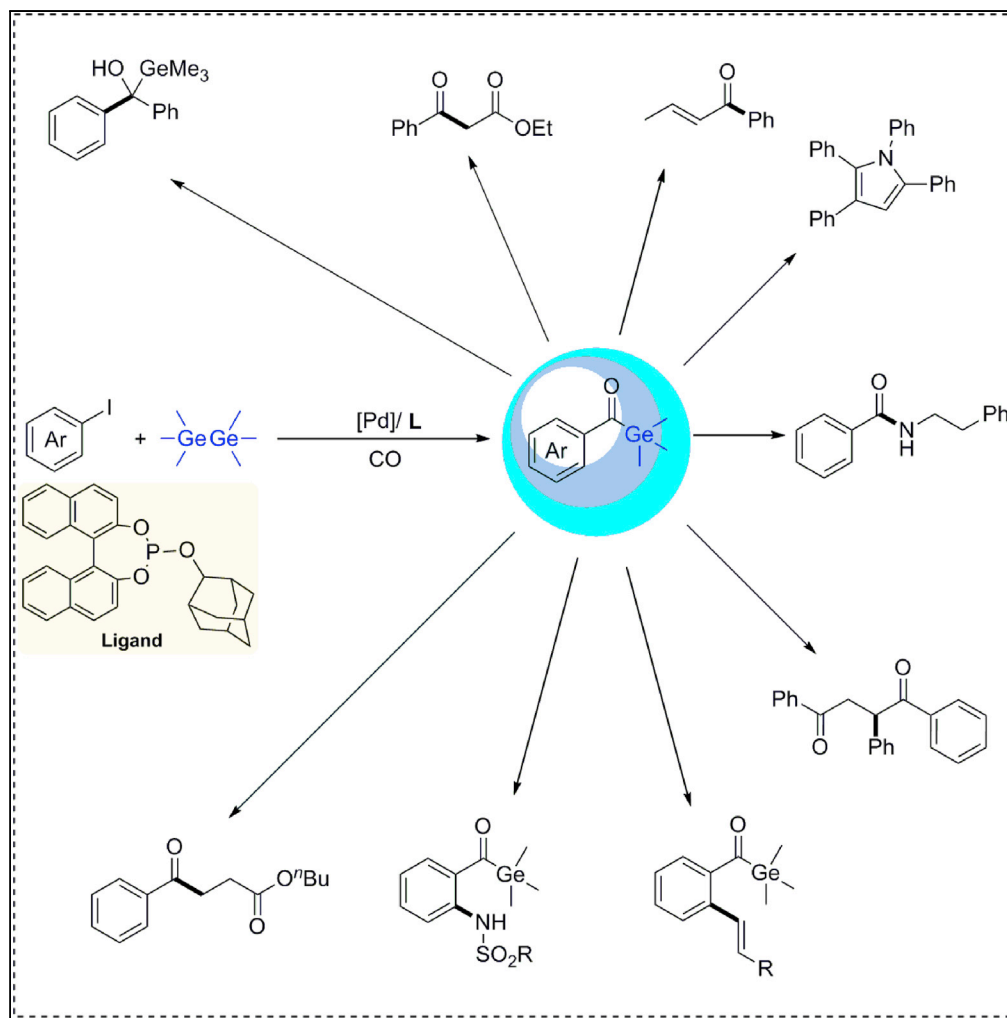


## Article

## The Exploration of Aryltrimethylgermane as Potent Synthetic Origins and Their Preparation



Yang Yuan,  
Youcan Zhang, Bo  
Chen, Xiao-Feng  
Wu

xiao-feng.wu@catalysis.de

## HIGHLIGHTS

The first carbonylation procedure for acylgermanes synthesis has been established

Synthetic transformations of acylgermanes have been developed

New BINOL-based monophosphite ligand is designed and applied

Yuan et al., iScience 23,  
100771  
January 24, 2020 © 2019 The  
Author(s).  
[https://doi.org/10.1016/  
j.isci.2019.100771](https://doi.org/10.1016/j.isci.2019.100771)

## Article

# The Exploration of Aroyltrimethylgermane as Potent Synthetic Origins and Their Preparation

Yang Yuan,<sup>1,2</sup> Youcan Zhang,<sup>1,2</sup> Bo Chen,<sup>1</sup> and Xiao-Feng Wu<sup>1,3,\*</sup>**SUMMARY**

The synthetic utilities of acylgermanes are surprisingly rarely explored compared with their analogues. In this communication, the survey of aroyltrimethylgermane as potent synthetic origins has been studied. A variety of novel chemical transformations have been realized, including using the acylgermane group as a directing group in Rh-catalyzed aromatic C-H alkenylation reaction and Ir-catalyzed aromatic C-H amidation reactions. Additionally, a general approach for acylgermanes preparation has been established as well. The catalytic system proceeds effectively in the presence of Pd(OAc)<sub>2</sub>/BINOL-based monophosphite (L11) and allows for the straightforward access to a wide range of functionalized acylgermanes in high yields.

**INTRODUCTION**

The acylsilanes, germanes, and stannanes have been well known as an electronically unique class of group-14 element compounds with remarkable  $n \rightarrow \pi^*$  redshifted transition band and their lower transition energy (Ramsey et al., 1974; Page et al., 1990). The electron inherent in these compounds leads to a distinct reactivity from other carbonyl compounds (Brook et al., 1960; Harnish and West, 1963; Yoshida et al. 1989, 1992). During the past decades, they have been explored as versatile synthetic intermediates in various novel chemical transformations (Brook, 1974; Moser, 2001; González et al., 2015). However, compared with the well understanding of the reactivity of acylsilanes and acylstannanes, the synthetic reactivity of acylgermanes is surprisingly much less explored (Cirillo and Panek, 1992; Galliford and Scheidt, 2008; Ito et al., 2011; Lettan et al., 2006; Matsuda et al., 2014; Mattson et al. 2004, 2006; Obora et al., 2002; Schmink and Krska, 2011; Yu et al., 2016; Matsumoto and Shindo, 2012; Shindo et al., 2007; Zhang et al., 2013).

Acylgermanes have been of great interest recently, because they showed the unique advantages in the field of photo-initiated free-radical polymerization reactions (Ganster et al., 2008; Jöckle et al., 2017, 2018; Lalevee et al., 2009; Moszner et al., 2009; Neshchadin et al., 2013; Radebner et al., 2017a, 2017b; Haas et al., 2018; Lappert et al., 1987; Jutzi and Hampel, 1986; Zhu et al., 2019). Due to the great achievements on chemical transformations of acylsilanes and acylstannanes, it is intriguing to discover the potential synthetic utilities of acylgermanes.

**RESULTS**

With this idea in mind, testings were performed and a set of new transformations of benzoyltrimethylgermane were succeeded (Scheme 1), for example, the intermolecular Schmidt reaction; palladium-catalyzed acylation of allylic trifluoroacetate; synthesis of  $\beta$ -keto ester by using diazo ester and benzoyltrimethylgermane as the reaction partner; rhodium-catalyzed arylation of benzoyltrimethylgermane with sodium tetraphenylborate; thiazolium-catalyzed additions of acylgermane to access 1,4-dicarbonyl products; and one-pot assembly of pyrrole ring.

With these promising results in hand, we start to look at the preparation of acylgermane compounds. Since the first acylgermane, benzoyl(triphenyl)germane, was synthesized in 1960 by Brook and co-workers (Brook et al., 1960), many synthetic methods toward acylgermanes were developed, including hydrolysis of germlydithianes (Brook et al., 1967; Corey and Seebach, 1965), reacting of acyl chlorides, esters, and amides with germlylithiums or other germlymetallic reagents (Bravo-Zhivotovskii et al., 1983; Castel et al. 1990, 1992; Iserloh and Curran, 1998; Kiyooka and Miyauchi, 1985; Yamamoto et al., 1987; Nanjo et al., 2001; Piers and Lemieux, 1995), and palladium-catalyzed transformation of alkynes with germanium hydride (Kinoshita

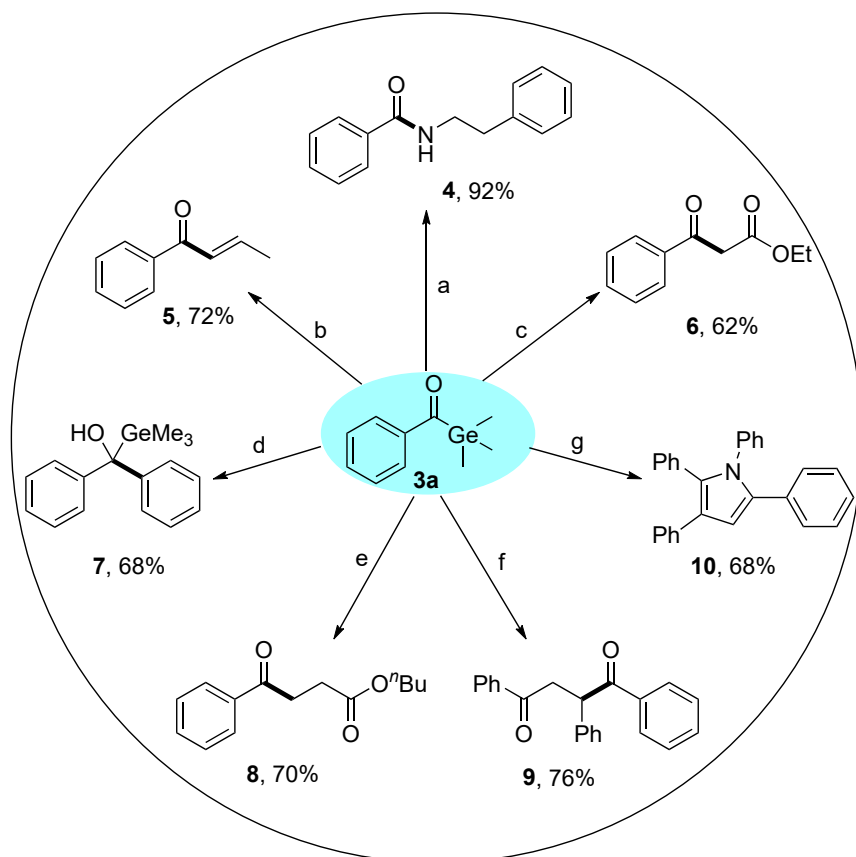
<sup>1</sup>Leibniz-Institut für Katalyse an der Universität Rostock, Albert-Einstein-Straße 29a, 18059 Rostock, Germany

<sup>2</sup>These authors contributed equally

<sup>3</sup>Lead Contact

\*Correspondence: xiao-feng.wu@catalysis.de  
<https://doi.org/10.1016/j.isci.2019.100771>





### Scheme 1. New Synthetic Transformations of Benzoyltrimethylgermane

[a] (2-Azidoethyl)benzene (1.5 equiv.), TfOH (2.0 equiv.), DCM, rt, 5 min. [b] Allyl trifluoroacetate (1.2 equiv.), Pd(TFA)<sub>2</sub> (5 mol%), THF, 70°C, 8 h. [c] (1) Ethyl diazoacetate (1.0 equiv.), LDA (1.0 equiv.), THF, -78°C; (2) MeOH, 0°C. [d] NaBPh<sub>4</sub> (2.0 equiv.), [Rh(cod)Cl]<sub>2</sub> (3.0 mol%), m-xylene, 130°C, 24 h. [e] (1) Thiazolium (30 mol%), butyl acrylate (1.0 equiv.), DBU (0.3 equiv.), i-PrOH (4.0 equiv.), THF, 70°C; (2) H<sub>2</sub>O. [f] (1) Thiazolium (30 mol%), chalcone (1.0 equiv.), DBU (0.3 equiv.), i-PrOH (4.0 equiv.), THF, 70°C; (2) H<sub>2</sub>O. [g] (1) Thiazolium (30 mol%), chalcone (1.0 equiv.), DBU (0.3 equiv.), i-PrOH (4.0 equiv.), THF, 70°C; (2) aniline (3.0 equiv.), *p*-toluenesulfonic acid (2.0 equiv.), EtOH, 4 Å MS, 70°C. See also Figures S9–S24.

et al., 2002). Given the importance of acylgermanes and its newly developed promising synthetic utilities in chemical transformations, we believe a practical approach to acylgermanes is under the current demand and could be achieved by carbonylative coupling of aryl halides with hexamethyldigermanium.

To verify our hypothesis, we decide to choose iodobenzene (1a) and hexamethyldigermanium (2) as the model substrates to establish the catalyst system. Initially, different palladium catalyst and phosphine ligands were tested; however, these reactions could give only traces of the desired product (see in Table S1). Gratifyingly, the desired product 3a was furnished in a promising yield of 54% when P(OMe)<sub>3</sub> (L1) was used as the ligand (Table 1, entry 1). This led us to examine the effect of different R groups (L2–L4, Table 1, entries 2–4). Notably, when ligand L4 with R of 2,4-ditBuPh group was used, 3a was obtained in 80% yield (Table 1, entry 4). The testing of the other palladium catalyst resulted in a decreased yield of 3a (Table 1, entries 5–7). We then turned our attention to the other ligands based on different backbones (L5–L12, Table 1, entries 8–13). When the modified ligands L11 and L12 based on the binaphthol (BINOL) backbone bearing R = 1-Ad and R = 2-Ad were used, resulting similar high yields in 87% and 89%, respectively (Table 1, entries 13–14). Other commonly used phosphite ligands such as monophos L12 only afforded the product in poor yield. The catalyst loading can be decreased to 2.5 mol% Pd(OAc)<sub>2</sub> and 5.0 mol% L11 as well and furnished 3a in 90% GC yield with 83% isolated yield (Table 1, entry 16). Remarkably, 3a also can be achieved in 80% isolated yield even under 1 bar CO pressure (Table 1, entry 17). Here it is also important to mention that Me<sub>3</sub>GeI can be obtained as the byproduct.

$$\text{Ar-I} + \text{GeMe}_6 \xrightarrow[\text{CO (20 bar)}]{[\text{Pd}] (5.0 \text{ mol } \%), \text{Ligand (10.0 mol } \%), 100 \text{ }^\circ\text{C, toluene, 12 h}} \text{Ar-GeMe}_2 + \text{Me}_3\text{GeI}$$

L1, R= Me  
 L2, R= Et  
 L3, R= Ph  
 L4, R= 2,4-di<sup>t</sup>BuPh

L7, R= <sup>n</sup>Bu  
 L8, R= <sup>t</sup>Bu  
 L9, R= 2,4-di<sup>t</sup>BuPh

L5, R= <sup>t</sup>Bu  
 L6, R= 1-Ad

L10, R= 1-Ad  
 L11, R= 2-Ad

L12

Entry	Ligand	Palladium	Yield (%) <sup>a</sup>
1	L1	Pd(OAc) <sub>2</sub>	54
2	L2	Pd(OAc) <sub>2</sub>	58
3	L3	Pd(OAc) <sub>2</sub>	60
4	L4	Pd(OAc) <sub>2</sub>	80
5	L4	Pd <sub>2</sub> (dba) <sub>3</sub>	75
6	L4	[PdCl(C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub>	70
7	L4	Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>	58
8	L5	Pd(OAc) <sub>2</sub>	30
9	L6	Pd(OAc) <sub>2</sub>	69
10	L7	Pd(OAc) <sub>2</sub>	59
11	L8	Pd(OAc) <sub>2</sub>	45
12	L9	Pd(OAc) <sub>2</sub>	70
13	L10	Pd(OAc) <sub>2</sub>	87
14	L11	Pd(OAc) <sub>2</sub>	89
15	L12	Pd(OAc) <sub>2</sub>	41
16 <sup>b</sup>	L11	Pd(OAc) <sub>2</sub>	90 (83) <sup>c</sup>
17 <sup>d</sup>	L11	Pd(OAc) <sub>2</sub>	80 <sup>d</sup>

**Table 1. Investigation of Reaction Conditions**

See also Table S1, Figures S1–S8.

Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), Pd(OAc)<sub>2</sub> (5.0 mol %), L (10.0 mol %), CO (20 bar), 100°C and toluene (1.0 mL).

<sup>a</sup>Yields were determined by GC with hexadecane as an internal standard.

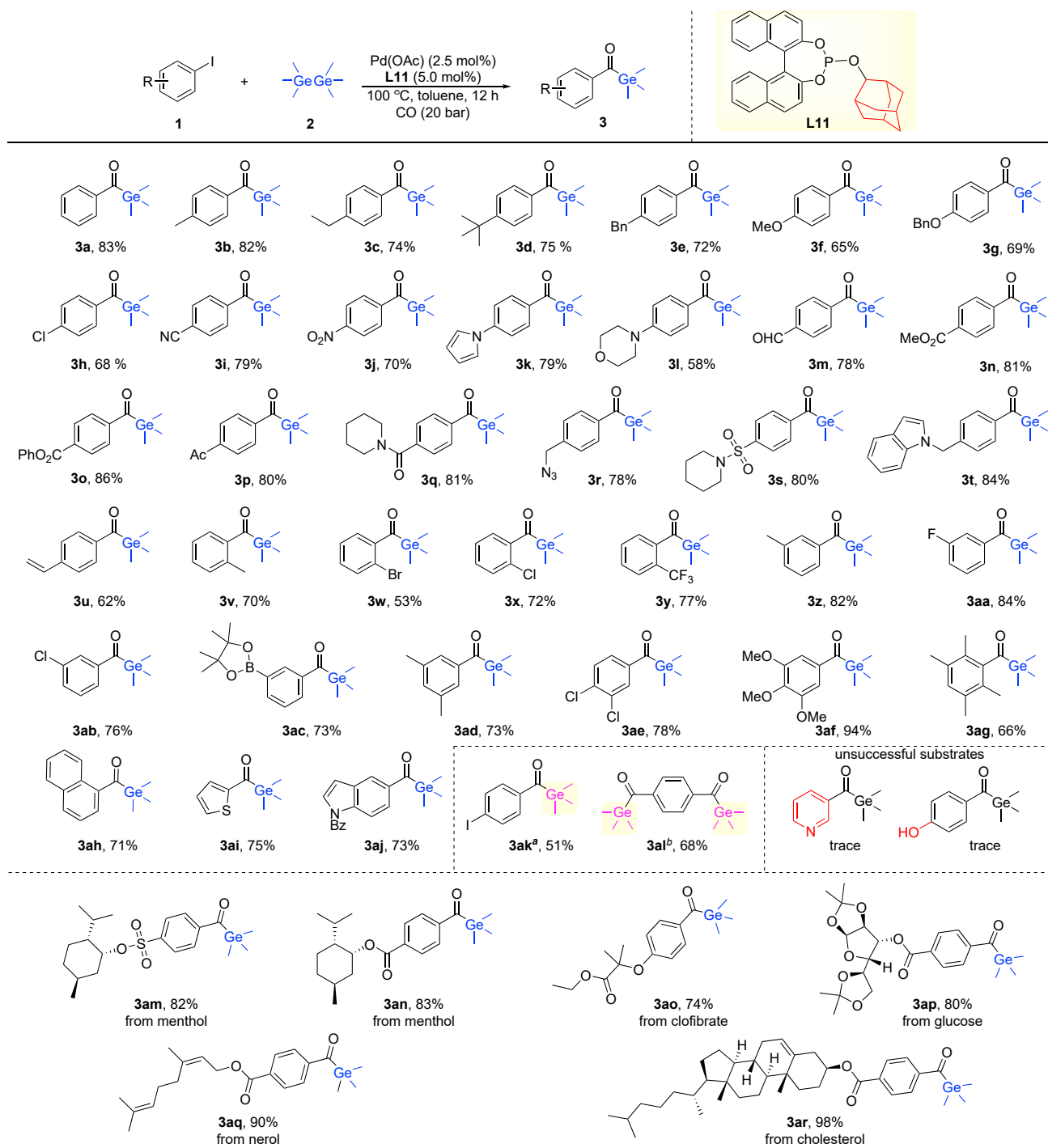
<sup>b</sup>Pd(OAc)<sub>2</sub> (2.5 mol %), L (5.0 mol %).

<sup>c</sup>Isolated yield.

<sup>d</sup>CO (1 bar).

## DISCUSSION

Having established the optimal conditions, we subjected the hexamethyldigermanium to the reaction with different (hetero)aryl iodides (Scheme 2). To our delight, the scope of this transformation is significantly broad. A variety of aryl iodides bearing electron-donating substituents at the para positions were successfully converted to the desired products **3a–3g** in good yields. Various electron-withdrawing functional

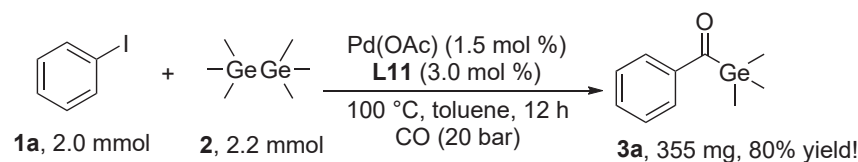


### Scheme 2. Synthesis of Aroyltrimethylgermanes

Reaction Conditions: **1a** (0.2 mmol), **2** (0.24 mmol), Pd(OAc)<sub>2</sub> (2.5 mol%), L11 (5.0 mol %), CO (20 bar), toluene (1.0 mL), 100 °C, 12 h, isolated yield. [**a**] **2** (0.2 mmol). [**b**] **2** (0.5 mmol). See also Figures S25–S111 and S140–144.

groups such as halogen, N-heterocycles, formyl, esters as well as ketones at the para positions of aryl iodides were all well tolerated and afforded the corresponding substituted products in 56%–86% isolated yields. Notably, the reaction proceeds smoothly with aryl iodides bearing cyano (**3i**), nitro (**3j**), azidomethyl (**3r**), and vinyl (**3u**). Ortho- or meta-substituted aryl iodides were able to give the corresponding products in

## 2 mmol scale reaction

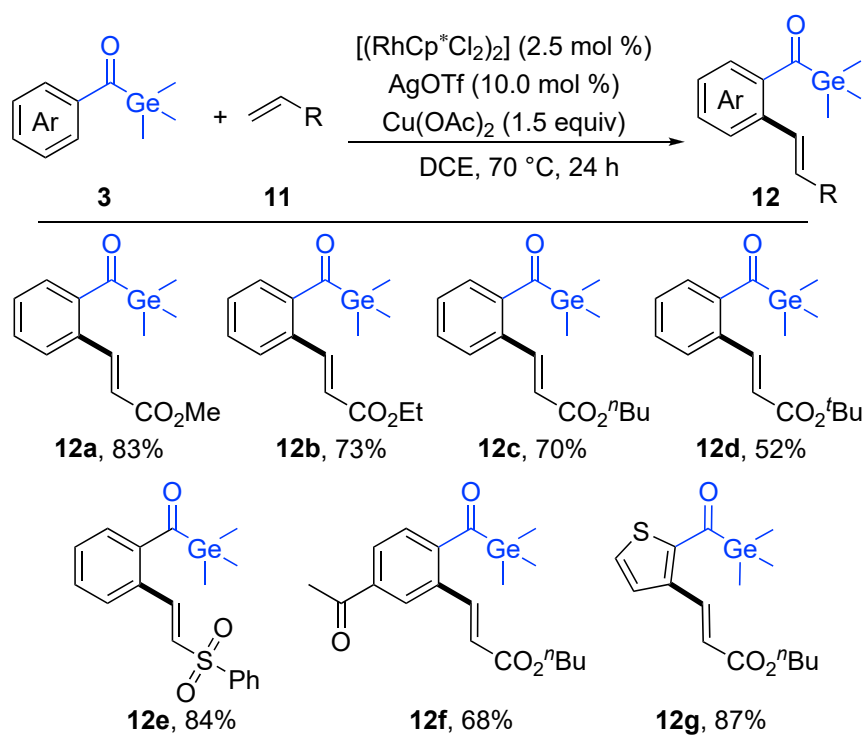


## Scheme 3. Scale-up Experiment

high yield as well (**3v-3ac**). Moreover, di-, tri-, and tetra-substituted aryl iodides also reacted smoothly to furnish the desired products **3ad-3ag** in good to excellent yields. Importantly, 1-iodonaphthalene, 2-iodothiophene, and indole-containing substrate were successfully compatible under the reaction conditions (**3ah-3aj**, 71%–75% yields). Interestingly, when applying 1,4-diiodobenzene as the substrate, mono- (**3ak**) and di-substituted (**3ai**) acylgermanes could be obtained respectively by controlling the equivalents of hexamethyldigermanium added. Nevertheless, 3-iodopyridines and 4-hydroxyiodobenzene did not work well under the reaction conditions. To demonstrate the potential applications, late-stage modification of various biologically active molecules, natural products, and pharmaceuticals derivatives were also conducted. Menthol derivative **3am** and **3an** can be isolated in 72% and 82% yield, respectively. Clofibrate-, glucose-, nerol-, and cholesterol-derived **3ao-3ar** were all obtained in good yields (74%–98% yield, [Scheme 2](#)).

The practicability of a synthetic methodology is the possibility for easy scale up. Hence, we performed the reaction in a 2 mmol scale in the presence of 1.5 mol% palladium catalyst and 3.0 mol% ligand (L11), and the desired product **3a** was obtained in 355 mg, 80% yield ([Scheme 3](#)).

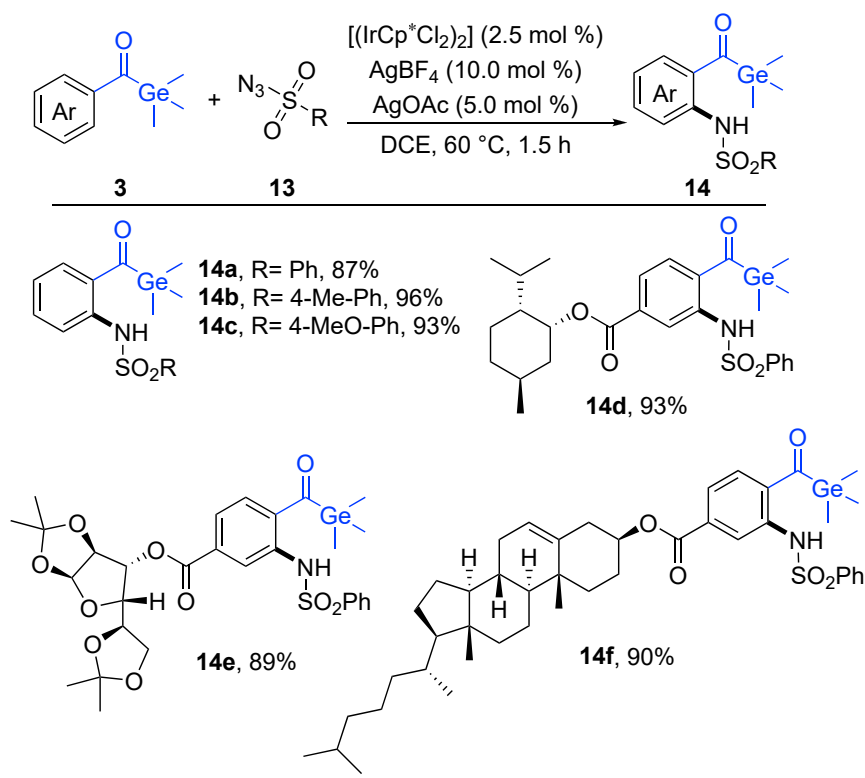
Furthermore, encouraged by the recent work on acylsilane-directed aromatic C-H functionalization by rhodium ([Becker et al., 2014](#)), iridium ([Becker et al., 2015](#)), and ruthenium catalysis ([Lu et al., 2019](#)), we



## Scheme 4. Rhodium-Catalyzed Alkenylation of Acylgermanes

[a] Reaction conditions: **3** (0.2 mmol), **11** (0.4 mmol),  $[\text{Cp}^*\text{RhCl}_2\text{]}_2$  (2.5 mol %), AgOTf (10.0 mol %), and  $\text{Cu}(\text{OAc})_2$  (1.5 equiv) in DCE (0.5 mL) under 70 °C for 24 h. Isolated yield for all products.

See also [Figures S112–S125](#).

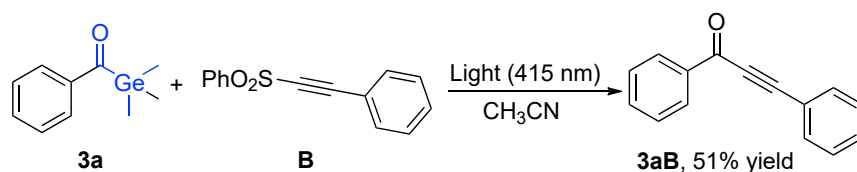


### Scheme 5. Iridium-Catalyzed Amidation of Acylgermanes

[a] Reaction conditions: 3 (0.2 mmol), 13 (0.24 mmol),  $[(\text{IrCp}^*\text{Cl}_2)_2]$  (2.5 mol %),  $\text{AgBF}_4$  (10.0 mol %),  $\text{AgOAc}$  (5.0 mol %) in DCE (0.5 mL) under 60 °C for 1.5 h. Isolated yield for all products. See also Figures S126–S137.

investigated the possibility of preparing the desired ortho-olefinated acylgermanes by utilizing acylgermane as a reactant. By using  $[(\text{RhCp}^*\text{Cl}_2)_2]$  (2.5 mol %),  $\text{AgOTf}$  (10 mol %), and  $\text{Cu}(\text{OAc})_2$  (1.5 equiv.) in DCE at 70 °C for 24 h, the desired ortho-olefinated benzoyltrimethylgermane **12a** can be obtained in 83% isolated yield. We then roughly examined the scope of this acylgermane-directed aromatic C-H alkylation reaction. Various acrylates such as methyl acrylate, ethyl acrylate, butyl acrylate, tert-butyl acrylate, and even phenyl vinyl sulfone were all efficiently reacted with benzoyltrimethylgermane (**3a**) to produce the corresponding products in moderate to good yields (12a–12e, Scheme 4). Two different substituted acylgermanes **3** were also investigated, and both were able to afford the desired products in good yields (12f–g, Scheme 4).

Meanwhile, inspired by the iridium-catalyzed ortho-amidation reaction of aroylsilanes with sulfonyl azides by Bolm and co-workers, benzoyltrimethylgermane (**3a**) and benzenesulfonyl azide were selected as representative substrates. A combination of  $[(\text{IrCp}^*\text{Cl}_2)_2]$  (2.5 mol %),  $\text{AgBF}_4$  (10 mol %), and  $\text{AgOAc}$  (5.0 mol %) was applied as the catalytic system in DCE at 60 °C. To our delight, the catalytic system was very efficient, and the desired product **14a** was obtained in 87% yield after 1.5 h. Subsequently, sulfonyl azide (**13**)



### Scheme 6. Alkynone Synthesis from Acylgermane

[a] Reaction conditions: **3a** (0.1 mmol), **B** (0.15 mmol) in  $\text{MeCN}$  (1.5 mL) under room temperature under light (415 nm) for 12 h, isolated yield.

See also Figures S138–S139.

substrates were tested, and the corresponding products (**14b-c**, Scheme 5) were all obtained in high yields. Menthol-, glucose-, and cholesterol-derived acylgermanes can be well tolerated as well and resulting the desired products **14d-f** in excellent yields (89%–93% yield, Scheme 5). Additionally, under the irradiation of light (415 nm), acylgermane can be activated to generate acyl radical and then captured by ((phenylethynyl)-sulfonyl)benzene to produce alkynone product (Scheme 6).

### Conclusions

In summary, we have demonstrated the versatility of acylgermanes in various new synthetic transformations and also developed a general approach to a variety of synthetically useful acylgermanes by palladium-catalyzed carbonylative reaction. The using of new BINOL-based monophosphite (L11) ligand enables the effective transformation of a broad range of aryl iodides, including drug-like molecules. It is noteworthy that, for the first time, the acylgermane group has been successfully explored as directing group in Rh-catalyzed aromatic C-H alkenylation reaction and Ir-catalyzed ortho-amidation reaction. These new synthetic applications highlight the usefulness of the obtained acylgermanes products. Further studies are ongoing in our laboratory to investigate the properties and reactivity of the acylgermanes compounds.

### Limitations of the Study

Aryl bromides and aryl chlorides are still not applicable as substrates in this system. The obtained acylgermanes is not stable under light and cannot be stored for long term.

### METHODS

All methods can be found in the accompanying [Transparent Methods supplemental file](#).

### SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at <https://doi.org/10.1016/j.isci.2019.100771>.

### ACKNOWLEDGMENTS

We thank the Chinese Scholarship Council (CSC) for financial support.

### AUTHOR CONTRIBUTIONS

X.W. designed and directed the project. X.W. and Y.Y. wrote this manuscript. Y.Y. performed the experiments and analyzed data for all the compounds. Y.Z. prepared the new phosphite ligands. B.C. prepared the aryl iodides and joined discussion. Y.Y. and Y.Z. contributed equally to this work.

### DECLARATION OF INTERESTS

The authors declare no competing interests.

Received: September 10, 2019

Revised: November 7, 2019

Accepted: December 9, 2019

Published: January 24, 2020

### REFERENCES

- Becker, P., Priebsenow, D.L., Pirwerdjan, R., and Bolm, C. (2014). Acylsilanes in rhodium(III)-catalyzed directed aromatic C–H alkenylations and siloxycarbene reactions with C–C double bonds. *Angew. Chem. Int. Ed.* **53**, 269–271.
- Becker, P., Pirwerdjan, R., and Bolm, C. (2015). Acylsilanes in iridium-catalyzed directed amidation reactions and formation of heterocycles via siloxycarbenes. *Angew. Chem. Int. Ed.* **54**, 15493–15496.
- Bravo-Zhivotovskii, D., Pigarev, S.D., Kalikhman, I., Vyazankina, O., and Vyazankin, N. (1983). Reactions of triethylgermyllithium with N,N-dialkylated carboxamides. *J. Organomet. Chem.* **248**, 51–60.
- Brook, A.G. (1974). Molecular rearrangements of organosilicon compounds. *Acc. Chem. Res.* **7**, 77–84.
- Brook, A., Quigley, M., Peddle, G., Schwartz, N., and Warner, C. (1960). The Spectral and chemical properties of  $\alpha$ -silyl ketones. *J. Am. Chem. Soc.* **82**, 5102–5106.
- Brook, A., Duff, J., Jones, P.F., and Davis, N. (1967). Synthesis of silyl and germyl ketones. *J. Am. Chem. Soc.* **89**, 431–434.
- Castel, A., Riviere, P., Satge, J., and Ko, H. (1990). New (diarylgemyl)lithiums. *Organometallics* **9**, 205–210.
- Castel, A., Rivière, P., Satgé, J., and Desor, D. (1992). Nouveaux aryldihydrogermyllithium. *J. Organomet. Chem.* **433**, 49–61.
- Cirillo, P.F., and Panek, J.S. (1992). Recent progress in the chemistry of acylsilanes. A review. *Org. Prep. Proced. Int.* **24**, 553–582.
- Corey, E.J., and Seebach, D. (1965). Synthesis of 1,n-dicarbonyl derivatives using carbanions from



- 1,3-dithianes. *Angew. Chem. Int. Ed.* **4**, 1077–1078.
- Galliford, C.V., and Scheidt, K.A. (2008). An unusual dianion equivalent from acylsilanes for the synthesis of substituted  $\beta$ -keto esters. *Chem. Commun. (Camb.)*, 1926–1928.
- Ganster, B., Fischer, U.K., Moszner, N., and Liska, R. (2008). New photocleavable structures. diacylgermane-based photoinitiators for visible light curing. *Macromolecules* **41**, 2394–2400.
- González, J., Santamaría, J., and Ballesteros, A. (2015). Gold(I)-catalyzed addition of silylacetylenes to acylsilanes: synthesis of indanones by C-H functionalization through a gold(I) carbenoid. *Angew. Chem. Int. Ed.* **54**, 13678–13681.
- Haas, M., Radebner, J., Eibel, A., Gescheidt, G., and Stueger, H. (2018). Recent advances in germanium-based photoinitiator chemistry. *Chem. Eur. J.* **24**, 8258–8267.
- Harnish, D.F., and West, R. (1963). The electronic spectra of  $\alpha$ -silyl ketones. *Inorg. Chem.* **2**, 1082–1084.
- Iserloh, U., and Curran, D.P. (1998). Radical cyclizations of acylgermane oxime ethers and hydrazones: Direct routes to cyclic hydrazones and oximes. *J. Org. Chem.* **63**, 4711–4716.
- Ito, K., Tamashima, H., Iwasawa, N., and Kusama, H. (2011). Photochemically promoted transition metal-free cross-coupling of acylsilanes with organoboron esters. *J. Am. Chem. Soc.* **133**, 3716–3719.
- Jöckle, P., Schweigert, C., Lamparth, I., Moszner, N., Unterreiner, A.-N., and Barner-Kowollik, C. (2017). An in-depth mechanistic investigation of the radical initiation behavior of monoacylgermanes. *Macromolecules* **50**, 8894–8906.
- Jöckle, P., Radebner, J., Haas, M., Lamparth, I., Stueger, H., Moszner, N., Unterreiner, A.-N., and Barner-Kowollik, C. (2018). A priori prediction of mass spectrometric product patterns of photoinitiated polymerizations. *ACS Macro Lett.* **7**, 132–136.
- Jutzi, P., and Hampel, B. (1986). Electrophilic attack at pentamethylcyclopentadienyl-substituted germynes. *Organometallics* **5**, 730–734.
- Kinoshita, H., Shinokubo, H., and Oshima, K. (2002). Pd(0)-catalyzed reaction of alkynes with trifurylgermane and CO providing acylgermanes: the example of hydrometalcarbonylation of alkynes. *J. Am. Chem. Soc.* **124**, 4220–4221.
- Kiyooka, S.-i., and Miyauchi, A. (1985). Facile synthesis of acylgermanes. *Chem. Lett.* **14**, 1829–1830.
- Lalevee, J., Allonas, X., and Fouassier, J.-P. (2009). Acylgermanes: Excited state processes and reactivity. *Chem. Phys. Lett.* **469**, 298–303.
- Lappert, M.F., Misra, M.C., Onyszczuk, M., Rowe, R.S., Power, P.P., and Slade, M.J. (1987). Subvalent group 14 metal compounds XI. Oxidative addition reactions of organic halides or acid anhydrides (including  $\text{CH}_4$ ,  $\text{Cl}_n$ ,  $\text{PhBr}$ ,  $\text{BrN}(\text{SiMe}_3)_2$ ,  $\text{ButCOCl}$ , or  $(\text{CF}_3\text{CO})_2\text{O}$ ) to some bivalent group 14 metal amides or alkyls. *J. Organomet. Chem.* **330**, 31–46.
- Lettan, R.B., Reynolds, T.E., Galliford, C.V., and Scheidt, K.A. (2006). Synthesis of tertiary  $\beta$ -hydroxy amides by enolate additions to acylsilanes. *J. Am. Chem. Soc.* **128**, 15566–15567.
- Lu, X., Shen, C., Meng, K., Zhao, L., Li, T., Sun, Y., Zhang, J., and Zhong, G. (2019). Acylsilane directed aromatic C-H alkenylations by ruthenium catalysis. *Chem. Commun. (Camb.)* **55**, 826–829.
- Matsuda, T., Mizuno, K., and Watanuki, S. (2014). Rhodium-catalyzed arylation of acylsilanes with sodium tetraarylborates. *J. Organomet. Chem.* **765**, 64–67.
- Matsumoto, K., and Shindo, M. (2012). Palladium-catalyzed fluoride-free cross-coupling of intramolecularly activated alkenylsilanes and alkenylgermanes: synthesis of tamoxifen as a synthetic application. *Adv. Synth. Catal.* **354**, 642–650.
- Mattson, A.E., Bharadwaj, A.R., and Scheidt, K.A. (2004). The thiazolium-catalyzed sila-stetter reaction: Conjugate addition of acylsilanes to unsaturated esters and ketones. *J. Am. Chem. Soc.* **126**, 2314–2315.
- Mattson, A.E., Bharadwaj, A.R., Zuhl, A.M., and Scheidt, K.A. (2006). Thiazolium-catalyzed additions of acylsilanes: A general strategy for acyl anion addition reactions. *J. Org. Chem.* **71**, 5715–5724.
- Moser, W.H. (2001). The brook rearrangement in tandem bond formation strategies. *Tetrahedron* **57**, 2065–2084.
- Moszner, N., Zeuner, F., Lamparth, I., and Fischer, U.K. (2009). Benzoylgermanium derivatives as novel visible-light photoinitiators for dental composites. *Macromol. Mater. Eng.* **294**, 877–886.
- Nanjo, M., Matsudo, K., and Mochida, K. (2001). Reactivities of triethylgermylborate in methanol. *Chem. Lett.* **30**, 1086–1087.
- Neshchadin, D., Rosspeintner, A., Griesser, M., Lang, B., Mosquera-Vazquez, S., Vauthey, E., Gorelik, V., Liska, R., Hametner, C., and Ganster, B. (2013). Acylgermanes: photoinitiators and sources for Ge-centered radicals. Insights into their reactivity. *J. Am. Chem. Soc.* **135**, 17314–17321.
- Obora, Y., Nakanishi, M., Tokunaga, M., and Tsuji, Y. (2002). Palladium complex catalyzed acylation of allylic esters with acylstannanes: Complementary method to the acylation with acylsilanes. *J. Org. Chem.* **67**, 5835–5837.
- Page, P.C.B., Klair, S.S., and Rosenthal, S. (1990). Synthesis and chemistry of acyl silanes. *Chem. Soc. Rev.* **19**, 147–195.
- Piers, E., and Lemieux, R. (1995). Reaction of (trimethylgermyl)copper(I)-dimethyl sulfide with acyl chlorides: efficient syntheses of functionalized acyltrimethylgermanes. *Organometallics* **14**, 5011–5012.
- Radebner, J., Leypold, M., Eibel, A., Maier, J., Schuh, L., Torvisco, A., Fischer, R., Moszner, N., Gescheidt, G., Stueger, H., and Haas, M. (2017a). Synthesis, spectroscopic behavior, and photoinduced reactivity of tetraacylgermanes. *Organometallics* **36**, 3624–3632.
- Radebner, J., Eibel, A., Leypold, M., Gorsche, C., Schuh, L., Fischer, R., Torvisco, A., Neshchadin, D., Geier, R., Moszner, N., et al. (2017b). Tetraacylgermanes: Highly efficient photoinitiators for visible-light-induced free-radical polymerization. *Angew. Chem. Int. Ed.* **56**, 3103–3107.
- Ramsey, B.G., Brook, A., Bassindale, A.R., and Bock, H. (1974).  $\sigma \rightarrow \pi^*$ , A Reassignment of the long wavelength uv transition in acyl-silanes and -germanes by photoelectron spectroscopy. *J. Organomet. Chem.* **74**, C41–C45.
- Schmink, J.R., and Krska, S.W. (2011). Reversed-polarity synthesis of diaryl ketones via palladium-catalyzed cross-coupling of acylsilanes. *J. Am. Chem. Soc.* **133**, 19574–19577.
- Shindo, M., Matsumoto, K., and Shishido, K. (2007). Hyperconjugative effect of C-Ge bonds: synthesis of multisubstituted alkenylgermanes via torquoselective olefination of acylgermanes with ynolates. *Tetrahedron* **63**, 4271–4277.
- Yamamoto, K., Hayashi, A., Suzuki, S., and Tsuji, J. (1987). Preparation of substituted benzoyltrimethylsilanes and -germanes by the reaction of benzoyl chlorides with hexamethyldisilane or -digermane in the presence of palladium complexes as catalysts. *Organometallics* **6**, 974–979.
- Yoshida, J.-i., Matsunaga, S.-i., and Isoe, S. (1989). Electrochemical oxidation of acylsilanes. *Tetrahedron Lett.* **30**, 5293–5296.
- Yoshida, J., Itoh, M., Matsunaga, S., and Isoe, S. (1992). Electrochemical oxidation of acylsilanes and their tosylhydrazones. *J. Org. Chem.* **57**, 4877–4882.
- Yu, C.-J., Li, R., and Gu, P. (2016). Intermolecular schmidt reaction of alkyl azides with acyl silanes. *Tetrahedron Lett.* **57**, 3568–3570.
- Zhang, H.-J., Priebbenow, D.L., and Bolm, C. (2013). Acylsilanes: Valuable organosilicon reagents in organic synthesis. *Chem. Soc. Rev.* **42**, 8540–8571.
- Zhu, H., Wie, N., Li, Z., Yang, Q., Xiao, X., Lai, G., and Kira, M. (2019). Reactions of an isolable dialkylgermylene with acyl chlorides forming acyl(chloro)germanes and diacylgermanes. *Organometallics* **38**, 1955–1962.

**iScience, Volume 23**

**Supplemental Information**

**The Exploration of Aroyltrimethylgermane  
as Potent Synthetic Origins  
and Their Preparation**

**Yang Yuan, Youcan Zhang, Bo Chen, and Xiao-Feng Wu**

# Transparent Methods

## General Comments

All commercial reagents were purchased from Sigma-Aldrich, Strem, Acros, TCI or Alfa Aesar and used as such unless stated otherwise. Solvents (Anhydrous and under inert atmosphere) were collected from The Solvent purification system by M BRAUN and used under standard schlenk technique. NMR spectra were recorded on Bruker Avance 300 MHz and Bruker ARX 400 MHz spectrometers. Multiplets were assigned as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet) and br. s (broad singlet). GC-yields were calculated using hexadecane as internal standard. All measurements were carried out at room temperature unless otherwise stated. Electron impact (EI) mass spectra were recorded on AMD 402 mass spectrometer (70 eV). The data are given as mass units per charge (m/z). Gas chromatography analysis was performed on an Agilent HP-7890A instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25  $\mu$ m film thickness) using argon as carrier gas. The products were isolated from the reaction mixture by column chromatography on silica gel 60, 0.063-0.2 mm, 70-230 mesh (Merck). The portable Lumatec Superlite 400 (150 W, 100-240 V, 50-60 Hz) with highly flexible fiber optic cable of 5 mm diameter was used as light source, and the power we used is about 1/4 of full power.

## Experimental procedures

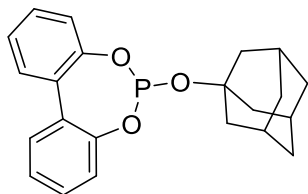
### General procedure for synthesis of L6, L10 and L11<sup>[1]</sup>

To an oven dried 100 mL Schlenk tube under an argon atmosphere was charged with distilled  $\text{PCl}_3$  (5.5 mmol, 1.1 equiv.), dry THF (10 mL) was added. The solution was cooled to 0 °C and  $\text{Et}_3\text{N}$  (2.2 equiv.) in abs. THF (5 mL) was added dropwise. In another 25 mL glass flask BINOL (1.43 g, 5 mmol) in dry THF (10 mL) was added over 10 min dropwise, the reaction was stirred at 0 °C for 30 min. The mixture was slowly warmed to room temperature and stirred overnight.

Another  $\text{Et}_3\text{N}$  (3.3 equiv.) in dry THF (5 mL) was added to the mixture solution, then ROH (5 equiv. in dry 10 mL THF) was added over 10 min drop wise. After addition, the reaction mixture was stirred overnight. Then the solution was filtered, concentrated to give the crude

products. Purification by column chromatography on silica gel (*n*-pentane/ethyl acetate 60:1), gave the corresponding ligands.

**6-(((3*s*,5*s*,7*s*)-Adamantan-1-yl)oxy)dibenzo[*d,f*][1,3,2]dioxaphosphepine (L6)**



72% yield, white solid.

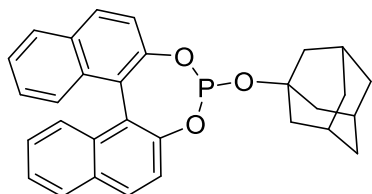
**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.44 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.33 (td, *J* = 7.6, 1.8 Hz, 2H), 7.27 – 7.21 (m, 2H), 7.16 (dt, *J* = 7.9, 1.2 Hz, 2H), 2.22 (s, 3H), 2.12 (d, *J* = 2.7 Hz, 6H), 1.67 (t, *J* = 3.1 Hz, 6H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 149.5, 149.4, 131.5, 131.5, 129.8, 128.8, 124.8, 122.2, 77.9, 77.8, 45.2, 45.0, 35.8, 31.0.

**<sup>31</sup>P NMR** (122 MHz, CDCl<sub>3</sub>) δ 151.1.

**HR-MS (EI)** calcd. for C<sub>22</sub>H<sub>23</sub>O<sub>3</sub>P [M]<sup>+</sup>: 366:13793; found: 366:13859.

**4-(((1*s*,3*s*)-Adamantan-1-yl)oxy)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine (L10)**



68% yield, white solid.

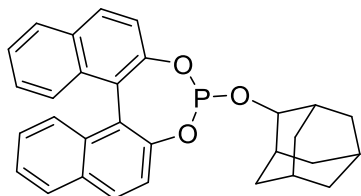
**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.97 – 7.91 (m, 2H), 7.91 – 7.87 (m, 2H), 7.50 (dd, *J* = 8.8, 0.9 Hz, 1H), 7.44 – 7.33 (m, 5H), 7.28 – 7.19 (m, 2H), 2.22 (s, 3H), 2.11 (s, 6H), 1.68 (t, *J* = 3.1 Hz, 6H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 148.0, 148.0, 147.9, 147.8, 132.8, 132.8, 131.4, 131.1, 130.1, 129.3, 128.3, 128.1, 127.1, 127.1, 126.1, 125.9, 124.8, 124.6, 122.4, 122.0, 122.0, 78.1, 78.0, 45.2, 45.1, 35.9, 31.0, 31.0.

**<sup>31</sup>P NMR** (122 MHz, CDCl<sub>3</sub>) δ 152.2.

**HRMS (EI)** calcd. for C<sub>30</sub>H<sub>27</sub>O<sub>9</sub>P [M]<sup>+</sup>: 466.16923; found: 466.16932.

**4-(((1R,3S,5r,7r)-Adamantan-2-yl)oxy)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine (L11)**



70% yield, white solid.

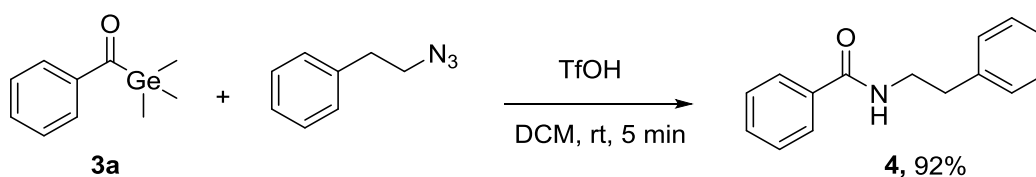
**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.95 (d, *J* = 9.0 Hz, 1H), 7.93 – 7.87 (m, 3H), 7.50 (dd, *J* = 8.8, 0.8 Hz, 1H), 7.44 – 7.34 (m, 5H), 7.27 – 7.20 (m, 2H), 4.38 (dt, *J* = 9.8, 3.1 Hz, 1H), 2.14 – 1.99 (m, 4H), 1.84 – 1.65 (m, 6H), 1.60 – 1.43 (m, 4H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 148.6, 148.6, 147.7, 147.7, 132.9, 132.8, 132.6, 132.6, 131.5, 130.9, 130.2, 129.5, 128.3, 128.2, 127.0, 126.1, 126.0, 124.9, 124.7, 124.4, 124.3, 122.7, 122.7, 122.0, 121.9, 121.7, 79.1, 78.9, 37.4, 36.4, 36.3, 34.3, 34.3, 34.1, 34.1, 31.2, 31.1, 27.2, 26.8.

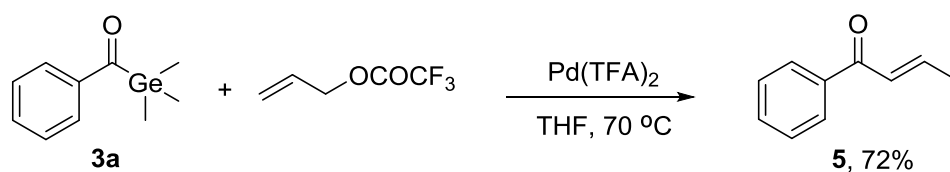
**<sup>31</sup>P NMR** (122 MHz, CDCl<sub>3</sub>) δ 145.8.

**HRMS (EI)** calcd. for C<sub>30</sub>H<sub>27</sub>O<sub>3</sub>P [M]<sup>+</sup>: 466:16923; found: 466:16946.

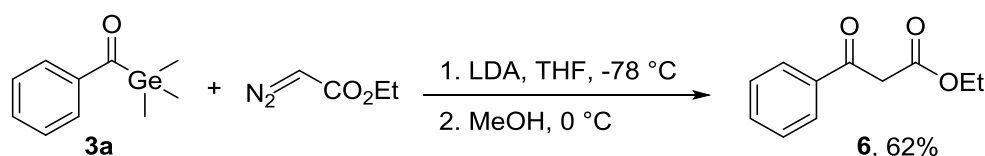
**Practical synthesis of compounds 4-10**



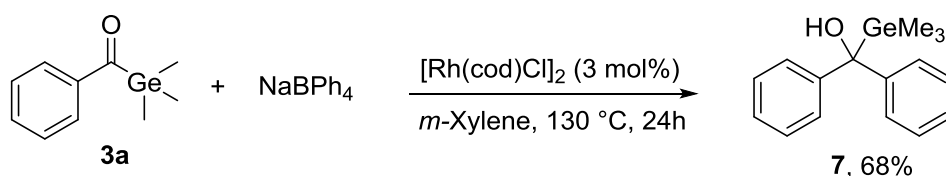
To a stirred mixture of **3a** (44.8 mg, 0.2 mmol) and (2-azidoethyl)benzene (44.2 mg, 0.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was slowly added TfOH (60.0 mg, 0.4 mmol). The reaction mixture was kept for 5 min at room temperature, then it was quenched with aqueous KOH (10%, 2 mL), extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by flash chromatography to give **4**<sup>[2]</sup> as a white solid (41.5 mg, 92% yield). **<sup>1</sup>H NMR** (300 MHz CDCl<sub>3</sub>) δ 7.71 – 7.66 (m, 2H), 7.50 – 7.29 (m, 5H), 7.27 – 7.19 (m, 3H), 6.26 (s, 1H), 3.71 (td, *J* = 6.9, 5.9 Hz, 2H), 2.93 (t, *J* = 6.9 Hz, 2H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 167.50, 138.93, 134.68, 131.39, 128.82, 128.72, 128.55, 126.83, 126.59, 41.16, 35.73.



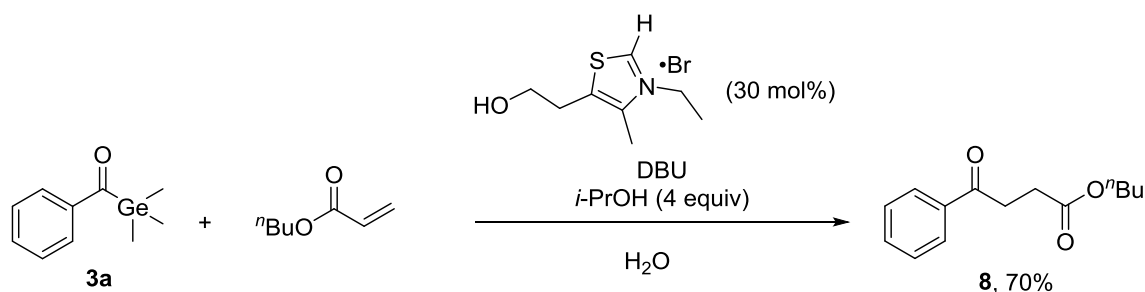
A mixture of **3a** (44.8 mg, 0.2 mmol), allyl trifluoroacetate (36.9 mg, 0.24 mmol), Pd(OCOCF<sub>3</sub>)<sub>2</sub> (3.3 mg, 0.01 mmol), and THF (0.5 mL) with a magnetic stirring bar was placed under an argon flow in a 10 mL round-bottomed flask. The reaction mixture was stirred for 8 h at 70 °C. After the reaction, the whole mixture was passed through a short silica gel column and concentrated. The residue was purified by flash chromatography to give **5**<sup>[3]</sup> as a colorless oil (21.0 mg, 72% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.97 – 7.87 (m, 2H), 7.59 – 7.40 (m, 3H), 7.15 – 6.99 (m, 1H), 6.95 – 6.83 (m, 1H), 1.99 (dd, *J* = 6.7, 1.5 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 190.76, 145.02, 137.93, 132.57, 128.50, 127.56, 18.59.



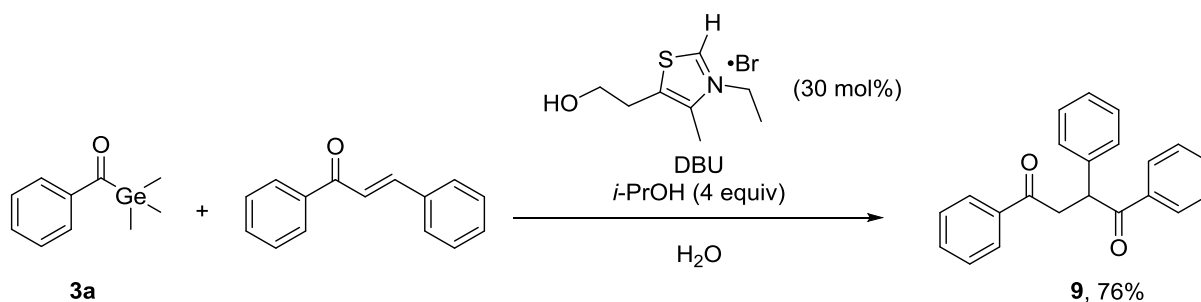
To a 10 mL Schlenk tube containing a magnetic stirring bar was added diazoester (23 mg, 0.2 mmol) and **3a** (44.8 mg, 0.2 mmol) in THF (1.5 mL). The mixture was cooled to –78 °C using a dry ice-acetone bath and a solution of LDA (110  $\mu$ L, 2M in THF) was added. After complete addition, the mixture was stirred for a further 30 min. At this point MeOH (100  $\mu$ L) was added and the mixture warmed to 0 °C and stirred until the reaction was judged to be complete by thin layer chromatography. The reaction mixture was partitioned between EtOAc and saturated ammonium chloride, and the aqueous layer extracted with EtOAc, washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by flash chromatography to give **6**<sup>[4]</sup> as a colorless oil (23.8 mg, 62% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97 – 7.92 (m, 2H), 7.62 – 7.56 (m, 1H), 7.51 – 7.42 (m, 3H), 4.29 – 4.15 (m, 2H), 3.99 (s, 2H), 1.28 – 1.19 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 192.54, 173.19, 171.42, 167.52, 136.01, 133.73, 131.23, 128.77, 128.53, 128.50, 126.03, 87.39, 61.47, 60.33, 46.00, 14.31, 14.08.



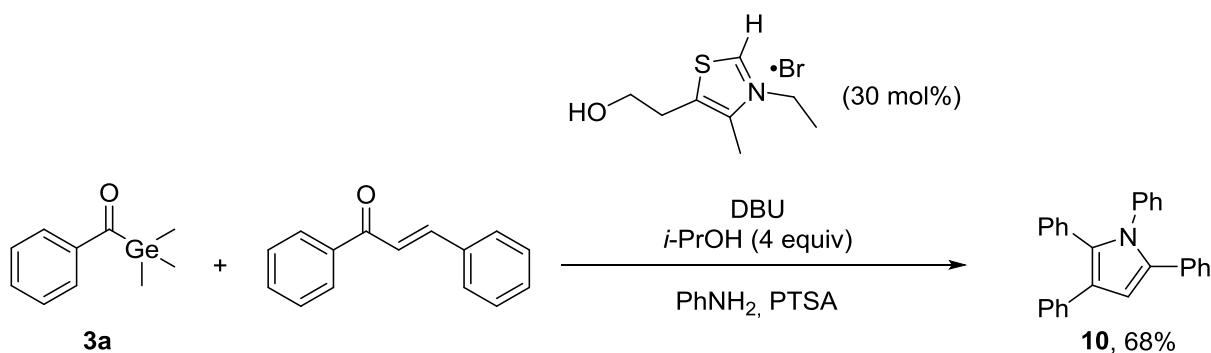
A Schlenk tube was charged with  $\text{NaBPh}_4$  (68.5 mg, 0.4 mmol) and  $[\text{Rh}(\text{cod})\text{Cl}]_2$  (2.9 mg, 3.0 mol%). The tube was evacuated and backfilled with argon, and then **3a** (44.8 mg, 0.2 mmol) and *m*-xylene (1.0 mL) were added via syringe through the septum. The mixture was heated at 130 °C for 24 h. After that the residue was directly purified by flash chromatography to give **7**<sup>[5]</sup> as a colorless oil (40.9 mg, 68% yield).  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 – 7.14 (m, 10H), 2.05 (s, 1H), 0.22 (s, 9H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  147.89, 129.32, 127.42, 127.41, 79.90, -1.06. **HRMS** (EI): Calcd. for  $\text{C}_{16}\text{H}_{20}\text{OGe}$ : 302.07205, Found: 302.07187.



A Schlenk tube was charged with the thiazolium salt (15 mg, 0.06 mmol) under argon, **3a** (67.2 mg, 0.3 mmol) in THF (0.5 mL) was added by syringe to the Schlenk tube followed by the addition of DBU (9  $\mu\text{L}$ , 0.06 mmol). The reaction mixture was heated to 70°C after which the butyl acrylate (25.6 mg, 0.2 mmol) was added by syringe followed by the addition of isopropanol (63  $\mu\text{L}$ , 0.8 mmol). The reaction was allowed to stir at 70°C for 24 hours. Upon completion by TLC, the reaction was cooled to room temperature, diluted with ethyl acetate (5 mL) and washed with water (10 mL). The aqueous layer was washed with ethyl acetate and the combined organic extracts were dried over  $\text{Na}_2\text{SO}_4$  and concentrated. The residue was purified by flash chromatography to give **8**<sup>[6]</sup> as a colorless oil (32.8 mg, 70% yield).  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 – 7.92 (m, 2H), 7.61 – 7.53 (m, 1H), 7.51 – 7.41 (m, 2H), 4.11 (t,  $J = 6.7$  Hz, 2H), 3.32 (t,  $J = 6.7$  Hz, 2H), 2.77 (t,  $J = 6.7$  Hz, 2H), 1.69 – 1.56 (m, 2H), 1.46 – 1.28 (m, 2H), 0.93 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  198.15, 172.99, 136.59, 133.20, 128.61, 128.03, 64.61, 33.41, 30.64, 28.30, 19.13, 13.72.



A Schlenk tube was charged with the thiazolium salt (15 mg, 0.06 mmol) under argon, **3a** (67.2 mg, 0.3 mmol) in THF (0.25 mL) was added by syringe to the Schlenk tube followed by the addition of DBU (9  $\mu$ L, 0.06 mmol). The reaction mixture was heated to 70°C after which the chalcone (41.6 mg, 0.2 mmol) in THF (0.25 mL) was added by syringe followed by the addition of isopropanol (63  $\mu$ L, 0.8 mmol). The reaction was allowed to stir at 70°C for 24 hours. Upon completion by TLC, the reaction was cooled to room temperature, diluted with ethyl acetate (5 mL) and washed with water (10 mL). The aqueous layer was washed with ethyl acetate and the combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by flash chromatography to give **9**<sup>[6]</sup> as a colorless solid (47.8 mg, 76% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 (m, 4H), 7.66 – 7.08 (m, 11H), 5.33 (dd,  $J$  = 10.1, 3.7 Hz, 1H), 4.22 (dd,  $J$  = 18.0, 10.1 Hz, 1H), 3.30 (dd,  $J$  = 18.0, 3.7 Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  198.92, 198.08, 138.65, 136.46, 133.27, 132.91, 129.21, 128.94, 128.59, 128.52, 128.25, 128.18, 127.38, 48.73, 43.91.



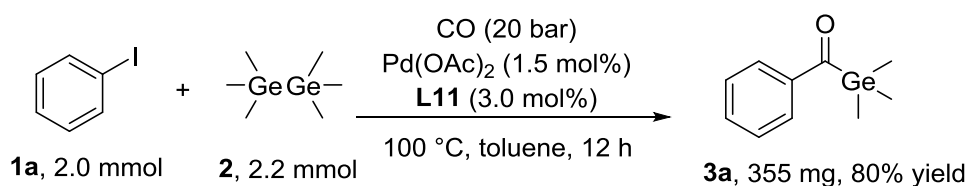
A Schlenk tube was charged with the thiazolium salt (15 mg, 0.06 mmol) under argon, **3a** (67.2 mg, 0.3 mmol) in THF (0.25 mL) was added by syringe to the Schlenk tube followed by the addition of DBU (9  $\mu$ L, 0.06 mmol). The reaction mixture was heated to 70 °C after which the chalcone (41.6 mg, 0.2 mmol) in THF (0.25 mL) was added by syringe followed by the addition of isopropanol (63  $\mu$ L, 0.8 mmol). The reaction was allowed to stir at 70 °C for 24 hours. After 24h, to the solution aniline (55.9 mg, 0.6 mmol) was added followed by addition of *p*-toluenesulfonic acid (75.6 mg, 0.4 mmol) in ethanol (0.3 mL) and 4Å molecular sieves



(50 mg). The reaction mixture remained heating at 70 °C for an additional 12 hours. Upon completion by TLC, the reaction was cooled to room temperature, diluted with ethyl acetate (5 mL) and washed with water (10 mL). The aqueous layer was washed with ethyl acetate and the combined organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by flash chromatography to give **10**<sup>[7]</sup> as a white solid (50.5 mg, 68% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.36 – 6.88 (m, 20H), 6.71 (s, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 138.83, 136.16, 134.85, 132.94, 132.70, 131.52, 129.14, 128.61, 128.51, 128.23, 128.18, 128.01, 127.89, 127.15, 126.99, 126.39, 125.53, 123.51, 110.02.

### General procedure for synthesis of acylgermanes **3**

A vial (4 mL) was charged with Pd(OAc)<sub>2</sub> (2.5 mol%), **L11** (5 mol%), aryl iodides **1** (0.2 mmol), hexamethyldigermanium **2** (0.24 mmol), and a stirring bar. The vial was closed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and connected with atmosphere with a needle. The vial was evacuated under vacuum and recharged with argon for three times. Then, toluene (1.0 mL) was injected under argon by using a syringe. The vial (or several vials) was placed in an alloy plate, which was transferred into a 300 mL autoclave of the 4560 series from Parr Instruments. After flushing the autoclave three times with CO, a pressure of 20 bar of CO was adjusted at ambient temperature. Then, the reaction was performed for 12 h at 100 °C. After the reaction was complete, the autoclave was cooled down with ice water to room temperature and the pressure was released carefully. After that the residue was directly purified by column chromatography to afford the corresponding products **3**.

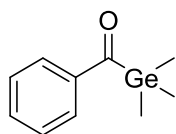


A vial (10 mL) was charged with Pd(OAc)<sub>2</sub> (1.5 mol%, 6.74 mg), **L11** (3.0 mol%, 28.0 mg), iodobenzene **1a** (2.0 mmol, 408 mg, 1.0 equiv.), hexamethyldigermanium **2** (2.2 mmol, 518 mg, 1.1 equiv.), and a stirring bar. The vial was closed by PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and connected with atmosphere with a needle. The vial was evacuated under vacuum and recharged with argon for three times. Then, toluene (5.0 mL) were injected under argon by using a syringe. The vial (or several vials) was placed in an alloy plate, which was transferred into a 300 mL autoclave of the 4560 series from Parr

Instruments. After flushing the autoclave three times with CO, a pressure of 20 bar of CO was adjusted at ambient temperature. Then, the reaction was performed for 12 h at 100 °C. After the reaction was complete, the autoclave was cooled down with ice water to room temperature and the pressure was released carefully. After that the residue was directly purified by column chromatography to afford the corresponding products **3a** (355 mg, yellow oil, 80% yield).

### Characterization of acylgermanes 3

#### Phenyl(trimethylgermyl)methanone (3a)



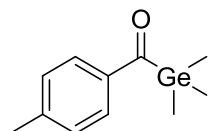
37.0 mg, 83% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.80 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.58 – 7.39 (m, 3H), 0.51 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 235.47, 141.77, 134.01, 129.88, 128.83, -0.00.

**HRMS** (EI): Calcd. for C<sub>10</sub>H<sub>14</sub>OGe: 224.02509, Found: 224.02530.

#### *p*-Tolyl(trimethylgermyl)methanone (3b)



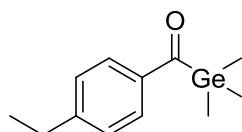
38.8 mg, 82% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.71 (dd, *J* = 8.4, 0.4 Hz, 2H), 7.28 (dd, *J* = 8.5, 0.7 Hz, 2H), 2.47 – 2.31 (m, 3H), 0.49 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 234.45, 144.78, 139.64, 130.51, 128.99, 22.75, 0.00.

**HRMS** (EI): Calcd. for C<sub>11</sub>H<sub>16</sub>OGe: 238.04074, Found: 238.04097.

#### (4-Ethylphenyl)(trimethylgermyl)methanone (3c)



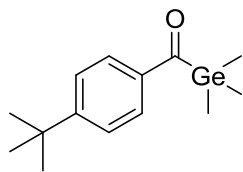
37.1 mg, 74% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.83 – 7.64 (m, 2H), 7.41 – 7.22 (m, 2H), 2.81 – 2.57 (m, 2H), 1.26 (t, *J* = 7.6 Hz, 3H), 0.50 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 234.43, 150.95, 139.83, 129.33, 129.09, 30.06, 16.26, -0.00.

**HRMS** (EI): Calcd. for C<sub>12</sub>H<sub>18</sub>OGe: 252.05639, Found: 252.05669.

**(4-(*tert*-Butyl)phenyl)(trimethylgermyl)methanone (3d)**



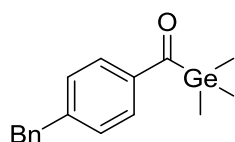
41.9 mg, 75% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.82 – 7.67 (m, 2H), 7.57 – 7.39 (m, 2H), 1.35 (s, 9H), 0.50 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 234.45, 157.69, 139.45, 128.81, 126.77, 32.18, 0.00.

**HRMS** (EI): Calcd. for C<sub>14</sub>H<sub>22</sub>OGe: 280.08770, Found: 280.08731.

**(4-Benzylphenyl)(trimethylgermyl)methanone (3e)**



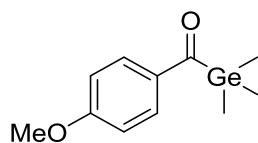
45.1 mg, 72% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.56 (dd, *J* = 8.5, 0.4 Hz, 2H), 7.19 – 6.87 (m, 7H), 3.86 (s, 2H), 0.31 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 234.56, 147.72, 141.09, 140.04, 130.37, 130.08, 129.71, 129.17, 127.50, 43.05, 0.00.

**HRMS** (EI): Calcd. for C<sub>17</sub>H<sub>20</sub>OGe: 314.07205, Found: 314.07062.

**(4-Methoxyphenyl)(trimethylgermyl)methanone (3f)**



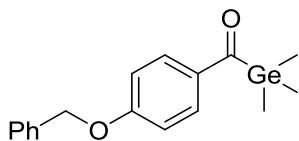
32.9 mg, 65% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.80 (d, *J* = 9.0 Hz, 2H), 6.97 (d, *J* = 9.0 Hz, 1H), 3.87 (s, 3H), 0.49 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 229.21, 161.16, 132.42, 127.87, 111.73, 53.29, -3.23.

**HRMS** (EI): Calcd. for C<sub>11</sub>H<sub>16</sub>O<sub>2</sub>Ge: 254.03566, Found: 254.03562.

**(4-(Benzyloxy)phenyl)(trimethylgermyl)methanone (3g)**



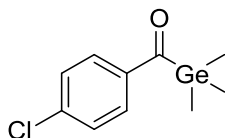
45.4 mg, 69% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.79 (d, *J* = 9.0 Hz, 2H), 7.49 – 7.29 (m, 5H), 7.04 (d, *J* = 9.0 Hz, 2H), 5.13 (d, *J* = 0.5 Hz, 2H), 0.49 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 232.44, 163.54, 137.25, 135.80, 131.10, 129.73, 129.26, 128.49, 115.81, 71.21, -0.00.

**HRMS** (EI): Calcd. for C<sub>17</sub>H<sub>20</sub>O<sub>2</sub>Ge: 330.06696, Found: 330.06694.

**(4-Chlorophenyl)(trimethylgermyl)methanone (3h)**



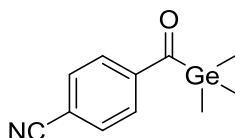
35.0 mg, 68% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.74 (d, *J* = 8.7 Hz, 2H), 7.52 – 7.42 (m, 2H), 0.50 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 232.59, 138.90, 138.53, 130.90, 128.77, -1.53.

**HRMS** (EI): Calcd. for C<sub>10</sub>H<sub>13</sub>OClGe: 257.98612, Found: 257.98638.

**4-((Trimethylgermyl)carbonyl)benzonitrile (3i)**



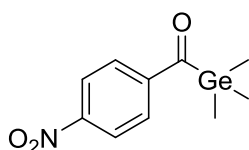
39.2 mg, 79% yield, yellow solid.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.89 – 7.83 (m, 2H), 7.81 – 7.78 (m, 2H), 0.53 (s, 9H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 235.45, 143.83, 134.11, 129.09, 119.32, 117.28, 0.00.

**HRMS** (EI): Calcd. for C<sub>11</sub>H<sub>13</sub>ONGe: 249.02034, Found: 249.02042.

**(4-Nitrophenyl)(trimethylgermyl)methanone (3j)**



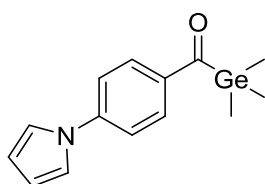
37.5 mg, 70% yield, pale yellow solid.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.35 (d,  $J = 9.0$  Hz, 2H), 7.91 (d,  $J = 8.9$  Hz, 2H), 0.54 (s, 9H).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  233.15, 139.41, 139.02, 129.28, 129.15, -1.01.

**HRMS** (EI): Calcd. for  $\text{C}_{10}\text{H}_{13}\text{O}_3\text{NGe}$ : 269.01017, Found: 269.00951.

**(4-(1H-pyrrol-1-yl)phenyl)(trimethylgermyl)methanone (3k)**



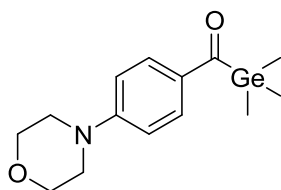
45.5 mg, 79% yield, yellow oil.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 8.8$  Hz, 2H), 7.50 (d,  $J = 8.8$  Hz, 2H), 7.25 – 7.09 (m, 2H), 6.46 – 6.33 (m, 2H), 0.53 (s, 9H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  233.58, 144.91, 138.80, 130.61, 120.76, 120.13, 112.67, -0.00.

**HRMS** (EI): Calcd. for  $\text{C}_{14}\text{H}_{17}\text{ONGe}$ : 289.05164, Found: 289.05175.

**(4-Morpholinophenyl)(trimethylgermyl)methanone (3l)**



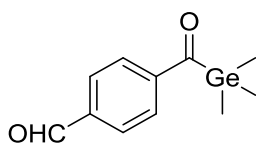
35.7 mg, 58% yield, yellow oil.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J = 9.1$  Hz, 2H), 6.90 (d,  $J = 9.0$  Hz, 2H), 3.94 – 3.71 (m, 4H), 3.40 – 3.19 (m, 4H), 0.48 (s, 9H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  231.52, 155.09, 133.61, 130.92, 114.45, 67.57, 48.51, -0.00.

**HRMS** (EI): Calcd. for  $\text{C}_{14}\text{H}_{21}\text{ONGe}$ : 309.07786, Found: 309.07806.

#### 4-((Trimethylgermyl)carbonyl)benzaldehyde (3m)



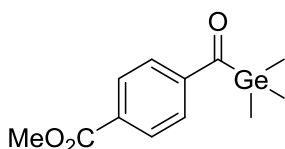
39.1 mg, 78% yield, yellow oil.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.11 (s, 1H), 8.07 – 7.97 (m, 2H), 7.94 – 7.89 (m, 2H), 0.53 (s, 9H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  236.29, 192.93, 145.15, 139.92, 131.41, 129.18, 0.00.

