Science Advances
AAAS

Supplementary Materials for

Reductive deaminative cross-coupling of alkyl bistriflimides enabled by electrocatalysis

Xiangzhang Tao *et al.*

Corresponding author: Sungwoo Hong, hongorg@kaist.ac.kr; Yi Wang, yiwang@nju.edu.cn

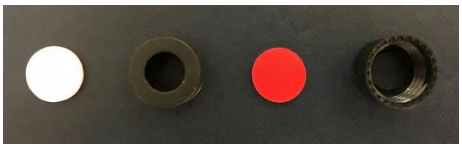
Sci. Adv. **10**, eads5410 (2024)
DOI: 10.1126/sciadv.ads5410

This PDF file includes:

General Methods

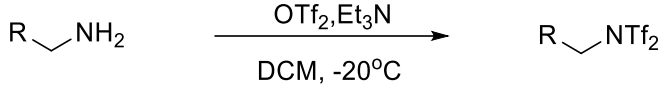
All reactions were performed in flame-dried glassware with magnetic stirring bar and sealed with a rubber septum. The solvents were distilled by standard methods. Reagents were obtained from commercial suppliers and used without further purification unlessotherwise noted. Silica gel column chromatography was carried out using silica Gel 60 (230–400 mesh). Analytical thin layer chromatography (TLC) was done using silica Gel (silica gel 60 F254). TLC plates were analyzed by an exposure to ultraviolet (UV) light. NMR experiments were measured on a Bruker AVANCE III-400 or 500 spectrometer and carried out indeuterochloroform ($CDCl_3$) ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz or 500 MHz and 100 MHz or 125 MHz spectrometers respectively. ^{19}F NMR spectra were recorded at 376 MHz or 470 MHz spectrometers. Chemical shifts are reported as δ valuesrelative to chloroform (δ 7.26 for ^{1}H NMR), chloroform (δ 77.16 for ^{13}C NMR). The following abbreviations are used for the multiplicities: s: singlet, d: doublet, dd:doublet of doublet, t: triplet, q: quadruplet, m: multiplet, br: broad signal for proton spectra; Coupling constants (J) are reported in Hertz (Hz). Infrared spectra were obtained on agilent Cary630. HRMS were recorded on a Bruker microTOF-Q111. GC-MS spectra were performed on Shimadzu QP2010 (EI Source). Unless otherwise noted, all reagents were weighed and handled in air, and all reactions were under argon.

All electrochemical reactions are carried out using the Electrasyn 2.0 setup and medium-sized screw-cap test tubes (8 mL) were used for 0.20 mmol scale reactions: Fisher 13 x 100 mm tubes (Cat. No.1495935C), Cap with Septa: Thermo Scientific ASM PHN CAP w/PTFE/SIL (Cat. No.03378316)



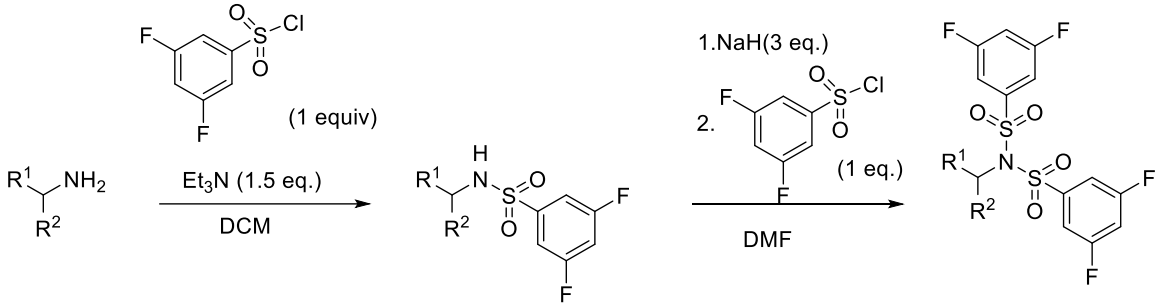
Synthesis of Starting Materials

Procedure 1 (From primary alkyl amines)



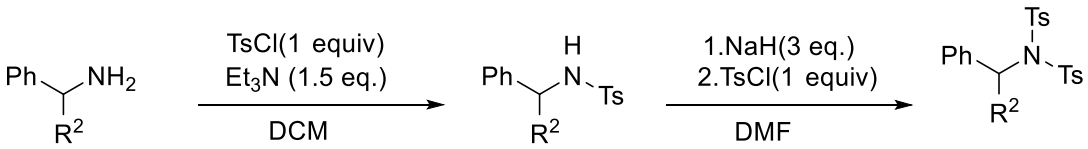
An oven dried round-bottom flask equipped with a stir bar was charged with amine (5.0 mmol, 1.0 equiv), CH_2Cl_2 (20 ml, 0.25M) and Et_3N (2.1 mL, 15 mmol, 3.0 equiv). The flask was cooled to -20 °C, and trifluoromethanesulfonic anhydride (1.7 mL, 2.8 g, 5.0 mmol, 2.0 equiv) was added dropwise. The reaction was stirred vigorously at -20 °C for 1 h and allowed to gradually warm up to room temperature. The reaction was then quenched with 20 mL H_2O. The reaction mixture was partitioned between H_2O and CH_2Cl_2 and layers were separated. The aqueous layer was extracted with CH_2Cl_2 (20 ml × 3). The organic layers were combined, dried over $NaSO_4$, filtered, and concentrated under reduced pressure. The reaction mixture was applied directly to a flash silica column for purification.

Procedure 2 (From secondary alkyl amines)



An oven dried round-bottom flask equipped with a stir bar was charged with amine (5.0 mmol, 1.0 equiv), CH_2Cl_2 (20 ml, 0.25M) and Et_3N (1.1 mL, 7.5 mmol, 1.5 equiv). The flask was cooled to 0 °C, and dry 3,5-difluorobenzenesulfonyl chloride (1.06 g, 5.0 mmol, 1.0 equiv) was added. The reaction was stirred vigorously at 0 °C for 1 h and allowed to gradually warm up to room temperature. The reaction was then quenched with 20 mL H_2O. The reaction mixture was partitioned between H_2O and CH_2Cl_2 and layers were separated. The aqueous layer was extracted with CH_2Cl_2 (20 ml × 3). The organic layers were combined, dried over $NaSO_4$, filtered, and concentrated under reduced pressure to give equivalent product of single substitution. Then the products were added DMF (10 mL) and sodium hydride (600 mg, 15.0 mmol). The mixture was stirred for 10 min, and added dry 3,5-difluorobenzenesulfonyl chloride (1.06 g, 5.0 mmol, 1.0 equiv). The mixture was stirred for 2 h, and quenched with ice water (50 mL). Crude sulfonimide was collected by filtration and purified by recrystallization from methanol.

Procedure 3 (From benzylamines)

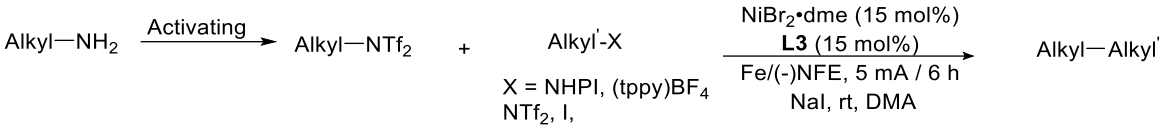


An oven dried round-bottom flask equipped with a stir bar was charged with amine (5.0 mmol,

1.0 equiv), CH_2Cl_2 (20 ml, 0.25M) and Et_3N (1.1 mL, 7.5 mmol, 1.5 equiv). The flask was cooled to 0 °C, and dry TsCl (0.95 g, 5.0 mmol, 1.0 equiv) was added. The reaction was stirred vigorously at 0 °C for 1 h and allowed to gradually warm up to room temperature. The reaction was then quenched with 20 mL H_2O. The reaction mixture was partitioned between H_2O and CH_2Cl_2 and layers were separated. The aqueous layer was extracted with CH_2Cl_2 (20 ml × 3). The organic layers were combined, dried over $NaSO_4$, filtered, and concentrated under reduced pressure to give equivalent product of single substitution. Then the products were added DMF (10 mL) and sodium hydride (600 mg, 15.0 mmol). The mixture was stirred for 10 min, and added dry TsCl (0.95 g, 5.0 mmol, 1.0 equiv). The mixture was stirred for 2 h, and quenched with ice water (50 mL). Crude sulfonimide was collected by filtration and purified by recrystallization from methanol.

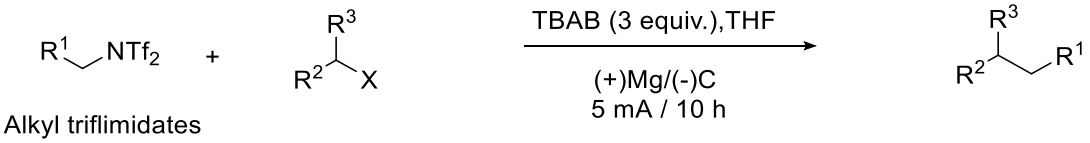
General Procedure for Nickel-electrocatalytic Deaminative Reaction

General Procedure 1 for e-XEC reaction of alkyl bistriflimides with C(sp^3) electrophiles utilizing electrocatalysis



In glove box, NaI (90.0 mg, 0.6 mmol), alkyl bistriflimides (0.3 mmol, 1 equiv.), alkyl electrophiles (0.9 mmol, 3 equiv.), $NiBr_2$·dme (13.8 mg, 0.045 mmol, 15 mol%), **L3** (9.4 mg, 0.045 mmol, 15 mol%), and dried DMA (3.0 mL) was added into the flame dried undivided ElectraSyn vial (5 mL) equipped with a stir bar. The resulting suspension was pre-stirred for about 1 min to dissolve the electrolyte (If the substrate was solid, it would be added to the vial before adding the solvent. If the substrate was sticky oil, it would be added as a solution in DMA). The vial was sealed with the ElectraSyn vial cap equipped with an iron plates anode and a nickel foam cathode, and then bring it out of glove box. After the reaction is completed, the mixture was transferred to separatory funnel. Then H_2O (20 mL) was added and the mixture was extracted with EtOAc (20 mL) for three times. The combined organic layer was washed with 1.0 M NaOH (20 mL), brine (20 mL) and H_2O (20 mL). The organic layer was dried with anhydrous Na_2SO_4, then concentrated under vacuum. The product was purified by flash column chromatography on silica gel or PTLC using petroleum ether/EtOAc as eluent.

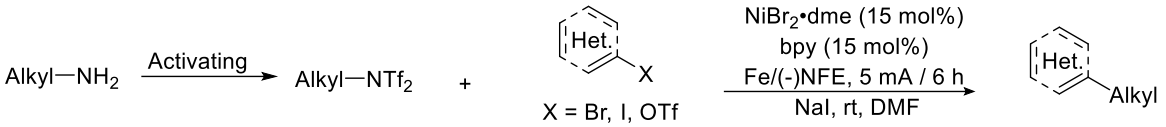
General Procedure 2 for e-XEC reaction with alkyl bistriflimides



Alkyl triflimidates

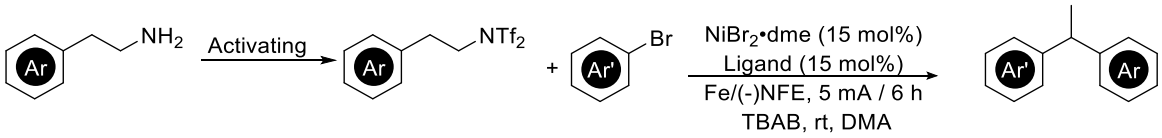
In glove box, TBAB (483.0 mg, 1.5 mmol, 3 equiv.) and dried THF (2.5 mL) was added into the flame dried undivided ElectraSyn vial (5 mL) equipped with a stir bar. The resulting suspension was pre-stirred for about 1 min to dissolve the electrolyte. Then the substrate with anion-stabilizing group (0.5 mmol, 1 equiv.) and alkyl bistriflimides (1.5 mmol, 3 equiv.) was sequentially added to the mixture. The vial was sealed with the ElectraSyn vial cap equipped with anode (Mg plate) and cathode (graphite plate), and then bring it out of glove box. Pre-stirring the resulting mixture for 2 minutes, and then the reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 10 h. After the reaction is completed, the mixture was transferred to separatory funnel, electrodes were washed with ethyl acetate. Then, the crude mixture was further diluted with Et_2O (If there were too much flocculent, filter it by celite). The resulting mixture was washed with brine. The organic layer was dried over with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to furnish the desired product.

General Procedure 3 for e-XEC reaction of alkyl bistriflimides with C(sp^2) electrophiles utilizing electrocatalysis



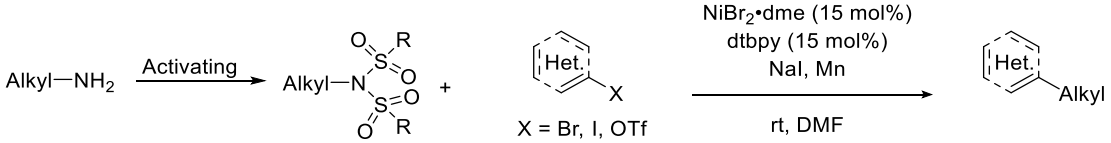
In glove box, NaI (90.0 mg, 0.6 mmol), alkyl bistriflimides (0.3 mmol, 1.5 equiv.), electrophiles (0.2 mmol, 1 equiv.), $NiBr_2$·dme (9.2 mg, 0.03 mmol, 15 mol%), bpy (4.7 mg, 0.03 mmol, 15 mol%), and dried DMF (3.0 mL) was added into the flame dried undivided ElectraSyn vial (5 mL) equipped with a stir bar. The resulting suspension was pre-stirred for about 1 min to dissolve the electrolyte (If the substrate was solid, it would be added to the vial before adding the solvent. If the substrate was sticky oil, it would be added as a solution in DMF). The vial was sealed with the ElectraSyn vial cap equipped with an iron plates anode and a nickel foam cathode, and then bring it out of glove box. After the reaction is completed, the mixture was transferred to separatory funnel. Then H_2O (20 mL) was added and the mixture was extracted with EtOAc (20 mL) for three times. The combined organic layer was washed with 1.0 M NaOH (20 mL), brine (20 mL) and H_2O (20 mL). The organic layer was dried with anhydrous Na_2SO_4, then concentrated under vacuum. The product was purified by flash column chromatography on silica gel or PTLC using petroleum ether/EtOAc as eluent.

General Procedure 4 for electrochemical reductive relay cross-coupling of alkyl bistriflimides to aryl halides



In glove box, TBAB (290.0 mg, 0.6 mmol), alkyl bistriflimides (0.3 mmol, 1.5 equiv.), aryl bromide (0.2 mmol, 1 equiv.), $NiBr_2$·dme (9.2 mg, 0.03 mmol, 15 mol%), ligand (0.03 mmol, 15 mol%), and dried DMA (3.0 mL) was added into the flame dried undivided ElectraSyn vial (5 mL) equipped with a stir bar. The resulting suspension was pre-stirred for about 1 min to dissolve the electrolyte (If the substrate was solid, it would be added to the vial before adding the solvent. If the substrate was sticky oil, it would be added as a solution in DMA). The vial was sealed with the ElectraSyn vial cap equipped with an iron plates anode and a nickel foam cathode, and then bring it out of glove box. After the reaction is completed, the mixture was transferred to separatory funnel. Then H_2O (20 mL) was added and the mixture was extracted with EtOAc (20 mL) for three times. The combined organic layer was washed with 1.0 M NaOH (20 mL), brine (20 mL) and H_2O (20 mL). The organic layer was dried with anhydrous Na_2SO_4, then concentrated under vacuum. The product was purified by flash column chromatography on silica gel or PTLC using petroleum ether/EtOAc as eluent.

General Procedure 5 for XEC reaction of alkyl bistriflimides with C(sp^2) electrophiles utilizing metal reductant Mn

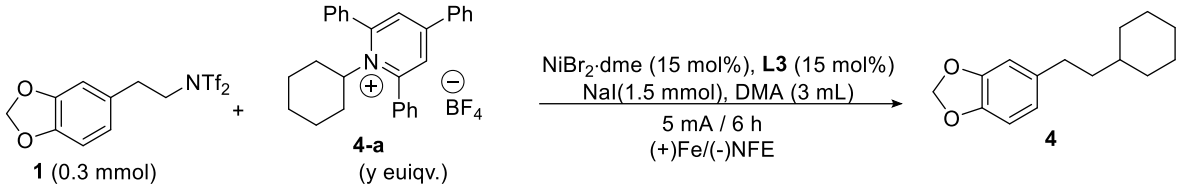


In glove box, a dry 8-mL vial equipped with a Teflon-coated magnetic stir bar was charged with electrophiles (0.2 mmol, 1 equiv., if solid), alkyl bistriflimides (0.3 mmol, 1.5 equiv., if solid),

$NiBr_2$·dme (9.2 mg, 0.03 mmol, 15 mol%), dtbpy (8.0 mg, 0.03 mmol, 15 mol%), NaI (45.0 mg, 0.3 mmol, 1.5 equiv.) and Mn (33 mg, 0.6 mmol, 2.5 equiv.). Anhydrous and degassed DMF (1.0 mL), electrophiles (0.2 mmol, 1 equiv., if liquid), alkyl bistriflimides (0.3 mmol, 1.5 equiv., if liquid), were added via syringe. The vial was capped and sealed with parafilm. The reaction mixture was stirred for 6 h at 60 ℃. After the reaction is completed, the mixture was transferred to separatory funnel. Then H_2O (20 mL) was added and the mixture was extracted with EtOAc (20 mL) for three times. The combined organic layer was washed with 1.0 M NaOH (20 mL), brine (20 mL) and H_2O (20 mL). The organic layer was dried with anhydrous Na_2SO_4, then concentrated under vacuum. The product was purified by flash column chromatography on silica gel or PTLC using petroleum ether/EtOAc as eluent.

Comparison with Other Alkyl Electrophiles

Table S1: Effect of concentration of **4-a**



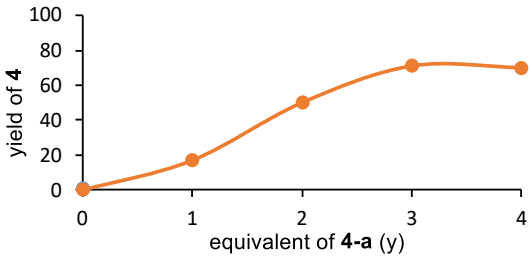
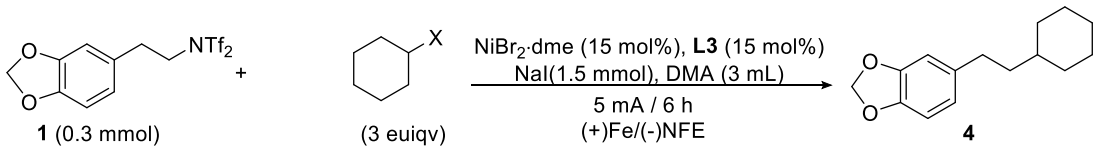
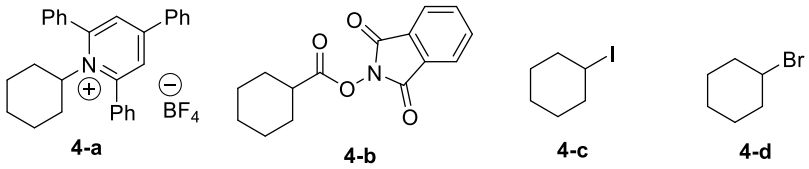


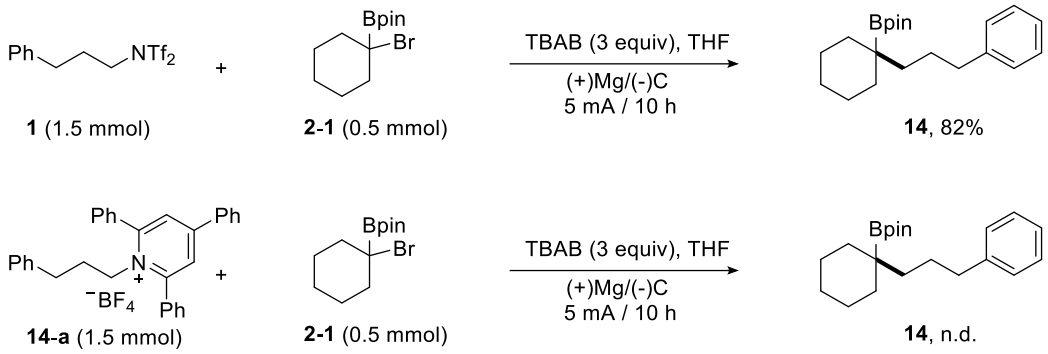
Table S2: Comparison with other alkyl electrophiles





y = 3	yield of **4** (%)
1 and **4-a**	71
1 and **4-b**	77
1 and **4-c**	54
1 and **4-d**	11

Table S3: Comparison with Katrizky salt under general procedure 2



In glove box, TBAB (483.0 mg, 1.5 mmol, 3 equiv.) and dried THF (2.5 mL) was added into the flame dried undivided ElectraSyn vial (5 mL) equipped with a stir bar. The resulting suspension was pre-stirred for about 1 min to dissolve the electrolyte. Then the **2-1** (0.5 mmol, 1 equiv.) and **14-a** (1.5 mmol, 3 equiv.) was sequentially added to the mixture. The vial was sealed with the ElectraSyn vial cap equipped with anode (Mg plate) and cathode (graphite plate), and then bring it out of glove box. Pre-stirring the resulting mixture for 2 minutes, and then the reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 10 h. After the reaction is completed, the reaction mixture was monitored by GCMS and TLC, and product **14** was not detected.

Cyclic Voltammetry Measurements

All measurements were performed under anhydrous conditions in argon-filled atmosphere. The cell for the analysis was equipped with a glass vial (working volume is 10 mL) and Teflon cap, equipped with O-ring for tight sealing. Glassy carbon was used as working electrodes (circle, d = 3 mm), platinum wire as a counter electrode, and Ag as a reference. All measurements were conducted in 0.1 M solutions of Bu_4NBF_4 in DMF. The potentials were given relative to the Fc/Fc+ redox couple with ferrocene as internal standard. For conversion to SCE as reference, it is known that SCE is 400 mV more negative than Fc/Fc+ in DMA with Bu_4NBF_4 as supporting electrolyte.

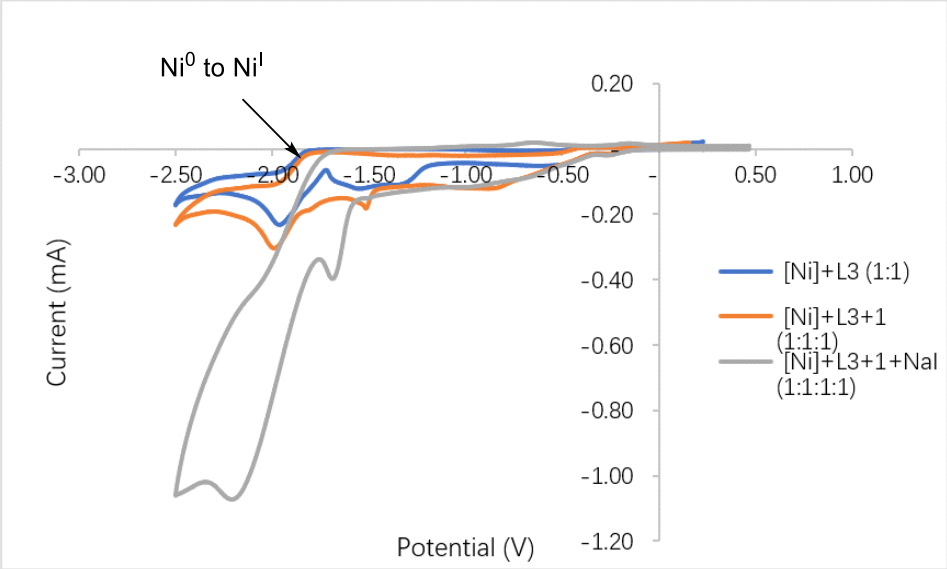
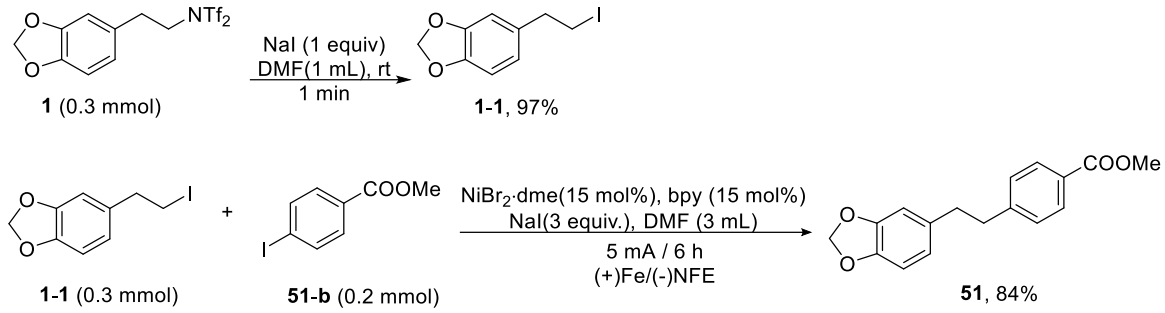


Figure S1: Cyclic voltammetry measurement

Intermediate and Sodium Iodide Effects



Under air conditions, 0.3 mmol of sodium iodide was added to an 8 mL tube, followed by 1 mL of DMF, and stirred until the NaI was dissolved. Then, 0.3 mmol of compound **1** was added, and stirring was continued for approximately 5 minutes. Subsequently, 20 mL of H_2O was added to the system. The resulting mixture was extracted with EtOAc (2×30 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by column chromatography to obtain the **1-1** in 97% yield. Compound **1-1**: **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.75 (m, 1H), 6.70 – 6.54 (m, 2H), 5.94 (s, 2H), 3.38 – 3.16 (m, 2H), 3.08 (t, *J* = 7.7 Hz, 2H).**^{13}C NMR (101 MHz, Chloroform-*d*)** δ 147.9, 146.5, 134.6, 121.5, 108.8, 108.5, 101.1, 40.2, 6.2.

In glove box, NaI (90.0 mg, 0.6 mmol), **1-1** (0.3 mmol, 1.5 equiv.), **51-b** (0.2 mmol, 1 equiv.), $NiBr_2$·dme (9.2 mg, 0.03 mmol, 15 mol%), bpy (4.7 mg, 0.02 mmol, 15 mol%), and dried DMF (3.0 mL) was added into the flame dried undivided ElectraSyn vial (5 mL) equipped with a stir bar. The resulting suspension was pre-stirred for about 1 min to dissolve the electrolyte. The vial was sealed with the ElectraSyn vial cap equipped with an iron plates anode and a nickel foam cathode, and then bring it out of glove box. After the reaction is completed, the yield 84% was detected by GC with dodecane as the internal standard.

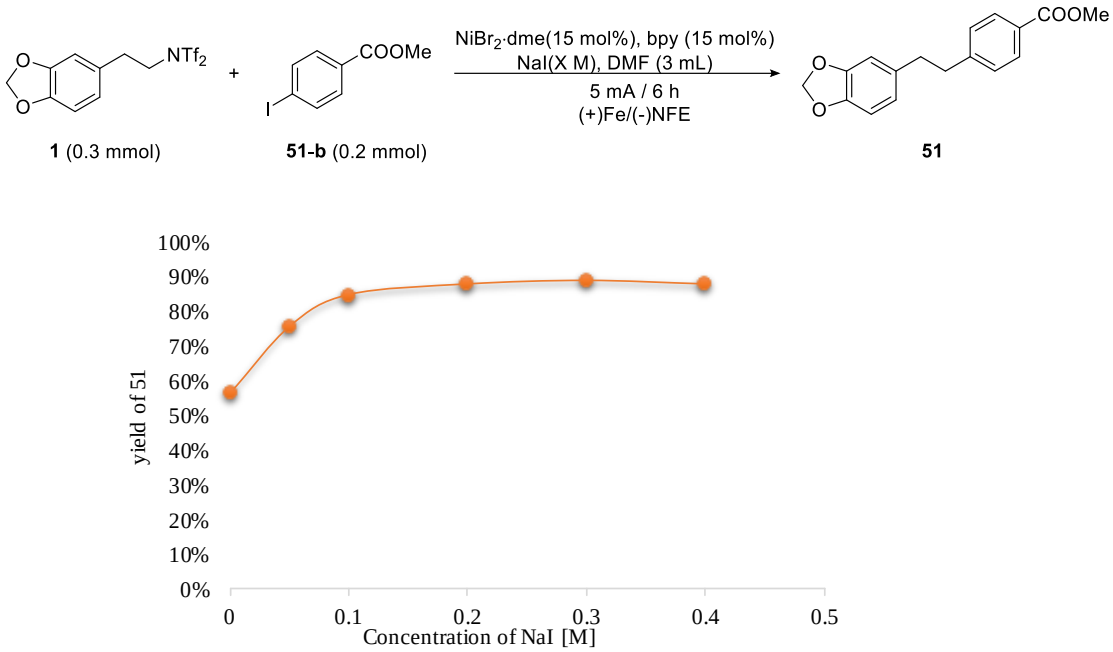


Figure S2: The effect of NaI

In glove box, NaI (X mmol), **1** (0.3 mmol, 1.5 equiv.), methyl 4-iodobenzoate **51-b** (0.2 mmol, 1 equiv.), $NiBr_2$·dme (9.2 mg, 0.03 mmol, 15 mol%), bpy (4.7 mg, 0.03 mmol, 15 mol%), and dried DMF (3.0 mL) was added into the flame dried undivided ElectraSyn vial (5 mL) equipped with a stir bar. The resulting suspension was pre-stirred for about 1 min to dissolve the electrolyte. The vial was sealed with the ElectraSyn vial cap equipped with an iron plates anode and a nickel foam cathode, and then bring it out of glove box. After the reaction is completed, the yield was detected by GC with dodecane as the internal standard.

Radical Inhibition Reaction

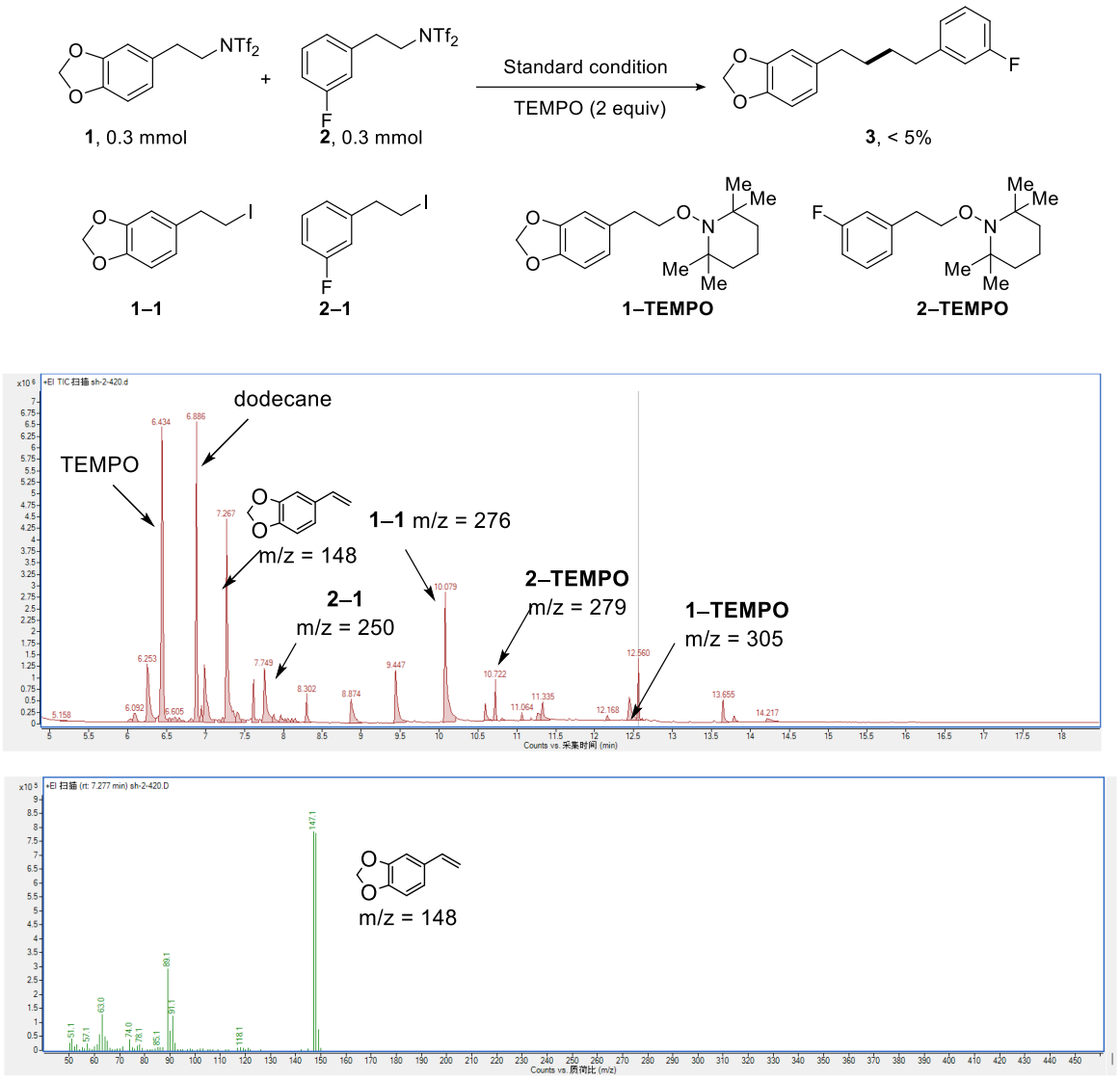
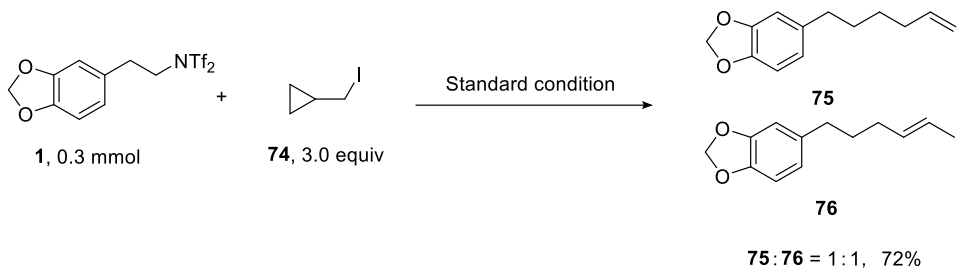


Figure S3: GCMS spectrum of TEMPO inhibition experiment

In glove box, NaI (1.5 mmol), **1** (0.3 mmol, 1.0 equiv.), **2** (0.3 mmol, 3.0 equiv.), $NiBr_2$·dme (13.8 mg, 0.045 mmol, 15 mol%), **L3** (9.4 mg, 0.045 mmol, 15 mol%), TEMPO (0.6 mmol), and dried DMA (3.0 mL) was added into a dry 5-mL vial equipped with a stir bar. The vial was sealed with the ElectraSyn vial cap equipped with an iron plates anode and a nickel foam cathode, and then bring it out of glove box. After the reaction is completed, the yield was detected by GC. In the reaction mixture, **1** primarily converts to alkenes (with alkenes derived from **2** having retention time before 5 minutes), and a small amount of TEMPO adducts is also present.



In glove box, NaI (1.5 mmol), **1** (0.3 mmol, 1.0 equiv.), **74** (0.9 mmol, 3.0 equiv.), $NiBr_2$·dme (13.8 mg, 0.045 mmol, 15 mol%), **L3** (9.4 mg, 0.045 mmol, 15 mol%), and dried DMA (3.0 mL) was added into a dry 5-mL vial equipped with a stir bar. The vial was sealed with the ElectraSyn vial cap equipped with an iron plates anode and a nickel foam cathode, and then bring it out of glove box. After the reaction is completed, the yield was detected by GC. After the reaction is completed, the mixture was transferred to separatory funnel. Then H_2O (20 mL) was added and the mixture was extracted with EtOAc (20 mL) for three times. The combined organic layer was washed with 1.0 M NaOH (20 mL), brine (20 mL) and H_2O (20 mL). The organic layer was dried with anhydrous Na_2SO_4, then concentrated under vacuum. The product was purified by flash column chromatography on silica gel or PTLC using petroleum ether/EtOAc as eluent. **75** and **76** cannot be separated by column chromatography.

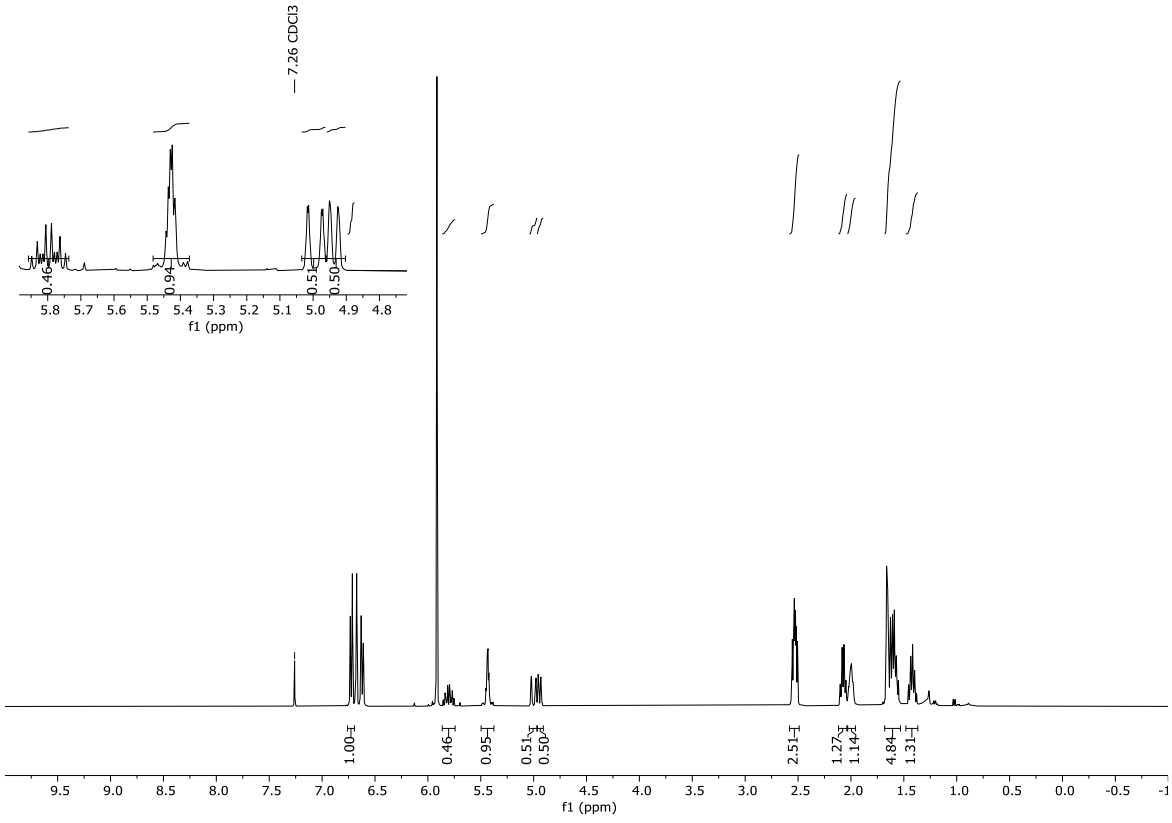
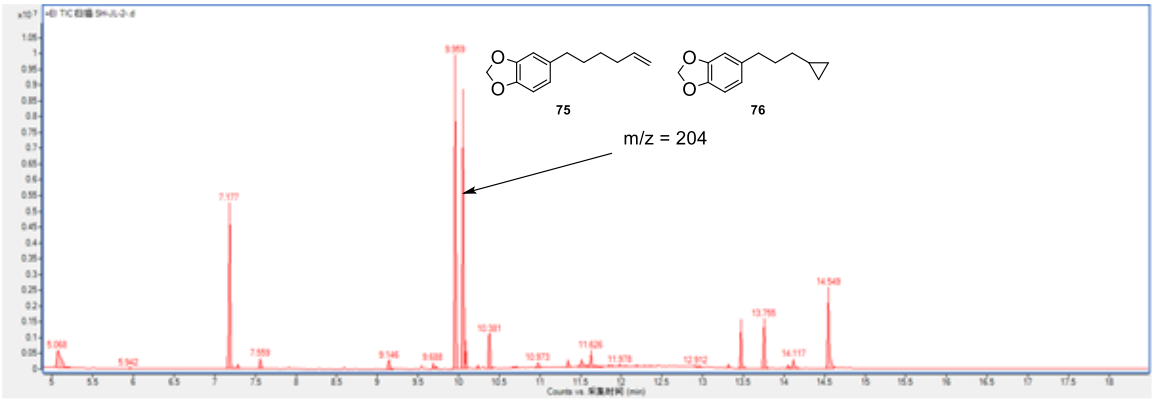
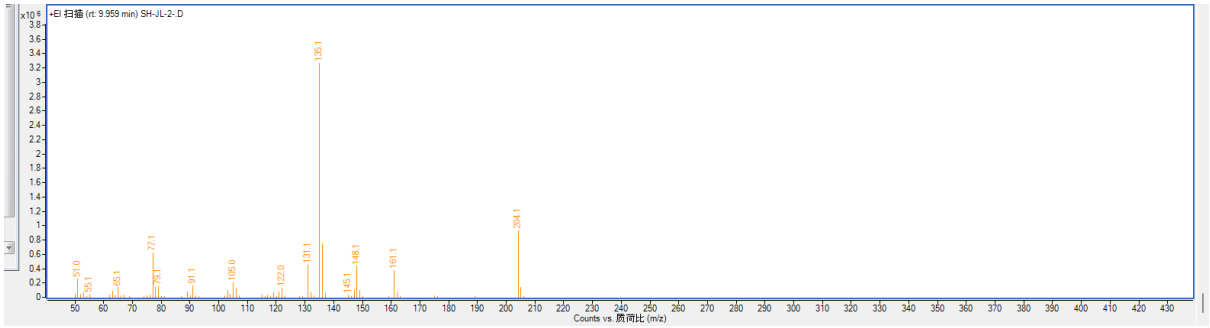


Figure S4: ^{1}H NMR of the mixture of **75** and **76**





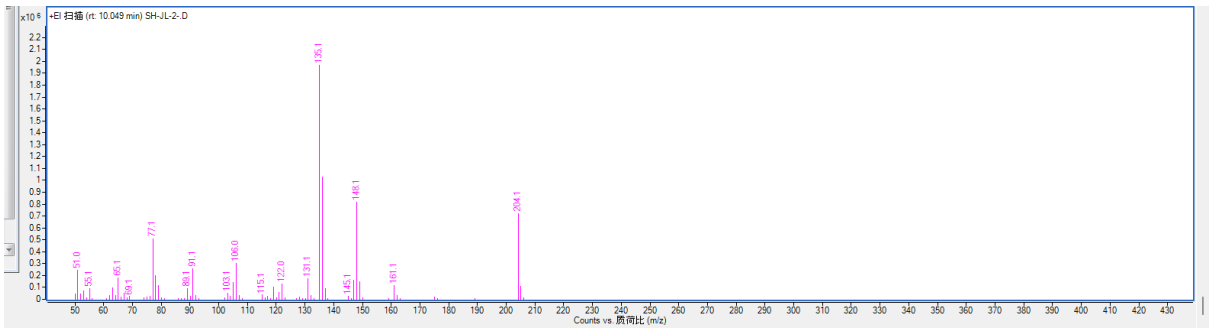
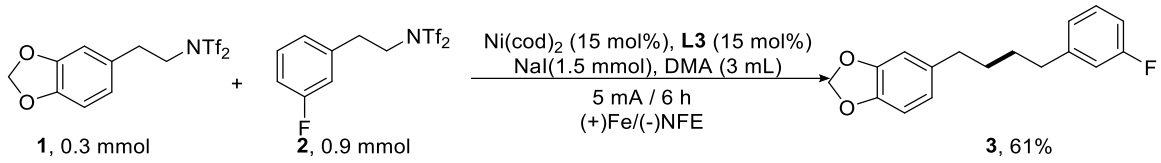


Figure S5: GCMS spectrum of radical clock experiment

Control experiments of [Ni]

Replacement of $Ni(cod)_2$ with $NiBr_2$·dme



In glove box, NaI (1.5 mmol), **1** (0.3 mmol, 1.0 equiv.), **2** (0.9 mmol, 3.0 equiv.), $Ni(cod)_2$ (12.4 mg, 0.045 mmol, 15 mol%), **L3** (9.5 mg, 0.045 mmol, 15 mol%), and dried DMA (3.0 mL) was added into the flame dried undivided ElectraSyn vial (5 mL) equipped with a stir bar. The resulting suspension was pre-stirred for about 1 min to dissolve the electrolyte. The vial was sealed with the ElectraSyn vial cap equipped with an iron plates anode and a nickel foam cathode, and then bring it out of glove box. After the reaction is completed, the yield was detected by GC with dodecane as the internal standard.

Effect of $Ni(cod)_2$ amounts on reactions as the catalyst and reducing agent:

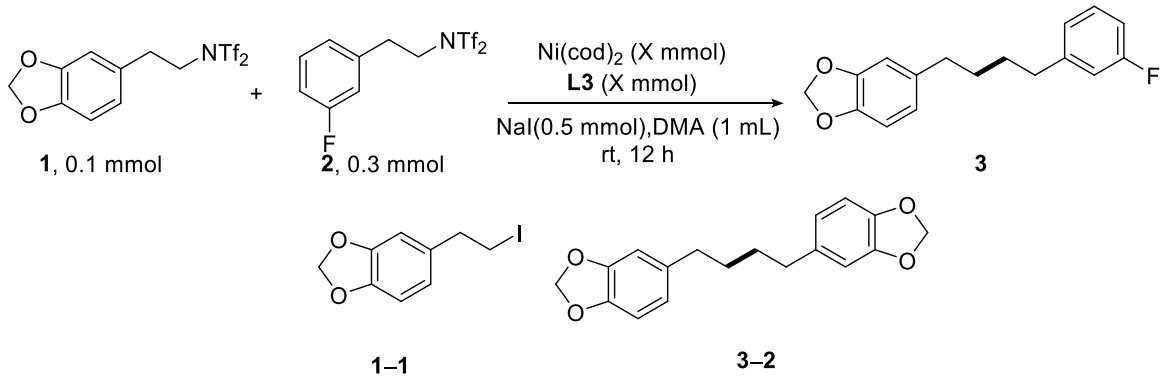


Table S4: Comparison of results for different equivalent amounts of $Ni(cod)_2$

	3	**1-1**	**3-2**	Mass banlance
0	0	100	0	100%
0.1	30	63	0	93%
0.2	51	34	3	91%
0.4	68	22	6	102%

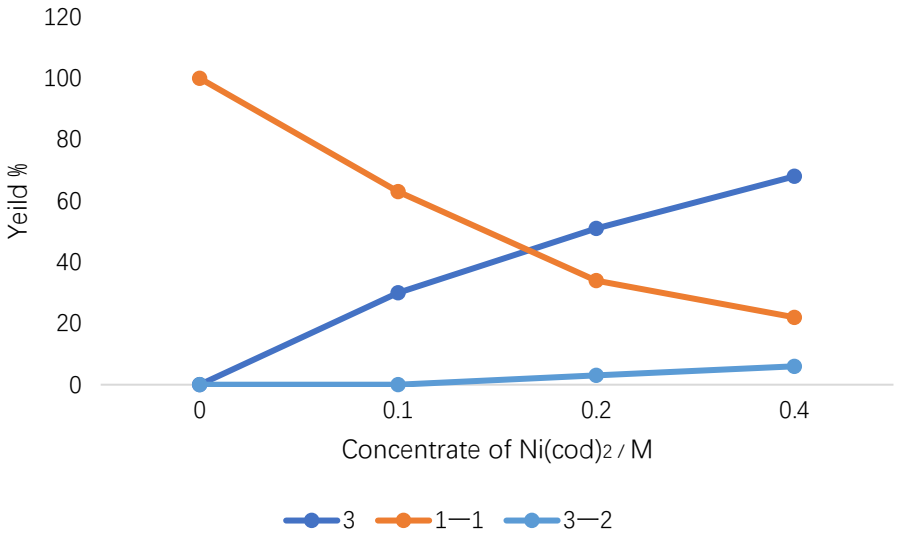
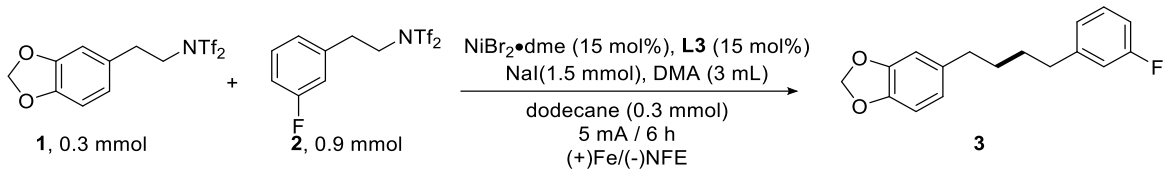


Figure S6: Effect of $Ni(cod)_2$

In glove box, NaI (1.5 mmol), **1** (0.1 mmol, 1.0 equiv.), **2** (0.3 mmol, 3.0 equiv.), $Ni(cod)_2$ (X mmol), **L3** (X mmol), and dried DMA (1.0 mL) was added into a dry 8-mL vial equipped with a stir bar. The reaction system was brought out of glove box and stir at room temperature for 12 h. After the reaction is completed, the yield was detected by GC with dodecane as the internal standard.



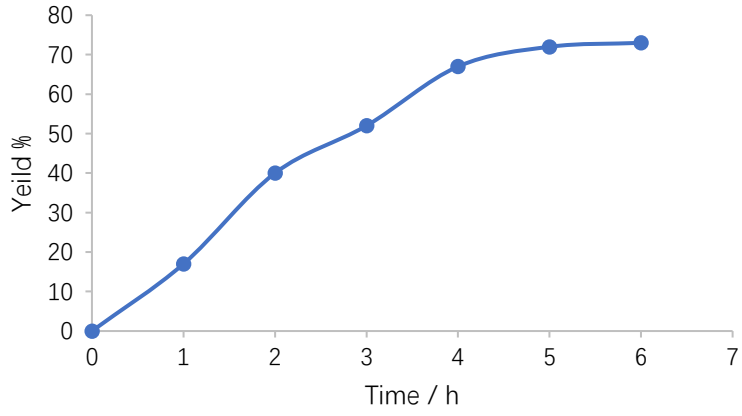
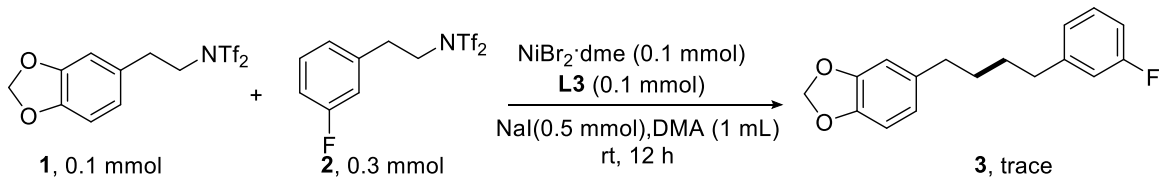


Figure S7: Effect of reaction time on yield

In glove box, NaI (1.5 mmol), **1** (0.3 mmol, 1.0 equiv.), **2** (0.9 mmol, 3.0 equiv.), $NiBr_2$·dme (13.8 mg, 0.045 mmol, 15 mol%), **L3** (9.4 mg, 0.045 mmol, 15 mol%), dodecane (0.3 mmol), and dried DMA (3.0 mL) was added into a dry 5-mL vial equipped with a stir bar. The vial was sealed with

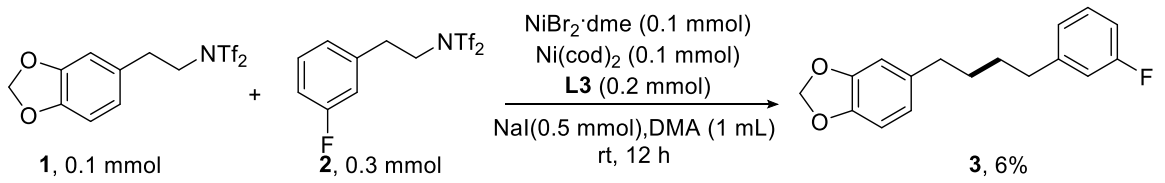
the ElectraSyn vial cap equipped with an iron plates anode and a nickel foam cathode, and then bring it out of glove box. After the reaction is completed, the yield was detected by GC.

1.0 equiv. $NiBr_2$·dme:



In glove box, NaI (1.5 mmol), **1** (0.1 mmol, 1.0 equiv.), **2** (0.3 mmol, 3.0 equiv.), $NiBr_2$·dme (30.9 mg, 0.1 mmol, 1.0 equiv), **L3** (21.1 mg, 0.1 mmol, 1.0 equiv), and dried DMA (1.0 mL) was added into a dry 8-mL vial equipped with a stir bar. The reaction system was brought out of glove box and stir at room temperature for 12 h. After the reaction is completed, the yield was detected by GC with dodecane as the internal standard.

1.0 equiv. $NiBr_2$·dme and 1.0 equiv. $Ni(cod)_2$:



In glove box, $Ni(cod)_2$ (27.5 mg, 0.1 mmol, 1.0 equiv), $NiBr_2$·dme (30.9 mg, 0.1 mmol, 1.0 equiv), **L3** (42.2 mg, 0.2 mmol, 2.0 equiv), and dried DMA (1.0 mL) was added into the flame dried vial (8 mL) equipped with a stir bar. The resulting suspension was pre-stirred for about 1 h, then NaI (1.5 mmol), **1** (0.1 mmol, 1.0 equiv.), **2** (0.3 mmol, 3.0 equiv.) was added. The reaction system was brought out of glove box and stir at room temperature for 11 h. After the reaction is completed, the yield was detected by GC with dodecane as the internal standard.

EPR analysis

[Ni(I)-Br] was generated

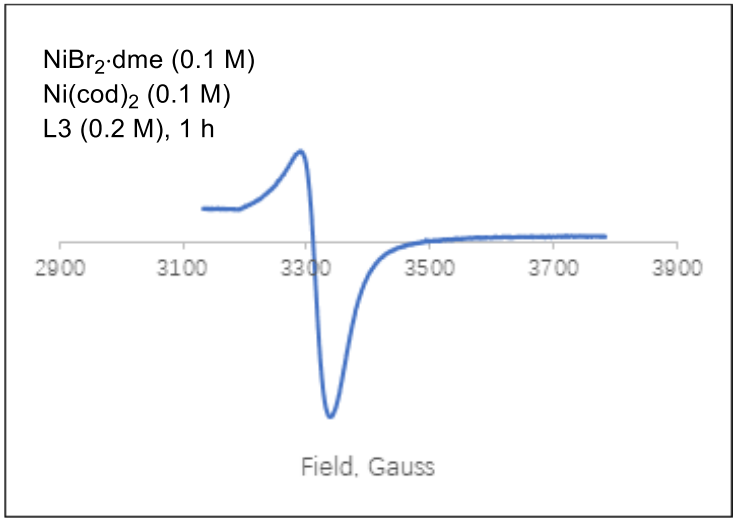


Figure S8: EPR signal of Ni

In glove box, $Ni(cod)_2$ (27.5 mg, 0.1 mmol, 1.0 equiv), $NiBr_2$·dme (30.9 mg, 0.1 mmol, 1.0 equiv), **L3** (42.2 mg, 0.2 mmol, 2.0 equiv), and dried DMA (1.0 mL) was added into the flame dried vial (8 mL) equipped with a stir bar. The resulting suspension was pre-stirred for about 1 h and transferred to the EPR tube. Then, outside the glovebox, the sample was frozen to 77 K with liquid nitrogen and introduced into the EPR instrument. An intense signal consistent with a nickel(I) was detected.

Proposed Mechanism

Path 1:

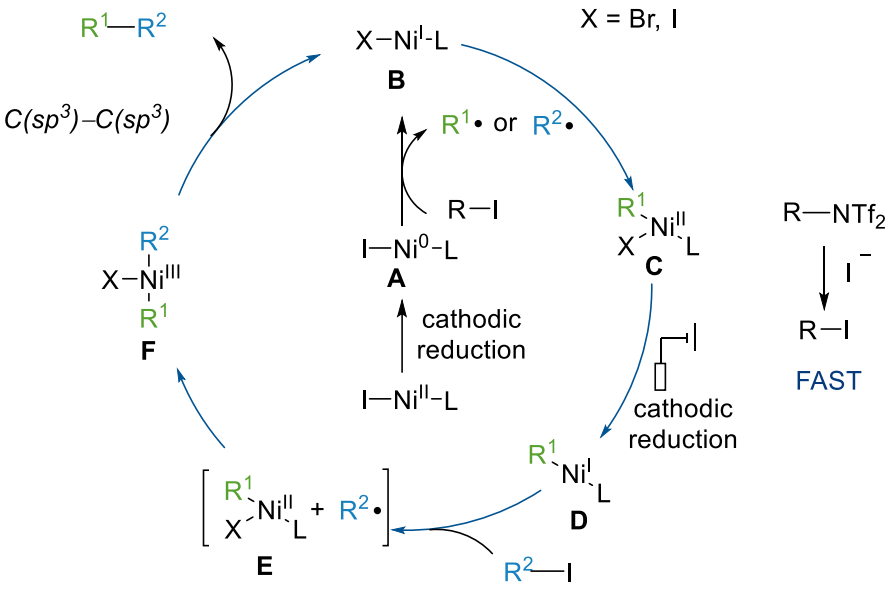


Figure S9: Proposed mechanism for construction of C(sp^3)-C(sp^3) (Path 1)

Path 2:

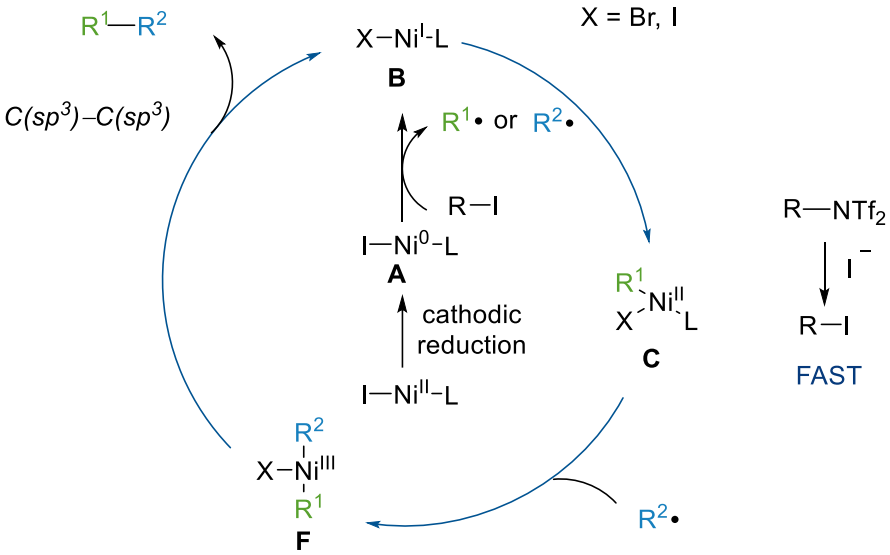


Figure S10: Proposed mechanism for construction of C(sp^3)-C(sp^3) (Path 2)

Path 3:

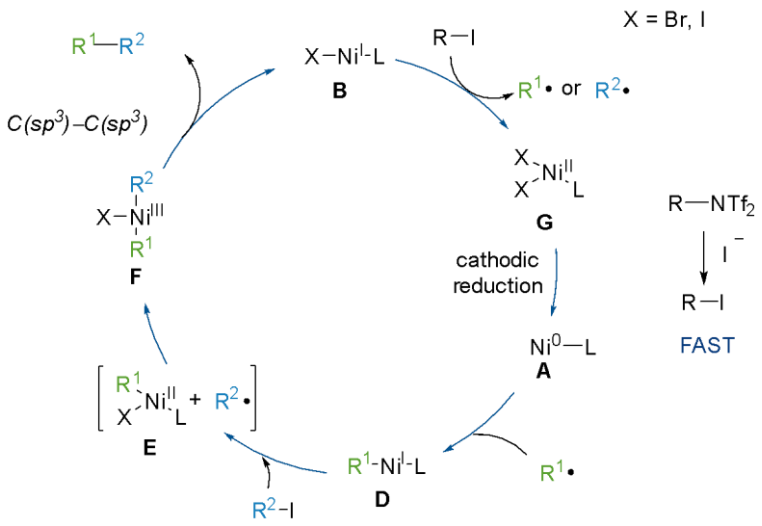


Figure S11: Proposed mechanism for construction of $C(sp^3)$-$C(sp^3)$ (Path 3)

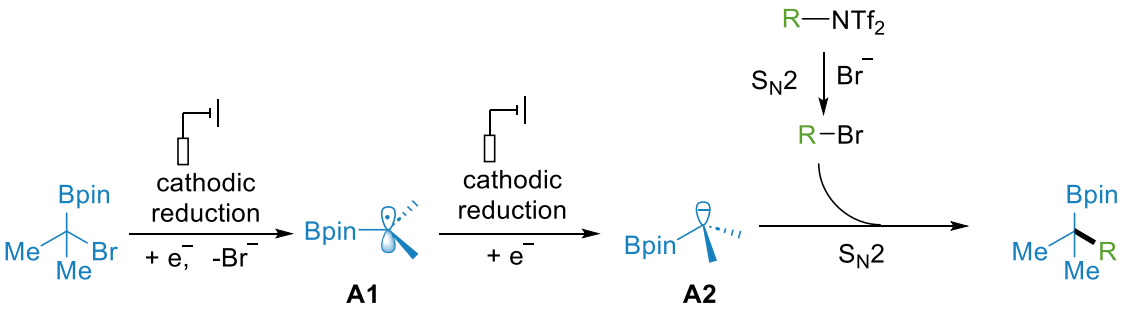


Figure S12: Proposed mechanism for cross-electrophile coupling of alkyl halides and alkyl bistriflimides

According to Lin's report, the mechanism for the formation of products **14-18** may proceed as follows: Initially, alkyl bistriflimides undergo nucleophilic substitution by bromide anions to generate less hindered alkyl bromides. The desired cross-electrophile coupling (XEC) can be envisioned via a radical-polar crossover pathway, which consists of the selective reduction of a more substituted alkyl halide to a carbon-centered radical (**A1**), followed by a second reduction to a carbanion (**A2**), and subsequent chemoselective nucleophilic substitution on a less hindered alkyl halide.

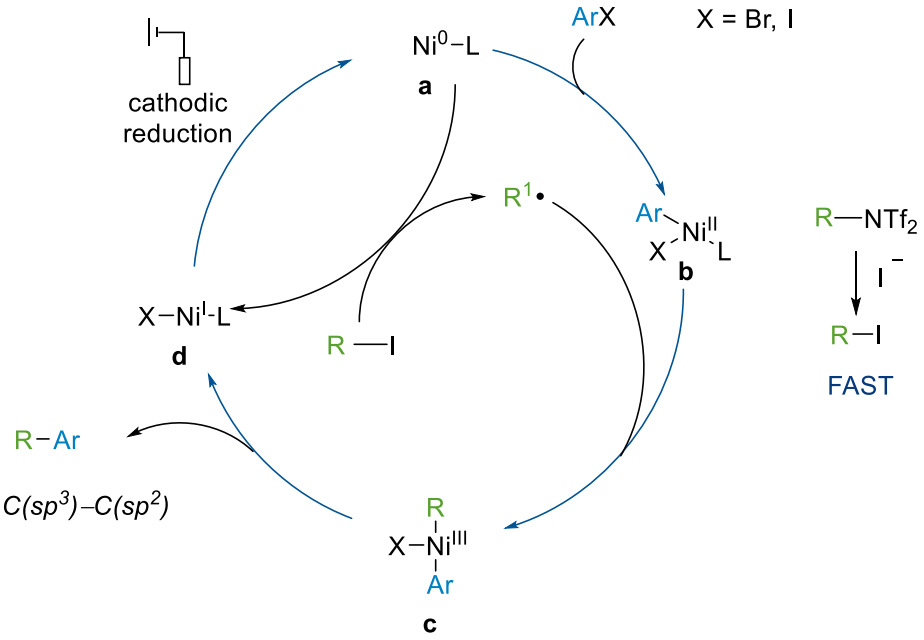


Figure S13: Proposed mechanism for construction of C(sp^3)-C(sp^2)

According to previous reports, the mechanism for the formation of products **19-45** and **51-73** may proceed as follows: Initially, alkyl bistriflimides undergo nucleophilic substitution by iodole anions to generate alkyl iodoles. On the other hand, the electroreduction of Ni(II) provide low-valent Ni(0) species (**a**) for the reduction of alkyl halides, generating alkyl radicals and Ni(I) species (**d**). At the same time, after oxidative addition of an aryl bromide to Ni(0), the aryl Ni(II) species (**b**) is formed. The resulting ArNi(II) species can react with an alkyl radical to generate a Ni(III) species (**c**). Upon reductive elimination, the desired cross-coupling product and a Ni(I) species (**d**) are formed. Upon cathodic reduction, the active Ni(0) is then regenerated.

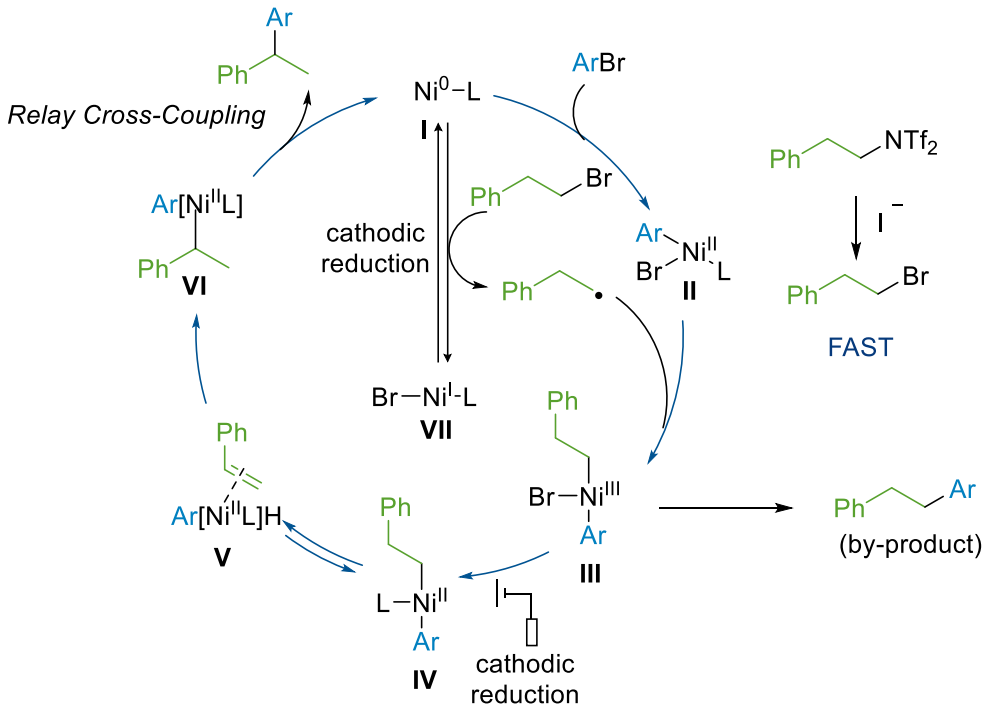


Figure S14: Proposed mechanism for relay cross-coupling of alkyl bistriflimides to aryl halides

According to Mei's report, the mechanism for the formation of products **46-50** may proceed as follows: Initially, alkyl bistriflimides undergo nucleophilic substitution by bromide anions to generate alkyl bromides. At the same time, the Ni(II) catalyst is reduced to Ni(0) by cathodic reduction. Then, after oxidative addition of an aryl bromide to Ni(0), the aryl Ni(II) species **II** is formed. The resulting ArNi(II) species can react with an alkyl radical to generate a Ni(III) species **III**. Direct reductive elimination from **III** can generate a linear by-product, and **III** can also be reduced by cathode to delivered **IV** and converted into the species **VI**, a more thermodynamically stable benzylic Ni(II) intermediate by multiple b-hydride elimination/reinsertion steps. Upon reductive elimination, the desired cross-coupling product and a Ni(0) species (**I**) are formed. **I** can react with an alkyl bromide, affording an alkyl radical species and Ni(I) species (**VII**). Upon cathodic reduction, the active Ni(0) is then regenerated.

DFT Calculation

All calculations except single point calculations were conducted using DFT *(78)* as implemented in the Gaussian 09 suite *(79)* of ab initio quantum chemistry programs with B3LYP-D3 levels of theory. *(80,81)* Geometry optimizations were proceeded using the 6-31G** basis set. After geometry optimizations, the energies were re-evaluated with optimized structures under M06-D3 level and 6-311G(d,p) basis set. Solvation energy corrections were carried out at the same level of the single point energy calculations using SMD *(82)* model (solvent = DMA), where the solution phase electronic energies (E_{Sol}) were evaluated. Vibrational frequency calculations were conducted at the same level as the geometry optimizations, to derive the thermochemistry correction term (G – E) as well as to confirm the stationary points as either minima (no imaginary frequencies) or saddle points (one imaginary frequency) on the potential energy surface. Final solution phase Gibbs free energies (G_{Sol}) were computed as follows:

$$G_{Sol} = E_{Sol} + (G - E) \qquad \text{(S1)}$$

$$\Delta G_{Sol} = \Sigma G_{Sol} \text{ for products} - \Sigma G_{Sol} \text{ for reactants} \qquad \text{(S2)}$$

1) S_N2 reaction

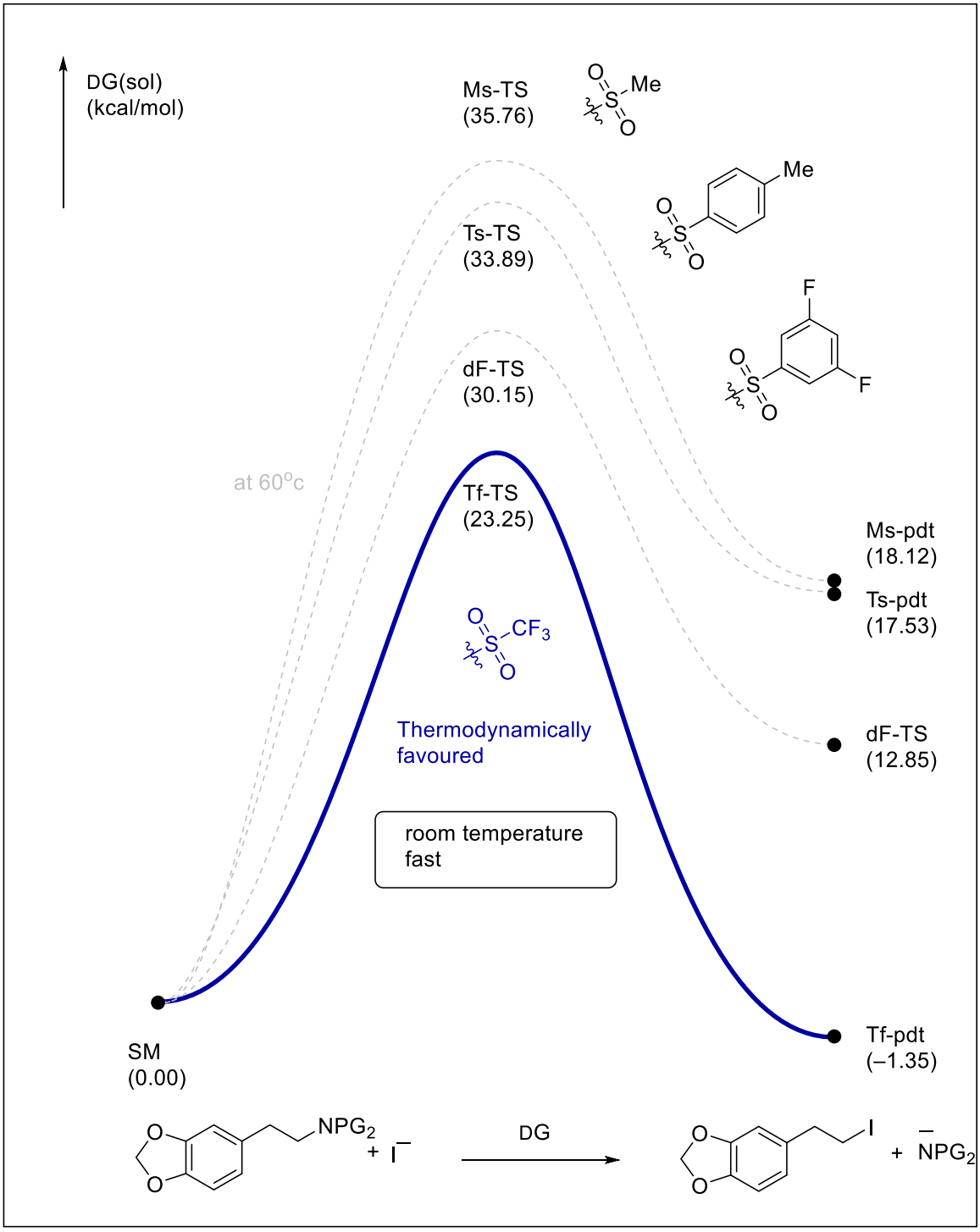
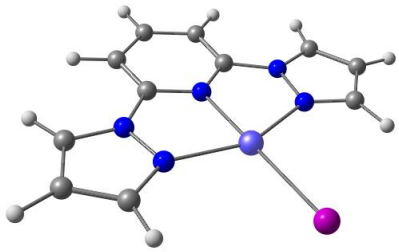


Figure S15: Energy profile of S_N2 reaction of various amine protection groups

From control experiment, we found out only the triflate protection group undergoes the reaction at room temperature. As shown in the calculation data above, other protection groups required high transition energy.

2) Ni regeneration



$E^{0,Theor}$[Ni(I)(L3)/Ni(0)] = –2.851V vs SCE

Figure S16: Calculated reduction potential of Ni(I)(L3)

3) Nickel catalyzed sp^3-sp^3 coupling reaction energy profile

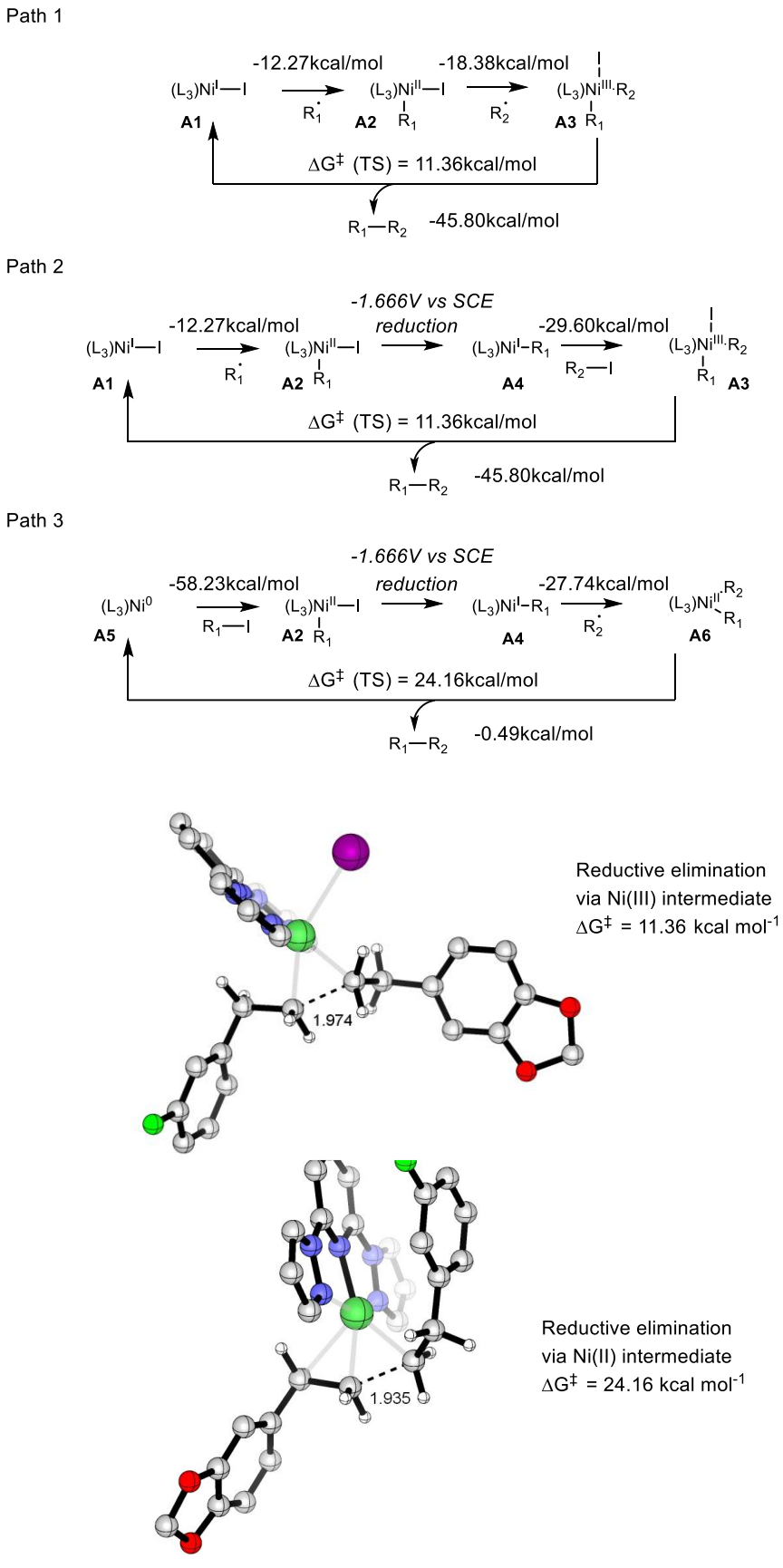


Figure S17: Possible energy profile of nickel catalyzed sp^3-sp^3 coupling reaction

Based on our experimental data, we proposed three possible reaction pathways to generate the desired product. Our findings indicate that the reductive elimination step may be the rate-determining step among all subsequent steps. Consequently, the reductive elimination rate of dialkyl-Ni(III) complexes is faster than that of dialkyl-Ni(II) complexes. Therefore, we propose that the pathway involving dialkyl-Ni(III) complexes is more favorable.

