Supporting Information

Regioselective C–H alkylation of anisoles with olefins by cationic imidazolin-2-iminato scandium(III) alkyl complexes

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Table of Contents

1. General remarks 2

2. Preparation of catalysts 2

3. Typical procedure for C–H activation of anisoles or 2-methyl anisole with alkenes 8

5. Experimental procedure for the scale-up reaction 15

6. Control experiments 15

7. X-ray crystallography data 29

8. The analytical and spectral characterization data of products 35

9. References 53

10. Copies of NMR spectra for catalysts and products 54

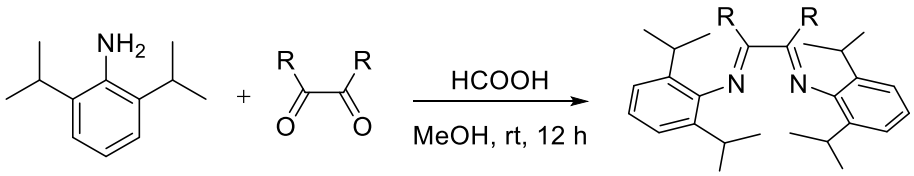
1. General remarks

^{1}H NMR spectra were recorded on Bruker ASCENDTM 400M (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26 ppm, $(CD_3)_2SO$, δ = 2.50 ppm, C_6D_6, δ = 7.16 ppm). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets), coupling constants (Hz), integration and assignment. $^{13}C\{^{1}H\}$ NMR spectra were collected on ASCENDTM 400M (101 MHz). Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0, $(CD_3)_2SO$, δ = 39.5 ppm, C_6D_6, δ = 128.1 ppm). High resolution mass spectra (HRMS) were performed on Thermo Q-Exactive Focus (FTMS+c ESI) and data were reported as (m/z). GC-MS analysis was performed on Shimadzu GCMS-2020 NX gas chromatograph with an SH-I-5MS column. Infrared spectra (IR) were recorded on Bruker Tensor II spectrometer with Plantium ATR accessory and the peaks were reported as absorption maxima (ν, cm^{-1}). Melting point ranges were determined on OptiMelt. X-ray crystallographic data were collected by a Bruker D8 Venture Photon II. All manipulations were performed under a dry and oxygen-free (< 0.01 ppm) argon atmosphere in a glovebox. All reported reaction temperatures correspond to temperatures of the oil bath. Solvents (including deuterated solvents used for NMR) were dried and distilled prior to use. $[Ph_3C][B(C_6F_5)_4]$ was purchased from Adamas. Anhydrous $ScCl_3(THF)_3$ was purchased from Yanfeng technology, Anhydrous YCl_3 were purchased from Aladdin. Anhydrous $GdCl_3$ and $LuCl_3$ were purchased from Alfa. 1,3-Bis(1-adamantyl)imidazolium chloride were purchased from Bidepharm. $Ln(CH_2C_6H_4NMe_2\text{-}o)_3$ (Ln = Sc, Y, Gd, Lu) were prepared according to the literatures.[1] Imidazolin-2-imine scandium neosilyl complexes $[NHISc(CH_2SiMe_3)_2(THF)]$ was prepared according to the reported procedure.[2] All substrates were distilled from CaH_2 and stored in molecular sieves before use. 4-Methyl[2-D]anisole and 1-methoxy-2-(methyl-d_3)benzene were prepared as described previously.[3] 1,3-Bis(2,4,6-trimethylphenyl)imidazolin-2-imine were prepared as described previously.[4]

2. Preparation of catalysts

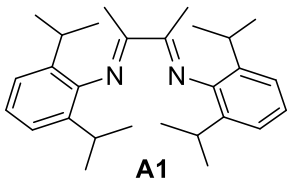
2.1 Preparation of imidazolin-2-imine ligands.

2.1.1 General procedure for synthesis of diimines



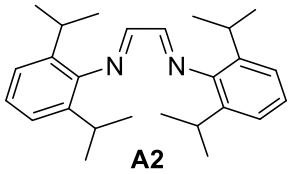
A1, R = Me
A2, R = H

General Procedure (GP): In a round bottom flask, aniline (2.0 equiv.) was dissolved in methanol (2M), 2,3-butanedione (1.0 equiv.) or glyoxal 40% in water (1.0 equiv.) and two drops of formic acid were added subsequently. The resulting solution was stirred at room temperature for 12 h. The yellow suspension was filtrated, washed with cold methanol. The solid was dried in vacuo to get product.



A1

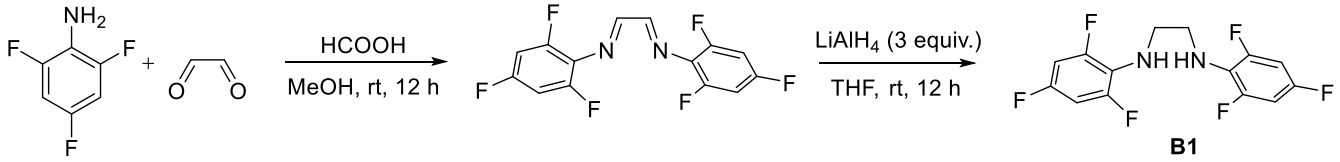
A1 ($C_{28}H_{40}N_2$) prepared according to the general procedure to yield 94% of yellow powder. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.19 – 7.17 (m, 4H), 7.13 – 7.09 (m, 2H), 2.76 – 2.69 (m, 4H), 2.08 (s, 6H), 1.22 – 1.18 (m, 24H). **$^{13}C\{^{1}H\}$ NMR** (101 MHz, Chloroform-*d*) δ 168.1, 146.1, 135.0, 123.7, 122.9, 28.5, 22.9, 22.6, 16.5. (Consistent with the data in previous literature) [5].



A2

A2 ($C_{26}H_{36}N_2$) prepared according to the general procedure to yield 90% of yellow powder. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.11 (s, 2H), 7.21 – 7.14 (m, 6H), 2.99 – 2.92 (m, 4H), 1.22 (d, J = 6.8 Hz, 24H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 163.0, 148.0, 136.7, 125.1, 123.1, 28.0, 23.3. (Consistent with the data in previous literature) [5].

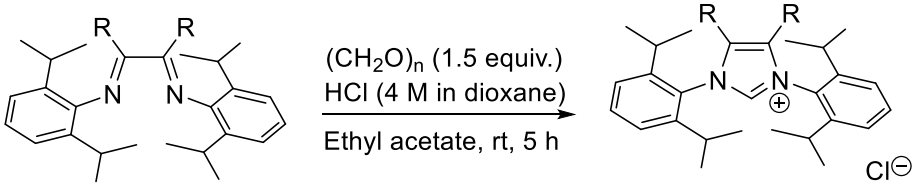
2.1.2 Synthesis of diamine (B1)



B1

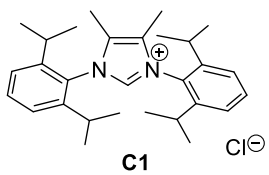
2,4,6-Trifluoroaniline (3.0 g, 20.0 mmol, 2.0 equiv.) was dissolved in methanol (5 mL), glyoxal 40% in water (1.14 mL, 10.0 mmol, 1.0 equiv.) and two drops of formic acid were added subsequently. The solution was stirred at room temperature for 12 h. The milky white suspension was filtrated, washed with cold methanol. The obtained solid was dried in vacuo to afford *N,N'*-bis(2,4,6-trifluorophenyl)ethane-1,2-diimine as a white powder. The powder was dissolved in THF, $LiAlH_4$ was added slowly at 0 °C. The solution was warmed to room temperature and stirred for 12 h. Then the reaction mixture was cooled to 0 °C. Ice water was added to quench the reaction, followed by addition of KOH solution. The aqueous phase was extracted with ethyl acetate. The combined organic layer was washed with H_2O, brine and dried with anhydrous magnesium sulfate. The mixture was filtered and the solvent was removed to afford *N,N'*-bis(2,4,6-trifluorophenyl)ethane-1,2-diamine (**B1**, 3.04 g, 9.5 mmol, 95%) as a colorless liquid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.63 (t, J = 8.4 Hz, 4H), 3.40 (s, 4H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 156.1, 154.9, 154.8, 154.7, 153.7, 152.5, 152.3, 152.2, 122.0, 100.5, 100.2, 100.0, 47.0. **^{19}F{^{1}H} NMR** (377 MHz, Chloroform-*d*) δ –120.93, –125.25. **IR** (film, cm^{-1}): 3410, 1610, 1505, 1440, 1242, 1173, 1113, 1018, 995, 837, 597, 511. **HRMS** (ESI-TOF) calcd for $C_{14}H_{10}F_6N_2^+$ ([M]+H$^+$) = 321.0821, found 321.0814.

2.1.3 General procedure for synthesis of imidazolium salts



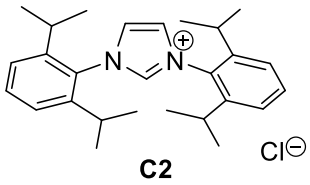
C1, R = Me
C2, R = H

General Procedure (GP): Paraformaldehyde (1.5 equiv.) was suspended in a solution of 4 M hydrochloric acid in dioxane (1.5 equiv.) and stirred until complete dissolution of the white solid. Diimine (1.0 equiv.) in Ethyl acetate (0.5 M) was added slowly. The resulting solution was stirred at room temperature for 5 h. Then the suspension was filtered, washed with diethyl ether to afford light pink solid. Then the obtained solid was dissolved in methanol and was neutralized with sodium bicarbonate. The suspension was filtered. The solvent was removed under reduced pressure. The residue was subjected to column chromatography on silica gel (eluent: DCM:MeOH = 10:1, v/v) to afford desired product.



C1

C1 prepared according to the general procedure (white powder, 55% yield). **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.01 (s, 1H), 7.69 (t, J = 7.8 Hz, 2H), 7.55 (d, J = 7.8 Hz, 4H), 2.33 – 2.29 (m, 4H), 2.08 (s, 6H), 1.26 (d, J = 6.8 Hz, 12H), 1.12 (d, J = 6.8 Hz, 12H). **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6) δ 145.2, 136.6, 132.1, 128.9, 127.8, 125.0, 28.4, 24.8, 22.6, 8.4. (Consistent with the data in previous literature). [6]

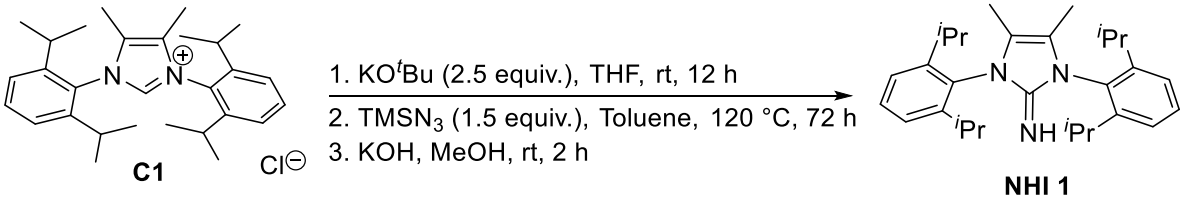


C2

C2 prepared according to the general procedure to yield 70% of white powder. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.22 (s, 1H), 8.57 (s, 2H), 7.69 (t, J = 7.8 Hz, 2H), 7.53 (d, J = 7.8 Hz, 4H), 2.39 – 2.32 (m, 4H), 1.26 (d, J = 6.8 Hz, 12H), 1.16 (d, J = 6.9 Hz, 12H). **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6) δ 144.8, 139.3, 131.8, 130.0, 126.2, 124.6, 28.6, 24.1, 23.1. (Consistent with the date in previous literature). [6]

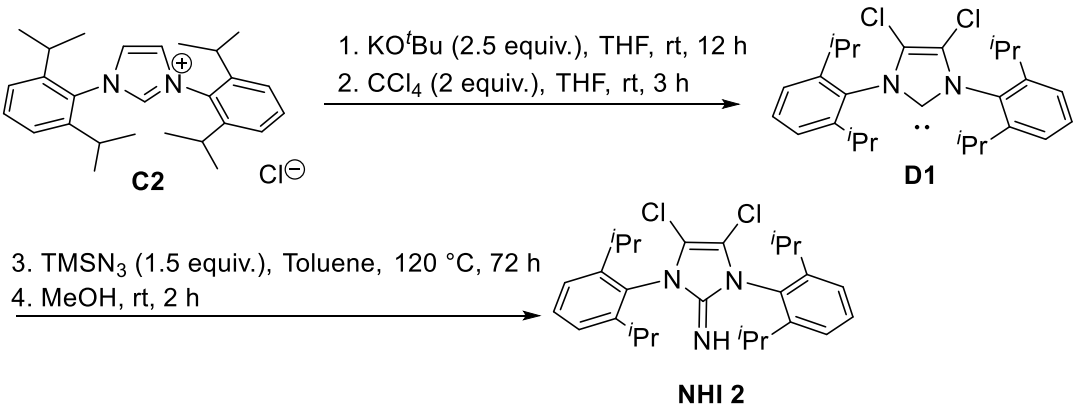
2.1.4 Synthesis of imidazolin-2-imine ligands

1,3-Bis(2,6-diisopropylphenyl)-4,5-dimethylimidazolin-2-imine (NHI 1)



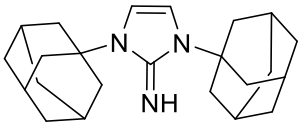
In a glovebox, [1,3-bis(2,6-diisopropylphenyl)-4,5-dimethyl]imidazolium chloride (**C1**) (4.53 g, 10.0 mmol, 1.0 equiv.) and KO^{t}Bu (2.81 g, 25.0 mmol, 2.5 equiv.) are added to a round-bottom flask. 40 mL of anhydrous THF was added. After stirring at room temperature for 12 h, the milky white suspension gradually turned into a light-yellow solution, and the solvent was removed under the vacuum, the off-white solid was obtained. Then toluene (20 mL) was added and the mixture was slightly heated to make it uniform. Hexane was added and a large amount of white solid was precipitated. Concentration of the combined filtrate gave a microcrystalline colorless solid (free NHC). A solution of the [1,3-bis(2,6-diisopropylphenyl)-4,5-dimethyl]imidazol-2-ylidene in toluene (20 mL) was treated dropwise with trimethylsilyl azide (2 mL, 15.0 mmol, 1.5 equiv.), and the resulting reaction mixture was heated at 120 °C for 72 h. Filtration and evaporation of the solvent afforded the TMS-protected imines as yellowish solids. Then the solid were treated with an excess of CH_3OH (10 mL) and KOH (840 mg) for 2 h. The solvent was then removed in reduced pressure. The residue was subjected to column chromatography on silica gel (eluent: DCM:MeOH = 10:1) to afford 1,3-bis(2,6-diisopropylphenyl)-4,5-dimethylimidazolin-2-imine (2.37 g, 5.5 mmol, 80 %) as a white powder. Melting point: 194 – 198 °C. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.57 (t, J = 7.8 Hz, 2H), 7.38 (d, J = 7.8 Hz, 4H), 2.61 – 2.54 (m, 4H), 1.91 (s, 6H) 1.28 – 1.25 m, 24H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-d) δ 147.0, 131.8, 125.2, 119.3, 117.7, 29.0, 24.2, 23.7, 8.9. **IR** (film, cm^{-1})): 3395, 2963, 2870, 2001, 1646, 1594, 1575, 1465, 1385, 1364, 1327, 1271, 1221, 1144, 1059, 940, 808, 761, 730, 699, 647, 441. **HRMS** (ESI-TOF) calcd for $C_{29}H_{42}N_3^+$ ([M]+H$^+$) = 432.3373, found 432.3367.

1,3-Bis(2,6-diisopropylphenyl)-4,5-dichloroimidazolin-2-imine (NHI 2)



In a glovebox, 1,3- bis-(2,6-diisopropylphenyl)imidazolium chloride (**C2**) (4.3 g, 10.0 mmol, 1.0 equiv.) and KO^{t}Bu (2.8 g, 25.0 mmol, 2.5 equiv.) are added to a round-bottom flask. 40 mL of anhydrous THF was added. After stirring at room temperature for 12 h, the milky white suspension gradually turned into a light-yellow solution, and the solvent was removed in the vacuo, the off-white solid was obtained. Then toluene (50 mL) was added and the mixture was slightly heated to make it uniform. Hexane was added and a large amount of white solid was precipitated. Concentration of the combined filtrate gave a microcrystalline colorless solid (free NHC). The obtained solid was dissolved in THF (5 mL), and CCl_4 (3.1 mL, 20.0 mmol, 2.0 equiv.) was added. The resulting solution was stirred an additional 12 h at room temperature. The solution turned into violet, and the solvent was drained under the vacuum, the violate solid was obtained. Recrystallized from hexane at −30 °C to provide [1,3-bis(2,6-diisopropylphenyl)-4,5-dichloro]imidazol-2-ylidene (**D1**) (3.7 g, 8.0 mmol, 80 %) as a violet powder. **^{1}H NMR** (400 MHz, Benzene-d_6) δ 7.29 – 7.25 m, 2H), 7.16 – 7.14 (m, 3H), 2.94 – 2.85 (m, 4H), 1.26 (d, J = 6.8 Hz, 12H), 1.21 (d, J = 7.0 Hz, 12H). **^{13}C{^{1}H} NMR** (101 MHz, Benzene-d_6) δ 146.4, 138.9, 129.6, 123.6, 116.6, 28.8, 24.4, 22.6. A solution of the [1,3-bis(2,6-diisopropylphenyl)-4,5-dichloro]imidazol-2-ylidene in toluene (20 mL) was treated dropwise with trimethylsilyl azide (1.4 mL, 12.0 mmol, 1.5 equiv.), and the resulting reaction mixture was subsequently heated at 120 °C for 72 h. The solvent was removed to the TMS-protected imines as yellowish solids. Then the solid were treated with an excess of CH_3OH 10 mL for 2 h. The solvent was then removed in reduced pressure. The residue was subject to column chromatography on silica gel (eluent: DCM:MeOH = 10:1, v/v) to afford 1,3-bis(2,6-diisopropylphenyl)-4,5-dichloroimidazolin-2-imine (1.89 g, 4.0 mmol, 50%) as a yellow powder. Melting point: 169 – 171 °C. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.42 (t, J = 7.8 Hz, 2H), 7.23 (d, J = 9.4 Hz, 4H), 2.92 – 2.85 (m, 4H), 1.23 (d, J = 6.8 Hz, 12H), 1.19 (d, J = 6.8 Hz, 12H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-d) δ 148.8, 130.4, 124.3, 29.0, 24.0, 23.5. **IR** (film, cm^{-1})): 3394, 2963, 2870, 1653, 1605, 1586, 1466, 1405, 1383, 1365, 1252, 1204, 1070, 936, 869, 802, 752, 680, 542, 430. **HRMS** (ESI-TOF) calcd for $C_{27}H_{36}Cl_2N_3^+$ ([M]+H$^+$) = 472.2281, found 472.2278.

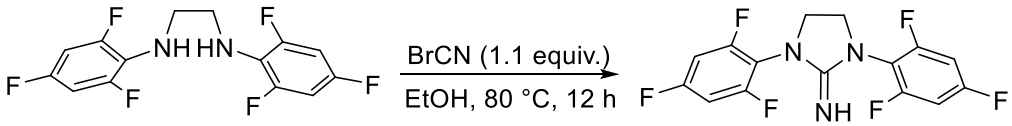
1,3-Bis(1-adamantyl)imidazolin-2-imine (NHI 3)



NHI 3

According to the same procedures of **NHI 1**, 1,3-bis(1-adamantyl)imidazolin-2-imine was afforded in 60% yield as a white powder. Melting point: 288 – 292 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.17 (s, 2H), 3.61 (s, 18H), 2.16 (s, 18H), 1.81 (d, J = 12.2 Hz, 6H), 1.62 (d, J = 12.2 Hz, 6H). **^{13}C{^{1}H} NMR** (101 MHz, DMSO-d_6) δ 143.4, 113.0, 59.7, 35.0, 29.6. **IR** (film, cm^{-1}): 3116, 2911, 2852, 2028, 1630, 1477, 1309, 1175, 1093, 735. **HRMS** (ESI-TOF) calcd for $C_{23}H_{34}N_3^+$ ([M]+H$^+$) = 352.2747, found 352.2743.

1,3-Bis(2,4,6-trifluorophenyl)imidazolidin-2-imine (NHI 4)

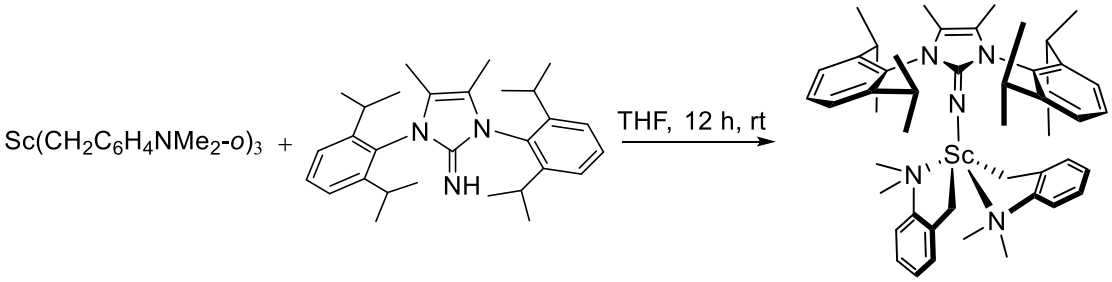


B1 **NHI 4**

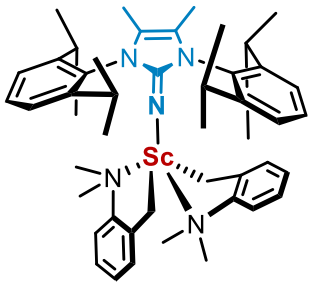
To a stirring solution of *N,N'*-bis(2,4,6-trifluorophenyl)ethane-1,2-diamine (**B1**, 2.6 g, 8.0 mmol) in 3 mL of ethanol was carefully added a solution of cyanogen bromide (932 mg, 8.8 mmol, 1.1 equiv.) in 1 mL of ethanol at 0 °C. The reaction mixture was warmed to 25 °C and heated at 80 °C for 12 h. The mixture was cooled to rt and was diluted with aqueous 1M NaOH (20 mL). The aqueous phase was extracted with DCM, the combined organic layer was washed with H_2O, brine and dried with anhydrous magnesium sulfate [7]. The mixture was filtered and the solvent was removed in vacuo and the residue was subjected to column chromatography on silica gel (eluent: DCM:MeOH = 10:1, v/v) to afford 1,3-bis(2,4,6-trifluorophenyl)imidazolidin-2-imine (829 mg, 2.4 mmol, 45%) as a white powder.

Melting point: 147 – 150 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.93 – 6.65 (m, 4H), 3.85 (s, 4H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 162.7, 161.9, 161.8, 161.7, 161.7, 160.2, 160.1, 159.3, 159.3, 159.2, 159.1, 156.7, 101.5, 101.2, 101.0, 46.8. **^{19}F{^{1}H} NMR** (377 MHz, Chloroform-*d*) δ -107.02, -113.41. **IR** (film, cm^{-1}): 3332, 3026, 1634, 1601, 1506, 1446, 1423, 1360, 1292, 1229, 1174, 1121, 1029, 995, 864, 841, 787, 739, 704, 651, 613, 582, 539, 510, 415. **HRMS** (ESI-TOF) calcd for $C_{15}H_{10}F_6N_3^+$ ([M]+H$^+$) = 346.0773, found 346.0768.

2.2 General procedure for the synthesis of imidazolin-2-iminato complexes of rare earth metals.

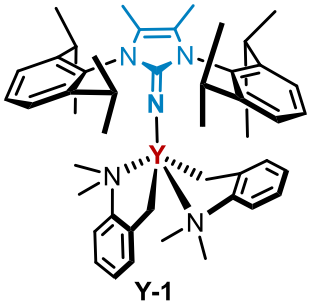


General procedure (GP): In a glovebox, Sc(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$ (224 mg, 0.5 mmol) and 1,3-bis(2,6-diisopropylphenyl)-4,5-dimethylimidazolin-2-imine (216 mg, 0.5 mmol, 1.0 equiv.) were dissolved in THF (5 mL). The resulting mixture was stirred at room temperature for 12 h. The solvent was removed in vacuo. The residue was dissolved in toluene and filtered. The solvent was removed in vacuo. The resulting residue was washed with hexane (0.5 mL*3) to finally give a pale-yellow solid. The obtained solid was dissolved in hexane at 70 °C. The solution was cooled to room temperature and crystalline compound precipitated. The crystals were filtered off and washed with hexane.



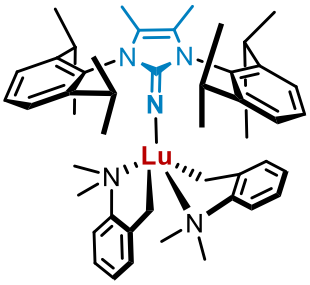
Sc-1

Sc-1 ($C_{47}H_{64}N_5Sc$) prepared according to the general procedure (colorless crystal, 298.0 mg, 80% yield). **^{1}H NMR** (400 MHz, Benzene-d_6) δ 7.21 (t, 2H), 7.17 (m, 2H), 7.10 (m, 2H), 7.00 (m, 2H), 6.98 (m, 2H), 6.80 (m, 2H), 6.71 (m, 2H), 3.35 (s, 2H), 2.86 (s, 2H), 2.28 (s, 6H), 1.88 (s, 6H), 1.56 (br, 2H), 1.55 (d, 6H), 1.46 (s, 6H), 1.27 (br, 2H), 1.14 (d, 12H), 0.90 (s, 6H). **^{13}C{^{1}H} NMR** (101 MHz, Benzene-d_6) δ 149.3, 148.5, 146.0, 145.6, 136.2, 135.1, 129.5, 128.7, 126.9, 124.0, 120.1, 118.1, 113.9, 47.2, 45.2, 44.1, 29.0, 24.2, 23.9, 22.6, 10.0.



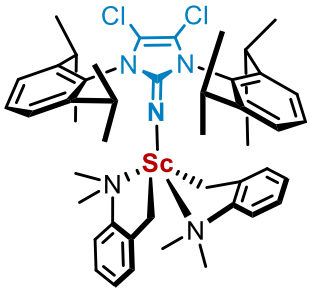
Y-1

Y-1 ($C_{47}H_{64}N_5Y$) prepared according to the general procedure (yellow crystal, 295.5 mg, 75% yield). **^{1}H NMR** (400 MHz, Benzene-d_6) δ 7.20 (t, 2H), 7.12 (m, 2H), 7.10 (m, 2H), 6.92 (m, 2H), 6.91 (m, 2H), 6.71 (m, 2H), 6.67 (m, 2H), 3.18 (s, 4H), 2.08 (s, 12H), 1.55 (s, 6H), 1.39 (s, 6H), 1.19 (m, 10H), 1.19 (d, 12H). **^{13}C{^{1}H} NMR** (101 MHz, Benzene-d_6) δ 149.0, 144.7, 140.3, 138.6, 138.5, 135.2, 128.9, 128.4, 127.4, 123.9, 119.1, 118.6, 113.6, 44.4, 43.32, 43.0, 29.0, 24.5, 10.0.



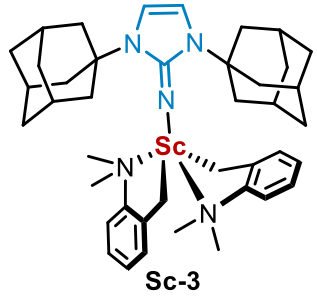
Lu-1

Lu-1 ($C_{47}H_{64}N_5Lu$) prepared according to the general procedure (pale yellow powder, 358.50 mg, 81% yield). **^{1}H NMR** (400 MHz, Benzene-d_6) δ 7.20 (t, 2H), 7.07 (br, 4H), 6.96 (m, 4H), 6.76 (m, 2H), 6.66 (d, 2H), 3.35 (s, 2H), 2.97 (s, 2H), 2.23 (s, 6H), 1.87 (s, 6H), 1.54 (s, 12H), 1.44 (br, 4H), 1.18 (d, 12H), 1.00 (br, 6H). **^{13}C{^{1}H} NMR** (101 MHz, Benzene-d_6) δ 149.6, 148.7, 144.9, 142.1, 141.9, 135.3, 129.6, 127.3, 123.9, 119.4, 118.6, 113.6, 48.6, 45.5, 44.7, 29.0, 24.9, 24.4, 24.1, 23.6, 22.6, 10.1, 9.5.



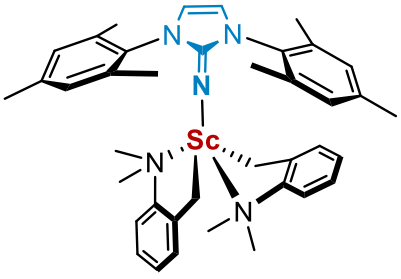
Sc-2

Sc-2 ($C_{45}H_{58}Cl_2N_5Sc$) prepared according to the general procedure (yellow crystal, 274.7 mg, 70%). **^{1}H NMR** (400 MHz, Benzene-d_6) δ 7.18 (t, 2H), 7.12 (br, 2H), 7.07 (s, 2H), 6.97 (s, 2H), 6.96 (m, 2H), 6.79 (m, 2H), 6.67 (d, 2H) , 3.33 (s, 2H), 2.96 (s, 2H), 2.23 (s, 6H), 1.81 (s, 6H), 1.47 (s, 6H), 1.35 (br, 4H), 1.20 (d, 12H), 0.87 (br, 6H). **^{13}C{^{1}H} NMR** (101 MHz, Benzene-d_6) δ 150.1, 149.3, 145.3, 145.1, 133.5, 129.8, 129.5, 127.1, 124.4, 123.8, 120.8, 118.3, 107.2, 47.1, 45.0, 44.8, 29.5, 29.2, 24.4, 23.9, 23.4, 22.7, 14.3.



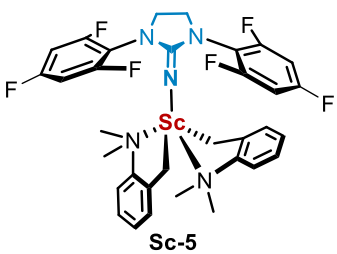
Sc-3

Sc-3 ($C_{41}H_{56}N_5Sc$) prepared according to the general procedure (pale yellow powder, 199.2 mg, 60% yield). **^{1}H NMR** (400 MHz, Benzene-d_6) δ 6.97 (m, 4H), 6.88 (m, 4H), 6.06 (s, 2H), 2.73 (s, 12H), 6.96 (m, 2H), 2.35 (s, 12H), 2.03 (s, 6H), 1.76 (d, 6H), 1.62 (d, 6H), 1.46 (br, 2H), 1.32 (br, 2H). **^{13}C{^{1}H} NMR** (101 MHz, Benzene-d_6) δ 144.7, 143.6, 136.2, 129.7, 128.6, 127.3, 120.1, 118.0, 105.8, 55.6, 46.1, 45.9, 43.7, 40.3, 36.6, 30.3, 30.2.



Sc-4

Sc-4 ($C_{39}H_{48}N_5Sc$) prepared according to the general procedure (pale yellow powder, 240.1 mg, 76% yield). **^{1}H NMR** (400 MHz, Benzene-d_6) δ 7.10 – 7.02 (m, 4H), 6.88 – 6.68 (m, 8H), 5.62 (s, 2H), 2.18 (d, J = 15.2 Hz, 24H), 1.98 (s, 6H), 1.69 (s, 2H), 1.31 (s, 2H). **^{13}C{^{1}H} NMR** (101 MHz, Benzene-d_6) δ 144.7, 143.2, 137.0, 136.3, 135.9, 135.7, 132.4, 131.4, 129.6, 126.9, 123.0, 119.8, 118.8, 118.4, 110.8, 110.6, 44.0, 27.1, 20.9, 18.5, 18.3.

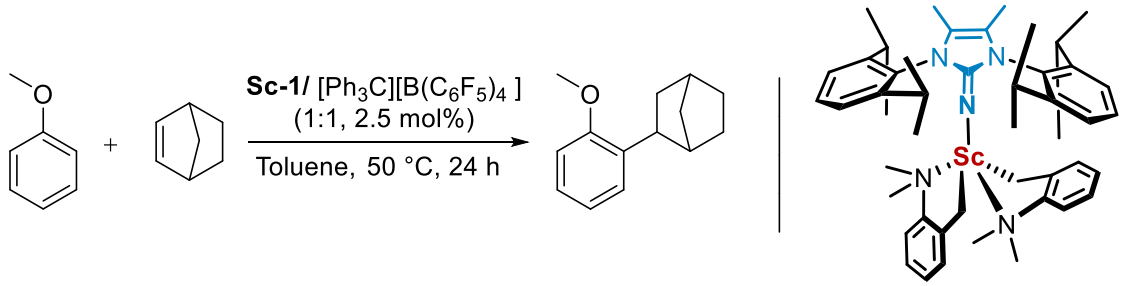


Sc-5

Sc-5 ($C_{33}H_{32}F_6N_5Sc$) prepared according to the general procedure (pale yellow powder, 230.2 mg, 70% yield). **^{1}H NMR** (400 MHz, Benzene-d_6) δ 7.10 (d, J = 7.4 Hz, 1H), 6.96 – 6.91 (m, 3H), 6.83 – 6.75 (m, 5H), 6.33 (t, J = 8.6 Hz, 3H), 3.27 (s, 4H), 2.44 (d, J = 7.8 Hz, 12H), 1.36 (s, 2H), 1.21 (s, 2H). **^{19}F{^{1}H} NMR** (376 MHz, Benzene-d_6) δ –107.86, –110.21, –113.91, –119.73, –137.21. **^{13}C{^{1}H} NMR** (101 MHz, Benzene-d_6) δ 143.6, 142.2, 129.9, 127.7, 120.6, 118.5, 45.2, 44.4.

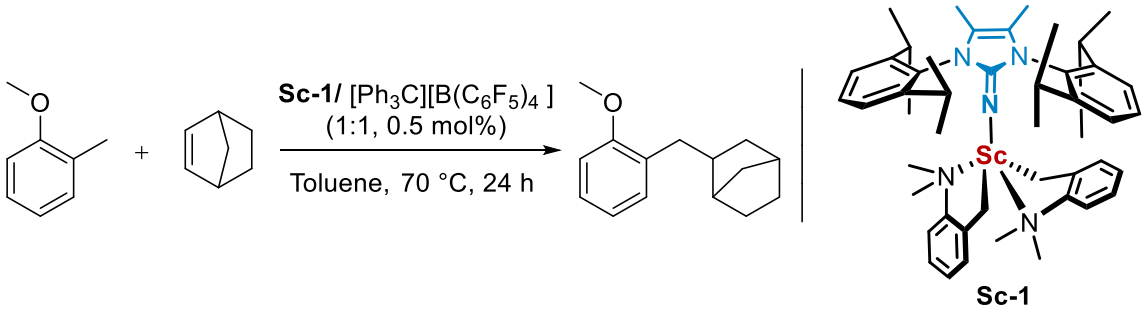
3. Typical procedure for C–H activation of anisoles and 2-methyl anisole with alkenes

3.1 General procedure for ortho C(sp^2)–H activation of anisoles with norbornene



In a glovebox, a dry reaction tube was charged with **Sc-1** (2.5 mol%, 3.7 mg) and $[Ph_3C][B(C_6F_5)_4]$ (2.5 mol%, 4.6 mg). Then, toluene (0.5 mL) was added. The resulting mixture was stirred at ambient temperature for 5 min. Anisole (21.6 mg, 0.2 mmol) and norbornene (28.2 mg, 0.3 mmol) were added. The closed tube was taken outside and heated at 50 °C for 24 h. After the tube was cooled to room temperature, all volatiles were removed under reduced pressure. The residue was subjected to column chromatography on silica gel and eluted with petroleum to afford the desired product.

3.2 General procedure for C(sp^3)–H activation of 2-methyl anisole with alkenes

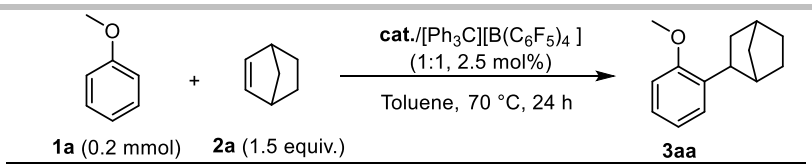


In a glovebox, a dry reaction tube was charged with **Sc-1** (0.5 mol%, 0.7 mg) and $[Ph_3C][B(C_6F_5)_4]$ (0.5 mol%, 0.9 mg). Then, 0.5 mL toluene was added under argon atmosphere. The resulting mixture was stirred at ambient temperature for 5 min. 2-Methyl anisole (24.4 mg, 0.2 mmol) and norbornene (28.2 mg, 0.3 mmol) were added successively. The closed tube was taken outside and heated at 70 °C for 24 h. After the tube was cooled to room temperature, all volatiles were removed under reduced pressure. The residue was subjected to column chromatography on silica gel and eluted with petroleum to afford the desired product.

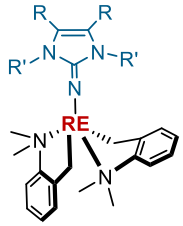
4. Optimization of the reaction conditions

4.1 Evaluation of the anisoles

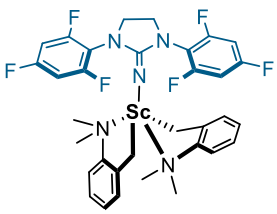
Table S1 Screening of catalysts.[a]



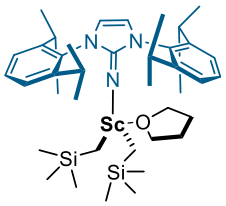
1a (0.2 mmol) **2a** (1.5 equiv.) **3aa**



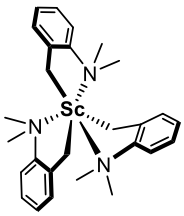
Sc-1, RE = Sc, R = Me, R' = 2,6-^{i}Pr$_2$C$_6$H$_3$
Y-1, RE = Y, R = Me, R' = 2,6-^{i}Pr$_2$C$_6$H$_3$
Gd-1, RE = Gd, R = Me, R' = 2,6-^{i}Pr$_2$C$_6$H$_3$
Lu-1, RE = Lu, R = Me, R' = 2,6-^{i}Pr$_2$C$_6$H$_3$
Sc-2, RE = Sc, R = Cl, R' = 2,6-^{i}Pr$_2$C$_6$H$_3$
Sc-3, RE = Sc, R = H, R' = 1-adamantyl
Sc-4, RE = Sc, R = H, R' = 2,4,6-Me$_3$C$_6$H$_2$



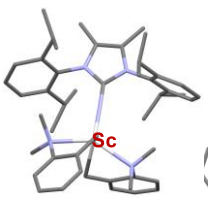
Sc-5



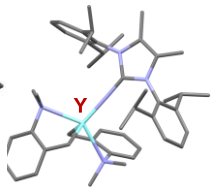
Sc-6



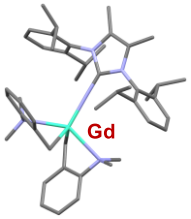
Sc-7



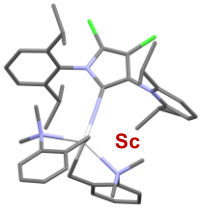
CCDC (2219242)
Sc-1



CCDC (2219245)
Y-1



CCDC (2219244)
Gd-1

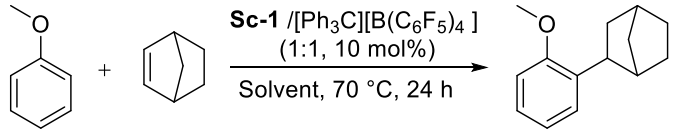


CCDC (2219243)
Sc-2

Entry	**Cat.**	Yield (%)[b]
1	**Sc-1**	**99**
2	**Y-1**	NR
3	**Gd-1**	NR
4	**Lu-1**	NR
5	**Sc-2**	**99**
6	**Sc-3**	NR
7	**Sc-4**	NR
8	**Sc-5**	NR
9	**Sc-6**	**99**
10	**Sc-7**	37

[a]Unless otherwise noted, all reactions were carried out with **Cat.**/[Ph$_3$C][B(C$_6$F$_5$)$_4$] (1:1, 10 mol%), anisole **1a** (0.20 mmol) and norbornene **2a** (0.30 mmol) at 70 °C for 24 h. [b]Yield was determined by ^{1}H NMR, with C$_2$H$_2$Br$_4$ as an internal standard.

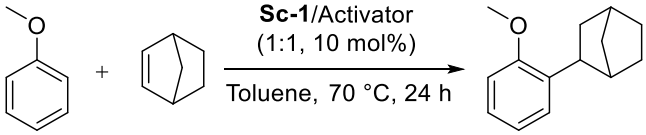
Table S2 Screening of the solvent.[a]



Entry	Solvent	Yield (%)[b]
1	**toluene**	**99**
2	benzene	80
3	THF	NR
4	cyclohexane	90
5	cyclohexane	65
6	benzotrifluoride	NR
7	*o*-xylene	80
8	*m*-xylene	92
9	*p*-xylene	92
10	*n*-hexane	86
11	*n*-pentane	95

[a]Unless otherwise noted, all reactions were carried out with **Sc-1**/$[Ph_3C][B(C_6F_5)_4]$ (1:1, 10 mol%), anisole (0.20 mmol) and norbornene (0.30 mmol) in solvent (0.5 mL) at 70 °C for 24 h. [b]Yield was determined by ^{1}H NMR, with $C_2H_2Br_4$ as an internal standard.

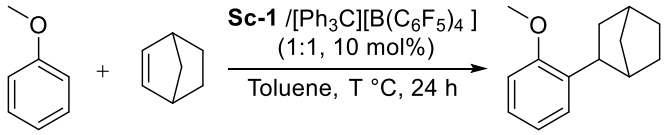
Table S3 Control experiments.[a]



Entry	**Cat**	Activator	Yield (%)[c]
1	**Sc-1**	**$[Ph_3C][B(C_6F_5)_4]$**	**99**
2[b]	**Sc-1**	$[Ph_3C][B(C_6F_5)_4]$	10
3	**-**	$[Ph_3C][B(C_6F_5)_4]$	30
4	**Sc-1**	$[PhNHMe_2][B(C_6F_5)_4]$	41
5	**Sc-1**	$B(C_6F_5)_3$	NR
6	**Sc-1**	-	NR

[a]Unless otherwise noted, all reactions were carried out with **Sc-1**/activator (1:1, 10 mol%), anisole (0.20 mmol) and norbornene (0.30 mmol) in toluene (0.5 mL) at 70 °C for 24 h. [b]**Sc-1**/$[Ph_3C][B(C_6F_5)_4]$ (1:2, 10 mol%). [c]Yield was determined by ^{1}H NMR, with $C_2H_2Br_4$ as an internal standard.

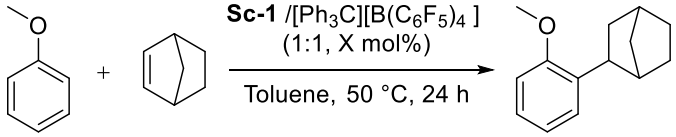
Table S4 Screening of reaction temperature.[a]



Entry	T (°C)	Yield (%)[b]
1	20	53
2	30	62
3	40	88
4	**50**	**99**
5	70	94

[a]All reactions were carried out with **Sc-1**/$[Ph_3C][B(C_6F_5)_4]$ (1:1, 10 mol%), anisole (0.20 mmol) and norbornene (0.30 mmol) in toluene (0.5 mL) at T °C for 24 h. [b]Yield was determined by ^1H NMR, with $C_2H_2Br_4$ being used as an internal standard.

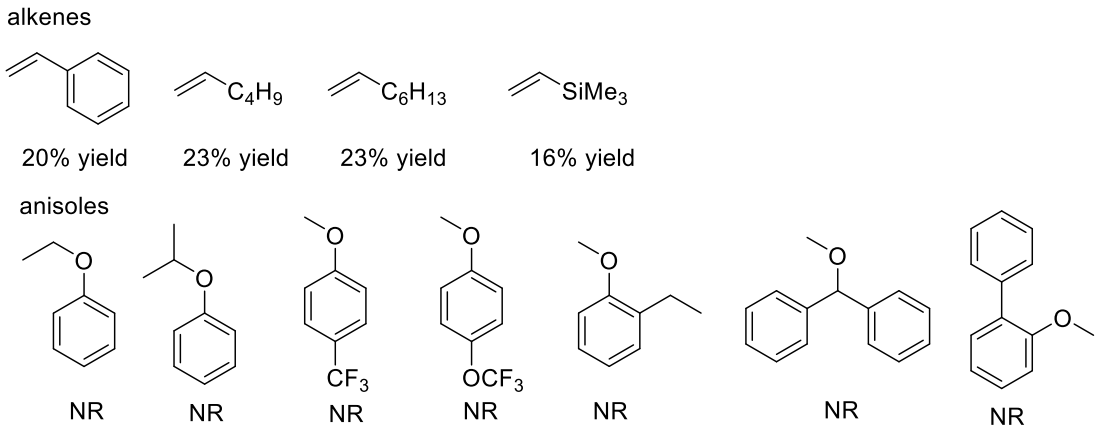
Table S5 Screening of the catalyst loading.[a]



Entry	x (mol%)	Yield (%)[b]
1	10	99
2	5	99
3	**2.5**	**99**
4	2	91
5	1	47

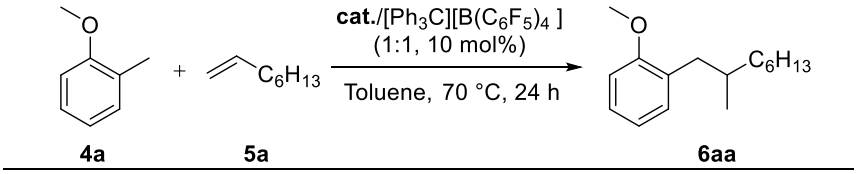
[a]All reactions were carried out with **Sc-1**/$[Ph_3C][B(C_6F_5)_4]$ (1:1, x mol%), anisole (0.20 mmol) and norbornene (0.30 mmol) in toluene (0.5 mL) at 70 °C for 24 h. [b]Yield was determined by ^1H NMR, with $C_2H_2Br_4$ as an internal standard.

Scope limitation.

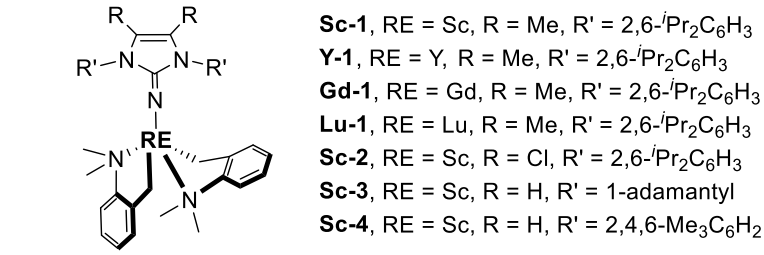


4.2 Optimization of the reaction with 2-methyl anisoles.

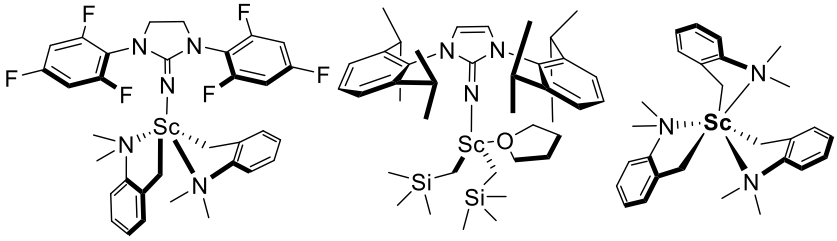
Table S6 Screening of catalysts.[a]



4a **5a** **6aa**



Sc-1, RE = Sc, R = Me, R' = 2,6-^{i}Pr$_2$C$_6$H$_3$
Y-1, RE = Y, R = Me, R' = 2,6-^{i}Pr$_2$C$_6$H$_3$
Gd-1, RE = Gd, R = Me, R' = 2,6-^{i}Pr$_2$C$_6$H$_3$
Lu-1, RE = Lu, R = Me, R' = 2,6-^{i}Pr$_2$C$_6$H$_3$
Sc-2, RE = Sc, R = Cl, R' = 2,6-^{i}Pr$_2$C$_6$H$_3$
Sc-3, RE = Sc, R = H, R' = 1-adamantyl
Sc-4, RE = Sc, R = H, R' = 2,4,6-Me$_3$C$_6$H$_2$

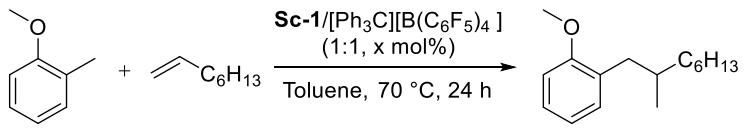


Sc-5 **Sc-6** **Sc-7**

Entry	cat.	Yield (%)[b]
1	**Sc-1**	**99**
2	**Y-1**	NR
3	**Gd-1**	NR
4	**Lu-1**	NR
5	**Sc-2**	**99**
6	**Sc-3**	NR
7	**Sc-4**	NR
8	**Sc-5**	NR
9	**Sc-6**	**99**
10	**Sc-7**	NR

[a]All reactions were carried out with **cat.**/[Ph$_3$C][B(C$_6$F$_5$)$_4$] (1:1, 10 mol%), 2-methyl anisole (0.20 mmol) and 1-octene (0.60 mmol) in toluene (0.5 mL) at 70 °C for 24 h. [b]Yield was determined by ^{1}H NMR, with $C_2H_2Br_4$ as an internal standard.

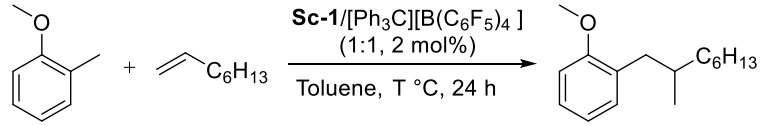
Table S7 Screening of the catalyst loading.[a]



Entry	x (mol%)	Yield (%)[b]
1	10	99
2	5	95
3	2.5	95
4	**2**	**94**
5	1	84

[a]All reactions were carried out with **Sc-1**/[Ph$_3$C][B(C$_6$F$_5$)$_4$] (1:1, x mol%), 2-methyl anisole (0.20 mmol) and 1-octene (0.60 mmol) in toluene (0.5 mL) at 70 °C for 24 h. [b]Yield was determined by 1H NMR, with $C_2H_2Br_4$ as an internal standard.

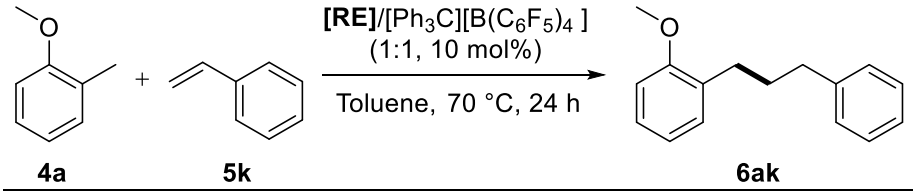
Table S8 Screening of reaction temperature.[a]



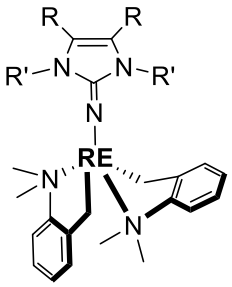
Entry	T (°C)	Yield (%)[b]
1	50	53
2	60	91
3	**70**	**94**
4	80	90
5	90	90

[a]All reactions were carried out with **Sc-1**/$[Ph_3C][B(C_6F_5)_4]$ (1:1, 2 mol%), 2-methyl anisole (0.20 mmol) and 1-octene (0.60 mmol) in toluene (0.5 mL) at T °C for 24 h. [b]Yield was determined by ^{1}H NMR, with $C_2H_2Br_4$ as an internal standard.

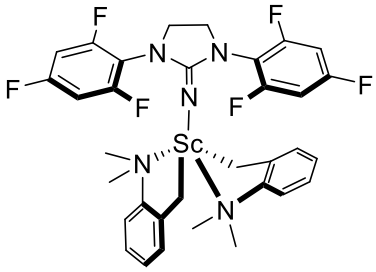
Table S9 Screening of catalysts.[a]

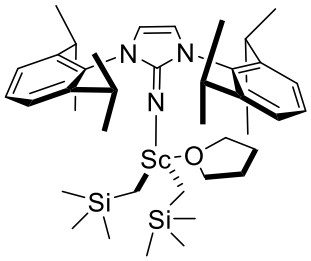


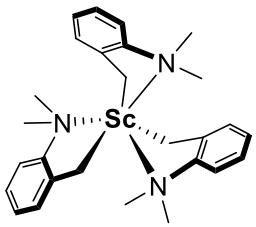
4a **5k** **6ak**



Sc-1, RE = Sc, R = Me, R' = 2,6-^{i}Pr$_2$C$_6$H$_3$
Y-1, RE = Y, R = Me, R' = 2,6-^{i}Pr$_2$C$_6$H$_3$
Gd-1, RE = Gd, R = Me, R' = 2,6-^{i}Pr$_2$C$_6$H$_3$
Lu-1, RE = Lu, R = Me, R' = 2,6-^{i}Pr$_2$C$_6$H$_3$
Sc-2, RE = Sc, R = Cl, R' = 2,6-^{i}Pr$_2$C$_6$H$_3$
Sc-3, RE = Sc, R = H, R' = 1-adamantyl
Sc-4, RE = Sc, R = H, R' = 2,4,6-Me$_3$C$_6$H$_2$





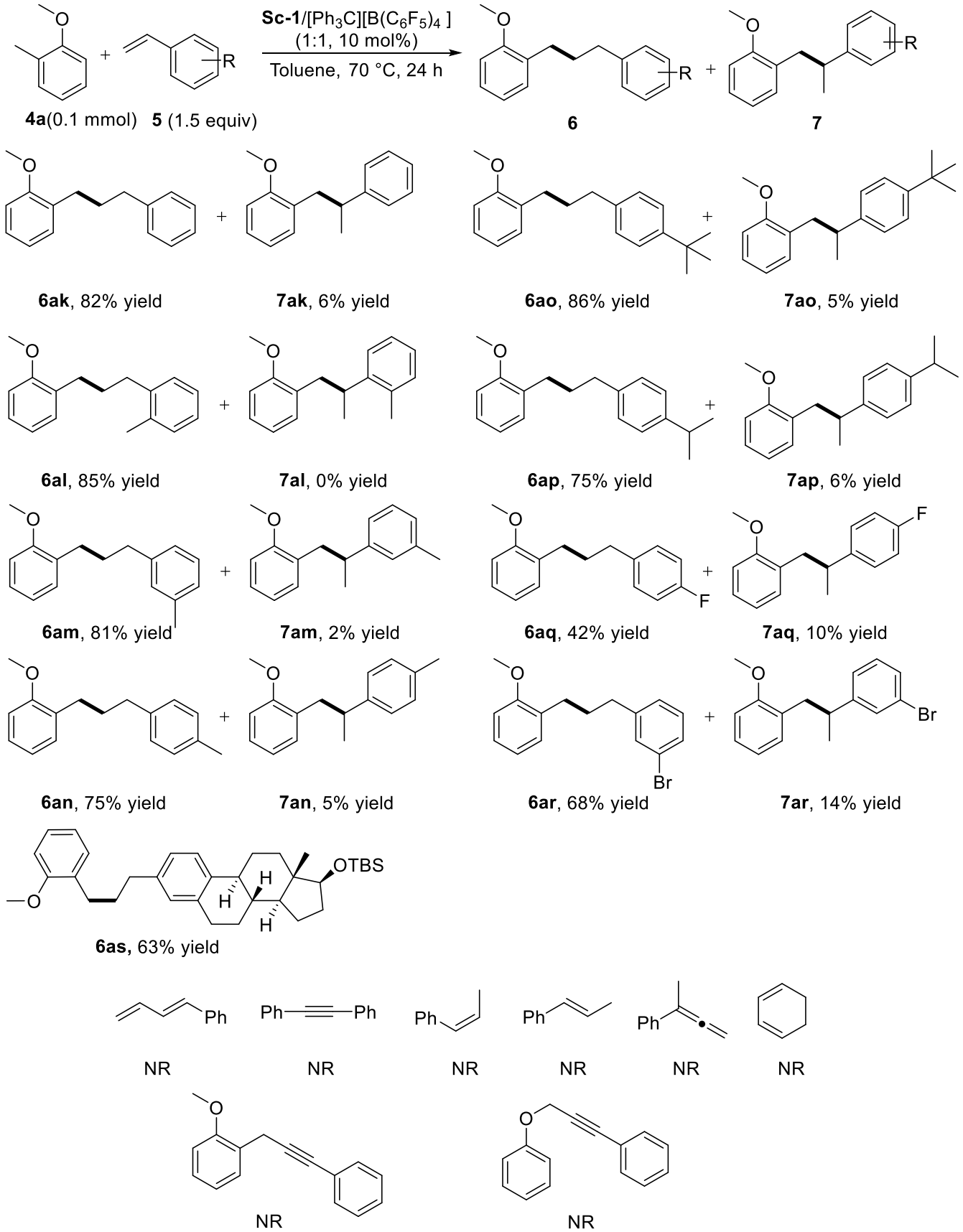


Sc-5 **Sc-6** **Sc-7**

Entry	**Cat**	Yield (%)[b]
1	**Sc-1**	**82**
2	**Y-1**	NR
3	**Gd-1**	NR
4	**Lu-1**	NR
5	**Sc-2**	45
6	**Sc-3**	NR
7	**Sc-4**	NR
8	**Sc-5**	NR
9	**Sc-6**	10
10	**Sc-7**	NR

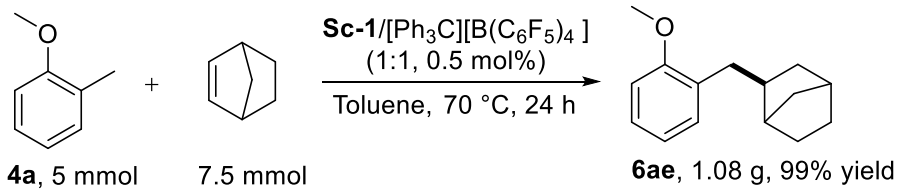
[a]All reactions were carried out with **Cat**/$[Ph_3C][B(C_6F_5)_4]$ (1:1, 10 mol%), 2-methyl anisole (0.10 mmol) and styrene (0.15 mmol) in toluene (0.5 mL) at 70 °C for 24 h. [b]Yield was determined by ^{1}H NMR, with $C_2H_2Br_4$ as an internal standard.

The substrate scope.[a]



[a]All reactions were carried out with **Sc-1**/[Ph_3C][$B(C_6F_5)_4$] (1:1, 10 mol%), 2-methyl anisole (0.1 mmol) and olefin (0.15 mmol) in toluene (0.5 mL) at 70 °C for 24 h. The branched chain product yield was determined by ^1H NMR, with $C_2H_2Br_4$ as an internal standard.

5. Experimental procedure for the scale-up reaction



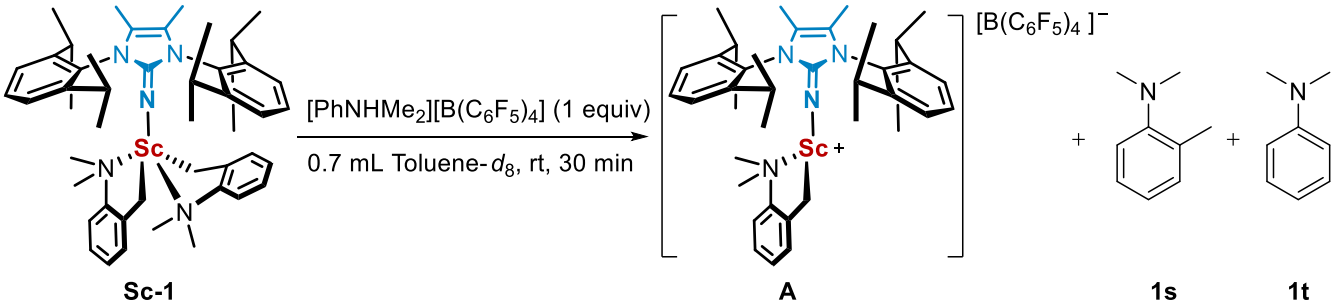
4a, 5 mmol 7.5 mmol **6ae**, 1.08 g, 99% yield

A Schlenk bottle was charged with **Sc-1**/[Ph_3C][$B(C_6F_5)_4$] (1:1, 0.5 mol%) in toluene (1 mL). The solution was stirred at room temperature for five minutes. Then, 2-methyl anisole (610.8 mg, 5.0 mmol) and norbornene (720.0 mg, 7.5 mmol) was added and the mixture was stirred at 70 °C for 24 h. After the tube was cooled to room temperature, all volatiles were removed under reduced pressure. The residue was subjected to column chromatography on silica gel and eluted with petroleum to afford desired product 1.08 g in 99% yield.

6. Control experiments

6.1 The formation of cationic intermediate monitored by ^{1}H NMR

In a glovebox, a dry reaction tube was charged with **Sc-1** (0.02 mmol, 14.9 mg) and [$PhNHMe_2$][$B(C_6F_5)_4$] (0.02 mmol, 16.0 mg). Toluene-d_8 (0.7 mL) was added under argon atmosphere. The resulting mixture was stirred at ambient temperature for 5 min. The mixture was transferred to a J. Young valve NMR tube. ^{1}H NMR analysis (Figure S1) indicated that the formation of ion-pair complex (**A**) along with *N*,*N*,2-trimethylaniline (**1s**) and *N*,*N*-dimethylaniline (**1t**). One equivalent of *N*,*N*,2-trimethylaniline (**1s**) and one equivalent of *N*,*N*-dimethyl-2-(methyl-*d*)aniline (**1s-D**) are obtained by quenching with deuterium water.