**HRMS** (EI): Calcd. for  $\text{C}_{11}\text{H}_{14}\text{O}_2\text{Ge}$ : 252.02001, Found: 252.02091.

#### Methyl 4-((trimethylgermyl)carbonyl)benzoate (3n)



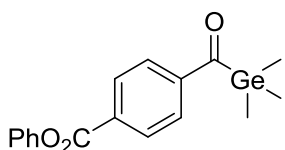
45.8 mg, 81% yield, yellow solid.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.22 – 8.08 (m, 2H), 7.92 – 7.76 (m, 2H), 3.95 (s, 3H), 0.52 (s, 9H).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  235.97, 167.50, 144.41, 134.75, 131.34, 128.58, 53.65, -0.00.

**HRMS** (EI): Calcd. for  $\text{C}_{12}\text{H}_{16}\text{O}_3\text{Ge}$ : 282.03057, Found: 282.03025.

#### Phenyl 4-((trimethylgermyl)carbonyl)benzoate (3o)



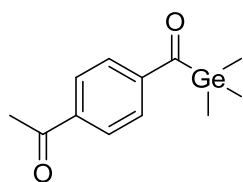
59.0 mg, 86% yield, yellow solid.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 (dd,  $J = 8.5, 1.3$  Hz, 2H), 7.90 (d,  $J = 8.8$  Hz, 2H), 7.65 (d,  $J = 7.4$  Hz, 1H), 7.57 – 7.49 (m, 2H), 7.40 – 7.32 (m, 2H), 0.53 (s, 9H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  233.85, 165.75, 155.53, 139.45, 135.01, 131.36, 130.42, 130.16, 129.78, 123.28, 0.00.

**HRMS** (EI): Calcd. for  $\text{C}_{17}\text{H}_{18}\text{O}_3\text{Ge}$ : 344.04622, Found: 344.04606.

### 1-(4-((Trimethylgermyl)carbonyl)phenyl)ethan-1-one (3p)



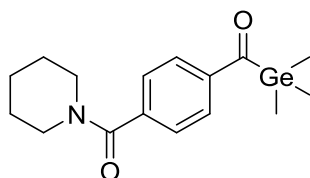
42.3 mg, 80% yield, yellow solid.

**<sup>1</sup>H NMR** (300 MHz, Chloroform-*d*)  $\delta$  8.10 – 8.02 (m, 2H), 7.88 – 7.81 (m, 2H), 2.65 (s, 3H), 0.52 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>)  $\delta$  236.03, 198.74, 144.27, 141.06, 130.03, 128.88, 28.13, 0.00.

**HRMS** (EI): Calcd. for C<sub>12</sub>H<sub>16</sub>O<sub>2</sub>Ge: 266.03566, Found: 266.03595.

### Piperidin-1-yl(4-((trimethylgermyl)carbonyl)phenyl)methanone (3q)



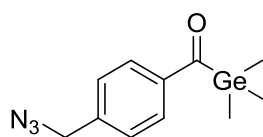
54.1 mg, 81% yield, yellow solid.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.94 – 7.72 (m, 2H), 7.58 – 7.43 (m, 2H), 3.73 (s, 2H), 3.31 (s, 2H), 1.69 (s, 4H), 1.52 (s, 2H), 0.51 (s, 9H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  235.29, 170.36, 142.03, 141.86, 129.56, 128.98, 128.37, 127.95, 49.83, 44.28, 27.72, 26.76, 25.69, -0.00.

**HRMS** (EI): Calcd. for C<sub>16</sub>H<sub>23</sub>O<sub>2</sub>NGe: 335.09351, Found: 335.09385.

### (4-(Azidomethyl)phenyl)(trimethylgermyl)methanone (3r)



43.4 mg, 78% yield, yellow oil.

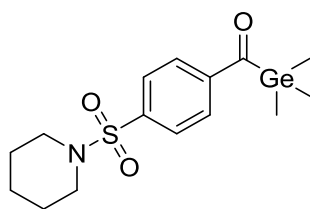
**<sup>1</sup>H NMR** (400 MHz, Chloroform-*d*)  $\delta$  7.80 – 7.76 (m, 1H), 7.73 (dt, *J* = 1.5, 0.7 Hz, 1H), 7.54 – 7.48 (m, 2H), 4.43 (s, 2H), 0.52 (s, 9H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  235.23, 142.20, 137.45, 133.44, 130.45, 129.09, 127.81, 55.54, -0.00.

**HRMS** (EI): Calcd. for C<sub>11</sub>H<sub>15</sub>ON<sub>3</sub>Ge: 279.04214, Found: 279.04136.



**(4-(Piperidin-1-ylsulfonyl)phenyl)(trimethylgermyl)methanone (3s)**



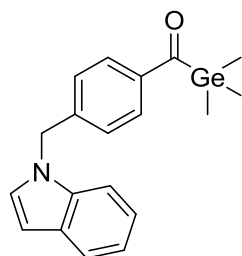
59.2 mg, 80% yield, yellow oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.02 – 7.72 (m, 4H), 3.15 – 2.86 (m, 4H), 1.74 – 1.57 (m, 4H), 1.53 – 1.37 (m, 2H), 0.53 (s, 9H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 235.59, 143.99, 141.32, 129.40, 129.12, 48.15, 26.40, 24.67, -0.00.

**HRMS** (ESI-TOF) m/z: Calcd. for C<sub>15</sub>H<sub>24</sub>O<sub>3</sub>NSGe [M+H]<sup>+</sup>: 372.0689, Found: 372.0684.

**(4-((1H-indol-1-yl)methyl)phenyl)(trimethylgermyl)methanone (3t)**



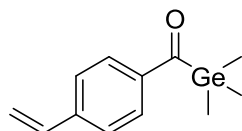
59.1 mg, 84% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.60 (ddd, *J* = 7.5, 1.5, 0.8 Hz, 2H), 7.36 (td, *J* = 7.6, 0.6 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.21 – 7.16 (m, 1H), 7.14 – 7.02 (m, 2H), 6.53 (dd, *J* = 3.2, 0.8 Hz, 1H), 5.35 (s, 2H), 0.21 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 235.82, 142.36, 139.96, 137.58, 132.19, 130.70, 130.25, 129.52, 127.72, 127.55, 123.40, 122.58, 121.41, 121.18, 110.97, 103.66, 51.05, 0.00.

**HRMS** (EI): Calcd. for C<sub>19</sub>H<sub>21</sub>ONGe: 353.08294, Found: 353.08344.

**(Trimethylgermyl)(4-vinylphenyl)methanone (3u)**



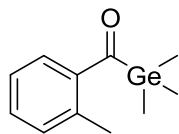
30.9 mg, 62% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.84 – 7.70 (m, 2H), 7.56 – 7.43 (m, 2H), 6.87 – 6.64 (m, 1H), 5.87 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.40 (dd, *J* = 10.9, 0.7 Hz, 1H), 0.50 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 233.36, 141.71, 135.86, 127.94, 126.38, 116.49, -1.28.

**HRMS** (EI): Calcd. for C<sub>12</sub>H<sub>16</sub>OGe: 250.04074, Found: 250.04133.

***o*-Tolyl(trimethylgermyl)methanone (3v)**



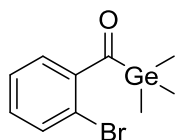
33.2 mg, 70% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.61 (d, *J* = 3.1 Hz, 1H), 7.34 (t, *J* = 3.4 Hz, 2H), 7.29 – 7.18 (m, 1H), 2.47 (s, 3H), 0.46 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 236.97, 138.36, 133.78, 129.89, 128.91, 128.74, 123.31, 18.64, -3.45.

**HRMS** (EI): Calcd. for C<sub>11</sub>H<sub>16</sub>O<sup>72</sup>Ge: 236.04164, Found: 236.04228.

**(2-Bromophenyl)(trimethylgermyl)methanone (3w)**



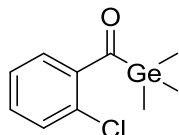
32.0 mg, 53% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.57 (ddd, *J* = 7.9, 1.2, 0.4 Hz, 1H), 7.37 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.14 (ddd, *J* = 7.5, 1.8, 0.4 Hz, 1H), 0.44 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 234.69, 134.63, 132.70, 129.16, 128.48, -0.00.

**HRMS** (EI): Calcd. for C<sub>10</sub>H<sub>14</sub>OBrGe: 302.94343, Found: 302.94492.

**(2-Chlorophenyl)(trimethylgermyl)methanone (3x)**



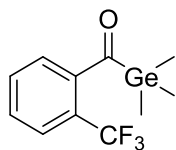
37.1 mg, 72% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.42 – 7.29 (m, 3H), 7.25 – 7.16 (m, 1H), 0.43 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 241.67, 144.22, 133.02, 132.14, 131.60, 128.78, 128.73, 0.00.

**HRMS** (EI): Calcd. for C<sub>10</sub>H<sub>13</sub>OClGe: 257.98612, Found: 257.98522.

**(2-(Trifluoromethyl)phenyl)(trimethylgermyl)methanone (3y)**



44.8 mg, 77% yield, brown oil.

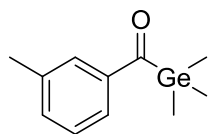
**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.70 (m, 1H), 7.62 (m, 1H), 7.56 – 7.47 (m, 1H), 7.26 – 7.22 (m, 1H), 0.40 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 238.52, 142.12, 129.54, 127.29, 124.73 (q, *J* = 5.1 Hz), 123.32, 122.92, 119.70, -4.31.

**<sup>19</sup>F NMR** (282 MHz, CDCl<sub>3</sub>) δ -57.50.

**HRMS** (ESI-TOF) *m/z*: Calcd. for C<sub>11</sub>H<sub>13</sub>OF<sub>3</sub>GeNa [M+Na]<sup>+</sup>: 315.0507, Found: 315.0502.

***m*-Tolyl(trimethylgermyl)methanone (3z)**



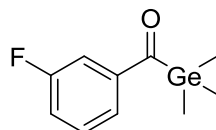
38.8 mg, 82% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.61 – 7.56 (m, 2H), 7.41 – 7.31 (m, 2H), 2.42 (s, 3H), 0.50 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 234.78, 141.18, 138.93, 133.98, 128.92, 127.99, 125.87, 21.72, -0.72.

**HRMS** (EI): Calcd. for C<sub>11</sub>H<sub>16</sub>OGe: 238.04074, Found: 238.04132.

**(3-Fluorophenyl)(trimethylgermyl)methanone (3aa)**



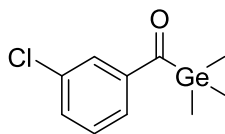
40.5 mg, 84% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.64 – 7.58 (m, 1H), 7.52 – 7.41 (m, 2H), 7.29 – 7.19 (m, 1H), 0.51 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 234.29, 164.29 (d, *J* = 248.9 Hz), 143.85 (d, *J* = 4.8 Hz), 131.59 (d, *J* = 7.6 Hz), 125.26 (d, *J* = 3.0 Hz), 121.02 (d, *J* = 21.9 Hz), 114.54 (d, *J* = 21.4 Hz), -0.00.

**HRMS** (EI): Calcd. for C<sub>10</sub>H<sub>13</sub>OFGe: 242.01567, Found: 242.01555.

**(3-Chlorophenyl)(trimethylgermyl)methanone (3ab)**



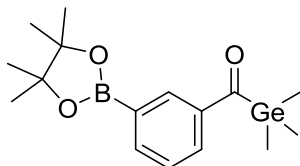
39.2 mg, 76% yield, brown oil.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 – 7.62 (m, 2H), 7.50 (dd,  $J = 2.1, 1.3$  Hz, 1H), 7.46 – 7.39 (m, 1H), 0.51 (s, 9H).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  231.46, 140.24, 133.48, 130.97, 128.33, 125.38, 124.47, -2.92.

**HRMS** (ED): Calcd. for  $\text{C}_{10}\text{H}_{13}\text{OCiGe}$ : 257.98612, Found: 257.98651.

**(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)(trimethylgermyl)methanone (3ac)**



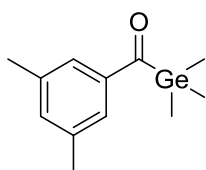
50.9 mg, 73% yield, yellow solid.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.24 (s, 1H), 7.96 (dt,  $J = 7.3, 1.3$  Hz, 1H), 7.89 – 7.82 (m, 1H), 7.52 – 7.43 (m, 1H), 1.35 (s, 12H), 0.50 (s, 9H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  235.79, 141.26, 140.11, 135.56, 131.16, 129.24, 85.19, 26.02, 0.00.

**HRMS** (ED): Calcd. for  $\text{C}_{16}\text{H}_{25}\text{O}_3\text{BGe}$ : 350.11030, Found: 350.10929.

**(3,5-Dimethylphenyl)(trimethylgermyl)methanone (3ad)**



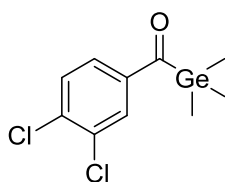
36.6 mg, 73% yield, yellow oil.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (dt,  $J = 1.7, 0.6$  Hz, 2H), 7.20 – 7.16 (m, 1H), 2.38 (d,  $J = 0.7$  Hz, 6H), 0.49 (s, 9H).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  234.43, 140.93, 138.27, 134.39, 125.43, 21.16, -1.11.

**HRMS** (ED): Calcd. for  $\text{C}_{12}\text{H}_{18}\text{OGe}$ : 252.05639, Found: 252.05640.

**(3,4-Dichlorophenyl)(trimethylgermyl)methanone (3ae)**



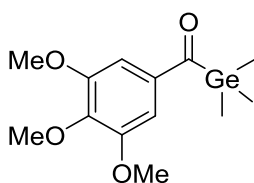
45.5 mg, 78% yield, brown oil.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (dd,  $J = 1.8, 0.5$  Hz, 1H), 7.69 – 7.52 (m, 2H), 0.51 (s, 9H).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  233.3, 141.0, 138.5, 134.8, 132.1, 130.3, 128.1, -0.0.

**HRMS** (ED): Calcd. for  $\text{C}_{10}\text{H}_{12}\text{OCl}_2\text{Ge}$ : 291.94715, Found: 291.94691.

**(3,4,5-Trimethoxyphenyl)(trimethylgermyl)methanone (3af)**



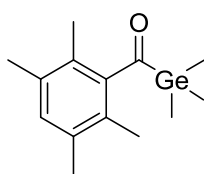
58.8 mg, 94% yield, yellow oil.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.03 (s, 2H), 3.85 (d,  $J = 1.1$  Hz, 9H), 0.45 (s, 9H).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  232.77, 154.22, 143.25, 136.98, 105.97, 61.82, 57.05, -0.00.

**HRMS** (ED): Calcd. for  $\text{C}_{13}\text{H}_{20}\text{O}_4\text{Ge}$ : 314.05679, Found: 314.05692.

**(2,3,5,6-Tetramethylphenyl)(trimethylgermyl)methanone (3ag)**



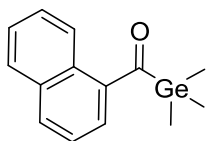
36.8 mg, 66% yield, colorless solid.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.91 (s, 1H), 2.19 (d,  $J = 0.6$  Hz, 6H), 1.96 (d,  $J = 0.5$  Hz, 6H), 0.33 (s, 9H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  255.34, 148.05, 136.71, 133.60, 128.99, 21.64, 17.91, 0.00.

**HRMS** (ED): Calcd. for  $\text{C}_{14}\text{H}_{22}\text{OGe}$ : 280.08770, Found: 280.08851.

### Naphthalen-1-yl(trimethylgermyl)methanone (3ah)



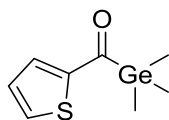
38.8 mg, 71% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 8.84 – 8.70 (m, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.89 – 7.80 (m, 2H), 7.62 – 7.48 (m, 3H), 0.51 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 240.21, 139.01, 135.04, 133.59, 132.17, 129.45, 129.24, 129.12, 127.48, 126.75, 125.37, -0.00.

**HRMS** (EI): Calcd. for C<sub>14</sub>H<sub>16</sub>OGe: 274.04074, Found: 274.04125.

### Thiophen-2-yl(trimethylgermyl)methanone (3ai)



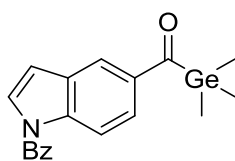
34.3 mg, 75% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.72 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.66 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.18 (dd, *J* = 4.9, 3.8 Hz, 1H), 0.52 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 223.81, 150.01, 133.68, 133.47, 128.35, -1.08.

**HRMS** (EI): Calcd. for C<sub>8</sub>H<sub>12</sub>OSGe: 229.98152, Found: 229.98180.

### (1-Benzoyl-1H-indol-5-yl)(trimethylgermyl)methanone (3aj)



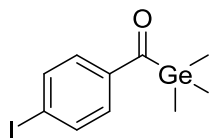
53.4 mg, 73% yield, slight yellow solid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 8.44 – 8.33 (m, 1H), 7.99 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.80 (ddd, *J* = 8.7, 1.7, 0.4 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.60 – 7.52 (m, 1H), 7.51 – 7.43 (m, 2H), 7.32 (dd, *J* = 3.7, 0.4 Hz, 1H), 6.66 (dd, *J* = 3.8, 0.8 Hz, 1H), 0.48 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 234.29, 169.59, 139.46, 138.19, 134.90, 133.27, 131.75, 130.23, 129.93, 129.66, 125.75, 122.16, 117.34, 110.12, -0.00.

**HRMS** (EI): Calcd. for C<sub>19</sub>H<sub>19</sub>O<sub>2</sub>NGe: 367.06221, Found: 367.06237.

**(4-Iodophenyl)(trimethylgermyl)methanone (3ak)**



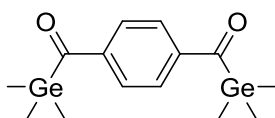
35.6 mg, 51% yield, yellow oil.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J = 8.6$  Hz, 2H), 7.50 (d,  $J = 8.6$  Hz, 2H), 0.50 (s, 9H).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  232.66, 138.76, 137.16, 128.03, 99.96, -2.12.

**HRMS** (EI): Calcd. for  $[\text{M}+\text{H}]^+$   $\text{C}_{10}\text{H}_{14}\text{OIGe}$ : 350.92956, Found: 350.92938.

**1,4-Phenylenebis((trimethylgermyl)methanone) (3al)**



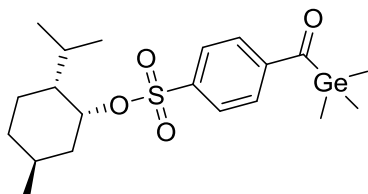
50.0 mg, 68% yield, yellow solid.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (s, 4H), 0.53 (s, 18H).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  236.06, 143.90, 129.19, -0.00.

**HRMS** (EI): Calcd. for  $\text{C}_{14}\text{H}_{22}\text{O}_2^{72}\text{GeGe}$ : 368.00469, Found: 368.00453.

**(1R,2R,5S)-2-Isopropyl-5-methylcyclohexyl 4-((trimethylgermyl)carbonyl)benzenesulfonate (3am)**



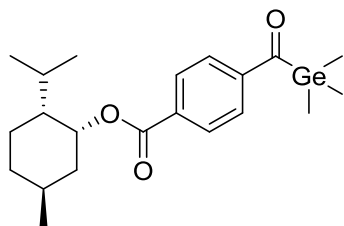
72.4 mg, 82% yield, yellow solid.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 – 7.94 (m, 2H), 7.86 – 7.79 (m, 2H), 4.41 (td,  $J = 10.8$ , 4.6 Hz, 1H), 2.06 (ddd,  $J = 10.7$ , 3.2, 1.7 Hz, 1H), 1.79 (td,  $J = 7.0$ , 2.5 Hz, 1H), 1.66 – 1.51 (m, 2H), 1.40 – 1.25 (m, 2H), 1.13 (td,  $J = 12.1$ , 10.9 Hz, 1H), 1.00 – 0.87 (m, 1H), 0.79 (dd,  $J = 14.3$ , 6.8 Hz, 7H), 0.46 (s, 12H).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  235.72, 144.60, 142.35, 129.54, 129.17, 86.08, 48.83, 43.31, 34.96, 32.98, 26.86, 24.25, 23.11, 22.08, 16.56, 0.00.

**HRMS** (EI): Calcd. for  $\text{C}_{20}\text{H}_{32}\text{O}_4\text{SGe}$ : 442.02276, Found: 442.02299.

**(1R,2R,5S)-2-Isopropyl-5-methylcyclohexyl 4-((trimethylgermyl)carbonyl)benzoate (3an)**



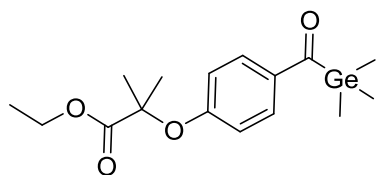
67.2 mg, 83% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 8.08 (d, *J* = 8.7 Hz, 2H), 7.76 (d, *J* = 8.7 Hz, 2H), 5.01 – 4.73 (m, 1H), 2.19 – 1.99 (m, 1H), 1.88 (td, *J* = 7.0, 2.8 Hz, 1H), 1.73 – 1.60 (m, 2H), 1.57 – 1.38 (m, 2H), 1.15 – 0.95 (m, 2H), 0.85 (dd, *J* = 6.8, 3.0 Hz, 7H), 0.72 (d, *J* = 6.9 Hz, 3H), 0.44 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 235.94, 166.50, 144.22, 135.48, 131.30, 128.58, 76.63, 48.46, 42.13, 35.48, 32.67, 27.74, 24.81, 23.25, 21.99, 17.71, -0.00.

**HRMS** (EI): Calcd. for C<sub>21</sub>H<sub>32</sub>O<sub>3</sub>Ge: 406.15577, Found: 406.15657.

**Ethyl 2-methyl-2-(4-((trimethylgermyl)carbonyl)phenoxy)propanoate (3ao)**



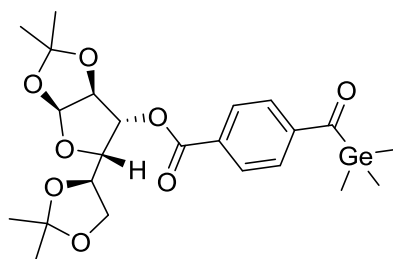
52.3 mg, 74% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 7.66 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.59 (s, 6H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.41 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 232.73, 174.77, 160.67, 135.98, 130.65, 118.58, 80.38, 62.74, 26.46, 15.08, -0.00.

**HRMS** (EI): Calcd. for C<sub>16</sub>H<sub>24</sub>O<sub>4</sub>Ge: 354.08809, Found: 354.08700.

**(3aS,5S,6R,6aS)-5-((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl 4-((trimethylgermyl)carbonyl)benzoate (3ap)**



81.5 mg, 80% yield, yellow foam.

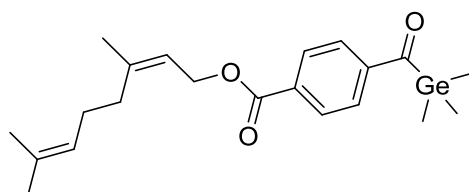


**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 8.14 (d, *J* = 8.7 Hz, 2H), 7.83 (d, *J* = 8.6 Hz, 2H), 5.95 (d, *J* = 3.7 Hz, 1H), 5.51 (d, *J* = 2.8 Hz, 1H), 4.69 – 4.58 (m, 1H), 4.42 – 4.25 (m, 2H), 4.19 – 4.00 (m, 2H), 1.55 (s, 3H), 1.41 (s, 3H), 1.32 (s, 3H), 1.26 (s, 3H), 0.51 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 236.04, 165.68, 144.68, 134.06, 131.51, 128.71, 113.68, 110.72, 106.36, 84.56, 81.16, 73.77, 68.59, 28.11, 27.96, 27.45, 26.46, -0.00.

**HRMS** (EI): Calcd. for C<sub>23</sub>H<sub>32</sub>O<sub>8</sub>Ge: 510.13035, Found: 510.13134.

**(Z)-3,7-Dimethylocta-2,6-dien-1-yl 4-((trimethylgermyl)carbonyl)benzoate (3aq)**



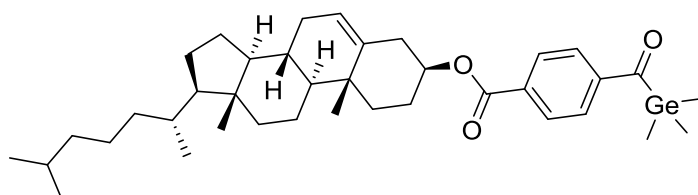
72.6 mg, 90% yield, yellow powder.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 8.23 – 8.08 (m, 2H), 7.90 – 7.72 (m, 2H), 5.62 – 5.38 (m, 1H), 5.18 – 5.02 (m, 1H), 4.84 (dd, *J* = 7.3, 1.0 Hz, 2H), 2.24 – 2.05 (m, 4H), 1.80 (d, *J* = 1.2 Hz, 3H), 1.67 (dd, *J* = 1.3, 0.6 Hz, 3H), 1.61 (dd, *J* = 1.3, 0.6 Hz, 3H), 0.51 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 236.01, 167.03, 144.42, 144.28, 135.14, 133.47, 131.35, 128.55, 124.72, 120.14, 63.20, 33.46, 27.88, 26.92, 24.77, 18.90, 0.00.

**HRMS** (EI): Calcd. for C<sub>21</sub>H<sub>30</sub>O<sub>3</sub>Ge: 404.14012, Found: 404.14080.

**(3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-((trimethylgermyl)carbonyl)benzoate (3ar)**



124.8 mg, 98% yield, yellow solid.

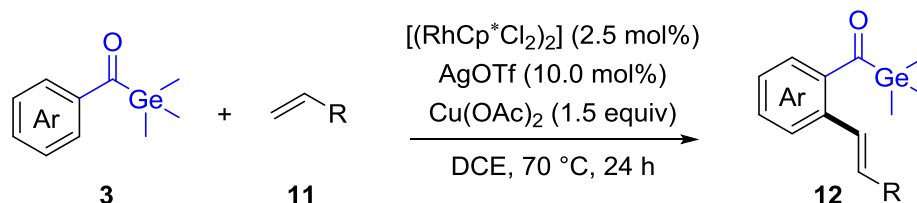
**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 8.15 (d, *J* = 8.7 Hz, 2H), 7.82 (d, *J* = 8.7 Hz, 2H), 5.43 (d, *J* = 5.2 Hz, 1H), 4.88 (m, 1H), 2.47 (d, *J* = 7.9 Hz, 2H), 2.11 – 0.97 (m, 29H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 1.4 Hz, 3H), 0.86 (d, *J* = 1.3 Hz, 3H), 0.69 (s, 3H), 0.51 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 235.48, 165.87, 143.74, 140.16, 134.95, 130.77, 128.01, 123.66, 75.83, 57.39, 56.84, 50.75, 43.03, 40.44, 40.22, 38.86, 37.70, 37.35, 36.89, 36.50,

32.64, 32.58, 28.93, 28.71, 28.55, 25.00, 24.53, 23.52, 23.26, 21.76, 20.06, 19.42, 12.57, -0.52.

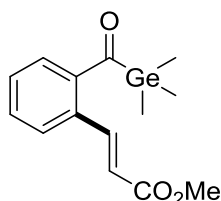
**HRMS** (EI): Calcd. for C<sub>38</sub>H<sub>58</sub>O<sub>3</sub>Ge: 636.35923, Found: 636.35975.

### General procedure for synthesis of *ortho*-olefinated acylgermanes (**12a-g**)



$[(\text{Cp}^*\text{RhCl}_2)_2]$  (2.5 mol%), AgOTf (10.0 mol%), Cu(OAc)<sub>2</sub> (1.5 equiv.) and DCE (0.5 mL) were added to a Schlenk tube under argon and the resulting mixture was stirred for 5 min. The acylgermane (0.2 mmol, 1.0 equiv.) was then added, followed by the acrylate (0.4 mmol, 2.0 equiv.). After sealing, the reaction was stirred at 70 °C for 24 h. After cooling to r.t., the crude reaction mixtures were purified by flash chromatography to give **12a-g** (20:1-10:1, pentane/EtOAc).

### Methyl (*E*)-3-(2-((trimethylgermyl)carbonyl)phenyl)acrylate (**12a**)



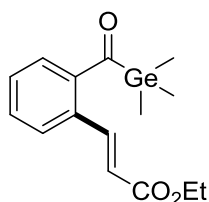
50.9 mg, 83% yield, yellow oil.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.04 (d, *J* = 15.9 Hz, 1H), 7.66 – 7.43 (m, 4H), 6.27 (d, *J* = 15.9 Hz, 1H), 3.81 (s, 3H), 0.46 (s, 9H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 237.22, 164.77, 141.69, 139.44, 130.21, 129.22, 127.79, 127.32, 126.10, 118.56, 49.58, -3.47.

**HRMS** (EI): Calcd. for C<sub>14</sub>H<sub>18</sub>O<sub>3</sub>Ge: 308.04622, Found: 308.04567.

### Ethyl (*E*)-3-(2-((trimethylgermyl)carbonyl)phenyl)acrylate (**12b**)



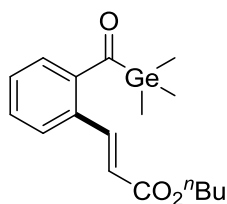
46.9 mg, 73% yield, yellow oil.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (dd,  $J = 15.9, 0.4$  Hz, 1H), 7.67 – 7.42 (m, 4H), 6.26 (dd,  $J = 15.9, 0.4$  Hz, 1H), 4.27 (qd,  $J = 7.2, 0.4$  Hz, 2H), 1.34 (td,  $J = 7.1, 0.4$  Hz, 3H), 0.46 (s, 9H).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  240.94, 167.81, 144.81, 143.15, 133.75, 132.63, 130.98, 130.78, 129.56, 122.58, 61.87, 15.65, 0.00.

**HRMS** (EI): Calcd. for  $\text{C}_{15}\text{H}_{20}\text{O}_3\text{Ge}$ : 322.06187, Found: 322.06181.

### Butyl (*E*)-3-(2-((trimethylgermyl)carbonyl)phenyl)acrylate (**12c**)



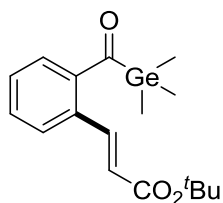
48.9 mg, 70% yield, yellow oil.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (dd,  $J = 15.9, 0.4$  Hz, 1H), 7.66 – 7.40 (m, 4H), 6.26 (d,  $J = 15.9$  Hz, 1H), 4.21 (t,  $J = 6.7$  Hz, 2H), 1.77 – 1.58 (m, 2H), 1.51 – 1.35 (m, 2H), 0.96 (t,  $J = 7.3$  Hz, 3H), 0.45 (s, 9H).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  239.41, 166.29, 143.14, 141.66, 132.10, 130.96, 129.24, 129.16, 127.93, 120.98, 64.19, 30.47, 18.91, 13.45, -1.64.

**HRMS** (EI): Calcd. for  $\text{C}_{17}\text{H}_{24}\text{O}_3\text{Ge}$ : 350.09317, Found: 350.09307.

### *tert*-Butyl (*E*)-3-(2-((trimethylgermyl)carbonyl)phenyl)acrylate (**12d**)



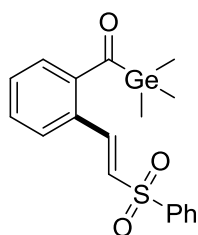
36.3 mg, 52% yield, yellow oil.

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (dd,  $J = 15.8, 0.6$  Hz, 1H), 7.61 – 7.39 (m, 4H), 6.19 (d,  $J = 15.8$  Hz, 1H), 1.53 (s, 9H), 0.44 (s, 9H).

$^{13}\text{C NMR}$  (75 MHz,  $\text{CDCl}_3$ )  $\delta$  237.83, 163.61, 140.08, 140.02, 130.36, 128.95, 127.11, 127.01, 126.04, 121.18, 78.43, 26.05, -3.50.

**HRMS** (ESI-TOF): Calcd. for  $\text{C}_{17}\text{H}_{24}\text{O}_3\text{GeNa}$  [ $\text{M}+\text{Na}$ ] $^+$ : 369.0860, Found: 369.0870.

**(E)-2-(2-(phenylsulfonyl)vinyl)phenyl(trimethylgermyl)methanone (12e)**



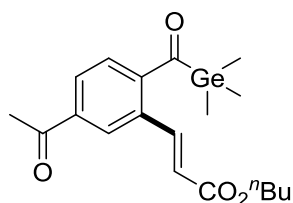
65.4 mg, 84% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 8.13 – 8.00 (m, 3H), 7.75 – 7.66 (m, 1H), 7.61 – 7.45 (m, 6H), 6.68 (d, *J* = 15.3 Hz, 1H), 0.49 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 239.62, 144.18, 142.56, 141.90, 134.52, 132.89, 131.89, 131.63, 131.40, 130.60, 130.50, 129.97, 129.02.

**HRMS** (ESI-TOF): Calcd. for C<sub>18</sub>H<sub>20</sub>O<sub>3</sub>GeSNa [M+Na]<sup>+</sup>: 409.0268, Found: 409.0274.

**Butyl (E)-3-(5-acetyl-2-((trimethylgermyl)carbonyl)phenyl)acrylate (12f)**



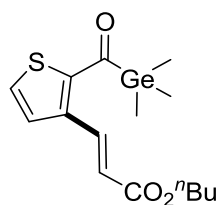
53.2 mg, 68% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 8.16 (s, 1H), 8.04 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.92 (d, *J* = 15.9 Hz, 1H), 7.56 (dd, *J* = 8.0, 0.5 Hz, 1H), 6.37 (d, *J* = 15.9 Hz, 1H), 4.22 (t, *J* = 6.6 Hz, 2H), 2.66 (s, 3H), 1.76 – 1.64 (m, 2H), 1.49 – 1.39 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.45 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 238.95, 194.83, 164.21, 143.54, 139.90, 136.47, 130.39, 127.15, 126.59, 125.97, 120.54, 62.67, 28.74, 24.80, 17.20, 11.74, -3.55.

**HRMS** (EI): Calcd. for C<sub>19</sub>H<sub>26</sub>O<sub>4</sub>Ge: 392.10374, Found: 392.10366.

**Butyl (E)-3-(2-((trimethylgermyl)carbonyl)thiophen-3-yl)acrylate (12g)**



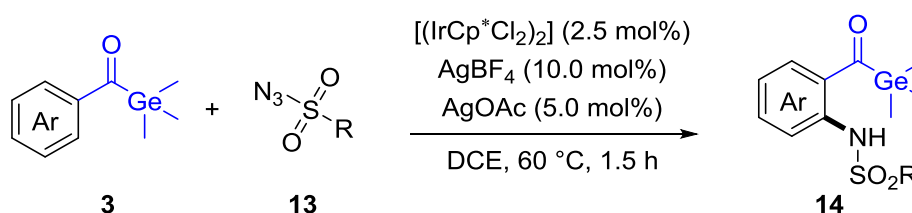
61.8 mg, 87% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 8.32 (d, *J* = 16.1 Hz, 1H), 7.54 (dd, *J* = 5.1, 0.7 Hz, 1H), 7.37 (dd, *J* = 5.2, 0.6 Hz, 1H), 6.37 (d, *J* = 16.1 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.75 – 1.64 (m, 2H), 1.48 – 1.36 (m, 2H), 1.01 – 0.89 (m, 3H), 0.52 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 225.56, 166.37, 144.55, 137.17, 136.63, 130.89, 126.76, 122.27, 64.21, 30.39, 18.79, 13.36, -1.64.

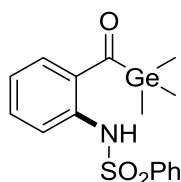
**HRMS** (EI): Calcd. for C<sub>15</sub>H<sub>22</sub>O<sub>3</sub>SGe: 356.04959, Found: 356.04967.

### General procedure for synthesis of *ortho*-amidation acylgermanes (**14a-f**)



[(IrCp\*Cl<sub>2</sub>)<sub>2</sub>] (2.5 mol%), AgBF<sub>4</sub> (10.0 mol%), AgOAc (5.0 mol%) and DCE (0.5 mL) were added to a Schlenk tube and the resulting mixture was stirred for 5 min. The acylgermane (0.2 mmol, 1.0 equiv.) was then added, followed by **13** (0.24 mmol, 1.2 equiv.). After sealing, the reaction was stirred at 60 °C for 1.5 h. After cooling to r.t., the crude reaction mixtures were purified by flash chromatography to give **14a-f** (10:1-4:1, pentane/EtOAc).

### *N*-(2-((Trimethylgermyl)carbonyl)phenyl)benzenesulfonamide (**14a**)



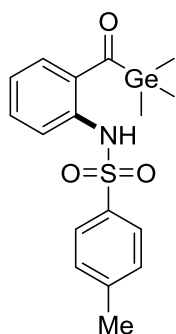
65.8 mg, 87% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 11.43 (s, 1H), 7.88 – 7.81 (m, 2H), 7.75 – 7.63 (m, 2H), 7.52 – 7.38 (m, 4H), 7.20 – 7.10 (m, 1H), 0.45 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 240.68, 140.50, 137.89, 135.50, 135.06, 133.79, 129.83, 128.07, 127.44, 123.74, 120.26, 0.00.

**HRMS** (EI): Calcd. for C<sub>16</sub>H<sub>19</sub>O<sub>3</sub>SNGe: 379.02919, Found: 379.02853.

#### 4-Methyl-*N*-(2-((trimethylgermyl)carbonyl)phenyl)benzenesulfonamide (14b)



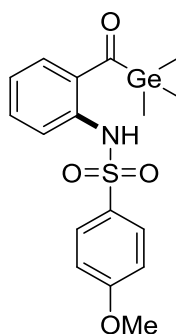
75.3 mg, 96% yield, yellow oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 11.38 (s, 1H), 7.71 (dq, *J* = 5.3, 1.9 Hz, 3H), 7.67 – 7.63 (m, 1H), 7.45 – 7.39 (m, 1H), 7.23 – 7.10 (m, 3H), 2.35 (s, 3H), 0.45 (s, 9H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 240.54, 144.67, 138.00, 137.50, 135.49, 135.05, 130.45, 128.14, 127.40, 123.61, 120.19, 22.38, 0.00.

**HRMS** (EI): Calcd. for C<sub>17</sub>H<sub>21</sub>O<sub>3</sub>SNGe: 393.04484, Found: 393.04433.

#### 4-Methoxy-*N*-(2-((trimethylgermyl)carbonyl)phenyl)benzenesulfonamide (14c)



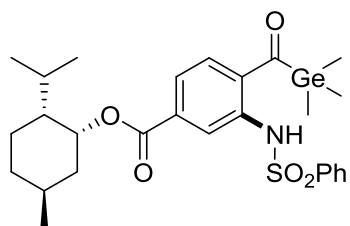
75.9 mg, 93% yield, yellow oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 11.36 (s, 1H), 7.79 – 7.70 (m, 3H), 7.64 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.42 (ddd, *J* = 8.5, 7.4, 1.5 Hz, 1H), 7.17 – 7.10 (m, 1H), 6.88 (d, *J* = 9.0 Hz, 2H), 3.81 (s, 3H), 0.46 (s, 9H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ 240.50, 163.90, 138.06, 135.51, 135.02, 132.01, 130.26, 127.30, 123.51, 120.07, 114.95, 56.43, 0.00.

**HRMS** (EI): Calcd. for C<sub>17</sub>H<sub>21</sub>O<sub>4</sub>SNGe: 409.03976, Found: 409.03976.

**(1*R*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl 3-(phenylsulfonamido)-4-((trimethylgermyl)carbonyl)benzoate (14d)**

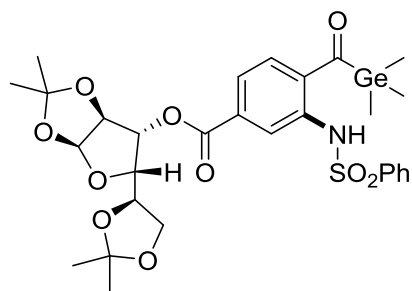


104.2 mg, 93% yield, yellow oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 11.36 (s, 1H), 8.27 (s, 1H), 7.94 – 7.85 (m, 2H), 7.81 – 7.76 (m, 2H), 7.57 – 7.40 (m, 3H), 4.92 (td, *J* = 10.8, 4.4 Hz, 1H), 2.16 – 2.07 (m, 1H), 1.93 (td, *J* = 7.0, 2.8 Hz, 1H), 1.76 (dt, *J* = 13.8, 3.5 Hz, 2H), 1.64 – 1.52 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 1H), 1.19 – 1.04 (m, 2H), 0.95 (dd, *J* = 6.8, 2.5 Hz, 6H), 0.79 (d, *J* = 6.9 Hz, 3H), 0.47 (s, 9H).  
**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 240.00, 164.06, 139.06, 136.55, 134.97, 133.98, 132.74, 128.65, 127.62, 127.04, 122.96, 119.65, 75.48, 46.85, 40.46, 33.85, 31.07, 26.17, 23.21, 21.63, 20.44, 16.14, -1.30.

**HRMS** (EI): Calcd. for C<sub>27</sub>H<sub>37</sub>O<sub>5</sub>SNGe: 561.15987, Found: 561.16000.

**(3*aS*,5*S*,6*R*,6*aS*)-5-((*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl 3-(phenylsulfonamido)-4-((trimethylgermyl)carbonyl)benzoate (14e)**

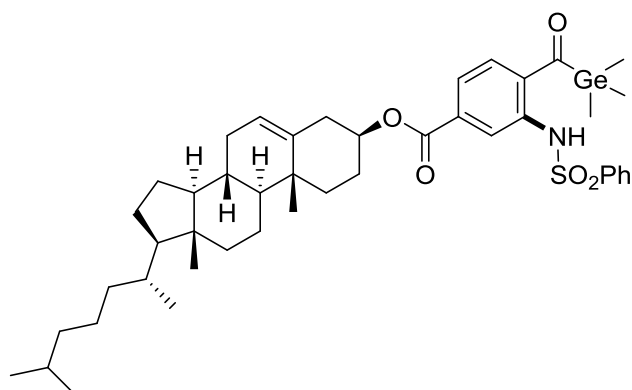


118.2 mg, 89% yield, yellow solid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 11.32 (s, 1H), 8.27 (dd, *J* = 1.5, 0.5 Hz, 1H), 7.92 – 7.71 (m, 4H), 7.60 – 7.40 (m, 3H), 5.94 (d, *J* = 3.7 Hz, 1H), 5.47 (d, *J* = 2.8 Hz, 1H), 4.61 (dd, *J* = 3.7, 0.6 Hz, 1H), 4.44 – 4.26 (m, 2H), 4.11 (dd, *J* = 8.1, 4.7 Hz, 2H), 1.56 (s, 3H), 1.41 (s, 3H), 1.33 (s, 3H), 1.26 (s, 3H), 0.47 (s, 9H).  
**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 239.00, 162.08, 137.98, 135.56, 132.90, 132.36, 131.65, 127.64, 126.81, 125.84, 121.81, 118.78, 111.01, 108.01, 103.61, 81.70, 78.47, 70.94, 65.92, 25.41, 25.22, 24.72, 23.65, -2.45.

**HRMS** (EI): Calcd. for C<sub>29</sub>H<sub>37</sub>O<sub>10</sub>SNGe: 665.13445, Found: 665.13464.

**(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-Tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl 3-(phenylsulfonamido)-4-((trimethylgermyl)carbonyl)benzoate (**14f**)**



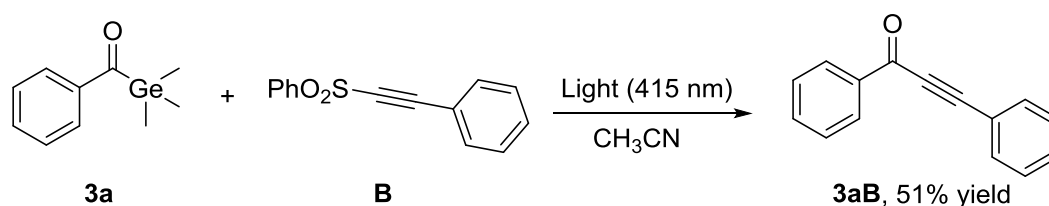
142.3 mg, 90% yield, yellow solid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 11.30 (s, 1H), 8.24 (s, 1H), 7.93 – 7.87 (m, 2H), 7.78 (d, *J* = 0.9 Hz, 2H), 7.57 – 7.40 (m, 3H), 5.43 (d, *J* = 4.9 Hz, 1H), 4.89 – 4.77 (m, 1H), 2.46 (d, *J* = 7.7 Hz, 2H), 2.10 – 1.05 (m, 29H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 1.3 Hz, 3H), 0.86 (d, *J* = 1.3 Hz, 3H), 0.70 (s, 3H), 0.46 (s, 9H).

**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 239.60, 163.54, 138.70, 138.59, 136.08, 134.56, 133.50, 132.39, 128.30, 127.41, 126.75, 122.64, 122.35, 119.54, 74.78, 55.97, 55.43, 49.32, 41.60, 39.01, 38.79, 37.39, 36.24, 35.92, 35.46, 35.06, 31.20, 31.15, 27.50, 27.28, 27.09, 23.56, 23.11, 22.08, 21.83, 20.33, 18.65, 18.00, 11.14, -1.67.

**HRMS** (EI): Calcd. for C<sub>44</sub>H<sub>63</sub>O<sub>5</sub>SNGe: 791.36386, Found: 791.36375.

**Procedure for alkynone synthesis.**

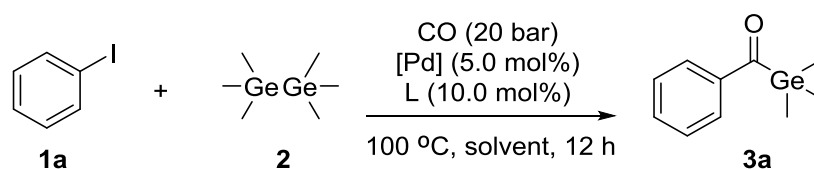


A mixture of phenyl(trimethylgermyl)methanone **3a** (0.10 mmol, 22.4 mg, 1.0 equiv.), ((phenylethynyl)-sulfonyl)benzene **B** (0.15 mmol, 36.3 mg, 1.5 equiv.) and CH<sub>3</sub>CN (1.5 mL) was stirred at room temperature with *the light (415 nm)*<sup>[S1]</sup> for 12 h. After quenching the reaction, the mixture was purified by flash chromatography on silica gel to give the products **3aB** (10.5 mg, 51% yield) as a brown oil. **<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ 8.26 – 8.19 (m, 2H), 7.71 – 7.58 (m, 3H), 7.56 – 7.36 (m, 5H). **<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ 178.01, 136.90, 134.17, 133.09, 130.85, 129.59, 128.73, 128.67, 120.12, 93.15, 86.95.



## References

- [1] a) S. Panda, J. M. Ready, *J. Am. Chem. Soc.* **2018**, *140*, 13242–13252; b) T. M. Beck, B. Breit, *Angew. Chem. Int. Ed.* **2017**, *56*, 1903–1907; c) B. Zhang, H. Jiao, D. Michalik, S. Kloß, L. M. Deter, D. Selent, A. Spannenberg, R. Franke, A. Börner, *ACS Catal.* **2016**, *6*, 7554–7565.
- [2] C.-J. Yu, R. Li, P. Gu, *Tetrahedron Lett.* **2016**, *57*, 3568-3570.
- [3] Y. Obora, M. Nakanishi, M. Tokunaga, Y. Tsuji, *J. Org. Chem.* **2002**, *67*, 5835-5837.
- [4] C. V. Galliford, K. A. Scheidt, *Chem. Commun.* **2008**, 1926-1928.
- [5] T. Matsuda, K. Mizuno, S. Watanuki, *J. Organomet. Chem.* **2014**, *765*, 64-67.
- [6] a) A. E. Mattson, A. R. Bharadwaj, K. A. Scheidt, *J. Am. Chem. Soc.* **2004**, *126*, 2314-2315; b) A. E. Mattson, A. R. Bharadwaj, A. M. Zuhl, K. A. Scheidt, *J. Org. Chem.* **2006**, *71*, 5715-5724.
- [7] A. R. Bharadwaj, K. A. Scheidt, *Org. Lett.* **2004**, *6*, 2465-2468.

**Table S1.** The optimization of reaction conditions <sup>a</sup>, related to Table 1.

Entry	[Pd]	Ligand	Solvent	Yield (%)
1	Pd(PPh <sub>3</sub> ) <sub>4</sub>	/	toluene	trace
2	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	/	toluene	trace
3	Pd(OAc) <sub>2</sub>	/	toluene	trace
4	Pd(OAc) <sub>2</sub>	PPh <sub>3</sub>	toluene	trace
5	Pd(OAc) <sub>2</sub>	DPEphos	toluene	trace
6	Pd(OAc) <sub>2</sub>	Xantphos	toluene	trace
7	Pd(OAc) <sub>2</sub>		toluene	trace
8	Pd(OAc) <sub>2</sub>	P(OMe) <sub>3</sub>	toluene	54
9	Pd(OAc) <sub>2</sub>	P(OEt) <sub>3</sub>	toluene	58
10	Pd(OAc) <sub>2</sub>	P(OPh) <sub>3</sub>	toluene	60
11	Pd(OAc) <sub>2</sub>	P(O-2,4-di <sup>t</sup> BuPh) <sub>3</sub>	toluene	80
12	Pd(OAc) <sub>2</sub>	P(2-furanyl) <sub>3</sub>	toluene	20
13	Pd(OAc) <sub>2</sub>	P(2,4-di <sup>t</sup> BuPh) <sub>3</sub>	THF	11
14	Pd(OAc) <sub>2</sub>	P(O-2,4-di <sup>t</sup> BuPh) <sub>3</sub>	CH <sub>3</sub> CN	26
15	Pd(OAc) <sub>2</sub>	P(O-2,4-di <sup>t</sup> BuPh) <sub>3</sub>	1,4-dioxane	31
16	Pd(cod)Cl <sub>2</sub>	P(O-2,4-di <sup>t</sup> BuPh) <sub>3</sub>	toluene	54
17	Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>	P(O-2,4-di <sup>t</sup> BuPh) <sub>3</sub>	toluene	58
18	PdCl <sub>2</sub>	P(O-2,4-di <sup>t</sup> BuPh) <sub>3</sub>	toluene	46
19	Pd <sub>2</sub> (dba) <sub>3</sub>	P(O-2,4-di <sup>t</sup> BuPh) <sub>3</sub>	toluene	75
20	(allylPdCl) <sub>2</sub>	P(O-2,4-di <sup>t</sup> BuPh) <sub>3</sub>	toluene	70

---

<b>21<sup>b</sup></b>	Pd(OAc) <sub>2</sub>	P(O-2,4-di <sup>t</sup> BuPh) <sub>3</sub>	toluene	NR
-----------------------	----------------------	--	---------	----

---

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.24 mmol), [Pd] (5.0 mol%), **L** (10.0 mol%), CO (20 bar), 100 °C and solvent (1.0 mL). Yields are determined by GC with hexadecane as an internal standard. [b] Use hexaethyldigermane instead of hexamethyldigermane **2**.

## Copies of NMR spectra

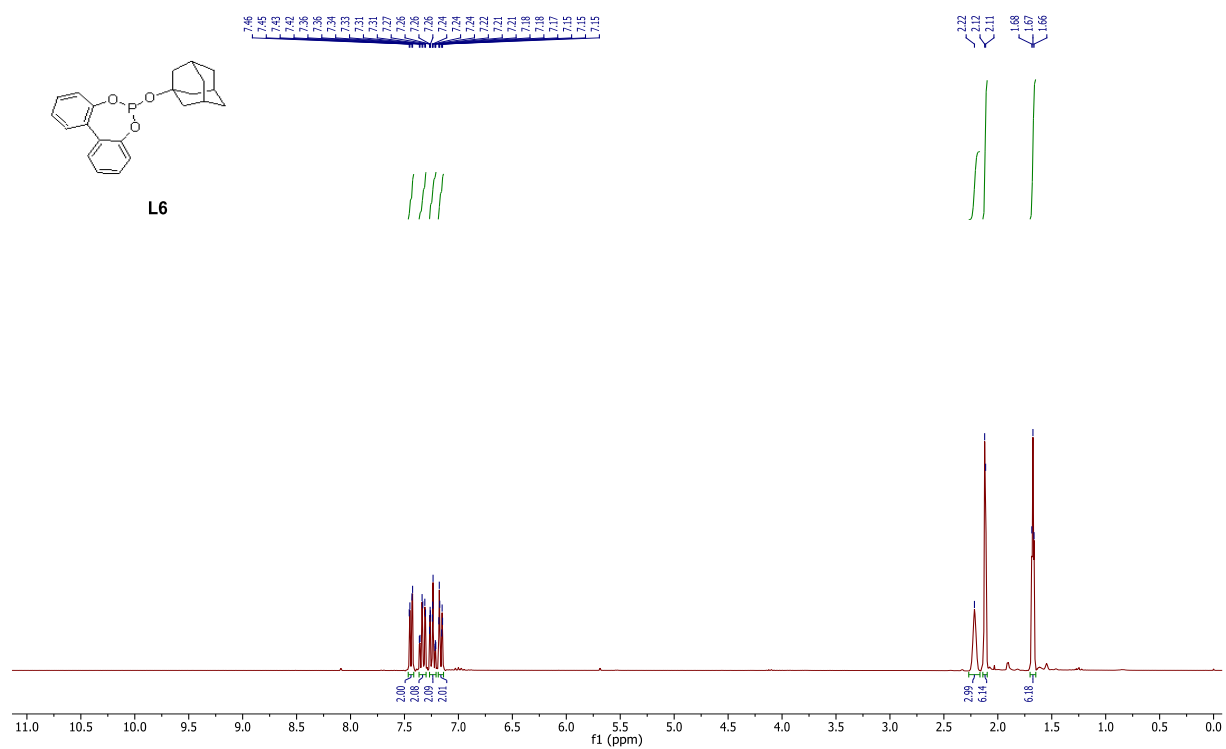


Figure S1. <sup>1</sup>H NMR spectrum of L6, related to Table 1.

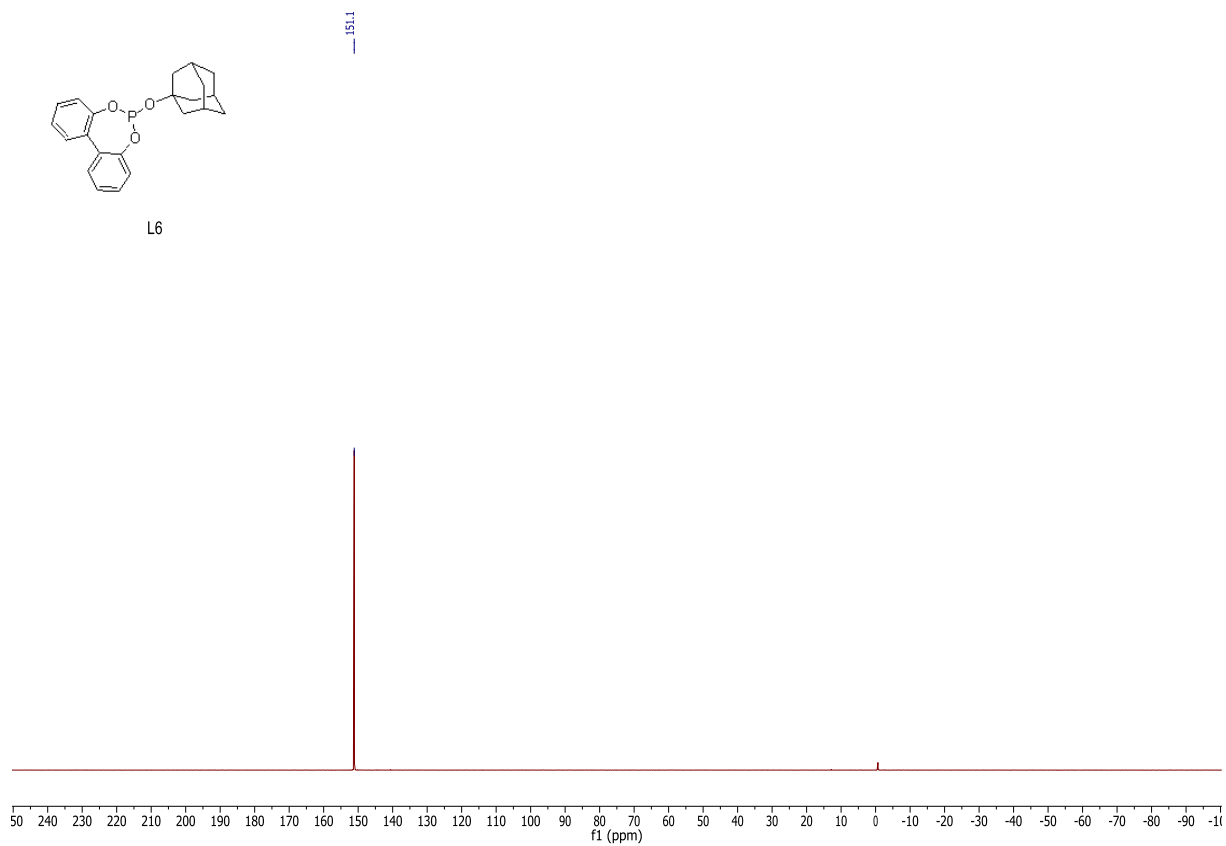
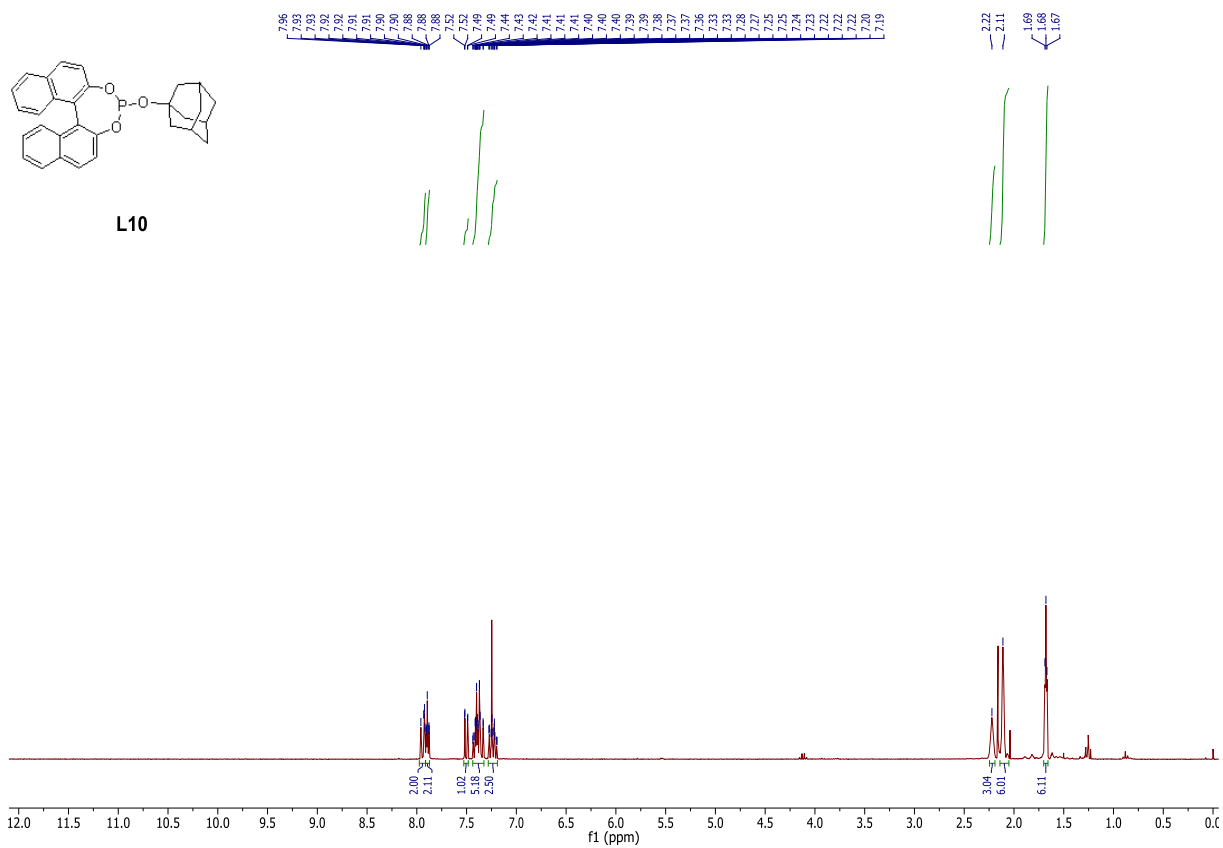
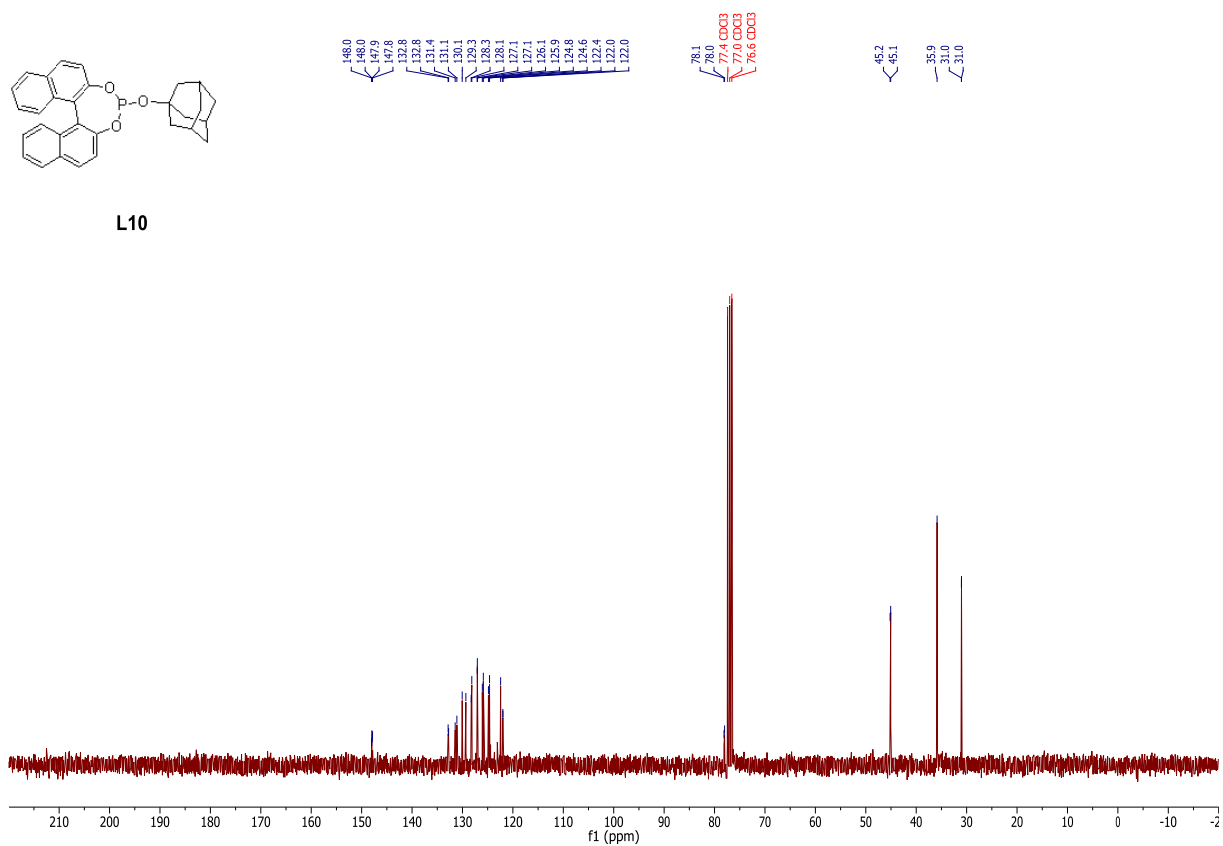


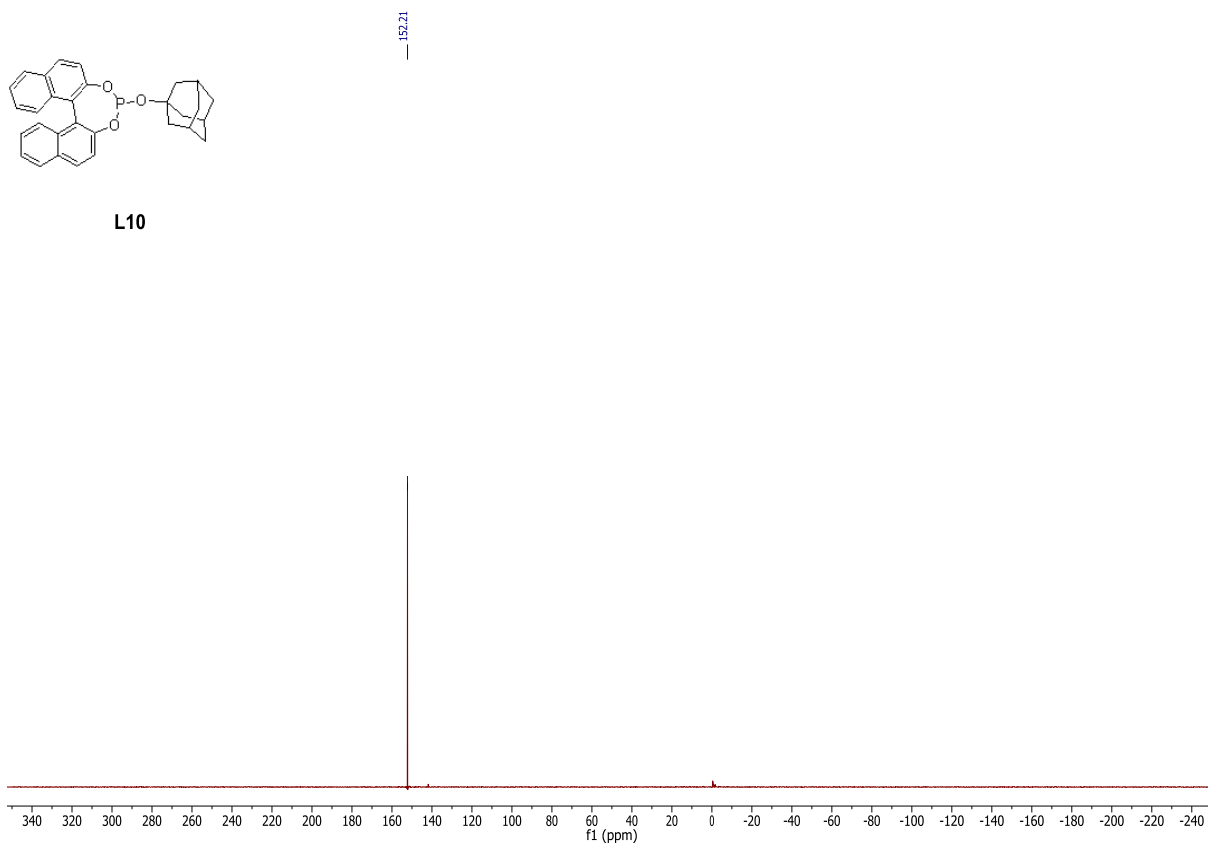
Figure S2. <sup>31</sup>P NMR spectrum of L6, related to Table 1.



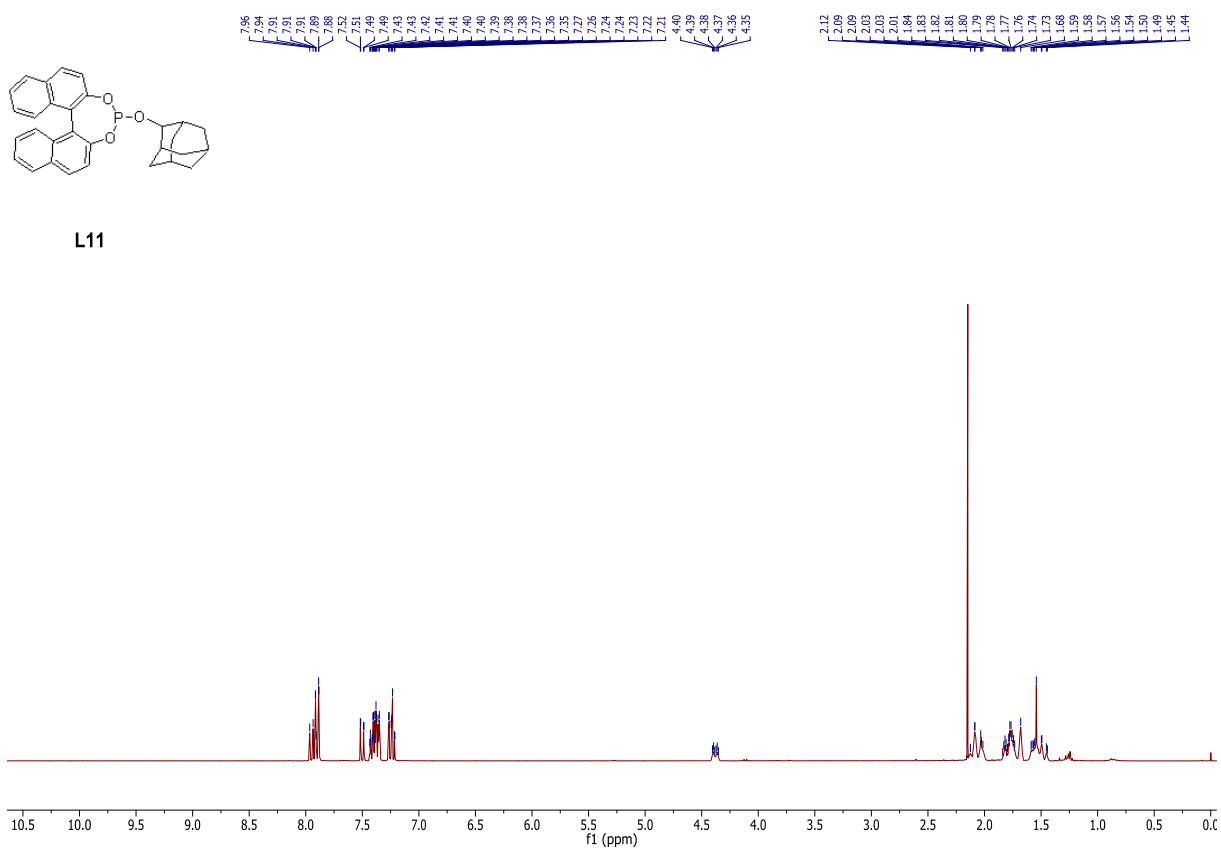
**Figure S3.**  $^1\text{H}$  NMR spectrum of L10, related to Table 1.



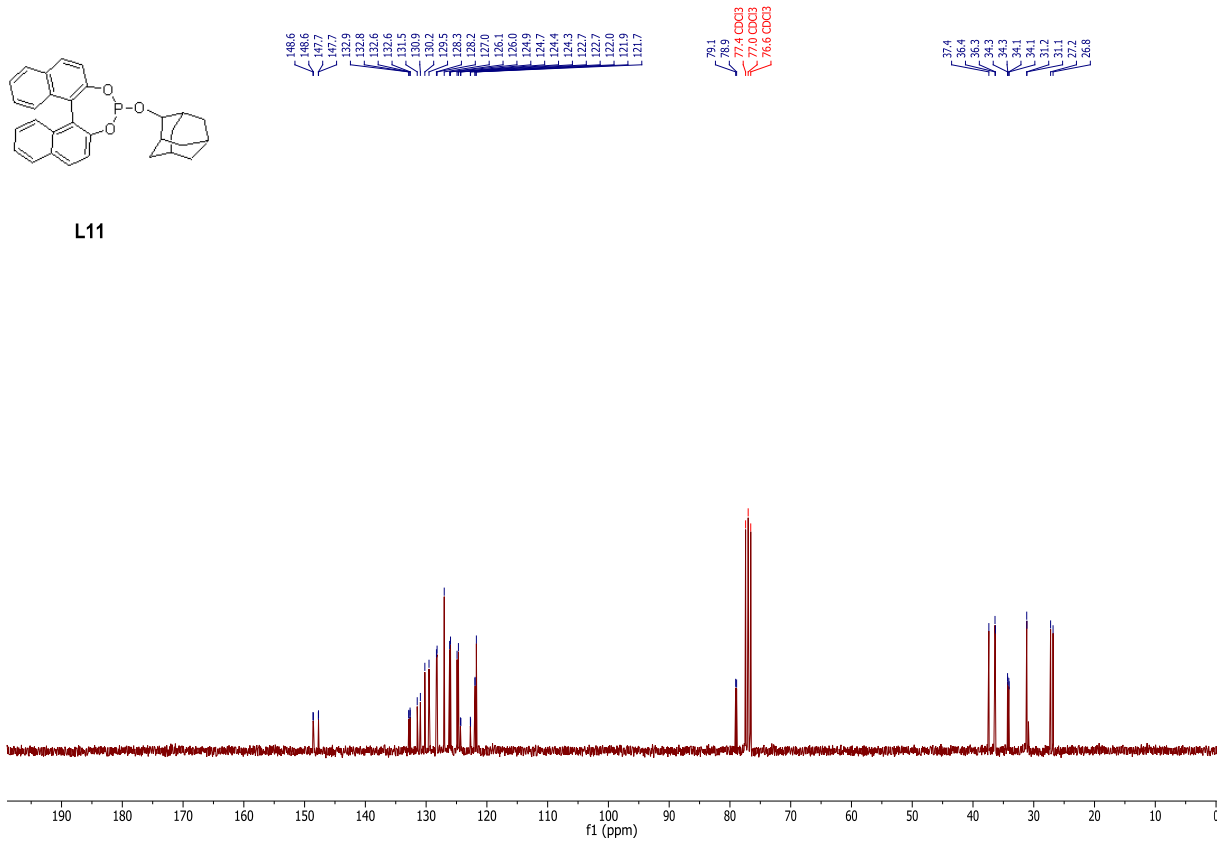
**Figure S4.**  $^{13}\text{C}$  NMR spectrum of L10, related to Table 1.



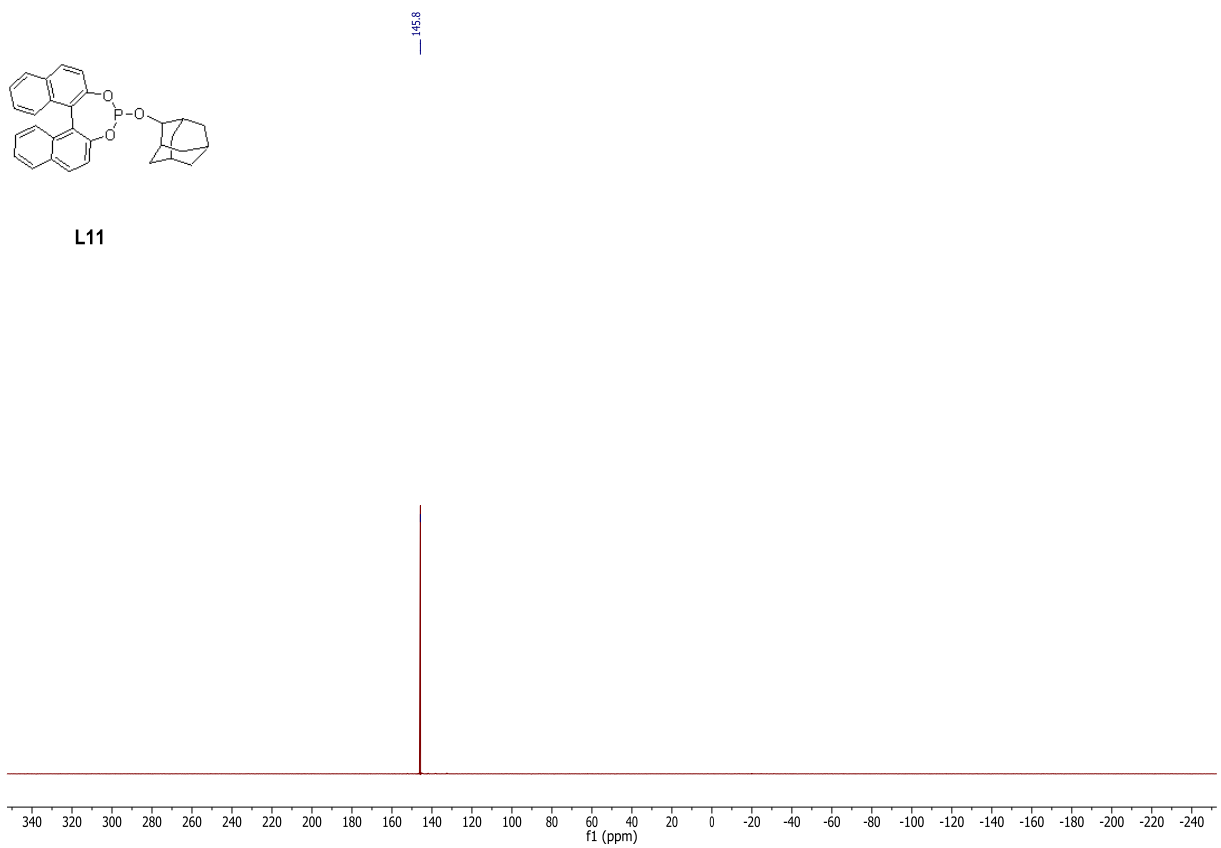
**Figure S5.**  $^{31}\text{P}$  NMR spectrum of L10, related to Table 1.



