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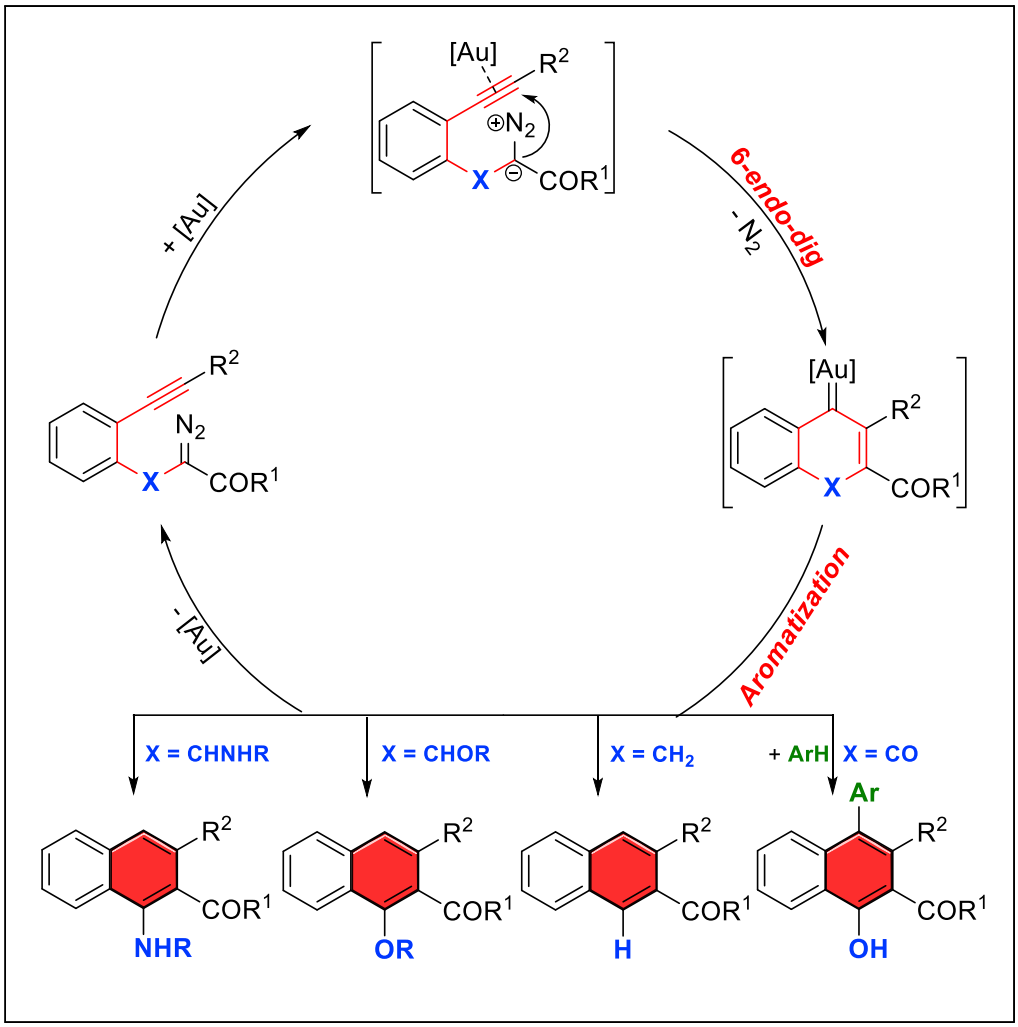

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HIGHLIGHTS

A general method for the construction of multi-functionalized naphthalenes

First *6-endo-dig* diazo-yne carbocyclization leading to the vinyl gold carbene

Expeditious access to naphthalenes with broad functional group compatibility

Applications for the synthesis of chiral 1,2′-binaphthalene ligands and CPHs

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Gold(I)-Catalyzed Aromatization: Expeditious Synthesis of Polyfunctionalized Naphthalenes

Cheng Zhang,[1,2] Kemiao Hong,[1,2] Shanliang Dong,[2] Chao Pei,[2] Xiaolu Zhang,[2] Ciwang He,[2] Wenhao Hu,[1,*] and Xinfang Xu[1,2,3,*]

SUMMARY

A gold-catalyzed 6-*endo-dig* carbocyclization of alkyne with the pendent diazo group is reported. It provides an expeditious approach for the synthesis of multi-functionalized naphthalene derivatives under mild conditions. Mechanistic studies suggest that a vinyl gold carbene is generated as the key intermediate in this cascade transformation that smoothly delivers naphthalene products through an unprecedented stepwise aromatization or an intermolecular aromatic substitution process. The unique endocyclic vinyl species is inaccessible with other precursors; thus, novel carbene cascade transformations could be envisioned with the current catalytic model. Functional groups, such as alkenyl, hydroxyl, amino, and carboxyl groups, remain untouched under these conditions. In addition, the utility of these generated 2-carboxyl naphthalenes is illustrated by the synthesis of chiral 1,2′-binaphthalene ligands and π-conjugated polycyclic hydrocarbons (CPHs).

INTRODUCTION

Naphthalene derivatives are one of the most prevalent key motifs in π-conjugated polycyclic hydrocarbons (CPHs) (Frederickson et al., 2017), and polycyclic systems related to naphthalene derivatives have shown versatile applications in physical organic chemistry (Frederickson et al., 2017; Huang et al., 2016), organometallic chemistry (Edelmann, 2017), materials science (Cao et al., 2015), and bioactive molecules (Stockdale and Williams, 2015). During the past decades, a variety of approaches for aromatic ring modification either through metal- (Tanaka, 2013; Phipps and Gaunt, 2009; Meng et al., 2017; Zhu et al., 2016; Della Ca' et al., 2016) or organo-catalysis (Qi et al., 2018) have been reported. Nevertheless, most of these methods are less efficient for sterically hindered substrates including naphthalenes and usually require a pre-installation of leaving groups or directional groups (Figure 1A, path a). On the other hand, transition-metal-catalyzed aromatization reactions provide a convenient way in the practical construction of substituted naphthalenes, including but not limited to the [2+2+2]-cycloaddition of benzyne intermediates with alkynes (path b) (Pérez et al., 2013), oxidative dehydrogenation of cyclic hydrocarbons (path c) (Iosub and Stahl, 2016; Wu and Jiang, 2012), ring-closing metathesis followed by aromatization (path d) (Donohoe et al., 2006; van Otterlo and de Koning, 2009), the electrocyclization reactions, and others (Tanaka, 2013). Recently, alkyne benzannulation has emerged as a straightforward approach for accessing densely functionalized naphthalene compounds, complementing the above-described methods (Hein et al., 2017). Despite these advances, polyfunctionalized naphthalenes of interest are still challenging to prepare and many of the substitution patterns are beyond the scope of the current synthetic methods; these include the methods for accessing naphthalenes with versatile functional groups such as the hydroxyl, amino, and carboxyl groups (Izawa et al., 2011; Hein et al., 2017; Raviola et al., 2016). These groups not only act as the key pharmacophores in pharmaceuticals (Stockdale and Williams, 2015) but also can be used for further transformations in preparing other complex molecules. Therefore, the development of novel and practical synthetic methods to construct naphthalenes with broad functional group compatibility still remains highly desirable and appealing.

In the last two decades, gold-catalyzed alkyne carbocyclizations have experienced explosive development in the construction of cyclic molecules with structural complexity (Pflästerer and Hashmi, 2016; Chen et al., 2018; Gorin and Toste, 2007; Dorel and Echavarren, 2015; Zheng et al., 2016). After the first reports of Hashmi on benzene ring formation by gold catalysis (Hashmi et al., 2000, 2001, 2002; Zeiler et al., 2015), another early example of 5-*exo-dig* diazo-yne carbocyclization was disclosed by Toste for the synthesis of indanone derivatives (Witham et al., 2007; Padwa et al., 1993; Mueller et al., 1993). Recently, Hashmi (Nösel et al., 2013) and Tang (Liu et al., 2013) have reported on the catalytic oxidative diyne 5-*exo-dig* cyclization in the presence of gold and rhodium catalysts, respectively. Although the catalytic 6-*endo-dig* carbocyclization of alkynes has also been studied (Yuan et al., 2016), no example of analogous diazo-yne cyclization has been reported for the construction of 6-membered carbocyclic rings.

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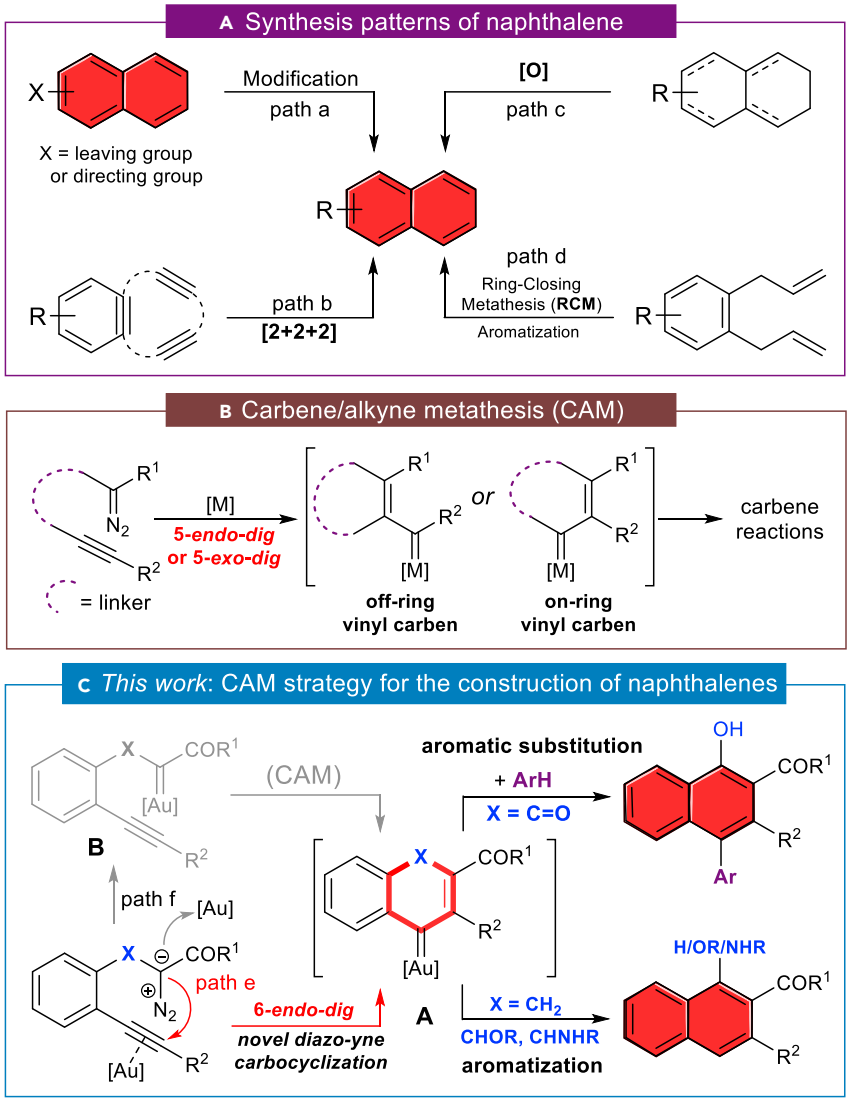


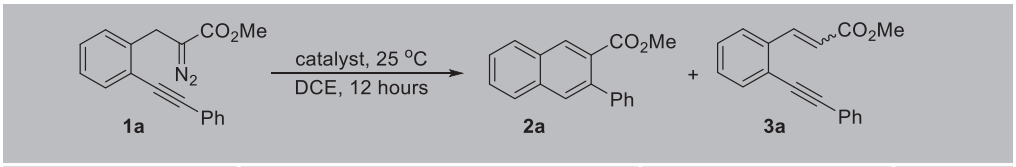
Figure 1. Strategy for Constructing Aromatic Rings

(A) General synthesis patterns of naphthalene.

(B) Carbene/alkyne metathesis (CAM).

(C) This work: CAM strategy for the construction of naphthalenes.

Inspired by these advances, and as the continuation of our interest in the carbene/alkyne metathesis (CAM) transformations (Figure 1B) (Pei et al., 2018; Le and May, 2015; González-Rodríguez et al., 2015; Torres et al., 2015; Zheng et al., 2015; Dong et al., 2018; Hashmi et al., 2008), we are intrigued by the possibility that nucleophilic addition of the diazo compound onto the gold-activated alkyne through an unprecedented *6-endo-dig* diazo-yne carbocyclization followed by the expulsion of dinitrogen can be used to generate the endocyclic vinyl gold carbene species A (Figure 1C, path e) (Hashmi et al., 2000; Lu et al., 2010). With this concept, the side reactions in general carbene/alkyne metathesis through carbene species B (path f), and in particular the β-*H* shift process of α-alkyl carbene intermediate B (X = CHR) (Lonca et al., 2017; Goto et al., 2011; Zhang et al., 2019), can be avoided, which would substantially expand the chemistry of the CAM process (Lauterbach et al., 2013, 2015; Rode et al., 2018). Herein, we report our recent results in this direction: the first example of gold-catalyzed *6-endo-dig* diazo-yne carbocyclization and the generated key intermediate **A** that is a versatile synthon for the construction of naphthalene frameworks via a stepwise aromatization or an intermolecular electrophilic aromatic substitution (Figure 1C). As a result of this new synthetic approach, naphthalene structures with a variety of



Entry	Catalyst	2a (%)[a]	3a (%)[a]
1	JohnPhosAu(CH_3CN)SbF_6	94 (91)[b]	<5
2[c]	JohnPhosAuCl	–	<10
3[c]	$Rh_2(OAc)_4$	<5	<5(70)[d]
4	$Cu(CH_3CN)_4BF_4$	<5	91
5	$Pd_2(dba)_3$	22	47
6	$AgSbF_6$	<5	96(90)[b]
7	JohnPhosAuCl + $AgSbF_6$	92	<5
8	JohnPhosAuCl + $AgNTf_2$	90	<5
9	PPh_3AuNTf_2	<5	87
10	PPh_3AuSbF_6	<5	86

Table 1. Reaction Optimization

Optimization conditions: **1a** (58 mg, 0.2 mmol) and catalyst (0.01 mmol) in DCE (1,2-dichloroethane, 2.0 mL) at 25°C for 12.0 h, unless otherwise stated.

[a]Yield determined by proton NMR using 1,3,5-trimethoxybenzene as the internal standard.

[b]Isolated yields.

[c]Most of **1a** (>90%) was recovered.

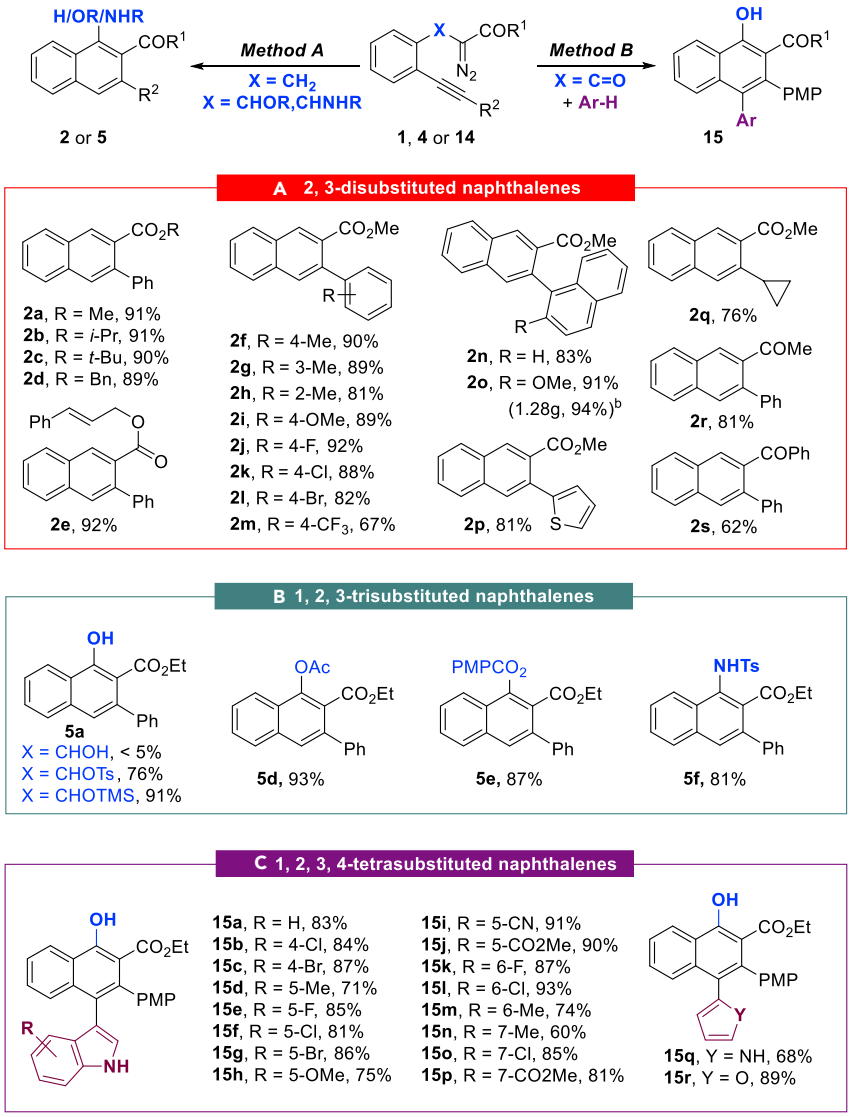
[d]The results in parentheses is the reaction that was conducted at 60°C instead of 25°C.

functional groups were uncovered, such as alkenyl, hydroxyl, amino, and carboxyl groups, remaining untouched under these conditions.

RESULTS AND DISCUSSION

To test the feasibility of our proposed approach for the construction of naphthalene frameworks, *o*-alkynylphenyl diazoacetate **1a** was used as a model substrate in the presence of various metal catalysts in 1,2-dichloroethane (DCE) at 25°C (Table 1). With its sterically demanding ligand, JohnPhos(CH_3CN)$AuSbF_6$ exhibited superior reactivity for the selective formation of naphthalene **2a** in 91% isolated yield (entry 1). The corresponding chloride salt, JohnPhosAuCl, showed very low reactivity, and most of **1a** was recovered (entry 2). All of the other metal catalysts including Rh-, Cu-, Pd-, and Ag-catalysts predominantly delivered the β-*H* shift product **3a** (entries 3–6). Further investigation of the ligands and counterions of the gold catalysts indicated that the steric effect of the ligand plays a crucial role in the selectivity control (entry 8 versus 9), and the gold catalyst bearing a triphenylphosphine ligand catalyzed the reaction to predominantly form the β-*H* shift product alkene **3a** (entries 9 and 10). For the extensive examination of the ligand effect, see Table S2. On the other hand, the counter anion of these catalysts shows no obvious effects on the reaction outcomes (entries 7–10) (Schießl et al., 2018a, 2018b). Notably, the observed 6-*endo*-*dig* diazo-yne cyclization process shows a unique effect for the gold catalysis that preferentially activates the C-C triple bond in the presence of a diazo group (Zheng et al., 2015). Reactions with other metal catalysts formed the β-*H* shift product **3a** as the major/only product, indicating that the reaction mechanism of this gold-catalyzed carbocyclization is distinctly different and that initial catalytic decomposition of the diazo group to form the corresponding carbenoid intermediate does not occur in this case.

Under the optimal reaction conditions, we investigated the scope of this unprecedented 6-*endo*-*dig* diazo-yne cyclization for the synthesis of 2,3-disubstituted naphthalenes (Scheme 1A). The impact of the ester part was examined first. It was found that the reaction could be applied to alkyl, benzyl, and 3-phenylallyl esters without a noticeable yield deterioration (**2a**-**2e**, 89%–92% yields). Then, the nature of the alkyne terminus was investigated. The electronic effects and the position of the substituent groups on the phenyl



Scheme 1. Scope for the Synthesis of Naphthalenes

Reaction conditions: **Method A**: **1** or **4** (0.2 mmol), JohnPhosAuSbF$_6$ (0.01 mmol) in DCE (1,2-dichloroethane, 2.0 mL) at 25°C,12 h, and yields are given in isolated yields. **Method B**: **14** (0.2 mmol), Ar-H (0.3 mmol), JohnPhosAuSbF$_6$ (0.01 mmol) in DCE (1,2-dichloroethane, 2.0 mL) at 60°C, 3 h, and yields are given in isolated yields.

The reaction was conducted on a 4.0-mmol scale.

(A) Synthesis of 2,3-disubstituted naphthalenes.

(B) Synthesis of 1,2,3-trisubstituted naphthalenes.

(C) Synthesis of 1,2,3,4-tetrasubstituted naphthalenes.

group of the substrates had little influence, and the corresponding products **2f**–**2m** were produced in high to excellent yields (67%–92%). Moreover, the 1-naphthyl-, 2-thienyl-, and alkyl-substituted substrates underwent the reaction smoothly, leading to naphthalene products **2n**–**2q** in >76% yields. Subsequently, diazoketones were used instead of diazoacetates, and it was found that they were also tolerated under these conditions. The corresponding products **2r** and **2s** were isolated in 81% and 62% yields, respectively. In addition, the reaction performed well on a gram scale with 94% isolated yield (note b, on 4.0 mmol).

Encouraged by these promising results, we envisioned that this catalytic system may also facilitate other challenging substrates for the synthesis of multi-functionalized naphthalene derivatives, with the results from these investigations summarized in Scheme 1B. Initially, α-hydroxyl substrate **4a** was used under the method A;

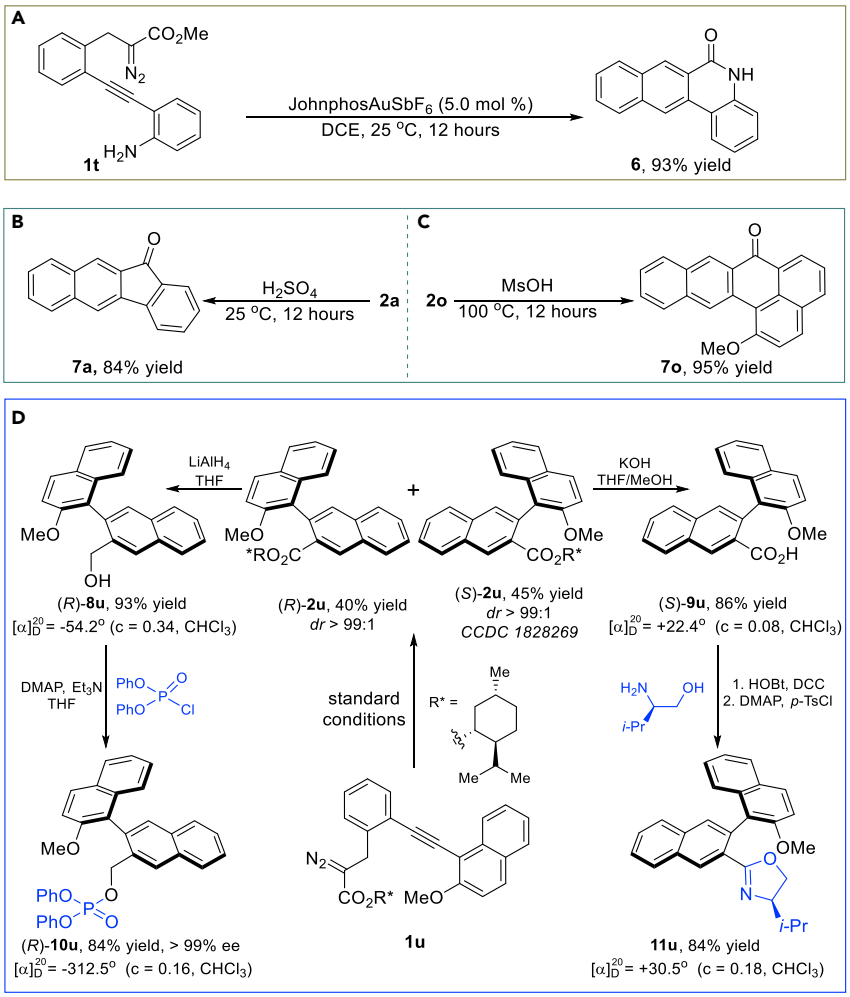


Figure 2. Synthesis of π-Conjugated Polycyclic Hydrocarbons (CPHs) and Chiral 1,2′-Dinaphthalene Ligands

(A) Synthesis of polycyclic lactam **6**.

(B) Synthesis of polycyclic ketone **7a**.

(C) Synthesis of polycyclic ketone **7o**.

(D) Synthesis of chiral 1,2′-dinaphthalene ligands.

however, no corresponding naphthalene product was observed. To our delight, when the substrates protected either with the Ts (**4b**) or TMS (**4c**) groups were used under the optimized reaction conditions, the reaction directly delivered the deprotected α-naphthol product **5a** in 76% and 91% yields, respectively. The ester variants, **4d** and **4e**, also provided the corresponding 1,2,3-trisubstituted naphthalenes in high yields (>87%). Notably, naphthylamine **5f** was isolated in 81% yield under the current conditions from **4f**.

To further demonstrate the generality of the present transformation, 1,3-dicarbonyl diazo compound **14** without α-methylene linkage was prepared and the interception reaction of the corresponding vinyl carbene intermediate **A** (Figure 1C, X = CO) was envisioned. To our delight, the C(sp^2)-H insertion products **15** were isolated in good to excellent yields (Scheme 1C, 53%–94% yields) when the reaction was performed at 60°C in the presence of nucleophiles such as indoles, furan, and pyrrole.

To demonstrate the synthetic utility of the present method, further transformations of carbocyclization products **2** were conducted for the synthesis of π-CPHs. For example, the tetracyclic fused lactam **6** was generated in one-pot from **1t** after the ester-amide exchange reaction with the internal amino group (Figure 2A). In addition, these 2-carbonyl naphthalenes were smoothly converted under acidic conditions to polycyclic hydrocarbons (Figures 2B and 2C), with **7a** and **7o** isolated in 84% and 95% yields, respectively.

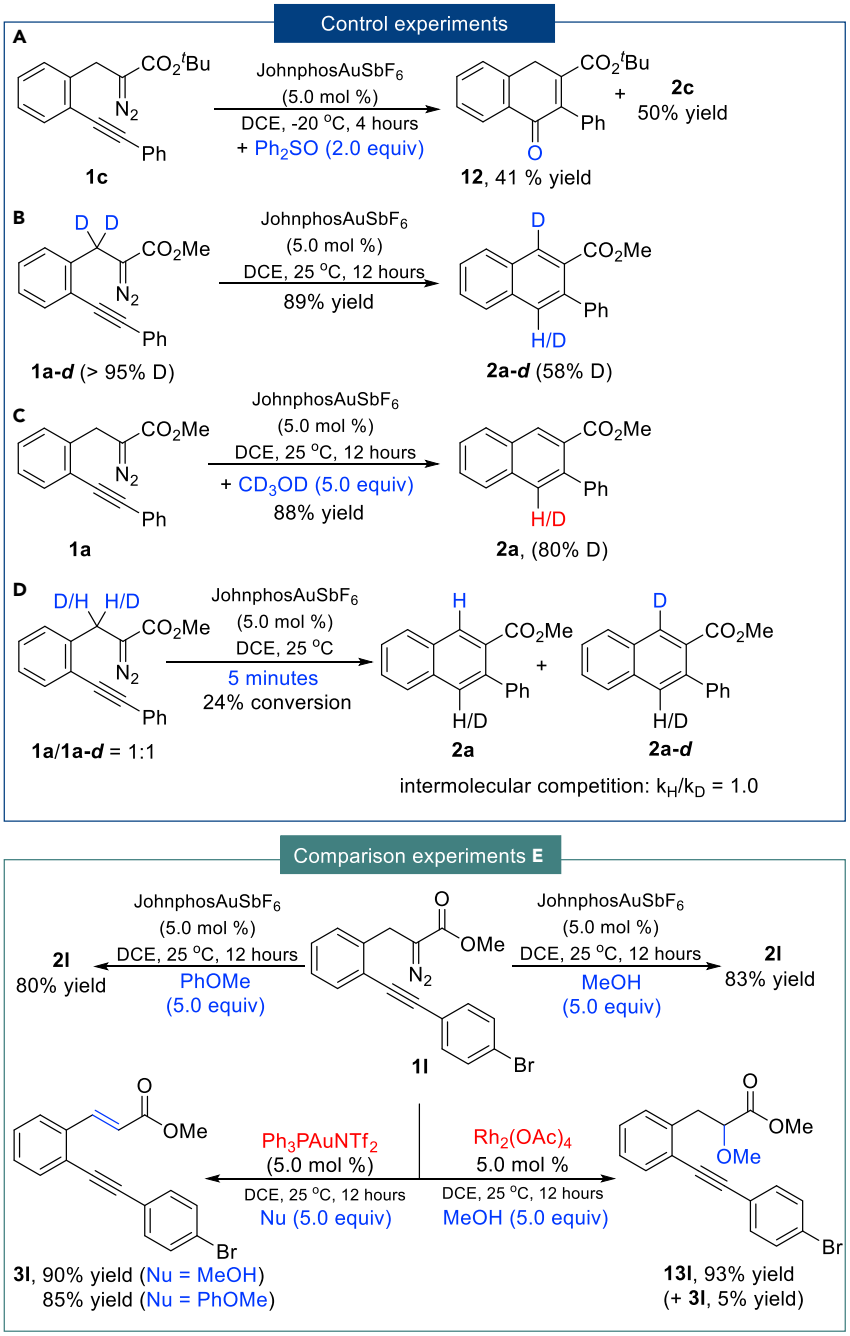


Figure 3. Control Experiments and Comparison Experiments

(A) Control reaction in the presence of dimethylsulfoxide.

(B) Control reaction with deuterated reagent.

(C) Control reaction in the presence of CD_3OD.

(D) Intermolecular kinetic isotope effect (KIE) experiment.

(E) The comparison experiments of carbene vs non carbene process.

Notably, chiral 1,2′-binaphthalene products could be prepared in high yield and 1:1 *dr* with (−)-L-menthol derived diazo compound **1u** (Figure 2D). The two diastereoisomers were separated by column chromatography with the (*S*)-isomer confirmed by single-crystal X-ray analysis. Moreover, the optically pure chiral phosphate derivative (*R*)-**10u** and chiral oxazole ligand **11u** with 1,2′-binaphthalene frameworks were

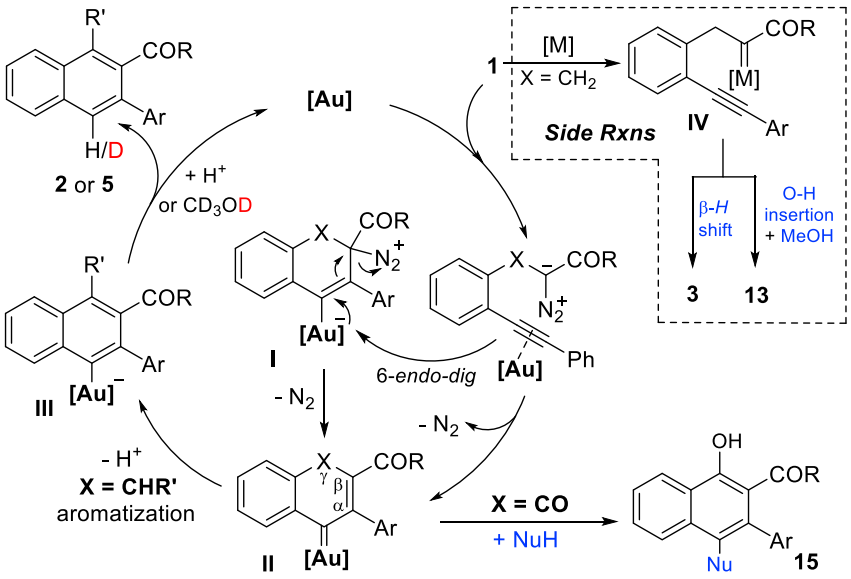


Figure 4. Proposed Reaction Mechanism

synthesized in high yields. Although ligands with the 1,1′-binaphthalene skeletons have been studied well and have broad applications, chiral ligands derived from 1,2′-binaphthalene motifs are rare, mainly because of the limited methods for access to this class of compounds (Lotter et al., 2016).

Control experiments were conducted to investigate the mechanism of this reaction. To verify the existence of the vinyl gold carbene intermediate, the interception reaction with **1c** in the presence of diphenyl sulfoxide was carried out at −20°C and the corresponding ketone product **12** was isolated in 41% yield combined with **2c** in 50% yield (Figure 3A) (Witham et al., 2007; Padwa et al., 1993; Mueller et al., 1993; Nösel et al., 2013; Liu et al., 2013). Evidence for the stepwise aromatization and protodeauration process was confirmed by an isotope-labeling experiment (Figure 3B, **2a-d** with 58% D). Moreover, the deuterated product **2a** was also obtained when the reaction was carried out in the presence of CD_3OD under standard conditions (Figure 3C, with 80% D). In addition, an intermolecular kinetic isotope effect (KIE) experiment (Figure 3D, k_H/k_D = 1.0) demonstrated that the deprotonation process is not the rate-limiting step. Based on these results and previously studied gold-catalyzed transformations (Witham et al., 2007; Padwa et al., 1993; Mueller et al., 1993; Nösel et al., 2013; Liu et al., 2013; Yuan et al., 2016; Pei et al., 2018; Le and May, 2015; González-Rodríguez et al., 2015; Torres et al., 2015; Zheng et al., 2015; Dong et al., 2018; Hashmi et al., 2008; Lu et al., 2010 Lonca et al., 2017; Goto et al., 2011; Qiu et al., 2016; Hashmi, 2010), a possible reaction mechanism is proposed in Figure 4. Initially, the gold catalyst coordinates the π-bond of alkyne to form a gold π-complex followed by a 6-*endo-dig* cyclization with the carbon on the diazo group to generate intermediate **I** that delivered the vinyl gold carbene **II** followed by a stepwise aromatization (deprotonation, X = CHR) and protodeauration process to form the naphthalene product **2** or **5** via **III**. Alternatively, direct formation of the key intermediate **III** from **I** through deprotonation with synchronous dinitrogen extrusion is also possible. Intermolecular electrophilic aromatic substitution interception of the vinyl gold carbene **II** would lead to the formation of C(sp^2)-H insertion product **15**. It should be noted that the reaction pathway through direct catalytic gold carbene formation followed by cyclopropenation and gold-catalyzed rearrangement of the cyclopropene to form the vinyl gold carbene intermediate **II** was ruled out in this reaction (Hashmi et al., 2000, 2001; 2002; Zeiler et al., 2015; Archambeau et al., 2015; Hoye et al., 1990; Bauer et al., 2008; Xu et al., 2013), which is consistent with the results of the comparison experiments (Figure 3E). For example, no corresponding direct carbene insertion product via **IV** was obtained when the reaction was carried out in the presence of MeOH or anisole, and the carbocyclization product **2l** was isolated as the only product in 83% and 80% yields, respectively. In addition, using the catalysts that prefer to activate the diazo group instead of the alkyne part, such as PPh_3AuNTf_2 and $Rh_2(OAc)_4$, the formation of carbene intermediate **IV** would occur initially (Figure 4, side reactions in dotted box), and the β-*H* shift product **3l** and O-H insertion product **13l** were generated predominantly via common carbene intermediate **IV** (Figure 3E).

Conclusion

In summary, we have developed a gold-catalyzed 6-*endo*-*dig* carbocyclization of alkyne with the pendent diazo groups that provides an expeditious approach for the synthesis of multi-functionalized naphthalene derivatives in high to excellent yields under mild conditions with broad substrate scope; functional groups, such as alkenyl, hydroxyl, amino, and carboxyl groups, are well tolerated under current conditions. The generated 2-carboxyl naphthalenes are useful for further diversification, as exemplified by the synthesis of chiral 1,2′-binaphthalene ligands and π-CPHs. Mechanistic studies indicate that the naphthyl-gold complex and the vinyl gold carbene species are the key intermediates in this cascade transformation, and side reactions in the usual carbene/alkyne metathesis process can be avoided under the current conditions, particularly for the β-*H* shift process. Synthetic applications based on the interception of these unique on-ring vinyl carbene intermediates, including the development of novel cascade reactions and synthesis of aromatic products with structural diversity, could be expected in due course.

Limitations of the Study

The asymmetric version for the formal C-H insertion reaction has not been realized, which is the main challenge in gold catalysis.

METHODS

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

DATA AND CODE AVAILABILITY

The crystallography data have been deposited at the Cambridge Crystallographic Data Center (CCDC) under accession number CCDC: 1828269 ((*S*)-**2u**) and can be obtained free of charge from www.ccdc.cam.ac.uk/getstructures.

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.10.042.

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AUTHOR CONTRIBUTIONS

X.X. supervised the project. C.Z., K.H., S.D., C.P., X.Z., and C.H. conducted the experimental work. C.Z., W.H., and X.X. co-wrote the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Supplemental Information

Gold(I)-Catalyzed Aromatization: Expeditious Synthesis of Polyfunctionalized Naphthalenes

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Supplemental Figures

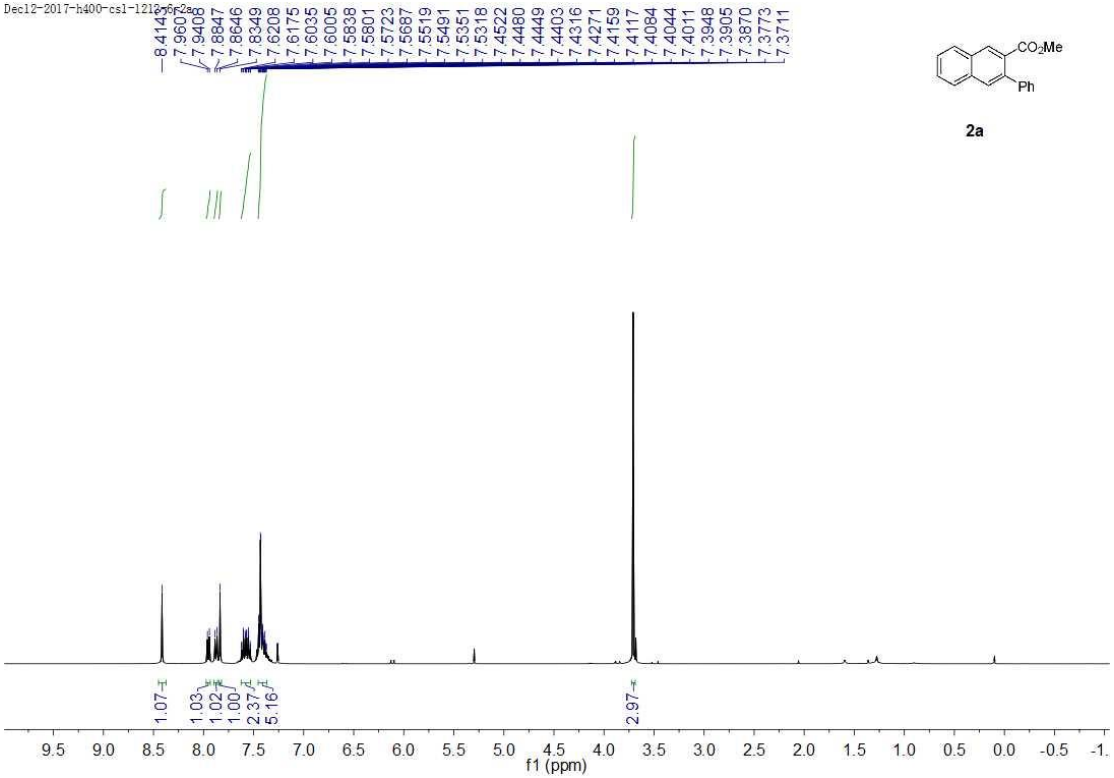


Figure S1. ^{1}H NMR spectra (400 MHz) of **2a** in $CDCl_3$, related to **Table 1** and **Scheme 1**.

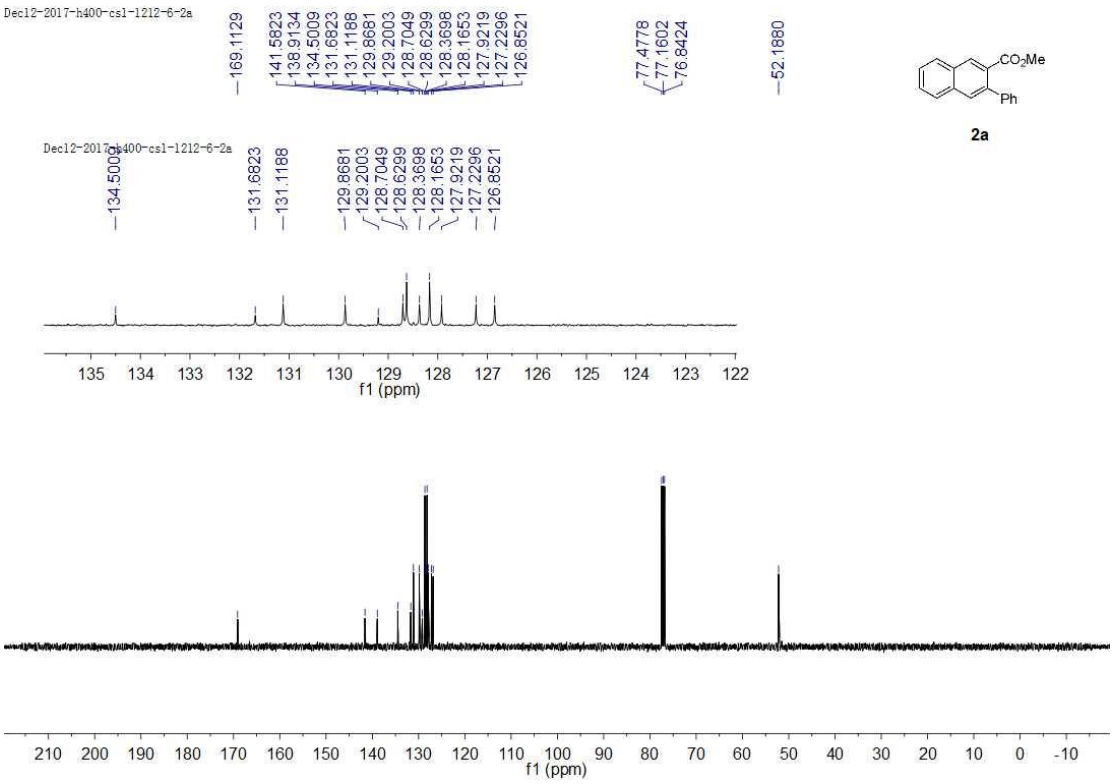


Figure S2. ^{13}C NMR spectra (400 MHz) of **2a** in $CDCl_3$, related to **Table 1** and **Scheme 1**.

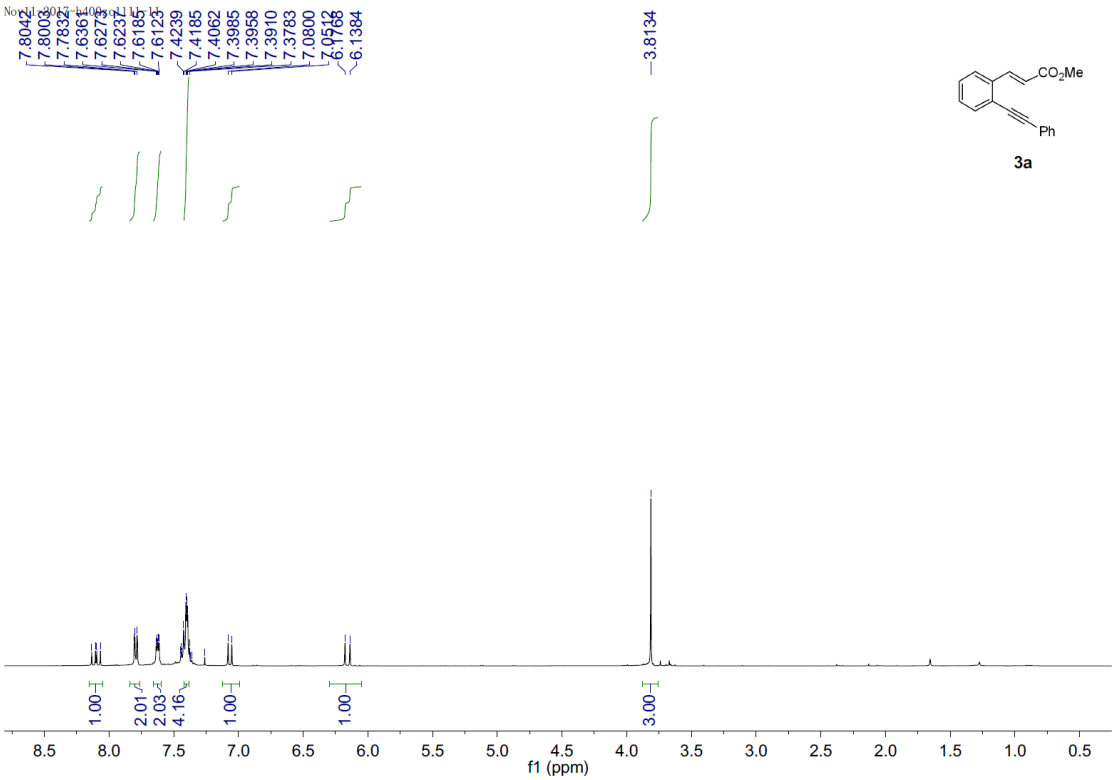


Figure S3. ^{1}H NMR spectra (400 MHz) of **3a** in $CDCl_3$, related to **Table 1**.

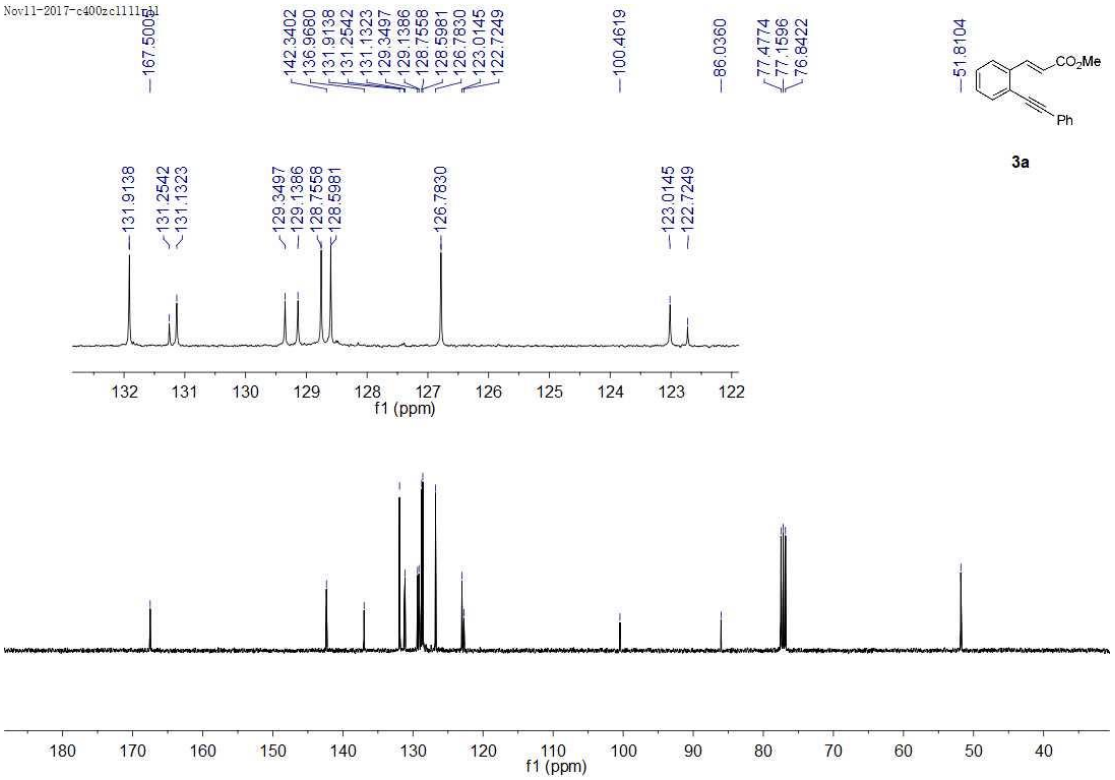


Figure S4. ^{13}C NMR spectra (400 MHz) of **3a** in $CDCl_3$, related to **Table 1**.

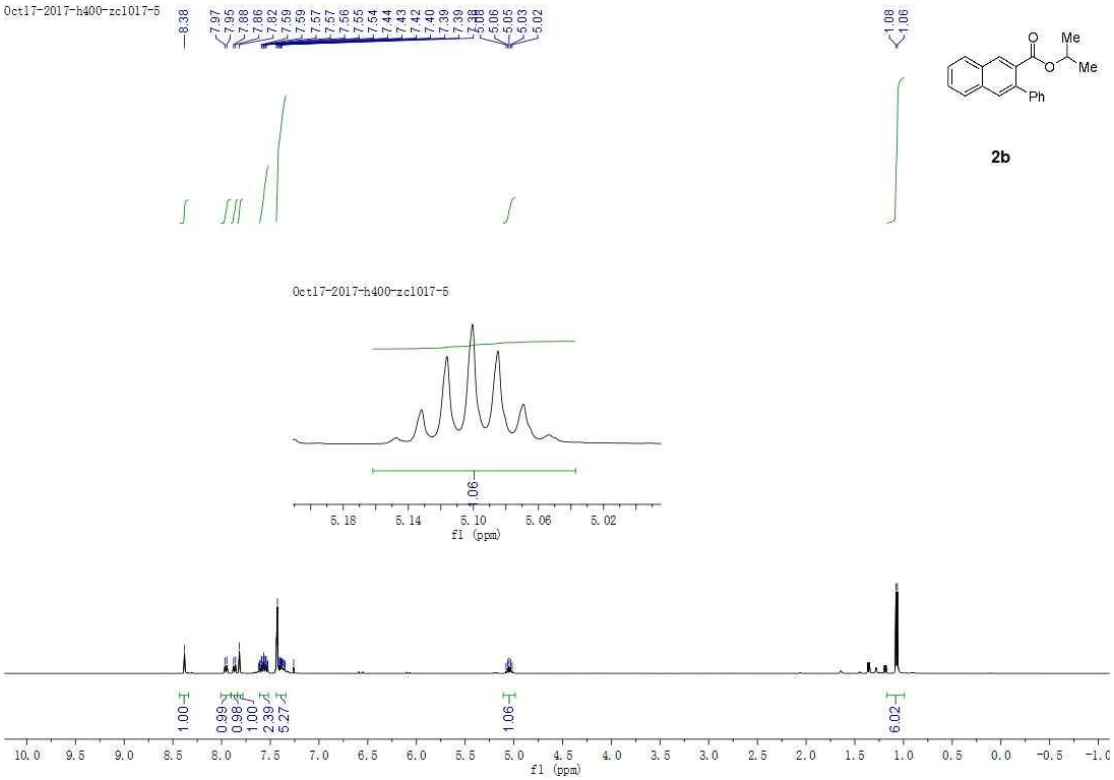


Figure S5. ^{1}H NMR spectra (400 MHz) of **2b** in $CDCl_3$, related to **Scheme 1**.

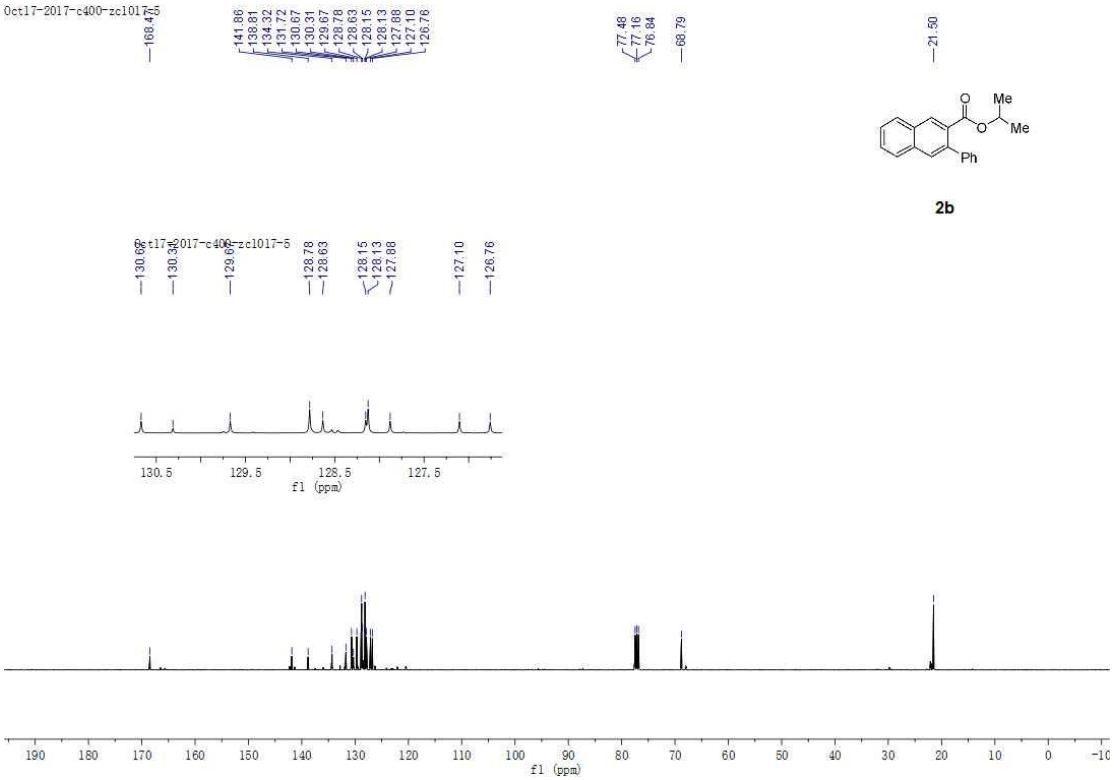


Figure S6. ^{13}C NMR spectra (400 MHz) of **2b** in $CDCl_3$, related to **Scheme 1**.

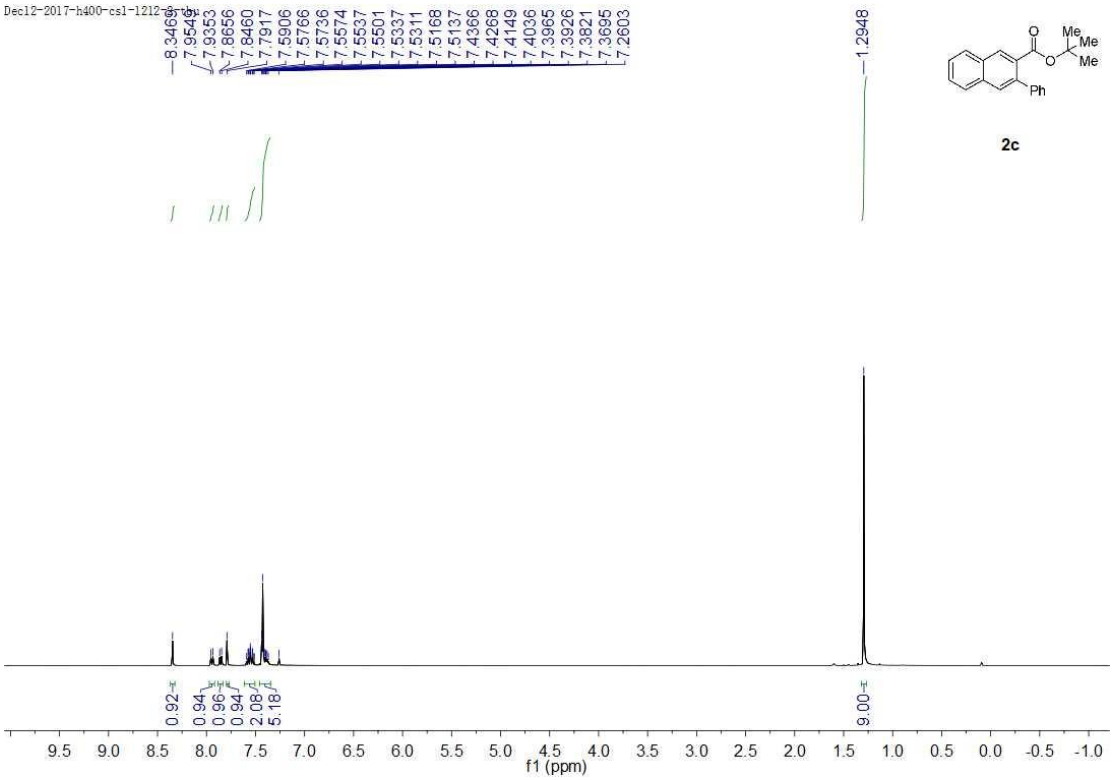


Figure S7. ^{1}H NMR spectra (400 MHz) of **2c** in $CDCl_3$, related to **Scheme 1**.

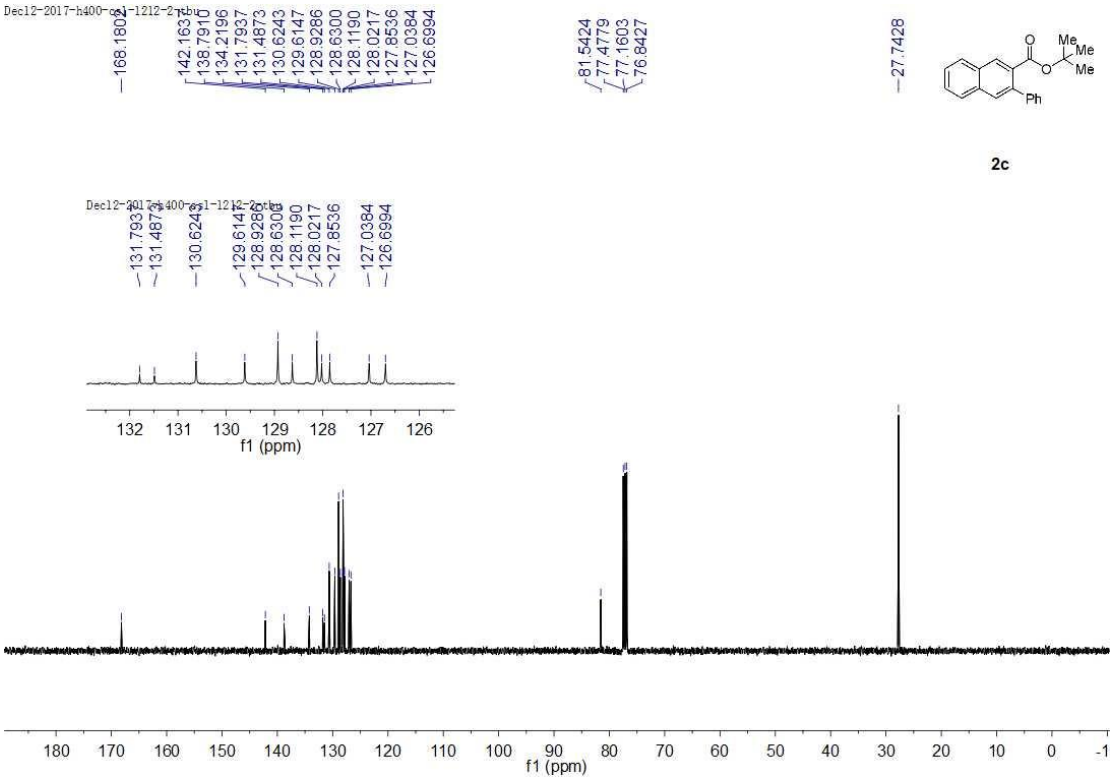


Figure S8. ^{13}C NMR spectra (400 MHz) of **2c** in $CDCl_3$, related to **Scheme 1**.

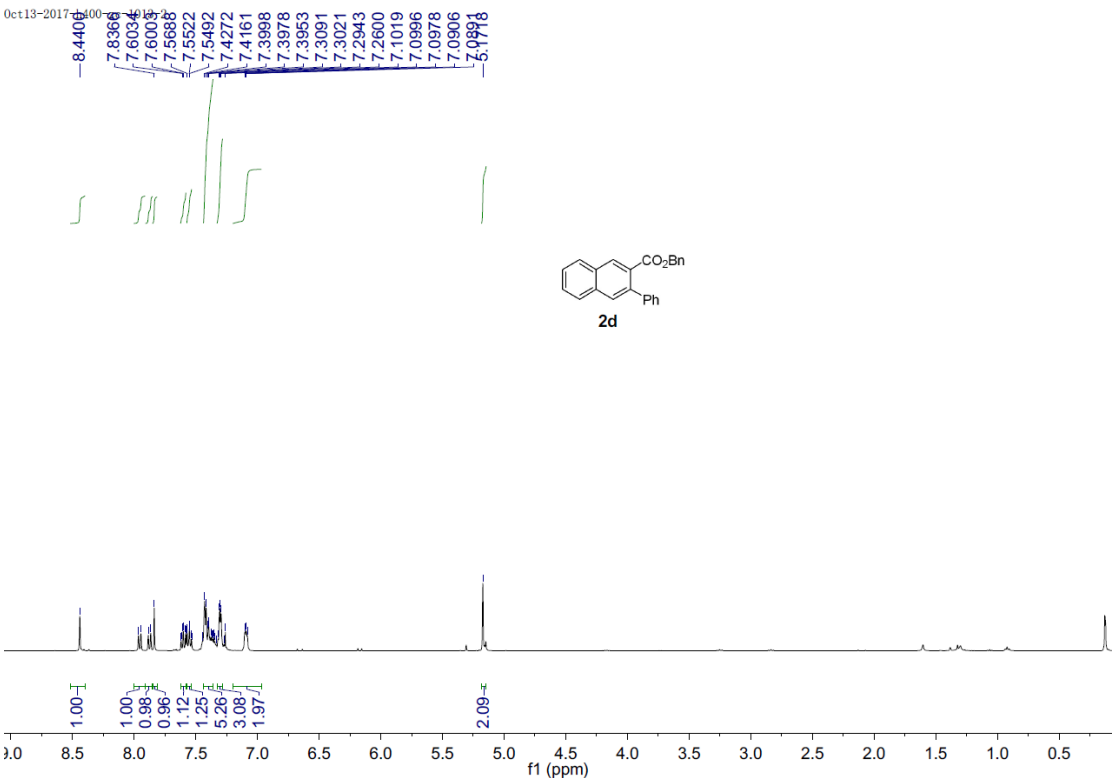


Figure S9. ^{1}H NMR spectra (400 MHz) of **2d** in $CDCl_3$, related to **Scheme 1**.

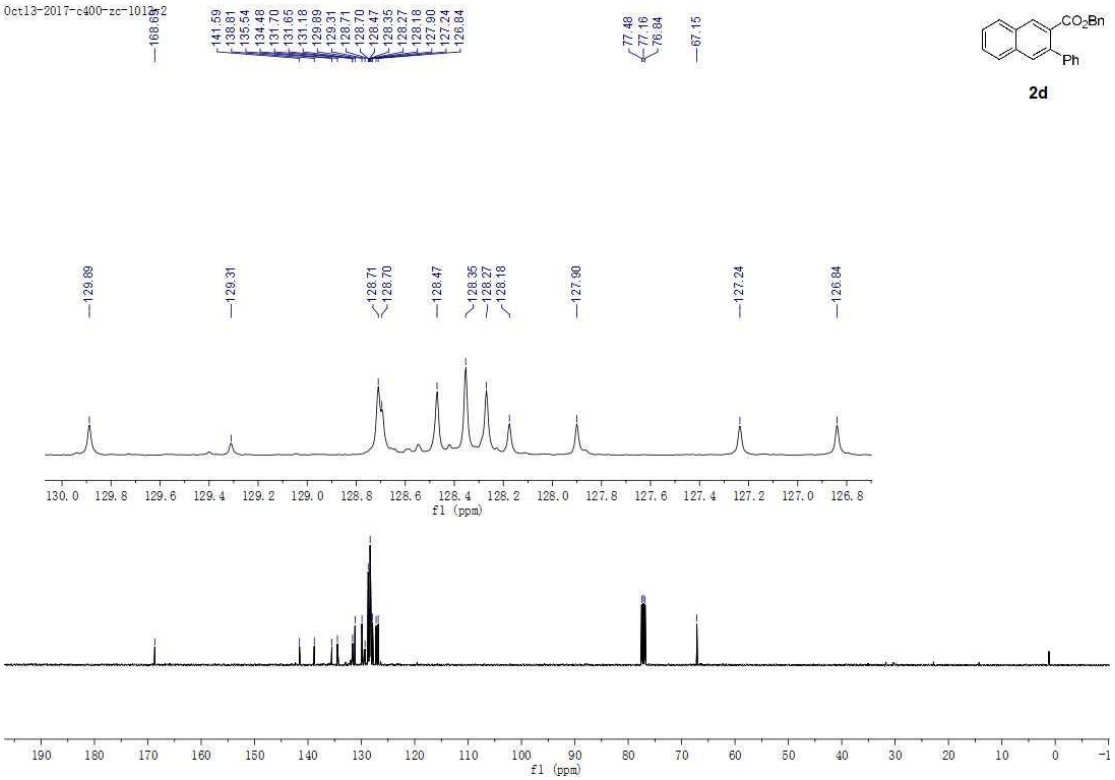


Figure S10. ^{13}C NMR spectra (400 MHz) of **2d** in $CDCl_3$, related to **Scheme 1**.