Sc-1 **A** **1s** **1t**

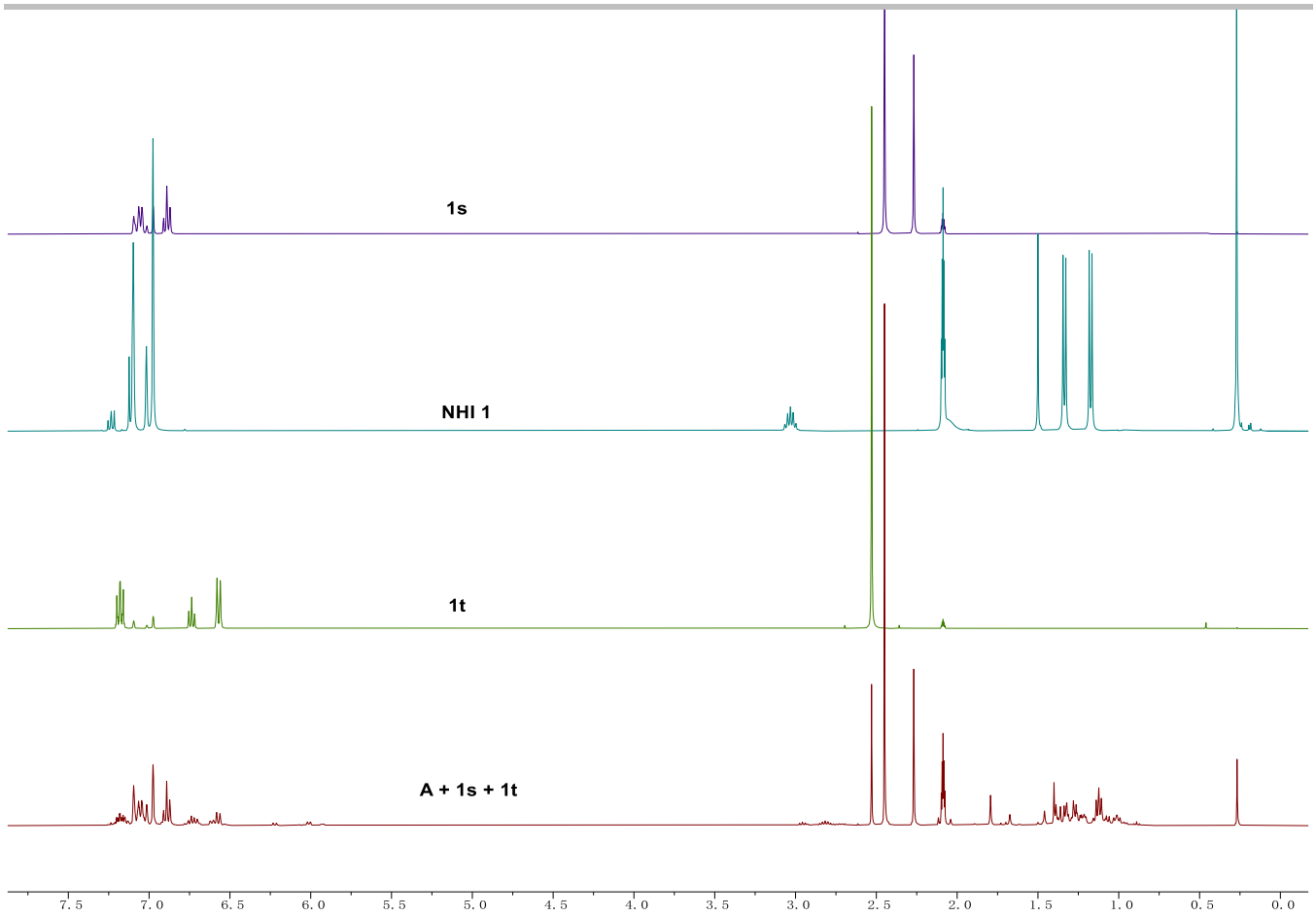


Figure S1. ^{1}H NMR spectrum (400 MHz) of **1s, A, NHI 1** and **1t** in Toluene-d_8.

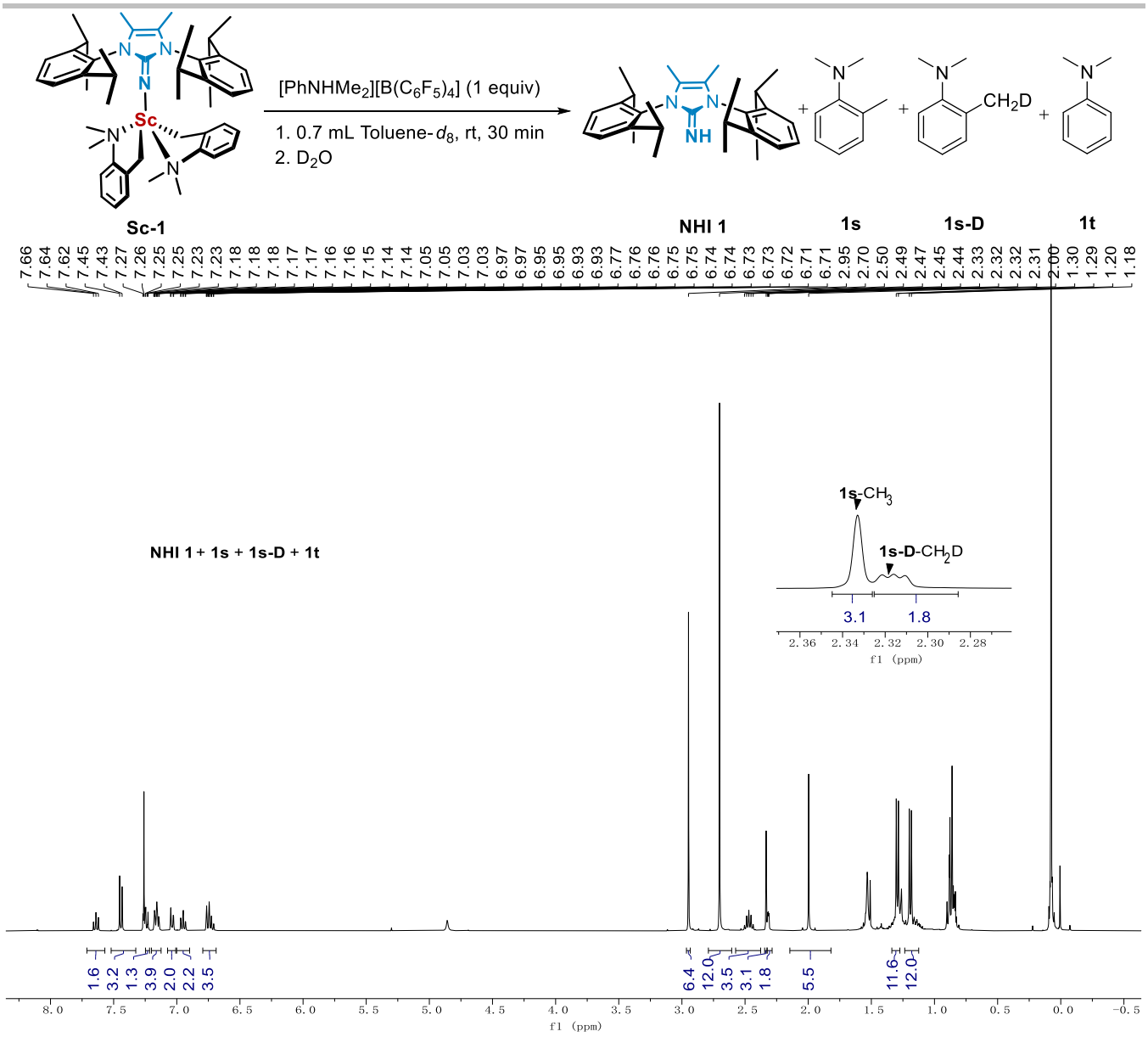
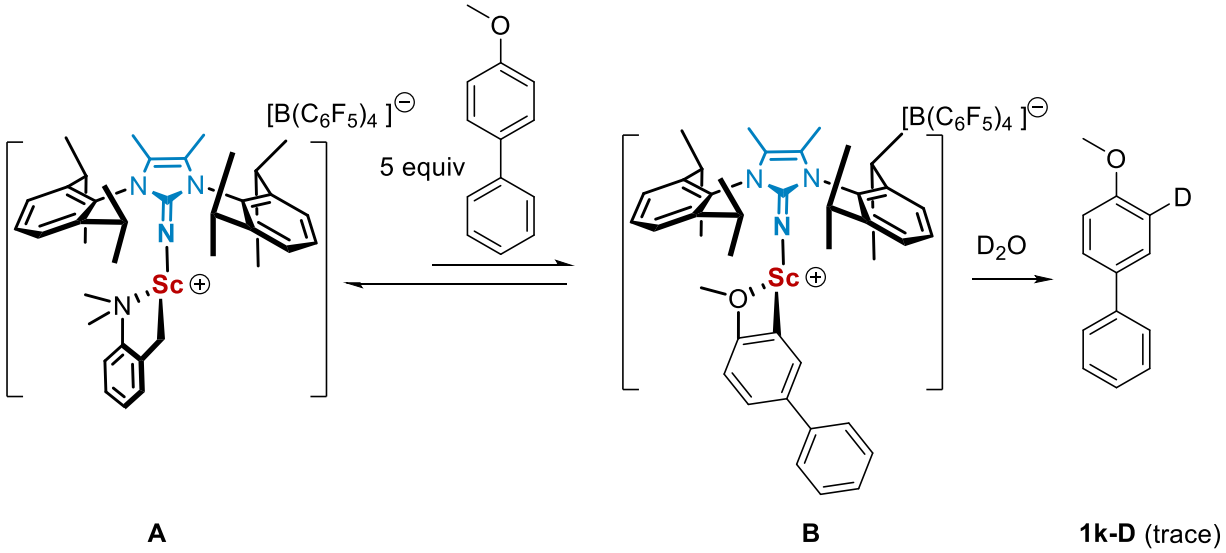


Figure S2. ^{1}H NMR spectrum (400 MHz) in $CDCl_3$.

6.2 The formation of cationic intermediate B monitored by ^{1}H NMR

In a glovebox, a dry reaction tube was charged with **Sc-1** (0.02 mmol, 14.9 mg) and $[Ph_3C][B(C_6F_5)_4]$ (0.02 mmol, 18.4 mg). Toluene-d_8 (0.7 mL) was added under argon atmosphere. The resulting mixture was stirred at ambient temperature for 5 min. 4-Methoxy-1,1'-biphenyl (**1k**, 18.4 mg, 0.10 mmol) was added and the mixture was stirred at 50 °C for 2 h. Quenched with deuterium water, high resolution mass spectra indicated that the formation of 4-methoxy-1,1'-biphenyl-3-*d* (**1k-D**). **HRMS** (ESI-TOF) calcd for $C_{13}H_{12}ONa^+$ ([M]+Na^+) = 208. 0843, found 208.0847.



A **B** **1k-D** (trace)

6.3 Intramolecular KIE Experiments

In a glovebox, a dry reaction tube was charged with **Sc-1** (2.5 mol%, 3.7 mg) and $[Ph_3C][B(C_6F_5)_4]$ (2.5 mol%, 4.6 mg). Then, 0.5 mL toluene was added under argon atmosphere. The resulting mixture was stirred at ambient temperature for 5 min. Then, 4-methyl[2-D]anisole (24.6 mg, 0.20 mmol) and norbornene (28.2 mg, 0.30 mmol) were added to the mixture subsequently The closed tube was taken outside and heated at 50 °C for 24 h. After the tube was cooled to room temperature, all volatiles were removed under reduced pressure. The residue was subjected to column chromatography on silica gel and eluted with petroleum to afford desired product (36.5 mg, 0.17 mmol) in 84% yield. The KIE value was determined to be 5.2 by analysis of its ^{1}H NMR spectrum (Figure S3).

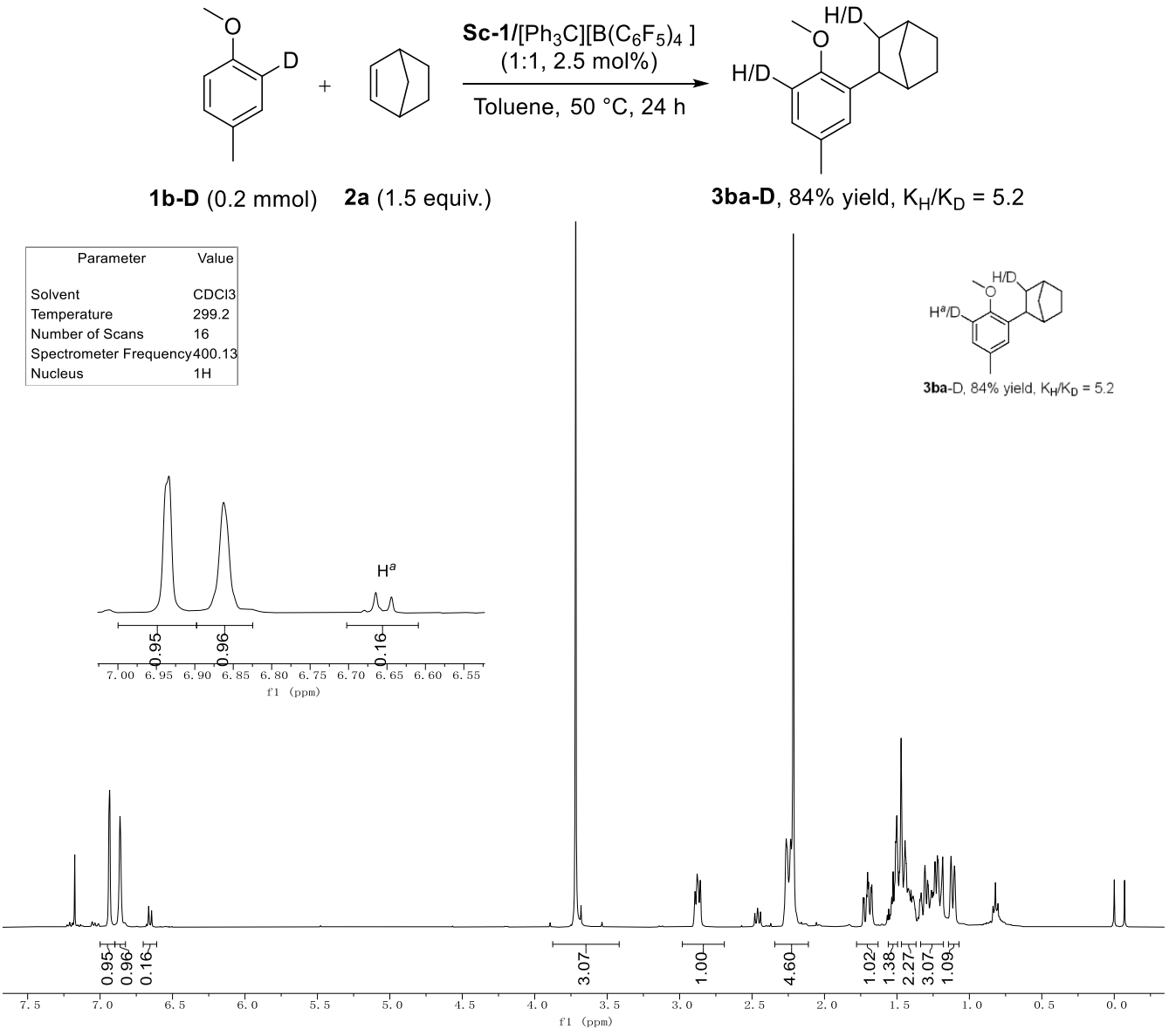


Figure S3. ^{1}H NMR spectrum (400 MHz) in $CDCl_3$.

In a glovebox, a dry reaction tube was charged with **Sc-1** (2.5 mol%, 3.7 mg) and $[Ph_3C][B(C_6F_5)_4]$ (2.5 mol%, 4.6 mg). Then, 0.5 mL toluene was added under argon atmosphere. The resulting mixture was stirred at ambient temperature for 5 min. Then 4-methyl[2-D]anisole (24.6 mg, 0.20 mmol) and norbornene (28.2 mg, 0.30 mmol) were added to the mixture subsequently. The closed tube was taken outside and heated at 50 °C for 90 min. After the tube was cooled to room temperature, all volatiles were removed under reduced pressure. The residue was subjected to column chromatography on silica gel and eluted with petroleum to afford desired product (12.6 mg, 0.06 mmol) in 29% yield. The KIE value was determined as 3.5 by analysis of its ^{1}H NMR spectrum (Figure S4).

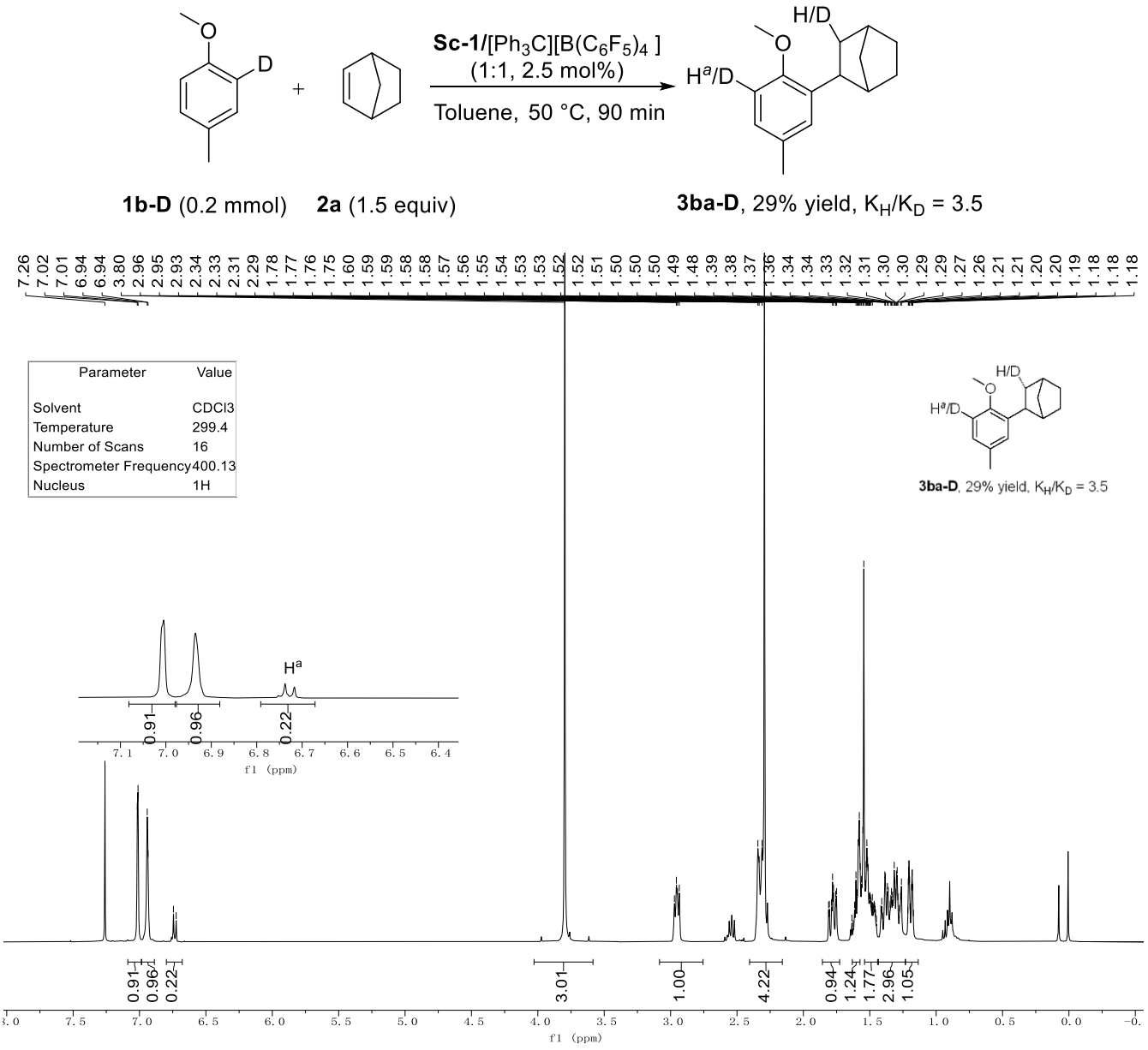


Figure S4. ^{1}H NMR spectrum (400 MHz) in $CDCl_3$.

6.4 Intermolecular KIE Experiments

In a glovebox, a dry reaction tube was charged with **Sc-1** (2.5 mol%, 3.7 mg) and $[Ph_3C][B(C_6F_5)_4]$ (2.5 mol%, 4.6 mg). Then, 0.5 mL toluene was added under argon atmosphere. The resulting mixture was stirred at ambient temperature for 5 min. Then 2-methyl anisole (12.2 mg, 0.10 mmol), 1-methoxy-2-(methyl-d_3) benzene (12.5 mg, 0.1 mmol) and norbornene (28.2 mg, 0.30 mmol) were added to the mixture successively. The closed tube was taken outside and heated at 40 °C for 0.5 h. After the tube was cooled to room temperature, all volatiles were removed under reduced pressure. The residue was subjected to column chromatography on silica gel and eluted with petroleum to afford desired product (10.8 mg, 0.05 mmol) in 27% yield. The KIE value was determined as 4.5 by analysis of its ^{1}H NMR spectrum (Figure S5).

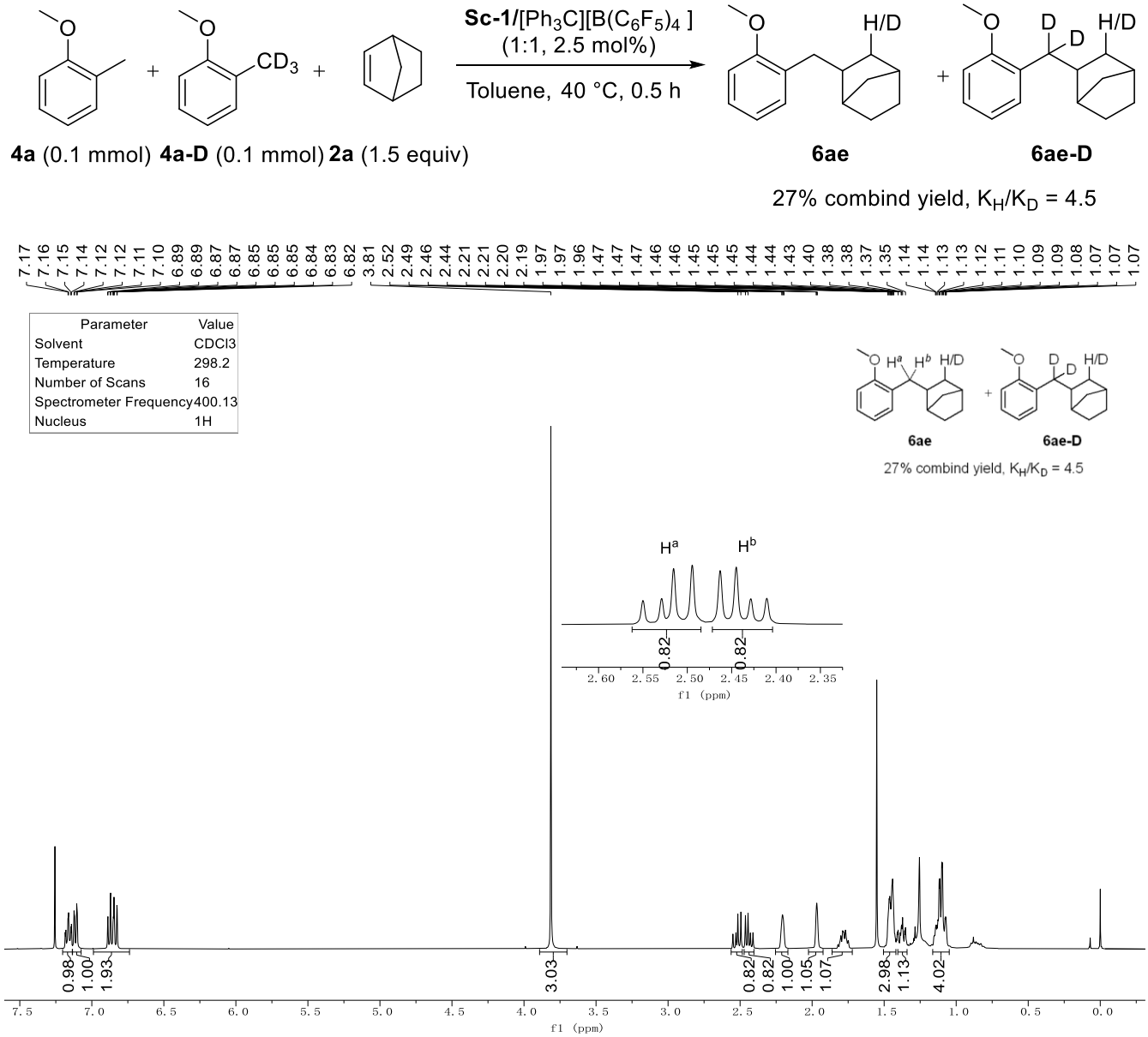


Figure S5. ^{1}H NMR spectrum (400 MHz) in $CDCl_3$.

A Schlenk bottle was charged with **Sc-1**/[Ph_3C][$B(C_6F_5)_4$] (1:1, 2 mol%), toluene (0.5 mL) was added. The resulting mixture was stirred at ambient temperature for 5 min. Then, 2-methyl anisole (12.2 mg, 0.10 mmol), 1-methoxy-2-(methyl-d_3)benzene (12.5 mg, 0.10 mmol) and 1-octene (33.66 mg, 0.30 mmol) was added and the mixture was stirred at 70 °C for 2 h. After the tube was cooled to room temperature, all volatiles were removed under reduced pressure. The residue was subjected to column chromatography on silica gel and eluted with petroleum to afford desired product (14 mg, 0.06 mmol) in 29% yield. The KIE value was determined as 5.7 by analysis of its ^{1}H NMR spectrum (Figure S6).

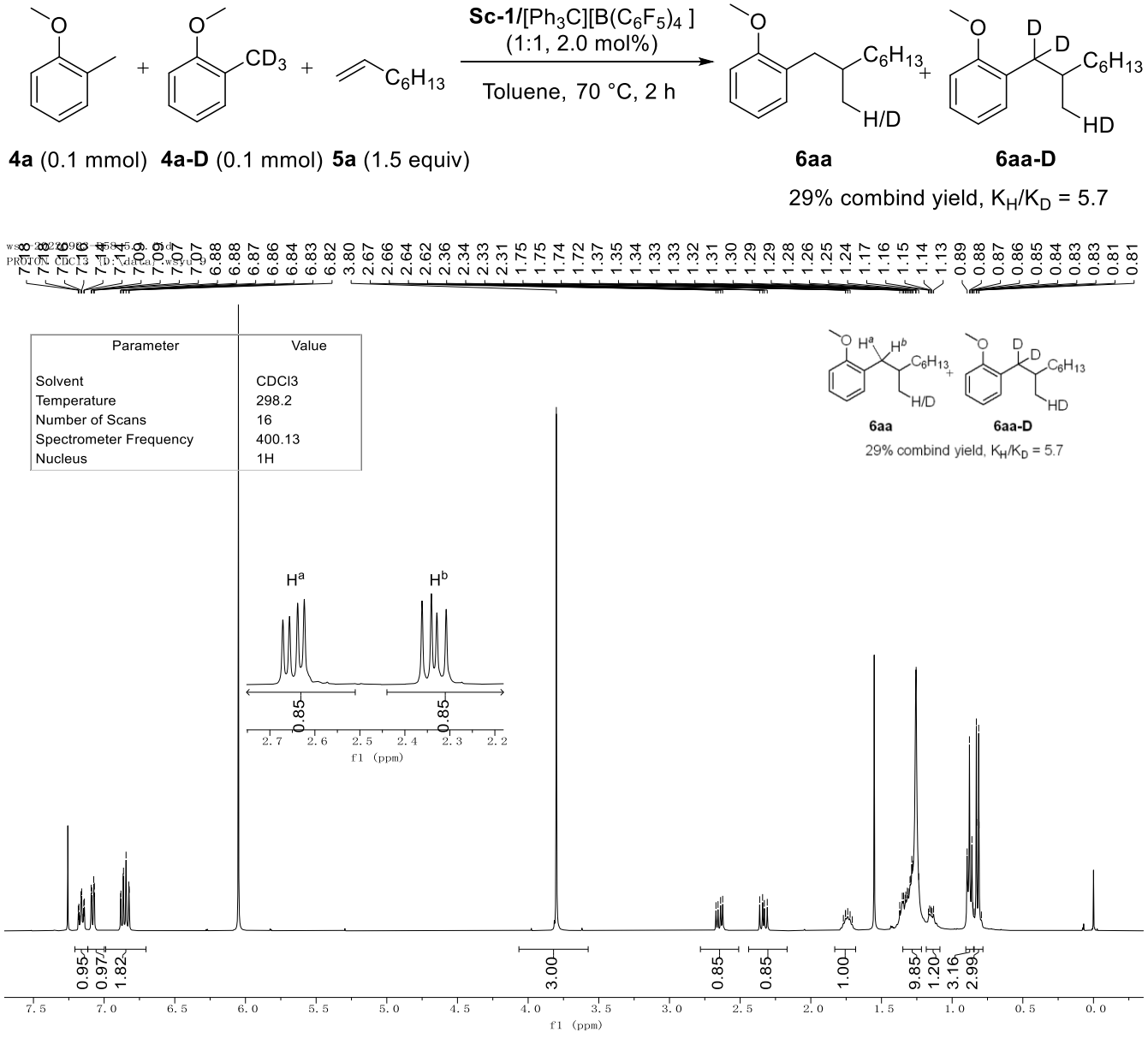
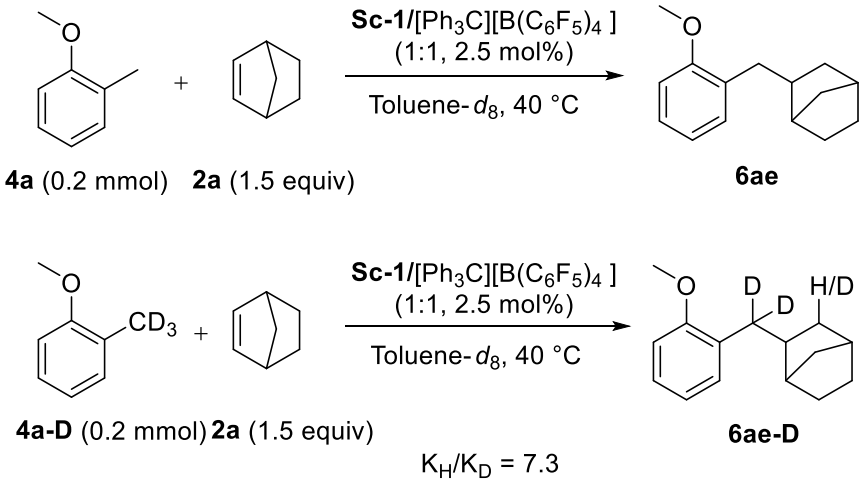


Figure S6. ^{1}H NMR spectrum (400 MHz) in $CDCl_3$.

In a glovebox, a dry reaction tube was charged with **Sc-1** (2.5 mol%, 3.7 mg) and [Ph_3C][$B(C_6F_5)_4$] (2.5 mol%, 4.6 mg). Toluene-d_8 (0.7 mL) was added under argon atmosphere. The resulting mixture was stirred at ambient temperature for 5 min. 2-Methyl anisole (24.4 mg, 0.20 mmol) or 1-methoxy-2-(methyl-d_3)benzene (25.0 mg, 0.20 mmol) and norbornene (28.2 mg, 0.30 mmol) were added to the mixture successively, then the mixture was transferred to a J. Young valve NMR tube. The closed NMR tube was taken outside and heated at 40 °C and was monitored by an NMR spectrometer. The yield was determined on the signal of OMe in the product based on **4a** and **4a-D**. A KIE value of 7.3 was found in these side-by-side reactions. These results suggest that the C–H activation of 2-methyl anisole was involved in the rate-determining step.



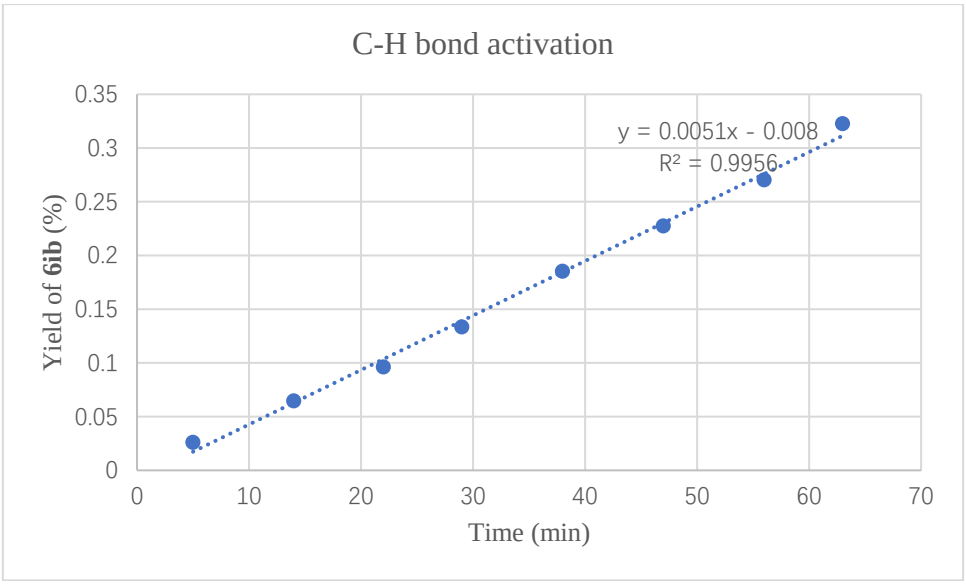


Figure S7. C–H bond activation of **4a** in C–H alkylation of **4a** with **2a**.

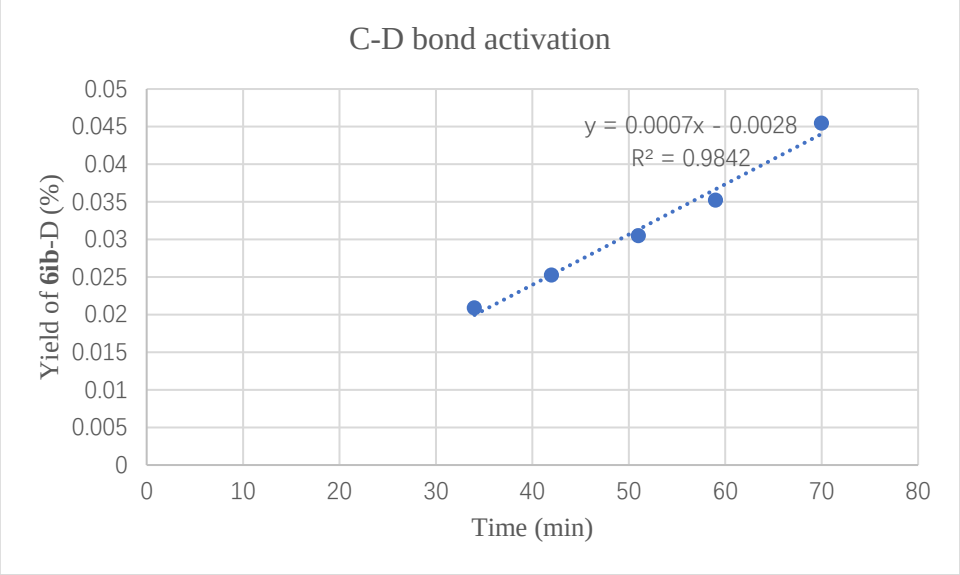
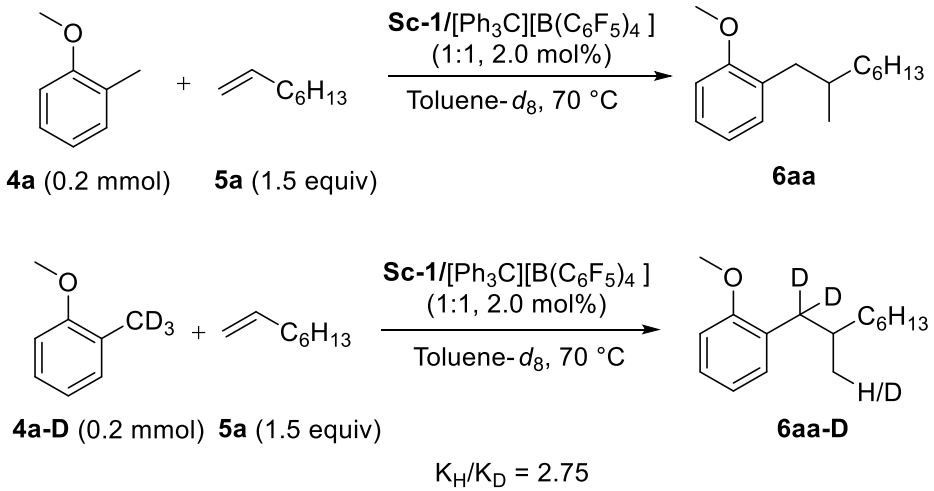


Figure S8. C–H bond activation of **4a-D** in C–H alkylation of **4a-D** with **2a**.

In a glovebox, a dry reaction tube was charged with **Sc-1** (2.0 mol%, 3.0 mg) and $[Ph_3C][B(C_6F_5)_4]$ (2.0 mol%, 3.7 mg). Toluene-d_8 (0.7 mL) was added under argon atmosphere. The resulting mixture was stirred at ambient temperature for 5 min. 2-Methyl anisole (24.4 mg, 0.20 mmol) or 1-methoxy-2-(methyl-d_3)benzene (25.0 mg, 0.20 mmol) and the 1-octene (33.66 mg, 0.30 mmol) were added, then the mixture was transferred to a J. Young valve NMR tube. The closed NMR tube was taken outside and heated at 70 °C and was monitored by an NMR spectrometer. The yield was determined on the signal of OMe in the product based on **4a** and **4a-D**. A KIE value of 2.75 was found in these side-by-side reactions. These results suggest that the C–H activation of 2-methyl anisole was probably involved in the rate-determining step.



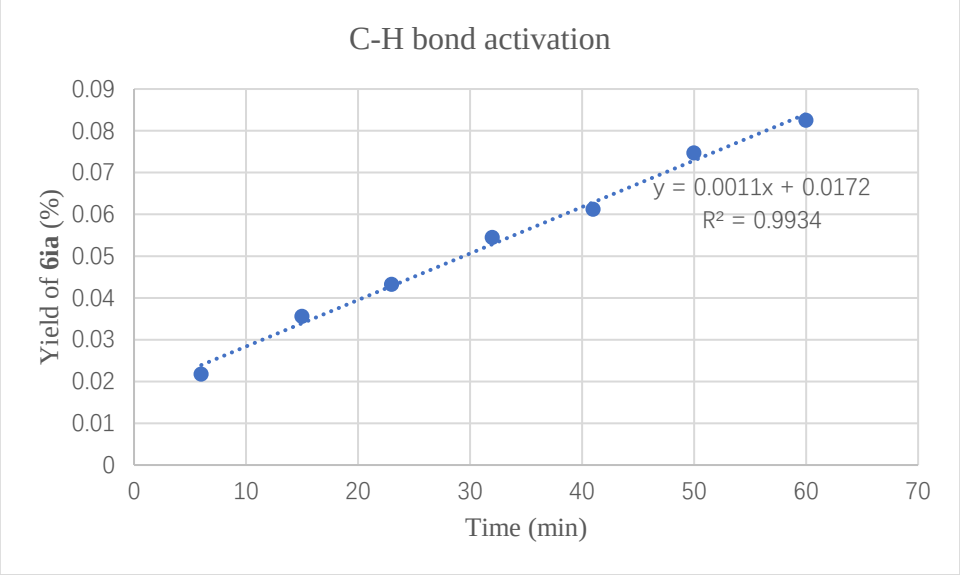


Figure S9. C–H bond activation of **4a** in C–H alkylation of **4a** with **5a**.

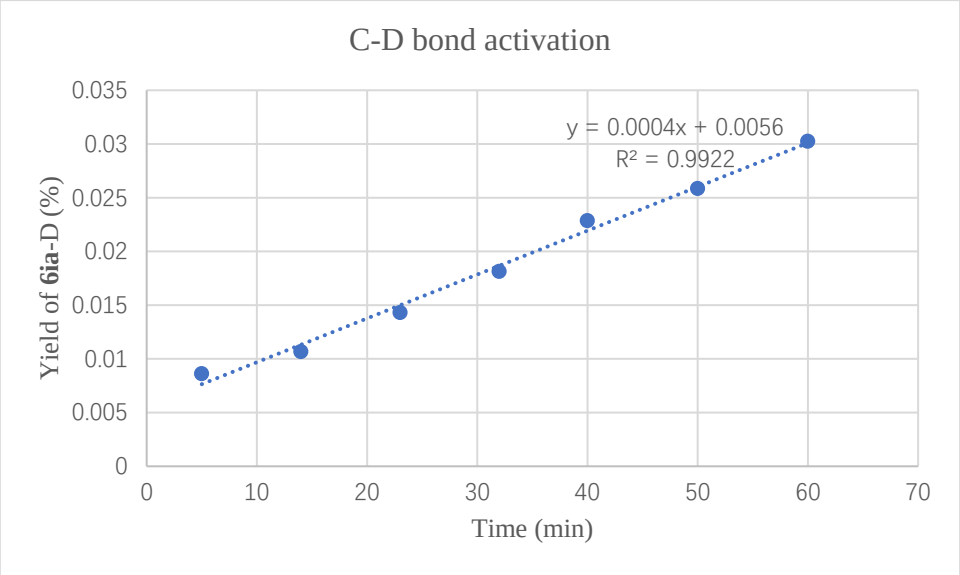
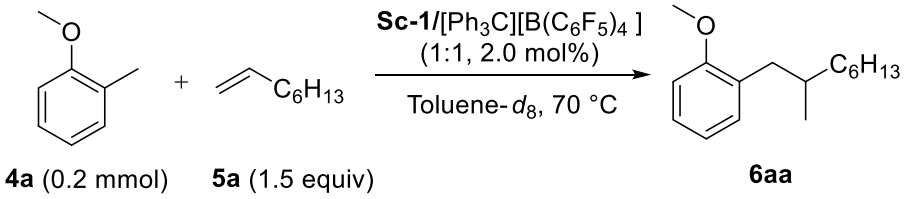


Figure S10. C–D bond activation of **4a-D** in C–H alkylation of **4a-D** with **5a**.

6.5 Kinetic Studies

In a glovebox, a dry reaction tube was charged with **Sc-1** (2.0 mol%, 3.0 mg) and [Ph_3C][$B(C_6F_5)_4$] (2.0 mol%, 3.7 mg). Toluene-d_8 (0.7 mL) was added under argon atmosphere. The resulting mixture was stirred at ambient temperature for 5 min. 2-Methyl anisole (0.10 mmol, 0.20 mmol, 0.40 mmol, 0.60 mmol) and 1-octene (33.7 mg, 0.30 mmol) were added to the mixture successively, then the mixture was transferred to a J. Young valve NMR tube. The closed NMR tube was taken outside and heated at 70 °C and was monitored by an NMR spectrometer. The yield was determined on the signal of OMe in the product based on **4a**. As depicted in Figure S12, a linear correlation was found between ln(rate) and ln[**4a**] and the slope was determined to be 0.96, indicating that the reaction order in **4a** is 1.



4a (0.2 mmol) **5a** (1.5 equiv) **6aa**

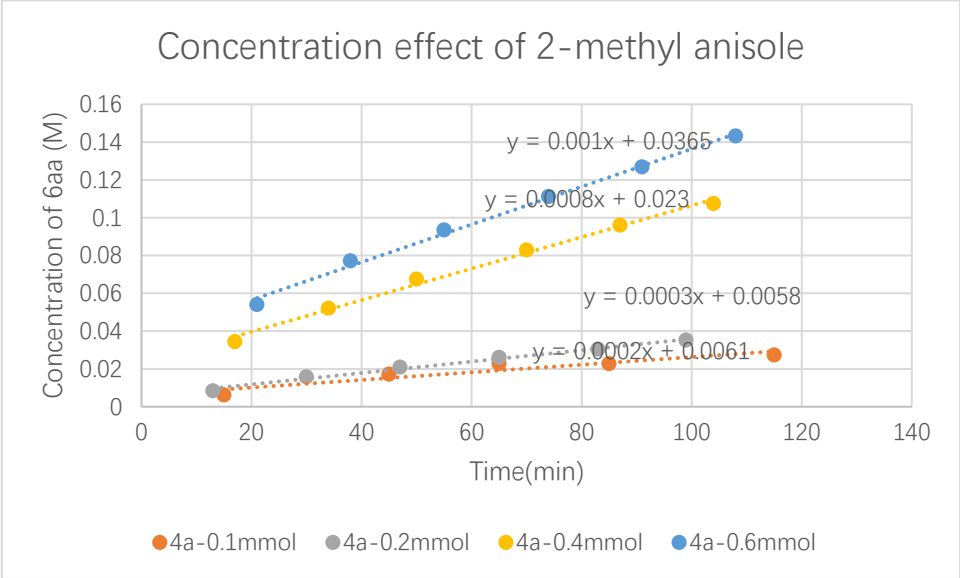


Figure S11. Concentration effect of **4a** in C–H alkylation of **4a** with **5a**.

Table S10 Concentration effect of **4a** in C–H alkylation of **4a** with **5a**

Concentration of **4a**/M	Reaction Rate/M·min^{-1}	ln(**4a**)	ln(rate)
0.14285	0.00020	1.94596	-8.51719
0.28571	0.00030	-1.25277	-8.11173
0.57143	0.00083	-0.55961	-7.09408
1.14286	0.00100	0.13353	-6.90775

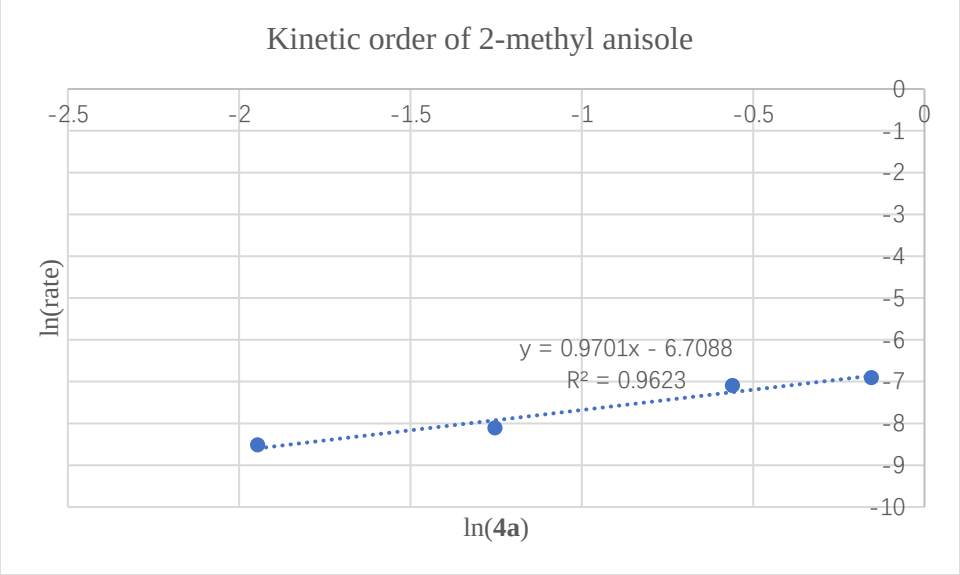


Figure S12. Kinetic order of **4a** in C–H alkylation of **4a** with **5a**.

In a glovebox, a dry reaction tube was charged with **Sc-1** (2.0 mol%, 3.0 mg) and $[Ph_3C][B(C_6F_5)_4]$ (2.0 mol%, 3.7 mg). Toluene-d_8 (0.7 mL) was added under argon atmosphere. The resulting mixture was stirred at ambient temperature for 5 min. 2-Methyl anisole (24.4 mg, 0.20 mmol) and 1-octene (0.10 mmol, 0.20 mmol, 0.30 mmol, 0.40 mmol) were added, then the mixture was transferred to a J. Young valve NMR tube. The closed NMR tube was taken outside and heated at 70 °C and was monitored by an NMR spectrometer. The yield was determined on the signal of OMe in the product based on **4a**. As depicted in Figure S14, a linear correlation was found between ln(rate) and ln[**5a**] and the slope was determined to be 0.75, indicating that the reaction order in **5a** is 1.

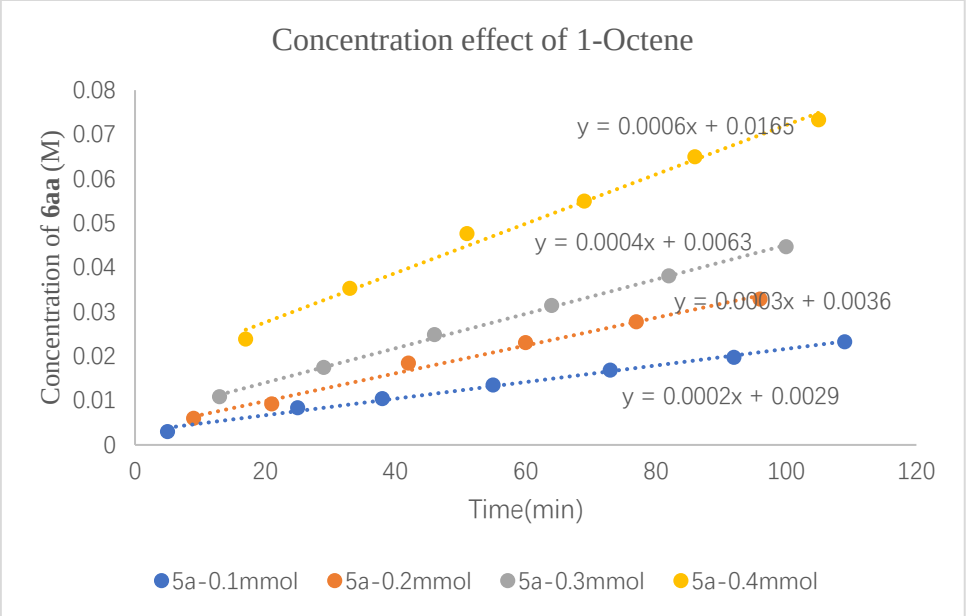


Figure S13. Concentration effect of **5a** in C–H alkylation of **4a** with **5a**.

Table S11 Concentration effect of **5a** in C–H alkylation of **4a** with **5a**

Concentration of **5a**/M	Reaction Rate/M·min^{-1}	ln(**5a**)	ln(rate)
0.14285	0.00019	-1.94596	-8.56849
0.28571	0.00031	-1.25277	-8.07894
0.42857	0.00039	-0.84730	-7.84936
0.57143	0.00056	-0.55961	-7.48757

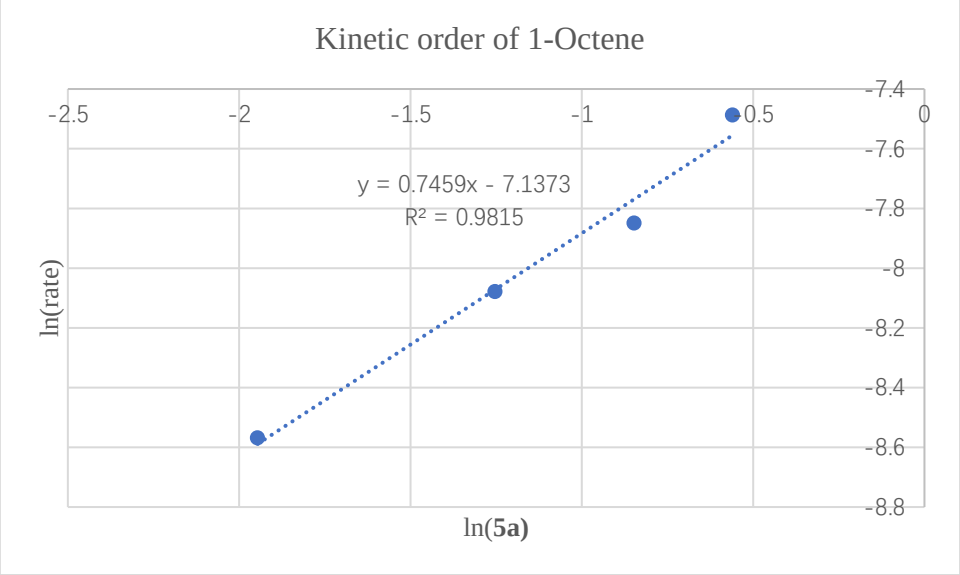


Figure S14. Kinetic order of **5a** in C–H alkylation of **4a** with **5a**.

In a glovebox, a dry reaction tube was charged with **Sc-1** (1.0 mol%, 2.0 mol%, 4.0 mol%) and $[Ph_3C][B(C_6F_5)_4]$ (1.0 mol%, 2.0 mol%, 4.0 mol%). Then, toluene-d_8 (0.7 mL) was added under argon atmosphere. The resulting mixture was stirred at ambient temperature for 5 min. 2-Methyl anisole (24.4 mg, 0.20 mmol) and 1-octene (33.7 mg, 0.30 mmol) were added, then the mixture was transferred to a J. Young valve NMR tube. The closed NMR tube was taken outside and heated at 70 °C and was monitored by an NMR spectrometer. The yield was determined on the signal of OMe in the product based on **4a**. As depicted in Figure S16, a linear correlation was found between ln(rate) and ln[**Cat**] and the slope was determined to be 0.63, indicating that the reaction order in **Sc-1** is 1.

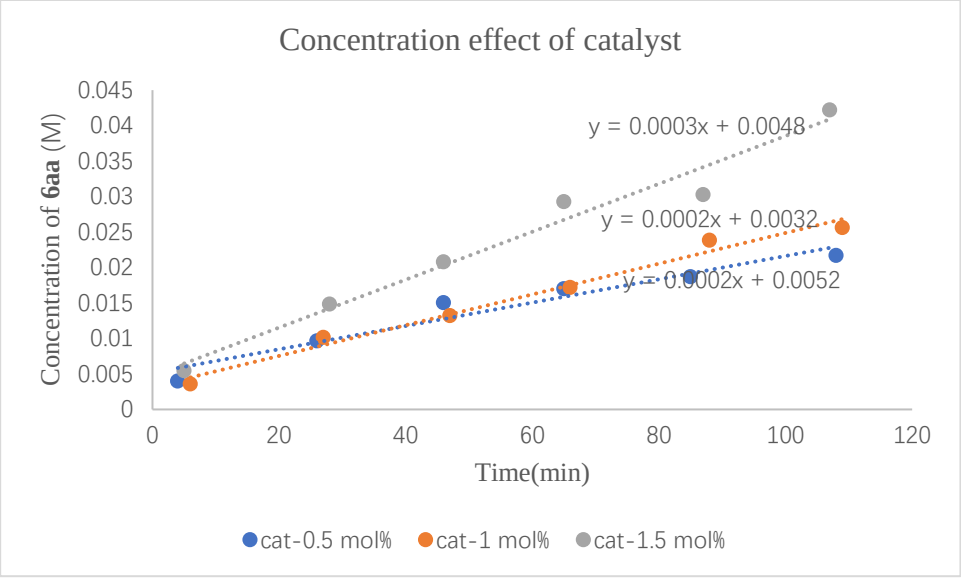


Figure S15. Concentration effect of catalyst in C–H alkylation of **4a** with **5a**.

Table S12 Concentration effect of catalyst in C–H alkylation of **4a** with **5a**.

Concentration of **cat**/M	Reaction Rate/M·min^{-1}	ln(**cat**)	ln(rate)
0.001429	0.00016	-6.55078	-8.71320
0.002857	0.00022	-5.85798	-8.43746
0.004286	0.00034	-5.45240	-7.99395

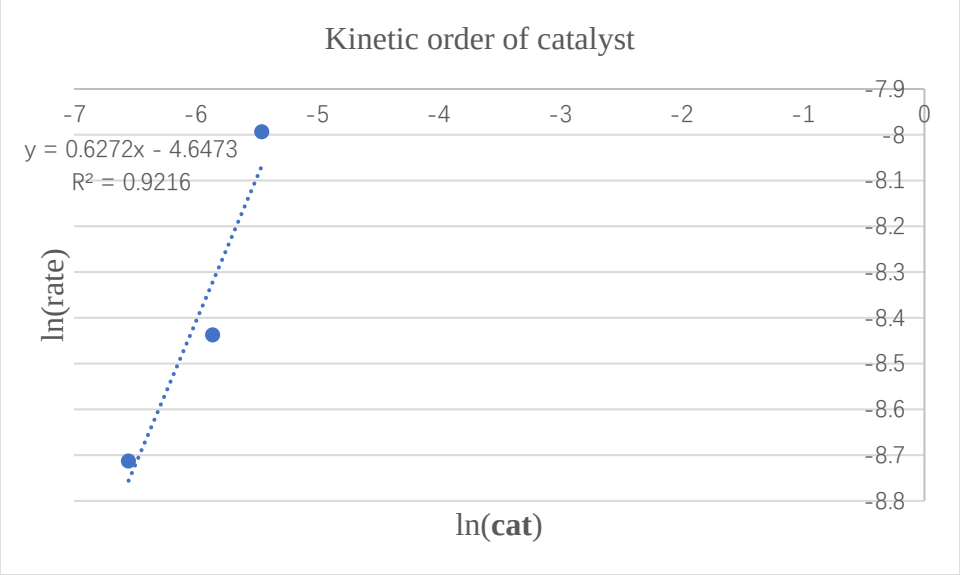
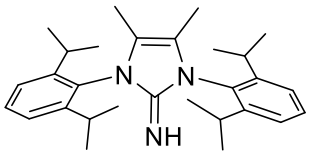


Figure S16. Kinetic order of catalyst in C–H alkylation of **4a** with **5a**.

7. X-ray crystallography data

7.1 Determination of the structure of imidazolin-2-imine NHI 1 by X-ray crystallography



NHI 1

Crystals of **NHI 1** for the X-ray crystal structure analysis were obtained from a concentrated solution of **NHI 1** in methyl alcohol and diethyl ether at room temperature. The colourless crystal in block-shape, with approximate dimensions of 0.098 × 0.212 × 0.473 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2) K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package[8]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[9]. The crystal data and further details are listed in Table S13. CCDC 2219241 which contains the crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK, which can be obtained free of charge via Fax: +44 (0)1223 336033; E-Mail: deposit@ccdc.cam.ac.uk, https://www.ccdc.cam.ac.uk/structures/.

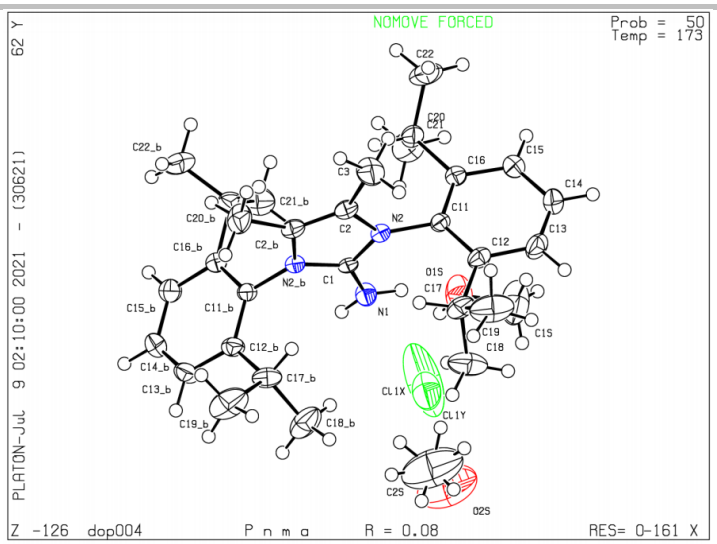


Figure S17. The thermal ellipsoid figure of **NHI 1** with 50% probabilities.

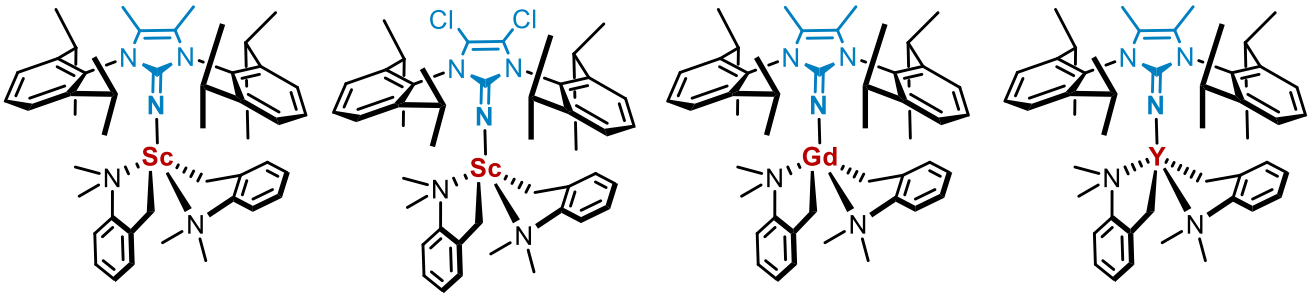
Table S13 Crystallographic Data for $C_{29}H_{41}N_3$.

Formula	$C_{29}H_{41}N_3$
Formula mass (amu)	431.33
Space group	P n m a
a (Å)	16.6840 (5)
b (Å)	19.1264 (5)
c (Å)	10.7020 (3)
α (deg)	90
β (deg)	90
γ (deg)	90
V (Å^3)	3415.06 (17)
Z	4
λ (Å)	1.54178
T (K)	173
ρ_{calcd} (g cm^{-3})	1.097
μ (mm^{-1})	1.240
Transmission factors	0.513–1.000
θ_{max} (deg)	68.285
No. of unique data, including $F_o^2 < 0$	3200
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	2703
No. of variables	209
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0800
$R_w(F_o^2)$ [b]	0.2029
Goodness of fit	1.062

[a] $R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.

[b] $R_w(F_o^2) = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

7.2 Determination of the structure of rare earth metals complexes by X-ray crystallography



Sc-1 **Sc-2** **Gd-1** **Y-1**

Crystals of **Sc-1** for the X-ray crystal structure analysis were obtained from a concentrated solution of **Sc-1** in hexane at room temperature. The colorless crystal in block-shape, with approximate dimensions of 0.208 × 0.340 × 0.659 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Mo radiation source (Kα = 0.71073Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package[8]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[9]. The crystal data and further details are listed in Table S14. CCDC 2219242 which contains the crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK, which can be obtained free of charge via Fax: +44 (0)1223 336033; E-Mail: deposit@ccdc.cam.ac.uk, https://www.ccdc.cam.ac.uk/structures/.

Crystals of **Sc-2** for the X-ray crystal structure analysis were obtained from a concentrated solution of **Sc-2** in hexane at room temperature. The yellow crystal in block-shape, with approximate dimensions of 0.126 × 0.198 × 0.347 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Cu radiation source (Kα = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package[8]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[9]. The crystal data and further details are listed in Table S14. CCDC 2219243 which contains the crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK, which can be obtained free of charge via Fax: +44 (0)1223 336033; E-Mail: deposit@ccdc.cam.ac.uk, https://www.ccdc.cam.ac.uk/structures/.

Crystals of **Gd-1** for the X-ray crystal structure analysis were obtained from a concentrated solution of **Gd-1** in hexane at room temperature. The yellow crystal in block-shape, with approximate dimensions of 0.171 × 0.210 × 0.241 mm3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Mo radiation source (Kα = 0.71073Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package[8]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[9]. The crystal data and further details are listed in Table S14. CCDC 2219244 which contains the crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK, which can be obtained free of charge via Fax: +44 (0)1223 336033; E-Mail: deposit@ccdc.cam.ac.uk, https://www.ccdc.cam.ac.uk/structures/.

Crystals of **Y-1** for the X-ray crystal structure analysis were obtained from a concentrated solution of **Y-1** in hexane at room temperature. The yellow crystal in block-shape, with approximate dimensions of 0.177 × 0.201 × 0.347 mm3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Mo radiation source (Kα = 0.71073Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package[8]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[9]. The crystal data and further details are listed in Table S14. CCDC 2219245 which contains the crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK, which can be obtained free of charge via Fax: +44 (0)1223 336033; E-Mail: deposit@ccdc.cam.ac.uk, https://www.ccdc.cam.ac.uk/structures/.