**Figure S6.**  $^1\text{H}$  NMR spectrum of L6, related to Table 1.



**Figure S7.**  $^{13}\text{C}$  NMR spectrum of L11, related to Table 1.



**Figure S8.**  $^{31}\text{P}$  NMR spectrum of L11, related to Table 1.

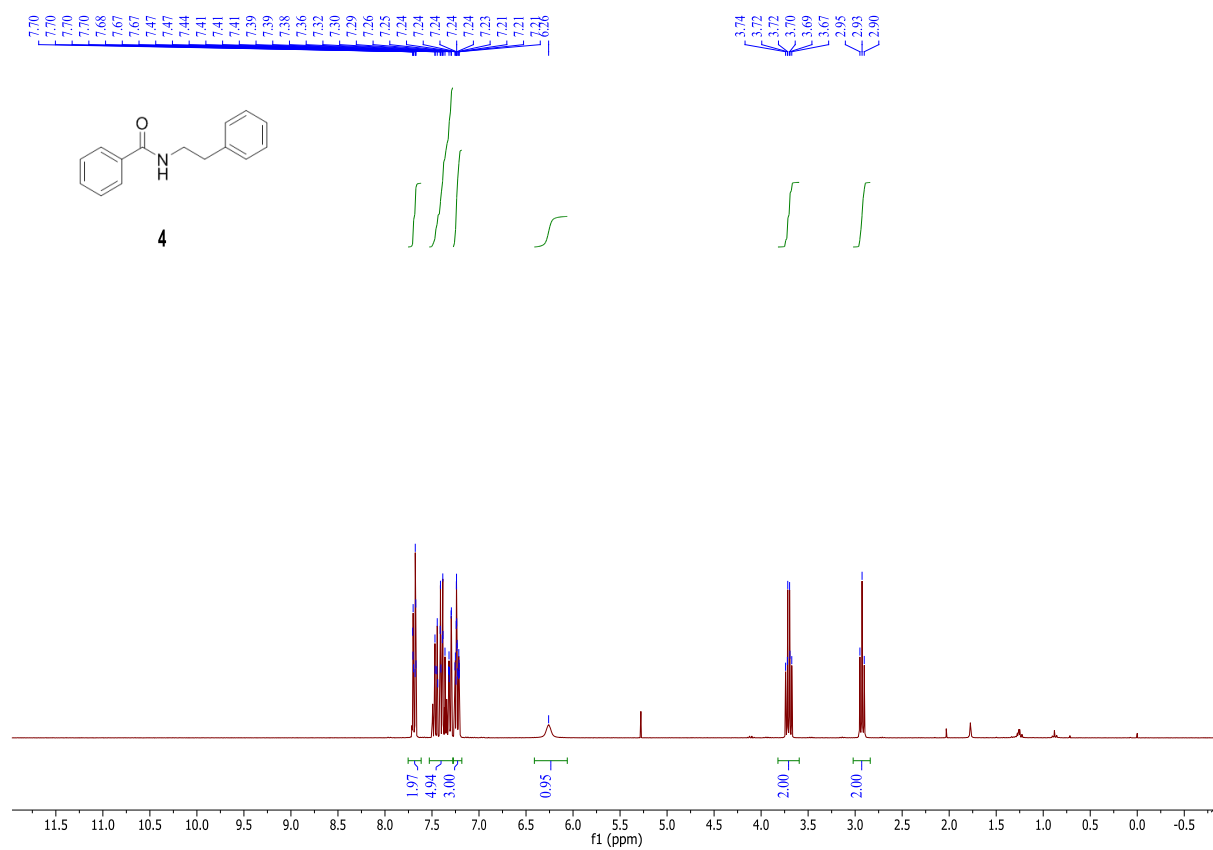


Figure S9. <sup>1</sup>H NMR spectrum of 4, related to Scheme 1.

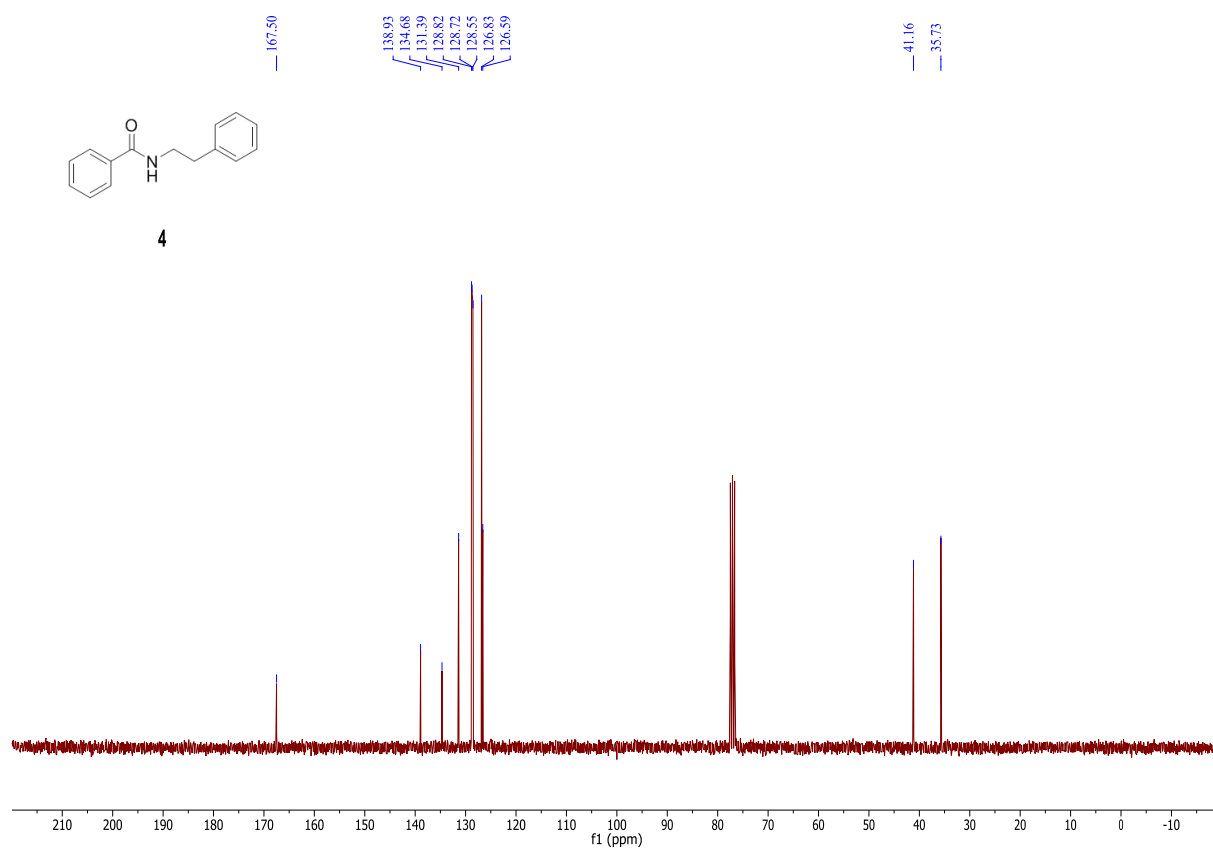


Figure S10. <sup>13</sup>C NMR spectrum of 4, related to Scheme 1.



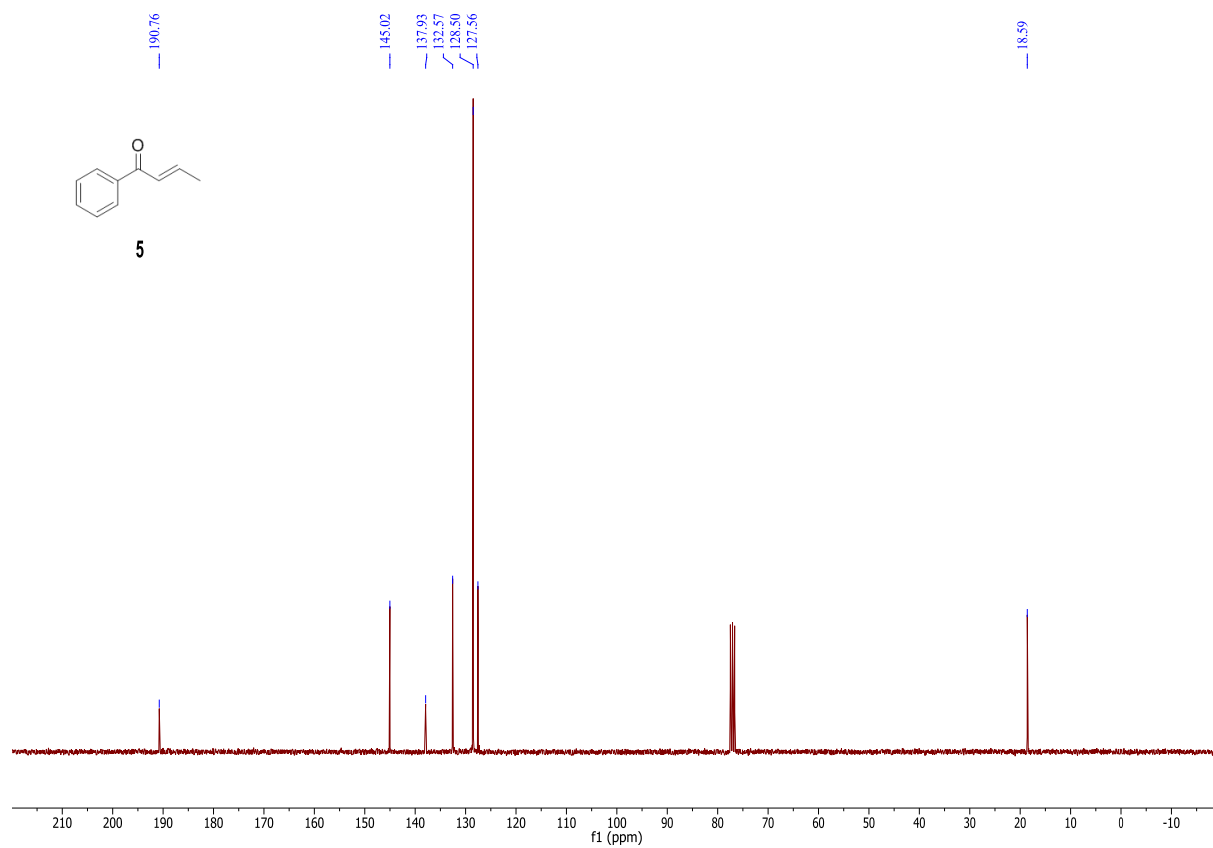


Figure S11. <sup>1</sup>H NMR spectrum of 5, related to Scheme 1.

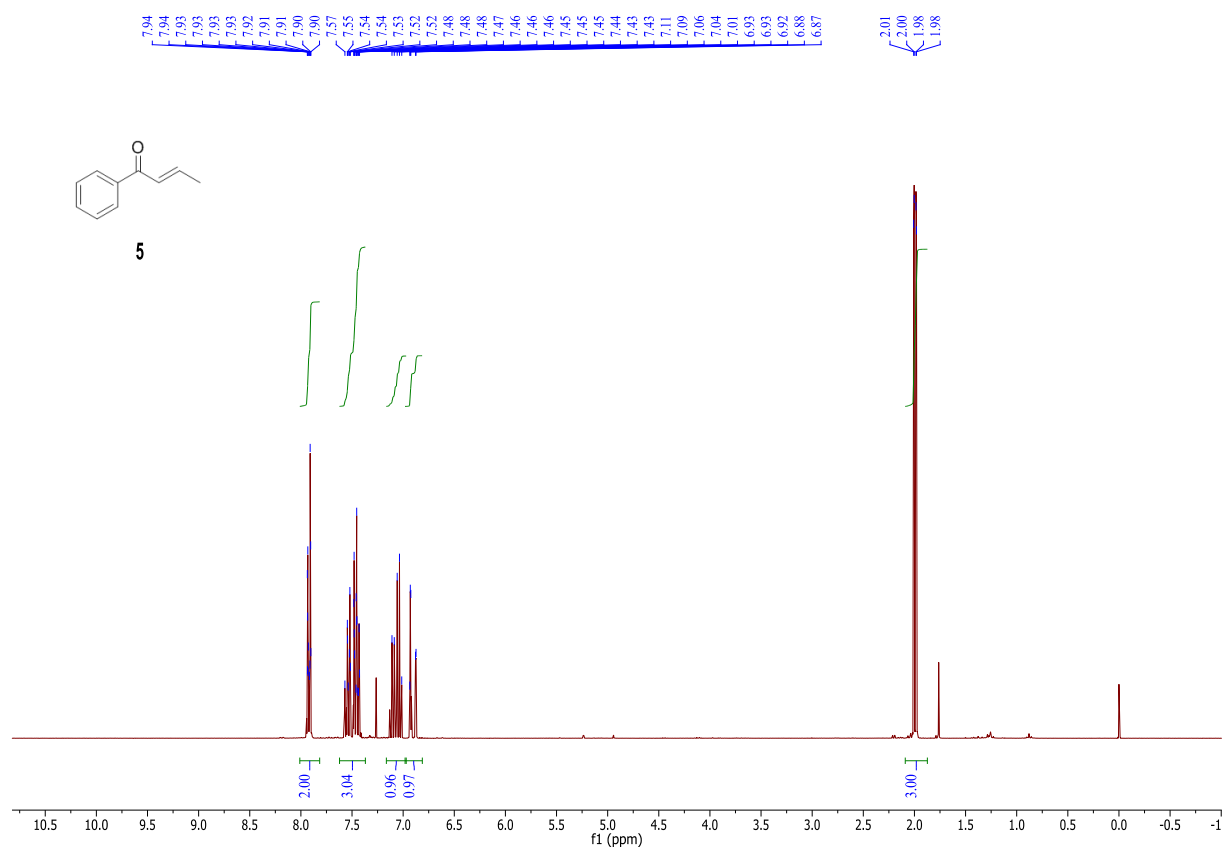
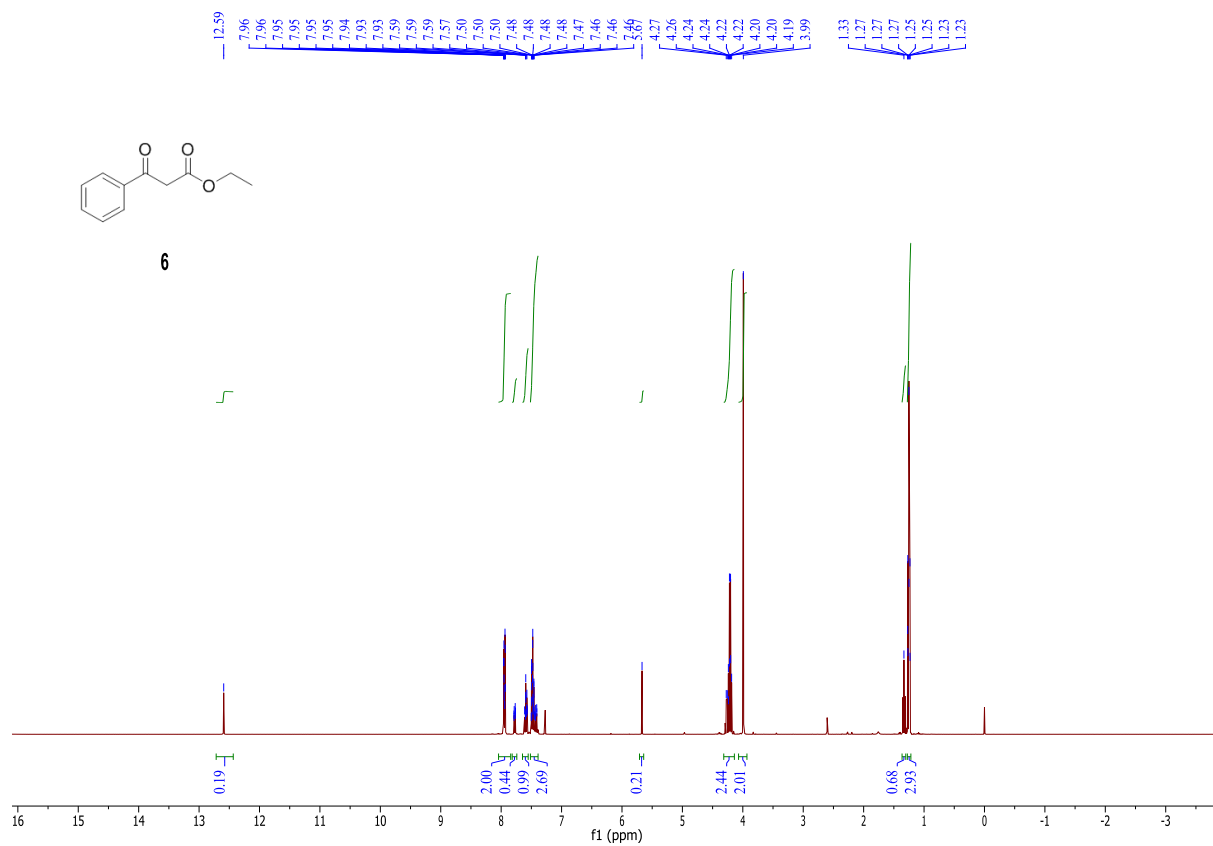
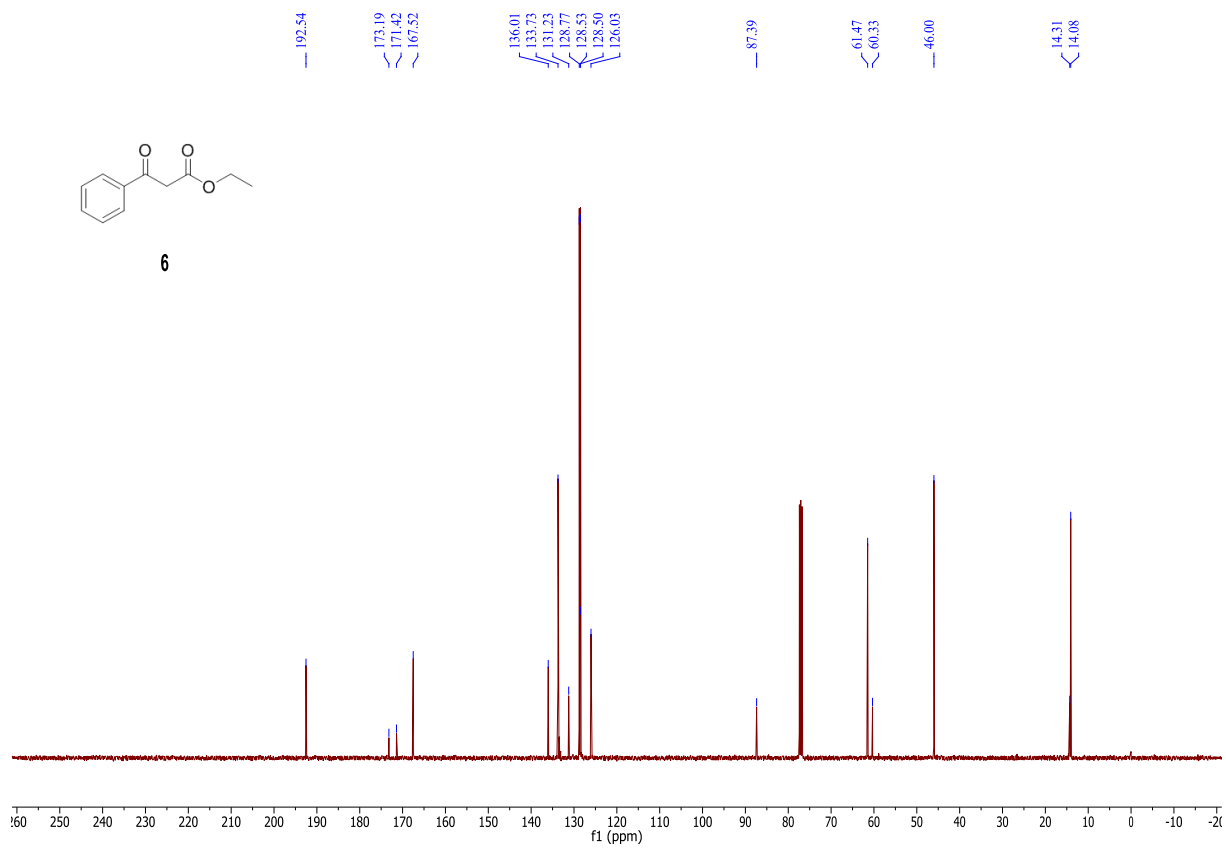


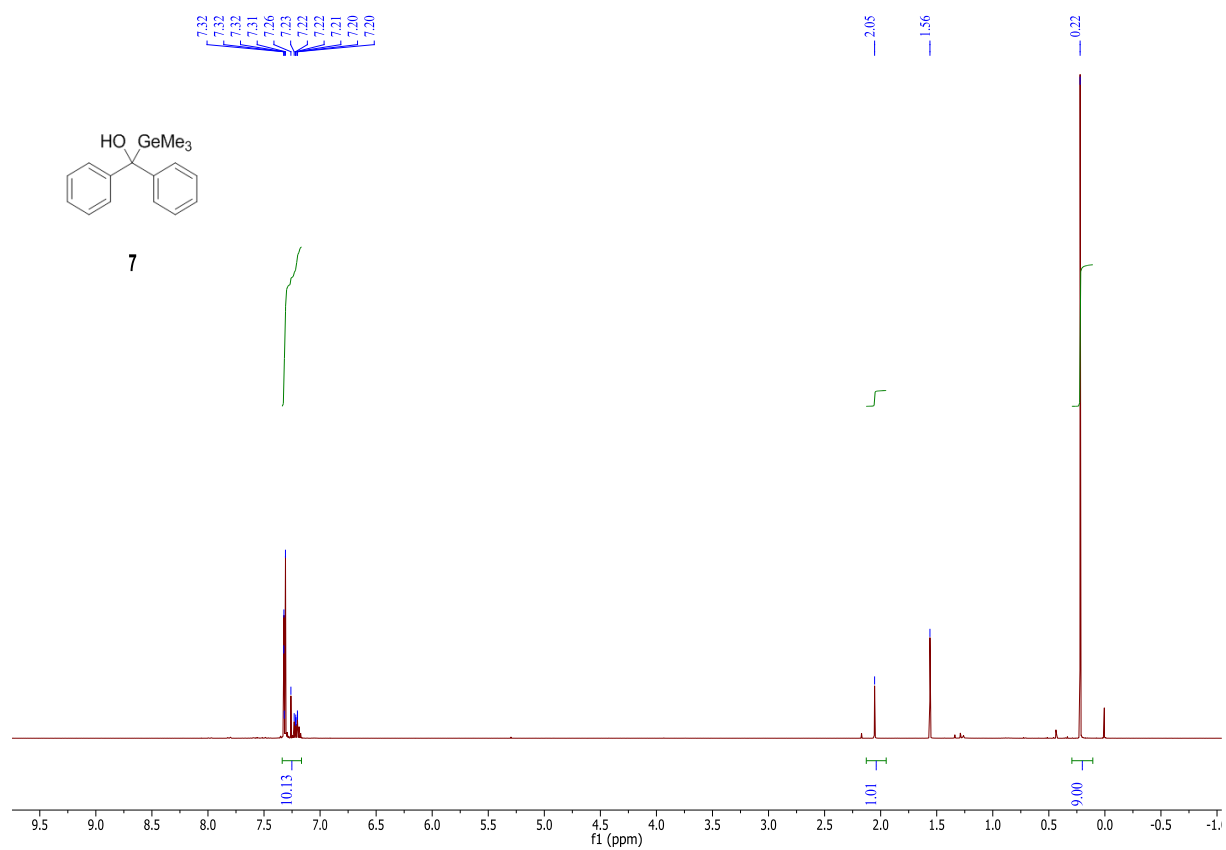
Figure S12. <sup>13</sup>C NMR spectrum of 5, related to Scheme 1.



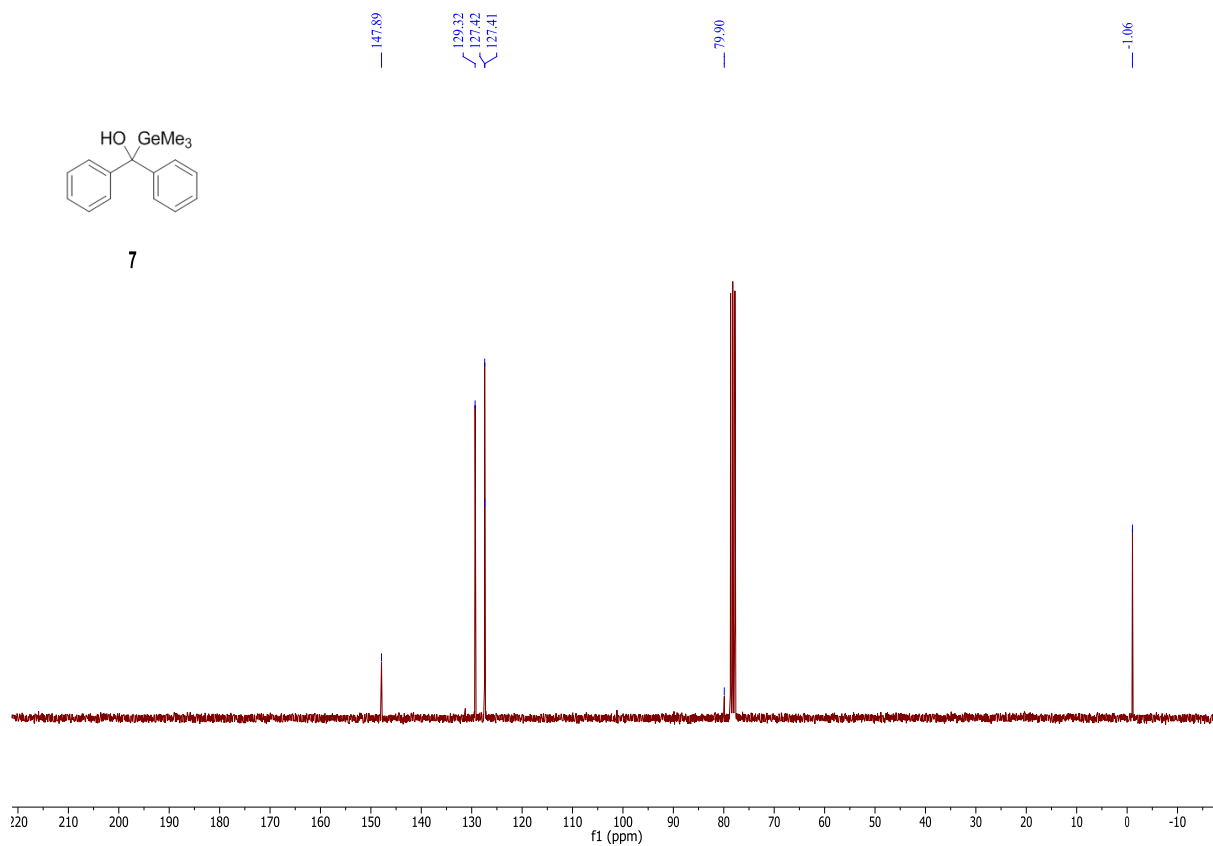
**Figure S13.**  $^1\text{H}$  NMR spectrum of 6, related to Scheme 1.



**Figure S14.**  $^{13}\text{C}$  NMR spectrum of 6, related to Scheme 1.



**Figure S15.** <sup>1</sup>H NMR spectrum of **7**, related to Scheme 1.



**Figure S16.** <sup>13</sup>C NMR spectrum of **7**, related to Scheme 1.

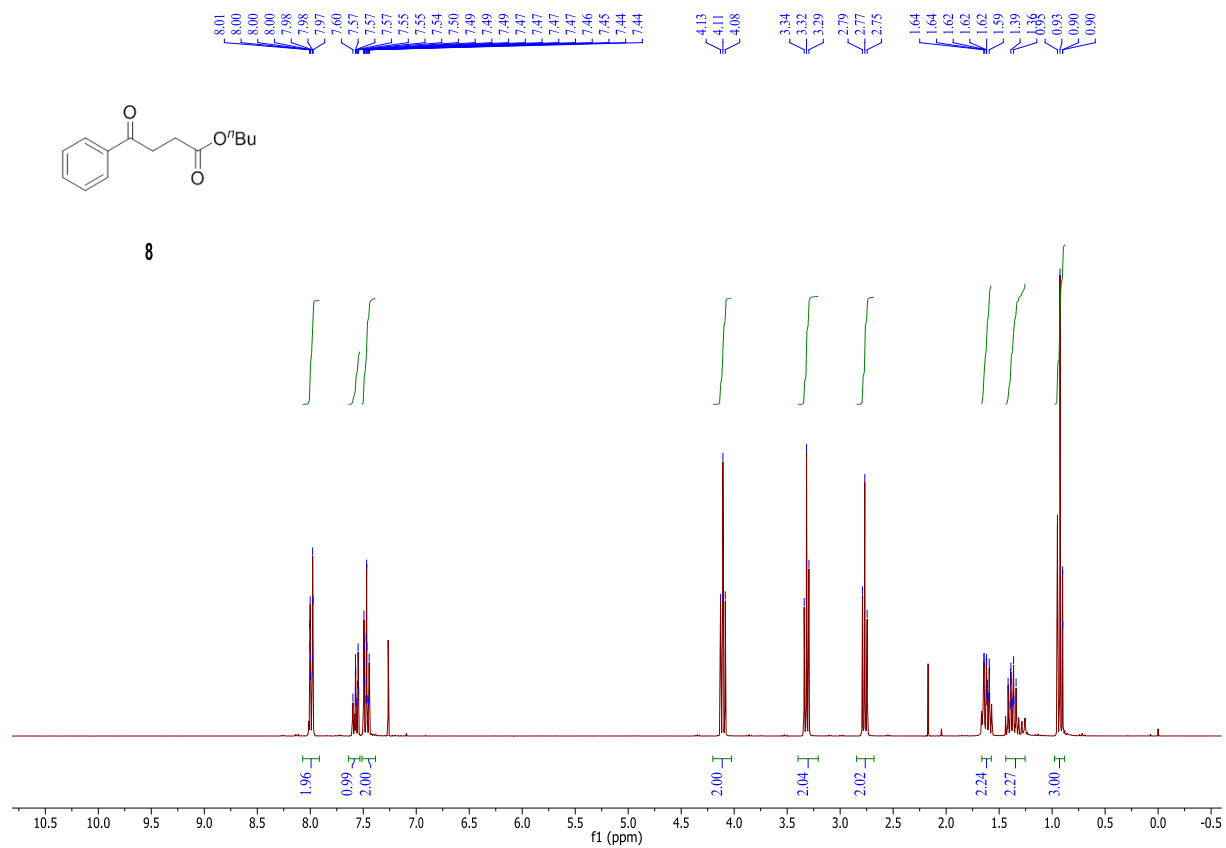


Figure S17. <sup>1</sup>H NMR spectrum of **8**, related to Scheme 1.

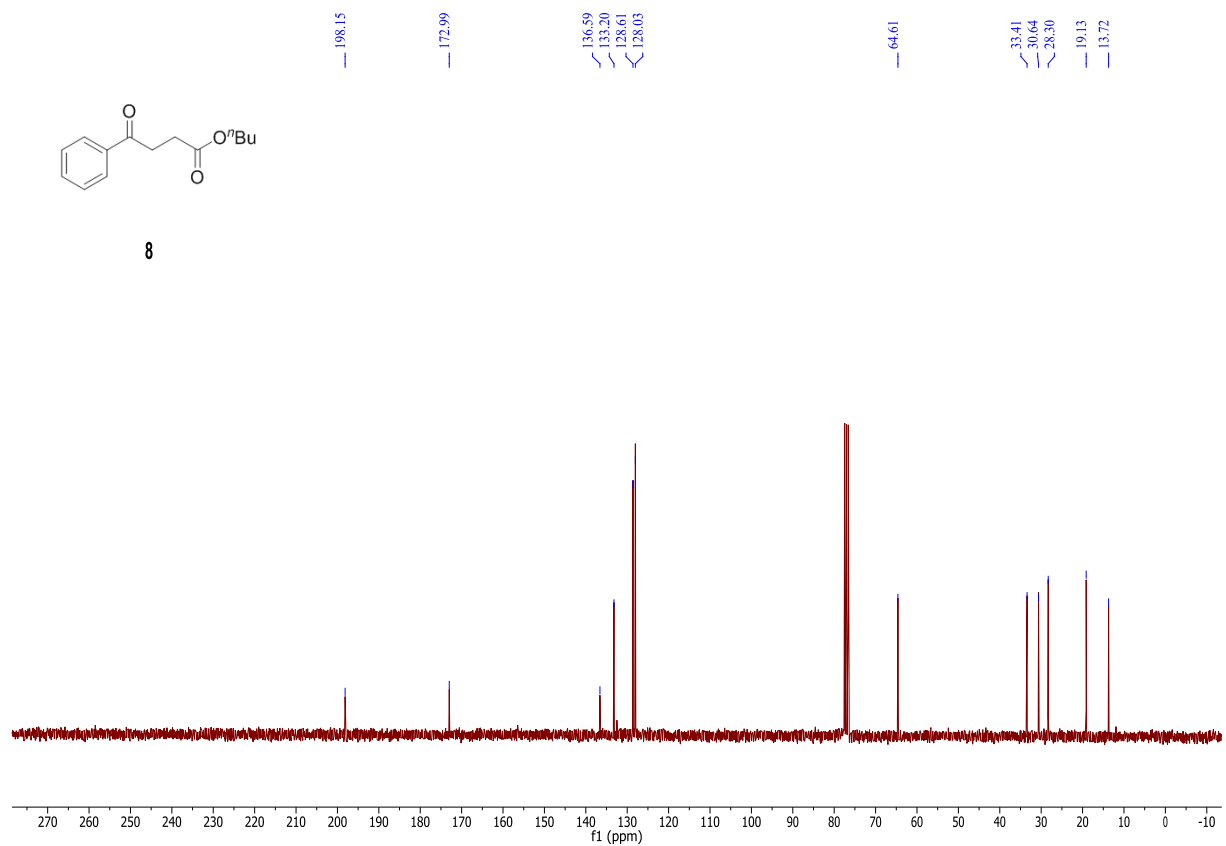


Figure S18. <sup>13</sup>C NMR spectrum of **8**, related to Scheme 1.

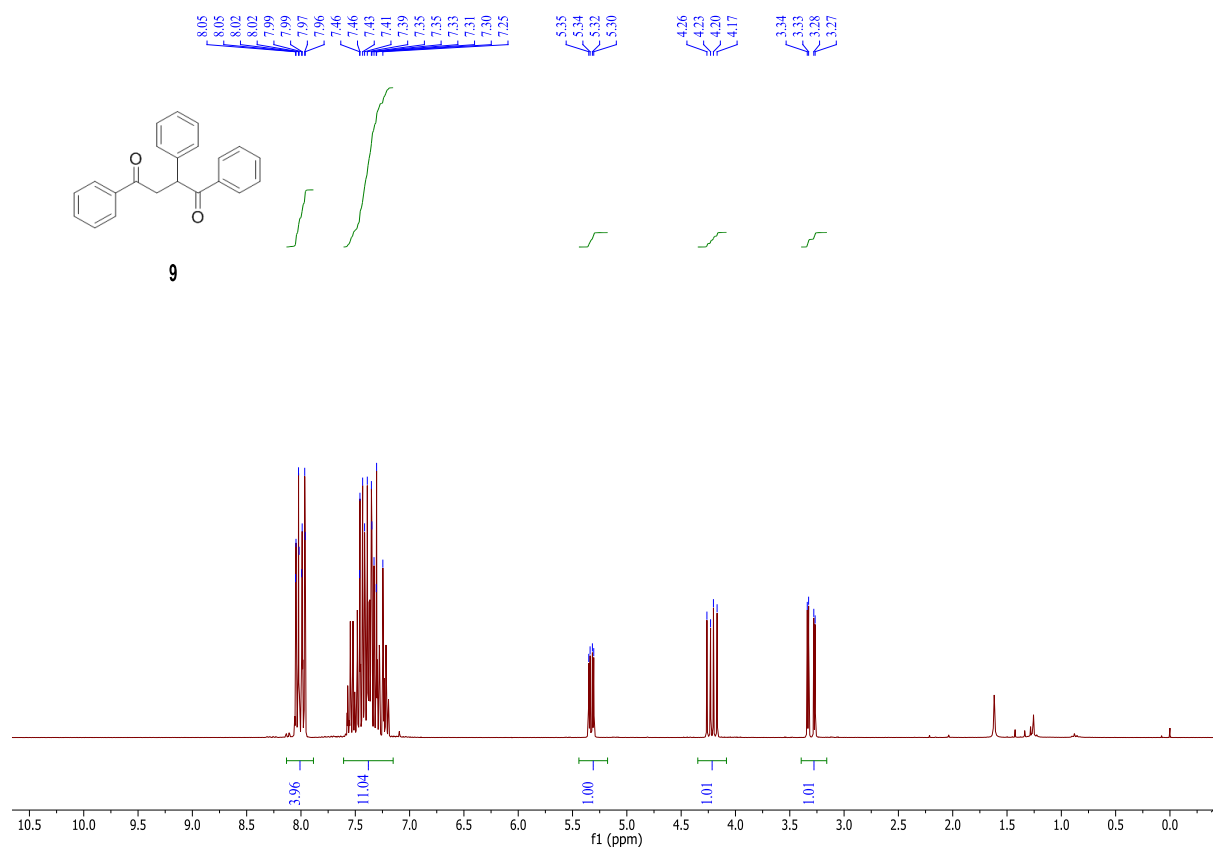


Figure S19. <sup>1</sup>H NMR spectrum of 9, related to Scheme 1.

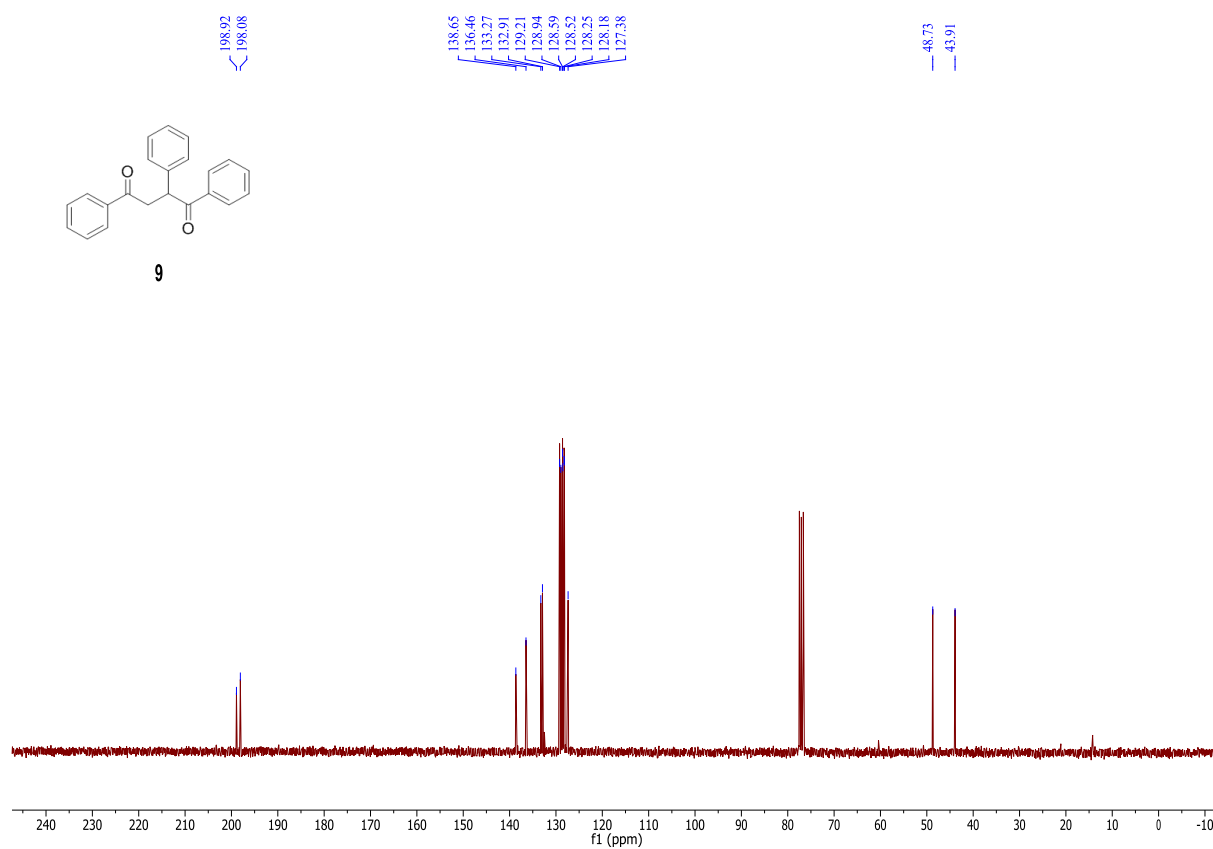
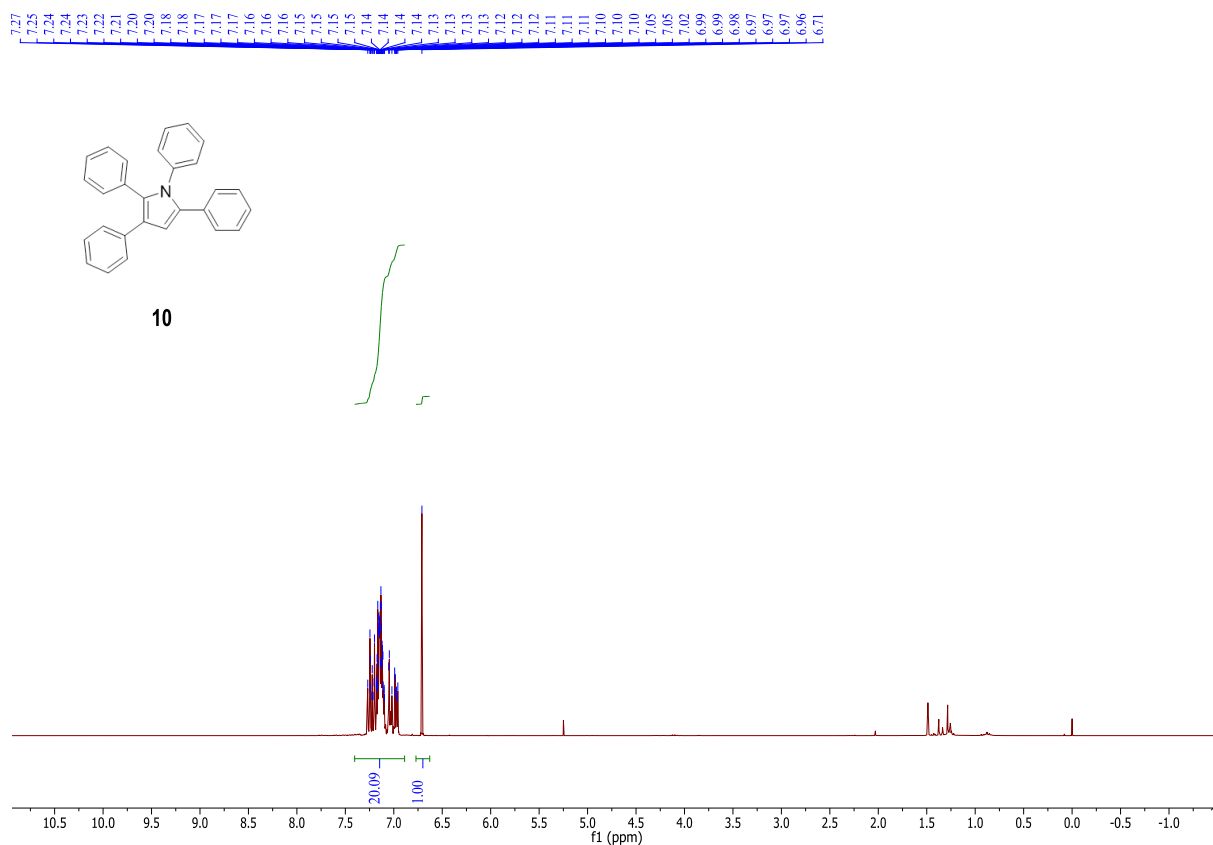
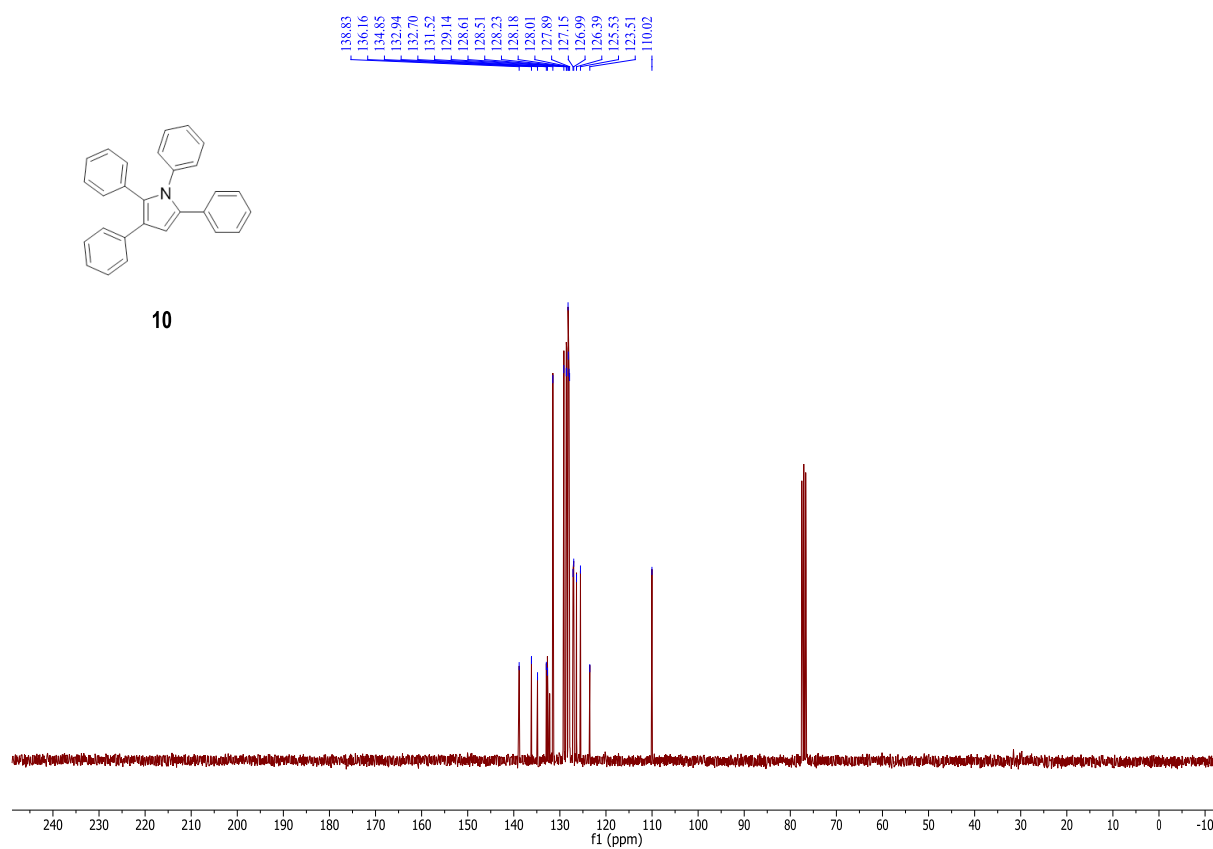


Figure S20. <sup>13</sup>C NMR spectrum of 9, related to Scheme 1.



**Figure S21.**  $^1\text{H}$  NMR spectrum of 10, related to Scheme 1.



**Figure S22.**  $^{13}\text{C}$  NMR spectrum of 10, related to Scheme 1.

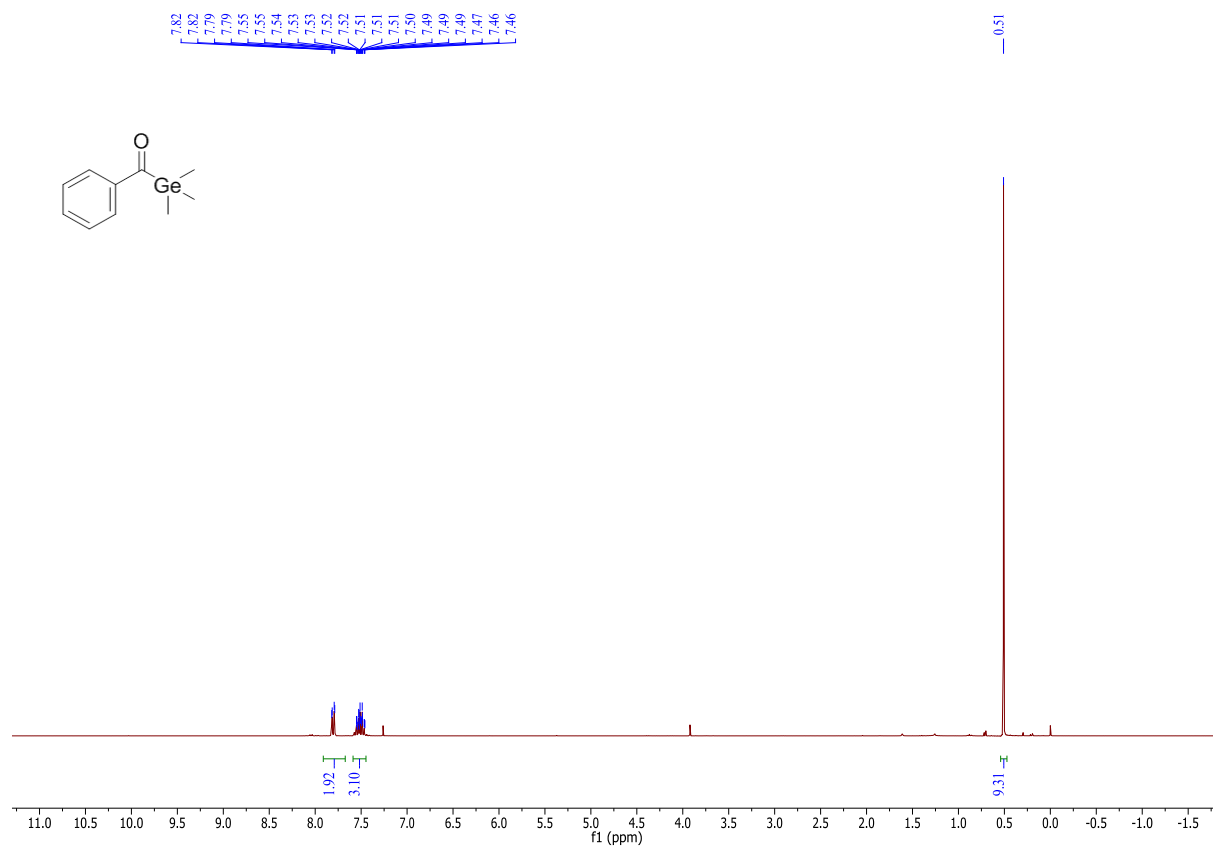


Figure S23. <sup>1</sup>H NMR spectrum of 3a, related to Scheme 1.

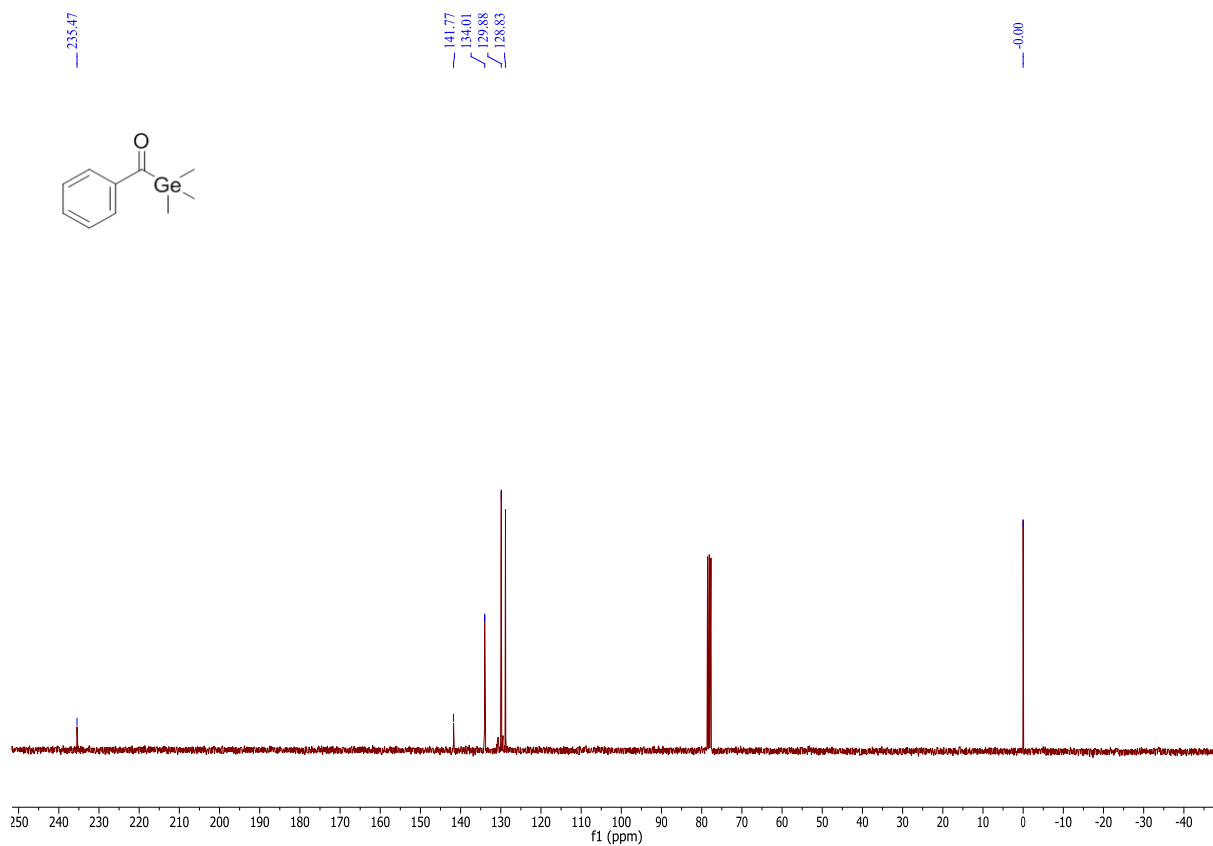
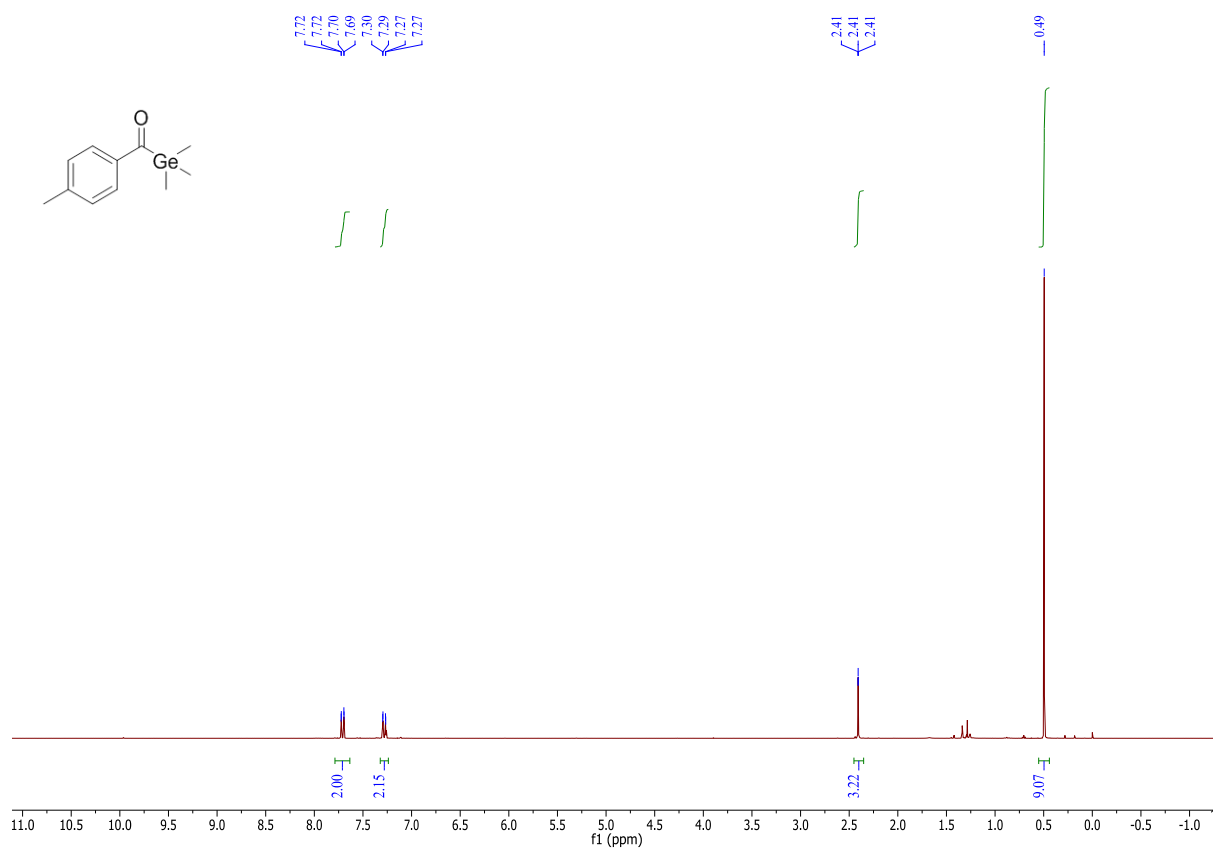
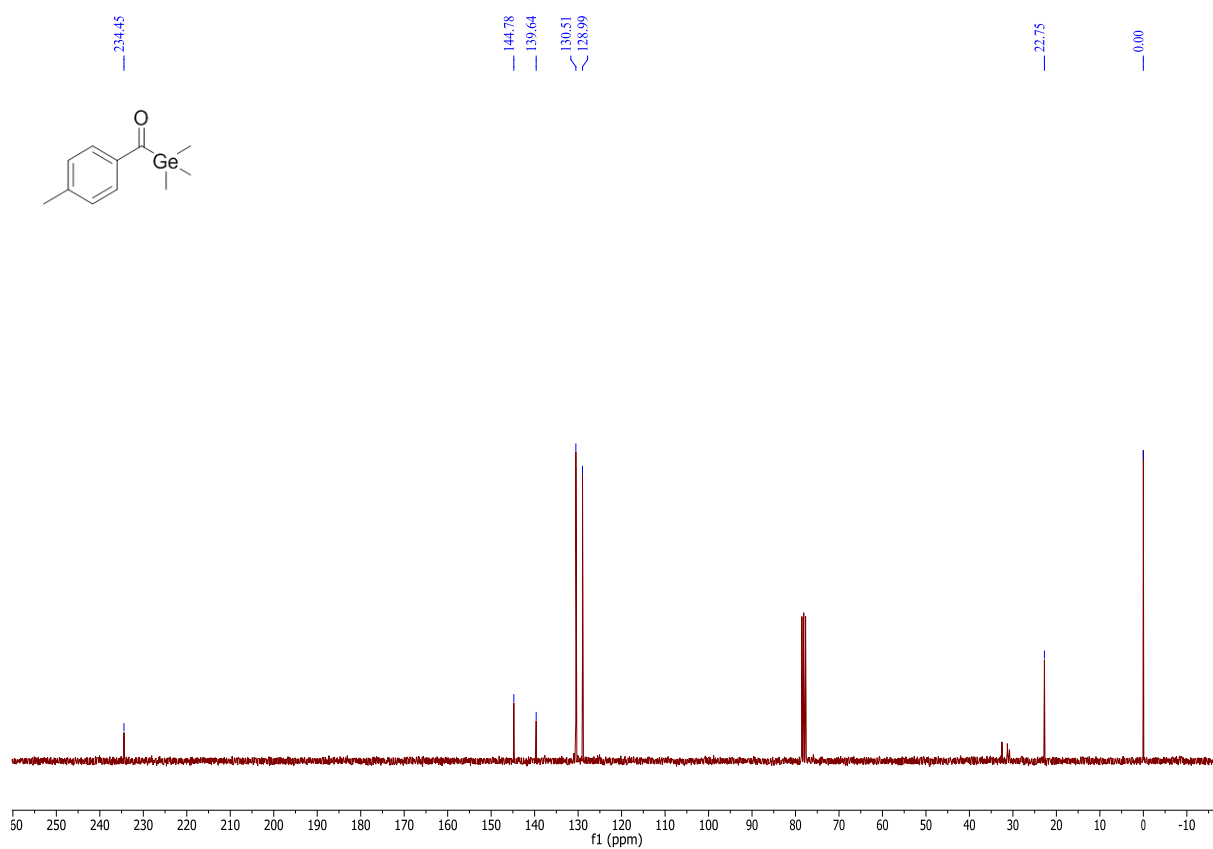


Figure S24. <sup>13</sup>C NMR spectrum of 3a, related to Scheme 1.



**Figure S25.**  $^1\text{H}$  NMR spectrum of 3b, related to Scheme 2.



**Figure S26.**  $^{13}\text{C}$  NMR spectrum of 3b, related to Scheme 2.



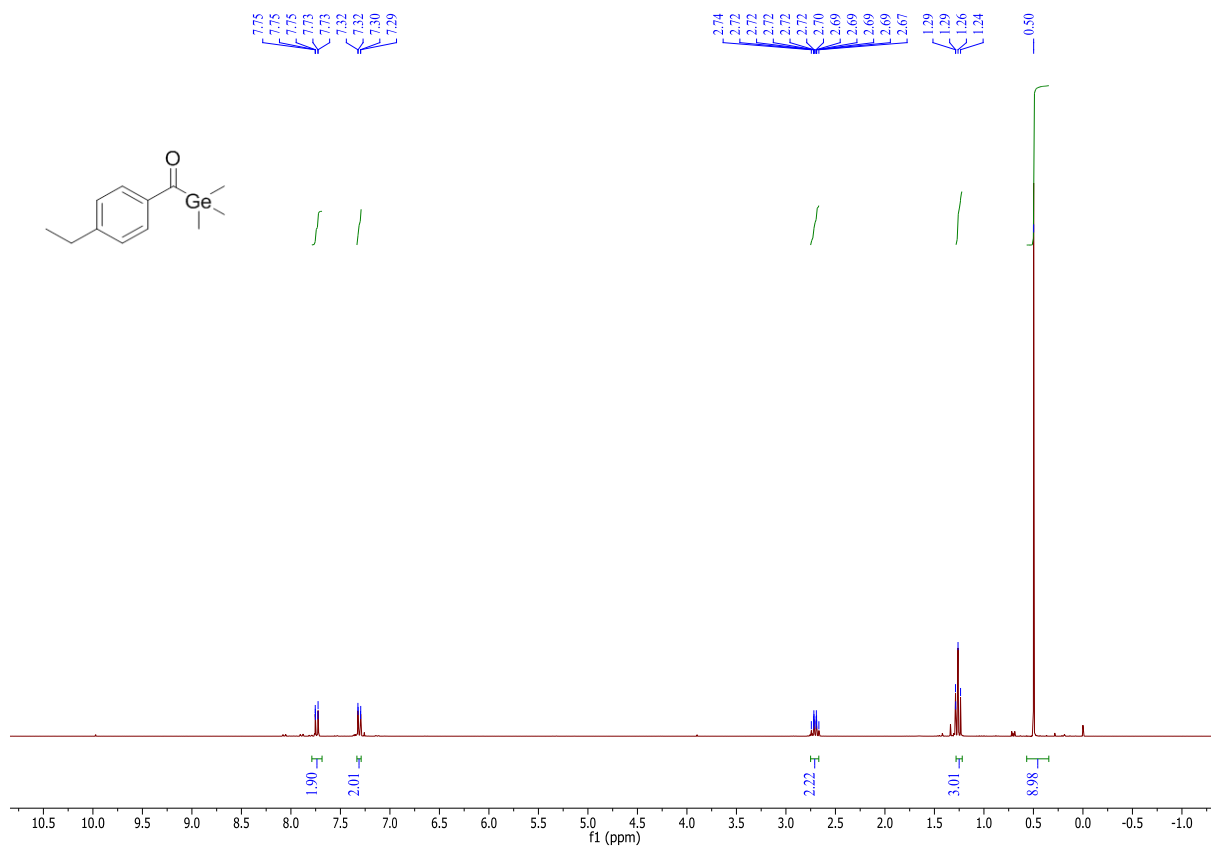


Figure S27. <sup>1</sup>H NMR spectrum of 3c, related to Scheme 2.

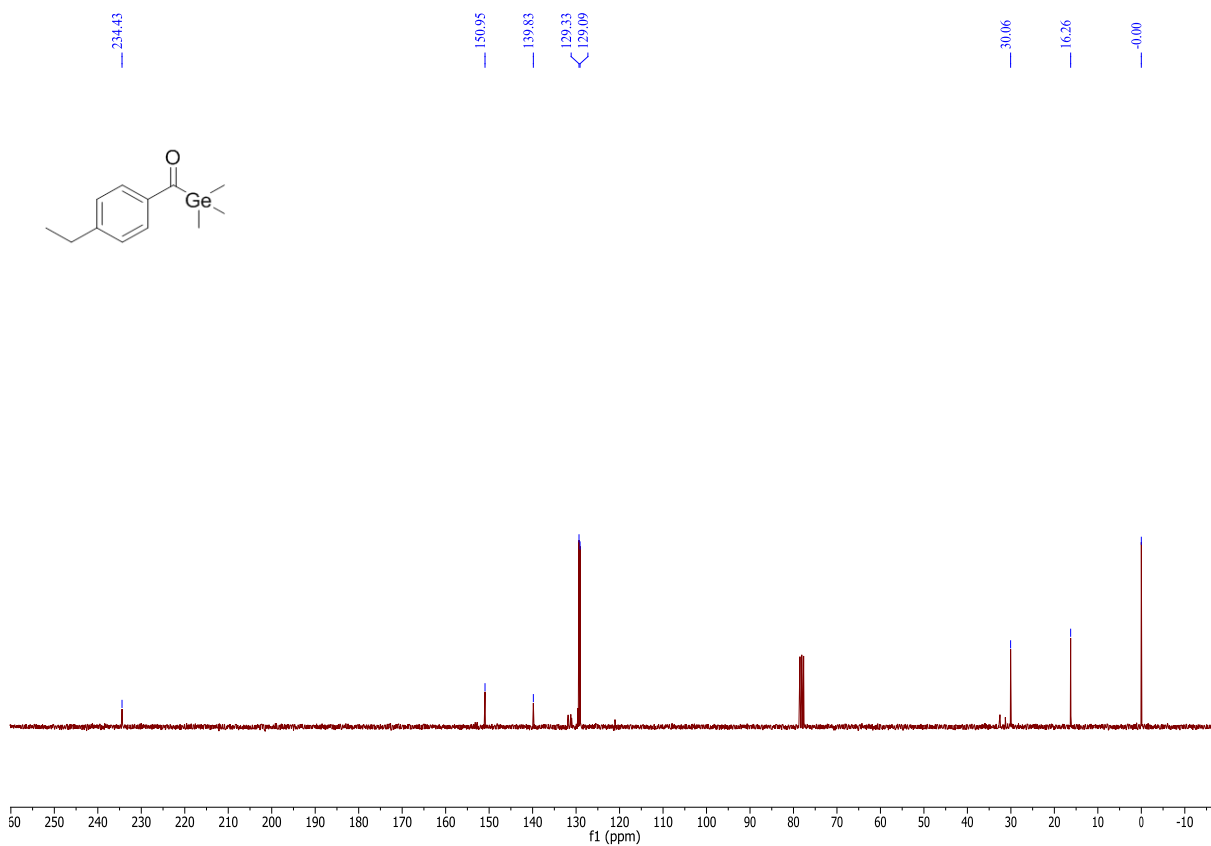


Figure S28. <sup>13</sup>C NMR spectrum of 3c, related to Scheme 2.

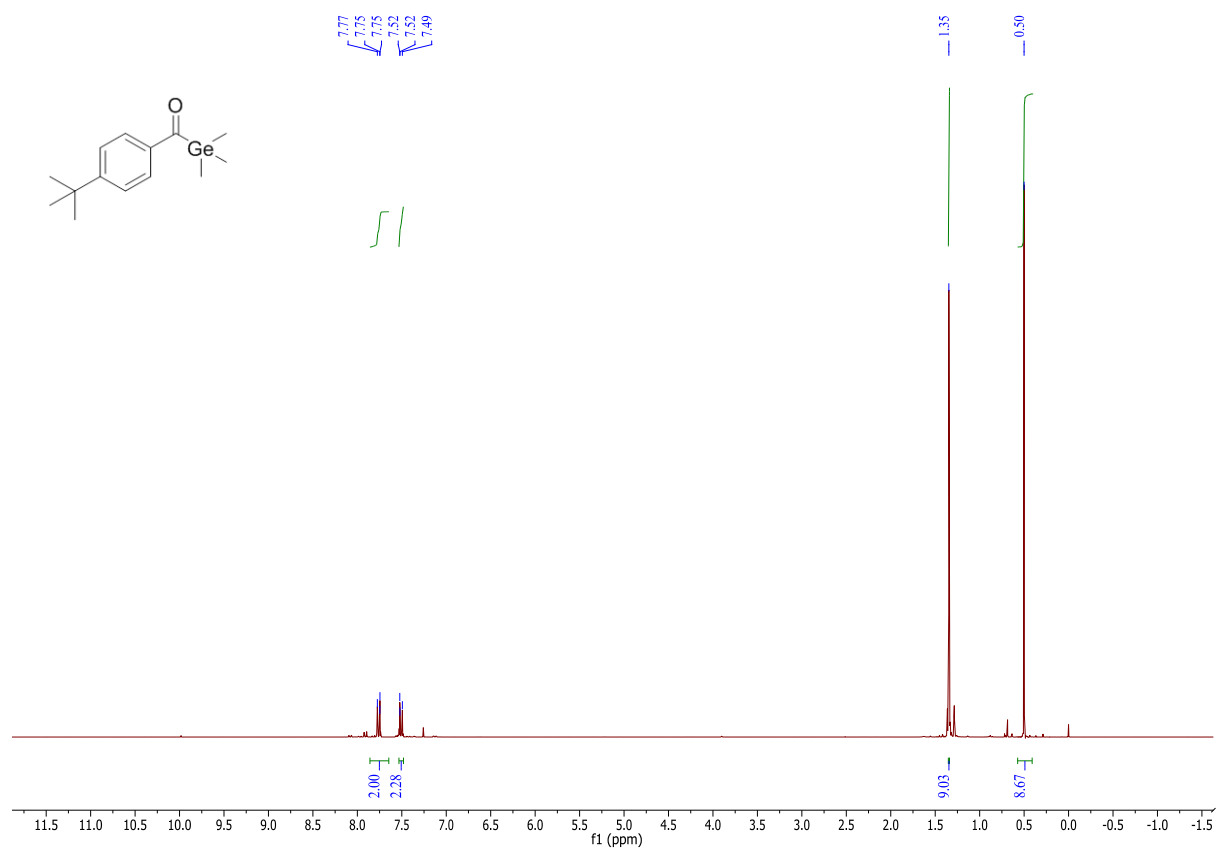


Figure S29. <sup>1</sup>H NMR spectrum of 3d, related to Scheme 2.