DFT-optimized structure's energy components

Table S5. Computed energy components for optimized structures

	E(SCF)/(eV)	Thermal correction	G(solv)/(eV)
	M06-D3/6-311G(d,p)	B3LYP-D3/6-31G*	M06-D3/6-311G(d,p)
Sub_NTf	-63284.267	4.379	-63279.888
Sub_NMs	-47082.395	5.864	-47076.531
Sub_NdF	-68313.330	7.481	-68305.849
Sub_NTs	-59650.292	9.845	-59640.447
NTf-	-49721.301	0.296	-49721.005
NMs-	-33518.556	1.753	-33516.803
NdF-	-54749.714	3.364	-54746.349
NTs-	-46086.510	5.764	-46080.745
TS_NTf	-63598.505	4.244	-63594.261
TS_NMs	-47396.048	5.687	-47390.361
TS_NdF	-68627.281	7.359	-68619.922
TS_NTs	-59964.107	9.748	-59954.359

Iodide_pdt	-13877.634	3.311	-13874.323
Iodide	-314.923	-0.458	-315.381
A1	-23959.365	4.000	-23955.365
A2	-37526.268	7.944	-37518.323
A3	-48664.869	11.470	-48653.400
A4	-37214.033	8.040	-37205.993
A5	-23645.618	4.143	-23641.476
A6	-48352.912	11.437	-48341.475
TS(A3/A1)	-48664.416	11.509	-48652.907
TS(A6/A5)	-48351.993	11.566	-48340.427

Table S6. Cartesian coordinates of the optimized geometries

The cartesian coordinates of optimized geometries are given below in the standard XYZ format, and units are in Å

Sub_NTf			
C	-2.670404	0.679678	0.784659
C	-3.033647	1.453444	-0.317141
C	-2.390184	1.333846	-1.532244
C	-1.345146	0.393991	-1.607376
C	-0.976128	-0.390599	-0.510596
C	-1.650580	-0.246879	0.723532
O	-3.484047	0.979787	1.849603
C	-4.292419	2.084373	1.422794
O	-4.089906	2.266544	0.015525
C	0.190760	-1.346588	-0.605788
C	1.469549	-0.661617	-0.115585
N	2.646430	-1.591962	-0.104537
S	2.947549	-2.439927	1.349984
O	3.869134	-3.534785	1.122622
O	1.651090	-2.592202	1.996566
C	3.874374	-1.131843	2.378184
F	5.166967	-1.426276	2.409752
F	3.374137	-1.145810	3.608291
F	3.701373	0.081511	1.838848
S	3.563962	-1.728568	-1.538926
O	2.724145	-1.188987	-2.599271
O	4.224877	-3.015132	-1.617440
C	4.883520	-0.440929	-1.211506
F	5.612632	-0.819419	-0.160135
F	5.657372	-0.328090	-2.284574
F	4.296858	0.729693	-0.947287
H	-2.683434	1.934002	-2.385871
H	-0.812738	0.272058	-2.546375
H	-1.382842	-0.848190	1.586299
H	-5.346849	1.859558	1.613495
H	-3.983155	2.993415	1.958923
H	0.018788	-2.233849	0.010500
H	0.345370	-1.674953	-1.637041
H	1.731094	0.190308	-0.743816
H	1.345399	-0.287903	0.901732

Sub_NMs			
C	-2.601728	0.551755	0.795457
C	-3.066359	1.354282	-0.245712
C	-2.446527	1.374377	-1.478389
C	-1.318161	0.547030	-1.635556
C	-0.846440	-0.265178	-0.600453
C	-1.500326	-0.265827	0.653682
O	-3.413516	0.703965	1.894645
C	-4.332628	1.750358	1.556764
O	-4.188261	2.038258	0.160787
C	0.399741	-1.102106	-0.772390
C	1.623058	-0.350958	-0.216694
N	2.860191	-1.173827	-0.089127
S	2.965789	-2.131175	1.337800
O	3.994963	-3.146270	1.110066
O	1.625570	-2.492375	1.801177
S	3.483657	-1.784062	-1.607027
O	3.157206	-0.716833	-2.555747
O	3.036958	-3.152668	-1.844948
H	-2.818176	1.995793	-2.285093
H	-0.801761	0.536615	-2.591117
H	-1.151781	-0.894278	1.466976
H	-5.355920	1.415399	1.756347
H	-4.095511	2.650120	2.143804
H	0.302727	-2.050785	-0.238665
H	0.571834	-1.327993	-1.828324
H	1.873859	0.504173	-0.846419
H	1.398455	0.031015	0.782833
C	3.628979	-0.907666	2.484644
H	3.711351	-1.406100	3.452360
H	4.607352	-0.591778	2.123497
H	2.941918	-0.063786	2.552091
C	5.256462	-1.771139	-1.311875
H	5.478602	-2.472179	-0.509395
H	5.711472	-2.090053	-2.251604
H	5.551902	-0.751054	-1.066780

Sub_NdF

C	-3.248548	-0.332728	0.721700
C	-3.868651	0.373062	-0.308698
C	-3.237786	0.600277	-1.514753
C	-1.934310	0.087613	-1.656001
C	-1.305024	-0.625630	-0.631722
C	-1.973835	-0.843300	0.595065
O	-4.104606	-0.435714	1.792125
C	-5.240461	0.372055	1.458591
O	-5.137254	0.737194	0.076883
C	0.116329	-1.114292	-0.785963
C	1.092047	-0.124722	-0.130014
N	2.509596	-0.585242	-0.125998
S	2.967207	-1.745516	1.060944
O	3.651563	-2.868897	0.425037
O	1.787638	-1.930679	1.905872
S	3.310006	-0.531645	-1.669270
O	2.856673	0.735008	-2.246418
O	3.152460	-1.786266	-2.397874
H	-3.728963	1.144342	-2.313315
H	-1.403683	0.249264	-2.589909
H	-1.503265	-1.396371	1.401538
H	-6.157244	-0.205372	1.615740
H	-5.239456	1.280273	2.079534
H	0.240555	-2.090459	-0.306631
H	0.375555	-1.233610	-1.842444
H	1.080381	0.838317	-0.643254
H	0.814000	0.044277	0.911254
C	4.197007	-0.819570	1.991103
C	3.840584	0.411237	2.544659
C	5.476587	-1.352612	2.103577
C	4.832815	1.123018	3.205700
C	6.429298	-0.586893	2.769682
C	6.138751	0.651984	3.325618
H	2.842004	0.820033	2.454364
H	5.736540	-2.301830	1.654315
C	5.020485	-0.364948	-1.163925
C	5.870039	-1.456467	-1.322902
C	5.433686	0.851484	-0.619202
C	7.186319	-1.298339	-0.899355
C	6.754517	0.938642	-0.199712
C	7.652335	-0.117305	-0.332059
H	5.513474	-2.394321	-1.728570
H	4.757380	1.689436	-0.508789
H	8.673794	-0.029380	0.015754
H	6.900473	1.236499	3.825761
F	7.182110	2.077064	0.371586
F	4.530920	2.317497	3.737915
F	8.035443	-2.329958	-1.022019
F	7.687884	-1.050563	2.847574

Sub_NTs

C	-2.634260	0.330969	1.040937
C	-3.189112	1.174247	0.079554
C	-2.658995	1.274004	-1.190580
C	-1.526798	0.485180	-1.470031
C	-0.964746	-0.367979	-0.515828
C	-1.528445	-0.450115	0.778587
O	-3.370156	0.404561	2.200903
C	-4.323820	1.452418	1.987294
O	-4.295458	1.806217	0.599771
C	0.287309	-1.157674	-0.816418
C	1.529039	-0.406571	-0.311673
N	2.771792	-1.207841	-0.382184
S	3.143218	-2.188400	0.971894
O	4.168315	-3.137809	0.545821
O	1.874976	-2.619519	1.563995
S	3.527616	-1.422294	-1.924355
O	2.963790	-0.329811	-2.723201
O	3.424660	-2.808735	-2.365096
H	-3.100411	1.926825	-1.934977
H	-1.078083	0.538929	-2.457774
H	-1.109851	-1.111016	1.530850
H	-5.324128	1.094644	2.252305
H	-4.049044	2.327601	2.595383
H	0.256336	-2.133609	-0.324252
H	0.394948	-1.326704	-1.892223
H	1.690120	0.507424	-0.885542
H	1.400262	-0.115938	0.734520
C	3.885132	-0.995932	2.079680
C	3.098261	-0.379410	3.053140
C	5.238978	-0.683747	1.934377
C	3.679472	0.580107	3.881150
C	5.798648	0.276928	2.770912
C	5.030864	0.927676	3.749296
H	2.058539	-0.665574	3.168095

H	5.841703	-1.191483	1.191027
H	3.074900	1.060562	4.645497
H	6.851861	0.522849	2.664579
C	5.233289	-1.047493	-1.556663
C	6.152686	-2.085598	-1.413106
C	5.603255	0.287654	-1.385612
C	7.467457	-1.770361	-1.074193
C	6.921350	0.581170	-1.048056
C	7.870354	-0.439883	-0.884343
H	5.825874	-3.110986	-1.533381
H	4.868442	1.075089	-1.512622
H	8.190510	-2.571422	-0.948229
H	7.218774	1.616531	-0.906289
C	9.302655	-0.111664	-0.539983
H	9.766798	-0.909824	0.046622
H	9.900610	0.013930	-1.450934
H	9.375930	0.820081	0.028659
C	5.645270	1.992248	4.625057
H	5.109609	2.091685	5.573279
H	6.694029	1.772381	4.846160
H	5.614881	2.969223	4.126902

NTf-

N	2.713427	-1.479709	-0.094898
S	2.670387	-2.248057	1.323343
O	2.964986	-3.685810	1.287986
O	1.483028	-1.776804	2.045383
C	4.085452	-1.516883	2.307938
F	5.274031	-1.845856	1.786321
F	4.039764	-1.977707	3.572921
F	3.996162	-0.177618	2.350002
S	3.764382	-1.804763	-1.282094
O	3.069034	-1.875270	-2.573659
O	4.828879	-2.775703	-0.991904
C	4.649978	-0.161299	-1.352884
F	5.248270	0.116959	-0.183633
F	5.598943	-0.203664	-2.307615
F	3.807697	0.839459	-1.646637

NMs-

N	3.160378	-1.084510	0.020428
S	3.188253	-2.096549	1.296036
O	4.389703	-2.975751	1.347913
O	1.896775	-2.747068	1.607848
S	3.466734	-1.636578	-1.482072
O	3.236592	-0.505136	-2.403009
O	2.831452	-2.931069	-1.810496
C	3.426233	-0.844283	2.584625
H	3.423643	-1.369804	3.542250
H	4.379557	-0.341479	2.419440
H	2.603118	-0.130699	2.535588
C	5.254915	-1.954327	-1.505382
H	5.470582	-2.678971	-0.719462
H	5.511900	-2.342182	-2.493635
H	5.772537	-1.012560	-1.314940

NdF-

N	2.509533	-0.572689	-0.138740
S	2.909946	-1.683117	0.973831
O	3.600328	-2.889583	0.467959
O	1.758868	-1.855516	1.874734
S	3.281335	-0.465959	-1.571533
O	2.902618	0.837198	-2.145834
O	3.172207	-1.664013	-2.422149
C	4.165316	-0.800969	1.955645
C	3.859810	0.465191	2.462742
C	5.422125	-1.373387	2.129845
C	4.857951	1.151309	3.136225
C	6.387613	-0.631852	2.800352
C	6.138771	0.632680	3.317306
H	2.887607	0.913172	2.298281
H	5.647016	-2.344586	1.708680
C	5.045073	-0.328253	-1.155088
C	5.856067	-1.457232	-1.256496
C	5.523816	0.882655	-0.651430
C	7.174199	-1.343551	-0.832991
C	6.844563	0.930190	-0.230571
C	7.699012	-0.165486	-0.313644
H	5.450289	-2.392729	-1.618719
H	4.878048	1.748623	-0.576494
H	8.721147	-0.110760	0.038381
H	6.910563	1.199934	3.821665
F	7.986760	-2.422986	-0.910020
F	7.331809	2.081211	0.289116
F	7.631555	-1.147848	2.938863
F	4.596048	2.383698	3.631092

NTs-

N	2.487610	-1.672728	-0.328934
S	3.108386	-2.523443	0.905753
O	4.084732	-3.577324	0.542648
O	1.994096	-2.890037	1.799147
S	3.284922	-1.503623	-1.745262
O	2.619938	-0.393274	-2.455559
O	3.499802	-2.764484	-2.480633
C	4.075155	-1.282764	1.814799
C	3.511121	-0.036461	2.098751
C	5.377944	-1.567897	2.213800
C	4.264049	0.924465	2.768061
C	6.124328	-0.597141	2.884207
C	5.585604	0.663566	3.161455
H	2.502398	0.176508	1.760702
H	5.798924	-2.535726	1.966801
H	3.828269	1.899840	2.975958
H	7.147765	-0.818503	3.181378
C	4.933473	-0.903917	-1.305339
C	5.995573	-1.800408	-1.204331
C	5.102286	0.438175	-0.961452
C	7.231570	-1.345323	-0.743190
C	6.338060	0.877355	-0.494953
C	7.415968	-0.009780	-0.366210
H	5.826995	-2.840328	-1.456818
H	4.260339	1.115687	-1.054877
H	8.059540	-2.045234	-0.649897
H	6.465959	1.918923	-0.207274
C	8.720691	0.456217	0.234346
H	9.555904	-0.188679	-0.057947
H	8.962081	1.482302	-0.064841
H	8.661895	0.442949	1.330820
C	6.423969	1.737636	3.814604
H	5.814485	2.409112	4.429063
H	7.203229	1.308202	4.453353
H	6.927435	2.356466	3.059766

TS_NTf

C	-2.171736	-0.986913	7.768543
C	-2.929716	-0.093871	7.013315
C	-2.611986	0.195984	5.703552
C	-1.476815	-0.444492	5.172367
C	-0.707018	-1.333947	5.925960
C	-1.063047	-1.629319	7.262092
O	-2.735627	-1.113686	9.024667
C	-3.703449	-0.069935	9.101140
O	-3.987696	0.374190	7.769980
C	0.522858	-1.974757	5.324648
C	1.816567	-1.629063	6.014624
H	-3.200704	0.894919	5.119836
H	-1.170742	-0.212036	4.159267
H	-0.476157	-2.324199	7.855545
H	-4.620411	-0.453680	9.559717
H	-3.296416	0.770941	9.687767
H	0.441785	-3.065914	5.362400
H	0.622853	-1.716087	4.268139
H	2.733792	-2.056669	5.641028
H	1.838905	-1.209018	7.008523
I	2.061737	-4.074843	7.773745
N	2.214990	0.209428	5.192515
S	2.461997	1.473941	6.245360
O	3.183866	2.599264	5.654925
O	2.831789	0.935423	7.553324
C	0.707380	2.101346	6.475308
F	0.774630	3.317415	7.035452
F	0.023654	1.292963	7.284093
F	0.074400	2.204833	5.301724
S	2.882117	0.182530	3.679852
O	2.684680	-1.176472	3.171212
O	4.181520	0.835639	3.559449
C	1.706652	1.229196	2.665750
F	1.668224	2.486301	3.110097
F	2.122608	1.229204	1.392632
F	0.469136	0.712589	2.708884

TS_NMs

C	-2.040344	-0.762694	7.557372
C	-2.657317	0.091625	6.645879
C	-2.225838	0.189765	5.337835
C	-1.121353	-0.603021	4.974675
C	-0.491895	-1.457430	5.885809
C	-0.961958	-1.554144	7.214955
O	-2.701757	-0.691150	8.769661
C	-3.569183	0.434723	8.647297
O	-3.721793	0.730896	7.255660
C	0.723778	-2.247261	5.461601
C	1.988485	-1.797490	6.146444

H	-2.714136	0.852800	4.631737
H	-0.721909	-0.543767	3.967141
H	-0.477570	-2.213582	7.929226
H	-4.546000	0.192487	9.077254
H	-3.121526	1.303379	9.159674
H	0.580599	-3.309607	5.675239
H	0.884838	-2.150542	4.386922
H	2.950805	-2.078848	5.747364
H	1.991495	-1.238475	7.066442
I	2.326477	-3.931559	8.042014
N	2.110057	0.155438	5.174893
S	2.439048	1.375560	6.247571
O	2.905110	2.607020	5.577422
O	3.213674	0.841929	7.377808
S	2.411692	0.321002	3.556872
O	1.801397	-0.866329	2.921126
O	3.810837	0.629480	3.234020
C	1.416666	1.740356	3.030962
H	1.516714	1.806947	1.946019
H	0.379226	1.551467	3.311211
H	1.806546	2.630620	3.522139
C	0.788381	1.733687	6.891630
H	0.156526	2.077124	6.072737
H	0.370519	0.825981	7.325719
H	0.903252	2.510238	7.650478

TS_NdF

C	-2.075577	-0.643874	7.882834
C	-2.859879	0.120357	7.023662
C	-2.551623	0.249686	5.686181
C	-1.408370	-0.433170	5.232985
C	-0.620189	-1.213817	6.082893
C	-0.956007	-1.325568	7.452483
O	-2.601269	-0.589354	9.156192
C	-3.715164	0.302561	9.088394
O	-3.899367	0.697586	7.721866
C	0.567377	-1.968640	5.530420
C	1.900020	-1.603284	6.125115
H	-3.149955	0.865919	5.024813
H	-1.127819	-0.342548	4.189610
H	-0.354757	-1.929148	8.125637
H	-4.617841	-0.214299	9.440581
H	-3.510889	1.192471	9.696142
H	0.431808	-3.043526	5.686988
H	0.646883	-1.829355	4.450215
H	2.794565	-2.053299	5.724017
H	2.001054	-1.023923	7.027900
I	2.160913	-3.736036	8.120641
N	2.251558	0.190761	5.038295
S	2.582547	1.533442	5.958969
O	3.349482	2.543101	5.212033
O	3.036991	1.092762	7.284205
S	2.830939	0.045822	3.491441
O	2.312450	-1.247493	3.015935
O	4.259434	0.340579	3.345538
C	0.938086	2.244303	6.214928
C	0.376838	3.032554	5.209644
C	0.286826	2.012052	7.423948
C	-0.878449	3.575497	5.441704
C	-0.959063	2.598048	7.601092
C	-1.571651	3.382185	6.632141
H	0.898354	3.232913	4.284605
H	0.735271	1.402512	8.197484
C	1.936304	1.325043	2.578983
C	2.567701	2.538179	2.310032
C	0.609038	1.079468	2.225586
C	1.812755	3.526055	1.687441
C	-0.097384	2.108343	1.618545
C	0.477348	3.344930	1.339115
H	3.591020	2.710185	2.615585
H	0.148255	0.118860	2.414717
H	-2.556322	3.802489	6.790968
H	-0.092882	4.135633	0.868379
F	-1.452437	4.327543	4.476881
F	-1.614507	2.393009	8.766453
F	-1.387293	1.908188	1.278118
F	2.387802	4.713768	1.408728

TS_NTs

C	-2.259448	-0.670825	7.681716
C	-2.889350	0.214526	6.813334
C	-2.423903	0.430839	5.534599
C	-1.281534	-0.292307	5.152172
C	-0.650557	-1.200507	6.008206
C	-1.146692	-1.399944	7.316705
O	-2.939549	-0.688093	8.889147
C	-3.845786	0.408201	8.818449

O	-3.981924	0.789799	7.444716
C	0.549083	-1.982740	5.523393
C	1.857174	-1.617658	6.170844
H	-2.894700	1.148307	4.872746
H	-0.859419	-0.120644	4.169237
H	-0.659542	-2.091191	7.997379
H	-4.822205	0.103670	9.208861
H	-3.446023	1.260426	9.394029
H	0.389758	-3.052926	5.685398
H	0.683258	-1.855836	4.446981
H	2.769243	-2.059930	5.802135
H	1.930125	-0.985155	7.039369
I	2.010377	-3.655697	8.217189
N	2.255572	0.180089	5.016867
S	2.624957	1.513449	5.938327
O	3.394140	2.517590	5.181773
O	3.119821	1.054062	7.245657
S	2.828978	0.014701	3.471809
O	2.288487	-1.278239	3.009690
O	4.267083	0.270584	3.326210
C	1.006378	2.243228	6.250380
C	0.410793	3.050310	5.281425
C	0.385605	2.028471	7.480985
C	-0.824878	3.637113	5.551535
C	-0.842838	2.631191	7.737119
C	-1.470585	3.437407	6.778249
H	0.910831	3.225210	4.336164
H	0.872486	1.405081	8.222244
H	-1.294640	4.261154	4.794553
H	-1.328358	2.463350	8.695587
C	1.968328	1.295225	2.540561
C	2.579940	2.529848	2.324654
C	0.670041	1.052278	2.091010
C	1.860546	3.539138	1.684512
C	-0.036989	2.071201	1.456239
C	0.541772	3.332688	1.255697
H	3.587389	2.690377	2.686871
H	0.235967	0.068233	2.229348
H	2.329242	4.506943	1.522695
H	-1.051017	1.885440	1.109971
C	-0.248098	4.451219	0.617537
H	0.404521	5.153766	0.089668
H	-0.983920	4.067549	-0.096514
H	-0.798156	5.024643	1.374819
C	-2.831941	4.027595	7.057648
H	-3.126821	4.746786	6.287349
H	-3.588119	3.234691	7.093440
H	-2.852779	4.542466	8.025312

Iodide

I	0.575442	0.000000	-2.144831

Iodide_pdt

C	-3.026657	0.456093	0.219098
C	-2.718337	1.813427	0.121798
C	-1.414298	2.250738	0.028157
C	-0.405571	1.265037	0.022996
C	-0.701316	-0.097263	0.120039
C	-2.051171	-0.516049	0.220325
O	-4.382363	0.298433	0.346577
C	-4.955482	1.605910	0.075161
O	-3.869083	2.560846	0.192299
C	0.364726	-1.185697	0.118274
C	1.792046	-0.669442	0.067963
H	-1.177115	3.306301	-0.038327
H	0.625172	1.596576	-0.053732
H	-2.312930	-1.566975	0.305051
H	-5.388753	1.632941	-0.980047
H	-5.755912	1.838642	0.838737
H	0.235676	-1.810958	1.008480
H	0.194639	-1.852390	-0.737720
H	2.014351	-0.123468	-0.850703
H	2.050980	-0.062656	0.934240
I	3.256582	-2.326499	0.092422

A1

C	-3.366951	-0.728052	-2.249397
C	-2.074365	-1.035074	-1.827964
N	-1.016470	-0.279374	-2.144682
C	-1.182618	0.817120	-2.893436
C	-2.430289	1.217321	-3.368615
C	-3.527168	0.419635	-3.030838
N	-1.727652	-2.145413	-1.039533
N	0.024868	1.494777	-3.133211
N	1.167151	0.968287	-2.593365

C	2.147717	1.779963	-2.959052
C	1.652691	2.850734	-3.745829
C	0.295954	2.638135	-3.837239
C	-2.491140	-3.150877	-0.508009
C	-1.635574	-3.979510	0.181642
C	-0.348707	-3.405699	0.022666
N	-0.408442	-2.304735	-0.711147
H	-4.213766	-1.349040	-1.985293
H	-2.549617	2.107255	-3.973802
H	-4.516576	0.695087	-3.380070
H	3.154005	1.550461	-2.637082
H	2.212413	3.663217	-4.183661
H	-0.481407	3.196172	-4.335558
H	-3.558369	-3.194756	-0.660017
H	-1.897754	-4.874341	0.725379
H	0.614419	-3.725136	0.395892
Ni	0.824563	-0.792404	-1.495354
I	3.199231	-1.454027	-0.657261

==========

A2

==========

C	-2.313675	-0.228675	-0.301865
C	-1.397838	-0.966811	-1.052799
N	-0.534809	-0.392096	-1.894031
C	-0.512542	0.936546	-2.023146
C	-1.383589	1.770581	-1.320873
C	-2.291570	1.158179	-0.456034
N	-1.278766	-2.365147	-0.990811
N	0.472775	1.400451	-2.910693
N	1.307389	0.487044	-3.491011
C	2.127215	1.181243	-4.262402
C	1.835708	2.567840	-4.193586
C	0.776323	2.672690	-3.323321
C	-1.997754	-3.292719	-0.281002
C	-1.464374	-4.524414	-0.579271
C	-0.408515	-4.263928	-1.490233
N	-0.302052	-2.968190	-1.732427
H	-3.007185	-0.704709	0.379234
H	-1.354768	2.846926	-1.431007
H	-2.984366	1.770010	0.112076
H	2.880228	0.652141	-4.829505
H	2.331546	3.374186	-4.712039
H	0.222973	3.531182	-2.976659
H	-2.816582	-3.008927	0.361158
H	-1.788474	-5.481006	-0.198831
H	0.273448	-4.942563	-1.983172
Ni	1.076404	-1.537277	-2.670870
C	2.381538	-1.345491	-1.104020
C	1.895434	-0.465727	0.035788
C	2.822165	-0.269060	1.234183
C	4.079370	-0.871267	1.316579
C	4.929716	-0.685034	2.425630
C	4.468935	0.127881	3.438937
C	3.216782	0.735883	3.370654
C	2.376818	0.557602	2.293128
O	5.076211	0.452315	4.635330
C	4.247477	1.463372	5.214036
O	2.994331	1.466005	4.519801
H	2.569013	-2.374259	-0.774912
H	3.296408	-0.951531	-1.561630
H	1.652123	0.535419	-0.352531
H	0.944446	-0.860568	0.425797
H	4.413701	-1.500835	0.499833
H	5.902996	-1.159630	2.483178
H	1.402879	1.037135	2.259202
H	4.077453	1.235602	6.271017
H	4.730944	2.446897	5.100140
I	2.175737	-3.015691	-4.568722

==========

A3

==========

C	-0.244747	-5.096886	4.666451
C	0.916303	-5.714816	4.197922
N	1.974808	-5.024495	3.772879
C	1.926241	-3.691018	3.755658
C	0.816868	-2.971223	4.199840
C	-0.274094	-3.704265	4.662436
N	1.059326	-7.110343	4.122369
N	3.078590	-3.076224	3.237058
N	4.077228	-3.861804	2.747071
C	5.000206	-3.032889	2.290154
C	4.608849	-1.682819	2.474732
C	3.375724	-1.747222	3.078380
C	0.169806	-8.095514	4.468519
C	0.763253	-9.295323	4.161970
C	2.027496	-8.951388	3.620337
N	2.200645	-7.640000	3.595494
H	-1.097128	-5.669514	5.006857

H	0.792102	-1.889835	4.173843
H	-1.160189	-3.185227	5.012342
H	5.896425	-3.435019	1.839974
H	5.152645	-0.791906	2.200455
H	2.703454	-0.969098	3.402476
H	-0.793830	-7.870816	4.896304
H	0.347966	-10.281729	4.300602
H	2.804262	-9.595890	3.237174
Ni	3.619342	-6.005161	2.852209
C	4.826347	-6.297524	4.422571
C	4.120371	-5.871084	5.715062
C	5.000445	-6.119380	6.921546
C	4.991563	-7.362149	7.572066
C	5.840318	-7.610038	8.651367
C	6.717887	-6.623448	9.106291
C	6.717047	-5.397390	8.451061
C	5.881271	-5.129080	7.374375
F	7.556775	-4.427451	8.879133
H	5.091671	-7.358116	4.460468
H	5.735236	-5.708430	4.275202
H	3.861530	-4.807681	5.664325
H	3.184089	-6.426952	5.831024
H	4.312957	-8.137149	7.225016
H	5.819622	-8.576348	9.147168
H	5.924400	-4.153870	6.898963
I	2.034606	-5.821592	0.543708
C	7.849597	-9.988218	0.064499
C	7.569132	-9.868938	-1.293810
C	6.413380	-9.261784	-1.744603
C	5.529249	-8.773075	-0.766484
C	5.798743	-8.891513	0.603033
C	6.992143	-9.509912	1.034808
O	9.069674	-10.608213	0.232426
C	9.446965	-11.057290	-1.073856
O	8.603756	-10.408212	-2.030160
C	4.835068	-8.299604	1.612585
C	5.124437	-6.820153	1.851555
H	6.201831	-9.170352	-2.804077
H	4.608915	-8.285661	-1.076091
H	7.228454	-9.607748	2.089511
H	10.490526	-10.787354	-1.264491
H	9.308132	-12.148171	-1.140967
H	3.809153	-8.406248	1.246695
H	4.911869	-8.843793	2.562560
H	6.098254	-6.673966	2.324763
H	5.081755	-6.252441	0.918193
H	7.387539	-6.785063	9.943603

==========

A4

==========

C	-3.448517	-0.640755	-2.129723
C	-2.157000	-1.055719	-1.882443
N	-1.072154	-0.375822	-2.351216
C	-1.253427	0.837038	-2.945831
C	-2.505909	1.333446	-3.238821
C	-3.627105	0.560136	-2.855568
N	-1.733843	-2.156088	-1.123376
N	-0.010635	1.453084	-3.151822
N	1.081559	0.847468	-2.560480
C	2.139514	1.602850	-2.886590
C	1.746041	2.691613	-3.681577
C	0.375040	2.567215	-3.838250
C	-2.387578	-3.224459	-0.581926
C	-1.441385	-3.993843	0.076197
C	-0.215243	-3.335571	-0.112462
N	-0.384262	-2.220883	-0.837198
H	-4.300141	-1.201206	-1.760254
H	-2.631034	2.294965	-3.724263
H	-4.627147	0.918220	-3.068017
H	3.119071	1.318464	-2.534055
H	2.375626	3.465392	-4.093476
H	-0.342002	3.162364	-4.381453
H	-3.449839	-3.353926	-0.716974
H	-1.617704	-4.911944	0.615465
H	0.775412	-3.597074	0.227245
Ni	0.641222	-0.810382	-1.668617
C	2.386138	-1.297058	-0.993414
C	2.548384	-0.778667	0.447104
C	3.866633	-1.181306	1.077671
C	3.948437	-2.290014	1.927064
C	5.166530	-2.725187	2.483645
C	6.293893	-2.001007	2.155217
C	6.228409	-0.893985	1.312001
C	5.040961	-0.462150	0.759583
O	7.601943	-2.217135	2.537016
C	8.324074	-1.075226	2.066037
O	7.492130	-0.372660	1.136038
H	2.496871	-2.391252	-1.012647

H	3.182619	-0.890499	-1.633133
H	2.458698	0.315602	0.448792
H	1.722433	-1.152837	1.064640
H	3.038189	-2.831152	2.172180
H	5.221858	-3.584939	3.142116
H	5.010369	0.400754	0.102235
H	8.563667	-0.415048	2.914725
H	9.237807	-1.404074	1.560960

==========

A5

==========

C	-3.388809	-0.798345	-2.397950
C	-2.188232	-0.920609	-1.722718
N	-1.182882	0.002549	-1.793663
C	-1.295920	0.932738	-2.788617
C	-2.454937	1.141289	-3.513501
C	-3.553189	0.298980	-3.262530
N	-1.768272	-2.040411	-0.983420
N	-0.048495	1.531699	-3.037729
N	1.064650	0.761323	-2.758794
C	2.114066	1.545232	-3.045236
C	1.693529	2.803404	-3.517247
C	0.311511	2.761666	-3.502650
C	-2.437818	-2.949090	-0.218849
C	-1.496677	-3.823039	0.293405
C	-0.258319	-3.382571	-0.211677
N	-0.411787	-2.305334	-0.995155
H	-4.161152	-1.552920	-2.292039
H	-2.495544	1.906422	-4.281644
H	-4.475547	0.424040	-3.817238
H	3.112959	1.152915	-2.927683
H	2.313323	3.628616	-3.833867
H	-0.434353	3.499174	-3.755385
H	-3.506469	-2.882099	-0.086157
H	-1.681498	-4.669092	0.937919
H	0.727636	-3.801812	-0.078833
Ni	0.569141	-0.830972	-1.776317

==========

A6

==========

C	0.779294	-1.284243	-6.421914
C	1.763450	-2.195312	-6.052219
N	3.076411	-1.897261	-6.039656
C	3.450640	-0.655207	-6.396861
C	2.549881	0.326888	-6.791918
C	1.190247	-0.002437	-6.797008
N	1.481219	-3.513106	-5.645645
N	4.839618	-0.444610	-6.337659
N	5.653227	-1.513877	-6.102787
C	6.888096	-1.029845	-6.090078
C	6.891520	0.366349	-6.319112
C	5.566426	0.709242	-6.468929
C	0.284901	-4.172377	-5.534725
C	0.570954	-5.456526	-5.123727
C	1.978699	-5.502470	-5.005672
N	2.524257	-4.331350	-5.319302
H	-0.269648	-1.552935	-6.419568
H	2.884591	1.313048	-7.087922
H	0.455223	0.735310	-7.098790
H	7.713958	-1.700307	-5.903836
H	7.741697	1.030381	-6.355438
H	5.092767	1.663486	-6.635113
H	-0.654292	-3.688235	-5.749331
H	-0.136925	-6.249289	-4.934768
H	2.621159	-6.320831	-4.714097
Ni	4.513362	-3.412858	-5.745297
C	5.810023	-4.549153	-4.696768
C	5.615607	-4.304991	-3.181668
C	5.608973	-2.820746	-2.890834
C	6.791169	-2.120241	-2.617683
C	6.796655	-0.725784	-2.536370
C	5.623591	0.004938	-2.740880
C	4.457157	-0.703946	-2.997403
C	4.422465	-2.089910	-3.052608
F	3.309900	-0.016623	-3.236705
H	5.689342	-5.615157	-4.928708
H	6.827103	-4.255678	-4.993984
H	4.656324	-4.736449	-2.866509
H	6.395859	-4.793236	-2.576114
H	7.716563	-2.674804	-2.487129
H	7.723227	-0.198181	-2.327828
H	3.484576	-2.592228	-3.264149
C	3.520637	-6.072059	-11.485253
C	4.420370	-5.555838	-12.415025
C	5.151220	-4.414397	-12.155121
C	4.946659	-3.800711	-10.905071
C	4.046673	-4.308058	-9.960620
C	3.309820	-5.476509	-10.259379

O	2.901418	-7.186175	-12.013441
C	3.622478	-7.478476	-13.214891
O	4.397172	-6.326807	-13.560401
C	3.900993	-3.660068	-8.597721
C	4.787612	-4.308584	-7.529818
H	5.844593	-4.011797	-12.885301
H	5.510709	-2.904297	-10.661412
H	2.605178	-5.892497	-9.546340
H	4.293310	-8.335280	-13.040600
H	2.914911	-7.697272	-14.020506
H	4.143234	-2.592504	-8.676616
H	2.849590	-3.717240	-8.284401
H	4.546820	-5.370585	-7.403824
H	5.849829	-4.215332	-7.783881
H	5.601786	1.088383	-2.706166

==========

TS(A3/A1)

==========

C	-0.498106	-5.030959	4.165769
C	0.731445	-5.666139	3.990501
N	1.858903	-4.996764	3.755174
C	1.820321	-3.670440	3.625155
C	0.649571	-2.929846	3.779029
C	-0.517274	-3.640159	4.062410
N	0.895221	-7.063195	4.019357
N	3.064346	-3.101279	3.291499
N	4.104198	-3.931078	2.991054
C	5.114682	-3.136563	2.667894
C	4.741437	-1.773583	2.751306
C	3.424337	-1.788539	3.148328
C	-0.026363	-8.040018	4.286314
C	0.612546	-9.247676	4.137104
C	1.937590	-8.915872	3.766040
N	2.106225	-7.602418	3.690520
H	-1.408066	-5.587350	4.349015
H	0.633666	-1.854267	3.658851
H	-1.454470	-3.106791	4.180722
H	6.059835	-3.572787	2.377723
H	5.349593	-0.905836	2.546823
H	2.731950	-0.985063	3.342670
H	-1.042110	-7.803907	4.559999
H	0.187890	-10.230790	4.270468
H	2.765026	-9.570889	3.538229
Ni	3.543431	-6.017343	3.023235
C	5.211044	-6.501185	4.332284
C	4.308411	-6.229332	5.583154
C	5.177016	-6.282593	6.821717
C	5.403526	-7.492531	7.493903
C	6.250680	-7.545964	8.601692
C	6.891503	-6.393739	9.061622
C	6.659664	-5.201896	8.384009
C	5.821592	-5.125722	7.278948
F	7.269135	-4.075389	8.816639
H	5.715291	-7.446328	4.540022
H	5.965639	-5.713049	4.303185
H	3.833545	-5.247730	5.516595
H	3.515642	-6.976830	5.653299
H	4.907833	-8.394868	7.145189
H	6.413083	-8.488899	9.115796
H	5.677121	-4.169336	6.785318
I	2.237723	-5.942270	0.472201
C	7.734083	-9.988202	0.040598
C	7.343728	-9.677174	-1.259027
C	6.185893	-8.970586	-1.519887
C	5.412823	-8.581486	-0.411728
C	5.795290	-8.893889	0.899193
C	6.988005	-9.610324	1.138926
O	8.930834	-10.671878	0.014542
C	9.172748	-10.954726	-1.368750
O	8.282467	-10.153032	-2.150417
C	4.953534	-8.402981	2.060079
C	5.332528	-6.965260	2.417756
H	5.889303	-8.728772	-2.534250
H	4.496644	-8.017755	-0.568324
H	7.307581	-9.860844	2.145546
H	10.207804	-10.699163	-1.616879
H	8.976747	-12.020878	-1.564602
H	3.898316	-8.439166	1.779050
H	5.098268	-9.052176	2.933846
H	6.406005	-6.887678	2.581845
H	5.106377	-6.289475	1.583598
H	7.553008	-6.403159	9.920668

==========

TS(A6/A5)

==========

C	1.226537	-0.564967	-5.031589
C	2.059697	-1.522096	-5.574190
N	3.317784	-1.250643	-6.033750

C	3.771275	0.028227	-5.897590
C	3.014488	1.052461	-5.370176
C	1.705422	0.756318	-4.928557
N	1.737258	-2.887144	-5.685221
N	5.104491	0.165188	-6.333684
N	5.763127	-0.954908	-6.757831
C	6.998384	-0.546713	-7.082738
C	7.145681	0.835105	-6.872891
C	5.917911	1.261690	-6.395632
C	0.610175	-3.570122	-5.321146
C	0.837194	-4.909268	-5.593323
C	2.137616	-4.963151	-6.122857
N	2.688078	-3.739602	-6.174731
H	0.241235	-0.824654	-4.662719
H	3.415529	2.055163	-5.274394
H	1.082343	1.533020	-4.502160
H	7.715177	-1.267013	-7.451243
H	8.019268	1.444628	-7.049015
H	5.567003	2.239395	-6.107058
H	-0.243203	-3.063617	-4.900756
H	0.151350	-5.727362	-5.432115
H	2.706015	-5.816080	-6.465598
Ni	4.556969	-2.705947	-6.514229
C	6.119778	-3.985272	-5.805581
C	5.417543	-4.297126	-4.466410
C	4.831231	-3.123931	-3.702714
C	5.582516	-1.963196	-3.459188
C	5.023891	-0.882268	-2.779574
C	3.706334	-0.934088	-2.317160
C	2.986914	-2.098746	-2.544357
C	3.526574	-3.195232	-3.202454
F	1.694917	-2.162033	-2.140836
H	6.750153	-4.847994	-6.014984
H	6.789701	-3.123945	-5.747661
H	4.633934	-5.040081	-4.643128
H	6.166163	-4.791483	-3.825391
H	6.597423	-1.890038	-3.837307
H	5.611627	0.016998	-2.620396
H	2.901807	-4.063862	-3.380058
C	3.677435	-6.585177	-10.965544
C	4.700454	-6.621760	-11.911923
C	5.731034	-5.703926	-11.900544
C	5.700381	-4.727517	-10.886996
C	4.677573	-4.678187	-9.934376
C	3.636341	-5.634380	-9.967715
O	2.799330	-7.619568	-11.194938
C	3.205360	-8.195386	-12.442508
O	4.501367	-7.680857	-12.768968
C	4.697693	-3.653755	-8.817898
C	5.449144	-4.298714	-7.593621
H	6.521790	-5.736811	-12.641497
H	6.491282	-3.983295	-10.849509
H	2.833466	-5.615145	-9.237367
H	3.260084	-9.283723	-12.340574
H	2.488341	-7.911518	-13.228018
H	5.220530	-2.748872	-9.141443
H	3.667188	-3.373101	-8.583109
H	5.000452	-5.273723	-7.390219
H	6.464873	-4.460747	-7.953936
H	3.232856	-0.096110	-1.819408

Table S7. Vibrational frequencies (in cm^{-1}) of the optimized structures

==========

Sub_NTf

==========

6.40 14.99 22.37 28.12 48.34 49.40 58.24 79.26 88.41
99.64 116.84 138.01 187.34 196.00 205.20 223.79 244.27
252.92 261.30 274.57 286.45 300.91 308.55 309.58
353.18 360.20 363.52 379.38 392.88 437.04 445.55
486.38 490.33 522.32 542.59 546.35 554.31 563.33
569.89 580.21 617.54 643.98 695.95 725.17 735.66
746.42 764.96 768.17 796.25 826.46 832.86 837.54
882.96 931.02 950.52 972.93 1018.69 1062.75 1065.13
1075.63 1105.20 1121.17 1130.06 1145.64 1155.47 1189.72
1201.72 1214.50 1220.92 1241.70 1249.88 1253.63 1274.72
1289.08 1297.70 1305.90 1328.27 1350.59 1380.53 1403.58
1409.53 1415.72 1442.23 1490.70 1505.11 1517.11 1538.82
1561.51 1663.80 1679.77 3013.04 3076.21 3092.35 3111.94
3127.57 3166.76 3189.76 3208.67 3225.09

Sub_NMs

==========

14.00 25.14 35.75 51.84 59.90 72.74 94.52 124.08
154.94 194.28 201.13 209.30 225.32 248.38 253.68
260.83 280.23 308.11 329.65 336.62 351.75 371.68
412.13 437.45 440.83 459.44 489.53 498.30 509.48
544.81 602.56 618.54 667.16 714.99 724.35 733.76
750.10 762.70 792.93 824.25 830.83 839.57 889.14
929.83 950.62 974.06 979.44 984.10 993.56 999.11
1024.26 1060.16 1068.18 1078.29 1127.47 1129.49 1145.78
1146.65 1154.49 1201.88 1220.65 1249.31 1296.59 1305.33
1329.77 1338.73 1344.81 1350.63 1362.09 1365.16 1409.37
1416.73 1442.29 1460.04 1462.89 1466.52 1480.51 1489.39
1494.60 1513.33 1537.71 1561.59 1663.77 1680.77 3007.62
3077.81 3079.90 3082.80 3088.63 3090.08 3129.41 3151.63
3183.99 3186.52 3190.37 3196.67 3208.10 3214.29 3223.45

Sub_NdF

==========

9.67 11.59 14.38 20.05 29.40 40.39 45.62 48.69 54.14
58.36 59.57 64.76 75.30 77.89 83.08 98.45 103.32
107.56 112.45 117.26 124.56 133.74 149.71 158.54
165.74 187.70 204.51 225.33 233.80 247.31 250.83
257.51 268.21 270.02 283.65 291.10 296.02 301.93
304.81 311.71 320.40 324.36 349.08 356.92 366.28
372.42 393.72 408.68 413.84 416.98 426.08 436.33
447.83 455.05 462.79 482.30 495.79 496.65 500.29
520.47 528.06 544.37 555.03 560.41 566.05 569.85
607.65 612.20 615.33 617.09 618.70 649.19 670.04
671.44 678.66 680.05 692.30 704.34 707.20 713.14
720.80 726.08 734.48 737.39 794.29 813.30 828.83
831.23 835.27 844.54 857.55 858.81 886.42 896.14
906.22 929.54 936.81 941.54 946.16 951.06 952.61
973.15 1012.87 1016.48 1018.90 1060.46 1063.29 1075.32
1103.70 1117.84 1123.44 1127.42 1129.33 1136.98 1139.49
1146.34 1151.57 1155.26 1158.75 1168.55 1177.20 1182.37
1191.35 1202.23 1221.21 1227.23 1233.69 1234.98 1242.58
1248.49 1294.18 1297.25 1302.52 1305.03 1309.34 1311.11
1330.25 1336.30 1348.42 1352.34 1372.20 1378.31 1381.53
1388.17 1408.52 1418.12 1442.11 1486.58 1490.03 1493.07
1493.68 1495.26 1497.81 1507.62 1538.17 1561.36 1650.46
1651.05 1664.02 1671.44 1672.94 1680.38 3010.04 3065.54
3092.97 3106.15 3113.21 3160.65 3190.09 3208.69 3224.27
3224.73 3238.81 3244.95 3246.35 3246.86 3247.00

Sub_NTs

==========

10.96 11.43 21.88 26.02 32.10 38.43 49.45 54.25
58.26 65.92 74.96 76.70 91.23 114.44 142.47 151.89
163.85 171.68 181.01 205.94 247.87 259.64 273.75
279.32 287.16 305.88 314.59 329.51 340.46 342.43
361.48 366.26 386.34 414.46 420.33 422.83 436.35
441.24 448.67 474.38 487.14 505.27 528.30 542.17
550.42 569.28 616.72 619.10 646.63 647.91 653.33
660.52 702.90 712.79 719.46 726.02 735.88 745.78
793.87 816.72 818.54 825.67 828.42 831.17 834.85
842.31 856.35 862.91 886.85 930.13 950.65 969.36
974.12 981.26 984.49 989.84 1020.27 1020.37 1032.37
1033.63 1035.88 1063.35 1064.03 1064.77 1075.56 1087.07
1091.91 1099.22 1127.76 1144.79 1146.79 1152.32 1154.43
1155.40 1156.85 1202.34 1220.23 1223.91 1224.72 1236.54
1237.87 1246.90 1294.94 1305.12 1327.38 1331.58 1339.90
1342.01 1344.39 1350.72 1355.90 1361.52 1408.65 1414.07
1427.52 1427.96 1441.99 1444.35 1444.43 1488.84 1496.03
1501.84 1502.73 1503.95 1504.59 1513.91 1537.21 1537.84
1539.32 1561.24 1627.45 1628.60 1653.97 1654.82 1663.78
1680.75 3003.63 3040.32 3041.32 3070.93 3089.54 3089.73

3102.83 3103.39 3121.67 3129.25 3130.92 3148.49 3185.05
3186.87 3188.03 3190.00 3190.33 3207.24 3220.88 3222.12
3222.94 3239.90 3244.13

NTf-

==========

35.85 52.36 64.44 79.80 117.35 156.98 191.03 194.25
196.63 264.79 267.16 291.81 309.43 315.14 336.55
383.17 409.08 495.04 515.46 534.71 544.66 555.68
564.37 581.16 630.46 716.14 749.91 768.08 1009.97
1115.91 1124.15 1201.59 1209.75 1216.58 1225.11 1230.04
1234.62 1304.92 1324.54

NMs-

==========

42.86 93.72 163.38 224.27 241.66 251.92 259.64 294.11
317.11 358.71 440.95 447.83 496.93 522.68 559.93
662.42 740.25 771.57 968.35 973.01 976.36 992.41
1010.65 1086.77 1129.73 1249.20 1282.03 1341.12 1343.45
1468.06 1468.77 1476.21 1486.86 3061.77 3068.12 3163.03
3169.21 3182.43 3183.51

NdF-

==========

19.31 29.24 38.75 45.61 46.43 56.08 59.02 72.57
79.57 101.78 104.25 109.44 113.33 115.96 123.33 143.37
155.99 166.11 176.66 211.69 233.86 243.64 250.47
266.98 273.43 284.06 291.03 294.52 300.57 312.36
321.42 342.55 348.44 354.35 384.08 406.90 413.66
417.73 426.31 453.87 469.38 491.02 495.83 496.22
512.43 530.00 546.25 561.96 565.09 569.39 591.98
607.63 610.88 619.78 643.93 667.38 669.32 677.68
679.10 701.14 706.09 708.69 710.31 737.86 823.65
834.50 853.57 854.85 887.43 897.66 920.93 927.00
946.40 954.53 988.61 1016.73 1019.00 1088.84 1113.70
1118.81 1121.20 1130.38 1133.55 1143.64 1149.52 1154.71
1160.06 1174.77 1181.80 1205.48 1209.81 1217.44 1224.26
1276.87 1291.87 1294.46 1303.63 1307.27 1310.22 1371.94
1376.36 1381.89 1386.55 1485.31 1486.89 1489.67 1492.98
1645.26 1646.00 1667.82 1669.28 3220.18 3235.26 3242.31
3243.58 3244.01 3244.49

NTs-

==========

32.74 42.11 47.30 63.57 67.22 80.13 85.61 117.81
141.70 158.18 169.91 177.29 223.33 264.43 276.99
303.32 313.48 319.56 349.10 349.62 383.17 410.19
415.34 418.15 438.55 481.65 507.56 533.70 550.42
558.77 596.02 634.19 648.87 650.22 651.61 711.40
715.25 748.55 812.79 815.04 822.25 828.92 846.16
852.22 956.10 957.77 966.67 972.46 986.75 1013.80
1014.74 1038.62 1040.98 1060.20 1061.47 1080.74 1098.85
1127.53 1137.65 1145.14 1148.34 1215.71 1216.61 1234.17
1234.61 1265.51 1282.00 1334.16 1334.66 1350.37 1352.53
1417.83 1421.47 1440.20 1441.63 1500.37 1501.69 1505.32
1509.65 1538.98 1539.70 1628.47 1629.59 1657.75 1658.29
3022.34 3023.75 3080.40 3081.82 3107.98 3108.66 3157.14
3160.12 3160.70 3162.56 3213.85 3215.73 3225.15 3237.15

TS_NTf

==========

-327.36 6.70 21.20 29.38 41.18 47.96 59.70 62.70
65.50 73.96 94.05 101.80 107.26 122.29 133.78 155.13
176.83 191.38 207.53 213.98 234.25 255.73 265.44
275.36 288.67 304.00 315.07 318.48 340.88 355.61
380.08 395.57 405.27 430.21 464.40 493.24 495.07
514.30 537.75 546.18 555.71 563.72 577.93 610.27
636.23 641.39 702.74 718.15 728.96 752.84 756.56
767.62 811.82 827.38 879.87 891.55 914.73 924.41
933.37 971.65 974.96 999.30 1065.74 1078.55 1083.67
1106.71 1122.13 1130.03 1150.70 1157.10 1199.96 1207.48
1211.14 1221.46 1225.94 1227.31 1233.04 1239.88 1256.65
1290.39 1307.28 1333.07 1355.91 1370.37 1417.54 1439.59
1465.14 1477.52 1489.89 1536.24 1557.69 1665.17 1682.98
2974.63 3074.03 3087.86 3124.69 3195.67 3210.59 3232.72
3235.98 3360.39

TS_NMs

==========

-325.09 12.75 22.30 31.25 42.09 52.63 65.05 74.63
101.21 109.86 123.08 146.10 161.76 190.26 221.54
230.78 237.47 247.84 263.53 266.27 297.84 304.63
327.45 350.23 366.99 391.93 396.43 431.54 464.20
464.77 493.37 494.86 508.09 554.23 609.73 644.39
661.15 722.89 728.68 737.60 753.23 770.96 824.34
829.04 878.09 894.00 920.29 925.99 948.87 959.22
973.45 978.80 981.83 987.85 995.00 999.98 1049.09
1067.19 1075.98 1101.65 1122.14 1128.71 1149.89 1156.83
1205.89 1218.53 1225.80 1285.56 1292.55 1299.87 1304.29
1347.31 1360.05 1367.72 1416.76 1438.51 1462.29 1466.17
1469.23 1472.32 1484.50 1491.40 1498.75 1533.84 1556.97
1659.92 1678.34 2971.64 3072.68 3077.23 3085.39 3091.93
3137.89 3173.08 3179.41 3196.98 3197.98 3198.93 3200.99
3213.66 3248.16 3371.73

TS_NdF

==========

-341.70 9.52 16.46 22.84 23.79 25.59 40.55 45.91
48.12 50.28 53.07 61.29 63.17 68.10 85.72 93.69 100.55
104.71 107.52 109.68 113.79 117.85 126.85 131.18
146.70 152.41 166.68 173.13 182.19 212.91 220.97
236.82 243.10 247.37 249.60 252.55 268.56 274.52
281.36 288.19 291.67 301.74 307.59 318.82 322.63
337.42 352.52 356.01 360.44 369.35 391.40 413.29
418.76 421.32 430.12 440.42 462.96 469.84 473.47
477.79 495.89 497.16 502.42 507.06 530.10 540.70
558.22 567.28 567.96 595.78 607.75 610.92 613.22
619.24 627.56 645.48 666.93 672.16 678.84 679.12
698.40 704.12 710.84 713.20 724.37 725.21 727.25
753.67 820.02 826.89 828.97 834.60 855.37 855.58
872.26 884.10 889.44 907.02 917.18 922.46 924.32
929.45 943.24 953.14 955.92 960.74 966.05 995.64
1017.28 1019.52 1063.27 1068.82 1076.09 1092.65 1116.54
1119.38 1122.08 1123.95 1133.50 1133.92 1145.83 1150.10
1152.70 1159.48 1163.82 1172.65 1183.11 1193.55 1206.91
1212.87 1215.80 1217.72 1220.12 1225.07 1233.89 1289.50
1295.56 1296.50 1299.39 1301.40 1304.25 1310.31 1319.90
1367.15 1376.39 1377.83 1378.89 1381.35 1418.05 1437.62
1469.55 1477.45 1488.21 1489.61 1490.09 1493.68 1496.38
1533.25 1556.60 1645.62 1649.59 1665.30 1668.07 1671.47
1681.25 2977.85 3071.99 3127.45 3156.51 3200.54 3224.82
3232.02 3245.14 3245.90 3247.71 3250.44 3251.59 3258.34
3280.88 3370.97

TS_NTs

==========

-323.62 14.08 18.12 26.99 31.05 39.78 41.18 48.82
54.80 64.56 74.69 89.54 98.68 100.05 106.54 115.19
132.62 143.48 151.35 160.69 168.89 172.31 190.21
219.29 226.57 240.65 269.94 276.22 295.38 301.15
311.34 340.09 344.62 346.09 365.24 375.70 391.56
415.61 418.83 429.25 433.90 447.82 460.24 471.98
491.25 496.59 528.18 547.35 555.67 597.40 609.87
636.84 639.26 649.40 649.91 669.65 708.47 716.25
716.66 729.28 731.50 752.79 804.67 816.78 819.79
825.19 826.69 830.79 851.93 857.01 890.45 891.84
905.99 922.30 927.15 950.52 963.65 971.71 974.64
977.06 982.97 994.34 1016.94 1019.73 1035.22 1037.04
1045.85 1062.62 1066.11 1071.19 1077.05 1080.84 1100.69
1117.85 1133.77 1142.02 1147.67 1150.77 1152.58 1157.14
1205.59 1216.32 1219.33 1220.04 1222.95 1235.12 1237.05
1284.82 1291.77 1302.12 1303.89 1336.98 1337.84 1351.59
1353.06 1370.07 1411.17 1424.80 1426.18 1438.83 1441.29
1443.37 1466.06 1482.81 1493.61 1499.74 1503.08 1505.13
1517.95 1535.08 1538.79 1541.30 1557.00 1627.51 1630.17
1655.81 1658.04 1664.20 1682.42 2969.38 3030.68 3033.89
3077.66 3085.59 3090.49 3095.85 3115.55 3118.09 3123.76
3167.88 3171.64 3172.12 3174.52 3202.64 3214.36 3219.11
3226.33 3231.91 3235.42 3247.42 3247.71 3373.71

Iodide_pdt

==========

6.83 76.42 91.93 146.23 169.68 241.03 299.08 306.96
352.72 427.84 438.12 492.23 594.82 600.69 656.59
716.00 725.52 762.68 771.01 814.85 825.80 877.15
893.77 921.19 939.64 981.37 1022.12 1067.77 1132.60
1154.95 1163.61 1201.25 1206.07 1228.54 1246.02 1283.29
1308.02 1326.20 1350.60 1417.80 1469.85 1490.35 1498.16
1503.41 1539.06 1581.60 1665.96 1682.08 2661.01 2783.32
3038.35 3079.70 3111.66 3188.18 3195.80 3196.36 3224.54

==========

A1

==========

28.15 48.11 49.46 92.45 93.52 107.72 111.18 139.83
176.38 200.85 234.96 265.77 267.96 271.57 359.94
390.23 464.66 484.48 574.00 599.33 608.67 632.92
652.78 668.80 671.60 722.24 745.84 746.58 781.25
793.13 850.37 851.67 867.42 924.61 924.72 929.81
934.40 952.72 971.01 974.70 1023.61 1055.74 1067.69
1070.30 1091.03 1104.17 1158.91 1173.01 1204.76 1238.45
1243.65 1305.78 1315.50 1370.72 1385.77 1404.37 1446.51
1450.95 1452.04 1470.67 1511.00 1523.80 1571.96 1576.58
1628.19 1638.47 3210.95 3232.17 3236.88 3269.76 3269.81
3280.59 3280.61 3296.03 3296.04

==========

A2

==========

5.10 19.88 23.96 30.98 37.13 40.99 43.87 73.54 76.34
96.27 105.90 111.08 121.76 139.03 142.43 154.38 163.82
183.45 197.89 233.68 238.62 263.25 269.13 293.15
300.04 340.92 389.76 410.22 427.44 432.13 465.00
473.84 519.85 569.95 592.53 594.82 601.05 608.49
633.97 647.91 648.64 657.90 673.53 687.10 717.22
727.66 731.54 747.46 750.38 760.77 786.50 793.44
805.42 828.27 853.16 854.78 858.35 868.37 883.23

923.02 923.22 928.84 932.16 934.11 943.18 972.86
977.42 982.50 984.53 1022.89 1049.27 1060.67 1063.38
1070.68 1072.72 1093.33 1101.59 1115.18 1128.58 1149.23
1153.12 1154.45 1162.90 1176.34 1195.00 1209.35 1215.09
1243.76 1251.92 1276.24 1290.25 1309.48 1310.45 1321.01
1322.02 1370.01 1385.51 1408.90 1409.81 1440.59 1449.97
1452.39 1467.48 1470.63 1478.60 1480.25 1484.19 1513.44
1528.00 1532.57 1559.46 1579.86 1591.68 1637.15 1652.26
1665.62 1681.66 2982.55 2989.64 3009.03 3041.33 3092.56
3103.56 3191.60 3209.57 3211.85 3222.93 3237.62 3241.42
3271.96 3272.01 3283.42 3283.42 3299.16 3299.19

==========

A3

==========

9.54 14.74 15.96 17.93 24.08 29.61 30.89 37.85 49.41
60.51 76.34 78.30 84.63 93.99 99.45 103.13 112.29
114.44 122.10 138.97 154.27 166.55 184.38 191.66
217.27 232.61 236.88 243.84 249.42 254.95 264.12
307.24 315.61 318.36 320.19 351.19 363.29 391.90
431.47 445.48 454.29 460.71 464.55 471.33 492.97
514.33 526.95 558.42 567.03 570.58 600.25 608.62
616.71 635.85 650.39 658.49 661.26 672.19 678.83
681.28 709.26 724.36 724.98 731.44 740.03 746.08
750.06 763.20 777.72 786.44 794.70 797.59 827.38
835.70 847.25 849.16 866.40 872.17 877.75 893.41
895.97 906.15 910.10 915.27 933.43 937.42 939.51
943.30 962.07 965.46 970.73 973.34 984.69 986.90
1010.75 1017.06 1026.59 1031.37 1067.73 1071.74 1074.57
1078.00 1098.46 1101.29 1104.12 1116.10 1119.32 1130.52
1149.68 1153.34 1156.96 1161.32 1171.11 1172.51 1180.01
1193.13 1201.84 1215.33 1218.10 1244.57 1247.09 1282.96
1291.28 1297.81 1298.41 1309.86 1315.67 1320.22 1325.33
1326.46 1334.27 1364.52 1366.72 1384.21 1402.10 1410.73
1440.49 1452.32 1455.96 1458.17 1467.44 1469.55 1486.47
1487.91 1489.44 1509.82 1517.21 1519.03 1529.90 1534.01
1535.33 1559.78 1585.33 1586.20 1645.68 1647.01 1660.59
1661.88 1663.90 1676.48 2990.59 3028.53 3044.83 3066.24
3073.24 3091.02 3091.22 3093.73 3136.65 3142.34 3175.87
3189.55 3195.16 3199.97 3203.55 3212.23 3220.05 3221.98
3241.34 3245.09 3271.79 3278.05 3285.12 3289.12 3302.25
3303.71

==========

A4

==========

9.49 14.53 23.09 41.56 47.52 56.36 79.54 92.92 116.88
123.33 138.00 143.72 193.55 209.12 217.27 242.04
254.40 269.49 280.09 301.49 324.39 347.46 356.86
370.28 398.83 429.05 436.64 448.05 502.96 504.37
558.57 577.76 590.54 608.31 611.17 616.32 632.05
642.46 651.41 662.32 681.88 705.26 717.53 722.65
724.02 724.32 731.06 774.18 789.53 803.17 804.21
821.93 829.11 855.54 869.73 870.79 871.37 873.86
875.28 920.13 920.59 924.09 942.64 950.16 965.44
973.58 1000.12 1016.08 1032.81 1048.00 1063.22 1071.26
1072.52 1080.90 1108.18 1110.95 1124.47 1131.26 1147.86
1149.06 1152.48 1173.79 1201.12 1217.76 1229.84 1234.08
1260.23 1278.94 1290.69 1291.08 1308.69 1320.63 1328.00
1369.50 1369.83 1405.12 1406.42 1424.64 1440.65 1459.09
1464.76 1480.19 1484.56 1489.06 1507.61 1513.87 1533.86
1536.38 1542.55 1559.86 1565.68 1623.69 1664.11 1678.37
2992.21 3005.12 3024.45 3045.52 3071.22 3091.89 3176.87
3203.63 3206.20 3211.63 3217.64 3229.72 3274.67 3275.37
3286.23 3287.49 3297.84 3298.21

==========

A5

==========

61.11 108.51 117.73 131.34 150.83 206.01 227.12
262.49 289.63 297.96 310.11 382.14 385.89 469.67
502.13 541.62 609.01 610.76 619.21 652.13 658.29
661.14 701.27 730.59 730.65 744.23 786.06 802.66
805.35 865.93 866.27 871.82 908.04 921.74 930.94
951.50 968.47 989.10 1039.22 1059.84 1075.13 1077.14
1094.38 1143.68 1149.62 1173.49 1225.09 1236.63 1280.09
1284.95 1348.61 1365.87 1367.37 1415.87 1421.52 1455.92
1465.73 1486.99 1505.01 1534.68 1546.90 1566.23 1631.00
3201.37 3206.66 3227.21 3270.32 3270.45 3282.32 3282.34
3294.51 3294.54

==========

A6

==========

7.73 12.34 13.98 21.22 28.50 37.68 41.35 54.06 57.83
64.50 71.22 79.69 95.28 108.79 111.43 119.41 127.73
143.72 148.69 156.72 176.43 193.64 213.60 233.90
239.51 251.21 253.92 263.51 292.05 306.37 308.14
339.90 359.94 390.26 411.14 429.99 441.73 447.49
460.25 470.55 477.29 480.05 503.94 520.59 538.17
551.54 566.75 599.15 609.52 611.05 612.10 626.90
643.57 655.34 659.12 667.27 668.47 680.46 709.71

716.49 719.57 731.46 736.76 739.65 748.51 768.77
773.34 790.92 792.08 822.55 827.58 830.88 832.23
861.92 863.07 872.51 885.19 887.59 889.83 892.20
902.50 922.04 933.87 934.88 937.35 940.47 940.98
963.78 972.30 973.77 976.01 981.28 1000.24 1016.44
1027.36 1054.01 1061.70 1071.43 1071.80 1079.50 1088.15
1097.96 1098.91 1110.20 1120.47 1124.63 1125.98 1150.28
1153.57 1162.80 1168.12 1174.31 1190.52 1200.54 1203.21
1219.03 1221.05 1239.17 1249.63 1276.08 1286.46 1289.68
1305.33 1309.97 1312.79 1315.98 1318.96 1329.13 1363.87
1365.48 1378.34 1399.51 1403.69 1437.85 1439.72 1442.96
1458.08 1461.03 1464.86 1468.08 1476.69 1483.62 1483.67
1500.99 1504.60 1514.24 1530.35 1531.97 1550.53 1558.61
1576.07 1593.24 1621.90 1640.05 1662.79 1662.89 1676.83
2978.43 2987.50 3010.43 3012.15 3040.11 3041.45 3052.87
3073.10 3095.05 3105.19 3176.32 3179.98 3193.43 3202.23
3210.36 3212.23 3216.52 3219.15 3230.08 3236.33 3268.95
3271.75 3281.92 3283.35 3299.14 3299.56

==========

TS(A3/A1)

==========

-348.39 15.20 17.22 19.82 21.49 25.87 29.06 31.02
40.33 51.50 56.52 74.80 76.30 80.31 89.59 100.58
104.67 111.01 122.55 127.40 140.23 154.10 167.66
188.09 193.87 201.45 229.20 235.21 244.52 259.11
267.24 283.71 293.98 311.31 315.92 351.88 361.81
390.01 428.48 437.24 450.59 454.14 459.55 463.08
473.99 487.44 525.52 537.77 568.88 570.16 600.44
610.34 618.86 635.17 647.71 651.27 660.89 672.48
675.27 696.38 711.97 721.47 725.27 732.10 744.32
747.89 749.89 767.59 782.73 784.37 793.73 797.18
828.55 843.69 844.99 846.08 854.95 865.90 870.07
886.41 898.66 899.72 904.22 933.82 937.40 937.88
952.36 959.32 961.15 971.43 972.37 978.01 978.44
984.20 1002.14 1016.98 1021.21 1047.41 1068.00 1071.98
1074.56 1077.29 1102.56 1103.09 1113.91 1118.74 1135.63
1149.95 1161.01 1166.50 1170.85 1178.35 1193.08 1200.95
1205.04 1212.08 1220.91 1235.18 1243.25 1247.10 1276.77
1287.55 1298.25 1302.64 1313.57 1315.54 1316.86 1322.84
1332.76 1356.85 1362.05 1370.16 1370.57 1383.19 1404.38
1405.05 1440.89 1450.19 1454.55 1456.60 1468.48 1471.18
1488.85 1491.36 1492.66 1510.08 1513.05 1519.97 1528.70
1530.42 1537.41 1559.98 1578.17 1580.37 1642.62 1645.70
1652.45 1661.88 1663.19 1677.26 2992.49 3024.44 3054.40
3071.96 3084.02 3091.43 3111.23 3129.23 3135.48 3151.05
3176.81 3184.55 3196.19 3199.00 3200.98 3211.48 3221.47
3222.52 3236.64 3240.94 3268.43 3276.92 3284.02 3287.96
3301.25 3302.64

==========

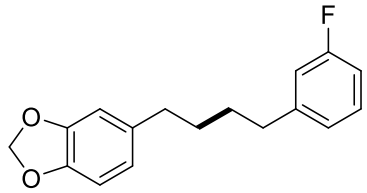
TS(A6/A5)

==========

-268.24 10.40 18.58 25.94 29.86 41.58 52.23 55.55
61.91 69.50 85.84 89.49 105.46 113.77 124.90 130.67
136.81 147.01 165.82 180.82 187.94 192.45 239.32
240.61 245.45 253.59 260.12 264.20 275.54 299.62
307.50 312.81 357.10 363.38 391.24 420.64 432.44
434.34 440.47 456.91 466.81 476.31 491.27 515.90
530.31 558.09 565.73 574.89 595.15 611.61 614.66
615.80 637.97 651.64 657.80 658.90 666.86 686.49
692.93 699.92 716.30 720.29 723.26 725.75 734.11
763.69 779.02 781.12 786.39 791.39 792.51 823.26
829.87 837.68 848.91 852.95 856.94 869.61 880.05
883.00 898.75 913.85 916.14 926.30 931.33 938.11
939.31 945.68 950.38 961.26 969.34 980.21 1008.24
1018.51 1020.23 1034.88 1049.90 1071.25 1071.40 1074.13
1077.94 1098.18 1105.10 1121.27 1141.90 1148.47 1151.91
1158.13 1171.96 1176.01 1195.19 1200.16 1204.40 1217.09
1224.43 1233.15 1248.48 1253.73 1268.66 1289.49 1292.81
1295.90 1298.57 1303.73 1325.31 1326.28 1330.20 1350.20
1362.13 1364.05 1365.29 1390.27 1401.88 1410.05 1424.48
1440.92 1460.10 1463.99 1470.58 1472.23 1477.40 1483.11
1484.76 1495.16 1497.72 1506.00 1531.72 1533.25 1533.84
1541.33 1558.56 1560.07 1624.58 1644.54 1662.84 1666.41
1677.05 2975.40 3002.06 3065.66 3076.19 3088.50 3095.17
3096.47 3113.77 3136.99 3149.80 3182.54 3183.61 3201.09
3202.22 3204.57 3211.05 3213.39 3220.97 3227.32 3229.38
3256.72 3257.81 3276.38 3277.43 3297.71 3301.47

Characterization Data

Compound 3



Followed general Procedure 1 (0.3 mmol scale), purification by pTLC (50:1 petroleum ether : EtOAc) afforded 52.1 mg (70%) of the title compound **3**.

Physical State: colorless oil.

R_f = 0.60 (50:1 petroleum ether : EtOAc).

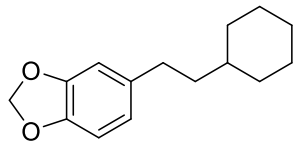
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.18 (m, 1H), 6.98 – 6.91 (m, 1H), 6.93 – 6.84 (m, 2H), 6.74 (d, *J* = 7.9 Hz, 1H), 6.67 (d, *J* = 1.7 Hz, 1H), 6.62 (dd, *J* = 7.7, 1.6 Hz, 1H), 5.92 (s, 2H), 2.63 (t, *J* = 7.1 Hz, 2H), 2.57 (t, *J* = 7.0 Hz, 2H), 1.68 – 1.60 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.04 (d, *J* = 245.1 Hz), 147.65, 145.65, 145.24 (d, *J* = 7.2 Hz), 136.38, 129.74 (d, *J* = 8.2 Hz), 124.17 (d, *J* = 2.7 Hz), 121.19, 115.30 (d, *J* = 20.8 Hz), 112.66 (d, *J* = 21.0 Hz), 108.95, 108.20, 100.85, 35.64, 35.59, 31.31, 30.71.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.97.

HRMS (ESI-TOF): calc'd for $C_{17}H_{17}FNaO_2$+ $[M+Na]^+$: 295.1105, found: 295.1104.

Compound 4



Followed general Procedure 1 (0.3 mmol scale), purification by pTLC (petroleum ether) afforded 49.6 mg (71%) of the title compound **4**.

Physical State: colorless oil.

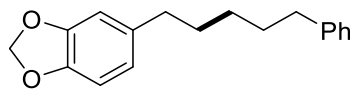
R_f = 0.40 (petroleum ether).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.72 (d, *J* = 7.9 Hz, 1H), 6.67 (d, *J* = 1.7 Hz, 1H), 6.62 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.91 (s, 2H), 2.57 – 2.49 (m, 2H), 1.78 – 1.63 (m, 5H), 1.49 – 1.41 (m, 2H), 1.30 – 1.14 (m, 4H), 0.92 (qd, *J* = 11.2, 10.2, 3.9 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.60, 145.48, 137.29, 121.08, 108.98, 108.19, 100.82, 39.80, 37.31, 33.45, 33.11, 26.85, 26.48.

HRMS (ESI-TOF): calc'd for $C_{15}H_{21}O_2^+$ $[M+H]^+$: 233.1536, found: 233.1537.

Compound 5



Followed general Procedure 1 (0.3 mmol scale), purification by pTLC (petroleum ether) afforded 53.8 mg (69%) of the title compound **5**.

Physical State: colorless oil.

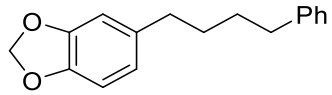
R_f = 0.35 (petroleum ether).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 2H), 7.26 – 7.18 (m, 3H), 6.76 (d, *J* = 7.8 Hz, 1H), 6.71 (d, *J* = 1.7 Hz, 1H), 6.65 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.94 (s, 2H), 2.67 – 2.62 (m, 2H), 2.59 – 2.54 (m, 2H), 1.73 – 1.56 (m, 4H), 1.46 – 1.38 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.60, 145.55, 142.86, 136.76, 128.51, 128.37, 125.74, 121.15, 108.96, 108.16, 100.80, 36.01, 35.72, 31.74, 31.49, 28.94.

HRMS (ESI-TOF): calc'd for $C_{18}H_{21}O_2$+ $[M+H]^+$: 269.1536, found: 269.1532.

Compound 6



Followed general Procedure 1 (0.3 mmol scale), purification by pTLC (petroleum ether) afforded 53.3 mg (70%) of the title compound **6**.

Physical State: colorless oil.

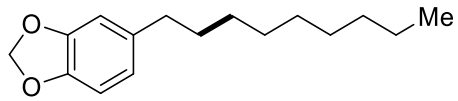
R_f = 0.35 (petroleum ether).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.20 (m, 2H), 7.17 – 7.11 (m, 3H), 6.68 (d, *J* = 7.8 Hz, 1H), 6.63 (d, *J* = 1.7 Hz, 1H), 6.58 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.88 (s, 2H), 2.60 (t, *J* = 7.1 Hz, 2H), 2.52 (t, *J* = 7.1 Hz, 2H), 1.60 (dt, *J* = 7.3, 2.9 Hz, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.62, 145.60, 142.69, 136.59, 128.55, 128.41, 125.80, 121.21, 109.00, 108.19, 100.84, 35.95, 35.67, 31.46, 31.08.

All data matched that reported in the literature *(61)*

Compound 7



Followed general Procedure 1 (0.3 mmol scale), purification by pTLC (petroleum ether) afforded 58.2 mg (78%) of the title compound **7**.

Physical State: colorless oil.

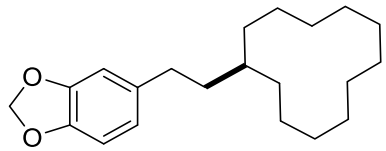
R_f = 0.40 (petroleum ether).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.73 (d, *J* = 7.9 Hz, 1H), 6.69 (d, *J* = 1.7 Hz, 1H), 6.63 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.92 (s, 2H), 2.57 – 2.49 (m, 2H), 1.62 – 1.53 (m, 2H), 1.34 – 1.27 (m, 12H), 0.94 – 0.86 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.59, 145.52, 136.98, 121.14, 108.99, 108.14, 100.80, 35.85, 32.04, 31.92, 29.71, 29.66, 29.48, 29.35, 22.82, 14.24.

All data matched that reported in the literature *(83)*

Compound 8



Followed general Procedure 1 (0.3 mmol scale), purification by pTLC (petroleum ether) afforded 62.7 mg (66%) of the title compound **8**.

Physical State: colorless oil.

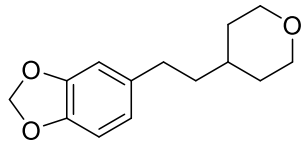
R_f = 0.45 (petroleum ether).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.73 (d, *J* = 7.9 Hz, 1H), 6.69 (d, *J* = 1.7 Hz, 1H), 6.64 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.92 (s, 2H), 2.56 – 2.52 (m, 2H), 1.51 – 1.47 (m, 2H), 1.38 – 1.28 (m, 23H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.59, 145.48, 137.27, 121.07, 108.96, 108.15, 100.78, 37.35, 33.84, 33.68, 29.04, 25.04, 24.42, 23.46, 23.38, 21.74.

HRMS (ESI-TOF): calc'd for $C_{21}H_{33}O_2$+ $[M+H]^+$: 317.2475, found: 317.2478.

Compound 9



Followed general Procedure 1 (0.3 mmol scale), purification by pTLC (petroleum ether) afforded 50.0 mg (71%) of the title compound **9**.

Physical State: colorless oil.

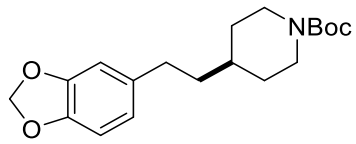
R_f = 0.35 (petroleum ether).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.72 (d, *J* = 7.9 Hz, 1H), 6.67 (d, *J* = 1.7 Hz, 1H), 6.61 (dd, *J* = 7.9, 1.8 Hz, 1H), 5.92 (s, 2H), 3.95 (dtd, *J* = 11.6, 2.5, 1.2 Hz, 2H), 3.36 (td, *J* = 11.8, 2.1 Hz, 2H), 2.58 – 2.53 (m, 2H), 1.65 – 1.61 (m, 2H), 1.54 – 1.49 (m, 2H), 1.36 – 1.25 (m, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.70, 145.65, 136.51, 121.08, 108.89, 108.26, 100.88, 68.20, 39.08, 34.50, 33.22, 32.52.

HRMS (ESI-TOF): calc'd for $C_{14}H_{19}O_3^+$ $[M+H]^+$: 235.1329, found: 235.1329.

Compound 10



Followed general Procedure 1 (0.3 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 69.4 mg (65%) of the title compound **10**.

Physical State: colorless oil.

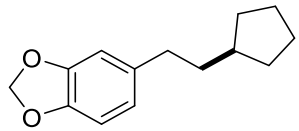
R_f = 0.40 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.71 (d, *J* = 7.9 Hz, 1H), 6.65 (d, *J* = 1.6 Hz, 1H), 6.60 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.90 (s, 2H), 4.07 (s, 2H), 2.66 (t, *J* = 12.7 Hz, 2H), 2.57 – 2.49 (m, 2H), 1.68 (d, *J* = 12.9 Hz, 2H), 1.54 – 1.48 (m, 2H), 1.45 (s, 9H), 1.44 – 1.34 (m, 1H), 1.11 (qd, *J* = 12.5, 4.4 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.99, 147.67, 145.63, 136.44, 121.04, 108.84, 108.22, 100.84, 79.29, 44.07, 38.65, 35.48, 32.73, 32.21, 28.58.

HRMS (ESI-TOF): calc'd for $C_{19}H_{27}NNaO_4^+$ $[M+Na]^+$: 356.1832, found: 356.1833.

Compound 11



Followed general Procedure 1 (0.3 mmol scale), purification by pTLC (petroleum ether) afforded 36.4 mg (55%) of the title compound **11**.

Physical State: colorless oil.

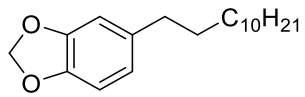
R_f = 0.35 (petroleum ether).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.72 (d, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 1.7 Hz, 1H), 6.63 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.91 (s, 2H), 2.57 – 2.51 (m, 2H), 1.84 – 1.71 (m, 3H), 1.63 – 1.54 (m, 4H), 1.55 – 1.46 (m, 2H), 1.17 – 1.08 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.58, 145.49, 137.11, 121.09, 108.98, 108.17, 100.81, 39.64, 38.53, 34.99, 32.78, 25.37.

HRMS (ESI-TOF): calc'd for $C_{14}H_{19}O_2^+$ $[M+H]^+$: 219.1380, found: 219.1379.

Compound 12



Followed general Procedure 1 (0.3 mmol scale), purification by pTLC (petroleum ether) afforded 57.6 mg (61%) of the title compound **12**.

Physical State: colorless oil.

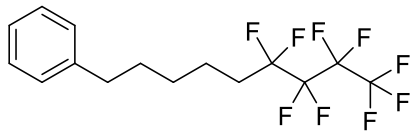
R_f = 0.60 (petroleum ether).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.72 (d, *J* = 7.9 Hz, 1H), 6.67 (d, *J* = 1.7 Hz, 1H), 6.62 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.91 (s, 2H), 2.52 (dd, *J* = 8.7, 6.7 Hz, 2H), 1.56 (p, *J* = 7.5, 6.2 Hz, 2H), 1.32-1.26 (m, 18H), 0.88 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.59, 145.52, 137.02, 121.16, 109.01, 108.16, 100.82, 35.85, 32.08, 31.92, 29.82, 29.79, 29.75, 29.66, 29.51, 29.35, 22.84, 14.27.

All data matched that reported in the literature *(84)*

Compound 13



Followed general Procedure 1 (0.3 mmol scale), purification by pTLC (petroleum ether) afforded 58.4 mg (57%) of the title compound **13**.

Physical State: colorless oil.

R_f = 0.65 (petroleum ether).

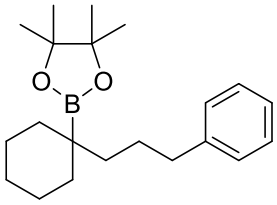
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.34 (m, 2H), 7.22 – 7.16 (m, 3H), 2.64 (t, *J* = 7.6 Hz, 2H), 1.74 – 1.71 (m, 8H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.41, 128.56, 128.53, 125.99, 35.84, 30.73 (t, *J* = 22.4 Hz), 28.86, 20.08 (t, *J* = 4.1 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -80.53 – -82.11 (m), -113.88 – -115.72 (m), -123.75 – -125.16 (m), -125.69 – -127.00 (m).

HRMS (APCI): calc'd for $C_{15}H_{15}F_9Na^+$ $[M+Na]^+$: 389.0922, found: 389.0924.

Compound 14



Followed general Procedure 2 (0.5 mmol scale), purification by flash column chromatography (20:1 petroleum ether : EtOAc) afforded 134.3 mg (82%) of the title compound **14**.

Physical State: white solid.

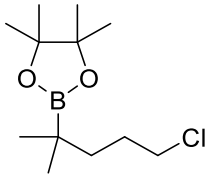
***R**$_f$* = 0.60 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.21 (m, 2H), 7.19 – 7.12 (m, 3H), 2.56 (t, *J* = 7.7 Hz, 2H), 1.86 (d, *J* = 12.7 Hz, 2H), 1.62 – 1.57 (m, 4H), 1.33 – 1.27 (m, 5H), 1.23 (s, 12H), 1.15 – 1.06 (m, 1H), 0.89 (td, *J* = 12.4, 3.4 Hz, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 143.01, 128.51, 128.31, 125.63, 83.02, 40.85, 37.05, 35.48, 27.58, 26.88, 25.41, 25.00, *Carbon attached to boron not observed.*

HRMS (ESI-TOF): calc'd for $C_{21}H_{34}BO_2^+$ $[M+H]^+$: 329.2646, found: 329.2643.

Compound 15



Followed general Procedure 2 (0.5 mmol scale), purification by flash column chromatography (petroleum ether) afforded 81.1 mg (66%) of the title compound **15**.

Physical State: colorless oil.

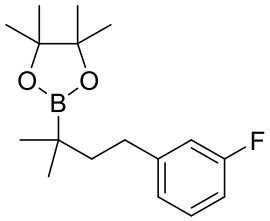
***R**$_f$* = 0.70 (50:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.49 (t, *J* = 6.9 Hz, 2H), 1.79 – 1.70 (m, 2H), 1.39 – 1.33 (m, 2H), 1.22 (s, 12H), 0.93 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 83.16, 46.01, 38.41, 30.00, 24.88, 24.82, *Carbon attached to boron not observed.*

All data matched that reported in the literature *(29)*

Compound 16



Followed general Procedure 2 (0.5 mmol scale), purification by flash column chromatography (petroleum ether) afforded 100.1 mg (69%) of the title compound **16**.

Physical State: colorless oil.

R_f = 0.40 (petroleum ether).

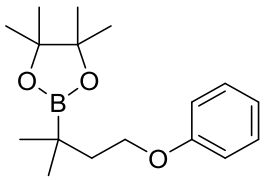
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 (td, *J* = 7.9, 6.1 Hz, 1H), 6.96 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.89 (dt, *J* = 10.2, 2.1 Hz, 1H), 6.87 – 6.81 (m, 1H), 2.60 – 2.52 (m, 2H), 1.61 – 1.54 (m, 2H), 1.26 (s, 12H), 1.00 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.04 (d, *J* = 244.8 Hz), 146.42 (d, *J* = 7.2 Hz), 129.68 (d, *J* = 8.3 Hz), 124.10 (d, *J* = 2.7 Hz), 115.27 (d, *J* = 20.7 Hz), 112.41 (d, *J* = 21.0 Hz), 83.18, 43.26, 33.00, 32.98, 24.88, *Carbon attached to boron not observed.*

^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.20.

HRMS (ESI-TOF): calc'd for $C_{17}H_{27}BFO_2^+$ $[M+H]^+$: 293.2083, found: 293.2082.

Compound 17



Followed general Procedure 2 (0.5 mmol scale), purification by flash column chromatography (30:1 petroleum ether : EtOAc) afforded 100.1 mg (69%) of the title compound **17**.

Physical State: colorless oil.

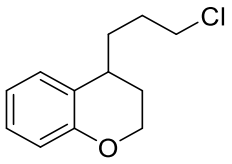
R_f = 0.50 (30:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.22 (m, 2H), 6.94 – 6.90 (m, 3H), 4.00 (t, *J* = 7.3 Hz, 2H), 1.80 (t, *J* = 7.4 Hz, 2H), 1.24 (s, 12H), 1.01 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.34, 129.48, 120.55, 114.92, 83.24, 66.39, 39.86, 25.25, 24.87, *Carbon attached to boron not observed.*

All data matched that reported in the literature *(85)*

Compound 18



Followed general Procedure 2 (0.2 mmol scale), purification by pTLC (petroleum ether) afforded 80.8 mg (76%) of the title compound **18**.

Physical State: colorless oil.

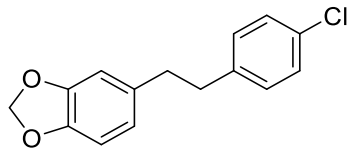
R_f = 0.60 (petroleum ether).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.12 (ddd, *J* = 15.6, 7.9, 1.7 Hz, 2H), 6.88 (td, *J* = 7.5, 1.3 Hz, 1H), 6.81 (dd, *J* = 8.1, 1.3 Hz, 1H), 4.26 – 4.13 (m, 2H), 3.66 – 3.53 (m, 2H), 2.90 – 2.78 (m, 1H), 2.13 – 2.05 (m, 1H), 1.99 – 1.92 (m, 2H), 1.92 – 1.85 (m, 1H), 1.84 – 1.79 (m, 1H), 1.76 – 1.68 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.64, 129.09, 127.58, 125.94, 120.31, 117.01, 63.54, 45.14, 33.58, 33.16, 30.09, 27.04.

HRMS (ESI-TOF): calc'd for $C_{12}H_{16}ClO^+$ $[M+H]^+$: 211.0884, found: 211.0886.

Compound 19



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (30:1 petroleum ether: EtOAc) afforded 26.4 mg (50%) of the title compound **19**.

Physical State: white solid.

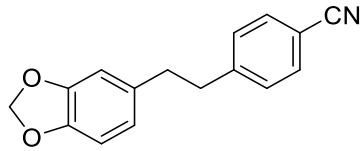
R_f = 0.60 (30:1 petroleum ether: EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.22 (m, 2H), 7.10 – 7.06 (m, 2H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.66 (d, *J* = 1.8 Hz, 1H), 6.59 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.93 (s, 2H), 2.89 – 2.79 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.68, 145.88, 140.09, 135.22, 131.77, 129.96, 128.52, 121.37, 109.01, 108.26, 100.92, 37.57, 37.55.

All data matched that reported in the literature *(48)*

Compound 20



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 34.6 mg (69%) of the title compound **20**.

Physical State: colorless oil.

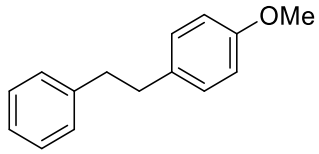
R_f = 0.50 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.51 (m, 2H), 7.25 – 7.20 (m, 2H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.62 (d, *J* = 1.7 Hz, 1H), 6.55 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.92 (s, 2H), 2.98 – 2.89 (m, 2H), 2.88 – 2.80 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.75, 147.20, 146.03, 134.49, 132.25, 129.43, 121.36, 119.18, 109.98, 108.91, 108.30, 100.97, 38.25, 37.03.

HRMS (ESI-TOF): calc'd for $C_{16}H_{14}NO_2^+$ $[M+H]^+$: 252.1019, found: 252.1019.

Compound 21



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded

37.3 mg (88%) of the title compound **21**.

Physical State: white solid.

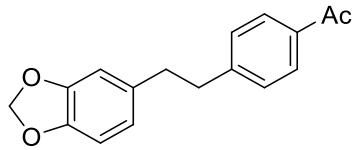
R_f = 0.3 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.22 (m, 2H), 7.23 – 7.12 (m, 3H), 7.11 – 7.04 (m, 2H), 6.84 – 6.78 (m, 2H), 3.77 (s, 3H), 2.90 – 2.85 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.98, 141.99, 134.02, 129.47, 128.61, 128.44, 125.99, 113.87, 55.38, 38.33, 37.16.

All data matched that reported in the literature *(86)*

Compound 22



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 41.8 mg (78%) of the title compound **22**.

Physical State: yellow oil.

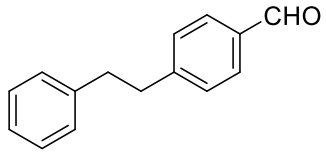
R_f = 0.25 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.83 (m, 2H), 7.25 – 7.21 (m, 2H), 6.71 (d, *J* = 7.9 Hz, 1H), 6.65 (d, *J* = 1.8 Hz, 1H), 6.58 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.92 (s, 2H), 2.98 – 2.89 (m, 2H), 2.88 – 2.84 (m, 2H), 2.58 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.96, 147.69, 147.42, 145.92, 135.28, 135.00, 128.83, 128.62, 121.34, 108.97, 108.26, 100.92, 38.18, 37.22, 26.66.

HRMS (ESI-TOF): calc'd for $C_{17}H_{17}O_3^+$ $[M+H]^+$: 269.1172, found: 269.1173.

Compound 23



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (petroleum ether) afforded 25.2 mg (60%) of the title compound **23**.

Physical State: colorless oil.

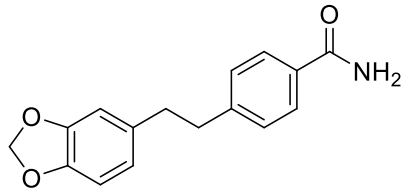
R_f = 0.50 (petroleum ether).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.98 (s, 1H), 7.81 – 7.77 (m, 2H), 7.34 – 7.27 (m, 4H), 7.23 – 7.20 (m, 1H), 7.18 – 7.14 (m, 2H), 3.05 – 3.00 (m, 2H), 2.98 – 2.93 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.12, 149.20, 141.04, 134.75, 130.04, 129.33, 128.56, 126.30, 38.17, 37.47.

All data matched that reported in the literature *(87)*

Compound 24



Followed general Procedure 3 (0.2 mmol scale), purification by recrystallization (petroleum ether and EA) afforded 30.1 mg (56%) of the title compound **24**.

Physical State: white solid.

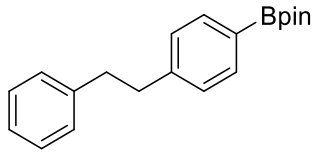
R_f = 0.1 (EtOAc).

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.81 – 7.74 (m, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.82 (d, *J* = 1.7 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.65 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.95 (s, 2H), 2.90-2.85 (m, 2H), 2.84-2.78 (m, 2H).

^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 167.77, 147.11, 145.26, 144.91, 135.11, 131.87, 128.20, 127.46, 121.17, 108.82, 107.96, 100.58, 37.01, 36.33.

HRMS (EI-TOF): calc'd for $C_{16}H_{16}NO_3^+$ $[M+H]^+$: 270.1125, found: 270.1124.

Compound 25



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (Petroleum ether) afforded 52.9 mg (86%) of the title compound **25**.

Physical State: colorless oil.

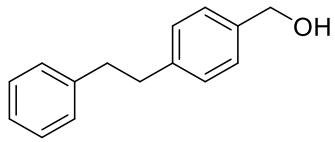
R_f = 0.30 (petroleum ether).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.72 (m, 2H), 7.32 – 7.26 (m, 2H), 7.23 – 7.17 (m, 5H), 2.98-2.90 (m, 4H), 1.36 (s, 12H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.30, 141.80, 135.04, 128.58, 128.48, 128.07, 126.06, 83.80, 38.28, 37.88, 25.01.

All data matched that reported in the literature *(88)*

Compound 26



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (10:1 petroleum ether: EtOAc) afforded 15.7 mg (37%) of the title compound **26**.

Physical State: colorless oil.

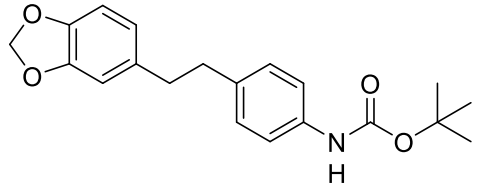
R_f = 0.20 (10:1 petroleum ether: EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.25 (m, 4H), 7.26 – 7.15 (m, 5H), 4.67 (s, 2H), 2.94 - 2.92 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.80, 141.46, 138.64, 128.81, 128.58, 128.48, 127.30, 126.08, 65.41, 38.05, 37.72.

All data matched that reported in the literature *(89)*

Compound 27



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (5:1 petroleum ether: EtOAc) afforded 55.9 mg (82%) of the title compound **27**.

Physical State: white solid.

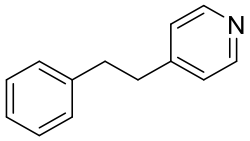
R_f = 0.40 (5:1 petroleum ether: EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.24 (m, 2H), 7.11 – 7.05 (m, 2H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.65 (d, *J* = 1.7 Hz, 1H), 6.59 (d, *J* = 1.7 Hz, 1H), 6.46 (s, 1H), 5.90 (s, 2H), 2.83-2.77(m, 4H), 1.51 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.99, 147.59, 145.73, 136.42, 136.37, 135.69, 129.04, 121.34, 118.76, 109.05, 108.20, 100.84, 80.47, 37.81, 37.57, 28.47.

HRMS (ESI-TOF): calc'd for $C_{20}H_{24}NO_4^+$ $[M+H]^+$: 342.1700, found: 342.1701.

Compound 28



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (2:1 petroleum ether: EtOAc) afforded 17.4 mg (42%) of the title compound **28**.

Physical State: white solid.

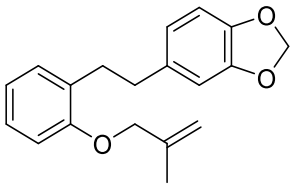
R_f = 0.20 (2:1 petroleum ether: EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 – 8.46 (m, 2H), 7.31 – 7.26 (m, 2H), 7.24 – 7.18 (m, 1H), 7.17 – 7.13 (m, 2H), 7.09 – 7.05 (m, 2H), 2.95-2.91 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.61, 149.83, 140.80, 128.60, 128.53, 126.38, 124.07, 37.17, 36.68.

All data matched that reported in the literature *(90)*

Compound 29



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 33.6 mg (58%) of the title compound **29**.

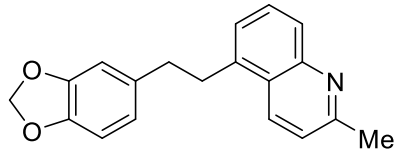
Physical State: colorless oil.

R_f = 0.30 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.16 (td, *J* = 7.8, 1.8 Hz, 1H), 7.11 (dd, *J* = 7.4, 1.8 Hz, 1H), 6.90 – 6.83 (m, 2H), 6.72 (d, *J* = 7.9 Hz, 2H), 6.64 (dd, *J* = 7.8, 1.8 Hz, 1H), 5.92 (s, 2H), 5.14 (dq, *J* = 2.3, 1.3 Hz, 1H), 5.01 (q, *J* = 1.4 Hz, 1H), 4.45 (s, 2H), 2.93 – 2.80 (m, 4H), 1.87 (s, 3H).

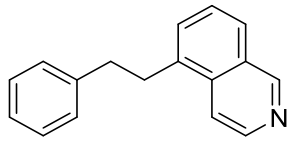
^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.69, 147.59, 145.67, 141.27, 136.55, 130.44, 130.17, 127.29, 121.30, 120.63, 112.34, 111.52, 109.13, 108.21, 100.84, 71.67, 36.25, 33.29, 19.70.
HRMS (ESI-TOF): calc'd for $C_{19}H_{21}O_3^+$ $[M+H]^+$: 297.1485, found: 297.1486.

Compound 30



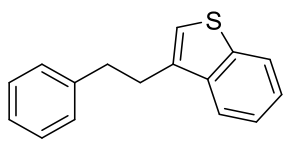
Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (5:1 petroleum ether : EtOAc) afforded 50.2 mg (83%) of the title compound **30**.
Physical State: white solid.
R_f = 0.70 (10:1 petroleum ether : EtOAc).
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (t, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 1H), 6.70 (d, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 1.8 Hz, 1H), 6.60 (dd, *J* = 7.8, 1.7 Hz, 1H), 5.91 (s, 2H), 3.03 (dd, *J* = 9.4, 6.4 Hz, 2H), 2.92 (dd, *J* = 9.4, 6.4 Hz, 2H), 2.73 (s, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 158.37, 147.67, 146.84, 145.85, 139.11, 135.85, 135.38, 130.96, 128.60, 126.57, 126.18, 122.11, 121.36, 109.03, 108.25, 100.89, 38.13, 37.53, 25.40.

Compound 31



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (2:1 petroleum ether : EtOAc) afforded 34.9 mg (75%) of the title compound **31**.
Physical State: white solid.
R_f = 0.30 (2:1 petroleum ether : EtOAc).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.28 (s, 1H), 8.57 (d, *J* = 6.0 Hz, 1H), 7.90 – 7.82 (m, 2H), 7.55 – 7.47 (m, 2H), 7.32 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 3.41 – 3.31 (m, 2H), 3.08 – 2.98 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.43, 142.96, 141.40, 137.22, 134.77, 130.51, 129.17, 128.63, 128.55, 127.20, 126.47, 126.36, 116.99, 37.03, 34.36.
All data matched that reported in the literature *(91)*

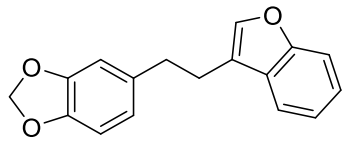
Compound 32



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 35.4 mg (74%) of the title compound **32**.
Physical State: white solid.
R_f = 0.65 (20:1 petroleum ether : EtOAc).