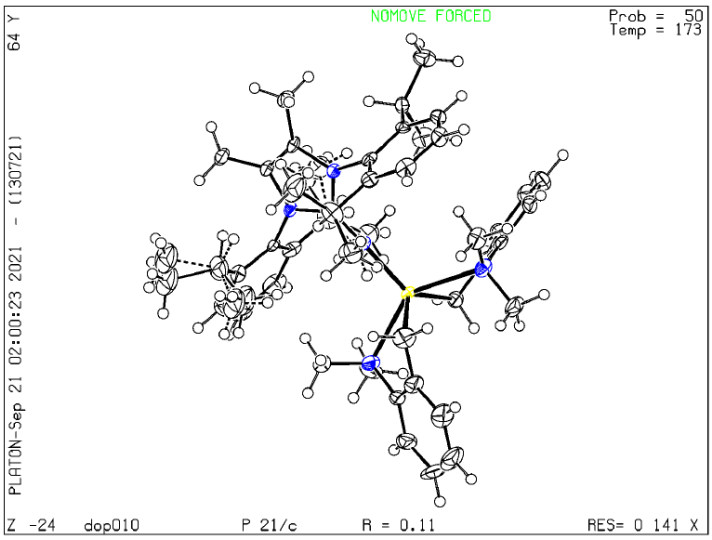


Figure S18. The thermal ellipsoid figure of **Sc-1** with 50% probabilities.

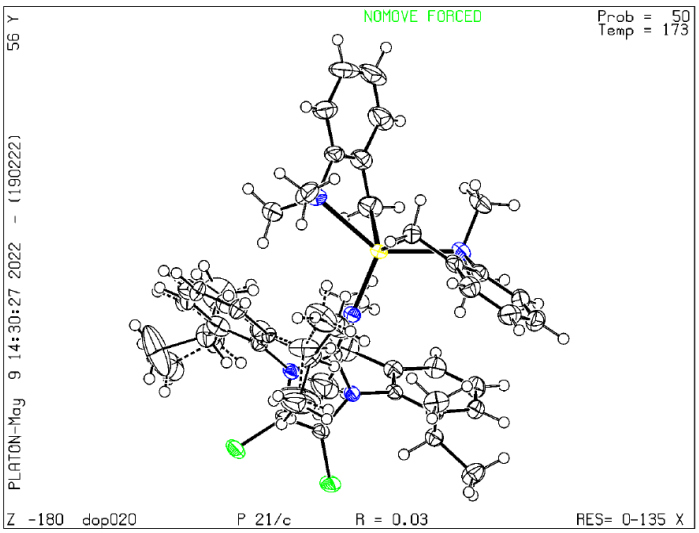


Figure S19. The thermal ellipsoid figure of **Sc-2** with 50% probabilities.

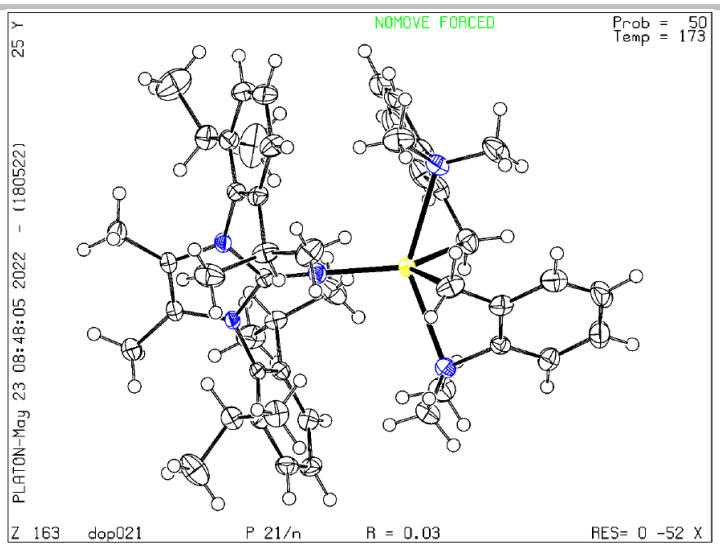


Figure S20. The thermal ellipsoid figure of **Gd-1** with 50% probabilities.

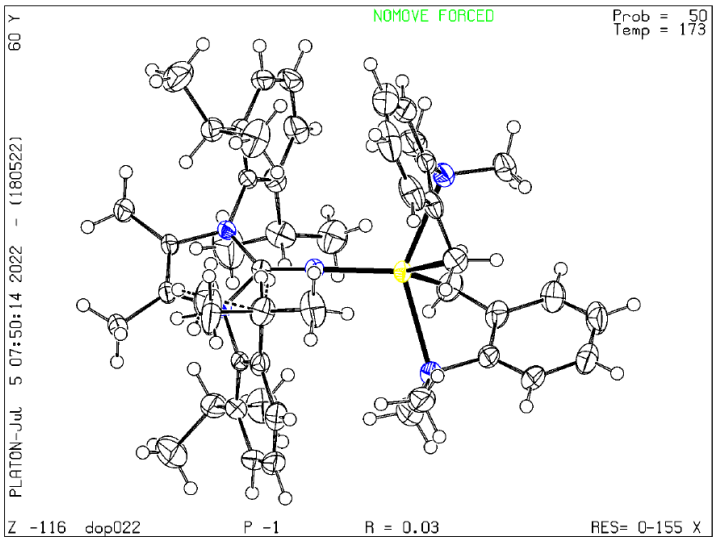


Figure S21. The thermal ellipsoid figure of **Y-1** with 50% probabilities.

Table S14 Crystallographic Data for rare earth metals complexes

Formula	$C_{47}H_{64}N_5Sc$	$C_{45}H_{58}Cl_2N_5Sc$	$C_{47}H_{64}N_5Gd$	$C_{47}H_{64}N_5Y$
Formula mass (amu)	743.99	784.82	856.28	787.94
Space group	P 21/c	P 21/c	P 21/n	P -1
a (Å)	19.891 (2)	19.8888 (5)	11.7634 (3)	10.8628 (7)
b (Å)	11.6240 (12)	11.5941 (3)	18.4422 (5)	11.7806 (7)
c (Å)	20.148 (2)	20.0988 (5)	19.7845 (6)	18.3075 (10)
α (deg)	90	90	90	86.193 (2)
β (deg)	112.715	112.329 (1)	93.583 (1)	83.654 (2)
γ (deg)	90	90	90	71.048 (2)
V (Å^3)	4297.3 (8)	4287.12 (19)	4283.7 (2)	2201.1 (2)

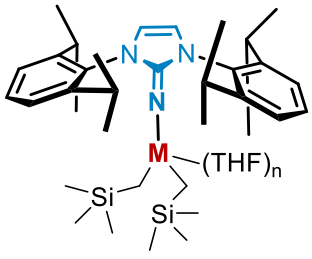
Z	4	4	4	2
λ (Å)	0.71073	1.54178	0.71073	0.71073
T (K)	173 K	173 K	173 K	173 K
ρ_{calcd} (g cm^{-3})	1.150	1.216	1.328	1.189
μ (mm^{-1})	0.208	2.886	1.585	1.361
Transmission factors	0.894–1.000	0.498–0.780	0.772–0.868	0.738–0.848
θ_{max} (deg)	25.612	68.326	27.497	25.435
No. of unique data, including $F_o^2 < 0$	7765	7744	9792	8092
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	6979	7070	8297	7224
No. of variables	498	573	492	503
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.1083	0.0336	0.0305	0.0302
$R_w(F_o^2)$ [b]	0.2142	0.0946	0.0580	0.0743
Goodness of fit	1.419	1.052	1.103	1.072

[a] $R(F) = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.

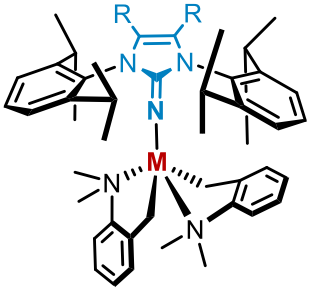
[b] $R_w(F_o^2) = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.

Table S15 Comparing rare-earth alkyl complexes supported by imidazolin-2-iminato ligands

Matthias Tamm	M-N1	M-N1-C1	Ours	M-N1	M-N1-C1
M = Sc	1.9520(18)	178.90(18)	M = Sc, R = Me	1.956(4)	178.6(4)
M = Lu	2.089(3)	176.4(2)	M = Sc, R = Cl	1.9711(13)	178.45(11)
M = Y	2.1255(13)	176.85(12)	M = Y, R = Me	2.1035(15)	178.12(14)
M = Gd	2.1643(13)	170.85(12)	M = Gd, R = Me	2.147(2)	178.91(19)



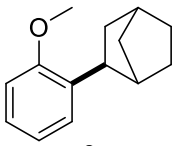
Matthias Tamm
M = Sc, n = 1
M = Y, n = 2
M = Lu, n = 2
M = Gd, n = 2



Ours
M = Sc, R = Me
M = Y, R = Me
M = Gd, R = Me
M = Sc, R = Cl

8. The analytical and spectral characterization data of products

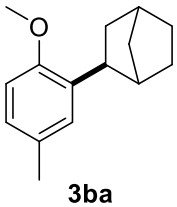
2-(2-Methoxyphenyl)bicyclo[2.2.1]heptane (3aa)



3aa

($C_{14}H_{18}O$) colorless oil; 39.2 mg, 97% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 9.4 Hz, 1H), 7.21 – 7.13 (m, 1H), 6.92 (t, *J* = 6.8 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 3.84 (s, 3H), 3.08 – 2.92 (m, 1H), 2.38 (s, 1H), 2.34 (s, 1H), 1.85 – 1.79 (m, 1H), 1.70 – 1.46 (m, 4H), 1.44 – 1.39 (m, 1H), 1.36 – 1.26 (m, 1H), 1.21 (d, *J* = 9.6, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 157.2, 135.9, 126.2, 125.7, 120.0, 110.1, 55.3, 41.1, 40.4, 38.7, 36.9, 36.3, 30.4, 29.1. **IR** (film, cm^{-1}): 2949, 2868, 2135, 1598, 1490, 1459, 1354, 1289, 1238, 1106, 1032, 747, 714. **HRMS** (ESI-TOF) calcd for $C_{14}H_{19}O^+$ ([M]+H$^+$) = 203.1430, found 203.1431. (Consistent with the data in previous literature)[10].

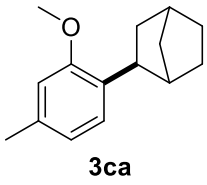
2-(2-Methoxy-5-methylphenyl)bicyclo[2.2.1]heptane (3ba)



3ba

($C_{15}H_{20}O$) colorless oil; 40.2 mg, 93% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.02 (s, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 3.80 (s, 3H), 2.98 – 2.94 (m, 1H), 2.34 (s, 1H), 2.32 (s, 1H), 2.30 (s, 3H), 1.82 – 1.76 (m, 1H), 1.62 – 1.45 (m, 4H), 1.41 – 1.37 (m, 1H), 1.33 – 1.26 (m, 1H), 1.20 (d, *J* = 11.6 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 155.2, 135.7, 129.1, 126.6, 126.3, 110.2, 55.5, 41.2, 40.4, 38.7, 36.9, 36.3, 30.5, 29.1, 20.8. **IR** (film, cm^{-1}): 2947, 2867, 1607, 1496, 1457, 1351, 1311, 1239, 1170, 1146, 1121, 1036, 923, 881, 802, 749, 562. **HRMS** (ESI-TOF) calcd for $C_{15}H_{21}O^+$ ([M]+H$^+$) = 217.1587, found 217.1587.

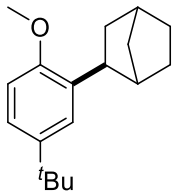
2-(2-Methoxy-4-methylphenyl)bicyclo[2.2.1]heptane (3ca)



3ca

($C_{15}H_{20}O$) colorless oil; 42.8 mg, 99% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.11 (d, *J* = 7.8 Hz, 1H), 6.74 (d, *J* = 7.8 Hz, 1H), 6.68 (s, 1H), 3.83 (s, 3H), 2.97 – 2.94 (m, 1H), 2.35 (s, 3H), 2.32 (s, 2H), 1.82 – 1.76 (m, 1H), 1.66 – 1.46 (m, 4H), 1.44 – 1.37 (m, 1H), 1.33 – 1.27 (m, 1H), 1.20 (d, *J* = 12.2 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 157.2, 136.0, 133.0, 125.6, 120.5, 111.3, 55.4, 41.3, 40.2, 38.7, 36.9, 36.3, 30.5, 29.1, 21.4. **IR** (film, cm^{-1}): 2947, 2867, 1611, 1578, 1502, 1456, 1310, 1286, 1252, 1193, 1119, 1042, 927, 806, 765, 725, 589. **HRMS** (ESI-TOF) calcd for $C_{15}H_{21}O^+$ ([M]+H$^+$) = 217.1587, found 217.1586.

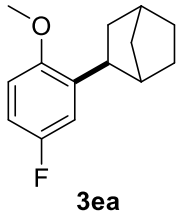
2-(5-(Tert-butyl)-2-methoxyphenyl)bicyclo[2.2.1]heptane (3da)



3da

($C_{18}H_{26}O$) colorless oil; 50.6 mg, 98% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.26 (s, 1H), 7.15 (d, *J* = 8.6, 1H), 6.77 (d, *J* = 8.6 Hz, 1H), 3.81 (s, 3H), 3.00 – 2.97 (m, 1H), 2.38 (s, 1H), 2.32 (s, 1H), 1.82 – 1.76 (m, 1H), 1.68 – 1.45 (m, 5H), 1.44 – 1.36 (m, 1H), 1.32 (s, 9H), 1.21 (d, *J* = 9.6 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 155.0, 142.4, 135.1, 123.0, 122.4, 109.5, 55.4, 41.2, 40.6, 38.7, 36.9, 36.3, 34.2, 31.6, 30.4, 29.1. **IR** (film, cm^{-1}): 2950, 2868, 1606, 1498, 1460, 1392, 1361, 1310, 1243, 1208, 1135, 1106, 1036, 921, 888, 808, 647. **HRMS** (ESI-TOF) calcd for $C_{18}H_{27}O^{+}$ ([M]+H^{+}) = 259.2056, found 259.2055.

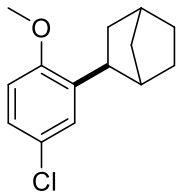
2-(5-Fluoro-2-methoxyphenyl)bicyclo[2.2.1]heptane (3ea)



3ea

($C_{14}H_{17}FO$) colorless oil; 41.9 mg, 95% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.94 – 6.91 (m, 1H), 6.83 – 6.78 (m, 1H), 6.75 – 6.71 (m, 1H), 3.80 (s, 3H), 3.01 – 2.88 (m, 1H), 2.31 (d, *J* = 4.4 Hz, 2H), 1.83 – 1.77 (m, 1H), 1.59 – 1.35(m, 5H), 1.32 – 1.25 (m, 1H), 1.21 (d, *J* = 9.8, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 158.2, 155.9, 153.3, 138.1, 113.2, 112.9, 111.6, 111.4, 110.8, 110.7, 55.9, 41.2, 38.8, 36.8, 36.2, 30.3, 28.9. **^{19}F{^{1}H} NMR** (376 MHz, Chloroform-*d*) δ –124.19. **IR** (film, cm^{-1}): 2950, 2870, 1598, 1492, 1462, 1423, 1354, 1273, 1243, 1200, 1178, 1149, 1101, 1035, 982, 941, 866, 840, 802, 748, 699. **HRMS** (ESI-TOF) calcd for $C_{14}H_{17}FONa^{+}$ ([M]+Na^{+}) = 243.1156, found 243.1158.

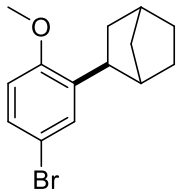
2-(5-Chloro-2-methoxyphenyl)bicyclo[2.2.1]heptane (3fa)



3fa

($C_{14}H_{17}ClO$) colorless oil; 43.6 mg, 92% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.15 (d, *J* = 2.6 Hz, 1H), 7.15 – 7.07 (m, 1H), 6.73 (d, *J* = 8.6 Hz, 1H), 3.80 (s, 3H), 2.94 – 2.91 (m, 1H), 2.35 – 2.28 (m, 2H), 1.82 – 1.76 (m, 1H), 1.66 – 1.55 (m, 2H), 1.49 (d, *J* = 9.8 Hz, 1H), 1.45 – 1.34 (m, 2H), 1.31 – 1.25 (m, 1H), 1.21 (d, *J* = 9.8 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 155.9, 137.9, 125.9, 125.7, 125.1, 111.2, 55.6, 40.9, 40.5, 38.7, 36.8, 36.3, 30.3, 28.9. **IR** (film, cm^{-1}): 2948, 2868, 1593, 1484, 1459, 1405, 1350, 1310, 1238, 1174, 1126, 1032, 968, 911, 879, 848, 803, 724, 643, 621, 555. **GC-MS** (EI): Calcd for $C_{14}H_{17}ClO$ = 236.09, found 236.05.

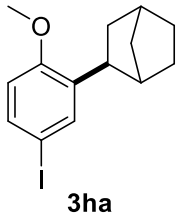
2-(5-Bromo-2-methoxyphenyl)bicyclo[2.2.1]heptane (3ga)



3ga

($C_{14}H_{17}BrO$) colorless oil; 43.6 mg, 80% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 – 7.21 (m, 2H), 6.69 (d, *J* = 8.6 Hz, 1H), 3.79 (s, 3H), 2.94 – 2.90 (m, 1H), 2.31 (s, 2H), 1.81 – 1.75 (m, 1H), 1.66 – 1.55 (m, 2H), 1.48 (d, *J* = 9.8 Hz, 1H), 1.45 – 1.33 (m, 2H), 1.31 – 1.24 (m, 1H), 1.21 (d, *J* = 9.8 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 156.4, 138.4, 128.8, 112.7, 111.8, 55.5, 40.9, 40.5, 38.6, 36.8, 36.3, 30.4, 28.9. **IR** (film, cm^{-1}): 2949, 2968, 1589, 1482, 1458, 1399, 1349, 1277, 1238, 1174, 1123, 1023, 907, 879, 844, 802, 721, 620, 522. **HRMS** (ESI-TOF) calcd for $C_{14}H_{17}BrONa^+$ ([M]+Na^+) = 303.0355, found 303.0360.

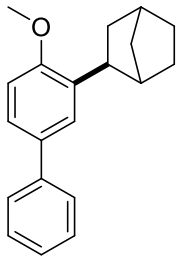
2-(5-Iodo-2-methoxyphenyl)bicyclo[2.2.1]heptane (3ha)



3ha

($C_{14}H_{17}IO$) colorless oil; 61.7 mg, 94% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 8.2 Hz, 1H), 3.79 (s, 3H), 2.99 – 2.83 (m, 1H), 2.31 (d, *J* = 4.4, 1.6 Hz, 2H), 1.81 – 1.75 (m, 1H), 1.66 – 1.52 (m, 2H), 1.48 (d, *J* = 9.6, 1H), 1.45 – 1.33 (m, 2H), 1.31 – 1.26 (m, 1H), 1.24 – 1.18 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 157.1, 138.8, 134.9, 134.6, 112.4, 82.9, 55.4, 40.9, 40.4, 38.6, 36.8, 36.2, 30.3, 28.9. **IR** (film, cm^{-1}): 2947, 2866, 1583, 1480, 1492, 1457, 1393, 1347, 1280, 1236, 1173, 1123, 1030, 954, 880, 843, 800, 720, 609, 551, 468. **HRMS** (ESI-TOF) calcd for $C_{14}H_{18}IO^+$ ([M]+H^+) = 329.0397, found 329.0383.

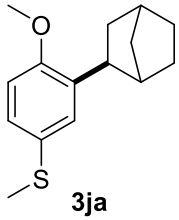
2-(4-Methoxy-[1,1'-biphenyl]-3-yl)bicyclo[2.2.1]heptane (3ia)



3ia

($C_{20}H_{22}O$) colorless oil; 55.1 mg, 99% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.60 – 7.52 (m, 2H), 7.48 – 7.34 (m, 4H), 7.34 – 7.28 (m, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 3.87 (s, 3H), 3.05 – 3.01 (m, 1H), 2.43 (d, *J* = 3.8 Hz, 1H), 2.34 (d, *J* = 4.4 Hz, 1H), 1.84 (t, *J* = 11.8 Hz, 1H), 1.69 – 1.56 (m, 3H), 1.43 (t, *J* = 10.4 Hz, 1H), 1.32 (t, *J* = 10.6 Hz, 1H), 1.27 – 1.19 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 156.9, 141.6, 136.2, 133.1, 128.6, 126.9, 126.4, 124.8, 124.8, 110.4, 55.5, 55.5, 41.1, 40.5, 38.7, 36.9, 36.4, 30.4, 29.1. **IR** (film, cm^{-1}): 3031, 2947, 2867, 2834, 1604, 1483, 1459, 1351, 1240, 1124, 1064, 1028, 890, 813, 762, 697, 599, 549. **HRMS** (ESI-TOF) calcd for $C_{20}H_{22}ONa^+$ ([M]+ Na^+) = 301.1563, found 301.1573.

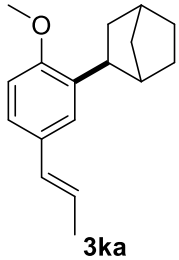
(3-(Bicyclo[2.2.1]heptan-2-yl)-4-methoxyphenyl)(methyl)sulfane (3ja)



3ja

($C_{15}H_{20}OS$) yellow oil; 49.2 mg, 99% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 7.22 (d, *J* = 2.4 Hz, 1H), 7.14 (d, *J* = 8.4, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 3.81 (s, 3H), 3.02 – 2.87 (m, 1H), 2.45 (s, 3H), 2.35 (s, 1H), 2.32 (s, 1H), 1.81 – 1.77 (m, 1H), 1.64 – 1.54 (m, 2H), 1.51 (d, *J* = 9.6 Hz, 1H), 1.49 – 1.41 (m, 1H), 1.41 – 1.35 (m, 1H), 1.29 (d, *J* = 12.4, 1H), 1.21 (d, *J* = 9.8, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 156, 136.7, 127.8, 127.1, 126.8, 110.7, 55.5, 40.9, 40.4, 38.6, 36.8, 36.3, 30.3, 28.9, 18.3. **IR** (film, cm^{-1}): 2947, 2867, 1590, 1485, 1458, 1337, 1293, 1236, 1175, 1132, 1095, 1031, 966, 918, 882, 803, 727, 641, 585, 559, 471. **HRMS** (ESI-TOF) calcd for $C_{15}H_{21}OS^+$ ([M]+H$^+$) = 249.1308, found 249.1309.

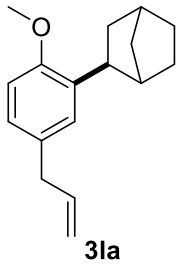
(E)-2-(2-Methoxy-5-(prop-1-en-1-yl)phenyl)bicyclo[2.2.1]heptane (3ka)



3ka

($C_{17}H_{22}O$) colorless oil; 47.0 mg, 97% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 7.19 (s, 1H), 7.13 – 7.08 (m, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 6.35 (d, *J* = 15.6 Hz, 1H), 6.12 – 6.06 (m, 1H), 3.81 (s, 3H), 2.95 – 2.93 (m, 1H), 2.35 (d, *J* = 4.0 Hz, 1H), 2.32 – 2.35 (m, 1H), 1.86 (d, *J* = 6.6 Hz, 3H), 1.80 – 1.76 (m, 1H), 1.65 – 1.51 (m, 5H), 1.51 – 1.44 (m, 1H), 1.42 – 1.35 (m, 1H), 1.31 – 1.25 (m, 1H), 1.20 (d, *J* = 10 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 156.4, 135.8, 130.9, 130.0, 123.6, 123.3, 123.0, 110.1, 55.4, 55.4, 41.0, 40.40, 38.6, 36.8, 36.3, 30.4, 29.0, 18.3. **IR** (film, cm^{-1}): 2948, 2868, 1691, 1601, 1494, 1456, 1353, 1310, 1242, 1169, 1143, 1117, 1032, 961, 888, 815, 785, 760, 552. **HRMS** (ESI-TOF) calcd for $C_{17}H_{23}O^+$ ([M]+H$^+$) = 243.1743, found 243.1741.

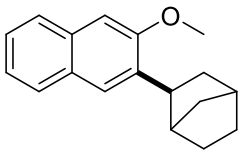
2-(5-Allyl-2-methoxyphenyl)bicyclo[2.2.1]heptane (3la)



3la

($C_{17}H_{22}O$) colorless oil; 48 mg, 99% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 7.02 (s, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.01 – 5.91 (m, 1H), 5.13 – 4.98 (m, 2H), 3.79 (s, 3H), 3.32 (d, *J* = 6.6 Hz, 2H), 2.95 (t, *J* = 9.2 Hz, 1H), 2.39 – 2.25 (m, 2H), 1.80 – 1.74 (m, 1H), 1.64 – 1.44 (m, 4H), 1.42 – 1.34 (m, 1H), 1.31 – 1.25 (m, 1H), 1.18 (d, *J* = 9.8 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 155.6, 138.1, 135.8, 131.3, 126.1, 125.8, 115.1, 110.1, 55.4, 41.1, 40.4, 39.7, 38.6, 36.8, 36.2, 30.4, 29.0. **IR** (film, cm^{-1}): 2948, 2868, 2833, 1638, 1605, 1495, 1459, 1353, 1241, 1171, 1146, 1119, 1035, 993, 911, 808, 785, 762, 644. **HRMS** (ESI-TOF) calcd for $C_{17}H_{23}O^+$ ([M]+H$^+$) = 243.1743, found 243.1743.

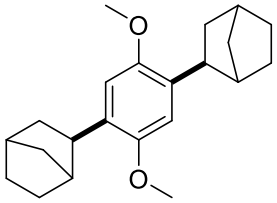
2-(Bicyclo[2.2.1]heptan-2-yl)-3-methoxynaphthalene (3ma)



3ma

($C_{18}H_{20}O$) colorless oil; 44.9 mg, 89% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 7.76 – 7.70 (m, 2H), 7.59 (s, 1H), 7.38 (t, *J* = 8.2, Hz, 1H), 7.32 (t, *J* = 8.2, Hz, 1H), 7.09 (s, 1H), 3.95 (s, 3H), 3.10 – 3.07 (m, 1H), 2.56 – 2.46 (m, 1H), 2.38 – 2.36 (m, 1H), 1.89 ‑ 1.83 (m, 1H), 1.69 – 1.54 (m, 4H), 1.50 – 1.42 (m, 1H), 1.38 – 1.32 (m, 1H), 1.25 (d, *J* = 9.8 Hz, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 156.5, 137.4, 132.8, 128.6, 127.3, 126.0, 125.3, 124.2, 123.4, 104.7, 55.3, 55.3, 41.0, 40.9, 38.5, 37.0, 36.1, 30.3, 29.1. **IR** (film, cm^{-1}): 2947, 2867, 1630, 1600, 1499, 1466, 1429, 1396, 1361, 1327, 890, 813, 762, 697, 599, 549. **HRMS** (ESI-TOF) calcd for $C_{18}H_{21}O^+$ ([M]+H$^+$) = 253.1587, found 253.1586.

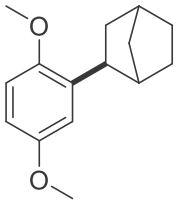
2,2'-(2,5-Dimethoxy-1,4-phenylene)bis(bicyclo[2.2.1]heptane) (3na)



3na

($C_{22}H_{30}O_2$) colorless solid; 64.6 mg, 99% yield, melting point: 92 – 98 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 6.76 (s, 2H), 3.82 (s, 6H), 3.00 – 2.96 (m, 2H), 2.40 – 2.29 (m, 4H), 1.83 – 1.78 (m, 2H), 1.64 – 1.54 (m, 6H), 1.52 – 1.46 (m, 2H), 1.44 – 1.37 (m, 2H), 1.30 (d, *J* = 11.2 Hz, 2H), 1.24 – 1.19 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 151.0, 133.5, 109.7, 56.4, 41.5, 41.4, 40.3, 40.2, 39.0, 38.9, 36.8, 36.4, 30.4, 28.9. **IR** (film, cm^{-1}): 2947, 2867, 1590, 1485, 1458, 1337, 1293, 1236, 1175, 1132, 1095, 1031, 966, 918, 882, 803, 727, 641, 585, 559, 471. **HRMS** (ESI-TOF) calcd for $C_{22}H_{31}O_2^+$ ([M]+H$^+$) = 327.2319, found 327.2314.

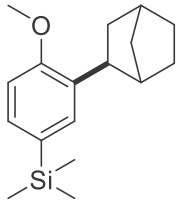
2-(2,5-Dimethoxyphenyl)bicyclo[2.2.1]heptane (3oa)



3oa

($C_{15}H_{20}O_2$) colorless oil; 46.0 mg, 99% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 6.82 (d, *J* = 3.0 Hz, 1H), 6.76 (d, *J* = 8.6 Hz, 1H), 6.67 – 6.64 (m, 1H), 3.78 (d, *J* = 4.2 Hz, 6H), 2.97 – 2.94 (m,1H), 2.34 – 2.30 (m, 2H), 1.83 – 1.77 (m, 1H), 1.61 – 1.52 (m, 3H), 1.49 – 1.36 (m, 2H), 1.32 – 1.26 (m, 1H), 1.22 – 1.18 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 153.3, 151.6, 137.5, 113.3, 110.8, 109.2, 55.9, 55.6, 41.1, 40.5, 38.8, 36.8, 36.3, 30.4, 28.9. **IR** (film, cm^{-1}): 2949, 2868, 2831, 1589, 1493, 1463, 1425, 1352, 1281, 1178, 1157, 1111, 1056, 1030, 974, 922, 875, 838, 796, 747, 731, 705, 634. **HRMS** (ESI-TOF) calcd for $C_{15}H_{21}O_2^+$ ([M]+H$^+$) = 233.1536, found 233.1536.

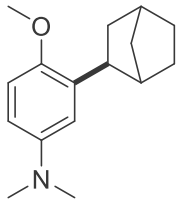
(3-(Bicyclo[2.2.1]heptan-2-yl)-4-methoxyphenyl)trimethylsilane (3pa)



3pa

($C_{17}H_{26}OSi$) colorless oil; 54.3 mg, 99% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 – 7.29 (m, 2H), 6.86 (d, *J* = 7.8 Hz, 1H), 3.84 (s, 3H), 3.01 – 2.98 (m, 1H), 2.44 – 2.27 (m, 2H), 1.83 – 1.77 (m, 1H), 1.64 – 1.60 (m, 2H), 1.55 – 1.47 (m, 2H), 1.45 – 1.37 (m, 1H), 1.35 – 1.30 (m, 1H), 1.24 – 1.20 (m, 1H), 0.27 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 158.0, 135.0, 131.6, 130.5, 130.3, 109.6, 55.1, 41.0, 40.4, 38.5, 36.9, 36.2, 30.4, 29.1. **IR** (film, cm^{-1}): 2950, 2869, 2835, 1591, 1566, 1493, 1460, 1388, 1344, 1292, 1275, 1263, 1241, 1211, 1165, 1149, 1134, 1104, 1034, 972, 932, 915, 861, 836, 808, 757, 725, 691, 650, 609, 581, 557, 534, 470. **GC-MS** (EI): Calcd for $C_{17}H_{26}OSi$ = 274.18, found 274.25.

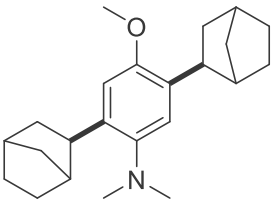
3-(Bicyclo[2.2.1]heptan-2-yl)-4-methoxy-*N,N*-dimethylaniline (3qa)



3qa

($C_{16}H_{23}NO$) colorless oil; 14.2 mg, 29% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.08 (d, *J* = 8.6 Hz, 1H), 6.85 (d, *J* = 3.0 Hz, 1H), 6.68 (dd, *J* = 8.8, 3.0 Hz, 1H), 3.78 (s, 3H), 3.25 – 3.19 (m, 1H), 2.62 (s, 6H), 2.34 (s, 1H), 2.22 (s, 1H), 1.88 – 1.82 (m, 1H), 1.73 – 1.69 (m, 1H), 1.60 – 1.55 (m, 2H), 1.53 – 1.50 (m, 1H), 1.43 – 1.39 (m, 1H), 1.33 – 1.29 (m, 1H), 1.26 – 1.22 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 155.9, 146.1, 145.5, 120.9, 113.0, 109.9, 46.0, 43.2, 40.8, 40.5, 36.8, 36.7, 31.1, 28.5. **IR** (film, cm^{-1}): 2949, 2868, 2820, 2776, 1724, 1658, 1605, 1576, 1497, 1452, 1424, 1351, 1289, 1233, 1189, 1155, 1101, 1042, 975, 944, 921, 872, 838, 809, 750, 690, 518. **HRMS** (ESI-TOF) calcd for $C_{16}H_{24}NO^{+}$ ($[M]+H^{+}$) = 246.1852, found 246.1853.

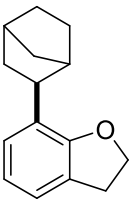
2,5-Di(bicyclo[2.2.1]heptan-2-yl)-4-methoxy-*N*,*N*-dimethylaniline (3ra)



3ra

($C_{23}H_{33}NO$) colorless oil; 37.3 mg, 55% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.04 (s, 1H), 6.77 (s, 1H), 3.82 (s, 3H), 3.34 – 3.15 (m, 1H), 2.97 – 2.93 (m, 1H), 2.64 (s, 6H), 2.41 – 2.28 (m, 3H), 2.23 (s, 1H), 1.90 – 1.82 (m, 1H), 1.80 – 1.70 (m, 2H), 1.64 – 1.49 (m, 7H), 1.42 – 1.37 (m, 1H), 1.35 – 1.24 (m, 4H), 1.22 – 1.18 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 153.6, 145.0, 141.5, 133.1, 55.6, 46.1, 43.3, 41.3, 40.9, 40.3, 38.6, 37.0, 36.8, 36.7, 36.3, 31.1, 30.3, 29.0, 28.5, 26.9. **IR** (film, cm^{-1}): 2947, 2867, 2817, 2772, 1607, 1501, 1452, 1395, 1352, 1296, 1261, 1238, 1208, 1190, 1169, 1113, 1093, 1046, 1019, 949, 924, 907, 838, 799, 634. **HRMS** (ESI-TOF) calcd for $C_{23}H_{34}NO^+$ ([M]+H$^+$) = 340.2635, found 340.2638.

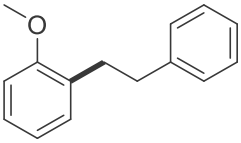
7-(Bicyclo[2.2.1]heptan-2-yl)-2,3-dihydrobenzofuran (3sa)



3sa

($C_{15}H_{18}O$) colorless oil; 34.3 mg, 80% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.04 – 7.01 (m, 2H), 6.80 (t, *J* = 7.4 Hz, 1H), 4.55 (t, *J* = 8.8 Hz, 2H), 3.20 (t, *J* = 8.8 Hz, 2H), 2.87 – 2.83 (m, 1H), 2.41 – 2.22 (m, 2H), 1.77 – 1.71 (m, 1H), 1.64 – 1.57 (m, 2H), 1.54 – 1.52 (m, 2H), 1.39 – 1.36 (m, 1H), 1.29 – 1.26 (m, 1H), 1.21 – 1.16 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 157.8, 129.4, 126.0, 124.4, 121.8, 120.0, 70.6, 41.6, 40.8, 37.8, 36.7, 36.1, 30.3, 30.0, 29.0. **IR** (film, cm^{-1}): 3036, 2949, 2868, 1593, 1477, 1451, 1364, 1314, 1299, 1262, 1209, 1178, 1159, 1062, 1024, 1002, 979, 946, 869, 757, 742. **HRMS** (ESI-TOF) calcd for $C_{15}H_{19}O^+$ ([M]+H$^+$) = 215.1430, found 215.1431. (Consistent with the data in previous literature)[10].

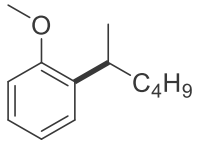
1-Methoxy-2-phenethylbenzene (3ab)



3ab

($C_{15}H_{16}O$) colorless oil; 8.5 mg, 20% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.26 – 7.17 (m, 3H), 7.17 – 7.07 (m, 4H), 7.05 – 7.00 (m, 1H), 6.80 (t, *J* = 7.4 Hz, 2H), 3.76 (s, 3H), 2.90 – 2.74 (m, 4H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 157.4, 142.4, 130.2, 129.8, 128.4, 128.2, 127.1, 125.7, 120.3, 110.2, 55.2, 55.2, 36.1, 32.4. **IR** (film, cm^{-1}): 3061, 3026, 3001, 2926, 2856, 2835, 1601, 1587, 1493, 1460, 1438, 1324, 1289, 1177, 1110, 1073, 1051, 1031, 929, 805, 750, 698. **HRMS** (ESI-TOF) calcd for $C_{15}H_{17}O^+$ ([M]+H$^+$) = 213.1274, found 213.1275. (Consistent with the data in previous literature)[10].

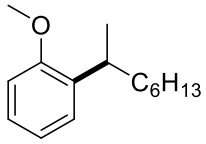
1-(Hexan-2-yl)-2-methoxybenzene (3ac)



3ac

($C_{13}H_{20}O$) colorless oil; 8.8 mg, 23% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 7.21 – 7.10 (m, 2H), 6.96 – 6.89 (m, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 3.17 (q, *J* = 7.0 Hz, 1H), 1.63 – 1.56 (m, 1H), 1.54 – 1.46 (m, 1H), 1.32 – 1.16 (m, 4H), 1.18 (d, *J* = 7.0 Hz, 3H), 0.86 (t, *J* = 7.0 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 156.9, 136.2, 126.7, 126.3, 120.5, 110.4, 55.4, 36.8, 31.6, 29.8, 22.8, 20.9, 14.0. **IR** (film, cm^{-1}): 3029, 2957, 2928, 2857, 2836, 1599, 1585, 1492, 1462, 1439, 1375, 1356, 1288, 1173, 1147, 1102, 1052, 1033, 802, 750, 497. **HRMS** (ESI-TOF) calcd for $C_{13}H_{20}OK^+$ ([M]+K^+) = 231.1146, found 231.1139. (Consistent with the data in previous literature)[10].

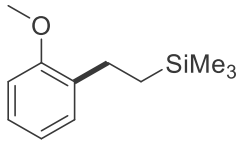
1-Methoxy-2-(octan-2-yl)benzene (3ad)



3ad

($C_{15}H_{24}O$) colorless oil; 10.1 mg, 20% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 7.22 – 7.11 (m, 2H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 3.18 (q, *J* = 7.2 Hz, 1H), 1.64 – 1.58 (m, 1H), 1.54 – 1.46 (m, 1H), 1.35 – 1.20 (m, 8H), 1.19 (d, *J* = 7.0 Hz, 3H), 0.87 (t, *J* = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 156.9, 136.2, 126.6, 126.3, 120.5, 110.4, 55.3, 37.1, 31.8, 31.6, 29.4, 27.6, 22.6, 20.9, 14.1. **IR** (film, cm^{-1}): 3029, 2956, 2925, 2854, 1599, 1585, 1491, 1462, 1439, 1375, 1357, 1288, 1174, 1146, 1104, 1052, 1033, 927, 801, 749, 497. **HRMS** (ESI-TOF) calcd for $C_{15}H_{25}O^+$ ([M]+H^+) = 221.1900, found 221.1901. (Consistent with the data in previous literature)[10].

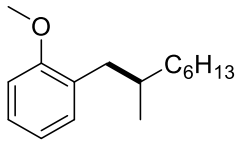
(2-Methoxyphenethyl)trimethylsilane (3ae)



3ae

($C_{12}H_{20}OSi$) colorless oil; 6.7 mg, 16% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 7.16 (t, *J* = 7.8 Hz, 2H), 6.88 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 2.64 – 2.58 (m, 2H), 0.85 – 0.79 (m, 2H), 0.02 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 157.1, 133.6, 128.7, 126.5, 120.3, 110.0, 29.7, 24.1, 16.8, -1.7. **IR** (film, cm^{-1})): 2997, 2952, 2925, 2854, 1599, 1492, 1463, 1440, 1289, 1176, 1139, 1092, 1051, 1033, 994, 906, 861, 835, 748, 690. **HRMS** (ESI-TOF) calcd for $C_{12}H_{21}OSi^+$ ([M]+H^+) = 209.1356, found 209.1350. (Consistent with the data in previous literature)[10].

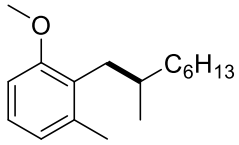
1-Methoxy-2-(2-methyloctyl)benzene (6aa)



6aa

($C_{16}H_{26}O$) colorless oil; 40.6 mg, 99% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.18 (t, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 6.97 – 6.80 (m, 2H), 3.82 (s, 3H), 2.68 (dd, *J* = 13.2, 5.9 Hz, 1H), 2.37 (dd, *J* = 13.2, 8.3 Hz, 1H), 1.85 – 1.72 (m, 1H), 1.41 – 1.26 (m, 9H), 1.22 – 1.13 (m, 1H), 0.91 (t, *J* = 6.6 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 157.7, 130.8, 130.2, 126.7, 120.0, 110.2, 55.2, 55.1, 37.7, 37.0, 33.3, 31.9, 29.5, 27.0, 22.7, 19.5, 14.1. **IR** (film, cm^{-1}): 2953, 2923, 2854, 1611, 1501, 1461, 1376, 1251, 1229, 1182, 1135, 1038, 884, 802, 714, 463. **HRMS** (ESI-TOF) calcd for $C_{16}H_{27}O^+$ ([M]+H$^+$) = 235.2056, found 235.2051. (Consistent with the data in previous literature)[10].

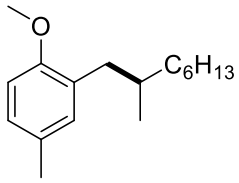
1-Methoxy-3-methyl-2-(2-methyloctyl)benzene (6ba)



6ba

($C_{17}H_{28}O$) colorless oil; 45.2 mg, 96% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.06 (t, *J* = 7.8 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 8.2 Hz, 1H), 3.79 (s, 3H), 2.63 (dd, *J* = 13.2, 5.8 Hz, 1H), 2.46 (dd, *J* = 13.2, 8.6 Hz, 1H), 2.30 (s, 3H), 1.76 – 1.71 (m, 1H), 1.40 – 1.14 (m, 10H), 0.89 (t, *J* = 6.6 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 157.9, 137.8, 129.0, 125.9, 122.5, 107.9, 55.3, 55.2, 37.3, 33.4, 33.3, 31.9, 29.6, 27.2, 22.7, 19.9, 19.5, 14.1. **IR** (film, cm^{-1}): 2953, 2924, 2854, 1582, 1467, 1376, 1313, 1261, 1178, 1119, 769, 692. **HRMS** (ESI-TOF) calcd for $C_{17}H_{29}O^+$ ([M]+H$^+$) = 249.2213, found 249.2208.

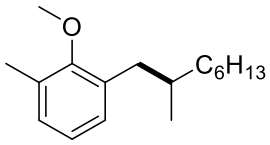
1-Methoxy-4-methyl-2-(2-methyloctyl)benzene (6ca)



6ca

($C_{17}H_{28}O$) colorless oil; 46.2 mg, 96% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.96 (d, *J* = 8.2 Hz, 1H), 6.91 (d, *J* = 2.4 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 3.78 (s, 3H), 2.62 (dd, *J* = 13.2, 5.8 Hz, 1H), 2.36 – 2.29 (m, 1H), 2.28 (s, 3H), 1.79 – 1.71 (m, 1H), 1.39 – 1.23 (m, 9H), 1.20 – 1.10 (m, 1H), 0.90 (t, *J* = 6.6 Hz, 3H), 0.84 (d, *J* = 6.6 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 155.6, 131.6, 130.0, 129.2, 126.9, 110.2, 55.4, 55.3, 37.6, 37.0, 33.4, 31.9, 29.5, 27.0, 22.7, 20.5, 20.4, 19.5, 14.1. **IR** (film, cm^{-1}): 2953, 2923, 2854, 1611, 1501, 1461, 1376, 1251, 1229, 1182, 1135, 1038, 802. **HRMS** (ESI-TOF) calcd for $C_{17}H_{29}O^+$ ([M]+H$^+$) = 249.2213, found 249.2209.

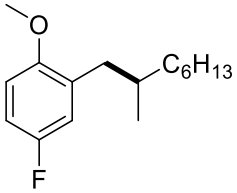
2-Methoxy-1-methyl-3-(2-methyloctyl)benzene (6da)



6da

($C_{17}H_{28}O$) colorless oil; 47.7 mg, 96% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 7.05 – 6.89 (m, 3H), 3.72 (s, 3H), 2.66 (dd, *J* = 13.4, 5.8 Hz, 1H), 2.35 (dd, *J* = 13.4, 8.5 Hz, 1H), 2.30 (s, 3H), 1.81 – 1.73 (m, 1H), 1.39 – 1.24 (m, 9H), 1.20 – 1.14 (m, 1H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.84 (d, *J* = 6.6 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 157.0, 134.5, 130.8, 128.8, 128.5, 123.5, 60.2, 37.5, 37.1, 34.1, 31.9, 29.5, 27.1, 22.6, 19.6, 16.2, 14.1. **IR** (film, cm^{-1}): 2954, 2923, 2853, 1465, 1376, 1258, 1212, 1168, 1086, 1016, 812, 766. **HRMS** (ESI-TOF) calcd for $C_{17}H_{29}O^+$ ([M]+H$^+$) = 249.2213, found 249.2210. (Consistent with the data in previous literature)[10].

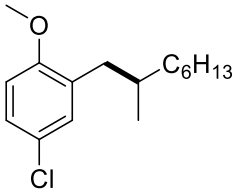
4-Fluoro-1-methoxy-2-(2-methyloctyl)benzene (6ea)



6ea

($C_{16}H_{25}FO$) colorless oil; 50.0 mg, 99% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 6.90 – 6.78 (m, 2H), 6.76 – 6.72 (m, 1H), 3.78 (s, 3H), 2.62 (dd, *J* = 13.2, 6.0 Hz, 1H), 2.32 (dd, *J* = 13.2, 8.3 Hz, 1H), 1.87 – 1.67 (m, 1H), 1.37 – 1.19 (m, 9H), 1.19 – 1.12 (m, 1H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.6 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 157.9, 155.6, 153.8, 153.8, 132.1, 132.0, 117.4, 117.2, 112.4, 112.1, 111.0, 110.9, 55.8, 37.6, 36.9, 33.2, 31.9, 29.5, 27.0, 22.6, 19.5, 14.1. **^{19}F{^{1}H} NMR** (376 MHz, Chloroform-*d*) *δ* –124.98. **IR** (film, cm^{-1}): 2955, 2925, 2854, 1601, 1496, 1463, 1424, 1377, 1259, 1217, 1036, 802, 713. **HRMS** (ESI-TOF) calcd for $C_{16}H_{25}FONa^+$ ([M]+Na$^+$) = 275.1782, found 275.1790.

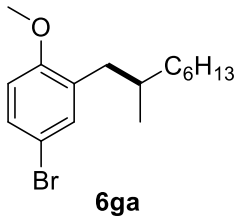
4-Chloro-1-methoxy-2-(2-methyloctyl)benzene (6fa)



6fa

($C_{16}H_{25}ClO$) colorless oil; 40.3 mg, 75% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 7.12 – 7.10 (m, 1H), 7.05 (d, *J* = 2.8 Hz, 1H), 6.74 (d, *J* = 8.8 Hz, 1H), 3.78 (s, 3H), 2.61 (dd, *J* = 13.2, 5.8 Hz, 1H), 2.30 (dd, *J* = 13.2, 8.4 Hz, 1H), 1.83 – 1.66 (m, 1H), 1.37 – 1.20 (m, 9H), 1.20 – 1.10 (m, 1H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.82 (d, *J* = 6.6 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 156.3, 132.1, 130.4, 126.3, 124.8, 111.3, 55.5, 37.5, 36.9, 33.2, 31.9, 29.5, 27.0, 22.6, 19.4, 14.1. **IR** (film, cm^{-1}): 2954, 2923, 2853, 1595, 1487, 1461, 1406, 1376, 1304, 1243, 1176, 1134, 1032, 879, 802, 724, 645. **HRMS** (ESI-TOF) calcd for $C_{16}H_{25}ClOK^+$ ([M]+K$^+$) = 307.1226, found 307.1222.

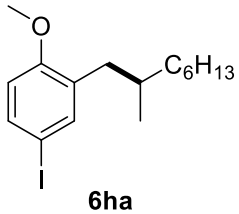
4-Bromo-1-methoxy-2-(2-methyloctyl)benzene (6ga)



6ga

($C_{16}H_{25}BrO$) colorless oil; 31.3 mg, 50% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.27 – 7.24 (m, 1H), 7.19 (d, *J* = 2.6 Hz, 1H), 6.70 (d, *J* = 8.8 Hz, 1H), 3.78 (s, 3H), 2.61 (dd, *J* = 13.2, 5.8 Hz, 1H), 2.29 (dd, *J* = 13.2, 8.4 Hz, 1H), 1.80 – 1.63 (m, 1H), 1.39 – 1.20 (m, 9H), 1.20 – 1.10 (m, 1H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.82 (d, *J* = 6.7 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 156.8, 133.3, 132.6, 129.3, 112.3, 111.9, 55.4, 37.4, 36.9, 33.2, 31.9, 29.5, 26.9, 22.6, 19.4, 14.1. **IR** (film, cm^{-1}): 2954, 2923, 2853, 1591, 1486, 1461, 1275, 1135,1032, 886, 864, 801, 723, 625. **HRMS** (ESI-TOF) calcd for $C_{16}H_{25}BrONa^+$ ([M]+Na$^+$) = 335.0981, found 335.0969.

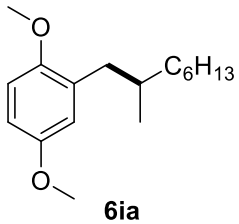
4-Iodo-1-methoxy-2-(2-methyloctyl)benzene (6ha)



6ha

($C_{16}H_{25}IO$) colorless oil; 33.9 mg, 47% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.45 – 7.42 (m, 1H), 7.37 (d, *J* = 2.4 Hz, 1H), 6.59 (d, *J* = 8.6 Hz, 1H), 3.77 (s, 3H), 2.58 (dd, *J* = 13.2, 5.8 Hz, 1H), 2.27 (dd, *J* = 13.2, 8.4 Hz, 1H), 1.76 – 1.67 (m, 1H), 1.41 – 1.21 (m, 9H), 1.20 – 1.09 (m, 1H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 6.6 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 157.6, 139.1, 135.4, 133.1, 112.5, 82.5, 55.3, 55.3, 37.3, 36.9, 33.2, 31.9, 29.5, 26.9, 22.6, 19.4, 14.1. **IR** (film, cm^{-1}): 2953, 2922, 2852, 1585, 1484, 1460, 1242, 1174, 1137, 1030, 801. **HRMS** (ESI-TOF) calcd for $C_{16}H_{26}IO^+$ ([M]+H$^+$) = 361.1023, found 361.1021.

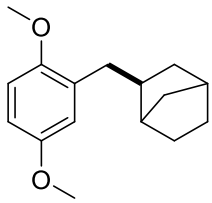
1,4-Dimethoxy-2-(2-methyloctyl)benzene (6ia)



6ia

($C_{17}H_{28}O_2$) colorless oil; 49.7 mg, 94% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.77 – 6.75 (m, 1H), 6.70 – 6.67 (m, 2H), 3.76 (s, 6H), 2.62 (dd, *J* = 13.2, 5.8 Hz, 1H), 2.32 (dd, *J* = 13.2, 8.4 Hz, 1H), 1.84 – 1.66 (m, 1H), 1.39 – 1.22 (m, 9H), 1.19 – 1.11 (m, 1H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.83 (d, *J* = 6.6 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 153.2, 152.1, 131.6, 117.2, 111.2, 110.6, 55.9, 55.6, 37.8, 37.0, 33.4, 31.9, 29.5, 27.0, 22.6, 19.5, 14.1. **IR** (film, cm^{-1}): 2923, 2853, 1590, 1497, 1462, 1376, 1280, 1221, 1178, 1157, 1130, 1049, 1028, 875, 797, 710. **HRMS** (ESI-TOF) calcd for $C_{17}H_{29}O_2^+$ ([M]+H$^+$) = 265.2162, found 265.2158.

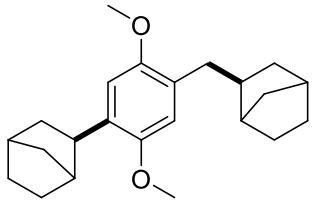
2-(2,5-Dimethoxybenzyl)bicyclo[2.2.1]heptane (6ja)



6ja

($C_{16}H_{22}O_2$) colorless oil; 48.8 mg, 99% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 6.83 – 6.63 (m, 3H), 3.78 (d, *J* = 2.8 Hz, 6H), 2.51 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.43 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.22 (s, 1H), 1.99 (s, 1H), 1.82 – 1.75 (m, 1H), 1.53 – 1.43 (m, 3H), 1.40 – 1.37 (m, 1H), 1.19 – 1.06 (m, 4H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 153.2, 152.0, 131.6, 116.8, 111.0, 110.3, 55.9, 55.8, 55.6, 55.6, 55.5, 41.8, 40.5, 37.9, 36.8, 35.1, 29.9, 28.9. **IR** (film, cm^{-1}): 2944, 2866, 1590, 1496, 1460, 1281, 1178, 1157, 1117, 1049, 874, 795, 709, 482. **HRMS** (ESI-TOF) calcd for $C_{16}H_{23}O_2^+$ ([M]+H$^+$) = 247.1693, found 247.1688.

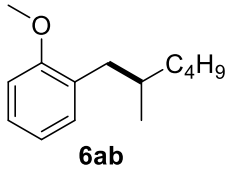
2-(4-(Bicyclo[2.2.1]heptan-2-yl)-2,5-dimethoxybenzyl)bicyclo[2.2.1]heptane (6jb)



6jb

($C_{23}H_{32}O_2$) colorless oil; 67.4 mg, 90% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 6.76 (s, 1H), 6.65 (s, 1H), 3.80 (s, 6H), 3.00 – 2.96 (m, 1H), 2.51 (ddd, *J* = 13.6, 8.4, 4.8 Hz, 1H), 2.41 (ddd, *J* = 13.6, 8.4, 4.8 Hz, 1H), 2.34 (s, 2H), 2.22 (s, 1H), 2.00 (s, 1H), 1.85 – 1.72 (m, 2H), 1.67 – 1.52 (m, 4H), 1.52 – 1.44 (m, 4H), 1.43 – 1.38 (m, 2H), 1.33 – 1.28 (m, 1H), 1.25 – 1.20 (m, 1H), 1.18 – 1.08 (m, 4H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 151.3, 150.9, 133.9, 127.6, 113.4, 109.7, 56.4, 56.3, 56.2, 42.2, 41.4, 40.5, 40.3, 39.0, 38.9, 38.0, 36.8, 36.5, 36.4, 36.4, 35.1, 30.4, 30.0, 28.9, 28.9. **IR** (film, cm^{-1}): 2945, 2866, 1501, 1458, 1399, 1352, 1203, 1047, 862, 735, 484. **HRMS** (ESI-TOF) calcd for $C_{23}H_{33}O_2^+$ ([M]+H$^+$) = 341.2475, found 341.2465.

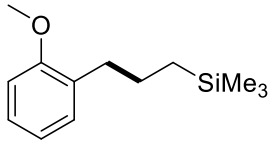
1-Methoxy-2-(2-methylhexyl)benzene (6ab)



6ab

($C_{14}H_{22}O$) colorless oil; 40.0 mg, 97% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 7.18 (t, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 6.97 – 6.80 (m, 2H), 3.82 (s, 3H), 2.68 (dd, *J* = 13.2, 5.9 Hz, 1H), 2.37 (dd, *J* = 13.2, 8.3 Hz, 1H), 1.85 – 1.72 (m, 1H), 1.41 – 1.26 (m, 9H), 1.22 – 1.13 (m, 1H), 0.91 (t, *J* = 6.7 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 157.7, 130.8, 130.2, 126.7, 120.0, 110.2, 55.2, 55.1, 37.7, 36.7, 33.3, 29.3, 22.9, 19.5, 14.1. **IR** (film, cm^{-1}): 2956, 2925, 2856, 1600, 1492, 1462, 1377, 1289, 1259, 1241, 1175, 1089, 1015, 799, 749, 725. **HRMS** (ESI-TOF) calcd for $C_{14}H_{23}O^+$ ([M]+H$^+$) = 207.1743, found 207.1741. (Consistent with the data in previous literature)[11].

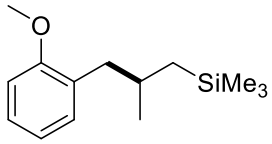
(3-(2-Methoxyphenyl)propyl)trimethylsilane (6ac)



6ac

($C_{13}H_{22}OSi$) colorless oil; 30.2 mg, 68% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.21 – 7.12 (m, 2H), 6.95 – 6.83 (m, 2H), 3.83 (s, 3H), 2.64 (t, *J* = 7.8 Hz, 2H), 1.69 – 1.57 (m, 2H), 0.65 – 0.50 (m, 2H), 0.00 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 157.4, 131.2, 129.8, 126.7, 120.2, 110.2, 55.2, 34.1, 24.4, 16.8, 1.0, -1.6, -1.7. **IR** (film, cm^{-1}): 2953, 1600, 1493, 1463, 1242, 1174, 1092, 1014, 797, 748, 691. **HRMS** (ESI-TOF) calcd for $C_{13}H_{23}OSi^+$ ([M]+H$^+$) = 223.1513, found 223.1516.

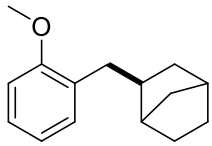
(3-(2-Methoxyphenyl)-2-methylpropyl)trimethylsilane (6ad)



6ad

($C_{14}H_{24}OSi$) colorless oil; 43 mg, 91% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.18 (t, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 7.4 Hz, 1H), 6.95 – 6.78 (m, 2H), 3.81 (s, 3H), 2.67 (dd, *J* = 13.0, 5.6 Hz, 1H), 2.36 (dd, *J* = 13.0, 8.6 Hz, 1H), 1.98 – 1.91 (m, 1H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.67 (dd, *J* = 14.8, 5.6 Hz, 1H), 0.49 (dd, *J* = 14.8, 8.2 Hz, 1H), 0.02 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 157.6, 130.9, 130.2, 126.8, 120.0, 110.1, 55.1, 41.3, 29.9, 25.1, 22.8, -0.7. **IR** (film, cm^{-1}): 2951, 1600, 1492, 1462, 1438, 1373, 1291, 1242, 1176, 1122, 1050, 1031, 860, 836, 750, 726, 692. **HRMS** (ESI-TOF) calcd for $C_{14}H_{25}OSi^+$ ([M]+H$^+$) = 237.1669, found 237.1670. (Consistent with the data in previous literature)[10].

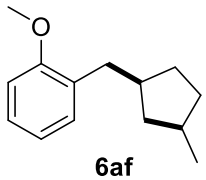
2-(2-Methoxybenzyl)bicyclo[2.2.1]heptane (6ae)



6ae

($C_{15}H_{20}O$) colorless oil; 42.8 mg, 99% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.24 – 7.08 (m, 2H), 7.05 – 6.65 (m, 2H), 3.83 (s, 3H), 2.55 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.47 (dd, *J* = 13.8, 7.2 Hz, 1H), 2.23 (s, 1H), 2.00 (s, 1H), 1.85 – 1.78 (m, 1H), 1.53 – 1.45 (m, 3H), 1.44 – 1.38 (m, 1H), 1.18 – 1.10 (m, 4H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 157.6, 130.3, 130.2, 126.7, 120.1, 110.1, 55.2, 41.8, 40.5, 38.0, 36.8, 36.7, 35.1, 30.1, 28.9. **IR** (film, cm^{-1}): 2945, 2866, 1600, 1492, 1456, 1437, 1289, 1239, 1174, 1136, 1107, 1083, 1050, 1031, 925, 803, 748, 715, 578, 484. **HRMS** (ESI-TOF) calcd for $C_{15}H_{21}O^+$ ([M]+H$^+$) = 217.1587, found 217.1586. (Consistent with the data in previous literature)[10].

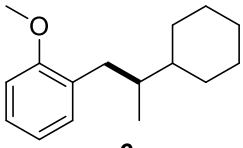
1-Methoxy-2-((3-methylcyclopentyl)methyl)benzene (6af)



6af

($C_{14}H_{20}O$) colorless oil; 40.6 mg, 99% yield, >98% *cis.* **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 7.22 – 7.09 (m, 2H), 6.94 – 6.79 (m, 2H), 3.81 (s, 3H), 2.71 – 2.53 (m, 2H), 2.23 – 2.15 (m, 1H), 1.96 – 1.79 (m, 2H), 1.79 – 1.64 (m, 2H), 1.38 – 1.29 (m, 1H), 1.23 – 1.14 (m, 1H), 0.98 (d, *J* = 6.4 Hz, 3H), 0.83 – 0.74 (m, 1H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 157.4, 130.7, 130.2, 126.6, 120.1, 110.1, 55.2, 55.1, 42.4, 40.5, 36.6, 34.4, 33.5, 31.7, 21.1. **IR** (film, cm^{-1}): 2944, 2863, 1600, 1492, 1461, 1289, 1240, 1176, 1134, 1050, 1032, 749,535. **HRMS** (ESI-TOF) calcd for $C_{14}H_{21}O^+$ ([M]+H$^+$) = 205.1587, found 205.1591.

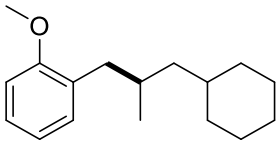
1-(2-Cyclohexylpropyl)-2-methoxybenzene (6ag)



6ag

($C_{16}H_{24}O$) colorless oil; 37.6 mg, 81% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 7.17 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.4 Hz, 1H), 6.92 – 6.79 (m, 2H), 3.81 (s, 3H), 2.76 (dd, *J* = 13.2, 5.2 Hz, 1H), 2.29 (dd, *J* = 13.2, 9.2 Hz, 1H), 1.83 – 1.70 (m, 3H), 1.70 – 1.60 (m, 3H), 1.28 – 1.04 (m, 6H), 0.77 (d, *J* = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 157.6, 130.7, 130.7, 126.6, 120.5, 110.2, 55.1, 42.6, 38.6, 34.7, 30.7, 28.5, 26.9, 26.8, 15.7. **IR** (film, cm^{-1}): 2921, 2850 , 1600, 1492, 1460, 1376, 1289, 1240, 1176, 1116, 1080, 1050, 1031, 888, 749, 727, 498. **HRMS** (ESI-TOF) calcd for $C_{16}H_{25}O^+$ ([M]+H$^+$) = 233.1900, found 233.1901.

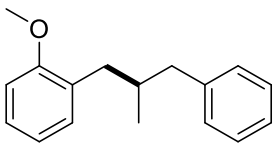
1-(3-Cyclohexyl-2-methylpropyl)-2-methoxybenzene (6ah)



6ah

($C_{17}H_{26}O$) colorless oil; 45.8 mg, 93% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 7.17 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.4 Hz, 1H), 6.94 – 6.76 (m, 2H), 3.80 (s, 3H), 2.67 (dd, *J* = 13.2, 5.4 Hz, 1H), 2.27 (dd, *J* = 13.2, 8.6 Hz, 1H), 1.96 – 1.82 (m, 1H), 1.76 – 1.61 (m, 5H), 1.41 – 1.34 (m, 1H), 1.29 – 1.14 (m, 4H), 1.09 – 1.02 (m, 1H), 0.91 – 0.74 (m, 5H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 157.6, 130.8, 130.2, 126.7, 120.0, 110.1, 55.1, 45.3, 37.9, 34.9, 33.9, 33.1, 30.0, 26.8, 26.5, 26.4, 19.8. **IR** (film, cm^{-1}): 3001, 2923, 2857, 1600, 1513, 1492, 1460, 1438, 1288, 1240, 1176, 1113, 1033, 928, 805, 749, 481. **HRMS** (ESI-TOF) calcd for $C_{17}H_{27}O^+$ ([M]+H$^+$) = 247.2056, found 247.2055.