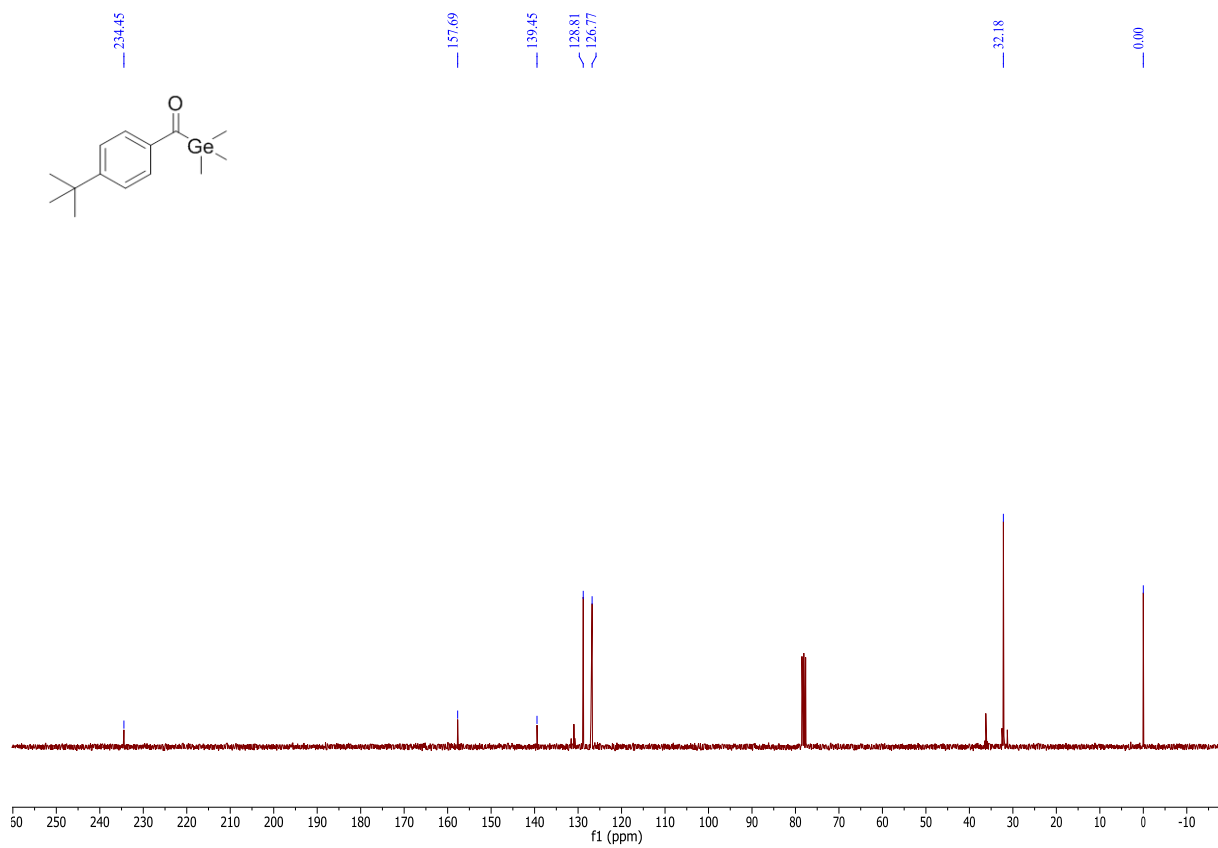
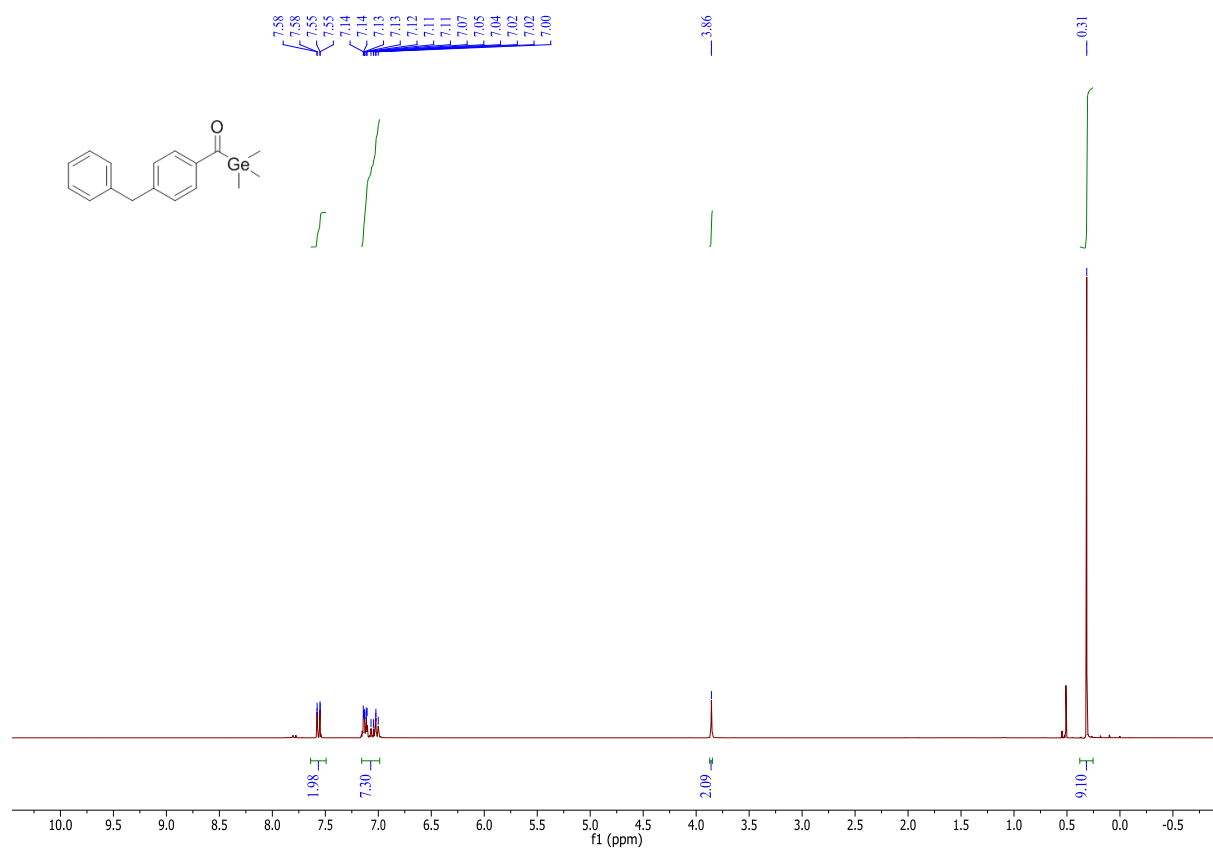
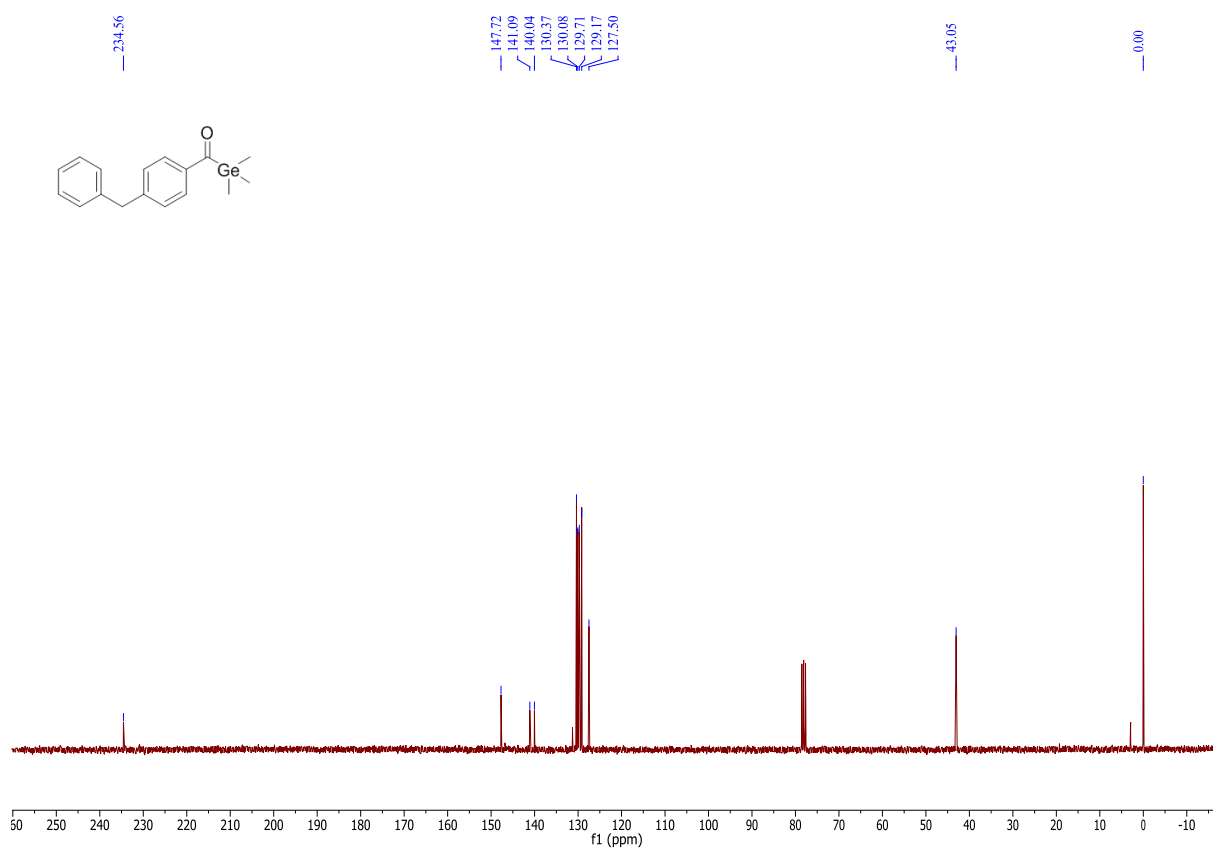


Figure S30. <sup>13</sup>C NMR spectrum of 3d, related to Scheme 2.



**Figure S31.**  $^1\text{H}$  NMR spectrum of 3e, related to Scheme 2.



**Figure S32.**  $^{13}\text{C}$  NMR spectrum of 3e, related to Scheme 2.

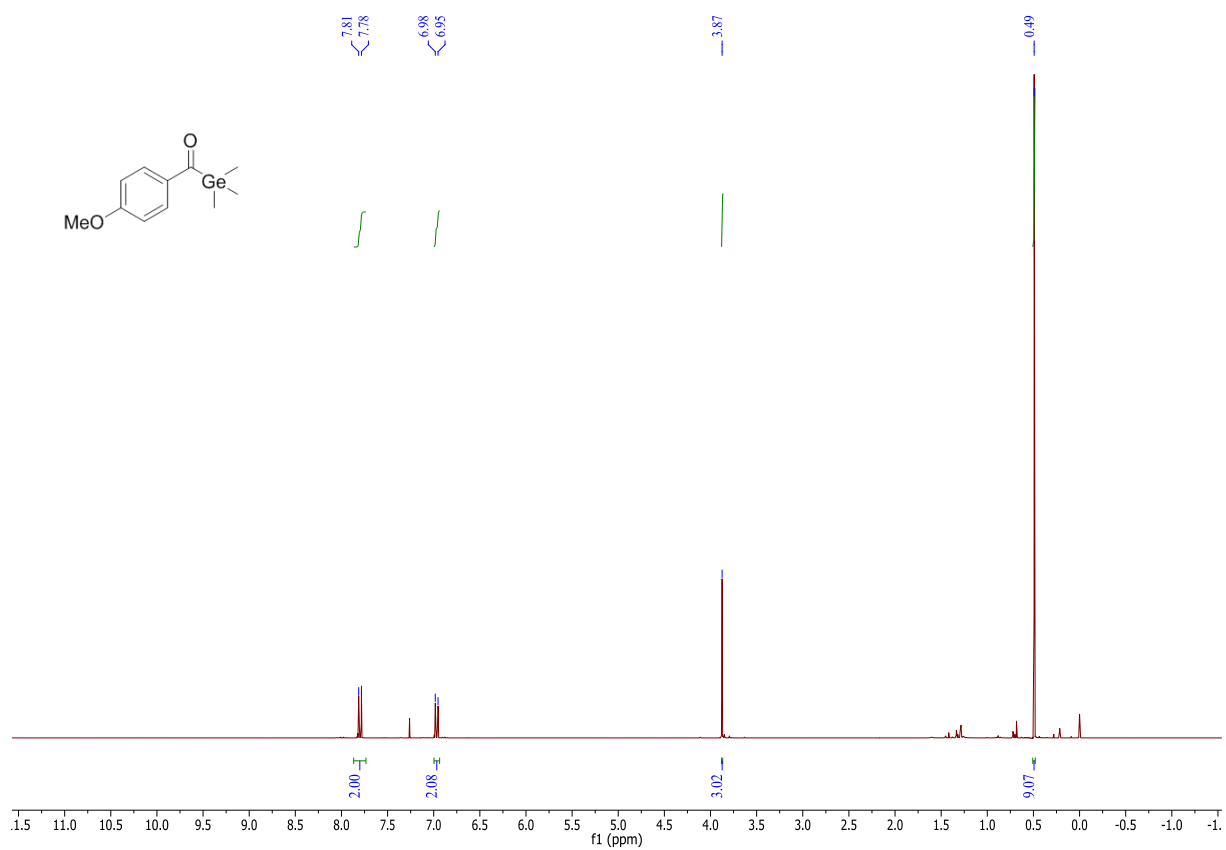


Figure S33. <sup>1</sup>H NMR spectrum of 3f, related to Scheme 2.

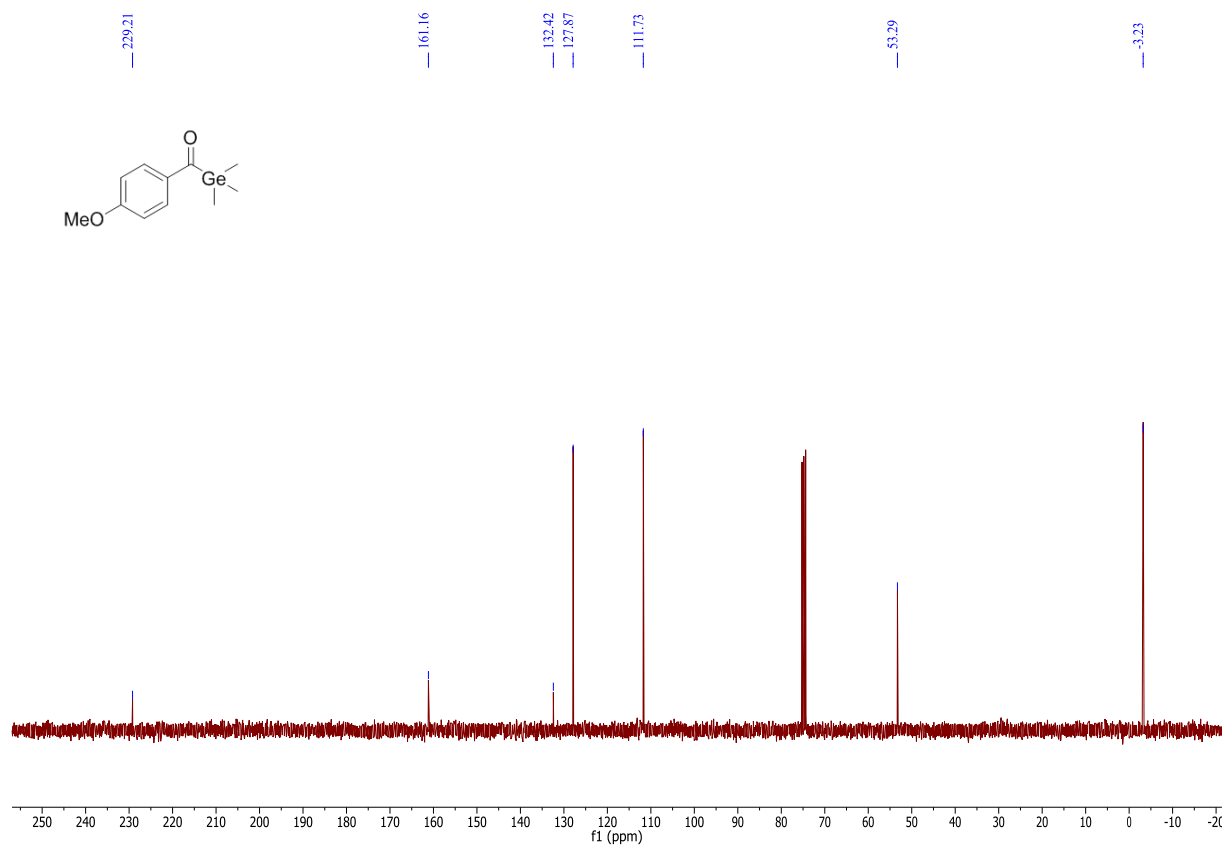


Figure S34. <sup>13</sup>C NMR spectrum of 3f, related to Scheme 2.

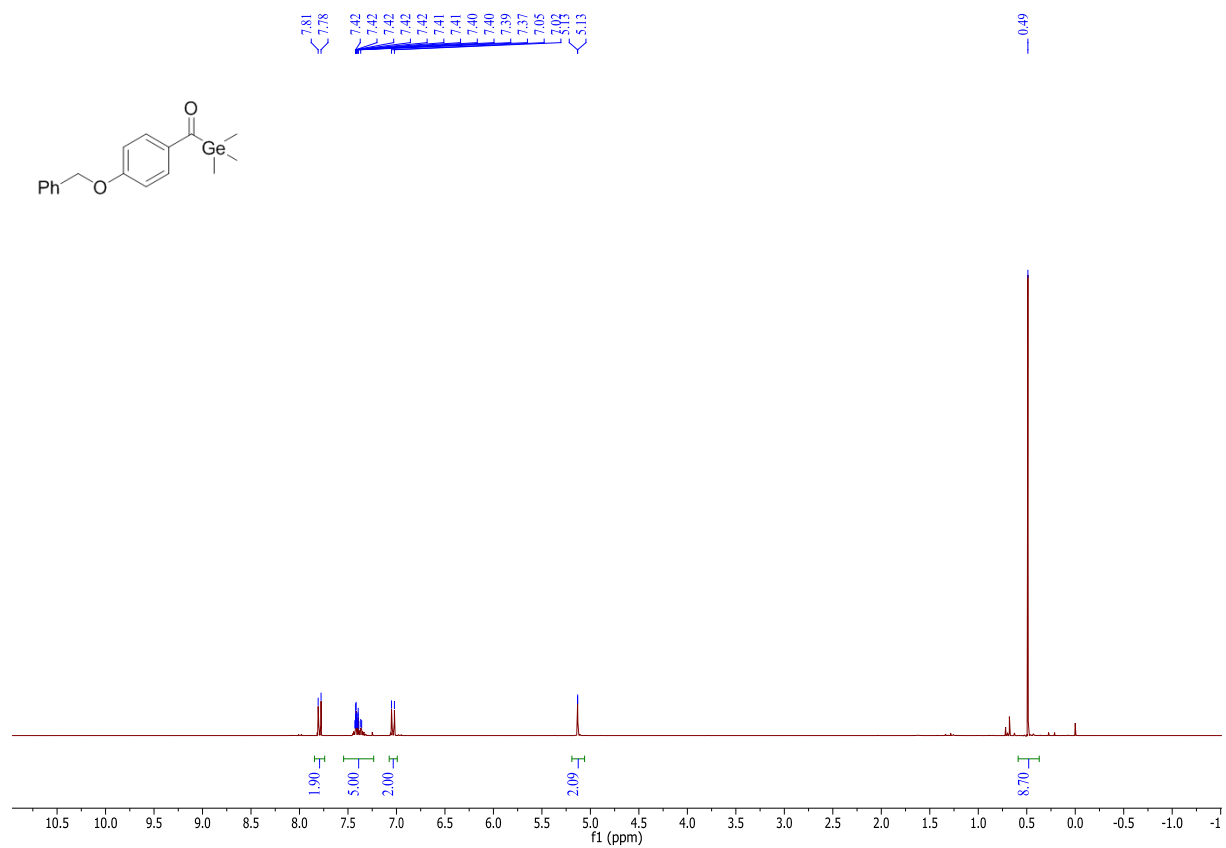


Figure S35. <sup>1</sup>H NMR spectrum of 3g, related to Scheme 2.

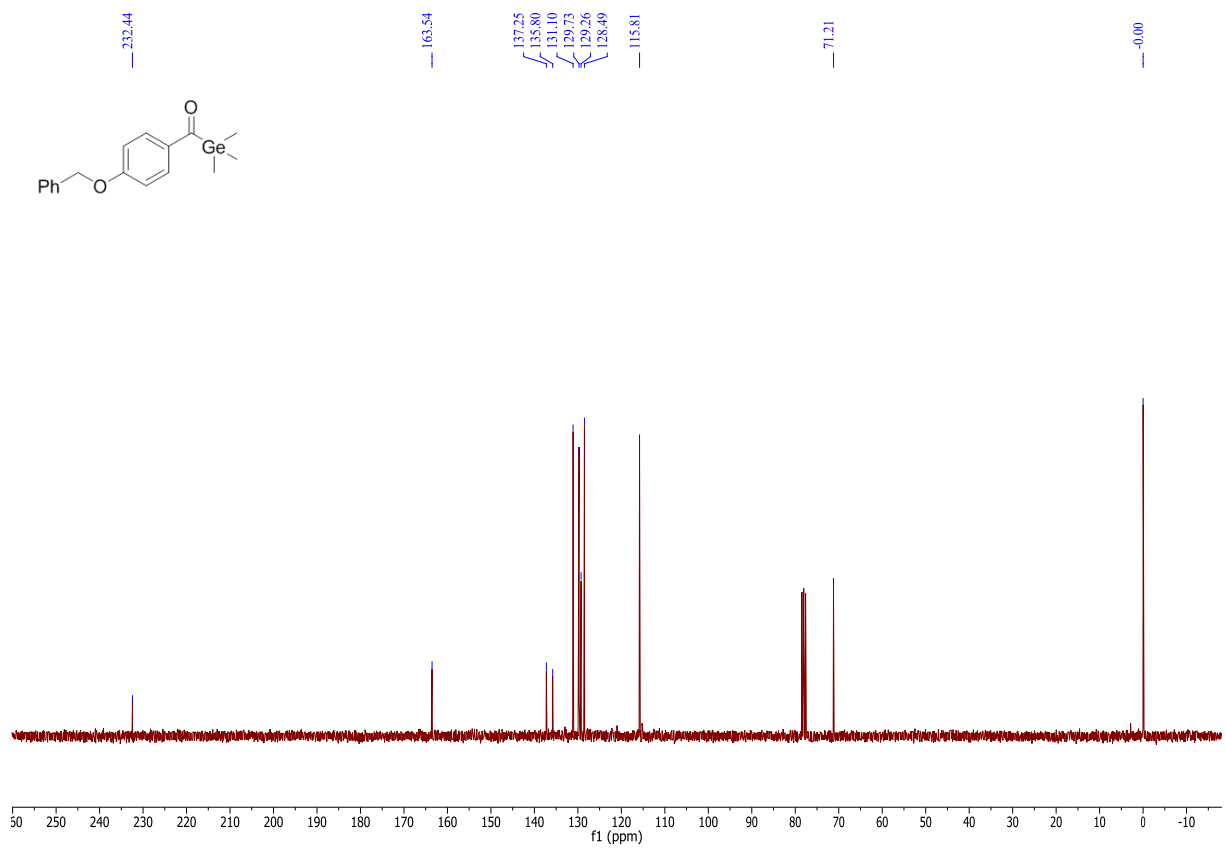


Figure S36. <sup>13</sup>C NMR spectrum of 3g, related to Scheme 2.

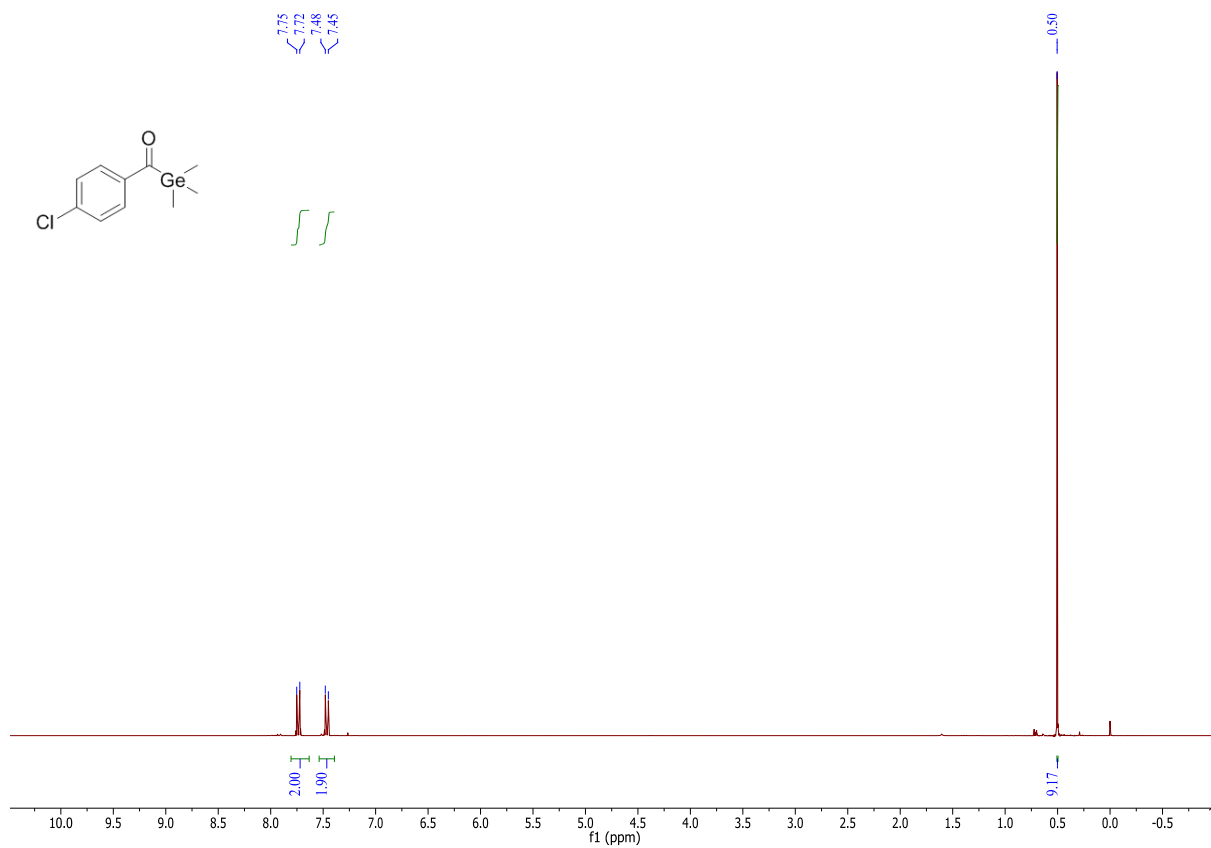


Figure S37. <sup>1</sup>H NMR spectrum of 3h, related to Scheme 2.

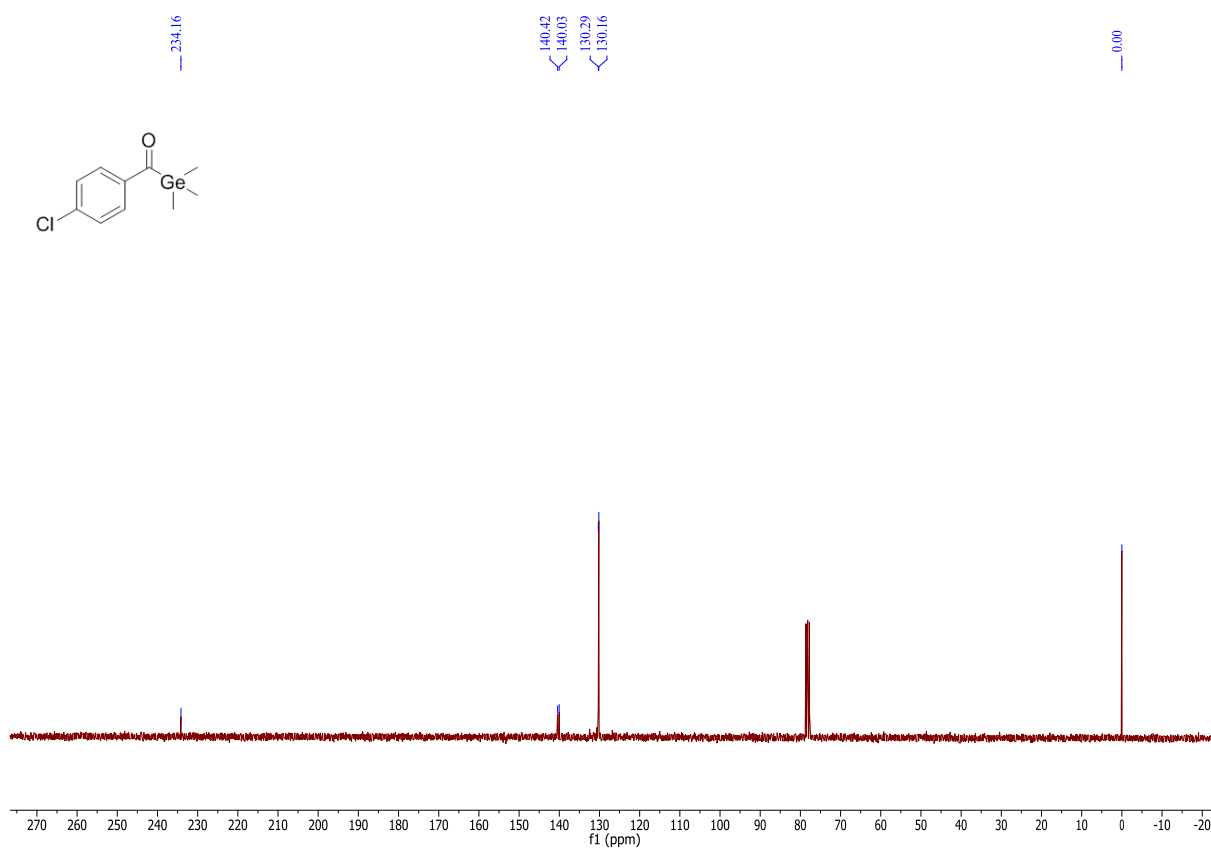


Figure S38. <sup>13</sup>C NMR spectrum of 3h, related to Scheme 2.

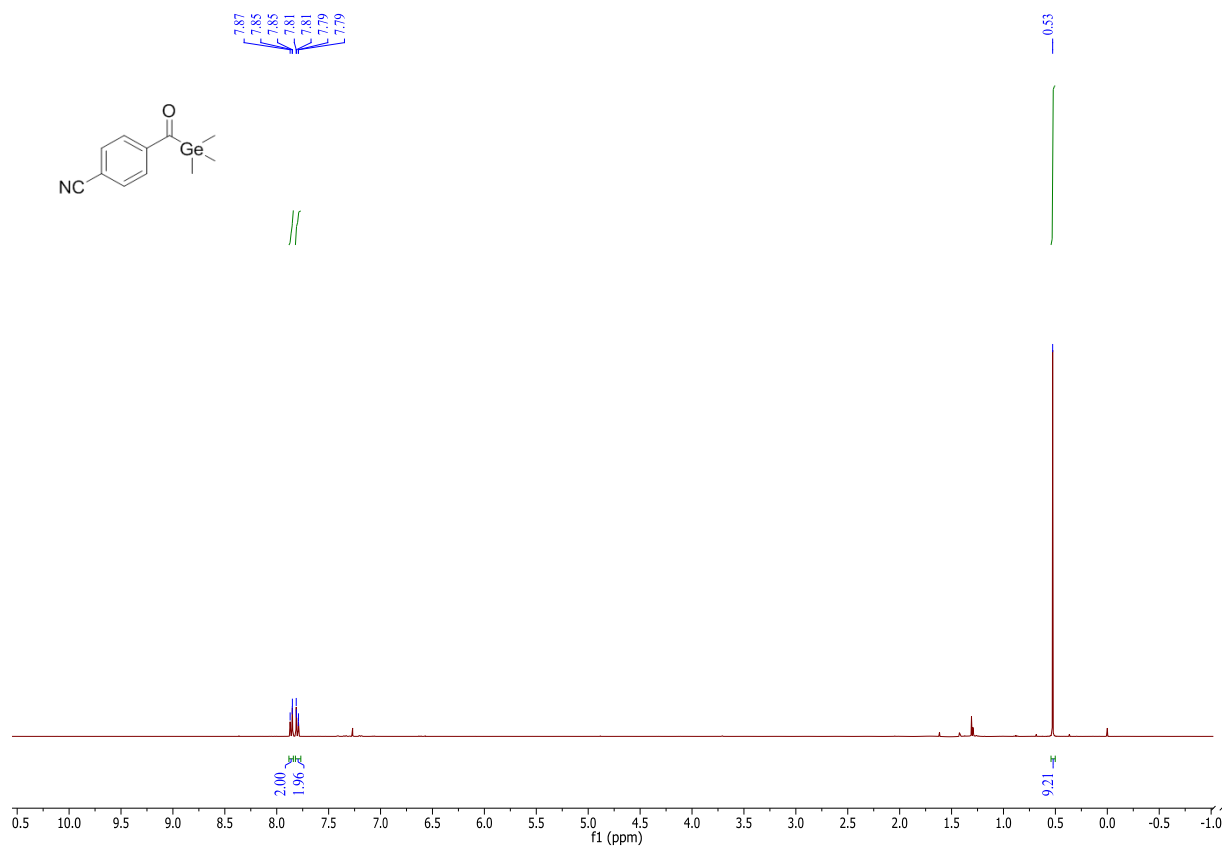


Figure S37. <sup>1</sup>H NMR spectrum of 3i, related to Scheme 2.

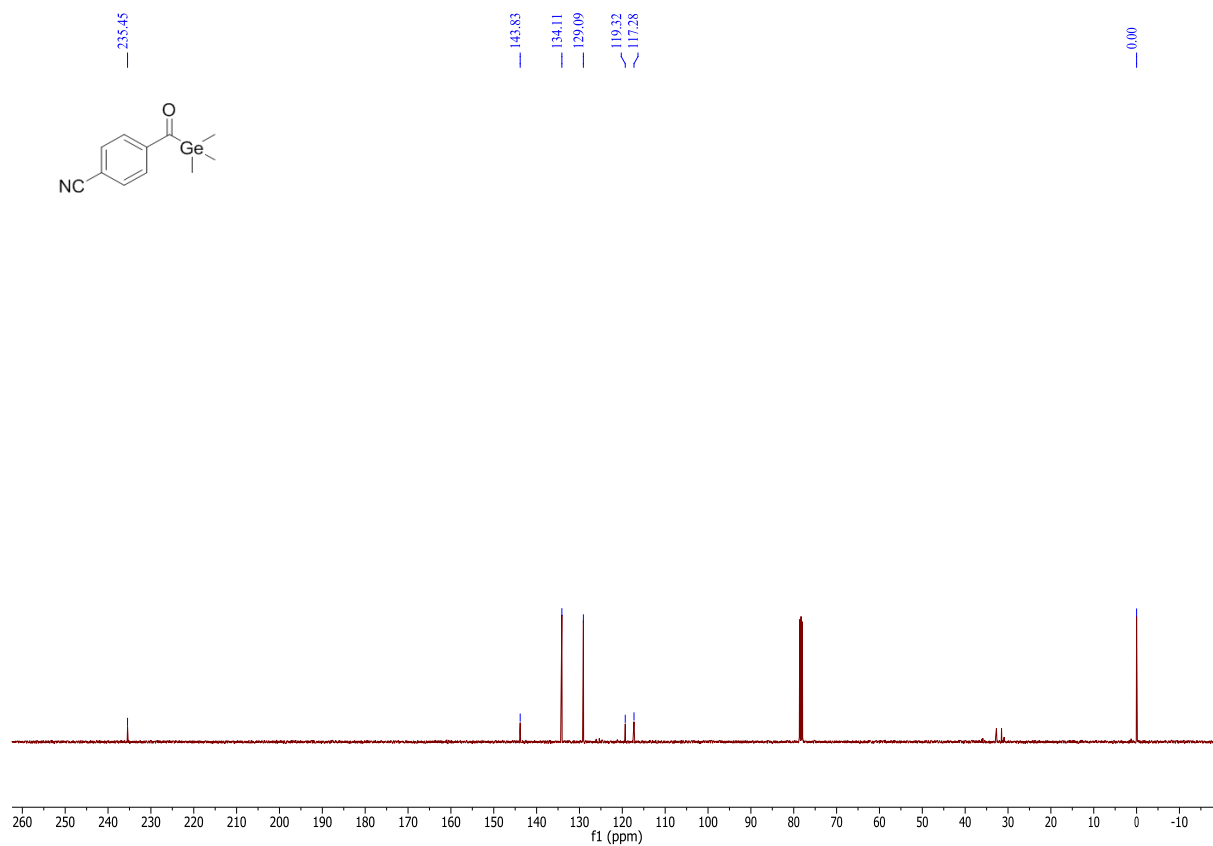


Figure S40. <sup>13</sup>C NMR spectrum of 3i, related to Scheme 2.

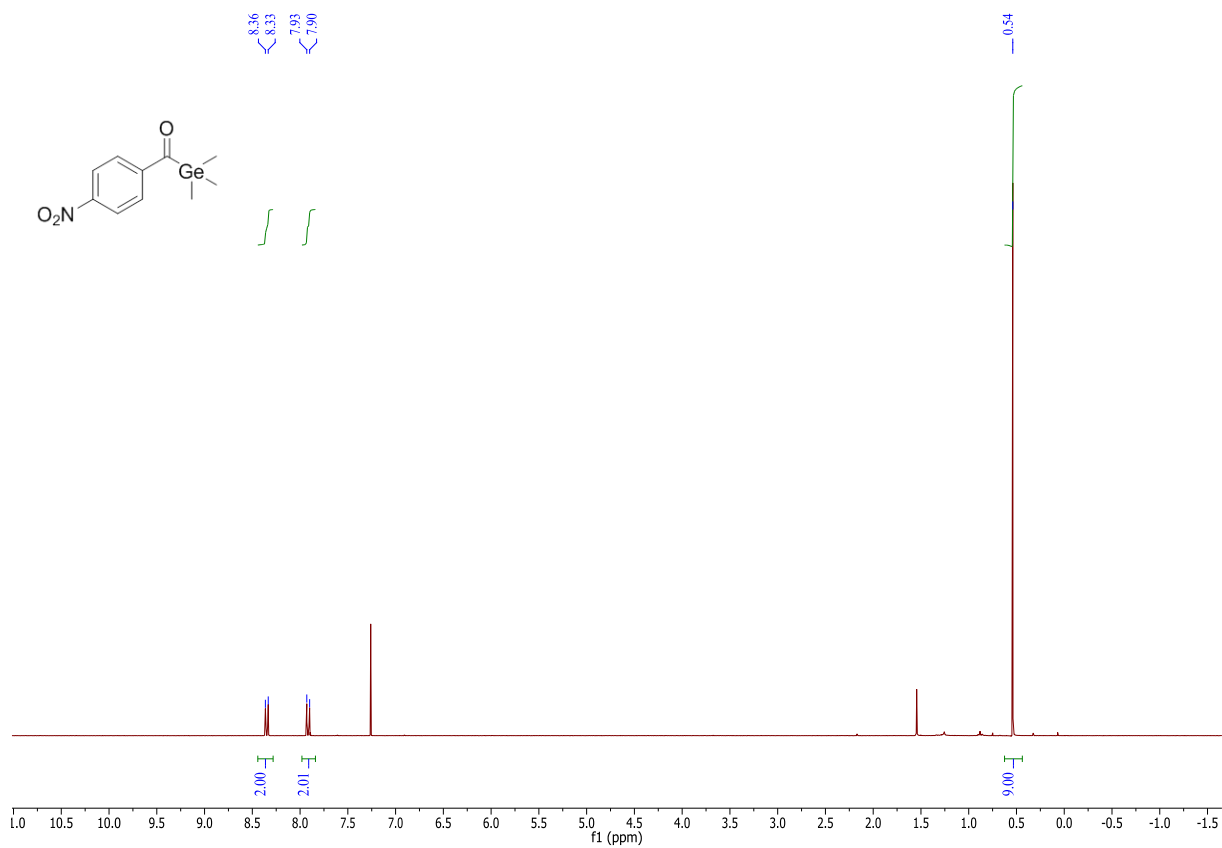


Figure S41. <sup>1</sup>H NMR spectrum of 3j, related to Scheme 2.

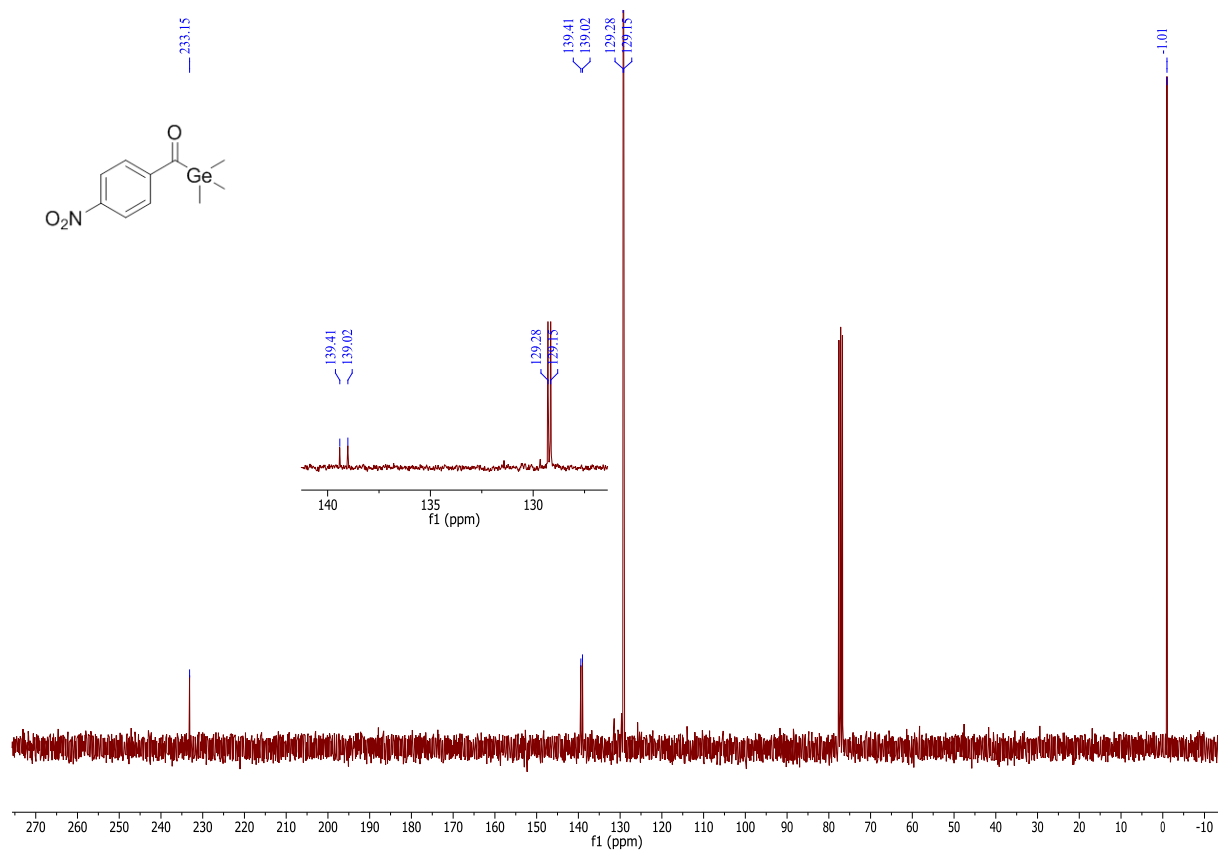
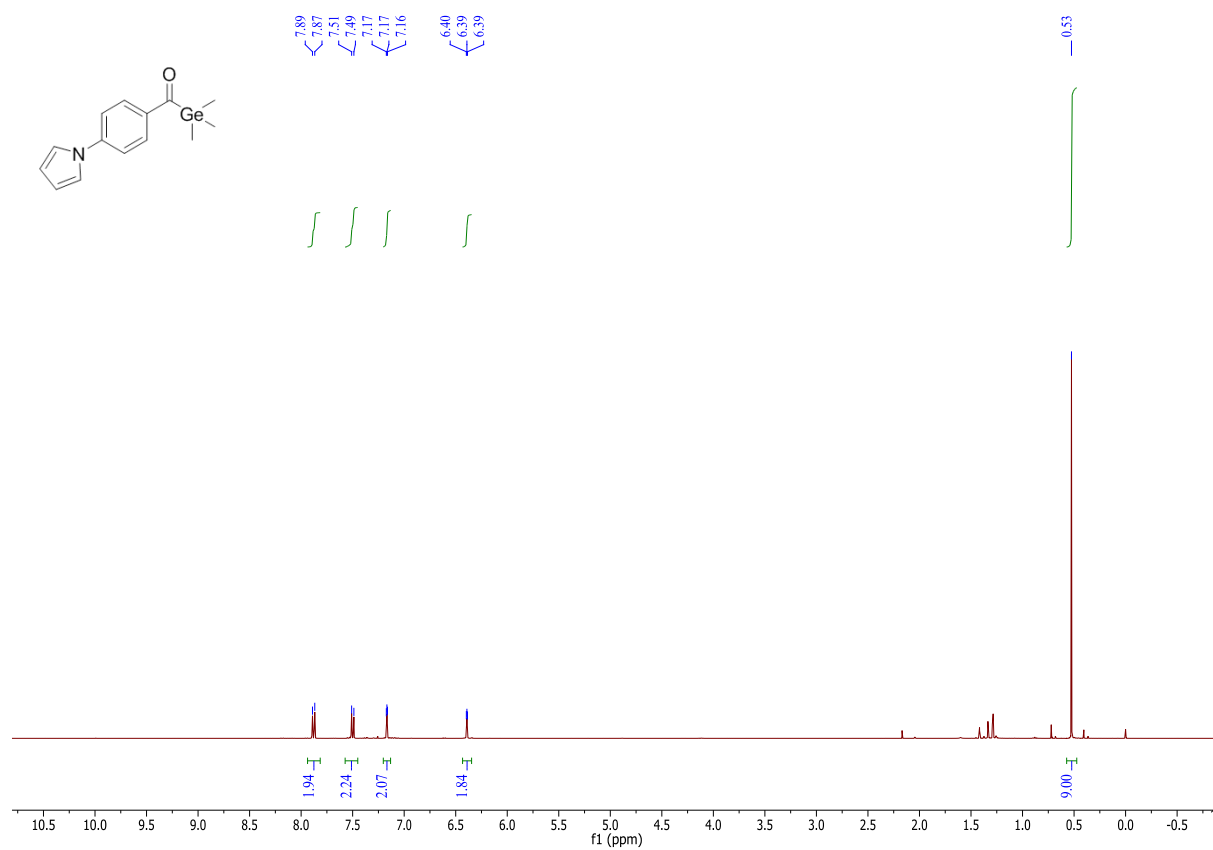
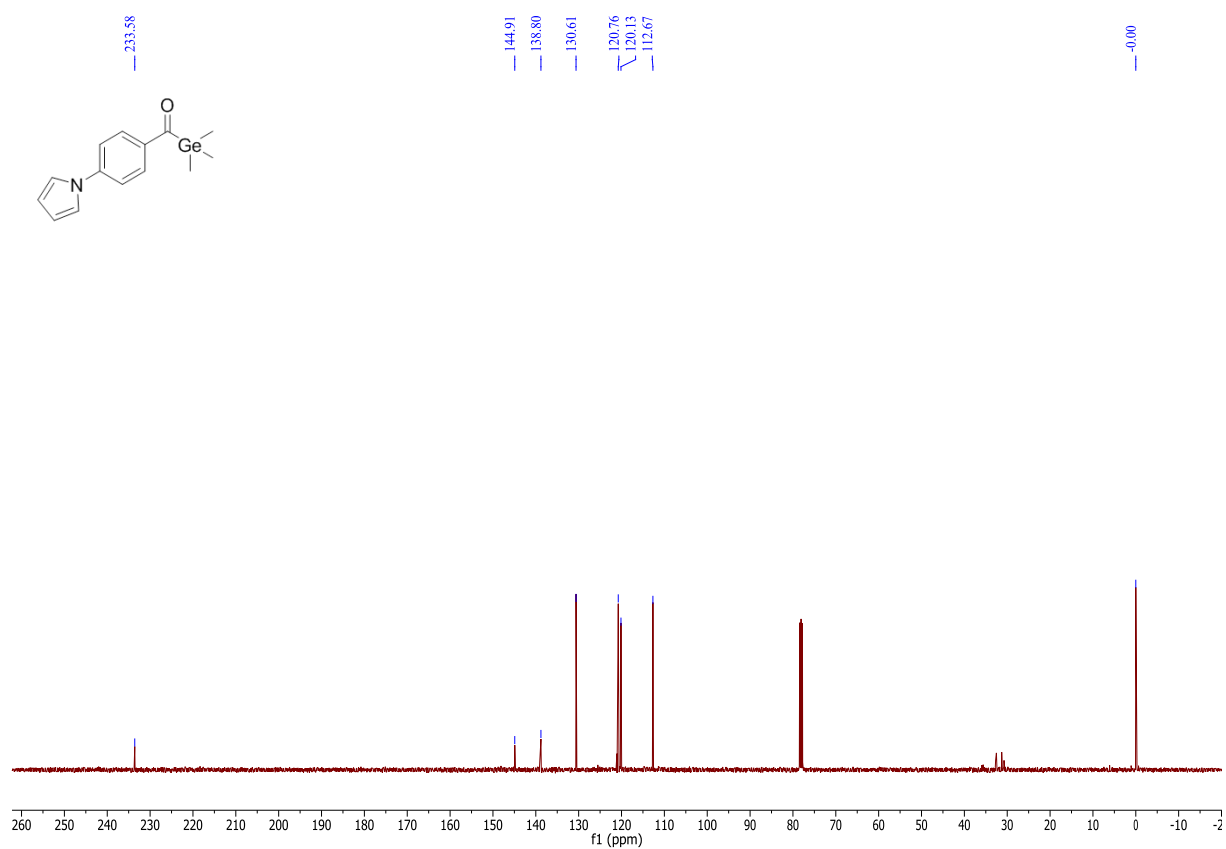


Figure S42. <sup>13</sup>C NMR spectrum of 3j, related to Scheme 2.

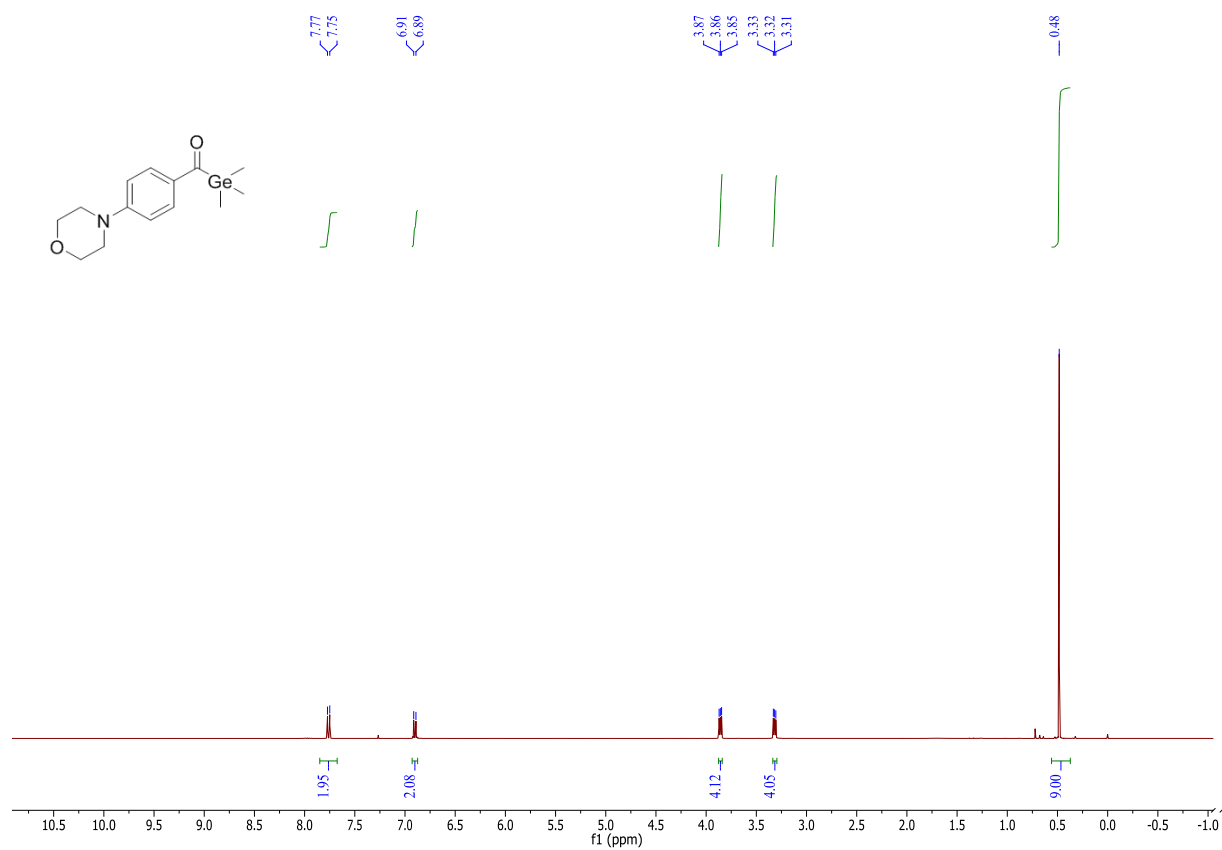




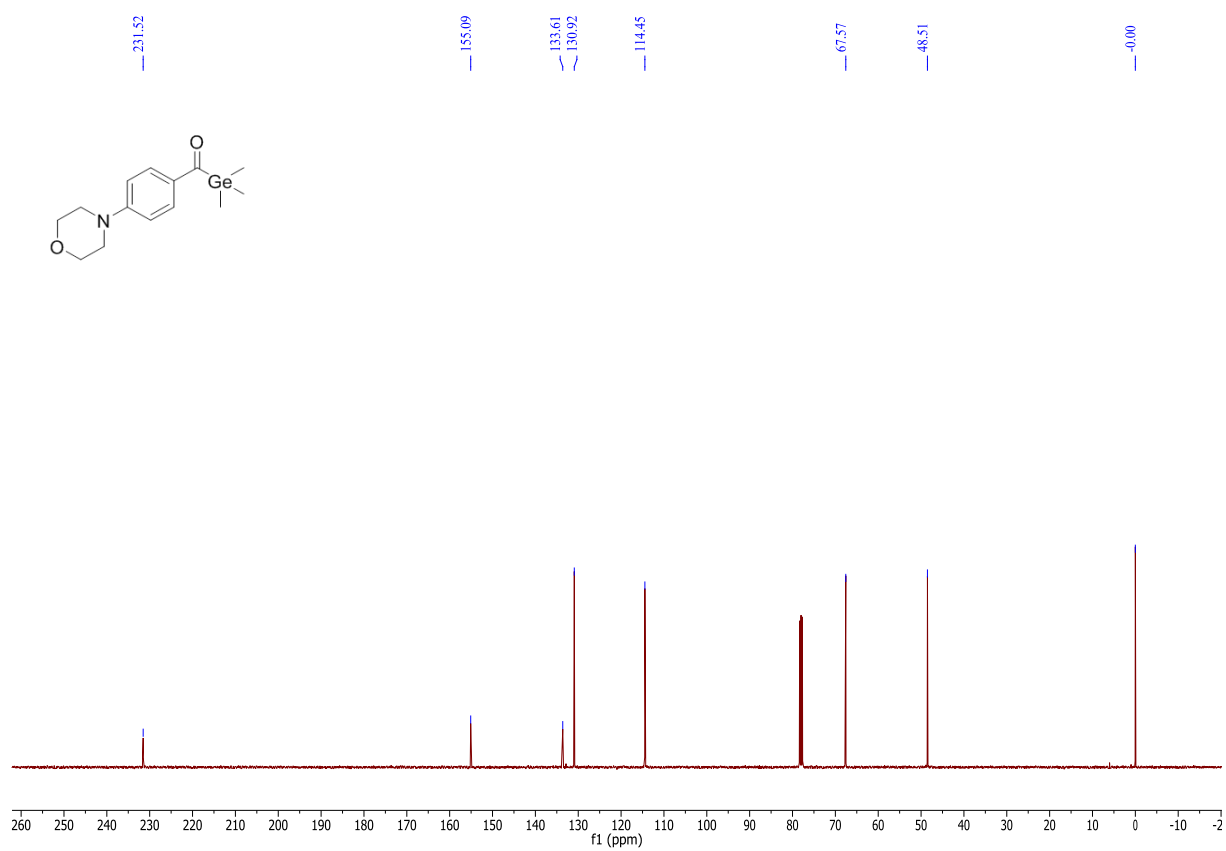
**Figure S43.**  $^1\text{H}$  NMR spectrum of 3k, related to Scheme 2.



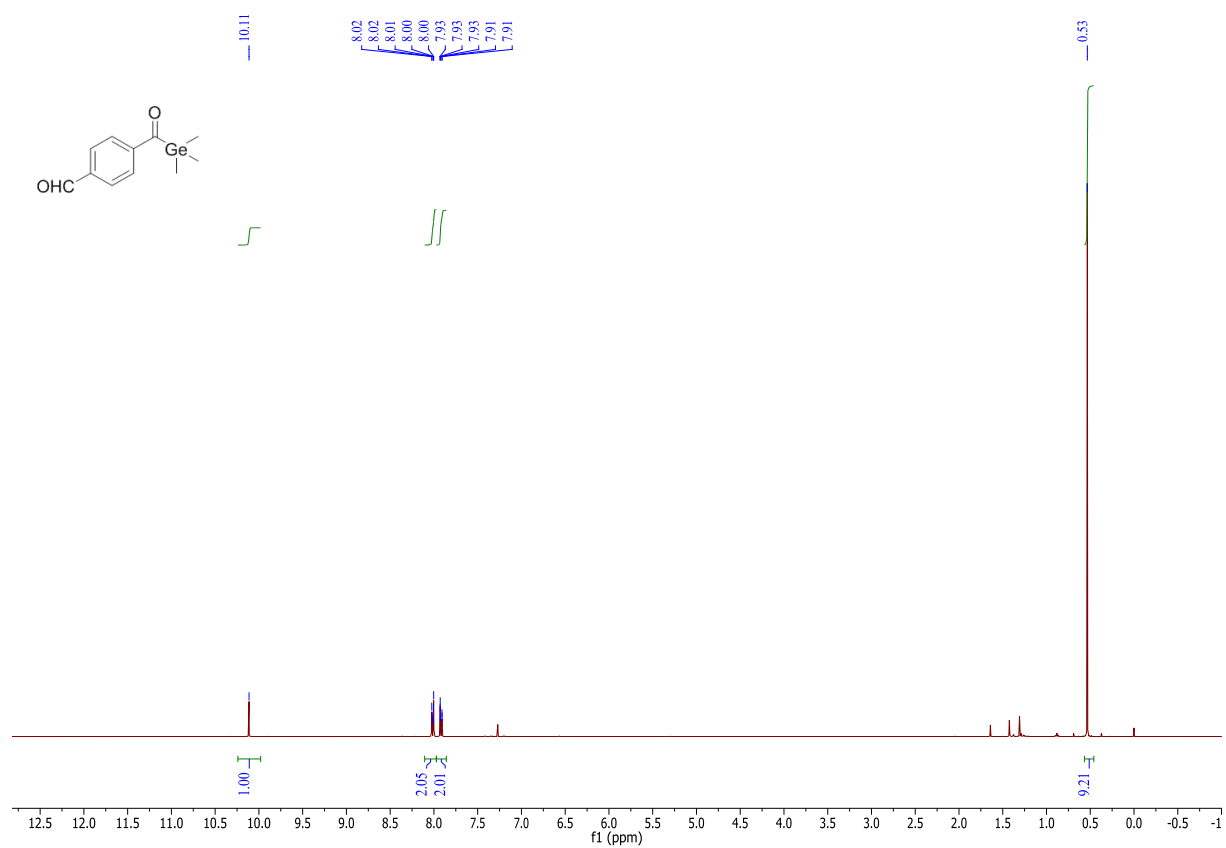
**Figure S44.**  $^{13}\text{C}$  NMR spectrum of 3k, related to Scheme 2.



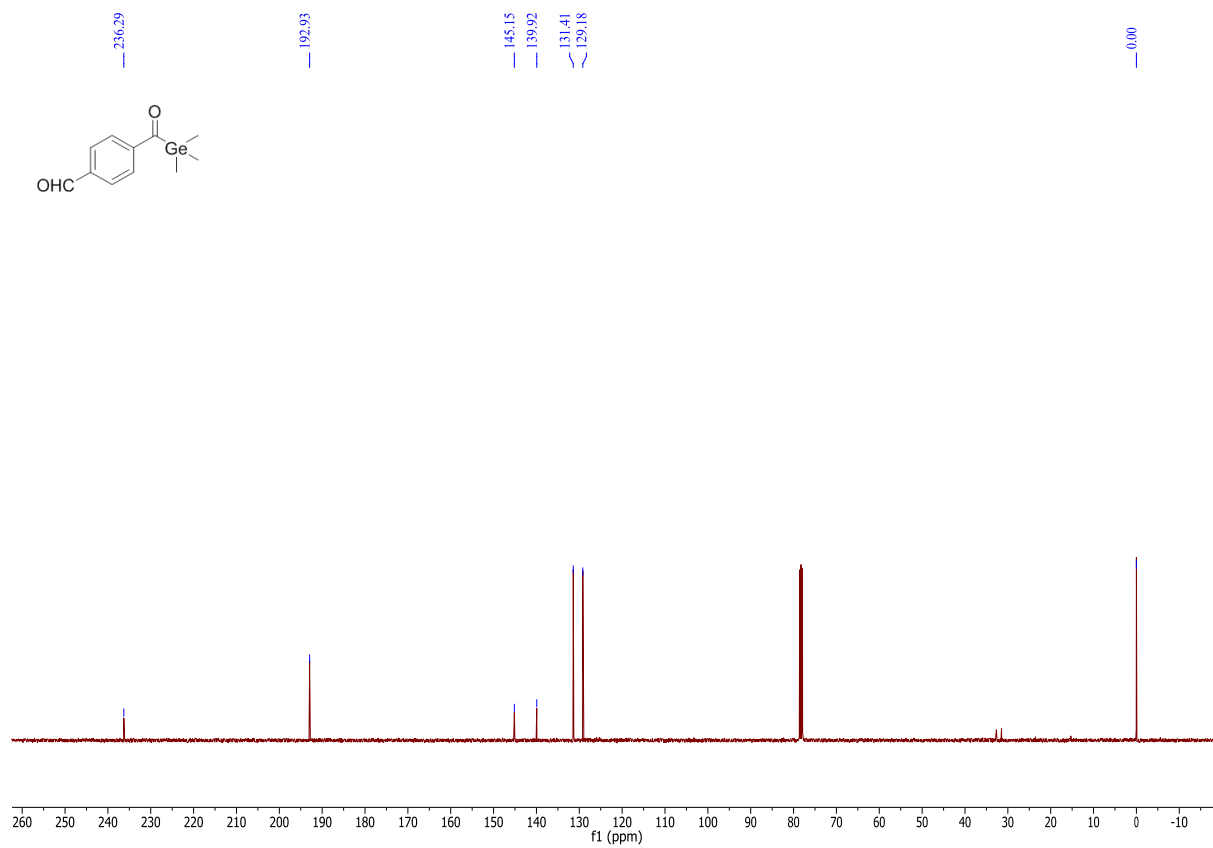
**Figure S45.**  $^1\text{H}$  NMR spectrum of 31, related to Scheme 2.



**Figure S46.**  $^{13}\text{C}$  NMR spectrum of 31, related to Scheme 2.



**Figure S47.** <sup>1</sup>H NMR spectrum of 3m, related to Scheme 2.



**Figure S48.** <sup>13</sup>C NMR spectrum of 3m, related to Scheme 2.

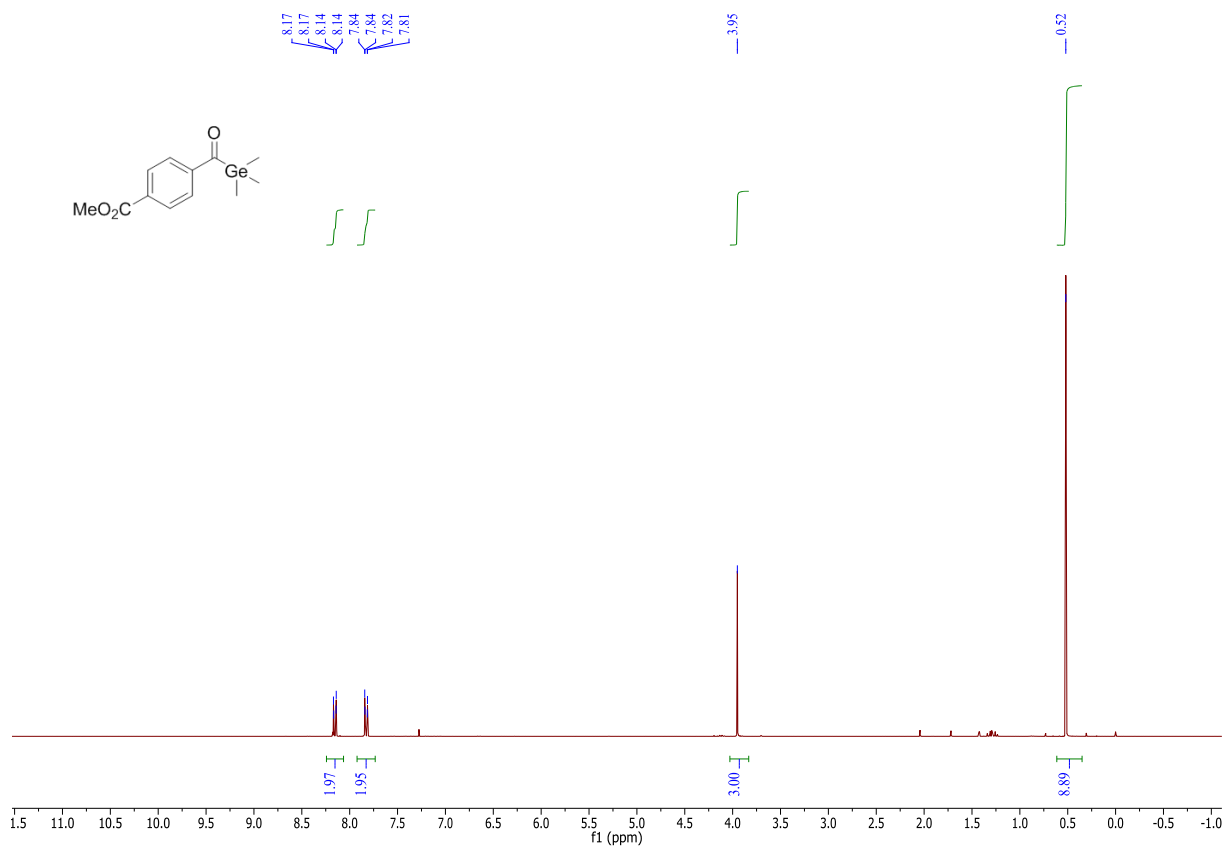


Figure S49. <sup>1</sup>H NMR spectrum of 3n, related to Scheme 2.

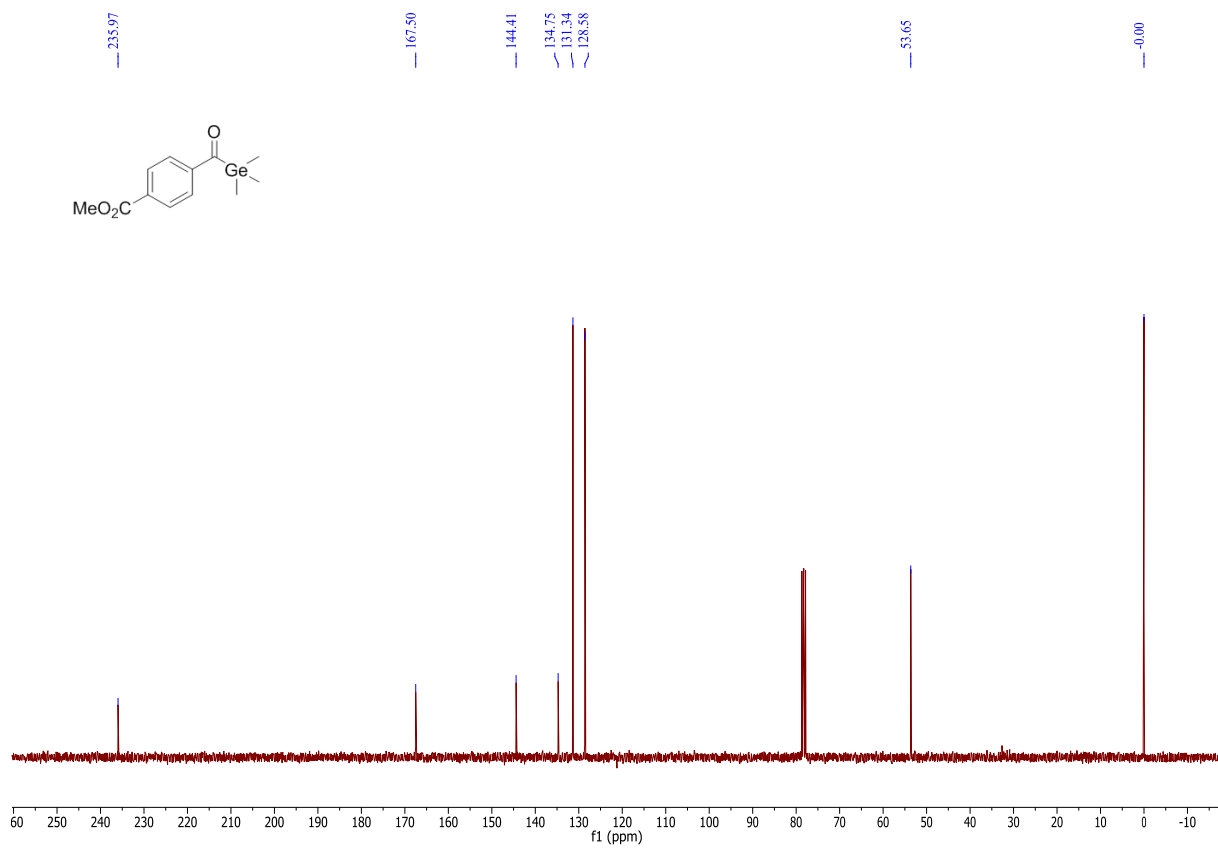


Figure S50. <sup>13</sup>C NMR spectrum of 3n, related to Scheme 2.

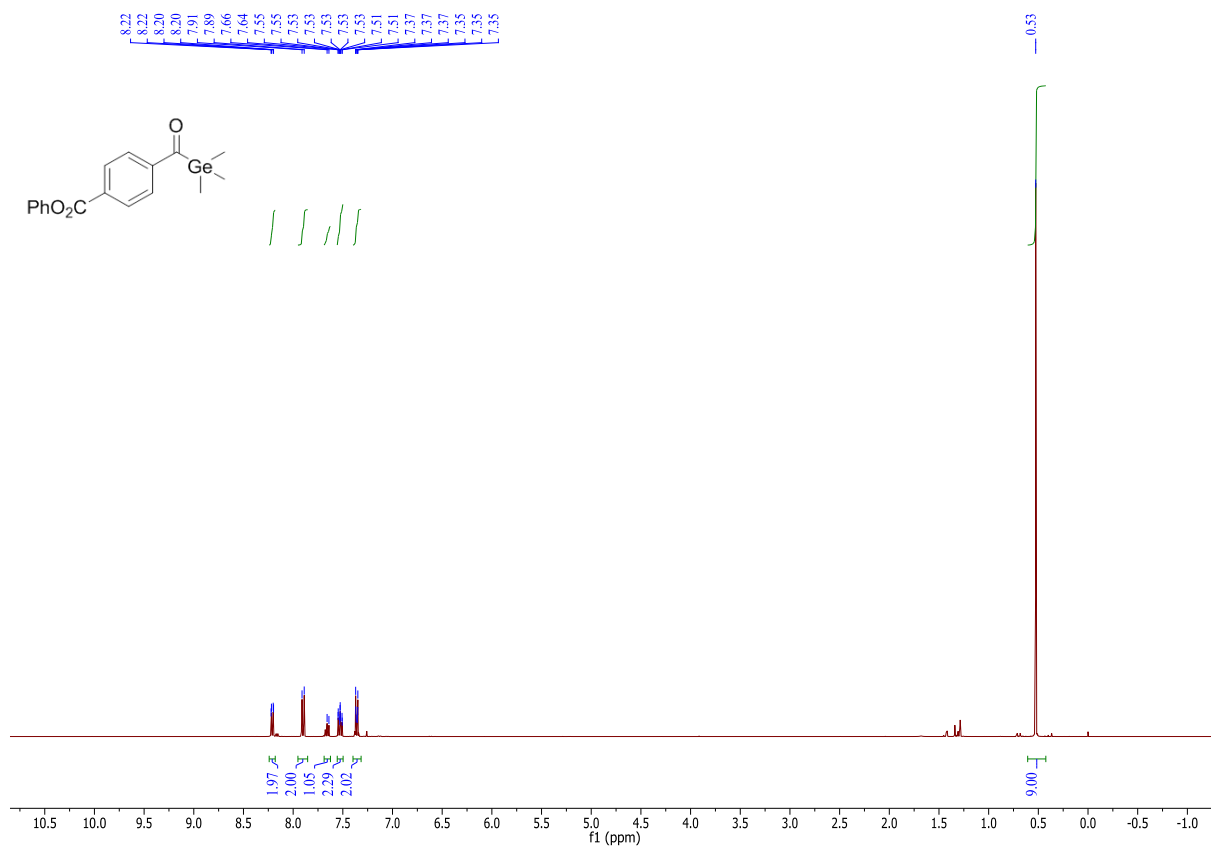


Figure S51. <sup>1</sup>H NMR spectrum of 3o, related to Scheme 2.

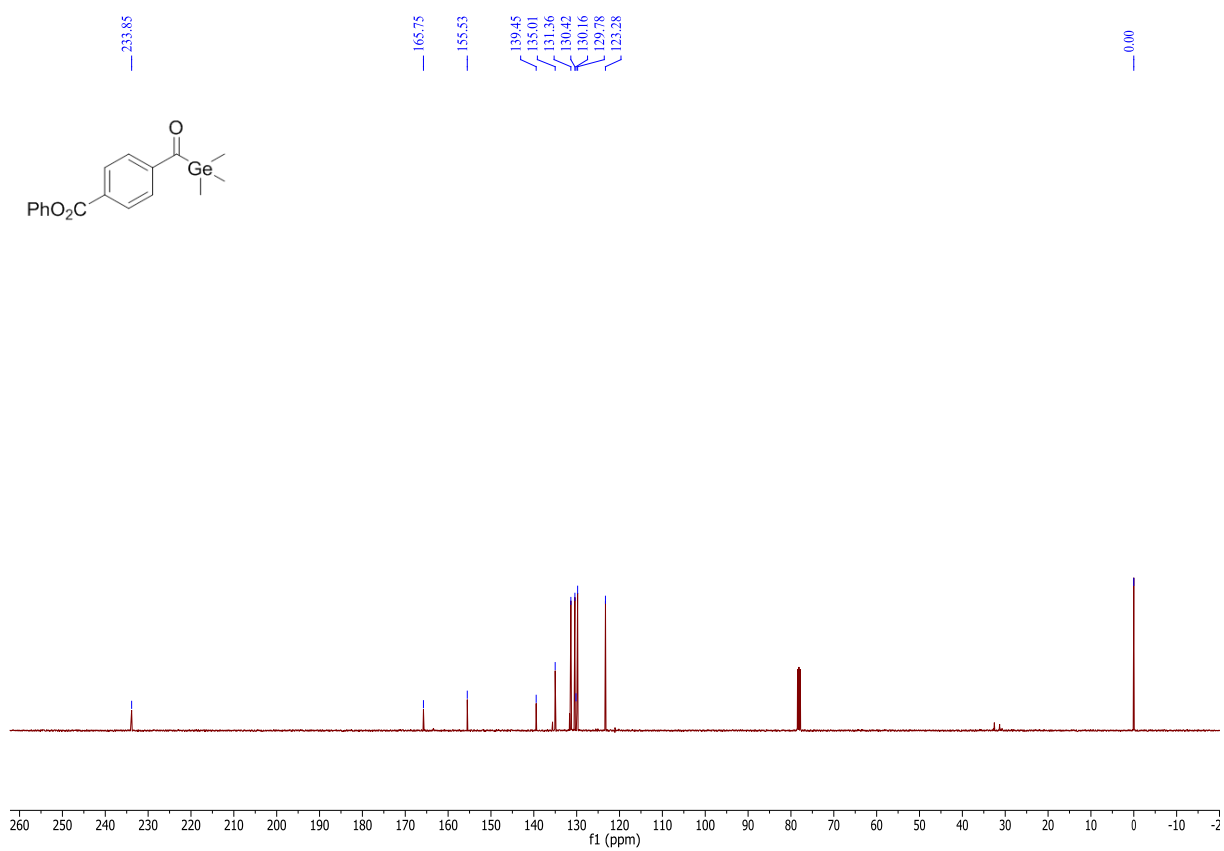


Figure S52. <sup>13</sup>C NMR spectrum of 3o, related to Scheme 2.

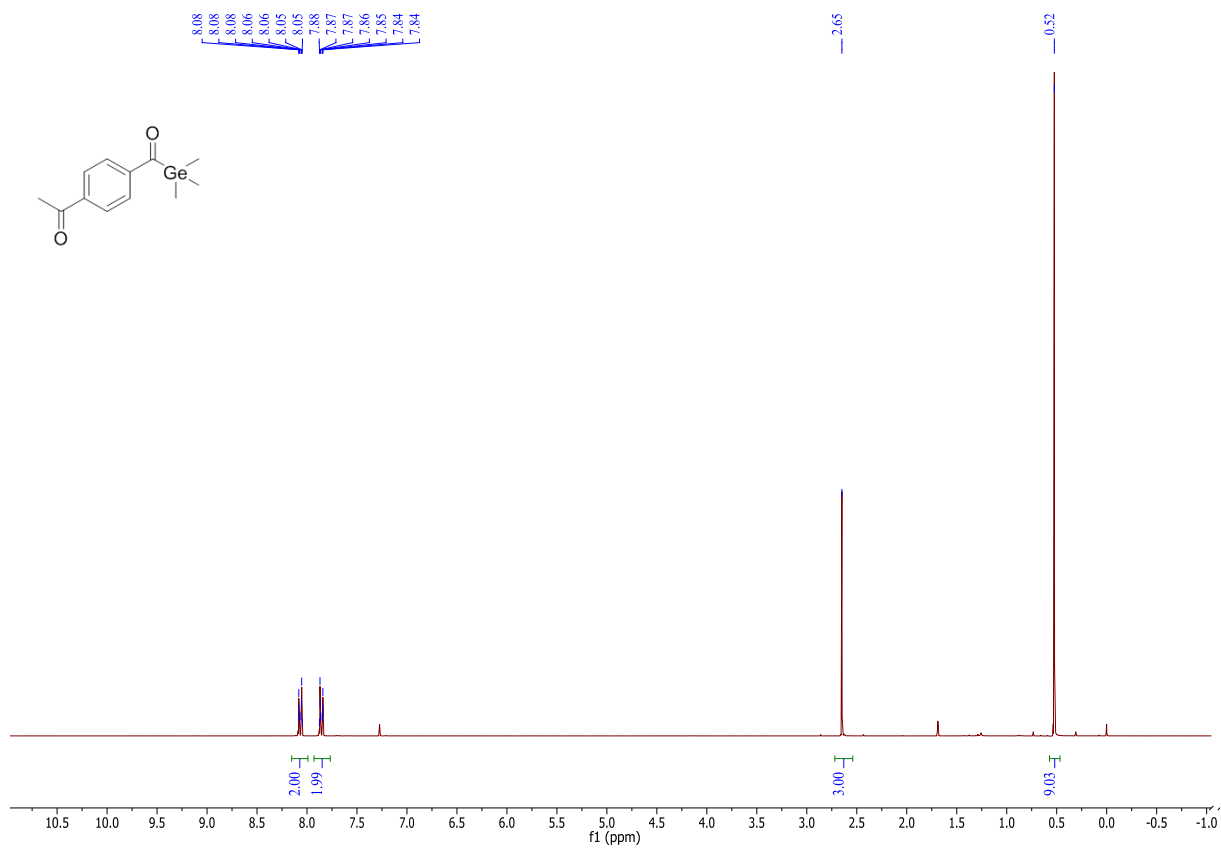


Figure S53. <sup>1</sup>H NMR spectrum of 3p, related to Scheme 2.