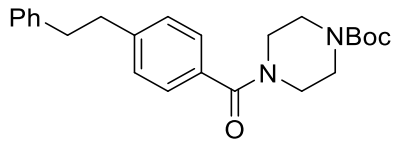
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (dt, *J* = 7.5, 0.9 Hz, 1H), 7.81 – 7.76 (m, 1H), 7.43 – 7.34 (m, 3H), 7.33 – 7.29 (m, 2H), 7.24 (d, *J* = 7.3 Hz, 2H), 7.07 (s, 1H), 3.18 – 3.13 (m, 2H), 3.10 – 3.05 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.81, 140.61, 139.06, 136.26, 128.59, 128.57, 126.24, 124.33, 124.02, 123.06, 121.72, 121.57, 35.63, 30.71.
All data matched that reported in the literature *(92)*

Compound 33



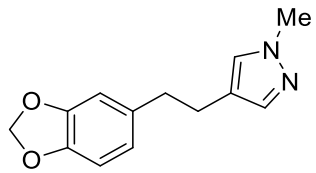
Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 21.0 mg (44%) of the title compound **33**.
Physical State: white solid.
***R**f* = 0.40 (20:1 petroleum ether : EtOAc).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.52 (m, 1H), 7.48 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.35 (s, 1H), 7.30 (ddd, *J* = 8.2, 7.2, 1.5 Hz, 1H), 7.27 – 7.22 (m, 1H), 6.78 – 6.70 (m, 2H), 6.66 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.93 (s, 2H), 2.95 (s, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.44, 147.74, 145.96, 141.43, 135.53, 128.24, 124.28, 122.40, 121.34, 119.81, 119.62, 111.61, 109.00, 108.33, 100.94, 35.25, 26.02.
HRMS (ESI-TOF): calc'd for $C_{17}H_{15}O_3$+ $[M+H]^+$: 267.1016, found: 267.1015.

Compound 34



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (5:1 petroleum ether : EtOAc) afforded 48.6 mg (62%) of the title compound **34**.
Physical State: white solid.
***R**f* = 0.40 (5:1 petroleum ether : EtOAc).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.64 (m, 2H), 7.26 (ddd, *J* = 7.7, 6.3, 1.5 Hz, 2H), 7.21 – 7.17 (m, 3H), 7.16 – 7.12 (m, 2H), 4.21 – 4.02 (m, 3H), 3.00 – 2.85 (m, 5H), 2.00 (dt, *J* = 12.3, 3.5 Hz, 2H), 1.46 (s, 9H), 1.42 – 1.38 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.86, 154.84, 145.70, 141.23, 132.32, 128.80, 128.55, 128.48, 127.08, 126.17, 79.79, 47.28, 37.74, 37.62, 32.26, 28.54.
HRMS (ESI-TOF): calc'd for $C_{24}H_{31}N_2O_3[M+H]^+$: 395.2329, found: 395.2330.

Compound 35



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (2:1 petroleum ether : EtOAc) afforded 16.2 mg (37%) of the title compound **35**.

Physical State: colorless oil.

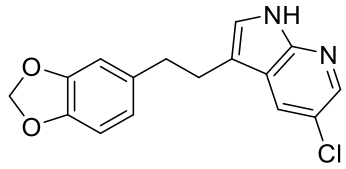
R_f = 0.30 (2:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.26 (m, 1H), 7.06 (s, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.67 (d, *J* = 1.7 Hz, 1H), 6.61 (dd, *J* = 7.8, 1.7 Hz, 1H), 5.91 (s, 2H), 3.83 (s, 3H), 2.80 – 2.67 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.62, 145.78, 138.79, 135.70, 128.37, 121.33, 121.08, 108.99, 108.20, 100.87, 38.87, 37.18, 26.42.

HRMS (ESI-TOF): calc'd for $C_{13}H_{14}ClN_2O_2^+$ $[M+H]^+$: 231.1128, found: 231.1130.

Compound 36



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (5:1 petroleum ether : EtOAc) afforded 26.5 mg (42%) of the title compound **36**.

Physical State: colorless oil.

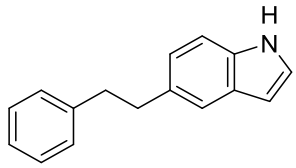
R_f = 0.30 (5:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-d) δ 9.99 (s, 1H), 8.23 (d, J = 2.3 Hz, 1H), 7.72 (d, J = 2.2 Hz, 1H), 7.08 (d, J = 2.2 Hz, 1H), 6.72 (d, J = 7.9 Hz, 1H), 6.66 (d, J = 1.7 Hz, 1H), 6.60 (dd, J = 7.9, 1.7 Hz, 1H), 5.92 (s, 2H), 3.01 – 2.94 (m, 2H), 2.92 – 2.86 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.72, 147.16, 145.96, 141.30, 135.64, 126.82, 123.94, 123.37, 121.44, 121.07, 114.33, 109.11, 108.31, 100.94, 36.38, 27.64.

HRMS (ESI-TOF): calc'd for $C_{16}H_{14}ClN_2O_2^+$ $[M+H]^+$: 301.0738, found: 301.0739.

Compound 37



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (10:1 petroleum ether : EtOAc) afforded 31.1 mg (68%) of the title compound **37**.

Physical State: white solid.

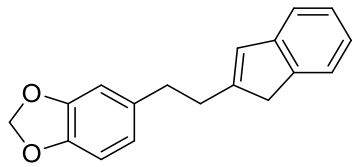
R_f = 0.70 (10:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (s, 1H), 7.46 (s, 1H), 7.28 (td, *J* = 8.1, 2.5 Hz, 3H), 7.24 – 7.18 (m, 3H), 7.17 – 7.14 (m, 1H), 7.04 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.51 – 6.46 (m, 1H), 3.04 – 2.93 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.45, 134.56, 133.43, 128.63, 128.43, 128.22, 125.91, 124.44, 123.16, 120.01, 110.90, 102.46, 38.98, 38.27.

All data matched that reported in the literature *(48)*

Compound 38



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (petroleum ether :) afforded 24.0 mg (48%) of the title compound **38**.

Physical State: colorless oil.

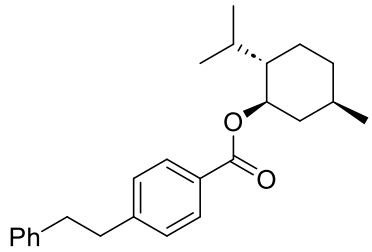
R_f = 0.30 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.35 (m, 1H), 7.26 (dt, *J* = 7.5, 1.1 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.10 (td, *J* = 7.3, 1.3 Hz, 1H), 6.75 – 6.71 (m, 2H), 6.66 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.55 – 6.51 (m, 1H), 5.91 (s, 2H), 3.35 – 3.23 (m, 2H), 2.89 – 2.81 (m, 2H), 2.79 – 2.70 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.79, 147.72, 145.83, 145.63, 143.17, 135.82, 126.81, 126.40, 123.85, 123.55, 121.19, 120.16, 108.89, 108.30, 100.91, 41.35, 35.25, 33.39.

HRMS (ESI-TOF): calc'd for $C_{18}H_{17}O_2$+ $[M+H]^+$: 265.1223, found: 265.1227.

Compound 39



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (5:1 petroleum ether : EtOAc) afforded 49.5 mg (68%) of the title compound **39**.

Physical State: white solid.

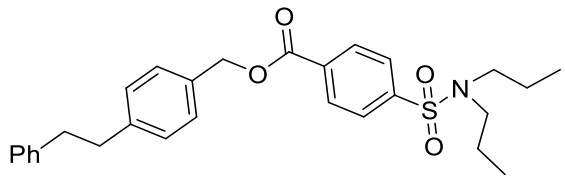
R_f = 0.50 (5:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.93 (m, 2H), 7.32 – 7.13 (m, 7H), 4.93 (td, *J* = 10.9, 4.4 Hz, 1H), 3.01 – 2.90 (m, 4H), 2.13 (ddt, *J* = 12.1, 4.0, 2.1 Hz, 1H), 1.97 (pd, *J* = 7.0, 2.7 Hz, 1H), 1.73 (dt, *J* = 11.7, 2.9 Hz, 2H), 1.55 (ddt, *J* = 13.9, 10.8, 3.1 Hz, 2H), 1.18 – 1.06 (m, 2H), 0.94 (d, *J* = 3.2 Hz, 3H), 0.92 (d, *J* = 3.6 Hz, 3H), 0.80 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.22, 147.05, 141.30, 129.79, 128.78, 128.57, 128.54, 128.51, 126.18, 74.74, 47.41, 41.13, 37.95, 37.61, 34.47, 31.56, 26.62, 23.78, 22.17, 20.90, 16.67.

HRMS (ESI-TOF): calc'd for $C_{25}H_{33}O_2^+$ $[M+H]^+$: 365.2475, found: 365.2475.

Compound 40



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (10:1 petroleum ether : EtOAc) afforded 53.1 mg (54%)of the title compound **40**.

Physical State: white solid.

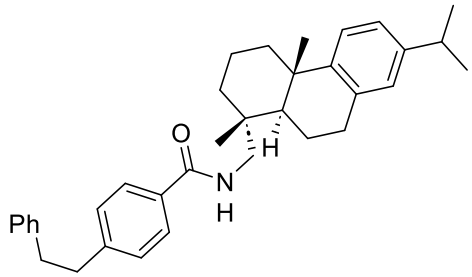
R_f = 0.60 (10:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 – 8.10 (m, 2H), 7.93 – 7.79 (m, 2H), 7.39 – 7.35 (m, 2H), 7.31 – 7.27 (m, 2H), 7.24 – 7.17 (m, 5H), 5.36 (s, 2H), 3.12 – 3.06 (m, 4H), 2.98-2.91 (m, 4H), 1.60 – 1.49 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.27, 144.47, 142.44, 141.65, 133.64, 133.21, 130.46, 128.92, 128.72, 128.55, 128.51, 127.13, 126.14, 67.40, 50.04, 37.91, 37.73, 22.04, 11.28.

HRMS (EI-TOF): calc'd for $C_{28}H_{34}NO_4S^+$ $[M+H]^+$: 480.2203, found: 480.2202.

Compound 41



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 51.3 mg (52%) of the title compound **41.**

Physical State: white solid.

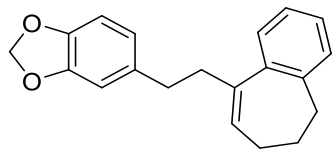
R_f = 0.4 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.64 (m, 2H), 7.32 – 7.27 (m, 2H), 7.24 – 7.15 (m, 5H), 7.02 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 6.21 (t, *J* = 6.4 Hz, 1H), 3.50 – 3.29 (m, 2H), 2.96 (tt, *J* = 7.3, 4.4 Hz, 5H), 2.90 – 2.80 (m, 2H), 2.32 (dt, *J* = 12.9, 3.4 Hz, 1H), 2.04 – 1.97 (m, 1H), 1.85 – 1.69 (m, 3H), 1.53 (ddt, *J* = 9.8, 6.6, 2.6 Hz, 2H), 1.41 (ddd, *J* = 13.1, 11.1, 4.0 Hz, 2H), 1.26 (d, *J* = 2.1 Hz, 6H), 1.24 (s, 3H), 1.03 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.76, 147.15, 145.71, 145.59, 141.28, 134.88, 132.54, 128.82, 128.54, 128.48, 127.05, 126.15, 124.33, 123.98, 50.41, 45.90, 38.46, 37.81, 37.75, 37.67, 37.63, 36.50, 33.51, 30.55, 25.55, 24.07, 19.20, 18.91, 18.76.

HRMS (ESI-TOF): calc'd for $C_{24}H_{31}N_2O_3^+$ $[M+H]^+$: 494.3417, found: 494.3417.

Compound 42



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 45.2 mg (77%) of the title compound **42**.

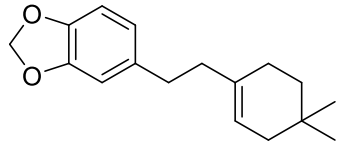
Physical State: colorless oil.

R_f = 0.60 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.21 (m, 2H), 7.21 – 7.13 (m, 2H), 6.68 (d, *J* = 7.9 Hz, 1H), 6.62 (d, *J* = 1.8 Hz, 1H), 6.53 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.95 (tt, *J* = 7.2, 1.4 Hz, 1H), 5.89 (s, 2H), 2.74 (dd, *J* = 9.7, 6.3 Hz, 2H), 2.58 (dd, *J* = 9.6, 6.2 Hz, 2H), 2.47 (t, *J* = 7.0 Hz, 2H), 2.04 (p, *J* = 7.1 Hz, 2H), 1.78 (q, *J* = 7.2 Hz, 2H).

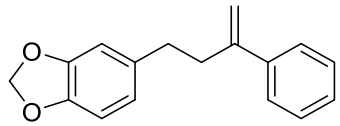
^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.58, 145.63, 141.77, 141.07, 140.69, 136.22, 129.01, 126.67, 126.44, 126.11, 125.98, 121.20, 108.97, 108.17, 100.82, 38.89, 35.13, 34.79, 32.40, 24.58.
HRMS (EI-TOF): calc'd for $C_{20}H_{21}O_2$ $[M+H]^+$: 293.1536, found: 293.1536.

Compound 43



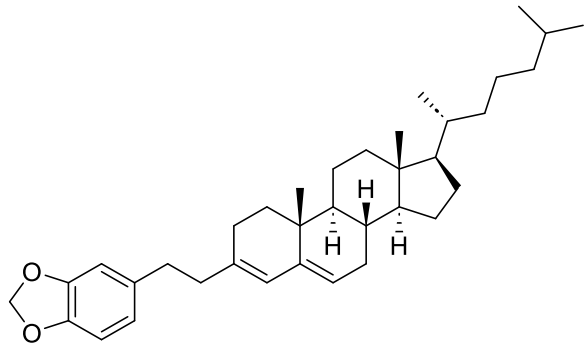
Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 35.4 mg (63%) of the title compound **43**.
Physical State: colorless oil.
R_f = 0.50 (20:1 petroleum ether : EtOAc).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.73 – 6.67 (m, 2H), 6.62 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.91 (s, 2H), 5.32 (tp, *J* = 3.0, 1.4 Hz, 1H), 2.68 – 2.61 (m, 2H), 2.21 (tt, *J* = 7.9, 3.8 Hz, 2H), 2.00 – 1.93 (m, 2H), 1.76 (dp, *J* = 3.9, 1.9 Hz, 2H), 1.36 (t, *J* = 6.4 Hz, 2H), 0.89 (s, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.57, 145.57, 136.63, 135.78, 121.16, 120.59, 108.99, 108.16, 100.82, 39.91, 39.43, 35.90, 34.44, 28.62, 28.34, 26.44.
HRMS (ESI-TOF): calc'd for $C_{17}H_{22}NaO_2$+ $[M+Na]^+$: 281.1512, found: 281.1514.

Compound 44



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (petroleum ether :) afforded 21.3 mg (41%) of the title compound **44**.
Physical State: colorless oil.
R_f = 0.30 (20:1 petroleum ether : EtOAc).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.38 (m, 2H), 7.35 – 7.30 (m, 2H), 7.29 – 7.23 (m, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 6.65 (d, *J* = 1.7 Hz, 1H), 6.59 (dd, *J* = 7.9, 1.8 Hz, 1H), 5.89 (s, 2H), 5.27 (d, *J* = 1.4 Hz, 1H), 5.03 (d, *J* = 1.4 Hz, 1H), 2.78 – 2.73 (m, 2H), 2.69 – 2.64 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.85, 147.63, 145.74, 141.19, 135.94, 128.50, 127.57, 126.27, 121.25, 112.91, 109.02, 108.23, 100.87, 37.72, 34.60.
HRMS (ESI-TOF): calc'd for $C_{17}H_{16}NaO_2$+ $[M+Na]^+$: 275.1043, found: 275.1044.

Compound 45



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 41.3 mg (40%) of the title compound **45**.

Physical State: white solid.

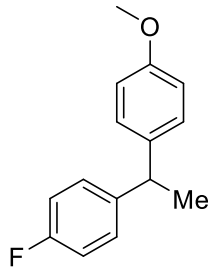
R_f = 0.50 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.71 (d, *J* = 7.9 Hz, 1H), 6.68 (d, *J* = 1.7 Hz, 1H), 6.62 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.91 (s, 2H), 5.73 (d, *J* = 2.2 Hz, 1H), 5.35 – 5.29 (m, 1H), 2.67 (td, *J* = 7.5, 3.6 Hz, 2H), 2.31 – 2.24 (m, 2H), 2.19 – 2.11 (m, 2H), 2.00 (td, *J* = 18.2, 17.0, 4.6 Hz, 2H), 1.89 – 1.77 (m, 2H), 1.71 – 1.61 (m, 2H), 1.59 – 1.47 (m, 4H), 1.44 – 1.30 (m, 4H), 1.22 – 1.09 (m, 7H), 1.07 – 0.97 (m, 3H), 0.93 (s, 3H), 0.91 (s, 3H), 0.88 (d, *J* = 1.8 Hz, 3H), 0.86 (d, *J* = 1.8 Hz, 3H), 0.70 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.60, 145.64, 141.97, 136.41, 136.24, 124.55, 121.82, 121.16, 108.96, 108.21, 100.85, 57.12, 56.32, 48.53, 42.62, 39.98, 39.78, 39.67, 36.34, 35.95, 35.03, 34.38, 31.99, 31.96, 28.40, 28.16, 26.59, 24.34, 23.98, 22.96, 22.71, 21.26, 19.06, 18.87, 12.13.

HRMS (ESI-TOF): calc'd for $C_{36}H_{53}O_2$+ $[M+H]^+$: 517.4040, found: 517.4042.

Compound 46



Followed general Procedure 4 (0.2 mmol scale), purification by pTLC (petroleum ether) afforded 36.8 mg (80%) of the title compound **46**.

Physical State: colorless oil.

R_f = 0.40 (petroleum ether).

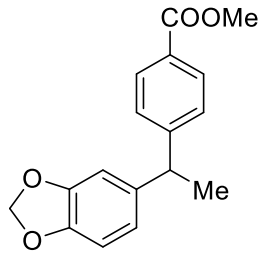
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 – 7.09 (m, 4H), 6.99 – 6.94 (m, 2H), 6.86 – 6.81 (m, 2H), 4.09 (q, *J* = 7.2 Hz, 1H), 3.79 (s, 3H), 1.60 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.33 (d, *J* = 240.4 Hz), 158.05, 142.59, 138.48, 129.01 (d, *J* = 7.8 Hz), 128.55, 115.16 (d, *J* = 21.2 Hz), 113.92, 55.38, 43.34, 22.35.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.66.

All data matched that reported in the literature *(93)*

Compound 47



Followed general Procedure 4 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 43.7 mg (82%) of the title compound **47**.

Physical State: colorless oil.

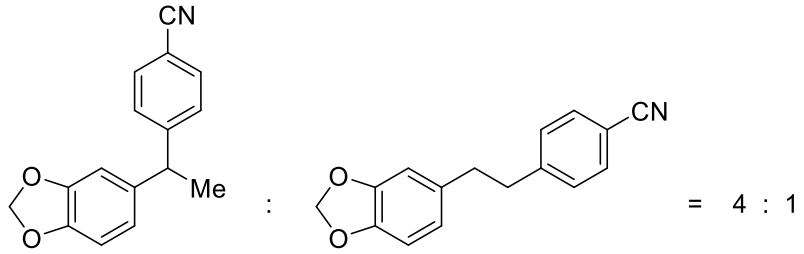
R_f = 0.40 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.89 (m, 2H), 7.31 – 7.24 (m, 2H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.69 – 6.63 (m, 2H), 5.89 (s, 2H), 4.11 (q, *J* = 7.2 Hz, 1H), 3.88 (s, 3H), 1.60 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.13, 151.88, 147.84, 146.06, 139.57, 129.87, 128.65, 128.13, 127.60, 120.52, 108.23, 101.01, 52.09, 44.59, 21.84.

HRMS (ESI-TOF): calc'd for $C_{17}H_{17}O_4$+ $[M+Na]^+$: 285.1121, found: 285.1122.

Compound 48



Followed general Procedure 4 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 35.6 mg (71%) of the title compound **48**.

Physical State: colorless oil.

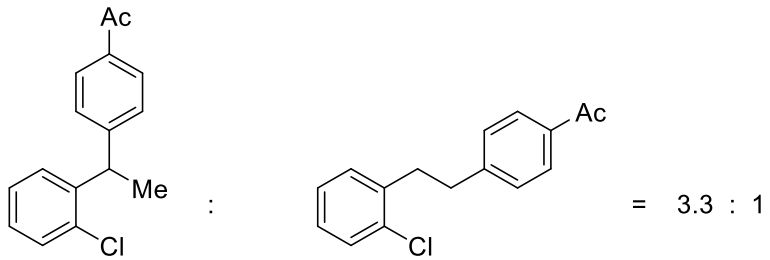
R_f = 0.45 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.28 (m, 2H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.66 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.63 (d, *J* = 1.8 Hz, 1H), 5.92 (s, 2H), 4.11 (q, *J* = 7.2 Hz, 1H), 1.60 (d, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.10, 148.01, 146.32, 138.78, 132.40, 128.40, 120.59, 119.13, 110.07, 108.39, 108.16, 101.15, 44.69, 21.71.

All data matched that reported in the literature *(94)*

Compound 49



Followed general Procedure 4 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 43.4 mg (84%) of the title compound **49**.

Physical State: colorless oil.

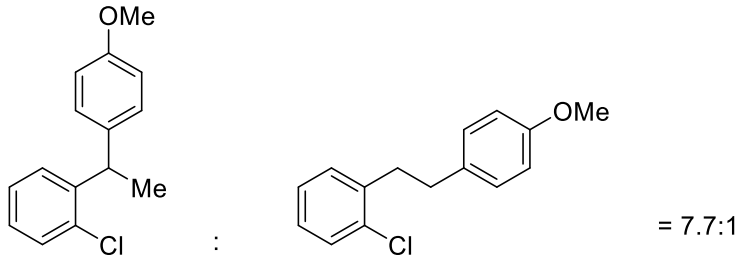
R_f = 0.20 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (t, *J* = 1.8 Hz, 1H), 7.78 (dt, *J* = 7.2, 1.7 Hz, 1H), 7.42 – 7.34 (m, 3H), 7.24 – 7.21 (m, 2H), 7.17 – 7.13 (m, 1H), 4.70 (q, *J* = 7.2 Hz, 1H), 2.58 (s, 3H), 1.65 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.39, 145.77, 143.01, 132.80, 129.86, 128.71, 128.56, 127.77, 127.49, 127.18, 126.60, 41.09, 26.82, 21.22.

HRMS (ESI-TOF): calc'd for $C_{16}H_{16}ClO^+$ $[M+Na]^+$: 259.0884, found: 259.0886.

Compound 50



Followed general Procedure 4 (0.2 mmol scale), purification by pTLC (30:1 petroleum ether : EtOAc) afforded 32.0 mg (65%) of the title compound **50**.

Physical State: colorless oil.

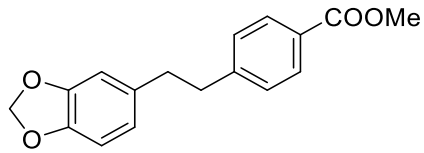
R_f = 0.30 (30:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (dt, *J* = 7.6, 0.9 Hz, 1H), 7.21 – 7.18 (m, 2H), 7.16 – 7.09 (m, 3H), 6.86 – 6.79 (m, 2H), 4.60 (q, *J* = 7.2 Hz, 1H), 3.77 (s, 3H), 1.58 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.05, 144.17, 137.21, 133.91, 129.71, 128.82, 128.60, 127.36, 127.02, 113.84, 55.35, 40.24, 21.38.

All data matched that reported in the literature *(95)*

Compound 51



Followed general Procedure 3 (0.2 mmol scale), purification by flash column chromatography (silica gel, 20:1 petroleum ether : EtOAc) afforded 49.9 mg (88%) of the title compound **51**.

Physical State: white solid.

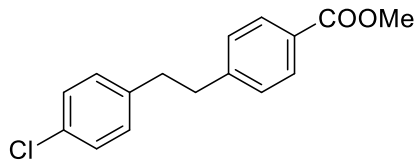
R_f = 0.35 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.71 (d, *J* = 7.9 Hz, 1H), 6.66 – 6.62 (m, 1H), 6.61 – 6.54 (m, 1H), 5.92 (s, 2H), 3.90 (s, 3H), 2.93 (dd, *J* = 9.2, 5.6 Hz, 2H), 2.85 (dd, *J* = 8.9, 5.9 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.25, 147.69, 147.14, 145.91, 135.08, 129.80, 128.67, 128.07, 121.36, 108.99, 108.27, 100.93, 52.10, 38.25, 37.29.

All data matched that reported in the literature *(59)*

Compound 52



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 52.6 mg (96%) of the title compound **52**.

Physical State: white solid.

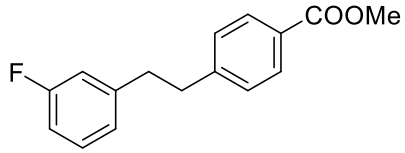
R_f = 0.40 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.92 (m, 2H), 7.25 – 7.17 (m, 4H), 7.07 – 7.02 (m, 2H), 3.90 (s, 3H), 2.94 – 2.88 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.19, 146.76, 139.61, 131.95, 129.94, 129.84, 128.67, 128.59, 128.20, 52.12, 37.81, 36.85.

All data matched that reported in the literature *(96)*

Compound 53



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 48.5 mg (95%) of the title compound **53**.

Physical State: white solid.

R_f = 0.55 (20:1 petroleum ether : EtOAc).

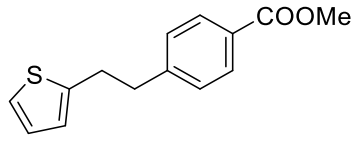
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.93 (m, 2H), 7.30 – 7.22 (m, 3H), 6.97 – 6.86 (m, 3H), 3.94 (s, 3H), 3.04 – 2.89 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.19, 163.00 (d, *J* = 245.5 Hz), 146.76, 143.76 (d, *J* = 7.2 Hz), 129.95, 129.87, 128.63, 128.22, 124.24 (d, *J* = 2.7 Hz), 115.40 (d, *J* = 20.9 Hz), 113.10 (d, *J* = 20.9 Hz), 52.11, 37.61, 37.21 (d, *J* = 1.8 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.58.

HRMS (ESI-TOF): calc'd for $C_{16}H_{16}FO_2^+$ $[M+Na]^+$: 259.1129, found: 259.1129.

Compound 54



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 29.5 mg (60%) of the title compound **54**.

Physical State: colorless oil.

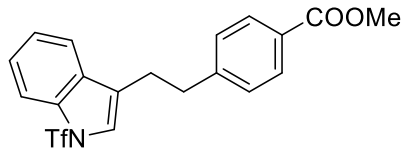
R_f = 0.40 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.94 (m, 2H), 7.28 – 7.21 (m, 2H), 7.12 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.90 (dd, *J* = 5.2, 3.4 Hz, 1H), 6.74 (dd, *J* = 3.4, 1.0 Hz, 1H), 3.90 (s, 3H), 3.18 – 3.13 (m, 2H), 3.04 (t, *J* = 8.1 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.19, 146.58, 143.87, 129.85, 128.63, 128.27, 126.86, 124.69, 123.39, 52.10, 38.14, 31.47.

HRMS (ESI-TOF): calc'd for $C_{14}H_{15}O_2S^+$ $[M+H]^+$: 247.0787, found: 247.0788.

Compound 55



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (10:1 petroleum ether : EtOAc) afforded 48.6 mg (59%) of the title compound **55**.

Physical State: white solid.

***R*$_f$** = 0.30 (10:1 petroleum ether : EtOAc).

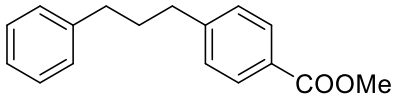
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.93 (m, 2H), 7.91 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.62 – 7.54 (m, 1H), 7.46 – 7.34 (m, 3H), 7.24 (s, 1H), 7.06 (s, 1H), 3.92 (s, 3H), 3.12 – 3.02 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.11, 146.34, 135.82, 131.02, 129.99, 128.55, 128.50, 126.08, 124.87, 124.59, 122.69, 119.94, 119.73 (q, *J* = 324.1 Hz), 114.10, 52.16, 35.02, 26.53.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -75.23.

HRMS (ESI-TOF): calc'd for $C_{19}H_{17}F_3NO_4S$+ $[M+H]^+$: 412.0825, found: 412.0825.

Compound 56



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 43.1 mg (85%) of the title compound **56**.

Physical State: colorless oil.

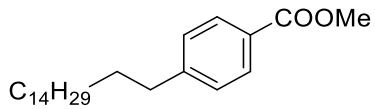
***R*$_f$** = 0.45 (20:1 petroleum ether : EtOAc)).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.93 (m, 2H), 7.30 – 7.23 (m, 4H), 7.23 – 7.13 (m, 3H), 3.89 (s, 3H), 2.66 (dt, *J* = 19.0, 7.7 Hz, 4H), 1.99 – 1.93 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.25, 147.94, 142.02, 129.80, 128.58, 128.53, 128.48, 127.92, 125.98, 52.06, 35.52, 35.45, 32.69.

All data matched that reported in the literature *(97)*

Compound 57



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (50:1 petroleum ether : EtOAc) afforded 57.7 mg (80%) of the title compound **57**.

Physical State: colorless oil.

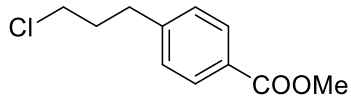
R_f = 0.30 (petroleum ether).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 3.90 (s, 3H), 2.73 – 2.42 (m, 2H), 1.65 – 1.59 (m, 2H), 1.28-1.26 (m, 26H), 0.88 (t, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.34, 148.66, 129.76, 128.56, 127.75, 60.86, 52.06, 36.16, 32.07, 31.30, 31.28, 29.84, 29.83, 29.80, 29.70, 29.60, 29.51, 29.40, 22.84, 14.50, 14.26.

HRMS (ESI-TOF): calc'd for $C_{24}H_{41}O_2^+$ $[M+H]^+$: 361.3101, found: 361.3101.

Compound 58



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 34.1 mg (79%) of the title compound **58**.

Physical State: colorless oil.

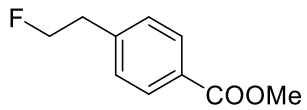
R_f = 0.45 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.95 (m, 2H), 7.30 – 7.25 (m, 2H), 3.91 (s, 3H), 3.52 (t, *J* = 6.4 Hz, 2H), 2.88 – 2.80 (m, 2H), 2.14 – 2.06 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.17, 146.32, 129.99, 128.72, 128.36, 52.16, 44.11, 33.75, 32.91.

All data matched that reported in the literature *(98)*

Compound 59



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (50:1 petroleum ether : EtOAc) afforded 24.5 mg (68%) of the title compound **59**.

Physical State: colorless oil.

R_f = 0.50 (20:1 petroleum ether : EtOAc).

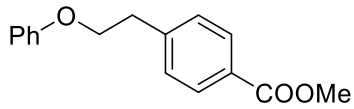
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 – 7.97 (m, 2H), 7.34 – 7.29 (m, 2H), 4.70 (t, *J* = 6.3 Hz, 1H), 4.61 (t, *J* = 6.3 Hz, 1H), 3.91 (s, 3H), 3.09 (t, *J* = 6.3 Hz, 1H), 3.04 (t, *J* = 6.3 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.10, 142.75 (d, *J* = 5.2 Hz), 130.01, 129.14, 128.86, 83.64 (d, *J* = 169.7 Hz), 52.20, 37.04 (d, *J* = 20.5 Hz).

^{19}F NMR (376 MHz, Chloroform-*d*) δ -216.09.

All data matched that reported in the literature *(99)*

Compound 60



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 40.6 mg (79%) of the title compound **60**.

Physical State: colorless oil.

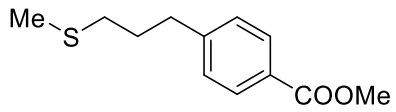
R_f = 0.45 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.30 – 7.22 (m, 2H), 6.97 – 6.91 (m, 1H), 6.88 (dt, *J* = 7.8, 1.1 Hz, 2H), 4.19 (t, *J* = 6.8 Hz, 2H), 3.90 (s, 3H), 3.14 (t, *J* = 6.8 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.15, 158.75, 144.00, 129.90, 129.60, 129.16, 128.60, 121.03, 114.69, 68.06, 52.15, 35.91.

HRMS (ESI-TOF): calc'd for $C_{16}H_{17}O_3$+ $[M+H]^+$: 257.1172, found: 257.1171.

Compound 61



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (50:1 petroleum ether : EtOAc) afforded 21.1 mg (47%) of the title compound **61**.

Physical State: colorless oil.

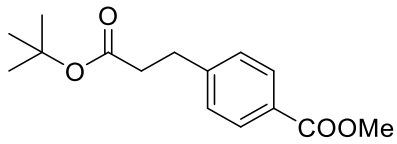
***R**f* = 0.50 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.93 (m, 2H), 7.29 – 7.23 (m, 2H), 3.90 (s, 3H), 2.83 – 2.72 (m, 2H), 2.55 – 2.45 (m, 2H), 2.09 (s, 3H), 1.97 – 1.88 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.24, 147.26, 129.88, 128.64, 128.10, 52.12, 34.83, 33.64, 30.38, 15.59.

HRMS (ESI-TOF): calc'd for $C_{12}H_{17}O_2S$+ $[M+H]^+$: 225.0944, found: 225.0945.

Compound 62



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 33.7 mg (61%) of the title compound **62**.

Physical State: colorless oil.

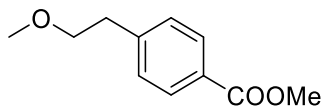
***R**f* = 0.42 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 3H), 2.96 (t, *J* = 7.7 Hz, 2H), 2.56 (t, *J* = 7.7 Hz, 2H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.97, 167.19, 146.38, 129.88, 128.51, 128.28, 80.72, 52.12, 36.64, 31.19, 28.18.

All data matched that reported in the literature *(100)*

Compound 63



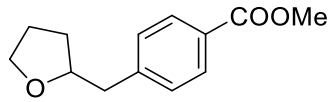
Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (petroleum ether :) afforded 24.8 mg (63%) of the title compound **63**.

Physical State: colorless oil.

***R**f* = 0.40 (petroleum ether).

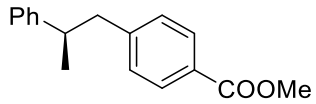
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 3.83 (s, 3H), 3.55 (t, *J* = 6.8 Hz, 2H), 3.27 (s, 3H), 2.86 (t, *J* = 6.8 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.23, 144.74, 129.83, 129.00, 128.34, 73.11, 58.84, 52.12, 36.35.
All data matched that reported in the literature *(101)*

Compound 64



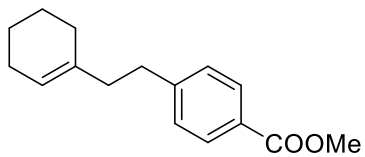
Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 35.3 mg (81%) of the title compound **64**.
Physical State: colorless oil.
***R**f* = 0.40 (20:1 petroleum ether : EtOAc).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 4.08 (dq, *J* = 7.8, 6.2 Hz, 1H), 3.90 (s, 3H), 3.88 – 3.84 (m, 1H), 3.73 (ddd, *J* = 8.4, 7.4, 6.4 Hz, 1H), 2.94 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.82 (dd, *J* = 13.7, 6.0 Hz, 1H), 2.00 – 1.88 (m, 1H), 1.89 – 1.82 (m, 2H), 1.58 – 1.51 (m, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.29, 144.67, 129.78, 129.42, 128.30, 79.65, 68.13, 52.12, 42.04, 31.17, 25.74.
HRMS (ESI-TOF): calc'd for $C_{13}H_{17}O_3^+$ $[M+H]^+$: 221.1172, found: 221.1171.

Compound 65



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (30:1 petroleum ether : EtOAc) afforded 40.1 mg (78%) of the title compound **65**.
Physical State: colorless oil.
***R**f* = 0.25 (30:1 petroleum ether : EtOAc).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.85 (m, 2H), 7.28 – 7.21 (m, 2H), 7.18 – 7.15 (m, 1H), 7.14 – 7.06 (m, 4H), 3.87 (s, 3H), 3.04 – 2.91 (m, 2H), 2.83 (dd, *J* = 12.8, 7.5 Hz, 1H), 1.24 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.29, 146.42, 146.37, 129.57, 129.29, 128.49, 127.98, 127.12, 126.32, 52.07, 45.16, 41.82, 21.40.
All data matched that reported in the literature *(102)*

Compound 66



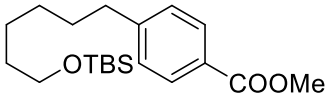
Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (50:1 petroleum ether : EtOAc) afforded 41.6 mg (85%) of the title compound **66**.
Physical State: colorless oil.
***R**f* = 0.50 (20:1 petroleum ether : EtOAc).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 5.39 (dp, *J* = 3.7,

1.7 Hz, 1H), 3.90 (s, 3H), 2.78 – 2.73 (m, 2H), 2.27 – 2.20 (m, 2H), 2.00 – 1.91 (m, 4H), 1.66 – 1.59 (m, 2H), 1.60 – 1.50 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.32, 148.28, 136.80, 129.70, 128.55, 127.78, 121.89, 52.05, 39.63, 34.57, 28.57, 25.32, 23.09, 22.60.

HRMS (ESI-TOF): calc'd for $C_{16}H_{21}O_2^+$ $[M+H]^+$: 245.1536, found: 245.1537.

Compound 67



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 61.6 mg (88%) of the title compound **67**.

Physical State: colorless oil.

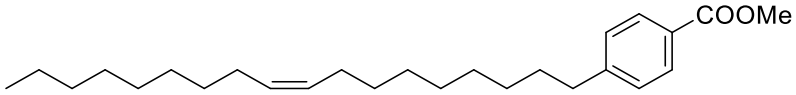
***R*$_f$** = 0.45 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.91 (m, 2H), 7.26 – 7.19 (m, 2H), 3.89 (s, 3H), 3.59 (t, *J* = 6.4 Hz, 2H), 2.69 – 2.61 (m, 2H), 1.71 – 1.56 (m, 2H), 1.57 – 1.43 (m, 2H), 1.43 – 1.30 (m, 4H), 0.89 (s, 12H), 0.04 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.32, 148.53, 129.76, 128.55, 127.78, 63.30, 52.05, 36.07, 32.87, 31.23, 29.14, 26.11, 26.09, 25.77, 18.49, -5.14.

HRMS (ESI-TOF): calc'd for $C_{20}H_{35}O_3Si+$ $[M+H]^+$: 351.2350, found: 351.2349.

Compound 68



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 44.7 mg (58%) of the title compound **68**.

Physical State: colorless oil.

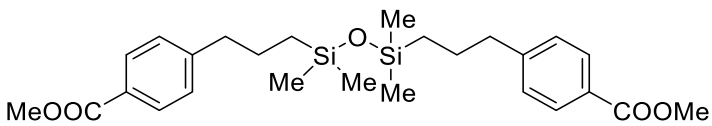
***R*$_f$** = 0.45 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.93 (m, 2H), 7.25 – 7.20 (m, 2H), 5.38 (q, *J* = 2.8, 1.8 Hz, 1H), 5.36 – 5.32 (m, 1H), 3.90 (s, 3H), 2.69 – 2.61 (m, 2H), 2.06 – 1.92 (m, 4H), 1.68 – 1.56 (m, 2H), 1.32 – 1.24 (m, 22H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.34, 148.63, 130.10, 129.96, 129.76, 128.56, 127.76, 52.06, 36.15, 32.75, 32.05, 31.27, 29.91, 29.88, 29.84, 29.80, 29.67, 29.58, 29.47, 29.39, 29.32, 27.36, 22.83, 14.25.

HRMS (ESI-TOF): calc'd for $C_{26}H_{42}NaO_2+$ $[M+Na]^+$: 409.3077, found: 409.3078.

Compound 69



Followed general Procedure 3 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 61.3 mg (63%) of the title compound **69**.

Physical State: colorless oil.

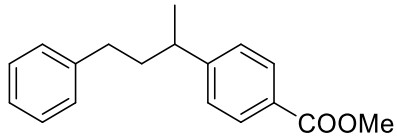
R_f = 0.45 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.92 (m, 4H), 7.23 – 7.18 (m, 4H), 3.90 (s, 6H), 2.66 (t, *J* = 7.6 Hz, 4H), 1.69 – 1.58 (m, 4H), 0.58 – 0.48 (m, 4H), 0.02 (s, 12H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.35, 148.34, 129.77, 128.65, 127.84, 52.09, 39.71, 25.23, 18.25, 0.49.

HRMS (ESI-TOF): calc'd for $C_{26}H_{39}O_5Si_2$+ $[M+H]^+$: 487.2331, found: 487.2335.

Compound 70



Followed general Procedure 5 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 49.3 mg (92%) of the title compound **70**.

Physical State: colorless oil.

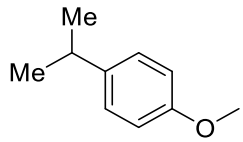
R_f = 0.41 (20:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.29 – 7.23 (m, 4H), 7.20 – 7.15 (m, 1H), 7.13 – 7.09 (m, 2H), 3.91 (s, 3H), 2.79 (q, *J* = 7.1 Hz, 1H), 2.54 – 2.45 (m, 2H), 1.93 (tdd, *J* = 8.5, 7.1, 1.7 Hz, 2H), 1.29 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.29, 152.94, 142.27, 129.96, 128.61, 128.47, 128.17, 127.27, 125.91, 52.11, 39.82, 39.70, 33.94, 22.33.

All data matched that reported in the literature *(103)*

Compound 71



Followed general Procedure 5 (0.2 mmol scale), purification by pTLC (30:1 petroleum ether : EtOAc) afforded 22.5 mg (75%) of the title compound **71**.

Physical State: colorless oil.

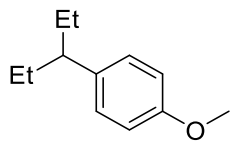
R_f = 0.30 (30:1 petroleum ether : EtOAc).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.14 (m, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 2.90 (p, *J* = 6.9 Hz, 1H), 1.32 – 1.21 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.78, 141.17, 127.37, 113.80, 55.35, 33.40, 24.35.

All data matched that reported in the literature *(103)*

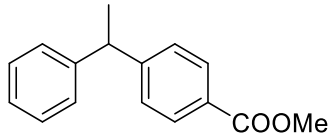
Compound 72



Followed general Procedure 5 (0.2 mmol scale), purification by pTLC (30:1 petroleum ether : EtOAc) afforded 22.1 mg (62%) of the title compound **72**.

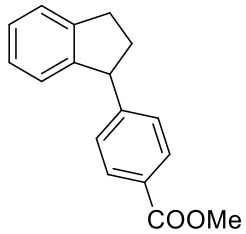
^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.08 – 7.02 (m, 2H), 6.87 – 6.81 (m, 2H), 3.79 (s, 3H), 2.29 – 2.22 (m, 1H), 1.70 – 1.63 (m, 2H), 1.53 – 1.45 (m, 2H), 0.76 (td, *J* = 7.4, 1.9 Hz, 3H).
^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.80, 138.00, 128.73, 113.65, 55.34, 48.97, 29.55, 12.34.
All data matched that reported in the literature *(104)*

Compound 73



Followed general Procedure 5 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 22.5 mg (85%) of the title compound **72**.
Physical State: colorless oil.
***R*$_f$** = 0.45 (20:1 petroleum ether : EtOAc).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.93 (m, 2H), 7.31 – 7.25 (m, 4H), 7.21 – 7.16 (m, 3H), 4.19 (q, *J* = 7.2 Hz, 1H), 3.87 (s, 3H), 1.64 (d, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.16, 151.83, 145.54, 129.86, 128.62, 128.12, 127.78, 127.70, 126.44, 52.09, 44.92, 21.70.
All data matched that reported in the literature *(105)*

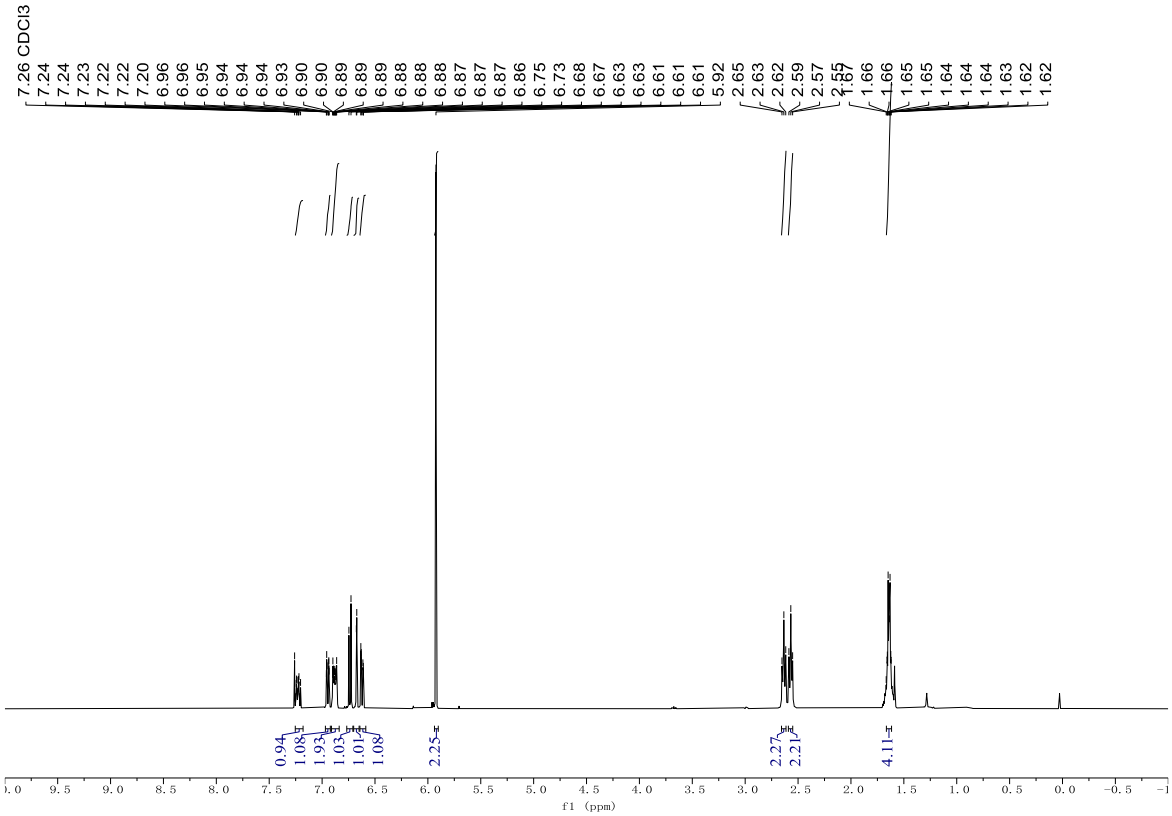
Compound 74



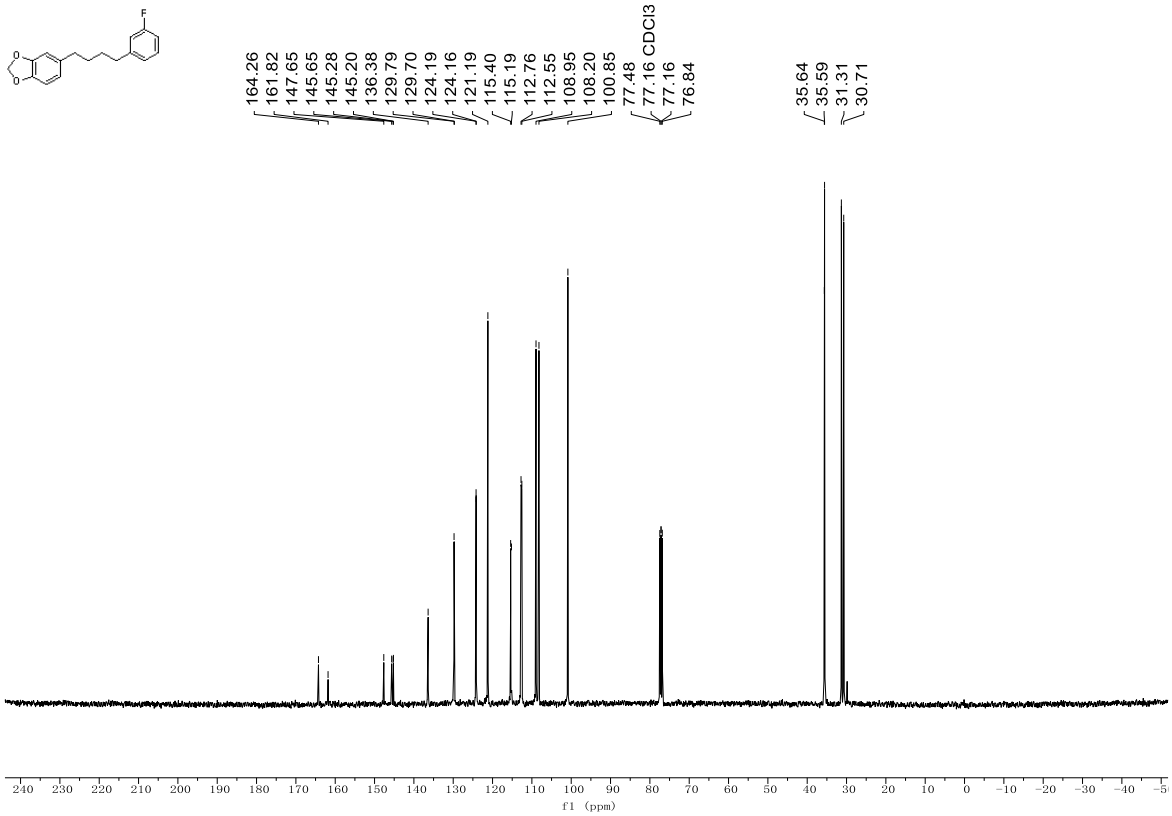
Followed general Procedure 5 (0.2 mmol scale), purification by pTLC (20:1 petroleum ether : EtOAc) afforded 32.3 mg (64%) of the title compound **73**.
Physical State: colorless oil.
***R*$_f$** = 0.38 (20:1 petroleum ether : EtOAc).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.22 – 7.17 (m, 1H), 7.13 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 7.4 Hz, 1H), 4.39 (t, *J* = 8.3 Hz, 1H), 3.90 (s, 3H), 3.07 (ddd, *J* = 15.8, 8.6, 3.8 Hz, 1H), 2.97 (dt, *J* = 16.0, 8.3 Hz, 1H), 2.60 (dtd, *J* = 11.9, 7.9, 3.8 Hz, 1H), 2.05 (dq, *J* = 12.7, 8.7 Hz, 1H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.22, 151.08, 146.17, 144.45, 129.98, 128.43, 128.25, 126.96, 126.63, 124.97, 124.61, 52.13, 51.75, 36.49, 31.97.
All data matched that reported in the literature *(105)*