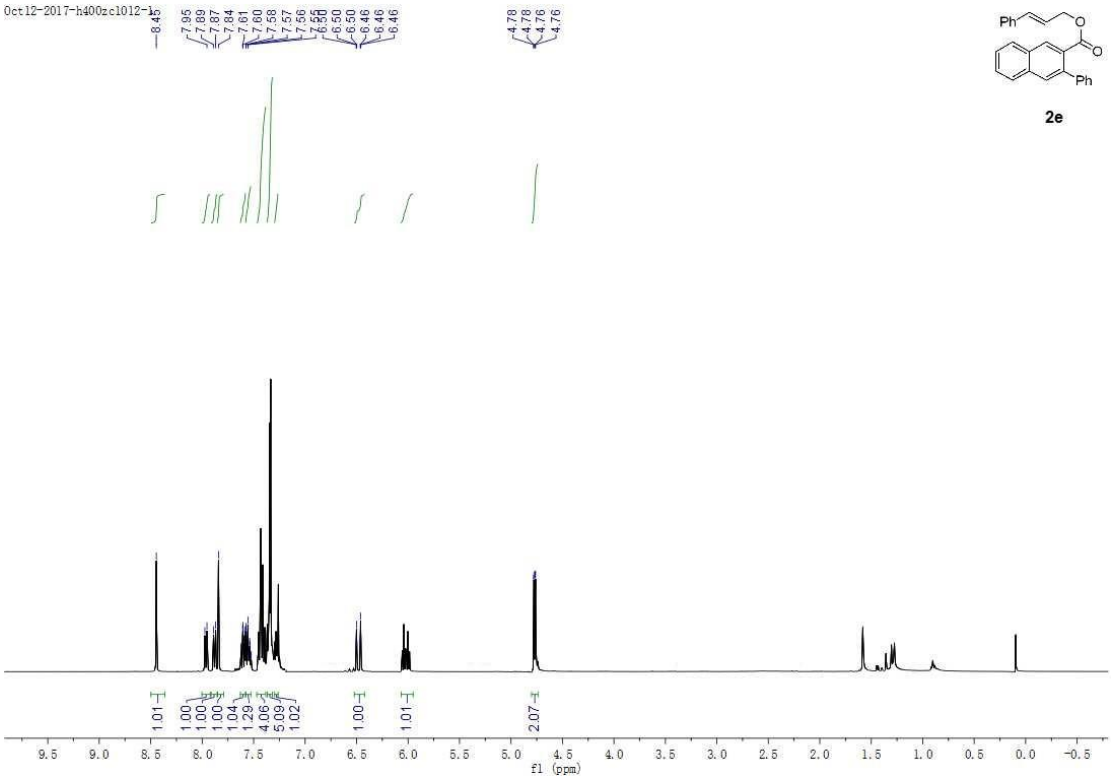


Figure S11. ^{1}H NMR spectra (400 MHz) of **2e** in $CDCl_3$, related to **Scheme 1**.

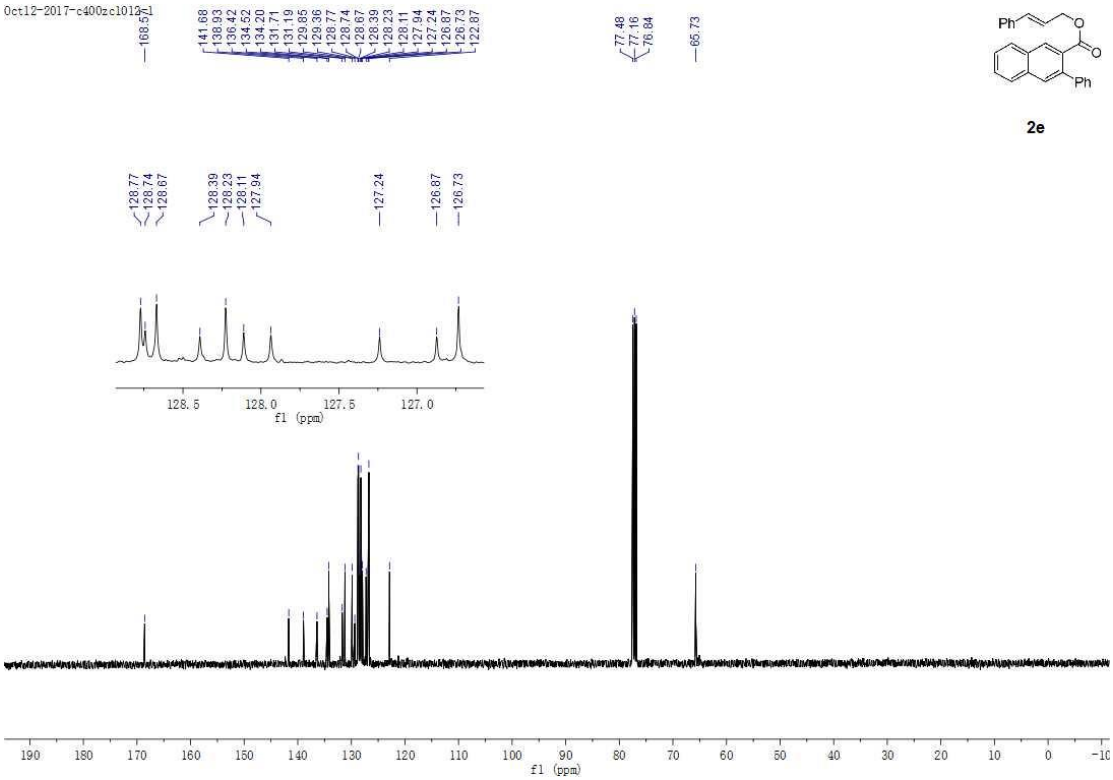


Figure S12. ^{13}C NMR spectra (400 MHz) of **2e** in $CDCl_3$, related to **Scheme 1**.

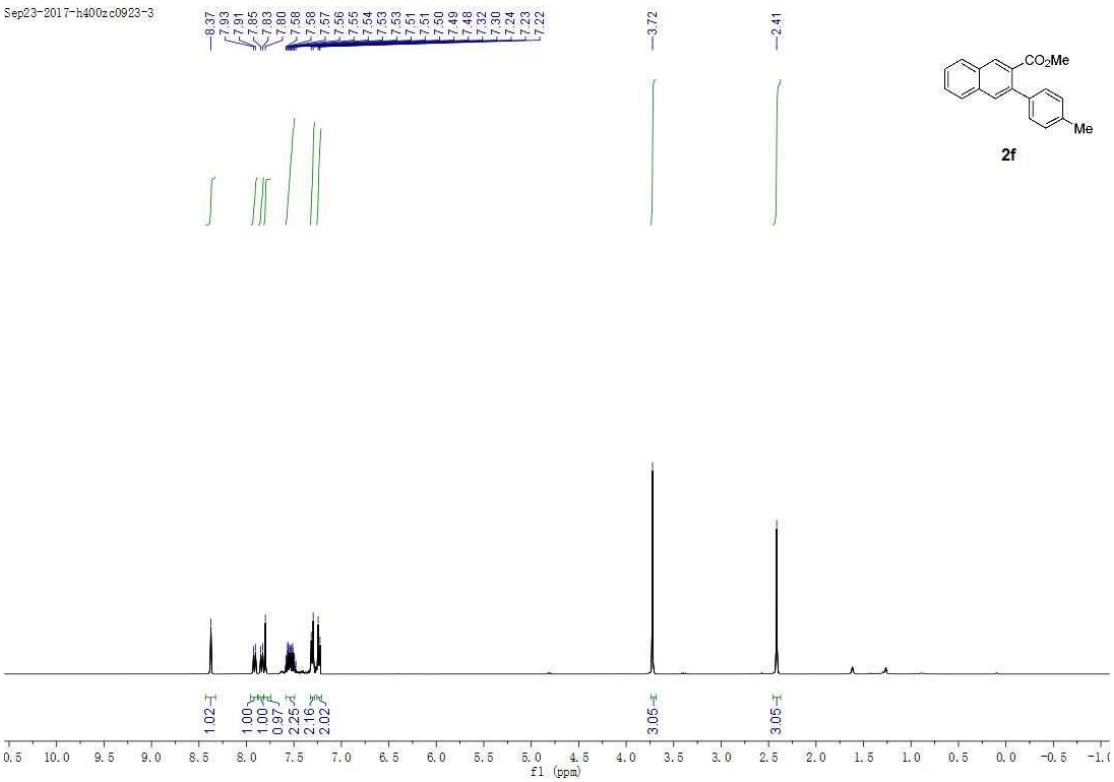


Figure S13. ^{1}H NMR spectra (400 MHz) of **2f** in $CDCl_3$, related to **Scheme 1**.

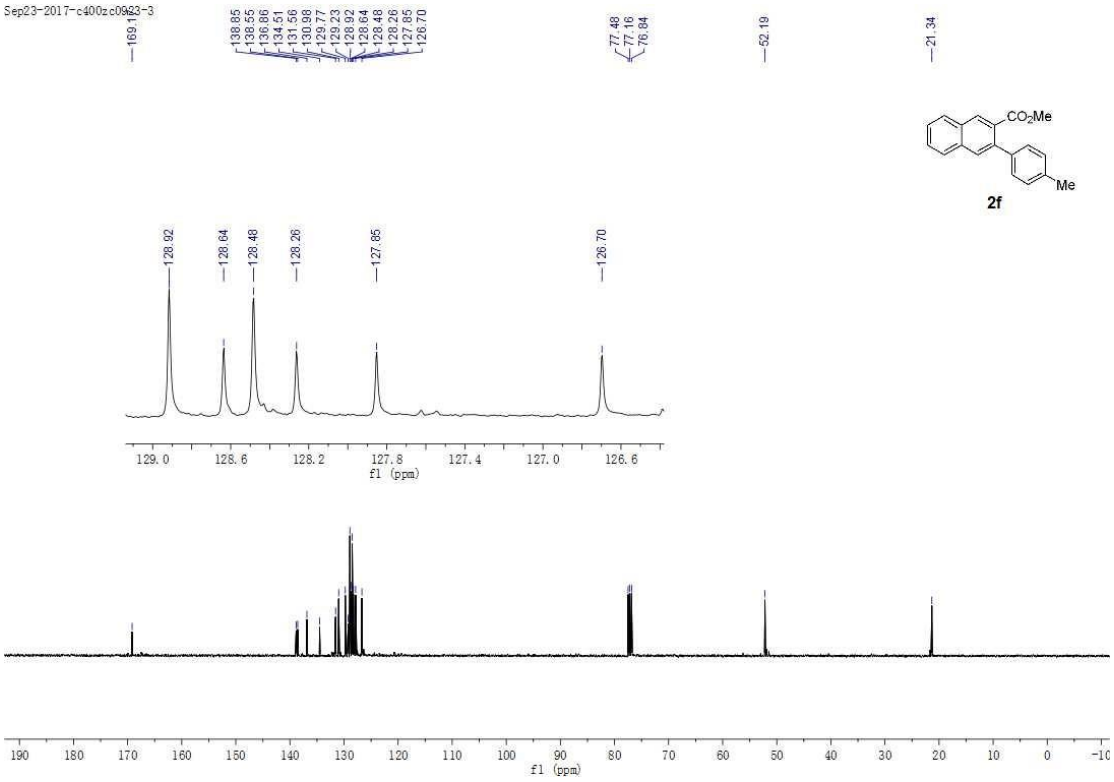


Figure S14. ^{13}C NMR spectra (400 MHz) of **2f** in $CDCl_3$, related to **Scheme 1**.

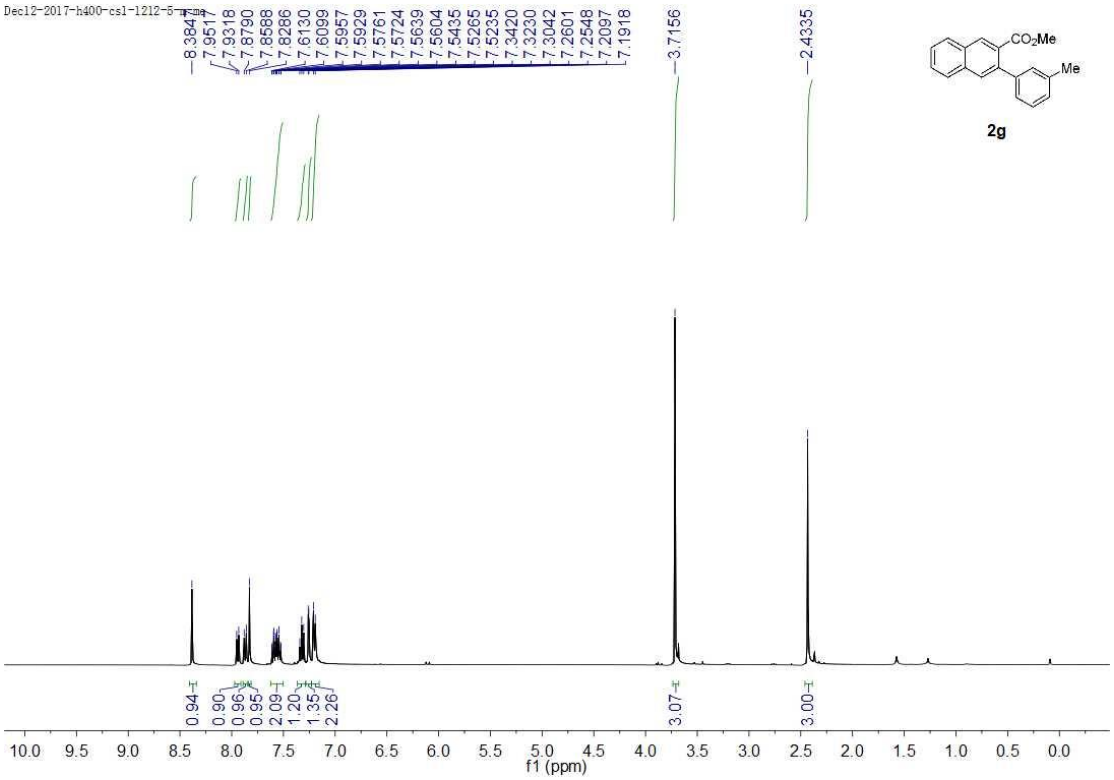


Figure S15. ^{1}H NMR spectra (400 MHz) of **2g** in $CDCl_3$, related to **Scheme 1**.

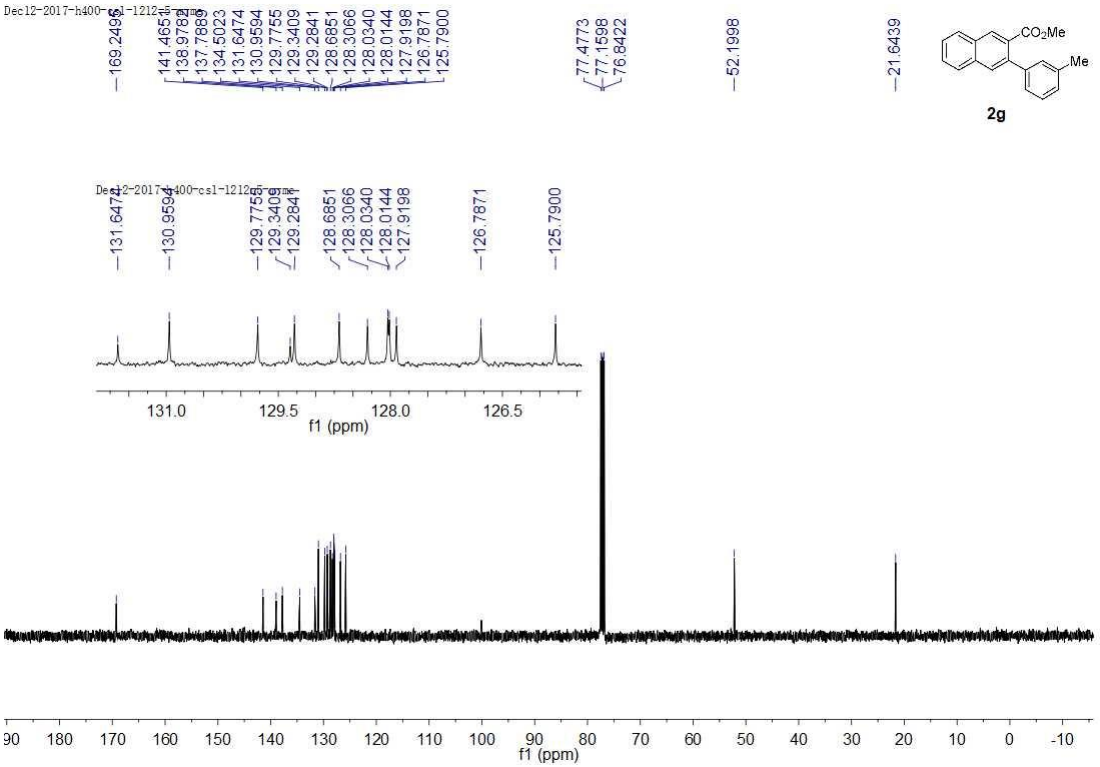


Figure S16. ^{13}C NMR spectra (400 MHz) of **2g** in $CDCl_3$, related to **Scheme 1**.

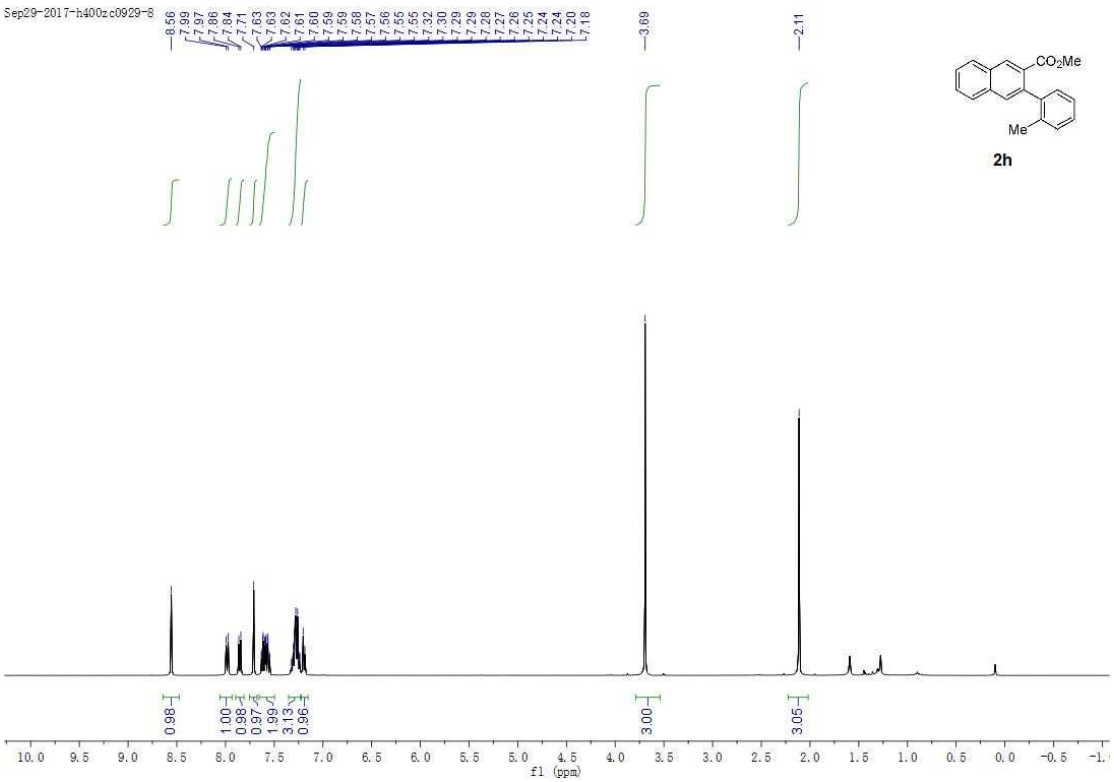


Figure S17. ^{1}H NMR spectra (400 MHz) of **2h** in $CDCl_3$, related to **Scheme 1**.

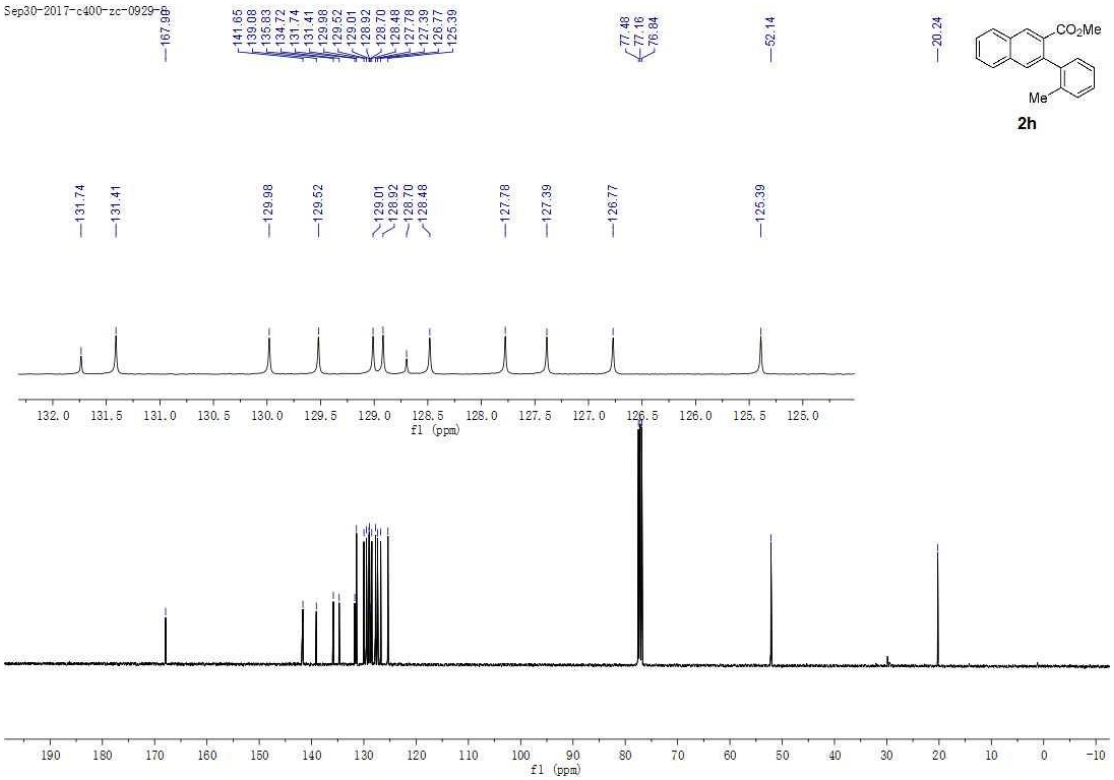


Figure S18. ^{13}C NMR spectra (400 MHz) of **2h** in $CDCl_3$, related to **Scheme 1**.

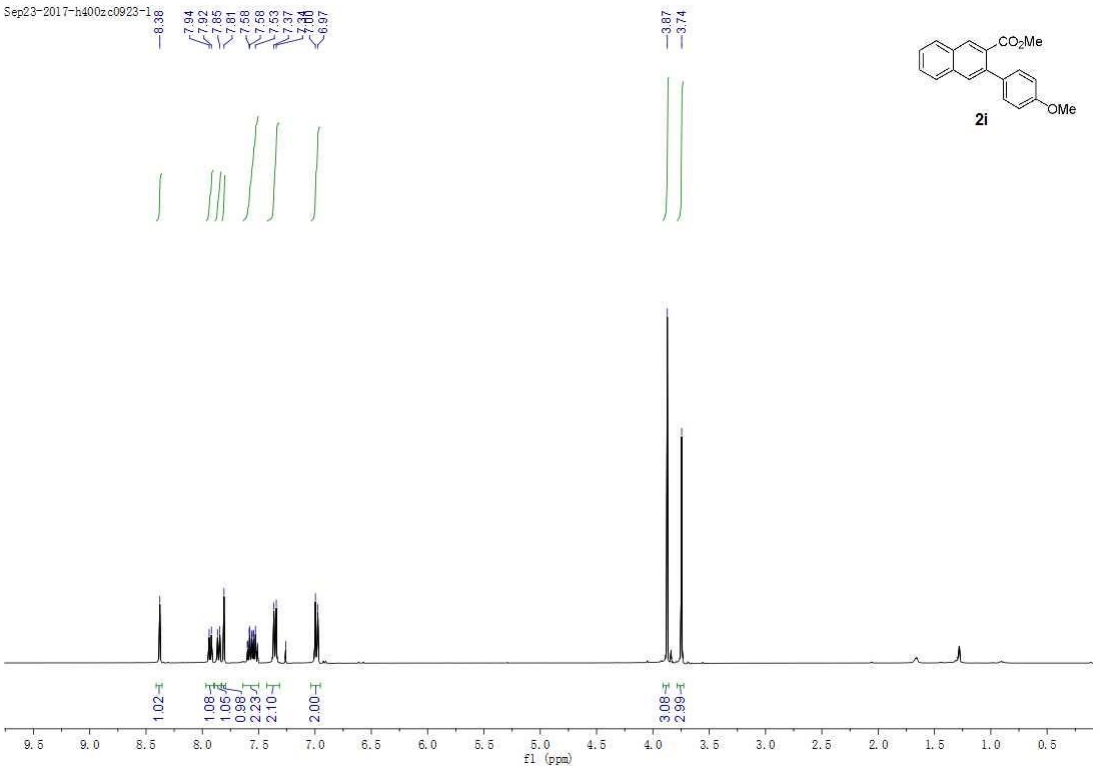


Figure S19. ^{1}H NMR spectra (400 MHz) of **2i** in $CDCl_3$, related to **Scheme 1**.

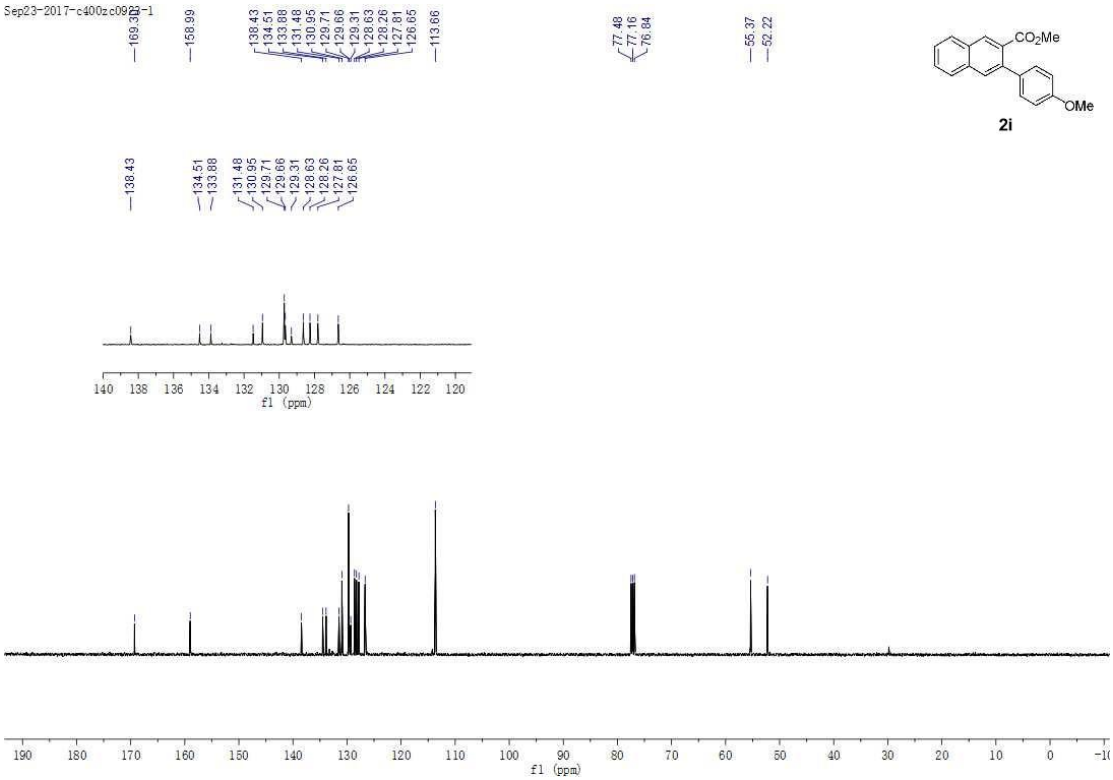


Figure S20. ^{13}C NMR spectra (400 MHz) of **2i** in $CDCl_3$, related to **Scheme 1**.

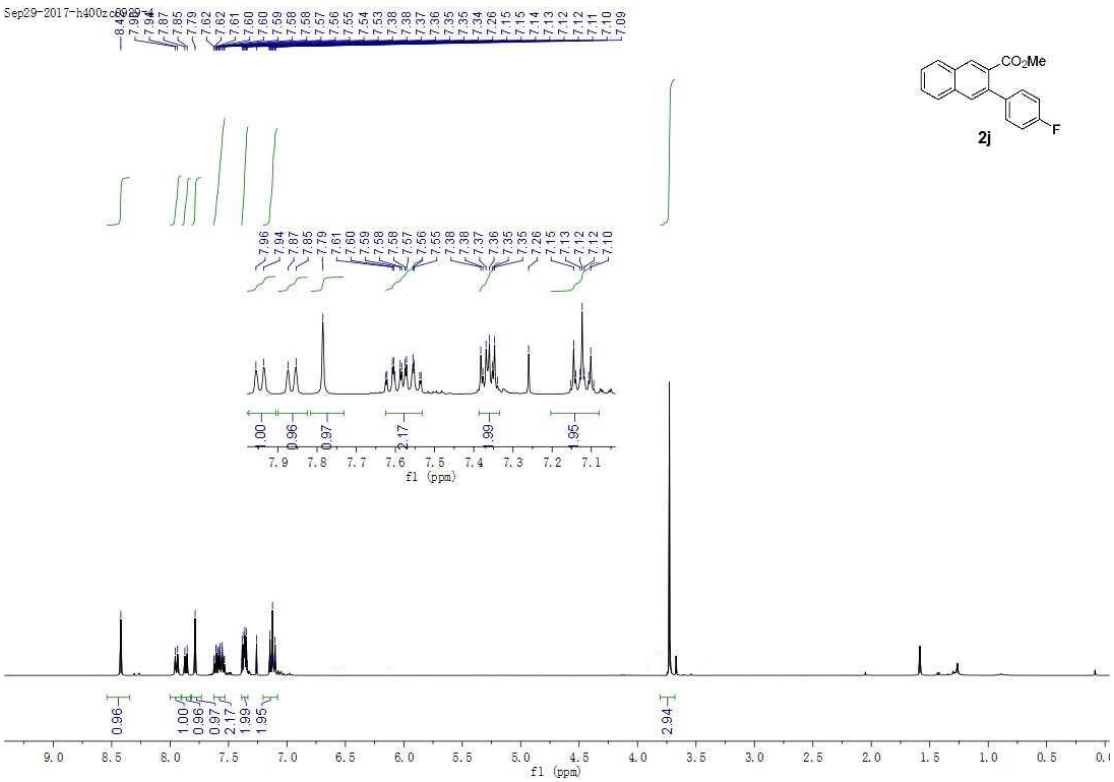


Figure S21. ^{1}H NMR spectra (400 MHz) of **2j** in $CDCl_3$, related to **Scheme 1**.

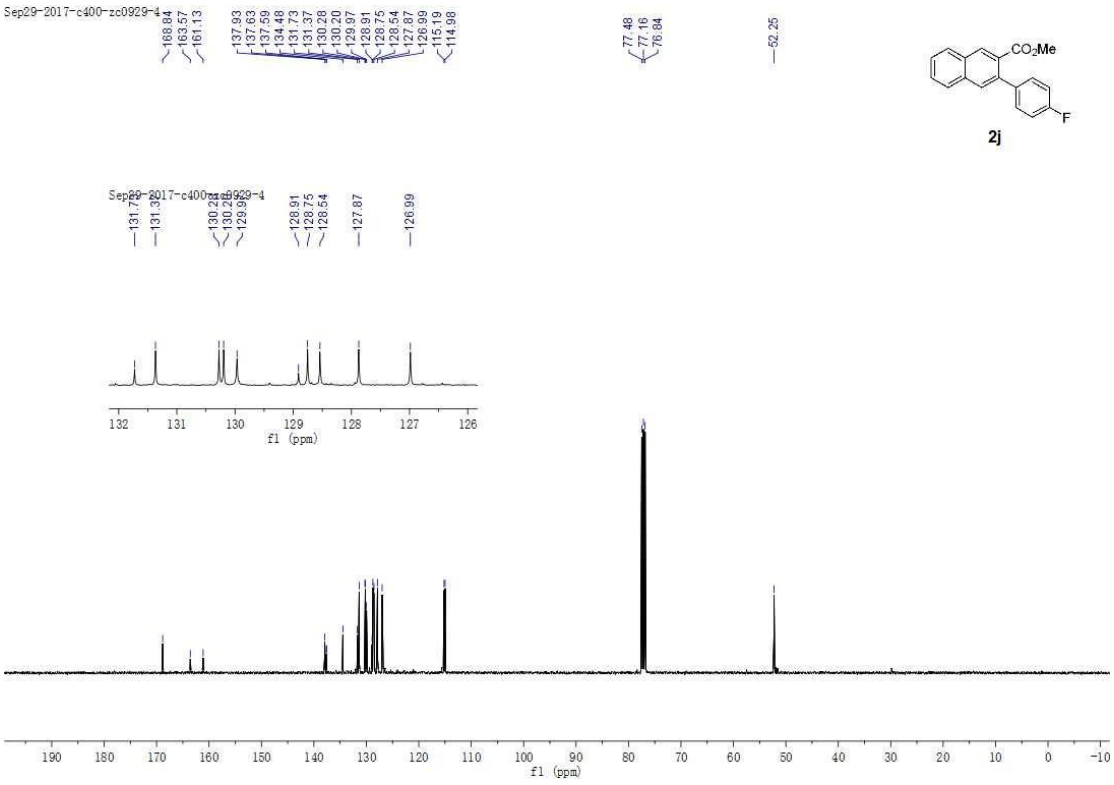


Figure S22. ^{13}C NMR spectra (400 MHz) of **2j** in $CDCl_3$, related to **Scheme 1**.

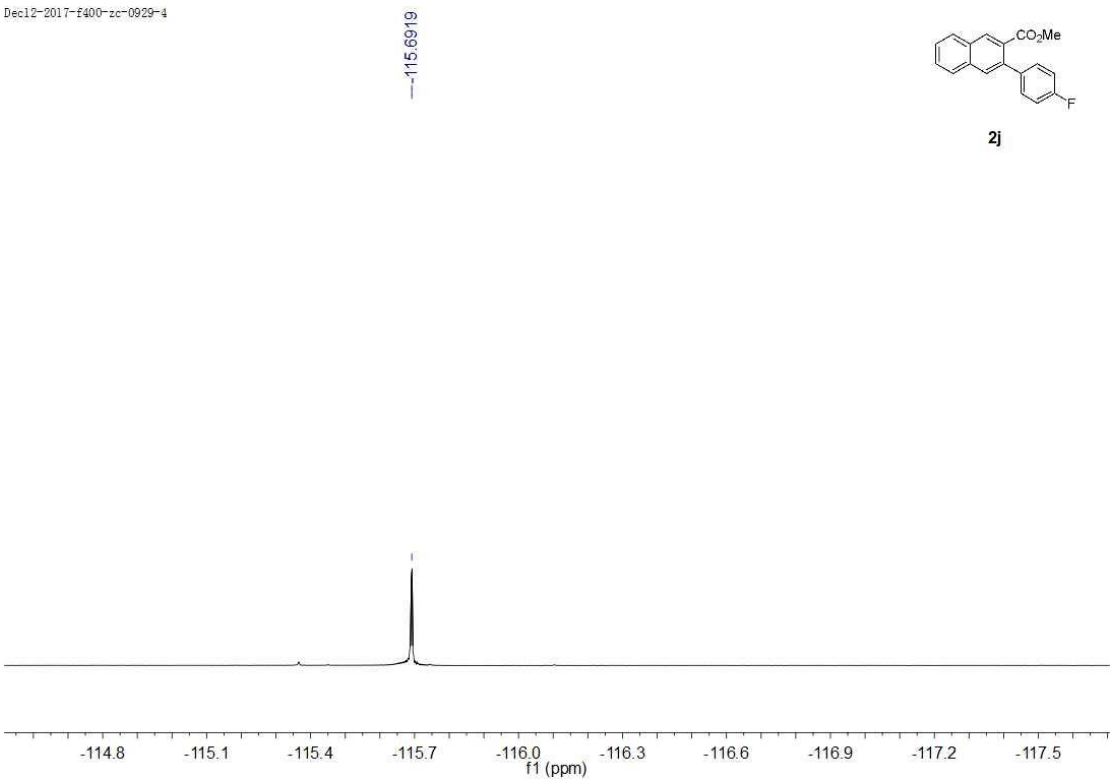


Figure S23. ^{19}F NMR spectra (400 MHz) of **2j** in $CDCl_3$, related to **Scheme 1**.

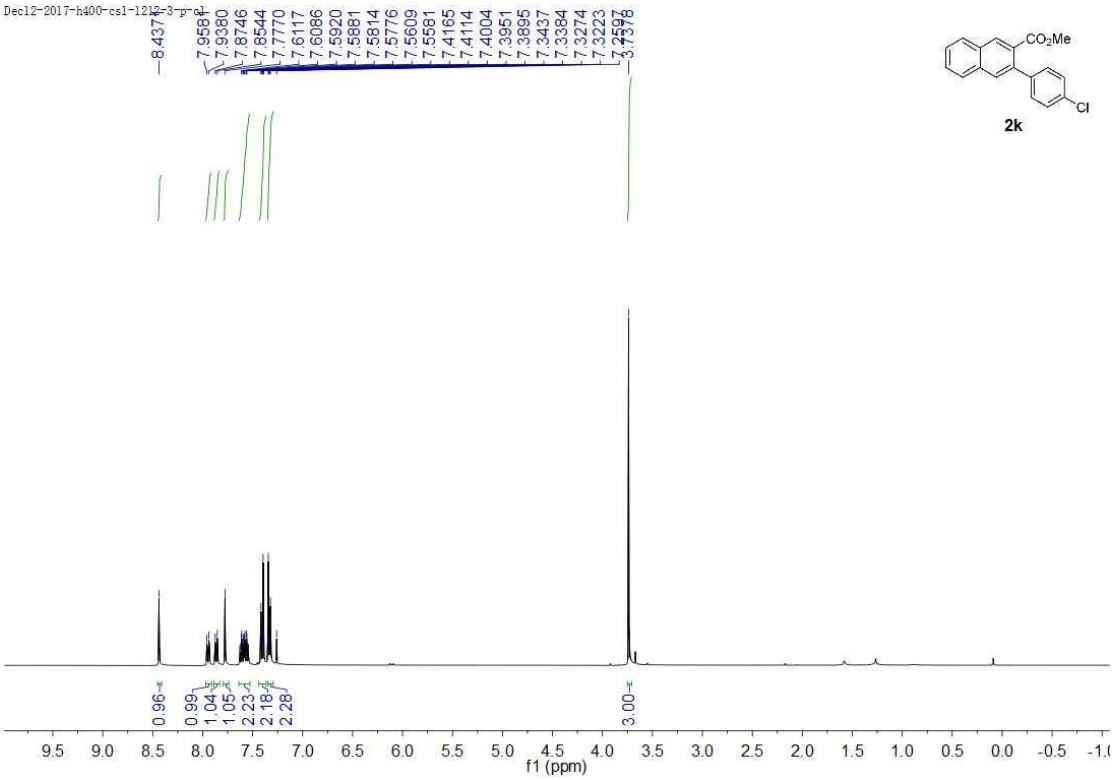


Figure S24. ^{1}H NMR spectra (400 MHz) of **2k** in $CDCl_3$, related to **Scheme 1**.

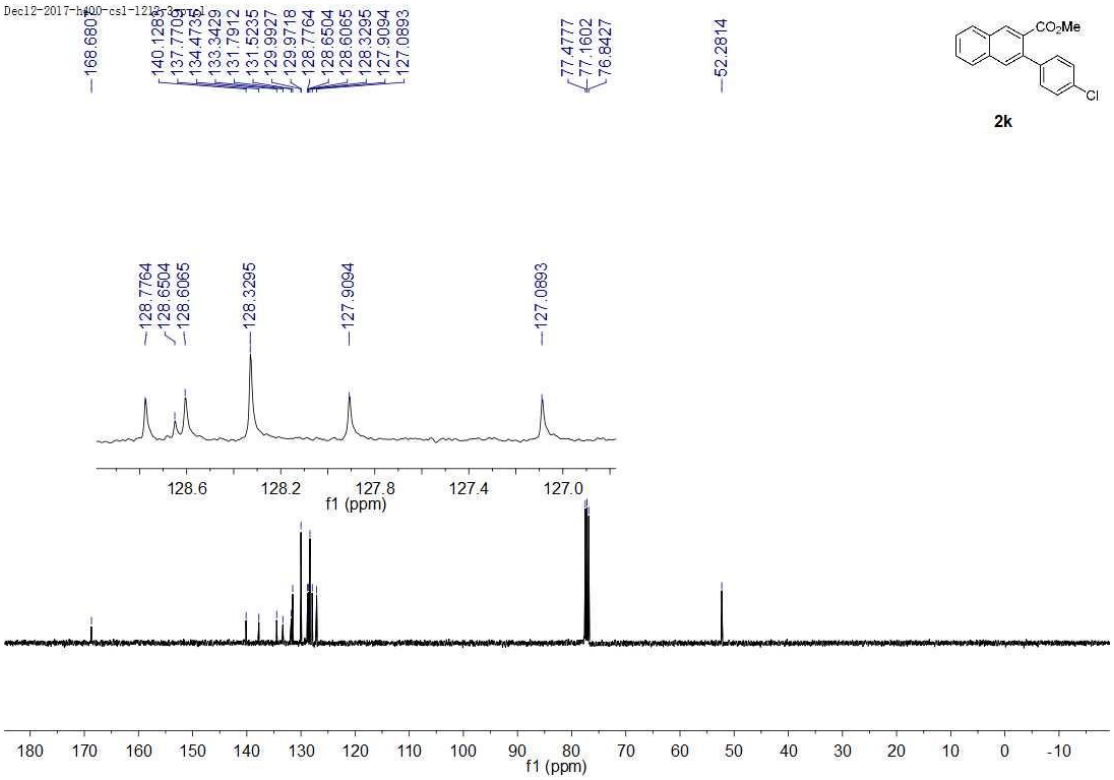


Figure S25. ^{13}C NMR spectra (400 MHz) of **2k** in $CDCl_3$, related to **Scheme 1**.

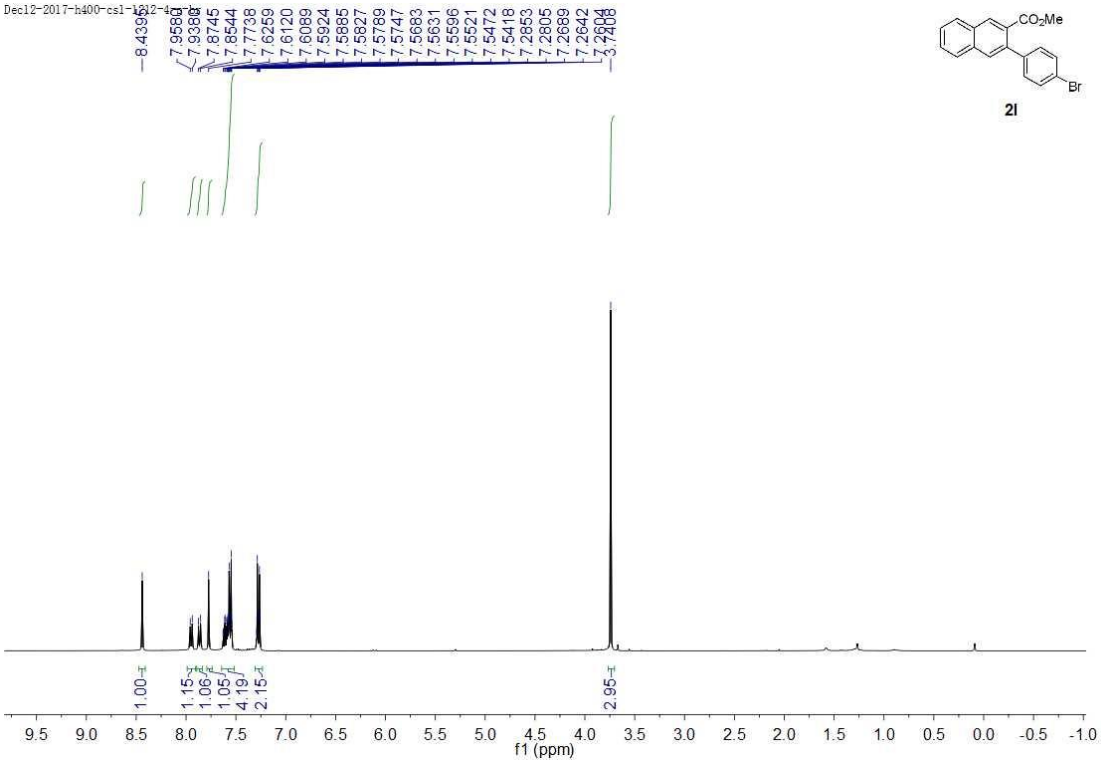


Figure S26. ^{1}H NMR spectra (400 MHz) of **2l** in $CDCl_3$, related to **Scheme 1**.

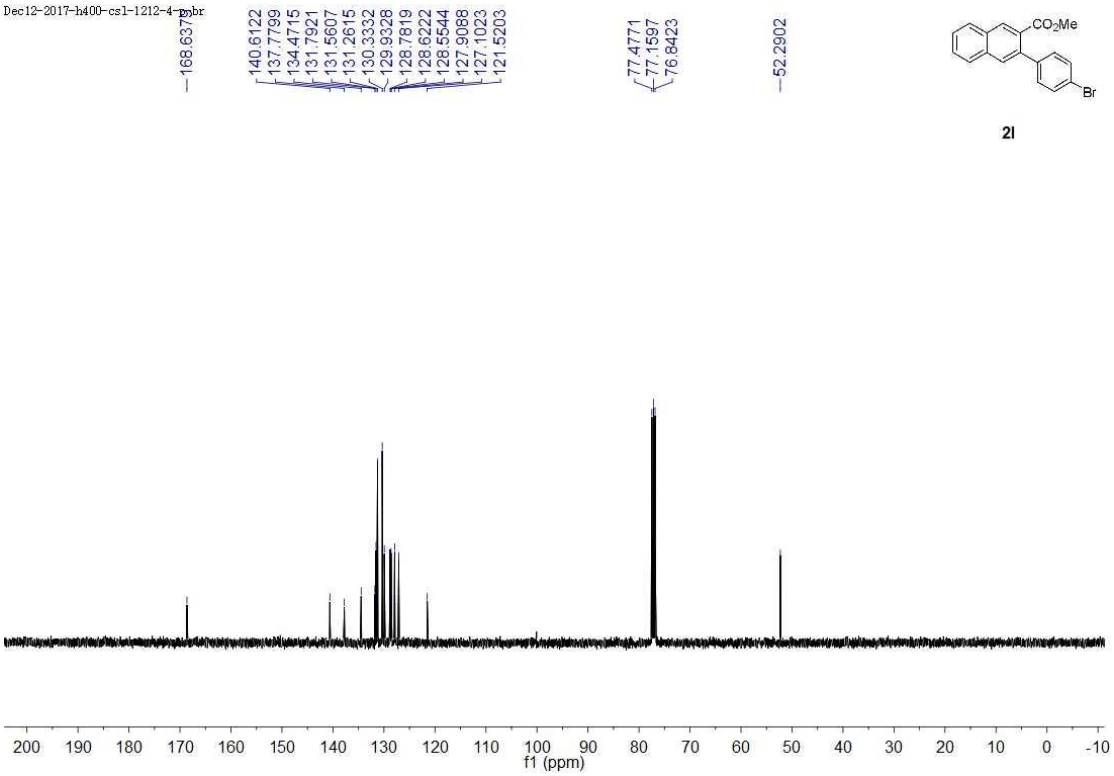


Figure S27. ^{13}C NMR spectra (400 MHz) of **2l** in $CDCl_3$, related to **Scheme 1**.

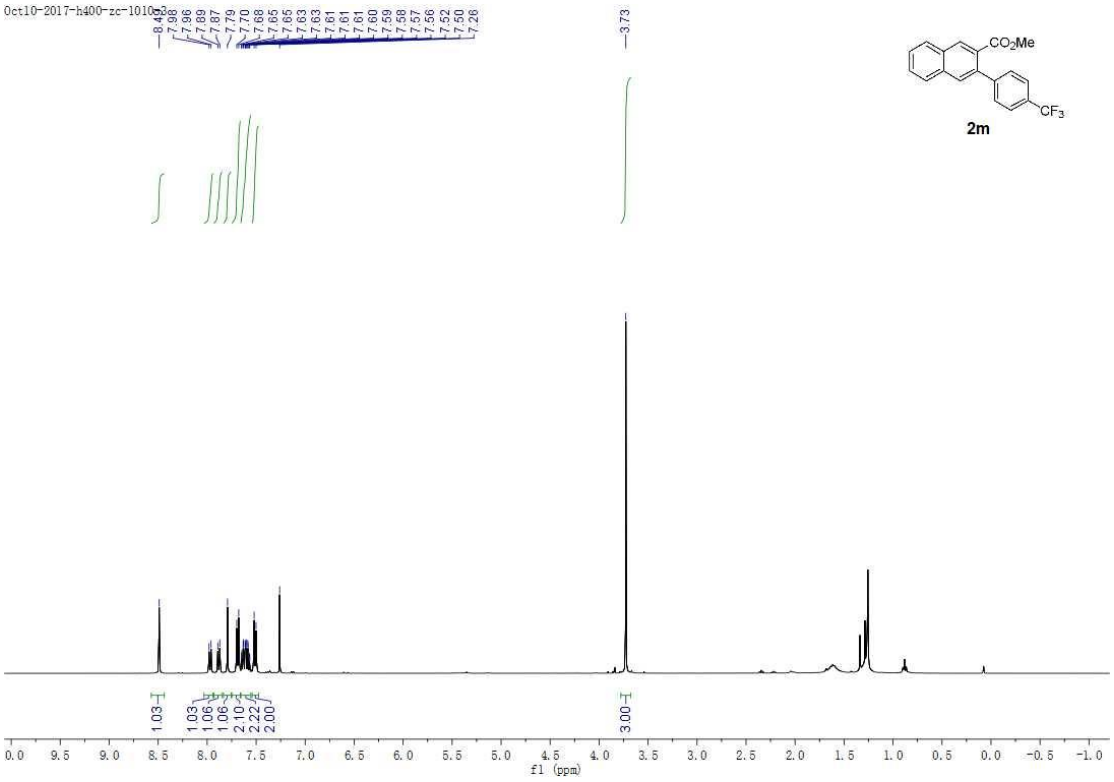


Figure S28. ^{1}H NMR spectra (400 MHz) of **2m** in $CDCl_3$, related to **Scheme 1**.

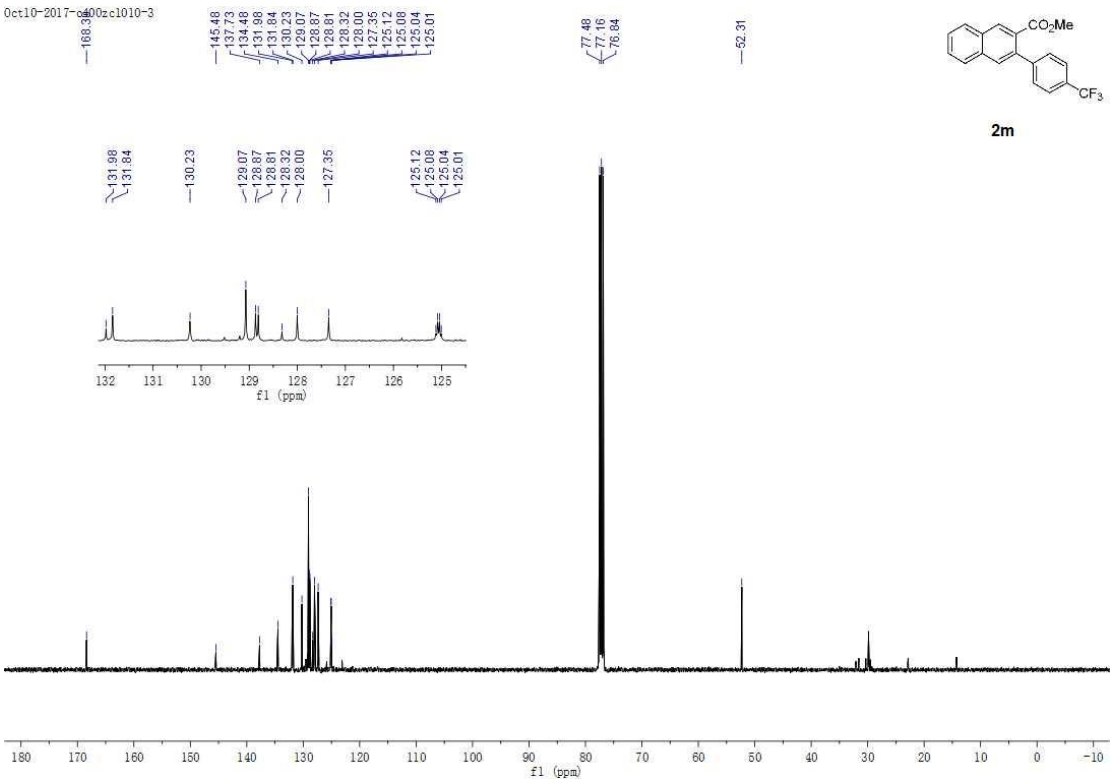


Figure S29. ^{13}C NMR spectra (400 MHz) of **2m** in $CDCl_3$, related to **Scheme 1**.

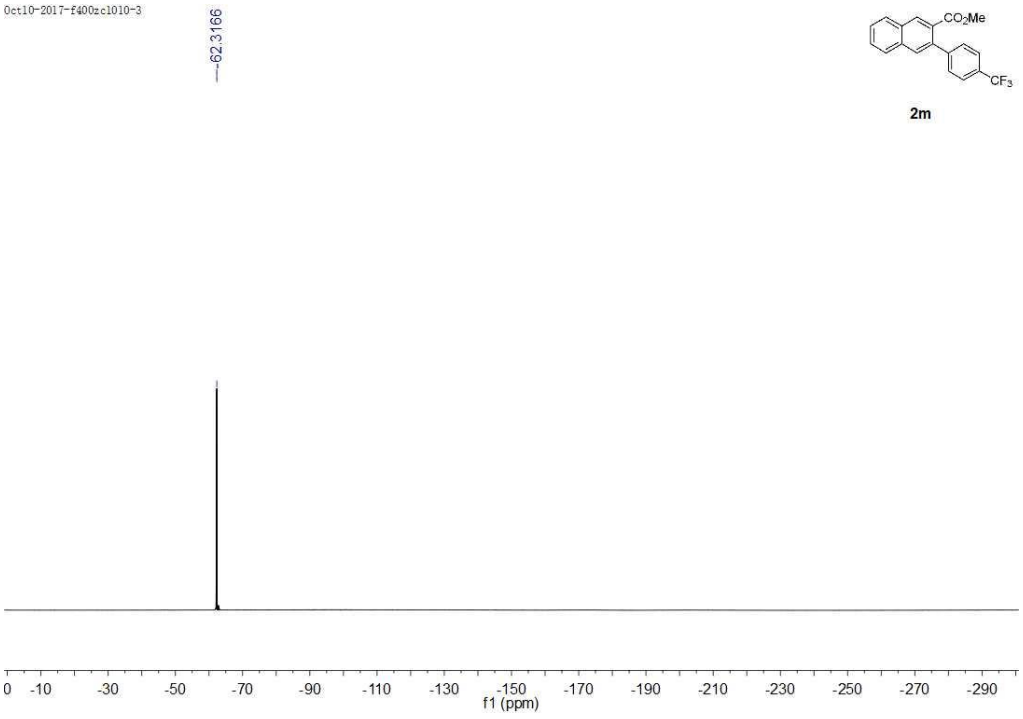


Figure S30. ^{19}F NMR spectra (400 MHz) of **2m** in $CDCl_3$, related to **Scheme 1**.

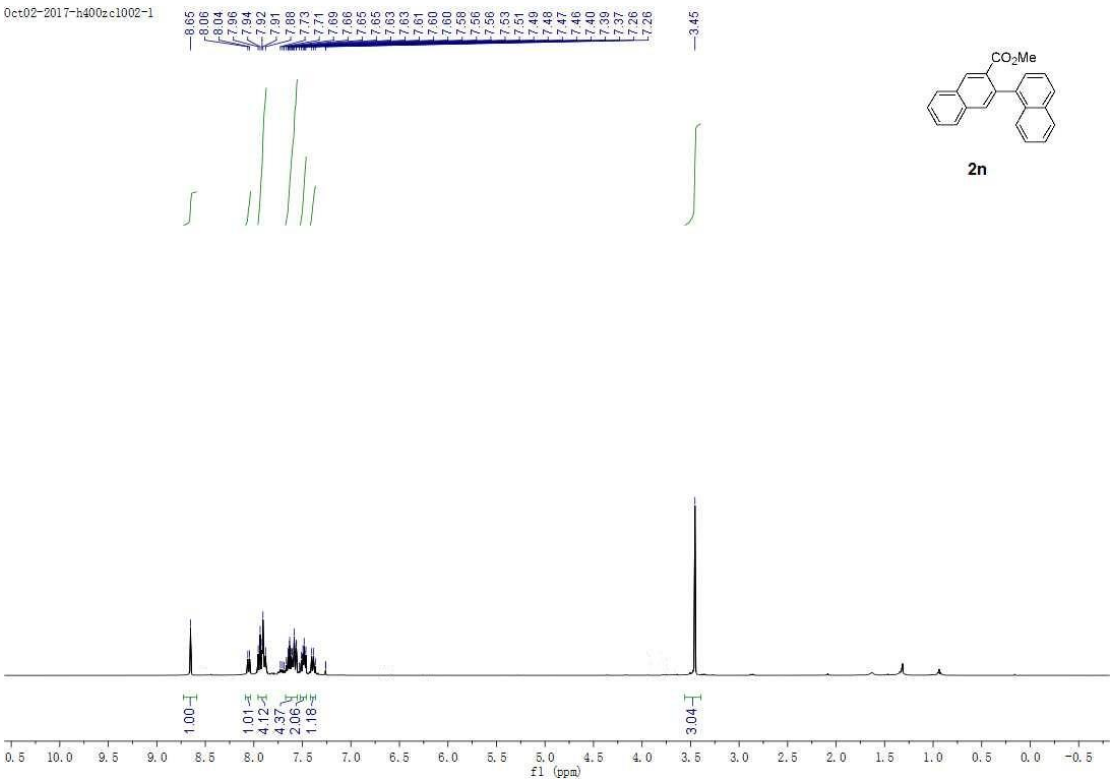


Figure S31. ^{1}H NMR spectra (400 MHz) of **2n** in $CDCl_3$, related to **Scheme 1**.

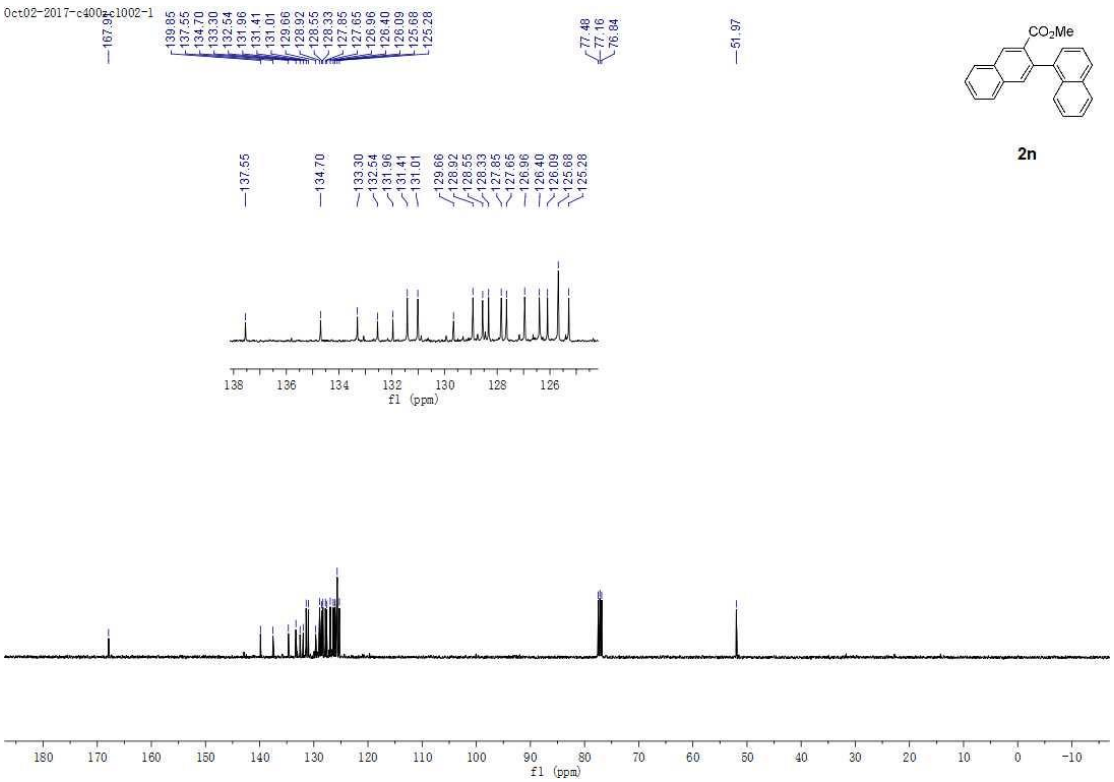


Figure S32. ^{13}C NMR spectra (400 MHz) of **2n** in $CDCl_3$, related to **Scheme 1**.

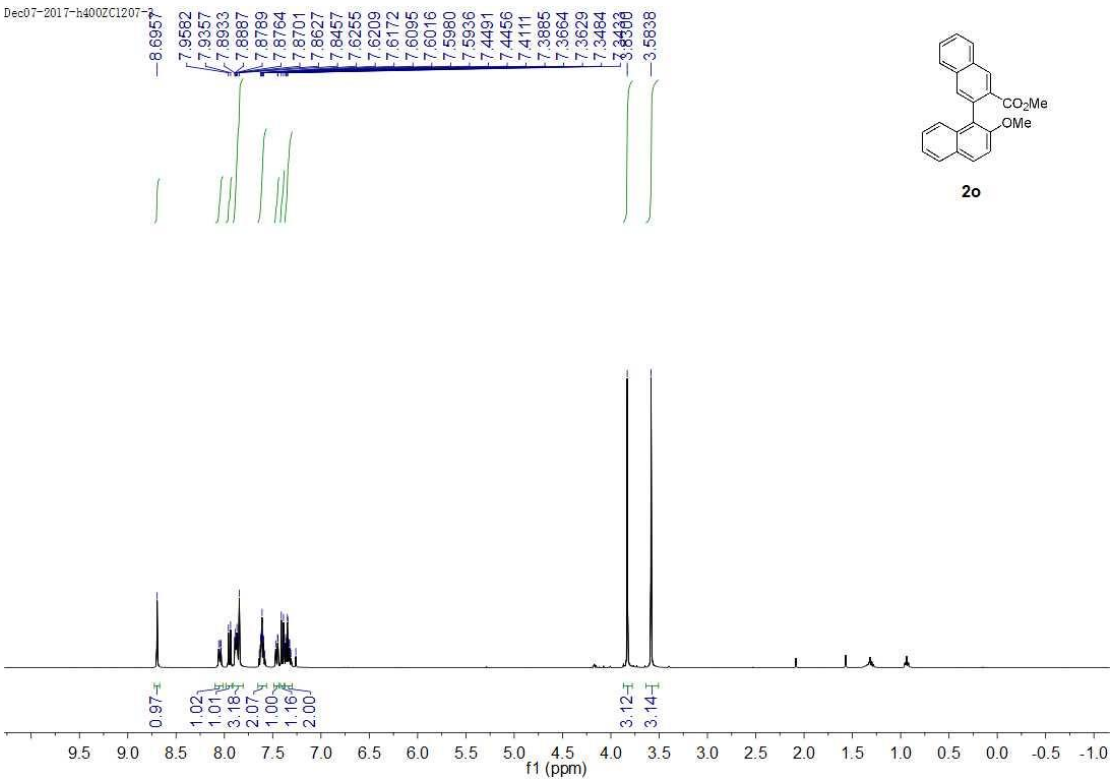


Figure S33. ^{1}H NMR spectra (400 MHz) of **2o** in $CDCl_3$, related to **Scheme 1**.

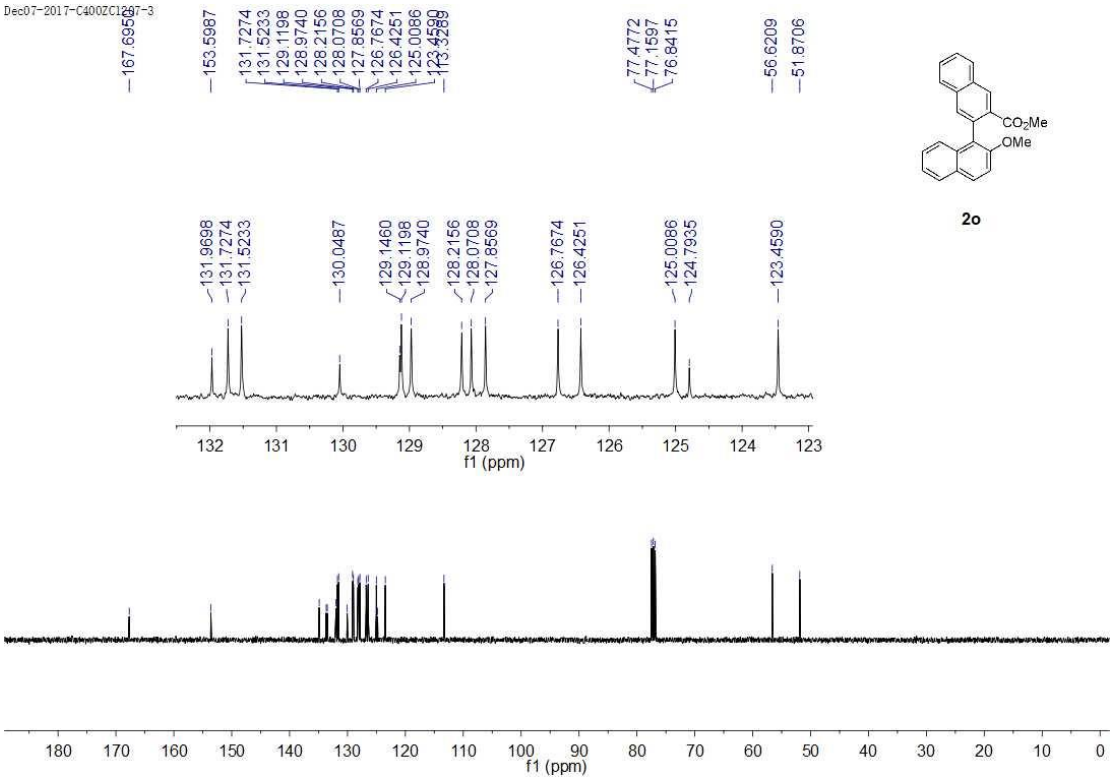


Figure S34. ^{13}C NMR spectra (400 MHz) of **2o** in $CDCl_3$, related to **Scheme 1**.