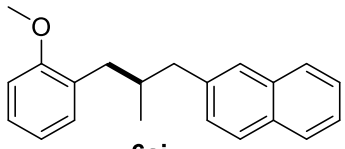
1-Methoxy-2-(2-methyl-3-phenylpropyl)benzene (6ai)



6ai

($C_{17}H_{20}O$) colorless oil; 34.6 mg, 72% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 7.30 – 7.26 (m, 1H), 7.25 (d, *J* = 1.8 Hz, 1H), 7.21 – 7.13 (m, 4H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.93 – 6.81 (m, 2H), 3.80 (s, 3H), 2.74 – 2.68 (m, 2H), 2.47 – 2.37 (m, 2H), 2.15 – 2.16 (m, 1H), 0.81 (d, *J* = 6.6 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 157.7, 141.6, 130.8, 129.7, 129.1, 128.0, 126.9, 125.5, 120.1, 110.3, 55.1, 43.5, 37.5, 35.5, 19.2. **IR** (film, cm^{-1}): 3025, 2953, 2922, 1600, 1492, 1457, 1375, 1289, 1241, 1178, 1119, 1045, 1029, 803, 747, 699, 495. **HRMS** (ESI-TOF) calcd for $C_{17}H_{21}O^+$ ([M]+H$^+$) = 241.1587, found 241.1588.

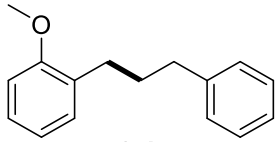
2-[3-(2-Methoxyphenyl)-2-methylpropyl]naphthalene (6aj)



6aj

($C_{21}H_{22}O$) colorless oil; 57.5 mg, 99% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.90 – 7.77 (m, 2H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.51 – 7.35 (m, 3H), 7.31 (d, *J* = 7.0 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 7.4 Hz, 1H), 6.97 – 6.79 (m, 2H), 3.75 (s, 3H), 3.26 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.80 (dd, *J* = 13.0, 6.4 Hz, 1H), 2.71 (dd, *J* = 13.6, 9.4 Hz, 1H), 2.59 (dd, *J* = 13.0, 7.8 Hz, 1H), 2.39 – 2.21 (m, 1H), 0.87 (d, *J* = 6.6 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 157.7, 137.8, 133.9, 132.1, 130.9, 129.7, 128.5, 127.1, 127.1, 126.4, 125.3, 125.2, 125.1, 124.2, 120.1, 110.2, 55.0, 40.6, 38.4, 34.7, 19.7. **IR** (film, cm^{-1}): 2921, 2850, 1600, 1492, 1460, 1376, 1289, 1240, 1176, 1116, 1080, 1050, 1031, 749, 727, 498. **HRMS** (ESI-TOF) calcd for $C_{21}H_{23}O^+$ ([M]+H$^+$) = 291.1743, found 291.1750.

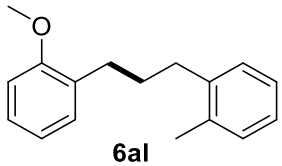
1-Methoxy-2-(3-phenylpropyl)benzene (6ak)



6ak

($C_{16}H_{18}O$) colorless oil; 18.6 mg, 82% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 – 7.25 (m, 2H), 7.25 – 7.08 (m, 5H), 6.96 – 6.78 (m, 2H), 3.82 (s, 3H), 2.79 – 2.53 (m, 4H), 2.06 – 1.79 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 157.4, 142.6, 130.7, 129.7, 128.4, 128.2, 126.9, 125.5, 120.2, 110.1, 55.2, 35.7, 31.3, 29.9. **IR** (film, cm^{-1}): 3025, 2927, 2855, 1600, 1493, 1459, 1241, 1176, 1111, 1032, 748, 698, 490. **HRMS** (ESI-TOF) calcd for $C_{16}H_{19}O^+$ ([M]+H$^+$) = 227.1430, found 227.1433. (Consistent with the data in previous literature)[12].

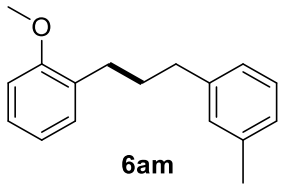
1-Methoxy-2-[3-(o-tolyl)propyl]benzene (6al)



6al

($C_{17}H_{20}O$) colorless oil; 20.4 mg, 85% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.24 – 7.03 (m, 6H), 6.93 – 6.80 (m, 2H), 3.82 (s, 3H), 2.78 – 2.57 (m, 4H), 2.28 (s, 3H), 2.00 – 1.79 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 157.4, 140.8, 135.9, 130.6, 130.0, 129.7, 128.6, 126.9, 125.7, 125.7, 120.3, 110.1, 55.2, 33.1, 30.2, 30.0, 19.2. **IR** (film, cm^{-1}): 2924, 2854, 1603, 1492, 1461, 1242, 1111, 1035, 849, 751, 698, 440. **HRMS** (ESI-TOF) calcd for $C_{17}H_{21}O^+$ ([M]+H$^+$) = 241.1587, found 241.1583.

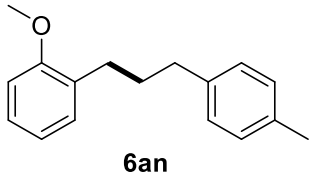
1-Methoxy-2-[3-(m-tolyl)propyl]benzene (6am)



6am

($C_{17}H_{20}O$) colorless oil; 19.5 mg, 75% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 7.25 – 7.09 (m, 3H), 7.08 – 6.93 (m, 3H), 6.93 – 6.76 (m, 2H), 3.82 (s, 3H), 2.68 – 2.61 (m, 4H), 2.33 (s, 3H), 2.00 – 1.81 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 157.4, 142.5, 137.7, 130.7, 129.7, 129.2, 128.0, 126.8, 126.3, 125.4, 120.2, 110.1, 55.2, 35.6, 31.3, 29.9, 21.4. **IR** (film, cm^{-1}): 2925, 2855, 1601, 1492, 1461, 1288, 1241, 1176, 1119, 1032, 748, 450. **HRMS** (ESI-TOF) calcd for $C_{17}H_{21}O^{+}$ ([M]+H^{+}) = 241.1587, found 241.1581.

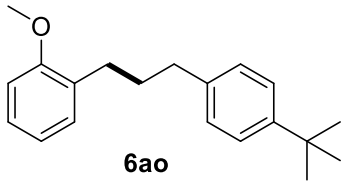
1-Methoxy-2-[3-(p-tolyl)propyl]benzene (6an)



6an

($C_{17}H_{20}O$) colorless oil; 18.0 mg, 75% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 7.23 – 7.04 (m, 6H), 6.95 – 6.81 (m, 2H), 3.83 (s, 3H), 2.70 – 2.63 (m, 4H), 2.34 (s, 3H), 2.01 – 1.85 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 157.4, 139.5, 134.9, 130.7, 129.7, 128.8, 128.2, 126.8, 120.2, 110.1, 55.1, 35.2, 31.3, 29.9, 20.9. **IR** (film, cm^{-1}): 3001, 2924, 2855, 1600, 1513, 1493, 1461, 1289, 1241, 1114, 1034, 806, 750, 543, 482. **HRMS** (ESI-TOF) calcd for $C_{17}H_{21}O^{+}$ ([M]+H^{+}) = 241.1587, found 241.1582.

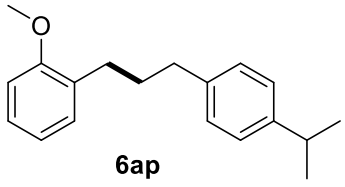
1-[3-(4-(Tert-butyl)phenyl)propyl]-2-methoxybenzene (6ao)



6ao

($C_{20}H_{26}O$) colorless oil; 24.3 mg, 82% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) *δ* 7.31 (d, *J* = 8.2 Hz, 2H), 7.23 – 7.11 (m, 4H), 6.94 – 6.81 (m, 2H), 3.82 (s, 3H), 2.71 – 2.63 (m, 4H), 1.98 – 1.90 (m, 2H), 1.32 (s, 9H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) *δ* 157.4, 148.3, 139.5, 130.8, 129.7, 128.0, 126.8, 125.0, 120.3, 110.2, 55.2, 35.1, 34.3, 31.4, 31.2, 30.0. **IR** (film, cm^{-1}): 2955, 2862, 1600, 1492, 1461,1438, 1240, 1108, 1034, 829, 750, 560. **HRMS** (ESI-TOF) calcd for $C_{20}H_{27}O^{+}$ ([M]+H^{+}) = 283.2056, found 283.2061. (Consistent with the data in previous literature)[13].

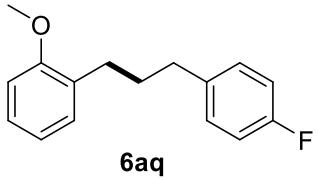
1-[3-(4-Isopropylphenyl)propyl]-2-methoxybenzene (6ap)



6ap

($C_{19}H_{24}O$) colorless oil; 20.1 mg, 75% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.23 – 7.05 (m, 6H), 6.94 – 6.80 (m, 2H), 3.82 (s, 3H), 2.92 – 2.85 (m, 1H), 2.70 – 2.65 (m, 4H), 2.03 – 1.81 (m, 2H), 1.25 (d, *J* = 6.8 Hz, 6H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 157.5, 146.0, 139.9, 130.8, 129.7, 128.2, 126.8, 126.2, 120.3, 110.2, 55.2, 55.2, 35.3, 33.6, 31.3, 29.9, 24.0. **IR** (film, cm^{-1}): 2957, 1600, 1511, 1493, 1461, 1438, 1288, 1241, 1176, 1113, 1052, 1034, 827, 751, 576. **HRMS** (ESI-TOF) calcd for $C_{19}H_{25}O^{+}$ ([M]+H^{+}) = 269.1900, found 269.1904.

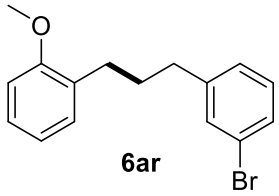
1-[3-(4-Fluorophenyl)propyl]-2-methoxybenzene (6aq)



6aq

($C_{16}H_{17}FO$) colorless oil; 10.3 mg, 42% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.23 – 7.07 (m, 4H), 6.99 – 6.92 (m, 2H), 6.91 – 6.80 (m, 2H), 3.81 (s, 3H), 2.66 – 2.61 (m, 4H), 1.99 – 1.80 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 129.7, 129.7, 129.6, 126.9, 120.3, 114.9, 114.7, 110.2, 55.2, 34.8, 31.4, 29.7. **^{19}F{^{1}H} NMR** (377 MHz, Chloroform-*d*) δ -118.23. **IR** (film, cm^{-1}): 2934, 2858, 1600, 1508, 1493, 1462, 1241, 1220, 1157, 1111, 1033, 829, 751, 494. **HRMS** (ESI-TOF) calcd for $C_{16}H_{18}FO^{+}$ ([M]+H^{+}) = 245.1336, found 245.1344.

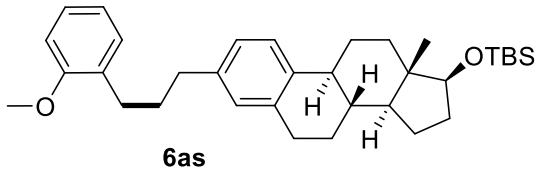
1-(3-(3-Bromophenyl)propyl)-2-methoxybenzene (6ar)



6ar

($C_{16}H_{17}BrO$) colorless oil; 20.8 mg, 68% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.36 (s, 1H), 7.32 – 7.29 (m, 1H), 7.23 – 7.04 (m, 4H), 6.95 – 6.79 (m, 2H), 3.82 (s, 3H), 2.67 – 2.61 (m, 4H), 1.94 – 1.87 (m, 2H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 157.4, 144.9, 131.4, 130.3, 129.7, 128.7, 127.1, 127.0, 122.2, 120.3, 110.2, 55.2, 35.2, 31.0, 29.7, 29.6. **IR** (film, cm^{-1}): 2924, 2854, 1596, 1566, 1492, 1463, 1438, 1289, 1241, 1034, 996, 776, 751, 691, 436. **HRMS** (ESI-TOF) calcd for $C_{16}H_{18}BrO^{+}$ ([M]+H^{+}) = 305.0536, found 305.0523.

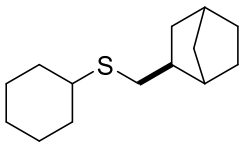
Tert-butyl({(8*R*,9*S*,13*S*,14*S*,17*S*)-2-[3-(2-methoxyphenyl)propyl]-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl}oxy)dimethylsilane (6as)



6as

($C_{34}H_{50}O_2Si$) colorless oil; 32.7 mg, 63% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.25 – 7.11 (m, 3H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.94 (s, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 3.83 (s, 3H), 3.70 – 3.62 (m, 1H), 2.90 – 2.79 (m, 2H), 2.76 – 2.65 (m, 2H), 2.65 – 2.54 (m, 2H), 2.35 – 2.33 (m, 1H), 2.27 – 2.18 (m, 1H), 1.97 – 1.87 (m, 4H), 1.71 – 1.63 (m, 1H), 1.54 – 1.14 (m, 8H), 0.91 (s, 9H), 0.75 (s, 3H), 0.05 (s, 3H), 0.04 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 157.4, 139.7, 137.7, 136.5, 130.8, 129.7, 128.9, 126.8, 125.6, 125.2, 120.2, 110.1, 81.7, 55.2, 55.2, 49.7, 44.4, 43.5, 38.7, 37.2, 35.1, 31.2, 30.9, 30.0, 29.6, 27.3, 26.2, 25.8, 23.2, 18.1, 11.3, -4.4, -4.8. **IR** (film, cm^{-1}): 2928, 2855, 1601, 1494, 1463, 1244, 1139, 1059, 1034, 880, 835, 775, 750. **HRMS** (ESI-TOF) calcd for $C_{34}H_{51}O_2Si^{+}$ ([M]+H^{+}) = 519.3653, found 519.3657.

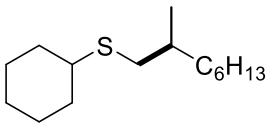
(Bicyclo[2.2.1]heptan-2-ylmethyl)(cyclohexyl)sulfane (9aa)



9aa

($C_{14}H_{24}S$) colorless oil; 44.4 mg, 99% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 2.62 – 2.57 (m, 1H), 2.47 (dd, *J* = 12.2, 8.0 Hz, 1H), 2.30 (dd, *J* = 12.2, 8.0 Hz, 1H), 2.20 (s, 1H), 2.12 (s, 1H), 2.00 – 1.91 (m, 2H), 1.77 – 1.73 (m, 2H), 1.63 – 1.54 (m, 2H), 1.48 – 1.41 (m, 3H), 1.34 – 1.22 (m, 6H), 1.17 – 1.04 (m, 4H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 43.6, 42.2, 40.9, 38.1, 36.8, 36.6, 35.1, 33.8, 33.7, 29.8, 28.6, 26.1, 25.8. **IR** (film, cm^{-1}): 2927, 2852, 1448, 1303, 1263, 1201, 999, 922, 885, 819, 746, 699. **HRMS** (ESI-TOF) calcd for $C_{14}H_{25}S^+$ ([M]+H$^+$) = 225.1671, found 225.1669.

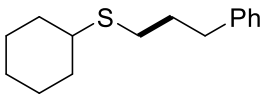
Cyclohexyl(2-methyloctyl)sulfane (9ab)



9ab

($C_{15}H_{30}S$) colorless oil; 34.9 mg, 72% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 2.59 – 2.50 (m, 2H), 2.36 (dd, *J* = 12.4, 7.4 Hz, 1H), 2.05 – 1.89 (m, 2H), 1.78 – 1.74 (m, 2H), 1.64 – 1.55 (m, 2H), 1.46 – 1.39 (m, 1H), 1.36 – 1.12 (m, 14H), 0.96 (d, *J* = 6.6 Hz, 3H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 44.0, 37.8, 36.3, 33.8, 33.6, 31.8, 29.5, 26.9, 26.1, 25.8, 22.6, 19.5, 14.1. **IR** (film, cm^{-1}): 2924, 2852, 1449, 1375, 1262, 1201, 999, 886. **HRMS** (ESI-TOF) calcd for $C_{15}H_{31}S^+$ ([M]+H$^+$) = 243.2141, found 243.2139.

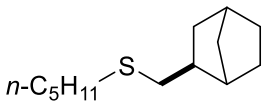
Cyclohexyl(3-phenylpropyl)sulfane (9ac)



9ac

($C_{15}H_{22}S$) colorless oil; 13.6 mg, 29% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.28 (t, *J* = 7.4 Hz, 2H), 7.22 – 7.15 (m, 3H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.65 – 2.60 (m, 1H), 2.55 (t, *J* = 7.4 Hz, 2H), 1.99 – 1.86 (m, 4H), 1.81 – 1.72 (m, 2H), 1.63 – 1.55 (m, 1H), 1.31 – 1.23 (m, 5H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 141.6, 128.4, 128.3, 125.8, 43.4, 34.9, 33.7, 31.5, 29.5, 26.1, 25.8. **IR** (film, cm^{-1}): 3026, 2851, 1603, 1459, 1449, 1261, 1202, 1028, 803, 744, 698, 492. **HRMS** (ESI-TOF) calcd for $C_{15}H_{23}S^+$ ([M]+H$^+$) = 235.1515, found 235.1510.

(Bicyclo[2.2.1]heptan-2-ylmethyl)(pentyl)sulfane (9ba)



9ba

($C_{13}H_{24}S$) colorless oil; 42.0 mg, 99% yield, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 2.56 – 2.35 (m, 3H), 2.27 (dd, *J* = 12.4, 7.6 Hz, 1H), 2.30 – 2.20 (m, 1H), 2.12 (d, *J* = 3.8 Hz, 1H), 1.62 – 1.52 (m, 3H), 1.51 – 1.41 (m, 3H), 1.39 – 1.26 (m, 5H), 1.19 – 1.07 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR** (101 MHz, Chloroform-*d*) δ 41.9, 40.8,

38.9, 38.0, 36.6, 35.1, 32.2, 31.1, 29.8, 29.4, 28.6, 22.3, 13.9. **IR** (film, cm^{-1}): 2947, 2867, 1454, 1378, 1303, 1246, 923, 731. **HRMS** (ESI-TOF) calcd for $C_{13}H_{25}S^+$ ([M]+H^+) = 213.1671, found 213.1670.

9. References

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10. Copies of NMR spectra for catalysts and products

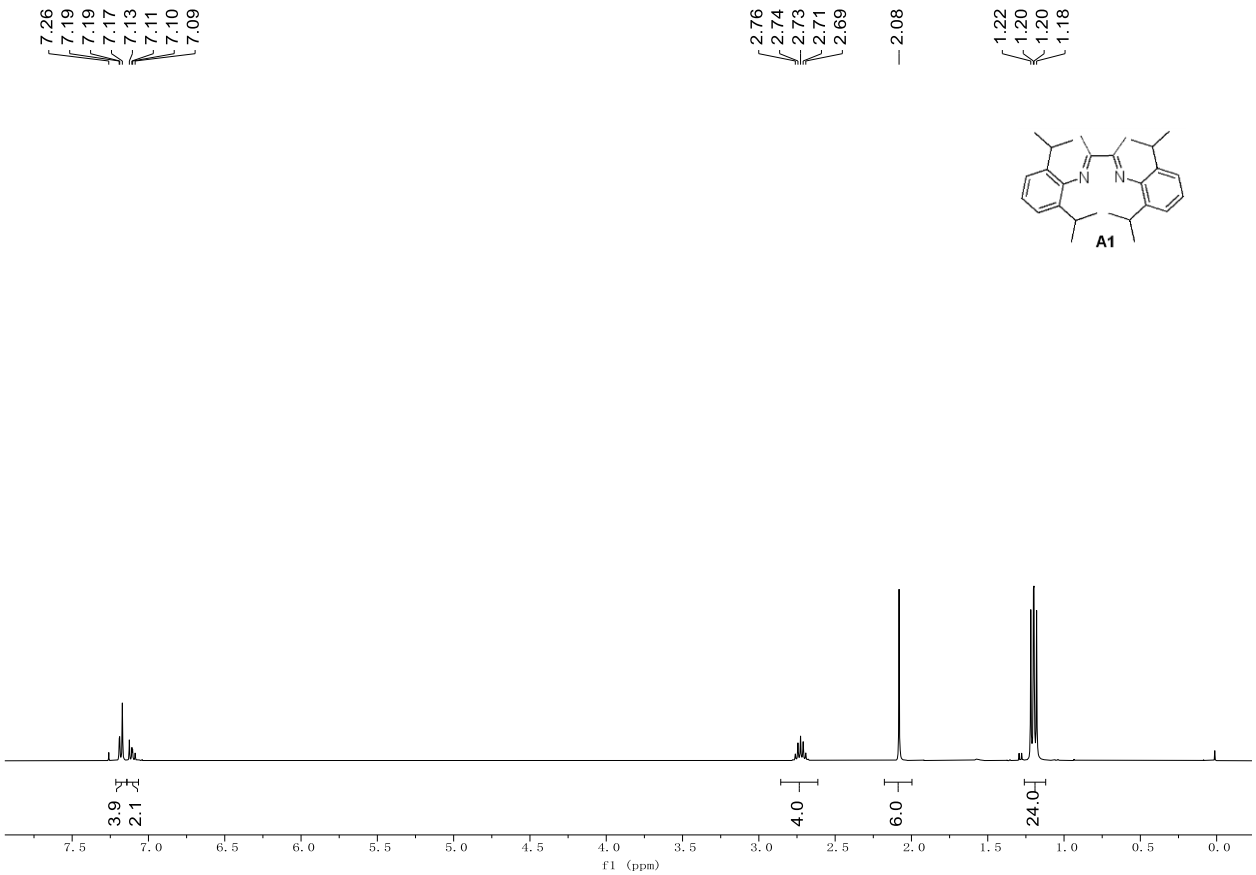

Figure S22. ^{1}H NMR spectrum (400 MHz) of **A1** in $CDCl_3$.

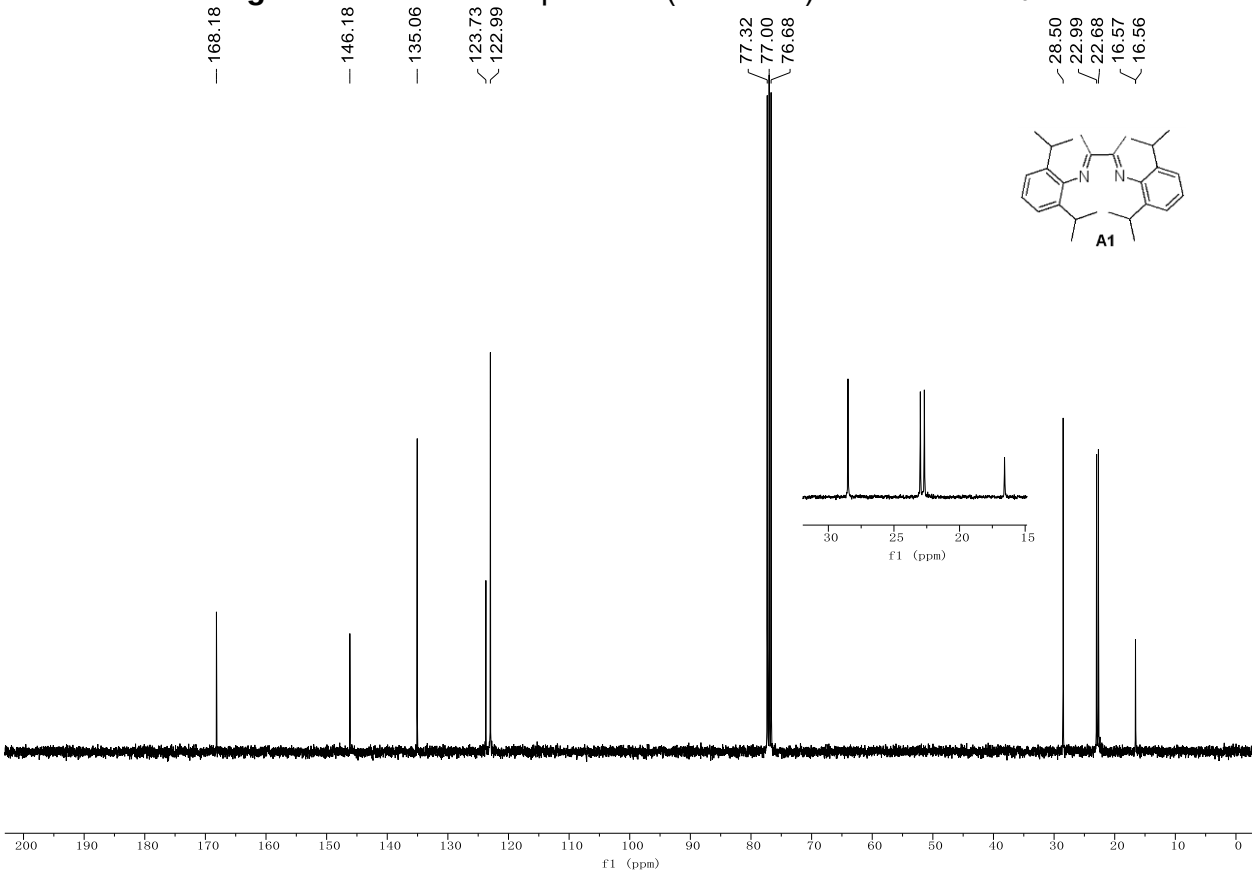

Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **A1** in $CDCl_3$.

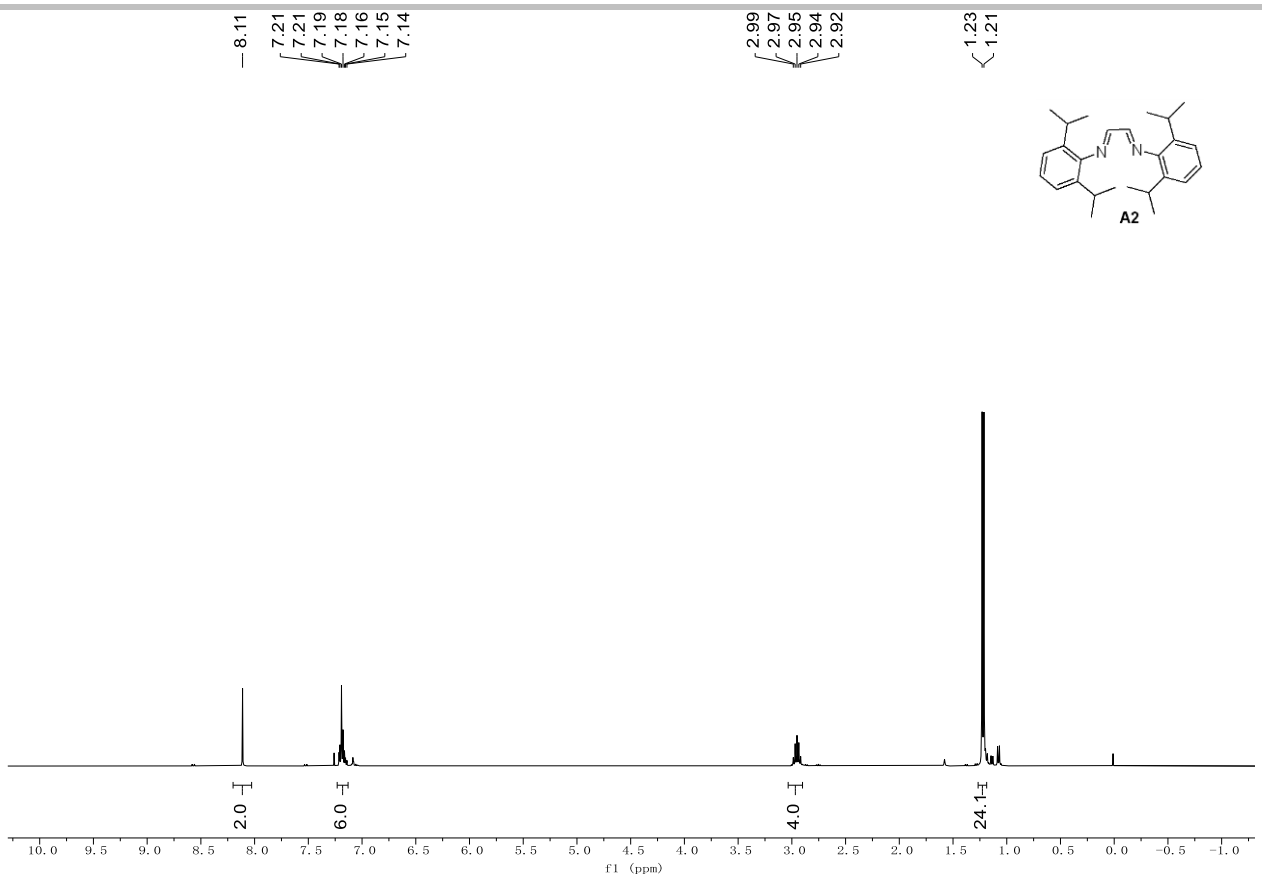

Figure S24. ^{1}H NMR spectrum (400 MHz) of **A2** in $CDCl_3$.

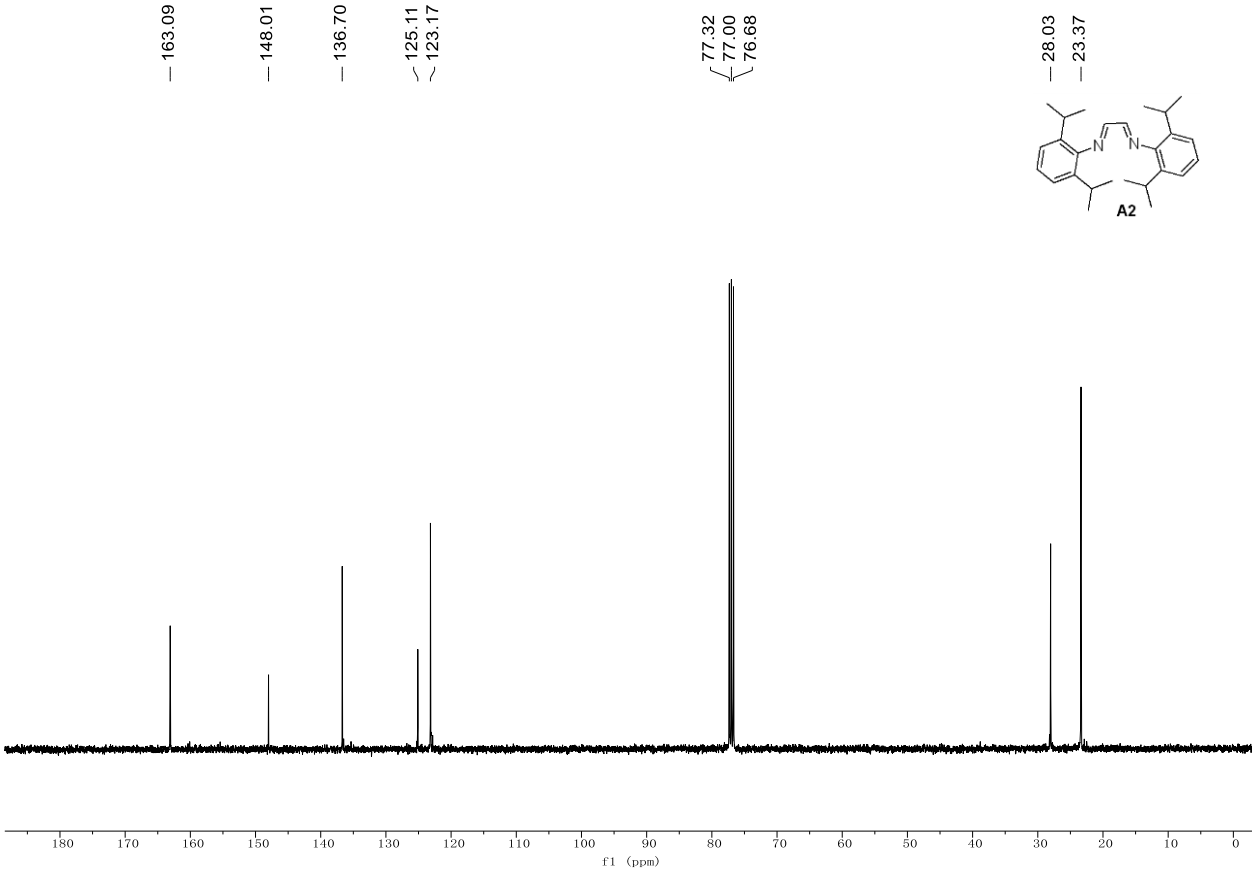

Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **A2** in $CDCl_3$.

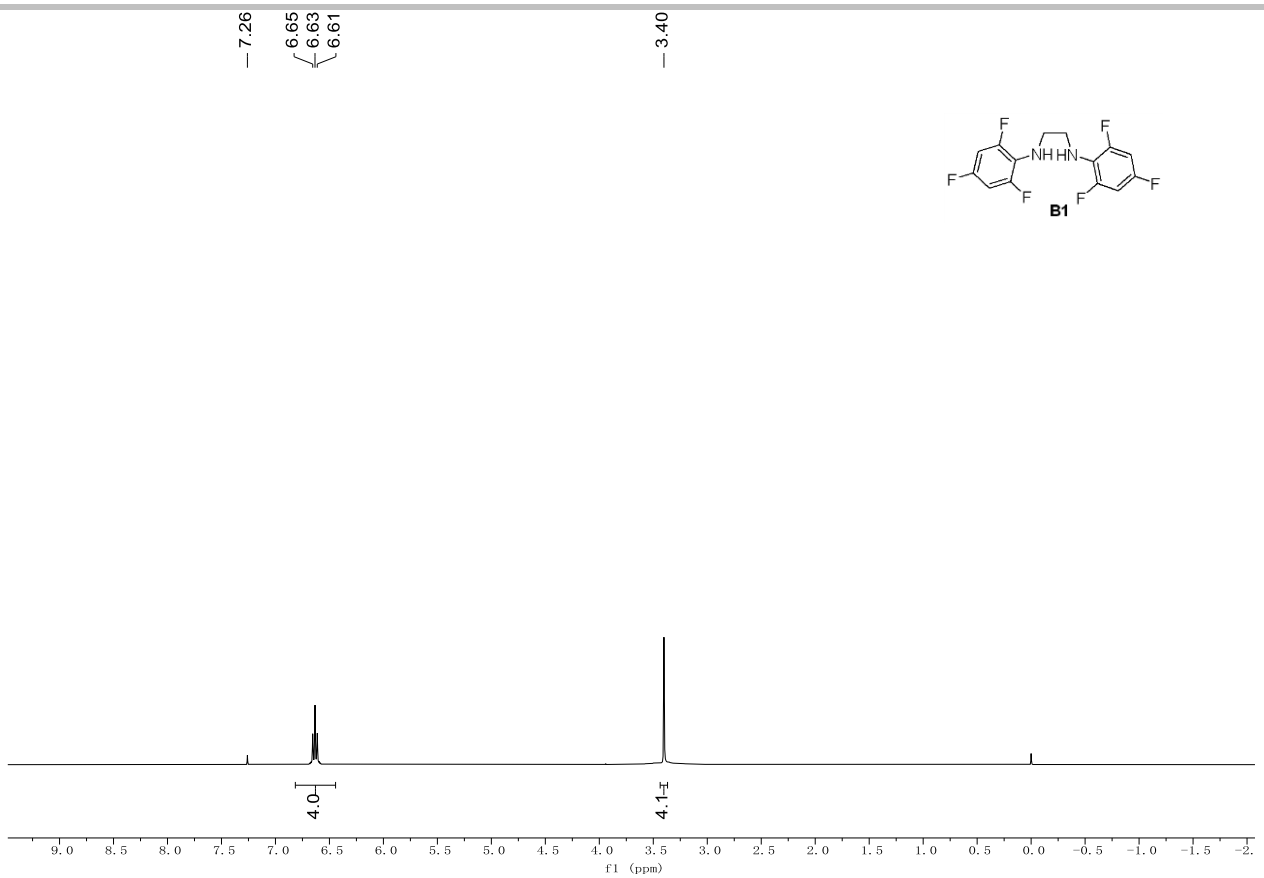

Figure S26. ^{1}H NMR spectrum (400 MHz) of **B1** in $CDCl_3$.

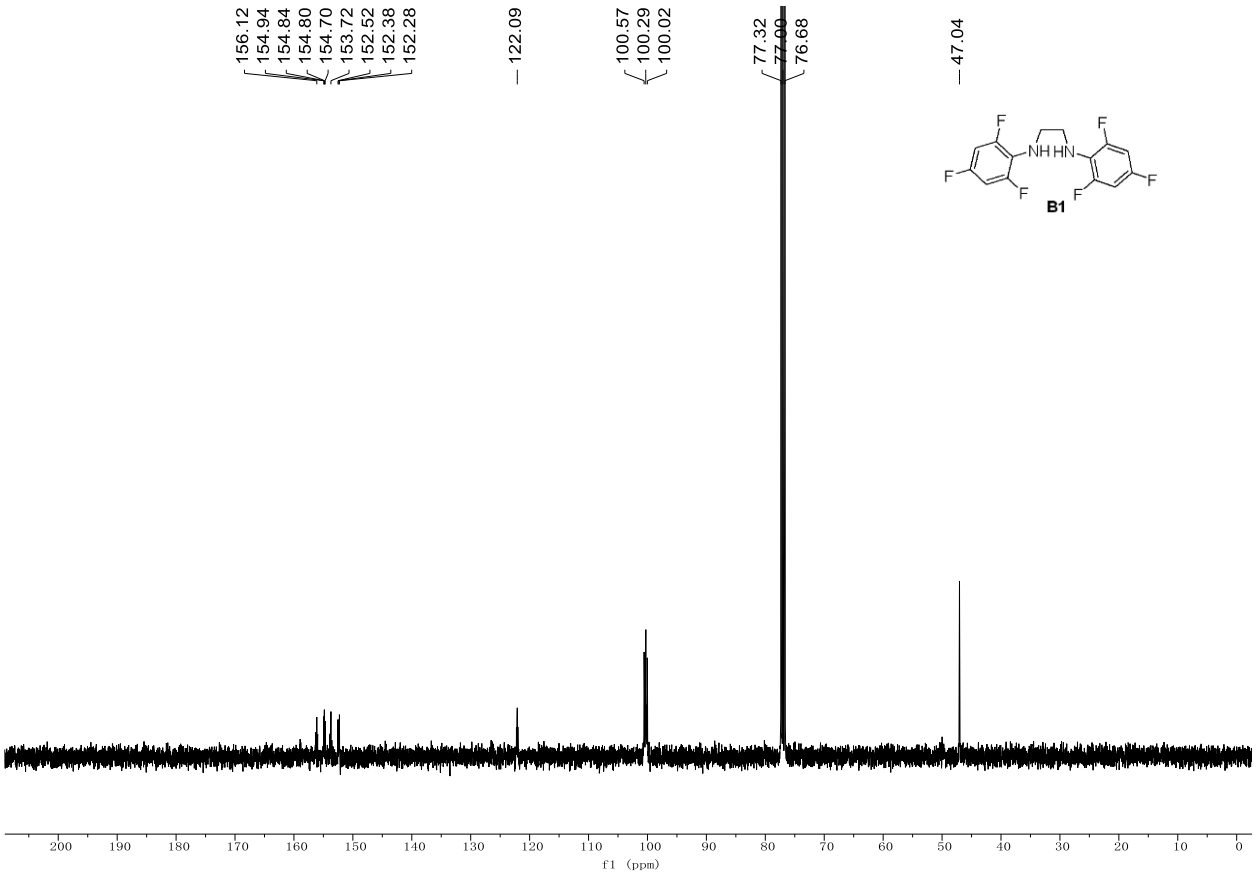

Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **B1** in $CDCl_3$.

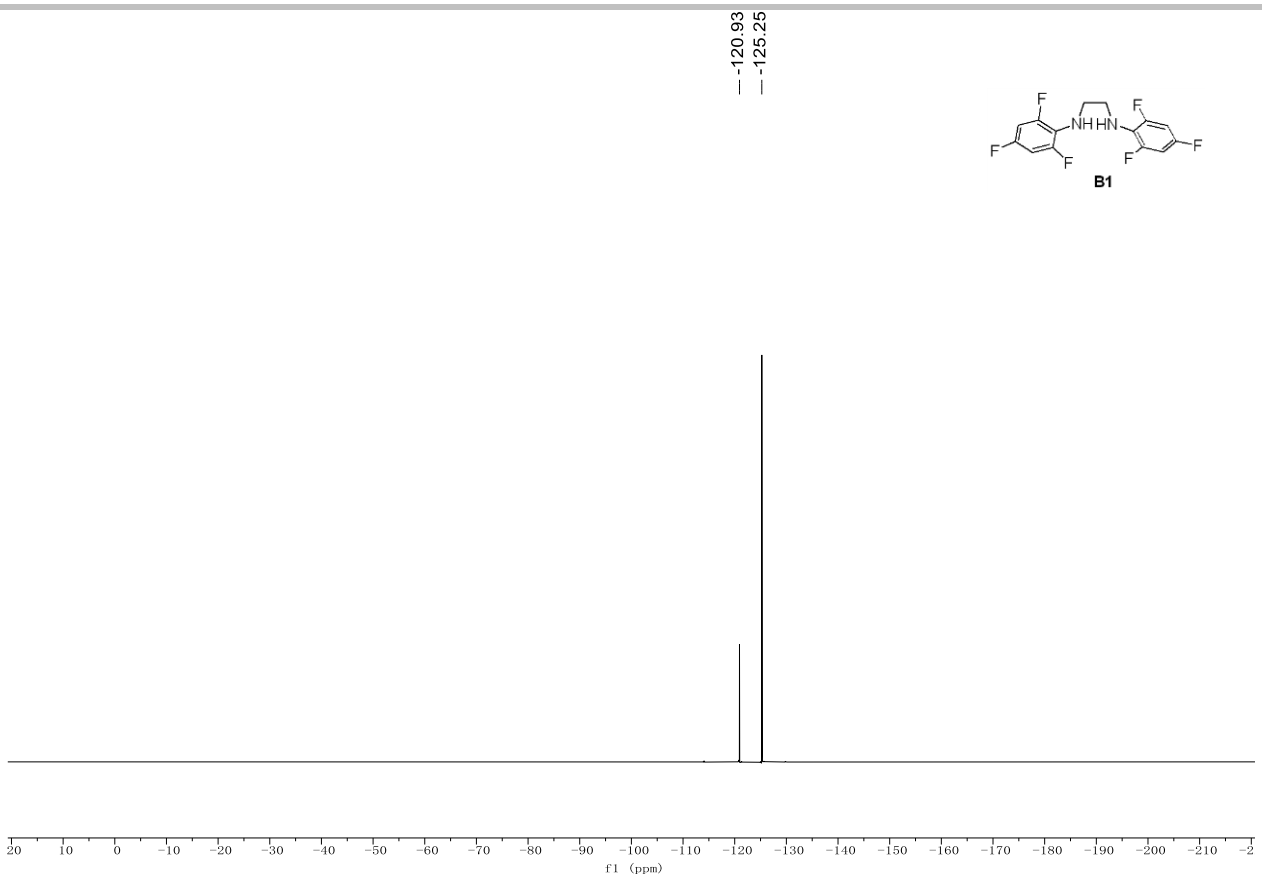

Figure S28. $^{19}F\{^{1}H\}$ NMR spectrum (377 MHz) of **B1** in $CDCl_3$.

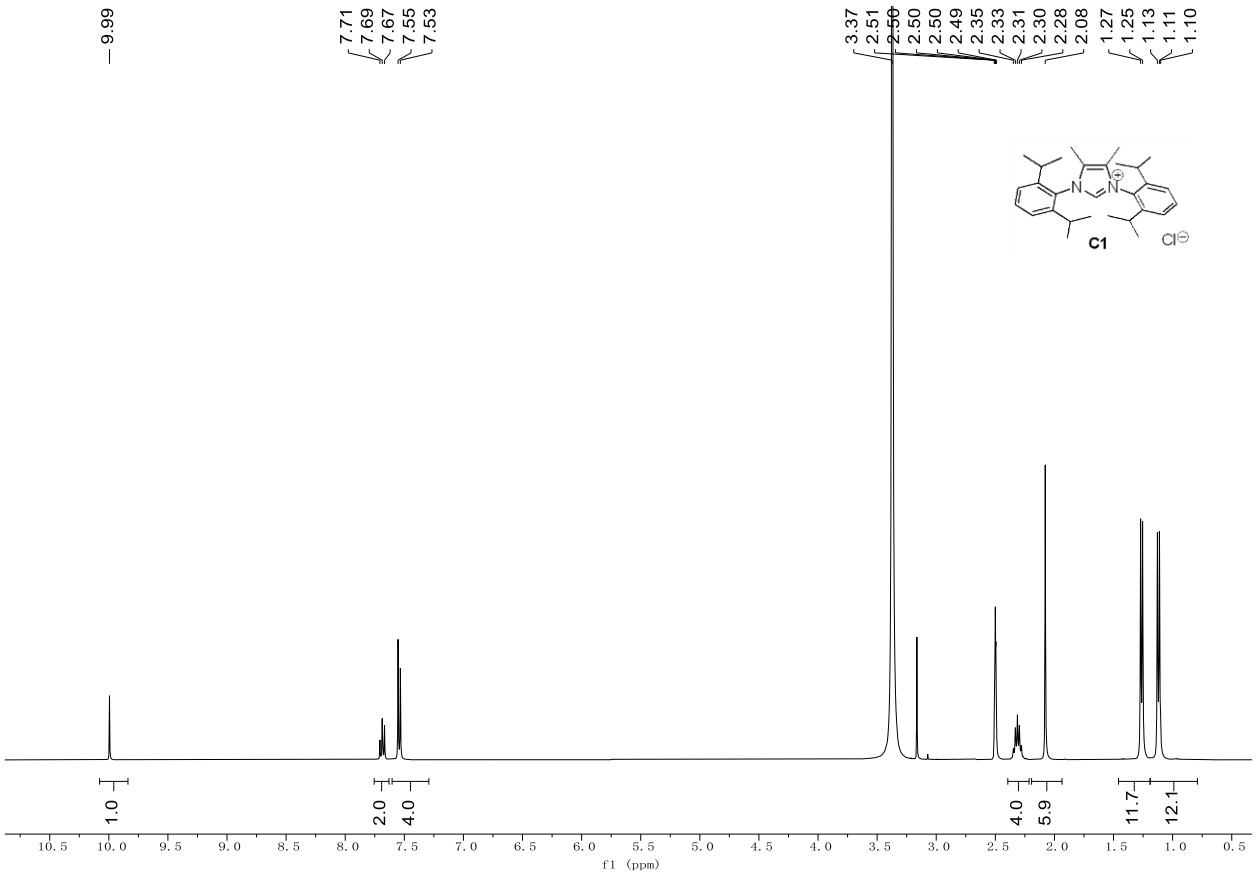

Figure S29. ^{1}H NMR spectrum (400 MHz) of **C1** in DMSO-d_6.

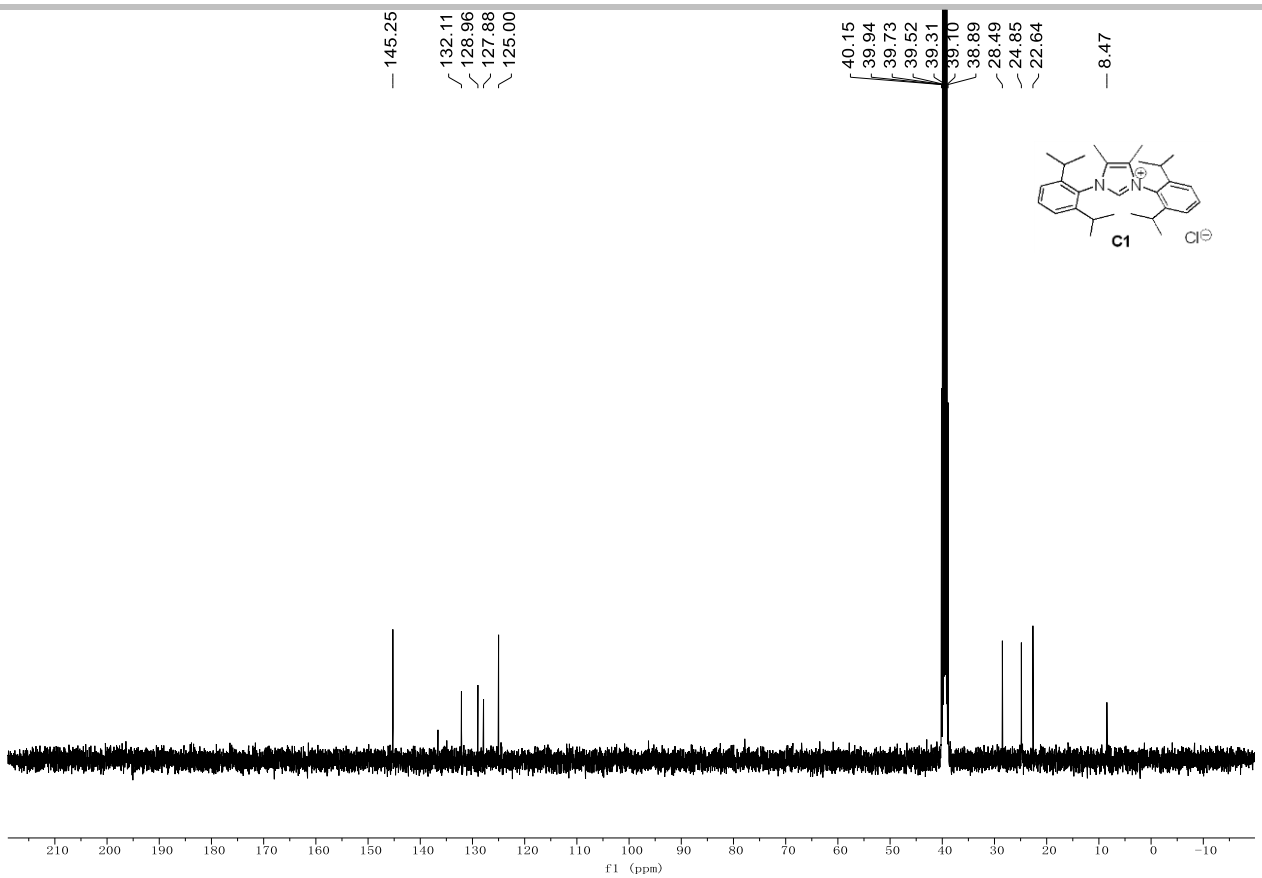

Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **C1** in DMSO-d_6.

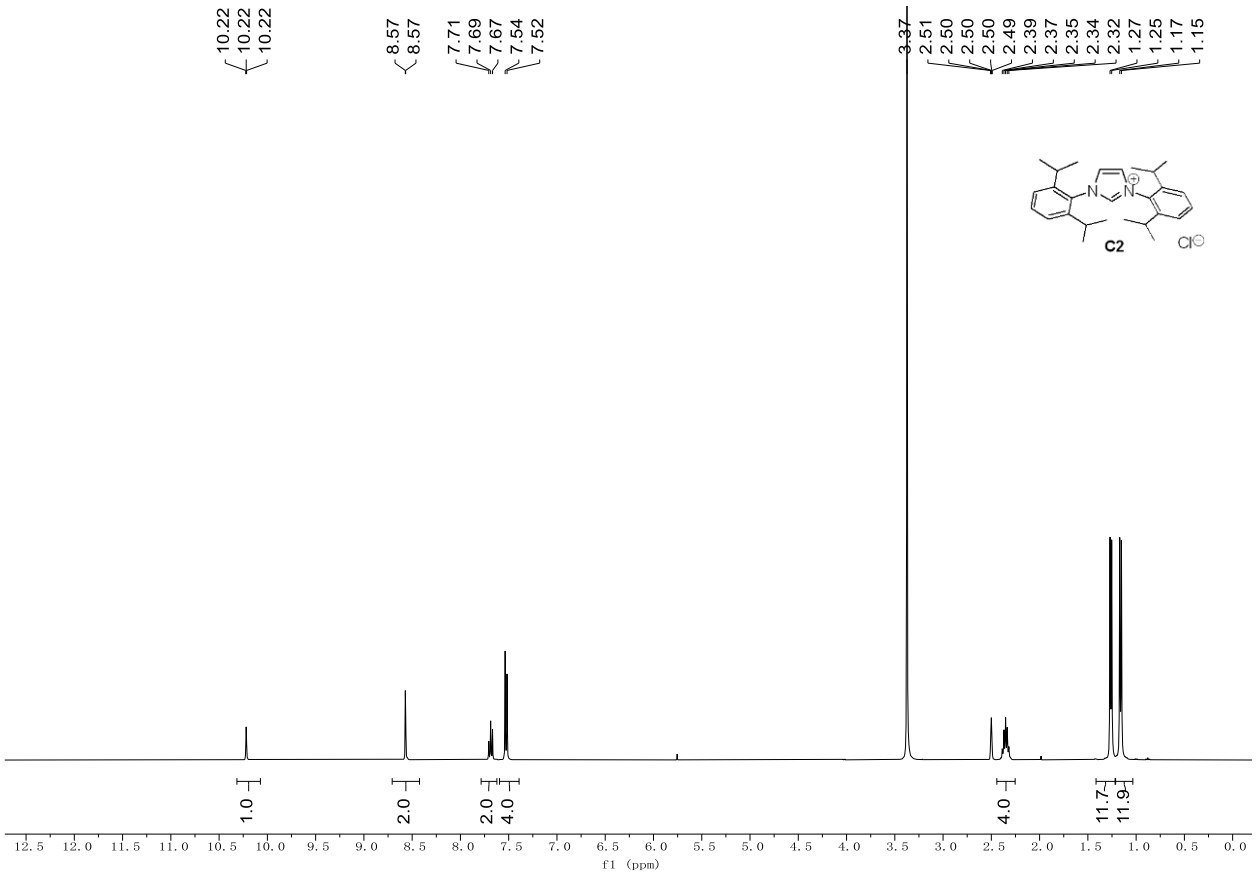

Figure S31. ^{1}H NMR spectrum (400 MHz) of **C2** in DMSO-d_6.

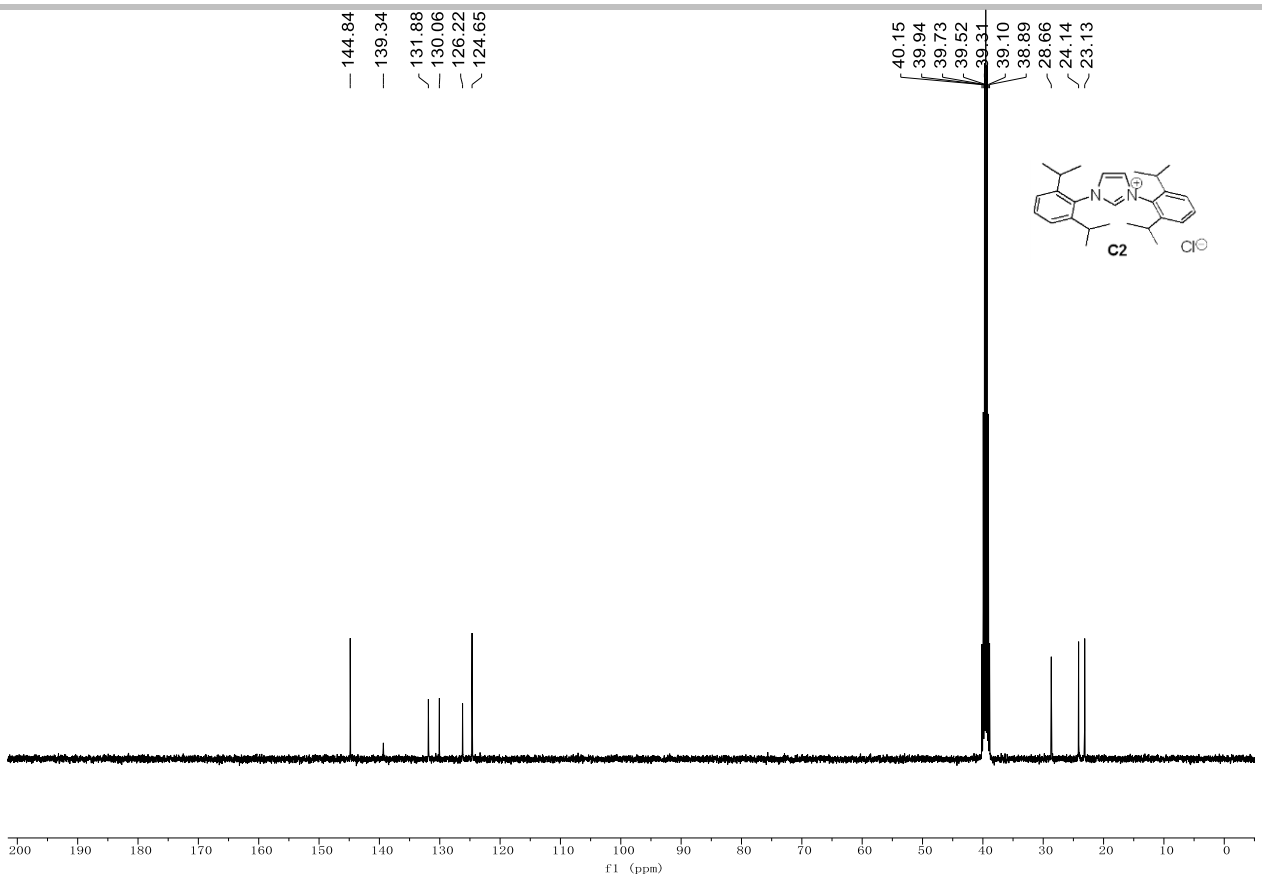

Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **C2** in DMSO-d_6.

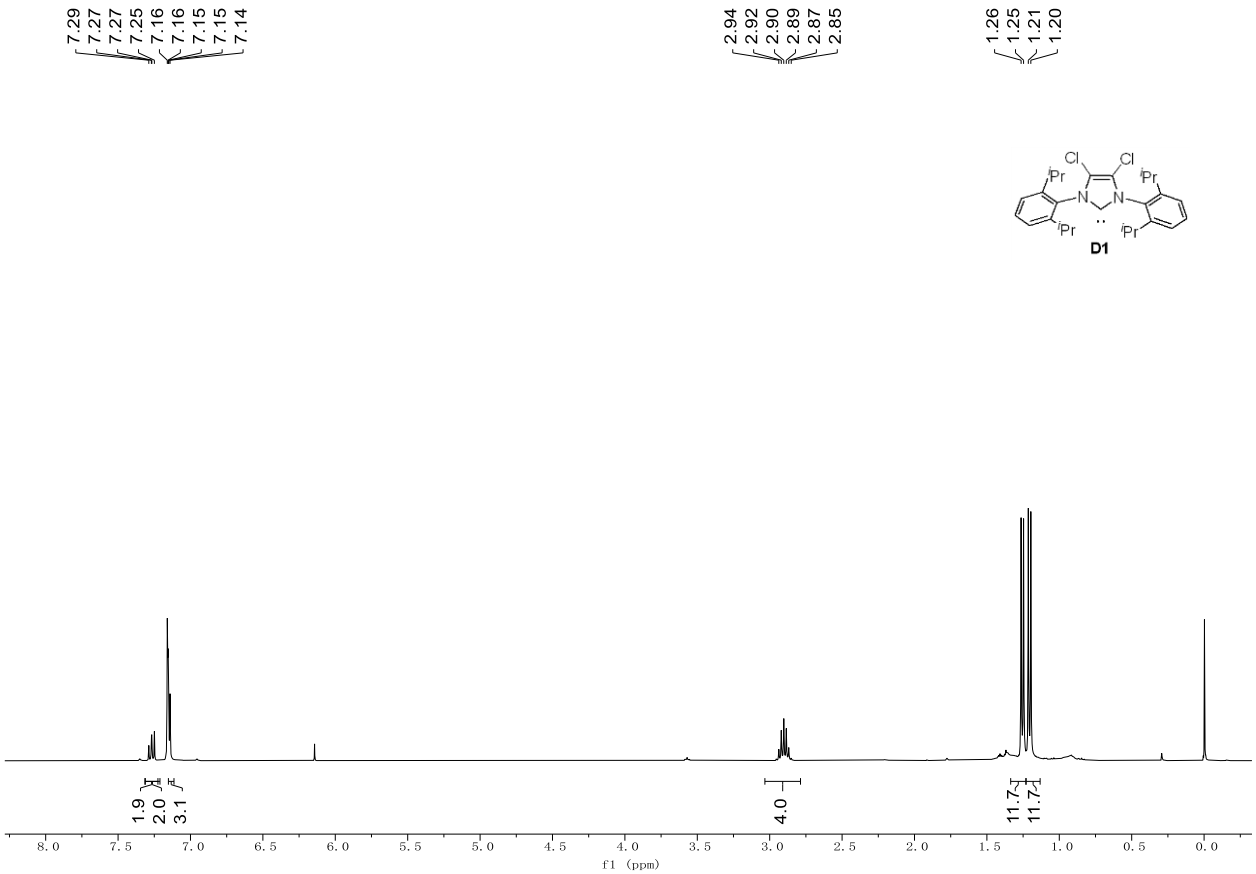

Figure S33. ^{1}H NMR spectrum (400 MHz) of **D1** in C_6D_6.

