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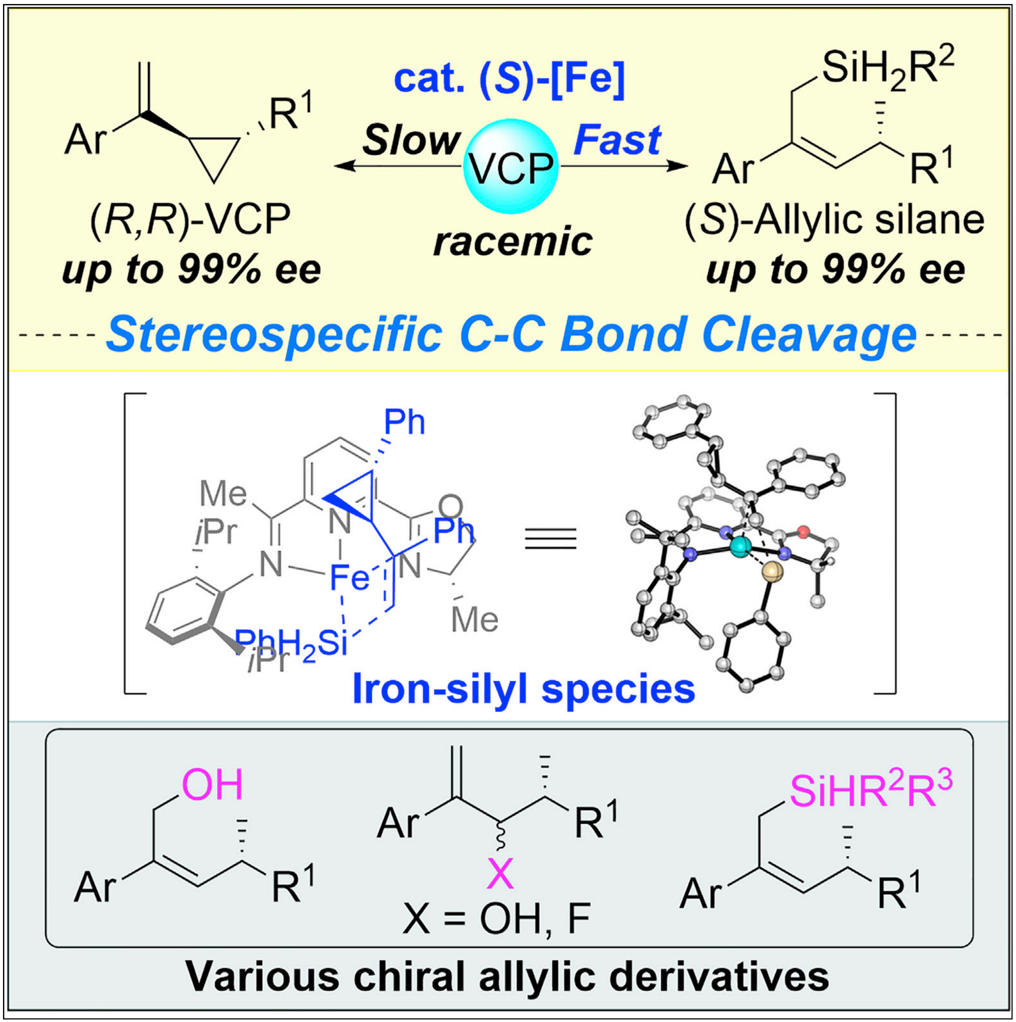

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HIGHLIGHTS

Iron-catalyzed 1,5-hydrosilylation of VCPs via C-C bond cleavage was first established

Chiral allyl silanes and chiral VCPs were obtained with high enantioselectivity

Various chiral allylic derivatives were delivered from chiral *Z*-allylic silanes

A possible mechanism via an iron-silyl species was proposed

DATA AND CODE AVAILABILITY

www.ccdc.cam.ac.uk/getstructures

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Iron-Catalyzed Asymmetric Hydrosilylation of Vinylcyclopropanes via Stereospecific C-C Bond Cleavage

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SUMMARY

An iron-catalyzed highly anti-Markovnikov selective, enantioselective hydrosilylation of vinylcyclopropanes with $PhSiH_3$ was reported for the preparation of valuable chiral allylic silanes via stereospecific C-C bond cleavage. Simultaneously, difficultly prepared chiral VCPs could be also obtained with moderate to excellent enantioselectivity via this kinetic resolution pathway. The chiral *Z*-allylic silanes could be converted to various chiral allylic derivatives. A possible mechanism via an iron-silyl species was proposed based on experimental and computational studies.

INTRODUCTION

Vinylcyclopropane (VCP) has been widely used in organic synthesis, particularly as a versatile organic synthon in cycloadditions (Lautens et al., 1996; Reissig and Zimmer, 2003; Rubin et al., 2007; Aïssa, 2011; Jiao and Yu, 2013; Wang and Yu, 2015; Fumagalli et al., 2017). Although the regio- and stereoselective ring-opening hydrofunctionalization reactions of VCPs could theoretically afford various potentially useful products, poor regioselectivity with eight possible regioisomers extremely limits their utility. Traditionally, in order to control the regioselectivity, gem-substituted electron-deficient groups have to be used to control the 1,4- or 3,4-regioselectivity via the cleavage of more substituted carbon-carbon bond (Crossley et al., 2016; Souillart and Cramer, 2015; Nairoukh et al., 2017; Wu and Zhu, 2019; Shigehisa et al., 2013; Sartori et al., 1983; Burgess, 1987; Sebelius et al., 2005; Sumida et al., 2008; Li et al., 2009; Dieskau et al., 2012; Wu et al., 2015; Zell et al., 2016; Meyer et al., 2017; Wang et al., 2019). To the best of our knowledge, asymmetric ring-opening hydrofunctionalization reactions of vinylcyclopropanes are still quite limited. Using donor-acceptor (D-A) vinylcyclopropanes, Krische and co-workers reported the iridium-catalyzed asymmetric alkylations with aldehydes or alcohols as electrophiles, affording the 3,4-regioselective hydrocarbonation products (Moran et al., 2011). Trost group recently disclosed the palladium-catalyzed asymmetric 1,4-hydrocarbonation of D-A vinylcyclopropanes with 3-substituted indoles as nucleophiles (Trost et al., 2018) (Figure 1A). Recently, our group reported an iron-catalyzed asymmetric 5,1-hydroboration of non-donor-acceptor (non-D-A) vinylcyclopropanes via iron-hydride intermediate (Chen et al., 2017). However, overstoichiometic amounts of VCPs were used to be converted to chiral boronic esters with less than 90% ee, and the ee values of recovered VCPs were extremely poor. So, the development of various regio- and enantioselective hydrofunctionalizations of vinylcyclopropanes via stereospecific C-C bond cleavage for the synthesis of chiral products is highly desirable.

Allylic silane is one of the most useful allylic reagents for organic transformations, such as Hosomi-Sakurai reaction (Masse and Panek, 1995; Fleming et al., 1997; Barbero and Pulido, 2004; Díez-Poza and Barbero, 2017). Chiral allylic silanes were used to be synthesized using stoichiometric chiral reagents via diastereoselective or stereospecific transformations (Sparks and Panek, 1991; Panek and Clark, 1992; Suginome et al., 1996; Bourque et al., 2007; Binanzer et al., 2010; Aggarwal et al., 2011). It is still a challenge for the catalytic enantioselective synthesis of chiral allylic silanes, which used to focus on the formation of chiral silicon-substituent carbon center (Hayashi et al., 1982; Hofstra et al., 2018; Wu et al., 2010; Ohmura et al., 2006; Da et al., 2018; Shintani et al., 2007; Lee et al., 2012; Kacprzynski et al., 2007; Sang et al., 2018; Wen et al., 2019).

Herein, we reported an iron-catalyzed 1,5-selective asymmetric hydrosilylation of vinylcyclopropanes via stereospecific C-C bond cleavage, affording chiral allylic silanes with excellent enantioselectivity and recovering VCPs with moderate to excellent enantioselectivity (Figure 1B).

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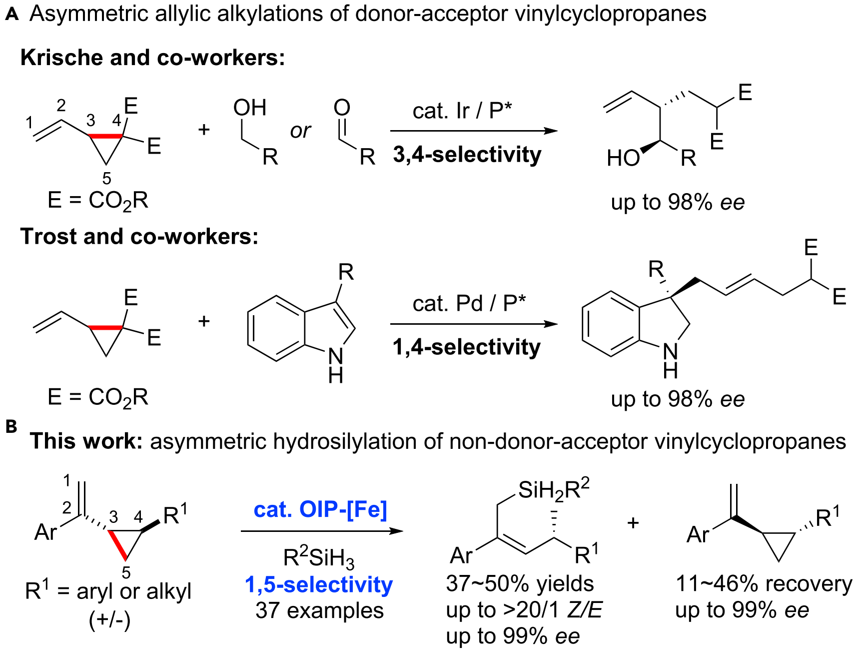


A Asymmetric allylic alkylations of donor-acceptor vinylcyclopropanes

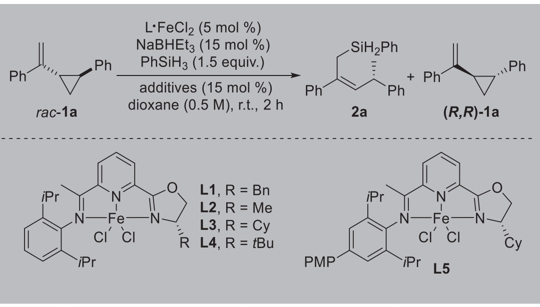
B This work: asymmetric hydrosilylation of non-donor-acceptor vinylcyclopropanes

Figure 1. Highly Enantioselective Hydrofunctionalizations of VCPs via C-C Bond Cleavage

RESULTS AND DISCUSSION

Initially, we chose the 1-phenyl-2-(1′-phenyl)vinylcyclopropane **1a** as a model substrate (Table 1). The reaction of **1a** with 1.5 equivalent of $PhSiH_3$ using 5 mol % of iron precatalyst **L1**·$FeCl_2$ and 15 mol % of $NaBHEt_3$ in a solution of dioxane (0.5 M) at ambient temperature for 24 h was carried out to afford the desired product **2a** in 6% yield (entry 1), whereas the reaction with Ph_2SiH_2 did not afford the hydrosilylation product (entry 2). The observation of **2a** illustrated the possibility of the generation of iron-silyl species. In our previous studies, free hydroxyl group was found to be tolerated in cobalt-catalyzed alkyne hydrosilylation in which cobalt-silyl species was proposed (Guo and Lu, 2016; Zuo et al., 2016). Ge and coworkers found that the addition of phenol could inhibit the *Z*/*E*-isomerization in Co-catalyzed alkyne hydrosilylation (Teo et al., 2017). These examples demonstrated that the addition of free hydroxyl group could promote the formation of cobalt silyl species. However, the proposed iron silyl species has not been reported for the tolerance of free hydroxyl group (Cheng et al., 2018; Hu et al., 2018; Chen et al., 2018; Obligacion and Chirik, 2018). With 15 mol % of water, the reaction afforded **2a** in an increasing yield (12%), which indicated that the addition of free hydroxyl group could also promote the formation of iron silyl species (entry 3). Using the phenol as an additive, the reaction was conducted for 2 h to afford **2a** in 28% yield with 98% *ee*, as well as **1a** in 65% recovery with 34% *ee* (entry 4). By further investigation of various phenols, 3-chlorophenol was found to accelerate reaction efficiently (entries 5–8). The reactivities were increased by increasing the steric hindrance of the group on oxazoline (Me, Bn, Cy) (entries 8–10). However, when **L4**·$FeCl_2$ was used as a precatalyst, the reaction was inhibited, which might be due to the overlarge steric hindrance (entry 11). When the 4-MeO-phenyl group was introduced into *para*-position of aniline, the reaction using L5·$FeCl_2$ as a precatalyst could be further accelerated to access **2a** in 48% yield with 13/1 *Z/E* and 98% *ee*, simultaneously with 28% recovery of chiral **1a** in 86% *ee* (entry 12). It should be noted that some dienes and hydrogenation products were observed as side products, which decreased the recovery of starting materials (see in Supplemental Information). The standard conditions were identified as 0.5 mmol of racemic vinylcyclopropane, 0.75 mmol of silane, 5 mol % of **L5**·$FeCl_2$, 15 mol % of $NaBHEt_3$, and 15 mol % of 3-chlorophenol in 1 mL of dioxane for 2 h.

With the optimal conditions in hand, the substrate scope was explored in Table 2. The scope of various substituents on alkene was first explored. The allylic silanes **2b**-**2j** with functional groups (methoxyl, methylthio, fluoro, chloro, bromo) at the *para*-, *meta*-, or *ortho*-position on the phenyl ring could be obtained in 39%–47% yields and 92%–98% *ee*, and chiral VCPs **1b**-**1j** could be observed in 15%–40% recoveries with



Entry	L	Additives	Yield of 2a (%)[a]	*ee* of 2a (%)[a]	Recovery of 1a (%)[a]	*ee* of 1a (%)[a]
1[b]	L1	–	6	–	89	–
2[b,c]	L1	–	0	–	48	–
3[b]	L1	H_2O	12	–	86	–
4	L1	C_6H_5OH	28	98	65	34
5	L1	4-MeOC_6H_4OH	18	97	76	21
6	L1	4-ClC_6H_4OH	30	98	62	38
7	L1	3-ClC_6H_4OH	35	97	59	41
8	L1	2-ClC_6H_4OH	15	98	82	14
9	L2	3-ClC_6H_4OH	32	96	60	37
10	L3	3-ClC_6H_4OH	41	98	45	63
11	L4	3-ClC_6H_4OH	2	–	90	–
12[d]	L5	3-ClC_6H_4OH	48	98	28	86

Table 1. Optimization of the Reaction Conditions

PMP, 4-methoxyphenyl. See also Table S1.

Using **1a** (0.5 mmol), $PhSiH_3$ (0.75 mmol), **L**·$FeCl_2$ (5 mol %), $NaBHEt_3$ (15 mol %), additives (15 mol %) and dioxane (0.5 M).

[a] Yields were determined by ^1H NMR analysis based on **1a** and *ee* value was determined by chiral HPLC. Unless noted, the ratio of *Z/E* was around 20/1.

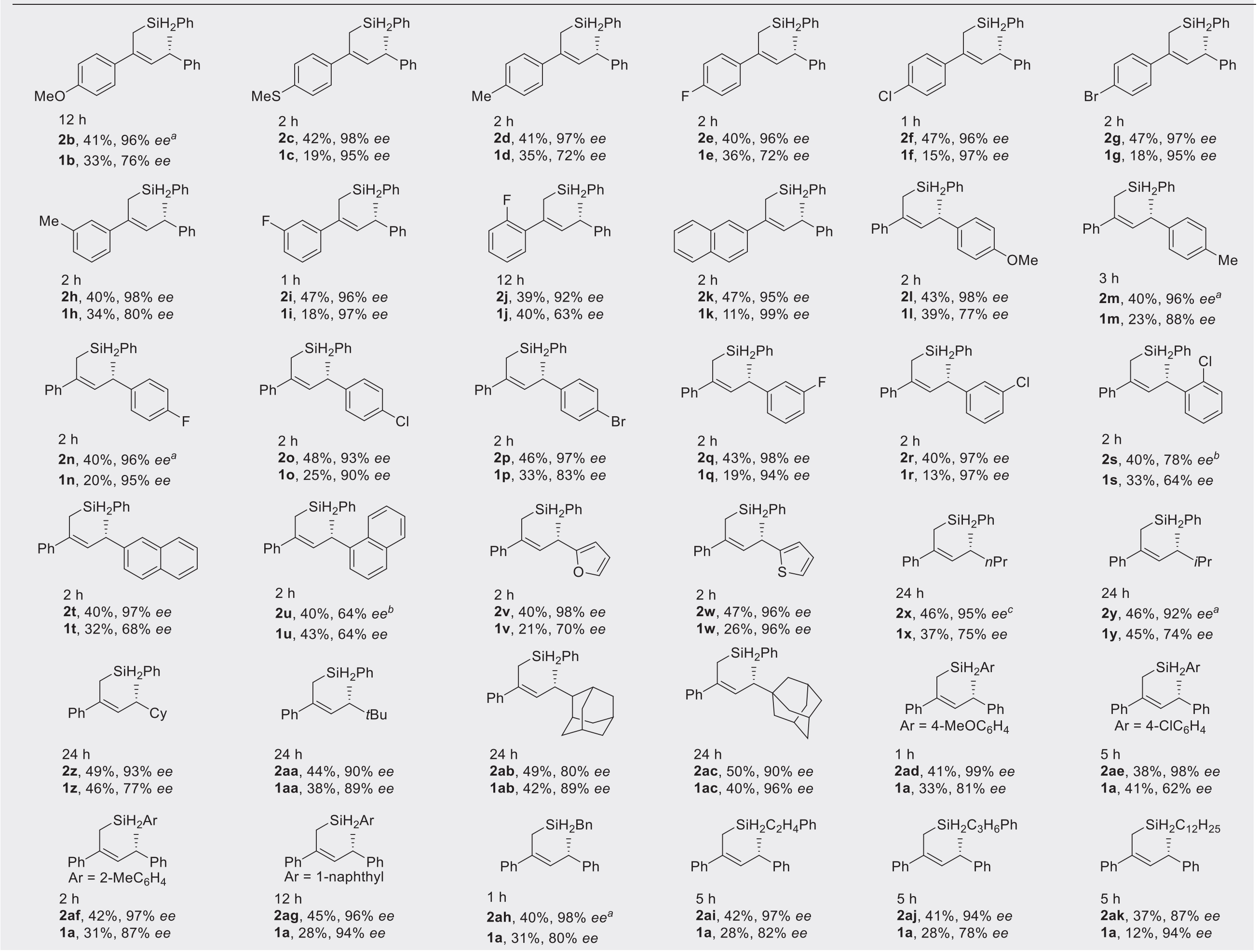
[b] 24 h.

[c] Using Ph_2SiH_2 instead of $PhSiH_3$, affording 14% yield of dienes without silicon group and 37% yield of hydrogenation products.

[d] *Z/E* = 13/1.

63%–97% *ee*. 2-Naphthyl substrate **1k** was also suitable, providing **2k** in 47% yield with 95% *ee* and 11% recovery of chiral **1k** in 99% *ee*. The reaction of alkyl-substituted VCPs did not occur. The scope of substituents on cyclopropanes was next examined. VCPs bearing electron-donating (**1l**, **1m**) or electron-withdrawing (**1n-1s**) groups at the different positions on the phenyl ring gave the corresponding products in 40%–48% yields with 78%–98% *ee*, and chiral VCPs **1l-1s** were observed in 13%–39% recoveries with 64%–97% *ee*. Additionally, 1-naphthyl, 2-naphthyl, 2-furyl, and 2-thienyl VCPs **1t-1w** were suitable for the catalytic system, affording **2t-2w** in 40%–47% yields with 64%–98% *ee* and chiral **1t-1w** in 21%–43% recoveries with 64%–96% *ee*. Owing to the sterically hindered groups, the selectivities of **1s** and **1u** were decreased. Notably, the reactions of 1°-, 2°-, 3°-alkyl substrates afforded **2x-2ac** in 44%–50% yields with 80%–95% *ee* and chiral **1x-1ac** in 37%–46% recoveries with 74%–96% *ee*.

To expand the utility of this strategy, a broad range of aryl and alkyl silanes were tested. Various aryl silanes were used in the reaction, affording **2ad-2ag** in 38%–45% with 96%–99% *ee* and chiral **1a** in 28%–41% recoveries with 62%–94% *ee*. When alkyl silanes were employed, the transformation also performed well, affording **2ah-2ak** in 37%–42% yields with 87%–98% *ee* and 12%–31% recoveries with 78%–94% *ee*. In general, VCPs bearing aryl or alkyl groups proceeded through a kinetic resolution (KR) pathway to deliver the desired chiral allylic silanes in good to excellent yields, moderate to excellent stereoselectivities and



12 h **2b**, 41%, 96% *ee*[a] **1b**, 33%, 76% *ee*	2 h **2c**, 42%, 98% *ee* **1c**, 19%, 95% *ee*	2 h **2d**, 41%, 97% *ee* **1d**, 35%, 72% *ee*	2 h **2e**, 40%, 96% *ee* **1e**, 36%, 72% *ee*	1 h **2f**, 47%, 96% *ee* **1f**, 15%, 97% *ee*	2 h **2g**, 47%, 97% *ee* **1g**, 18%, 95% *ee*
2 h **2h**, 40%, 98% *ee* **1h**, 34%, 80% *ee*	1 h **2i**, 47%, 96% *ee* **1i**, 18%, 97% *ee*	12 h **2j**, 39%, 92% *ee* **1j**, 40%, 63% *ee*	2 h **2k**, 47%, 95% *ee* **1k**, 11%, 99% *ee*	2 h **2l**, 43%, 98% *ee* **1l**, 39%, 77% *ee*	3 h **2m**, 40%, 96% *ee*[a] **1m**, 23%, 88% *ee*
2 h **2n**, 40%, 96% *ee*[a] **1n**, 20%, 95% *ee*	2 h **2o**, 48%, 93% *ee* **1o**, 25%, 90% *ee*	2 h **2p**, 46%, 97% *ee* **1p**, 33%, 83% *ee*	2 h **2q**, 43%, 98% *ee* **1q**, 19%, 94% *ee*	2 h **2r**, 40%, 97% *ee* **1r**, 13%, 97% *ee*	2 h **2s**, 40%, 78% *ee*[b] **1s**, 33%, 64% *ee*
2 h **2t**, 40%, 97% *ee* **1t**, 32%, 68% *ee*	2 h **2u**, 40%, 64% *ee*[b] **1u**, 43%, 64% *ee*	2 h **2v**, 40%, 98% *ee* **1v**, 21%, 70% *ee*	2 h **2w**, 47%, 96% *ee* **1w**, 26%, 96% *ee*	24 h **2x**, 46%, 95% *ee*[c] **1x**, 37%, 75% *ee*	24 h **2y**, 46%, 92% *ee*[a] **1y**, 45%, 74% *ee*
24 h **2z**, 49%, 93% *ee* **1z**, 46%, 77% *ee*	24 h **2aa**, 44%, 90% *ee* **1aa**, 38%, 89% *ee*	24 h **2ab**, 49%, 80% *ee* **1ab**, 42%, 89% *ee*	24 h **2ac**, 50%, 90% *ee* **1ac**, 40%, 96% *ee*	Ar = 4-MeOC$_6$H$_4$ 1 h **2ad**, 41%, 99% *ee* **1a**, 33%, 81% *ee*	Ar = 4-ClC$_6$H$_4$ 5 h **2ae**, 38%, 98% *ee* **1a**, 41%, 62% *ee*
Ar = 2-MeC$_6$H$_4$ 2 h **2af**, 42%, 97% *ee* **1a**, 31%, 87% *ee*	Ar = 1-naphthyl 12 h **2ag**, 45%, 96% *ee* **1a**, 28%, 94% *ee*	1 h **2ah**, 40%, 98% *ee*[a] **1a**, 31%, 80% *ee*	5 h **2ai**, 42%, 97% *ee* **1a**, 28%, 82% *ee*	5 h **2aj**, 41%, 94% *ee* **1a**, 28%, 78% *ee*	5 h **2ak**, 37%, 87% *ee* **1a**, 12%, 94% *ee*

Table 2. Substrate Scope

Reaction conditions: **1** (0.5 mmol), PhSiH$_3$ (0.75 mmol), **L5**·FeCl$_2$ (5 mol %), NaBHEt$_3$ (15 mol %), 3-ClC$_6$H$_4$OH (15 mol %) and dioxane (0.5 M), r.t. Isolated yield of *Z*-isomer. The ratio of *Z/E* and recovery of **1** were determined by ^{1}H NMR analysis and *ee* value was determined by chiral HPLC. Unless noted, the ratio of *Z/E* was better than 10/1.

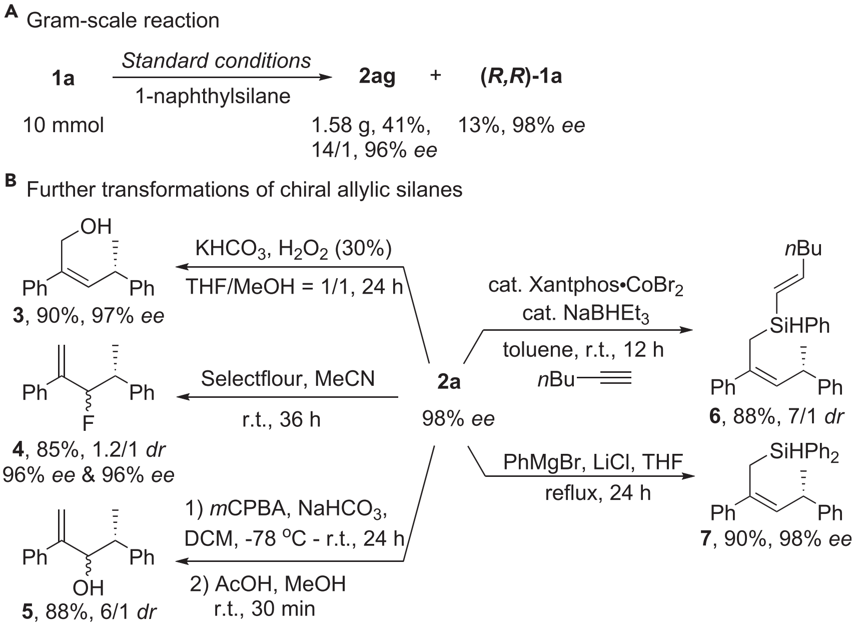
[a] *Z/E* = 9/1.

[b] *Z/E* = 8/1.

[c] *Z/E* = 4/1.

excellent enantioselectivities, and recover chiral VCPs in moderate to excellent yields with moderate to excellent enantioselectivities (Keith et al., 2001; Vedejs and Jure, 2005; Muller and Schreiner, 2011; Miller and Sarpong, 2011; Gao et al., 2014; Xiao et al., 2016; Hu et al., 2016; Das et al., 2017; Shimoda and Yamamoto, 2017; Jones et al., 2019; Brauns and Cramer, 2019; Zheng et al., 2019; Deng et al., 2019; Wu et al., 2019; Rajkumar et al., 2019).

To demonstrate the utility of this method, a gram-scale reaction could be carried out to afford **2ag** in 41% yield with 14/1 *Z/E*, 95% *ee* and recover chiral **1a** in 13% yield with 98% *ee* (Scheme 1A). The further derivatizations of products were illustrated in Scheme 1B. The Fleming-Tamao oxidation of **2a** delivered chiral allylic alcohol **3** in 90% yield with 97% *ee* (Wen et al., 2019). The absolute configuration was confirmed by X-ray diffraction of **3**. Obviously, the Hosomi-Sakurai reaction of **2a** with selectfluor and *meta*-chloroperoxybenzoic acid gave **4** and **5** in 85% and 88% yields with 1.2/1 and 6/1 *dr*, respectively (Hayashi et al., 1984; Thibaudeau and Gouverneur, 2003; Tredwell et al., 2008). Moreover, the hydrosilylation of *n*-hexyne with silane **2a** accessed a tertiary silane with silicon-stereocenter **6** in 88% yield with 7/1 *dr* (Cheng et al.,

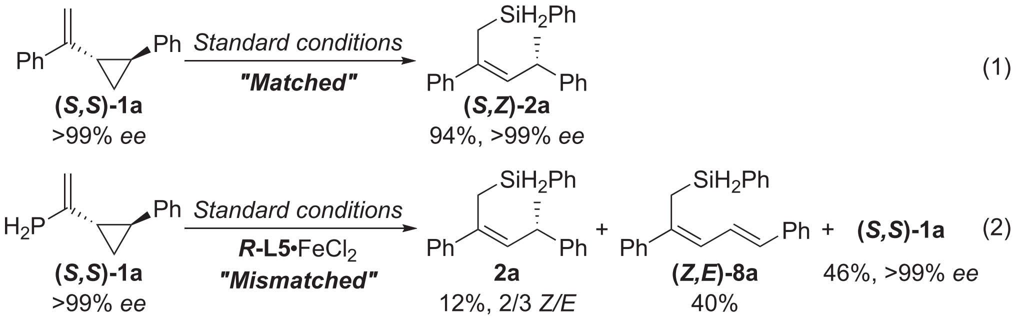


Scheme 1. Gram-Scale Reaction and Further Transformations

2017). The cross-coupling reaction of **2a** with phenylmagnesium bromide afforded **7** in 90% yield with 98% *ee* (Hirone et al., 2010).

Two control experiments were conducted to elucidate the possible reaction pathway (Scheme 2, eq. 1 and 2). The reaction of (***S***,***S***)-**1a** under standard conditions afforded (***S***,***Z***)-**2a** in 94% yield with >99% *ee* (Scheme 2, eq. 1), whereas the reaction of (***S***,***S***)-**1a** under standard conditions using ***R*-L5**·$FeCl_2$ as precatalyst afforded **2a** in 12% yield with a 2/3 ratio of *Z/E* and 46% recovery of (***S***,***S***)-**1a**. The diene (***Z***,***E***)-**8a** was observed as a side product, which also demonstrated the reason of poor recovery (scheme 2, eq. 2). These two control experiments well indicated the phenomenon of "matched and mismatched" between the substrate and iron precatalyst.

Inspired by the control experiments and the previously reported literatures on metal-silyl species (Wei and Darcel, 2019; Randolph and Wrighton, 1986; Lee et al., 2010; Lee and Peters, 2011; Tondreau et al., 2012; Zhang et al., 2014; Jia and Huang, 2016) and hydrosilylation (Chen et al., 2015, 2019; Xi and Lu, 2016; Guo et al., 2017, 2019; Cheng et al., 2019; Sun and Deng, 2016; Du and Huang, 2017; Trost and Ball, 2001; Mo et al., 2014; Ding et al., 2015; Du et al., 2016; Schuster et al., 2016; Pappas et al., 2016; Wang et al., 2017; Gribble et al., 2017; Liu et al., 2018; Wen et al., 2018; Zhan et al., 2018; Hu et al., 2019), we proposed that the iron-silyl species might promote this new 1,5-selective type of hydrosilylation of VCPs, which was different from the hydroboration of VCPs through iron-hydride species. The possible mechanism was proposed (Figure 2). The iron-silyl species is generated from OIP·$FeCl_2$ in the presence of $NaBHEt_3$, 3-chlorophenol, and silanes (Teo et al., 2017). In the matched catalytic



Scheme 2. Control Experiments

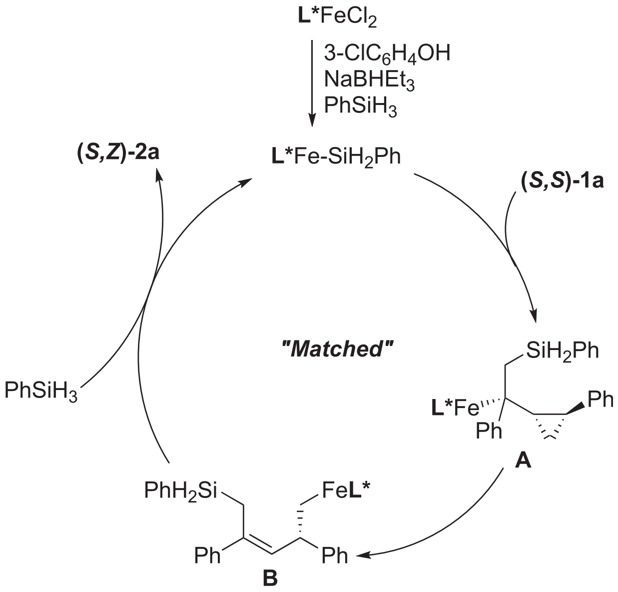


Figure 2. Proposed Mechanism

cycle, 1,2-insertion of (***S***,***S***)-**1a** into the iron-silicon bond delivers the tertiary alkyl iron species **A**. Subsequent β-carbon elimination generates the primary alkyl iron species **B**. Iron species **B** undergoes δ-bond metathesis with hydrosilane to access the product and regenerate iron silyl species. The mismatched catalytic cycle was discussed in Supplemental Information.

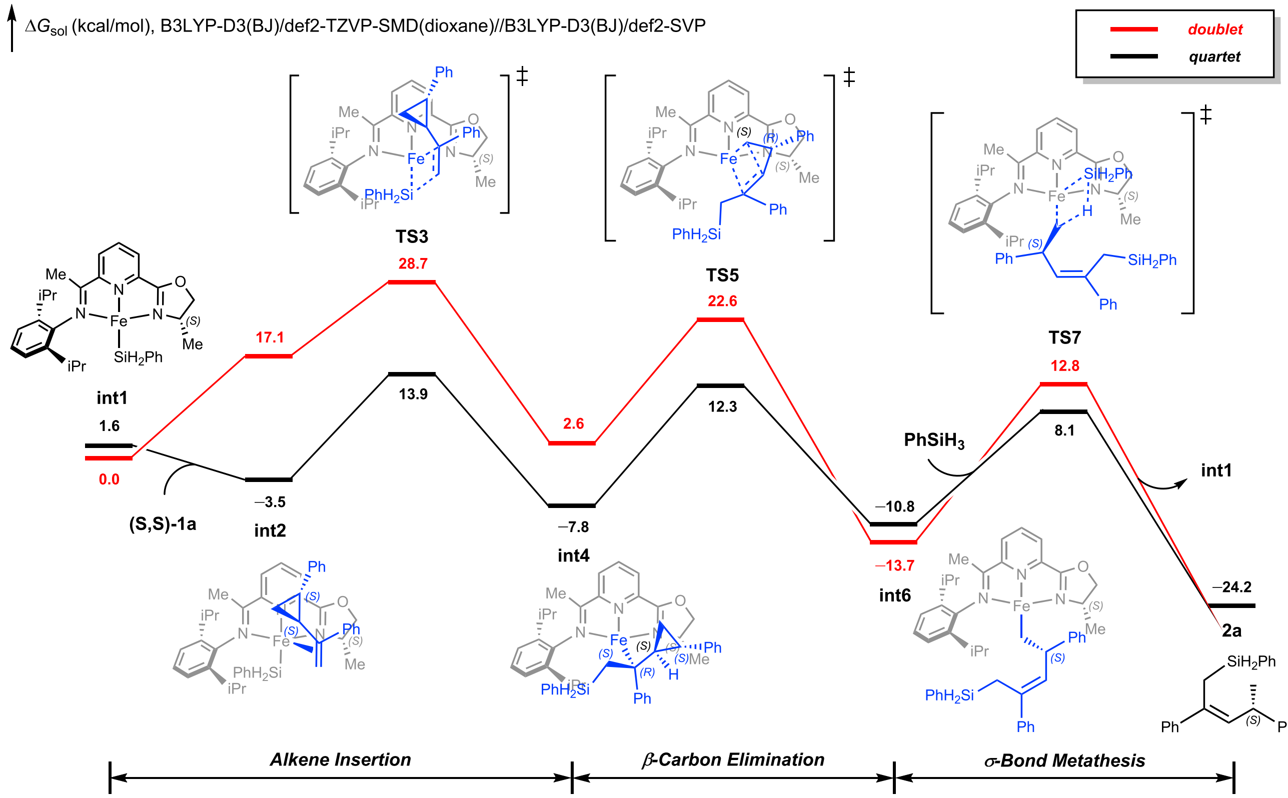


Figure 3. Free Energy Diagram for the Most Favorable Reaction Pathway for 1,5-Selective Hydrosilylation of 1a

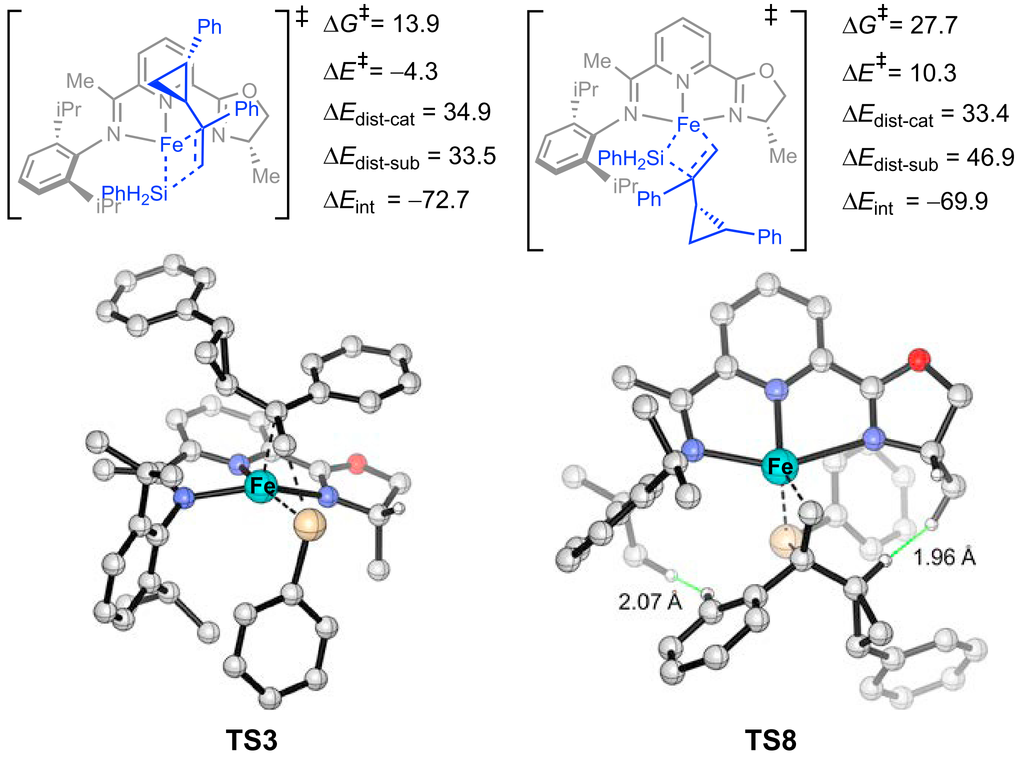


Figure 4. Optimized Structures, Energies, and Distortion/Interaction Analysis of the Regioisomeric Alkene Insertion Transition States

Energy barriers in kcal/mol are compared with int1 and 1a. Trivial hydrogens are omitted for clarity.

The proposed mechanism is also supported by density functional theory (DFT) calculations. The computed free energy changes of the most favorable pathway for iron-catalyzed 1,5-selective hydrosilylation of VCP **1a** with OIP ligand **L2** are shown in Figure 3. From the (OIP)Fe-silyl active species **int1**, alkene coordinates to allow the subsequent alkene insertion via **TS3**. This generates the tertiary alkyl-iron intermediate **int4**, which undergoes the proposed β-carbon elimination through **TS5** to give the primary alkyl-iron intermediate **int6**. From **int6**, the 1,5-selective hydrosilylation product **2a** is produced through a σ-bond metathesis via **TS7**, accompanied by the regeneration of **int1**. Based on the free energy changes of the whole catalytic cycle, the irreversible alkene insertion determines the overall regioselectivity of hydrosilylation.

We next explored the regioselectivity of alkene insertion, and the energies and optimized structures of the competing insertion transition states (**TS3** and **TS8**) are shown in Figure 4. **TS3** is 13.8 kcal/mol more favorable than **TS8**, which is consistent with the experimental observations of the exclusive 1,5-selective hydrosilylation. The distortion/interaction analysis (Bickelhaupt and Houk, 2017) is performed to further elucidate the origins of regioselectivity. The distortion energies ΔE_{dist} are the energy penalty associated with the geometric change from the ground state to the corresponding geometry in alkene insertion transition state. ΔE_{int} reflects the strength of interaction between the two distorted fragments in the transition state. $\Delta E_{\mathrm{dist\text{-}sub}}$ is the leading cause that differentiates the two transition states. This is due to the steric repulsions between the inserting VCP substrate and OIP ligand in **TS8**. The closet H-H distances between the substrate and ligand are highlighted in Figure 4. Therefore, the sterically demanding OIP ligand forces the *anti*-Markovnikov insertion of VCP, leading to the excellent regioselectivity of hydrosilylation.

Conclusion

In summary, we have first developed an iron-catalyzed asymmetric *anti*-Markovnikov-selective hydrosilylation of vinylcyclopropanes via stereospecific C-C bond cleavage. The addition of 3-chlorophenol has been found to promote the formation of proposed iron silyl species to accelerate the reaction. The transformation with a wide range of VCPs and silanes proceeds through a kinetic resolution pathway to generate the chiral allylic silanes in excellent *ee* and recover chiral VCPs in moderate to excellent *ee*. The chiral allylic silanes can be used in the Hosomi-Sakurai reaction, hydrosilylation, and cross-coupling reaction. An iron-silyl species was proposed based on experimental and computational studies. The studies on novel difunctionalization of VCPs are underway in our laboratory.

Limitations of Study

In this study, the scope of substrate is well explored but the vinylcyclopropanes with alkyl-substituents on alkene did not work. It is still a challenge for the highly enantioselective earth abundant metal-catalyzed hydrosilylation of 1,1-disubstituted alkenes with alkyl substituents.

METHODS

All methods can be found in the accompanying Transparent Methods supplemental file.

DATA AND CODE AVAILABILITY

The crystallography data have been deposited at the Cambridge Crystallographic Data Center (CCDC) under accession number CCDC: 1900765 (**3**) and can be obtained free of charge from www.ccdc.cam.ac.uk/getstructures.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2020.100985.

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AUTHOR CONTRIBUTIONS

Z.L. conceived and designed the study. X.H. designed the computational studies. Z.L. and C.C. co-wrote the paper. X.H. and H.W. wrote the computational part of the manuscript. C.C. principally performed the experiments. H.W. performed the computational studies. Y.S., J.C., J.X., Y.S., and S.Y. helped to conduct some experiments and collect data.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Supplemental Information

Iron-Catalyzed Asymmetric Hydrosilylation of Vinylcyclopropanes via Stereospecific C-C Bond Cleavage

Chenhui Chen, Hongliang Wang, Yufeng Sun, Jiayan Cui, Jianbo Xie, Yang Shi, Shijia Yu, Xin Hong, and Zhan Lu

Transparent Methods

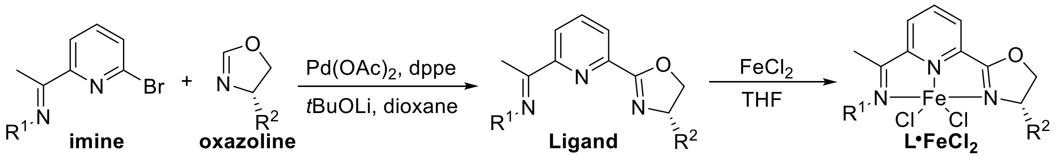
A. General Information

Ether, THF, and dioxane were distilled from sodium benzophenone ketyl prior to use. $NaHBEt_3$ (1.0 M in THF) and $FeCl_2$ (99.7%) were purchased from Aldrich and used as received. $Pd(OAc)_2$ (99%) were purchased from strem and used as received. The other commercially available chemicals were used as received. NMR spectra were recorded on Bruker-400 instrument and WNMR-I 400 instrument. ^1H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm), ^{13}C NMR chemical shifts were referenced to the solvent resonance (77.00 ppm, $CDCl_3$), ^{19}F NMR chemical shifts were referenced to the solvent resonance. The following abbreviations (or combinations) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m= multiplet, br = broad, q = quadruplet. HPLC analyses were performed on a Shimadzu SPD-20A. High-resolution mass spectra (HRMS) were recorded on Waters GCT Premier (EI) and Waters XEVO (ESI). IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with diamond ATR accessory. The X-ray diffraction data was obtained on Rigaku Gemini A Ultra. Optical rotation data was obtained on PerkinElmer Model 341 Polarimeter. Melting point data was obtained on WRR melting point apparatus.

B. Computational Details

All DFT calculations were performed using Gaussian 09 program (Frisch et al., 2013). Geometry optimizations were carried out using B3LYP (Lee et al., 1988; Becke, 1993; Stephens et al., 1994) -D3 (Becke-Johnson damping function) (Grimme et al., 2010; Grimme et al., 2011) functional, with def2-SVP basis set (Schäfer et al., 1992) for all elements. The vibrational frequency was calculated at the same level of theory to identify each optimized stationary point as an energy minimum or a transition state, and to evaluate the zero-point vibrational energy and thermal corrections at 298 K. Based on the gas-phase optimized structures, the single-point energies and solvent effects of dioxane were calculated using B3LYP-D3 functional and def2-TZVP basis set for all elements, using the SMD solvent model (Marenich et al., 2009). The 3D diagrams of computed species were generated by CYLView (Legault, 2009). In order to adjust the Gibbs free energies from 1 atm to 1 mol/L, a correction of $RT\ln(c_s/c_g)$ (1.9 kcal/mol) is added to energies of all species. c_s is the standard molar con-centration in solution (1 mol/L), c_g is standard molar con-centration in gas phase (0.040876 mol/L), and *R* is the gas constant.

C. Experimental procedures



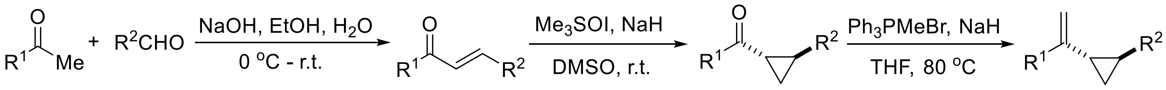
L1, **L2**, **L3**, **L4**, **L5** and L·$FeCl_2$ complexes were prepared according to the previously reported procedure in our group (Chen et al., 2014; Chen et al., 2014; Xi et al., 2015; Guo et al., 2016).

Synthesis of imine: 1-(6-bromopyridin-2-yl)ethan-1-one (1.0 equiv.), aniline (1.0 equiv.), *p*-toluenesulfonic acid monohydrate (10 mol %) and toluene (0.5 M) was mixed in a 500 mL three-necked round-bottom flask. The reaction mixture was refluxed at 110-130 °C until the starting material disappeared (monitored by TLC with PE/EA (10/1)). The reaction mixture was filtered and washed with petroleum ether. The combined solution was concentrated in vacuo and further purified by crystallized from ethanol.

Synthesis of oxazoline: amino alcohol (1.0 equiv.), *N,N*-dimethylformamide dimethyl acetal (DMF-DMA, 1.2 equiv.), IR-120 (9 wt %) and toluene (0.4-0.5 M) was mixed in a 500 mL three-necked round-bottom flask. The reaction mixture was refluxed at 110-130 °C until the starting material disappeared. The reaction mixture was washed with saturated $NaHCO_3$, brine, dried over Na_2SO_4, concentrated by rotary evaporation and further purified by distillation.

Synthesis of OIP ligand: to a flame-dried Schlenk tube were added oxazoline (1.2 equiv.), $Pd(OAc)_2$ (2.5 mol %), dppe (2.8 mol %) and *t*BuOLi (2.0 equiv.) under N_2. The tube was degassed with N_2 three times, and imine (1.0 equiv.) and anhydrous 1,4-dioxane (0.2 M) were added in sequence. The reaction mixture was stirred in an oil bath at 100 °C for 24 h until the starting material disappeared (monitored by TLC with PE/EA (10/1)). The reaction mixture was then cooled to room temperature, filtered through a pad of silica gel and washed by dichloromethane (10 mL x 3). The combined solution was concentrated in vacuo and further purified by flash chromatography on silica gel (PE/EA/Et_3N).

Synthesis of iron catalyst: to a flame-dried Schlenk tube were added OIP ligand (1.02 equiv.), anhydrous $FeCl_2$ (1.0 equiv.) and THF (0.1 M) under N_2. The reaction mixture was stirred at room temperature for 3 h, then ether (0.1 M) was injected to precipitate the complex and stirred for 30 min. The resulting mixture was filtered, washed with ether and dried in vacuo to give the iron catalyst.

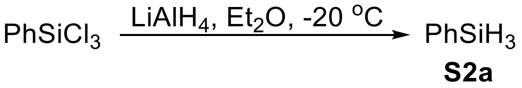


1a-1ac were prepared according to the previously reported procedure in our group (Chen et al., 2017).

Synthesis of vinylcyclopropanes: acetophenone (100 mmol) was dissolved in ethanol (150 mL) in a 500 mL round-bottom flask and cooled to 0 ºC, a solution of sodium hydroxide (200 mmol) in water (60 mL) was added. Then the solution of alcohol (150 mL) containing benzaldehyde (100 mmol) was added drop wise with stirring over a period of 10 min. The reaction mixture was stirred at room temperature for about 4-12 h until the starting material disappeared (monitored by TLC with PE/EA (10/1)). The reaction mixture was concentrated by rotary evaporation and extracted with DCM (50 mL x 3). The combined organic layers were washed with saturated $NaHCO_3$ and then brine, dried over Na_2SO_4, concentrated by rotary evaporation and further purified by flash chromatography on silica gel or crystallized from ethanol.

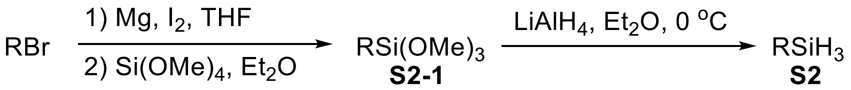
Me_3SOI (1.2 equiv.) and NaH (1.2 equiv., 60% dispersion in mineral oil) was mixed in a 250 mL three-necked flame-dried round-bottom flask under the atmosphere of nitrogen. 150 mL of DMSO were added dropwise and stirred at room temperature for 30 min. Then chalcone was added in portion and stirred at room temperature for about 4-12 h until the starting material disappeared (monitored by TLC withPE/EA (10/1)). The mixture was then treated with water (150 mL) and extracted with DCM (50 mL x 3). The combined organic layers were washed with water (50 mL x 2) and saturated $NaHCO_3$ (50 mL x 2) and then brine, dried over Na_2SO_4, concentrated by rotary evaporation and further purified by flash chromatography on silica gel or crystallized from ethanol.

A 250 mL of three-necked flame-dried round-bottom flask was cooled at room temperature under the atmosphere of nitrogen, charged with Methyltriphenylphosphonium bromide (1.2 equiv.), NaH (1.3 equiv., 60% dispersion in mineral oil), THF (150 mL). The mixture was refluxed at 80ºC for 1 h and then cooled to 0 ºC, a solution of cyclopropyl ketone in THF (20 mL) was added dropwise and continued to reflux for about 4-12 h until the starting material disappeared (monitored by TLC with PE). The reaction was quenched by 1.0 mL saturated NH_4Cl, concentrated by rotary evaporation and filtrated on silica gel. The combined filtrates were concentrated by rotary evaporation and further purified by flash chromatography on silica gel.



$$\mathrm{PhSiCl_3} \xrightarrow{\mathrm{LiAlH_4,\ Et_2O,\ -20\ ^oC}} \underset{\textbf{S2a}}{\mathrm{PhSiH_3}}$$

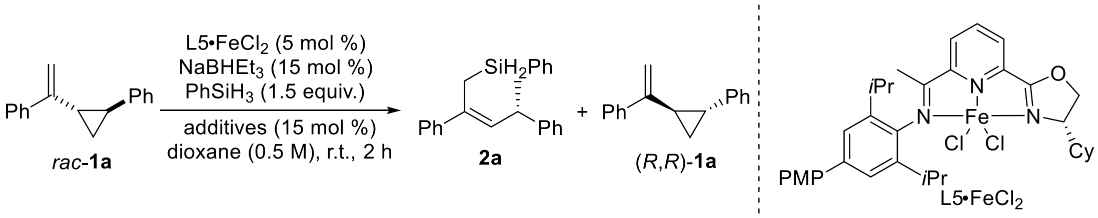
Synthesis of phenylsilane (S2a): prepared according to the previously reported procedure (Sakurai et al., 1984), a 1000 mL of three-necked flame-dried round-bottom flask was cooled at -20 ºC under the atmosphere of nitrogen, charged with lithium aluminum hydride (28.90 g, 750 mmol) and ether (400 mL). Phenyltrichlorosilane (80 mL, 500 mmol) dissolved in 200 mL ether was added dropwise. The mixture was stirred at room temperature for 12 h and then cooled to -20 ºC, quenched with water (100 mL), extracted with ether (50 mL x 3). The organic layers were combined, washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The resulting oil was purified via distillation to give 42.27 g (393.4 mmol, 79% yield) of the title compound as a colorless oil.



$$\mathrm{RBr} \xrightarrow[\text{2) Si(OMe)}_4\text{, Et}_2\text{O}]{\text{1) Mg, I}_2\text{, THF}} \underset{\textbf{S2-1}}{\mathrm{RSi(OMe)_3}} \xrightarrow{\mathrm{LiAlH_4,\ Et_2O,\ 0\ ^oC}} \underset{\textbf{S2}}{\mathrm{RSiH_3}}$$

Synthesis of other silanes: prepared according to the previously reported procedure (Visco et al., 2016), a 250 mL of three-necked flame-dried round-bottom flask was cooled at -20 ºC under the atmosphere of nitrogen, charged with magnesium turnings (1.05 equiv.), several iodine crystals and THF (10 mL). bromide (50 mmol, 1.0 equiv.) dissolved in 40 mL THF was added dropwise over 30 min. After completing addition of bromide, the mixture was refluxing for another one hour. The resulting Grignard reagent was cooled to room temperature and added dropwise to a solution of $Si(OMe)_4$ (3.0 equiv.) and ether (100 mL) at 0 °C. After finishing addition, the mixture was warm to room temperature and stirred overnight. The reaction was quenched with water (10 mL), extracted with ether (50 mL x 3). The organic layers were combined, washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The mixture (**S2-1**) was used in next step after removing excess $Si(OMe)_4$ by distillation.

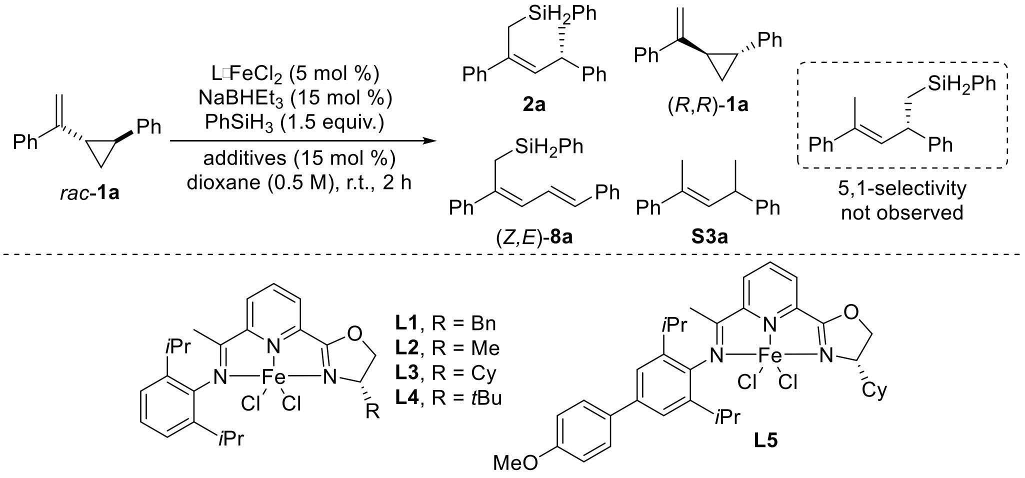
A 500 mL of three-necked flame-dried round-bottom flask was cooled at 0 °C under the atmosphere of nitrogen, charged with lithium aluminium hydride (1.5 equiv.) and ether (150 mL). **S2-1** dissolved in 50 mL ether was added dropwise carefully at 0 °C and stirred at room temperature overnight. The reaction mixture was then diluted with 200 mL of PE, stirred for 30 min, filtered through Celite and concentrated in vacuo. The resulting residue was diluted with an additional 200 mL of PE, filtered through Celite and concentrated in vacuo. The resulting oil was purified via distillation to give the corresponding compound.



Asymmetric hydrosilylation of vinylcyclopropanes: to a 25 mL flame-dried Schlenk flask cooled under nitrogen, **L5**·$FeCl_2$ complex (0.025 mmol, 5 mol%) and vinylcyclopropane (0.5 mmol, 1.0 equiv.) were added. The mixture was vacuumed and flushed with nitrogen for three times, and then 1.0 mL of dioxane (0.5 M) containing 5 mol% of 3-chlorophenol (0.075 mmol) and silane (0.75 mmol, 1.5 equiv.) were added in sequence. The mixture was injected with $NaBHEt_3$ (1.0 M in THF, 75 μL, 0.075 mmol) by dropwise. The reaction was run at ambient temperature for 2 h. Then the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity (the ratio of *Z/E*) was monitored by ^1H NMR analysis. The resulting mixture was purified by flash column chromatography using PE as the eluent to give the corresponding product and recover the chiral vinylcyclopropane.

Tables and Figures

Table S1. Optimization for asymmetric hydrosilylation of vinylcyclopropanes.[a] Related to Table 1.

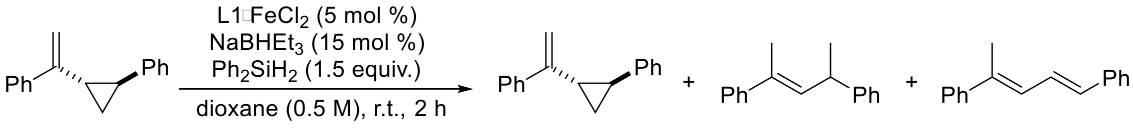


entry	ligands	additives	2a			(R,R)-1a		yield of (Z,E)-8a (%)[b]	yield of S3a (%)[b]
			yield (%)[b]	Z/E[b]	ee (%)[b]	recovery (%)[b]	ee (%)[b]		
1[c]	**L1**	-	6	-	-	89	-	<1	3
2[c,d]	**L1**	-	0	-	-	48	-	0	37
3[c]	**L1**	H_2O	12	-	-	86	-	<1	<1
4	**L1**	PhOH	28	20/1	98	65	34	5	3
5	**L1**	4-$MeOC_6H_4OH$	18	20/1	97	76	21	3	3
6	**L1**	4-ClC_6H_4OH	30	>20/1	98	62	38	5	3
7	**L1**	3-ClC_6H_4OH	35	19/1	97	59	41	6	2
8	**L1**	2-ClC_6H_4OH	15	>20/1	98	82	14	2	<1
9	**L2**	3-ClC_6H_4OH	32	20/1	96	60	37	6	3
10	**L3**	3-ClC_6H_4OH	41	19/1	98	45	63	11	3
11	**L4**	3-ClC_6H_4OH	2	-	-	90	-	0	8
12	**L5**	3-ClC_6H_4OH	50 (48)	13/1	98	28	86	18	4

[a] Using **1a** (0.5 mmol), $PhSiH_3$ (0.75 mmol), **L**·$FeCl_2$ (5 mol %), $NaBHEt_3$ (15 mol %), additives

(15 mol %) and dioxane (0.5 M). [b] Yields, recovery and ratio of *Z/E* were determined by ^{1}H NMR analysis based on **1a**, isolated yield was in the parenthesis and *ee* value was determined by chiral HPLC. [c] 24 h. [d] Using Ph_2SiH_2 instead of $PhSiH_3$, affording 14% yield of dienes without silicon group and 37% yield of hydrogenation products.

Entry 2: using Ph_2SiH_2 instead of $PhSiH_3$.



rac-**1a**

48% of **1a**

37% of **S3a**

15% of **S4a**

Table S2. Zero-point correction (*ZPE*), thermal correction to enthalpy (*TCH*), thermal correction to Gibbs free energy (*TCG*), energies(*E*), enthalpies (*H*), and Gibbs free energies (*G*) (in Hartree) of the structures for all the figures calculated at the B3LYP-D3(BJ)/def2-TZVP-SMD(dioxane)//B3LYP-D3(BJ)/def2-SVP level of theory. Spin states are shown in parentheses, Related to Figure 3.

Structures	*ZPE*	*TCH*	*TCG*	*E*	*H*	*G*	Imaginary Frequency
Int1(doublet)	0.587657	0.623888	0.519882	-2920.263623	-2919.639735	-2919.743741	
Int1(quartet)	0.587119	0.623417	0.518708	-2920.259963	-2919.636546	-2919.741255	
(S,S)-1a	0.277168	0.292318	0.232535	-657.71446	-657.422142	-657.481925	
2a	0.398044	0.421186	0.342902	-1180.865933	-1180.444747	-1180.523031	
$PhSiH_3$	0.115387	0.123326	0.083212	-523.088626	-522.9653	-523.005414	
Int2(doublet)	0.86992	0.920396	0.788193	-3577.98363	-3577.063234	-3577.195437	
Int2(quartet)	0.866489	0.918559	0.780368	-3578.008611	-3577.090052	-3577.228243	
TS3(doublet)	0.871965	0.921265	0.791429	-3577.968384	-3577.047119	-3577.176955	87.8*i*
TS3(quartet)	0.867833	0.918259	0.784545	-3577.985015	-3577.066756	-3577.20047	153.7*i*
Int4(doublet)	0.868908	0.919716	0.784	-3578.002525	-3577.082809	-3577.218525	
Int4(quartet)	0.866381	0.918178	0.777166	-3578.012161	-3577.093983	-3577.234995	
TS5(doublet)	0.868955	0.919307	0.784562	-3577.971201	-3577.051894	-3577.186639	289.1*i*
TS5(quartet)	0.865556	0.916545	0.778204	-3577.981282	-3577.064737	-3577.203078	311.2*i*
Int6(doublet)	0.867417	0.918593	0.781556	-3578.026051	-3577.107458	-3577.244495	
Int6(quartet)	0.866569	0.917983	0.779604	-3578.019383	-3577.1014	-3577.239779	
TS7(doublet)	0.987109	1.045466	0.894527	-4101.099158	-4100.053692	-4100.204631	780.6*i*
TS7(quartet)	0.982705	1.041923	0.887834	-4101.100001	-4100.058078	-4100.212167	863.6*i*
TS8(doublet)	0.86891	0.918589	0.788132	-3577.943066	-3577.024477	-3577.154934	119.4*i*
TS8(quartet)	0.866023	0.916803	0.783065	-3577.961626	-3577.044823	-3577.178561	229.0*i*

The mismatched catalytic cycle: in the mismatched catalytic cycle (Figure S1), the iron-silyl species is generated from OIP·$FeCl_2$ in the presence of $NaBHEt_3$, 3-chlorophenol and silanes. Another tertiary alkyl iron species **C** is formed by 1,2-insertion of (*R*,*R*)-**1a** into the iron-silicon bond. Due to the overlarge steric hindrance, **C** tends to form iron species and carbon radical intermediate **D** through iron carbon bond cleavage. Then carbon radical intermediate **D** is generated through radical ring-opening pathway (Gui et al., 2015), coupling with iron species to deliver iron-silyl species **F**. β-Hydrogen elimination of iron-silyl species **F** generates (*Z*,*E*)**-8a** and iron-hydride species. Finally, iron-hydride species regenerates the iron-silyl species with silanes. Moreover, radical-radical coupling reaction between carbon radical intermediate **D** and iron species affords iron-silyl species **C'**. Subsequent β-carbon elimination generates the primary alkyl iron species **B'**. Iron species **B'** undergoes δ-bond metathesis with hydrosilane to access ***R*-2a** and regenerate iron silyl species.

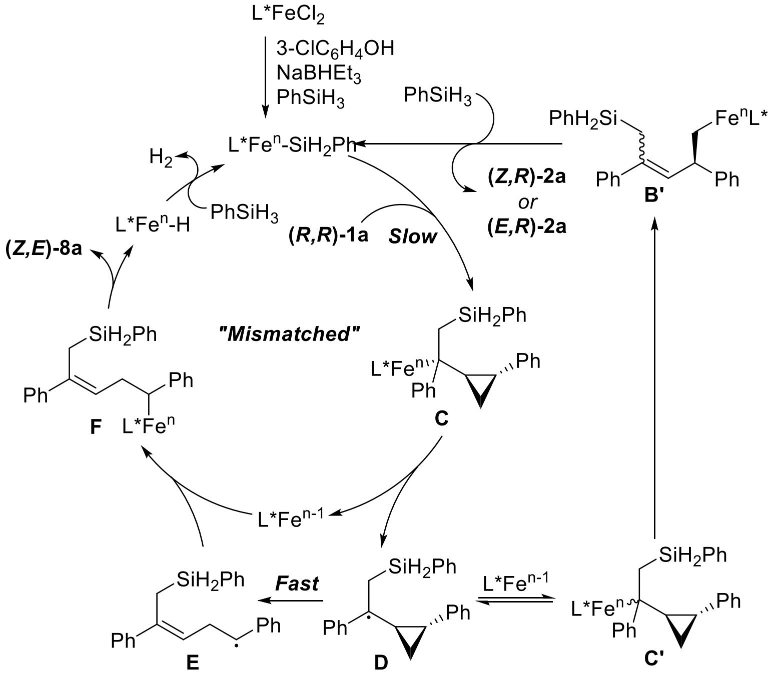


Figure S1. Proposed mechanism of the mismatched catalytic cycle, Related to Figure 2.

Figure S2 shows the protocol of distortion/interaction analysis using **TS3** as an example. The optimized structure of **TS3** is separated into two fragments: the (OIP)Fe-silyl catalyst fragment (**cat**) and the VCP substrate fragment (**sub**). The energies of these distorted fragments were computed at the B3LYP-D3(BJ)/def2-TZVP level, without the inclusion of solvation energy corrections. Comparing the energies of the distorted fragments and those of the corresponding optimized species, we obtained the distortion energies of the catalyst and substrate ($\Delta E_{\text{dist-sub}}$ and $\Delta E_{\text{dist-cat}}$). The interaction energy, ΔE_{int}, is the difference between the total distortion energy and the electronic reaction barrier, $\Delta E_{\text{int}} = \Delta E^{\ddagger} - (\Delta E_{\text{dist-sub}} + \Delta E_{\text{dist-cat}})$.

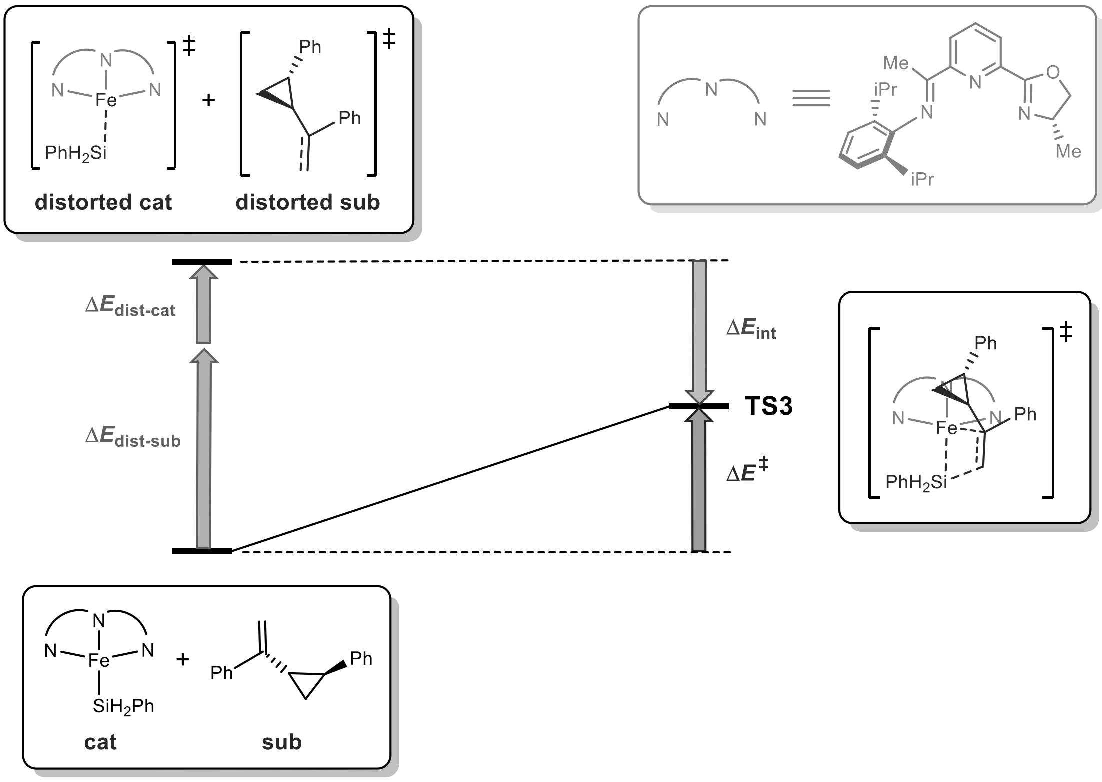


Figure S2. Illustration of distortion/interaction analysis using **TS3** as an example, Related to Figure 4.