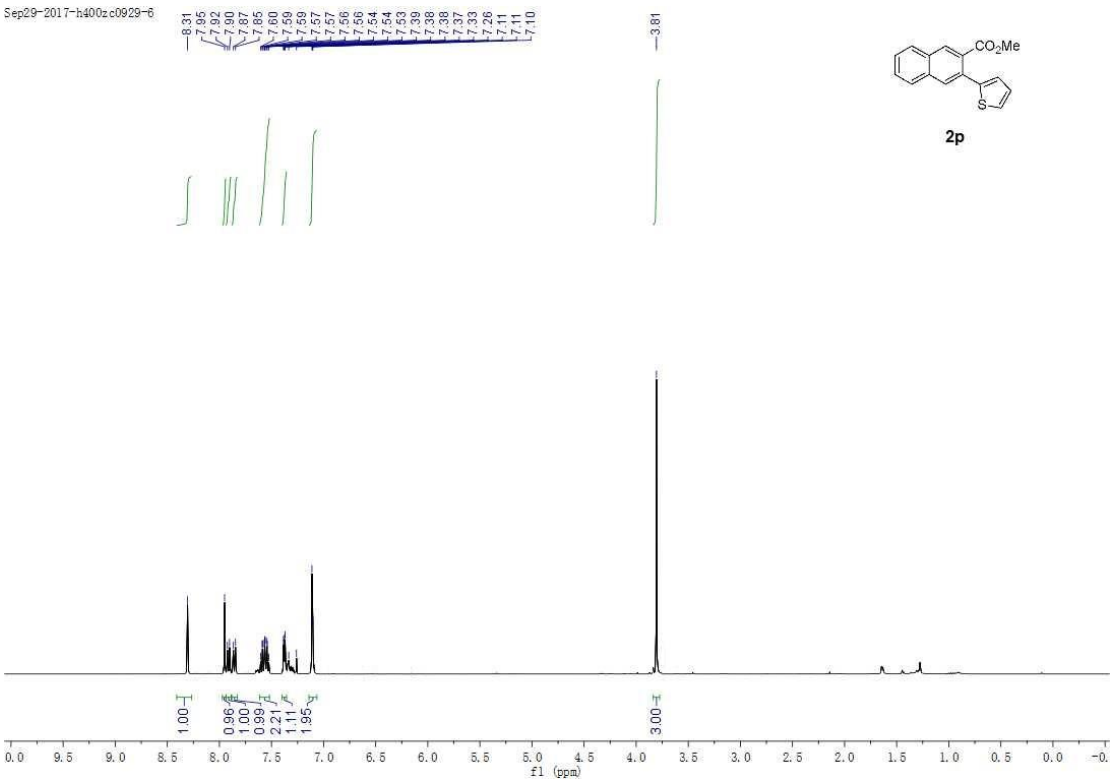


Figure S35. ^{1}H NMR spectra (400 MHz) of **2p** in $CDCl_3$, related to **Scheme 1**.

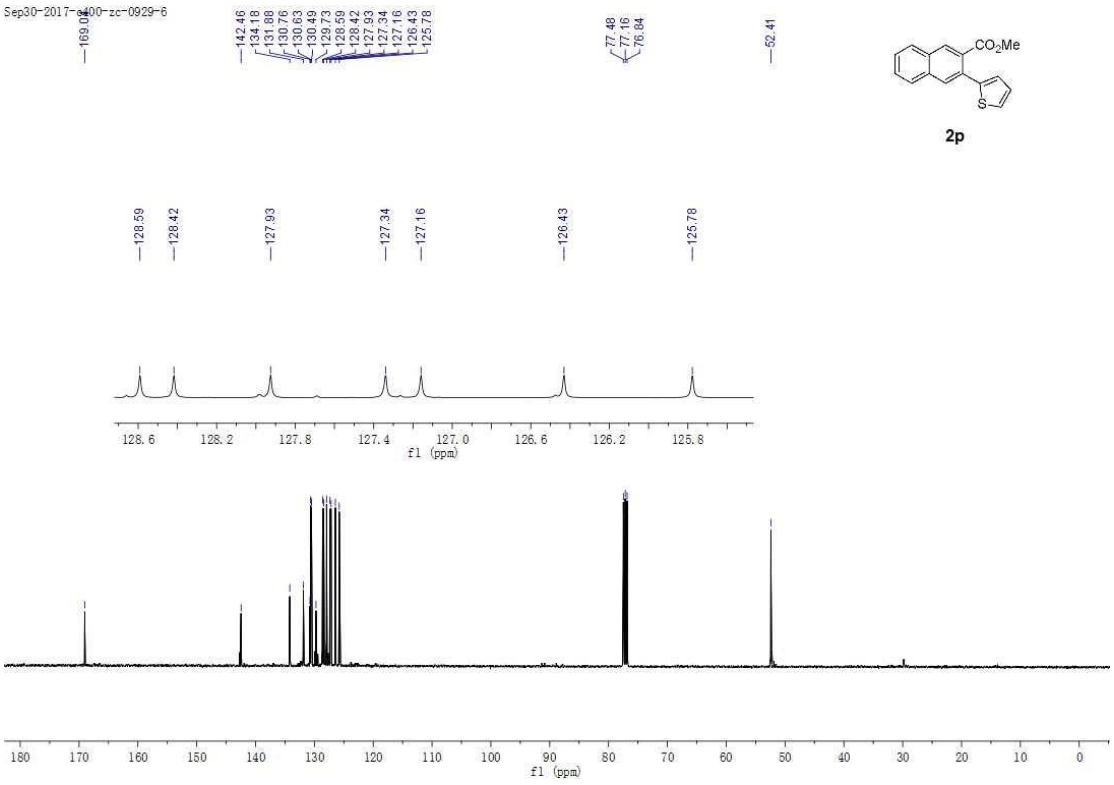


Figure S36. ^{13}C NMR spectra (400 MHz) of **2p** in $CDCl_3$, related to **Scheme 1**.

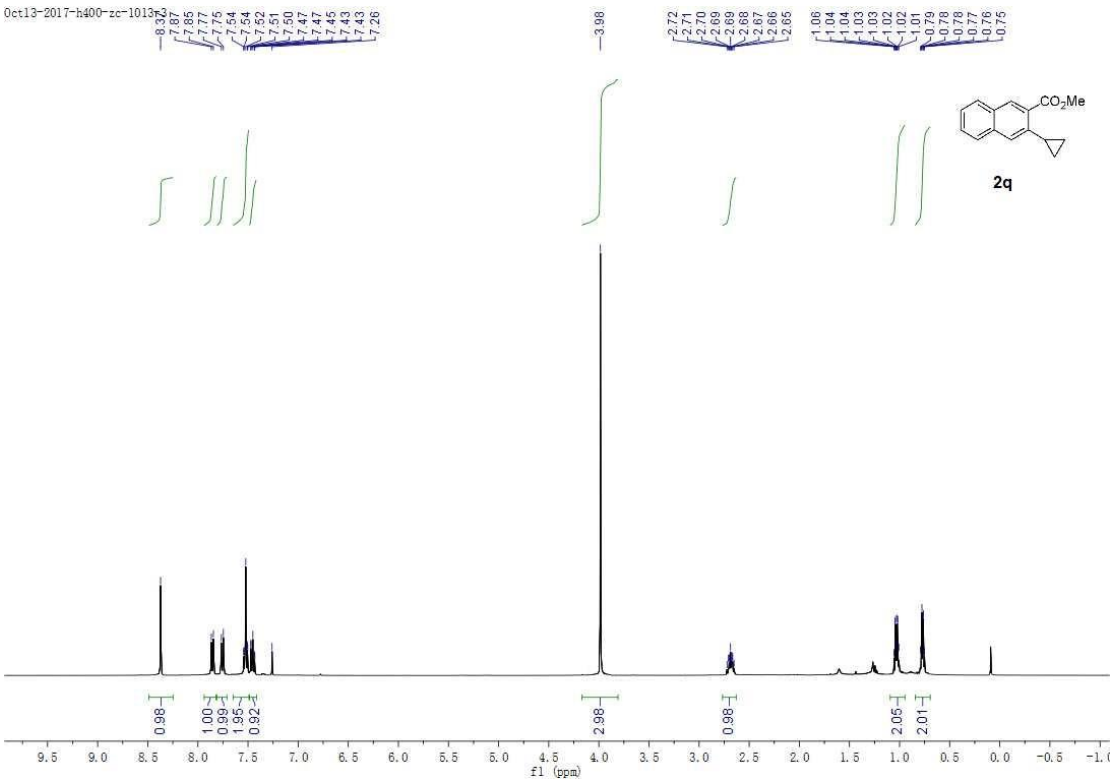


Figure S37. ^{1}H NMR spectra (400 MHz) of **2q** in $CDCl_3$, related to **Scheme 1**.

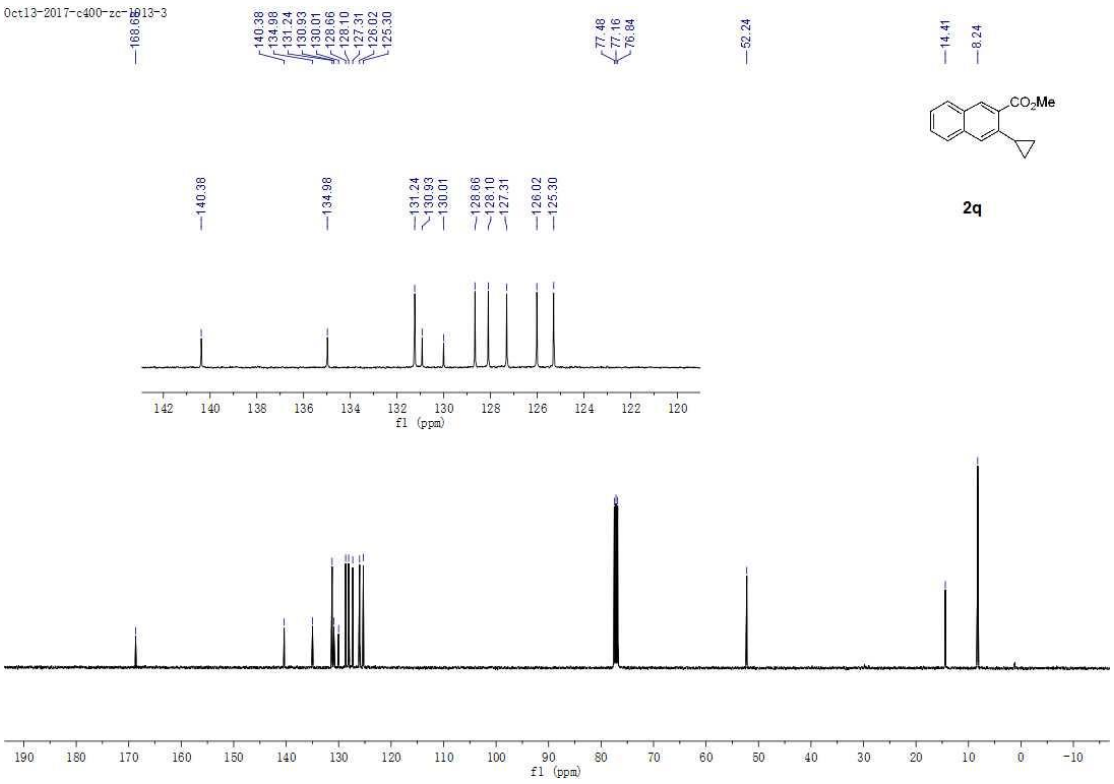


Figure S38. ^{13}C NMR spectra (400 MHz) of **2q** in $CDCl_3$, related to **Scheme 1**.

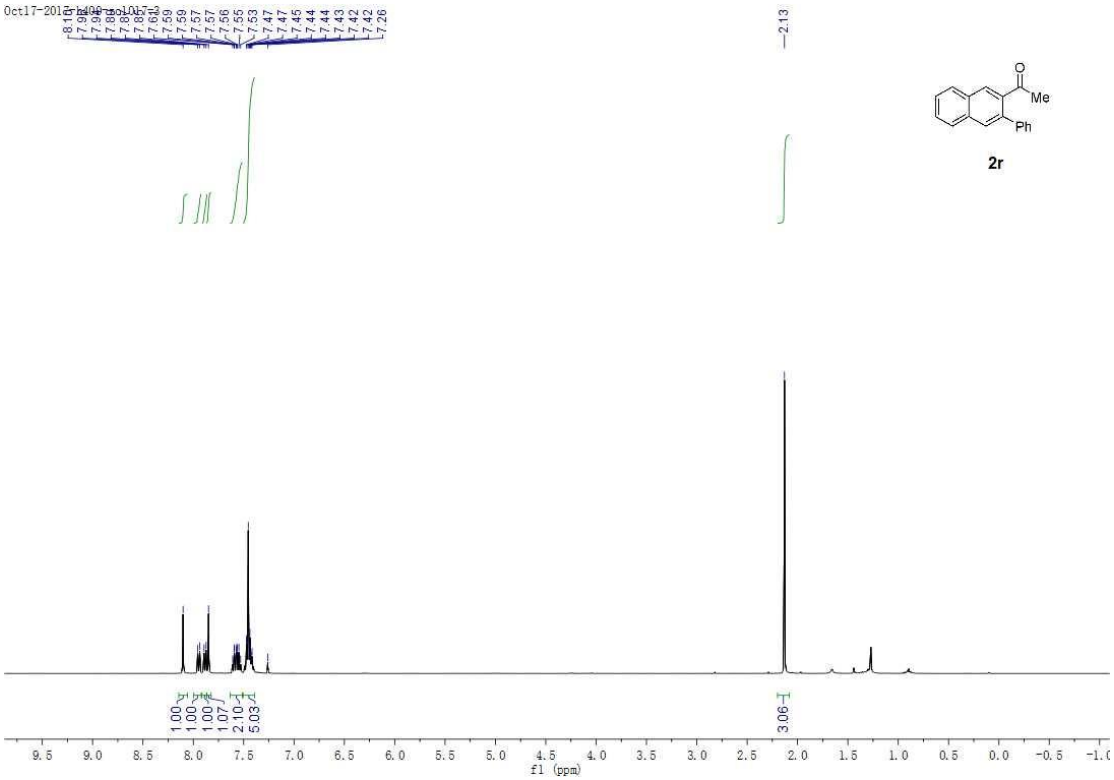


Figure S39. ^{1}H NMR spectra (400 MHz) of **2r** in $CDCl_3$, related to **Scheme 1**.

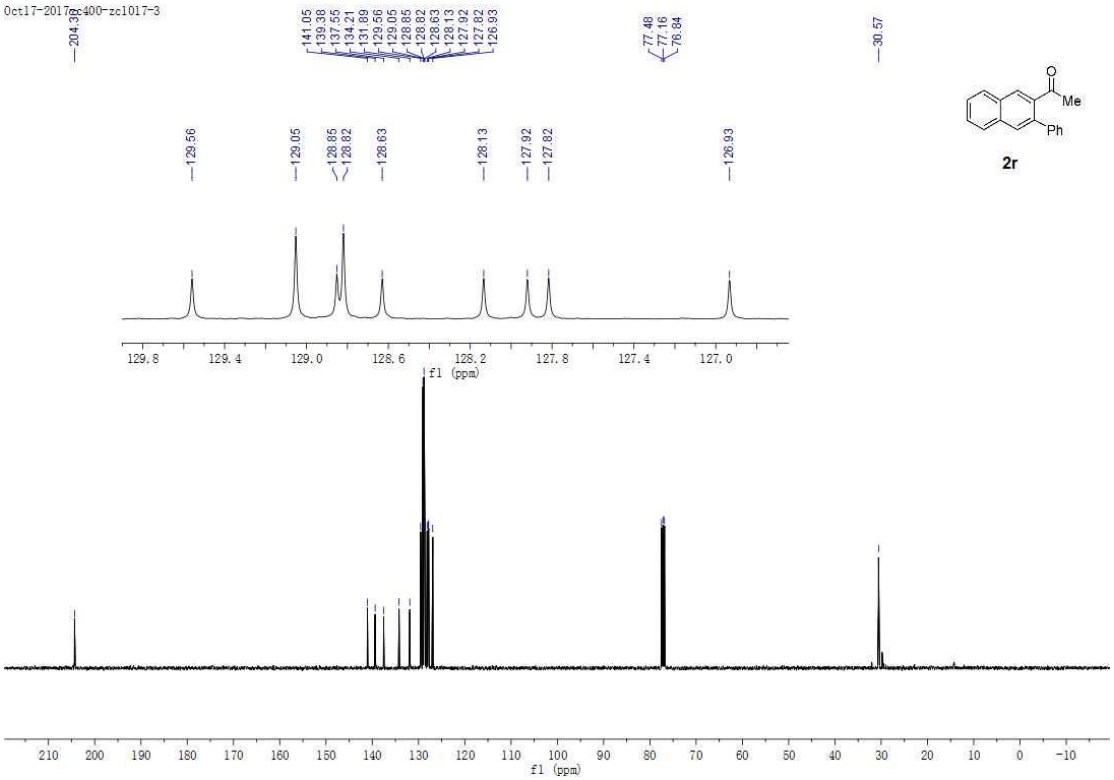


Figure S40. ^{13}C NMR spectra (400 MHz) of **2r** in $CDCl_3$, related to **Scheme 1**.

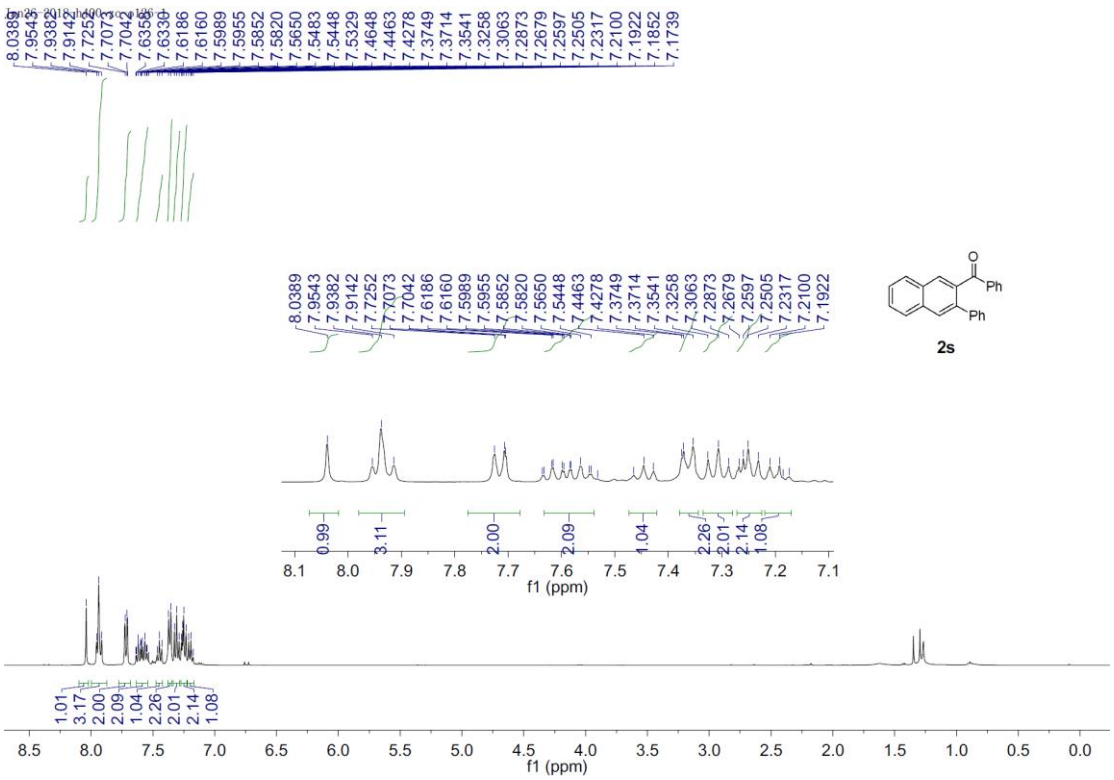


Figure S41. ^{1}H NMR spectra (400 MHz) of **2s** in $CDCl_3$, related to **Scheme 1**.

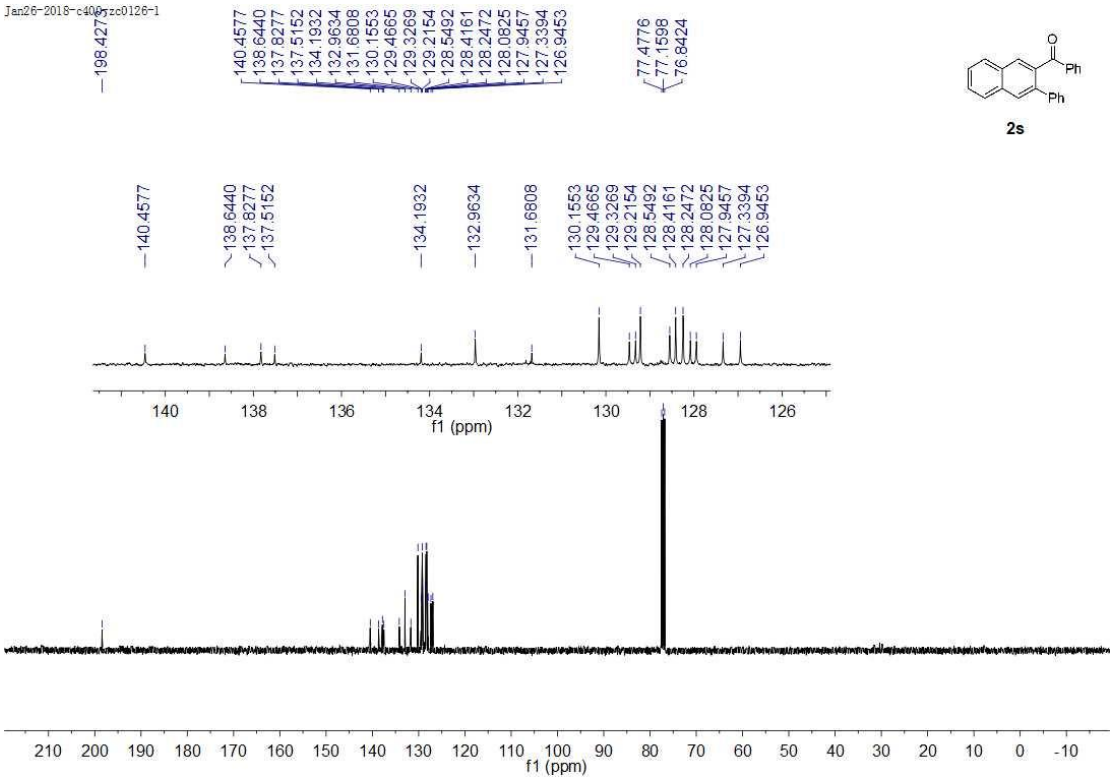


Figure S42. ^{13}C NMR spectra (400 MHz) of **2s** in $CDCl_3$, related to **Scheme 1**.

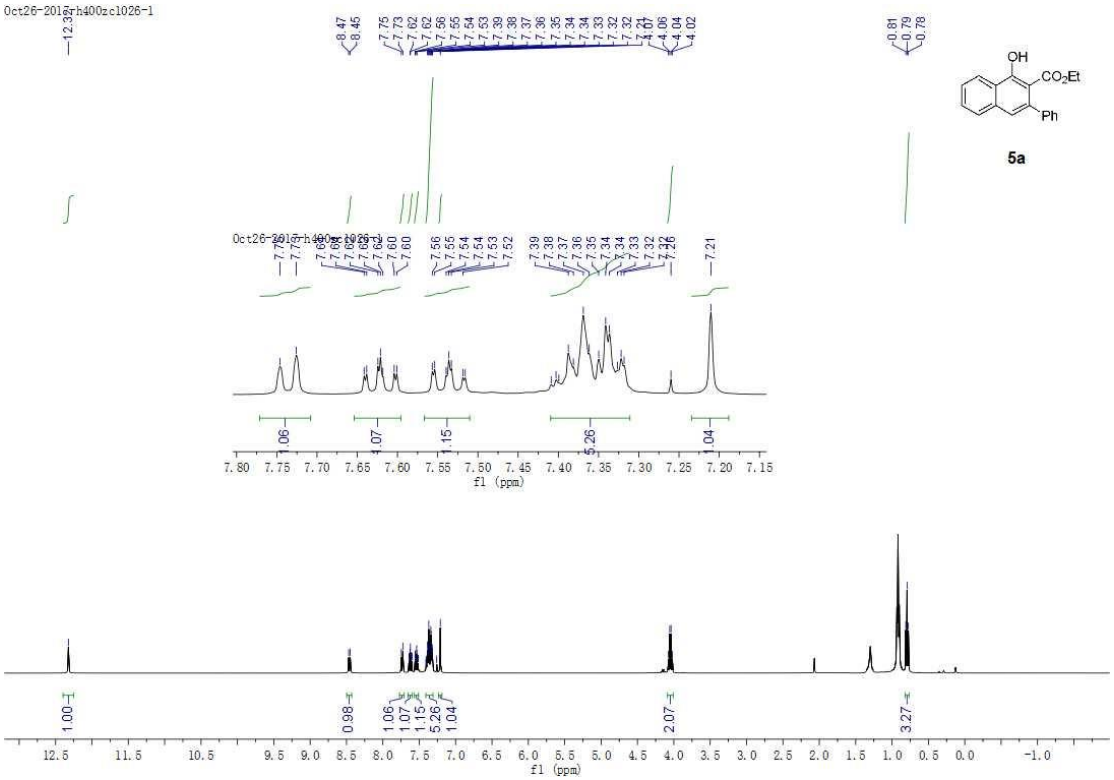


Figure S43. ^{1}H NMR spectra (400 MHz) of **5a** in $CDCl_3$, related to **Scheme 1**.

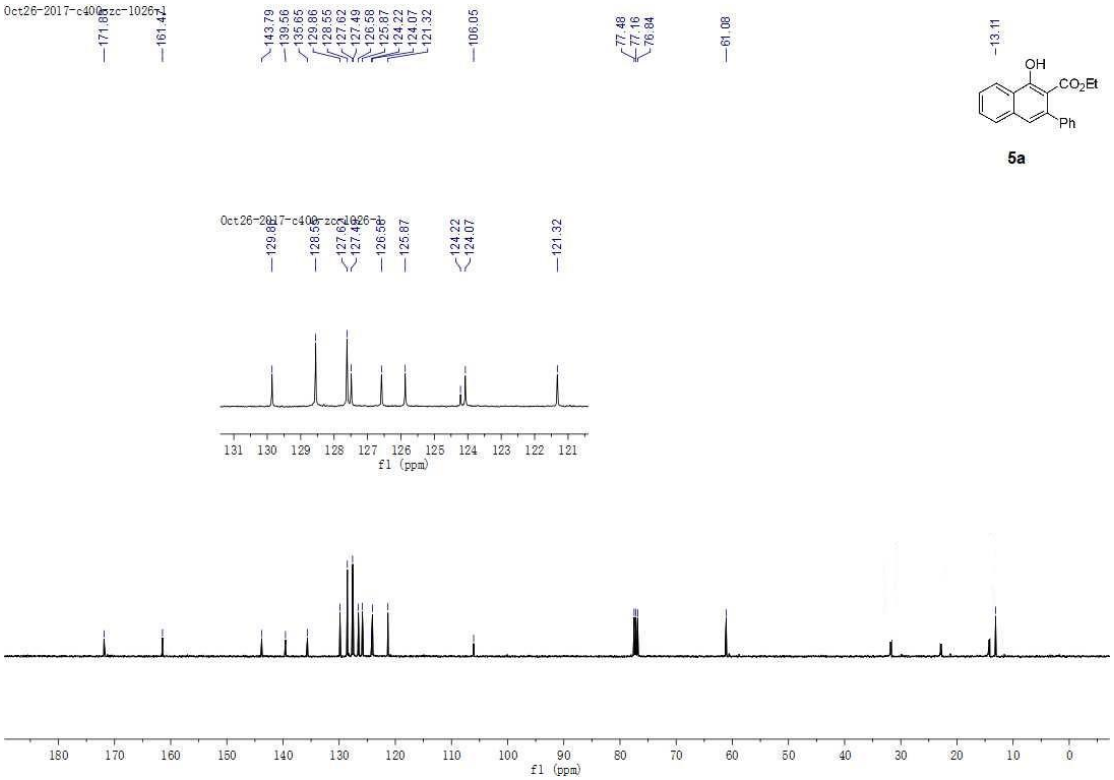


Figure S44. ^{13}C NMR spectra (400 MHz) of **5a** in $CDCl_3$, related to **Scheme 1**.

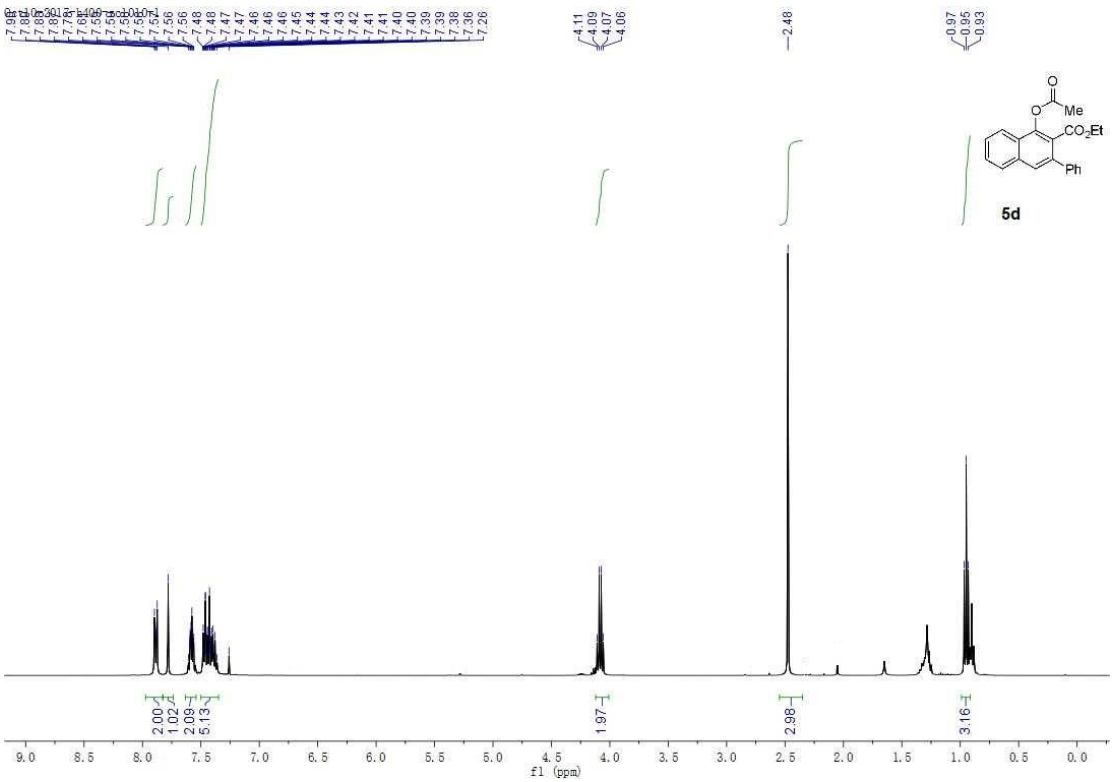


Figure S45. ^{1}H NMR spectra (400 MHz) of **5d** in $CDCl_3$, related to **Scheme 1**.

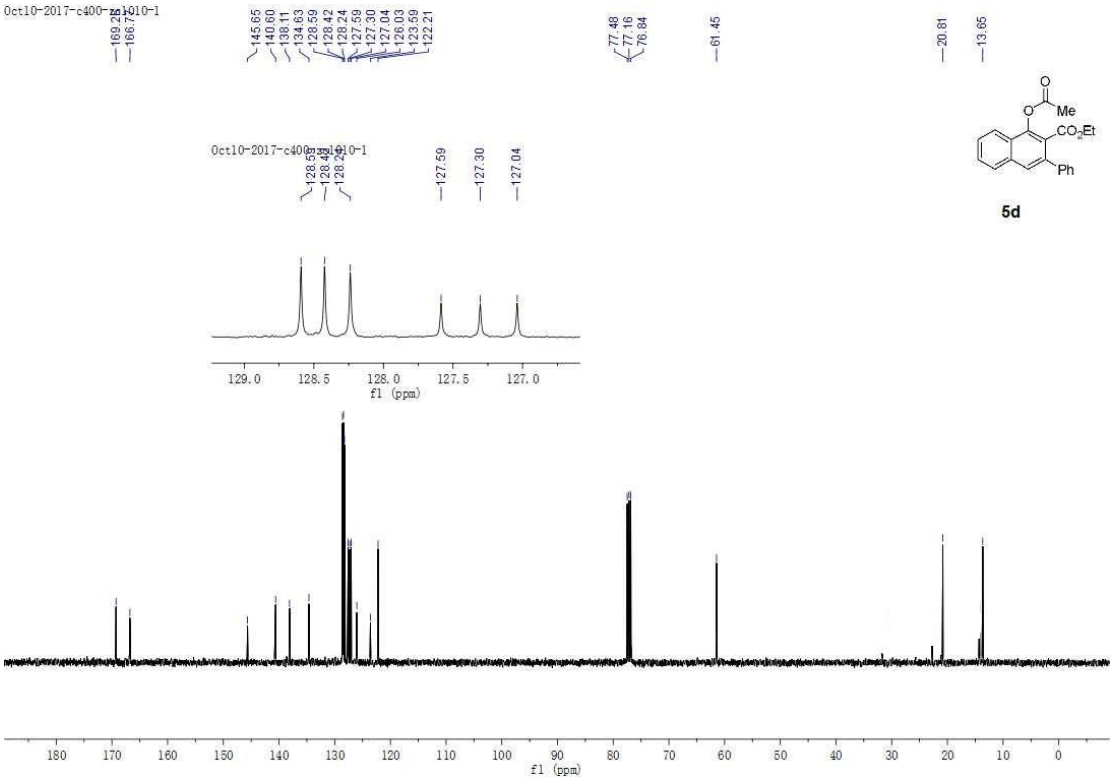


Figure S46. ^{13}C NMR spectra (400 MHz) of **5d** in $CDCl_3$, related to **Scheme 1**.

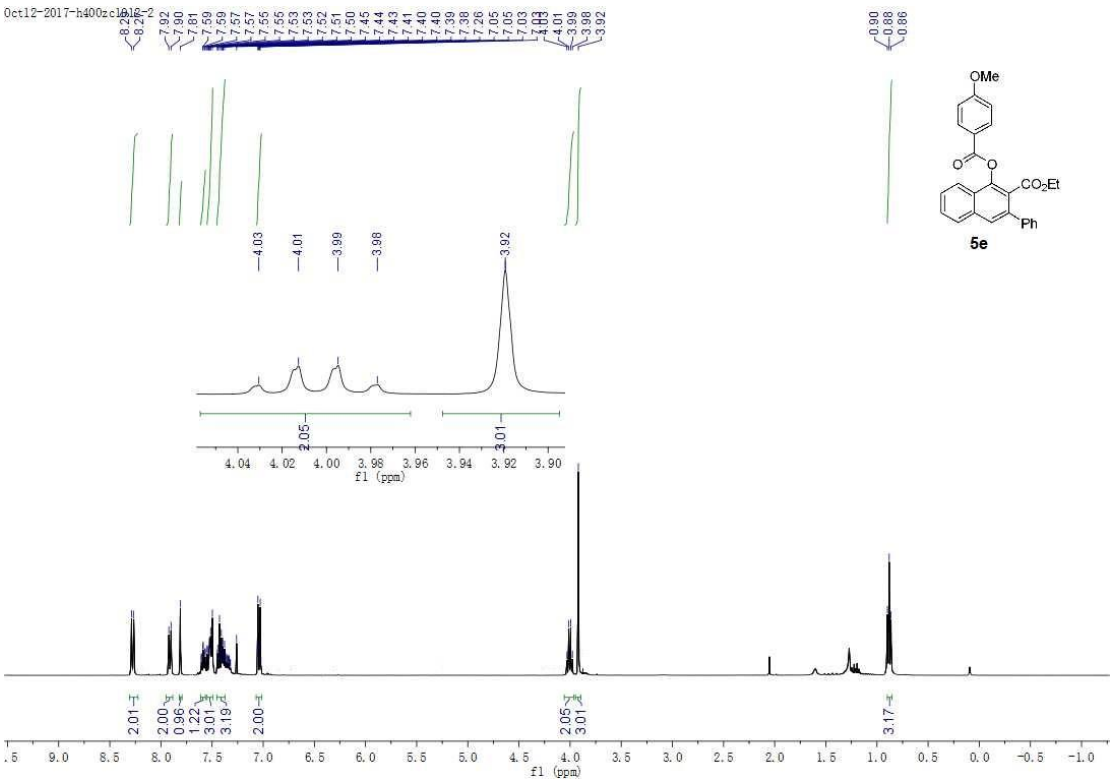


Figure S47. ^{1}H NMR spectra (400 MHz) of **5e** in $CDCl_3$, related to **Scheme 1**.

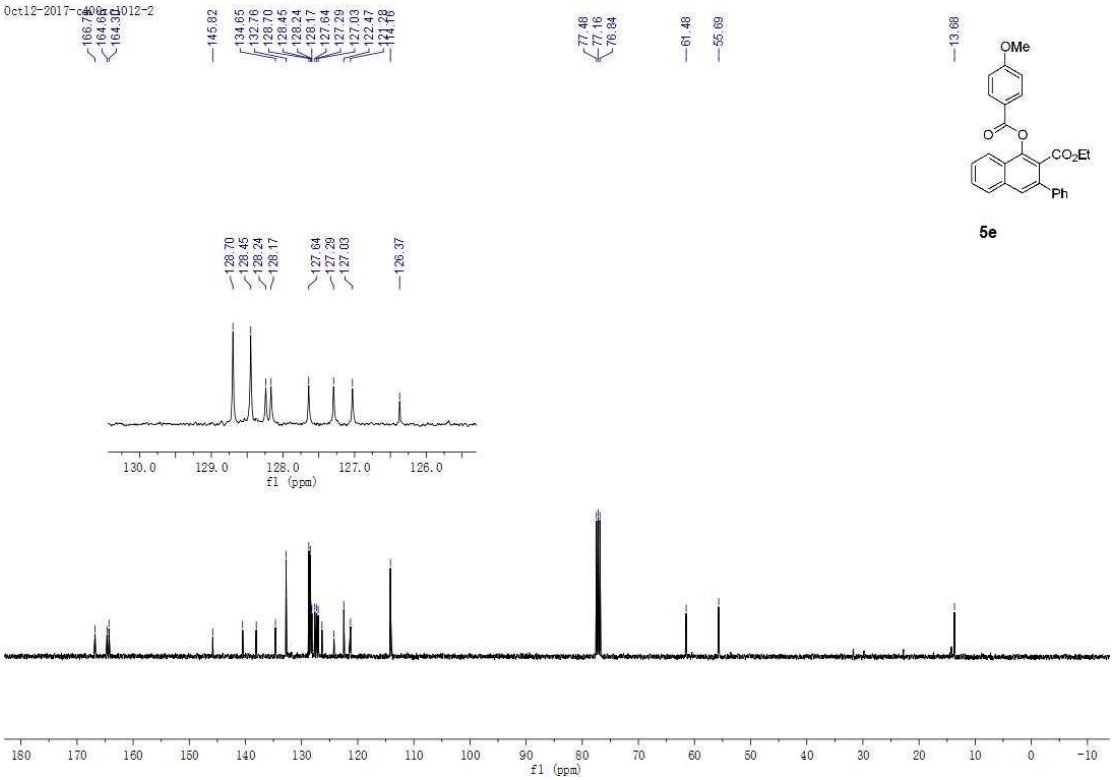


Figure S48. ^{13}C NMR spectra (400 MHz) of **5e** in $CDCl_3$, related to **Scheme 1**.

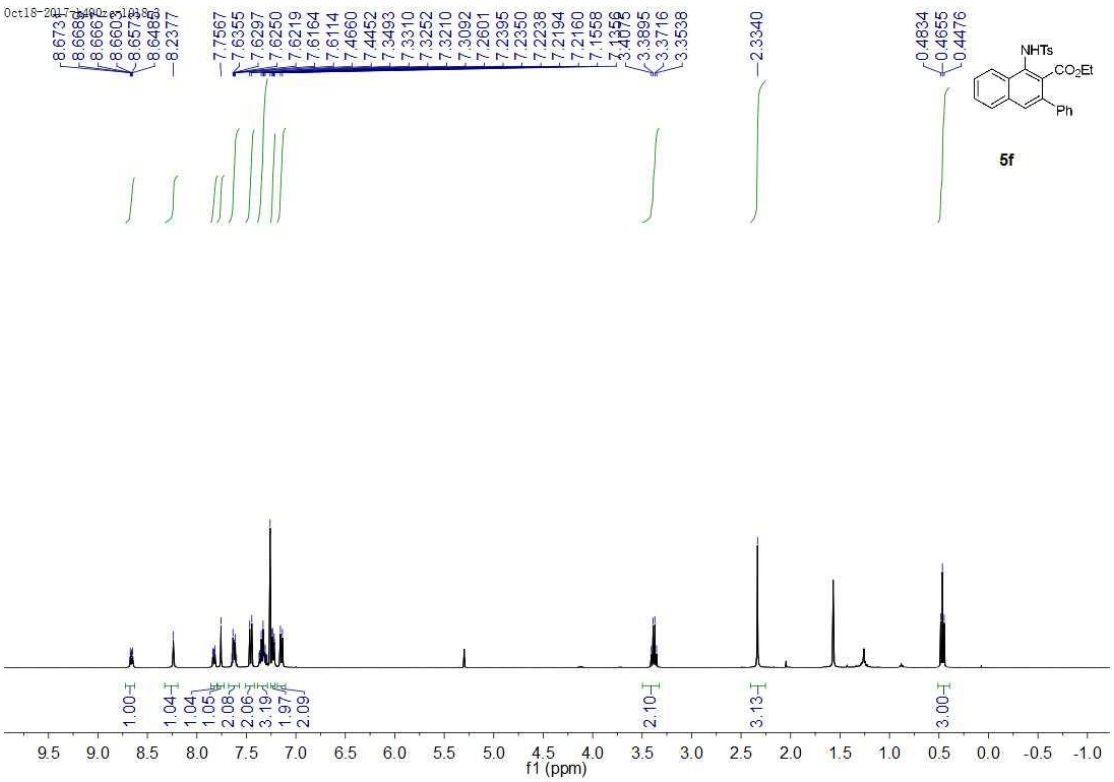


Figure S49. ^{1}H NMR spectra (400 MHz) of **5f** in $CDCl_3$, related to **Scheme 1**.

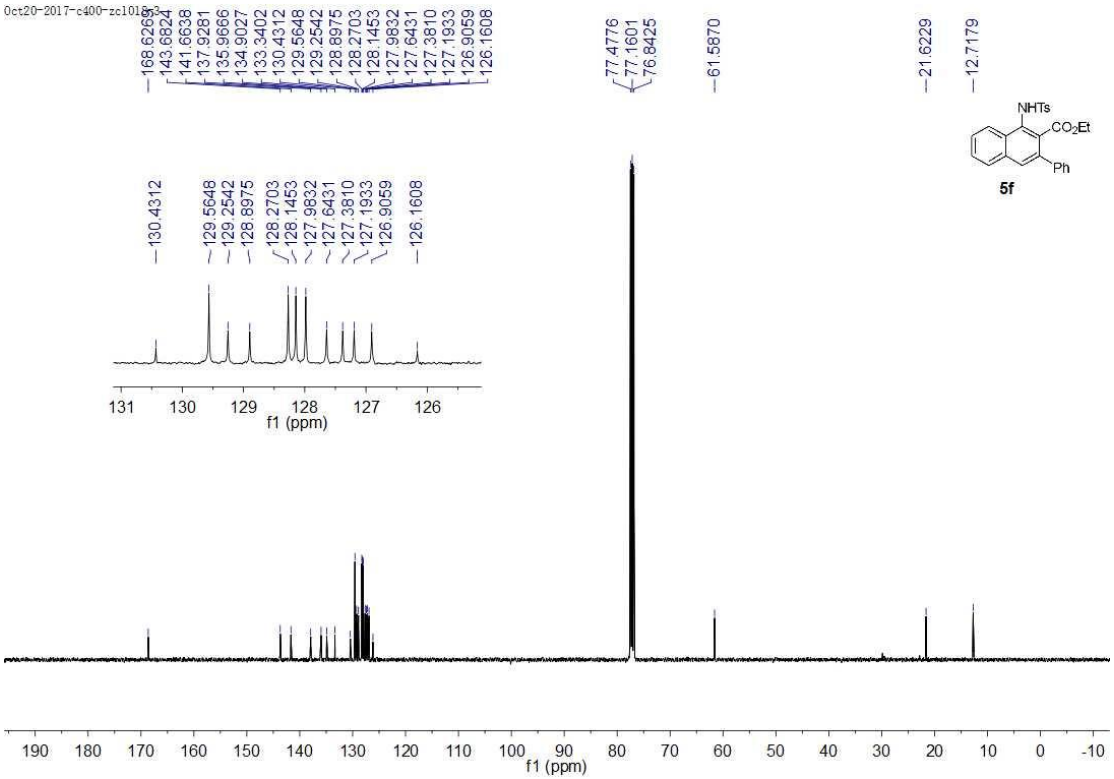


Figure S50. ^{13}C NMR spectra (400 MHz) of **5f** in $CDCl_3$, related to **Scheme 1**.

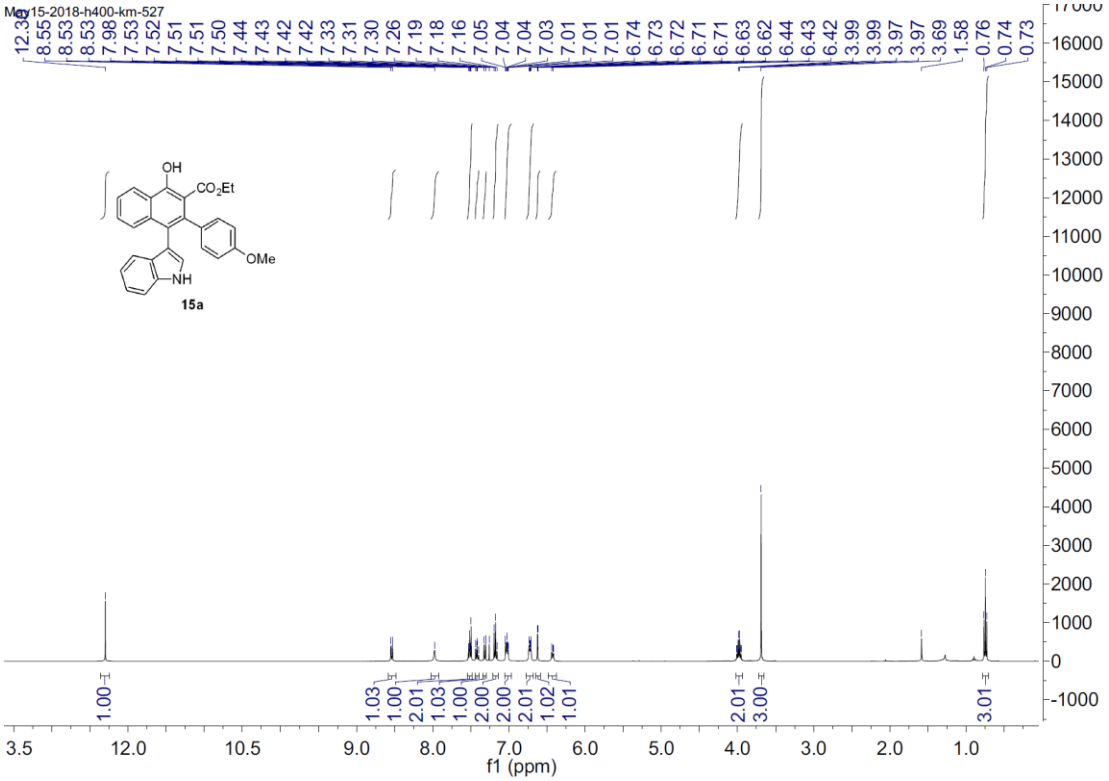


Figure S51. ^{1}H NMR spectra (400 MHz) of **15a** in $CDCl_3$, related to **Scheme 1**.

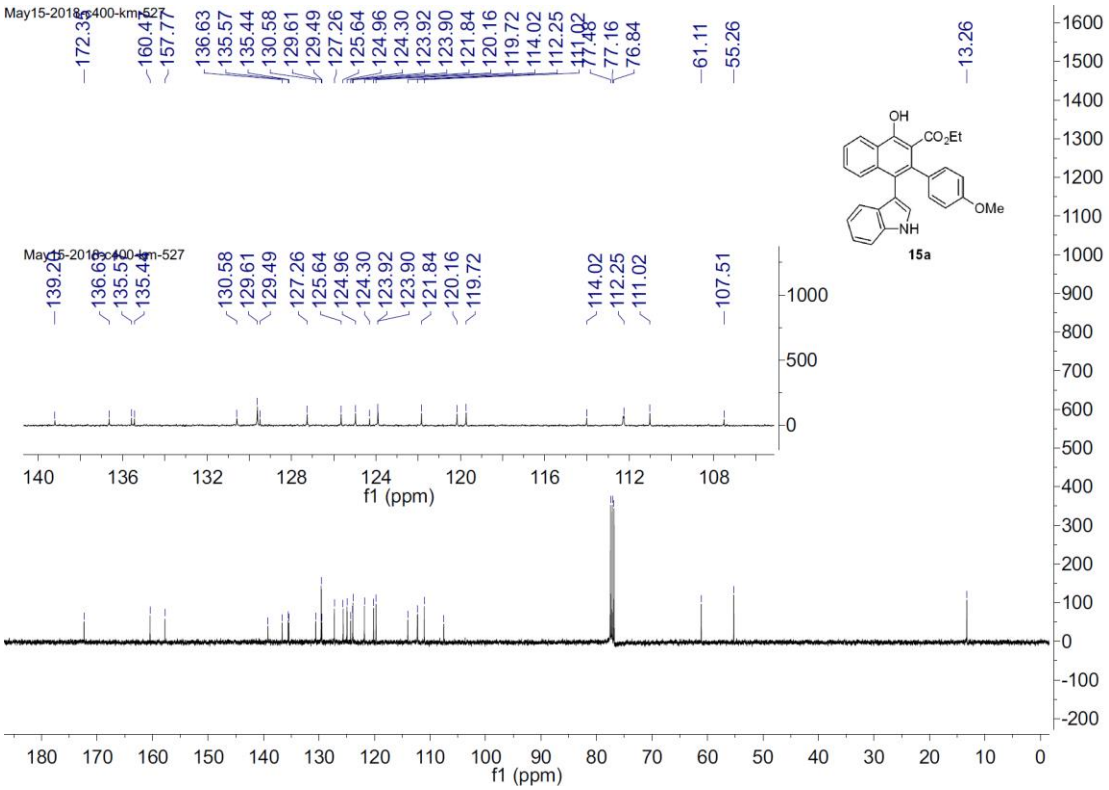


Figure S52. ^{13}C NMR spectra (400 MHz) of **15a** in $CDCl_3$, related to **Scheme 1**.

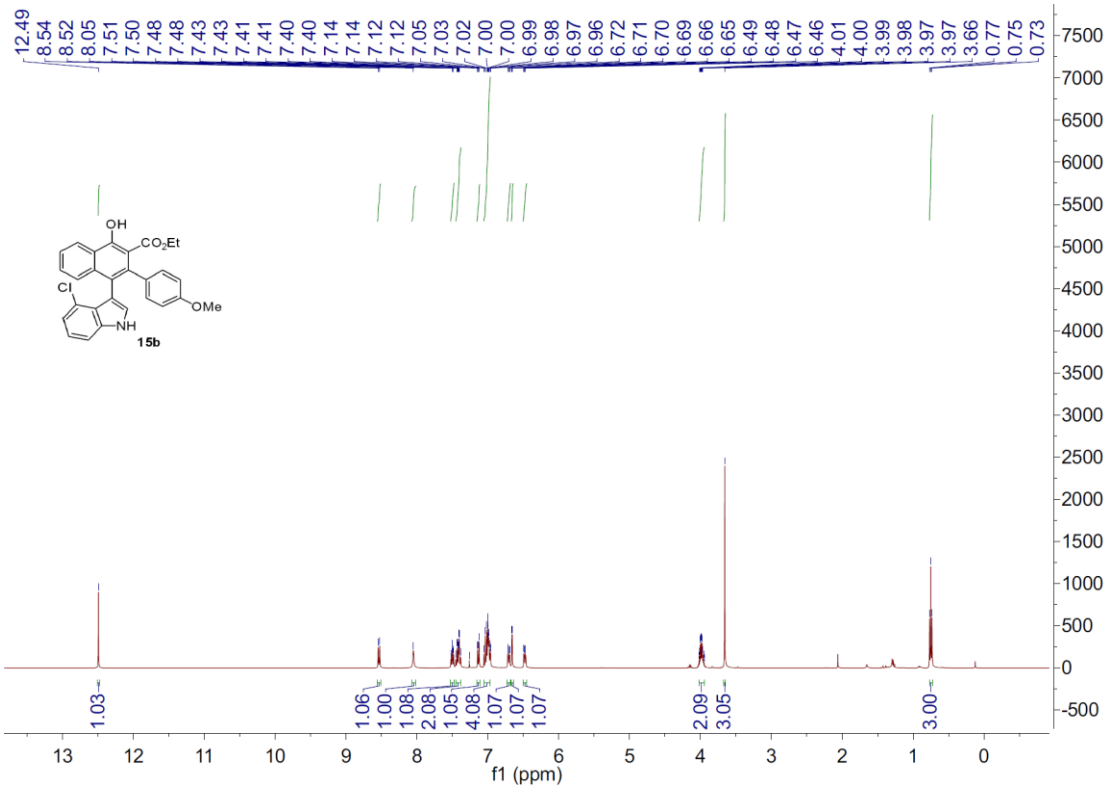


Figure S53. ^{1}H NMR spectra (400 MHz) of **15b** in $CDCl_3$, related to **Scheme 1**.

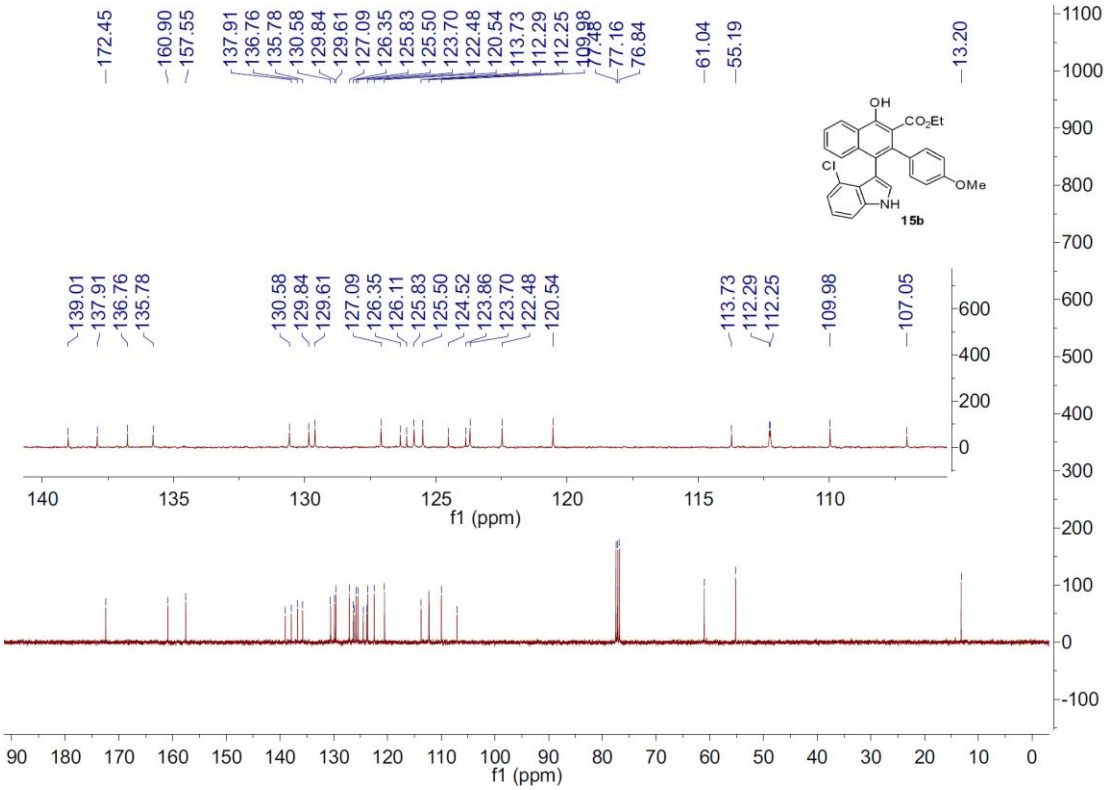


Figure S54. ^{13}C NMR spectra (400 MHz) of **15b** in $CDCl_3$, related to **Scheme 1**.

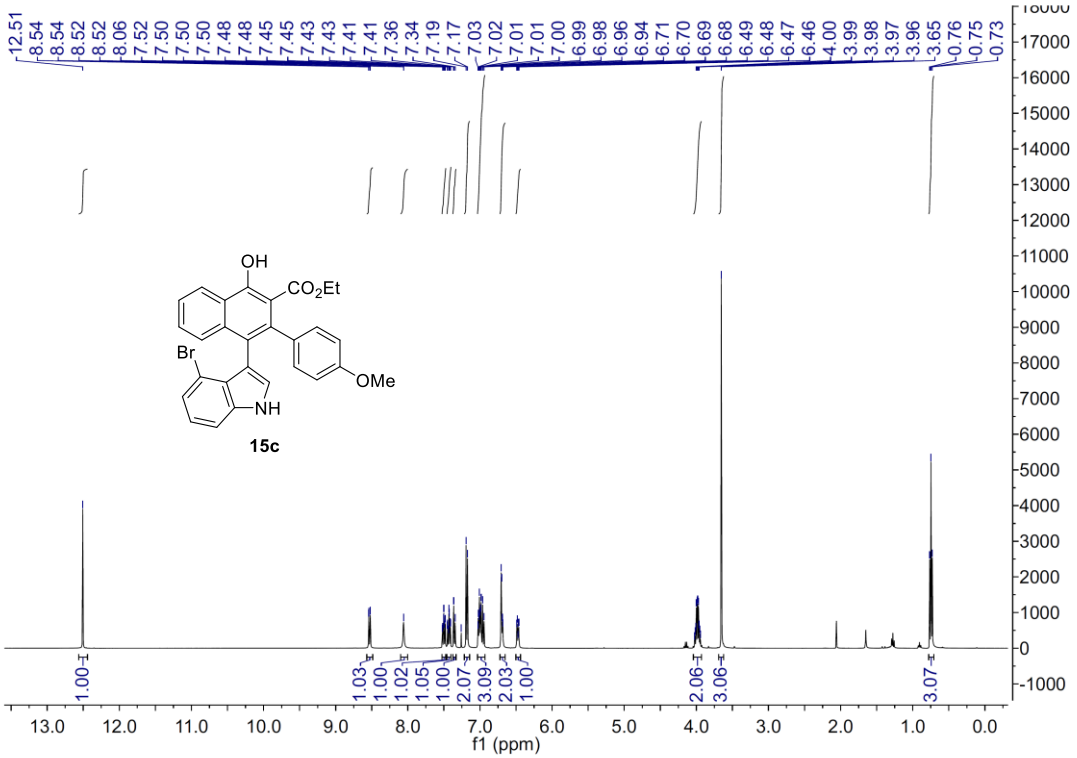


Figure S55. ^{1}H NMR spectra (400 MHz) of **15c** in $CDCl_3$, related to **Scheme 1**.

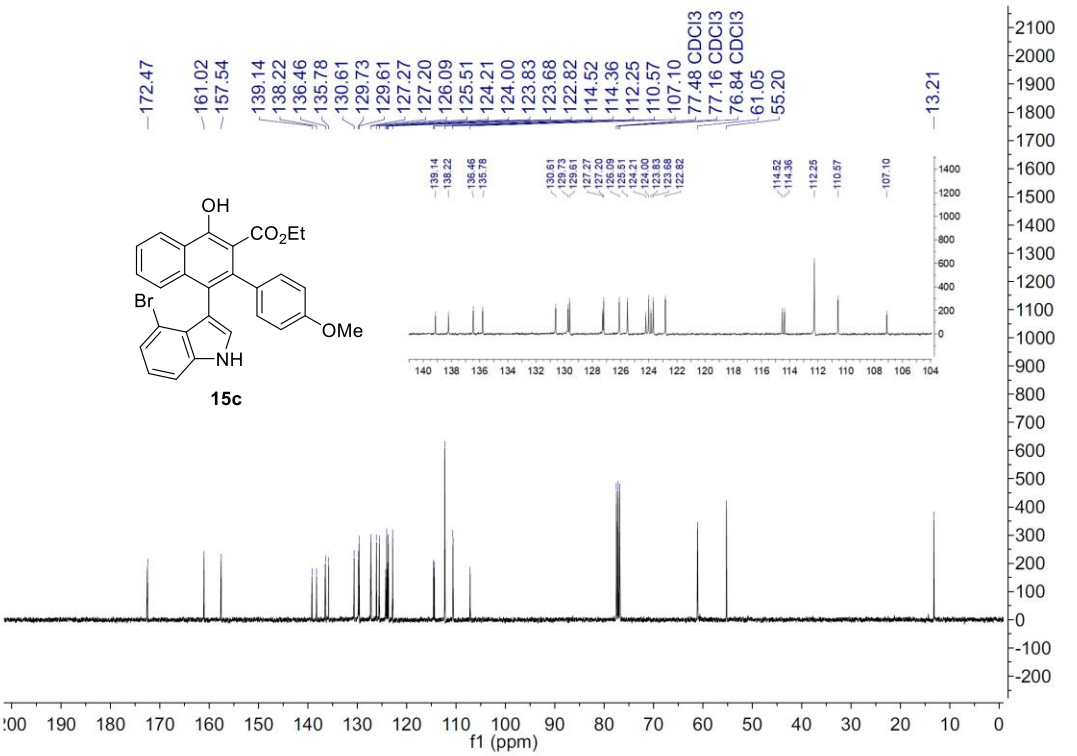


Figure S56. ^{13}C NMR spectra (400 MHz) of **15c** in $CDCl_3$, related to **Scheme 1**.

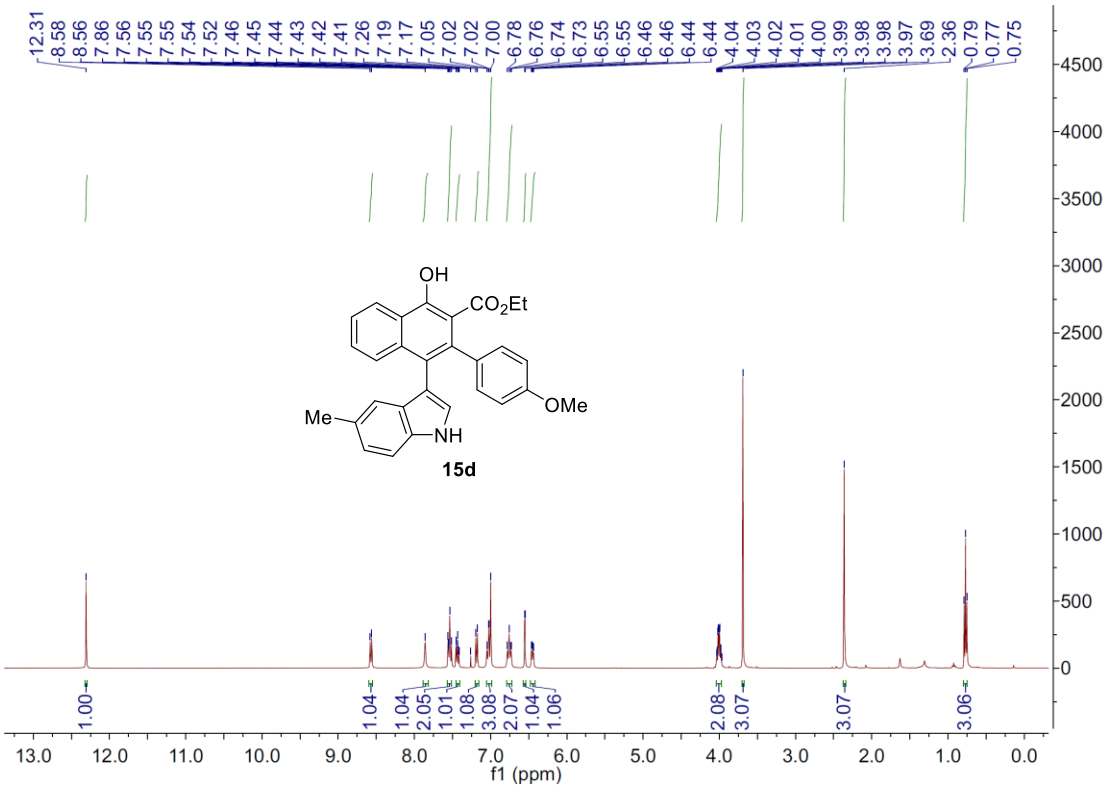


Figure S57. ^{1}H NMR spectra (400 MHz) of **15d** in $CDCl_3$, related to **Scheme 1**.