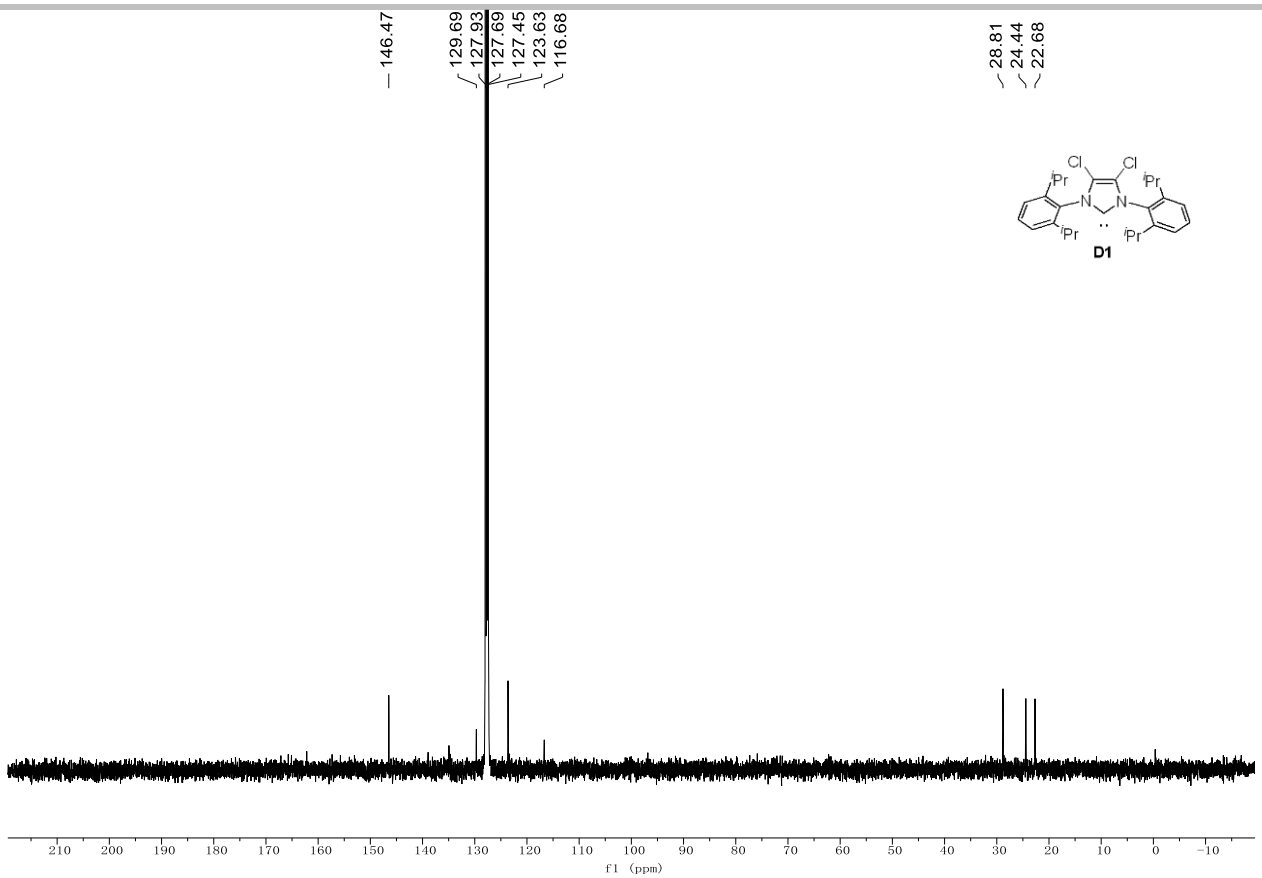

Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **D1** in C_6D_6.

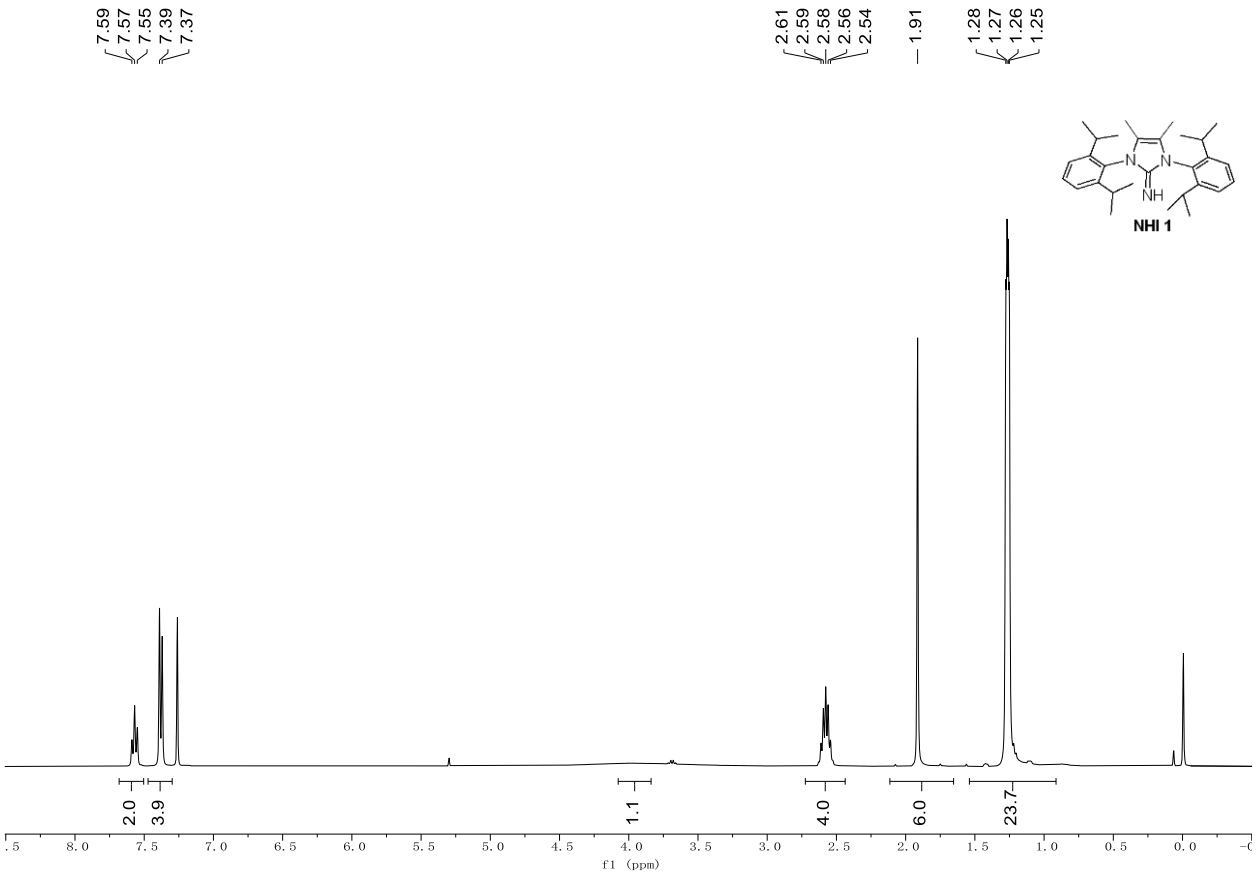

Figure S35. ^{1}H NMR spectrum (400 MHz) of **NHI 1** in $CDCl_3$.

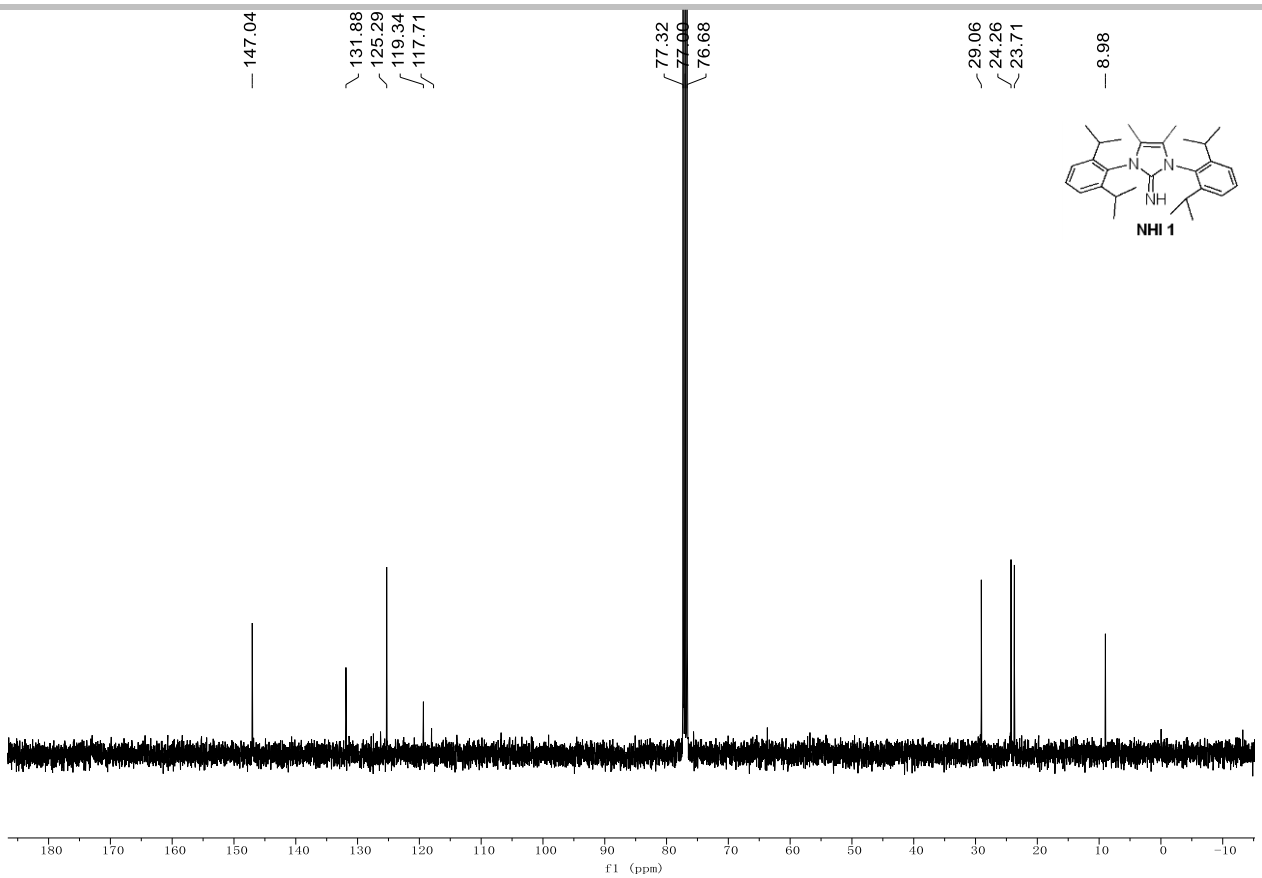

Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **NHI 1** in $CDCl_3$.

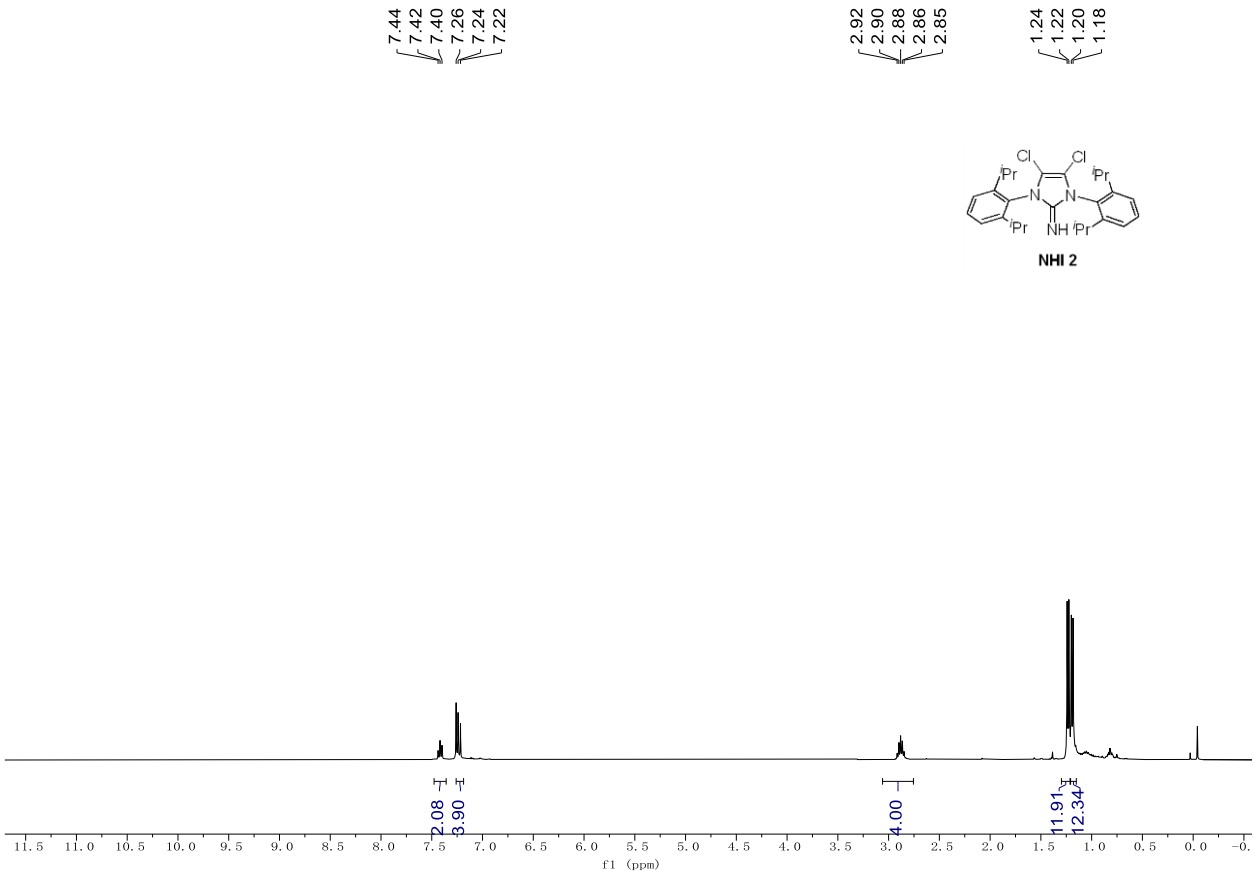

Figure S37. ^{1}H NMR spectrum (400 MHz) of **NHI 2** in $CDCl_3$.

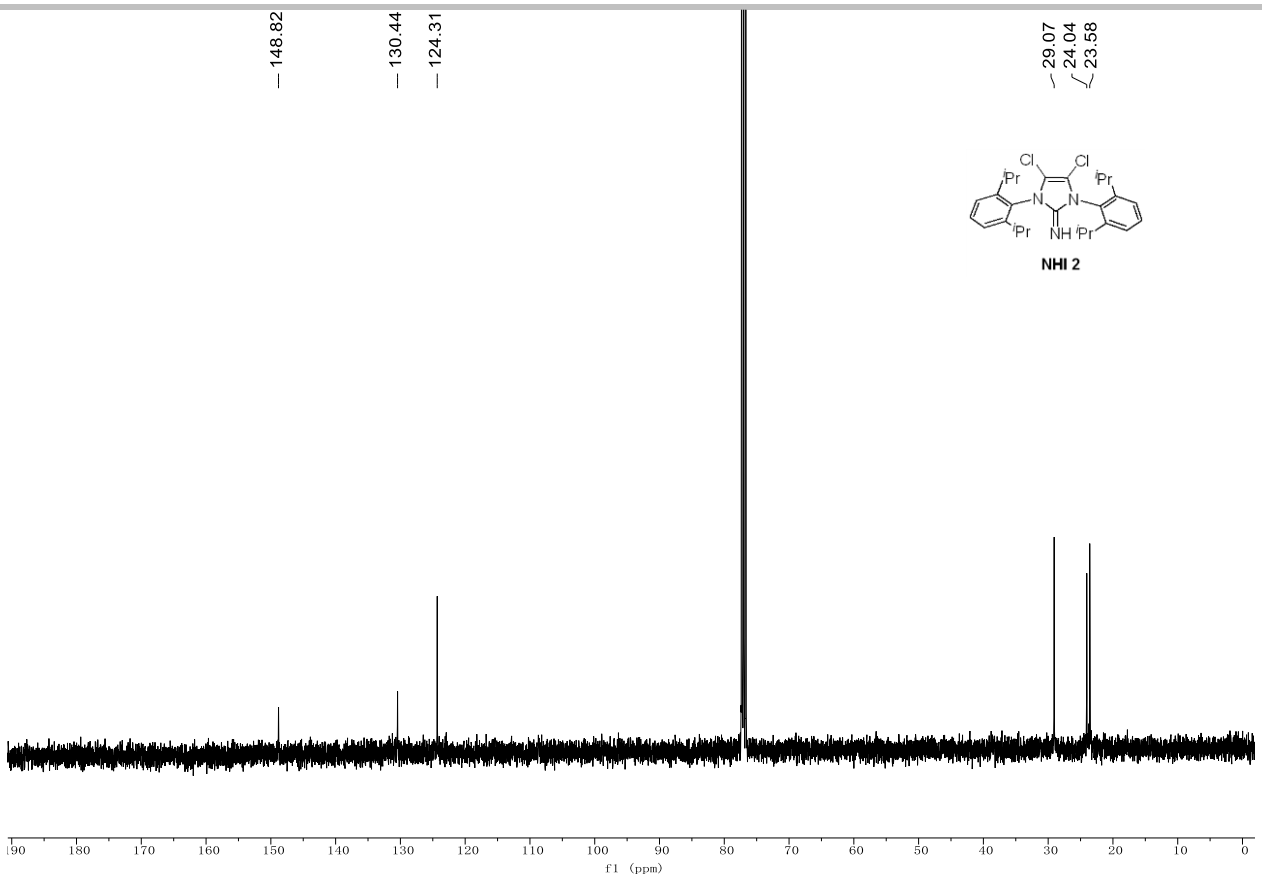

Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **NHI 2** in $CDCl_3$.

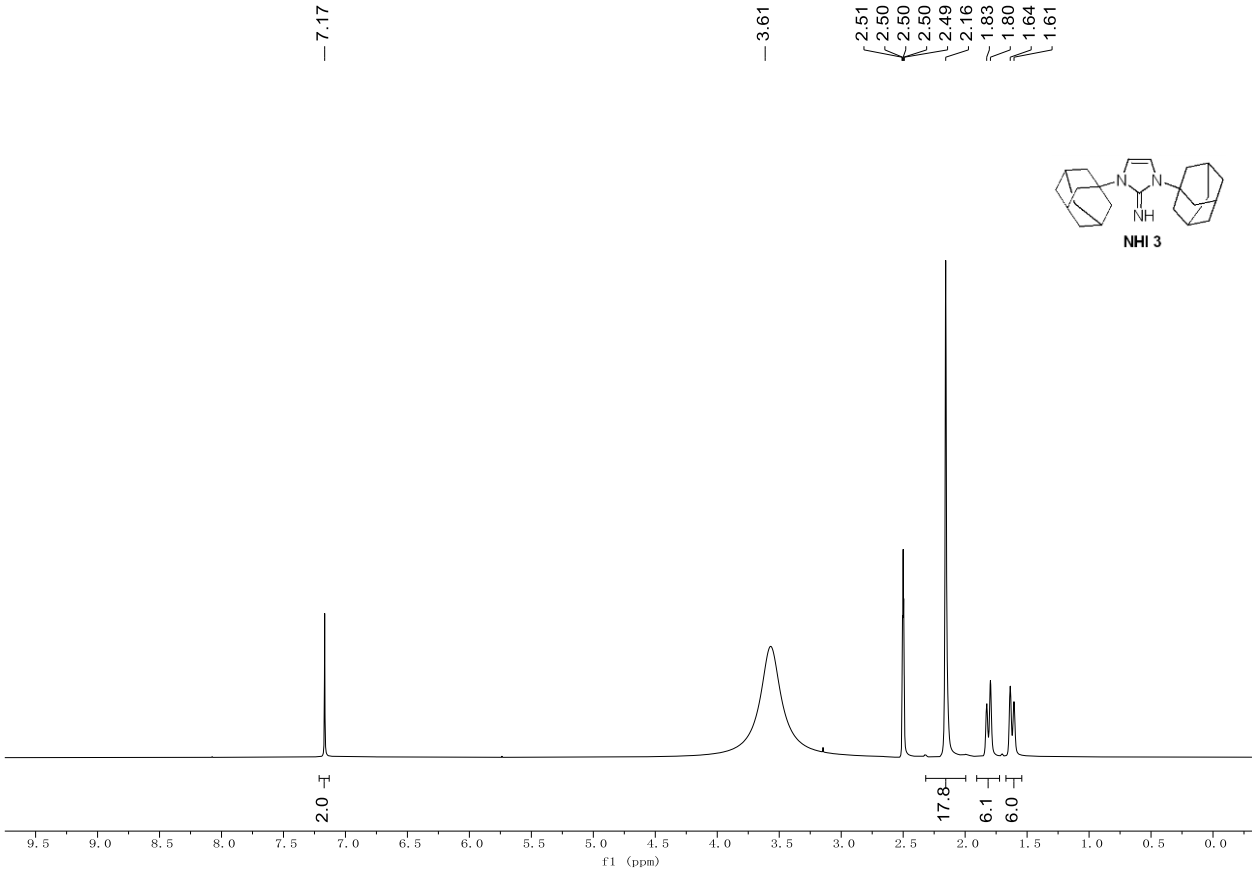

Figure S39. ^{1}H NMR spectrum (400 MHz) of **NHI 3** in DMSO-d_6.

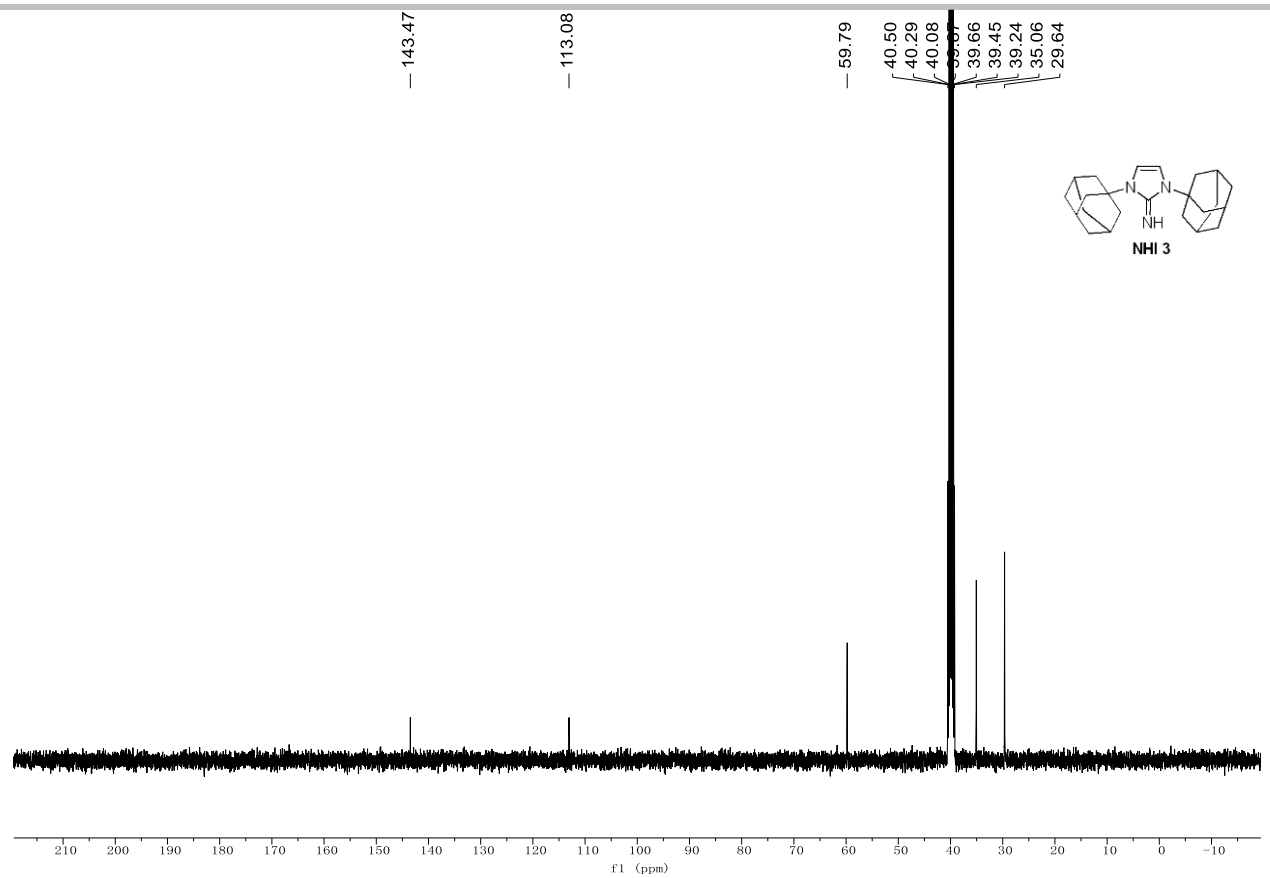

Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **NHI 3** in DMSO-d_6.

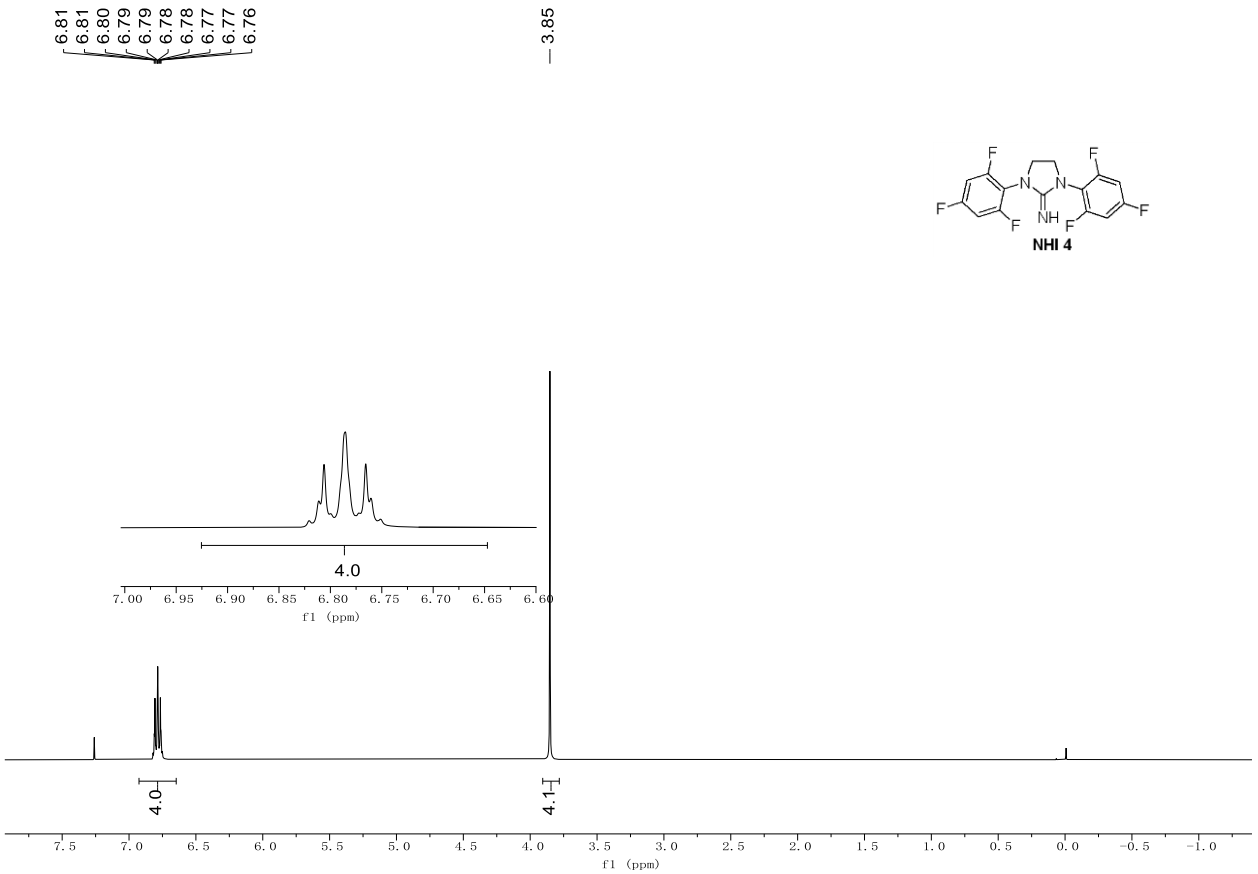

Figure S41. ^{1}H NMR spectrum (400 MHz) of **NHI 4** in $CDCl_3$.

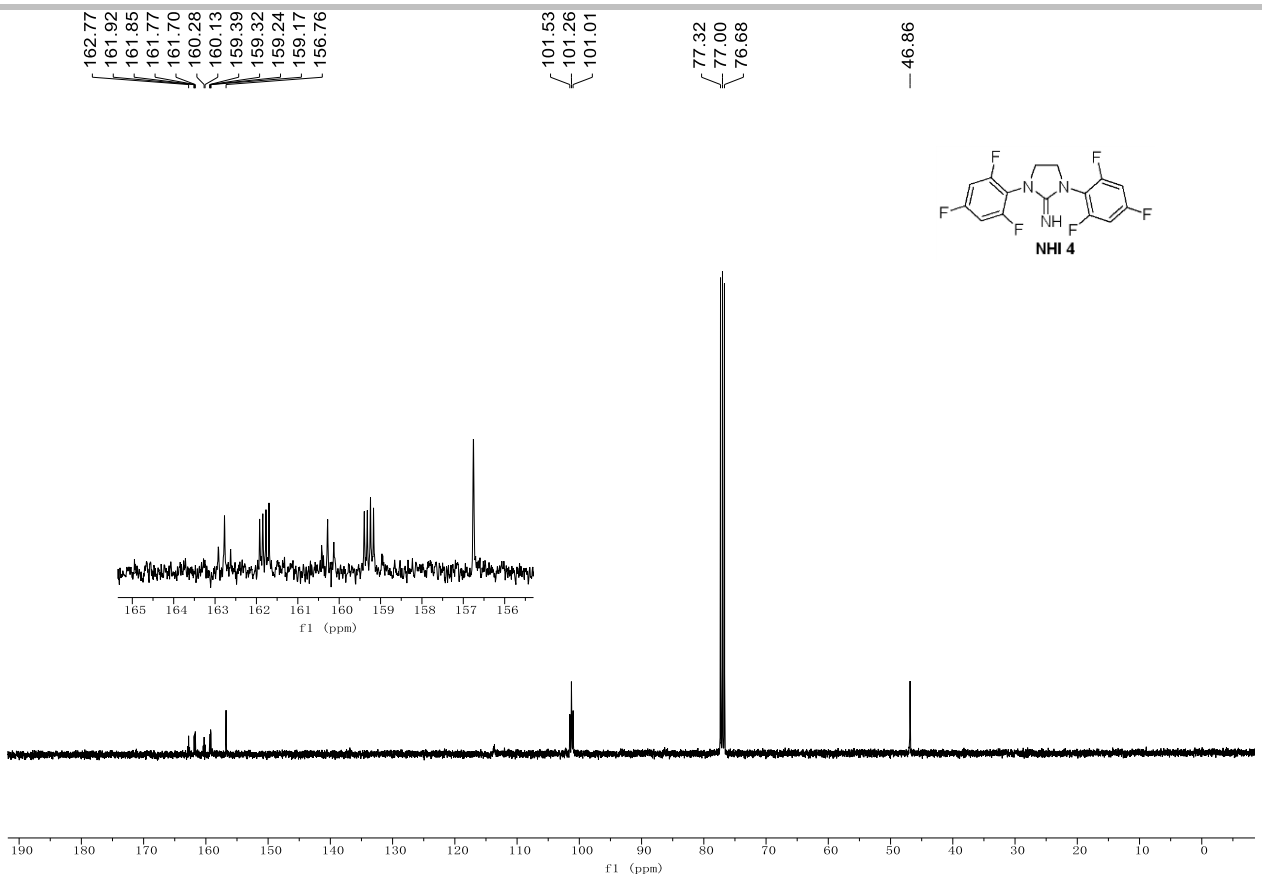

Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **NHI 4** in $CDCl_3$.

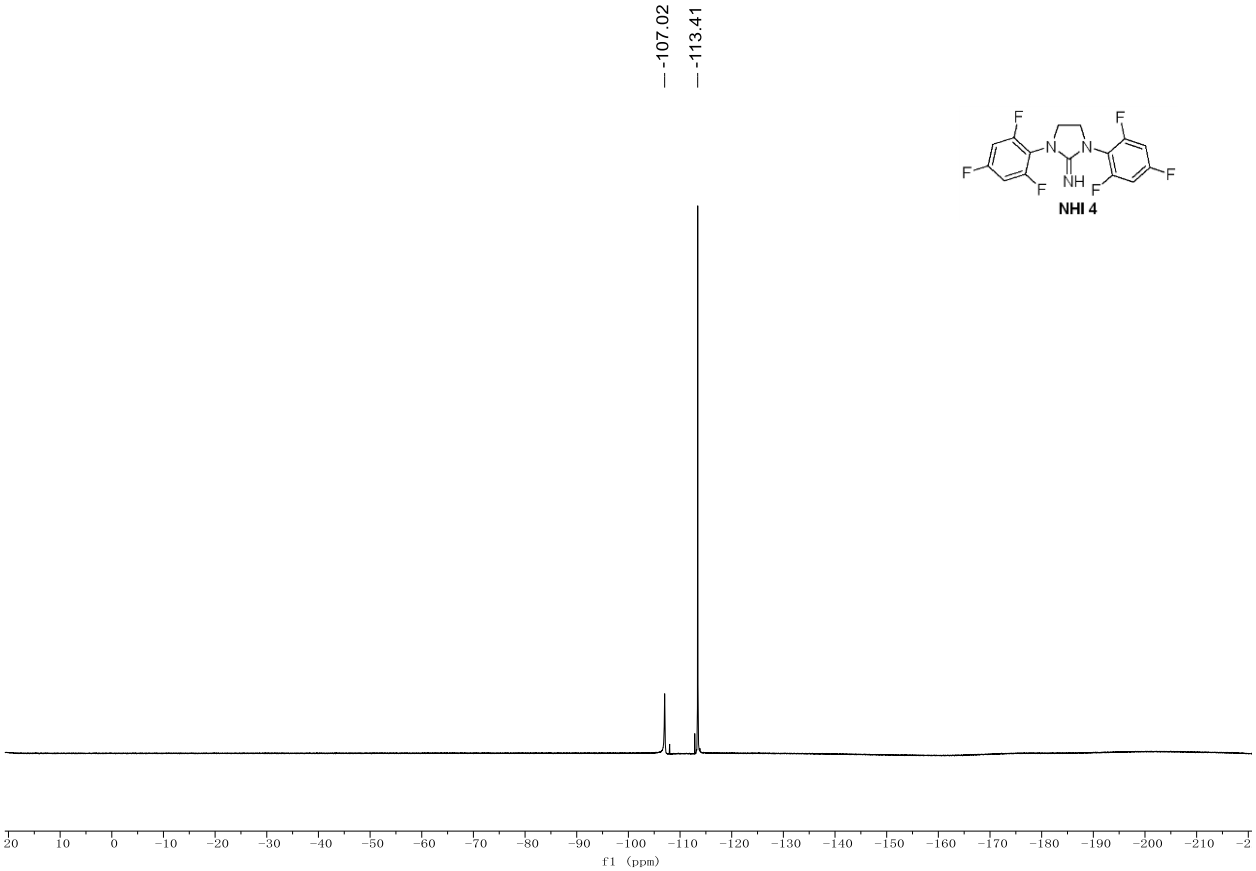

Figure S43. $^{19}F\{^{1}H\}$ NMR spectrum (377 MHz) of **NHI 4** in $CDCl_3$.

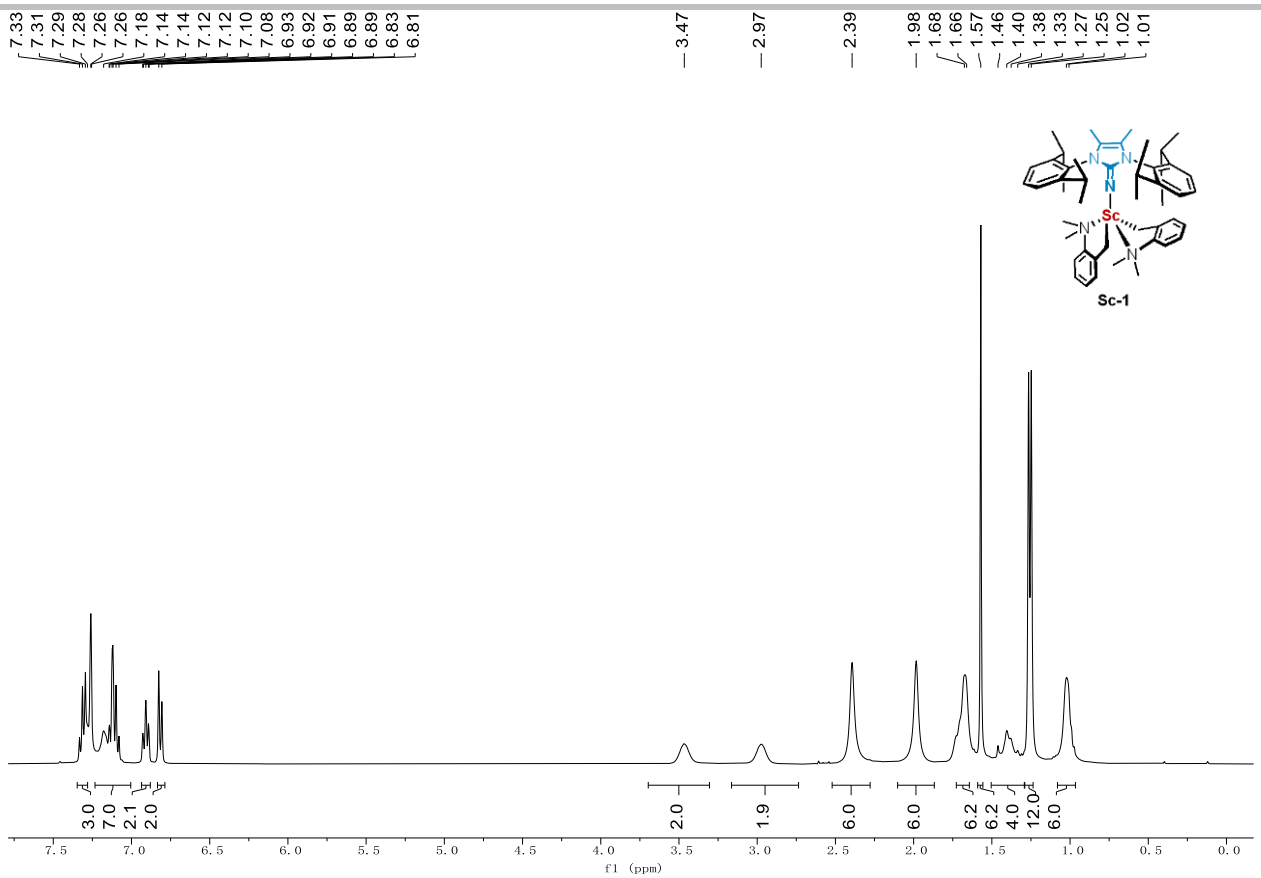

Figure S44. ^{1}H NMR spectrum (400 MHz) of **Sc-1** in C_6D_6.

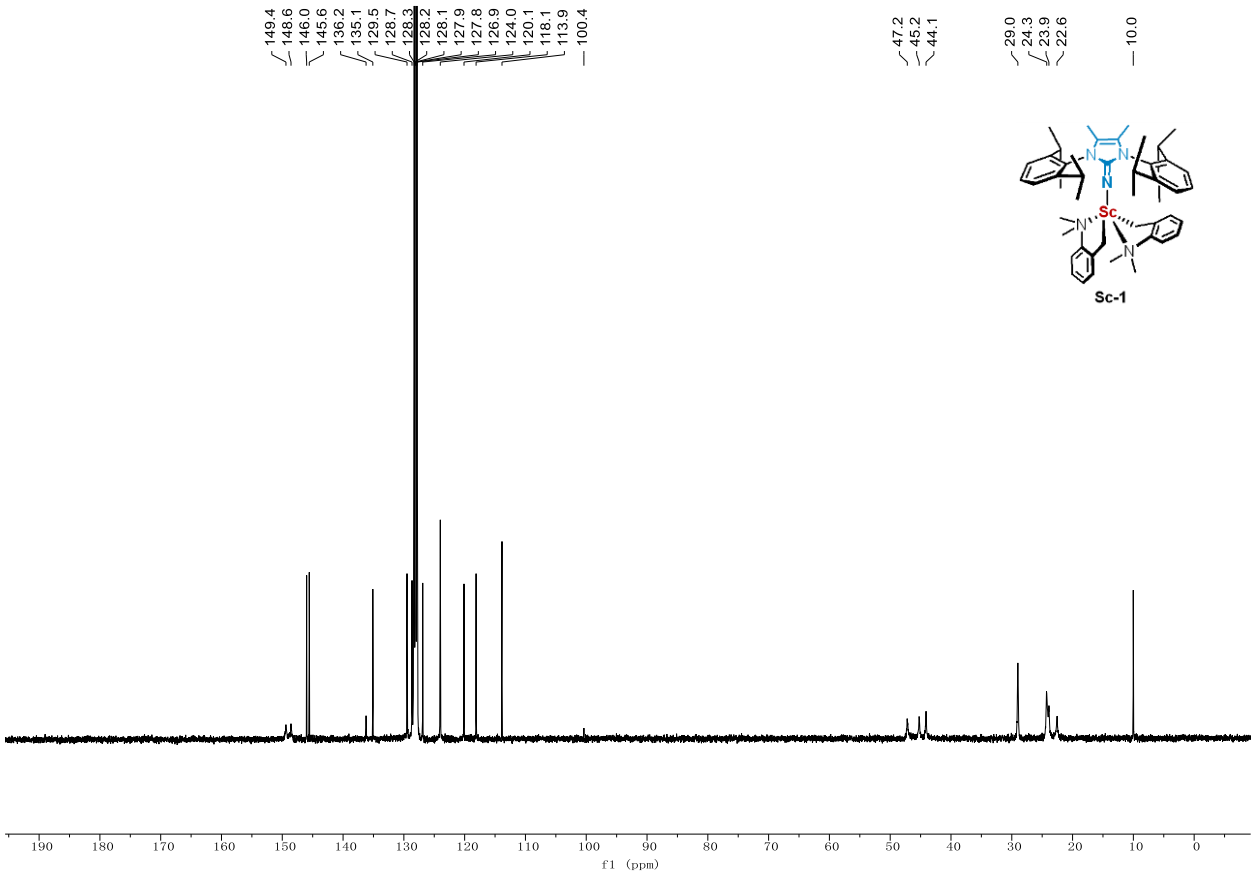

Figure S45. ^{13}C{^{1}H} NMR spectrum (101 MHz) of **Sc-1** in C_6D_6.

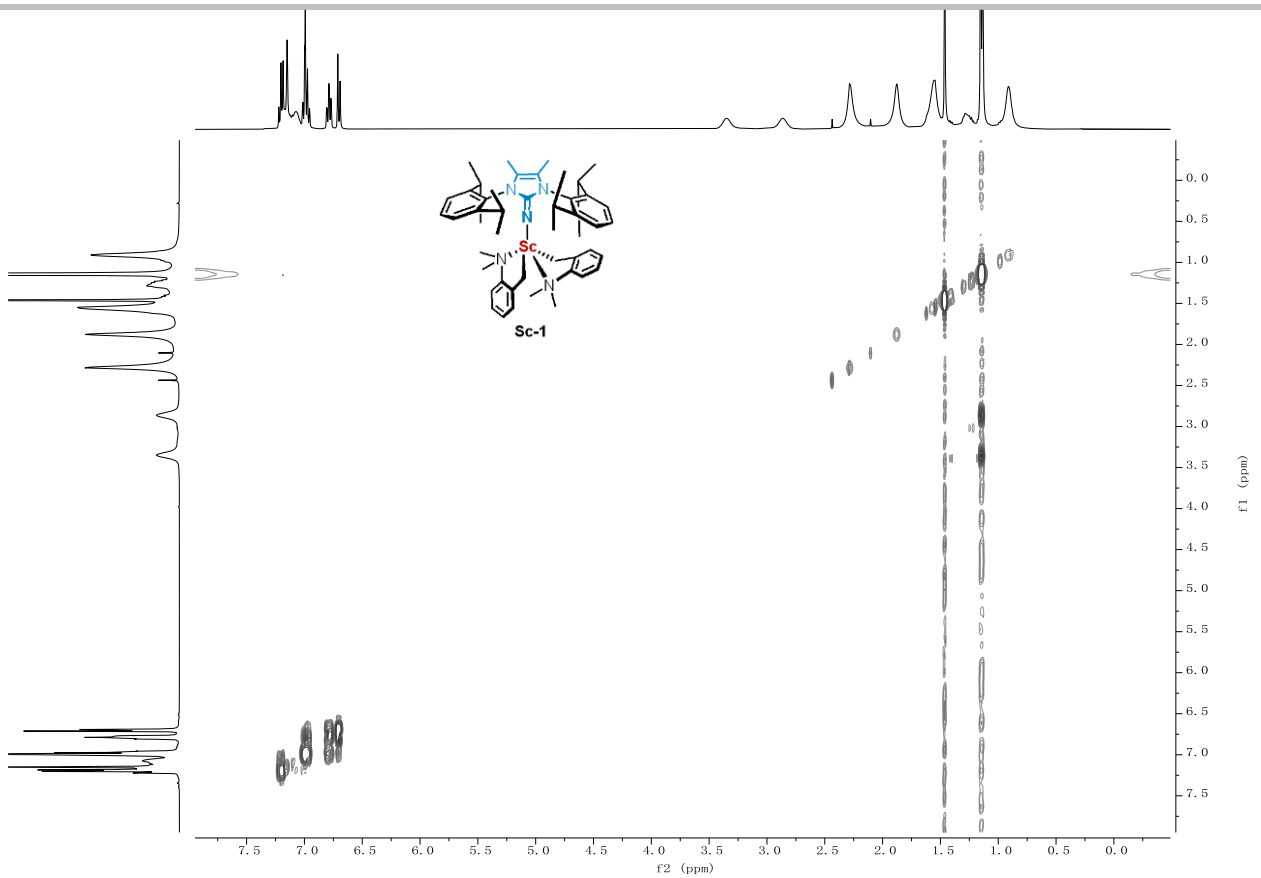

Figure S46. 2D ^{1}H-^{1}H COSY NMR spectrum of **Sc-1** in C_6D_6.

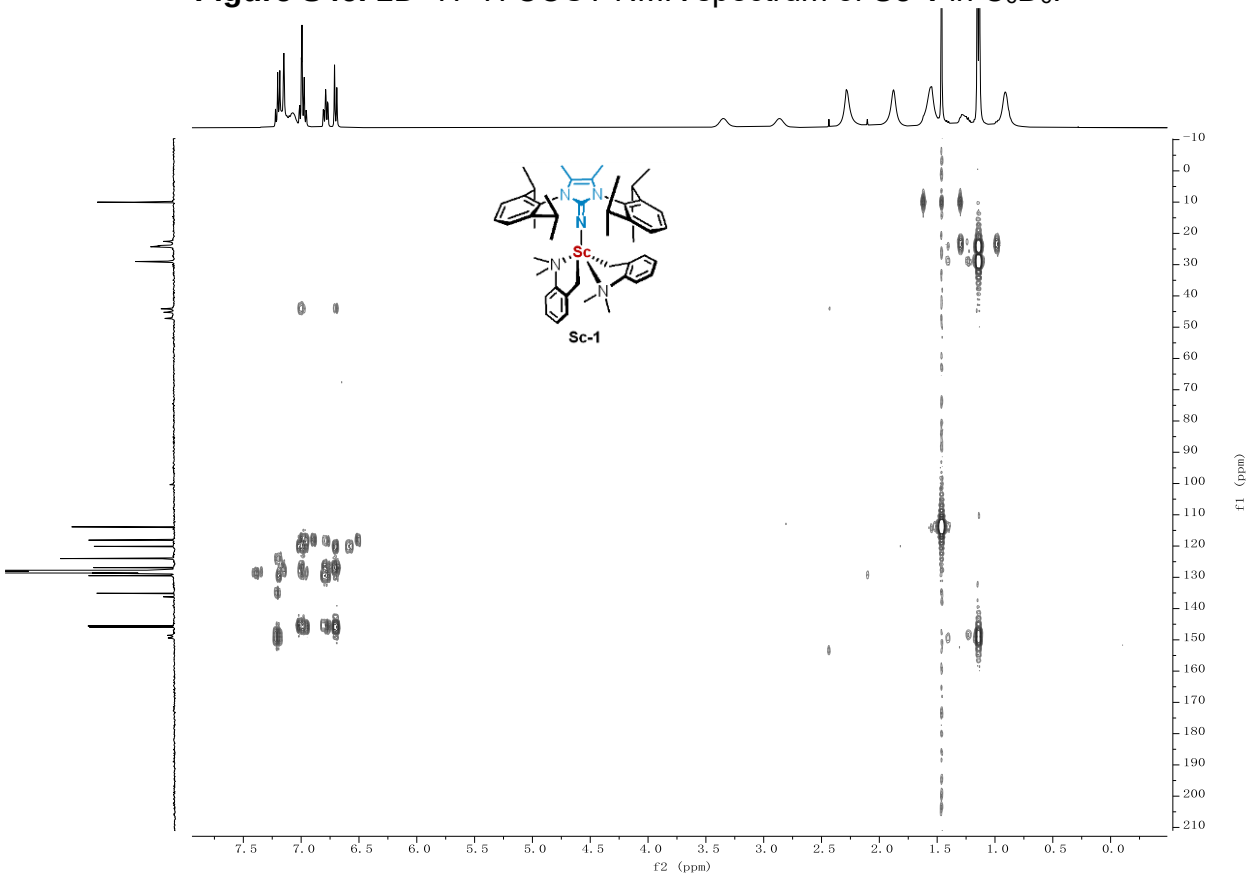

Figure S47. 2D ^{1}H-^{13}C HMBC NMR spectrum of **Sc-1** in C_6D_6.

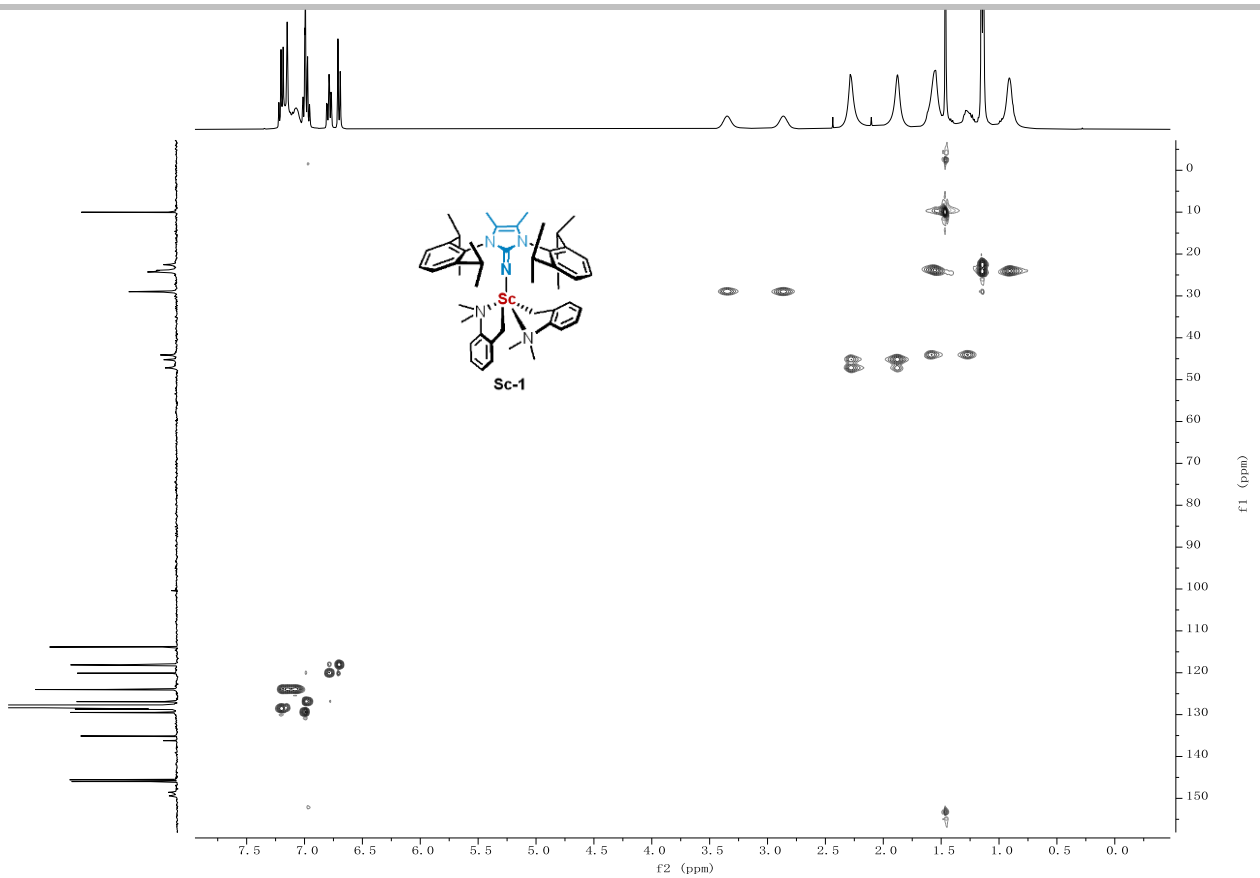

Figure S48. 2D ^{1}H-^{13}C HSQC NMR spectrum of **Sc-1** in C_6D_6.

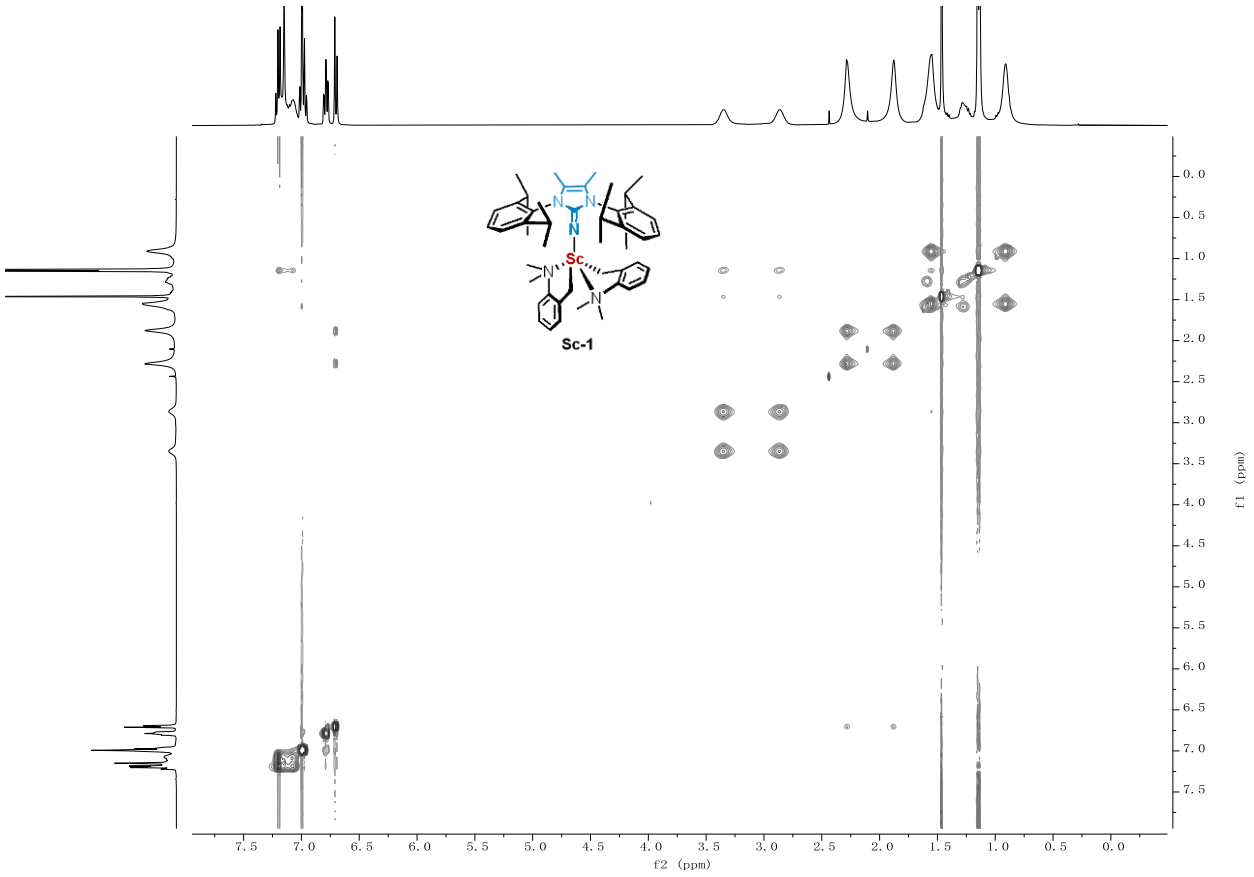

Figure S49. 2D NOESY NMR spectrum of **Sc-1** in C_6D_6.

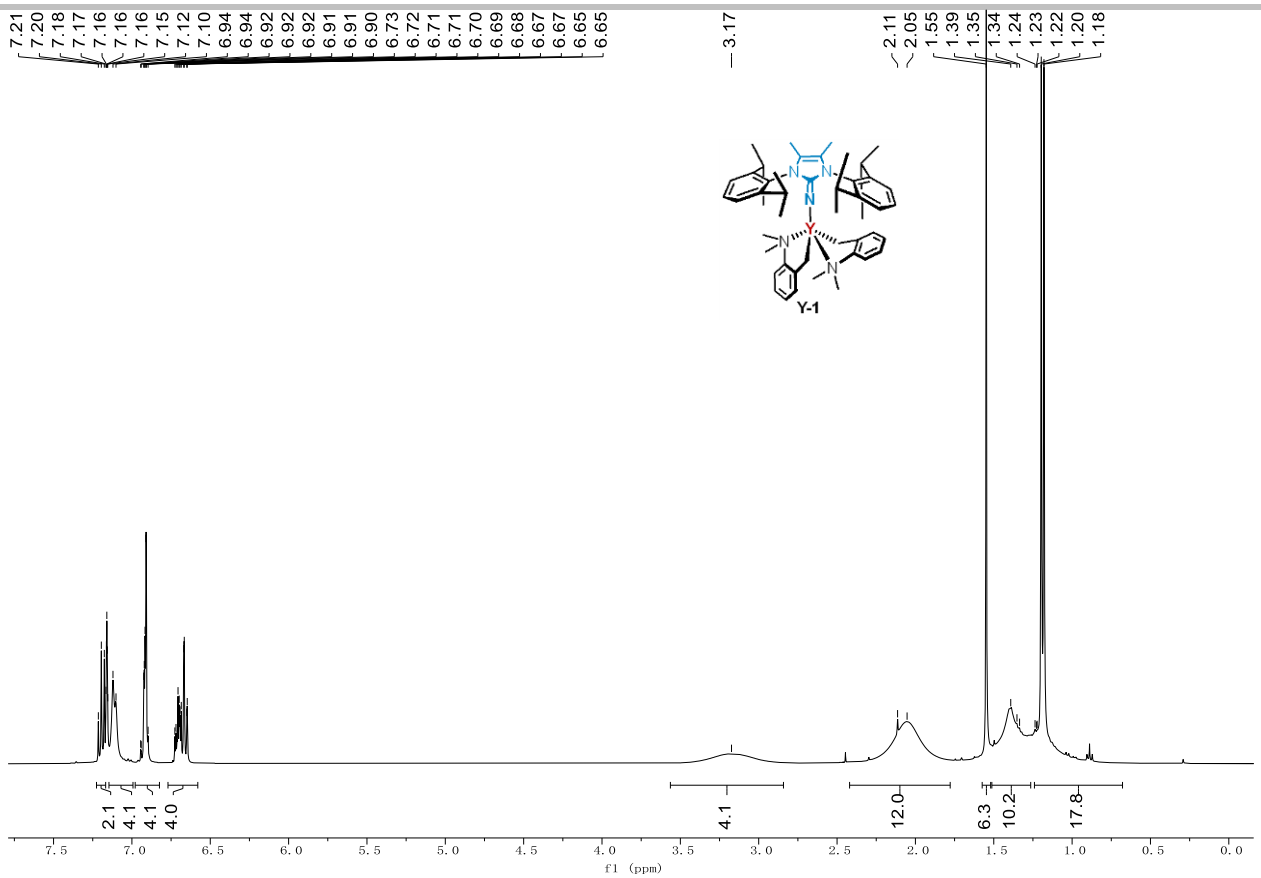

Figure S50. ^{1}H NMR spectrum (400 MHz) of **Y-1** in C_6D_6.

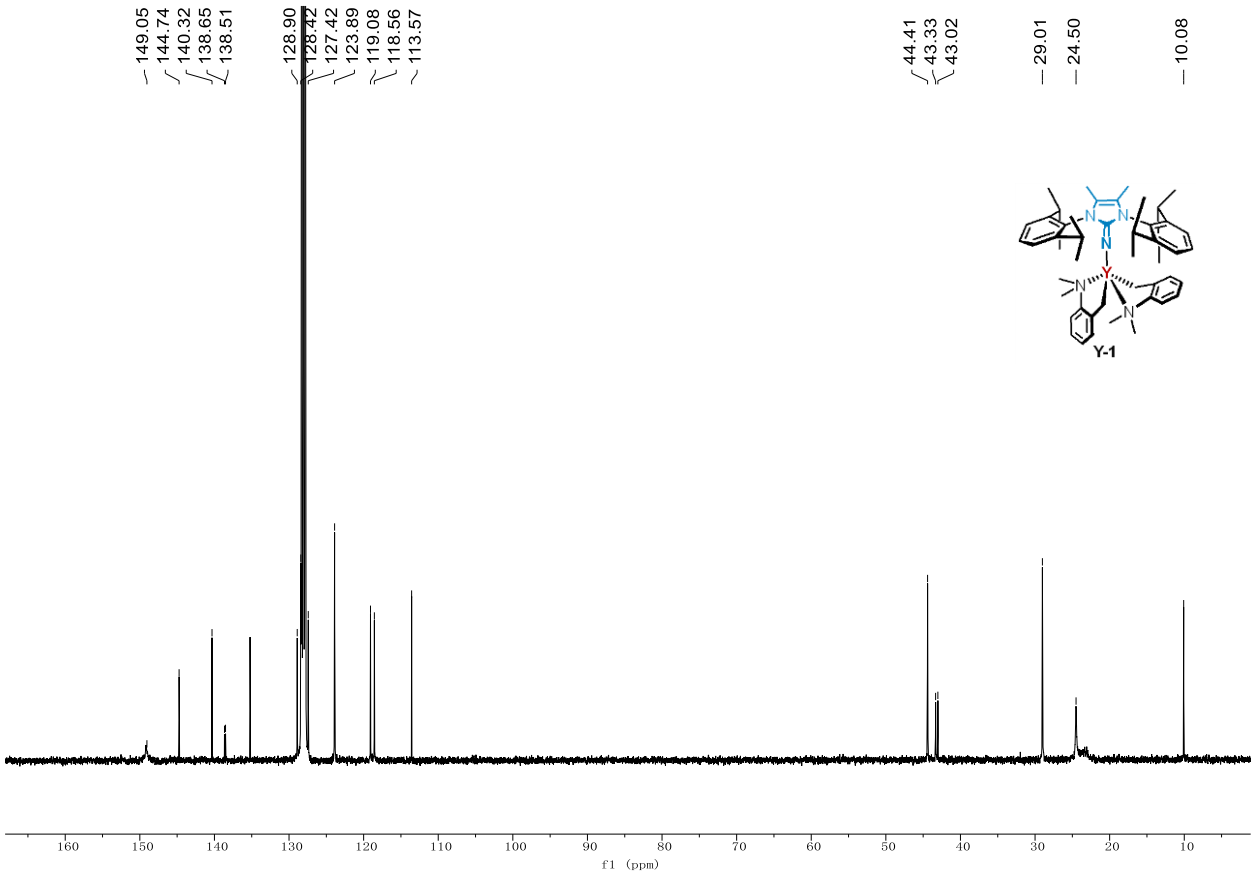

Figure S51. ^{13}C{^{1}H} NMR spectrum (101 MHz) of **Y-1** in C_6D_6.