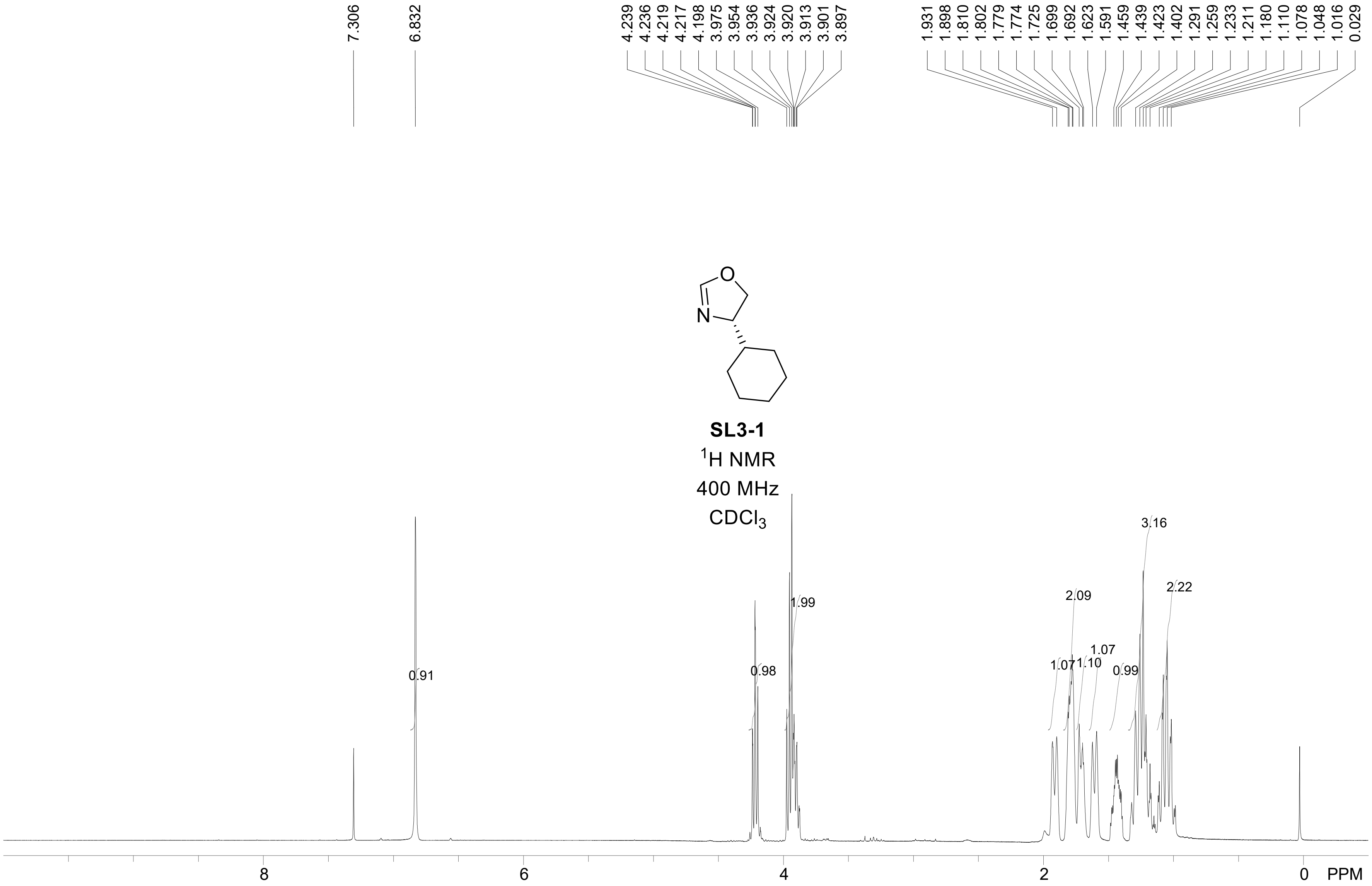


Figure S3. ^{1}H NMR spectra of **SL3-1**, Related to Table 1

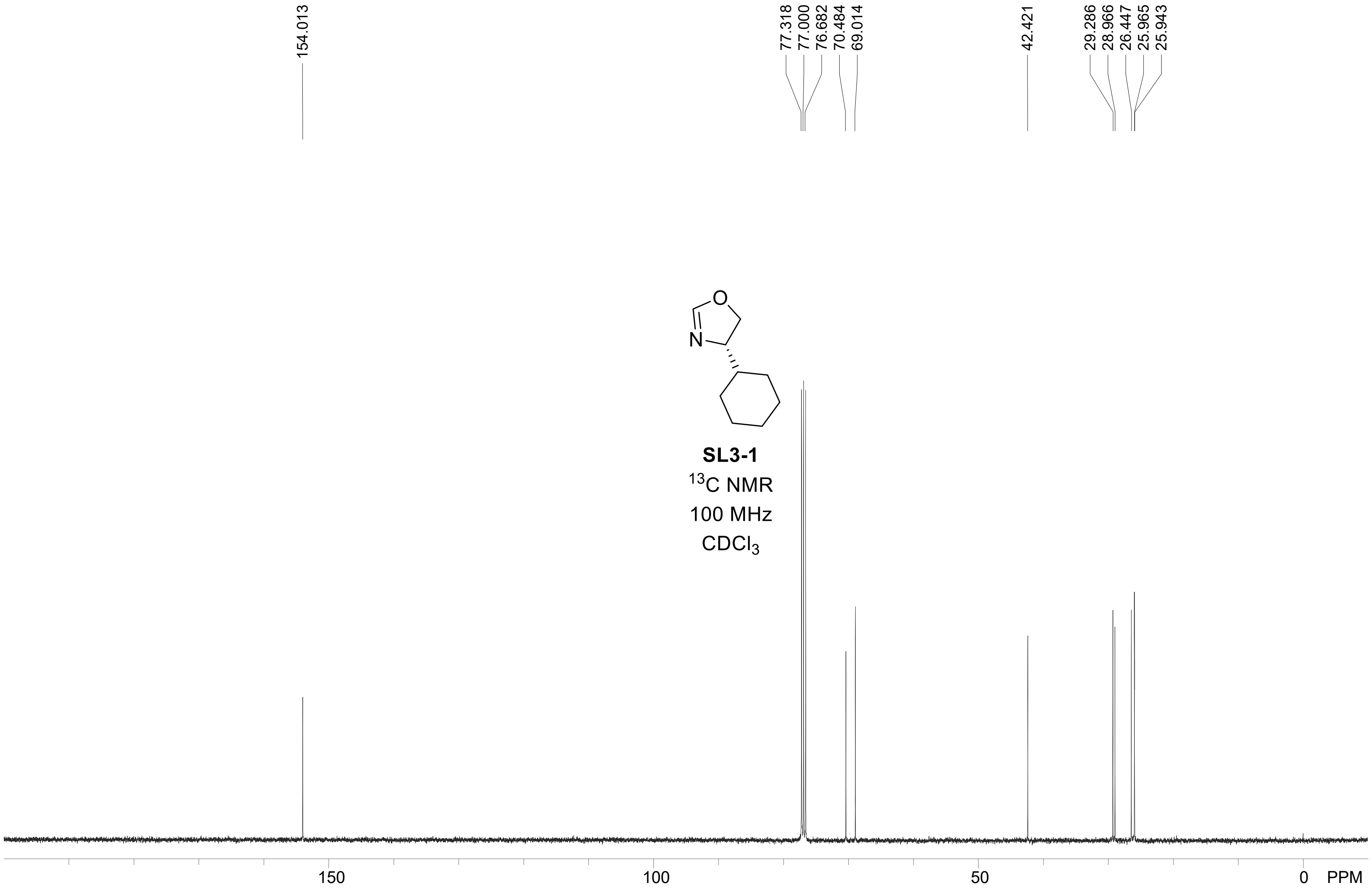


Figure S4. ^{13}C NMR spectra of **SL3-1**, Related to Table 1

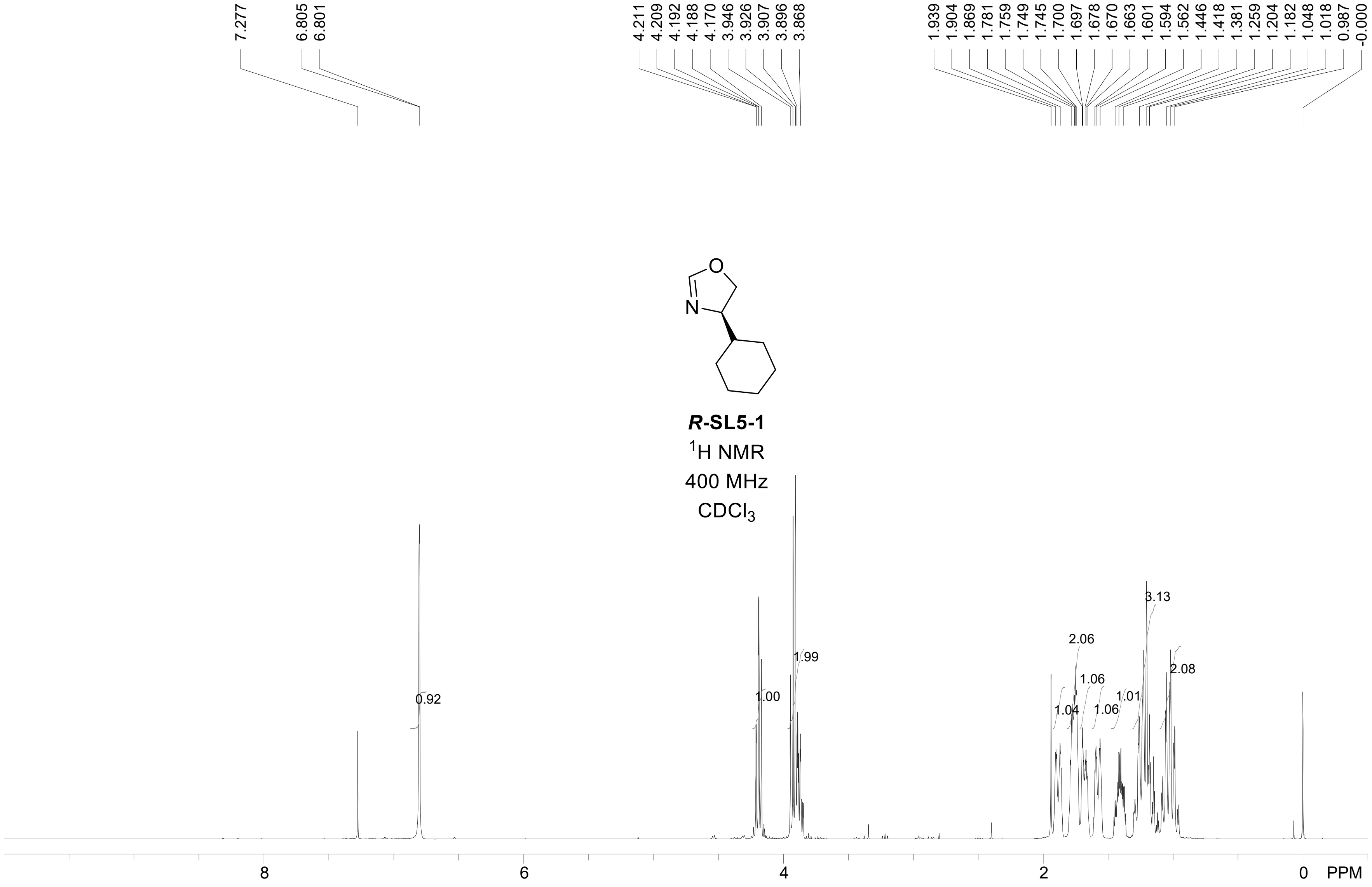


Figure S5. ^{1}H NMR spectra of ***R*-SL5-1**, Related to Table 1

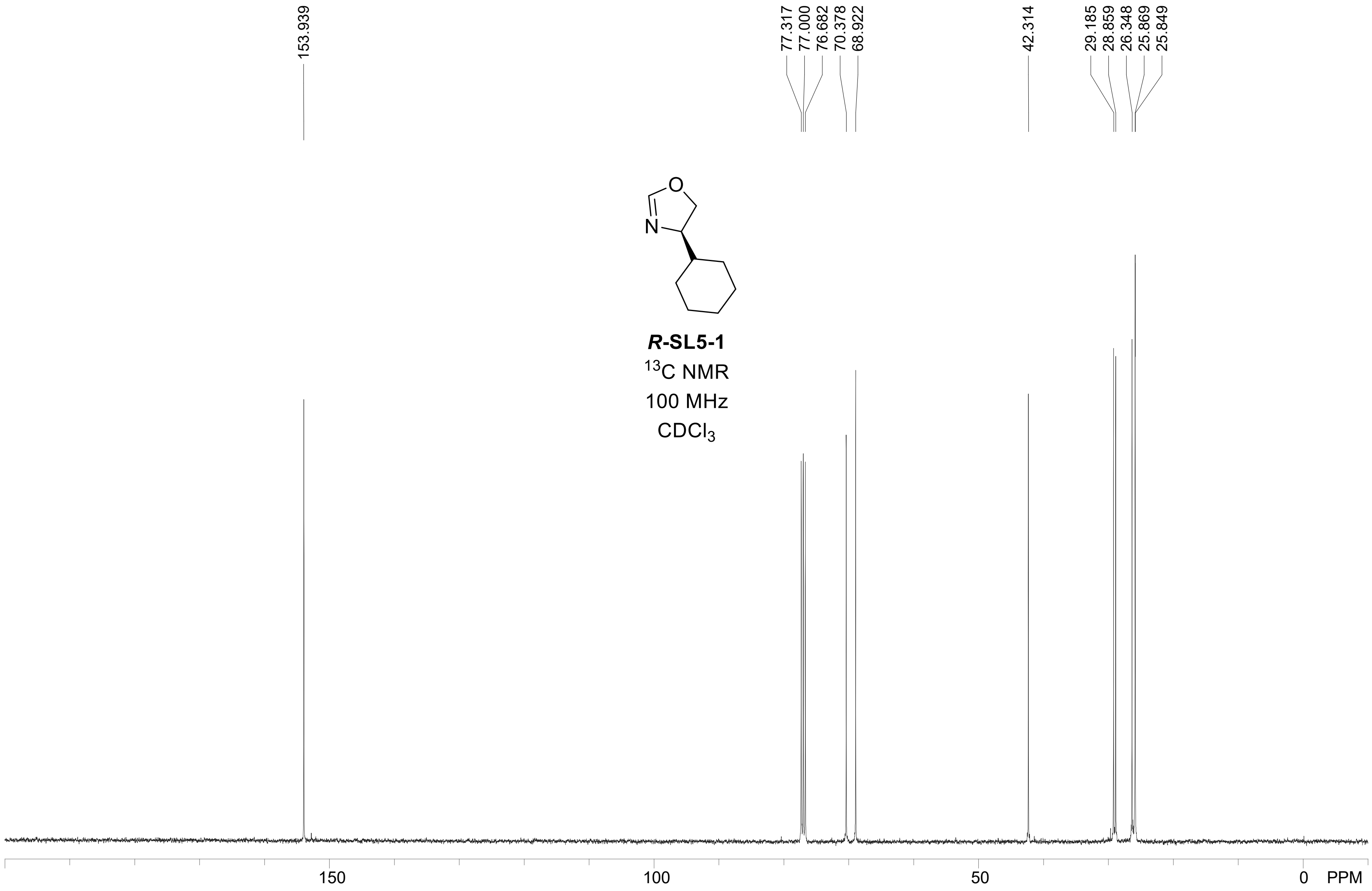


Figure S6. ^{13}C NMR spectra of ***R*-SL5-1**, Related to Table 1

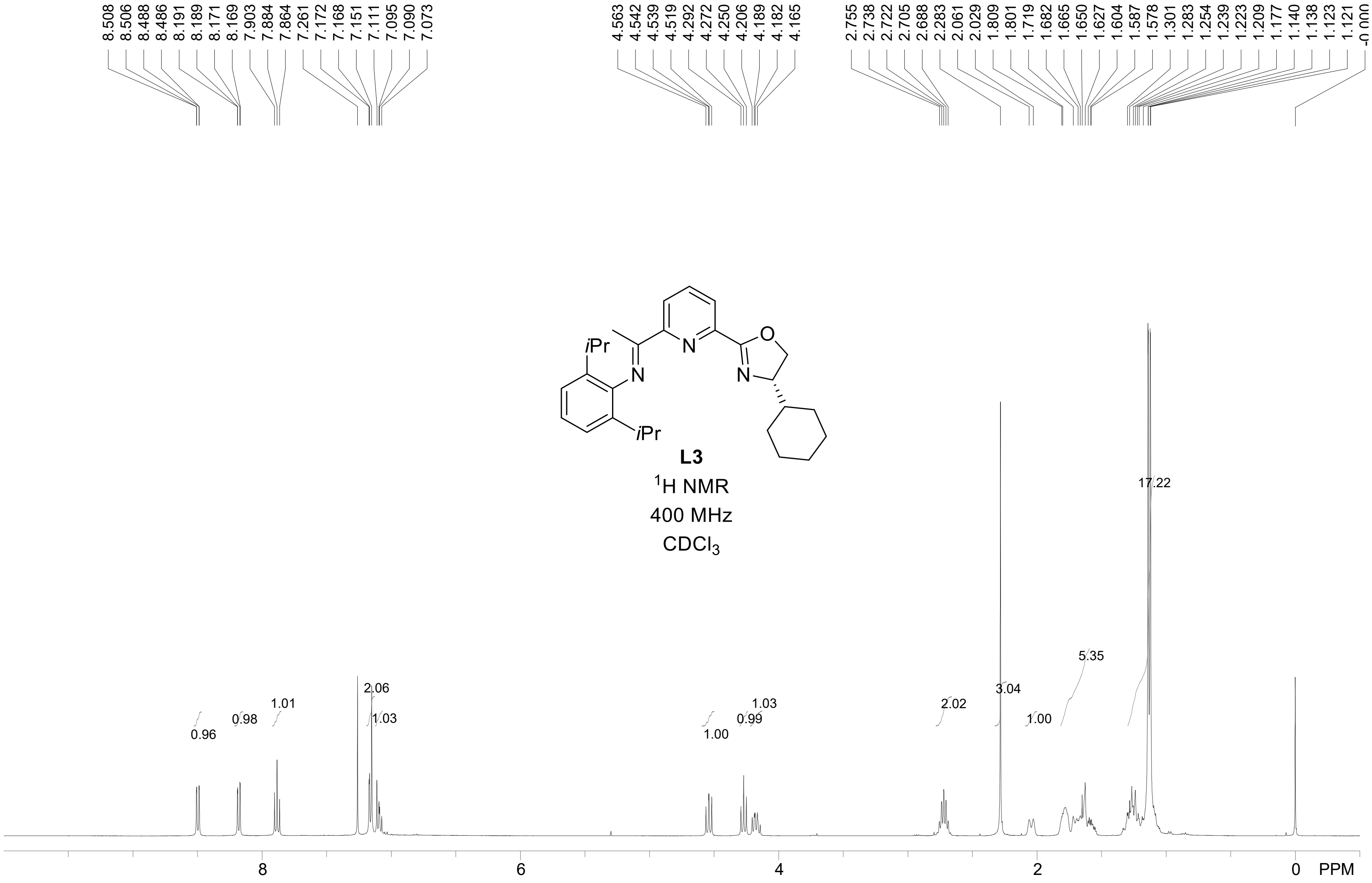


Figure S7. ^{1}H NMR spectra of **L3**, Related to Table 1

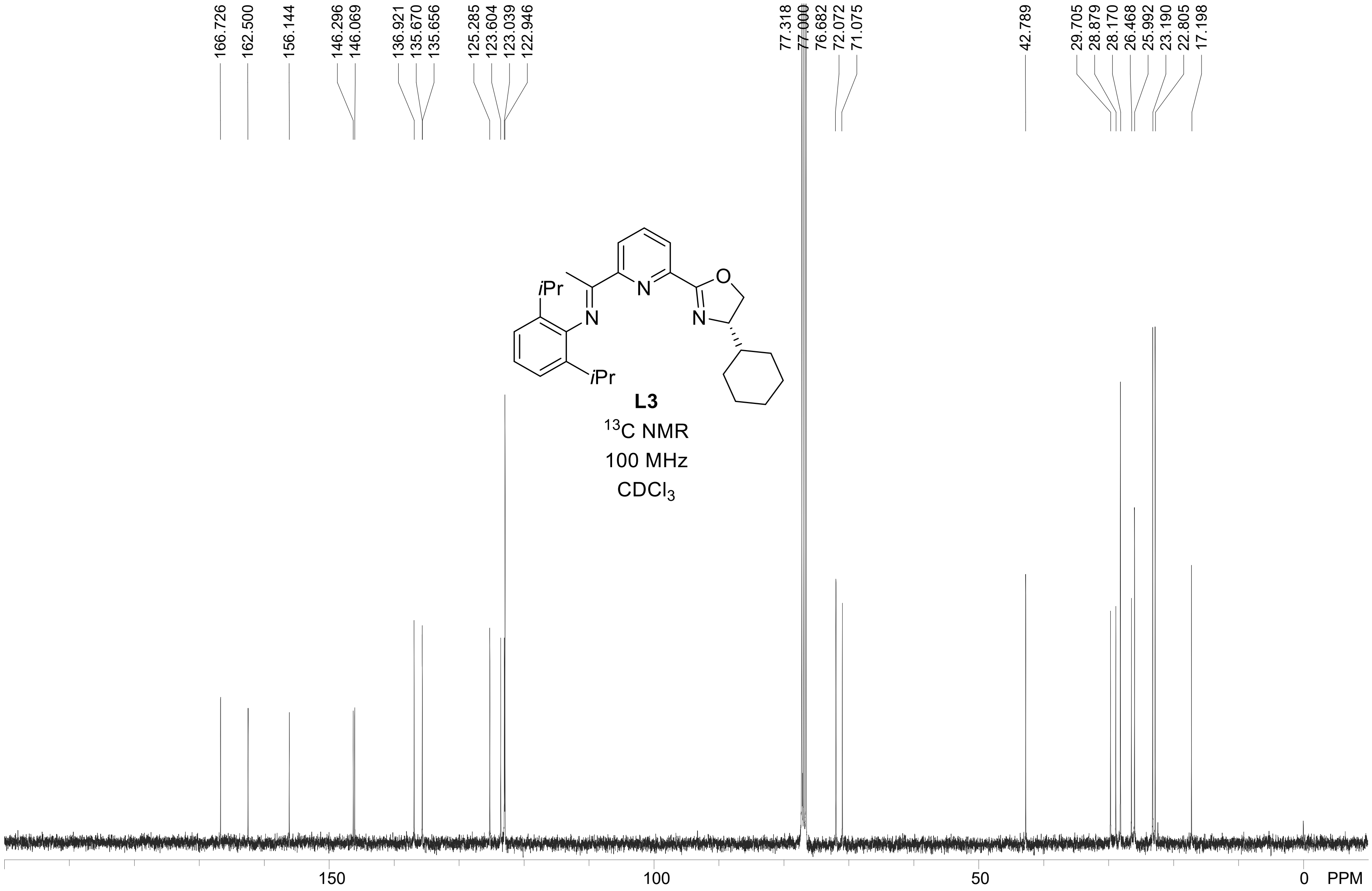


Figure S8. ^{13}C NMR spectra of **L3**, Related to Table 1

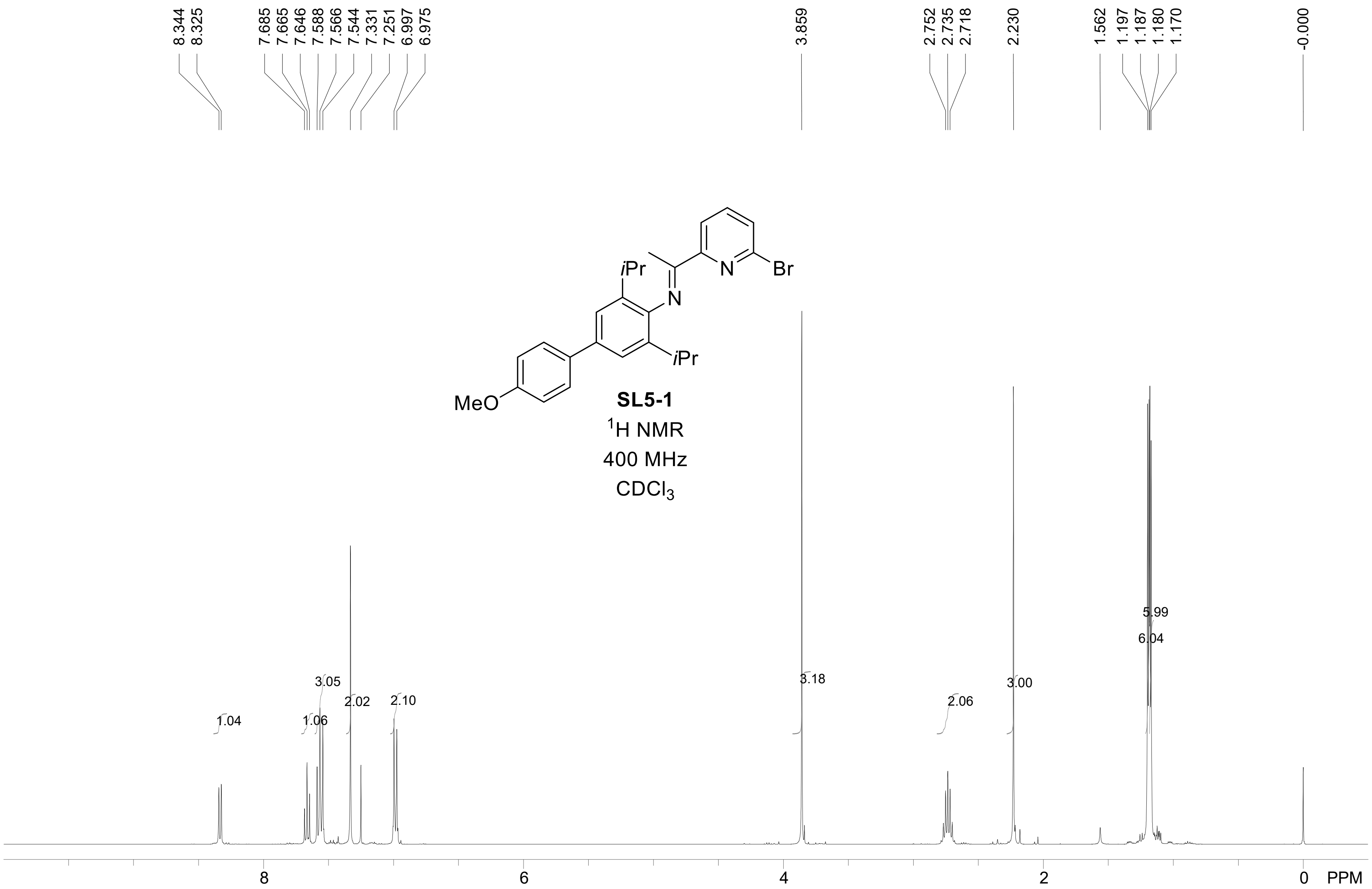


Figure S9. ^{1}H NMR spectra of **SL5-1**, Related to Table 1

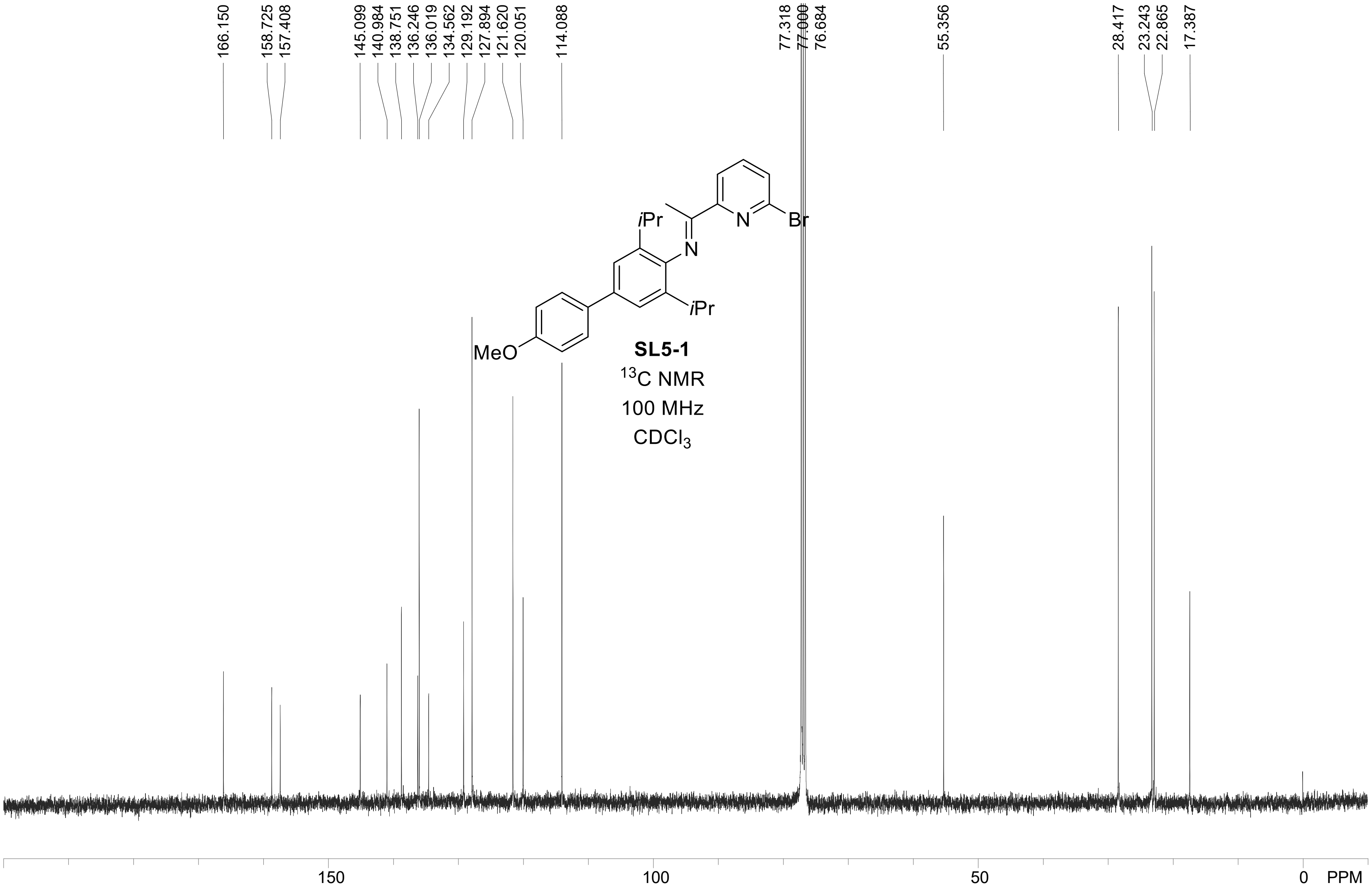


Figure S10. ^{13}C NMR spectra of **SL5-1**, Related to Table 1

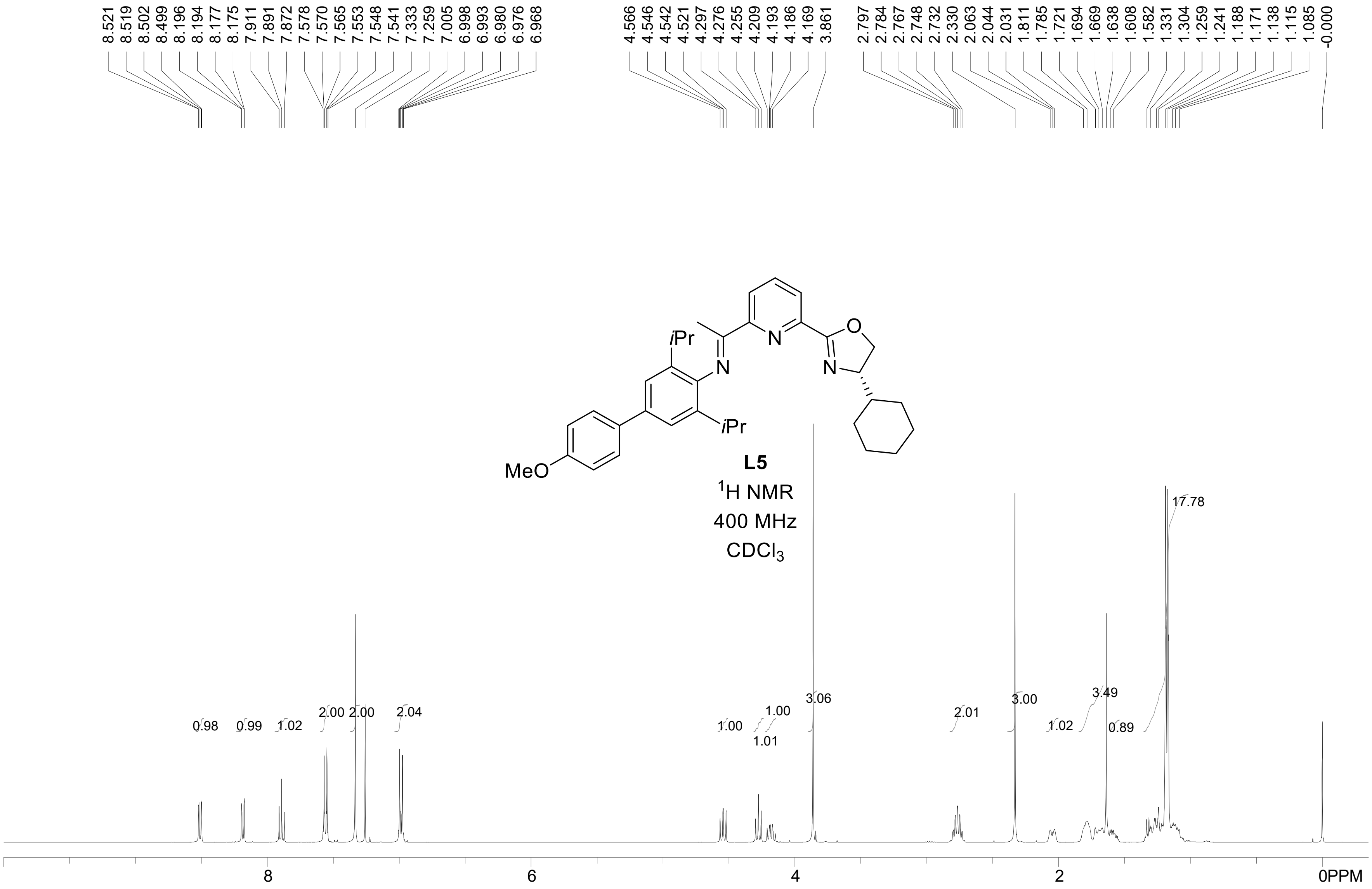


Figure S11. ^{1}H NMR spectra of **L5**, Related to Table 1

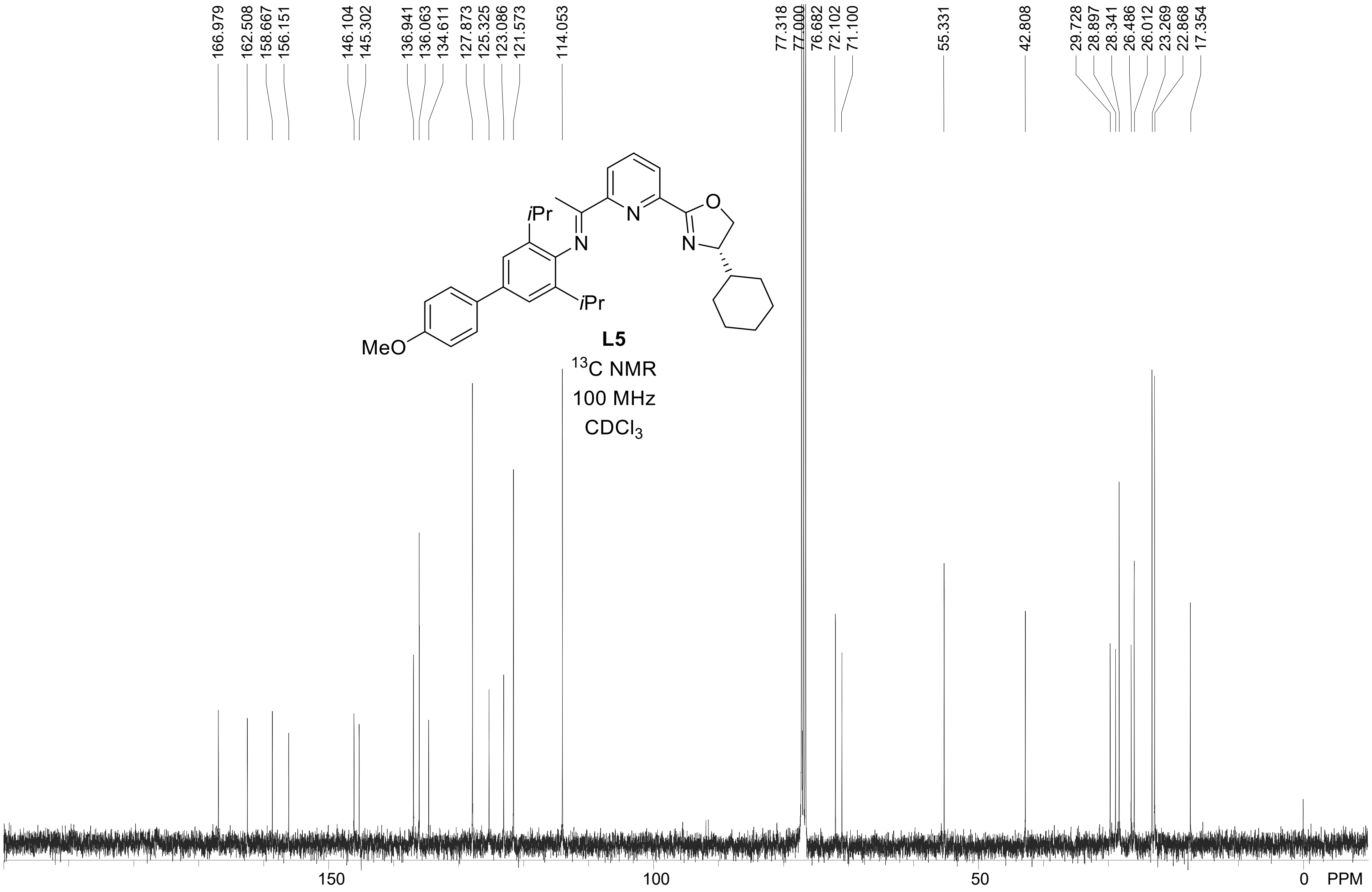


Figure S12. ^{13}C NMR spectra of **L5**, Related to Table 1

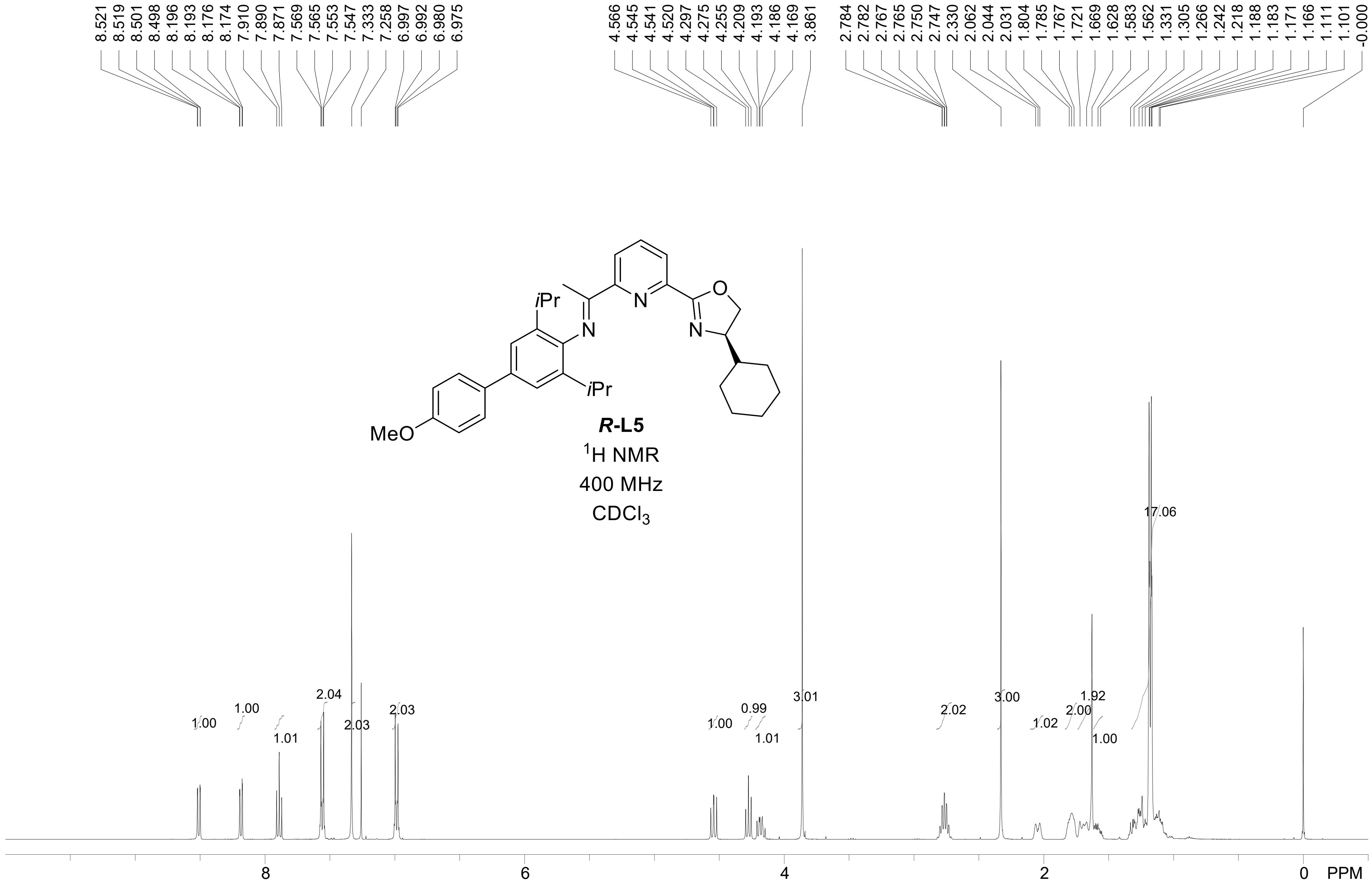


Figure S13. ^{1}H NMR spectra of ***R*-L5**, Related to Scheme 2

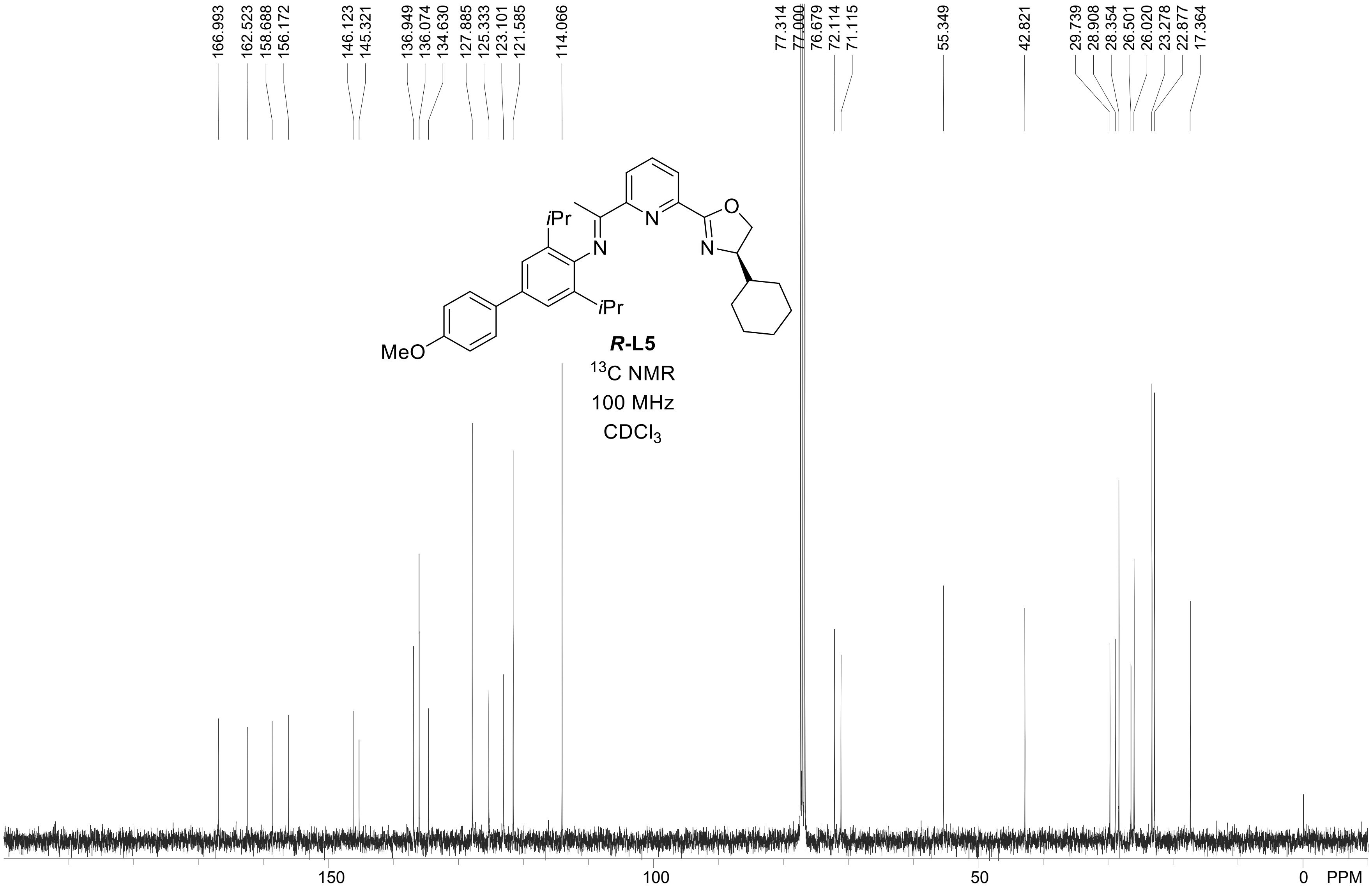


Figure S14. ^{13}C NMR spectra of ***R*-L5**, Related to Scheme 2

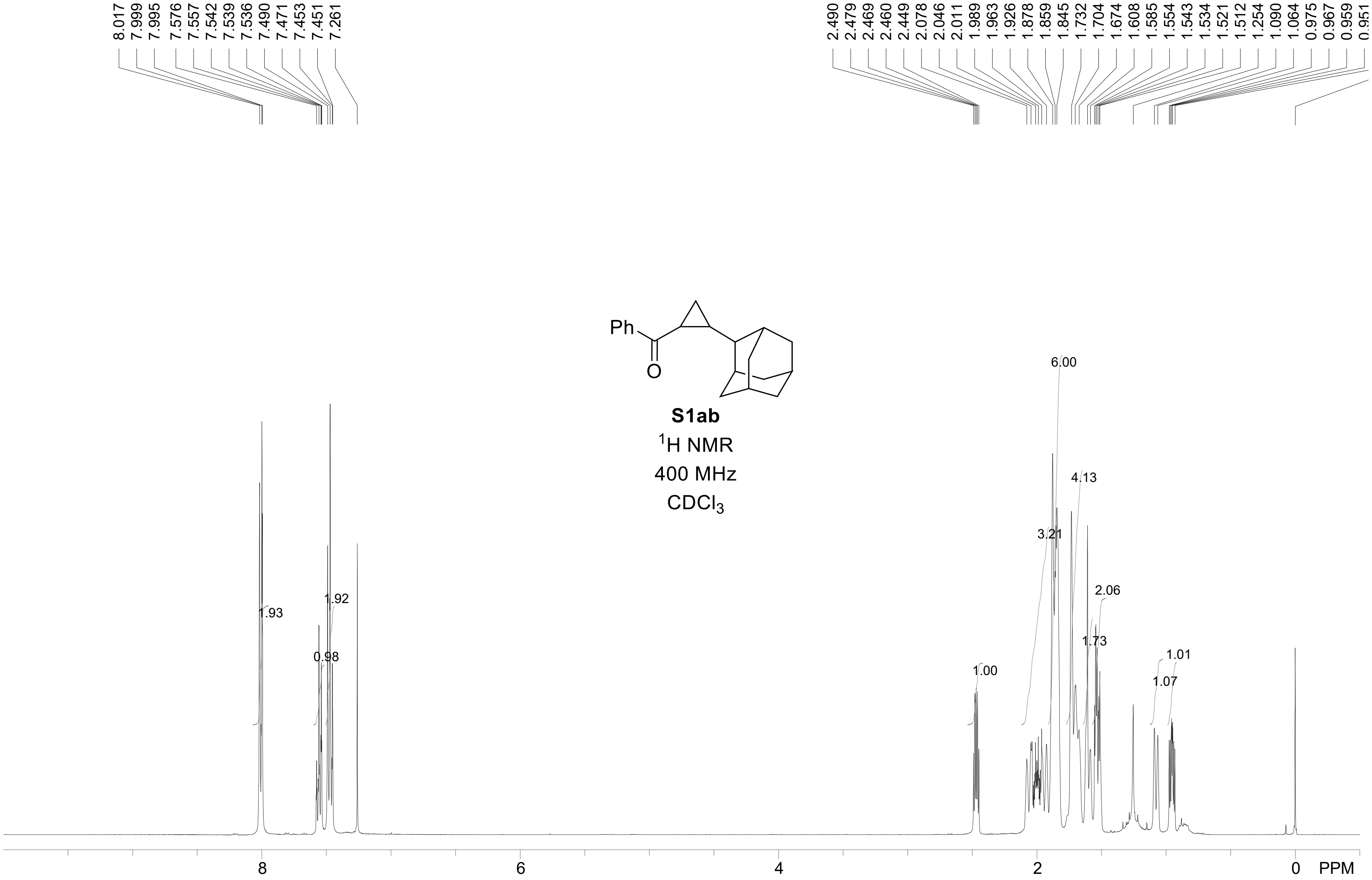


Figure S15. ^{1}H NMR spectra of **S1ab**, Related to Table 2

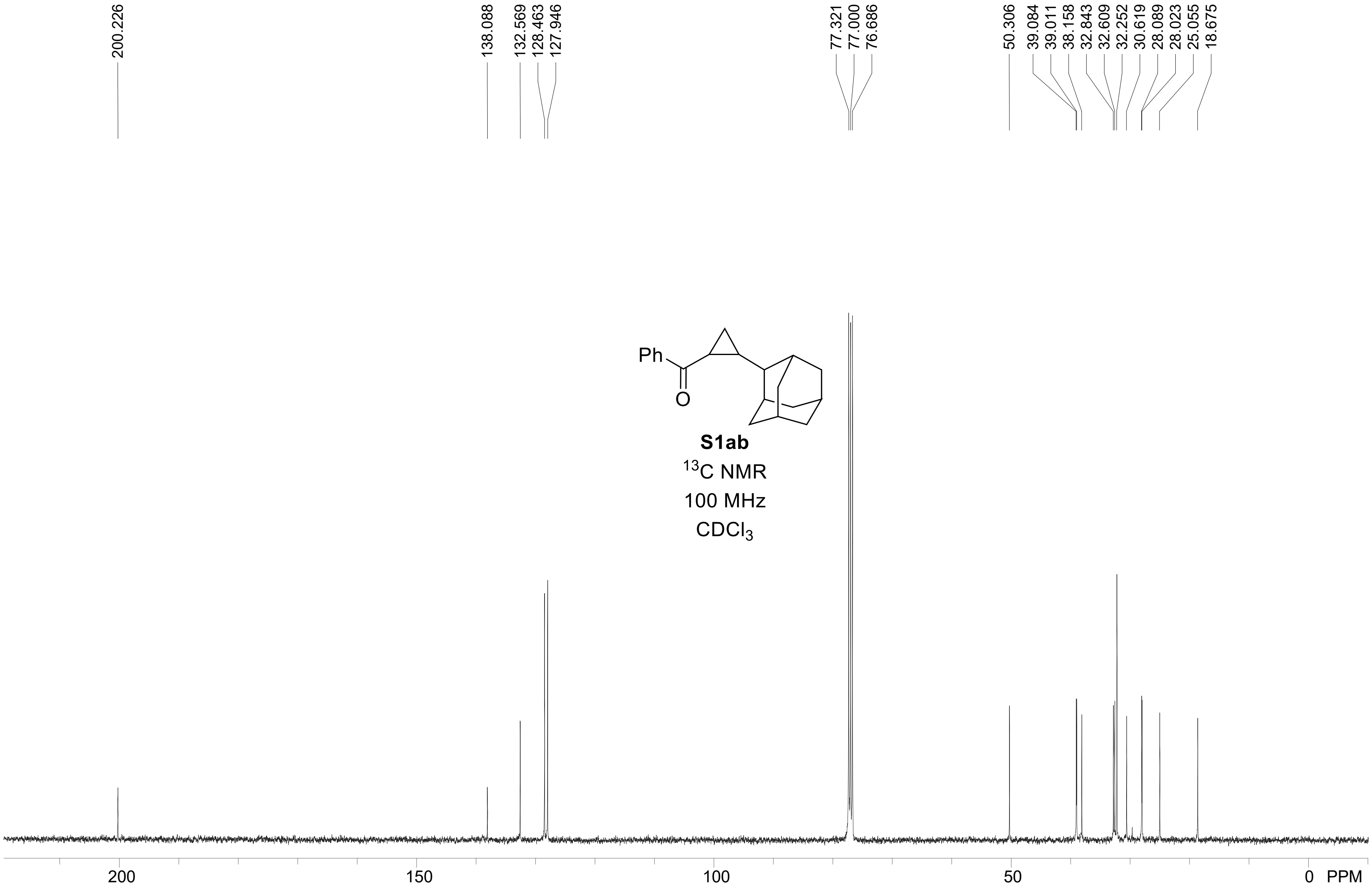


Figure S16. ^{13}C NMR spectra of **S1ab**, Related to Table 2

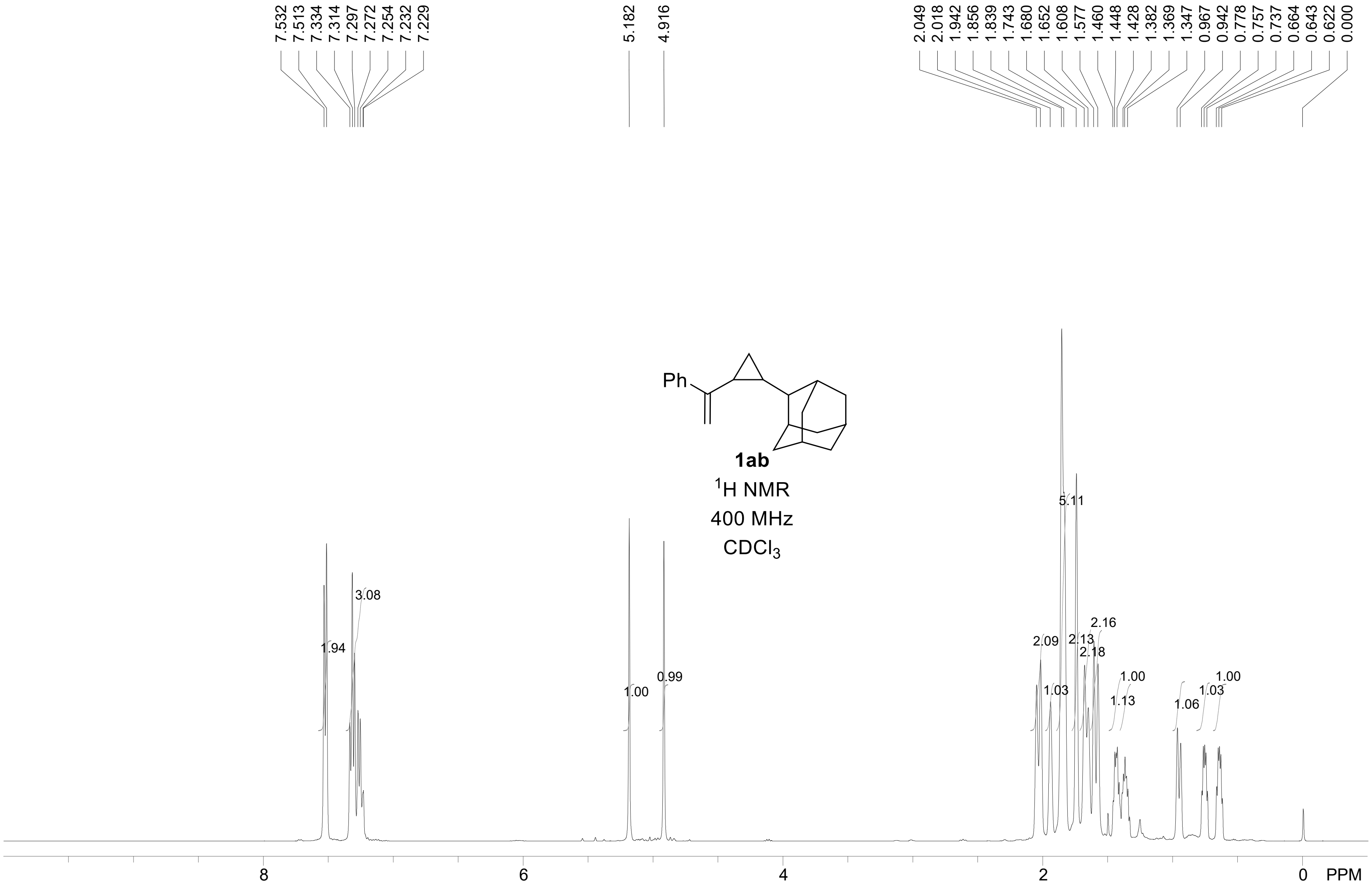


Figure S17. ^{1}H NMR spectra of **1ab**, Related to Table 2

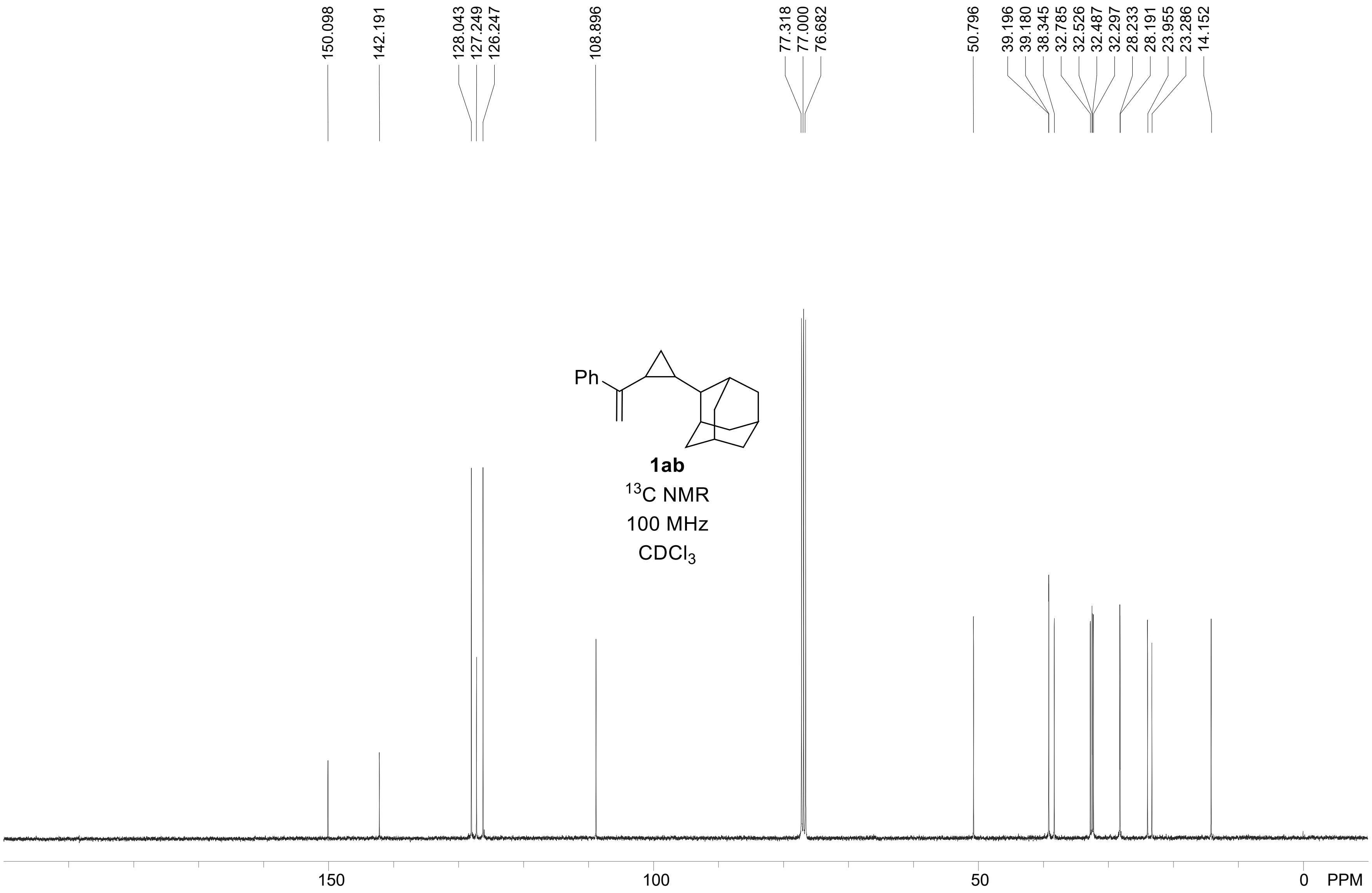


Figure S18. ^{13}C NMR spectra of **1ab**, Related to Table 2

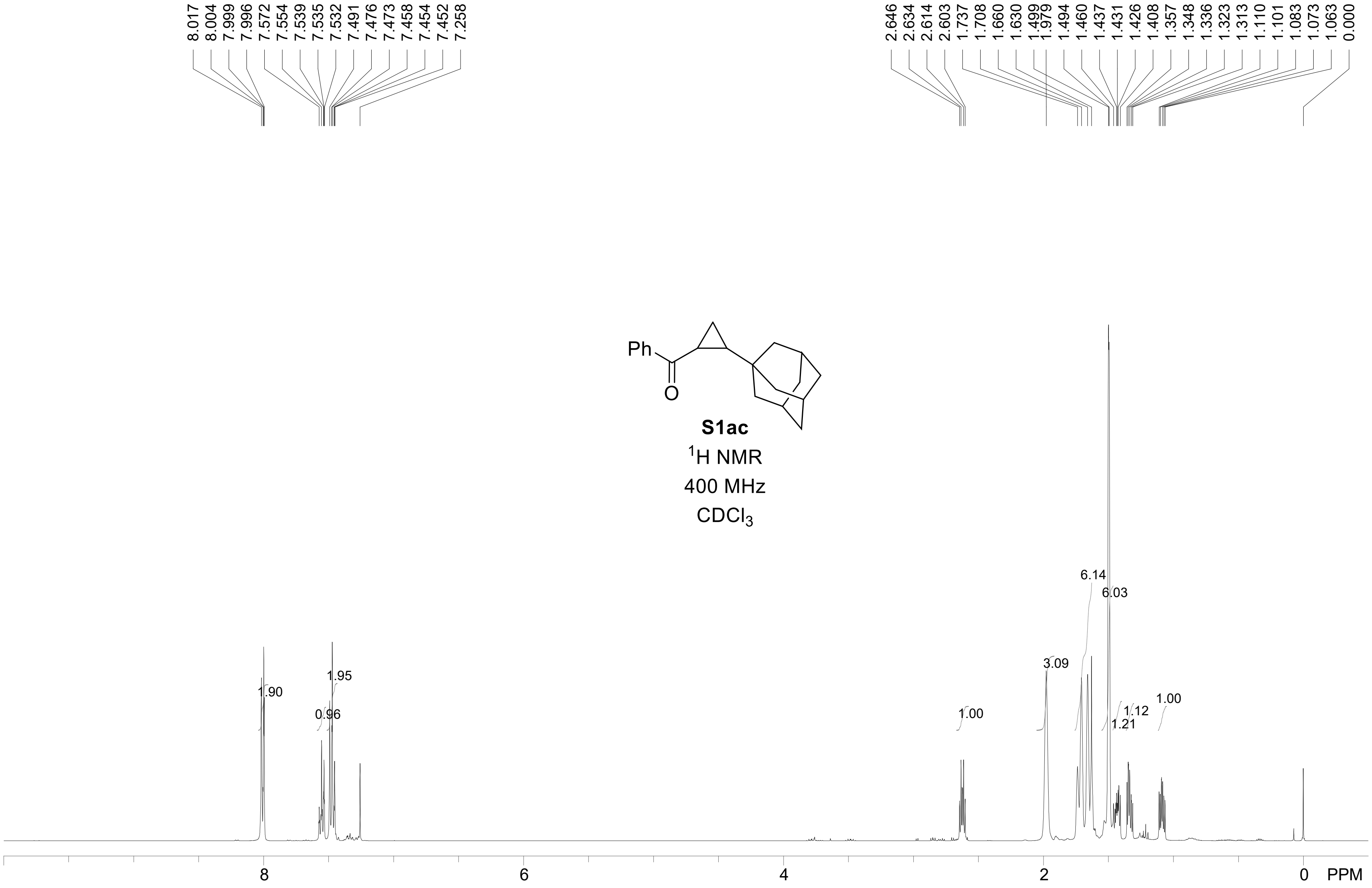


Figure S19. ^{1}H NMR spectra of **S1ac**, Related to Table 2

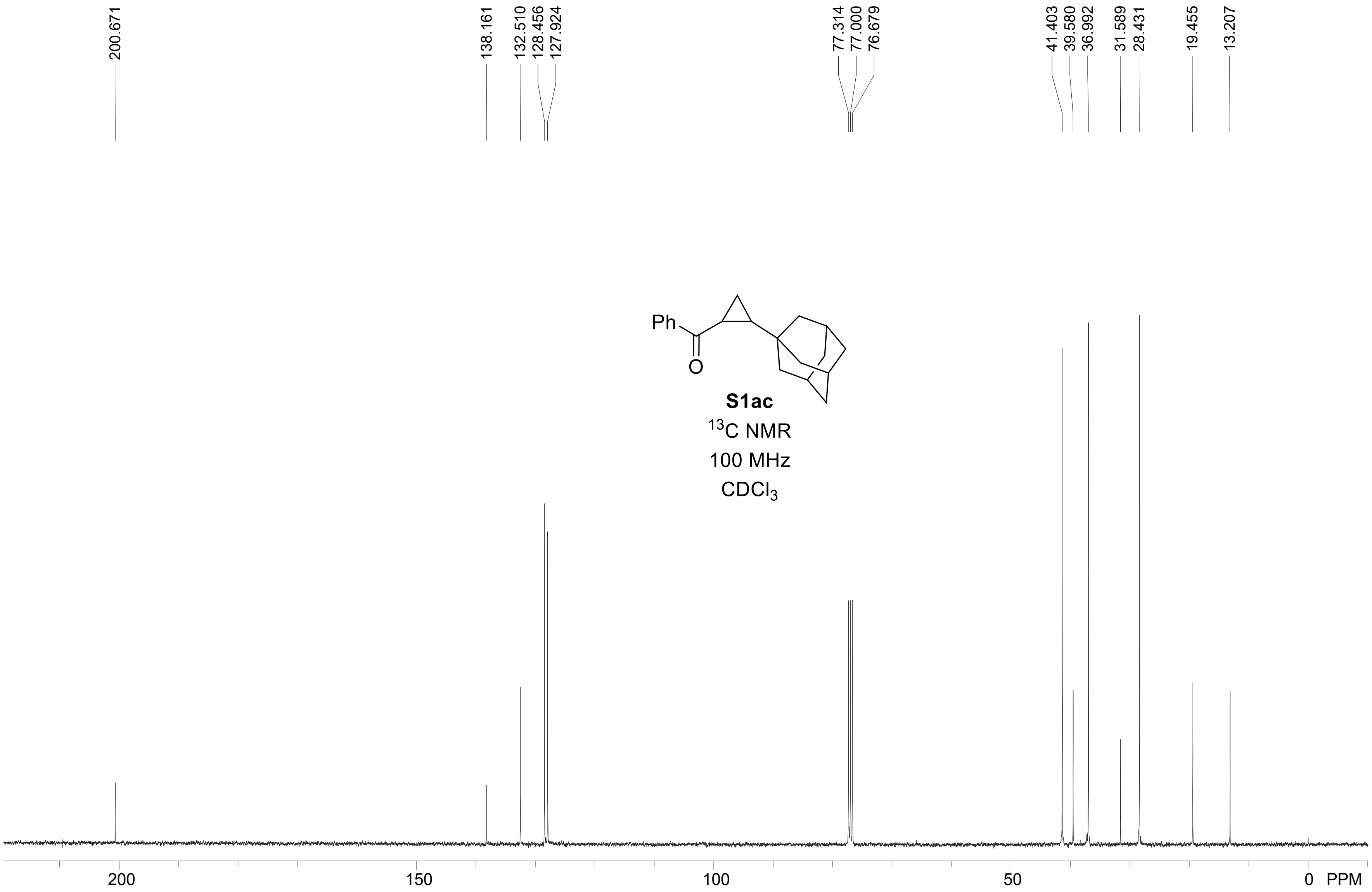


Figure S20. ^{13}C NMR spectra of **S1ac**, Related to Table 2

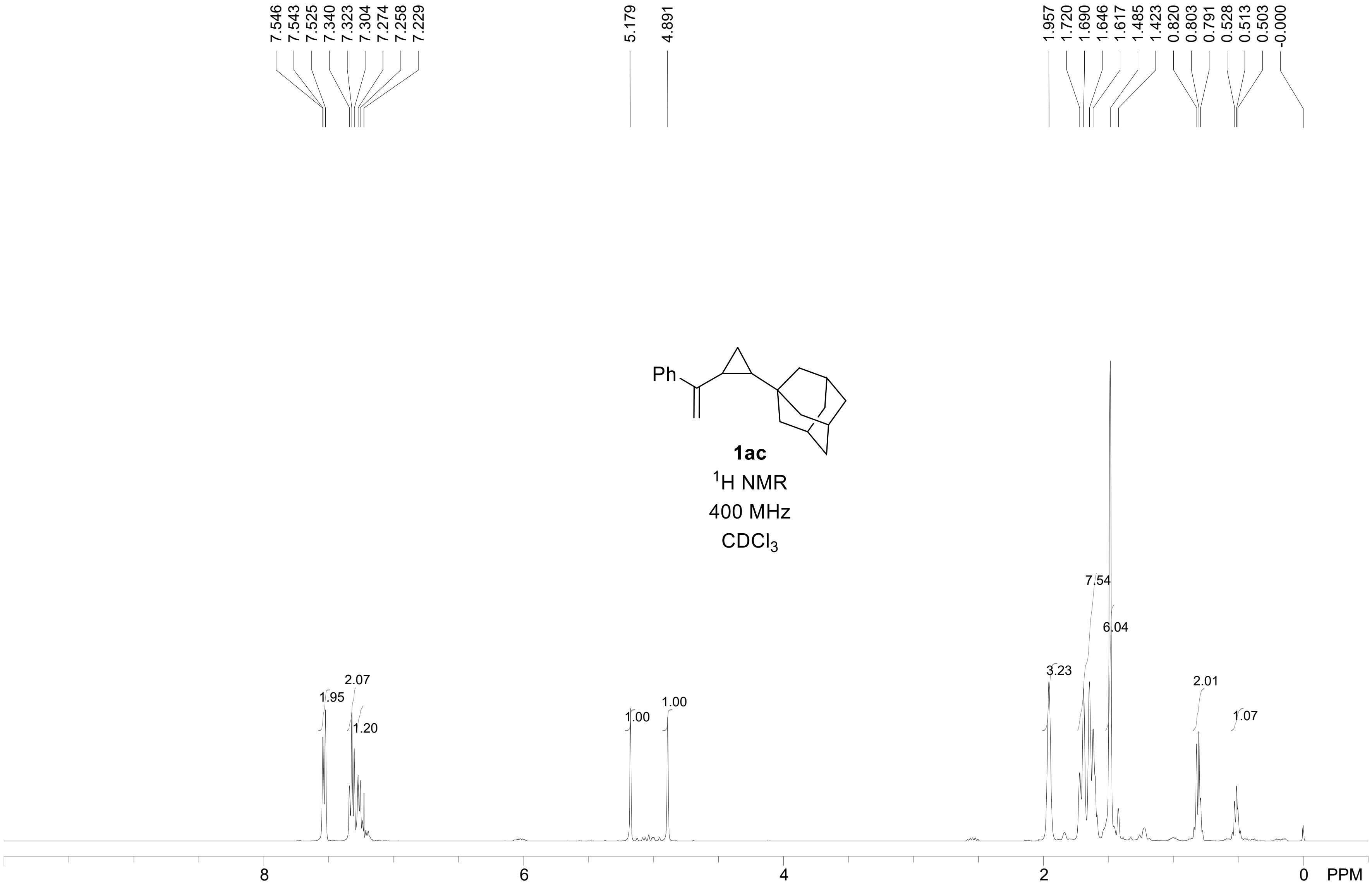


Figure S21. ^{1}H NMR spectra of **1ac**, Related to Table 2

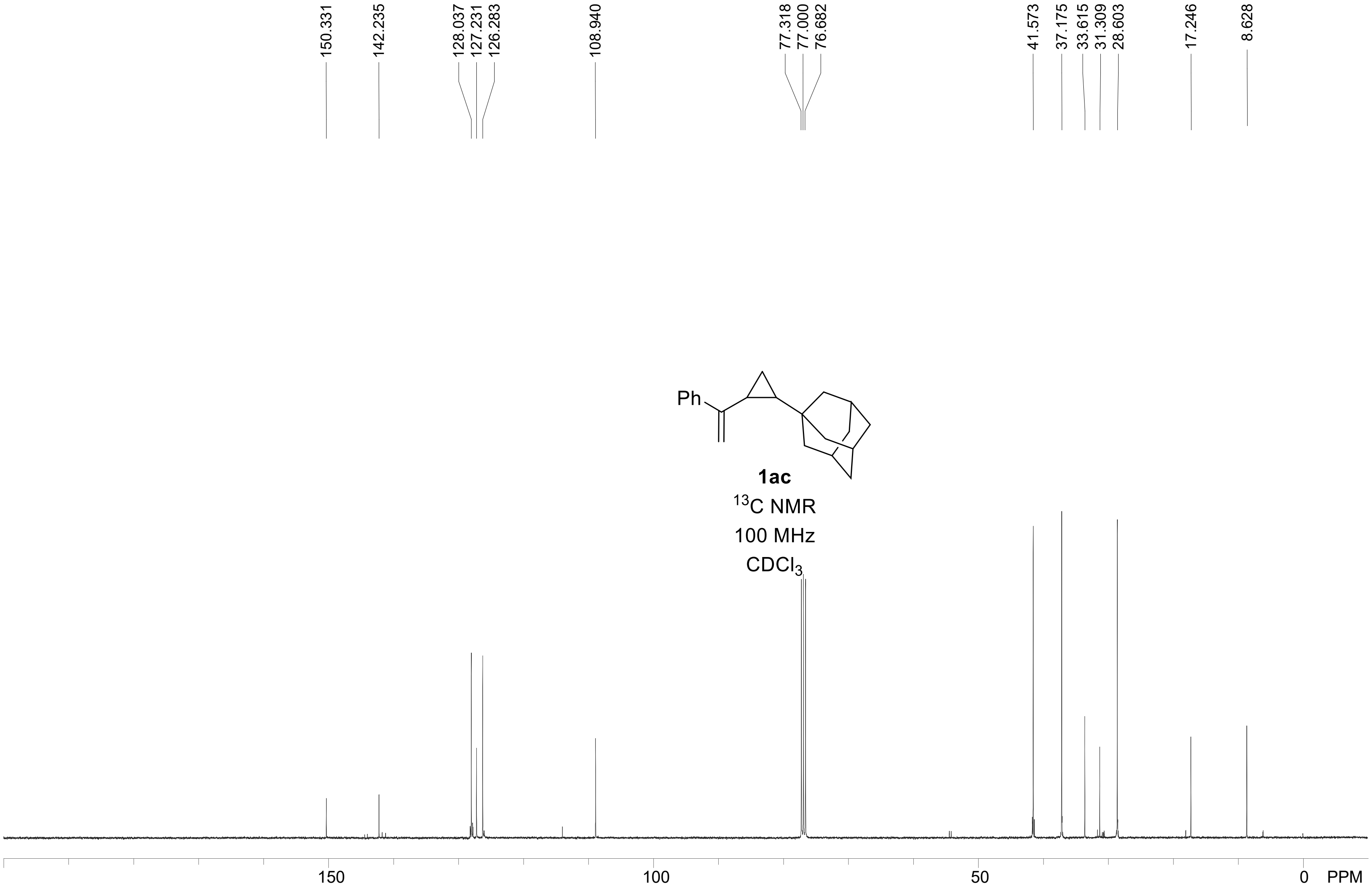


Figure S22. ^{13}C NMR spectra of **1ac**, Related to Table 2

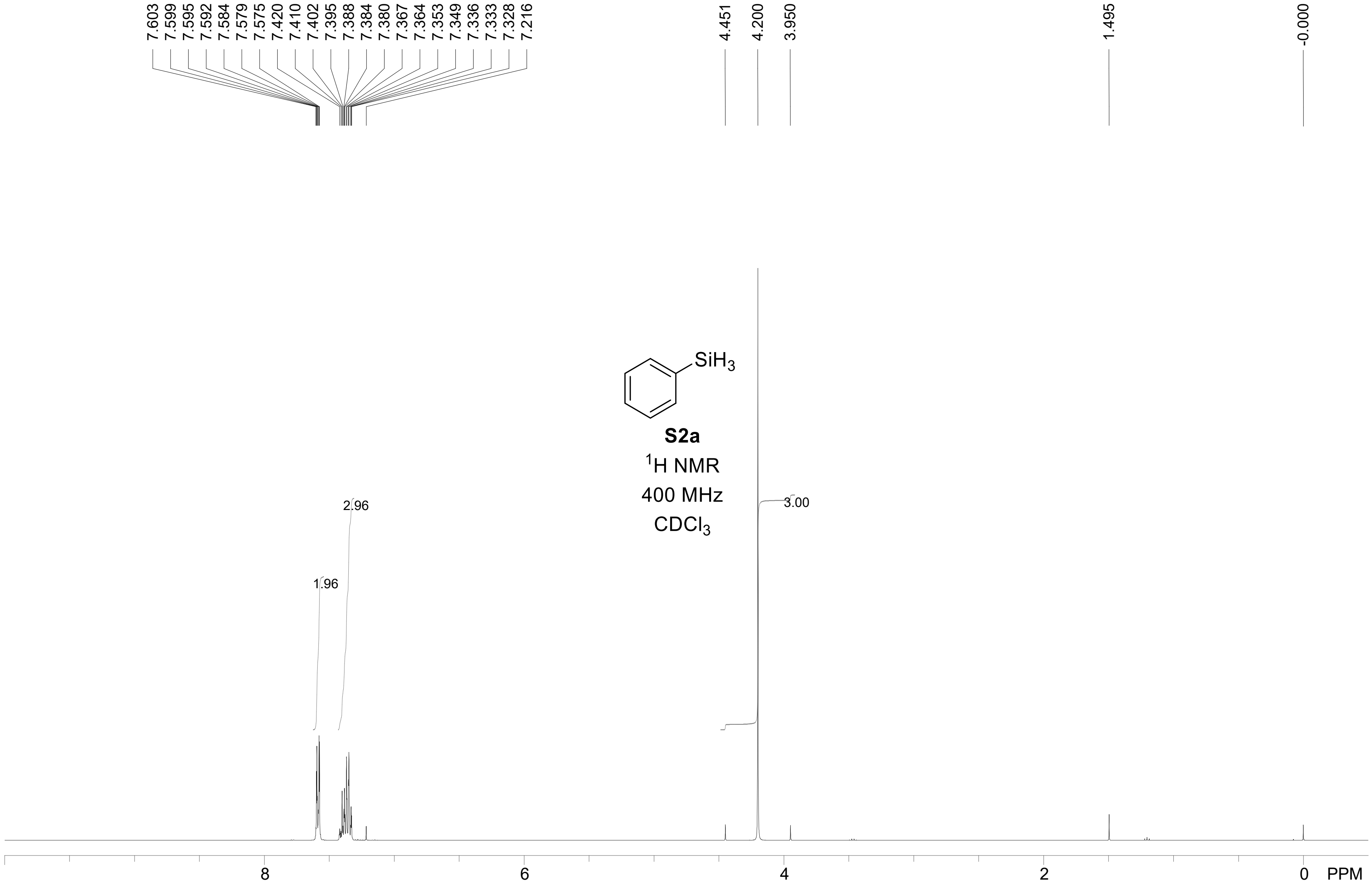


Figure S23. ^{1}H NMR spectra of **S2a**, Related to Table 2

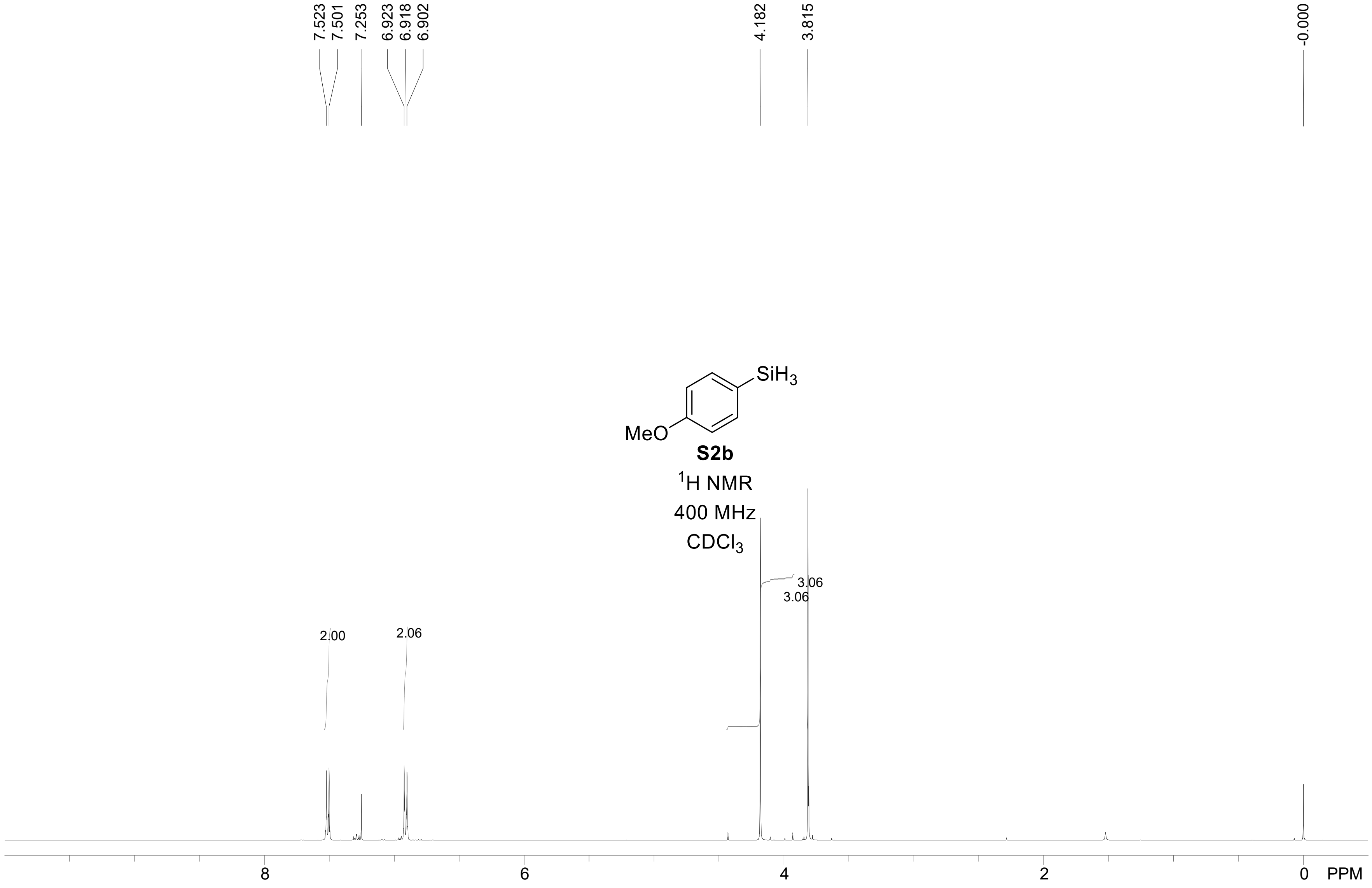


Figure S24. ^{1}H NMR spectra of **S2b**, Related to Table 2

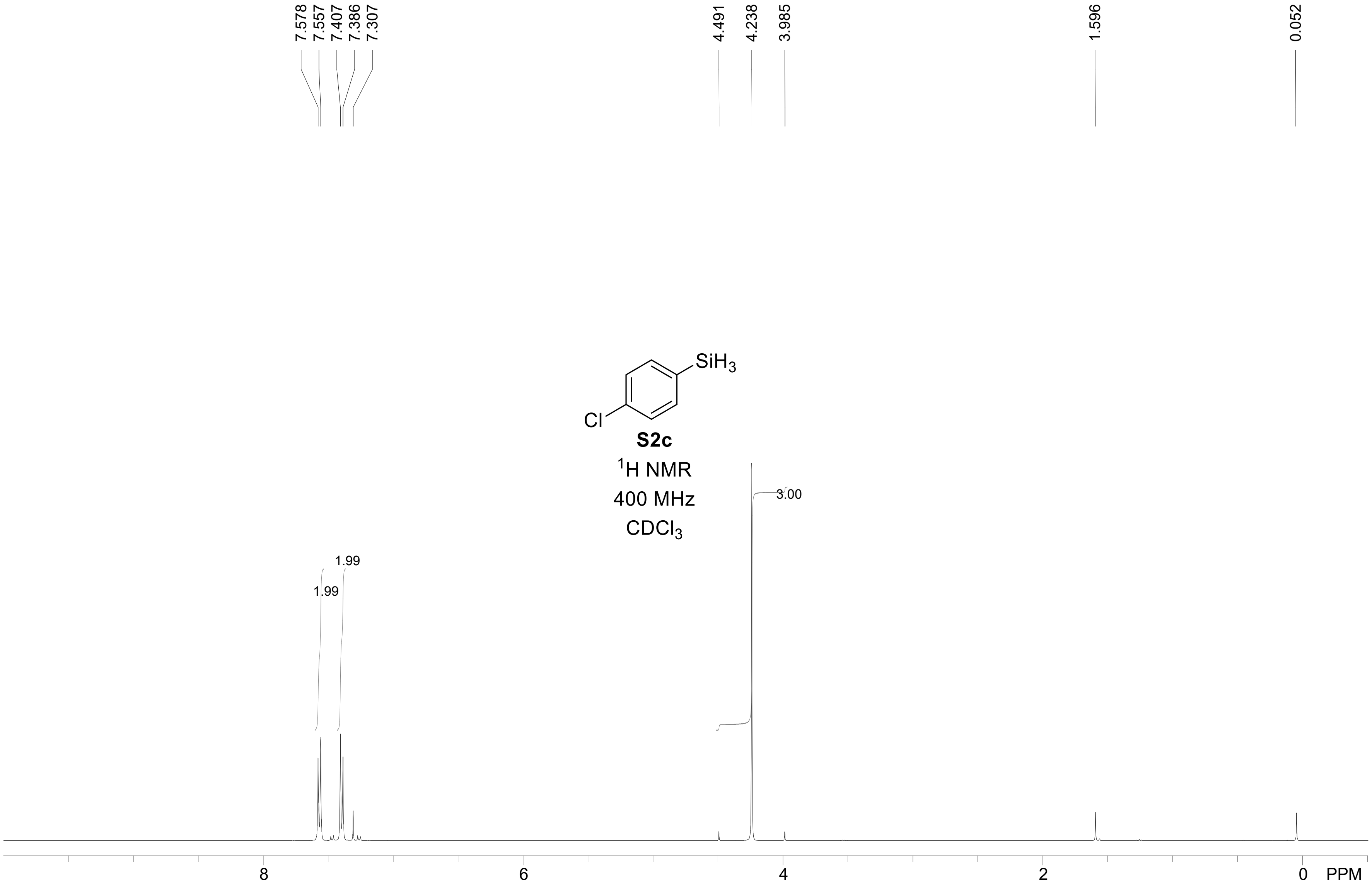


Figure S25. ^{1}H NMR spectra of **S2c**, Related to Table 2

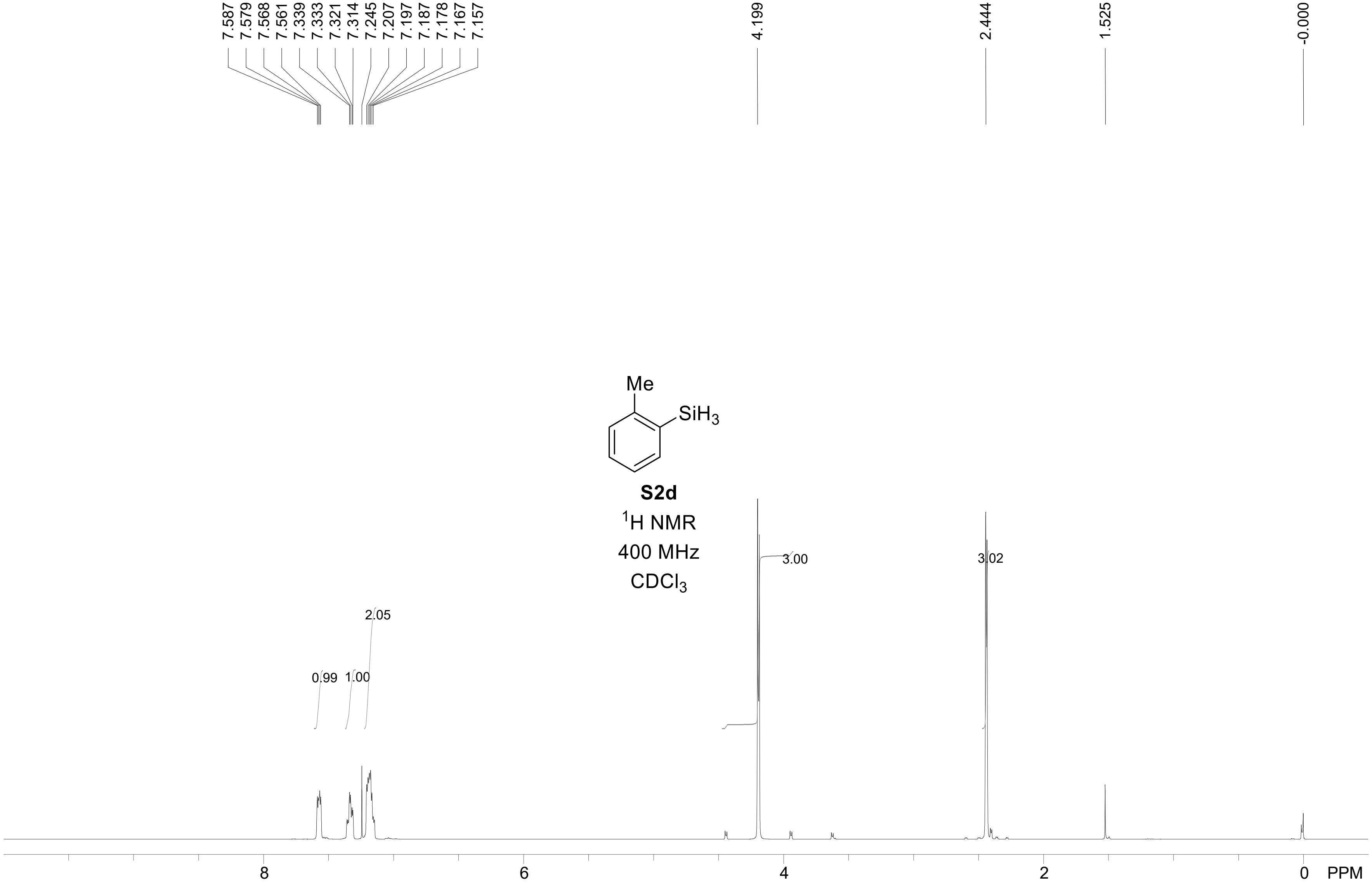


Figure S26. ^{1}H NMR spectra of **S2d**, Related to Table 2

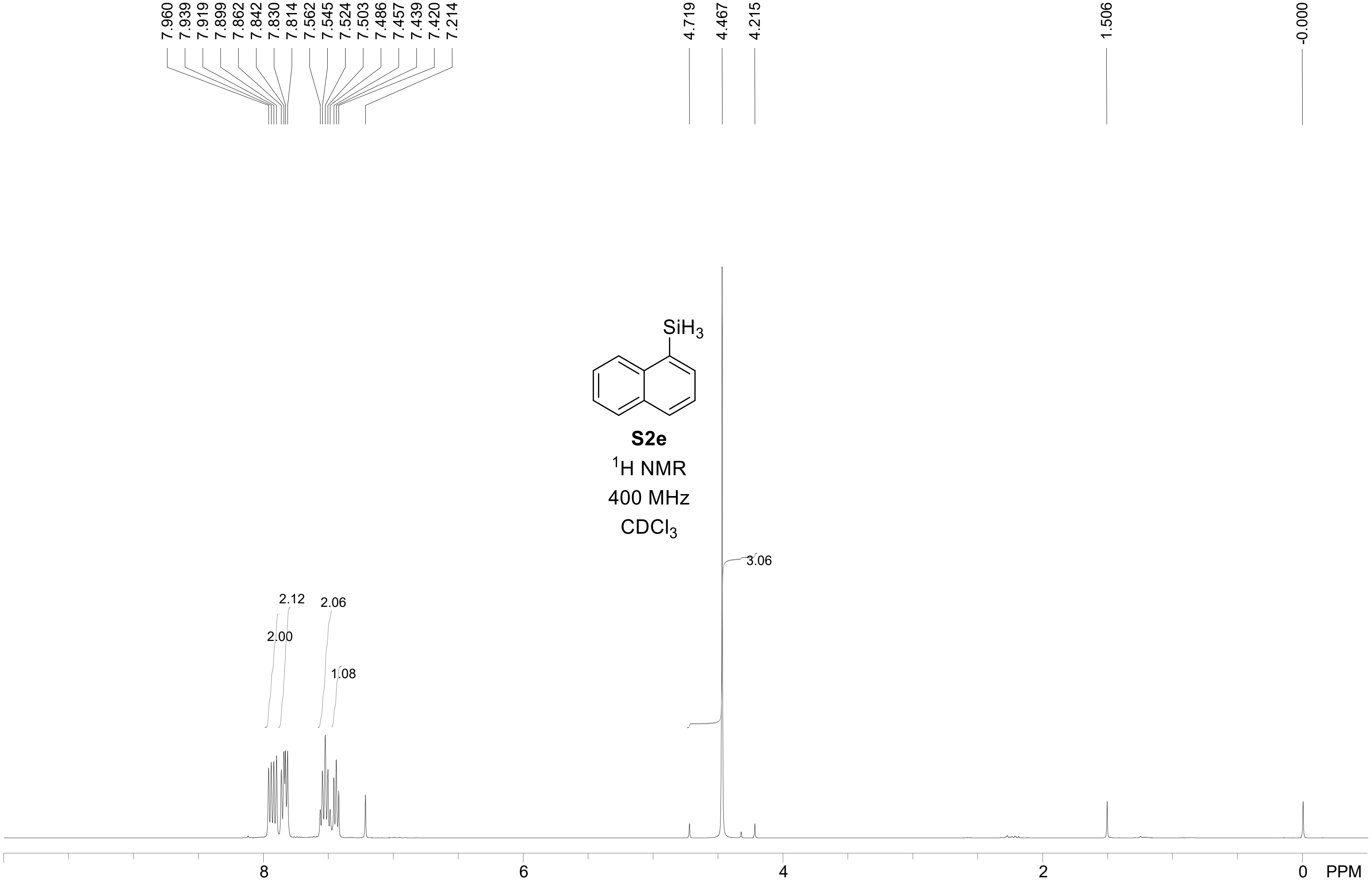


Figure S27. ^{1}H NMR spectra of **S2e**, Related to Table 2

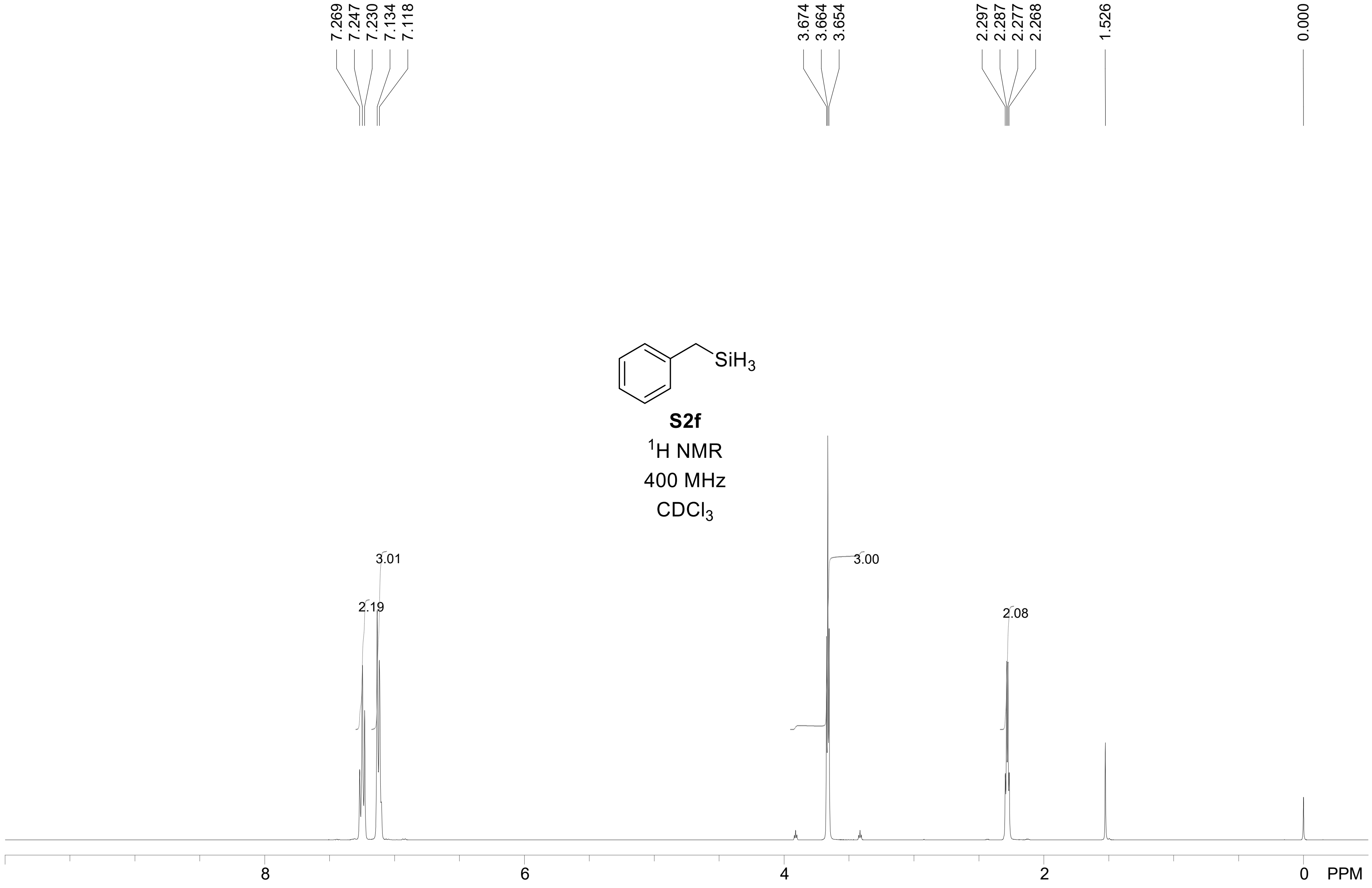


Figure S28. ^{1}H NMR spectra of **S2f**, Related to Table 2

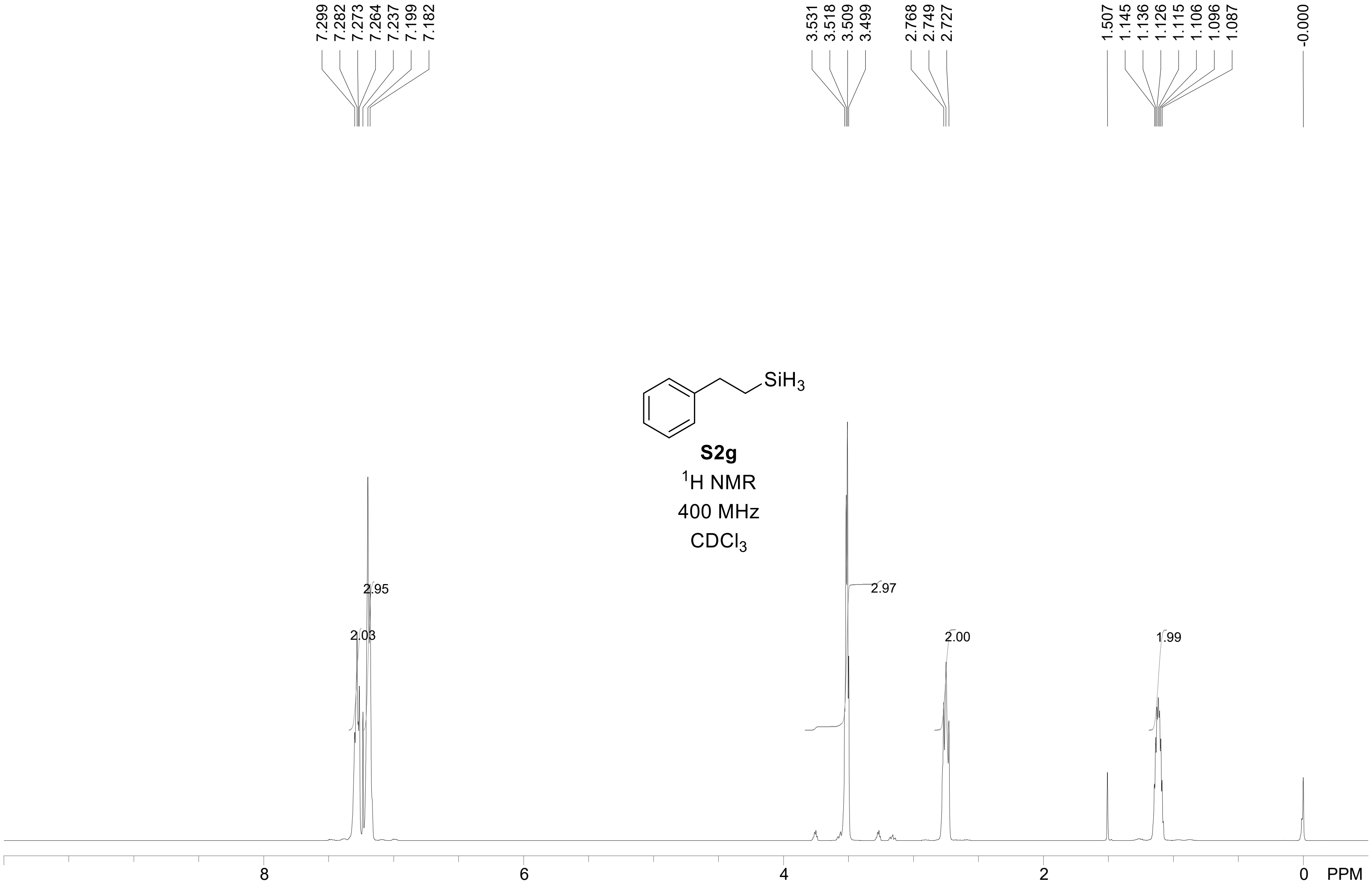


Figure S29. ^{1}H NMR spectra of **S2g**, Related to Table 2

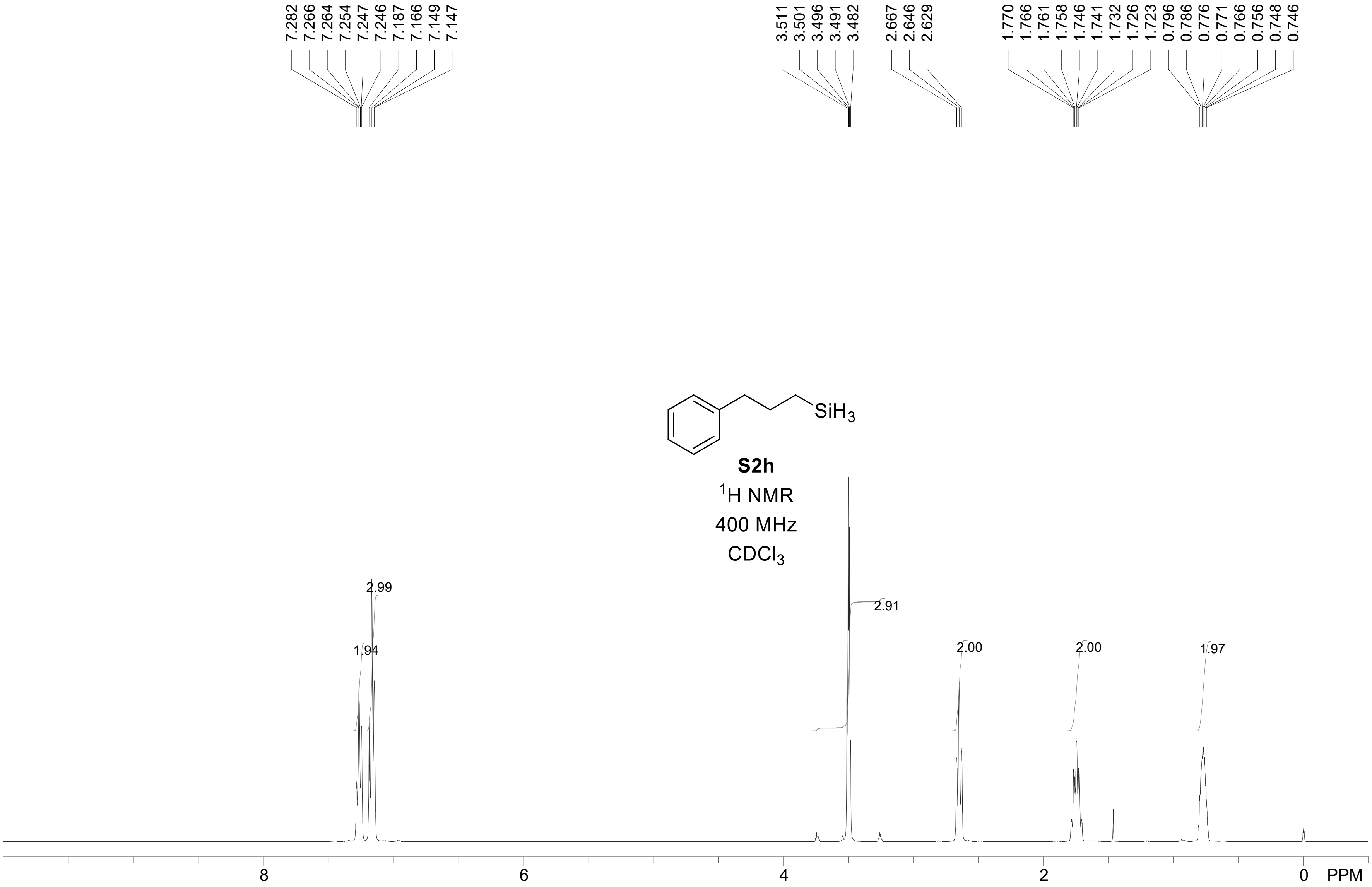


Figure S30. ^{1}H NMR spectra of **S2h**, Related to Table 2

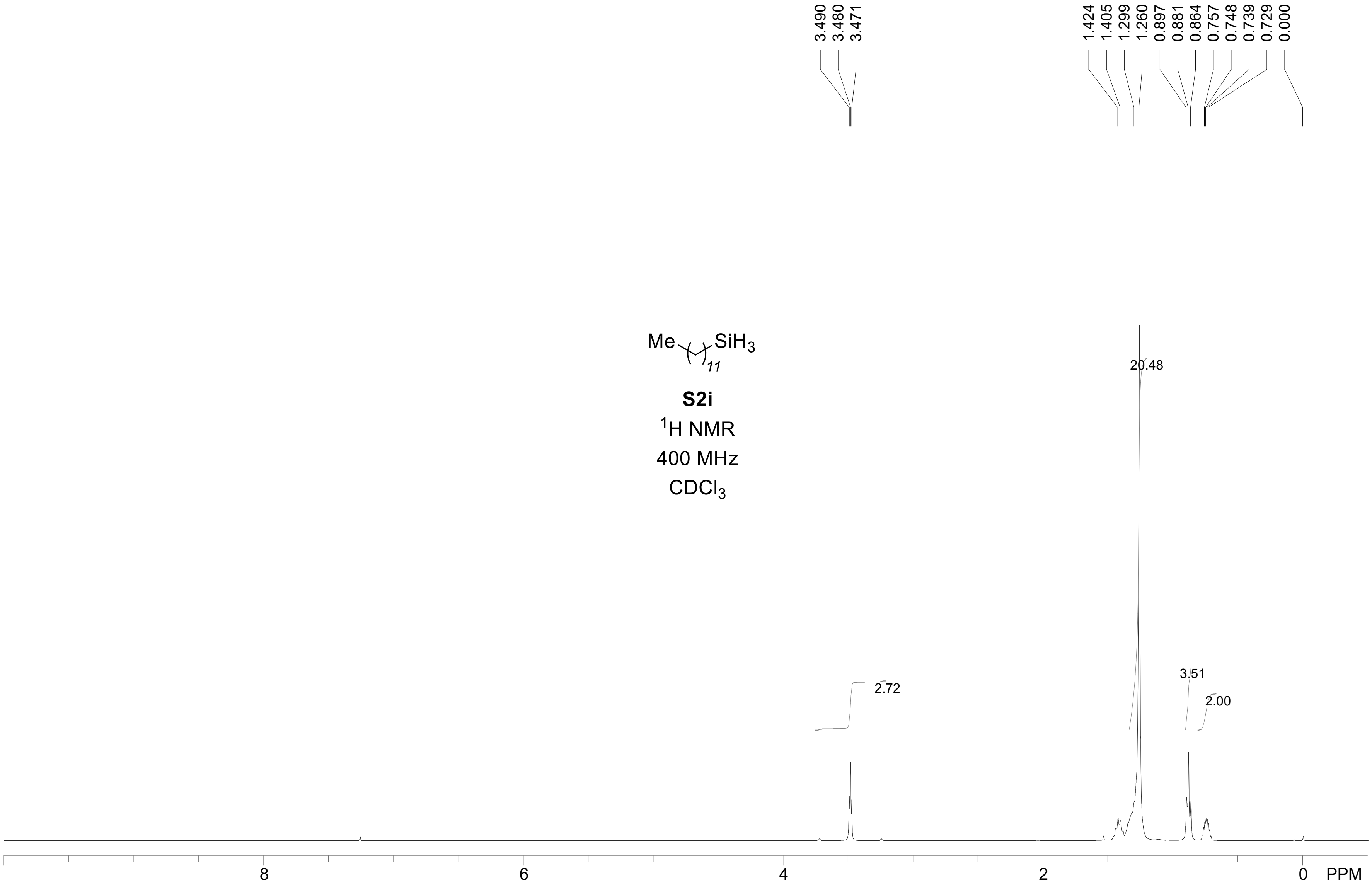


Figure S31. ^{1}H NMR spectra of **S2i**, Related to Table 2

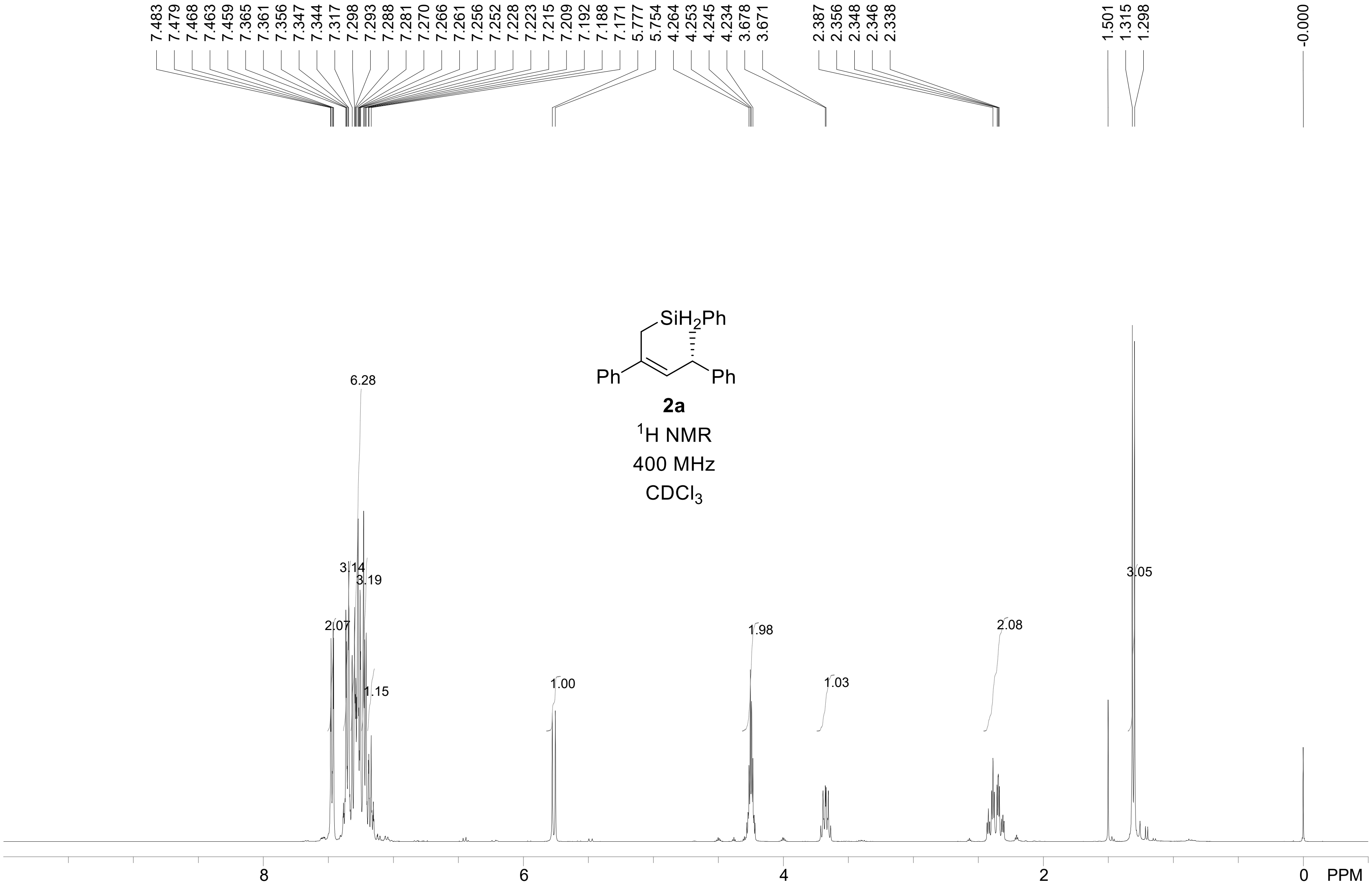


Figure S32. ^{1}H NMR spectra of **2a**, Related to Table 1

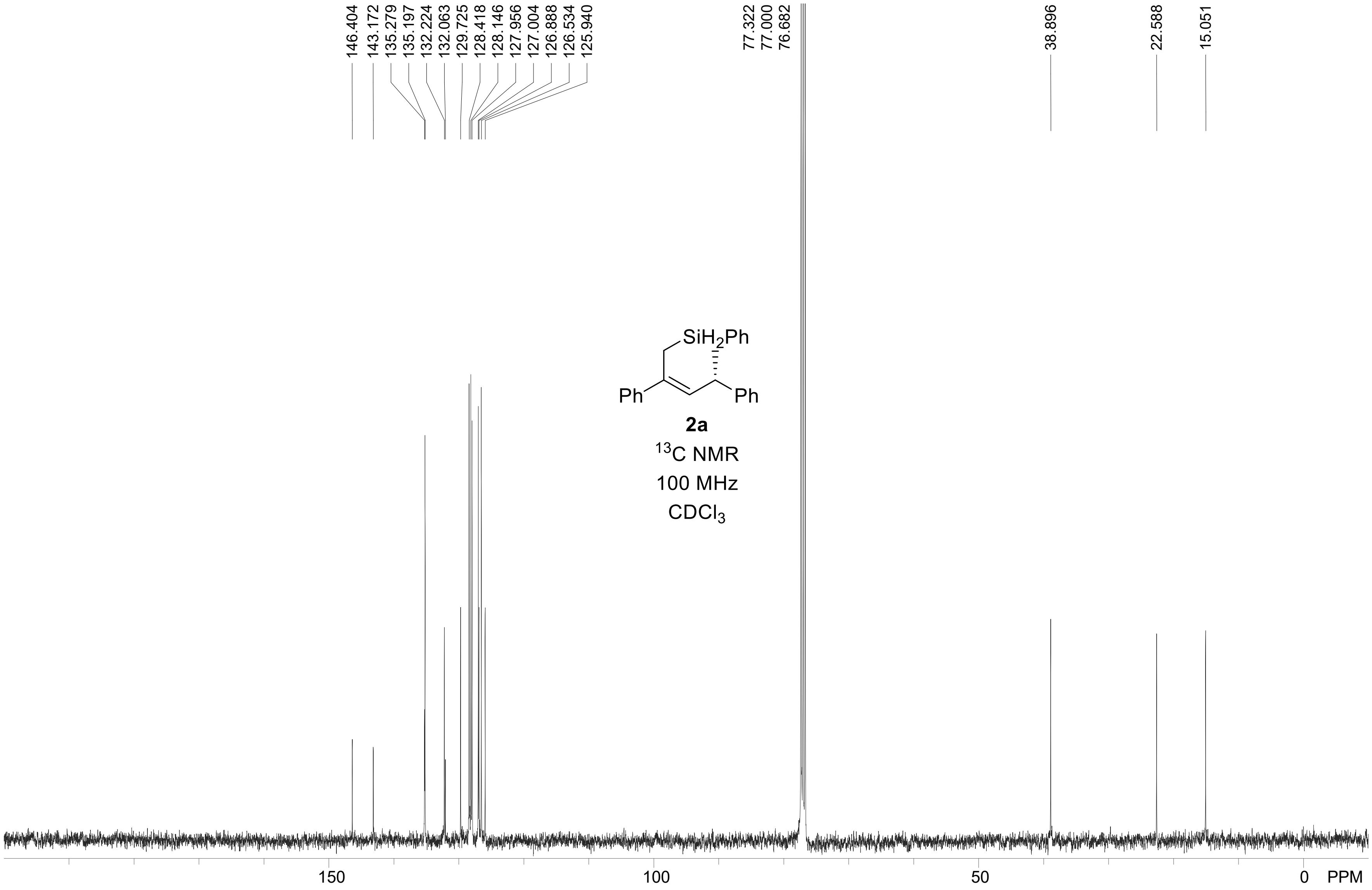


Figure S33. ^{13}C NMR spectra of **2a**, Related to Table 1

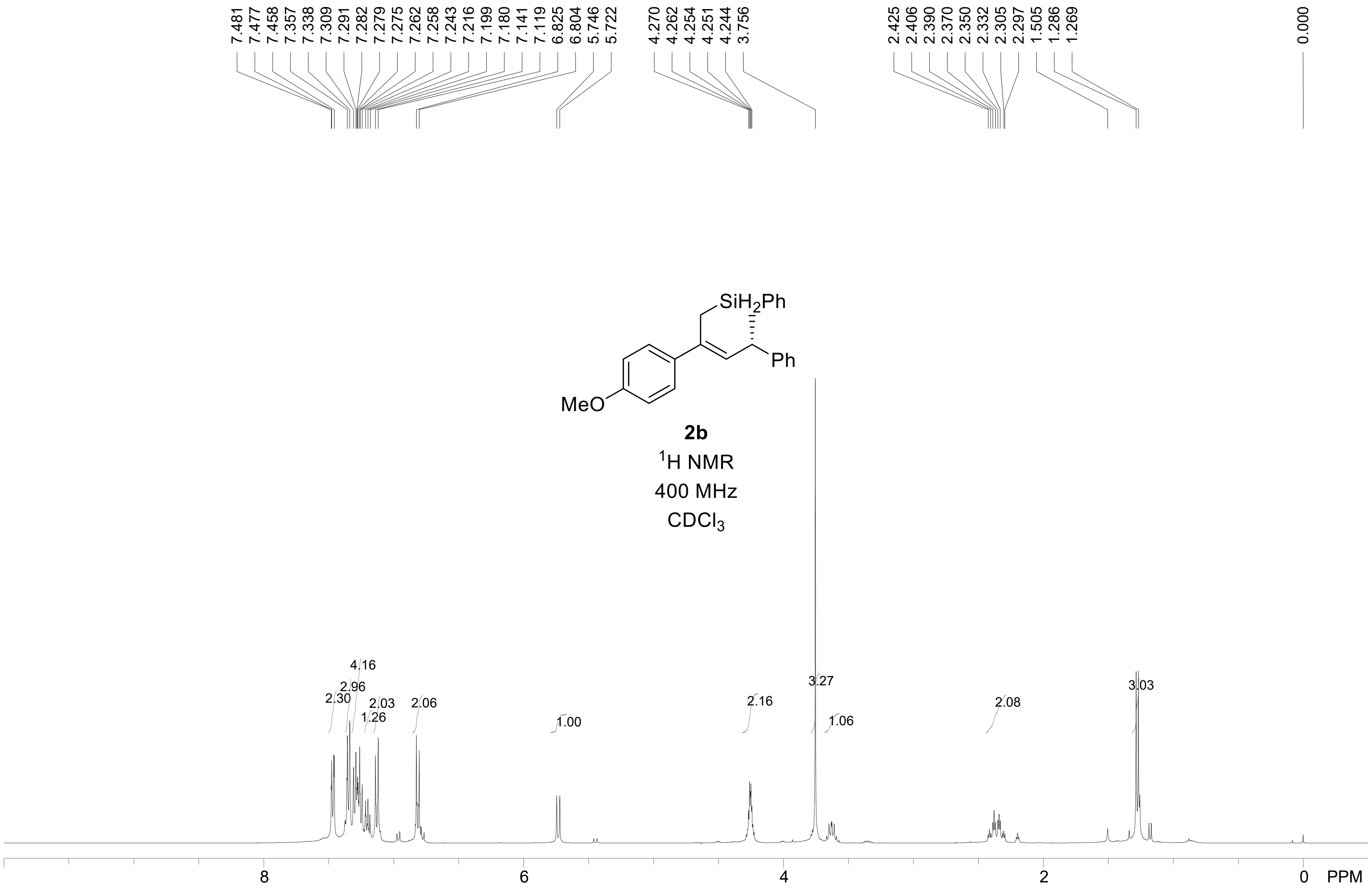


Figure S34. ^{1}H NMR spectra of **2b**, Related to Table 2

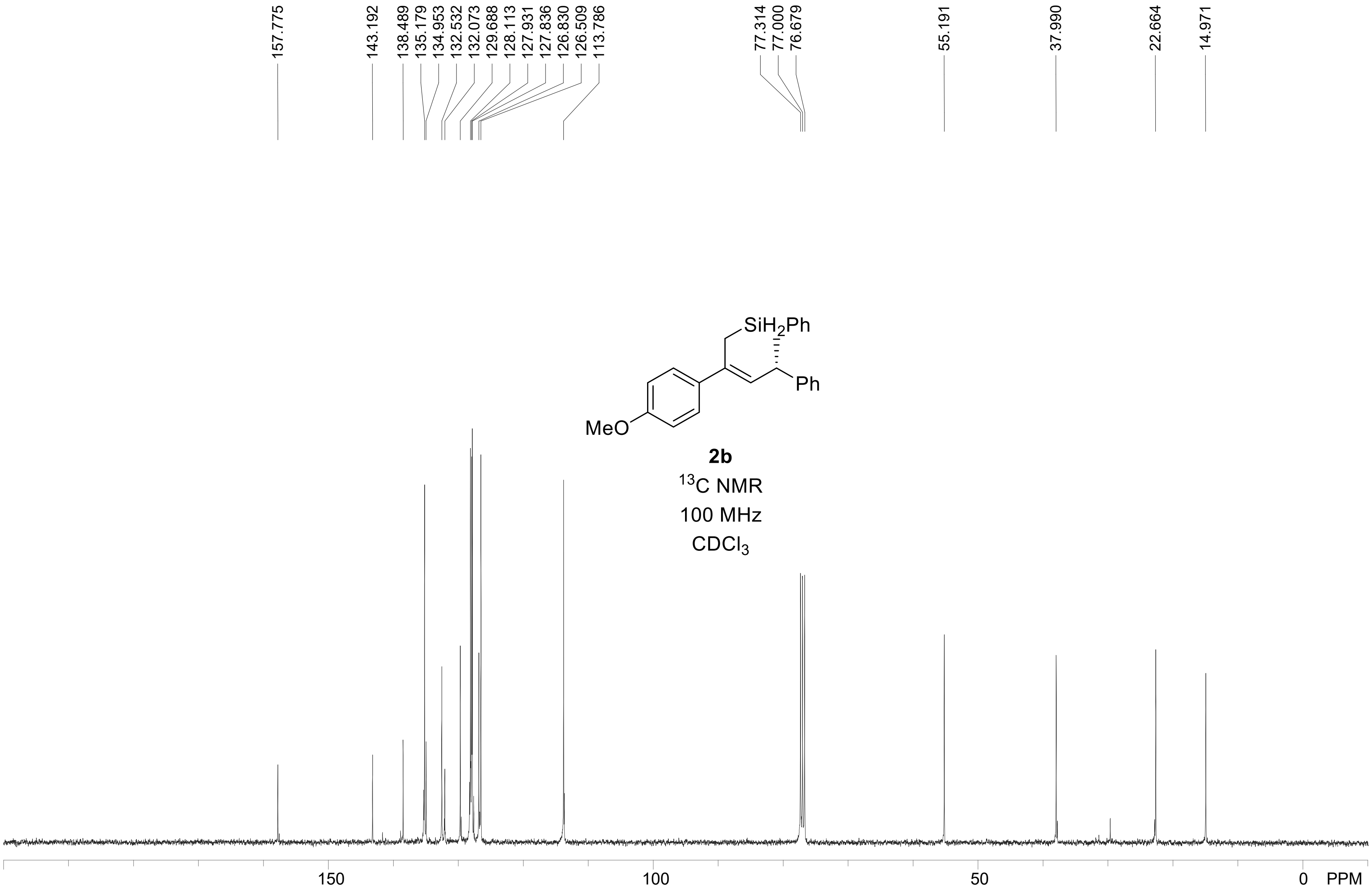


Figure S35. ^{13}C NMR spectra of **2b**, Related to Table 2

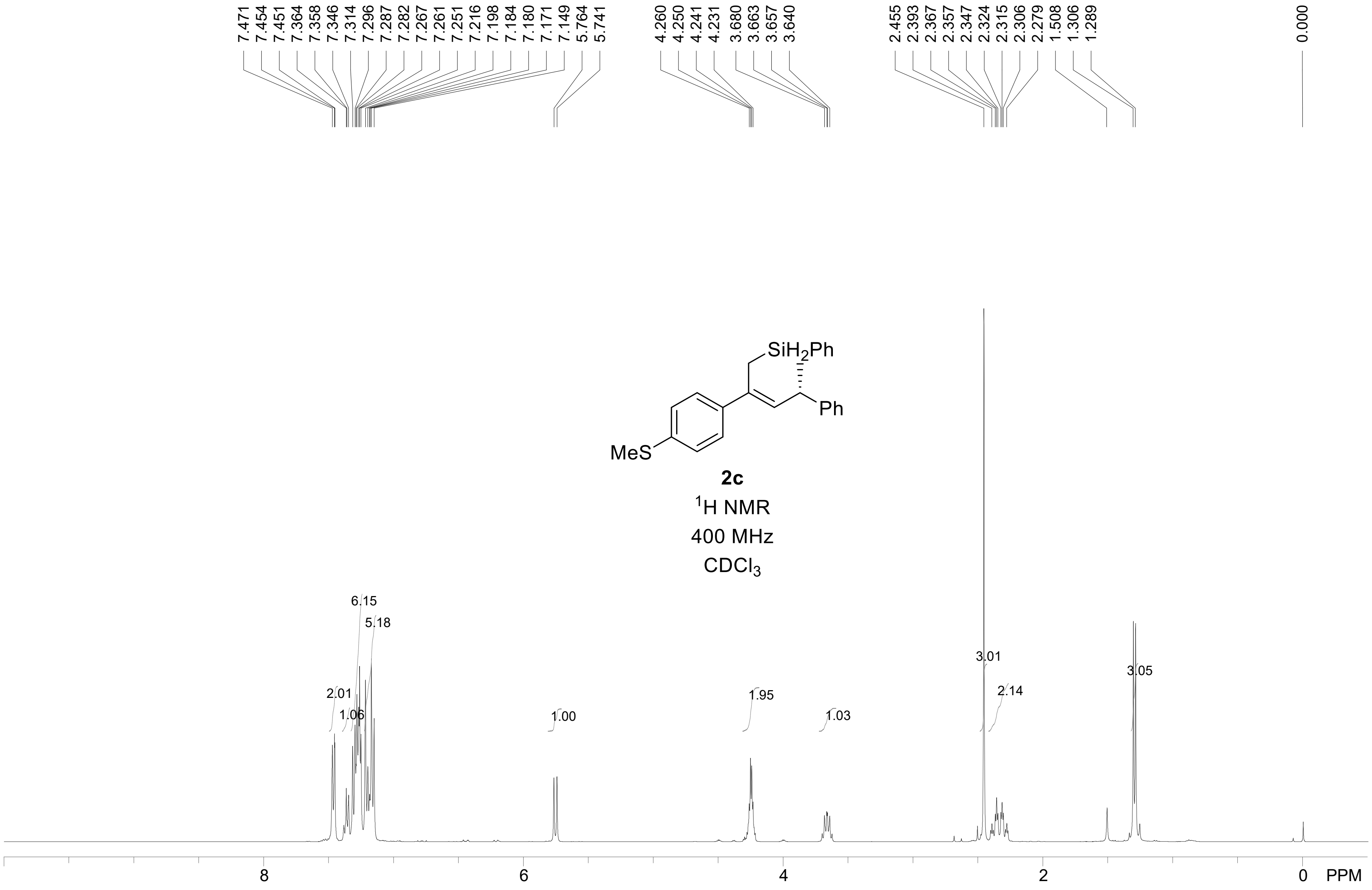


Figure S36. ^{1}H NMR spectra of **2c**, Related to Table 2

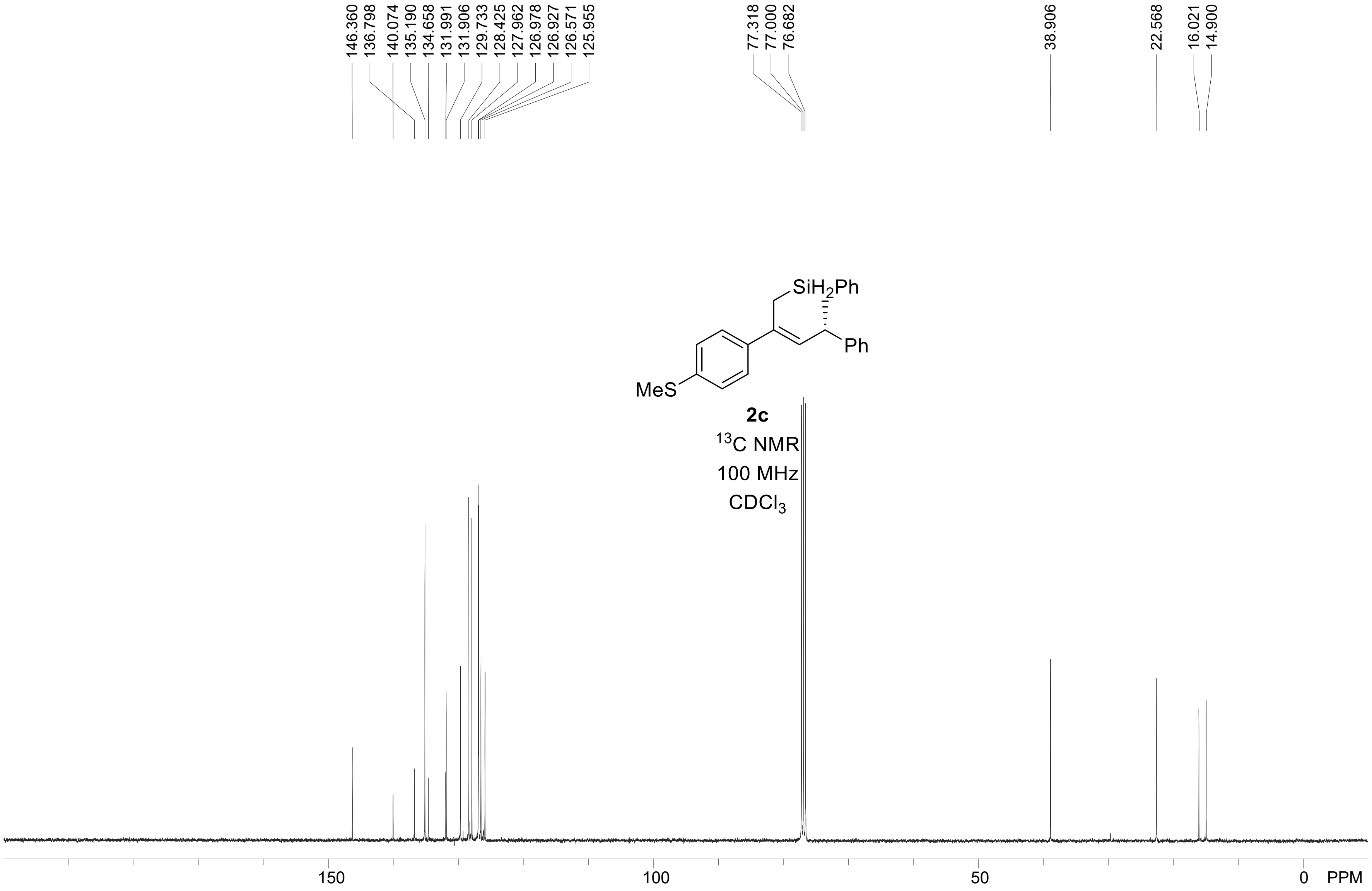


Figure S37. ^{13}C NMR spectra of **2c**, Related to Table 2

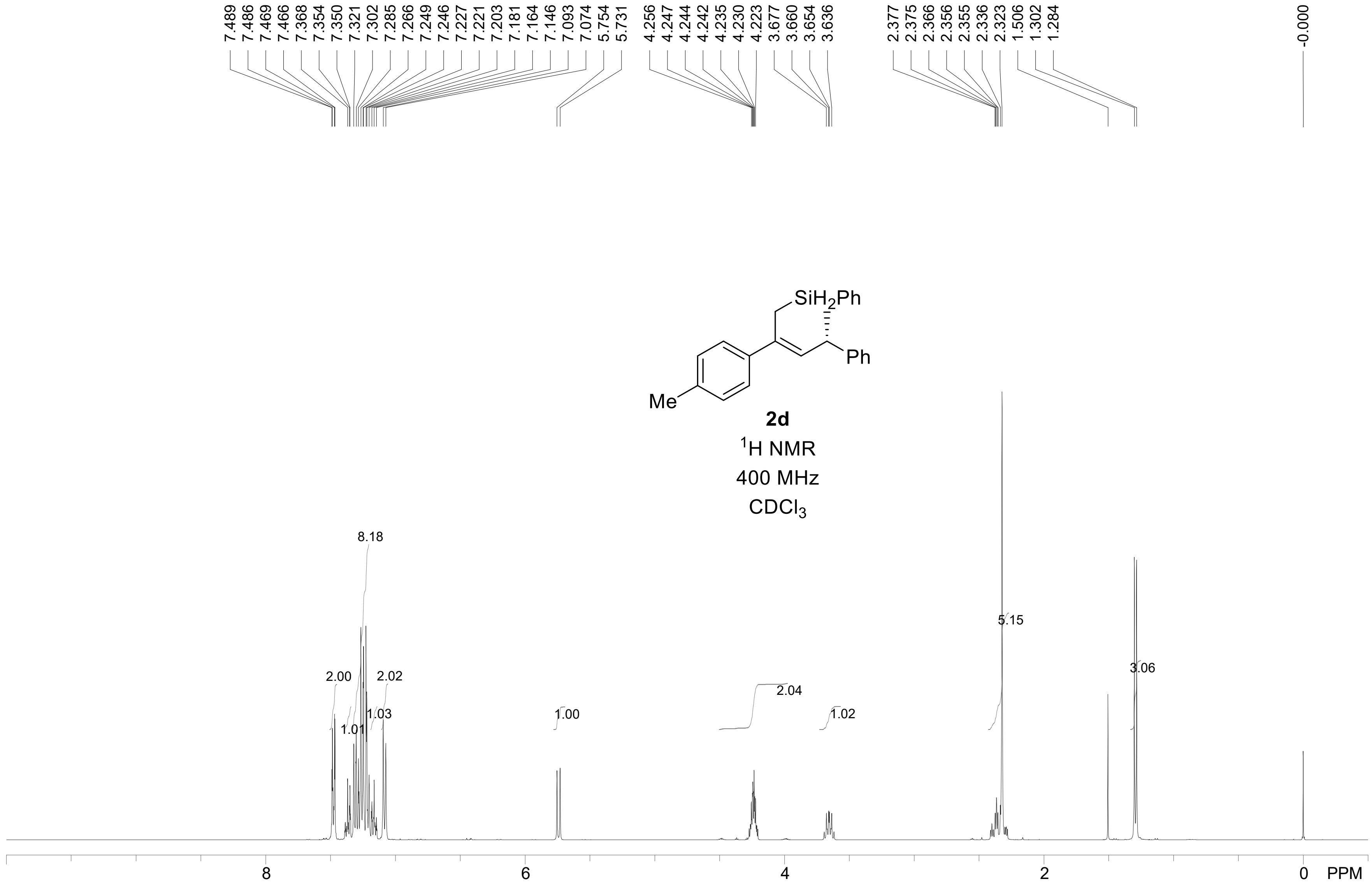


Figure S38. ^{1}H NMR spectra of **2d**, Related to Table 2

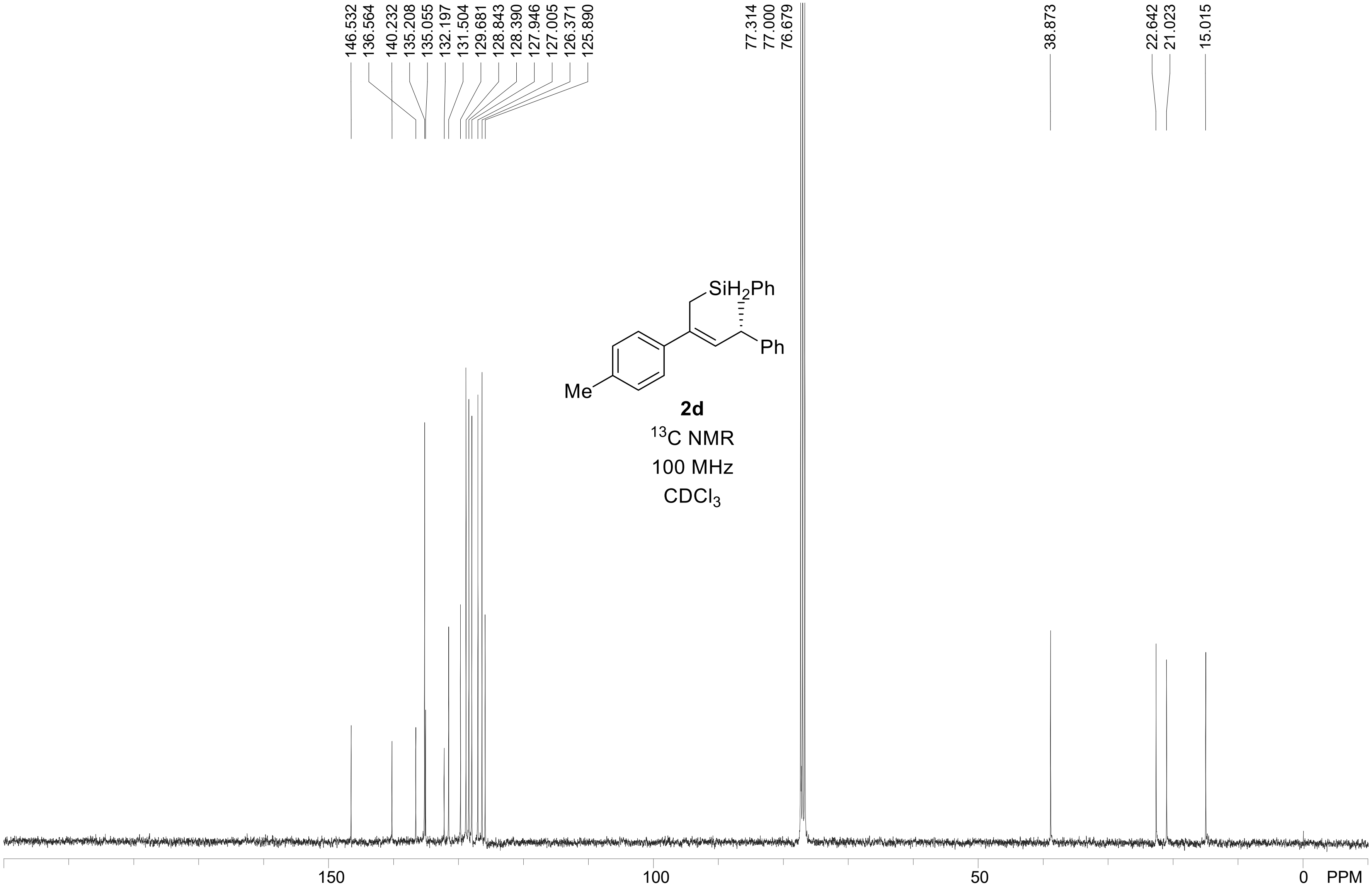


Figure S39. ^{13}C NMR spectra of **2d**, Related to Table 2

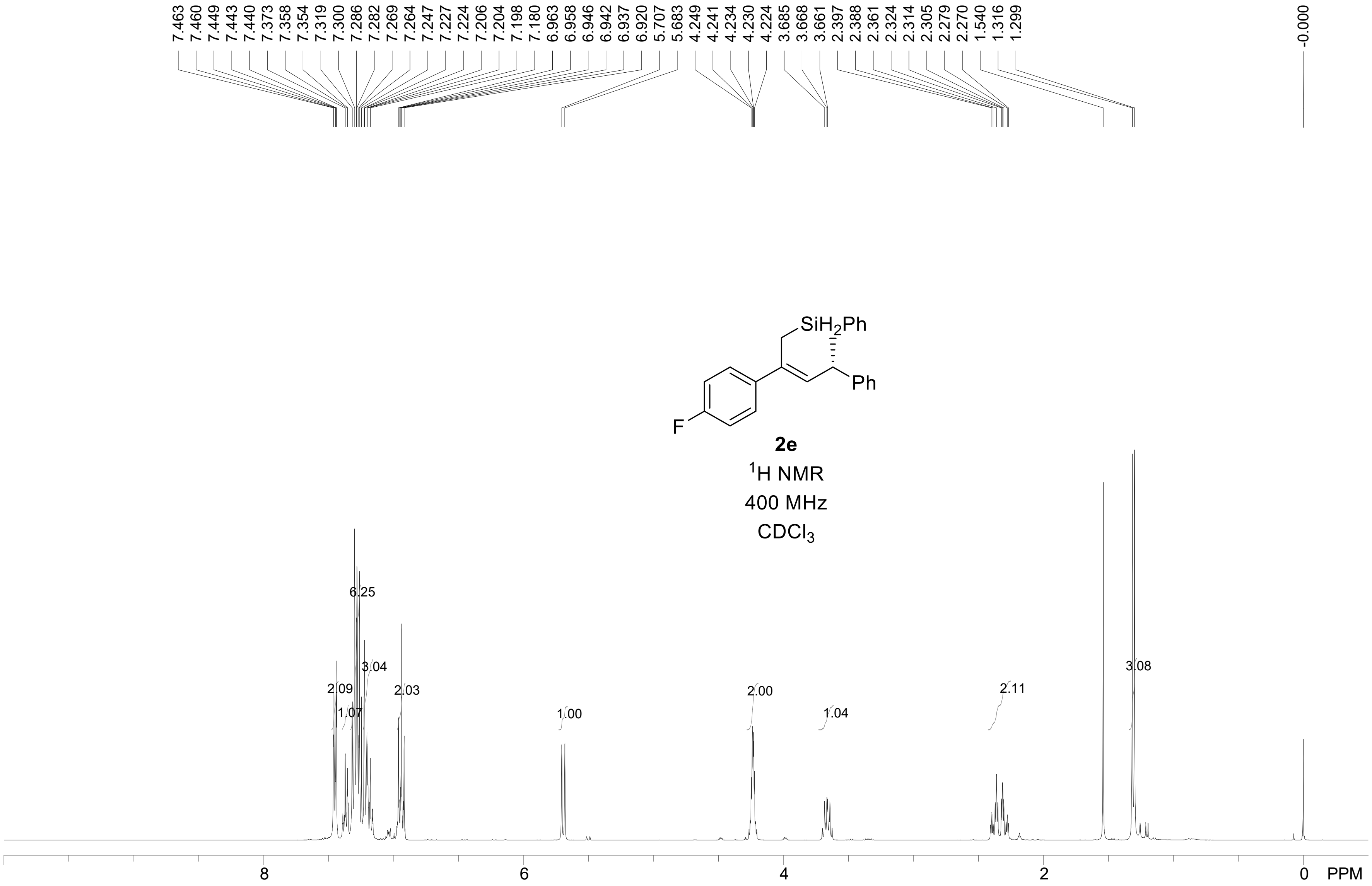


Figure S40. ^{1}H NMR spectra of **2e**, Related to Table 2

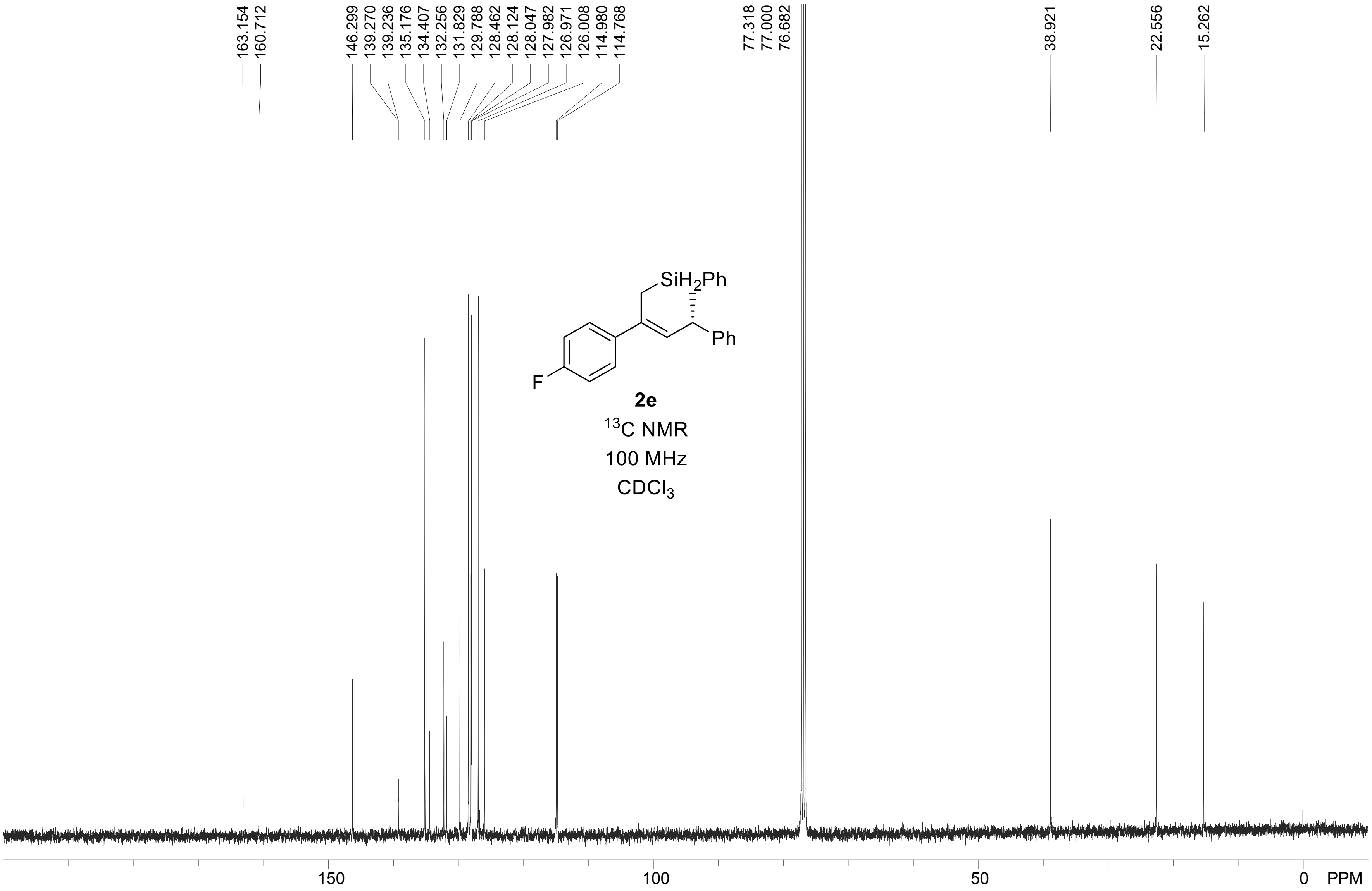


Figure S41. ^{13}C NMR spectra of **2e**, Related to Table 2

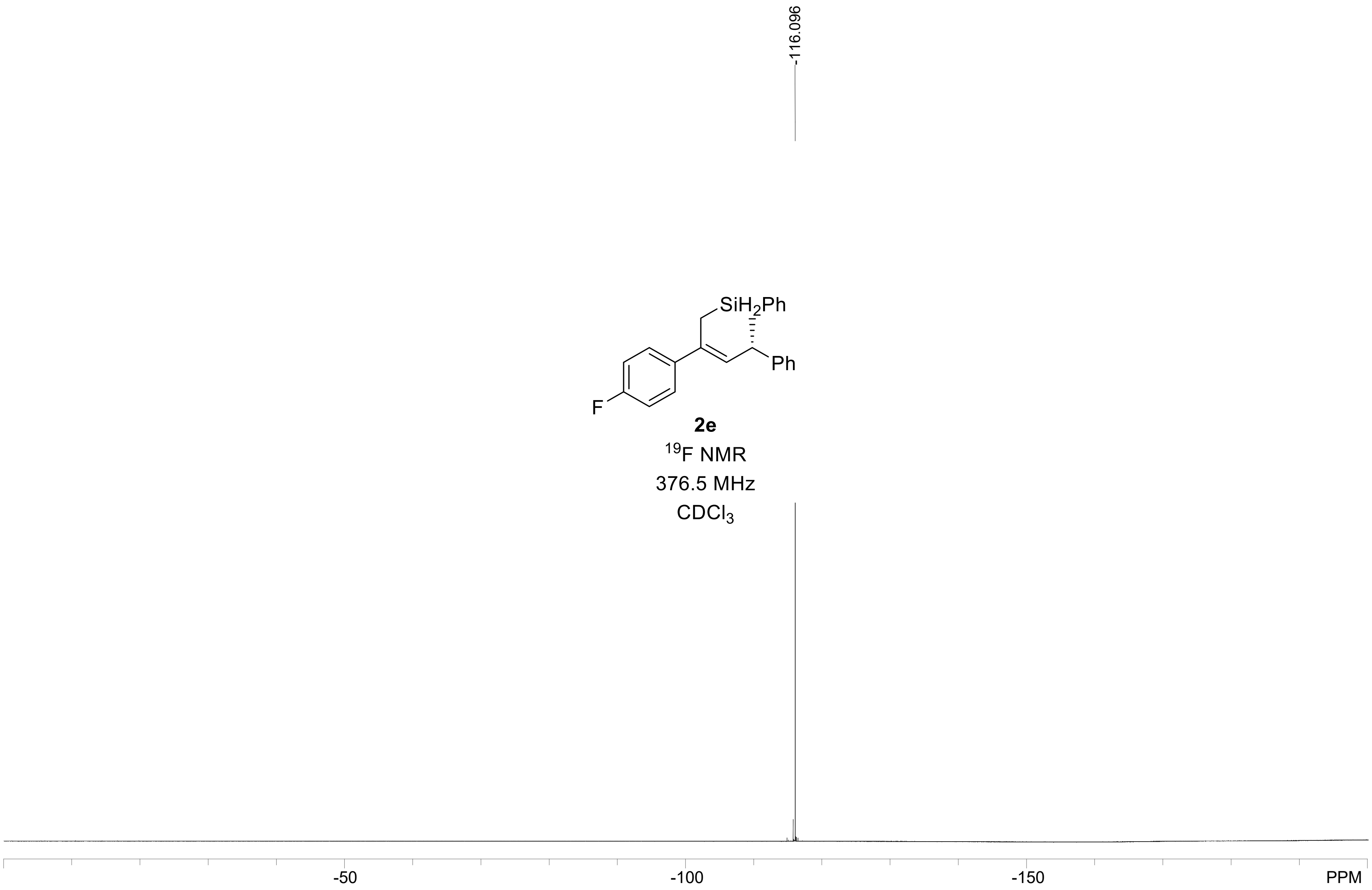


Figure S42. ^{19}F NMR spectra of **2e**, Related to Table 2

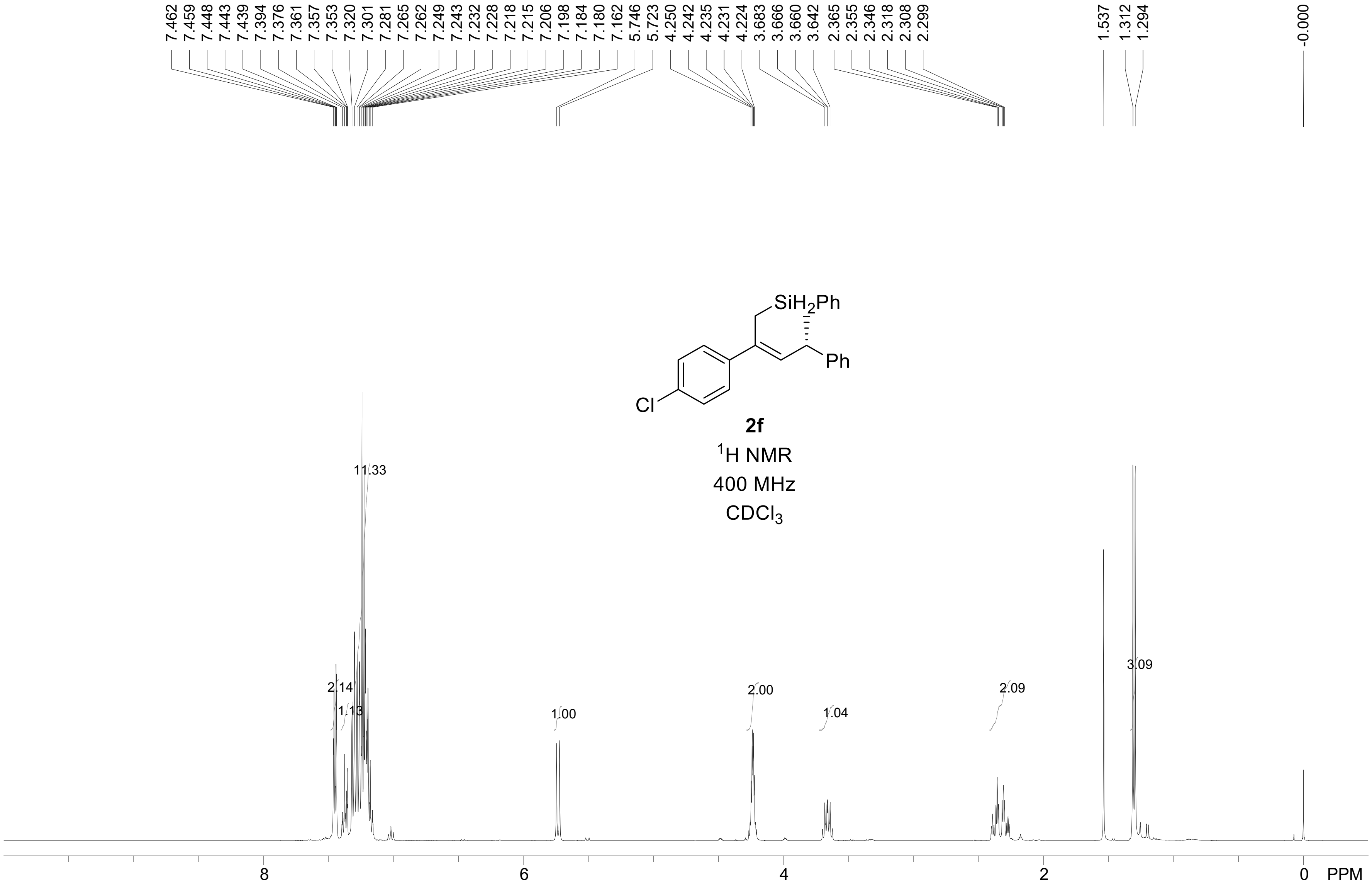


Figure S43. ^{1}H NMR spectra of **2f**, Related to Table 2

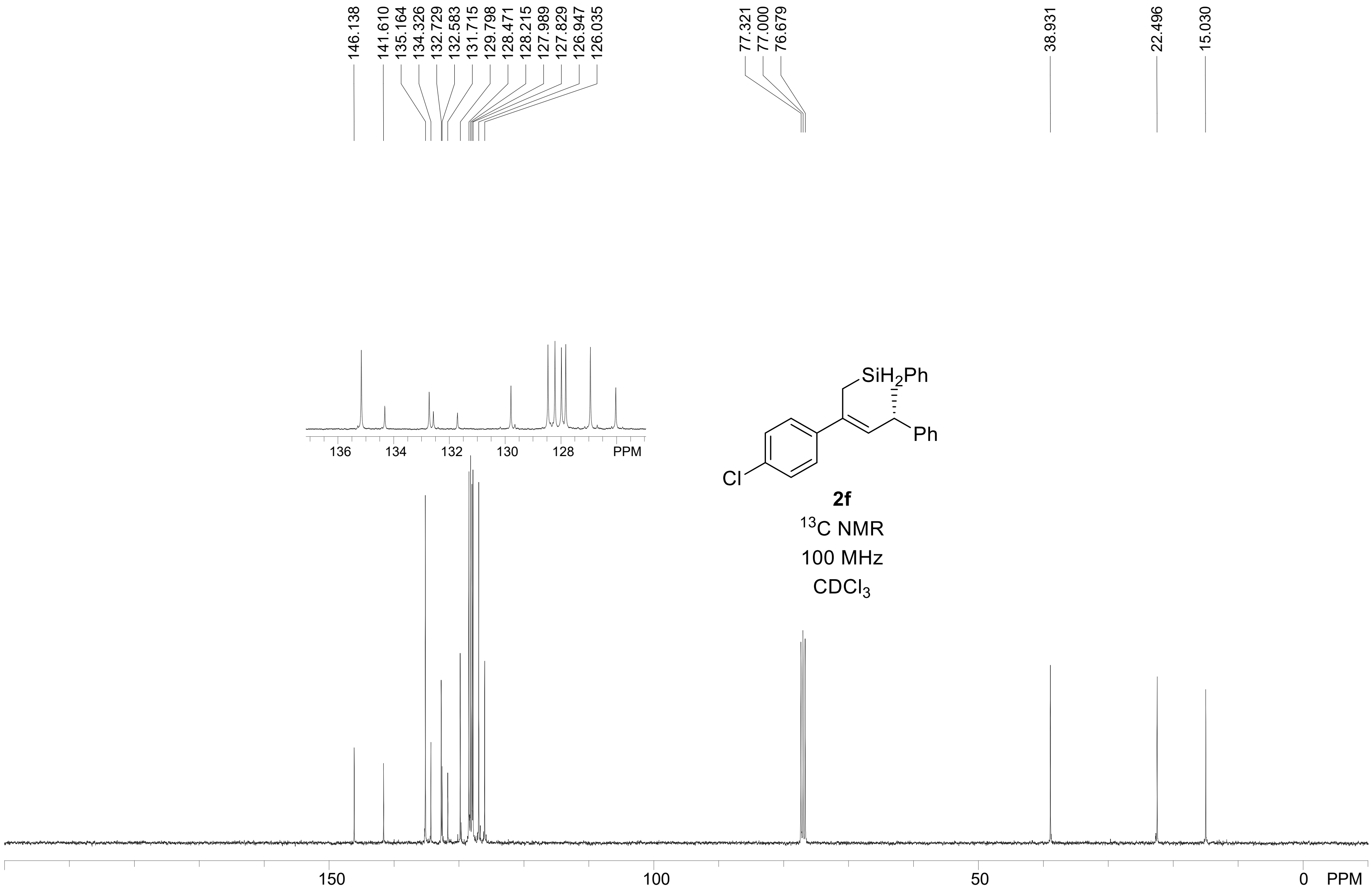


Figure S44. ^{13}C NMR spectra of **2f**, Related to Table 2

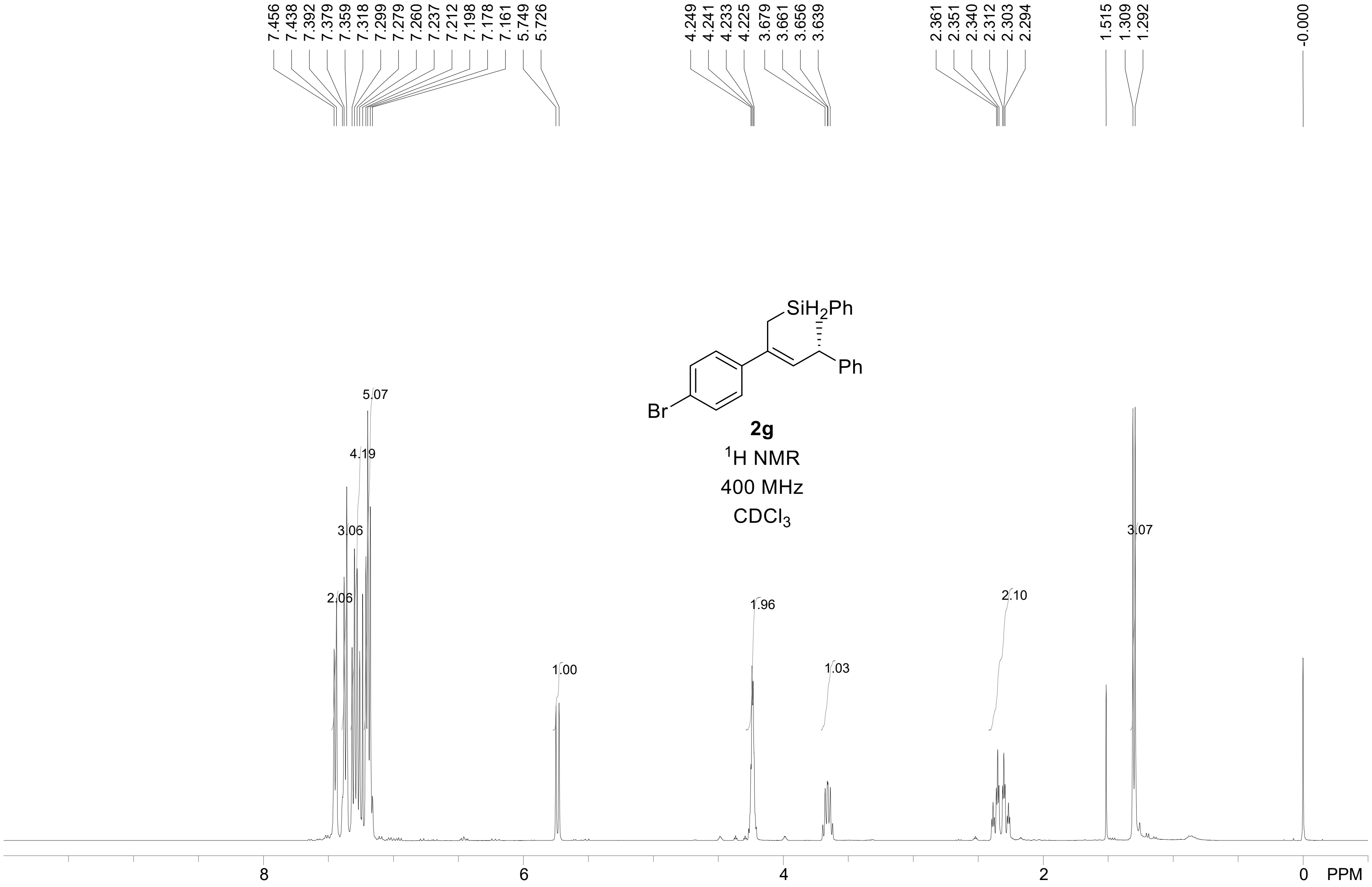


Figure S45. ^{1}H NMR spectra of **2g**, Related to Table 2

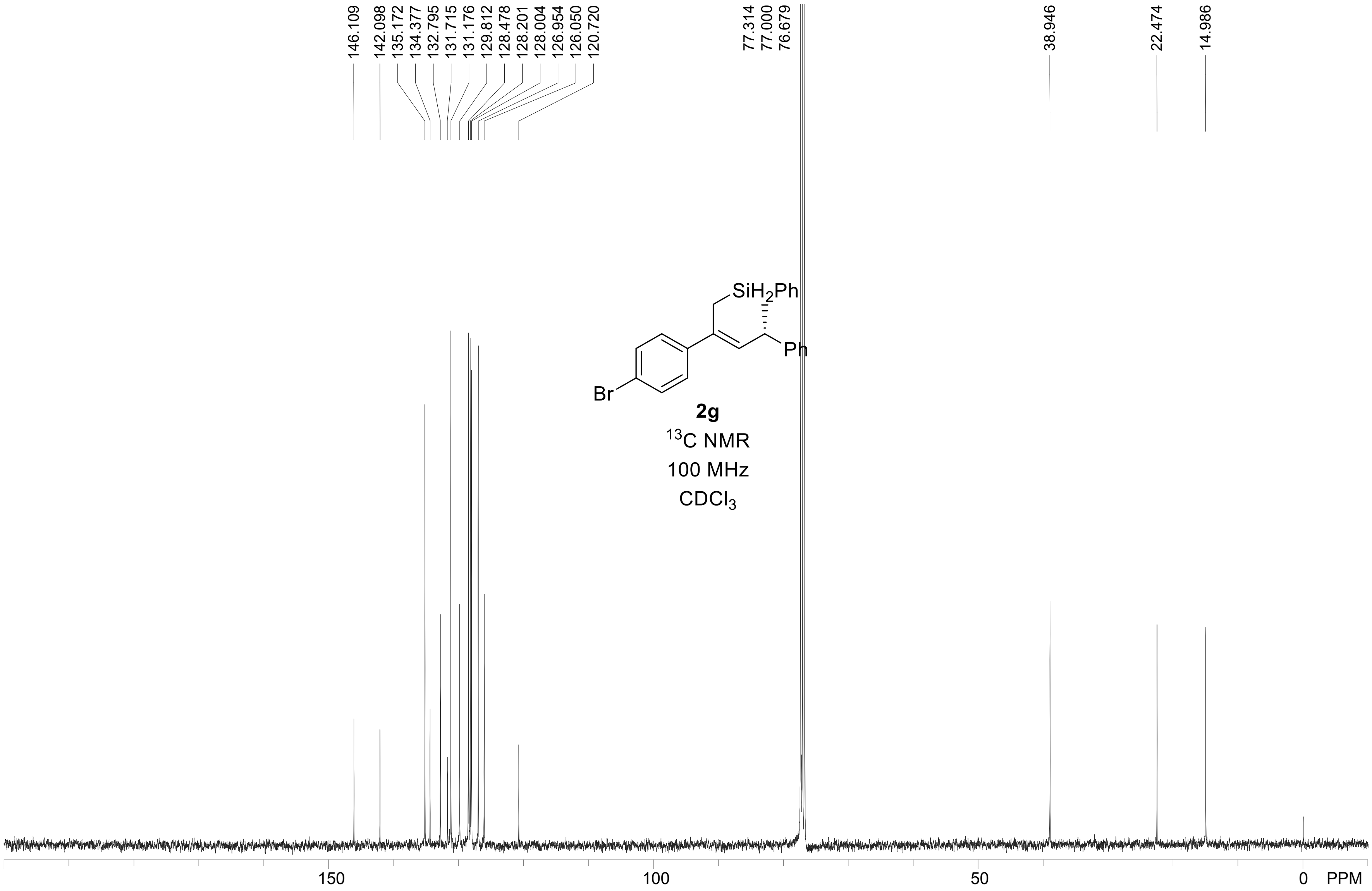


Figure S46. ^{13}C NMR spectra of **2g**, Related to Table 2

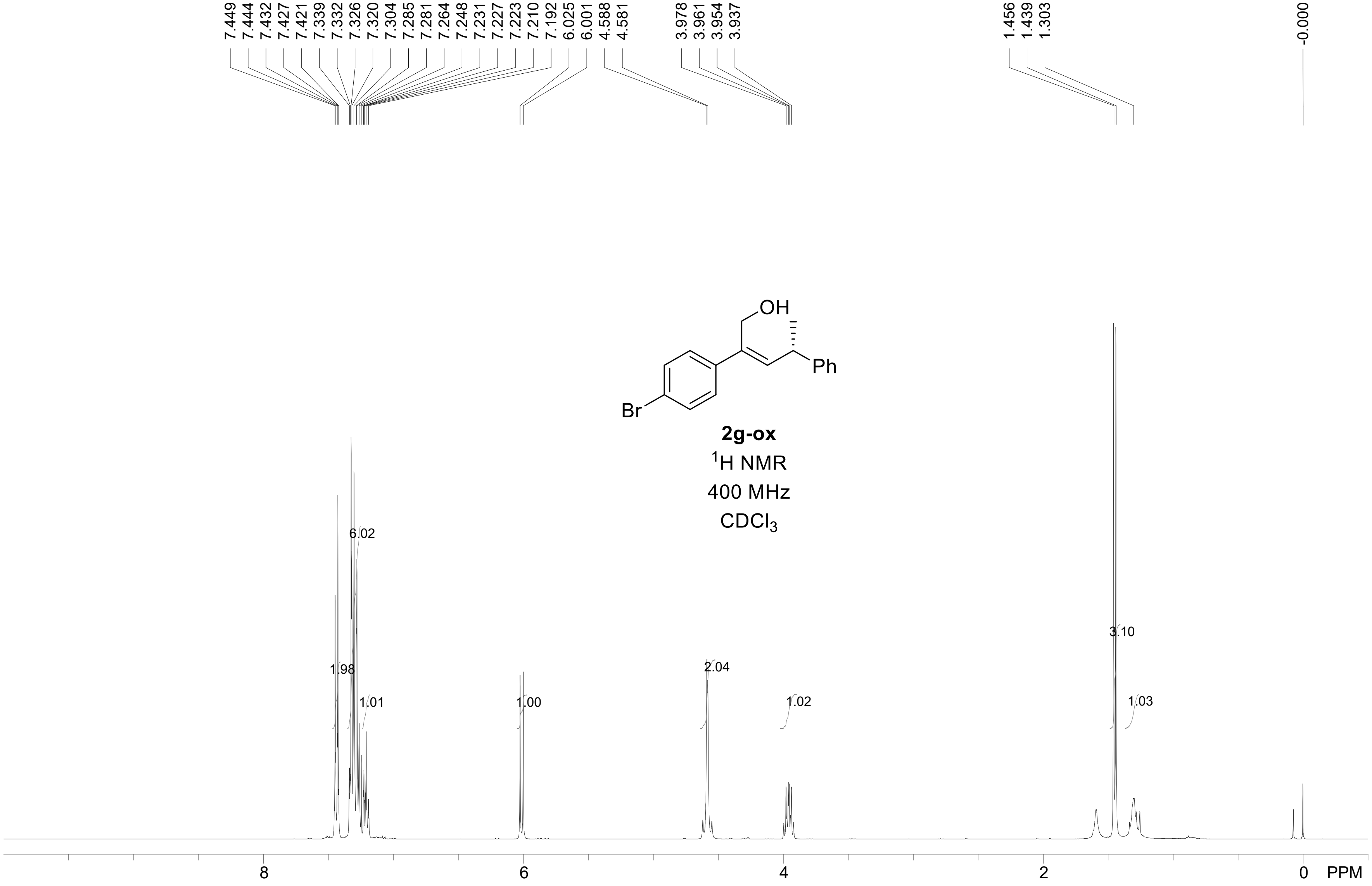


Figure S47. ^{1}H NMR spectra of **2g-ox**, Related to Table 2

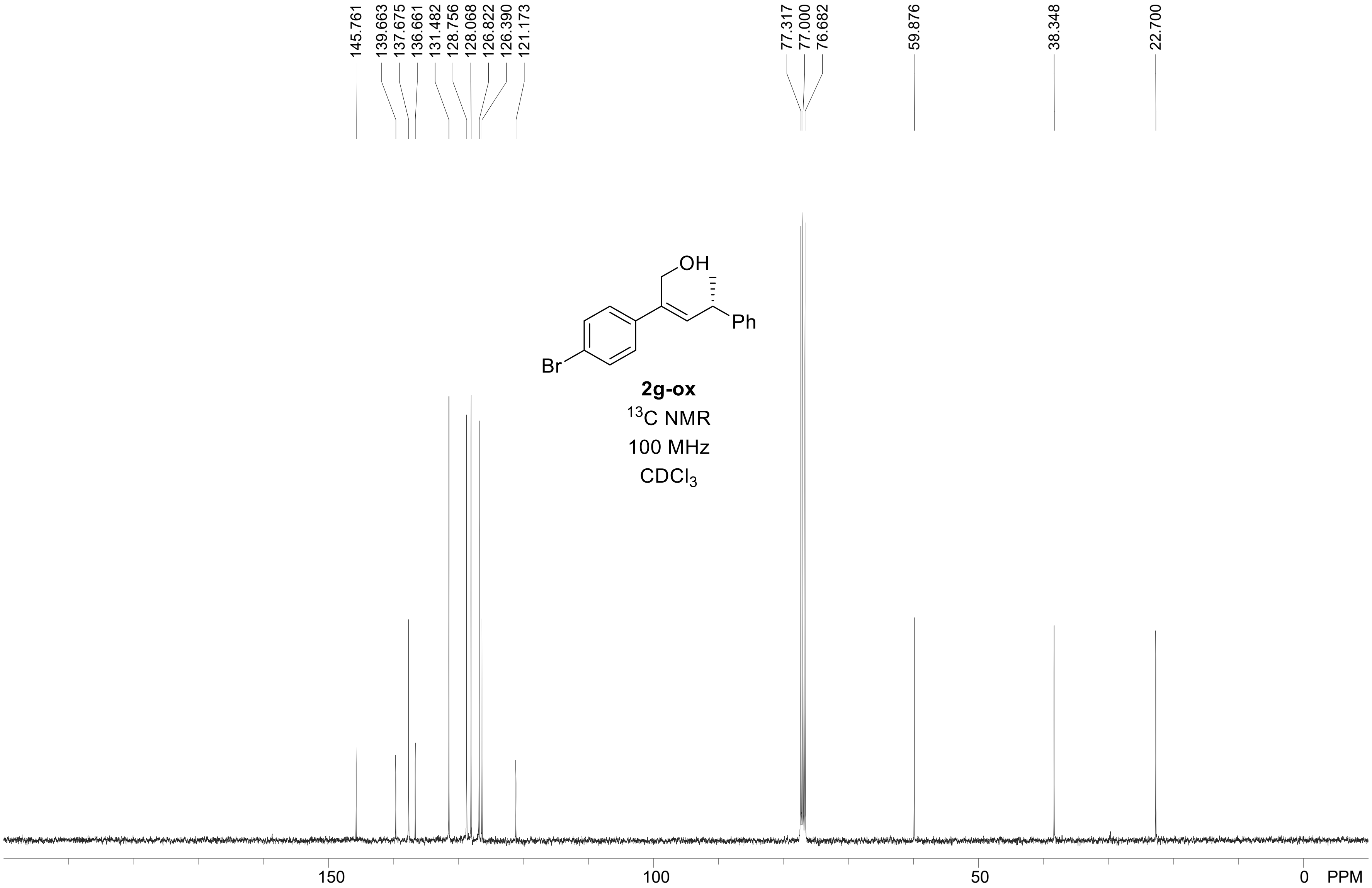


Figure S48. ^{13}C NMR spectra of **2g-ox**, Related to Table 2

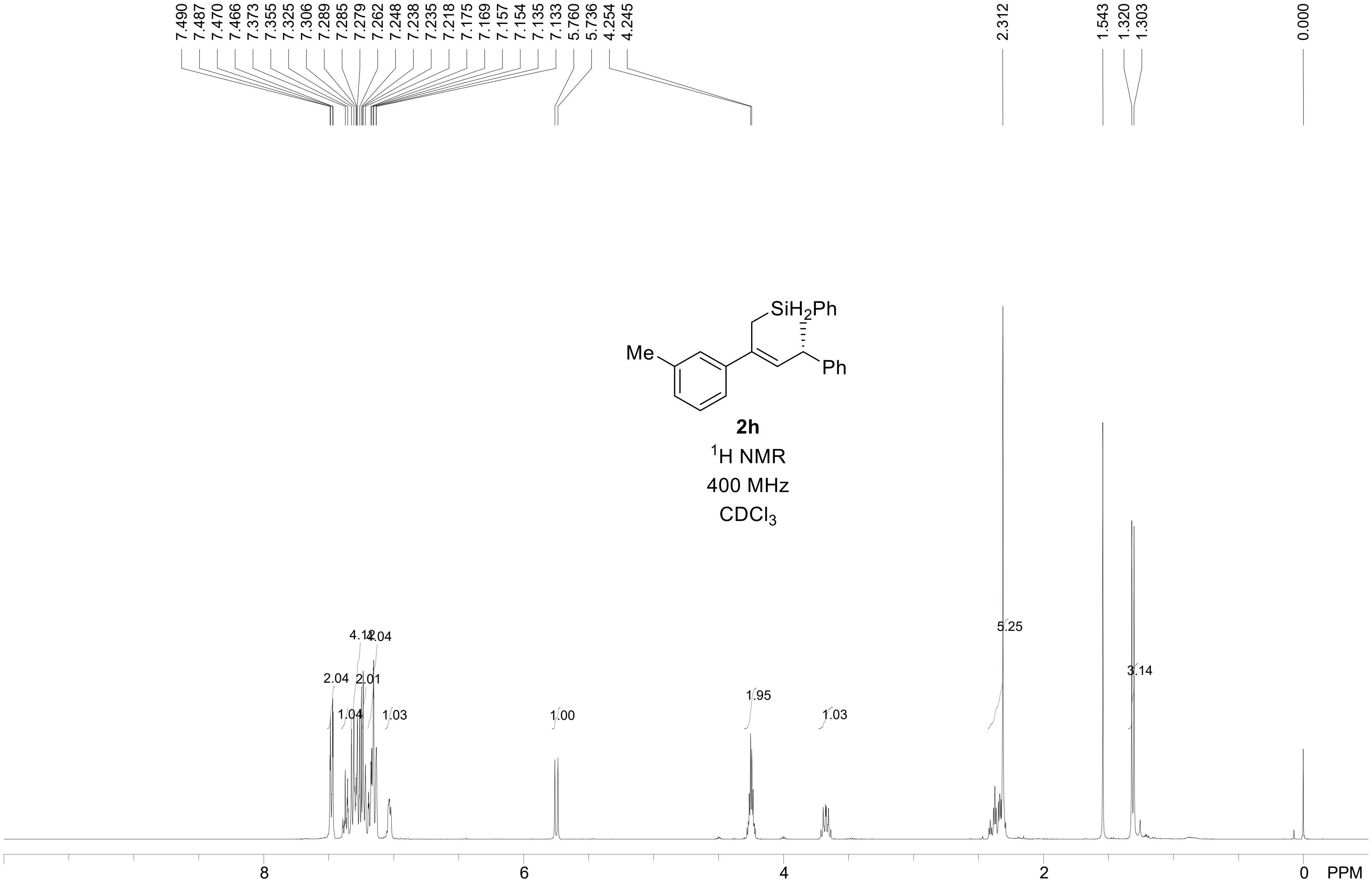


Figure S49. ^{1}H NMR spectra of **2h**, Related to Table 2

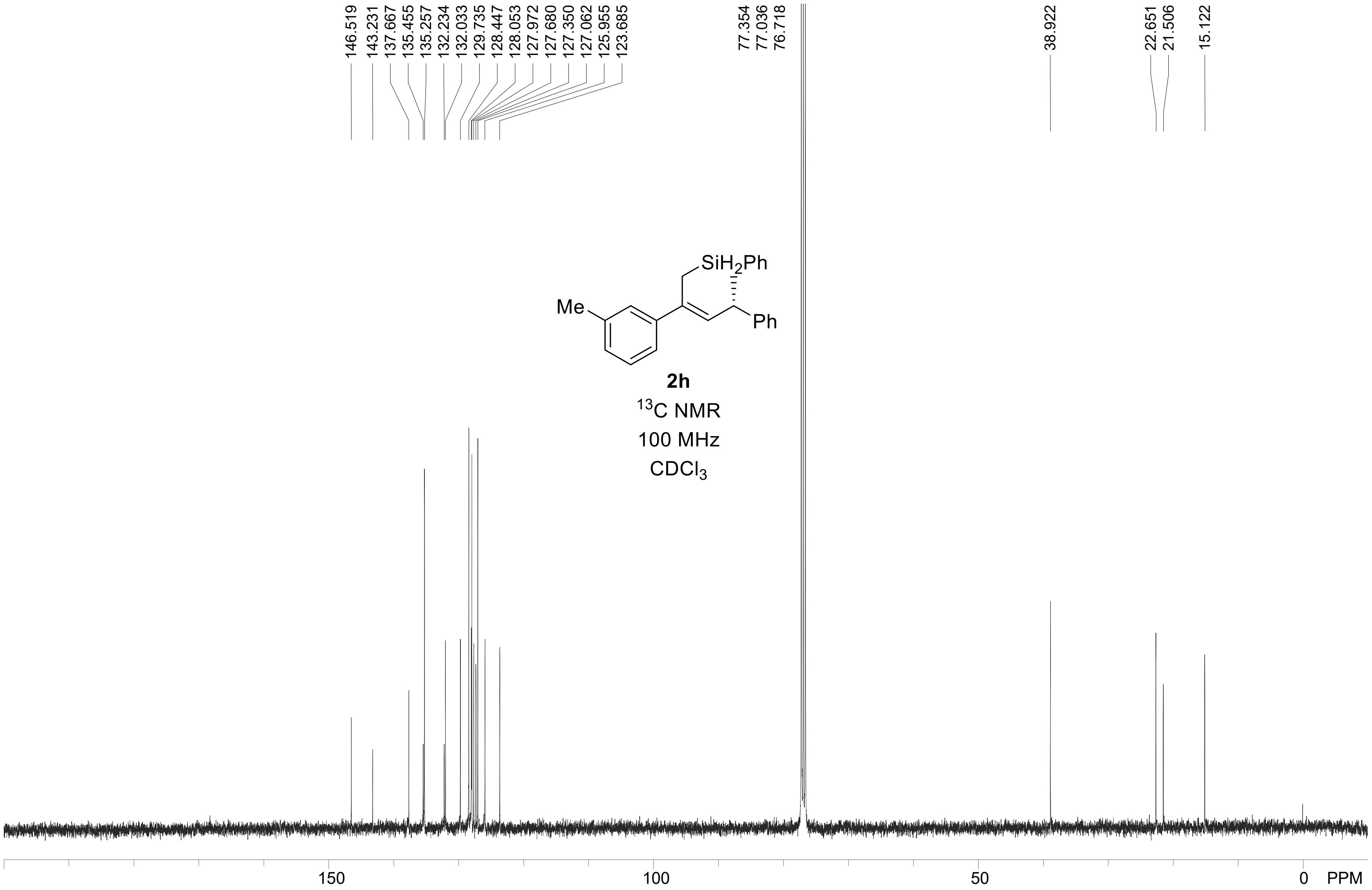


Figure S50. ^{13}C NMR spectra of **2h**, Related to Table 2

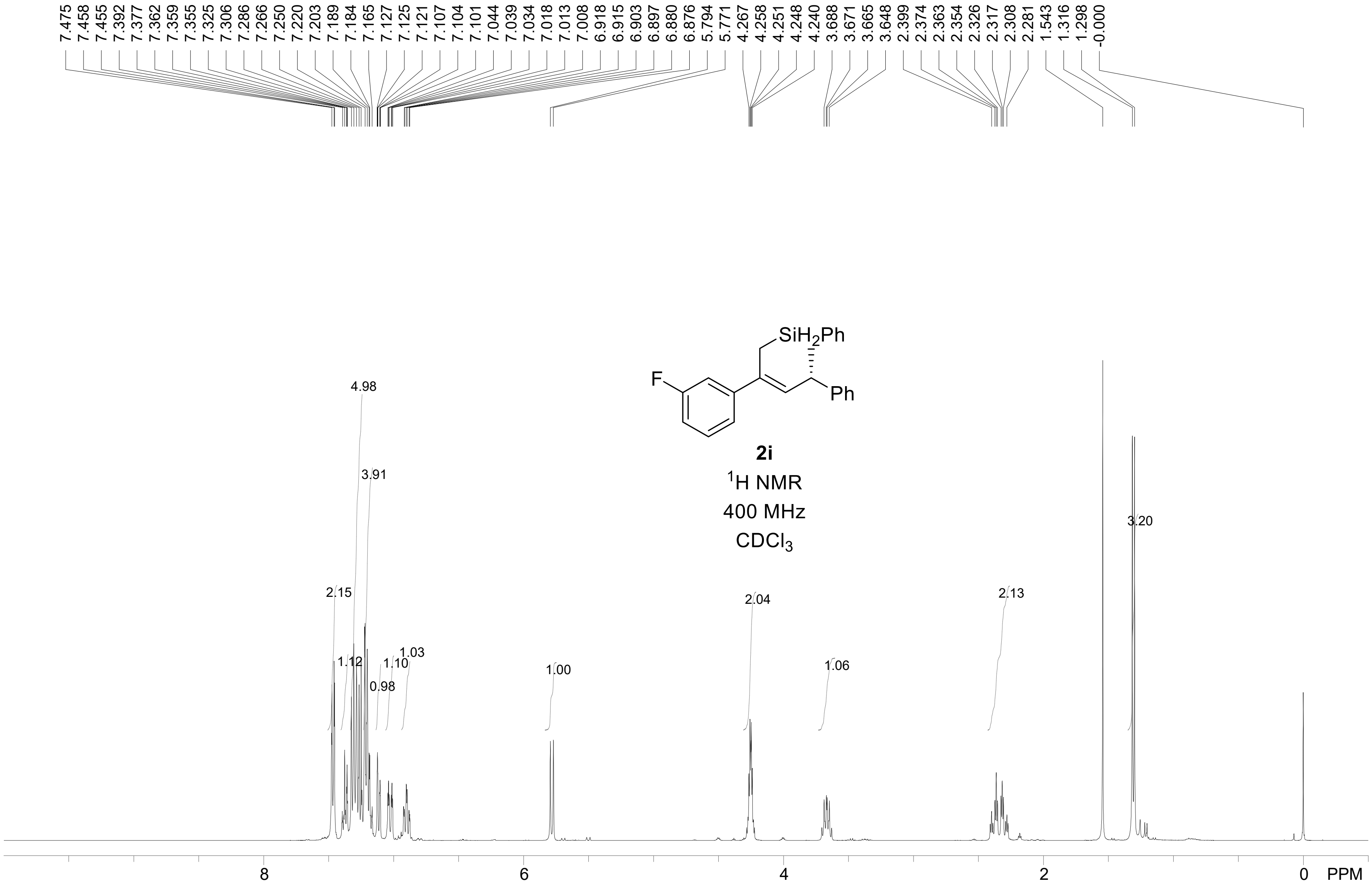


Figure S51. ^{1}H NMR spectra of **2i**, Related to Table 2

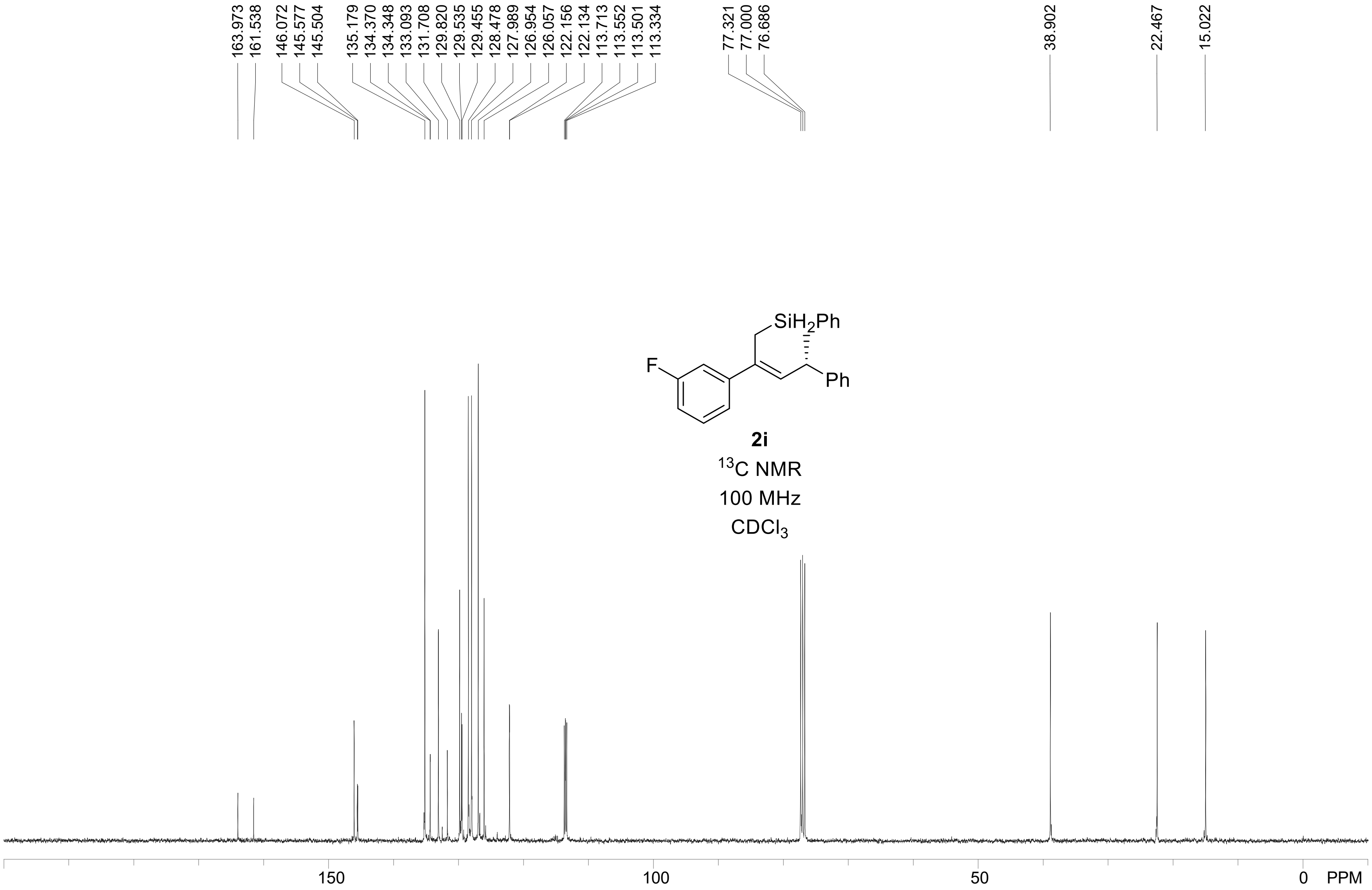


Figure S52. ^{13}C NMR spectra of **2i**, Related to Table 2

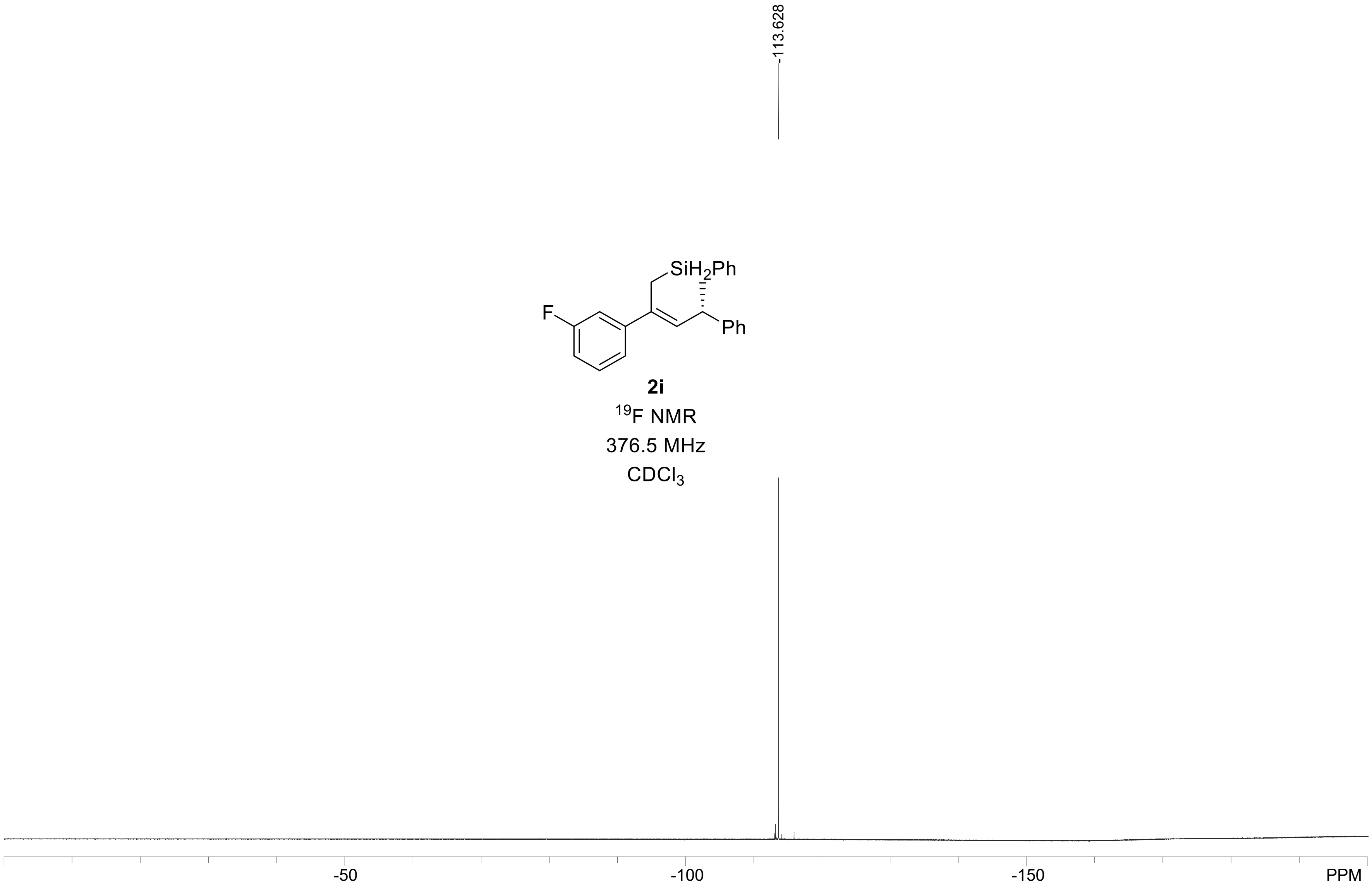


Figure S53. ^{19}F NMR spectra of **2i**, Related to Table 2

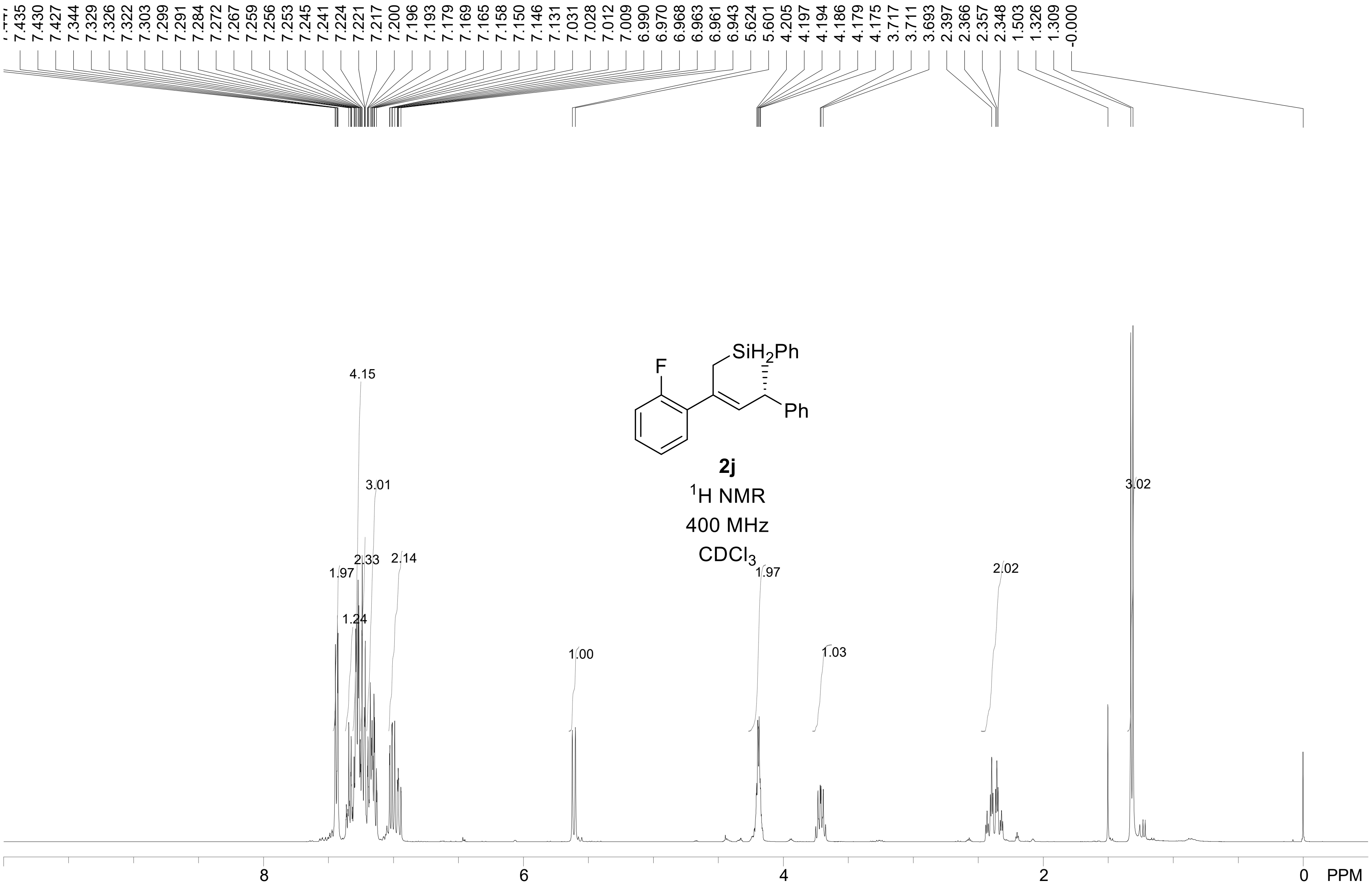


Figure S54. ^{1}H NMR spectra of **2j**, Related to Table 2

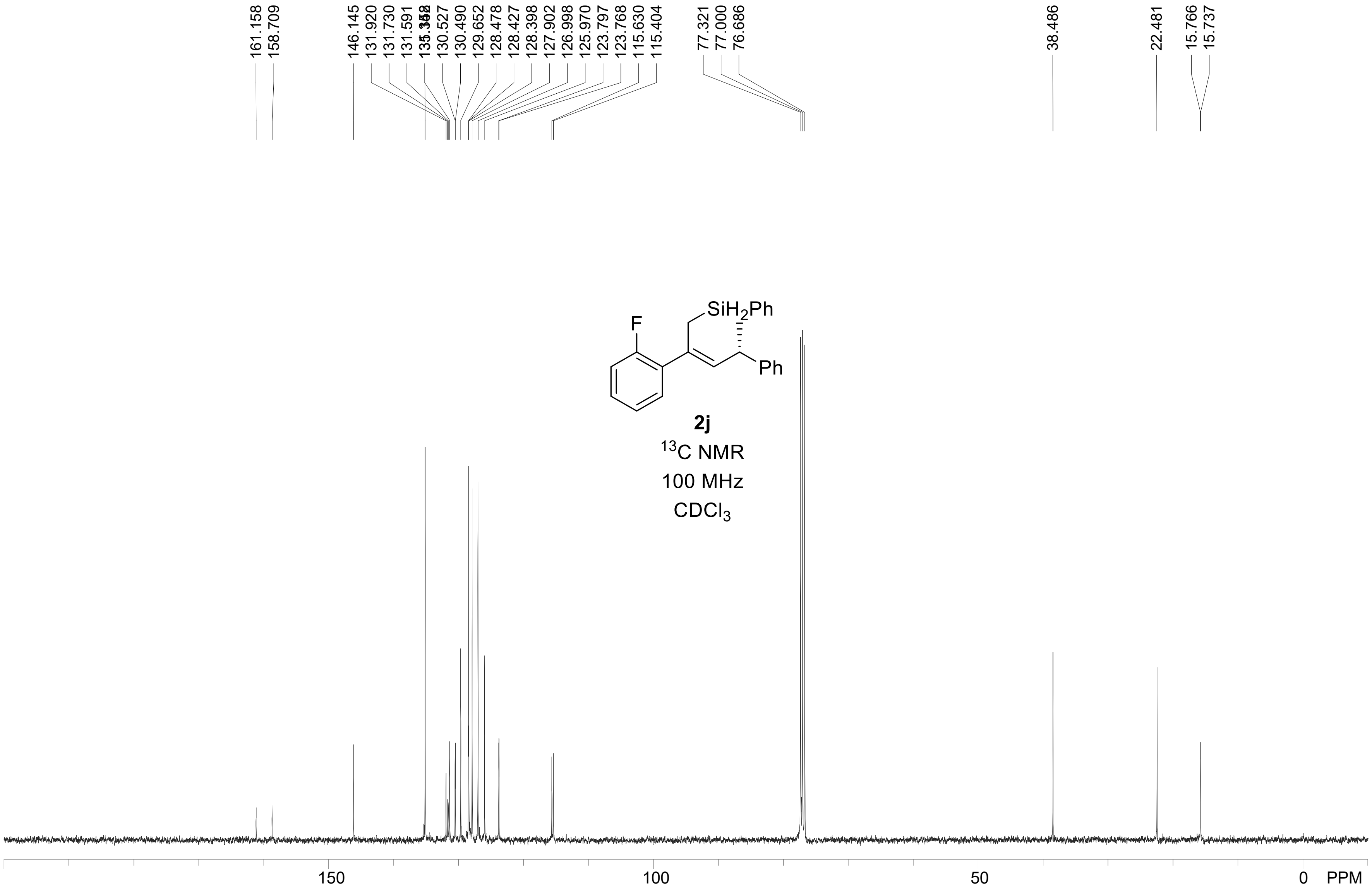


Figure S55. ^{13}C NMR spectra of **2j**, Related to Table 2

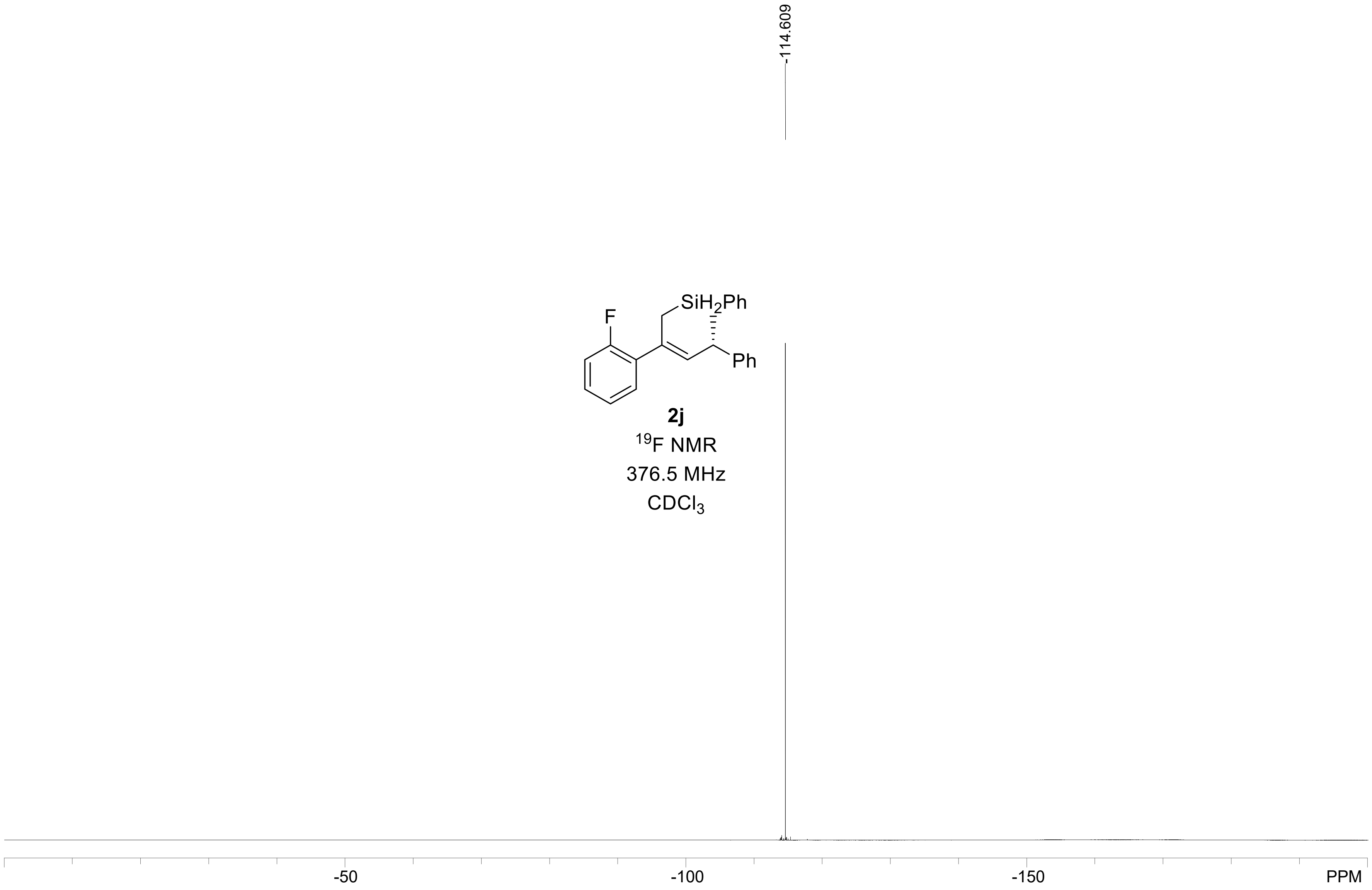


Figure S56. ^{19}F NMR spectra of **2j**, Related to Table 2

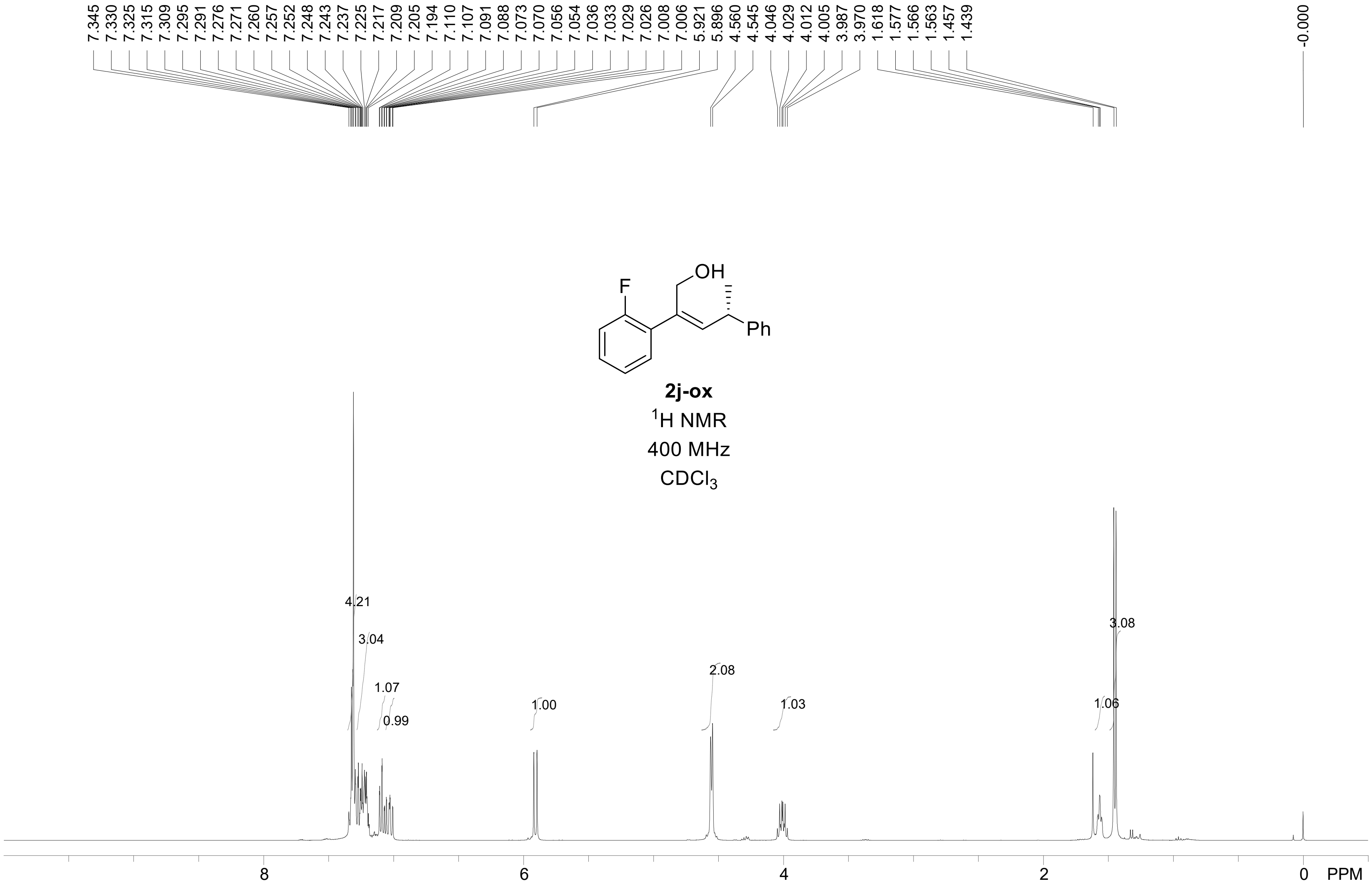


Figure S57. ^{1}H NMR spectra of **2j-ox**, Related to Table 2

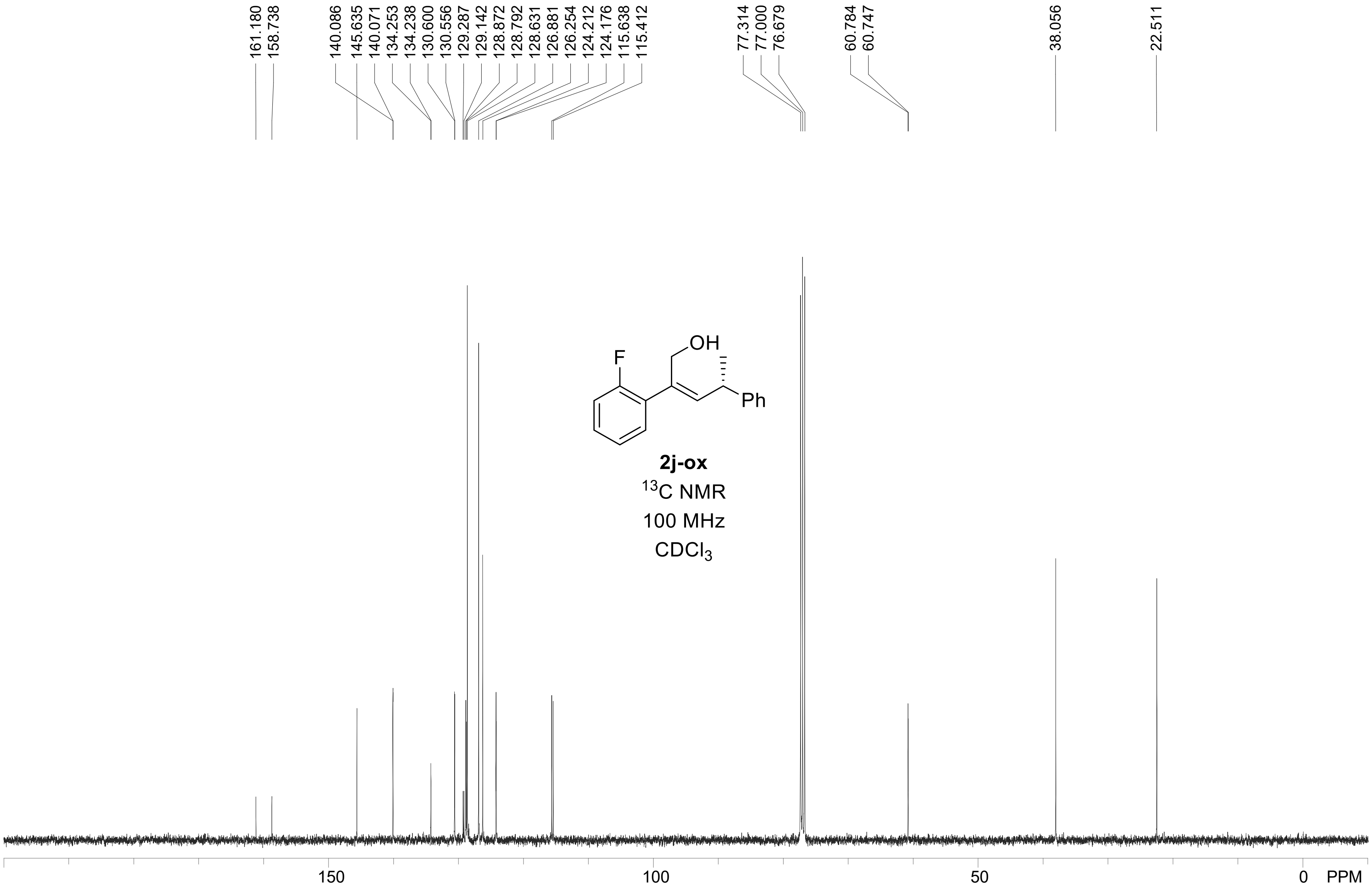


Figure S58. ^{13}C NMR spectra of **2j-ox**, Related to Table 2

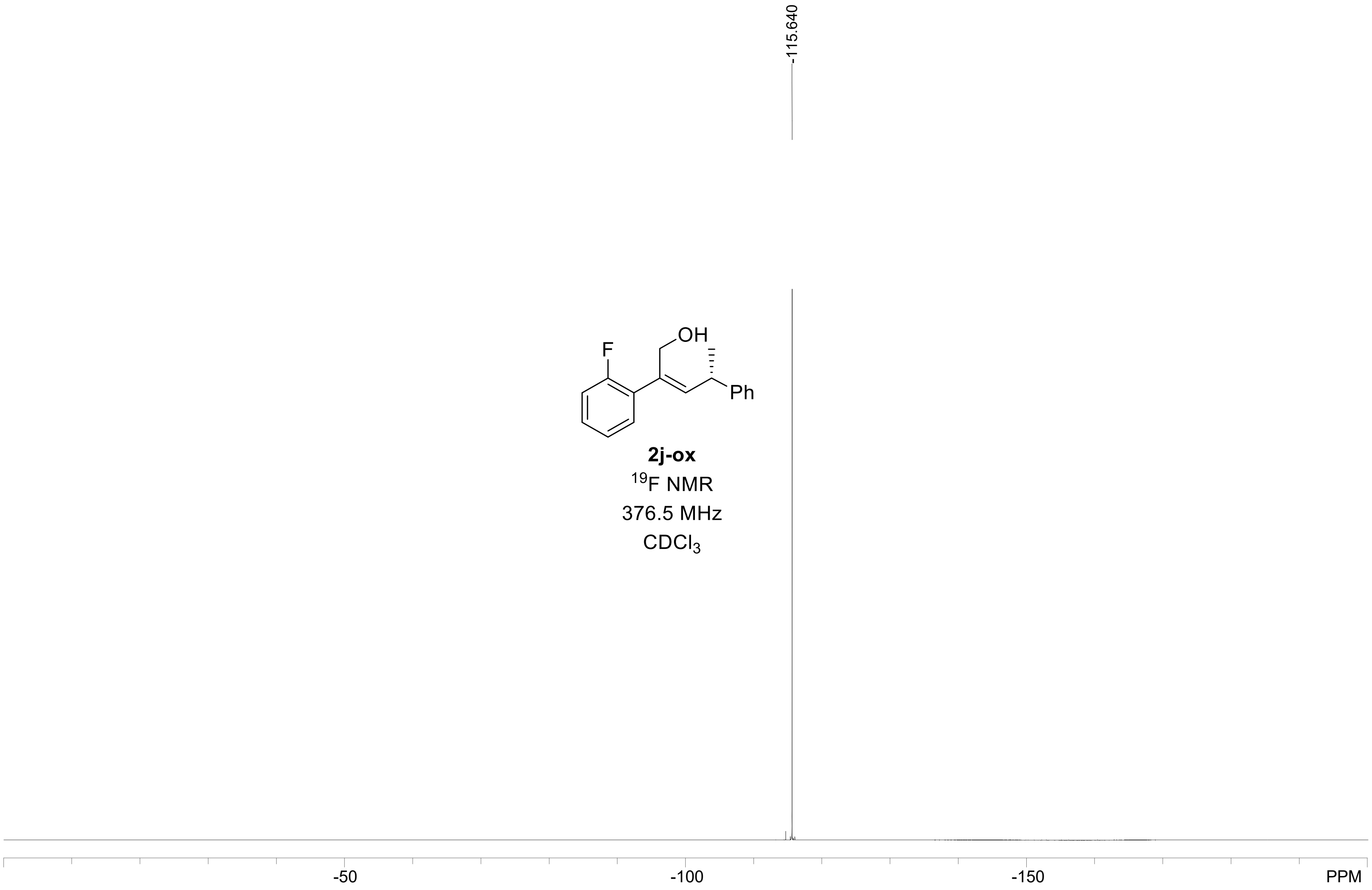


Figure S59. ^{19}F NMR spectra of **2j-ox**, Related to Table 2

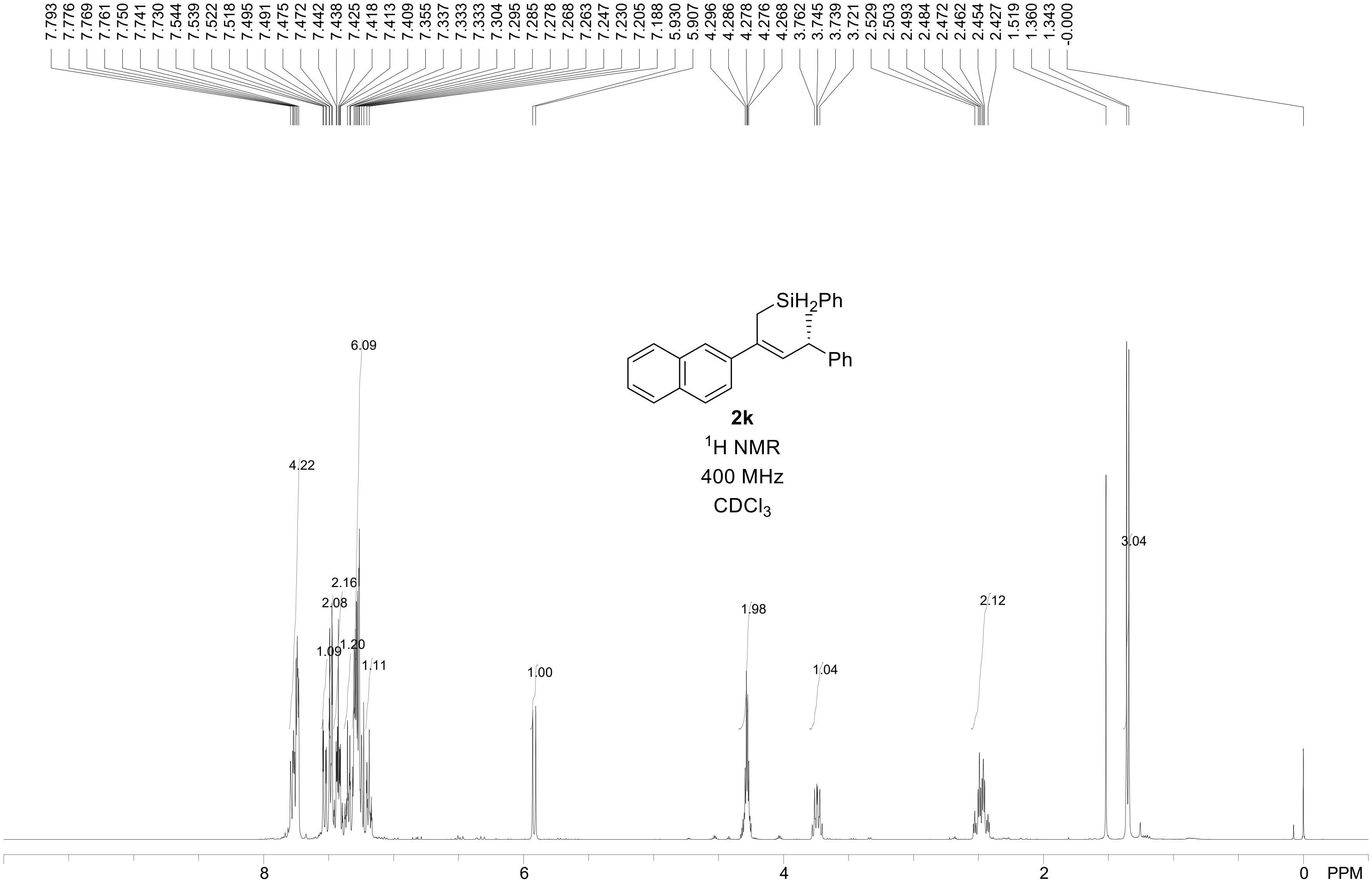


Figure S60. ^{1}H NMR spectra of **2k**, Related to Table 2

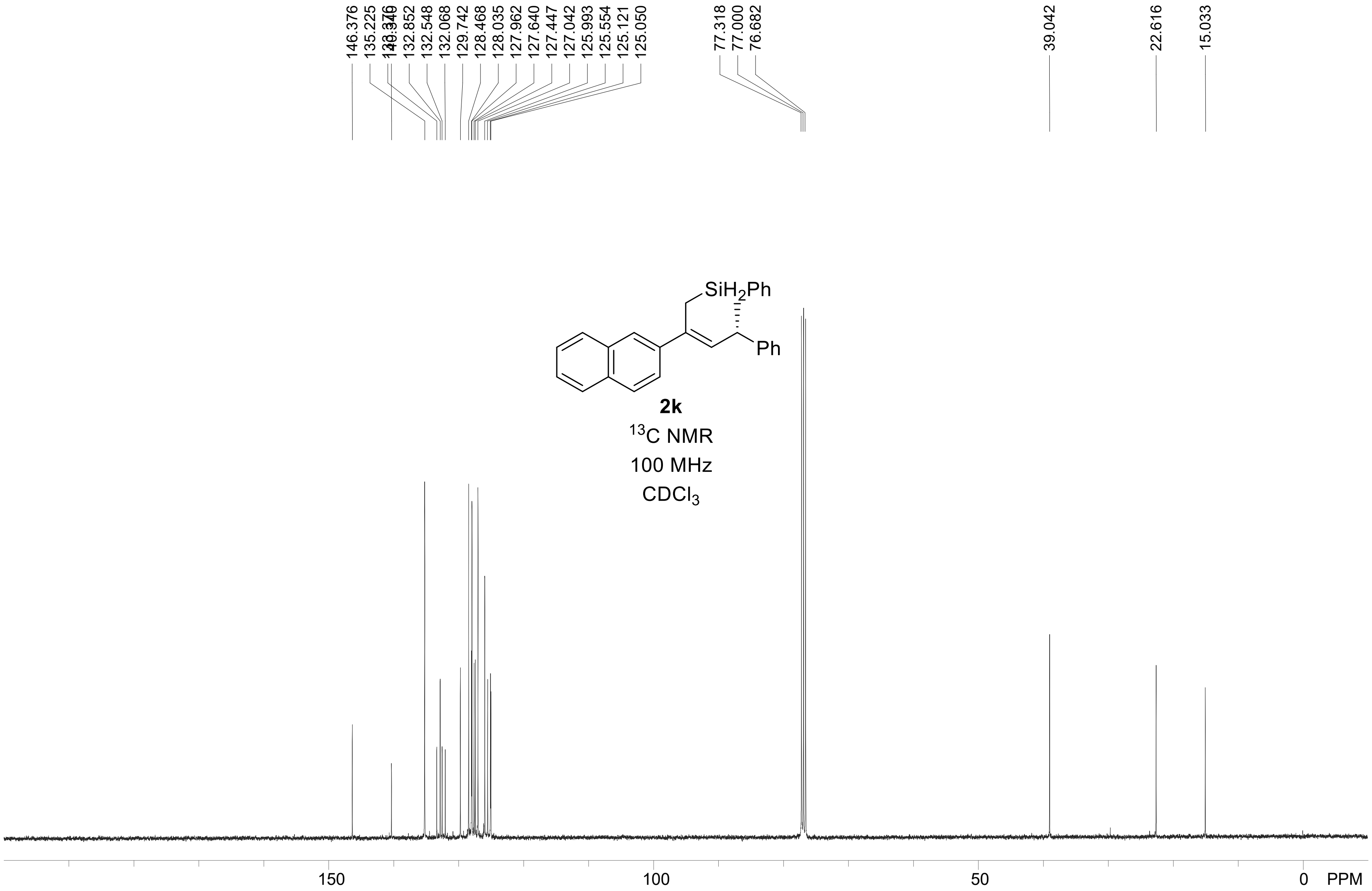


Figure S61. ^{13}C NMR spectra of **2k**, Related to Table 2

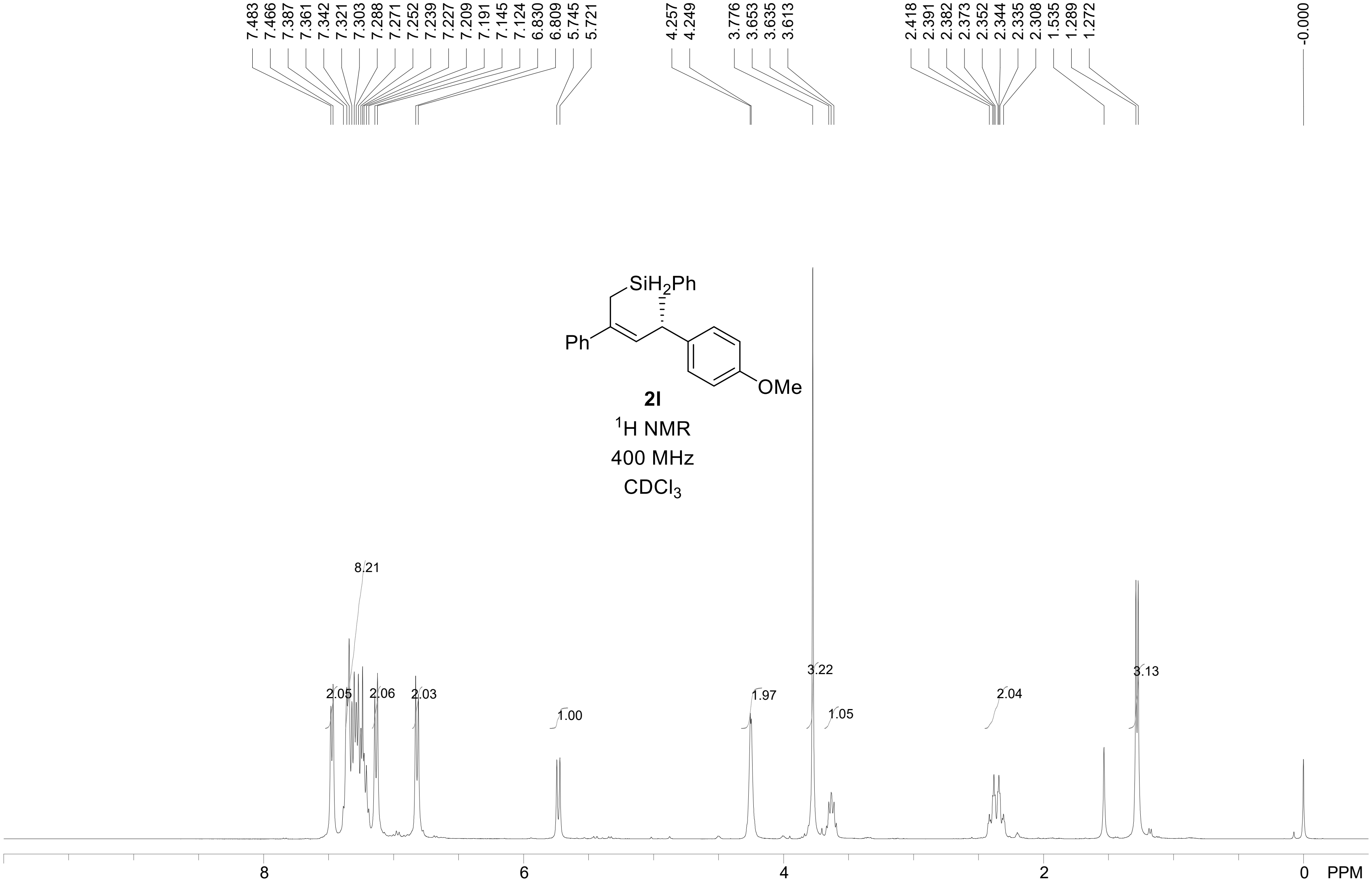


Figure S62. ^{1}H NMR spectra of **2l**, Related to Table 2

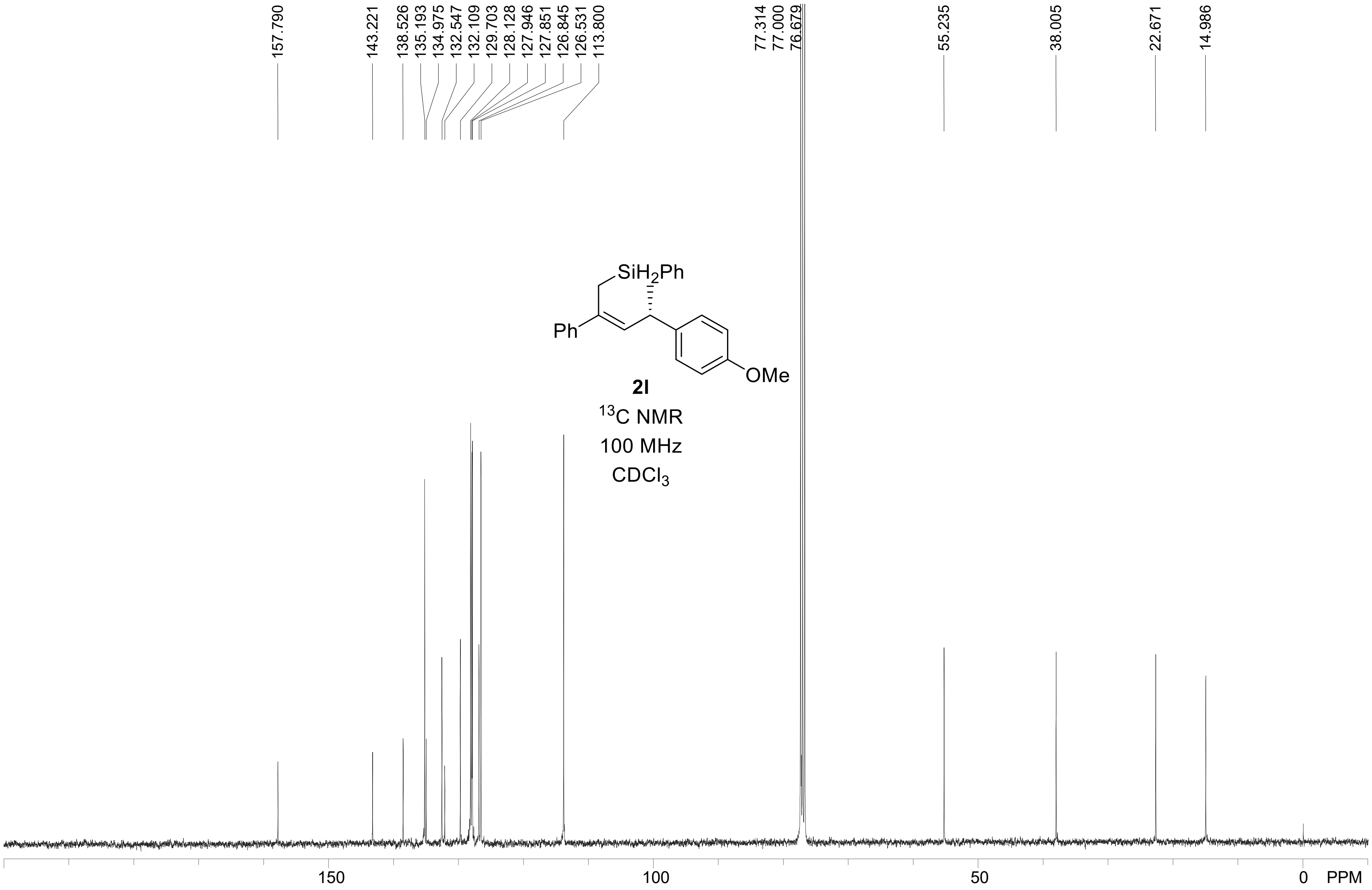


Figure S63. ^{13}C NMR spectra of **2l**, Related to Table 2

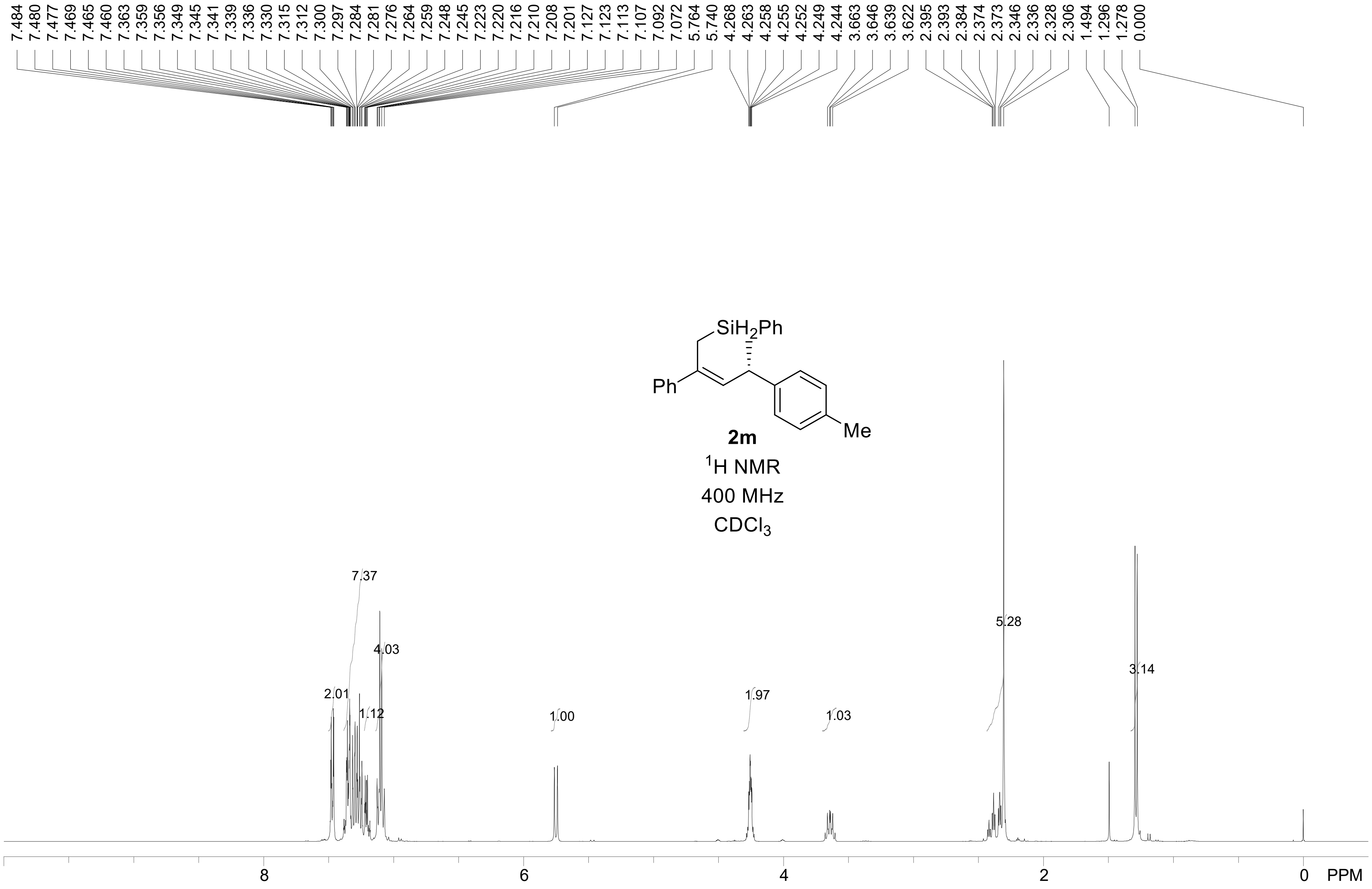


Figure S64. ^{1}H NMR spectra of **2m**, Related to Table 2

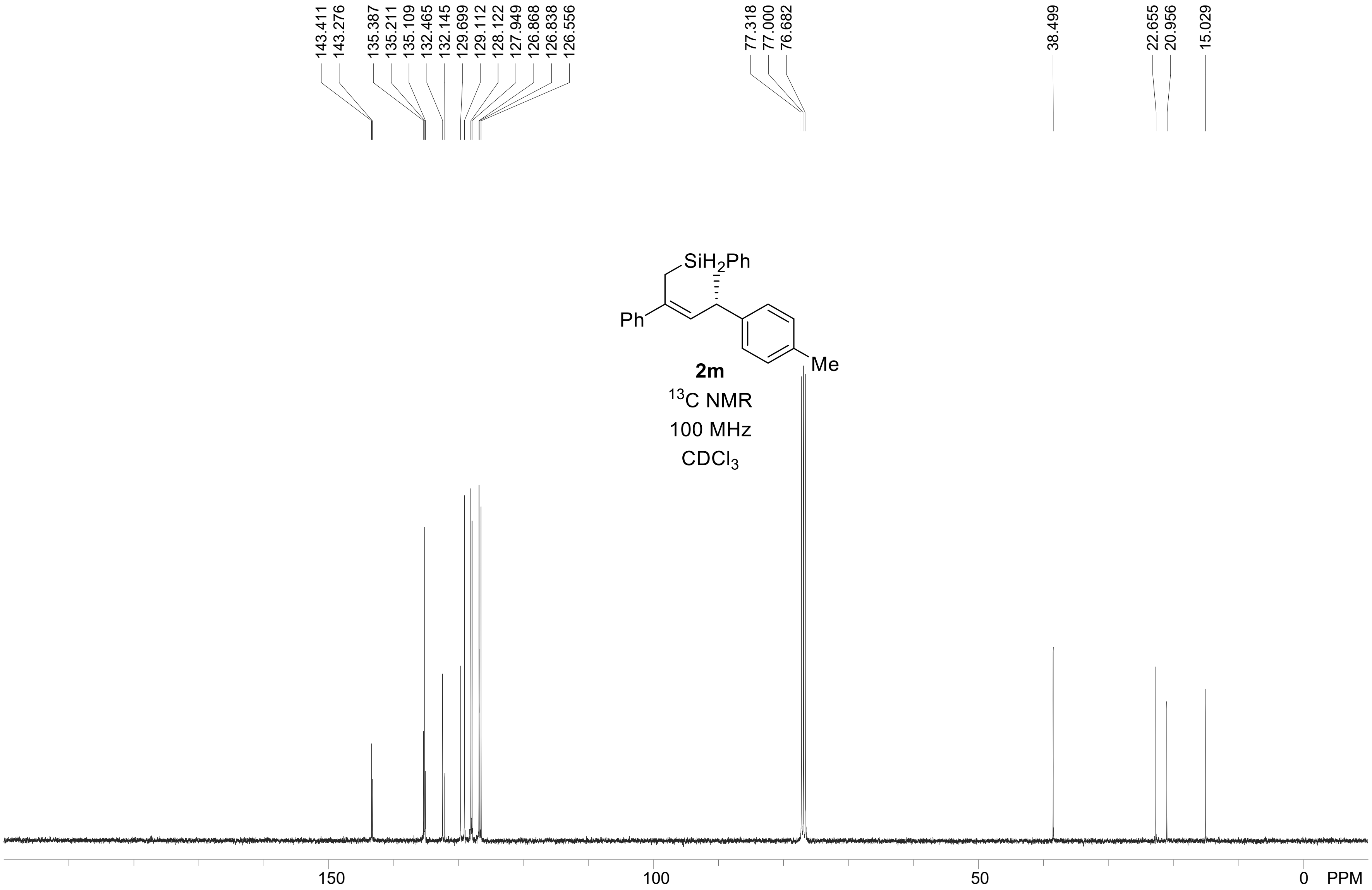


Figure S65. ^{13}C NMR spectra of **2m**, Related to Table 2

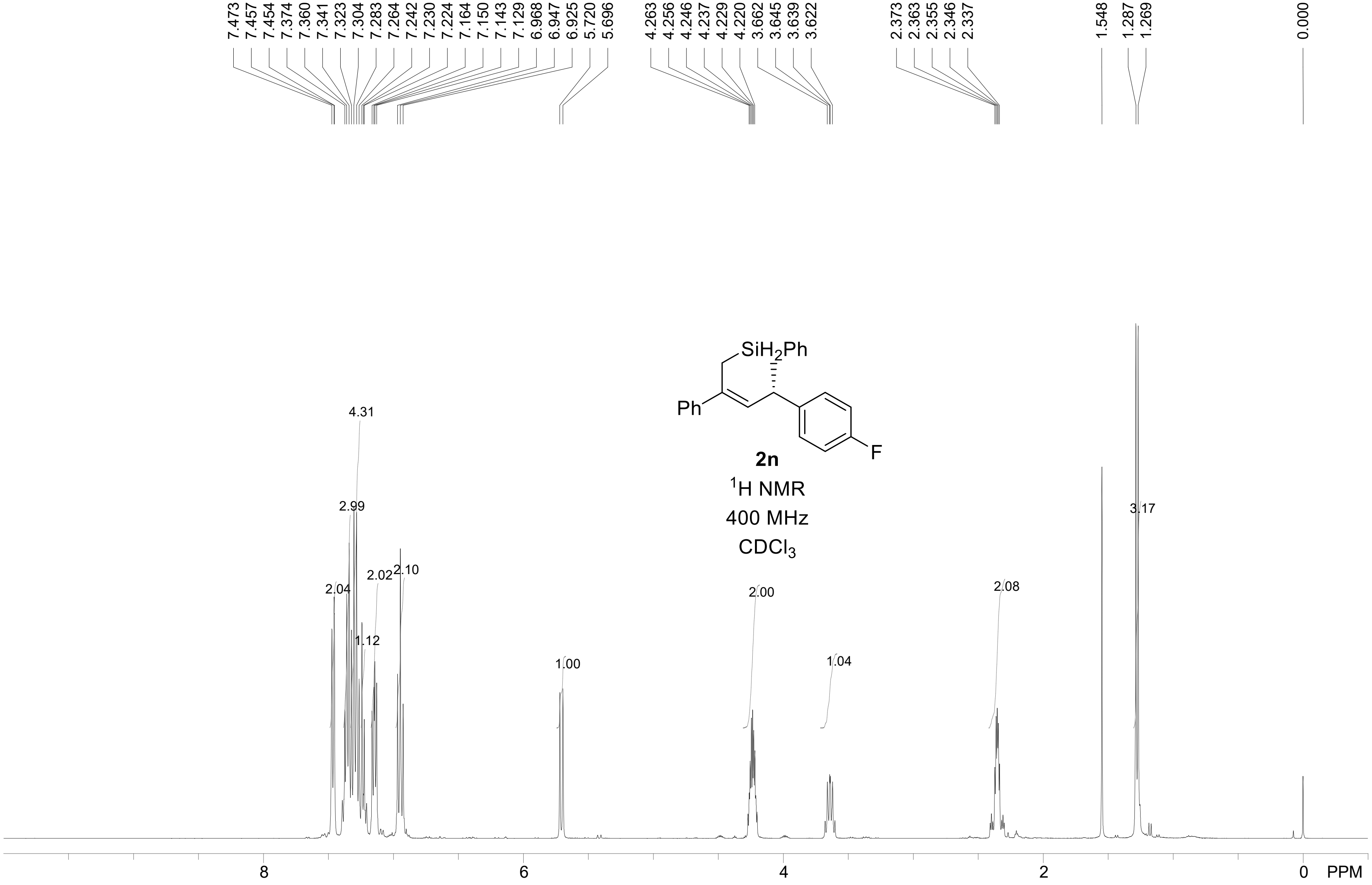


Figure S66. ^{1}H NMR spectra of **2n**, Related to Table 2

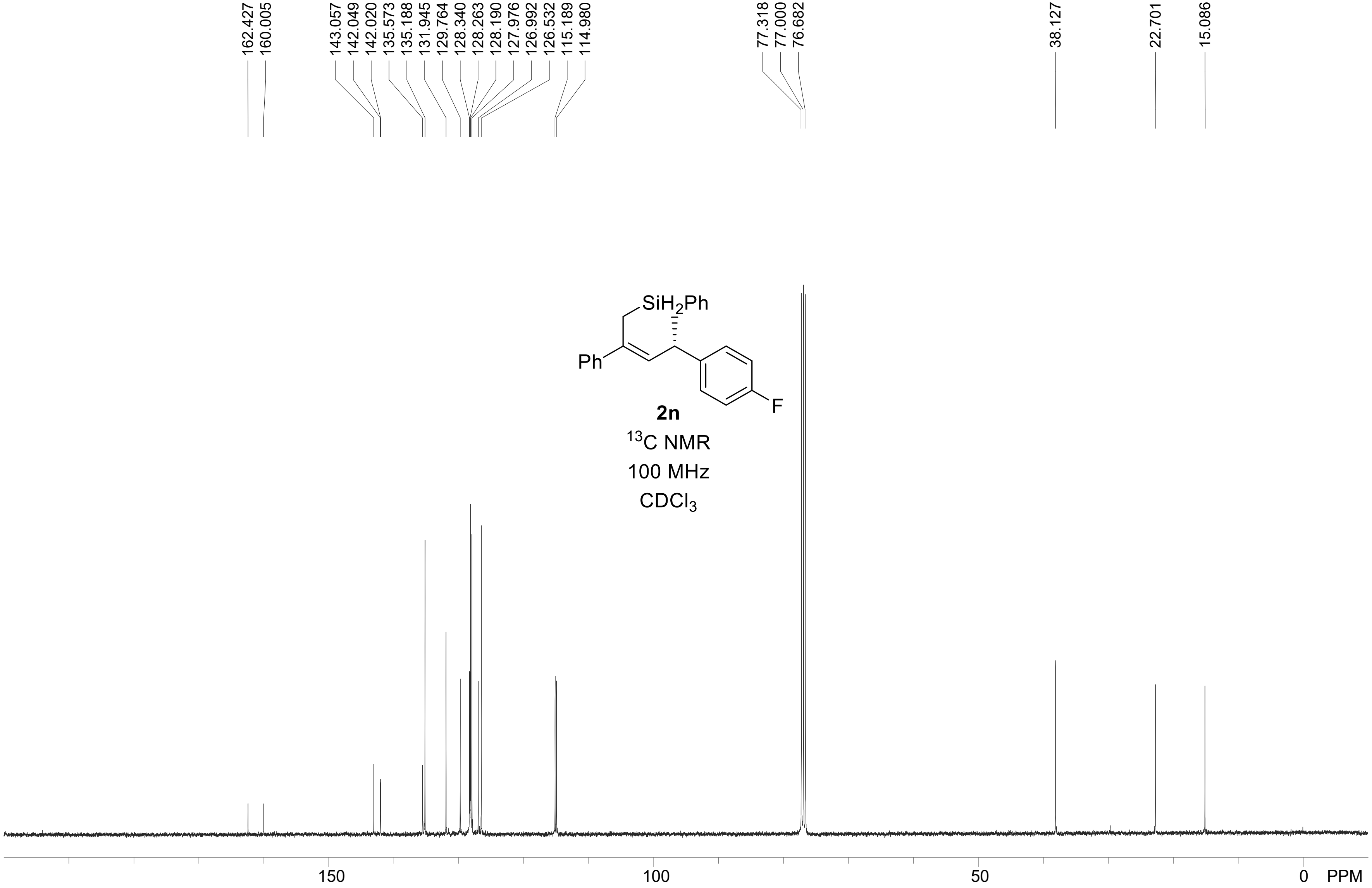


Figure S67. ^{13}C NMR spectra of **2n**, Related to Table 2

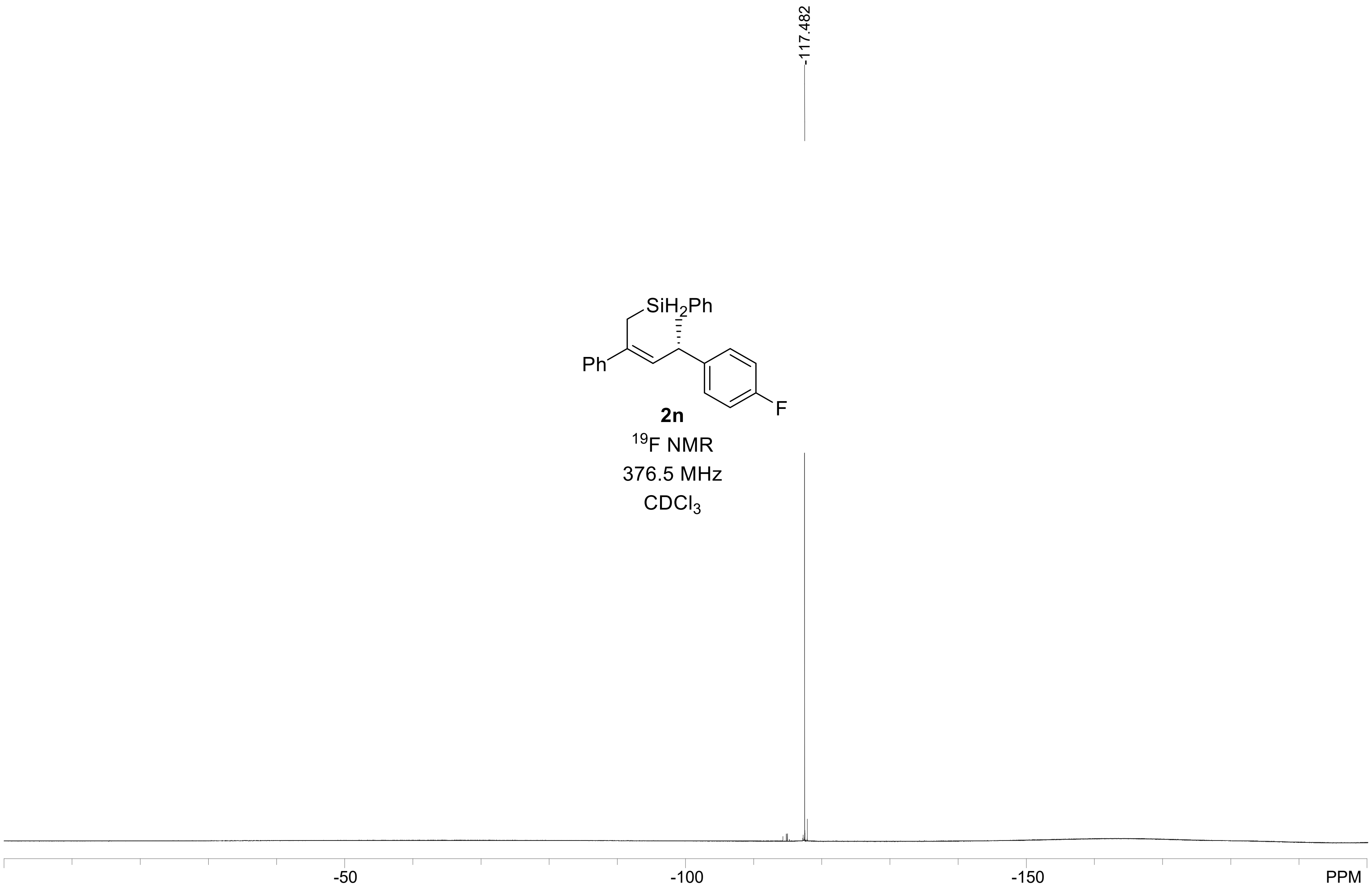


Figure S68. ^{19}F NMR spectra of **2n**, Related to Table 2

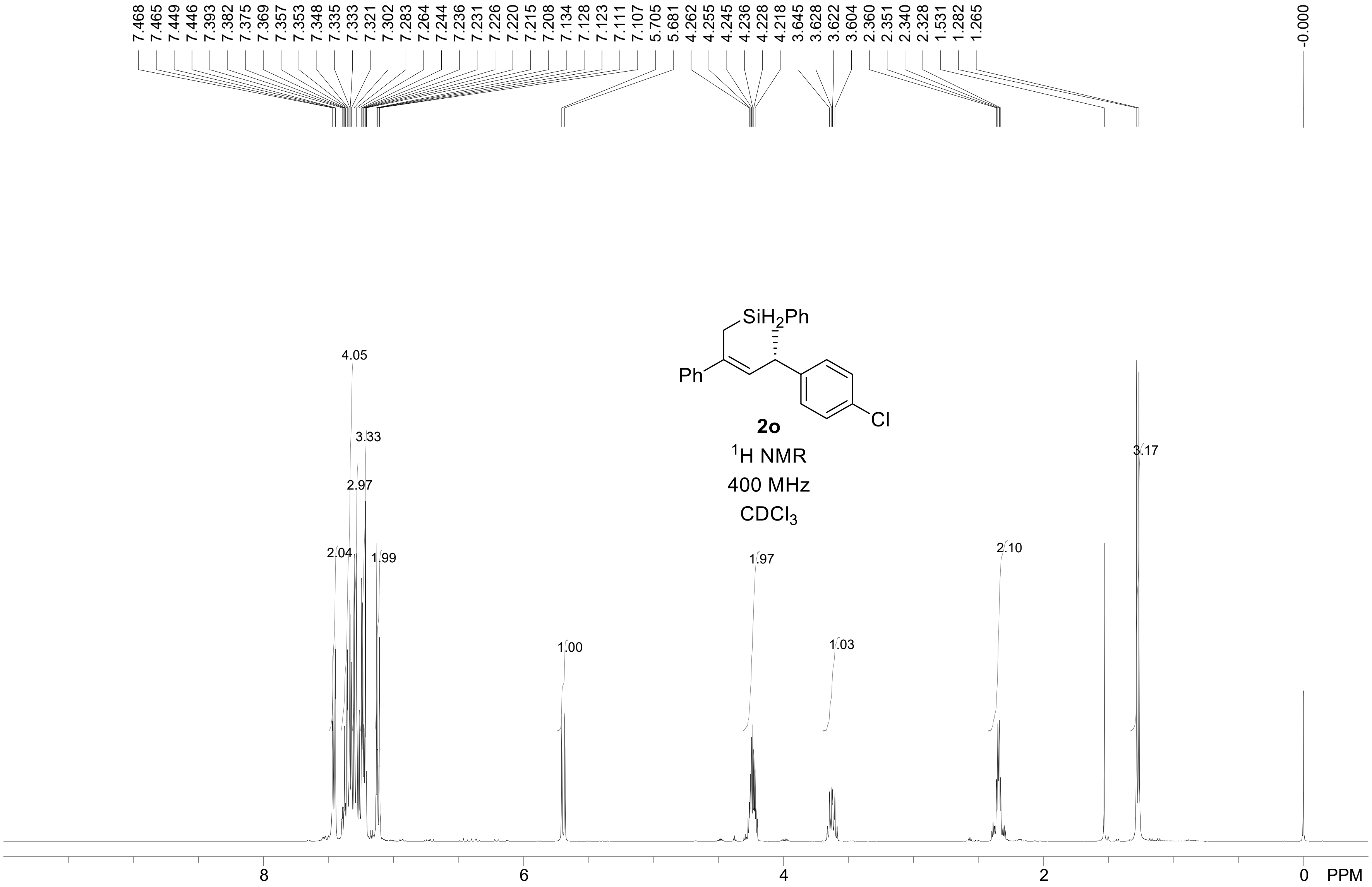


Figure S69. ^{1}H NMR spectra of **2o**, Related to Table 2

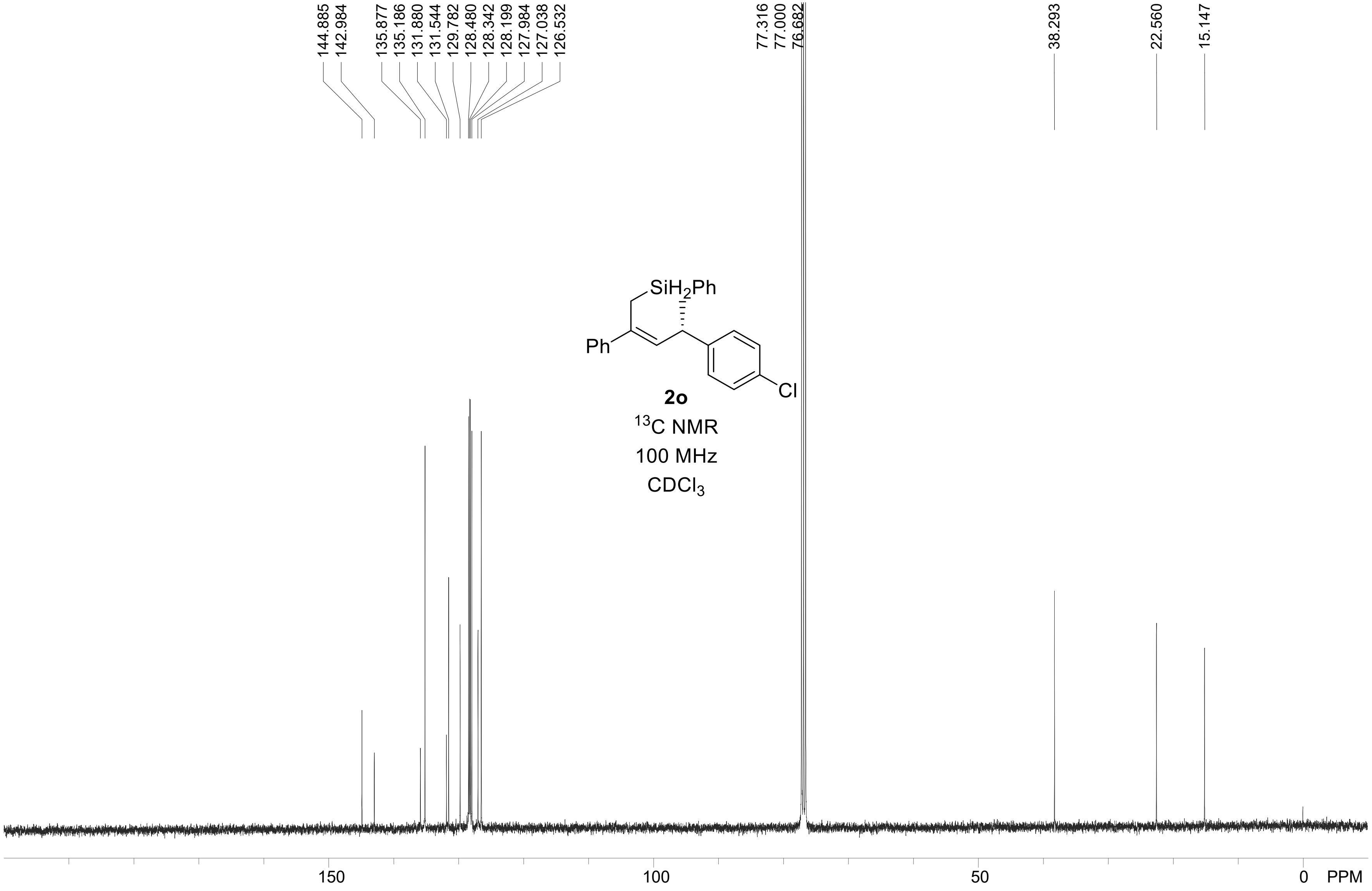


Figure S70. ^{13}C NMR spectra of **2o**, Related to Table 2

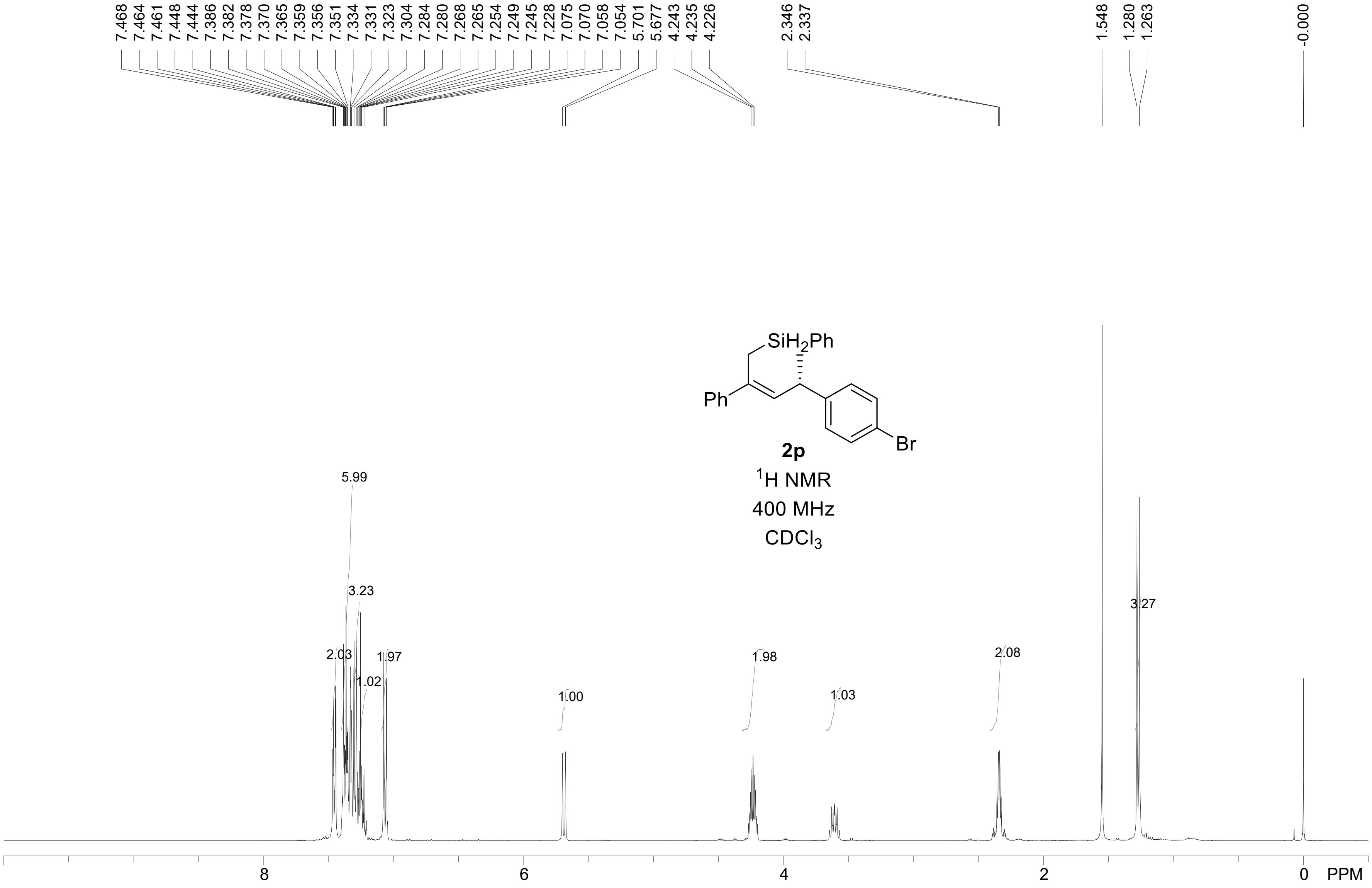


Figure S71. ^{1}H NMR spectra of **2p**, Related to Table 2

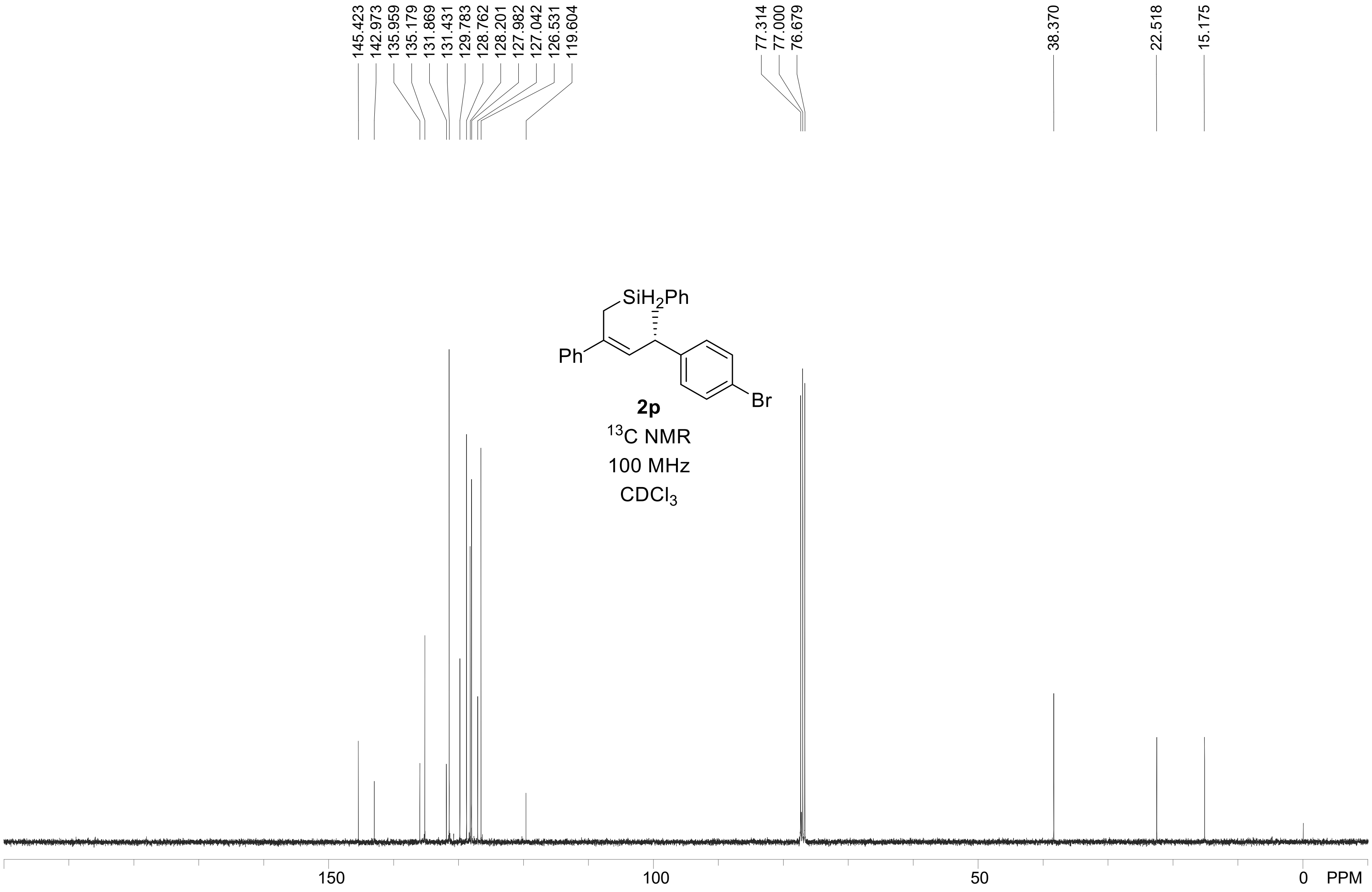


Figure S72. ^{13}C NMR spectra of **2p**, Related to Table 2

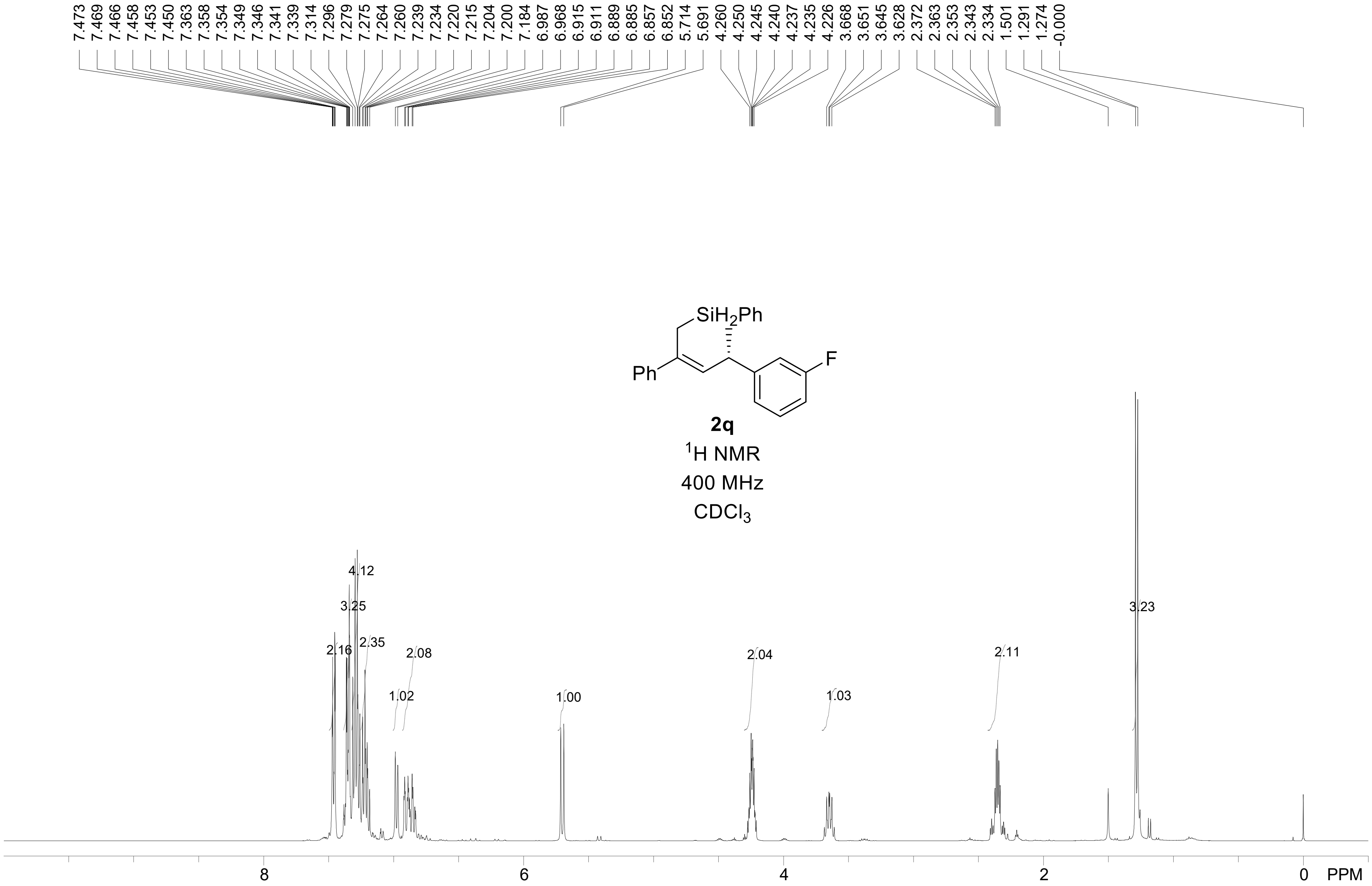


Figure S73. ^{1}H NMR spectra of **2q**, Related to Table 2

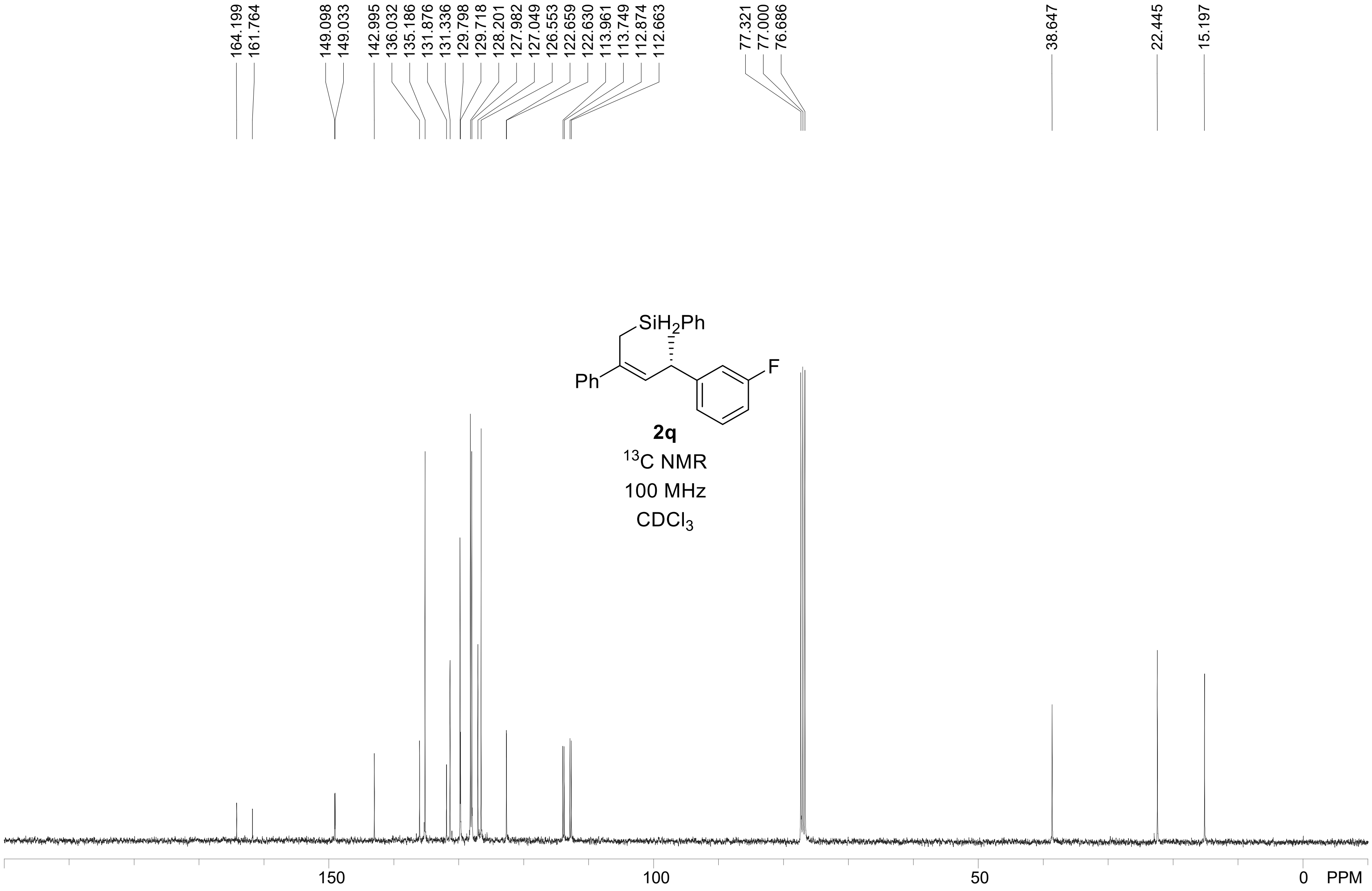


Figure S74. ^{13}C NMR spectra of **2q**, Related to Table 2

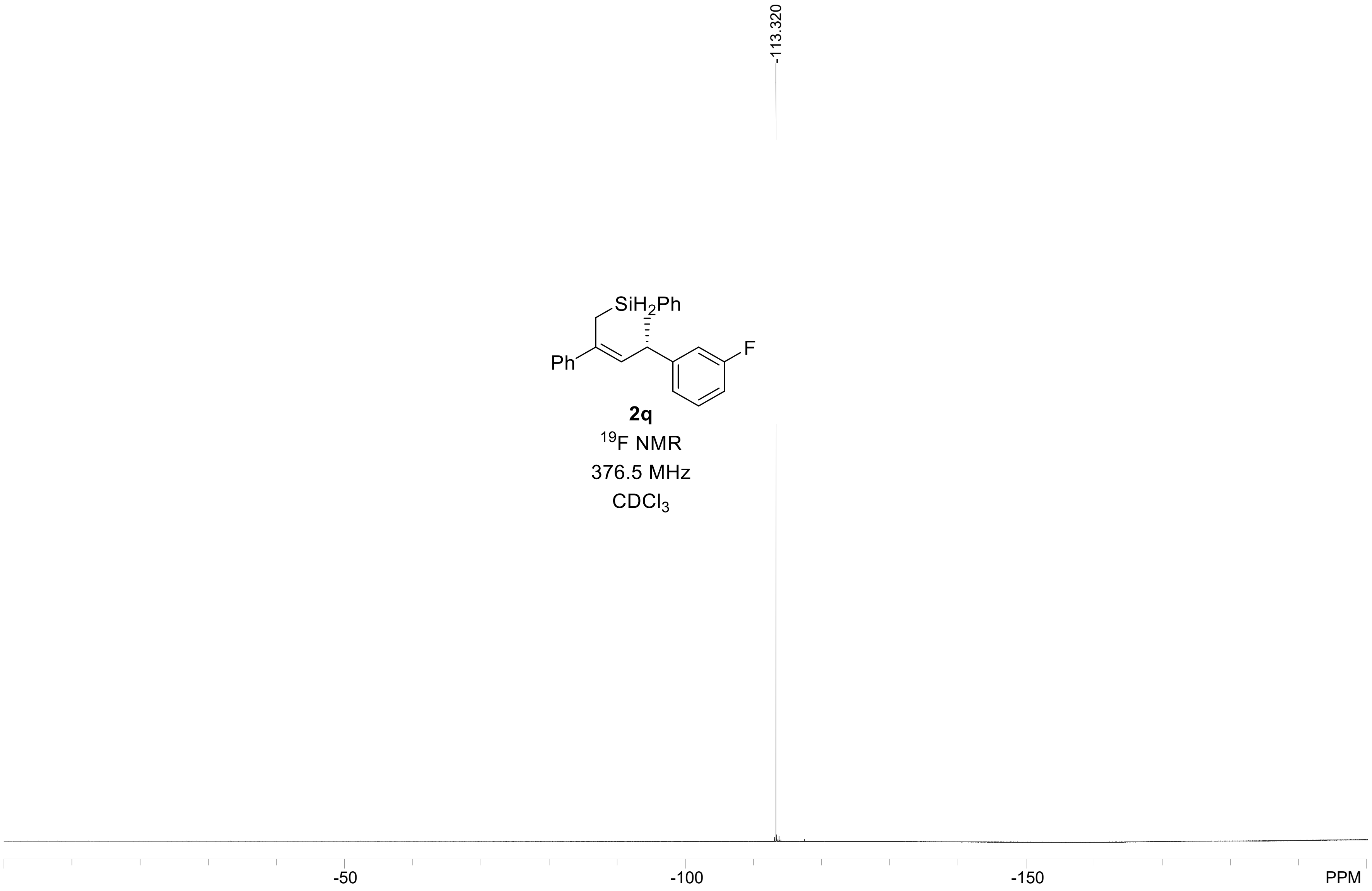


Figure S75. ^{19}F NMR spectra of **2q**, Related to Table 2

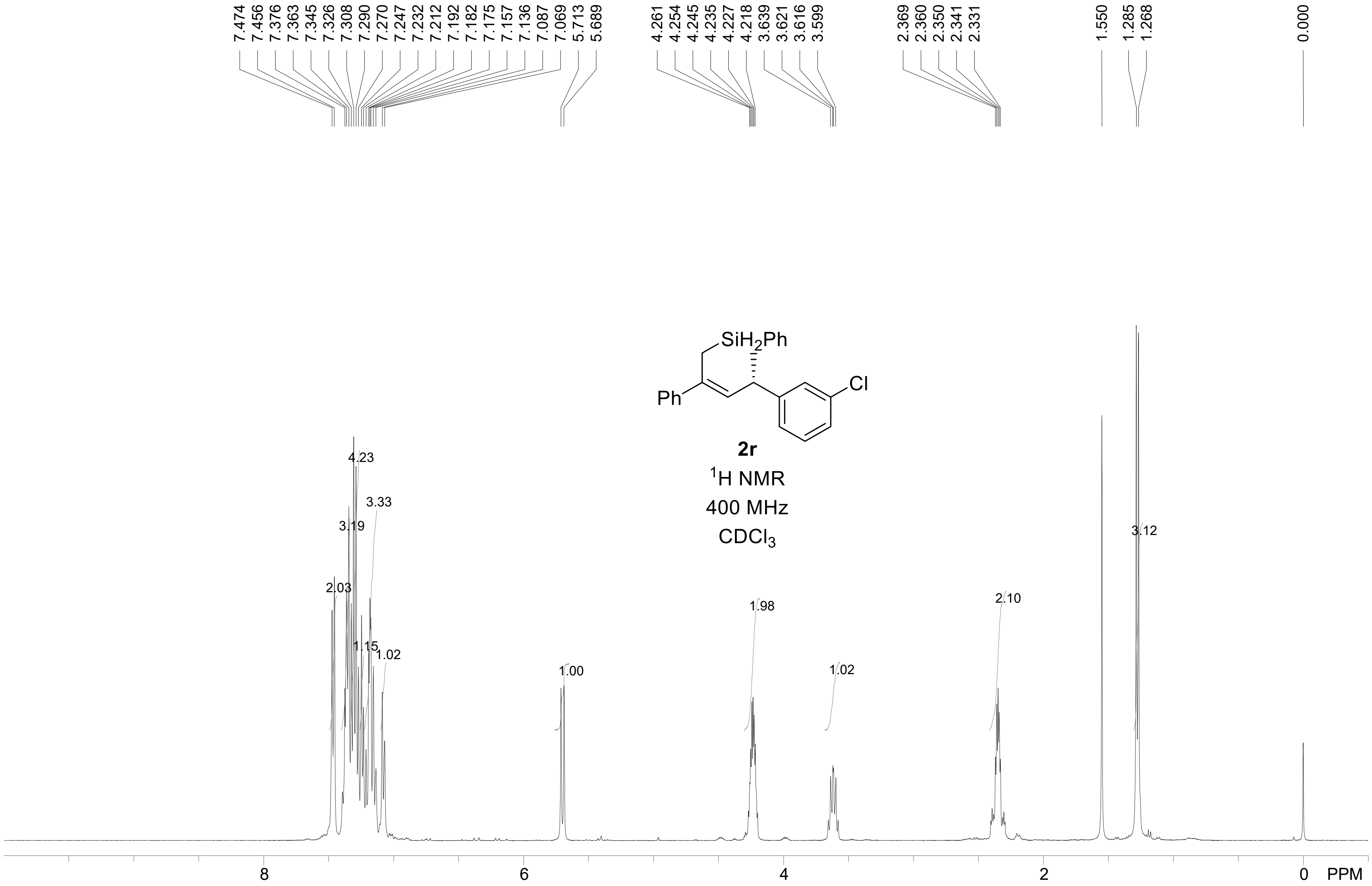


Figure S76. ^{1}H NMR spectra of **2r**, Related to Table 2

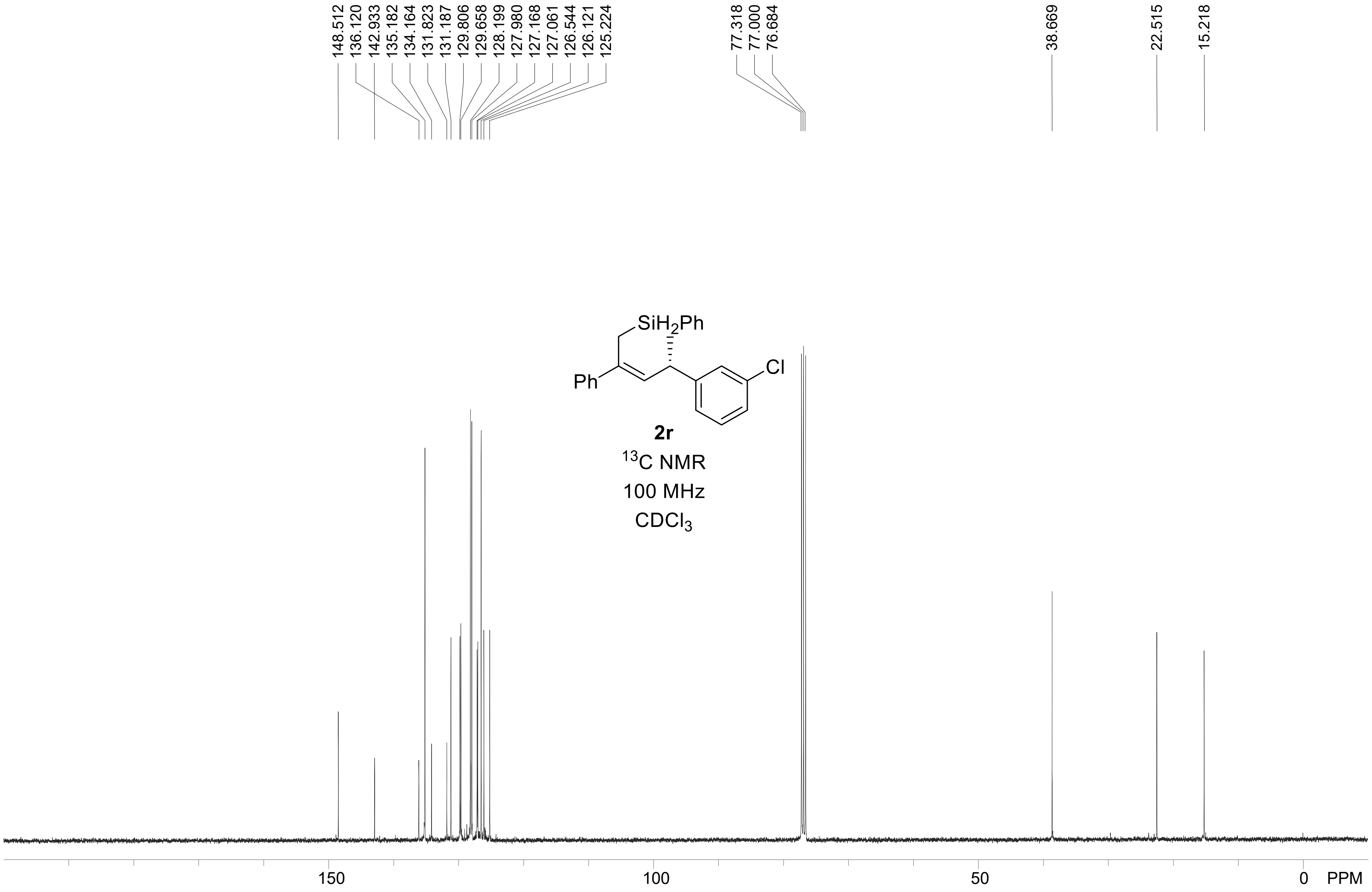


Figure S77. ^{13}C NMR spectra of **2r**, Related to Table 2

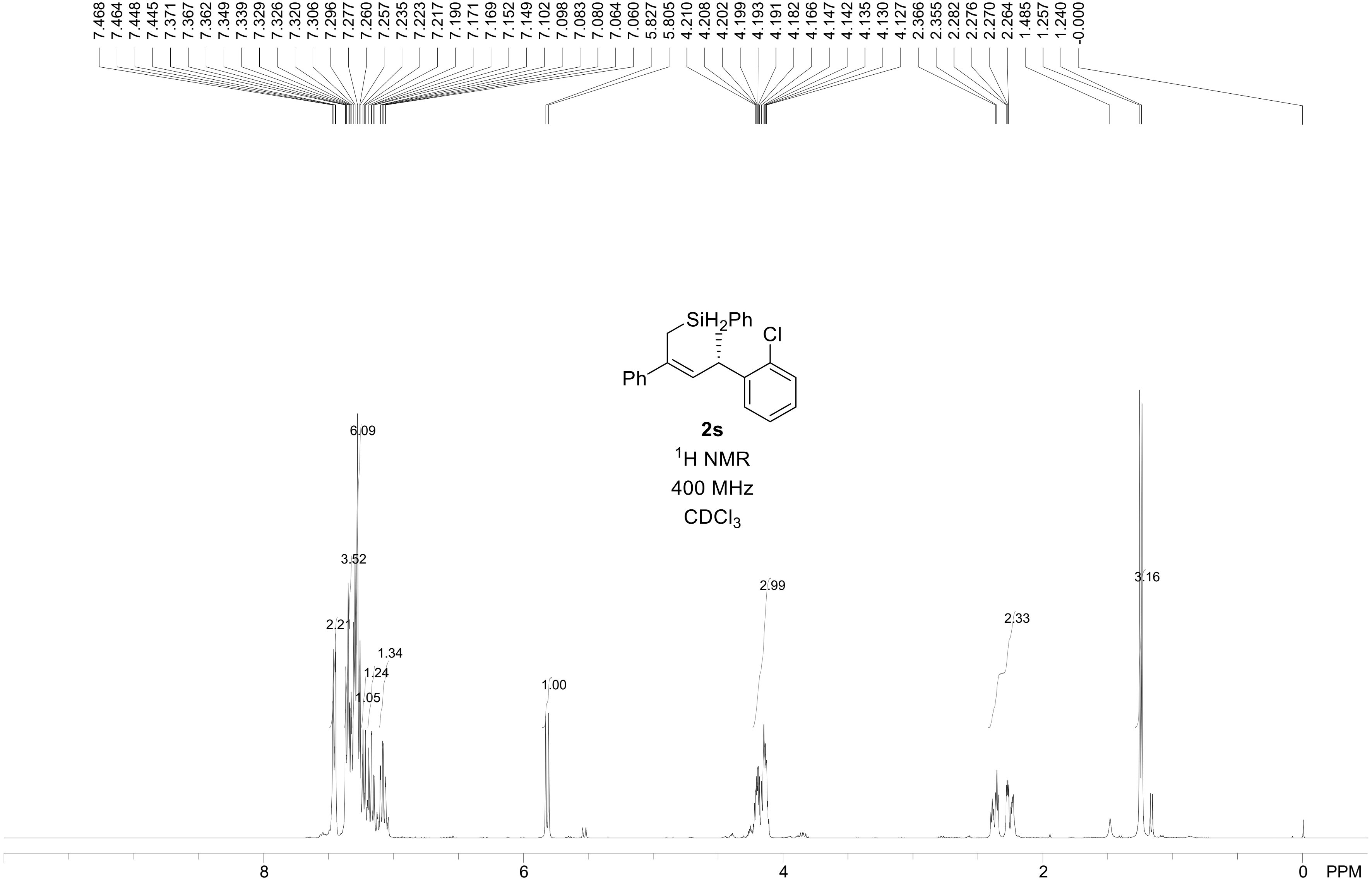


Figure S78. ^{1}H NMR spectra of **2s**, Related to Table 2

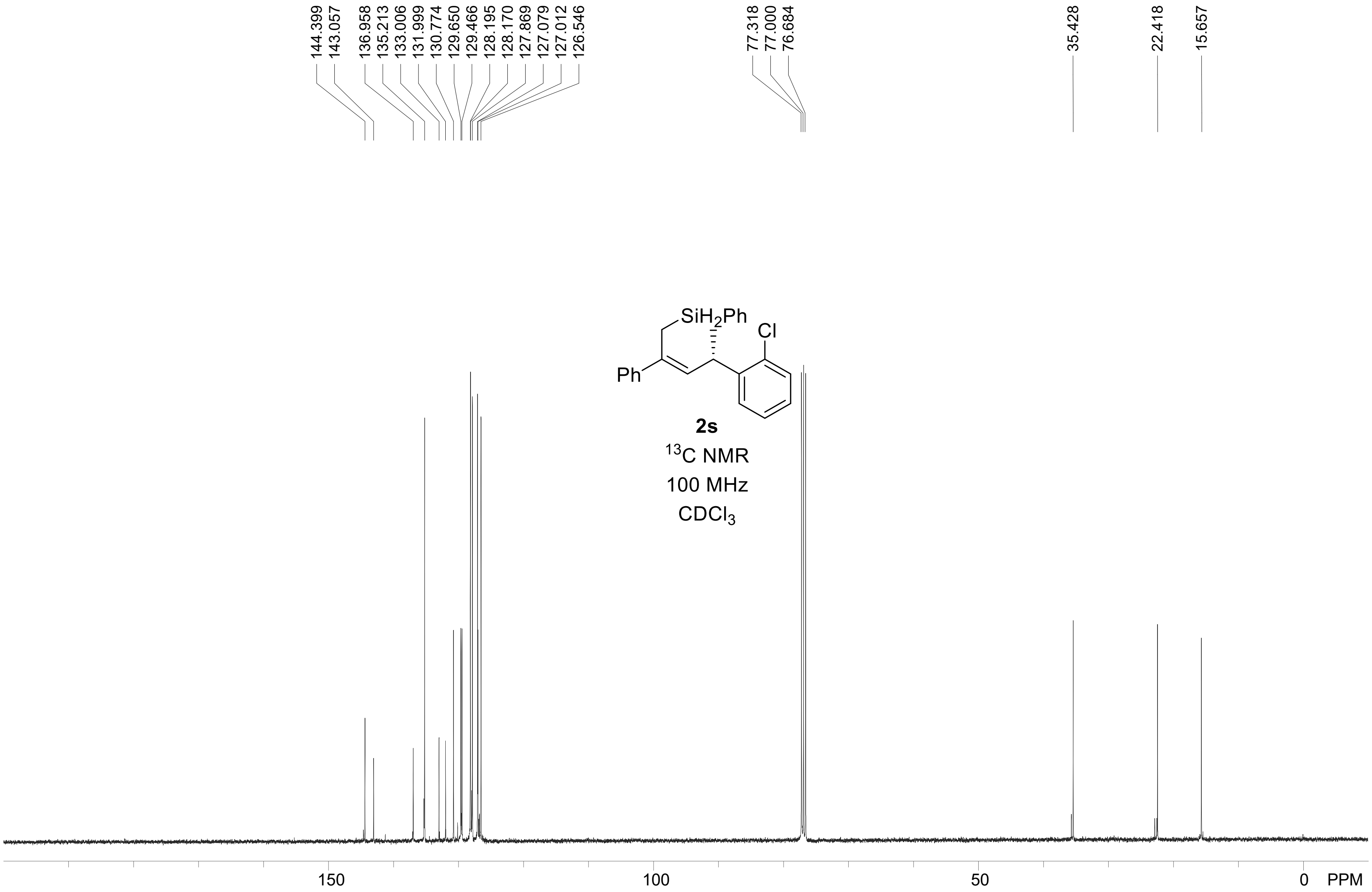


Figure S79. ^{13}C NMR spectra of **2s**, Related to Table 2

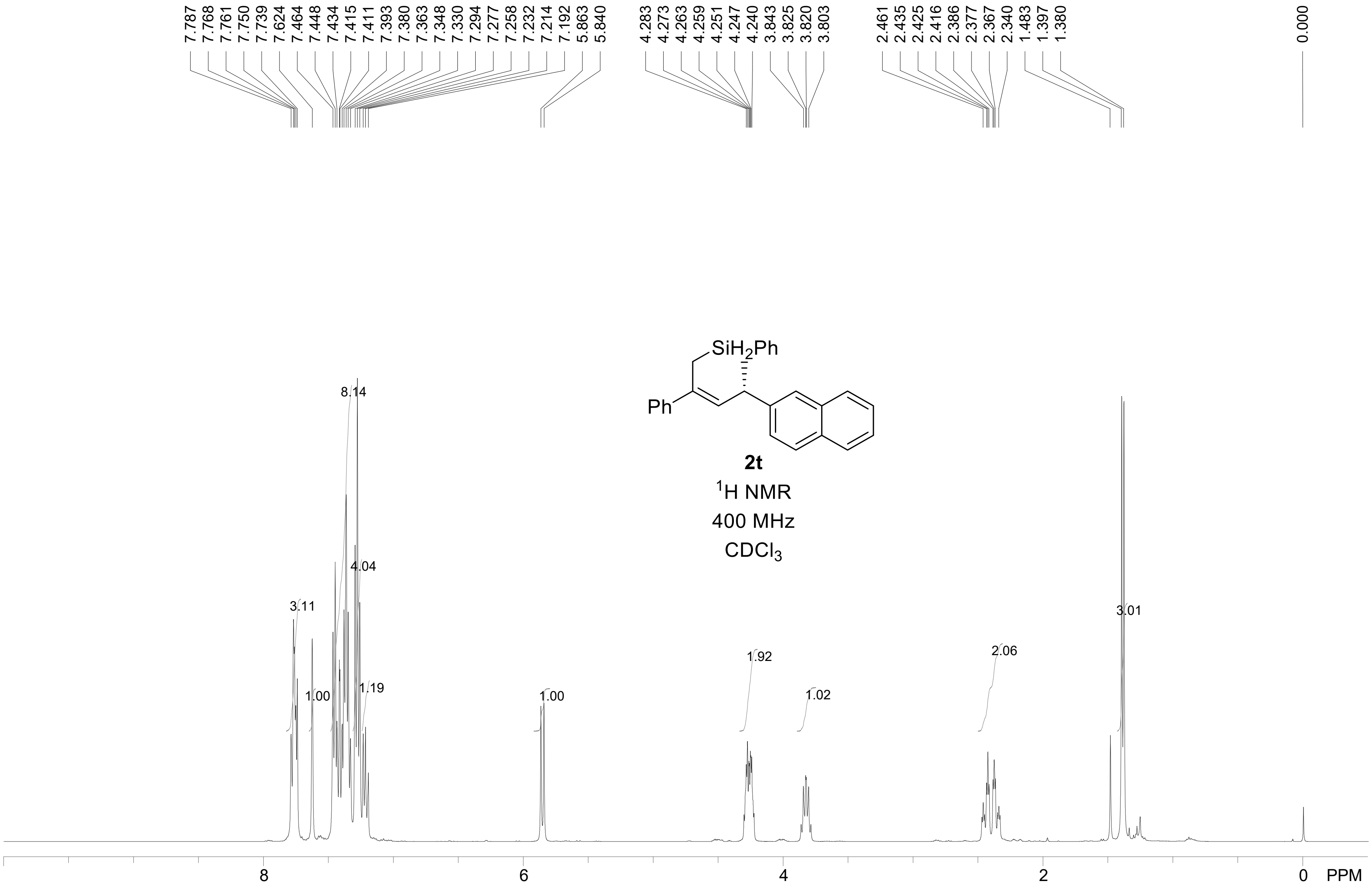


Figure S80. ^{1}H NMR spectra of **2t**, Related to Table 2

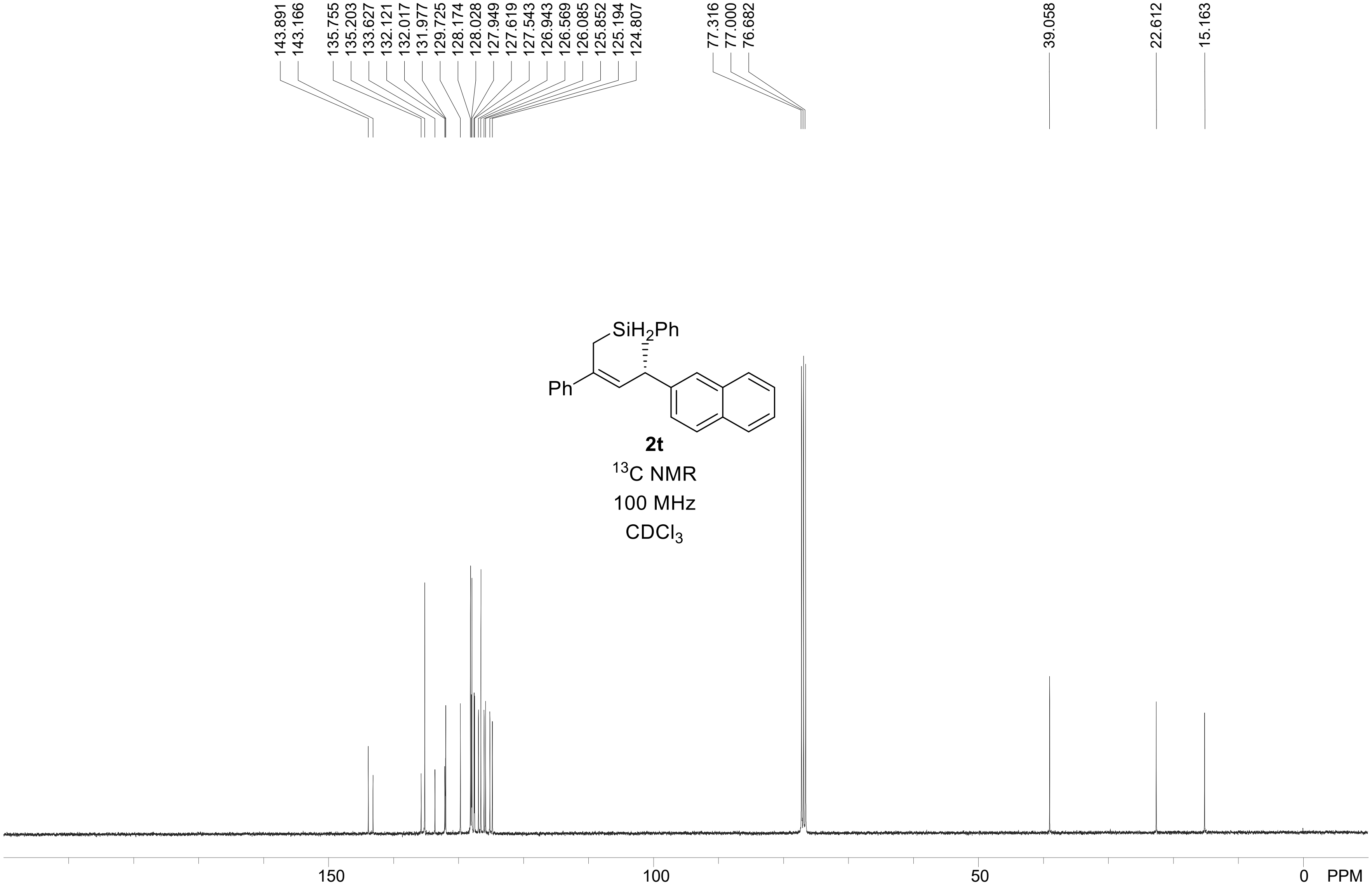


Figure S81. ^{13}C NMR spectra of **2t**, Related to Table 2

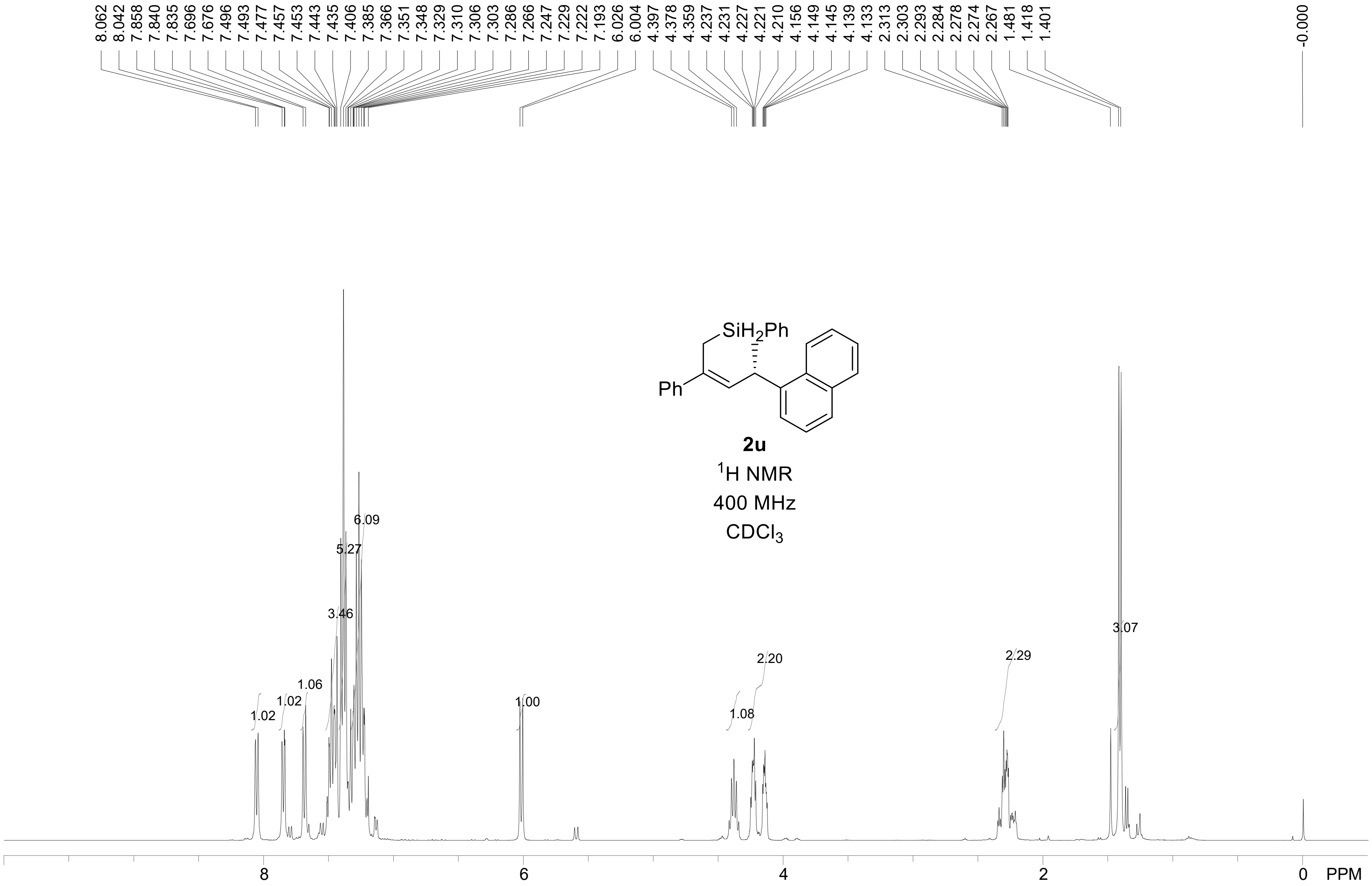


Figure S82. ^{1}H NMR spectra of **2u**, Related to Table 2

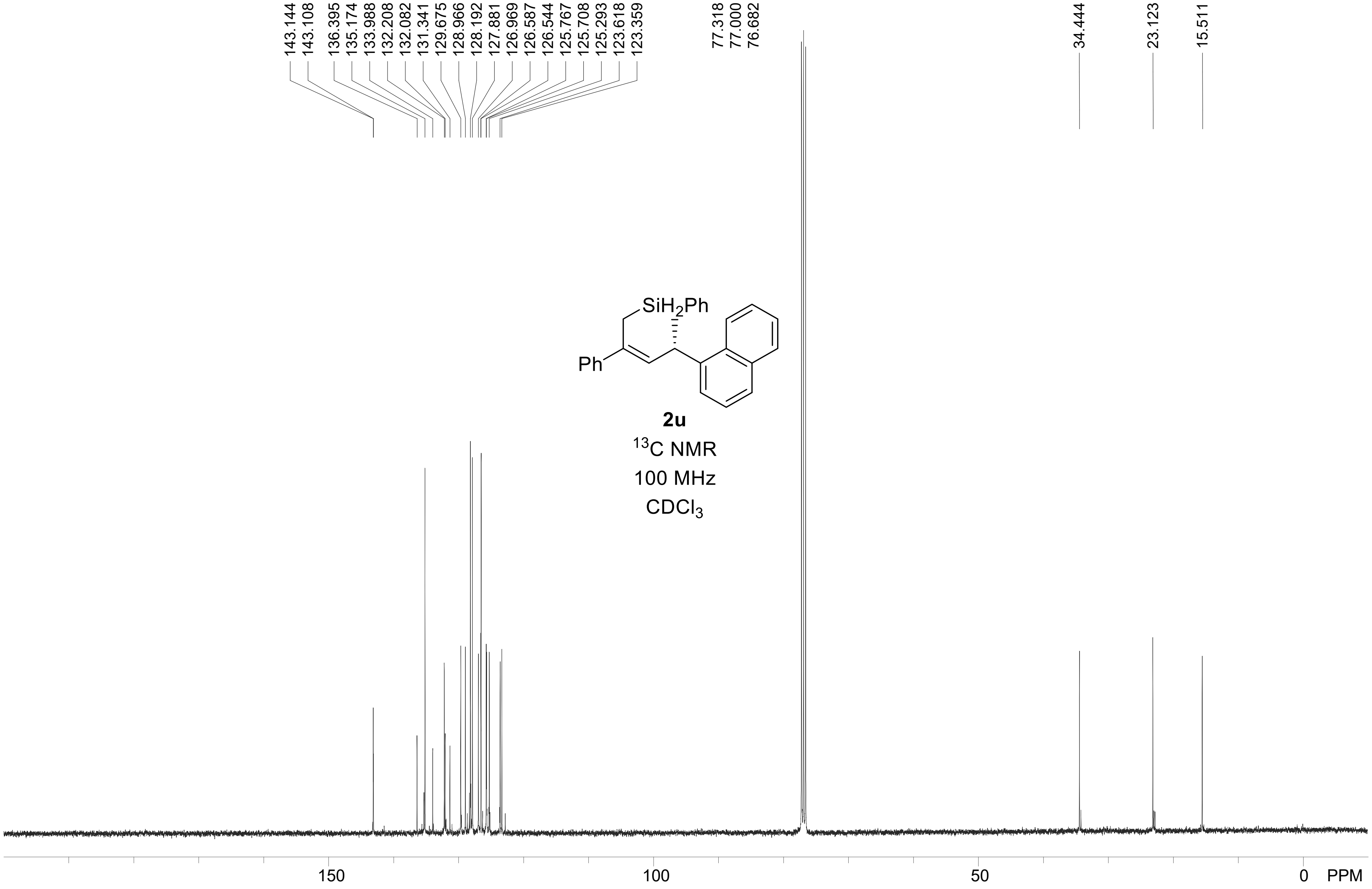


Figure S83. ^{13}C NMR spectra of **2u**, Related to Table 2

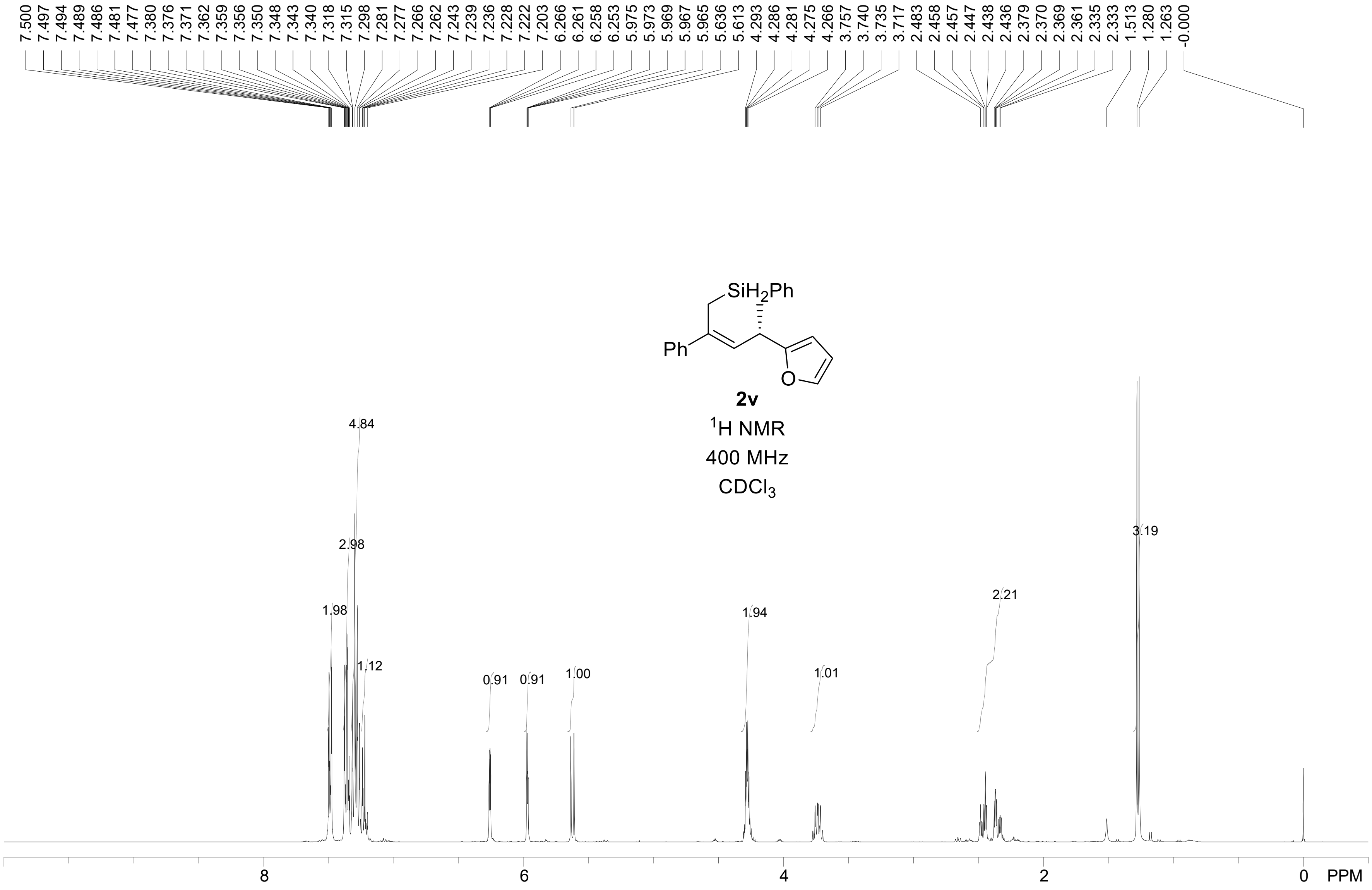


Figure S84. ^{1}H NMR spectra of **2v**, Related to Table 2

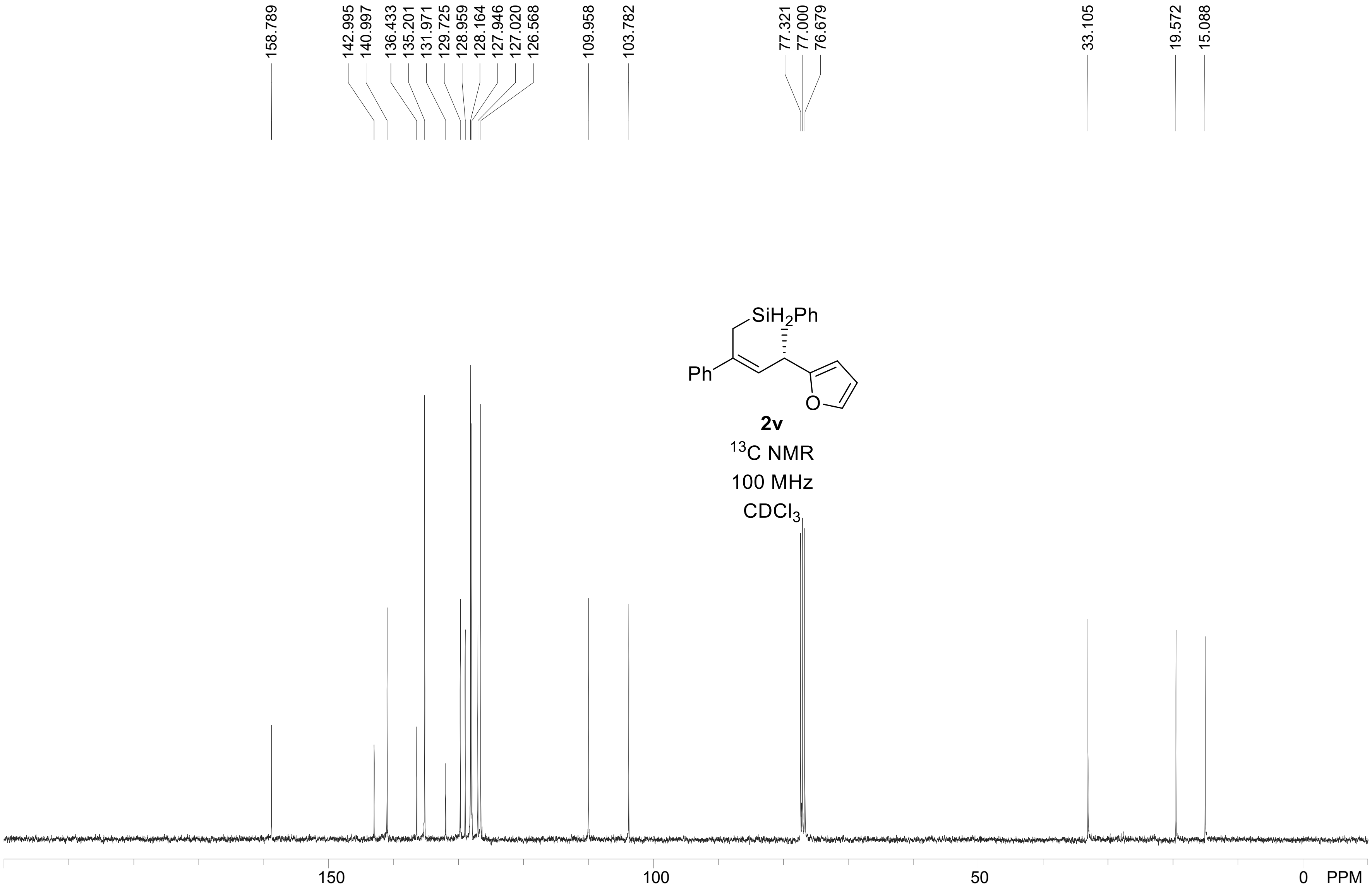


Figure S85. ^{13}C NMR spectra of **2v**, Related to Table 2