Spectral Data

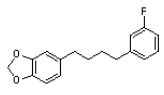
Compound **3** ^{1}H NMR



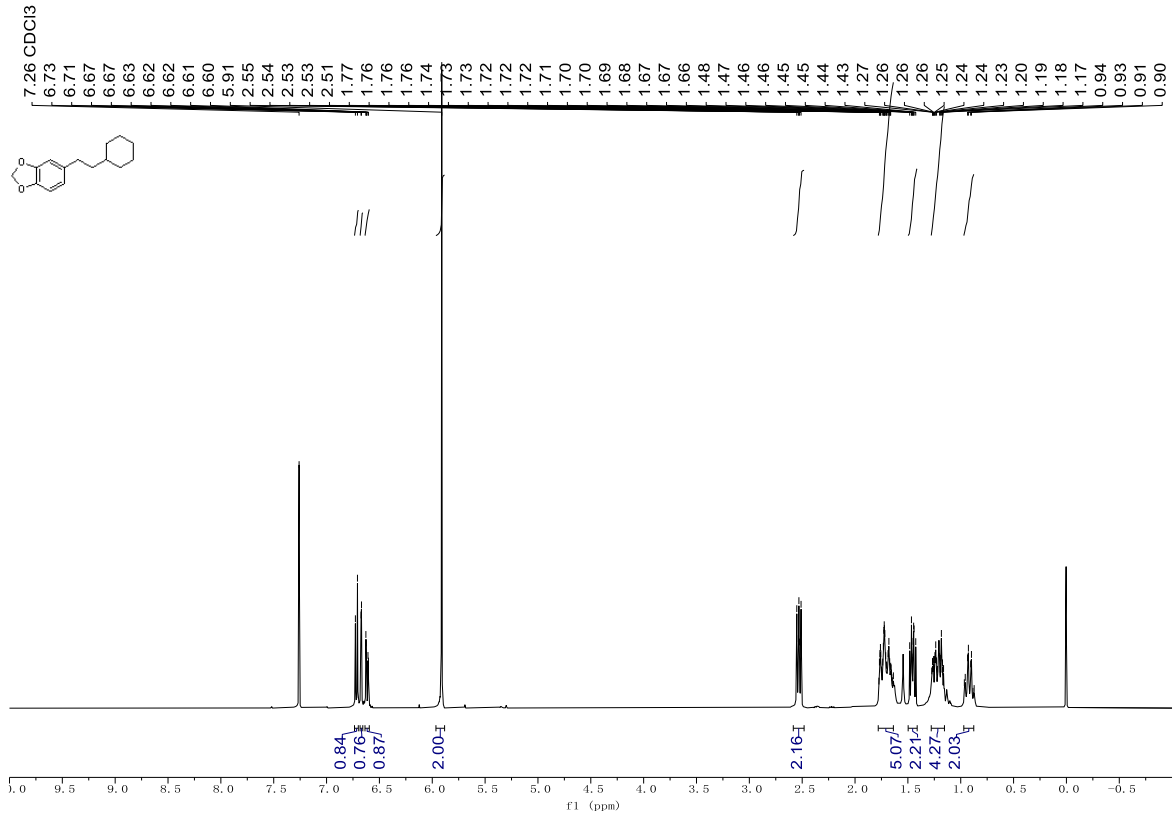
Compound **3** ^{13}C NMR



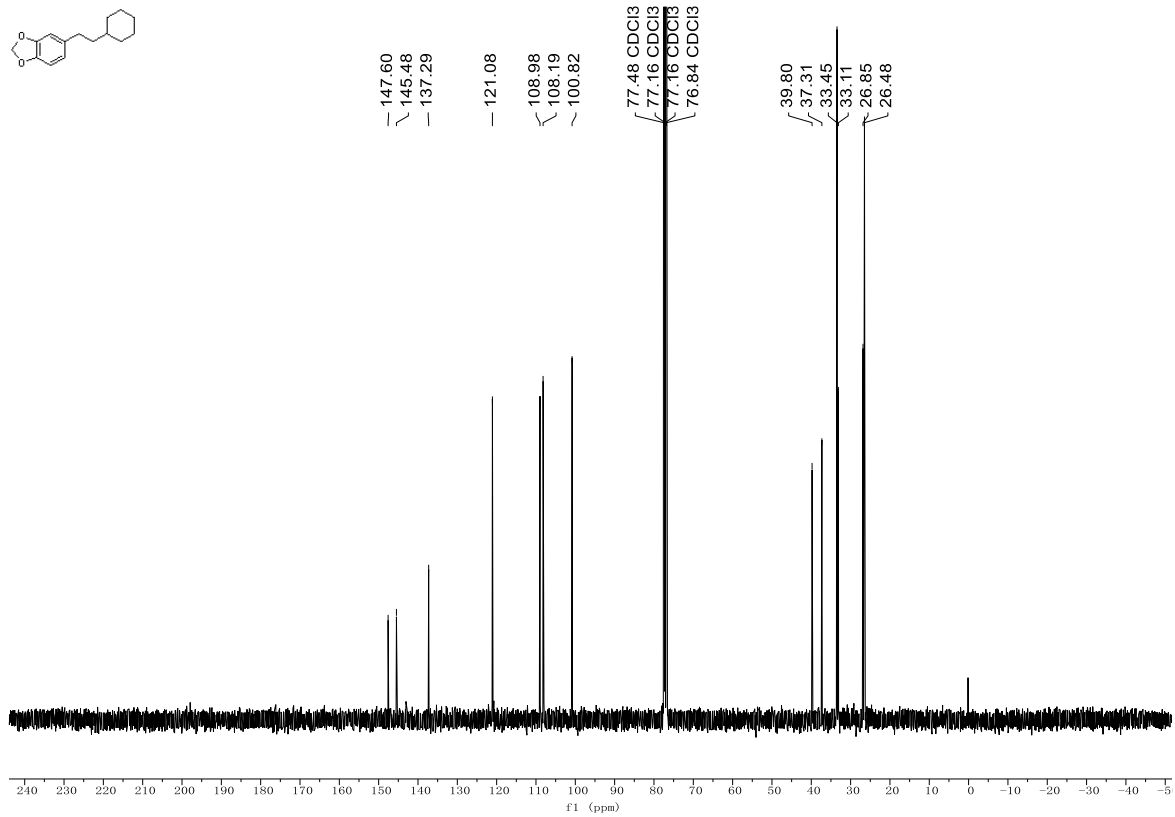
Compound **3** ^{19}F NMR



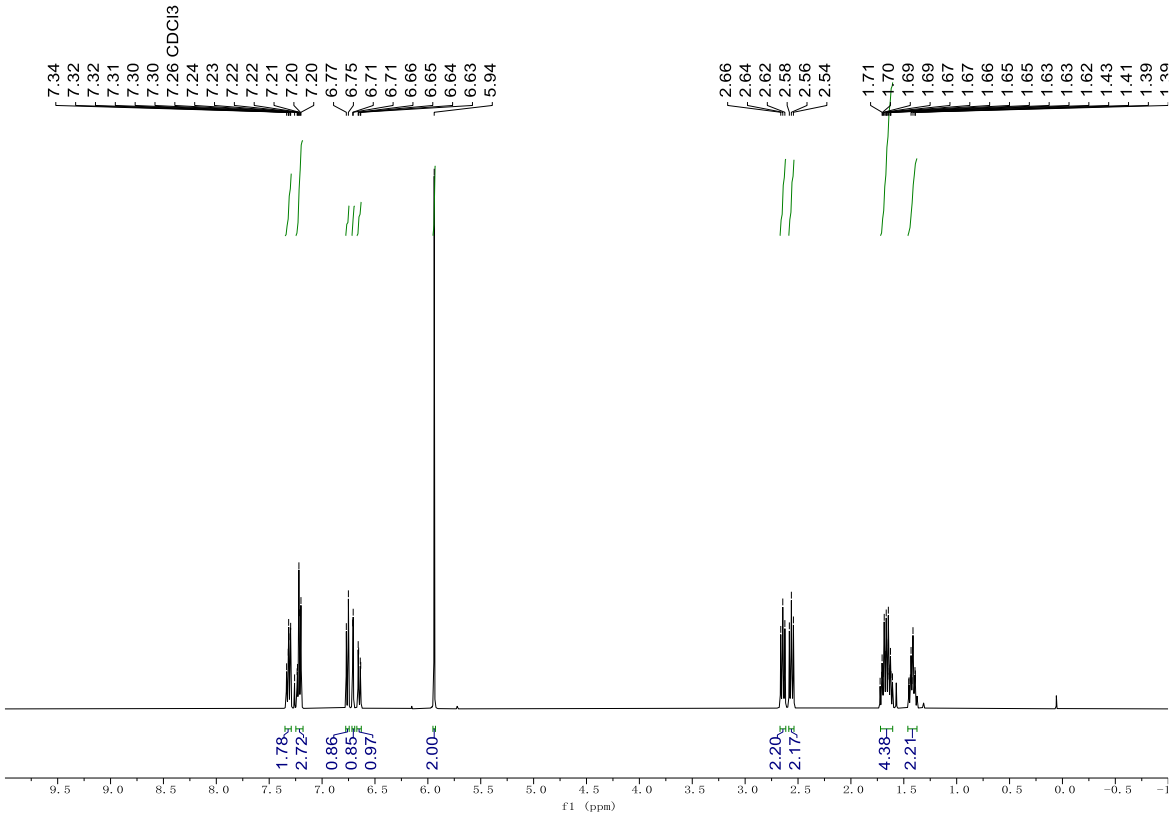
Compound **4** ^{1}H NMR



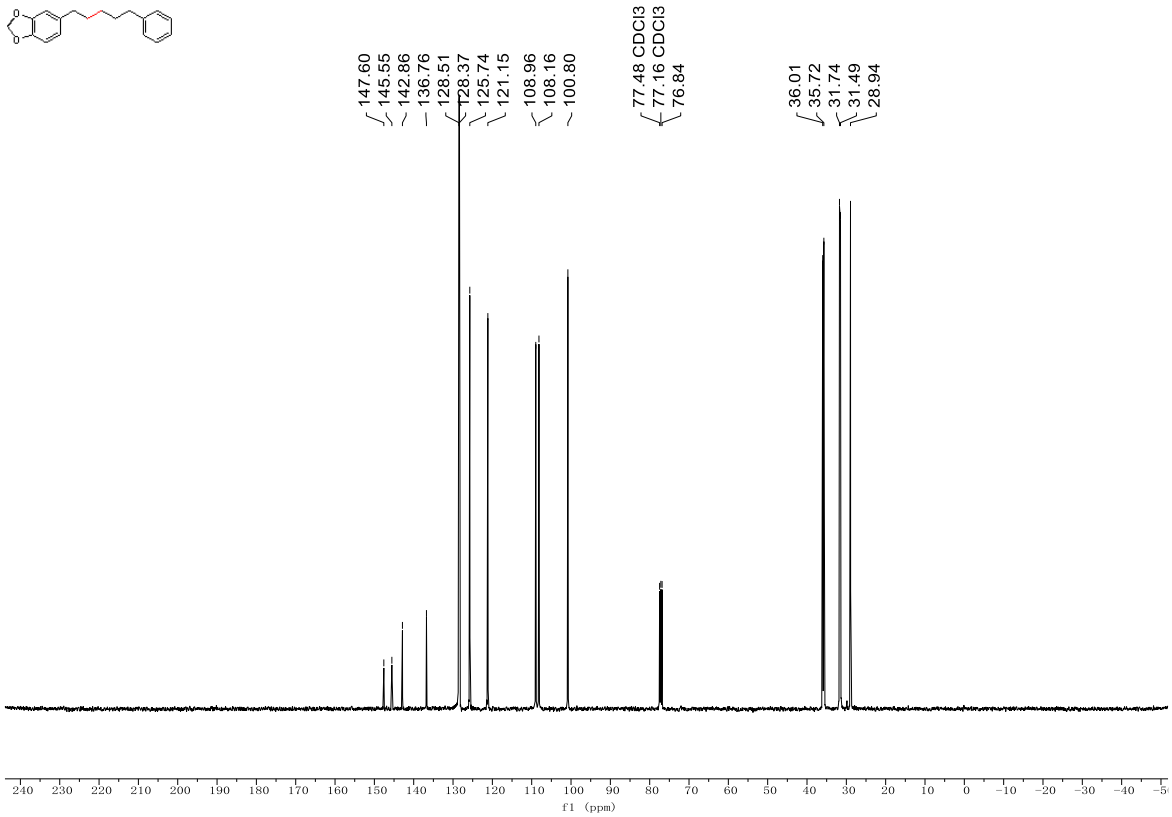
Compound **4** ^{13}C NMR



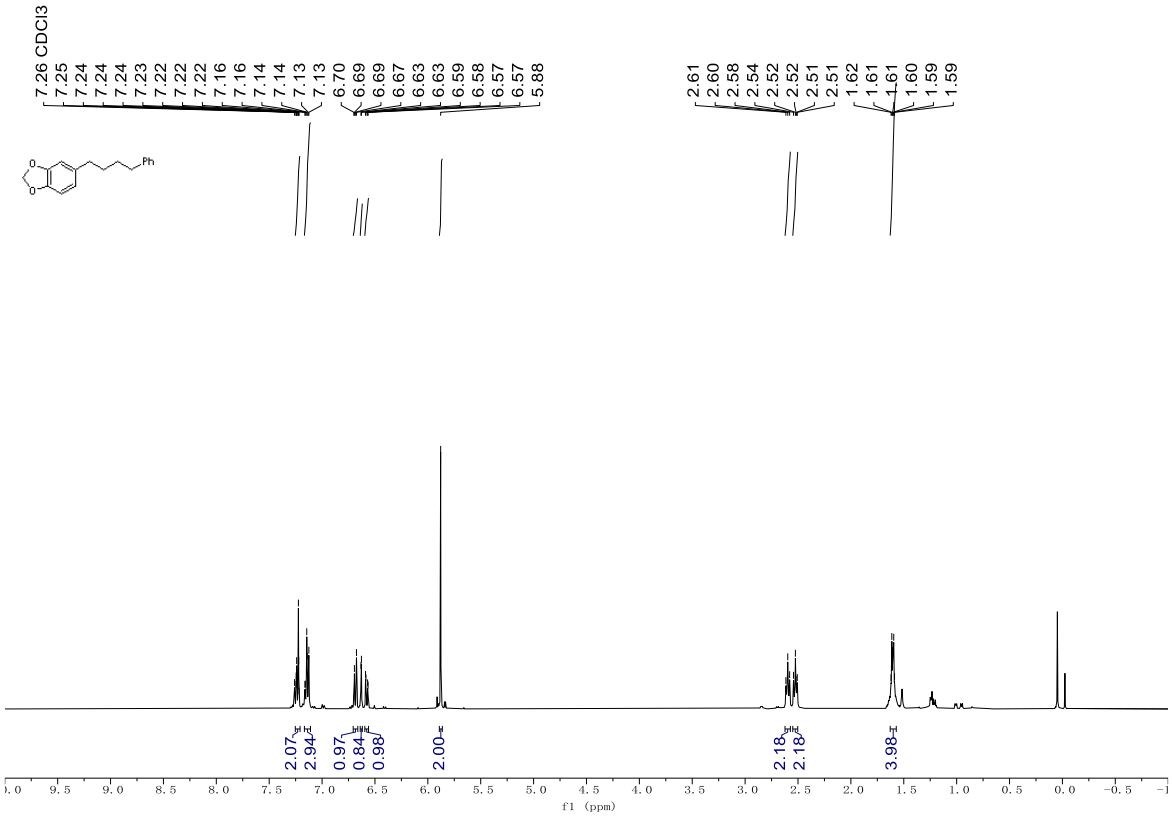
Compound **5** ^{1}H NMR



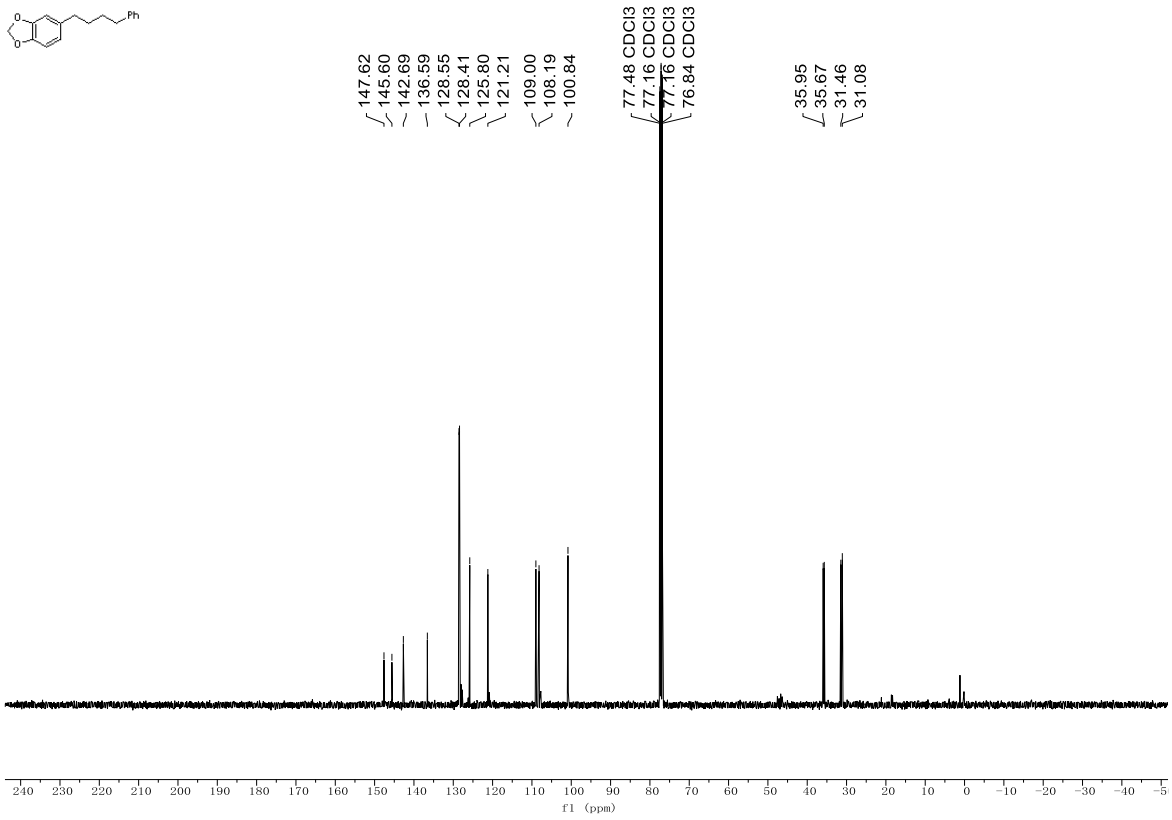
Compound **5** ^{13}C NMR



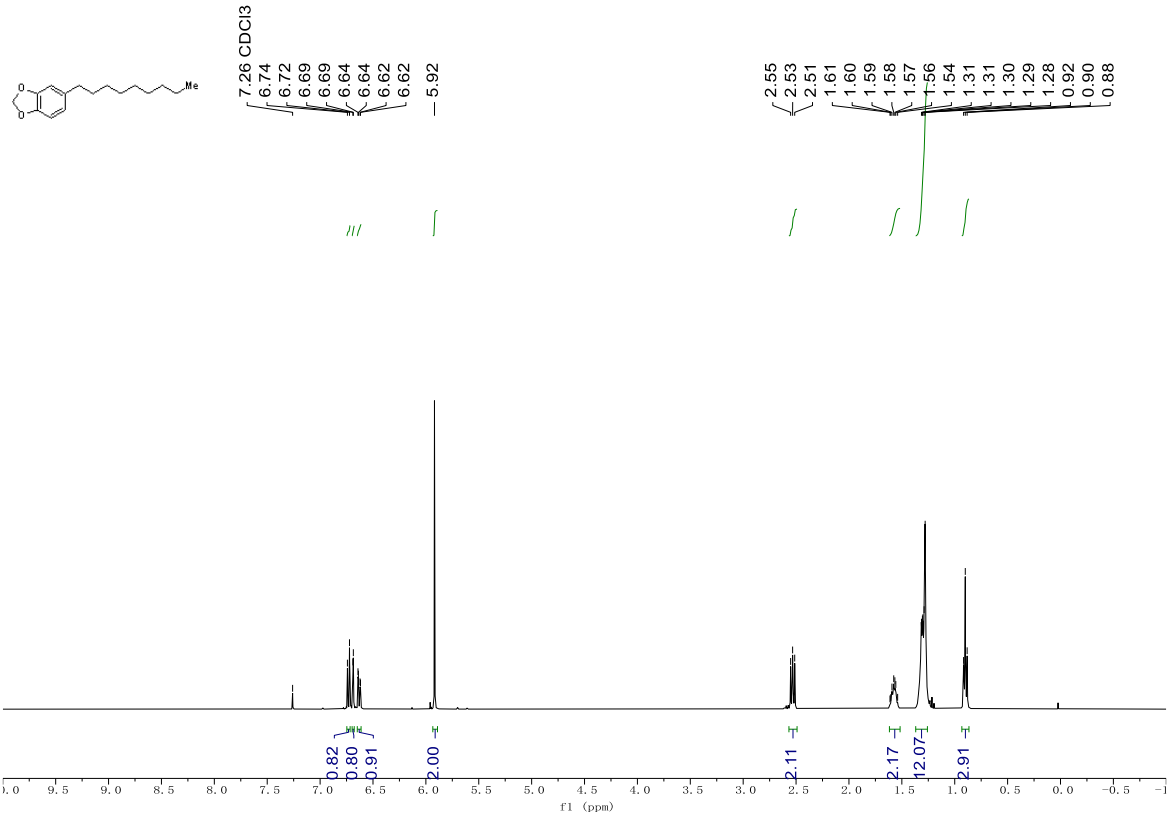
Compound **6** ^{1}H NMR



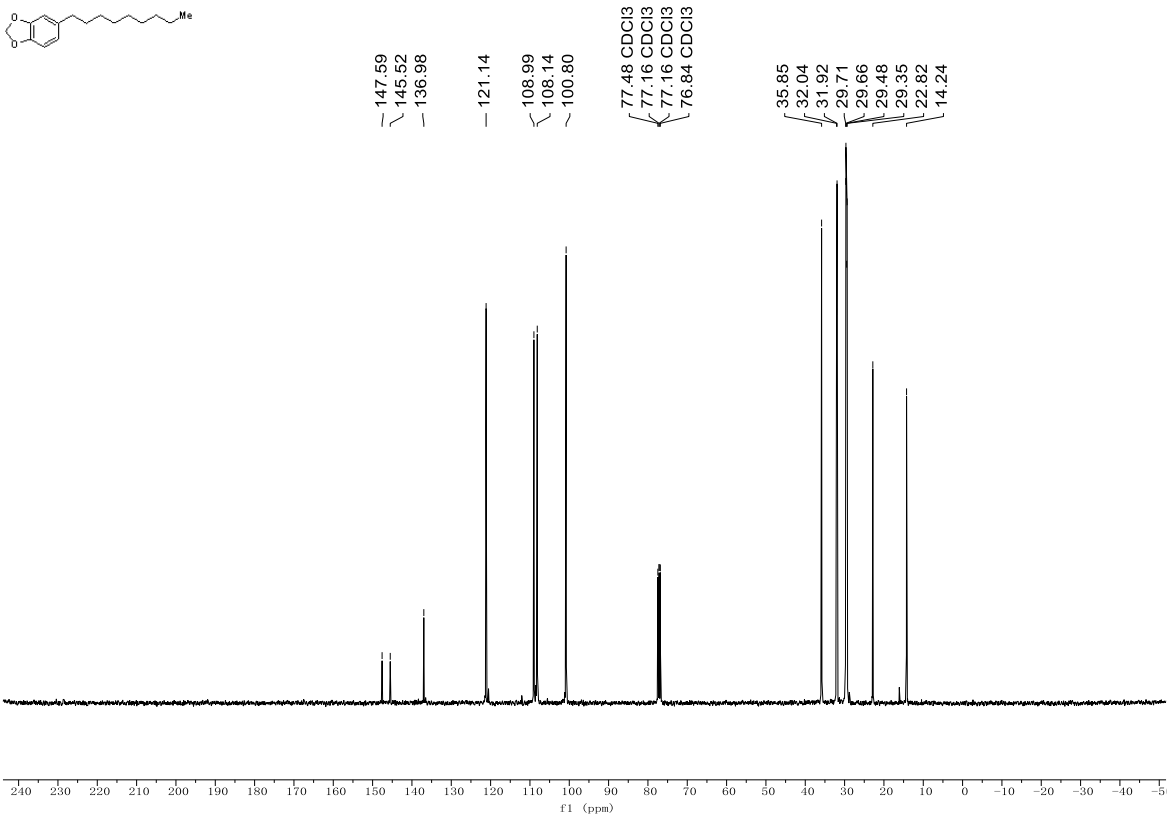
Compound **6** ^{13}C NMR



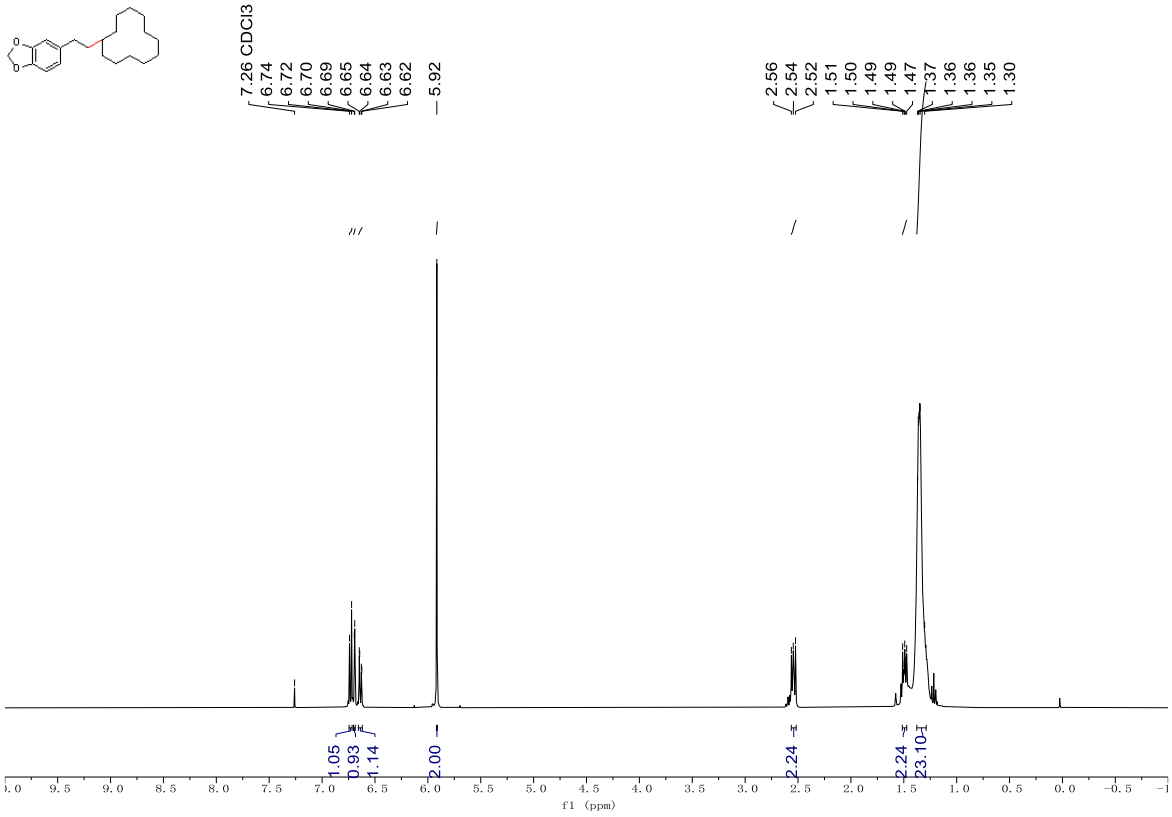
Compound **7** ^{1}H NMR



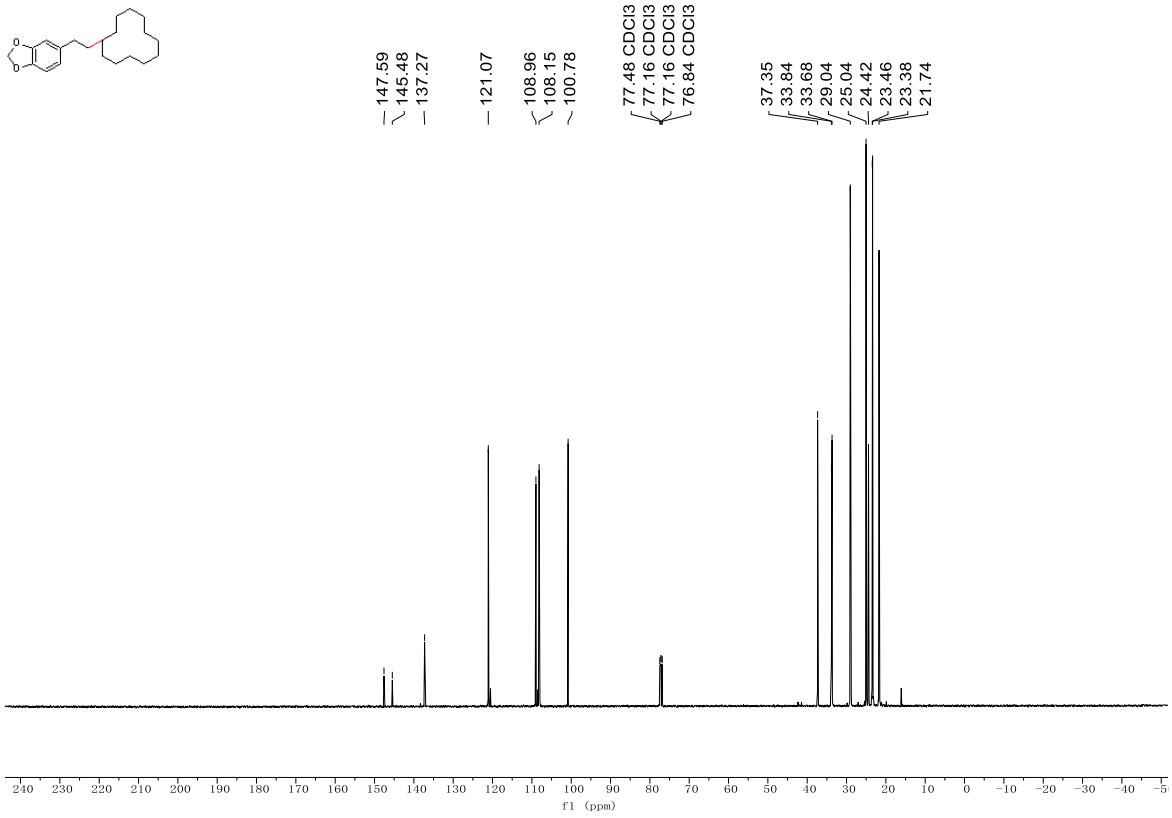
Compound **7** ^{13}C NMR



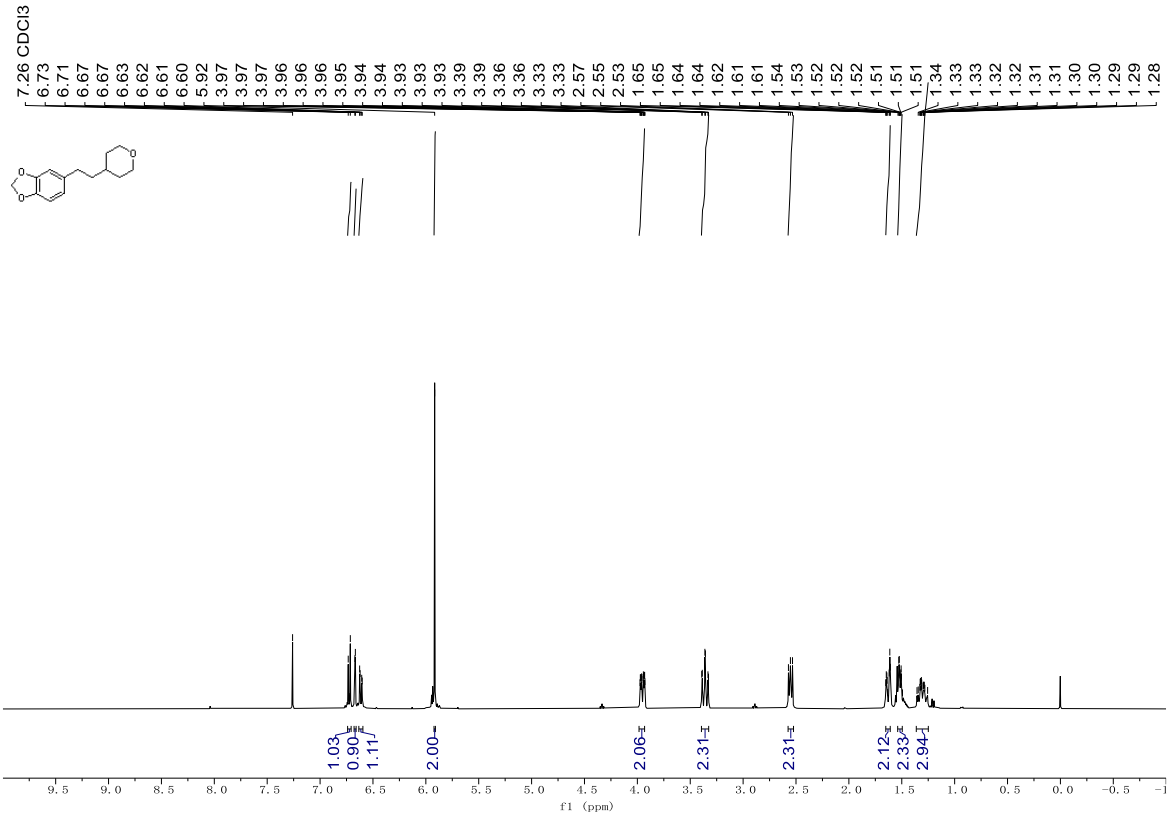
Compound **8** ^{1}H NMR



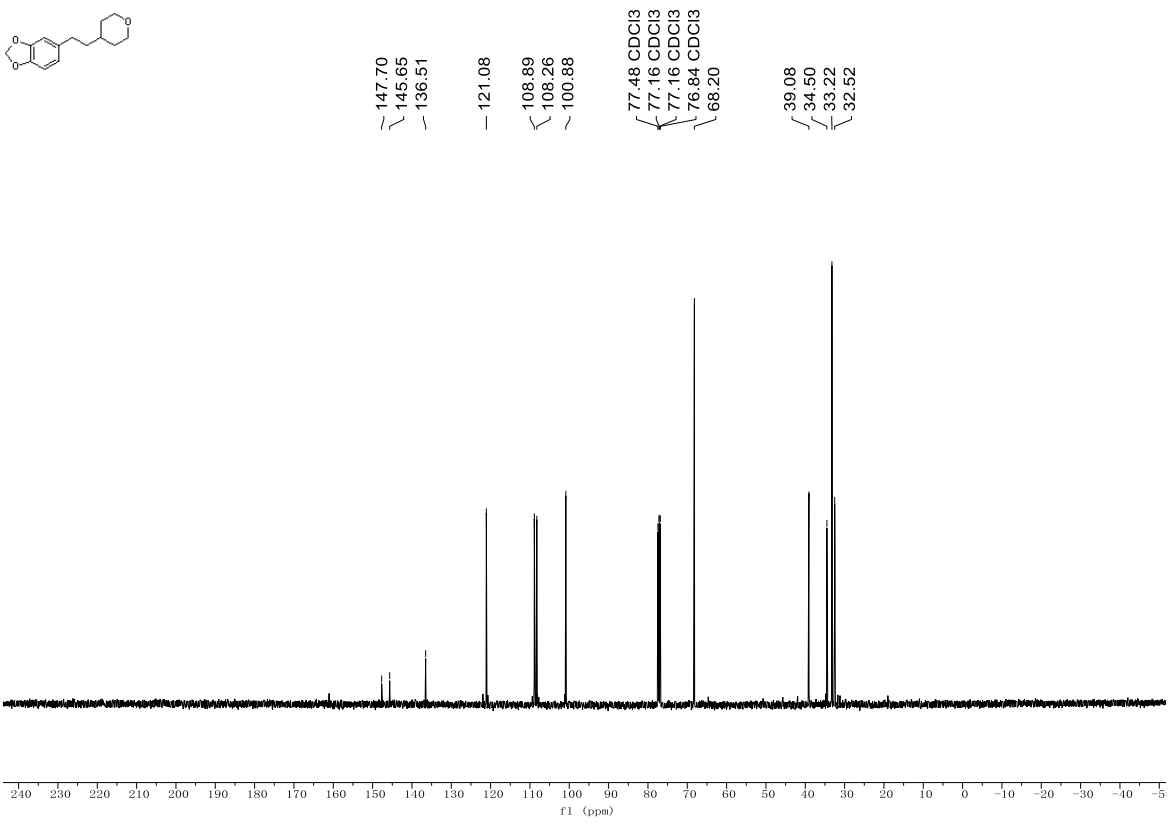
Compound **8** ^{13}C NMR



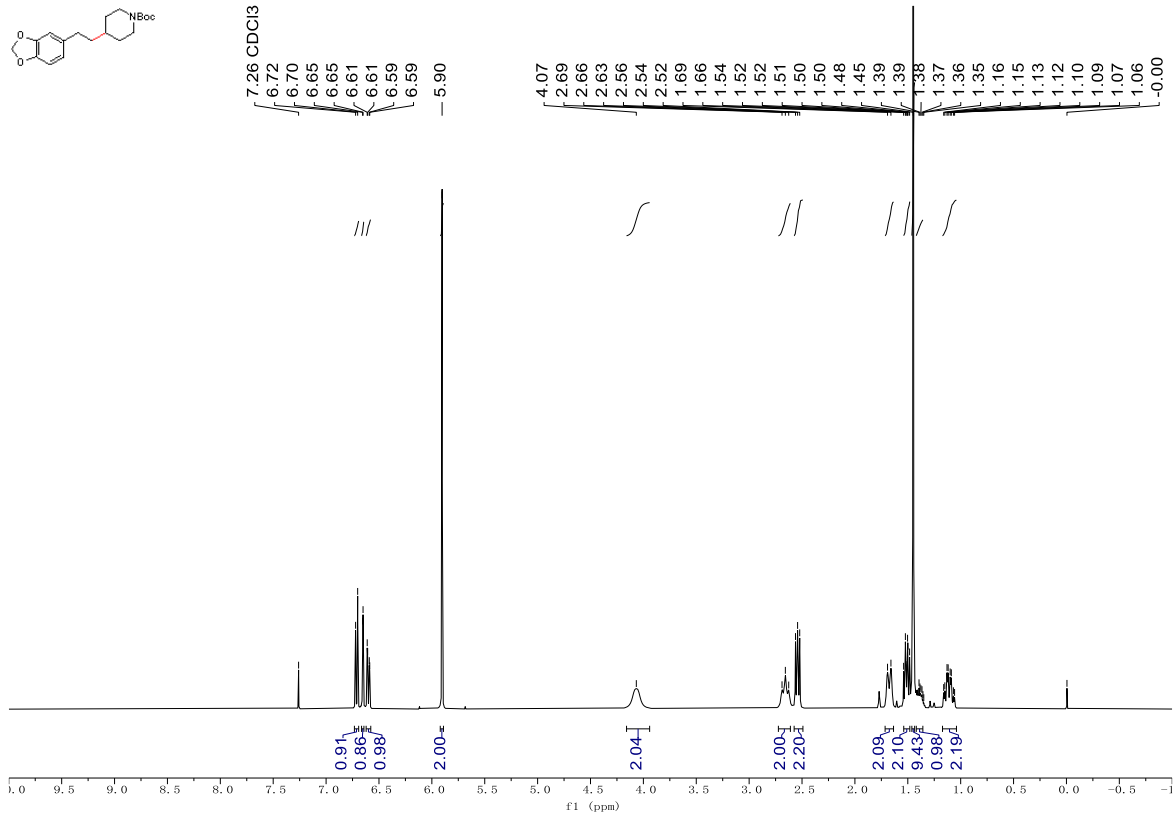
Compound **9** ^{1}H NMR



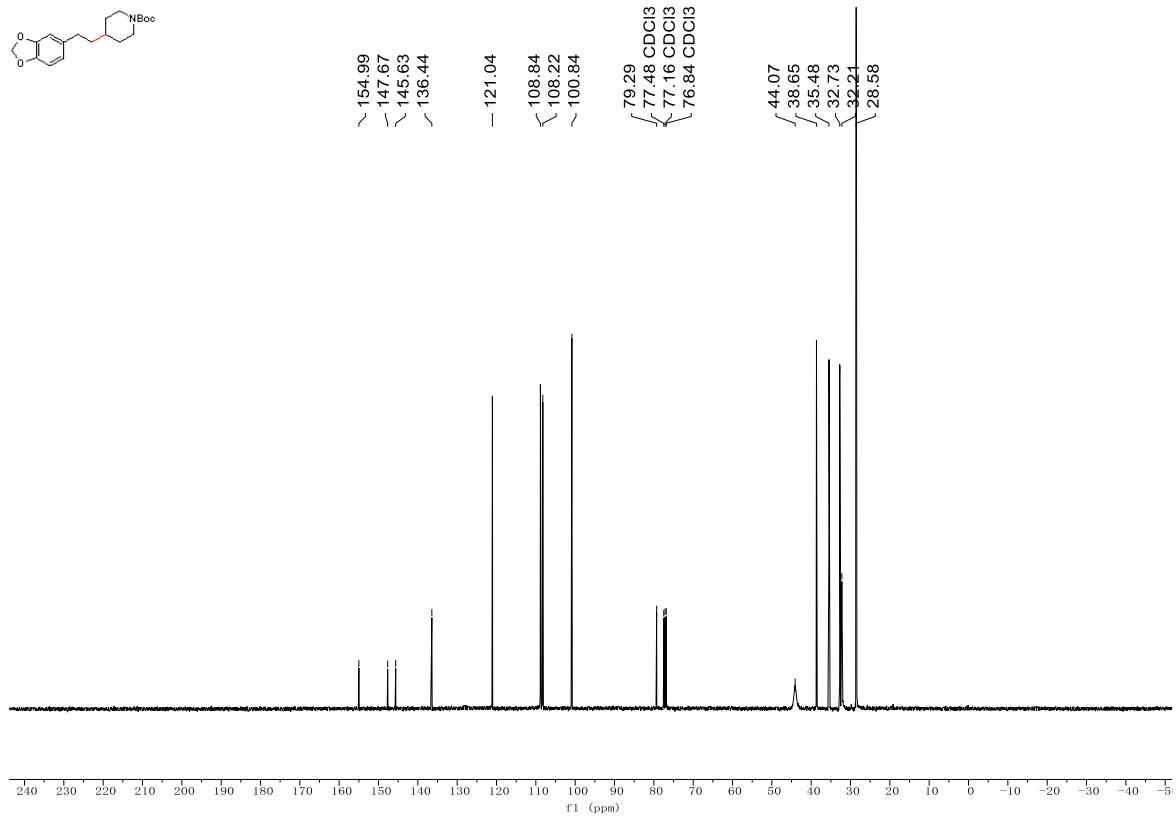
Compound **9** ^{13}C NMR



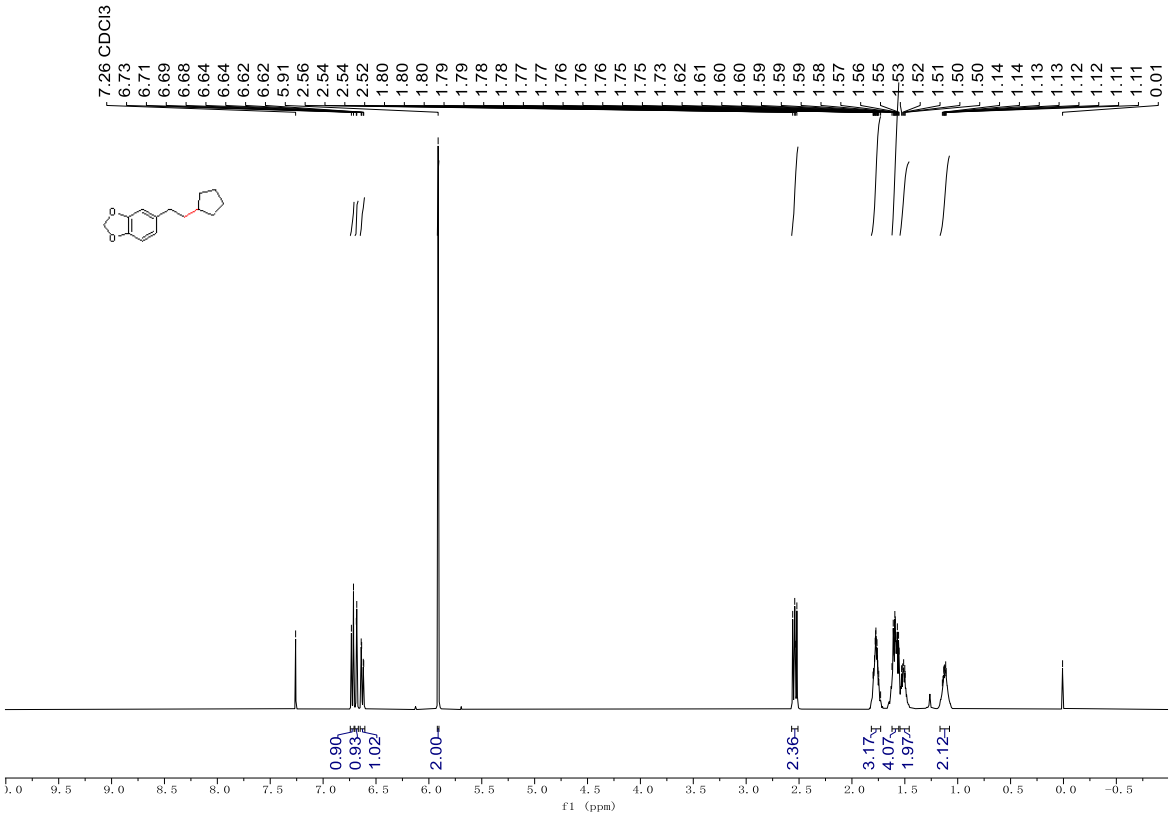
Compound **10** ^{1}H NMR



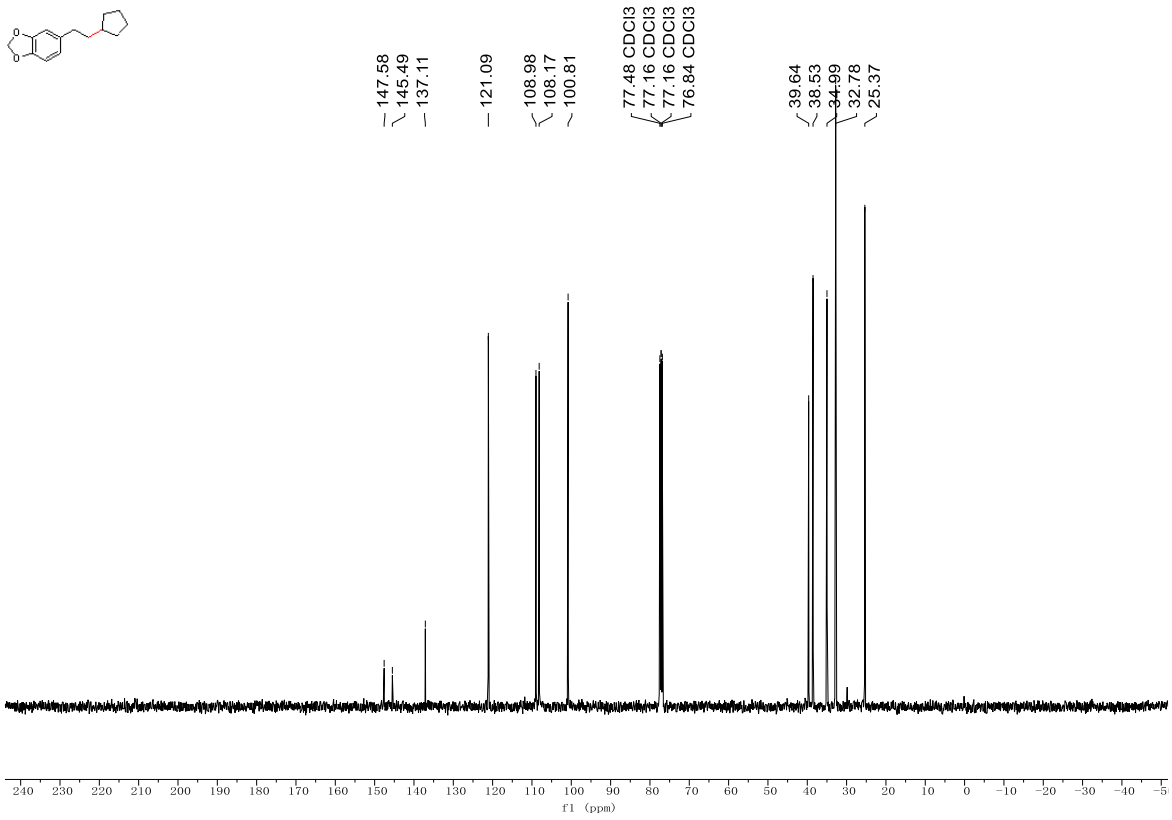
Compound **10** ^{13}C NMR



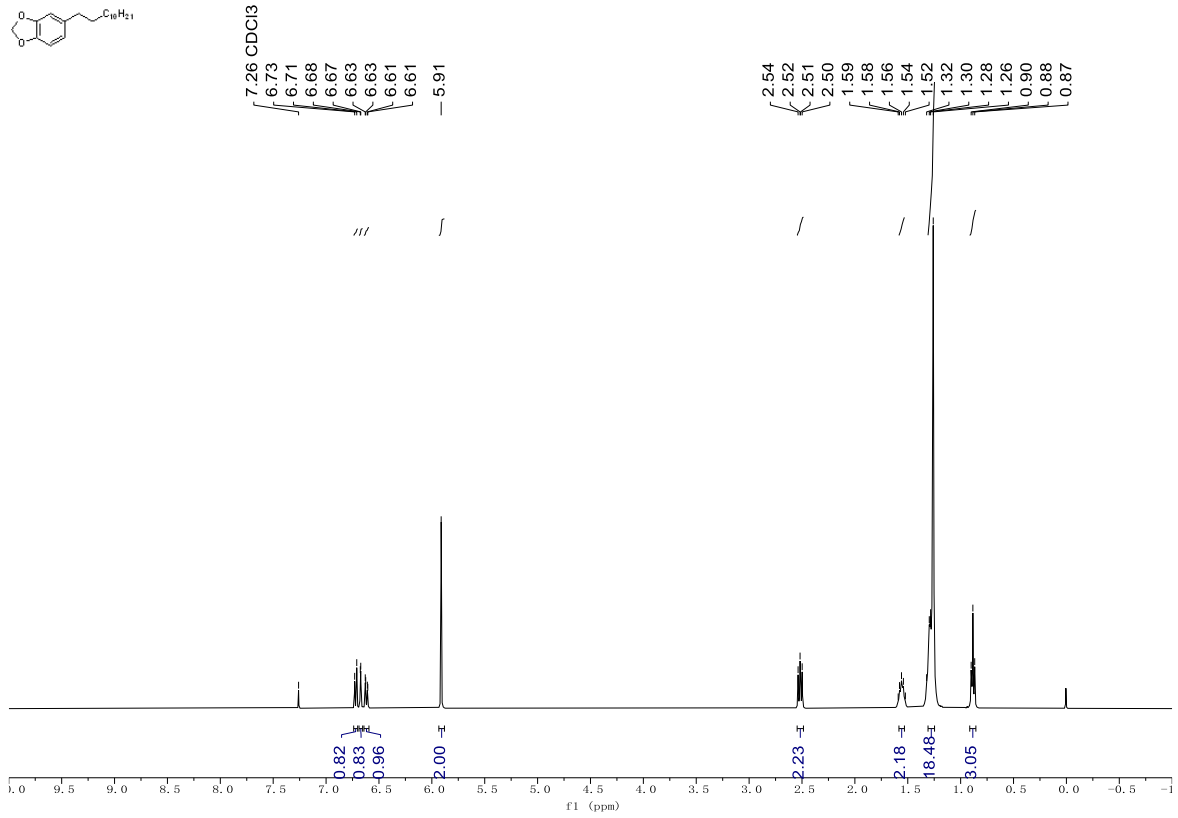
Compound **11** ^{1}H NMR



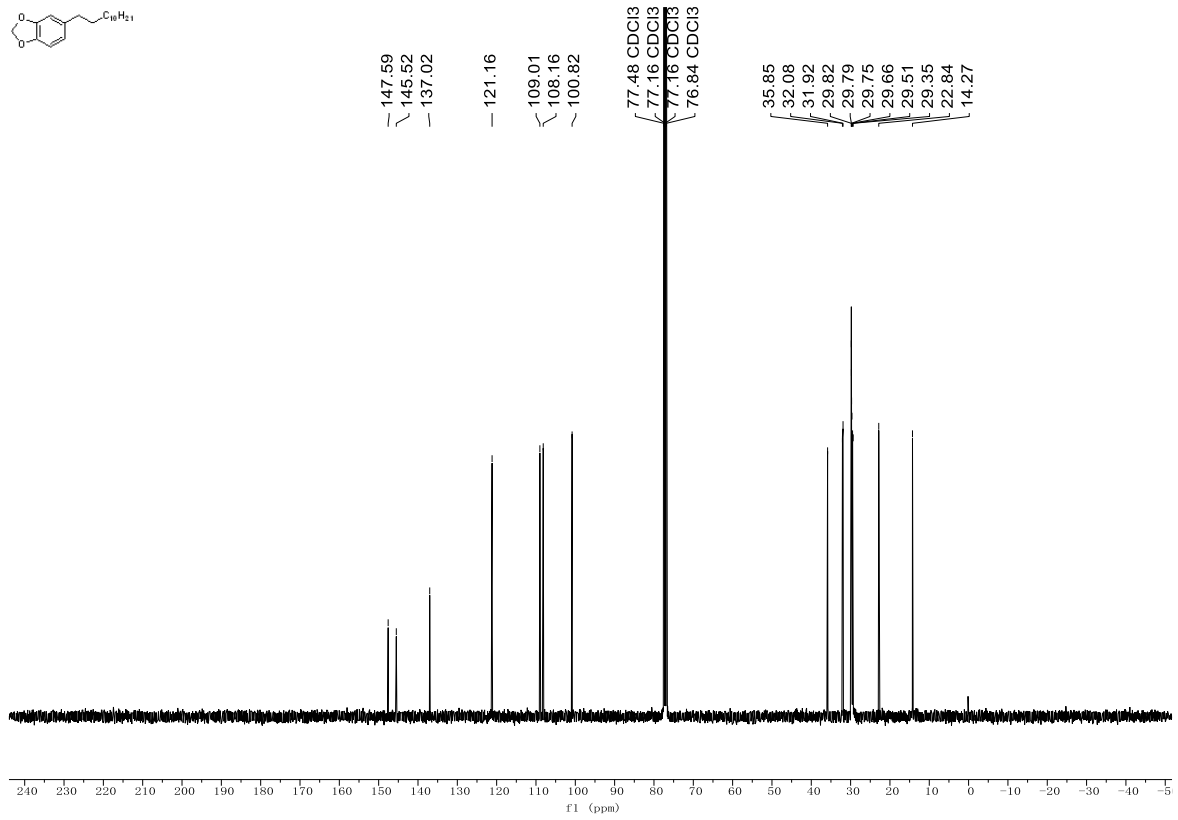
Compound **11** ^{13}C NMR



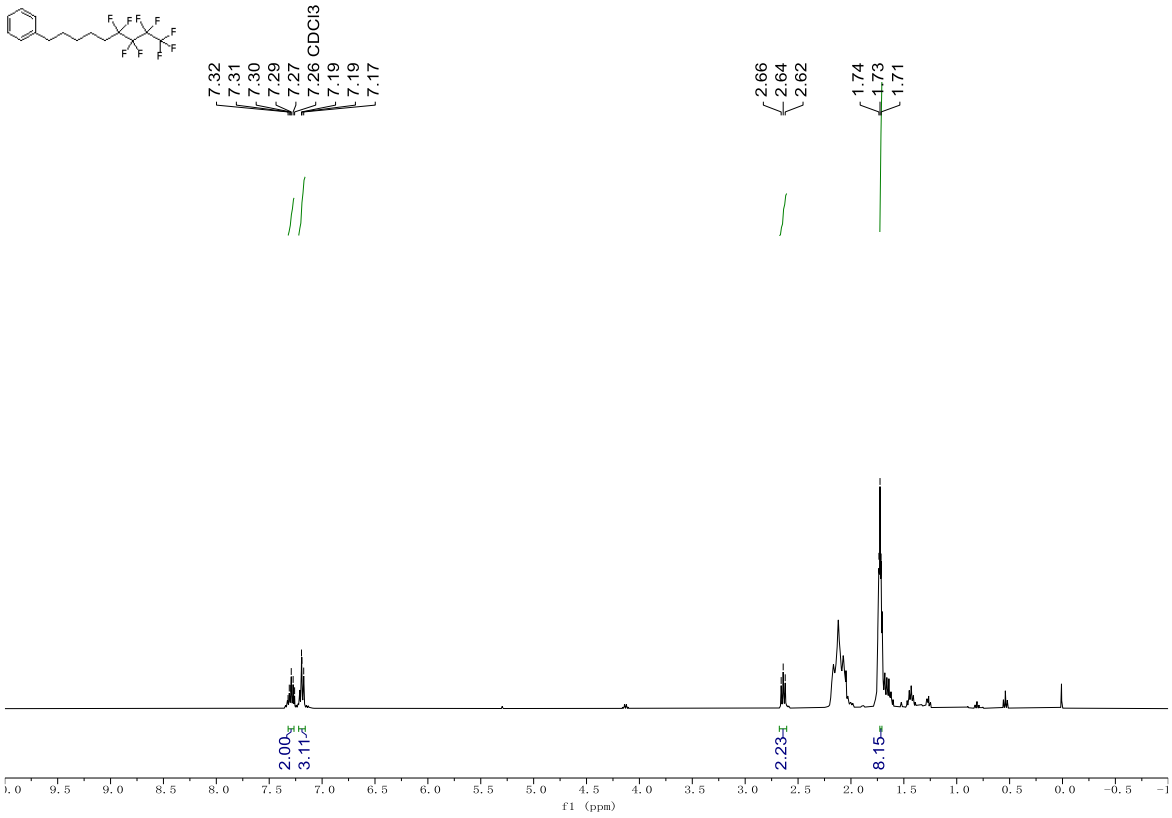
Compound **12** ^{1}H NMR



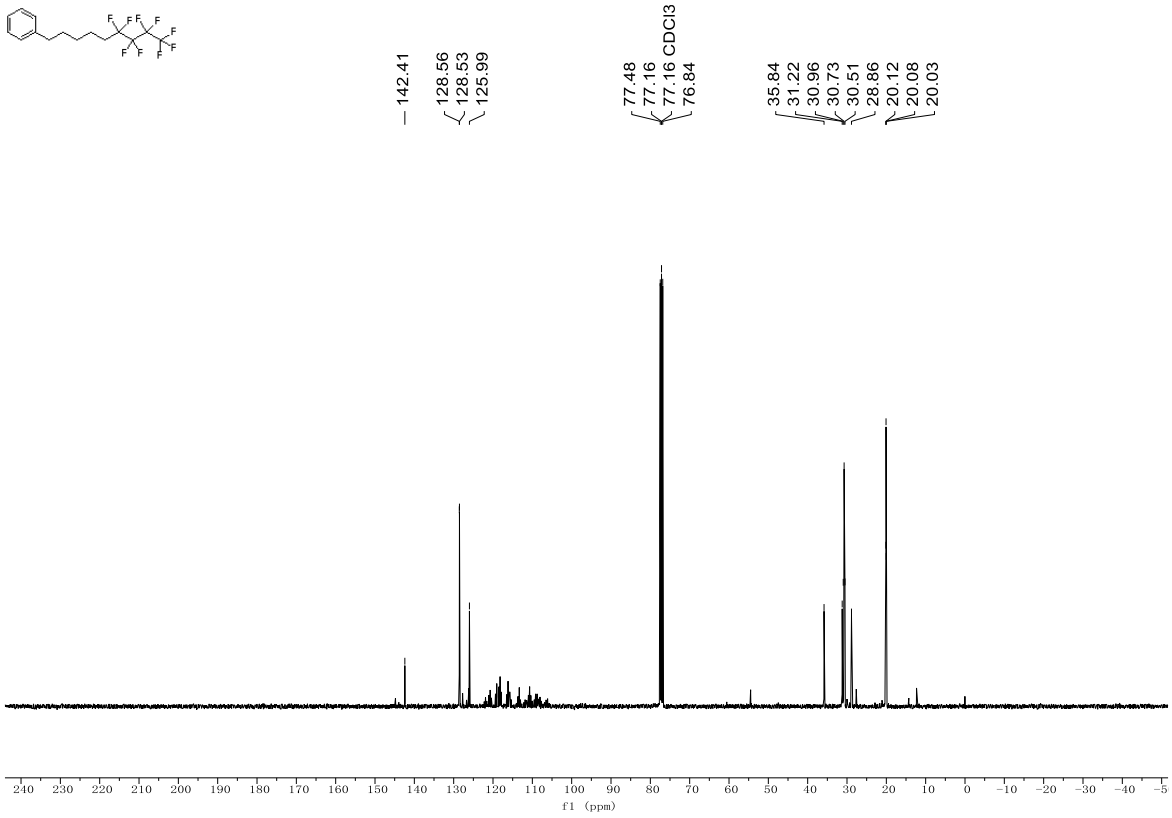
Compound **12** ^{13}C NMR



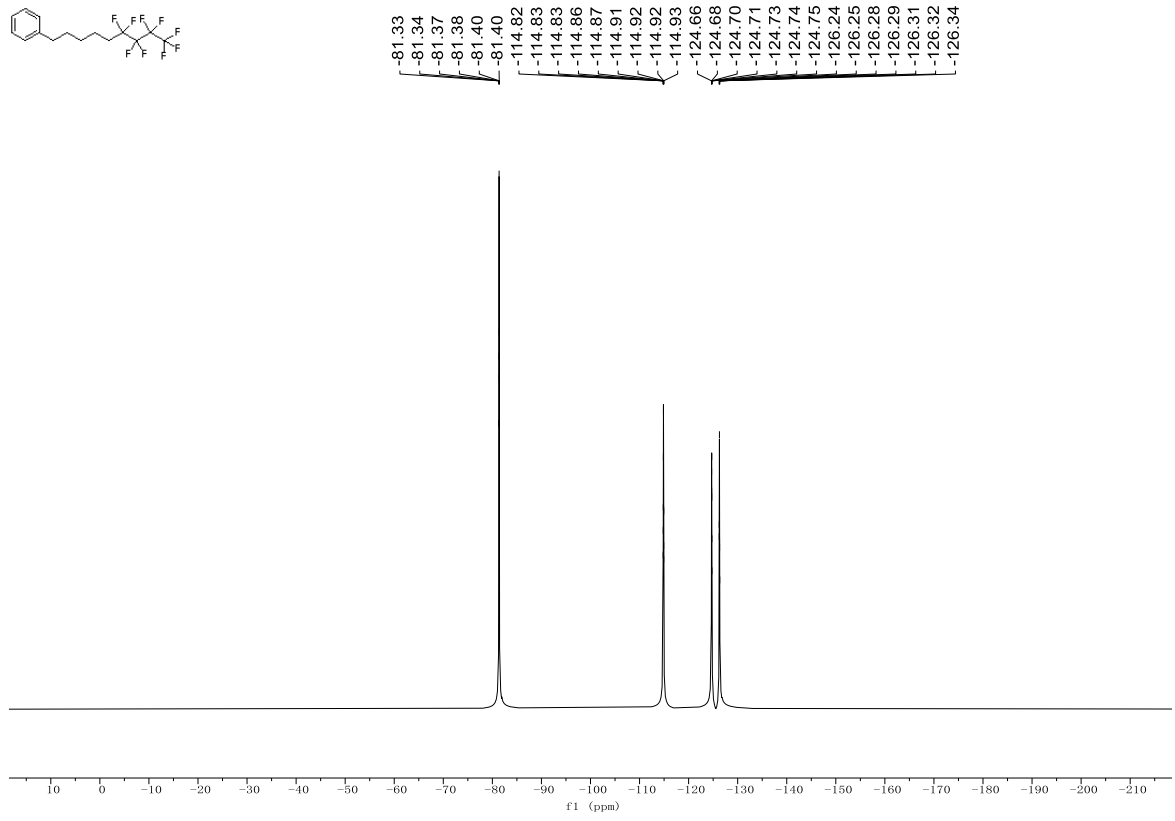
Compound **13** ^{1}H NMR



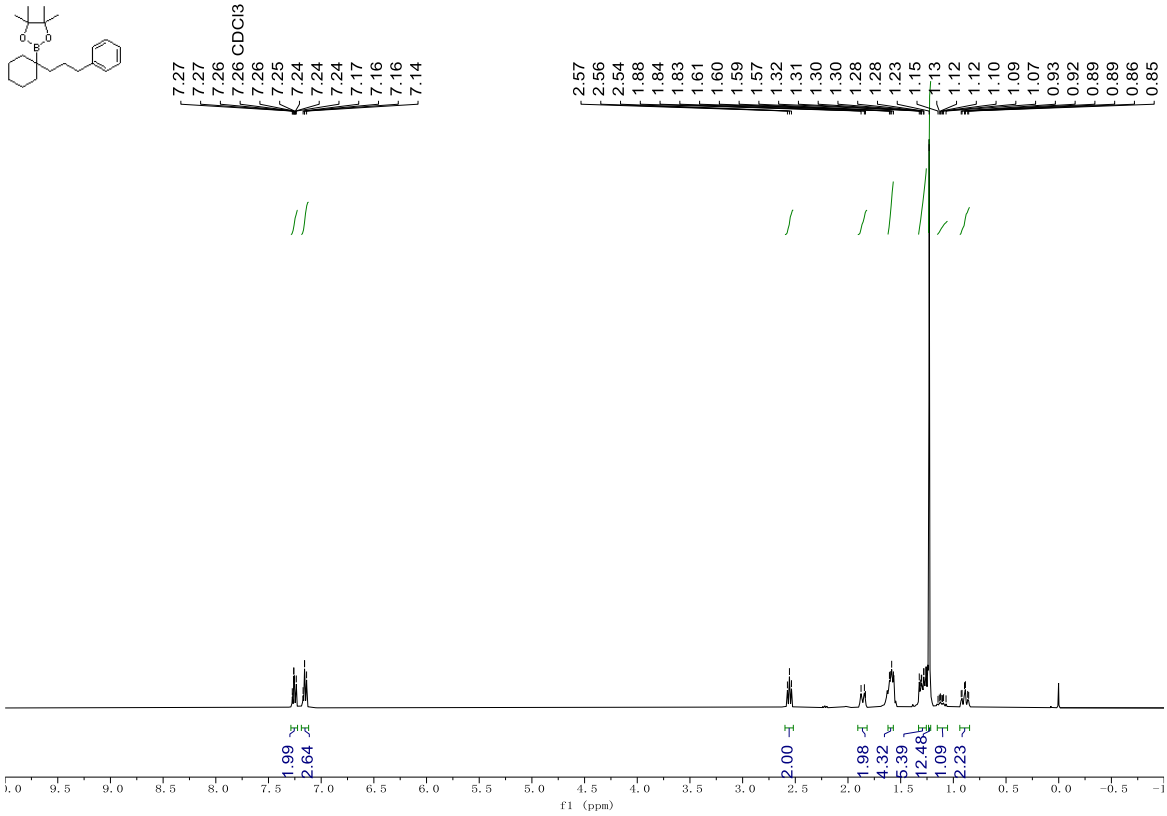
Compound **13** ^{13}C NMR



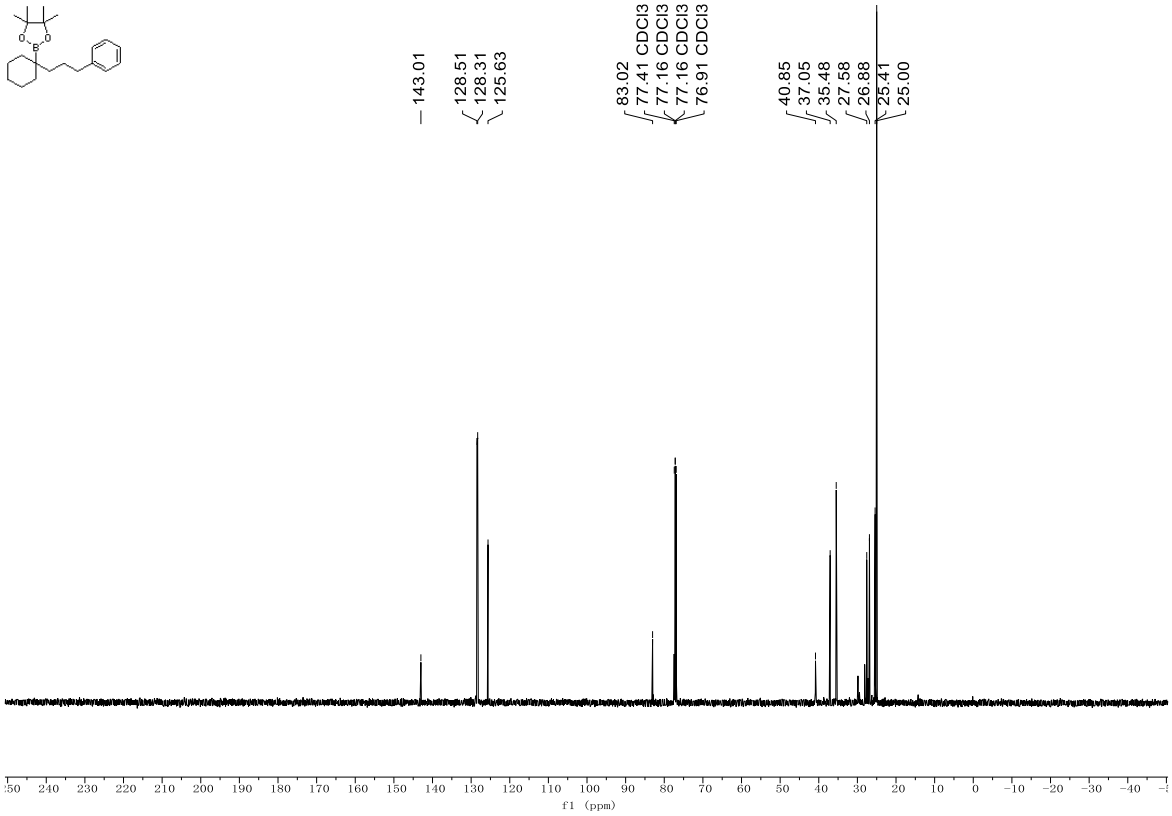
Compound **13** ^{19}F NMR



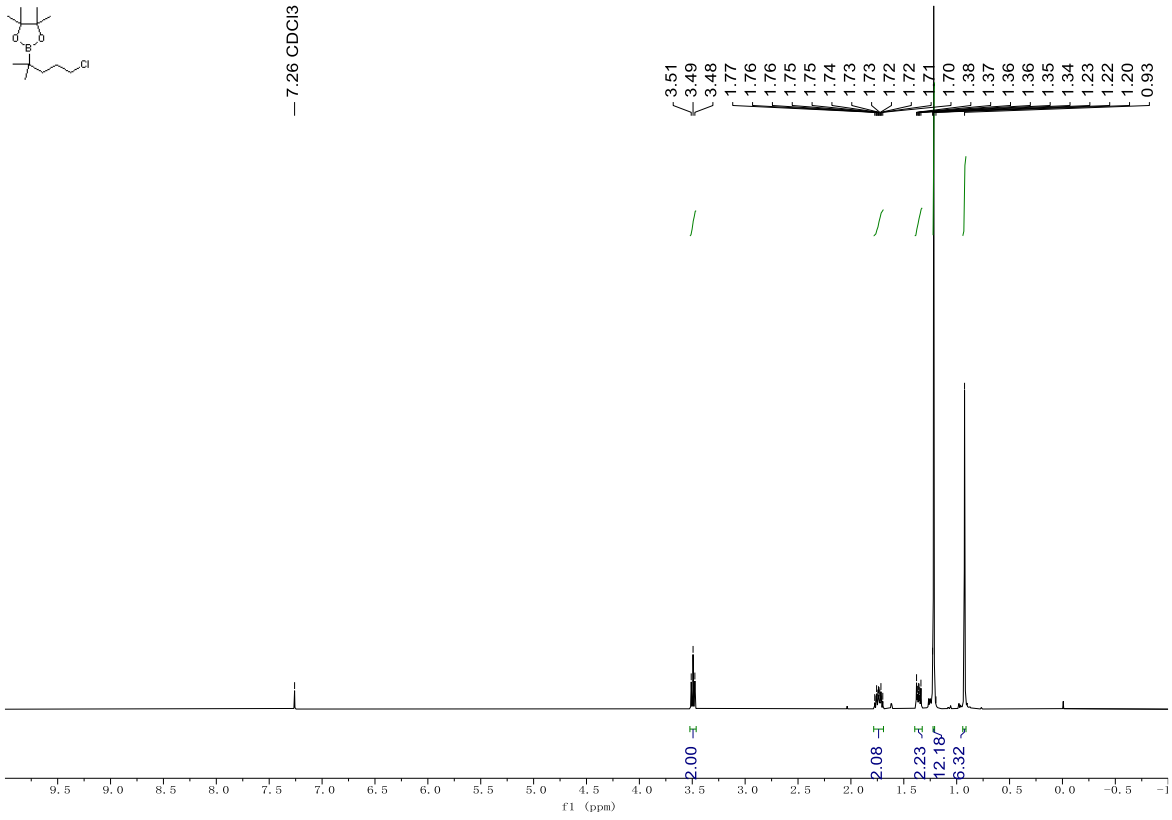
Compound **14** ^{1}H NMR



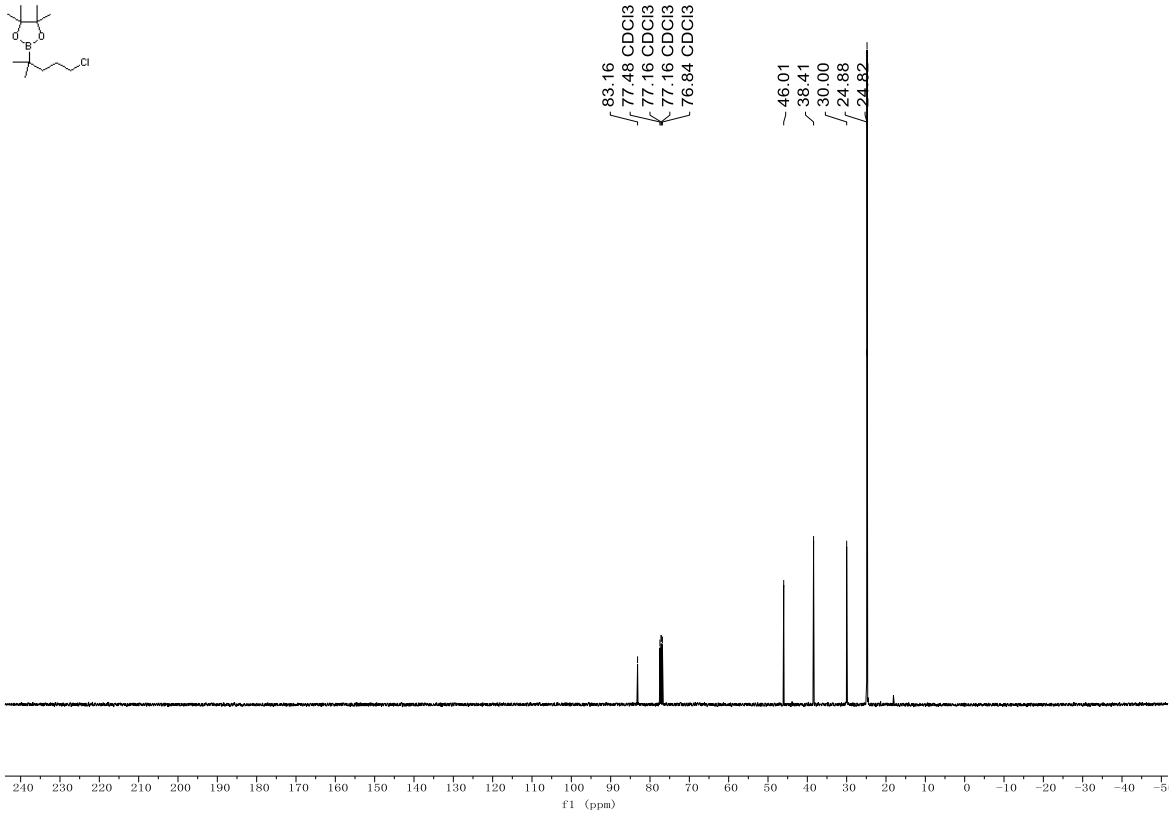
Compound **14** ^{13}C NMR



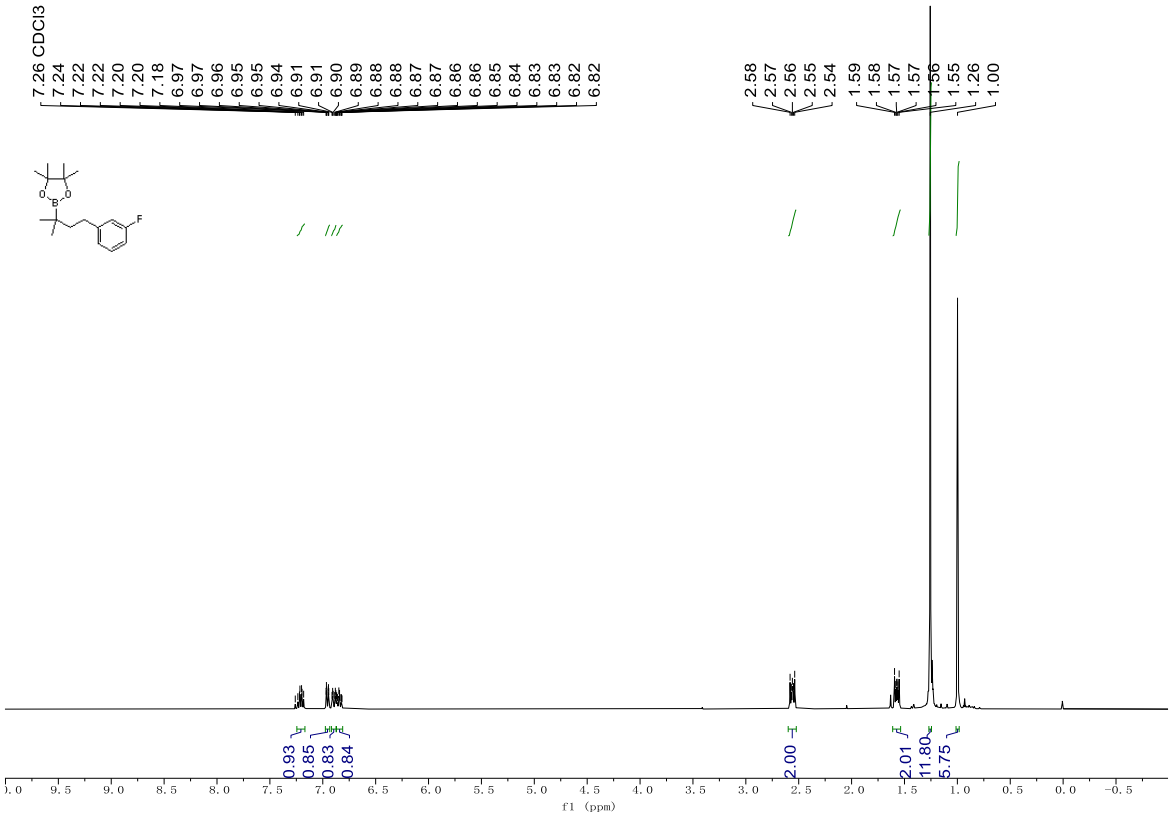
Compound **15** ^{1}H NMR



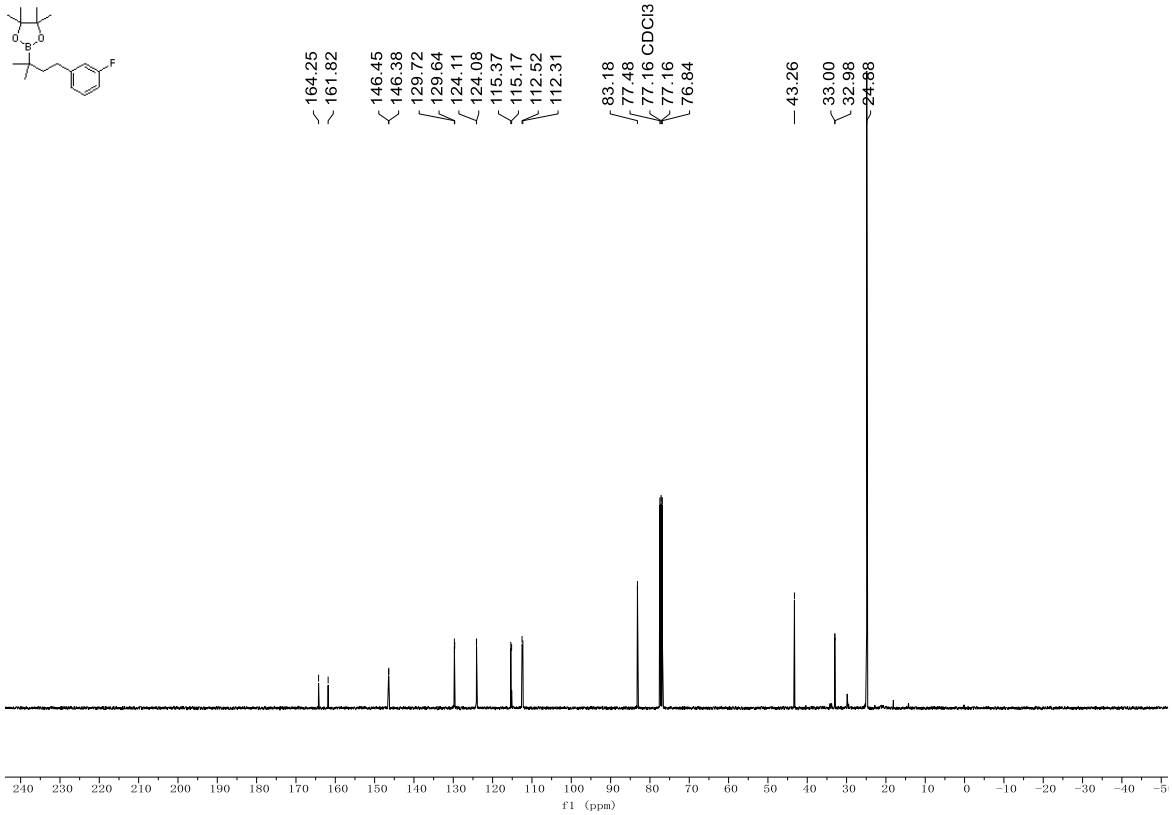
Compound **15** ^{13}C NMR



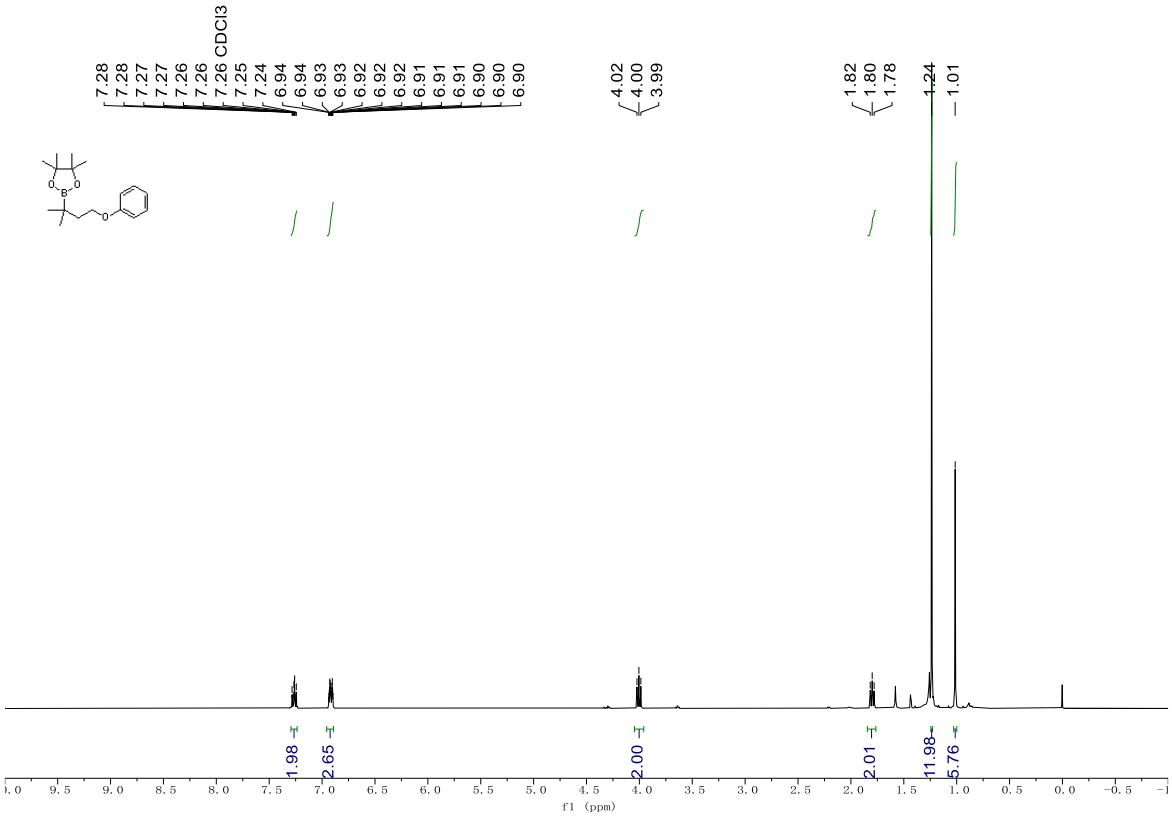
Compound **16** ^{1}H NMR



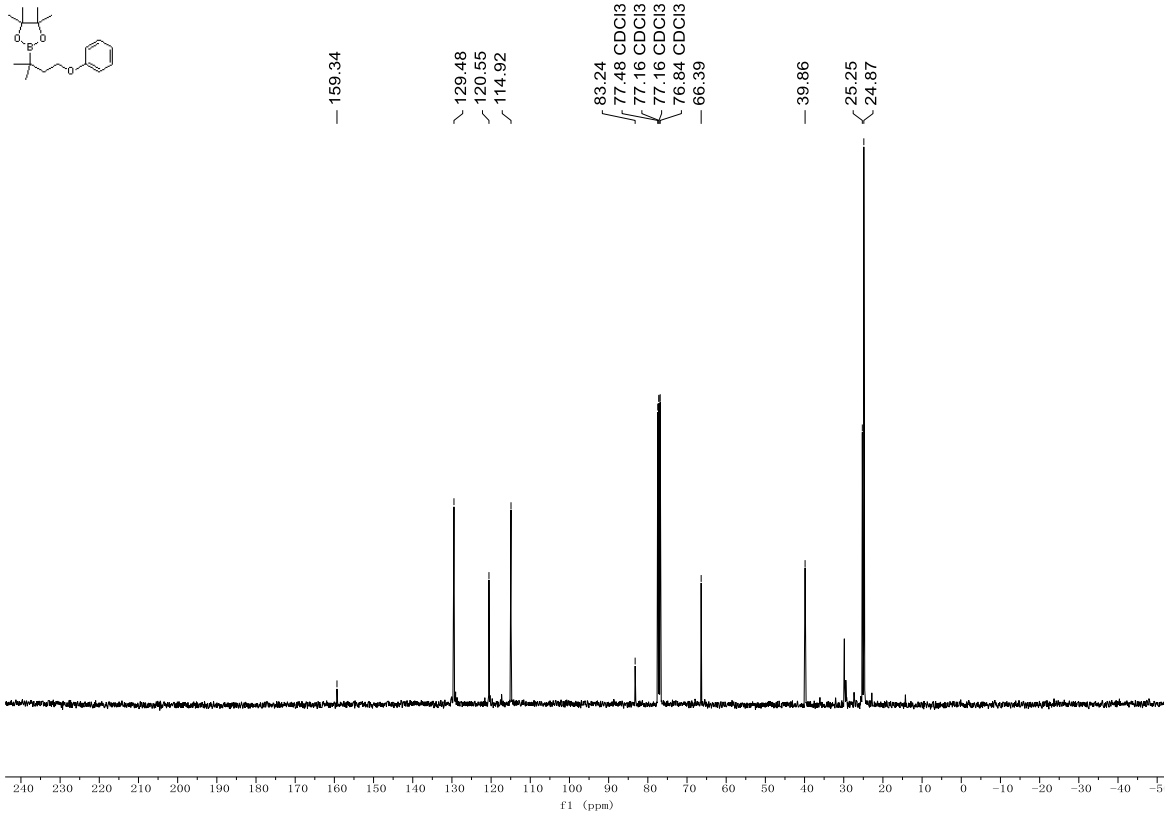
Compound **16** ^{13}C NMR



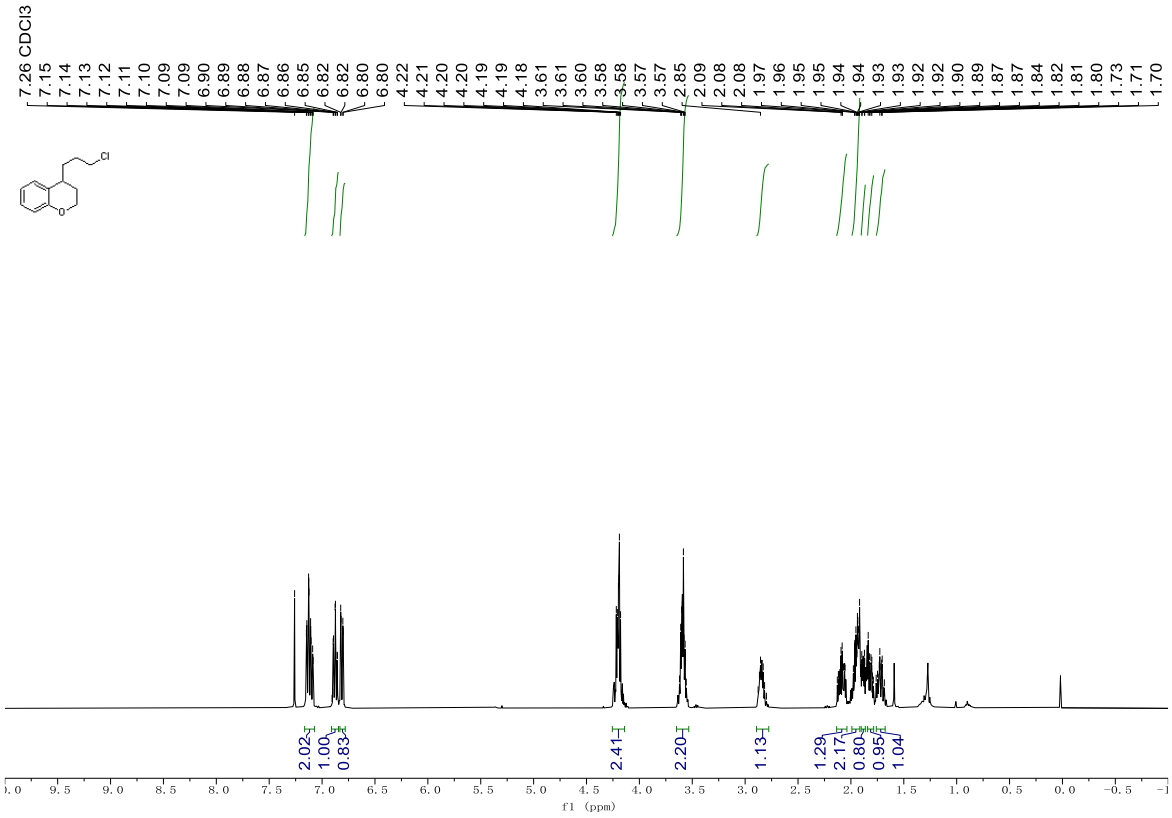
Compound **17** ^{1}H NMR



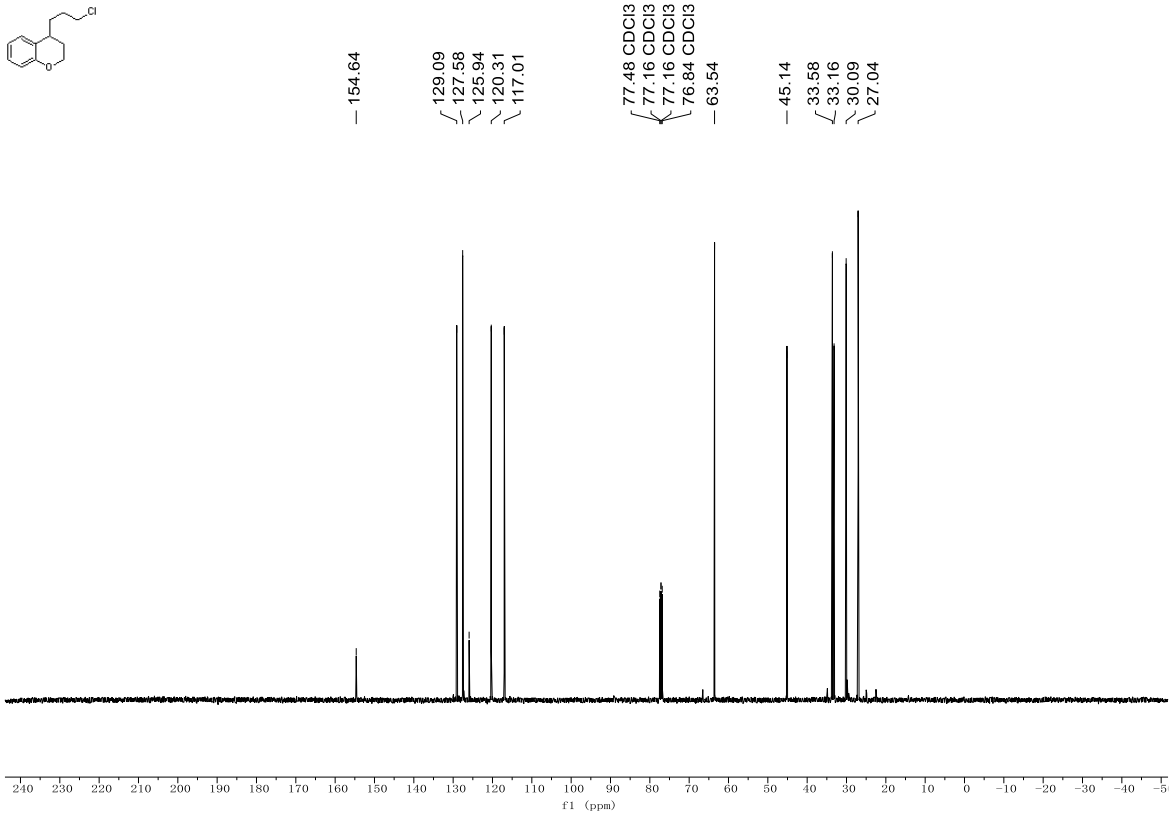
Compound **17** ^{13}C NMR



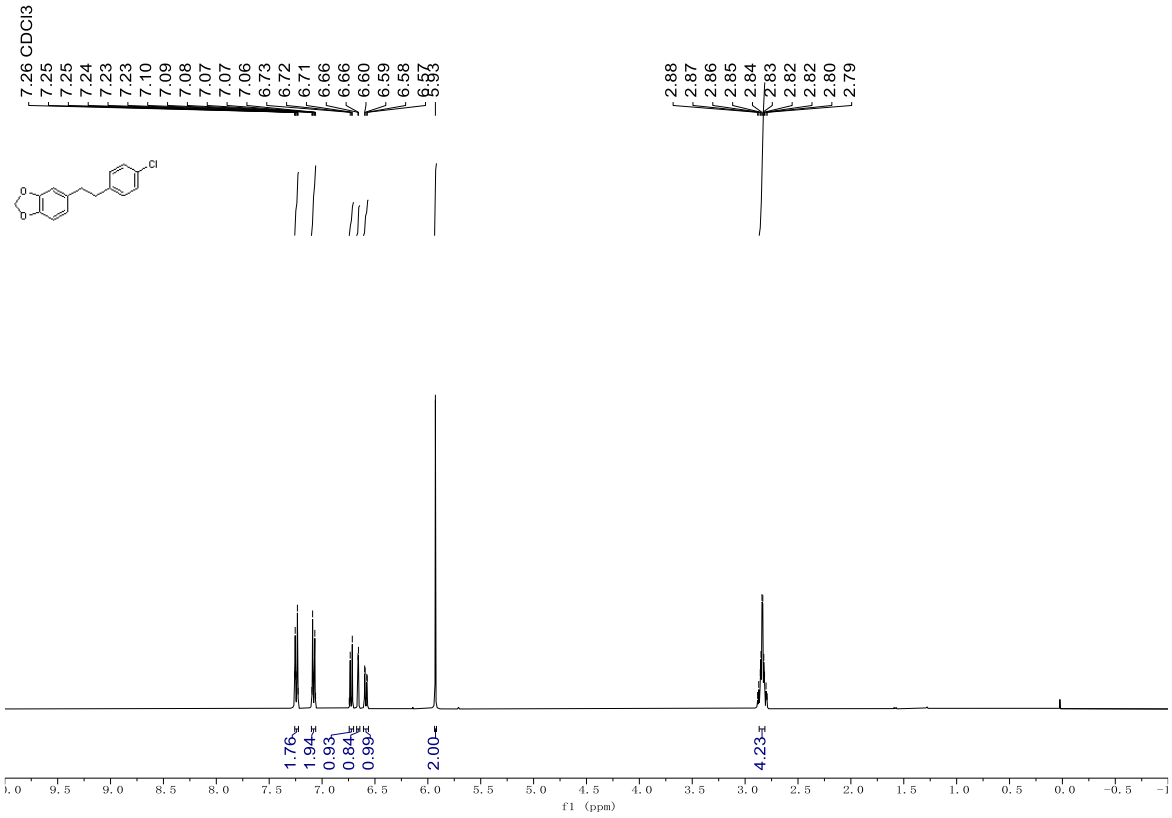
Compound **18** ^{1}H NMR



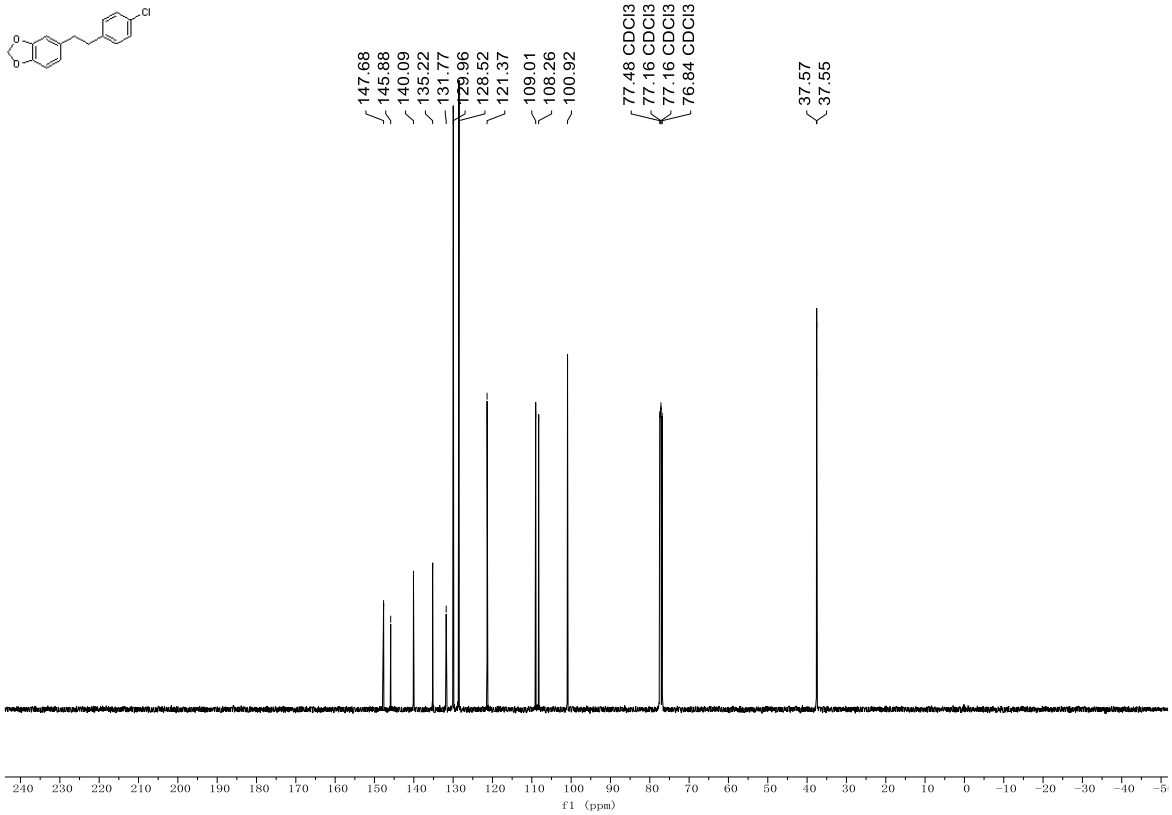
Compound **18** ^{13}C NMR



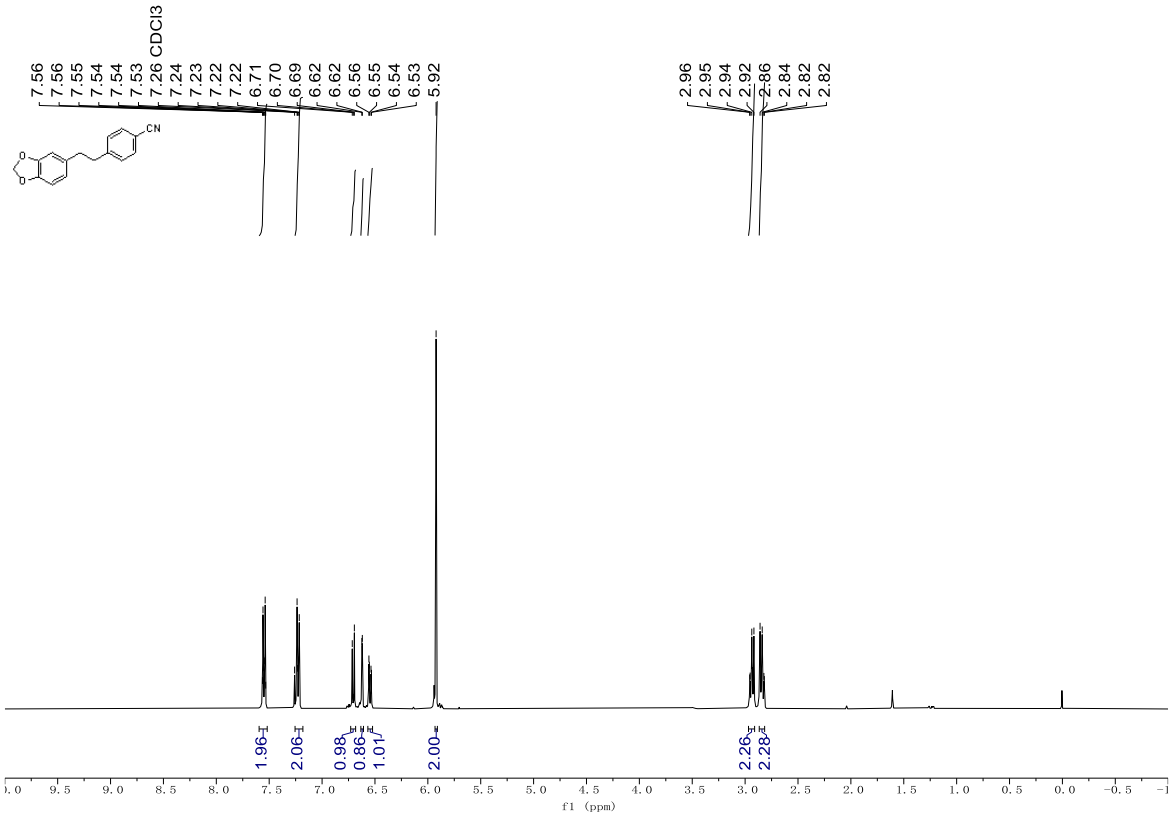
Compound **19** ^{1}H NMR



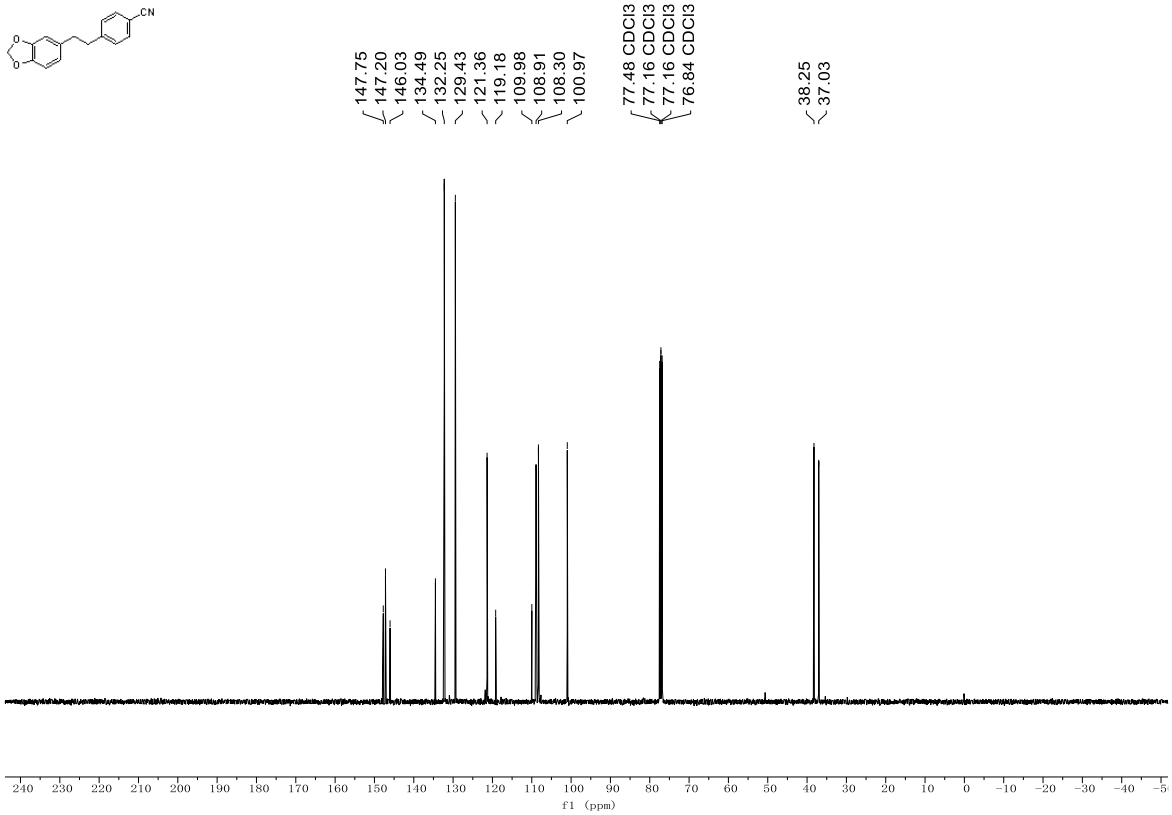
Compound **19** ^{13}C NMR



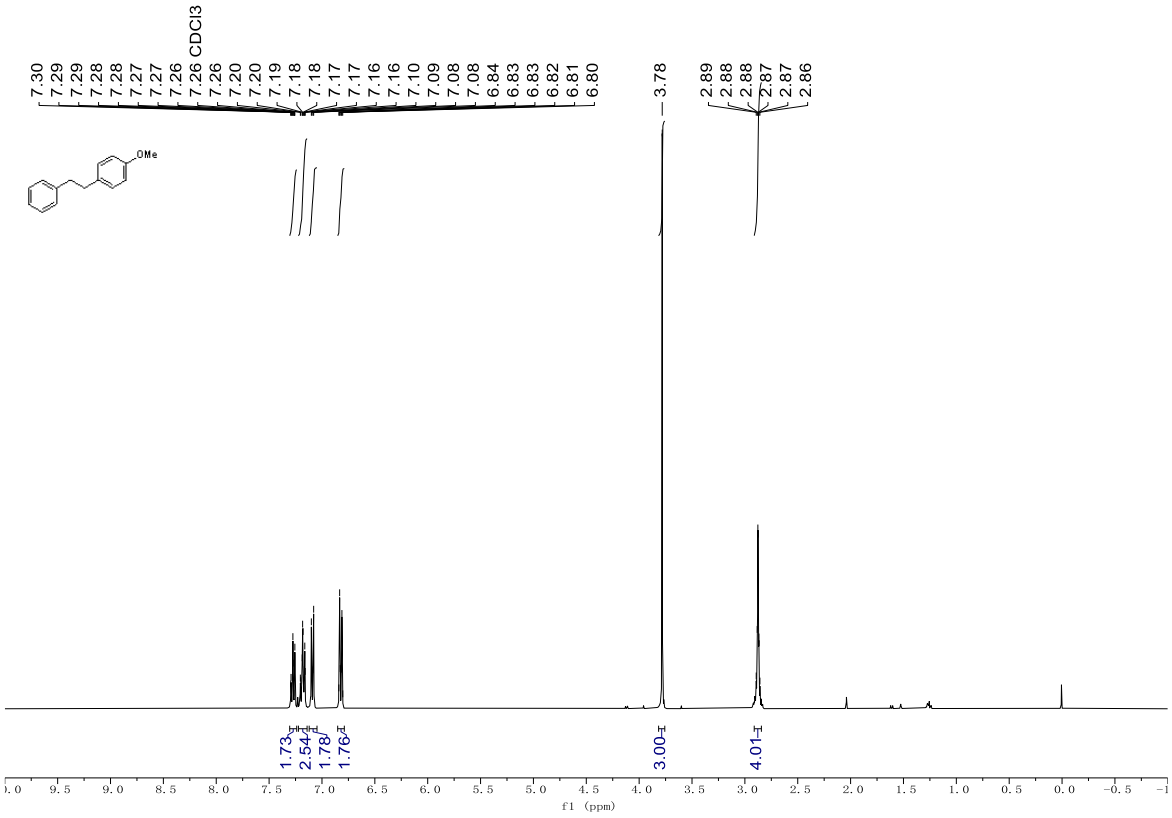
Compound **20** ^{1}H NMR



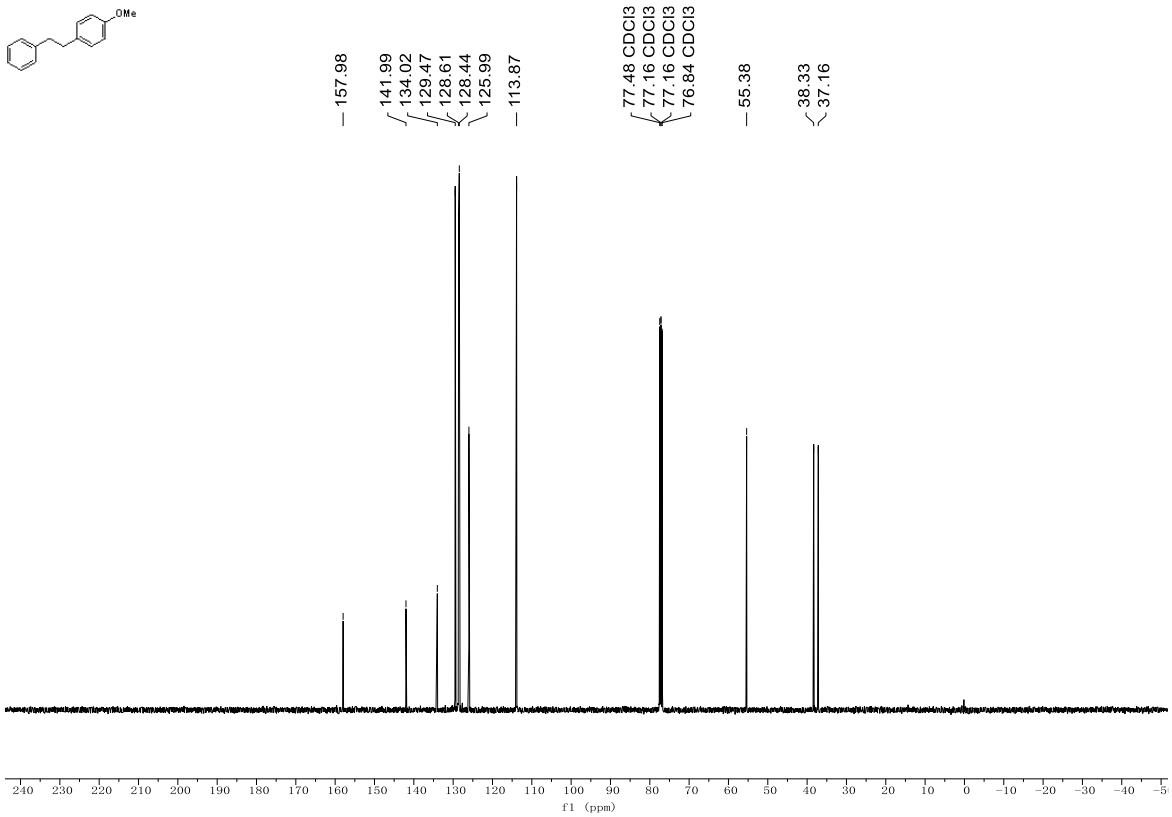
Compound **20** ^{13}C NMR



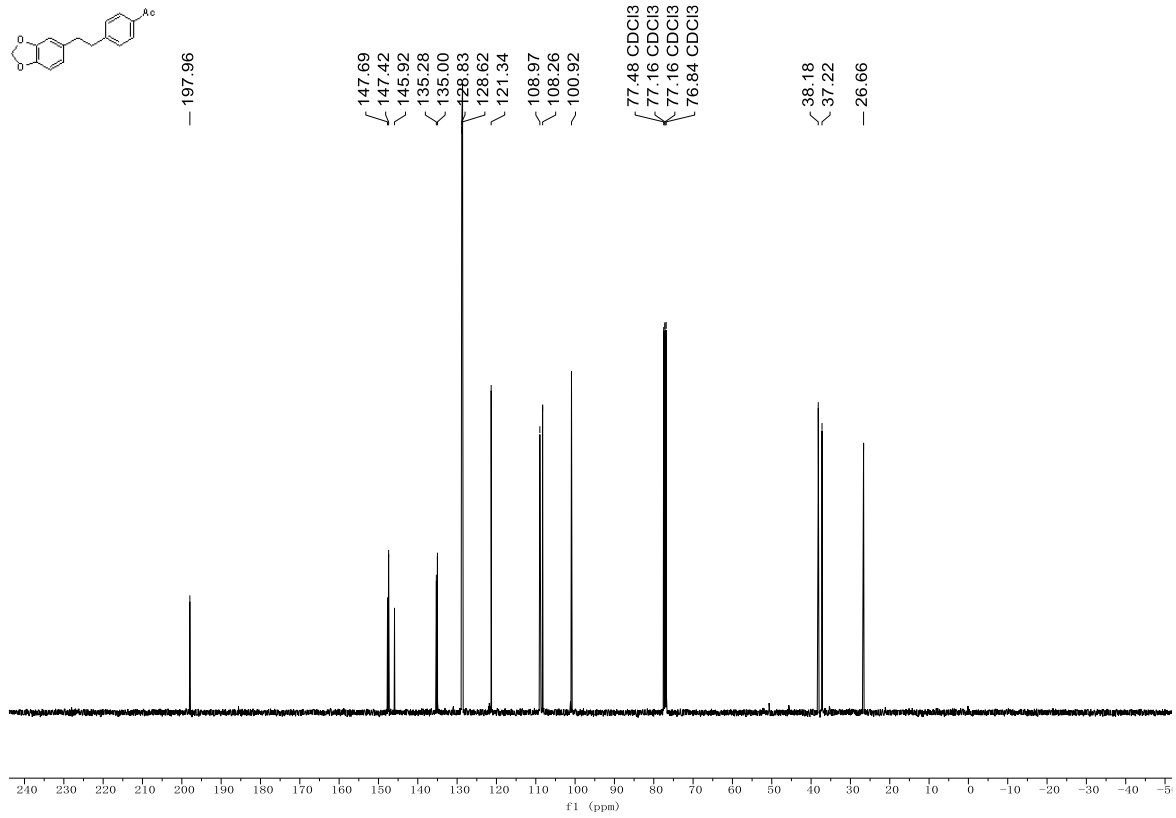
Compound **21** ^{1}H NMR



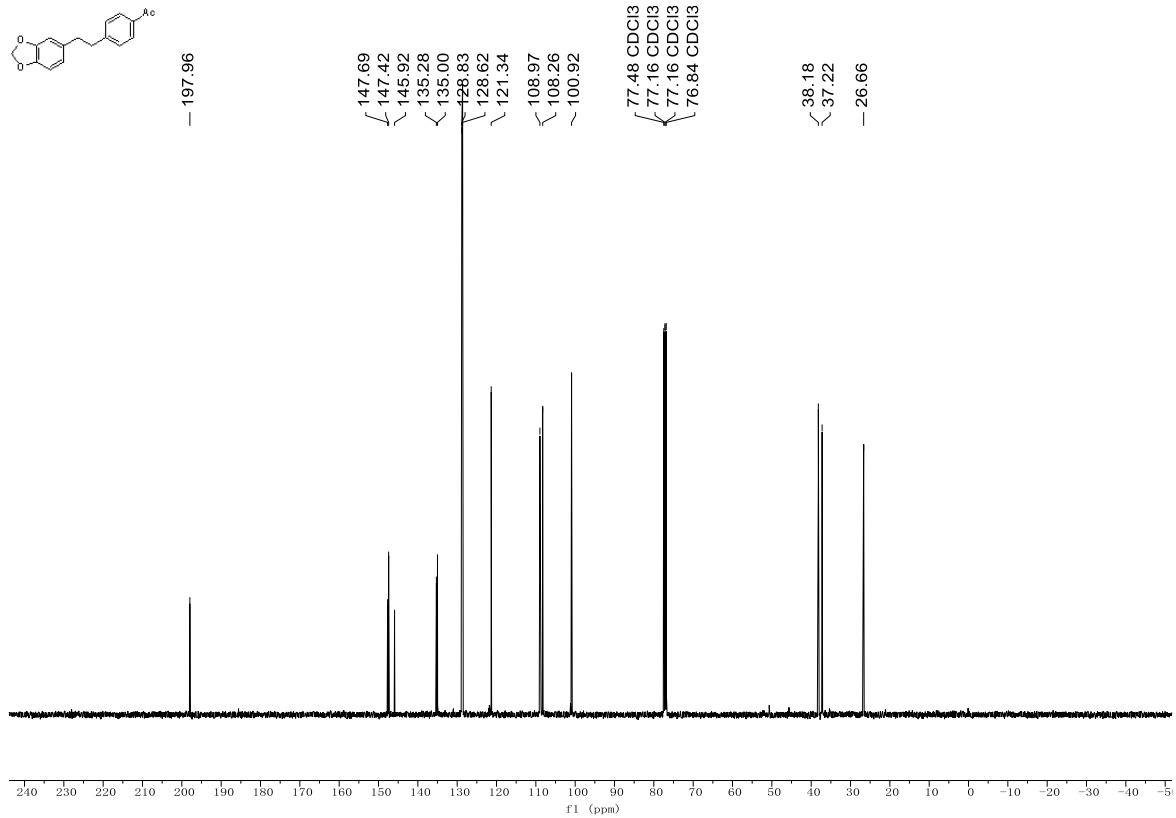
Compound **21** ^{13}C NMR



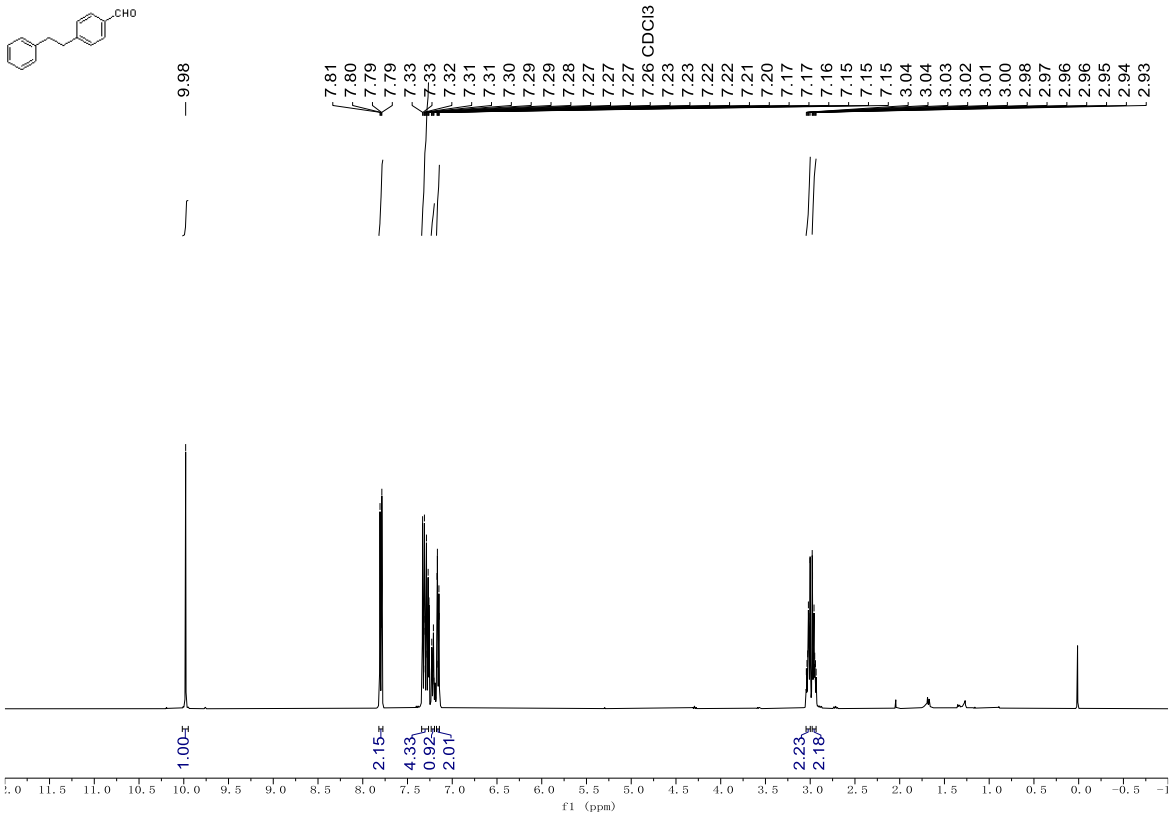
Compound **22** ^{1}H NMR



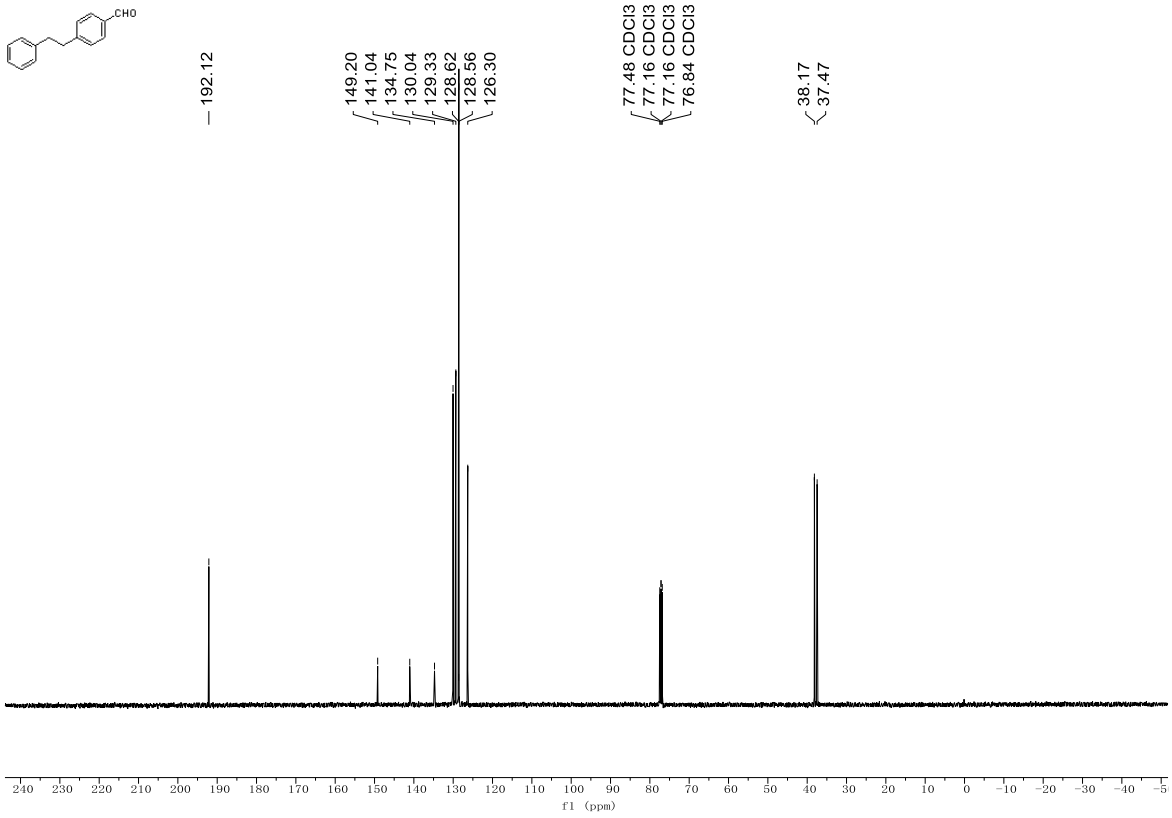
Compound **22** ^{13}C NMR



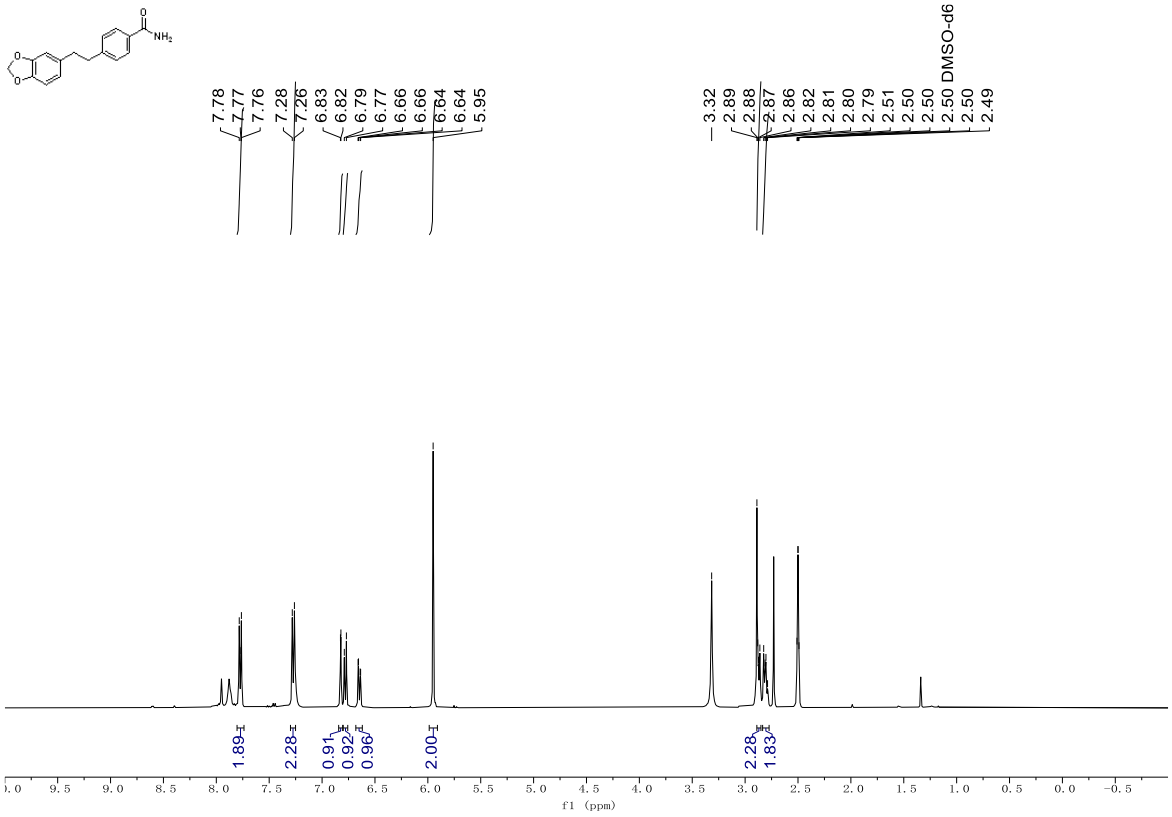
Compound **23** ^{1}H NMR



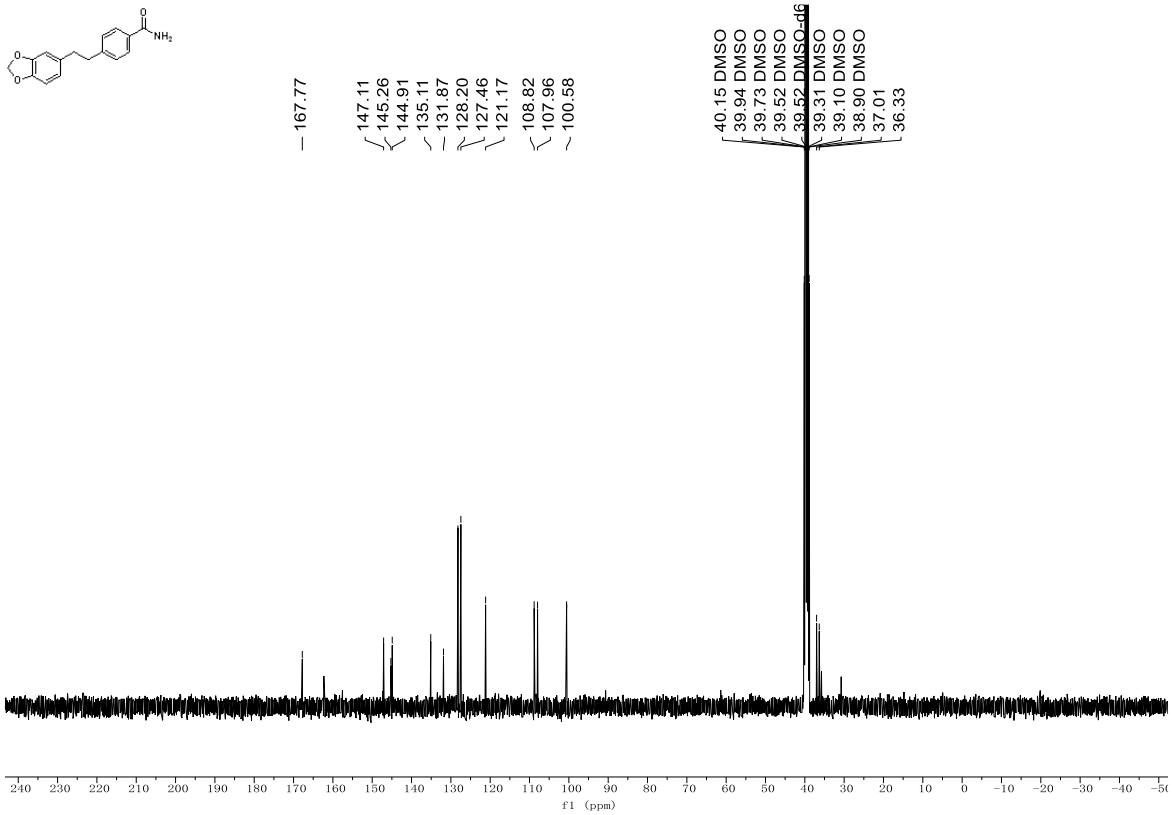
Compound **23** ^{13}C NMR



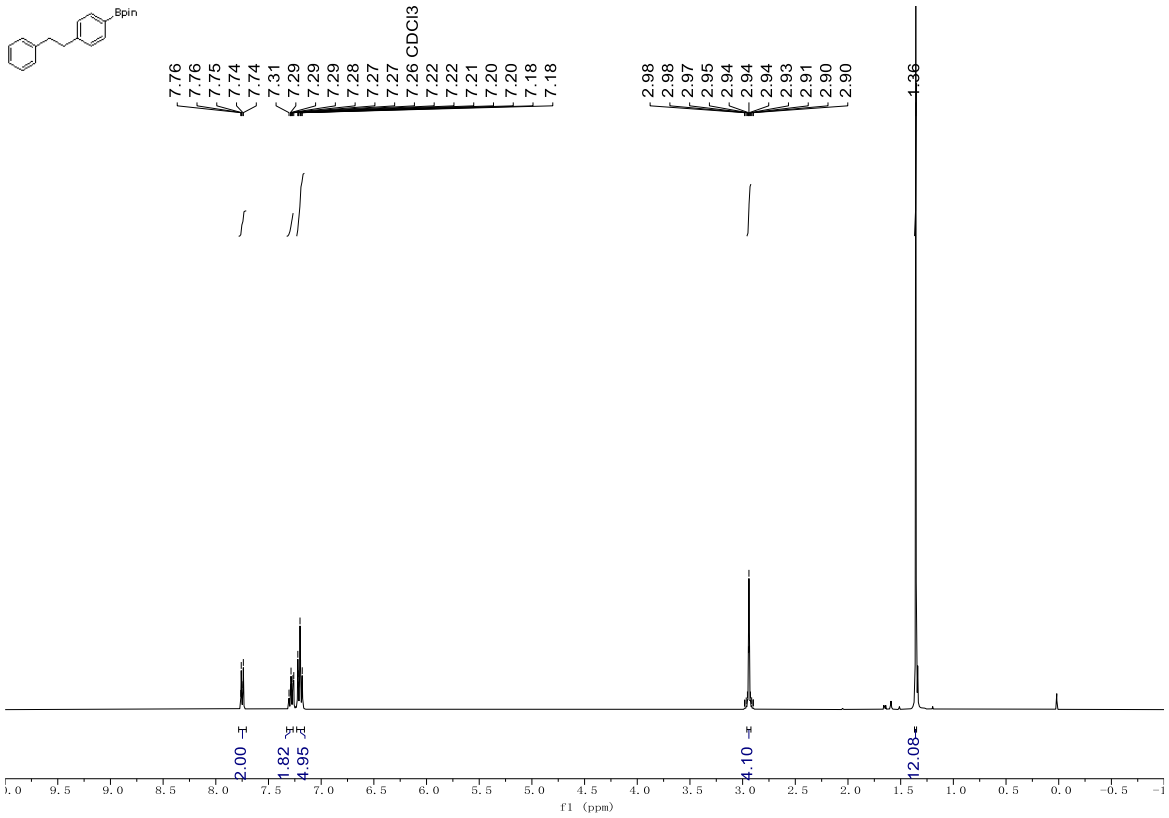
Compound **24** ^{1}H NMR



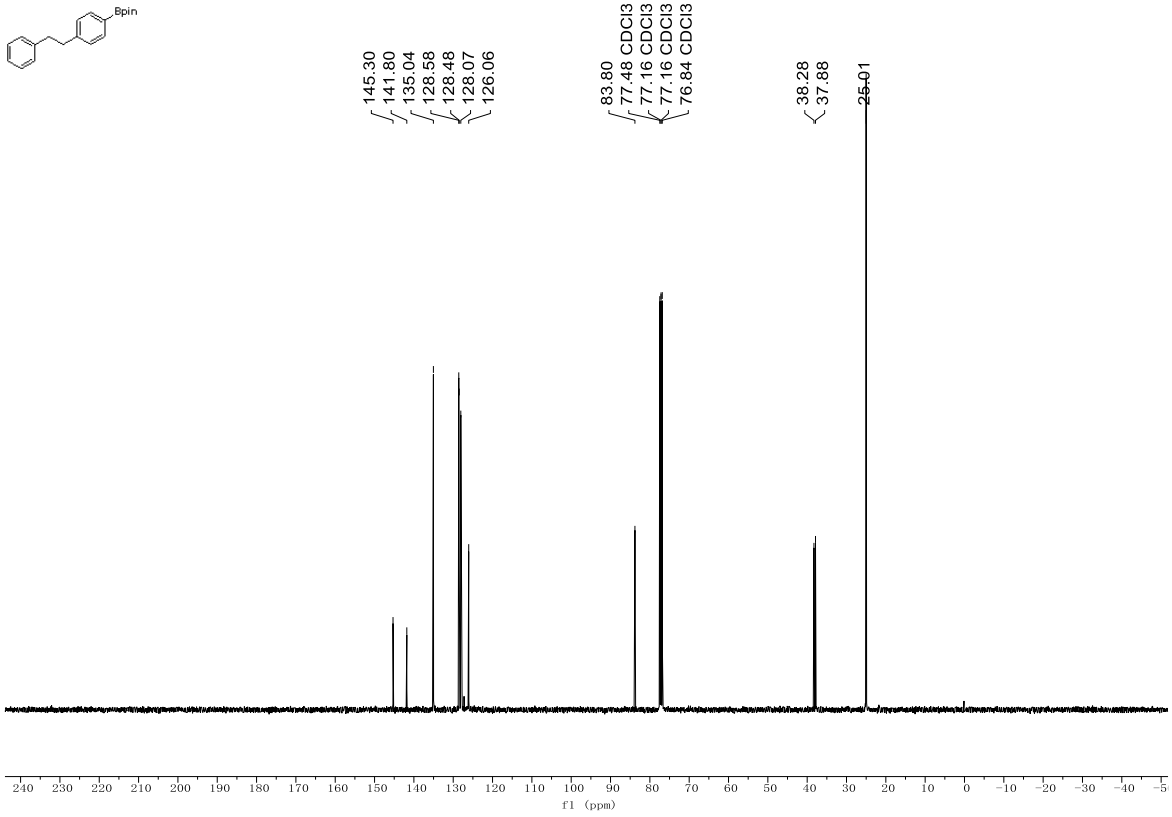
Compound **24** ^{13}C NMR



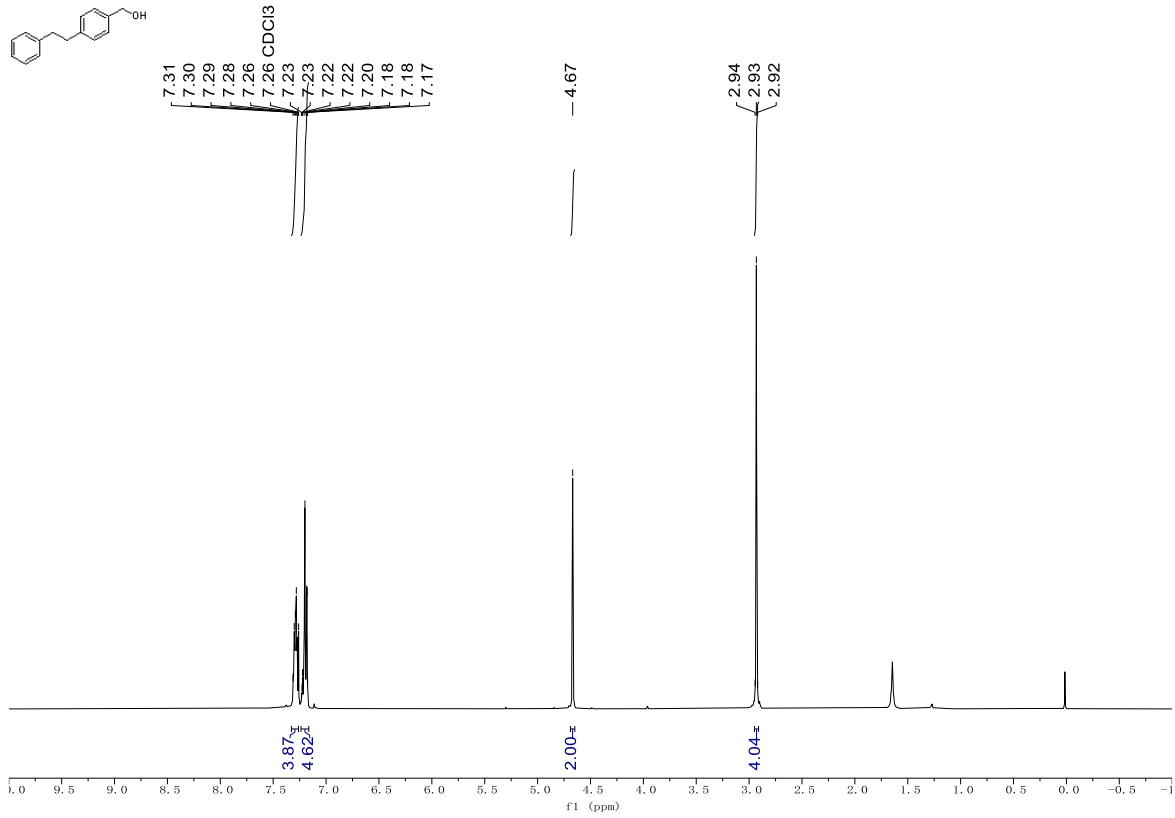
Compound **25** ^{1}H NMR



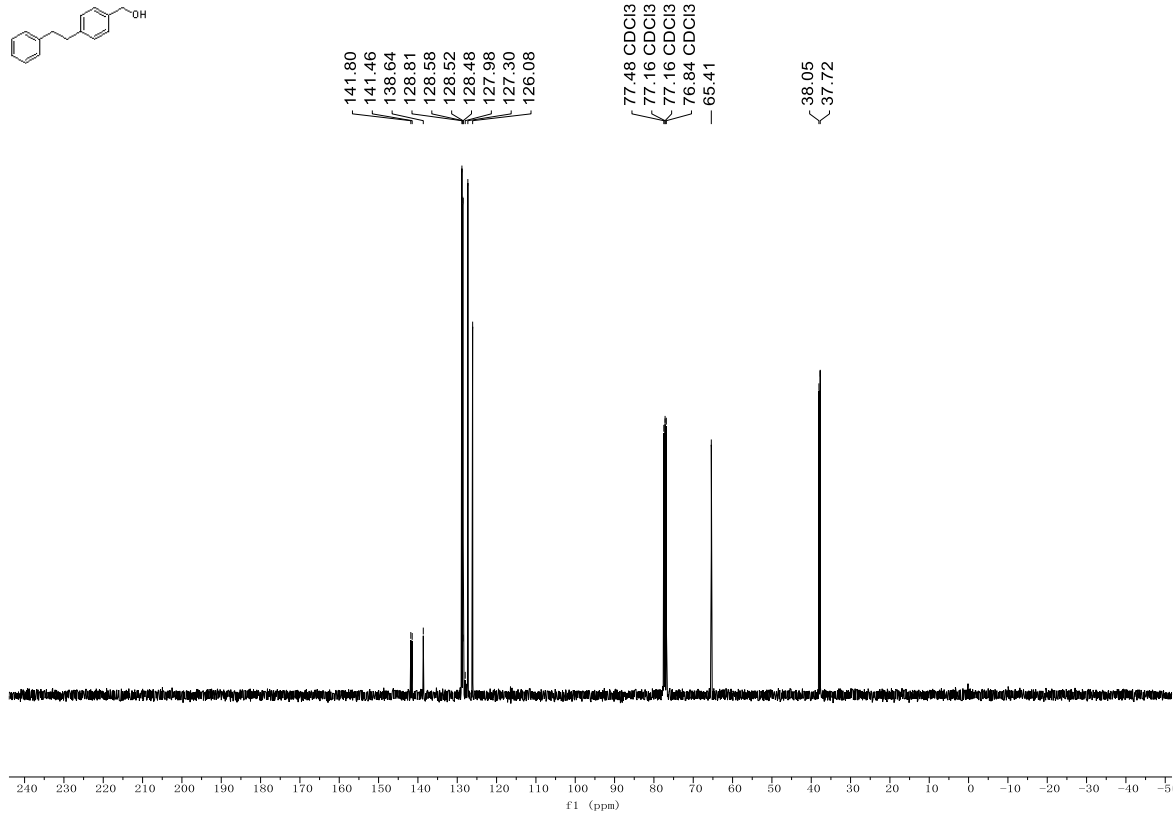
Compound **25** ^{13}C NMR



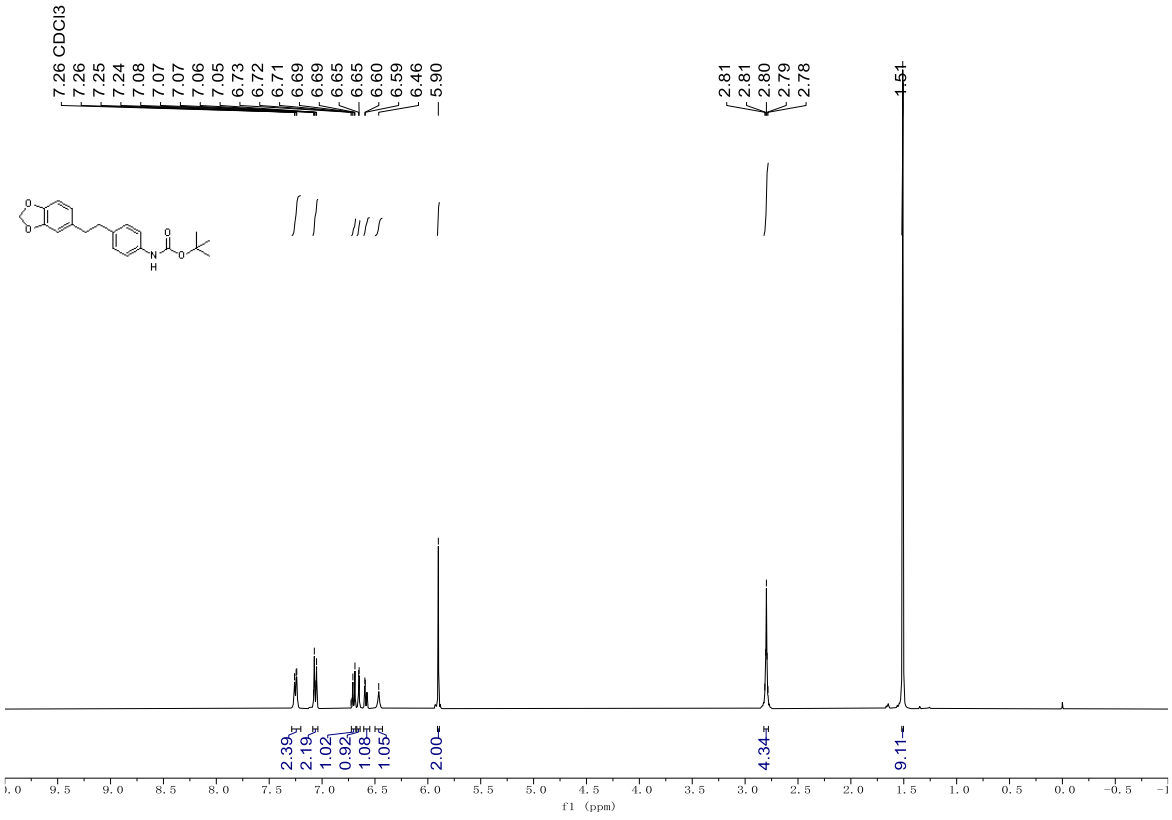
Compound **26** ^{1}H NMR



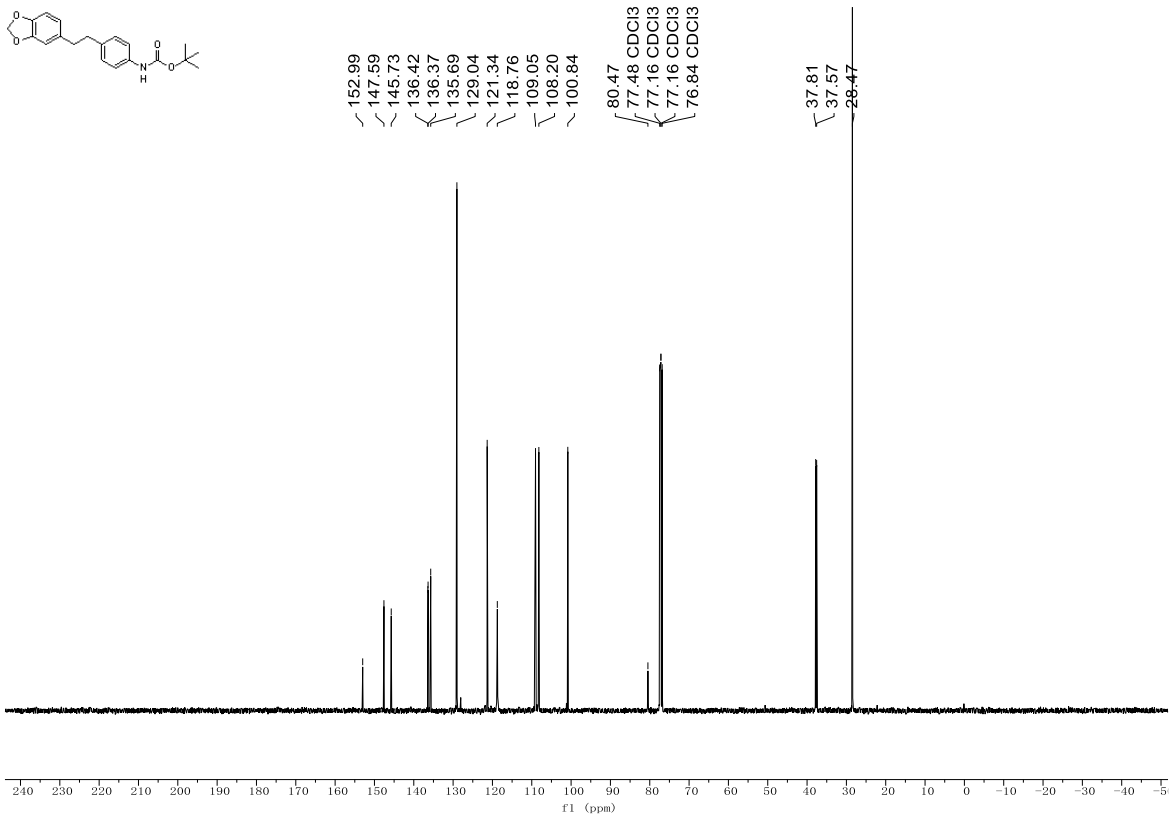
Compound **26** ^{13}C NMR



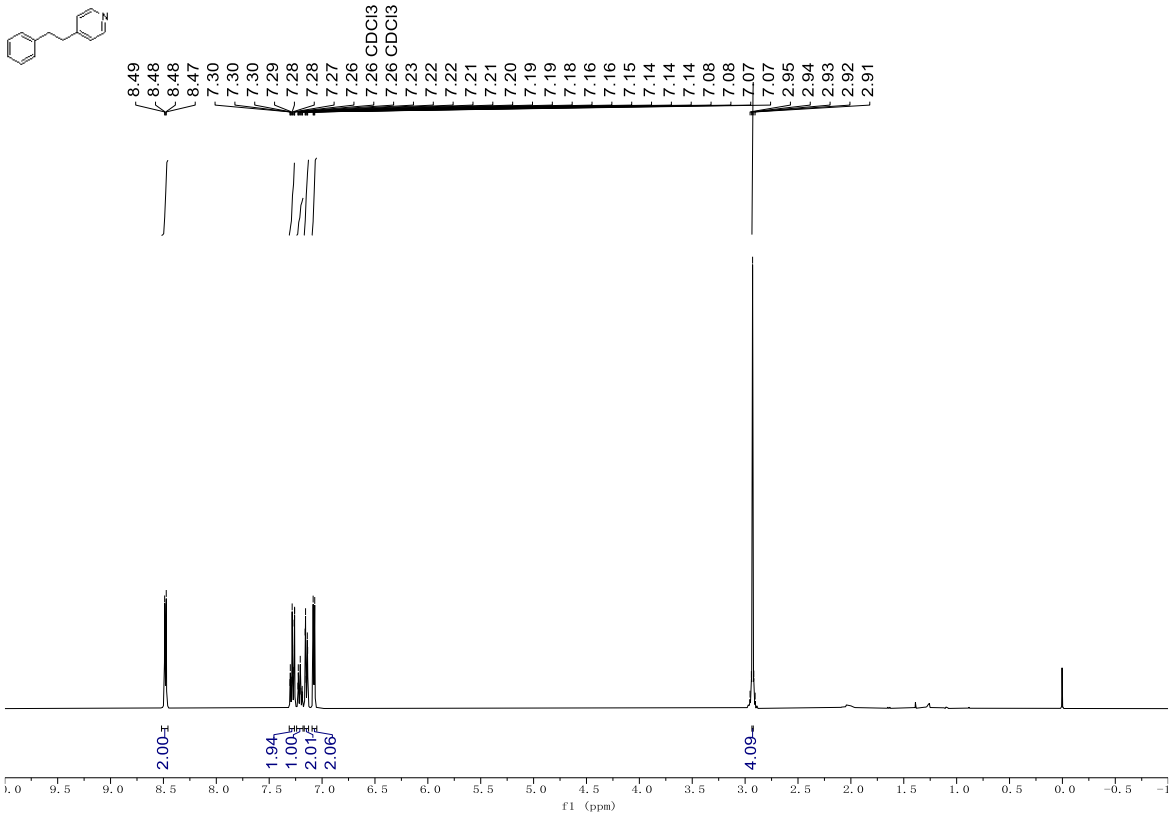
Compound **27** ^{1}H NMR



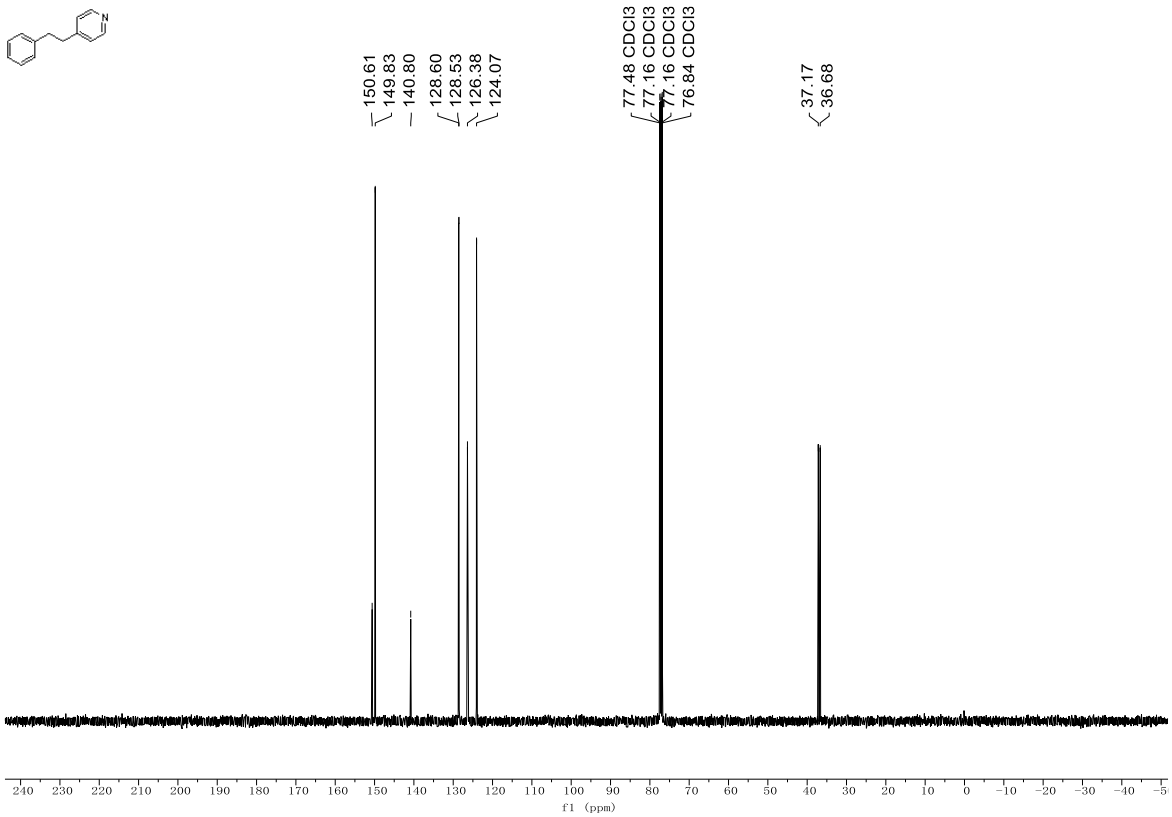
Compound **27** ^{13}C NMR



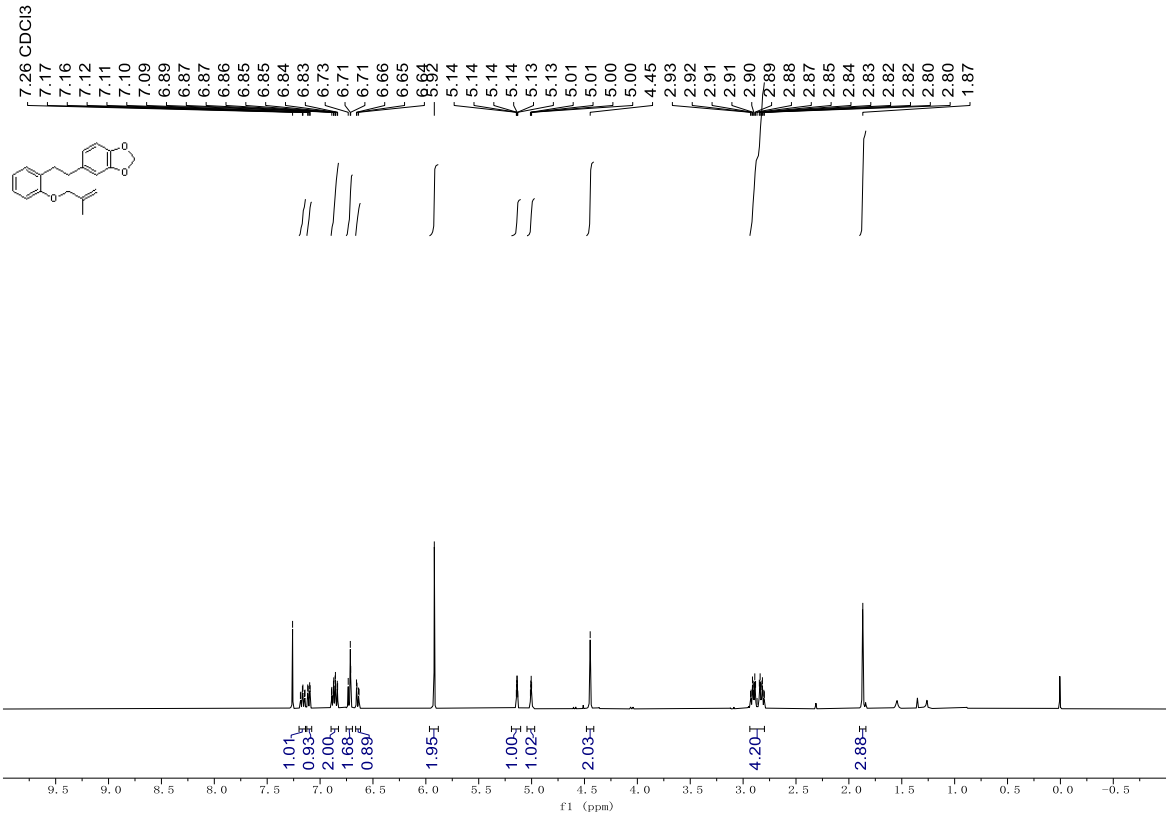
Compound **28** ^{1}H NMR



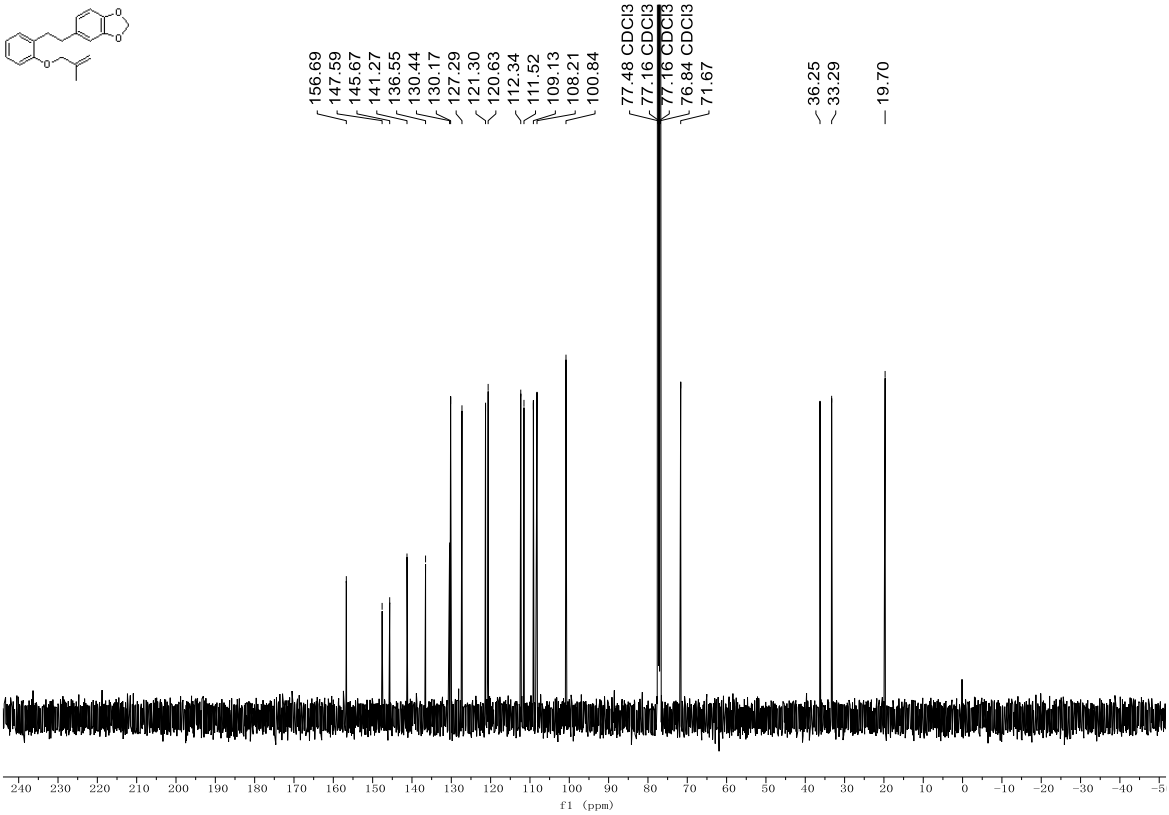
Compound **28** ^{13}C NMR



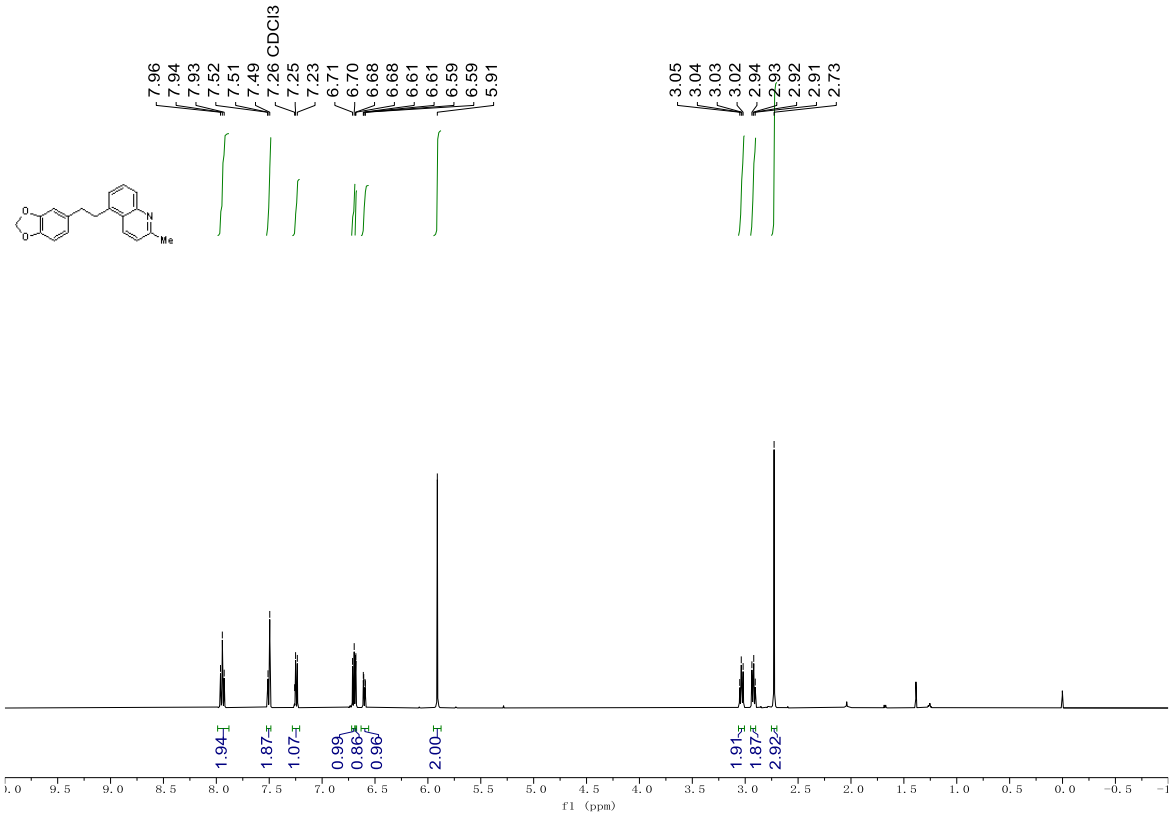
Compound **29** ^{1}H NMR



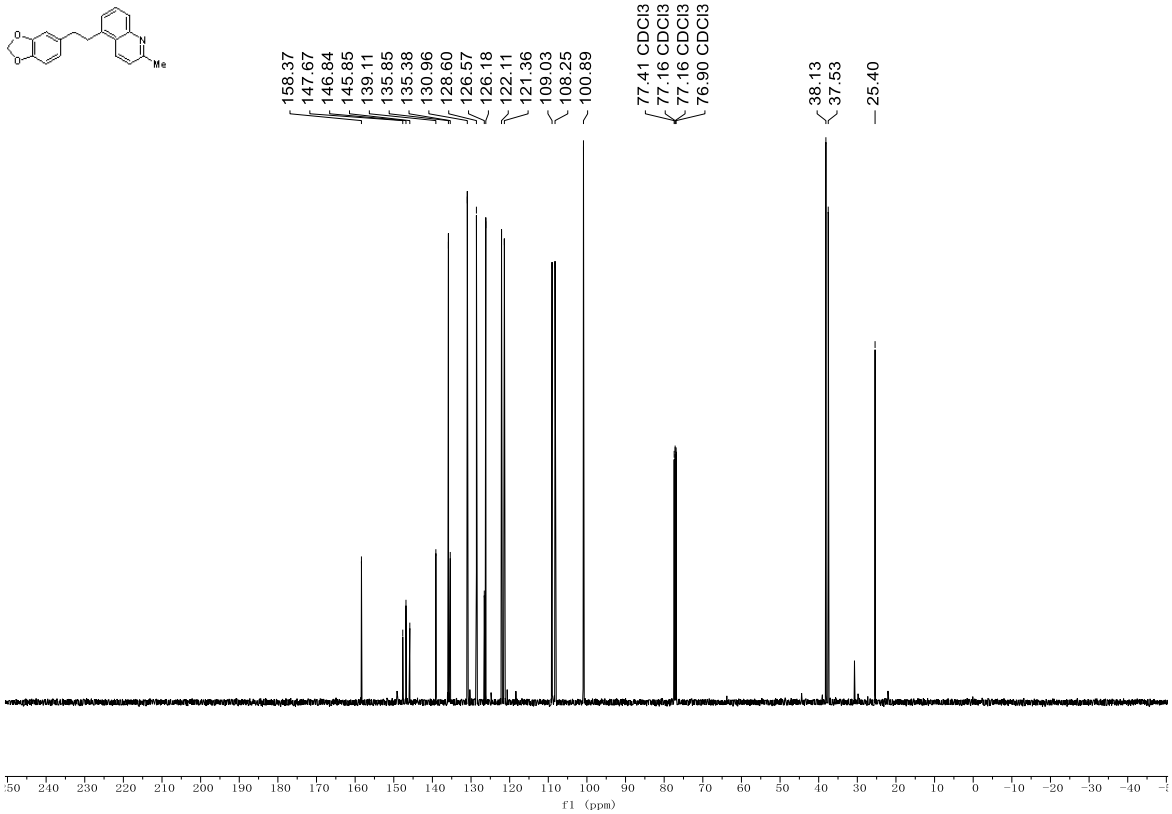
Compound **29** ^{13}C NMR



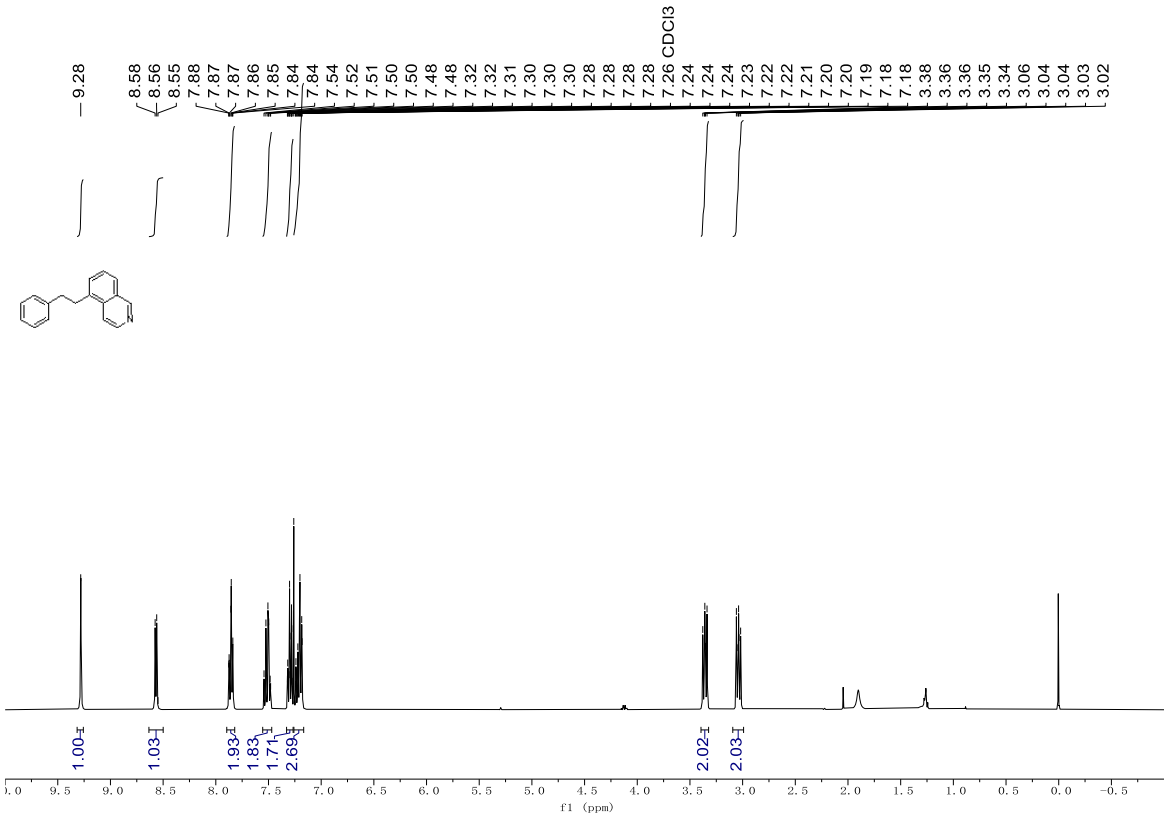
Compound **30** ^{1}H NMR



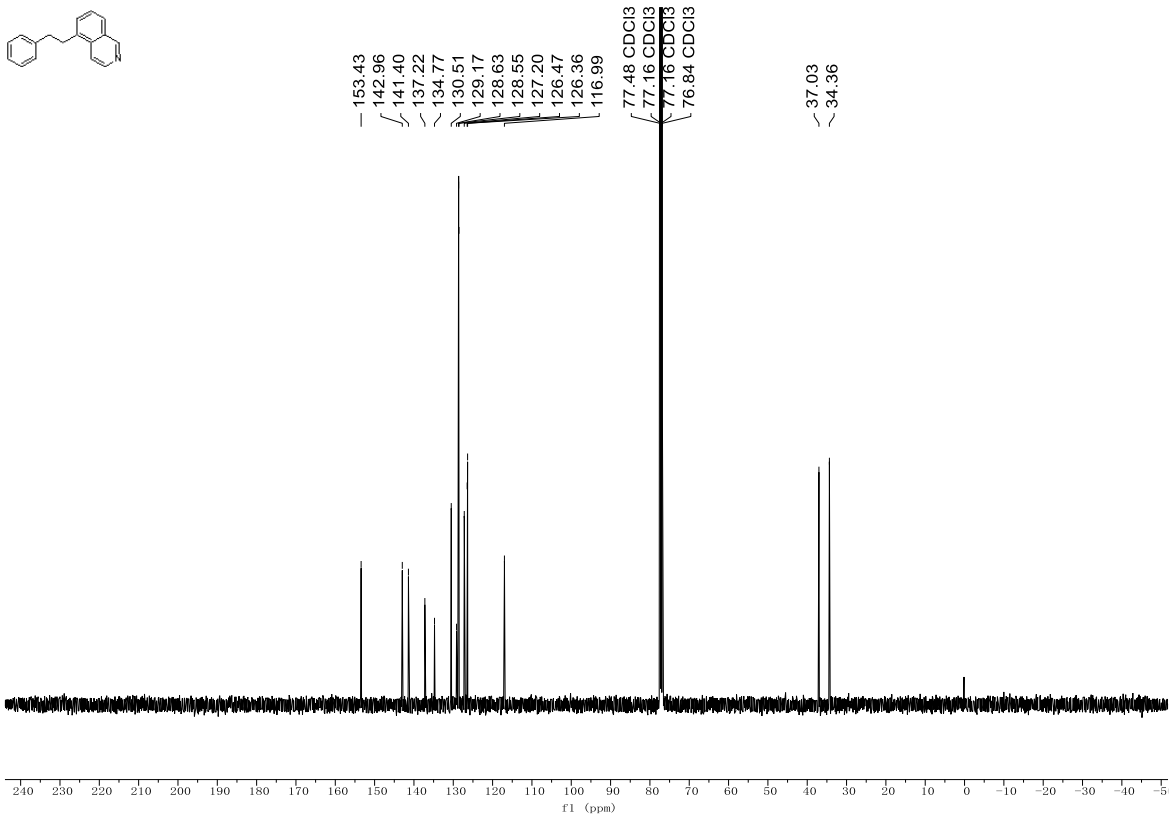
Compound **30** ^{13}C NMR



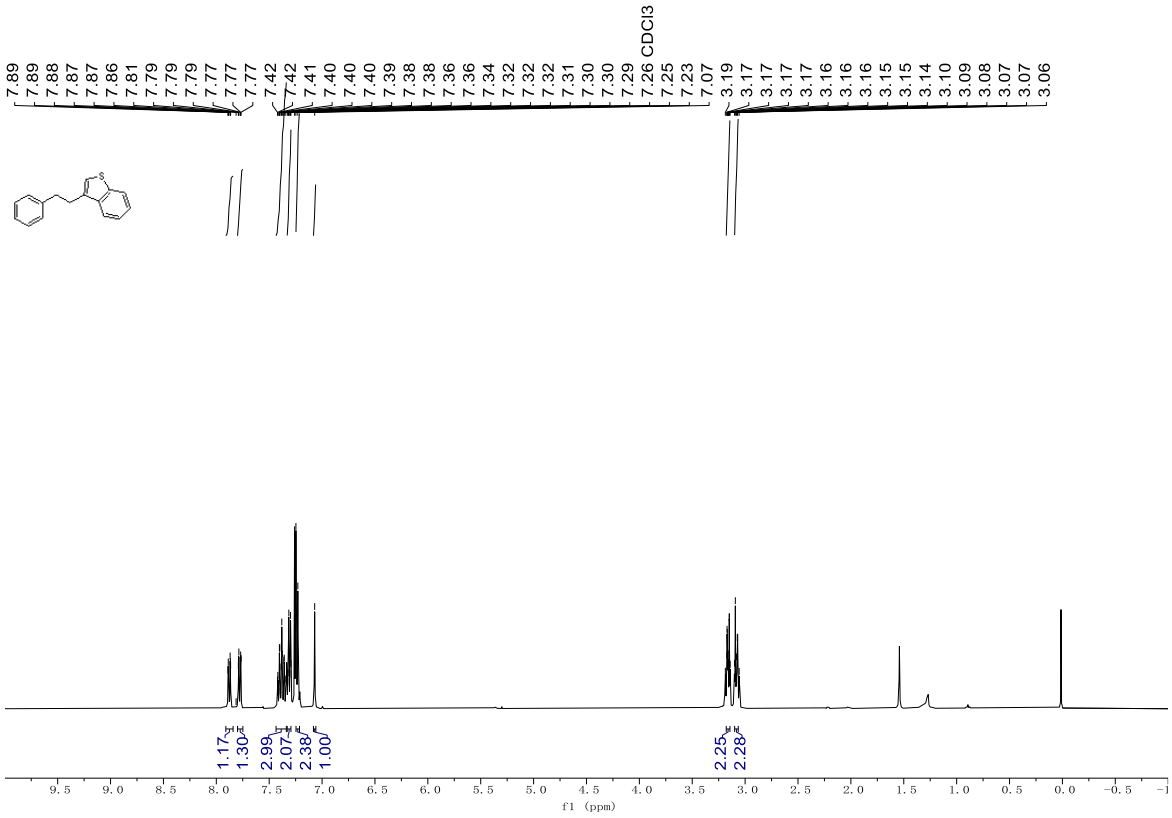
Compound **31** ^{1}H NMR



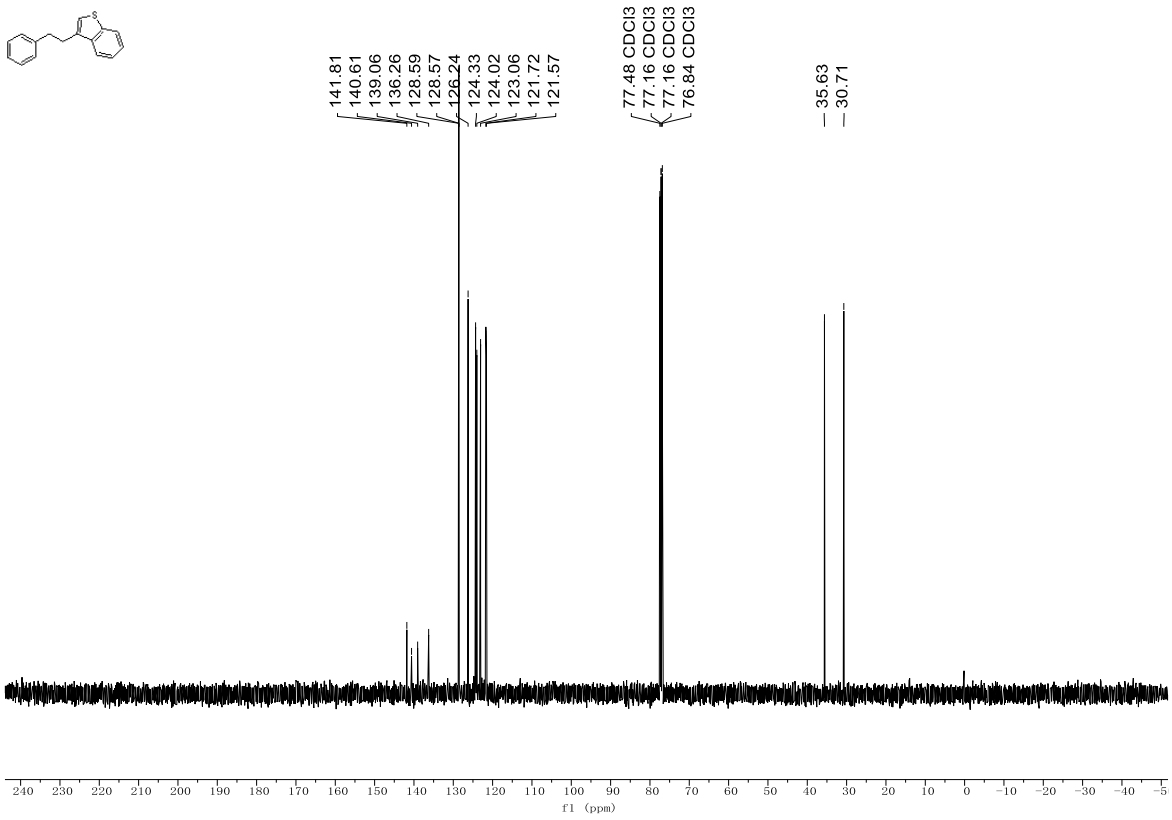
Compound **31** ^{13}C NMR



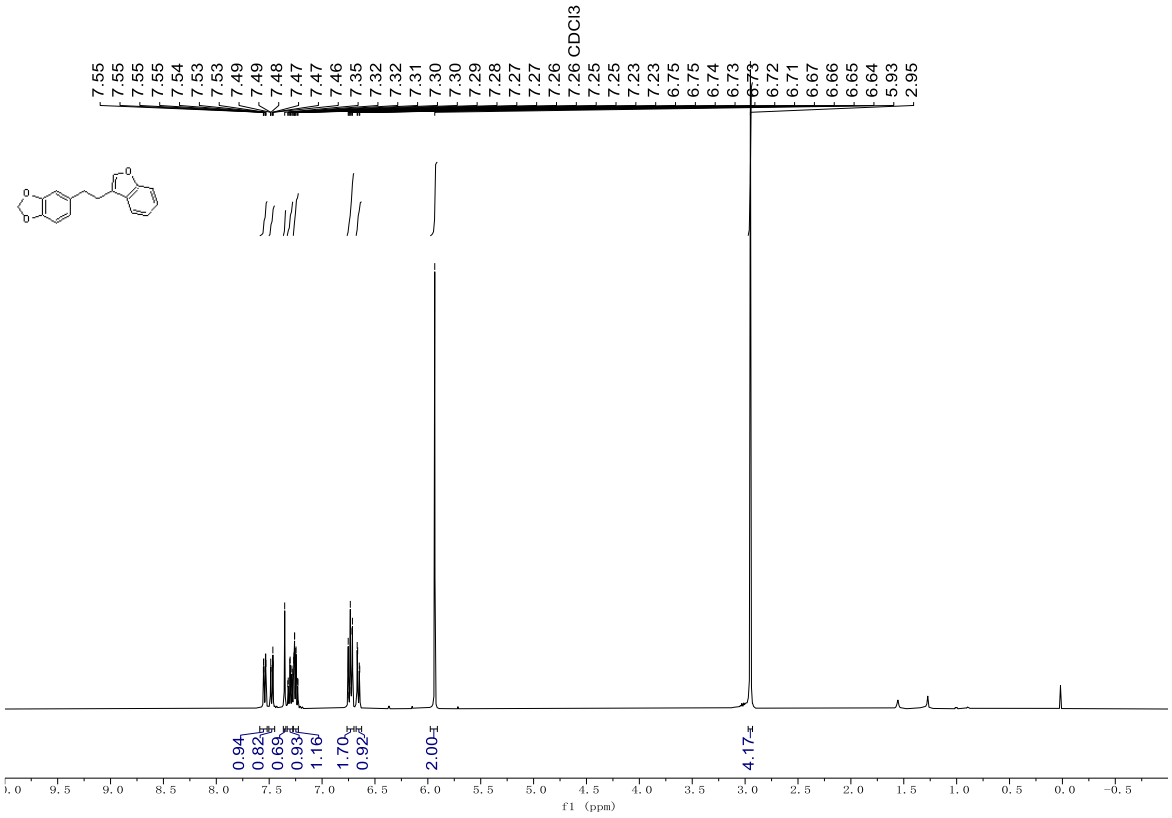
Compound **32** ^{1}H NMR



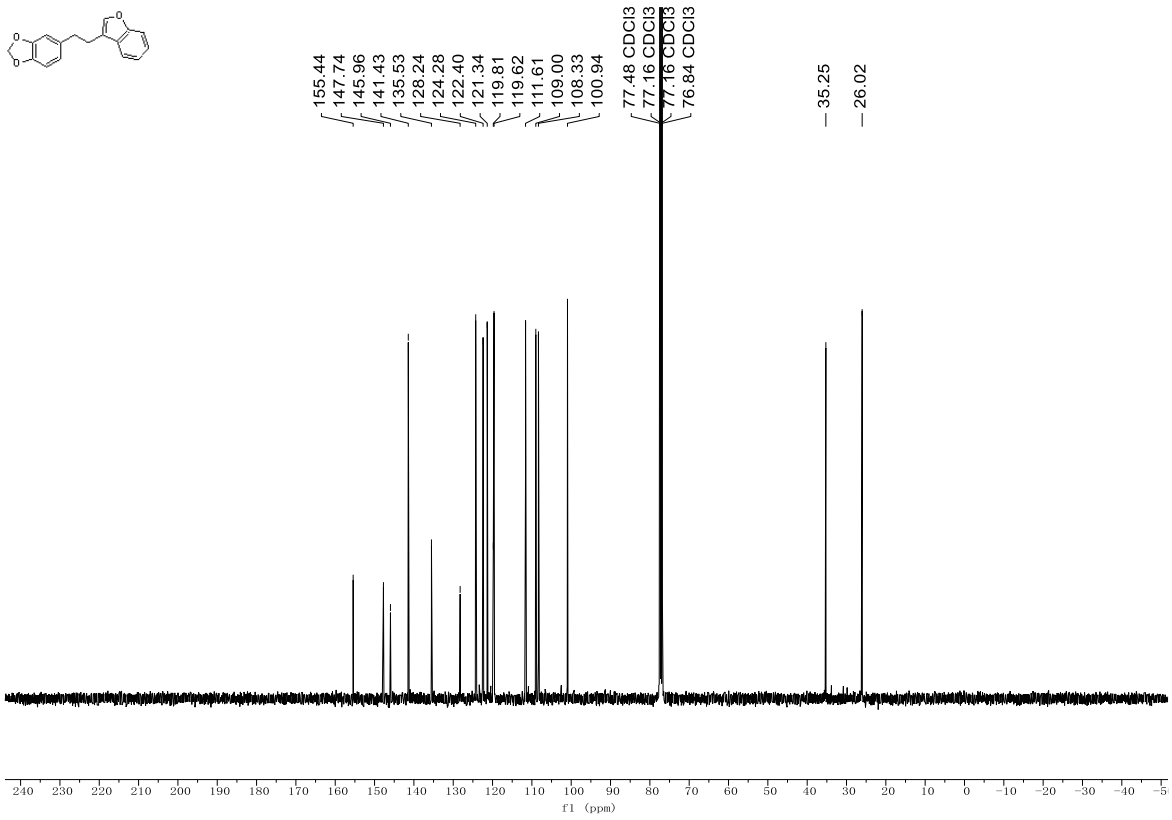
Compound **32** ^{13}C NMR



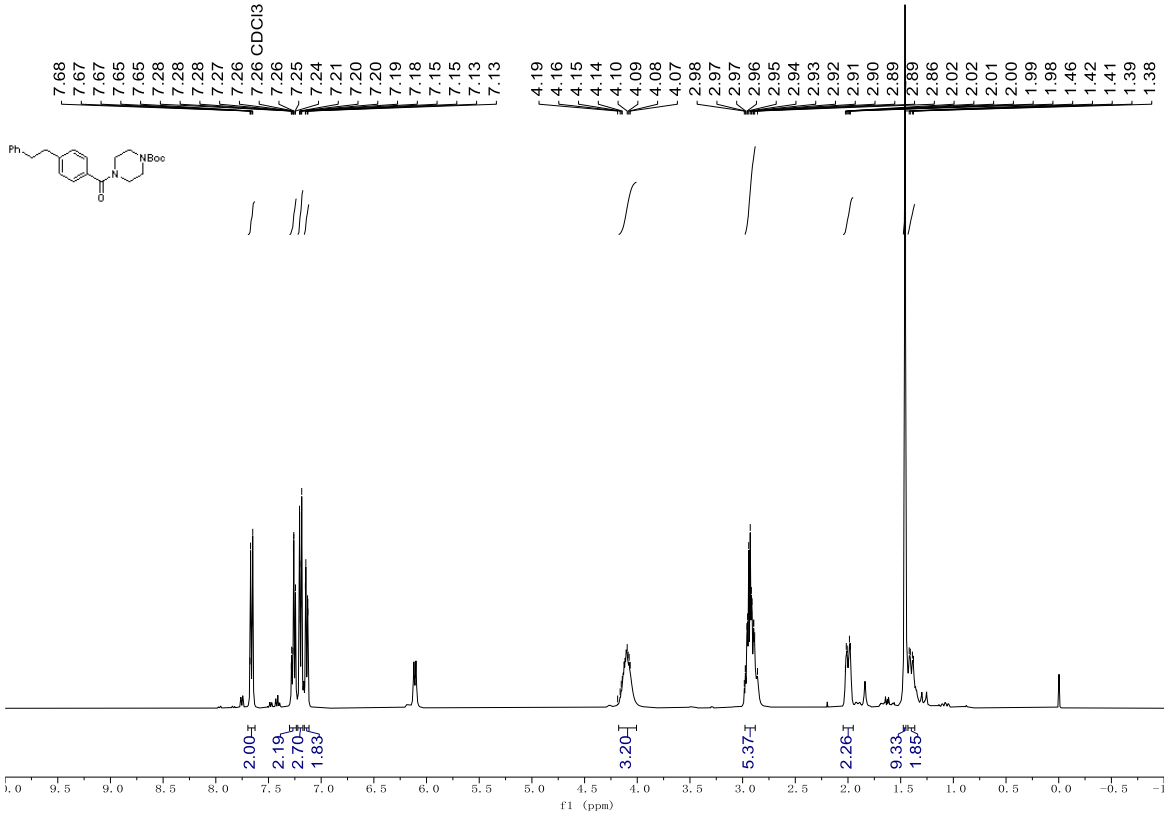
Compound **33** ^{1}H NMR



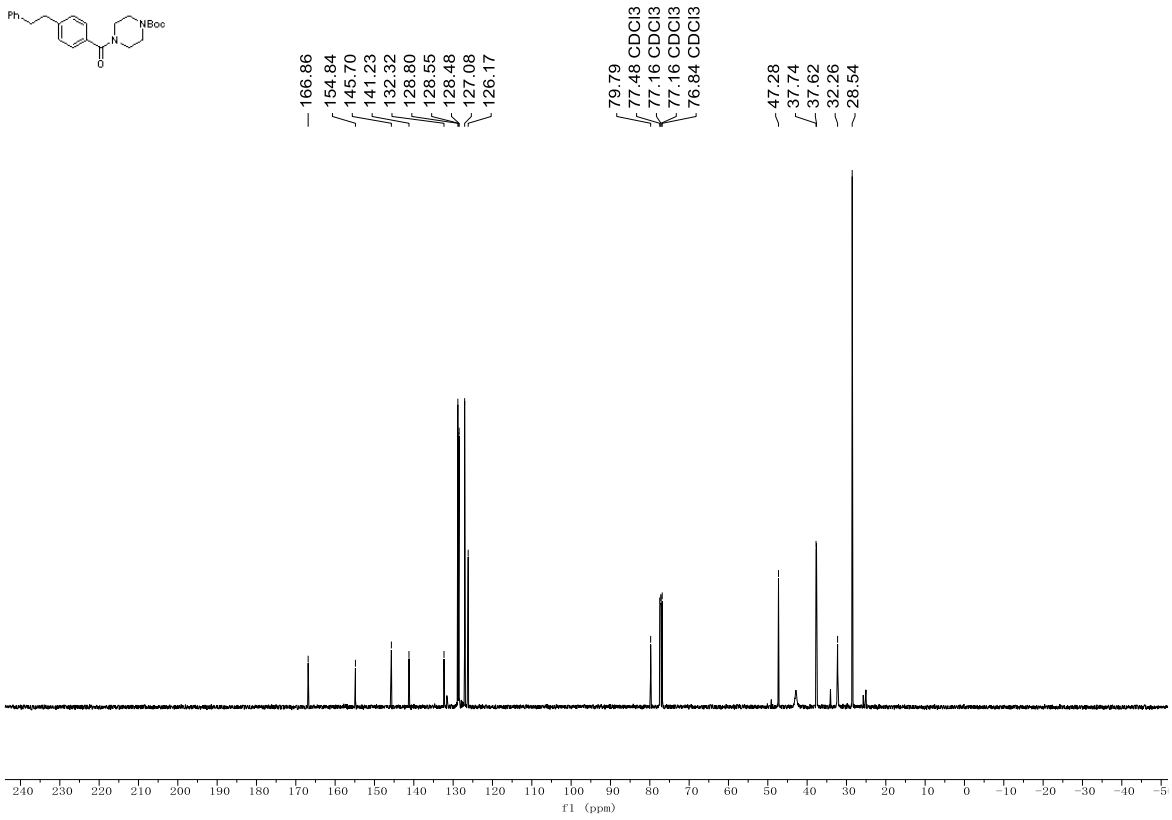
Compound **33** ^{13}C NMR



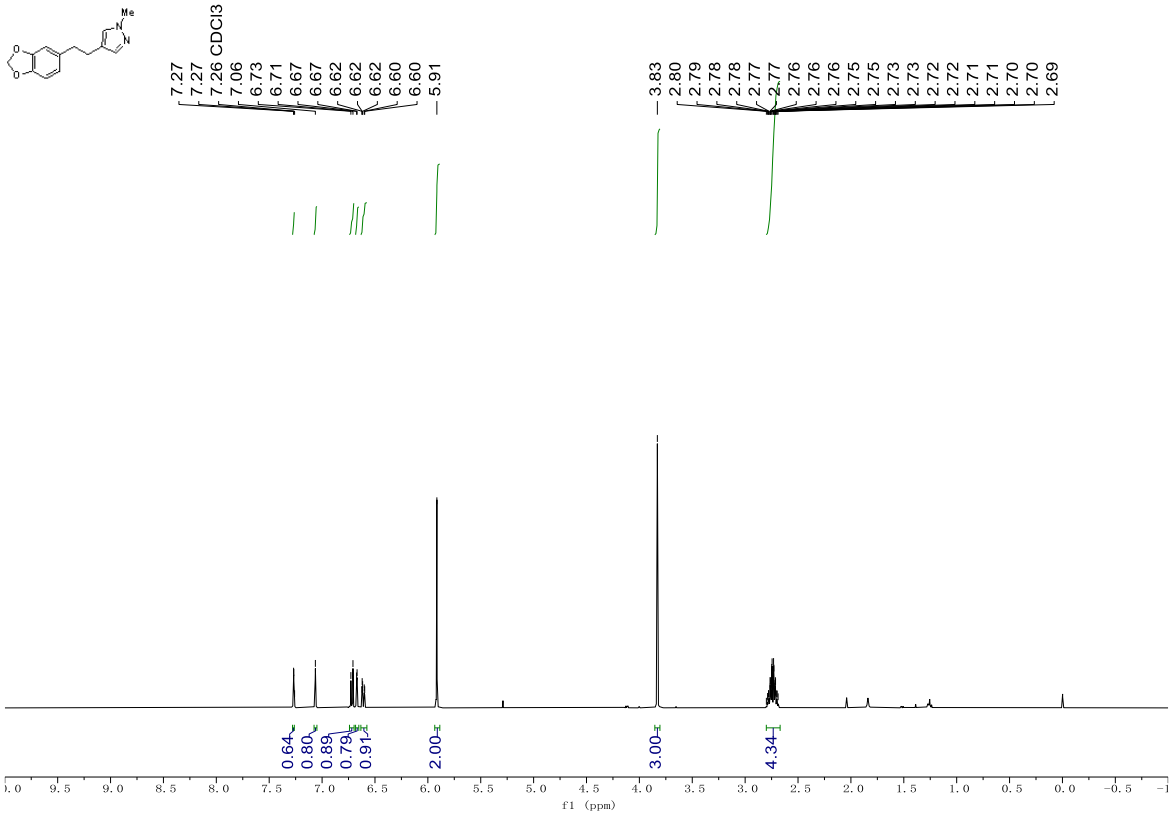
Compound **34** ^{1}H NMR



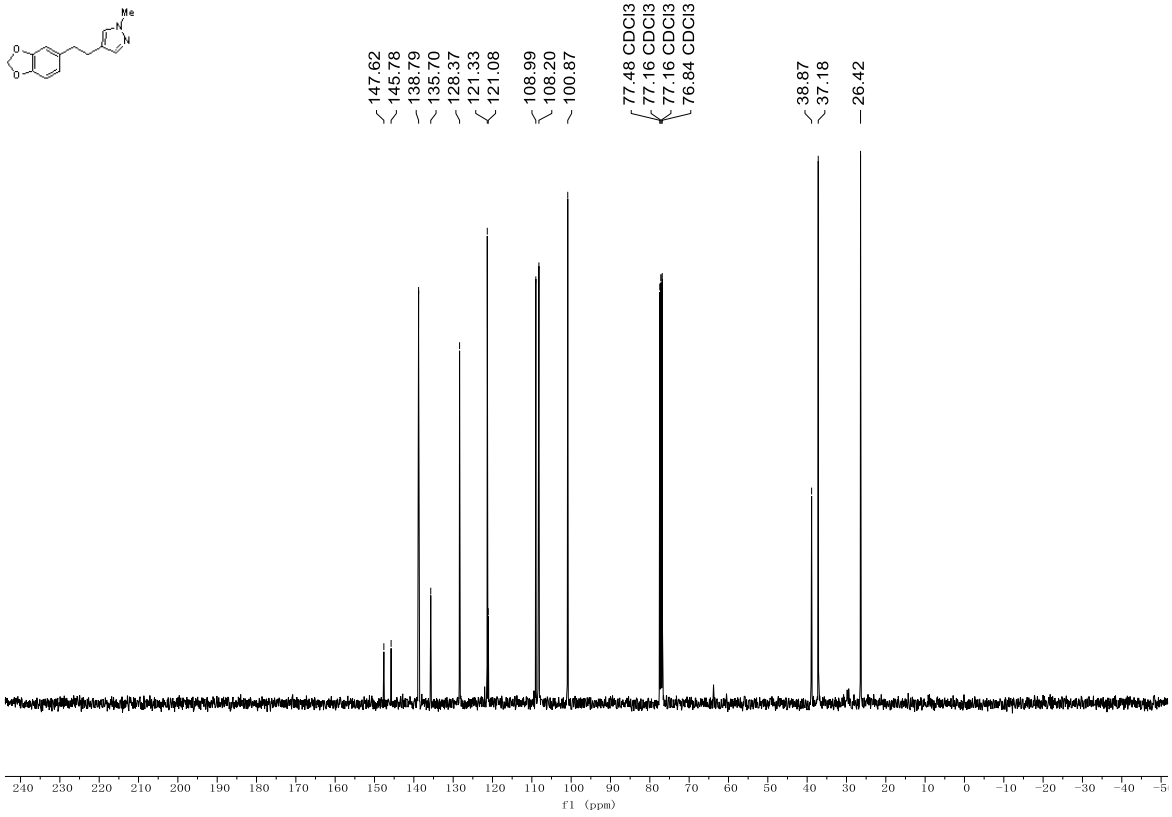
Compound **34** ^{13}C NMR



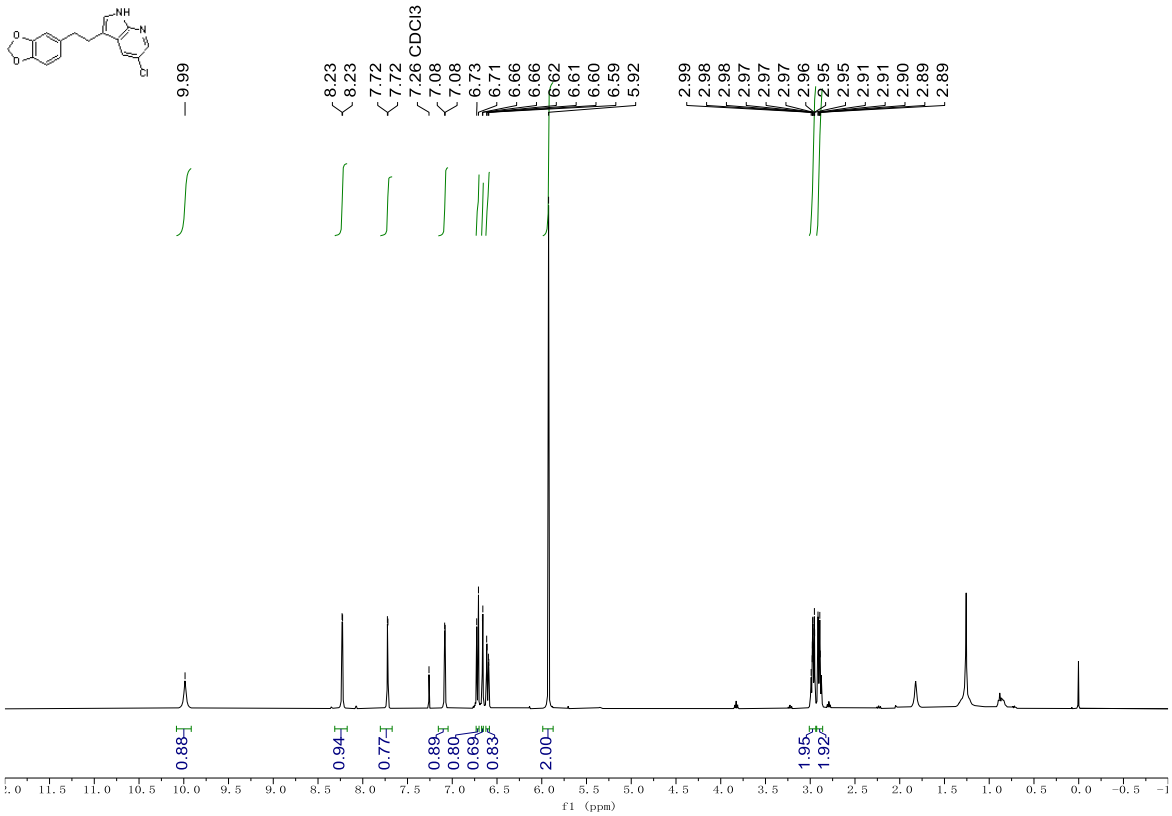
Compound **35** ^{1}H NMR



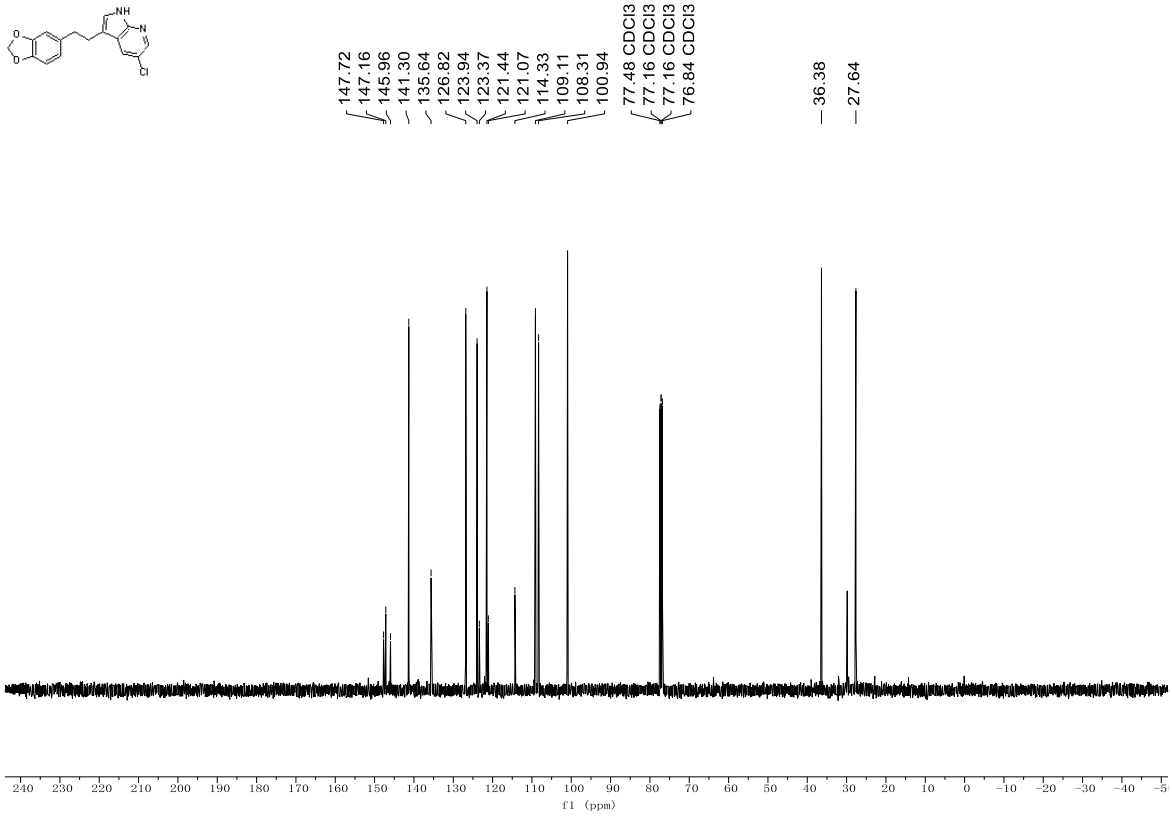
Compound **35** ^{13}C NMR



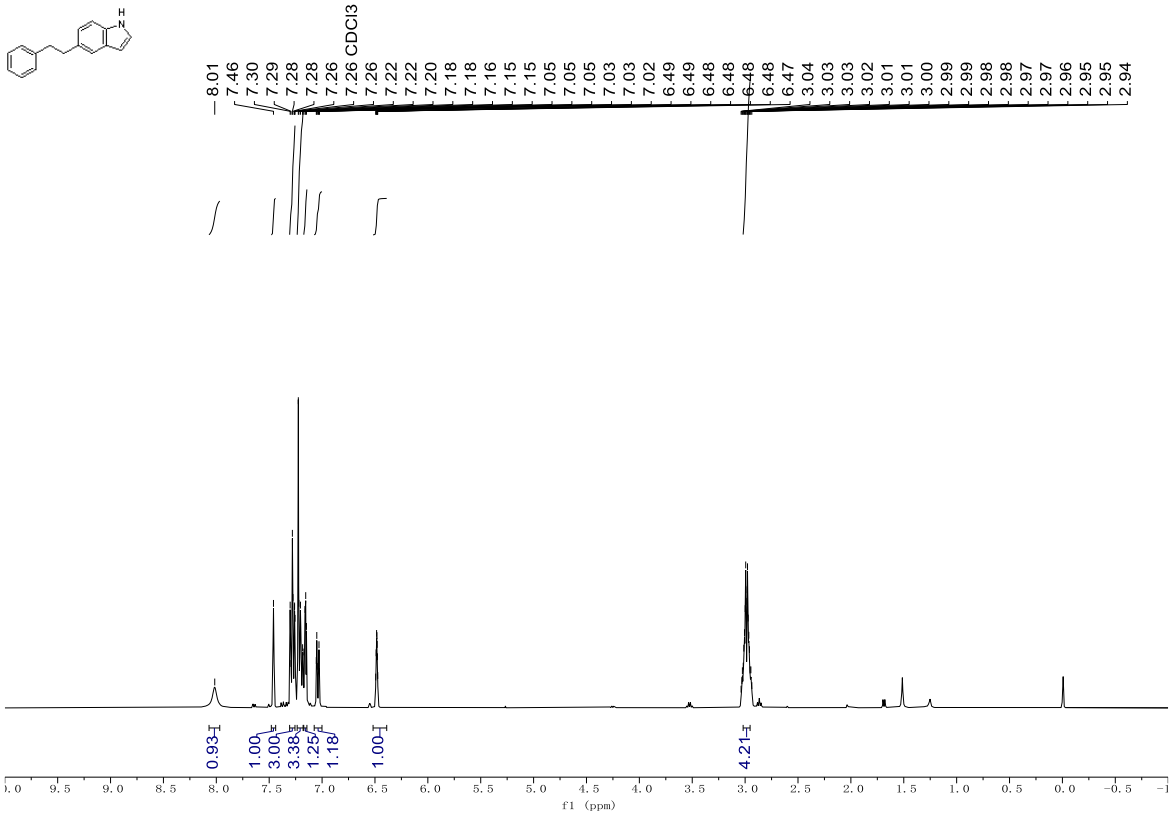
Compound **36** ^{1}H NMR



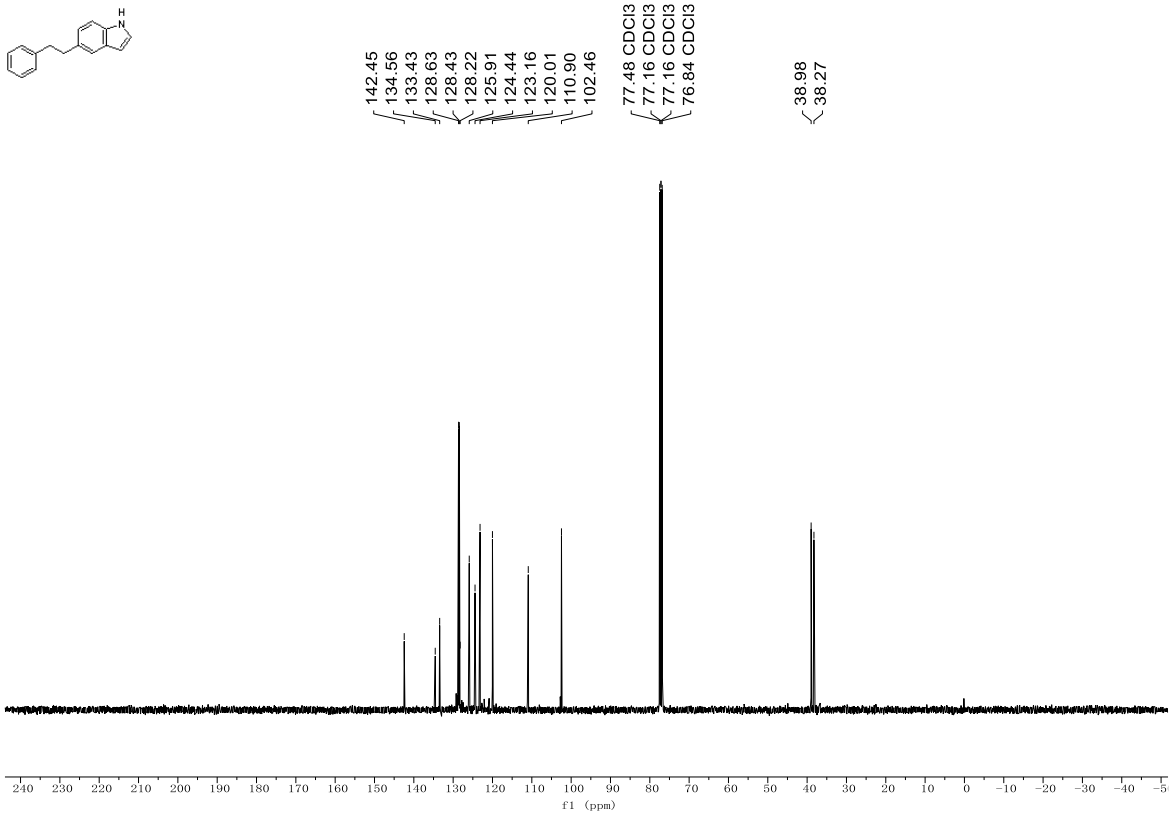
Compound **36** ^{13}C NMR



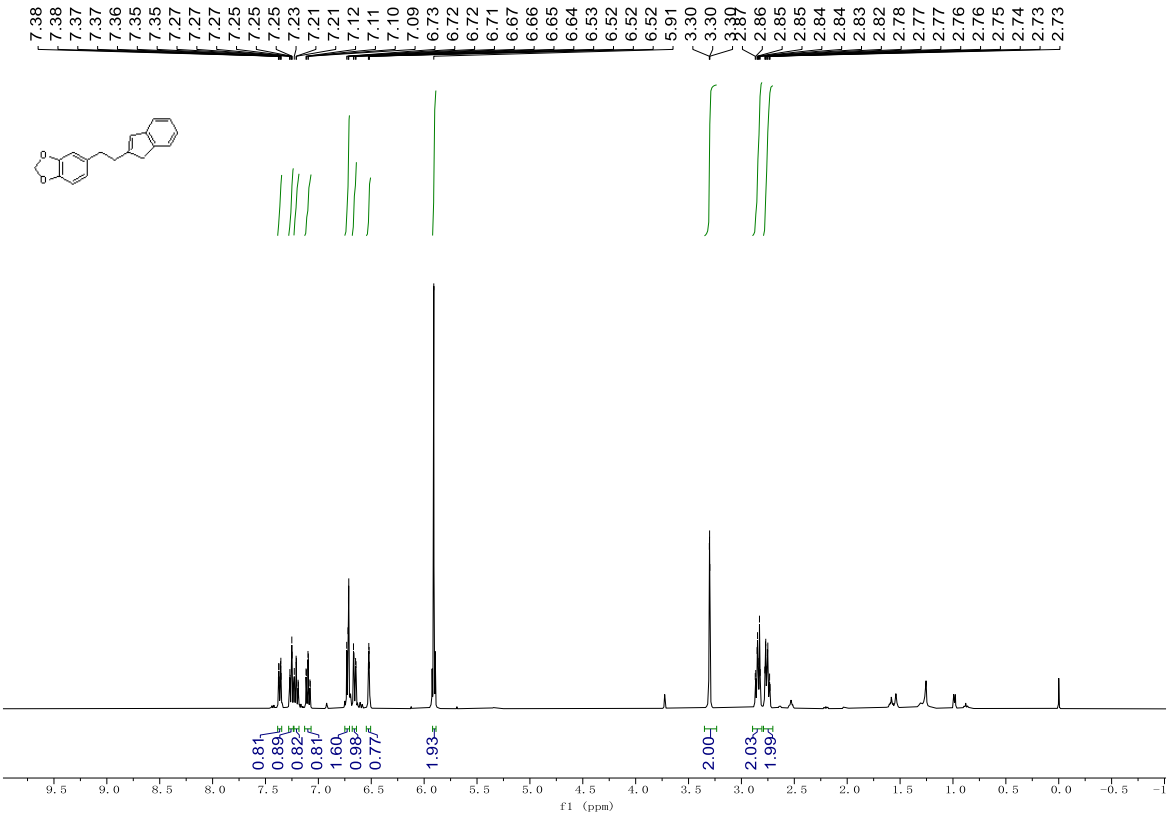
Compound **37** ^{1}H NMR



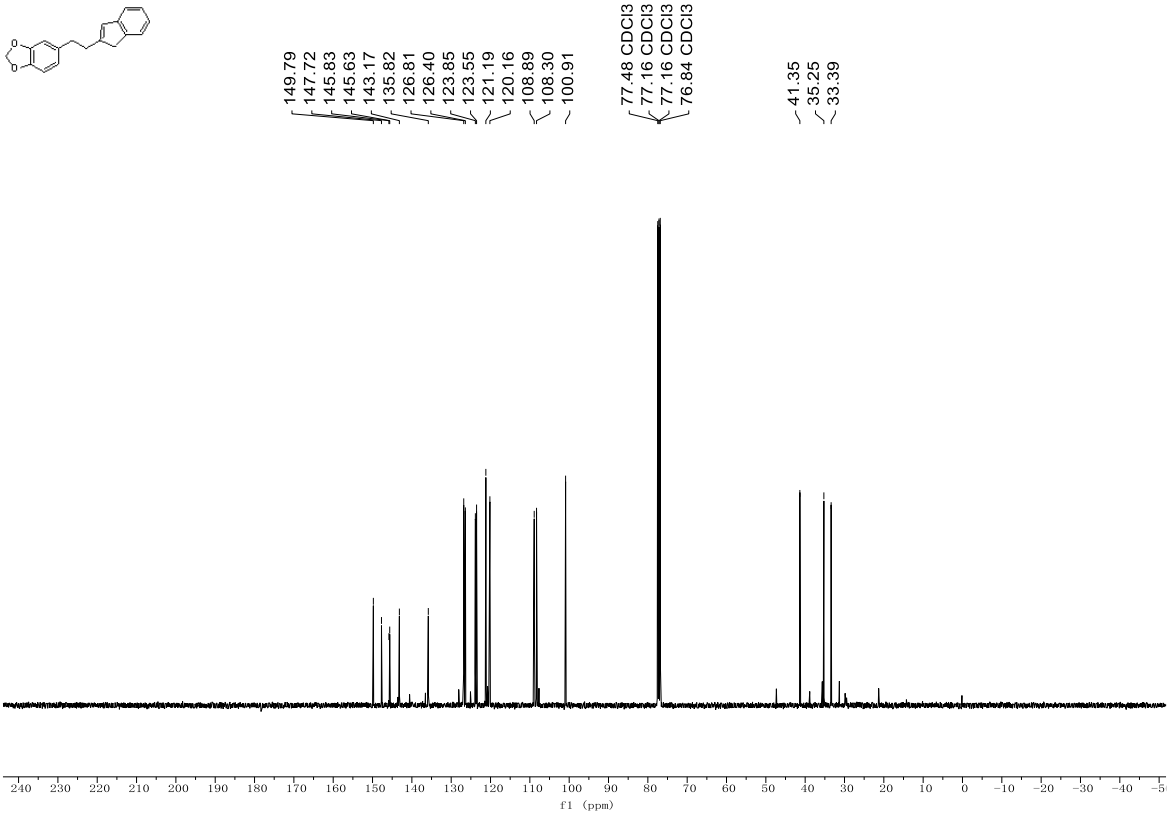
Compound **37** ^{13}C NMR



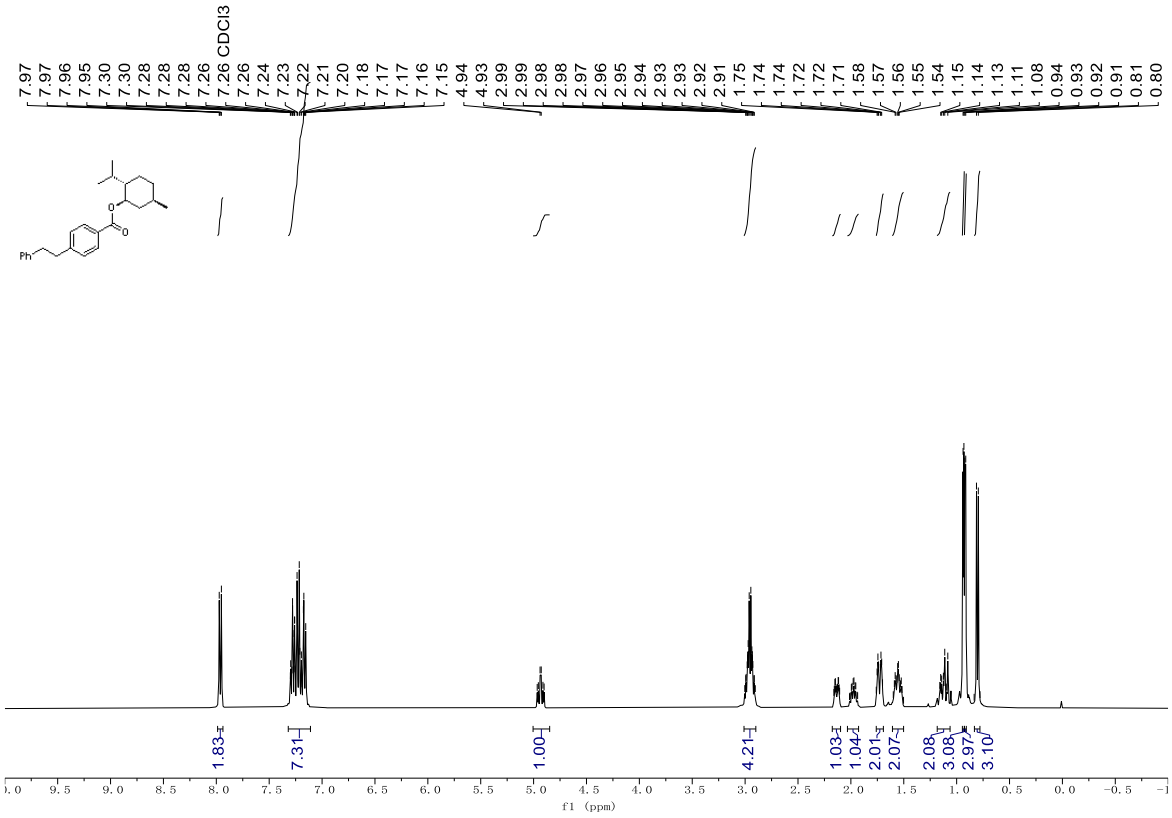
Compound **38** ^{1}H NMR



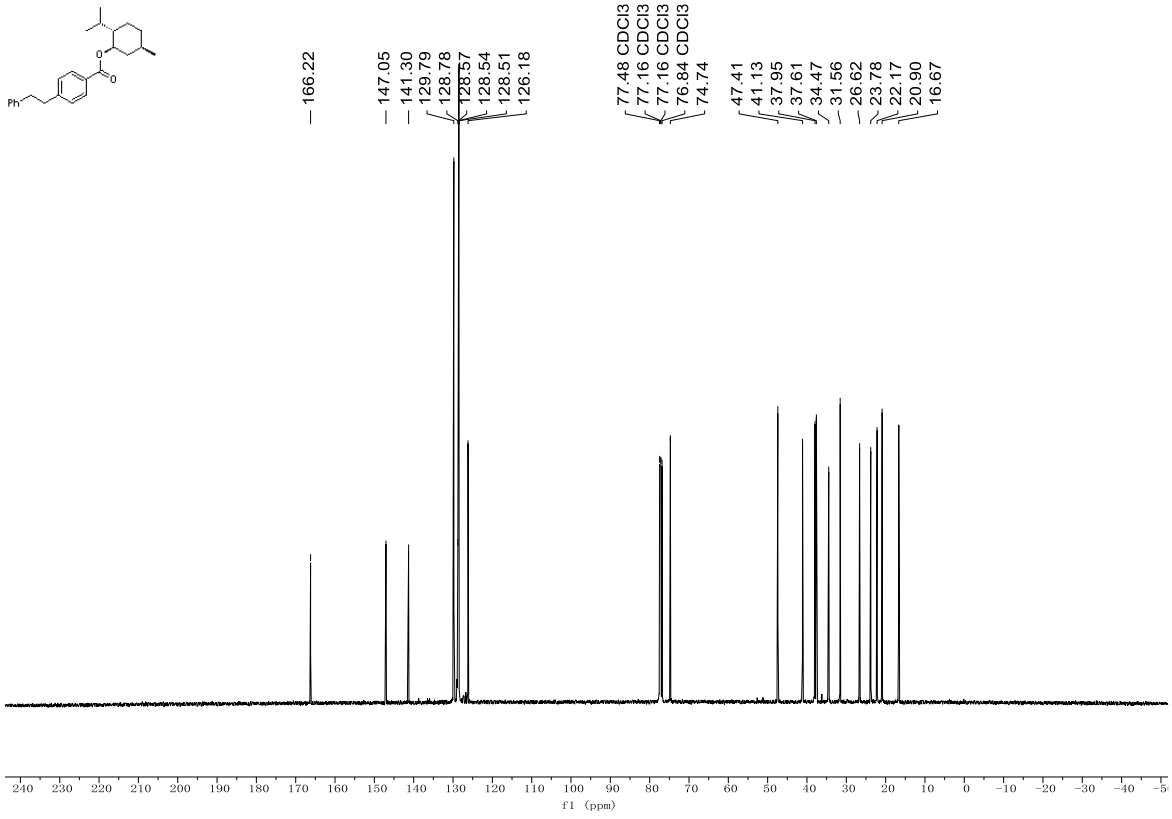
Compound **38** ^{13}C NMR



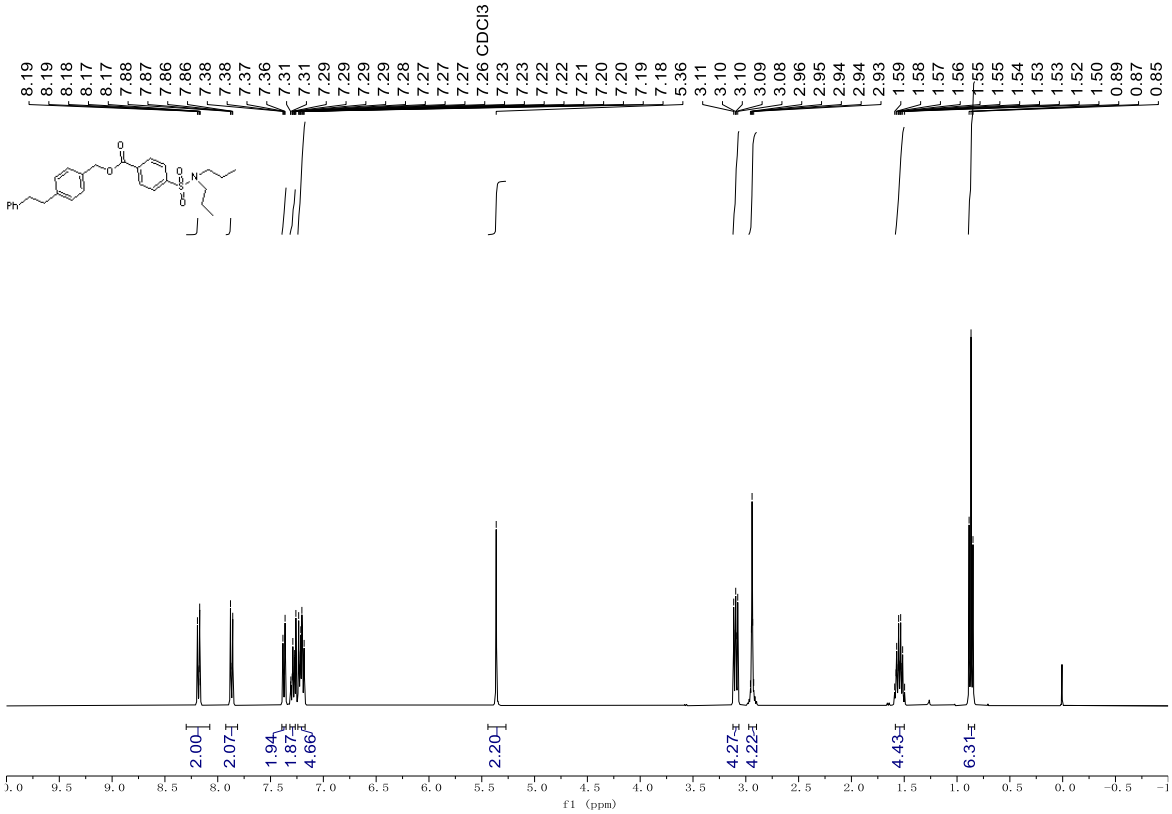
Compound **39** ^{1}H NMR



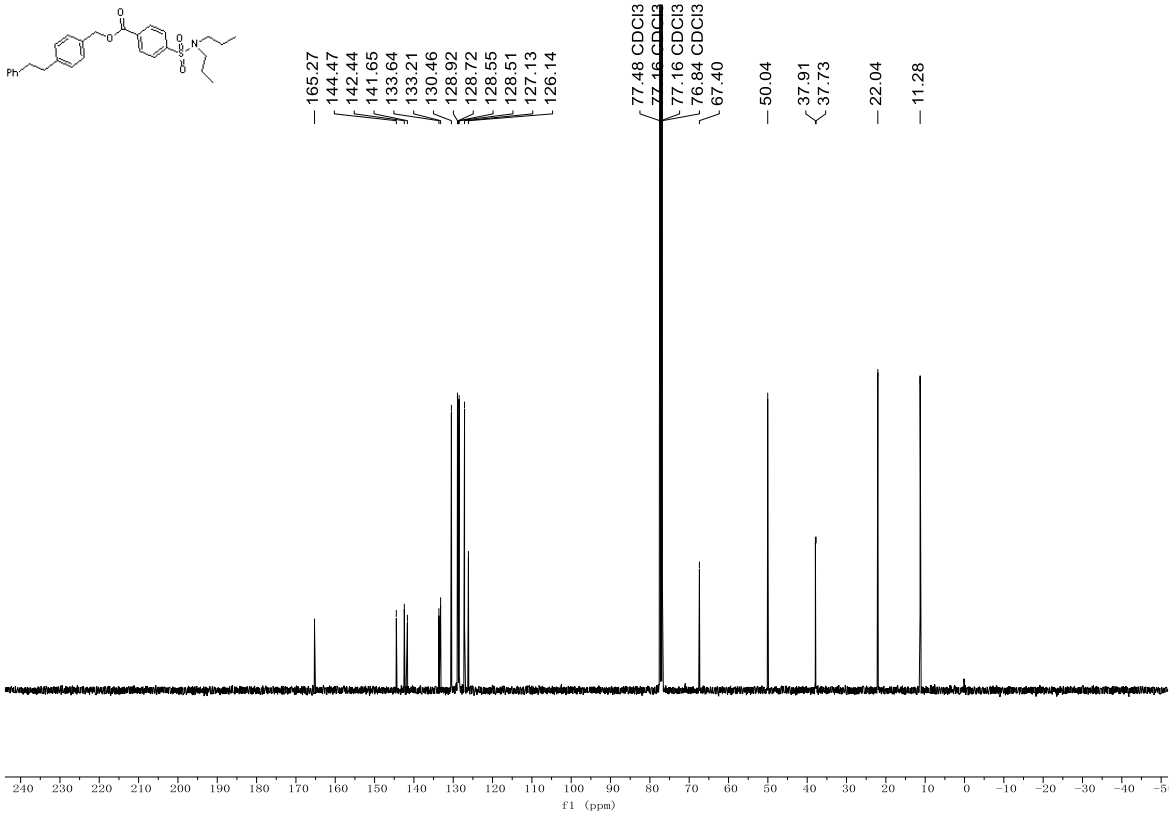
Compound **39**^{13}C NMR



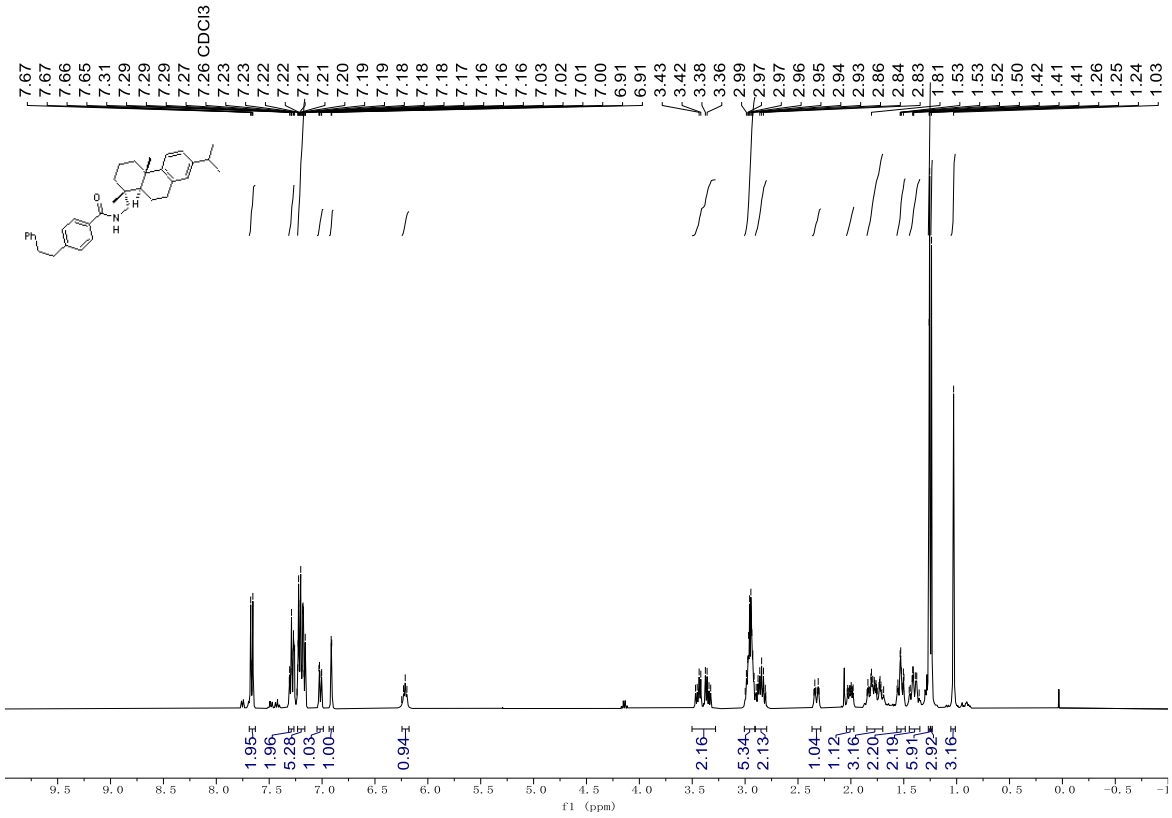
Compound **40** ^{1}H NMR



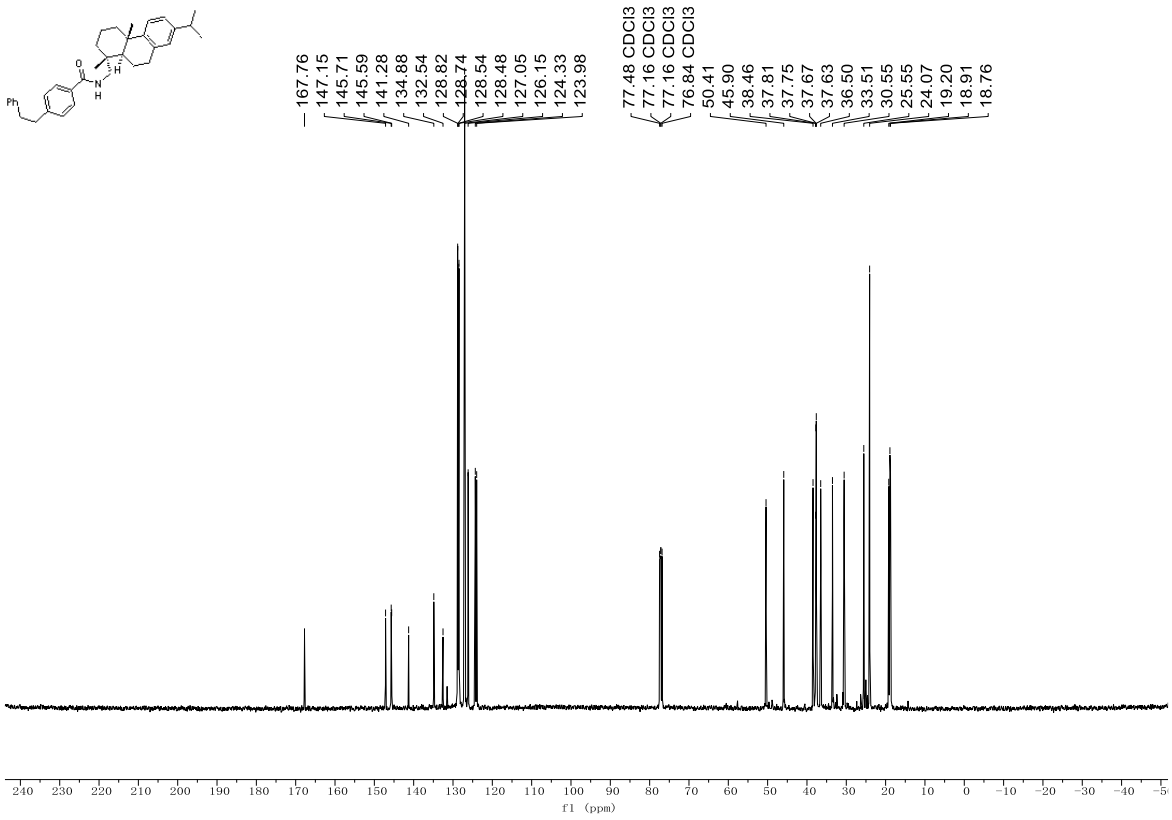
Compound **40** ^{13}C NMR



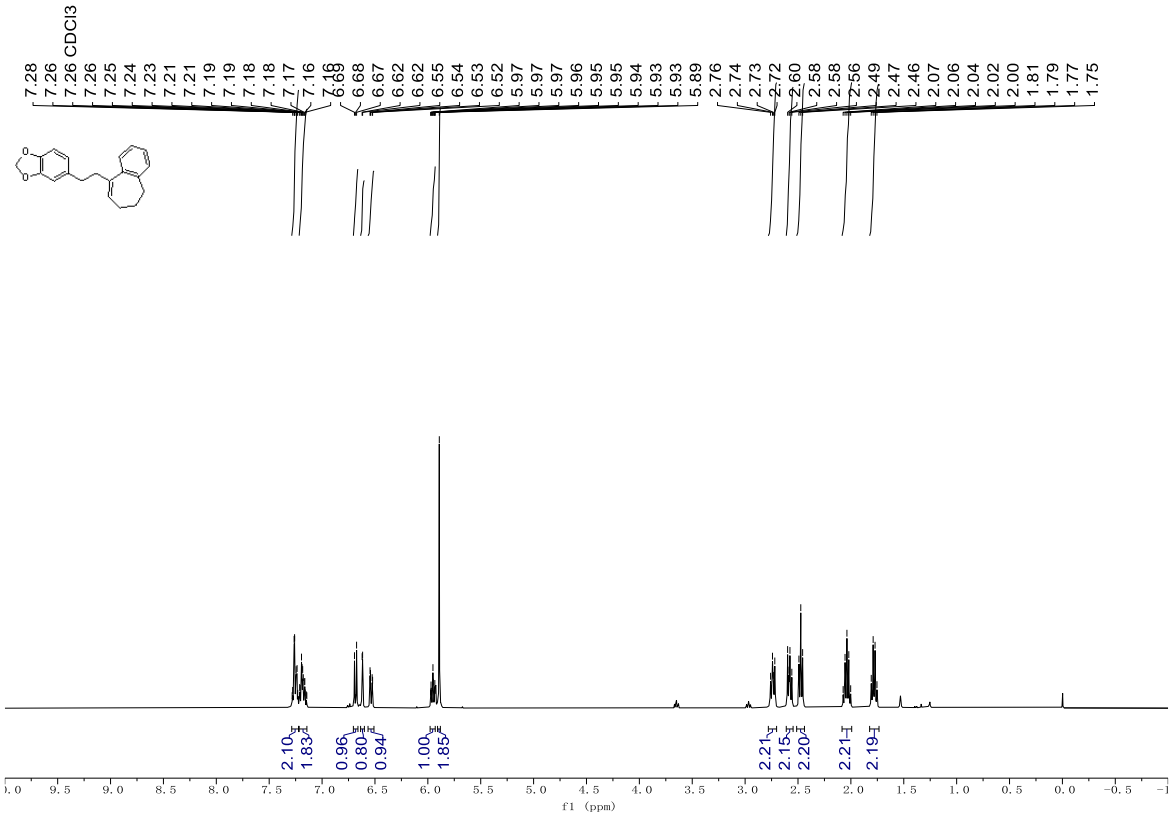
Compound **41** ^{1}H NMR



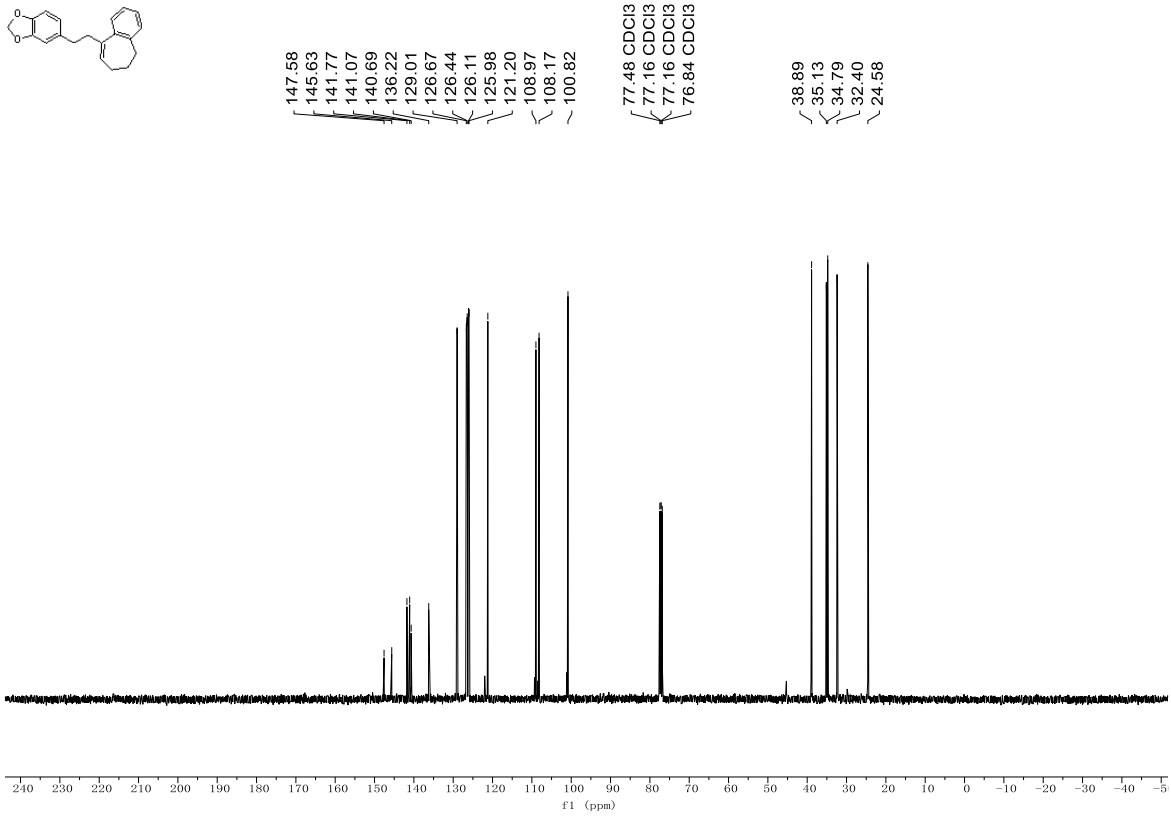
Compound **41** ^{13}C NMR



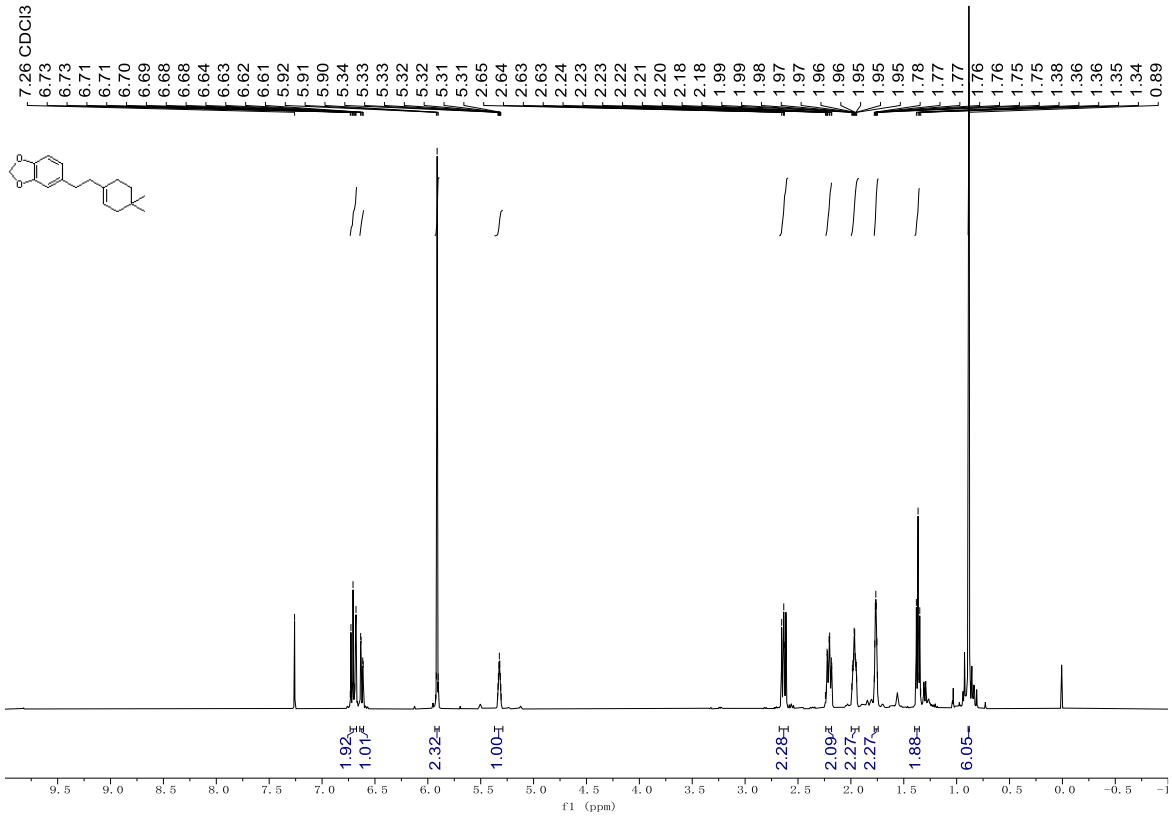
Compound **42** ^{1}H NMR



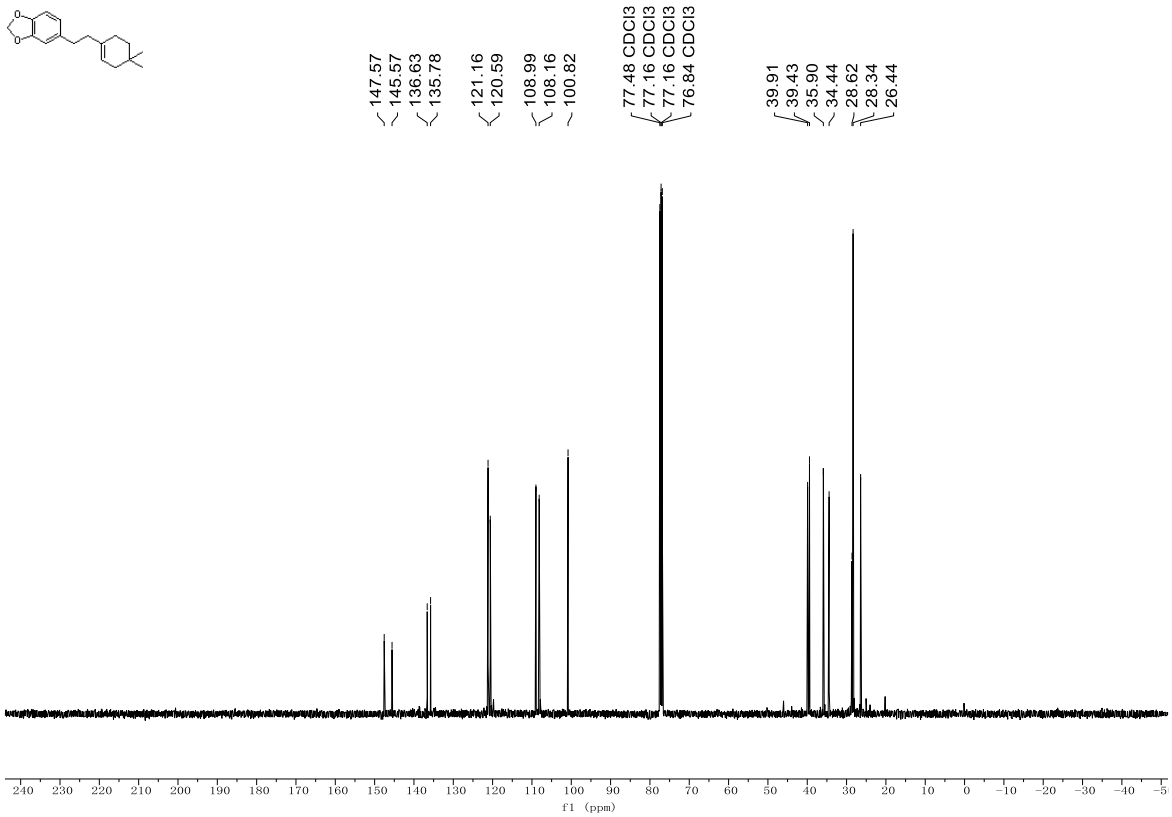
Compound **42** ^{13}C NMR



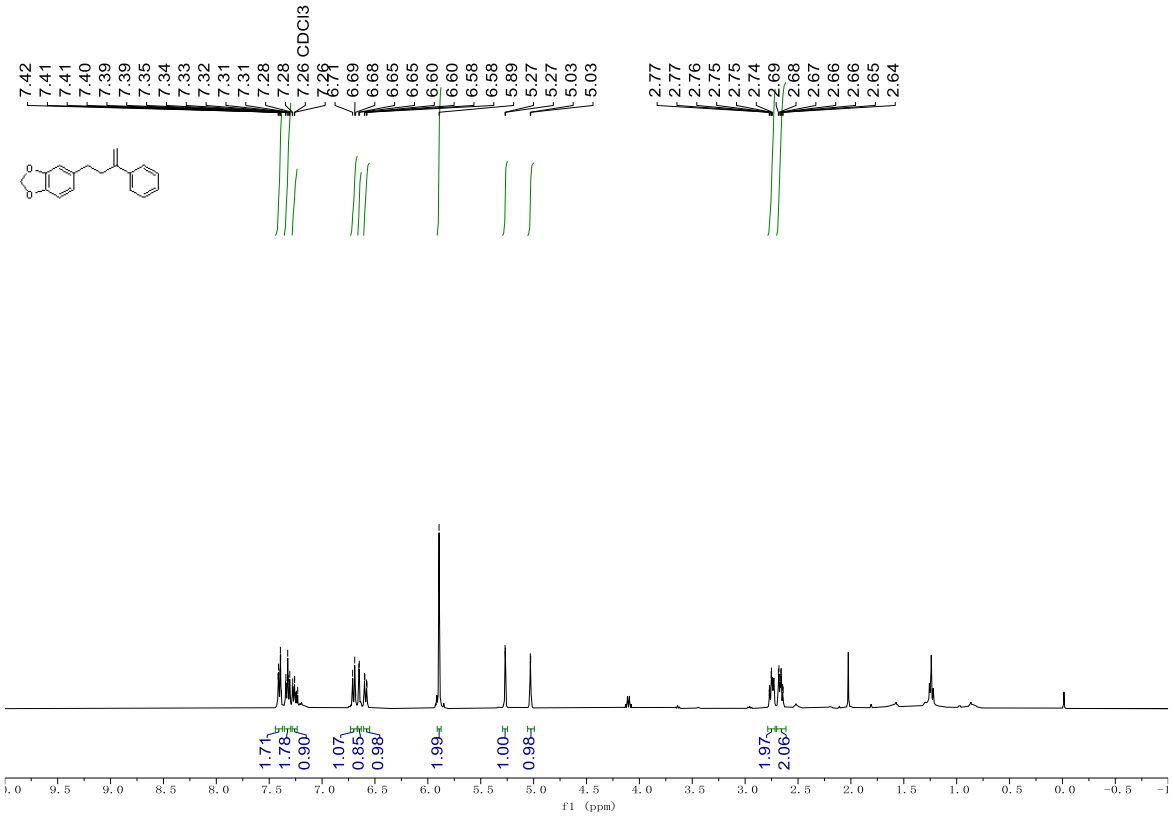
Compound **43** ^{1}H NMR



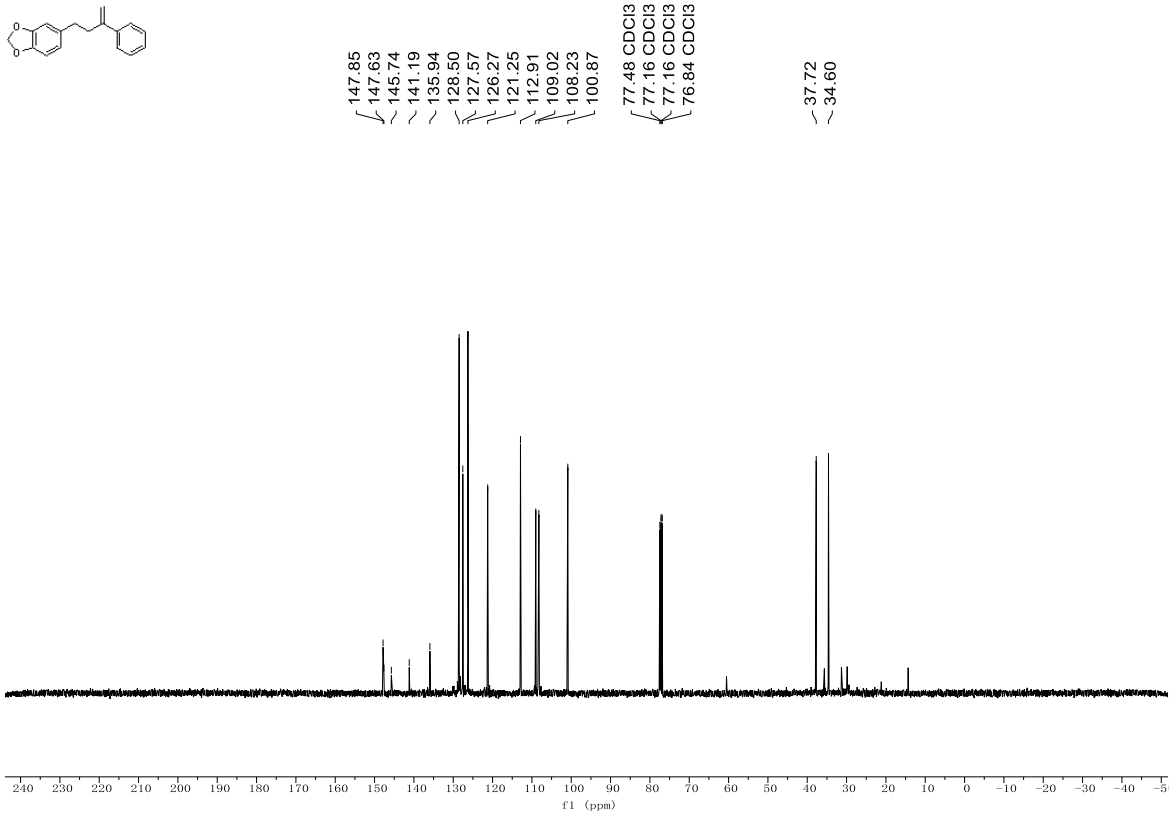
Compound **43** ^{13}C NMR



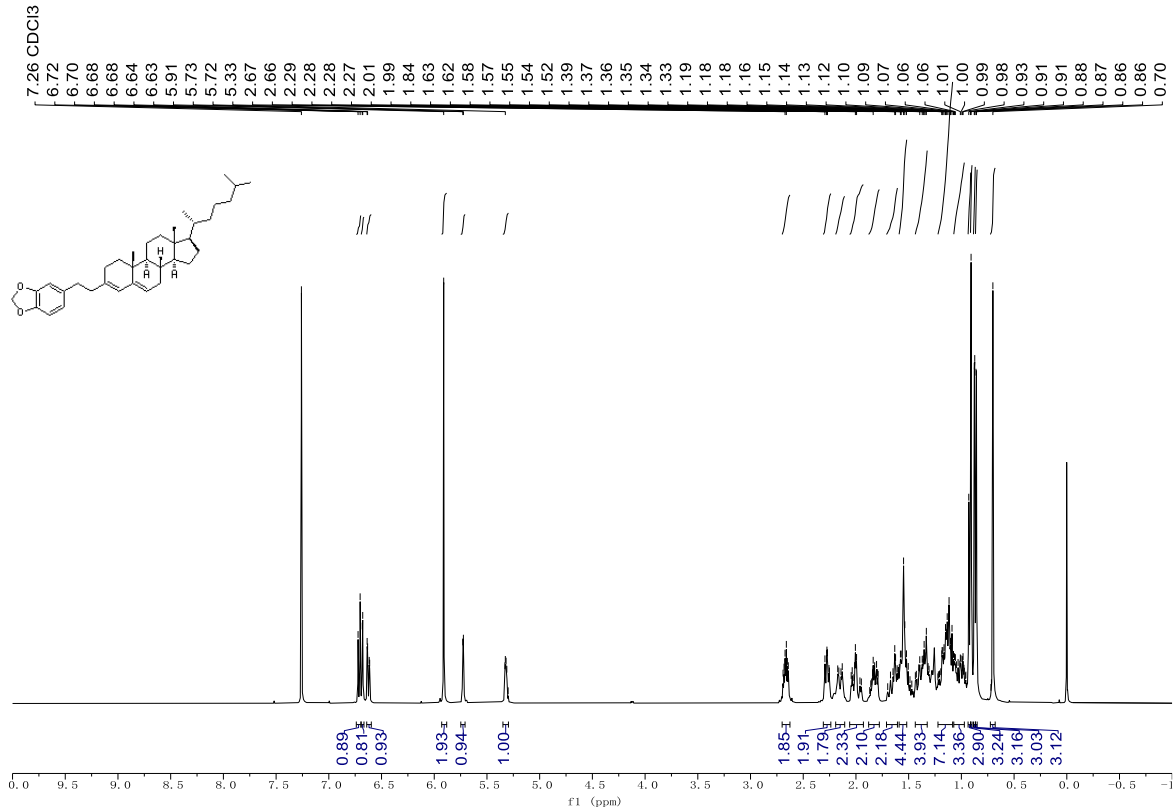
Compound **44** ^{1}H NMR



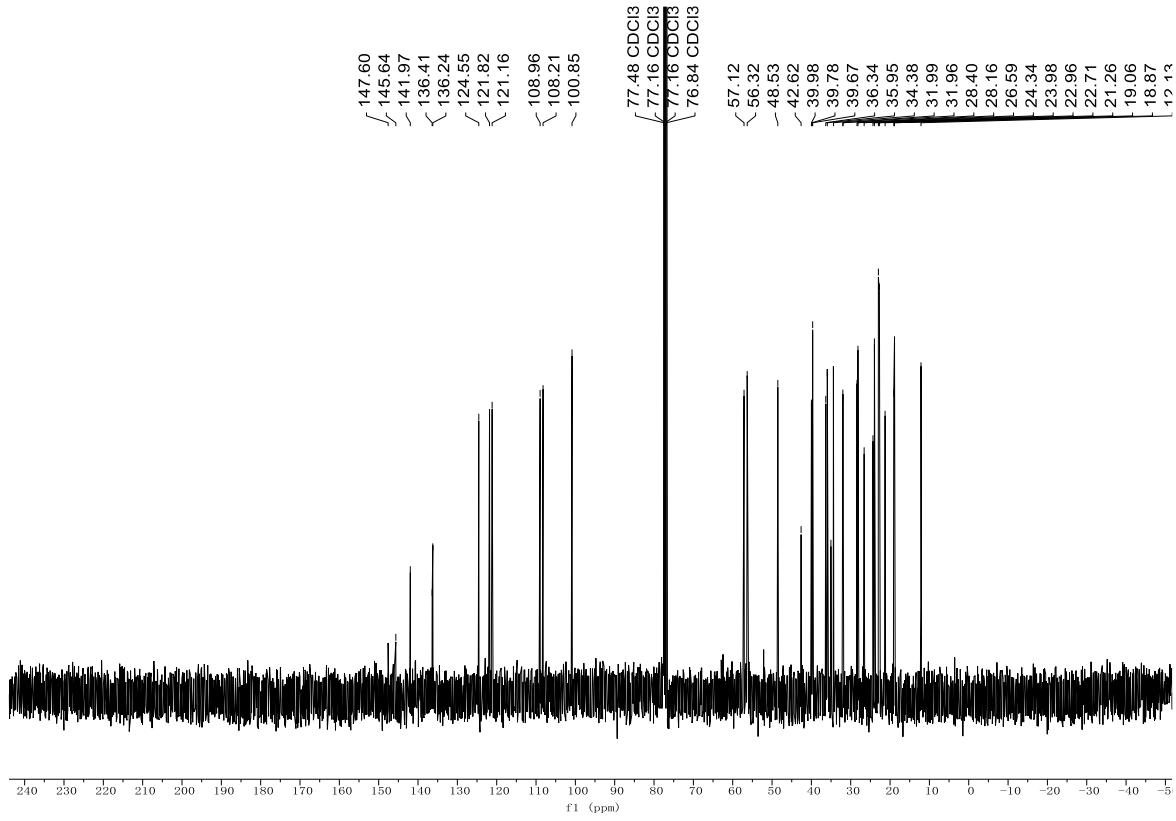
Compound **44** ^{13}C NMR



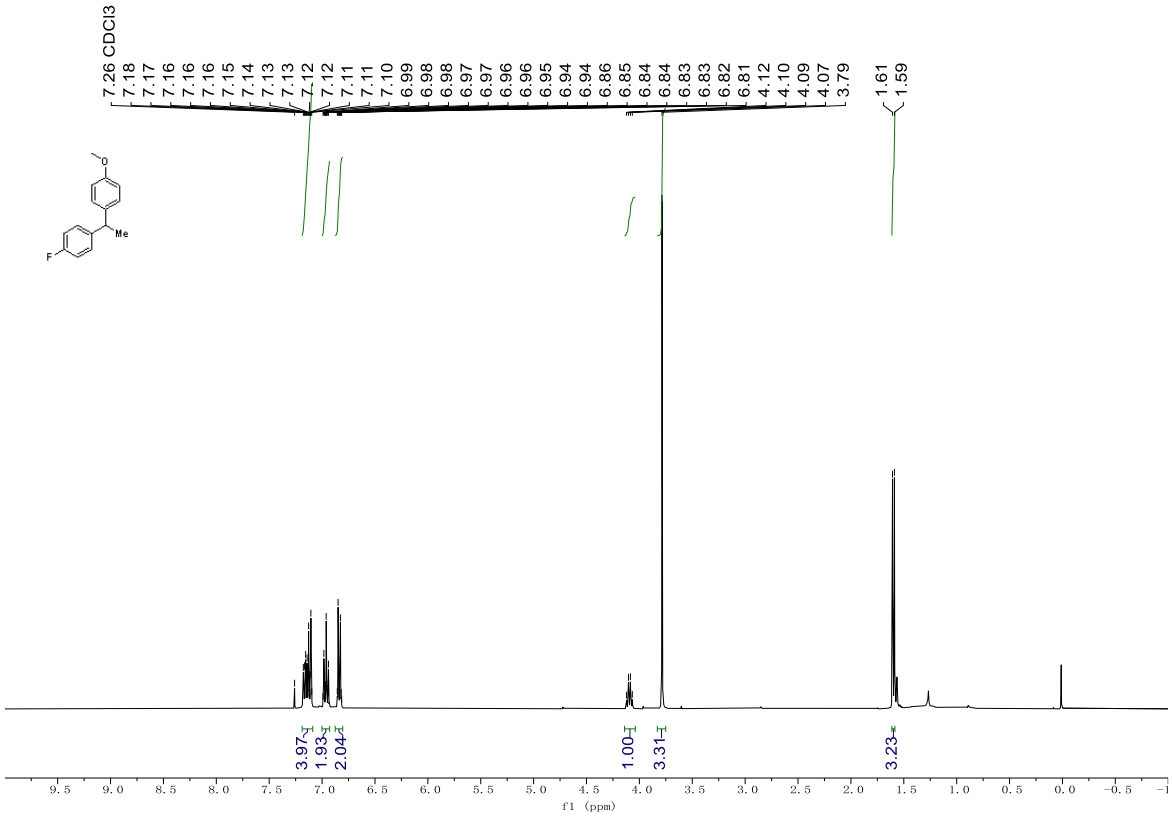
Compound **45** ^{1}H NMR



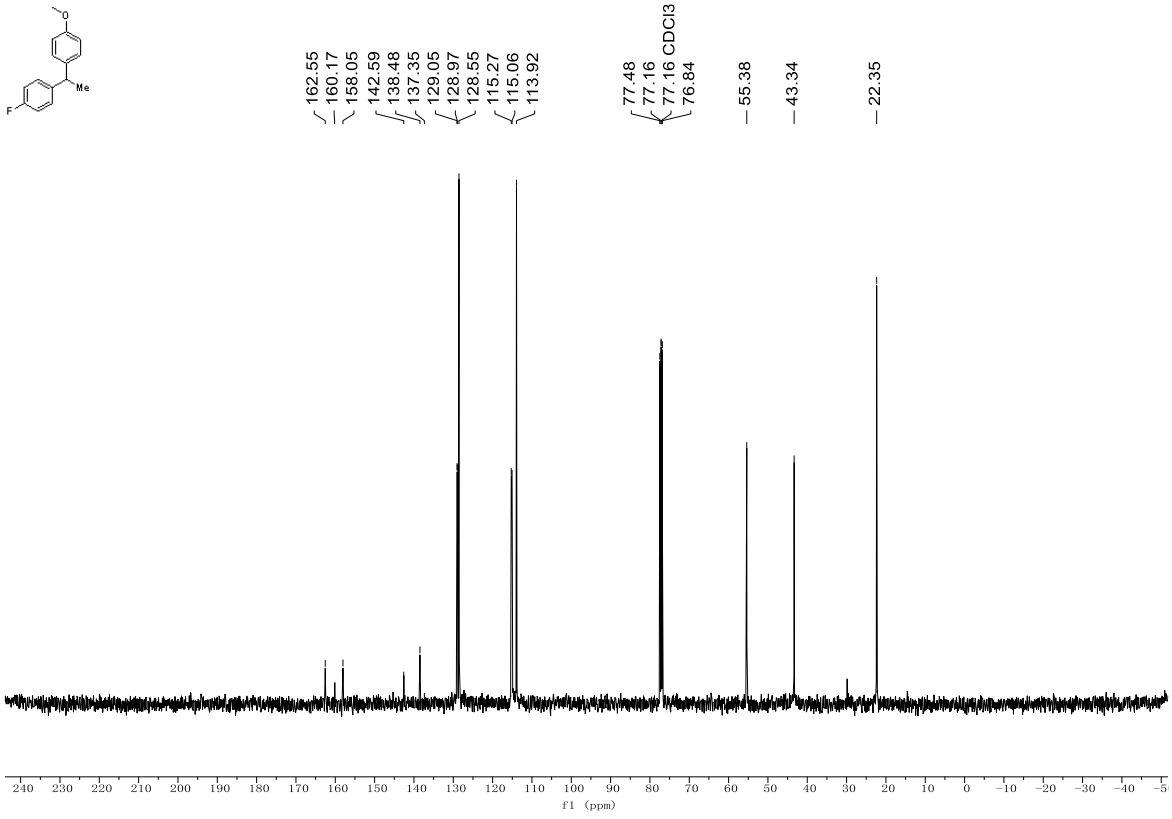
Compound **45** ^{13}C NMR



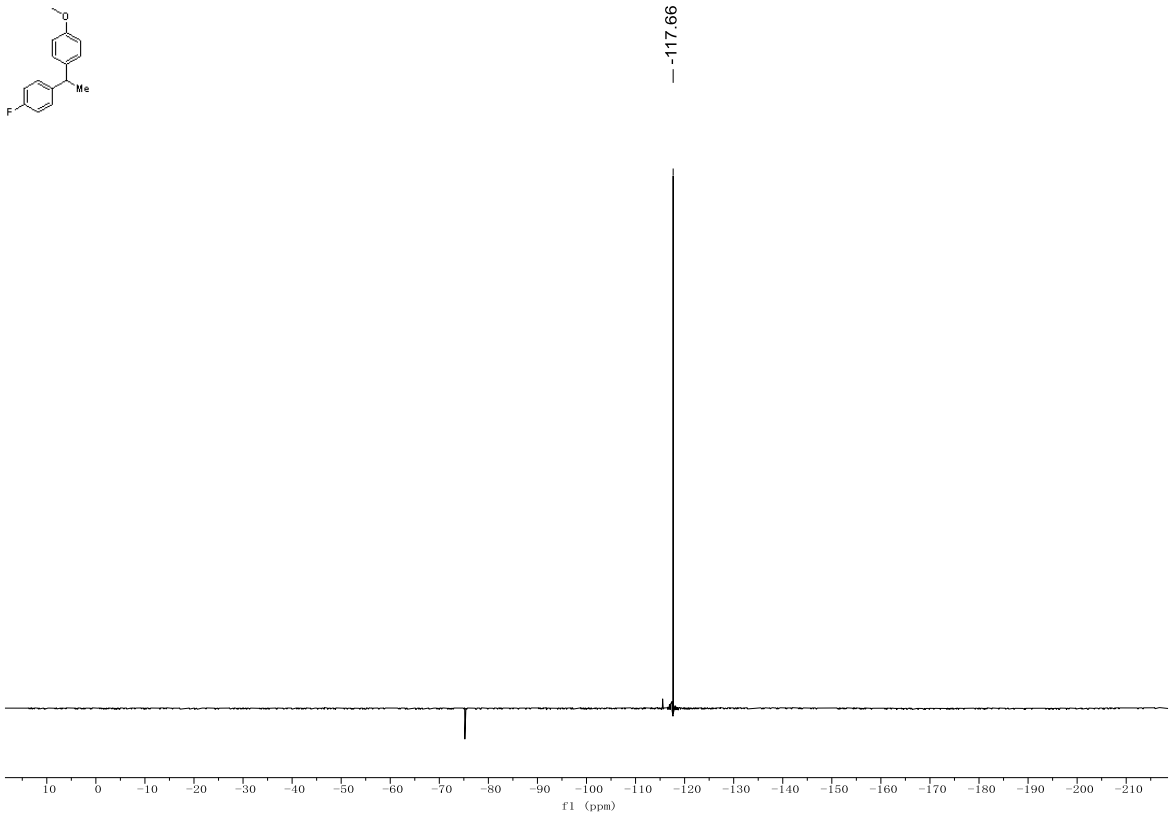