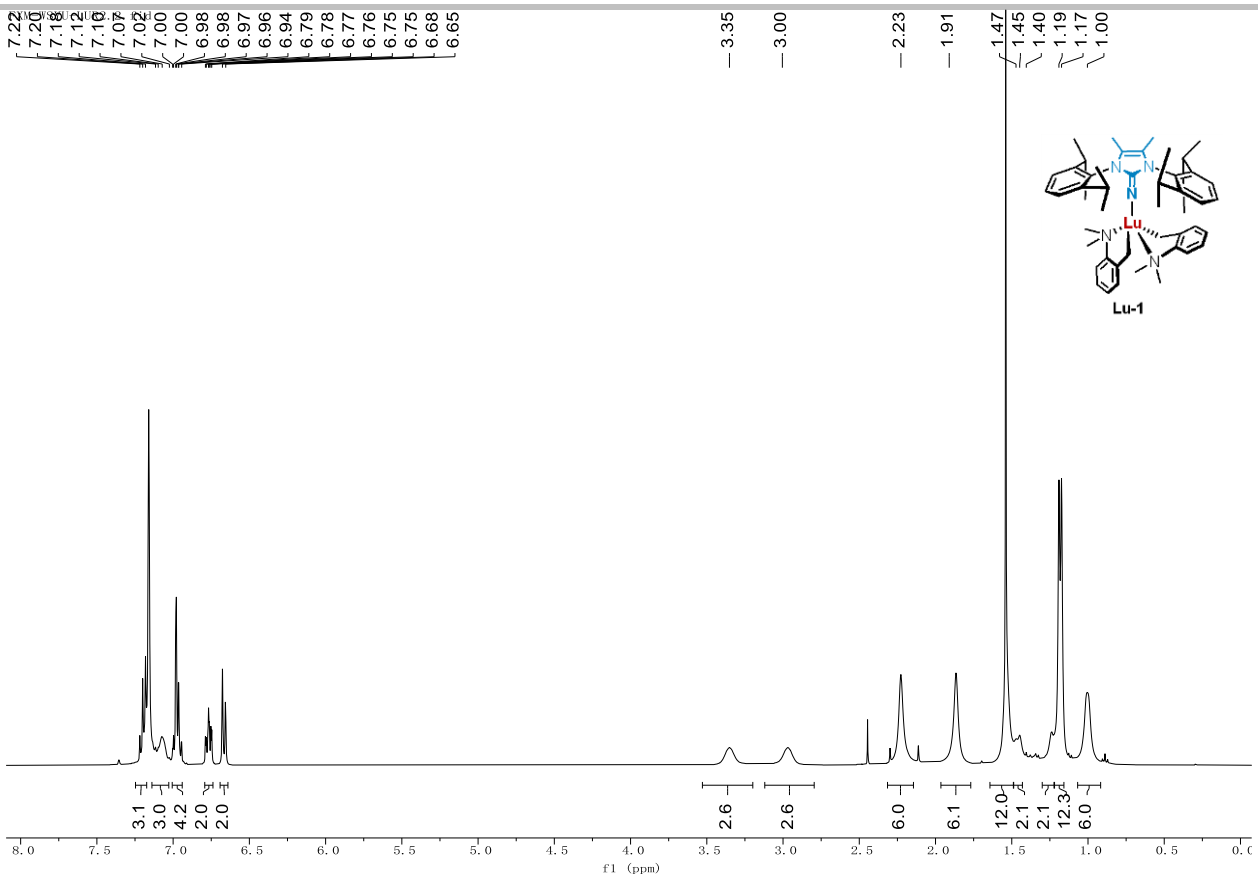

Figure S52. ^{1}H NMR spectrum (400 MHz) of **Lu-1** in C_6D_6.

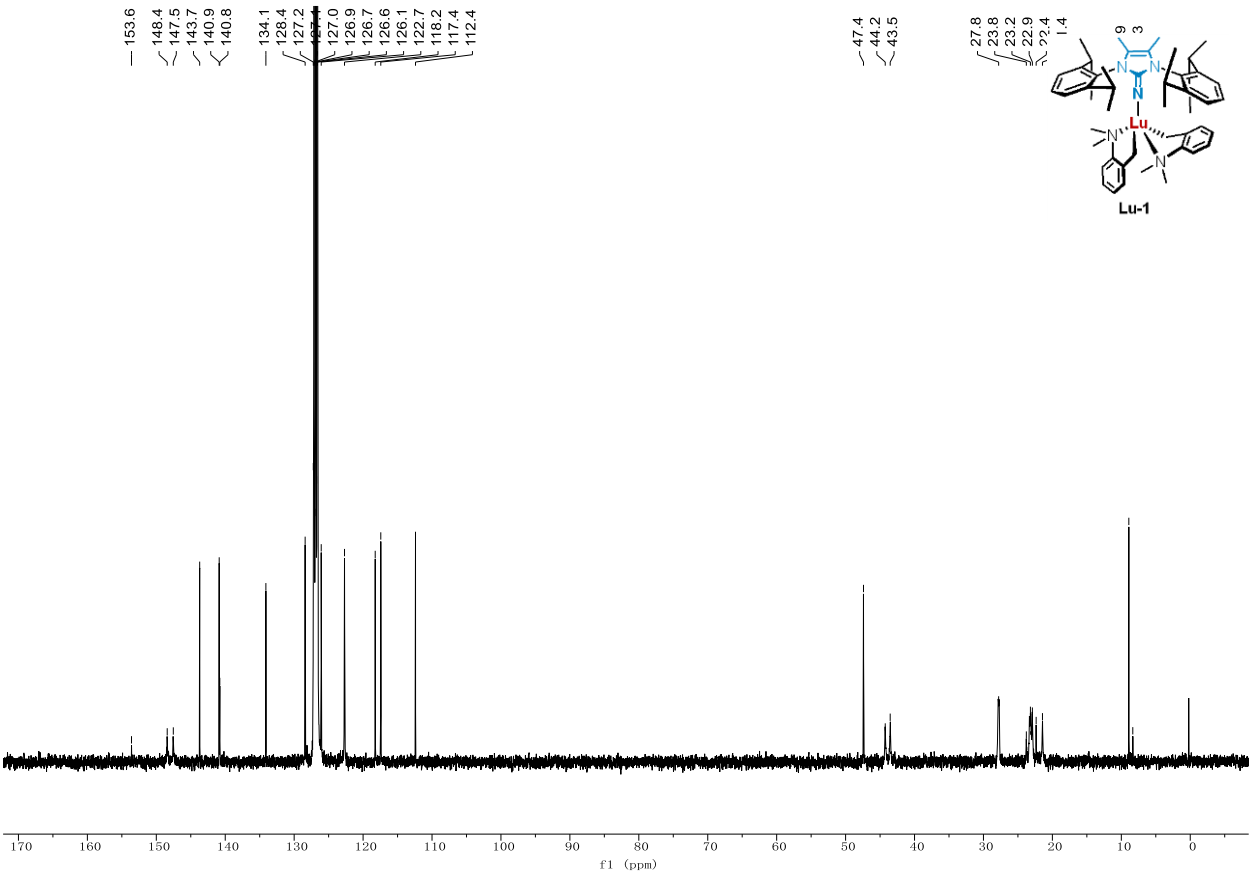

Figure S53. ^{13}C{^{1}H} NMR spectrum (101 MHz) of **Lu-1** in C_6D_6.

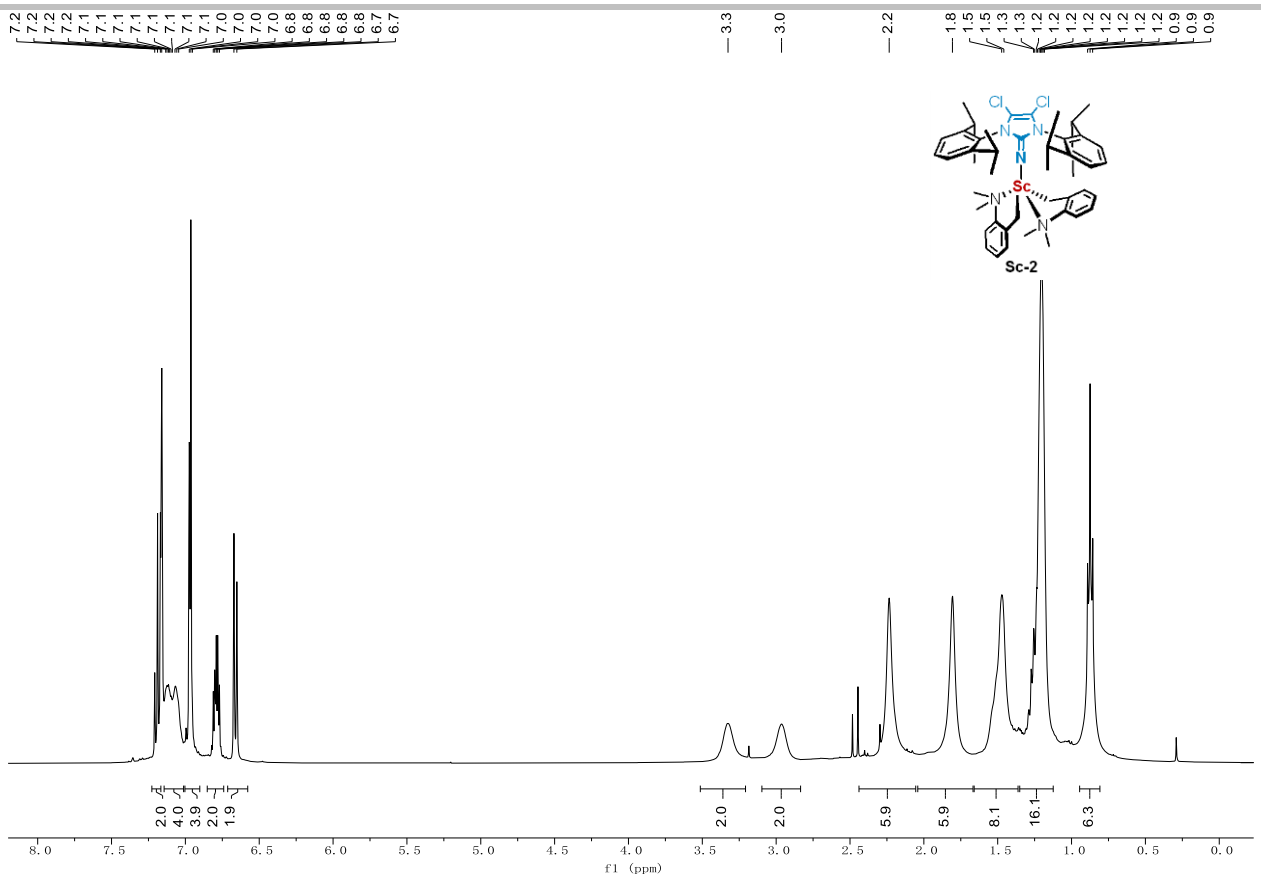

Figure S54. ^{1}H NMR spectrum (400 MHz) of **Sc-2** in C_6D_6.

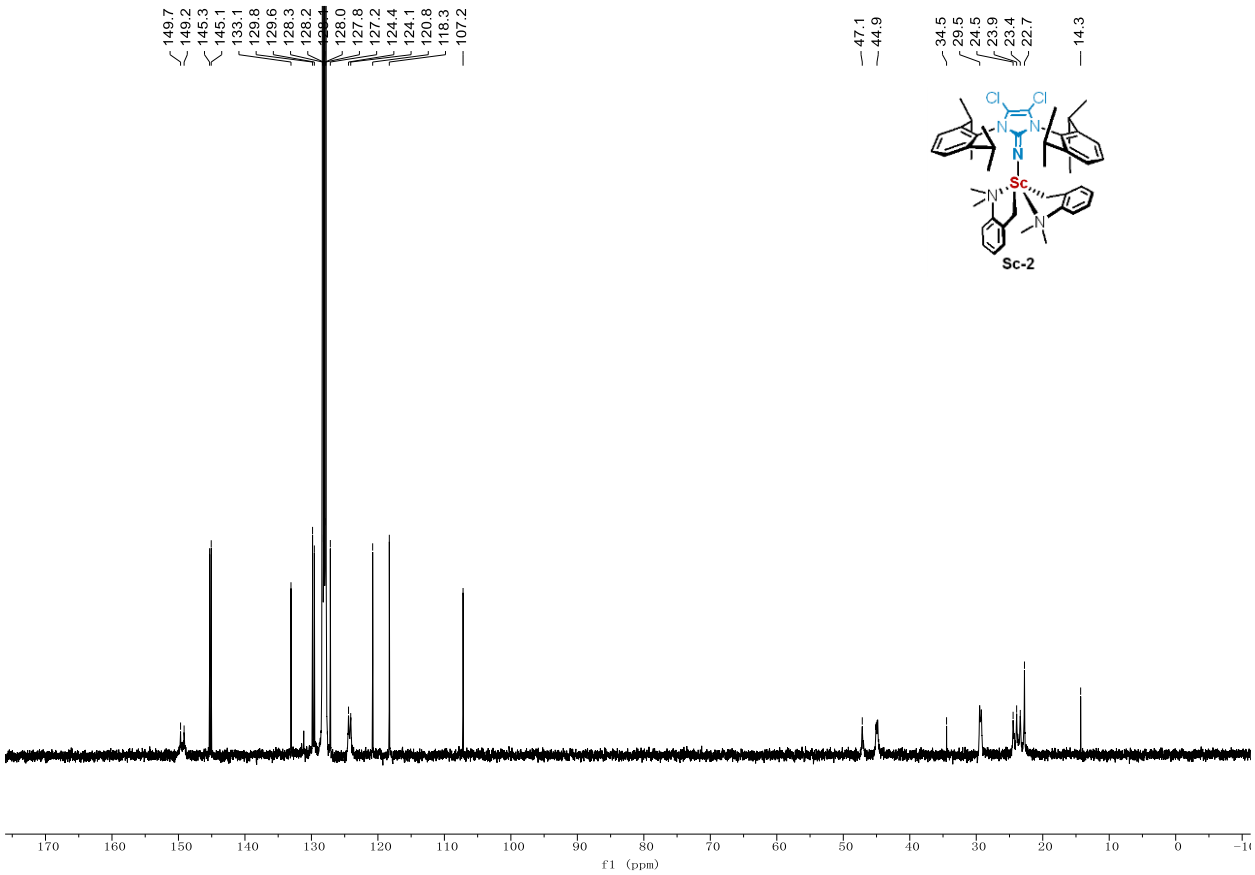

Figure S55. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **Sc-2** in C_6D_6.

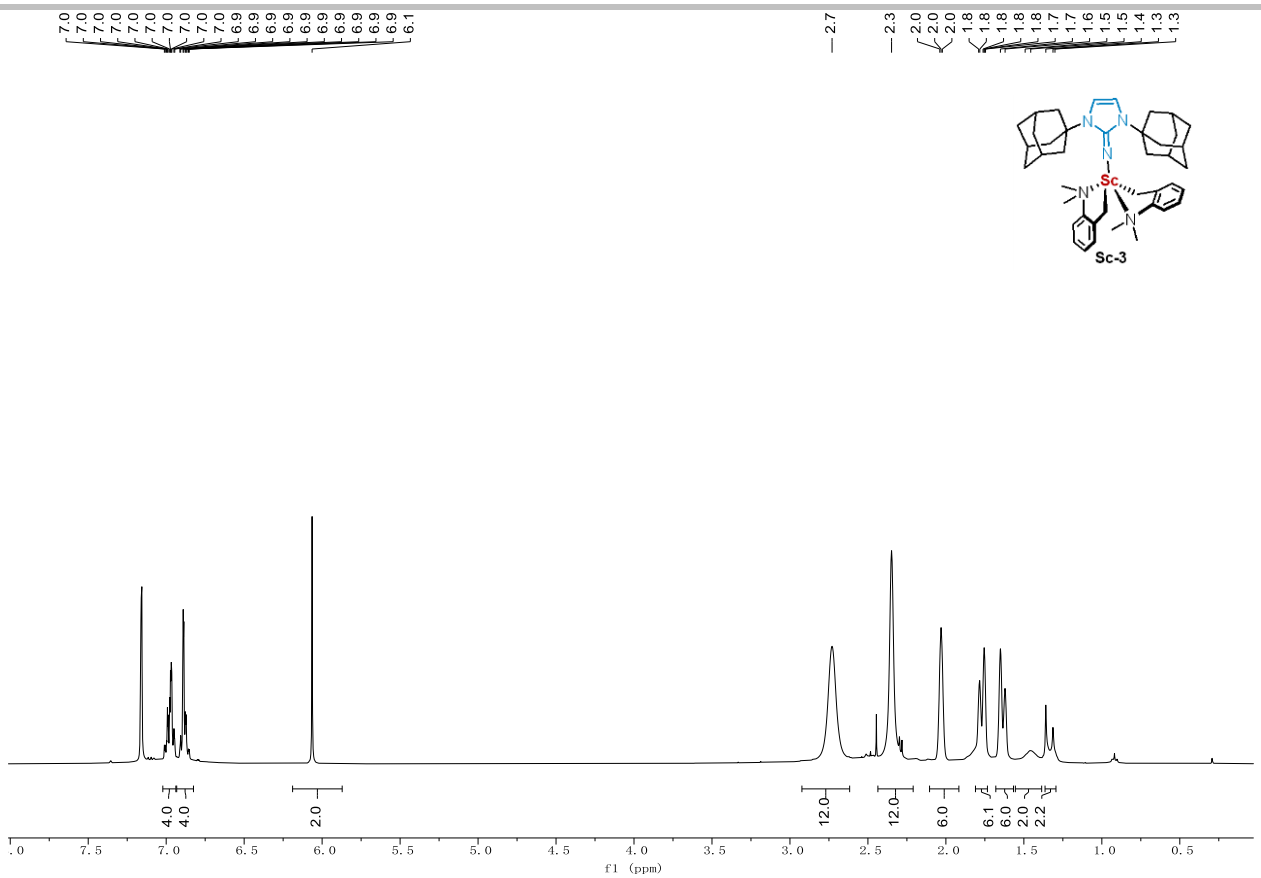

Figure S56. ^{1}H NMR spectrum (400 MHz) of **Sc-3** in C_6D_6.

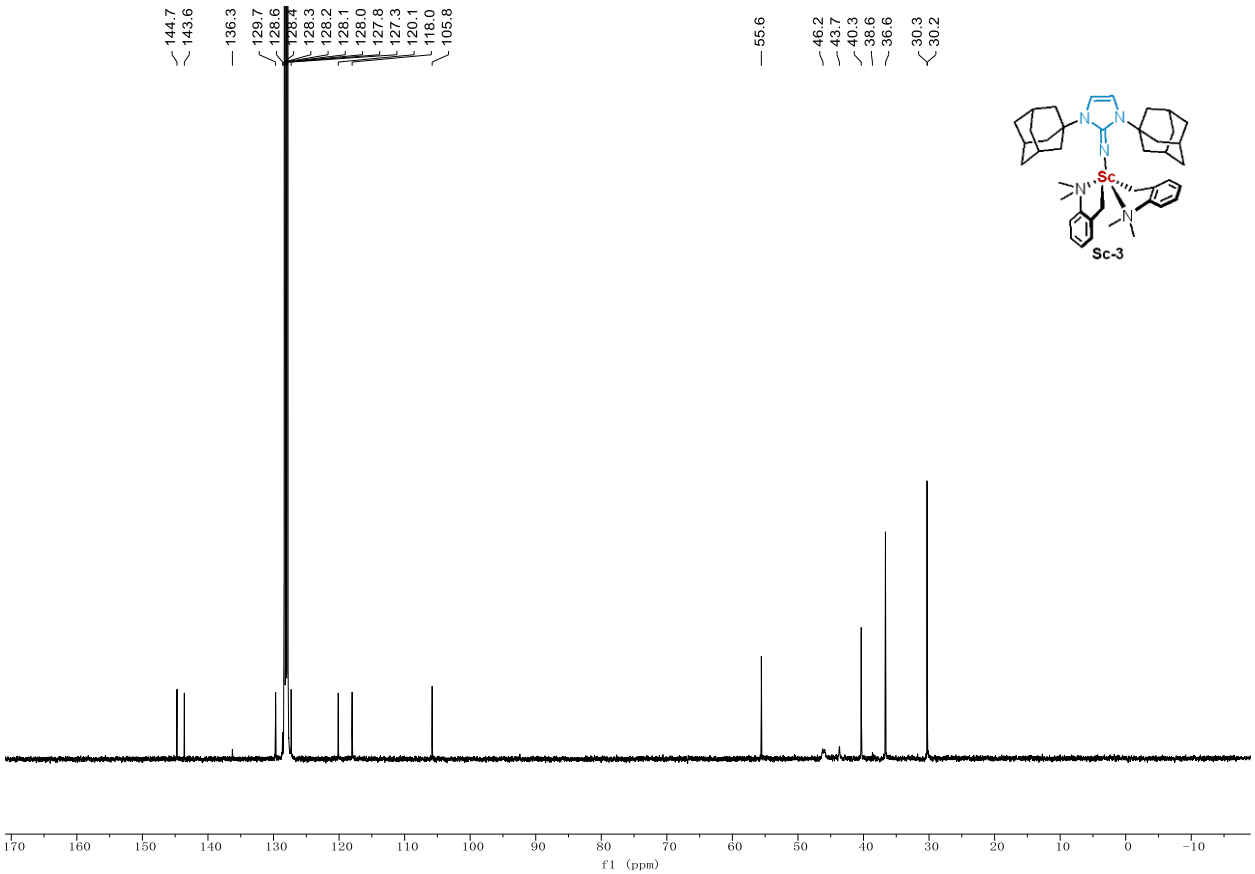

Figure S57. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **Sc-3** in C_6D_6.

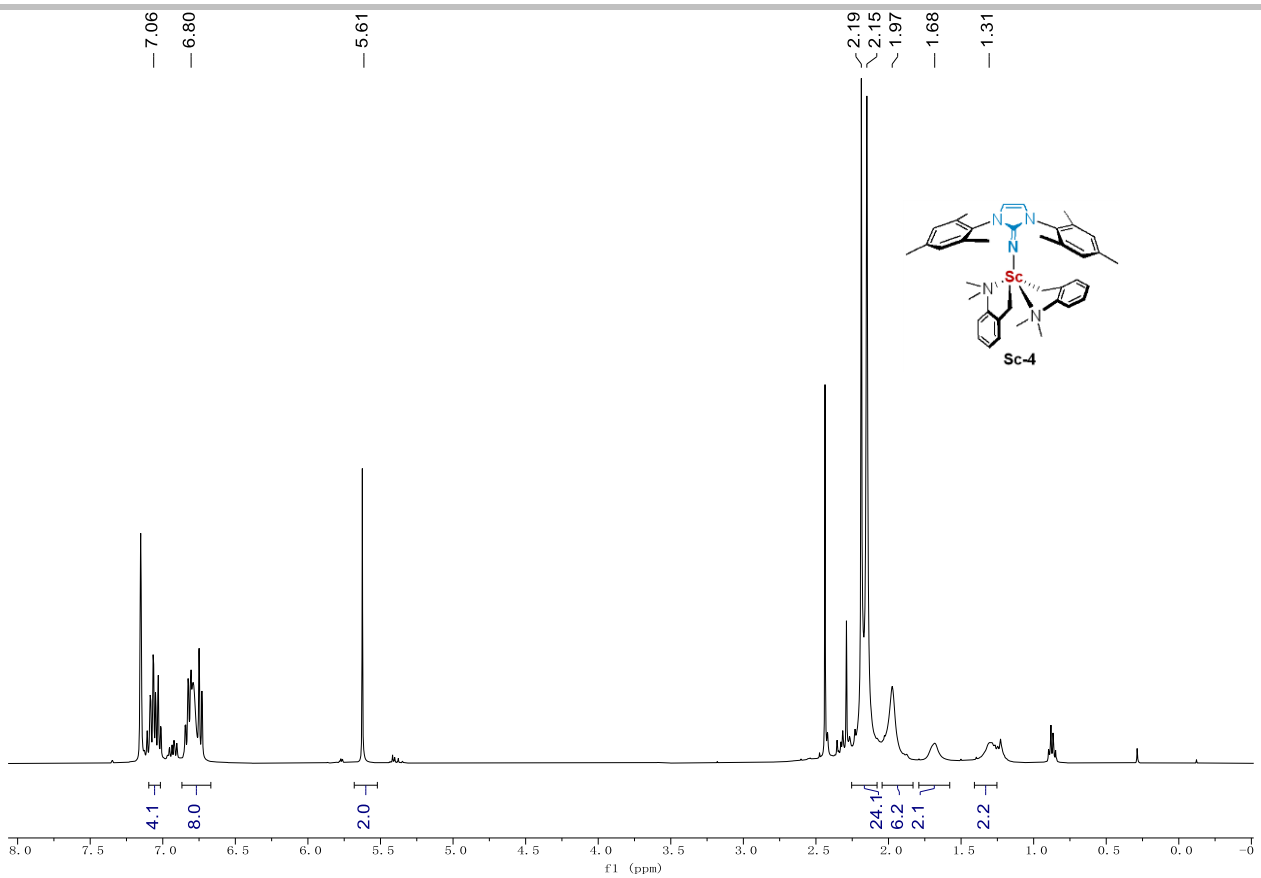

Figure S58. ^{1}H NMR spectrum (400 MHz) of **Sc-4** in C_6D_6.

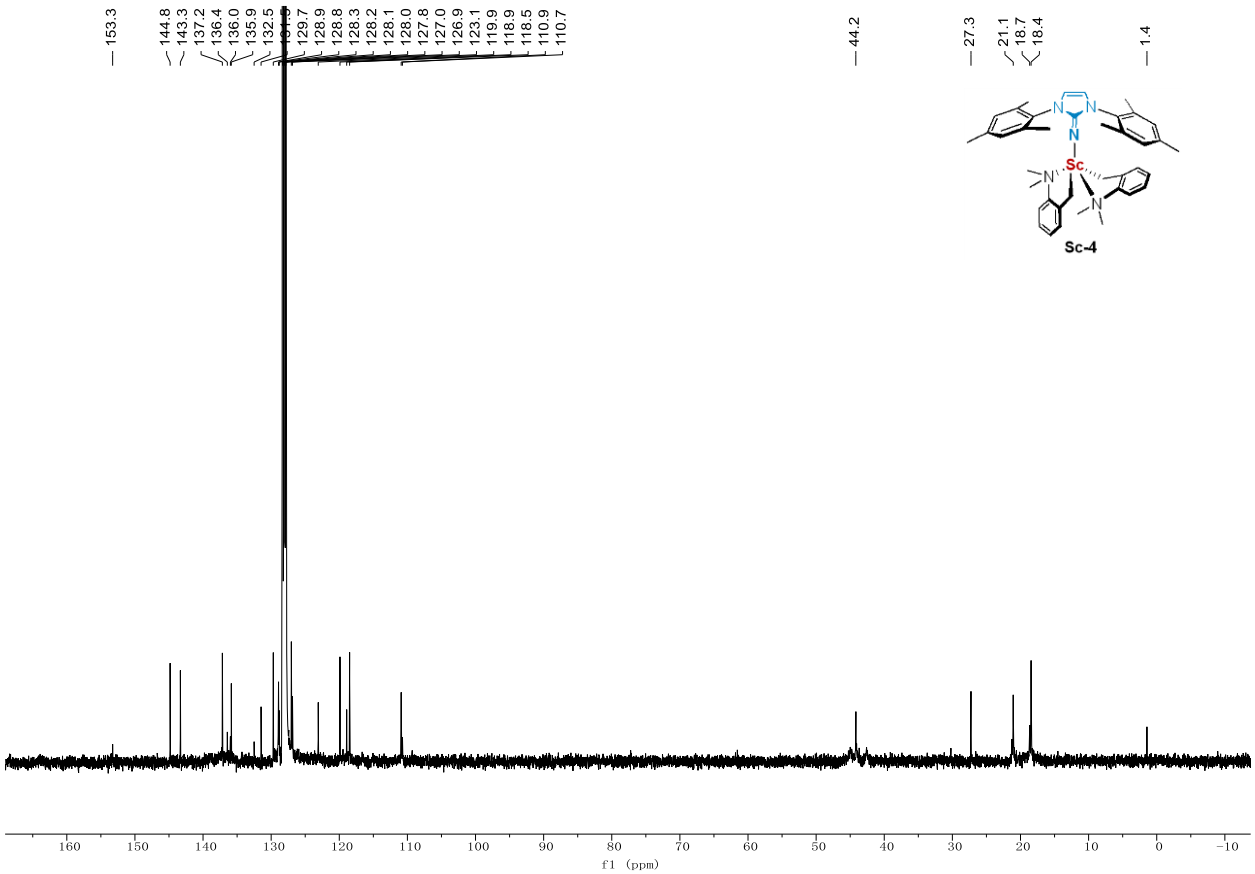

Figure S59. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **Sc-4** in C_6D_6.

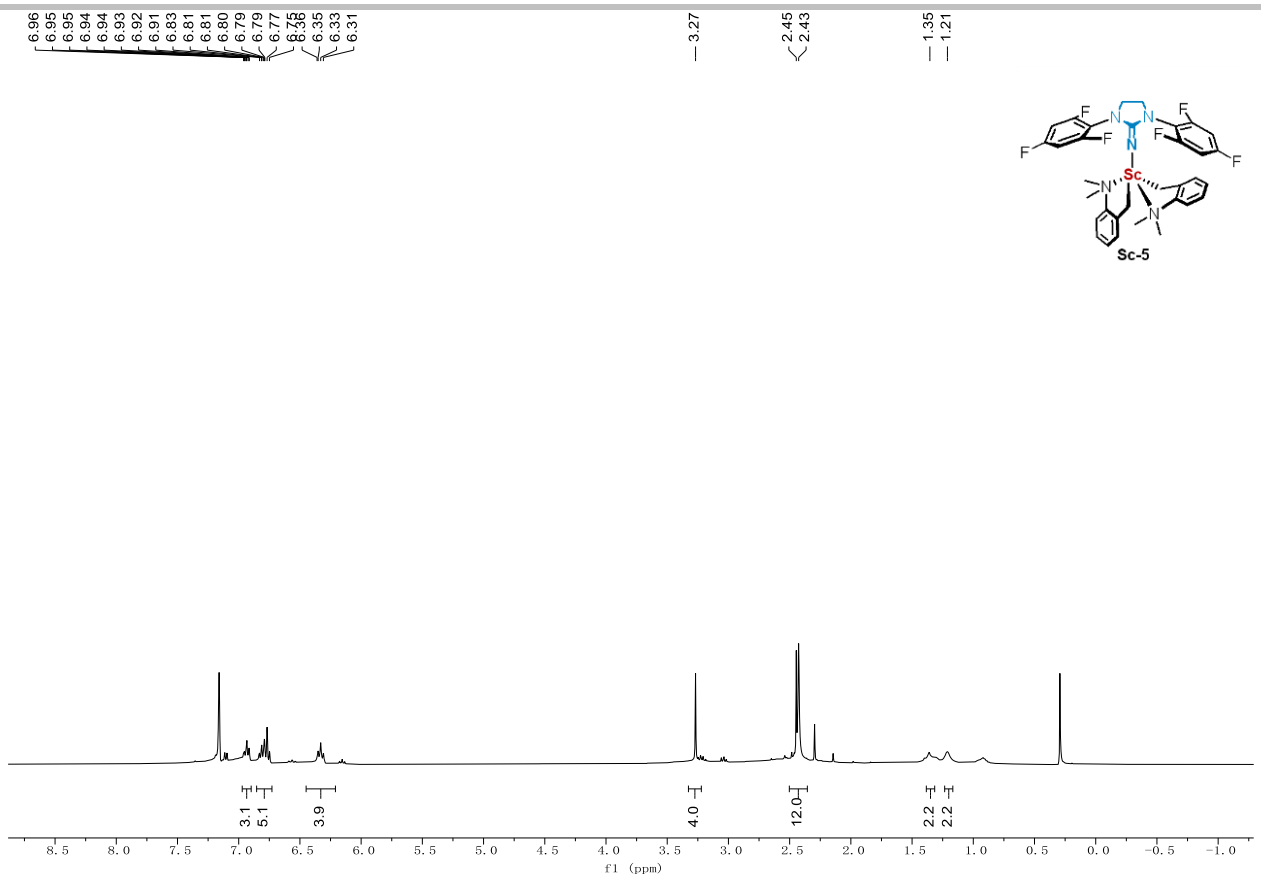

Figure S60. ^{1}H NMR spectrum (400 MHz) of **Sc-5** in C_6D_6.

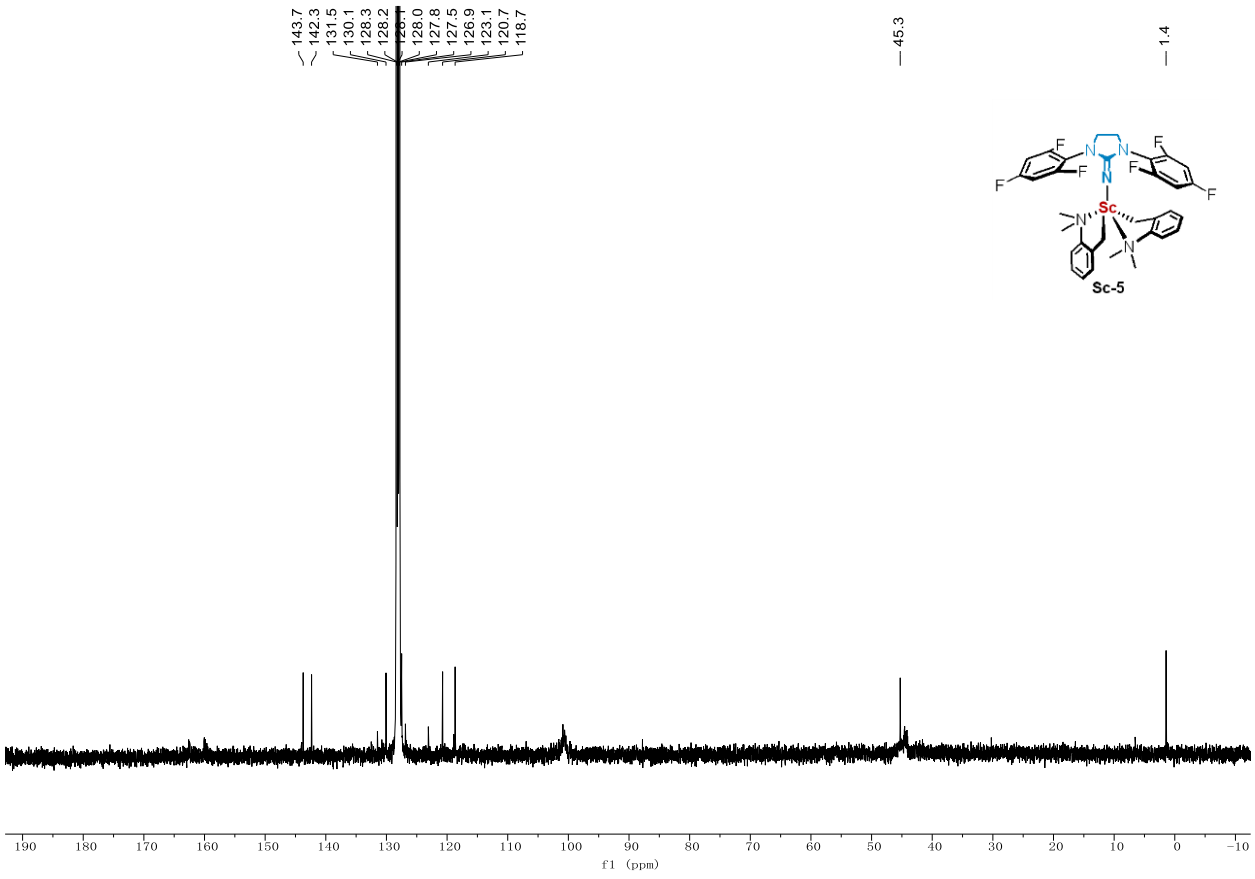

Figure S61. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **Sc-5** in $CDCl_3$.

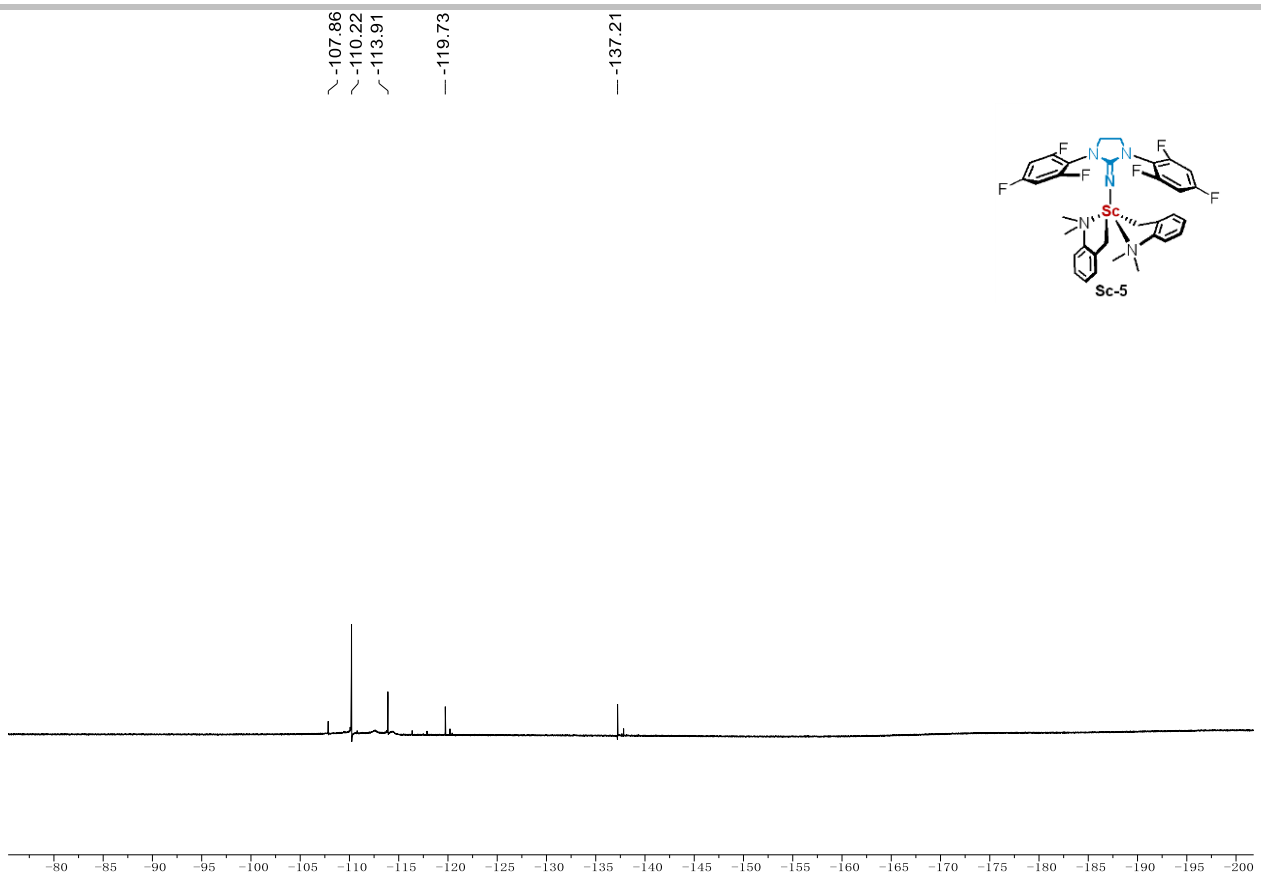

Figure S62. $^{19}F\{^{1}H\}$ NMR spectrum (377 MHz) of **Sc-5** in $CDCl_3$.

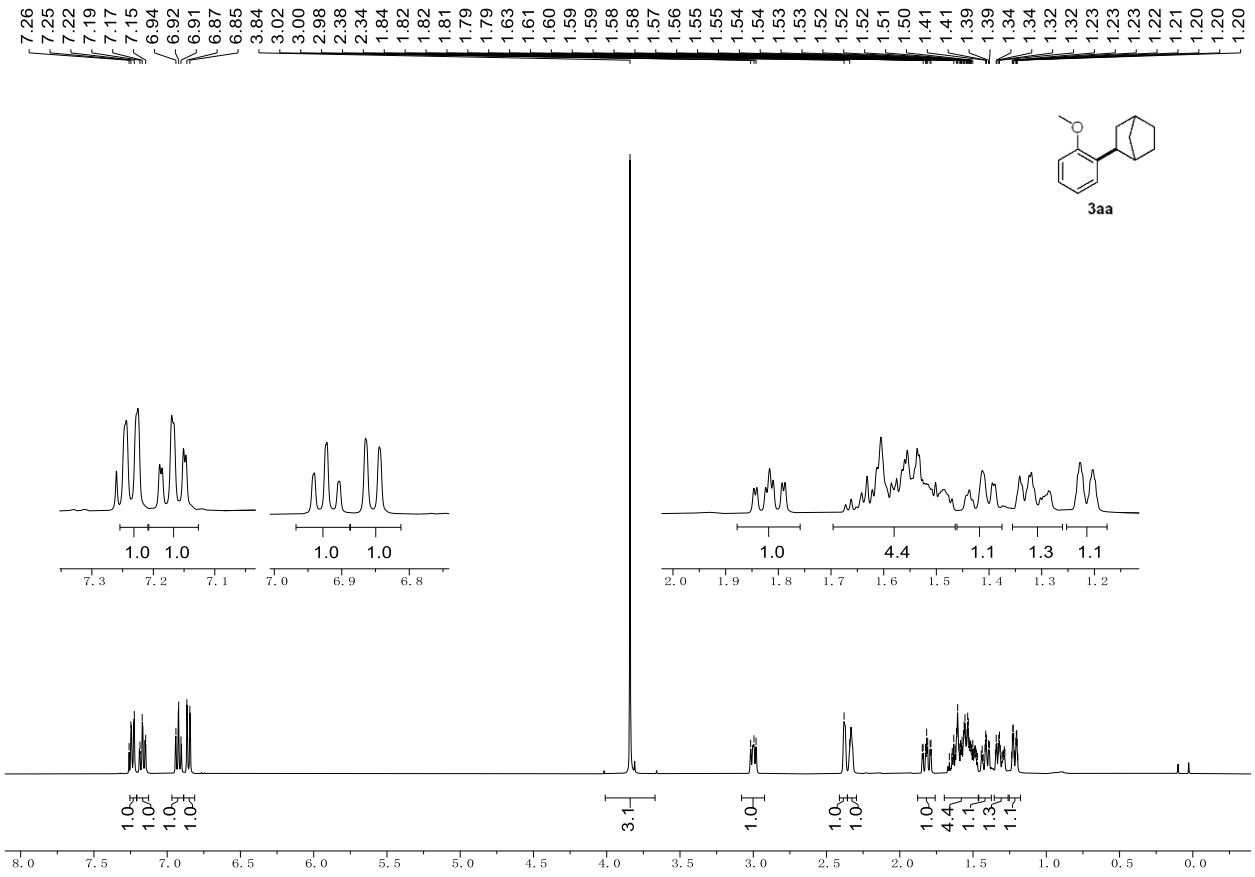

Figure S63. ^{1}H NMR spectrum (400 MHz) of **3aa** in $CDCl_3$.

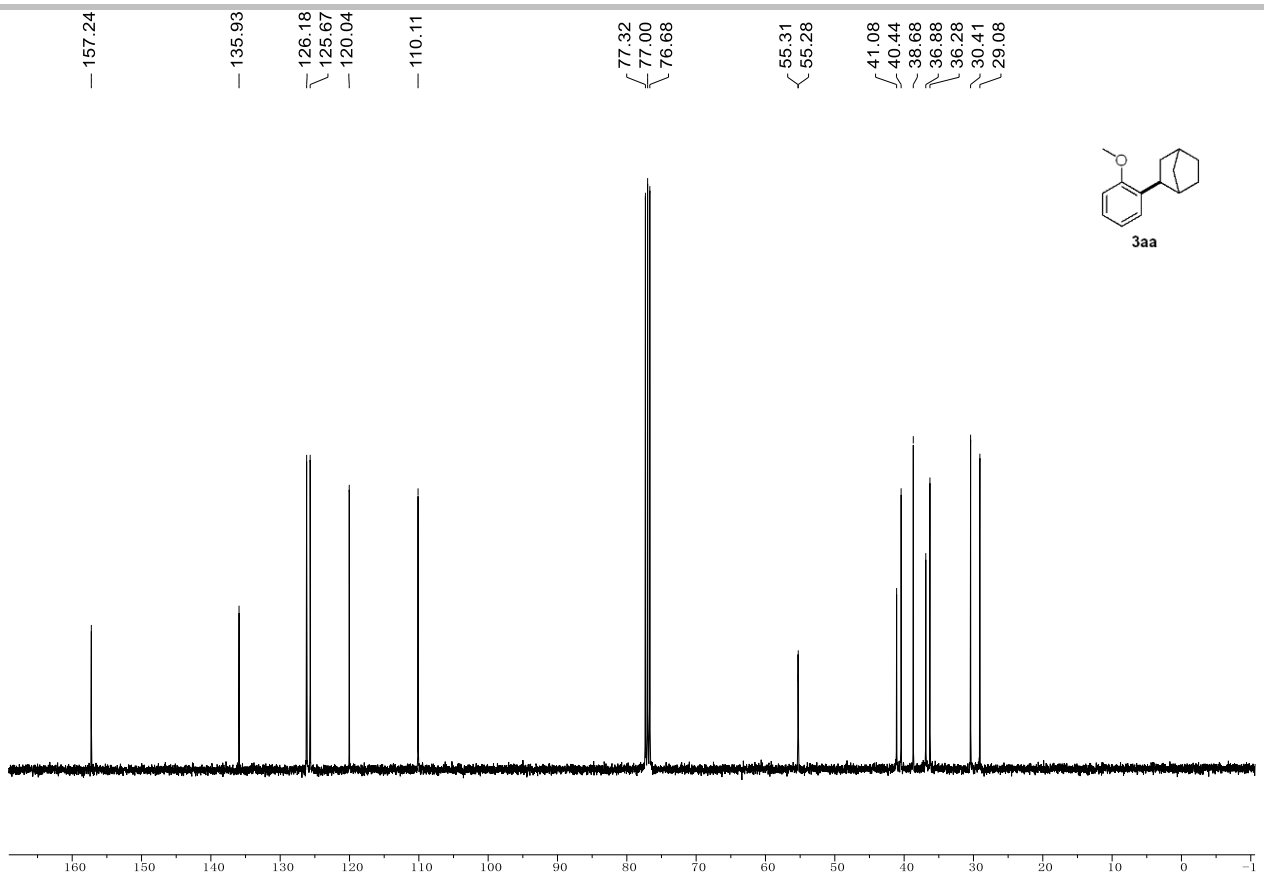

Figure S64. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3aa** in $CDCl_3$.

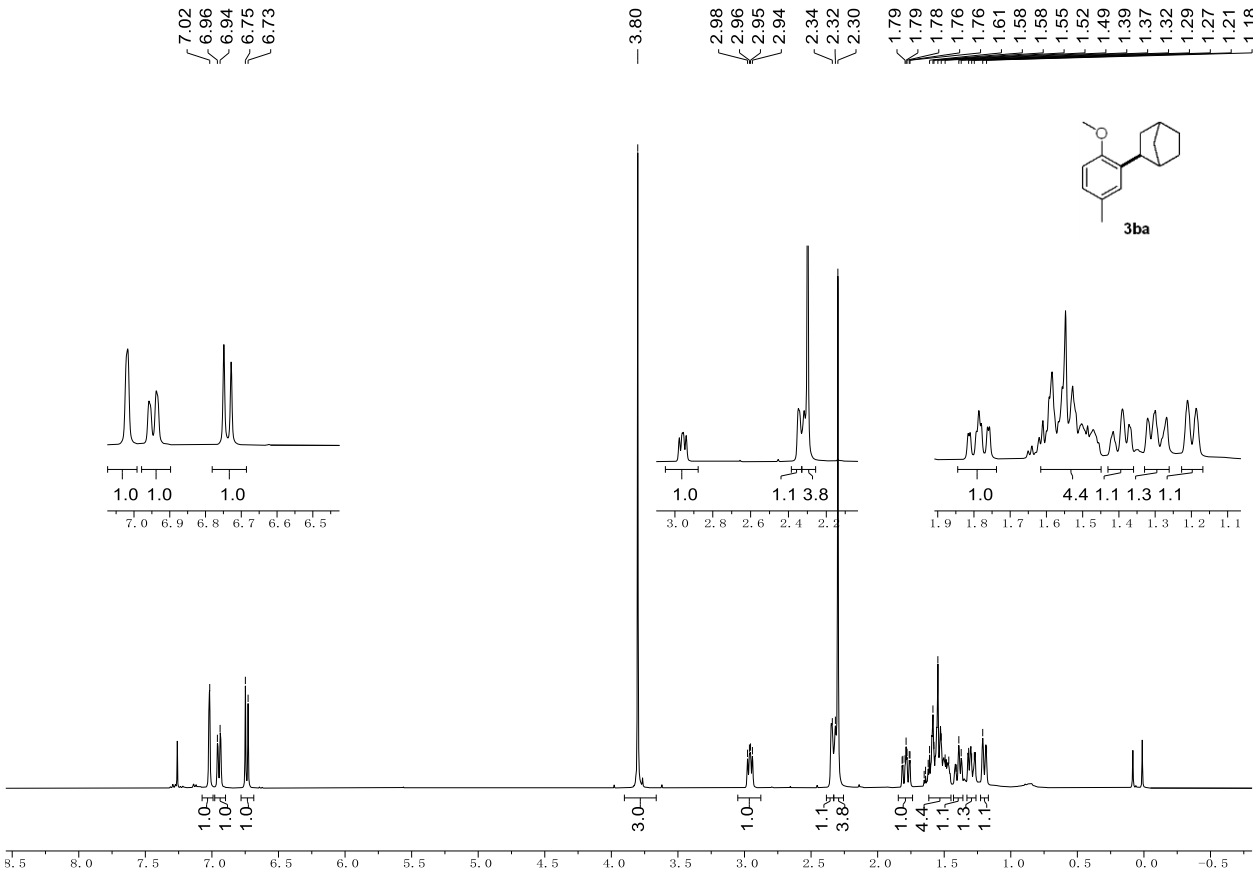

Figure S65. ^{1}H NMR spectrum (400 MHz) of **3ba** in $CDCl_3$.

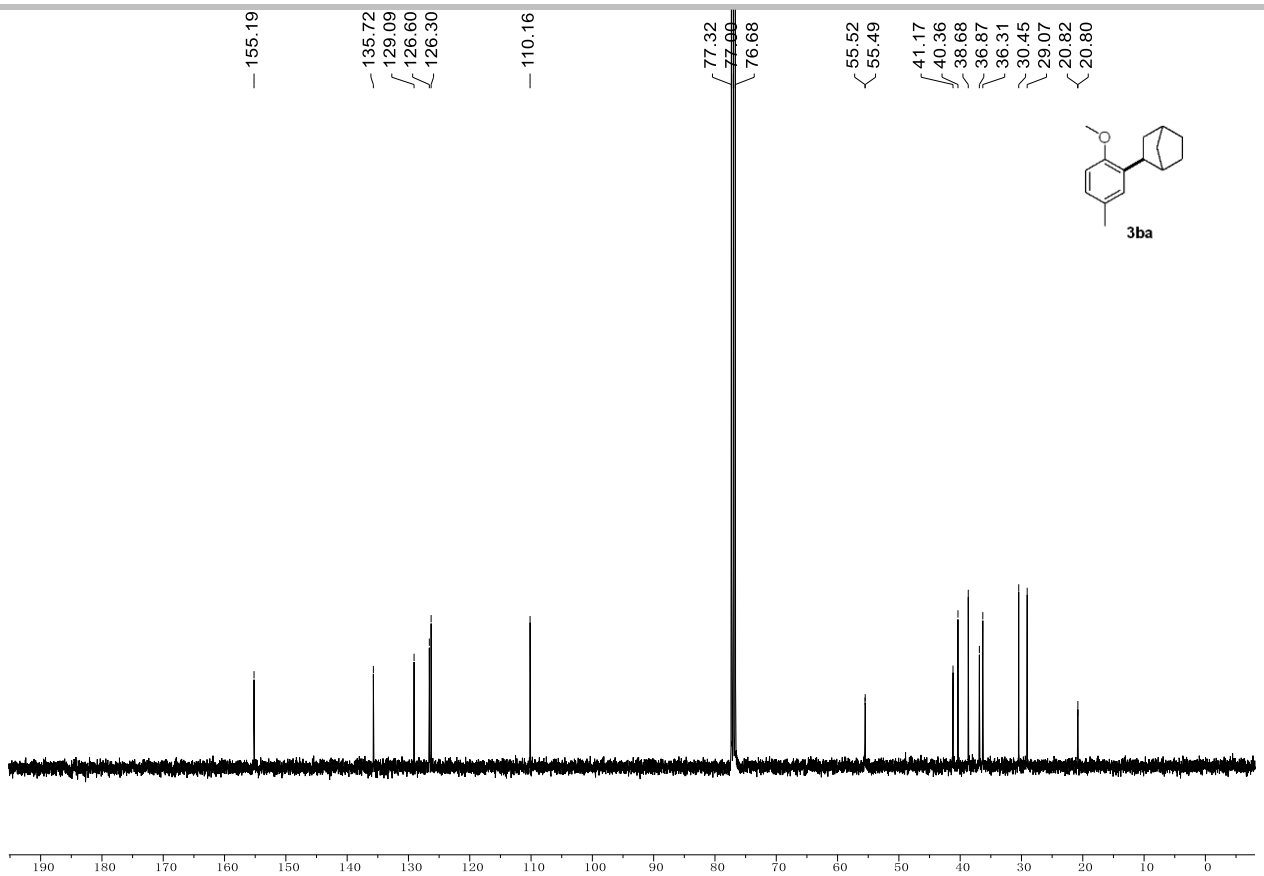

Figure S66. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3ba** in $CDCl_3$.

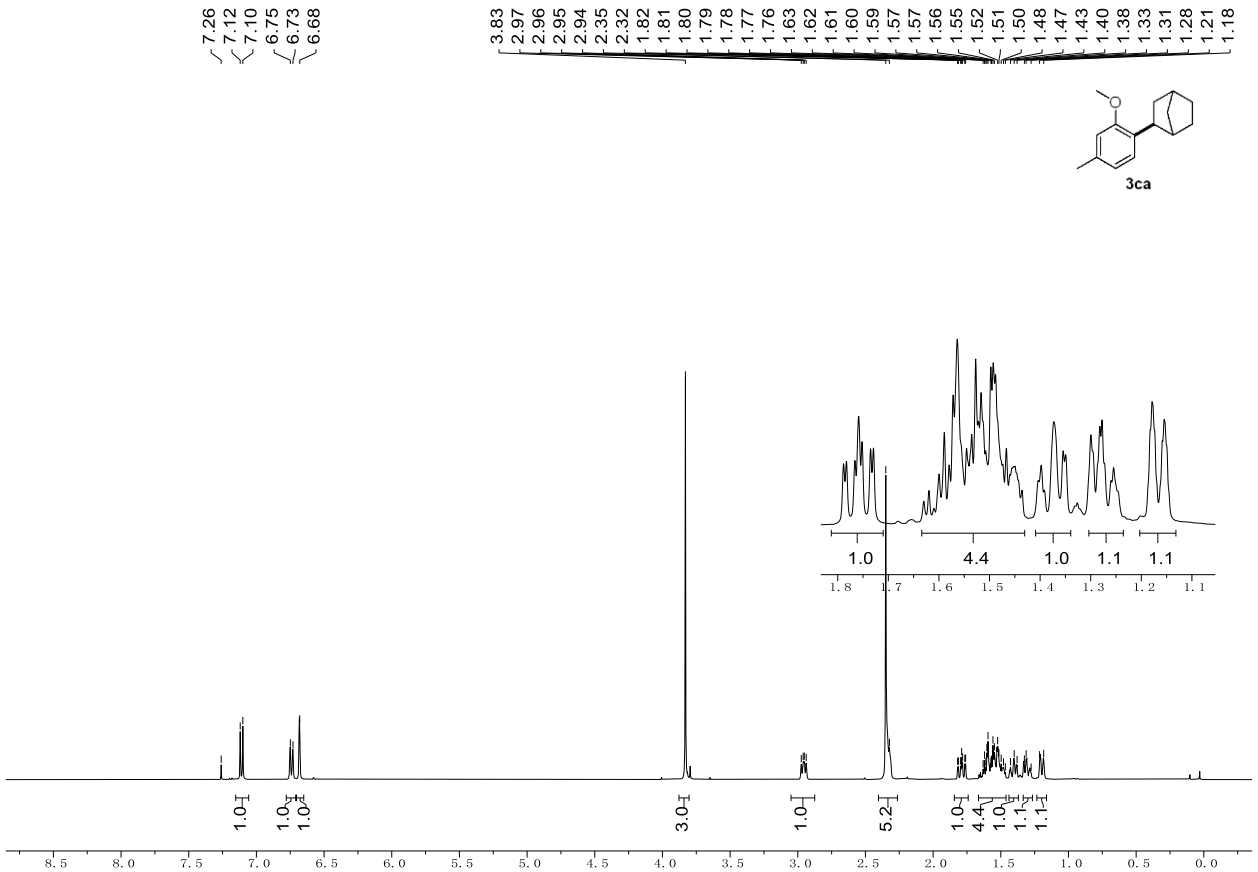

Figure S67. ^{1}H NMR spectrum (400 MHz) of **3ca** in $CDCl_3$.

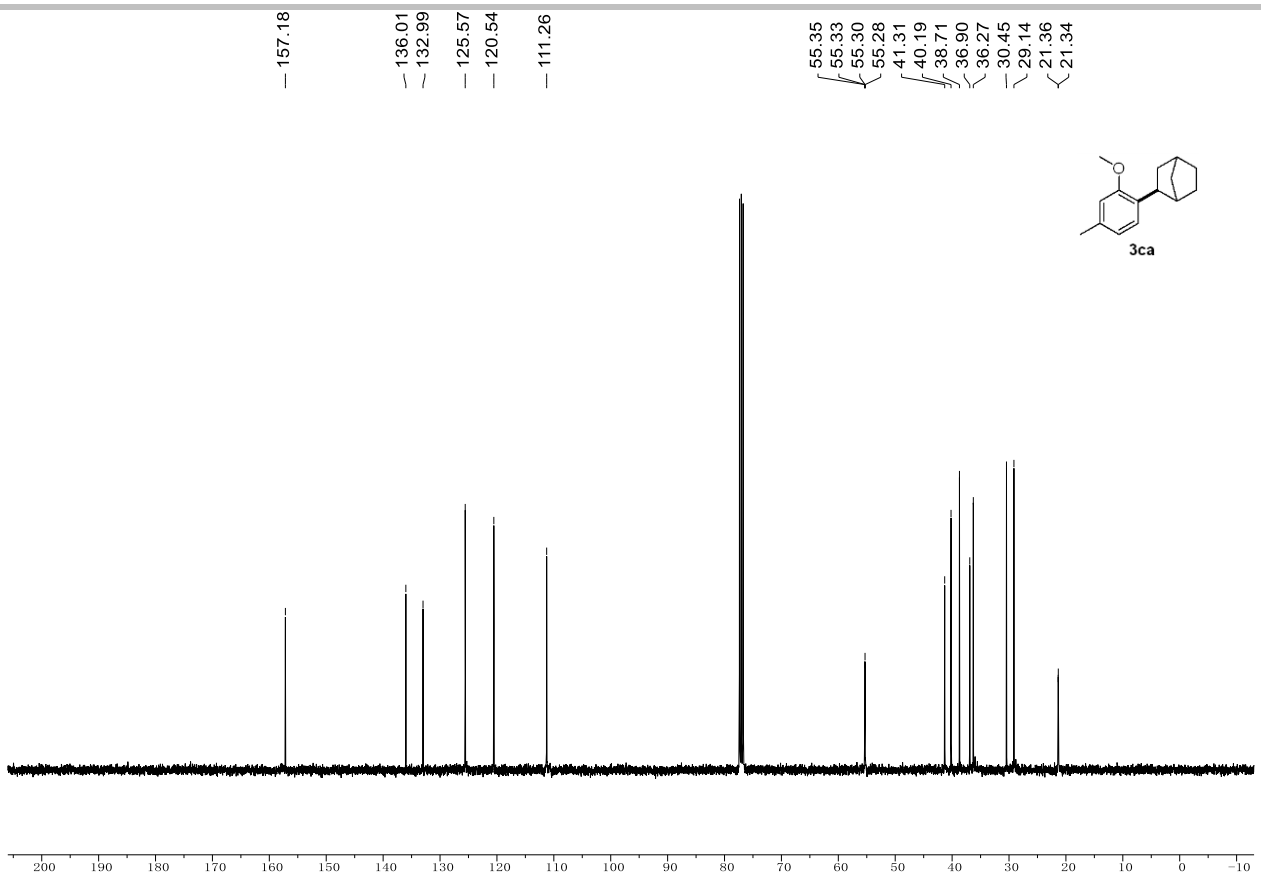

Figure S68. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3ca** in $CDCl_3$.

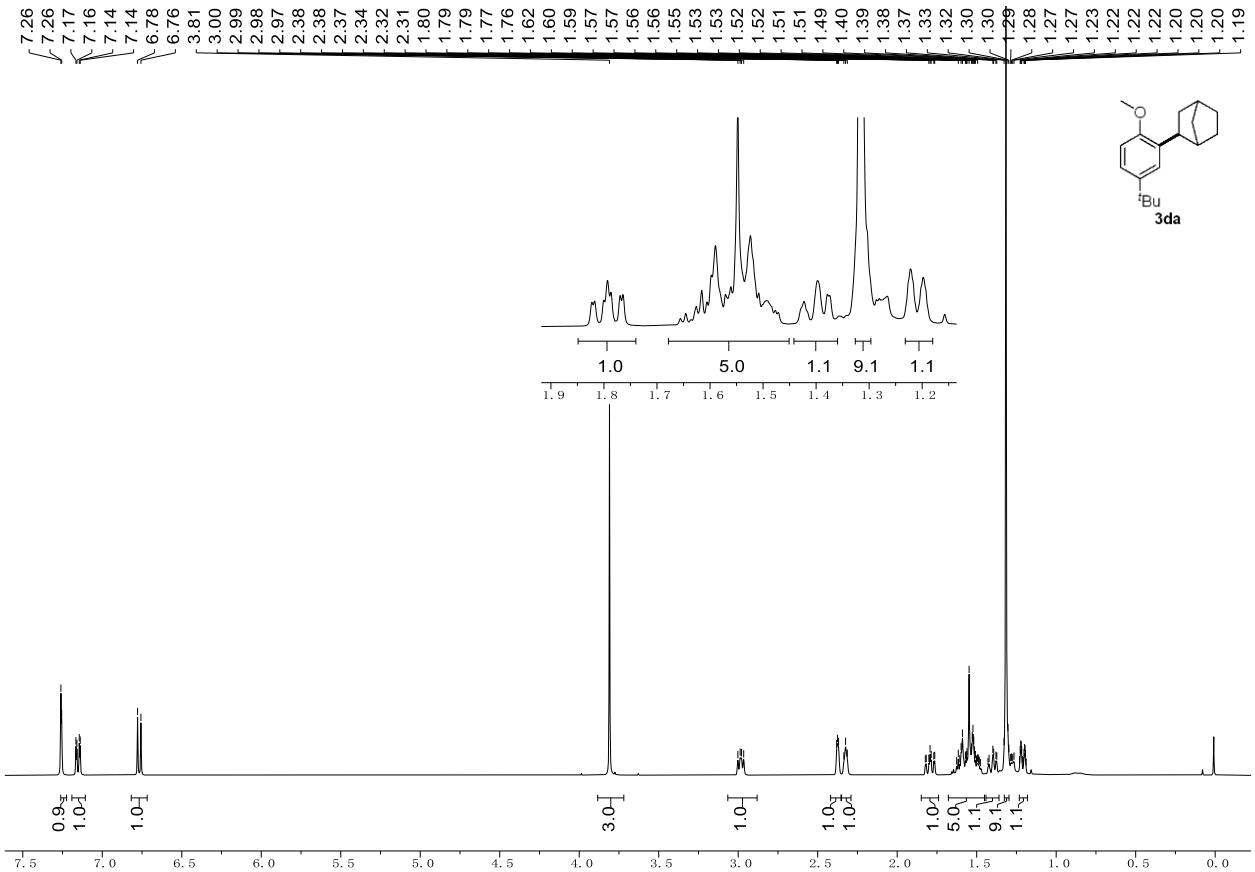

Figure S69. ^{1}H NMR spectrum (400 MHz) of **3da** in $CDCl_3$.