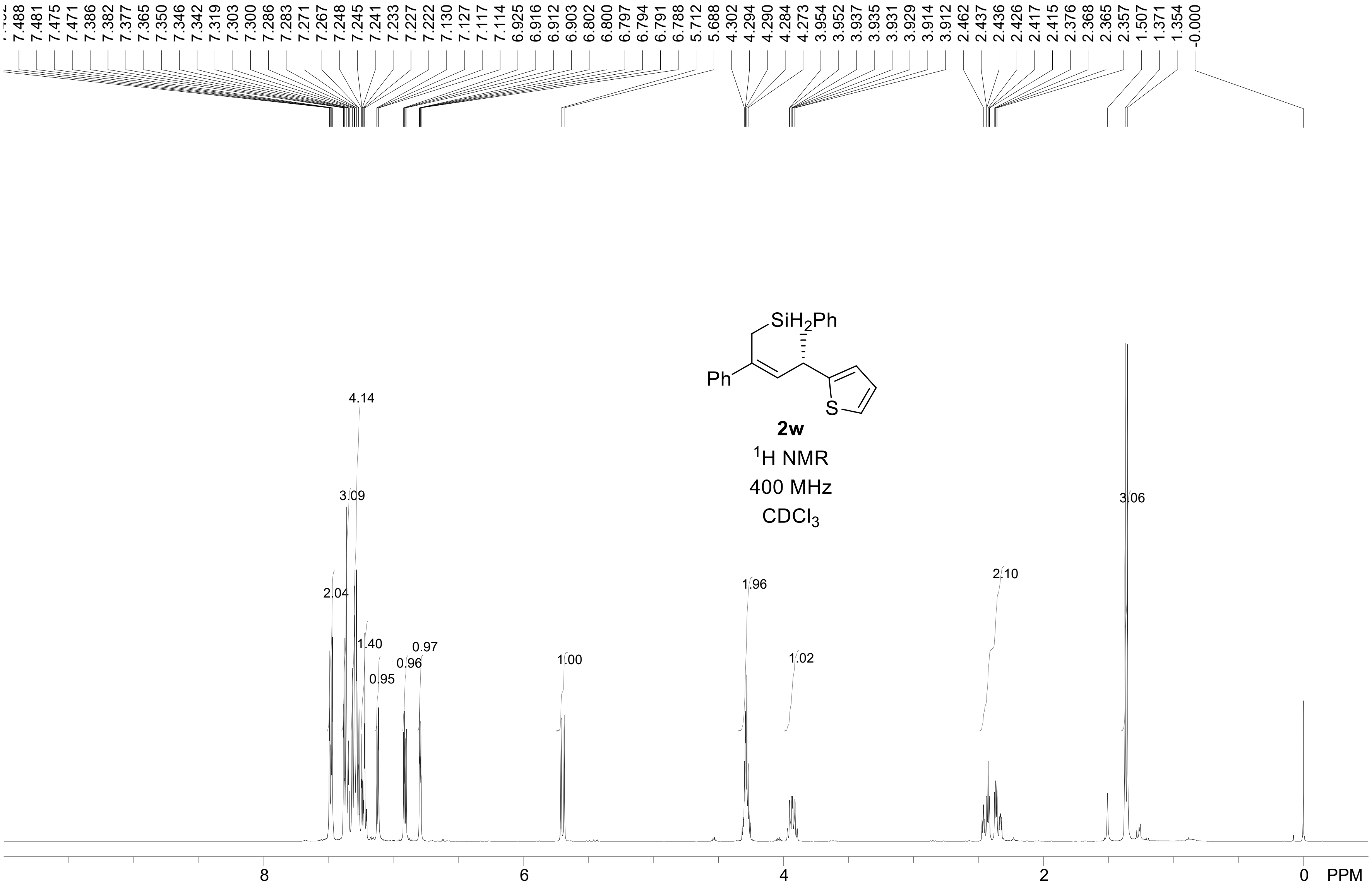


Figure S86. ^{1}H NMR spectra of **2w**, Related to Table 2

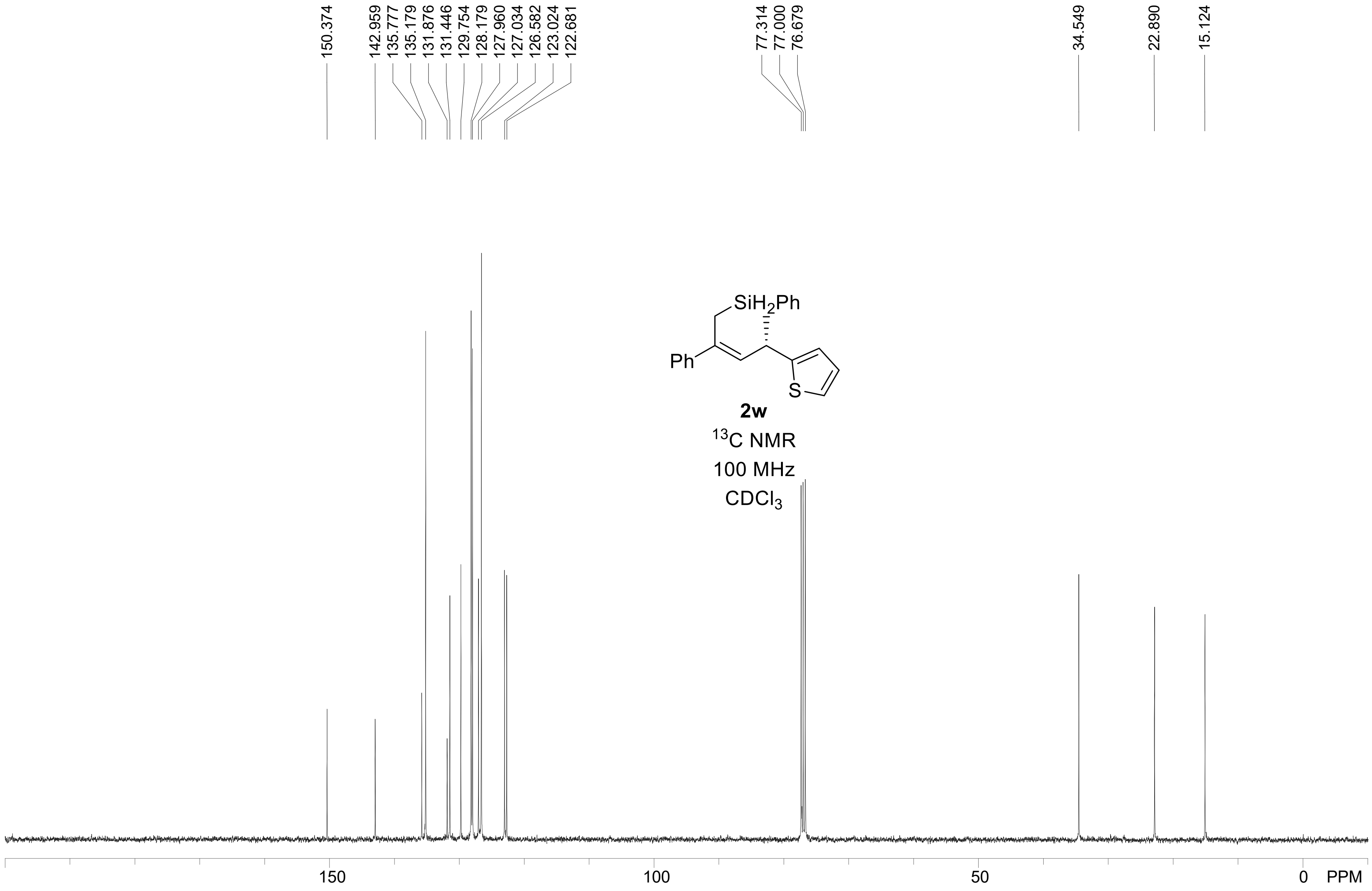


Figure S87. ^{13}C NMR spectra of **2w**, Related to Table 2

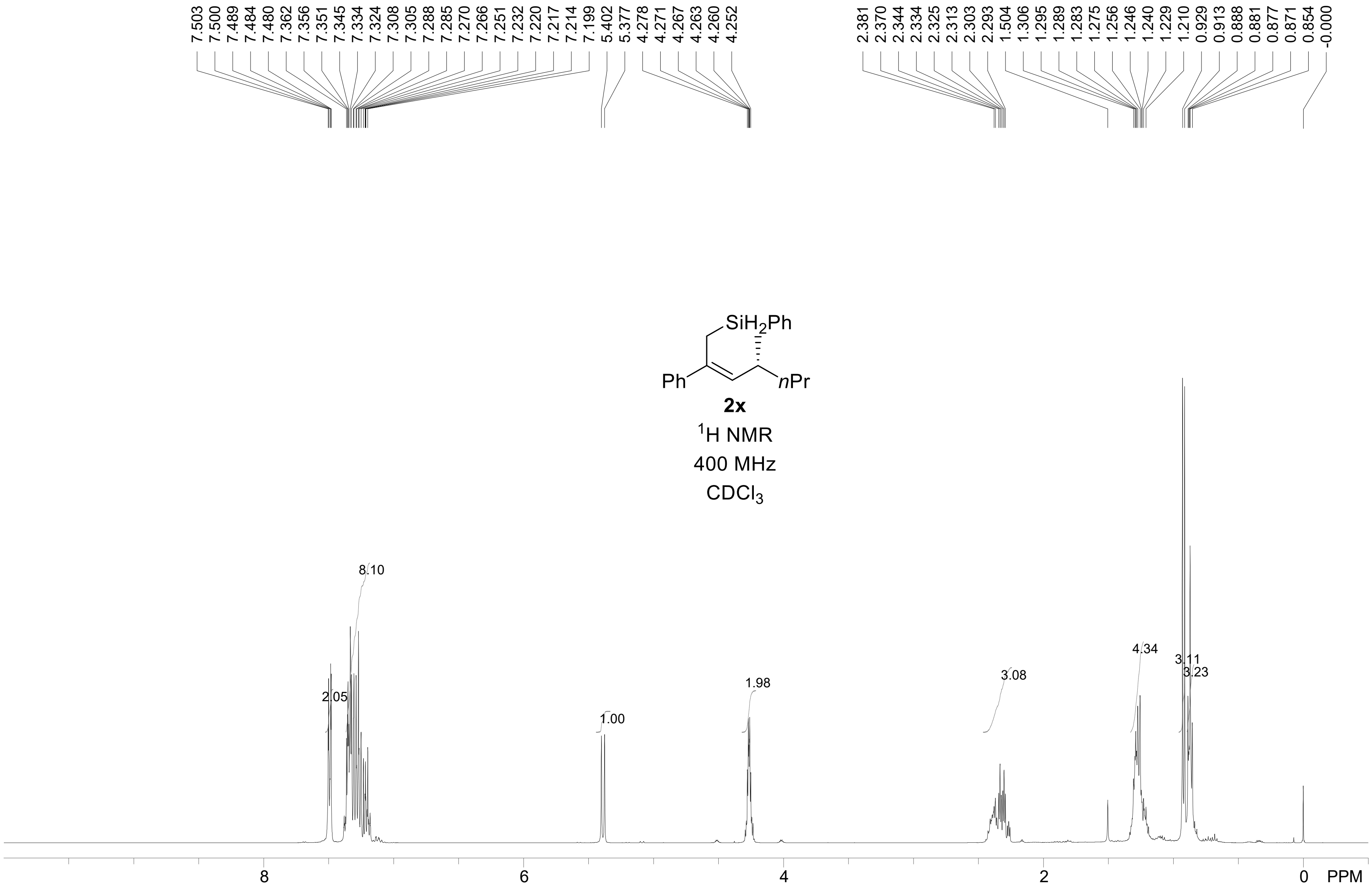


Figure S88. ^{1}H NMR spectra of **2x**, Related to Table 2

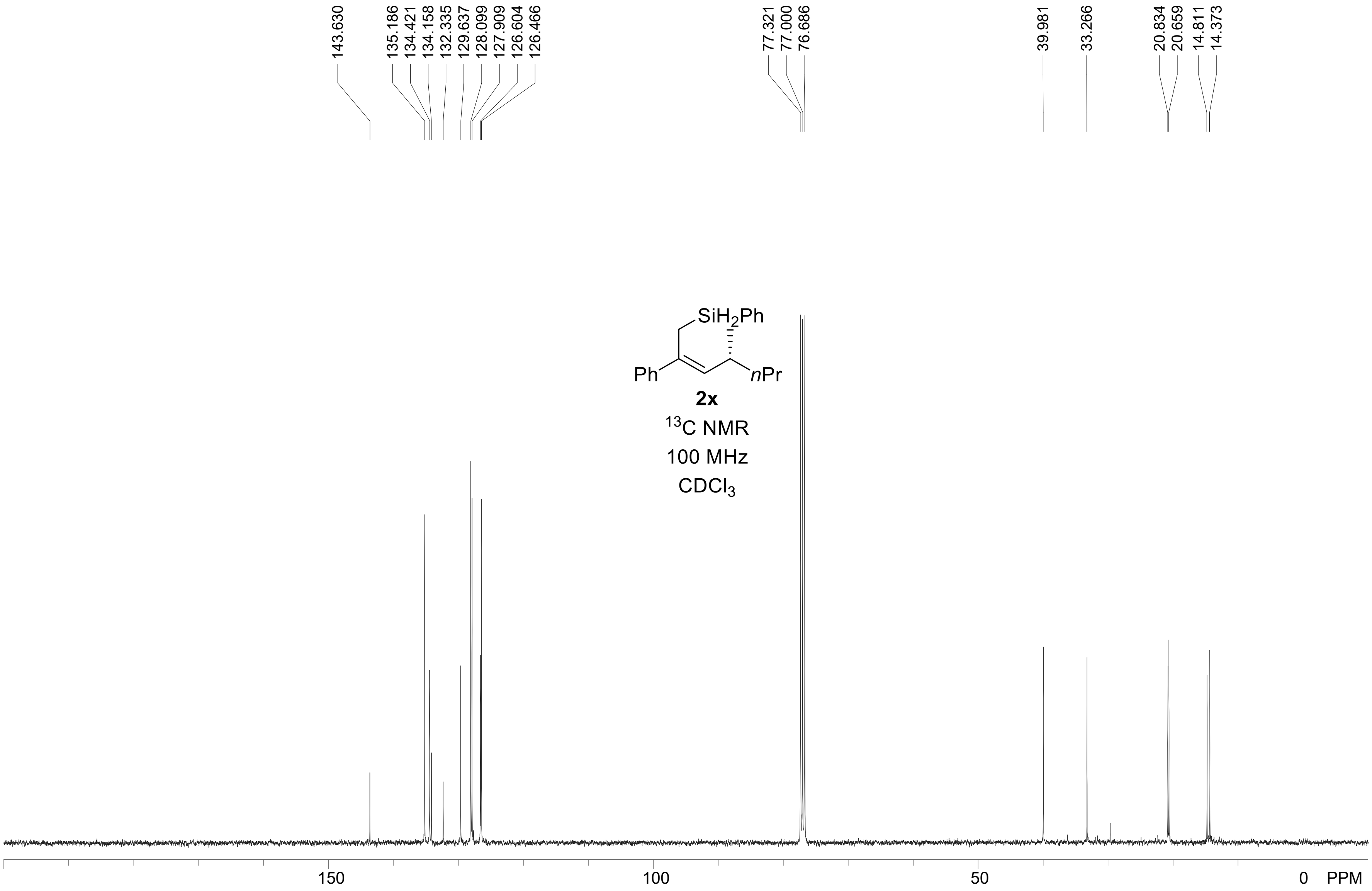


Figure S89. ^{13}C NMR spectra of **2x**, Related to Table 2

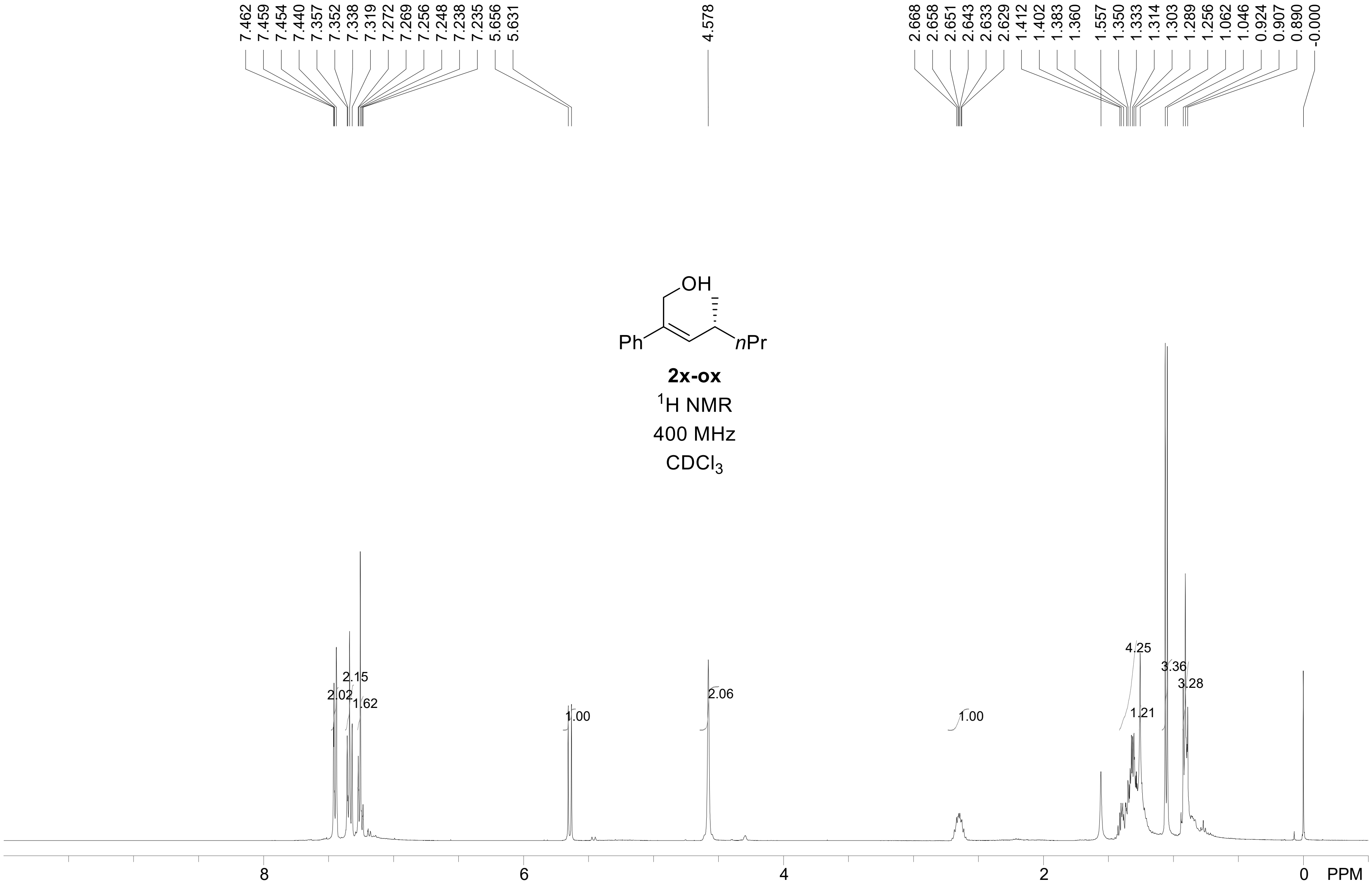


Figure S90. ^{1}H NMR spectra of **2x-ox**, Related to Table 2

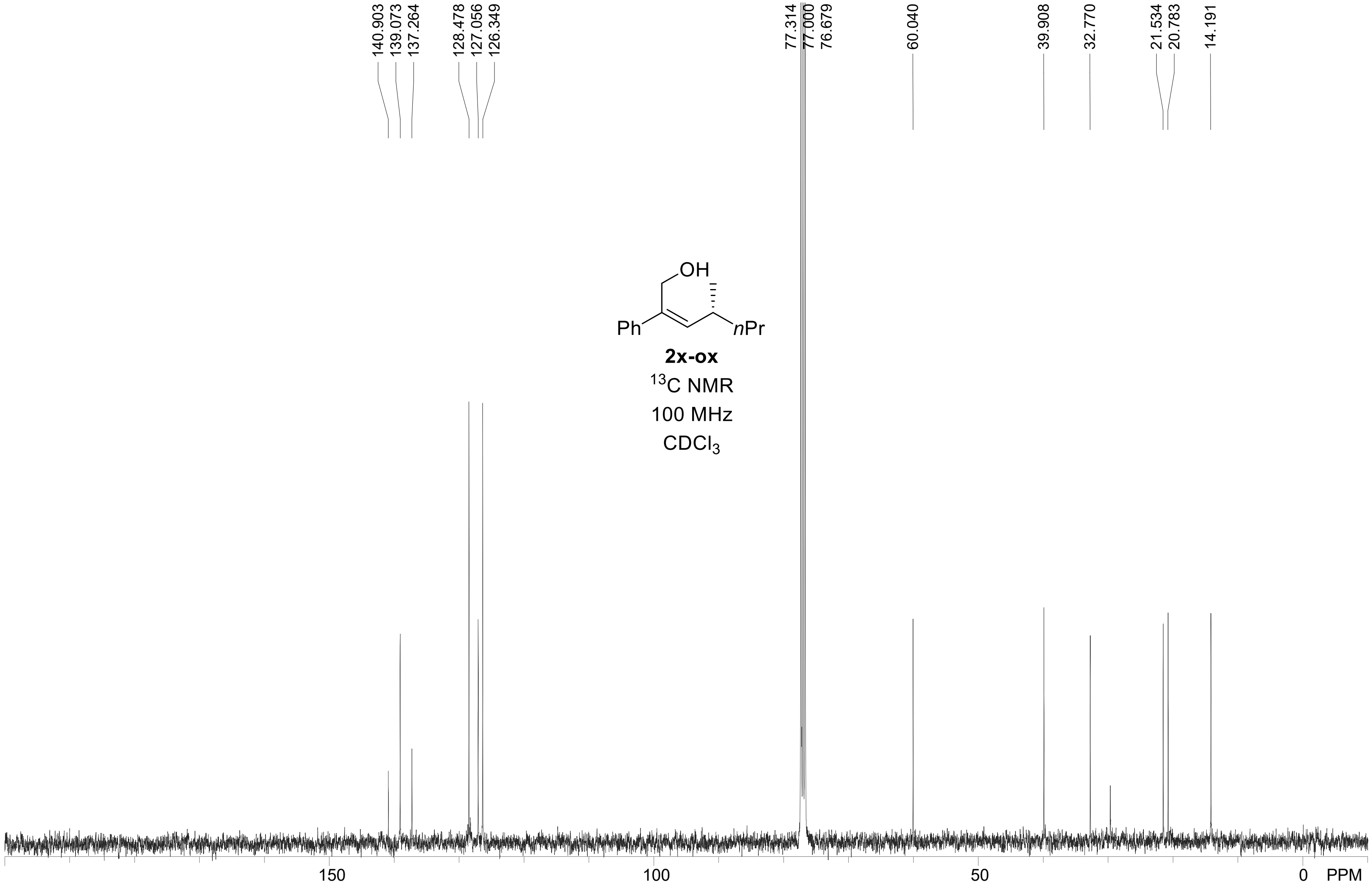


Figure S91. ^{13}C NMR spectra of **2x-ox**, Related to Table 2

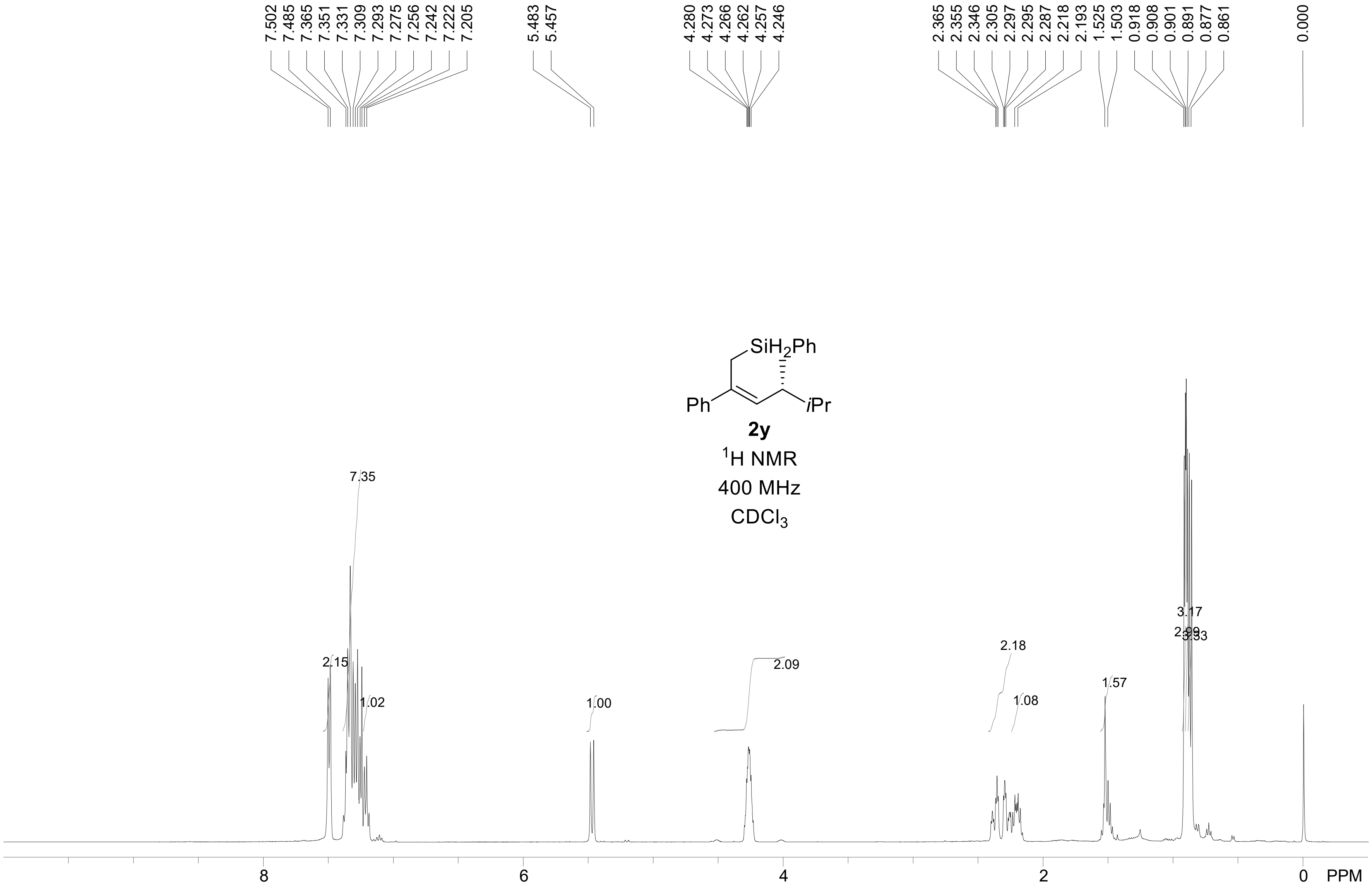


Figure S92. ^{1}H NMR spectra of **2y**, Related to Table 2

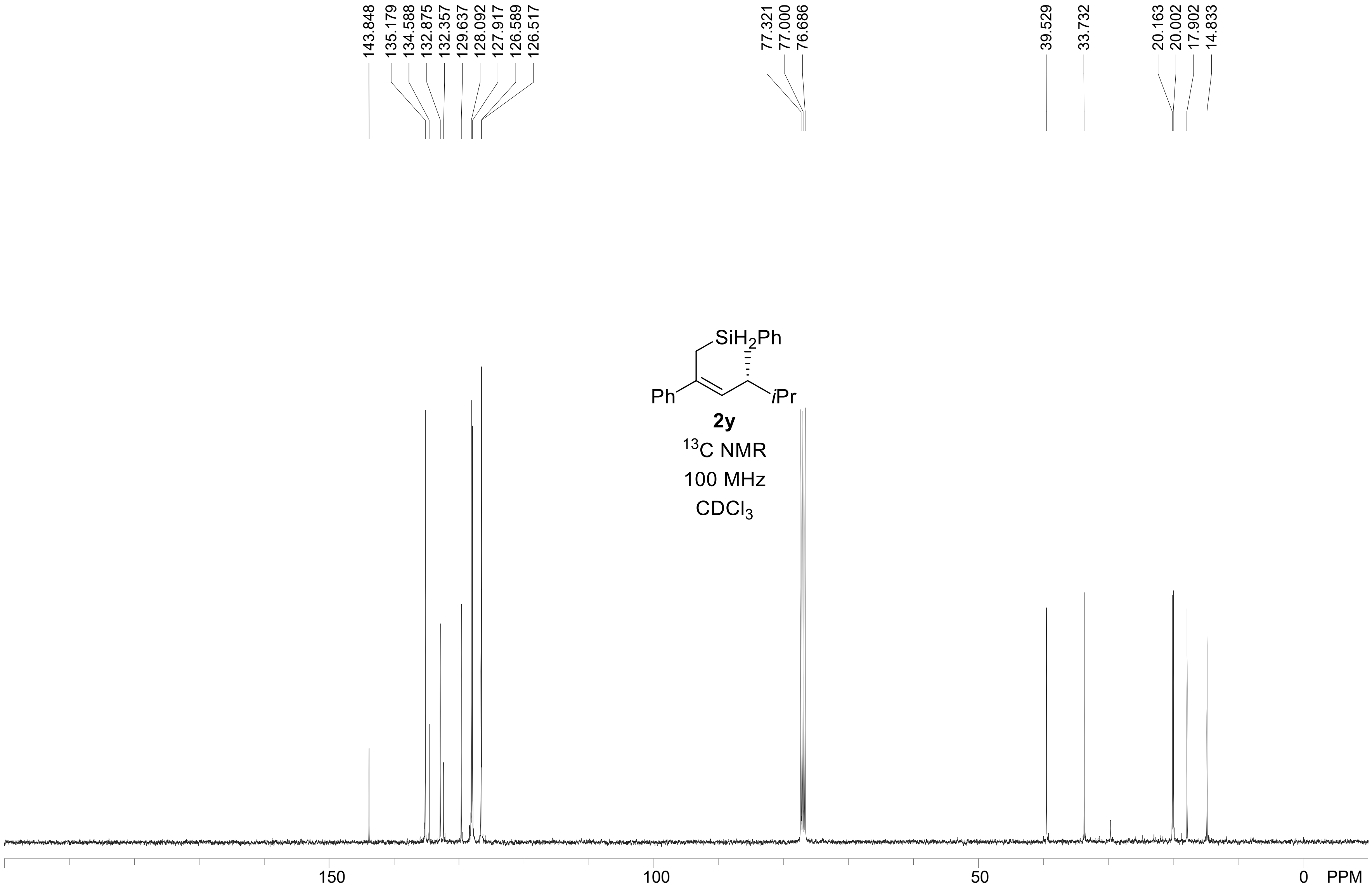


Figure S93. ^{13}C NMR spectra of **2y**, Related to Table 2

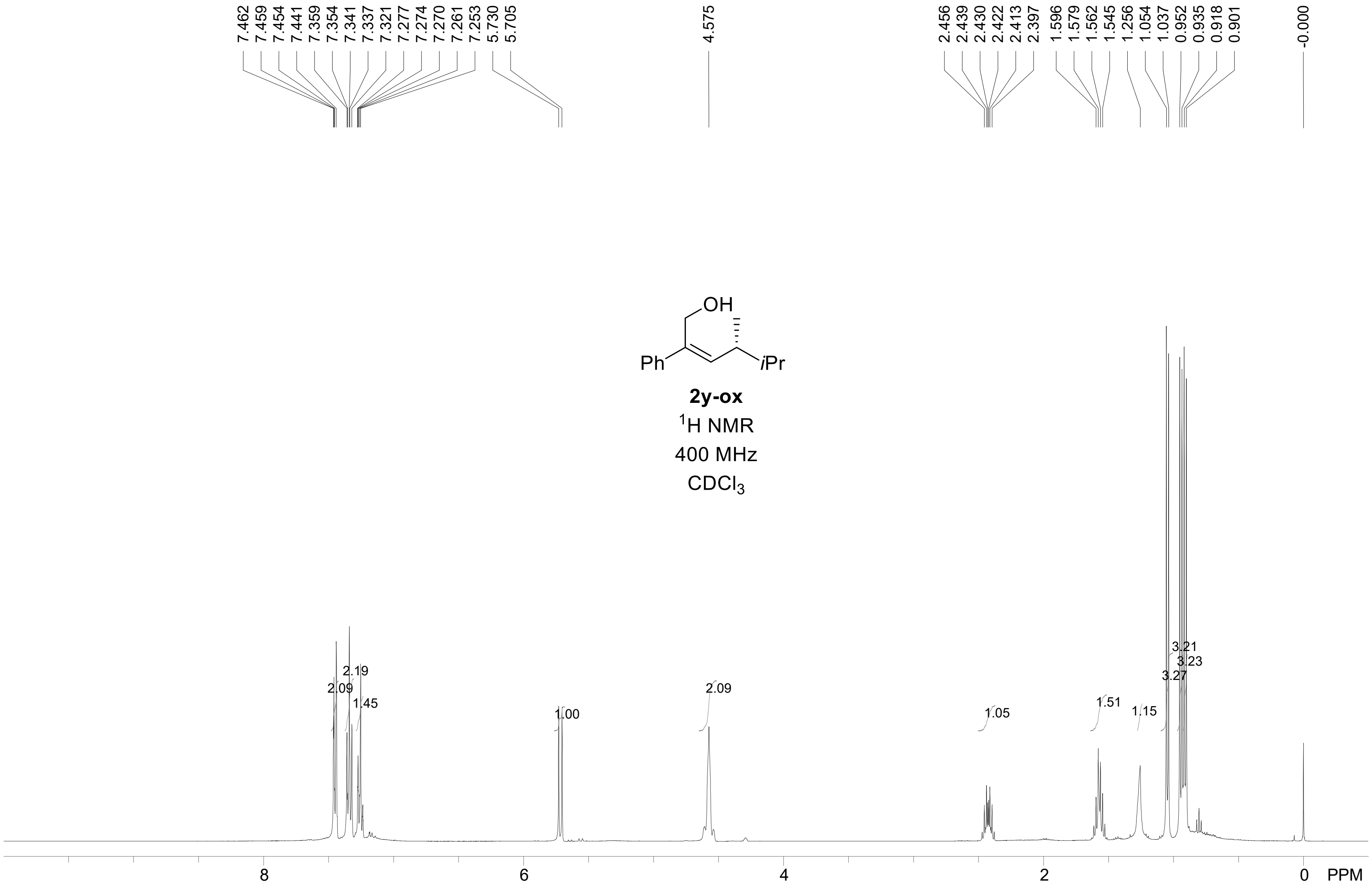


Figure S94. ^{1}H NMR spectra of **2y-ox**, Related to Table 2

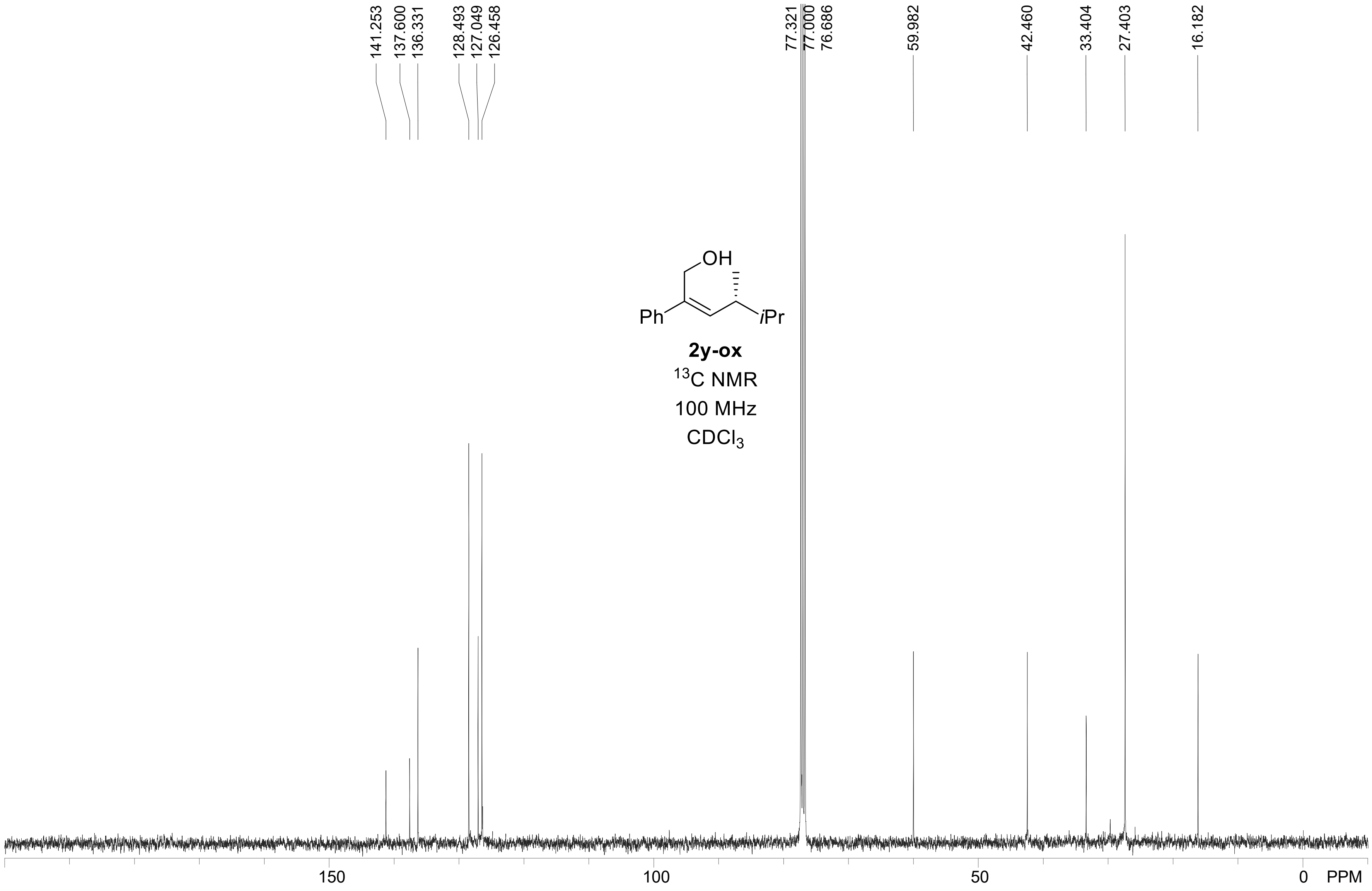


Figure S95. ^{13}C NMR spectra of **2y-ox**, Related to Table 2

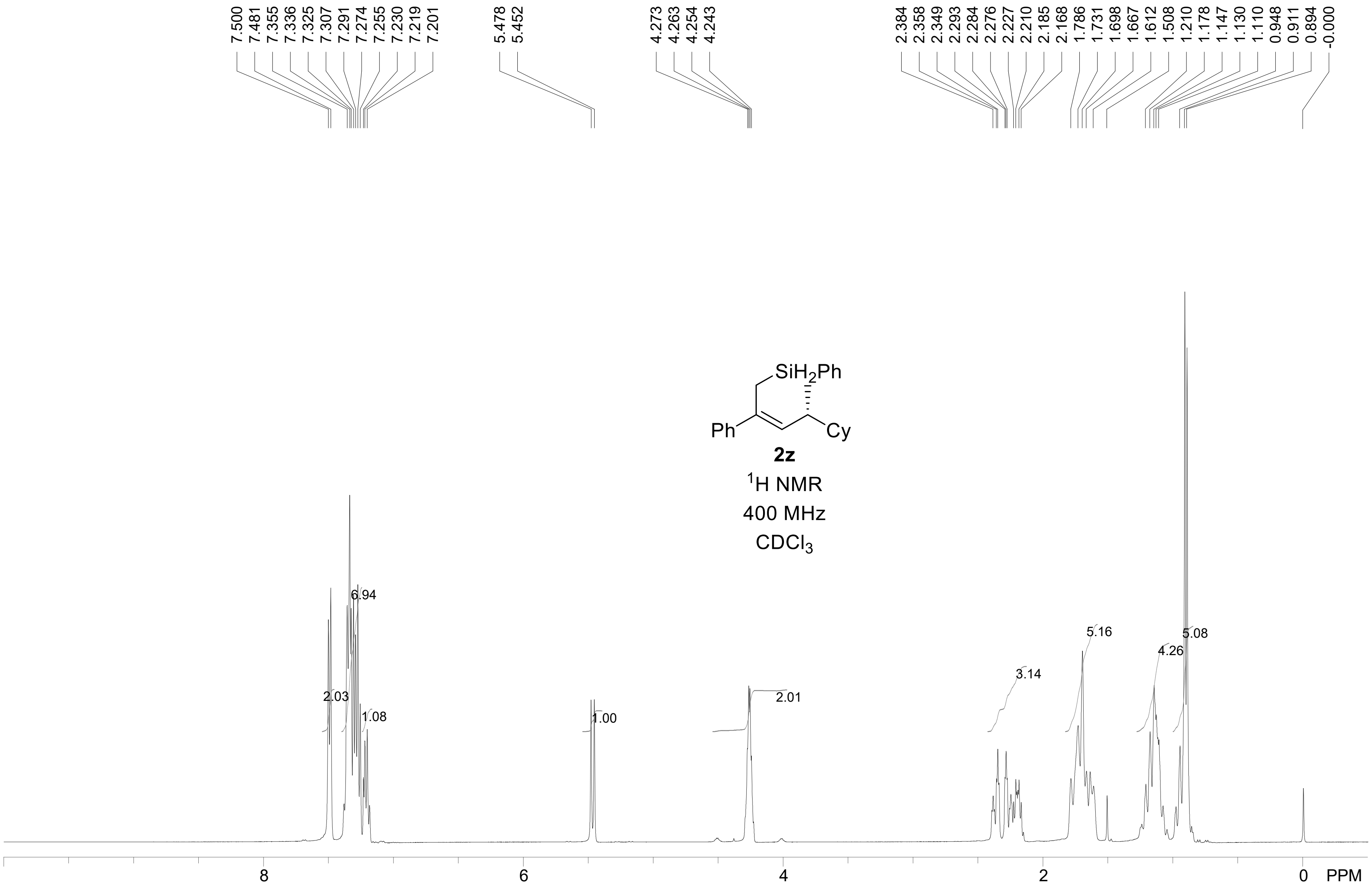


Figure S96. ^{1}H NMR spectra of **2z**, Related to Table 2

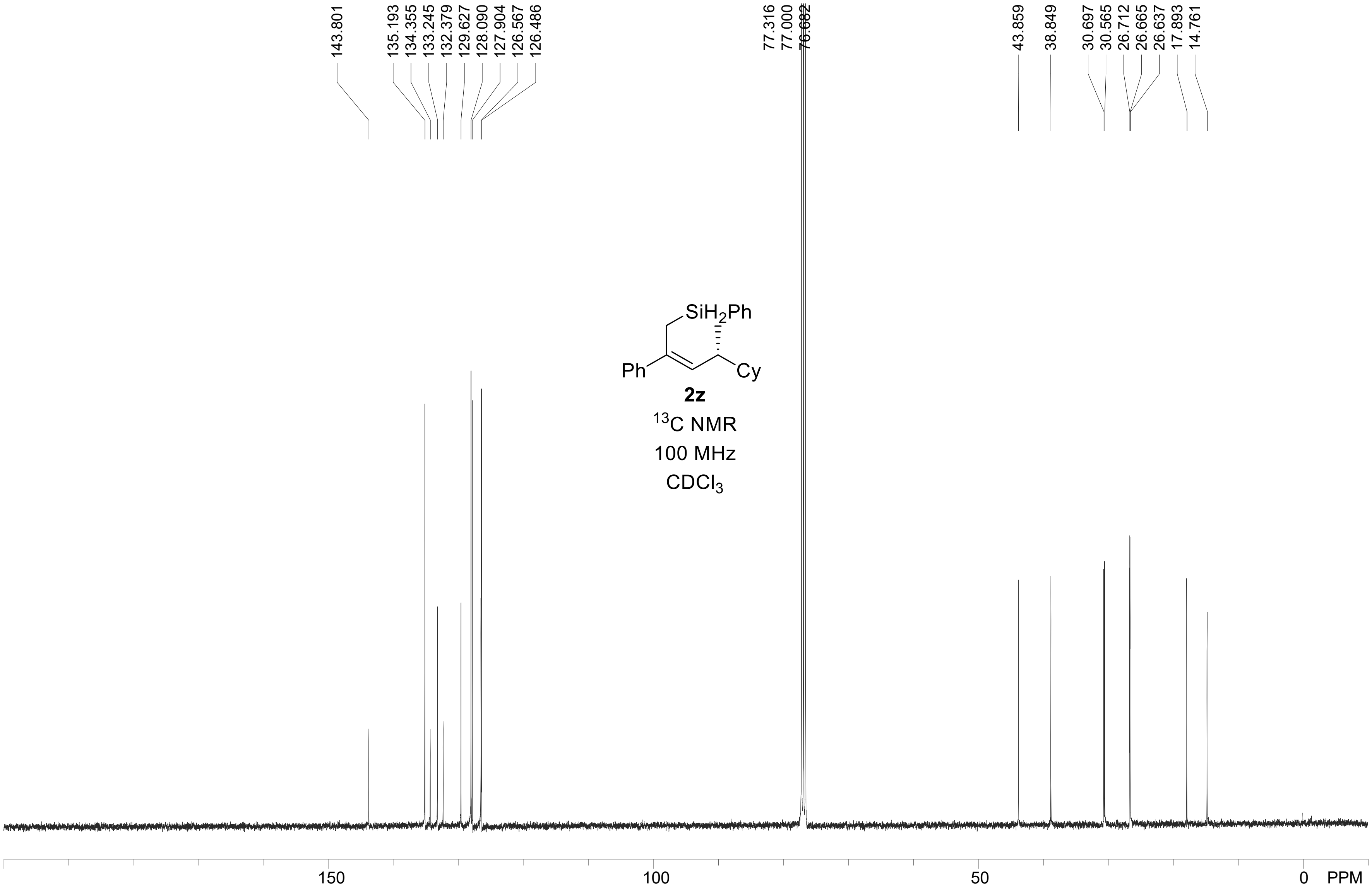


Figure S97. ^{13}C NMR spectra of **2z**, Related to Table 2

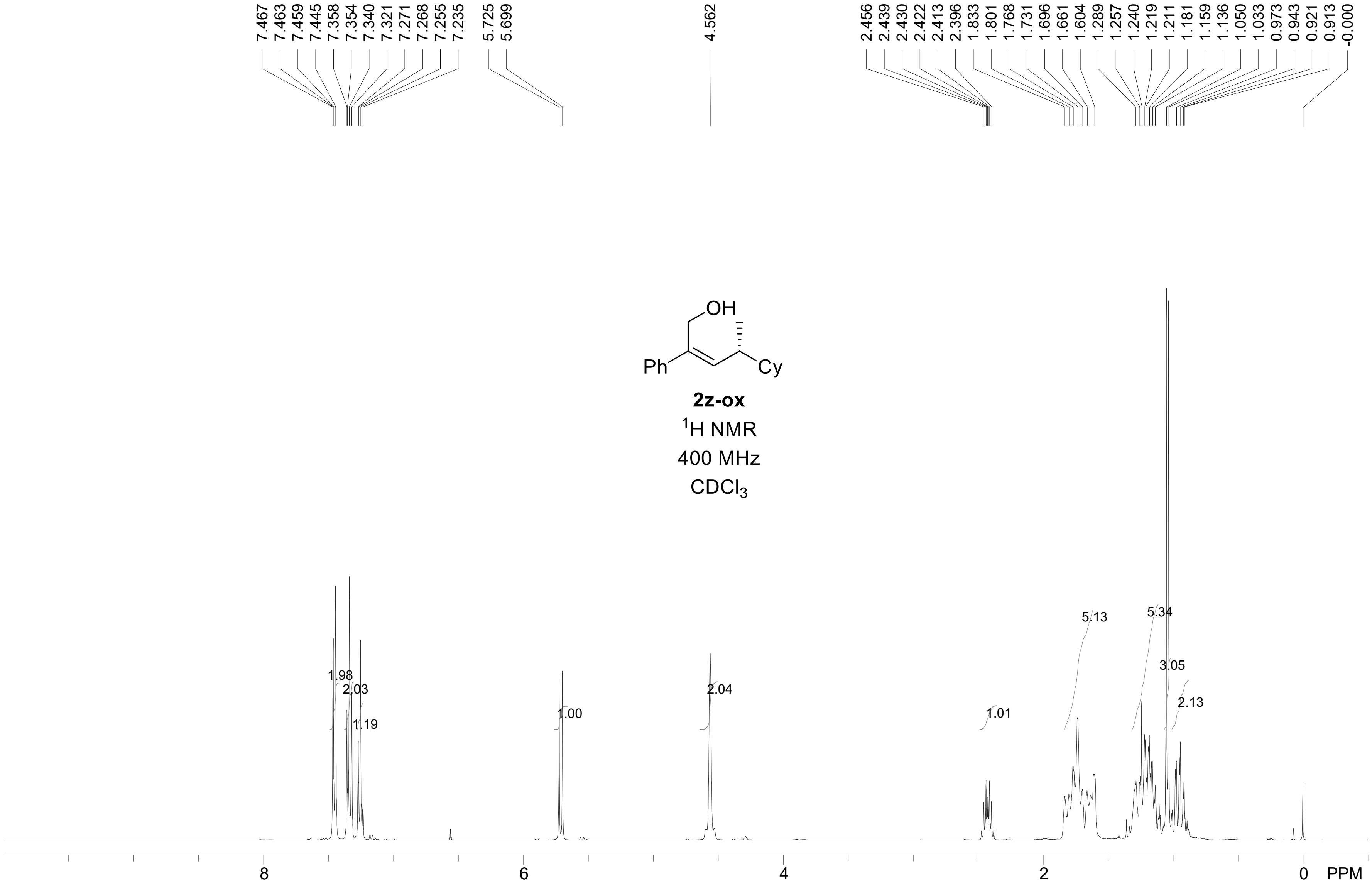


Figure S98. ^{1}H NMR spectra of **2z-ox**, Related to Table 2

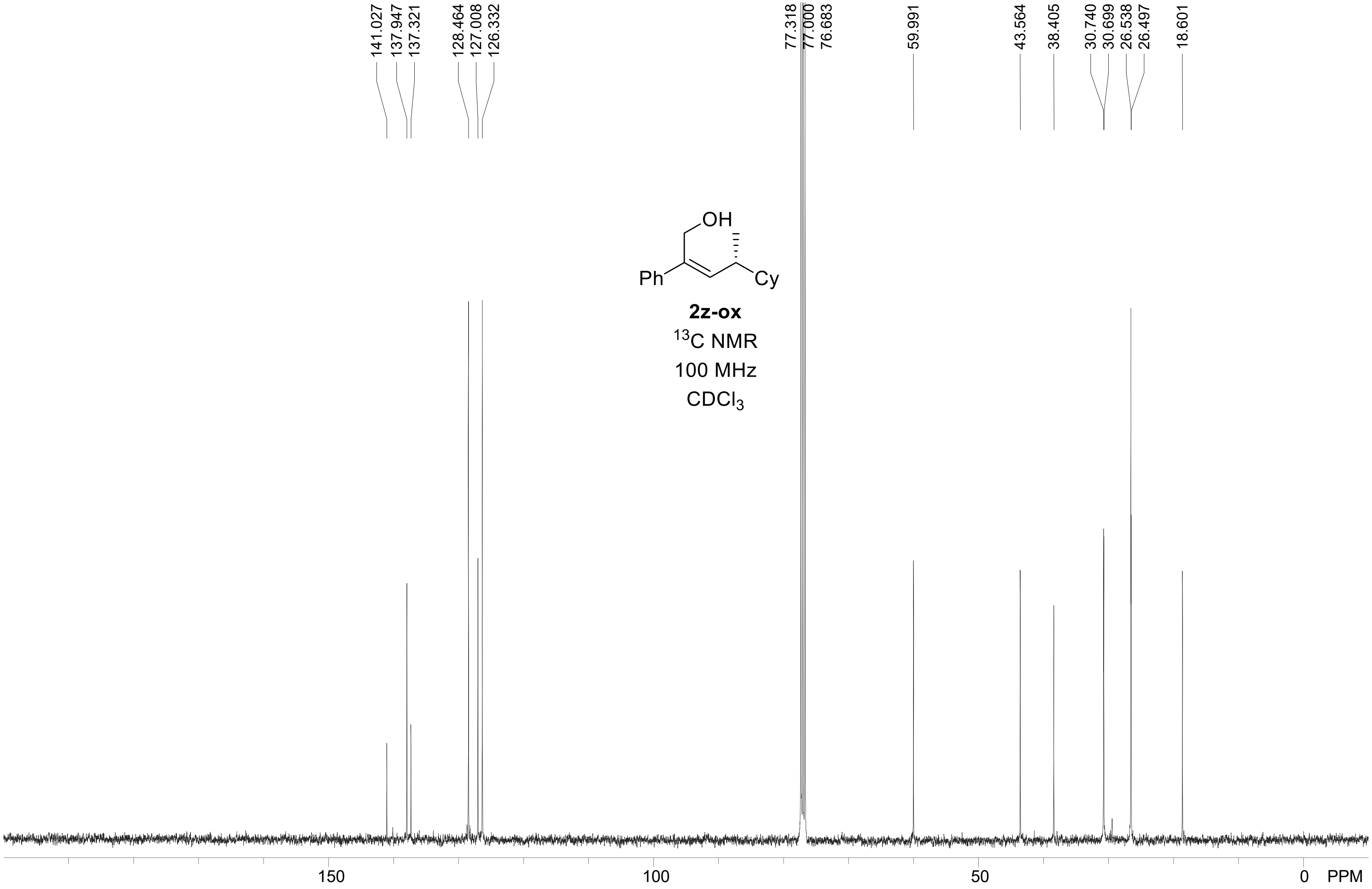


Figure S99. ^{13}C NMR spectra of **2z-ox**, Related to Table 2

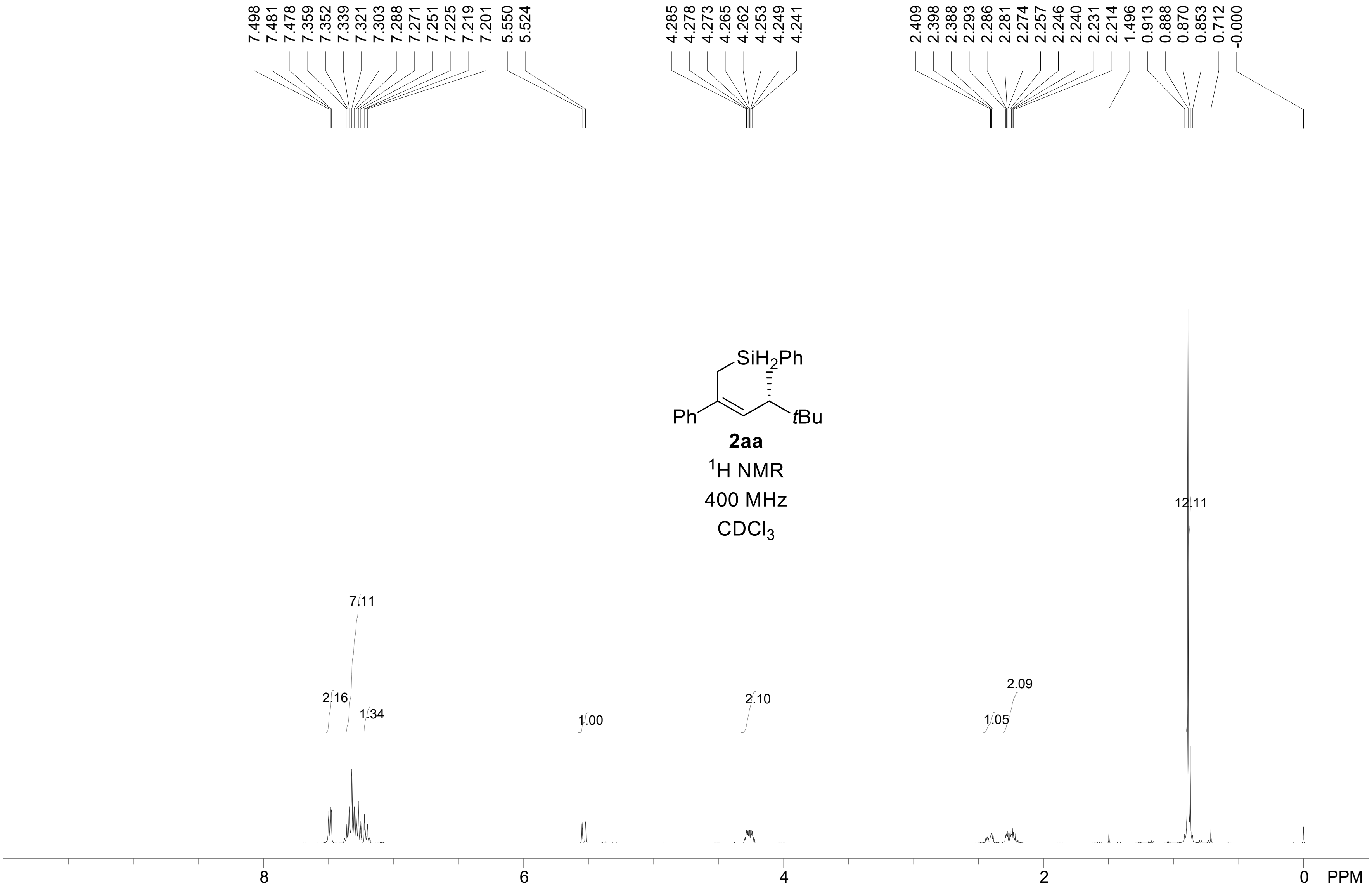


Figure S100. ^{1}H NMR spectra of **2aa**, Related to Table 2

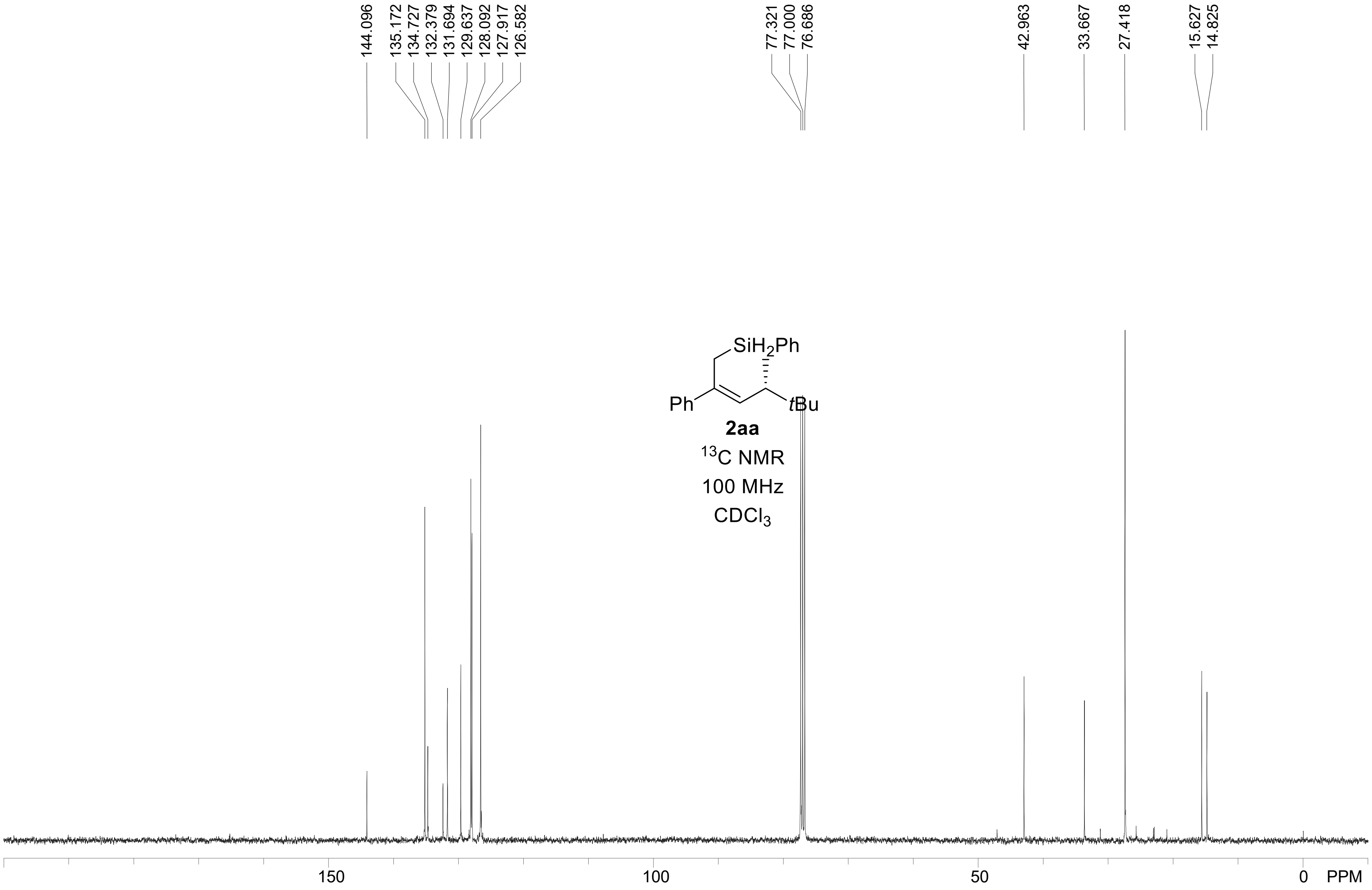


Figure S101. ^{13}C NMR spectra of **2aa**, Related to Table 2

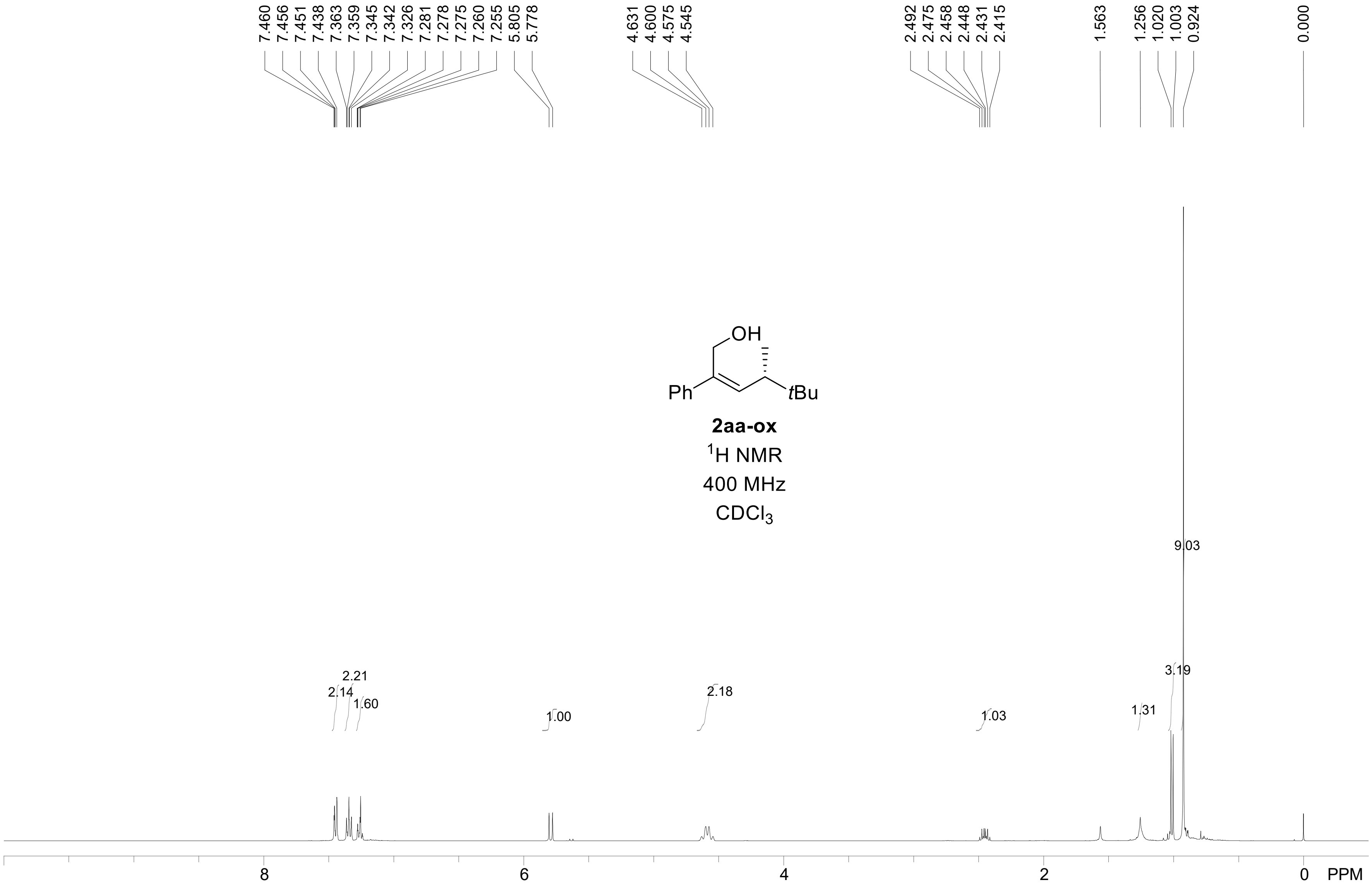


Figure S102. ^{1}H NMR spectra of **2aa-ox**, Related to Table 2

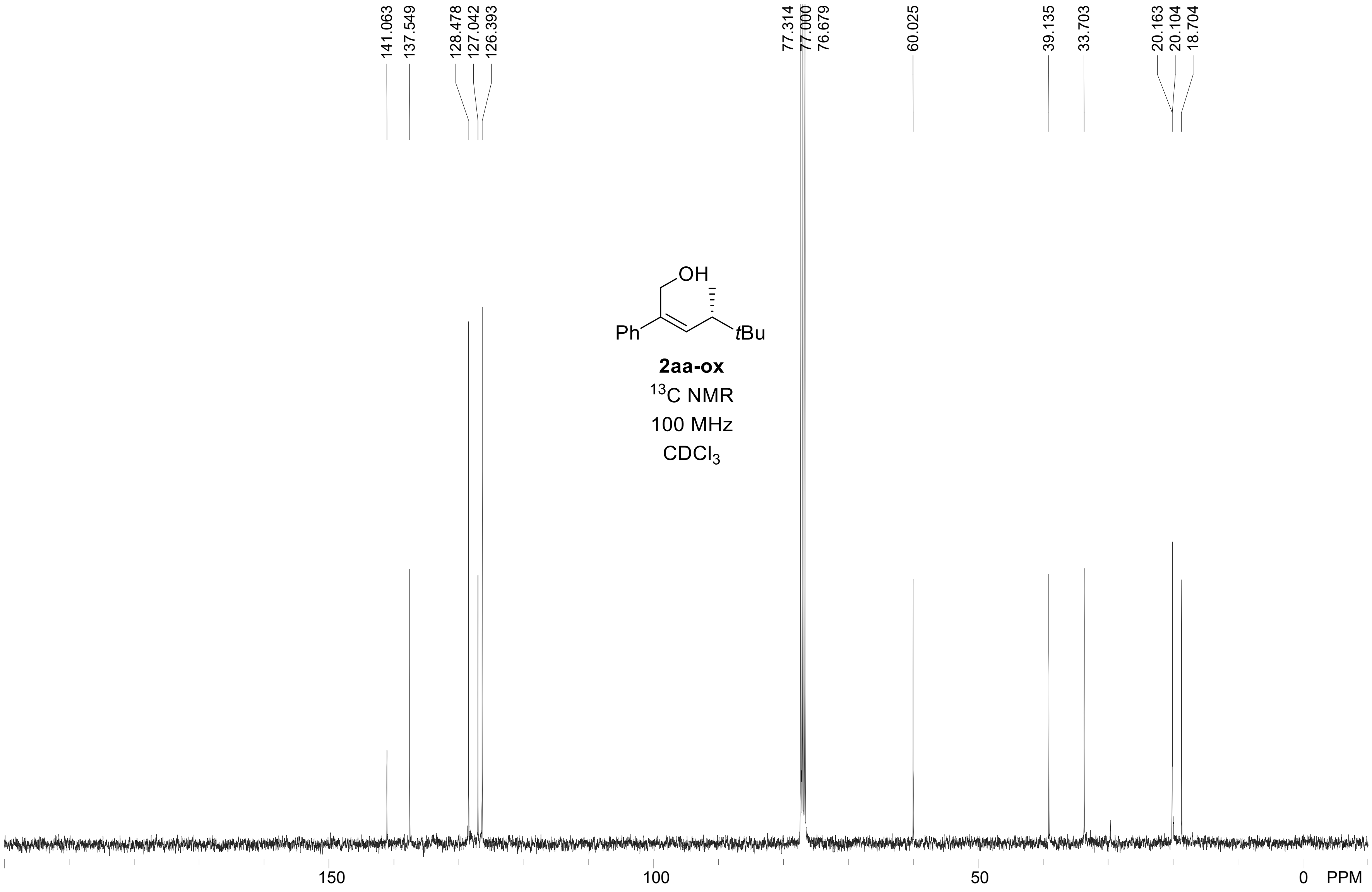


Figure S103. ^{13}C NMR spectra of **2aa-ox**, Related to Table 2

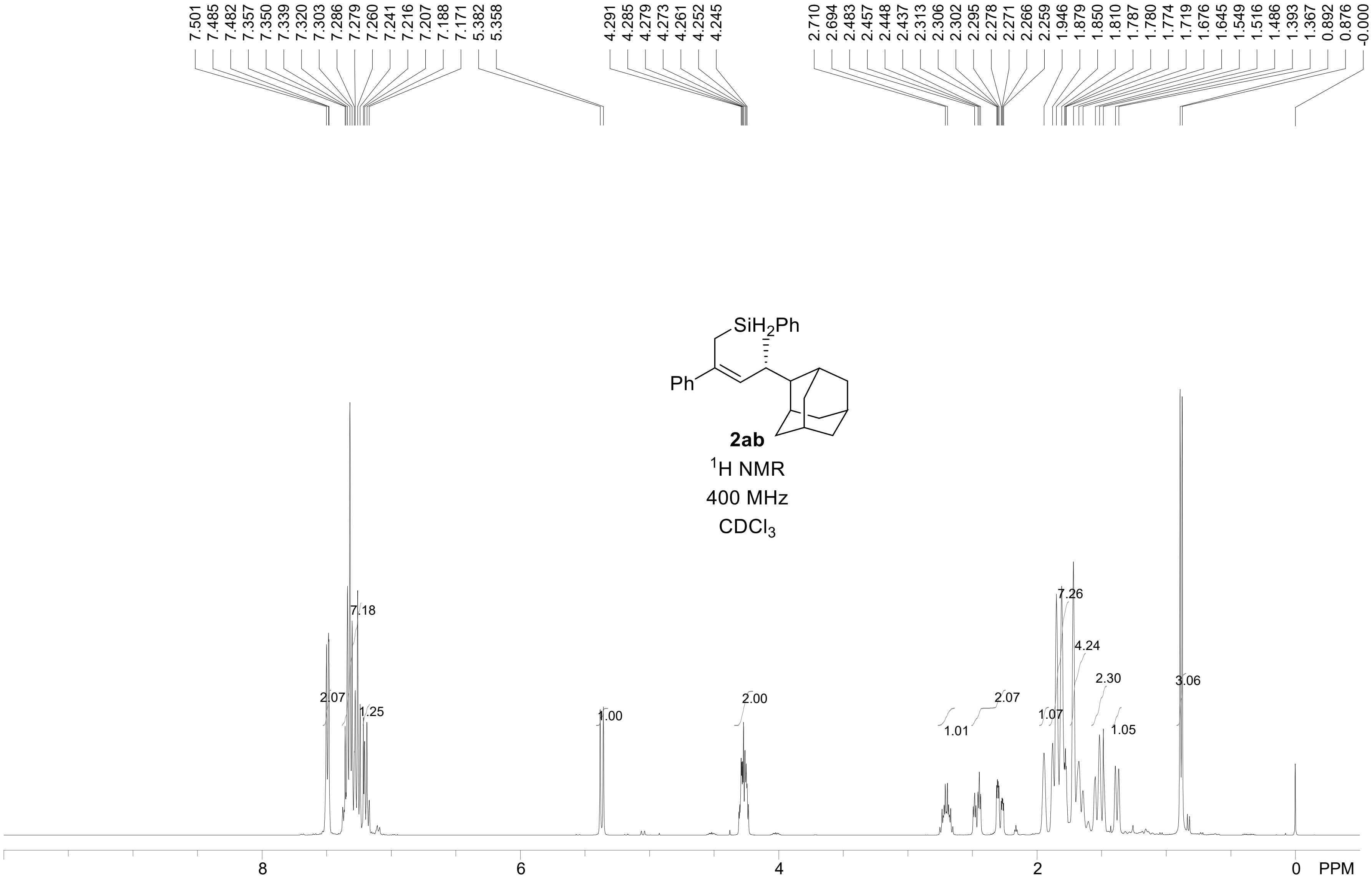


Figure S104. ^{1}H NMR spectra of **2ab**, Related to Table 2

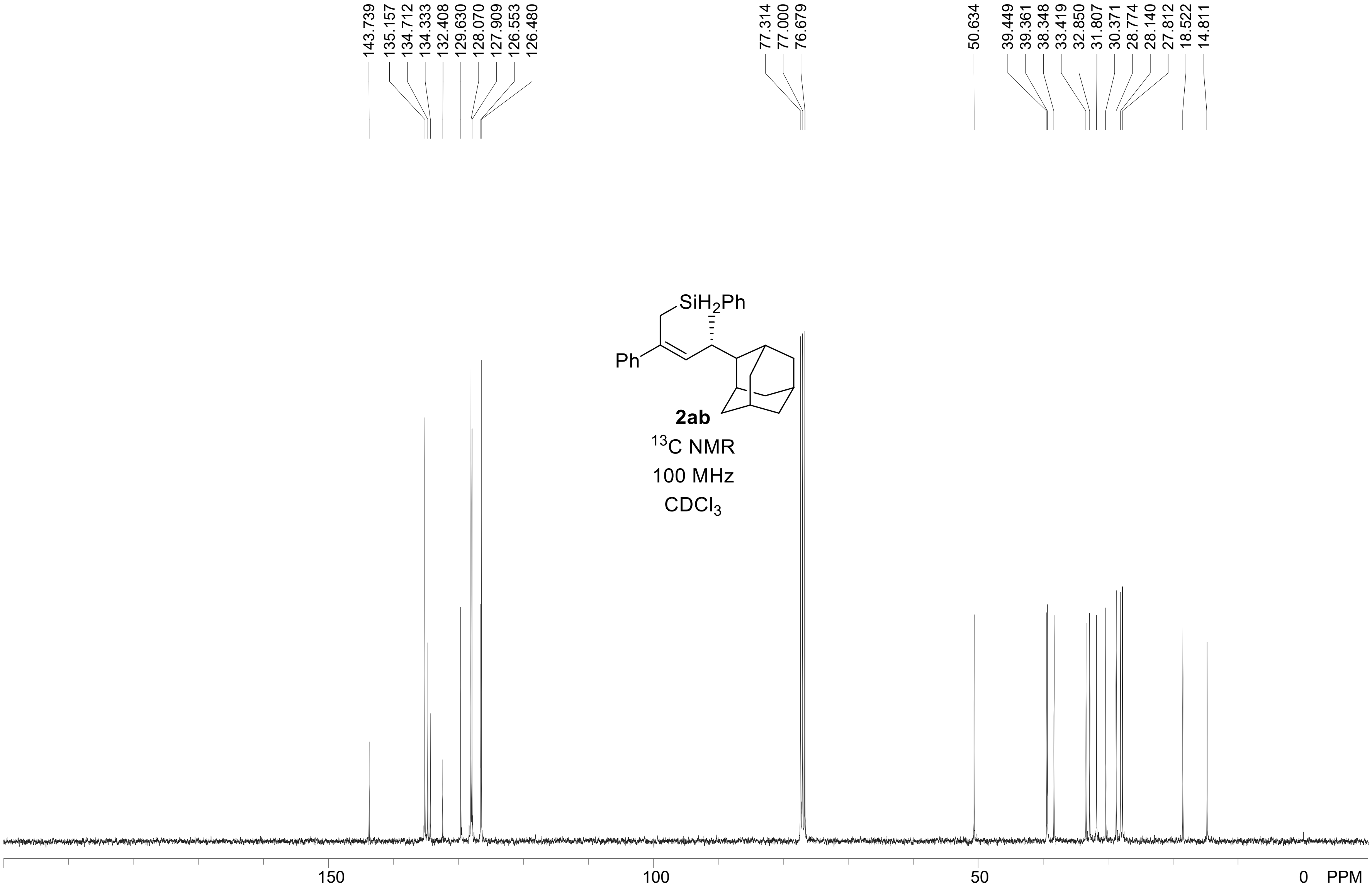


Figure S105. ^{13}C NMR spectra of **2ab**, Related to Table 2

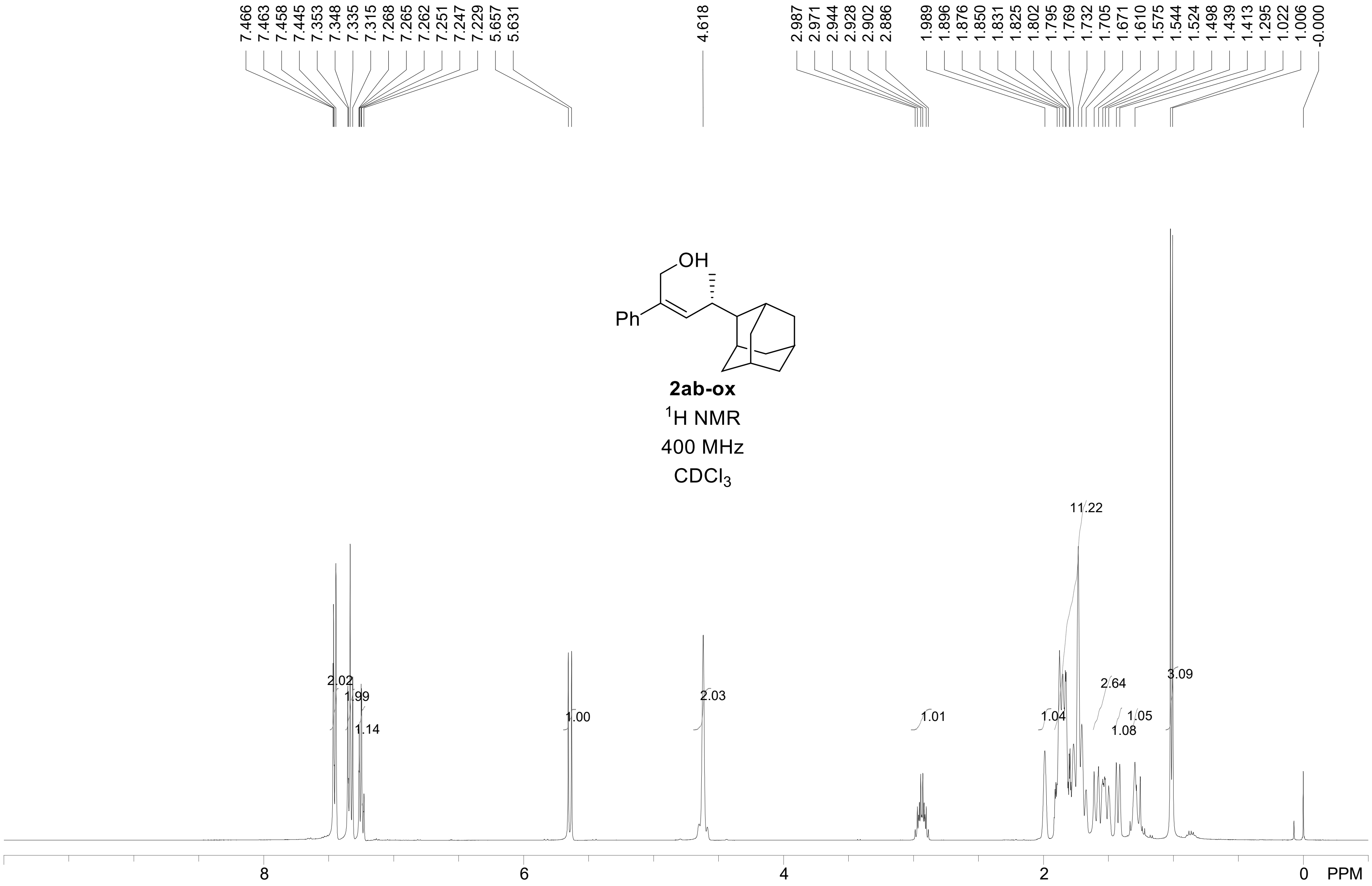


Figure S106. ^{1}H NMR spectra of **2ab-ox**, Related to Table 2

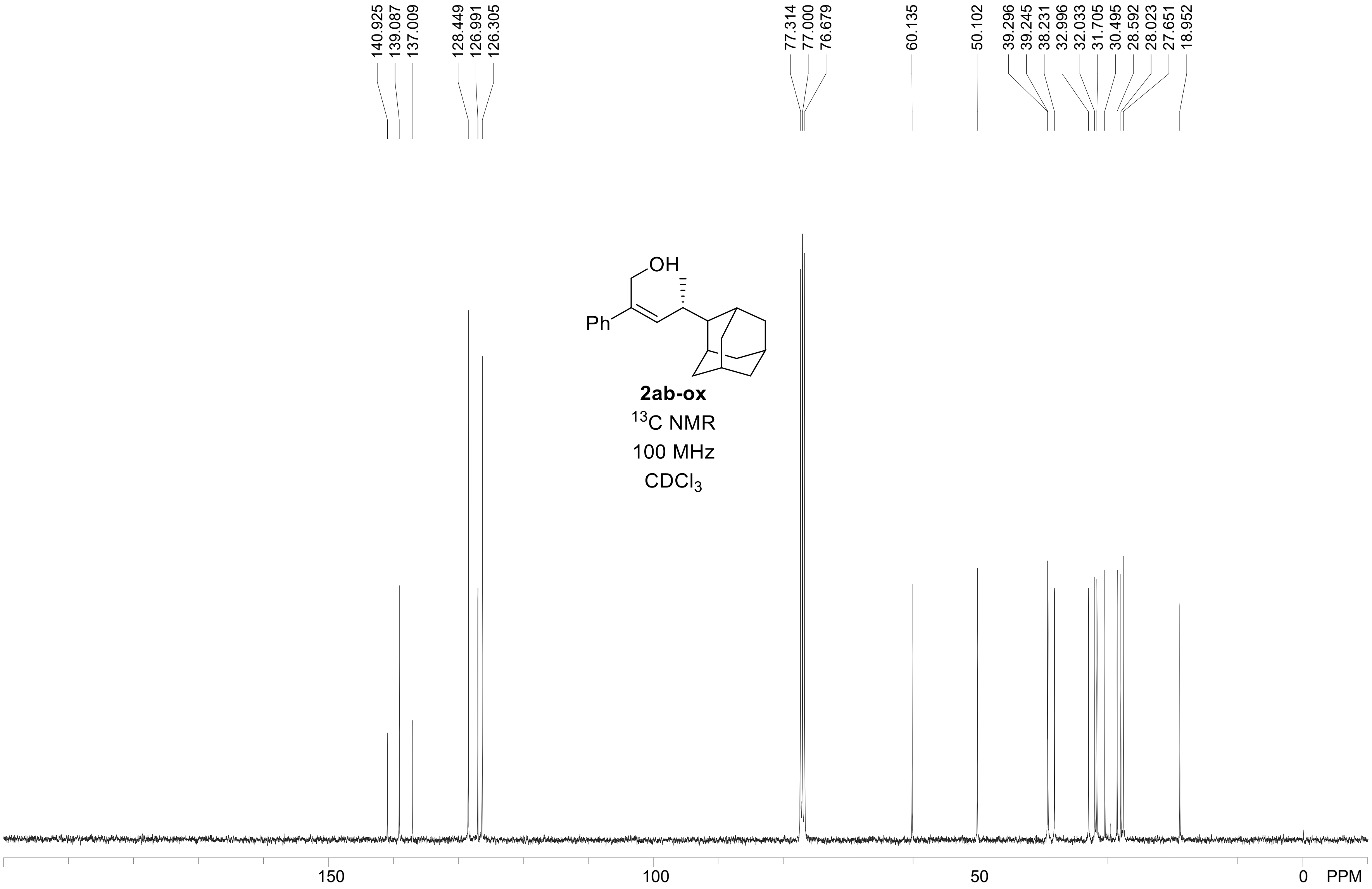


Figure S107. ^{13}C NMR spectra of **2ab-ox**, Related to Table 2

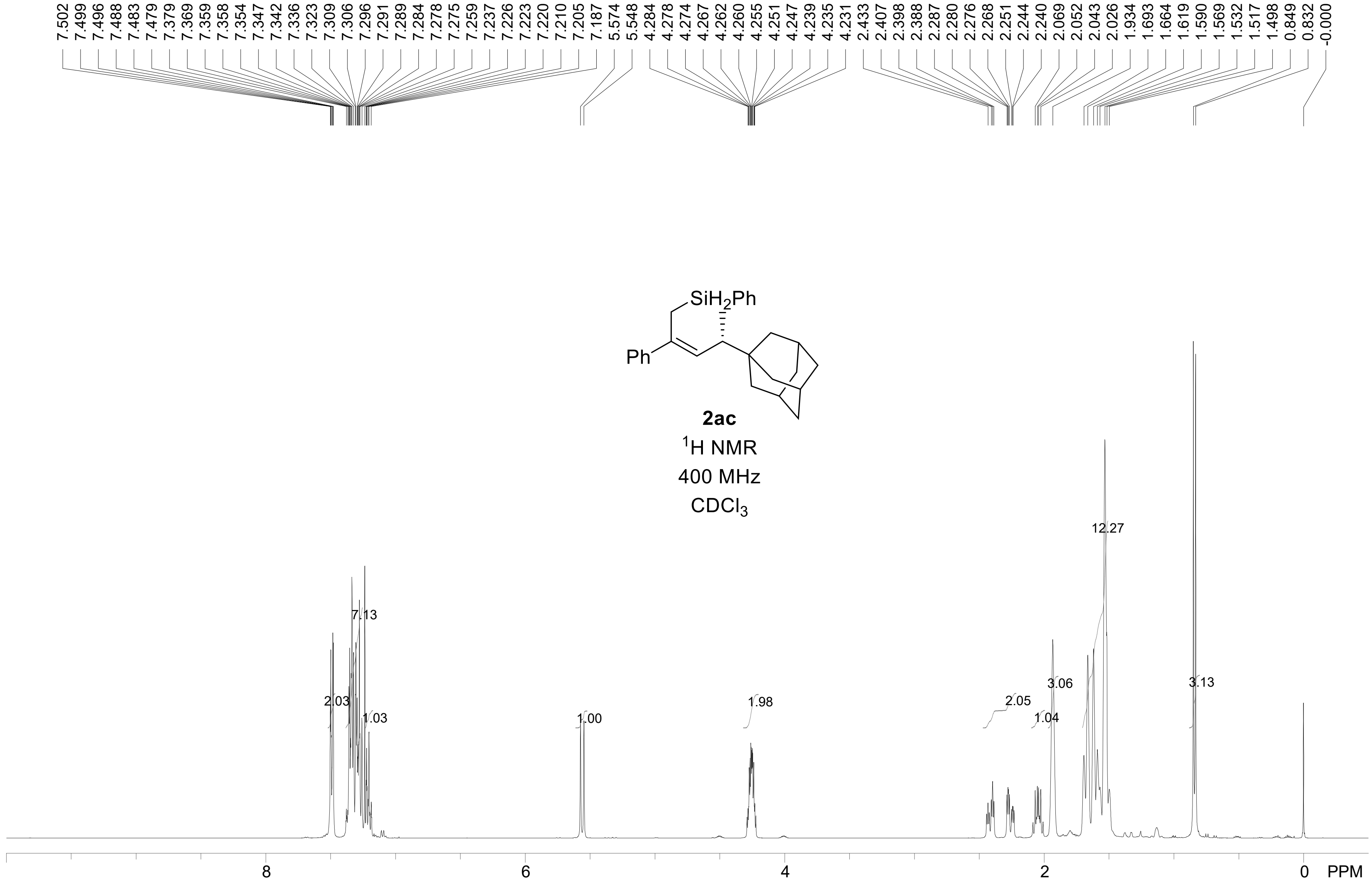


Figure S108. ^{1}H NMR spectra of **2ac**, Related to Table 2

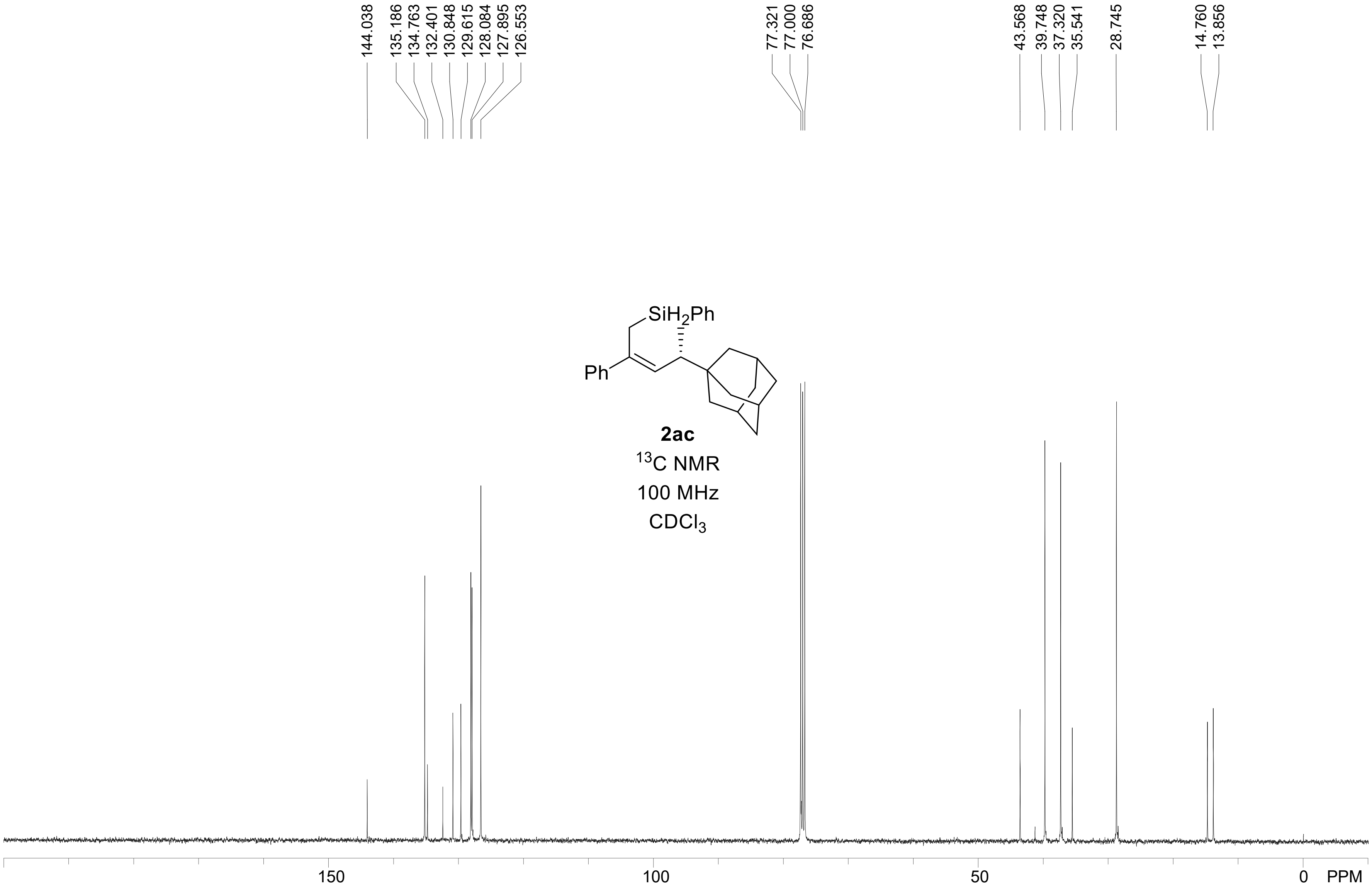


Figure S109. ^{13}C NMR spectra of **2ac**, Related to Table 2

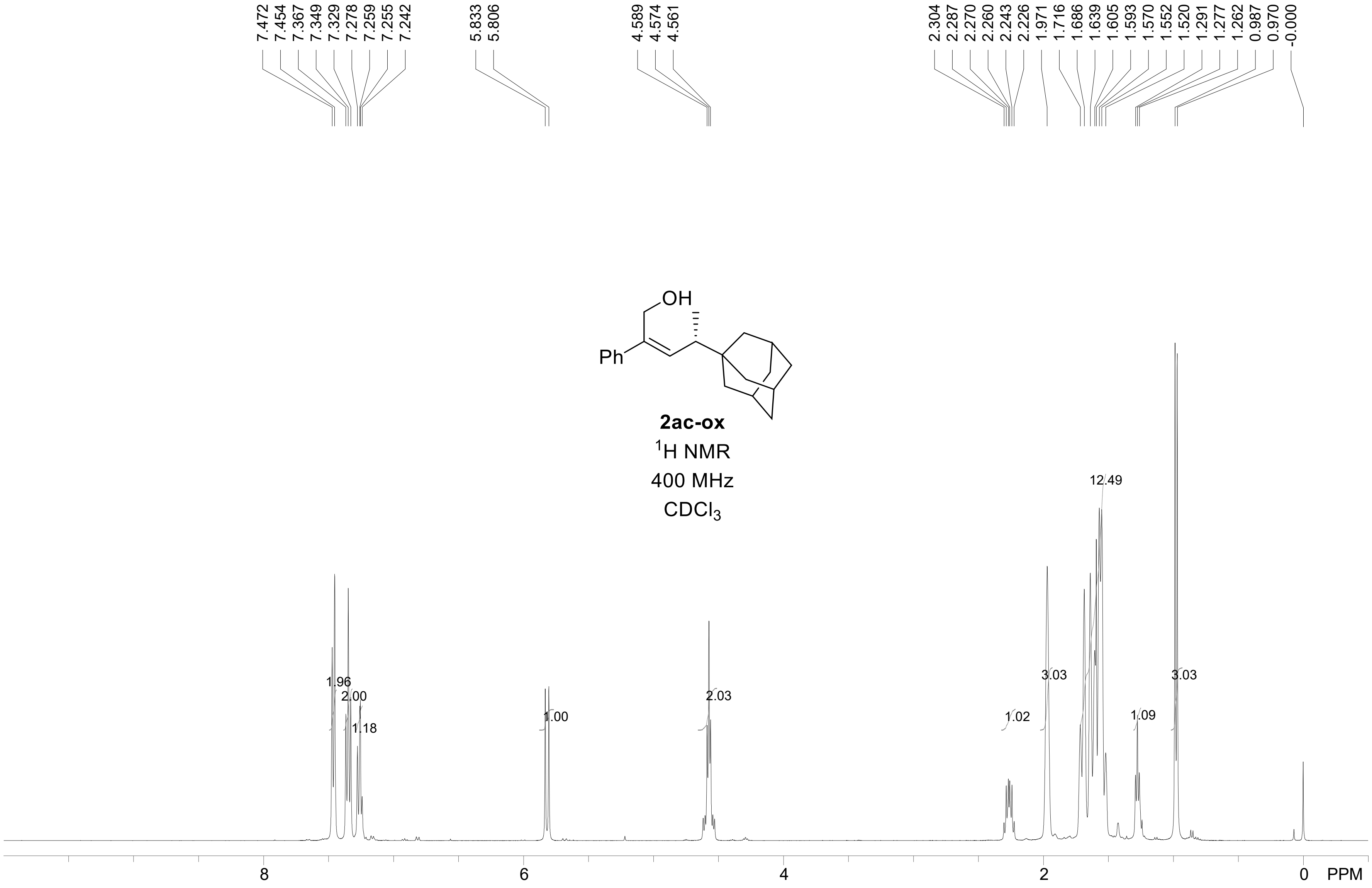


Figure S110. ^{1}H NMR spectra of **2ac-ox**, Related to Table 2

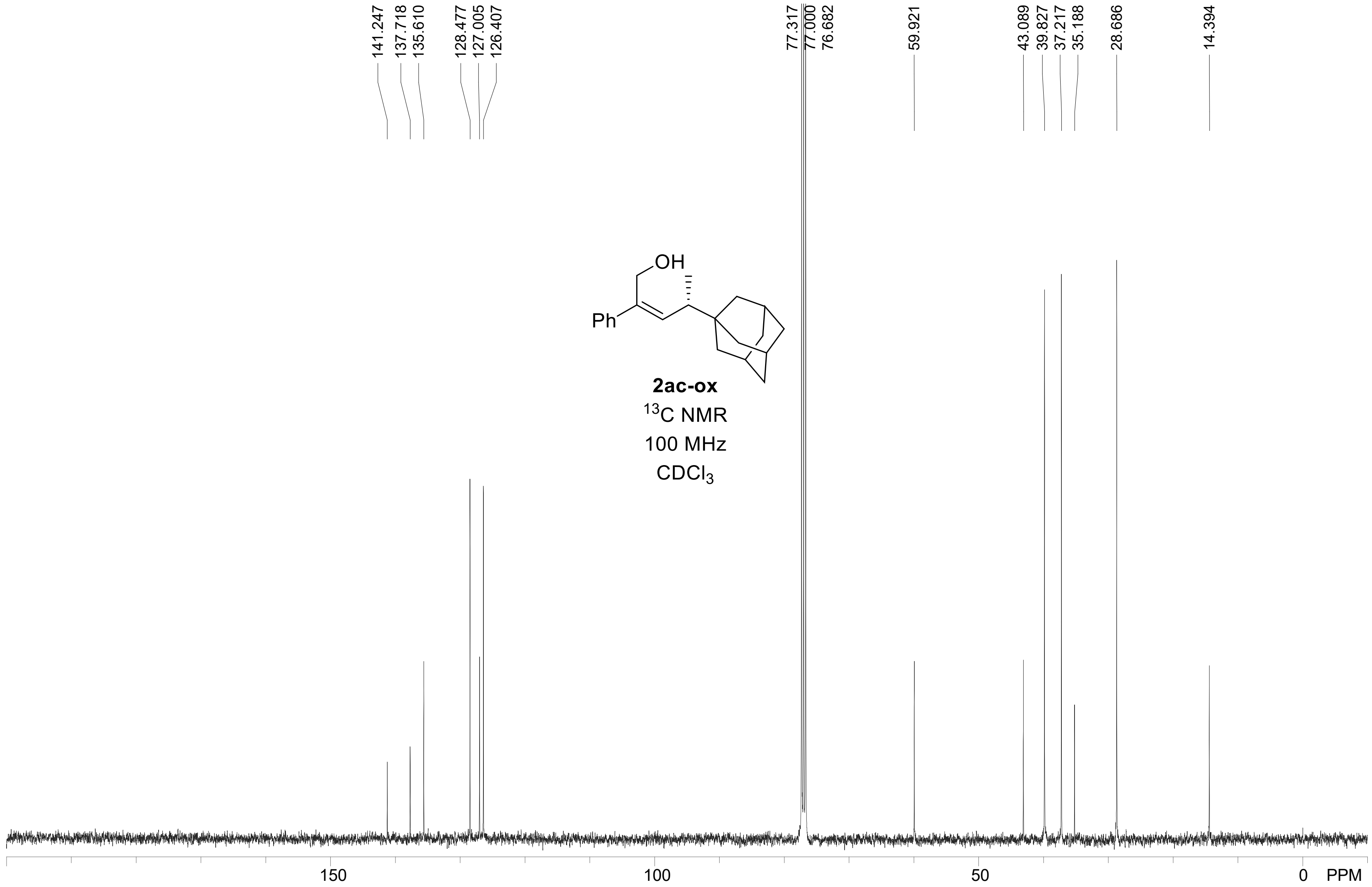


Figure S111. ^{13}C NMR spectra of **2ac-ox**, Related to Table 2

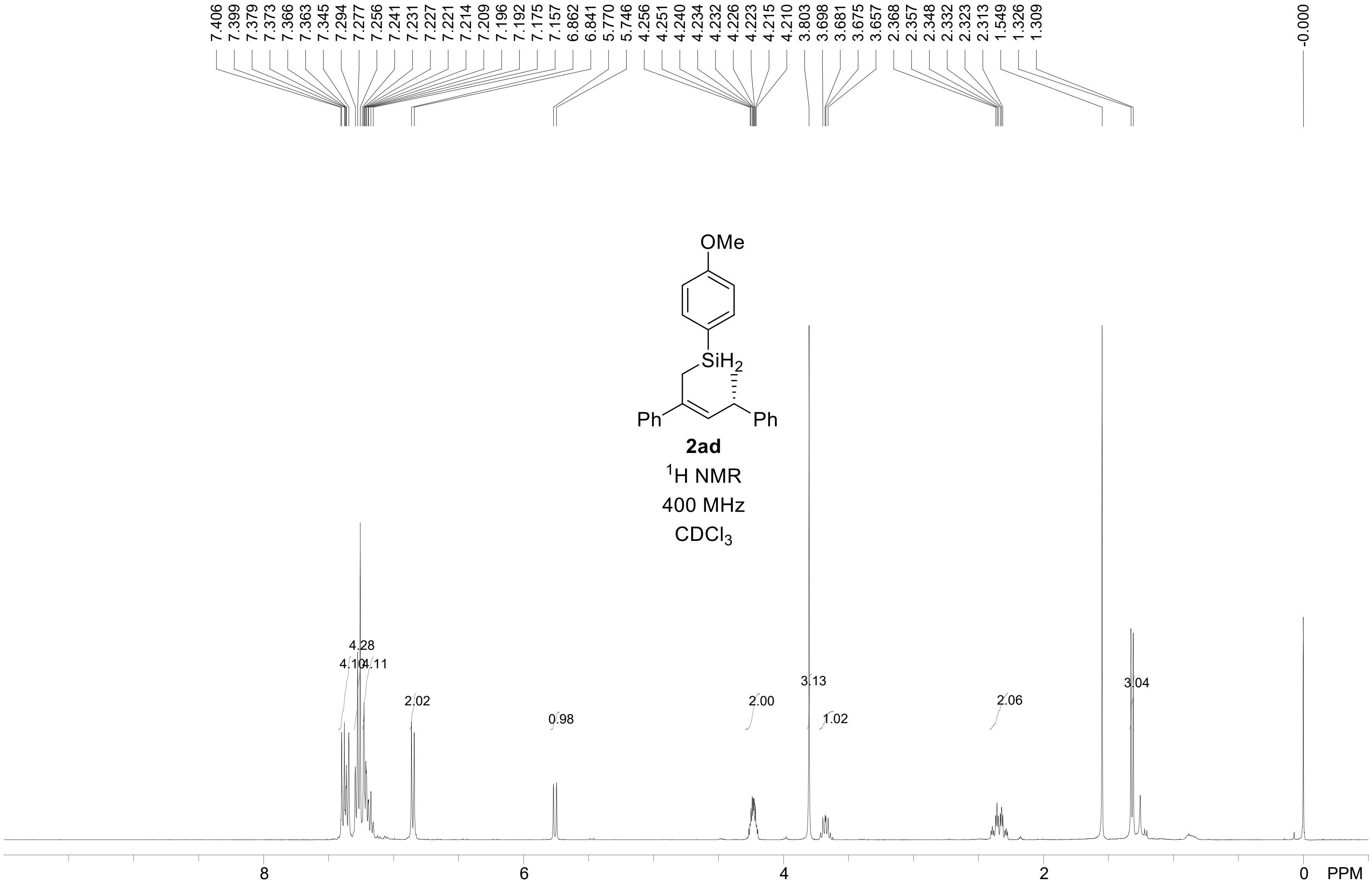


Figure S112. ^{1}H NMR spectra of **2ad**, Related to Table 2

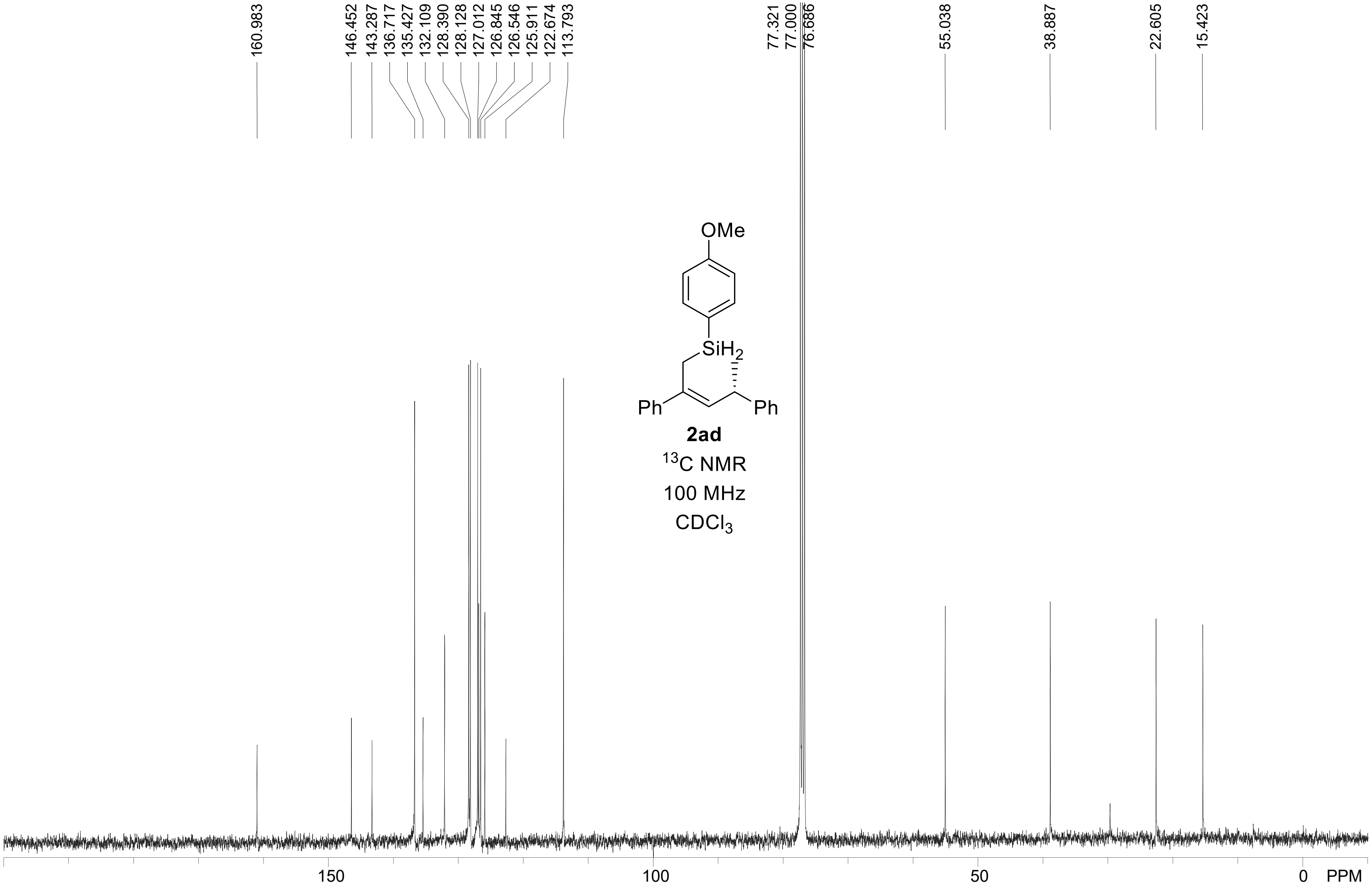


Figure S113. ^{13}C NMR spectra of **2ad**, Related to Table 2

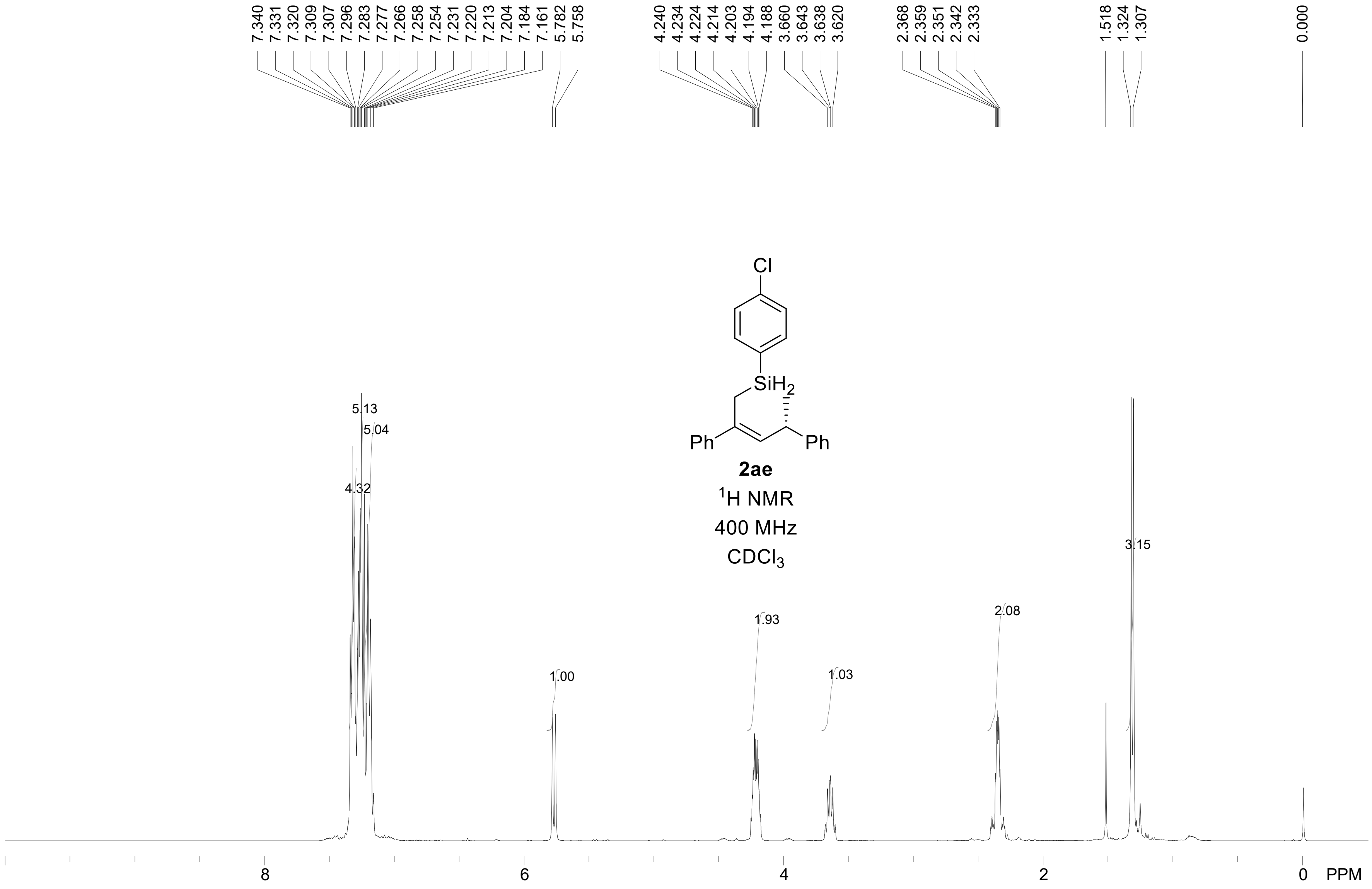


Figure S114. ^{1}H NMR spectra of **2ae**, Related to Table 2

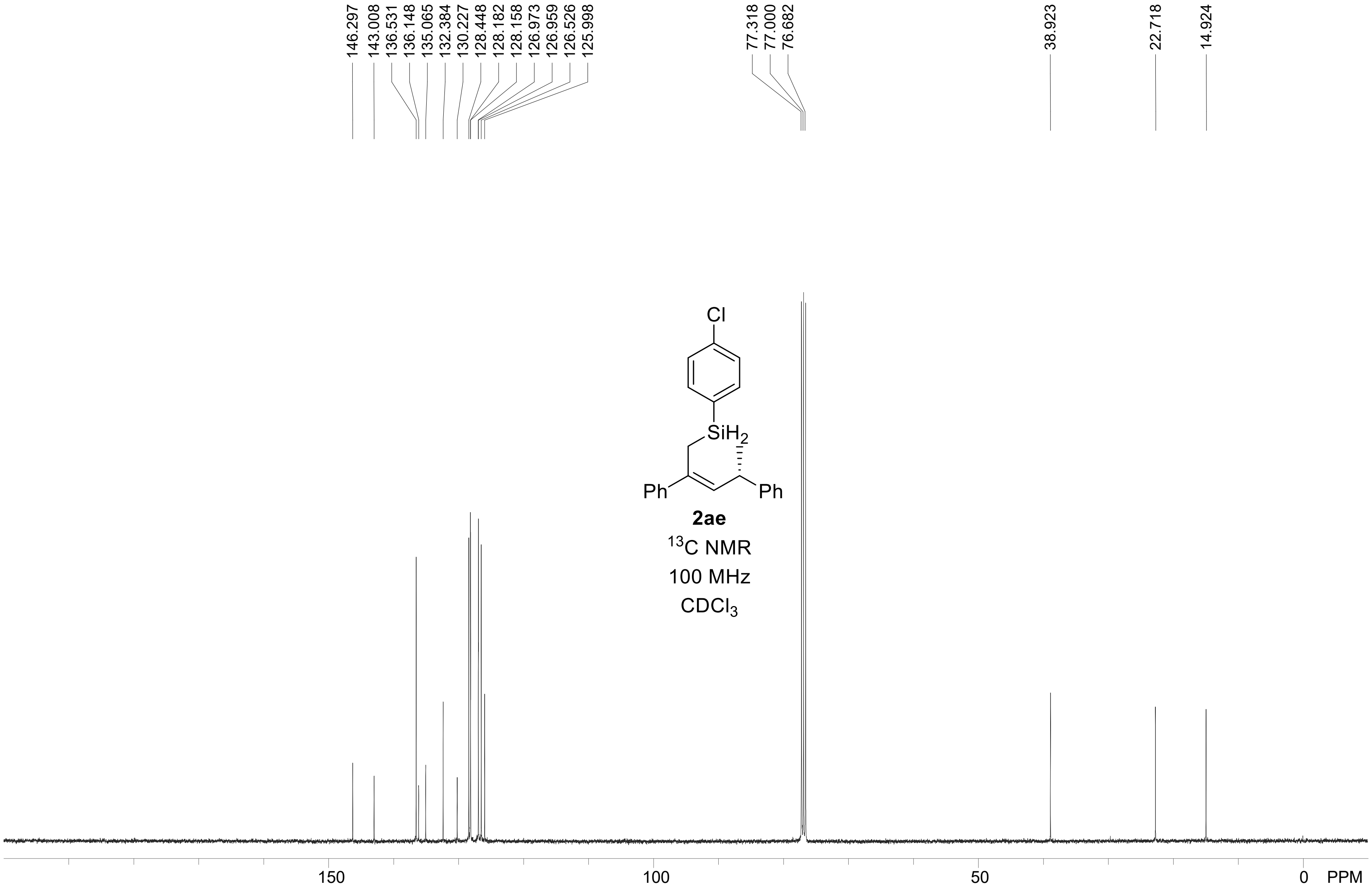


Figure S115. ^{13}C NMR spectra of **2ae**, Related to Table 2

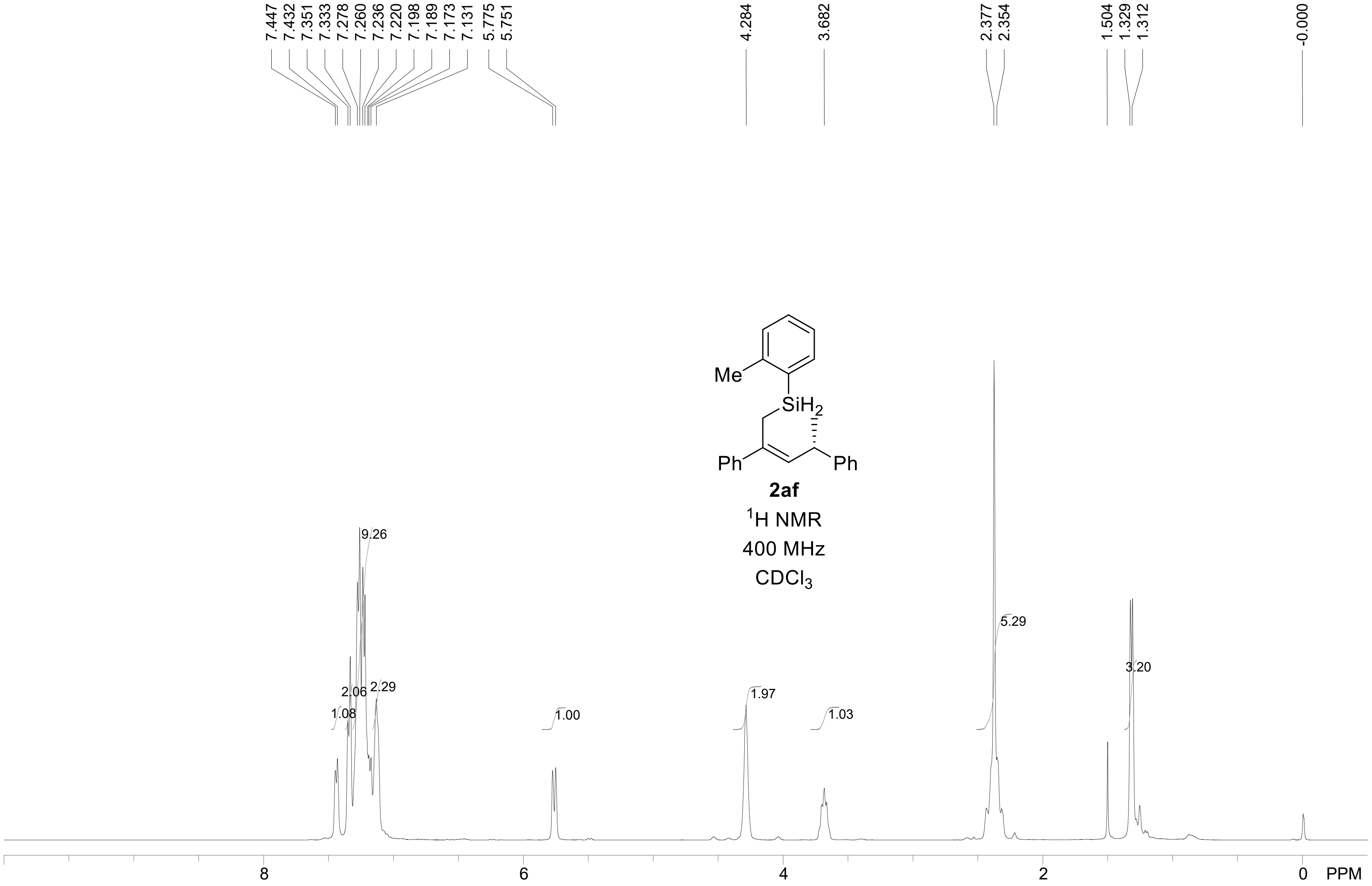


Figure S116. ^{1}H NMR spectra of **2af**, Related to Table 2

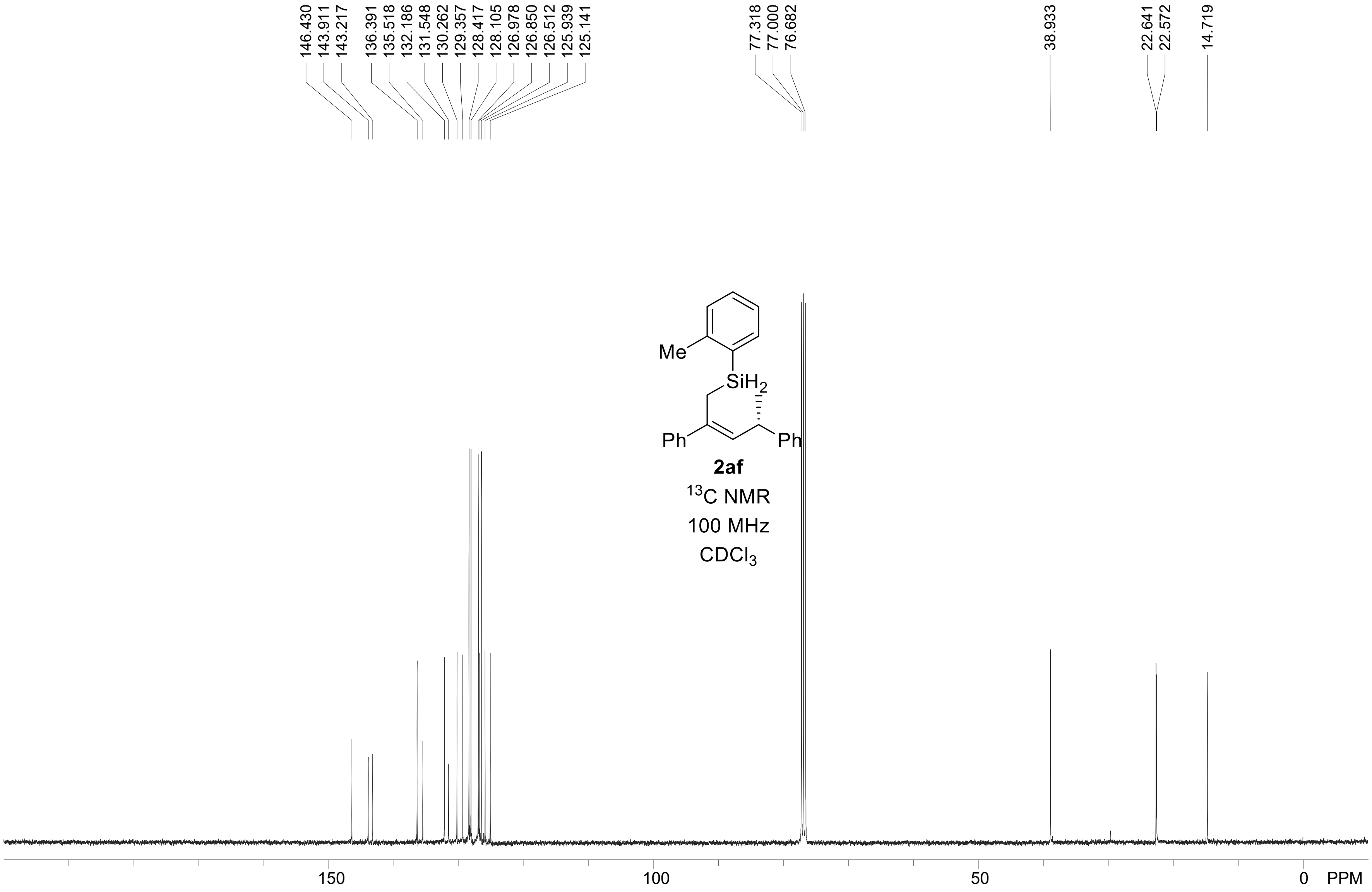


Figure S117. ^{13}C NMR spectra of **2af**, Related to Table 2

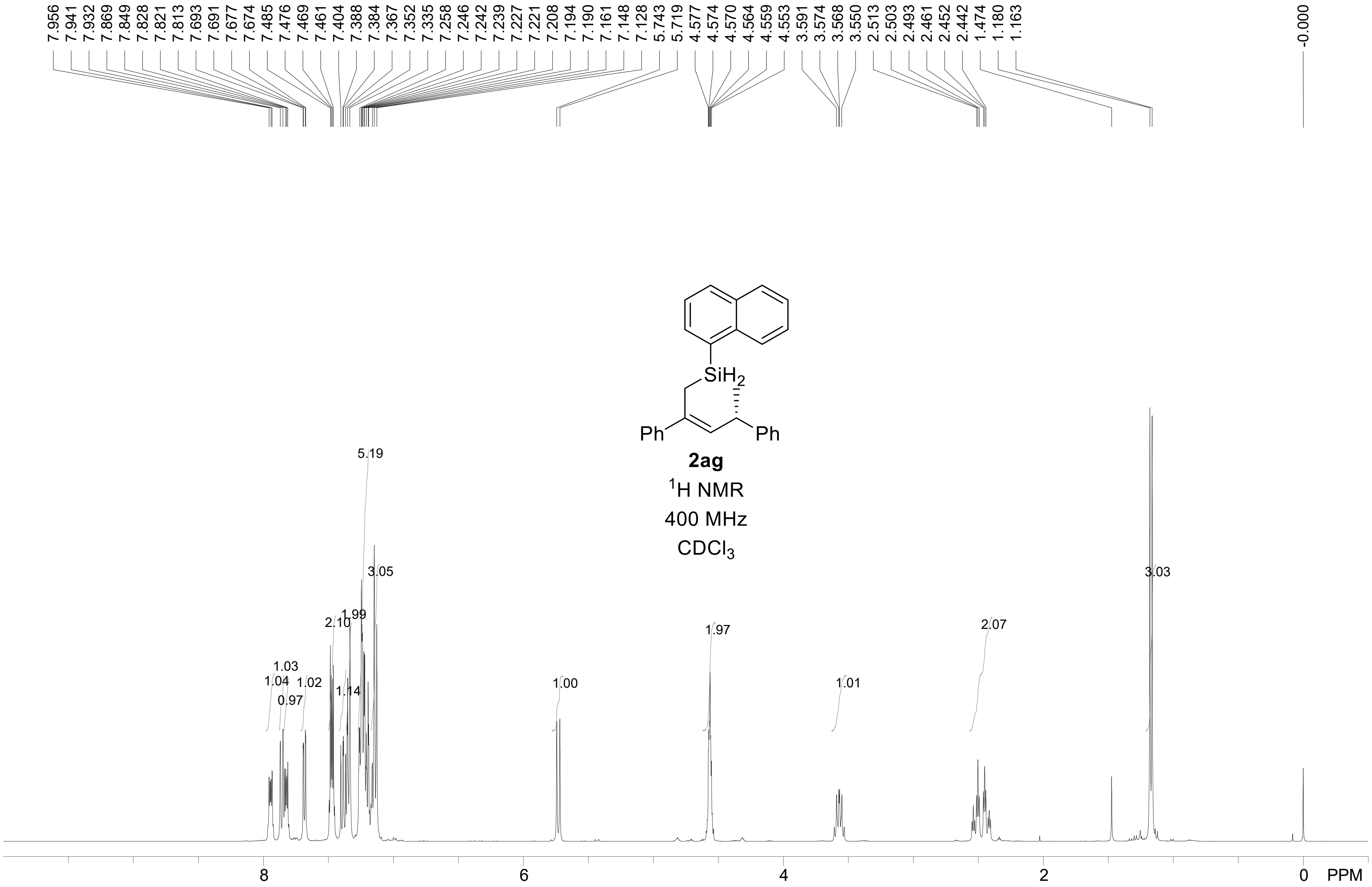


Figure S118. ^{1}H NMR spectra of **2ag**, Related to Table 2

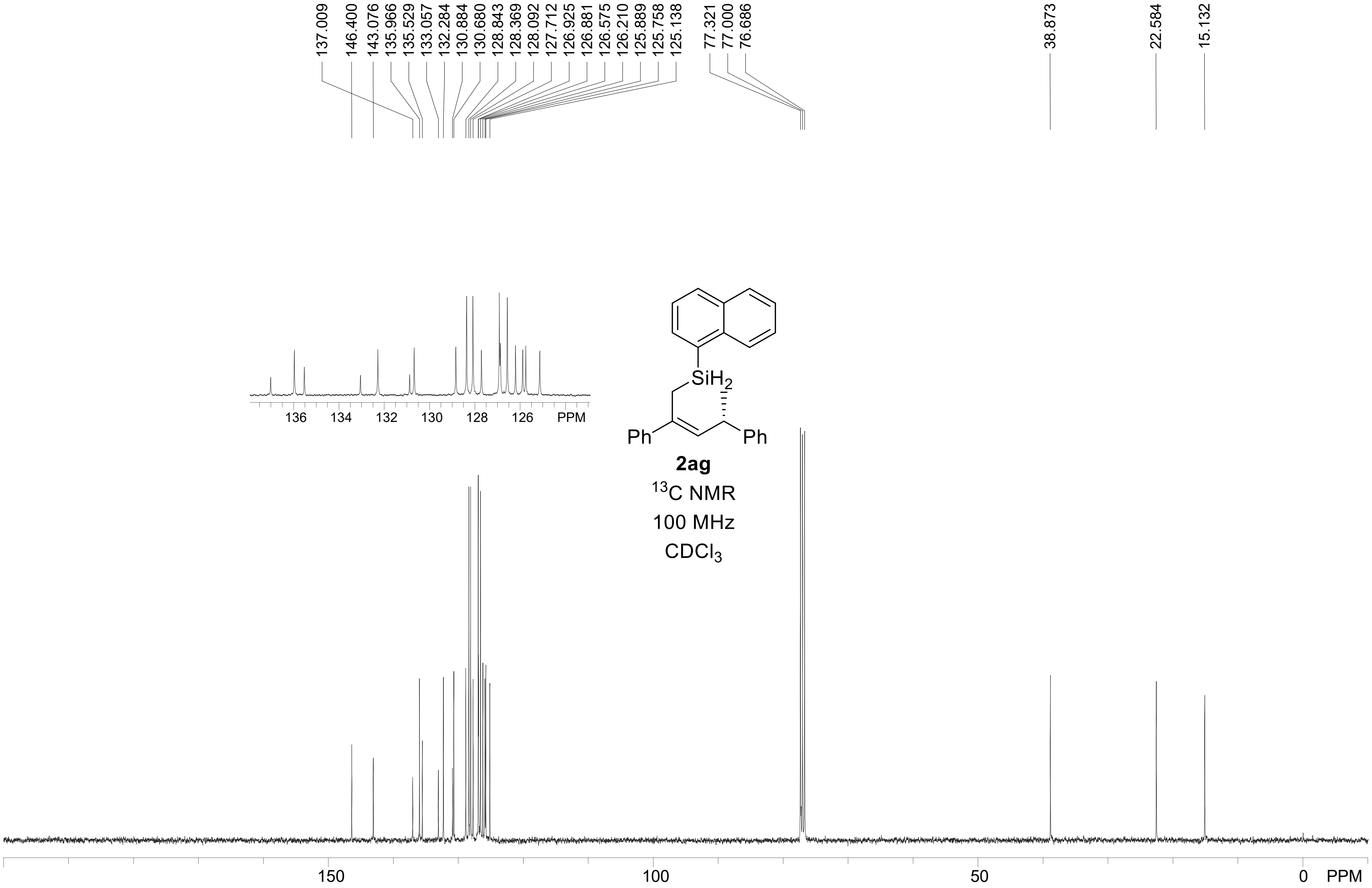


Figure S119. ^{13}C NMR spectra of **2ag**, Related to Table 2

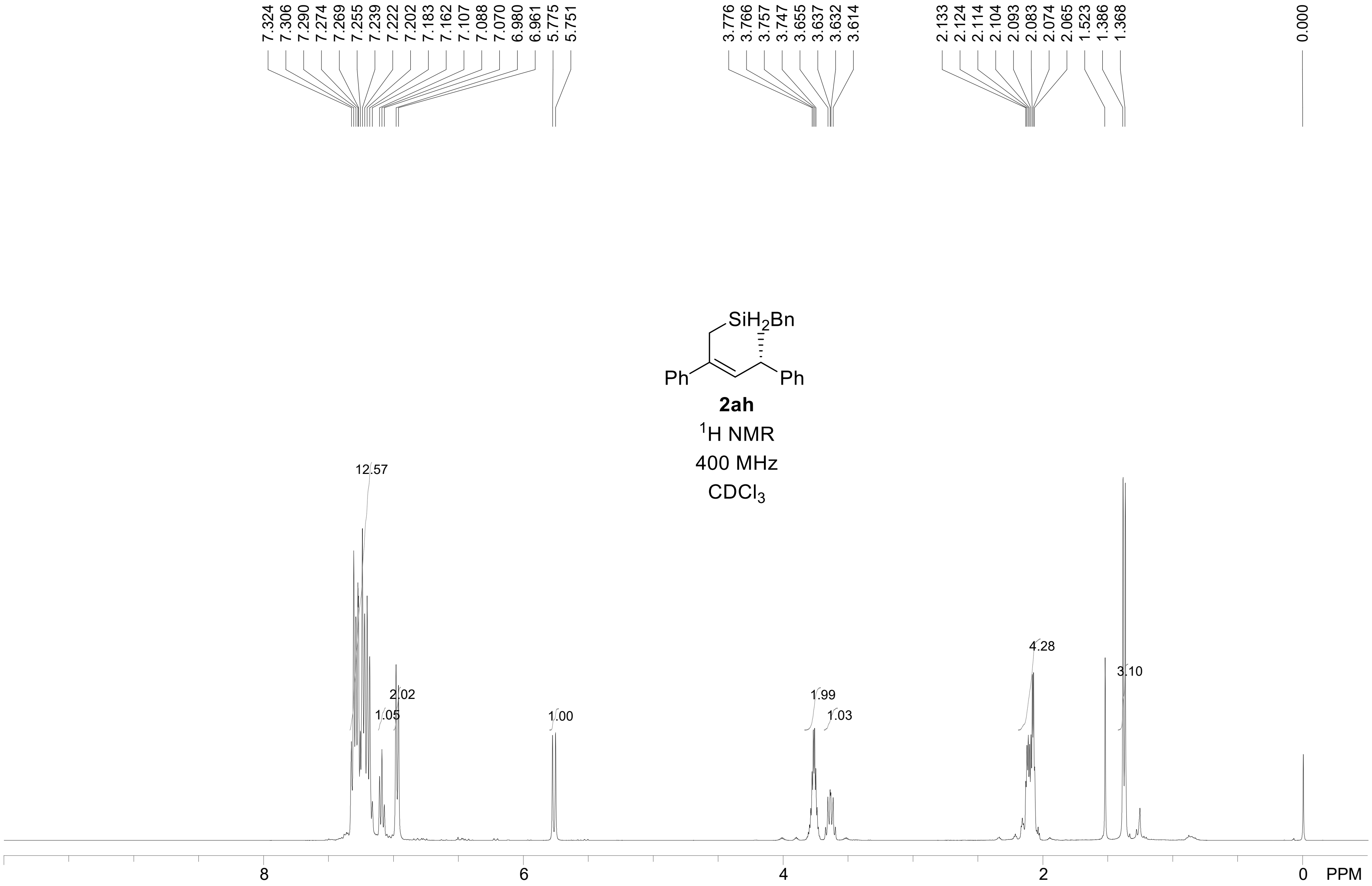


Figure S120. ^{1}H NMR spectra of **2ah**, Related to Table 2

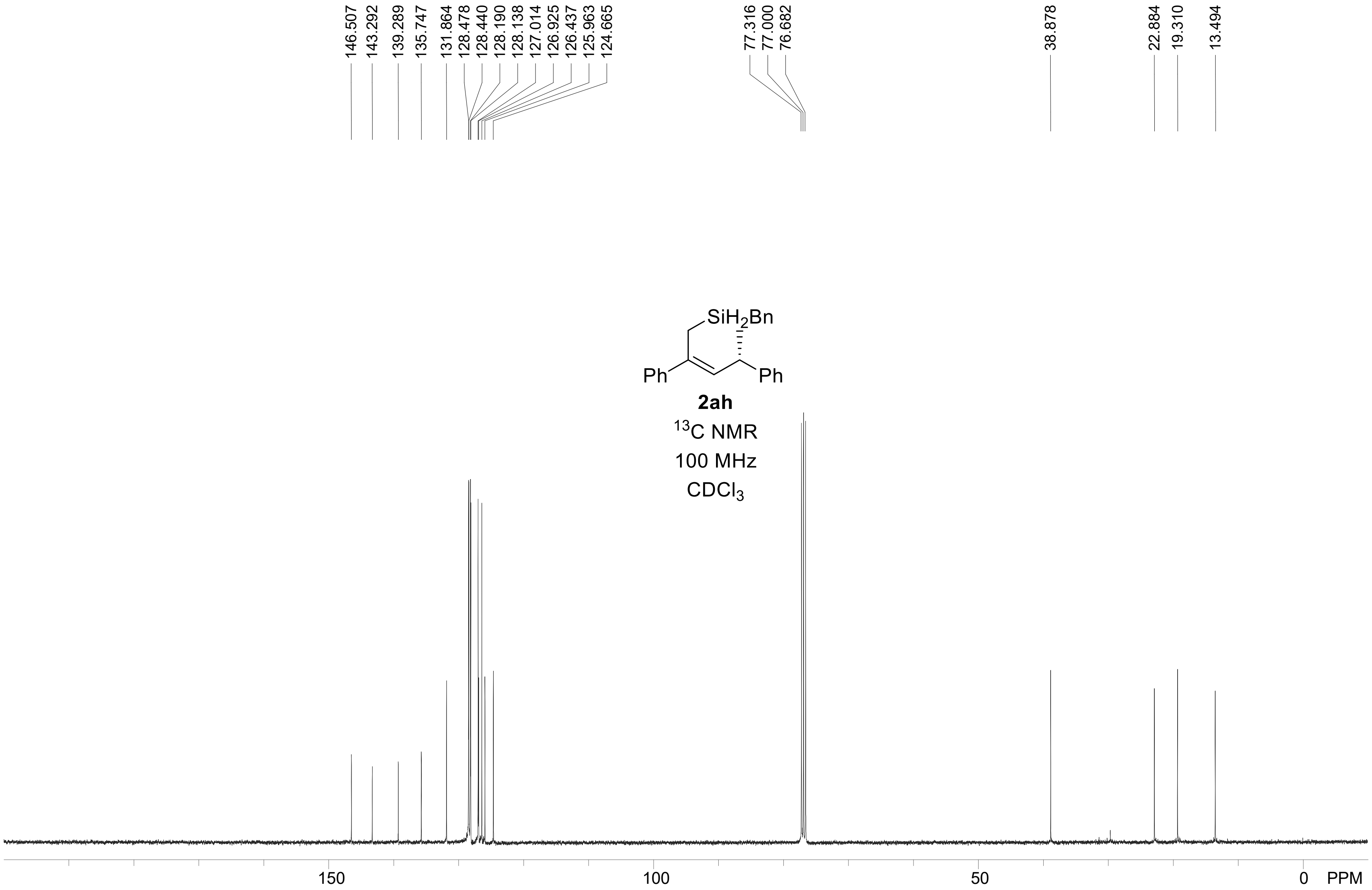


Figure S121. ^{13}C NMR spectra of **2ah**, Related to Table 2

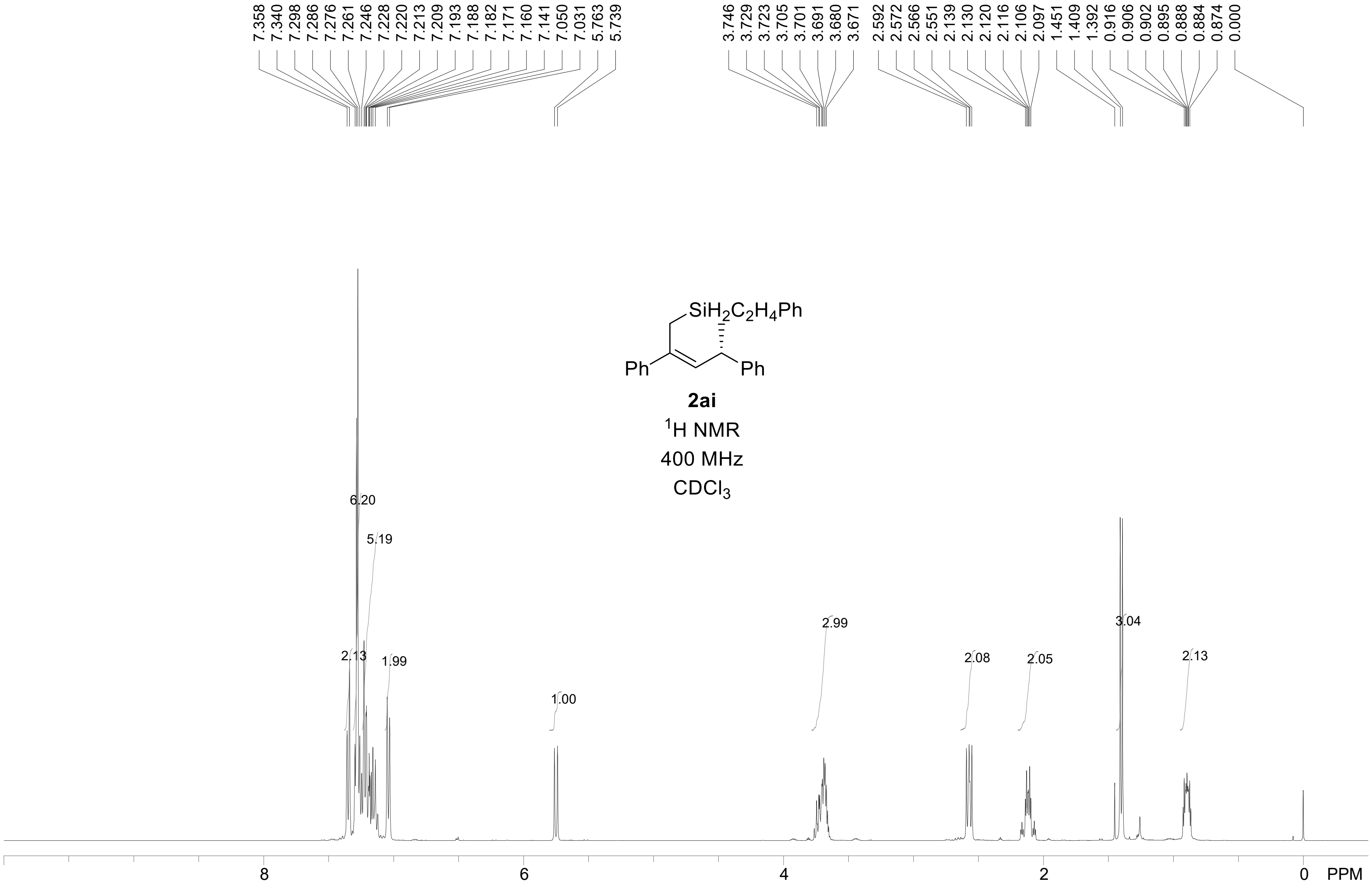


Figure S122. ^{1}H NMR spectra of **2ai**, Related to Table 2

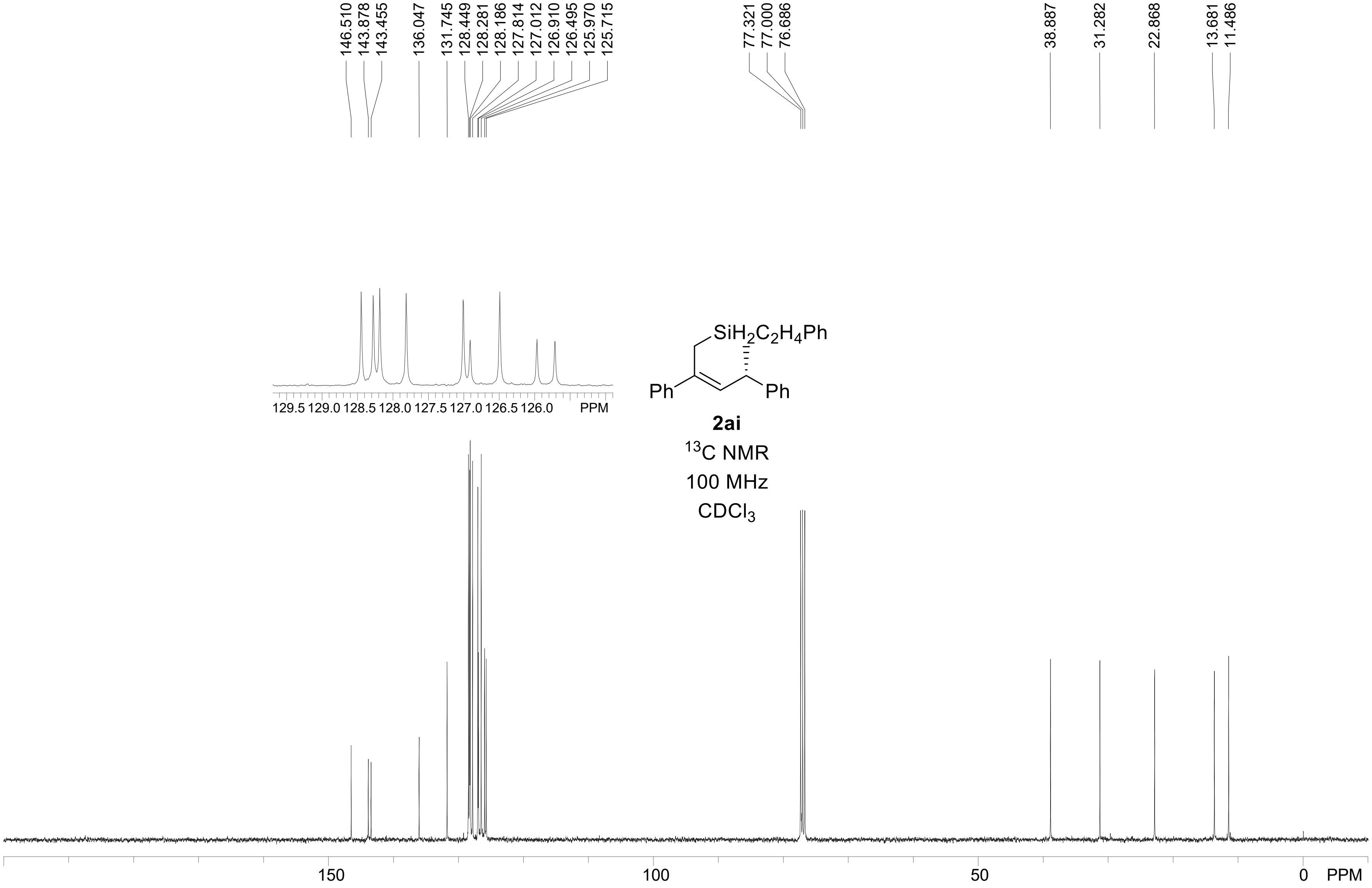


Figure S123. ^{13}C NMR spectra of **2ai**, Related to Table 2

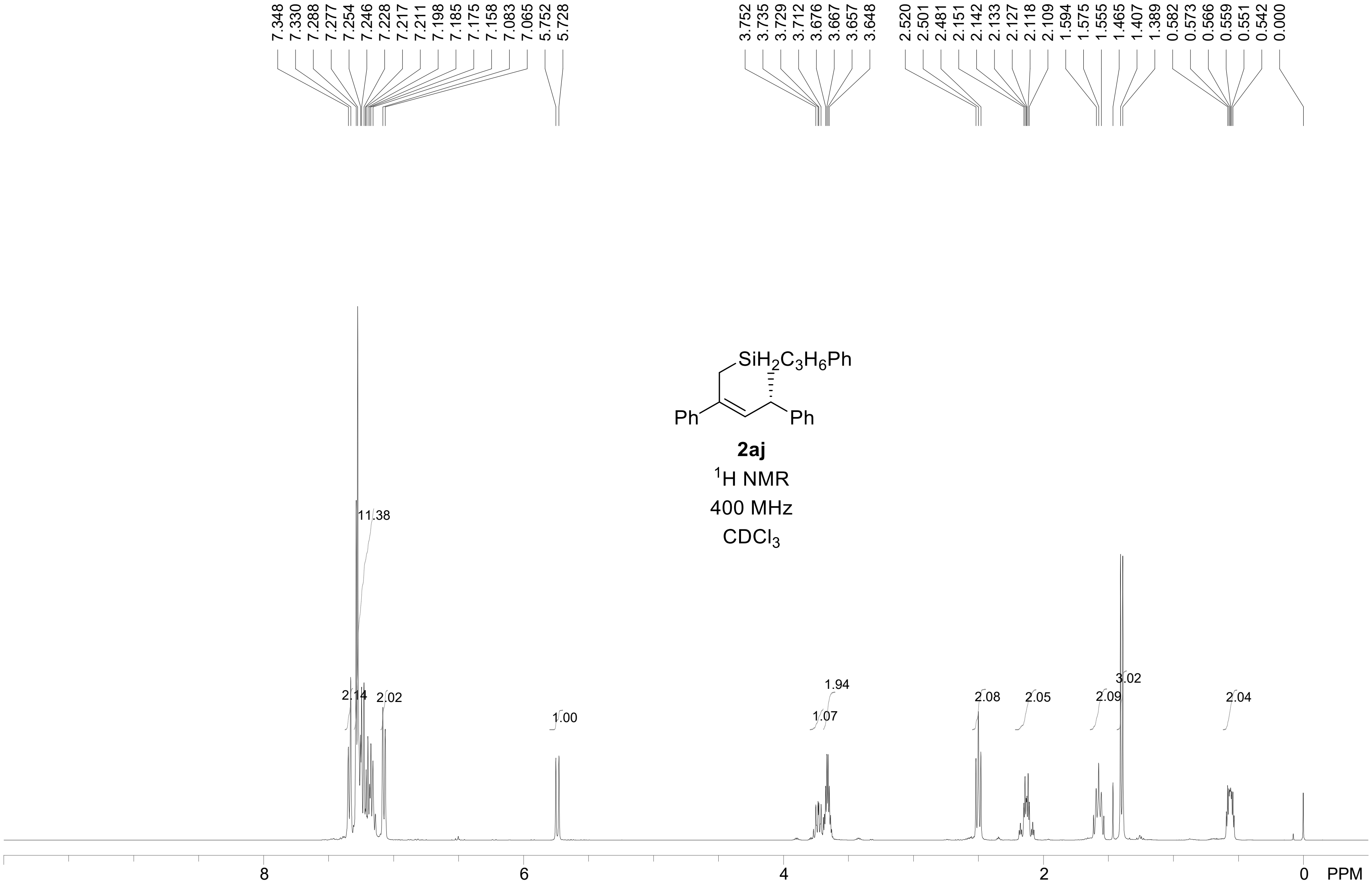


Figure S124. ^{1}H NMR spectra of **2aj**, Related to Table 2

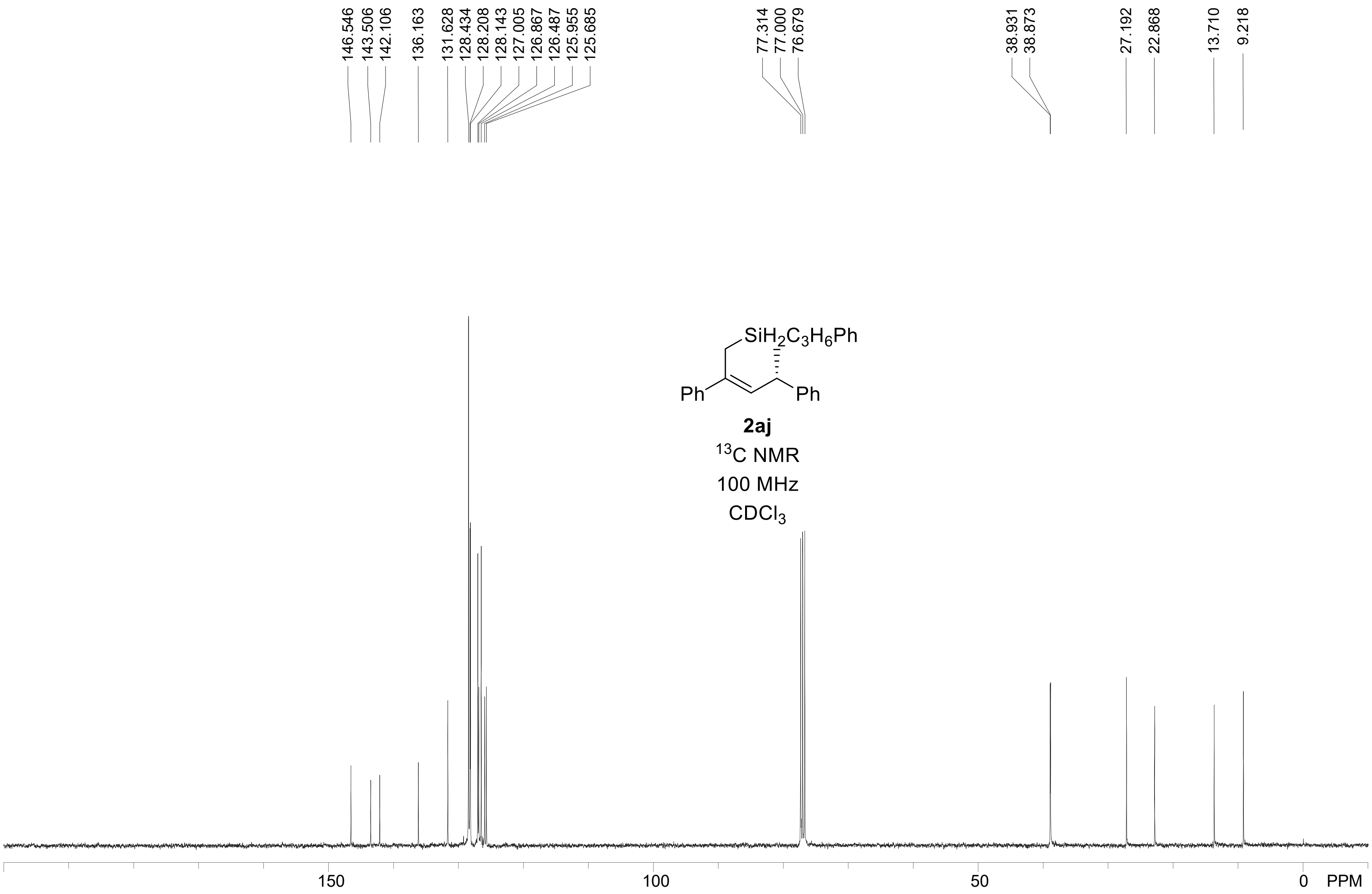


Figure S125. ^{13}C NMR spectra of **2aj**, Related to Table 2

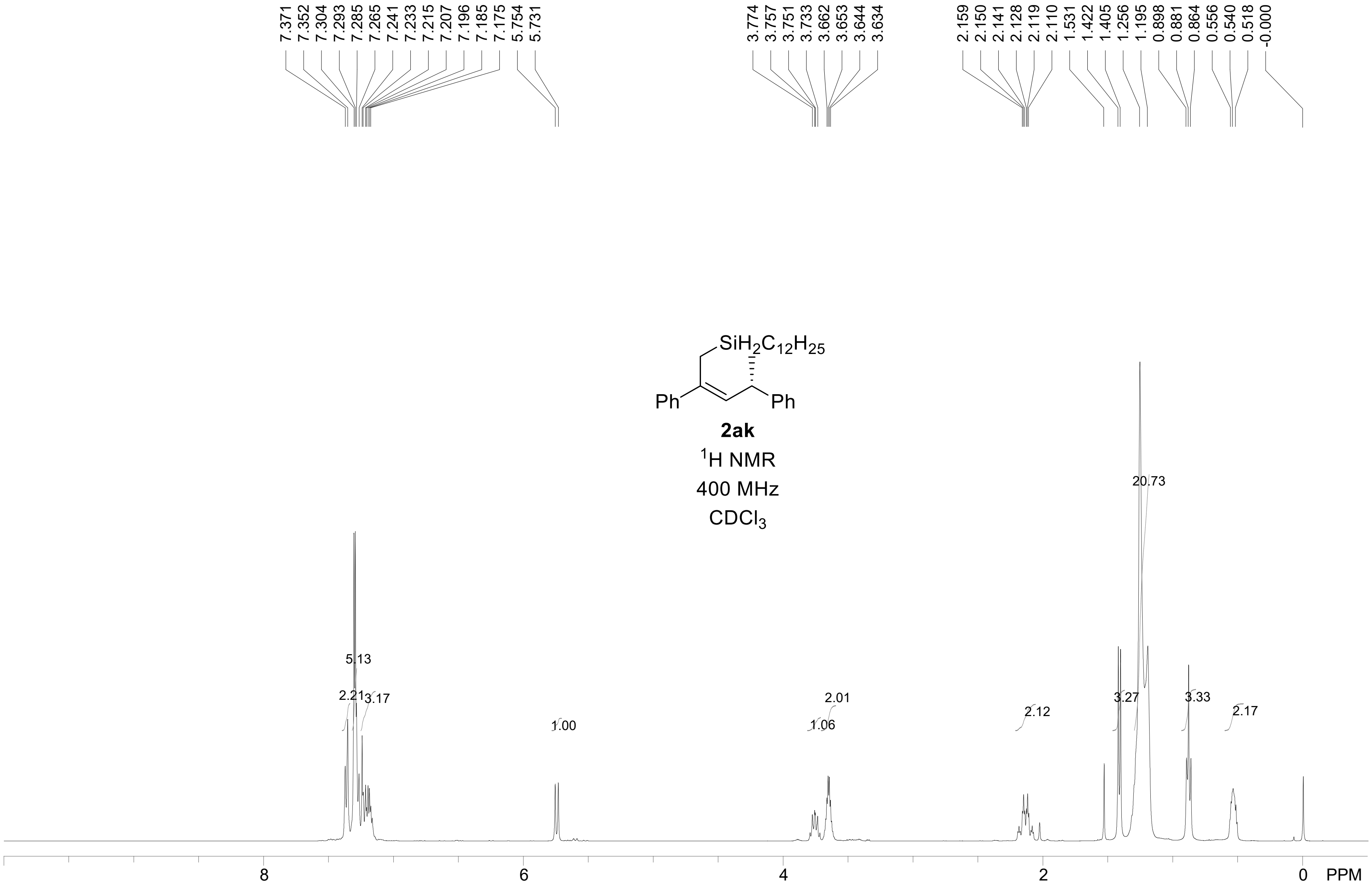


Figure S126. ^{1}H NMR spectra of **2ak**, Related to Table 2

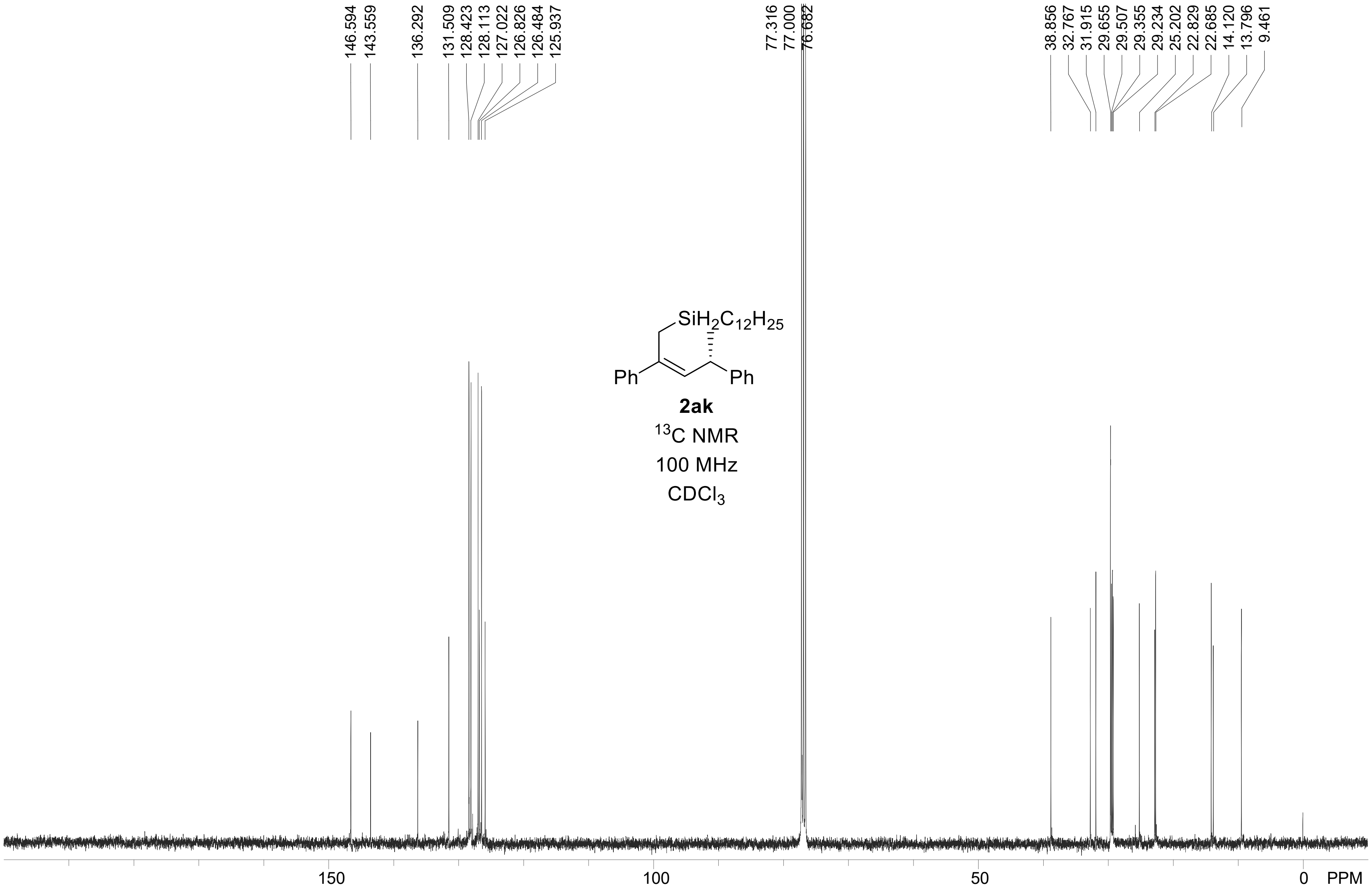


Figure S127. ^{13}C NMR spectra of **2ak**, Related to Table 2

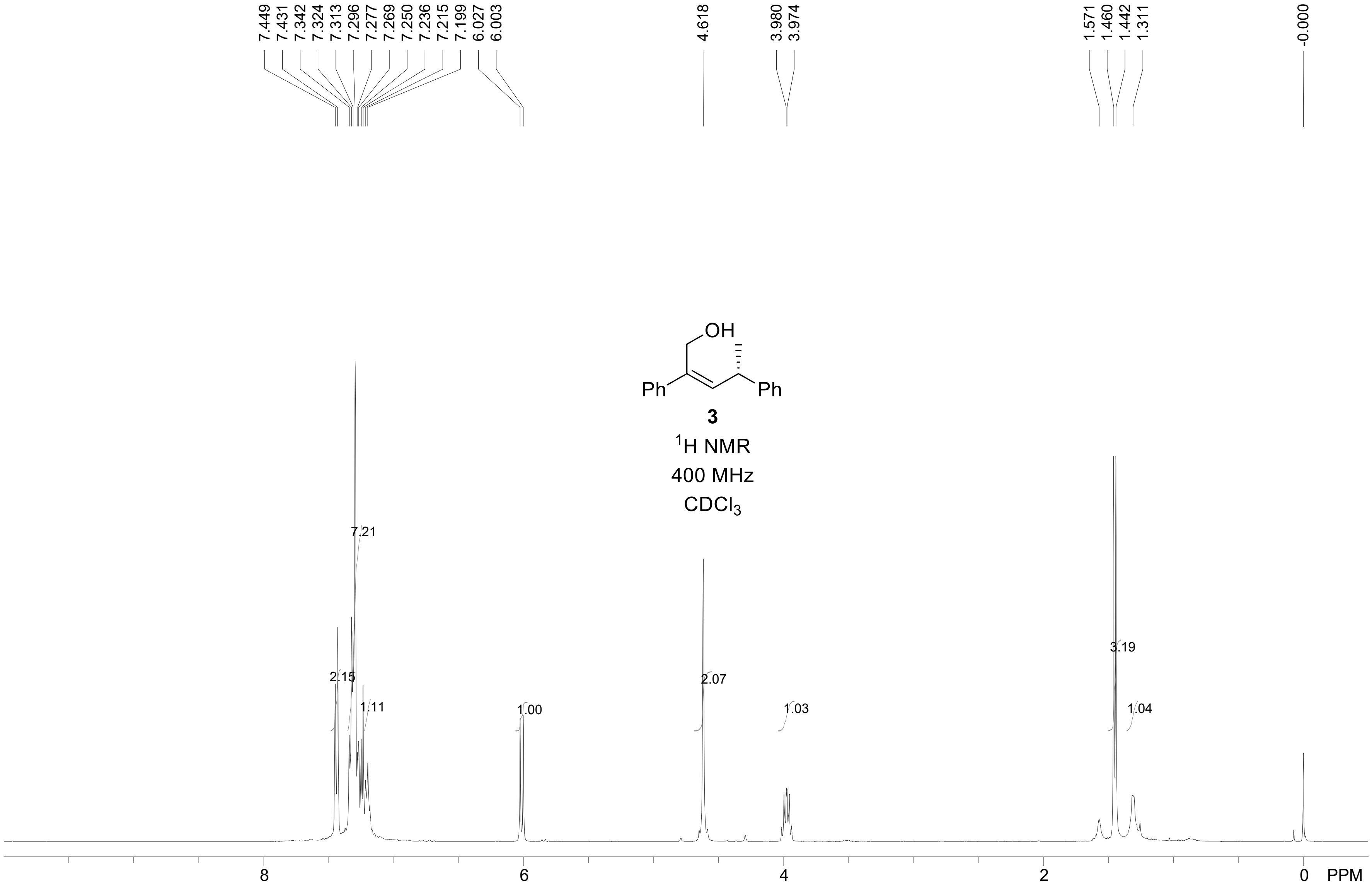


Figure S128. ^{1}H NMR spectra of **3**, Related to Scheme 1

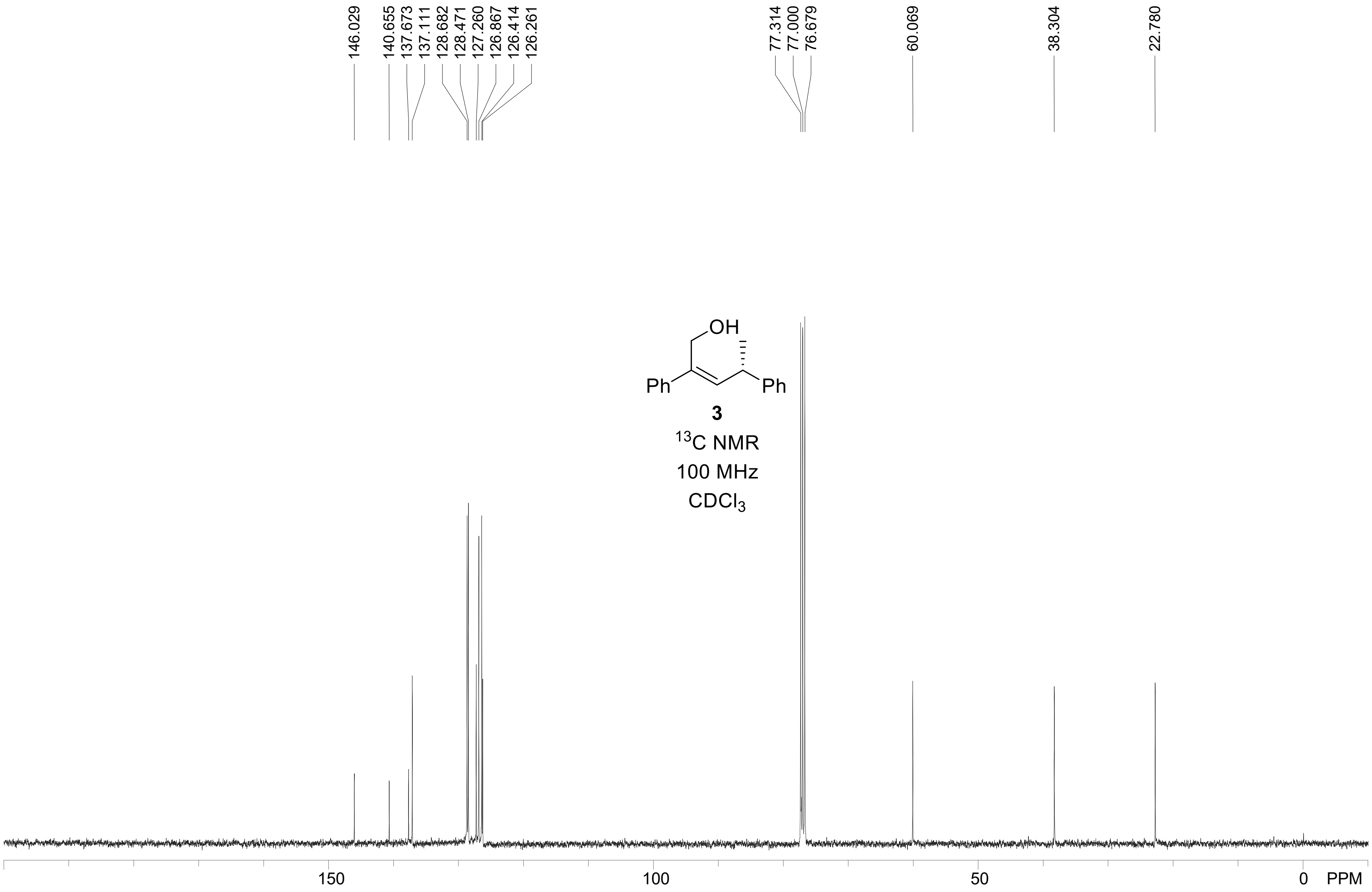


Figure S129. ^{13}C NMR spectra of **3**, Related to Scheme 1

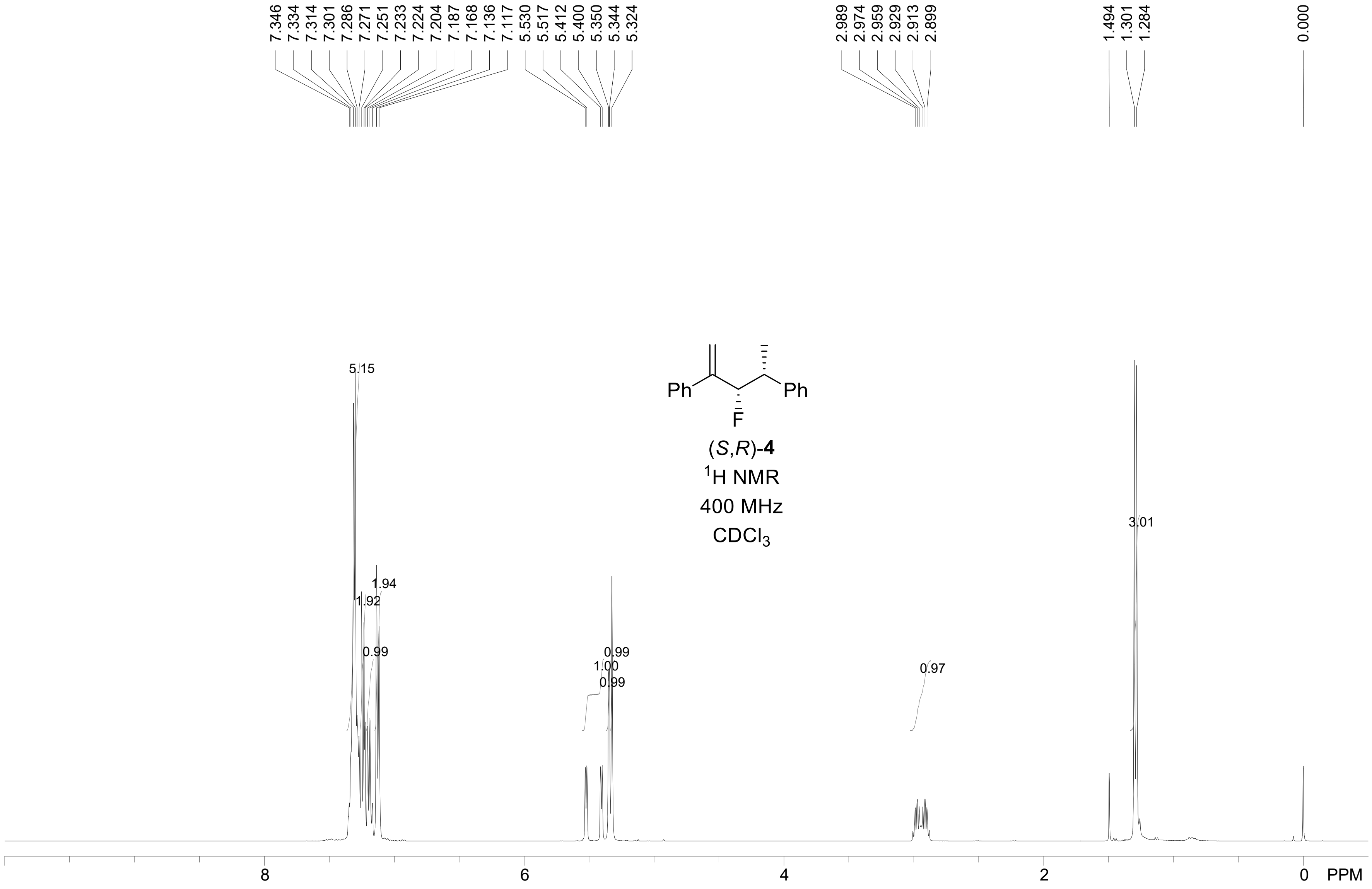


Figure S130. ^{1}H NMR spectra of (*S,R*)-**4**, Related to Scheme 1

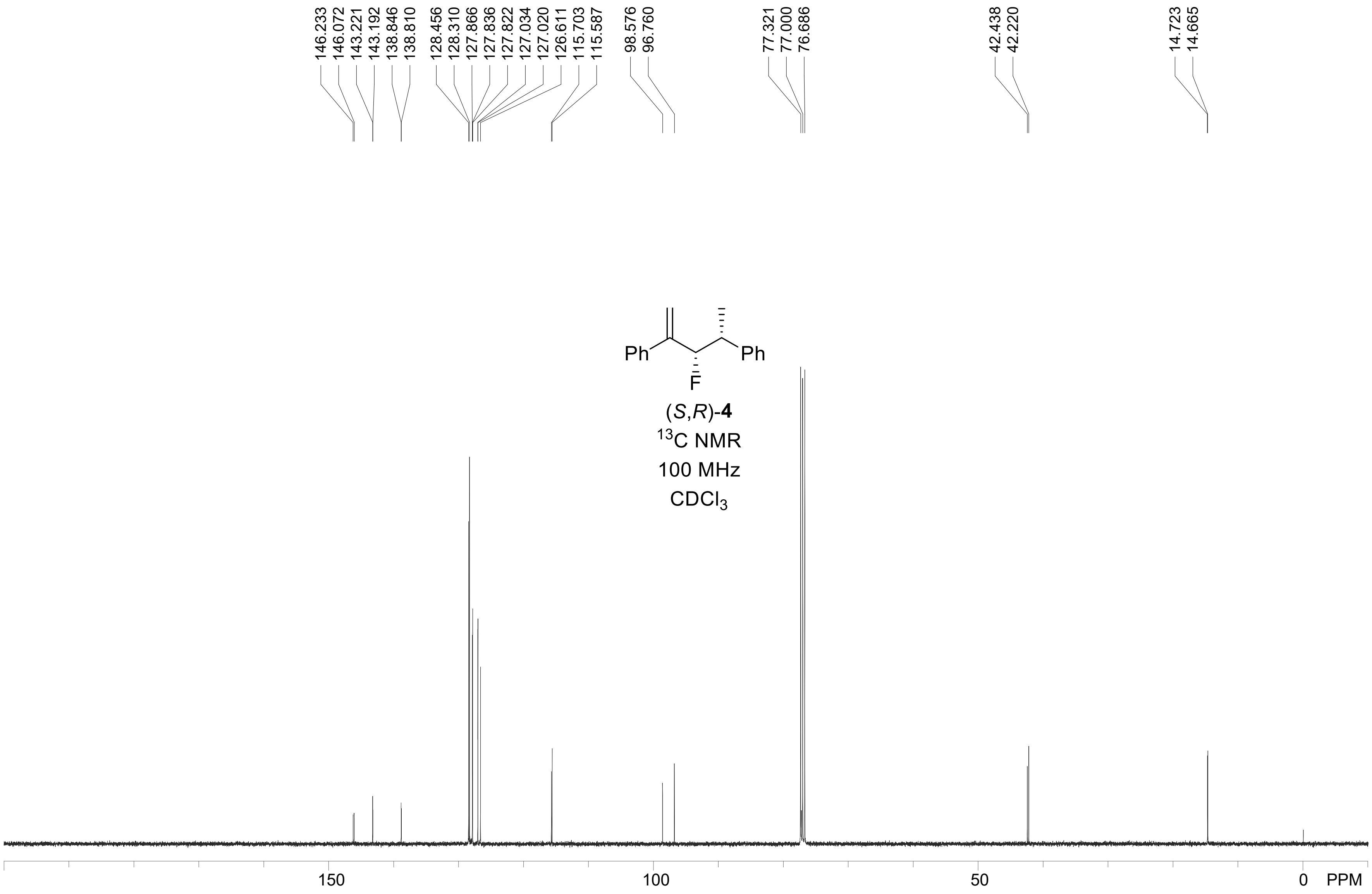


Figure S131. ^{13}C NMR spectra of (*S,R*)-**4**, Related to Scheme 1

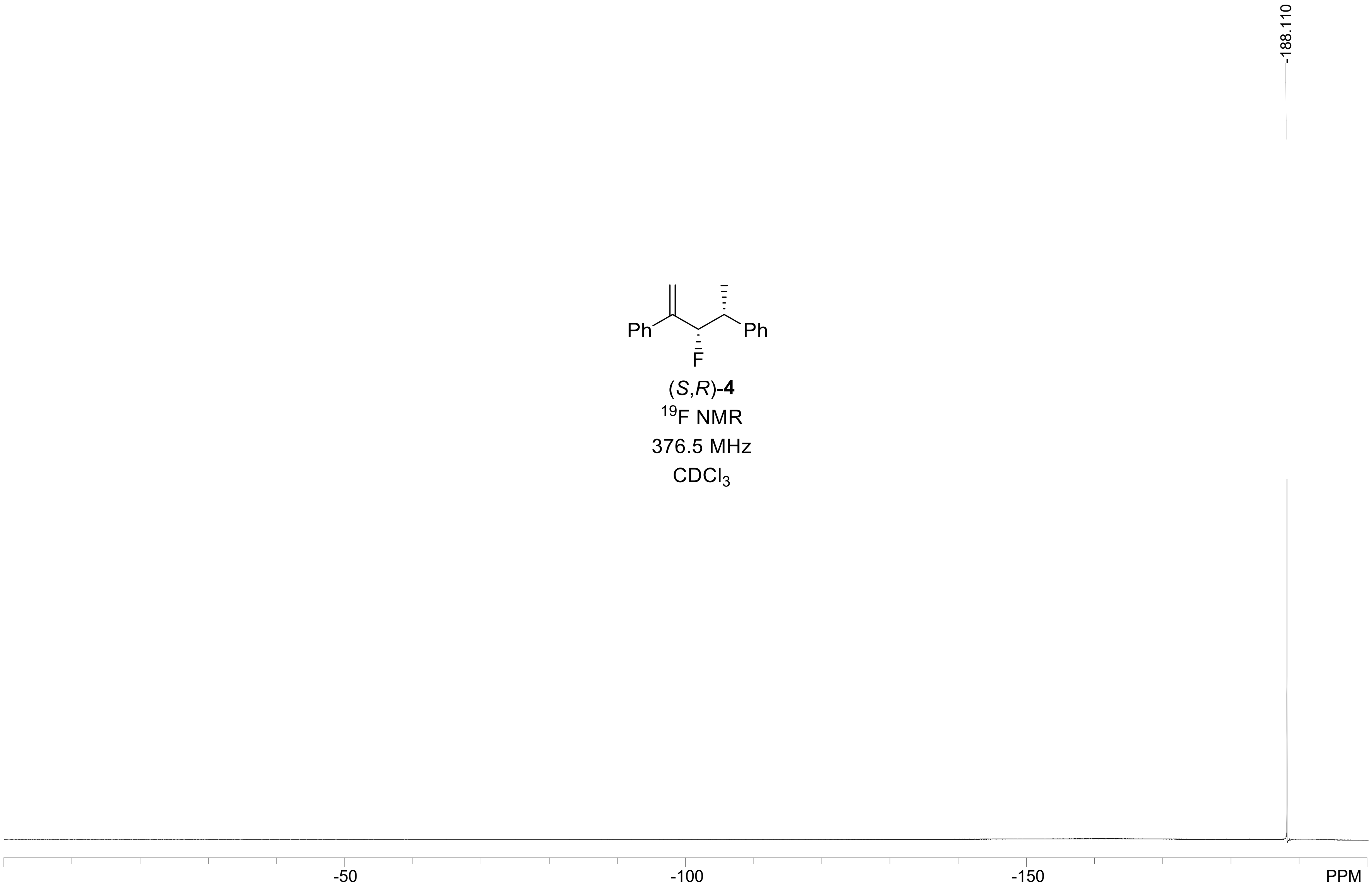


Figure S132. ^{19}F NMR spectra of (*S*,*R*)-**4**, Related to Scheme 1

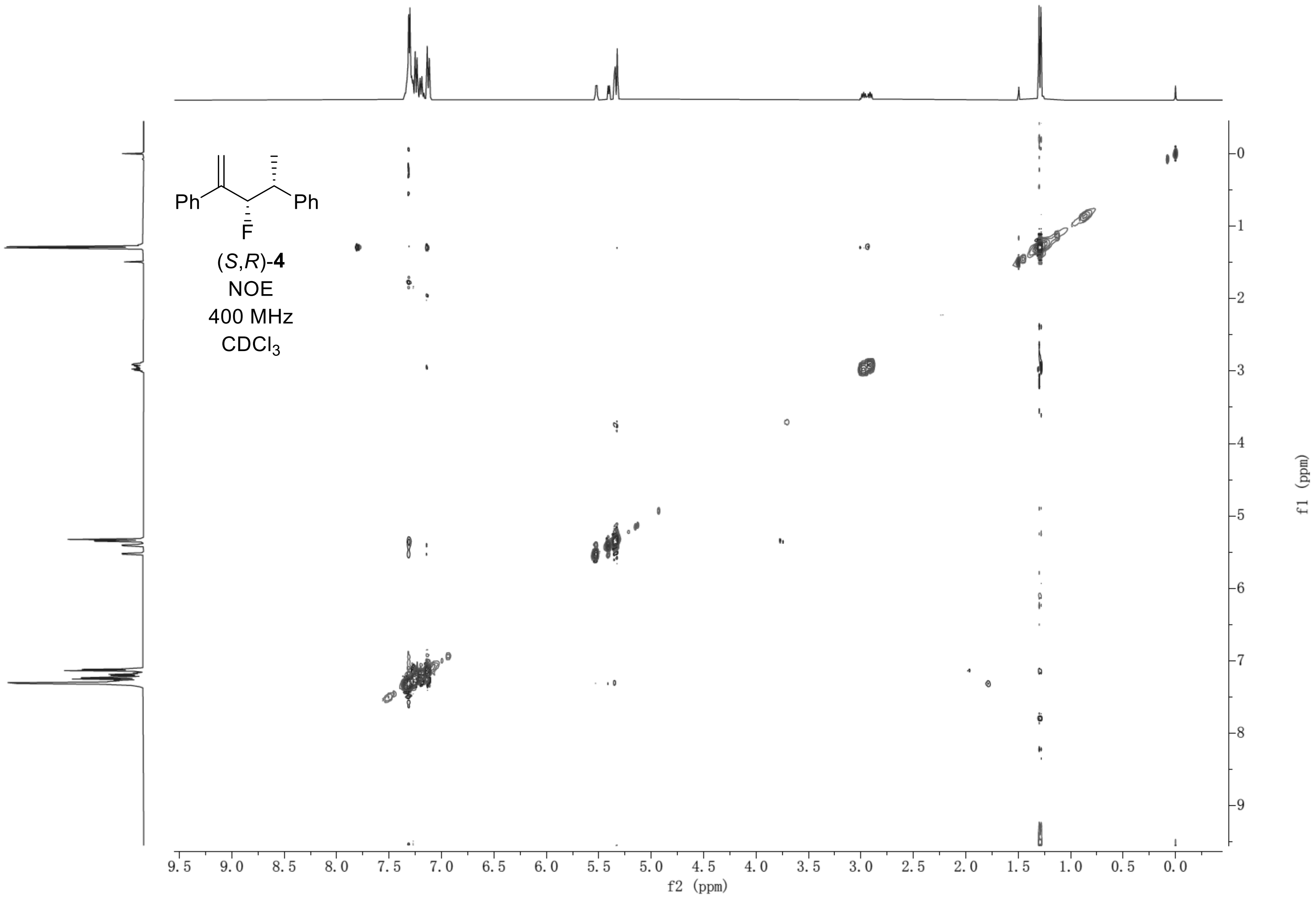


Figure S133. NOE spectra of (*S,R*)-**4**, Related to Scheme 1

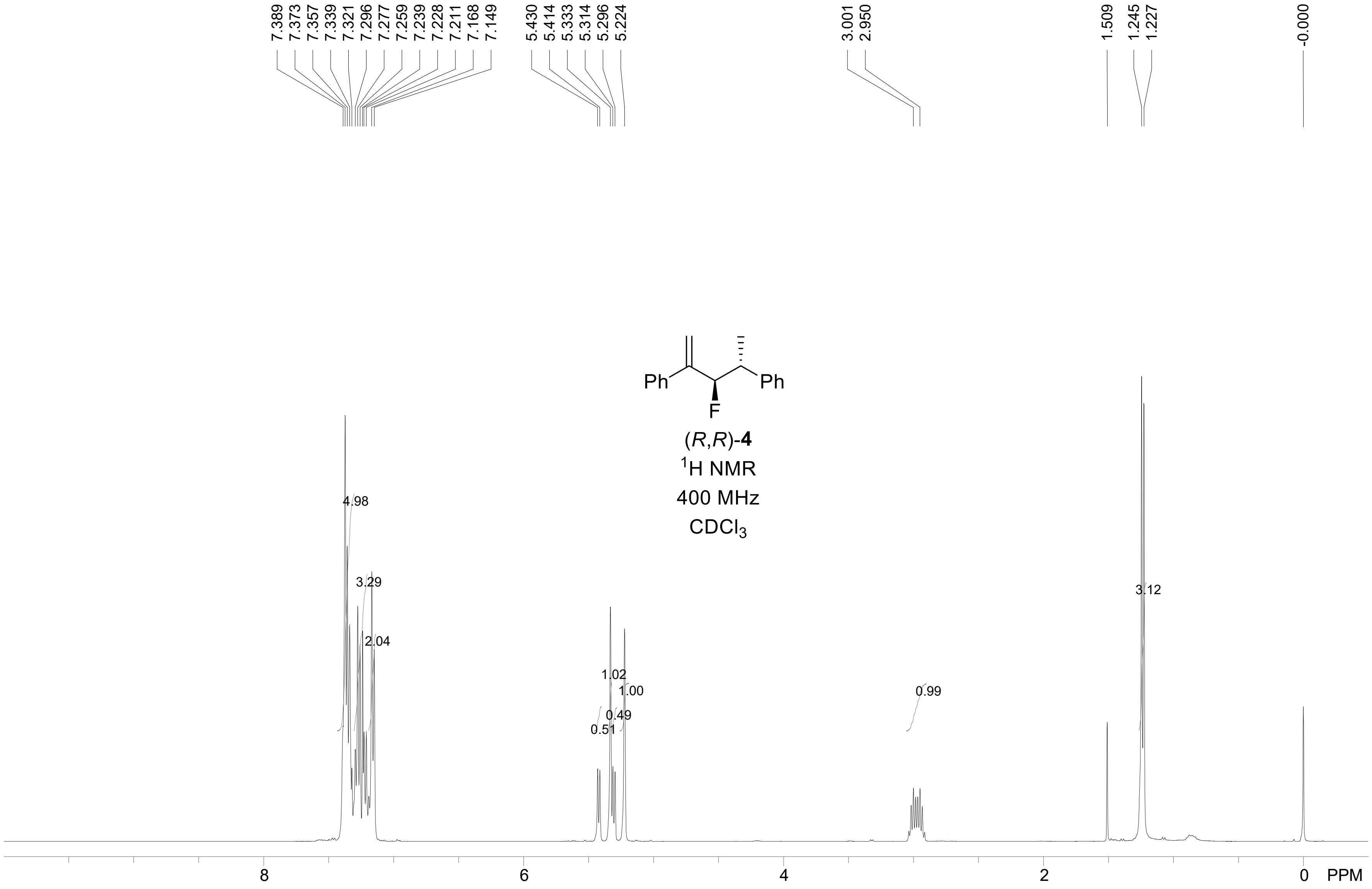


Figure S134. ^{1}H NMR spectra of (*R,R*)-**4**, Related to Scheme 1

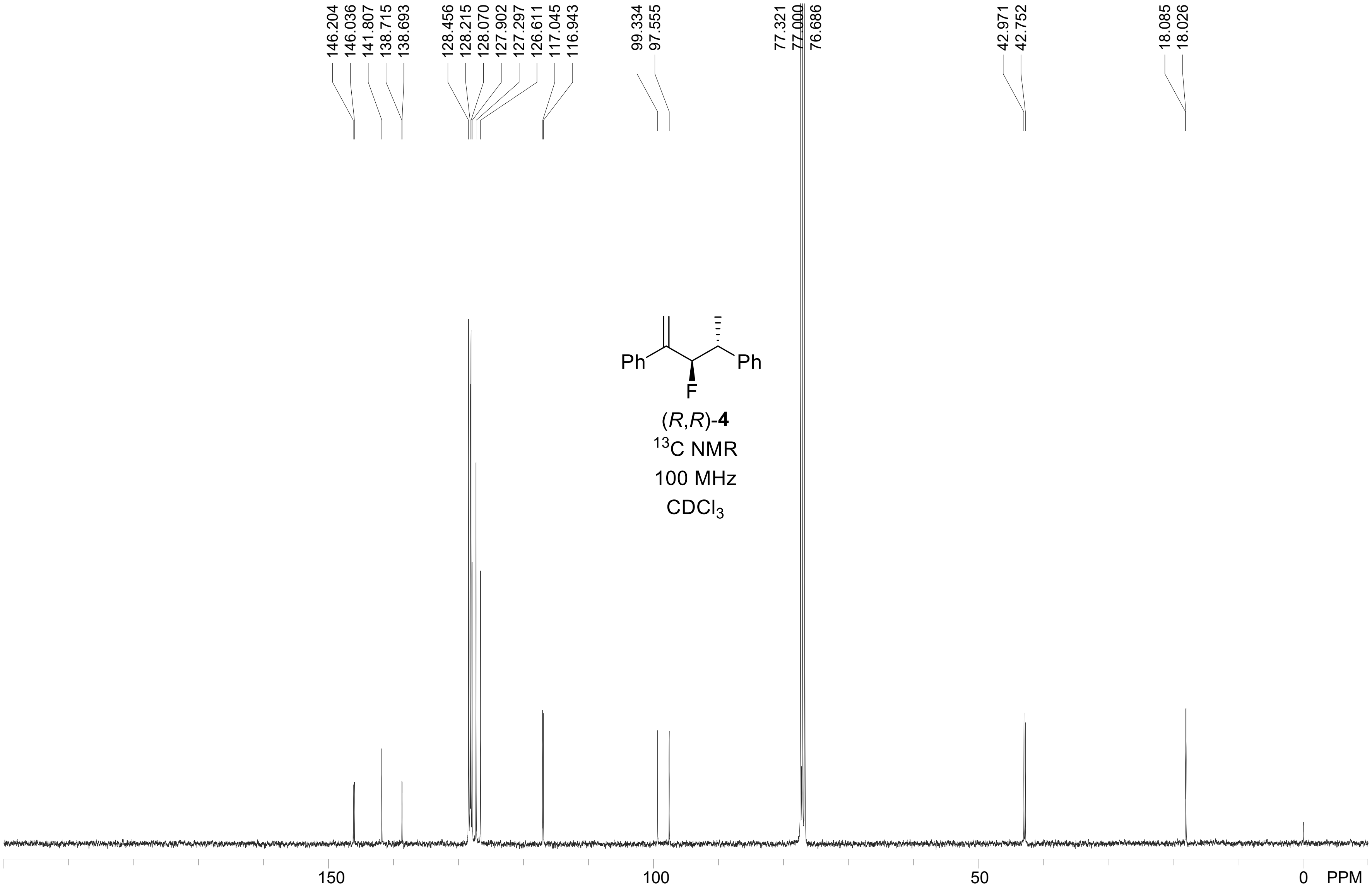


Figure S135. ^{13}C NMR spectra of (*R,R*)-**4**, Related to Scheme 1

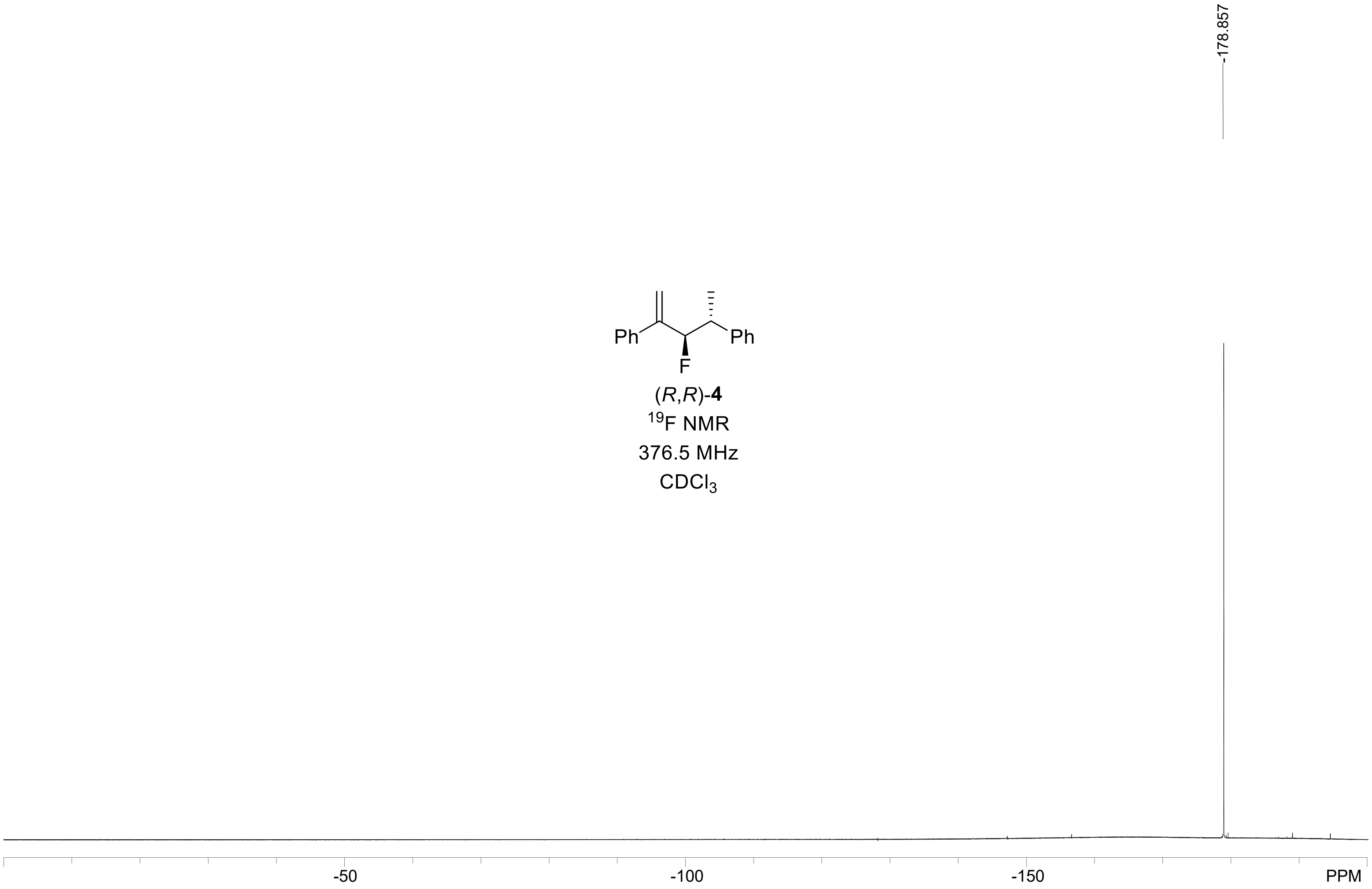


Figure S136. ^{19}F NMR spectra of (*R,R*)-**4**, Related to Scheme 1

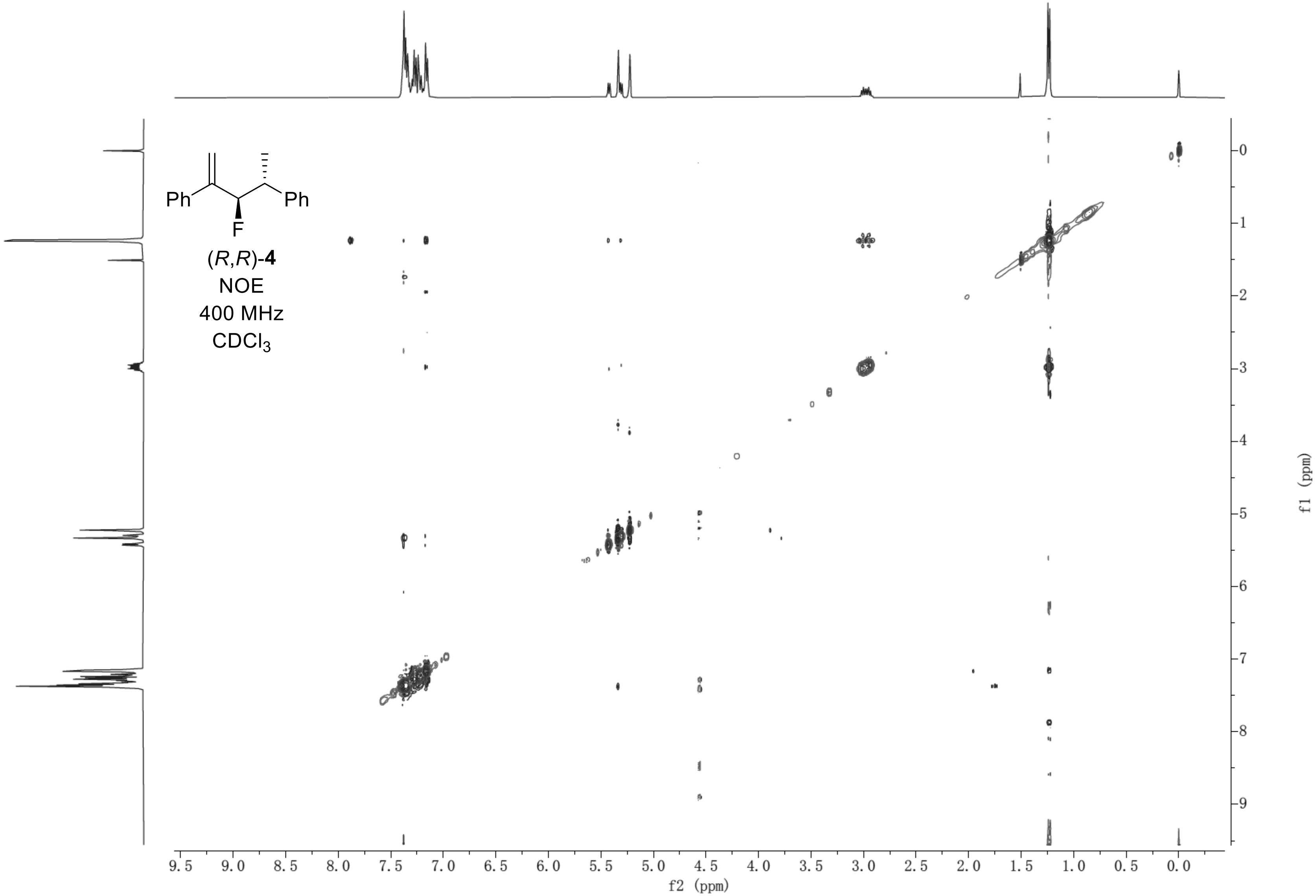


Figure S137. NOE spectra of (*R,R*)-**4**, Related to Scheme 1

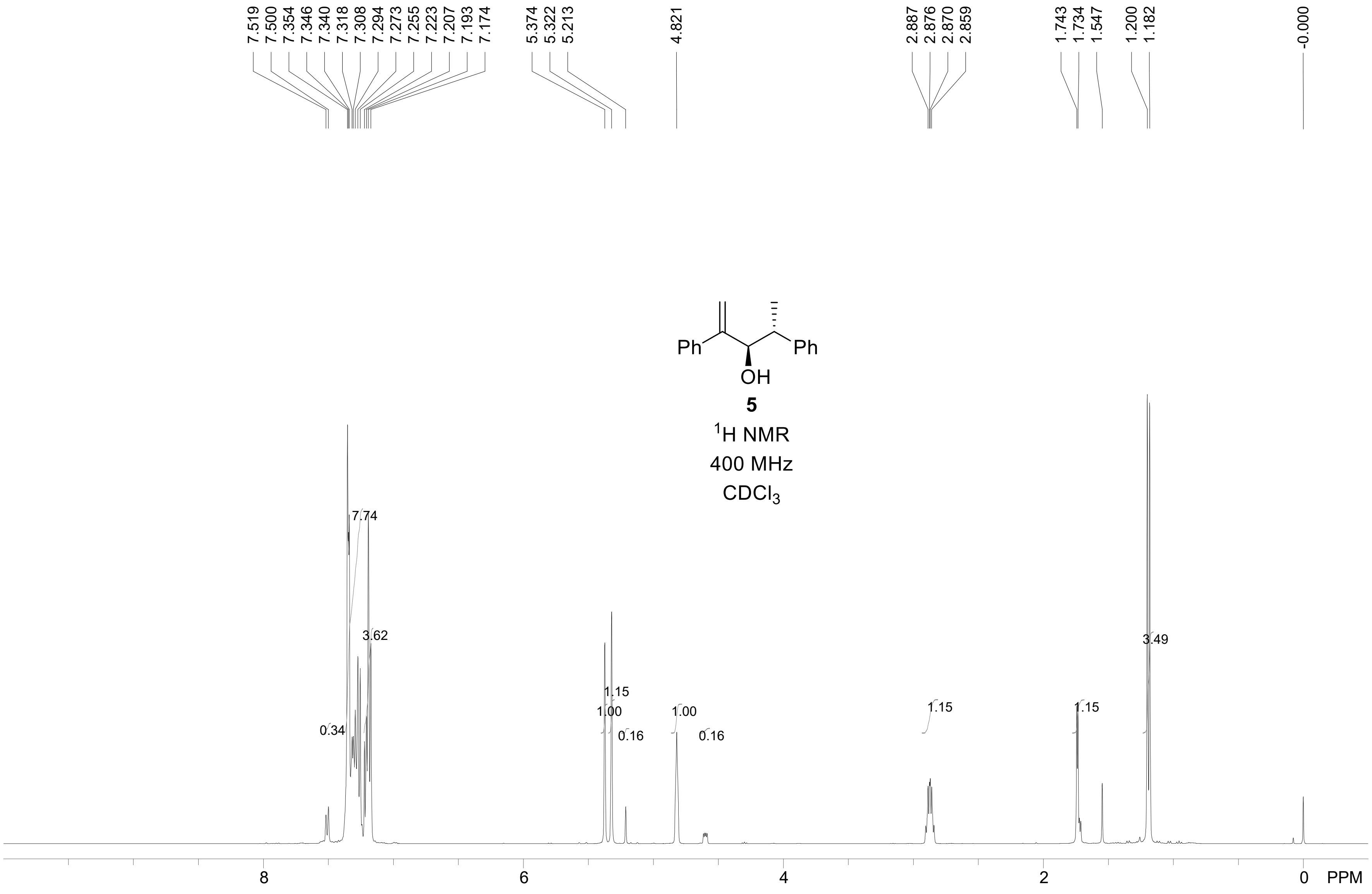


Figure S138. ^{1}H NMR spectra of **5**, Related to Scheme 1

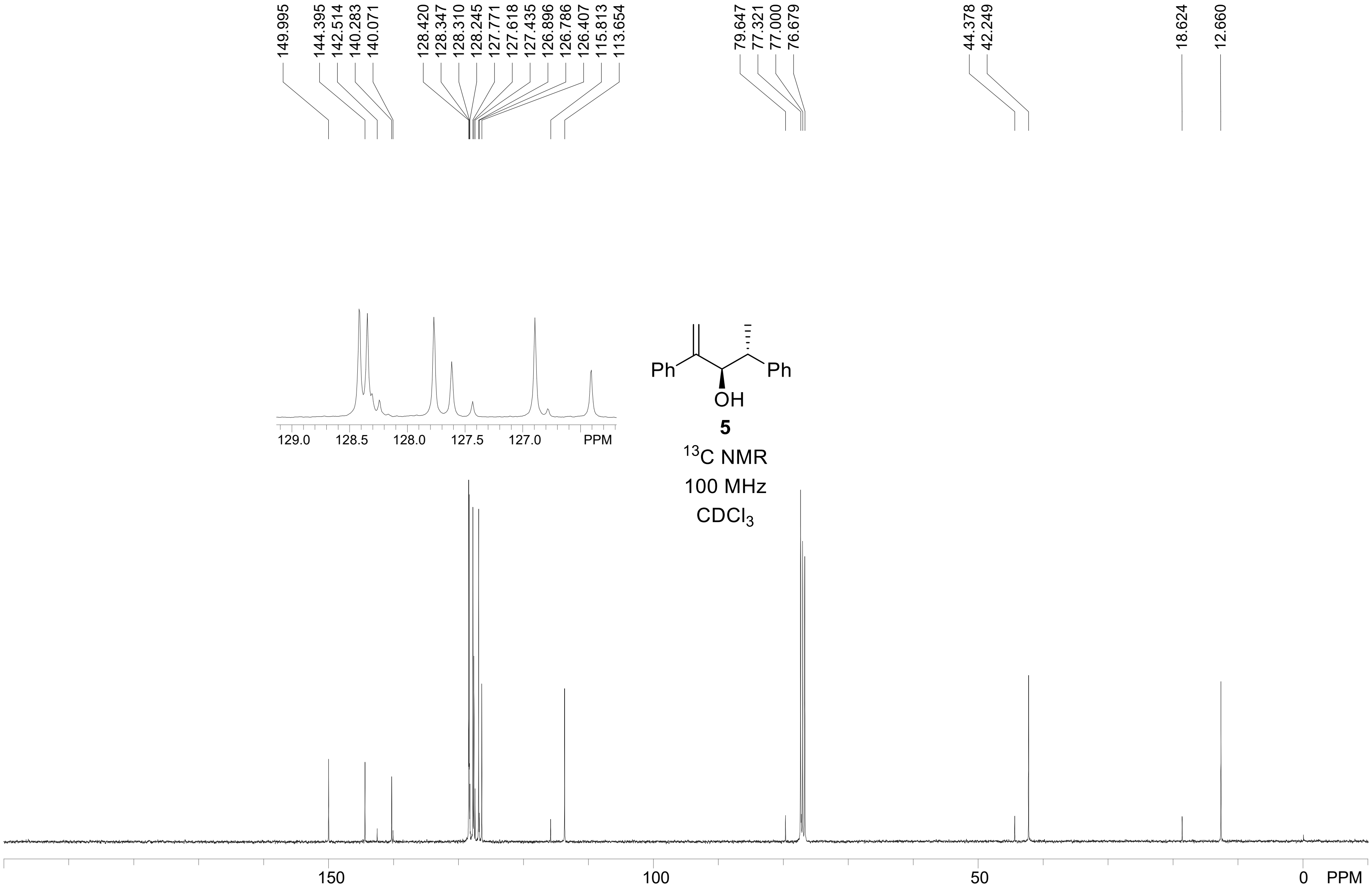


Figure S139. ^{13}C NMR spectra of **5**, Related to Scheme 1

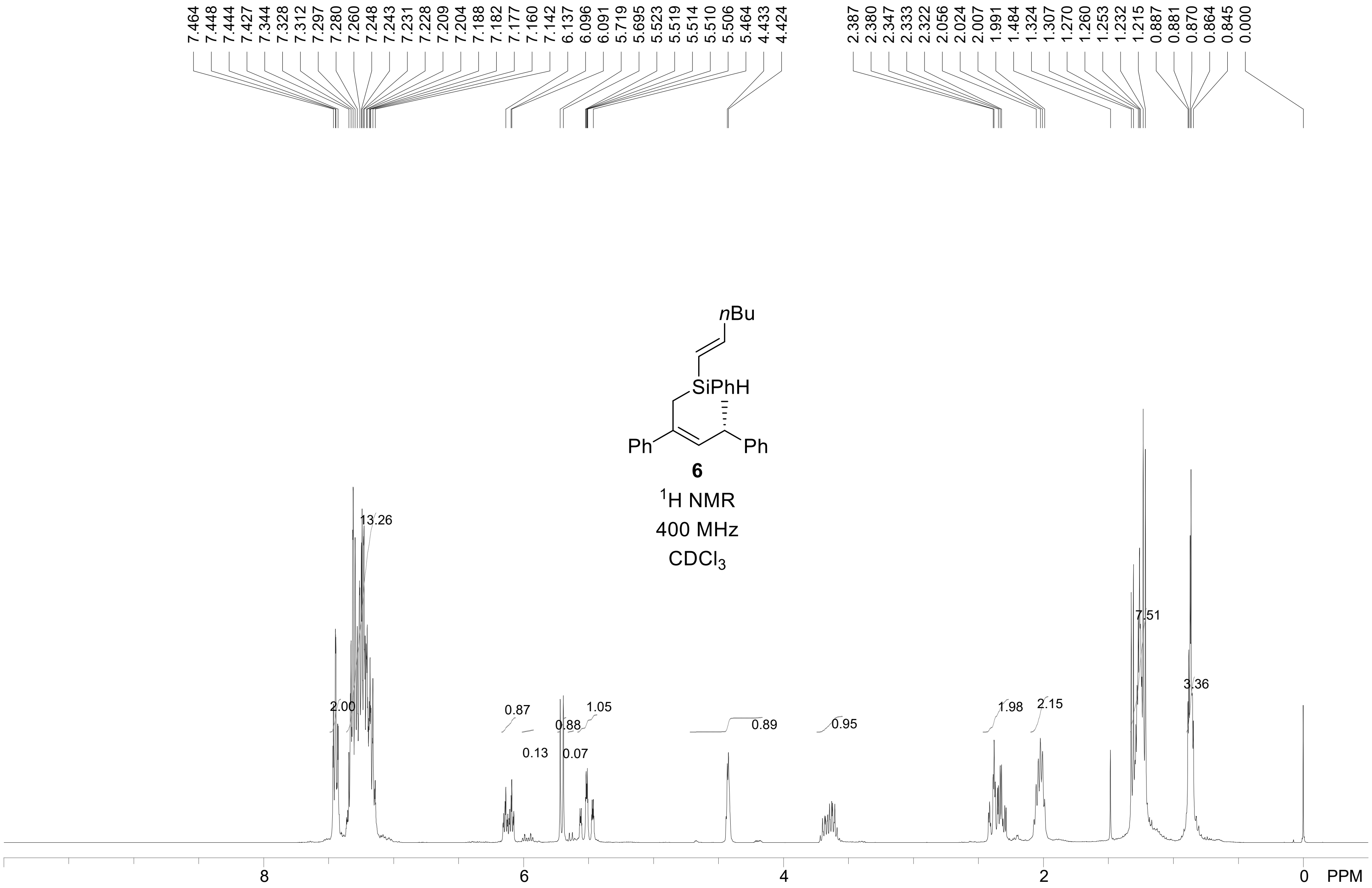


Figure S140. ^{1}H NMR spectra of **6**, Related to Scheme 1

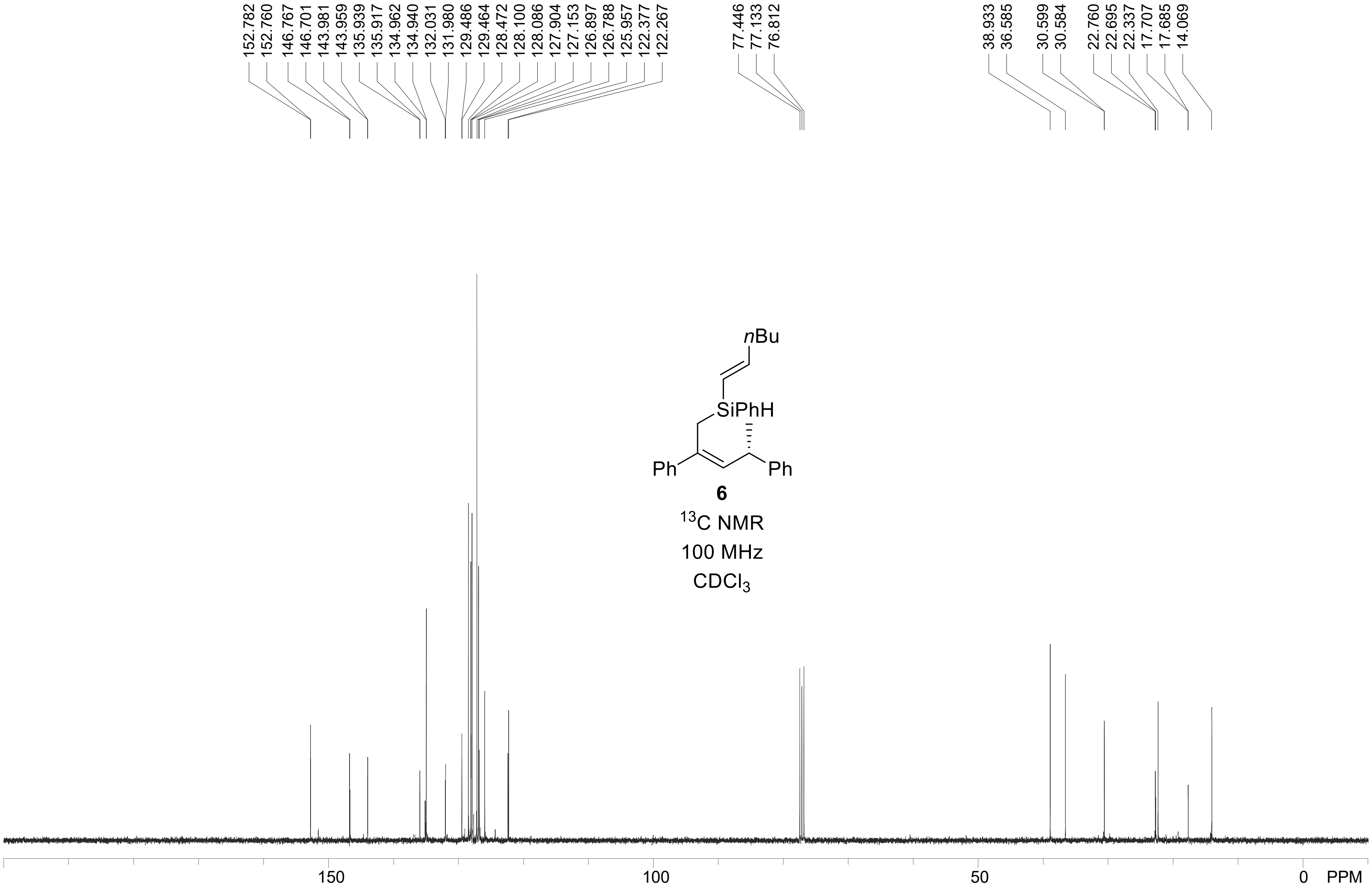


Figure S141. ^{13}C NMR spectra of **6**, Related to Scheme 1

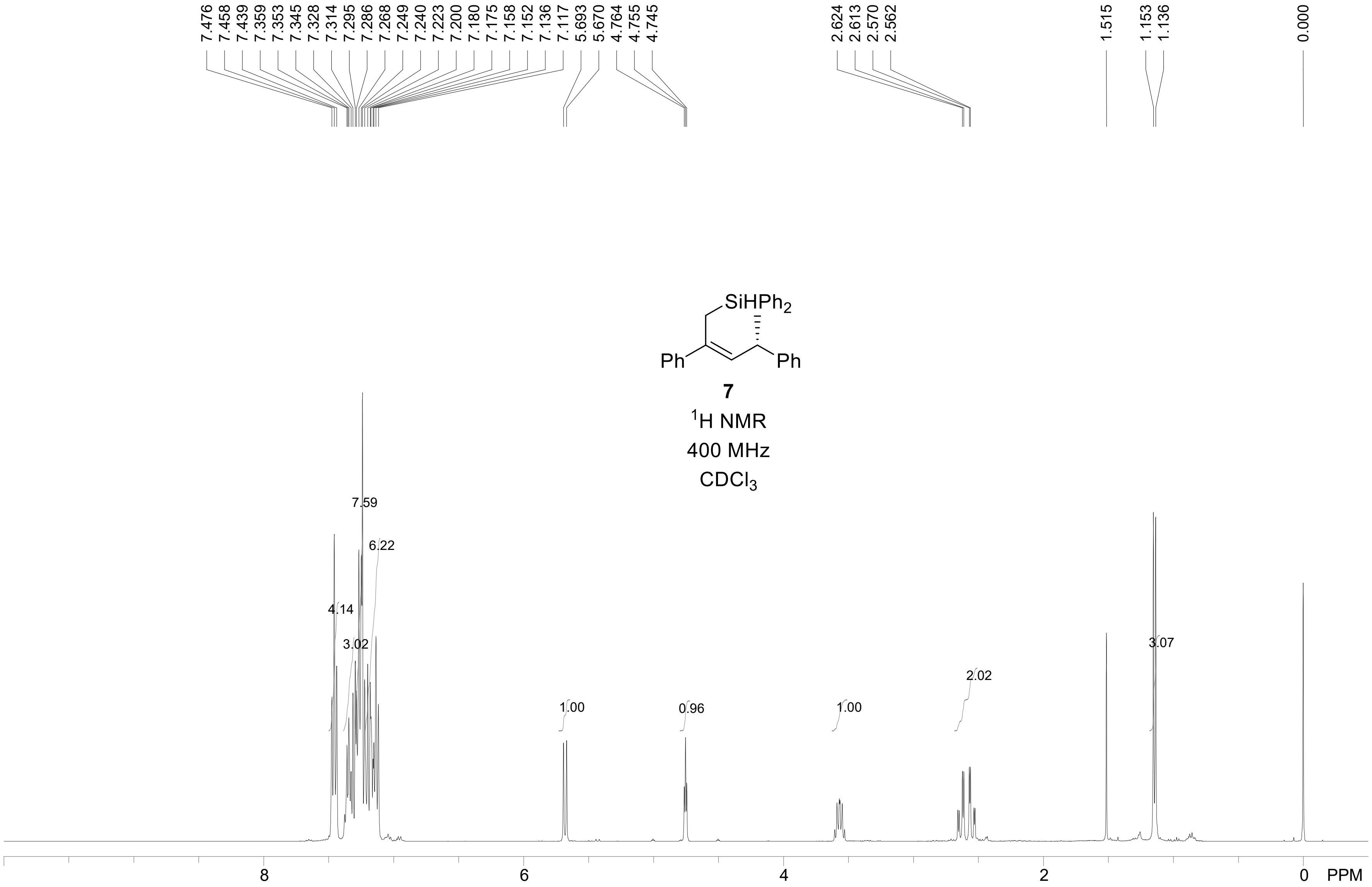


Figure S142. ^{1}H NMR spectra of **7**, Related to Scheme 1

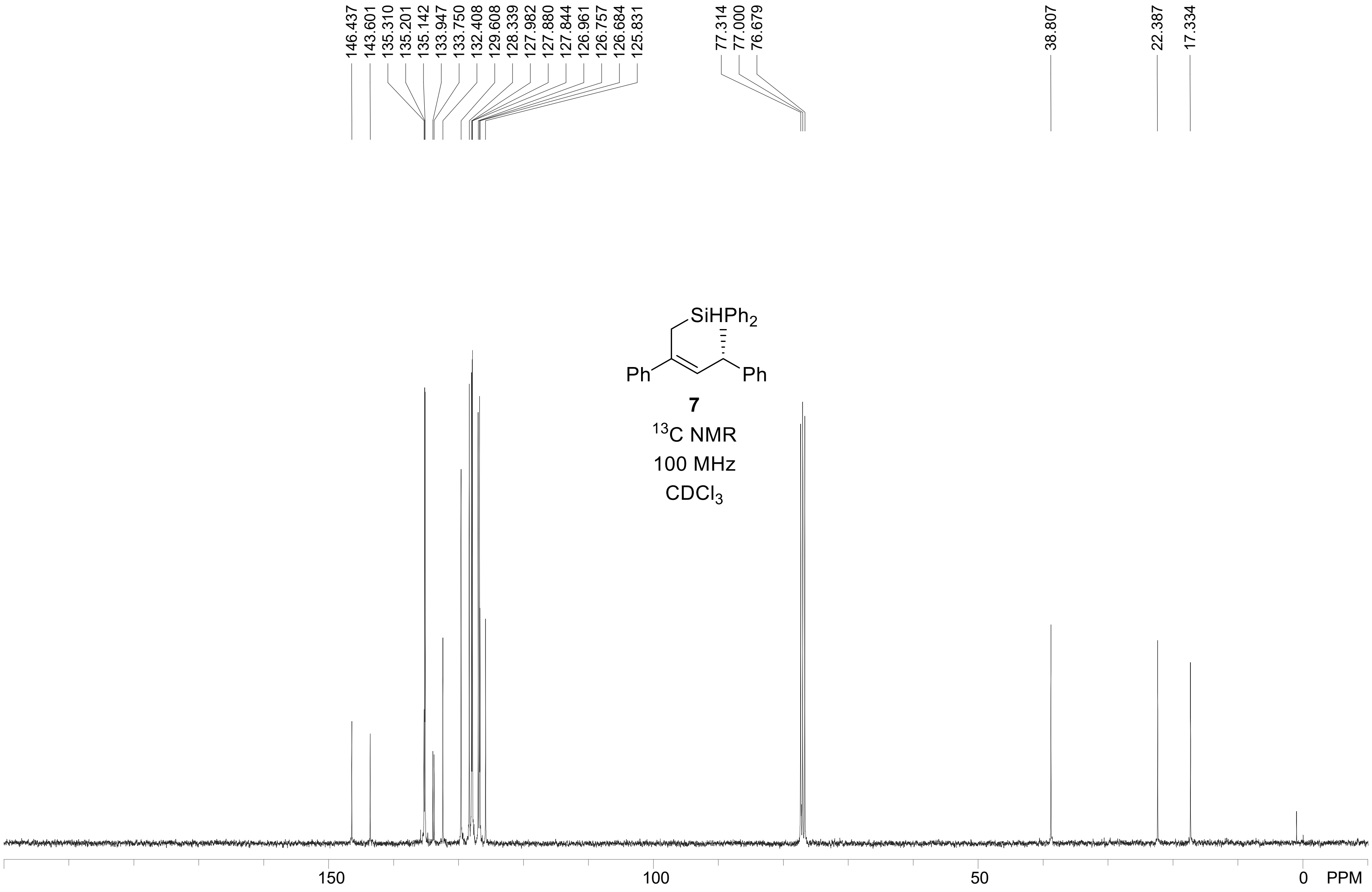


Figure S143. ^{13}C NMR spectra of **7**, Related to Scheme 1

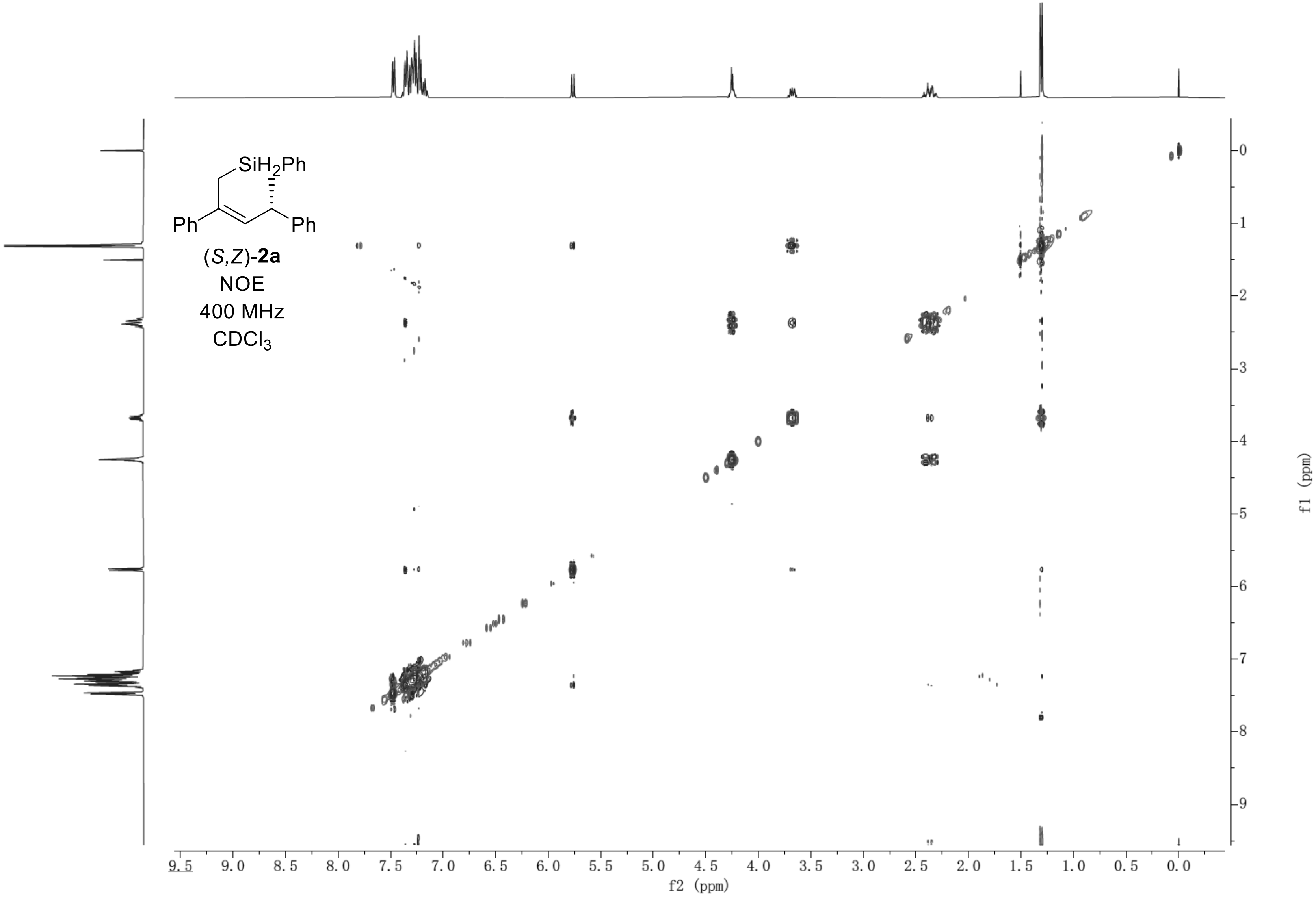


Figure S144. NOE spectra of (*S*,*Z*)-**2a**, Related to Scheme 2

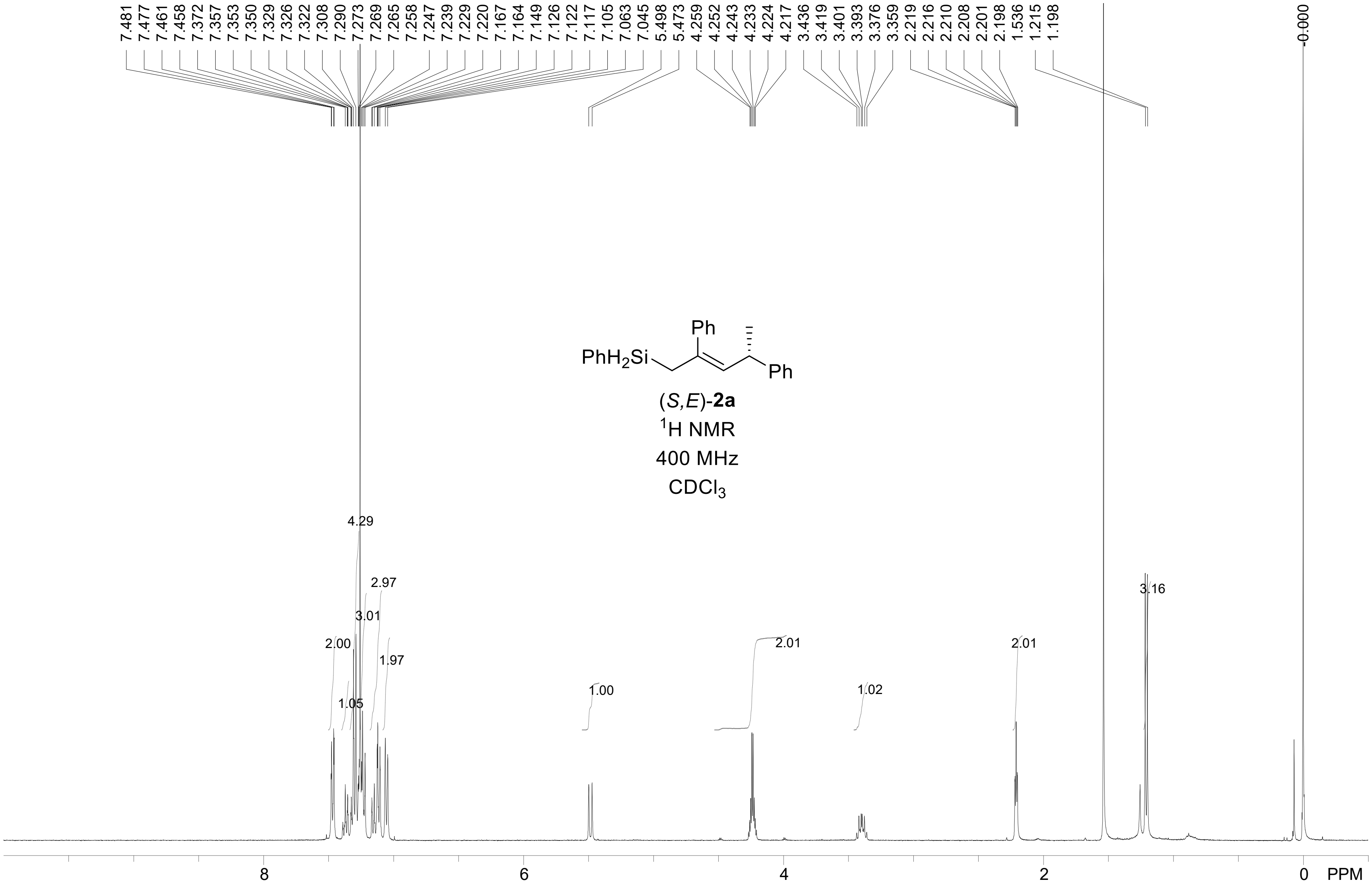


Figure S145. ^{1}H NMR spectra of (*S,E*)-**2a**, Related to Scheme 2

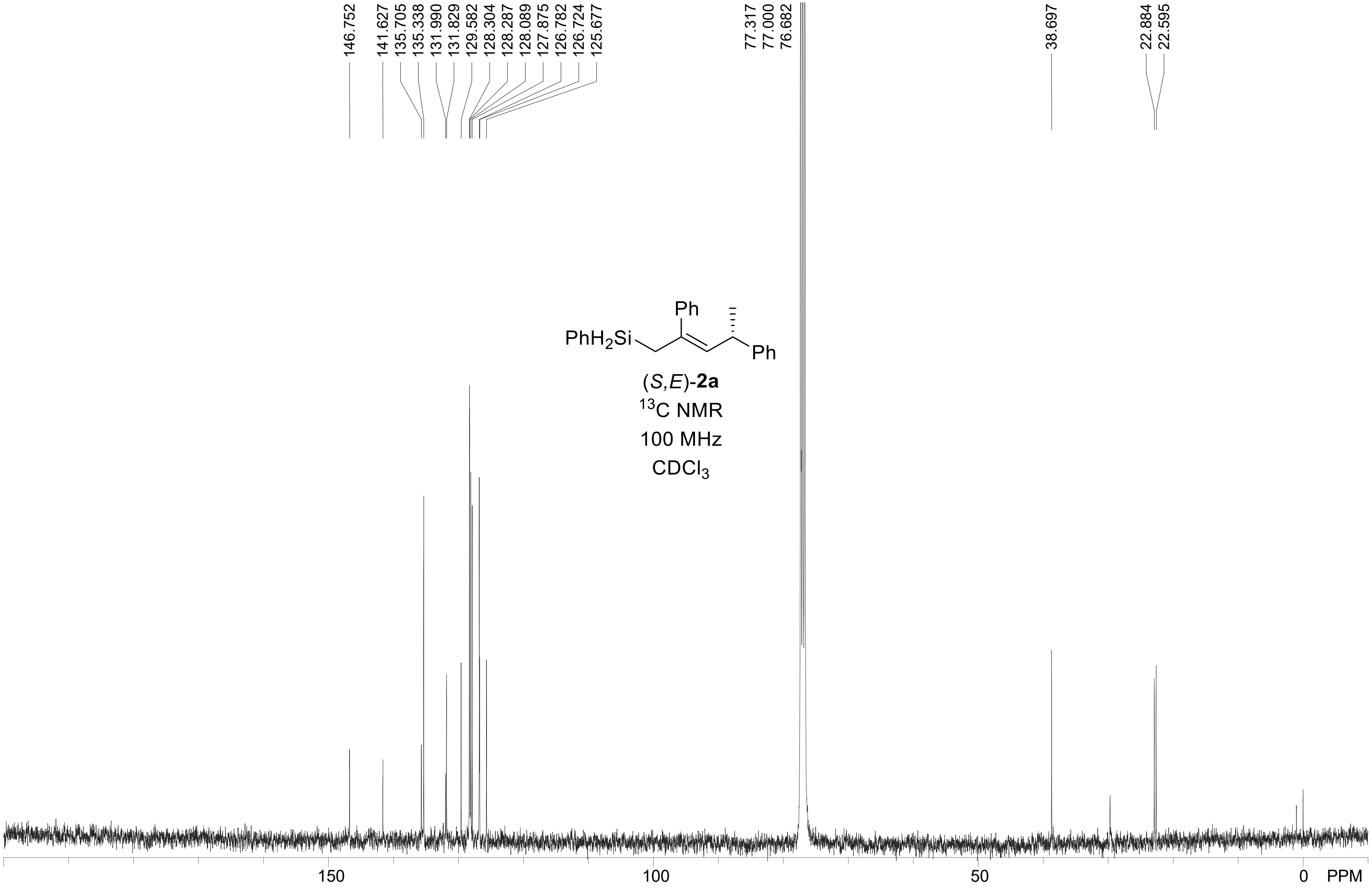


Figure S146. ^{13}C NMR spectra of (*S,E*)-**2a**, Related to Scheme 2

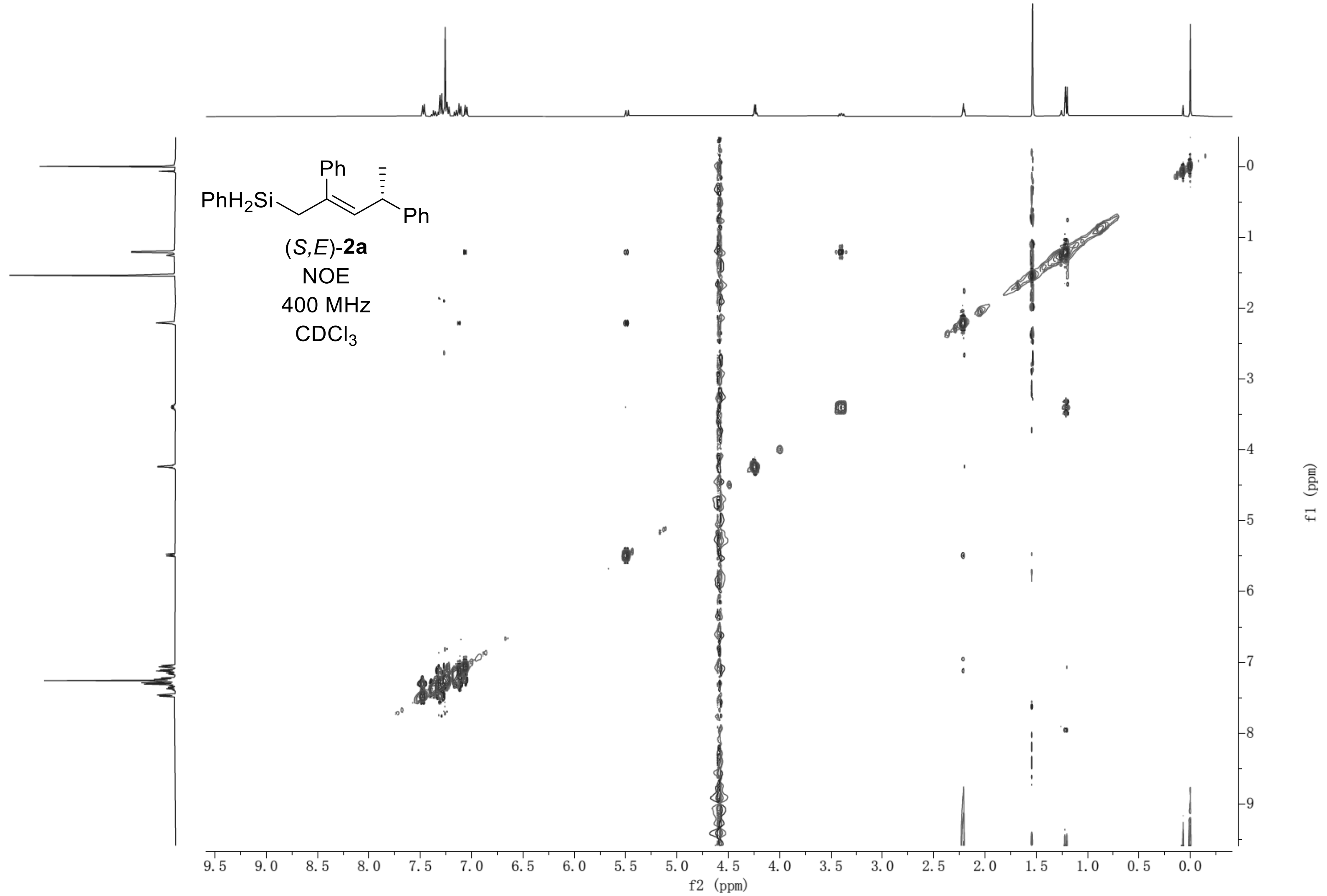


Figure S147. NOE spectra of (*S,E*)-**2a**, Related to Scheme 2

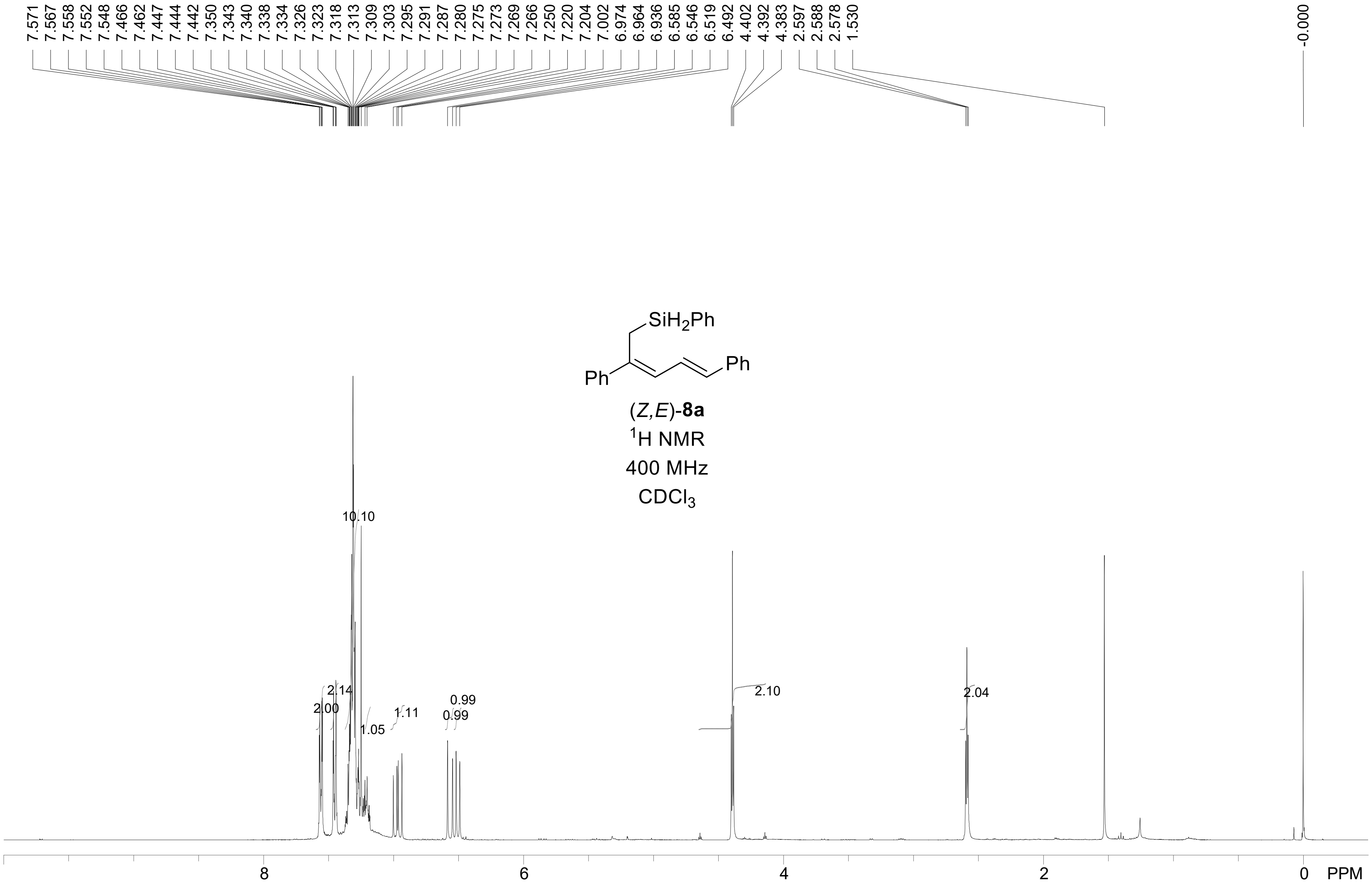


Figure S148. ^{1}H NMR spectra of (*Z,E*)-**8a**, Related to Scheme 2

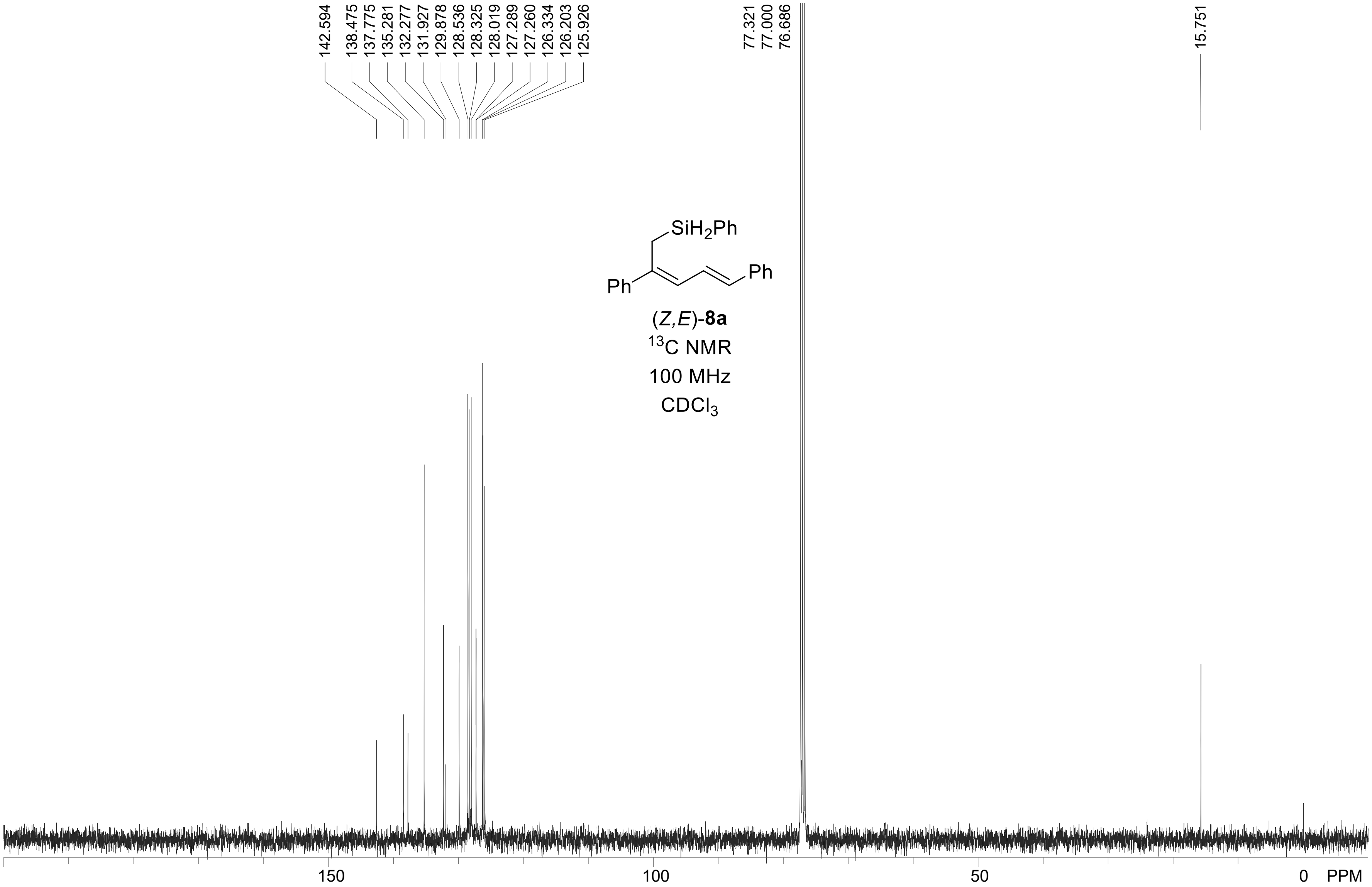


Figure S149. ^{13}C NMR spectra of (*Z,E*)-**8a**, Related to Scheme 2

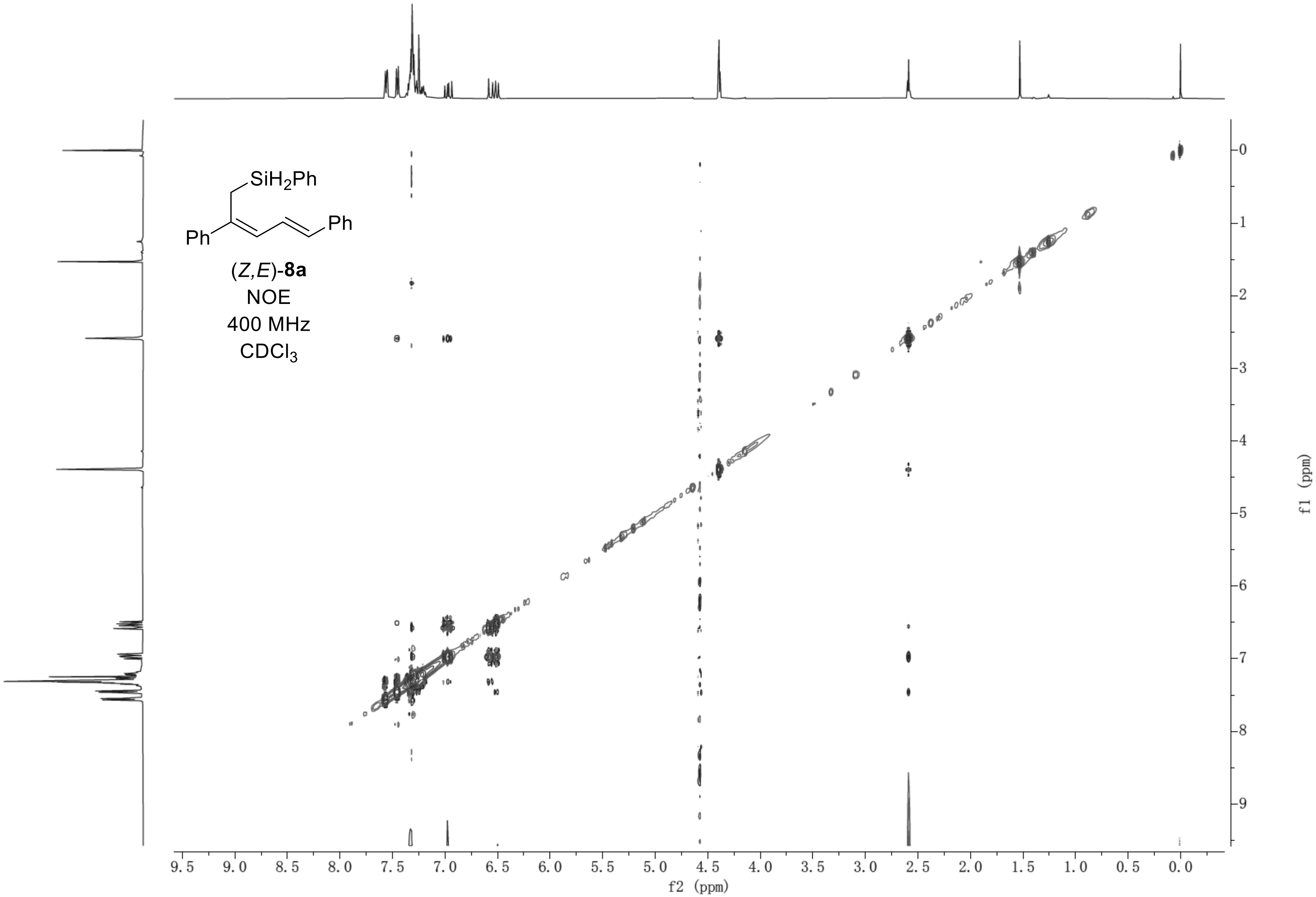
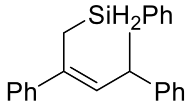


Figure S150. NOE spectra of (*Z,E*)-**8a**, Related to Scheme 2

Translation of Chinese characters in HPLC spectra to English

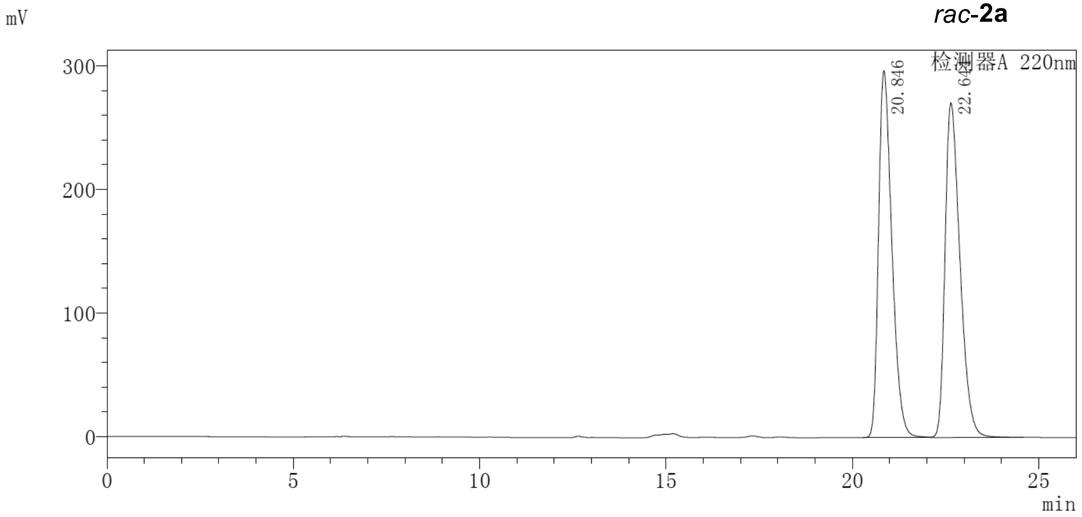
Chinese characters	English
分析日期	Date of Analysis
处理日期	Date of Processing
描述	HPLC Condition
色谱图	HPLC Spectra
检测器	Detector
峰表	Area Percent Report
峰号	Peak
保留时间	Remiaining Time
面积	Area
高度	Height
标记	Note
总计	Total

分析日期　　: 2019/12/27 16:10:14
处理日期　　: 2019/12/27 16:56:01
描述　　　　: 2*OD-H, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



rac-**2a**

色谱图

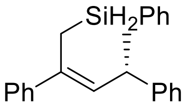


峰表

检测器A 220nm

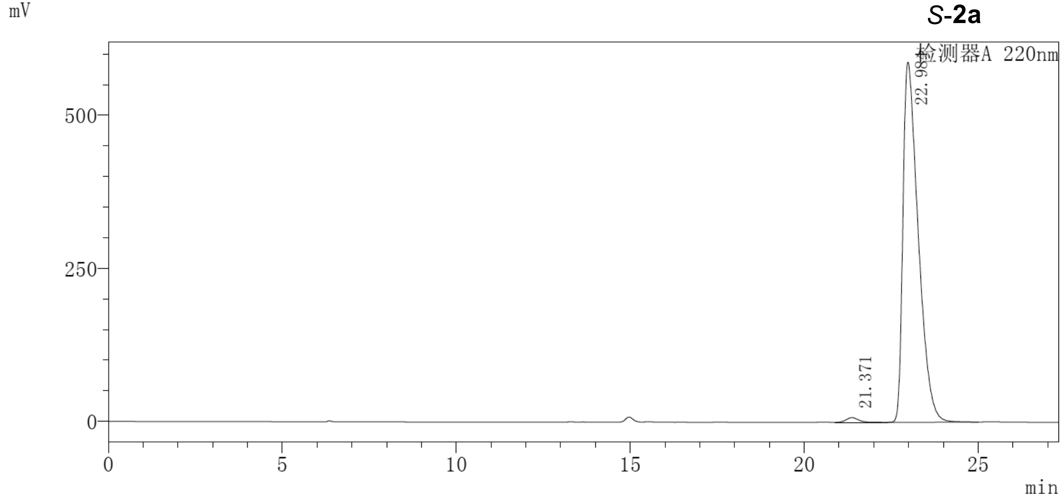
峰号	保留时间	面积	高度	标记	面积%
1	20.846	7380067	296711		49.433
2	22.644	7549362	270816	V	50.567
总计		14929429	567527		100.000

分析日期　　: 2019/12/27 9:43:28
处理日期　　: 2019/12/27 10:10:49
描述　　　　: 2*OD-H, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



S-**2a**

色谱图



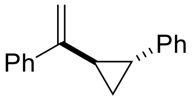
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	21.371	182899	7594		1.009
2	22.984	17952304	587732		98.991
总计		18135203	595327		100.000

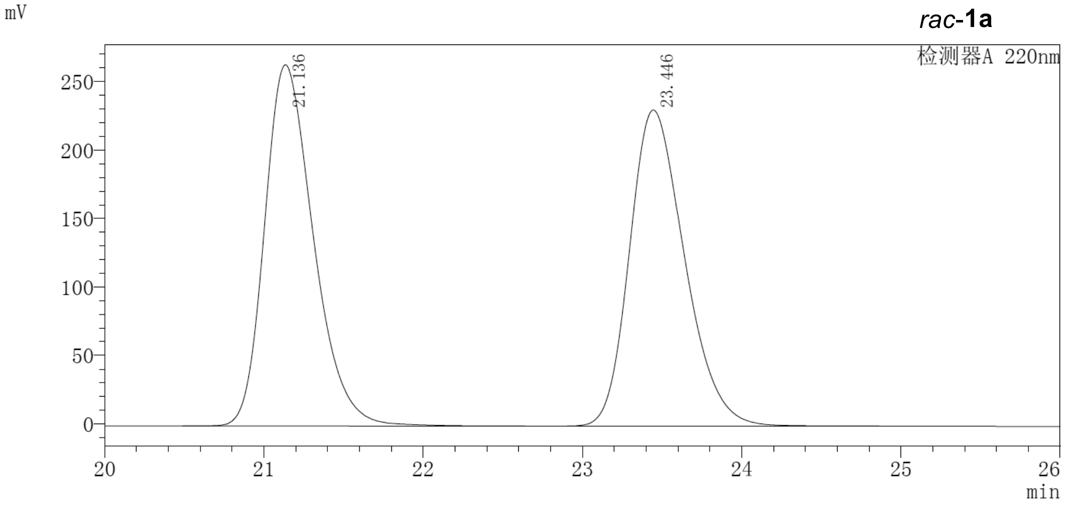
Figure S151. HPLC spectra of *S*-**2a**, Related to Table 1

分析日期　　　: 2019/7/30 10:03:21
处理日期　　　: 2019/7/30 10:30:57
描述　　　　　: OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



rac-**1a**

色谱图

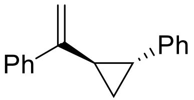


峰表

检测器A 220nm

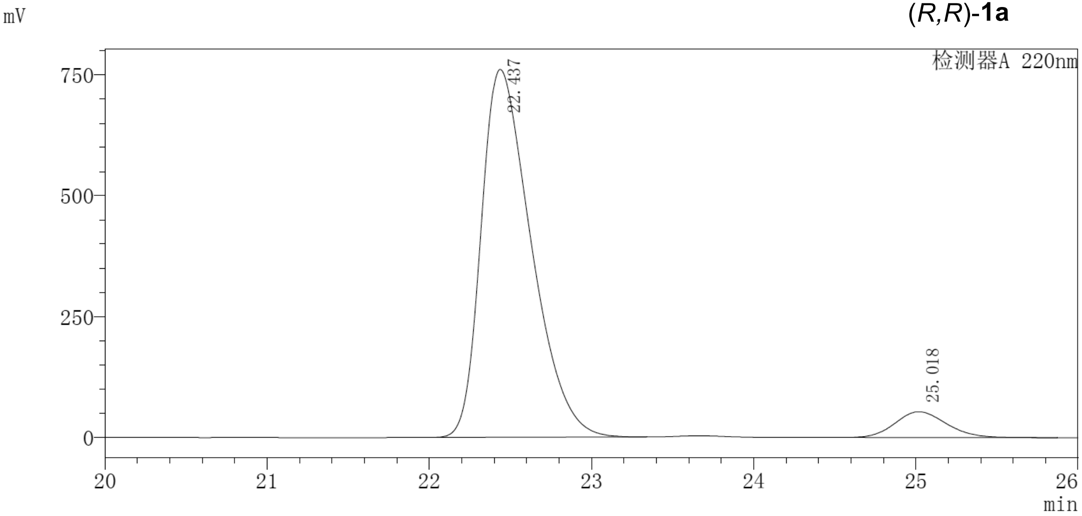
峰号	保留时间	面积	高度	标记	面积%
1	21.136	5614292	263846		50.337
2	23.446	5539092	230827	M	49.663
总计		11153384	494673		100.000

分析日期　　　: 2019/7/30 19:30:05
处理日期　　　: 2019/7/30 19:57:52
描述　　　　　: OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



(*R*,*R*)-**1a**

色谱图



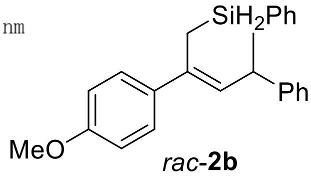