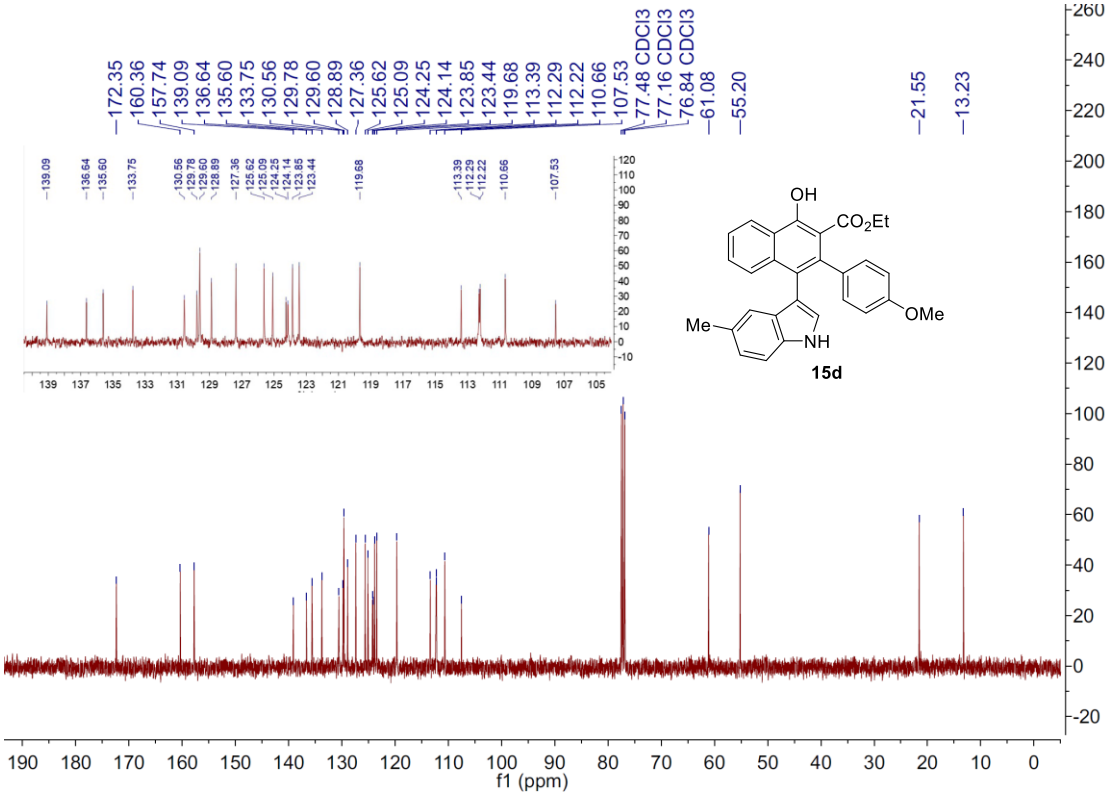


Figure S58. ^{13}C NMR spectra (400 MHz) of **15d** in $CDCl_3$, related to **Scheme 1**.

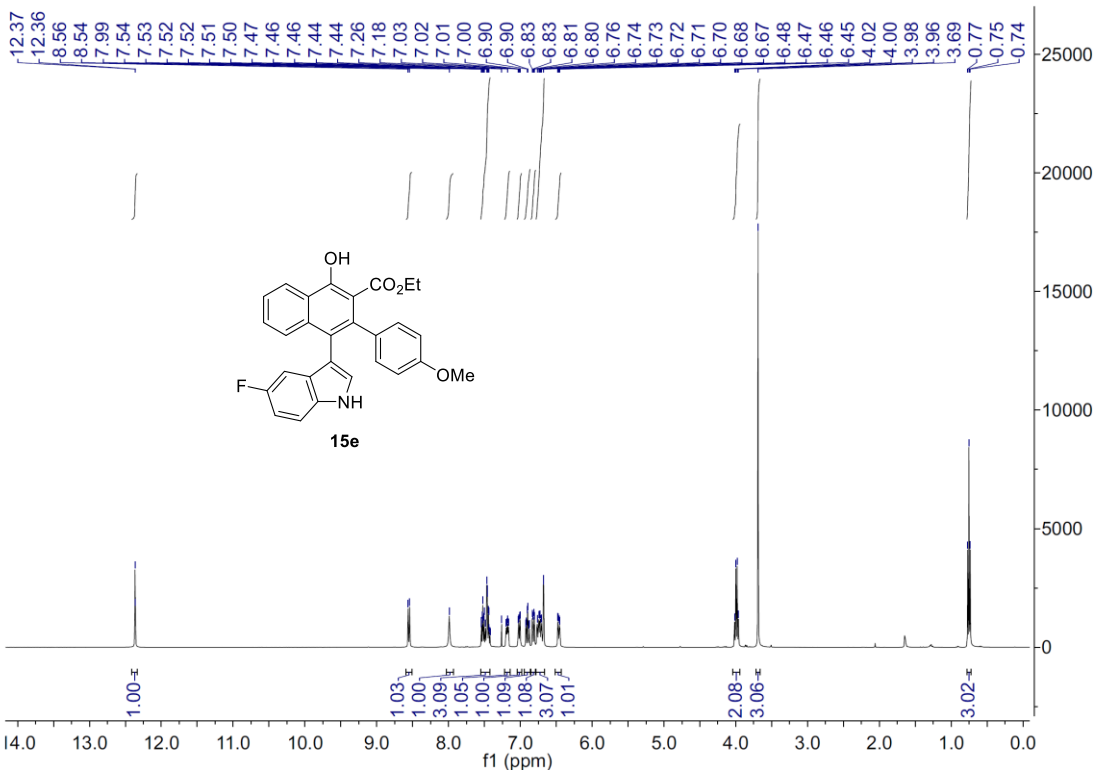


Figure S59. ^{1}H NMR spectra (400 MHz) of **15e** in $CDCl_3$, related to **Scheme 1**.

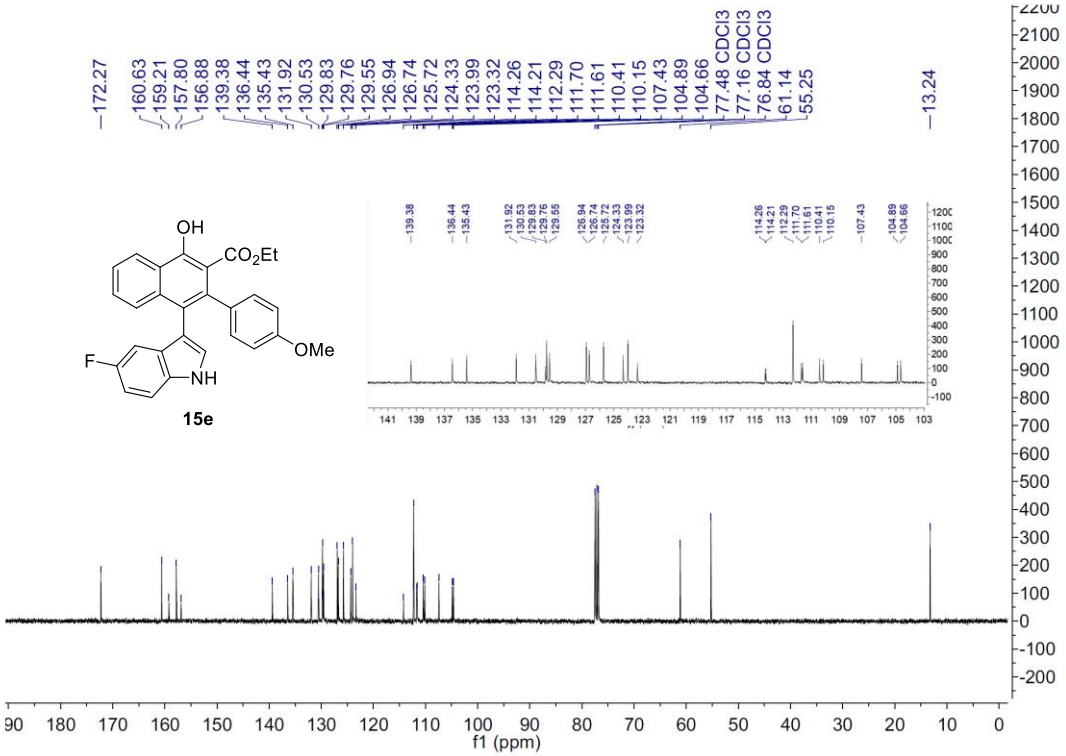


Figure S60. ^{13}C NMR spectra (400 MHz) of **15e** in $CDCl_3$, related to **Scheme 1**.

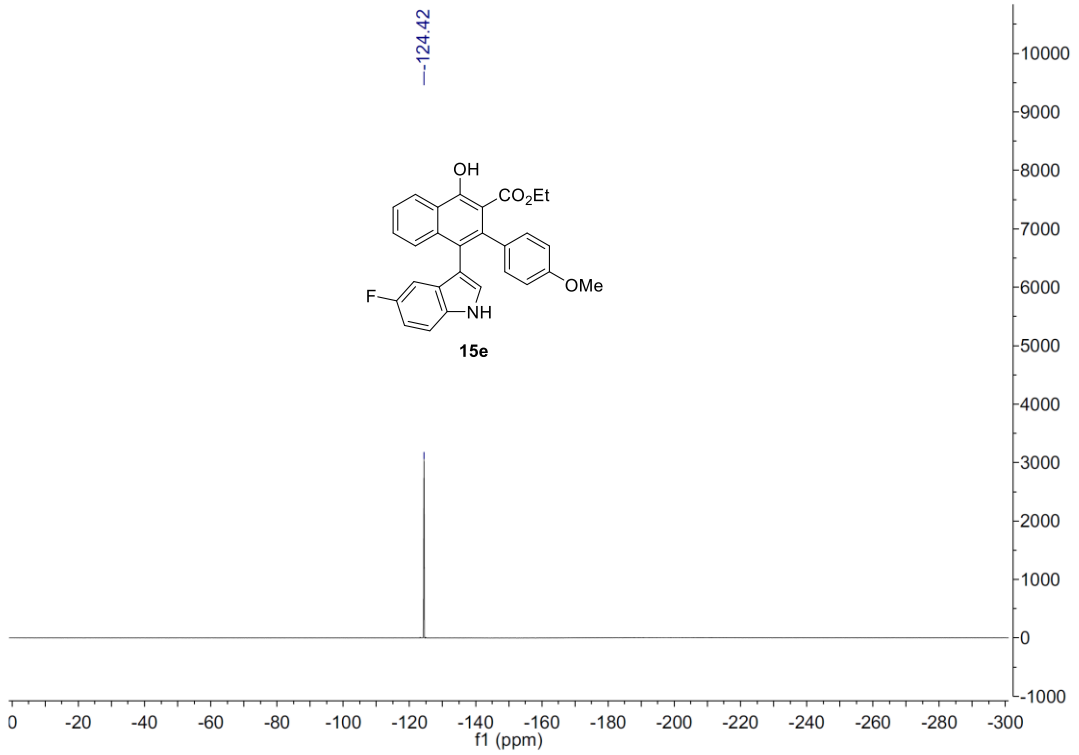


Figure S61. ^{19}F NMR spectra (400 MHz) of **15e** in $CDCl_3$, related to **Scheme 1**.

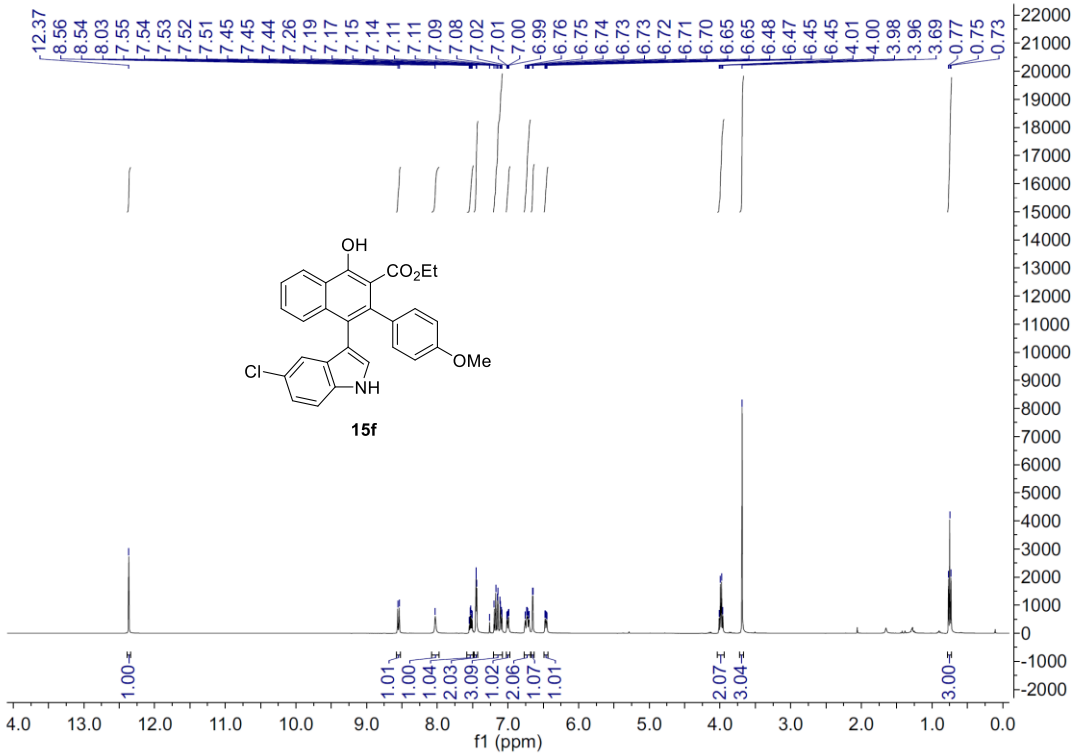


Figure S62. ^{1}H NMR spectra (400 MHz) of **15f** in $CDCl_3$, related to **Scheme 1**.

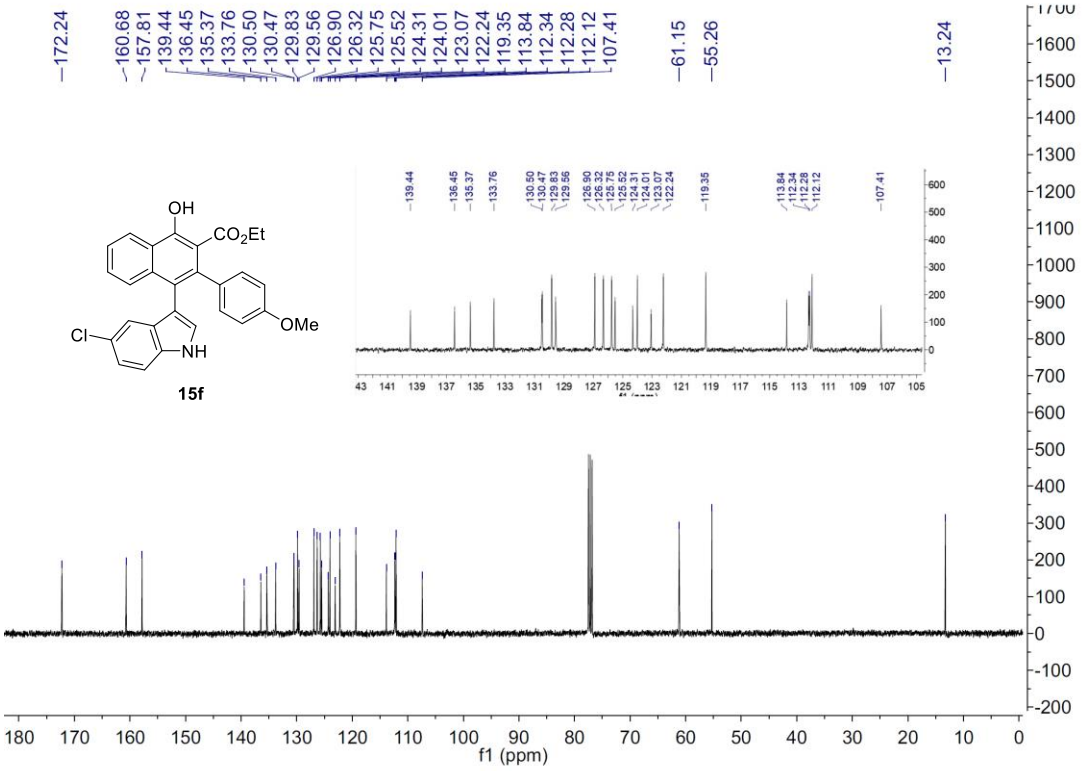


Figure S63. ^{13}C NMR spectra (400 MHz) of **15f** in $CDCl_3$, related to **Scheme 1**.

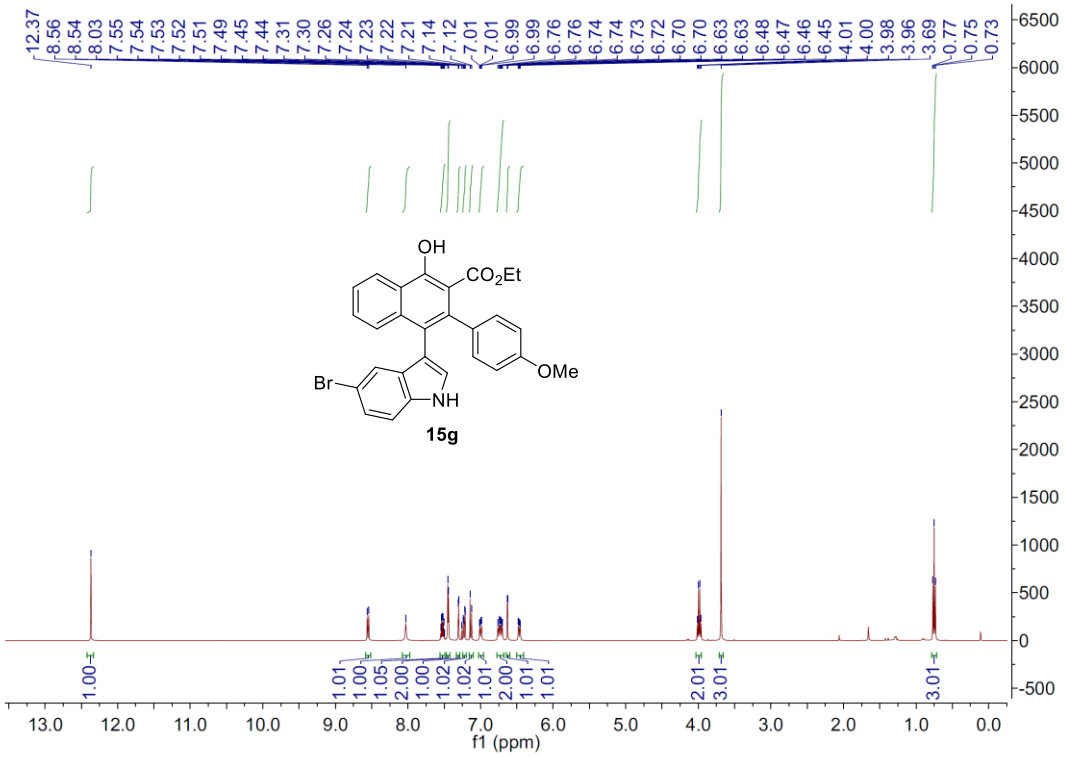


Figure S64. ^{1}H NMR spectra (400 MHz) of **15g** in $CDCl_3$, related to **Scheme 1**.

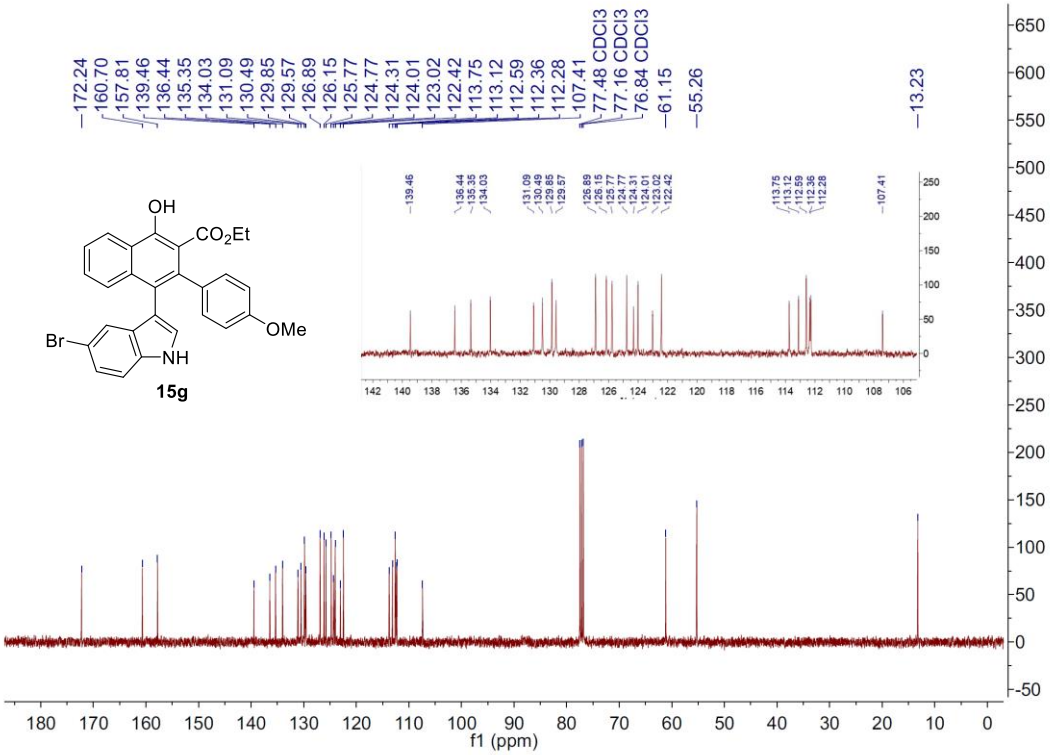


Figure S65. ^{13}C NMR spectra (400 MHz) of **15g** in $CDCl_3$, related to **Scheme 1**.

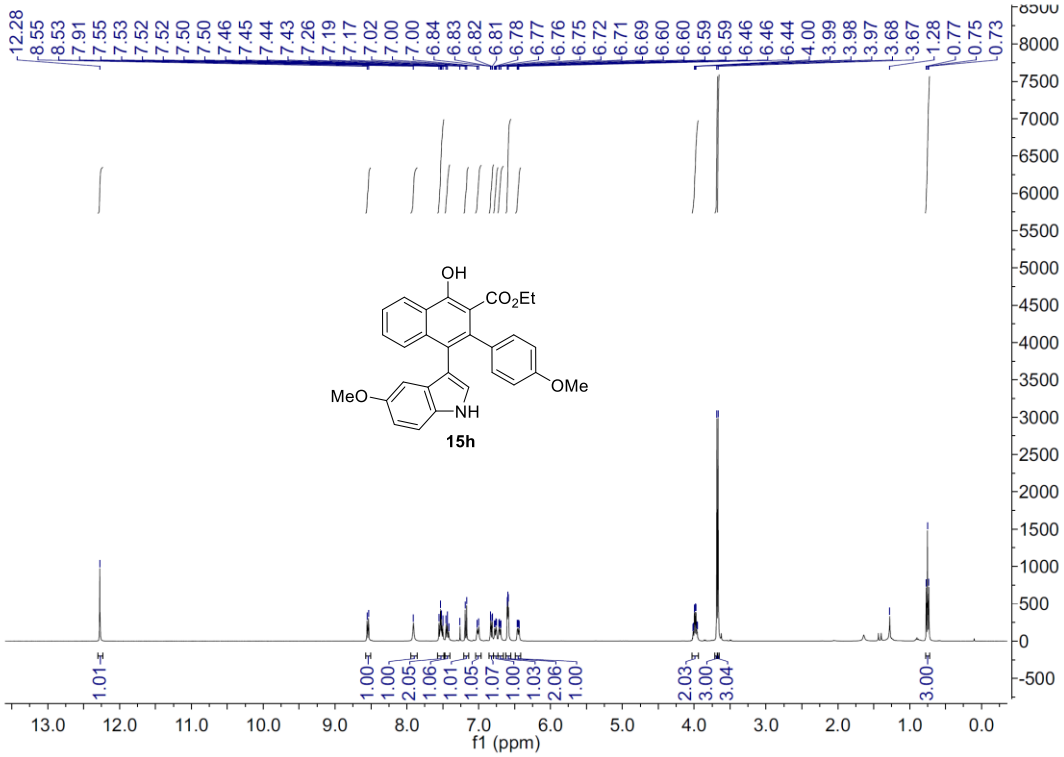


Figure S66. ^{1}H NMR spectra (400 MHz) of **15h** in $CDCl_3$, related to **Scheme 1**.

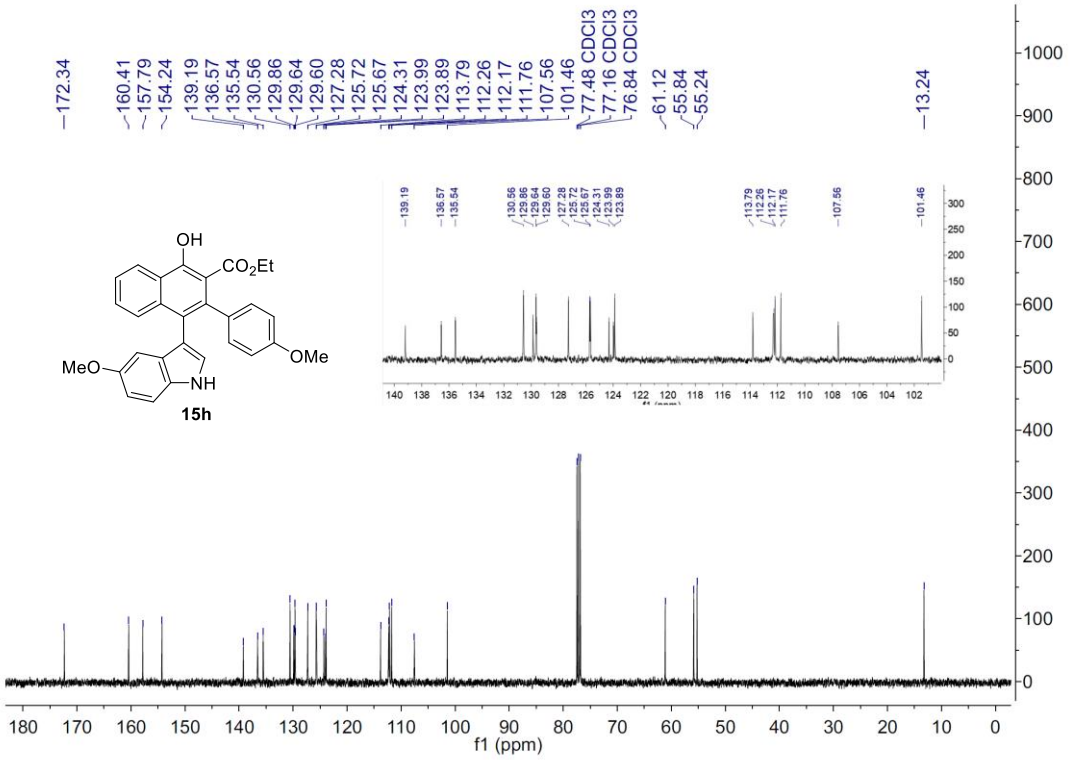


Figure S67. ^{13}C NMR spectra (400 MHz) of **15h** in $CDCl_3$, related to **Scheme 1**.

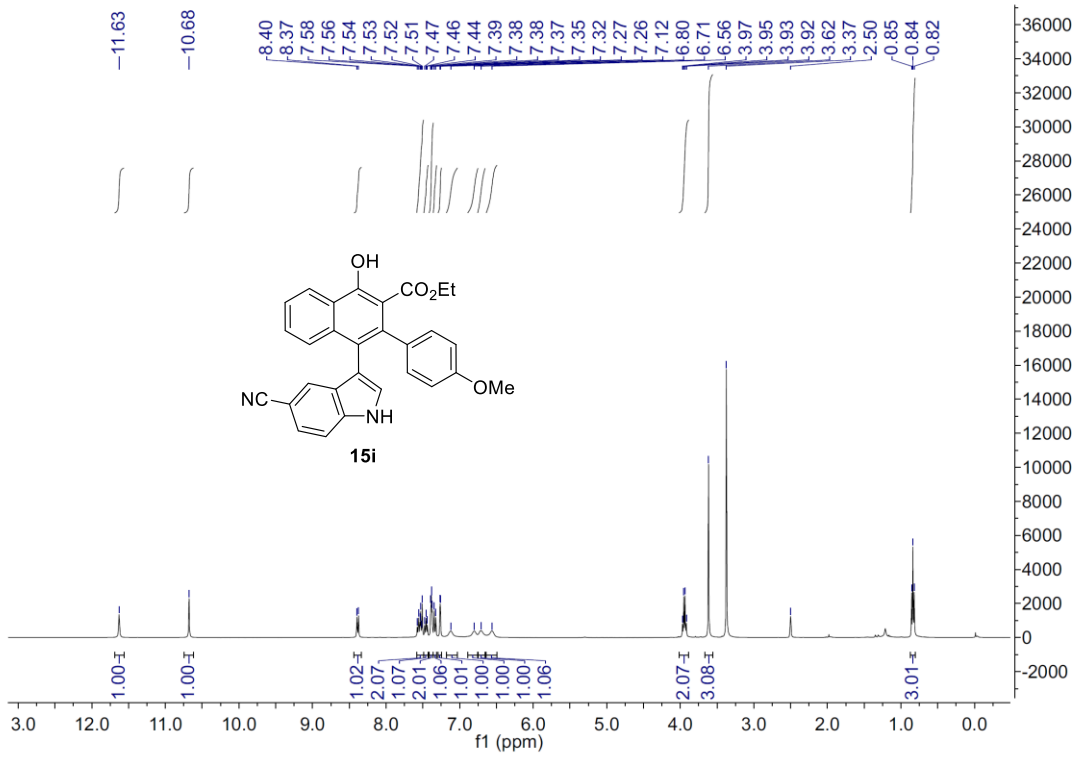


Figure S68. ^{1}H NMR spectra (400 MHz) of **15i** in DMSO-d_6, related to **Scheme 1**.

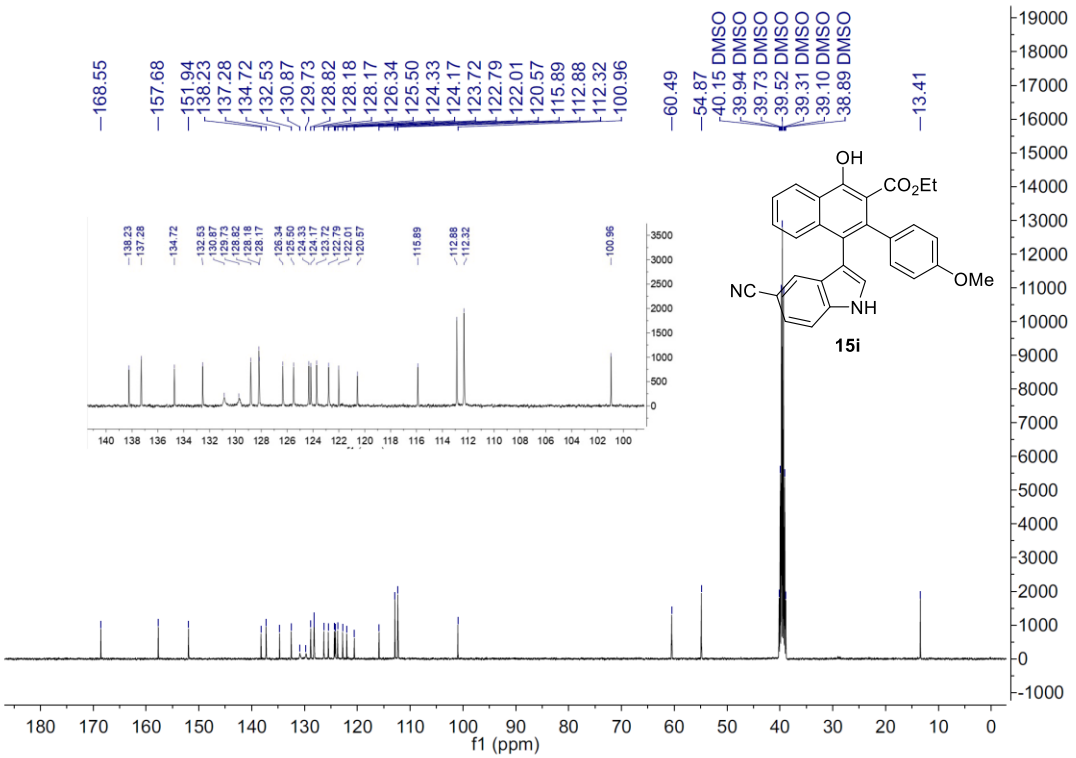


Figure S69. ^{13}C NMR spectra (400 MHz) of **15i** in DMSO-d_6, related to **Scheme 1**.

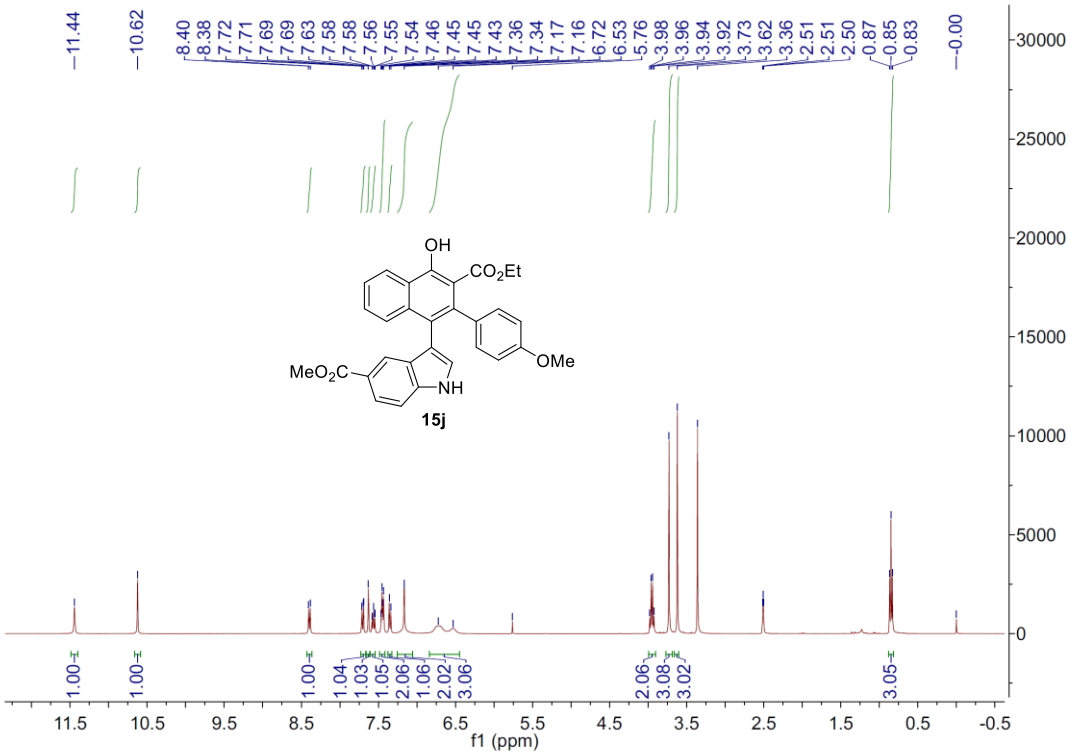


Figure S70. ^{1}H NMR spectra (400 MHz) of **15j** in DMSO-d_6, related to **Scheme 1**.

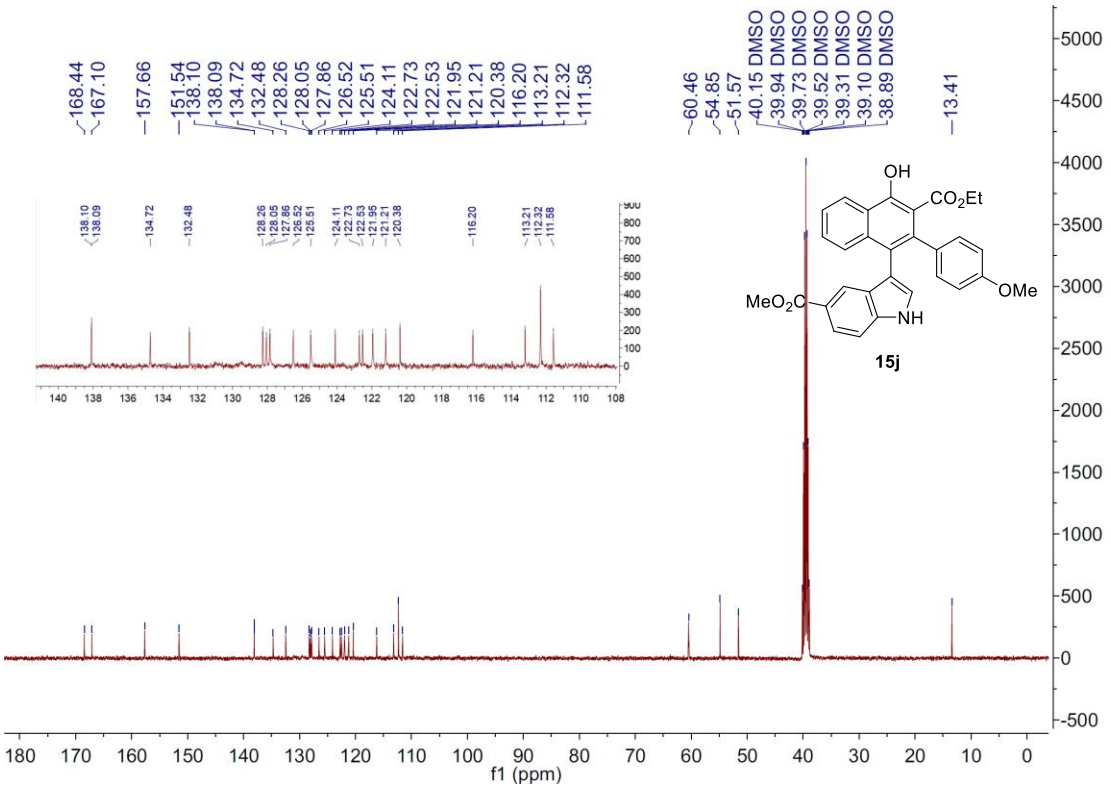


Figure S71. ^{13}C NMR spectra (400 MHz) of **15j** in DMSO-d_6, related to **Scheme 1**.

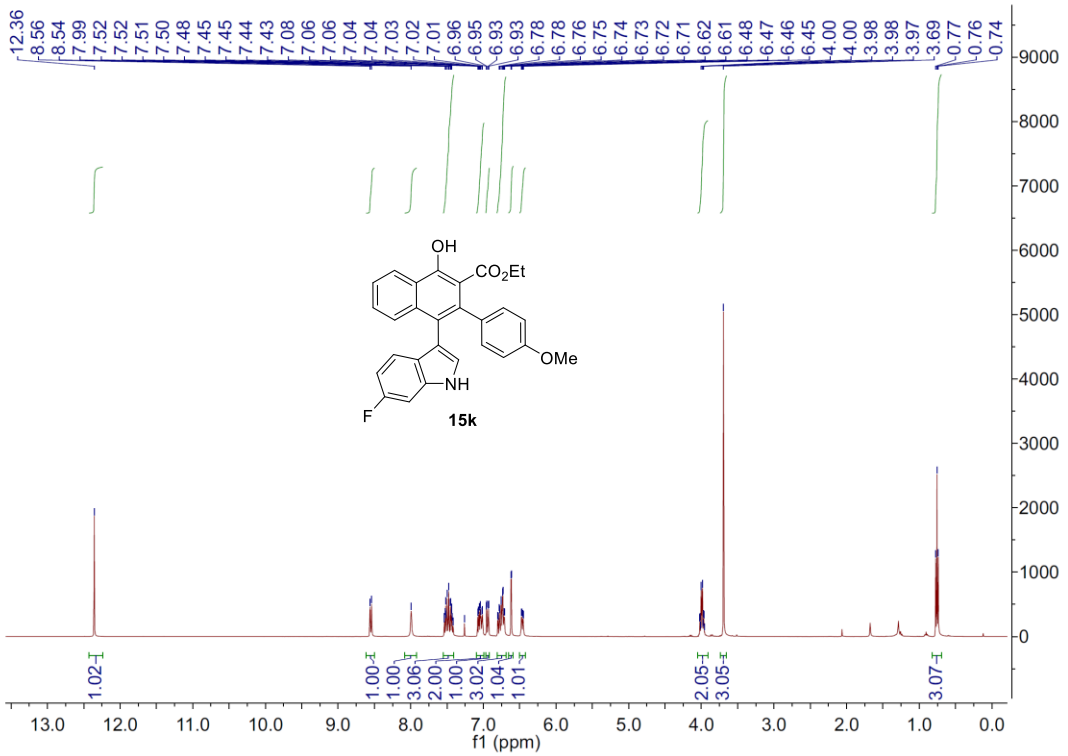


Figure S72. ^{1}H NMR spectra (400 MHz) of **15k** in $CDCl_3$, related to **Scheme 1**.

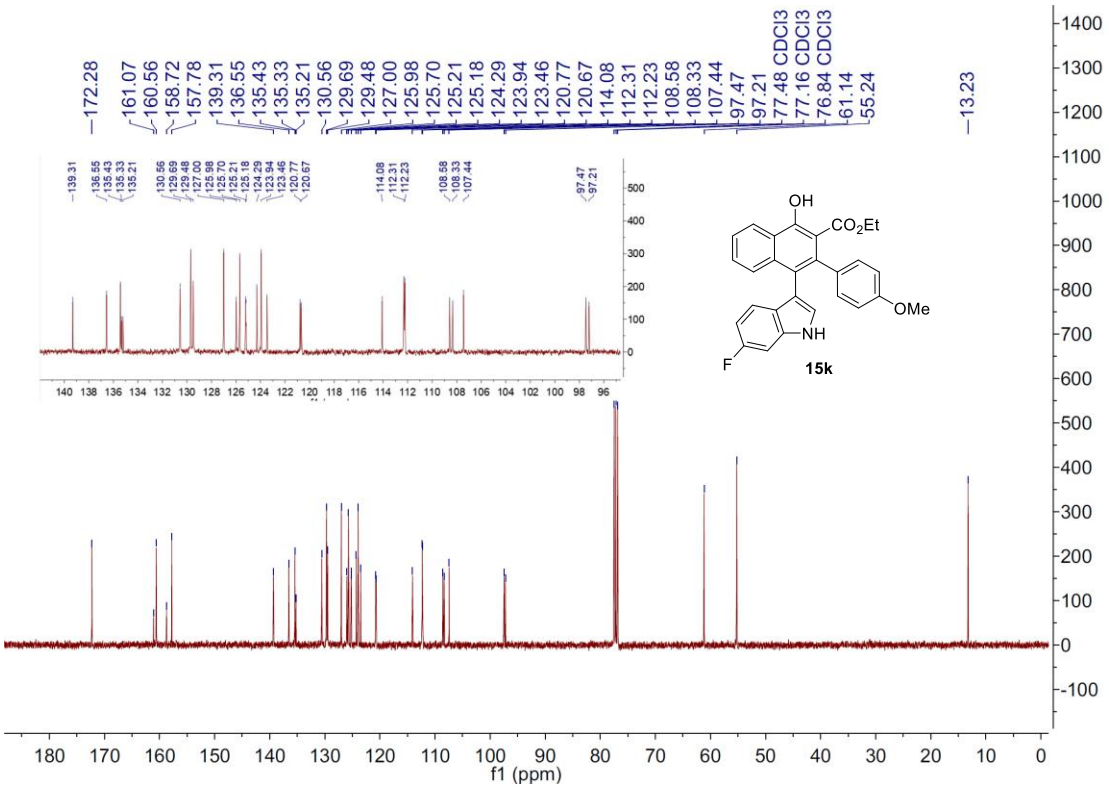


Figure S73. ^{13}C NMR spectra (400 MHz) of **15k** in $CDCl_3$, related to **Scheme 1**.

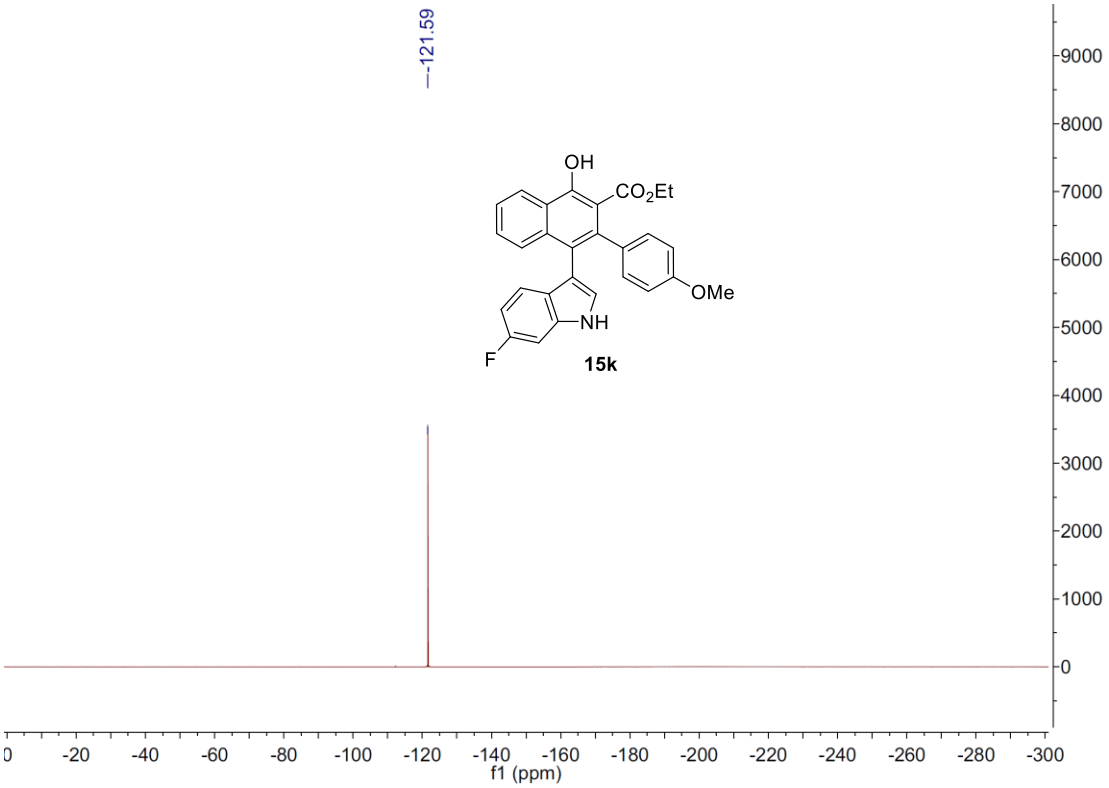


Figure S74. ^{19}F NMR spectra (400 MHz) of **15k** in $CDCl_3$, related to **Scheme 1**.

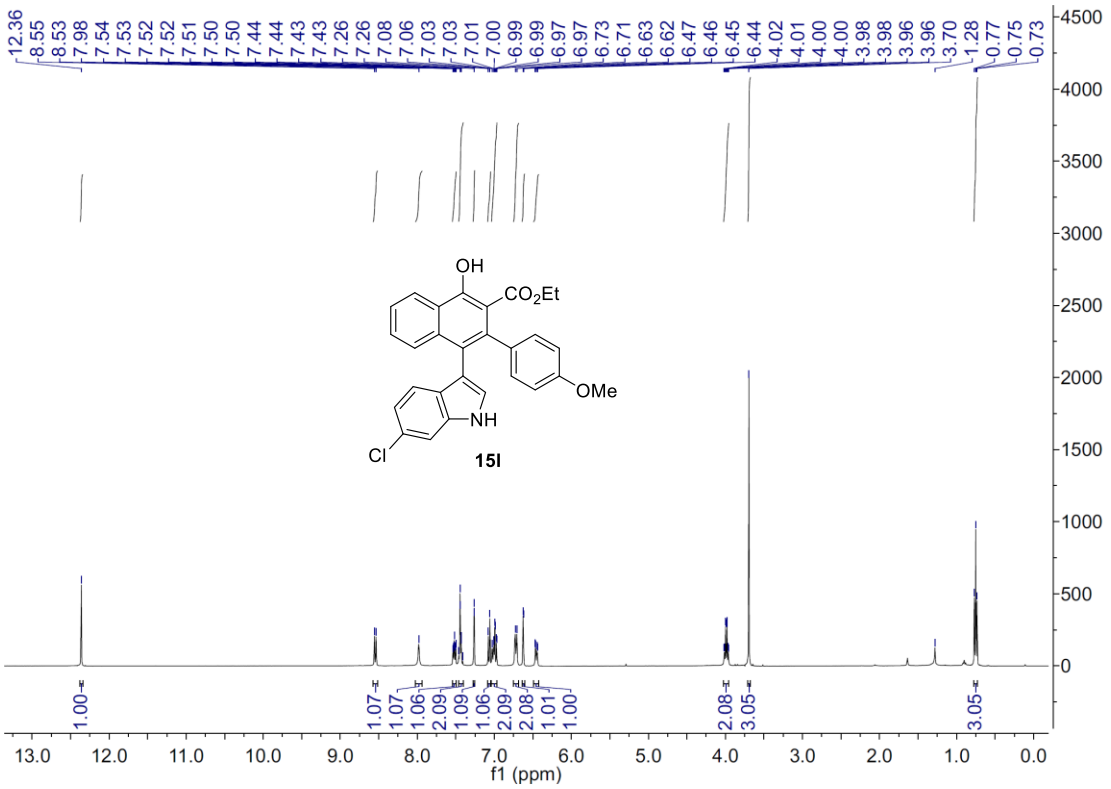


Figure S75. ^{1}H NMR spectra (400 MHz) of **15l** in $CDCl_3$, related to **Scheme 1**.

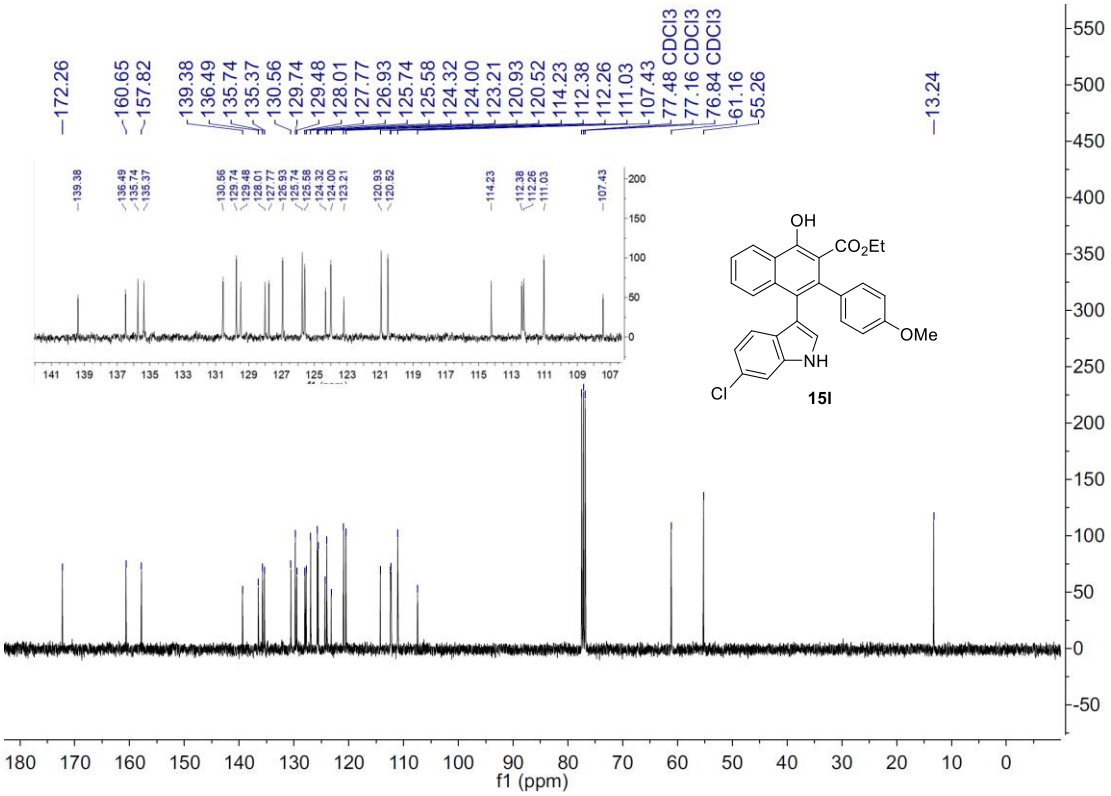


Figure S76. ^{13}C NMR spectra (400 MHz) of **15l** in $CDCl_3$, related to **Scheme 1**.

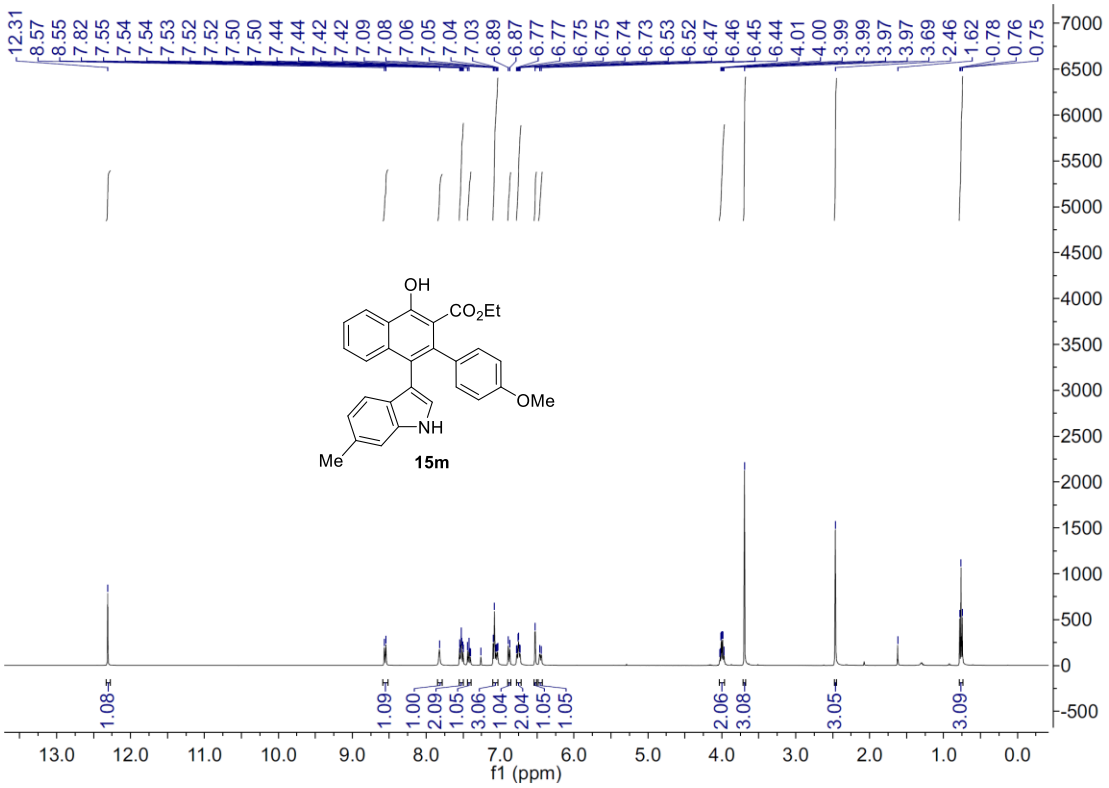


Figure S77. ^{1}H NMR spectra (400 MHz) of **15m** in $CDCl_3$, related to **Scheme 1**.

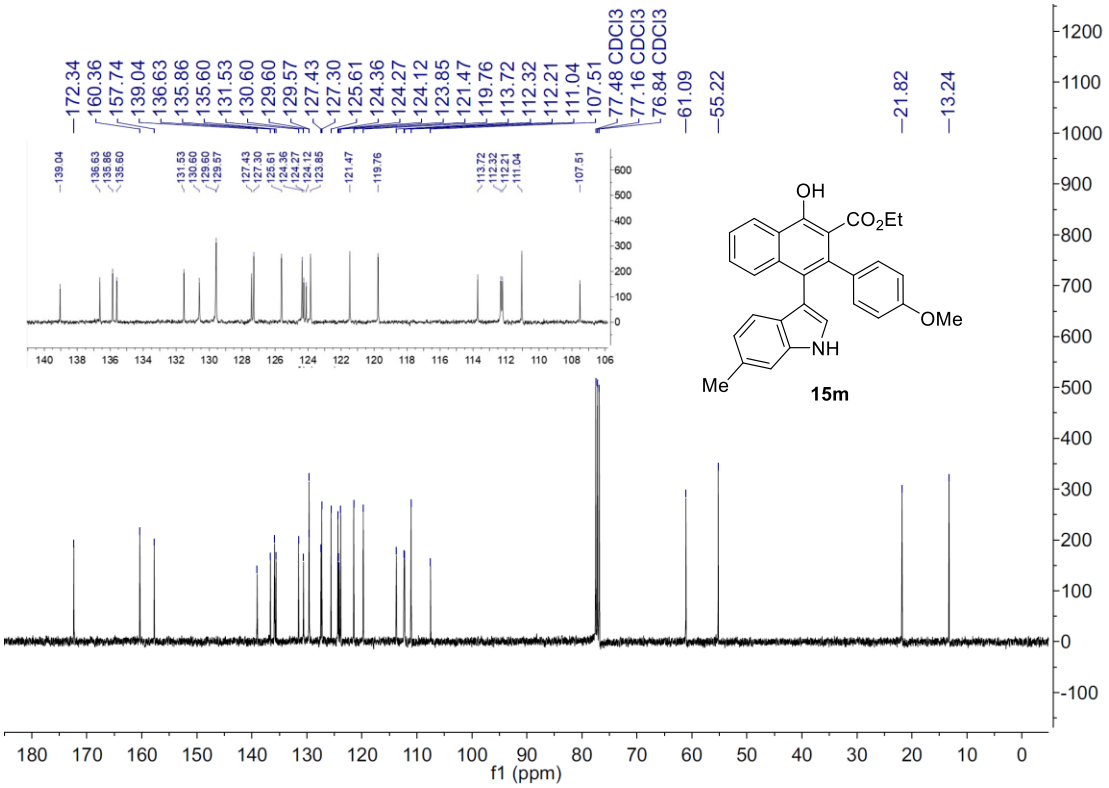


Figure S78. ^{13}C NMR spectra (400 MHz) of **15m** in $CDCl_3$, related to **Scheme 1**.

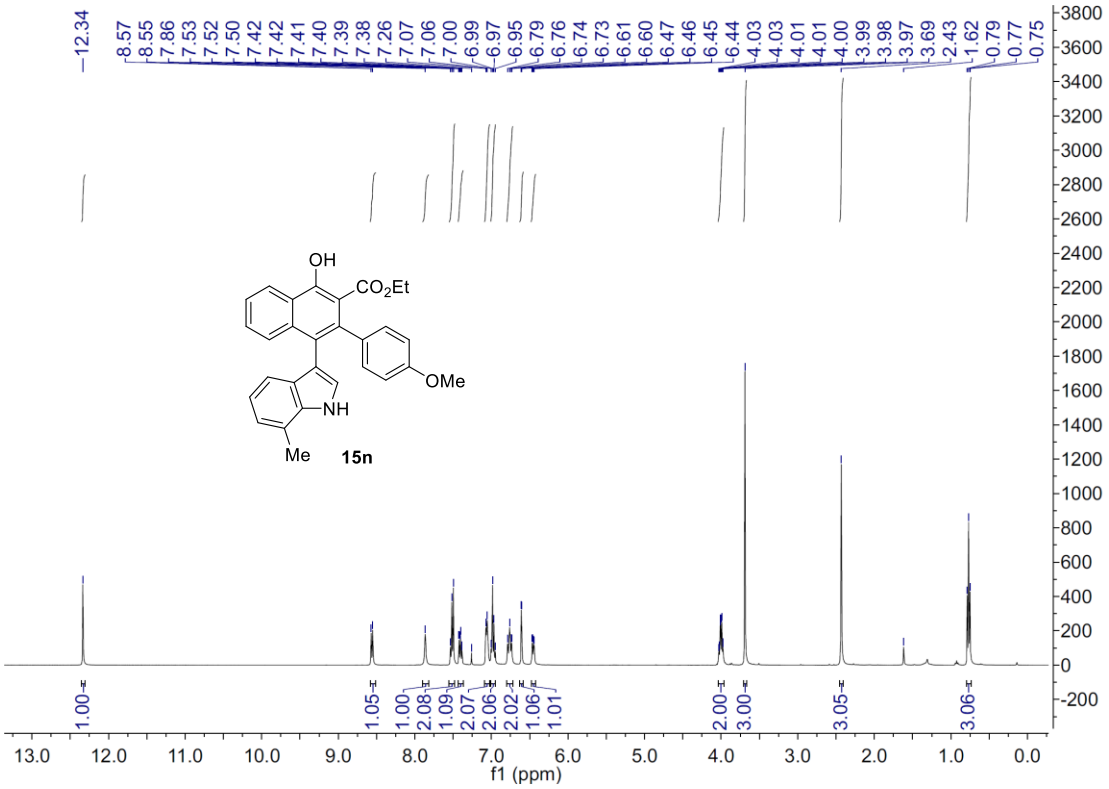


Figure S79. ^{1}H NMR spectra (400 MHz) of **15n** in $CDCl_3$, related to **Scheme 1**.

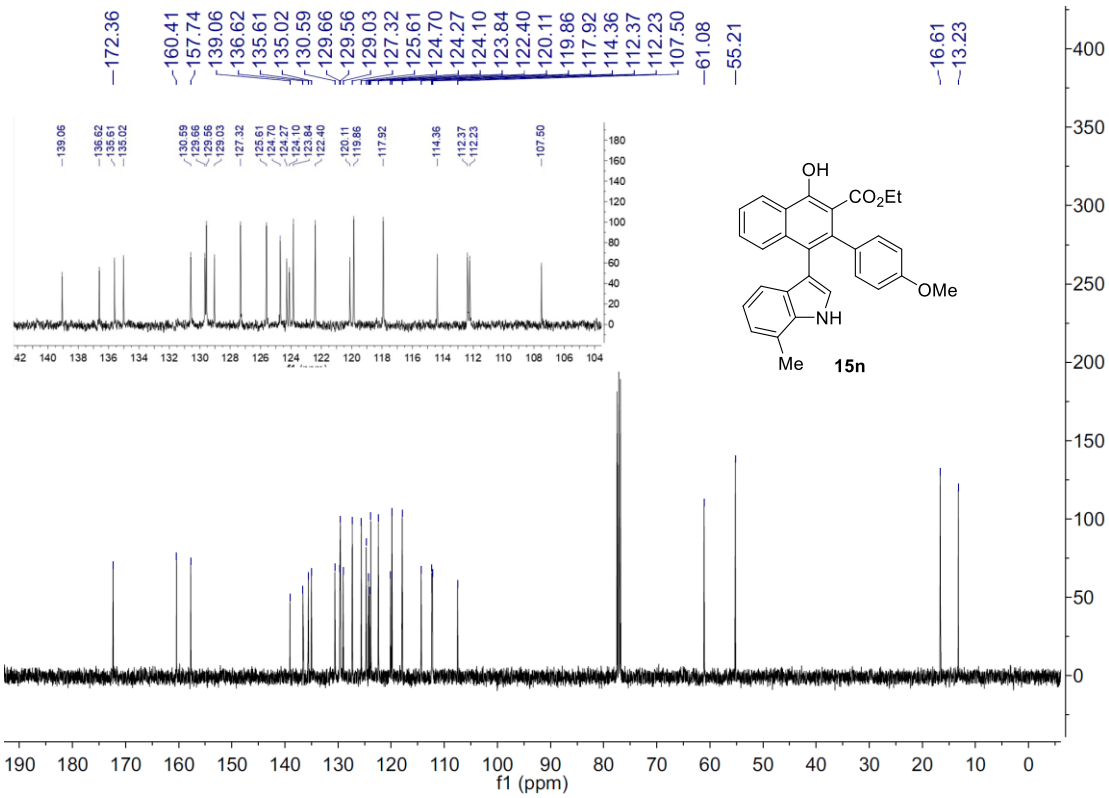


Figure S80. ^{13}C NMR spectra (400 MHz) of **15n** in $CDCl_3$, related to **Scheme 1**.

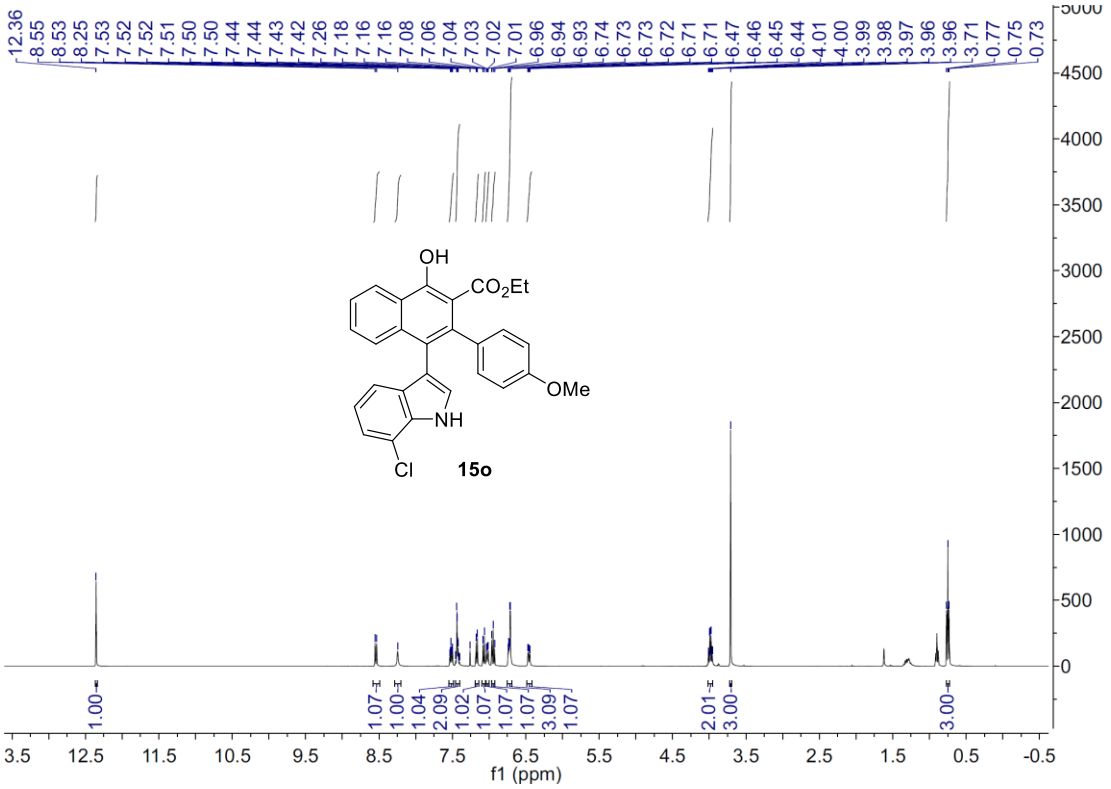


Figure S81. ^{1}H NMR spectra (400 MHz) of **15o** in $CDCl_3$, related to **Scheme 1**.