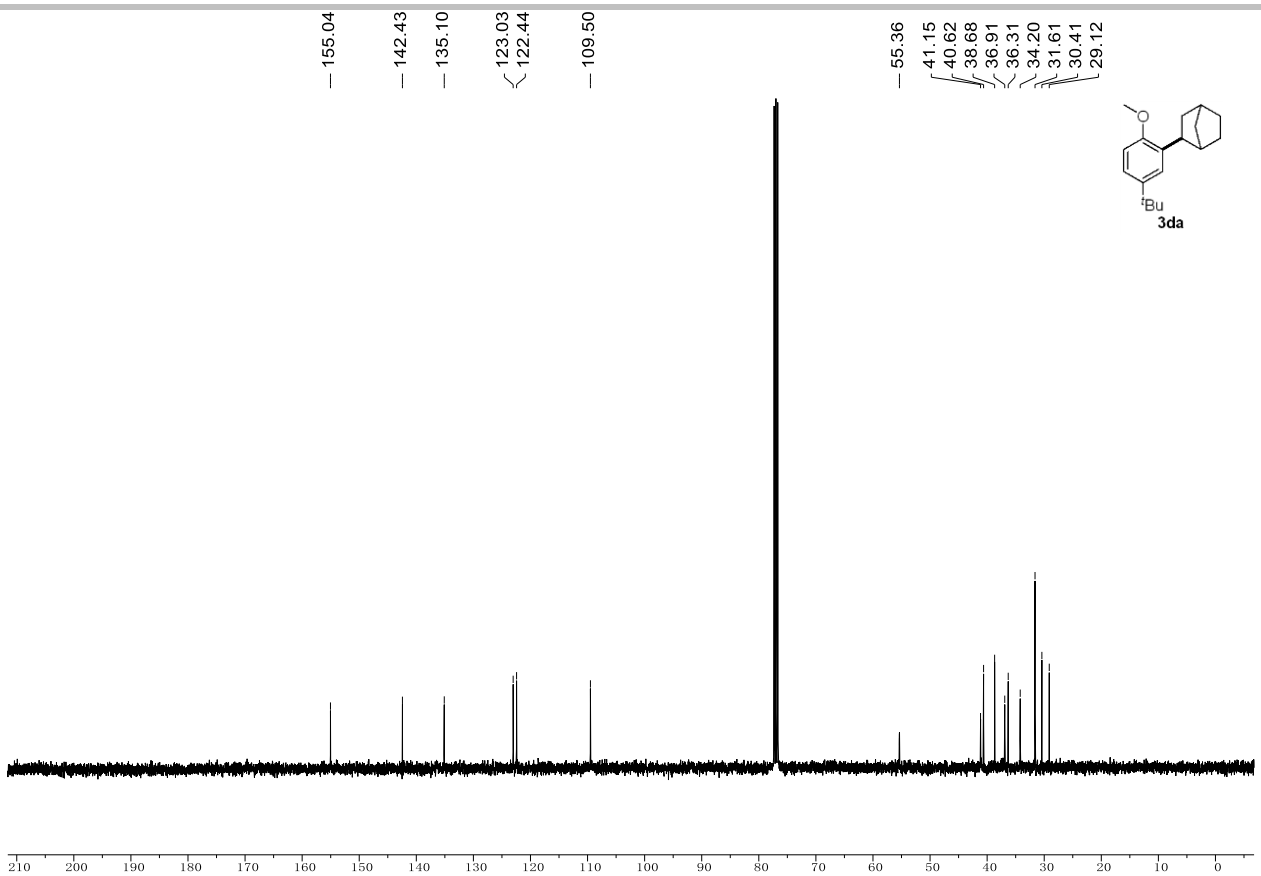

Figure S70. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3da** in $CDCl_3$.

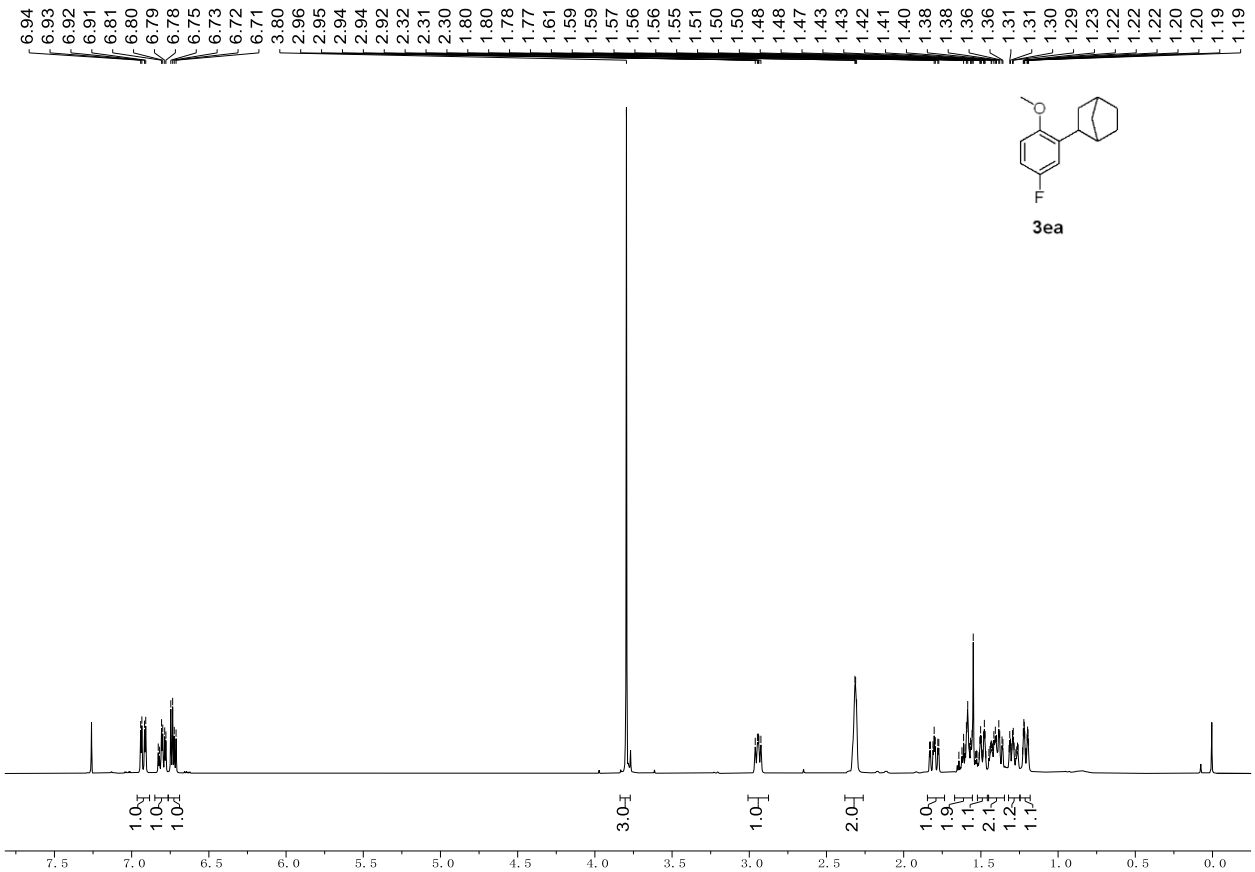

Figure S71. ^{1}H NMR spectrum (400 MHz) of **3ea** in $CDCl_3$.

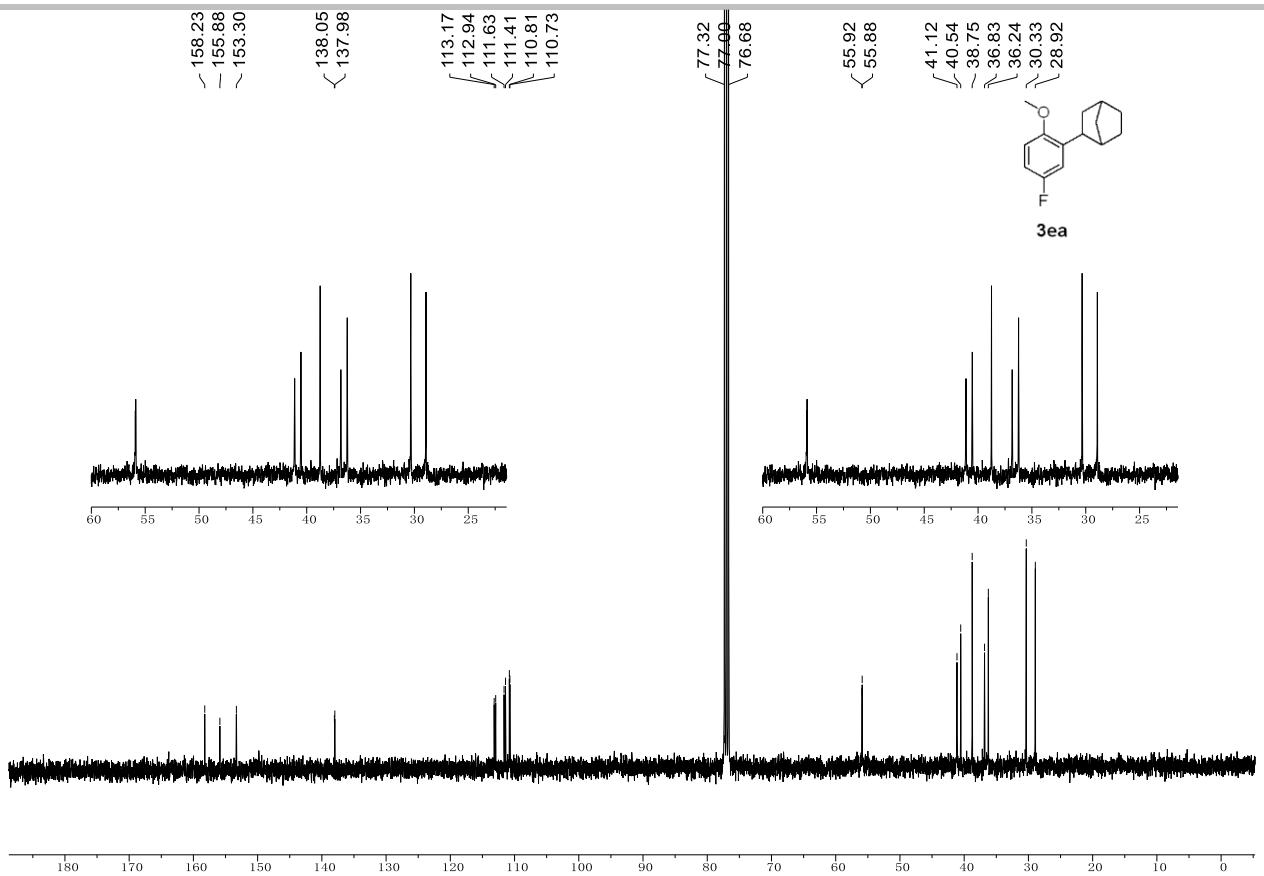

Figure S72. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3ea** in $CDCl_3$.

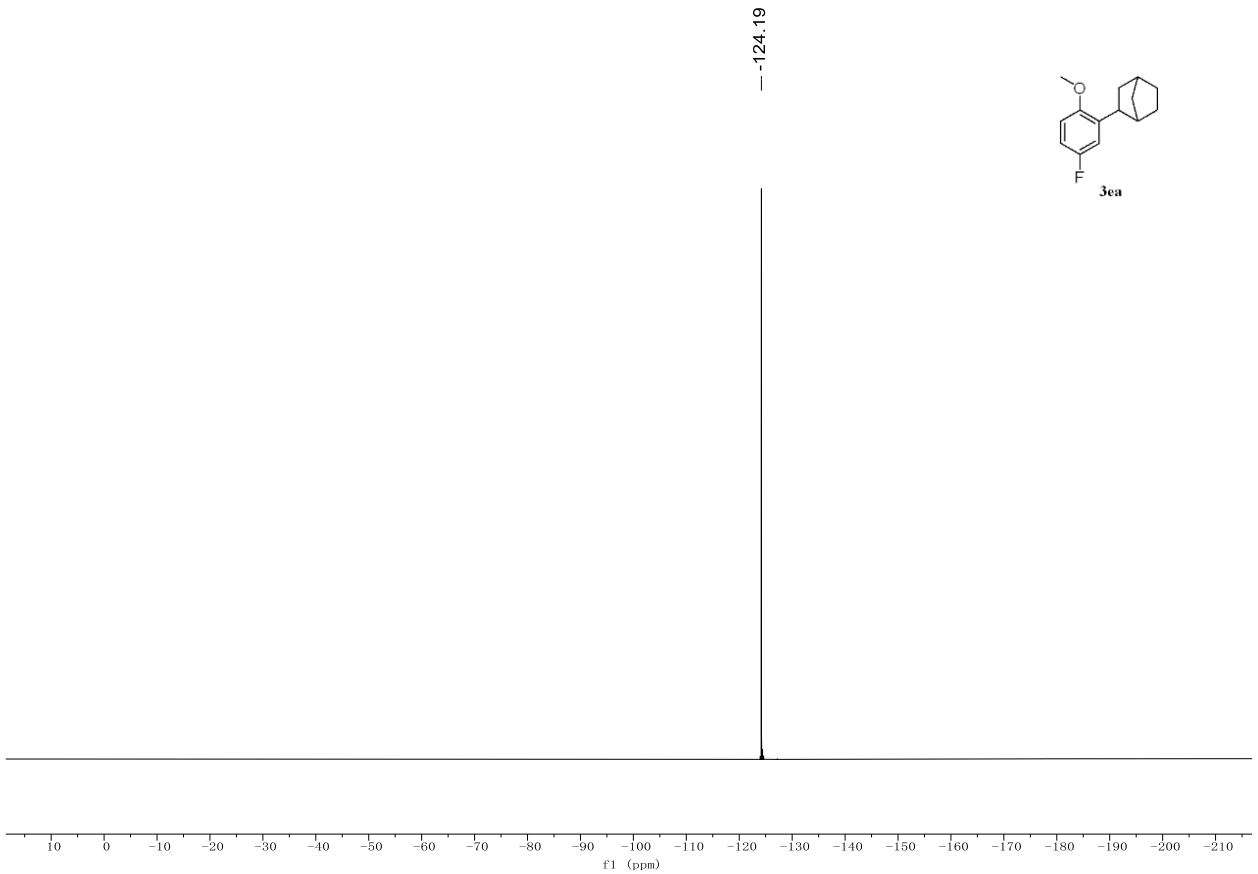

Figure S73. $^{19}F\{^{1}H\}$ NMR spectrum (377 MHz) of **3ea** in $CDCl_3$.

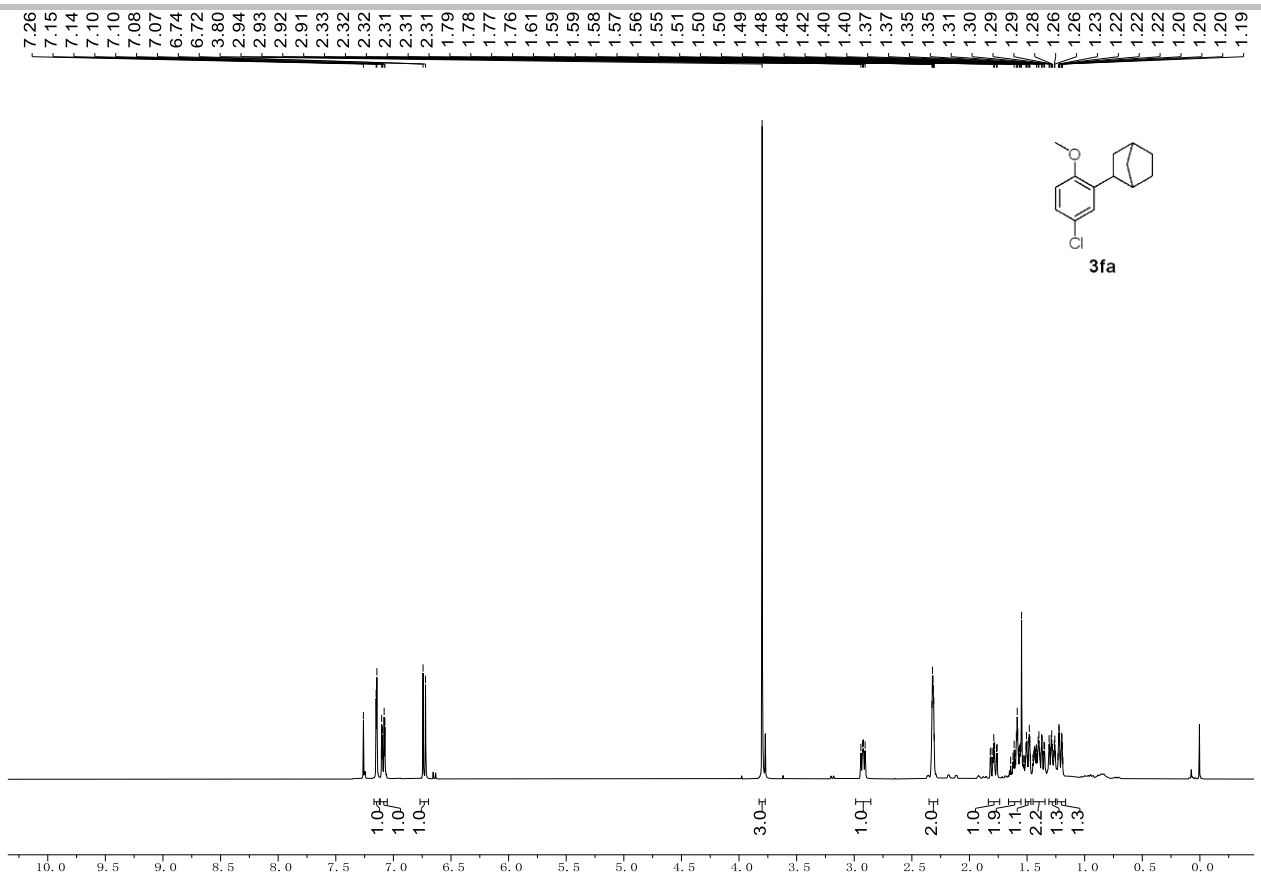

Figure S74. ^{1}H NMR spectrum (400 MHz) of **3fa** in $CDCl_3$.

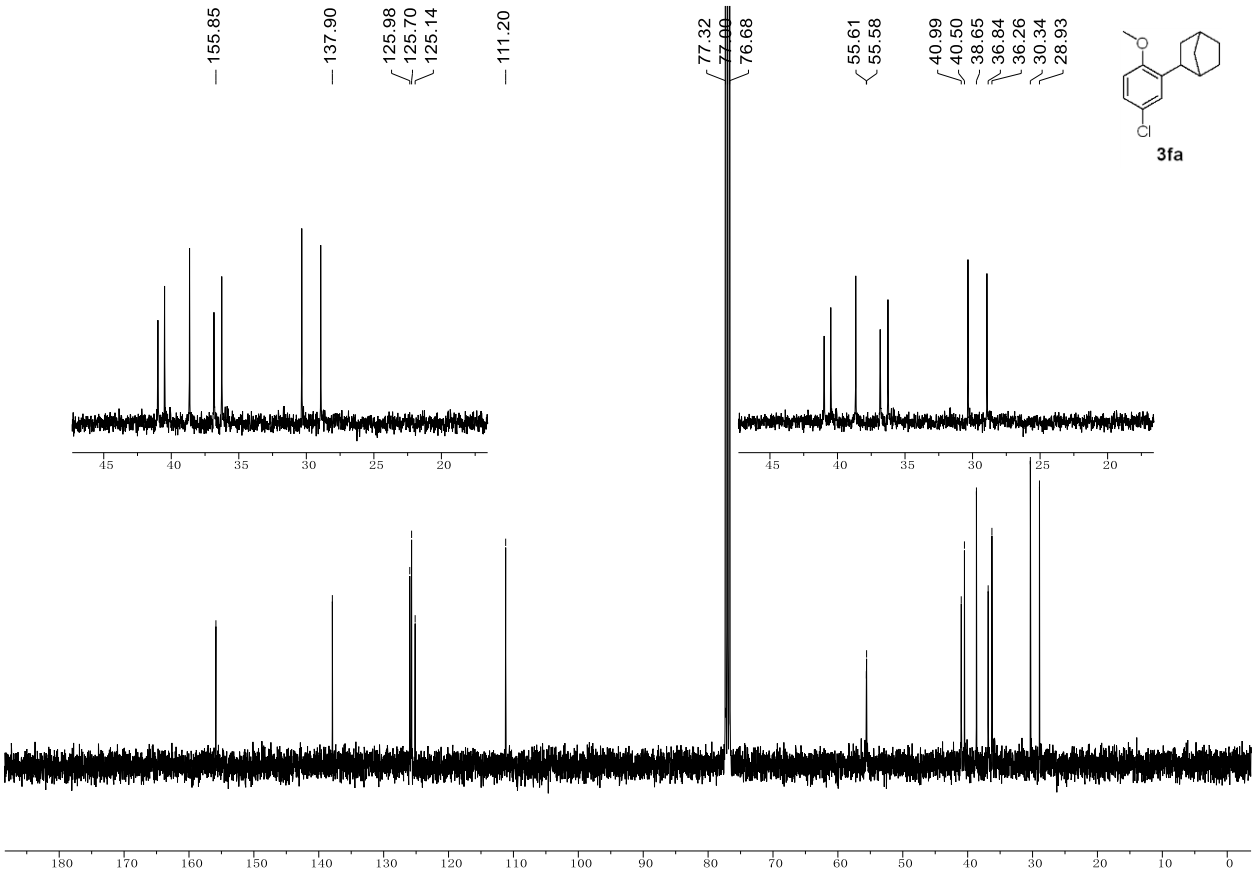

Figure S75. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3fa** in $CDCl_3$.

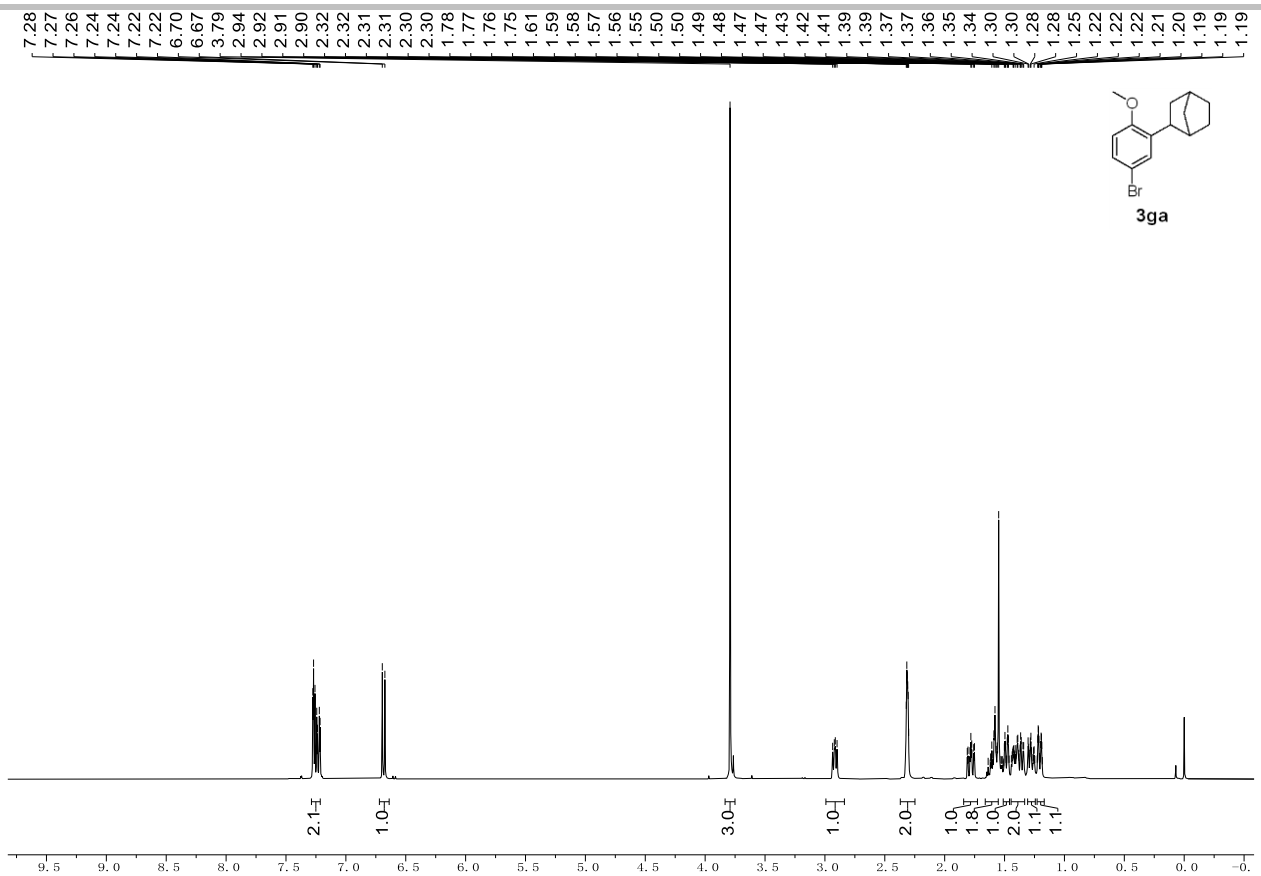

Figure S76. ^{1}H NMR spectrum (400 MHz) of **3ga** in $CDCl_3$.

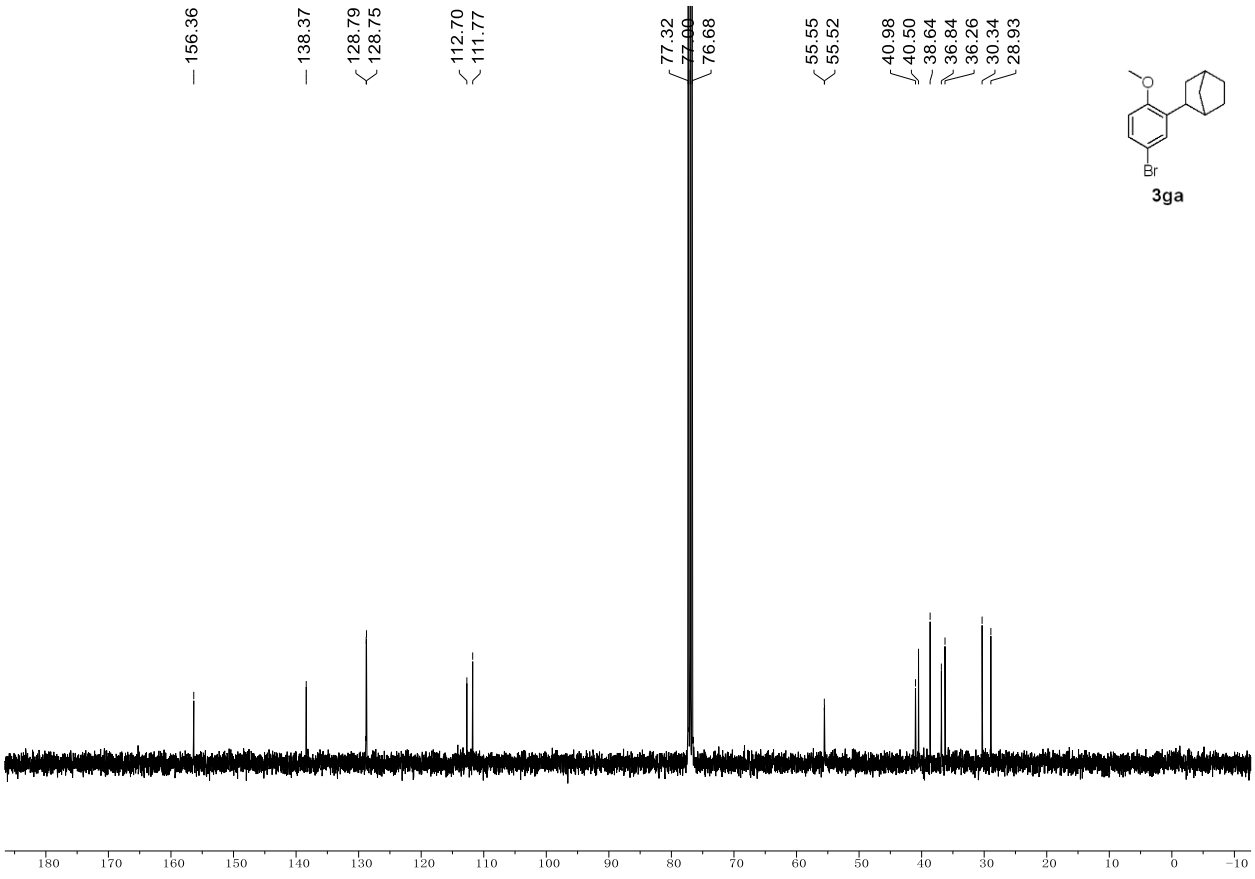

Figure S77. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3ga** in $CDCl_3$.

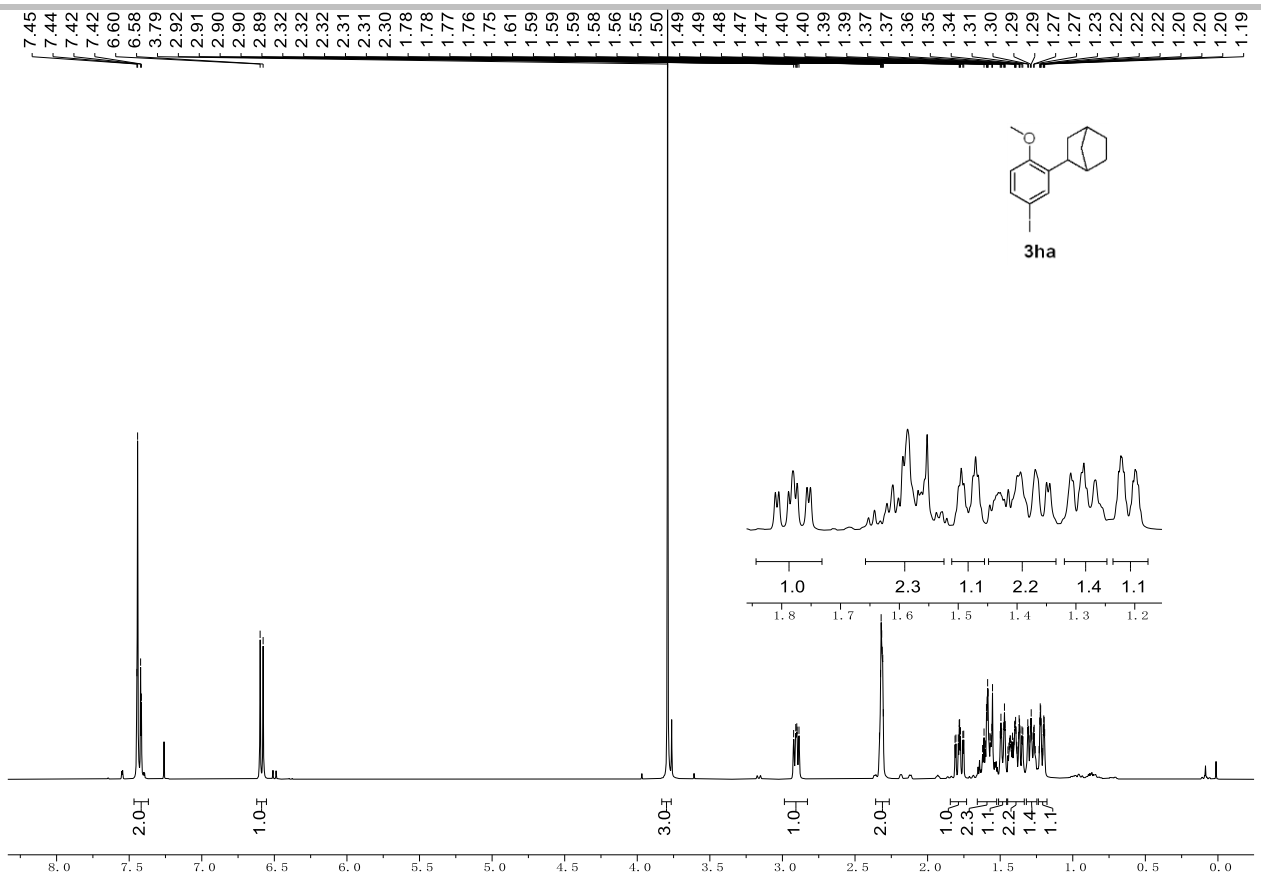

Figure S78. ^{1}H NMR spectrum (400 MHz) of **3ha** in $CDCl_3$.

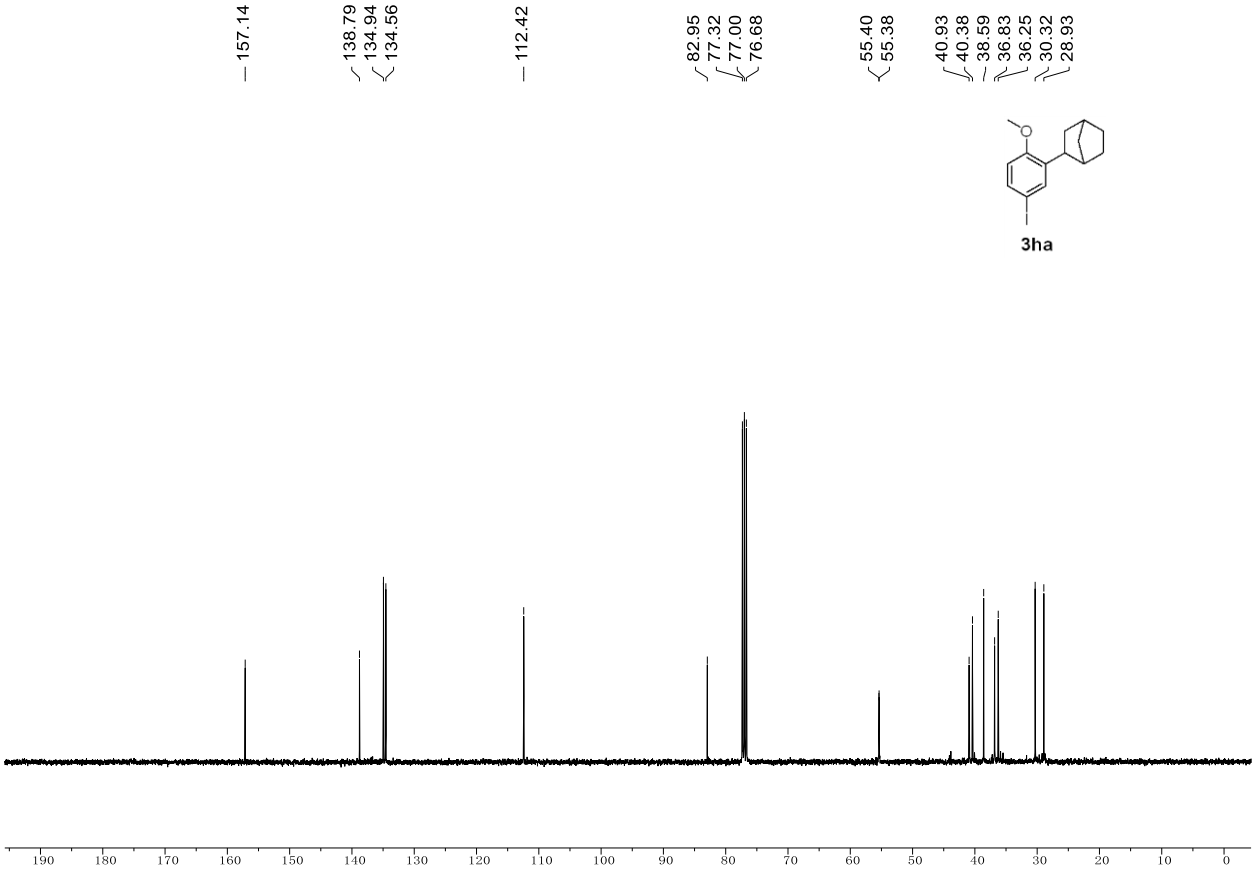

Figure S79. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3ha** in $CDCl_3$.

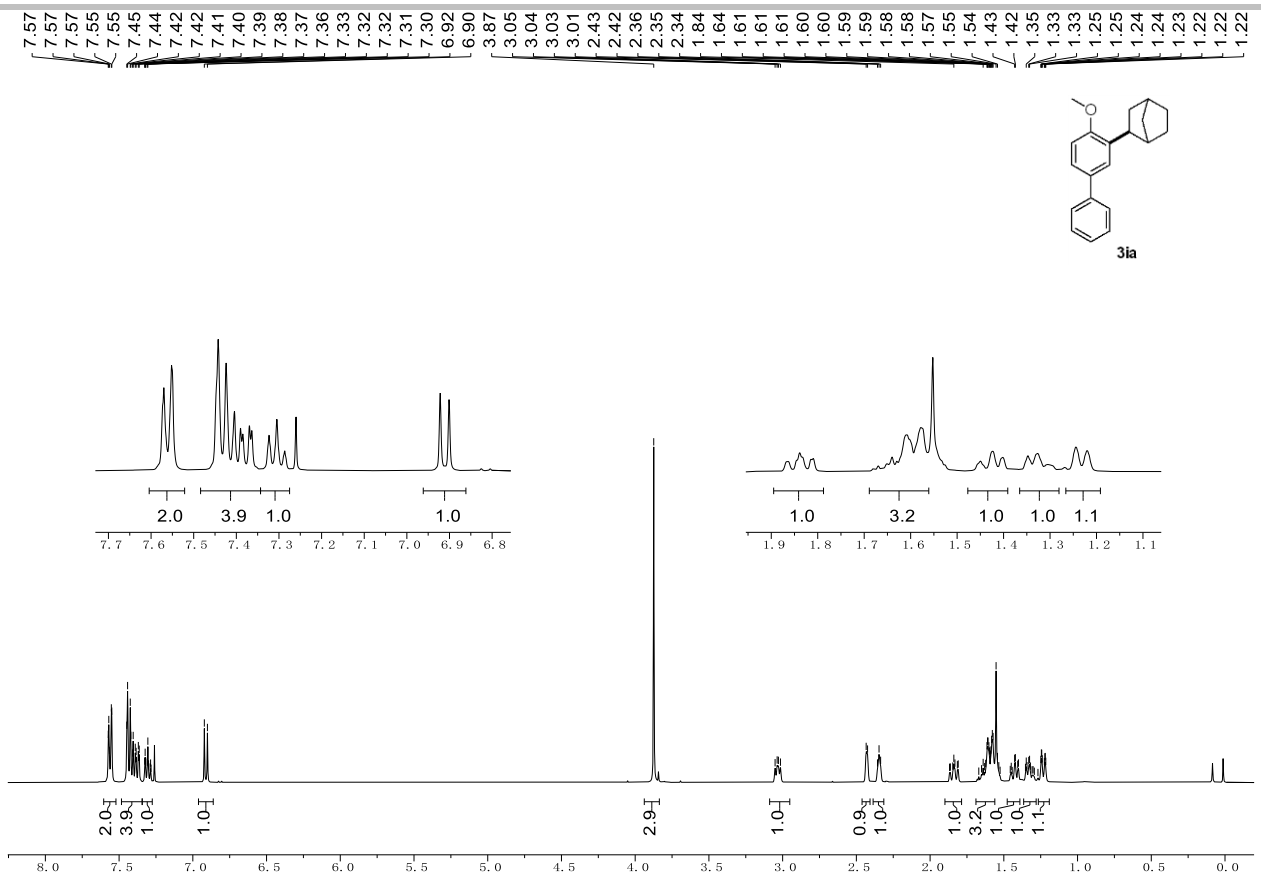

Figure S80. ^{1}H NMR spectrum (400 MHz) of **3ia** in $CDCl_3$.

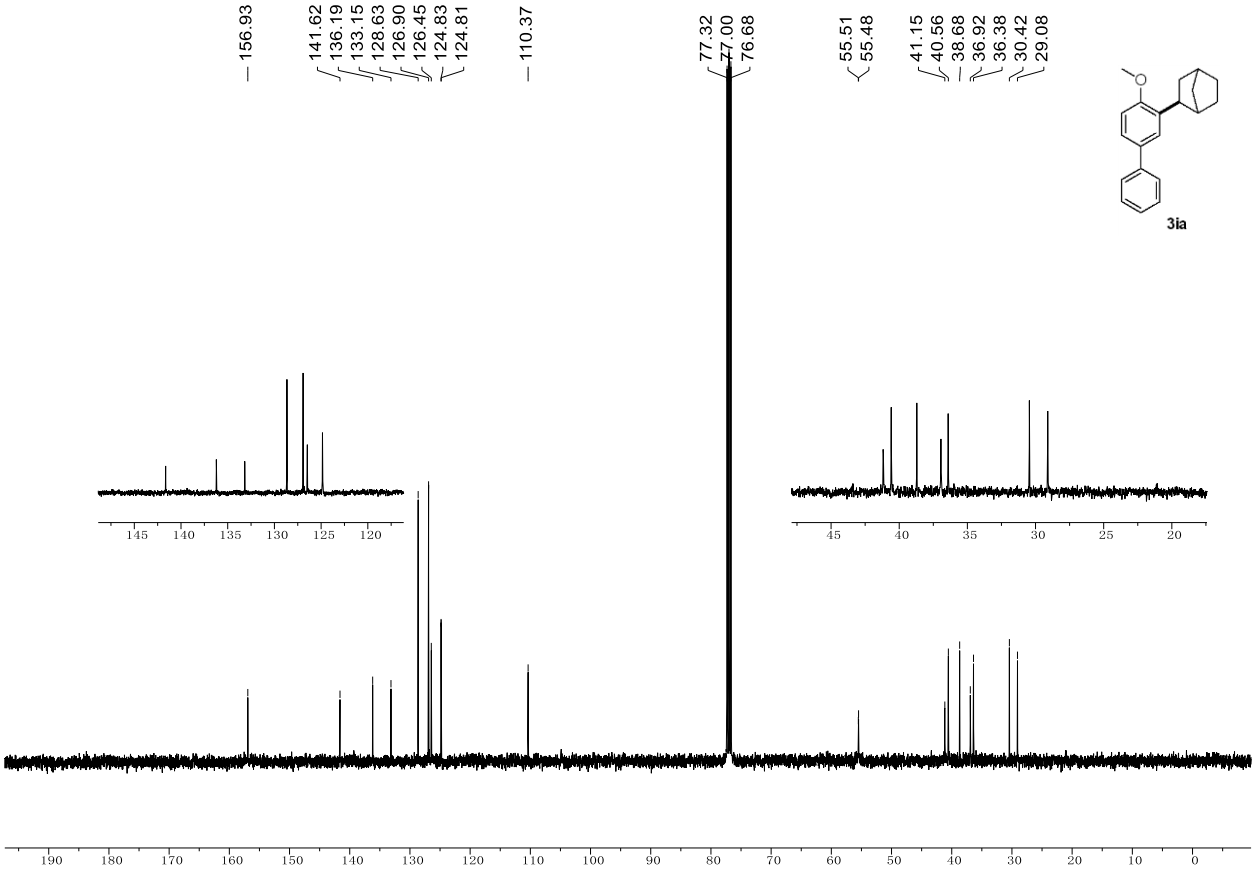

Figure S81. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3ia** in $CDCl_3$.

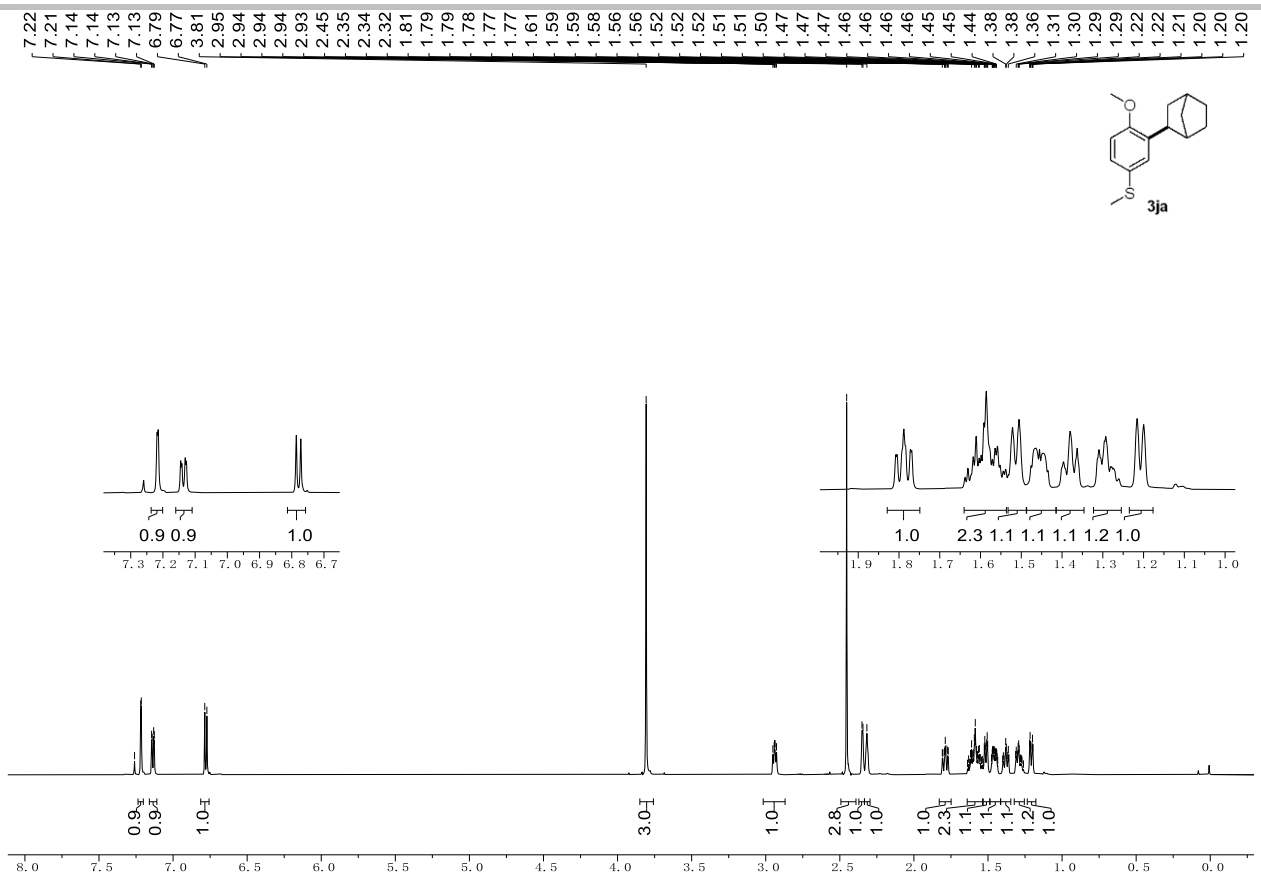

Figure S82. ^{1}H NMR spectrum (400 MHz) of **3ja** in $CDCl_3$.

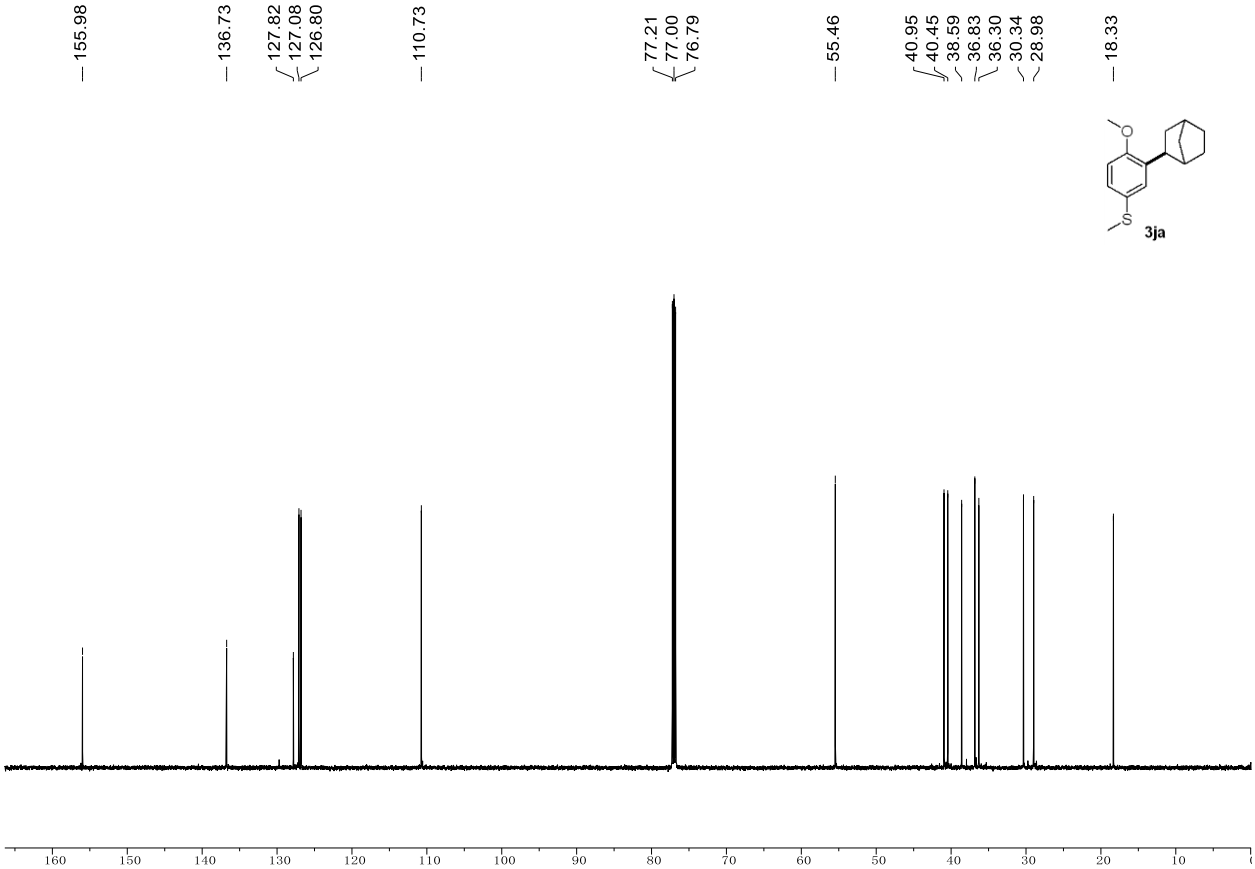

Figure S83. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3ja** in $CDCl_3$.

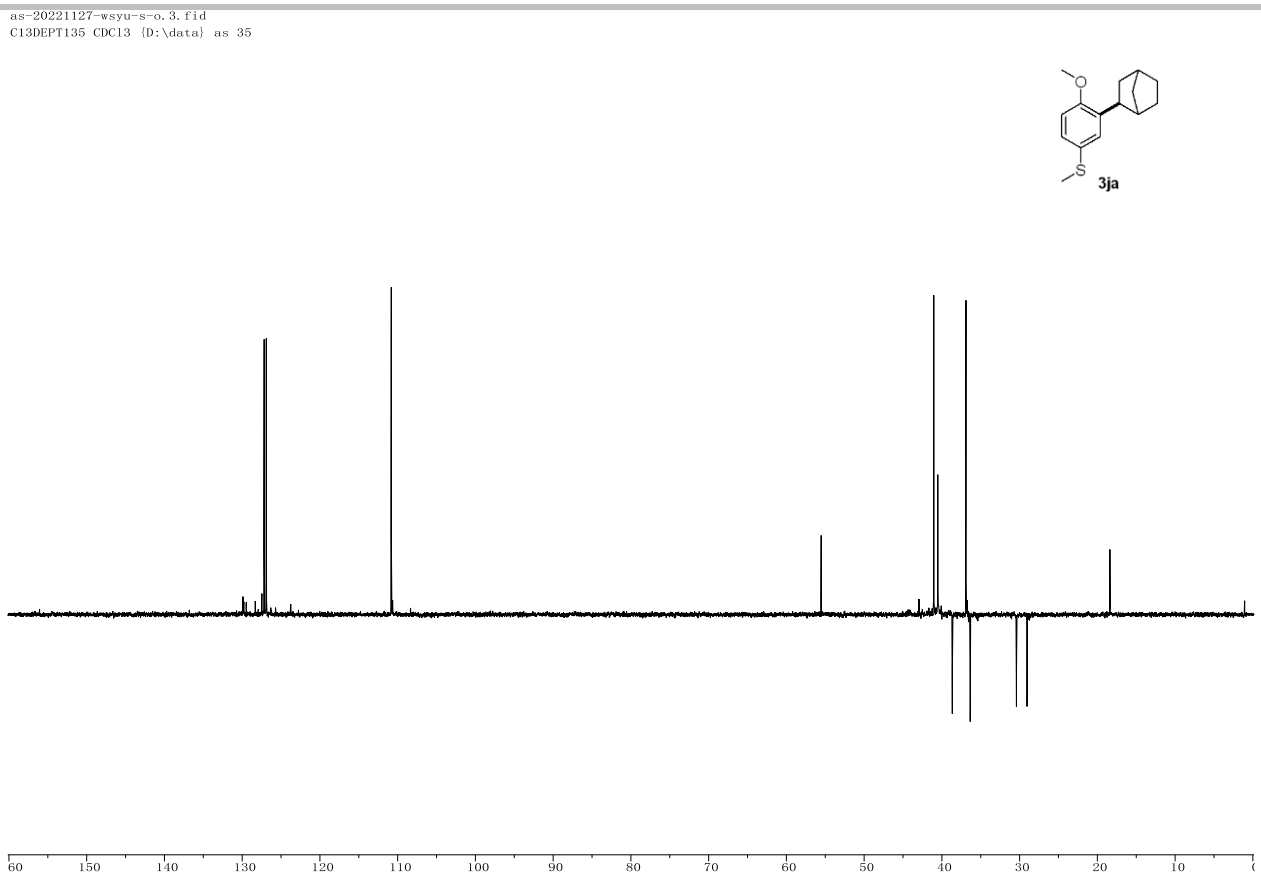

Figure S84. ^{135}Dept NMR spectrum (101 MHz) of **3ja** in $CDCl_3$.

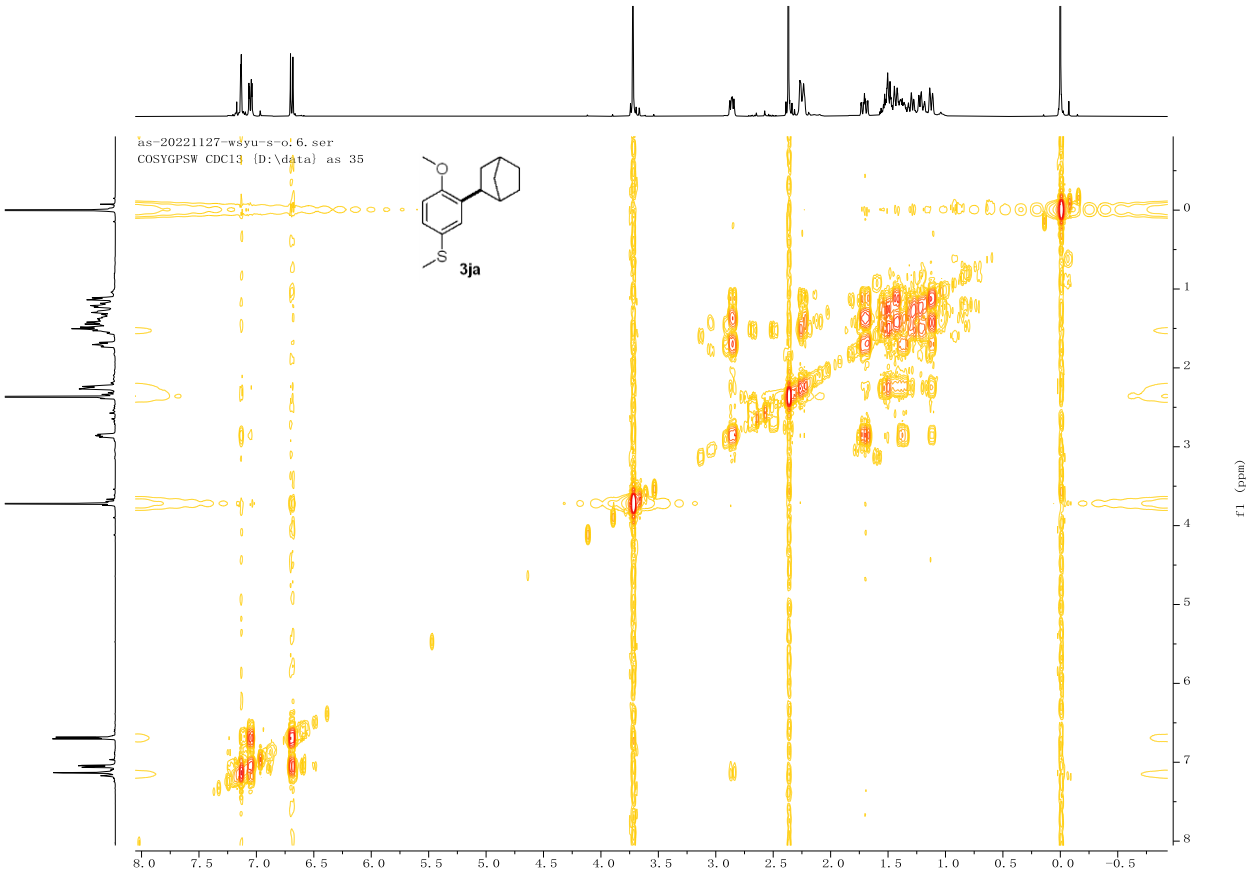

Figure S85. 2D ^{1}H-^{1}H COSY NMR spectrum of **3ja** in $CDCl_3$.

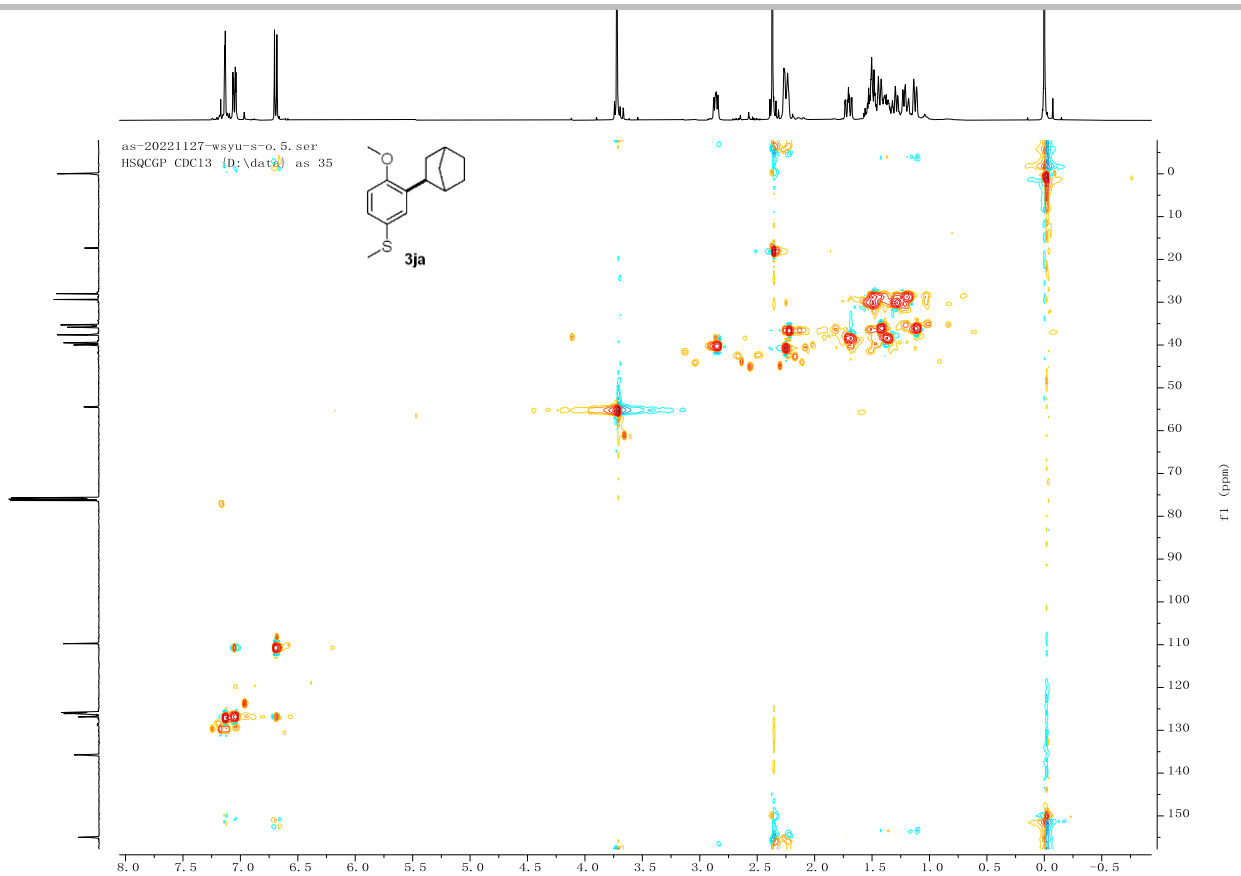

Figure S86. 2D ^{1}H-^{13}C HSQC NMR spectrum of **3ja** in $CDCl_3$.