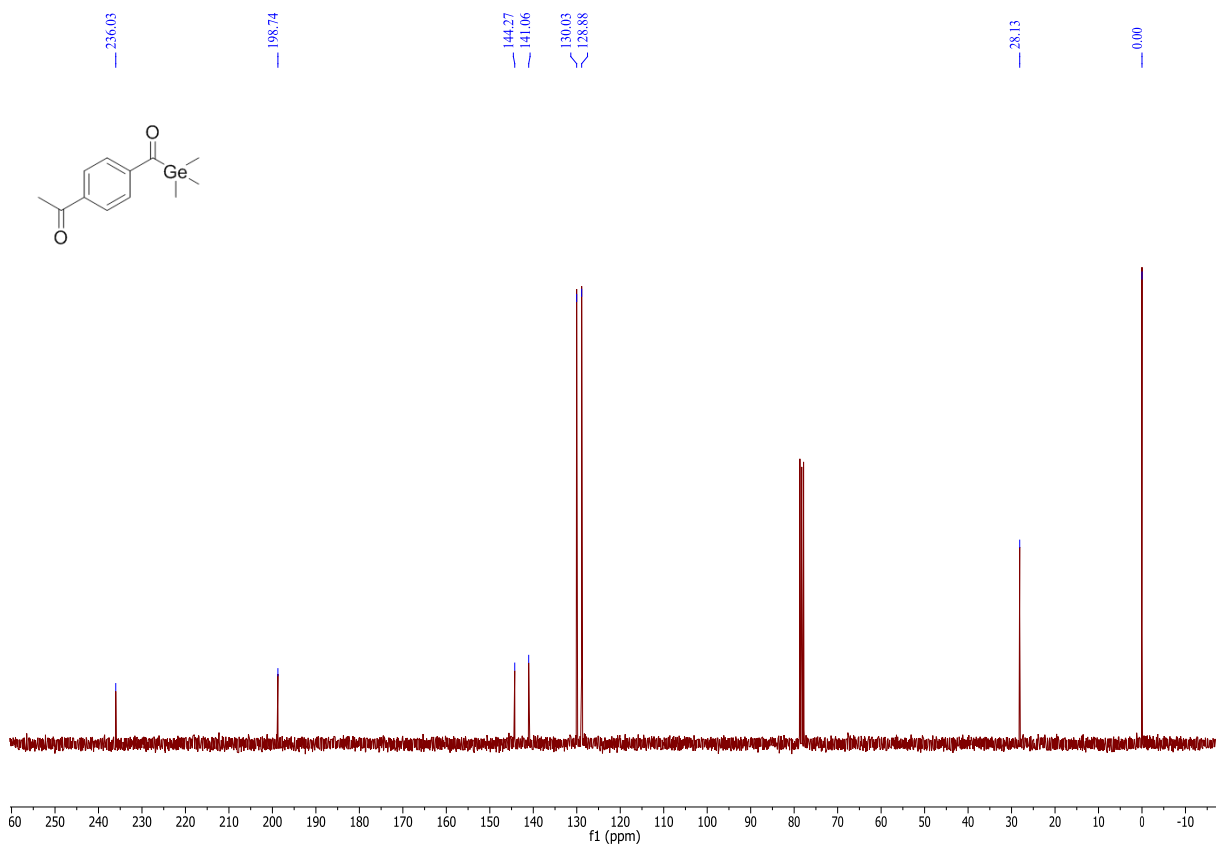


Figure S54. <sup>13</sup>C NMR spectrum of 3p, related to Scheme 2.

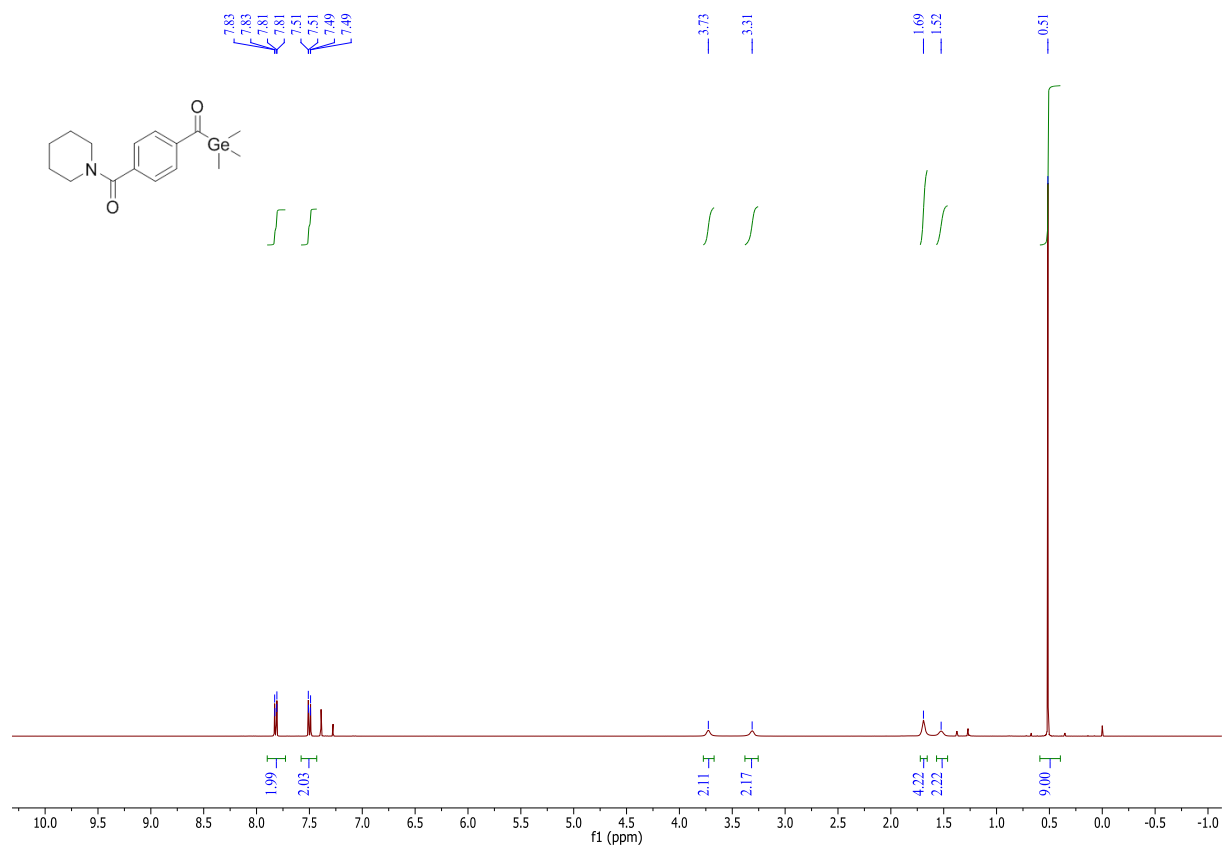


Figure S55. <sup>1</sup>H NMR spectrum of 3q, related to Scheme 2.

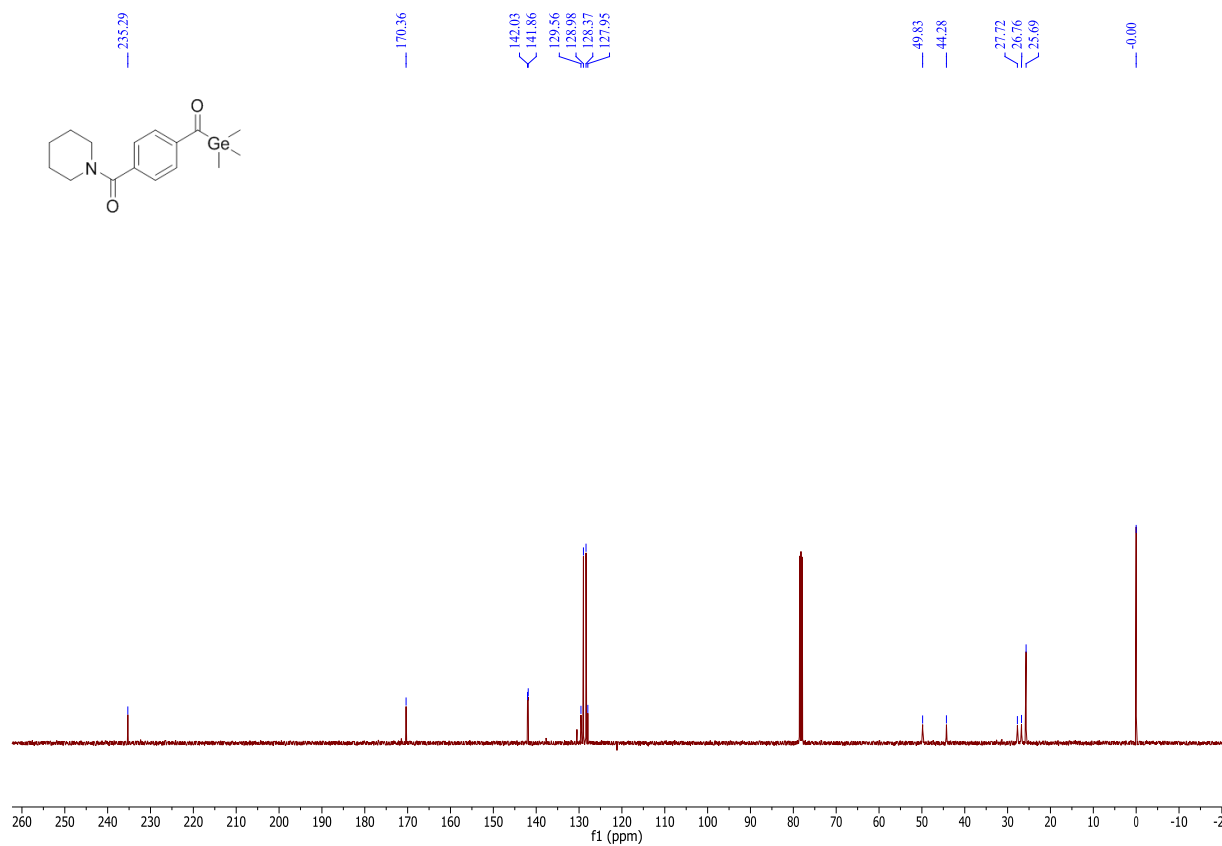


Figure S56. <sup>13</sup>C NMR spectrum of 3q, related to Scheme 2.

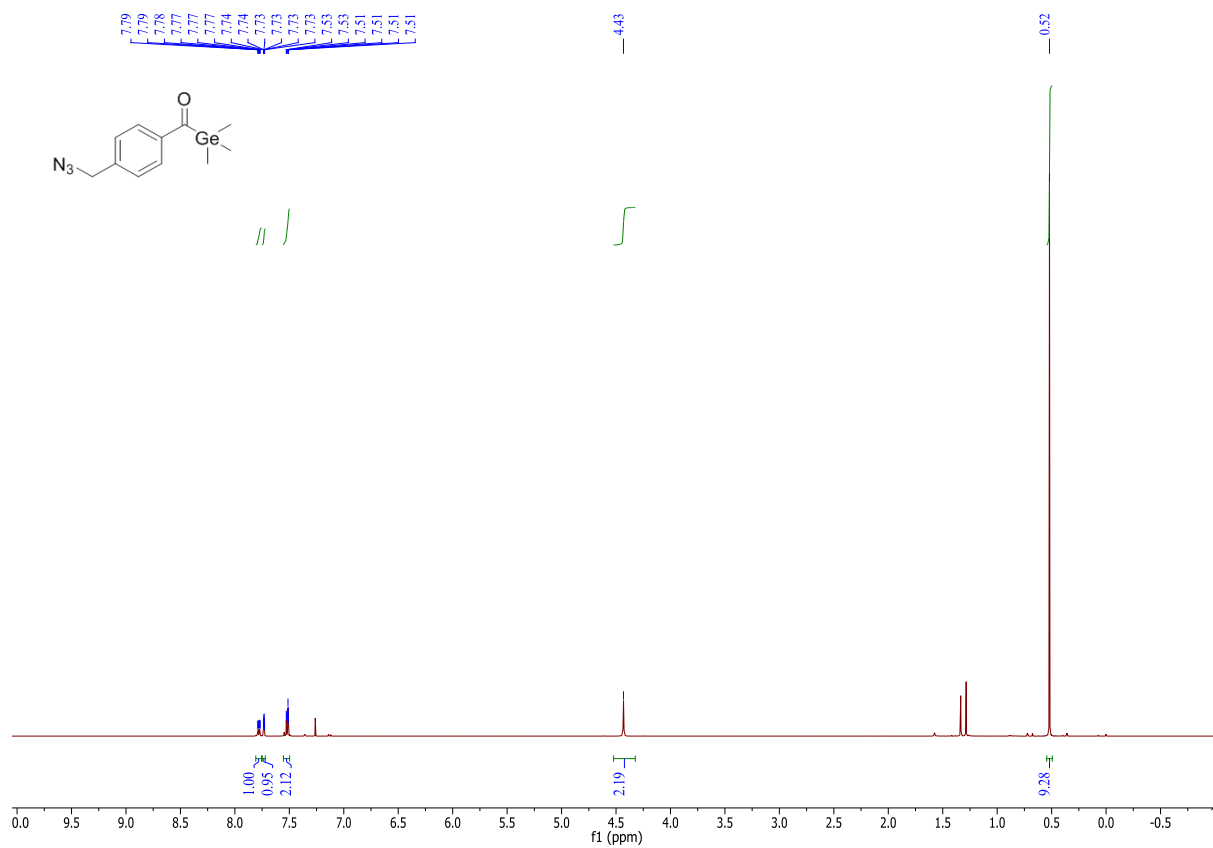


Figure S57. <sup>1</sup>H NMR spectrum of 3r, related to Scheme 2.

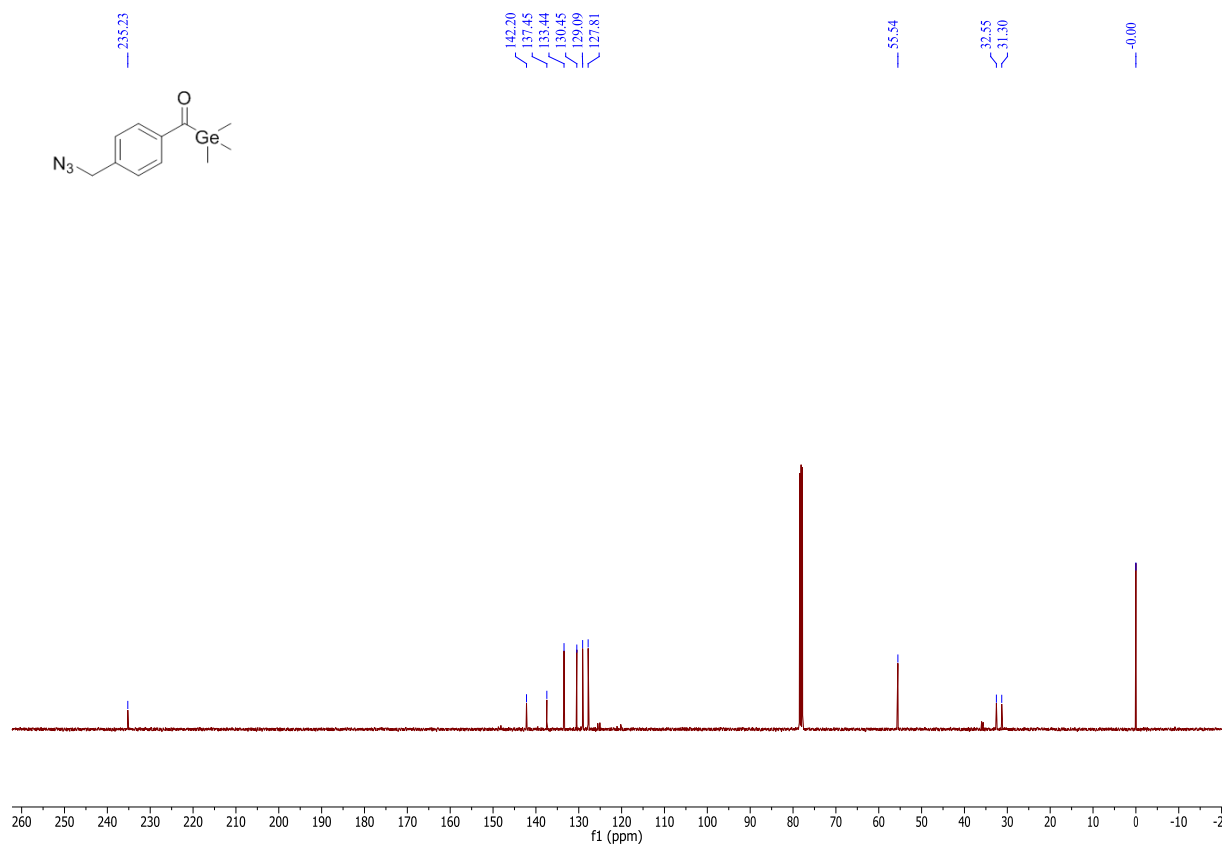


Figure S58. <sup>13</sup>C NMR spectrum of 3r, related to Scheme 2.



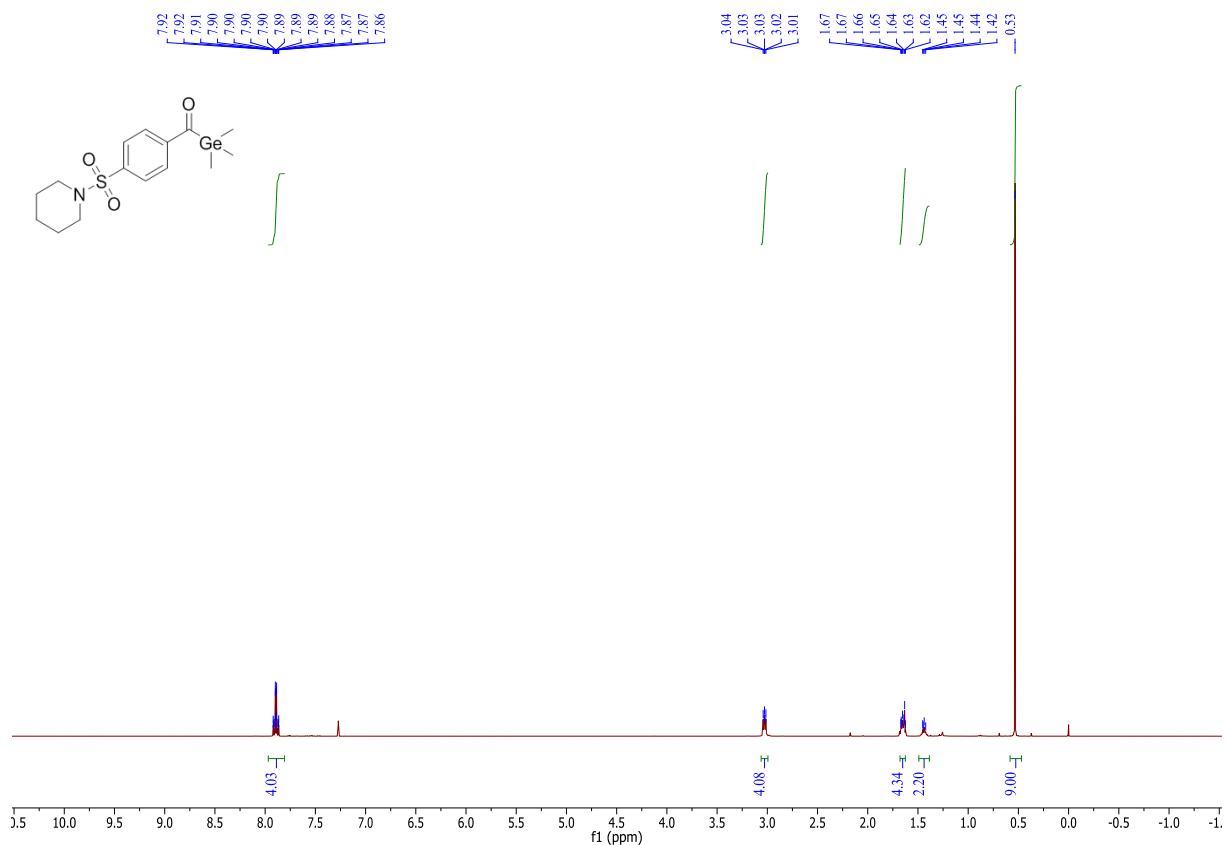


Figure S59. <sup>1</sup>H NMR spectrum of 3s, related to Scheme 2.

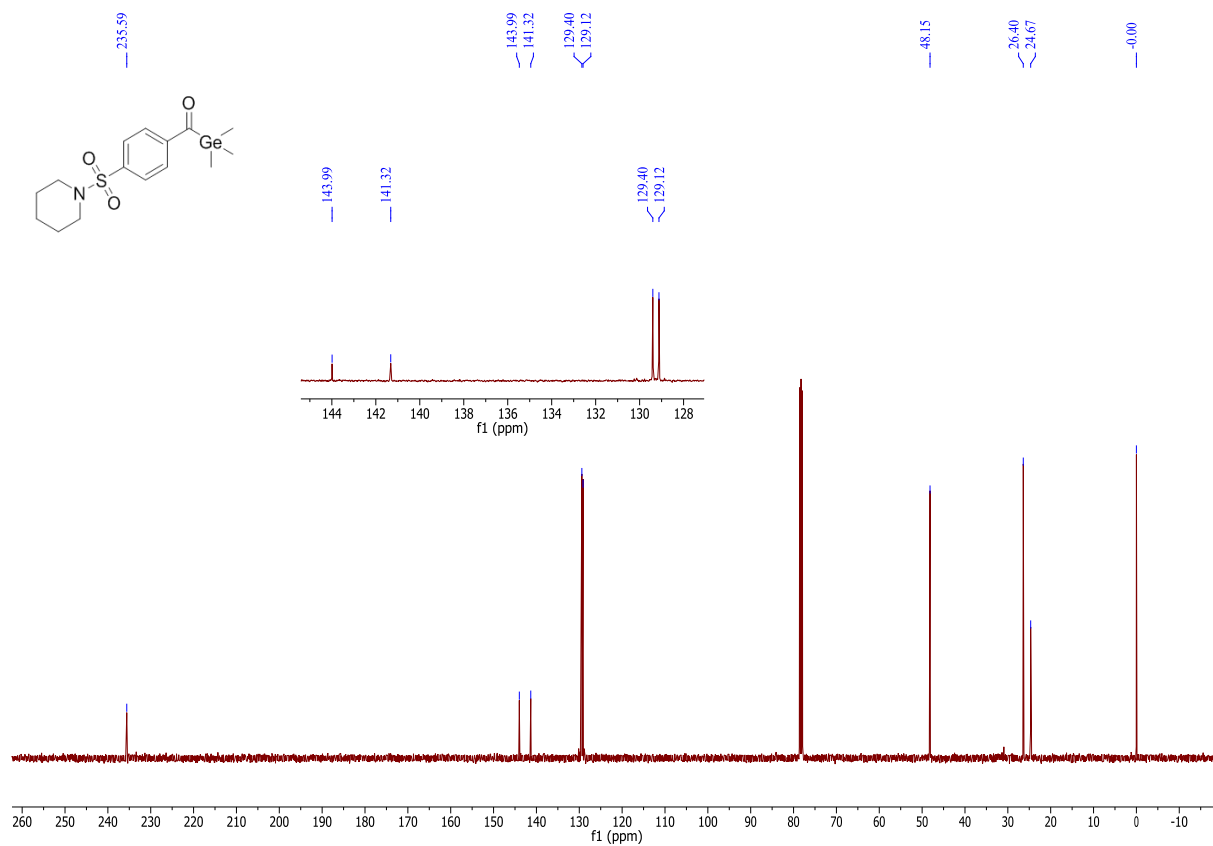


Figure S60. <sup>13</sup>C NMR spectrum of 3s, related to Scheme 2.

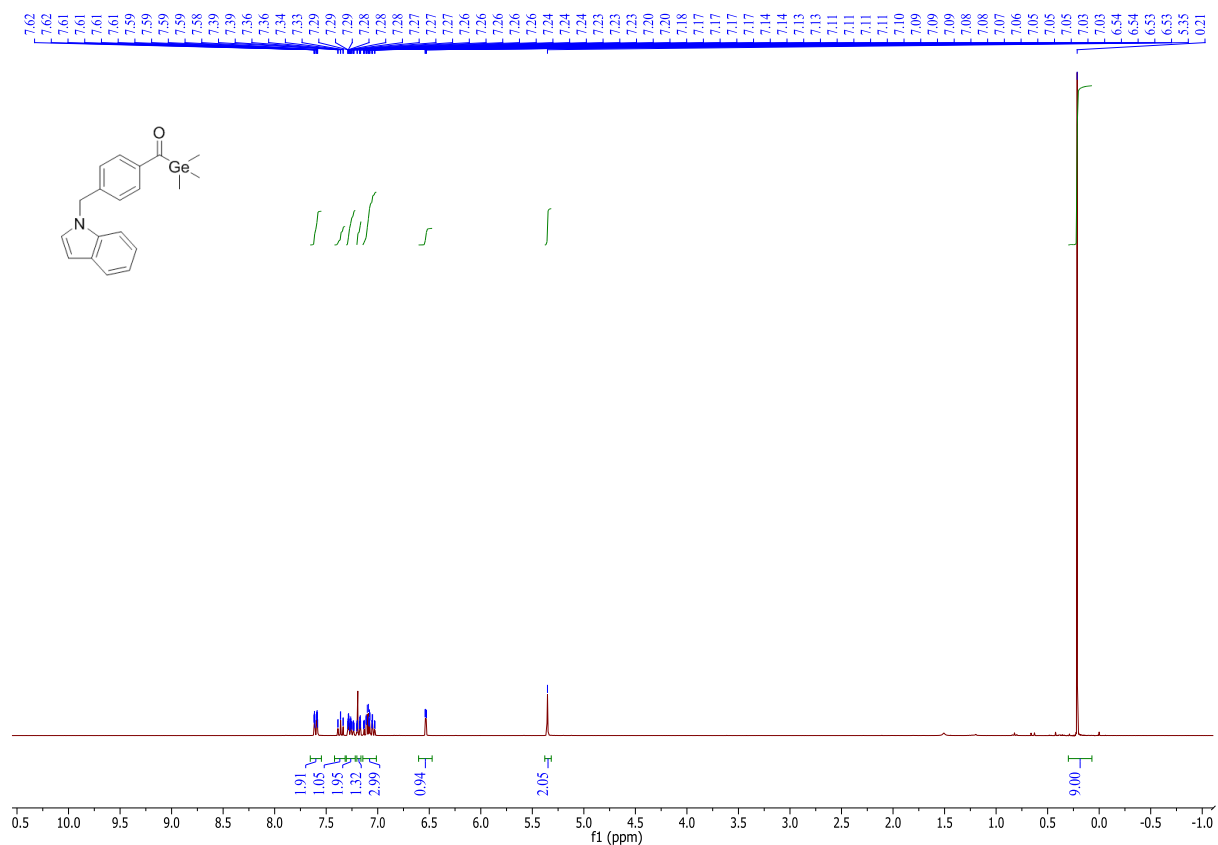


Figure S61. <sup>1</sup>H NMR spectrum of 3t, related to Scheme 2.

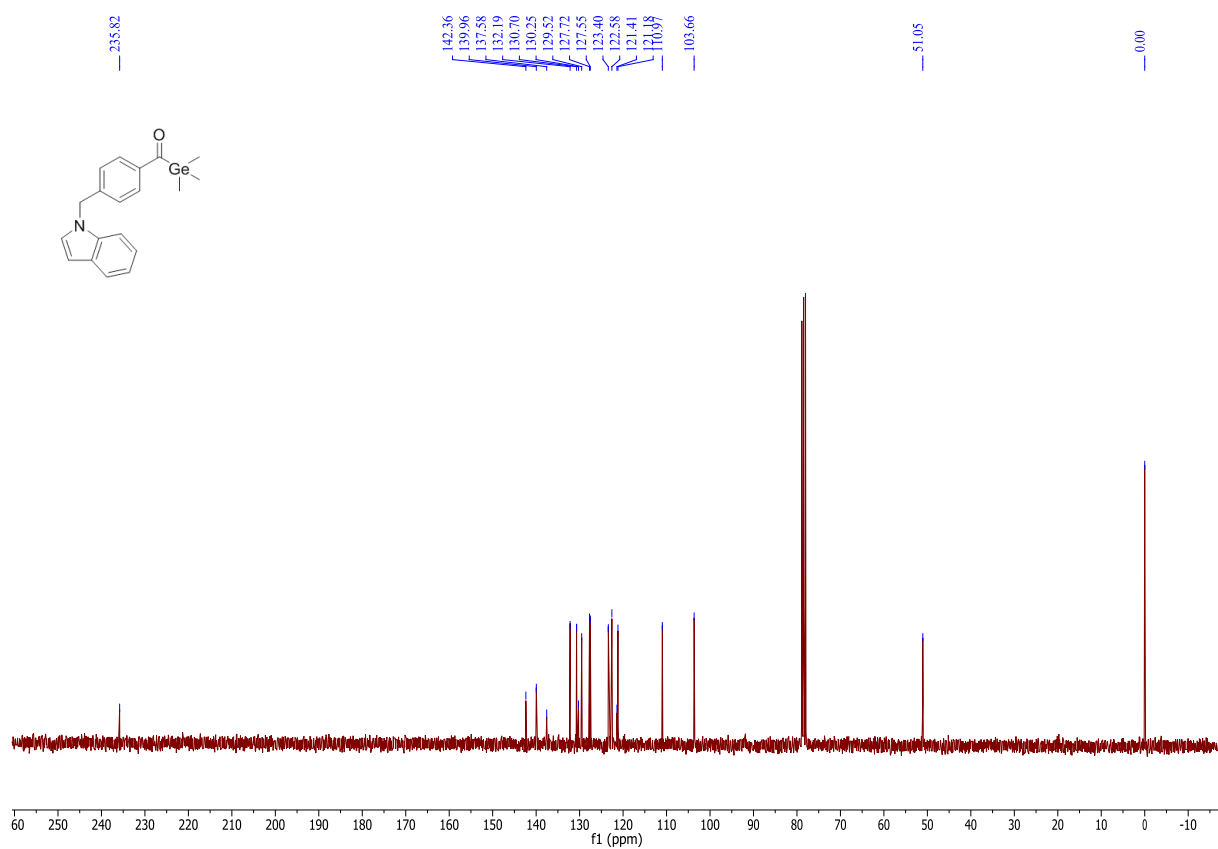


Figure S62. <sup>13</sup>C NMR spectrum of 3t, related to Scheme 2.

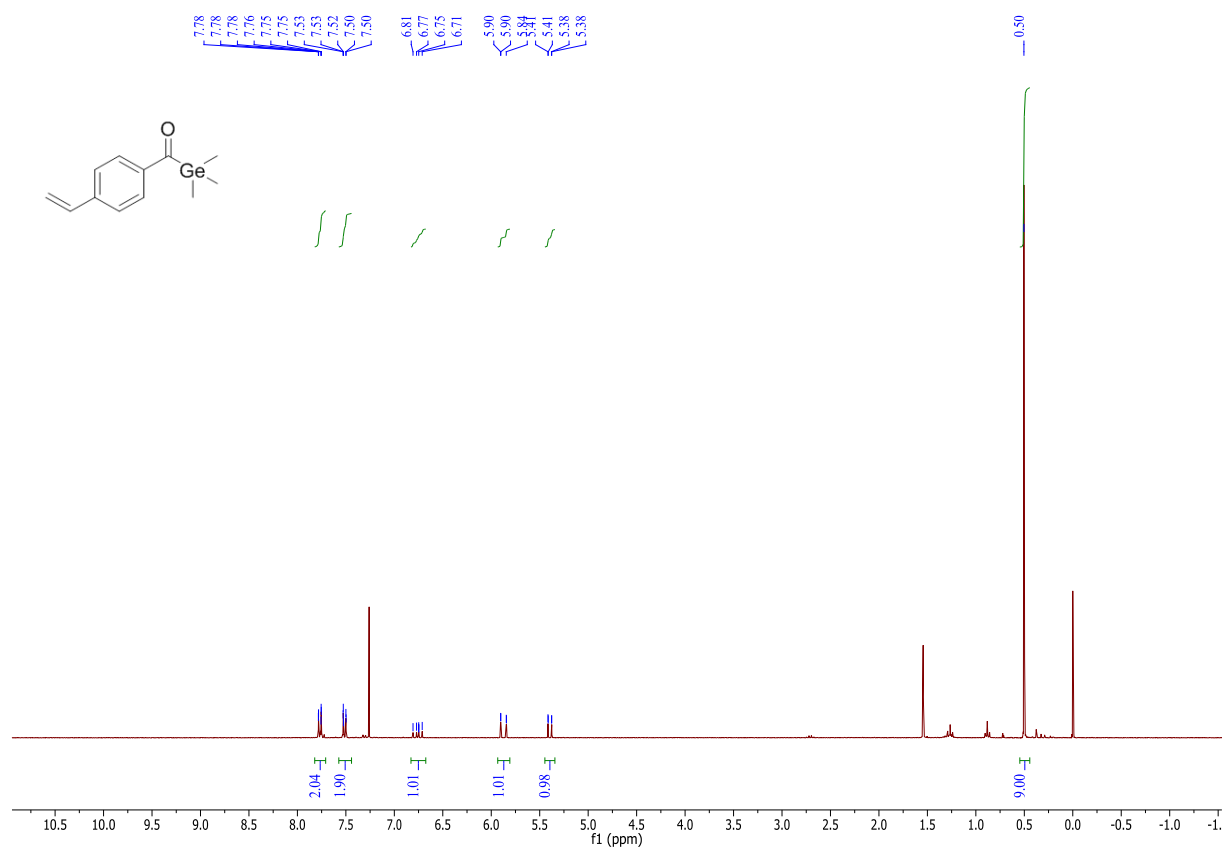


Figure S63. <sup>1</sup>H NMR spectrum of 3u, related to Scheme 2.

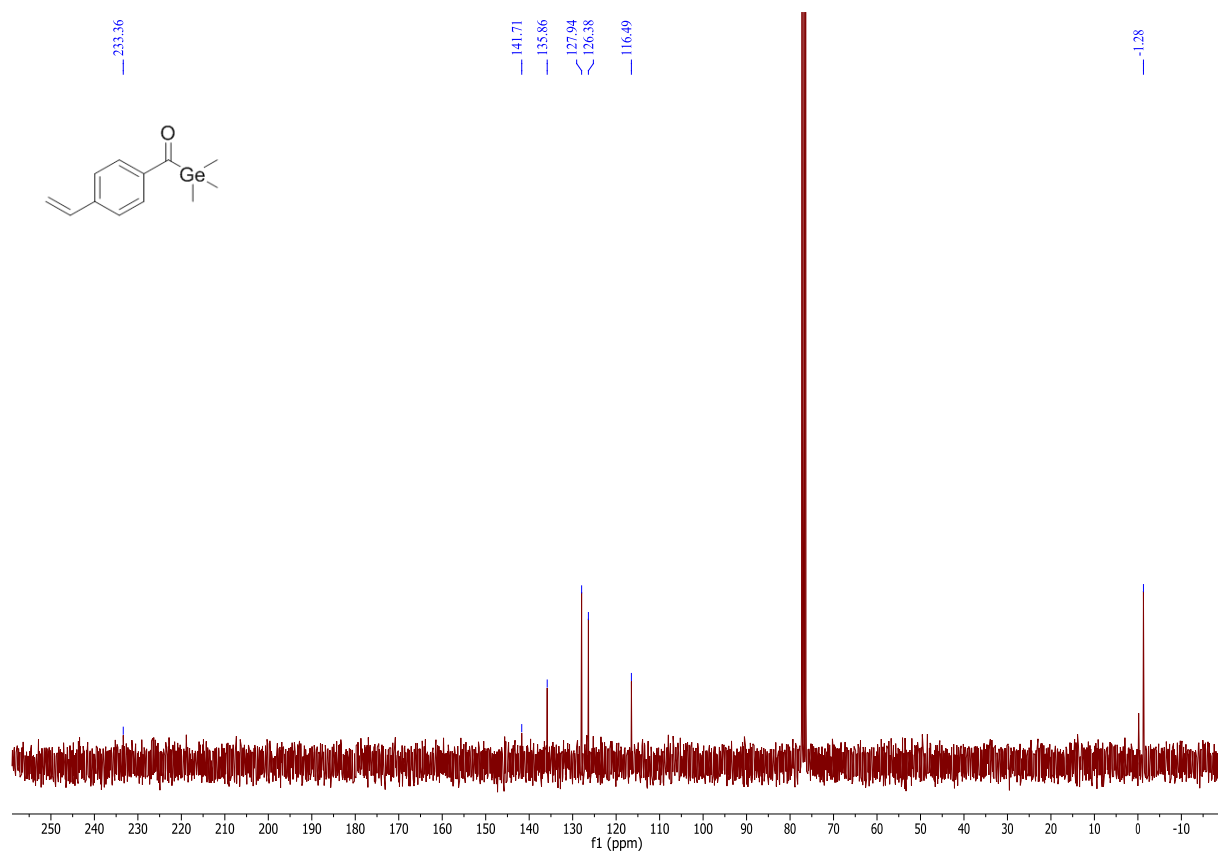


Figure S64. <sup>13</sup>C NMR spectrum of 3u, related to Scheme 2.

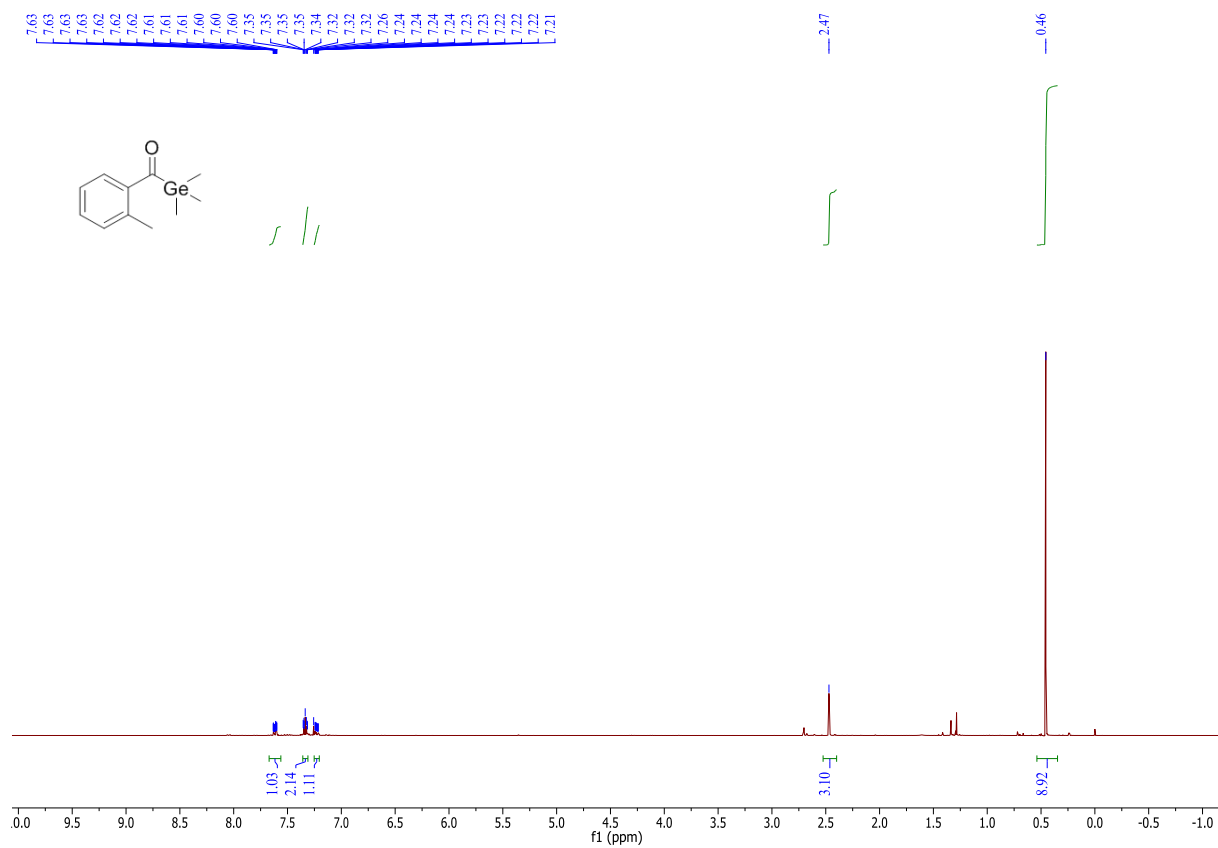


Figure S65.  $^1\text{H NMR}$  spectrum of 3v, related to Scheme 2.

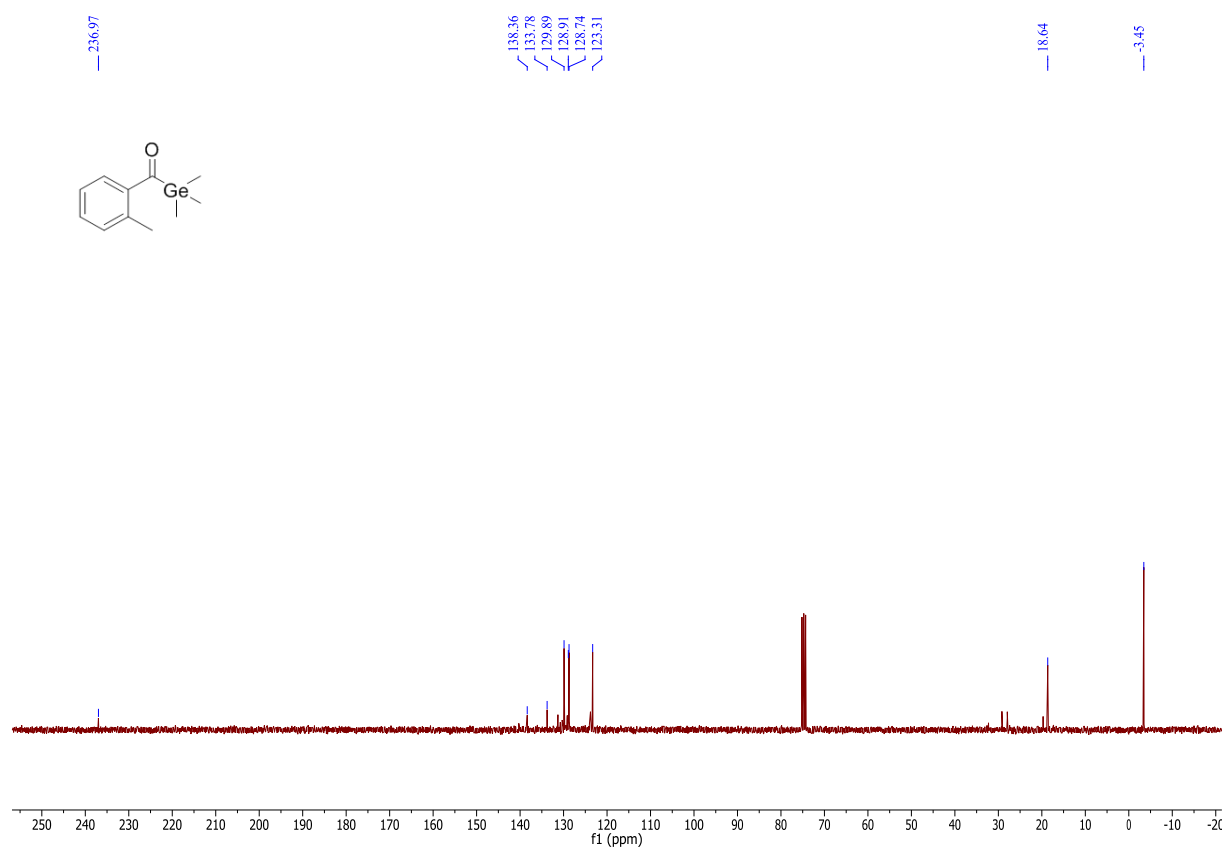


Figure S66.  $^{13}\text{C NMR}$  spectrum of 3v, related to Scheme 2.

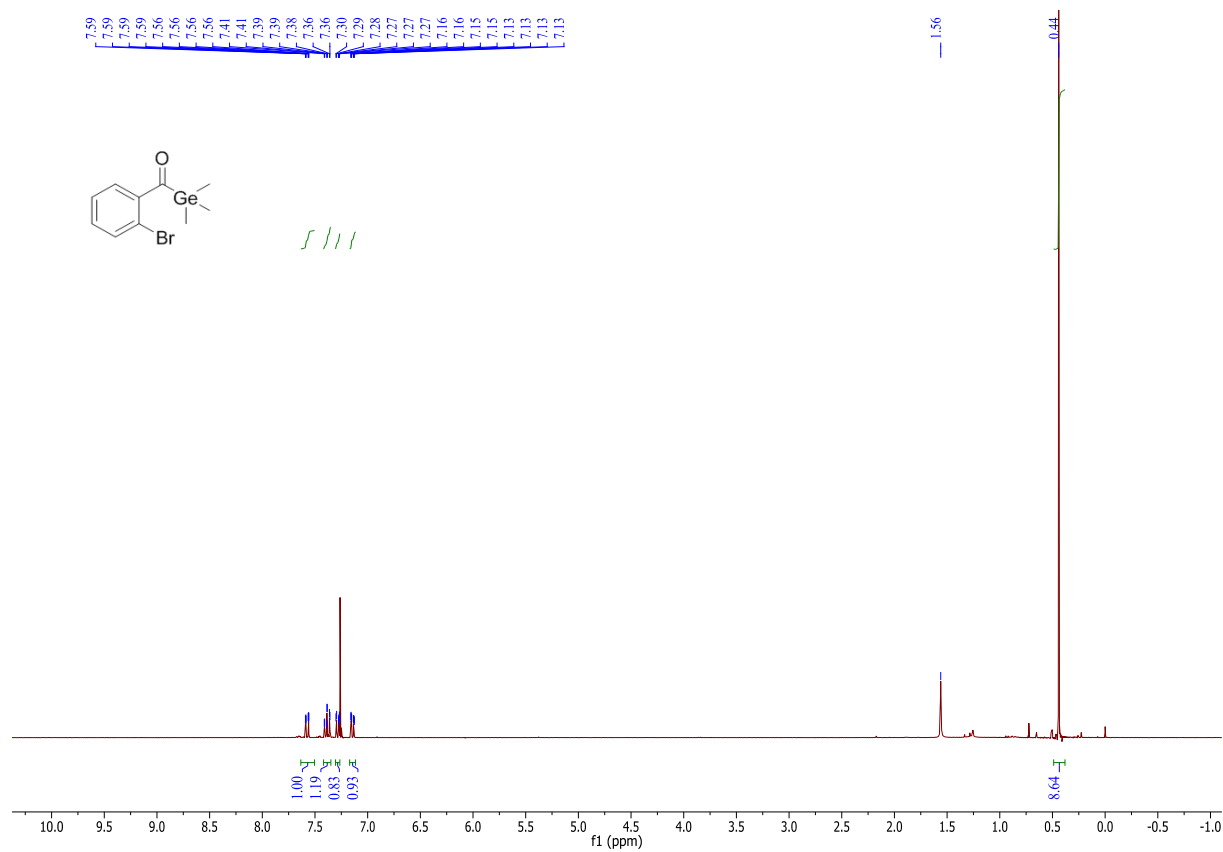


Figure S67. <sup>1</sup>H NMR spectrum of 3w, related to Scheme 2.

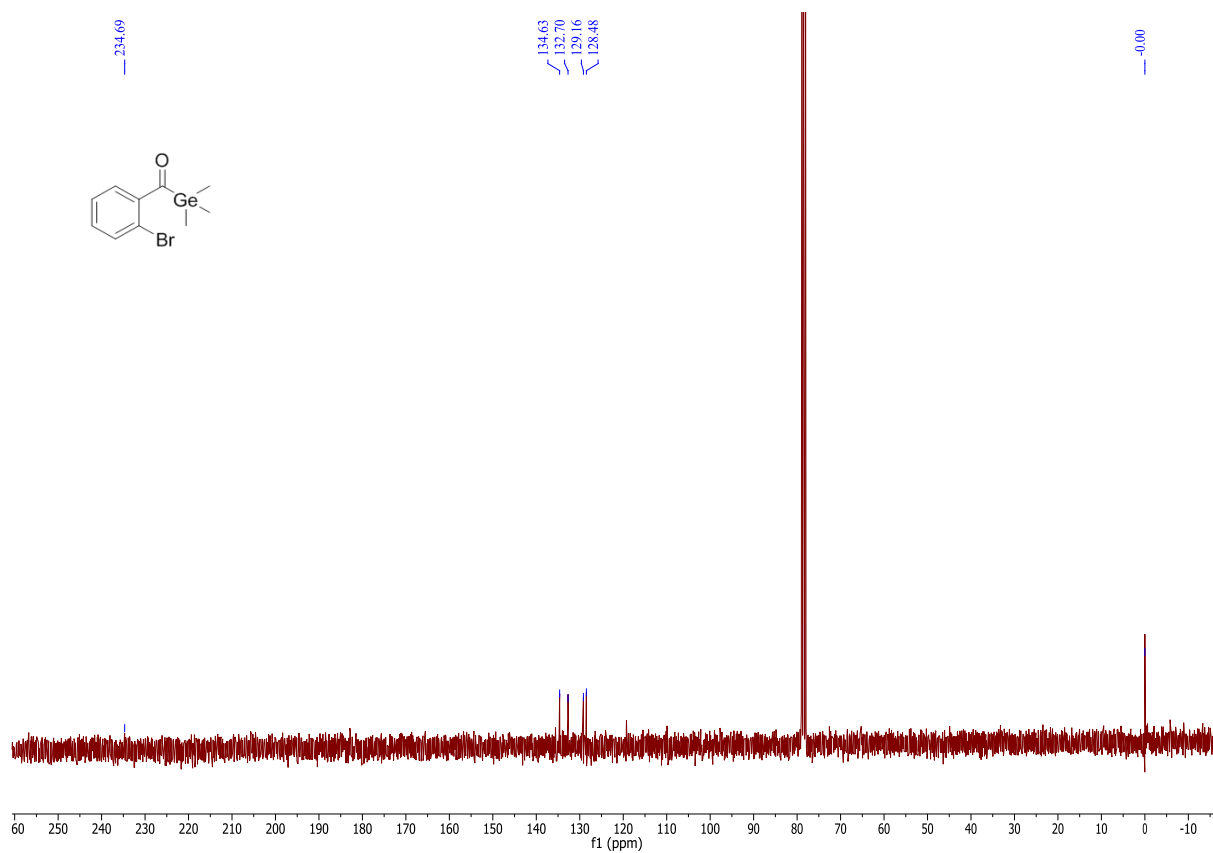


Figure S68. <sup>13</sup>C NMR spectrum of 3w, related to Scheme 2.

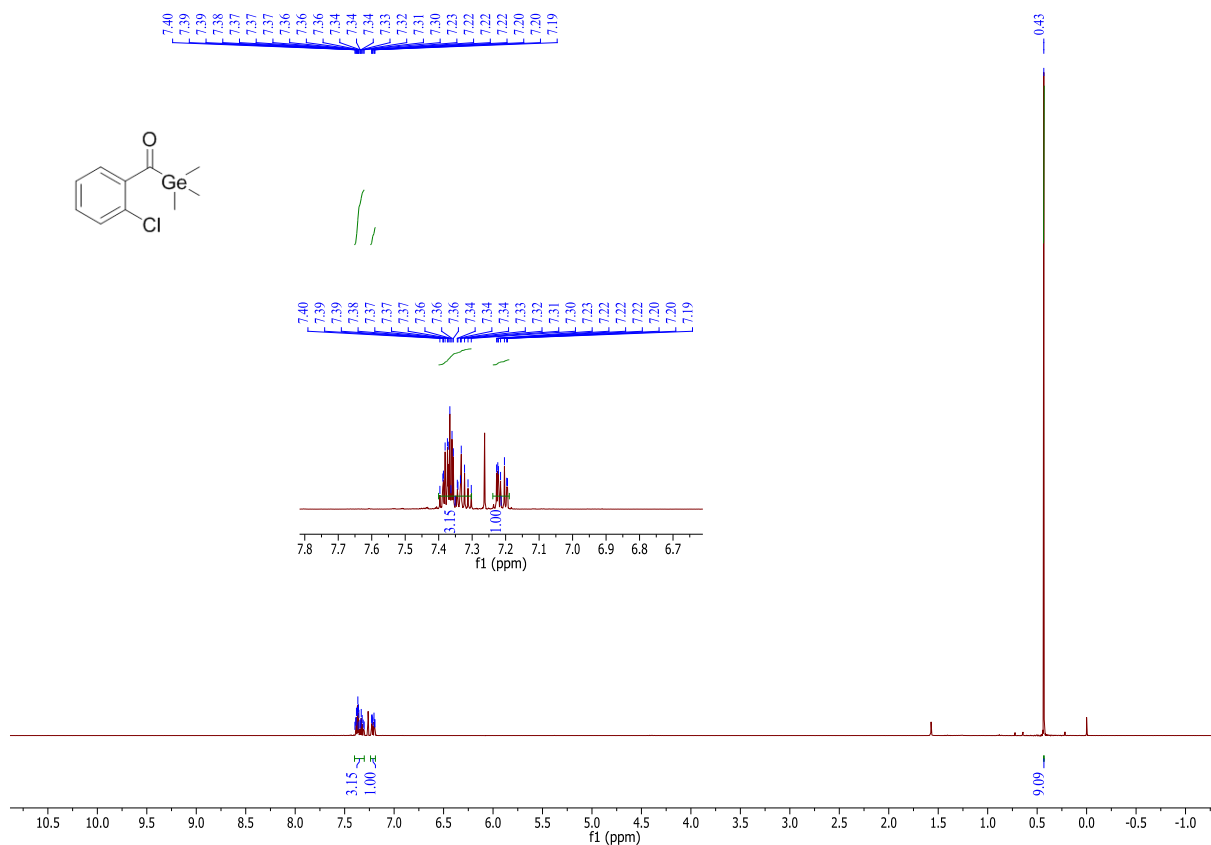


Figure S69. <sup>1</sup>H NMR spectrum of 3x, related to Scheme 2.

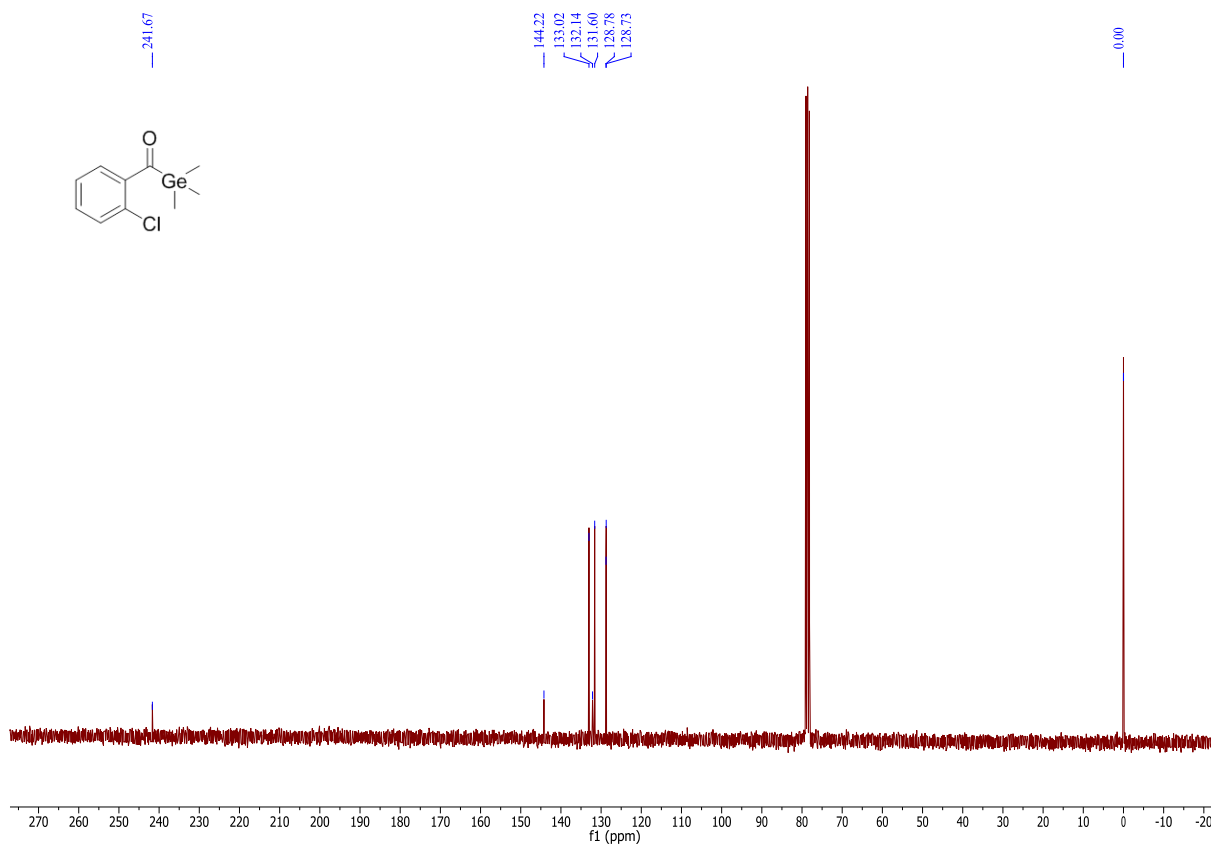


Figure S70. <sup>13</sup>C NMR spectrum of 3x, related to Scheme 2.

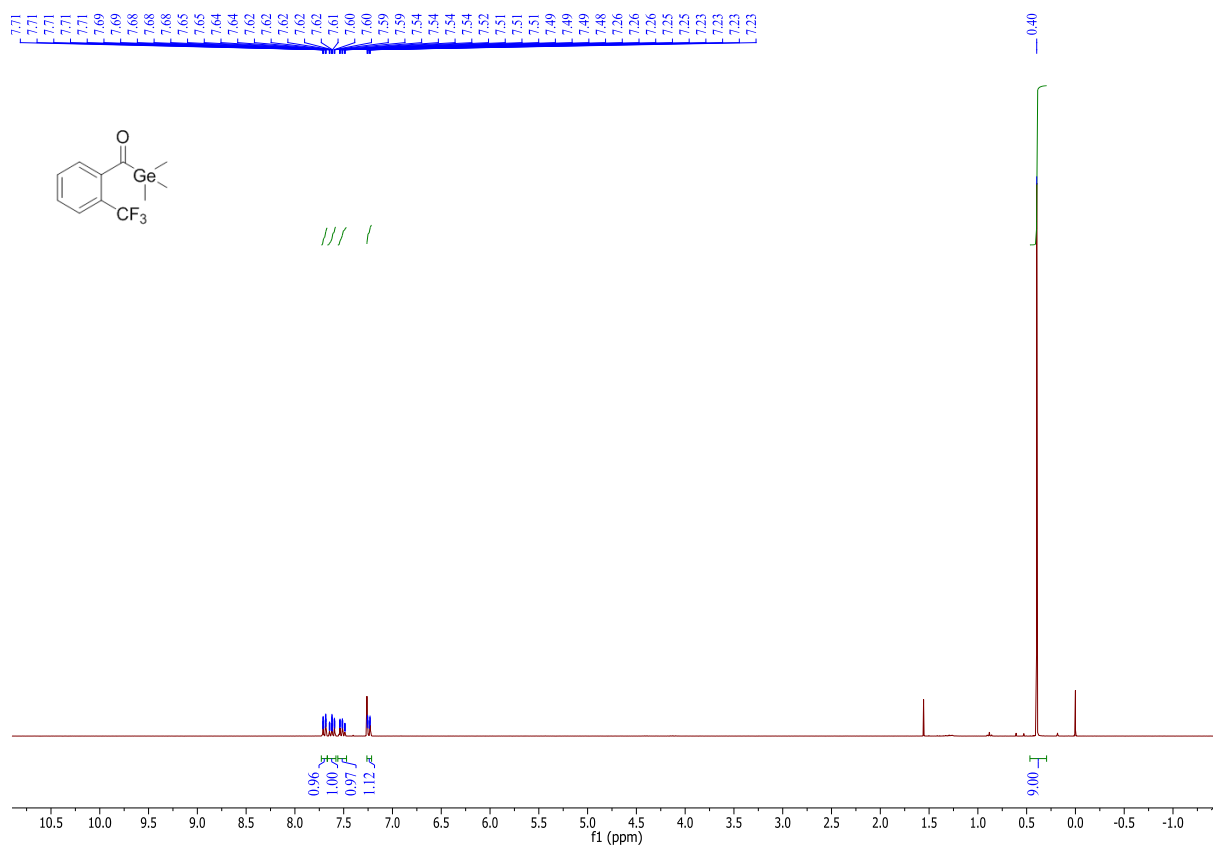


Figure S71. <sup>1</sup>H NMR spectrum of 3y, related to Scheme 2.

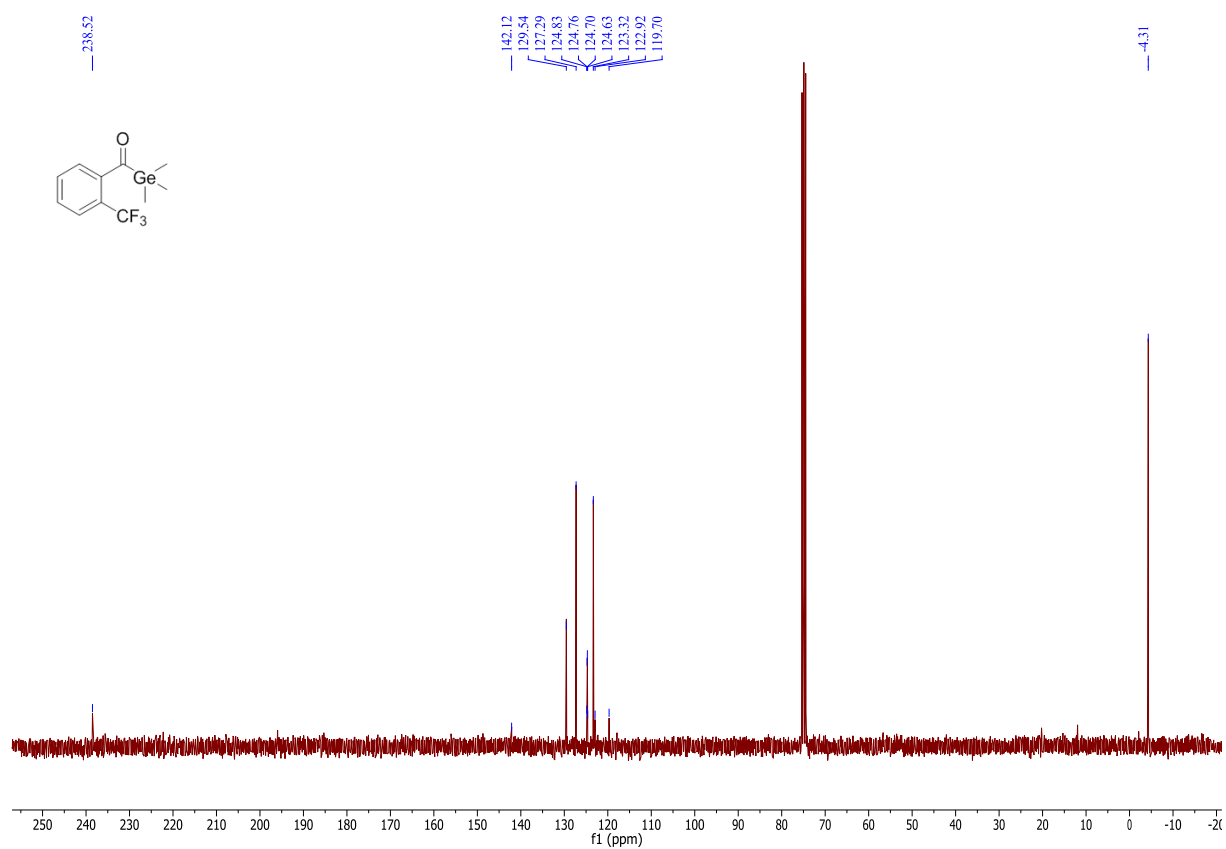


Figure S72. <sup>13</sup>C NMR spectrum of 3y, related to Scheme 2.

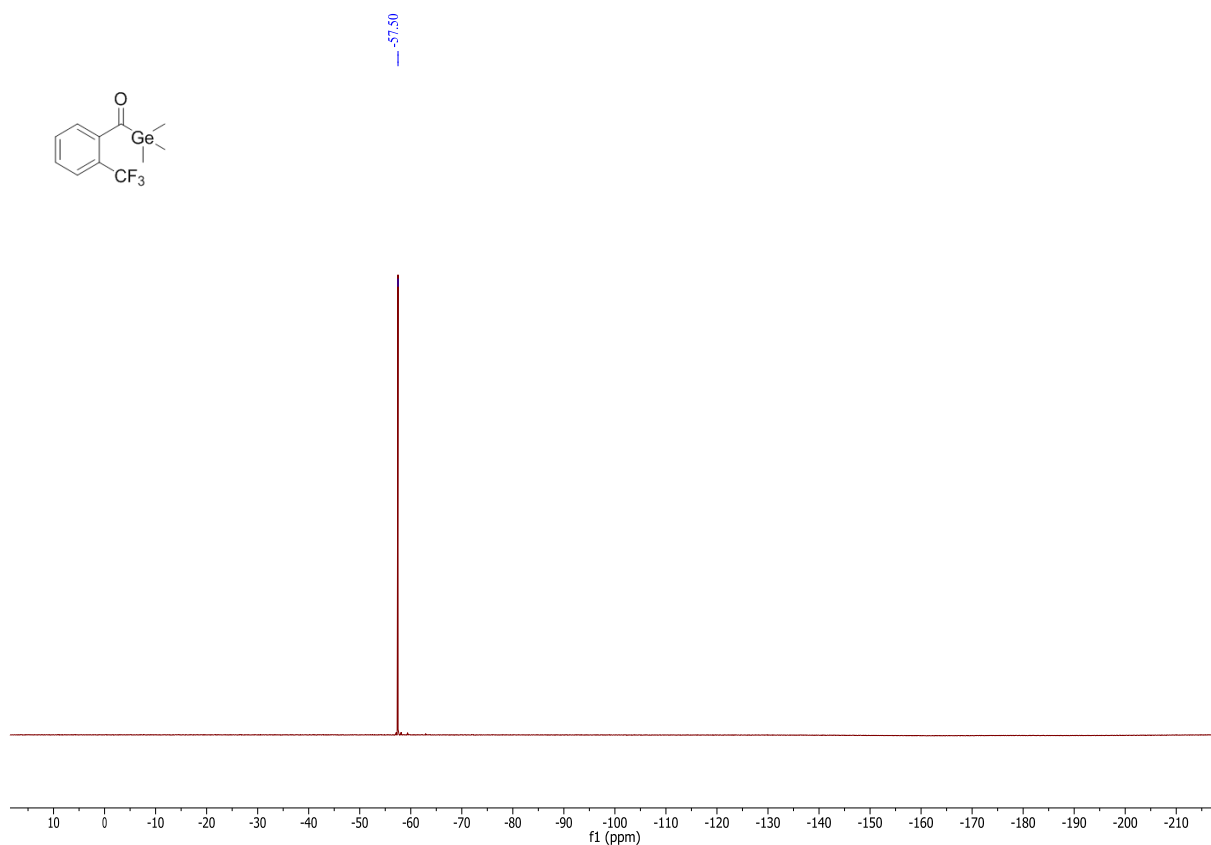


Figure S73.  $^{19}\text{F}$  NMR spectrum of 3y, related to Scheme 2.

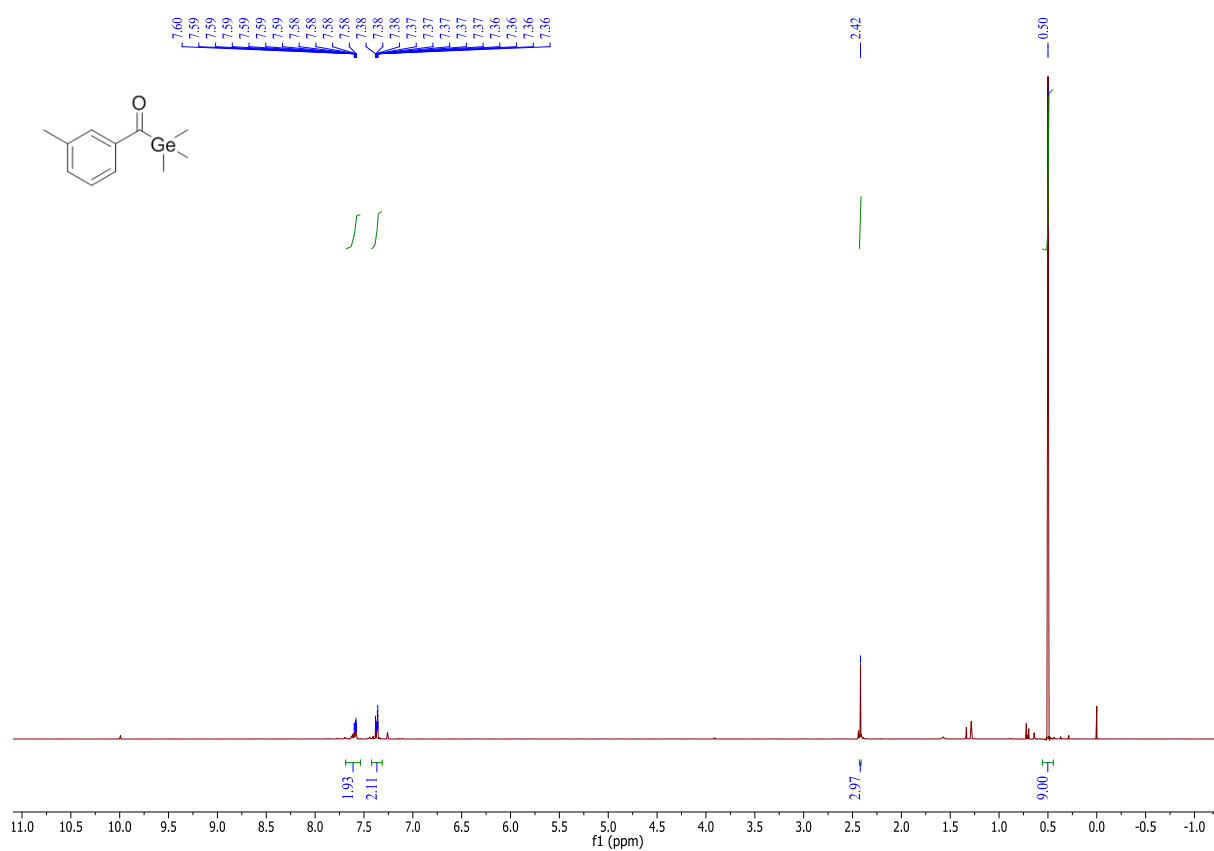


Figure S74.  $^1\text{H}$  NMR spectrum of 3z, related to Scheme 2.



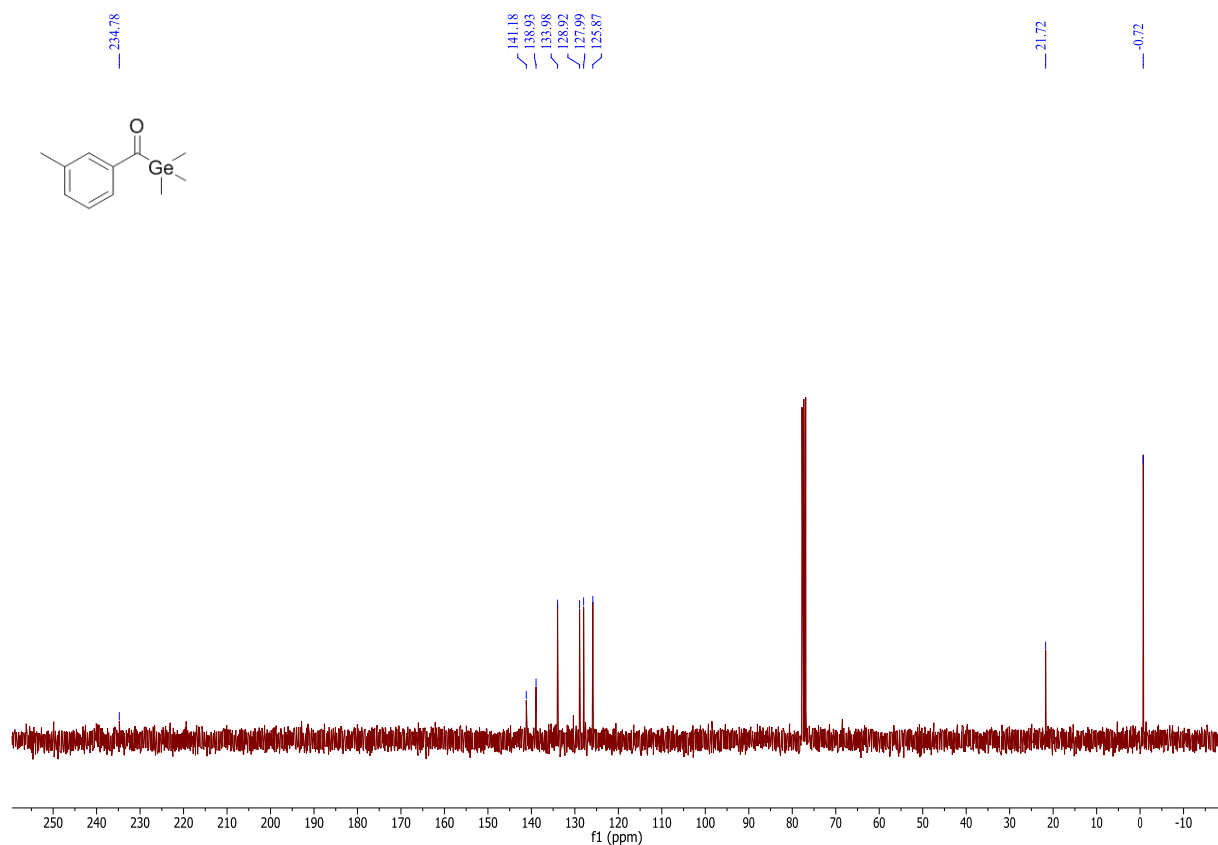


Figure S75.  $^{13}\text{C}$  NMR spectrum of 3z, related to Scheme 2.