Compound **46** ^{1}H NMR



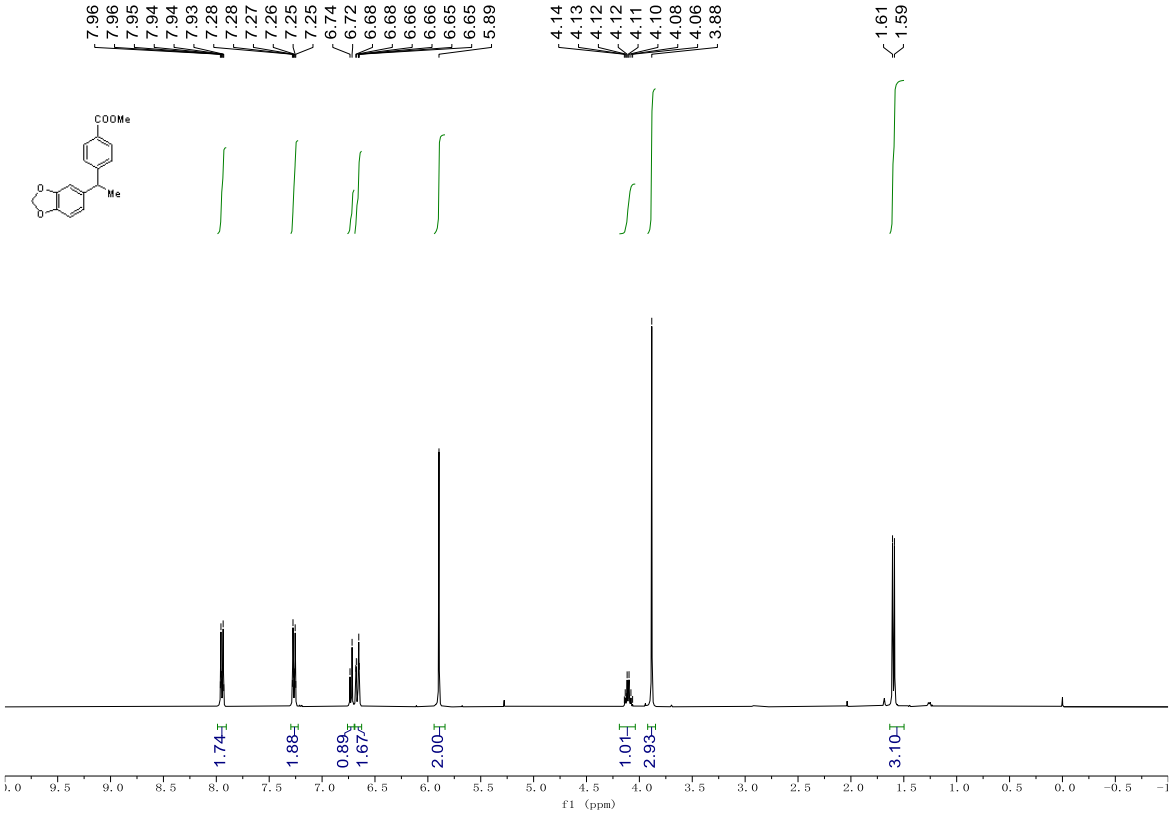
Compound **46** ^{13}C NMR



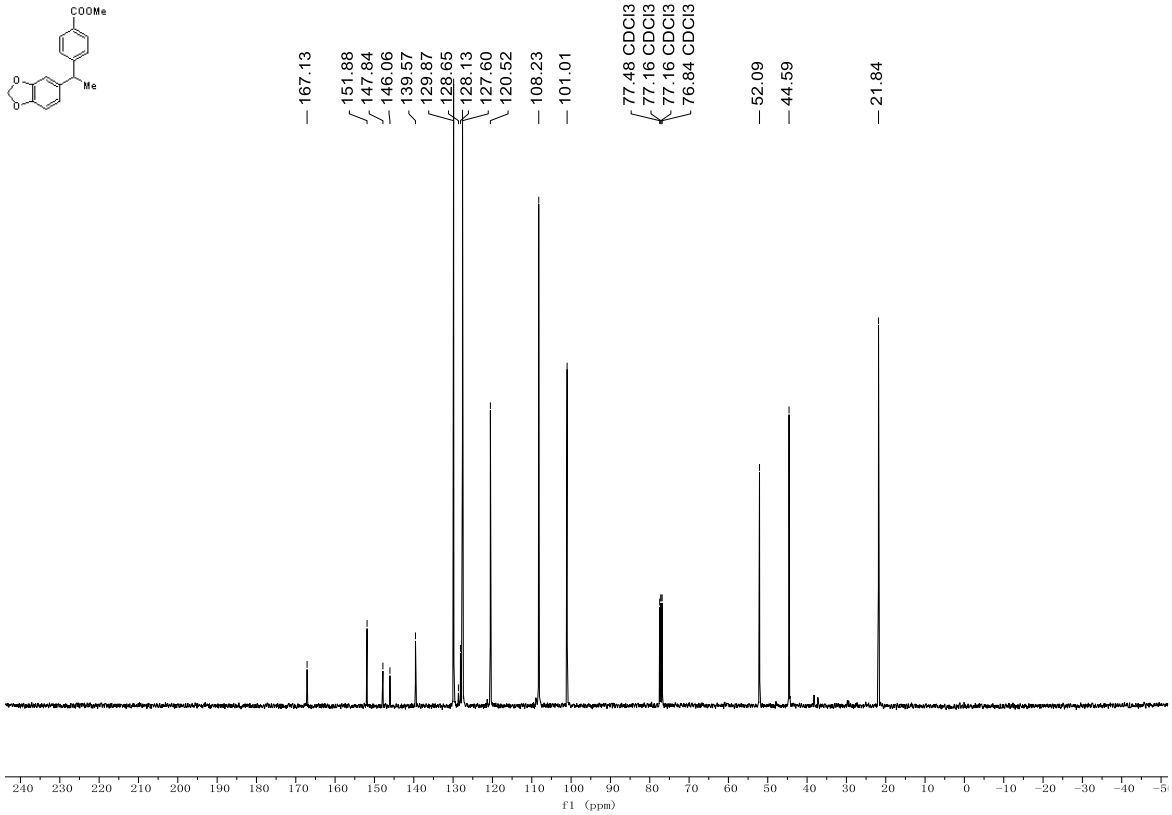
Compound **46** ^{19}F NMR



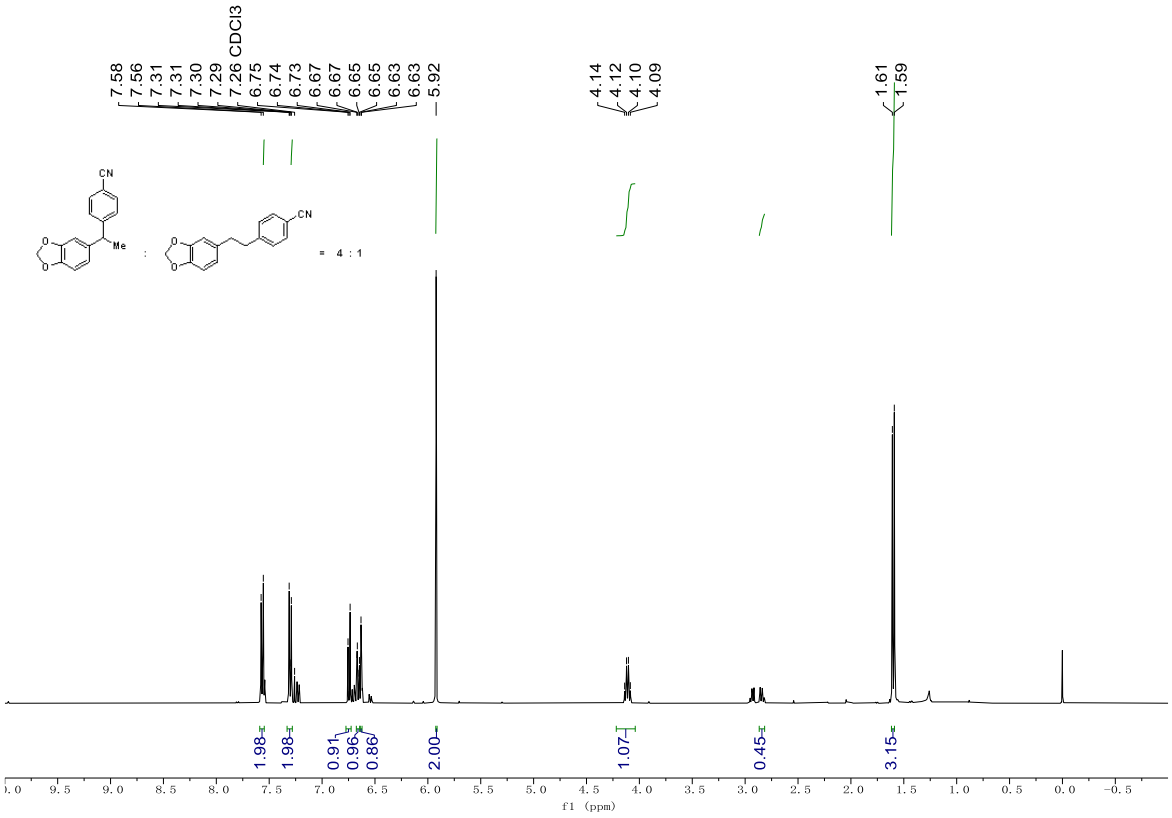
Compound **47** ^{1}H NMR



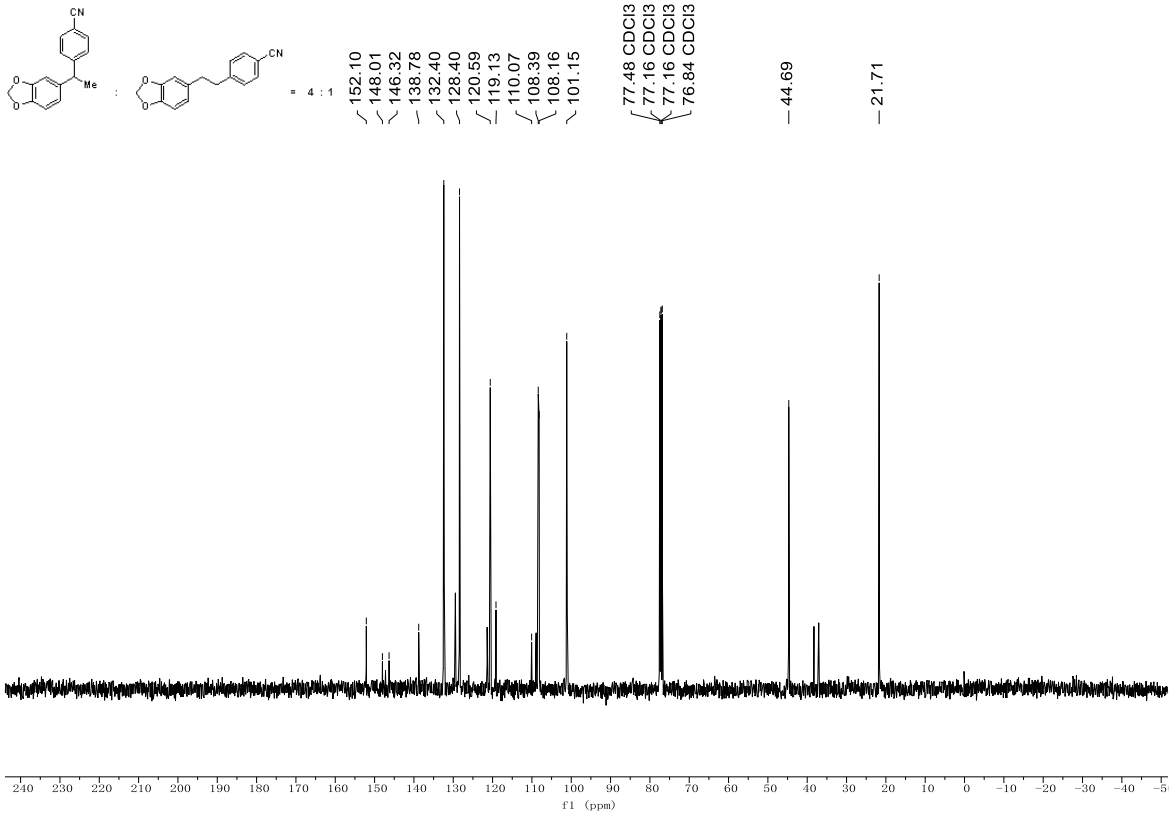
Compound **47** ^{13}C NMR



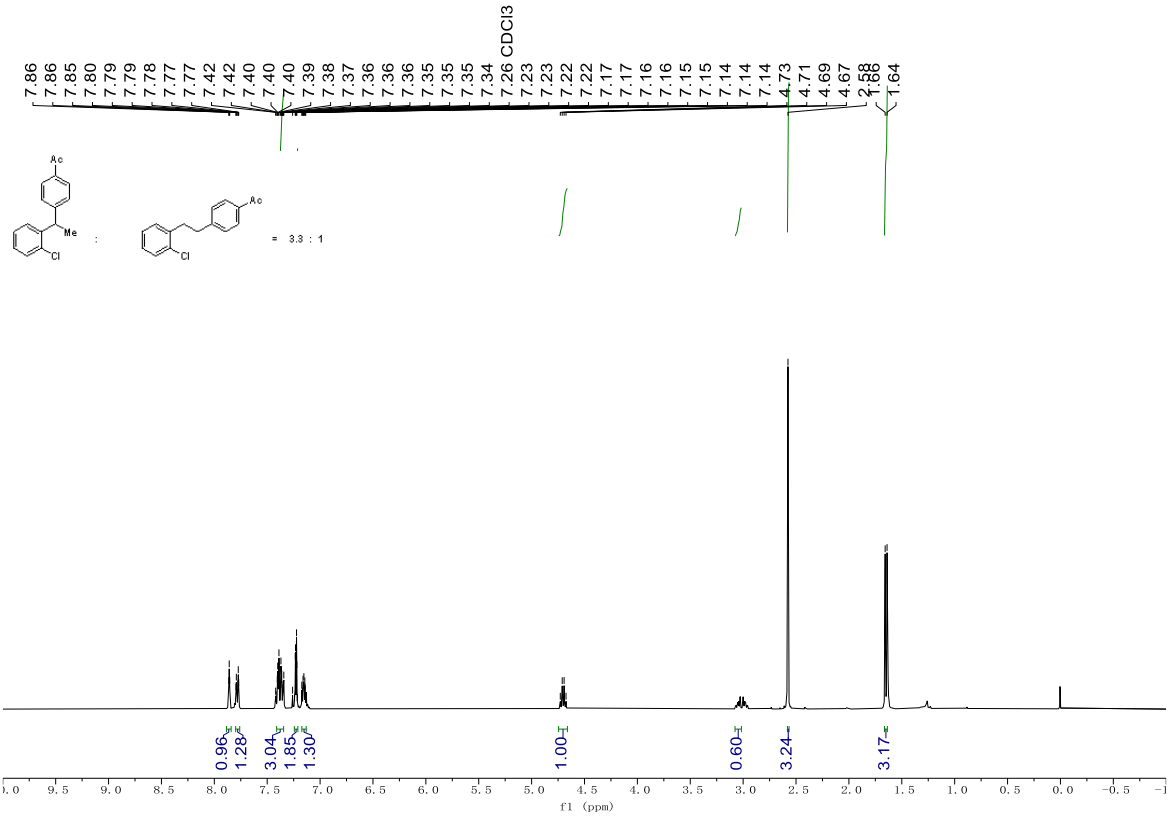
Compound **48** ^{1}H NMR



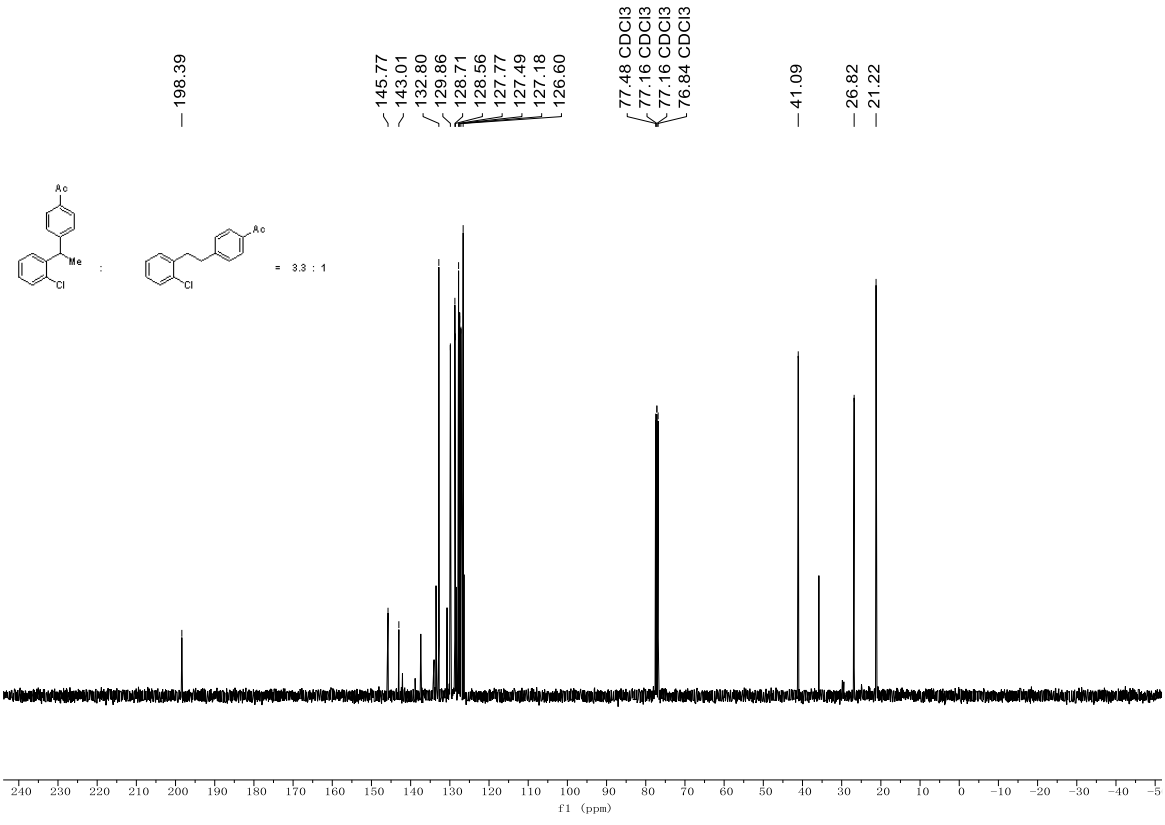
Compound **48** ^{13}C NMR



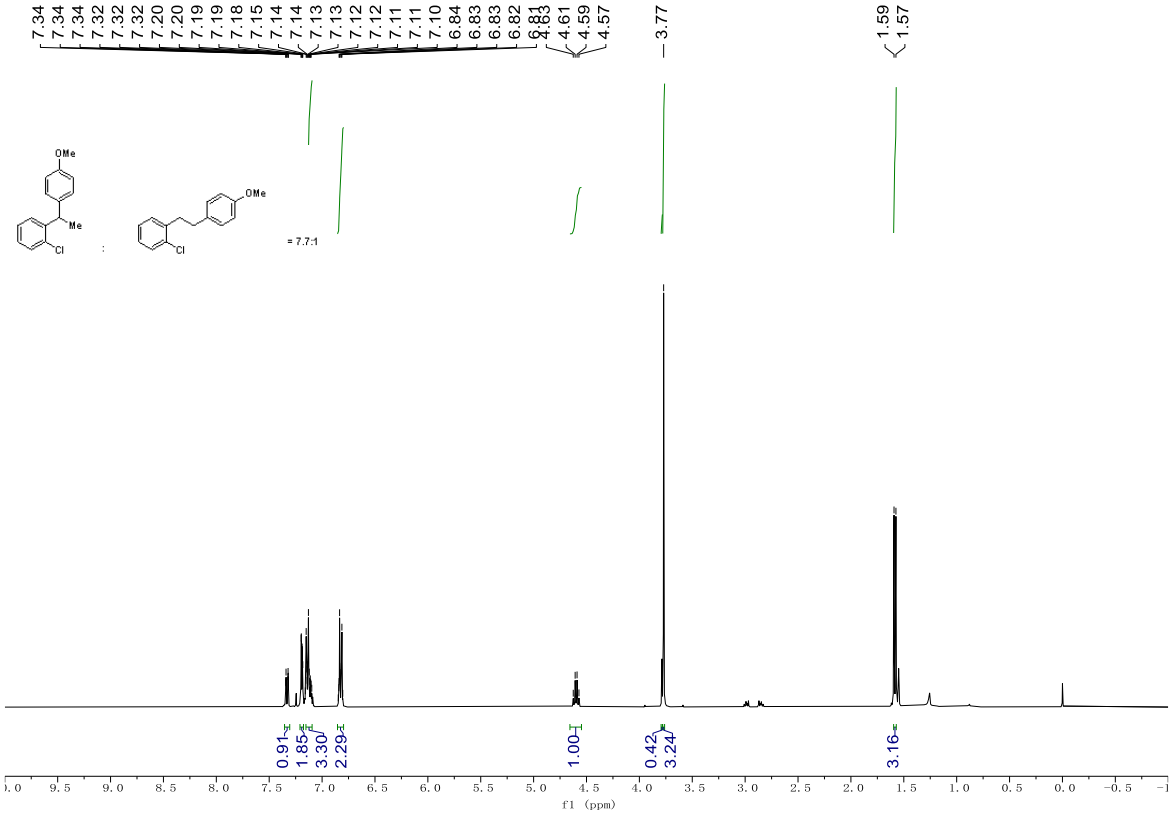
Compound **49** ^{1}H NMR



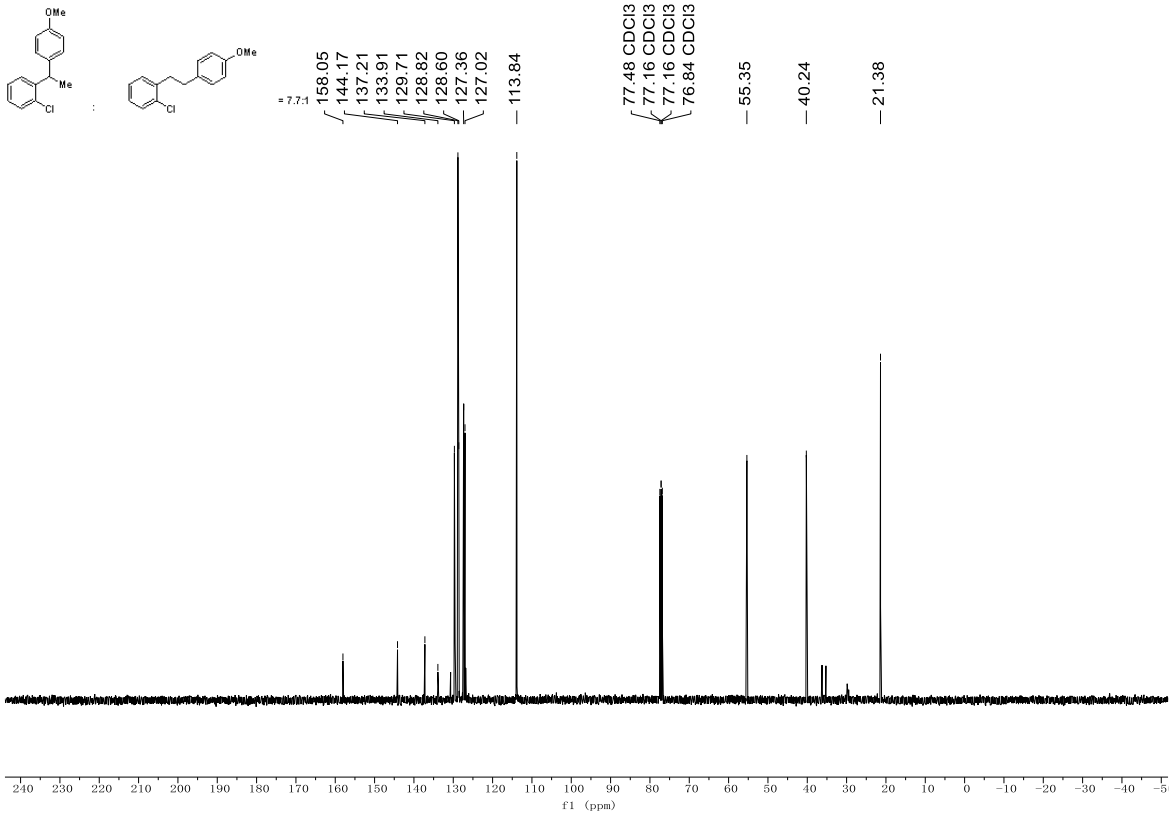
Compound **49** ^{13}C NMR



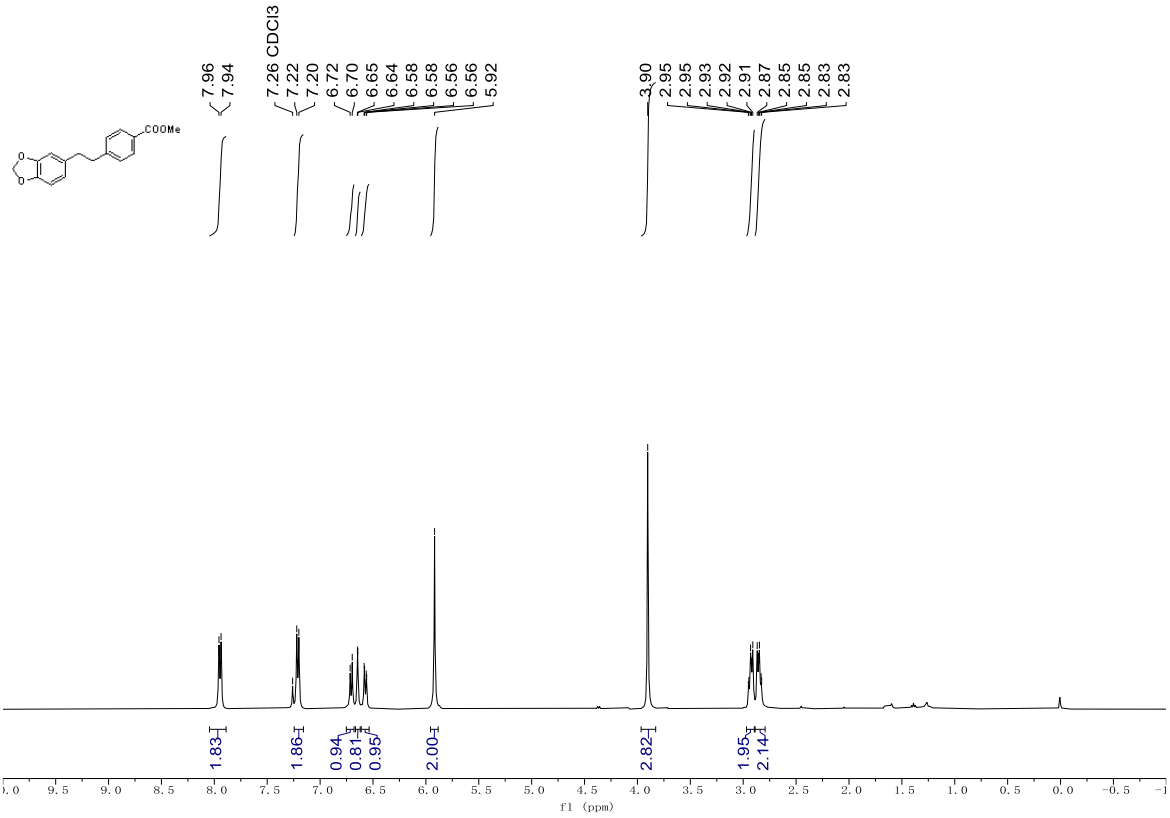
Compound **50** ^{1}H NMR



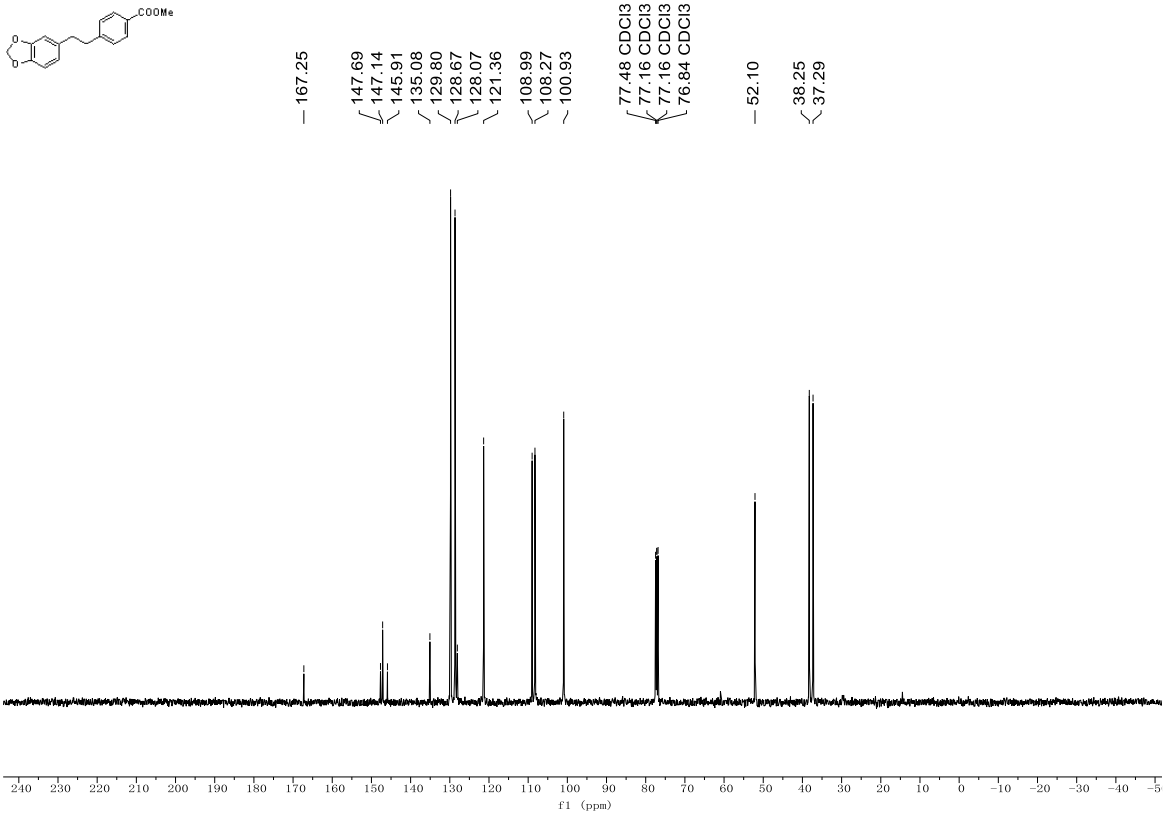
Compound **50** ^{13}C NMR



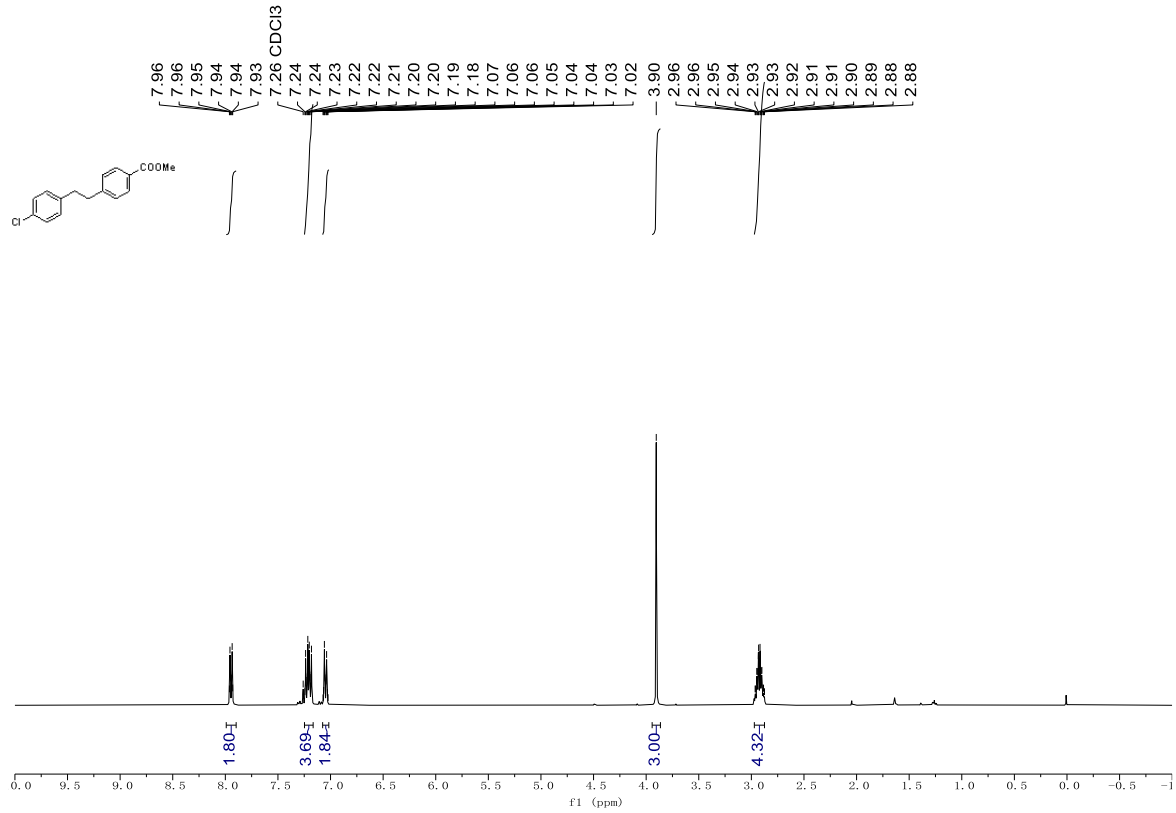
Compound **51** ^{1}H NMR



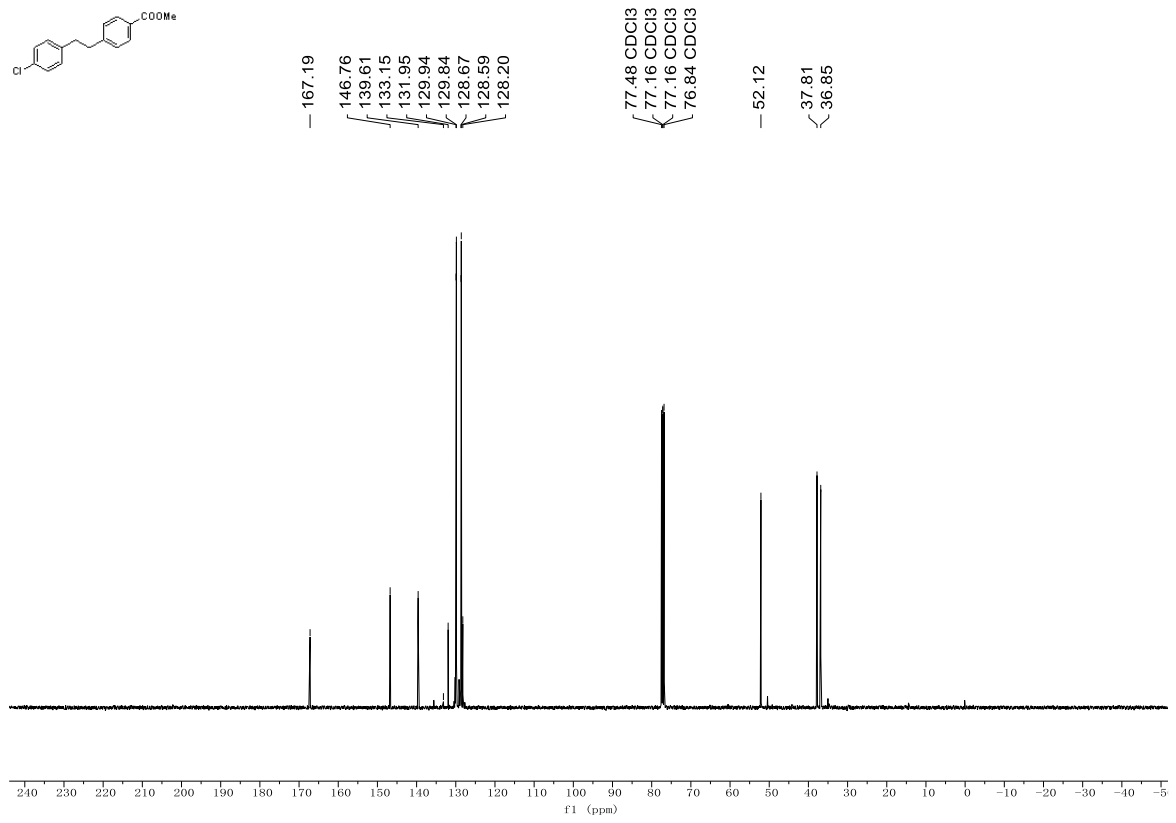
Compound **51** ^{13}C NMR



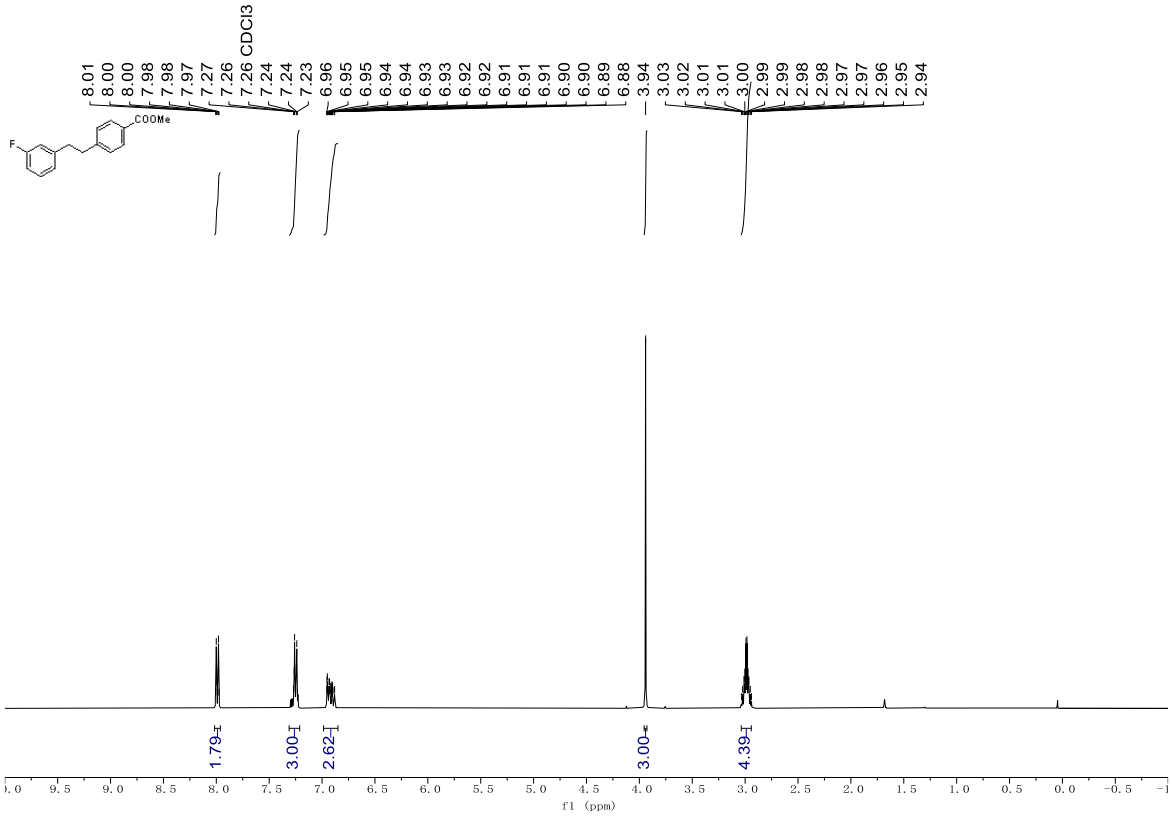
Compound **52** ^{1}H NMR



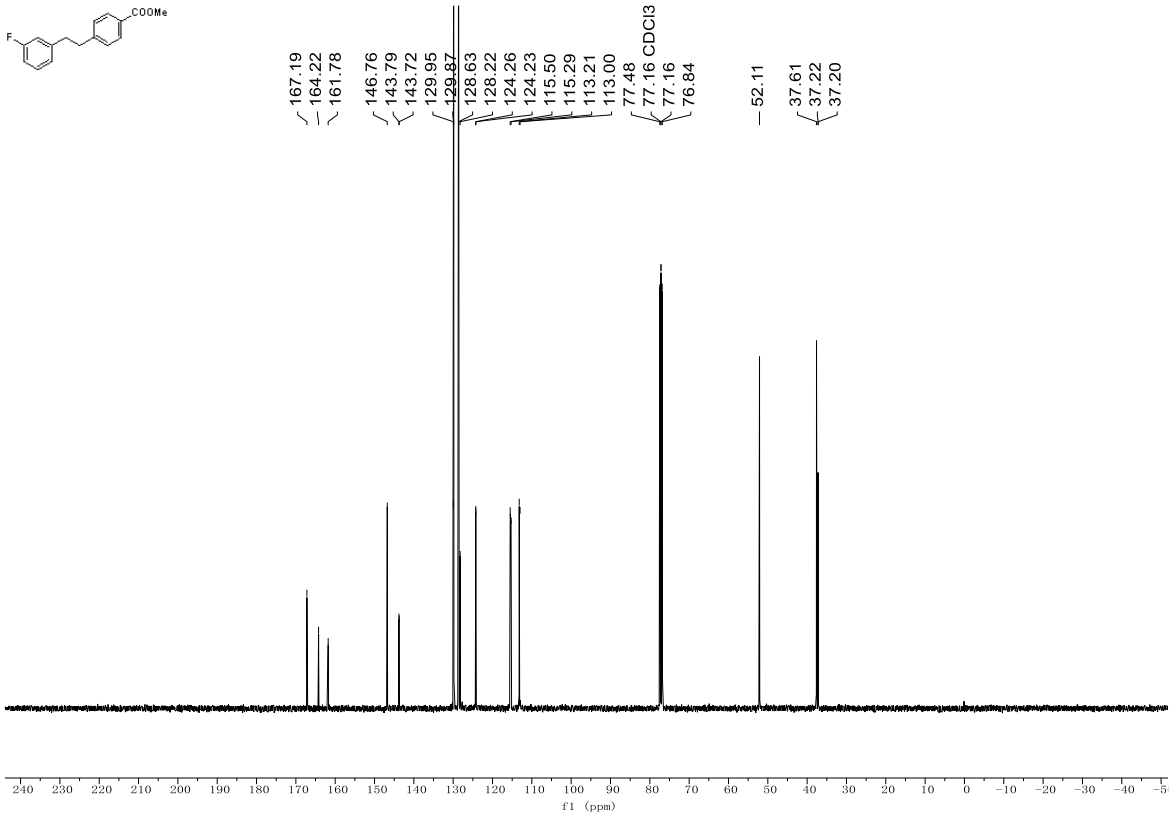
Compound **52** ^{13}C NMR



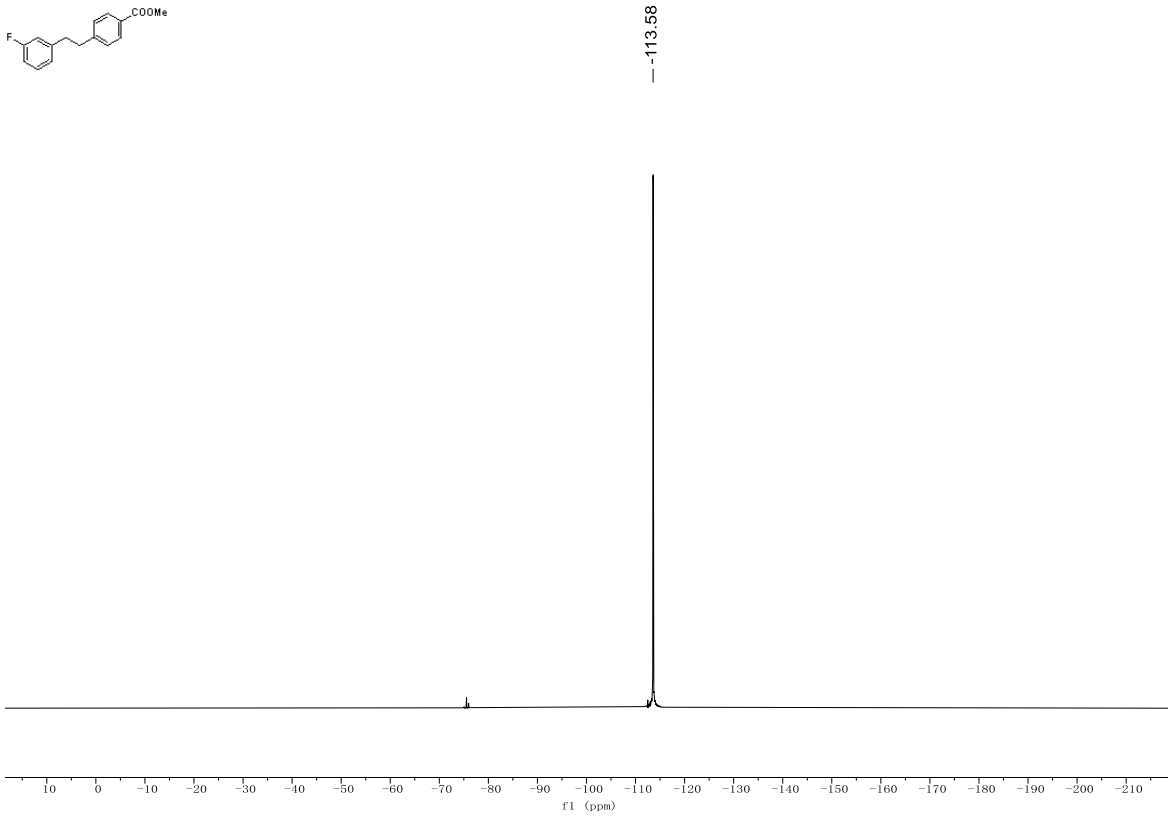
Compound **53** ^{1}H NMR



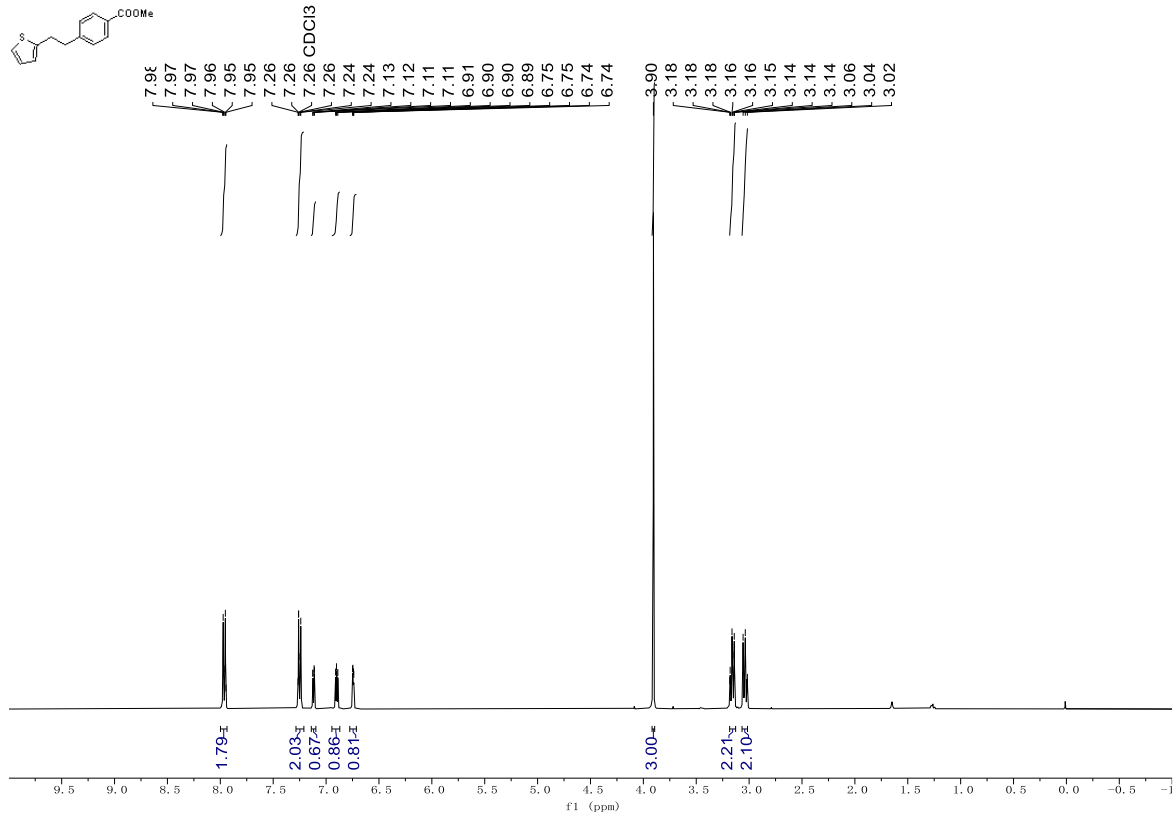
Compound **53** ^{13}C NMR



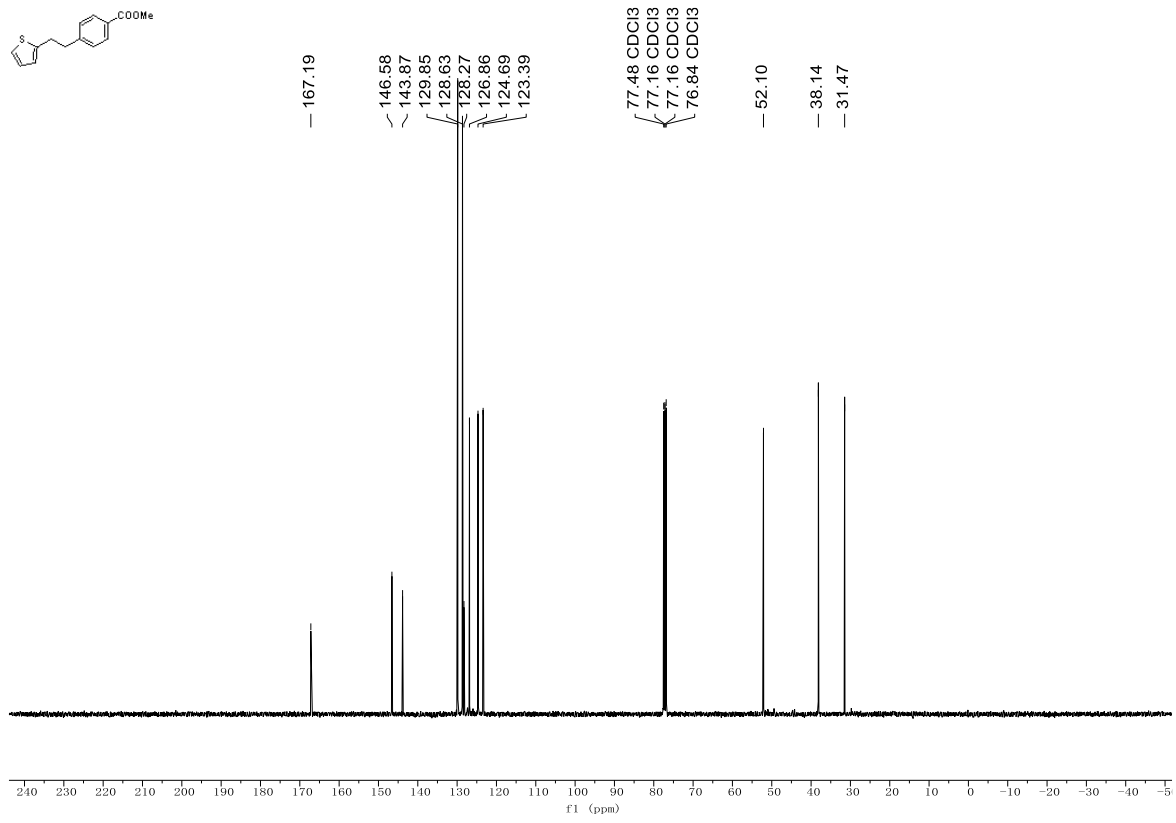
Compound **53** ^{19}F NMR



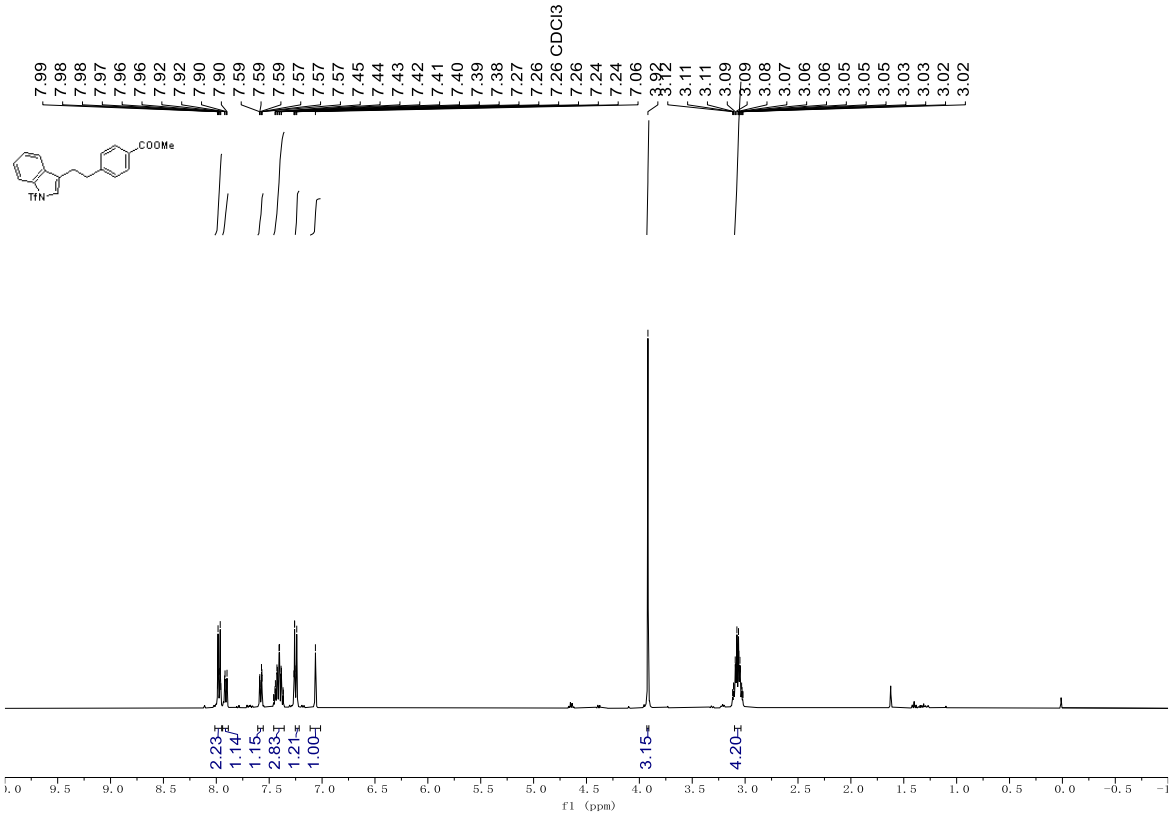
Compound **54** ^{1}H NMR



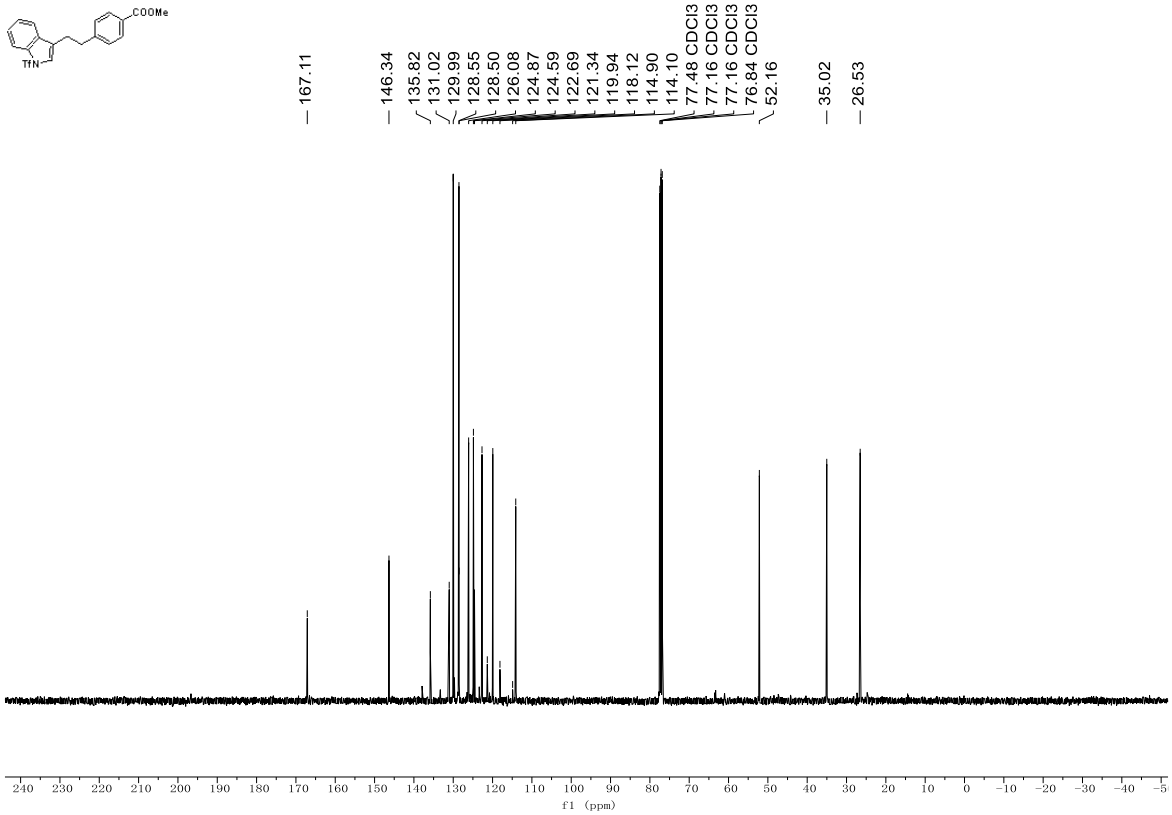
Compound **54** ^{13}C NMR



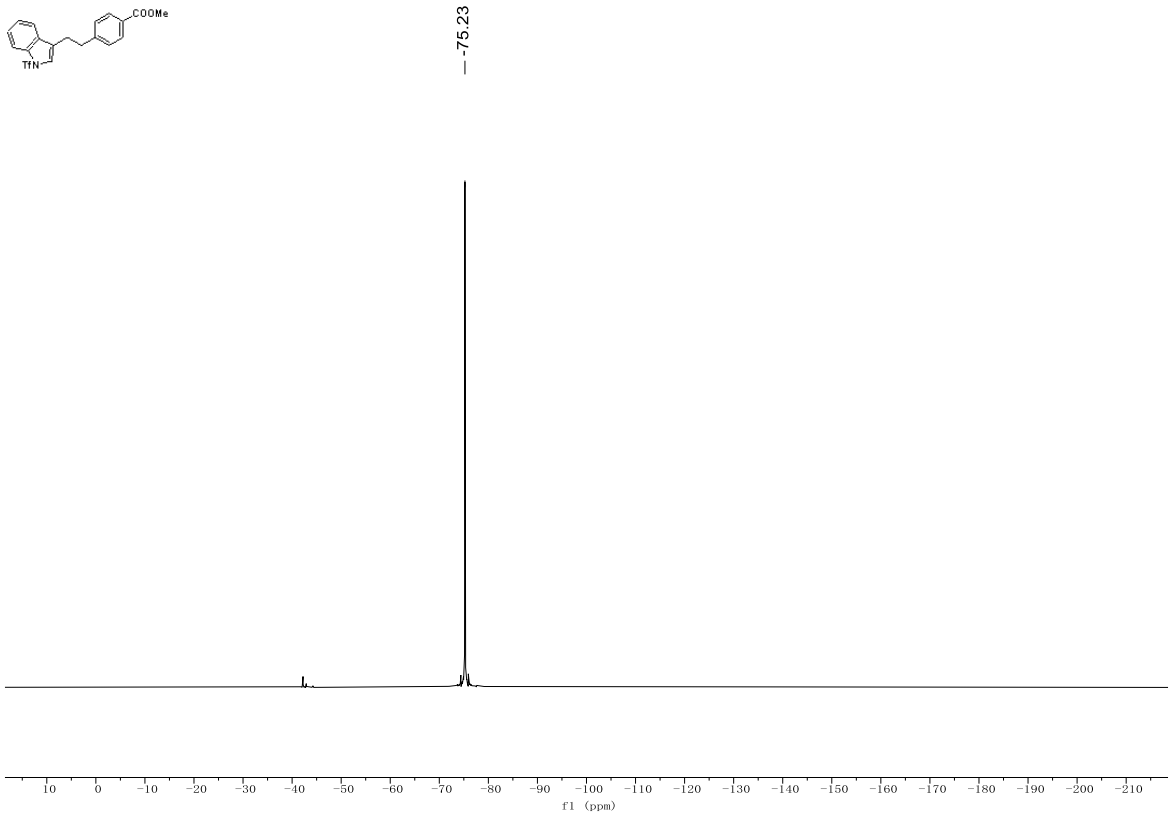
Compound **55** ^{1}H NMR



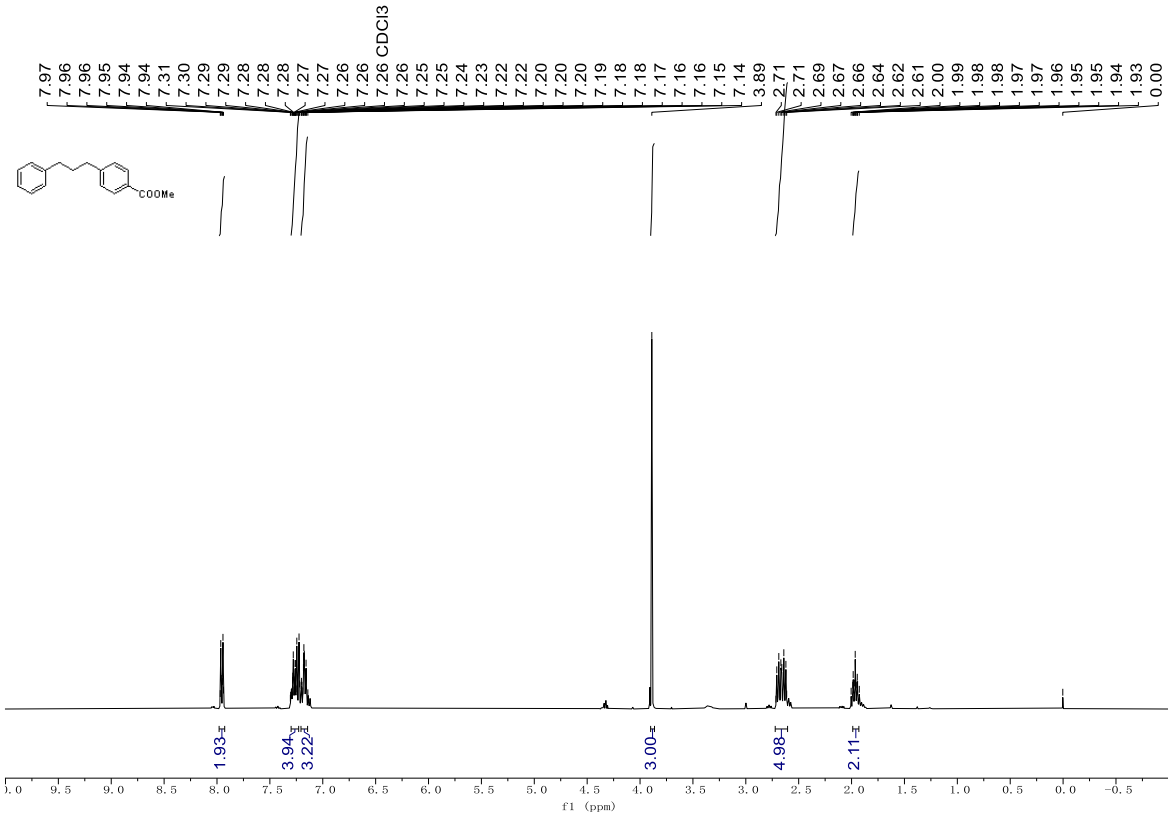
Compound **55** ^{13}C NMR



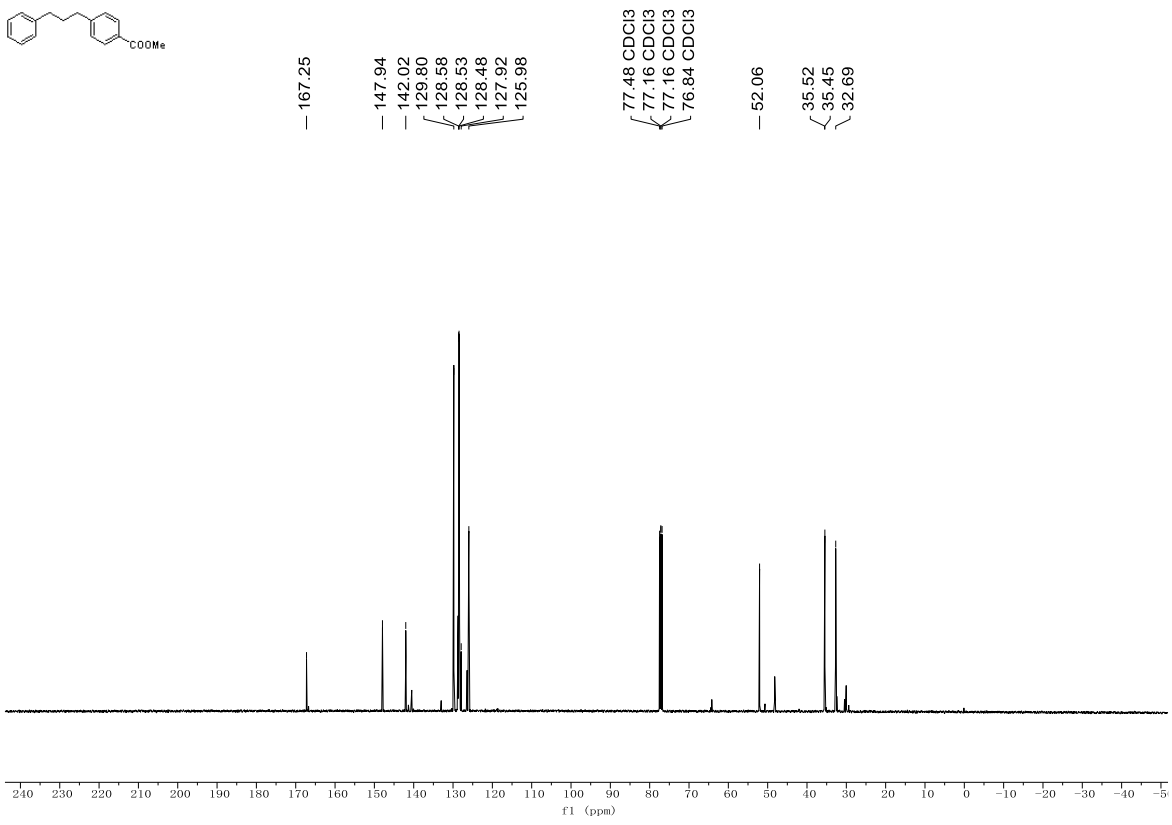
Compound **55** ^{19}F NMR



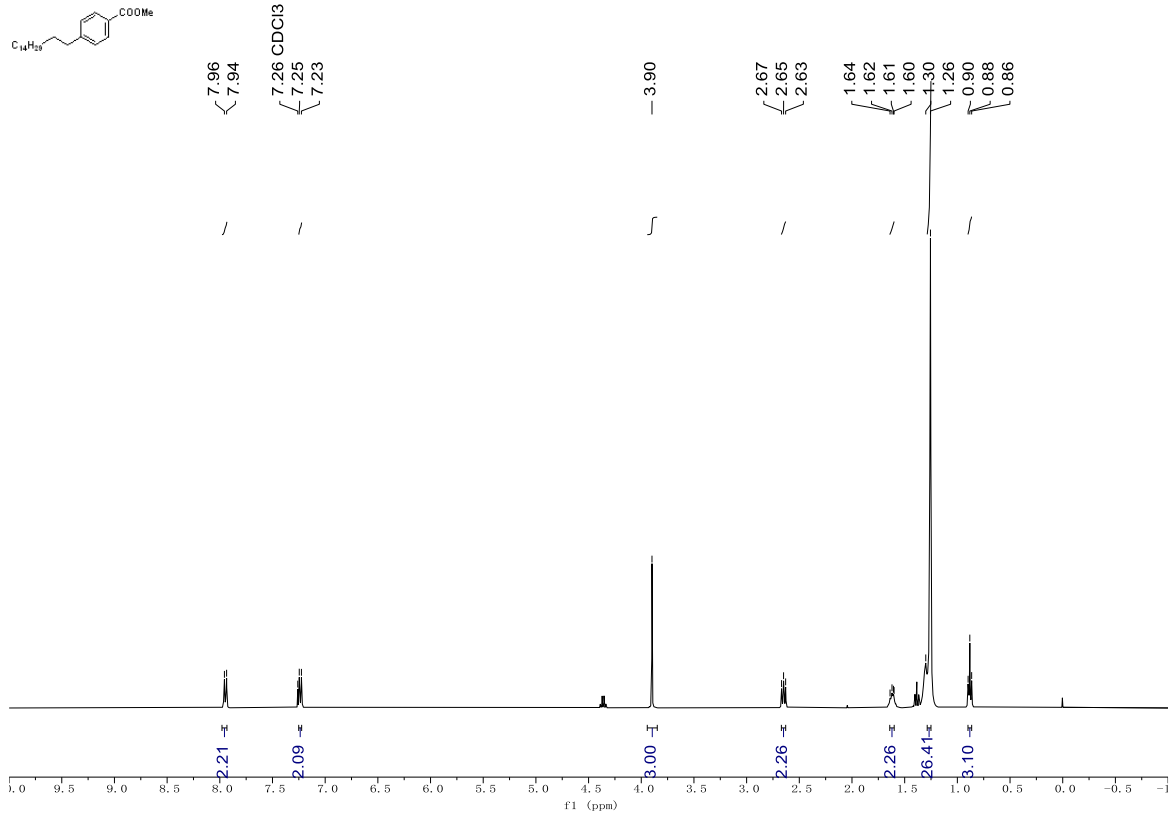
Compound **56** ^{1}H NMR



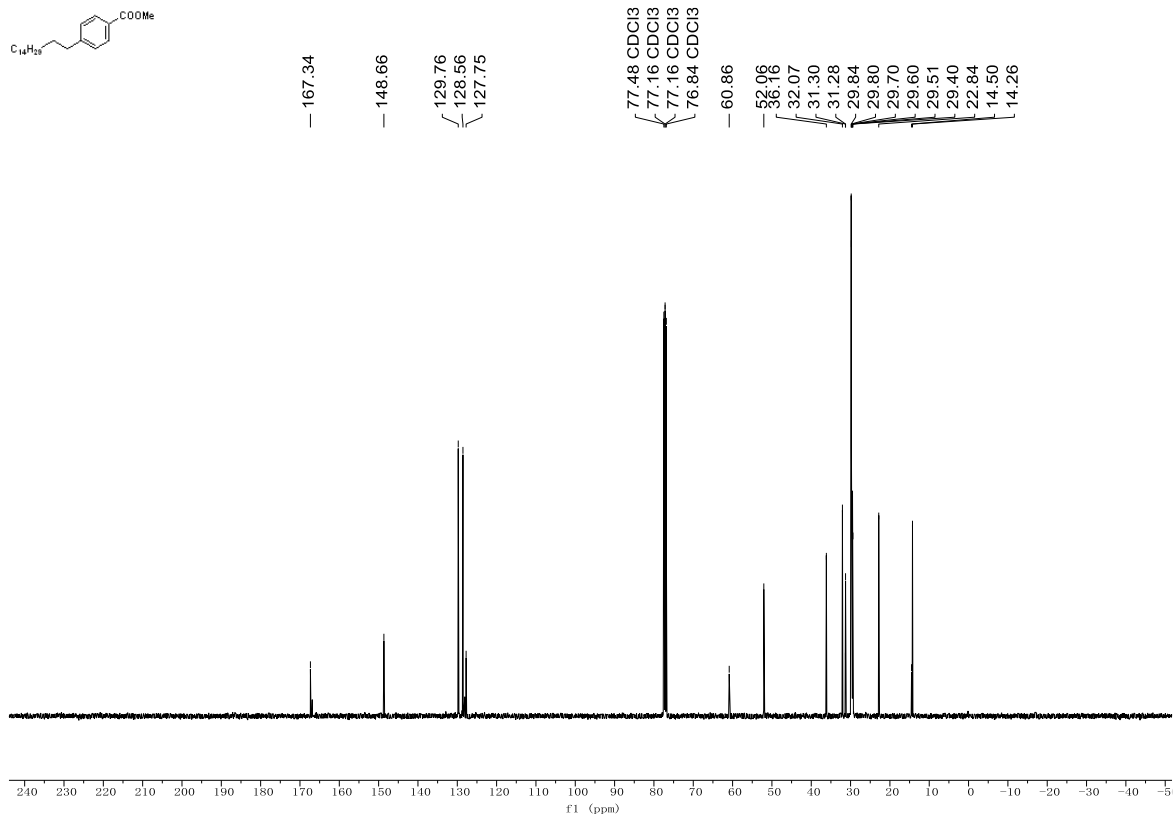
Compound **56** ^{13}C NMR



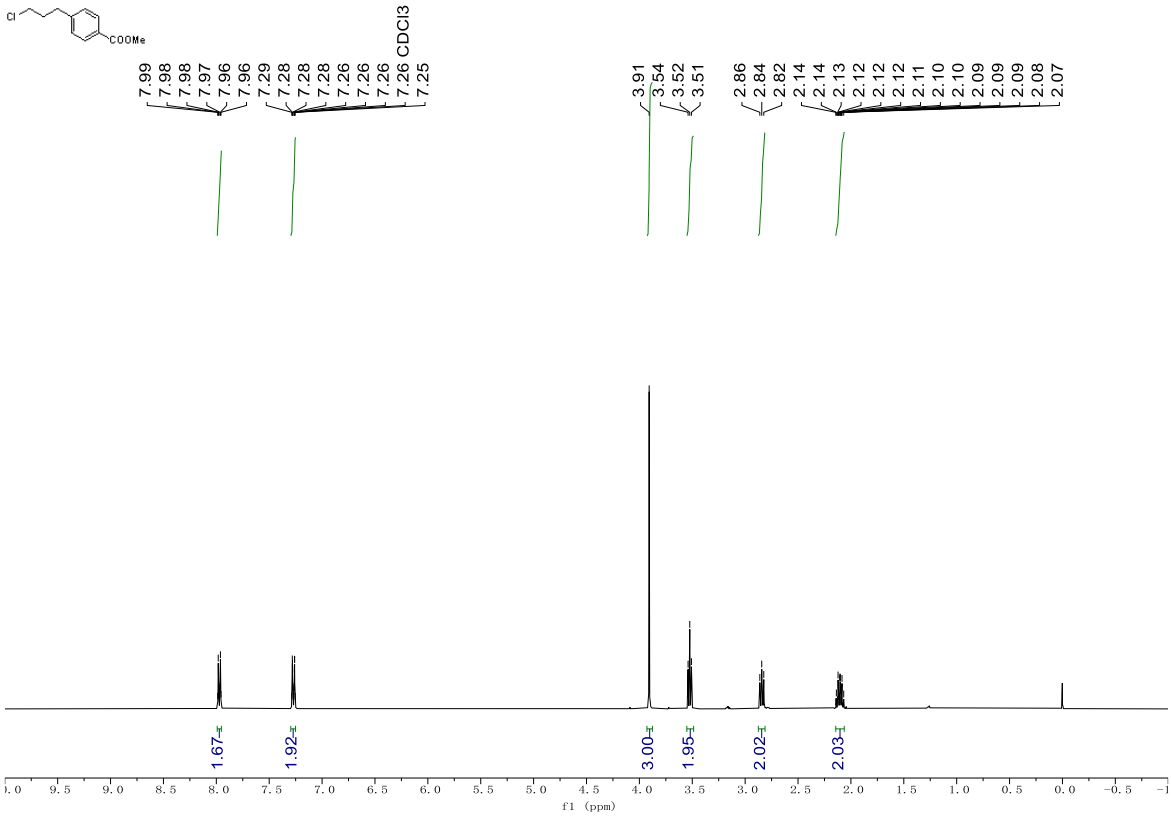
Compound **57** ^{1}H NMR



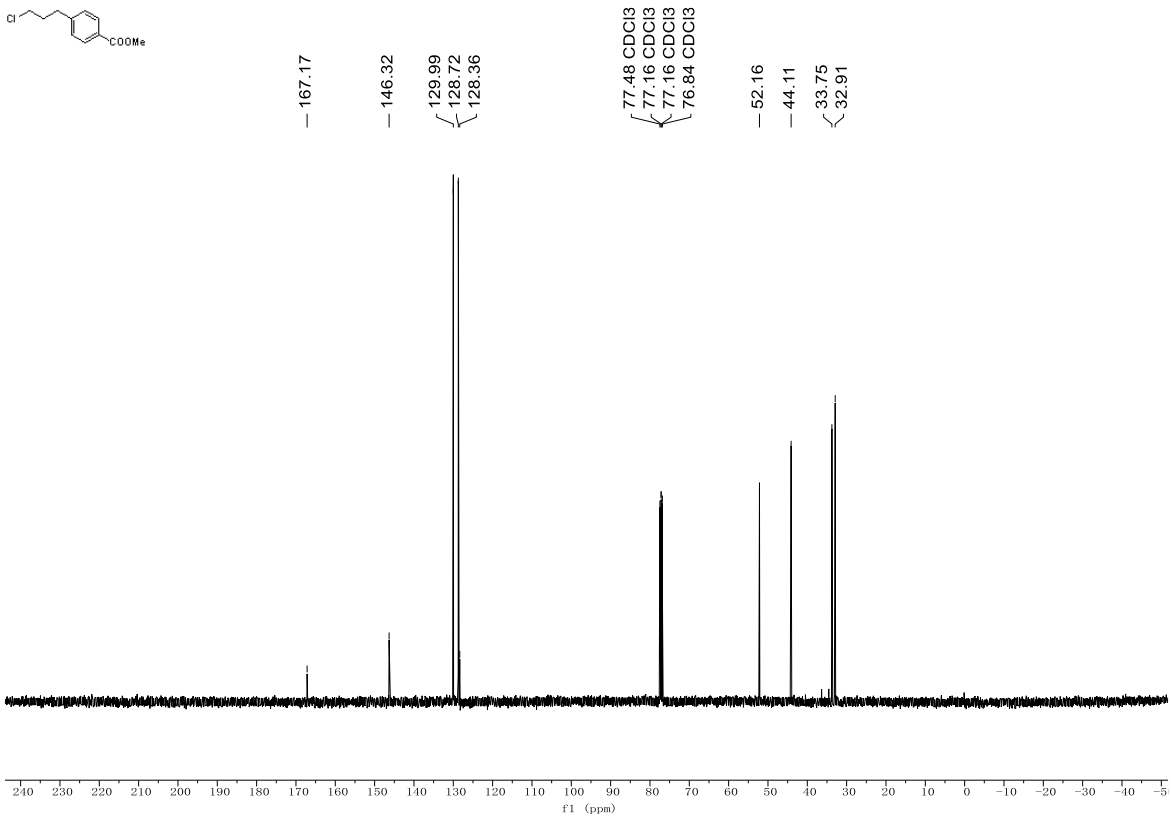
Compound **57** ^{13}C NMR



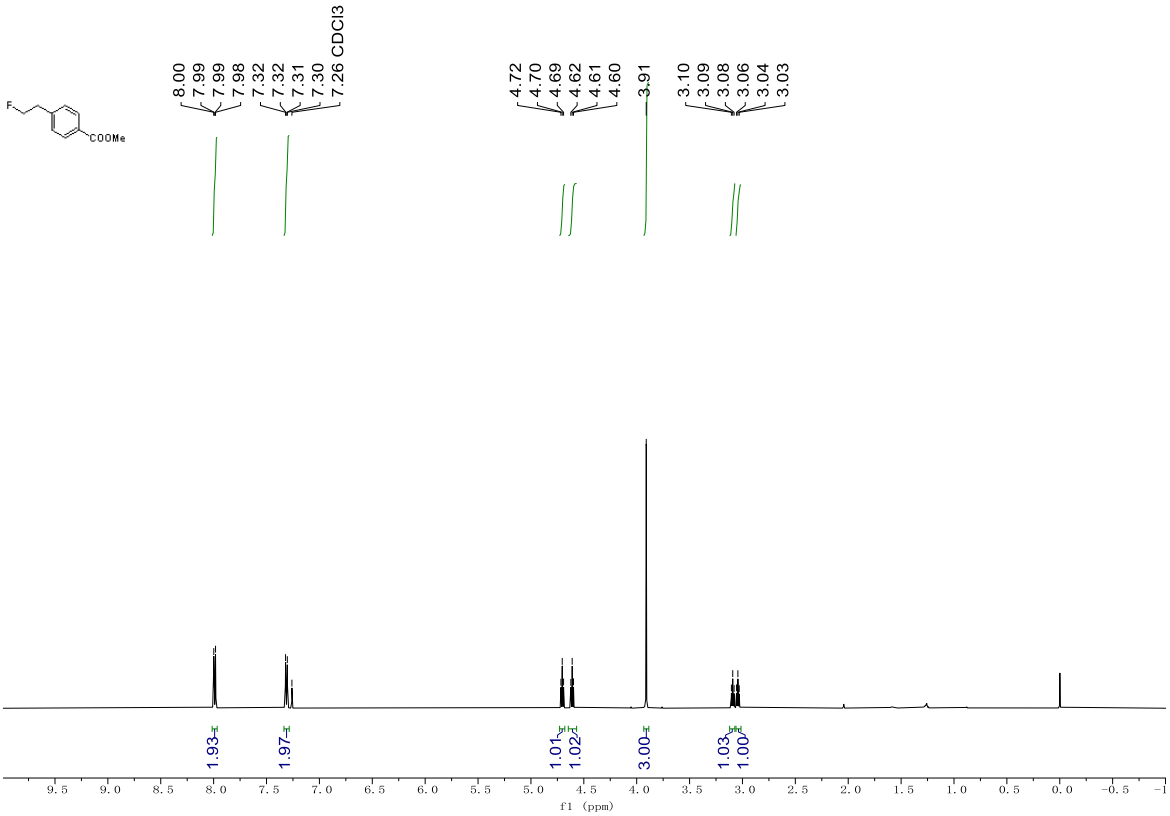
Compound **58** ^{1}H NMR



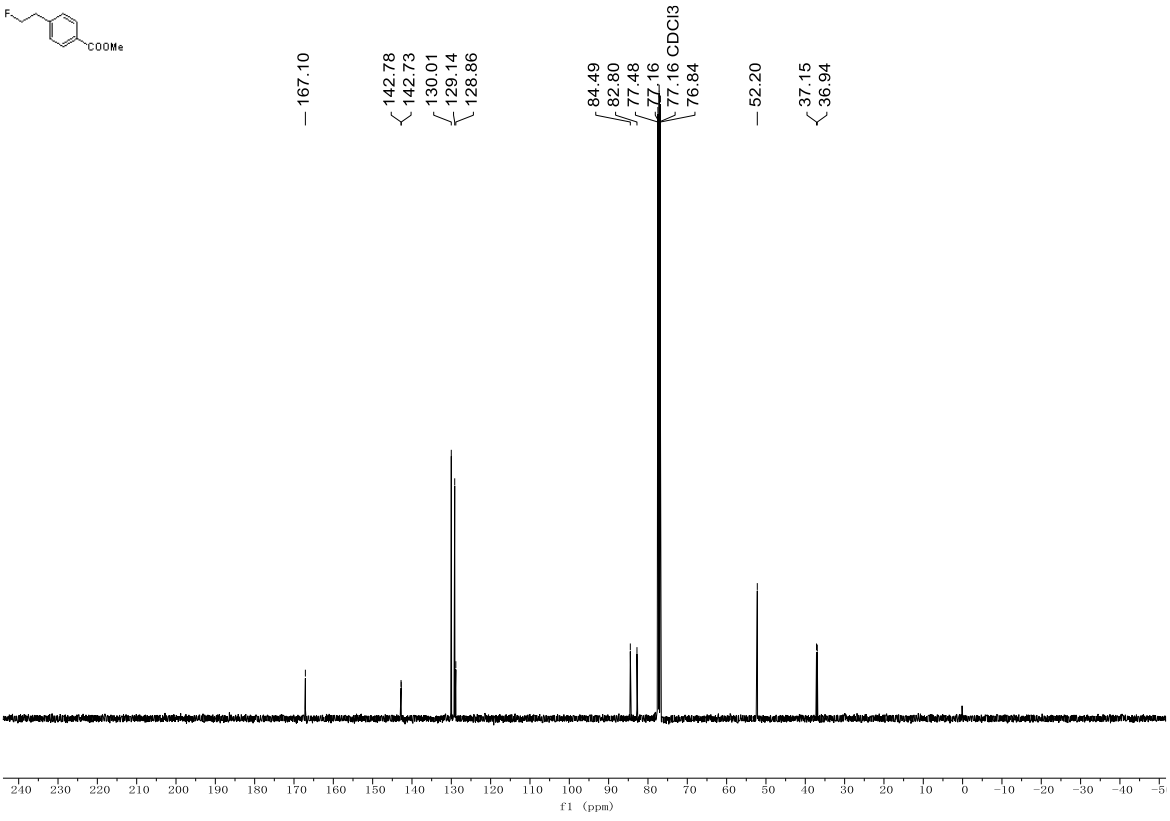
Compound **58** ^{13}C NMR



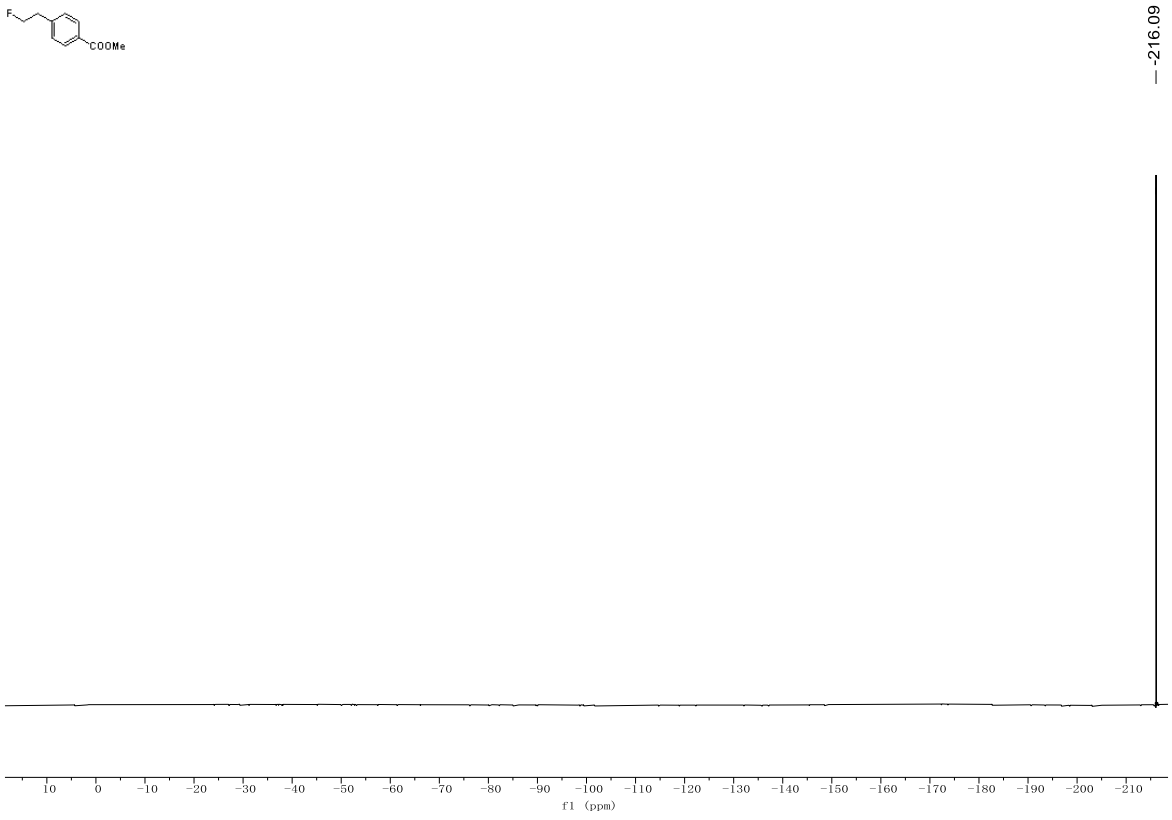
Compound **59** ^{1}H NMR



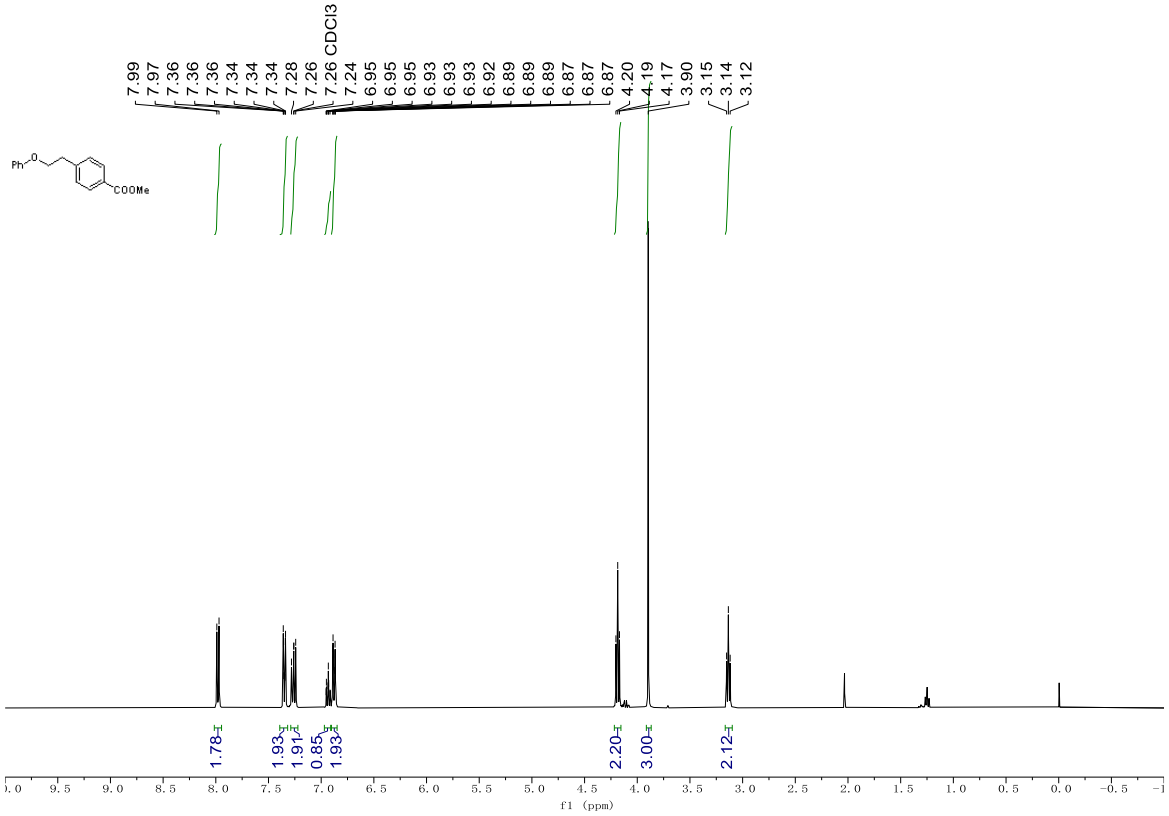
Compound **59** ^{13}C NMR



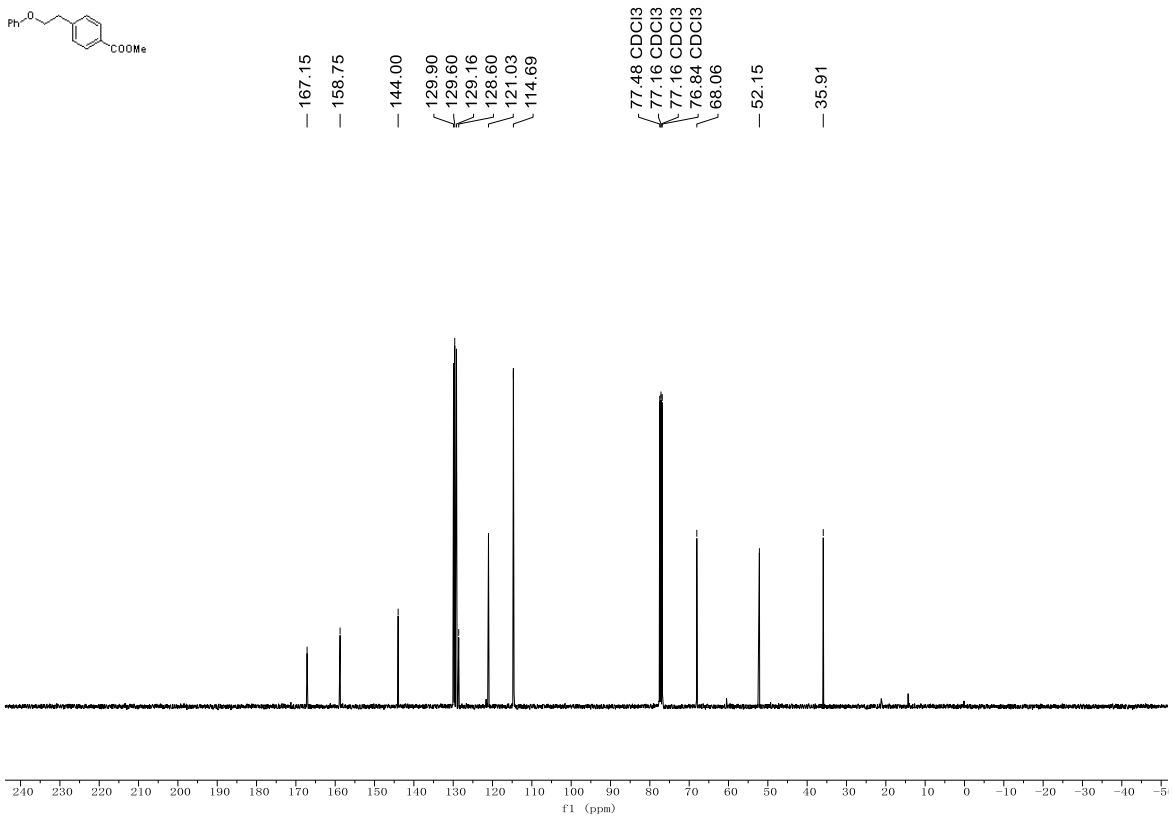
Compound **59** ^{19}F NMR



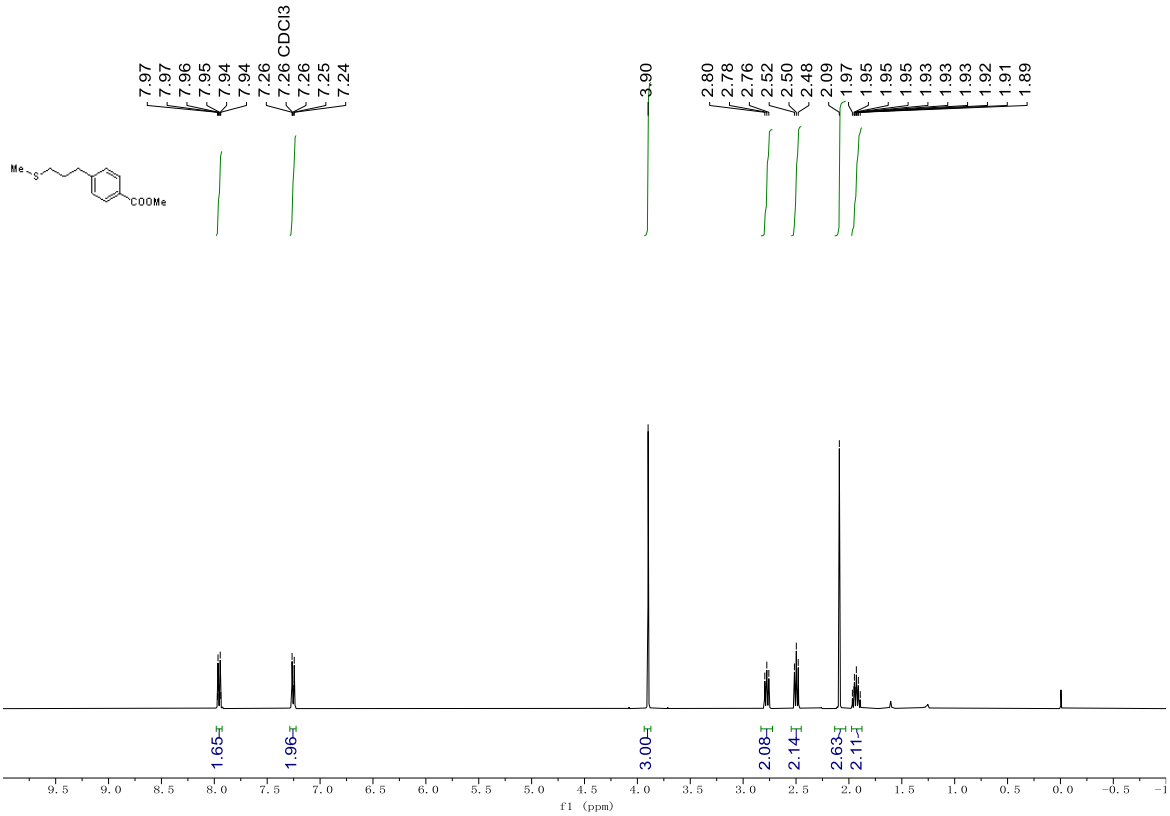
Compound **60** ^{1}H NMR



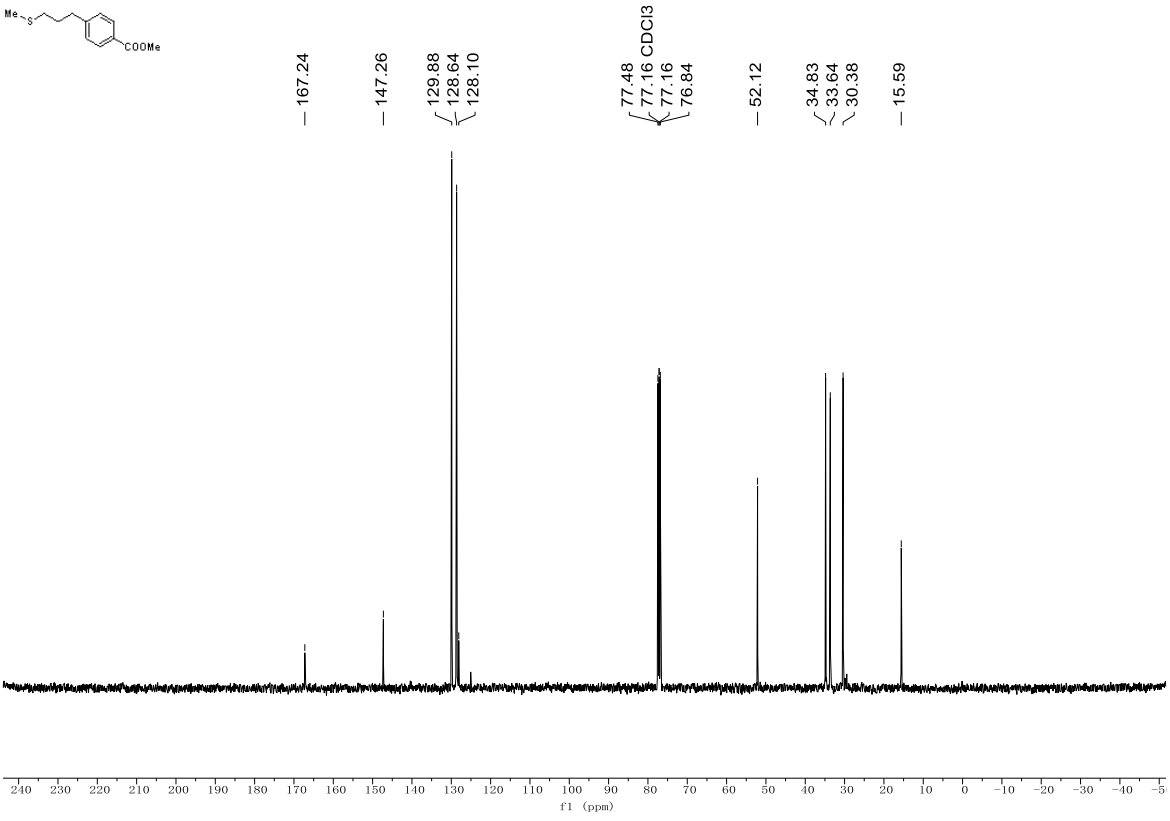
Compound **60** ^{13}C NMR



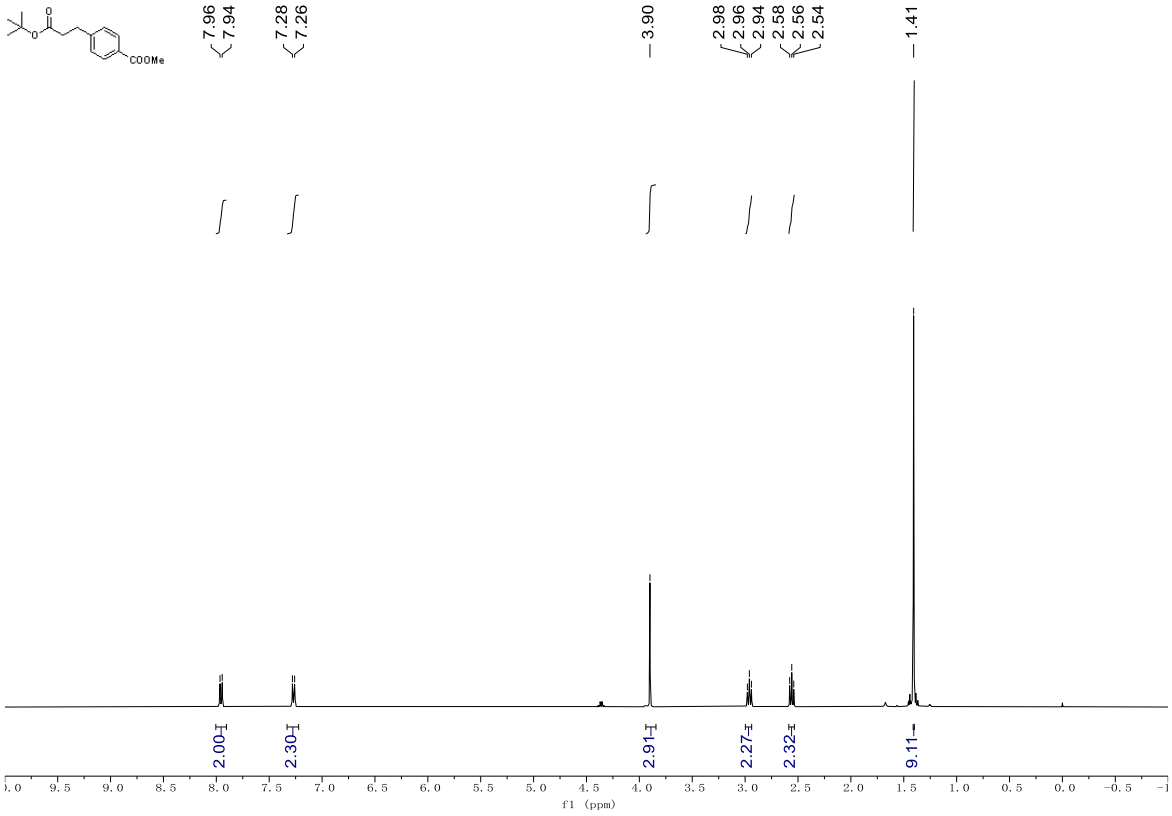
Compound **61** ^{1}H NMR



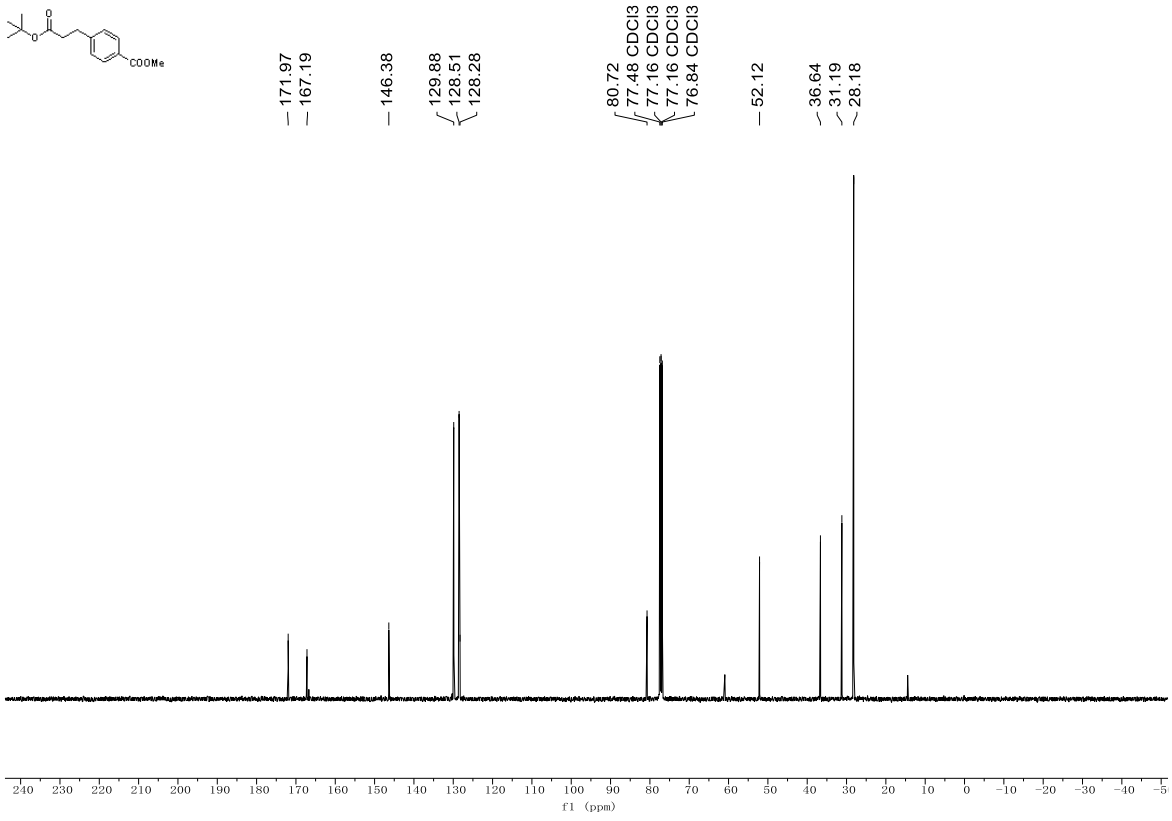
Compound **61** ^{13}C NMR



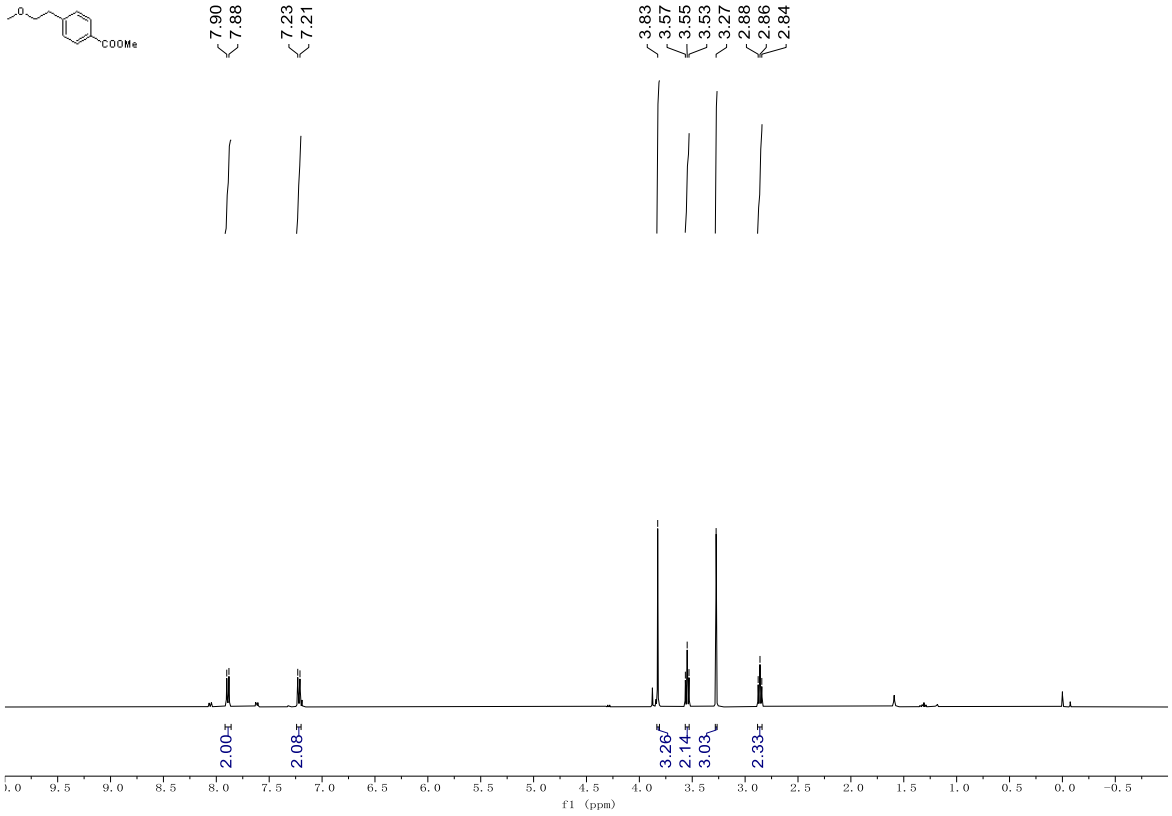
Compound **62** ^{1}H NMR



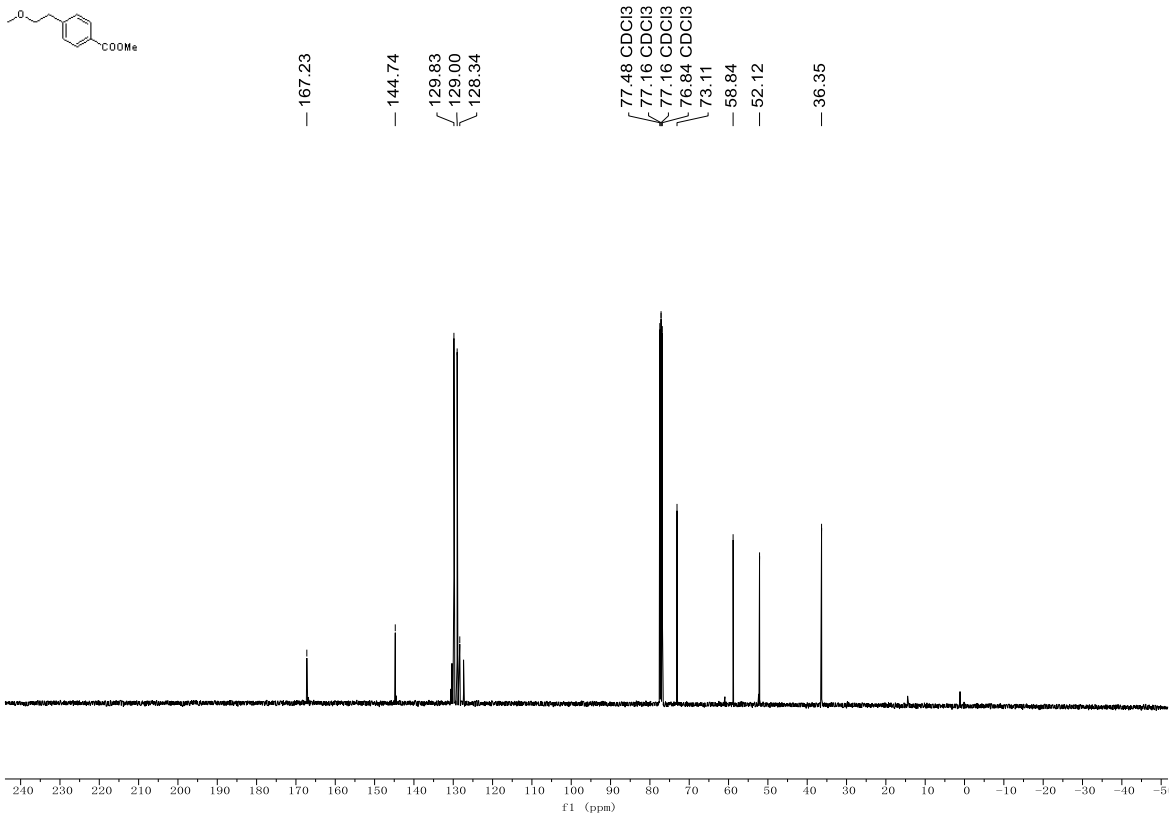
Compound **62** ^{13}C NMR



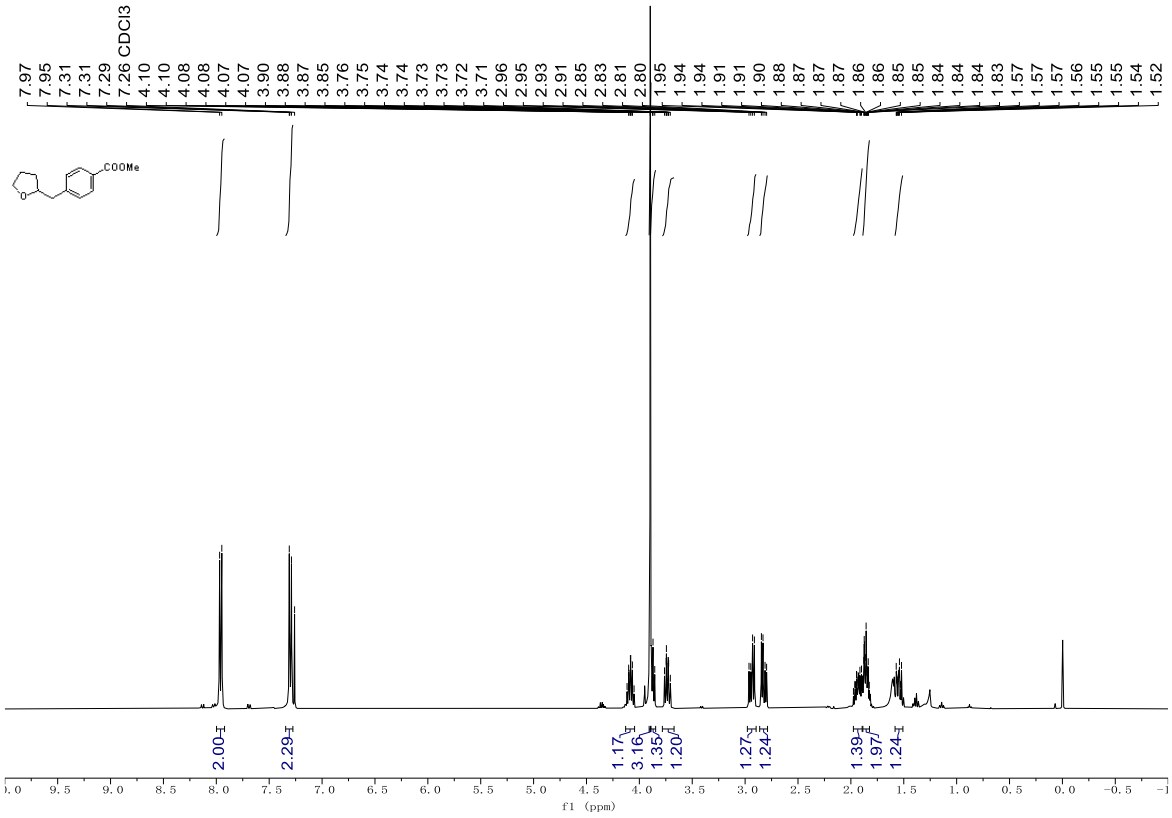
Compound **63** ^{1}H NMR



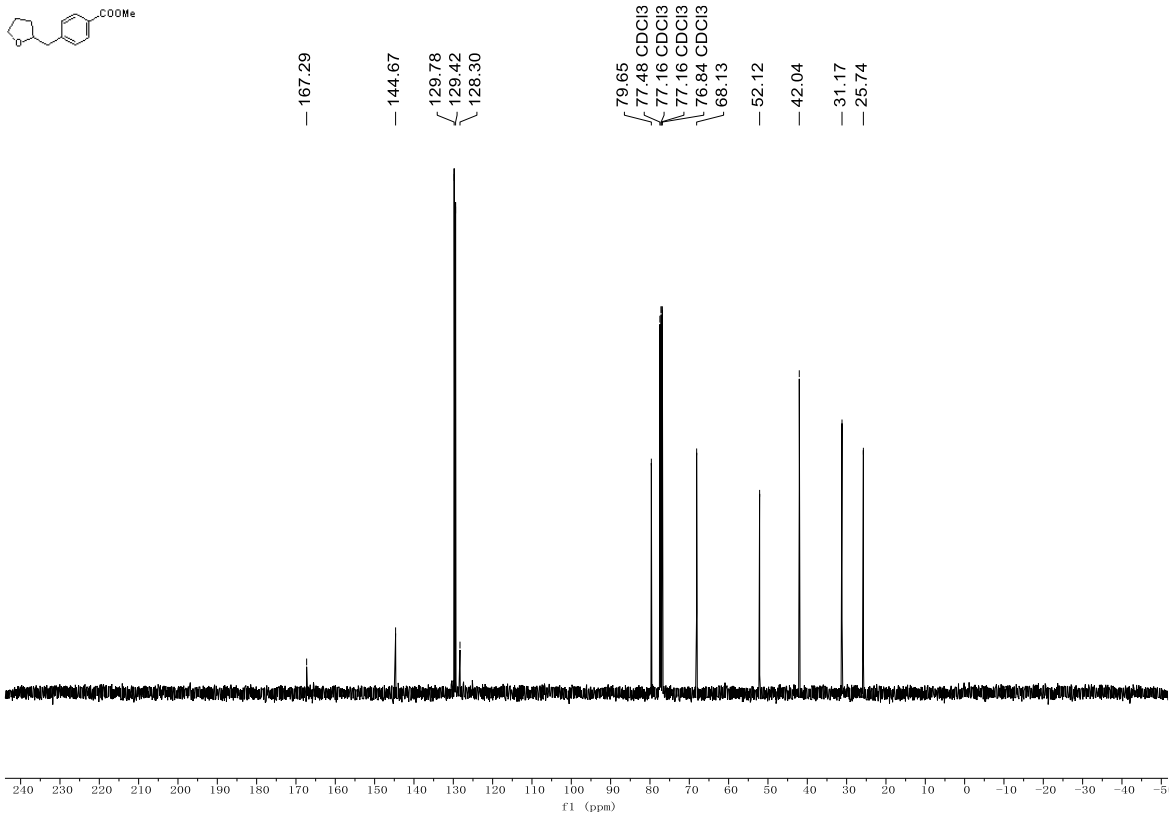
Compound **63** ^{13}C NMR



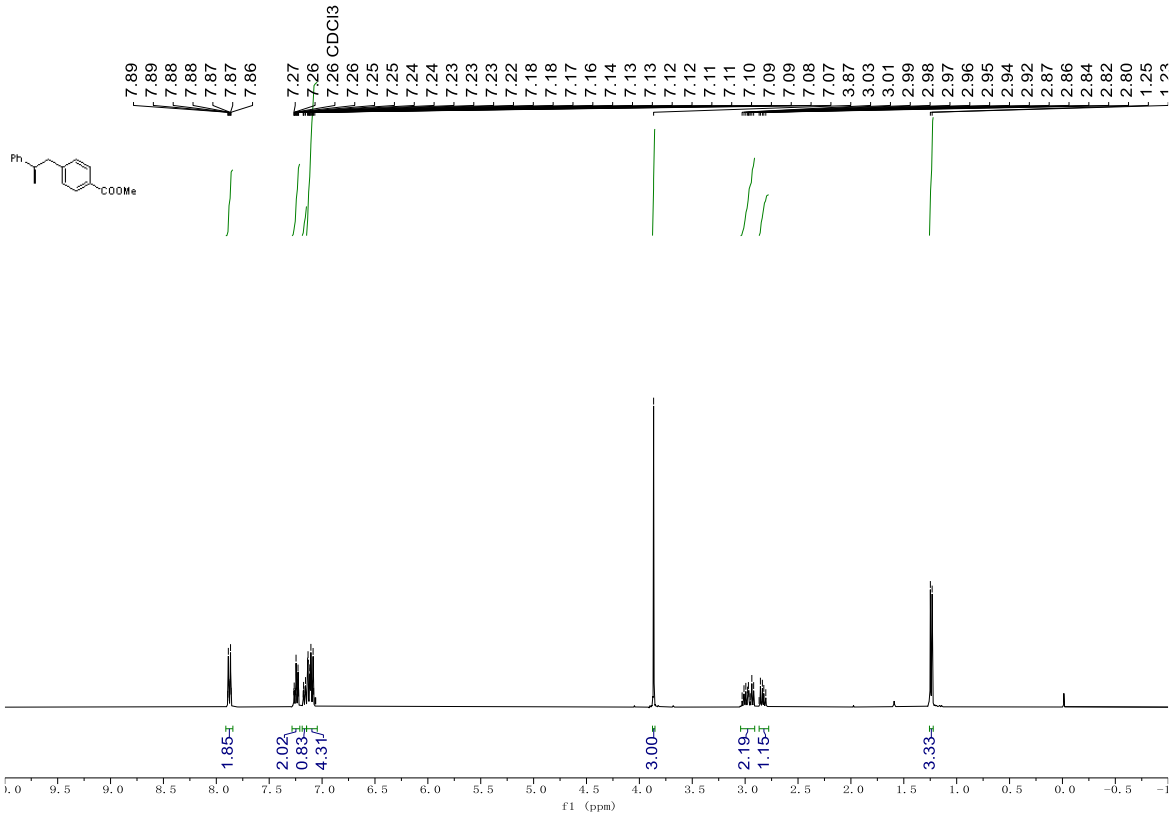
Compound **64** ^{1}H NMR



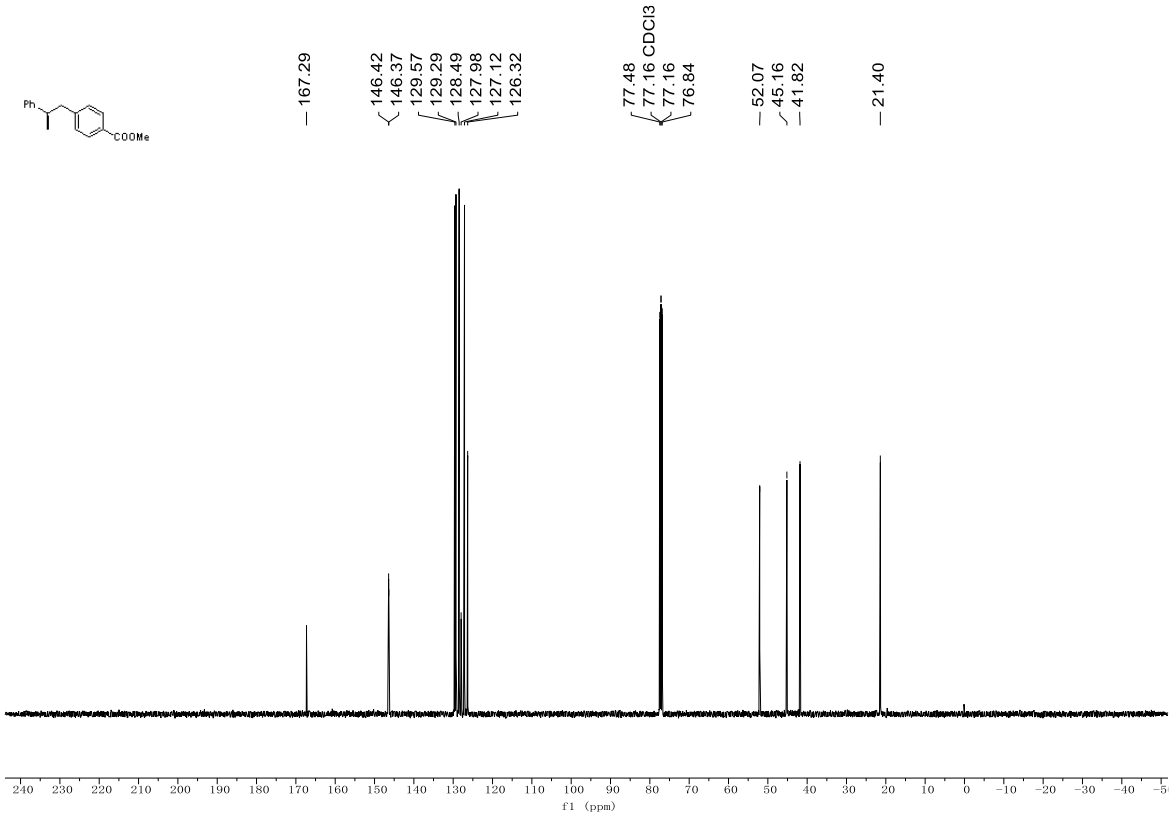
Compound **64** ^{13}C NMR



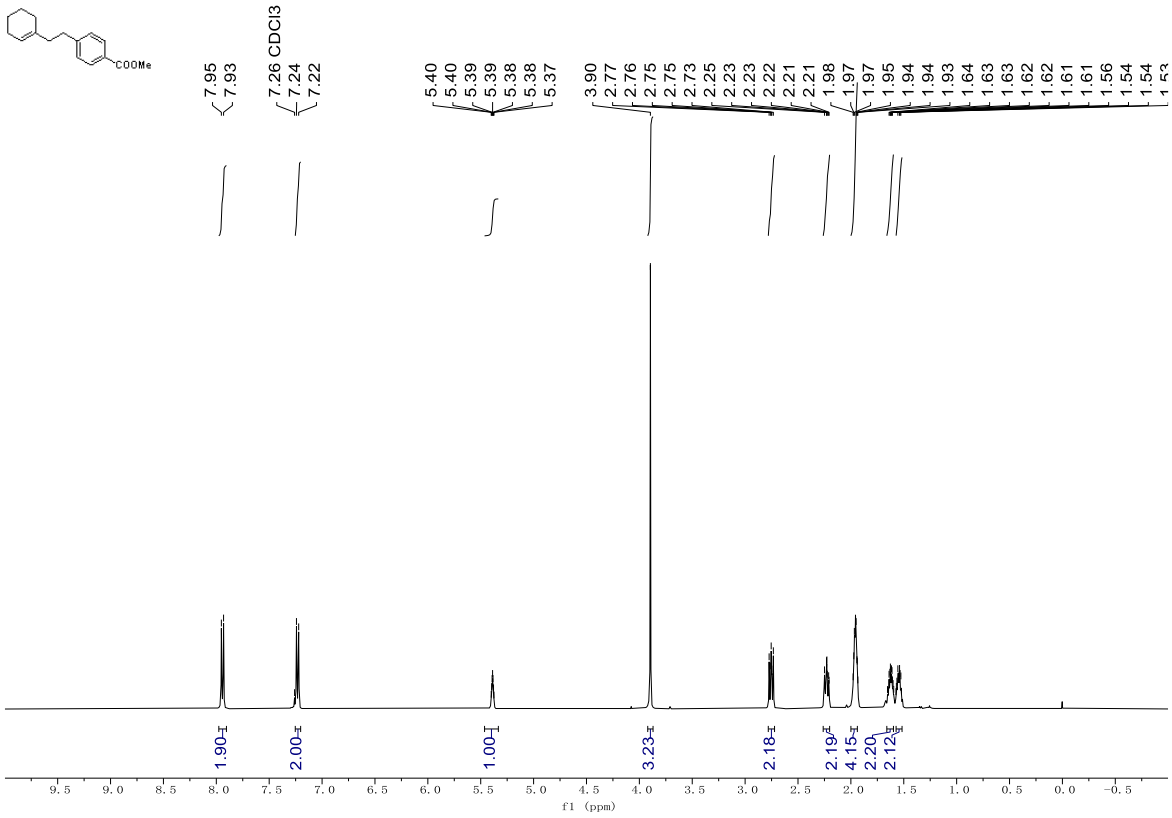
Compound **65** ^{1}H NMR



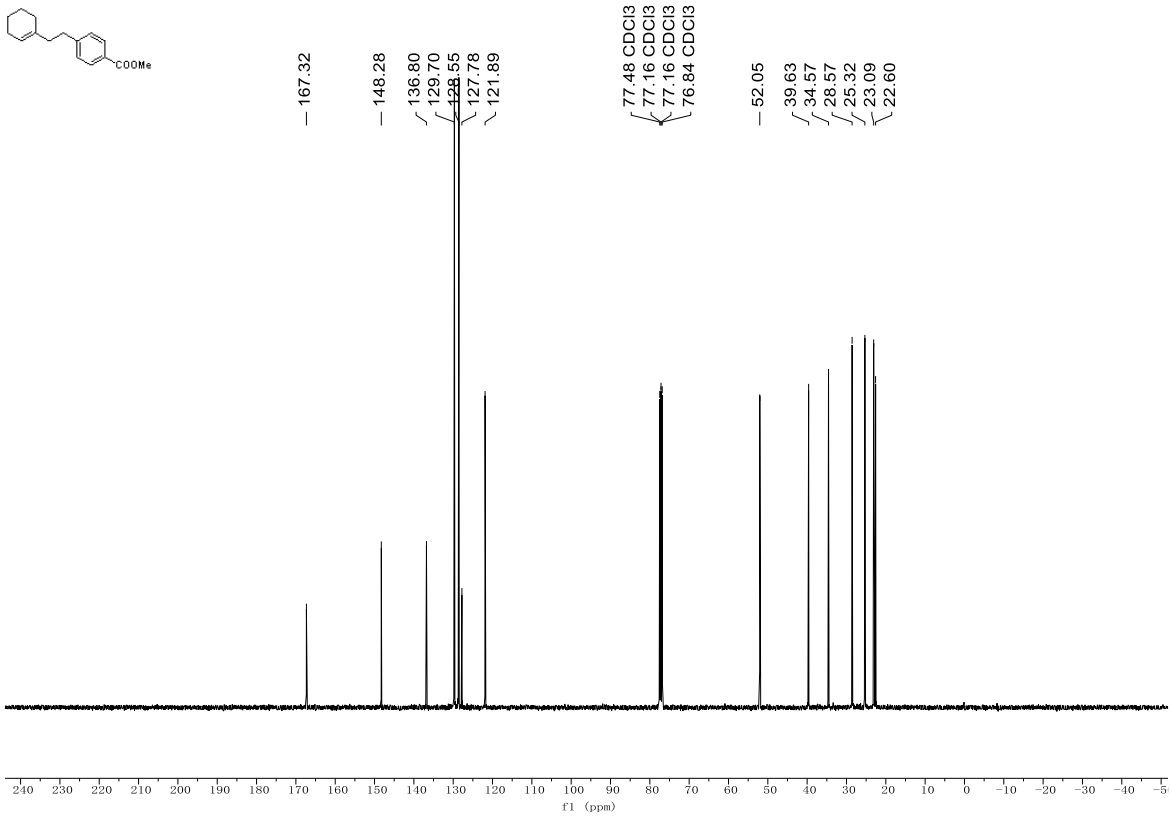
Compound **65** ^{13}C NMR



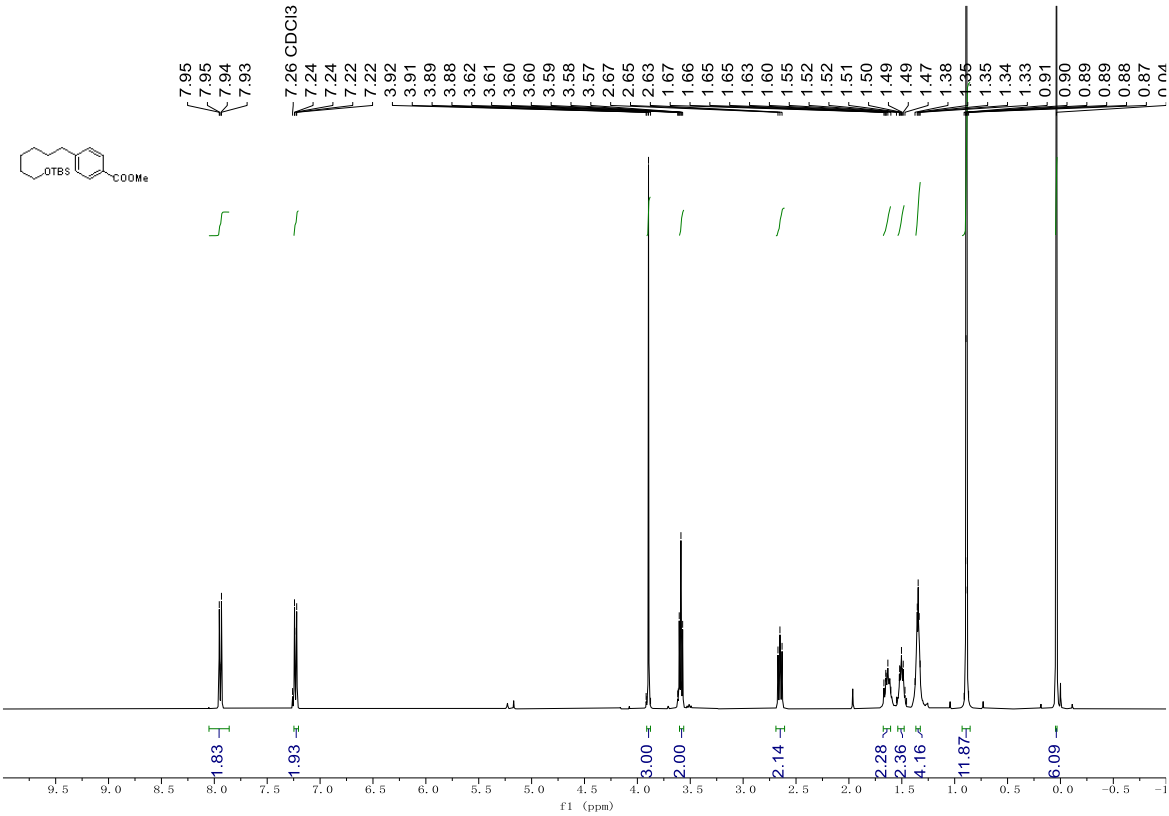
Compound **66** ^{1}H NMR



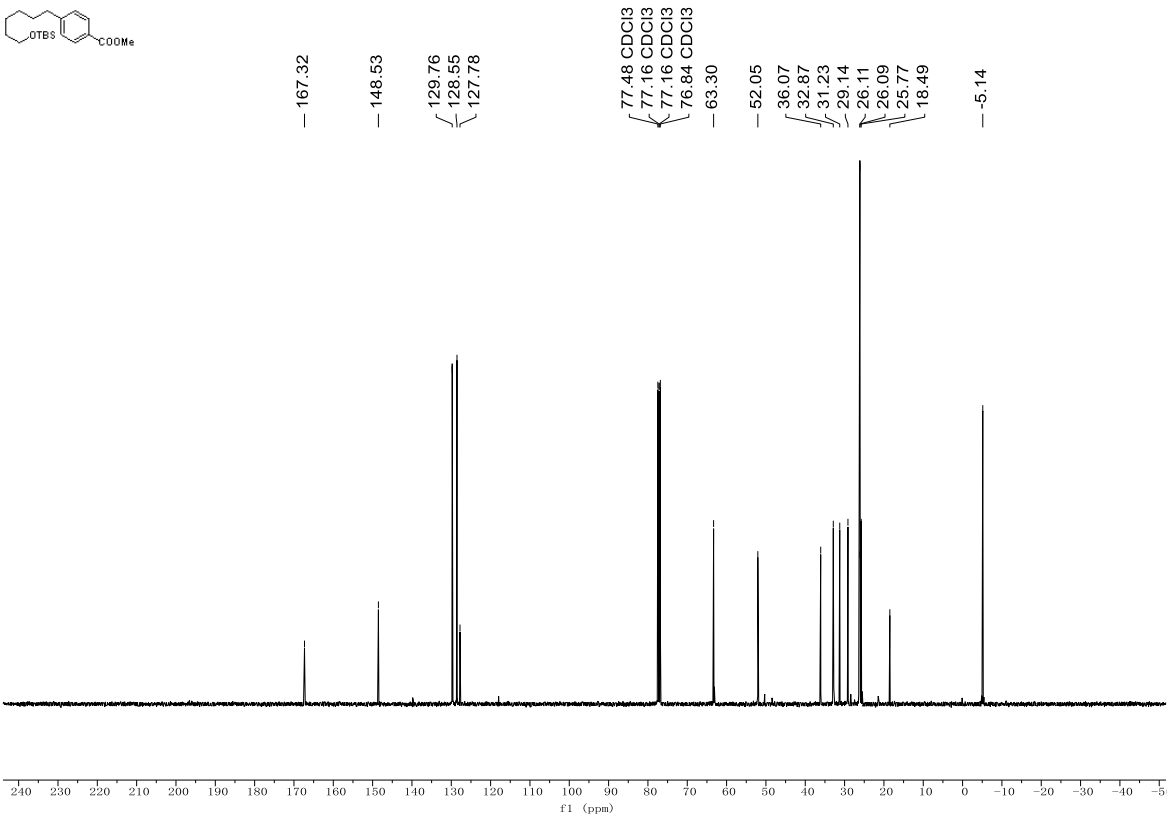
Compound **66** ^{13}C NMR



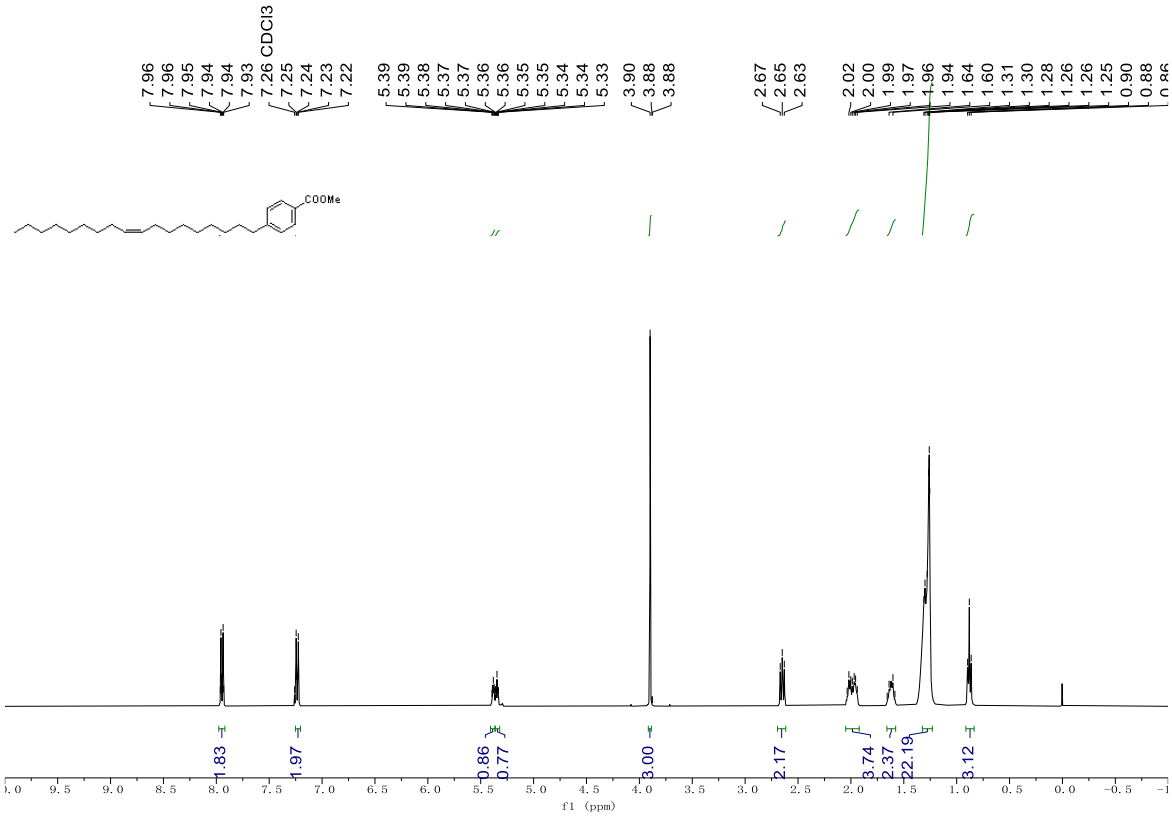
Compound **67** ^{1}H NMR



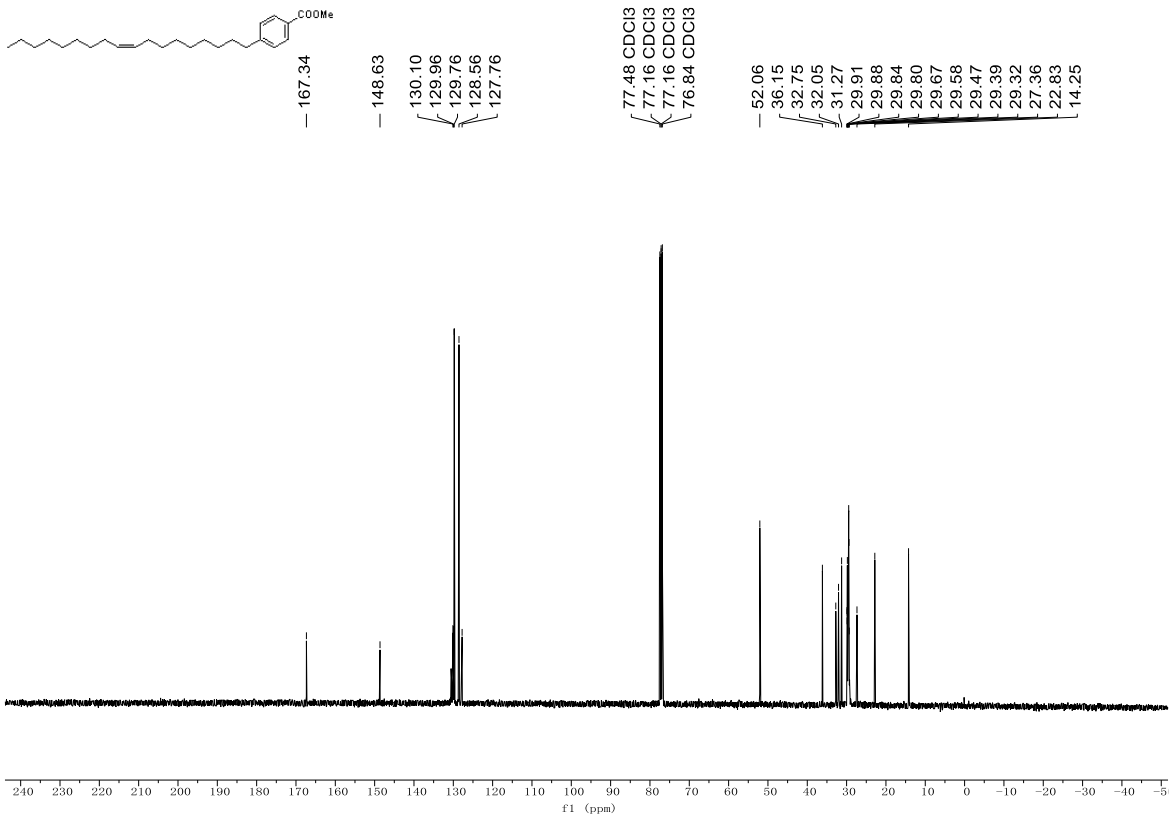
Compound **67** ^{13}C NMR



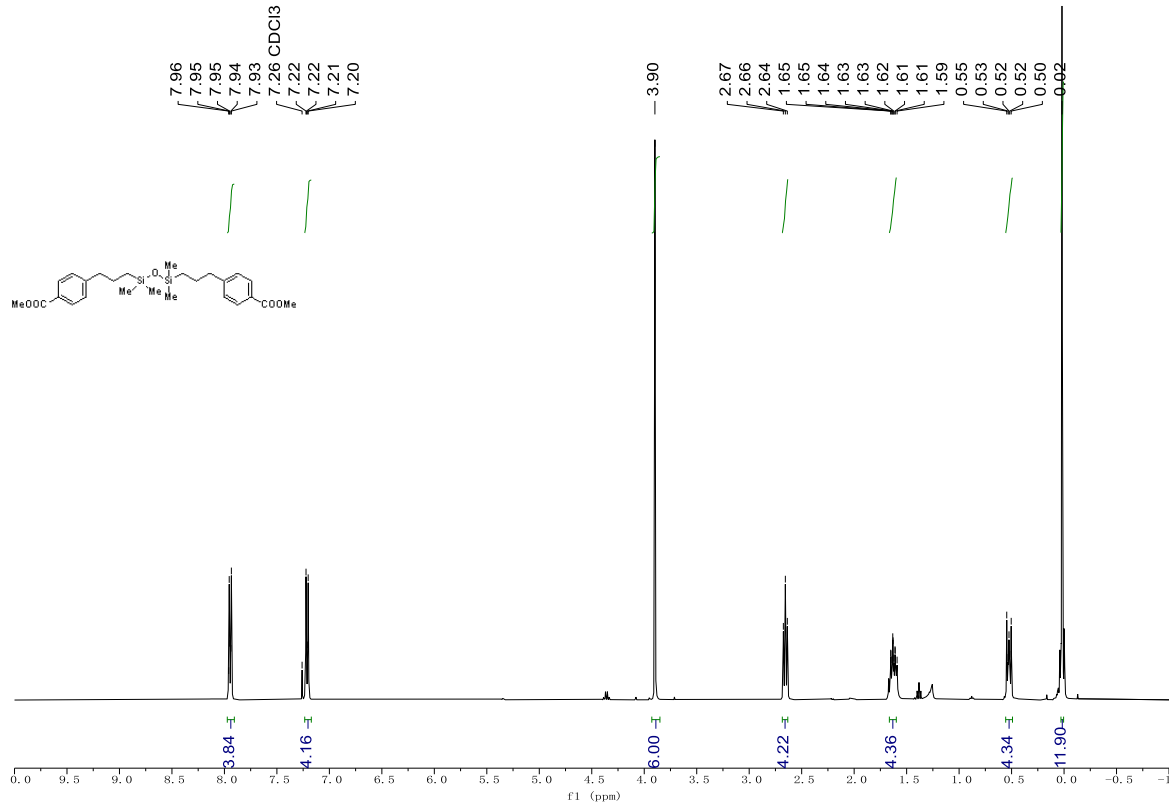
Compound **68** ^{1}H NMR



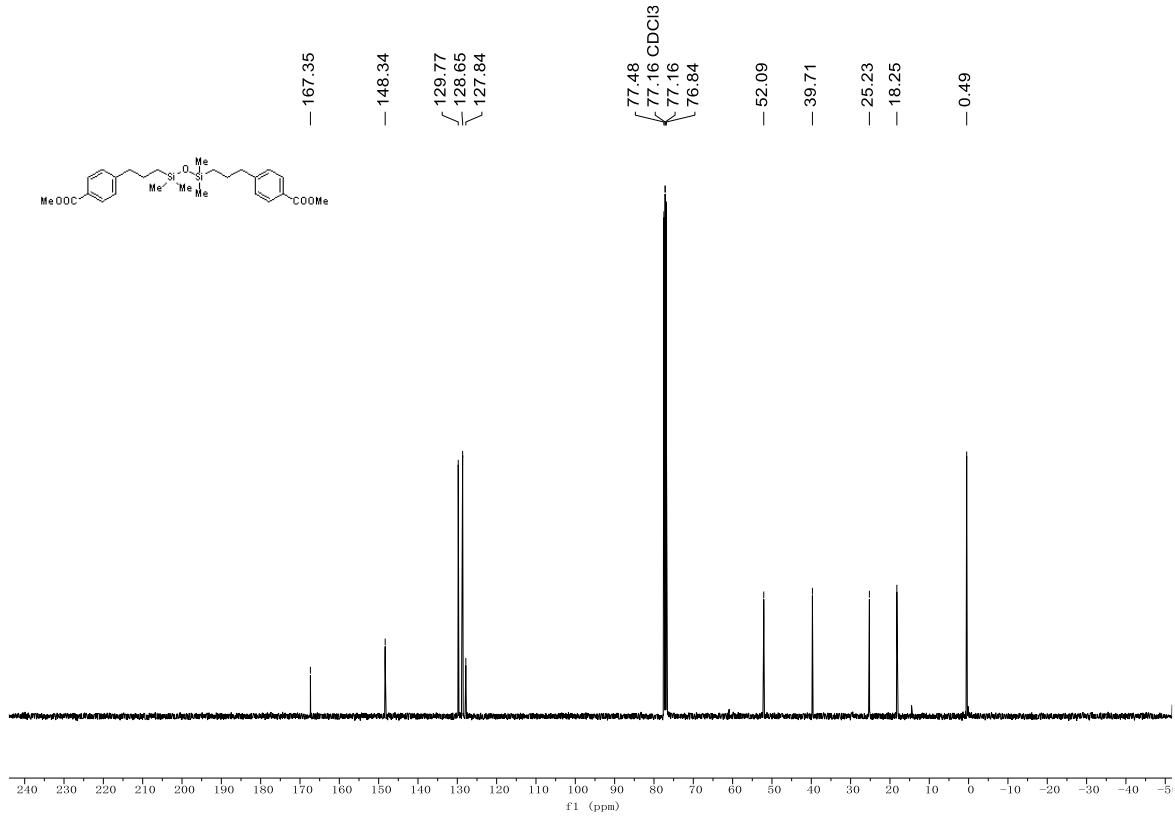
Compound **68** ^{13}C NMR



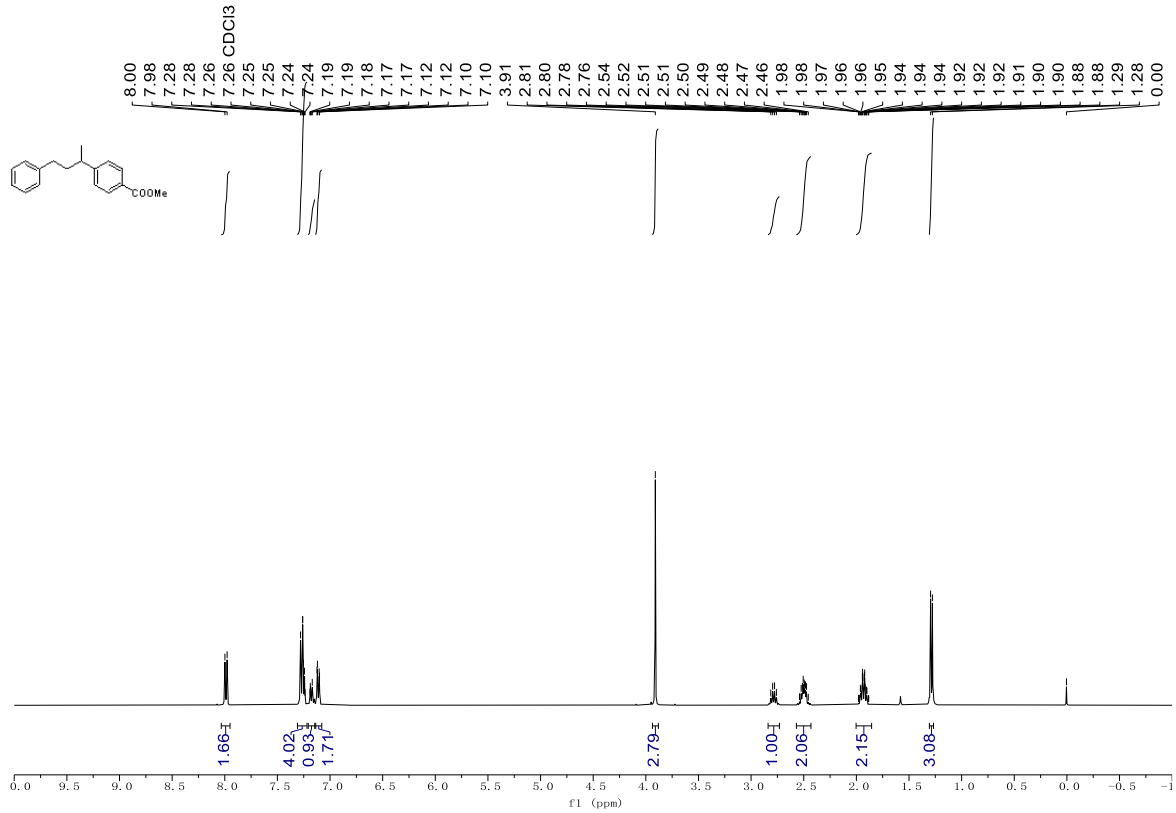
Compound **69** ^{1}H NMR



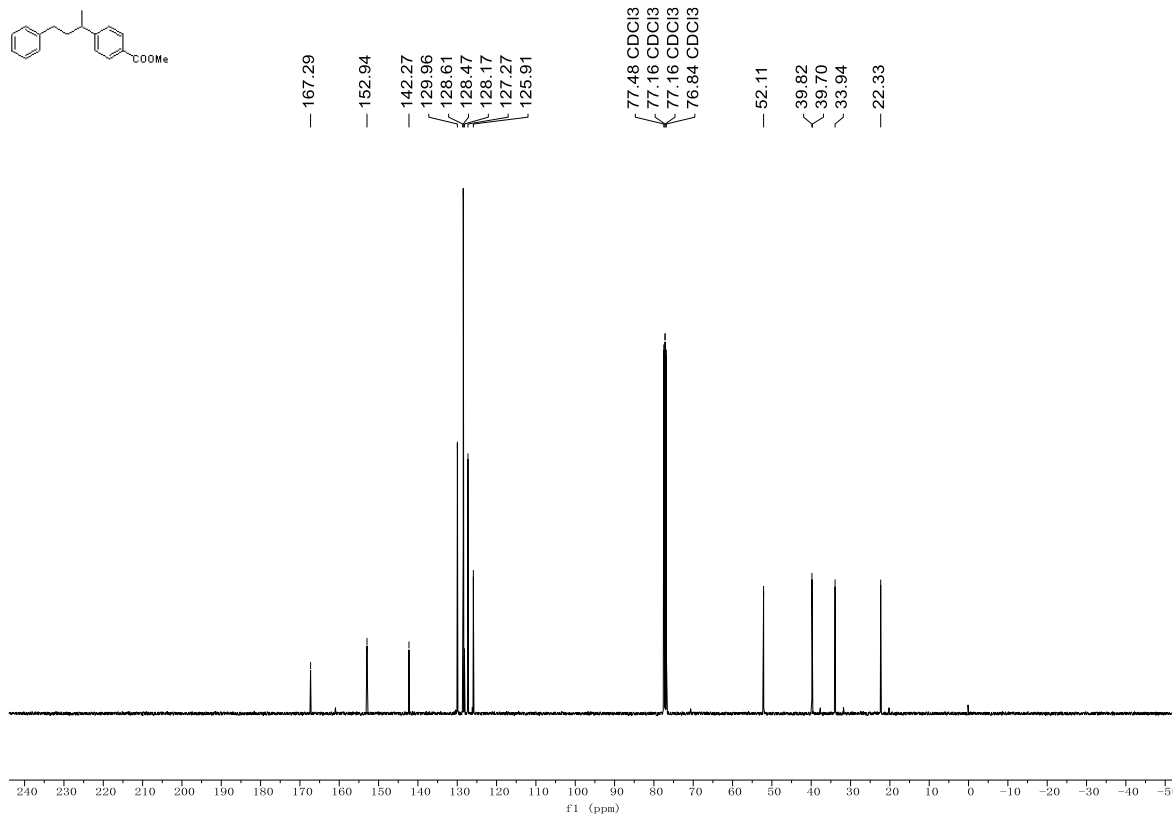
Compound **69** ^{13}C NMR



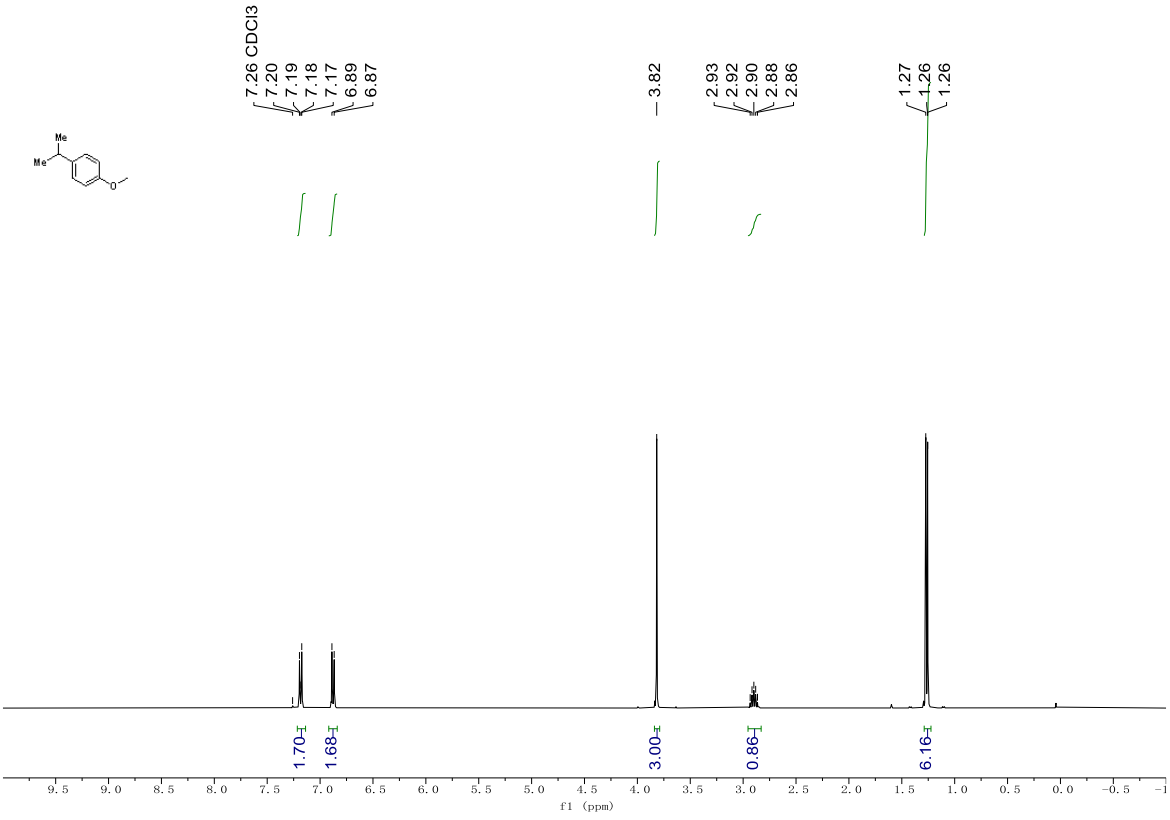
Compound **70** ^{1}H NMR



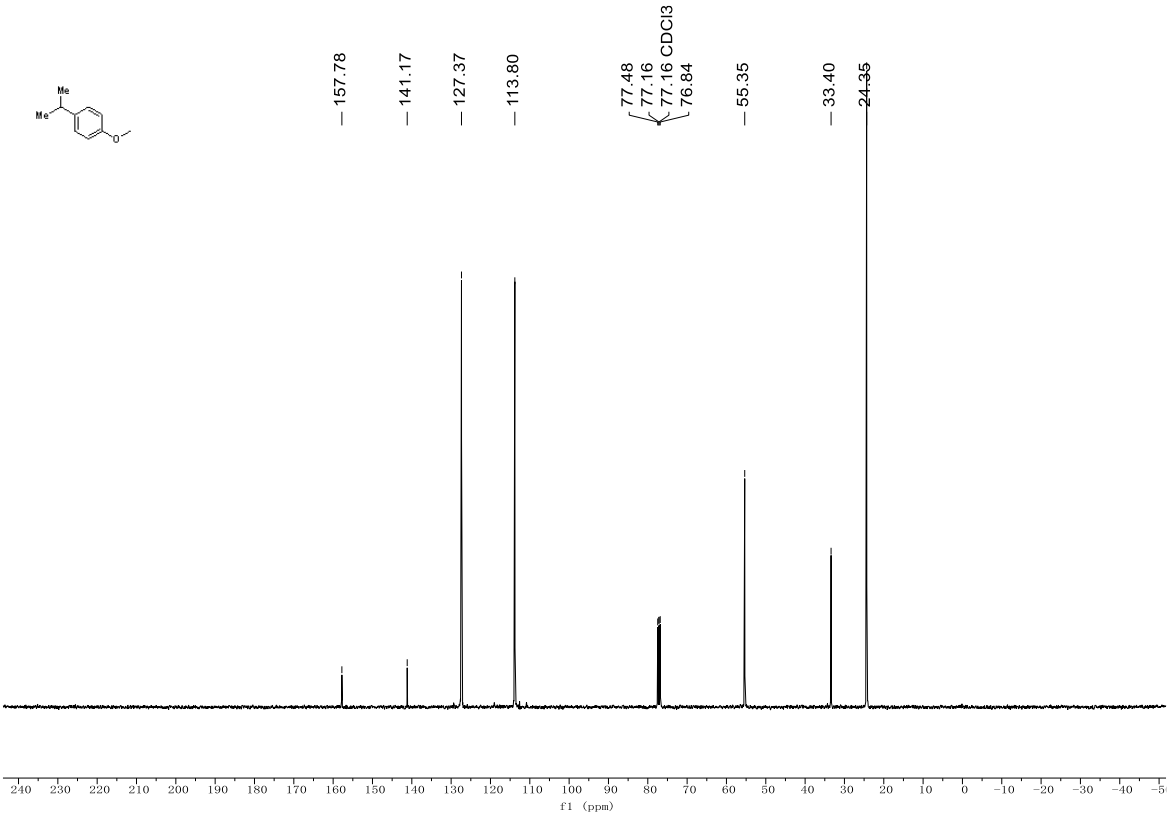
Compound **70** ^{13}C NMR



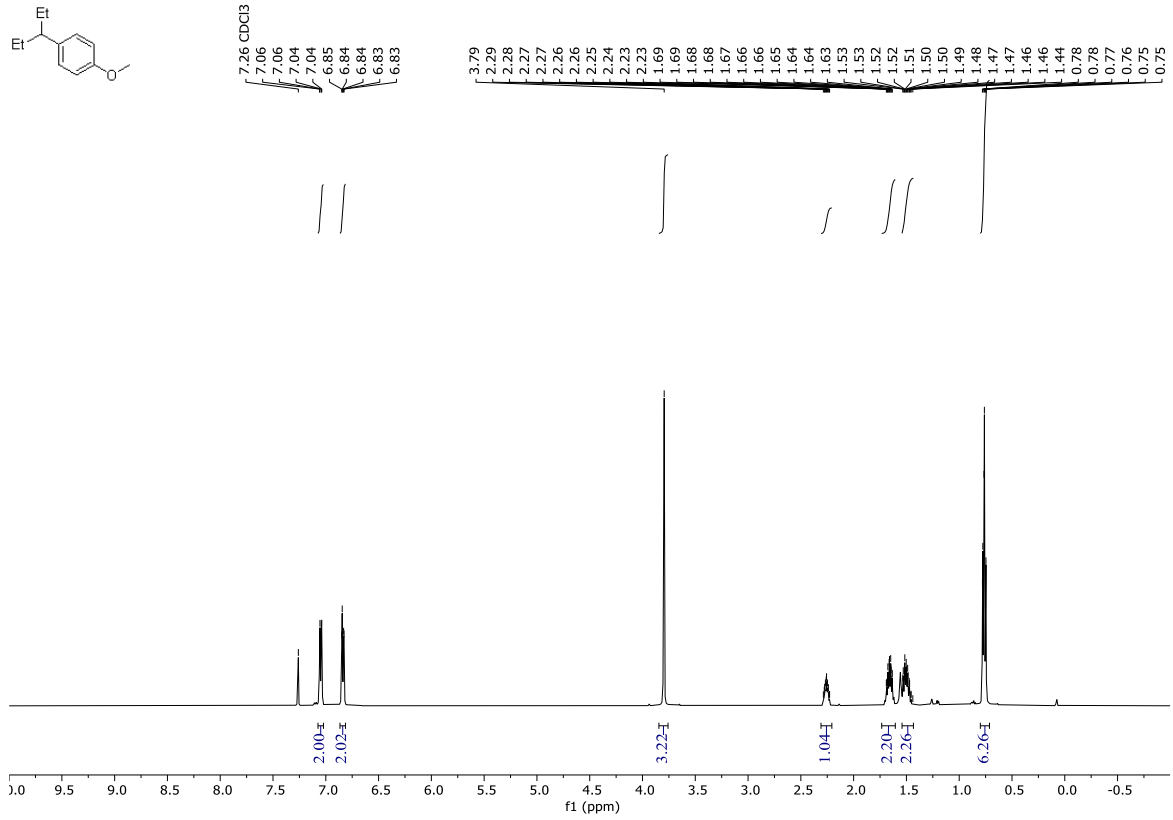
Compound **71** ^{1}H NMR



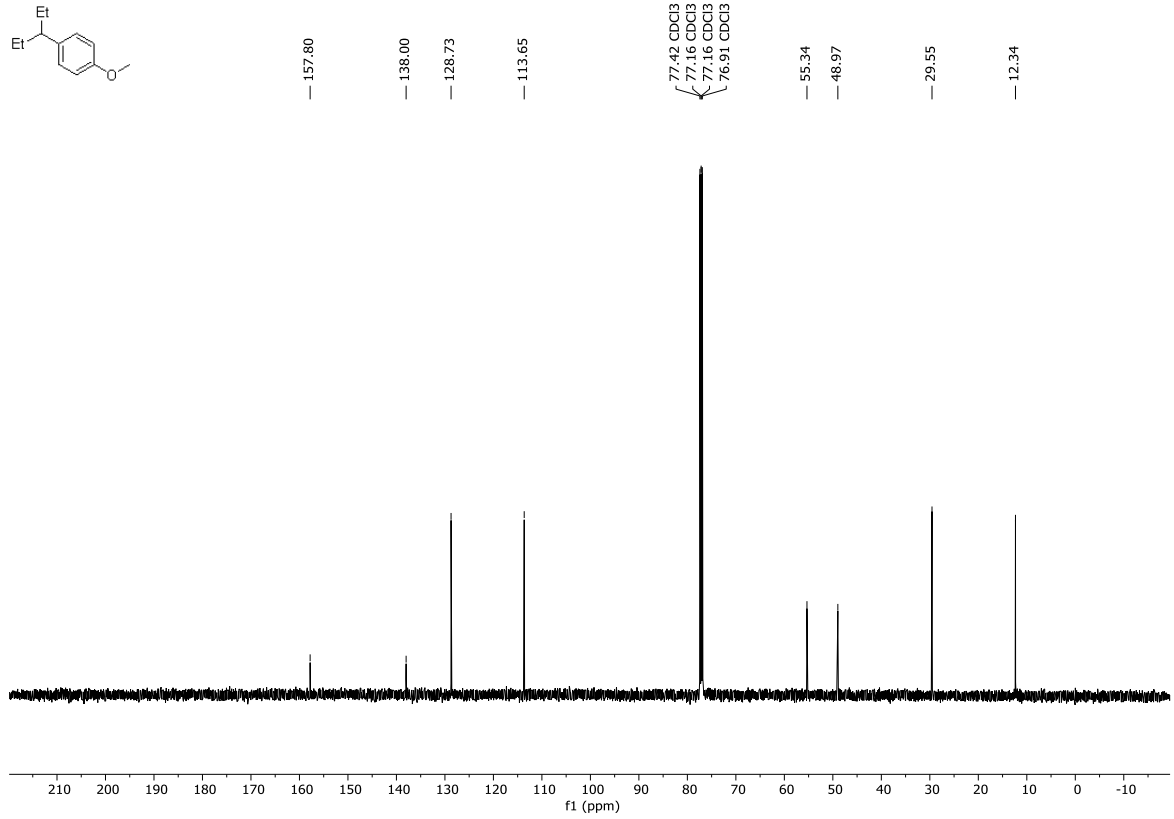
Compound **71** ^{13}C NMR



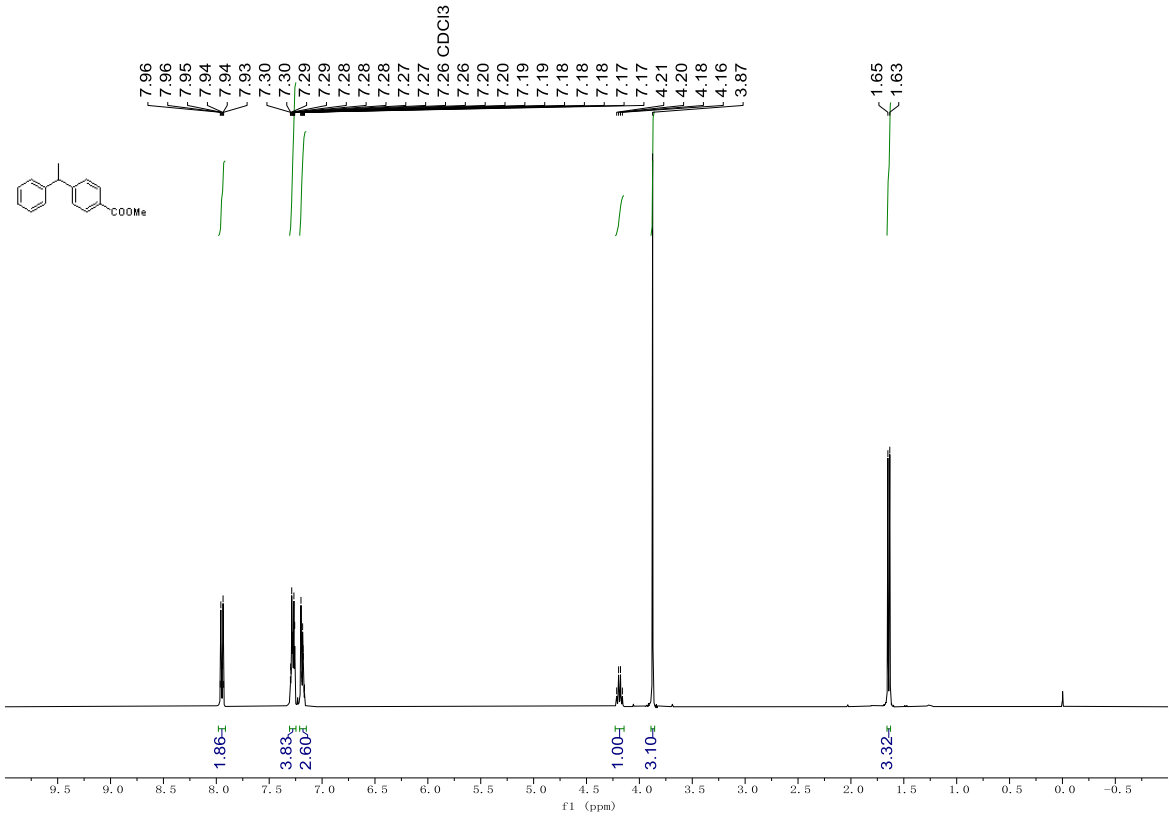
Compound **72** ^{1}H NMR



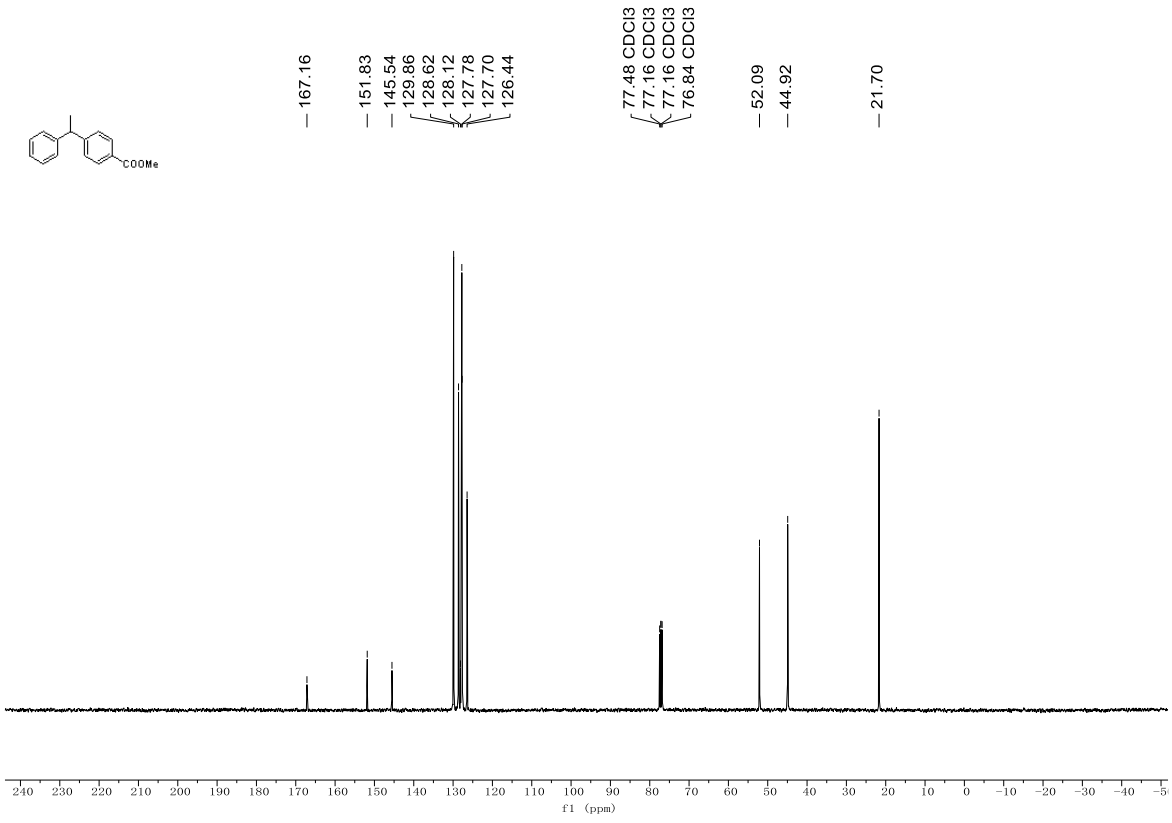
Compound **72** ^{13}C NMR



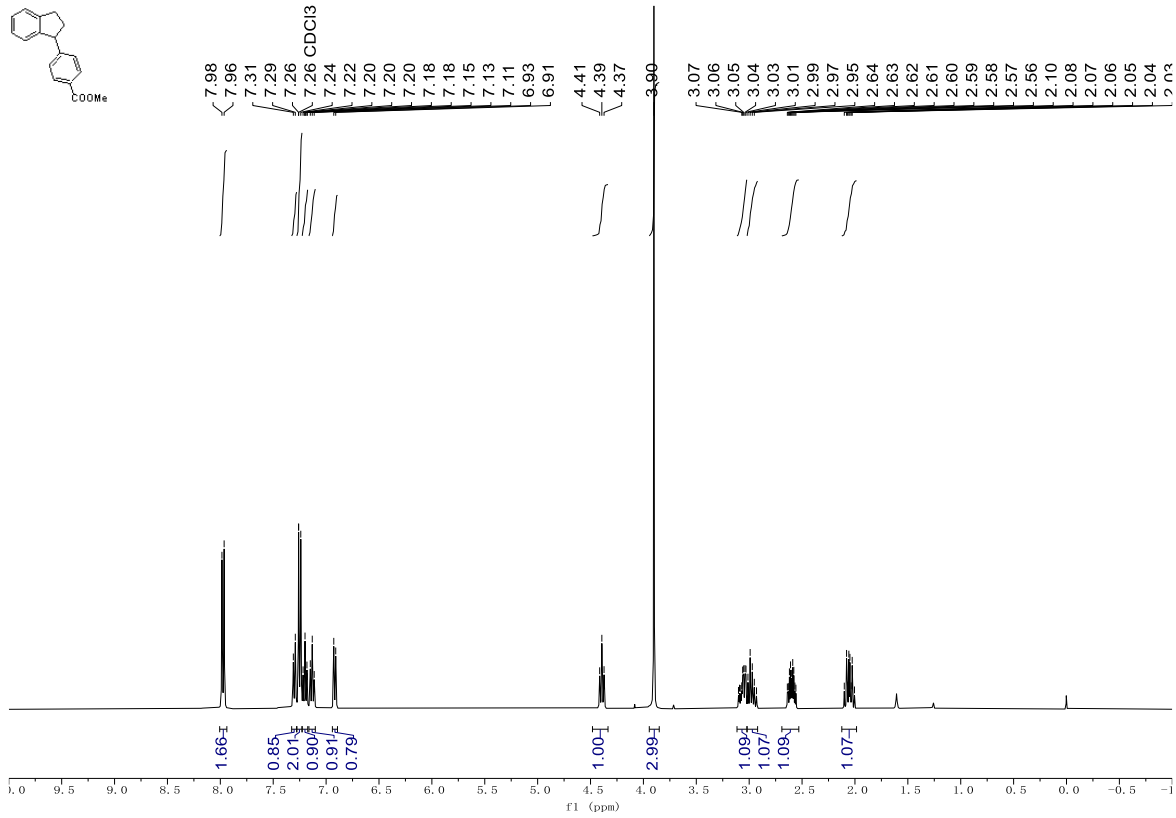
Compound **73** ^{1}H NMR



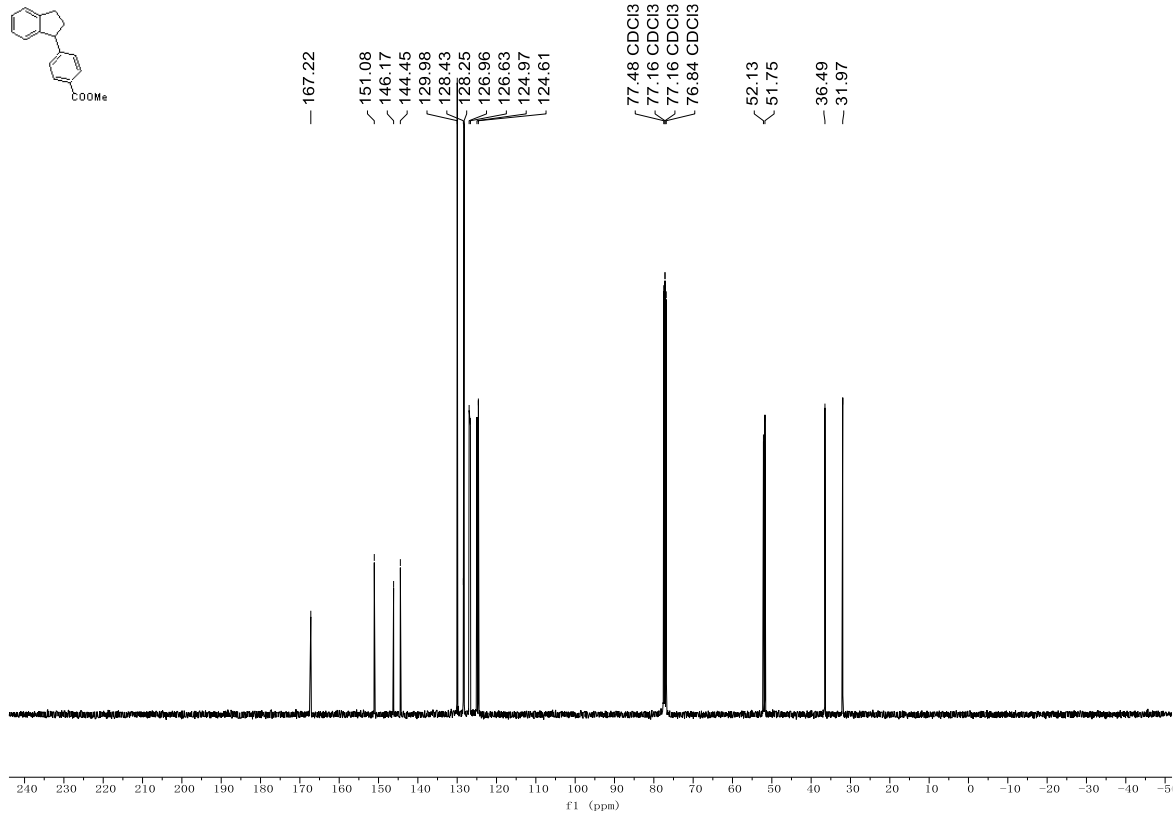
Compound **73** ^{13}C NMR



Compound **74** ^{1}H NMR



Compound **74** ^{13}C NMR



REFERENCES AND NOTES

1. J.-P. Corbet, G. Mignani, Selected patented cross-coupling reaction technologies. *Chem. Rev.* **106**, 2651–2710 (2006).

2. J. Twilton, M. R. Johnson, V. Sidana, M. C. Franke, C. Bottecchia, D. Lehnherr, F. Lévesque, S. M. M. Knapp, L. Wang, J. B. Gerken, C. M. Hong, T. P. Vickery, M. D. Weisel, N. A. Strotman, D. J. Weix, T. W. Root, S. S. Stahl, Quinone-mediated hydrogen anode for non-aqueous reductive electrosynthesis. *Nature* **623**, 71–76 (2023).

3. Y. Liu, P. Li, Y. Wang, Y. Qiu, Electroreductive cross-electrophile coupling (eXEC) reactions. *Angew. Chem. Int. Ed. Engl.* **62**, e202306679 (2023).

4. S. A. Zubaydi, S. Waske, V. Akyildiz, H. F. Starbuck, M. Majumder, C. E. Moore, D. Kalyani, C. S. Sevov, Reductive alkyl-alkyl coupling from isolable nickel-alkyl complexes. *Nature* **634**, 585–591 (2024).

5. L. P. Dinh, H. F. Starbuck, T. B. Hamby, M. J. LaLama, C. Q. He, D. Kalyani, C. S. Sevov, Persistent organonickel complexes as general platforms for Csp2–Csp3 coupling reactions. *Nat. Chem.* **16**, 1515–1522 (2024).

6. T. Shen, T. H. Lambert, Electrophotocatalytic diamination of vicinal C–H bonds. *Science* **371**, 620–626 (2021).

7. J.-i. Yoshida, K. Kataoka, R. Horcajada, A. Nagaki, Modern strategies in electroorganic synthesis. *Chem. Rev.* **108**, 2265–2299 (2008).

8. Y. Yuan, A. Lei, Electrochemical oxidative cross-coupling with hydrogen evolution reactions. *Acc. Chem. Res.* **52**, 3309–3324 (2019).

9. R. Francke, R. D. Little, Redox catalysis in organic electrosynthesis: Basic principles and recent developments. *Chem. Soc. Rev.* **43**, 2492–2521 (2014).

10. J. L. Röckl, D. Pollok, R. Franke, S. R. Waldvogel, A decade of electrochemical dehydrogenative C,C-coupling of aryls. *Acc. Chem. Res.* **53**, 45–61 (2020).

11. M. Yan, Y. Kawamata, P. S. Baran, Synthetic organic electrochemical methods since 2000: On the verge of a renaissance. *Chem. Rev.* **117**, 13230–13319 (2017).