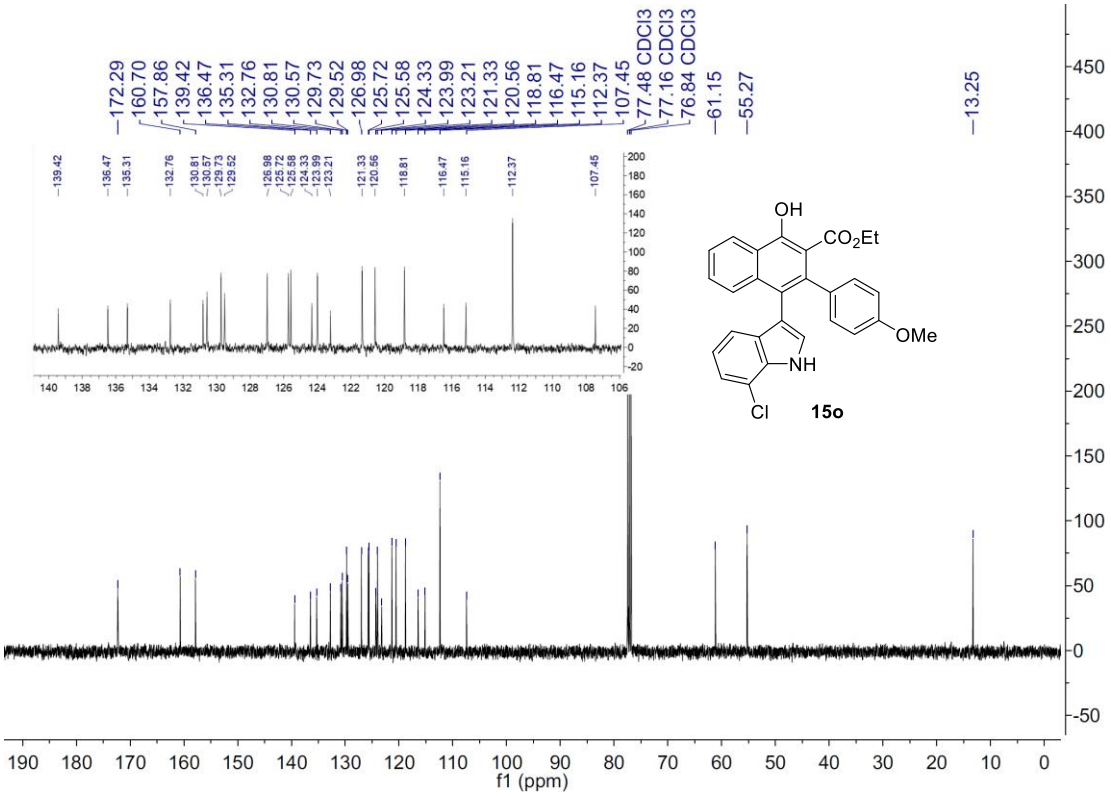


Figure S82. ^{13}C NMR spectra (400 MHz) of **15o** in $CDCl_3$, related to **Scheme 1**.

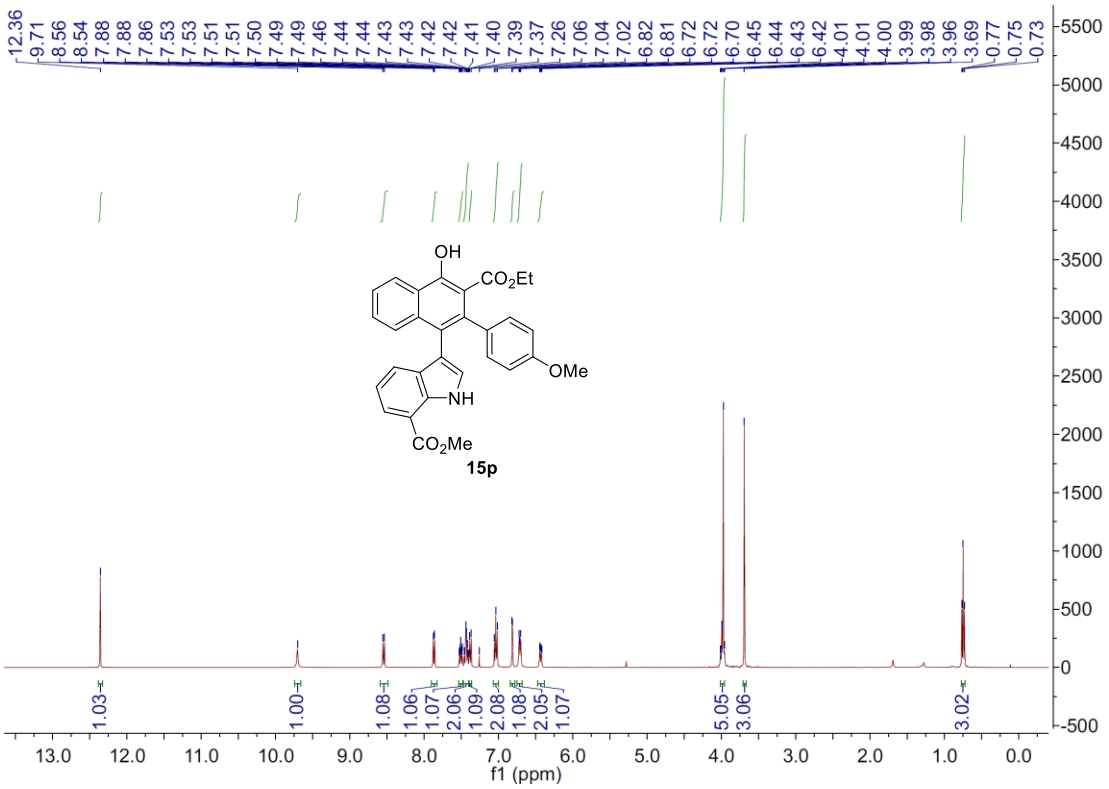


Figure S83. ^{1}H NMR spectra (400 MHz) of **15p** in $CDCl_3$, related to **Scheme 1**.

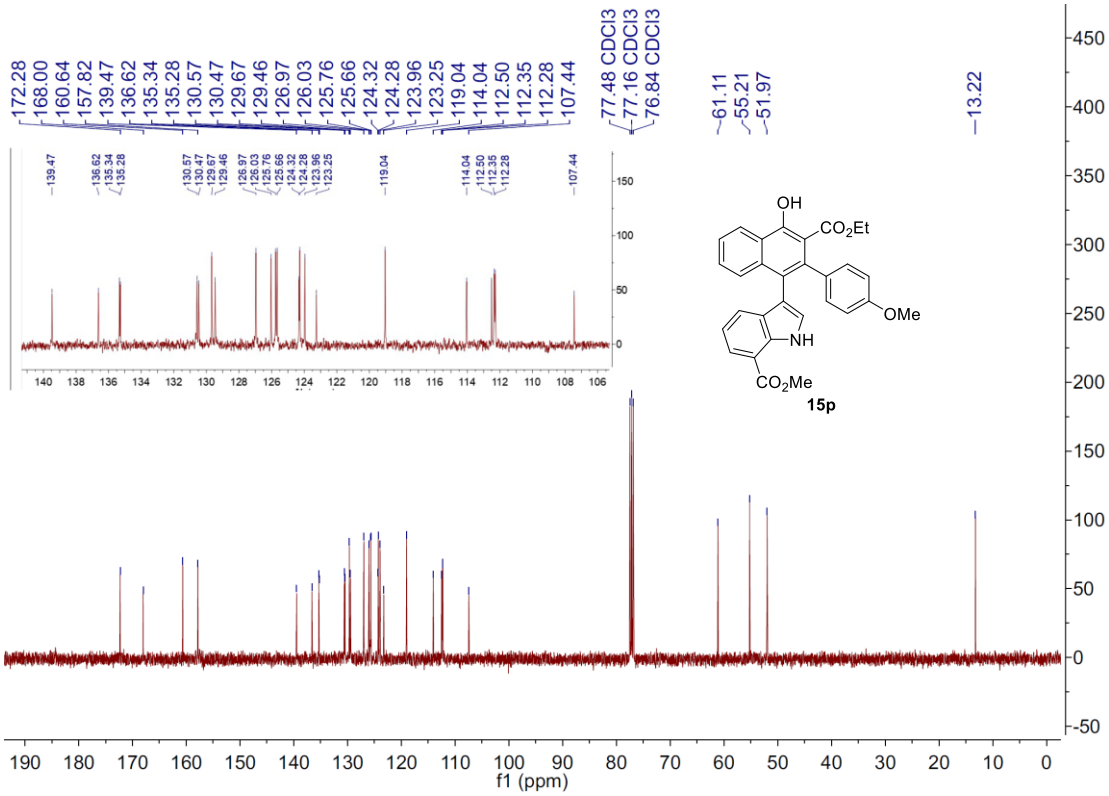


Figure S84. ^{13}C NMR spectra (400 MHz) of **15p** in $CDCl_3$, related to **Scheme 1**.

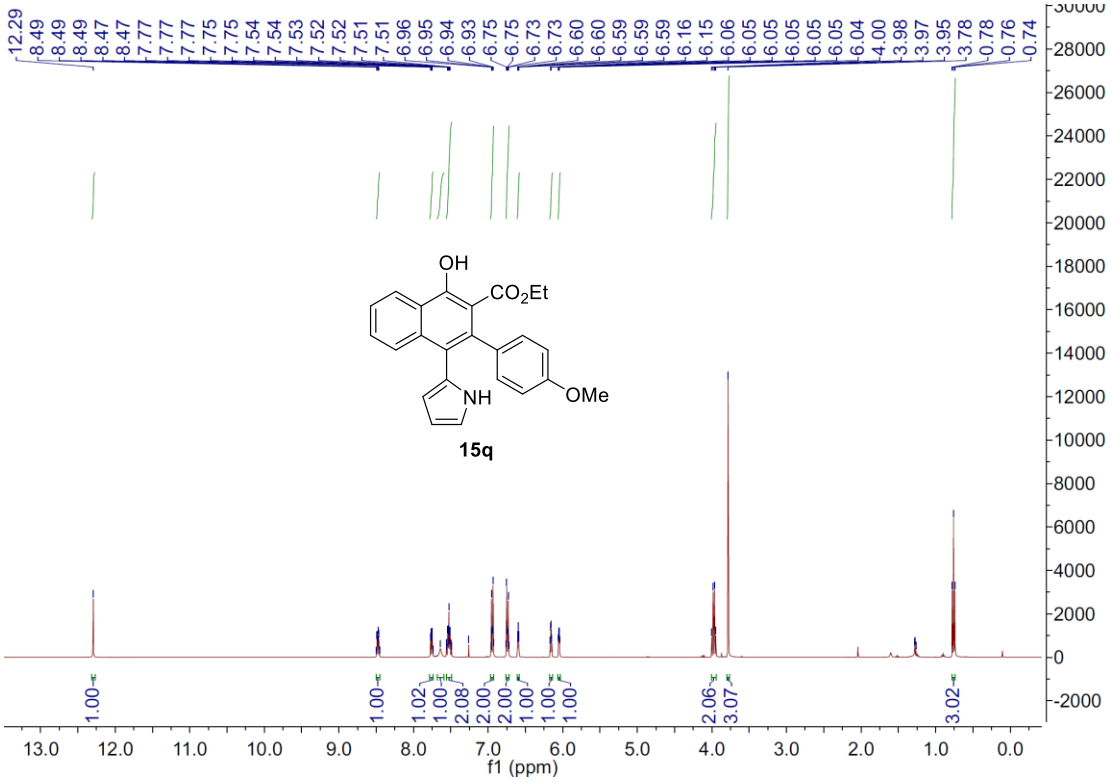


Figure S85. ^{1}H NMR spectra (400 MHz) of **15q** in $CDCl_3$, related to **Scheme 1**.

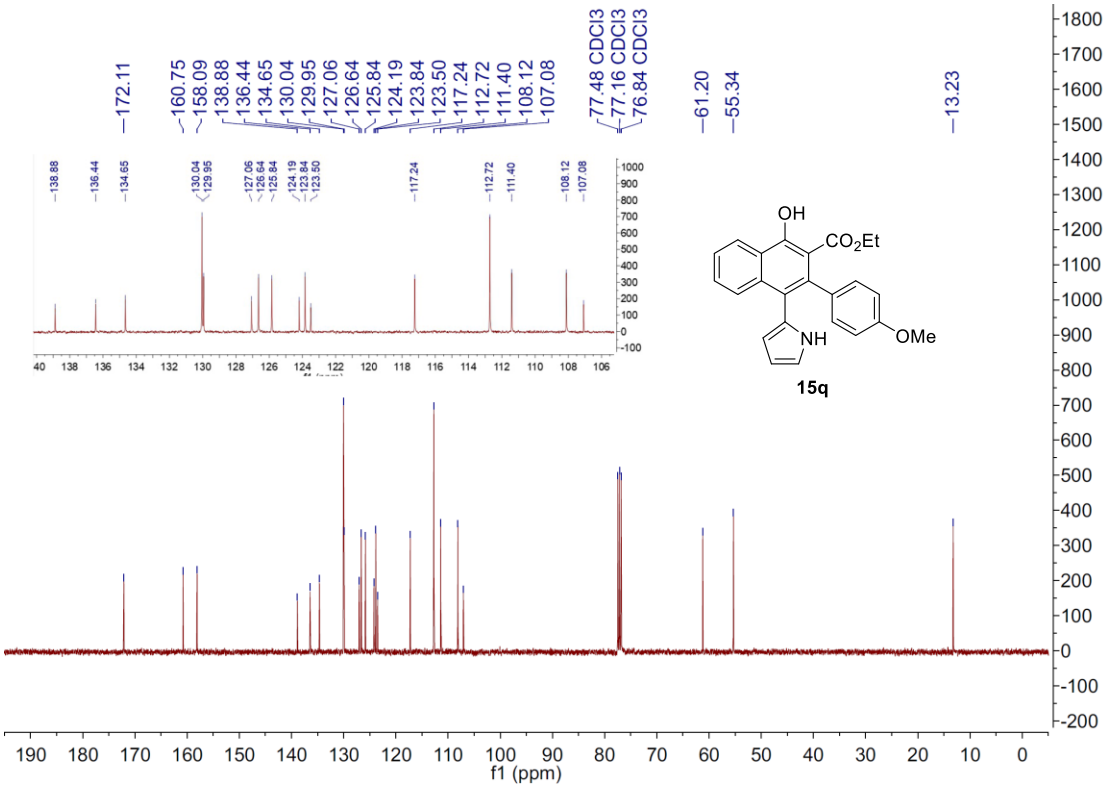


Figure S86. ^{13}C NMR spectra (400 MHz) of **15q** in $CDCl_3$, related to **Scheme 1**.

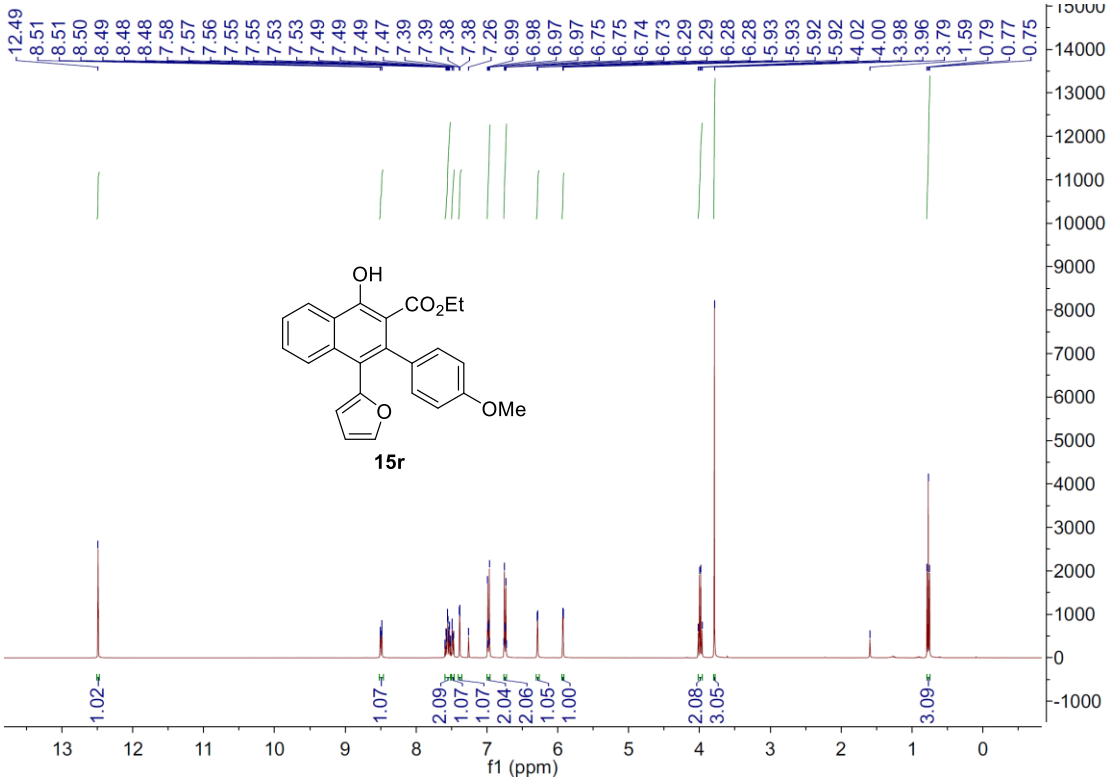


Figure S87. ^{1}H NMR spectra (400 MHz) of **15r** in $CDCl_3$, related to **Scheme 1**.

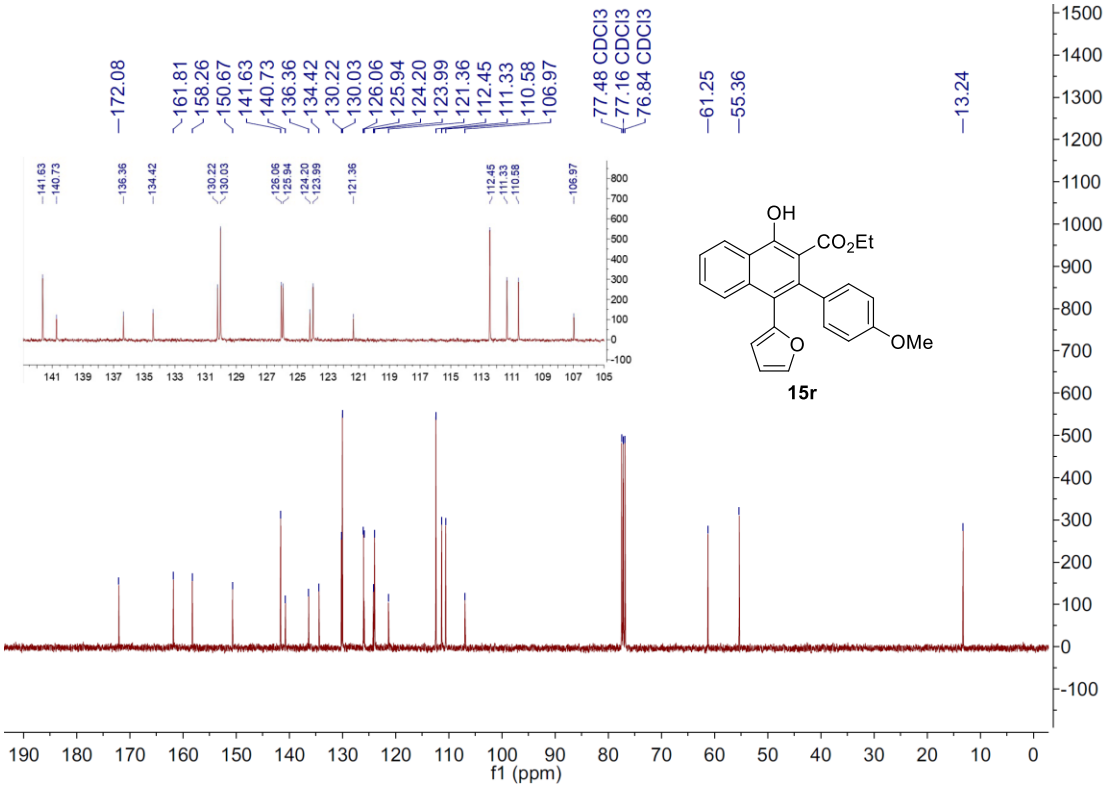


Figure S88. ^{13}C NMR spectra (400 MHz) of **15r** in $CDCl_3$, related to **Scheme 1**.

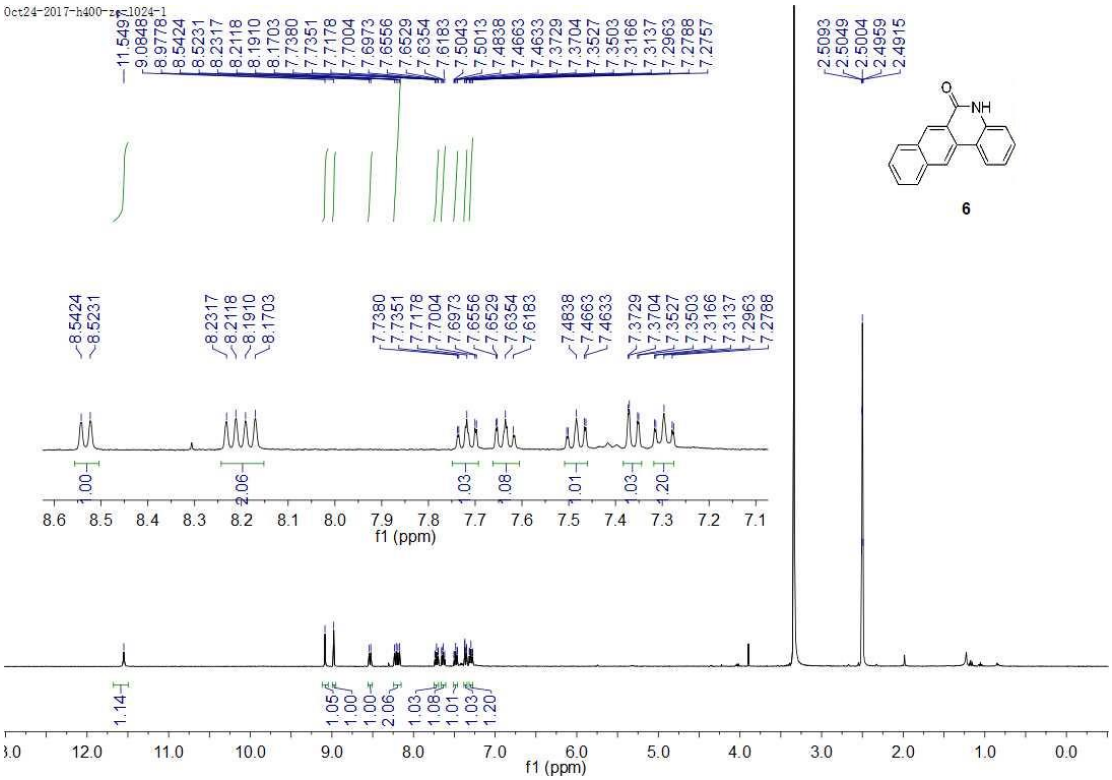


Figure S89. ^{1}H NMR spectra (400 MHz) of **6** in DMSO-d_6, related to **Figure 2A**.

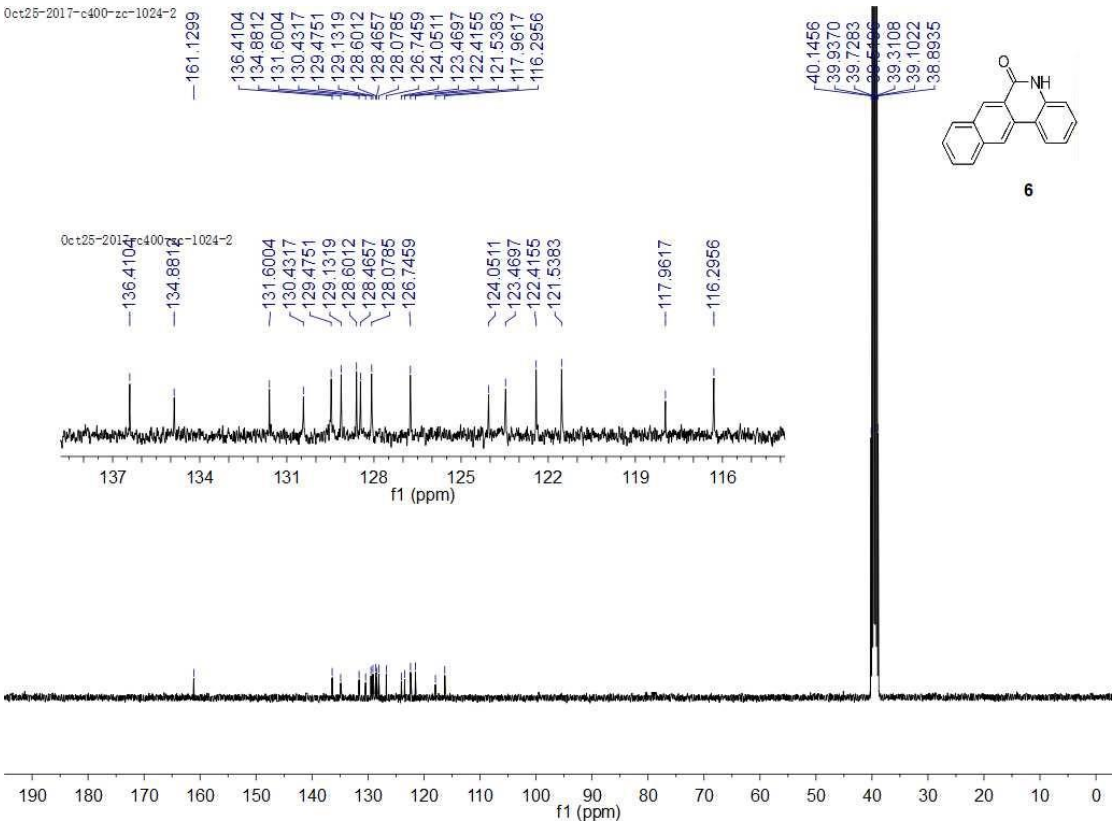


Figure S90. ^{13}C NMR spectra (400 MHz) of **6** in DMSO-d_6, related to **Figure 2A**.

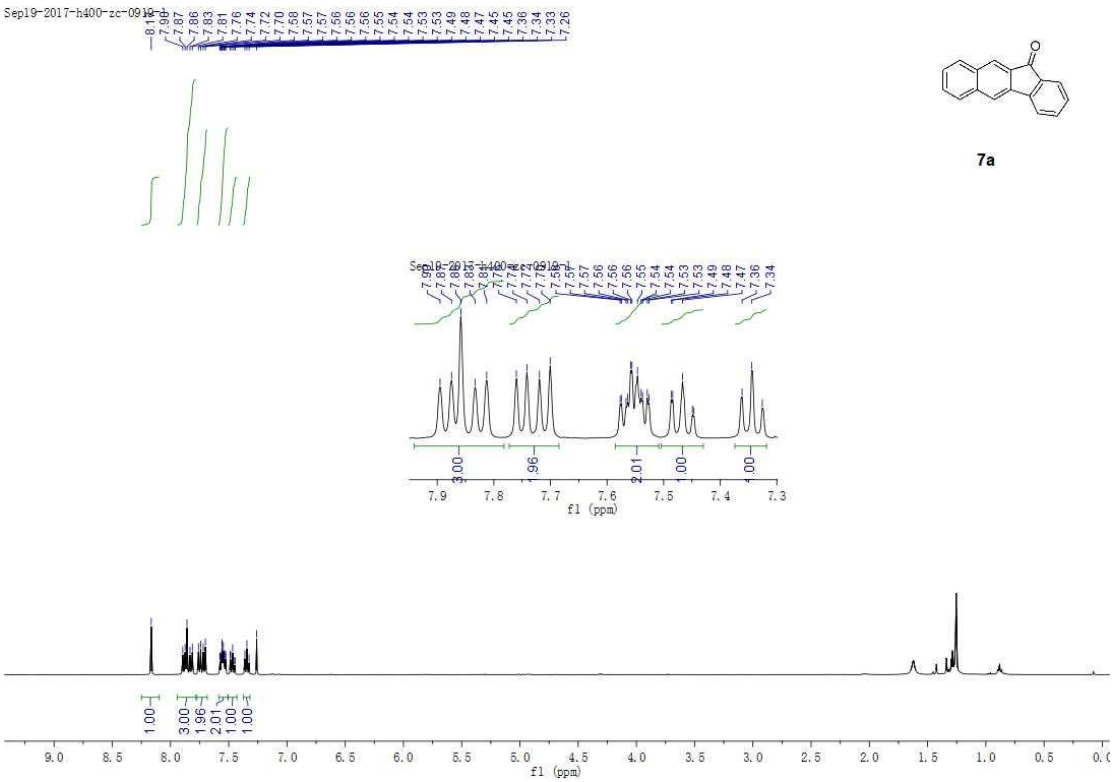


Figure S91. ^{1}H NMR spectra (400 MHz) of **7a** in $CDCl_3$, related to **Figure 2B**.

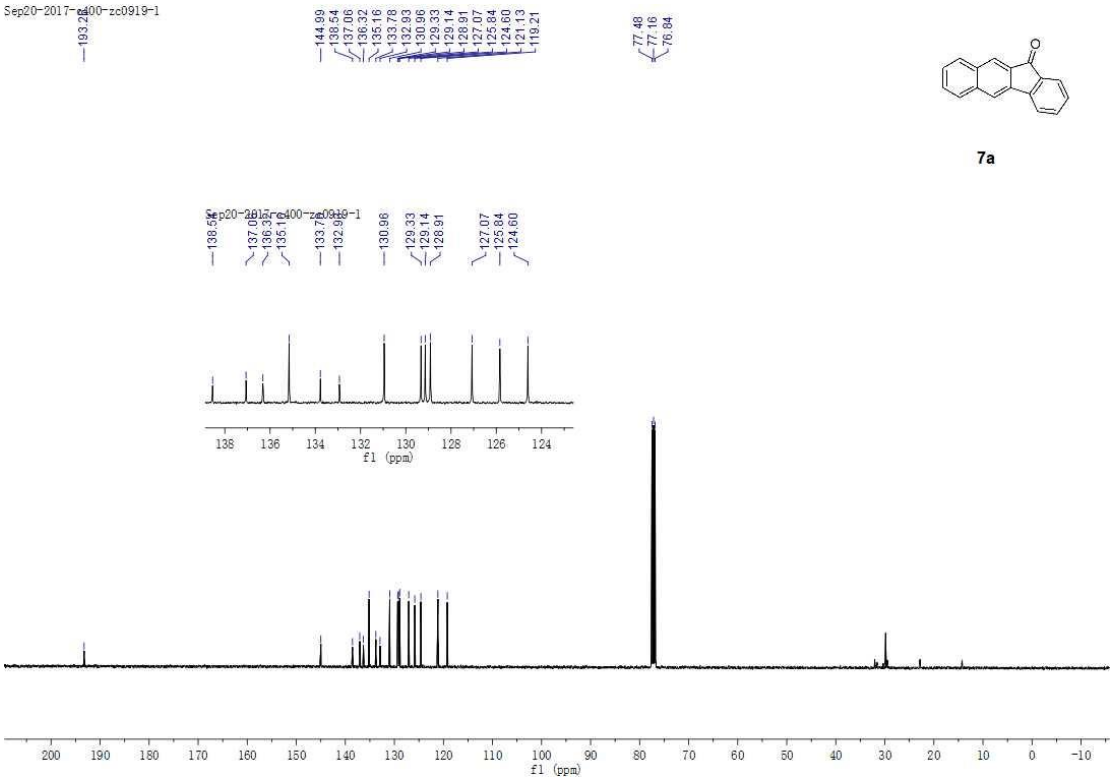


Figure S92. ^{13}C NMR spectra (400 MHz) of **7a** in $CDCl_3$, related to **Figure 2B**.

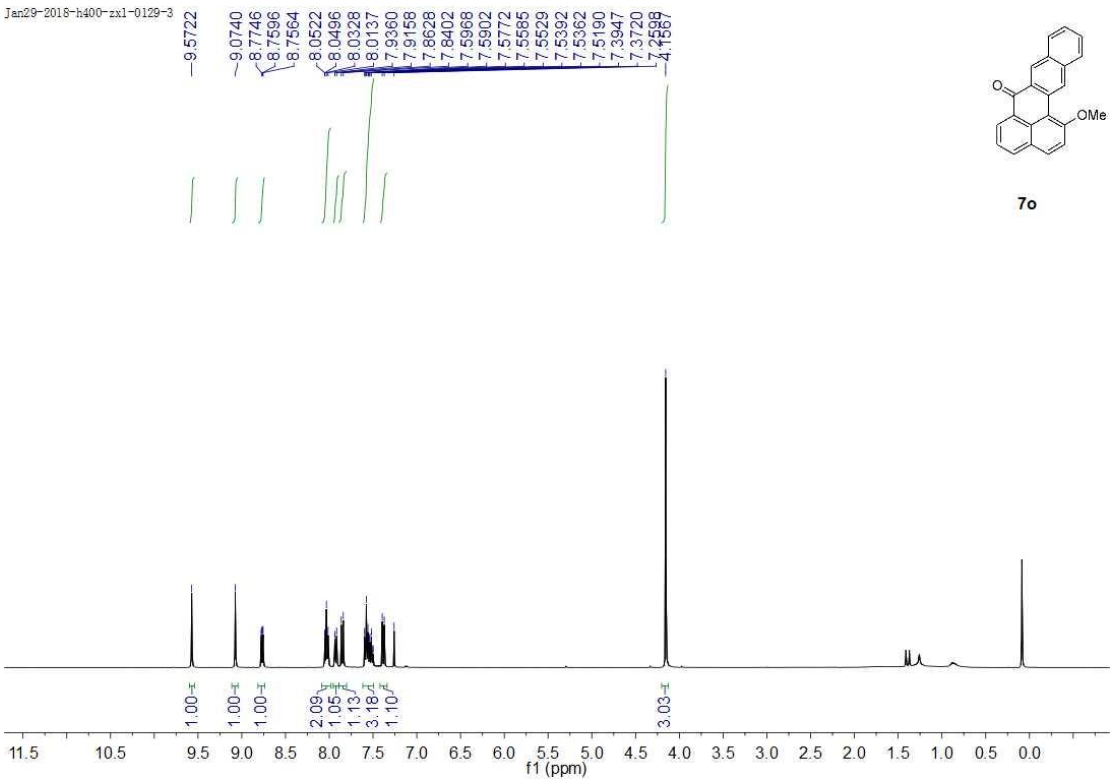


Figure S93. ^{1}H NMR spectra (400 MHz) of **7o** in $CDCl_3$, related to **Figure 2C**.

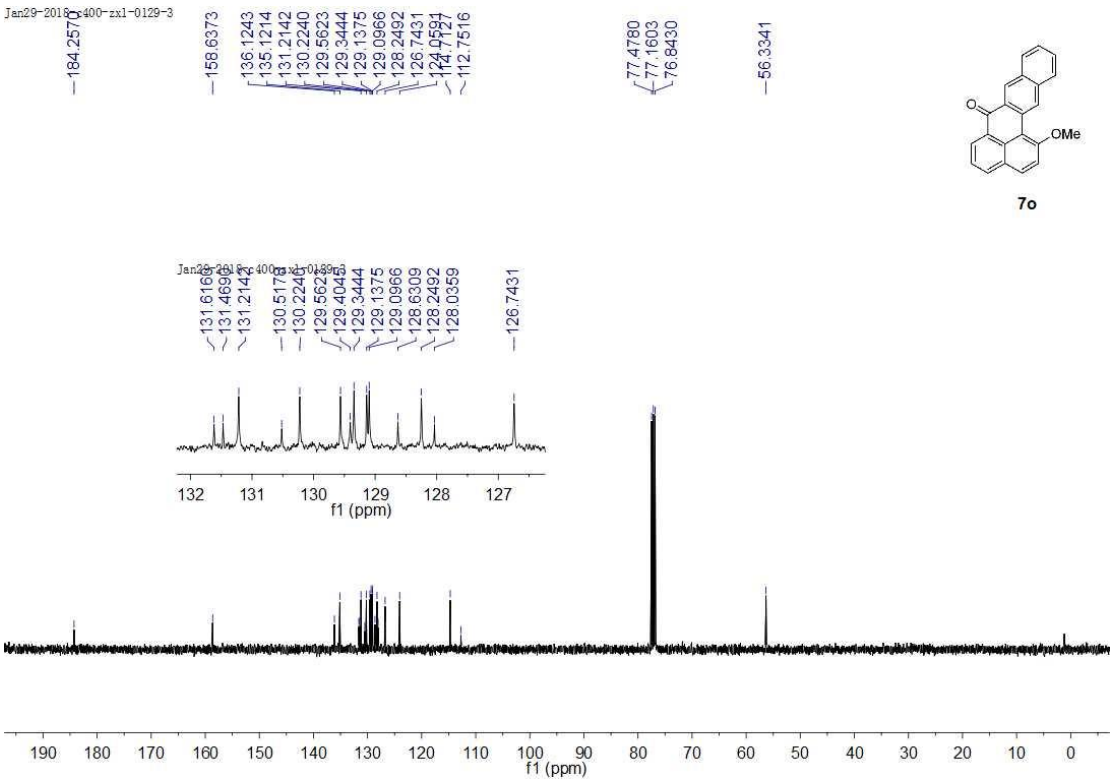


Figure S94. ^{13}C NMR spectra (400 MHz) of **7o** in $CDCl_3$, related to **Figure 2C**.

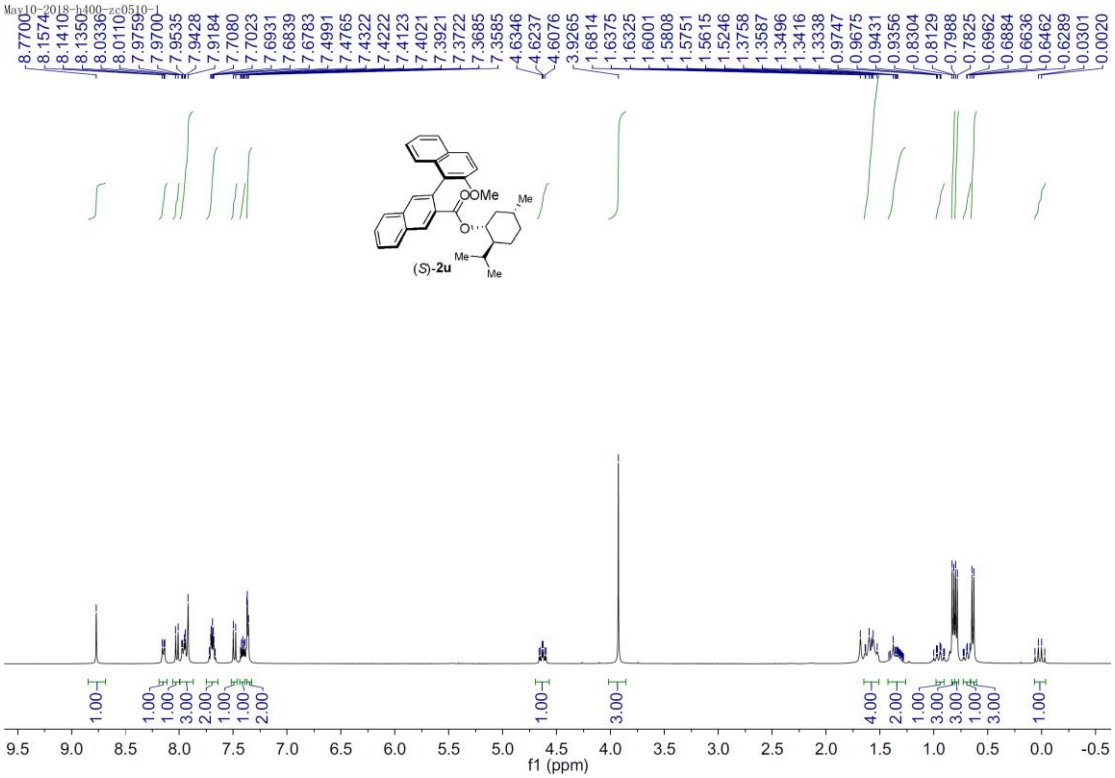


Figure S95. ^{1}H NMR spectra (400 MHz) of (*S*)-**2u** in $CDCl_3$, related to **Figure 2D**.

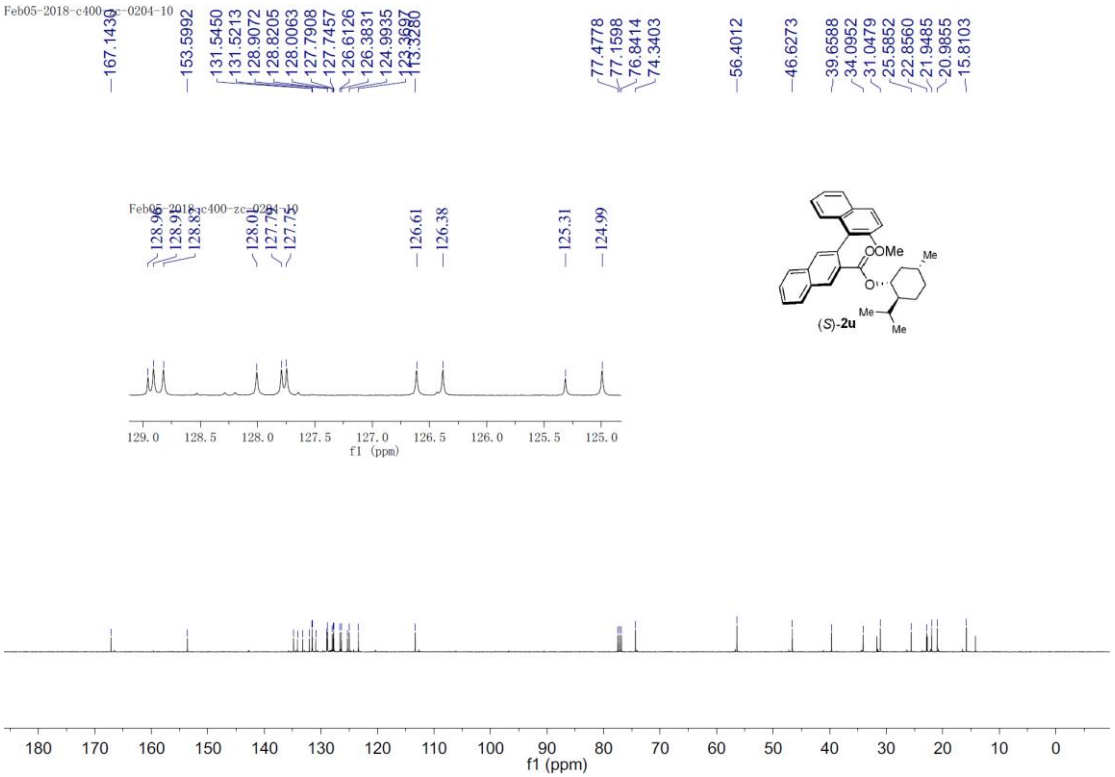


Figure S96. ^{13}C NMR spectra (400 MHz) of (*S*)-**2u** in $CDCl_3$, related to **Figure 2D**.

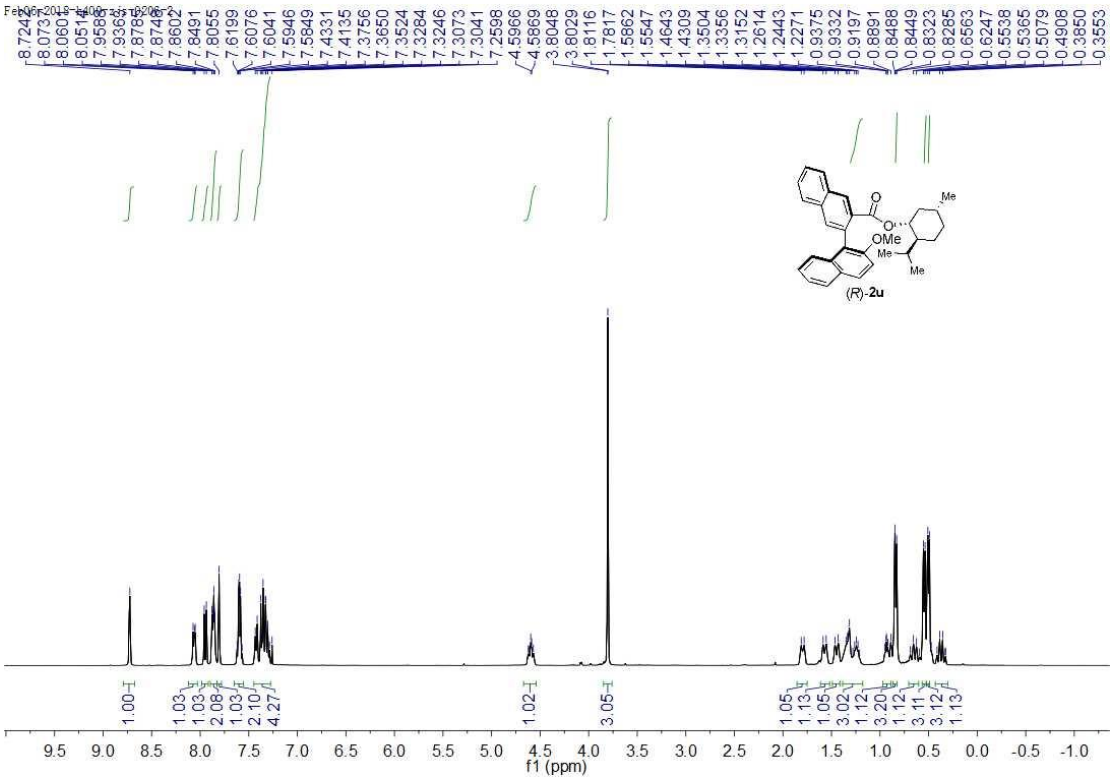


Figure S97. ^{1}H NMR spectra (400 MHz) of (*R*)-**2u** in $CDCl_3$, related to **Figure 2D**.

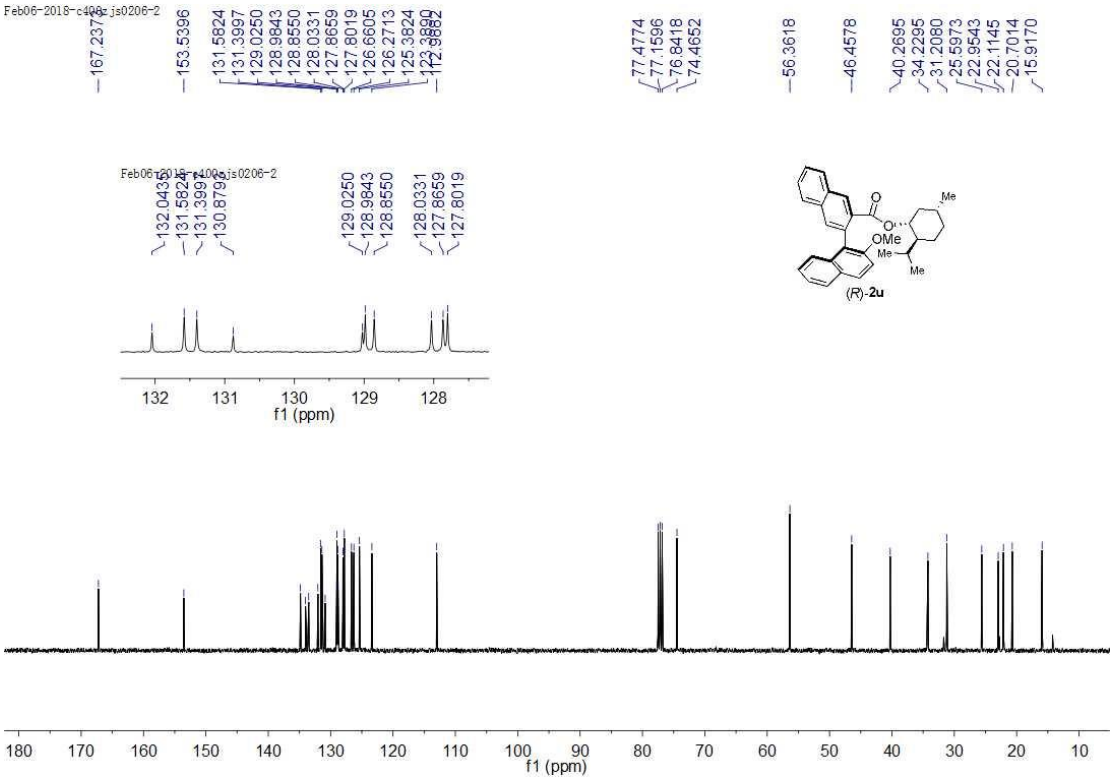


Figure S98. ^{13}C NMR spectra (400 MHz) of (*R*)-**2u** in $CDCl_3$, related to **Figure 2D**.

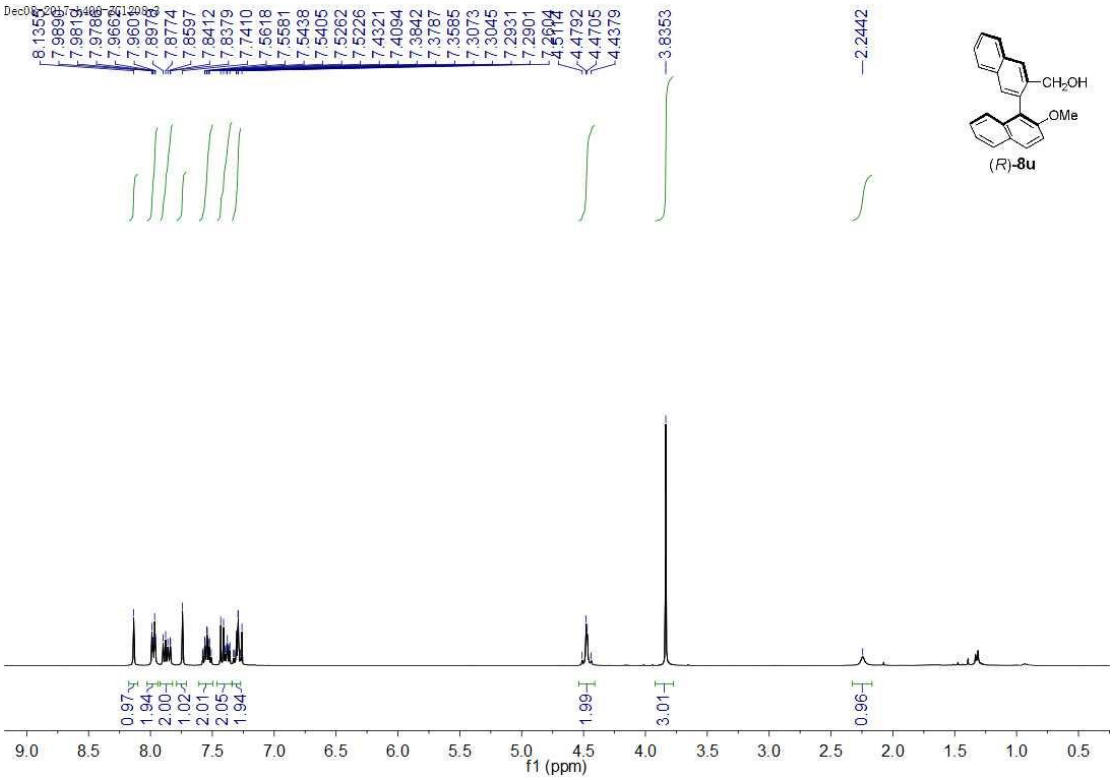


Figure S99. ^{1}H NMR spectra (400 MHz) of (*R*)-**8u** in $CDCl_3$, related to **Figure 2D**.

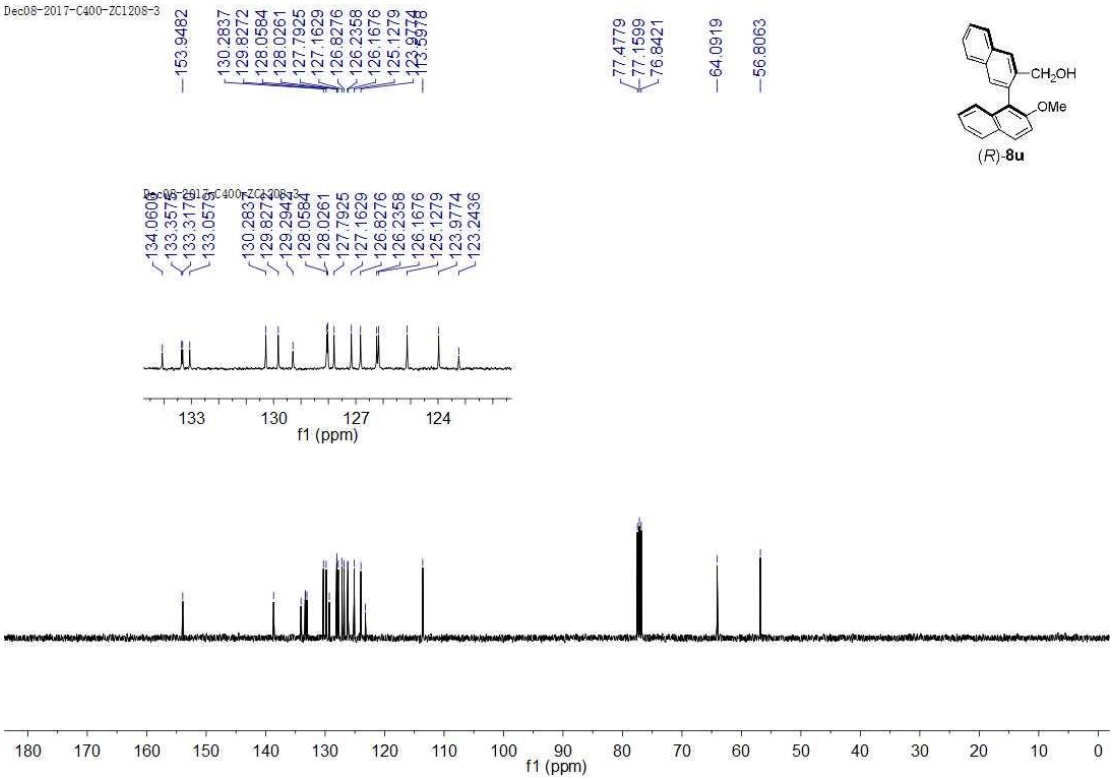


Figure S100. ^{13}C NMR spectra (400 MHz) of (*R*)-**8u** in $CDCl_3$, related to **Figure 2D**.

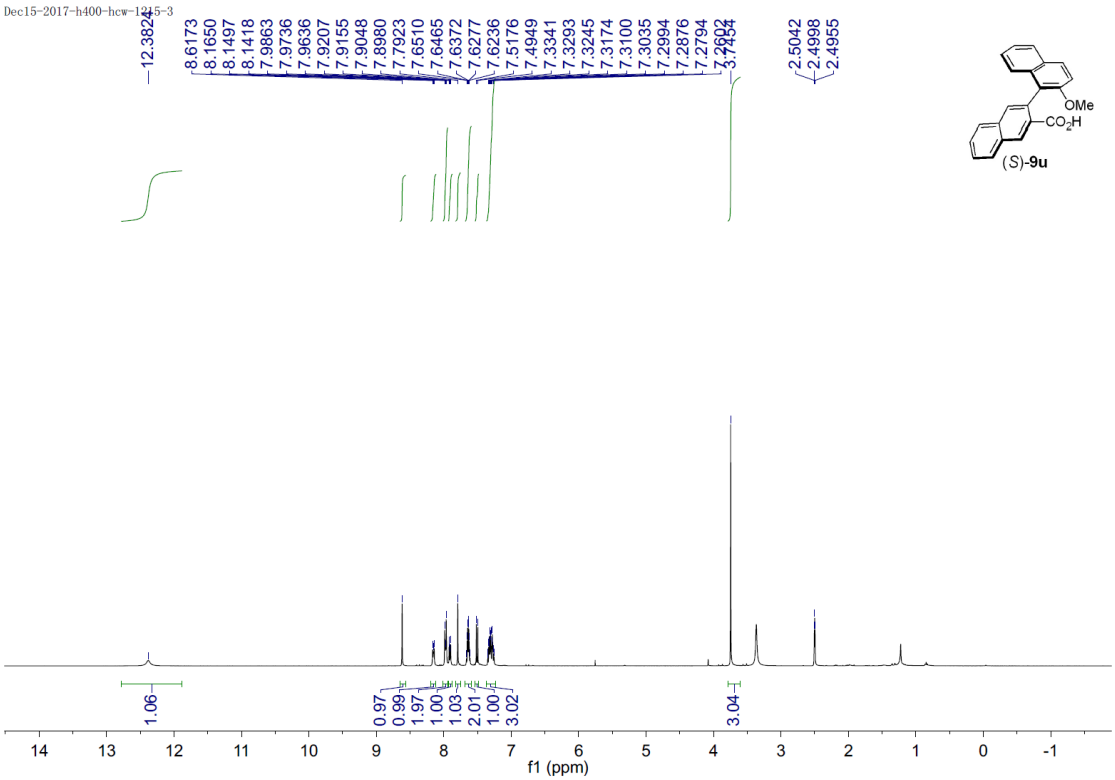


Figure S101. ^{1}H NMR spectra (400 MHz) of (*S*)-**9u** in DMSO-d_6, related to **Figure 2D**.

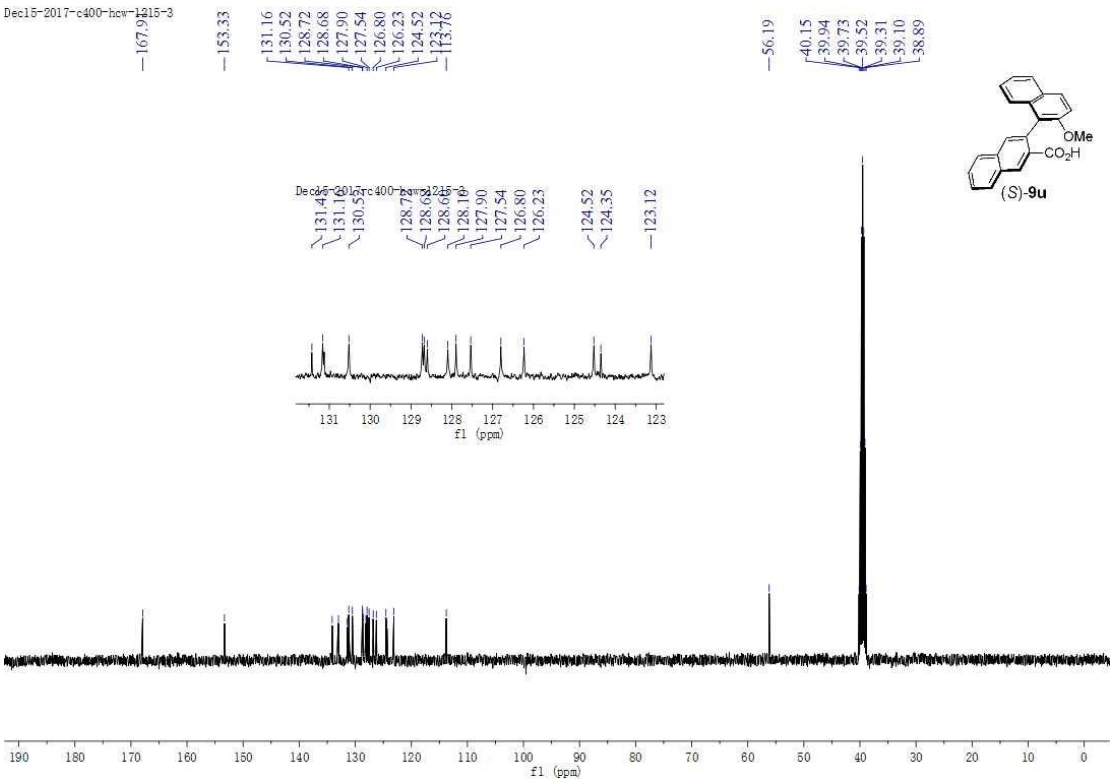


Figure S102. ^{13}C NMR spectra (400 MHz) of (*S*)-**9u** in DMSO-d_6, related to **Figure 2D**.

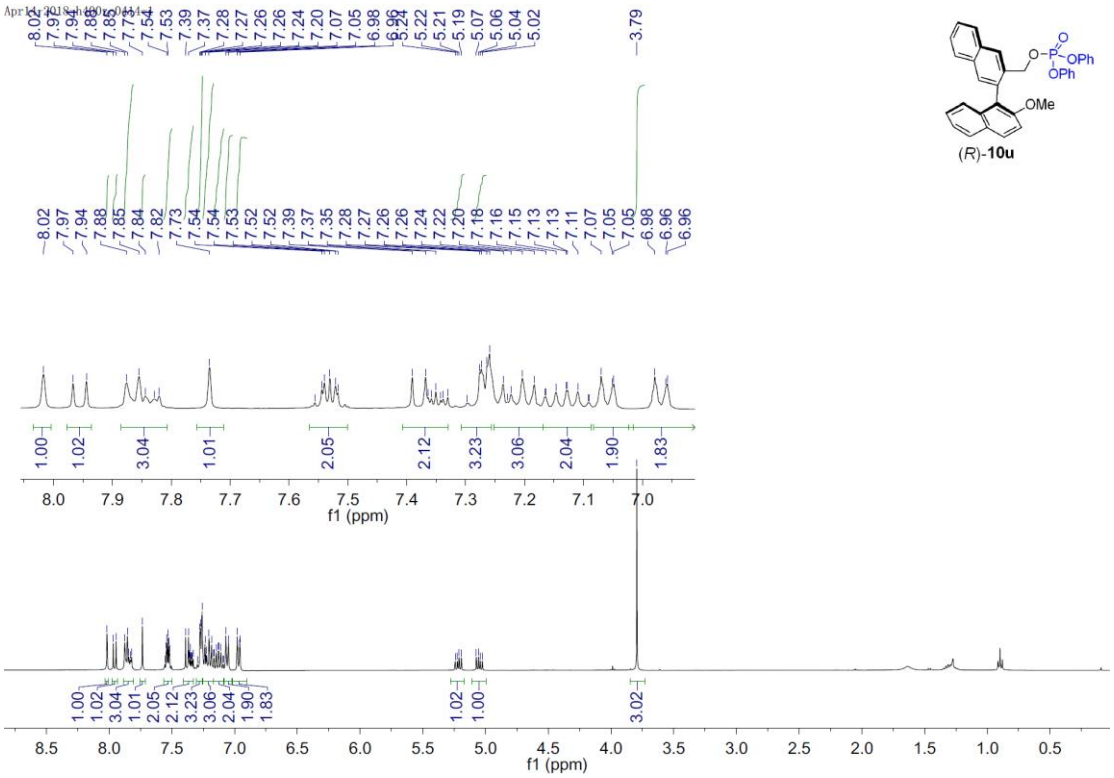


Figure S103. ^{1}H NMR spectra (400 MHz) of (*R*)-**10u** in $CDCl_3$, related to **Figure 2D**.

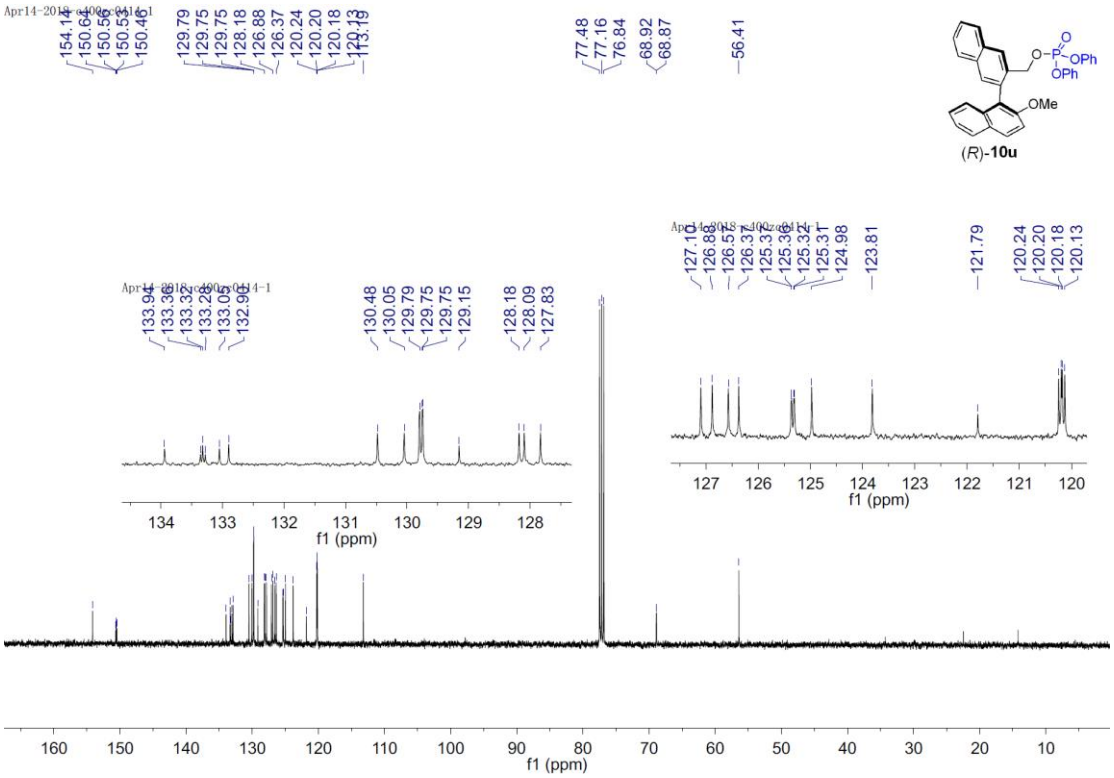


Figure S104. ^{13}C NMR spectra (400 MHz) of (*R*)-**10u** in $CDCl_3$, related to **Figure 2D**.