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	22.437	16284755	761727		93.224
2	25.018	1183569	53588	M	6.776
总计		17468324	815314		100.000

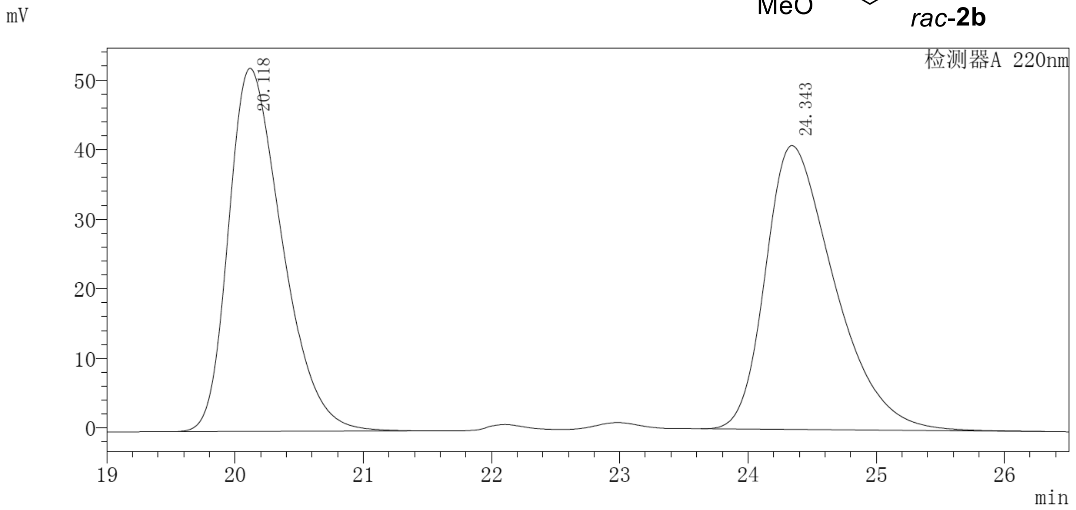
Figure S152. HPLC spectra of (*R*,*R*)-**1a**, Related to Table 1

分析日期　　　: 2018/7/16 23:16:26
处理日期　　　: 2018/7/16 23:42:58
描述　　　　　: OD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



rac-**2b**

色谱图

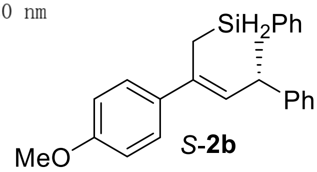


峰表

检测器A 220nm

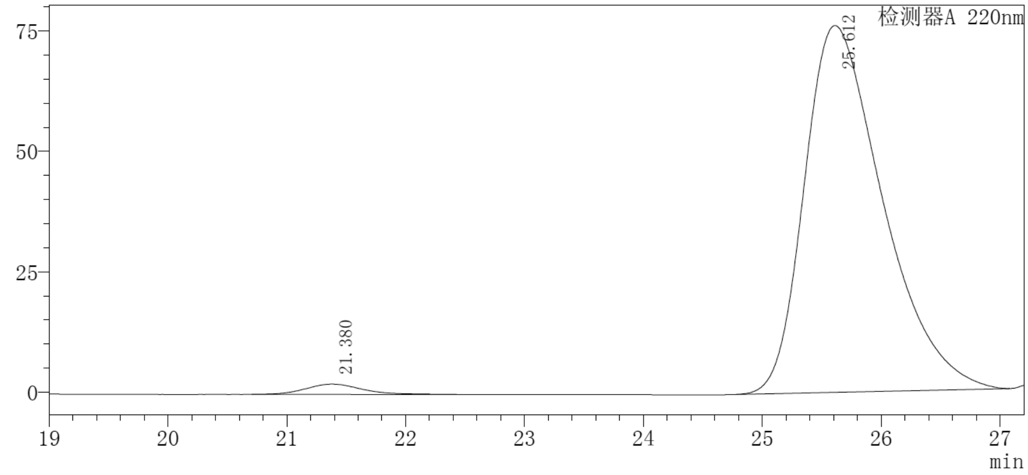
峰号	保留时间	面积	高度	标记	面积%
1	20.118	1516316	52204		49.812
2	24.343	1527790	40808		50.188
总计		3044106	93012		100.000

分析日期　　　: 2018/7/16 22:43:37
处理日期　　　: 2018/7/16 23:13:06
描述　　　　　: OD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



S-**2b**

色谱图



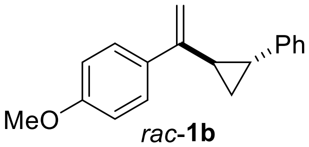
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	21.380	71044	2141		1.991
2	25.612	3497925	76183		98.009
总计		3568968	78324		100.000

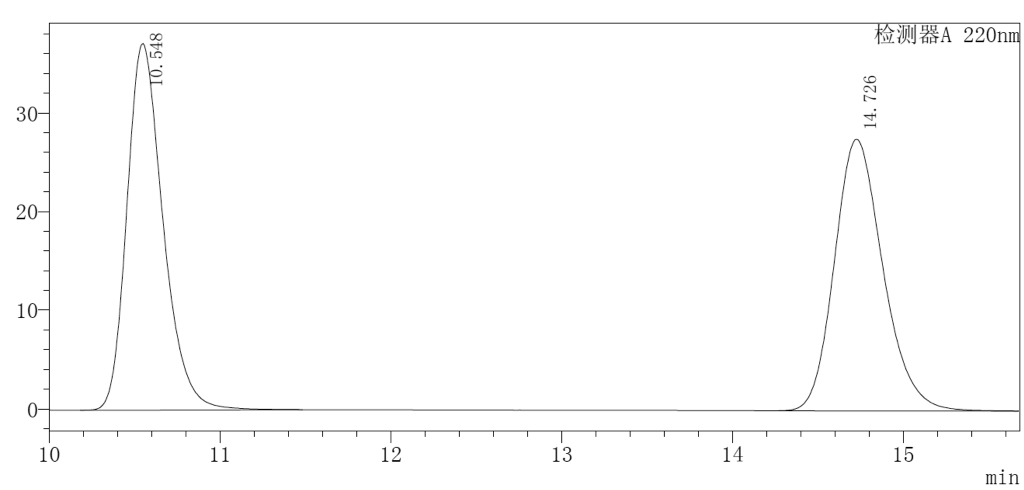
Figure S153. HPLC spectra of *S*-**2b**, Related to Table 2

分析日期　　　: 2018/7/16 20:25:00
处理日期　　　: 2018/7/16 20:40:42
描述　　　　　: OJ-H , n-hexane/iPrOH = 95/5, 1.0 mL/min, 220 nm



rac-**1b**

色谱图

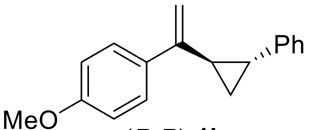


峰表

检测器A 220nm

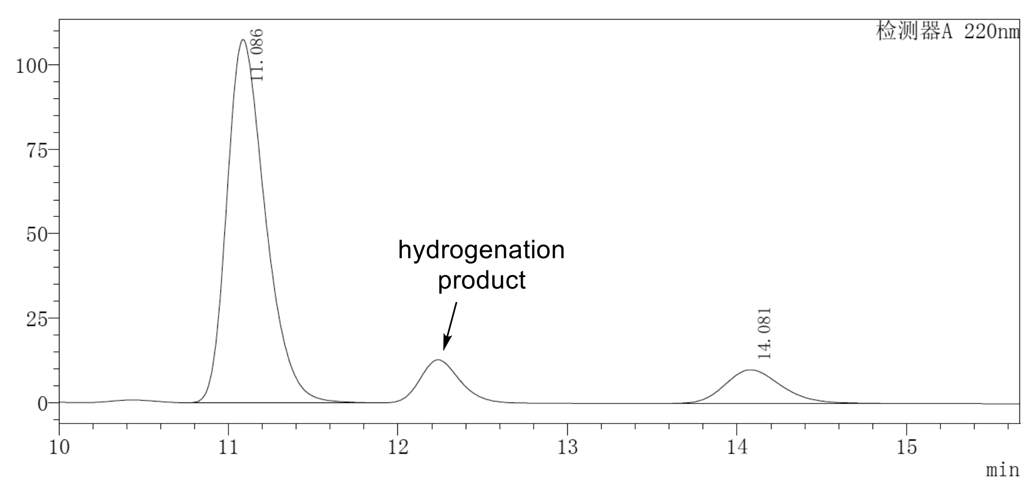
峰号	保留时间	面积	高度	标记	面积%
1	10.548	545884	37152		50.078
2	14.726	544185	27533		49.922
总计		1090069	64685		100.000

分析日期　　　: 2018/7/16 20:42:54
处理日期　　　: 2018/7/16 20:59:29
描述　　　　　: OJ-H , n-hexane/iPrOH = 95/5, 1.0 mL/min, 220 nm



(*R*,*R*)-**1b**

色谱图



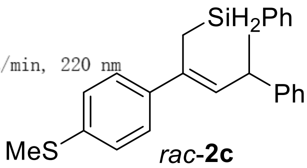
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	11.086	1699408	107575		87.952
2	14.081	232802	9979		12.048
总计		1932210	117553		100.000

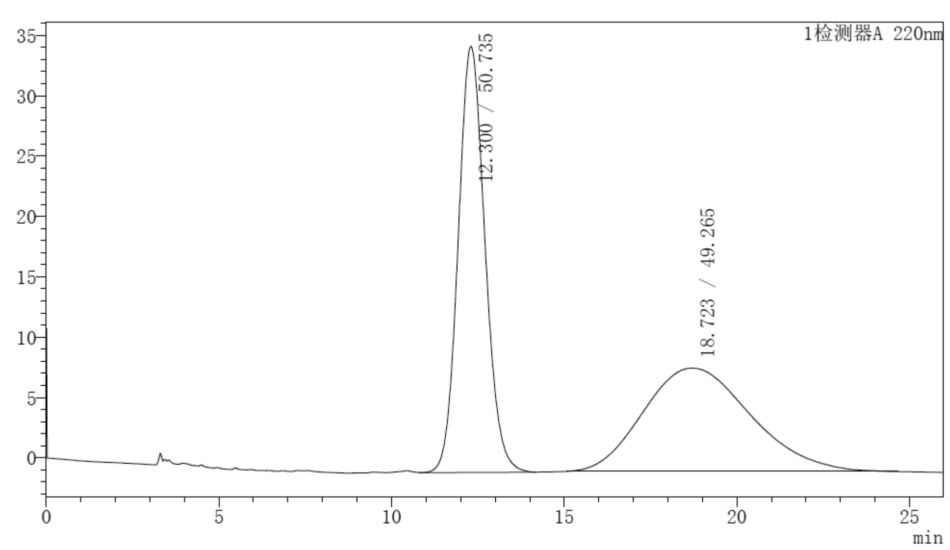
Figure S154. HPLC spectra of (*R*,*R*)-**1b**, Related to Table 2

分析日期/时间 : 2018/8/4 14:52:04
处理日期/时间 : 2018/8/4 15:18:04
描述 : OJ-H , n-hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm



rac-**2c**

色谱图

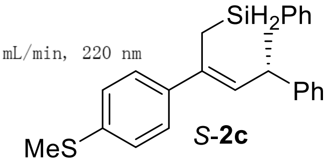


峰表

检测器A 220nm

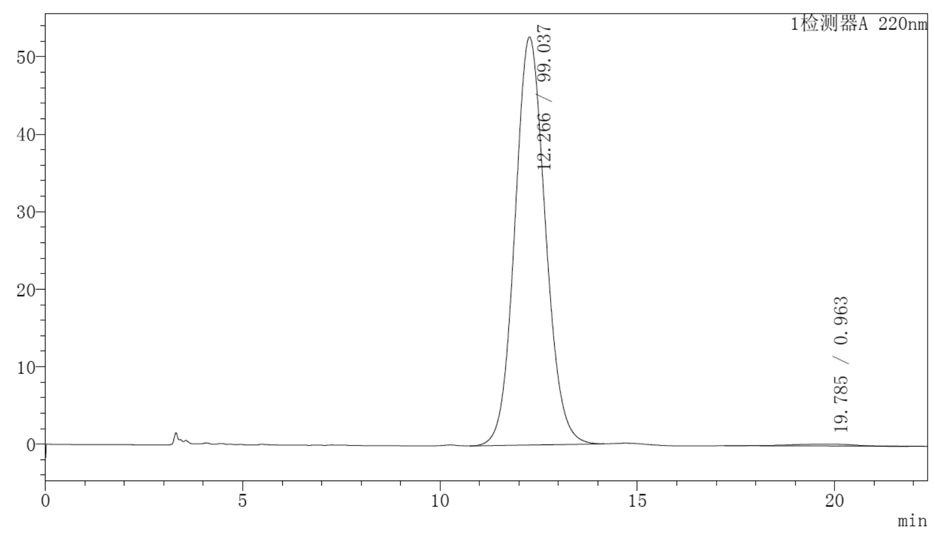
峰号	保留时间	面积	高度	标记	面积%
1	12.300	1904518	35284		50.735
2	18.723	1849325	8560	M	49.265
总计		3753844	43844		100.000

分析日期/时间 : 2018/8/4 15:27:15
处理日期/时间 : 2018/8/4 15:58:46
描述 : OJ-H , n-hexane/iPrOH = 90/10, 1.0 mL/min, 220 nm



S-**2c**

色谱图



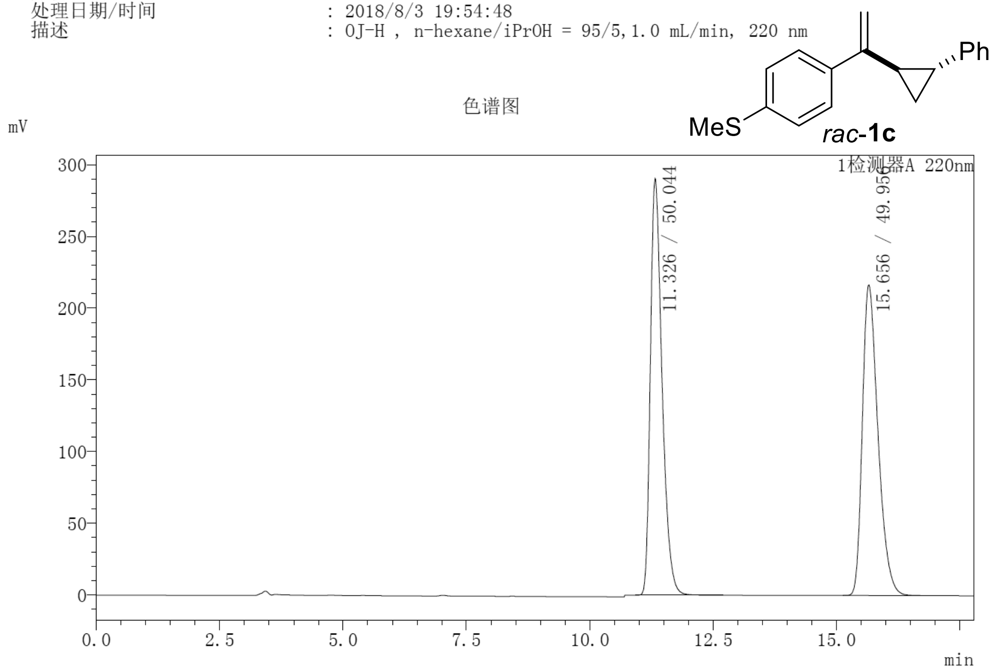
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	12.266	2830764	52654		99.037
2	19.785	27516	261	M	0.963
总计		2858280	52915		100.000

Figure S155. HPLC spectra of *S*-**2c**, Related to Table 2

分析日期/时间　　　　: 2018/8/3 19:37:00
处理日期/时间　　　　: 2018/8/3 19:54:48
描述　　　　　　　　: OJ-H , n-hexane/iPrOH = 95/5, 1.0 mL/min, 220 nm

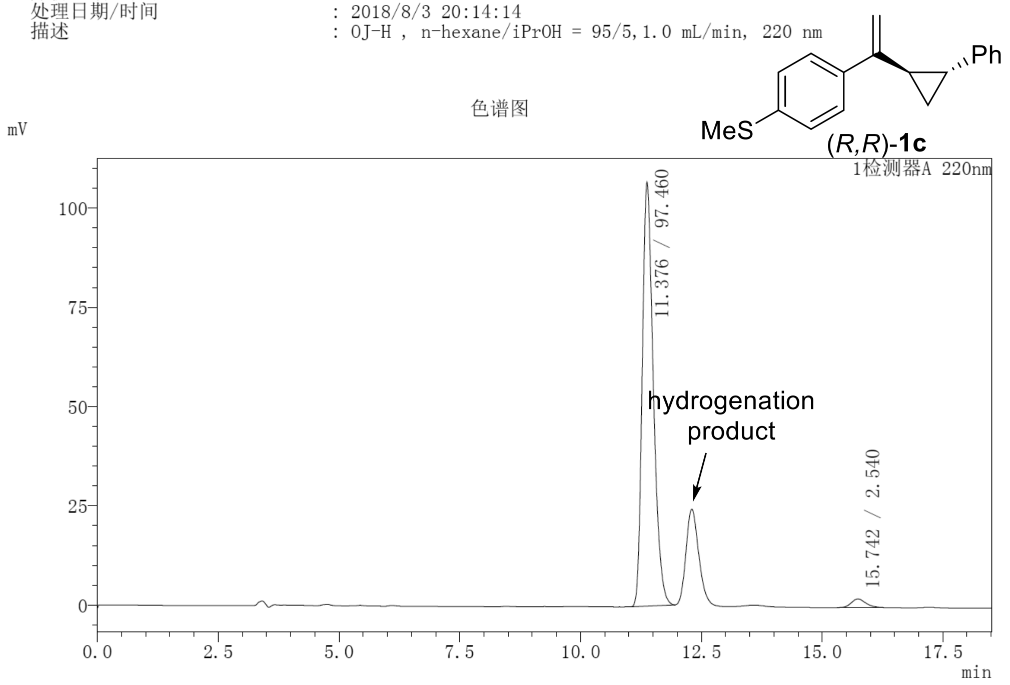


峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	11.326	4774968	290409		50.044
2	15.656	4766556	216535	M	49.956
总计		9541524	506944		100.000

分析日期/时间　　　　: 2018/8/3 19:55:41
处理日期/时间　　　　: 2018/8/3 20:14:14
描述　　　　　　　　: OJ-H , n-hexane/iPrOH = 95/5, 1.0 mL/min, 220 nm



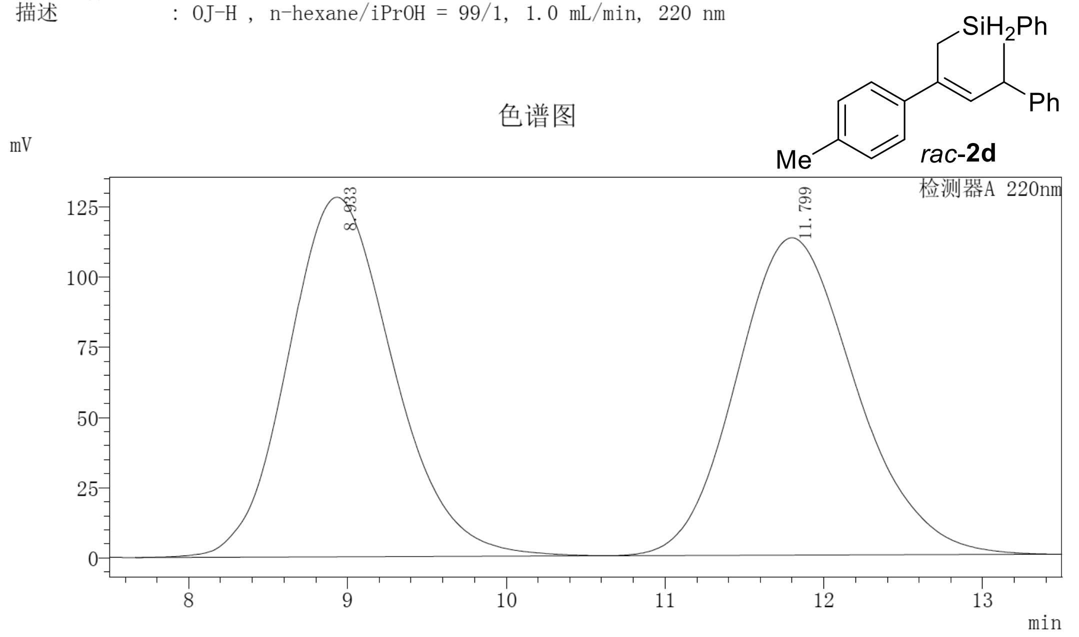
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	11.376	1704661	106833		97.460
2	15.742	44423	2145	M	2.540
总计		1749084	108978		100.000

Figure S156. HPLC spectra of (*R,R*)-**1c**, Related to Table 2

分析日期　　: 2018/7/6 15:36:12
处理日期　　: 2018/7/6 15:51:28
描述　　　　: OJ-H , n-hexane/iPrOH = 99/1, 1.0 mL/min, 220 nm

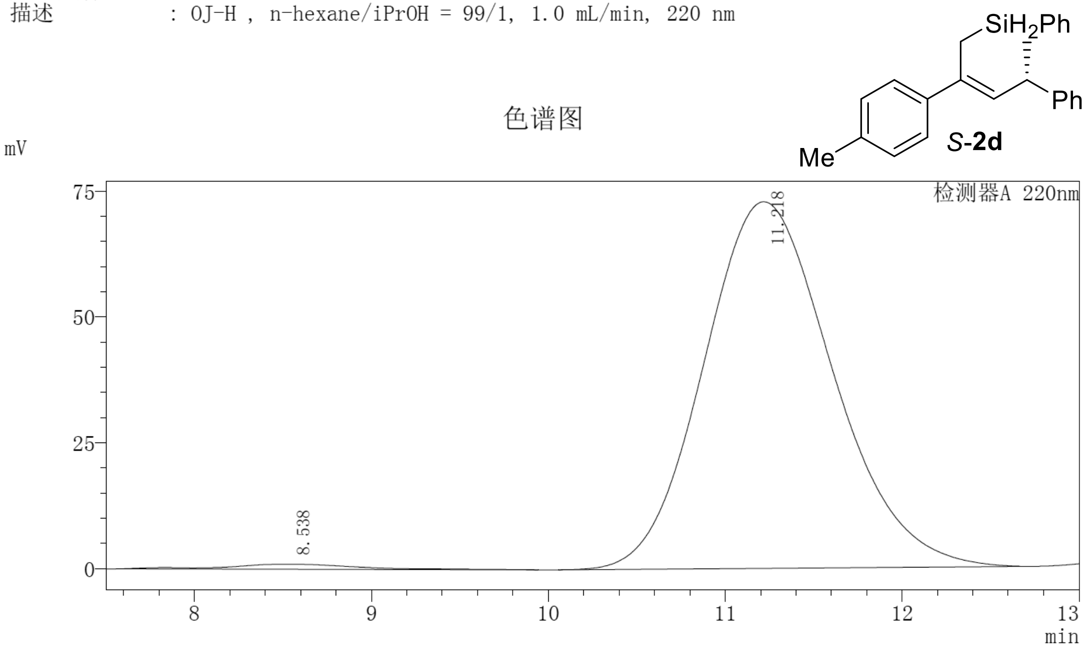


峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.933	5911574	128048		49.993
2	11.799	5913124	113020	V	50.007
总计		11824698	241068		100.000

分析日期　　: 2018/7/6 15:53:02
处理日期　　: 2018/7/6 16:07:38
描述　　　　: OJ-H , n-hexane/iPrOH = 99/1, 1.0 mL/min, 220 nm



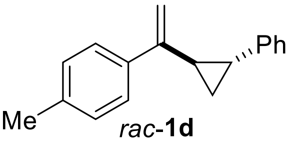
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.538	52994	1022	M	1.418
2	11.218	3685230	72828		98.582
总计		3738224	73851		100.000

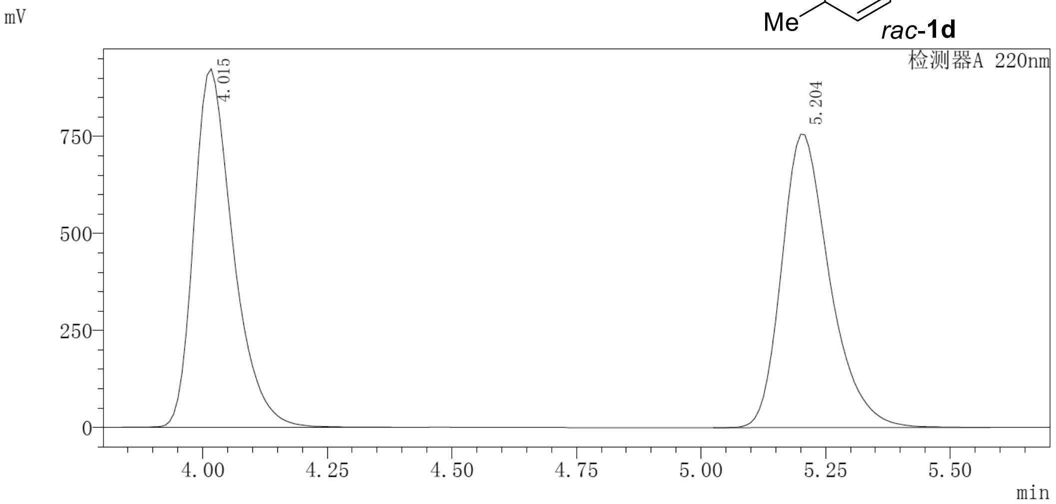
Figure S157. HPLC spectra of *S*-**2d**, Related to Table 2

分析日期　　　: 2018/7/8 18:38:46
处理日期　　　: 2018/7/8 18:45:16
描述　　　　　: AD-H , n-hexane/iPrOH = 98/2, 1.0 mL/min, 220 nm



rac-**1d**

色谱图

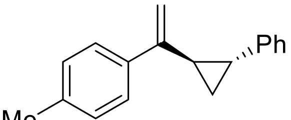


峰表

检测器A 220nm

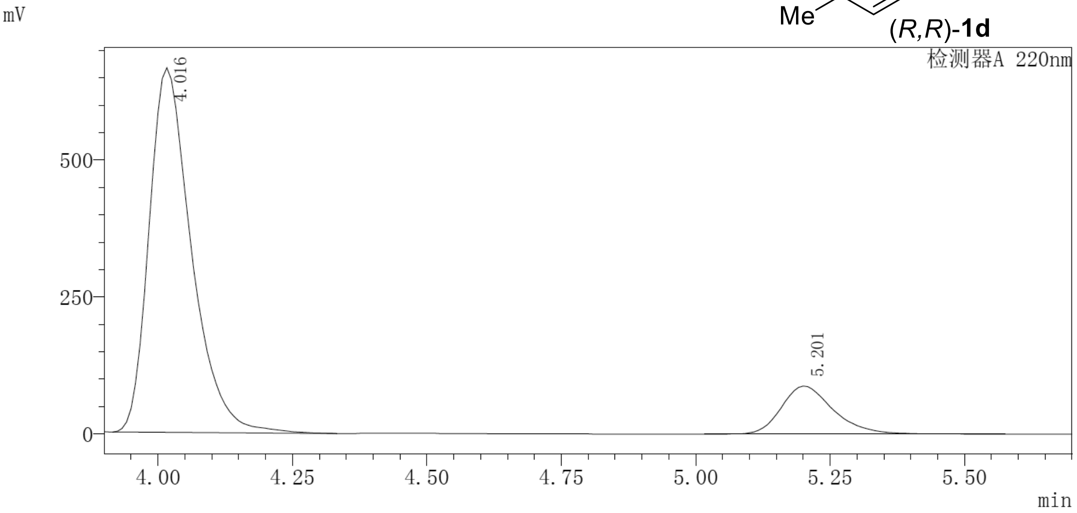
峰号	保留时间	面积	高度	标记	面积%
1	4.015	5066532	923668		49.938
2	5.204	5079194	755669	M	50.062
总计		10145726	1679337		100.000

分析日期　　　: 2018/7/8 18:46:40
处理日期　　　: 2018/7/8 18:52:38
描述　　　　　: AD-H , n-hexane/iPrOH = 98/2, 1.0 mL/min, 220 nm



(*R*,*R*)-**1d**

色谱图



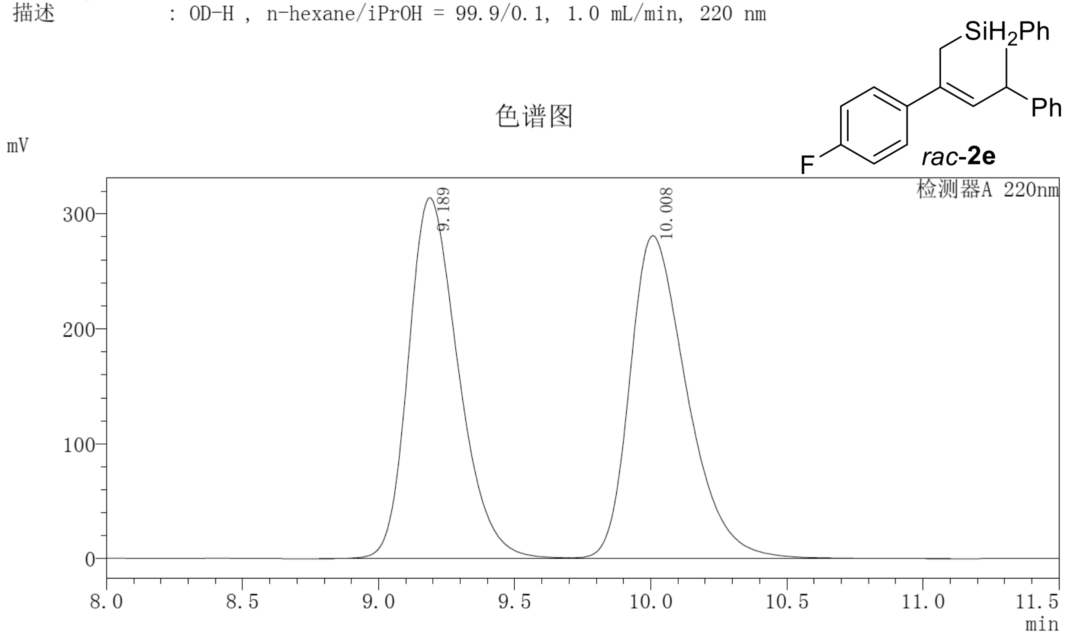
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	4.016	3642186	665414		86.113
2	5.201	587356	87707	M	13.887
总计		4229542	753122		100.000

Figure S158. HPLC spectra of (*R*,*R*)-**1d**, Related to Table 2

分析日期　　: 2018/7/7 16:21:34
处理日期　　: 2018/7/7 16:33:32
描述　　　　: OD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm

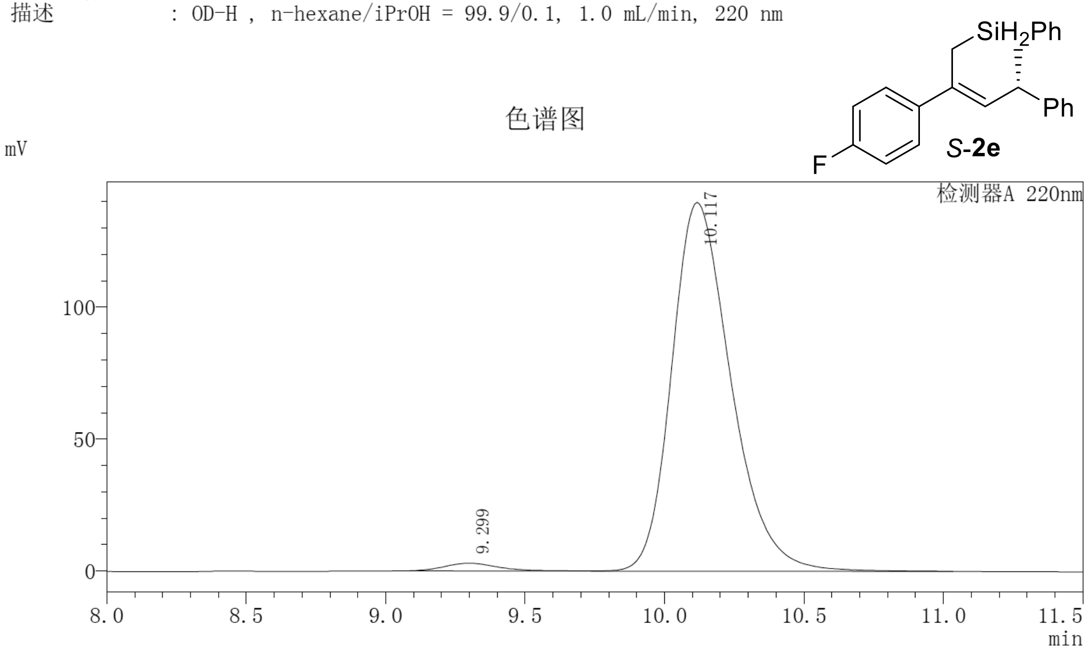


峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.189	4012972	313938		49.430
2	10.008	4105575	281080	V	50.570
总计		8118546	595017		100.000

分析日期　　: 2018/7/7 16:36:25
处理日期　　: 2018/7/7 16:48:47
描述　　　　: OD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



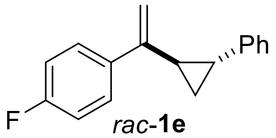
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.299	40602	2945	M	1.928
2	10.117	2065469	139800	V M	98.072
总计		2106071	142744		100.000

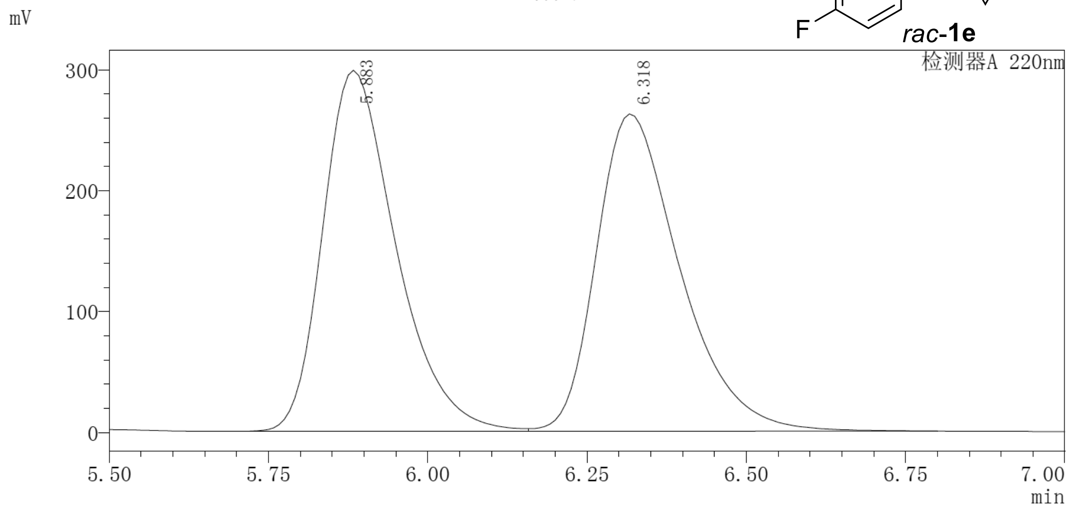
Figure S159. HPLC spectra of *S*-**2e**, Related to Table 2

分析日期　: 2018/7/9 9:40:16
处理日期　: 2018/7/9 9:47:28
描述　: AD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



rac-**1e**

色谱图

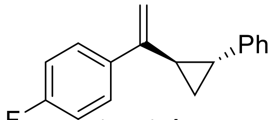


峰表

检测器A 220nm

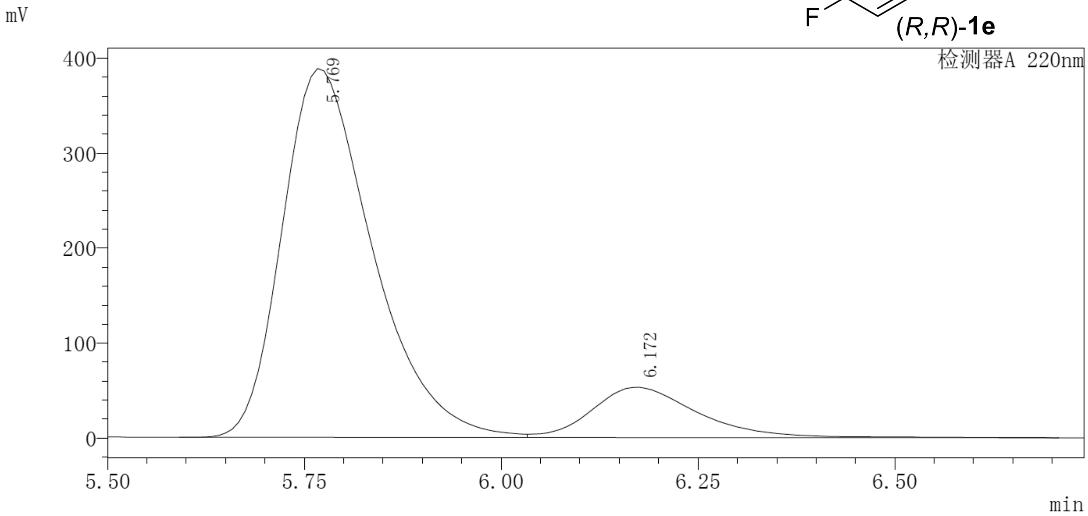
峰号	保留时间	面积	高度	标记	面积%
1	5.883	2388939	298714		49.913
2	6.318	2397223	262607	V M	50.087
总计		4786162	561322		100.000

分析日期　: 2018/7/9 9:58:18
处理日期　: 2018/7/9 10:05:05
描述　: AD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



(*R*,*R*)-**1e**

色谱图



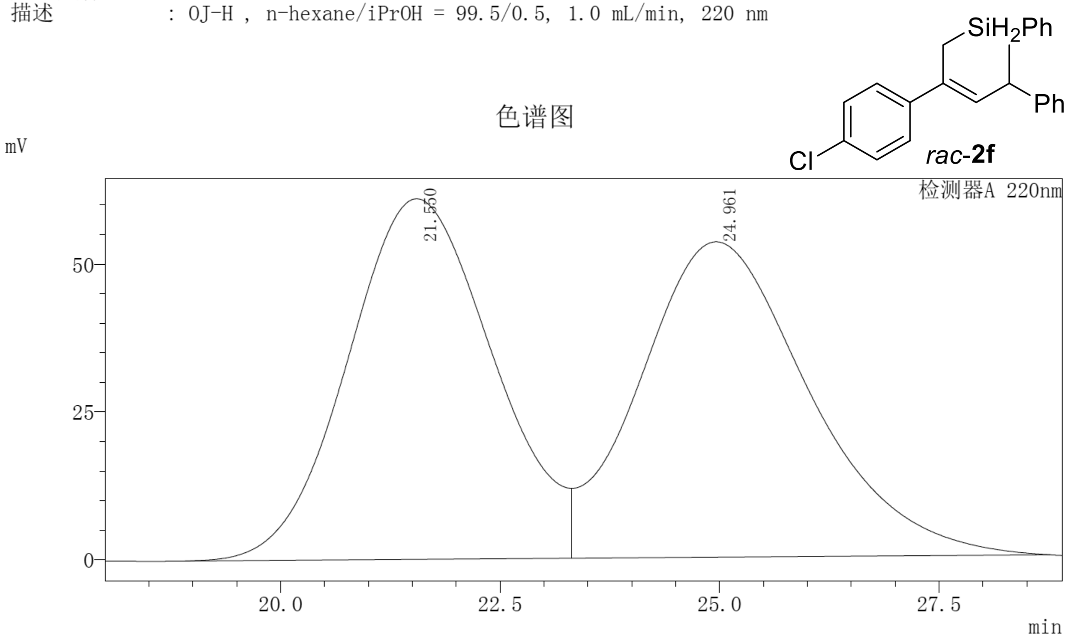
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	5.769	3096343	388191		86.238
2	6.172	494135	52899	V	13.762
总计		3590478	441090		100.000

Figure S160. HPLC spectra of (*R,R*)-**1e**, Related to Table 2

分析日期　　: 2018/7/21 19:58:07
处理日期　　: 2018/7/21 20:27:08
描述　　　　: OJ-H , n-hexane/iPrOH = 99.5/0.5, 1.0 mL/min, 220 nm

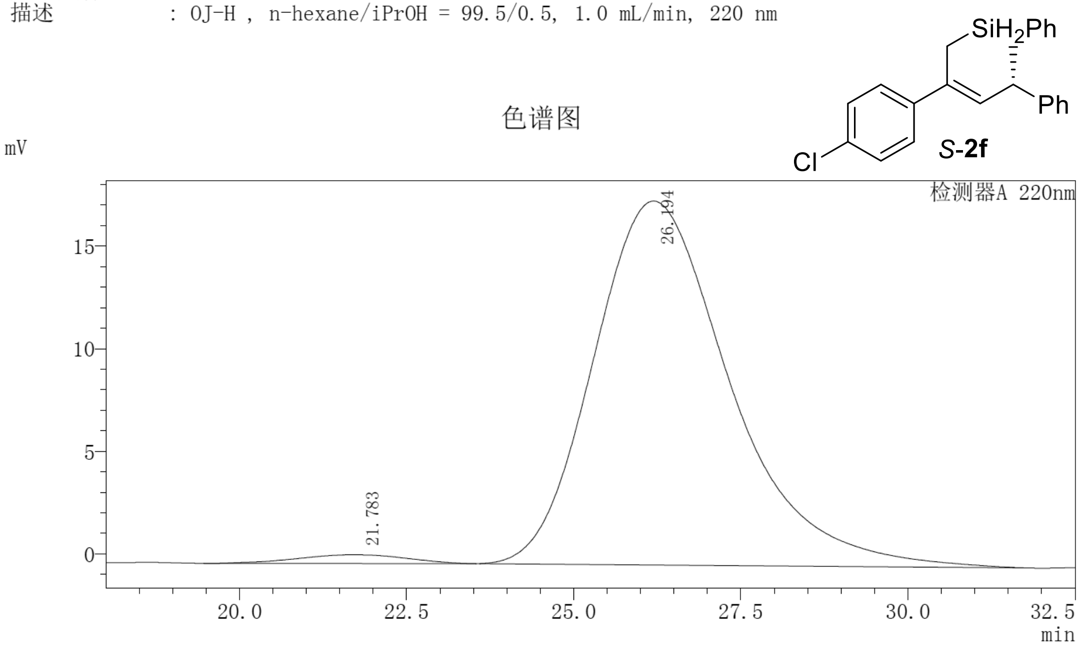


峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	21.550	7024363	61064		49.537
2	24.961	7155664	53412	V M	50.463
总计		14180026	114476		100.000

分析日期　　: 2018/7/17 9:12:58
处理日期　　: 2018/7/17 9:46:15
描述　　　　: OJ-H , n-hexane/iPrOH = 99.5/0.5, 1.0 mL/min, 220 nm



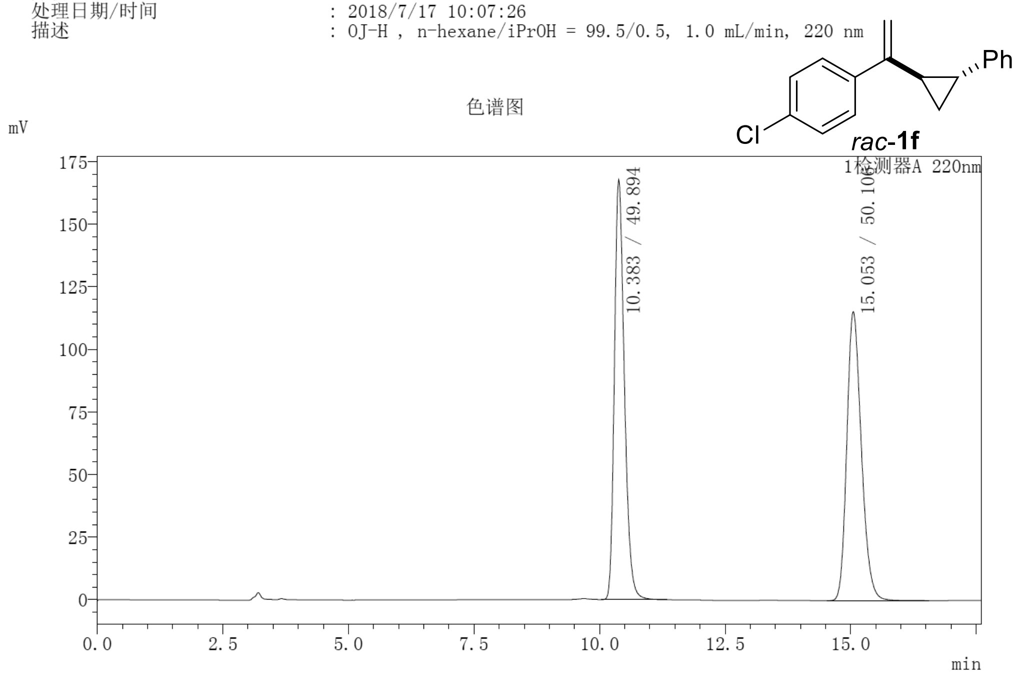
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	21.783	48164	428	M	1.877
2	26.194	2517759	17745		98.123
总计		2565923	18173		100.000

Figure S161. HPLC spectra of *S*-**2f**, Related to Table 2

分析日期/时间　　: 2018/7/17 9:49:49
处理日期/时间　　: 2018/7/17 10:07:26
描述　　　　　　: OJ-H , n-hexane/iPrOH = 99.5/0.5, 1.0 mL/min, 220 nm

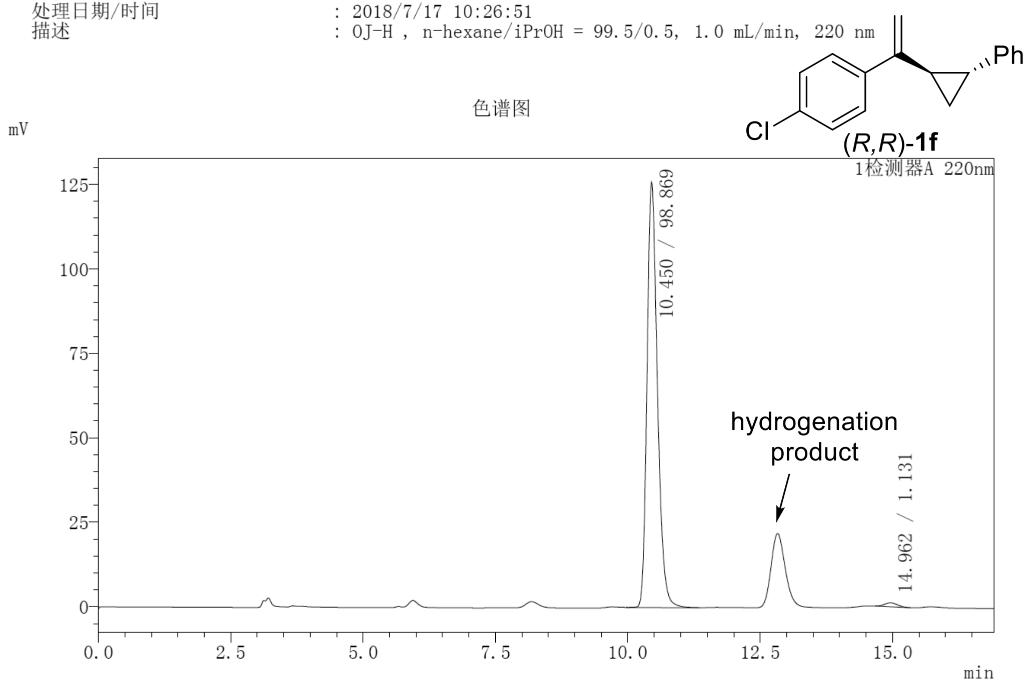


峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	10.383	2317471	167815		49.894
2	15.053	2327346	115470		50.106
总计		4644817	283285		100.000

分析日期/时间　　: 2018/7/17 10:09:54
处理日期/时间　　: 2018/7/17 10:26:51
描述　　　　　　: OJ-H , n-hexane/iPrOH = 99.5/0.5, 1.0 mL/min, 220 nm



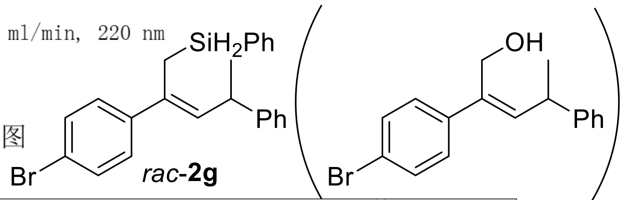
峰表

检测器A 220nm

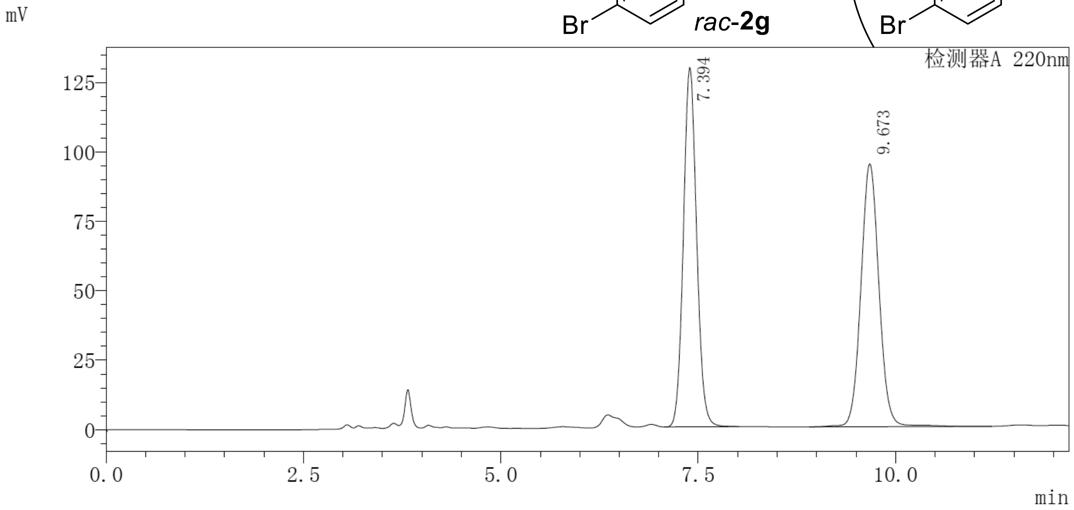
峰号	保留时间	面积	高度	标记	面积%
1	10.450	1723907	125911		98.869
2	14.962	19726	1162		1.131
总计		1743633	127072		100.000

Figure S162. HPLC spectra of (*R,R*)-**1f**, Related to Table 2

分析日期　　　: 2019/1/3 10:05:07
处理日期　　　: 2019/1/3 10:17:20
描述　　　　　: OD-H, n-hexane/iPrOH =90/10, 1.0 ml/min, 220 nm


rac-**2g**

色谱图

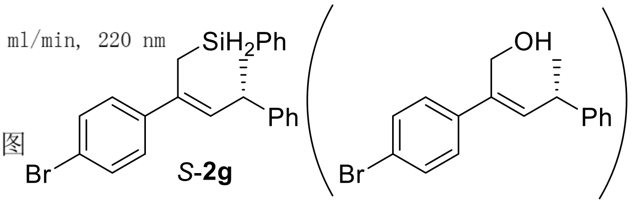


峰表

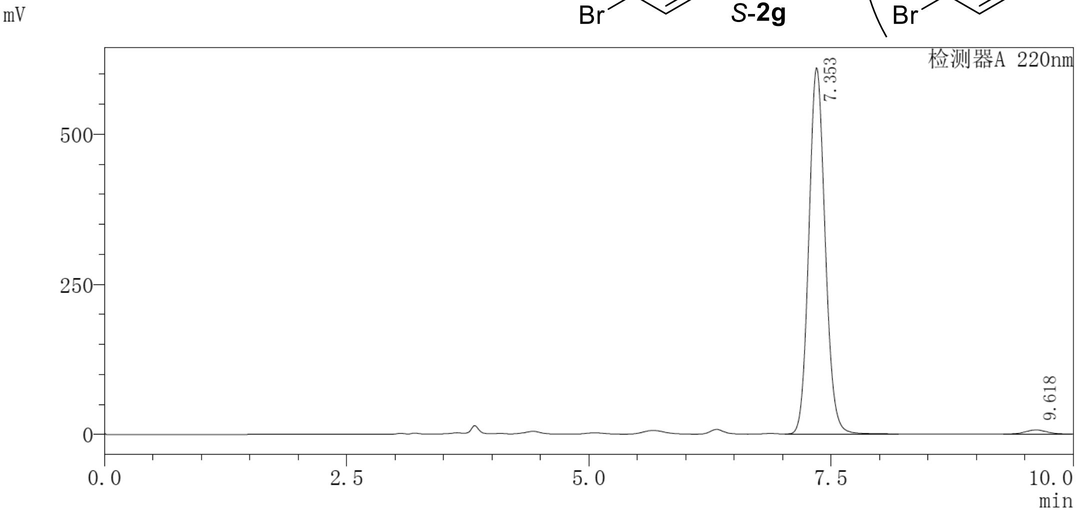
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	7.394	1508959	129377	M	50.059
2	9.673	1505384	94686	S	49.941
总计		3014344	224063		100.000

分析日期　　　: 2019/1/3 10:19:07
处理日期　　　: 2019/1/3 10:31:21
描述　　　　　: OD-H, n-hexane/iPrOH =90/10, 1.0 ml/min, 220 nm


S-**2g**

色谱图



峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	7.353	7148701	609987	M	98.591
2	9.618	102182	6769		1.409
总计		7250884	616756		100.000

Figure S163. HPLC spectra of *S*-**2g**, Related to Table 2

```
分析日期        : 2018/12/26 16:04:22
处理日期        : 2018/12/26 16:20:16
描述            : OJ-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm
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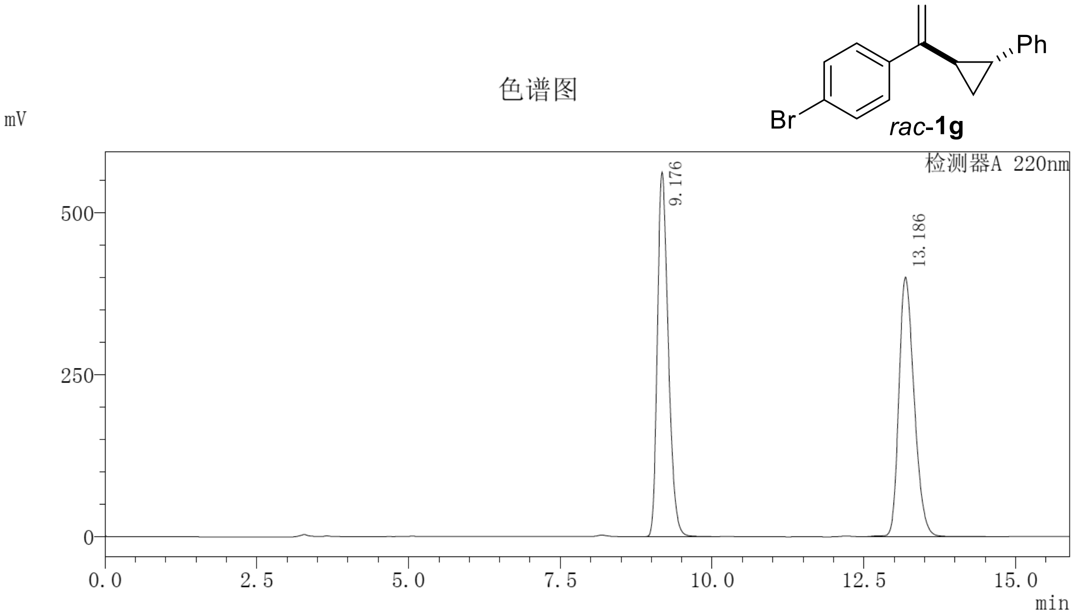

峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.176	7011073	562463		49.986
2	13.186	7015124	400345	S	50.014
总计		14026197	962808		100.000

```
分析日期        : 2018/12/26 16:22:22
处理日期        : 2018/12/26 16:36:58
描述            : OJ-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm
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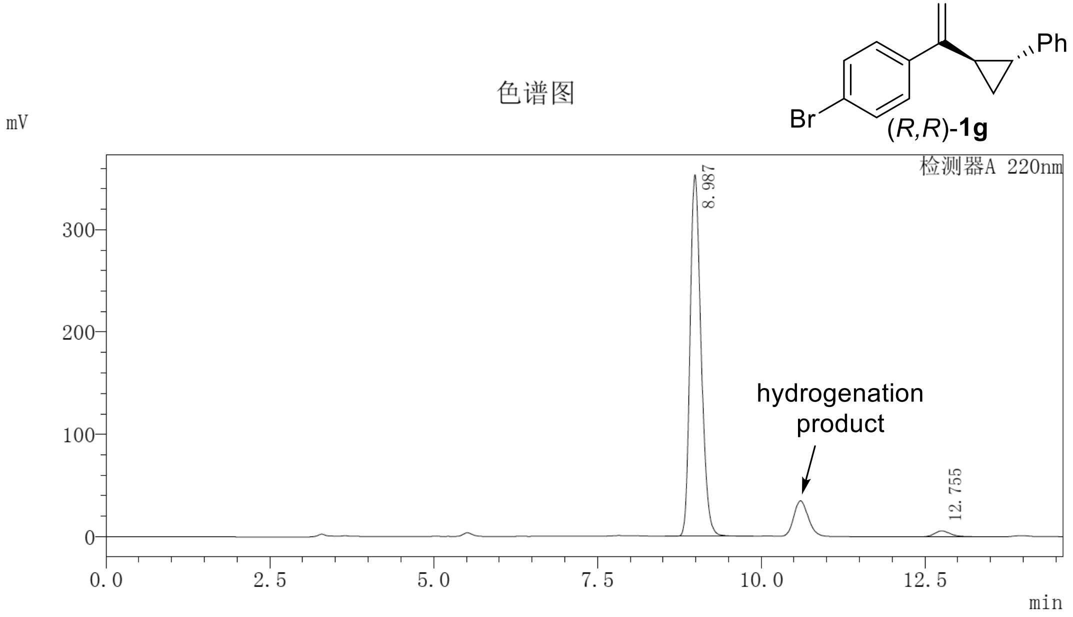