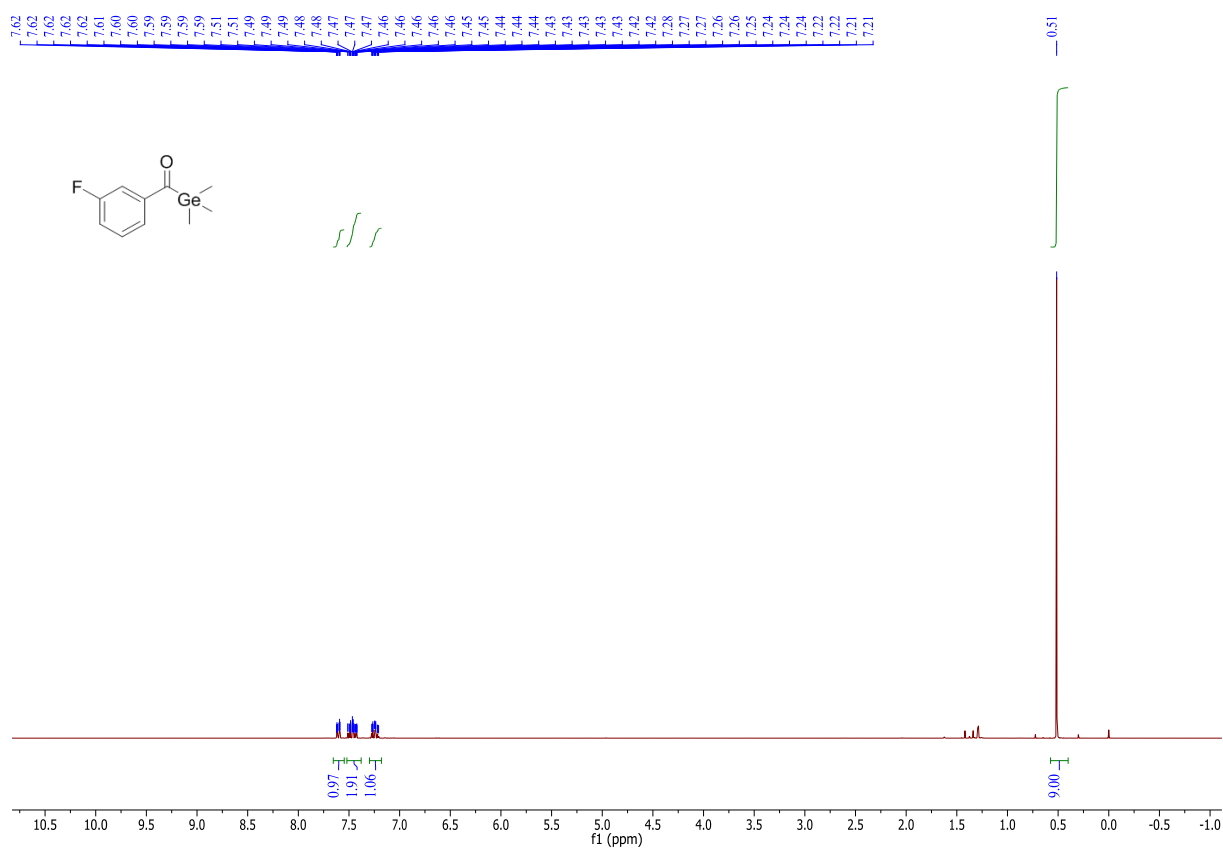


Figure S76.  $^1\text{H}$  NMR spectrum of 3aa, related to Scheme 2.

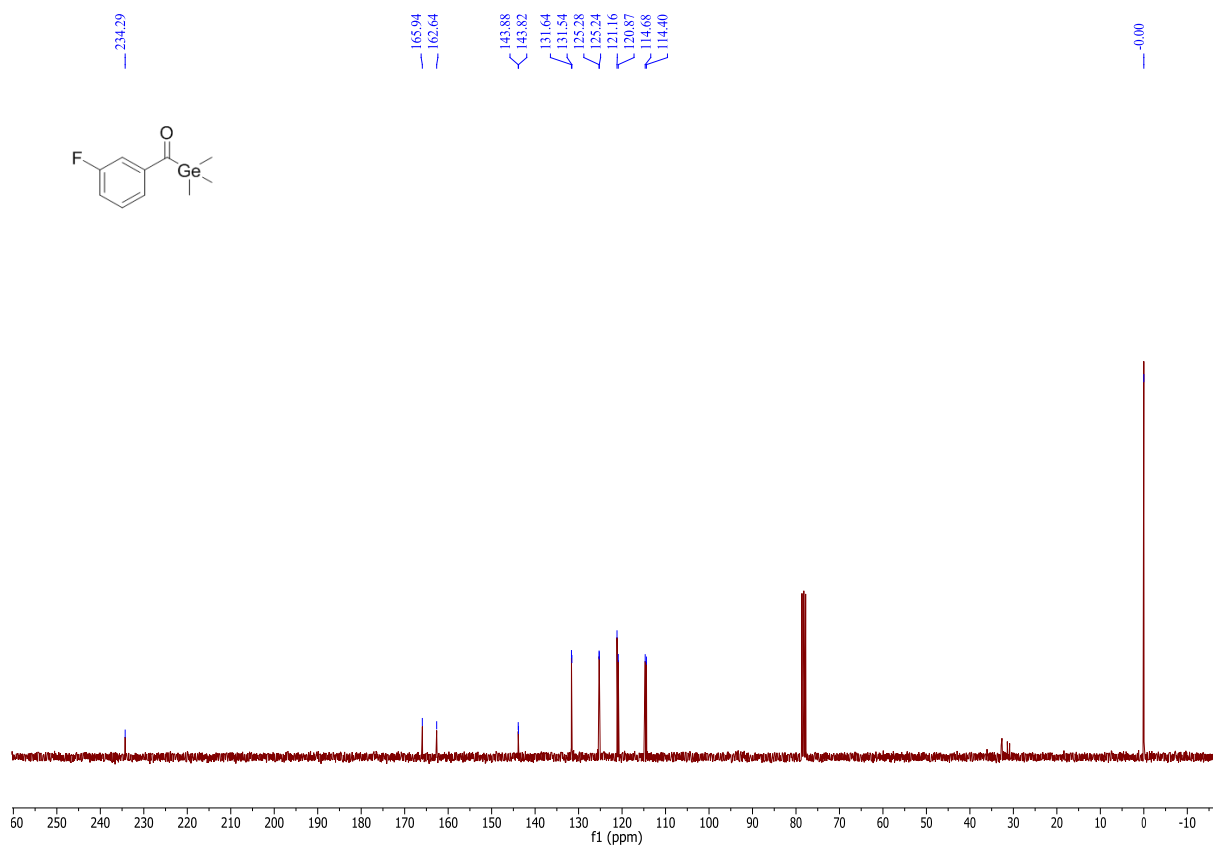


Figure S77.  $^{13}\text{C}$  NMR spectrum of 3aa, related to Scheme 2.

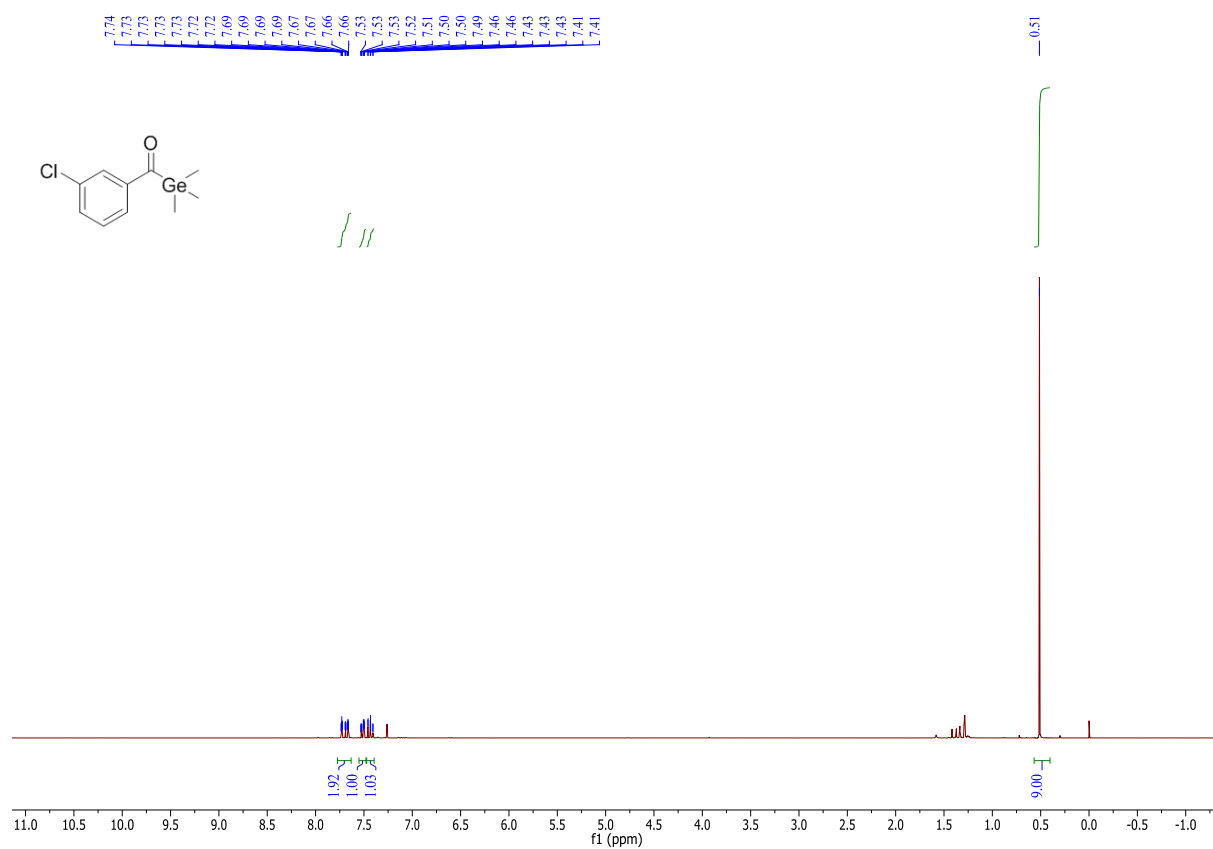


Figure S78.  $^1\text{H}$  NMR spectrum of 3ab, related to Scheme 2.

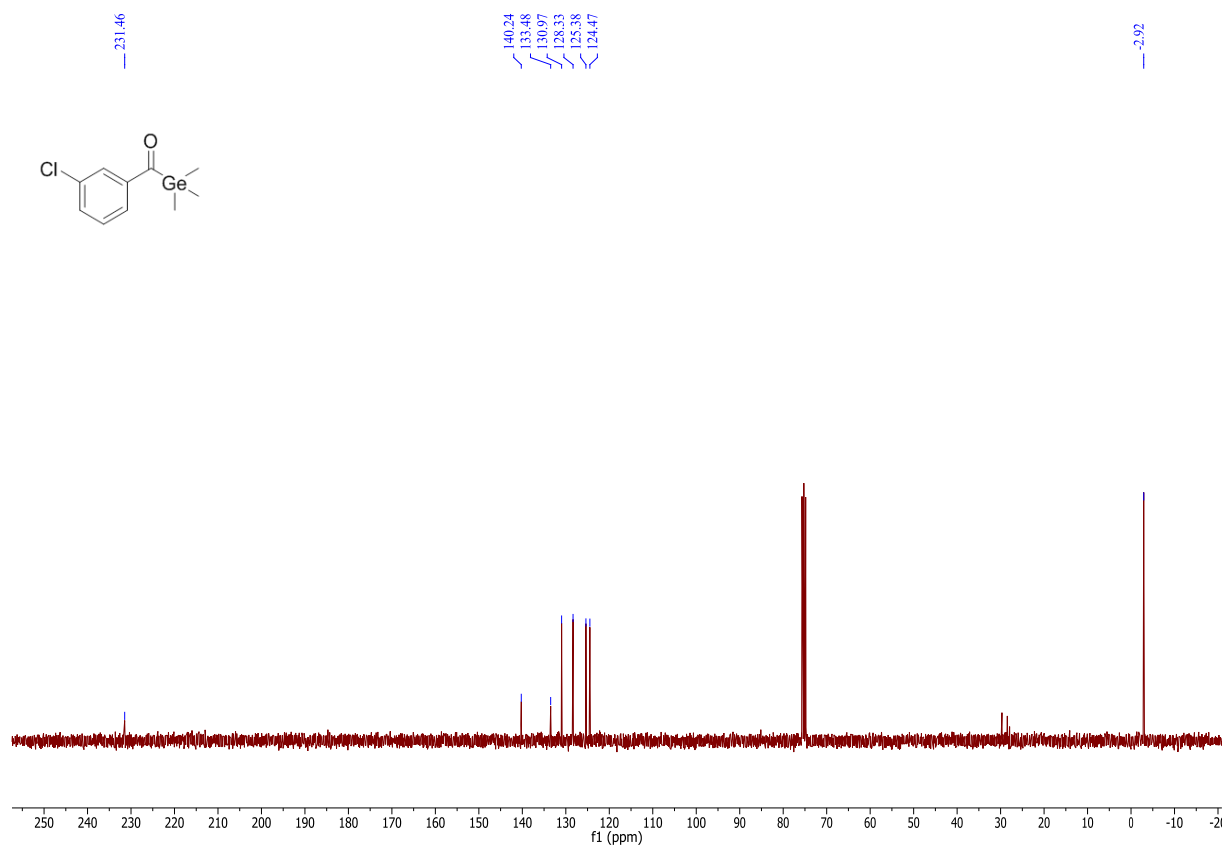


Figure S79.  $^{13}\text{C}$  NMR spectrum of 3ab, related to Scheme 2.

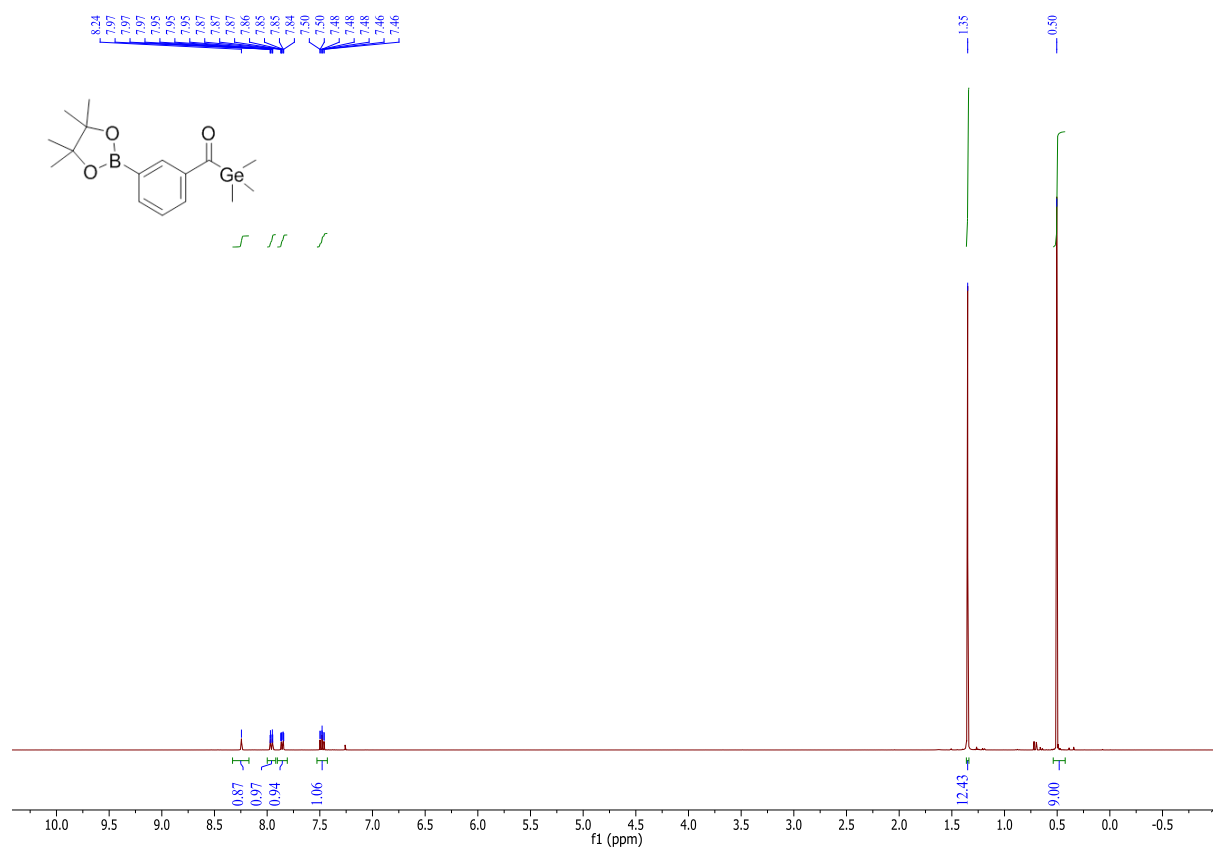


Figure S80.  $^1\text{H}$  NMR spectrum of 3ac, related to Scheme 2.

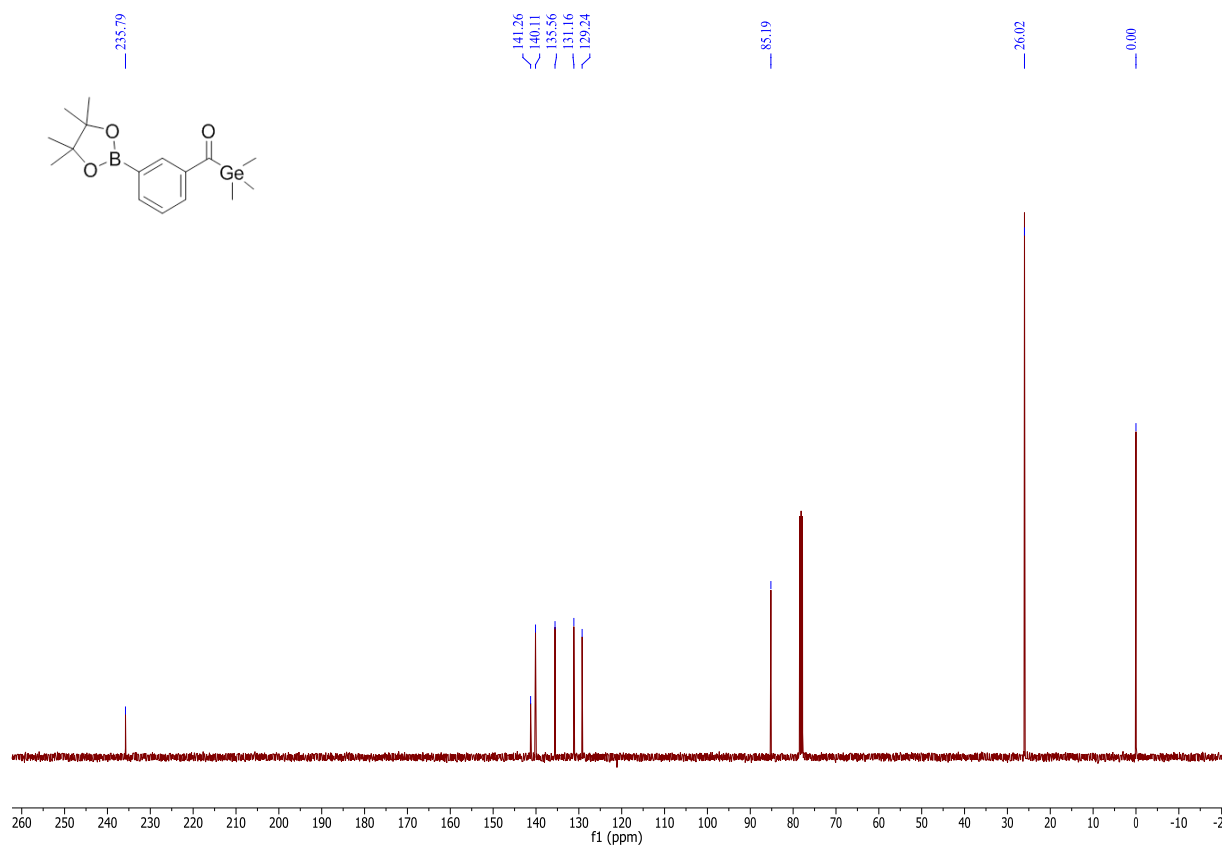


Figure S81.  $^{13}\text{C}$  NMR spectrum of 3ac, related to Scheme 2.

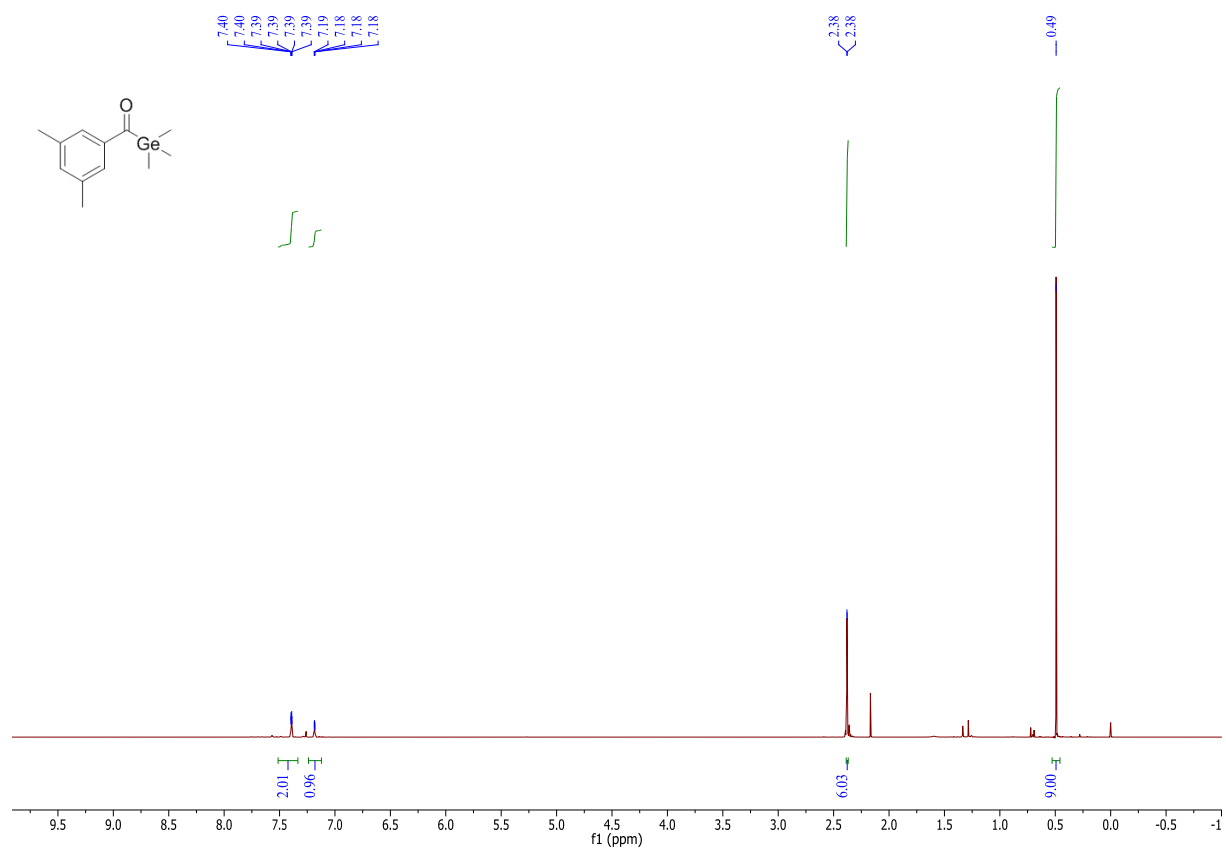


Figure S82.  $^1\text{H}$  NMR spectrum of 3ad, related to Scheme 2.

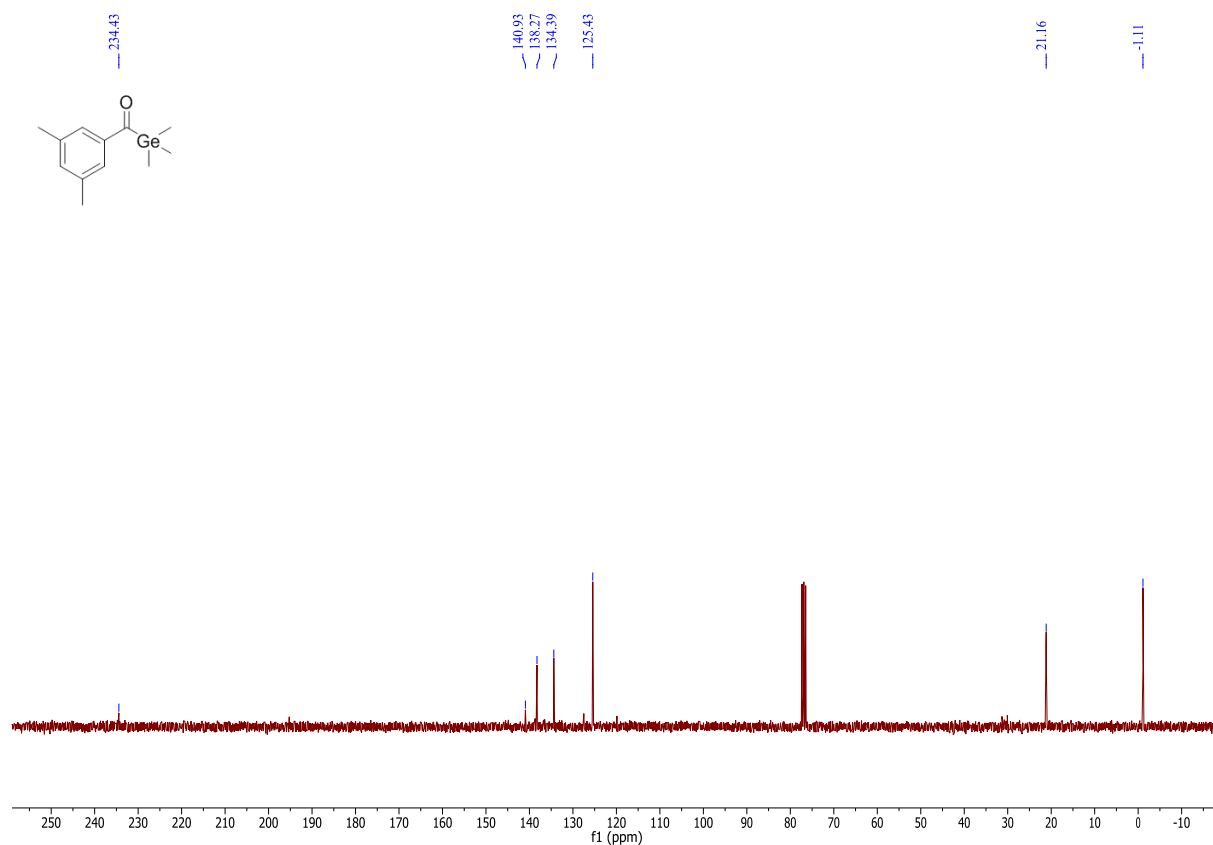


Figure S83.  $^{13}\text{C}$  NMR spectrum of 3ad, related to Scheme 2.

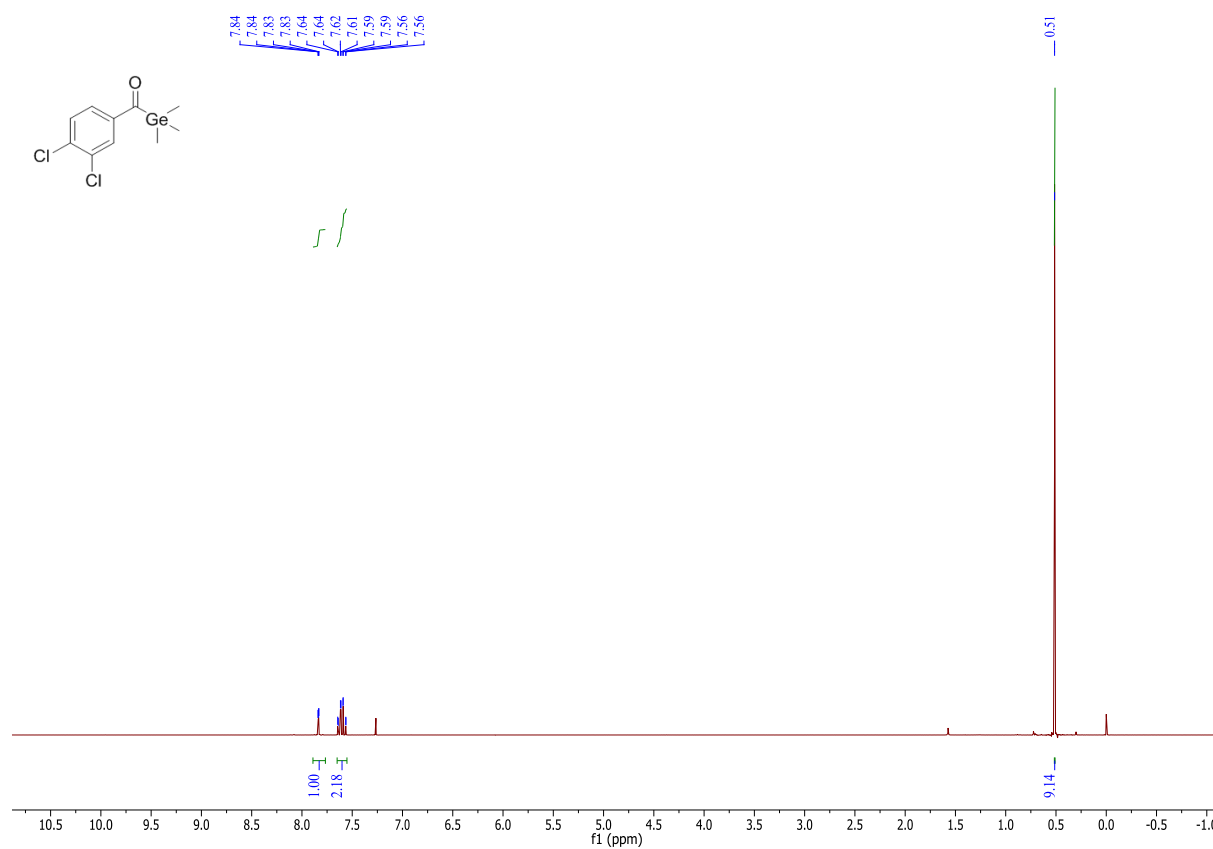


Figure S84.  $^1\text{H}$  NMR spectrum of 3ae, related to Scheme 2.

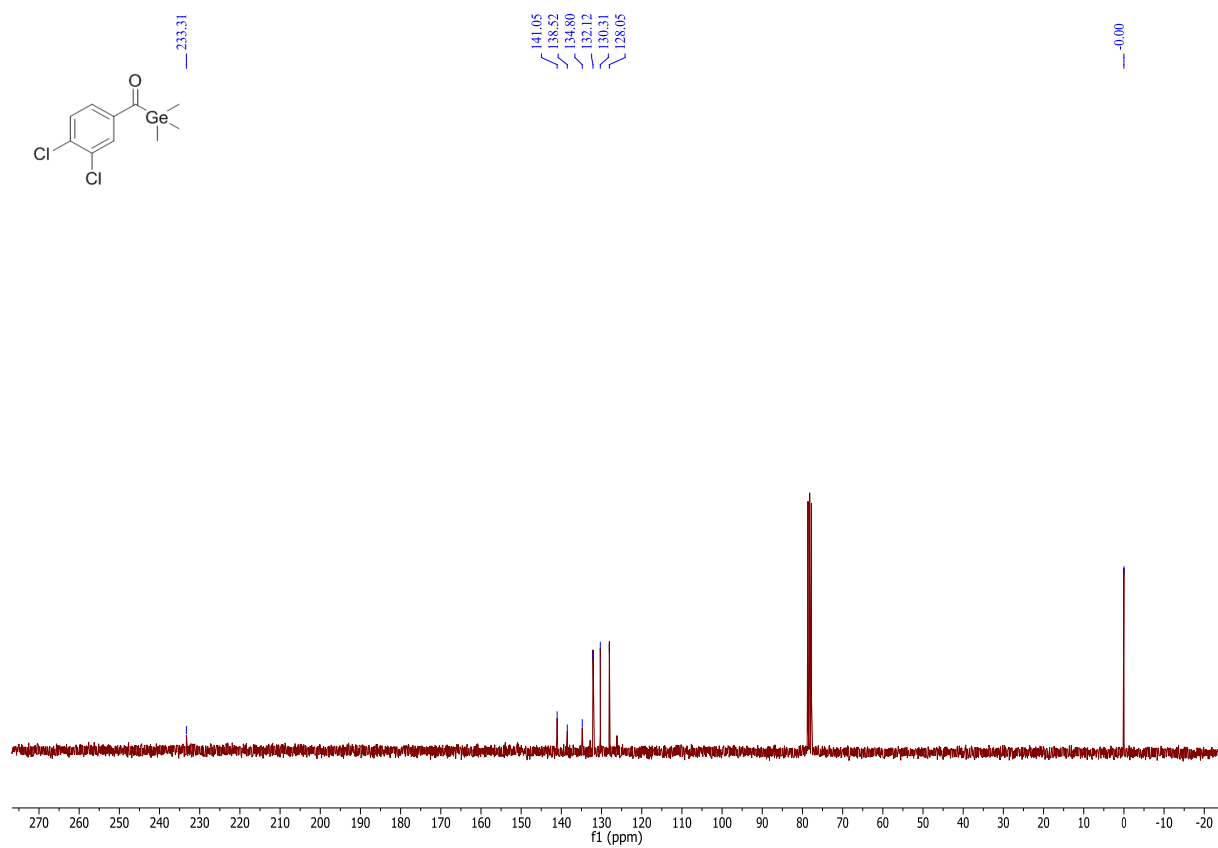


Figure S85.  $^{13}\text{C}$  NMR spectrum of 3ae, related to Scheme 2.

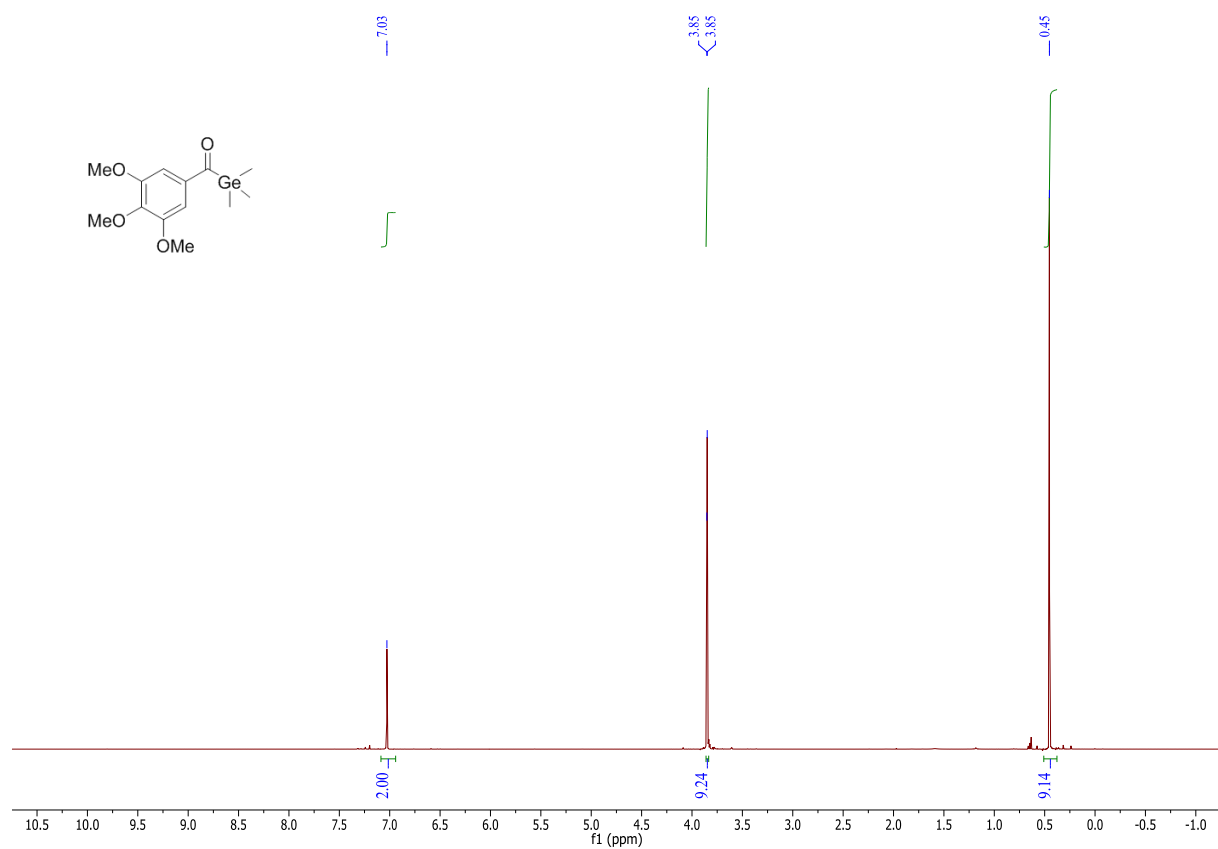


Figure S86.  $^1\text{H}$  NMR spectrum of 3af, related to Scheme 2.

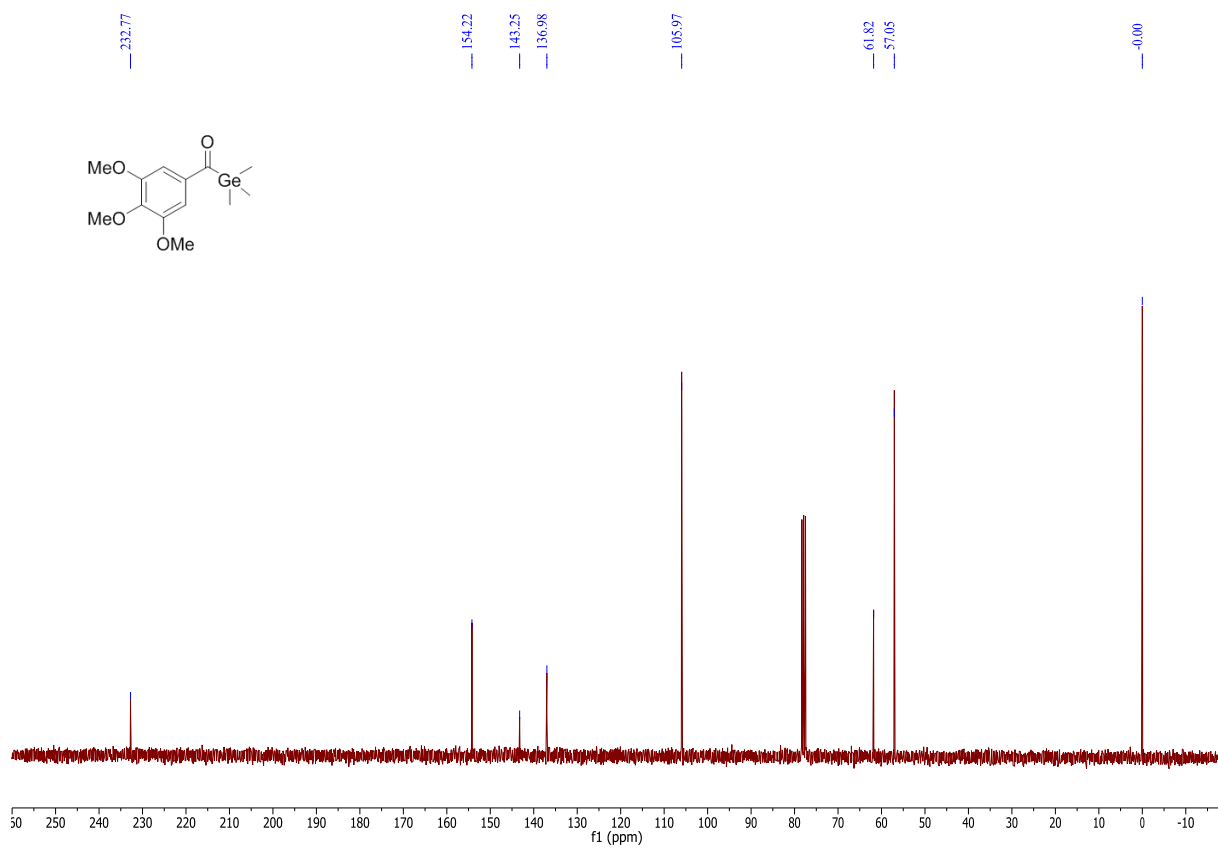


Figure S87.  $^{13}\text{C}$  NMR spectrum of 3af, related to Scheme 2.

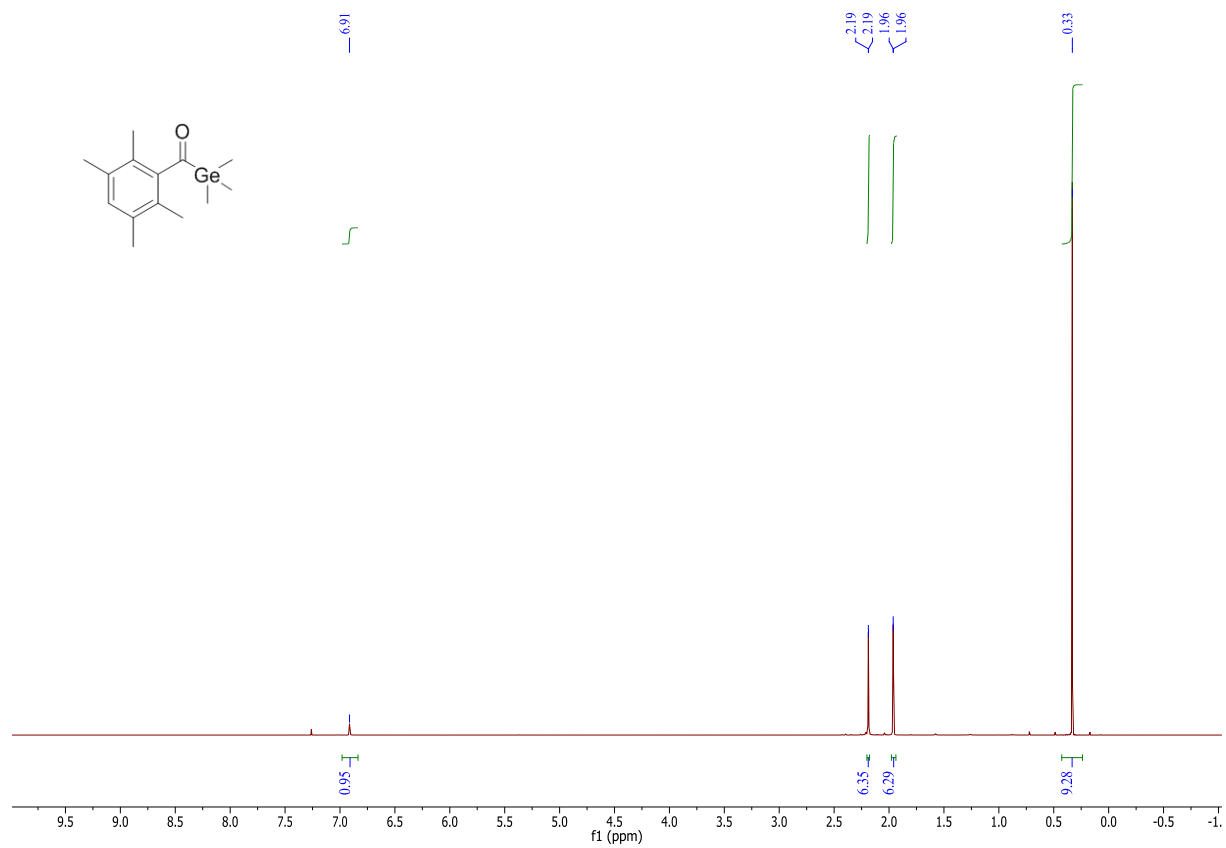


Figure S88.  $^1\text{H}$  NMR spectrum of 3ag, related to Scheme 2.

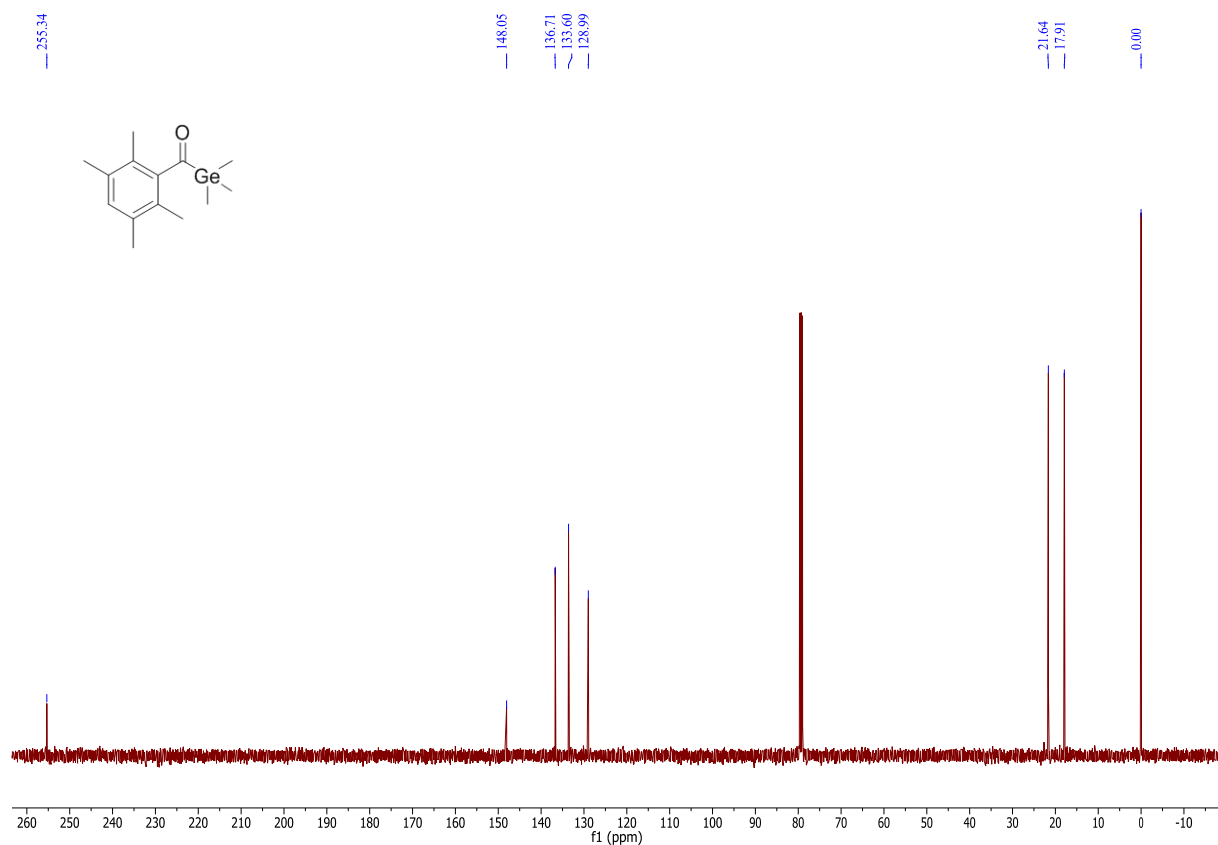


Figure S89.  $^{13}\text{C}$  NMR spectrum of 3ag, related to Scheme 2.

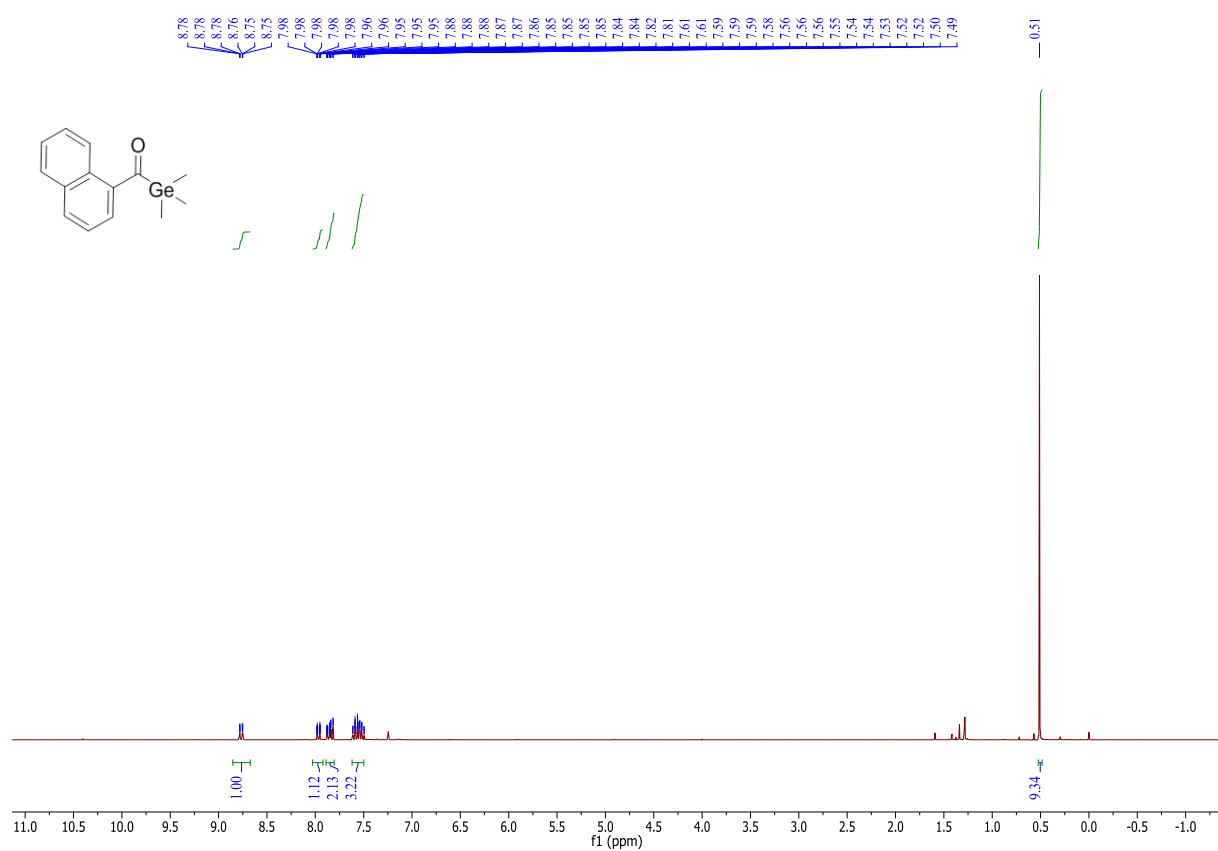


Figure S90.  $^1\text{H}$  NMR spectrum of 3ah, related to Scheme 2.



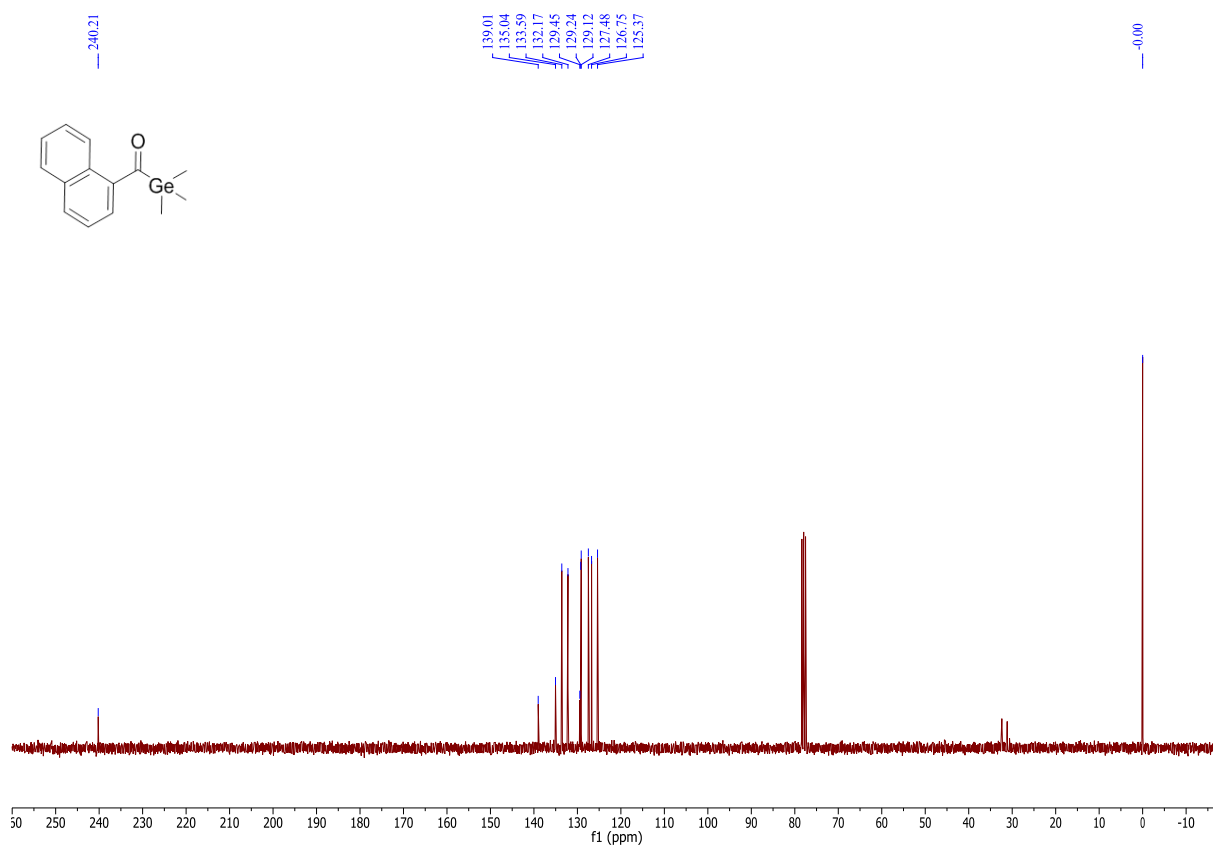


Figure S91.  $^{13}\text{C}$  NMR spectrum of 3ah, related to Scheme 2.

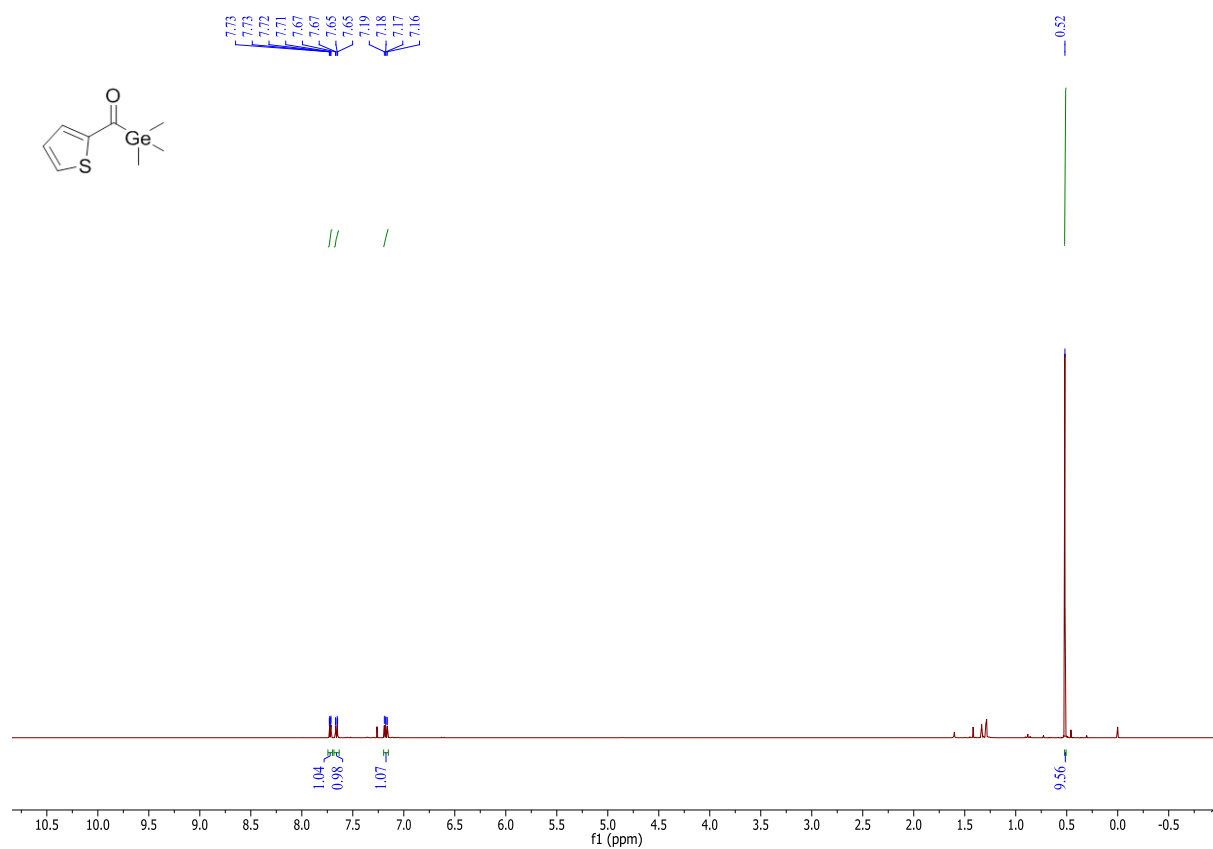


Figure S92.  $^1\text{H}$  NMR spectrum of 3ai, related to Scheme 2.

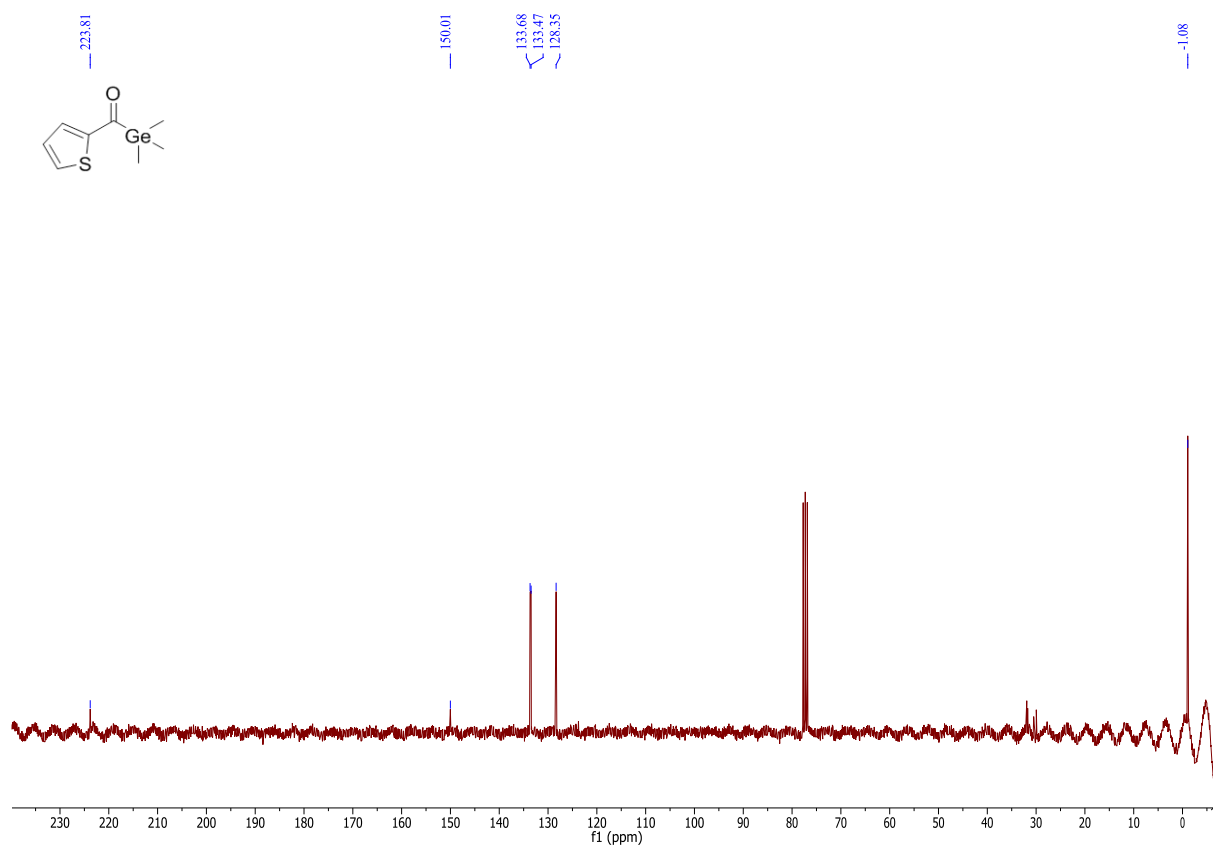


Figure S93.  $^{13}\text{C}$  NMR spectrum of 3ai, related to Scheme 2.

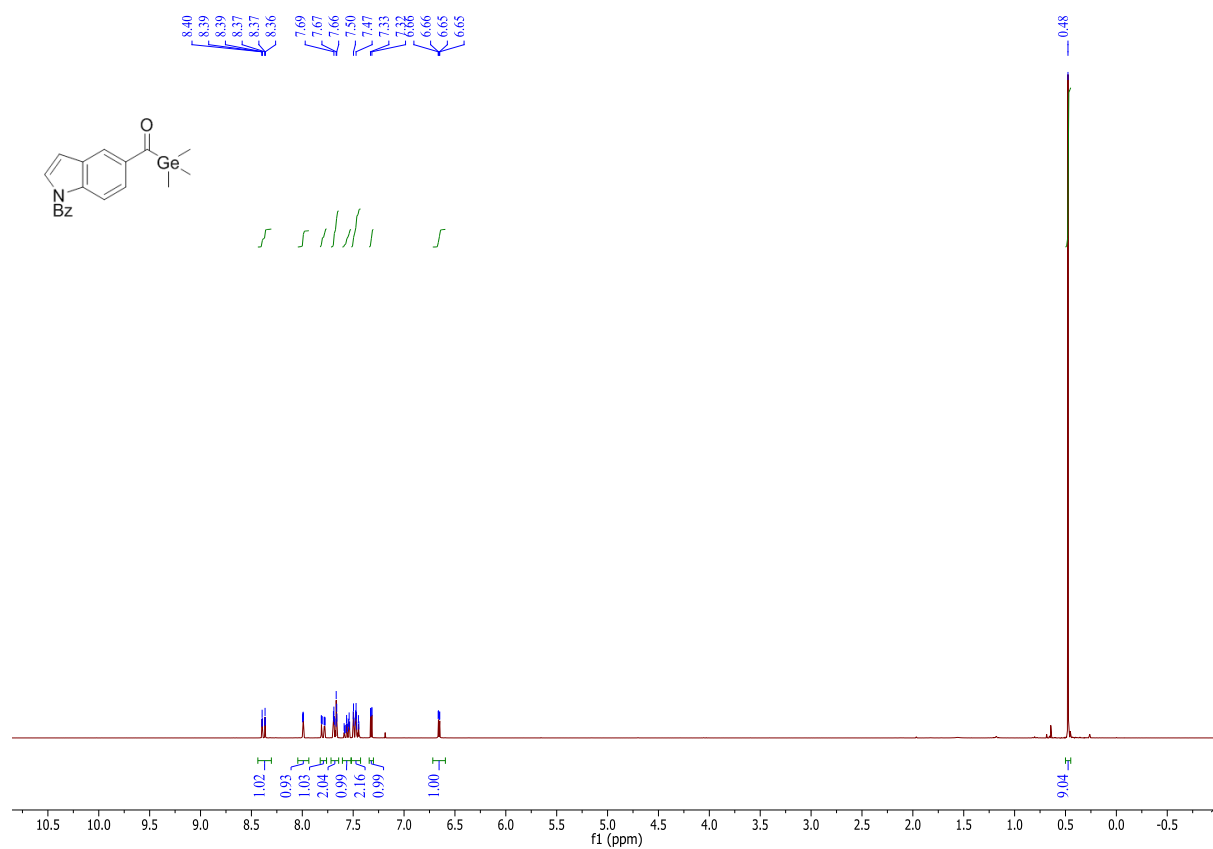


Figure S94.  $^1\text{H}$  NMR spectrum of 3aj, related to Scheme 2.

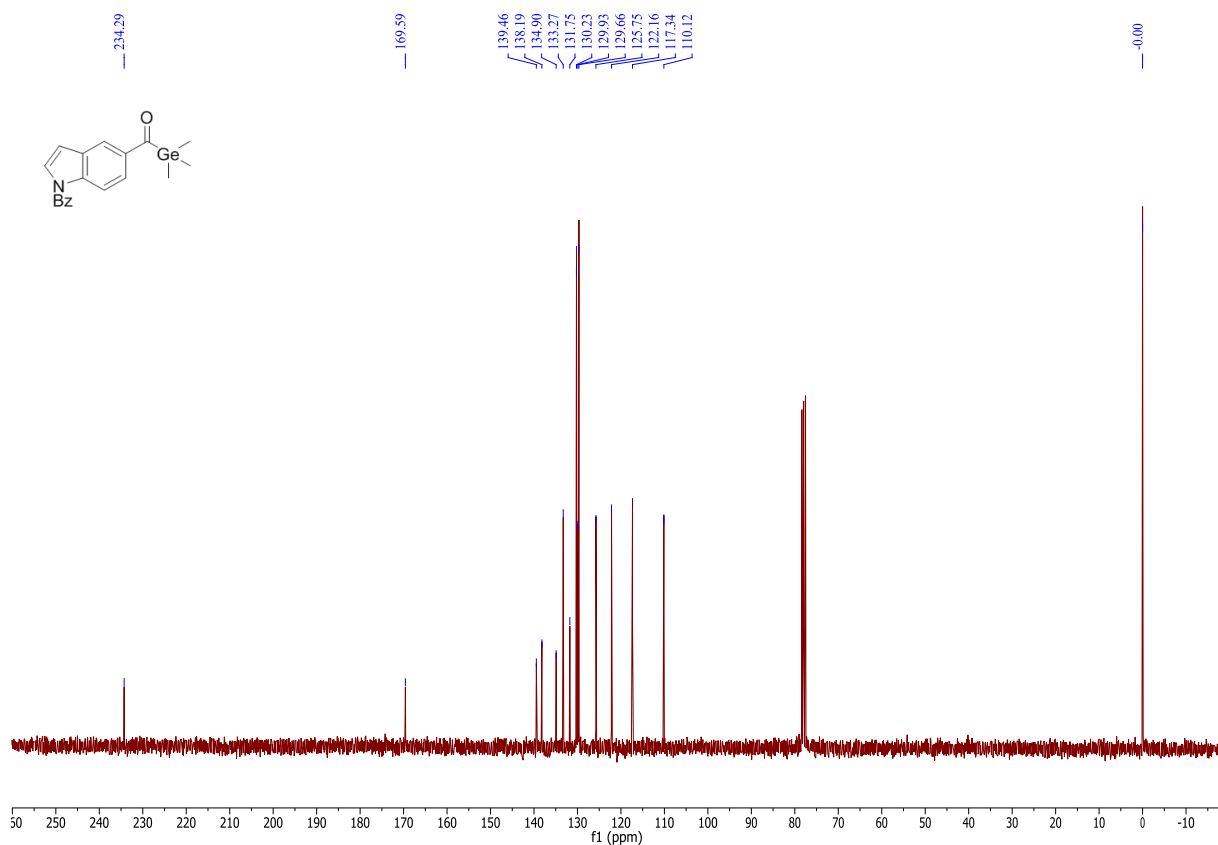


Figure S95.  $^{13}\text{C}$  NMR spectrum of 3aj, related to Scheme 2.

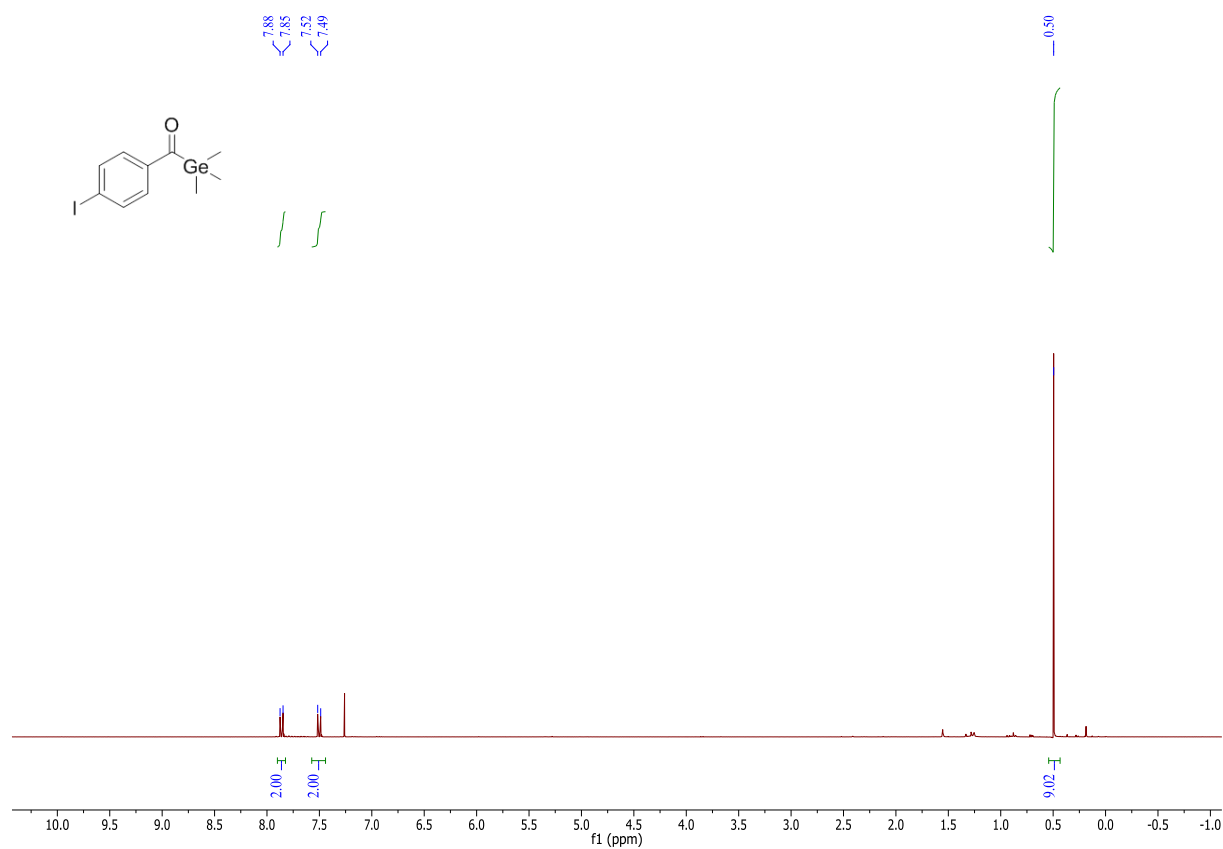


Figure S96.  $^1\text{H}$  NMR spectrum of 3ak, related to Scheme 2.

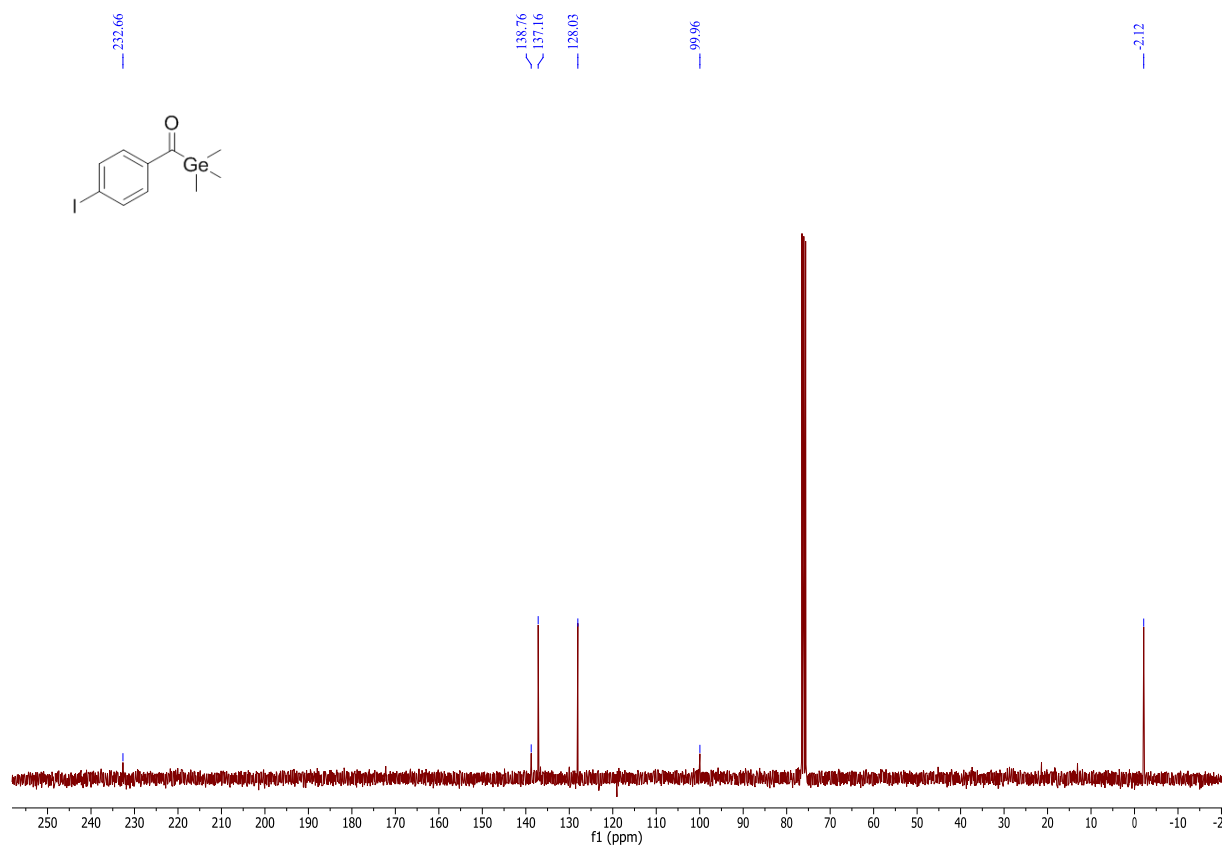


Figure S97. <sup>13</sup>C NMR spectrum of 3ak, related to Scheme 2.

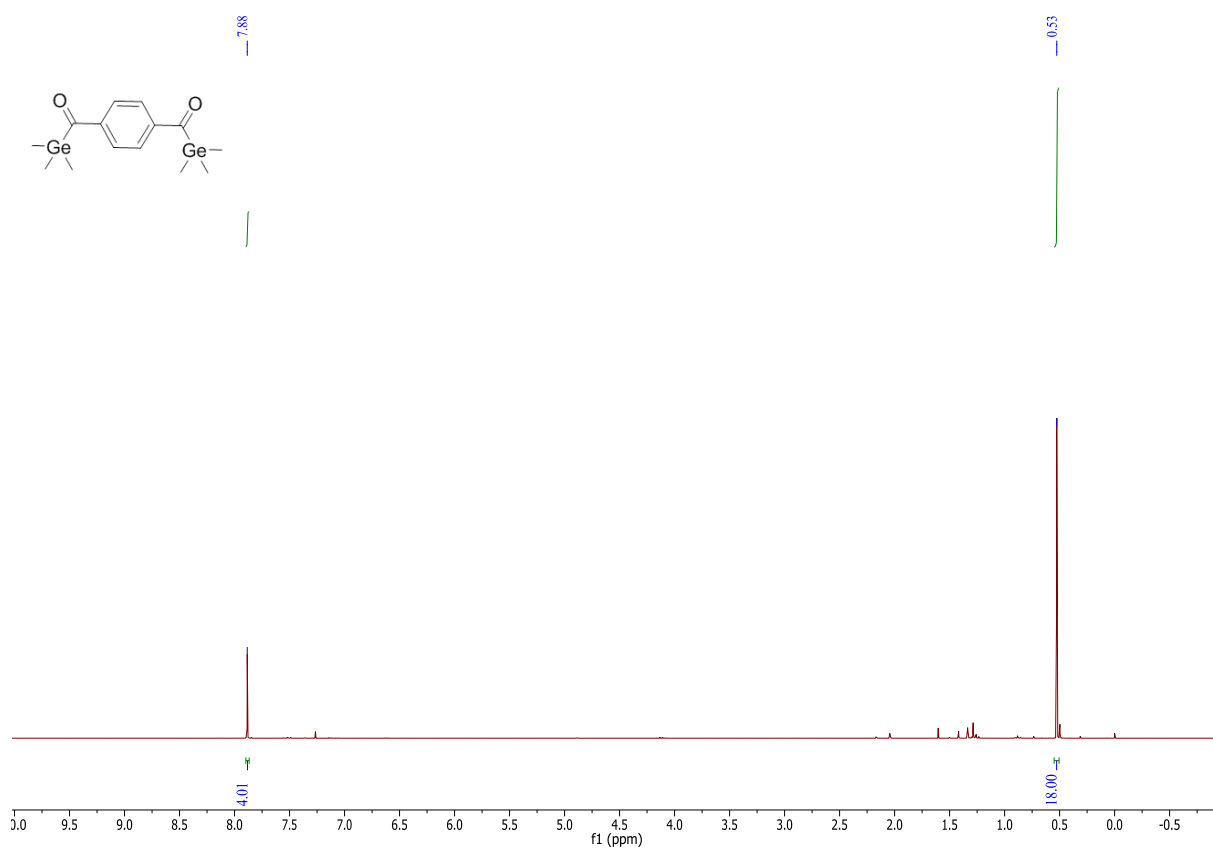


Figure S98. <sup>1</sup>H NMR spectrum of 3al, related to Scheme 2.