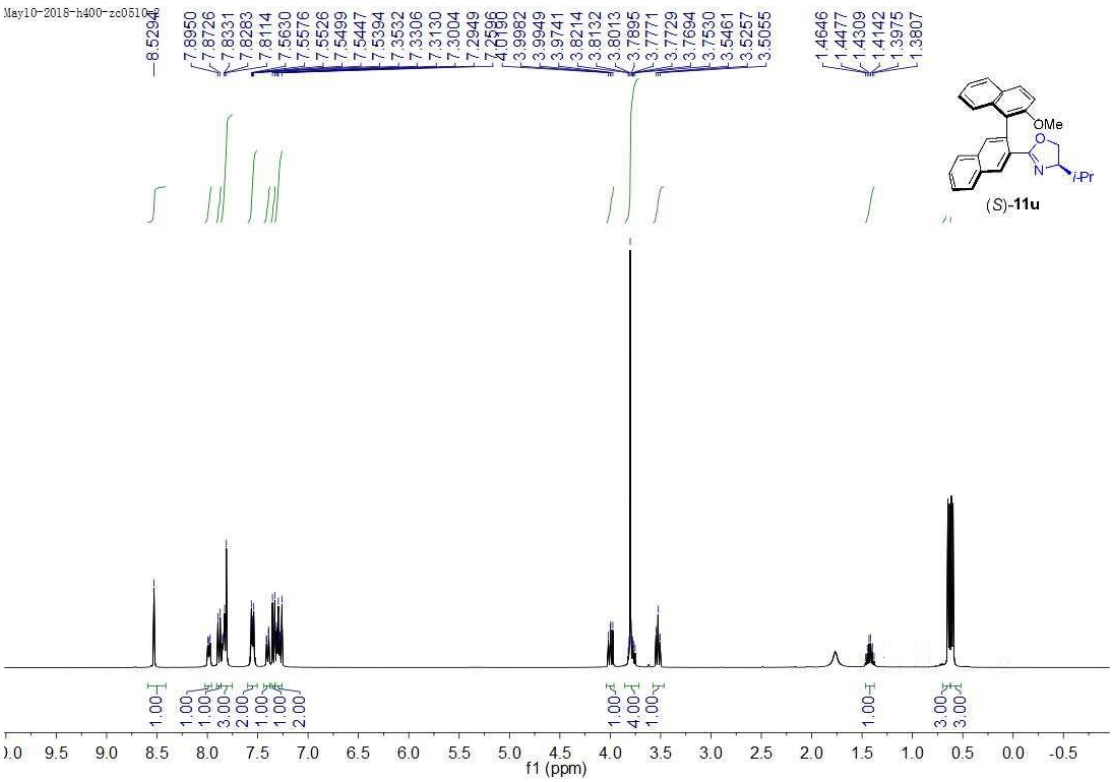


Figure S105. ^{1}H NMR spectra (400 MHz) of (*S*)-**11u** in $CDCl_3$, related to **Figure 2D**.

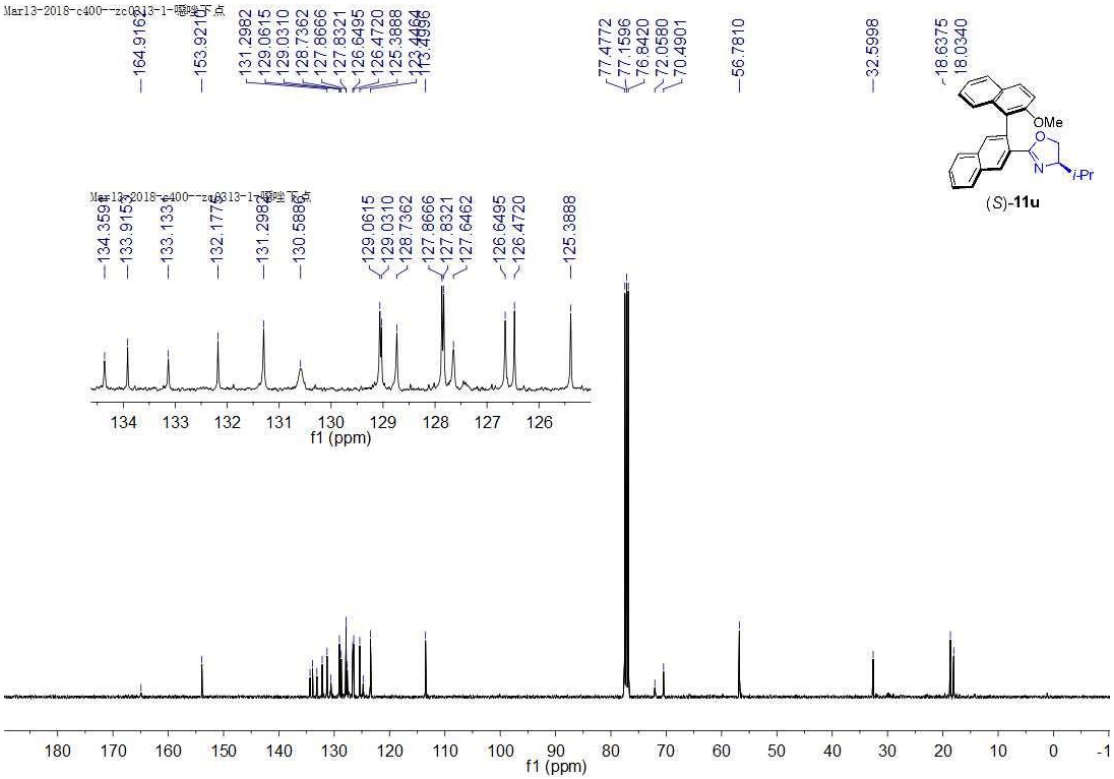


Figure S106. ^{13}C NMR spectra (400 MHz) of (*S*)-**11u** in $CDCl_3$, related to **Figure 2D**.

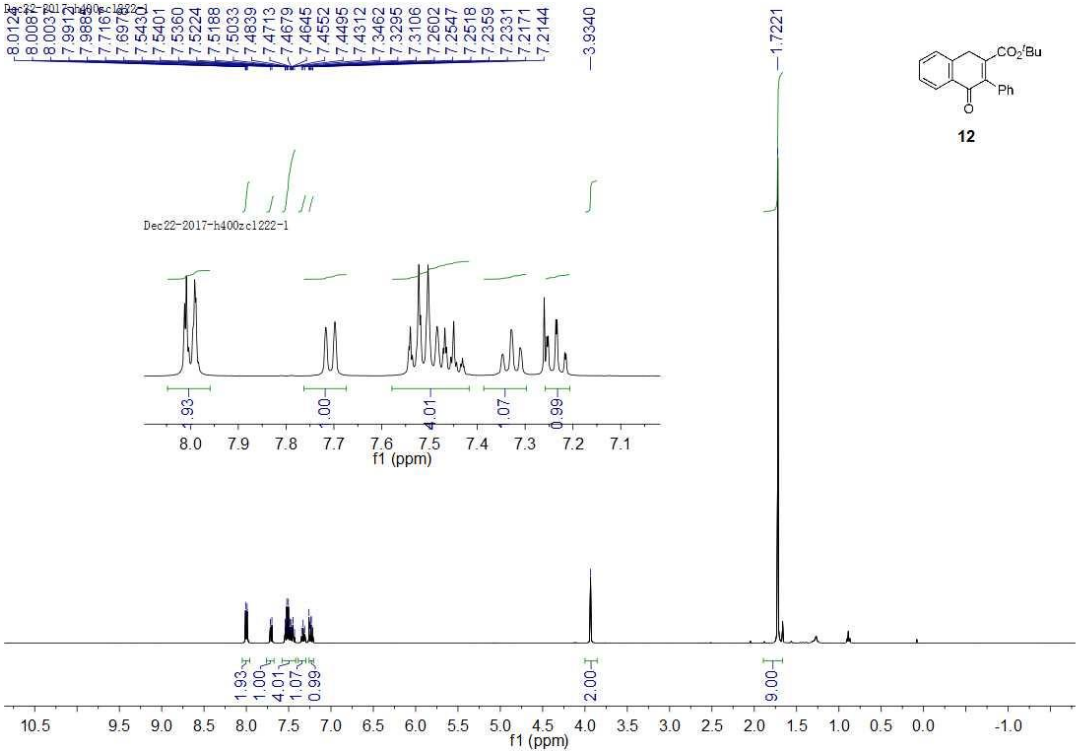


Figure S107. ^{1}H NMR spectra (400 MHz) of **12** in $CDCl_3$, related to **Figure 3A**.

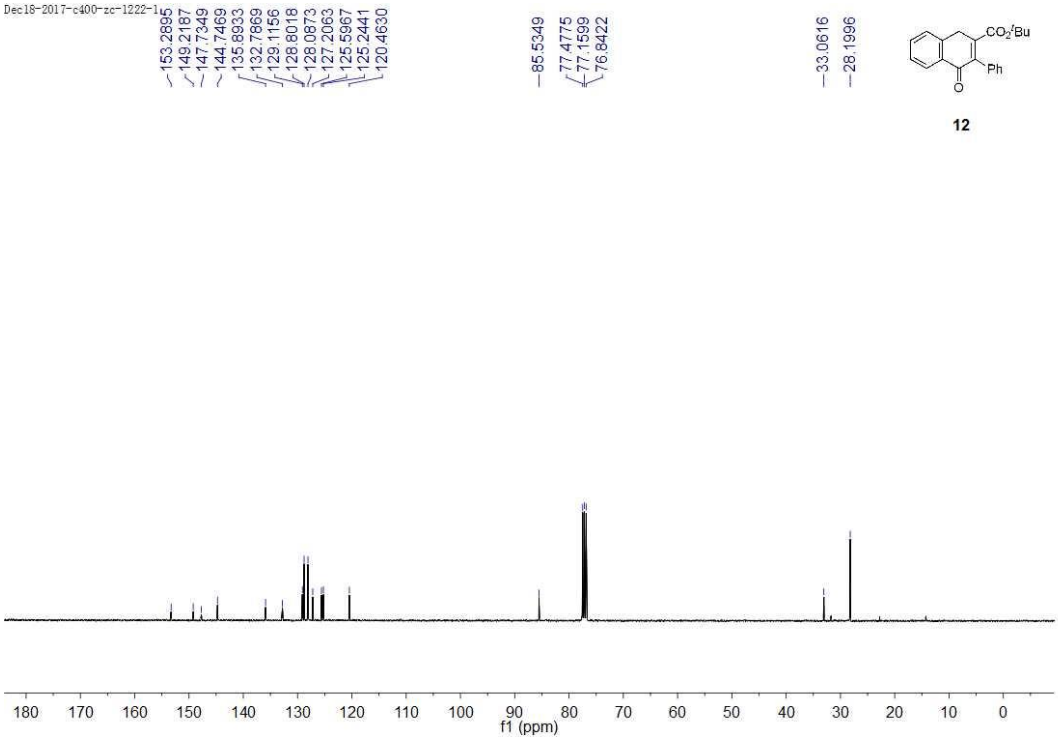


Figure S108. ^{13}C NMR spectra (400 MHz) of **12** in $CDCl_3$, related to **Figure 3A**.

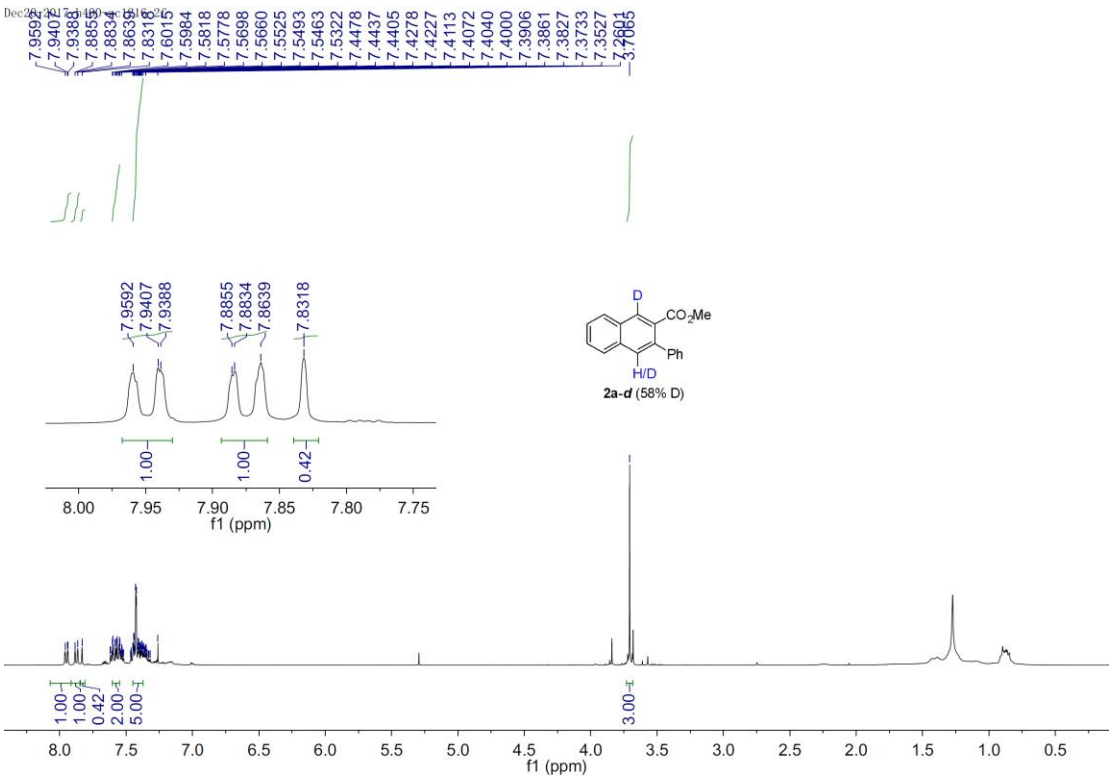


Figure S109. Proton NMR of **2a-*d*** with 58% D, related to **Figure 3B**

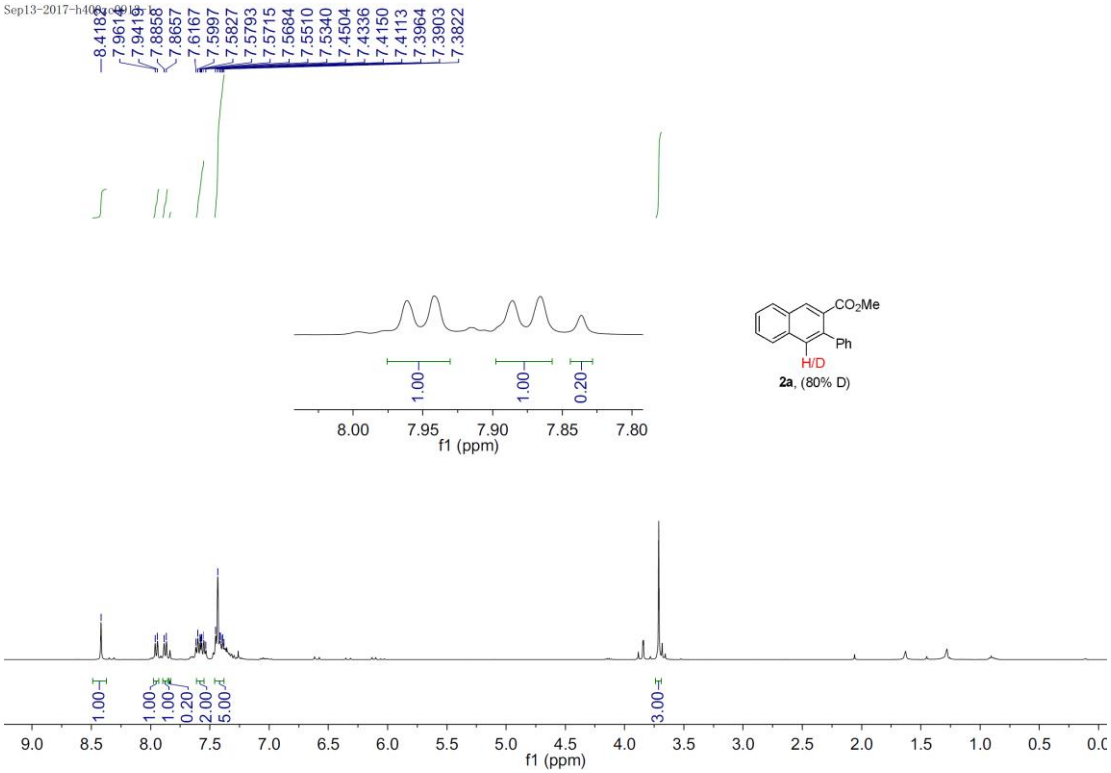


Figure S110. Proton NMR of **2a** with 80% D, related to **Figure 3C.**

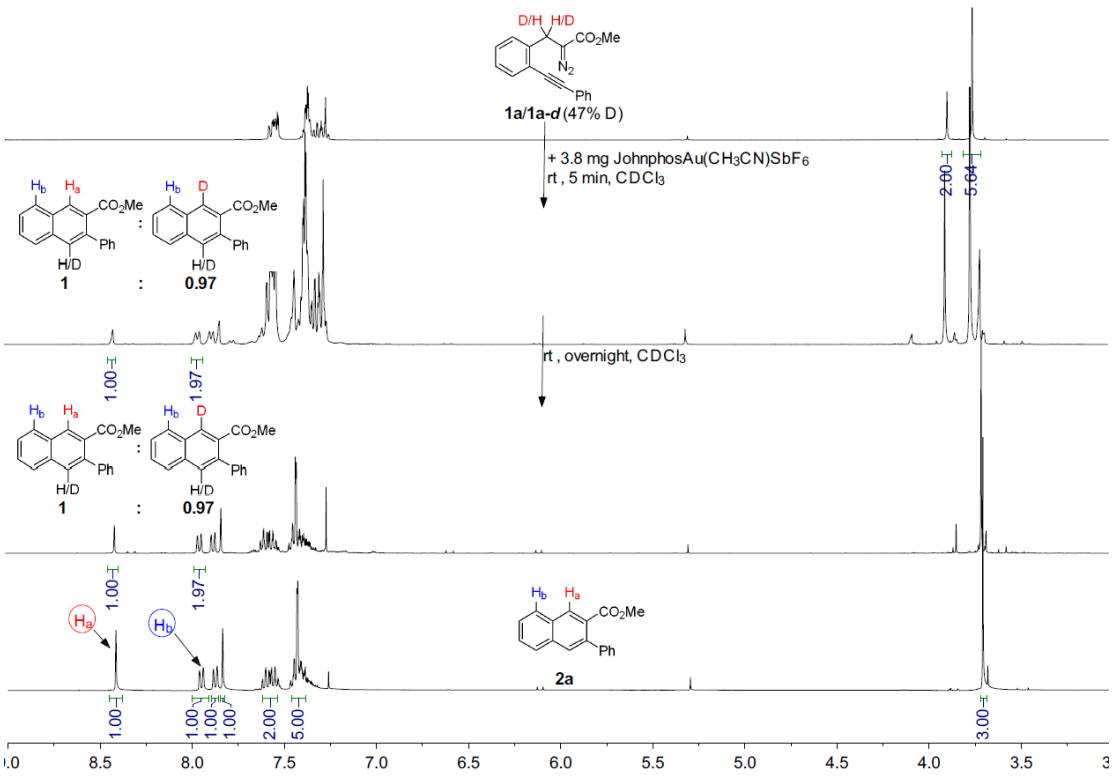


Figure S111. Intermolecular Kinetic Isotope Effect (KIE) Experiment, related to **Figure 3D.**

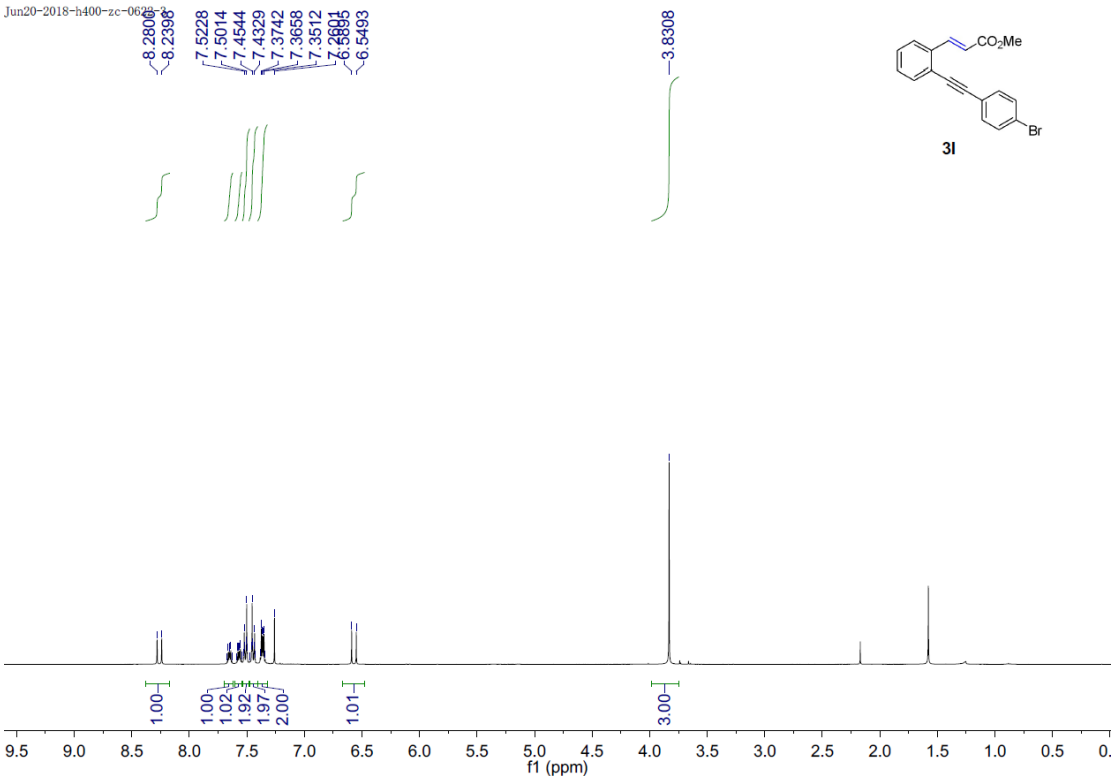


Figure S112. ^{1}H NMR spectra (400 MHz) of **3l** in $CDCl_3$, related to **Figure 3E**.

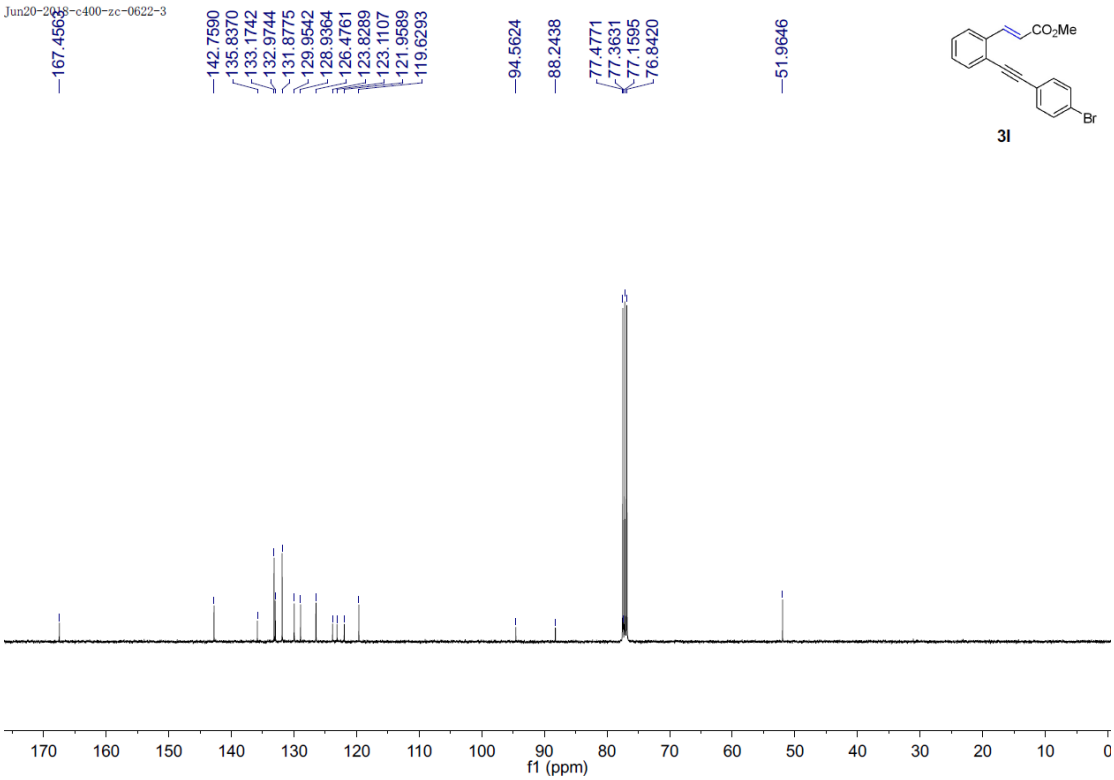


Figure S113. ^{13}C NMR spectra (400 MHz) of **3l** in $CDCl_3$, related to **Figure 3E**.

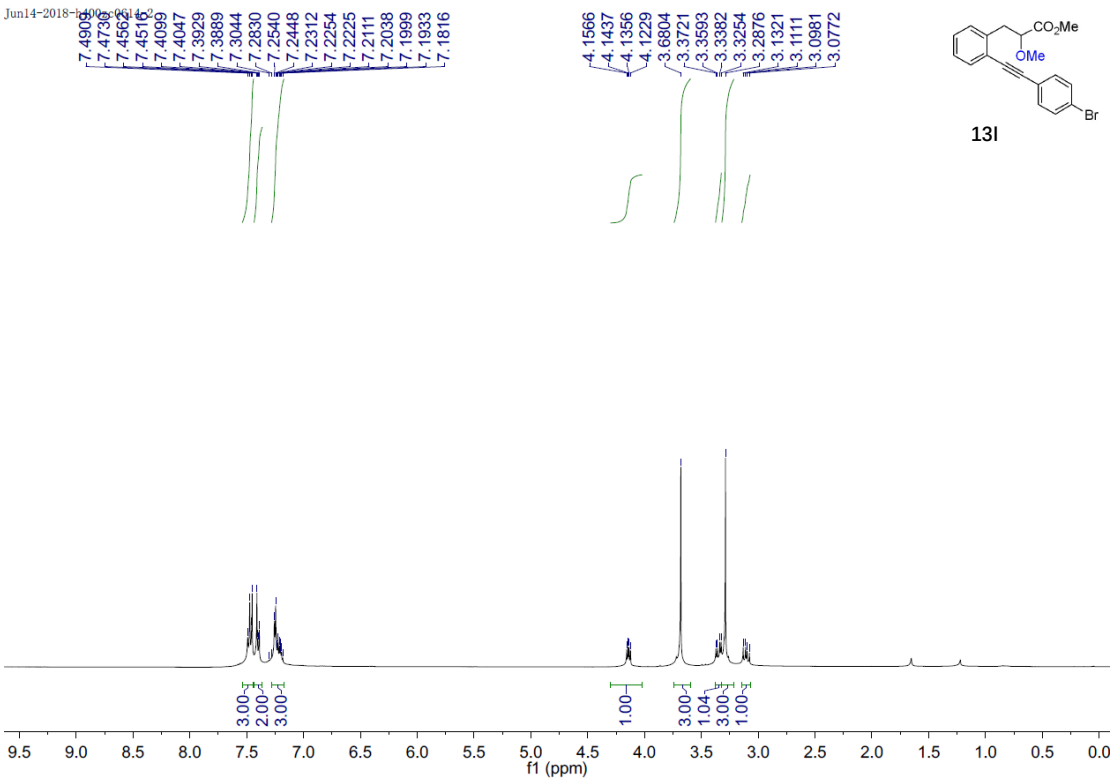


Figure S114. ^{1}H NMR spectra (400 MHz) of **13l** in $CDCl_3$, related to **Figure 3E**.

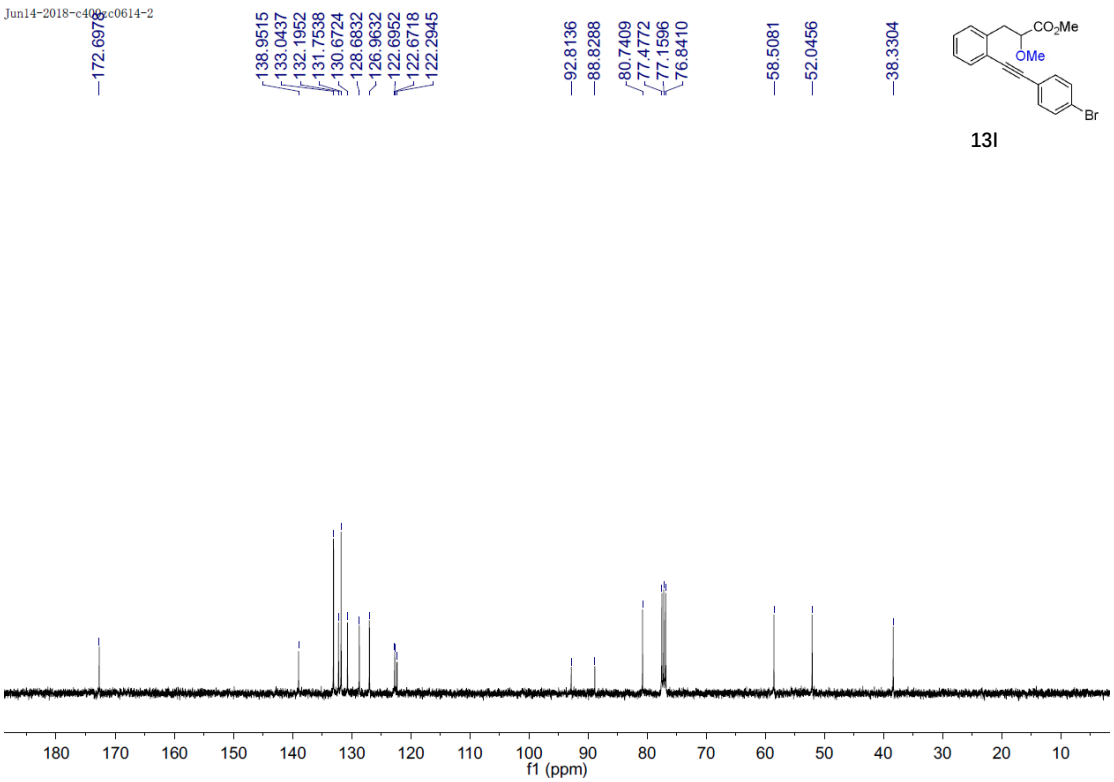
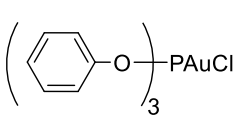


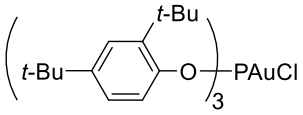
Figure S115. ^{13}C NMR spectra (400 MHz) of **13l** in $CDCl_3$, related to **Figure 3E**.

Supplemental Tables

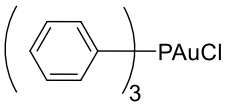
Table S1. Preparation of Au(I)-Catalysts, related to **Table 1**.



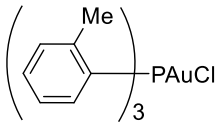
L1AuCl



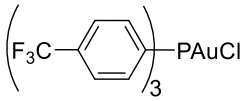
L2AuCl



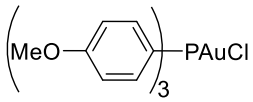
L3AuCl



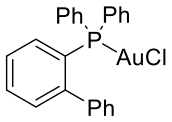
L4AuCl



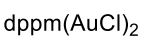
L5AuCl



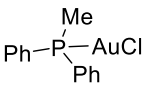
L6AuCl



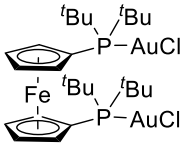
L7AuCl



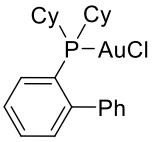
L8$(AuCl)_2$



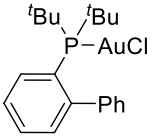
L9AuCl



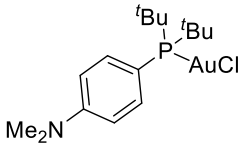
L10$(AuCl)_2$



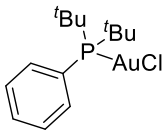
L11 AuCl



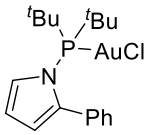
L12 AuCl



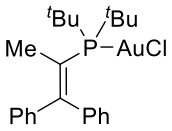
L13 AuCl



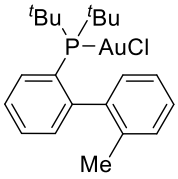
L14 AuCl



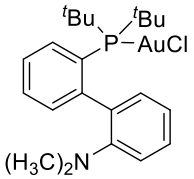
L15 AuCl



L16 AuCl



L17 AuCl



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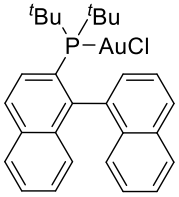
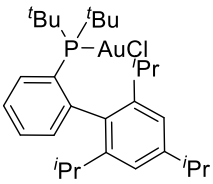
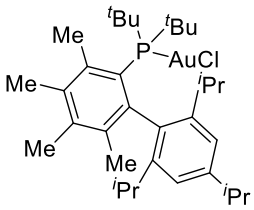


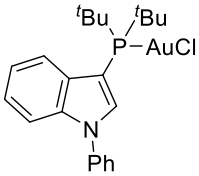
L19 AuCl



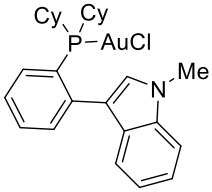
L20 AuCl



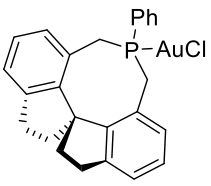
L21 AuCl



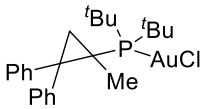
L22 AuCl



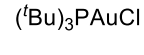
L23 AuCl



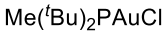
L24 AuCl



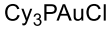
L25 AuCl



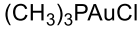
L26 AuCl



L27 AuCl

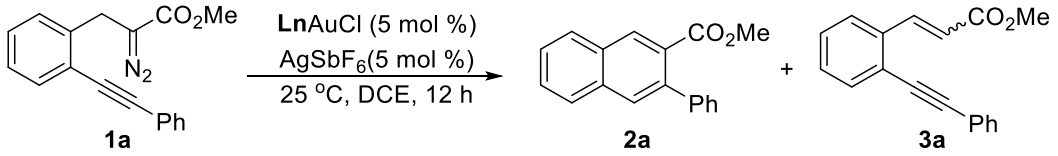


L28 AuCl



L29 AuCl

Table S2. Ligand Effects on Product Distribution, related to **Table 1**.



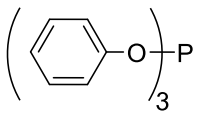
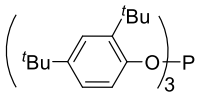
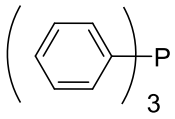
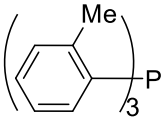
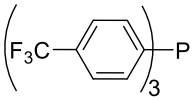
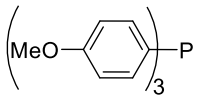
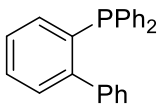
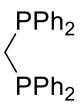
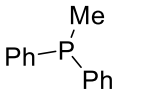
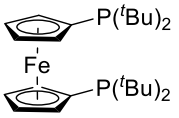
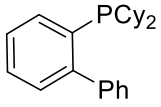
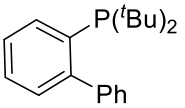
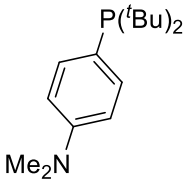
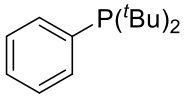
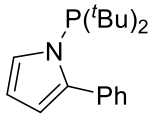
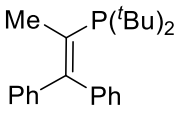
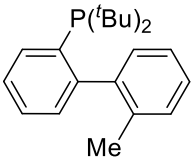
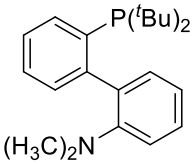
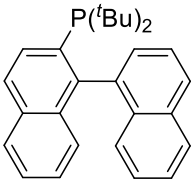
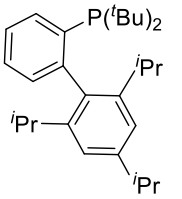
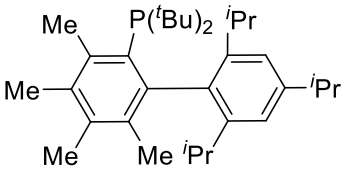
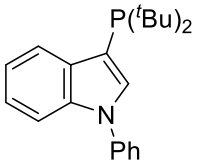
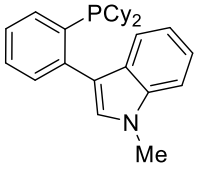
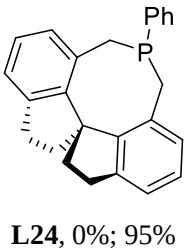
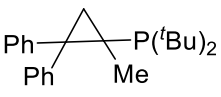
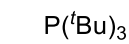
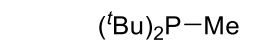
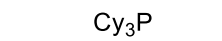
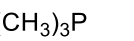
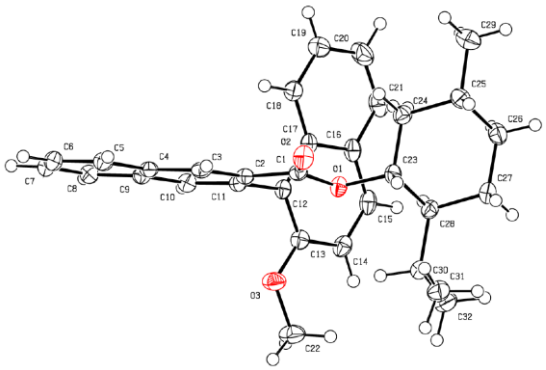
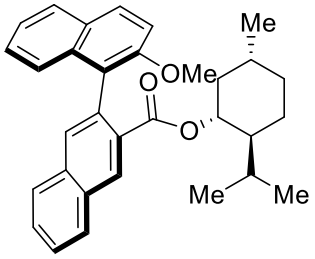
				
L1, 0%; 89%	**L2**, 0%; 87%	**L3**, 0%; 86%	**L4**, < 5%; 85%	**L5**, 0%; 65%
				
L6, 0%; 88%	**L7**, < 5%; 75%	**L8**, 0%; 85%	**L9**, 0%; 84%	**L10**, < 5%; 86%
				
L11, 41%; 55%	**L12**, 92%; < 5%	**L13**, 0%; 78%	**L14**, 0%; 73%	**L15**, 75/25
				
L16, 70%; 26%	**L17**, 92%; < 5%	**L18**, 52%; 42%	**L19**, 92%; < 5%	**L20**, 94%; < 5%
				
L21, 92%; < 5%	**L22**, 56%; 40%	**L23**, 45%; 50%	**L24**, 0%; 95%	
				
L25, 71%; 25%	**L26**, 0%; 93%	**L27**, < 5%; 81%	**L28**, 0%; 95%	**L29**, 0%; 79%

Table S3. X-ray crystal structures of (*S*)-2u, related to Figure 2D.





(*S*)-**2u**, ***CCDC:*** *1828269*

Datablock: cu_zc20180305_0m

Bond precision: C-C = 0.0020 A Wavelength=1.54178

Cell: a=8.6525(3) b=11.6262(3) c=25.3640(7)
alpha=90 beta=90 gamma=90
Temperature: 120 K

	Calculated	Reported
Volume	2551.51(13)	2551.51(13)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C32 H34 O3	C32 H34 O3
Sum formula	C32 H34 O3	C32 H34 O3
Mr	466.59	466.59
Dx,g cm-3	1.215	1.215
Z	4	4
Mu (mm-1)	0.597	0.597
F000	1000.0	1000.0
F000'	1002.79	
h,k,lmax	10,14,32	10,14,32
Nref	5446[3096]	5403
Tmin,Tmax	0.867,0.887	0.698,0.754
Tmin'	0.788	

Correction method= # Reported T Limits: Tmin=0.698 Tmax=0.754
AbsCorr = MULTI-SCAN

Data completeness= 1.75/0.99 Theta(max)= 77.963

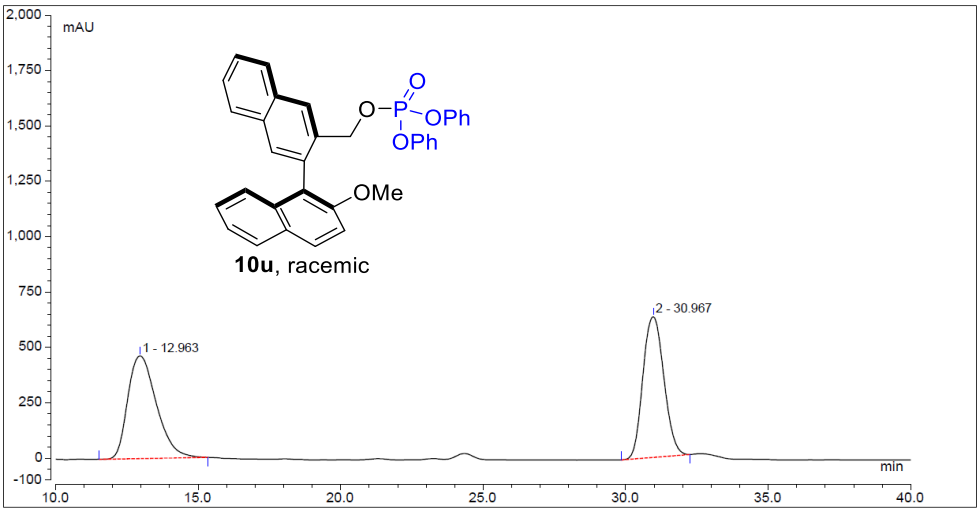
R(reflections)= 0.0281(5338) wR2(reflections)= 0.0772(5403)

S = 1.055 Npar= 320

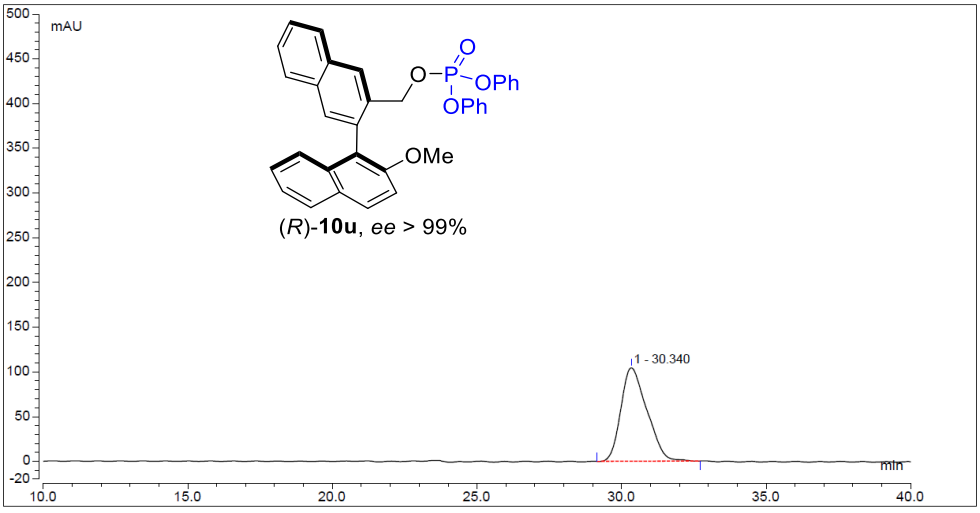
Table S4. HPLC spectra of compound (*R*)-10u, related to Figure 2D.

Condition: hexane : 2-propanol = 90:10.

Flow rate = 1.0 mL/min, λ = 272 nm, Chiral IA-3.



Entry	RT min	Area mAU*min	Height mAU	% Area %	% Height %
1	12.963	540.076	464.056	49.88	42.21
2	30.967	542.598	635.364	50.12	57.79



Entry	RT min	Area mAU*min	Height mAU	% Area %	% Height %
1	30.340	108.702	104.607	100.00	100.00

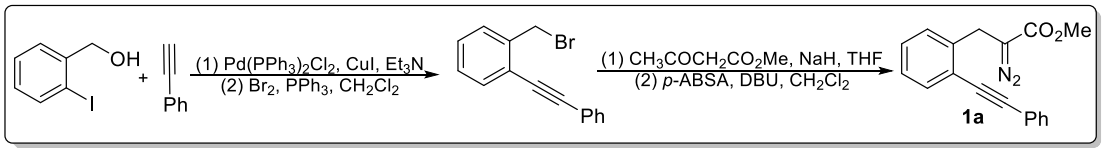
Transparent Methods

General Information

All of the reactions were carried out under argon atmosphere using oven-dried glassware. Super dry dichloroethane (DCE), ethyl diazoacetate, indoles, phosphine ligand, and metal catalysts were purchased from chemical companies and were used without further treatment. Flash column chromatography was performed using a silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates precoated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). All of the new compounds were fully characterized. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 using a 400/600 MHz spectrometer, and chemical shifts are reported in ppm with the solvent signals as the reference, and coupling constants (*J*) are given in Hz. The peak information is described as: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet, and comp = composite. High-resolution mass spectra (HRMS) were recorded using a commercial apparatus (ESI Source).

Experimental Procedures

General Procedure for the Preparation of Diazo Compounds 1a - 1u, related to Scheme 1.



Synthesis of 1-(bromomethyl)-2-(phenylethynyl)benzene: To a solution of (2-iodophenyl)methanol (9.36 g, 40.0 mmol), $Pd(PPh_3)_2Cl_2$ (280.8 mg, 1.0 mol %), CuI (76.2 mg, 1.0 mol%) in Et_3N (40.0 mL), was added a solution of phenylacetylene (4.91 g, 48.0 mmol) in Et_3N (20.0 mL) slowly at 0 ℃ under argon atmosphere. The reaction mixture was stirred overnight and the reaction temperature was warmed to room temperature slowly. Upon completion (monitored by TLC), the solvent was evaporated under vacuum after filtering through Celite, and the obtained (2-(phenylethynyl)phenyl)methanol was directly used for the next step without further purification.

To a 100 mL oven-dried round-bottom flask containing a magnetic stirring bar, triphenylphosphine (12.60 g, 48.0 mmol) in CH_2Cl_2 (40.0 mL), was added bromine (7.67 g, 48.0 mmol) dropwise, and the mixture was stirred vigorously at ambient temperature for 30 min. Then a solution of the above obtained product in CH_2Cl_2 (16.0 mL) was added to the reaction mixture dropwise and the reaction mixture was stirred for additional 1 hour. *n*-Hexane (40.0 mL) was then added to quench the reaction, and the solvent was evaporated under vacuum after filtering through Celite. The residue was purified by flash chromatography on Al_2O_3 (ethyl acetate/petroleum ether = 1/20) to afford the product 1-(bromomethyl)-2-(phenylethynyl)benzene (9.65 g, 89 % based on (2-iodophenyl)methanol).

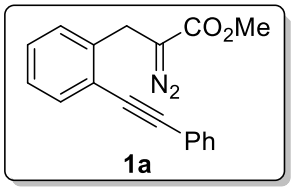
Synthesis of 1a: To a 100 mL oven-dried round-bottom flask containing a magnetic stirring bar, sodium hydride (60 % dispersion in mineral oil, 0.60 g, 15.0 mmol) in dry THF (30 mL), was added methyl acetoacetate (1.74 g, 15.0 mmol) dropwise at 0 ºC under nitrogen atmosphere. After the mixture turned clear, a solution of 1-(bromomethyl)- 2-(phenylethynyl)benzene (2.71 g, 10.0 mmol) in THF (10.0 mL) was added dropwise at ambient temperature, and the reaction was refluxed for 4 hours. Saturated NH_4Cl (20.0 mL) was added to quench the reaction, the organic phase was separated, and the aqueous layer was extracted with Et_2O (3 × 20.0 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum after filtration, and the residue was directly used for the next step without further purification.

To a 50-mL oven-dried flask containing a magnetic stirring bar, the above obtained crude product, 4-acetamidobenzenesulfonyl azide (*p*-ABSA, 2.89 g, 12.0 mmol) in DCM (20.0 mL), was added a solution of 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU, 2.29 mg, 15.0 mmol) in DCM (5.0 mL) slowly at 0 ℃. The reaction mixture was

stirred at 0 ℃ for 12 hours. Upon completion (monitored by TLC), the solvent was evaporated under vacuum after filtering through Celite, and the resulting residues was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1/10) to give the pure diazoacetate **1a** (2.06 g, 71% yields based on 1-(bromomethyl)-2-(phenylethynyl)benzene).

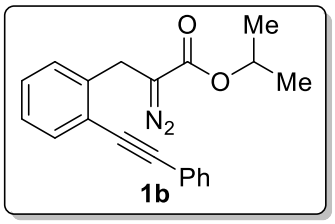
The synthesis of other substrates (**1b**-**1u**) is similar to that of **1a**.

Methyl 2-diazo-3-(2-(phenylethynyl)phenyl)propanoate.



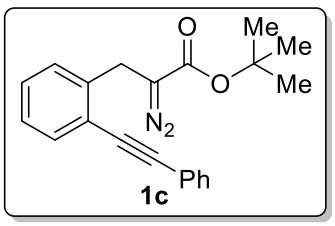
2.06 g, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.50 – 7.43 (comp, 3H), 7.31 – 7.24 (comp, 4H), 7.23 – 7.16 (comp, 2H), 3.81 (s, 2H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.8, 139.4, 132.7, 131.7, 129.3, 128.8, 128.6, 128.5, 127.3, 123.1, 123.0, 94.2, 87.4, 52.1, 28.3. HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{14}N_2NaO_2^+$ $[M+Na]^+$: 313.0953, found 313.0939.

Isopropyl 2-diazo-3-(2-(phenylethynyl)phenyl)propanoate.



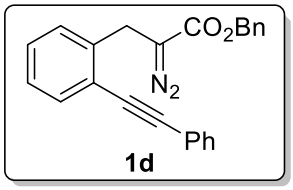
1.97 g, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.58 – 7.51 (comp, 3H), 7.39 – 7.34 (comp, 4H), 7.33 – 7.24 (comp, 2H), 5.18 – 4.98 (m, 1H), 3.88 (s, 2H), 1.23 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.9, 139.6, 132.7, 131.7, 129.4, 128.7, 128.6, 128.5, 127.2, 123.2, 123.1, 94.1, 87.5, 68.5, 28.3, 22.2. HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{19}N_2O_2^+$ $[M+H]^+$: 319.1441, found 319.1438.

***tert*-Butyl 2-diazo-3-(2-(phenylethynyl)phenyl)propanoate**.



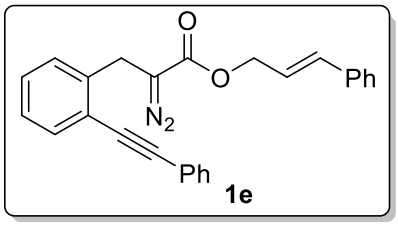
2.30 g, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.58 – 7.53 (comp, 3H), 7.40 – 7.33 (comp, 5H), 7.33 – 7.23 (m, 2H), 3.85 (s, 2H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.9, 139.6, 132.7, 131.7, 129.4, 128.7, 128.6, 128.5, 127.2, 123.2, 123.1, 94.1, 87.5, 68.5, 28.3, 22.2. HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{21}N_2O_2^+$ $[M+H]^+$: 333.1598, found 333.1596.

Benzyl 2-diazo-3-(2-(phenylethynyl)phenyl)propanoate.



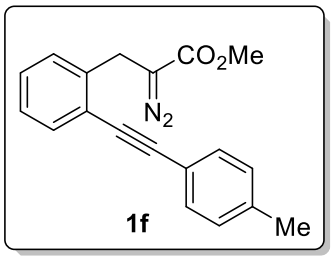
2.20 g, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.64 – 7.55 (comp, 4H), 7.42 – 7.39 (comp, 4H), 7.38 – 7.36 (comp, 4H), 7.34 – 7.29 (comp, 2H), 5.26 (s, 2H), 3.96 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.1, 139.3, 136.1, 132.7, 131.6, 129.3, 128.7, 128.6, 128.4, 128.2, 128.1, 127.3, 122.61, 122.56, 94.2, 87.4, 66.5, 28.3. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{19}N_2O_2^+$ $[M+H]^+$: 367.1441, found 367.1435.

Cinnamyl 2-diazo-3-(2-(phenylethynyl)phenyl)propanoate.



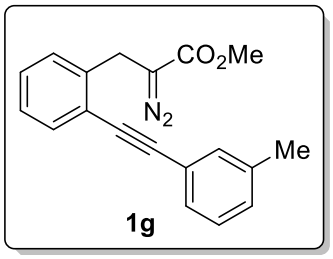
2.28 g, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.61 – 7.53 (comp, 4H), 7.40 – 7.35 (comp, 8H), 7.30 – 7.27 (comp, 2H), 6.67 – 6.59 (m, 1H), 6.32 – 6.23 (m, 1H), 4.86 – 4.81 (m, 2H), 3.93 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.1, 139.3, 136.3, 134.1, 132.7, 131.7, 129.4, 128.8, 128.7, 128.6, 128.5, 128.1, 127.3, 126.7, 123.5, 123.11, 123.06, 94.2, 87.4, 65.4, 28.4. HRMS (TOF MS ESI$^+$) calculated for $C_{26}H_{21}N_2O_2^+$ $[M+H]^+$: 393.1598, found 393.1599.

Methyl 2-diazo-3-(2-(*p*-tolylethynyl)phenyl)propanoate.



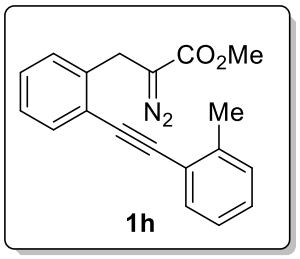
2.19 g, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.55 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.37 – 7.33 (m, 1H), 7.31 – 7.24 (comp, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 3.88 (s, 2H), 3.75 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.7, 139.3, 138.8, 132.6, 131.6, 129.31, 129.26, 128.6, 127.3, 123.2, 120.1, 94.4, 86.8, 52.0, 28.3, 21.6. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{16}N_2NaO_2^+$ $[M+Na]^+$: 327.1104, found 327.1098.

Methyl 2-diazo-3-(2-(*m*-tolylethynyl)phenyl)propanoate.



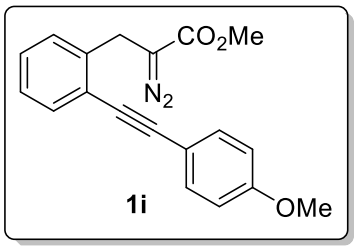
2.22 g, 73% yield. ^{1}H NMR (600 MHz, $CDCl_3$) (δ, ppm) 7.58 – 7.54 (m, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.33 – 7.27 (comp, 2H), 7.26 – 7.23 (comp, 2H), 7.21 – 7.16 (m, 1H), 3.90 (s, 2H), 3.75 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 167.8, 145.9, 140.2, 139.0, 132.8, 132.1, 129.7, 128.8, 128.7, 127.3, 125.8, 123.4, 123.0, 93.2, 91.3, 52.1, 28.3, 21.0. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{16}N_2NaO_2^+$ $[M+Na]^+$: 327.1104, found 327.1102.

Methyl 2-diazo-3-(2-(*o*-tolylethynyl)phenyl)propanoate.



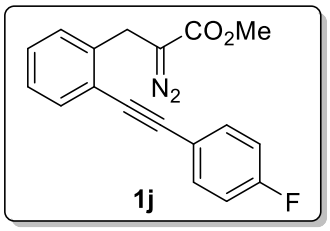
1.98 g, 65% yield. ^{1}H NMR (600 MHz, $CDCl_3$) (δ, ppm) 7.51 – 7.47 (m, 1H), 7.30 – 7.28 (comp, 2H), 7.27 – 7.24 (m, 1H), 7.23 – 7.21 (m, 1H), 7.21 – 7.17 (comp, 2H), 7.11 (d, *J* = 7.6 Hz, 1H), 3.83 (s, 2H), 3.70 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.3, 139.4, 138.2, 132.7, 132.3, 129.5, 129.3, 128.8, 128.7, 128.4, 127.3, 123.2, 123.0, 94.4, 87.1, 52.1, 28.3, 21.4. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{16}N_2NaO_2^+$ $[M+Na]^+$: 327.1104, found 327.1107.

Methyl 2-diazo-3-(2-((4-methoxyphenyl)ethynyl)phenyl)propanoate.



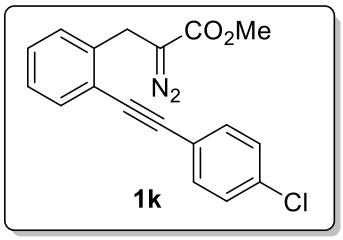
1.67 g, 52% yield. ^{1}H NMR (600 MHz, $CDCl_3$) (δ, ppm) 7.54 (d, *J* = 7.3 Hz, 1H), 7.48 – 7.45 (m, 2H), 7.34 (d, *J* = 7.3 Hz, 1H), 7.30 – 7.23 (m, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 2H), 3.83 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 167.7, 159.9, 139.1, 133.2, 132.5, 129.3, 128.4, 127.3, 123.4, 115.2, 114.1, 94.3, 86.2, 55.4, 52.0, 28.3. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{17}N_2O_3^+$ $[M+H]^+$: 321.1234, found 321.1227.

Methyl 2-diazo-3-(2-((4-fluorophenyl)ethynyl)phenyl)propanoate.



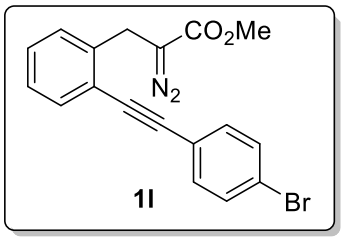
2.16 g, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.45 – 7.38 (comp, 3H), 7.25 – 7.21 (m, 1H), 7.21 – 7.17 (m, 1H), 7.17 – 7.12 (m, 1H), 6.98 – 6.91 (comp, 2H), 3.76 (s, 2H), 3.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.6, 162.7 (d, *J* = 249.9 Hz), 139.3, 133.6 (d, *J* = 8.4 Hz), 132.7, 129.3, 128.8, 127.3, 122.8, 119.2 (d, *J* = 3.5 Hz), 115.8 (d, *J* = 22.1 Hz), 93.1, 87.1, 52.0, 28.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.46. HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{14}FN_2O_2^+$ $[M+H]^+$: 309.1034, found 309.1029.

Methyl 3-(2-((4-Chlorophenyl)ethynyl)phenyl)-2-diazopropanoate.



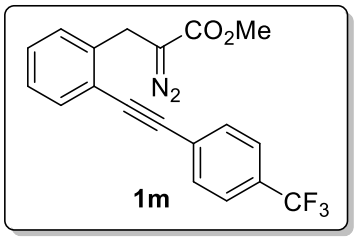
2.14 g, 66% yield. ^{1}H NMR (600 MHz, $CDCl_3$) (δ, ppm) 7.54 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.29 (m, 4H), 7.28 – 7.24 (m, 1H), 3.86 (s, 2H), 3.74 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 167.5, 139.4, 134.6, 132.9, 132.7, 129.3, 129.0, 128.8, 127.3, 122.7, 121.6, 93.0, 88.4, 52.0, 28.3. HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{13}ClN_2NaO_2^+$ $[M+Na]^+$: 347.0558, found 347.0550.

Methyl 3-(2-((4-bromophenyl)ethynyl)phenyl)-2-diazopropanoate.



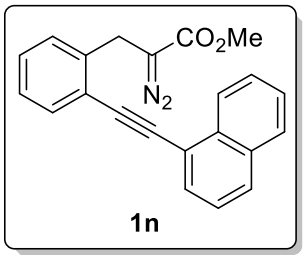
1.96 g, 53% yield. ^{1}H NMR (600 MHz, $CDCl_3$) (δ, ppm) 7.49 (d, *J* = 7.4 Hz, 1H), 7.46 – 7.42 (comp, 2H), 7.35 – 7.31 (comp, 2H), 7.30 – 7.24 (comp, 2H), 7.23 – 7.19 (m, 1H), 3.81 (s, 2H), 3.69 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 167.7, 139.4, 133.1, 132.8, 131.8, 129.4, 129.0, 127.4, 122.9, 122.7, 122.1, 93.1, 88.6, 52.1, 28.4. HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{13}BrN_2NaO_2^+$ $[M+Na]^+$: 391.0053, found 391.0145.

Methyl 2-diazo-3-(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)propanoate.



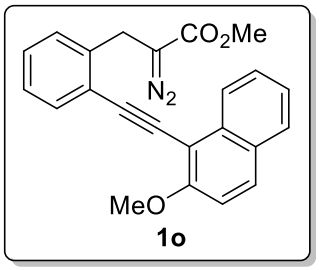
1.97 g, 55% yield. ^{1}H NMR (600 MHz, $CDCl_3$) (δ, ppm) 7.70 – 7.47 (comp, 5H), 7.39 – 7.26 (comp, 2H), 7.26 – 7.18 (m, 1H), 3.87 (s, 2H), 3.72 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 167.3, 139.5, 132.8, 131.8, 130.0 (q, *J* = 32.7 Hz), 129.3, 129.2, 127.2, 126.8, 125.2 (q, *J* = 3.8 Hz), 122.2, 92.6, 89.7, 51.8, 28.2. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{13}F_3N_2NaO_2^+$ $[M+Na]^+$: 381.0821, found 381.0828.

Methyl 2-diazo-3-(2-(naphthalen-1-ylethynyl)phenyl)propanoate.



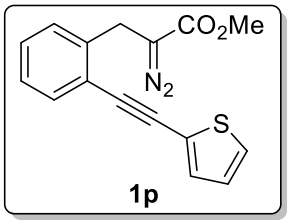
1.67 g, 49% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.45 (d, *J* = 8.3 Hz, 1H), 7.92 – 7.86 (comp, 2H), 7.83 – 7.79 (m, 1H), 7.74 – 7.70 (m, 1H), 7.68 – 7.61 (m, 1H), 7.60 – 7.54 (m, 1H), 7.53 – 7.47 (m, 1H), 7.45 – 7.40 (m, 1H), 7.39 – 7.32 (comp, 2H), 4.02 (s, 2H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.7, 139.2, 133.3, 133.2, 132.8, 130.7, 129.3, 129.1, 128.9, 128.4, 127.4, 127.0, 126.5, 126.1, 125.4, 123.1, 120.7, 92.3, 92.2, 52.0, 28.4. HRMS (TOF MS ESI$^+$) calculated for $C_{22}H_{17}N_2O_2^+$ $[M+H]^+$: 341.1285, found 341.1297.

Methyl 2-diazo-3-(2-((2-methoxynaphthalen-1-yl)ethynyl)phenyl)propanoate.



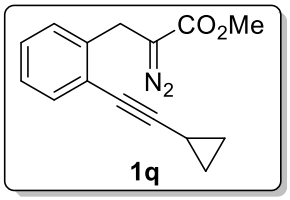
2.11 g, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.30 (d, *J* = 8.3 Hz, 1H), 7.85 – 7.74 (comp, 2H), 7.70 – 7.65 (m, 1H), 7.59 – 7.52 (m, 1H), 7.45 – 7.33 (comp, 2H), 7.33 – 7.26 (comp, 2H), 7.27 – 7.22 (m, 1H), 4.04 (s, 2H), 4.01 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 168.2, 159.2, 139.4, 134.3, 132.4, 130.5, 129.3, 128.7, 128.6, 128.2, 127.5, 127.2, 125.3, 124.3, 123.7, 112.6, 106.2, 97.0, 88.9, 56.5, 52.0, 28.0. HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{19}N_2O_3^+$ $[M+H]^+$: 371.1390, found 371.1400.

Methyl 2-diazo-3-(2-(thiophen-2-ylethynyl)phenyl)propanoate.



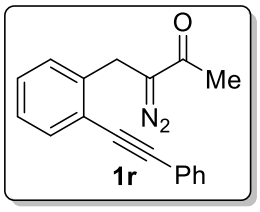
1.24 g, 42% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.52 – 7.48 (m, 1H), 7.34 – 7.26 (comp, 4H), 7.24 – 7.19 (m, 1H), 7.00 – 6.96 (m, 1H), 3.81 (s, 2H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.3, 139.4, 132.5, 132.2, 129.3, 128.9, 127.7, 127.3, 127.2, 123.0, 122.6, 91.1, 87.4, 52.0, 28.4. HRMS (TOF MS ESI$^+$) calculated for $C_{16}H_{13}N_2O_2S^+$ $[M+H]^+$: 297.0698, found 297.0694.

Methyl 3-(2-(cyclopropylethynyl)phenyl)-2-diazopropanoate.



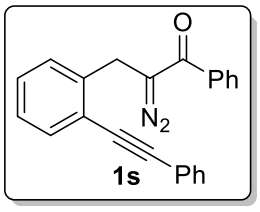
1.35 g, 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.43 – 7.38 (m, 1H), 7.32 – 7.26 (m, 1H), 7.26 – 7.16 (comp, 2H), 3.79 (s, 3H), 3.77 (s, 2H), 1.52 – 1.44 (m, 1H), 0.94 – 0.80 (comp, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.7, 139.3, 132.6, 129.1, 127.8, 127.0, 123.7, 98.5, 73.9, 51.9, 28.2, 8.7, 0.4. HRMS (TOF MS ESI$^+$) calculated for $C_{15}H_{14}N_2NaO_2^+$ $[M+Na]^+$: 277.0947, found 277.0961.

3-Diazo-4-(2-(phenylethynyl)phenyl)butan-2-one.



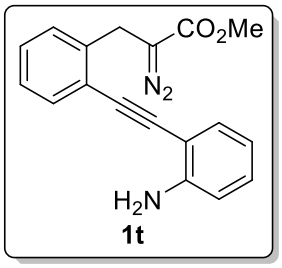
1.67 g, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.60 – 7.53 (comp, 3H), 7.41 – 7.27 (comp, 6H), 3.94 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 190.5, 139.0, 132.6, 131.6, 129.6, 128.8, 128.6, 128.5, 127.3, 123.0, 94.0, 87.4, 68.2, 27.5. HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{14}N_2NaO^+$ $[M+Na]^+$: 297.0998, found 297.0994.

2-Diazo-1-phenyl-3-(2-(phenylethynyl)phenyl)propan-1-one.