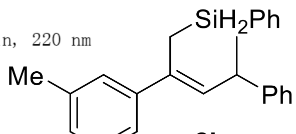
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.987	4135486	353054		97.732
2	12.755	95986	5672	M	2.268
总计		4231473	358726		100.000

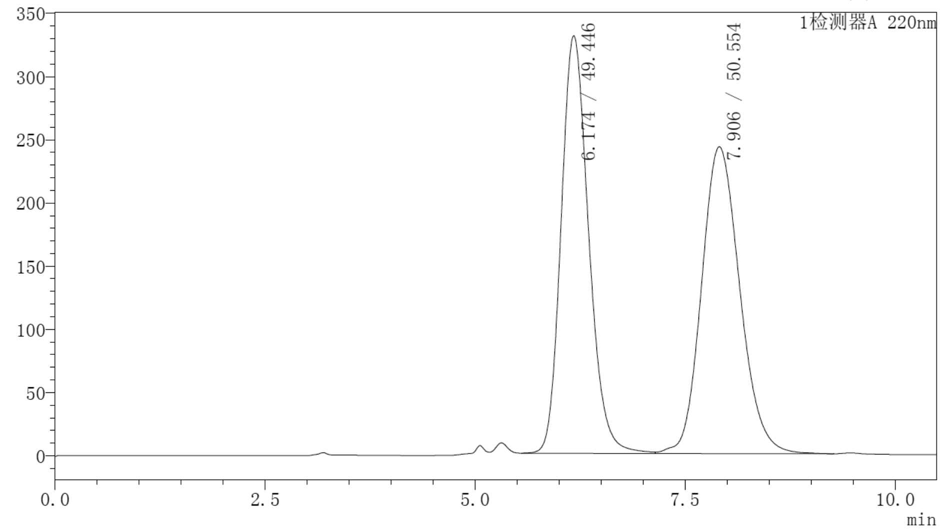
Figure S164. HPLC spectra of (*R*,*R*)-**1g**, Related to Table 2

分析日期/时间　　　　　: 2018/7/6 16:47:13
处理日期/时间　　　　　: 2018/7/6 16:57:43
描述　　　　　　　　　: OJ-H , n-hexane/iPrOH = 99/1, 1.0 mL/min, 220 nm



rac-**2h**

色谱图

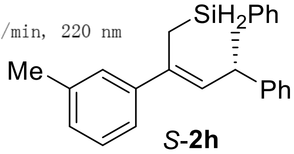


峰表

检测器A 220nm

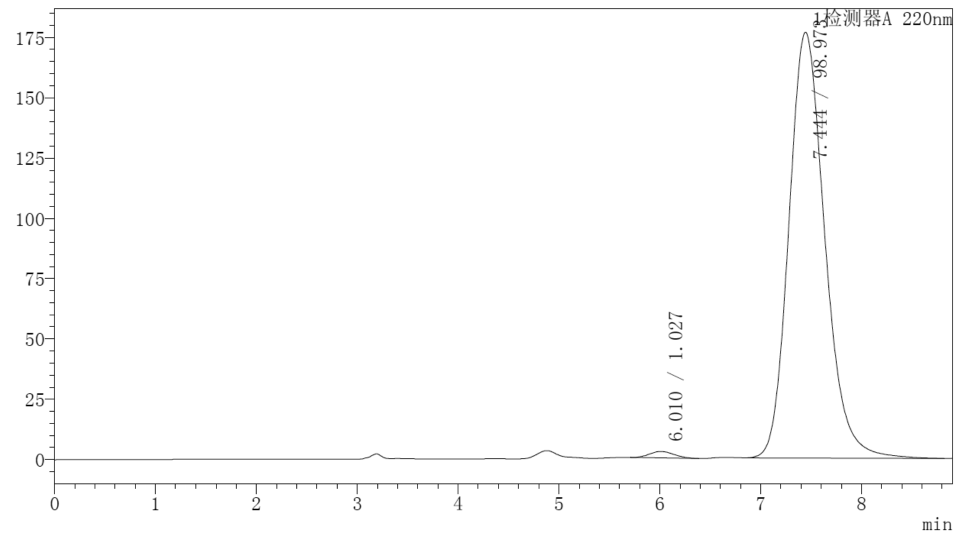
峰号	保留时间	面积	高度	标记	面积%
1	6.174	7533256	330563		49.446
2	7.906	7701939	242865	V	50.554
总计		15235195	573428		100.000

分析日期/时间　　　　　: 2018/7/6 18:33:43
处理日期/时间　　　　　: 2018/7/6 18:47:02
描述　　　　　　　　　: OJ-H , n-hexane/iPrOH = 99/1, 1.0 mL/min, 220 nm



S-**2h**

色谱图



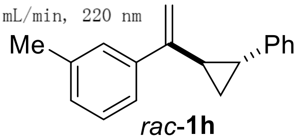
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	6.010	45344	2677		1.027
2	7.444	4369178	176537		98.973
总计		4414522	179214		100.000

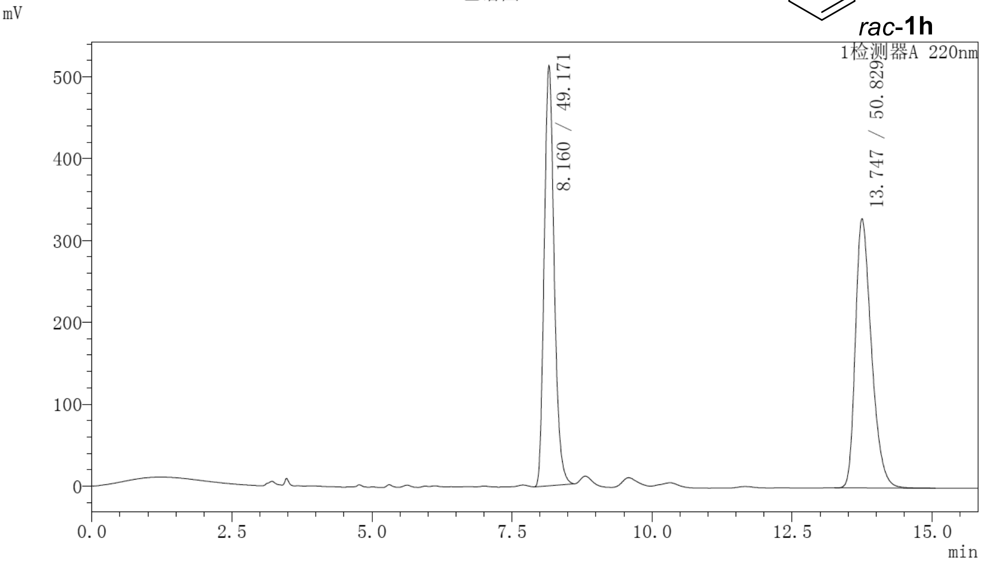
Figure S165. HPLC spectra of *S*-**2h**, Related to Table 2

分析日期/时间　　　　　　　: 2018/7/21 17:48:21
处理日期/时间　　　　　　　: 2018/7/21 18:04:11
描述　　　　　　　　　　　: OJ-H , n-hexane/iPrOH = 99.5/0.5, 1.0 mL/min, 220 nm



rac-**1h**

色谱图

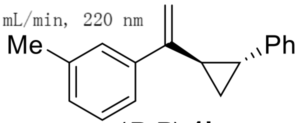


峰表

检测器A 220nm

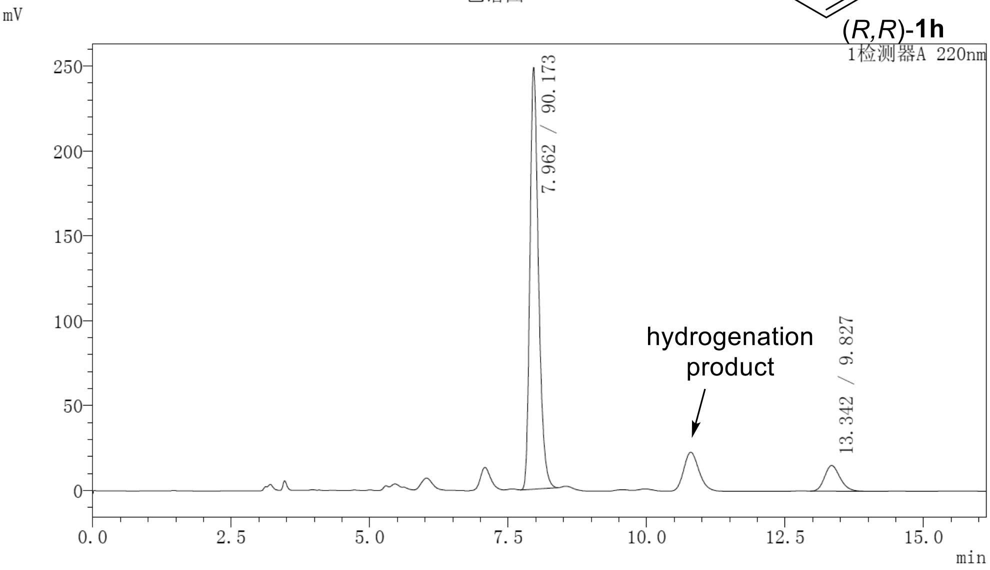
峰号	保留时间	面积	高度	标记	面积%
1	8.160	6342895	513241		49.171
2	13.747	6556698	328854		50.829
总计		12899593	842095		100.000

分析日期/时间　　　　　　　: 2018/7/21 18:05:28
处理日期/时间　　　　　　　: 2018/7/21 18:21:37
描述　　　　　　　　　　　: OJ-H , n-hexane/iPrOH = 99.5/0.5, 1.0 mL/min, 220 nm



(*R,R*)-**1h**

色谱图



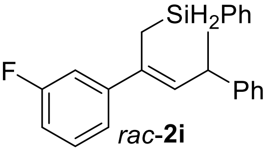
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	7.962	2684280	248374		90.173
2	13.342	292524	15124		9.827
总计		2976804	263497		100.000

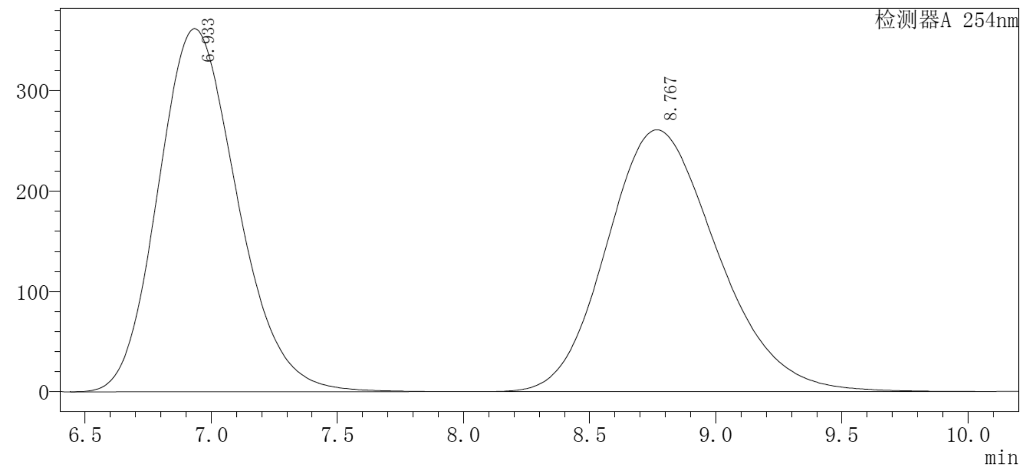
Figure S166. HPLC spectra of (*R,R*)-**1h**, Related to Table 2

分析日期　: 2018/10/10 13:41:50
处理日期　: 2018/10/10 13:56:25
描述　: OJ-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm



rac-**2i**

色谱图

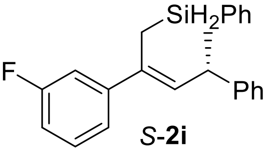


峰表

检测器A 254nm

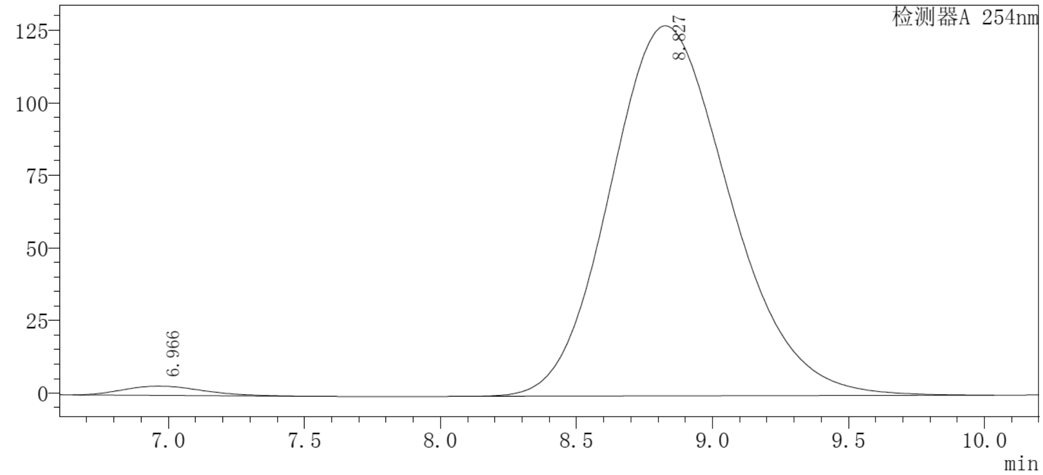
峰号	保留时间	面积	高度	标记	面积%
1	6.933	7912722	361966		49.796
2	8.767	7977500	260913	V	50.204
总计		15890222	622879		100.000

分析日期　: 2018/10/10 14:01:40
处理日期　: 2018/10/10 14:14:23
描述　: OJ-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm



S-**2i**

色谱图



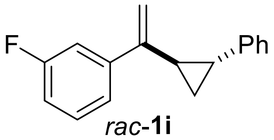
峰表

检测器A 254nm

峰号	保留时间	面积	高度	标记	面积%
1	6.966	65827	3220		1.655
2	8.827	3912400	127531		98.345
总计		3978227	130751		100.000

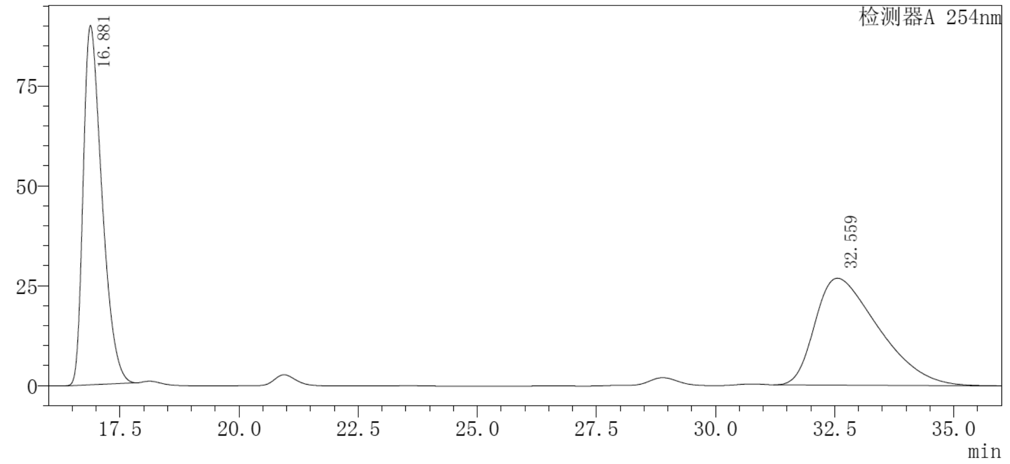
Figure S167. HPLC spectra of *S*-**2i**, Related to Table 2

分析日期　　: 2018/10/10 16:34:26
处理日期　　: 2018/10/10 17:12:28
描述　　　　: OJ-H, n-hexane/iPrOH =99.9/0.1, 1.0 ml/min, 220 nm



rac-**1i**

色谱图

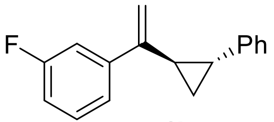


峰表

检测器A 254nm

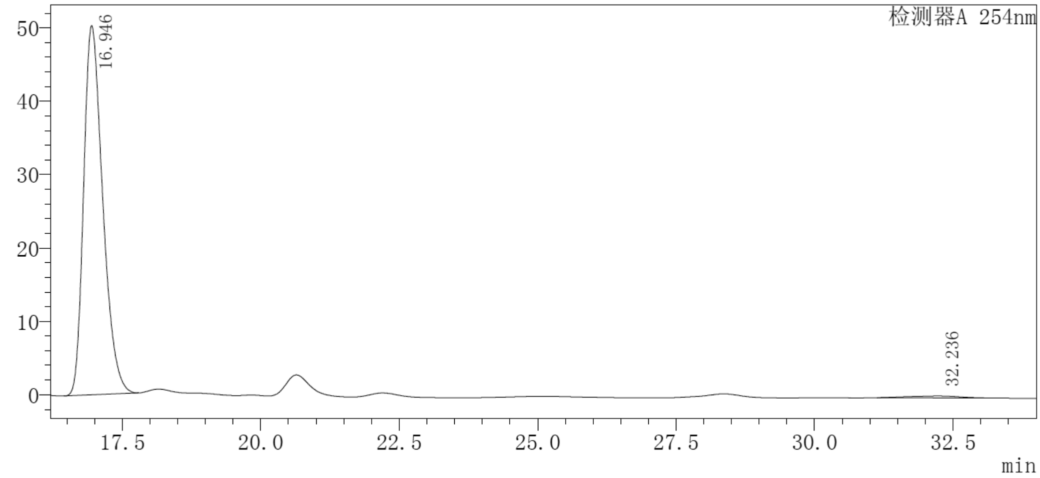
峰号	保留时间	面积	高度	标记	面积%
1	16.881	2473583	89952		49.906
2	32.559	2482904	26775		50.094
总计		4956487	116728		100.000

分析日期　　: 2018/10/10 15:56:25
处理日期　　: 2018/10/10 16:32:26
描述　　　　: OJ-H, n-hexane/iPrOH =99.9/0.1, 1.0 ml/min, 220 nm



(*R*,*R*)-**1i**

色谱图



峰表

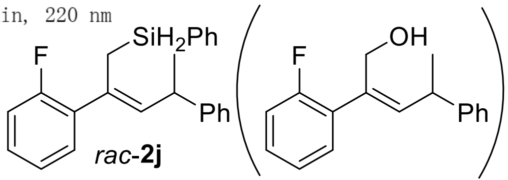
检测器A 254nm

峰号	保留时间	面积	高度	标记	面积%
1	16.946	1208293	50318		98.589
2	32.236	17292	271		1.411
总计		1225585	50589		100.000

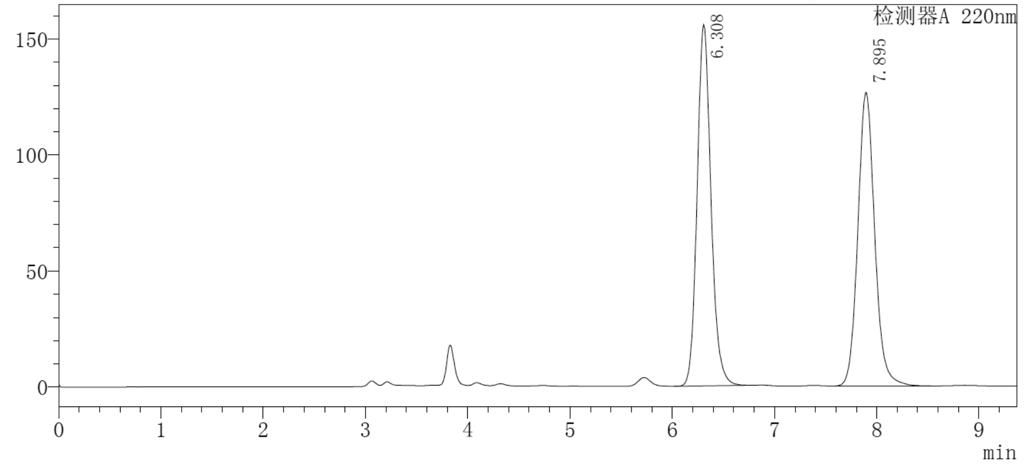
Figure S168. HPLC spectra of (*R,R*)-**1i**, Related to Table 2

分析日期 : 2019/1/3 10:34:43
处理日期 : 2019/1/3 10:44:06
描述 : OD-H, n-hexane/iPrOH =90/10, 1.0 ml/min, 220 nm

色谱图



rac-**2j**



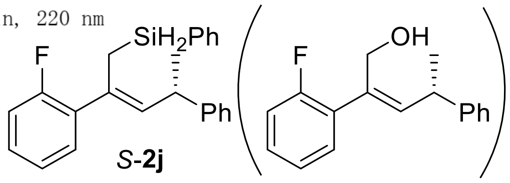
峰表

检测器A 220nm

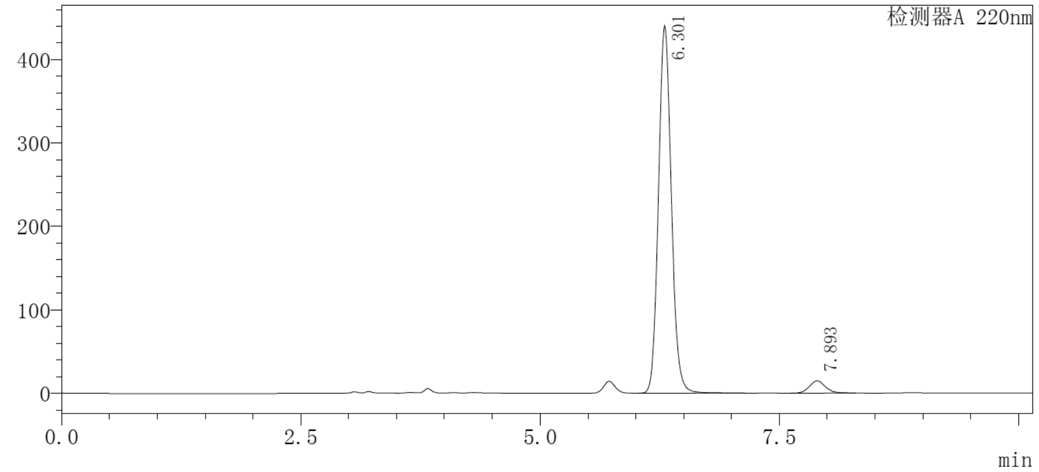
峰号	保留时间	面积	高度	标记	面积%
1	6.308	1470932	155649		50.350
2	7.895	1450485	126512		49.650
总计		2921417	282161		100.000

分析日期 : 2019/1/3 10:45:55
处理日期 : 2019/1/3 10:56:05
描述 : OD-H, n-hexane/iPrOH =90/10, 1.0 ml/min, 220 nm

色谱图



S-**2j**



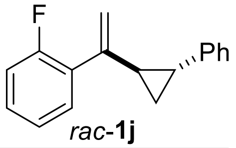
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	6.301	4111690	440573	M	95.958
2	7.893	173189	14638	M	4.042
总计		4284878	455211		100.000

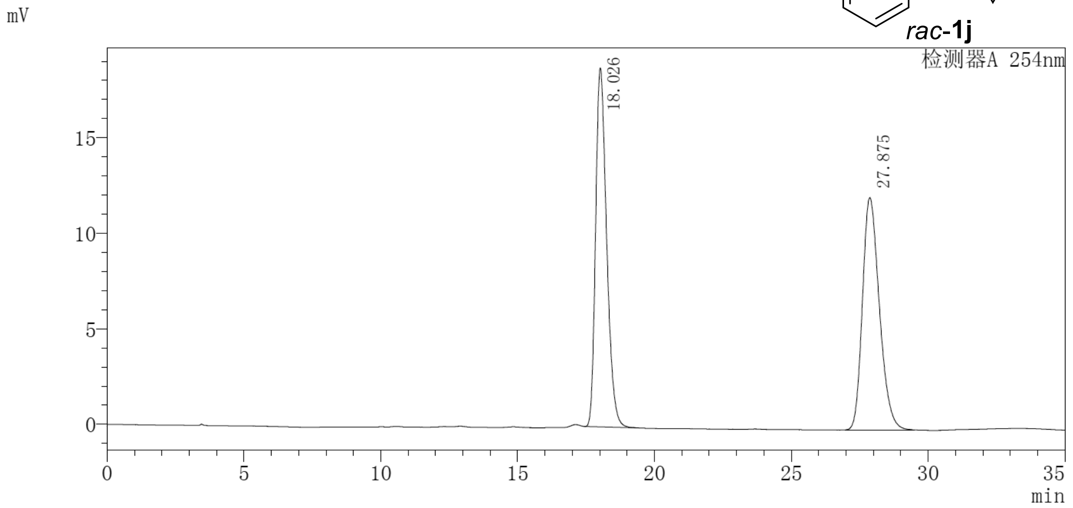
Figure S169. HPLC spectra of *S*-**2j**, Related to Table 2

分析日期　　　: 2018/10/10 17:14:28
处理日期　　　: 2018/10/10 18:24:23
描述　　　　　: OJ-H, n-hexane/iPrOH =99.9/0.1, 1.0 ml/min, 220 nm



rac-**1j**

色谱图

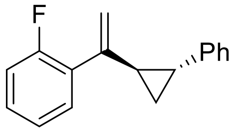


峰表

检测器A 254nm

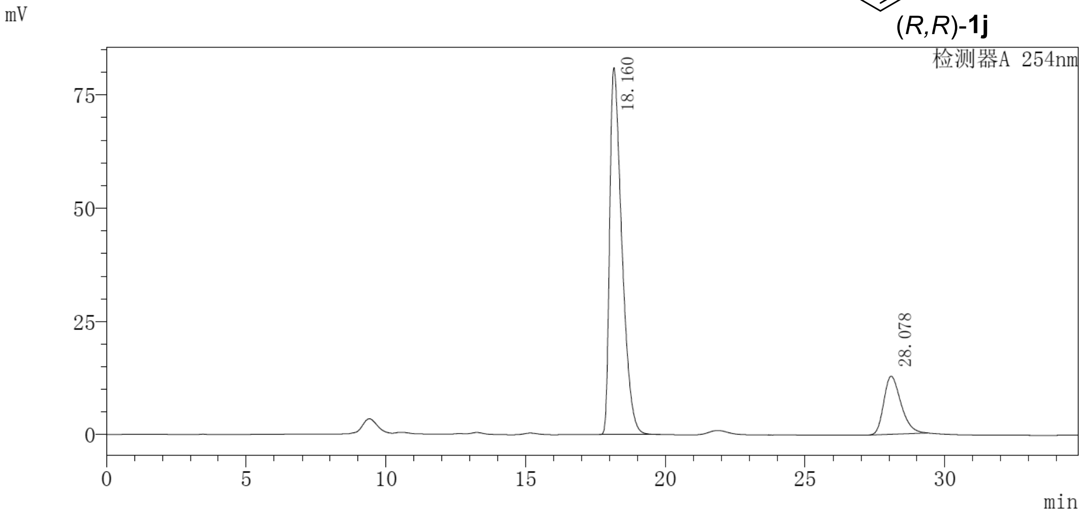
峰号	保留时间	面积	高度	标记	面积%
1	18.026	524314	18792		50.061
2	27.875	523040	12161		49.939
总计		1047353	30952		100.000

分析日期　　　: 2018/10/10 18:59:29
处理日期　　　: 2018/10/10 19:34:16
描述　　　　　: OJ-H, n-hexane/iPrOH =99.9/0.1, 1.0 ml/min, 220 nm



(*R,R*)-**1j**

色谱图



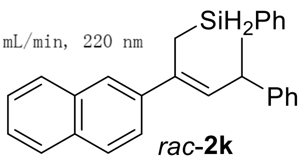
峰表

检测器A 254nm

峰号	保留时间	面积	高度	标记	面积%
1	18.160	2459480	81051		81.757
2	28.078	548792	12822	M	18.243
总计		3008273	93873		100.000

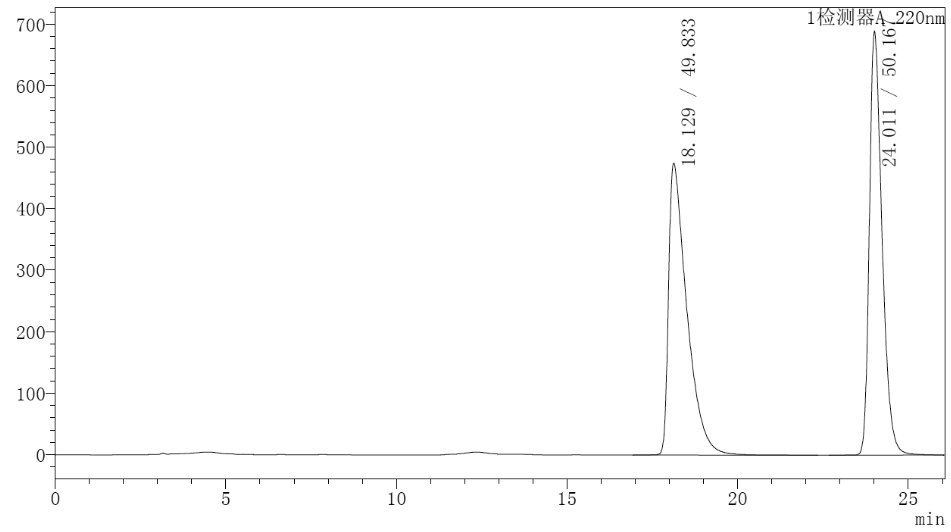
Figure S170. HPLC spectra of (*R,R*)-**1j**, Related to Table 2

分析日期/时间　　: 2018/7/7 10:28:37
处理日期/时间　　: 2018/7/7 10:54:44
描述　　: OD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



rac-**2k**

色谱图

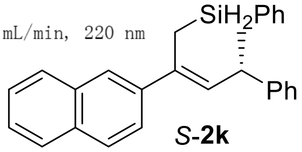


峰表

检测器A 220nm

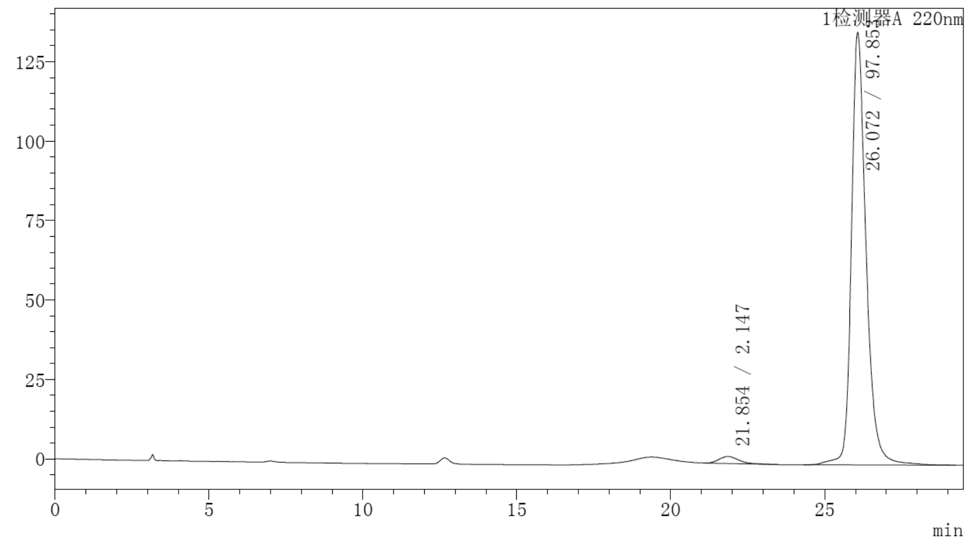
峰号	保留时间	面积	高度	标记	面积%
1	18.129	17685408	474514		49.833
2	24.011	17804296	689309		50.167
总计		35489704	1163823		100.000

分析日期/时间　　: 2018/7/7 12:09:07
处理日期/时间　　: 2018/7/7 12:42:18
描述　　: OD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



S-**2k**

色谱图



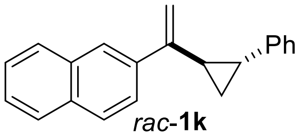
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	21.854	98996	2202		2.147
2	26.072	4512152	136105		97.853
总计		4611149	138306		100.000

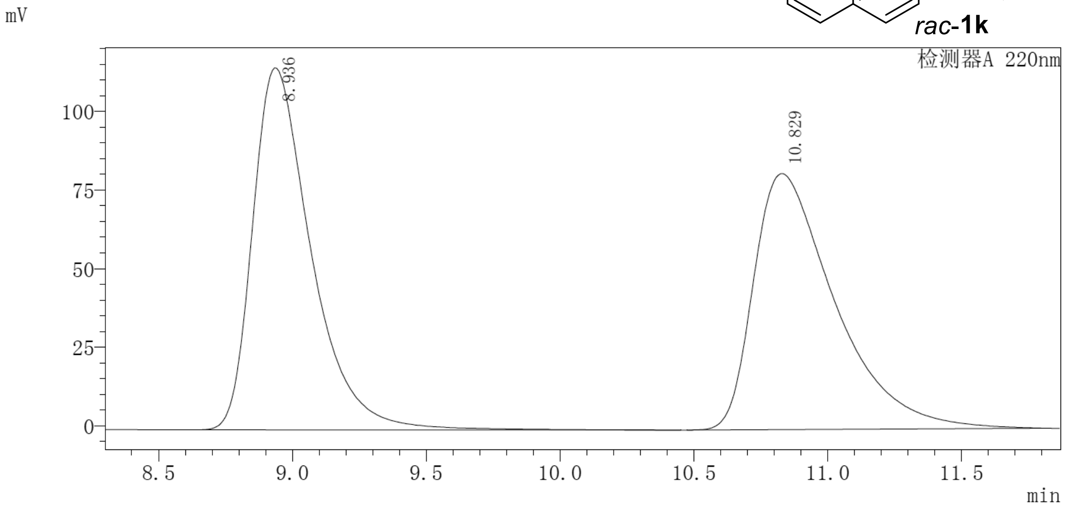
Figure S171. HPLC spectra of *S*-**2k**, Related to Table 2

分析日期　　: 2018/7/9 10:14:23
处理日期　　: 2018/7/9 10:26:16
描述　　　　: AD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



rac-**1k**

色谱图

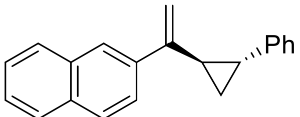


峰表

检测器A 220nm

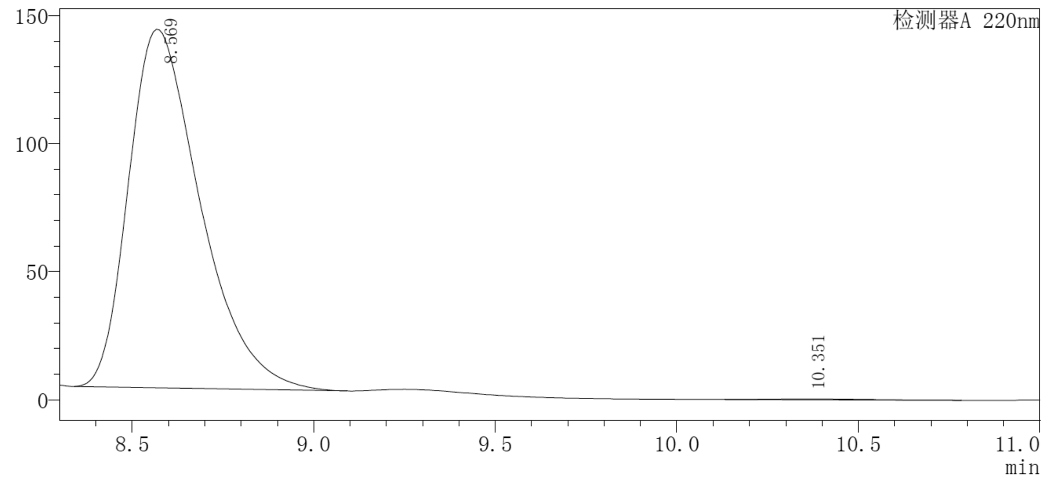
峰号	保留时间	面积	高度	标记	面积%
1	8.936	1754101	115137		50.426
2	10.829	1724439	81354		49.574
总计		3478540	196491		100.000

分析日期　　: 2018/7/9 10:27:16
处理日期　　: 2018/7/9 10:39:53
描述　　　　: AD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



(*R*,*R*)-**1k**

色谱图



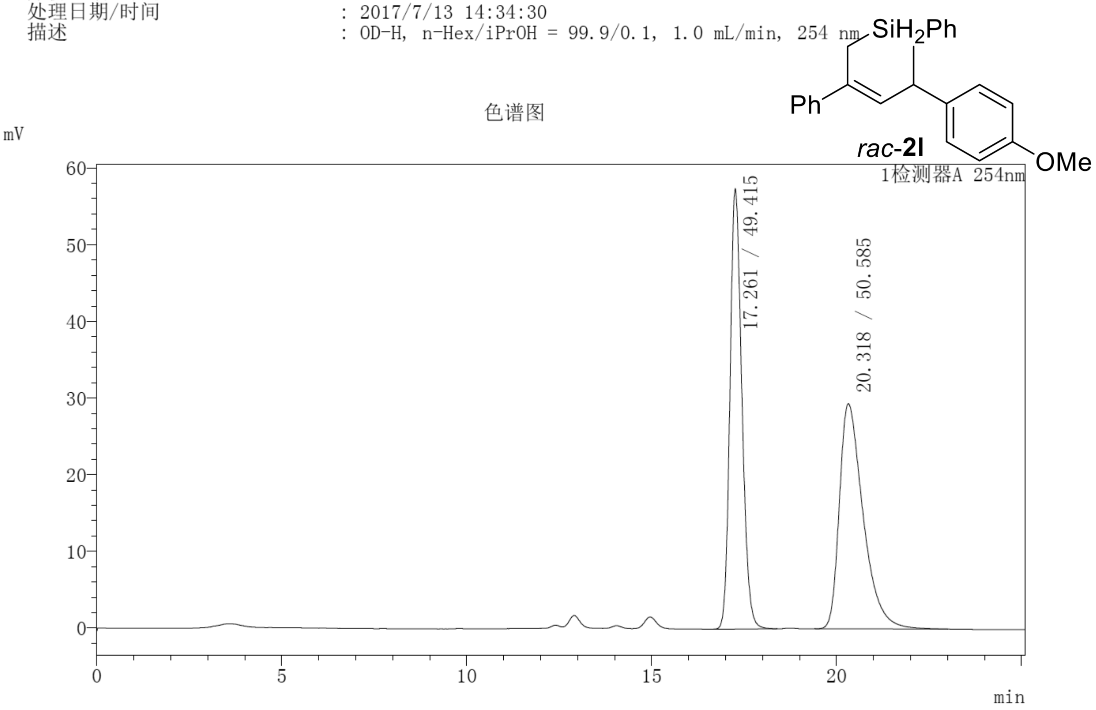
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.569	1925259	140038		99.713
2	10.351	5544	334		0.287
总计		1930803	140372		100.000

Figure S172. HPLC spectra of (*R,R*)-**1k**, Related to Table 2

分析日期/时间　　　　　　　: 2017/7/13 14:09:23
处理日期/时间　　　　　　　: 2017/7/13 14:34:30
描述　　　　　　　　　　　: OD-H, n-Hex/iPrOH = 99.9/0.1, 1.0 mL/min, 254 nm

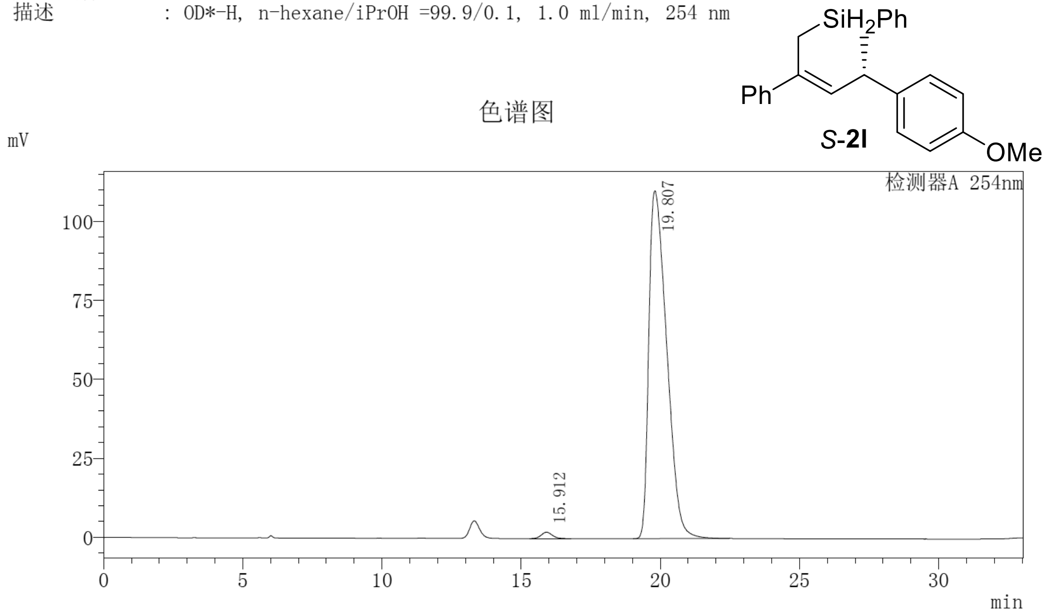


峰表

检测器A 254nm

峰号	保留时间	面积	高度	标记	面积%
1	17.261	1284040	57429		49.415
2	20.318	1314439	29379		50.585
总计		2598479	86807		100.000

分析日期　　　: 2018/12/28 16:18:10
处理日期　　　: 2018/12/28 16:51:13
描述　　　　　: OD*-H, n-hexane/iPrOH =99.9/0.1, 1.0 ml/min, 254 nm



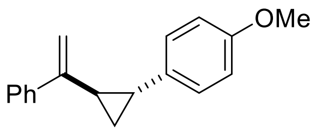
峰表

检测器A 254nm

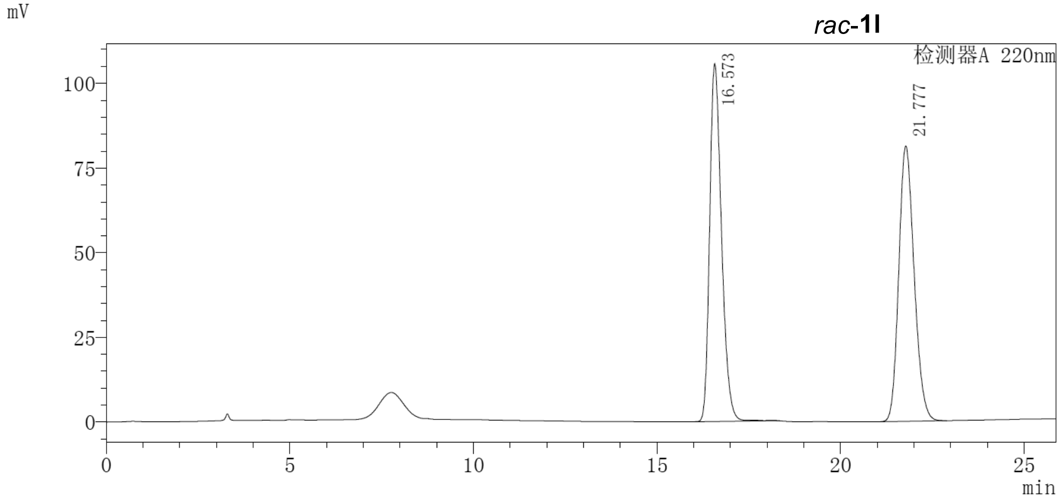
峰号	保留时间	面积	高度	标记	面积%
1	15.912	55868	2010		1.124
2	19.807	4916785	110150		98.876
总计		4972653	112160		100.000

Figure S173. HPLC spectra of *S*-**2l**, Related to Table 2

分析日期　　: 2018/12/26 16:38:23
处理日期　　: 2018/12/26 17:04:15
描述　　　　: OJ-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm



色谱图

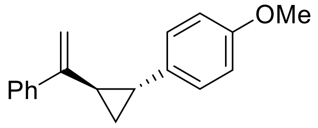

rac-**1l**

峰表

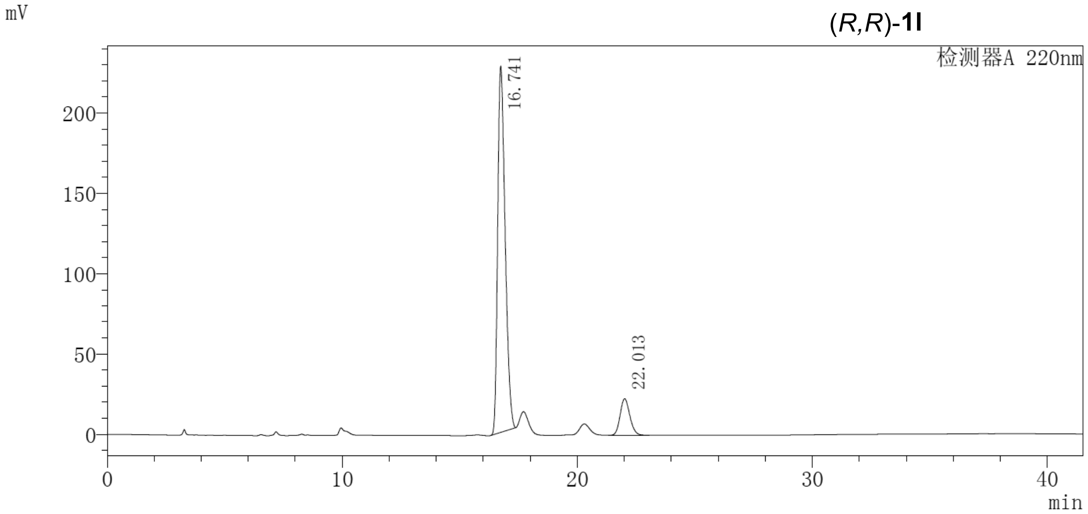
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	16.573	2370686	105610	M	50.084
2	21.777	2362753	81279		49.916
总计		4733439	186889		100.000

分析日期　　: 2018/12/26 17:05:40
处理日期　　: 2018/12/26 17:47:11
描述　　　　: OJ-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm



色谱图


(*R*,*R*)-**1l**

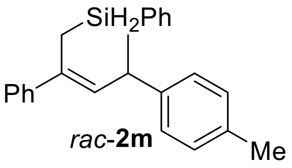
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	16.741	5030468	227872		88.540
2	22.013	651120	22801		11.460
总计		5681588	250673		100.000

Figure S174. HPLC spectra of (*R*,*R*)-**1l**, Related to Table 2

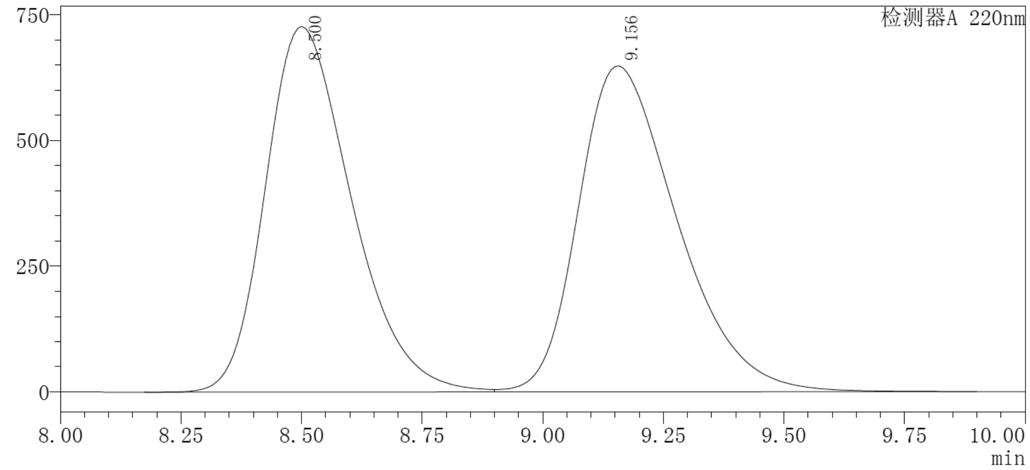
分析日期　　: 2018/7/16 22:16:24
处理日期　　: 2018/7/16 22:28:04
描述　　　　: OD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



rac-**2m**

色谱图

mV

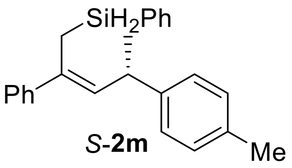


峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.500	9012793	726397		49.443
2	9.156	9215796	647663	V M	50.557
总计		18228589	1374060		100.000

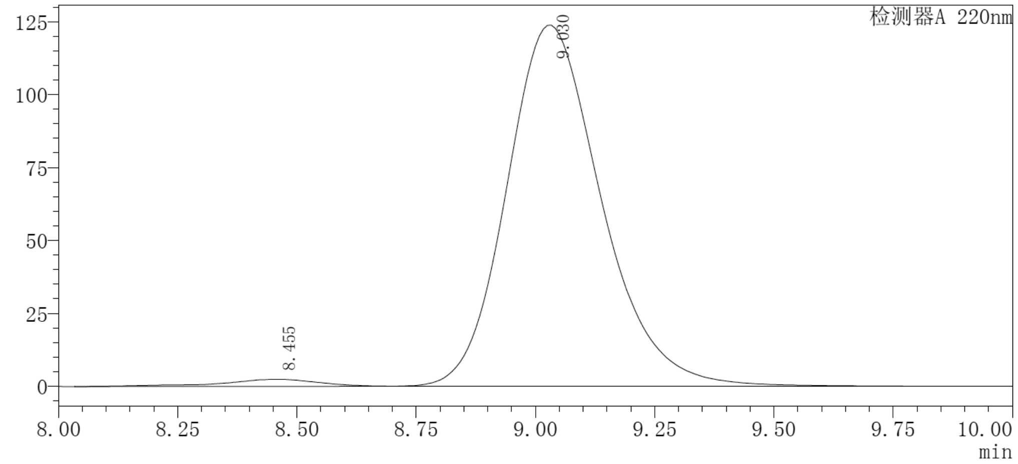
分析日期　　: 2018/8/4 10:15:07
处理日期　　: 2018/8/4 10:49:23
描述　　　　: OD-H , n-hexane/iPrOH = 99.9/0.1,1.0 mL/min, 220 nm



S-**2m**

色谱图

mV



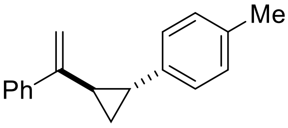
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.455	35244	2444		2.020
2	9.030	1709891	123792	V	97.980
总计		1745135	126236		100.000

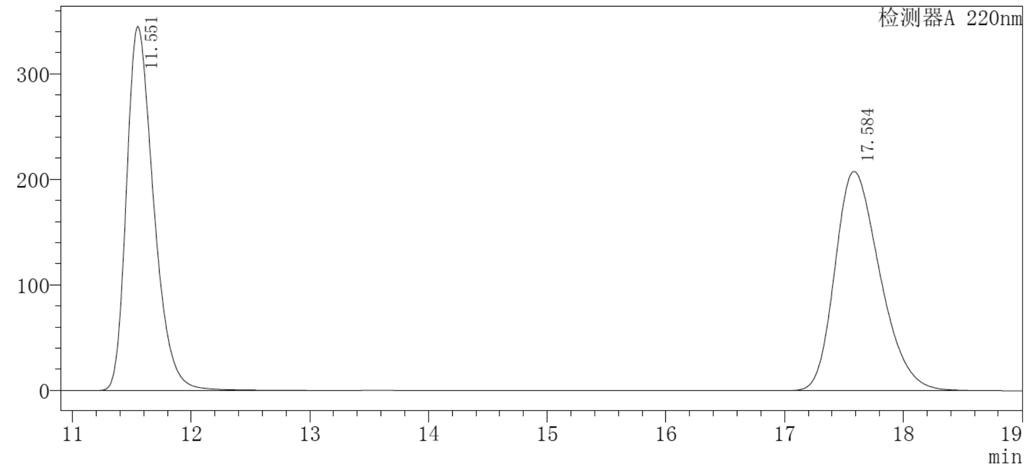
Figure S175. HPLC spectra of *S*-**2m**, Related to Table 2