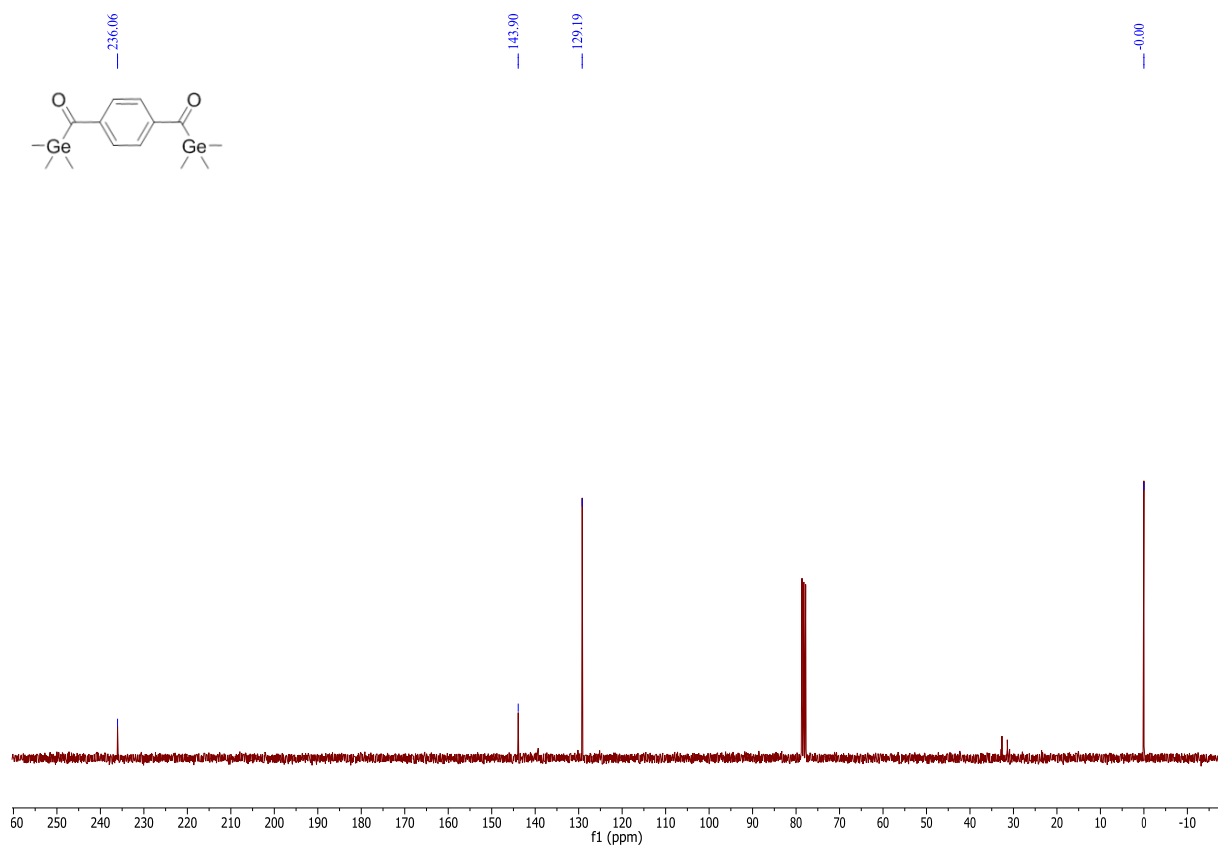


Figure S99.  $^{13}\text{C}$  NMR spectrum of 3al, related to Scheme 2.

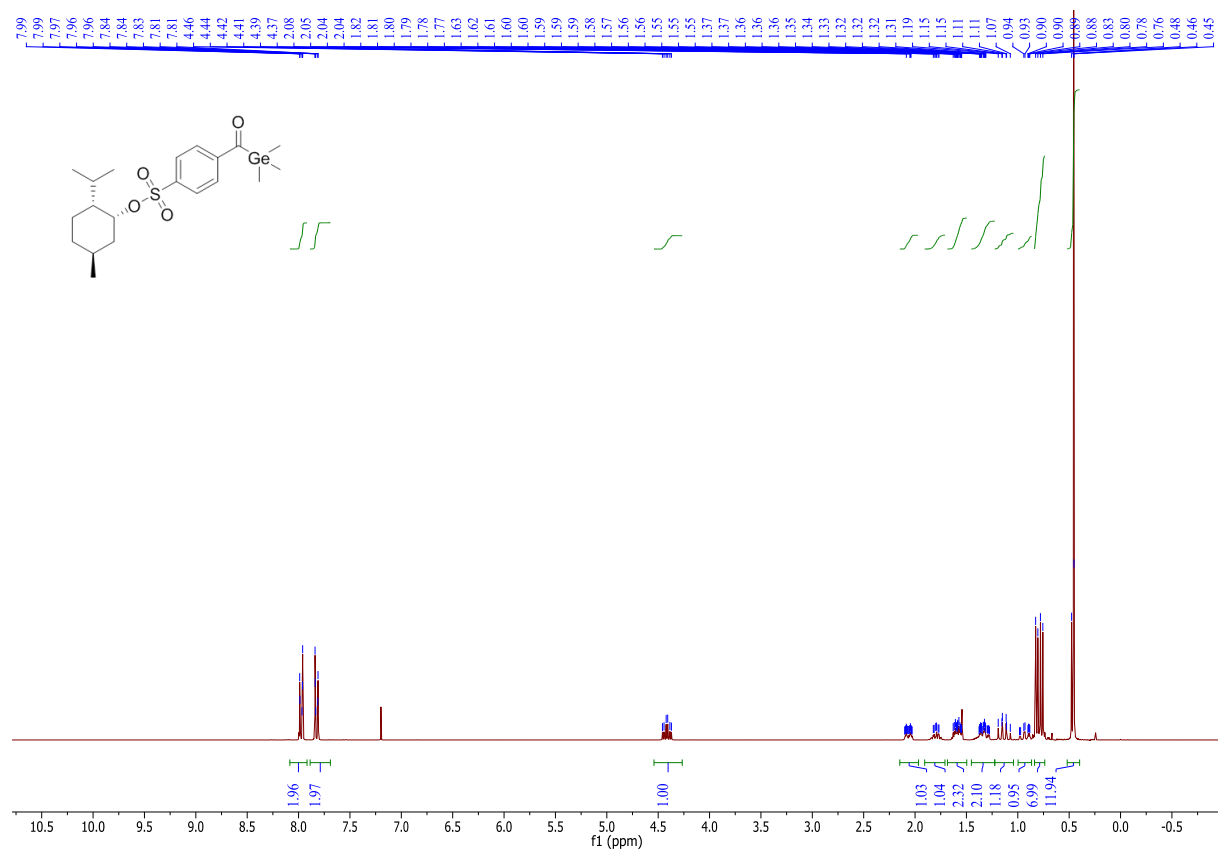


Figure S100.  $^1\text{H}$  NMR spectrum of 3am, related to Scheme 2.

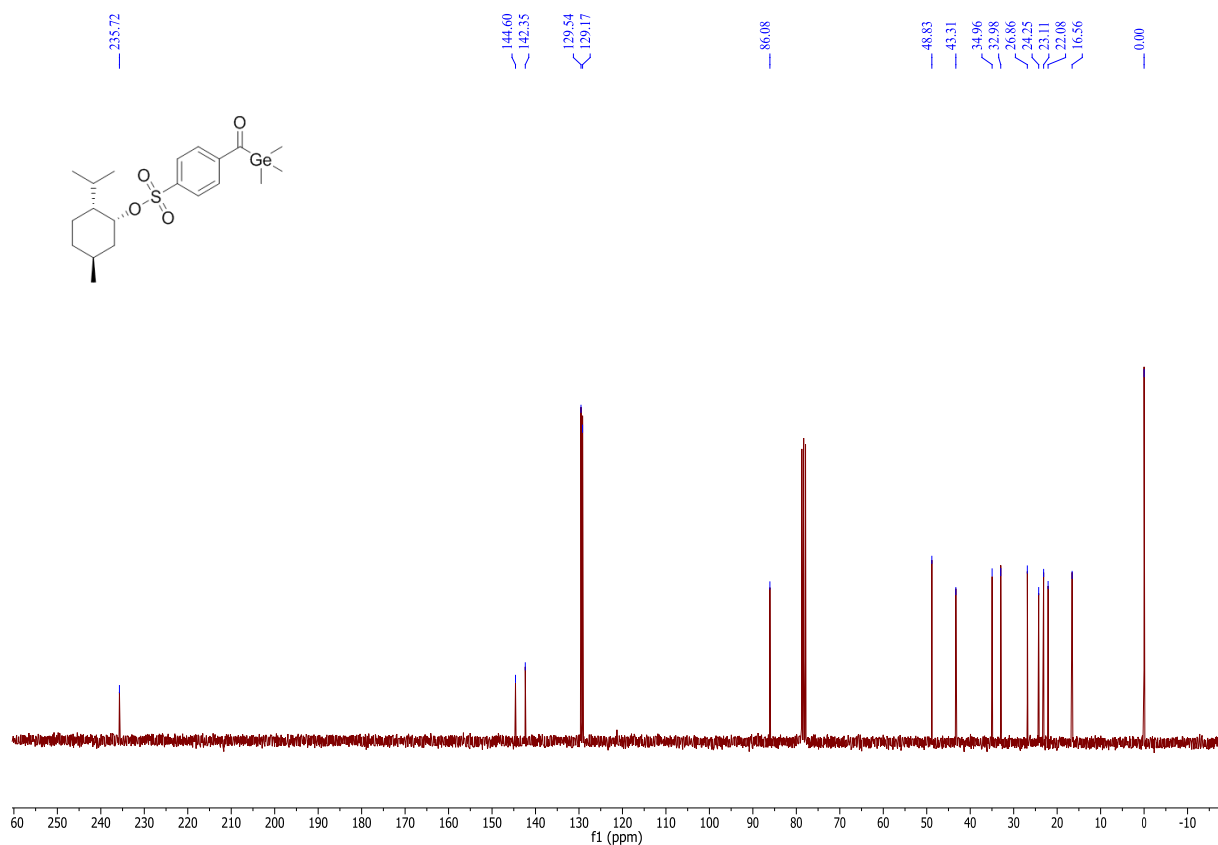


Figure S101.  $^{13}\text{C}$  NMR spectrum of 3am, related to Scheme 2.

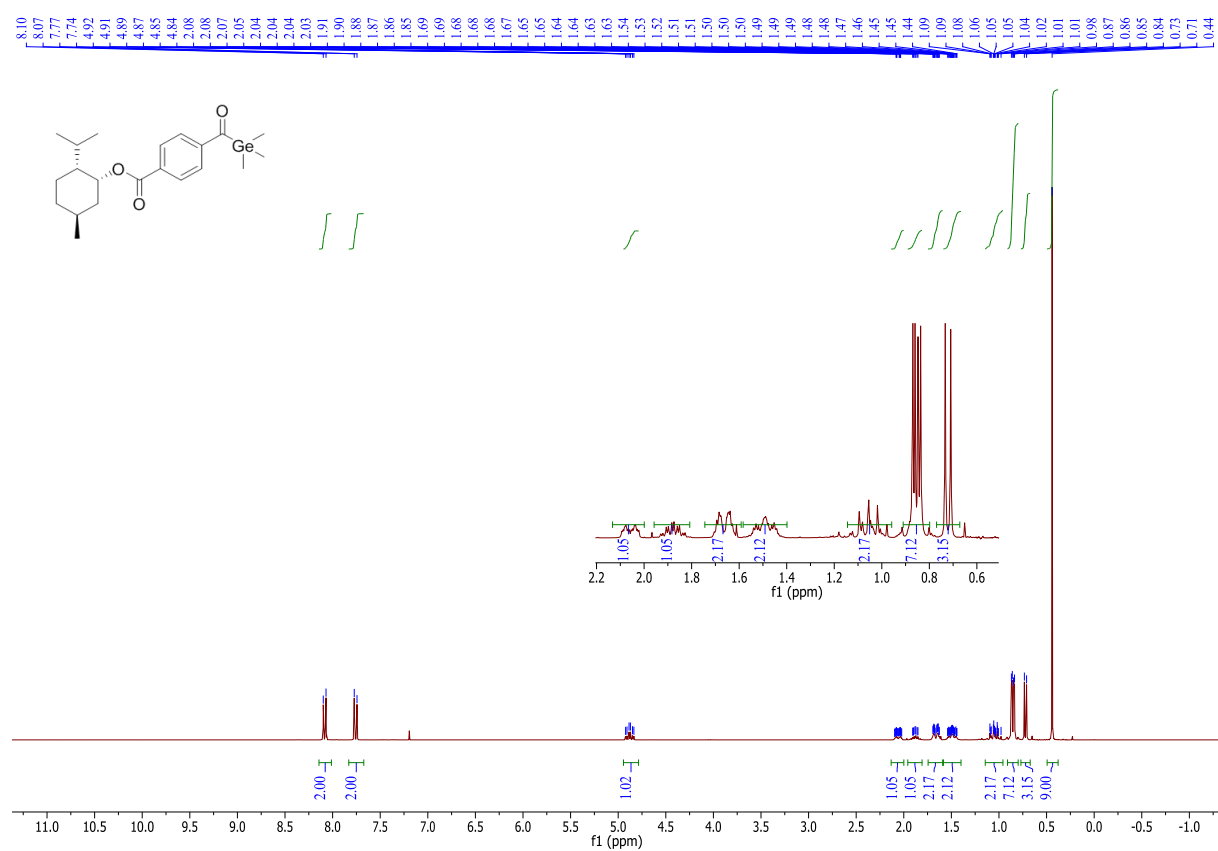


Figure S102.  $^1\text{H}$  NMR spectrum of 3an, related to Scheme 2.

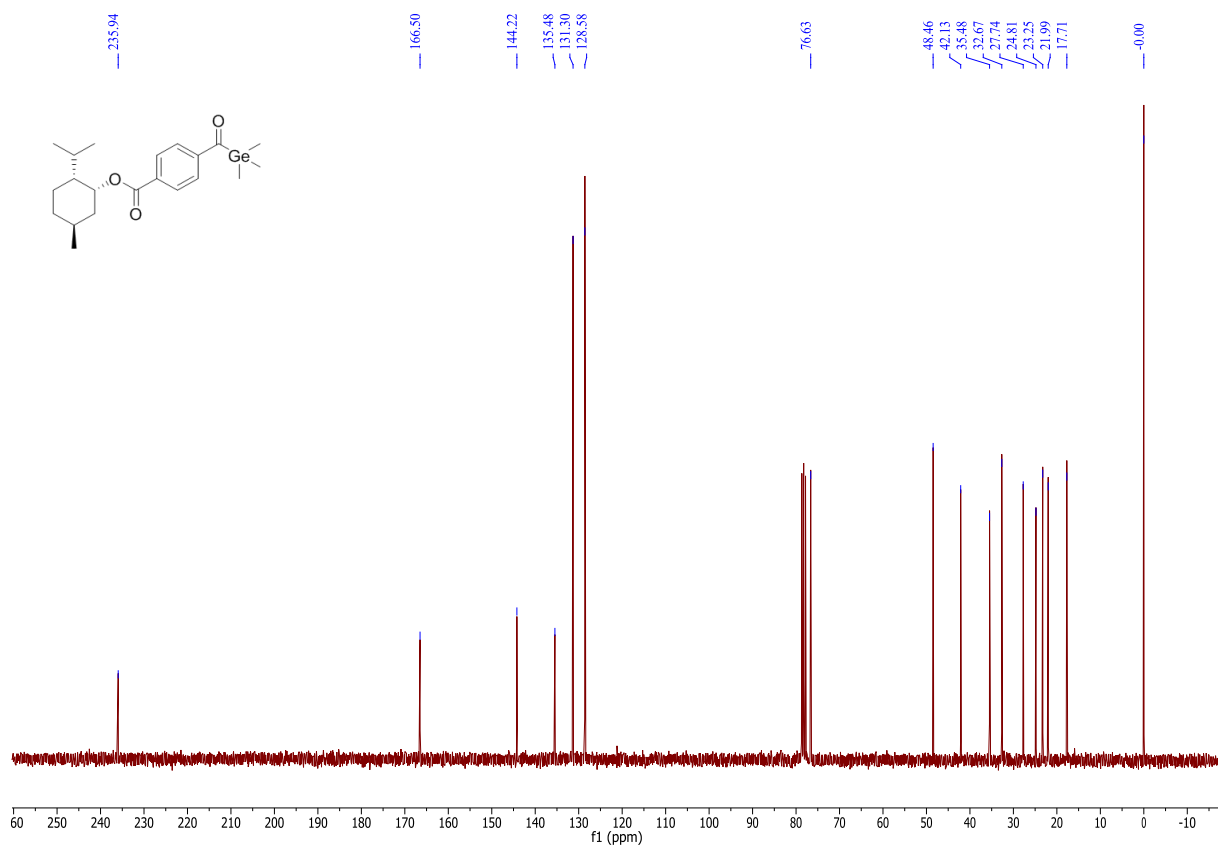


Figure S103. <sup>13</sup>C NMR spectrum of 3an, related to Scheme 2.

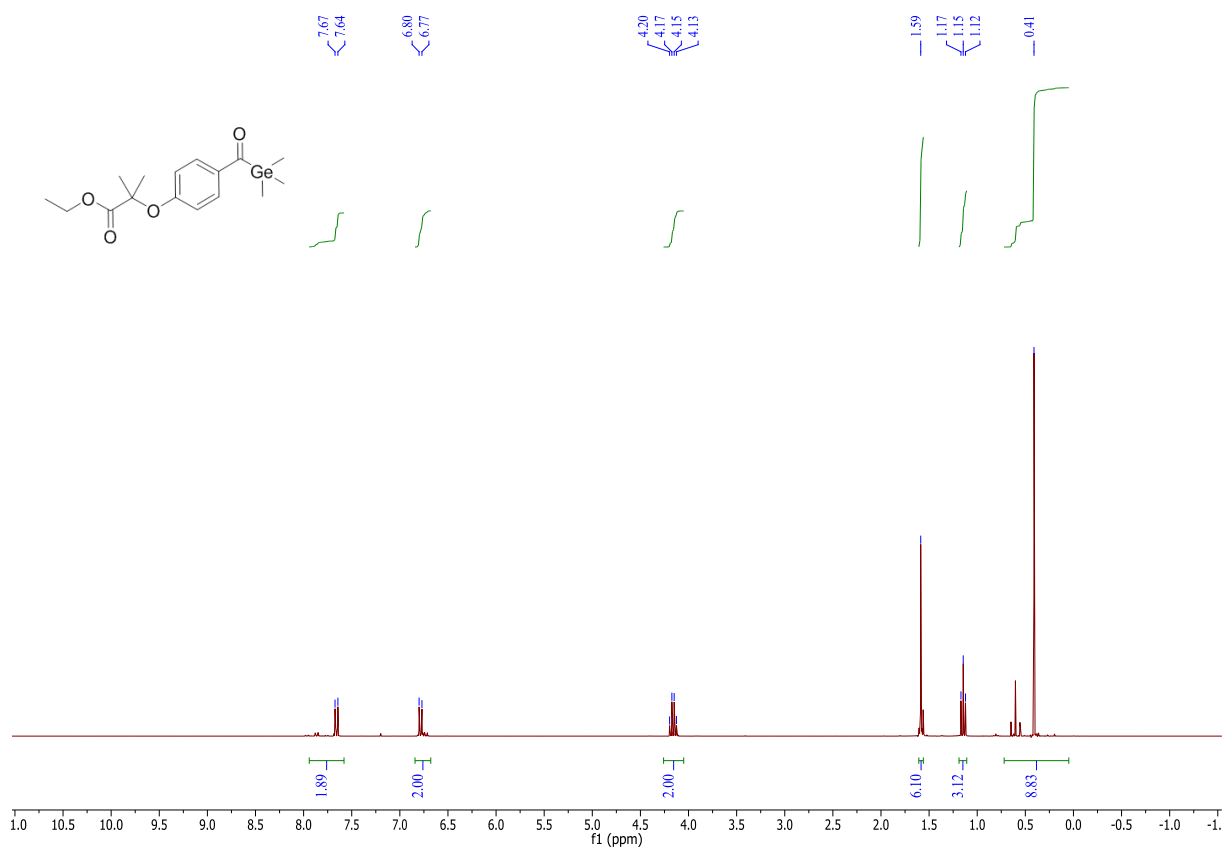


Figure S104. <sup>1</sup>H NMR spectrum of 3ao, related to Scheme 2.

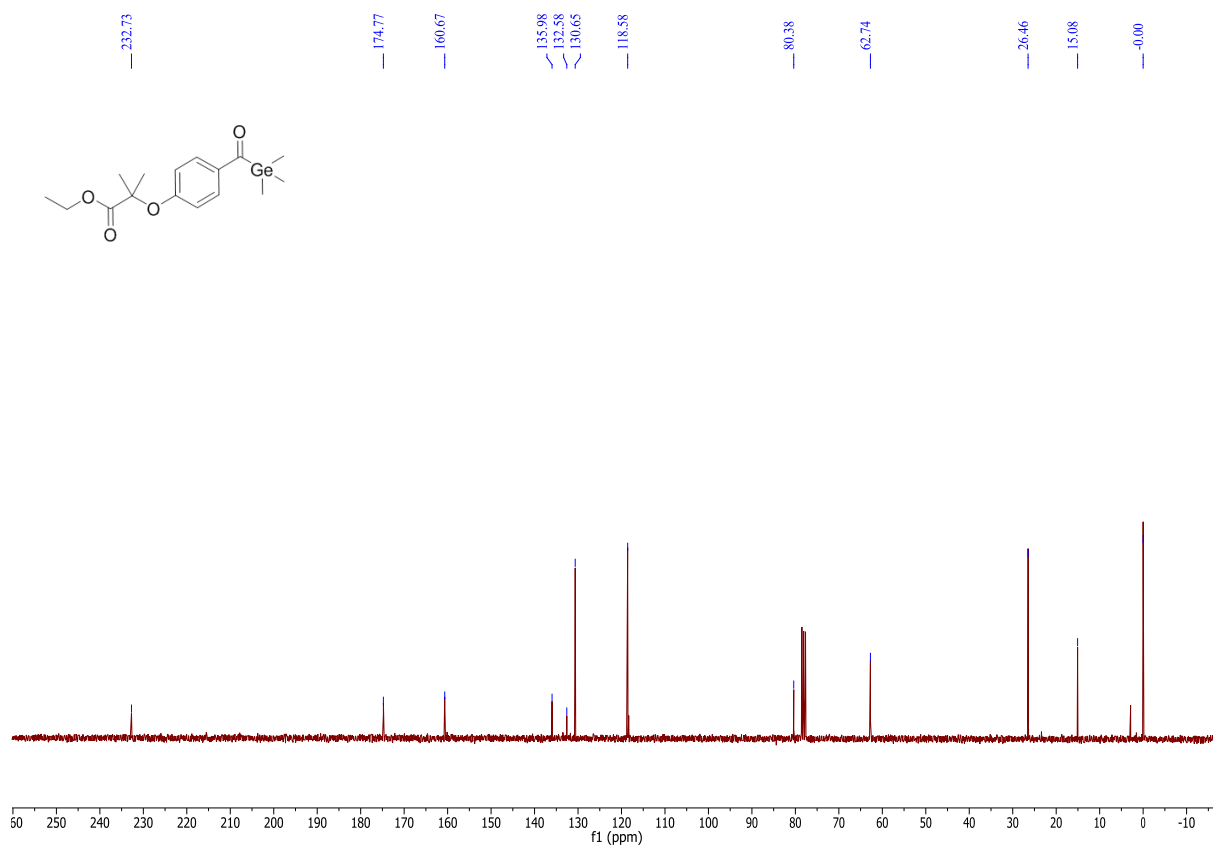


Figure S105.  $^{13}\text{C}$  NMR spectrum of 3ao, related to Scheme 2.

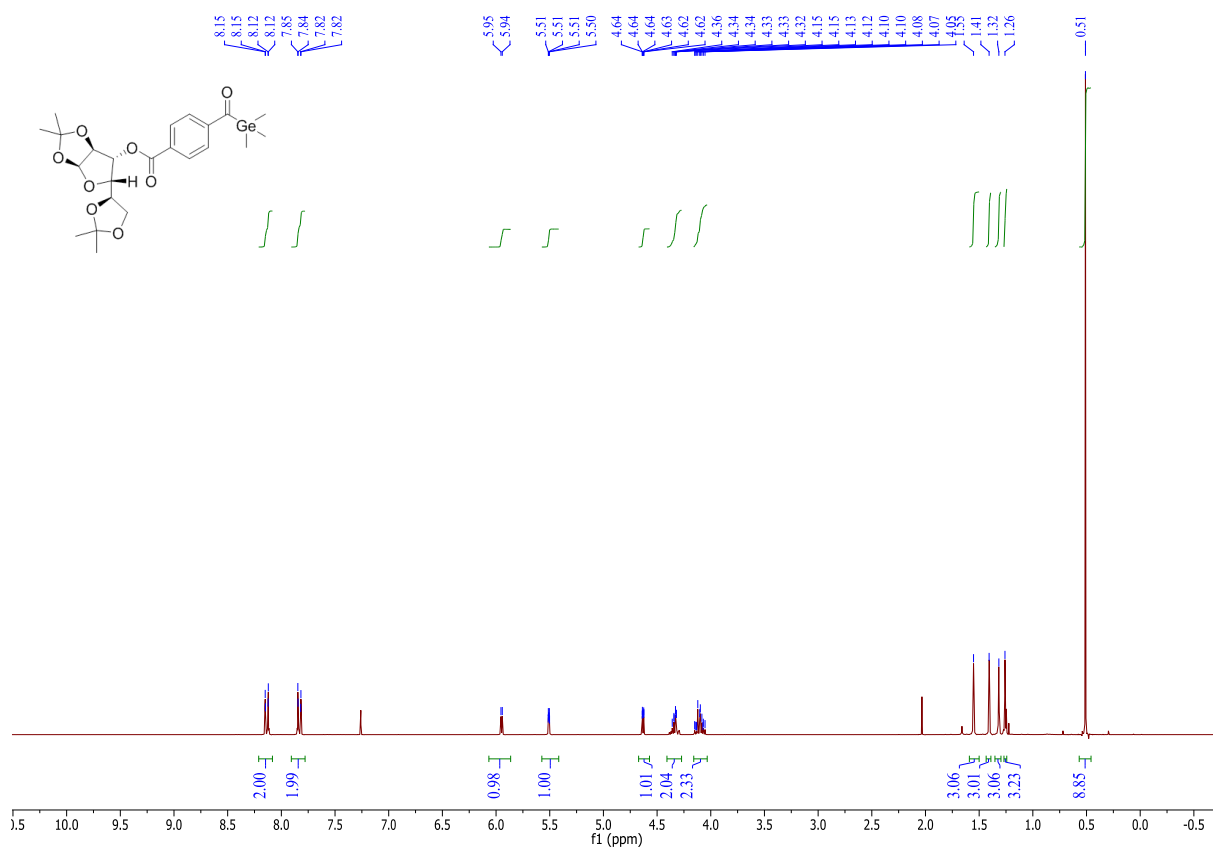


Figure S106.  $^1\text{H}$  NMR spectrum of 3ap, related to Scheme 2.





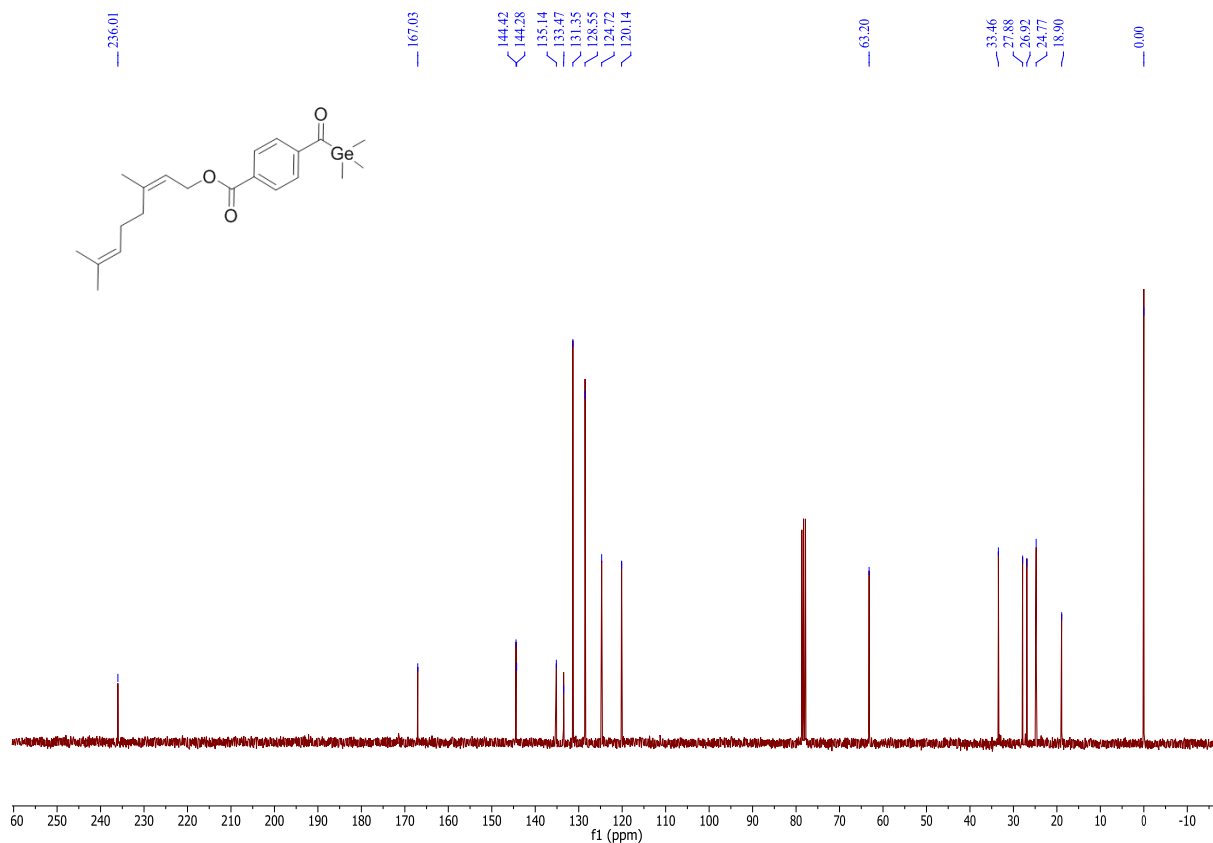


Figure S109.  $^{13}\text{C}$  NMR spectrum of 3aq, related to Scheme 2.

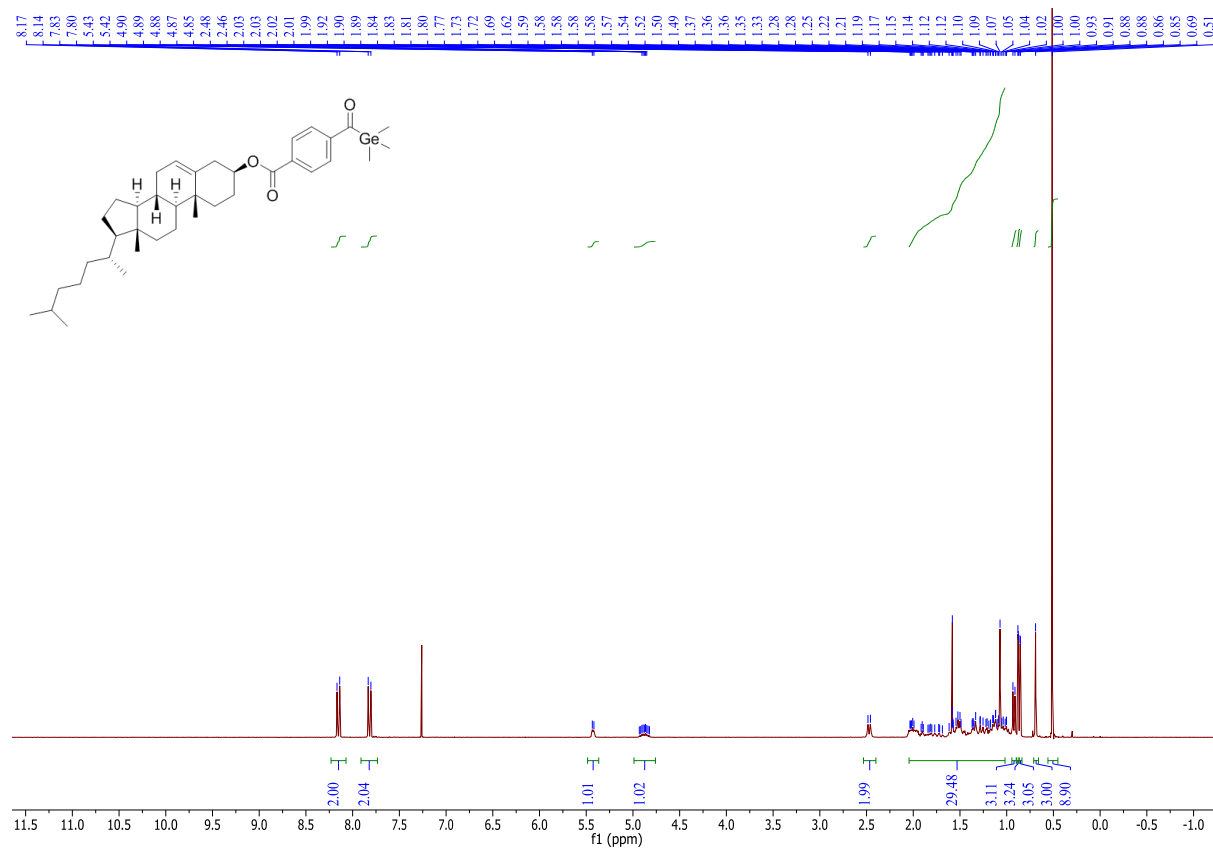


Figure S110.  $^1\text{H}$  NMR spectrum of 3ar, related to Scheme 2.

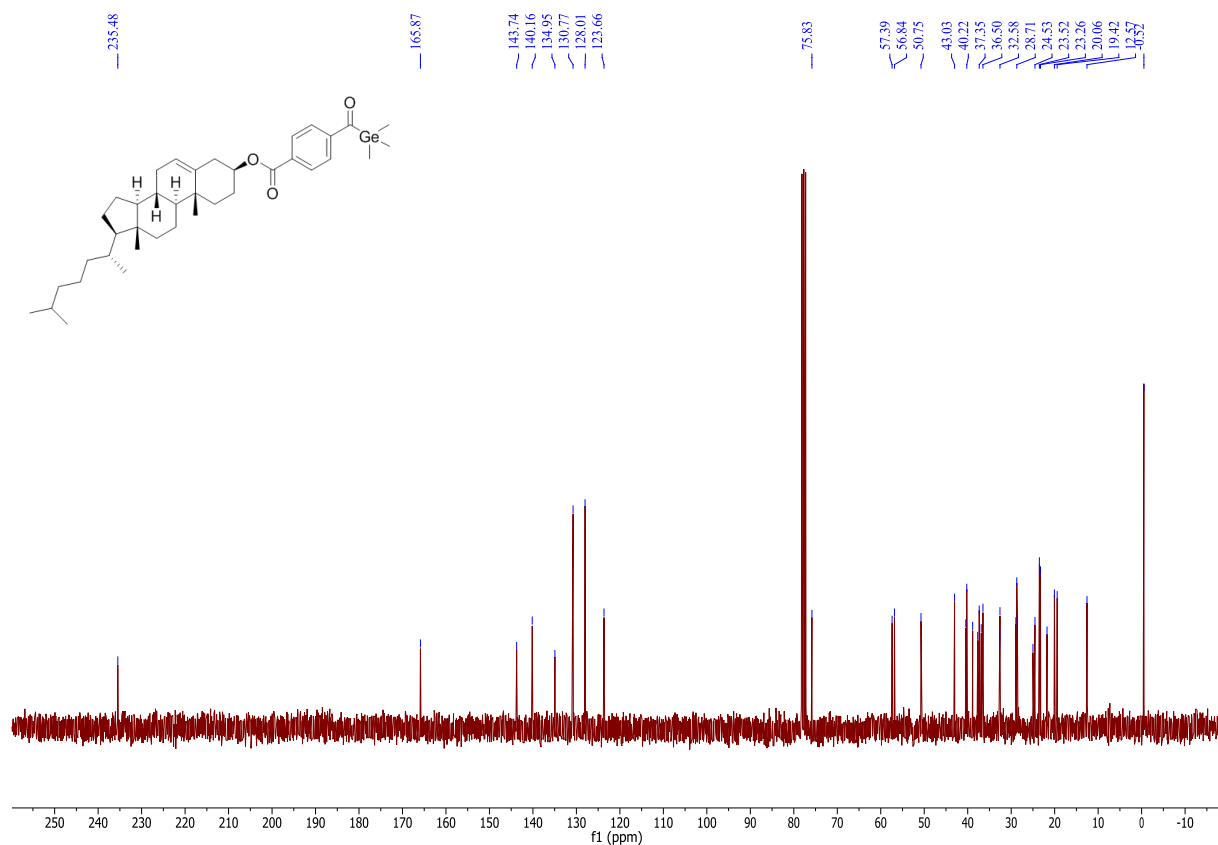


Figure S111.  $^{13}\text{C}$  NMR spectrum of 3ar, related to Scheme 2.

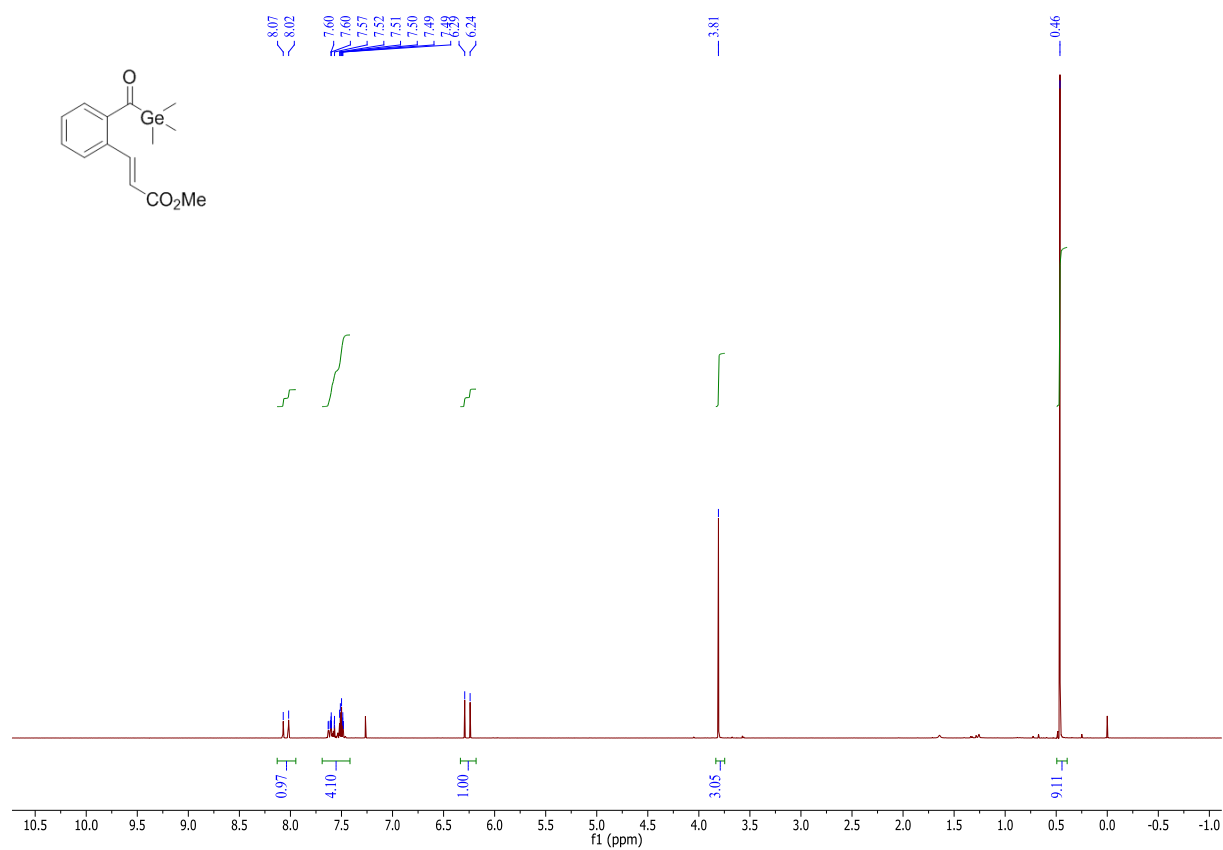


Figure S112.  $^1\text{H}$  NMR spectrum of 12a, related to Scheme 4.

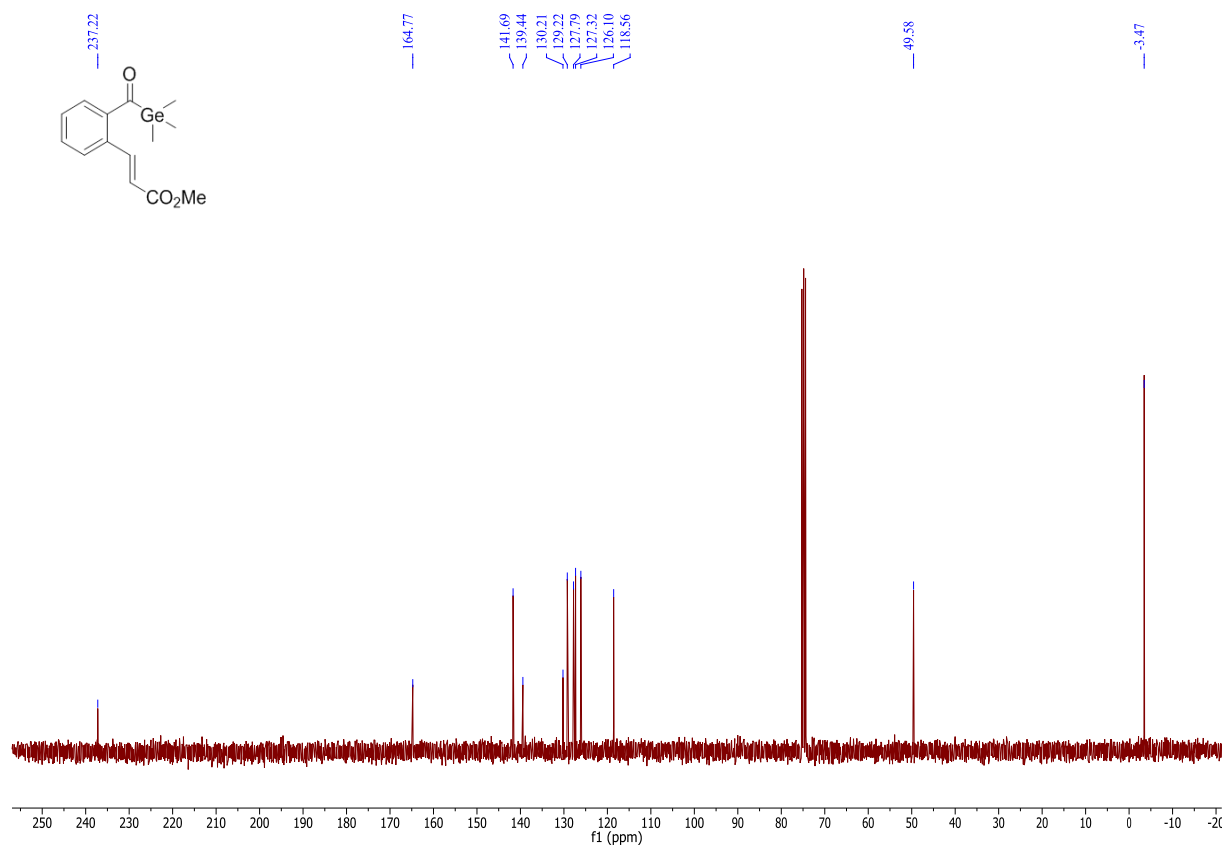


Figure S113.  $^{13}\text{C}$  NMR spectrum of 12a, related to Scheme 4.

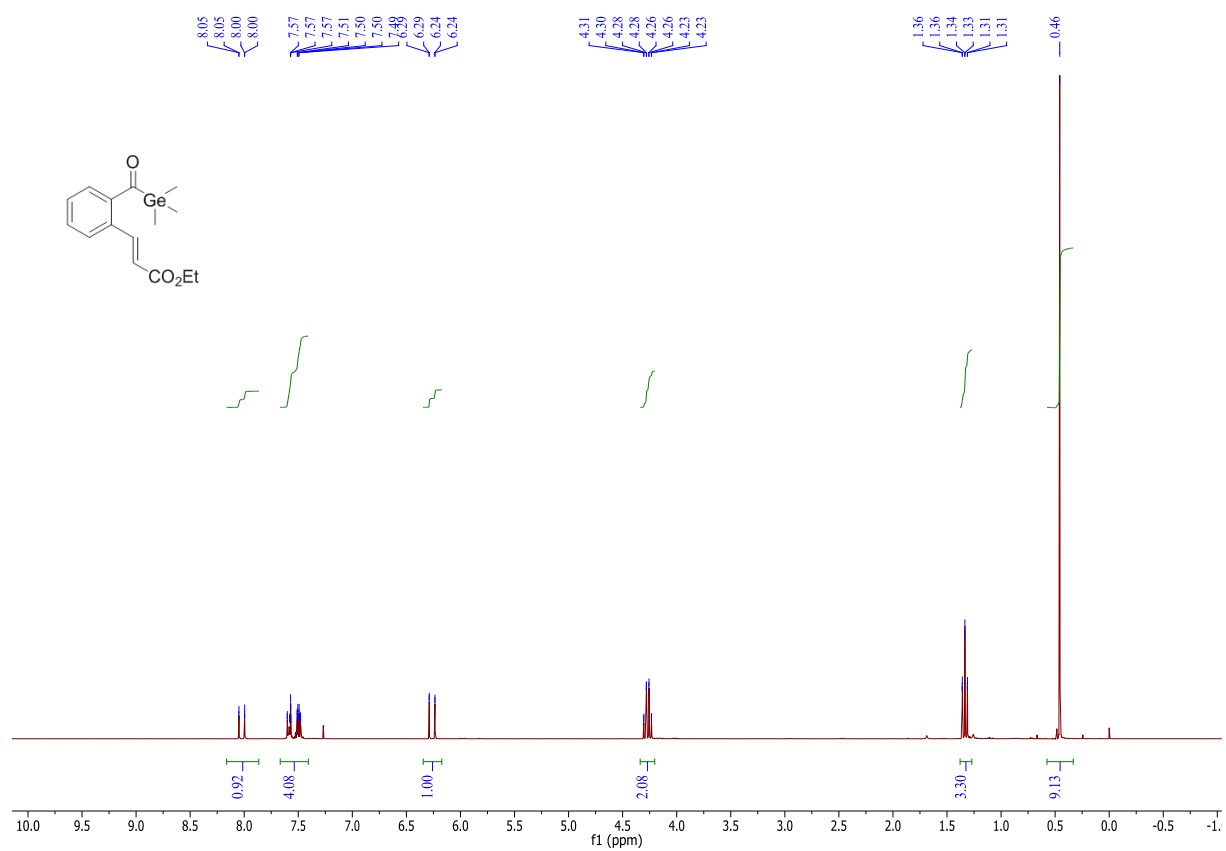


Figure S114.  $^1\text{H}$  NMR spectrum of 12b, related to Scheme 4.

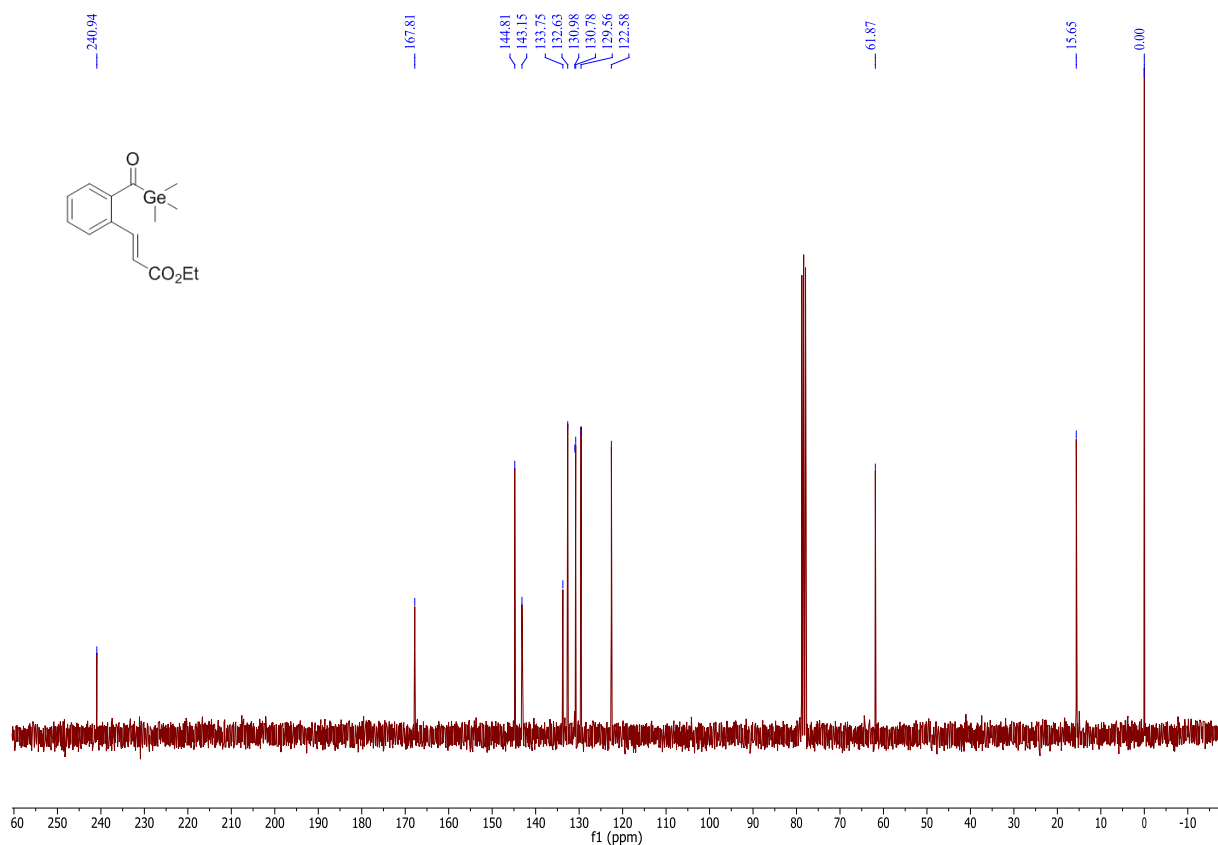


Figure S115.  $^{13}\text{C}$  NMR spectrum of 12b, related to Scheme 4.

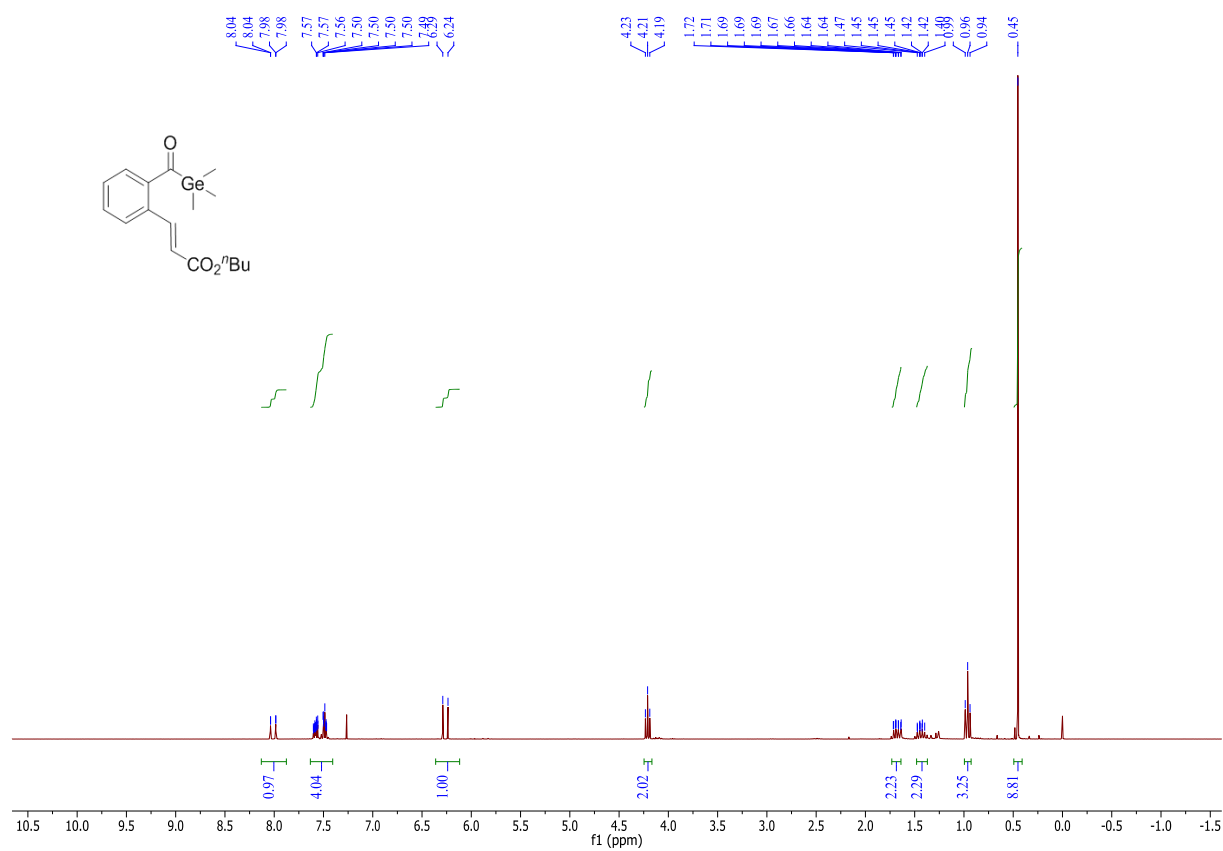


Figure S116.  $^1\text{H}$  NMR spectrum of 12c, related to Scheme 4.

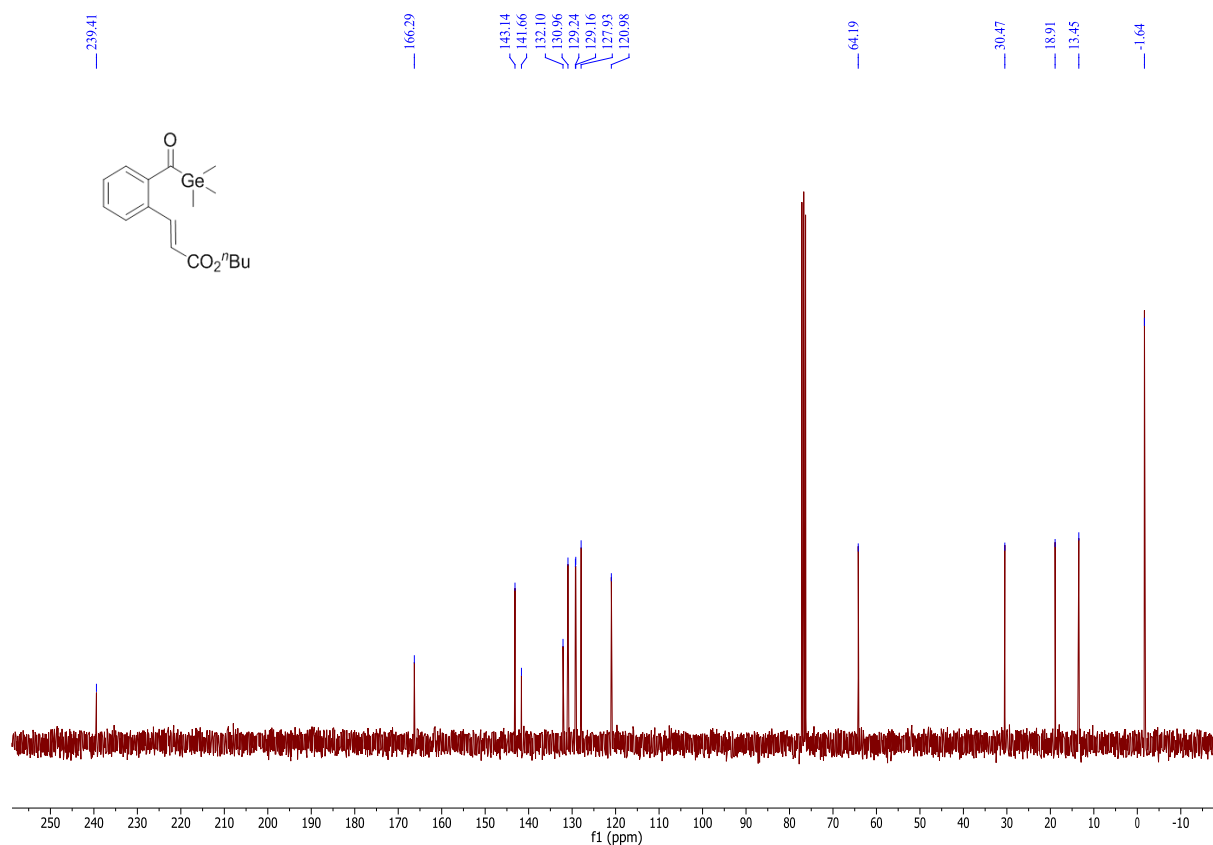


Figure S117. <sup>13</sup>C NMR spectrum of 12c, related to Scheme 4.

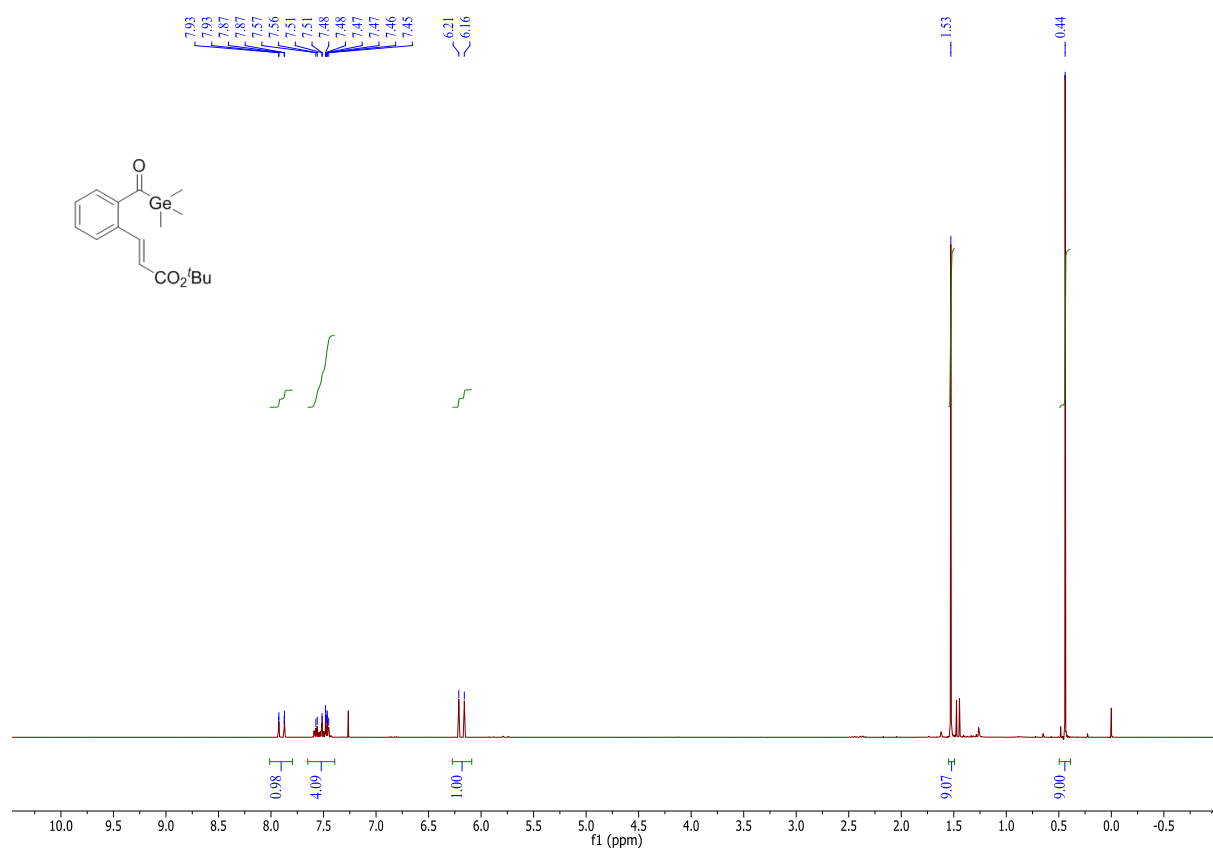


Figure S118. <sup>1</sup>H NMR spectrum of 12d, related to Scheme 4.

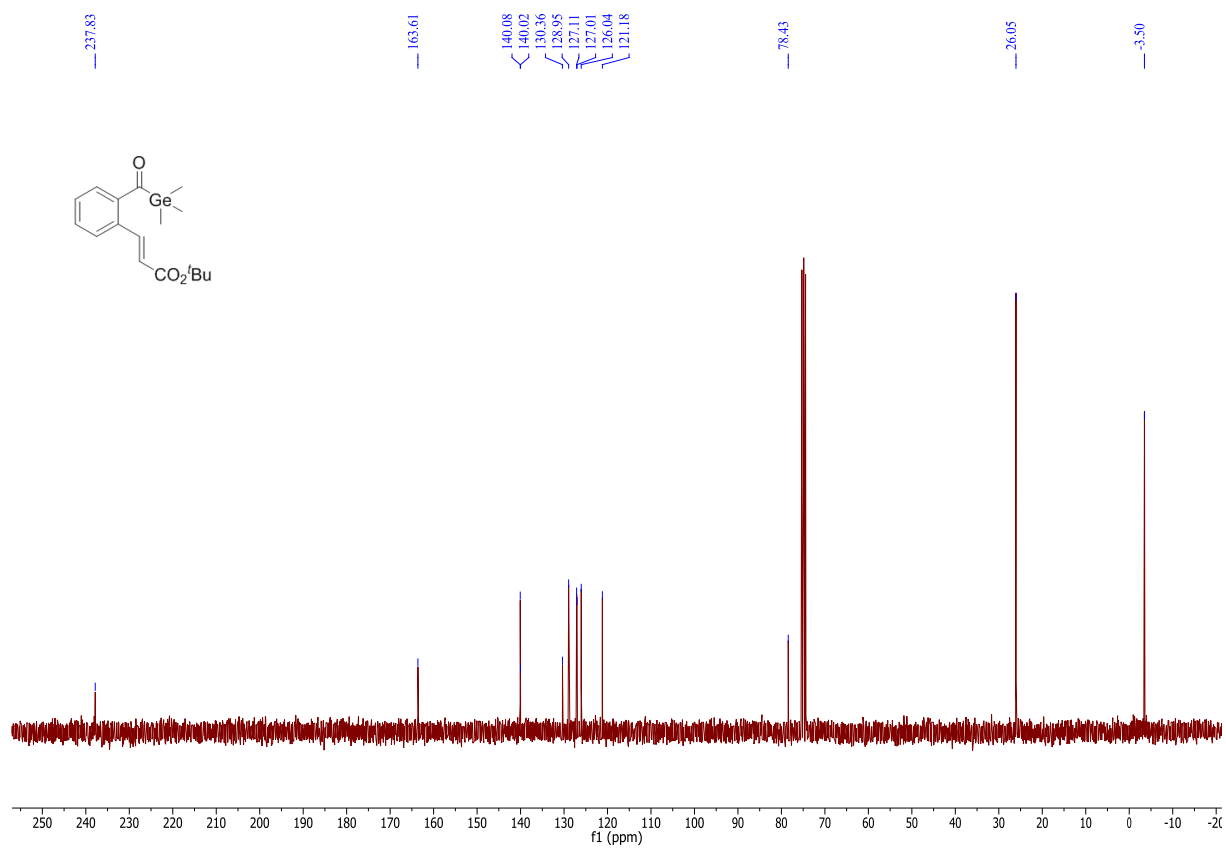


Figure S119.  $^{13}\text{C}$  NMR spectrum of 12d, related to Scheme 4.

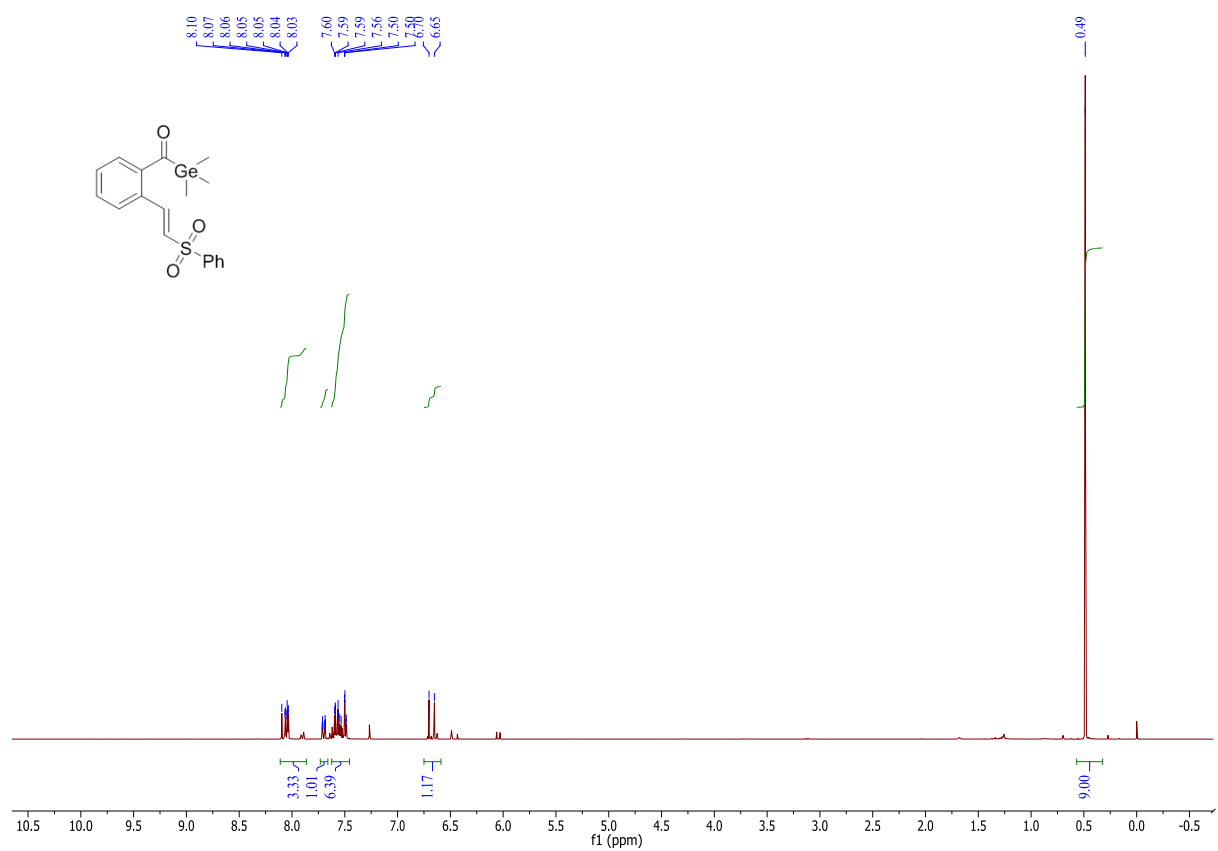


Figure S120.  $^1\text{H}$  NMR spectrum of 12e, related to Scheme 4.

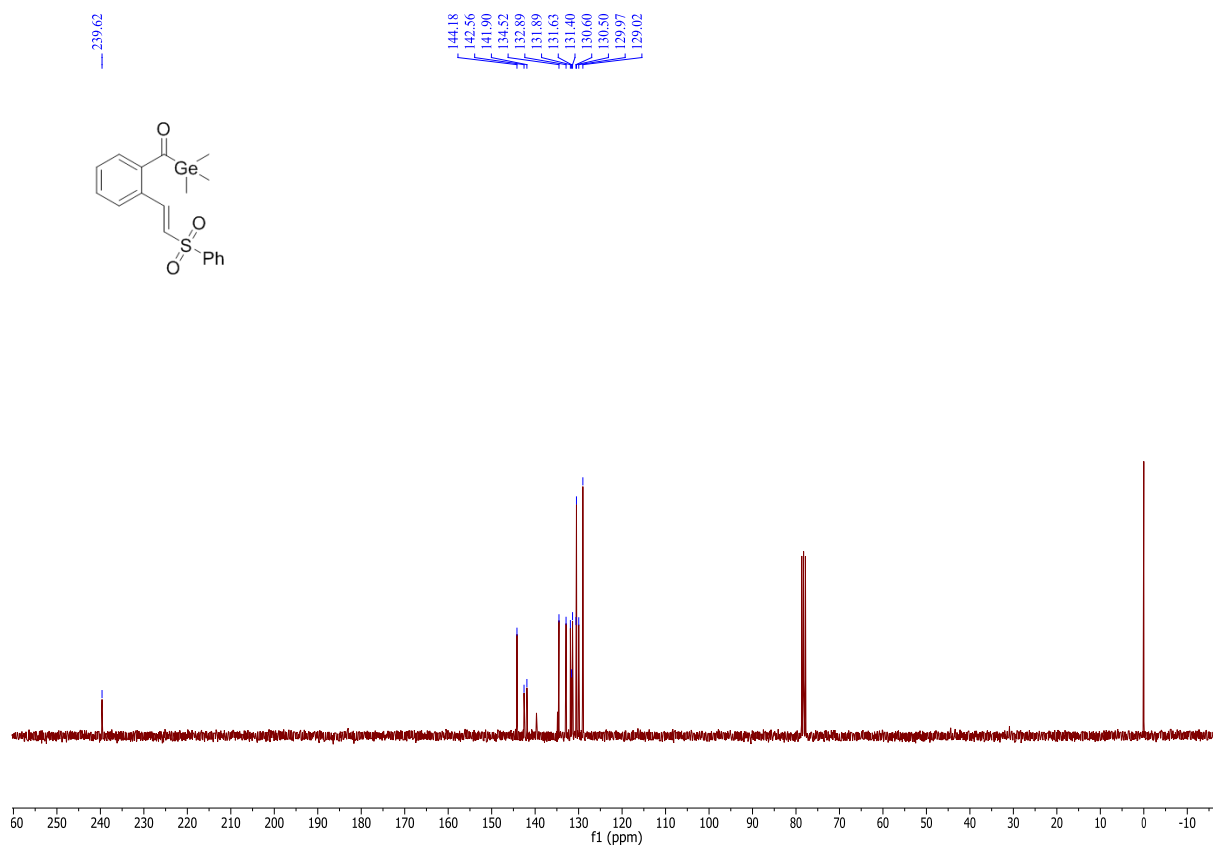


Figure S121. <sup>13</sup>C NMR spectrum of 12e, related to Scheme 4.

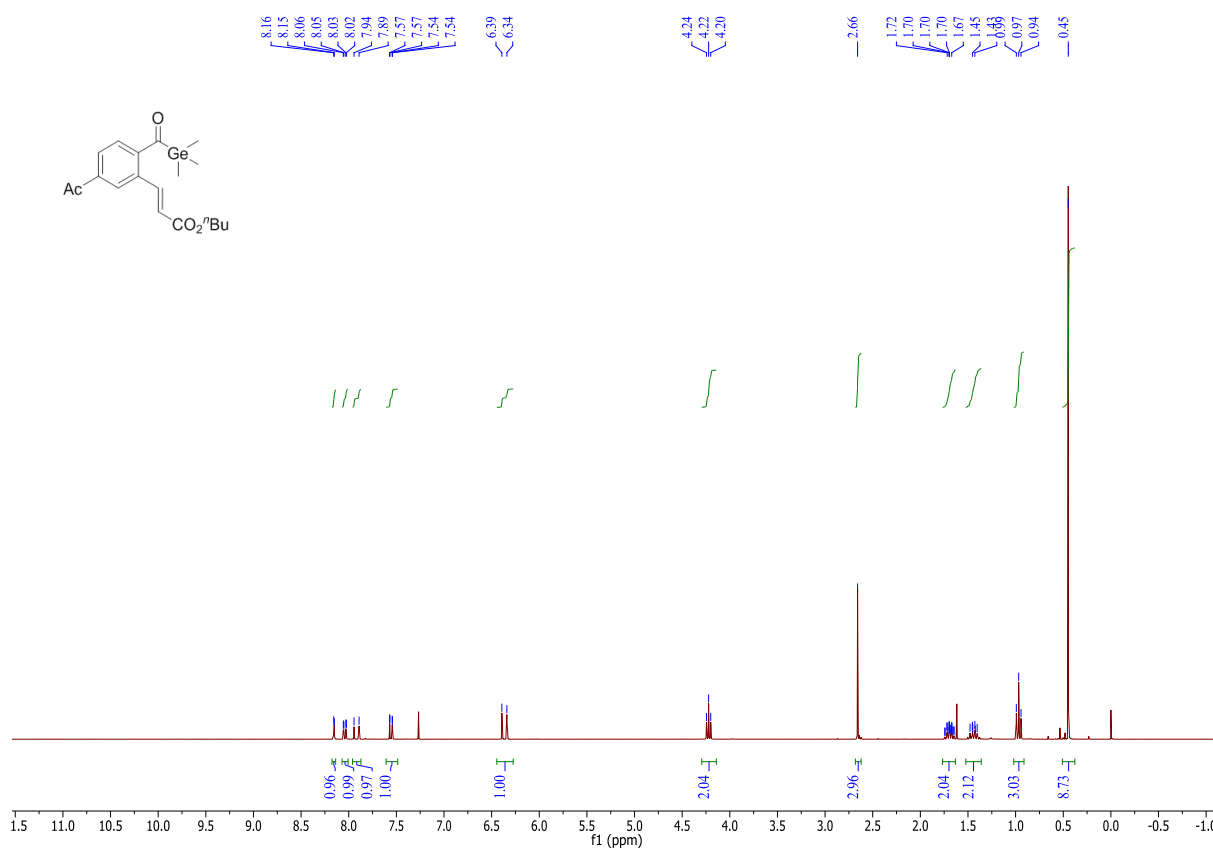


Figure S122. <sup>1</sup>H NMR spectrum of 12f, related to Scheme 4.