2.42 g, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.61 – 7.55 (comp, 3H), 7.55 – 7.50 (comp, 2H), 7.49 – 7.39 (comp, 3H), 7.39 – 7.32 (comp, 5H), 7.31 – 7.27 (m, 1H), 4.12 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 189.2, 138.9, 137.7, 132.8, 131.7, 131.5, 129.7, 128.9, 128.6, 128.5, 127.5, 127.3, 123.2, 123.0, 94.3, 87.4, 28.8. HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{17}N_2O^+$ $[M+H]^+$: 337.1335, found 337.1330.

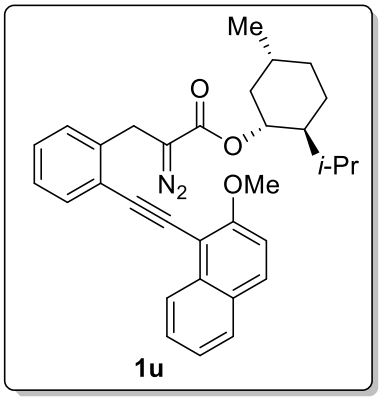
Methyl 3-(2-((2-aminophenyl)ethynyl)phenyl)-2-diazopropanoate.



1t

1.22 g, 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.58 – 7.53 (m, 1H), 7.38 – 7.24 (comp, 4H), 7.18 – 7.12 (m, 1H), 6.76 – 6.70 (comp, 2H), 4.35 (s, 2H), 3.89 (s, 2H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.7, 148.0, 138.8, 132.6, 132.3, 130.0, 129.1, 128.7, 127.2, 123.1, 117.9, 114.5, 107.6, 92.4, 90.9, 52.0, 28.2. HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{15}N_3NaO_2^+$ $[M+Na]^+$: 328.1056, found 328.1064.

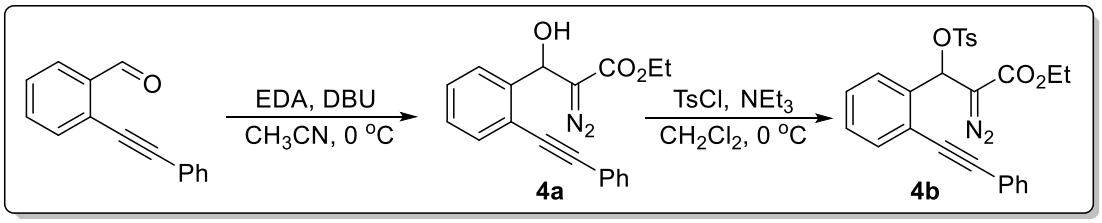
(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 2-diazo-3-(2-((2-methoxynaphthalen-1-yl)ethynyl)phenyl)propanoate.



1u

2.92 g, 59% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.32 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.78 (comp, 2H), 7.72 – 7.66 (m, 1H), 7.60 – 7.54 (m, 1H), 7.46 – 7.37 (comp, 2H), 7.36 – 7.27 (comp, 3H), 4.76 (td, *J* = 10.9, 4.4 Hz, 1H), 4.06 (s, 2H), 4.05 (s, 3H), 2.04 – 1.95 (m, 1H), 1.70 – 1.60 (comp, 2H), 1.54 – 1.40 (m, 1H), 1.40 – 1.27 (comp, 2H), 1.14 – 1.06 (m, 1H), 1.05 – 0.99 (m, 1H), 0.98 – 0.95 (m, 1H), 0.90 – 0.81 (comp, 6H), 0.75 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.2, 159.2, 144.7, 139.8, 134.4, 132.4, 130.5, 128.64, 128.61, 128.3, 127.6, 127.1, 125.3, 124.3, 123.7, 112.6, 106.4, 97.1, 88.8, 74.9, 56.6, 53.6, 47.2, 41.4, 34.7, 34.3, 31.5, 26.0, 22.1, 20.8, 16.2. HRMS (TOF MS ESI$^+$) calculated for $C_{32}H_{35}N_2O_3^+$ $[M+H]^+$: 495.2642, found 495.2650.

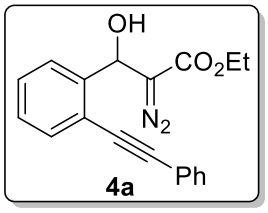
The preparation of diazo compounds 4a – 4e, related to Scheme 1.



Synthesis of 4a: To a solution of ethyl diazoacetate (EDA, 1.37 g, 12.0 mmol) in CH_3CN (10.0 mL), a solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU 1.53 g, 10.0 mmol) and 2-(phenylethynyl)benzaldehyde (2.07 g, 10.0 mmol) in CH_3CN (10.0 mL) were added in sequence at 0 ℃ under nitrogen atmosphere. After the mixture was stirred at 0 ℃ for 15 hours, the reaction was quenched with saturated aqueous $NaHCO_3$ and then extracted with CH_2Cl_2 (3 × 20.0 mL). The combined organic phase was dried over Na_2SO_4 and the solvent was evaporated under vacuum after filtration. The resulting residues was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1/3) to afford the pure diazoacetate **4a** (2.85 g, 89% yield based on 2-(phenylethynyl)benzaldehyde).
The synthesis of other substrate **4g** is similar to that of **4a**.

Synthesis of 4b: To a solution of diazoacetate **4a** (0.32 g, 1.0 mmol) and 4-toluenesulfonyl chloride (TsCl, 0.19 g, 1.0 mmol) in dry CH_2Cl_2 (5.0 mL), and triethylamine (0.12 g, 1.2 mmol) in dry CH_2Cl_2 (1.0 mL) were added in sequence at 0 ℃ under argon atmosphere. After the mixture was stirred at 0 ℃ for 15 hours, the reaction was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2 (2 × 5.0 mL). Then the combined organic phase was washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo after filtration, and the resulting residues was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1/10) to afford the pure diazoacetates **4b** (370 mg, 78% yield based on **4a**).
The synthesis of other substrates (**4c**-**4e**) is similar to that of **4b**.

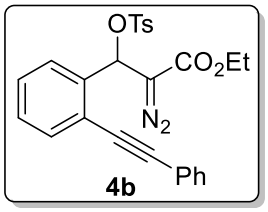
Ethyl 2-diazo-3-hydroxy-3-(2-(phenylethynyl)phenyl)propanoate.



2.85 g, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.74 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.50 (comp, 3H), 7.45 – 7.38 (m, 1H), 7.37 – 7.28 (comp, 4H), 6.37 (s, 1H), 4.26 – 4.17 (m, 2H), 3.96 (s, 1H), 1.23 – 1.16 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.4, 140.9, 132.3, 131.7, 128.7, 128.5, 128.3, 127.9, 125.6, 122.9, 120.7,

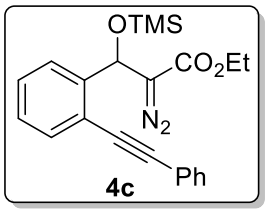
95.6, 86.0, 67.5, 61.1, 14.4. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{16}N_2NaO_3^+$ [M+Na]$^+$: 343.1053, found 343.1051.

Ethyl 2-diazo-3-(2-(phenylethynyl)phenyl)-3-(tosyloxy)propanoate.



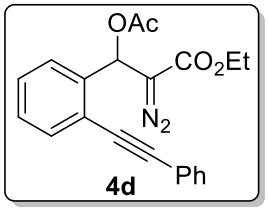
370.0 mg, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.80 – 7.67 (m, 1H), 7.65 – 7.55 (m, 1H), 7.54 – 7.48 (m, 1H), 7.47 – 7.33 (comp, 4H), 7.33 – 7.15 (comp, 6H), 6.22 (s, 1H), 4.11 – 4.01 (m, 2H), 2.39 (s, 3H), 1.38 – 1.19 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 139.2, 132.5, 131.8, 129.7, 128.6, 128.5, 128.30, 128.25, 128.2, 127.2, 126.4, 125.8, 123.0, 121.6, 95.5, 86.0, 73.1, 61.1, 22.3, 14.4. HRMS (TOF MS ESI$^+$) calculated for $C_{26}H_{22}N_2NaO_5S^+$ [M+Na]$^+$: 497.1147, found 497.1141.

Ethyl 2-diazo-3-(2-(phenylethynyl)phenyl)-3-((trimethylsilyl)oxy)propanoate.



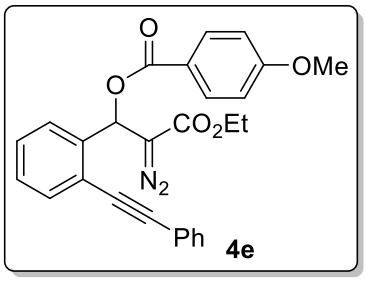
326.0 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.68 – 7.62 (m, 1H), 7.62 – 7.53 (comp, 3H), 7.42 – 7.32 (comp, 4H), 7.33 – 7.27 (m, 1H), 6.35 (d, *J* = 1.6 Hz, 1H), 4.46 – 3.99 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 3H), 0.19 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.6, 142.4, 132.4, 131.8, 128.6, 128.5, 128.4, 127.8, 125.9, 123.1, 120.5, 95.7, 86.2, 68.2, 60.9, 14.5, 0.01. HRMS (TOF MS ESI$^+$) calculated for $C_{22}H_{24}N_2NaO_3Si^+$ [M+Na]$^+$: 415.1448, found 415.1454.

Ethyl 3-acetoxy-2-diazo-3-(2-(phenylethynyl)phenyl)propanoate.



631.0 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.63 – 7.51 (comp, 3H), 7.49 – 7.44 (m, 1H), 7.41 – 7.29 (comp, 5H), 7.21 (s, 1H), 4.26 – 4.08 (m, 2H), 2.17 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 169.6, 164.7, 138.1, 132.7, 131.8, 128.7, 128.5, 128.4, 128.3, 125.4, 122.8, 121.2, 96.2, 85.8, 70.0, 61.2, 21.0, 14.3. HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{18}N_2NaO_4^+$ [M+Na]$^+$: 385.1159, found 385.1169.

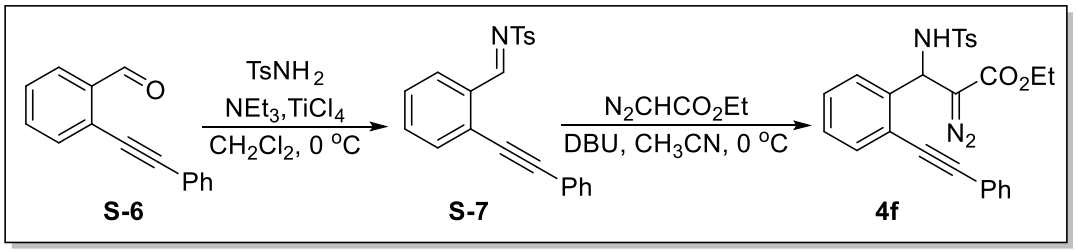
2-Diazo-3-ethoxy-3-oxo-1-(2-(phenylethynyl)phenyl)propyl 4-methoxybenzoate.



4e

818.0 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.18 – 8.07 (comp, 2H), 7.67 – 7.52 (comp, 4H), 7.43 (s, 1H), 7.40 – 7.29 (comp, 5H), 7.02 – 6.90 (comp, 2H), 4.25 – 4.09 (m, 2H), 3.85 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.2, 165.0, 163.8, 138.5, 132.8, 132.0, 131.9, 128.7, 128.5, 128.4, 128.3, 125.6, 122.9, 122.2, 121.2, 113.8, 96.2, 86.0, 70.4, 61.2, 55.5, 14.2. HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{22}N_2NaO_5^+$ $[M+Na]^+$: 477.1426, found 477.1432.

The preparation of diazo compound 4f, related to Scheme 1.



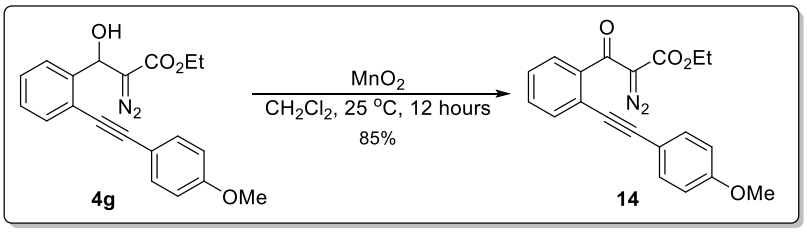
S-6 **S-7** **4f**

<u>Synthesis of 4f</u>: To a solution of 2-alkynylbenzaldehyde **S-6** (412.5 mg, 2.0 mmol), arylsulfonamide (342.5mg, 2.0 mmol) and triethylamine (506.0 mg, 5.0 mmol) in dry CH_2Cl_2 (10.0 mL), was added titanium tetrachloride (455.2 mg, 2.4 mmol) at 0 °C under argon atmosphere. The reaction mixture was stirred under these conditions for 12 h, and then quenched with brine. The aqueous phase was extracted with CH_2Cl_2 (10.0 mL X 2), and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo after filtration, and the resulting residues was purified by recrystallization (solvents: CH_2Cl_2/petroleum ether = 5 : 1) to afford 432.0 mg of **S-7** in 60% yield (based on **S-6**).

To a solution of ethyl diazoacetate (0.14 g, 1.2 mmol) in anhydrous CH_3CN (1.0 mL), was added a solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.15 g, 1.0 mmol) in anhydrous CH_3CN (1.0 mL) and **S-7** (0.36 g, 1.0 mmol) in anhydrous CH_3CN (1.0 mL) in sequence at 0 °C under nitrogen atmosphere. After the mixture was stirred at room temperature for 15 h, the reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (2 X 5.0 mL). Then the combined organic phase was washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo after filtration, and the precipitated solid was washed with petroleum ether (6.0 mL X 2). Then the solid was dried under vacuum to give the corresponding diazoacetate **4f**

(407.0 mg, 86% yield based on **S-7**) without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.82 – 7.79 (comp, 2H), 7.71 – 7.69 (m, 1H), 7.53 – 7.45 (comp, 3H), 7.37 – 7.35 (comp, 2H), 7.30 – 7.27 (comp, 2H), 7.25 – 7.22 (m, 1H), 7.19 – 7.14 (comp, 2H), 6.00 (d, *J* = 5.6 Hz, 1H), 5.84 (d, *J* = 7.6 Hz, 1H), 4.05 – 3.98 (m, 2H), 2.32 (s, 3H), 1.34 – 1.31 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 165.4, 143.6, 139.6, 137.0, 132.9, 131.8, 129.8, 129.7, 128.8, 128.5, 128.1, 127.3, 127.0, 126.5, 122.0, 95.9, 86.4, 61.2, 52.6, 21.6, 14.3. HRMS (TOF MS CI$^+$) calculated for $C_{26}H_{23}N_3NaO_4S^+$ $[M+Na]^+$: 496.1301, found 496.1311.

The preparation of diazo compounds 14, related to Scheme 1.

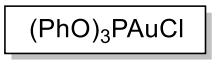


To a 50-mL oven-dried flask containing a magnetic stirring bar, **4g** (2.38 g, 6.8 mmol, prepared according to the above method for **4a**) in CH_2Cl_2 (20 mL) was added MnO_2 (8.88 g, 102.0 mmol) at 25 °C, and the reaction mixture was stirred under this condition for 12 hours. After the reaction was finished, the mixture was filtered through a short pad of silica, then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel (ethyl acetate/petroleum ether = 1/10) to give pure diazoacetate **14** (2.0 g, 85% yield based on **4g**). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.53-7.51 (m, 1H), 8.45-8.35 (comp, 5H), 6.89-6.85 (m, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.80 (s, 3H), 1.09 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.4, 161.1, 160.0, 140.4, 133.1, 131.9, 130.5, 127.9, 127.2, 121.5, 114.8, 114.1, 94.3, 85.5, 61.7, 55.3, 14.0. HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{17}N_2O_4^+$ $[M+H]^+$: 349.1183, found 349.1192.

General Procedure for the Preparation of Au(I)-Catalysts, related to Table S1.

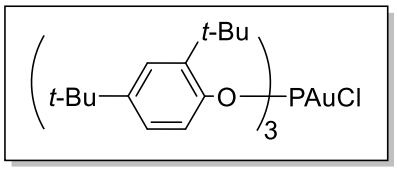
$(Me_2S)AuCl$ (294.5 mg, 1.0 equiv) was added to a solution of the corresponding phosphine (1.0 equiv) in CH_2Cl_2 (2.0 mL) under argon at 25 ºC and the solution was left stirring for 6 hours. After TLC indicated complete consumption of the starting material, the reaction solution was concentrated under reduced pressure to yield the desired Au(I) complexes (Mauleón et al., 2009; Gorin et al., 2005; Hashmi et al., 2014).

Chloro(triphenyl phosphite)gold(I) (**L1**AuCl)



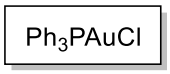
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.45 – 7.37 (comp, 6H), 7.33 – 7.27 (m, 3H), 7.25 – 7.15 (comp, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 149.49 (d, *J* = 4.5 Hz), 130.58 (d, *J* = 1.2 Hz), 126.78 (d, *J* = 1.8 Hz), 121.24 (d, *J* = 5.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 110.49.

Chloro[tris(2,4-di-tert-butylphenyl) phosphite]gold(I) (**L2**AuCl)



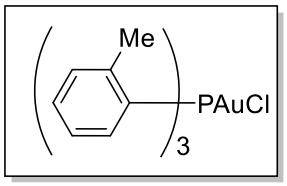
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.59 – 7.34 (comp, 6H), 7.19 – 7.03 (m, 3H), 1.45 (s, 27H), 1.30 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 148.27 (s), 147.39 (d, *J* = 5.9 Hz), 139.26 (d, *J* = 6.9 Hz), 124.89 (d, *J* = 121.3 Hz), 119.34 (d, *J* = 8.9 Hz), 35.00 (d, *J* = 43.1 Hz), 31.10 (d, *J* = 83.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 101.26.

Chloro(triphenylphosphine)gold(I) (**L3**AuCl)



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.63 – 7.39 (comp, 15H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 134.25 (d, *J* = 13.7 Hz), 132.12 (d, *J* = 1.7 Hz), 129.36 (d, *J* = 11.9 Hz), 128.81 (d, *J* = 62.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 33.77.

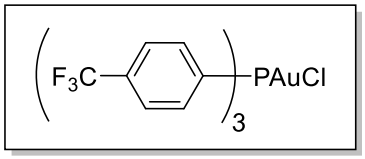
Chloro(tri-*o*-tolylphosphine)gold(I) (**L4**AuCl)



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.54 – 7.40 (m, 3H), 7.42 – 7.29 (m, 3H), 7.20 (t, *J* = 7.6 Hz, 3H), 7.05 – 6.77 (m, 3H), 2.68 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

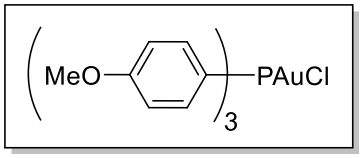
143.09 (d, *J* = 11.8 Hz), 133.65 (d, *J* = 9.7 Hz), 132.57 (d, *J* = 9.1 Hz), 132.12 (d, *J* = 2.4 Hz), 126.85 (d, *J* = 10.4 Hz), 125.17 (d, *J* = 61.1 Hz), 23.43 (d, *J* = 11.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 8.85.

Chloro[tris(4-(trifluoromethyl)phenyl)phosphine]gold(I) (**L5**AuCl)



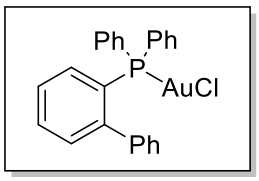
^{1}H NMR (600 MHz, $CDCl_3$) (δ, ppm) 7.85 – 7.77 (m, 6H), 7.74 – 7.59 (m, 6H); ^{13}C NMR (150MHz; $CDCl_3$) (δ, ppm)134.8 (qd, J = 33 , 2.7 Hz, Ar-C(CF3)), 134.7 (d, J = 14.6 Hz, ArCH), 131.8 (d, J = 60.6 Hz, Ar-CP), 126.7 (dq, J = 12.2, 3.5 Hz, Ar-CH), 123.2 (d, J = 271.1 Hz, CF3); ^{19}F NMR (564 MHz; $CDCl_3$) (δ, ppm): -63.4 (m); ^{31}PNMR (162 MHz; $CDCl_3$) (δ, ppm) 33.6.

Chloro[tris(4-methoxyphenyl)phosphine]gold(I) (**L6**AuCl)



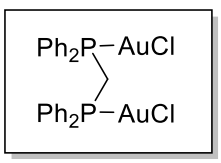
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.52 – 7.31 (m, 6H), 7.01 – 6.85 (m, 6H), 3.82 (s, 9H); ^{13}C NMR (150 MHz, $cdcl_3$) (δ, ppm) 162.42 (s), 135.61 (d, *J* = 15.3 Hz), 120.41 (d, *J* = 68.4 Hz), 114.83 (d, *J* = 13.0 Hz), 55.55 (s); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 29.77.

Chloro[(1,1'-biphenyl)-2-yldiphenylphosphine]gold(I) (**L7**AuCl)



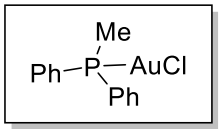
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.65 – 7.30 (comp, 14H), 7.28 – 7.24 (m, 2H), 7.10 – 6.90 (comp, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 148.22 (d, *J* = 15.0 Hz), 140.06 (d, *J* = 6.7 Hz), 134.58 (d, *J* = 14.0 Hz), 133.79 (d, *J* = 6.7 Hz), 132.12 (d, *J* = 8.2 Hz), 131.88 (d, *J* = 2.3 Hz), 131.53 (d, *J* = 2.2 Hz), 129.94 (d, *J* = 62.1 Hz), 129.82, 129.26 (d, *J* = 12.0 Hz), 128.58, 128.54, 127.66 (d, *J* = 8.9 Hz) , 127.658 (d, *J* = 61.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 60.51.

dppm(AuCl)$_2$ (**L8**$(AuCl)_2$)



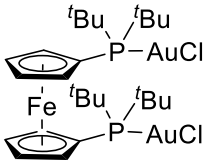
^{1}H NMR (600 MHz, DMSO-d_6) (δ, ppm) 7.80 – 7.73 (m, 8H), 7.51 (t, J = 7.4 Hz, 4H), 7.47 – 7.40 (m, 8H), 4.67 (t, J = 12.8 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) (δ, ppm) 133.36 (t, J = 7.0 Hz), 132.16 (s), 129.16 (t, J = 5.9 Hz), 128.76 (d, J = 33.3 Hz), 24.55 (t, J = 33.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.61.

Chloro(methyldiphenylphosphine)gold(I) (**L9**AuCl)



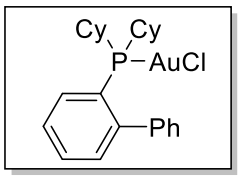
^{1}H NMR (600 MHz, $CDCl_3$) (δ, ppm) 7.66 – 7.58 (m, 4H), 7.55 – 7.48 (m, 2H), 7.48 – 7.44 (m, 4H), 2.13 (d, J = 10.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 132.80 (d, J = 13.4 Hz), 132.09 (d, J = 2.6 Hz), 130.50 (d, J = 62.3 Hz), 129.41 (d, J = 11.7 Hz), 14.90 (d, J = 39.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 17.44.

1,1'-Bis(di-*tert*-butylphosphino)ferrocene-(AuCl)$_2$ (**L10**$(AuCl)_2$)



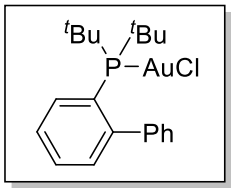
^{1}H NMR (600 MHz, $CDCl_3$) (δ, ppm) 4.84 (s, 4H), 4.53 (d, J = 1.6 Hz, 4H), 1.39 (d, J = 15.5 Hz, 36H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 75.37 (d, J = 7.0 Hz), 74.69 (d, J = 9.5 Hz), 72.51 (d, J = 49.4 Hz), 37.20 (d, J = 28.4 Hz), 30.62 (d, J = 5.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 68.92.

Chloro[(1,1'-biphenyl)-2-yldicyclohexylphosphine]gold(I) (**L11**AuCl)



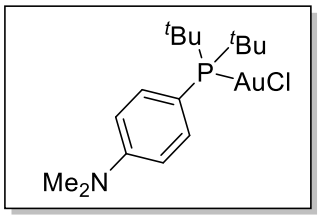
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.81 – 7.65 (m, 1H), 7.64 – 7.37 (m, 5H), 7.35 – 7.27 (m, 1H), 7.23 – 7.07 (m, 2H), 2.17 – 1.90 (m, 4H), 1.87 – 1.71 (m, 4H), 1.68 – 1.55 (m, 4H), 1.51 – 1.39 (m, 2H), 1.35 – 1.11 (m, 8H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 148.97 (d, J = 10.5 Hz), 141.45 (d, J = 5.2 Hz), 134.32 (d, J = 7.3 Hz), 132.55 (d, J = 7.4 Hz), 130.82 (s), 129.02 (d, J = 94.3 Hz), 128.41 (s), 127.57 (d, J = 8.9 Hz), 124.91 (d, J = 51.6 Hz), 36.66 (d, J = 33.6 Hz), 31.26 (d, J = 3.7 Hz), 29.51 (s), 26.563 (s), 26.556 (d, J = 26.0 Hz), 25.69 (s); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 44.51.

Chloro[(1,1'-biphenyl)-2-yldi-*tert*-butylphosphine]gold(I) (**L12**AuCl)



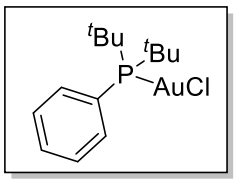
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.89 – 7.82 (m, 1H), 7.59 – 7.54 (m, 1H), 7.54 – 7.46 (m, 2H), 7.45 – 7.39 (m, 2H), 7.33 – 7.28 (m, 1H), 7.16 – 7.10 (m, 2H), 1.41 (d, *J* = 15.6 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 150.30 (d, *J* = 13.5 Hz), 142.25 (d, *J* = 6.5 Hz), 133.62 (d, *J* = 2.7 Hz), 133.37 (d, *J* = 7.4 Hz), 130.68 (d, *J* = 2.3 Hz), 129.07 (d, *J* = 52.4 Hz), 128.35 (s), 126.84 (d, *J* = 6.7 Hz), 126.21 (d, *J* = 45.5 Hz), 37.91 (d, *J* = 25.9 Hz), 31.00 (d, *J* = 6.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 26.74.

Chloro[4-(di-*tert*-butylphosphaneyl)-*N*, *N*-dimethylaniline]gold(I) (**L13**AuCl)



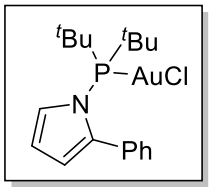
^{1}H NMR (600 MHz, $CDCl_3$) (δ, ppm) 7.77 – 7.76 (m, 2H), 6.70 (d, *J* = 8.0 Hz, 2H), 3.02 (s, 6H), 1.37 (d, *J* = 15.4 Hz, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 152.26 (s), 138.29 (s), 111.83 (s), 111.44 (d, *J* = 11.5 Hz), 40.06 (s), 36.64 (d, *J* = 28.0 Hz), 30.37 (d, *J* = 5.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 76.69.

Chloro[di-*tert*-butyl(phenyl)phosphane]gold(I) (**L14**AuCl)



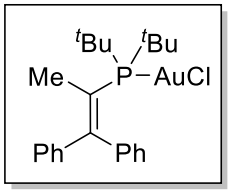
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.12 – 7.82 (m, 2H), 7.62 – 7.51 (m, 1H), 7.50 – 7.37 (m, 2H), 1.40 (d, *J* = 15.6 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 136.37 (s), 131.94 (d, *J* = 2.3 Hz), 128.59 (d, *J* = 10.7 Hz), 127.67 (d, *J* = 47.6 Hz), 36.43 (d, *J* = 26.2 Hz), 30.22 (d, *J* = 5.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 79.65.

Chloro[1-(di-*tert*-butylphosphaneyl)-2-phenyl-1*H*-pyrrole]gold(I) (**L15**AuCl)



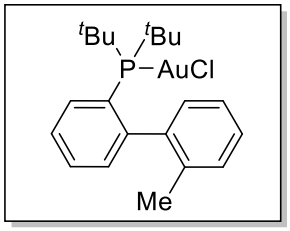
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.62 (t, *J* = 7.5 Hz, 1H), 7.56 – 7.41 (m, 2H), 7.24 – 7.10 (m, 2H), 7.08 – 6.97 (m, 1H), 6.87 (d, *J* = 3.9 Hz, 1H), 6.49 – 6.31 (m, 1H), 1.35 (d, *J* = 16.1 Hz, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 140.22 (s), 130.66 (d, *J* = 3.8 Hz), 129.87 (s), 129.20 (d, *J* = 173.4 Hz), 120.38 (d, *J* = 5.5 Hz), 118.79 (d, *J* = 64.9 Hz), 109.25 (d, *J* = 7.4 Hz), 37.91 (d, *J* = 31.0 Hz), 30.22 (d, *J* = 6.5 Hz); ^{31}P NMR (162 MHz) (δ, ppm) 46.64.

Chloro[di-*tert*-butyl(1,1-diphenylprop-1-en-2-yl)phosphine]gold(I) (**L16**AuCl)



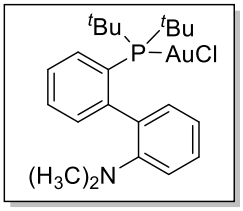
^{1}H NMR (600 MHz, $CDCl_3$) (δ, ppm) 7.46 – 7.39 (m, 1H), 7.39 – 7.26 (comp, 4H), 7.24 – 7.20 (m, 1H), 7.17 – 7.00 (comp, 4H), 2.07 (d, *J* = 7.5 Hz, 3H), 1.51 (d, *J* = 15.3 Hz, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 162.32 (d, *J* = 13.9 Hz), 143.59 (d, *J* = 11.9 Hz), 142.49 (d, *J* = 9.9 Hz), 129.22 (d, *J* = 46.0 Hz), 127.73 (d, *J* = 100.5 Hz) 127.42 (d, *J* = 177.3 Hz), 123.27 (d, *J* = 38.8 Hz), 37.66 (d, *J* = 25.7 Hz), 31.46 (d, *J* = 6.6 Hz), 22.01 (d, *J* = 2.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 66.93.

Chloro{di-*tert*-butyl(2'-methyl-[1,1'-biphenyl]-2-yl)phosphine}gold(I) (**L17**AuCl)



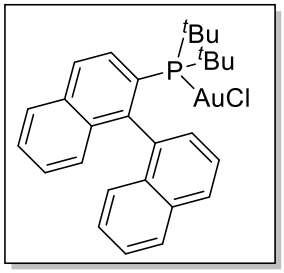
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.01 – 7.79 (m, 1H), 7.62 – 7.40 (m, 3H), 7.37 – 7.28 (m, 1H), 7.27 – 7.17 (m, 2H), 7.07 – 6.76 (m, 1H), 2.03 (s, 3H), 1.43 (dd, *J* = 15.5, 9.7 Hz, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 149.68 (d, *J* = 13.8 Hz), 141.28 (d, *J* = 6.3 Hz), 135.50 (s), 133.95 (d, *J* = 2.2 Hz), 133.41 (d, *J* = 7.6 Hz), 131.31 (s), 130.99 (s), 130.24 (s), 128.70 (s), 127.03 (s), 126.74 (d, *J* = 6.6 Hz), 125.43 (s), 38.01 (dd, *J* = 26.0, 14.0 Hz), 31.18 (dd, *J* = 122.0, 6.5 Hz), 20.81 (s); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 60.40.

Chloro[2'-(di-*tert*-butylphosphaneyl)-*N*,*N*-dimethyl-[1,1'-biphenyl]-2-amine]gold(I) (**L18**AuCl)



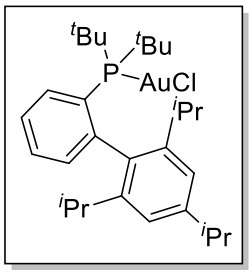
^{1}H NMR (600 MHz, $CDCl_3$) (δ, ppm) 7.89 – 7.82 (m, 1H), 7.59 – 7.49 (comp, 2H), 7.48 – 7.42 (m, 1H), 7.37 – 7.31 (m, 1H), 7.13 (d, *J* = 8.1 Hz, 1H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 7.3 Hz, 1H), 2.46 (s, 6H), 1.53 (d, *J* = 15.6 Hz, 9H), 1.25 (d, *J* = 15.3 Hz, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 151.23 (s), 149.24 (d, *J* = 13.3 Hz), 136.37 (d, *J* = 5.5 Hz), 134.52 (d, *J* = 7.8 Hz), 133.94 (s), 131.13 (d, *J* = 76.3 Hz), 129.43 (s), 127.10 (d, *J* = 46.2 Hz), 126.37 (d, *J* = 5.9 Hz), 122.44 (s), 121.18 (s), 44.05 (s), 38.14 (d, *J* = 26.1 Hz), 37.65 (d, *J* = 25.8 Hz), 31.70 (d, *J* = 6.8 Hz), 30.34 (d, *J* = 6.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 62.01.

Chloro[(1,1'-binaphthalen)-2-yldi-*tert*-butylphosphine]gold(I) (**L19**AuCl)



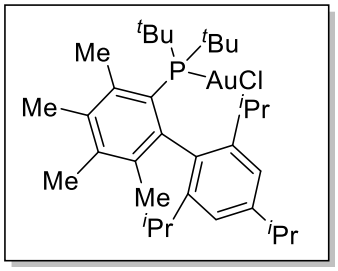
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.23 (d, *J* = 8.3 Hz, 1H), 8.11 – 7.97 (comp, 3H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.62 – 7.51 (comp, 2H), 7.50 – 7.42 (m, 1H), 7.36 – 7.30 (m, 1H), 7.26 – 7.18 (comp, 2H), 7.03 – 6.86 (comp, 2H), 1.44 (dd, *J* = 15.5, 11.5 Hz, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 147.90 (d, *J* = 13.2 Hz), 136.26 (d, *J* = 7.9 Hz), 134.69 (d, *J* = 9.0 Hz), 134.13 (d, *J* = 1.9 Hz), 133.56 (s), 129.44 (d, *J* = 13.0 Hz), 128.87 (d, *J* = 3.3 Hz), 128.65 (d, *J* = 1.0 Hz), 127.44 (d, *J* = 7.1 Hz), 124.98 (s), 38.16 (dd, *J* = 25.3, 22.9 Hz), 31.38 (dd, *J* = 89.8, 6.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 62.51.

Chloro{di-*tert*-butyl(2',4',6'-triisopropyl-[1,1'-biphenyl]-2-yl)phosphine}gold(I) (**L20**AuCl)



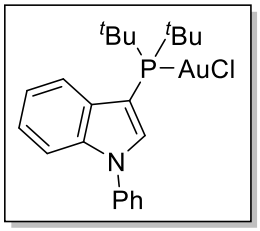
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.93 – 7.82 (m, 1H), 7.57 – 7.43 (comp, 2H), 7.36 – 7.28 (m, 1H), 7.06 (s, 2H), 2.98 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.33 (dt, *J* = 13.4, 6.7 Hz, 2H), 1.41 (d, *J* = 15.4 Hz, 18H), 1.37 (d, *J* = 6.9 Hz, 6H), 1.28 (d, *J* = 6.8 Hz, 6H), 0.91 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 150.21 (s), 148.65 (d, *J* = 14.3 Hz), 145.77 (s), 135.61 (d, *J* = 5.6 Hz), 135.03 (d, *J* = 8.0 Hz), 134.53 (d, *J* = 3.1 Hz), 130.29 (d, *J* = 2.3 Hz), 128.43 (d, *J* = 43.1 Hz), 126.48 (d, *J* = 7.0 Hz), 121.94 (s), 38.43 (d, *J* = 26.4 Hz), 34.31 (s), 31.39 (d, *J* = 6.5 Hz), 30.94 (s), 26.29 (s), 24.46 (s), 23.11 (s); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 59.17.

Chloro{di-*tert*-butyl(2',4',6'-triisopropyl-3,4,5,6-tetramethyl-[1,1'-biphenyl]-2-yl) phosphine}gold(I) (**L21**AuCl)



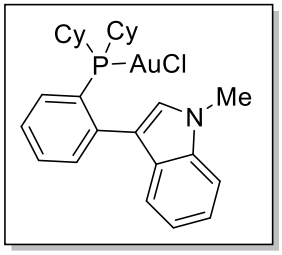
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.04 (s, 2H), 3.03 – 2.94 (m, 1H), 2.61 (s, 3H), 2.41 – 2.34 (m, 2H), 2.30 (s, 3H), 2.23 (s, 3H), 1.57 – 1.45 (comp, 21H), 1.38 (d, *J* = 6.9 Hz, 6H), 1.29 (d, *J* = 6.8 Hz, 6H), 0.85 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 150.38 (s), 146.31 (d, *J* = 20.4 Hz), 145.88 (s), 140.34 (d, *J* = 2.5 Hz), 138.17 (d, *J* = 3.4 Hz), 137.78 (d, *J* = 1.4 Hz), 137.69 (d, *J* = 2.7 Hz), 135.66 (d, *J* = 7.1 Hz), 128.32 (d, *J* = 35.6 Hz), 122.68 (s), 41.98 (d, *J* = 20.5 Hz), 34.36 (s), 33.58 (d, *J* = 8.3 Hz), 30.80 (s), 28.12 (d, *J* = 1.6 Hz), 25.31 (s), 25.17 (s), 24.76 (s), 22.33 (d, *J* = 2.7 Hz), 17.65 (d, *J* = 47.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 77.67.

Chloro[3-(di-*tert*-butylphosphaneyl)-1--phenyl-1*H*-indole]gold(I) (**L22**AuCl)



^{1}H NMR (600 MHz, $CDCl_3$) (δ, ppm) 7.77 – 7.69 (comp, 2H), 7.63 – 7.57 (comp, 2H), 7.26 – 7.25 (m, 1H), 7.25 – 7.19 (comp, 4H), 6.90 – 6.85 (m, 1H), 1.44 (d, *J* = 16.3 Hz, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 141.65 (d, *J* = 4.7 Hz), 137.83 (s), 130.42 (s), 130.24 (s), 130.04 (s), 126.52 (d, *J* = 7.6 Hz), 126.15 (d, *J* = 58.0 Hz), 124.65 (s), 121.34 (d, *J* = 34.8 Hz), 113.56 (d, *J* = 4.6 Hz), 111.98 (s), 38.08 (d, *J* = 29.4 Hz), 30.37 (d, *J* = 6.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 48.86.

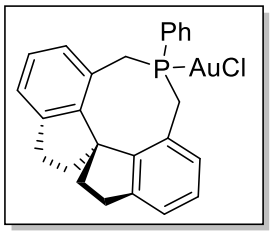
Chloro[3-(di-*tert*-butylphosphaneyl)-1--phenyl-1*H*-indole]gold(I) (**L23**AuCl)



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.93 – 7.78 (m, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.49 (m, 2H), 7.47 – 7.33 (comp, 2H), 7.34 – 7.26 (m, 1H), 7.24 – 7.13 (m, 1H), 6.68 – 6.20 (m, 1H), 3.50 (s, 3H), 2.50 – 2.19 (m, 1H), 2.02 – 1.88 (m, 2H), 1.88 –

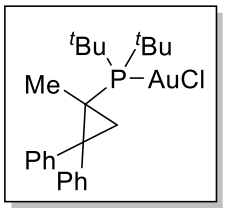
1.49 (m, 10H), 1.41 – 1.09 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 139.33 (d, *J* = 9.9 Hz), 137.49 (s), 137.41 (d, *J* = 5.6 Hz), 135.14 (d, *J* = 9.1 Hz), 134.05 (d, *J* = 7.0 Hz), 130.88 (d, *J* = 2.2 Hz), 128.90 (d, *J* = 9.0 Hz), 127.54 (s), 122.46 (s), 120.72 (s), 120.37 (s), 110.24 (s), 104.97 (s), 37.02 (d, *J* = 32.9 Hz), 35.82 (d, *J* = 33.9 Hz), 31.82 (d, *J* = 5.6 Hz), 30.96 (s), 30.25 (d, *J* = 2.0 Hz), 29.75 (d, *J* = 2.9 Hz), 26.73 (dd, *J* = 12.4, 7.5 Hz), 26.45 (dd, *J* = 20.7, 12.9 Hz), 25.68 (s). ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 46.55.

Chloro[*S*-dimethylene-[7,7′-(1,1′-spiroindan)]-phenylphospholine]gold(I) (**L24**AuCl)



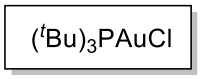
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.53 – 7.45 (m, 1H), 7.38 – 7.27 (comp, 4H), 7.26 – 7.22 (m, 1H), 7.21 – 7.11 (comp, 3H), 6.85 (t, *J* = 7.5 Hz, 1H), 5.94 (d, *J* = 7.6 Hz, 1H), 3.76 (dd, *J* = 16.0, 12.9 Hz, 1H), 3.50 (dd, *J* = 14.5, 8.6 Hz, 1H), 3.12 – 2.98 (comp, 3H), 2.98 – 2.84 (comp, 3H), 2.32 (dd, *J* = 12.4, 6.4 Hz, 1H), 2.24 (dd, *J* = 12.4, 6.5 Hz, 1H), 2.06 – 1.94 (m, 1H), 1.94 – 1.83 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) (δ, ppm) 147.94 (d, *J* = 4.6 Hz), 147.71 (d, *J* = 5.3 Hz), 143.98 (d, *J* = 3.6 Hz), 143.80 (d, *J* = 3.1 Hz), 133.73 (d, *J* = 12.6 Hz), 132.38 (d, *J* = 2.5 Hz), 130.69 (d, *J* = 6.2 Hz), 129.89 (d, *J* = 4.6 Hz), 128.84 (d, *J* = 3.8 Hz), 128.56 (d, *J* = 11.1 Hz), 127.21 (d, *J* = 4.3 Hz), 127.07 (d, *J* = 2.9 Hz), 126.73 (s), 125.64 (d, *J* = 11.4 Hz), 124.96 (d, *J* = 4.1 Hz), 124.69 (d, *J* = 3.5 Hz), 61.78 (d, *J* = 2.1 Hz), 38.21 (d, *J* = 42.4 Hz), 31.75 (d, *J* = 28.4 Hz), 30.48 (d, *J* = 23.2 Hz), 26.21 (d, *J* = 34.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 27.00.

Chloro[di-*tert*-butyl(1-methyl-2,2-diphenylcyclopropyl)phosphine]gold(I) (**L25**AuCl)



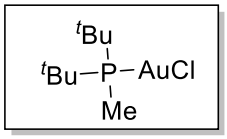
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.56 – 7.45 (m, 2H), 7.45 – 7.37 (m, 2H), 7.32 – 7.24 (m, 5H), 7.21 – 7.14 (m, 1H), 2.45 (dd, *J* = 15.3, 5.3 Hz, 1H), 1.67 – 1.49 (m, 19H), 1.42 (d, *J* = 7.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 143.21 (s), 141.37 (d, *J* = 5.9 Hz), 130.47 (s), 129.65 (d, *J* = 1.6 Hz), 129.34 (s), 128.84 (s), 127.72 (s), 126.87 (s), 42.40 (s), 39.51 (dd, *J* = 309.9, 25.3 Hz), 32.22 (dd, *J* = 97.0, 5.1 Hz), 27.40 (s), 25.37 (d, *J* = 35.8 Hz), 24.26 (s); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 77.64.

Chloro[tri-*tert*-butylphosphine]gold(I) (**L26**AuCl)



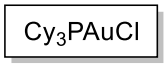
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 1.52 (d, *J* = 13.9 Hz, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 39.61 (d, *J* = 20.9 Hz), 32.38 (d, *J* = 4.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 91.18.

Chloro[di-*tert*-butyl(methyl)phosphine]gold(I) (**L27**AuCl)



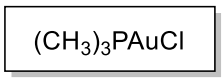
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 1.49 (d, *J* = 9.3 Hz, 3H), 1.33 (d, *J* = 15.2 Hz, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 34.48 (d, *J* = 29.6 Hz), 29.16 (d, *J* = 5.2 Hz), 5.77 (d, *J* = 31.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 58.18.

Chloro(tricyclohexylphosphine)gold(I) (**L28**AuCl)



^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 2.04 – 1.90 (m, 9H), 1.90 – 1.78 (m, 6H), 1.75 – 1.67 (m, 3H), 1.52 – 1.38 (m, 6H), 1.36 – 1.18 (m, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 33.44 (d, *J* = 31.0 Hz), 30.89 (s), 27.10 (d, *J* = 12.2 Hz), 25.94 (d, *J* = 1.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) 54.65.

Chloro(trimethylphosphine)gold(I) (**L29**AuCl)



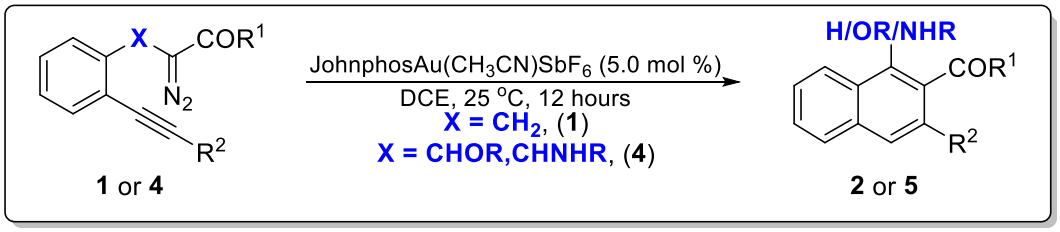
^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 1.62 (d, *J* = 11.3 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 16.25 (d, *J* = 40.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) -9.80.

General Procedure for the Optimization of Ligands, related to Table S2.

The **Ln**AuCl complex (0.01 mmol) and $AgSbF_6$ (3.34mg, 0.01 mmol) were suspended in DCE (0.5 mL). The reaction was stirred at room temperature for 2.0 hours. The solvent was evaporated and the mixture dissolved in 0.5 mL of DCE. Then the mixture was filtered through a pad of Celite, which was added into a solution of **1a** (58mg, 0.2mmol) in DCE (0.5 mL) at 25 ℃ for 12.0 hours. Afterwards, 1,3,5-trimethoxybenzene (16.8 mg, 0.1mmol) was added into the reaction mixture, and yield determined by proton *NMR* using 1,3,5-trimethoxybenzene as the internal standard. E.g., "**L1**, 0%; 89%" is equal to "**L1**AuCl, 0% **2a**; 89% **3a**".

General Procedure for the Gold-Catalyzed Aromatization, related to Scheme1

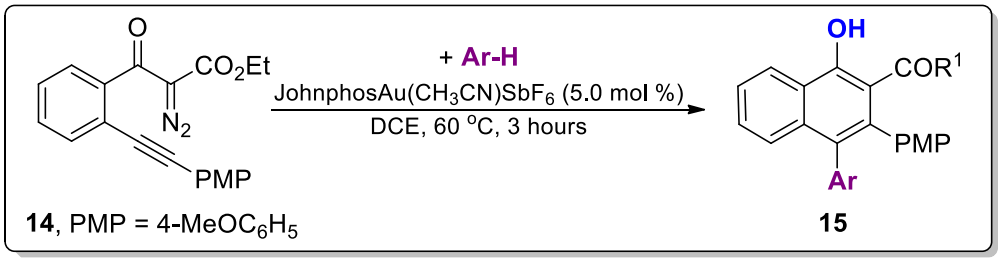
Method A



A solution of diazoacetate **1** or **4** (0.2 mmol) in 1,2-dichloroethane (2.0 mL) was added over 5 min to a 10-mL oven-dried flask containing a magnetic stirring bar, and JohnphosAu(CH_3CN)SbF_6 (7.7 mg, 0.01 mmol, 5.0 mol %) in dry 1,2-dichloroethane (2.0 mL) using a syringe at room temperature under argon atmosphere. After the addition, the reaction mixture was stirred at 25 ℃ for 12 hours. Then, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on a silica gel (solvents: ethyl acetate/petroleum ether = 1/10) to afford the pure naphthalene derivatives **2** or **5** in 62%-94% yields.

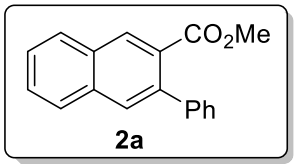
(The experimental procedure for the synthesis of **6** is same to that mentioned above in Method A, related to **Figure 2A**.)

Method B



A solution of diazoacetate **14** (69.6 mg, 0.2 mmol) in dry 1,2-dichloroethane (2.0 mL) was added over 5 min to a 10-mL oven-dried flask containing a magnetic stirring bar, JohnphosAu (CH_3CN)SbF_6 (7.7 mg, 0.01 mmol, 5.0 mol %), and nucleophiles (0.3 mmol, 1.5 equiv) in dry 1,2-dichloroethane (2.0 mL) using a syringe at room temperature under argon atmosphere. After the addition, the reaction mixture was stirred at 60 ℃ for 3 hours (performed for 12 h in the case of **15i**). Then, the solvent was removed under reduced pressure and the crude product was purified by column chromatography on a silica gel (solvents: ethyl acetate/petroleum ether = 1/10 to 1/5) to afford the pure products **15** in 53%-94% yields.

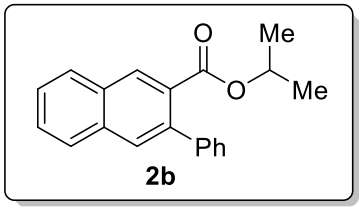
Methyl 3-phenyl-2-naphthoate.



2a

47.7 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.41 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.83 (s, 1H), 7.63 – 7.52 (comp, 2H), 7.48 – 7.35 (comp, 5H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 169.1, 141.6, 138.9, 134.5, 131.7, 131.1, 129.9, 129.2, 128.7, 128.6, 128.4, 128.2, 127.9, 127.2, 126.9, 52.2. HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{14}NaO_2^+$ [M+Na]$^+$: 285.0886, found 285.0881.

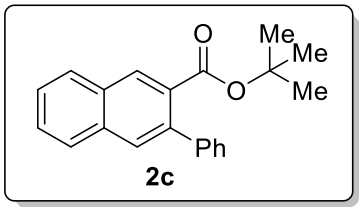
Isopropyl 3-phenyl-2-naphthoate.



2b

52.8 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.38 (s, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.82 (s, 1H), 7.61 – 7.52 (comp, 2H), 7.44 – 7.34 (comp, 5H), 5.05 (dt, *J* = 12.5, 6.3 Hz, 1H), 1.07 (d, *J* = 6.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 168.5, 141.7, 138.8, 134.3, 131.7, 130.7, 130.3, 129.7, 128.8, 128.6, 128.2, 128.1, 127.9, 127.1, 126.8, 68.8, 21.5. HRMS (TOF MS CI$^+$) calculated for $C_{20}H_{18}NaO_2^+$ [M+Na]$^+$: 313.1199, found 313.1215.

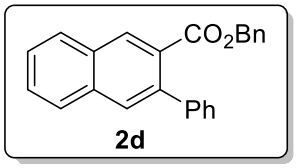
***tert*-Butyl 3-phenyl-2-naphthoate**.



2c

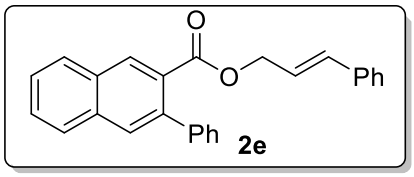
54.8 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.35 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.79 (s, 1H), 7.61 – 7.51 (m, 2H), 7.46 – 7.35 (m, 5H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 168.2, 142.2, 138.8, 134.2, 131.8, 131.5, 130.6, 129.6, 128.9, 128.6, 128.1, 128.0, 127.9, 127.0, 126.7, 81.5, 27.7. HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{20}NaO_2^+$ [M+Na]$^+$: 327.1356, found 327.1351.

Benzyl 3-phenyl-2-naphthoate.



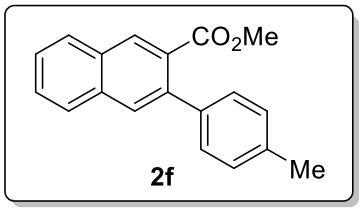
60.2 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.44 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.84 (s, 1H), 7.62 – 7.58 (m, 1H), 7.57 – 7.53 (m, 1H), 7.44 – 7.36 (comp, 5H), 7.33 – 7.28 (comp, 3H), 7.20 – 6.97 (comp, 2H), 5.17 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 168.7, 141.6, 138.8, 135.5, 134.5, 131.70, 131.65, 131.2, 129.9, 129.3, 128.71, 128.70, 128.5, 128.4, 128.3, 128.2, 127.9, 127.2, 126.8 67.2. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{18}NaO_2^+$ $[M+Na]^+$: 361.1199, found 361.1194.

Cinnamyl 3-phenyl-2-naphthoate.



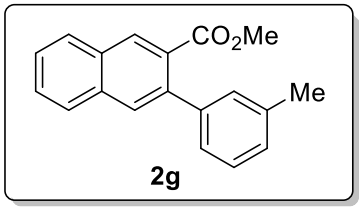
67.1 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.45 (s, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.84 (s, 1H), 7.63 – 7.58 (m, 1H), 7.58 – 7.53 (m, 1H), 7.47 – 7.38 (comp, 4H), 7.37 – 7.32 (comp, 5H), 7.30 – 7.26 (m, 1H), 6.52 – 6.42 (m, 1H), 6.07 – 5.95 (m, 1H), 4.77 (dd, *J* = 6.4, 1.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 168.6, 141.7, 138.9, 136.4, 134.5, 134.2, 131.7, 131.2, 129.9, 129.4, 128.8, 128.74, 128.67, 128.4, 128.2, 128.1, 127.9, 127.2, 126.9, 126.7, 122.9 65.7 HRMS (TOF MS ESI$^+$) calculated for $C_{26}H_{20}NaO_2^+$ $[M+Na]^+$: 387.1356, found 387.1370.

Methyl 3-(*p*-tolyl)-2-naphthoate.



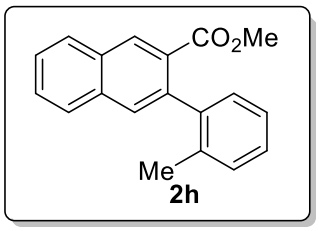
49.8 mg, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.37 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.80 (s, 1H), 7.59 – 7.49 (comp, 2H), 7.32 – 7.28 (comp, 2H), 7.26 – 7.21 (comp, 2H), 3.72 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 169.2, 138.9, 138.6, 136.9, 134.5, 131.6, 131.0, 129.8, 129.2, 128.9, 128.6, 128.5, 128.3, 127.9, 126.7, 52.2, 21.3. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{16}NaO_2^+$ $[M+Na]^+$: 299.1043, found 299.1044.

Methyl 3-(*m*-tolyl)-2-naphthoate.



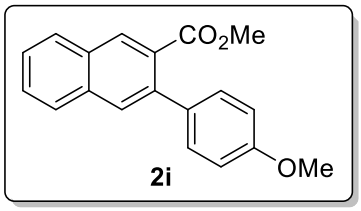
49.2 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.38 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.83 (s, 1H), 7.62 – 7.50 (comp, 2H), 7.37 – 7.29 (m, 1H), 7.28 – 7.23 (m, 1H), 7.23 – 7.15 (comp, 2H), 3.72 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 169.3, 141.5, 139.0, 137.8, 134.5, 131.7, 131.0, 129.8, 129.34, 129.28, 128.7, 128.3, 128.03, 128.01, 127.9, 126.8, 125.8, 52.2, 21.6. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{16}NaO_2^+$ $[M+Na]^+$: 299.1043, found 299.1049.

Methyl 3-(*o*-tolyl)-2-naphthoate.



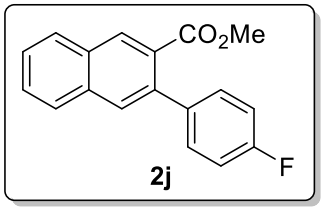
44.8 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.56 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.71 (s, 1H), 7.66 – 7.50 (comp, 2H), 7.35 – 7.23 (comp, 3H), 7.19 (d, *J* = 7.2 Hz, 1H), 3.69 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.9, 141.7, 139.1, 135.8, 134.7, 131.7, 131.4, 130.0, 129.5, 129.0, 128.9, 128.7, 128.5, 127.8, 127.4, 126.8, 125.4, 52.1, 20.2. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{16}NaO_2^+$ $[M+Na]^+$: 299.1043, found 299.1042.

Methyl 3-(4-methoxyphenyl)-2-naphthoate (**2i**).



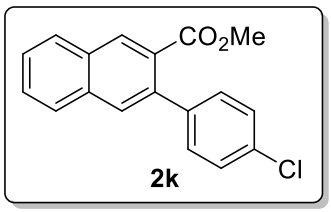
52.0 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.38 (s, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.81 (s, 1H), 7.64 – 7.50 (comp, 2H), 7.43 – 7.32 (comp, 2H), 7.04 – 6.95 (comp, 2H), 3.87 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 169.3, 159.0, 138.4, 134.5, 133.9, 131.5, 131.0, 129.71, 129.66, 129.3, 128.6, 128.3, 127.8, 126.7, 113.7, 55.4, 52.2. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{16}NaO_3^+$ $[M+Na]^+$: 315.0992, found 315.0986.

Methyl 3-(4-fluorophenyl)-2-naphthoate.



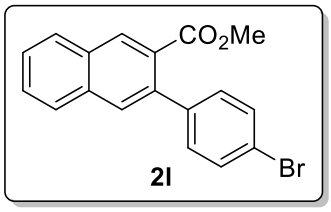
51.6 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.42 (s, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.79 (s, 1H), 7.62 – 7.53 (comp, 2H), 7.39 – 7.33 (comp, 2H), 7.20 – 7.08 (comp, 2H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 168.8, 162.4 (d, *J* = 246.0 Hz), 137.9, 137.6 (d, *J* = 3.4 Hz), 134.5, 131.7, 131.4, 130.2 (d, *J* = 8.0 Hz), 130.0, 128.9, 128.8, 128.5, 127.9, 127.0, 115.1 (d, *J* = 21.5 Hz), 52.3; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -115.69. HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{13}FNaO_2^+$ $[M+Na]^+$: 303.0792, found 303.0785.

Methyl 3-(4-chlorophenyl)-2-naphthoate.



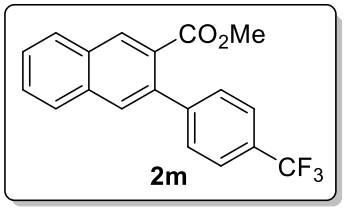
52.2 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.44 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.78 (s, 1H), 7.64 – 7.53 (comp, 2H), 7.44 – 7.37 (comp, 2H), 7.35 – 7.29 (comp, 2H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 168.7, 140.1, 137.8, 134.5, 133.3, 131.8, 131.5, 129.99, 129.97, 128.8, 128.7, 128.6, 128.3, 127.9, 127.1, 52.3. HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{13}ClNaO_2^+$ $[M+Na]^+$: 319.0496, found 319.0500.

Methyl 3-(4-bromophenyl)-2-naphthoate.



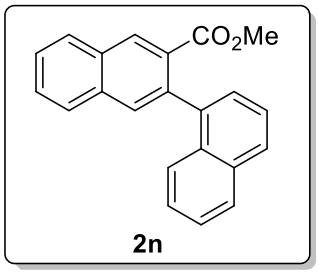
56.0 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.44 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.77 (s, 1H), 7.64 – 7.52 (comp, 4H), 7.31 – 7.23 (comp, 2H), 3.74 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 168.6, 140.6, 137.8, 134.5, 131.8, 131.6, 131.3, 130.3, 129.9, 128.8, 128.62, 128.55, 127.9, 127.1, 121.5, 52.3. HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{13}BrNaO_2^+$ $[M+Na]^+$: 362.9991, found 362.9992.

Methyl 3-(4-(trifluoromethyl)phenyl)-2-naphthoate.



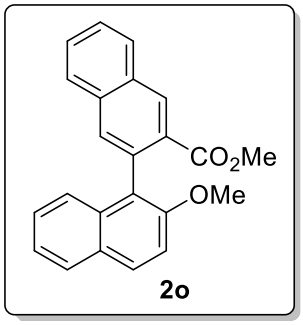
44.3 mg, 67% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.49 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.79 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.66 – 7.55 (comp, 2H), 7.54 – 7.47 (comp, 2H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 168.4, 145.5, 137.7, 134.5, 132.0, 131.8, 130.2, 129.1, 128.9, 128.8, 128.3, 128.0, 127.4, 125.1 (q, *J* = 3.7 Hz), 52.3; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -62.32. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{13}F_3NaO_2^+$ $[M+Na]^+$: 353.0760, found 353.0755.

Methyl [1,2'-binaphthalene]-3'-carboxylate.



51.9 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.65 (s, 1H), 8.05 (d, *J* = 7.4 Hz, 1H), 7.96 – 7.87 (comp, 4H), 7.67 – 7.55 (comp, 4H), 7.52 – 7.46 (comp, 2H), 7.42 – 7.36 (m, 1H), 3.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.9, 139.9, 137.6, 134.7, 133.3, 132.5, 132.0, 131.4, 131.0, 129.7, 128.9, 128.6, 128.3, 127.9, 127.7, 127.0, 126.4, 126.1, 125.7, 125.3, 52.0. HRMS (TOF MS ESI$^+$) calculated for $C_{22}H_{16}NaO_2^+$ $[M+Na]^+$: 335.1048, found 335.1041.

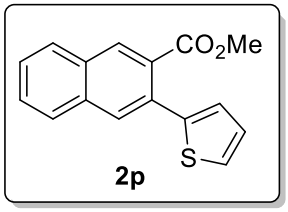
Methyl 2-methoxy-[1,2'-binaphthalene]-3'-carboxylate.



62.3 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.70 (s, 1H), 8.10 – 8.01 (m, 1H), 7.95 (d, *J* = 9.0 Hz, 1H), 7.91 – 7.81 (comp, 3H), 7.65 – 7.56 (comp, 2H), 7.49 – 7.43 (m, 1H), 7.42 – 7.38 (m, 1H), 7.37 – 7.30 (comp, 2H), 3.83 (s, 3H), 3.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.7, 153.6, 134.9, 133.7, 133.5, 132.0, 131.7, 131.5, 130.1, 129.2, 129.1, 129.0, 128.2, 128.1, 127.9, 126.8, 126.4,

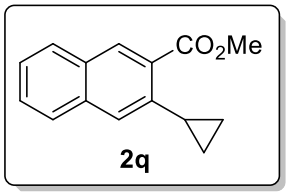
125.0, 124.8, 123.5, 113.3, 56.6, 51.9. HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{18}NaO_3^+$ [M+Na]$^+$: 365.1154, found 365.1151.

Methyl 3-(thiophen-2-yl)-2-naphthoate.



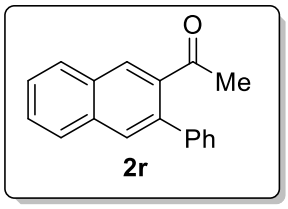
43.5 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.31 (s, 1H), 7.95 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.61 – 7.52 (comp, 2H), 7.40 – 7.35 (m, 1H), 7.14 – 7.06 (comp, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 169.0, 142.5, 134.2, 131.9, 130.8, 130.6, 130.5, 129.7, 128.6, 128.4, 127.9, 127.3, 127.2, 126.4, 125.8, 52.4. HRMS (TOF MS ESI$^+$) calculated for $C_{16}H_{12}NaO_2S^+$ [M+Na]$^+$: 291.0456, found 291.0457.

Methyl 3-cyclopropyl-2-naphthoate.



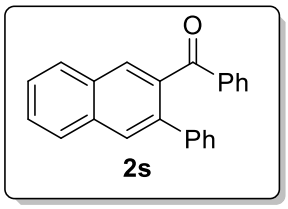
34.4 mg, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.37 (s, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.49 (comp, 2H), 7.48 – 7.42 (m, 1H), 3.98 (s, 3H), 2.77 – 2.63 (m, 1H), 1.09 – 0.95 (comp, 2H), 0.84 – 0.69 (comp, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 168.9, 140.4, 135.0, 131.2, 130.9, 130.0, 128.7, 128.1, 127.3, 126.0, 125.3, 52.2, 14.4, 8.2. HRMS (TOF MS ESI$^+$) calculated for $C_{15}H_{14}NaO_2^+$ [M+Na]$^+$: 249.0892, found 249.0876.

1-(3-Phenylnaphthalen-2-yl)ethan-1-one.



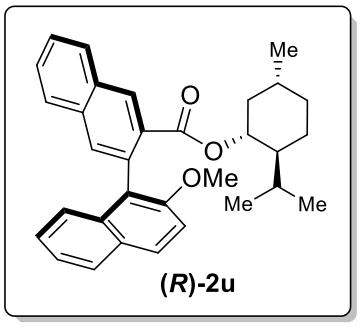
39.9 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.10 (s, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.85 (s, 1H), 7.63 – 7.51 (comp, 2H), 7.51 – 7.39 (comp, 5H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 204.4, 141.1, 139.4, 137.6, 134.2, 131.9, 129.6, 129.1, 128.9, 128.8, 128.6, 128.1, 127.9, 127.8, 126.9, 30.6. HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{14}NaO^+$ [M+Na]$^+$: 269.0937, found 269.0941.

Phenyl (3-phenylnaphthalen-2-yl)methanone.



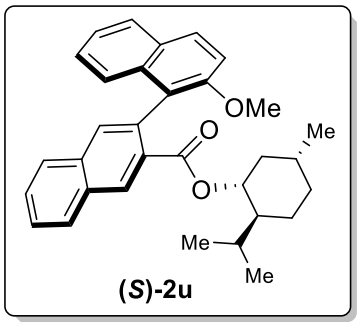
38.2 mg, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.04 (s, 1H), 8.00 – 7.87 (comp, 3H), 7.78 – 7.68 (comp, 2H), 7.63 – 7.54 (comp, 2H), 7.47 – 7.42 (m, 1H), 7.38 – 7.34 (comp, 2H), 7.33 – 7.28 (comp, 2H), 7.27 – 7.22 (comp, 2H), 7.22 – 7.17 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 198.4, 140.5, 138.6, 137.8, 137.5, 134.2, 133.0, 131.7, 130.2, 129.5, 129.3, 129.2, 128.6, 128.4, 128.3, 128.1, 128.0, 127.3, 127.0. HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{16}NaO^+$ $[M+Na]^+$: 331.1093, found 331.1089.

(*R*)-(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 2-methoxy-[1,2'-binaphthalene]-3'-carboxylate.