分析日期　　　: 2018/7/16 19:22:50
处理日期　　　: 2018/7/16 19:42:00
描述　　　　　: OJ-H , n-hexane/iPrOH = 99.5/0.5, 1.0 mL/min, 220 nm



rac-**1m**

色谱图

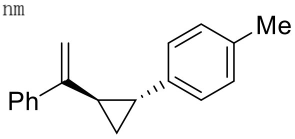


峰表

检测器A 220nm

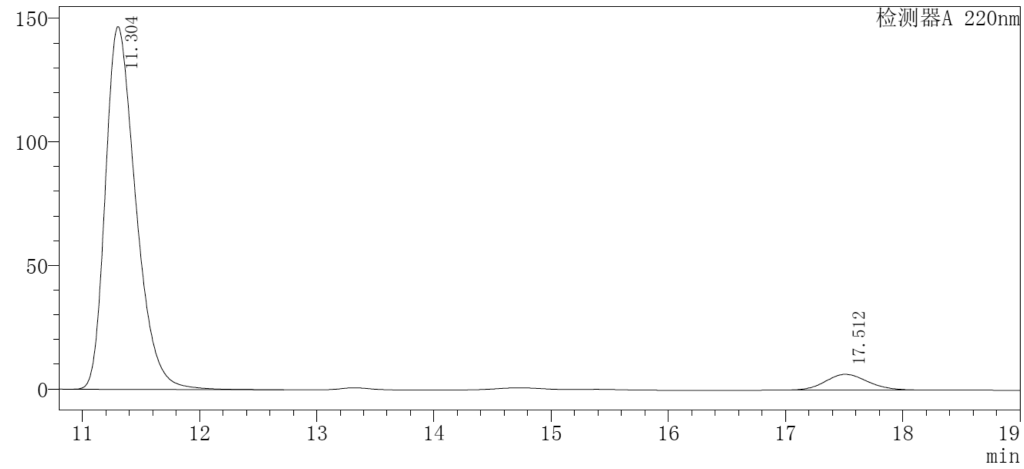
峰号	保留时间	面积	高度	标记	面积%
1	11.551	5496623	345272		50.126
2	17.584	5469096	207992	M	49.874
总计		10965719	553264		100.000

分析日期　　　: 2018/7/16 19:43:00
处理日期　　　: 2018/7/16 20:07:33
描述　　　　　: OJ-H , n-hexane/iPrOH = 99.5/0.5, 1.0 mL/min, 220 nm



(*R*,*R*)-**1m**

色谱图



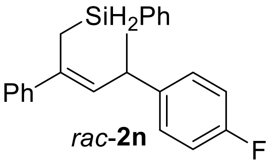
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	11.304	2646452	146823		94.200
2	17.512	162940	6413		5.800
总计		2809392	153236		100.000

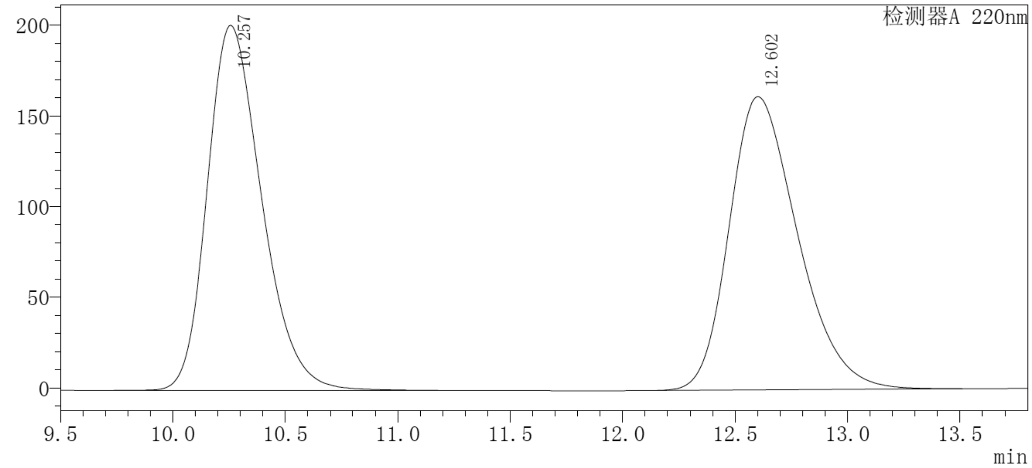
Figure S176. HPLC spectra of (*R*,*R*)-**1m**, Related to Table 2

分析日期　　　: 2018/7/7 20:14:56
处理日期　　　: 2018/7/7 20:28:50
描述　　　　　: OD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



rac-**2n**

色谱图

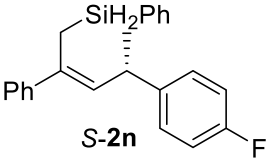


峰表

检测器A 220nm

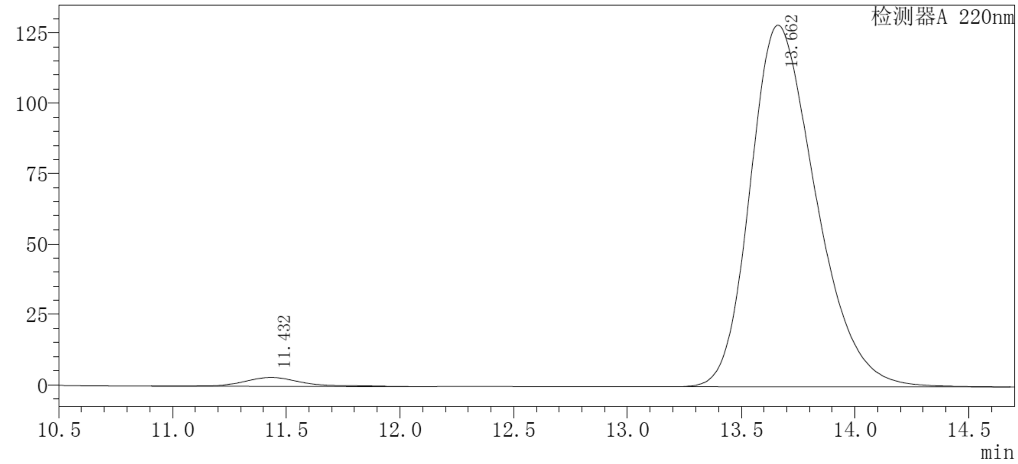
峰号	保留时间	面积	高度	标记	面积%
1	10.257	3386046	201287		49.694
2	12.602	3427766	161647		50.306
总计		6813813	362934		100.000

分析日期　　　: 2018/7/7 20:30:19
处理日期　　　: 2018/7/7 20:45:41
描述　　　　　: OD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



S-**2n**

色谱图



峰表

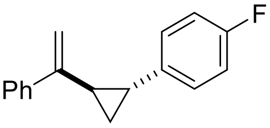
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	11.432	55343	3162		2.103
2	13.662	2576703	128412		97.897
总计		2632046	131573		100.000

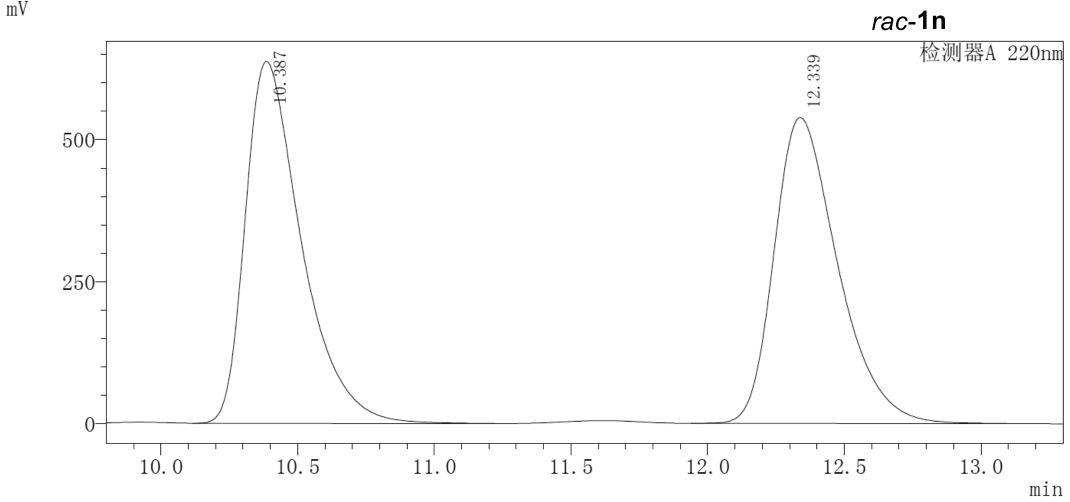
Figure S177. HPLC spectra of *S*-**2n**, Related to Table 2

分析日期　　: 2018/7/21 20:54:45
处理日期　　: 2018/7/21 21:10:19
描述　　　　: OJ-H , n-hexane/iPrOH = 99.5/0.5, 1.0 mL/min, 220 nm

色谱图



rac-**1n**



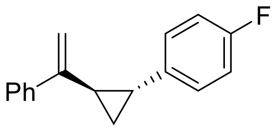
峰表

检测器A 220nm

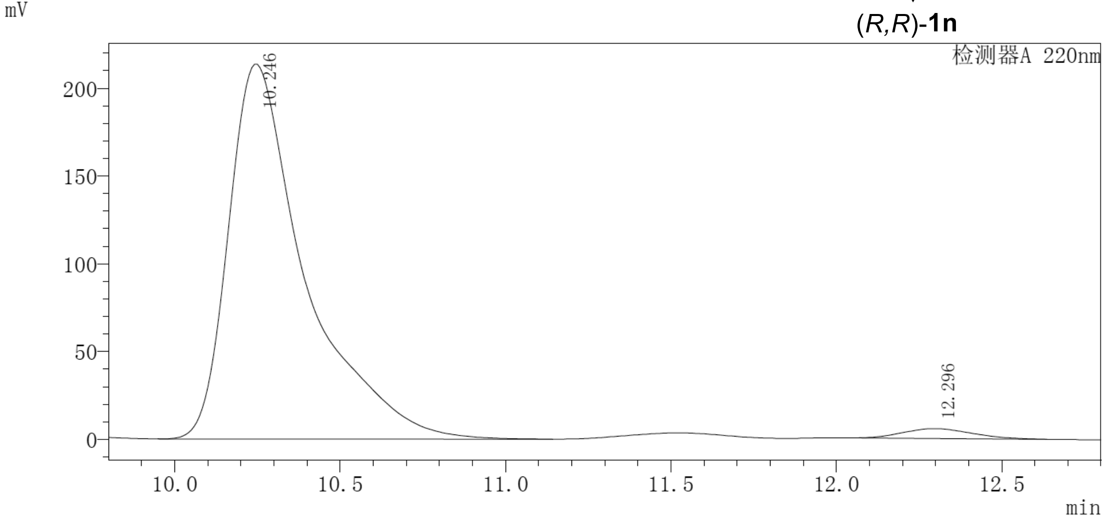
峰号	保留时间	面积	高度	标记	面积%
1	10.387	9103993	636680		51.066
2	12.339	8723805	538284	M	48.934
总计		17827797	1174964		100.000

分析日期　　: 2018/7/21 21:11:46
处理日期　　: 2018/7/21 21:24:50
描述　　　　: OJ-H , n-hexane/iPrOH = 99.5/0.5, 1.0 mL/min, 220 nm

色谱图



(*R*,*R*)-**1n**



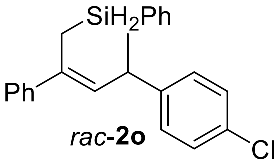
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	10.246	3436274	213481		97.663
2	12.296	82216	5618		2.337
总计		3518490	219098		100.000

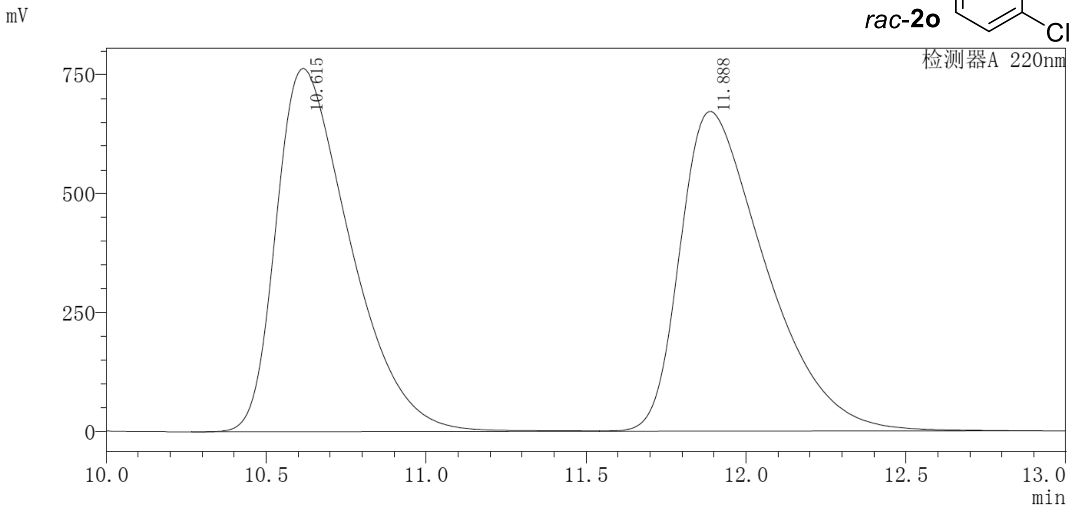
Figure S178. HPLC spectra of (*R*,*R*)-**1n**, Related to Table 2

分析日期　　　: 2018/7/7 15:50:37
处理日期　　　: 2018/7/7 16:04:52
描述　　　　　: OD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



rac-**2o**

色谱图

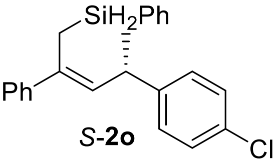


峰表

检测器A 220nm

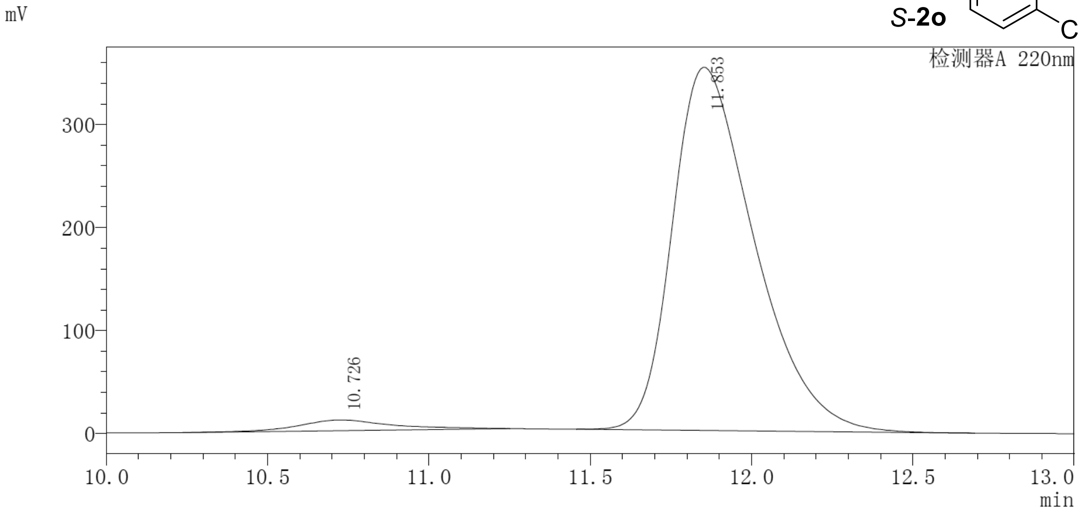
峰号	保留时间	面积	高度	标记	面积%
1	10.615	12282408	763785		49.525
2	11.888	12517890	672063	V M	50.475
总计		24800299	1435848		100.000

分析日期　　　: 2018/7/7 16:06:14
处理日期　　　: 2018/7/7 16:19:53
描述　　　　　: OD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



S-**2o**

色谱图



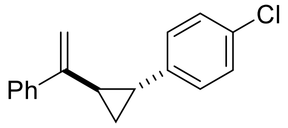
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	10.726	210053	10340	M	3.257
2	11.853	6239242	352354		96.743
总计		6449295	362694		100.000

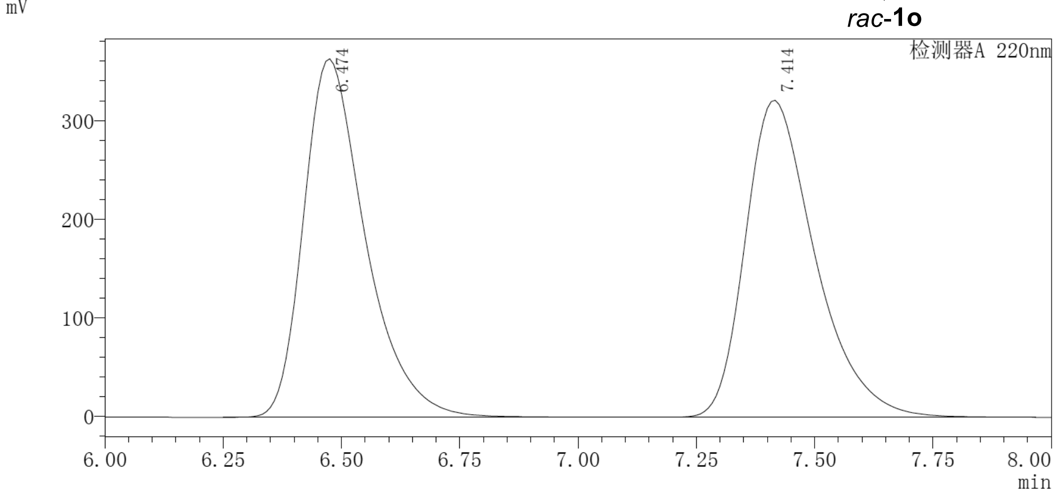
Figure S179. HPLC spectra of *S*-**2o**, Related to Table 2

分析日期　　: 2018/7/9 9:04:01
处理日期　　: 2018/7/9 9:12:10
描述　　　　: AD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



rac-**1o**

色谱图

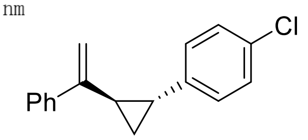


峰表

检测器A 220nm

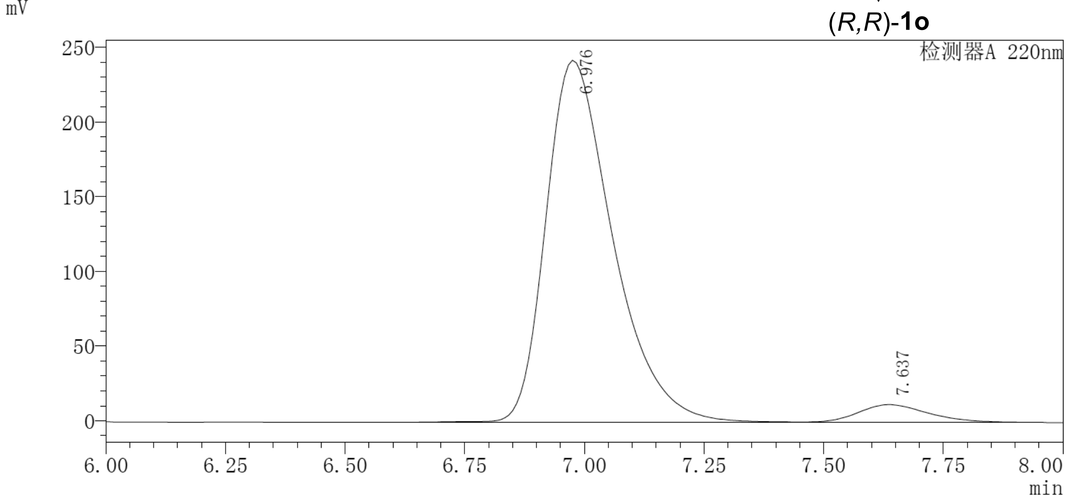
峰号	保留时间	面积	高度	标记	面积%
1	6.474	3304897	363222	S	50.047
2	7.414	3298693	321179	V M	49.953
总计		6603590	684402		100.000

分析日期　　: 2018/7/9 9:13:13
处理日期　　: 2018/7/9 9:22:01
描述　　　　: AD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



(*R*,*R*)-**1o**

色谱图



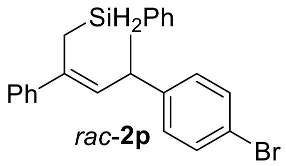
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	6.976	2363551	242254		95.061
2	7.637	122808	11912	V M	4.939
总计		2486360	254167		100.000

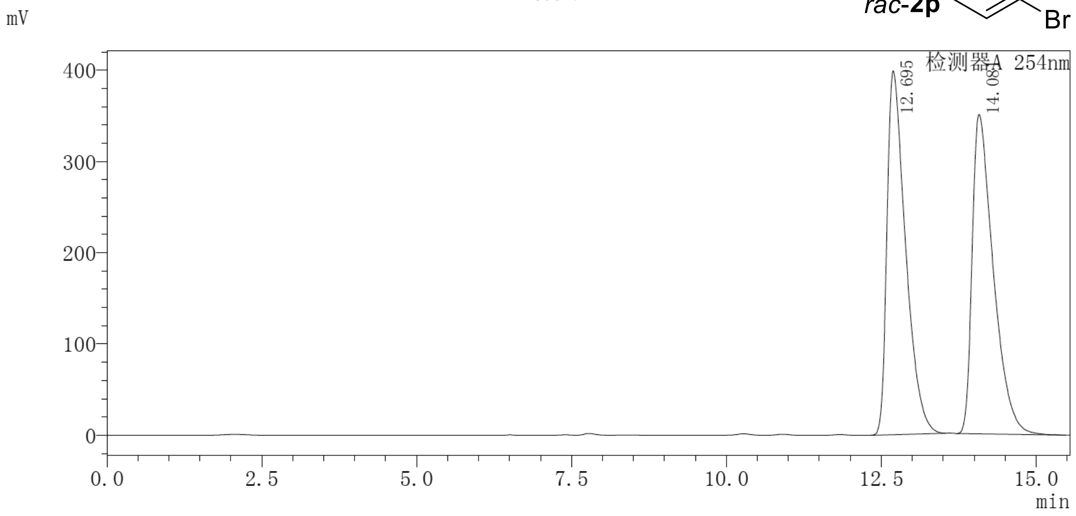
Figure S180. HPLC spectra of (*R,R*)-**1o**, Related to Table 2

分析日期　　　: 2018/12/28 18:15:14
处理日期　　　: 2018/12/28 18:30:48
描述　　　　　: OD*-H, n-hexane/iPrOH =99.9/0.1, 1.0 ml/min, 254 nm



rac-**2p**

色谱图

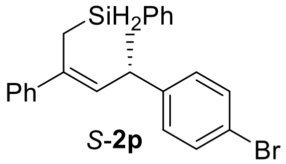


峰表

检测器A 254nm

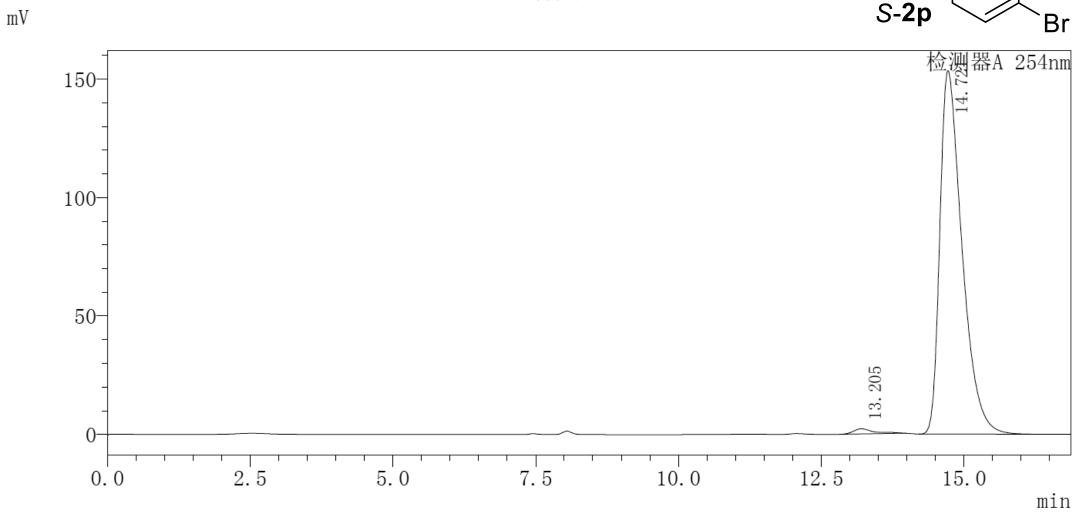
峰号	保留时间	面积	高度	标记	面积%
1	12.695	8300233	398133		49.989
2	14.081	8303788	349705		50.011
总计		16604021	747838		100.000

分析日期　　　: 2018/12/28 17:55:47
处理日期　　　: 2018/12/28 18:12:41
描述　　　　　: OD*-H, n-hexane/iPrOH =99.9/0.1, 1.0 ml/min, 254 nm



S-**2p**

色谱图



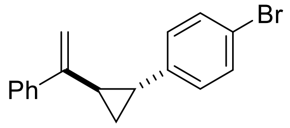
峰表

检测器A 254nm

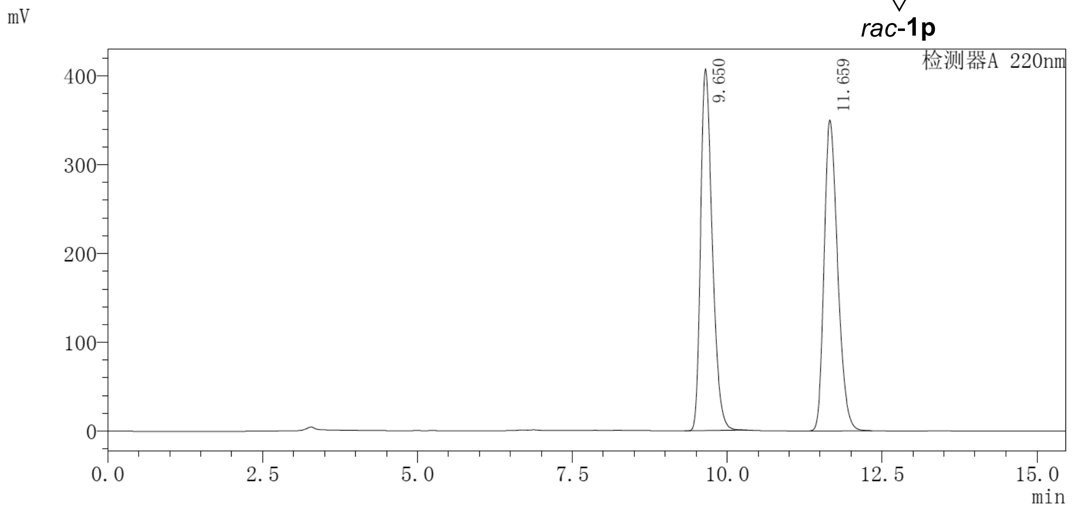
峰号	保留时间	面积	高度	标记	面积%
1	13.205	56492	2188	M	1.344
2	14.721	4147445	153502		98.656
总计		4203937	155690		100.000

Figure S181. HPLC spectra of *S*-**2p**, Related to Table 2

分析日期　　: 2018/12/26 14:23:18
处理日期　　: 2018/12/26 14:38:47
描述　　　　: OJ-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm


rac-**1p**

色谱图

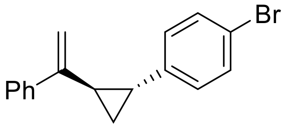


峰表

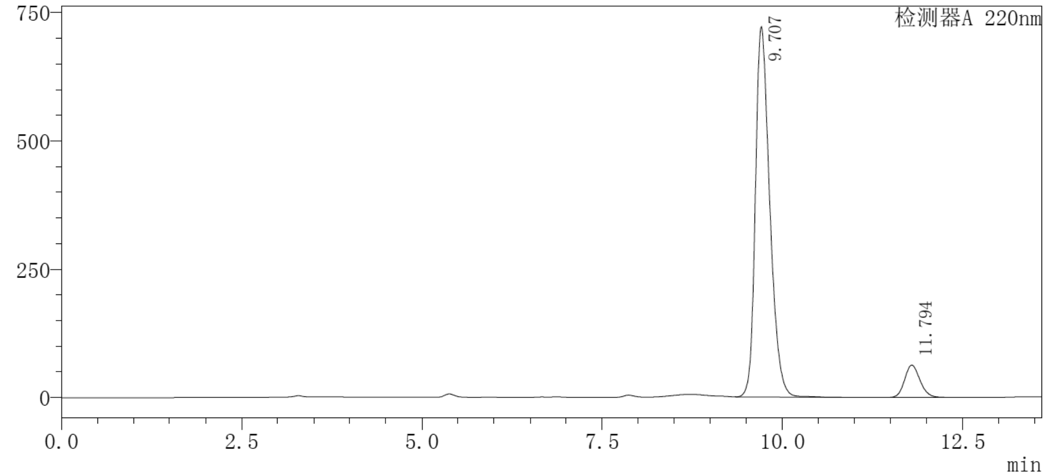
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.650	5330346	406932	M	49.991
2	11.659	5332349	349958	M	50.009
总计		10662695	756889		100.000

分析日期　　: 2018/12/26 14:41:17
处理日期　　: 2018/12/26 14:54:54
描述　　　　: OJ-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm


(*R*,*R*)-**1p**

色谱图



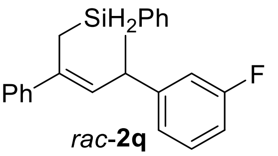
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.707	10045436	721345		91.462
2	11.794	937750	62969		8.538
总计		10983186	784314		100.000

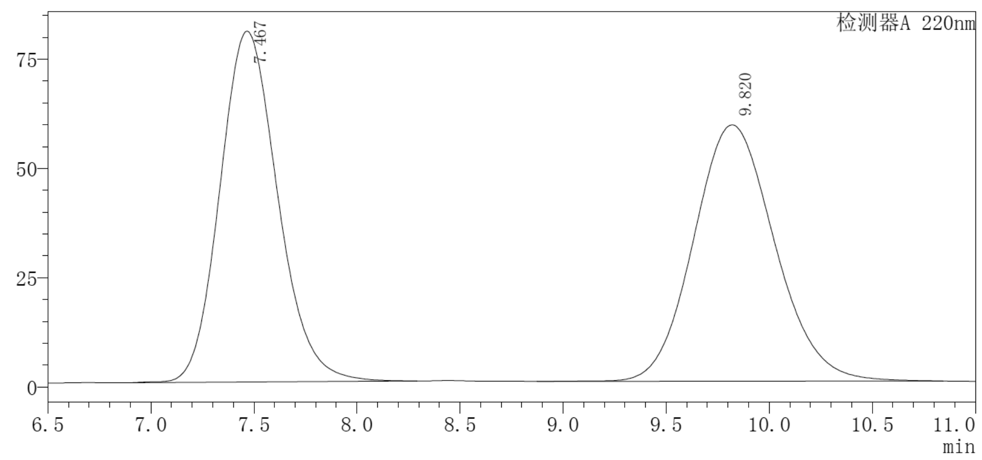
Figure S182. HPLC spectra of (*R*,*R*)-**1p**, Related to Table 2

分析日期　　: 2018/8/4 16:20:00
处理日期　　: 2018/8/4 16:31:07
描述　　　　: OJ-H , n-hexane/iPrOH = 99/1, 1.0 mL/min, 220 nm



rac-**2q**

色谱图

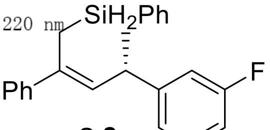


峰表

检测器A 220nm

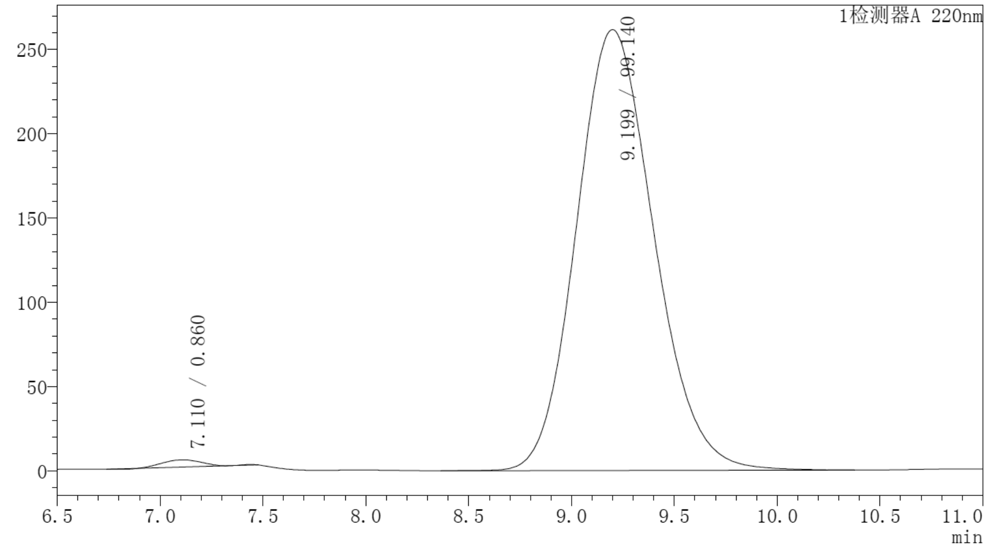
峰号	保留时间	面积	高度	标记	面积%
1	7.467	1567140	80323		49.379
2	9.820	1606546	58683	M	50.621
总计		3173686	139007		100.000

分析日期/时间　　: 2018/8/4 16:35:40
处理日期/时间　　: 2018/8/4 16:48:55
描述　　　　　　: OJ-H , n-hexane/iPrOH = 99/1, 1.0 mL/min, 220 nm



S-**2q**

色谱图



峰表

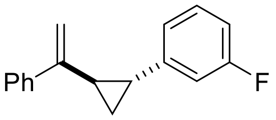
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	7.110	59464	4342	M	0.860
2	9.199	6853435	261658		99.140
总计		6912899	266001		100.000

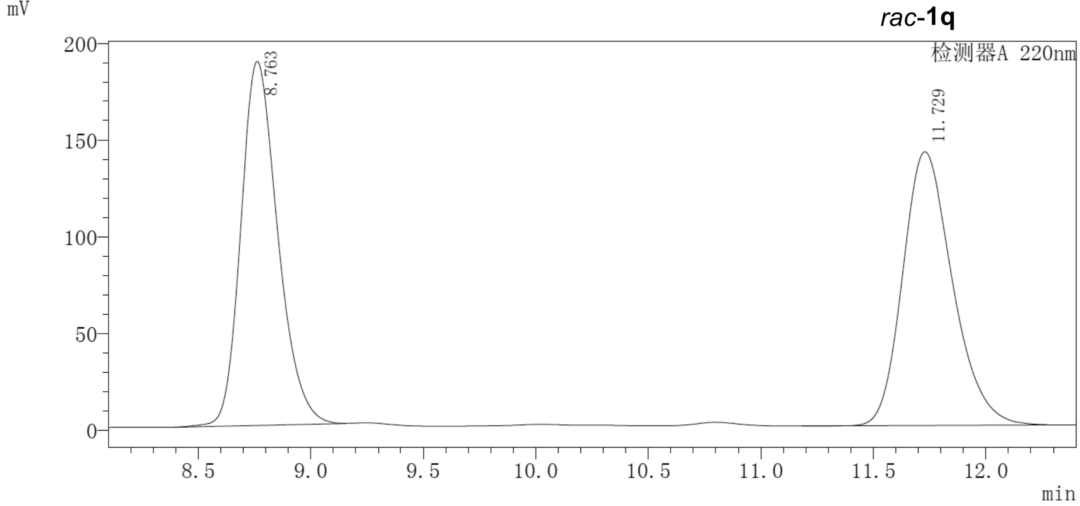
Figure S183. HPLC spectra of *S*-**2q**, Related to Table 2

分析日期　　　　: 2018/8/3 20:30:35
处理日期　　　　: 2018/8/3 20:43:25
描述　　　　　　: OJ-H , n-hexane/iPrOH = 99.5/0.5,1.0 mL/min, 220 nm

色谱图



rac-**1q**



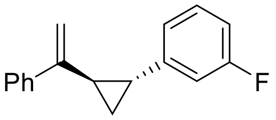
峰表

检测器A 220nm

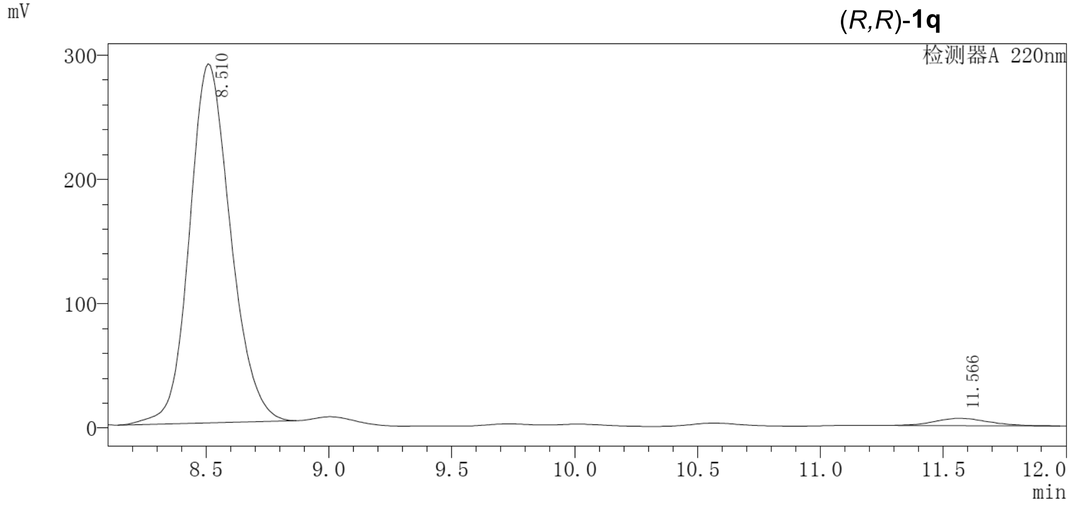
峰号	保留时间	面积	高度	标记	面积%
1	8.763	2154508	187845		49.700
2	11.729	2180524	141388		50.300
总计		4335032	329233		100.000

分析日期　　　　: 2018/8/3 20:44:20
处理日期　　　　: 2018/8/3 20:56:59
描述　　　　　　: OJ-H , n-hexane/iPrOH = 99.5/0.5,1.0 mL/min, 220 nm

色谱图



(*R*,*R*)-**1q**



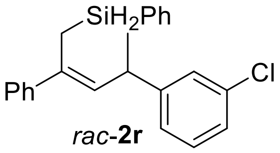
峰表

检测器A 220nm

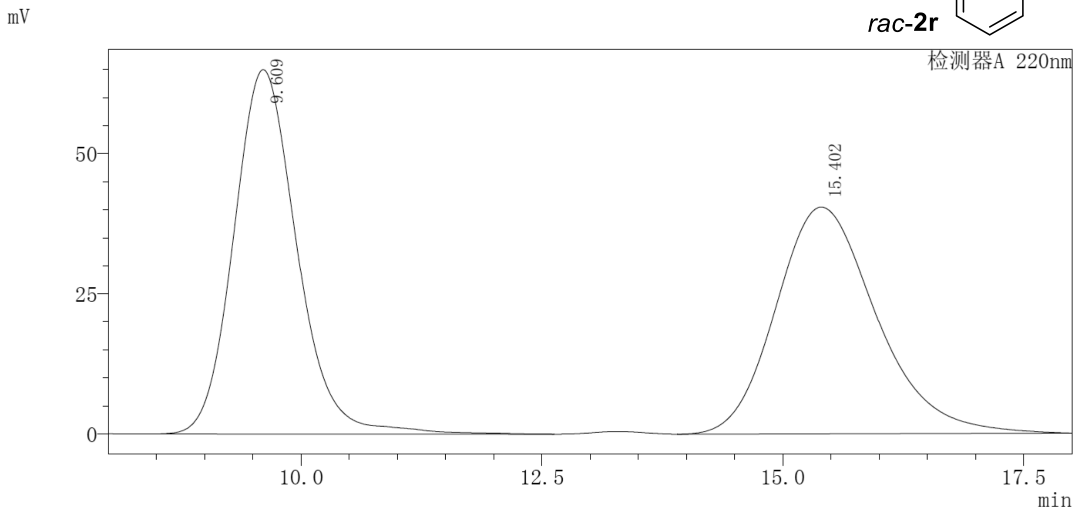
峰号	保留时间	面积	高度	标记	面积%
1	8.510	3368662	288809		97.339
2	11.566	92106	5968		2.661
总计		3460768	294777		100.000

Figure S184. HPLC spectra of (*R*,*R*)-**1q**, Related to Table 2

分析日期　　: 2018/7/10 19:33:18
处理日期　　: 2019/7/29 15:24:42
描述　　　　: OJ-H , n-hexane/iPrOH = 99.5/0.5, 1.0 mL/min, 220 nm


rac-**2r**

色谱图

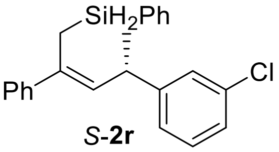


峰表

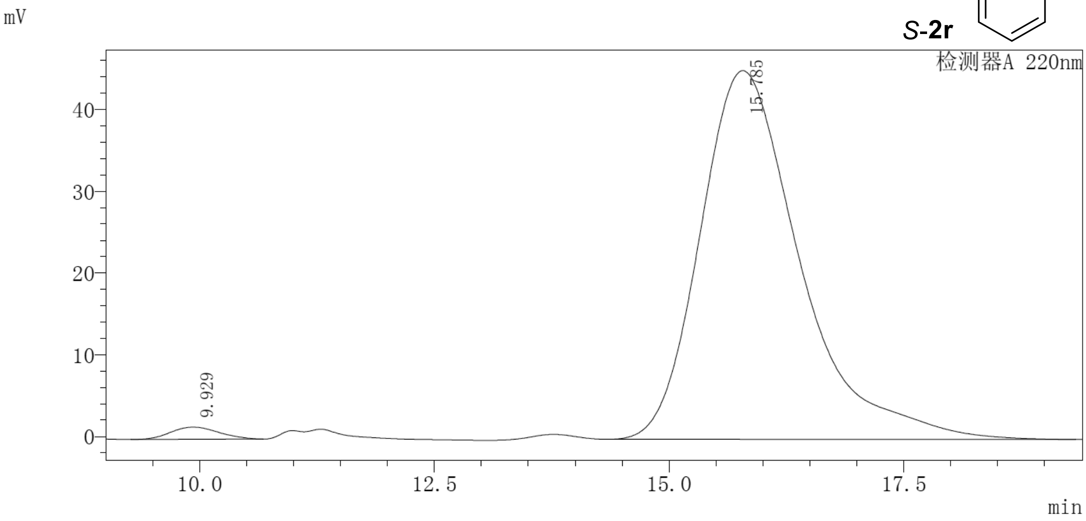
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.609	2967839	65035		50.233
2	15.402	2940319	40455	M	49.767
总计		5908158	105490		100.000

分析日期　　: 2018/7/10 22:27:33
处理日期　　: 2018/7/10 22:47:00
描述　　　　: OJ-H , n-hexane/iPrOH = 99.5/0.5, 1.0 mL/min, 220 nm


S-**2r**

色谱图



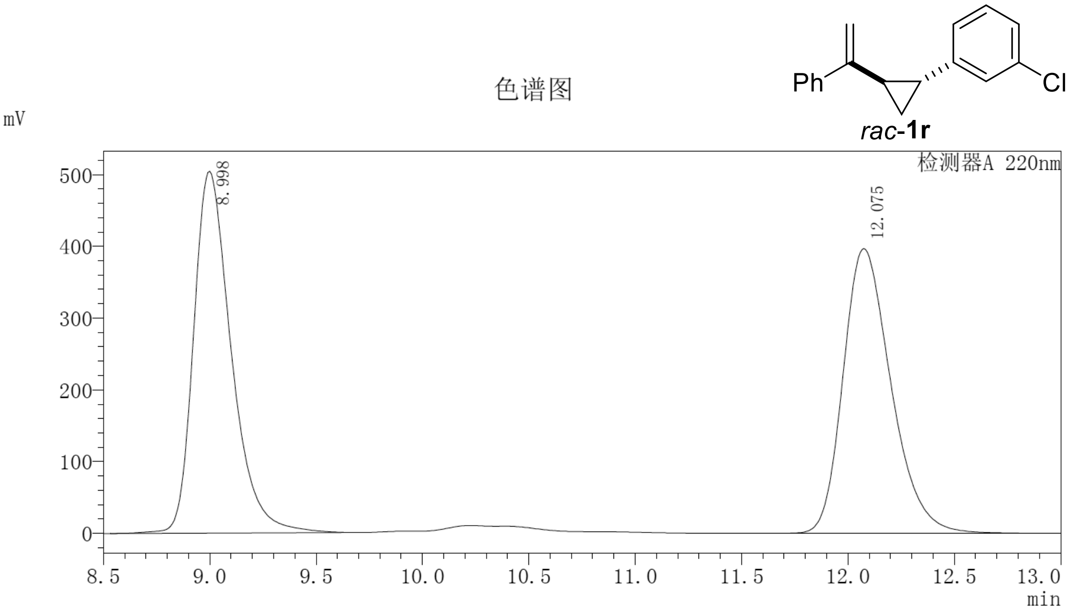
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.929	53716	1494		1.585
2	15.785	3334825	45114		98.415
总计		3388541	46609		100.000

Figure S185. HPLC spectra of *S*-**2r**, Related to Table 2

分析日期　　　: 2018/7/10 20:50:00
处理日期　　　: 2018/7/10 21:03:34
描述　　　　　: OJ-H , n-hexane/iPrOH = 99.5/0.5, 1.0 mL/min, 220 nm


色谱图

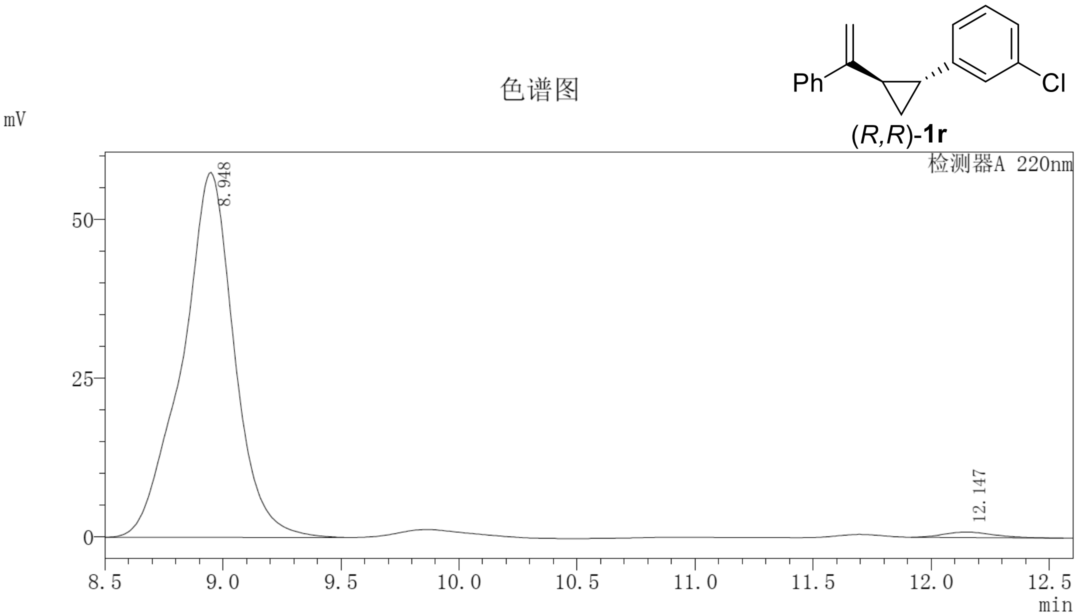
rac-**1r**

峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.998	6210755	504414		50.005
2	12.075	6209540	396936	V	49.995
总计		12420296	901350		100.000

分析日期　　　: 2018/7/10 21:04:28
处理日期　　　: 2018/7/10 21:22:54
描述　　　　　: OJ-H , n-hexane/iPrOH = 99.5/0.5, 1.0 mL/min, 220 nm


色谱图

(*R*,*R*)-**1r**

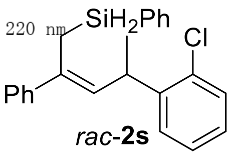
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.948	887375	57516		98.584
2	12.147	12744	863		1.416
总计		900120	58378		100.000

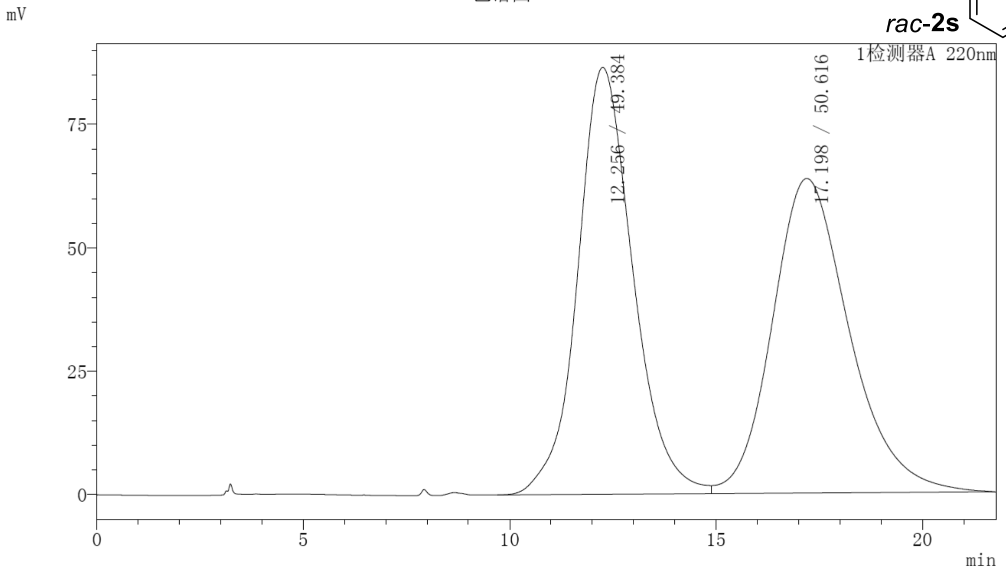
Figure S186. HPLC spectra of (*R*,*R*)-**1r**, Related to Table 2

分析日期/时间　　　　　　　: 2018/7/10 23:07:27
处理日期/时间　　　　　　　: 2018/7/10 23:29:15
描述　　　　　　　　　　　: OJ-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



rac-**2s**

色谱图

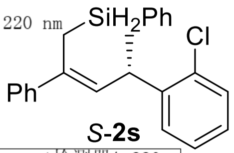


峰表

检测器A 220nm

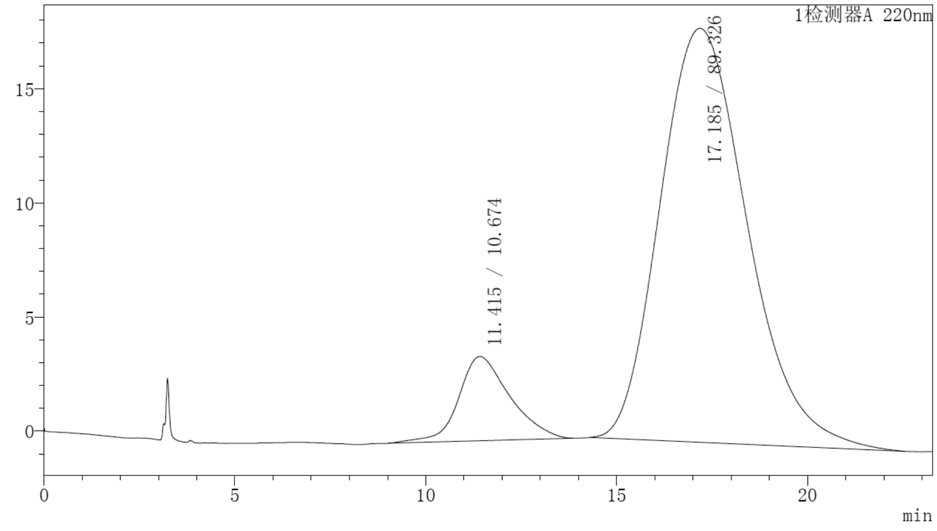
峰号	保留时间	面积	高度	标记	面积%
1	12.256	8061718	86464		49.384
2	17.198	8262922	63708	V	50.616
总计		16324640	150172		100.000

分析日期/时间　　　　　　　: 2018/7/10 23:30:06
处理日期/时间　　　　　　　: 2018/7/10 23:53:23
描述　　　　　　　　　　　: OJ-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



S-**2s**

色谱图



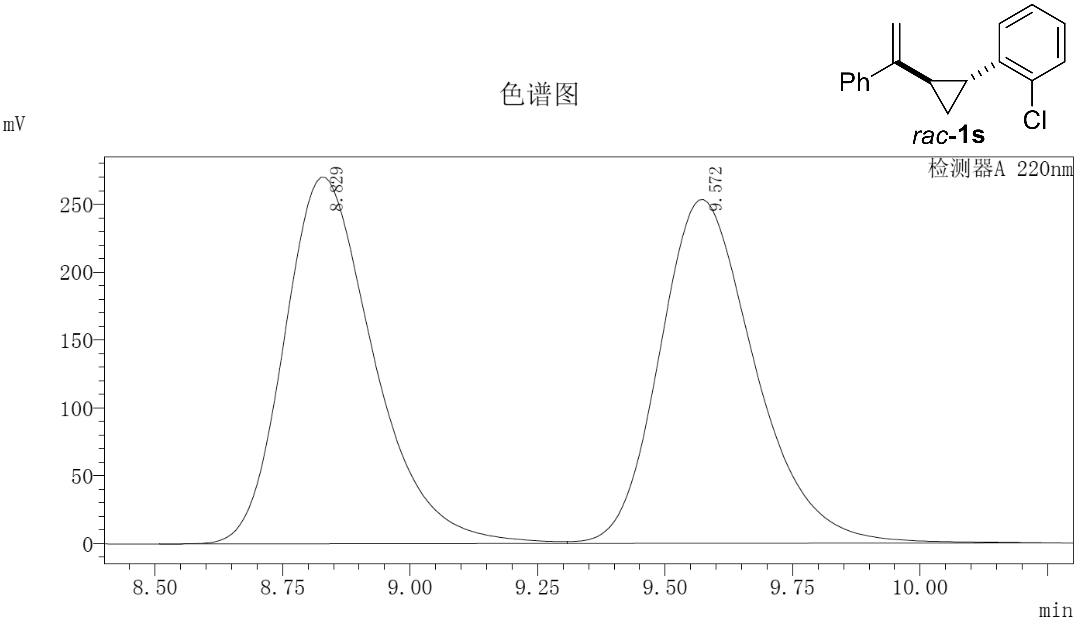
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	11.415	344552	3695		10.674
2	17.185	2883342	18126		89.326
总计		3227894	21821		100.000

Figure S187. HPLC spectra of *S*-**2s**, Related to Table 2

分析日期　　　: 2018/7/10 21:25:53
处理日期　　　: 2018/7/10 21:36:48
描述　　　　　: OJ-H , n-hexane/iPrOH = 99.5/0.5, 1.0 mL/min, 220 nm

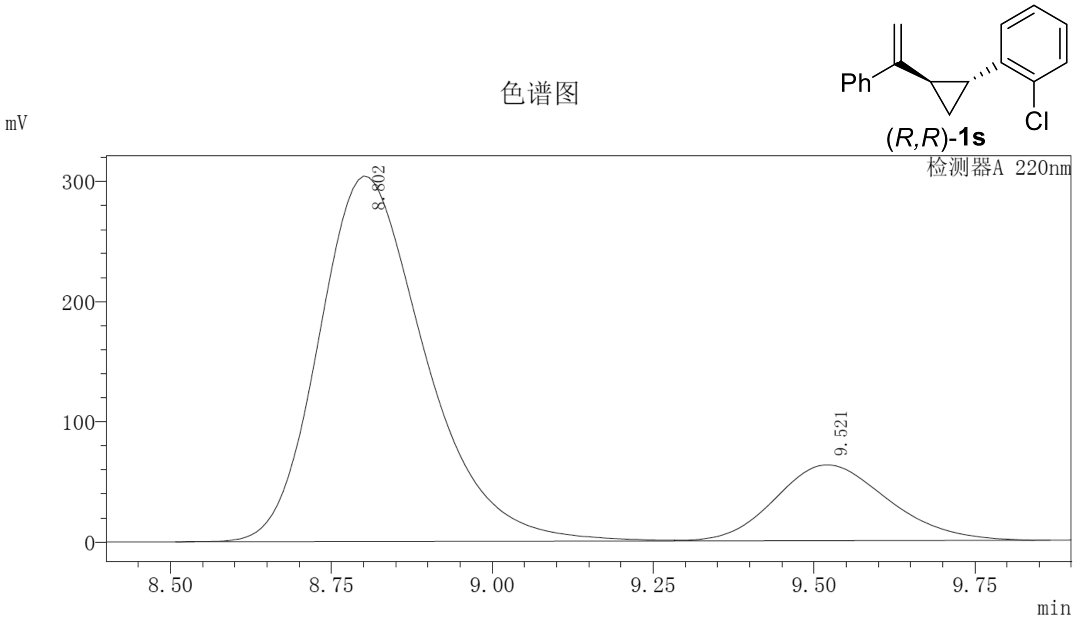


峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.829	3301115	269837		50.033
2	9.572	3296697	253189	V M	49.967
总计		6597812	523026		100.000

分析日期　　　: 2018/7/10 21:38:48
处理日期　　　: 2018/7/10 22:01:54
描述　　　　　: OJ-H , n-hexane/iPrOH = 99.5/0.5, 1.0 mL/min, 220 nm



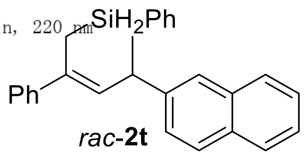
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.802	3488944	303957		81.908
2	9.521	770651	63085	V	18.092
总计		4259595	367041		100.000

Figure S188. HPLC spectra of (*R,R*)-**1s**, Related to Table 2

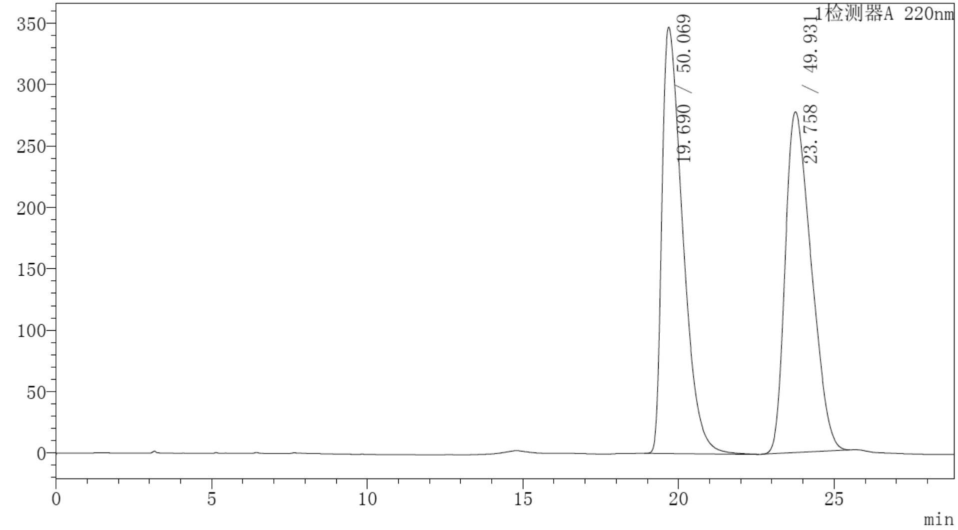
分析日期/时间　　　　　　　　: 2018/7/7 12:44:34
处理日期/时间　　　　　　　　: 2018/7/7 13:13:26
描述　　　　　　　　　　　　: OD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



rac-**2t**

色谱图

mV

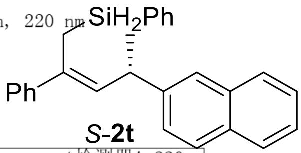


峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	19.690	16157173	347281		50.069
2	23.758	16112572	277516		49.931
总计		32269744	624797		100.000

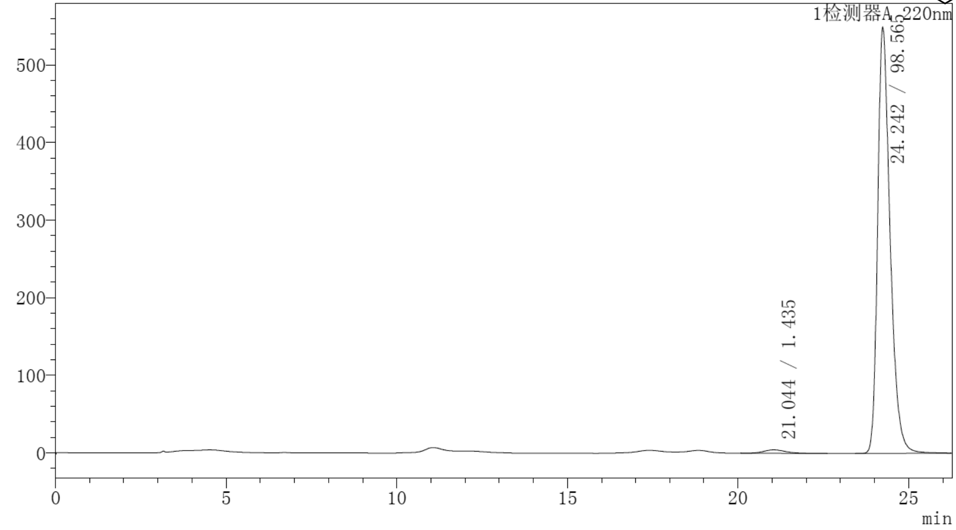
分析日期/时间　　　　　　　　: 2018/7/7 13:16:08
处理日期/时间　　　　　　　　: 2018/7/7 13:42:25
描述　　　　　　　　　　　　: OD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



S-**2t**

色谱图

mV



峰表

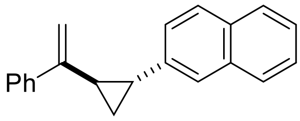
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	21.044	203498	4512		1.435
2	24.242	13973714	549819		98.565
总计		14177212	554331		100.000

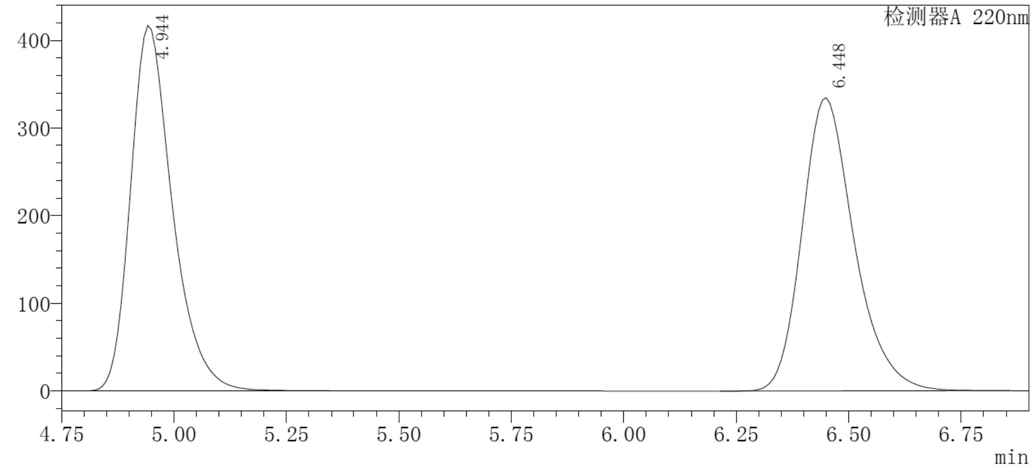
Figure S189. HPLC spectra of *S*-**2t**, Related to Table 2

分析日期　　: 2018/7/8 17:52:28
处理日期　　: 2018/7/8 18:00:17
描述　　　　: AD-H , n-hexane/iPrOH = 98/2, 1.0 mL/min, 220 nm

色谱图



rac-**1t**



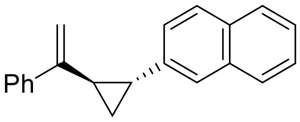
峰表

检测器A 220nm

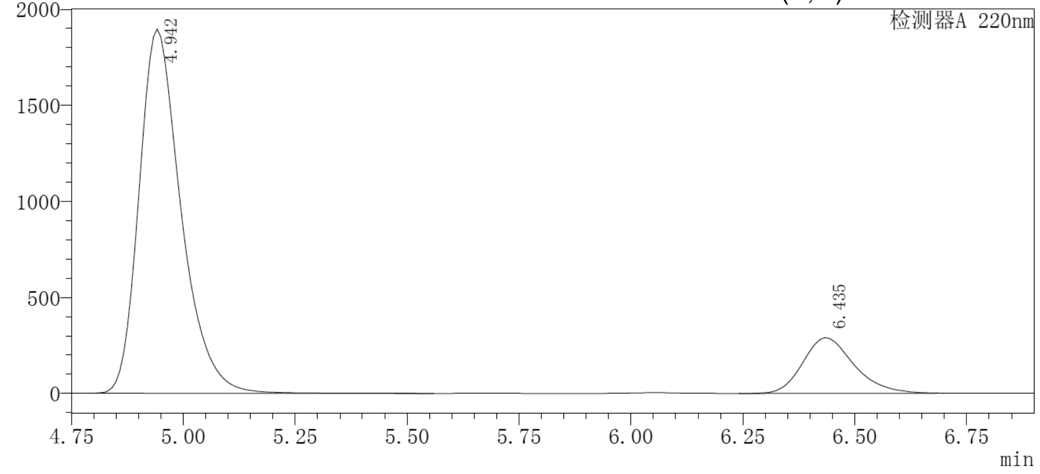
峰号	保留时间	面积	高度	标记	面积%
1	4.944	2698021	417196		50.032
2	6.448	2694577	334761	M	49.968
总计		5392598	751957		100.000

分析日期　　: 2018/7/8 18:01:13
处理日期　　: 2018/7/8 18:08:39
描述　　　　: AD-H , n-hexane/iPrOH = 98/2, 1.0 mL/min, 220 nm

色谱图



(*R*,*R*)-**1t**



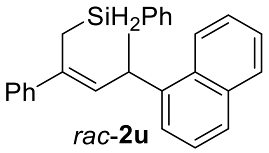
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	4.942	12318655	1896101		84.232
2	6.435	2306021	289877		15.768
总计		14624676	2185979		100.000

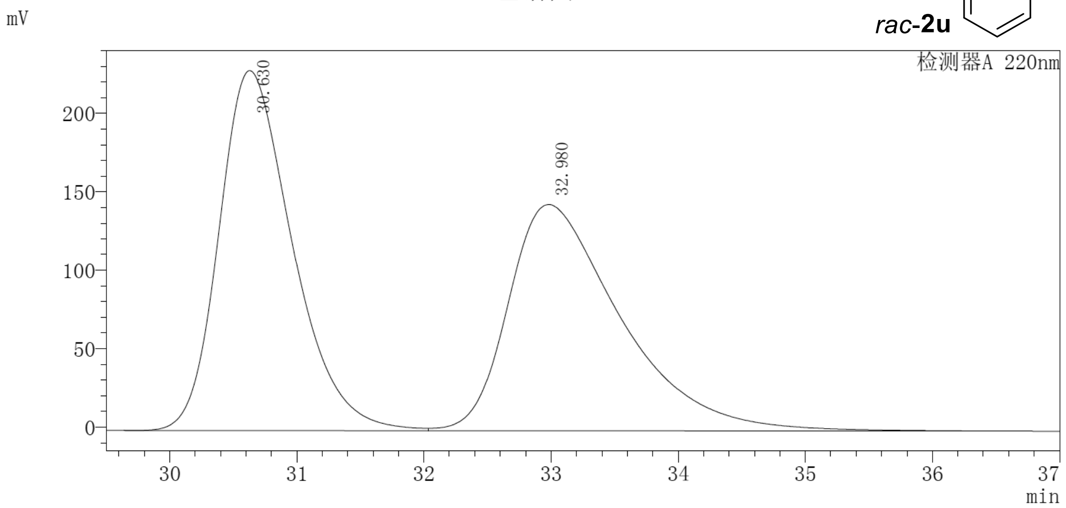
Figure S190. HPLC spectra of (*R*,*R*)-**1t**, Related to Table 2

分析日期　　　: 2018/7/7 14:31:21
处理日期　　　: 2018/7/7 15:08:39
描述　　　　　: OD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



rac-**2u**

色谱图

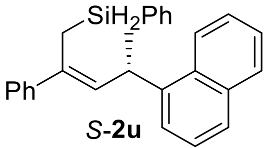


峰表

检测器A 220nm

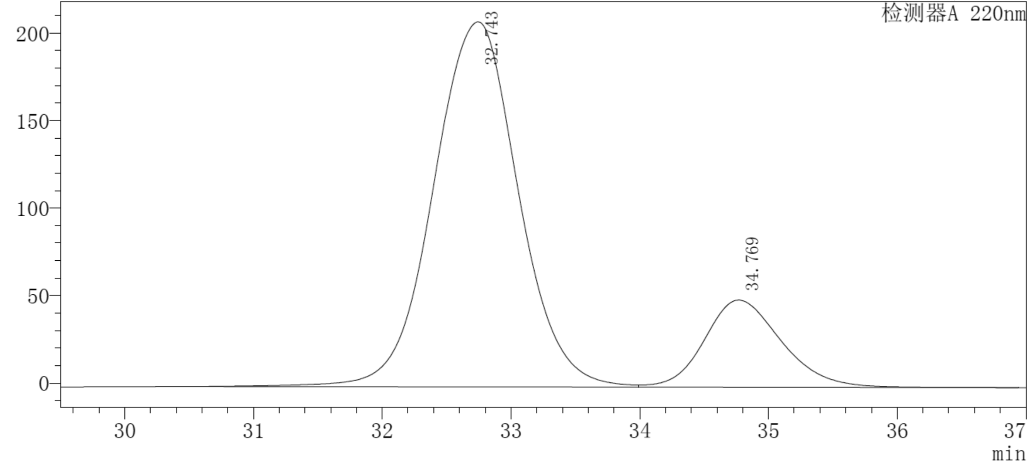
峰号	保留时间	面积	高度	标记	面积%
1	30.630	9212034	229504		50.879
2	32.980	8893718	144243	V M	49.121
总计		18105751	373746		100.000

分析日期　　　: 2018/7/7 15:10:00
处理日期　　　: 2018/7/7 15:47:03
描述　　　　　: OD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



S-**2u**

色谱图



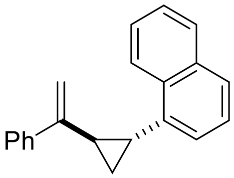
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	32.743	9576128	208563	M	82.183
2	34.769	2076055	49799	V M	17.817
总计		11652183	258363		100.000

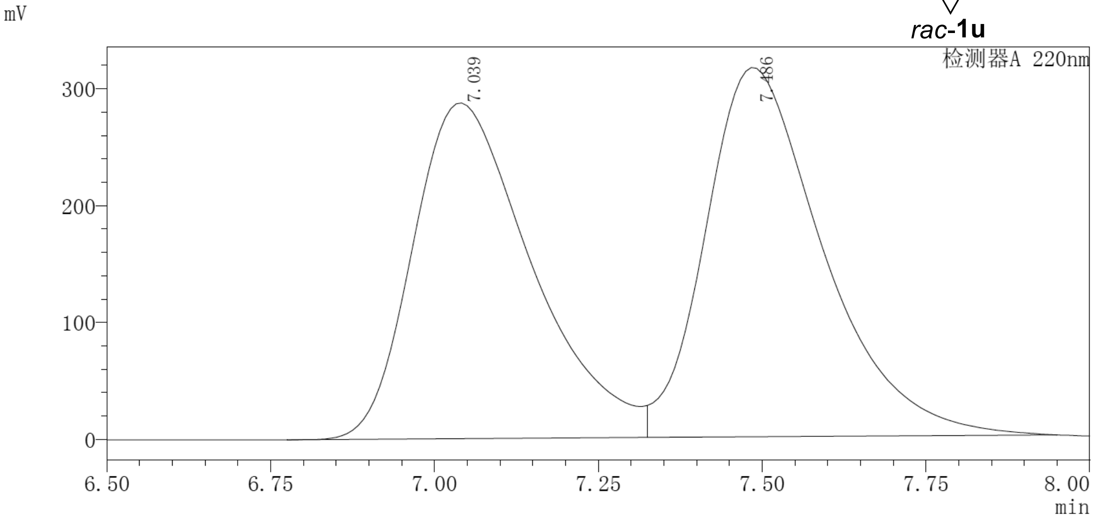
Figure S191. HPLC spectra of *S*-**2u**, Related to Table 2

分析日期　　: 2018/7/9 10:41:01
处理日期　　: 2018/7/9 10:49:21
描述　　　　: AD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



rac-**1u**

色谱图

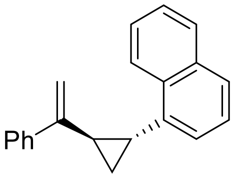


峰表

检测器A 220nm

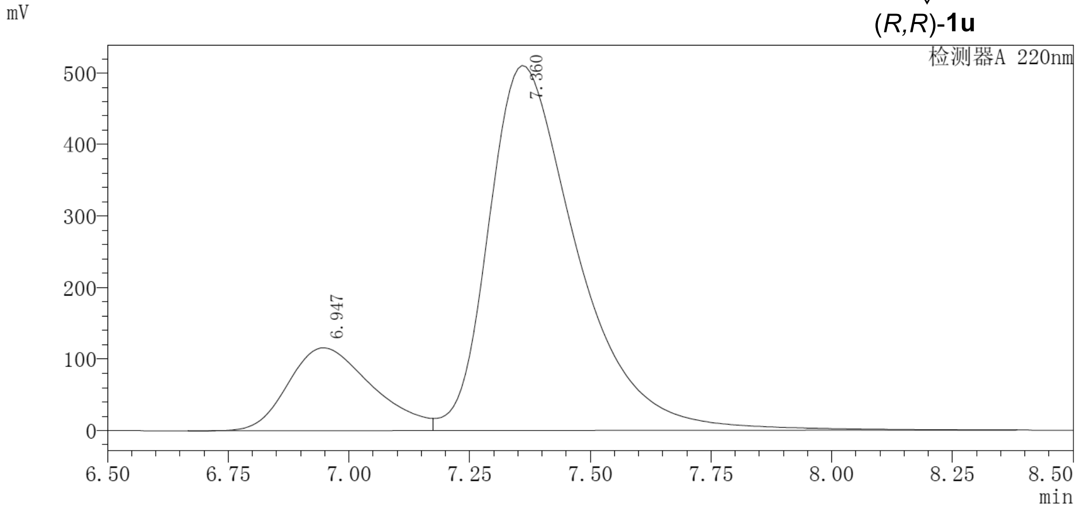
峰号	保留时间	面积	高度	标记	面积%
1	7.039	3634427	287188	M	48.004
2	7.486	3936631	315763	V M	51.996
总计		7571058	602951		100.000

分析日期　　: 2018/7/9 10:50:14
处理日期　　: 2018/7/9 10:59:02
描述　　　　: AD-H , n-hexane/iPrOH = 99.9/0.1, 1.0 mL/min, 220 nm



(*R*,*R*)-**1u**

色谱图



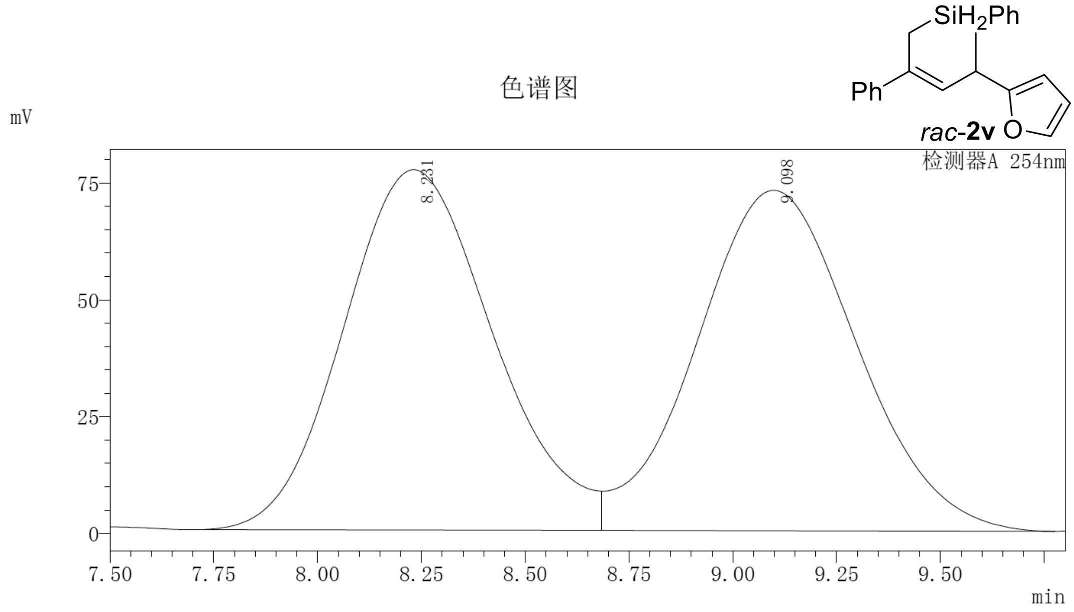
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	6.947	1408210	115790		17.747
2	7.360	6526896	510334	V M	82.253
总计		7935105	626124		100.000

Figure S192. HPLC spectra of (*R*,*R*)-**1u**, Related to Table 2

分析日期　　: 2018/10/10 14:15:20
处理日期　　: 2018/10/10 14:27:24
描述　　　　: OJ-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm

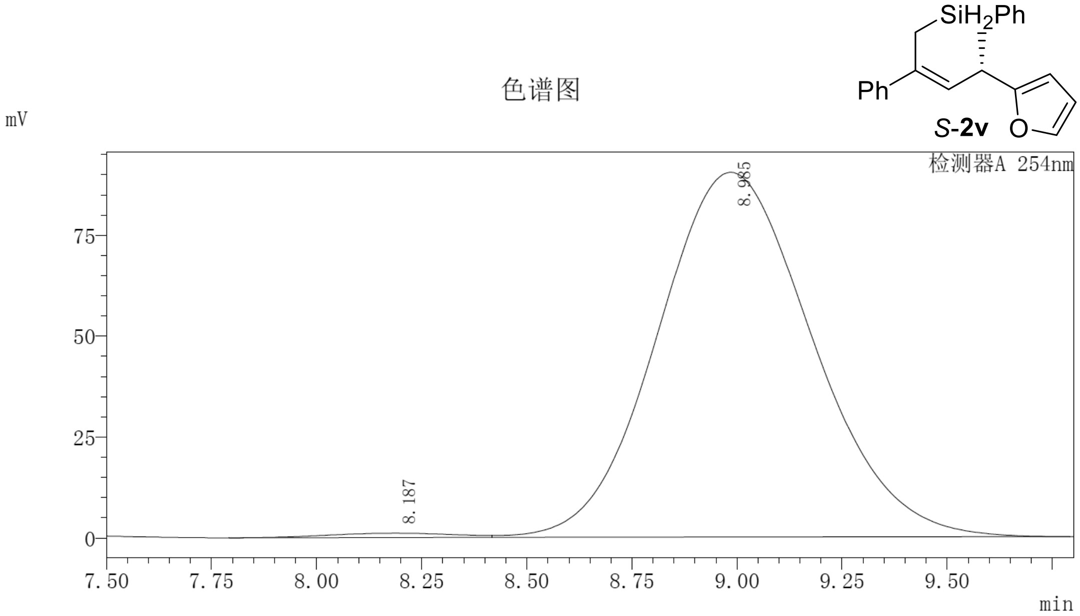


峰表

检测器A 254nm

峰号	保留时间	面积	高度	标记	面积%
1	8.231	1932004	77164		49.780
2	9.098	1949061	72915	V	50.220
总计		3881065	150080		100.000

分析日期　　: 2018/10/10 14:36:51
处理日期　　: 2018/10/10 14:50:39
描述　　　　: OJ-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm



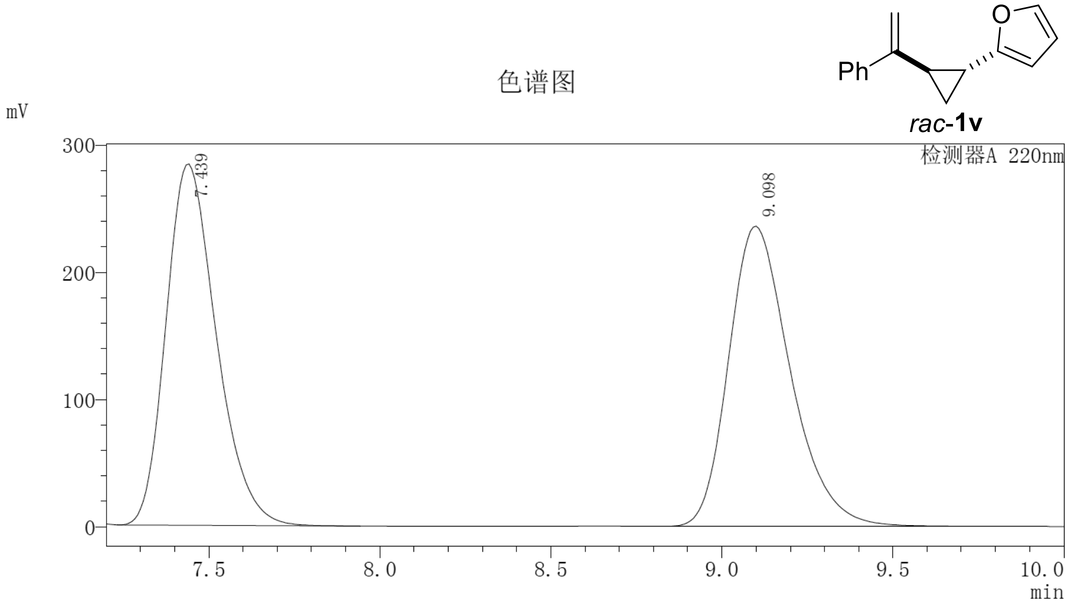
峰表

检测器A 254nm

峰号	保留时间	面积	高度	标记	面积%
1	8.187	22771	1084		0.973
2	8.985	2316403	90364	V	99.027
总计		2339174	91448		100.000

Figure S193. HPLC spectra of *S*-**2v**, Related to Table 2

分析日期　　: 2018/10/10 11:43:21
处理日期　　: 2018/10/10 11:55:36
描述　　　　: OJ-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm

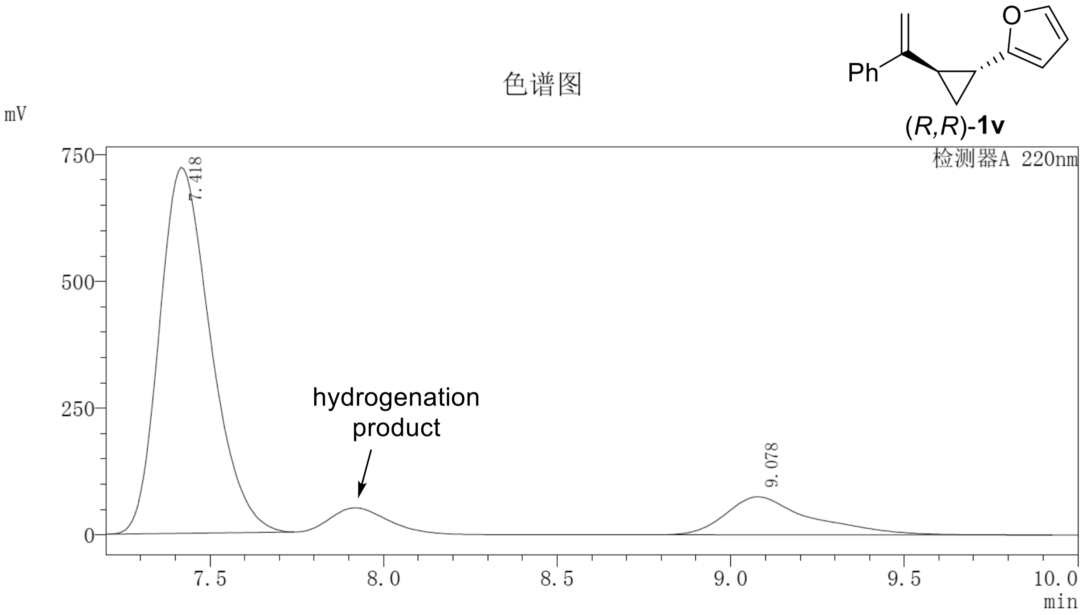


峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	7.439	2907454	283965		49.572
2	9.098	2957710	235931	M	50.428
总计		5865164	519896		100.000

分析日期　　: 2018/10/10 11:57:32
处理日期　　: 2018/10/10 12:12:48
描述　　　　: OJ-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm



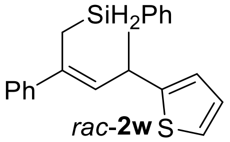
峰表

检测器A 220nm

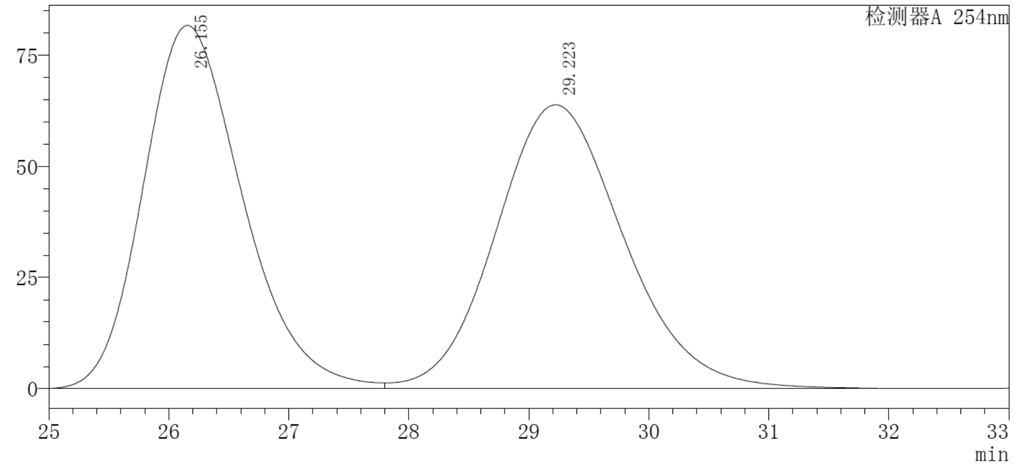
峰号	保留时间	面积	高度	标记	面积%
1	7.418	7400218	721645	M	85.293
2	9.078	1275994	74941		14.707
总计		8676212	796586		100.000

Figure S194. HPLC spectra of (*R,R*)-**1v**, Related to Table 2

分析日期　　: 2018/10/13 9:37:58
处理日期　　: 2018/10/13 10:11:57
描述　　　　: 2*OJ-H, n-hexane/iPrOH =99.5/0.5, 1.0 ml/min, 220 nm


rac-**2w**

色谱图

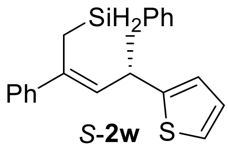


峰表

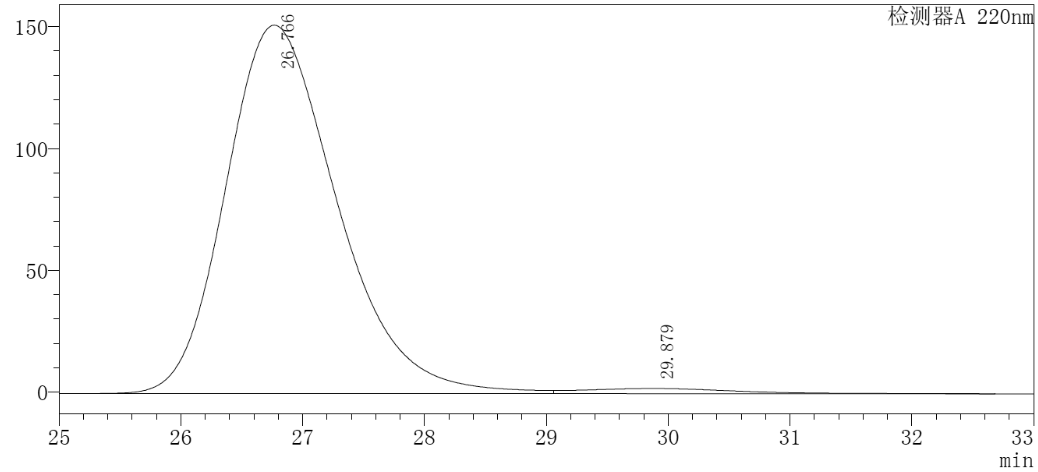
检测器A 254nm

峰号	保留时间	面积	高度	标记	面积%
1	26.155	4693451	81637	M	49.810
2	29.223	4729200	63794	V	50.190
总计		9422651	145430		100.000

分析日期　　: 2018/10/15 20:59:46
处理日期　　: 2018/10/15 21:37:01
描述　　　　: OJ-H*2, n-hexane/iPrOH =99.5/0.5, 1.0 ml/min, 220 nm


S-**2w**

色谱图



峰表

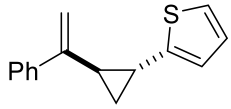
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	26.766	9610627	151201		98.093
2	29.879	186798	2118	V	1.907
总计		9797425	153319		100.000

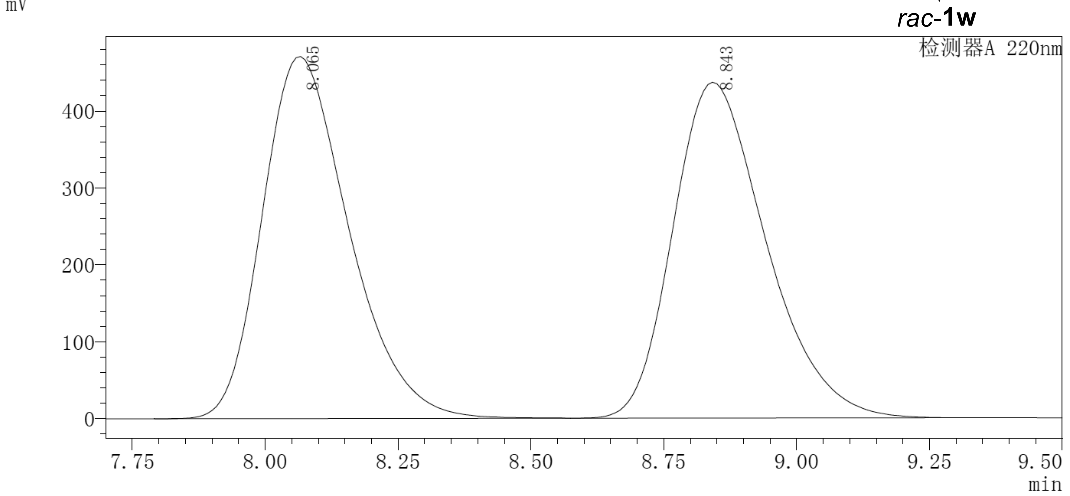
Figure S195. HPLC spectra of *S*-**2w**, Related to Table 2

分析日期　　: 2018/10/10 12:14:18
处理日期　　: 2018/10/10 12:26:05
描述　　　　: OJ-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm

色谱图



rac-**1w**



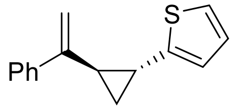
峰表

检测器A 220nm

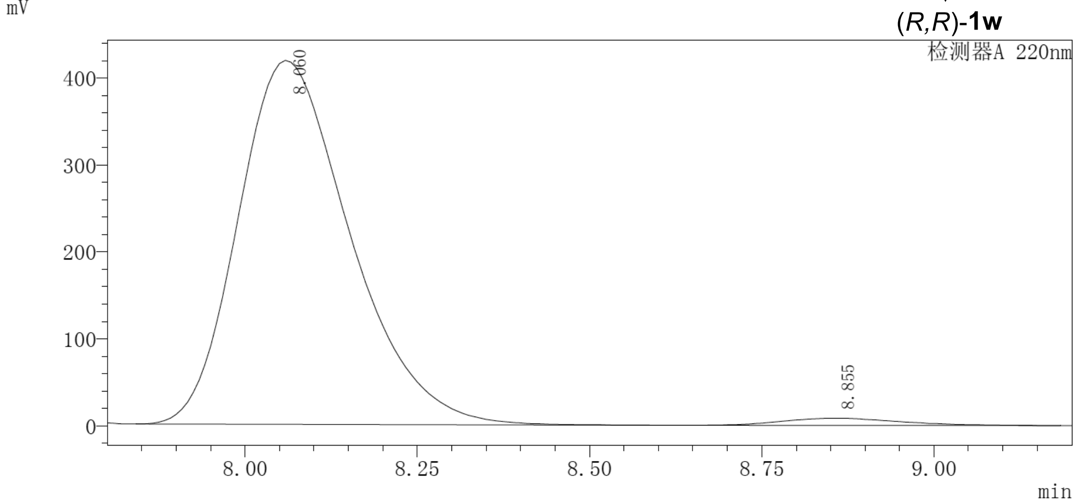
峰号	保留时间	面积	高度	标记	面积%
1	8.065	5343543	470861		50.074
2	8.843	5327701	436826	V	49.926
总计		10671245	907687		100.000

分析日期　　: 2018/10/10 12:27:19
处理日期　　: 2018/10/10 12:42:26
描述　　　　: OJ-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm

色谱图



(*R*,*R*)-**1w**



峰表

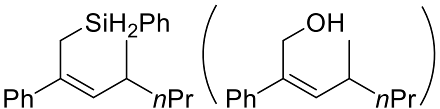
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	8.060	4726750	418757		98.023
2	8.855	95344	8166		1.977
总计		4822094	426924		100.000

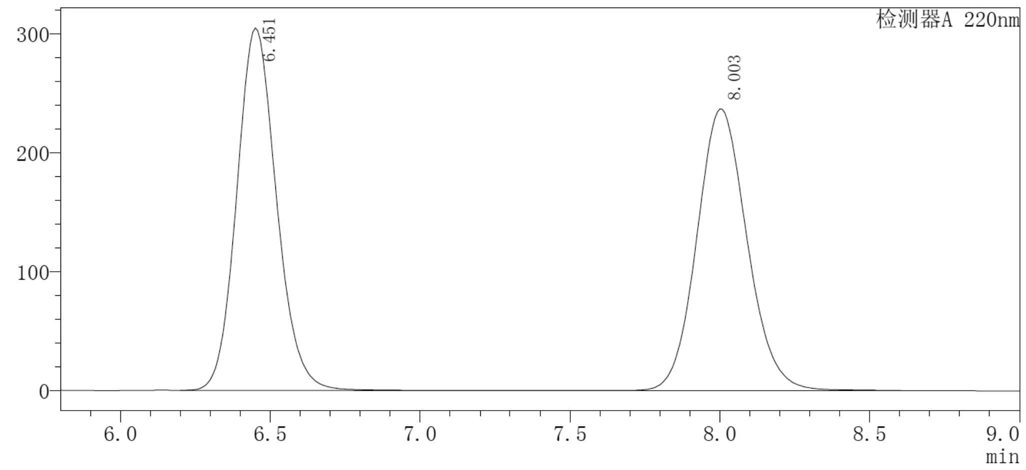
Figure S196. HPLC spectra of (*R*,*R*)-**1w**, Related to Table 2

分析日期　　: 2018/3/2 19:23:51
处理日期　　: 2018/3/2 19:33:12
描述　　　　: OD-H, n-Hexane/iPrOH = 95/5, 1.0 mL/min, 220 nm

色谱图



rac-**2x**



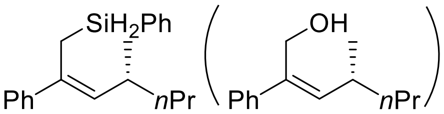
峰表

检测器A 220nm

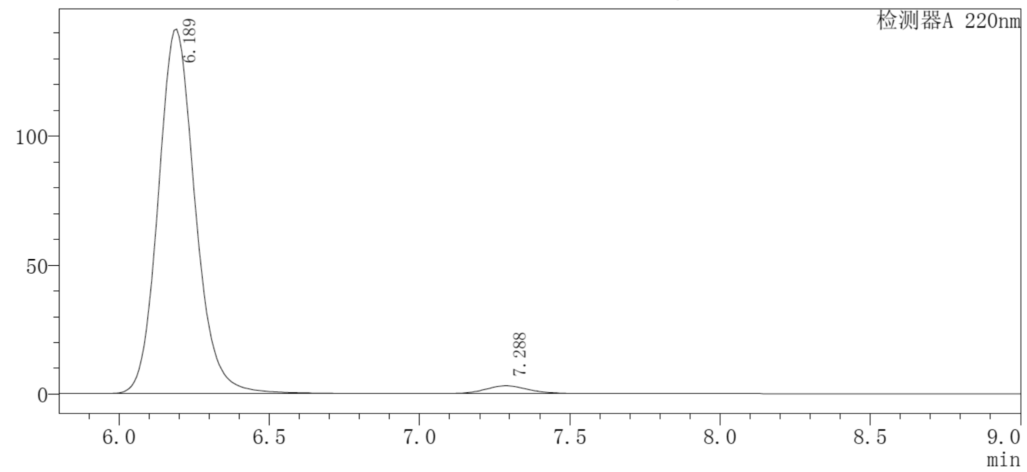
峰号	保留时间	面积	高度	标记	面积%
1	6.451	2810631	304582		50.404
2	8.003	2765613	236799	V M	49.596
总计		5576244	541381		100.000

分析日期　　: 2019/1/16 19:05:37
处理日期　　: 2019/1/16 19:18:33
描述　　　　: OD-H, n-hexane/iPrOH =95/5, 1.0 ml/min, 220 nm

色谱图



S-**2x**



峰表

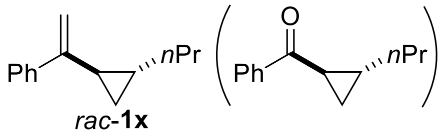
检测器A 220nm

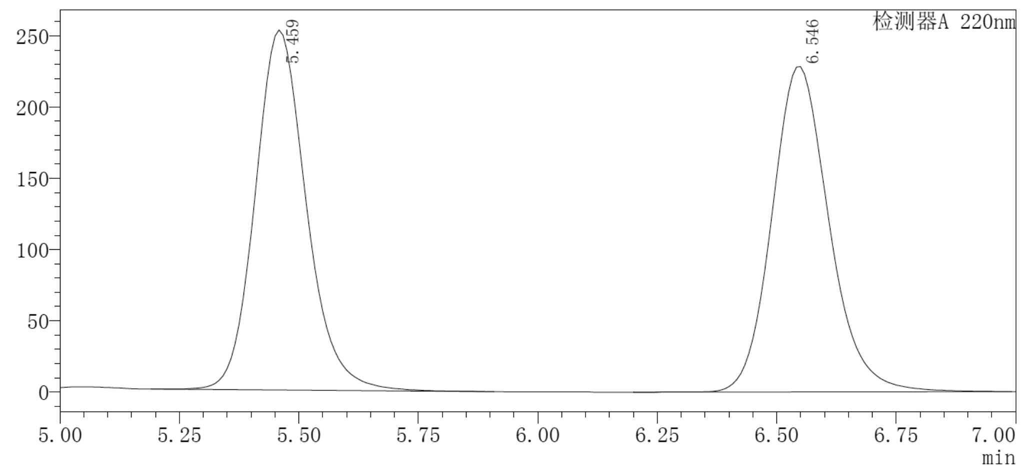
峰号	保留时间	面积	高度	标记	面积%
1	6.189	1207869	141267		97.600
2	7.288	29706	3000		2.400
总计		1237575	144267		100.000

Figure S197. HPLC spectra of *S*-**2x**, Related to Table 2

分析日期　　: 2019/1/16 16:09:13
处理日期　　: 2019/1/16 16:18:42
描述　　　　: OD-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm

色谱图


rac-**1x**



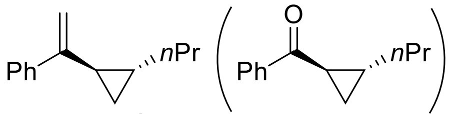
峰表

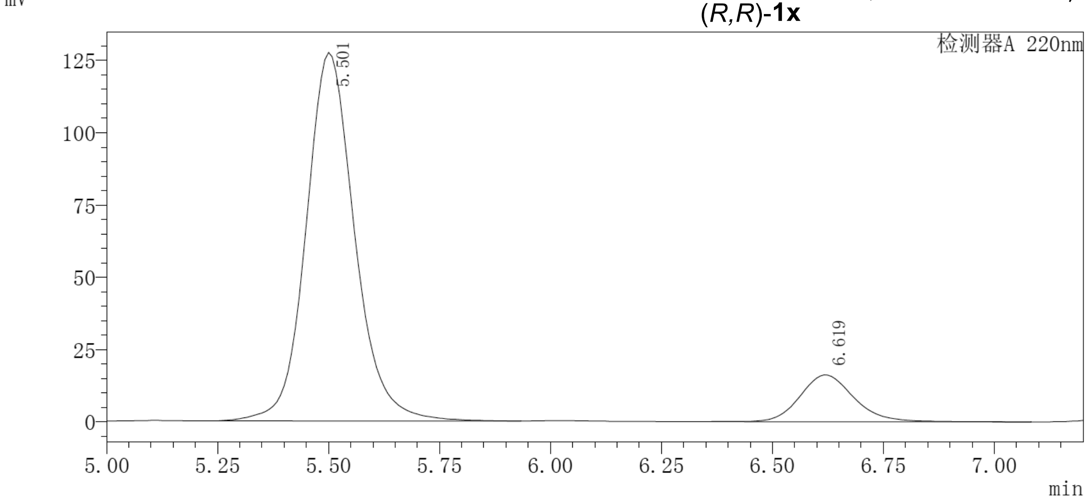
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	5.459	1884603	252766		49.839
2	6.546	1896755	228479	M	50.161
总计		3781358	481245		100.000

分析日期　　: 2019/1/16 17:47:56
处理日期　　: 2019/1/16 17:56:20
描述　　　　: OD-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm

色谱图


(*R*,*R*)-**1x**



峰表

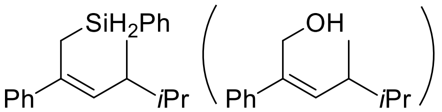
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	5.501	969381	127402		87.587
2	6.619	137381	16178		12.413
总计		1106761	143580		100.000

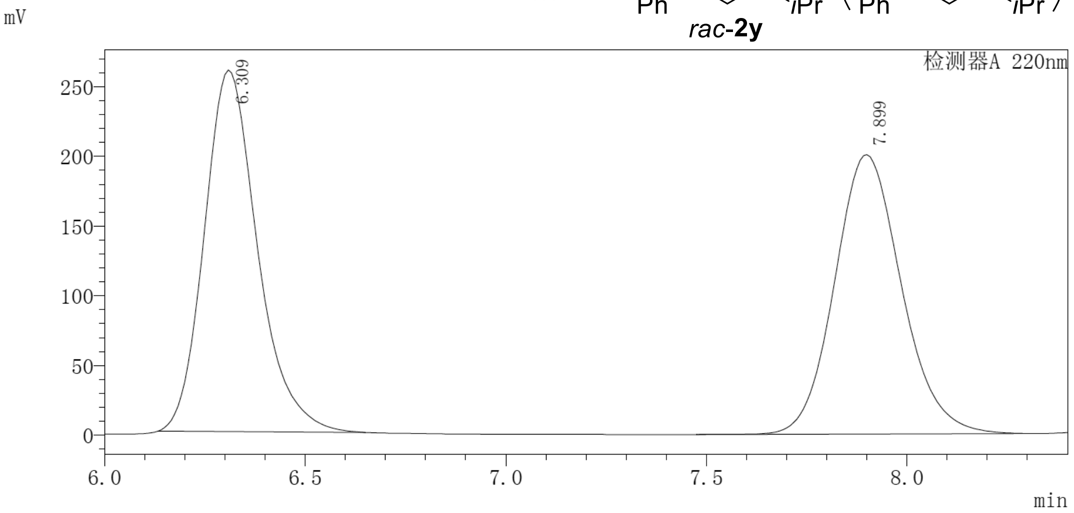
Figure S198. HPLC spectra of (*R*,*R*)-**1x**, Related to Table 2

分析日期　　　: 2018/3/2 20:12:12
处理日期　　　: 2018/3/2 20:21:52
描述　　　　　: OD-H, n-Hexane/iPrOH = 95/5, 1.0 mL/min, 220 nm

色谱图



rac-**2y**



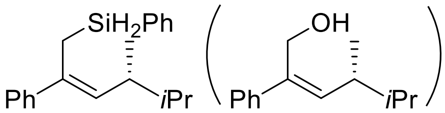
峰表

检测器A 220nm

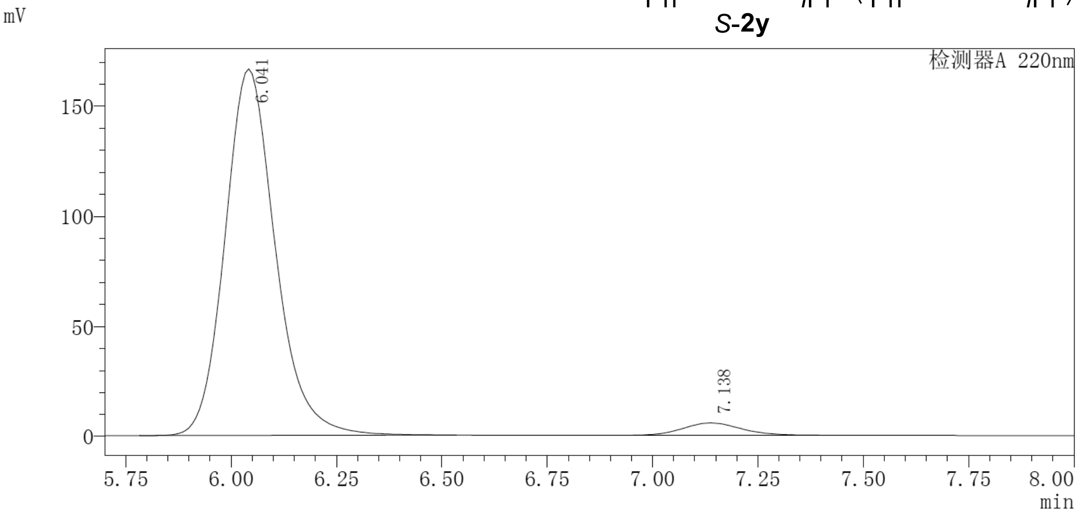
峰号	保留时间	面积	高度	标记	面积%
1	6.309	2389966	259373	M	50.755
2	7.899	2318824	200507		49.245
总计		4708790	459880		100.000

分析日期　　　: 2019/1/16 19:20:30
处理日期　　　: 2019/1/16 19:35:39
描述　　　　　: OD-H, n-hexane/iPrOH =95/5, 1.0 ml/min, 220 nm

色谱图



S-**2y**



峰表

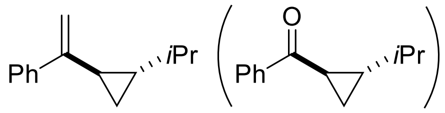
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	6.041	1383771	166400	M	96.244
2	7.138	54000	5607	M	3.756
总计		1437771	172007		100.000

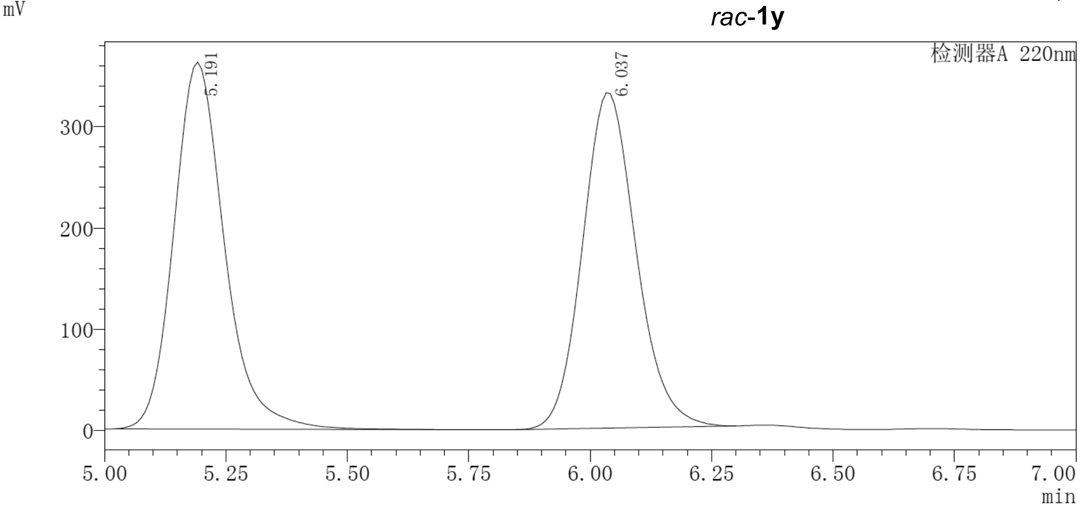
Figure S199. HPLC spectra of *S*-**2y**, Related to Table 2

分析日期　　　: 2019/1/16 16:29:45
处理日期　　　: 2019/1/16 16:43:35
描述　　　　　: OD-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm

色谱图



rac-**1y**



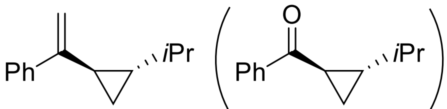
峰表

检测器A 220nm

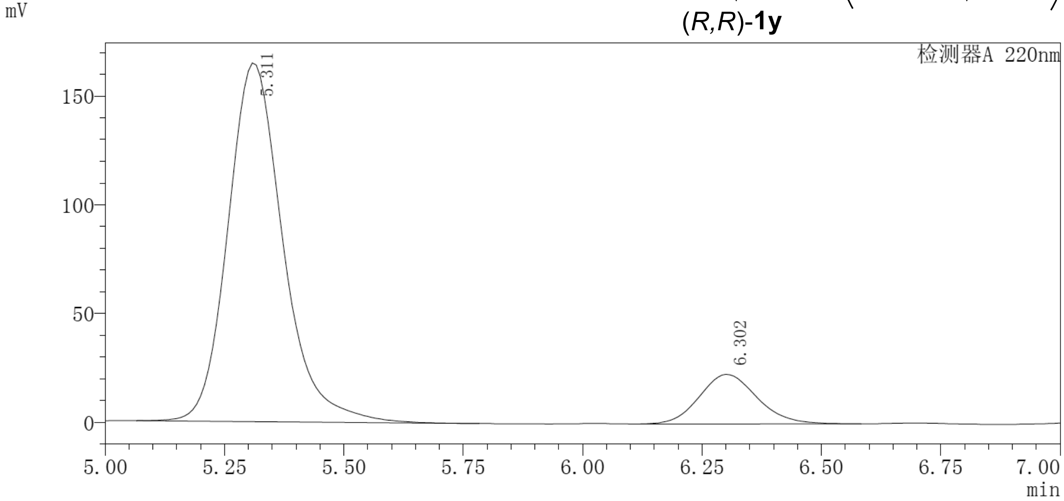
峰号	保留时间	面积	高度	标记	面积%
1	5.191	2627795	362100	M	50.803
2	6.037	2544734	330999	M	49.197
总计		5172530	693099		100.000

分析日期　　　: 2019/1/16 16:19:41
处理日期　　　: 2019/1/16 16:28:32
描述　　　　　: OD-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm

色谱图



(*R*,*R*)-**1y**



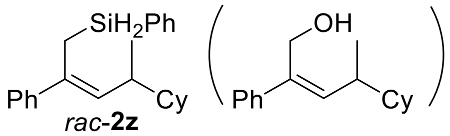
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	5.311	1320671	164998		87.299
2	6.302	192140	22803		12.701
总计		1512811	187802		100.000

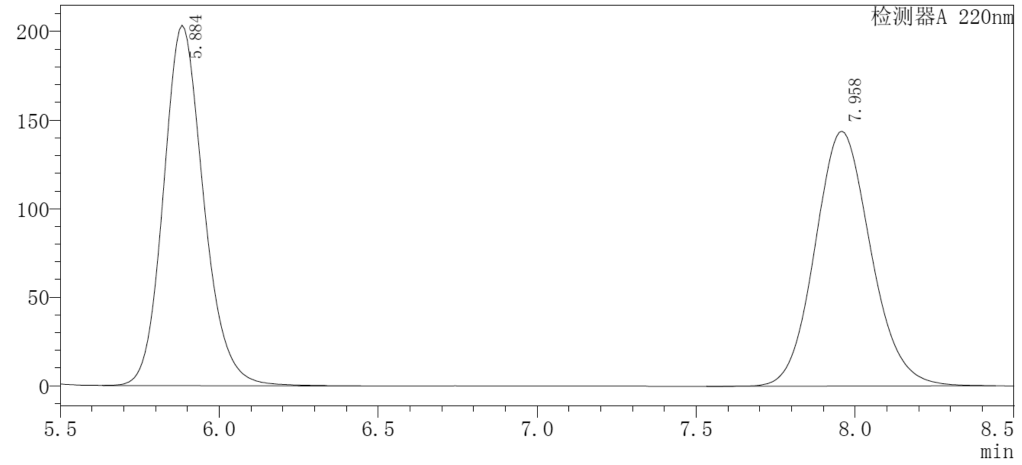
Figure S200. HPLC spectra of (*R*,*R*)-**1y**, Related to Table 2

分析日期　　　: 2018/2/7 15:24:31
处理日期　　　: 2018/2/7 15:37:01
描述　　　　　: OD-H, n-hexane/iPrOH =95/5, 1.0 ml/min, 220 nm



rac-**2z**

色谱图

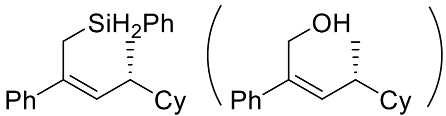


峰表

检测器A 220nm

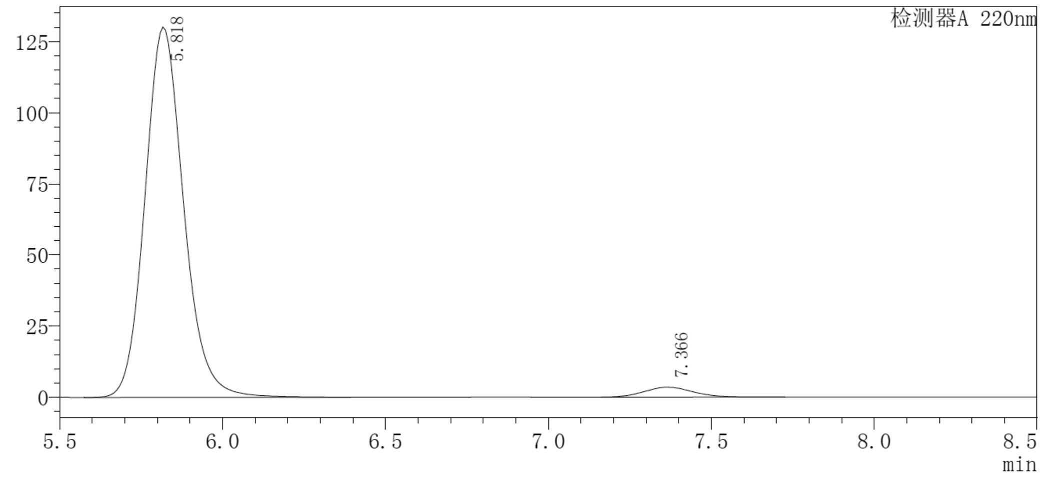
峰号	保留时间	面积	高度	标记	面积%
1	5.884	1792011	203323		50.550
2	7.958	1753036	143827	M	49.450
总计		3545047	347149		100.000

分析日期　　　: 2019/1/16 19:37:14
处理日期　　　: 2019/1/16 19:58:33
描述　　　　　: OD-H, n-hexane/iPrOH =95/5, 1.0 ml/min, 220 nm



S-**2z**

色谱图



峰表

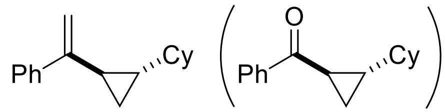
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	5.818	1076758	130160		96.703
2	7.366	36716	3487		3.297
总计		1113473	133647		100.000

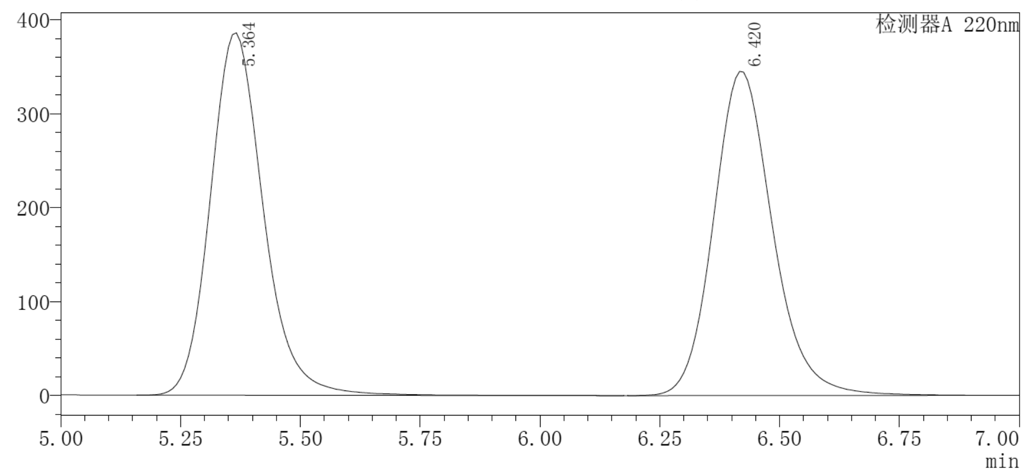
Figure S201. HPLC spectra of *S*-**2z**, Related to Table 2

分析日期　　: 2019/1/16 16:57:27
处理日期　　: 2019/1/16 17:05:41
描述　　　　: OD-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm

色谱图



rac-**1z**



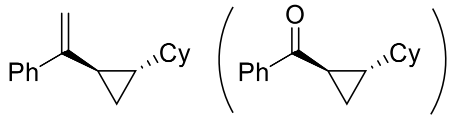
峰表

检测器A 220nm

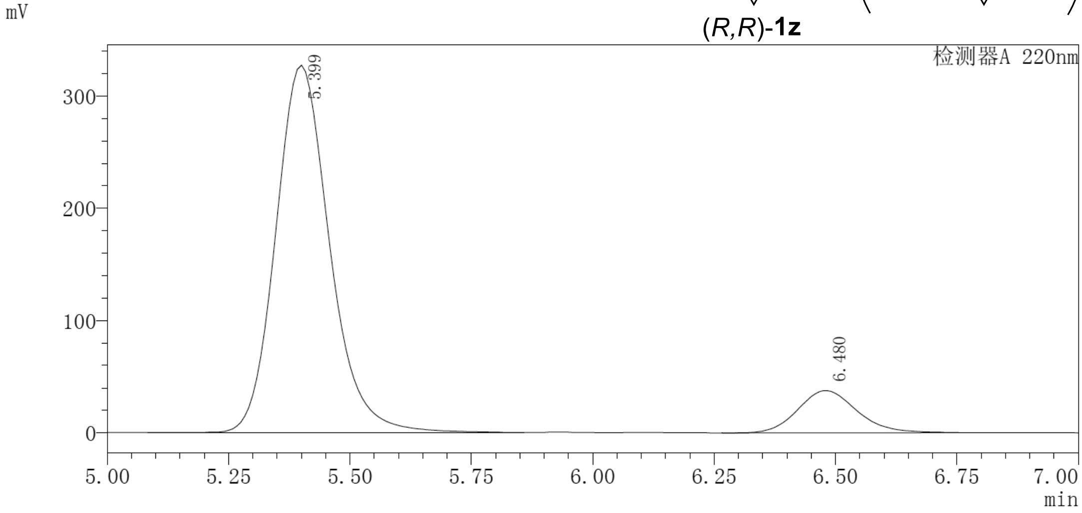
峰号	保留时间	面积	高度	标记	面积%
1	5.364	2961691	385784	S	49.994
2	6.420	2962430	345185	M	50.006
总计		5924121	730969		100.000

分析日期　　: 2019/1/16 16:45:21
处理日期　　: 2019/1/16 16:53:05
描述　　　　: OD-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm

色谱图



(*R*,*R*)-**1z**



峰表

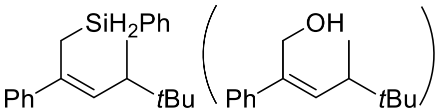
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	5.399	2510548	327245		88.769
2	6.480	317647	37536	M	11.231
总计		2828195	364781		100.000

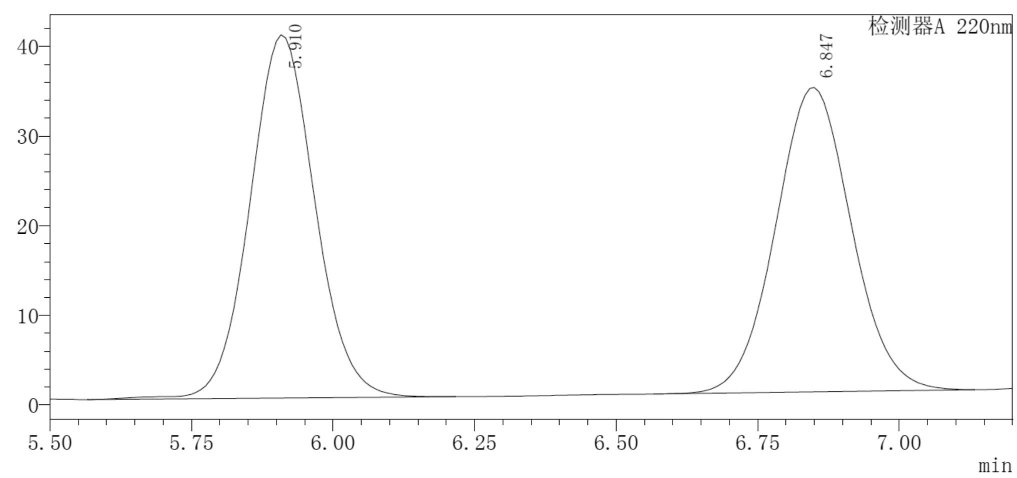
Figure S202. HPLC spectra of (*R*,*R*)-**1z**, Related to Table 2

分析日期　　　: 2019/2/16 10:06:42
处理日期　　　: 2019/2/16 10:15:15
描述　　　　　: OD-H, n-hexane/iPrOH = 95/5, 1.0 ml/min, 220 nm

色谱图



rac-**2aa**



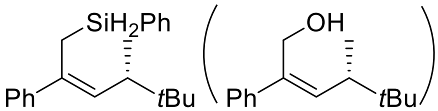
峰表

检测器A 220nm

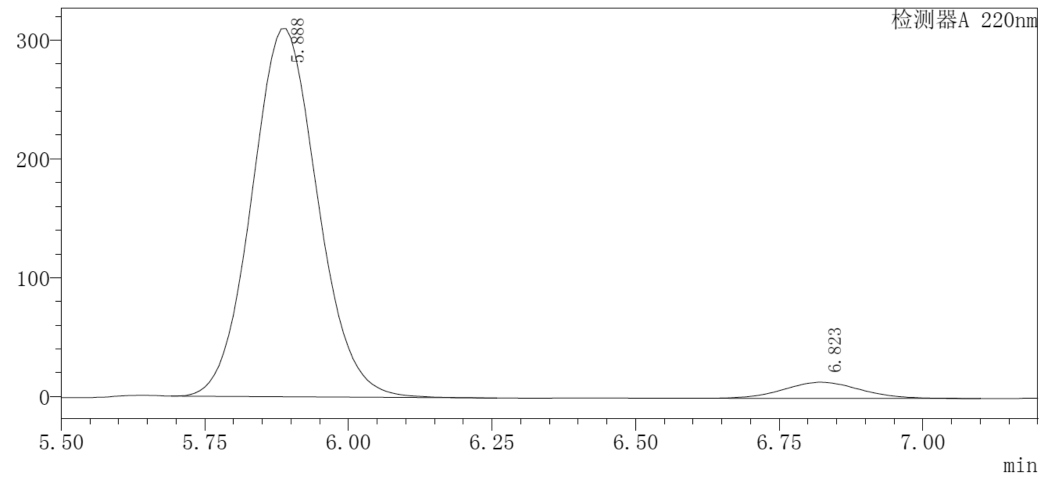
峰号	保留时间	面积	高度	标记	面积%
1	5.910	323881	40534		50.537
2	6.847	316999	33996		49.463
总计		640880	74531		100.000

分析日期　　　: 2019/2/16 10:26:45
处理日期　　　: 2019/2/16 10:34:22
描述　　　　　: OD-H, n-hexane/iPrOH = 95/5, 1.0 ml/min, 220 nm

色谱图



S-**2aa**



峰表

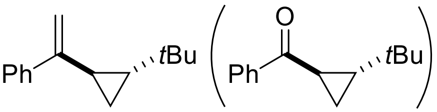
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	5.888	2470836	309699		95.134
2	6.823	126379	13613		4.866
总计		2597215	323313		100.000

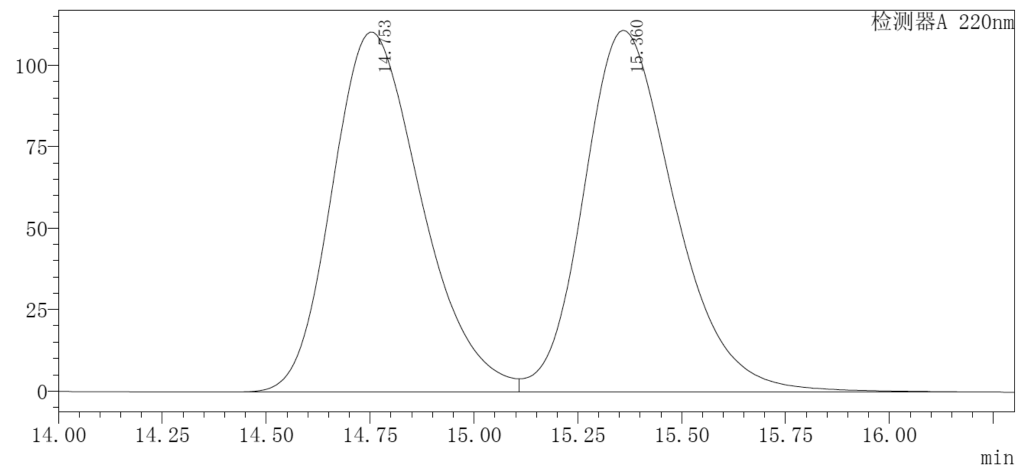
Figure S203. HPLC spectra of *S*-**2aa**, Related to Table 2

分析日期　　: 2019/2/22 11:17:36
处理日期　　: 2019/2/22 11:36:21
描述　　　　: 2*OJ-H, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm

色谱图



rac-**1aa**



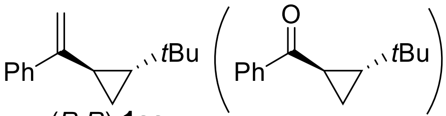
峰表

检测器A 220nm

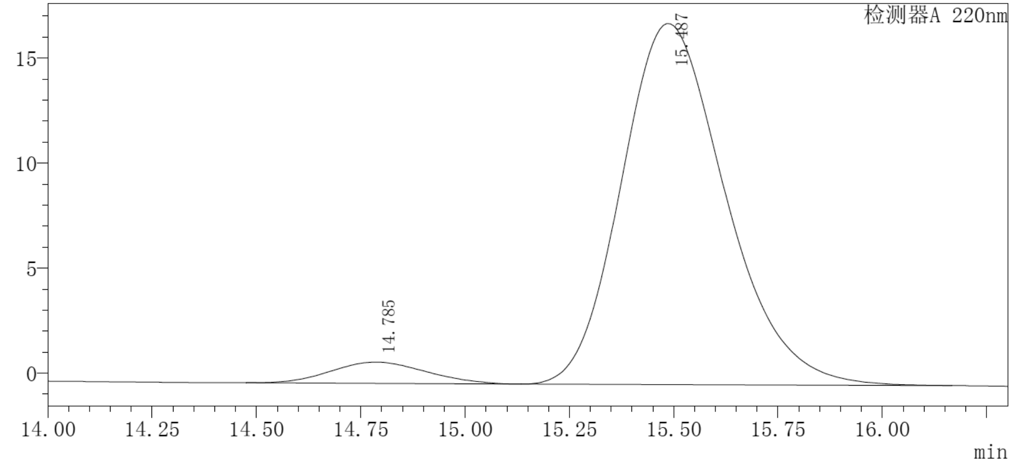
峰号	保留时间	面积	高度	标记	面积%
1	14.753	1655008	110527		49.430
2	15.360	1693155	111030	V M	50.570
总计		3348163	221556		100.000

分析日期　　: 2019/2/22 11:42:23
处理日期　　: 2019/2/22 12:02:43
描述　　　　: 2*OJ-H, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm

色谱图



(*R*,*R*)-**1aa**



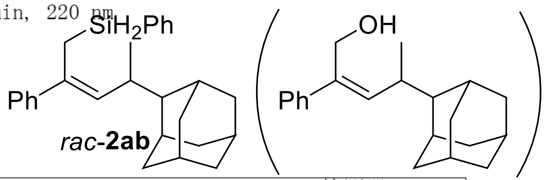
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	14.785	16205	1016		5.154
2	15.487	298217	17188	M	94.846
总计		314422	18204		100.000

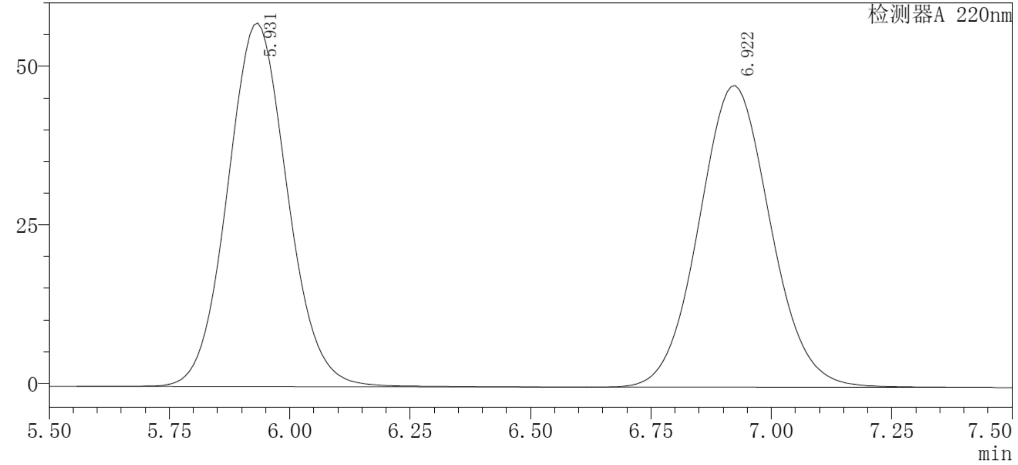
Figure S204. HPLC spectra of (*R,R*)-**1aa**, Related to Table 2

分析日期　　　: 2019/2/16 10:38:55
处理日期　　　: 2019/2/16 10:48:56
描述　　　　　: OD-H, n-hexane/iPrOH = 95/5, 1.0 ml/min, 220 nm



rac-**2ab**

色谱图

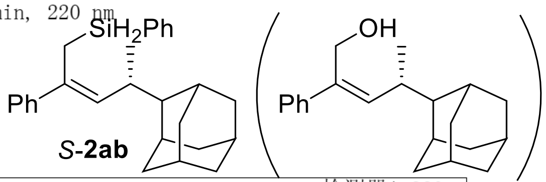


峰表

检测器A 220nm

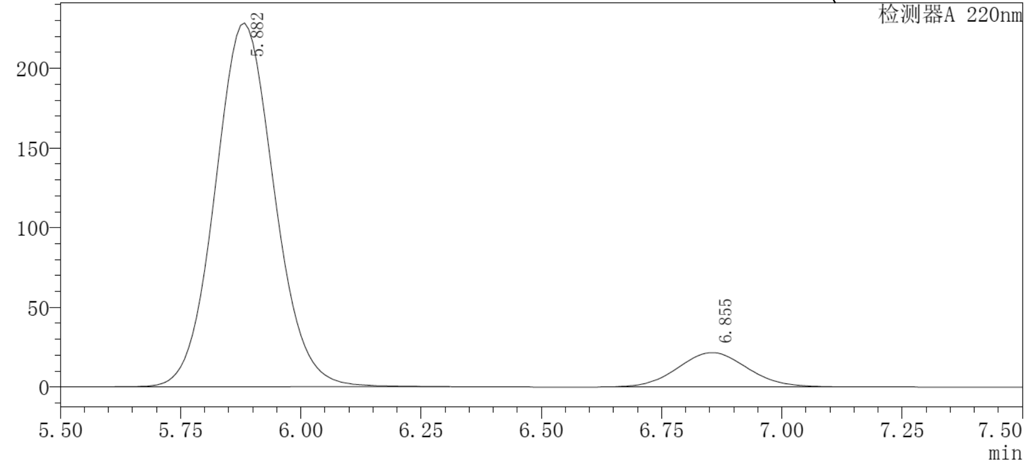
峰号	保留时间	面积	高度	标记	面积%
1	5.931	496310	57352		50.190
2	6.922	492556	47577	M	49.810
总计		988865	104929		100.000

分析日期　　　: 2019/2/16 10:49:44
处理日期　　　: 2019/2/16 10:57:29
描述　　　　　: OD-H, n-hexane/iPrOH = 95/5, 1.0 ml/min, 220 nm



S-**2ab**

色谱图



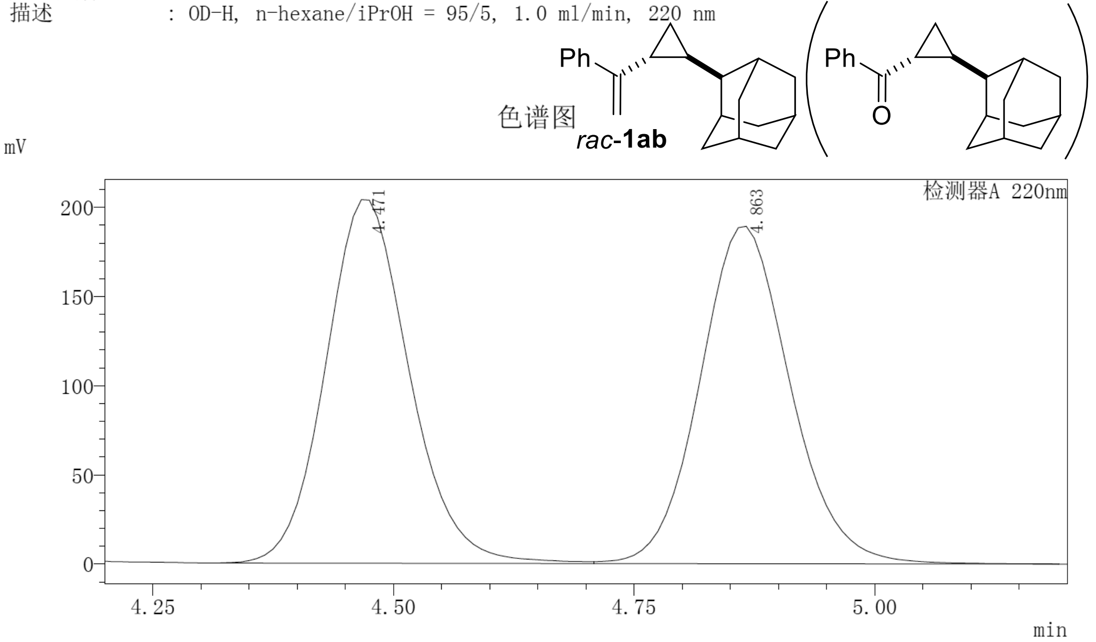
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	5.882	1950240	228343	M	89.993
2	6.855	216869	21498	M	10.007
总计		2167109	249841		100.000

Figure S205. HPLC spectra of *S*-**2ab**, Related to Table 2

分析日期　　　: 2019/2/16 11:51:04
处理日期　　　: 2019/2/16 11:57:07
描述　　　　　: OD-H, n-hexane/iPrOH = 95/5, 1.0 ml/min, 220 nm

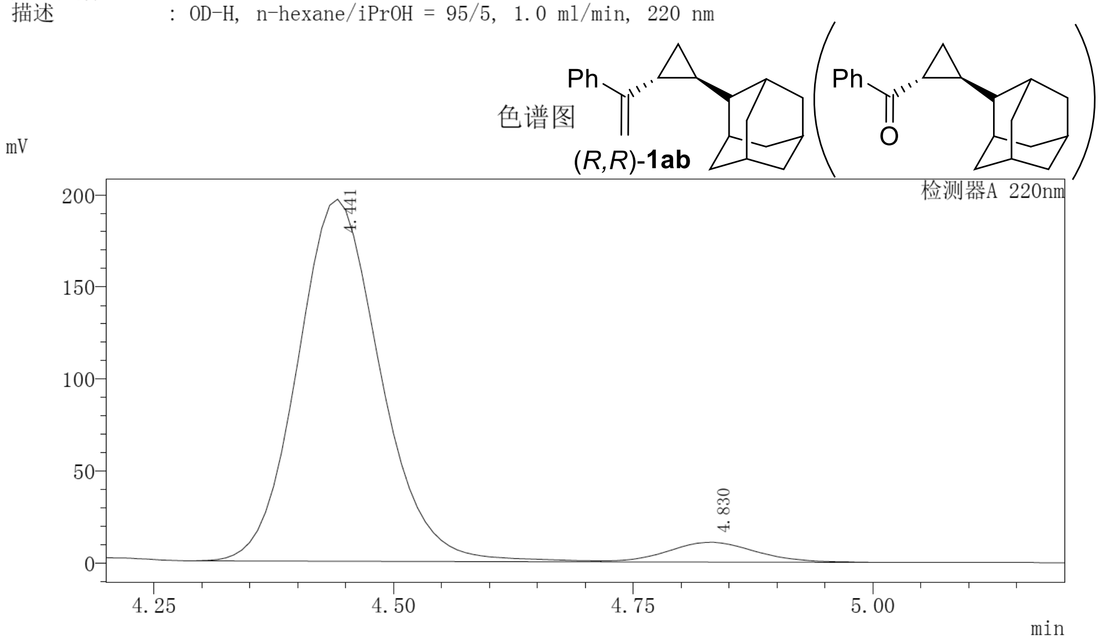


峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	4.471	1235495	203776		49.993
2	4.863	1235831	189033	V M	50.007
总计		2471326	392808		100.000

分析日期　　　: 2019/2/16 12:00:12
处理日期　　　: 2019/2/16 12:06:09
描述　　　　　: OD-H, n-hexane/iPrOH = 95/5, 1.0 ml/min, 220 nm



峰表

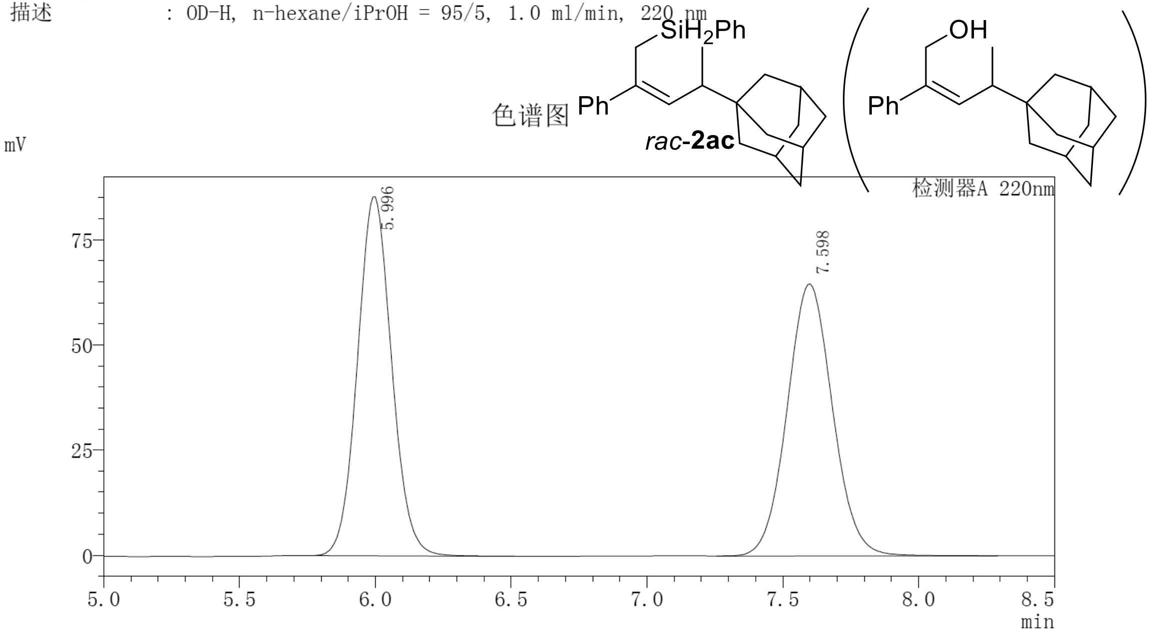
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	4.441	1181674	196450		94.511
2	4.830	68634	10762	V M	5.489
总计		1250308	207212		100.000

Figure S206. HPLC spectra of (*R,R*)-**1ab**, Related to Table 2

分析日期　　: 2019/2/16 11:04:21
处理日期　　: 2019/2/16 11:13:06
描述　　　　: OD-H, n-hexane/iPrOH = 95/5, 1.0 ml/min, 220 nm

色谱图



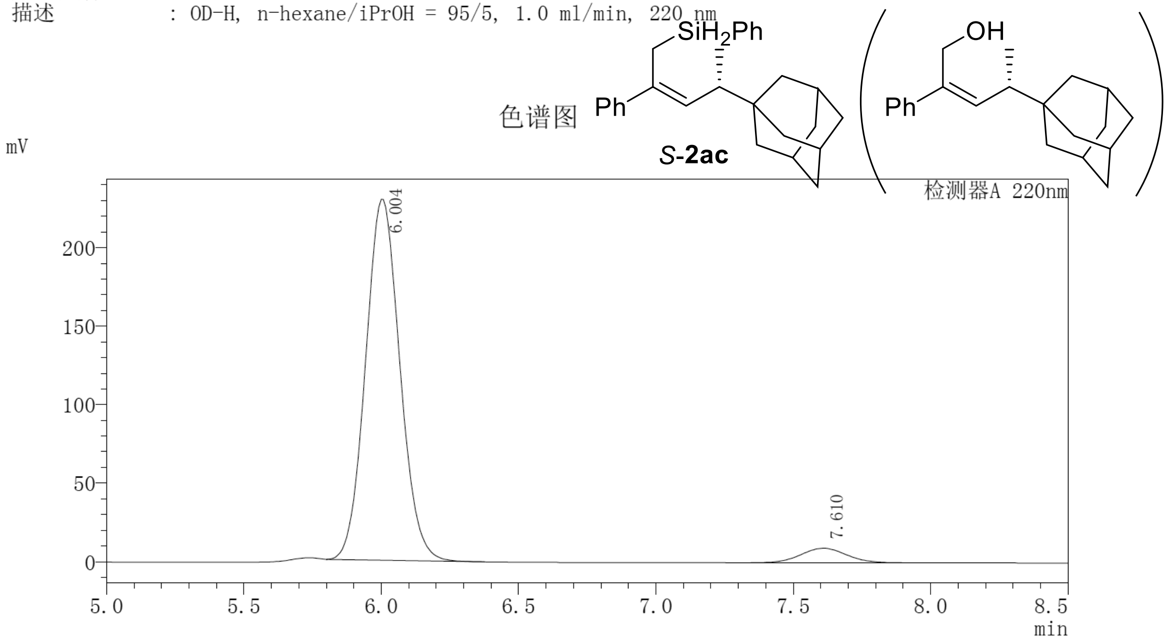
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	5.996	748187	85333		49.867
2	7.598	752183	64659	M	50.133
总计		1500371	149992		100.000

分析日期　　: 2019/2/16 11:16:40
处理日期　　: 2019/2/16 11:26:17
描述　　　　: OD-H, n-hexane/iPrOH = 95/5, 1.0 ml/min, 220 nm

色谱图



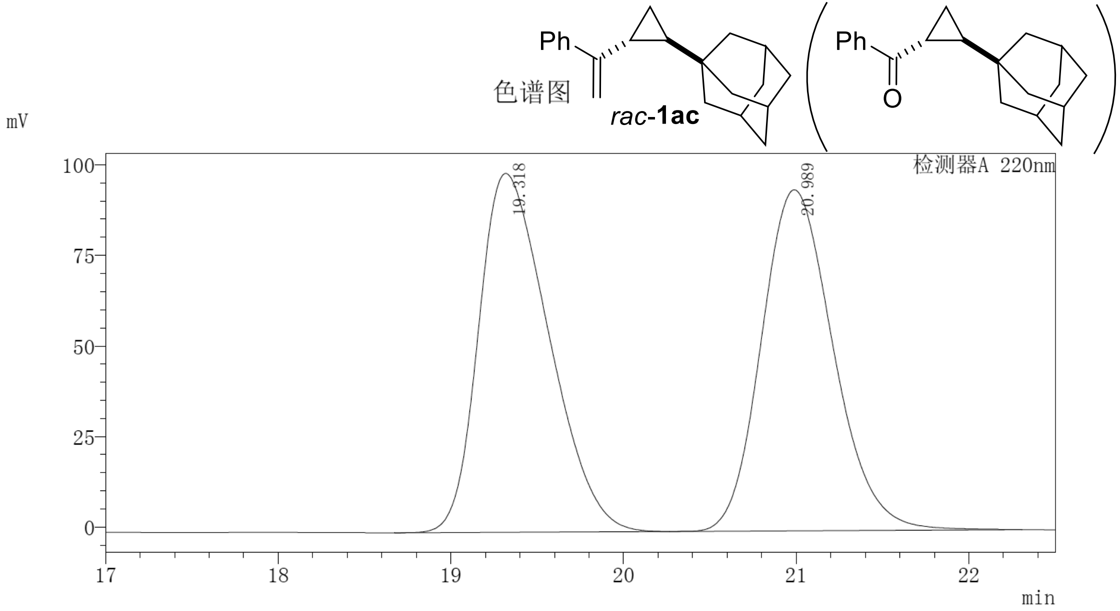
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	6.004	1996553	229830		94.913
2	7.610	106999	9252	M	5.087
总计		2103552	239082		100.000

Figure S207. HPLC spectra of *S*-**2ac**, Related to Table 2

分析日期　　: 2019/2/16 12:47:14
处理日期　　: 2019/2/16 13:10:18
描述　　　　: OD-H, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm

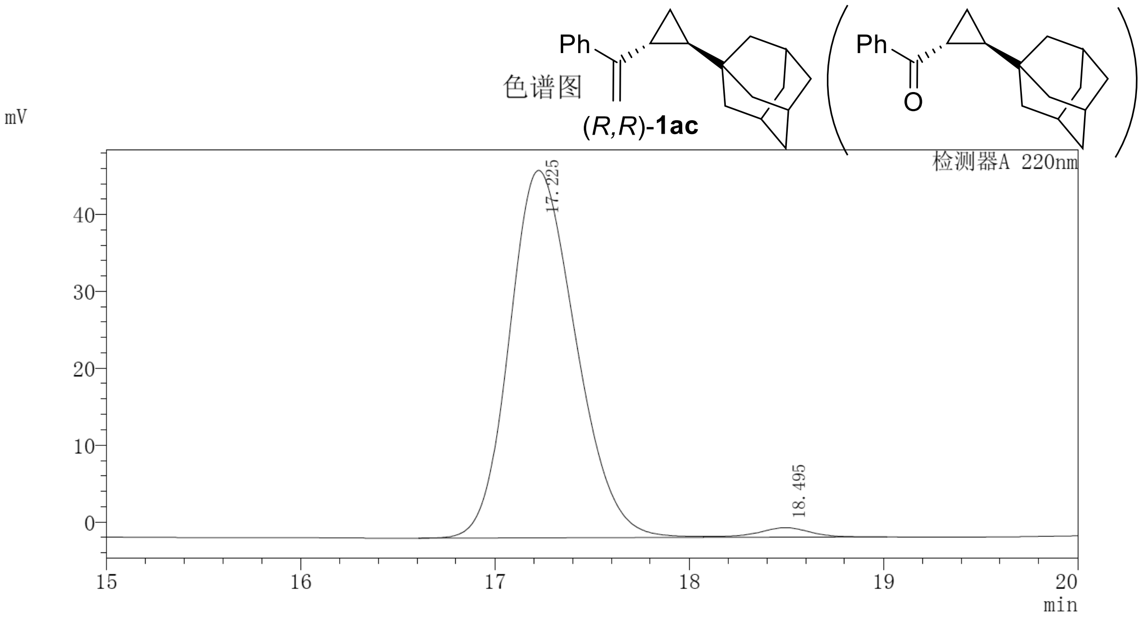


峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	19.318	2796464	99023		50.676
2	20.989	2721825	94098	M	49.324
总计		5518289	193121		100.000

分析日期　　: 2019/2/16 14:22:10
处理日期　　: 2019/2/16 14:42:17
描述　　　　: OD-H, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



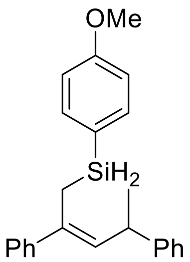
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	17.225	1131564	47789		97.946
2	18.495	23731	1247	V	2.054
总计		1155295	49036		100.000

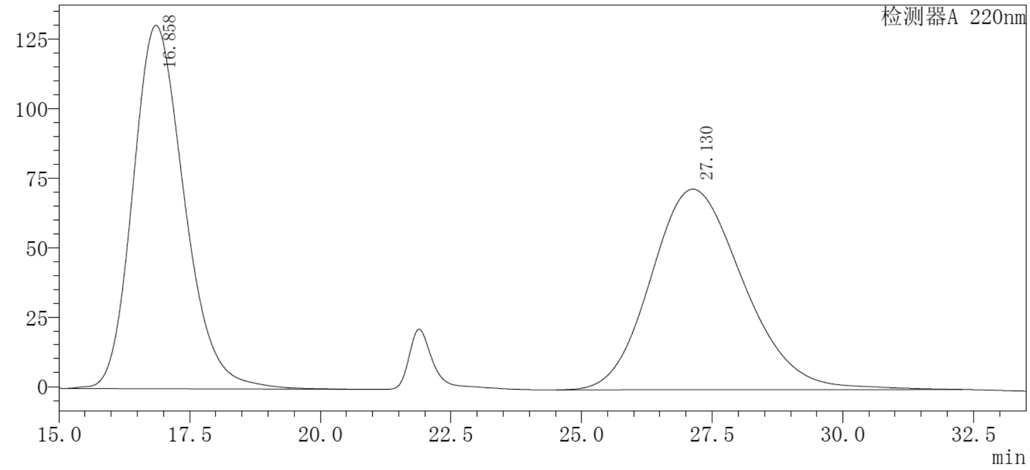
Figure S208. HPLC spectra of (*R*,*R*)-**1ac**, Related to Table 2