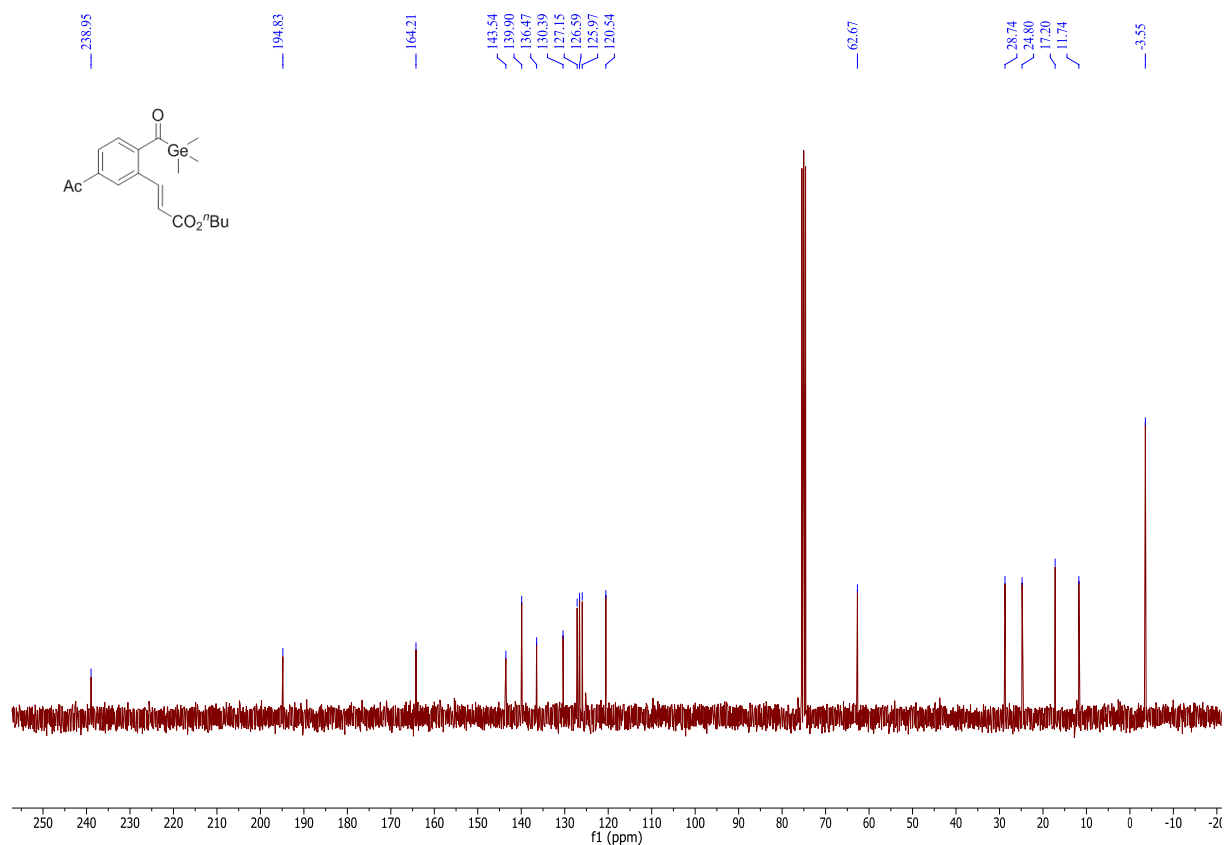


Figure S123. <sup>13</sup>C NMR spectrum of 12f, related to Scheme 4.

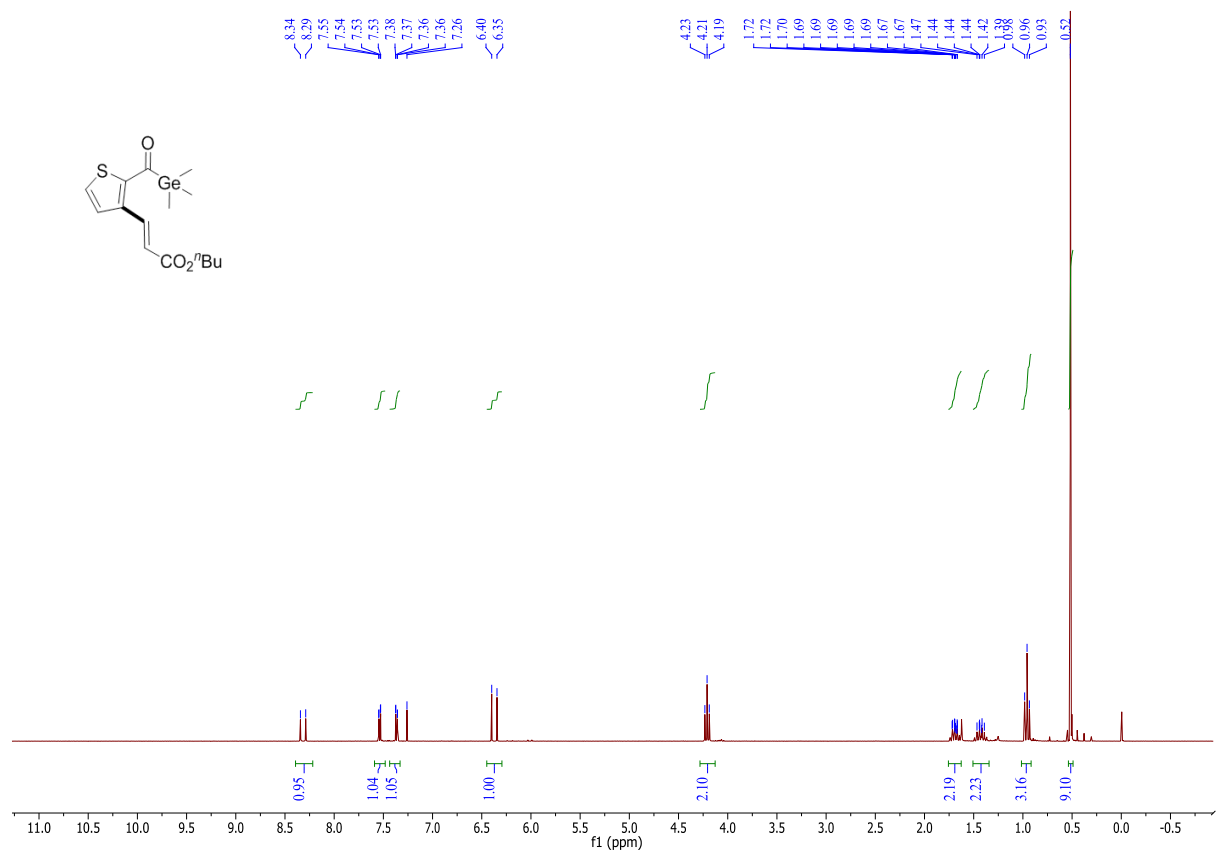


Figure S124. <sup>1</sup>H NMR spectrum of 12g, related to Scheme 4.

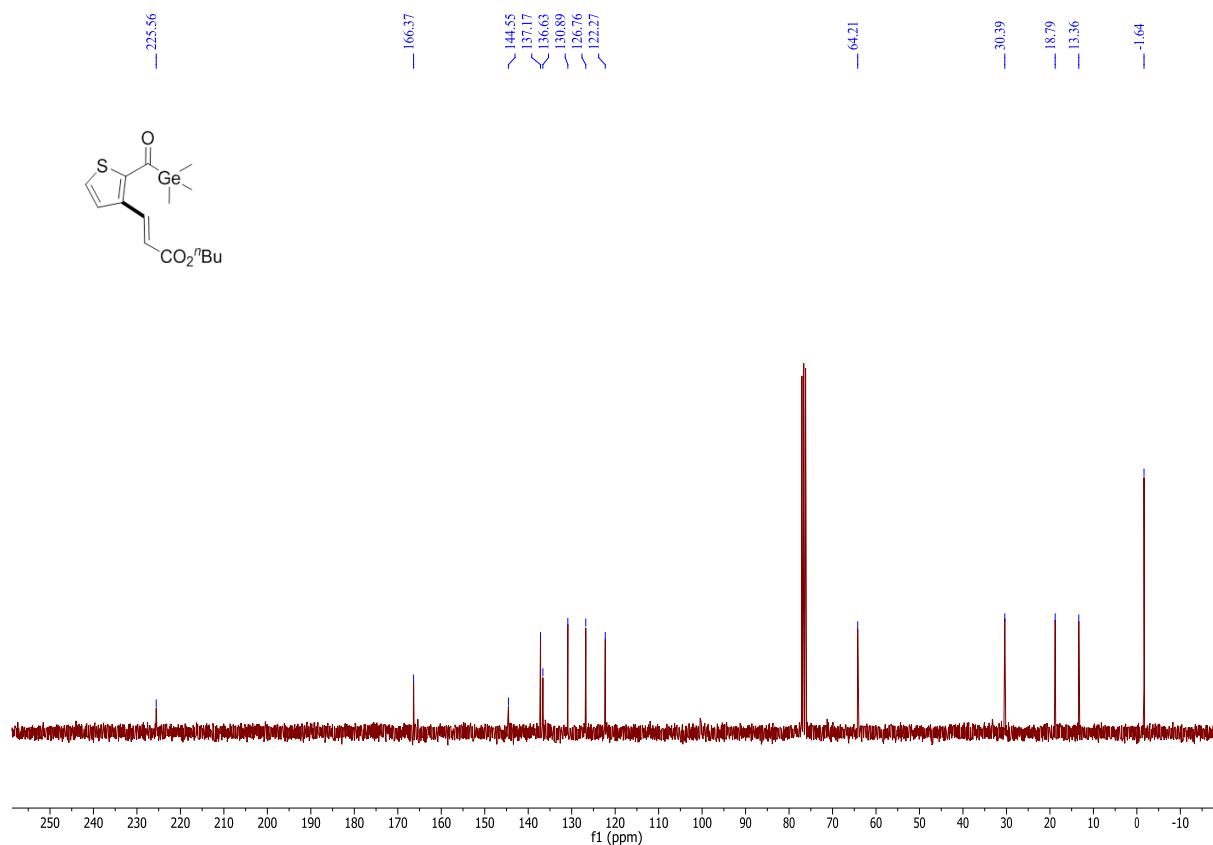


Figure S125. <sup>13</sup>C NMR spectrum of 12g, related to Scheme 4.

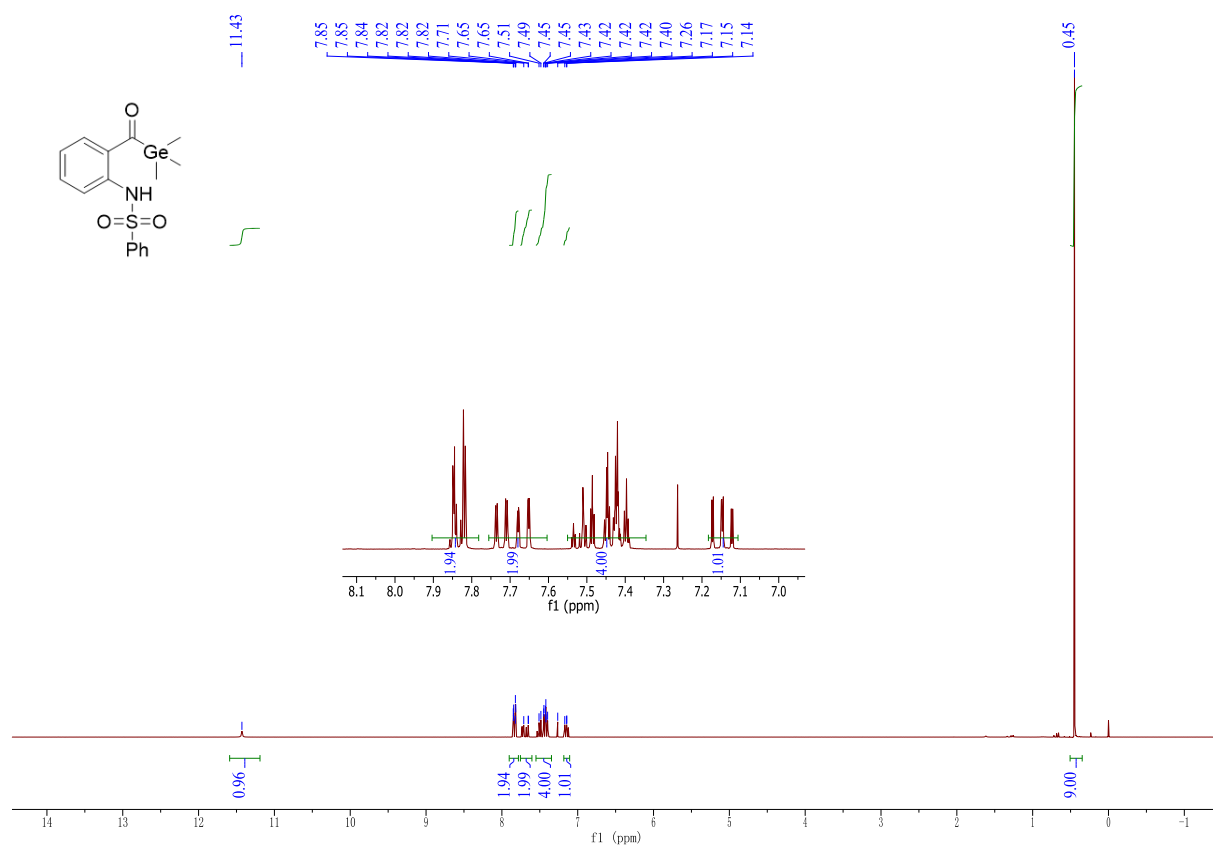
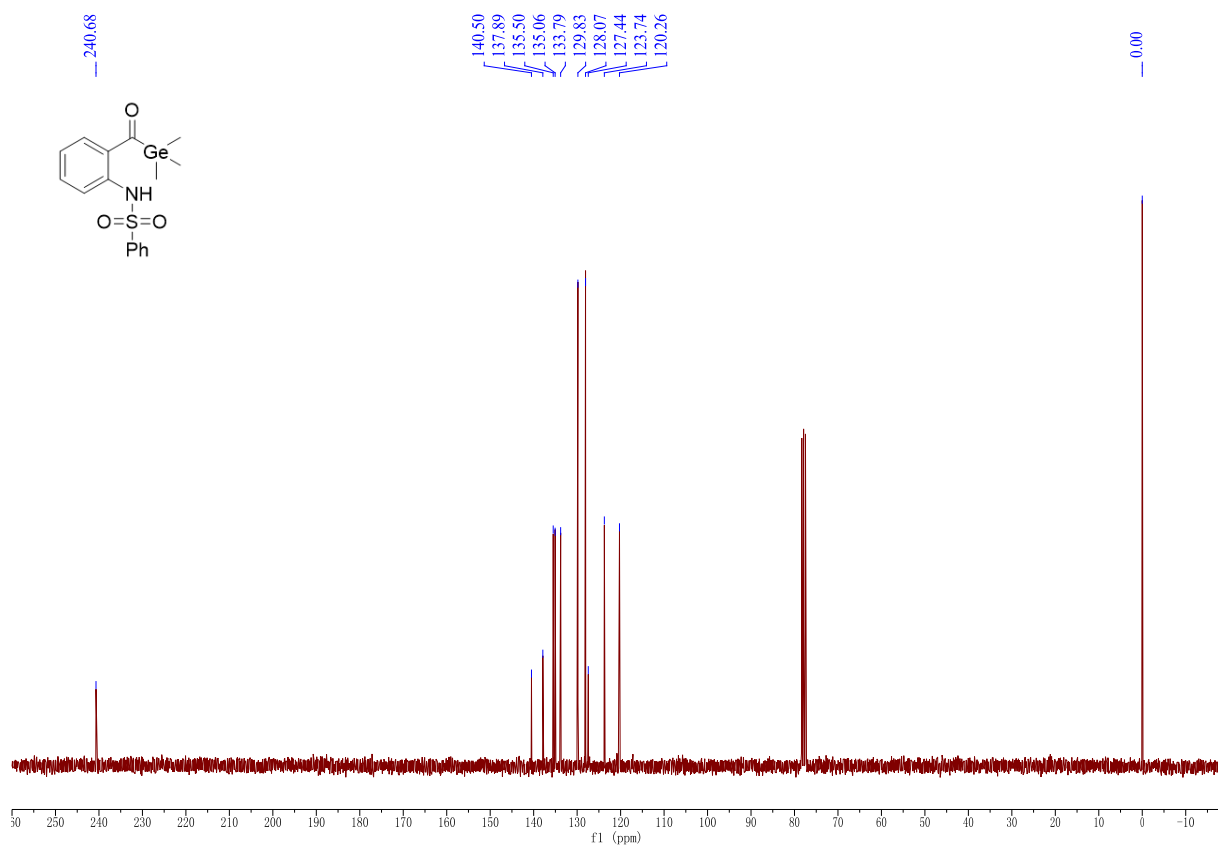
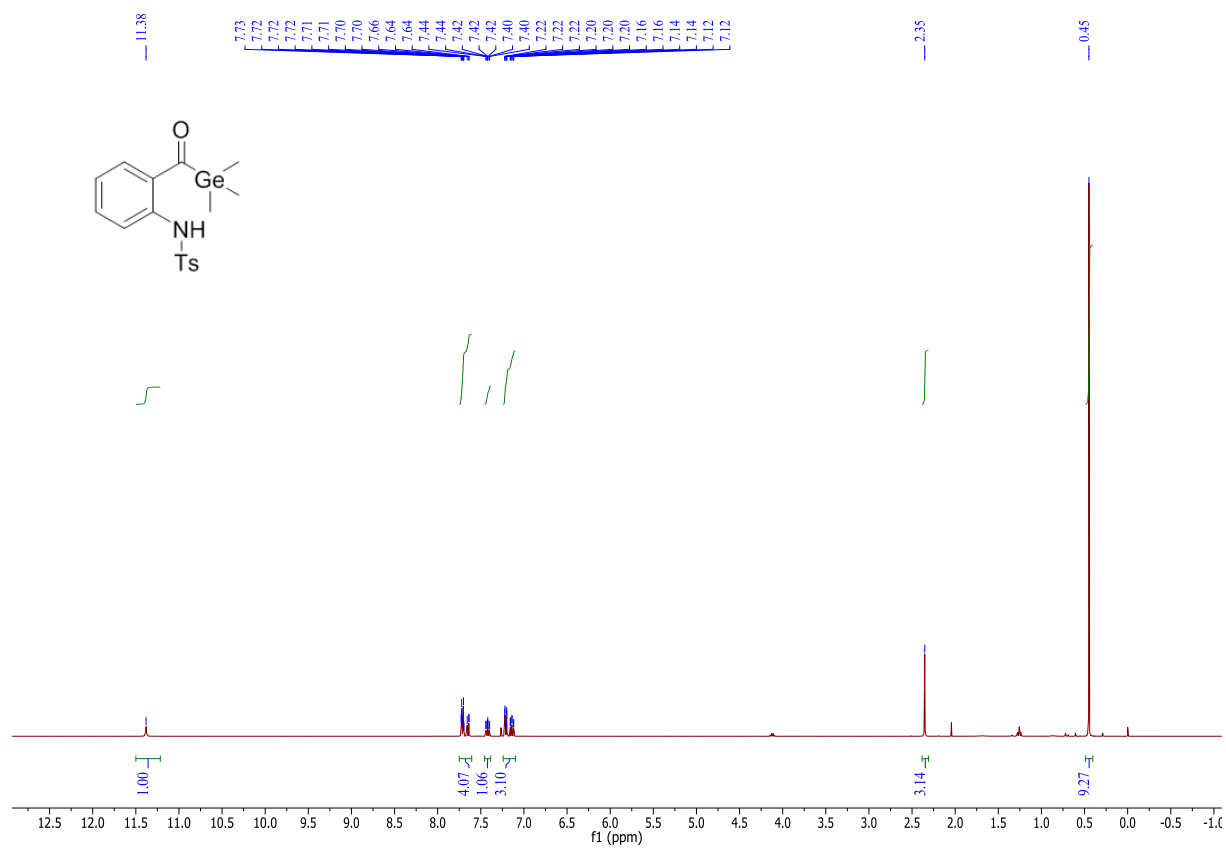


Figure S126. <sup>1</sup>H NMR spectrum of 14a, related to Scheme 5.



**Figure S127.**  $^{13}\text{C}$  NMR spectrum of 14a, related to Scheme 5.



**Figure S128.**  $^1\text{H}$  NMR spectrum of 14b, related to Scheme 5.

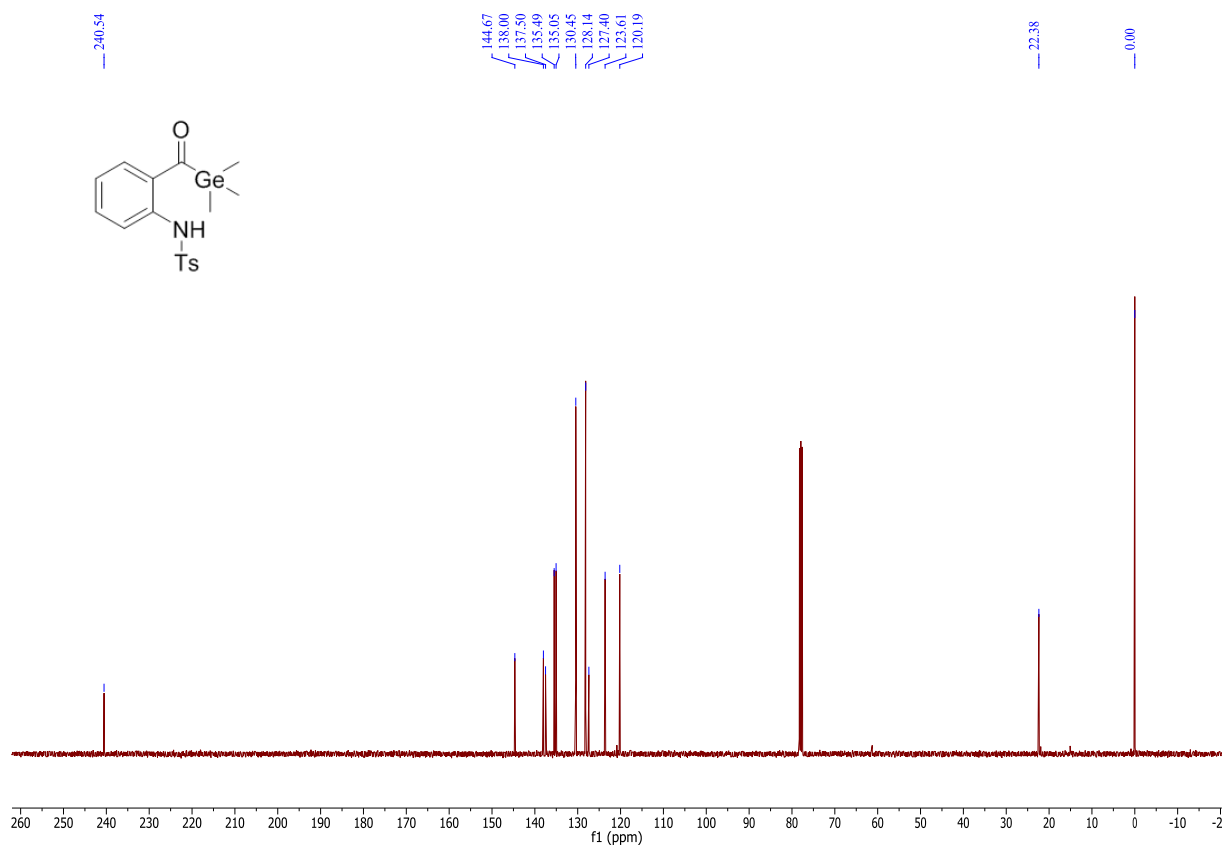


Figure S129. <sup>13</sup>C NMR spectrum of 14b, related to Scheme 5.

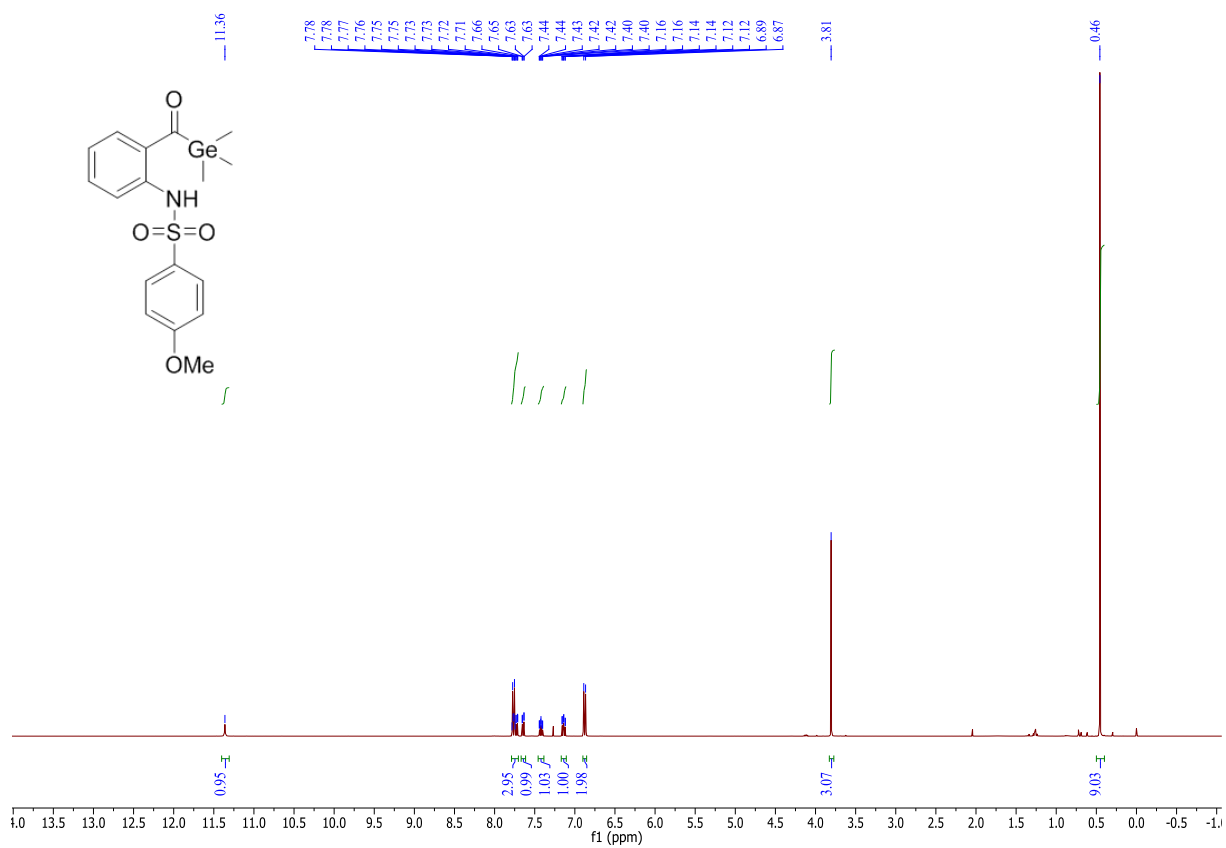
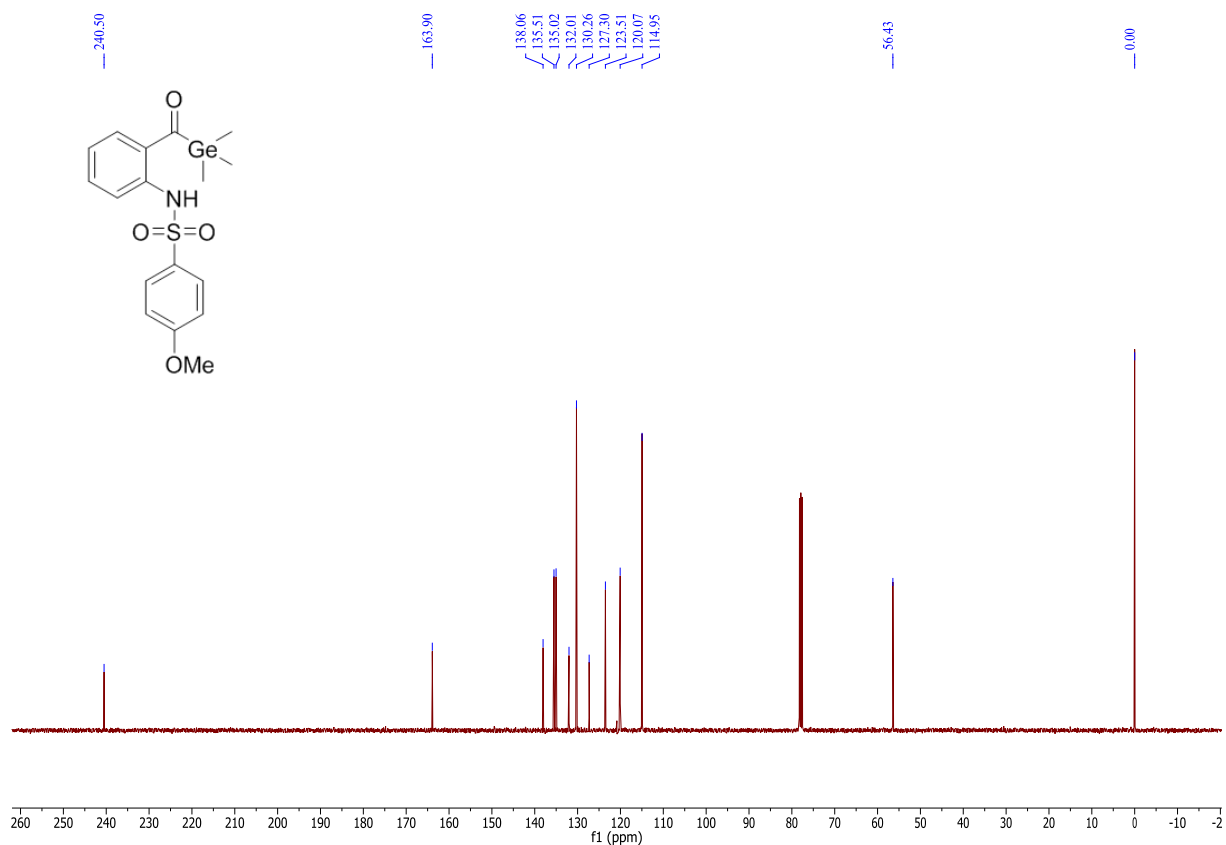
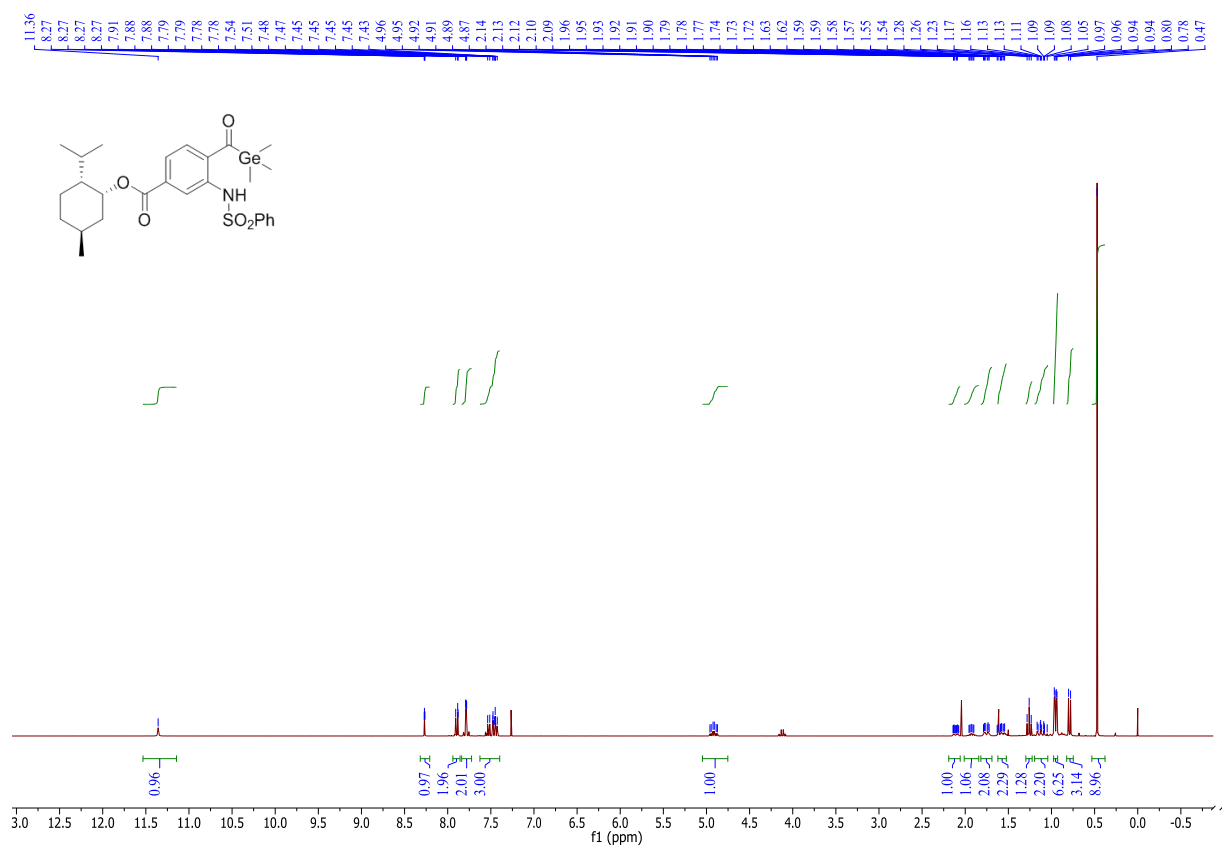


Figure S130. <sup>1</sup>H NMR spectrum of 14c, related to Scheme 5.



**Figure S131.**  $^{13}\text{C}$  NMR spectrum of 14c, related to Scheme 5.



**Figure S132.**  $^1\text{H}$  NMR spectrum of 14d, related to Scheme 5.

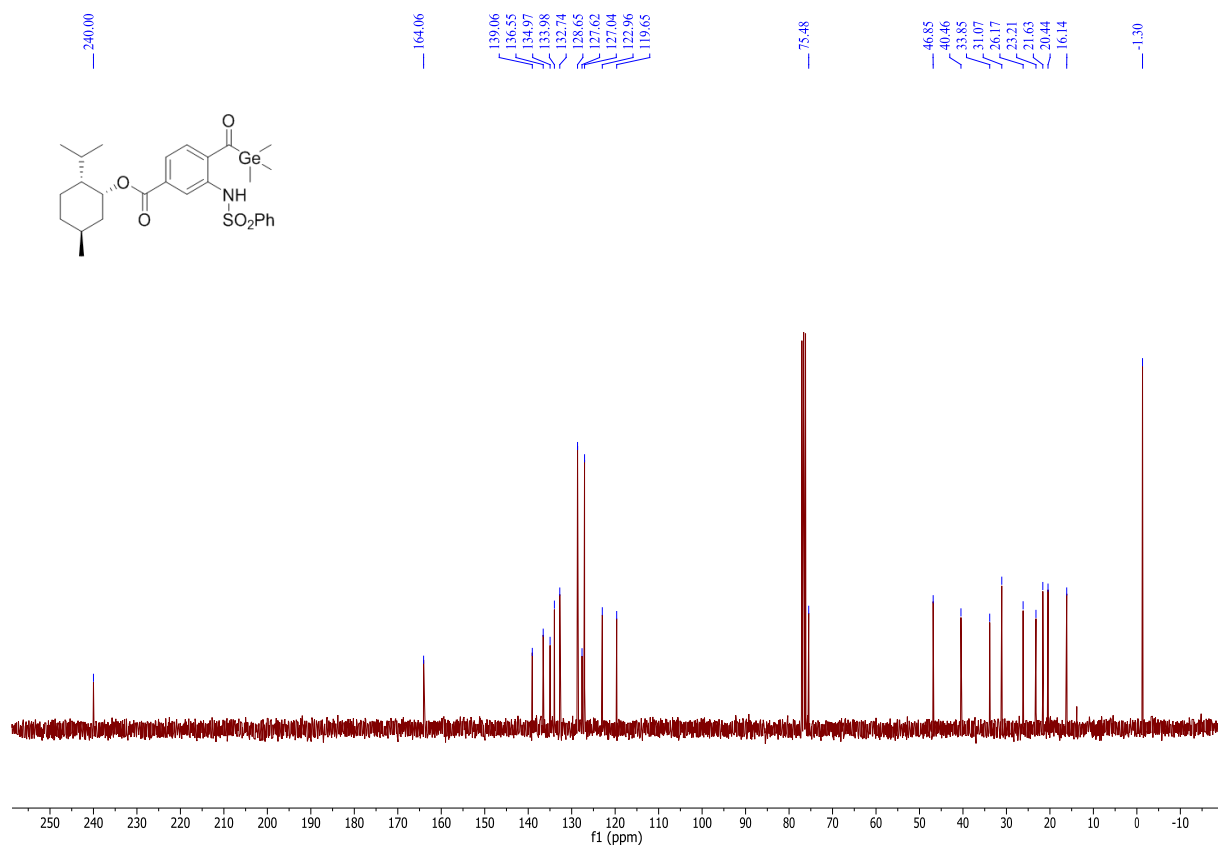


Figure S133.  $^{13}\text{C}$  NMR spectrum of 14d, related to Scheme 5.

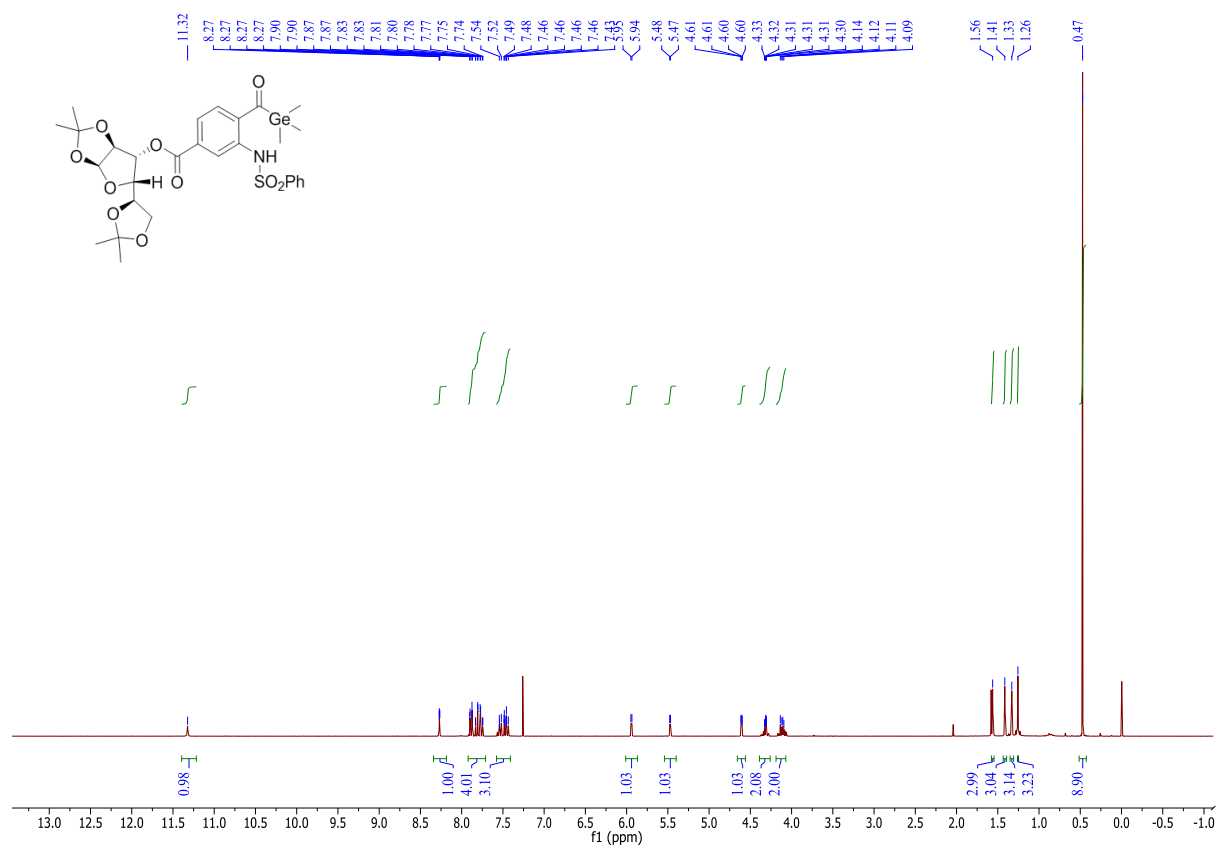
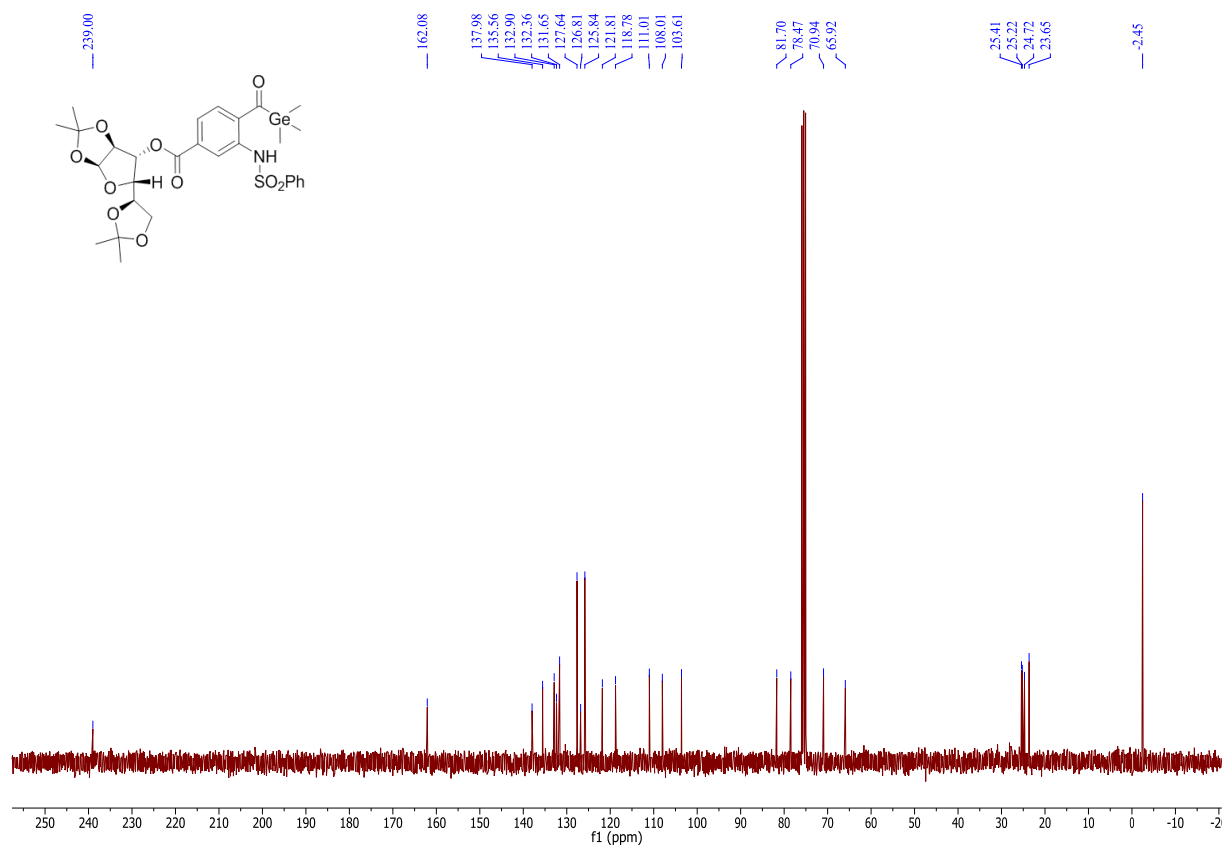
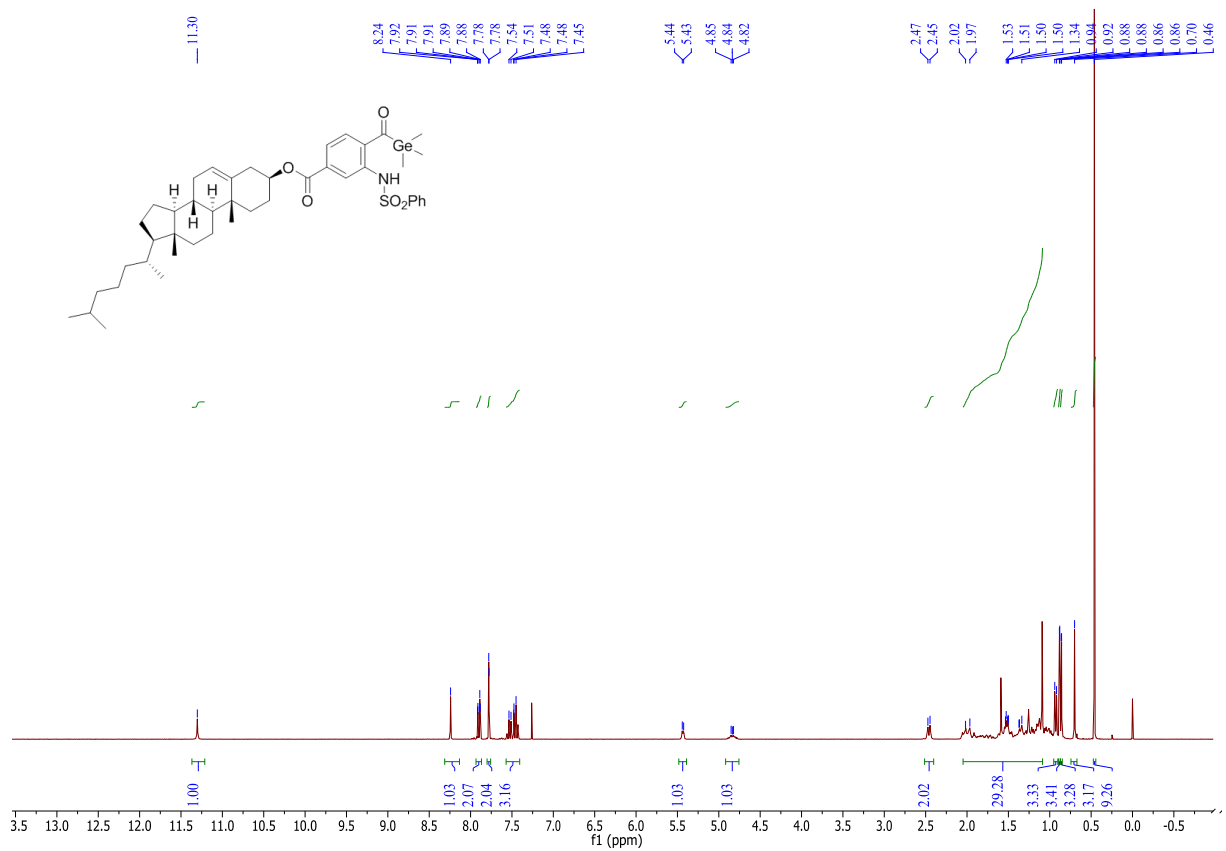


Figure S134.  $^1\text{H}$  NMR spectrum of 14e, related to Scheme 5.



**Figure S135.**  $^{13}\text{C}$  NMR spectrum of 14e, related to Scheme 5.



**Figure S136.**  $^1\text{H}$  NMR spectrum of 14f, related to Scheme 5.

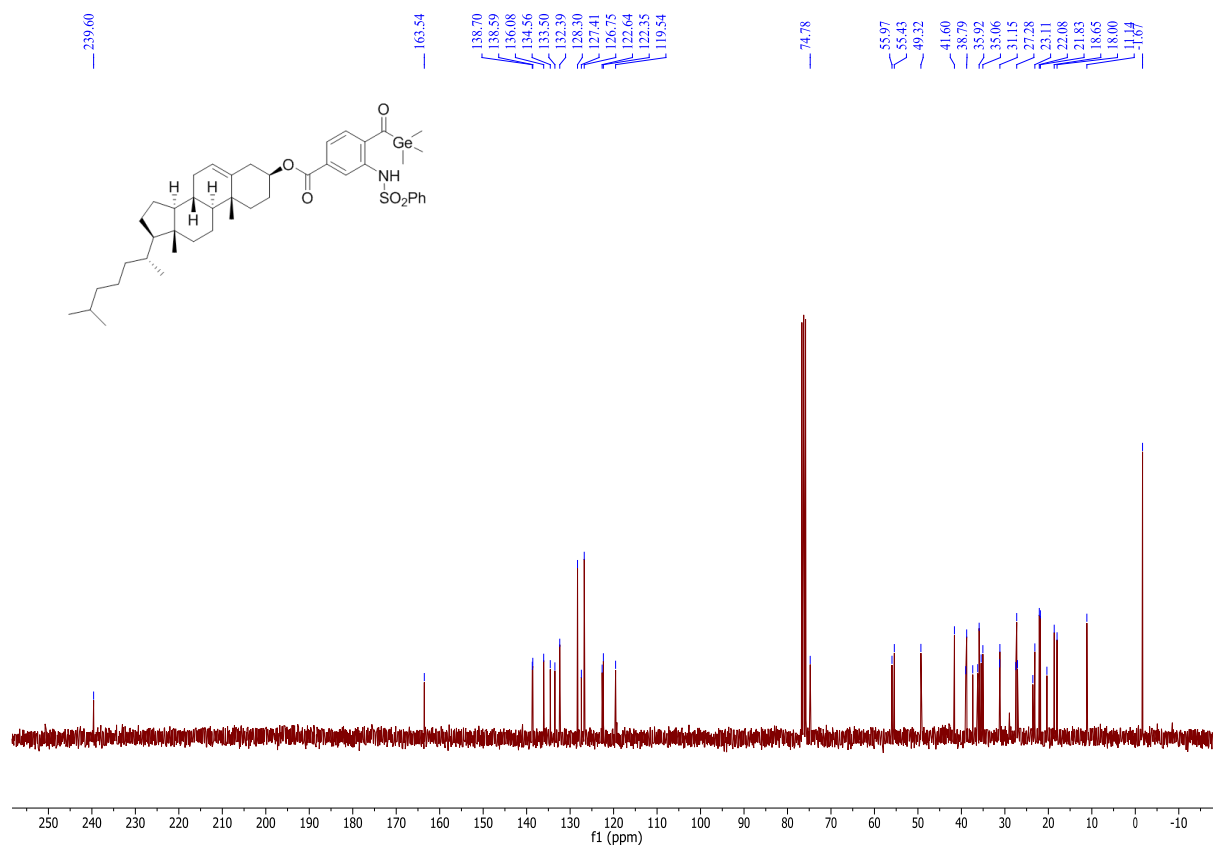


Figure S137. <sup>13</sup>C NMR spectrum of 14f, related to Scheme 5.

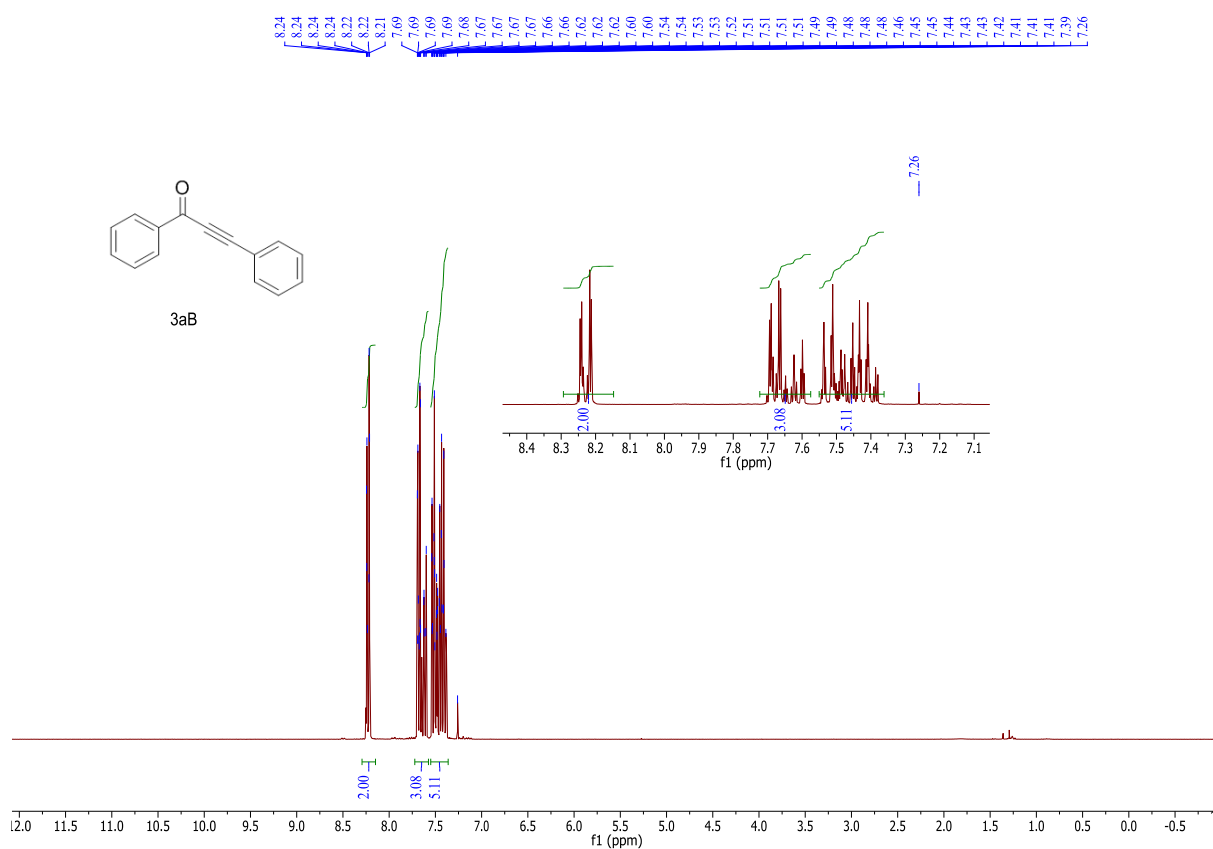
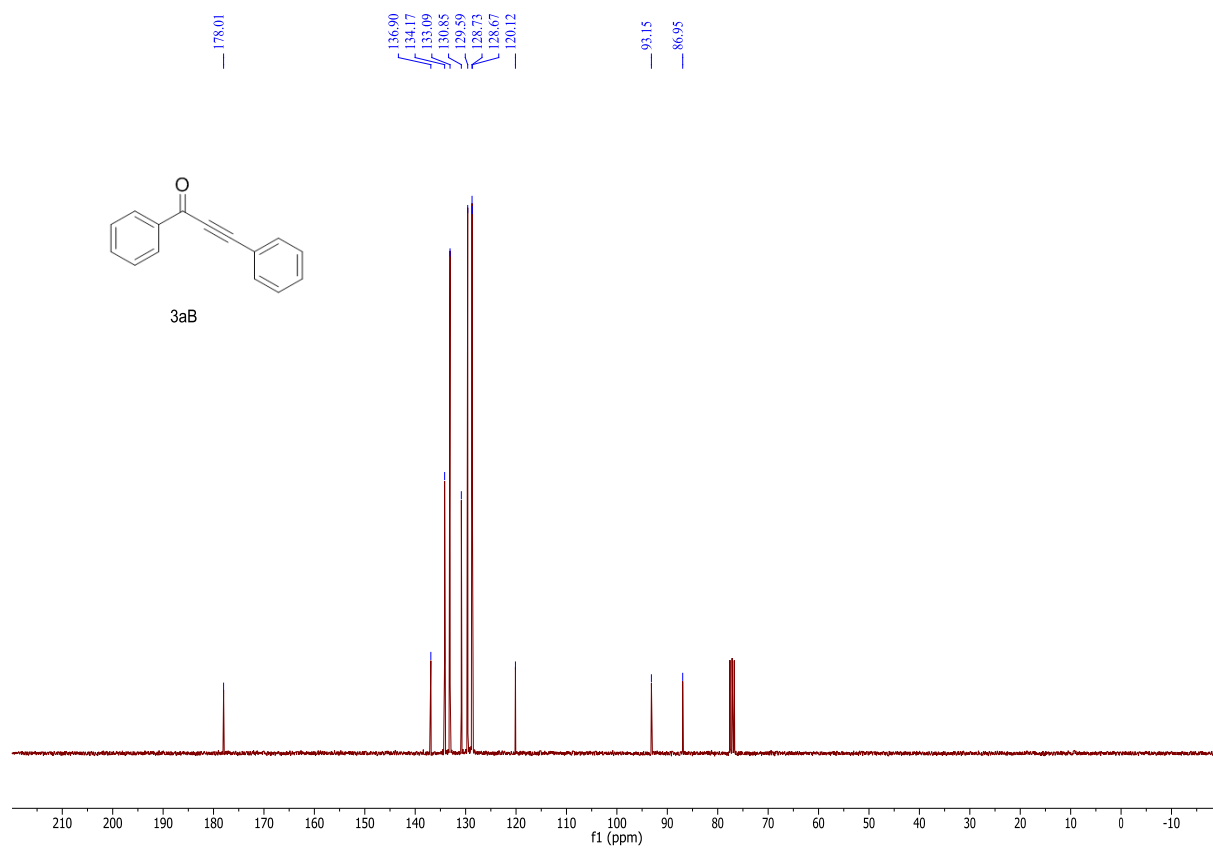
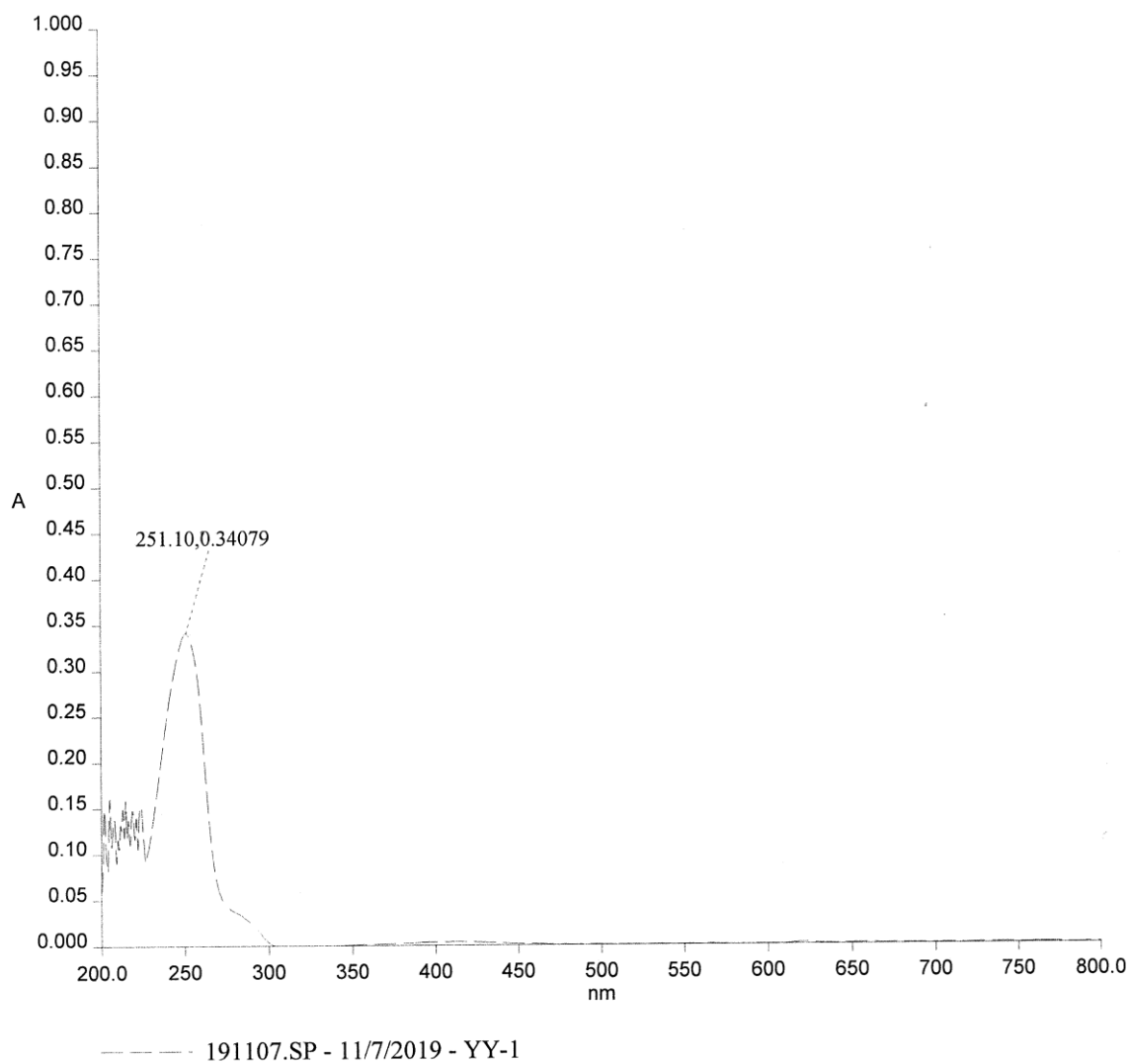
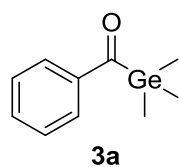


Figure S138. <sup>1</sup>H NMR spectrum of 3aB, related to Scheme 6.

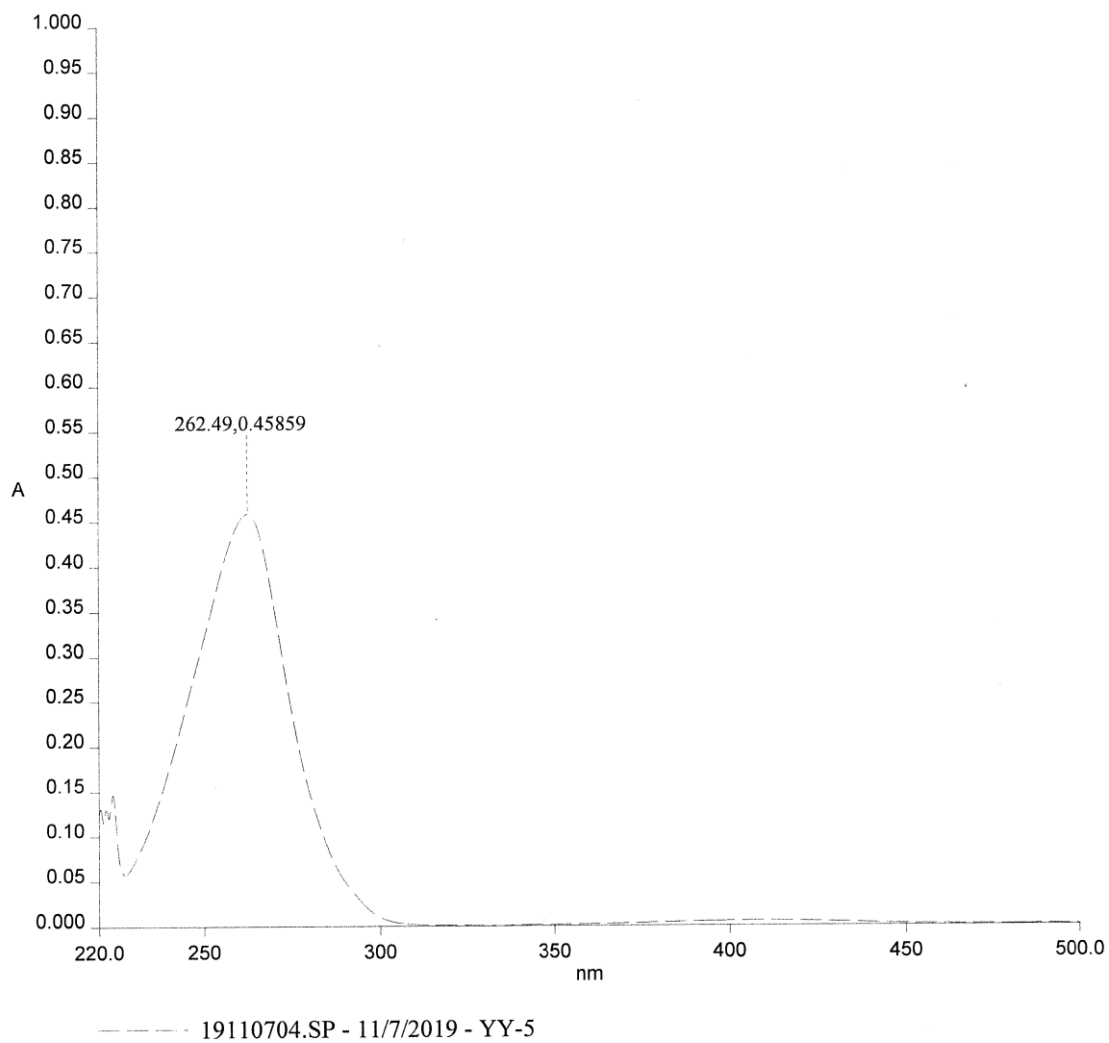
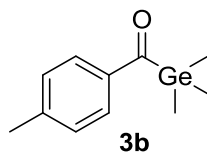




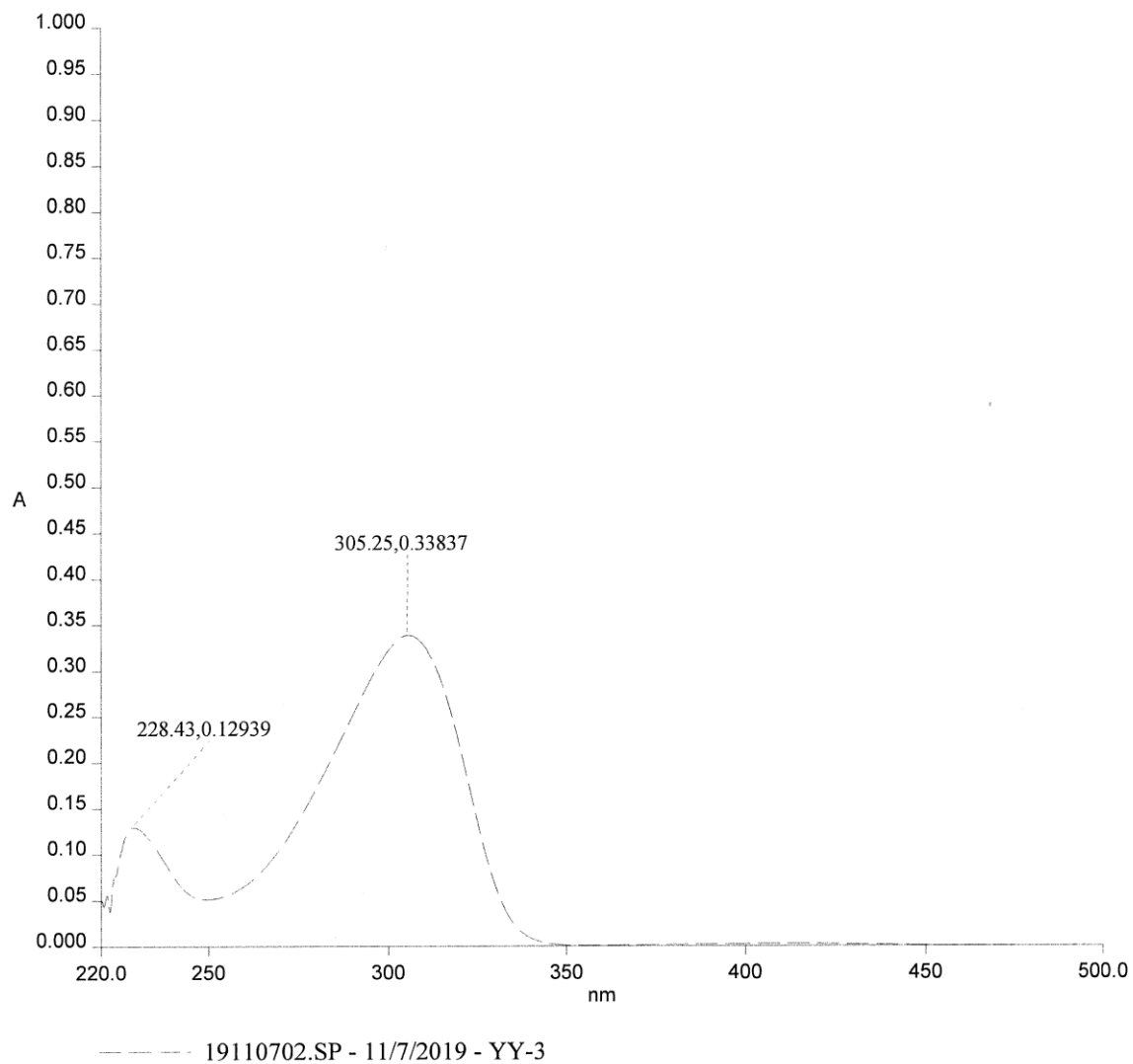
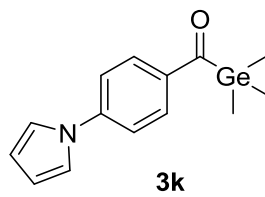
**Figure S139.** <sup>13</sup>C NMR spectrum of 3aB, related to Scheme 6.



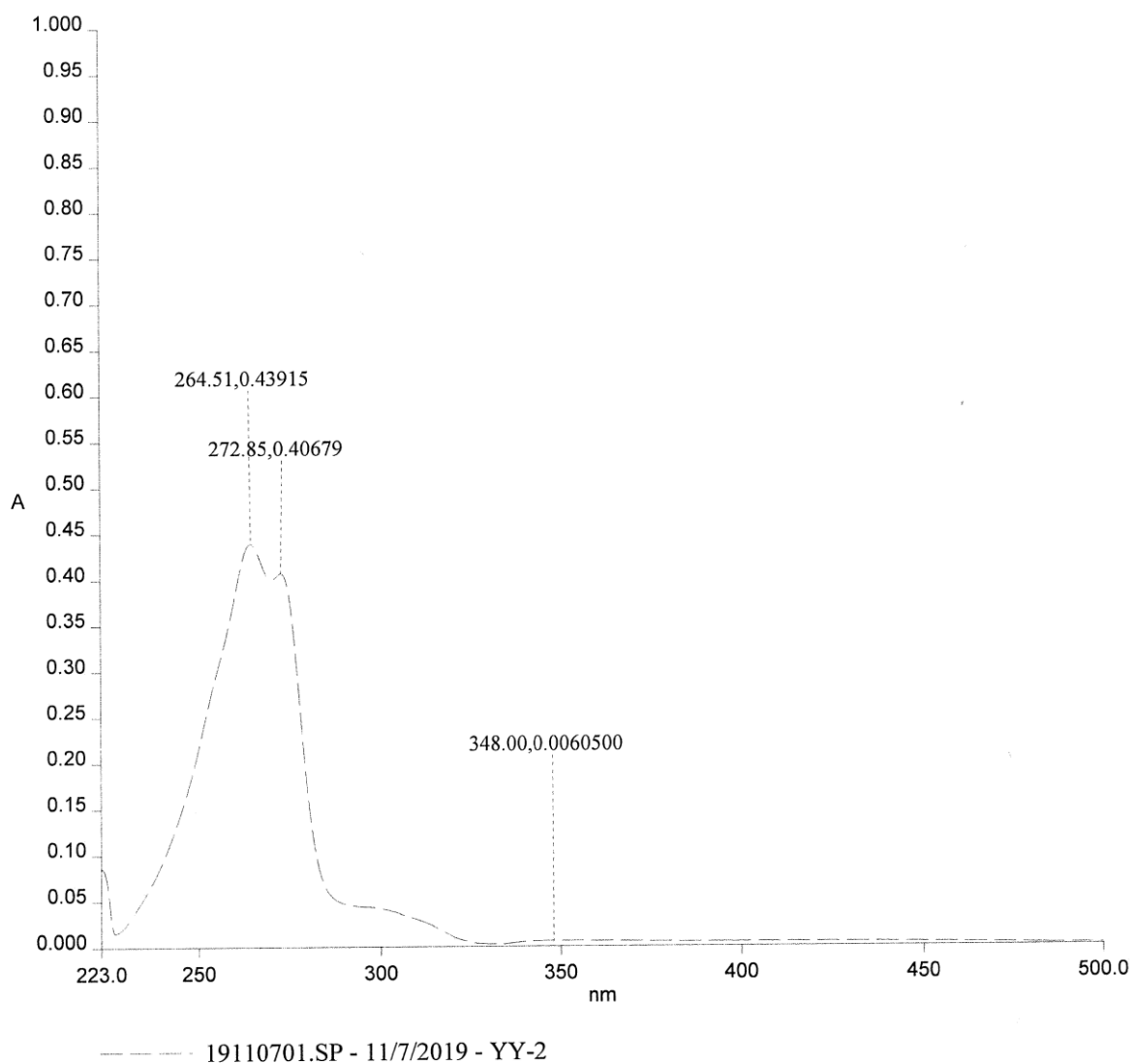
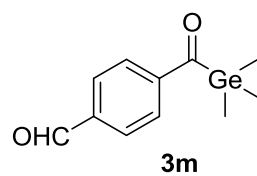
**Figure S140.** UV/Vis spectroscopy of 3a, related to Scheme 2.



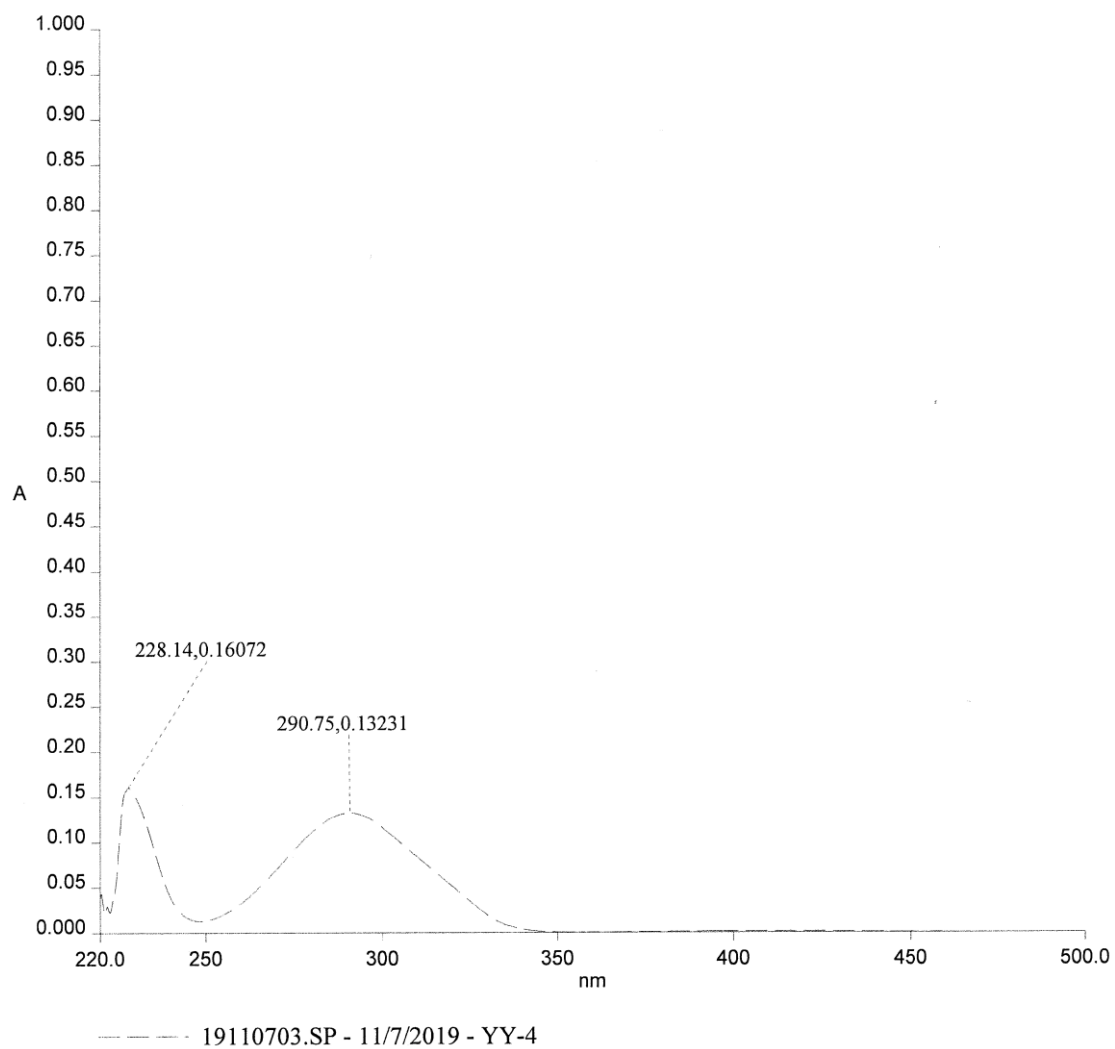
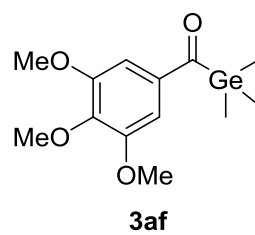
**Figure S141.** UV/Vis spectroscopy of 3b, related to Scheme 2.



**Figure S142.** UV/Vis spectroscopy of 3k, related to Scheme 2.



**Figure S143.** UV/Vis spectroscopy of 3m, related to Scheme 2.



**Figure S144.** UV/Vis spectroscopy of 3af, related to Scheme 2.