12. K.-J. Jiao, Y.-K. Xing, Q.-L. Yang, H. Qiu, T.-S. Mei, Site-selective C–H functionalization via synergistic use of electrochemistry and transition metal catalysis. *Acc. Chem. Res.* **53**, 300–310 (2020).

13. P. Xiong, H.-C. Xu, Chemistry with electrochemically generated N-centered radicals. *Acc. Chem. Res.* **52**, 3339–3350 (2019).

14. T. B. Hamby, M. J. LaLama, C. S. Sevov, Controlling Ni redox states by dynamic ligand exchange for electroreductive Csp3–Csp2 coupling. *Science* **376**, 410–416 (2022).

15. T. S.-B. Lou, Y. Kawamata, T. Ewing, G. A. Correa-Otero, M. R. Collins, P. S. Baran, Scalable, chemoselective nickel electrocatalytic sulfinylation of aryl halides with SO2. *Angew. Chem. Int. Ed. Engl.* **61**, e202208080 (2022).

16. Y.-M. Cai, X.-T. Liu, L.-L. Xu, M. Shang, Electrochemical Ni-catalyzed decarboxylative C(sp3)−N cross-electrophile coupling. *Angew. Chem. Int. Ed. Engl.* **63**, e202315222 (2024).

17. Q. Wang, J. Xu, Z. Xu, Z. Wang, X. Tao, S. Ni, Y. Pan, Y. Wang, Catalyst-free electroreductive carboxylic acid–nitroarene coupling. *Green Chem.* **25**, 7084–7091 (2023).

18. P. Li, C. Guo, S. Wang, D. Ma, T. Feng, Y. Wang, Y. Qiu, Facile and general electrochemical deuteration of unactivated alkyl halides. *Nat. Commun.* **13**, 3774 (2022).

19. X. Yu, T. Yang, S. Wang, H. Xu, H. Gong, Nickel-catalyzed reductive cross-coupling of unactivated alkyl halides. *Org. Lett.* **13**, 2138–2141 (2011).

20. J. Liu, Y. Ye, J. L. Sessler, H. Gong, Cross-electrophile couplings of activated and sterically hindered halides and alcohol derivatives. *Acc. Chem. Res.* **53**, 1833–1845 (2020).

21. X. Wang, Y. Dai, H. Gong, Nickel-catalyzed reductive couplings. *Top. Curr. Chem.* **374**, 43 (2016).

22. D. J. Weix, Methods and mechanisms for cross-electrophile coupling of Csp2 halides with alkyl electrophiles. *Acc. Chem. Res.* **48**, 1767–1775 (2015).

23. C. E. I. Knappke, S. Grupe, D. Gärtner, M. Corpet, C. Gosmini, A. Jacobi von Wangelin, Reductive cross-coupling reactions between two electrophiles. *Chemistry* **20**, 6828–6842 (2014).

24. T. Moragas, A. Correa, R. Martin, Metal-catalyzed reductive coupling reactions of organic halides with carbonyl-type compounds. *Chemistry* **20**, 8242–8258 (2014).

25. T. Iwasaki, N. Kambe, Ni-catalyzed C–C couplings using alkyl electrophiles. *Top. Curr. Chem.* **374**, 66 (2016).

26. B. Zhang, Y. Gao, Y. Hioki, M. S. Oderinde, J. X. Qiao, K. X. Rodriguez, H.-J. Zhang, Y. Kawamata, P. S. Baran, Ni-electrocatalytic Csp3–Csp3 doubly decarboxylative coupling. *Nature* **606**, 313–318 (2022).

27. Y. Gao, B. Zhang, J. He, P. S. Baran, Ni-electrocatalytic enantioselective doubly decarboxylative C(sp3)–C(sp3) cross coupling. *J. Am. Chem. Soc.* **145**, 11518–11523 (2023).

28. P. Li, Z. Zhu, C. Guo, G. Kou, S. Wang, P. Xie, D. Ma, T. Feng, Y. Wang, Y. Qiu, Nickel-electrocatalysed C(sp3)–C(sp3) cross-coupling of unactivated alkyl halides. *Nat. Catal.* **7**, 412–421 (2024).

29. W. Zhang, L. Lu, W. Zhang, Y. Wang, S. D. Ware, J. Mondragon, J. Rein, N. Strotman, D. Lehnherr, K. A. See, S. Lin, Electrochemically driven cross-electrophile coupling of alkyl halides. *Nature* **604**, 292–297 (2022).

30. Z. Zhang, T. Cernak, The formal cross-coupling of amines and carboxylic acids to form sp3–sp3 carbon–carbon bonds. *Angew. Chem. Int. Ed. Engl.* **60**, 27293–27298 (2021).

31. T. Yang, Y. Wei, M. J. Koh, Photoinduced nickel-catalyzed deaminative cross-electrophile coupling for C(sp2)–C(sp3) and C(sp3)–C(sp3) bond formation. *ACS Catal.* **11**, 6519–6525 (2021).

32. Z. Dong, D. W. C. MacMillan, Metallaphotoredox-enabled deoxygenative arylation of alcohols. *Nature* **598**, 451–456 (2021).

33. X. Zhang, D. W. C. MacMillan, Alcohols as latent coupling fragments for metallaphotoredox catalysis: sp3–sp2 cross-coupling of oxalates with aryl halides. *J. Am. Chem. Soc.* **138**, 13862–13865 (2016).

34. Y. Wei, B. Ben-zvi, T. Diao, Diastereoselective synthesis of aryl C-glycosides from glycosyl esters via C−O bond homolysis. *Angew. Chem. Int. Ed. Engl.* **60**, 9433–9438 (2021).

35. B. K. Chi, J. K. Widness, M. M. Gilbert, D. C. Salgueiro, K. J. Garcia, D. J. Weix, In-situ bromination enables formal cross-electrophile coupling of alcohols with aryl and alkenyl halides. *ACS Catal.* **12**, 580–586 (2022).

36. N. Rodríguez, L. J. Goossen, Decarboxylative coupling reactions: A modern strategy for C–C-bond formation. *Chem. Soc. Rev.* **40**, 5030–5048 (2011).

37. Z. Zuo, D. T. Ahneman, L. Chu, J. A. Terrett, A. G. Doyle, D. W. C. MacMillan, Merging photoredox with nickel catalysis: Coupling of α-carboxyl sp3-carbons with aryl halides. *Science* **345**, 437–440 (2014).

38. A. Y. Chan, I. B. Perry, N. B. Bissonnette, B. F. Buksh, G. A. Edwards, L. I. Frye, O. L. Garry, M. N. Lavagnino, B. X. Li, Y. Liang, E. Mao, A. Millet, J. V. Oakley, N. L. Reed, H. A. Sakai, C. P. Seath, D. W. C. MacMillan, Metallaphotoredox: The merger of photoredox and transition metal catalysis. *Chem. Rev.* **122**, 1485–1542 (2022).

39. Z. Zuo, H. Cong, W. Li, J. Choi, G. C. Fu, D. W. C. MacMillan, Enantioselective decarboxylative arylation of α-amino acids via the merger of photoredox and nickel catalysis. *J. Am. Chem. Soc.* **138**, 1832–1835 (2016).

40. N. A. McGrath, M. Brichacek, J. T. Njardarson, A graphical journey of innovative organic architectures that have improved our lives. *J. Chem. Educ.* **87**, 1348–1349 (2010).

41. K. Sanderson, Amino acid provides shortcut to drugs. *Nature* **488**, 266–266 (2012).

42. K. A. Steiniger, M. C. Lamb, T. H. Lambert, Cross-coupling of amines via photocatalytic denitrogenation of in situ generated diazenes. *J. Am. Chem. Soc.* **145**, 11524–11529 (2023).

43. K. M. Baker, D. Lucas Baca, S. Plunkett, M. E. Daneker, M. P. Watson, Engaging alkenes and alkynes in deaminative alkyl-alkyl and alkyl-vinyl cross-couplings of alkylpyridinium salts. *Org. Lett.* **21**, 9738–9741 (2019).

44. C. H. Basch, J. Liao, J. Xu, J. J. Piane, M. P. Watson, Harnessing alkyl amines as electrophiles for nickel-catalyzed cross couplings via C–N bond activation. *J. Am. Chem. Soc.* **139**, 5313–5316 (2017).