分析日期　　: 2018/10/2 11:38:34
处理日期　　: 2018/10/2 13:08:33
描述　　　　: OJ-H, n-hexane/iPrOH = 99/1, 1.0 ml/min, 220 nm



rac-**2ad**

色谱图

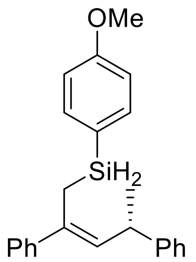


峰表

检测器A 220nm

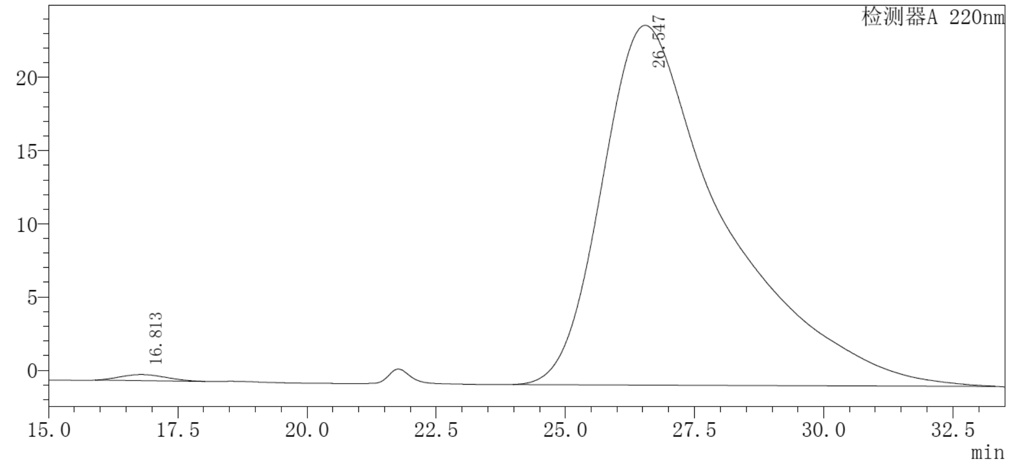
峰号	保留时间	面积	高度	标记	面积%
1	16.858	8957109	130763		50.103
2	27.130	8920303	72218	M	49.897
总计		17877412	202981		100.000

分析日期　　: 2018/10/2 16:27:02
处理日期　　: 2018/10/2 17:00:42
描述　　　　: OJ-H, n-hexane/iPrOH = 99/1, 1.0 ml/min, 220 nm



S-**2ad**

色谱图



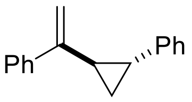
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	16.813	25313	412		0.621
2	26.547	4052785	24567	M	99.379
总计		4078098	24979		100.000

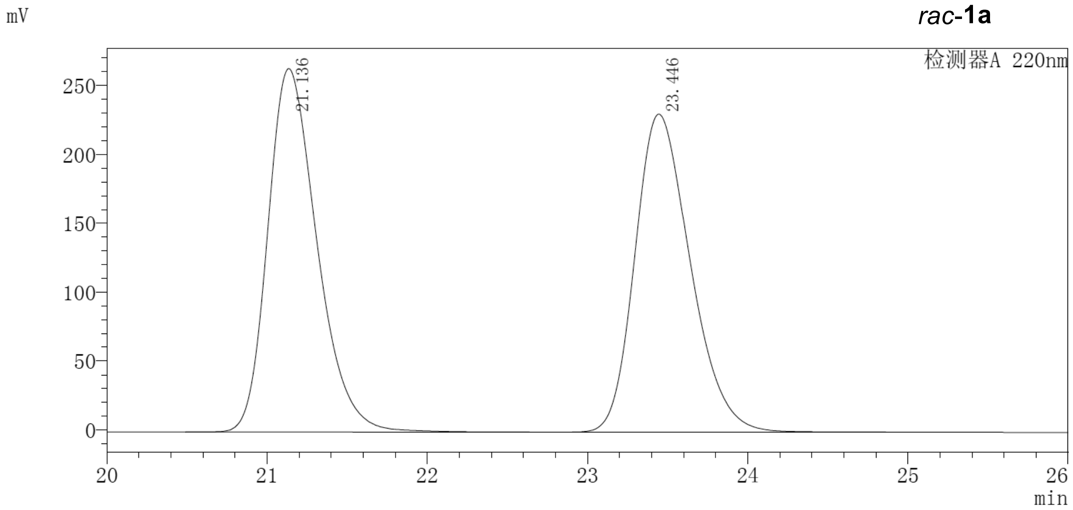
Figure S209. HPLC spectra of *S*-**2ad**, Related to Table 2

分析日期　　: 2019/7/30 10:03:21
处理日期　　: 2019/7/30 10:30:57
描述　　　　: OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



rac-**1a**

色谱图

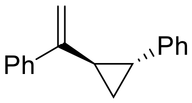


峰表

检测器A 220nm

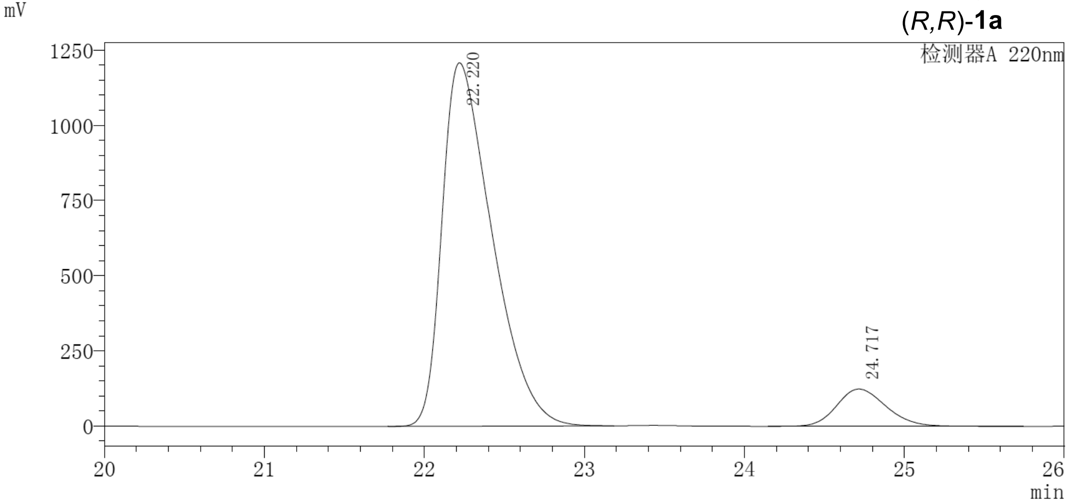
峰号	保留时间	面积	高度	标记	面积%
1	21.136	5614292	263846		50.337
2	23.446	5539092	230827	M	49.663
总计		11153384	494673		100.000

分析日期　　: 2019/7/30 15:21:08
处理日期　　: 2019/7/30 15:57:56
描述　　　　: OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



(*R*,*R*)-**1a**

色谱图



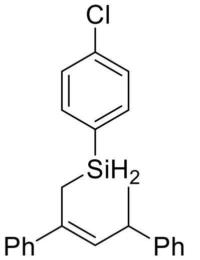
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	22.220	26221956	1208486		90.816
2	24.717	2651874	124162		9.184
总计		28873830	1332648		100.000

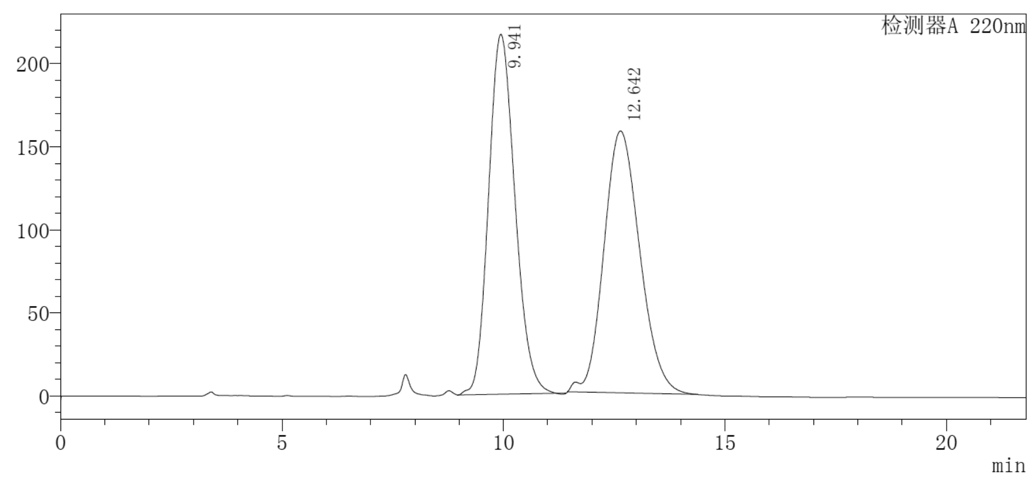
Figure S210. HPLC spectra of (*R*,*R*)-**1a**, Related to Table 2

分析日期　　　: 2018/10/2 12:15:54
处理日期　　　: 2018/10/2 12:37:43
描述　　　　　: OJ-H, n-hexane/iPrOH = 99/1, 1.0 ml/min, 220 nm



rac-**2ae**

色谱图

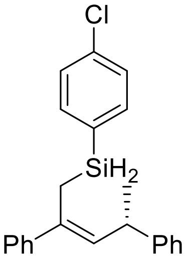


峰表

检测器A 220nm

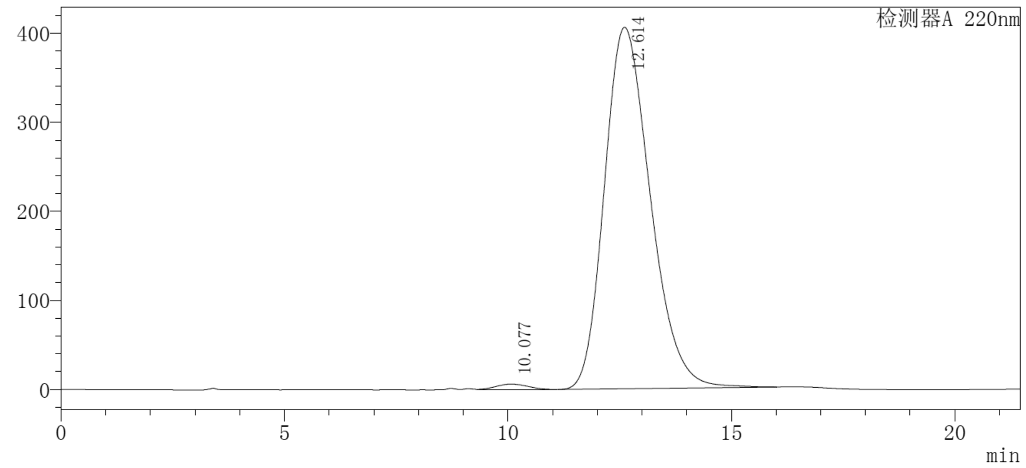
峰号	保留时间	面积	高度	标记	面积%
1	9.941	8993426	216680		50.262
2	12.642	8899492	157714	M	49.738
总计		17892918	374395		100.000

分析日期　　　: 2018/10/8 20:06:13
处理日期　　　: 2018/10/8 20:27:42
描述　　　　　: OJ-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm



S-**2ae**

色谱图



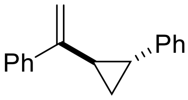
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	10.077	290196	5989		0.991
2	12.614	29004851	405670		99.009
总计		29295047	411659		100.000

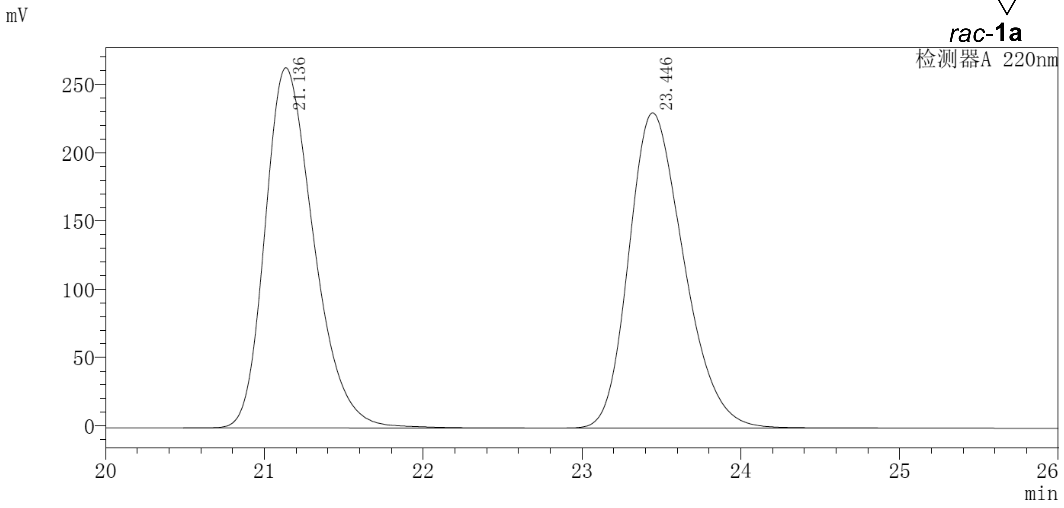
Figure S211. HPLC spectra of *S*-**2ae**, Related to Table 2

分析日期　　　: 2019/7/30 10:03:21
处理日期　　　: 2019/7/30 10:30:57
描述　　　　　: OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



rac-**1a**

色谱图

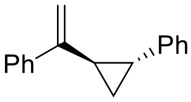


峰表

检测器A 220nm

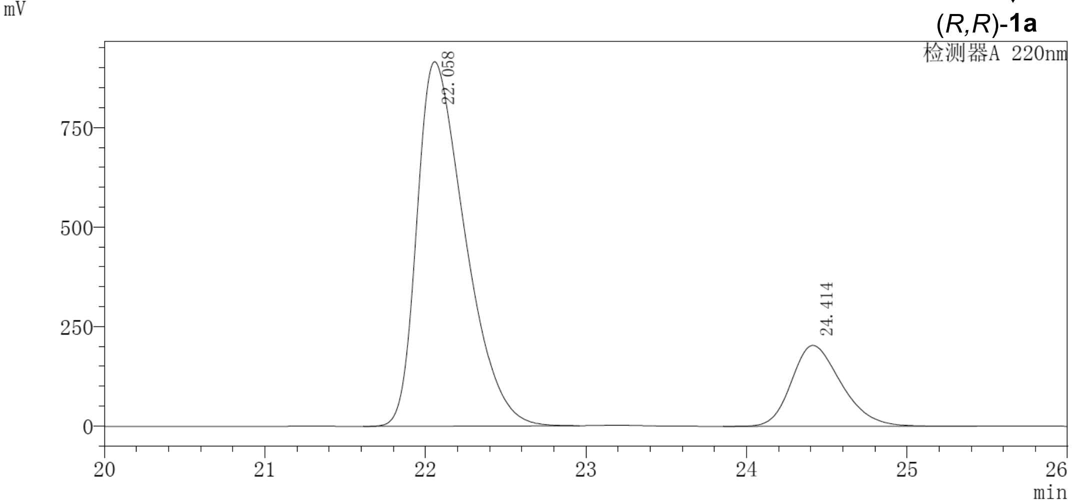
峰号	保留时间	面积	高度	标记	面积%
1	21.136	5614292	263846		50.337
2	23.446	5539092	230827	M	49.663
总计		11153384	494673		100.000

分析日期　　　: 2019/7/30 15:59:39
处理日期　　　: 2019/7/30 16:25:51
描述　　　　　: OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



(*R*,*R*)-**1a**

色谱图



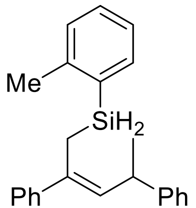
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	22.058	19060615	916239		81.246
2	24.414	4399810	203311		18.754
总计		23460424	1119551		100.000

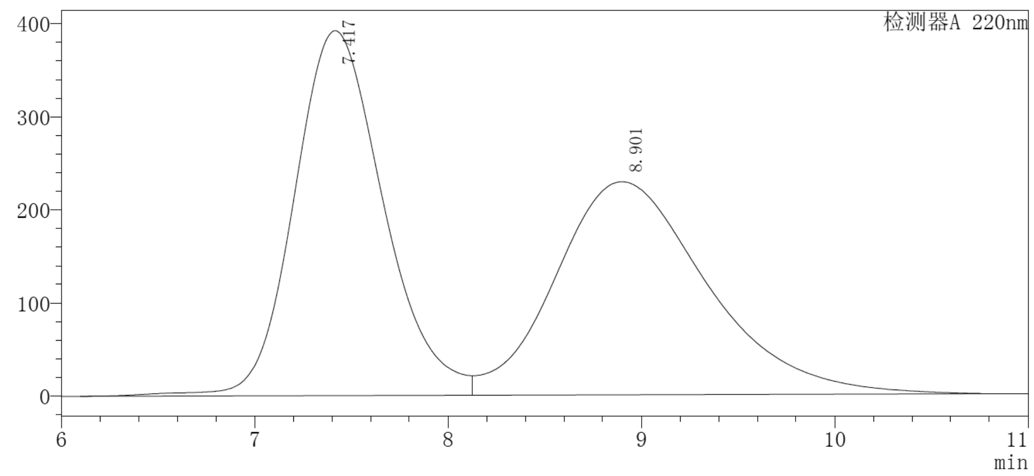
Figure S212. HPLC spectra of (*R*,*R*)-**1a**, Related to Table 2

分析日期　　　: 2018/10/2 15:19:32
处理日期　　　: 2018/10/2 15:32:41
描述　　　　　: OJ-H, n-hexane/iPrOH = 99/1, 1.0 ml/min, 220 nm



rac-**2af**

色谱图

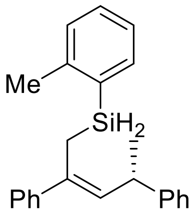


峰表

检测器A 220nm

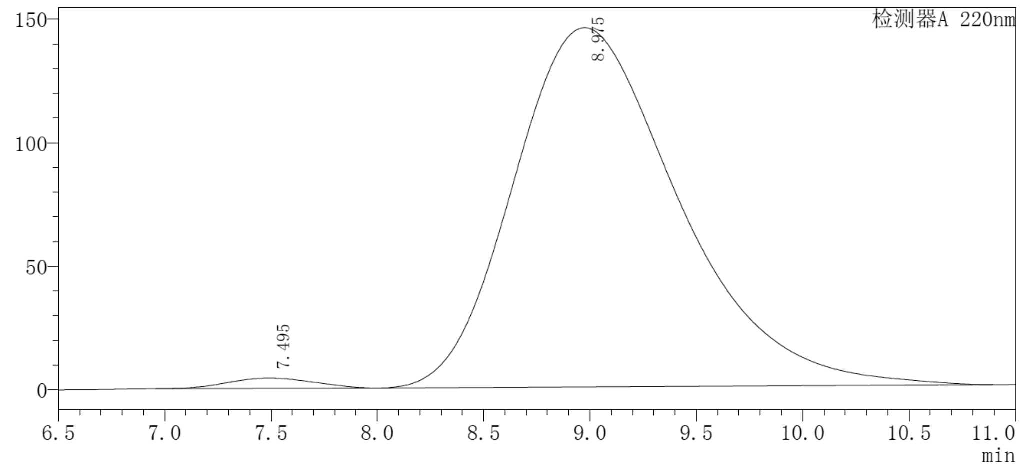
峰号	保留时间	面积	高度	标记	面积%
1	7.417	12561537	391826		50.088
2	8.901	12517572	228901	V	49.912
总计		25079109	620727		100.000

分析日期　　　: 2018/10/2 15:35:31
处理日期　　　: 2018/10/2 15:49:11
描述　　　　　: OJ-H, n-hexane/iPrOH = 99/1, 1.0 ml/min, 220 nm



S-**2af**

色谱图



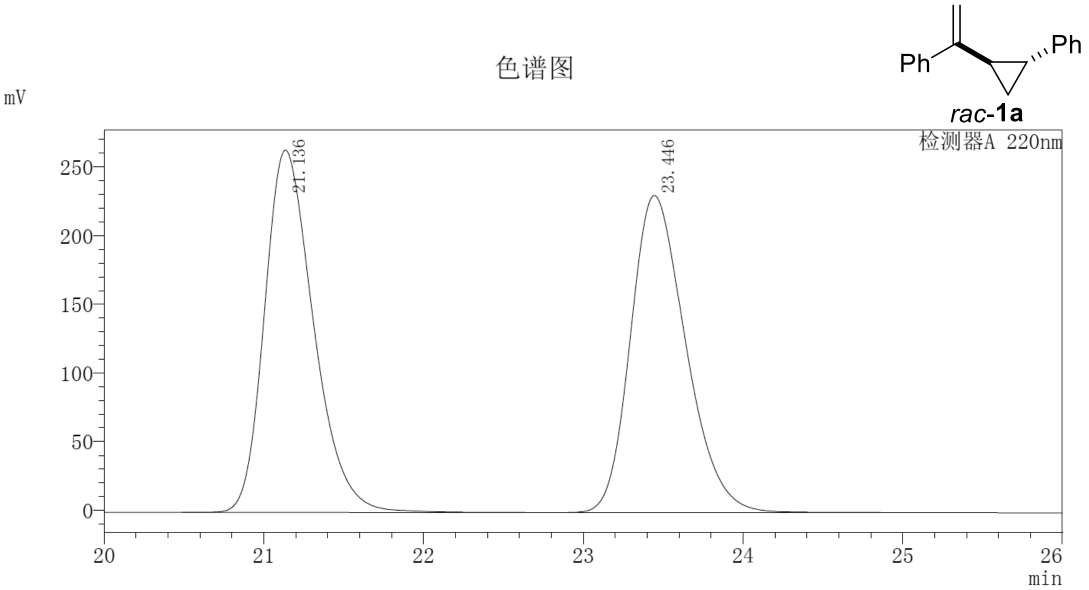
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	7.495	116641	4189	M	1.460
2	8.975	7874970	145497		98.540
总计		7991611	149686		100.000

Figure S213. HPLC spectra of *S*-**2af**, Related to Table 2

分析日期 : 2019/7/30 10:03:21
处理日期 : 2019/7/30 10:30:57
描述 : OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm

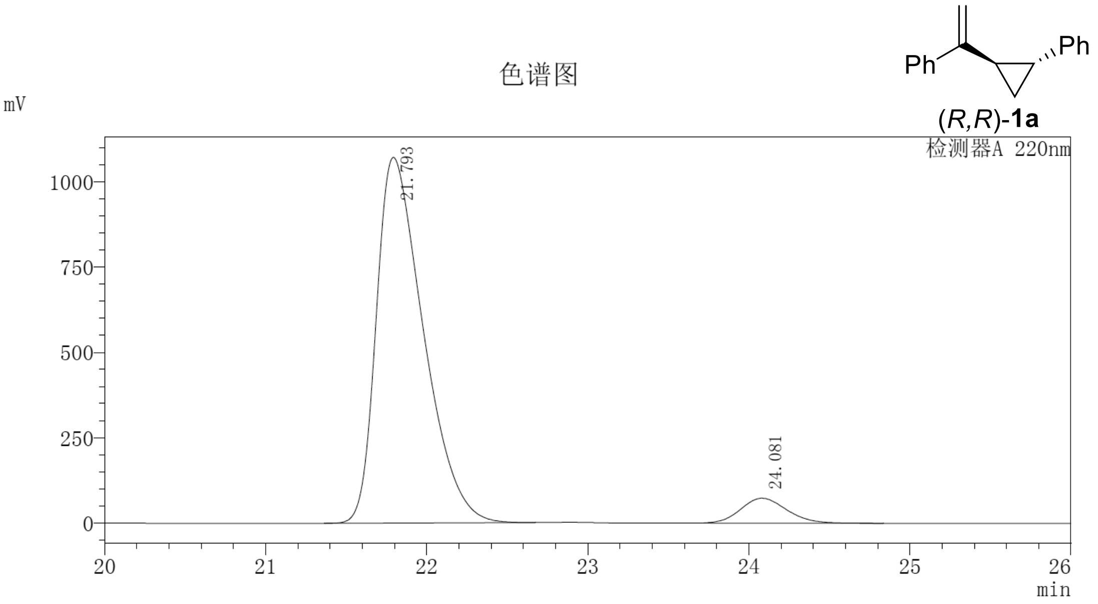


峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	21.136	5614292	263846		50.337
2	23.446	5539092	230827	M	49.663
总计		11153384	494673		100.000

分析日期 : 2019/7/30 13:24:44
处理日期 : 2019/7/30 13:51:12
描述 : OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



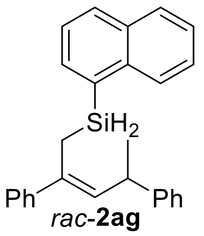
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	21.793	21759956	1072160		93.690
2	24.081	1465537	73356	M	6.310
总计		23225493	1145515		100.000

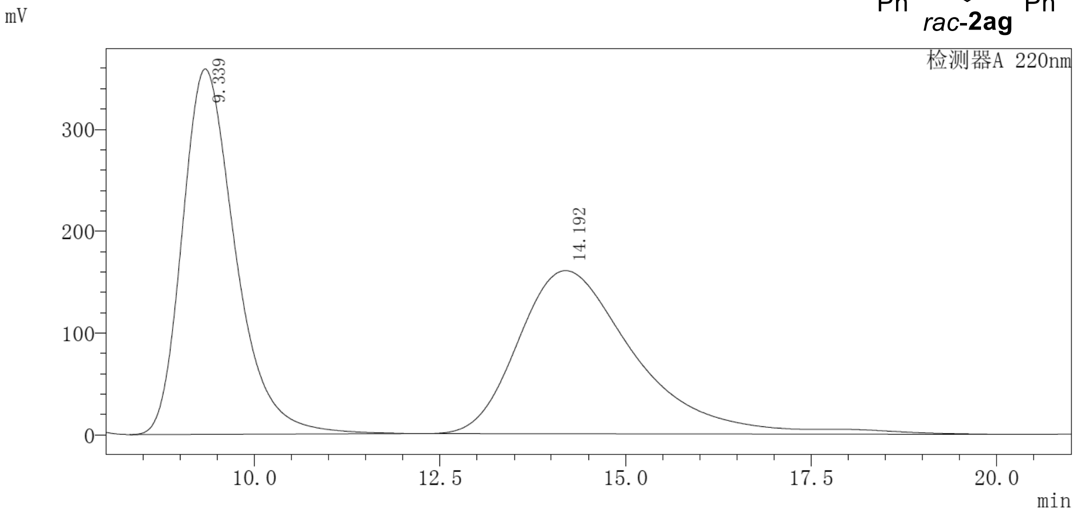
Figure S214. HPLC spectra of (*R*,*R*)-**1a**, Related to Table 2

分析日期　　　: 2018/11/5 16:47:50
处理日期　　　: 2018/11/5 17:28:02
描述　　　　　: OJ-H, n-hexane/iPrOH = 99/1, 1 ml/min, 220 nm



rac-**2ag**

色谱图

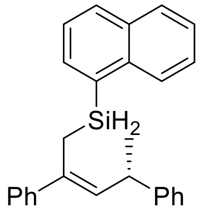


峰表

检测器A 220nm

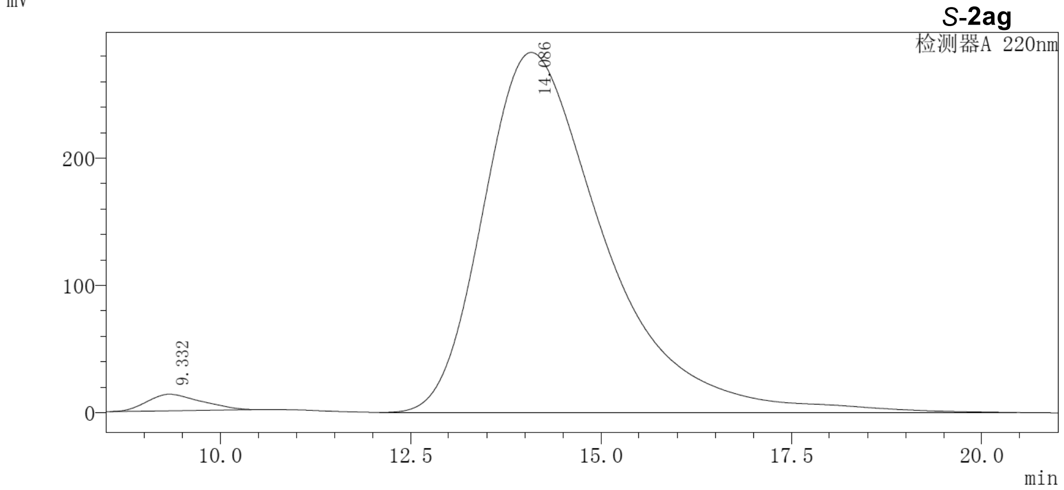
峰号	保留时间	面积	高度	标记	面积%
1	9.339	17865012	358878		50.330
2	14.192	17630632	160277	M	49.670
总计		35495643	519155		100.000

分析日期　　　: 2018/11/5 17:29:44
处理日期　　　: 2018/11/5 17:56:34
描述　　　　　: OJ-H, n-hexane/iPrOH = 99/1, 1 ml/min, 220 nm



S-**2ag**

色谱图



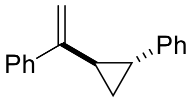
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.332	645096	13090		2.016
2	14.086	31359781	282856	M	97.984
总计		32004878	295946		100.000

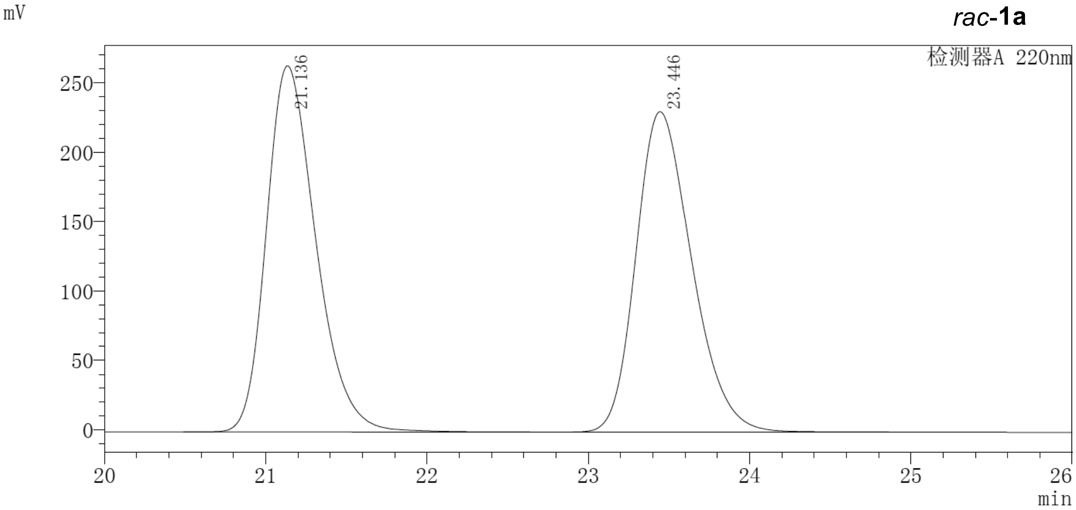
Figure S215. HPLC spectra of *S*-**2ag**, Related to Table 2

分析日期　　　: 2019/7/30 10:03:21
处理日期　　　: 2019/7/30 10:30:57
描述　　　　　: OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



rac-**1a**

色谱图

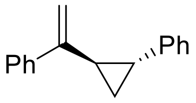


峰表

检测器A 220nm

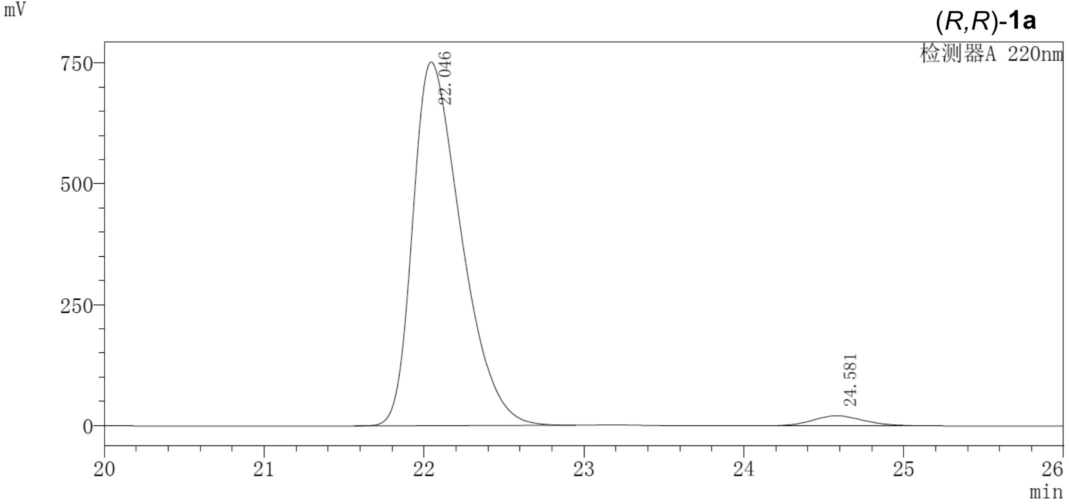
峰号	保留时间	面积	高度	标记	面积%
1	21.136	5614292	263846		50.337
2	23.446	5539092	230827	M	49.663
总计		11153384	494673		100.000

分析日期　　　: 2019/7/30 10:32:04
处理日期　　　: 2019/7/30 10:58:51
描述　　　　　: OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



(*R*,*R*)-**1a**

色谱图



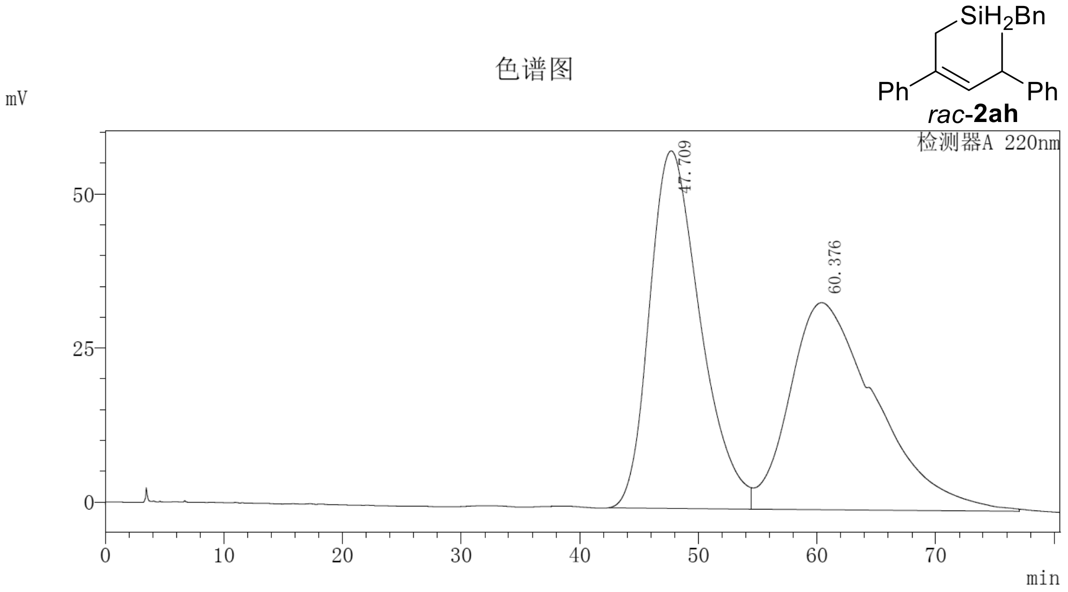
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	22.046	15864682	751807		97.218
2	24.581	453936	20631	M	2.782
总计		16318617	772438		100.000

Figure S216. HPLC spectra of (*R,R*)-**1a**, Related to Table 2

分析日期　　　: 2018/10/8 15:13:24
处理日期　　　: 2018/10/8 16:33:56
描述　　　　　: OJ-H, n-hexane/iPrOH =99.9/0.1, 1.0 ml/min, 220 nm

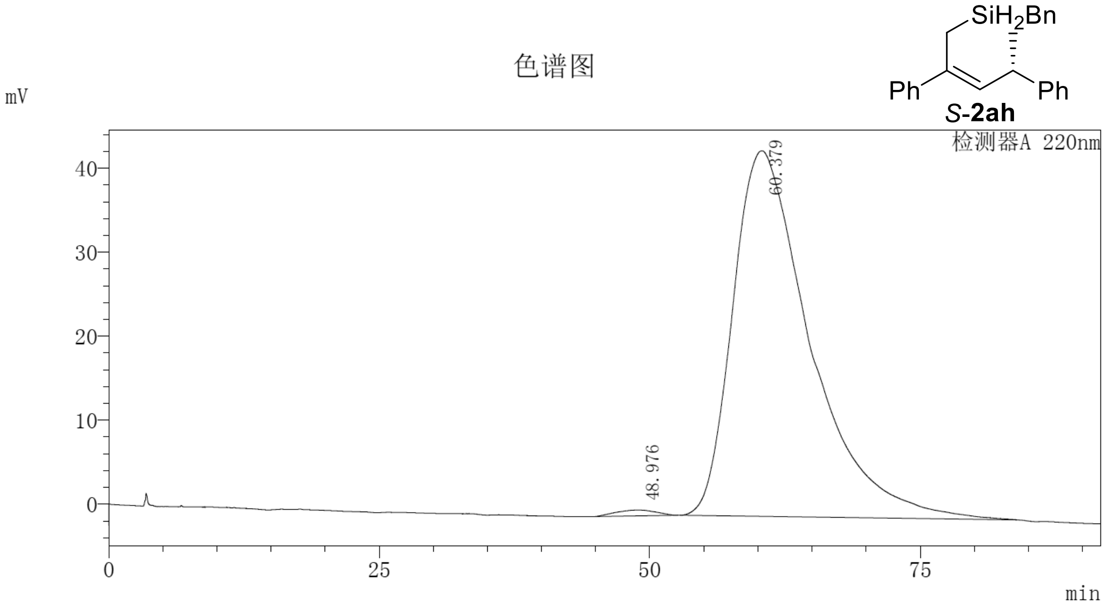


峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	47.709	17314519	58072	M	50.283
2	60.376	17119463	33615	V M	49.717
总计		34433982	91687		100.000

分析日期　　　: 2018/10/8 18:05:16
处理日期　　　: 2018/10/8 19:36:57
描述　　　　　: OJ-H, n-hexane/iPrOH =99.9/0.1, 1.0 ml/min, 220 nm



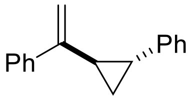
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	48.976	178783	699	M	0.820
2	60.379	21627177	43495	M	99.180
总计		21805959	44194		100.000

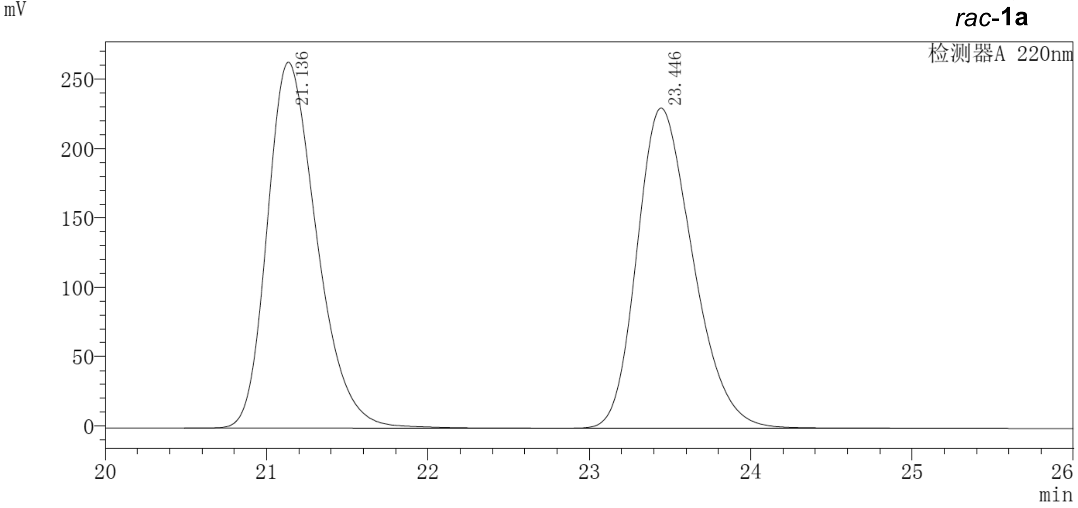
Figure S217. HPLC spectra of *S*-**2ah**, Related to Table 2

分析日期　　　: 2019/7/30 10:03:21
处理日期　　　: 2019/7/30 10:30:57
描述　　　　　: OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



rac-**1a**

色谱图

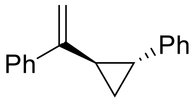


峰表

检测器A 220nm

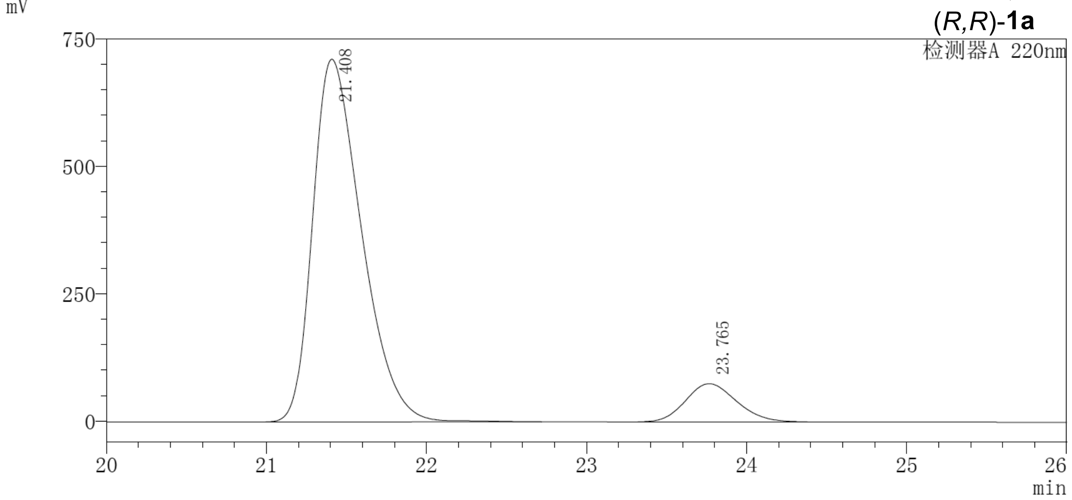
峰号	保留时间	面积	高度	标记	面积%
1	21.136	5614292	263846		50.337
2	23.446	5539092	230827	M	49.663
总计		11153384	494673		100.000

分析日期　　　: 2019/7/30 12:15:43
处理日期　　　: 2019/7/30 12:52:05
描述　　　　　: OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



(*R*,*R*)-**1a**

色谱图



峰表

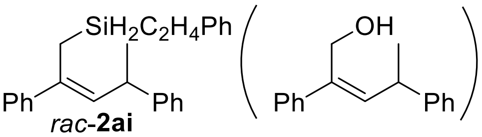
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	21.408	15102597	711937		90.023
2	23.765	1673803	75210	M	9.977
总计		16776400	787147		100.000

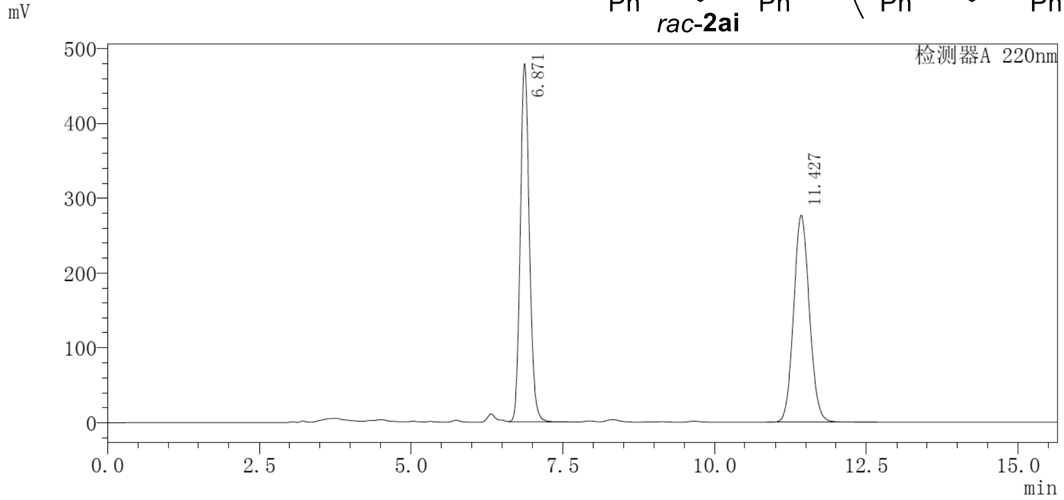
Figure S218. HPLC spectra of (*R*,*R*)-**1a**, Related to Table 2

分析日期　　: 2018/12/28 11:21:13
处理日期　　: 2018/12/28 11:36:53
描述　　: OD*-H, n-hexane/iPrOH =90/10, 1.0 ml/min, 220 nm

色谱图



rac-**2ai**



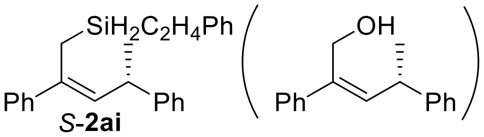
峰表

检测器A 220nm

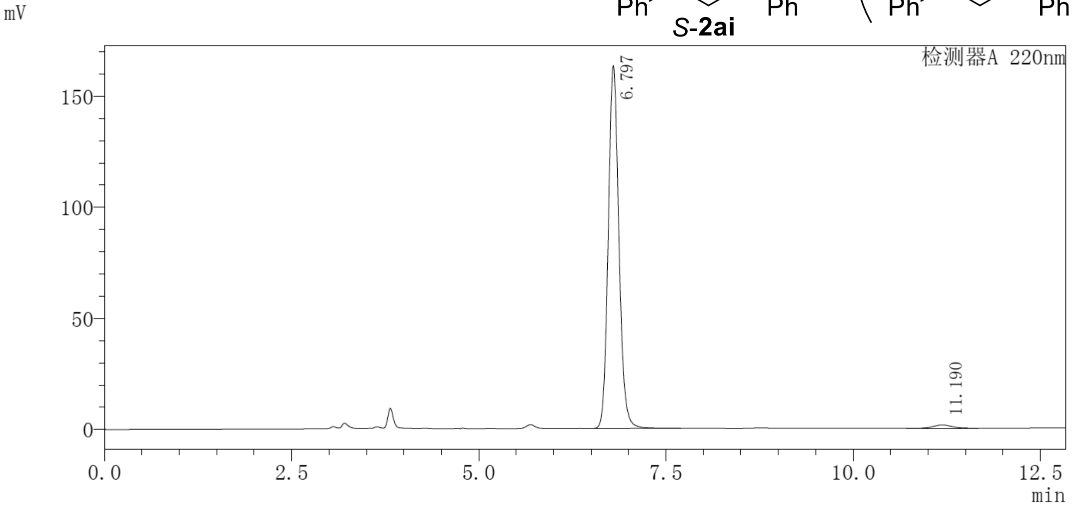
峰号	保留时间	面积	高度	标记	面积%
1	6.871	4972293	478138	S	49.815
2	11.427	5009162	276849		50.185
总计		9981455	754987		100.000

分析日期　　: 2019/1/16 21:10:48
处理日期　　: 2019/1/16 21:23:39
描述　　: OD-H, n-hexane/iPrOH =90/10, 1.0 ml/min, 220 nm

色谱图



S-**2ai**



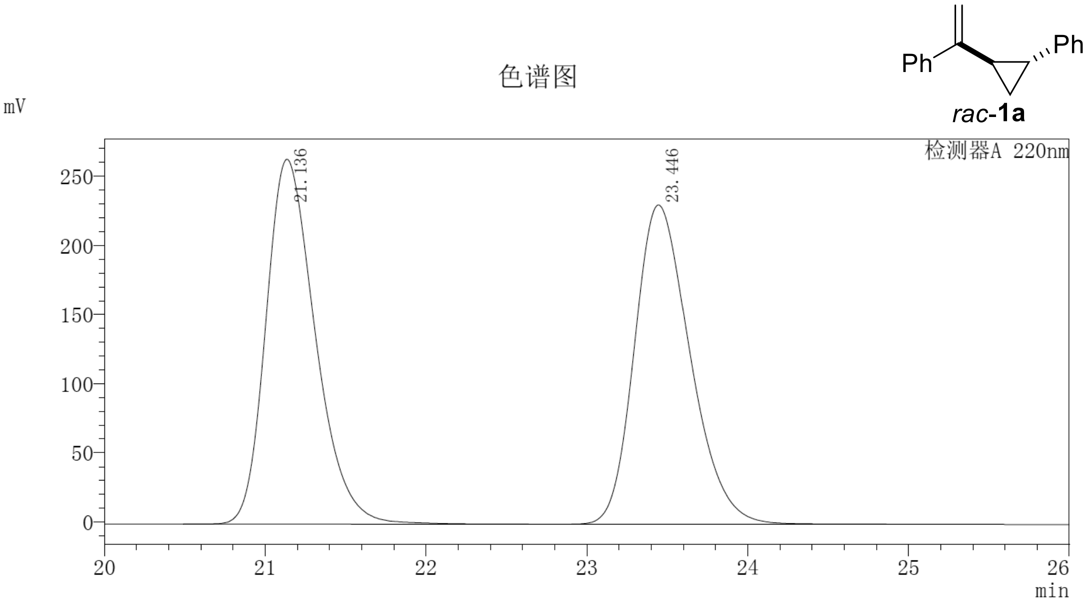
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	6.797	1623469	163225	S	98.452
2	11.190	25525	1484		1.548
总计		1648994	164709		100.000

Figure S219. HPLC spectra of *S*-**2ai**, Related to Table 2

分析日期　　　: 2019/7/30 10:03:21
处理日期　　　: 2019/7/30 10:30:57
描述　　　　　: OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm

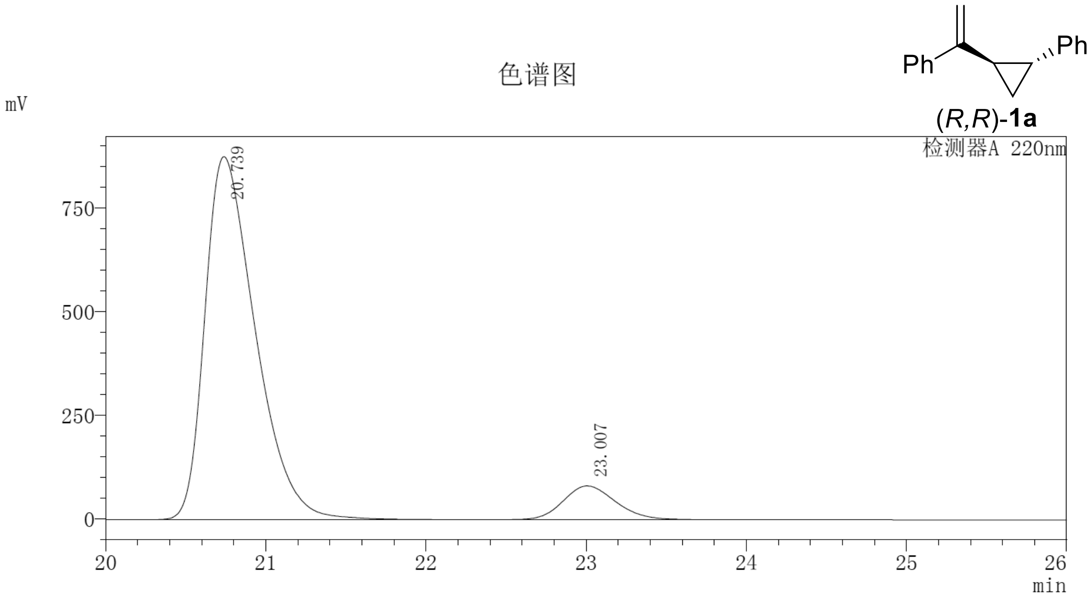


峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	21.136	5614292	263846		50.337
2	23.446	5539092	230827	M	49.663
总计		11153384	494673		100.000

分析日期　　　: 2019/7/30 14:38:08
处理日期　　　: 2019/7/30 15:18:27
描述　　　　　: OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



峰表

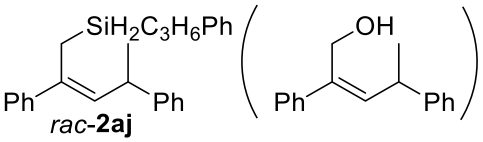
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	20.739	19168968	875442		91.129
2	23.007	1866051	81488	V	8.871
总计		21035019	956930		100.000

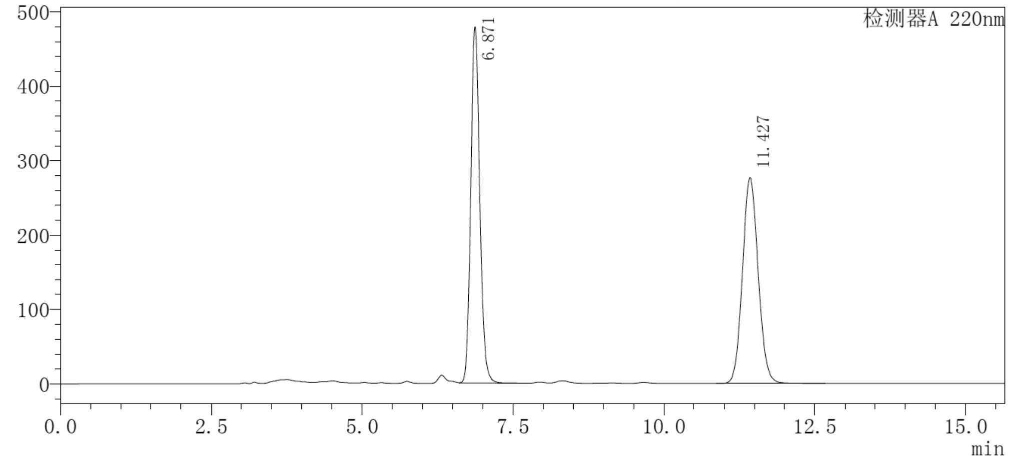
Figure S220. HPLC spectra of (*R*,*R*)-**1a**, Related to Table 2

分析日期　　: 2018/12/28 11:21:13
处理日期　　: 2018/12/28 11:36:53
描述　　　　: OD*-H, n-hexane/iPrOH =90/10, 1.0 ml/min, 220 nm

色谱图



rac-**2aj**



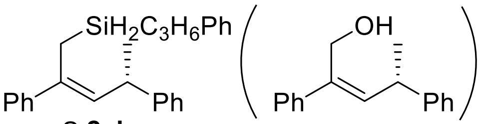
峰表

检测器A 220nm

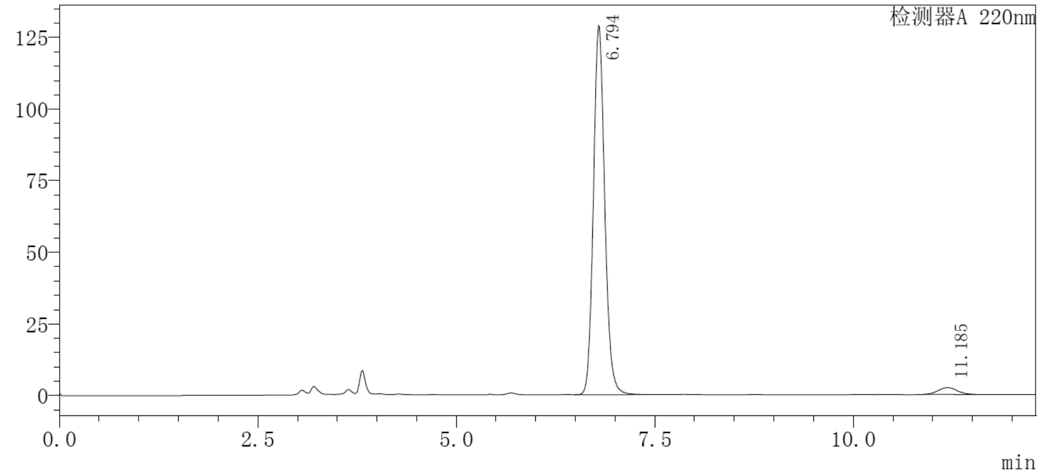
峰号	保留时间	面积	高度	标记	面积%
1	6.871	4972293	478138	S	49.815
2	11.427	5009162	276849		50.185
总计		9981455	754987		100.000

分析日期　　: 2019/1/16 21:25:15
处理日期　　: 2019/1/16 21:37:35
描述　　　　: OD-H, n-hexane/iPrOH =90/10, 1.0 ml/min, 220 nm

色谱图



S-**2aj**



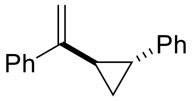
峰表

检测器A 220nm

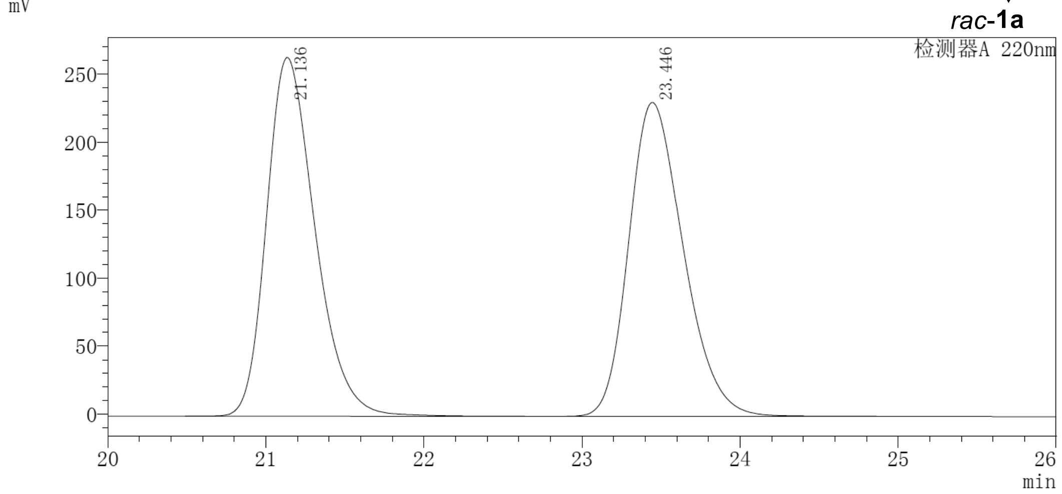
峰号	保留时间	面积	高度	标记	面积%
1	6.794	1282657	128856	V	97.004
2	11.185	39617	2373	M	2.996
总计		1322275	131228		100.000

Figure S221. HPLC spectra of *S*-**2aj**, Related to Table 2

分析日期　　　: 2019/7/30 10:03:21
处理日期　　　: 2019/7/30 10:30:57
描述　　　　　: OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



rac-**1a**

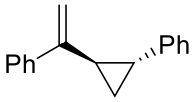


峰表

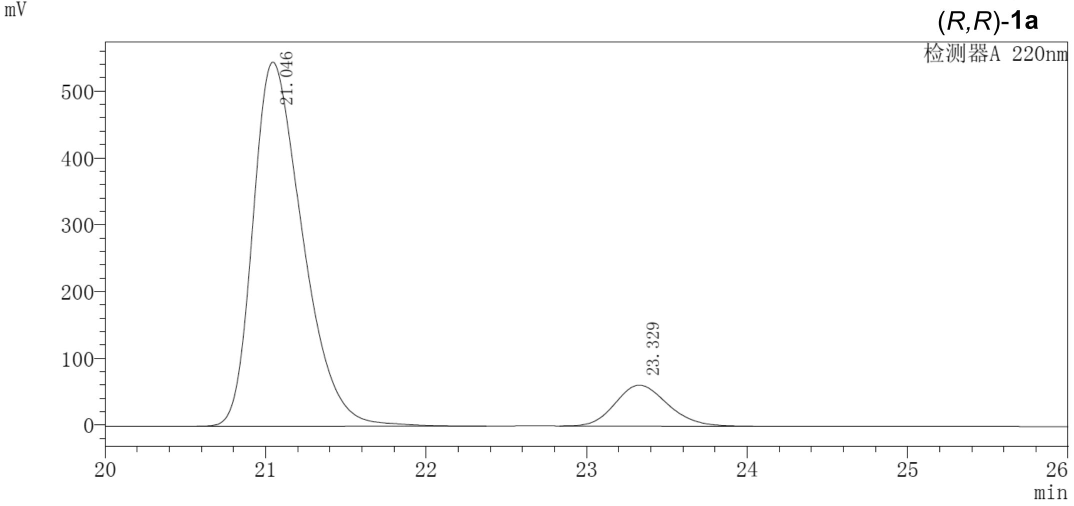
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	21.136	5614292	263846		50.337
2	23.446	5539092	230827	M	49.663
总计		11153384	494673		100.000

分析日期　　　: 2019/7/30 20:43:05
处理日期　　　: 2019/7/30 21:10:06
描述　　　　　: OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



(*R*,*R*)-**1a**



峰表

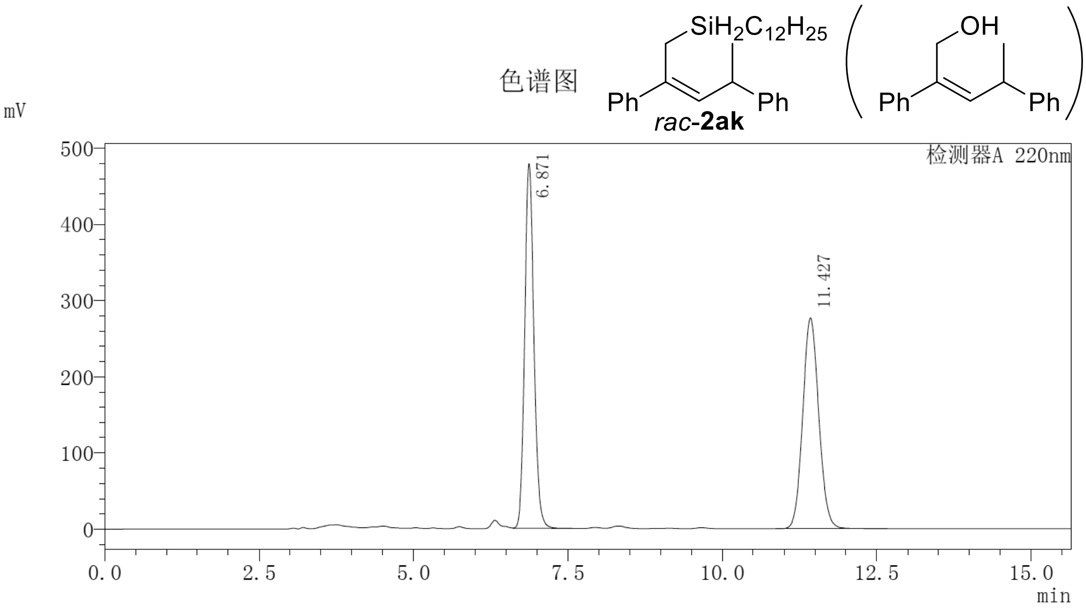
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	21.046	11706009	545090		89.345
2	23.329	1396012	61332		10.655
总计		13102021	606422		100.000

Figure S222. HPLC spectra of (*R*,*R*)-**1a**, Related to Table 2

分析日期　　　: 2018/12/28 11:21:13
处理日期　　　: 2018/12/28 11:36:53
描述　　　　　: OD*-H, n-hexane/iPrOH =90/10, 1.0 ml/min, 220 nm

色谱图



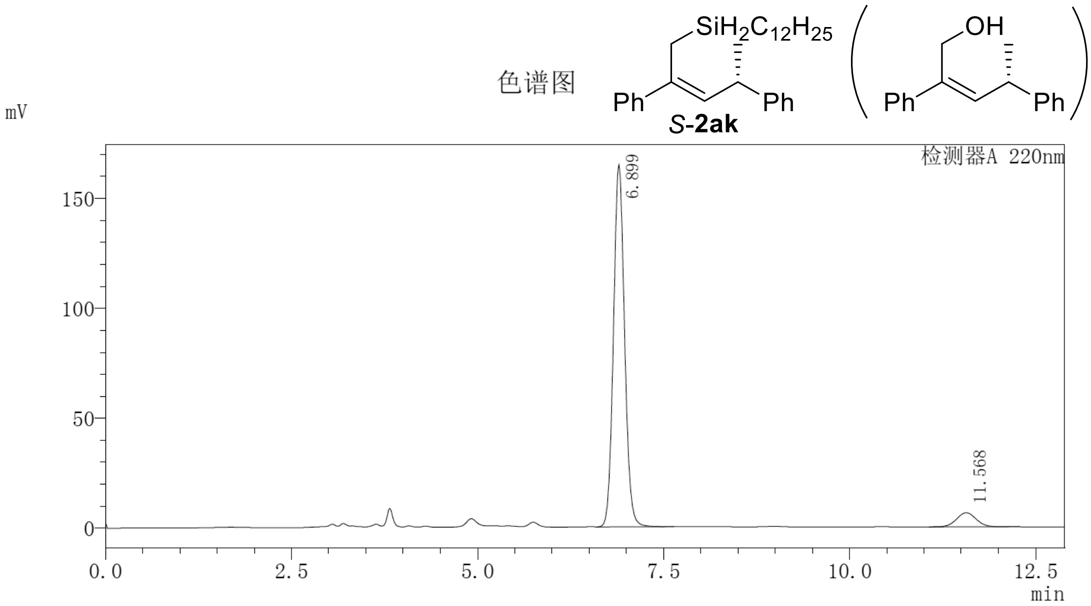
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	6.871	4972293	478138	S	49.815
2	11.427	5009162	276849		50.185
总计		9981455	754987		100.000

分析日期　　　: 2019/1/3 9:46:24
处理日期　　　: 2019/1/3 9:59:19
描述　　　　　: OD-H, n-hexane/iPrOH =90/10, 1.0 ml/min, 220 nm

色谱图



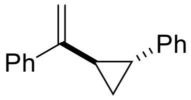
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	6.899	1707844	164722		93.562
2	11.568	117525	6426		6.438
总计		1825370	171148		100.000

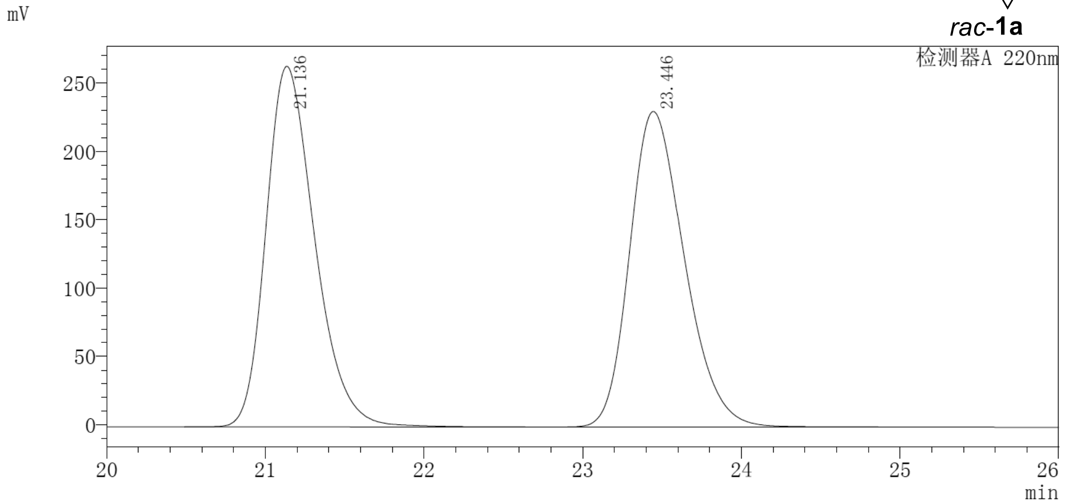
Figure S223. HPLC spectra of *S*-**2ak**, Related to Table 2

分析日期　　: 2019/7/30 10:03:21
处理日期　　: 2019/7/30 10:30:57
描述　　　　: OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



rac-**1a**

色谱图

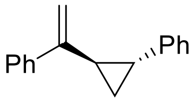


峰表

检测器A 220nm

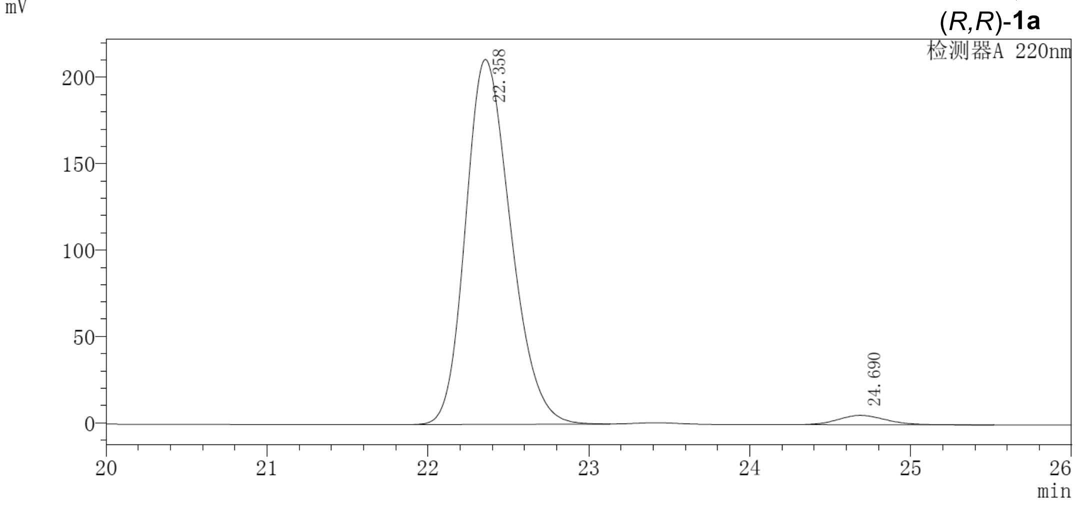
峰号	保留时间	面积	高度	标记	面积%
1	21.136	5614292	263846		50.337
2	23.446	5539092	230827	M	49.663
总计		11153384	494673		100.000

分析日期　　: 2019/7/30 12:54:26
处理日期　　: 2019/7/30 13:22:54
描述　　　　: OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



(*R*,*R*)-**1a**

色谱图



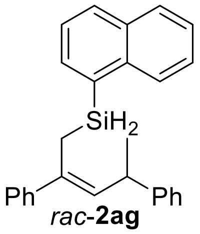
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	22.358	4106497	211269		97.368
2	24.690	111007	5420	M	2.632
总计		4217505	216689		100.000

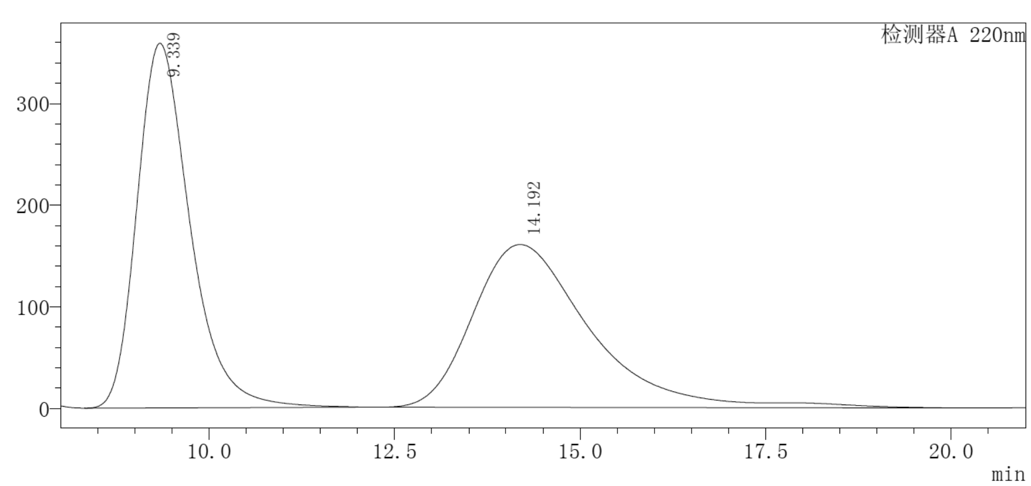
Figure S224. HPLC spectra of (*R*,*R*)-**1a**, Related to Table 2

分析日期　　：2018/11/5 16:47:50
处理日期　　：2018/11/5 17:28:02
描述　　　　：OJ-H, n-hexane/iPrOH = 99/1, 1 ml/min, 220 nm



rac-**2ag**

色谱图

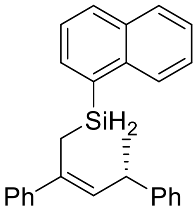


峰表

检测器A 220nm

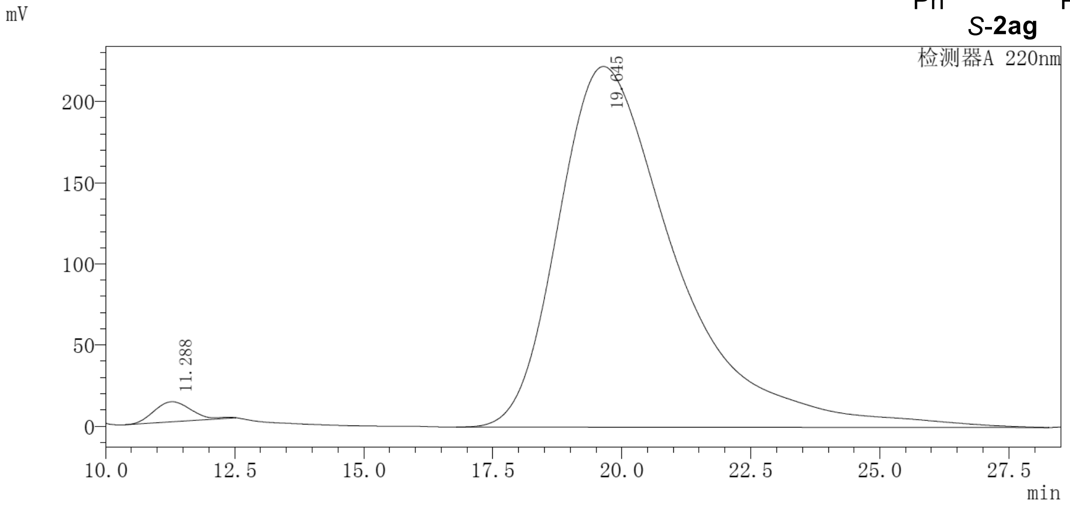
峰号	保留时间	面积	高度	标记	面积%
1	9.339	17865012	358878		50.330
2	14.192	17630632	160277	M	49.670
总计		35495643	519155		100.000

分析日期　　：2018/12/10 14:04:14
处理日期　　：2018/12/10 14:36:34
描述　　　　：OJ-H, n-hexane/iPrOH = 99/1, 1.0 ml/min, 220 nm



S-**2ag**

色谱图



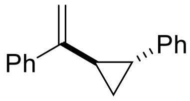
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	11.288	619673	12378	M	1.723
2	19.645	35351154	222229		98.277
总计		35970827	234607		100.000

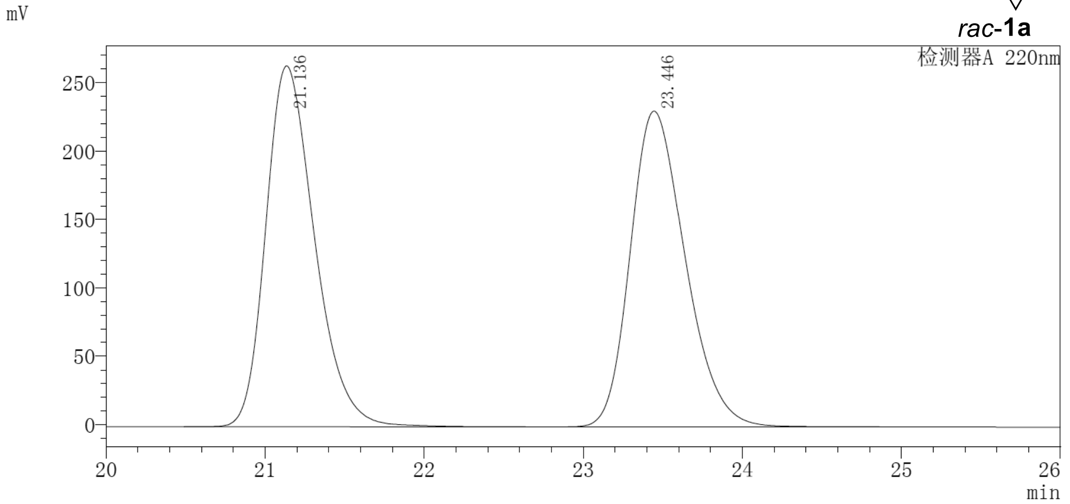
Figure S225. HPLC spectra of *S*-**2ag**, Related to Scheme 1

分析日期　　　: 2019/7/30 10:03:21
处理日期　　　: 2019/7/30 10:30:57
描述　　　　　: OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



rac-**1a**

色谱图

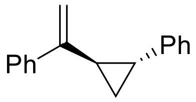


峰表

检测器A 220nm

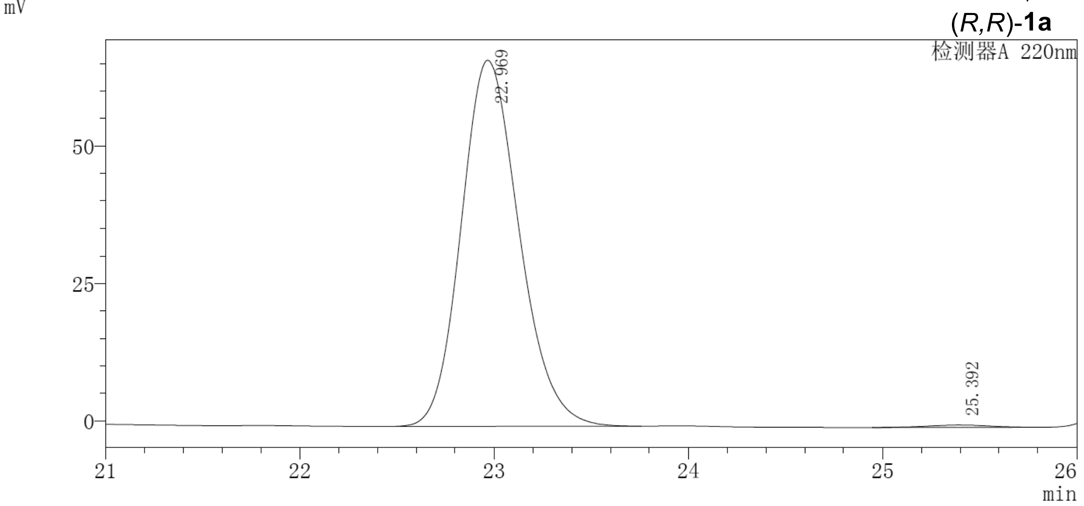
峰号	保留时间	面积	高度	标记	面积%
1	21.136	5614292	263846		50.337
2	23.446	5539092	230827	M	49.663
总计		11153384	494673		100.000

分析日期　　　: 2018/12/15 15:51:06
处理日期　　　: 2018/12/15 16:21:47
描述　　　　　: 2*OD-H, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm



(*R*,*R*)-**1a**

色谱图



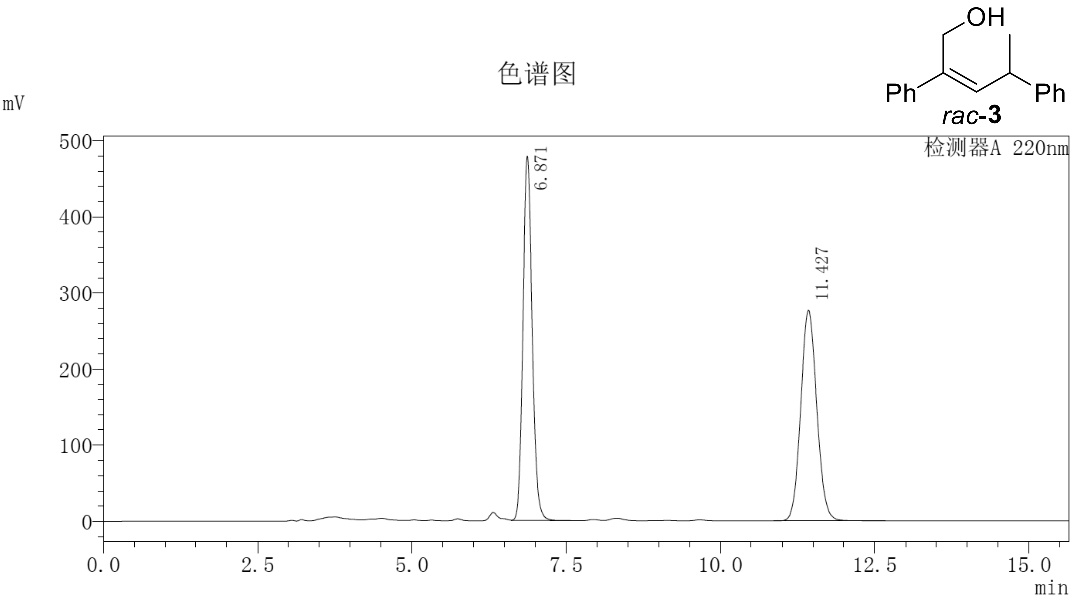
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	22.969	1379135	66616		99.320
2	25.392	9442	438		0.680
总计		1388577	67054		100.000

Figure S226. HPLC spectra of (*R,R*)-**1a**, Related to Scheme 1

分析日期　　　: 2018/12/28 11:21:13
处理日期　　　: 2018/12/28 11:36:53
描述　　　　　: OD*-H, n-hexane/iPrOH =90/10, 1.0 ml/min, 220 nm

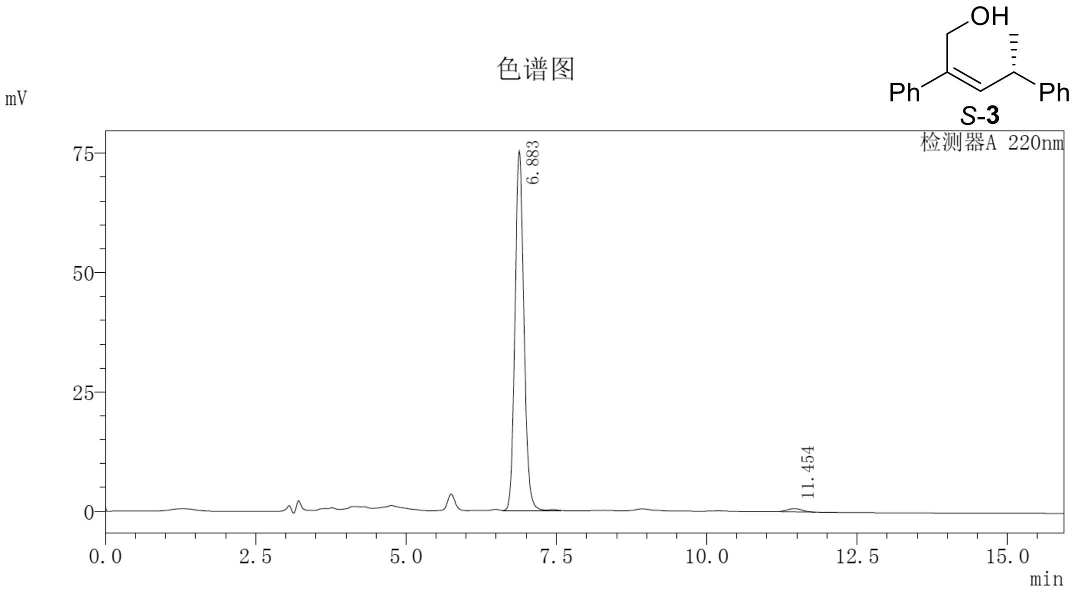


峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	6.871	4972293	478138	S	49.815
2	11.427	5009162	276849		50.185
总计		9981455	754987		100.000

分析日期　　　: 2018/12/28 11:37:49
处理日期　　　: 2018/12/28 11:53:46
描述　　　　　: OD*-H, n-hexane/iPrOH =90/10, 1.0 ml/min, 220 nm



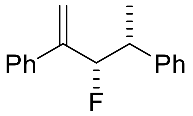
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	6.883	779396	75335	M	98.475
2	11.454	12073	686	M	1.525
总计		791469	76022		100.000

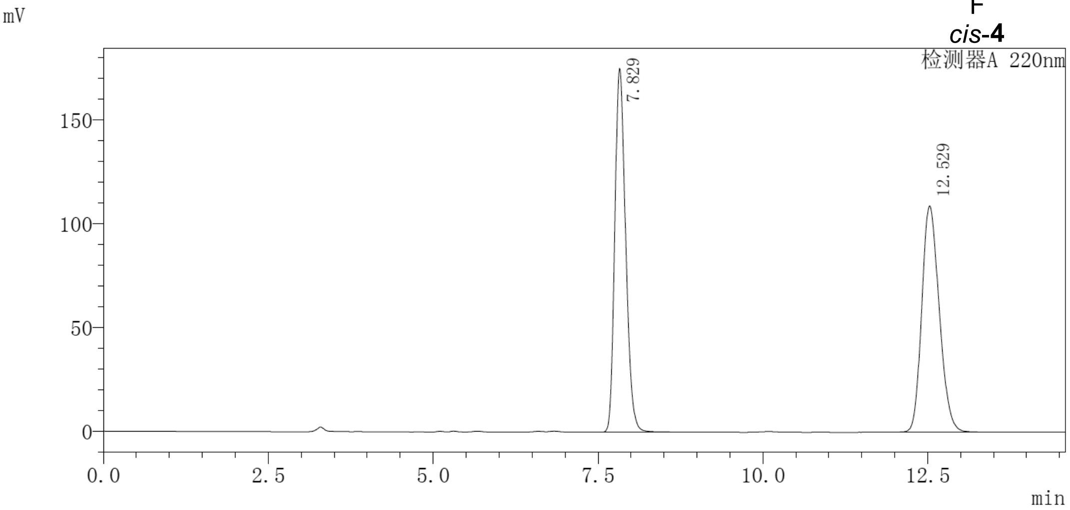
Figure S227. HPLC spectra of *S*-**3**, Related to Scheme 1

分析日期　　　: 2018/12/26 19:22:11
处理日期　　　: 2018/12/26 19:36:47
描述　　　　　: OJ-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm



cis-**4**

色谱图

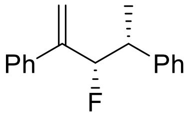


峰表

检测器A 220nm

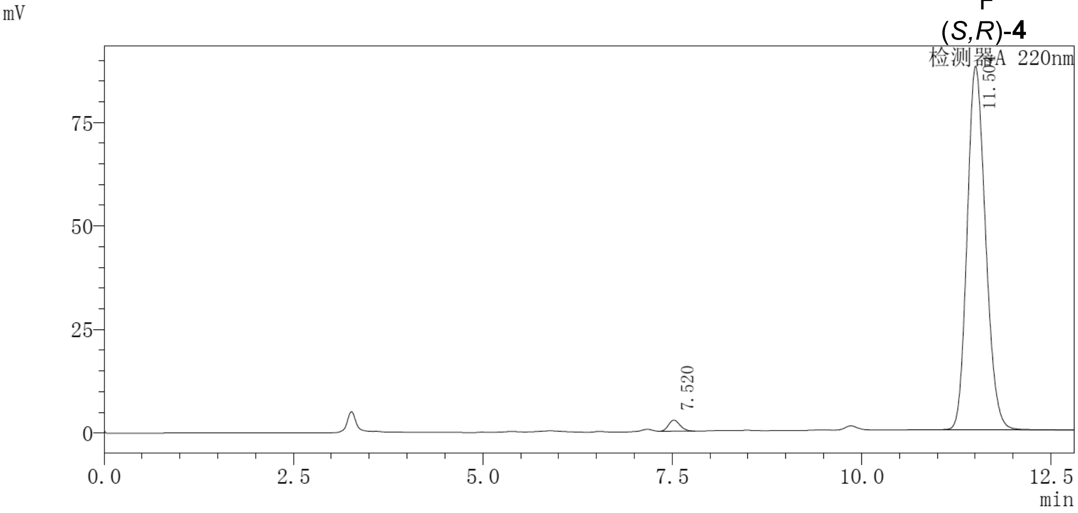
峰号	保留时间	面积	高度	标记	面积%
1	7.829	2003448	175064	S	49.897
2	12.529	2011710	108879		50.103
总计		4015158	283943		100.000

分析日期　　　: 2018/12/26 19:55:54
处理日期　　　: 2018/12/26 20:08:44
描述　　　　　: OJ-H, n-hexane/iPrOH =99/1, 1.0 ml/min, 220 nm



(*S*,*R*)-**4**

色谱图



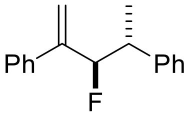
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	7.520	27873	2649		1.841
2	11.504	1486043	87756		98.159
总计		1513916	90405		100.000

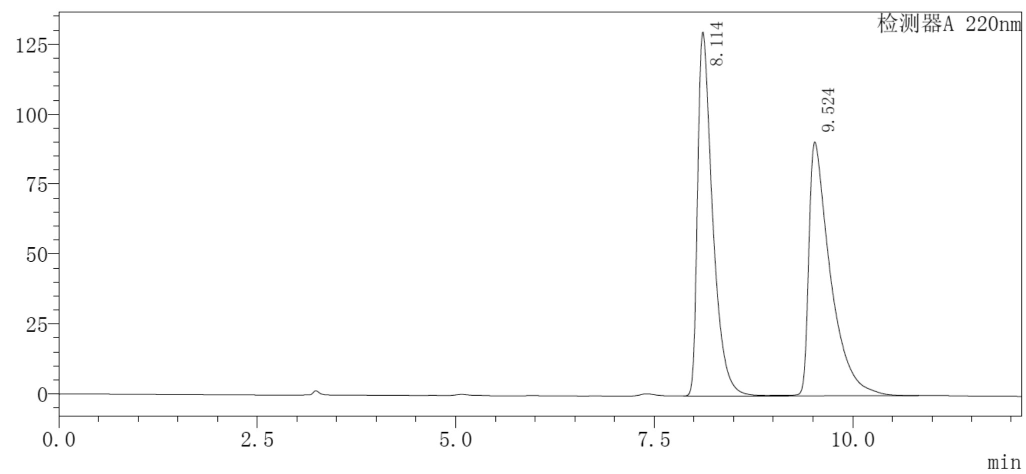
Figure S228. HPLC spectra of (*S,R*)-**4**, Related to Scheme 1

分析日期　　: 2018/12/28 12:10:12
处理日期　　: 2018/12/28 12:22:21
描述　　　　: OD*-H, n-hexane/iPrOH =99.9/0.1, 1.0 ml/min, 220 nm



trans-**4**

色谱图

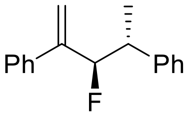


峰表

检测器A 220nm

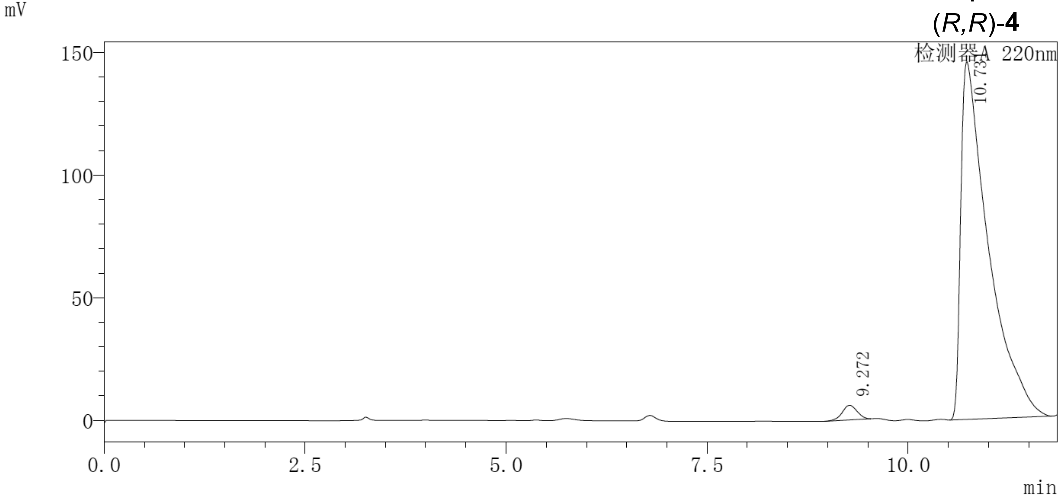
峰号	保留时间	面积	高度	标记	面积%
1	8.114	1715911	130023	S	50.016
2	9.524	1714812	90762	V	49.984
总计		3430723	220784		100.000

分析日期　　: 2018/12/28 12:24:00
处理日期　　: 2018/12/28 12:40:42
描述　　　　: OD*-H, n-hexane/iPrOH =99.9/0.1, 1.0 ml/min, 220 nm



(*R*,*R*)-**4**

色谱图



峰表

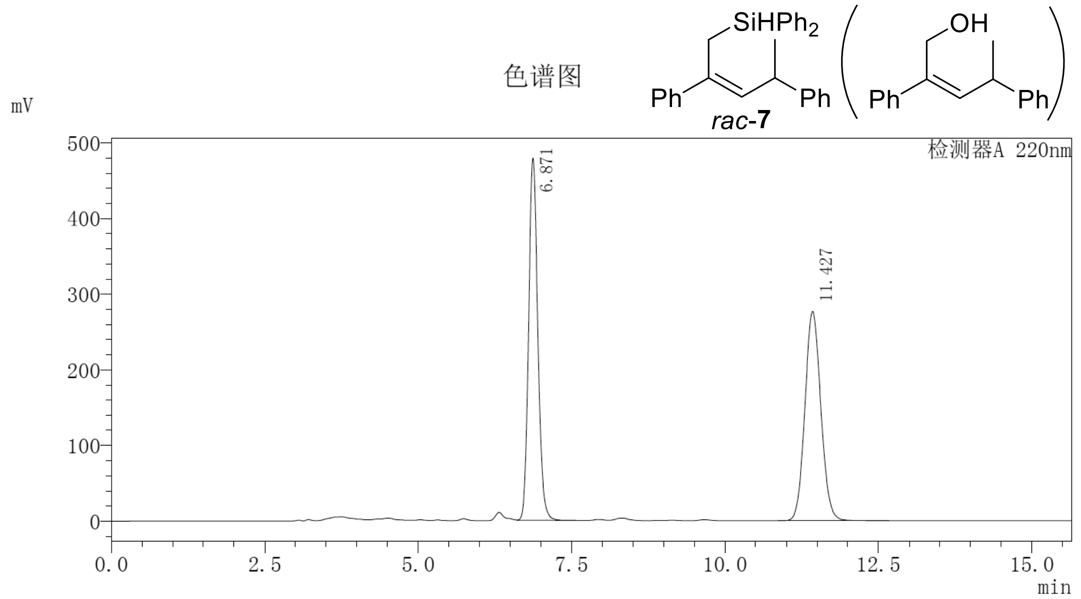
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	9.272	77343	6001		2.168
2	10.731	3490549	145847		97.832
总计		3567892	151848		100.000

Figure S229. HPLC spectra of (*R*,*R*)-**4**, Related to Scheme 1

分析日期　　　: 2018/12/28 11:21:13
处理日期　　　: 2018/12/28 11:36:53
描述　　　　　: OD*-H, n-hexane/iPrOH =90/10, 1.0 ml/min, 220 nm

色谱图



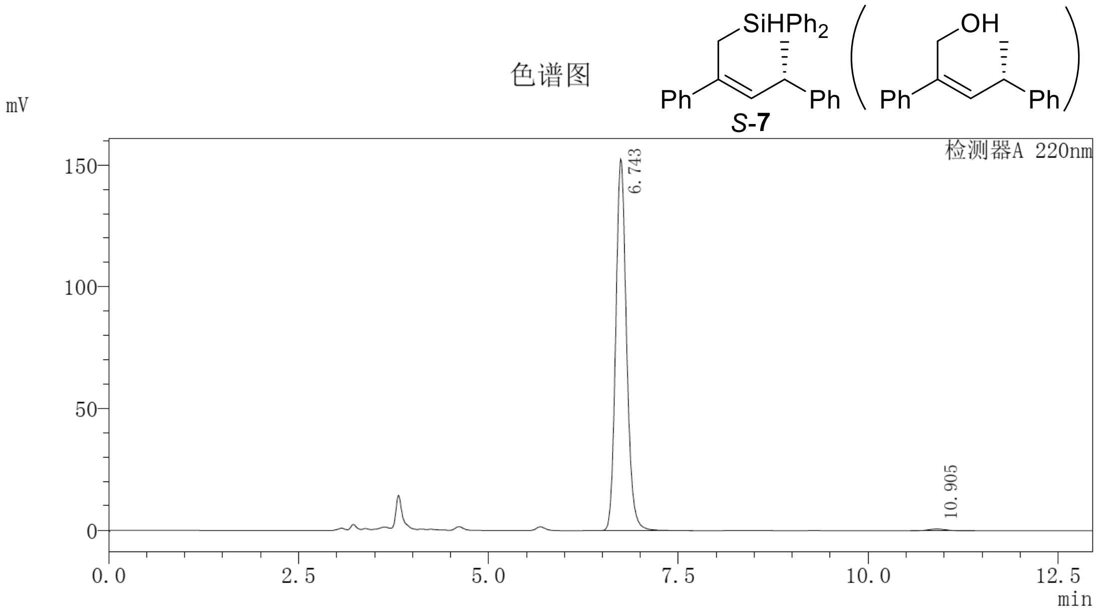
峰表

检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	6.871	4972293	478138	S	49.815
2	11.427	5009162	276849		50.185
总计		9981455	754987		100.000

分析日期　　　: 2019/7/27 18:11:18
处理日期　　　: 2019/7/27 18:24:17
描述　　　　　: OD-H, n-hexane/iPrOH = 90/10, 1.0 ml/min, 220 nm

色谱图



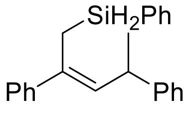
峰表

检测器A 220nm

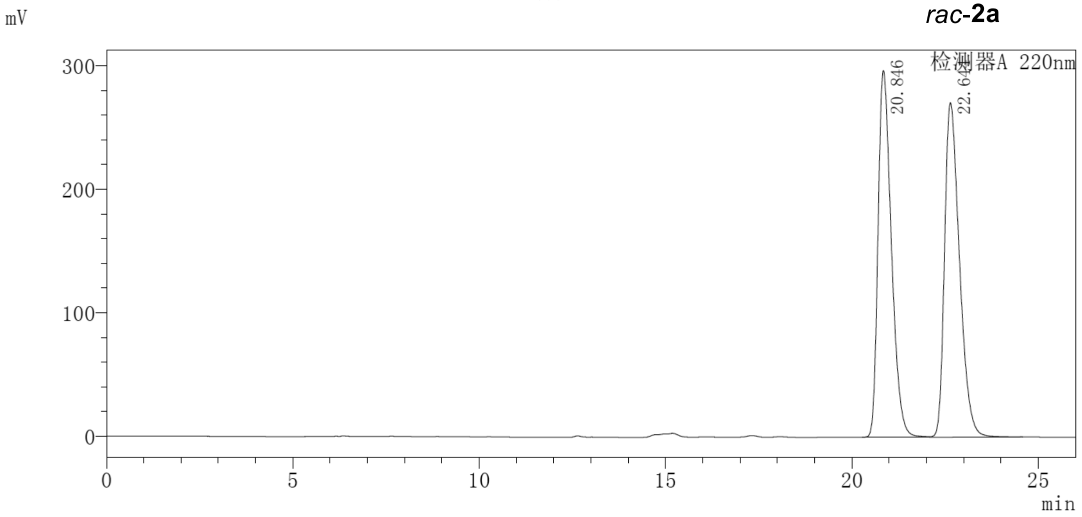
峰号	保留时间	面积	高度	标记	面积%
1	6.743	1512641	152610	V	99.184
2	10.905	12438	763		0.816
总计		1525080	153373		100.000

Figure S230. HPLC spectra of *S*-**7**, Related to Scheme 1

分析日期　　　: 2019/12/27 16:10:14
处理日期　　　: 2019/12/27 16:56:01
描述　　　　　: 2*OD-H, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm


rac-**2a**

色谱图

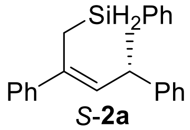


峰表

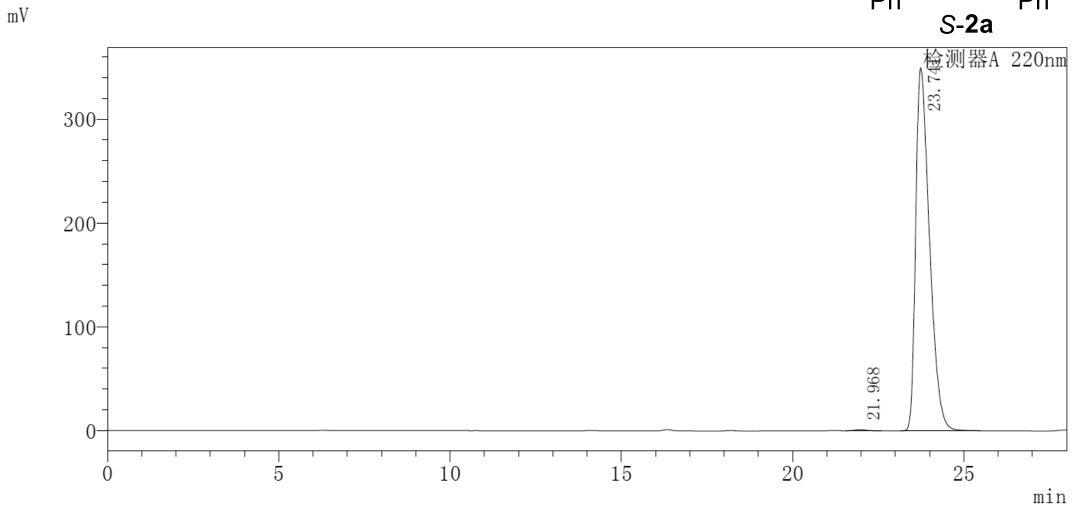
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	20.846	7380067	296711		49.433
2	22.644	7549362	270816	V	50.567
总计		14929429	567527		100.000

分析日期　　　: 2019/12/27 13:38:45
处理日期　　　: 2019/12/27 14:24:22
描述　　　　　: 2*OD-H, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm


S-**2a**

色谱图



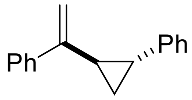
峰表

检测器A 220nm

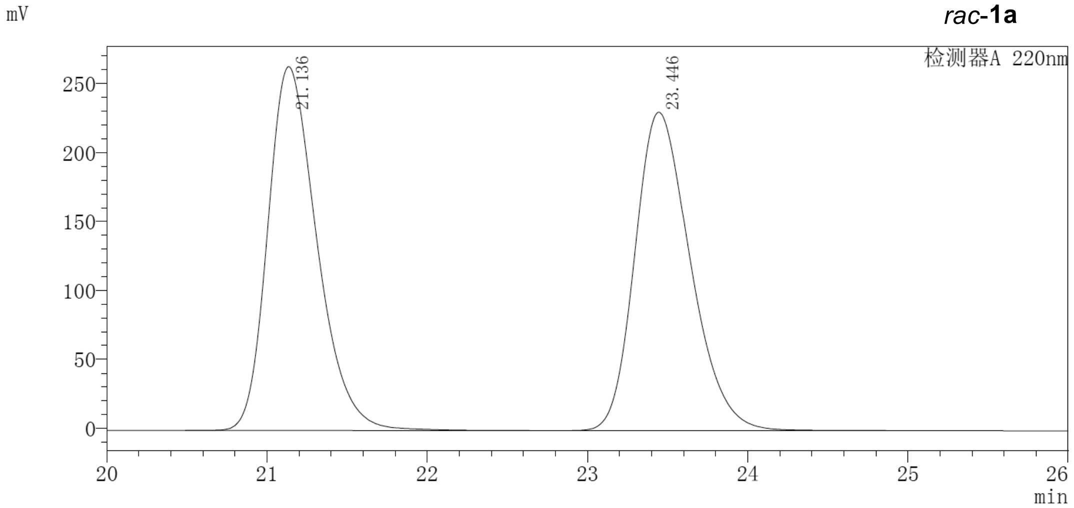
峰号	保留时间	面积	高度	标记	面积%
1	21.968	25407	1103		0.258
2	23.741	9807493	349771		99.742
总计		9832901	350875		100.000

Figure S231. HPLC spectra of *S*-**2a**, Related to Scheme 2

分析日期　　　　: 2019/7/30 10:03:21
处理日期　　　　: 2019/7/30 10:30:57
描述　　　　　　: OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm


rac-**1a**

色谱图

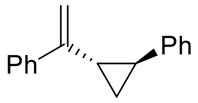


峰表

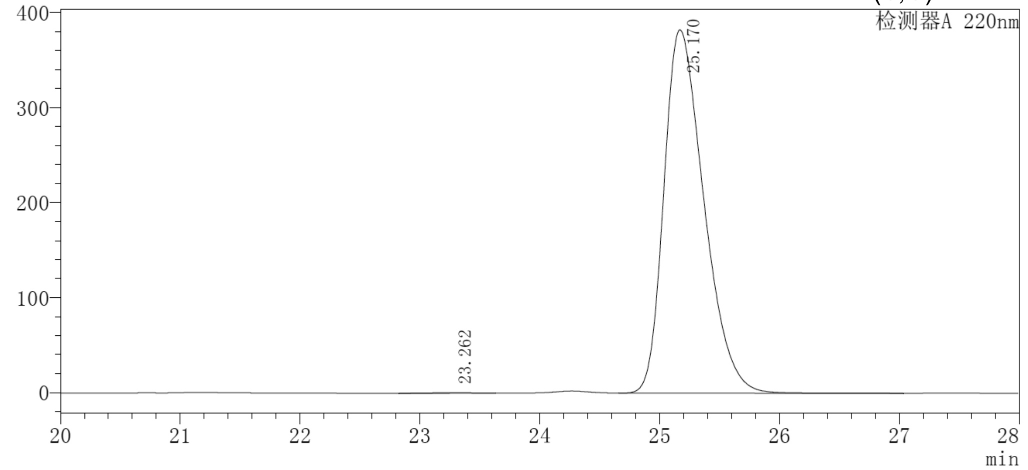
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	21.136	5614292	263846		50.337
2	23.446	5539092	230827	M	49.663
总计		11153384	494673		100.000

分析日期　　　　: 2020/1/6 19:20:56
处理日期　　　　: 2020/1/6 19:48:57
描述　　　　　　: OD-H*2, n-hexane/iPrOH = 99.9/0.1, 1.0 ml/min, 220 nm


(*S*,*S*)-**1a**

色谱图



峰表

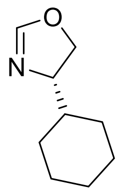
检测器A 220nm

峰号	保留时间	面积	高度	标记	面积%
1	23.262	10384	487		0.117
2	25.170	8866524	382616		99.883
总计		8876908	383103		100.000

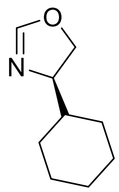
Figure S232. HPLC spectra of (*S,S*)-**1a**, Related to Scheme 2

Data S1. Related to Table 1, Table 2, Scheme 1 and Scheme 2.

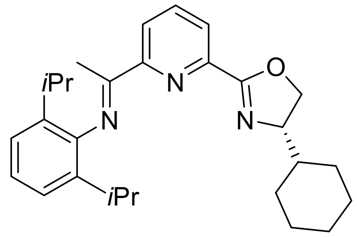
A. Data of Ligands and Metal Complexes



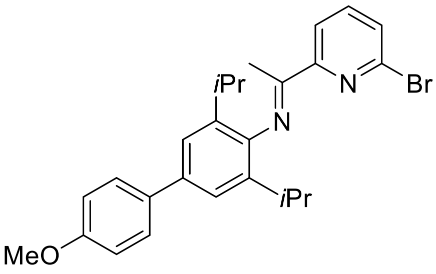
(*S*)-4-cyclohexyloxazoline (SL3-1) Using 16.31 g (114 mmol) of (*S*)-2-amino-2-cyclohexylethan-1-ol (Podhajsky et al., 2011), 18.2 ml (137 mmol) of *N,N*-dimethylformamide dimethyl acetal, 1.47 g of IR-120 an d 300 mL of toluene to give 11.52 g (75 mmol, 66% yield) of **SL3-1** as a colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = -120.8 (c 1.02, $CHCl_3$). IR (cm^{-1}): 2927, 2855, 1635, 1453, 1349. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.83 (s, 1H), 4.26-4.17 (m, 1H), 3.99-3.87 (m, 2H), 1.95-1.87 (m, 1H), 1.84-1.75 (m, 2H), 1.74-1.67 (m, 1H), 1.65-1.56 (m, 1H), 1.49-1.38 (m, 1H), 1.34-1.16 (m, 3H), 1.13-0.97 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.0, 70.5, 69.0, 42.4, 29.3, 29.0, 26.4, 26.0, 25.9. HRMS (EI) calculated for $[C_9H_{15}NO]^+$ requires m/z 153.1154, found m/z 153.1153.



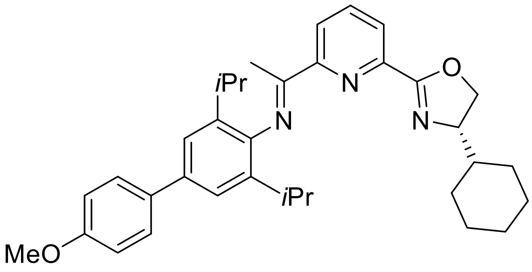
(*R*)-4-cyclohexyloxazoline (*R*-SL5-1) Using 23.53 g (164 mmol) of (*R*)-2-amino-2-cyclohexylethan-1-ol (Podhajsky et al., 2011), 26.2 ml (197 mmol) of *N,N*-dimethylformamide dimethyl acetal, 2.11 g of IR-120 and 300 mL of toluene to give 9.17 g (60 mmol, 36% yield) of ***R*-SL5-1** as a colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +118.0 (c 1.00, $CHCl_3$). IR (cm^{-1}): 2925, 2853, 1633, 1451, 1346. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.80 (d, J = 1.6 Hz, 1H), 4.24-4.14 (m, 1H), 3.96-3.84 (m, 2H), 1.92-1.84 (m, 1H), 1.81-1.72 (m, 2H), 1.71-1.64 (m, 1H), 1.62-1.54 (m, 1H), 1.46-1.36 (m, 1H), 1.31-1.14 (m, 3H), 1.10-0.95 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.9, 70.4, 68.9, 42.3, 29.2, 28.9, 26.3, 25.9, 25.8. HRMS (EI) calculated for $[C_9H_{15}NO]^+$ requires m/z 153.1154, found m/z 153.1152.



(*S*,*E*)-1-(6-(4-cyclohexyl-4,5-dihydrooxazol-2-yl)pyridin-2-yl)-*N*-(2,6-diisopropylphenyl)ethan-1-imine (L3) Using 1.8209 g (5.1 mmol) of (*E*)-1-(6-bromopyridin-2-yl)-N-(2,6-diisopropylphenyl)ethan-1-imine (Chen et al., 2014), 1.0256 g (6.7 mmol) of **SL3-1**, 0.0552 g (0.25 mmol) of Pd(OAc)$_2$, 0.1225 g (0.31 mmol) of 1,2-bis(diphenylphosphino)ethane, 0.8168 g (10.2 mmol) of *t*BuOLi and 40 mL of 1,4-dioxane to give 1.6644 g (3.9 mmol, 76% yield) of **L3** as a yellow solid, mp: 153.2-154.0 ºC. Optical Rotation: $[\alpha]_{20}^{D}$ = -63.4 (c 1.05, CHCl$_3$). IR (cm^{-1}): 2962, 2925, 1643, 1573, 1455, 1369. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.50 (dd, J = 8.0, 1.0 Hz, 1H), 8.18 (dd, J = 7.8, 1.0 Hz, 1H), 7.88 (dd, J = 8.0, 7.8 Hz, 1H), 7.18-7.14 (m, 2H), 7.12-7.07 (m, 1H), 4.54 (dd, J = 9.6, 8.4 Hz, 1H), 4.27 (dd, J = 8.2, 8.4 Hz, 1H), 4.21-4.13 (m, 1H), 2.76-2.67 (m, 2H), 2.28 (s, 3H), 2.08-2.00 (m, 1H), 1.88-1.55 (m, 5H), 1.31-1.07 (m, 17H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 166.7, 162.5, 156.1, 146.3, 146.1, 136.9, 135.67, 135.66, 125.3, 123.6, 123.0, 122.9, 72.1, 71.1, 42.8, 29.7, 28.9, 28.2, 26.5, 26.0, 23.2, 22.8, 17.2. HRMS (EI) calculated for $[C_{28}H_{37}N_3O]^+$ requires m/z 431.2937, found m/z 431.2937.

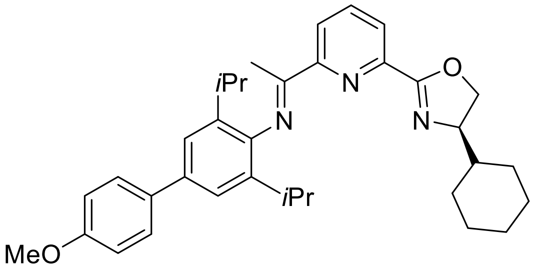


(*E*)-1-(6-bromopyridin-2-yl)-*N*-(3,5-diisopropyl-4'-methoxy-[1,1'-biphenyl]-4-yl)ethan-1-imine (SL5-1) Using 10.00 g (50 mmol) of 1-(6-bromopyridin-2-yl)ethan-1-one (Chen et al., 2014), 14.17 g (50 mmol) of 3,5-diisopropyl-4'-methoxy-[1,1'-biphenyl]-4-amine (Yoshida et al., 2018), 0.97 g (5.1 mmol) of *p*-toluenesulfonic acid monohydrate and 100 mL of toluene to give 16.04 g (34 mmol, 69% yield) of **SL5-1** as a yellow solid, mp: 151.6-152.9 ºC. IR (cm^{-1}): 2960, 1644, 1515, 1439, 1248. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.33 (d, J = 7.4 Hz, 1H), 7.67 (dd, J = 7.8, 7.6 Hz, 1H), 7.60-7.53 (m, 3H), 7.33 (s, 2H), 7.01-6.95 (m, 2H), 3.86 (s, 3H), 2.79-2.68 (m, 2H), 2.23 (s, 3H), 1.19 (d, J = 4.2 Hz, 6H), 1.17 (d, J = 3.8 Hz, 6H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 166.2, 158.7, 157.4, 145.1, 141.0, 138.8, 136.2, 136.0, 134.6, 129.2, 127.9, 121.6, 120.1, 114.1, 55.4, 28.4, 23.2, 22.9, 17.4. HRMS (EI) calculated for $[C_{26}H_{29}BrN_2O]^+$ requires m/z 464.1463, found m/z 464.1459.

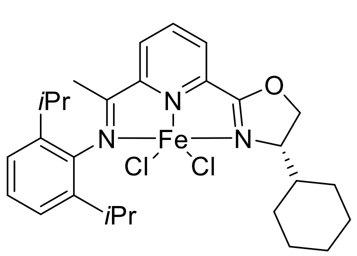


(*S*,*E*)-1-(6-(4-cyclohexyl-4,5-dihydrooxazol-2-yl)pyridin-2-yl)-*N*-(3,5-diisopropyl-4'-methoxy-[1,1'-biphenyl]-4-yl)ethan-1-imine (L5) Using 2.11 g (4.5 mmol) of **SL5-1**, 0.8297 g

(5.4 mmol) of **SL3-1**, 0.0267 g (0.12 mmol) of Pd(OAc)$_2$, 0.0536 g (0.13 mmol) of 1,2-bis(diphenylphosphino)ethane, 1.2244 g (15.3 mmol) of *t*BuOLi and 30 mL of 1,4-dioxane to give 1.7582 g (3.3 mmol, 72% yield) of **L5** as a yellow solid, mp: 186.3-187.6 ºC. Optical Rotation: $[\alpha]_{20}^{D}$ = -55.5 (c 1.00, CHCl$_3$). IR (cm^{-1}): 2960, 2925, 1642, 1572, 1515, 1458, 1368. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.51 (dd, J = 8.0, 1.0 Hz, 1H), 8.18 (dd, J = 7.8, 1.0 Hz, 1H), 7.89 (dd, J = 8.0, 7.8 Hz, 1H), 7.58-7.53 (m, 2H), 7.33 (s, 2H), 7.01-6.96 (m, 2H), 4.54 (dd, J = 9.8, 8.4 Hz, 1H), 4.28 (dd, J = 8.4, 8.6 Hz, 1H), 4.22-4.14 (m, 1H), 3.86 (s, 3H), 2.81-2.72 (m, 2H), 2.33 (s, 3H), 2.09-2.00 (m, 1H), 1.84-1.55 (m, 4H), 1.35-1.05 (m, 18H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 167.0, 162.5, 158.7, 156.2, 146.1, 145.3, 136.9, 136.1, 134.6, 127.9, 125.3, 123.1, 121.6, 114.1, 72.1, 71.1, 55.3, 42.8, 29.7, 28.9, 28.3, 26.5, 26.0, 23.3, 22.9, 17.4. HRMS (EI) calculated for $[C_{35}H_{43}N_3O_2]^+$ requires m/z 537.3355, found m/z 537.3357.

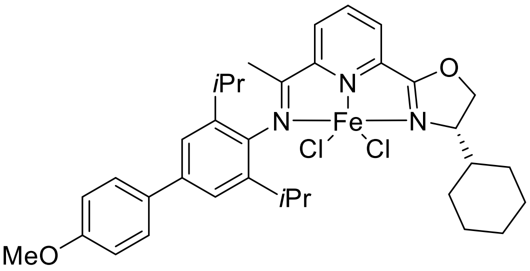


(*R*,*E*)-1-(6-(4-cyclohexyl-4,5-dihydrooxazol-2-yl)pyridin-2-yl)-*N*-(3,5-diisopropyl-4'-methoxy-[1,1'-biphenyl]-4-yl)ethan-1-imine (*R*-L5) Using 0.4659 g (1.0 mmol) of **SL5-1**, 0.2163 g (1.2 mmol) of ***R*-SL5-1**, 0.0117 g (0.05 mmol) of Pd(OAc)$_2$, 0.0238 g (0.06 mmol) of 1,2-bis(diphenylphosphino)ethane, 0.3551 g (4.0 mmol) of *t*BuOLi and 6 mL of 1,4-dioxane to give 0.2830 g (0.53mmol, 53% yield) of ***R*-L5** as a yellow solid. IR (cm^{-1}): 2960, 2925, 1645, 1574, 1515, 1454, 1370. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.51 (dd, J = 8.0, 1.0 Hz, 1H), 8.19 (dd, J = 7.8, 1.0 Hz, 1H), 7.89 (dd, J = 8.0, 7.8 Hz, 1H), 7.58-7.53 (m, 2H), 7.33 (s, 2H), 7.01-6.96 (m, 2H), 4.54 (dd, J = 9.8, 8.4 Hz, 1H), 4.28 (t, J = 8.4 Hz, 1H), 4.22-4.14 (m, 1H), 3.86 (s, 3H), 2.82-2.70 (m, 2H), 2.33 (s, 3H), 2.09-2.00 (m, 1H), 1.84-1.74 (m, 2H), 1.74-1.63 (m, 2H), 1.61-1.54 (m, 1H), 1.35-1.08 (m, 17H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 167.0, 162.5, 158.7, 156.2, 146.1, 145.3, 136.9, 136.1, 134.6, 127.9, 125.3, 123.1, 121.6, 114.1, 72.1, 71.1, 55.3, 42.8, 29.7, 28.9, 28.4, 26.5, 26.0, 23.3, 22.9, 17.4. HRMS (EI) calculated for $[C_{35}H_{43}N_3O_2]^+$ requires m/z 537.3355, found m/z 537.3352.

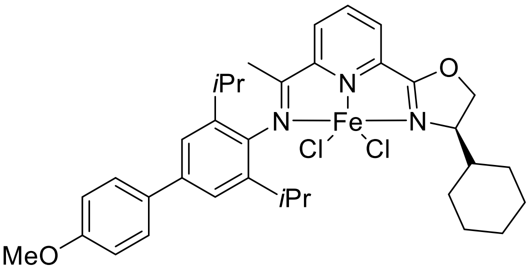


L3·FeCl$_2$ A 50 mL Schlenk flask was charged with 0.8253 g

(1.91 mmol) of **L3**, 0.2060 g (1.63 mmol) of $FeCl_2$ and 10 mL of THF under the atmosphere of nitrogen, then the mixture was stirred at room temperature for 3 h, then 10 mL of ether was injected to precipitate the complex and stirred for 30 min. The resulting mixture was filtered, washed with ether and dried in vacuo to give 0.7111 g (1.27 mmol, 78% yield) of blue powder. Anal. Calcd for $C_{28}H_{37}Cl_2FeN_3O$: C, 60.23; H, 6.68; N, 7.53; Found: C, 59.72; H, 6.90; N, 7.39.

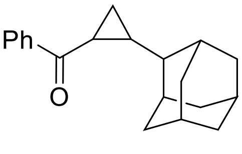


L5·FeCl₂ A 50 mL Schlenk flask was charged with 1.7582 g (3.27 mmol) of **L5**, 0.4066 g (3.20 mmol) of $FeCl_2$ and 33 mL of THF under the atmosphere of nitrogen, then the mixture was stirred at room temperature for 3 h, then 33 mL of ether was injected to precipitate the complex and stirred for 30 min. The resulting mixture was filtered, washed with ether and dried in vacuo to give 1.7111 g (2.58 mmol, 80% yield) of green powder. Anal. Calcd for $C_{35}H_{47}Cl_2FeN_3O_4$: C, 63.26; H, 6.52; N, 6.32; Found: C, 60.55; H, 6.48; N, 6.09.



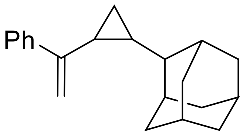
***R*-L5·FeCl₂** A 50 mL Schlenk flask was charged with 0.5403 g (1.00 mmol) of ***R*-L5**, 0.0.1261 g (0.99 mmol) of $FeCl_2$ and 10 mL of THF under the atmosphere of nitrogen, then the mixture was stirred at room temperature for 4 h, then 10 mL of ether was injected to precipitate the complex and stirred for 30 min. The resulting mixture was filtered, washed with ether and dried in vacuo to give 0.5190 g (0.78 mmol, 79% yield) of green powder. Anal. Calcd for $C_{35}H_{47}Cl_2FeN_3O_4$: C, 63.26; H, 6.52; N, 6.32; Found: C, 61.82; H, 6.46; N, 6.00.

B. Data of Vinylcyclopropanes

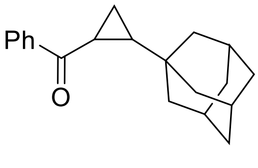


(2-(adamantan-2-yl)cyclopropyl)(phenyl)methanone (S1ab) Using 5.03 g (18.9 mmol) of (*E*)-3-(adamantan-2-yl)-1-phenylprop-2-en-1-one

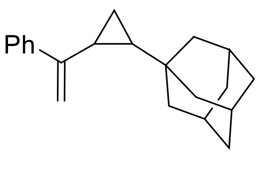
(Wang et al., 2017) to give 4.03 g (14.4 mmol, 76% yield) of **S1ab**. colorless oil; IR (cm^{-1}): 2906, 1668, 1451, 1376, 1219. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.03-7.98 (m, 2H), 7.58-7.53 (m, 1H), 7.50-7.44 (m, 2H), 2.50-2.44 (m, 1H), 2.10-1.91 (m, 3H), 1.91-1.81 (m, 6H), 1.76-1.65 (m, 4H), 1.64-1.57 (m, 1H), 1.56-1.50 (m, 2H), 1.11-1.05 (m, 1H), 0.98-0.93 (m, 1H); ^{13}C NMR: (CDCl$_3$, 100 MHz): δ 200.2, 138.1, 132.6, 128.5, 127.9, 50.3, 39.1, 39.0, 38.2, 32.8, 32.6, 32.3, 30.6, 28.1, 28.0, 25.1, 18.7; HRMS (EI) calculated for [$C_{20}H_{24}O$]$^+$ requires m/z 280.1827, found m/z 280.1828.



2-(2-(1-phenylvinyl)cyclopropyl)adamantane (1ab) Using 4.03 g (14.4 mmol) of **S1ab** to give 3.52 g (12.6 mmol, 88% yield) of **1ab**. colorless oil; IR (cm^{-1}): 2902, 2849, 1621, 1493, 1451. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.52 (d, J = 7.8 Hz, 2H), 7.35-7.22 (m, 3H), 5.18 (s, 1H), 4.92 (s, 1H), 2.16-2.00 (m, 2H), 1.97-1.92 (m, 1H), 1.88-1.81 (m, 5H), 1.76-1.72 (m, 2H), 1.70-1.63 (m, 2H), 1.63-1.56 (m, 2H), 1.47-1.40 (m, 1H), 1.40-1.33 (m, 1H), 0.99-0.92 (m, 1H), 0.79-0.73 (m, 1H), 0.67-0.61 (m, 1H); ^{13}C NMR: (CDCl$_3$, 100 MHz): δ 150.1, 142.2, 128.0, 127.2, 126.2, 108.9, 50.8, 39.20, 39.18, 38.3, 32.8, 32.53, 32.49, 32.3, 28.23, 28.19, 24.0, 23.3, 14.2; HRMS (EI) calculated for [$C_{21}H_{26}$]$^+$ requires m/z 278.2035, found m/z 278.2032.



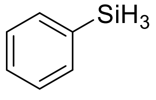
(2-(-adamantan-1-yl)cyclopropyl)(phenyl)methanone (S1ac) Using 22.95 g (86.2 mmol) of (*E*)-3-(adamantan-1-yl)-1-phenylprop-2-en-1-one (Wang et al., 2017) to give 8.25 g (29.4 mmol, 34% yield) of **S1ac**. colorless oil; IR (cm^{-1}): 2901, 1667, 1450, 1399, 1333, 1221. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.03-7.99 (m, 2H), 7.58-7.53 (m, 1H), 7.50-7.44 (m, 2H), 2.65-2.60 (m, 1H), 1.98 (s, 3H), 1.76-1.61 (m, 6H), 1.52-1.48 (m, 6H), 1.46-1.40 (m, 1H), 1.36-1.31 (m, 1H), 1.11-1.06 (m, 1H); ^{13}C NMR: (CDCl$_3$, 100 MHz): δ 200.7, 138.2, 132.5, 128.5, 127.9, 41.4, 39.6, 37.0, 31.6, 28.4, 19.5, 13.2; HRMS (EI) calculated for [$C_{20}H_{24}O$]$^+$ requires m/z 280.1827, found m/z 280.1831.



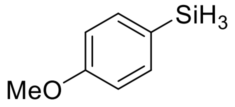
1-(2-(1-phenylvinyl)cyclopropyl)adamantane (1ac) Using 8.25 g (29.4

mmol) of **S1ac** to give 3.80 g (13.7 mmol, 46% yield) of **1ac**. colorless oil; IR (cm^{-1}): 2900, 2846, 1621, 1493, 1449. ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.56-7.51 (m, 2H), 7.35-7.29 (m, 2H), 7.29-7.23 (m, 1H), 5.18 (s, 1H), 4.89 (s, 1H), 1.96 (s, 3H), 1.74-1.58 (m, 7H), 1.53-1.45 (m, 6H), 0.84-0.77 (m, 2H), 0.55-0.48 (m, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 150.3, 142.2, 128.0, 127.2, 126.3, 108.9, 41.6, 37.2, 33.6, 31.3, 28.6, 17.2, 8.6; HRMS (EI) calculated for $[C_{21}H_{26}]^+$ requires m/z 278.2035, found m/z 278.2033.

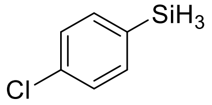
C. Data of Silanes



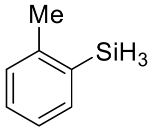
Phenylsilane (S2a) (Sakurai et al., 1984) colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61-7.66 (m, 2H), 7.43-7.32 (m, 3H), 4.20 (s, 3H).



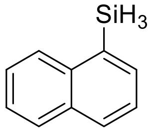
(4-Methoxyphenyl)silane (S2b) (Visco et al., 2016) colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53-7.49 (m, 2H), 6.93-6.89 (m, 2H), 4.18 (s, 3H), 3.81 (s, 3H).



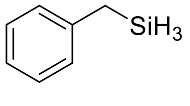
(4-Chlorophenyl)silane (S2c) (Sakurai et al., 1984) colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.0 Hz, 2H), 4.24 (s, 3H).



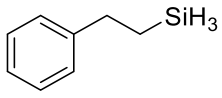
***o*-Tolylsilane (S2d)** (Banovetz et al., 1993) colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60-7.55 (m, 1H), 7.35-7.30 (m, 1H), 7.21-7.14 (m, 2H), 4.20 (s, 3H), 2.44 (s, 3H).



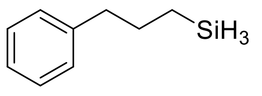
Naphthalen-1-ylsilane (S2e) (Visco et al., 2016) colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97-7.89 (m, 2H), 7.87-7.80 (m, 2H), 7.57-7.48 (m, 2H), 7.47-7.41 (m, 1H), 4.47 (s, 3H).



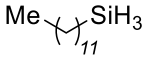
Benzylsilane (S2f) (Sakurai et al., 1984) colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28-7.21 (m, 2H), 7.15-7.09 (m, 3H), 3.66 (t, J = 4.0 Hz, 3H), 2.28 (q, J = 4.0 Hz, 2H).



Phenethylsilane (S2g) (Sakurai et al., 1984) colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.32-7.25 (m, 2H), 7.22-7.15 (m, 3H), 3.55-3.49 (m, 3H), 2.80-2.71 (m, 2H), 1.16-1.07 (m, 2H).

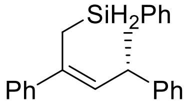


(3-Phenylpropyl)silane (S2h) (Smirnov and Oestreich, 2016) colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.30-7.23 (m, 2H), 7.20-7.13 (m, 3H), 7.52-7.47 (m, 3H), 2.65 (t, J = 8.4 Hz, 2H), 1.79-1.69 (m, 2H), 0.81-0.72 (m, 2H).



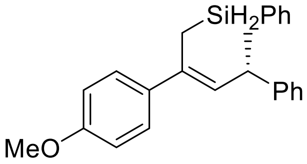
Dodecylsilane (S2i) (Rosenberg and Kobus, 2003) colorless oil. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 3.48 (t, J = 3.8 Hz, 3H), 1.34-1.20 (m, 20H), 0.88 (t, J = 6.4 Hz, 3H), 0.78-0.70 (m, 2H).

D. Iron-Catalyzed Asymmetric Hydrosilylation of Vinylcyclopropanes

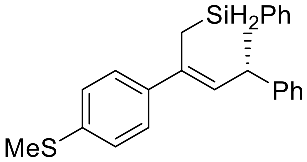


(*S*,*Z*)-(2,4-Diphenylpent-2-en-1-yl)(phenyl)silane (2a) Prepared according to the general procedure, using 0.1117 g (0.5 mmol) of **1a**, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH$_3$, 0.0167 g (0.025 mmol) of **L5**·FeCl$_2$, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt$_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0795 g (0.24 mmol, 13/1 *E/Z*, 48% yield) of the title compound (*Z*) and recover chiral **1a** in 28% NMR yield. (*R*,*R*)-**1a**: 86.4% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 22.4 (major), 25.0 (minor). **2a**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +28.5 (c 1.03, CHCl$_3$), 98.0% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 21.4 (minor), 23.0 (major). IR (cm^{-1}): 2962, 2144, 1599, 1492, 1428. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.50-7.45 (m, 2H), 7.40-7.33 (m, 3H), 7.33-7.24 (m, 6H), 7.24-7.20 (m, 3H), 7.20-7.14 (m, 1H), 5.76 (d, J = 9.6 Hz, 1H), 4.29-4.21 (m, 2H), 3.72-3.63 (m, 1H), 2.44-2.29 (m, 2H), 1.31 (d, J = 6.8 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz):

δ 146.4, 143.2, 135.3, 135.2, 132.2, 132.1, 129.7, 128.4, 128.1, 128.0, 127.0, 126.9, 126.5, 125.9, 38.9, 22.6, 15.1. HRMS (EI) calculated for $[C_{23}H_{24}Si]^+$ requires m/z 328.1647, found m/z 328.1649.

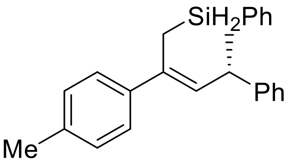


(*S*,*Z*)-(2-(4-Methoxyphenyl)-4-phenylpent-2-en-1-yl)(phenyl)silane (2b) Prepared according to the general procedure, using 0.1253 g (0.5 mmol) of **1b**, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH$_3$, 0.0167 g (0.025 mmol) of **L5**·FeCl$_2$, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt$_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0741 g (0.21 mmol, 9/1 *E/Z*, 41% yield) of the title compound (*Z*) and recover chiral **1b** in 33% NMR yield. (*R*,*R*)-**1b**: 75.9% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 95/5, 1.0 mL/min, n = 220 nm, tr 11.1 (major), 14.1 (minor). **2b**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +31.6 (c 0.98, CHCl$_3$), 96.0% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 21.4 (minor), 25.6 (major). IR (cm^{-1}): 2957, 2924, 2143, 1511, 1247. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.49-7.45 (m, 2H), 7.38-7.32 (m, 3H), 7.32-7.24 (m, 4H), 7.22-7.17 (m, 1H), 7.15-7.10 (m, 2H), 6.84-6.78 (m, 2H), 5.73 (d, J = 9.6 Hz, 1H), 4.30-4.21 (m, 2H), 3.76 (s, 3H), 3.68-3.57 (m, 1H), 2.44-2.28 (m, 2H), 1.28 (d, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 157.8, 143.2, 138.5, 135.2, 135.0, 132.5, 132.1, 129.7, 128.1, 127.9, 127.8, 126.8, 126.5, 113.8, 55.2, 38.0, 22.7, 15.0. HRMS (EI) calculated for $[C_{24}H_{26}OSi]^+$ requires m/z 358.1753, found m/z 358.1756.



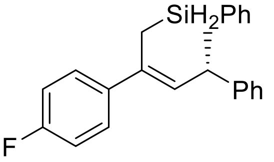
(*S*,*Z*)-(2-(4-(Methylthio)phenyl)-4-phenylpent-2-en-1-yl)(phenyl) silane (2c) Prepared according to the general procedure, using 0.1343 g (0.5 mmol) of **1c**, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH$_3$, 0.0166 g (0.025 mmol) of **L5**·FeCl$_2$, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt$_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by

PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0785 g (0.21 mmol, 11/1 *E/Z*, 42% yield) of the title compound (*Z*) and recover chiral **1c** in 19% NMR yield. (*R*,*R*)-**1c**: 94.9% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 95/5, 1.0 mL/min, n = 220 nm, tr 11.4 (major), 15.7 (minor). **2c**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = -25.2 (c 1.03, $CHCl_3$), 98.1% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 90/10, 1.0 mL/min, n = 220 nm, tr 12.3 (major), 19.8 (minor). IR (cm^{-1}): 2965, 2143, 1596, 1492, 1435. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49-7.44 (m, 2H), 7.39-7.33 (m, 1H), 7.33-7.24 (m, 6H), 7.23-7.13 (m, 5H), 5.75 (d, 1H), 4.30-4.20 (m, 2H), 3.71-3.61 (m, 1H), 2.46 (s, 3H), 2.41-2.24 (m, 2H), 1.30 (d, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.4, 140.1, 136.8, 135.2, 134.7, 132.0, 131.9, 129.7, 128.4, 128.0, 127.0, 126.9, 126.6, 126.0, 38.9, 22.6, 16.0, 14.9. HRMS (ESI) calculated for $[C_{24}H_{27}SSi]^+$ (M + H$^+$) requires m/z 375.1603, found m/z 375.1603.

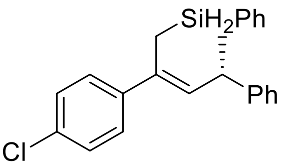


(*S*,*Z*)-Phenyl(4-phenyl-2-(p-tolyl)pent-2-en-1-yl)silane (2d)

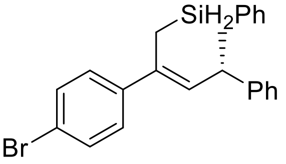
Prepared according to the general procedure, using 0.1172 g (0.5 mmol) of **1d**, 96 μL (0.75 mmol, 1.5 equiv.) of $PhSiH_3$, 0.0167 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0703 g (0.21 mmol, 17/1 *E/Z*, 41% yield) of the title compound (*Z*) and recover chiral **1d** in 35% NMR yield. (*R*,*R*)-**1d**: 72.2% *ee* determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*hexane/*i*PrOH = 98/2, 1.0 mL/min, n = 220 nm, tr 4.0 (major), 5.2 (minor). **2d**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +16.7 (c 1.04, $CHCl_3$), 97.2% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 8.5 (minor), 11.2 (major). IR (cm^{-1}): 2922, 2144, 1511, 1452, 1429. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50-7.46 (m, 2H), 7.40-7.34 (m, 1H), 7.33-7.20 (m, 8H), 7.19-7.14 (m, 1H), 7.08 (d, J = 7.8 Hz, 2H), 5.74 (d, J = 9.4 Hz, 1H), 4.28-4.20 (m, 2H), 3.70-3.61 (m, 1H), 2.42-2.27 (m, 5H), 1.29 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.5, 140.2, 136.6, 135.2, 135.1, 132.2, 131.5, 129.7, 128.8, 128.4, 127.9, 127.0, 126.4, 125.9, 38.9, 22.6, 21.0, 15.0. HRMS (EI) calculated for $[C_{24}H_{26}Si]^+$ requires m/z 342.1804, found m/z 342.1804.



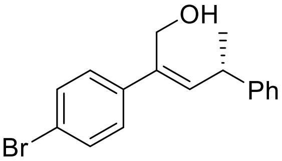
***(S,Z)*-(2-(4-Fluorophenyl)-4-phenylpent-2-en-1-yl)(phenyl)silane (2e)** Prepared according to the general procedure, using 0.1192 g (0.5 mmol) of **1e**, 96 μL (0.75 mmol, 1.5 equiv.) of $PhSiH_3$, 0.0167 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0701 g (0.20 mmol, 11/1 *E/Z*, 40% yield) of the title compound (*Z*) and recover chiral **1e** in 36% NMR yield. (*R*,*R*)-**1e**: 72.5% *ee* determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 5.8 (major), 6.2 (minor). **2e**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +28.9 (c 1.00, $CHCl_3$), 96.1% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 9.3 (minor), 10.1 (major). IR (cm^{-1}): 2960, 2924, 2144, 1601, 1507, 1230. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48-7.43 (m, 2H), 7.40-7.34 (m, 1H), 7.33-7.25 (m, 6H), 7.25-7.15 (m, 3H), 6.98-6.90 (m, 2H), 5.69 (d, *J* = 9.4 Hz, 1H), 4.27-4.19 (m, 2H), 3.71-3.61 (m, 1H), 2.42-2.26 (m, 2H), 1.30 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.0 (d, *J* = 246.4 Hz), 146.3, 139.3 (d, *J* = 3.4 Hz), 135.2, 134.4, 132.3, 131.8, 129.8, 128.5, 128.1 (d, *J* = 7.8 Hz), 128.0, 127.0, 126.0, 114.9 (d, *J* = 21.2 Hz), 38.9, 22.6, 15.3; ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ -116.1. HRMS (EI) calculated for $[C_{23}H_{23}FSi]^+$ requires m/z 346.1553, found m/z 346.1551.



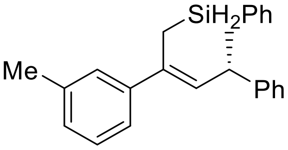
***(S,Z)*-(2-(4-Chlorophenyl)-4-phenylpent-2-en-1-yl)(phenyl)silane (2f)** Prepared according to the general procedure, using 0.1272 g (0.5 mmol) of **1f**, 96 μL (0.75 mmol, 1.5 equiv.) of $PhSiH_3$, 0.0168 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 1 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0857 g (0.24 mmol, 11/1 *E/Z*, 47% yield) of the title compound (*Z*) and recover chiral **1f** in 15% NMR yield. (*R*,*R*)-**1f**: 97.7% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99.5/0.5, 1.0 mL/min, n = 220 nm, tr 10.5 (major), 15.0 (minor). **2f**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D} = -2.1$ (c 1.01, $CHCl_3$), 96.2% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99.5/0.5, 1.0 mL/min, n = 220 nm, tr 21.8 (minor), 26.2 (major). IR (cm^{-1}): 2963, 2924, 2144, 1491, 1428. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46-7.41 (m, 2H), 7.39-7.33 (m, 1H), 7.31-7.14 (m, 11H), 5.73 (d, *J* = 9.4 Hz, 1H), 4.28-4.20 (m, 2H), 3.70-3.61 (m, 1H), 2.40-2.25 (m, 2H), 1.30 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.1, 141.6, 135.2, 134.3, 132.7, 132.6, 131.7, 129.8, 128.5, 128.2, 128.0, 127.8, 126.9, 126.0, 38.9, 22.5, 15.0. HRMS (EI) calculated for $[C_{23}H_{23}ClSi]^+$ requires m/z 362.1258, found m/z 362.1259.



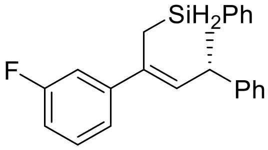
(*S*,*Z*)-(2-(4-Bromophenyl)-4-phenylpent-2-en-1-yl)(phenyl)silane (2g) Prepared according to the general procedure, using 0.1510 g (0.5 mmol) of **1g**, 96 μL (0.75 mmol, 1.5 equiv.) of $PhSiH_3$, 0.0168 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0956 g (0.23 mmol, 18/1 *E/Z*, 47% yield) of the title compound (*Z*) and recover chiral **1g** in 18% NMR yield. (*R*,*R*)-**1g**: 95.5% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 9.0 (major), 12.8 (minor). **2g**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D} = -5.5$ (c 1.04, $CHCl_3$), 97.2% *ee* determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 90/10, 1.0 mL/min, n = 220 nm, tr 7.4 (major), 9.6 (minor). IR (cm^{-1}): 3022, 2964, 2143, 1488, 1439. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47-7.42 (m, 2H), 7.41-7.34 (m, 3H), 7.33-7.25 (m, 4H), 7.22-7.15 (m, 5H), 5.74 (d, *J* = 9.6 Hz, 1H), 4.27-4.20 (m, 2H), 3.71-3.61 (m, 1H), 2.41-2.25 (m, 2H), 1.30 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): *δ* 146.1, 142.1, 135.2, 134.4, 132.8, 131.7, 131.2, 129.8, 128.5, 128.2, 128.0, 127.0, 126.0, 120.7, 38.9, 22.5, 15.0. HRMS (EI) calculated for $[C_{23}H_{23}BrSi]^+$ requires m/z 406.0752, found m/z 406.0750.



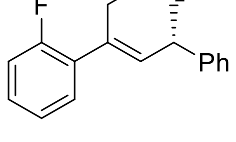
(*S*,*Z*)-2-(4-Bromophenyl)-4-phenylpent-2-en-1-ol (2g-ox) colorless oil. IR (cm^{-1}): 3360, 2973, 2908, 1486, 1394. ^{1}H NMR (CDCl$_3$, 400 MHz): *δ* 7.46-7.41 (m, 2H), 7.35-7.25 (m, 6H), 7.24-7.18 (m, 1H), 6.01 (d, *J* = 9.8 Hz, 1H), 4.58 (d, *J* = 2.8 Hz, 2H), 4.01-3.91 (m, 1H), 1.45 (d, *J* = 7.0 Hz, 3H), 1.30 (brs, 1H); ^{13}C NMR (CDCl$_3$, 100 MHz): *δ* 145.8, 139.7, 137.7, 136.7, 131.5, 128.8, 128.1, 126.8, 126.4, 121.2, 59.9, 38.3, 22.7. HRMS (EI) calculated for $[C_{17}H_{17}BrO]^+$ requires m/z 316.0463, found m/z 316.0460.



(*S*,*Z*)-Phenyl(4-phenyl-2-(m-tolyl)pent-2-en-1-yl)silane (2h) Prepared according to the general procedure, using 0.1173 g (0.5 mmol) of **1h**, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH$_3$, 0.0165 g (0.025 mmol) of **L5**·FeCl$_2$, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt$_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0688 g (0.20 mmol, 14/1 *E/Z*, 40% yield) of the title compound (*Z*) and recover chiral **1h** in 34% NMR yield. (*R*,*R*)-**1h**: 80.3% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99.5/0.5, 1.0 mL/min, n = 220 nm, tr 8.0 (major), 13.3 (minor). **2h**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +26.2 (c 1.03, CHCl$_3$), 97.9% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 6.0 (minor), 7.4 (major). IR (cm^{-1}): 2958, 2923, 2142, 1601, 1452, 1428. ^{1}H NMR (CDCl$_3$, 400 MHz): *δ* 7.50-7.45 (m, 2H), 7.40-7.35 (m, 1H), 7.34-7.25 (m, 4H), 7.25-7.21 (m, 2H), 7.20-7.12 (m, 4H), 7.05-7.01 (m, 1H), 5.75 (d, *J* = 9.6 Hz, 1H), 4.28-4.21 (m, 2H), 3.72-3.63 (m, 1H), 2.43-2.30 (m, 2H), 2.31 (s, 3H), 1.31 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): *δ* 146.5, 143.2, 137.7, 135.5, 135.3, 132.2, 132.0, 129.7, 128.4, 128.1, 128.0, 127.7, 127.4, 127.1, 126.0, 123.7, 38.9, 22.7, 21.5, 15.1. HRMS (EI) calculated for $[C_{24}H_{26}Si]^+$ requires m/z 342.1804, found m/z 342.1806.

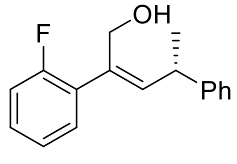


(*S*,*Z*)-(2-(3-Fluorophenyl)-4-phenylpent-2-en-1-yl)(phenyl)silane (2i) Prepared according to the general procedure, using 0.1206 g (0.5 mmol) of **1i**, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH$_3$, 0.0167 g (0.025 mmol) of **L5**·FeCl$_2$, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt$_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 1 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0831 g (0.24 mmol, 12/1 *E/Z*, 47% yield) of the title compound (*Z*) and recover chiral **1i** in 18% NMR yield. (*R*,*R*)-**1i**: 97.2% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 16.9 (major), 32.2 (minor). **2i**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +19.5 (c 1.04, CHCl$_3$), 96.7% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99 /1, 1.0 mL/min, n = 220 nm, tr 7.0 (minor), 8.8 (major). IR (cm^{-1}): 3024, 2964, 2143, 1582, 1488, 1438. ^{1}H NMR (CDCl$_3$, 400 MHz): *δ* 7.48-7.43 (m, 2H), 7.40-7.34 (m, 1H), 7.33-7.25 (m, 4H), 7.24-7.15 (m, 4H), 7.13-7.11 (m, 1H), 7.06-7.00 (m, 1H), 6.92-6.85 (m, 1H), 5.78 (d, *J* = 9.6 Hz, 1H), 4.29-4.22 (m, 2H), 3.71-3.62 (m, 1H), 2.41-2.25 (m, 2H), 1.30 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): *δ* 162.8 (d, *J* = 245.0 Hz), 146.1, 145.6 (d, *J* = 7.4 Hz), 135.2, 134.4 (d, *J* = 2.2 Hz), 133.1, 131.7, 129.8, 129.5 (d, *J* = 8.2 Hz), 128.5, 128.0, 127.0, 126.1, 122.2 (d, *J* = 2.2 Hz), 113.7 (d, *J* = 16.2 Hz), 113.4 (d, *J* = 17.0 Hz), 38.9, 22.5, 15.0; ^{19}F NMR (CDCl$_3$, 376.5 MHz): *δ* -113.6. HRMS (ESI) calculated for $[C_{23}H_{24}FSi]^+$ (M + H$^+$) requires m/z 347.1631, found m/z 347.1608.

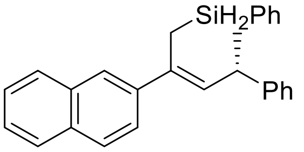


(*S*,*Z*)-(2-(2-Fluorophenyl)-4-phenylpent-2-en-1-yl)(phenyl)silane (2j) Prepared according to the general procedure, using 0.1201 g (0.5 mmol) of

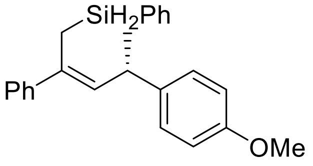
1j, 96 μL (0.75 mmol, 1.5 equiv.) of $PhSiH_3$, 0.0167 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 12 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0687 g (0.20 mmol, >20/1 *E/Z*, 39% yield) of the title compound (*Z*) and recover chiral **1j** in 40% NMR yield. (*R*,*R*)-**1j**: 63.5% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 18.2 (major), 28.1 (minor). **2j**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +38.6 (c 1.20, $CHCl_3$), 91.9% *ee* determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 90/10, 1.0 mL/min, n = 220 nm, tr 6.3 (major), 7.9 (minor). IR (cm^{-1}): 3063, 2965, 2143, 1489, 1445, 1212. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46-7.41 (m, 2H), 7.37-7.31 (m, 1H), 7.31-7.25 (m, 4H), 7.25-7.21 (m, 2H), 7.21-7.11 (m, 3H), 7.04-6.93 (m, 2H), 5.61 (d, *J* = 9.4 Hz, 1H), 4.23-4.15 (m, 2H), 3.76-3.66 (m, 1H), 2.45-2.30 (m, 2H), 1.32 (d, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.0 (d, *J* = 247.2 Hz), 146.1, 135.1, 131.9, 131.7 (d, *J* = 13.4 Hz), 131.4, 130.5 (d, *J* = 3.8 Hz), 129.7, 128.5, 128.43, 128.40, 127.9, 127.0, 126.0, 123.8 (d, *J* = 3.0 Hz), 115.5 (d, *J* = 22.8 Hz), 38.5, 22.5, 15.8 (d, *J* = 3.0 Hz); ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ -114.6. HRMS (ESI) calculated for $[C_{23}H_{23}FSiNa]^+$ (M + Na$^+$) requires m/z 369.1451, found m/z 369.1464.



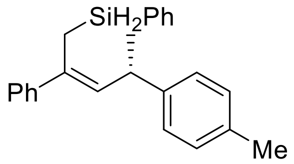
(*S*,*Z*)-2-(2-Fluorophenyl)-4-phenylpent-2-en-1-ol (2j-ox) colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35-7.28 (m, 4H), 7.28-7.18 (m, 3H), 7.09 (td, *J* = 7.4, 1.2 Hz, 1H), 7.03 (ddd, *J* = 11.0, 8.2, 0.8 Hz, 1H), 5.91 (d, *J* = 9.8 Hz, 1H), 4.55 (d, *J* = 5.8 Hz, 2H), 4.05-3.96 (m, 1H), 1.57 (t, *J* = 4.6 Hz, 1H), 1.45 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.0 (d, *J* = 245.7 Hz), 145.6, 140.1 (d, *J* = 1.5 Hz), 134.3 (d, *J* = 1.5 Hz), 130.6 (d, *J* = 4.4 Hz), 129.2 (d, *J* = 14.7 Hz), 128.9 (d, *J* = 8.2 Hz), 128.6, 126.9, 126.3, 124.2 (d, *J* = 3.8 Hz), 115.5 (d, *J* = 22.7 Hz), 60.8 (d, *J* = 3.7 Hz), 38.1, 22.5; ^{19}F NMR: ($CDCl_3$, 376.5 MHz) δ -115.6. HRMS (EI) calculated for $[C_{17}H_{17}FO]^+$ requires m/z 256.1263, found m/z 256.1263.