42.0 mg, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.72 (s, 1H), 8.12 – 8.03 (m, 1H), 7.95 (d, *J* = 9.0 Hz, 1H), 7.90 – 7.83 (comp, 2H), 7.81 (s, 1H), 7.65 – 7.55 (comp, 2H), 7.45 – 7.28 (comp, 4H), 4.67 – 4.54 (m, 1H), 3.80 (s, 3H), 1.86 – 1.75 (m, 1H), 1.61 – 1.52 (m, 1H), 1.49 – 1.41 (m, 1H), 1.39 – 1.18 (comp, 3H), 0.97 – 0.89 (m, 1H), 0.87 – 0.83 (m, 3H), 0.70 – 0.60 (m, 1H), 0.50 (d, *J* = 6.9 Hz, 3H), 0.63 (d, *J* = 6.9 Hz, 3H), 0.43 – 0.30 (m, 1H);^{13}C NMR (100 MHz, $CDCl_3$) 167.2, 153.5, 134.8, 134.0, 133.5, 132.0, 131.6, 131.4, 130.9, 129.03, 128.98, 128.9, 128.0, 127.9, 127.8, 126.7, 126.3, 125.4, 123.4, 113.0, 74.5, 56.4, 46.5, 40.3, 34.2, 31.2, 25.6, 23.0, 22.1, 20.7, 15.9. (δ, ppm) HRMS (TOF MS ESI$^+$) calculated for $C_{32}H_{35}O_3^+$ $[M+H]^+$: 467.2581, found 467.2593.

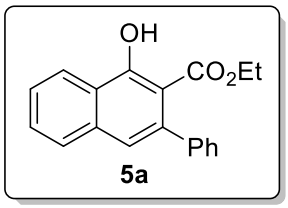
(*S*)-(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2-methoxy-[1,2'-binaphthalene] -3'-carboxylate.



(*S*)-2u

42.0 mg, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) 8.77 (s, 1H), 8.19 – 8.11 (m, 1H), 8.02 (d, *J* = 9.0 Hz, 1H), 7.99 – 7.87 (comp, 3H), 7.75 – 7.64 (comp, 2H), 7.49 (d, *J* = 9.0 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.37 – 7.33 (comp, 2H), 4.63 (td, *J* = 10.8, 4.4 Hz, 1H), 3.93 (s, 3H), 1.65 – 1.51 (comp, 4H), 1.43 – 1.26 (comp, 2H), 0.98 – 0.90 (m, 1H), 0.82 (d, *J* = 7.0 Hz, 3H), 0.79 (d, *J* = 6.5 Hz, 3H), 0.73 – 0.66 (m, 1H), 0.64 (d, *J* = 7.0 Hz, 3H), 0.07 – -0.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.1, 153.6, 134.9, 134.2, 133.3, 132.0, 131.6, 131.5, 130.9, 129.0, 128.9, 128.8, 128.0, 127.79, 127.75, 126.6, 126.4, 125.3, 125.0, 123.4, 113.3, 74.3, 56.4, 46.6, 39.7, 34.1, 31.1, 25.6, 22.9, 22.0, 21.0, 15.8. HRMS (TOF MS ESI$^+$) calculated for $C_{32}H_{35}O_3^+$ $[M+H]^+$: 467.2581, found 467.2593.

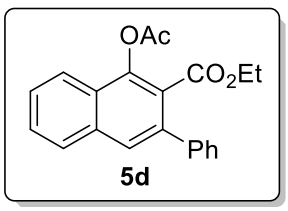
Ethyl 1-hydroxy-3-phenyl-2-naphthoate.



5a

76% yield with **4b** and 91% yield with **4c**. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 12.32 (s, 1H), 8.46 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.57 – 7.51 (m, 1H), 7.41 – 7.31 (comp, 5H), 7.21 (s, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 0.79 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.9, 161.5, 143.8, 139.6, 135.7, 129.9, 128.6, 127.6, 127.5, 126.6, 125.9, 124.2, 124.1, 121.3, 106.1, 61.1, 13.1. HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{16}NaO_3^+$ $[M+Na]^+$: 315.0992, found 315.0986.

Ethyl 1-acetoxy-3-phenyl-2-naphthoate.

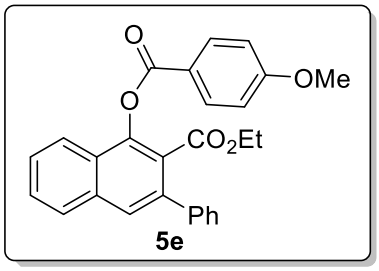


5d

62.2 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.97 – 7.83 (comp, 2H),

7.78 (s, 1H), 7.63 – 7.54 (comp, 2H), 7.50 – 7.35 (comp, 5H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.48 (s, 3H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 169.3, 166.8, 145.7, 140.6, 138.1, 134.6, 128.6, 128.4, 128.2, 127.6, 127.3, 127.0, 126.0, 123.6, 122.2, 61.5, 20.8, 13.7. HRMS (TOF MS ESI$^+$) calculated for $C_{21}H_{18}NaO_4^+$ $[M+Na]^+$: 357.1097, found 357.1105.

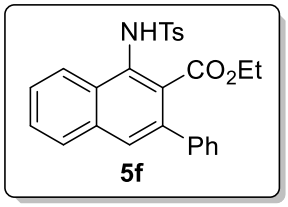
Ethyl 1-((4-methoxybenzoyl)oxy)-3-phenyl-2-naphthoate



5e

74.1 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.28 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.6 Hz, 2H), 7.81 (s, 1H), 7.61 – 7.56 (m, 1H), 7.55 – 7.49 (comp, 3H), 7.45 – 7.37 (comp, 3H), 7.07 – 7.01 (comp, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.8, 164.7, 164.3, 145.8, 140.5, 138.1, 134.7, 132.8, 128.7, 128.5, 128.2, 128.2, 127.6, 127.3, 127.0, 126.4, 124.2, 122.5, 121.3, 114.2, 61.5, 55.7, 13.7. HRMS (TOF MS ESI$^+$) calculated for $C_{27}H_{22}NaO_5^+$ $[M+Na]^+$: 449.1359, found 449.1359.

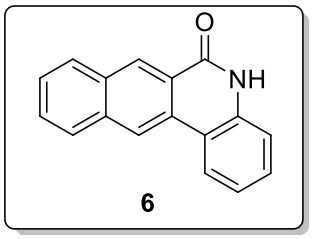
Ethyl 1-((4-methylphenyl)sulfonamido)-3-phenyl-2-naphthoate.



5f

72.2 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.72 – 8.63 (m, 1H), 8.24 (s, 1H), 7.86 – 7.79 (m, 1H), 7.76 (s, 1H), 7.68 – 7.57 (comp, 2H), 7.51 – 7.42 (comp, 2H), 7.39 – 7.29 (comp, 3H), 7.25 – 7.21 (comp, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 3.38 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 0.47 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 168.6, 143.7, 141.7, 137.9, 136.0, 134.9, 133.3, 130.4, 129.6, 129.3, 128.9, 128.3, 128.2, 128.0, 127.6, 127.4, 127.2, 126.9, 126.2, 61.6, 21.6, 12.7. HRMS (TOF MS ESI$^+$) calculated for $C_{26}H_{23}NNaO_4S^+$ $[M+Na]^+$: 468.1240, found 468.1257.

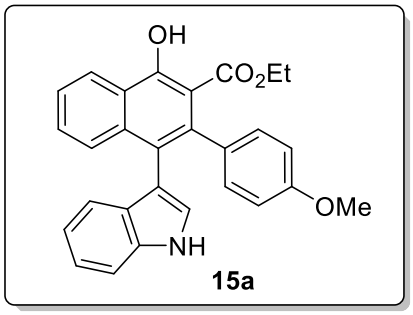
Benzo[*j*]phenanthridin-6(5*H*)-one (Gao, et al., 2019).



6

45.6 mg, 93% yield. ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 11.55 (s, 1H), 9.08 (s, 1H), 8.98 (s, 1H), 8.56 – 8.50 (m, 1H), 8.24 – 8.15 (comp, 2H), 7.75 – 7.69 (m, 1H), 7.66 – 7.61 (m, 1H), 7.51 – 7.46 (m, 1H), 7.38 – 7.34 (m, 1H), 7.32 – 7.28 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm) 161.1, 136.4, 134.9, 131.6, 130.4, 129.5, 129.1, 128.6, 128.5, 128.1, 126.8, 124.1, 123.5, 122.4, 121.5, 118.0, 116.3. HRMS (TOF MS ESI$^+$) calculated for $C_{17}H_{11}NNaO^+$ [M+Na]$^+$: 268.0733, found 268.0720.

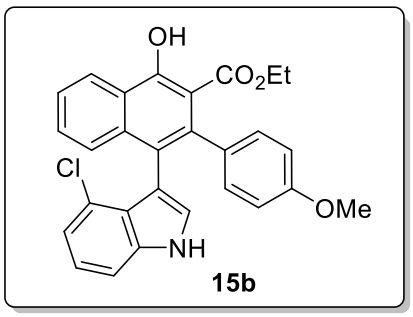
Ethyl 1-hydroxy-4-(1*H*-indol-3-yl)-3-(4-methoxyphenyl)-2-naphthoate (15a).



15a

72.6 mg, 83% yield. White solid, mp: 175-176 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 12.30 (s, 1H), 8.55 – 8.53 (m, 1H), 7.98 (s, 1H), 7.53 – 7.50 (m, 2H), 7.44 – 7.40 (m, 1H), 7.33 – 7.30 (m, 1H), 7.19 – 7.16 (m, 2H), 7.05 – 7.01 (m, 2H), 6.74 – 6.71 (m, 2H), 6.62 (d, J = 2.4 Hz, 1H), 6.43 (dd, J = 8.5, 2.5 Hz, 1H), 4.01 – 3.95 (m, 2H), 3.69 (s, 3H), 0.74 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.4, 160.5, 157.8, 139.2, 136.6, 135.6, 135.4, 130.6, 129.6, 129.5, 127.3, 125.6, 125.0, 124.3, 123.92, 123.90, 121.8, 120.2, 119.7, 114.0, 112.2, 111.0, 107.5, 61.1, 55.3, 13.3. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{23}NO_4Na^+$ [M+Na]$^+$: 460.1519, found 460.1508.

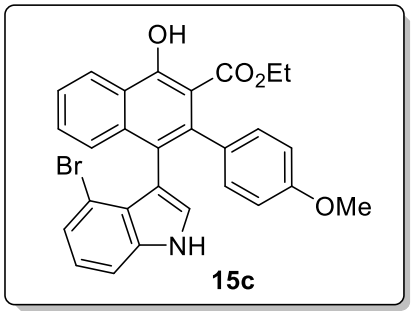
Ethyl 4-(4-chloro-1*H*-indol-3-yl)-1-hydroxy-3-(4-methoxyphenyl)-2-naphthoate.



15b

79.1 mg, 84% yield. White solid, mp: 204-205 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 12.49 (s, 1H), 8.53 (d, J = 8.1 Hz, 1H), 8.05 (s, 1H), 7.52 – 7.48 (m, 1H), 7.45 – 7.38 (m, 2H), 7.14 – 7.12 (m, 1H), 7.05 – 6.96 (comp, 4H), 6.70 (dd, J = 8.3, 2.6 Hz, 1H), 6.66 (d, J = 2.3 Hz, 1H), 6.48 (dd, J = 8.4, 2.6 Hz, 1H), 4.02 – 3.95 (m, 2H), 3.66 (s, 3H), 0.75 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.5, 160.9, 157.6, 139.0, 137.9, 136.8, 135.8, 130.6, 129.8, 129.6, 127.1, 126.4, 126.1, 125.8, 125.5, 124.5, 123.9, 123.7, 122.5, 120.5, 113.7, 112.29, 112.25, 109.9, 107.1, 61.0, 55.2, 13.2. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{22}ClNO_4Na^+$ [M+Na]$^+$: 494.1130, found 494.1096.

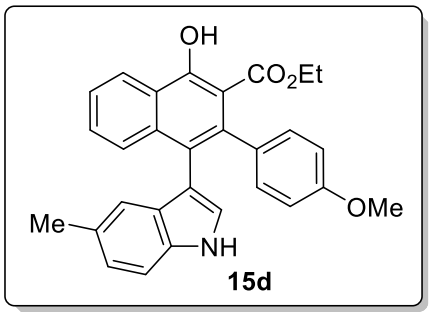
Ethyl 4-(4-bromo-1*H*-indol-3-yl)-1-hydroxy-3-(4-methoxyphenyl)-2-naphthoate.



15c

89.8 mg, 87% yield. White solid, mp: 215-216 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 12.51 (s, 1H), 8.57 – 8.49 (m, 1H), 8.06 (s, 1H), 7.52 – 7.48 (m, 1H), 7.45 – 7.41 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.03 – 6.93 (comp, 3H), 6.71 – 6.68 (m, 2H), 6.50 – 6.44 (m, 1H), 4.03 – 3.94 (m, 2H), 3.65 (s, 3H), 0.75 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.5, 161.0, 157.5, 139.1, 138.2, 136.5, 135.8, 130.6, 129.7, 129.6, 127.3, 127.2, 126.1, 125.5, 124.2, 124.0, 123.8, 123.7, 122.8, 114.5, 114.4, 112.3, 110.6, 107.1, 61.1, 55.2, 13.2. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{22}BrNO_4Na^+$ $[M+Na]^+$: 538.0624, found 538.0589.

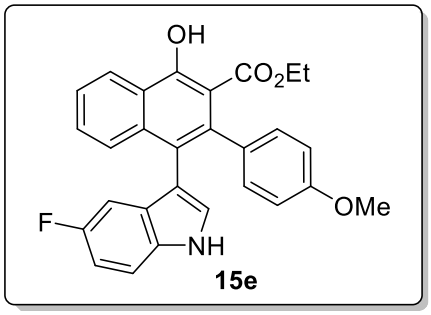
Ethyl 1-hydroxy-3-(4-methoxyphenyl)-4-(5-methyl-1*H*-indol-3-yl)-2-naphthoate.



15d

64.4 mg, 71% yield. White solid, mp: 184-185 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 12.31 (s, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 7.86 (s, 1H), 7.56 – 7.51 (m, 2H), 7.46 – 7.40 (m, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 7.05 – 6.99 (comp, 3H), 6.79 – 6.72 (m, 2H), 6.55 (d, *J* = 2.3 Hz, 1H), 6.45 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.04 – 3.97 (m, 2H), 3.69 (s, 3H), 2.36 (s, 3H), 0.77 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.4, 160.4, 157.7, 139.1, 136.6, 135.6, 133.8, 130.6, 129.8, 129.6, 128.9, 127.4, 125.6, 125.1, 124.3, 124.1, 123.9, 123.4, 119.7, 113.4, 112.3, 112.2, 110.7, 107.5, 61.1, 55.2, 21.6, 13.2. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{25}NO_4Na^+$ $[M+Na]^+$: 474.1676, found 474.1695.

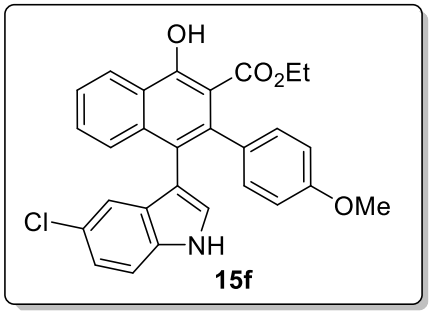
Ethyl 4-(5-fluoro-1*H*-indol-3-yl)-1-hydroxy-3-(4-methoxyphenyl)-2-naphthoate.



15e

77.4 mg, 85% yield. White solid, mp: 172-173 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 12.37 (s, 1H), 8.55 (d, *J* = 8.2 Hz, 1H), 7.99 (s, 1H), 7.54 – 7.42 (comp, 3H), 7.20 – 7.16 (m, 1H), 7.02 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.92 – 6.87 (m, 1H), 6.82 (dd, *J* = 9.6, 2.3 Hz, 1H), 6.76 – 6.70 (m, 2H), 6.68 (d, *J* = 2.3 Hz, 1H), 6.46 (dd, *J* = 8.4, 2.5 Hz, 1H), 3.99 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 3H), 0.75 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.3, 159.2 (d, *J* = 284.0 Hz), 158.1(d, *J* = 234.6 Hz), 139.4, 136.4, 135.4, 131.9, 130.5, 129.8, 129.7, 129.6, 126.9, 126.7, 125.7, 124.3, 123.9, 123.3, 114.2 (d, *J* = 4.6 Hz), 112.3, 111.7 (d, *J* = 9.6 Hz), 110.3 (d, *J* = 26.5 Hz), 107.4, 104.8 (d, *J* = 23.5 Hz), 61.1, 55.3, 13.2; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -124.4. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{22}FNO_4Na^+$ $[M+Na]^+$: 478.1425, found 478.1464.

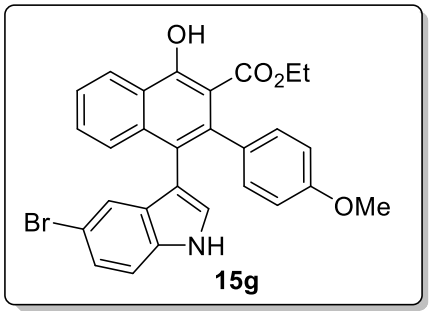
Ethyl 4-(5-chloro-1*H*-indol-3-yl)-1-hydroxy-3-(4-methoxyphenyl)-2-naphthoate (15f)



15f

76.3 mg, 81% yield. White solid, mp: 195-196 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 12.37 (s, 1H), 8.55 (d, *J* = 8.3 Hz, 1H), 8.03 (s, 1H), 7.55 – 7.51 (m, 1H), 7.45 – 7.44 (m, 2H), 7.19 – 7.08 (comp, 3H), 7.00 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.76 – 6.70 (m, 2H), 6.65 (d, *J* = 2.4 Hz, 1H), 6.46 (dd, *J* = 8.4, 2.6 Hz, 1H), 3.99 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 3H), 0.75 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.2, 160.7, 157.8, 139.4, 136.5, 135.4, 133.8, 130.5, 130.4, 129.8, 129.6, 126.9, 126.3, 125.8, 125.5, 124.3, 124.0, 123.1, 122.2, 119.4, 113.8, 112.3, 112.2, 112.1, 10`7.4, 61.2, 55.3, 13.2. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{22}ClNO_4Na^+$ $[M+Na]^+$: 494.1130, found 494.1160.

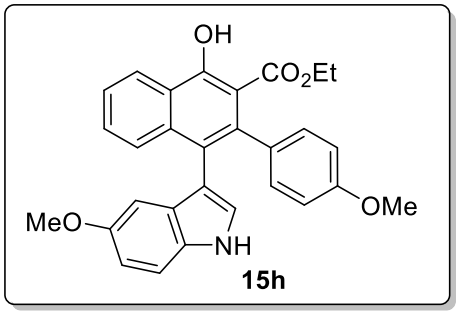
Ethyl 4-(5-bromo-1*H*-indol-3-yl)-1-hydroxy-3-(4-methoxyphenyl)-2-naphthoate.



15g

88.5 mg, 86% yield. White solid, mp: 210-211 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 12.37 (s, 1H), 8.55 (d, *J* = 8.3 Hz, 1H), 8.03 (s, 1H), 7.55 – 7.51 (m, 1H), 7.45 (d, *J* = 3.4 Hz, 2H), 7.30 (d, *J* = 1.7 Hz, 1H), 7.23 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.13 (d, *J* = 8.6 Hz, 1H), 7.00 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.76 – 6.70 (m, 2H), 6.63 (d, *J* = 2.4 Hz, 1H), 6.47 (dd, *J* = 8.5, 2.6 Hz, 1H), 3.99 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 3H), 0.75 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.2, 160.7, 157.8, 139.5, 136.4, 135.4, 134.0, 131.1, 130.5, 129.9, 129.6, 126.9, 126.2, 125.8, 124.8, 124.3, 124.0, 123.0, 122.4, 113.8, 113.1, 112.6, 112.4, 112.3, 107.4, 61.2, 55.3, 13.2. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{22}BrNO_4Na^+$ $[M+Na]^+$:538.0624, found 538.0642.

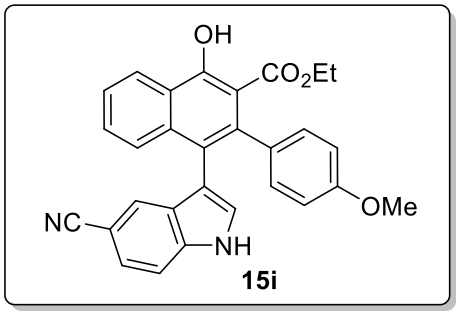
Ethyl 1-hydroxy-4-(5-methoxy-1*H*-indol-3-yl)-3-(4-methoxyphenyl)-2-naphthoate



15h

70.0 mg, 75% yield. White solid, mp: 177-178 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 12.28 (s, 1H), 8.54 (d, *J* = 8.3 Hz, 1H), 7.91 (s, 1H), 7.55 – 7.50 (m, 2H), 7.46 – 7.41 (m, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 7.02 – 7.00 (m, 1H), 6.82 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.78 – 6.75 (m, 1H), 6.72 – 6.69 (m, 1H), 6.60 – 6.59 (m, 2H), 6.46 – 6.44 (m, 1H), 4.02 – 3.96 (m, 2H), 3.68 (s, 3H), 3.67 (s, 3H), 0.75 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.3, 160.4, 157.8, 154.2, 139.2, 136.6, 135.5, 130.6, 129.9, 129.64, 129.60, 127.3, 125.7, 125.6, 124.3, 124.0, 123.9, 113.8, 112.3, 112.2, 111.8, 107.6, 101.5, 61.1, 55.8, 55.2, 13.2. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{25}NO_5Na^+$ $[M+Na]^+$: 490.1625, found 490.1601.

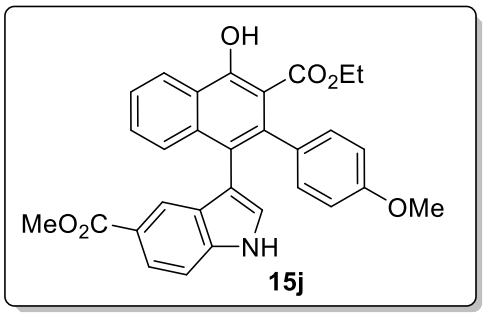
Ethyl 4-(5-cyano-1*H*-indol-3-yl)-1-hydroxy-3-(4-methoxyphenyl)-2-naphthoate



15i

84.1 mg, 91% yield. White solid, mp: 289-290 °C. ^{1}H NMR (400 MHz, DMSO) (δ, ppm) 11.63 (s, 1H), 10,68 (s, 1H), 8.38 (d, *J* = 8.3 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.39 – 7.37 (m, 2H), 7.33 (d, *J* = 8.4, 1H), 7.26 (d, *J* = 2.2, 1H), 7.12 (s, 1H), 6.80 (s, 1H), 6.71 (s, 1H), 6.56 (s, 1H), 3.94 (q, *J* = 7.1 Hz, 2H), 3.62 (s, 3H), 0.84 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO) (δ, ppm) 168.6, 157.7, 151.9, 138.2, 137.3, 134.7, 132.5, 130.9, 129.7, 128.8, 128.18, 128.17, 126.3, 125.5, 124.3, 124.2, 123.7, 122.8, 122.0, 120.6, 115.9, 112.9, 112.3, 100.9, 60.5, 54.9, 13.4. HRMS (TOF MS ESI^{+}) calculated for $C_{29}H_{22}N_2O_4Na^{+}$ $[M+Na]^{+}$: 485.1472, found 485.1484.

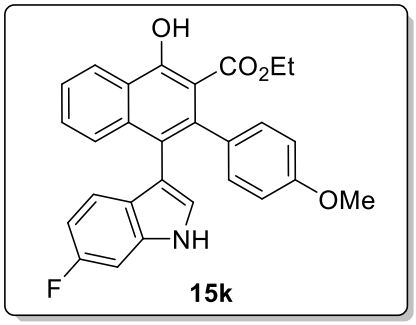
Methyl 3-(3-(ethoxycarbonyl)-4-hydroxy-2-(4-methoxyphenyl)naphthalen-1-yl) -1*H*-indole-5-carboxylate



15j

88.7 mg, 90% yield. White solid, mp: 320-321 °C. ^{1}H NMR (400 MHz, DMSO) (δ, ppm) 11.44 (s, 1H), 10.62 (s, 1H), 8.39 (d, *J* = 8.3 Hz, 1H), 7.70 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.63 (s, 1H), 7.60 – 7.54 (m, 1H), 7.46 – 7.43 (m, 2H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 2.2 Hz, 2H), 6.72 – 6.53 (comp, 3H), 3.95 (q, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 3.62 (s, 3H), 0.85 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO) (δ, ppm) 168.4, 167.1, 157.7, 151.5, 138.10, 138.09, 134.7, 132.5, 128.3, 128.1, 127.9, 126.5, 125.5, 124.1, 122.7, 122.5, 122.0, 121.2, 120.4, 116.2, 113.2, 112.3, 111.6, 60.5, 54.9, 51.6, 13.4. HRMS (TOF MS ESI^{+}) calculated for $C_{30}H_{25}NO_6Na^{+}$ $[M+Na]^{+}$: 518.1574, found 518.1528.

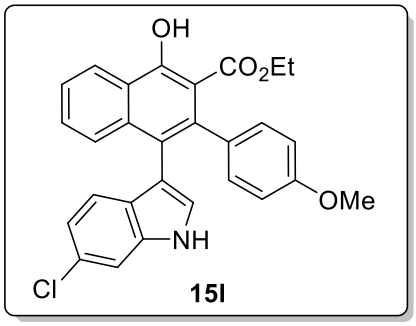
Ethyl 4-(6-fluoro-1*H*-indol-3-yl)-1-hydroxy-3-(4-methoxyphenyl)-2-naphthoate.



15k

79.2 mg, 87% yield. White solid, mp: 178-179 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 12.36 (s, 1H), 8.55 (d, *J* = 8.3 Hz, 1H), 7.99 (s, 1H), 7.57 – 7.39 (comp, 3H), 7.08 – 7.01 (m, 2H), 6.94 (dd, *J* = 9.6, 2.2 Hz, 1H), 6.80 – 6.71 (comp, 3H), 6.62 (d, *J* = 2.3 Hz, 1H), 6.46 (dd, *J* = 8.4, 2.6 Hz, 1H), 3.99 (m, 2H), 3.69 (s, 3H), 0.76 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.3, 160.8 (d, *J* = 51.4 Hz), 158.3 (d, *J* = 93.7 Hz), 139.3, 136.6, 135.4, 135.27 (d, *J* = 12.6 Hz), 130.6, 129.7, 129.5, 127.0, 126.0, 125.7, 125.2 (d, *J* = 3.5 Hz), 124.3, 123.9, 123.5, 120.7 (d, *J* = 10.1 Hz), 114.1, 112.3 (d, *J* = 8.1 Hz), 108.5 (d, *J* = 24.4 Hz), 107.4, 97.34 (d, *J* = 26.1 Hz), 61.1, 55.2, 13.2; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -121.6. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{22}FNO_4Na^+$ $[M+Na]^+$:478.1431, found 478.1452.

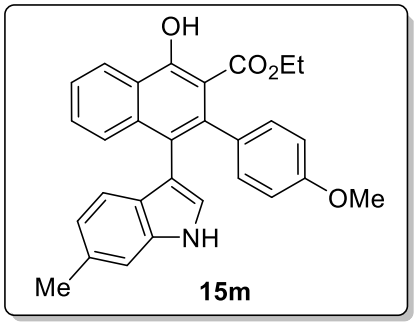
Ethyl 4-(6-chloro-1*H*-indol-3-yl)-1-hydroxy-3-(4-methoxyphenyl)-2-naphthoate.



15l

87.6 mg, 93% yield. White solid, mp: 198-199 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 12.36 (s, 1H), 8.54 (d, *J* = 8.3 Hz, 1H), 7.98 (s, 1H), 7.54 – 7.50 (m, 1H), 7.46 – 7.41 (m, 2H), 7.26 (s, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 7.03 – 6.97 (m, 2H), 6.72 (d, *J* = 8.3 Hz, 2H), 6.62 (d, *J* = 2.3 Hz, 1H), 6.45 (dd, *J* = 8.5, 2.6 Hz, 1H), 4.02 – 3.96 (m, 2H), 3.70 (s, 3H), 0.75 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.3, 160.7, 157.8, 139.4, 136.5, 135.7, 135.4, 130.6, 129.7, 129.5, 128.0, 127.8, 126.9, 125.7, 125.6, 124.3, 124.0, 123.2, 120.9, 120.5, 114.2, 112.4, 112.3, 111.0, 107.4, 61.2, 55.3, 13.2. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{22}ClNO_4Na^+$ $[M+Na]^+$: 494.1130, found 494.1088.

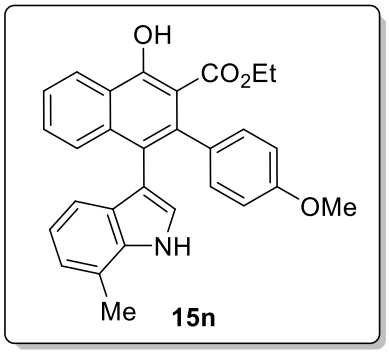
Ethyl 1-hydroxy-3-(4-methoxyphenyl)-4-(6-methyl-1*H*-indol-3-yl)-2-naphthoate.



15m

66.7 mg, 74% yield. White solid, mp: 216-217 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 12.31 (s, 1H), 8.56 (d, *J* = 8.3 Hz, 1H), 7.82 (s, 1H), 7.55 – 7.50 (m, 2H), 7.44 – 7.40 (m, 1H), 7.10 – 7.03 (comp, 3H), 6.88 (d, *J* = 8.6 Hz, 1H), 6.77 – 6.73 (m, 2H), 6.53 (d, *J* = 2.3 Hz, 1H), 6.45 (dd, *J* = 8.4, 2.5 Hz, 1H), 4.03 – 3.97 (m, 2H), 3.69 (s, 3H), 2.46 (s, 3H), 0.76 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.3, 160.4, 157.7, 139.0, 136.6, 135.9, 135.6, 131.5, 130.6, 129.60, 129.57, 127.4, 127.3, 125.6, 124.4, 124.3, 124.1, 123.9, 121.5, 119.8, 113.7, 112.3, 112.2, 111.0, 107.5, 61.1, 55.2, 21.8, 13.2. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{25}NO_4Na^+$ $[M+Na]^+$: 474.1676, found 474.1658.

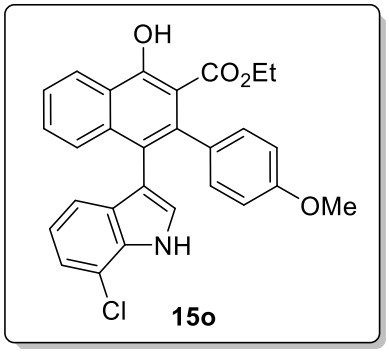
Ethyl 1-hydroxy-3-(4-methoxyphenyl)-4-(7-methyl-1*H*-indol-3-yl)-2-naphthoate



15n

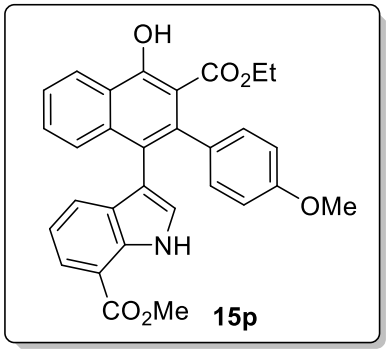
54.1 mg, 60% yield. White solid, mp: 161-162 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 12.34 (s, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 7.86 (s, 1H), 7.51 (d, *J* = 7.9 Hz, 2H), 7.44 – 7.37 (m, 1H), 7.06 (d, *J* = 6.7 Hz, 2H), 7.00 – 6.95(m, 2H), 6.80 – 6.72 (m, 2H), 6.61 (d, *J* = 2.3 Hz, 1H), 6.45 (dd, *J* = 8.4, 2.3 Hz, 1H), 4.00 (m, 2H), 3.69 (s, 3H), 2.43 (s, 3H), 0.77 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.4, 160.4, 157.7, 139.1, 136.6, 135.6, 135.0, 130.6, 129.7, 129.6, 129.0, 127.3, 125.6, 124.7, 124.3, 124.1, 123.8, 122.4, 120.1, 119.9, 117.9, 114.4, 112.4, 112.2, 107.5, 61.1, 55.2, 16.6, 13.2. HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{25}NO_4Na^+$ $[M+Na]^+$: 474.1676, found 474.1627.

Ethyl 4-(7-chloro-1*H*-indol-3-yl)-1-hydroxy-3-(4-methoxyphenyl)-2-naphthoate



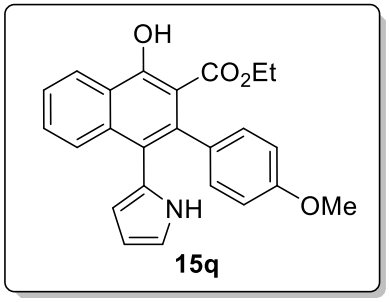
80.1 mg, 85% yield. White solid, mp: 144-145 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 12.36 (s, 1H), 8.54 (d, *J* = 8.2 Hz, 1H), 8.25 (s, 1H), 7.54 – 7.50 (m, 1H), 7.45 – 7.40 (m, 2H), 7.18 – 7.16 (m, 1H), 7.07 (d, *J* = 7.9 Hz, 1H), 7.02 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.94 (t, *J* = 7.7 Hz, 1H), 6.74 – 6.71 (comp, 3H), 6.46 (dd, *J* = 8.5, 2.6 Hz, 1H), 4.01 – 3.96 (m, 2H), 3.71 (s, 3H), 0.75 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.3, 160.7, 157.9, 139.4, 136.5, 135.3, 132.8, 130.8, 130.6, 129.7, 129.5, 127.0, 125.7, 125.6, 124.3, 124.0, 123.2, 121.3, 120.6, 118.8, 116.5, 115.2, 112.4, 107.5, 61.2, 55.3, 13.3. HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{22}ClNO_4Na^+$ [M+Na]$^+$: 494.1130, found 494.1093.

Methyl 3-(3-(ethoxycarbonyl)-4-hydroxy-2-(4-methoxyphenyl)naphthalen-1-yl) -1*H*-indole-7-carboxylate



80.2 mg, 81% yield. White solid, mp: 189-190 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 12.36 (s, 1H), 9.71 (s, 1H), 8.55 (d, *J* = 8.2 Hz, 1H), 7.90 – 7.82 (m, 1H), 7.53 – 7.49 (m, 1H), 7.47 – 7.41 (m, 2H), 7.40 – 7.36 (m, 1H), 7.04 (t, *J* = 7.7 Hz, 2H), 6.82 (d, *J* = 2.2 Hz, 1H), 6.75 – 6.68 (m, 2H), 6.43 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.99 (comp, 5H), 3.69 (s, 3H), 0.75 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.3, 168.0, 160.6, 157.8, 139.5, 136.6, 135.34, 135.28, 130.6, 130.5, 129.7, 129.5, 127.0, 126.0, 125.8, 125.7, 124.3, 124.3, 124.0, 123.3, 119.0, 114.0, 112.5, 112.4, 112.3, 107.4, 61.1, 55.2, 52.0, 13.2. HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{25}NO_6Na^+$ [M+Na]$^+$: 518.1574, found 518.1541.

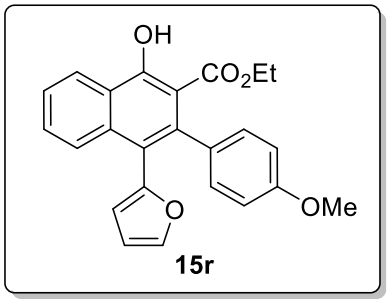
Ethyl 1-hydroxy-3-(4-methoxyphenyl)-4-(1*H*-pyrrol-2-yl)-2-naphthoate



15q

52.7 mg, 68% yield. White solid, mp: 146-147 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 12.29 (s, 1H), 8.50 – 8.45 (m, 1H), 7.78 – 7.74 (m, 1H), 7.64 (s, 1H), 7.56 – 7.49 (m, 2H), 6.97 – 6.93 (m, 2H), 6.76 – 6.72 (m, 2H), 6.60 – 6.59 (m, 1H), 6.17 – 6.15 (m, 1H), 6.06 – 6.04 (m, 1H), 3.97 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 0.76 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.1, 160.8, 158.1, 138.9, 136.4, 134.7, 130.04, 129.95, 127.1, 126.6, 125.8, 124.2, 123.8, 123.5, 117.2, 112.7, 111.4, 108.1, 107.1, 61.2, 55.3, 13.2. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{21}NO_4Na^+$ $[M+Na]^+$: 410.1363, found 410.1375.

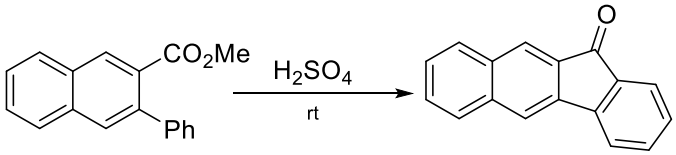
Ethyl 4-(furan-2-yl)-1-hydroxy-3-(4-methoxyphenyl)-2-naphthoate



15r

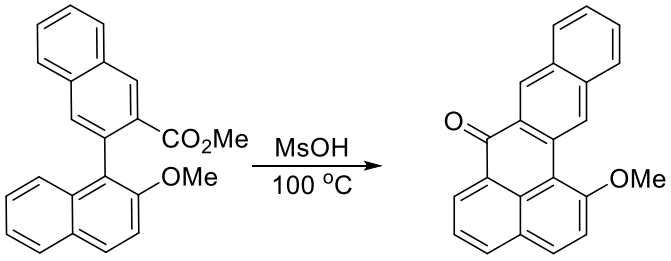
69.3 mg, 89% yield. White solid, mp: 116-117 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 12.49 (s, 1H), 8.52 – 8.46 (m, 1H), 7.59 – 7.51 (m, 2H), 7.50 – 7.46 (m, 1H), 7.39 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.00 – 6.96 (m, 2H), 6.76 – 6.72 (m, 2H), 6.29 (dd, *J* = 3.2, 1.9 Hz, 1H), 5.93 (dd, *J* = 3.2, 0.7 Hz, 1H), 3.99 (q, *J* = 7.1 Hz, 2H), 3.79 (s, 3H), 0.77 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.1, 161.8, 158.3, 150.7, 141.6, 140.7, 136.4, 134.4, 130.2, 130.0, 126.1, 125.9, 124.2, 124.0, 121.4, 112.5, 111.3, 110.6, 107.0, 61.3, 55.4, 13.2. HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{20}O_5Na^+$ $[M+Na]^+$: 411.1203, found 411.1189.

The Preparation of π-conjugated polycyclic hydrocarbons (CPHs), related to Figure 2B.



2a **7a**, 84% yield

Synthesis of **7a:** To a 50-mL oven-dried round-bottom flask containing a magnetic stirring bar, **2a** (52.5 mg, 0.2 mmol) was added sulphuric acid (8.0 ml) in 5 min at 0 ℃. The reaction mixture was stirred overnight and the reaction temperature was warmed to room temperature slowly. Then, water (50 mL) was added to the reaction mixture and the reaction mixture was stirred for 1-2 h. The yellow solid precipitated out and was filtered under vacuum. The crude product was purified by column chromatography on silica gel (solvents: petroleum ether/ethyl acetate = 20 : 1) to afford 38.7 mg **7a** in 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.17 (s, 1H), 7.94 – 7.78 (comp, 3H), 7.77 – 7.68 (comp, 2H), 7.59 – 7.51 (comp, 2H), 7.50 – 7.43 (m, 1H), 7.37 – 7.32 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 193.3, 145.0, 138.5, 137.1, 136.3, 135.2, 133.8, 132.9, 131.0, 129.3, 129.1, 128.9, 127.1, 125.8, 124.6, 121.1, 119.2. HRMS (TOF MS CI$^+$) calculated for $C_{17}H_{10}NaO^+$ $[M+Na]^+$: 253.0624, found 253.0630.

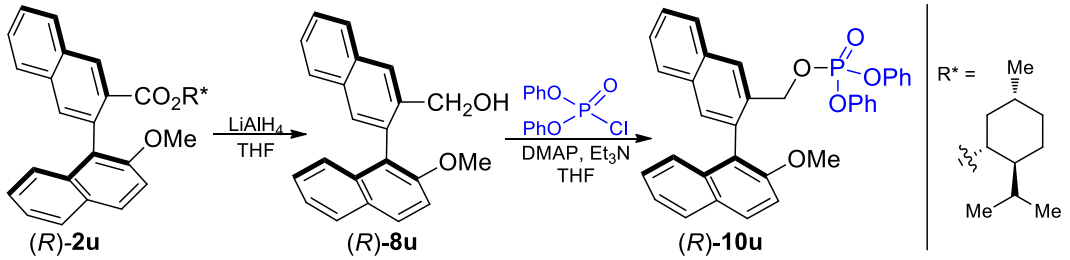


2o **7o**, 95% yield

Synthesis of **7o**: To a 25-mL oven-dried round-bottom flask containing a magnetic stirring bar, **2o** (68.5 mg, 0.2 mmol), and methanesulphonic acid (8.0 mL) were added in sequence under argon at room temperature. Then the reaction mixture was refluxed at 100 ℃ for 2 h. After cooling to room temperature, water (50 mL) was added to the reaction mixture and the reaction mixture was stirred for 1-2 h. The yellow solid precipitated out and was filtered under vacuum. The crude product was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1/3) to give 59.0 mg **7o** in 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 9.57 (s, 1H), 9.07 (s, 1H), 8.81 – 8.74 (m, 1H), 8.09 – 7.98 (comp, 2H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 9.1 Hz, 1H), 7.62 – 7.49 (comp, 3H), 7.38 (d, *J* = 9.1 Hz, 1H), 4.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 184.3, 158.6, 136.1, 135.1, 131.6, 131.5, 131.2, 130.5, 130.2, 129.6, 129.4, 129.3, 129.14, 129.10, 128.6, 128.3, 128.0, 126.7, 124.1,

114.7, 112.8, 56.3. HRMS (TOF MS CI$^+$) calculated for $C_{22}H_{14}NaO_2^+$ $[M+Na]^+$: 333.0886, found 333.0891.

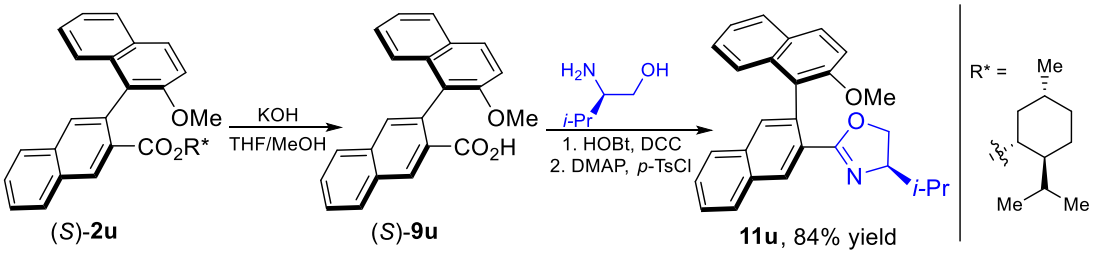
The Preparation of chiral 1,2'-dinaphthalene ligands, related to 2D.



Synthesis of (*R*)-**8u**: To a 10-mL oven-dried flask containing a magnetic stirring bar, compound **(*R*)-2u** (93.3 mg, 0.2 mmol) in dry THF (4.0 mL), was added $LiAlH_4$ (15.2 mg, 0.4 mmol) portion-wise at 0 °C under argon atmosphere. After completion of addition, the reaction mixture was allowed to warm up to room temperature and stirred for 2 h. After the consumption of starting material (monitored by TLC analysis), the reaction mixture was quenched by addition of $Na_2SO_4 \cdot 10H_2O$ followed by saturated NH_4Cl, and extracted with DCM (2 X 5 mL). The combined organic phase was dried over Na_2SO_4 and the solvent was evaporated under vacuum after filtration. The resulting residues was purified by column chromatography on silica gel (eluent: petroleum ether /EtOAc = 1 : 1) to give 61.0 mg (*R*)-**8u** in 97% yield. $[\alpha]_D^{20}$ = -54.2°, (*c* = 0.34, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.14 (s, 1H), 8.03 – 7.94 (comp, 2H), 7.92 – 7.82 (comp, 2H), 7.74 (s, 1H), 7.61 – 7.50 (comp, 2H), 7.46 – 7.34 (comp, 2H), 7.34 – 7.27 (comp, 2H), 4.54 – 4.41 (comp, 2H), 3.84 (s, 3H), 2.24 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 154.0, 138.7, 134.1, 133.4, 133.3, 133.1, 130.3, 129.8, 129.3, 128.1, 128.0, 127.8, 127.2, 126.8, 126.2, 126.2, 125.1, 124.0, 123.2, 113.6, 64.1, 56.8. HRMS (TOF MS CI$^+$) calculated for $C_{22}H_{18}NaO_2^+$ $[M+Na]^+$: 337.1199, found 337.1210.

Synthesis of (*R*)-**10u**: To a 10-mL oven-dried flask containing a magnetic stirring bar, (*R*)-**8u** (31.4 mg, 0.1 mmol), triethylamine (0.02 mL, 0.3 mmol), and DMAP (1.3 mg, 0.01 mmol) in THF (1.0 mL), was added diphenyl phosphorochloridate (26.9 mg, 0.1 mmol, 100 mol %) over 30 min at 0 °C under argon atmosphere. The reaction mixture was stirred overnight and the reaction temperature was warmmed to room temperature slowlly. After the consumption of starting material (monitored by TLC analysis), the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (eluent: petroleum ether /EtOAc = 1:1) to give 46.0 mg (*R*)-**10u** in 84%. > 99% ee, $[\alpha]_D^{20}$ = -312.5°, (*c* = 0.16, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.02 (s, 1H), 7.96 (d, *J* = 9.1 Hz, 1H), 7.89 – 7.81 (m, 3H), 7.73 (s, 1H), 7.57 – 7.50 (comp, 2H), 7.41 – 7.33 (comp, 2H), 7.31 – 7.26 (comp,

3H), 7.25 – 7.17 (comp, 3H), 7.17 – 7.09 (comp, 2H), 7.08 – 7.02 (comp, 2H), 7.02 – 6.90 (comp, 2H), 5.22 (dd, *J* = 12.7, 7.3 Hz, 1H), 5.05 (dd, *J* = 12.6, 7.0 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 154.1, 150.6 (d, *J* = 7.3 Hz), 150.50 (d, *J* = 7.3 Hz), 133.9, 133.4, 133.32, 133.28, 133.1, 132.9, 130.5, 130.1, 129.79, 129.749, 129.750, 129.2, 128.2, 128.1, 127.8, 127.1, 126.9, 126.6, 126.4, 125.4 (d, *J* = 1.0 Hz), 125.3 (d, *J* = 1.1 Hz), 125.0, 123.8, 121.8, 120.22 (d, *J* = 4.9 Hz), 120.15 (d, *J* = 4.9 Hz), 113.2, 68.89 (d, *J* = 5.6 Hz), 56.4; ^{31}P NMR (162 MHz, $CDCl_3$) (δ, ppm) -12.04. HRMS (TOF MS CI$^+$) calculated for $C_{34}H_{28}O_5P^+$ $[M+H]^+$: 547.1669, found 547.1681. HPLC conditions for determination of enantiomeric excess: Chiral IB-3, λ = 272 nm, hexane : 2-propanol = 95:5, flow rate = 1.0 mL/min, t_S = 27.7 min, t_R = 35.2 min.



Synthesis of (*S*)-**9u**: To a 10-mL oven-dried flask containing a magnetic stirring bar, and KOH (112.0 mg, 2.0 mmol) in THF (6.0 mL) and CH_3OH (2.0 mL), was added the white solid (*S*)-**2u** (93.3 mg, 0.2 mmol) at 0 ℃. The reaction mixture was stirred at room temperature overnight. Then the solvent was removed under vaccum and the reaction mixture was acidified with 6 N HCl (10.0 mL). The precipitated solid was filtrated and washed with water (3 X 15 mL) to give 58.5 mg pure (*S*)-**9u** in 86% yield.

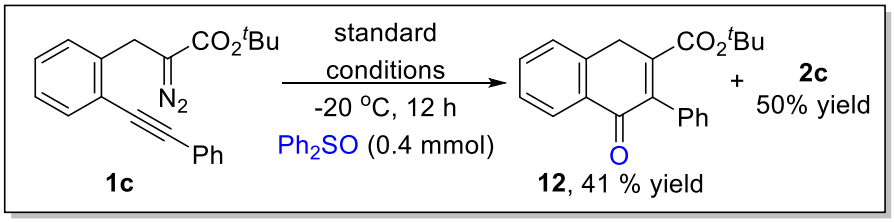
$[\alpha]_D^{20}$ = +22.4°, (*c* = 0.08, $CHCl_3$). ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm) 12.38 (s, 1H), 8.62 (s, 1H), 8.19 – 8.11 (m, 1H), 8.01 – 7.94 (comp, 2H), 7.93 – 7.87 (m, 1H), 7.79 (s, 1H), 7.68 – 7.59 (comp, 2H), 7.51 (d, *J* = 9.1 Hz, 1H), 7.37 – 7.23 (comp, 3H), 3.75 (s, 3H).; ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm) 167.9, 153.3, 134.1, 133.1, 133.0, 131.4, 131.2, 131.1, 130.5, 128.72, 128.68, 128.6, 128.1, 127.9, 127.5, 126.8, 126.2, 124.5, 124.4, 123.1, 113.8, 56.2. HRMS (TOF MS CI$^+$) calculated for $C_{22}H_{16}NaO_3^+$ $[M+Na]^+$: 351.0992, found 351.1000.

Synthesis of **11u**: To a 10-mL oven-dried flask containing a magnetic stirring bar, (*S*)-**9u** (32.8 mg, 0.1 mmol), *N*,*N*'-dicyclohexylcarbodimide (DCC, 41.2 mg, 0.2 mmol), benzotriazol-1-ol (16.2 mg, 0.12 mmol), and (*R*)-2- amino-3-methylbutan-1-ol (12.4 mg, 0.12 mmol), and dry THF (1.0 mL) were added in sequence at -5 ℃. The reaction mixture was stirred for 1 h under these conditions, and then stirred at room temperature overnight. The solvent was evaporated under vacuum after filtration, the obtained white solid was directly used for the next step without further purification.

To a 10-mL oven-dried flask containing a magnetic stirring bar, the above obtained white solid, 4-(dimethylamino)pyridine (1.3 mg, 0.01 mmol), and CH_2Cl_2 (1.0 mL), was added triethylamine (22.2 mg, 0.22 mmol) under argon atmosphere at 0 ℃. Then

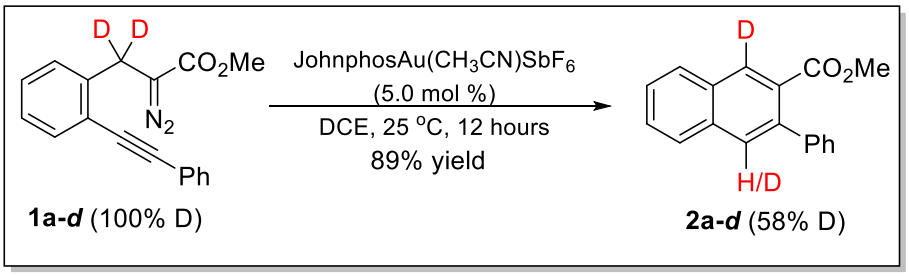
a solution of *p*-toluenesulfonyl chloride (38.2 mg, 0.2 mmol) in CH_2Cl_2 (0.5 mL) was added to the above reaction mixture at 0 ℃. The reaction mixture was stirred at room temperature for 12 h. Then the solvent was evaporated under reduced pressure, and the resulting residues was purified by silica gel column chromatography (petroleum ester/ethyl acetate = 1:1) to give 33.2 mg **11u** in 84% yield. 98% ee, $[\alpha]_D^{20}$ = +30.5°, (*c* = 0.18, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.59 (s, 1H), 8.03 – 7.97 (m, 1H), 7.89 – 7.78 (comp, 4H), 7.60 – 7.53 (comp, 2H), 7.42 – 7.28 (comp, 4H), 4.06 – 3.98 (m, 1H), 3.85 – 3.77 (comp, 4H), 3.55 (t, *J* = 8.1 Hz, 1H), 1.47 (td, *J* = 13.3, 6.6 Hz, 1H), 0.65 (d, *J* = 6.7 Hz, 3H), 0.62 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.9, 153.9, 134.4, 133.9, 133.1, 132.2, 131.3, 130.6, 129.1, 129.0, 128.7, 127.9, 127.8, 127.7, 126.7, 126.5, 125.4, 124.8, 123. 5, 113.5, 72.1, 70.5, 56. 8, 32.6, 18.6, 18.0. HRMS (TOF MS CI$^+$) calculated for $C_{27}H_{26}NO_2^+$ [M+H]$^+$: 396.1958, found 396.1969.

Experimental procedure for the interception reaction of vinyl gold carbenoid intermediate, related to Figure 3A.



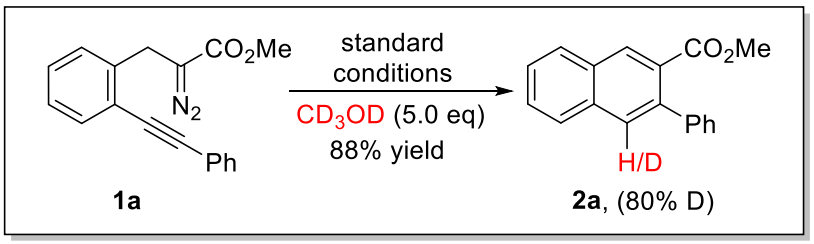
To a 10-mL oven-dried flask containing a magnetic stirring bar, JohnphosAu $(CH_3CN)SbF_6$ (7.7 mg, 0.01 mmol, 5.0 mol %), and Ph_2SO (81.0 mg, 0.4 mmol) in dry 1,2-dichloroethane (2.0 mL), was added a solution of diazoacetate **1c** (66.5 mg, 0.2 mmol) in dry 1,2-dichloroethane (2.0 mL) by a syringe in 5 mins at -20 ℃ under argon atmosphere. After addition, the reaction mixture was stirred at -20 ℃ for 12 h. Then the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (solvents: petroleum ether/ethyl acetate = 10 : 1) to afford **2c** (30.5 mg, 50% yield) and **12** (26.3 mg, 41% yield). Compound **12**: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.05 – 7.96 (comp, 2H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.58 – 7.42 (comp, 4H), 7.39 – 7.30 (m, 1H), 7.26 – 7.21 (m, 1H), 3.93 (s, 2H), 1.72 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 153.3, 149.2, 147.7, 144.8, 135. 9, 132.8, 129.1, 128.8, 128.1, 127.2, 125.6, 125.2, 120.5, 85.5, 33.1, 28.2. HRMS (TOF MS CI$^+$) calculated for $C_{21}H_{21}O_3^+$ $[M+H]^+$: 321.1485, found 321.1490.

Experimental procedure for the deuterated reaction of 1a-d to 2a-d, related to Figure 3B.



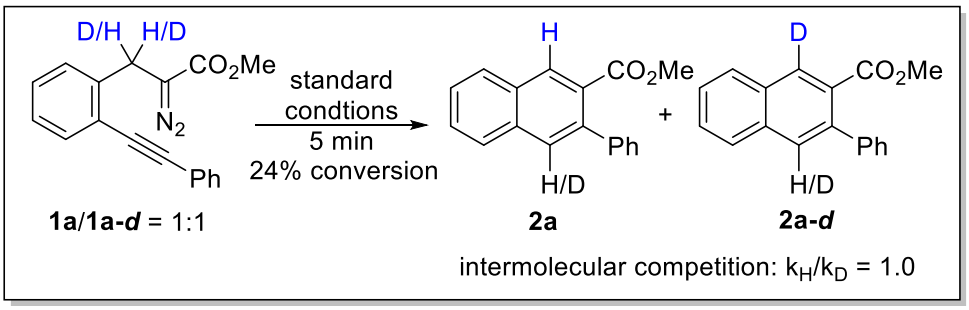
To a 10-mL oven-dried flask containing a magnetic stirring bar, JohnphosAu $(CH_3CN)SbF_6$ (7.7 mg, 0.01 mmol, 5.0 mol %) in dry 1,2-dichloroethane (2.0 mL), was added a solution of diazoacetate **1a-*d*** (58.4 mg, 0.2 mmol) in dry 1,2-dichloroethane (2.0 mL) by a syringe in 5 mins at room temperature under argon atmosphere. After addition, the reaction mixture was stirred at room temperature for 12 h. Then the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (solvents: petroleum ether/ethyl acetate = 10 : 1) to afford 47.0 mg **2a-*d*** (58% D, see Figure S2) in 89% yield.

Experimental procedure for the deuterated reaction of 1a to 2a, related to Figure 3C.



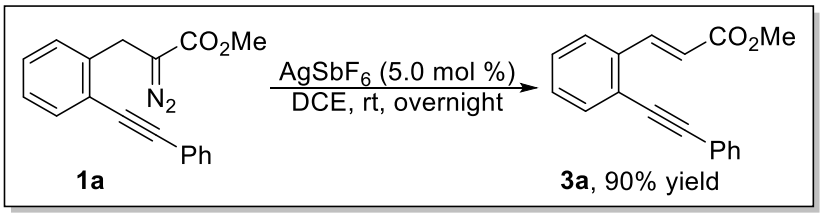
To a 10-mL oven-dried flask containing a magnetic stirring bar, JohnphosAu $(CH_3CN)SbF_6$ (7.7 mg, 0.01 mmol, 5.0 mol %) and CD_3OD (36.1 mg, 1.0 mmol) in dry 1,2-dichloroethane (2.0 mL), was added a solution of diazoacetate **1a** (58.0 mg, 0.2 mmol) in dry 1,2-dichloroethane (2.0 mL) by a syringe in 5 mins at room temperature under argon atmosphere. After addition, the reaction mixture was stirred at room temperature for 12 h. Then the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (solvents: petroleum ether/ethyl acetate = 10 : 1) to give 46.5 mg **2a** (80% D, see Figure S1) in 88% yield.

Intermolecular kinetic isotope effect (KIE) experiment, **related to Figure 3C**.



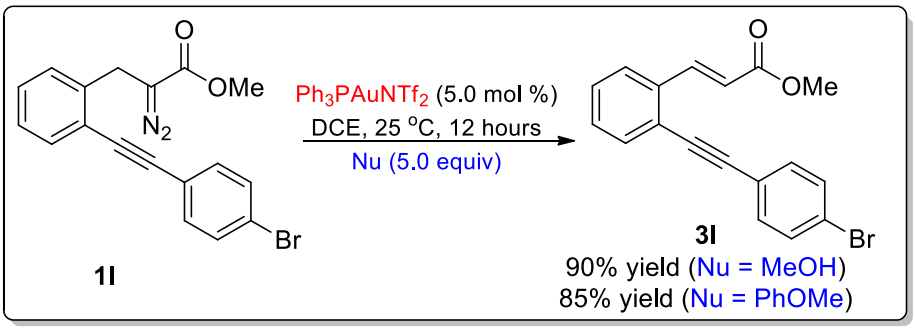
To a dried NMR tube, **1a** (14.5 mg, 0.05 mmol) and **1a-*d*** (14.6 mg, 0.05 mmol) in dry $CDCl_3$ (1.0 mL), was added JohnphosAu$(CH_3CN)SbF_6$ (3.8 mg, 0.005 mmol, 5.0 mol %). And the reaction mixture was analyzed by proton NMR after 5 minutes at room temperature (Figure S3). And these results intermolecular kinetic isotope effect (KIE) experiment turned out that k_H/k_D = 1:1.

Experimental procedure for the β-*H* shift reaction of 1a to 3a, related to Table 1.



To a 10-mL oven-dried flask containing a magnetic stirring bar, $AgSbF_6$ (3.4 mg, 0.01 mmol, 5.0 mol %) in dry 1,2-dichloroethane (2.0 mL), was added a solution of diazoacetate **1a** (58.0 mg, 0.2 mmol) in 1,2-dichloroethane (2.0 mL) by a syringe in 5 mins at room temperature under argon atmosphere. After addition, the reaction mixture was stirred at room temperature for 12 h. Then the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (solvents: petroleum ether/ethyl acetate = 10 : 1) to give 47.5 mg **3a** in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.15 – 8.05 (m, 1H), 7.87 – 7.74 (comp, 2H), 7.68 – 7.58 (comp, 2H), 7.42 – 7.39 (comp, 4H), 7.07 (d, *J* = 11.5 Hz, 1H), 6.16 (d, *J* = 15.3 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.5, 142.3, 137.0, 131.9, 131.3, 131.1, 129.4, 129.1, 128.8, 128.6, 126.8, 123.0, 122.7, 100.5, 86.0, 51.8. HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{14}NaO_2^+$ $[M+Na]^+$: 285.0886, found 285.0890.

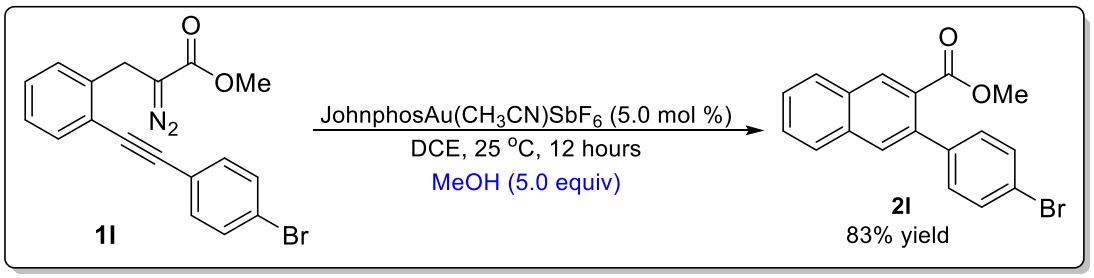
Experimental procedure for the β-*H* shift reaction of 11 to 31, related to Figure 3E.



To a 10-mL oven-dried flask containing a magnetic stirring bar, $Ph_3PAuNTf_2$ (7.4 mg, 0.01 mmol, 5.0 mol %) and MeOH (32.0 mg, 1.0 mmol, 5.0 equiv.) or anisole (108.1 mg, 1.0 mmol, 5.0 equiv.) in dry 1,2-dichloroethane (1.0 mL), was added a solution of diazoacetate **1l** (73.8 mg, 0.2 mmol) in dry 1,2-dichloroethane (1.0 mL) by a syringe in 5 minutes at room temperature under argon atmosphere. After addition, the reaction mixture was stirred overnight at room temperature. Then the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1/10) to afford

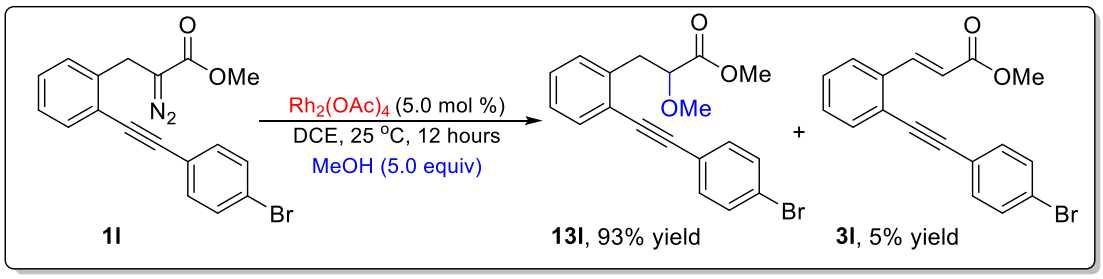
61.5 mg **3l** in 90% yield with MeOH (85% yield with anisole). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.26 (d, *J* = 16.1 Hz, 1H), 7.70 – 7.62 (m, 1H), 7.60 – 7.54 (m, 1H), 7.54 – 7.48 (comp, 2H), 7.48 – 7.41 (comp, 2H), 7.41 – 7.32 (comp, 2H), 6.57 (d, *J* = 16.1 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.5, 142.8, 135.8, 133.2, 133.0, 131.9, 130.0, 128.9, 126.5, 123.8, 123.1, 122.0, 119.6, 94. 6, 88.2, 77.5, 52.0. HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{14}BrO_2^+$ $[M+H]^+$: 341.0172, found 341.0164.

Experimental procedure for the carbocyclization of 1l to 2l with MeOH, related to Figure 3E.



To a 10-mL oven-dried flask containing a magnetic stirring bar, JohnphosAu(CH_3CN)SbF_6 (7.7 mg, 0.01 mmol, 5.0 mol %) and CH_3OH (32.0 mg, 1.0 mmol, 5.0 equiv.) in dry 1,2-dichloroethane (1.0 mL), was added a solution of diazoacetate **1l** (73.8 mg, 0.2 mmol) in dry 1,2-dichloroethane (1.0 mL) by a syringe in 5 minutes at room temperature under argon atmosphere. After addition, the reaction mixture was stirred overnight at room temperature. Then the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1/10) to afford 56.6 mg **2l** in 83% yield.

Experimental procedure for the Comparison with $Rh_2(OAc)_4$, related to Figure 3E.



To a 10-mL oven-dried flask containing a magnetic stirring bar, $Rh_2(OAc)_4$ (4.4 mg, 0.01 mmol, 5.0 mol %) and CH_3OH (32.0 mg, 1.0 mmol, 5.0 equiv.) in dry 1,2-dichloroethane (1.0 mL), was added a solution of diazoacetate **1l** (73.8 mg, 0.2 mmol) in dry 1,2-dichloroethane (1.0 mL) by a syringe in 5 minutes at 25℃ under

argon atmosphere. After addition, the reaction mixture was stirred at 25℃ for 12 hours. Then the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1/10) to afford **13l** (69.4 mg, 93% yield) and **3l** (3.4 mg, 5% yield). Compound **13l**: ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.54 – 7.44 (comp, 3H), 7.43 – 7.36 (comp, 2H), 7.28 – 7.17 (comp, 3H), 4.14 (dd, *J* = 8.4, 5.1 Hz, 1H), 3.68 (s, 3H), 3.35 (dd, *J* = 13.6, 5.1 Hz, 1H), 3.29 (s, 3H), 3.10 (dd, *J* = 13.6, 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 172.7, 139.0, 133.0, 132.2, 131.8, 130.7, 128.7, 127.0, 122.7, 122.7, 122.3, 92.8, 88.8, 80.7, 58.5, 52.1, 38.3. HRMS (TOF MS CI^{+}) calculated for $C_{19}H_{18}BrO_3^{+}$ $[M+H]^{+}$: 373.0434, found 373.0450.

Supplemental References.

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