45. J. Hu, G. Wang, S. Li, Z. Shi, Selective C-N borylation of alkyl amines promoted by Lewis base. *Angew. Chem. Int. Ed. Engl.* **57**, 15227–15231 (2018).

46. X. Jiang, M. M. Zhang, W. Xiong, L. Q. Lu, W. J. Xiao, Deaminative (carbonylative) alkyl-Heck-type reactions enabled by photocatalytic C-N bond activation. *Angew. Chem. Int. Ed. Engl.* **58**, 2402–2406 (2019).

47. F. J. R. Klauck, M. J. James, F. Glorius, Deaminative strategy for the visible-light-mediated generation of alkyl radicals. *Angew. Chem. Int. Ed. Engl.* **56**, 12336–12339 (2017).

48. J. Liao, C. H. Basch, M. E. Hoerrner, M. R. Talley, B. P. Boscoe, J. W. Tucker, M. R. Garnsey, M. P. Watson, Deaminative reductive cross-electrophile couplings of alkylpyridinium salts and aryl bromides. *Org. Lett.* **21**, 2941–2946 (2019).

49. R. Martin-Montero, V. R. Yatham, H. Yin, J. Davies, R. Martin, Ni-catalyzed reductive deaminative arylation at sp(3) carbon centers. *Org. Lett.* **21**, 2947–2951 (2019).

50. S. Plunkett, C. H. Basch, S. O. Santana, M. P. Watson, Harnessing alkylpyridinium salts as electrophiles in deaminative alkyl-alkyl cross-couplings. *J. Am. Chem. Soc.* **141**, 2257–2262 (2019).

51. F. Sandfort, F. Strieth-Kalthoff, F. J. R. Klauck, M. J. James, F. Glorius, Deaminative borylation of aliphatic amines enabled by visible light excitation of an electron donor-acceptor complex. *Chemistry* **24**, 17210–17214 (2018).

52. S. Z. Sun, Y. M. Cai, D. L. Zhang, J. B. Wang, H. Q. Yao, X. Y. Rui, R. Martin, M. Shang, Enantioselective deaminative alkylation of amino acid derivatives with unactivated olefins. *J. Am. Chem. Soc.* **144**, 1130–1137 (2022).

53. S. Z. Sun, C. Romano, R. Martin, Site-selective catalytic deaminative alkylation of unactivated olefins. *J. Am. Chem. Soc.* **141**, 16197–16201 (2019).

54. C. Wang, R. Qi, H. Xue, Y. Shen, M. Chang, Y. Chen, R. Wang, Z. Xu, Visible-light-promoted C(sp^3)-H alkylation by intermolecular charge transfer: Preparation of unnatural α-amino acids and late-stage modification of peptides. *Angew. Chem. Int. Ed. Engl.* **59**, 7461–7466 (2020).

55. J. Wang, M. E. Hoerrner, M. P. Watson, D. J. Weix, Nickel-catalyzed synthesis of dialkyl ketones from the coupling of N-alkyl pyridinium salts with activated carboxylic acids. *Angew. Chem. Int. Ed. Engl.* **59**, 13484–13489 (2020).

56. J. Wu, P. S. Grant, X. Li, A. Noble, V. K. Aggarwal, Catalyst-free deaminative functionalizations of primary amines by photoinduced single-electron transfer. *Angew. Chem. Int. Ed. Engl.* **58**, 5697–5701 (2019).

57. J. Wu, L. He, A. Noble, V. K. Aggarwal, Photoinduced deaminative borylation of alkylamines. *J. Am. Chem. Soc.* **140**, 10700–10704 (2018).

58. J. Yi, S. O. Badir, L. M. Kammer, M. Ribagorda, G. A. Molander, Deaminative reductive arylation enabled by nickel/photoredox dual catalysis. *Org. Lett.* **21**, 3346–3351 (2019).

59. H. Yue, C. Zhu, L. Shen, Q. Geng, K. J. Hock, T. Yuan, L. Cavallo, M. Rueping, Nickel-catalyzed C-N bond activation: Activated primary amines as alkylating reagents in reductive cross-coupling. *Chem. Sci.* **10**, 4430–4435 (2019).

60. X. Zeng, W. Yan, S. B. Zacate, A. Cai, Y. Wang, D. Yang, K. Yang, W. Liu, Copper-catalyzed deaminative difluoromethylation. *Angew. Chem. Int. Ed. Engl.* **59**, 16398–16403 (2020).

61. S. Ni, C.-X. Li, Y. Mao, J. Han, Y. Wang, H. Yan, Y. Pan, Ni-catalyzed deaminative cross-electrophile coupling of Katritzky salts with halides via C─N bond activation. *Sci. Adv.* **5**, eaaw9516 (2019).

62. M. A. Ashley, T. Rovis, Photoredox-catalyzed deaminative alkylation via C-N bond activation of primary amines. *J. Am. Chem. Soc.* **142**, 18310–18316 (2020).

63. J. R. Dorsheimer, M. A. Ashley, T. Rovis, Dual nickel/photoredox-catalyzed deaminative cross-coupling of sterically hindered primary amines. *J. Am. Chem. Soc.* **143**, 19294–19299 (2021).

64. J. R. Dorsheimer, T. Rovis, Late-stage isotopic exchange of primary amines. *J. Am. Chem. Soc.* **145**, 24367–24374 (2023).

65. A. D. Marchese, J. R. Dorsheimer, T. Rovis, Photoredox-catalyzed generation of tertiary anions from primary amines via a radical polar crossover. *Angew. Chem. Int. Ed. Engl.* **63**, e202317563 (2024).

66. C.-H. Xu, L. Zeng, M. Hu, J.-H. Qin, X.-H. Xu, J.-H. Li, Photoreductive alkylative dearomatization of N-alkyl pyridin-1-ium salts: Site selective access to 4-alkyl 1,4-dihydropyridines. *European J. Org. Chem.* **27**, e202301120 (2024).

67. R. Scholz, G. Hellmann, S. Rohs, D. Özdemir, G. Raabe, C. Vermeeren, H.-J. Gais, Enantioselective synthesis, configurational stability, and reactivity of lithium α-tert-butylsulfonyl carbanion salts. *European J. Org. Chem.* **2010**, 4588–4616 (2010).

68. P. Müller, M. P. N. Thi, Conversion of amines into phenylsulfides and phenylselenides via ditosylamides. *Helv. Chim. Acta* **63**, 2168–2172 (1980).

69. Q. Qin, Z. Cheng, N. Jiao, Recent applications of trifluoromethanesulfonic anhydride in organic synthesis. *Angew. Chem. Int. Ed. Engl.* **62**, e202215008 (2023).

70. D. Sun, Y. Gong, Y. Wu, Y. Chen, H. Gong, Bis(pinacolato)diboron-enabled Ni-catalyzed reductive arylation/vinylation of alkyl electrophiles. *Adv. Sci.* **11**, 2404301 (2024).

71. L. Lu, Y. Wang, W. Zhang, W. Zhang, K. A. See, S. Lin, Three-component cross-electrophile coupling: Regioselective electrochemical dialkylation of alkenes. *J. Am. Chem. Soc.* **145**, 22298–22304 (2023).

72. M. D. Palkowitz, G. Laudadio, S. Kolb, J. Choi, M. S. Oderinde, T. E.-H. Ewing, P. N. Bolduc, T. Chen, H. Zhang, P. T. W. Cheng, B. Zhang, M. D. Mandler, V. D. Blasczak, J. M. Richter, M. R. Collins, R. L. Schioldager, M. Bravo, T. G. M. Dhar, B. Vokits, Y. Zhu, P.-G. Echeverria, M. A. Poss, S. A. Shaw, S. Clementson, N. N. Petersen, P. K. Mykhailiuk, P. S. Baran, Overcoming limitations in decarboxylative arylation via Ag–Ni electrocatalysis. *J. Am. Chem. Soc.* **144**, 17709–17720 (2022).

73. G. S. Kumar, A. Peshkov, A. Brzozowska, P. Nikolaienko, C. Zhu, M. Rueping, Nickel-catalyzed chain-walking cross-electrophile coupling of alkyl and aryl halides and olefin hydroarylation enabled by electrochemical reduction. *Angew. Chem. Int. Ed. Engl.* **59**, 6513–6519 (2020).