(*S*,*Z*)-(2-(Naphthalen-2-yl)-4-phenylpent-2-en-1-yl)(phenyl)silane (2k) Prepared according to the general procedure, using 0.1362 g (0.5 mmol) of **1k**, 96 μL (0.75 mmol, 1.5 equiv.) of $PhSiH_3$, 0.0166 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0903 g (0.24 mmol, 13/1 *E/Z*, 47% yield) of the title compound (*Z*) and recover chiral **1k** in 11% NMR yield. (*R*,*R*)-**1k**: 99.4% *ee* determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 8.6 (major), 10.4 (minor). **2k**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = -19.2 (c 1.03, $CHCl_3$), 95.7% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 21.9 (minor), 26.1 (major). IR (cm^{-1}): 2958, 2923, 2143, 1597, 1452, 1428. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.80-7.70 (m, 4H), 7.55-7.51 (m, 1H), 7.50-7.45 (m, 2H), 7.45-7.37 (m, 2H), 7.36-7.31 (m, 1H), 7.31-7.23 (m, 6H), 7.21-7.15 (m, 1H), 5.92 (d, *J* = 9.4 Hz, 1H), 4.32-4.25 (m, 2H), 3.78-7.69 (m, 1H), 2.55-2.40 (m, 2H), 1.35 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.4, 140.3, 135.2, 133.4, 132.9, 132.5, 132.1, 129.7, 128.5, 128.04, 127.96, 127.6, 127.4, 127.0, 126.0, 125.6, 125.12, 125.05, 39.0, 22.6, 15.0. HRMS (EI) calculated for $[C_{27}H_{26}Si]^+$ requires m/z 378.1804, found m/z 378.1805.

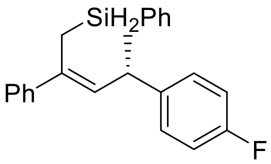


(*S*,*Z*)-(4-(4-Methoxyphenyl)-2-phenylpent-2-en-1-yl)(phenyl)silane (2l) Prepared according to the general procedure, using 0.1251 g (0.5 mmol) of **1l**, 96 μL (0.75 mmol, 1.5 equiv.) of $PhSiH_3$, 0.0166 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0764 g (0.21 mmol, 16/1 *E/Z*, 43% yield) of the title compound (*Z*) and recover chiral **1l** in 39% NMR yield. (*R*,*R*)-**1l**: 77.1% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 16.7 (major), 22.0 (minor). **2l**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +39.2 (c 1.01, $CHCl_3$), 97.8% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 254 nm, tr 15.9 (minor), 19.8 (major). IR (cm^{-1}): 2960, 2143, 1605, 1507, 1247. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.47 (d, J = 7.0 Hz, 2H), 7.40-7.19 (m, 8H), 7.13 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 5.73 (d, J = 9.6 Hz, 1H), 4.29-4.21 (m, 2H), 3.78 (s, 3H), 3.68-3.58 (m, 1H), 2.44-2.29 (m, 2H), 1.28 (d, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.8, 143.2, 138.5, 135.2, 135.0, 132.5, 132.1, 129.7, 128.1, 127.95, 127.85, 126.8, 126.5, 113.8, 55.2, 38.0, 22.7, 15.0. HRMS (ESI) calculated for $[C_{24}H_{27}OSi]^+$ (M + H^+) requires m/z 359.1831, found m/z 359.1842.

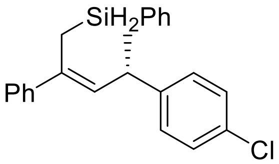


(*S*,*Z*)-Phenyl(2-phenyl-4-(p-tolyl)pent-2-en-1-yl)silane (2m) Prepared according to the general procedure, using 0.1175 g (0.5 mmol) of **1m**, 96 μL (0.75 mmol, 1.5 equiv.) of $PhSiH_3$, 0.0166 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 3 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0694 g (0.20 mmol, 9/1 *E/Z*, 40% yield) of the title compound (*Z*) and recover chiral **1m** in 23% NMR yield. (*R*,*R*)-**1m**: 88.4% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99.5/0.5, 1.0 mL/min, n = 220 nm, tr 11.3 (major), 17.5 (minor). **2m**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +40.4 (c 1.01, $CHCl_3$), 96.0% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 8.5 (minor), 9.0 (major). IR (cm^{-1}): 2963, 2922, 2143, 1504, 1440. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.50-7.45 (m, 2H), 7.39-7.23 (m, 7H), 7.23-7.17 (m, 1H), 7.14-7.06 (m, 4H), 5.75 (d, J = 9.6 Hz, 1H), 4.29-4.22 (m, 2H), 3.69-3.60 (m, 1H), 2.44-2.28 (m, 2H), 2.31 (s, 3H), 1.29 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.4, 143.3, 135.4, 135.2, 135.1, 132.5, 132.1, 129.7, 129.1, 128.1, 127.9, 126.9, 126.8, 126.6, 38.5, 22.7, 21.0, 15.0. HRMS (EI) calculated for $[C_{24}H_{26}Si]^+$

requires m/z 342.1804, found m/z 342.1801.

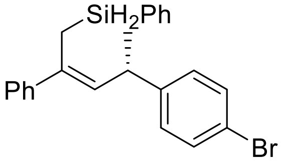


(*S*,*Z*)-(4-(4-Fluorophenyl)-2-phenylpent-2-en-1-yl)(phenyl)silane (2n) Prepared according to the general procedure, using 0.1193 g (0.5 mmol) of **1n**, 96 μL (0.75 mmol, 1.5 equiv.) of $PhSiH_3$, 0.0166 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0704 g (0.20 mmol, 9/1 *E/Z*, 40% yield) of the title compound (*Z*) and recover chiral **1n** in 20% NMR yield. (*R*,*R*)-**1n**: 95.3% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99.5/0.5, 1.0 mL/min, n = 220 nm, tr 10.2 (major), 12.3 (minor). **2n**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +24.6 (c 1.01, $CHCl_3$), 95.8% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 11.4 (minor), 13.7 (major). IR (cm^{-1}): 2970, 2144, 1601, 1508, 1428, 1226. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.50-7.44 (m, 2H), 7.40-7.33 (m, 3H), 7.33-7.25 (m, 4H), 7.33-7.19 (m, 1H), 7.17-7.11 (m, 2H), 6.99-3.91 (m, 2H), 5.71 (d, *J* = 9.4 Hz, 1H), 4.30-4.20 (m, 2H), 3.69-3.59 (m, 1H), 2.42-2.29 (m, 2H), 1.28 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.2 (d, *J* = 243.6 Hz), 143.1, 142.0 (d, *J* = 3.0 Hz), 135.6, 135.2, 131.9, 129.8, 128.3 (d, *J* = 7.8 Hz), 128.2, 128.0, 127.0, 126.5, 115.1 (d, *J* = 21.2 Hz), 38.1, 22.7, 15.1; ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ -117.5. HRMS (EI) calculated for $[C_{23}H_{23}FSi]^+$ requires m/z 346.1553, found m/z 346.1552.

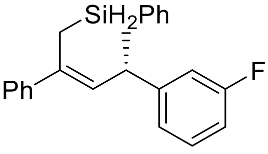


(*S*,*Z*)-(4-(4-Chlorophenyl)-2-phenylpent-2-en-1-yl)(phenyl)silane (2o) Prepared according to the general procedure, using 0.1284 g (0.5 mmol) of **1o**, 96 μL (0.75 mmol, 1.5 equiv.) of $PhSiH_3$, 0.0168 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H

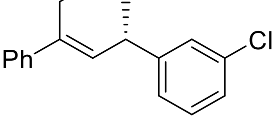
NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0873 g (0.24 mmol, 11/1 *E/Z*, 48% yield) of the title compound (*Z*) and recover chiral **1o** in 25% NMR yield. (*R*,*R*)-**1o**: 90.1% *ee* determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 7.0 (major), 7.6 (minor). **2o**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +48.5 (c 1.01, $CHCl_3$), 93.5% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 10.7 (minor), 11.9 (major). IR (cm^{-1}): 2963, 2923, 2144, 1491, 1428. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49-7.44 (m, 2H), 7.40-7.31 (m, 4H), 7.31-7.26 (m, 3H), 7.25-7.20 (m, 3H), 7.14-7.09 (m, 2H), 5.69 (d, J = 9.4 Hz, 1H), 4.28-4.19 (m, 2H), 3.67-3.58 (m, 1H), 2.40-2.29 (m, 2H), 1.27 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.9, 143.0, 135.9, 135.2, 131.9, 131.5, 129.8, 128.5, 128.3, 128.2, 128.0, 127.0, 126.5, 38.3, 22.6, 15.1. HRMS (EI) calculated for $[C_{23}H_{23}ClSi]^+$ requires m/z 362.1258, found m/z 362.1259.



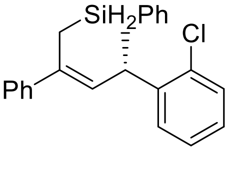
(*S*,*Z*)-(4-(4-Bromophenyl)-2-phenylpent-2-en-1-yl)(phenyl)silane (2p) Prepared according to the general procedure, using 0.1499 g (0.5 mmol) of **1p**, 96 μL (0.75 mmol, 1.5 equiv.) of $PhSiH_3$, 0.0166 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0927 g (0.23 mmol, 17/1 *E/Z*, 46% yield) of the title compound (*Z*) and recover chiral **1p** in 33% NMR yield. (*R*,*R*)-**1p**: 82.9% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 9.7 (major), 11.8 (minor). **2p**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +52.3 (c 1.07, $CHCl_3$), 97.3% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 13.2 (minor), 14.7 (major). IR (cm^{-1}): 3059, 2964, 2143, 1487, 1438. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48-7.43 (m, 2H), 7.40-7.31 (m, 6H), 7.31-7.25 (m, 3H), 7.21-7.21 (m, 1H), 7.08-7.04 (m, 2H), 5.69 (d, J = 9.4 Hz, 1H), 4.28-2.19 (m, 2H), 3.65-3.56 (m, 1H), 2.40-2.28 (m, 2H), 1.27 (d, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.4, 143.0, 136.0, 135.2, 131.9, 131.4, 129.8, 128.8, 128.2, 128.0, 127.0, 126.5, 119.6, 38.4, 22.5, 15.2. HRMS (ESI) calculated for $[C_{23}H_{24}BrSi]^+$ (M + H^+) requires m/z 407.0831, found m/z 407.0823.



(*S,Z*)-(4-(3-Fluorophenyl)-2-phenylpent-2-en-1-yl)(phenyl)silane (2q) Prepared according to the general procedure, using 0.1195 g (0.5 mmol) of **1q**, 96 μL (0.75 mmol, 1.5 equiv.) of $PhSiH_3$, 0.0167 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0741 g (0.21 mmol, 12/1 *E/Z*, 43% yield) of the title compound (*Z*) and recover chiral **1q** in 19% NMR yield. (*R*,*R*)-**1q**: 94.7% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99.5/0.5, 1.0 mL/min, n = 220 nm, tr 8.5 (major), 11.6 (minor). **2q**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +26.2 (c 1.06, $CHCl_3$), 98.3% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 7.1 (minor), 9.2 (major). IR (cm^{-1}): 3061, 2965, 2143, 1597, 1490, 1441. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.50-7.44 (m, 2H), 7.39-7.33 (m, 3H), 7.33-7.25 (m, 4H), 7.25-7.18 (m, 2H), 7.00-6.96 (m, 1H), 6.93-6.82 (m, 2H), 5.70 (d, J = 9.4 Hz, 1H), 4.28-4.20 (m, 2H), 3.70-3.60 (m, 1H), 2.42-2.29 (m, 2H), 1.28 (d, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.5 (d, J = 245.8 Hz), 149.1 (d, J = 6.2 Hz), 143.0, 136.0, 135.2, 131.9, 131.3, 129.8, 128.2, 128.0, 127.9, 127.0, 126.6, 122.7 (d, J = 3.0 Hz), 113.9 (d, J = 21.6 Hz), 112.8 (d, J = 21.6 Hz), 38.6, 22.4, 15.2; ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ -113.3. HRMS (ESI) calculated for $[C_{23}H_{24}FSi]^+$ (M + H^+) requires m/z 347.1631, found m/z 347.1617.

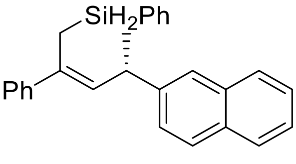


(*S,Z*)-(4-(3-Chlorophenyl)-2-phenylpent-2-en-1-yl)(phenyl)silane (2r) Prepared according to the general procedure, using 0.1284 g (0.5 mmol) of **1r**, 96 μL (0.75 mmol, 1.5 equiv.) of $PhSiH_3$, 0.0167 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0740 g (0.20 mmol, 12/1 *E/Z*, 40% yield) of the title compound (*Z*) and recover chiral **1r** in 13% NMR yield. (*R*,*R*)-**1r**: 97.2% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99.5/0.5, 1.0 mL/min, n = 220 nm, tr 8.9 (major), 12.1 (minor). **2r**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +39.3 (c 0.98, CHCl$_3$), 96.8% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99.5/0.5, 1.0 mL/min, n = 220 nm, tr 9.9 (minor), 15.8 (major). IR (cm^{-1}): 2958, 2924, 2144, 1594, 1461, 1428. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.50-7.43 (m, 2H), 7.39-7.33 (m, 3H), 7.32-7.25 (m, 4H), 7.25-7.21 (m, 1H), 7.21-7.11 (m, 3H), 7.10-7.05 (m, 1H), 5.70 (d, *J* = 9.4 Hz, 1H), 4.28-4.19 (m, 2H), 3.66-3.56 (m, 1H), 2.41-2.28 (m, 2H), 1.27 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 148.5, 142.9, 136.1, 135.2, 134.2, 131.8, 131.2, 129.8, 129.7, 128.2, 128.0, 127.2, 127.1, 126.5, 126.1, 125.2, 38.7, 22.5, 15.2. HRMS (EI) calculated for $[C_{23}H_{23}ClSi]^+$ requires m/z 362.1258, found m/z 362.1258.

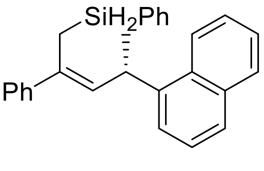


(*S*,*Z*)-(4-(2-Chlorophenyl)-2-phenylpent-2-en-1-yl)(phenyl)silane (2s) Prepared according to the general procedure, using 0.1278 g (0.5 mmol) of **1s**, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH$_3$, 0.0167 g (0.025 mmol) of **L5**·FeCl$_2$, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt$_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0735 g (0.20 mmol, 8/1 *E/Z*, 40% yield) of the title compound (*Z*) and recover chiral **1s** in 33% NMR yield. (*R*,*R*)-**1s**: 63.8% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99.5/0.5, 1.0 mL/min, n = 220 nm, tr 8.8 (major), 9.5 (minor). **2s**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = -40.0 (c 1.02, CHCl$_3$), 78.7% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 11.4 (minor), 17.2 (major). IR (cm^{-1}): 2957, 2924, 2145, 1470, 1443. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.49-7.43 (m, 2H), 7.39-7.31 (m, 3H), 7.31-7.25 (m, 6H), 7.25-7.21 (m, 1H), 7.21-7.14 (m, 1H), 7.11-7.03

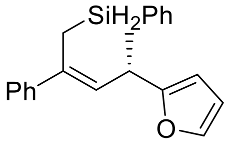
(m, 1H), 5.82 (d, *J* = 9.0 Hz, 1H), 4.24-4.10 (m, 3H), 2.41-2.21 (m, 2H), 1.25 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 144.4, 143.1, 137.0, 135.2, 133.0, 132.0, 130.8, 129.6, 129.5, 128.20, 128.17, 127.9, 127.1, 127.0, 126.5, 35.4, 22.4, 15.7. HRMS (EI) calculated for [$C_{23}H_{23}ClSi$]$^+$ requires m/z 362.1258, found m/z 362.1260.



(*S*,*Z*)-(4-(Naphthalen-2-yl)-2-phenylpent-2-en-1-yl)(phenyl)silane (2t) Prepared according to the general procedure, using 0.1352 g (0.5 mmol) of **1t**, 96 µL (0.75 mmol, 1.5 equiv.) of PhSiH$_3$, 0.0167 g (0.025 mmol) of **L5**·FeCl$_2$, 75 µL (1.0 M in THF, 0.075 mmol) of NaBHEt$_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0761 g (0.20 mmol, 14/1 *E/Z*, 40% yield) of the title compound (*Z*) and recover chiral **1t** in 32% NMR yield. (*R*,*R*)-**1t**: 68.5% *ee* determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*hexane/*i*PrOH = 98/2, 1.0 mL/min, n = 220 nm, tr 4.9 (major), 6.4 (minor). **2t**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +72.7 (c 1.01, CHCl$_3$), 97.1% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 21.0 (minor), 24.2 (major). IR (cm^{-1}): 2960, 2922, 2142, 1599, 1445. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.80-7.73 (m, 3H), 7.62 (s, 1H), 7.48-7.32 (m, 8H), 7.31-7.25 (m, 4H), 7.24-7.18 (m, 1H), 5.85 (d, *J* = 9.4 Hz, 1H), 4.31-4.21 (m, 2H), 3.87-3.78 (m, 1H), 2.48-2.32 (m, 2H), 1.39 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 143.9, 143.2, 135.8, 135.2, 133.6, 132.1, 132.02, 131.98, 129.7, 128.2, 128.0, 127.9, 127.6, 127.5, 126.9, 126.6, 126.1, 125.9, 125.2, 124.8, 39.1, 22.6, 15.2. HRMS (EI) calculated for [$C_{27}H_{26}Si$]$^+$ requires m/z 378.1804, found m/z 378.1806.

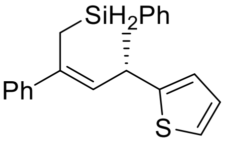


(*S*,*Z*)-(4-(Naphthalen-1-yl)-2-phenylpent-2-en-1-yl)(phenyl)silane (2u) Prepared according to the general procedure, using 0.1353 g (0.5 mmol) of **1u**, 96 µL (0.75 mmol, 1.5 equiv.) of PhSiH$_3$, 0.0166 g (0.025 mmol) of **L5**·FeCl$_2$, 75 µL (1.0 M in THF, 0.075 mmol) of NaBHEt$_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0761 g (0.20 mmol, 8/1 *E/Z*, 40% yield) of the title compound (*Z*) and recover chiral **1u** in 43% NMR yield. (*R*,*R*)-**1u**: 64.5% *ee* determined by HPLC, HPLC conditions: Chiralcel AD-H, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 6.9 (minor), 7.4 (major). **2u**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = -83.0 (c 0.98, $CHCl_3$), 64.4% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 32.7 (major), 34.8 (minor). IR (cm^{-1}): 2959, 2924, 2143, 1596, 1446, 1428. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (d, J = 8.0 Hz, 1H), 7.87-7.83 (m, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.52-7.42 (m, 3H), 7.42-7.35 (m, 5H), 7.32-7.20 (m, 6H), 6.01 (d, J = 8.6 Hz, 1H), 4.42-4.33 (m, 1H), 4.26-4.11 (m, 2H), 2.36-2.19 (m, 2H), 1.41 (d, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.14, 143.11, 136.4, 135.2, 134.0, 132.2, 132.1, 131.3, 129.7, 129.0, 128.2, 127.9, 127.0, 126.6, 126.5, 125.8, 125.7, 125.3, 123.6, 123.4, 34.4, 23.1, 15.5. HRMS (EI) calculated for $[C_{27}H_{26}Si]^+$ requires m/z 378.1804, found m/z 378.1805.

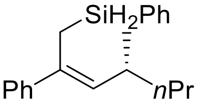


(*S*,*Z*)-(4-(Furan-2-yl)-2-phenylpent-2-en-1-yl)(phenyl)silane (2v)

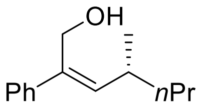
Prepared according to the general procedure, using 0.1053 g (0.5 mmol) of **1v**, 96 μL (0.75 mmol, 1.5 equiv.) of $PhSiH_3$, 0.0167 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0645 g (0.20 mmol, 11/1 *E/Z*, 40% yield) of the title compound (*Z*) and recover chiral **1v** in 21% NMR yield. (*R*,*R*)-**1v**: 70.6% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 7.4 (major), 9.1 (minor). **2v**: yellow oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +59.3 (c 0.97, $CHCl_3$), 98.1% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 8.2 (minor), 9.0 (major). IR (cm^{-1}): 2971, 2144, 1591, 1498, 1439. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51-7.47 (m, 2H), 7.39-7.33 (m, 3H), 7.33-7.25 (m, 5H), 7.25-7.19 (m, 1H), 6.27-6.25 (m, 1H), 5.97-5.95 (m, 1H), 5.62 (d, *J* = 9.6 Hz, 1H), 4.31-4.25 (m, 2H), 3.78-7.69 (m, 1H), 2.50-2.30 (m, 2H), 1.27 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 158.8, 143.0, 141.0, 136.4, 135.2, 132.0, 129.7, 129.0, 128.2, 127.9, 127.0, 126.6, 110.0, 103.8, 33.1, 19.6, 15.1. HRMS (ESI) calculated for [C$_{21}$H$_{23}$OSi]$^+$ (M + H$^+$) requires m/z 319.1518, found m/z 319.1525.



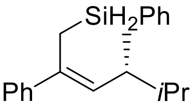
(*S*,*Z*)-Phenyl(2-phenyl-4-(thiophen-2-yl)pent-2-en-1-yl)silane (2w) Prepared according to the general procedure, using 0.1146 g (0.5 mmol) of **1w**, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH$_3$, 0.0168 g (0.025 mmol) of **L5**·FeCl$_2$, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt$_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0794 g (0.24 mmol, 10/1 *E/Z*, 47% yield) of the title compound (*Z*) and recover chiral **1w** in 26% NMR yield. (*R*,*R*)-**1w**: 96.0% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 8.1 (major), 8.9 (minor). **2w**: yellow oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +28.4 (c 1.33, CHCl$_3$), 96.2% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H x 2, *n*hexane/*i*PrOH = 99.5/0.5, 1.0 mL/min, n = 220 nm, tr 26.8 (major), 29.9 (minor). IR (cm^{-1}): 2965, 2144, 1493, 1439. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.51-7.46 (m, 2H), 7.40-7.33 (m, 3H), 7.33-7.26 (m, 4H), 7.25-7.20 (m, 1H), 7.12 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.91 (dd, *J* = 5.2, 3.4 Hz, 1H), 6.81-6.78 (m, 1H), 5.70 (d, *J* = 9.6 Hz, 1H), 4.32-4.25 (m, 2H), 3.98-3.89 (m, 1H), 2.48-2.31 (m, 2H), 1.36 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 150.4, 143.0, 135.8, 135.2, 131.9, 131.4, 129.8, 128.2, 128.0, 127.0, 126.6, 123.0, 122.7, 34.5, 22.9, 15.1. HRMS (ESI) calculated for [C$_{21}$H$_{23}$SSi]$^+$ (M + H$^+$) requires m/z 335.1290, found m/z 335.1298.



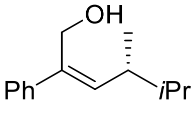
(*R*,*Z*)-(4-Methyl-2-phenylhept-2-en-1-yl)(phenyl)silane (2x) Prepared according to the general procedure, using 0.0951 g (0.5 mmol) of **1x**, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH$_3$, 0.0167 g (0.025 mmol) of **L5**·FeCl$_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 24 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^1H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0683 g (0.23 mmol, 4/1 *E/Z*, 46% yield) of the title compound (*Z*) and recover chiral **1x** in 37% NMR yield. (*R*,*R*)-**1x**: 75.2% *ee* determined by HPLC after oxidation to the corresponding ketone (Hossain et al., 2014), HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 5.5 (major), 6.6 (minor). **2x**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = -16.2 (c 1.10, $CHCl_3$), 95.2% *ee* determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 95/5, 1.0 mL/min, n = 220 nm, tr 6.2 (major), 7.3 (minor). IR (cm^{-1}): 2956, 2925, 2145, 1456, 1429. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.52-7.47 (m, 2H), 7.39-7.17 (m, 8H), 5.39 (d, J = 9.8 Hz, 1H), 4.30-4.23 (m, 2H), 2.43-2.25 (m, 3H), 1.34-1.22 (m, 4H), 0.92 (d, J = 6.6 Hz, 3H), 0.90-0.85 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.6, 135.2, 134.4, 134.2, 132.3, 129.6, 128.1, 127.9, 126.6, 126.5, 40.0, 33.3, 20.8, 20.7, 14.8, 14.4. HRMS (EI) calculated for $[C_{20}H_{26}Si]^+$ requires m/z 294.1804, found m/z 294.1807.



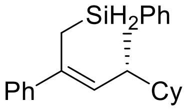
(*R*,*Z*)-4-Methyl-2-phenylhept-2-en-1-ol (2x-ox) colorless oil. IR (cm^{-1}): 3378, 2956, 2925, 1493, 1462, 1377. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.47-7.42 (m, 2H), 7.37-7.30 (m, 2H), 7.28-7.23 (m, 1H), 5.64 (d, J = 10.0 Hz, 1H), 4.58 (s, 2H), 2.71-2.59 (m, 1H), 1.43-1.28 (m, 4H), 1.26 (brs, 1H), 1.05 (d, J = 6.6 Hz, 3H), 0.91 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.9, 139.1, 137.3, 128.5, 127.1, 126.3, 60.0, 39.9, 32.8, 21.5, 20.8, 14.2. HRMS (EI) calculated for $[C_{14}H_{20}O]^+$ requires m/z 204.1514, found m/z 204.1514.



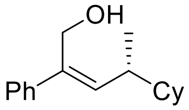
(*R*,*Z*)-(4,5-Dimethyl-2-phenylhex-2-en-1-yl)(phenyl)silane (2y) Prepared according to the general procedure, using 0.0935 g (0.5 mmol) of **1y**, 96 μL (0.75 mmol, 1.5 equiv.) of $PhSiH_3$, 0.0167 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 24 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0680 g (0.23 mmol, 9/1 *E/Z*, 46% yield) of the title compound (*Z*) and recover chiral **1y** in 45% NMR yield. (*R*,*R*)-**1y**: 74.6% *ee* determined by HPLC after oxidation to the corresponding ketone (Hossain et al., 2014), HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 5.3 (major), 6.3 (minor). **2y**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = -27.9 (c 0.90, CHCl$_3$), 92.5% *ee* determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 95/5, 1.0 mL/min, n = 220 nm, tr 6.0 (major), 7.1 (minor). IR (cm^{-1}): 2957, 2143, 1458, 1428. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.52-7.47 (m, 2H), 7.39-7.25 (m, 7H), 7.23-7.18 (m, 1H), 5.47 (d, *J* = 10.2 Hz, 1H), 4.31-4.22 (m, 2H), 2.41-2.24 (m, 2H), 2.24-2.15 (m, 1H), 1.56-1.46 (m, 1H), 0.91 (d, *J* = 4.2 Hz, 3H), 0.90 (d, *J* = 4.2 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 143.8, 135.2, 134.6, 132.9, 132.4, 129.6, 128.1, 127.9, 126.6, 126.5, 39.5, 33.7, 20.2, 20.0, 17.9, 14.8. HRMS (EI) calculated for $[C_{20}H_{26}Si]^+$ requires m/z 294.1804, found m/z 294.1807.



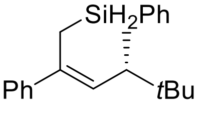
(*R*,*Z*)-4,5-Dimethyl-2-phenylhex-2-en-1-ol (2y-ox) colorless oil. IR (cm^{-1}): 3398, 2959, 2871, 1493, 1462, 1369. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.48-7.43 (m, 2H), 7.37-7.31 (m, 2H), 7.29-7.23 (m, 1H), 5.72 (d, *J* = 10.4 Hz, 1H), 4.57 (s, 2H), 2.48-2.37 (m, 1H), 1.63-1.50 (m, 1H), 1.26 (brs, 1H), 1.04 (d, *J* = 7.0 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 141.3, 137.6, 136.3, 128.5, 127.0, 126.5, 60.0, 42.5, 33.4, 27.4, 16.2. HRMS (EI) calculated for $[C_{14}H_{20}O]^+$ requires m/z 204.1514, found m/z 204.1511.



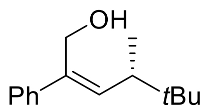
(*R*,*Z*)-(4-Cyclohexyl-2-phenylpent-2-en-1-yl)(phenyl)silane (2z) Prepared according to the general procedure, using 0.1151 g (0.5 mmol) of **1z**, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH$_3$, 0.0168 g (0.025 mmol) of **L5**·FeCl$_2$, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt$_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 24 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0836 g (0.25 mmol, 10/1 *E/Z*, 49% yield) of the title compound (*Z*) and recover chiral **1z** in 46% NMR yield. (*R*,*R*)-**1z**: 77.5% *ee* determined by HPLC after oxidation to the corresponding ketone (Hossain et al., 2014), HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 5.4 (major), 6.5 (minor). **2z**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = -20.4 (c 1.00, $CHCl_3$), 93.4% *ee* determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 95/5, 1.0 mL/min, n = 220 nm, tr 5.8 (major), 7.4 (minor). IR (cm^{-1}): 2922, 2850, 2142, 1446, 1428. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52-7.46 (m, 2H), 7.39-7.24 (m, 7H), 7.24-7.17 (m, 1H), 5.46 (d, *J* = 10.2 Hz, 1H), 4.30-4.22 (m, 2H), 2.41-2.15 (m, 3H), 1.81-1.58 (m, 5H), 1.26-1.06 (m, 4H), 1.00-0.85 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.8, 135.2, 134.4, 133.2, 132.4, 129.6, 128.1, 127.9, 126.6, 126.5, 43.9, 38.8, 30.7, 30.6, 26.71, 26.67, 26.64, 17.9, 14.8. HRMS (EI) calculated for $[C_{23}H_{30}Si]^+$ requires m/z 334.2117, found m/z 334.2114.



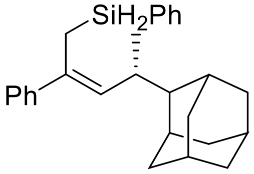
(*R,Z*)-4-Cyclohexyl-2-phenylpent-2-en-1-ol (2z-ox) colorless oil. IR (cm^{-1}): 3357, 2972, 2919, 1484, 1450, 1396. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48-7.43 (m, 2H), 7.38-7.29 (m, 2H), 7.28-7.22 (m, 1H), 5.71 (d, *J* = 10.6 Hz, 1H), 4.56 (s, 2H), 2.48-2.37 (m, 1H), 1.85-1.58 (m, 5H), 1.33-1.09 (m, 5H), 1.04 (d, *J* = 6.8 Hz, 3H), 1.02-0.87 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.0, 137.9, 137.3, 128.5, 127.0, 126.3, 60.0, 43.6, 38.4, 30.74, 30.70, 26.54, 26.50, 18.6. HRMS (EI) calculated for $[C_{17}H_{24}O]^+$ requires m/z 244.1827, found m/z 244.1828.



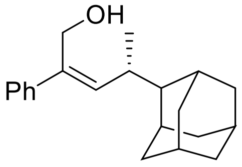
(*S*,*Z*)-Phenyl(4,5,5-trimethyl-2-phenylhex-2-en-1-yl)silane (2aa) Prepared according to the general procedure, using 0.1012 g (0.5 mmol) of **1aa**, 96 μL (0.75 mmol, 1.5 equiv.) of $PhSiH_3$, 0.0167 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 24 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0682 g (0.22 mmol, 12/1 *E/Z*, 44% yield) of the title compound (*Z*) and recover chiral **1aa** in 38% NMR yield. (*R*,*R*)-**1aa**: 89.7% *ee* determined by HPLC after oxidation to the corresponding ketone (Hossain et al., 2014), HPLC conditions: Chiralcel OJ-H x 2, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 14.8 (minor), 15.5 (major). **2aa**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = -30.1 (c 1.02, CHCl$_3$), 90.3% *ee* determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 95/5, 1.0 mL/min, n = 220 nm, tr 5.9 (major), 6.8 (minor). IR (cm^{-1}): 2963, 2145, 1492, 1367. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.51-7.46 (m, 2H), 7.39-7.24 (m, 7H), 7.22-7.17 (m, 1H), 5.54 (d, J = 10.6 Hz, 1H), 4.31-4.22 (m, 2H), 2.45-2.37 (m, 1H), 2.30-2.19 (m, 2H), 0.90-0.86 (m, 12H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 144.1, 135.2, 134.7, 132.4, 131.7, 129.6, 128.1, 127.9, 126.6, 43.0, 33.7, 27.4, 15.6, 14.8. HRMS (EI) calculated for $[C_{21}H_{28}Si]^+$ requires m/z 308.1960, found m/z 308.1961.



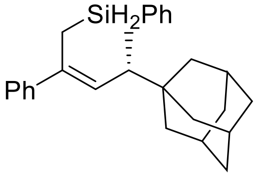
(*S,Z*)-4,5,5-Trimethyl-2-phenylhex-2-en-1-ol (2aa-ox) colorless oil. IR (cm^{-1}): 3365, 2961, 2870, 1493, 1470, 1366. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.47-7.43 (m, 2H), 7.37-7.31 (m, 2H), 7.29-7.23 (m, 1H), 5.79 (d, J = 10.8 Hz, 1H), 4.59 (q, J = 9.8 Hz, 2H), 2.50-2.40 (m, 1H), 1.26 (brs, 1H), 1.01 (d, J = 7.0 Hz, 3H), 0.92 (s, 9H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 141.1, 137.5, 128.5, 127.0, 126.4, 60.0, 39.1, 33.7, 20.2, 20.1, 18.7. HRMS (EI) calculated for $[C_{15}H_{22}O]^+$ requires m/z 218.1671, found m/z 218.1673.



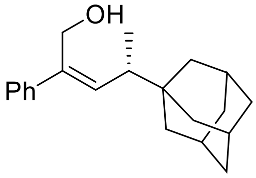
((*R,Z*)-4-(Adamantan-2-yl)-2-phenylpent-2-en-1-yl)(phenyl)silane (2ab) Prepared according to the general procedure, using 0.1395 g (0.5 mmol) of **1ab**, 96 μL (0.75 mmol, 1.5 equiv.) of PhSiH$_3$, 0.0168 g (0.025 mmol) of **L5**·FeCl$_2$, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt$_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 24 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0962 g (0.25 mmol, 11/1 *E/Z*, 49% yield) of the title compound (*Z*) and recover chiral **1ab** in 42% NMR yield. (*R*,*R*)-**1ab**: 89.0% *ee* determined by HPLC after oxidation to the corresponding ketone (Hossain et al., 2014), HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 95/5, 1.0 mL/min, n = 220 nm, tr 4.4 (major), 4.8 (minor). **2ab**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = -11.3 (c 1.02, $CHCl_3$), 80.0% *ee* determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 95/5, 1.0 mL/min, n = 220 nm, tr 5.9 (major), 6.9 (minor). IR (cm^{-1}): 2905, 2849, 2144, 1492, 1450. ^1H NMR ($CDCl_3$, 400 MHz): *δ* 7.52-7.47 (m, 2H), 7.38-7.23 (m, 7H), 7.22-7.16 (m, 1H), 5.37 (d, *J* = 9.8 Hz, 1H), 4.31-4.22 (m, 2H), 2.76-2.65 (m, 1H), 2.50-2.25 (m, 2H), 1.95 (s, 1H), 1.90-1.76 (m, 7H), 1.74-1.62 (m, 4H), 1.57-1.46 (m, 2H), 1.41-1.35 (m, 1H), 0.88 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 143.7, 135.2, 134.7, 134.3, 132.4, 129.6, 128.1, 127.9, 126.6, 126.5, 50.6, 39.45, 39.36, 38.3, 33.4, 32.8, 31.8, 30.4, 28.8, 28.1, 27.8, 18.5, 14.8. HRMS (EI) calculated for $[C_{27}H_{34}Si]^+$ requires m/z 386.2430, found m/z 386.2431.



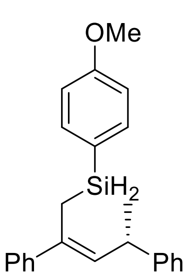
(*R*,*Z*)-4-(Adamantan-2-yl)-2-phenylpent-2-en-1-ol (2ab-ox) colorless oil. IR (cm^{-1}): 3365, 2905, 2850, 1493, 1453, 1372. ^1H NMR ($CDCl_3$, 400 MHz): *δ* 7.48-7.43 (m, 2H), 7.37-7.30 (m, 2H), 7.28-7.22 (m, 1H), 5.64 (d, *J* = 10.2 Hz, 1H), 4.62 (s, 2H), 3.00-2.88 (m, 1H), 1.99 (s, 1H), 1.93-1.65 (m, 11H), 1.63-1.47 (m, 2H), 1.43 (d, *J* = 10.6 Hz, 1H), 1.30 (brs, 1H), 1.01 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): *δ* 140.9, 139.1, 137.0, 128.4, 127.0, 126.3, 60.1, 50.1, 39.3, 39.2, 38.2, 33.0, 32.0, 31.7, 30.5, 28.6, 28.0, 27.7, 19.0. HRMS (EI) calculated for $[C_{21}H_{28}O]^+$ requires m/z 296.2140, found m/z 296.2140.



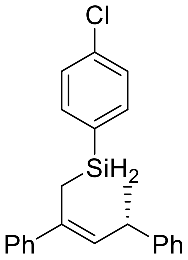
((*S*,*Z*)-4-(Adamantan-1-yl)-2-phenylpent-2-en-1-yl)(phenyl)silane (2ac) Prepared according to the general procedure, using 0.1410 g (0.5 mmol) of **1ac**, 96 μL (0.75 mmol, 1.5 equiv.) of $PhSiH_3$, 0.0168 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 24 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0976 g (0.25 mmol, 15/1 *E/Z*, 50% yield) of the title compound (*Z*) and recover chiral **1ac** in 40% NMR yield. (*R*,*R*)-**1ac**: 95.9% *ee* determined by HPLC after oxidation to the corresponding ketone (Hossain et al., 2014), HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 17.2 (najor), 18.5 (minor). **2ac**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = -17.2 (c 1.05, $CHCl_3$), 89.8% *ee* determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 95/5, 1.0 mL/min, n = 220 nm, tr 6.0 (major), 7.6 (minor). IR (cm^{-1}): 2902, 2846, 2142, 1491, 1448, 1359. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52-7.47 (m, 2H), 7.38-7.25 (m, 7H), 7.23-7.18 (m, 1H), 5.56 (d*, J* = 10.6 Hz, 1H), 4.30-4.21 (m, 2H), 2.45-2.22 (m, 2H), 2.10-2.00 (m, 1H), 1.93 (s, 3H), 1.71-1.48 (m, 12H), 0.84 (d*, J* = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.0, 135.2, 134.8, 132.4, 130.8, 129.6, 128.1, 127.9, 126.6, 43.6, 39.7, 37.3, 35.5, 28.7, 14.8, 13.9. HRMS (EI) calculated for $[C_{27}H_{34}Si]^+$ requires m/z 386.2430, found m/z 386.2431.



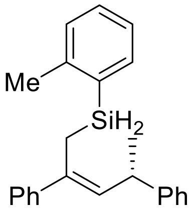
(*S,Z*)-4-(Adamantan-1-yl)-2-phenylpent-2-en-1-ol (2ac-ox) colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 (d, *J* = 7.4 Hz, 2H), 7.35 (dd, *J* = 7.4, 7.2 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 1H), 5.82 (d, *J* = 10.8 Hz, 1H), 4.63-4.52 (m, 2H), 2.31-2.21 (m, 1H), 1.97 (s, 3H), 1.74-1.50 (m, 12H), 1.28 (t, *J* = 5.8 Hz, 1H), 0.98 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.2, 137.7, 135.6, 128.5, 127.0, 126.4, 59.9, 43.1, 39.8, 37.2, 35.2, 28.7, 14.4. HRMS (EI) calculated for $[C_{21}H_{28}O]^+$ requires m/z 296.2140, found m/z 296.2140.



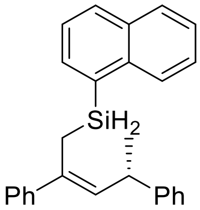
(*S,Z*)-(2,4-Diphenylpent-2-en-1-yl)(4-methoxyphenyl)silane (2ad) Prepared according to the general procedure, using 0.1107 g (0.5 mmol) of **1a**, 0.1145 g (0.75 mmol, 1.5 equiv.) of 4-$MeOC_6H_4SiH_3$, 0.0164 g (0.025 mmol) of **L5**·$FeCl_2$, 75 µL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 1 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0741 g (0.21 mmol, 11/1 *E/Z*, 41% yield) of the title compound (*Z*) and recover chiral **1a** in 33% NMR yield. (*R*,*R*)-**1a**: 81.6% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 22.2 (major), 24.7 (minor). **2ad**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +30.9 (c 1.07, $CHCl_3$), 98.8% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 16.8 (minor), 26.5 (major). IR (cm^{-1}): 3021, 2960, 2138, 1594, 1498, 1248. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41-7.33 (m, 4H), 7.30-7.25 (m, 4H), 7.24-7.15 (m, 4H), 6.87-6.83 (m, 2H), 5.76 (d, *J* = 9.6 Hz, 1H), 4.27-4.19 (m, 2H), 3.80 (s, 3H), 3.72-3.62 (m, 1H), 2.41-2.27 (m, 2H), 1.32 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.0, 146.5, 143.3, 136.7, 135.4, 132.1, 128.4, 128.1, 127.0, 126.8, 126.5, 125.9, 122.7, 113.8, 55.0, 38.9, 22.6, 15.4. HRMS (ESI) calculated for $[C_{24}H_{27}OSi]^+$ (M + H$^+$) requires m/z 359.1831, found m/z 359.1823.



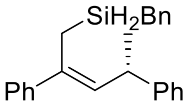
(*S*,*Z*)-(4-Chlorophenyl)(2,4-diphenylpent-2-en-1-yl)silane (2ae) Prepared according to the general procedure, using 0.1110 g (0.5 mmol) of **1a**, 0.1190 g (0.75 mmol, 1.5 equiv.) of 4-$ClC_6H_4SiH_3$, 0.0167 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 5 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0694 g (0.19 mmol, 10/1 *E/Z*, 38% yield) of the title compound (*Z*) and recover chiral **1a** in 41% NMR yield. (*R*,*R*)-**1a**: 62.5% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 22.1 (major), 24.4 (minor). **2ae**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +24.0 (c 0.97, $CHCl_3$), 98.0% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 10.1 (minor), 12.6 (major). IR (cm^{-1}): 3025, 2963, 2147, 1583, 1488, 1449. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35-7.29 (m, 4H), 7.29-7.24 (m, 5H), 7.24-7.15 (m, 5H), 5.77 (d, *J* = 9.4 Hz, 1H), 4.26-4.17 (m, 2H), 3.69-3.59 (m, 1H), 2.41-2.29 (m, 2H), 1.31 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 146.3, 143.0, 136.5, 136.1, 135.1, 132.4, 130.2, 128.4, 128.18, 128.16, 126.97, 126.96, 126.5, 126.0, 38.9, 22.7, 14.9. HRMS (ESI) calculated for [$C_{23}H_{24}ClSi$]$^+$ (M + H$^+$) requires m/z 363.1336, found m/z 363.1301.



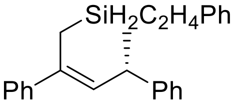
(*S*,*Z*)-(2,4-Diphenylpent-2-en-1-yl)(o-tolyl)silane (2af) Prepared according to the general procedure, using 0.1109 g (0.5 mmol) of **1a**, 0.0923 g (0.75 mmol, 1.5 equiv.) of 2-MeC$_6$H$_4$SiH$_3$, 0.0166 g (0.025 mmol) of **L5**·FeCl$_2$, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt$_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0718 g (0.21 mmol, >20/1 *E/Z*, 42% yield) of the title compound (*Z*) and recover chiral **1a** in 31% NMR yield. (*R*,*R*)-**1a**: 87.4% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 21.7 (major), 24.1 (minor). **2af**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +33.4 (c 0.97, CHCl$_3$), 97.1% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 7.5 (minor), 9.0 (major). IR (cm^{-1}): 2962, 2924, 2142, 1596, 1490, 1449. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.44 (d, *J* = 6.4 Hz, 1H), 7.37-7.32 (m, 2H), 7.31-7.16 (m, 9H), 7.16-7.09 (m, 2H), 5.76 (d, *J* = 9.4 Hz, 1H), 4.33-4.24 (m, 2H), 3.74-3.63 (m, 1H), 2.47-2.29 (m, 5H), 1.32 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 146.4, 143.9, 143.2, 136.4, 135.5, 132.2, 131.5, 130.3, 129.4, 128.4, 128.1, 127.0, 126.9, 126.5, 125.9, 125.1, 38.9, 22.6, 22.6, 14.7. HRMS (ESI) calculated for [$C_{24}H_{27}Si$]$^+$ (M + H$^+$) requires m/z 343.1882, found m/z 343.1897.



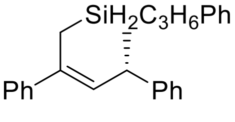
(*S*,*Z*)-(2,4-Diphenylpent-2-en-1-yl)(naphthalen-1-yl)silane (2ag) Prepared according to the general procedure, using 0.1110 g (0.5 mmol) of **1a**, 0.1197 g (0.75 mmol, 1.5 equiv.) of naphthalen-1-ylsilane, 0.0166 g (0.025 mmol) of **L5**·FeCl$_2$, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt$_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 12 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0835 g (0.22 mmol, 13/1 *E/Z*, 45% yield) of the title compound (*Z*) and recover chiral **1a** in 28% NMR yield. (*R*,*R*)-**1a**: 94.4% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 22.0 (major), 24.6 (minor). **2ag**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +36.4 (c 0.96, CHCl$_3$), 96.0% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 9.3 (minor), 14.1 (major). IR (cm^{-1}): 3052, 2963, 2144, 1497, 1449. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.97-7.92 (m, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.84-7.80 (m, 1H), 7.68 (dd, *J* = 6.6, 1.0 Hz, 1H), 7.50-7.45 (m, 2H), 7.39 (dd, *J* = 8.2, 6.6 Hz, 1H), 7.36-7.32 (m, 2H), 7.27-7.18 (m, 5H), 7.17-7.11 (m, 3H), 5.73 (d, *J* = 9.6 Hz, 1H), 4.60-4.53 (m, 2H), 3.62-3.52 (m, 1H), 2.56-2.40 (m, 2H), 1.17 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 146.4, 143.1, 137.0, 136.0, 135.5, 133.1, 132.3, 130.9, 130.7, 128.8, 128.4, 128.1, 127.7, 126.93, 126.88, 126.6, 126.2, 125.9, 125.8, 125.1, 38.9, 22.6, 15.1. HRMS (ESI) calculated for $[C_{27}H_{27}Si]^+$ (M + H$^+$) requires m/z 379.1882, found m/z 379.1879.



(*S*,*Z*)-Benzyl(2,4-diphenylpent-2-en-1-yl)silane (2ah) Prepared according to the general procedure, using 0.1103 g (0.5 mmol) of **1a**, 0.0920 g (0.75 mmol, 1.5 equiv.) of BnSiH$_3$, 0.0168 g (0.025 mmol) of **L5**·FeCl$_2$, 75 μL (1.0 M in THF, 0.075 mmol) of NaBHEt$_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 1 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0687 g (0.20 mmol, 9/1 *E/Z*, 40% yield) of the title compound (*Z*) and recover chiral **1a** in 31% NMR yield. (*R*,*R*)-**1a**: 80.0% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 21.4 (major), 23.8 (minor). **2ah**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +12.5 (c 0.96, CHCl$_3$), 98.4% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 49.0 (minor), 60.4 (major). IR (cm^{-1}): 3025, 2963, 2141, 1599, 1493, 1450. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34-7.15 (m, 12H), 7.09 (t, J = 7.4 Hz, 1H), 6.97 (d, J = 7.4 Hz, 2H), 5.76 (d, J = 9.4 Hz, 1H), 3.80-3.72 (m, 2H), 3.68-3.59 (m, 1H), 2.18-2.05 (m, 4H), 1.38 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.5, 143.3, 139.3, 135.7, 131.9, 128.5, 128.4, 128.2, 128.1, 127.0, 126.9, 126.4, 126.0, 124.7, 38.9, 22.9, 19.3, 13.5. HRMS (ESI) calculated for $[C_{24}H_{27}Si]^+$ (M + H$^+$) requires m/z 343.1882, found m/z 343.1880.

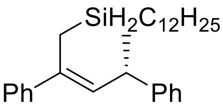


(*S*,*Z*)-(2,4-Diphenylpent-2-en-1-yl)(phenethyl)silane (2ai) Prepared according to the general procedure, using 0.1104 g (0.5 mmol) of **1a**, 0.1035 g (0.75 mmol, 1.5 equiv.) of $PhC_2H_4SiH_3$, 0.0167 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 5 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0751 g (0.21 mmol, 10/1 *E/Z*, 42% yield) of the title compound (*Z*) and recover chiral **1a** in 28% NMR yield. (*R*,*R*)-**1a**: 82.3% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 20.7 (major), 23.0 (minor). **2ai**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +8.5 (c 1.00, $CHCl_3$), 96.9% *ee* determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 90/10, 1.0 mL/min, n = 220 nm, tr 6.8 (major), 11.2 (minor). IR (cm^{-1}): 3026, 2923, 2135, 1599, 1493, 1450. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37-7.33 (m, 2H), 7.31-7.25 (m, 6H), 7.24-7.12 (m, 5H), 7.04 (d, J = 7.4 Hz, 2H), 5.75 (d, J = 9.6 Hz, 1H), 3.77-3.65 (m, 3H), 2.60-2.54 (m, 2H), 2.18-2.05 (m, 2H), 1.40 (d, J = 7.0 Hz, 3H), 0.93-0.86 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.5, 143.9, 143.5, 136.0, 131.7, 128.4, 128.3, 128.2, 127.8, 127.0, 126.9, 126.5, 126.0, 125.7, 38.9, 31.3, 22.9, 13.7, 11.5. HRMS (ESI) calculated for $[C_{25}H_{29}Si]^+$ (M + H$^+$) requires m/z 357.2039, found m/z 357.2044.



(*S*,*Z*)-(2,4-Diphenylpent-2-en-1-yl)(3-phenylpropyl)silane (2aj) Prepared according to the general procedure, using 0.1105 g (0.5 mmol) of **1a**, 0.1032 g (0.75 mmol, 1.5 equiv.) of $PhC_3H_6SiH_3$, 0.0167 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL

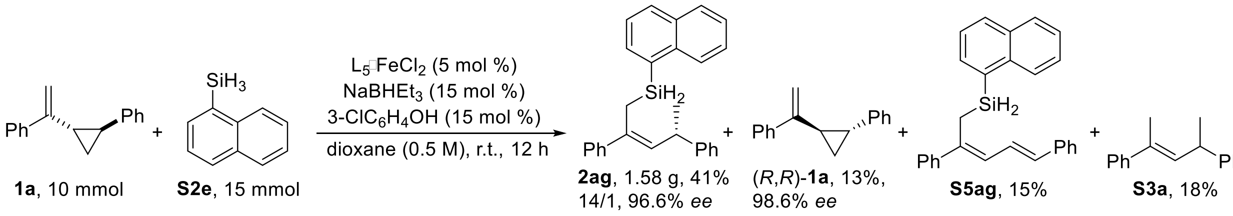
(1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 5 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0763 g (0.21 mmol, 12/1 *E/Z*, 41% yield) of the title compound (*Z*) and recover chiral **1a** in 28% NMR yield. (*R*,*R*)-**1a**: 78.7% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 21.0 (major), 23.3 (minor). **2aj**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +9.5 (c 0.95, $CHCl_3$), 94.0% *ee* determined by HPLC after Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 90/10, 1.0 mL/min, n = 220 nm, tr 6.8 (major), 11.2 (minor). IR (cm^{-1}): 2924, 2131, 1598, 1493, 1450. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36-7.32 (m, 2H), 7.30-7.15 (m, 11H), 7.07 (d, J = 7.4 Hz, 2H), 5.74 (d, J = 9.6 Hz, 1H), 3.78-3.70 (m, 1H), 3.70-3.62 (m, 2H), 2.50 (t, J = 7.8 Hz, 2H), 2.19-2.07 (m, 2H), 1.62-1.53 (m, 2H), 1.40 (d, J = 7.2 Hz, 3H), 0.60-0.53 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.5, 143.5, 142.1, 136.2, 131.6, 128.4, 128.2, 128.1, 127.0, 126.9, 126.5, 126.0, 125.7, 38.93, 38.87, 27.2, 22.9, 13.7, 9.2. HRMS (ESI) calculated for $[C_{26}H_{30}SiNa]^+$ (M + Na$^+$) requires m/z 393.2014, found m/z 393.2017.



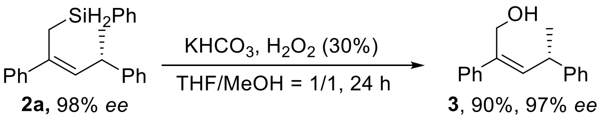
(*S*,*Z*)-(2,4-Diphenylpent-2-en-1-yl)(dodecyl)silane (2ak) Prepared according to the general procedure, using 0.1113 g (0.5 mmol) of **1a**, 0.1524 g (0.75 mmol, 1.5 equiv.) of $C_{12}H_{25}SiH_3$, 0.0166 g (0.025 mmol) of **L5**·$FeCl_2$, 75 μL (1.0 M in THF, 0.075 mmol) of $NaBHEt_3$, and 1.0 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.075 mmol). After 5 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0770 g (0.18 mmol, 11/1 *E/Z*, 37% yield) of the title compound (*Z*) and recover chiral **1a** in 12% NMR yield. (*R*,*R*)-**1a**: 94.7% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 22.4 (major), 24.7 (minor). **2ak**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = -1.7 (c 1.00, toluene), 87.1% *ee* determined by HPLC after

Fleming-Tamao oxidation to the corresponding alcohol (Wang et al., 2017), HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 90/10, 1.0 mL/min, n = 220 nm, tr 6.9 (major), 11.6 (minor). IR (cm^{-1}): 2923, 2855, 2132, 1494, 1455. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39-7.34 (m, 2H), 7.32-7.27 (m, 5H), 7.25-7.15 (m, 3H), 5.74 (d, J = 9.6 Hz, 1H), 3.80-3.71 (m, 1H), 3.69-3.61 (m, 2H), 2.20-2.07 (m, 2H), 1.41 (d, J = 7.0 Hz, 3H), 1.31-1.17 (m, 20H), 0.88 (t, J = 6.4 Hz, 3H), 0.58-0.50 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.6, 143.6, 136.3, 131.5, 128.4, 128.1, 127.0, 126.8, 126.5, 125.9, 38.9, 32.8, 31.9, 29.7, 29.5, 29.4, 29.2, 25.2, 22.8, 22.7, 14.1, 13.8, 9.5. HRMS (ESI) calculated for $[C_{29}H_{45}Si]^+$ ($M + H^+$) requires m/z 421.3291, found m/z 421.3300.

E. Data of Gram Scale Reaction and Further Transformations



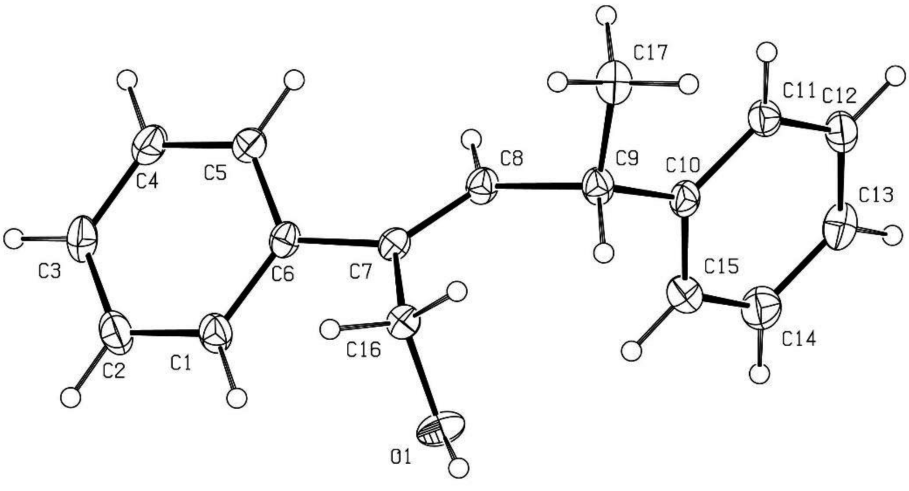
Gram scale reaction (2ag) Prepared according to the general procedure, using 2.2091 g (10.0 mmol) of **1a**, 2.3731 g (15.0 mmol, 1.5 equiv.) of naphthalen-1-ylsilane, 0.3333 g (0.5 mmol) of **L5**·$FeCl_2$, 1.5 mL (1.0 M in THF, 1.5 mmol) of $NaBHEt_3$, and 20 mL (0.5 M) of dioxane containing 5 mol% of 3-chlorophenol (0.1928 g, 1.5 mmol). After 12 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 1.58 g (4.17 mmol, 14/1 *E/Z*, 41% yield) of the title compound (*Z*) and recover chiral **1a** in 13% NMR yield. **2ag**: colorless oil. 96.6% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 11.3 (minor), 19.6 (major). (*R*,*R*)-**1a**: 98.6% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 23.0 (major), 25.4 (minor).

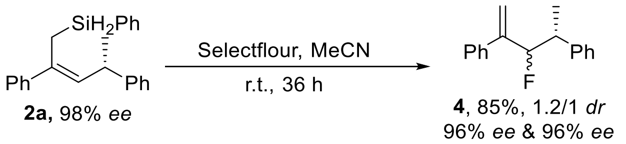


(*S*,*Z*)-2,4-Diphenylpent-2-en-1-ol (3): Prepared according to a previously reported procedure

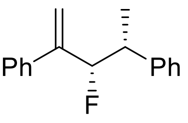
(Wang et al., 2017),a 10 mL Schlenk flask was charged with **2a** (0.0667 g, 0.2 mmol), $KHCO_3$ (0 .0205 g, 0.2 mmol) and THF/MeOH (1/1, 4 mL), and then 30% aqueous H_2O_2 (0.4 ml, 3.6 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 24 h. The reaction was quenched with water (2 mL), extracted with ether (5 mL x 3). The organic layers were combined, washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography using PE/EA (10/1) as the eluent to give 0.0434 g (0.18 mmol, 90% yield) of the title compound as a white solid. mp: 75.5-76.3 ºC. Optical Rotation: $[\alpha]_{20}^{D}$ = -44.8 (c 0.85, $CHCl_3$), 97.0% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 90/10, 1.0 mL/min, n = 220 nm, tr 6.9 (major), 11.5 (minor). IR (cm^{-1}): 3358, 2965, 1599, 1491, 1450. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.44 (d, J = 7.6 Hz, 2H), 7.35-7.24 (m, 7H), 7.23-7.17 (m, 1H), 6.01 (d, J = 9.6 Hz, 1H), 4.62 (s, 2H), 4.01-3.93 (m, 1H), 1.45 (d, J = 7.0 Hz, 3H), 1.34-1.27 (brs, 1H); ^{13}C NMR: ($CDCl_3$, 100 MHz) : δ 146.0, 140.7, 137.7, 137.1, 128.7, 128.5, 127.3, 126.9, 126.4, 126.3, 60.1, 38.3, 22.8. HRMS (ESI) calculated for $[C_{17}H_{18}ONa]^+$ (M + Na^+) requires m/z 261.1255, found m/z 261.1265.

X-ray diffraction of 3; CCDC 1900765

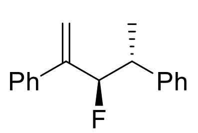




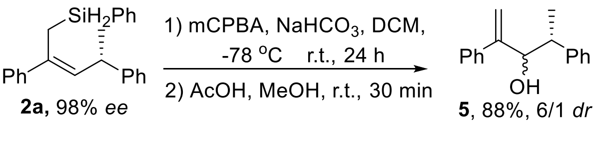
((4*R*)-3-Fluoropent-1-ene-2,4-diyl)dibenzene (4): Prepared according to a previously reported procedure (Thibaudeau and Gouverneur, 2003; Tredwell et al., 2008), a 10 mL flame-dried Schlenk flask cooled under nitrogen was charged with **2a** (0.1651 g, 0.5 mmol) and MeCN (5 mL), and then 0.2136 g of selectflour (0.6 mmol, 1.2 equiv.) was added. The reaction mixture was stirried at room temperature for 36 h and at room temperature for 30 min. The reaction was quenched with ether (5 mL) and filtered through a pad of silica gel, washed by ether (5 mL x 3). The organic layers was concentrated in vacuo and purified by column chromatography using PE as the eluent to give 0.0458 g (0.19 mmol, 38% yield) of (*S*,*R*)-**4** and 0.0566 g (0.24 mmol, 47% yield) of (*R*,*R*)-**4**.



((3*S*,*4*R)-3-fluoropent-1-ene-2,4-diyl)dibenzene (*S*,*R*)-**4**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +68.9 (c 0.99, $CHCl_3$), 96.3% *ee* determined by HPLC, HPLC conditions: Chiralcel OJ-H, *n*hexane/*i*PrOH = 99/1, 1.0 mL/min, n = 220 nm, tr 7.5 (minor), 11.5 (major). IR (cm^{-1}): 2977, 2929, 1496, 1452. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36-7.26 (m, 5H), 7.26-7.21 (m, 2H), 7.21-7.16 (m, 1H), 7.13 (d, J = 7.6 Hz, 2H), 5.47 (dd, J = 47.2, 5.2 Hz, 1H), 5.35 (d, J = 2.4 Hz, 1H), 5.32 (s, 1H), 3.01-2.87 (m, 1H), 1.29 (d, J = 7.0 Hz, 3H); ^{13}C NMR: ($CDCl_3$, 100 MHz) : δ 146.2 (d, J = 16.2 Hz), 143.2 (d, J = 3.0 Hz), 138.8 (d, J = 3.8 Hz), 128.5, 128.3, 127.9 (d, J = 4.4 Hz), 127.8, 127.0 (d, J = 1.6 Hz), 126.6, 115.7 (d, J = 11.8 Hz), 97.7 (d, J = 182.8 Hz), 42.3 (d, J = 22.0 Hz), 14.7 (d, J = 6.0 Hz); ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ -188.1. HRMS (ESI) calculated for $[C_{17}H_{17}FNa]^+$ ($M + Na^+$) requires m/z 263.1212, found m/z 263.1205.

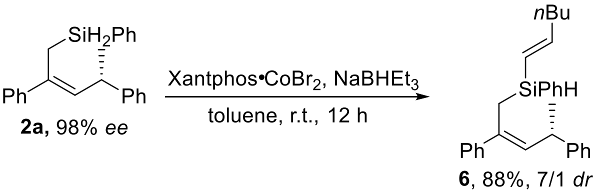


((3*R*,4*R*)-3-fluoropent-1-ene-2,4-diyl)dibenzene (*R*,*R*)-**4**: colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +38.3 (c 1.03, $CHCl_3$), 95.7% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 9.3 (minor), 10.7 (major). IR (cm^{-1}): 2972, 2926, 1495, 1451. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41-7.31 (m, 5H), 7.30-7.20 (m, 3H), 7.16 (d, J = 7.6 Hz, 2H), 5.36 (dd, J = 46.8, 6.6 Hz, 1H), 5.33 (s, 1H), 5.22 (s, 1H), 3.05-2.91 (m, 1H), 1.24 (d, J = 7.2 Hz, 3H); ^{13}C NMR: ($CDCl_3$, 100 MHz) : δ 146.1 (d, J = 17.0 Hz), 141.8, 138.7 (d, J = 2.2 Hz), 128.5, 128.2, 128.1, 127.9, 127.3, 126.6, 117.0 (d, J = 10.4 Hz), 98.5 (d, J = 179.2 Hz), 42.9 (d, J = 22.2 Hz), 18.1 (d, J = 6.0 Hz); ^{19}F NMR ($CDCl_3$, 376.5 MHz): δ -178.9. HRMS (ESI) calculated for $[C_{17}H_{18}F]^+$ ($M + H^+$) requires m/z 241.1393, found m/z 241.1388.

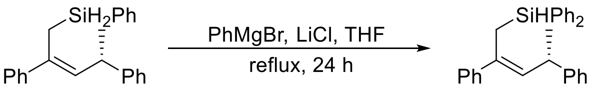


(3*R*,4*R*)-2,4-Diphenylpent-1-en-3-ol (5): Prepared according to a previously reported procedure (Hayashi et al., 1984), a 10 mL flame-dried Schlenk flask cooled under nitrogen was charged with **2a** (0.0663 g, 0.2 mmol) and DCM (1 mL), and $NaHCO_3$ (0.0343 g, 0.4 mmol) was added. The reaction mixture was cooled to -78 ºC and a solution of *m*CPBA (0.0663 g, 0.4 mmol in 2 mL DCM) was added dropwise. The reaction mixture was allowed to stir to room temperature and at room temperature for 24 h. Then 2 mL of MeOH and 140 uL of acetic acid were added and stirred at room temperature for 30 min. The reaction was quenched with water (2 mL), extracted with

DCM (5 mL x 3). The organic layers were combined, washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography using PE/EA (10/1) as the eluent to give 0.0426 g (0.18 mmol, 88% yield, 6/1 *dr*) of the title compound as a colorless oil. Optical Rotation: $[\alpha]_{20}^{D} = +91.2$ (c 0.97, $CHCl_3$). IR (cm^{-1}): 3456, 2974, 1494, 1450. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.38-7.24 (m, 7H), 7.23-7.16 (m, 3H), 5.37 (s, 1H), 5.32 (s, 1H), 4.82 (s, 1H), 2.92-2.83 (m, 1H), 1.74 (d, J = 3.4 Hz, 1H), 1.19 (d, J = 7.2 Hz, 3H); ^{13}C NMR: ($CDCl_3$, 100 MHz) : δ 150.0, 144.4, 140.3, 128.4, 128.3, 127.8, 127.6, 126.9, 126.4, 113.7, 77.3, 42.2, 12.7. HRMS (ESI) calculated for $[C_{17}H_{19}O]^+$ (M + H^+) requires m/z 239.1436, found m/z 239.1434.



((*S*,*Z*)-2,4-Diphenylpent-2-en-1-yl)((*E*)-hex-1-en-1-yl)(phenyl)silane (6): Prepared according to a previously reported procedure (Cheng et al., 2017), a 10 mL flame-dried Schlenk flask cooled under nitrogen was charged with **2a** (0.0662 g, 0.2 mmol) and xantphos·$CoBr_2$ (0.0163 g, 10 mol%). The mixture was vacuumed and flushed with nitrogen for three times, and then 1.0 mL of toluene (0.2 M), $NaBHEt_3$ (1.0 M in THF, 60 μL, 0.06 mmol) and 1-butyne (46 uL, 0.4 mmol) were added in sequence. The reaction was run at room temperature for 12 h. Then the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and purified by flash column chromatography using PE as the eluent to give 0.0726 g (0.18 mmol, 88% yield, 7/1 *dr*) of the title compound as a colorless oil. Optical Rotation: $[\alpha]_{20}^{D} = +40.0$ (c 1.03, $CHCl_3$). IR (cm^{-1}): 2959, 2924, 2126, 1610, 1454. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.47-7.42 (m, 2H), 7.35-7.13 (m, 13H), 6.16-6.07 (m, 1H), 5.71 (d, J = 9.6 Hz, 1H), 5.57-5.45 (m, 1H), 4.45-4.40 (m, 1H), 3.72-3.58 (m, 1H), 2.43-2.28 (m, 2H), 2.08-1.97 (m, 2H), 1.33-1.20 (m, 7H), 0.90-0.83 (m, 3H). HRMS (ESI) calculated for $[C_{29}H_{35}Si]^+$ (M + H^+) requires m/z 411.2508, found m/z 411.2520.

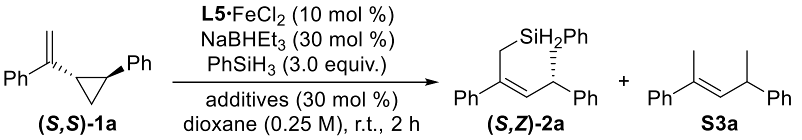


2a, 98% *ee* **7**, 90%, 98% *ee*

(*S,Z*)-(2,4-Diphenylpent-2-en-1-yl)diphenylsilane (7): Prepared according to a previously reported procedure (Hirone et al., 2010), a 10 mL flame-dried Schlenk flask cooled under nitrogen was charged with **2a** (0.1654 g, 0.5 mmol) and THF (1 mL). Lithium chloride (0.0431 g, 1.0 mmol) and phenylmagnesium bromide (5 mL, 1 M in THF) were added in sequence. The reaction mixture was run at room temperure for 24 h and quenched with water (0.5 mL), filtered through a pad of silica gel, washed by ether (5 mL x 3) and concentrated in vacuo. The crude product was purified by column chromatography using PE as the eluent to give 0.1836 g (0.45 mmol, 90% yield) of the title compound as a colorless oil. Optical Rotation: $[\alpha]_{20}^{D}$ = +42.2 (c 1.00, $CHCl_3$), 98.4% *ee* determined by HPLC after oxidation (Cheng et al., 2019), HPLC conditions: Chiralcel OD-H, *n*hexane/*i*PrOH = 90/10, 1.0 mL/min, n = 220 nm, tr 6.7 (major), 10.9 (minor). IR (cm^{-1}): 3059, 2964, 2133, 1491, 1438. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.49-7.43 (m, 4H), 7.39-7.30 (m, 3H), 7.30-7.23 (m, 7H), 7.21-7.10 (m, 6H), 5.68 (d, J = 9.6 Hz, 1H), 4.75 (t, J = 3.8 Hz, 1H), 3.61-3.52 (m, 1H), 2.67-2.52 (m, 2H), 1.14 (d, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 146.4, 143.6, 135.3, 135.2, 135.1, 133.9, 133.7, 132.4, 129.6, 128.3, 128.0, 127.9, 127.8, 127.0, 126.8, 126.7, 125.8, 38.8, 22.4, 17.3. HRMS (ESI) calculated for $[C_{29}H_{29}Si]^+$ (M + H^+) requires m/z 405.2039, found m/z 405.2041.

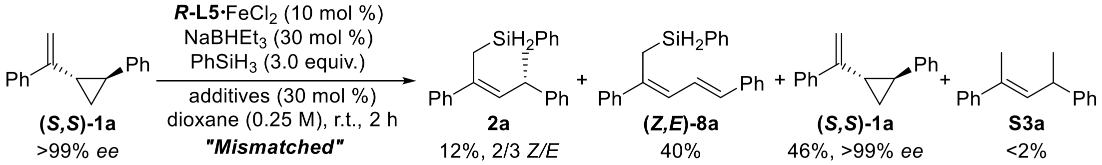
F. Mechanism Studies

Control experiments

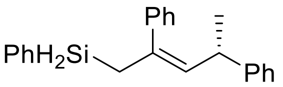


(*S*,*S*)-1a >99% *ee* ***"Matched"*** **(*S*,*Z*)-2a** 94%, >99% *ee* **S3a** <2%

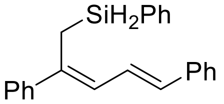
Prepared according to the general procedure, using 0.0445 g (0.2 mmol) of (*S,S*)-**1a**, 77 μL (0.6 mmol, 3.0 equiv.) of $PhSiH_3$, 0.0134 g (0.02 mmol) of **L5**·$FeCl_2$, 60 μL (1.0 M in THF, 0.06 mmol) of $NaBHEt_3$, and 0.8 mL (0.25 M) of dioxane containing 5 mol% of 3-chlorophenol (0.06 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. The crude mixture was purified by flash column chromatography using PE as the eluent to give 0.0623 g (0.19 mmol, 94% yield) of the title compound (*Z*). (*S,Z*)-**2a**: 99.5% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 22.0 (minor), 23.7 (major).



Prepared according to the general procedure, using 0.0449 g (0.2 mmol) of (*S,S*)-**1a**, 77 μL (0.6 mmol, 3.0 equiv.) of $PhSiH_3$, 0.0134 g (0.02 mmol) of ***R*-L5**·$FeCl_2$, 60 μL (1.0 M in THF, 0.06 mmol) of $NaBHEt_3$, and 0.8 mL (0.25 M) of dioxane containing 5 mol% of 3-chlorophenol (0.06 mmol). After 2 h, the resulting solution was added 10 mL of PE/EA (10/1) and filtered through a pad of silica gel, washed by PE/EA (10/1, 10 mL x 3). The combined filtrates were concentrated and stereoselectivity was monitored by ^{1}H NMR analysis. A mixture of product **2a** (12% yield, 2/3 *Z/E*), (*Z,E*)-**8a** (40% yield), (*S,S*)-**1a** (46% yield, >99% *ee*) and **S3a** (<2% yield) was observed. (*S,S*)-**1a**: 99.8% *ee* determined by HPLC, HPLC conditions: Chiralcel OD-H x 2, *n*hexane/*i*PrOH = 99.9/0.1, 1.0 mL/min, n = 220 nm, tr 23.3 (minor), 25.2 (major).



(*S,E*)-(2,4-diphenylpent-2-en-1-yl)(phenyl)silane (*S,E*)-**2a**: colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49-7.45 (m, 2H), 7.40-7.34 (m, 1H), 7.34-7.26 (m, 4H), 7.25-7.21 (m, 3H), 7.18-7.09 (m, 3H), 7.08-7.03 (m, 2H), 5.49 (d, *J* = 10.2 Hz, 1H), 4.28-4.20 (m, 2H), 3.45-3.35 (m, 1H), 2.21 (td, *J* = 3.6, 0.8 Hz, 2H), 1.21 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR: ($CDCl_3$, 100 MHz) : δ 146.8, 141.6, 135.7, 135.3, 132.0, 131.8, 129.6, 128.30, 128.29, 128.1, 127.9, 126.8, 126.7, 125.7, 38.7, 22.9, 22.6. HRMS (EI) calculated for $[C_{23}H_{24}Si]^+$ requires m/z 328.1647, found m/z 328.1647.



((*2Z,4E*)-2,5-diphenylpenta-2,4-dien-1-yl)(phenyl)silane (*Z,E*)-**8a**: colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58-7.54 (m, 2H), 7.48-7.43 (m, 2H), 7.38-7.26 (m, 10H), 7.24-7.17 (m, 1H), 6.97 (dd, *J* = 15.4, 11.2 Hz, 1H), 6.57 (d, *J* = 15.4

Hz, 1H), 6.50 (d, *J* = 11.2 Hz, 1H), 4.39 (t, *J* = 3.8 Hz, 2H), 2.59 (t, *J* = 3.8 Hz, 2H); ^{13}C NMR: (CDCl$_3$, 100 MHz) : δ 142.6, 138.5, 137.8, 135.3, 132.3, 131.9, 129.9, 128.5, 128.3, 128.0, 127.29, 127.26, 126.3, 126.2, 125.9, 15.8. HRMS (EI) calculated for $[C_{23}H_{22}Si]^+$ requires m/z 326.1491, found m/z 326.1491.

Data S2. Cartesian coordinates of the calculated species, Related to Figure 3.

Int1(doublet)

C	-3.540691	-0.020772	-0.631331
C	-4.63781	-0.590392	-1.243851
C	-4.440182	-1.83264	-1.910295
C	-3.190764	-2.440414	-1.908762
C	-2.103174	-1.818373	-1.254371
N	-2.31573	-0.602429	-0.653423
H	-5.27946	-2.315068	-2.41398
H	-5.613829	-0.105859	-1.207084
H	-3.050227	-3.402605	-2.40436
C	-3.458027	1.21025	0.153622
O	-4.513574	1.972953	0.41623
C	-2.519442	2.812983	1.424028
C	-4.050103	3.046903	1.280005
H	-4.295655	4.000168	0.789692
N	-2.313162	1.571193	0.656669
H	-4.601189	2.973884	2.22826
C	-1.674909	3.969257	0.906251
H	-1.894681	4.883576	1.480007
H	-0.605003	3.750906	1.011507
H	-1.88877	4.162703	-0.156853
C	-0.75971	-2.270347	-1.069216
C	-0.279772	-3.60142	-1.567411
H	-0.393899	-4.378669	-0.791924
H	-0.845229	-3.925232	-2.452238
H	0.786816	-3.564806	-1.825829
N	0.013872	-1.431248	-0.358899
C	1.347098	-1.801118	-0.025816
C	2.422198	-1.221484	-0.740034
C	1.568608	-2.683594	1.055019
C	3.725588	-1.55583	-0.353208
C	2.891049	-2.984748	1.403406
C	3.962387	-2.431602	0.705708
H	4.572566	-1.119235	-0.882708
H	3.086749	-3.655798	2.241827
H	4.987768	-2.676021	0.993465
C	0.408784	-3.226885	1.880555
C	0.144437	-2.319552	3.092812
C	0.601046	-4.687059	2.306833
H	-0.495429	-3.187685	1.257446
H	-0.08074	-1.294018	2.765428
H	-0.709958	-2.691039	3.682342
H	1.027174	-2.274726	3.750299
H	0.825862	-5.33382	1.443714
H	1.422484	-4.800252	3.031929
H	-0.312409	-5.066529	2.792025
C	2.155158	-0.260015	-1.891138
C	1.70349	-0.99252	-3.166038
C	3.337643	0.657167	-2.21147
H	1.316559	0.37904	-1.566785

H	0.76575	-1.543291	-3.018236
H	1.537683	-0.270888	-3.9824
H	2.473997	-1.707689	-3.498413
H	3.705071	1.178178	-1.317539
H	4.174433	0.096448	-2.659957
H	3.029626	1.423291	-2.937848
Fe	-0.857828	0.214877	0.286231
H	-2.244908	2.612237	2.47166
Si	0.912837	1.216722	1.560903
H	0.418986	2.042093	2.737474
H	1.959439	0.340311	2.193693
C	1.940242	2.467588	0.53162
C	1.429633	3.044236	-0.646254
C	3.246067	2.83204	0.911726
C	2.174107	3.954022	-1.402927
H	0.429537	2.763413	-0.989696
C	4.001908	3.735168	0.158795
H	3.682958	2.392277	1.81281
C	3.465921	4.302738	-1.001647
H	1.749532	4.382492	-2.315141
H	5.015239	3.996356	0.476398
H	4.05603	5.007171	-1.593576

Int1(quartet)

C	-3.532874	-0.059277	-0.657743
C	-4.611385	-0.632142	-1.298263
C	-4.3888	-1.86376	-1.978165
C	-3.133613	-2.45877	-1.963472
C	-2.062215	-1.835943	-1.282748
N	-2.301309	-0.6301	-0.667281
H	-5.214016	-2.346824	-2.503966
H	-5.59284	-0.157627	-1.274558
H	-2.975453	-3.412097	-2.471011
C	-3.478309	1.161635	0.141082
O	-4.54123	1.924004	0.383396
C	-2.572554	2.768857	1.433485
C	-4.108493	2.967313	1.297205
H	-4.382126	3.936045	0.855263
N	-2.345682	1.522486	0.680397
H	-4.655275	2.831844	2.241733
C	-1.756395	3.933285	0.887358
H	-1.981396	4.851381	1.453015
H	-0.681423	3.733463	0.976684
H	-1.991806	4.10964	-0.174341
C	-0.719384	-2.269345	-1.085637
C	-0.211169	-3.595898	-1.5672
H	-0.267766	-4.357603	-0.770204
H	-0.796401	-3.961528	-2.422165
H	0.843497	-3.531838	-1.86745
N	0.039011	-1.411413	-0.369136
C	1.370683	-1.767135	-0.016096
C	2.450774	-1.188221	-0.723656
C	1.586503	-2.637878	1.075486

C	3.751656	-1.510908	-0.318692
C	2.906294	-2.928074	1.44253
C	3.981865	-2.37454	0.751784
H	4.602235	-1.074572	-0.842716
H	3.096449	-3.590014	2.289548
H	5.005492	-2.608969	1.053773
C	0.419494	-3.183969	1.888896
C	0.141388	-2.283564	3.103257
C	0.609957	-4.645183	2.312683
H	-0.477856	-3.143631	1.255846
H	-0.076705	-1.252783	2.785222
H	-0.719742	-2.657988	3.680918
H	1.016262	-2.242693	3.77143
H	0.84307	-5.288674	1.449458
H	1.425884	-4.759028	3.043905
H	-0.306862	-5.027869	2.788933
C	2.192792	-0.241499	-1.889612
C	1.769289	-0.992369	-3.16379
C	3.371606	0.68341	-2.200855
H	1.343346	0.392499	-1.587015
H	0.831717	-1.545913	-3.026528
H	1.615638	-0.281655	-3.992047
H	2.550004	-1.706981	-3.472631
H	3.720969	1.216023	-1.306645
H	4.220056	0.126055	-2.631186
H	3.067967	1.439508	-2.939513
Fe	-0.866381	0.188511	0.326897
H	-2.286193	2.592578	2.481971
Si	0.883906	1.235352	1.563866
H	0.366579	2.081094	2.715352
H	1.929463	0.382707	2.230458
C	1.908934	2.477069	0.523625
C	1.392725	3.040323	-0.657814
C	3.211025	2.85612	0.901463
C	2.128207	3.951661	-1.421359
H	0.393601	2.750133	-0.997176
C	3.957671	3.761995	0.142676
H	3.651812	2.426487	1.805578
C	3.416264	4.316096	-1.0218
H	1.699525	4.369936	-2.336343
H	4.968232	4.035694	0.458506
H	3.999369	5.022427	-1.618342

(S,S)-1a

C	0.000713	0.013751	-0.089807
C	1.235472	0.240144	-0.917473
C	0.340081	-0.936803	-1.216903
H	0.191057	-0.388361	0.912518
H	1.171243	1.060324	-1.642012
H	-0.275896	-0.890125	-2.118556
H	0.695272	-1.936841	-0.953868
C	-1.193507	0.917731	-0.166237
C	-1.03187	2.233477	-0.392904

H	-1.869059	2.932654	-0.426776
H	-0.035926	2.65643	-0.538691
C	-2.526374	0.288742	0.048689
C	-2.626014	-1.03523	0.515641
C	-3.727554	0.979511	-0.208554
C	-3.867804	-1.636202	0.734665
H	-1.720421	-1.608821	0.712001
C	-4.966978	0.381045	0.00566
H	-3.695435	1.998665	-0.596447
C	-5.045736	-0.931959	0.482799
H	-3.911385	-2.664377	1.102351
H	-5.880617	0.94167	-0.207153
H	-6.017999	-1.401595	0.649534
C	2.597022	0.05727	-0.32078
C	2.97102	0.769667	0.828996
C	3.53505	-0.80111	-0.912506
C	4.250076	0.63017	1.372449
H	2.244413	1.43624	1.301277
C	4.815529	-0.943452	-0.37181
H	3.252797	-1.364026	-1.805936
C	5.177101	-0.227485	0.772772
H	4.523831	1.190758	2.269854
H	5.533539	-1.618317	-0.844647
H	6.177232	-0.339865	1.198368

2a

C	0.958304	-3.134296	2.359308
C	0.498754	-2.015448	1.409256
H	0.098058	-3.683183	2.770133
C	1.68666	-1.22185	0.905968
H	-0.143214	-1.331162	1.991845
C	-0.383283	-2.593827	0.308847
H	2.674399	-1.599071	1.187897
C	1.630804	-0.099013	0.157374
C	-1.774992	-2.638559	0.476925
C	0.164216	-3.125592	-0.867093
C	2.881192	0.629714	-0.193068
C	0.323377	0.486933	-0.30771
C	-2.602009	-3.189675	-0.505769
H	-2.215955	-2.226905	1.389578
C	-0.657914	-3.678939	-1.851295
H	1.245381	-3.084806	-1.01868
C	3.068661	1.190361	-1.46976
C	3.917292	0.776251	0.748398
H	0.443137	1.06854	-1.23375
H	-0.411774	-0.300944	-0.52604
C	-2.044781	-3.711186	-1.676175
H	-3.684772	-3.207339	-0.357821
H	-0.213364	-4.083229	-2.764259
C	4.251979	1.853148	-1.799257
H	2.287465	1.087569	-2.225732
C	5.099973	1.440857	0.421664
H	3.777015	0.381991	1.756825

H	-2.687631	-4.138317	-2.449488
C	5.274192	1.981986	-0.855109
H	4.37704	2.269563	-2.801926
H	5.885672	1.547869	1.173781
H	6.197658	2.507068	-1.110542
H	1.594999	-3.856783	1.823787
H	1.540514	-2.720361	3.198088
Si	-0.467532	1.658574	0.959957
H	0.313203	2.924486	1.075598
H	-0.477327	0.996446	2.298799
C	-2.222279	2.059108	0.410599
C	-2.701056	3.38069	0.3687
C	-3.09573	1.025012	0.020789
C	-4.006608	3.662382	-0.044294
H	-2.04405	4.20542	0.659687
C	-4.400514	1.301885	-0.392558
H	-2.756437	-0.014811	0.033845
C	-4.858754	2.622639	-0.425282
H	-4.358991	4.696673	-0.071054
H	-5.061317	0.484607	-0.692631
H	-5.879171	2.841144	-0.750083

PhSiH3

Si	-2.34908	0.00002	0.006645
H	-2.864512	-1.214885	-0.689684
H	-2.86378	1.223804	-0.674456
H	-2.876524	-0.008862	1.404715
C	-0.467979	0.000085	-0.016165
C	0.255411	-1.206805	-0.0111
C	0.255503	1.206853	-0.01113
C	1.652437	-1.209286	0.003552
H	-0.27756	-2.162141	-0.023265
C	1.652593	1.209189	0.003573
H	-0.277392	2.162214	-0.023271
C	2.353397	-0.000059	0.011522
H	2.196161	-2.157306	0.005478
H	2.196364	2.157181	0.005504
H	3.446197	-0.000147	0.02044

Int2(doublet)

N	0.931797	-0.336827	-1.231295
C	-4.564188	2.95829	0.561442
C	2.701437	0.308056	-3.248612
C	1.95856	1.308178	-2.633932
C	1.00342	0.965262	-1.65042
H	-2.226045	-0.771679	-1.614015
H	3.430029	0.568395	-4.018276
H	3.037256	-1.861411	-3.385272
H	2.100443	2.353051	-2.912158
C	1.275459	-2.601384	-1.275663
O	1.912614	-3.719965	-1.608956
C	1.419926	-4.756128	-0.723416
H	1.045012	-5.581832	-1.34549

N	0.35951	-2.667592	-0.356593
H	2.266064	-5.100122	-0.114182
C	-1.062642	-4.711639	-0.085304
H	-1.016499	-5.776358	0.194287
Fe	-0.172632	-0.727852	0.295533
H	-1.383067	-4.639605	-1.136356
C	-0.008306	1.774186	-1.061727
C	-0.159714	3.21778	-1.450624
H	-0.472801	3.32194	-2.503683
H	-0.909464	3.725297	-0.83384
H	0.801471	3.742797	-1.343516
N	-0.843955	1.111819	-0.227863
C	-2.095557	1.738089	0.057549
C	-3.074922	1.786536	-0.972263
C	-2.338254	2.332997	1.315216
C	-4.300632	2.399139	-0.688505
C	-3.585637	2.927671	1.550544
C	2.50222	-1.048568	-2.894527
H	-5.072859	2.434362	-1.456382
H	-3.784229	3.389539	2.519534
H	-5.532622	3.423757	0.759671
C	-1.234144	2.442105	2.353114
C	-1.707583	2.211118	3.791753
C	-0.522039	3.799926	2.229282
H	-0.499697	1.667403	2.113028
H	-2.268048	1.269608	3.87902
H	-0.84125	2.159902	4.470864
H	-2.351396	3.030103	4.150845
H	-0.067524	3.927037	1.236603
H	-1.231777	4.629342	2.380361
H	0.273934	3.895796	2.984934
C	-2.802631	1.19963	-2.356984
C	-3.690814	1.789377	-3.457397
C	-2.89316	-0.332181	-2.366065
H	-1.766492	1.453178	-2.622327
H	-3.663283	2.890452	-3.464556
H	-3.350418	1.432875	-4.442192
H	-4.740905	1.475127	-3.346347
C	1.613444	-1.314303	-1.866395
H	-3.915915	-0.665752	-2.14405
H	-2.604766	-0.725305	-3.354773
H	-1.81112	-4.227379	0.551326
C	0.302477	-4.066766	0.107854
C	1.605768	-0.53582	1.681284
H	0.250145	-1.83701	2.756706
H	-0.051627	-0.045264	2.973262
C	0.424202	-0.827117	2.381207
C	2.620158	-1.580336	1.400019
C	3.566576	-1.42678	0.364732
C	2.696777	-2.759361	2.171197
C	4.516196	-2.411609	0.094223
H	3.546471	-0.526331	-0.244238
C	3.651268	-3.741949	1.906377

H	2.013595	-2.894983	3.010932
C	4.565588	-3.578906	0.859771
H	5.219271	-2.265359	-0.729476
H	3.68999	-4.637188	2.532702
H	5.312919	-4.347959	0.651428
C	2.016568	0.912404	1.555309
C	3.456592	1.392567	1.55803
C	2.549337	1.705504	2.720487
H	1.398998	1.511701	0.885165
H	4.213195	0.632782	1.762116
H	2.750774	1.163548	3.64828
H	2.192299	2.7281	2.861463
C	3.857918	2.377658	0.516225
C	4.922293	2.074627	-0.348409
C	3.154813	3.574988	0.304864
C	5.260839	2.926332	-1.402185
H	5.485789	1.15085	-0.195295
C	3.493846	4.430776	-0.745026
H	2.327748	3.842722	0.964827
C	4.544439	4.107858	-1.609857
H	6.09002	2.664993	-2.064534
H	2.934865	5.359429	-0.886366
H	4.808734	4.777742	-2.431458
Si	-2.113882	-1.388536	1.514661
H	-2.454927	-0.496073	2.669878
H	-1.900791	-2.741107	2.153128
C	-3.799238	-1.548849	0.634787
C	-4.750961	-0.527087	0.79838
C	-4.151397	-2.629345	-0.196061
C	-5.991979	-0.572591	0.157525
H	-4.514341	0.328592	1.432942
C	-5.392996	-2.689784	-0.832326
H	-3.44166	-3.439849	-0.365818
C	-6.319323	-1.655501	-0.66187
H	-6.703117	0.245714	0.298287
H	-5.637447	-3.543853	-1.470015
H	-7.289502	-1.695702	-1.164018
H	0.560956	-4.074743	1.178244

Int2(quartet)

N	0.9424	0.365184	1.278413
C	-4.480782	-3.114596	-0.465107
C	2.949657	-0.24935	3.088946
C	2.159039	-1.257802	2.565031
C	1.103578	-0.933481	1.673182
H	-2.451795	0.773194	1.435642
H	3.761899	-0.496153	3.775159
H	3.284802	1.926233	3.14403
H	2.346234	-2.298289	2.829462
C	1.330402	2.650167	1.268601
O	1.957473	3.757433	1.67849
C	1.411697	4.849804	0.897822
H	1.029248	5.608561	1.596325

N	0.415273	2.767723	0.37322
H	2.229493	5.273332	0.299272
C	-1.103316	4.730357	0.321827
H	-1.151461	5.80897	0.102559
Fe	-0.427337	0.725902	-0.297236
H	-1.372856	4.574046	1.37825
C	0.10198	-1.819455	1.162334
C	0.006773	-3.235373	1.655639
H	0.977562	-3.745893	1.562554
H	-0.278742	-3.274575	2.721322
H	-0.742724	-3.802006	1.090115
N	-0.767869	-1.264497	0.303662
C	-2.006275	-1.90805	0.042313
C	-3.014597	-1.885438	1.043029
C	-2.236166	-2.536851	-1.200531
C	-4.240172	-2.497665	0.763114
C	-3.484058	-3.130048	-1.436741
C	2.703033	1.100137	2.736969
H	-5.031131	-2.481336	1.51327
H	-3.670328	-3.623651	-2.393051
H	-5.449024	-3.580537	-0.663191
C	-1.121696	-2.658671	-2.225379
C	-1.566689	-2.313284	-3.650533
C	-0.488884	-4.058637	-2.162917
H	-0.346922	-1.940479	-1.934131
H	-2.052486	-1.326996	-3.684447
H	-0.698106	-2.295972	-4.328984
H	-2.276806	-3.054356	-4.051279
H	-0.07735	-4.267232	-1.163479
H	-1.235905	-4.838313	-2.383547
H	0.32608	-4.158274	-2.898187
C	-2.778741	-1.178282	2.37399
C	-3.584915	-1.772043	3.533872
C	-3.036914	0.331803	2.255026
H	-1.716766	-1.298836	2.629926
H	-3.443639	-2.861525	3.613898
H	-3.269128	-1.314476	4.484675
H	-4.663541	-1.576343	3.425542
C	1.698228	1.338279	1.810479
H	-4.095669	0.537448	2.041297
H	-2.762032	0.846508	3.190138
H	-1.842521	4.218968	-0.307962
C	0.29454	4.192916	0.037048
C	1.700888	0.522163	-1.882453
H	0.205188	1.749895	-2.829868
H	-0.042918	-0.077347	-2.977988
C	0.51265	0.746469	-2.531534
C	2.636185	1.618388	-1.544521
C	3.593311	1.472996	-0.5211
C	2.613022	2.841251	-2.247605
C	4.467892	2.510439	-0.197
H	3.637347	0.545071	0.043485
C	3.492377	3.874542	-1.92946

H	1.910811	2.974158	-3.071884
C	4.424971	3.717612	-0.897095
H	5.182128	2.37304	0.618156
H	3.458239	4.806292	-2.499918
H	5.1149	4.526938	-0.647388
C	2.10686	-0.899918	-1.603833
C	3.537419	-1.40131	-1.674481
C	2.527242	-1.834694	-2.705475
H	1.539509	-1.384883	-0.806548
H	4.279845	-0.679863	-2.023294
H	2.63994	-1.411828	-3.707037
H	2.154656	-2.860443	-2.687405
C	4.01373	-2.282384	-0.571554
C	5.148255	-1.915571	0.169923
C	3.319185	-3.442151	-0.18993
C	5.569159	-2.672641	1.265722
H	5.703521	-1.018348	-0.115436
C	3.741606	-4.203824	0.900988
H	2.434426	-3.757395	-0.746483
C	4.865645	-3.820438	1.639142
H	6.453427	-2.364338	1.829124
H	3.190269	-5.107158	1.174485
H	5.195136	-4.417294	2.492794
Si	-2.428674	1.507278	-1.618984
H	-2.646756	0.670246	-2.853996
H	-2.233058	2.897208	-2.189012
C	-4.131927	1.542533	-0.77762
C	-4.9539	0.401494	-0.820663
C	-4.574058	2.630451	-0.001033
C	-6.158174	0.343282	-0.115392
H	-4.640851	-0.466314	-1.405619
C	-5.777833	2.581151	0.706238
H	-3.965127	3.536995	0.06022
C	-6.575015	1.432682	0.654982
H	-6.76972	-0.561656	-0.163716
H	-6.096384	3.441429	1.301638
H	-7.516072	1.389764	1.209553
H	0.517704	4.308368	-1.035679

TS3(doublet)

N	-0.831932	-0.259042	1.390762
C	4.978332	2.32154	-0.416061
C	-2.742913	0.6584	3.195517
C	-1.858292	1.550975	2.604651
C	-0.855491	1.08091	1.730891
H	1.838109	-0.738047	1.949364
H	-3.515494	1.021756	3.874989
H	-3.306805	-1.458575	3.358125
H	-1.936477	2.620395	2.804385
C	-1.509193	-2.477938	1.480615
O	-2.337413	-3.457145	1.858356
C	-2.021579	-4.605263	1.041005
H	-1.797509	-5.449692	1.710026

N	-0.607332	-2.751458	0.590779
H	-2.905435	-4.836402	0.430838
C	0.426327	-5.040089	0.420396
H	0.174383	-6.090056	0.200681
Fe	0.153907	-0.740516	-0.136891
H	0.767766	-4.978196	1.46584
C	0.21501	1.816979	1.151559
C	0.43845	3.263386	1.496743
H	0.489232	3.421837	2.586287
H	1.370486	3.63699	1.056231
H	-0.395511	3.878367	1.121121
N	1.000286	1.103442	0.320218
C	2.322874	1.56032	0.073215
C	3.277815	1.500481	1.129886
C	2.689971	2.068759	-1.192166
C	4.597209	1.869743	0.848177
C	4.023251	2.436139	-1.420056
C	-2.640744	-0.722232	2.908613
H	5.350051	1.809828	1.63371
H	4.310669	2.832169	-2.39643
H	6.016868	2.602836	-0.606798
C	1.636363	2.330736	-2.253517
C	2.064479	1.907677	-3.662821
C	1.20622	3.806785	-2.230334
H	0.758016	1.74217	-1.974676
H	2.407392	0.862342	-3.684705
H	1.219717	2.00184	-4.363859
H	2.881141	2.536415	-4.051959
H	0.813142	4.091134	-1.243521
H	2.05758	4.469971	-2.454491
H	0.420578	3.998183	-2.979462
C	2.868957	1.097431	2.547943
C	3.868742	1.535761	3.623378
C	2.568207	-0.399785	2.694917
H	1.930503	1.625122	2.76818
H	4.101337	2.610042	3.558507
H	3.450008	1.338053	4.622522
H	4.816261	0.977248	3.554471
C	-1.684216	-1.128743	1.99285
H	3.482856	-0.992999	2.56805
H	2.15147	-0.607991	3.693613
H	1.253019	-4.752206	-0.240245
C	-0.797056	-4.159807	0.194123
C	-1.288916	-0.406089	-1.52042
H	-0.344105	-1.514432	-3.145433
H	0.291523	0.117346	-2.90576
C	-0.119623	-0.749546	-2.383871
C	-2.418967	-1.367262	-1.429909
C	-3.455703	-1.154847	-0.489722
C	-2.520373	-2.528594	-2.224386
C	-4.512461	-2.050023	-0.346032
H	-3.415448	-0.275674	0.149534
C	-3.587397	-3.421024	-2.092066

H	-1.758217	-2.746427	-2.973785
C	-4.591911	-3.194088	-1.147853
H	-5.279749	-1.854644	0.407551
H	-3.631574	-4.302187	-2.738082
H	-5.425169	-3.892521	-1.041495
C	-1.660452	1.064991	-1.538978
C	-3.067388	1.620713	-1.665667
C	-2.078536	1.796999	-2.789306
H	-1.068036	1.688779	-0.869567
H	-3.86057	0.897486	-1.861162
H	-2.262865	1.196949	-3.684954
H	-1.660437	2.787342	-2.988819
C	-3.453528	2.702613	-0.718917
C	-4.568593	2.526335	0.1164
C	-2.687097	3.8695	-0.561123
C	-4.89717	3.472008	1.090089
H	-5.178426	1.626235	0.005274
C	-3.015249	4.818482	0.409059
H	-1.817133	4.037903	-1.19895
C	-4.118714	4.622099	1.245626
H	-5.766477	3.308338	1.732099
H	-2.405144	5.719744	0.511361
H	-4.374441	5.364421	2.005424
Si	1.545928	-1.892413	-2.007984
H	2.135687	-1.569058	-3.341926
H	1.044311	-3.294922	-2.066936
C	3.055708	-1.844766	-0.870232
C	4.154813	-1.04841	-1.243867
C	3.199821	-2.681108	0.251228
C	5.35636	-1.09922	-0.53704
H	4.077663	-0.383824	-2.105946
C	4.409024	-2.753633	0.945624
H	2.359537	-3.284527	0.589576
C	5.491775	-1.962824	0.553293
H	6.190423	-0.4653	-0.844093
H	4.501797	-3.42343	1.804347
H	6.436825	-2.014264	1.099739
H	-1.054637	-4.168922	-0.875731

TS3(quartet)

N	-0.860316	-0.369901	1.406999
C	4.476092	3.282289	-0.001093
C	-3.097815	0.152796	2.94428
C	-2.309621	1.201344	2.494236
C	-1.149649	0.926805	1.729314
H	3.538609	-0.843065	1.675246
H	-3.998094	0.360262	3.525127
H	-3.335784	-2.033587	2.984465
H	-2.589855	2.232427	2.710795
C	-1.090951	-2.664036	1.382937
O	-1.649032	-3.819743	1.754727
C	-0.986916	-4.850497	0.975937
H	-0.761194	-5.691538	1.645414

N	-0.06528	-2.712036	0.597701
H	-1.682985	-5.166681	0.187297
C	1.534917	-4.473379	1.214909
H	1.856522	-5.508965	1.019653
Fe	0.315053	-0.596214	-0.230857
H	1.348495	-4.363657	2.295243
C	-0.162299	1.848475	1.257012
C	-0.156777	3.274289	1.731917
H	-1.095597	3.780517	1.451986
H	-0.075938	3.330543	2.830193
H	0.679947	3.837399	1.301872
N	0.768107	1.321644	0.438844
C	2.003463	1.998445	0.276179
C	2.983145	1.856908	1.290292
C	2.263876	2.7696	-0.878375
C	4.209037	2.511358	1.129957
C	3.507893	3.403851	-0.997066
C	-2.744237	-1.185398	2.640413
H	4.975041	2.406301	1.901919
H	3.718122	4.009461	-1.881631
H	5.43974	3.786272	-0.107904
C	1.202964	2.94527	-1.950779
C	1.734287	2.654572	-3.360183
C	0.562981	4.340121	-1.876537
H	0.414524	2.215202	-1.734367
H	2.220139	1.66814	-3.412077
H	0.909842	2.666386	-4.091047
H	2.471158	3.406378	-3.68527
H	0.093263	4.511754	-0.896596
H	1.315281	5.131081	-2.029713
H	-0.21161	4.458566	-2.651399
C	2.7316	1.00237	2.526434
C	2.829392	1.830449	3.815886
C	3.661594	-0.21842	2.570456
H	1.707423	0.614516	2.458925
H	2.148916	2.69554	3.789743
H	2.567092	1.215426	4.691892
H	3.850241	2.215073	3.974166
C	-1.621721	-1.384844	1.85527
H	4.721073	0.077554	2.623359
H	3.438775	-0.836638	3.455379
H	2.351725	-3.792627	0.94662
C	0.270708	-4.136032	0.425769
C	-1.280274	-0.46187	-1.662438
H	-0.051249	-1.285201	-3.258442
H	0.264447	0.429209	-2.870514
C	-0.047183	-0.531973	-2.454495
C	-2.126716	-1.651563	-1.518969
C	-3.272549	-1.635621	-0.684751
C	-1.840918	-2.875977	-2.173713
C	-4.083813	-2.758412	-0.532341
H	-3.517518	-0.728571	-0.136864
C	-2.662672	-3.991546	-2.029611

H	-0.961473	-2.960542	-2.812243
C	-3.795365	-3.948192	-1.206963
H	-4.950703	-2.70138	0.131436
H	-2.414271	-4.910066	-2.569093
H	-4.435612	-4.825543	-1.091674
C	-1.890742	0.897856	-1.464493
C	-3.330071	1.228545	-1.832273
C	-2.187977	1.824853	-2.613316
H	-1.607219	1.435584	-0.553441
H	-3.886321	0.436048	-2.337444
H	-2.039109	1.437715	-3.62496
H	-1.971611	2.890127	-2.504001
C	-4.121137	1.993253	-0.830114
C	-5.340835	1.475932	-0.364227
C	-3.643732	3.182152	-0.251209
C	-6.050406	2.110804	0.657655
H	-5.728398	0.5533	-0.803601
C	-4.352126	3.819711	0.768698
H	-2.702985	3.616577	-0.596127
C	-5.557006	3.284289	1.234345
H	-6.995002	1.684981	1.005673
H	-3.960642	4.74411	1.201854
H	-6.110866	3.782866	2.033325
Si	1.897613	-1.482222	-2.102739
H	2.291297	-0.939523	-3.440895
H	1.587199	-2.933894	-2.276385
C	3.534582	-1.406234	-1.143621
C	4.282929	-0.217526	-1.065325
C	4.101354	-2.577175	-0.605553
C	5.546293	-0.200127	-0.471198
H	3.882595	0.711066	-1.475787
C	5.361062	-2.56253	-0.001649
H	3.564856	-3.524386	-0.689557
C	6.087482	-1.370289	0.067445
H	6.103633	0.737216	-0.424154
H	5.781135	-3.486275	0.404897
H	7.074196	-1.354701	0.536986
H	0.412627	-4.346278	-0.644581

Int4(doublet)

C	2.61077	-3.352582	-0.185185
C	3.107132	-4.564973	-0.61931
C	2.18616	-5.478205	-1.203178
C	0.844756	-5.1395	-1.308012
C	0.393533	-3.879668	-0.848473
N	1.303035	-3.008972	-0.305485
H	2.535467	-6.448318	-1.560669
H	4.164341	-4.805235	-0.50471
H	0.134229	-5.842065	-1.746795
C	3.322635	-2.280844	0.499921
O	4.616052	-2.357827	0.810488
C	3.597702	-0.408793	1.692485
C	4.962447	-1.075424	1.40154

H	5.565209	-1.266197	2.299477
N	2.673893	-1.218027	0.873095
H	5.561936	-0.519101	0.664342
C	3.179871	-0.44231	3.158465
H	3.850988	0.187147	3.762624
H	2.158857	-0.054744	3.269727
H	3.212523	-1.472952	3.547593
C	-0.933876	-3.361325	-0.827289
C	-2.094011	-4.242115	-1.193945
H	-2.180429	-4.361719	-2.286272
H	-1.968743	-5.24813	-0.765624
H	-3.039488	-3.826853	-0.825835
N	-1.048025	-2.094018	-0.3903
C	-2.340799	-1.543732	-0.16376
C	-2.75645	-1.393302	1.186884
C	-3.159122	-1.084852	-1.224628
C	-3.974601	-0.756804	1.447553
C	-4.368003	-0.450153	-0.906554
C	-4.775662	-0.279062	0.410929
H	-4.304479	-0.619123	2.477353
H	-4.998709	-0.066377	-1.710659
H	-5.708563	0.241277	0.631408
C	-2.790772	-1.252191	-2.696679
C	-2.733879	0.081036	-3.463436
C	-3.786666	-2.18476	-3.412429
H	-1.789722	-1.706189	-2.743671
H	-2.000062	0.778566	-3.041292
H	-2.461917	-0.097239	-4.51589
H	-3.711335	0.588031	-3.455083
H	-3.921013	-3.137838	-2.885187
H	-4.777492	-1.70843	-3.485786
H	-3.447307	-2.402717	-4.438129
C	-1.889679	-1.927015	2.322604
C	-1.952346	-3.461031	2.419432
C	-2.208588	-1.317707	3.691693
H	-0.843452	-1.666472	2.073719
H	-1.600555	-3.945878	1.500758
H	-1.320146	-3.820065	3.247651
H	-2.985519	-3.793994	2.610174
H	-2.250775	-0.219687	3.663078
H	-3.174893	-1.678914	4.079353
H	-1.435113	-1.606597	4.419751
Fe	0.736627	-1.227965	0.170224
C	1.561238	1.047919	-1.021766
C	1.359625	1.080773	-2.504188
C	1.816582	2.344898	-1.817193
H	2.521776	0.608874	-0.734974
H	0.337097	1.080948	-2.887848
H	2.070181	0.550984	-3.144929
H	1.06406	3.129425	-1.715609
C	3.205508	2.858953	-1.891116
C	3.469365	4.199975	-1.560491
C	4.299677	2.032152	-2.208007

C	4.773779	4.696959	-1.54302
H	2.633222	4.856532	-1.306044
C	5.604984	2.527746	-2.190078
H	4.130786	0.986688	-2.477319
C	5.851008	3.862966	-1.856086
H	4.949927	5.743642	-1.281826
H	6.437168	1.866193	-2.445566
H	6.872432	4.250468	-1.843883
C	0.774075	1.491351	1.323016
C	-0.101462	1.301676	2.414526
C	1.871498	2.350207	1.536735
C	0.117965	1.901482	3.652822
H	-0.974475	0.66556	2.278818
C	2.09734	2.952804	2.778717
H	2.550649	2.574395	0.714718
C	1.228699	2.731071	3.849012
H	-0.581568	1.717213	4.472921
H	2.958768	3.615085	2.902301
H	1.406	3.204072	4.817686
C	-0.93077	1.19464	-0.459921
H	-1.663622	0.84475	0.277211
H	-1.179845	0.635339	-1.365991
C	0.478144	0.828685	0.010172
Si	-1.445417	3.005577	-0.729332
H	-1.312392	3.424397	-2.160352
H	-0.645364	3.94499	0.109022
C	-3.264513	3.145657	-0.25414
C	-4.287919	3.184225	-1.216673
C	-3.635385	3.116252	1.103234
C	-5.634509	3.196117	-0.840888
H	-4.030233	3.203413	-2.279726
C	-4.978181	3.133252	1.485548
H	-2.860609	3.074823	1.875426
C	-5.982026	3.173286	0.512506
H	-6.415058	3.226886	-1.605763
H	-5.24451	3.112856	2.545628
H	-7.033954	3.186352	0.80948
H	3.586879	0.628271	1.336877

Int4(quartet)

C	2.259039	-3.042282	-1.274303
C	2.635186	-4.123903	-2.048301
C	1.602207	-4.880772	-2.66253
C	0.27446	-4.575143	-2.398275
C	-0.047369	-3.472008	-1.571817
N	0.966938	-2.660977	-1.127827
H	1.853215	-5.733366	-3.296064
H	3.686198	-4.397457	-2.14496
H	-0.521551	-5.199154	-2.808341
C	3.135312	-2.252013	-0.408313
O	4.468617	-2.367879	-0.46152
C	3.747971	-0.847057	1.219367
C	5.000162	-1.508707	0.579784

H	5.565383	-2.138457	1.284169
N	2.634591	-1.444939	0.469174
H	5.677991	-0.782013	0.110626
C	3.593189	-1.076703	2.717187
H	4.434035	-0.625753	3.267786
H	2.663486	-0.610489	3.073777
H	3.560307	-2.154139	2.945048
C	-1.332635	-3.143187	-1.024549
C	-2.512822	-4.046295	-1.247455
H	-2.98906	-3.889974	-2.228912
H	-2.206756	-5.102086	-1.196663
H	-3.274462	-3.87667	-0.4762
N	-1.336558	-2.095962	-0.19582
C	-2.431972	-1.653121	0.571902
C	-2.229845	-1.624233	1.985316
C	-3.620998	-1.120288	0.007541
C	-3.21754	-1.06685	2.798652
C	-4.570487	-0.553807	0.872436
C	-4.381325	-0.523668	2.249328
H	-3.076004	-1.038988	3.879033
H	-5.477252	-0.117799	0.449038
H	-5.137358	-0.075593	2.898414
C	-3.930008	-1.137667	-1.487144
C	-4.13917	0.264794	-2.076413
C	-5.173064	-1.9985	-1.781249
H	-3.068879	-1.578396	-2.006936
H	-3.247641	0.888697	-1.967901
H	-4.3743	0.193484	-3.150522
H	-4.969372	0.797347	-1.588904
H	-5.108119	-2.999143	-1.332862
H	-6.079949	-1.517125	-1.381726
H	-5.314469	-2.116029	-2.867911
C	-0.94632	-2.195689	2.579204
C	-0.878471	-3.725002	2.435911
C	-0.679893	-1.792567	4.03067
H	-0.09833	-1.779169	1.995557
H	-0.975861	-4.046306	1.391571
H	0.082276	-4.106147	2.817587
H	-1.687237	-4.19484	3.018659
H	-0.685034	-0.70216	4.158604
H	-1.422089	-2.232406	4.716345
H	0.309797	-2.16232	4.340872
Fe	0.484022	-1.032403	-0.021318
C	1.791842	1.273977	-1.165821
C	1.892819	1.792086	-2.565003
C	2.405594	2.659348	-1.439408
H	2.59299	0.570368	-0.922695
H	0.983012	2.134603	-3.062924
H	2.621722	1.338777	-3.242655
H	1.77974	3.513832	-1.168549
C	3.848246	2.838286	-1.145659
C	4.276623	3.932028	-0.372795
C	4.815548	1.892401	-1.537816

C	5.614373	4.074662	0.0003
H	3.540502	4.673658	-0.052087
C	6.153975	2.033542	-1.164404
H	4.522269	1.033307	-2.145936
C	6.562113	3.124022	-0.390169
H	5.918461	4.934408	0.602885
H	6.886142	1.289329	-1.489879
H	7.609355	3.234859	-0.099482
C	0.534582	1.427991	1.021269
C	-0.640891	1.352021	1.814302
C	1.703856	1.888881	1.676947
C	-0.643071	1.702075	3.16271
H	-1.57172	1.002044	1.370645
C	1.70033	2.224152	3.030778
H	2.621755	2.01827	1.106797
C	0.529294	2.135777	3.790877
H	-1.577116	1.630921	3.726114
H	2.625389	2.579925	3.493137
H	0.527842	2.410552	4.847932
C	-0.79026	1.386142	-1.136233
H	-1.643346	0.880208	-0.662902
H	-0.774122	1.003128	-2.168405
C	0.510872	1.027658	-0.408394
Si	-1.262117	3.242902	-1.166367
H	-0.915669	3.866827	-2.482005
H	-0.524305	3.97763	-0.099935
C	-3.120018	3.437096	-0.907031
C	-3.70552	3.054518	0.31479
C	-3.97228	3.868664	-1.938819
C	-5.089218	3.093215	0.496526
H	-3.073463	2.711295	1.137844
C	-5.358576	3.909031	-1.763184
H	-3.5476	4.171038	-2.900435
C	-5.920515	3.518443	-0.544494
H	-5.519915	2.785236	1.452604
H	-6.002668	4.244103	-2.58036
H	-7.004366	3.54613	-0.405834
H	3.755544	0.235952	1.026516

TS5(doublet)

Fe	-0.935639	0.824737	-0.170277
C	-2.997496	4.434415	0.333616
C	-4.215294	4.017409	0.92727
C	-4.469853	2.665679	1.092336
C	-3.511169	1.701723	0.692424
C	0.657308	2.727826	-3.42356
H	-4.954446	4.758011	1.237851
H	-2.770741	5.484514	0.149538
H	-5.412481	2.334309	1.530579
C	-0.839243	3.653921	-0.743459
O	-0.432083	4.871368	-1.128259
C	0.940641	3.149352	-1.984683
C	0.862512	4.676803	-1.749786

H	0.893817	5.271046	-2.673073
N	-0.114509	2.639142	-1.090052
H	1.631567	5.043936	-1.051221
H	1.466099	3.062288	-4.091346
N	-2.312898	2.127192	0.164963
H	0.588569	1.634741	-3.492873
H	-0.293024	3.165159	-3.770406
C	-3.644797	0.286637	0.69983
C	-4.960435	-0.344164	1.065586
H	-5.143248	-0.309267	2.152552
H	-5.795275	0.185889	0.580521
H	-5.000851	-1.394467	0.753967
N	-2.5635	-0.393296	0.26141
C	-2.6561	-1.798983	0.101853
C	-2.70946	-2.317932	-1.220036
C	-2.642086	-2.673428	1.216341
C	-2.720227	-3.705596	-1.396746
C	-2.647476	-4.056199	0.984854
C	-2.681487	-4.574917	-0.305324
H	-2.758494	-4.122064	-2.403514
H	-2.623256	-4.740185	1.836337
H	-2.682295	-5.655731	-0.464504
C	-2.609383	-2.1724	2.657605
C	-1.326046	-2.587506	3.395838
C	-3.833561	-2.655392	3.454792
H	-2.633042	-1.073858	2.631193
H	-0.423167	-2.232554	2.883668
H	-1.317796	-2.174942	4.417344
H	-1.247862	-3.683266	3.476881
H	-4.7776	-2.415058	2.947621
H	-3.804377	-3.747223	3.599634
H	-3.851726	-2.191007	4.454068
C	-2.754059	-1.369677	-2.413252
C	-4.112115	-0.656776	-2.536498
C	-2.412307	-2.033184	-3.751402
H	-1.992961	-0.594847	-2.212397
H	-4.348467	-0.064245	-1.64498
H	-4.108978	0.027077	-3.400807
H	-4.920029	-1.391232	-2.688144
H	-1.482159	-2.618206	-3.708982
H	-3.216459	-2.710716	-4.08158
H	-2.290723	-1.264777	-4.530249
C	0.728588	-0.543133	-0.322772
C	1.09293	0.412117	0.690373
C	-0.128953	1.079552	1.888859
C	1.121361	0.270389	2.171327
H	1.635023	1.296052	0.355761
H	-1.0535	0.623641	2.254614
H	-0.049359	2.154029	2.078025
H	0.89796	-0.740006	2.522715
C	2.279161	0.859994	2.914105
C	2.986	0.077682	3.839784
C	2.716216	2.174345	2.682921

C	4.102929	0.586418	4.507413
H	2.659837	-0.948125	4.028179
C	3.831402	2.685935	3.348612
H	2.180075	2.808829	1.972427
C	4.532574	1.893036	4.262539
H	4.640681	-0.043	5.220774
H	4.155935	3.711256	3.153399
H	5.406543	2.292883	4.782033
C	1.409433	-0.407455	-1.643201
C	0.91082	-1.099276	-2.765992
C	2.596604	0.328756	-1.834179
C	1.5369	-1.037594	-4.010328
H	0.010927	-1.699567	-2.65304
C	3.225376	0.397867	-3.077016
H	3.077915	0.807155	-0.981444
C	2.700159	-0.279902	-4.180115
H	1.109532	-1.585934	-4.854266
H	4.156604	0.961737	-3.173122
H	3.19763	-0.232934	-5.151531
C	0.482072	-1.984633	0.108483
H	0.006836	-2.557195	-0.698396
H	-0.244182	-2.026394	0.925712
C	-2.093809	3.451918	-0.032795
H	1.915212	2.750323	-1.676413
Si	2.019554	-2.948338	0.688504
H	2.151803	-2.842016	2.17541
H	1.865964	-4.397726	0.351297
C	3.612557	-2.294275	-0.067184
C	4.032056	-2.7018	-1.345898
C	4.374031	-1.319015	0.601538
C	5.167041	-2.15017	-1.94139
H	3.453518	-3.449062	-1.896257
C	5.510733	-0.762054	0.008692
H	4.075675	-0.978296	1.595614
C	5.908474	-1.176606	-1.264962
H	5.468349	-2.471668	-2.941256
H	6.08524	-0.002669	0.545614
H	6.795937	-0.741511	-1.732019

TS5(quartet)

Fe	-1.04968	-0.38487	-0.456233
C	-4.603425	-1.805055	-2.218942
C	-4.639034	-3.16321	-1.804142
C	-3.566236	-3.702797	-1.118339
C	-2.436342	-2.898197	-0.800414
C	-1.034401	2.083546	-3.867538
H	-5.50391	-3.784692	-2.044361
H	-5.397164	-1.355975	-2.815006
H	-3.581254	-4.751772	-0.819126
C	-3.208492	0.309277	-2.27801
O	-4.087109	1.003328	-3.016984
C	-2.042295	2.154781	-2.723988
C	-3.511242	2.321332	-3.189452

H	-3.611359	2.605515	-4.246026
N	-2.081368	0.873949	-1.999336
H	-4.085094	3.025646	-2.566102
H	-0.962433	3.053967	-4.382942
N	-2.466941	-1.56224	-1.131682
H	-0.040082	1.824224	-3.48292
H	-1.33947	1.317076	-4.598181
C	-1.214365	-3.331279	-0.214125
C	-1.008576	-4.795112	0.07622
H	-1.610111	-5.127634	0.938871
H	-1.309453	-5.414629	-0.783351
H	0.042841	-5.011516	0.300651
N	-0.274632	-2.390116	0.001659
C	0.966717	-2.72919	0.573229
C	2.126548	-2.706164	-0.25068
C	1.088112	-2.998763	1.961368
C	3.381055	-2.894579	0.339047
C	2.367425	-3.172706	2.505579
C	3.509892	-3.11169	1.711914
H	4.278209	-2.869724	-0.280288
H	2.470668	-3.35942	3.577374
H	4.498405	-3.244651	2.15764
C	-0.124125	-3.109526	2.880503
C	-0.145867	-2.029842	3.973432
C	-0.207882	-4.503803	3.525446
H	-1.024366	-2.968354	2.266675
H	-0.179488	-1.019521	3.545286
H	-1.032336	-2.147908	4.616991
H	0.746744	-2.088424	4.616309
H	-0.164825	-5.304054	2.773484
H	0.625038	-4.66576	4.228295
H	-1.14621	-4.61435	4.092936
C	1.984341	-2.490905	-1.751381
C	1.439444	-3.746164	-2.454111
C	3.275543	-2.034368	-2.440697
H	1.224984	-1.701131	-1.88046
H	0.453889	-4.032227	-2.067293
H	1.335287	-3.567723	-3.536811
H	2.125921	-4.597039	-2.313483
H	3.749351	-1.182993	-1.92964
H	4.016945	-2.848308	-2.487275
H	3.06093	-1.730608	-3.477152
C	0.358337	0.939085	0.315287
C	-0.91099	1.413187	0.794197
C	-2.169042	0.16162	1.303678
C	-1.539403	1.259812	2.137444
H	-1.429439	2.14688	0.176717
H	-1.959427	-0.853554	1.662171
H	-3.210681	0.321424	1.010109
H	-0.856743	0.892077	2.910377
C	-2.375866	2.394633	2.642618
C	-2.103492	2.964108	3.895015
C	-3.424867	2.935341	1.880366

C	-2.853932	4.040351	4.37459
H	-1.289345	2.556432	4.500103
C	-4.176132	4.011452	2.356128
H	-3.662575	2.509196	0.902351
C	-3.894124	4.56958	3.606556
H	-2.624009	4.467481	5.353896
H	-4.989693	4.415333	1.74807
H	-4.482761	5.410802	3.979993
C	0.993761	1.747159	-0.771071
C	1.95088	1.156233	-1.615821
C	0.746796	3.122923	-0.942011
C	2.616158	1.887593	-2.595784
H	2.182326	0.10427	-1.481743
C	1.404411	3.861137	-1.930841
H	0.056706	3.634472	-0.267899
C	2.341618	3.248765	-2.765029
H	3.363967	1.394327	-3.220568
H	1.196106	4.929508	-2.033454
H	2.86604	3.828608	-3.527918
C	1.344964	0.341506	1.307308
H	1.980431	-0.407543	0.815167
H	0.823727	-0.217888	2.091108
C	-3.488964	-1.063058	-1.856824
H	-1.749589	2.959977	-2.03438
Si	2.548361	1.585613	2.081754
H	1.887856	2.896471	2.362144
H	3.069295	1.033743	3.3721
C	3.972513	1.843312	0.876775
C	4.723442	0.727881	0.457273
C	4.253172	3.088119	0.292078
C	5.714354	0.852047	-0.517809
H	4.519807	-0.25905	0.883317
C	5.244332	3.217661	-0.684809
H	3.670629	3.966348	0.581726
C	5.975492	2.100182	-1.093538
H	6.28249	-0.027114	-0.833248
H	5.437313	4.193346	-1.137784
H	6.746704	2.199429	-1.861751

Int6(doublet)

C	4.763673	0.127391	-0.449149
C	5.927788	-0.360074	-1.021142
C	5.998975	-1.75987	-1.24601
C	4.932741	-2.586903	-0.913446
C	3.757578	-2.030431	-0.352338
N	3.726147	-0.678829	-0.125593
H	6.900197	-2.189834	-1.687541
H	6.748438	0.310056	-1.276839
H	4.992939	-3.661546	-1.094188
C	4.417391	1.491587	-0.070478
O	5.22957	2.540347	-0.222323
C	3.217657	3.116702	0.898987
C	4.458607	3.703479	0.181309

H	5.093595	4.326001	0.826332
N	3.260469	1.708741	0.482572
H	4.193061	4.257147	-0.731265
C	3.254256	3.227214	2.420884
H	3.198868	4.281164	2.736789
H	2.401816	2.686736	2.856718
H	4.182126	2.788512	2.821324
C	2.538472	-2.669444	0.026851
C	2.412738	-4.165192	-0.00492
H	2.335425	-4.548759	-1.036415
H	3.298687	-4.637825	0.448604
H	1.523899	-4.503315	0.542016
N	1.560918	-1.829342	0.439096
C	0.293414	-2.334081	0.827915
C	-0.061842	-2.262178	2.199547
C	-0.614554	-2.861536	-0.123293
C	-1.307245	-2.75711	2.599115
C	-1.85417	-3.33844	0.325561
C	-2.196553	-3.302402	1.673696
H	-1.589085	-2.717291	3.652237
H	-2.572139	-3.735399	-0.394766
H	-3.165617	-3.684583	1.999379
C	-0.298672	-2.915476	-1.613351
C	-1.198304	-1.961235	-2.412773
C	-0.416387	-4.339905	-2.179998
H	0.740475	-2.584436	-1.750594
H	-1.125698	-0.932719	-2.035434
H	-0.911944	-1.951929	-3.476901
H	-2.252271	-2.267543	-2.346257
H	0.184413	-5.059926	-1.606452
H	-1.46108	-4.688998	-2.160078
H	-0.079533	-4.368339	-3.228996
C	0.925198	-1.694884	3.207156
C	1.966528	-2.747437	3.618185
C	0.262917	-1.064023	4.434179
H	1.465025	-0.888902	2.681693
H	2.501084	-3.144254	2.743565
H	2.71428	-2.312691	4.301998
H	1.483505	-3.593394	4.134619
H	-0.499835	-0.326603	4.141168
H	-0.218601	-1.816872	5.079391
H	1.018537	-0.548727	5.048124
Fe	2.079212	0.084671	0.517222
C	-1.39134	2.488738	-0.101787
C	-0.376009	1.408611	-0.342736
H	-1.003712	3.391467	0.382417
H	-0.887806	0.50802	-0.708196
C	-3.595675	3.563966	0.073405
C	-4.633956	4.042163	-0.747072
C	-3.408926	4.184154	1.323391
C	-5.438291	5.109855	-0.345332
H	-4.801486	3.58748	-1.72585
C	-4.212938	5.250619	1.727764

H	-2.636053	3.800474	1.992462
C	-5.231916	5.720857	0.894544
H	-6.230626	5.468763	-1.00722
H	-4.052023	5.708157	2.707373
H	-5.866191	6.551827	1.212528
C	-3.382173	1.248925	-1.003653
H	-4.298844	1.53718	-1.538961
H	-2.723018	0.758454	-1.734796
C	-2.715771	2.443867	-0.360278
C	0.666495	1.76688	-1.398339
C	1.372138	0.728885	-2.038612
C	1.03167	3.087236	-1.69866
C	2.441616	0.998285	-2.896202
H	1.075694	-0.305492	-1.861664
C	2.101604	3.360672	-2.557207
H	0.47276	3.9136	-1.256175
C	2.824171	2.317961	-3.146161
H	2.980641	0.170974	-3.363612
H	2.368008	4.398914	-2.77435
H	3.665118	2.533752	-3.809243
C	0.334735	0.997947	0.980021
H	0.557646	1.91851	1.556575
H	-0.379799	0.412102	1.58185
H	2.295619	3.57304	0.514423
Si	-3.851133	-0.001676	0.345359
H	-4.737259	0.663565	1.346242
H	-2.618317	-0.444798	1.045946
C	-4.753456	-1.491827	-0.380091
C	-4.814687	-1.715883	-1.76606
C	-5.342934	-2.448943	0.466411
C	-5.41654	-2.864972	-2.28943
H	-4.380654	-0.98738	-2.455408
C	-5.94568	-3.598486	-0.047618
H	-5.324395	-2.298083	1.549745
C	-5.97671	-3.812865	-1.429894
H	-5.446377	-3.0204	-3.370925
H	-6.392055	-4.331192	0.629642
H	-6.444169	-4.713804	-1.8351

Int6(quartet)

C	4.868076	-0.147751	-0.461581
C	5.971479	-0.731114	-1.044988
C	5.933953	-2.14842	-1.230572
C	4.817681	-2.878065	-0.860238
C	3.69244	-2.220198	-0.293439
N	3.782637	-0.863077	-0.08555
H	6.791303	-2.654995	-1.677656
H	6.831243	-0.132392	-1.345823
H	4.790293	-3.957805	-1.020569
C	4.636017	1.263675	-0.139958
O	5.509652	2.232893	-0.403842
C	3.586098	3.043793	0.73219
C	4.848261	3.481008	-0.053556

H	5.5534	4.084304	0.534356
N	3.5252	1.60676	0.439579
H	4.604699	3.997969	-0.993172
C	3.65793	3.28149	2.237279
H	3.665823	4.359424	2.46418
H	2.785277	2.826207	2.727357
H	4.567458	2.826274	2.661027
C	2.43202	-2.741936	0.08902
C	2.154337	-4.21821	0.079722
H	2.003892	-4.608409	-0.940578
H	2.997351	-4.775155	0.51817
H	1.251821	-4.452701	0.658869
N	1.537252	-1.805495	0.500145
C	0.218386	-2.149157	0.885328
C	-0.135585	-1.979472	2.250644
C	-0.748523	-2.573175	-0.05989
C	-1.451834	-2.233254	2.642999
C	-2.058991	-2.81016	0.382898
C	-2.411817	-2.644996	1.718026
H	-1.738755	-2.107084	3.68789
H	-2.819442	-3.128353	-0.331849
H	-3.437386	-2.834796	2.036873
C	-0.4263	-2.797375	-1.534215
C	-1.191974	-1.834259	-2.454169
C	-0.718619	-4.247797	-1.95764
H	0.647018	-2.610824	-1.679672
H	-0.960834	-0.784564	-2.232415
H	-0.929522	-2.017226	-3.508786
H	-2.277717	-1.972633	-2.348503
H	-0.232709	-4.976355	-1.293936
H	-1.801007	-4.451145	-1.937166
H	-0.366977	-4.429874	-2.986216
C	0.925536	-1.573113	3.262585
C	1.769196	-2.785358	3.68799
C	0.3727	-0.831367	4.481245
H	1.603002	-0.872814	2.744972
H	2.240428	-3.269173	2.820795
H	2.569389	-2.481948	4.382915
H	1.141247	-3.535407	4.196232
H	-0.255546	0.020548	4.180167
H	-0.230141	-1.489077	5.128364
H	1.201536	-0.445829	5.0959
Fe	2.224279	0.052111	0.598754
C	-1.296406	2.401507	-0.062404
C	-0.232486	1.361328	-0.269292
H	-0.926629	3.345318	0.352556
H	-0.700256	0.404508	-0.540856
C	-3.505167	3.461804	0.083525
C	-4.597118	3.829306	-0.724704
C	-3.27465	4.212254	1.252324
C	-5.406887	4.917023	-0.394777
H	-4.810583	3.265788	-1.634869
C	-4.0839	5.29915	1.585114

H	-2.461706	3.916937	1.918703
C	-5.153903	5.660015	0.761405
H	-6.242432	5.185502	-1.046224
H	-3.886316	5.859434	2.502666
H	-5.792196	6.507156	1.023774
C	-3.300785	1.09191	-0.854346
H	-3.830486	1.347262	-1.78941
H	-2.562428	0.326582	-1.124443
C	-2.626307	2.313074	-0.276274
C	0.753955	1.708879	-1.381798
C	1.461839	0.673298	-2.021611
C	1.085598	3.029452	-1.717132
C	2.494822	0.944511	-2.921318
H	1.210017	-0.363736	-1.797578
C	2.117324	3.306648	-2.621312
H	0.533368	3.855186	-1.265228
C	2.837462	2.266876	-3.217013
H	3.036485	0.117421	-3.386157
H	2.356457	4.345622	-2.865186
H	3.647181	2.484984	-3.917439
C	0.568285	1.119517	1.0414
H	0.855446	2.109	1.449216
H	-0.110852	0.655606	1.777057
H	2.687666	3.523474	0.320129
Si	-4.566126	0.281103	0.305424
H	-5.757505	1.164152	0.47596
H	-3.973427	0.048234	1.651623
C	-5.109853	-1.374277	-0.422452
C	-4.940039	-1.666924	-1.787144
C	-5.663167	-2.374576	0.397747
C	-5.283537	-2.917356	-2.310095
H	-4.518533	-0.914768	-2.458496
C	-6.008069	-3.626441	-0.116219
H	-5.814078	-2.179339	1.463733
C	-5.811344	-3.9036	-1.472951
H	-5.131757	-3.123801	-3.372584
H	-6.425438	-4.391338	0.543538
H	-6.072278	-4.885126	-1.87635

TS7(doublet)

C	-0.739871	-2.764047	0.730625
C	-0.901043	-3.638069	1.791282
C	-1.763682	-3.262421	2.845642
C	-2.411705	-2.04008	2.785879
C	-2.172696	-1.157177	1.710802
N	-1.335439	-1.540116	0.682739
H	-1.935391	-3.938532	3.684657
H	-0.394991	-4.602988	1.772811
H	-3.106172	-1.747202	3.573271
C	-0.011546	-3.10844	-0.489362
O	0.490453	-4.350586	-0.639001
C	0.640979	-3.076743	-2.613801
C	1.195814	-4.332917	-1.905717

H	2.273727	-4.247086	-1.692553
N	0.094479	-2.304617	-1.487139
H	0.98926	-5.276373	-2.426695
C	1.641887	-2.316962	-3.466424
H	1.96258	-2.932958	-4.321354
H	1.180095	-1.400284	-3.861036
H	2.530729	-2.044284	-2.882488
C	-2.711268	0.162721	1.579599
C	-3.778458	0.64197	2.523668
H	-4.678364	0.014679	2.411373
H	-3.464894	0.57297	3.576314
H	-4.056962	1.681685	2.31662
N	-2.252696	0.875492	0.543427
C	-2.495716	2.278748	0.471177
C	-1.848914	3.166862	1.375974
C	-3.335945	2.808271	-0.54116
C	-2.042401	4.54739	1.224084
C	-3.485615	4.194653	-0.658023
C	-2.84175	5.069589	0.212569
H	-1.543757	5.229853	1.91506
H	-4.134648	4.593737	-1.440092
H	-2.969374	6.149643	0.109664
C	-4.150681	1.899673	-1.439707
C	-4.052625	2.265347	-2.923354
C	-5.612654	1.853056	-0.970137
H	-3.733142	0.89541	-1.323854
H	-3.004778	2.285414	-3.258781
H	-4.588059	1.523023	-3.534355
H	-4.495263	3.251701	-3.135939
H	-5.681768	1.550877	0.08637
H	-6.092629	2.840999	-1.064633
H	-6.192794	1.134618	-1.571415
C	-0.952386	2.704434	2.518814
C	-1.592067	2.972423	3.892664
C	0.428096	3.375396	2.469876
H	-0.810295	1.618914	2.419087
H	-2.592587	2.531784	3.980637
H	-0.962493	2.560048	4.697785
H	-1.690997	4.055433	4.069754
H	0.912776	3.257695	1.493258
H	0.35502	4.455997	2.66628
H	1.088502	2.952634	3.242858
Fe	-1.183563	-0.322672	-0.835307
C	1.710052	0.391251	-0.896929
C	0.799727	1.589883	-0.958938
H	1.947665	-0.051771	-1.866416
H	0.373509	1.770775	0.038657
C	3.049774	-1.433639	0.052145
C	2.871956	-2.553834	0.882522
C	4.067813	-1.485412	-0.915611
C	3.667866	-3.691099	0.737695
H	2.082866	-2.548212	1.636245
C	4.874421	-2.614312	-1.053305

H	4.255966	-0.607497	-1.534064
C	4.67601	-3.726657	-0.229805
H	3.495308	-4.556216	1.38232
H	5.675044	-2.617615	-1.796429
H	5.310186	-4.610286	-0.333463
C	1.984447	0.281648	1.6048
H	1.027965	0.80844	1.713094
H	1.977704	-0.543486	2.331625
C	2.193704	-0.224746	0.202034
C	1.504607	2.882384	-1.355525
C	0.818091	4.100813	-1.222487
C	2.818551	2.905057	-1.840767
C	1.431934	5.307176	-1.559654
H	-0.203933	4.102842	-0.837507
C	3.433951	4.113004	-2.185234
H	3.375115	1.970863	-1.931174
C	2.744215	5.319029	-2.044833
H	0.882727	6.244393	-1.438639
H	4.460949	4.109779	-2.560036
H	3.226256	6.263535	-2.308514
C	-0.389746	1.282158	-1.918299
H	-1.050439	2.157355	-1.977794
H	0.014923	1.104497	-2.928909
H	-0.223262	-3.348603	-3.248815
Si	3.412793	1.461564	2.06552
H	3.419332	1.663555	3.547334
H	3.238355	2.767684	1.380345
C	5.041165	0.730571	1.478007
C	5.712171	1.303241	0.383243
C	5.567154	-0.448829	2.035725
C	6.866697	0.714555	-0.141837
H	5.320256	2.216162	-0.073685
C	6.716409	-1.042569	1.513443
H	5.061506	-0.925965	2.880242
C	7.368162	-0.46111	0.42109
H	7.373872	1.173441	-0.994571
H	7.100448	-1.966688	1.951803
H	8.266337	-0.927454	0.008324
Si	-2.854525	-1.411557	-2.116464
H	-3.833979	-0.64464	-2.950235
H	-2.256353	-2.415601	-3.05744
H	-1.577975	0.201408	-2.19995
C	-3.898851	-2.391729	-0.877312
C	-4.937974	-1.769028	-0.160567
C	-3.574253	-3.717491	-0.533569
C	-5.625334	-2.439341	0.854201
H	-5.217515	-0.741566	-0.398669
C	-4.252746	-4.390952	0.484435
H	-2.770344	-4.233567	-1.06619
C	-5.279979	-3.752644	1.185647
H	-6.434467	-1.934204	1.389372
H	-3.975567	-5.418205	0.7357
H	-5.811431	-4.278129	1.983139

TS7(quartet)

C	-0.563588	-2.672749	0.766216
C	-0.637816	-3.548266	1.835124
C	-1.465867	-3.192243	2.925359
C	-2.180503	-2.009718	2.875809
C	-2.028163	-1.129535	1.776505
N	-1.187921	-1.473045	0.746009
H	-1.570414	-3.86438	3.778731
H	-0.106135	-4.49864	1.795758
H	-2.865047	-1.746914	3.682175
C	0.074716	-2.993753	-0.507615
O	0.661865	-4.189512	-0.689913
C	0.549661	-2.925234	-2.677114
C	1.251872	-4.133283	-2.012671
H	2.334668	-3.969184	-1.890842
N	0.006719	-2.199074	-1.51549
H	1.07161	-5.094351	-2.510911
C	1.443959	-2.087101	-3.575559
H	1.740412	-2.665485	-4.464767
H	0.907595	-1.189159	-3.91377
H	2.355672	-1.77844	-3.046048
C	-2.677651	0.133068	1.629751
C	-3.734713	0.564849	2.607428
H	-4.588927	-0.13105	2.557959
H	-3.372884	0.561841	3.646529
H	-4.101882	1.571676	2.375645
N	-2.341035	0.838595	0.538346
C	-2.614749	2.229865	0.454973
C	-1.990621	3.14609	1.349869
C	-3.452933	2.72474	-0.578385
C	-2.21223	4.518798	1.171465
C	-3.632561	4.105101	-0.717861
C	-3.01558	5.006884	0.145574
H	-1.730588	5.22373	1.852145
H	-4.28005	4.478676	-1.513642
H	-3.164831	6.082167	0.02385
C	-4.22595	1.780048	-1.478196
C	-4.146929	2.145802	-2.962545
C	-5.680909	1.653823	-1.002747
H	-3.766499	0.7918	-1.365563
H	-3.101108	2.227523	-3.296019
H	-4.636162	1.36979	-3.570697
H	-4.6475	3.102647	-3.181348
H	-5.726697	1.349697	0.054555
H	-6.212668	2.615065	-1.095621
H	-6.223277	0.903568	-1.600473
C	-1.08318	2.723461	2.50114
C	-1.708778	3.050873	3.869056
C	0.302976	3.378457	2.414896
H	-0.943121	1.634916	2.444122
H	-2.721236	2.641868	3.975549
H	-1.086539	2.646733	4.683973

H	-1.776984	4.14094	4.014556
H	0.789108	3.197385	1.449673
H	0.240724	4.469717	2.545988
H	0.958089	2.993338	3.212076
Fe	-1.363053	-0.310559	-0.92949
C	1.738886	0.406393	-0.919527
C	0.792449	1.571868	-0.960034
H	2.001335	0.003919	-1.899419
H	0.340272	1.705519	0.032636
C	3.12393	-1.402142	-0.020175
C	3.014301	-2.537505	0.800868
C	4.108824	-1.410951	-1.024848
C	3.837228	-3.648609	0.610012
H	2.256673	-2.565524	1.585018
C	4.940716	-2.513937	-1.210447
H	4.250831	-0.518925	-1.635595
C	4.806468	-3.64311	-0.396252
H	3.715965	-4.525801	1.250027
H	5.712406	-2.4836	-1.983159
H	5.460757	-4.506638	-0.537415
C	1.977092	0.231023	1.578338
H	0.999346	0.720127	1.684036
H	1.983975	-0.614325	2.281523
C	2.228947	-0.22637	0.164722
C	1.472166	2.896037	-1.302916
C	0.741991	4.089847	-1.176468
C	2.801959	2.971992	-1.73729
C	1.327829	5.321723	-1.467566
H	-0.293855	4.053738	-0.832173
C	3.389783	4.205206	-2.037768
H	3.392348	2.058273	-1.821339
C	2.656401	5.385663	-1.90192
H	0.74349	6.238055	-1.350842
H	4.429618	4.241745	-2.373483
H	3.116503	6.350196	-2.129947
C	-0.359433	1.271168	-1.954228
H	-1.077106	2.104234	-1.965191
H	0.053317	1.186557	-2.971505
H	-0.32171	-3.263578	-3.267184
Si	3.356832	1.443662	2.096391
H	3.337804	1.601006	3.583945
H	3.152093	2.765788	1.451493
C	5.011703	0.777736	1.503601
C	5.680891	1.406667	0.439147
C	5.556117	-0.412496	2.018821
C	6.850857	0.86145	-0.098641
H	5.275317	2.329937	0.016423
C	6.721013	-0.963008	1.483928
H	5.052354	-0.933317	2.838221
C	7.370055	-0.326282	0.421238
H	7.35604	1.363695	-0.92781
H	7.119042	-1.896659	1.888287
H	8.279822	-0.75923	-0.002371

Si	-3.027625	-1.598035	-2.185877
H	-4.121818	-0.904372	-2.937166
H	-2.441425	-2.592305	-3.144238
H	-1.471263	0.052619	-2.430204
C	-3.852863	-2.593383	-0.805992
C	-4.853065	-2.01325	-0.000108
C	-3.379212	-3.867614	-0.438251
C	-5.36697	-2.681046	1.113347
H	-5.238692	-1.021473	-0.247647
C	-3.88337	-4.535582	0.679525
H	-2.598055	-4.34716	-1.035111
C	-4.879877	-3.944747	1.461512
H	-6.152181	-2.213069	1.713918
H	-3.493296	-5.521807	0.94474
H	-5.275683	-4.466896	2.336145

TS8(doublet)

N	0.700776	2.524675	-0.315183
C	4.641025	-2.878073	-0.961728
C	1.392573	5.197729	0.001617
C	2.329585	4.200955	0.234591
C	1.986345	2.84544	0.03797
H	1.733739	-2.570476	2.333492
H	1.656118	6.246018	0.150848
H	-0.647639	5.602585	-0.711117
H	3.337498	4.461425	0.561235
C	-1.406772	2.923916	-1.13766
O	-2.3928	3.68163	-1.633793
C	-3.233377	2.768581	-2.382932
H	-4.276717	3.090646	-2.277261
N	-1.546565	1.631884	-1.220741
H	-2.92903	2.821067	-3.441488
C	-3.907898	1.117301	-0.596311
H	-4.884367	0.814678	-1.000662
Fe	0.268952	0.67239	-0.633965
H	-4.047315	2.01864	0.018028
C	2.843335	1.70951	0.076771
C	4.307305	1.876808	0.369407
H	4.727992	2.712136	-0.211313
H	4.475503	2.106955	1.434332
H	4.873589	0.971324	0.125266
N	2.257429	0.541454	-0.246008
C	3.078995	-0.6074	-0.446287
C	3.555621	-1.387619	0.632873
C	3.404342	-0.951658	-1.785575
C	4.335113	-2.51726	0.346202
C	4.176892	-2.094513	-2.018505
C	0.10115	4.849473	-0.465756
H	4.701828	-3.131576	1.170931
H	4.428674	-2.372145	-3.043515
H	5.245136	-3.766714	-1.160363
C	2.971865	-0.062224	-2.943232
C	2.593316	-0.841587	-4.207027

C	4.048994	0.990046	-3.252591
H	2.073744	0.474928	-2.605791
H	1.855198	-1.6275	-3.987177
H	2.152873	-0.160964	-4.952893
H	3.467859	-1.316669	-4.680727
H	4.273706	1.607401	-2.371859
H	4.987638	0.508693	-3.573631
H	3.717214	1.663279	-4.060058
C	3.280071	-1.040076	2.089511
C	4.561343	-0.611124	2.82644
C	2.624405	-2.201007	2.849034
H	2.577327	-0.19539	2.095865
H	5.080073	0.216832	2.326859
H	4.324401	-0.295632	3.855622
H	5.269909	-1.452551	2.893117
C	-0.189566	3.506499	-0.606146
H	3.321111	-3.046154	2.966035
H	2.325323	-1.875087	3.857968
H	-3.55447	0.31139	0.054912
C	-2.925345	1.410128	-1.729887
C	-0.652139	-1.626758	-0.331583
H	1.01407	-1.519363	-1.773422
H	-0.56763	-0.9976	-2.422369
C	0.063973	-1.049896	-1.522695
C	-0.023207	-2.865525	0.298813
C	-0.563463	-3.451526	1.465472
C	1.07504	-3.524011	-0.281262
C	-0.052237	-4.63095	2.005834
H	-1.389577	-2.969186	1.983443
C	1.594098	-4.703199	0.258709
H	1.549663	-3.120197	-1.171572
C	1.032832	-5.270696	1.401957
H	-0.501652	-5.044914	2.911842
H	2.453713	-5.171938	-0.225346
H	1.43945	-6.19278	1.82401
C	-2.098136	-1.877699	-0.769133
C	-3.179872	-2.741878	-0.14228
C	-2.502127	-3.172815	-1.41809
H	-2.509953	-1.003092	-1.265688
H	-2.897965	-3.31135	0.743093
H	-1.804276	-4.009019	-1.332242
H	-3.05076	-3.140674	-2.362308
C	-4.576587	-2.221716	-0.097332
C	-5.12557	-1.839018	1.138793
C	-5.355744	-2.039696	-1.249937
C	-6.398694	-1.274083	1.218673
H	-4.532235	-1.973443	2.046646
C	-6.63291	-1.476763	-1.173662
H	-4.963987	-2.342687	-2.222703
C	-7.159217	-1.085515	0.059836
H	-6.80052	-0.978427	2.1911
H	-7.222182	-1.347831	-2.085374
H	-8.157242	-0.644973	0.119944

Si	-0.789002	-0.340872	1.485307
H	0.209485	-1.007475	2.35418
H	-2.162075	-0.808178	1.855011
C	-0.75997	1.441922	2.159061
C	-1.882996	2.286472	2.137951
C	0.427788	1.951963	2.717556
C	-1.816423	3.597994	2.615932
H	-2.830663	1.911899	1.750464
C	0.501644	3.258891	3.197633
H	1.318114	1.320015	2.757473
C	-0.619178	4.093664	3.138655
H	-2.704305	4.235316	2.58172
H	1.440421	3.632877	3.614367
H	-0.560269	5.121695	3.504316
H	-2.919658	0.597089	-2.468672

TS8(quartet)

N	0.785477	2.799953	-0.243944
C	4.848011	-2.579908	0.760264
C	1.336927	5.493583	0.329155
C	2.239346	4.500749	0.675804
C	1.969667	3.147405	0.376084
H	1.123171	-1.700812	3.13363
H	1.542982	6.539097	0.563439
H	-0.581935	5.871127	-0.674164
H	3.168513	4.761231	1.183957
C	-1.250031	3.298153	-1.317542
O	-2.071141	4.177199	-1.929921
C	-2.942779	3.382932	-2.761088
H	-3.966293	3.769774	-2.663567
N	-1.514449	2.045081	-1.437001
H	-2.609253	3.488896	-3.806484
C	-3.951066	1.517956	-1.343445
H	-4.86393	1.459168	-1.957814
Fe	0.479854	0.846734	-0.685147
H	-4.11708	2.239512	-0.530733
C	2.859242	2.057479	0.635187
C	4.228929	2.330475	1.19989
H	4.751256	3.09644	0.605805
H	4.169202	2.707512	2.233342
H	4.845084	1.424358	1.204533
N	2.419889	0.848349	0.293775
C	3.240934	-0.295166	0.484392
C	3.426296	-0.873058	1.766162
C	3.875987	-0.85774	-0.653817
C	4.236992	-2.012047	1.873138
C	4.663968	-2.001022	-0.493893
C	0.147965	5.129851	-0.349112
H	4.388221	-2.465247	2.855712
H	5.148404	-2.444267	-1.365
H	5.465896	-3.474497	0.867589
C	3.772883	-0.173855	-2.009144
C	3.770164	-1.150018	-3.189865

C	4.887816	0.872489	-2.174828
H	2.817846	0.369542	-2.017872
H	3.041435	-1.9589	-3.039965
H	3.513458	-0.61893	-4.120174
H	4.758925	-1.612215	-3.343768
H	4.85622	1.627291	-1.377202
H	5.880182	0.392898	-2.144855
H	4.790175	1.3965	-3.139731
C	2.812968	-0.297486	3.038842
C	3.894635	0.220151	4.004069
C	1.927336	-1.316497	3.774093
H	2.176555	0.551216	2.749933
H	4.573681	0.934554	3.520932
H	3.432978	0.718642	4.871839
H	4.50853	-0.610864	4.38707
C	-0.079091	3.791231	-0.604804
H	2.5176	-2.175123	4.132177
H	1.454439	-0.849588	4.652816
H	-3.787342	0.541448	-0.877216
C	-2.768129	1.944154	-2.209948
C	-0.364125	-1.332516	-1.175005
H	1.063021	-0.734264	-2.719246
H	-0.61727	-0.066661	-2.947719
C	0.13249	-0.428112	-2.236403
C	0.557009	-2.523937	-0.951405
C	1.086228	-2.920047	0.283422
C	0.90209	-3.30023	-2.076653
C	1.893972	-4.053151	0.402302
H	0.896024	-2.334054	1.176647
C	1.701728	-4.437791	-1.964001
H	0.547203	-2.991332	-3.060441
C	2.198373	-4.825871	-0.717366
H	2.299378	-4.31571	1.380737
H	1.94548	-5.016693	-2.858466
H	2.832975	-5.710298	-0.624163
C	-1.835372	-1.699897	-1.368374
C	-2.486962	-2.935233	-0.781064
C	-2.301188	-2.806727	-2.274925
H	-2.475099	-0.815964	-1.389734
H	-1.787405	-3.621032	-0.295595
H	-1.559954	-3.46413	-2.730655
H	-3.183442	-2.620588	-2.893587
C	-3.815615	-2.857333	-0.118321
C	-4.004332	-3.470476	1.130698
C	-4.888296	-2.137667	-0.670815
C	-5.215104	-3.351315	1.816661
H	-3.179814	-4.032388	1.576043
C	-6.097596	-2.012638	0.014022
H	-4.776549	-1.653805	-1.643287
C	-6.266889	-2.615223	1.264403
H	-5.334394	-3.830196	2.791644
H	-6.913282	-1.436981	-0.430416
H	-7.212695	-2.51485	1.801817

Si	-0.86179	-0.496942	1.003295
H	0.311072	-0.096988	1.831636
H	-1.26121	-1.849244	1.471994
C	-2.274027	0.638521	1.52706
C	-3.560266	0.139652	1.798097
C	-2.045616	2.015526	1.715052
C	-4.589736	0.989316	2.214454
H	-3.767581	-0.9238	1.684336
C	-3.066175	2.865161	2.141448
H	-1.05151	2.425521	1.52651
C	-4.347919	2.354997	2.382874
H	-5.582496	0.575335	2.407655
H	-2.862792	3.929944	2.282677
H	-5.151597	3.020566	2.708591
H	-2.625251	1.220787	-3.028469
H	-2.625251	1.220787	-3.028469

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