74. K. J. Jiao, D. Liu, H. X. Ma, H. Qiu, P. Fang, T. S. Mei, Nickel-catalyzed electrochemical reductive relay cross-coupling of alkyl halides to aryl halides. *Angew. Chem. Int. Ed. Engl.* **59**, 6520–6524 (2020).

75. H. Wu, S.-Q. Zhang, X. Hong, Mechanisms of nickel-catalyzed reductive cross-coupling reactions. *Chem. Synth.* **3**, 39 (2023).

76. H. Xu, C. Zhao, Q. Qian, W. Deng, H. Gong, Nickel-catalyzed cross-coupling of unactivated alkyl halides using bis(pinacolato)diboron as reductant. *Chem. Sci.* **4**, 4022–4029 (2013).

77. T. J. Anderson, D. A. Vicic, Direct observation of noninnocent reactivity of ZnBr2 with alkyl halide complexes of nickel. *Organometallics* **23**, 623–625 (2004).

78. R. G. Parr, Y. Weitao, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, 1994).

79. M. J. Frisch, G. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. Sonnenberg, M. Hada, D. Fox, Gaussian 09 Revision A.1. Gaussian Inc. (2009).

80. C. Lee, W. Yang, R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B Condens Matter* **37**, 785–789 (1988).

81. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J Chem Phys* **132**, 154104 (2010).

82. A. V. Marenich, C. J. Cramer, D. G. Truhlar, Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *J. Phys. Chem. B* **113**, 6378–6396 (2009).

83. B. P. Moore, P. S. Hewlett, Insecticidal synergism with the pyrethrins: Studies on the relationship between chemical structure and synergistic activity in the 3:4-methylenedioxyphenyl compounds. *J. Sci. Food Agric.* **9**, 666–672 (1958).

84. K. Komeyama, R. Ohata, S. Kiguchi, I. Osaka, Highly nucleophilic vitamin B12-assisted nickel-catalysed reductive coupling of aryl halides and non-activated alkyl tosylates. *Chem. Commun.* **53**, 6401–6404 (2017).

85. W. Su, R.-X. Qiao, Y.-Y. Jiang, X.-L. Zhen, X. Tian, J.-R. Han, S.-M. Fan, Q. Cheng, S. Liu, Ligand-Free Iron-Catalyzed Regioselectivity-Controlled Hydroboration of Aliphatic Terminal Alkenes. *ACS Catal.* **10**, 11963–11970 (2020).

86. J. Nguyen, A. Chong, G. Lalic, Nickel-catalyzed anti-Markovnikov hydroarylation of alkenes. *Chem. Sci.* **10**, 3231–3236 (2019).

87. Q.-H. Xu, L.-P. Wei, B. Xiao, Alkyl-GeMe3: Neutral metalloid radical precursors upon visible-light photocatalysis. *Angew. Chem. Int. Ed.* **61**, e202115592 (2022).

88. T. Koyanagi, A. Herath, A. Chong, M. Ratnikov, A. Valiere, J. Chang, V. Molteni, J. Loren, One-pot electrochemical nickel-catalyzed decarboxylative Sp^2–Sp^3 cross-coupling. *Org. Lett.* **21**, 816–820 (2019).

89. J. A. Fuentes, S. M. Smith, M. T. Scharbert, I. Carpenter, D. B. Cordes, A. M. Z. Slawin, M. L. Clarke, On the functional group tolerance of ester hydrogenation and polyester depolymerisation catalysed by ruthenium complexes of tridentate aminophosphine ligands. *Chem. Eur. J.* **21**, 10851–10860 (2015).

90. J. Choi, G. Laudadio, E. Godineau, P. S. Baran, Practical and Regioselective Synthesis of C-4-Alkylated Pyridines. *J. Am. Chem. Soc.* **143**, 11927–11933 (2021).

91. A. Ray Choudhury, S. Mukherjee, Enantioselective dearomatization of isoquinolines by anion-binding catalysis en route to cyclic α-aminophosphonates. *Chem. Sci.* **7**, 6940–6945 (2016).

92. W. E. Truce, D. D. Emrick, R. E. Miller, The Internal Condensation of 2,4-Diphenyl-1-butanesulfonylSulfone1. *J. Am. Chem. Soc.* **75**, 3359–3361 (1953).

93. Y. He, Y. Cai, S. Zhu, Mild and regioselective benzylic C–H functionalization: Ni-catalyzed reductive arylation of remote and proximal olefins. *J. Am. Chem. Soc.* **139**, 1061–1064 (2017).

94. X. Wu, C. N. Gannett, J. Liu, R. Zeng, L. F. T. Novaes, H. Wang, H. D. Abruña, S. Lin, Intercepting hydrogen evolution with hydrogen-atom transfer: Electron-initiated hydrofunctionalization of alkenes. *J. Am. Chem. Soc.* **144**, 17783–17791 (2022).

95. G. Sun, H. Sun, Z. Wang, M.-M. Zhou, A novel $InCl_3/SiO_2$-catalyzed hydroarylation of arenes with styrenes under solvent-free conditions. *Synlett* **2008**, 1096–1100 (2008).

96. P. Basnet, S. Thapa, D. A. Dickie, R. Giri, The copper-catalysed Suzuki–Miyaura coupling of alkylboron reagents: disproportionation of anionic(alkyl)(alkoxy)borates to

anionic dialkylborates prior to transmetalation. *Chem. Commun.* **52**, 11072–11075 (2016).

97. Q. Lin, G. Ma, H. Gong, Ni-catalyzed formal cross-electrophile coupling of alcohols with aryl halides. *ACS Catal.* **11**, 14102–14109 (2021).

98. C.-L. Ji, J. Han, T. Li, C.-G. Zhao, C. Zhu, J. Xie, Photoinduced gold-catalyzed divergent dechloroalkylation of gem-dichloroalkanes. *Nat. Catal.* **5**, 1098–1109 (2022).

99. Y. Yang, Q. Zhou, J. Cai, T. Xue, Y. Liu, Y. Jiang, Y. Su, L. Chung, D. A. Vicic, Exploiting the trifluoroethyl group as a precatalyst ligand in nickel-catalyzed Suzuki-type alkylations. *Chem. Sci.* **10**, 5275–5282 (2019).

100. W. Hang, N. Liang, Y. Liu, C. Xi, Cobalt-catalyzed highly regioselective three-component arylcarboxylation of acrylate with aryl bromides and carbon dioxide. *ChemSusChem* **14**, 4941–4946 (2021).

101. A. Luridiana, D. Mazzarella, L. Capaldo, J. A. Rincón, P. García-Losada, C. Mateos, M. O. Frederick, M. Nuño, W. Jan Buma, T. Noël, The merger of benzophenone HAT photocatalysis and silyl radical-induced XAT enables both nickel-catalyzed cross-electrophile coupling and 1,2-dicarbofunctionalization of olefins. *ACS Catal.* **12**, 11216–11225 (2022).

102. H. Li, S. Li, H. Hu, R. Sun, M. Liu, A. Ding, X. Liu, W. Luo, Z. Fu, S. Guo, H. Cai, Visible-light-induced C(sp^3)–C(sp^3) bond formation via radical/radical cross-coupling. *Chem. Commun.* **59**, 1205–1208 (2023).

103. G. S. Yedase, A. K. Jha, V. R. Yatham, Visible-Light Enabled C(sp^3)–C(sp^2) Cross-Electrophile Coupling via Synergistic Halogen-Atom Transfer (XAT) and Nickel Catalysis. *J. Org. Chem.* **87**, 5442–5450 (2022).

104. R. R. Chowdhury, A. K. Crane, C. Fowler, P. Kwong, C. M. Kozak, Iron(iii) amine-bis(phenolate) complexes as catalysts for the coupling of alkyl halides with aryl Grignard reagents. *Chem. Commun.* , 94–96 (2008).

105. Y. Pan, Y. Gong, Y. Song, W. Tong, H. Gong, Retracted Article: Deoxygenative cross-electrophile coupling of benzyl chloroformates with aryl iodides. *Org. Biomol. Chem.* **17**, 4230–4233 (2019).