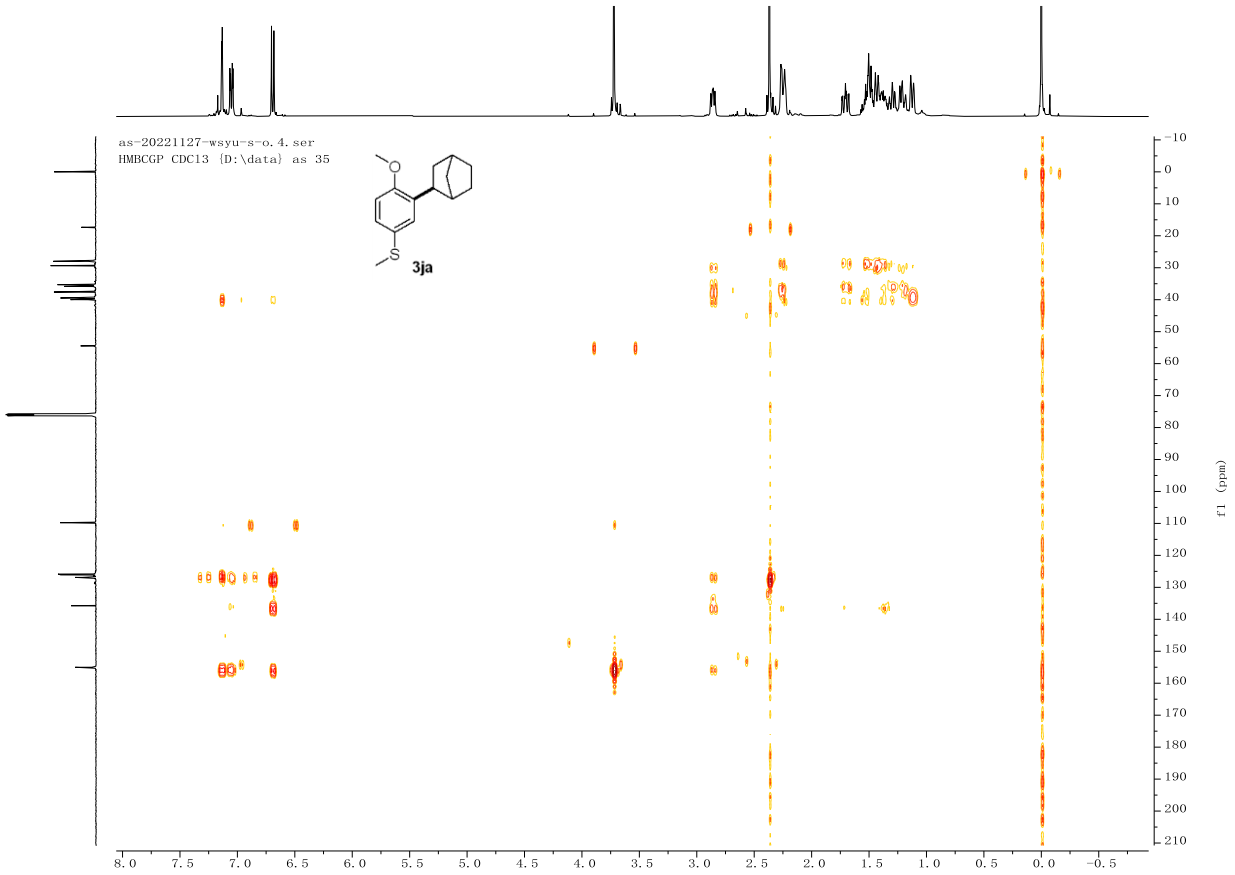

Figure S87. 2D ^{1}H-^{13}C HMBC NMR spectrum of **3ja** in $CDCl_3$.

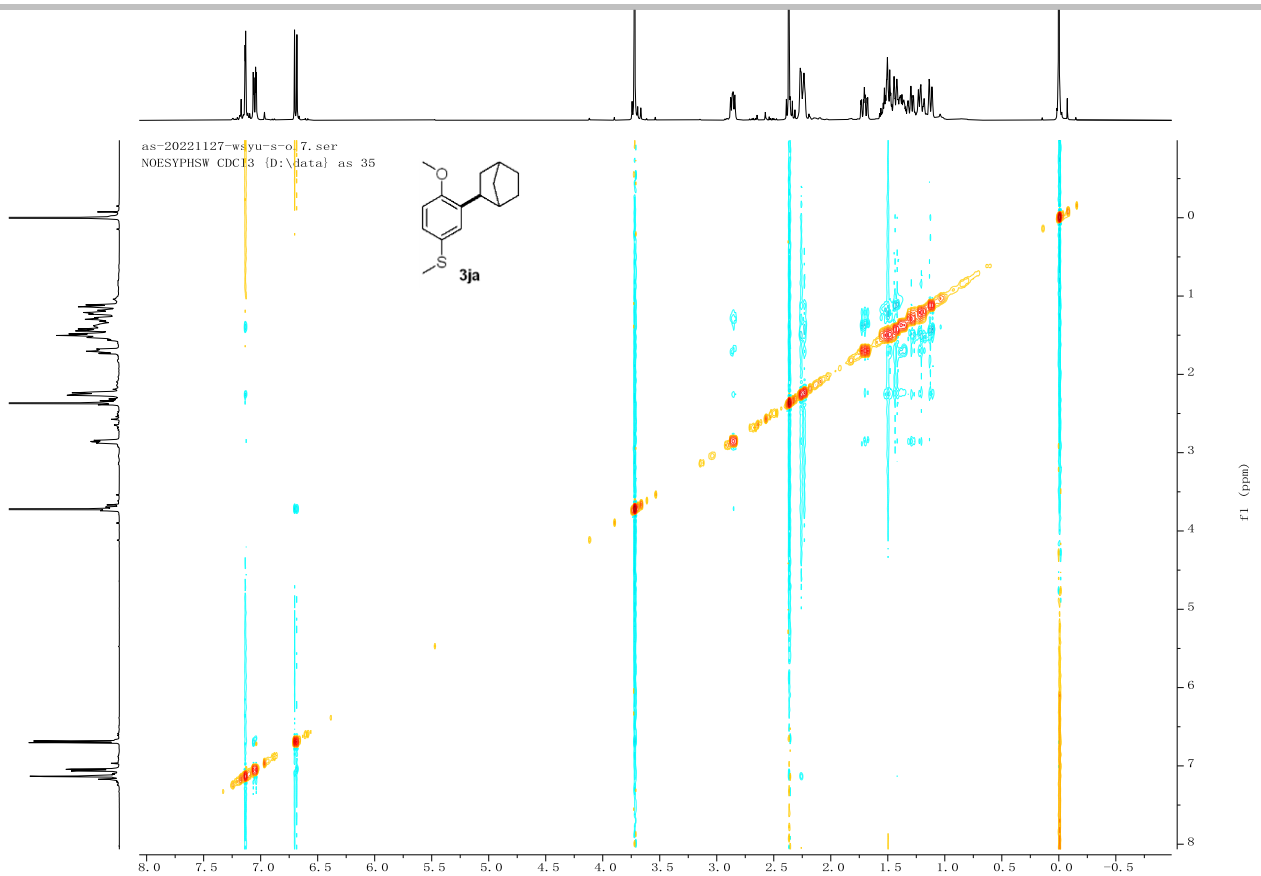

Figure S88. 2D NOESY NMR spectrum of **3ja** in $CDCl_3$.

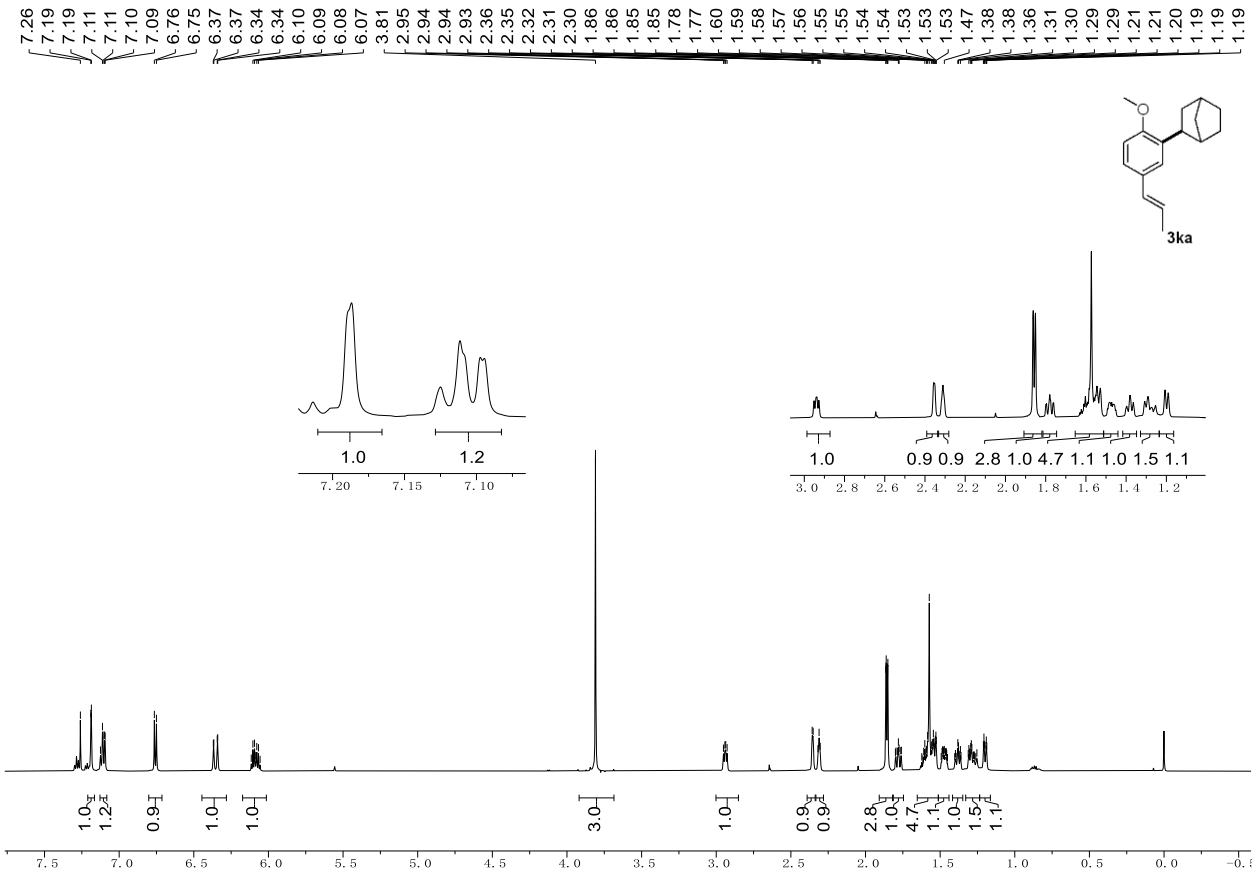

Figure S89. ^1H NMR spectrum (400 MHz) of **3ka** in $CDCl_3$.

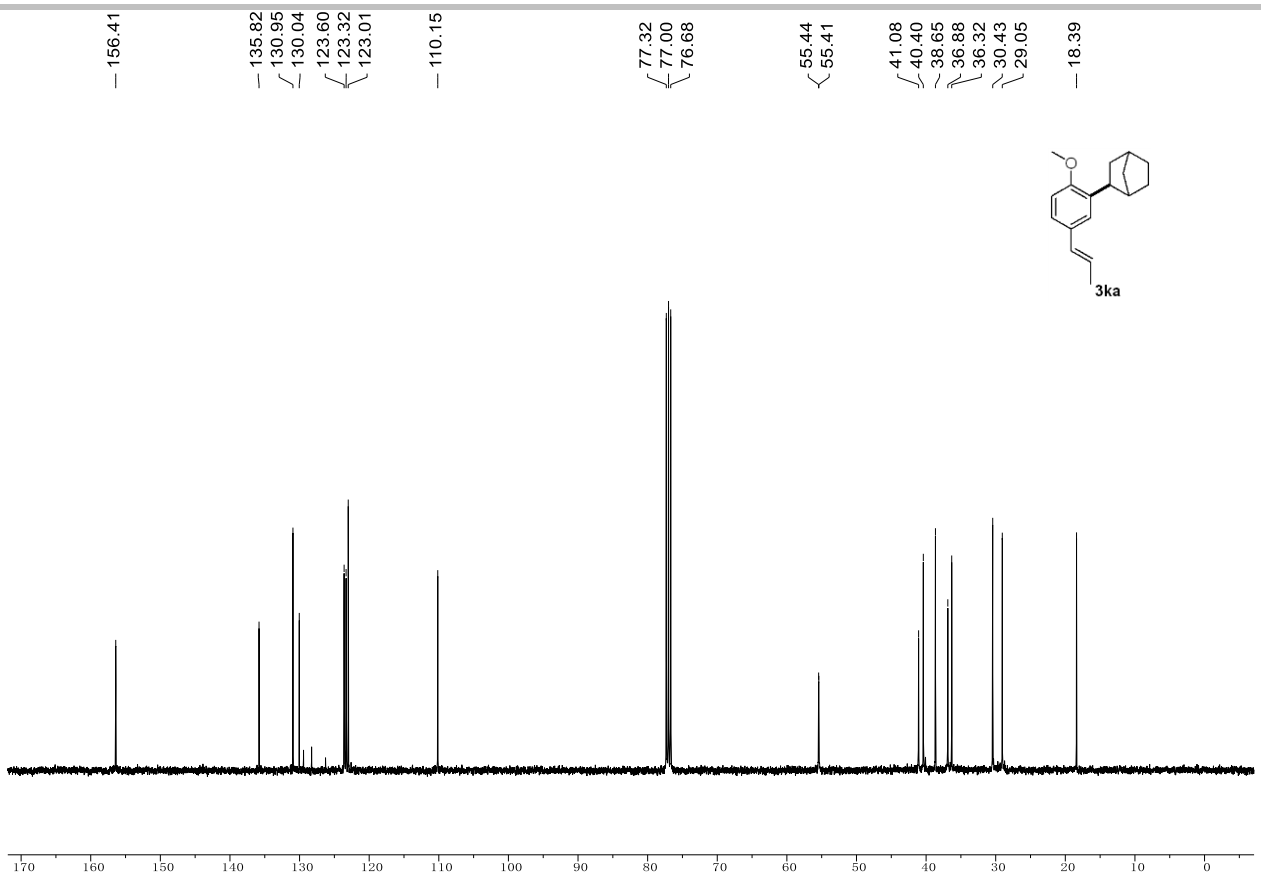

Figure S90. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3ka** in $CDCl_3$.

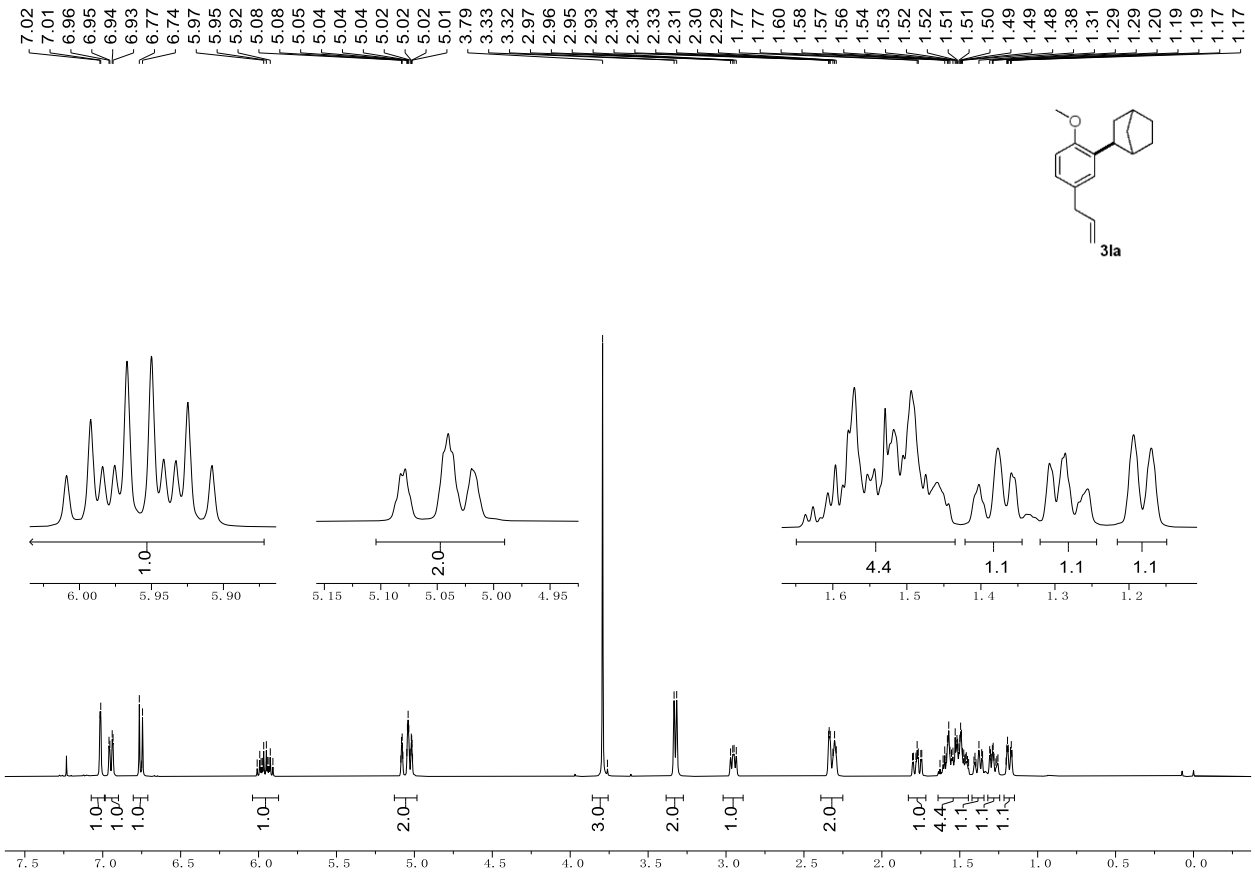

Figure S91. ^{1}H NMR spectrum (400 MHz) of **3la** in $CDCl_3$.

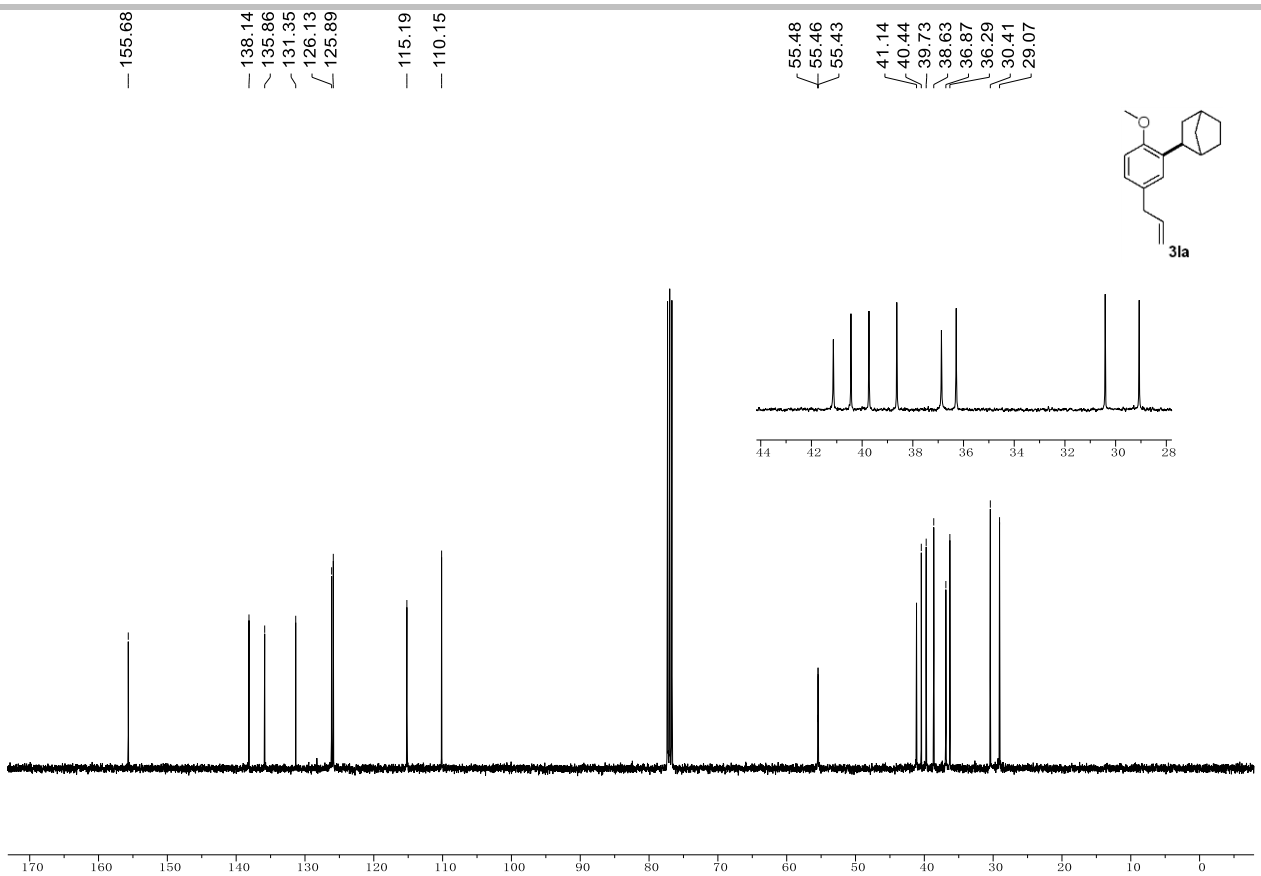

Figure S92. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3la** in $CDCl_3$.

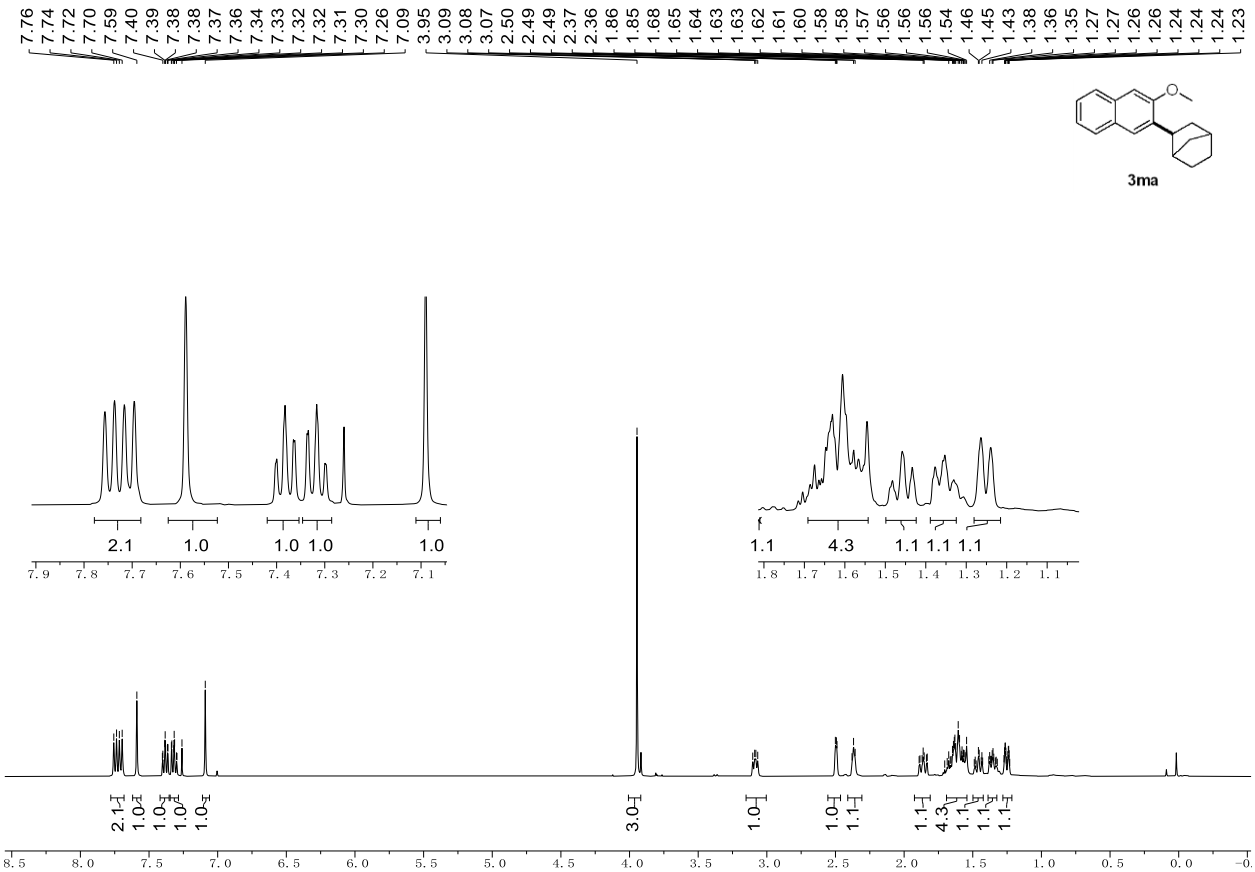

Figure S93. ^{1}H NMR spectrum (400 MHz) of **3ma** in $CDCl_3$.

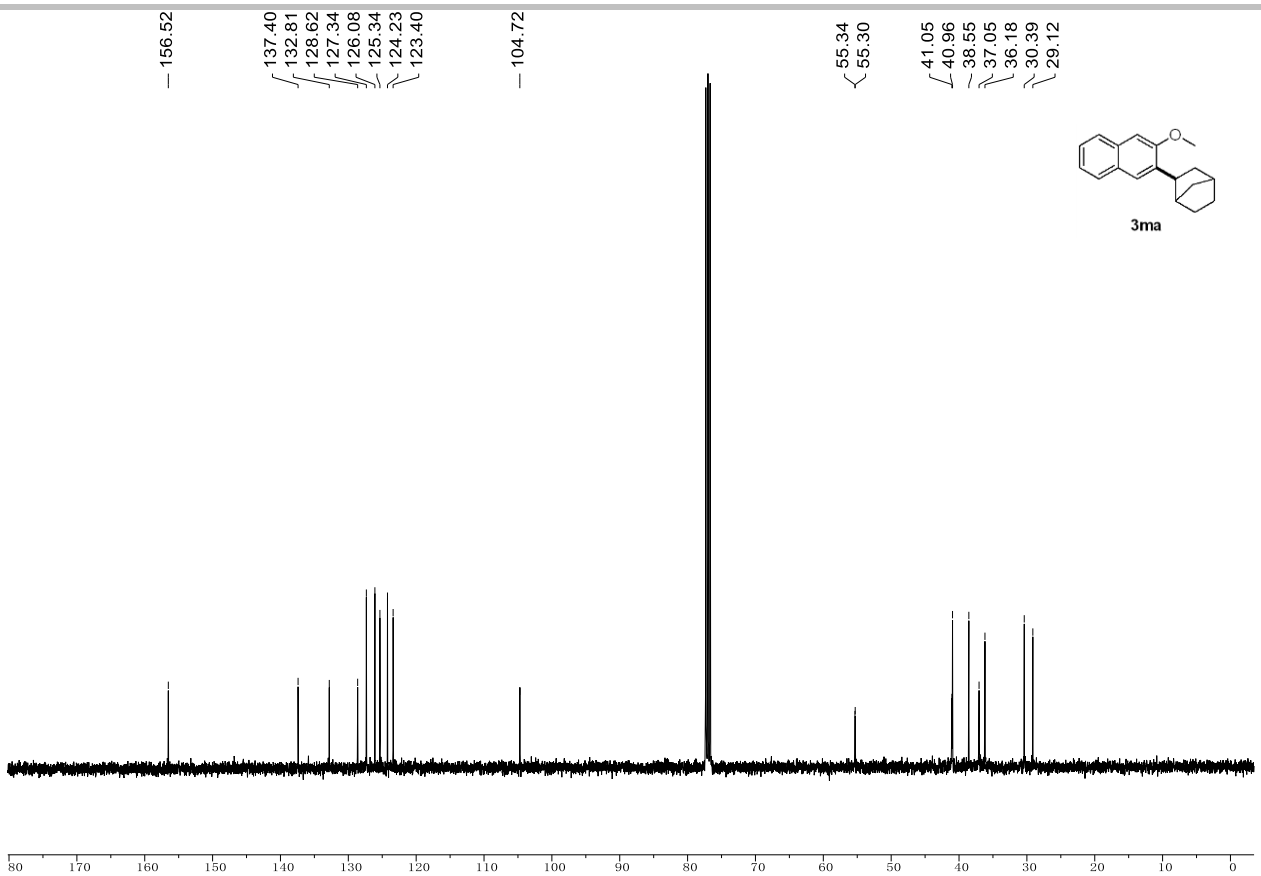

Figure S94. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3ma** in $CDCl_3$.

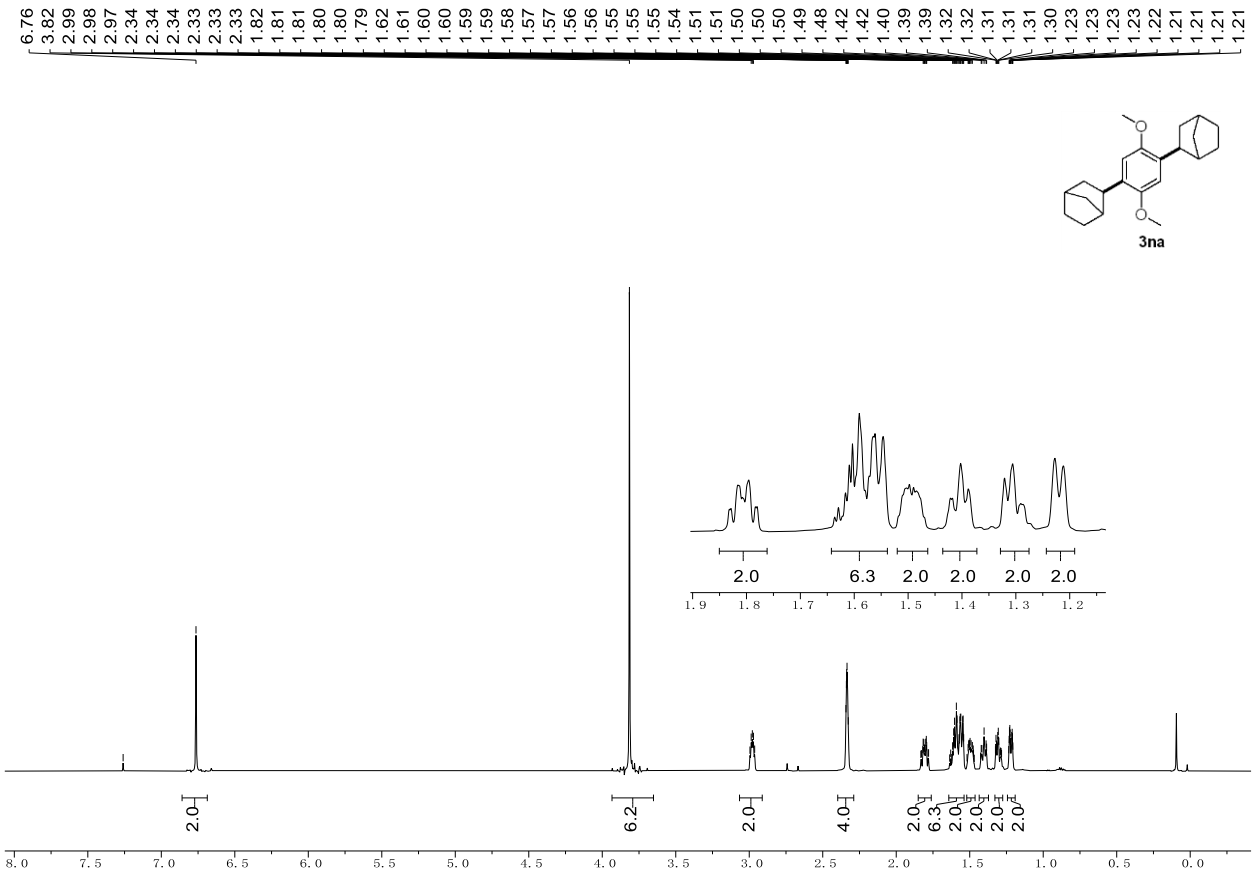

Figure S95. ^{1}H NMR spectrum (400 MHz) of **3na** in $CDCl_3$.

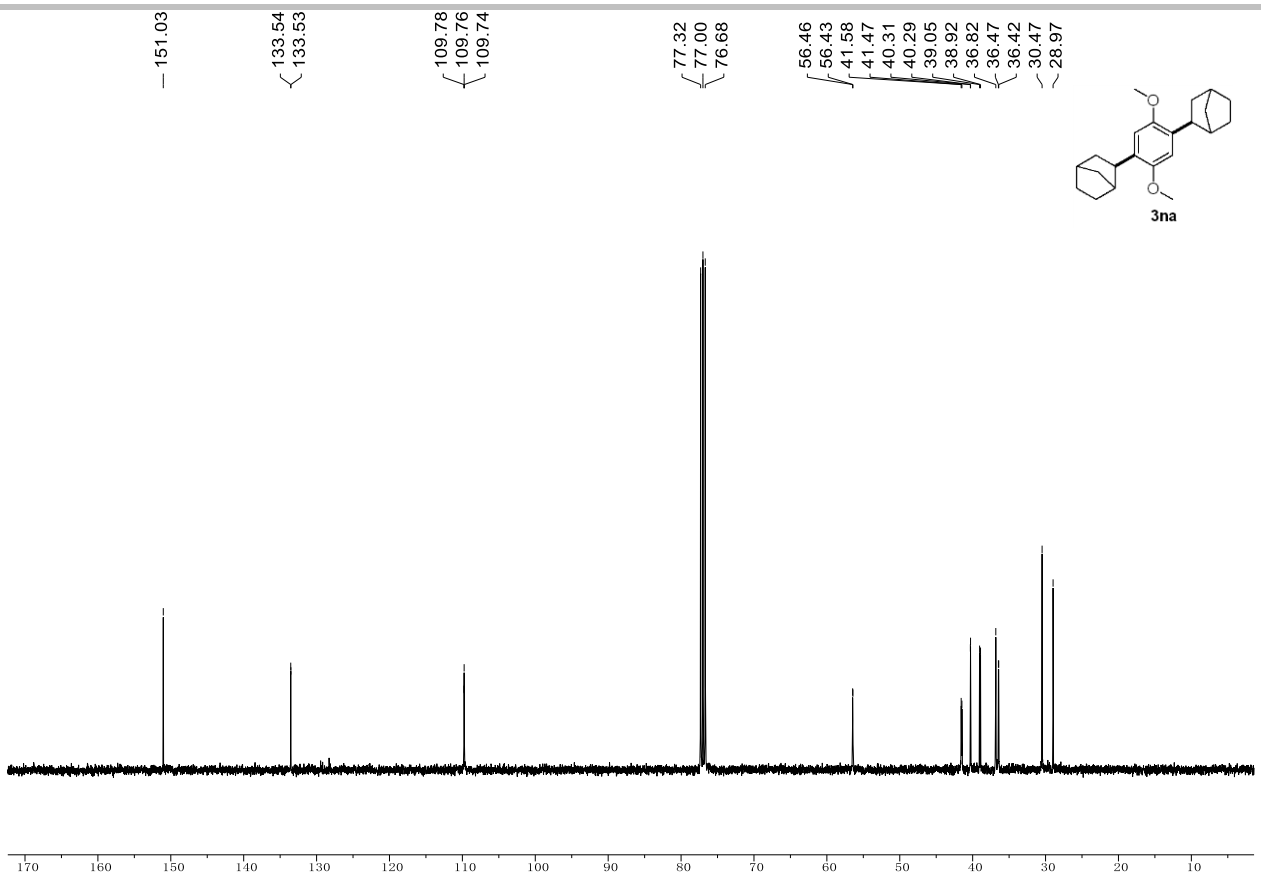

Figure S96. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3na** in $CDCl_3$.

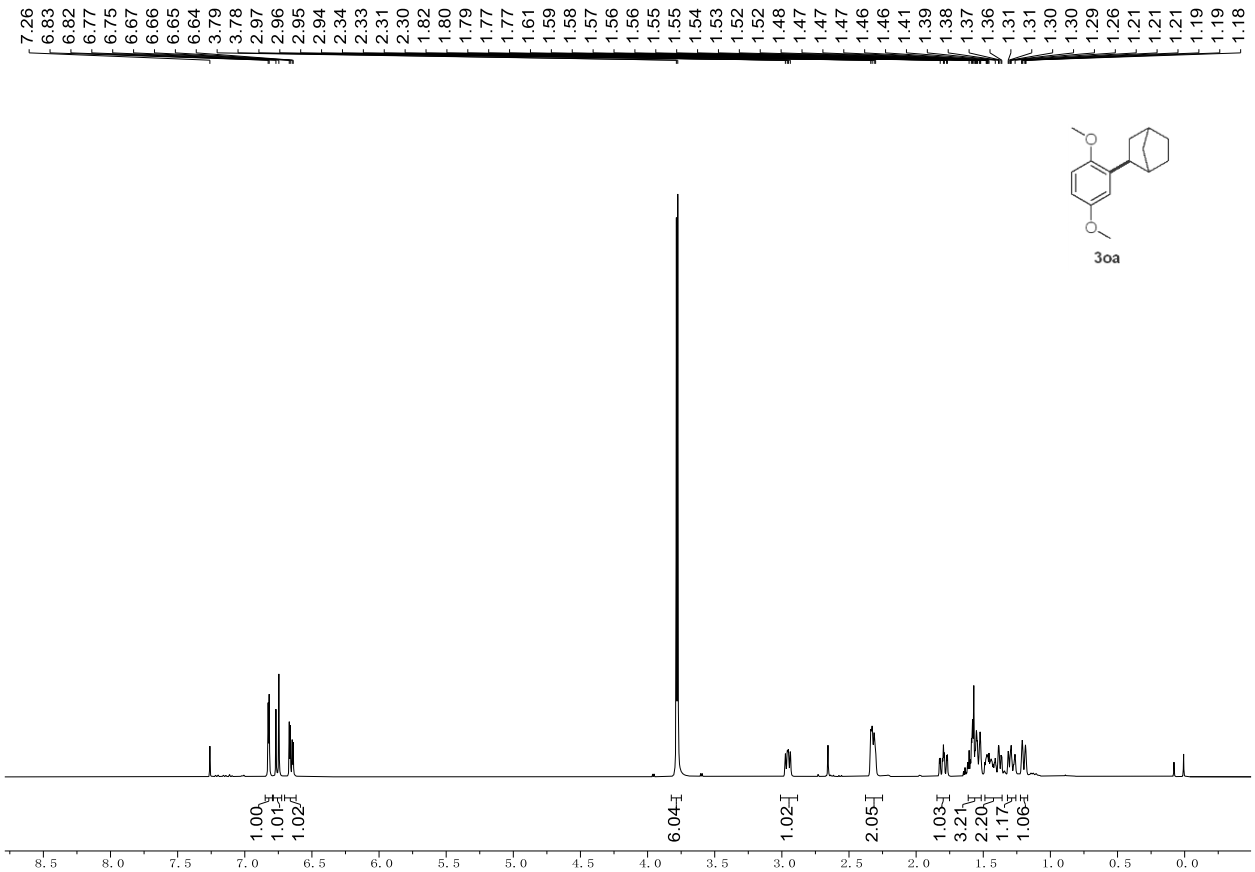

Figure S97. ^{1}H NMR spectrum (400 MHz) of **3oa** in $CDCl_3$.

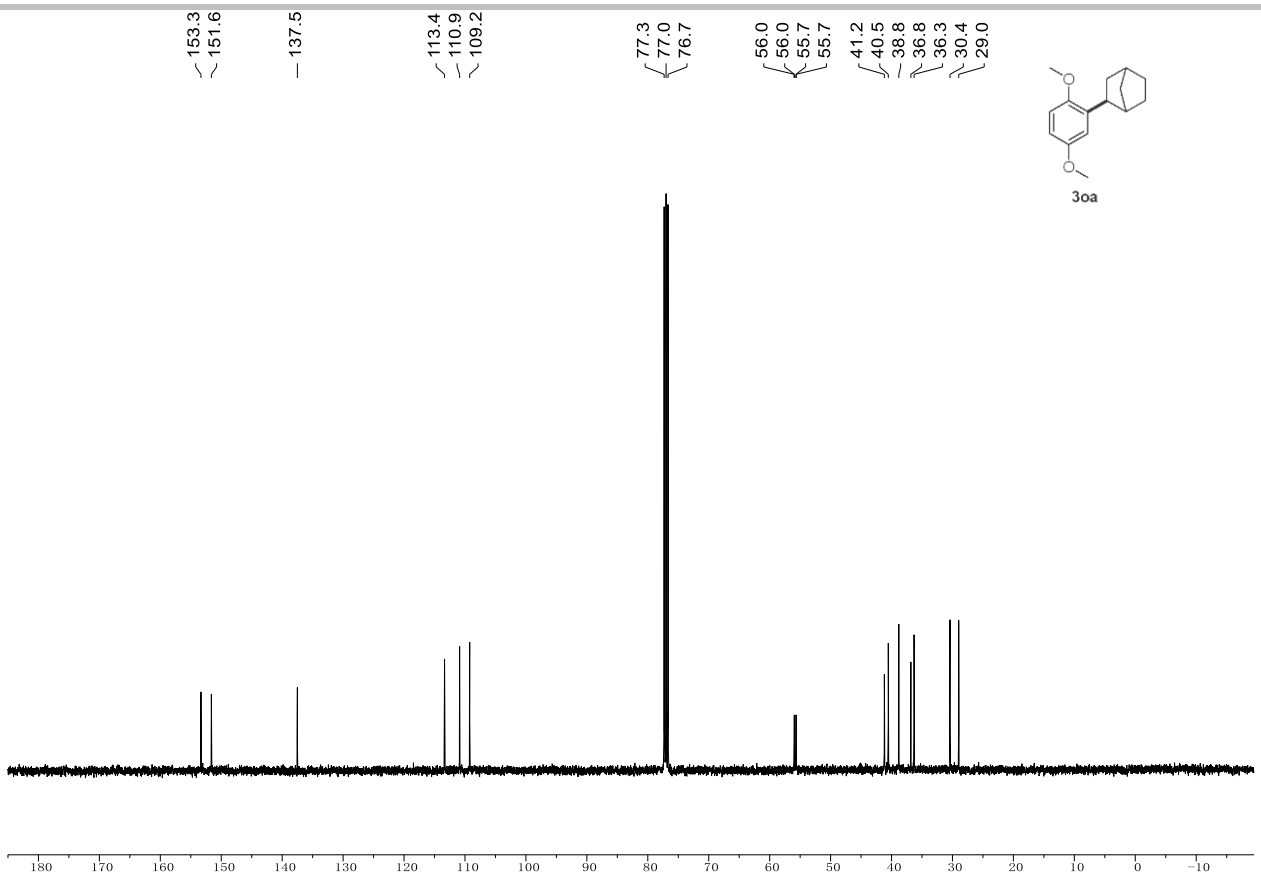

Figure S98. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3oa** in $CDCl_3$.

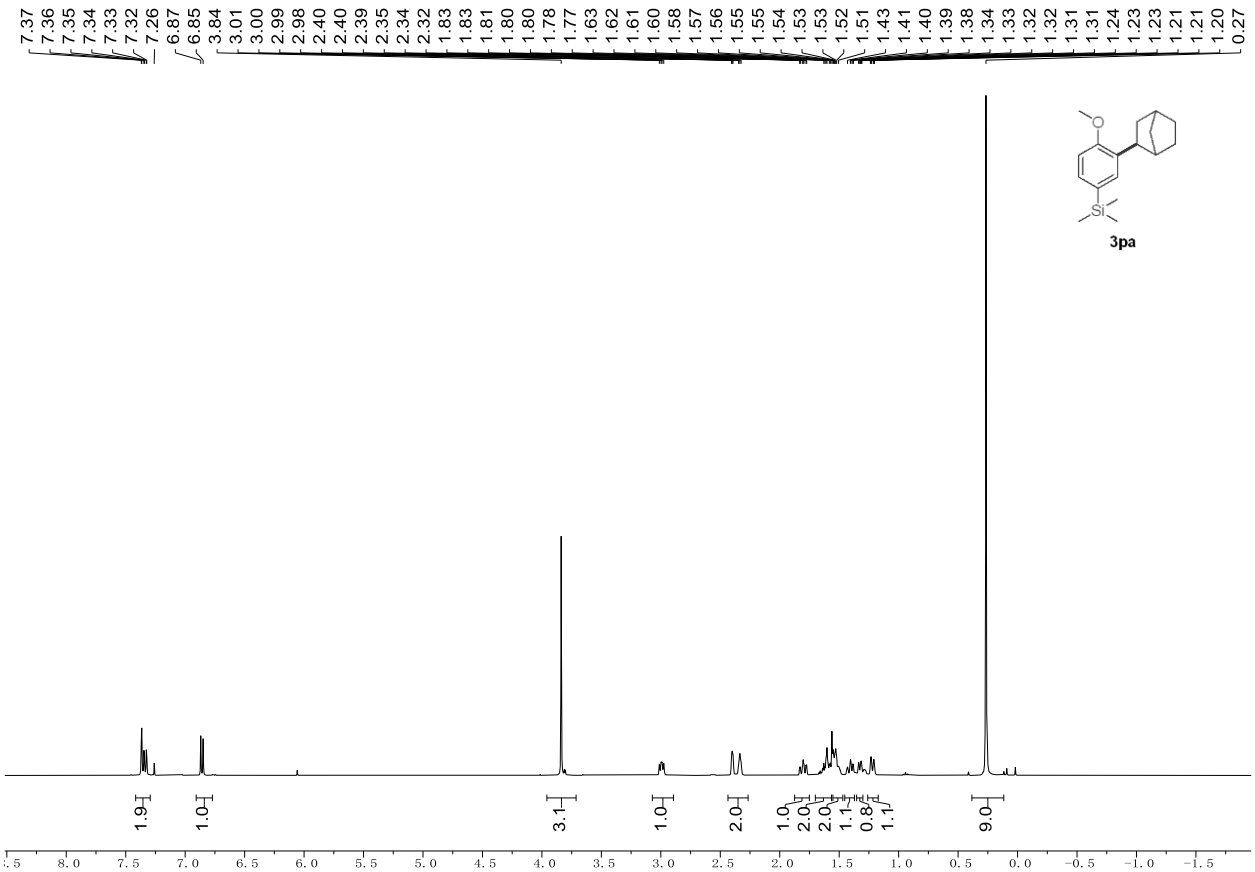

Figure S99. ^{1}H NMR spectrum (400 MHz) of **3pa** in $CDCl_3$.

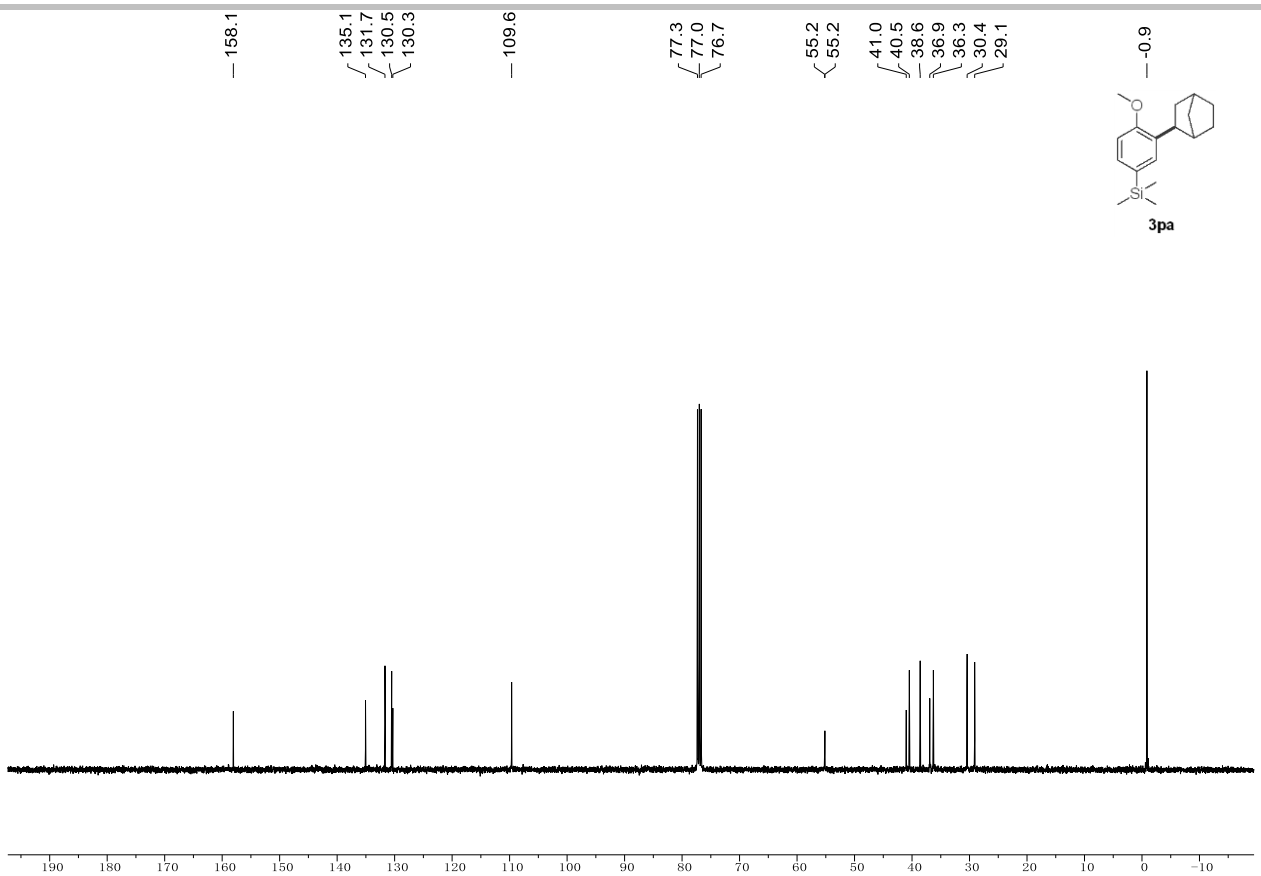

Figure S100. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3pa** in $CDCl_3$.

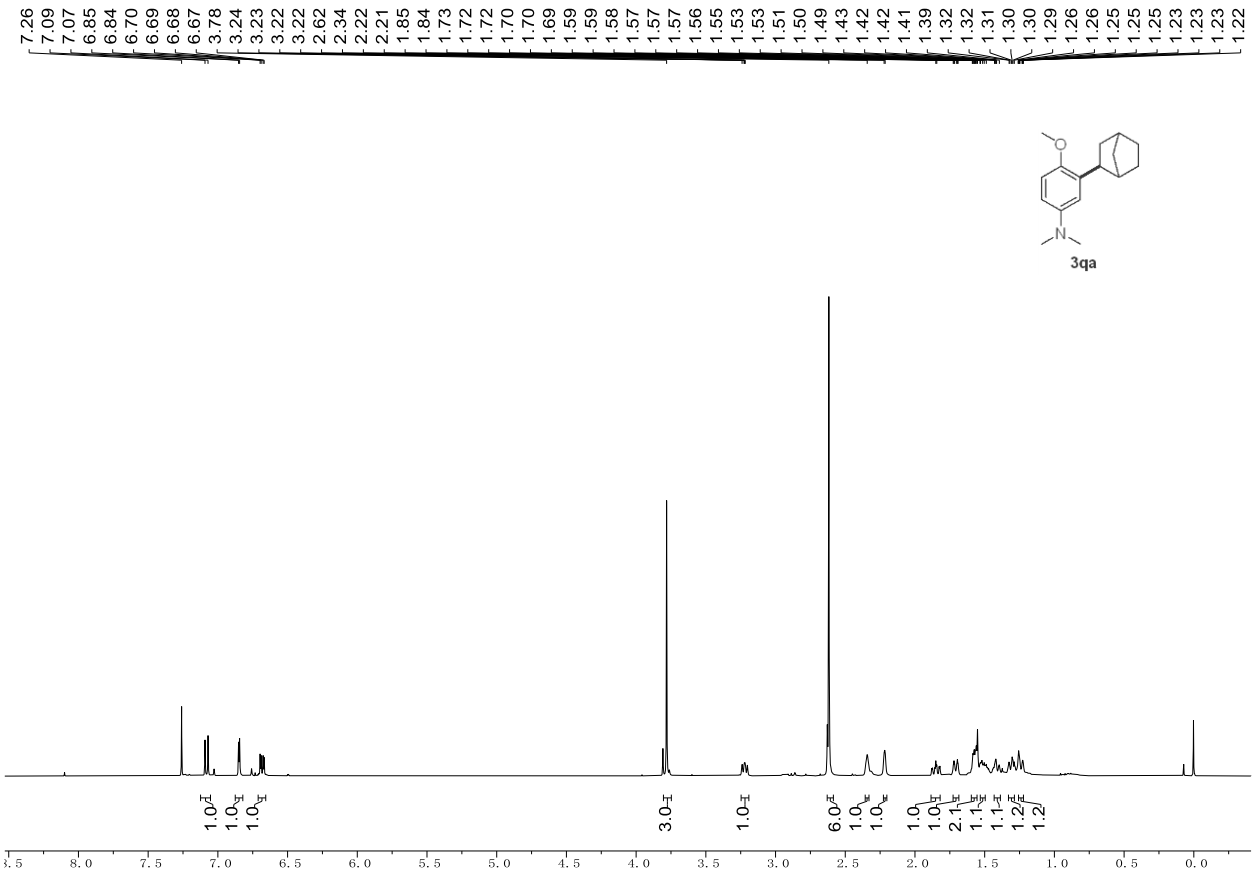

Figure S101. ^{1}H NMR spectrum (400 MHz) of **3qa** in $CDCl_3$.

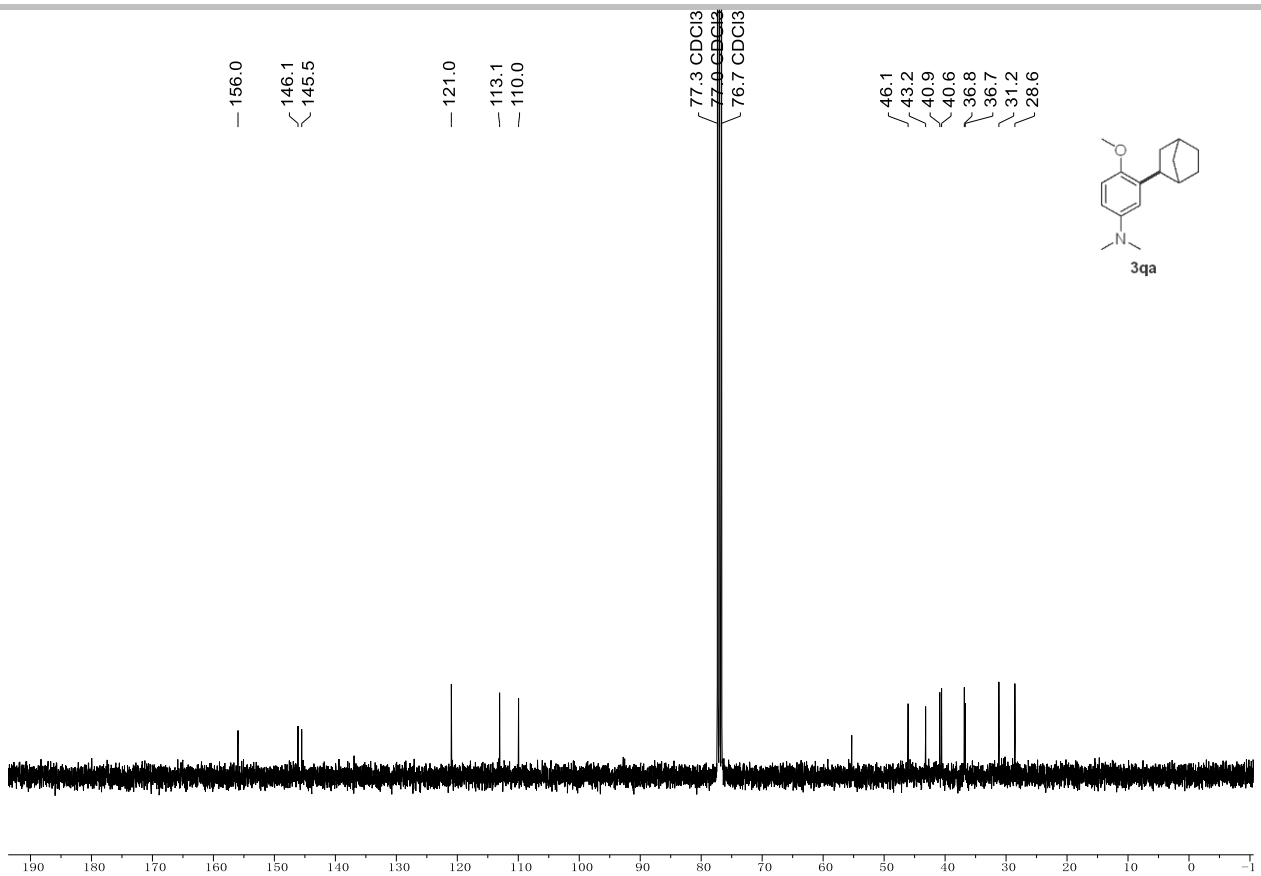

Figure S102. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3qa** in $CDCl_3$.

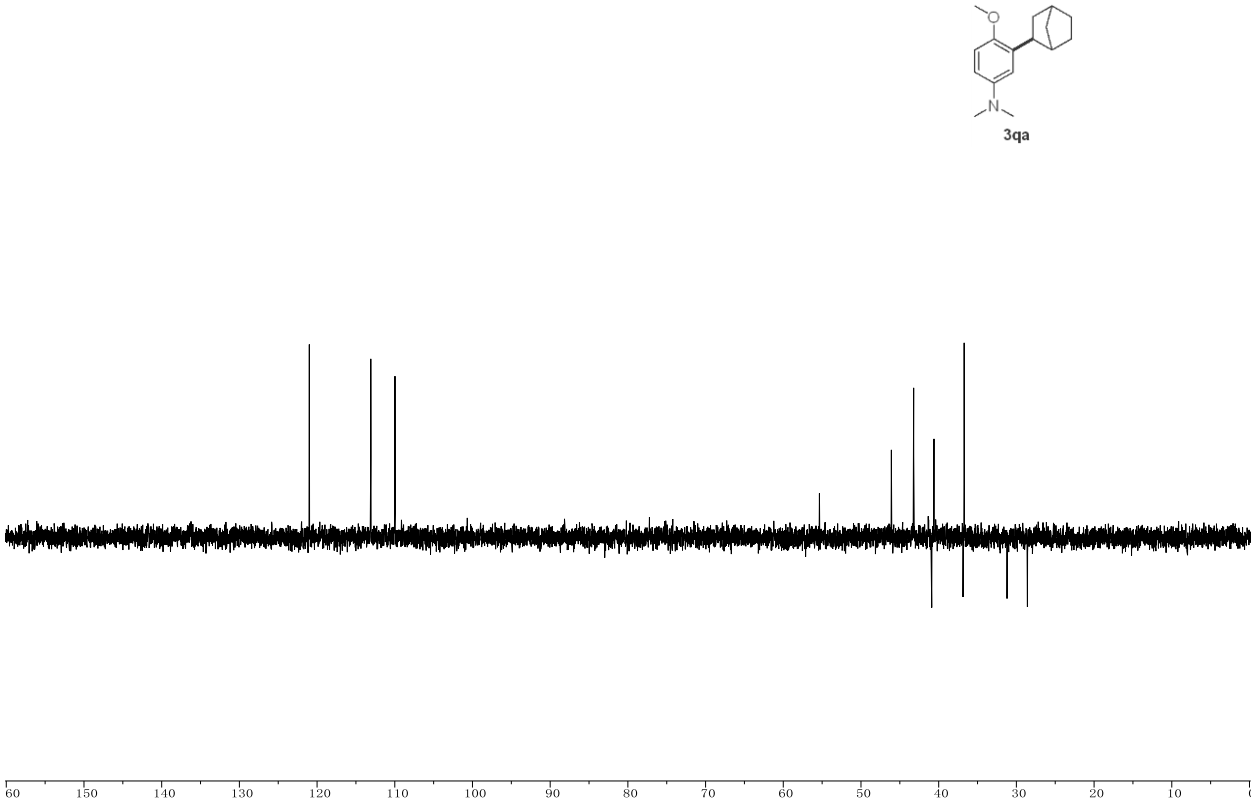

Figure S103. ^{135}Dept NMR spectrum (101 MHz) of **3qa** in $CDCl_3$.

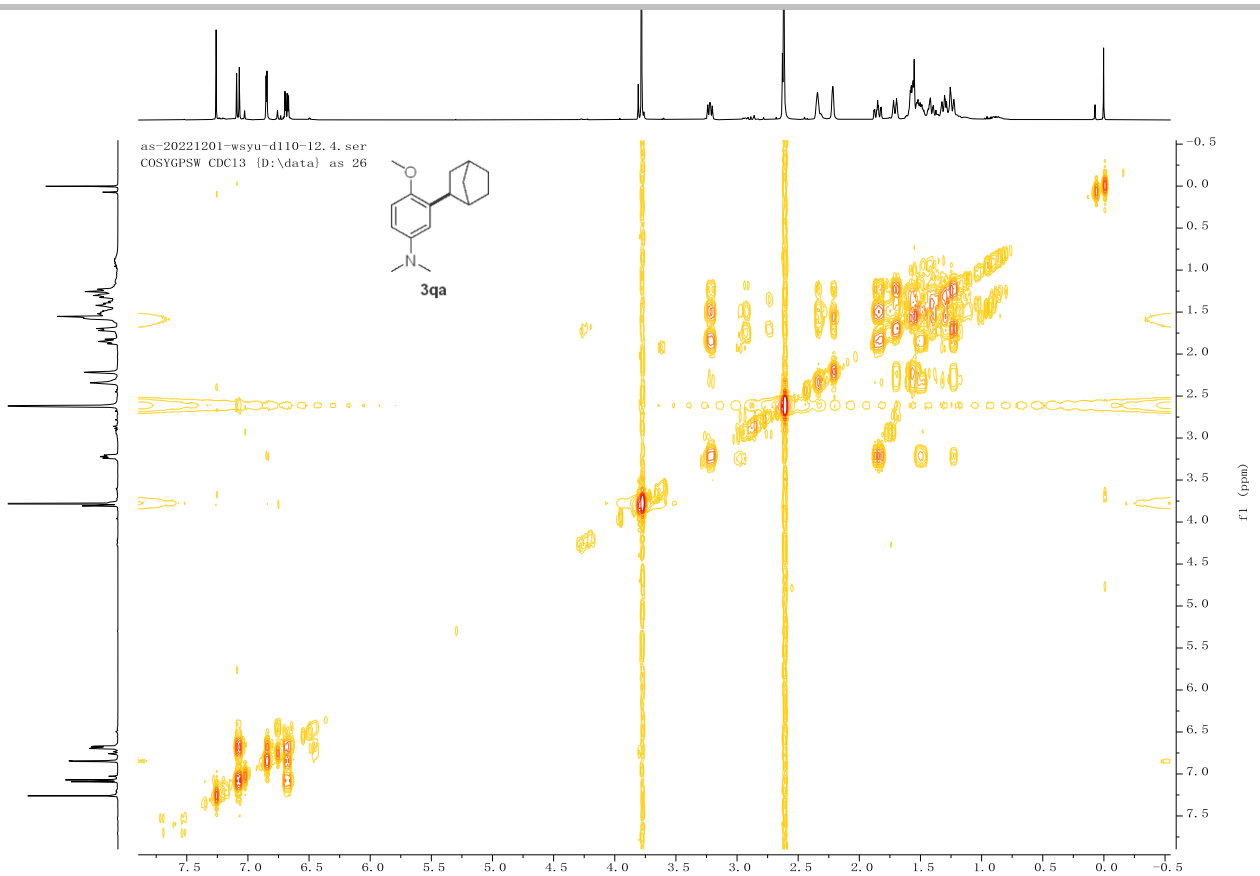

Figure S104. 2D ^{1}H-^{1}H COSY NMR spectrum of **3qa** in $CDCl_3$.

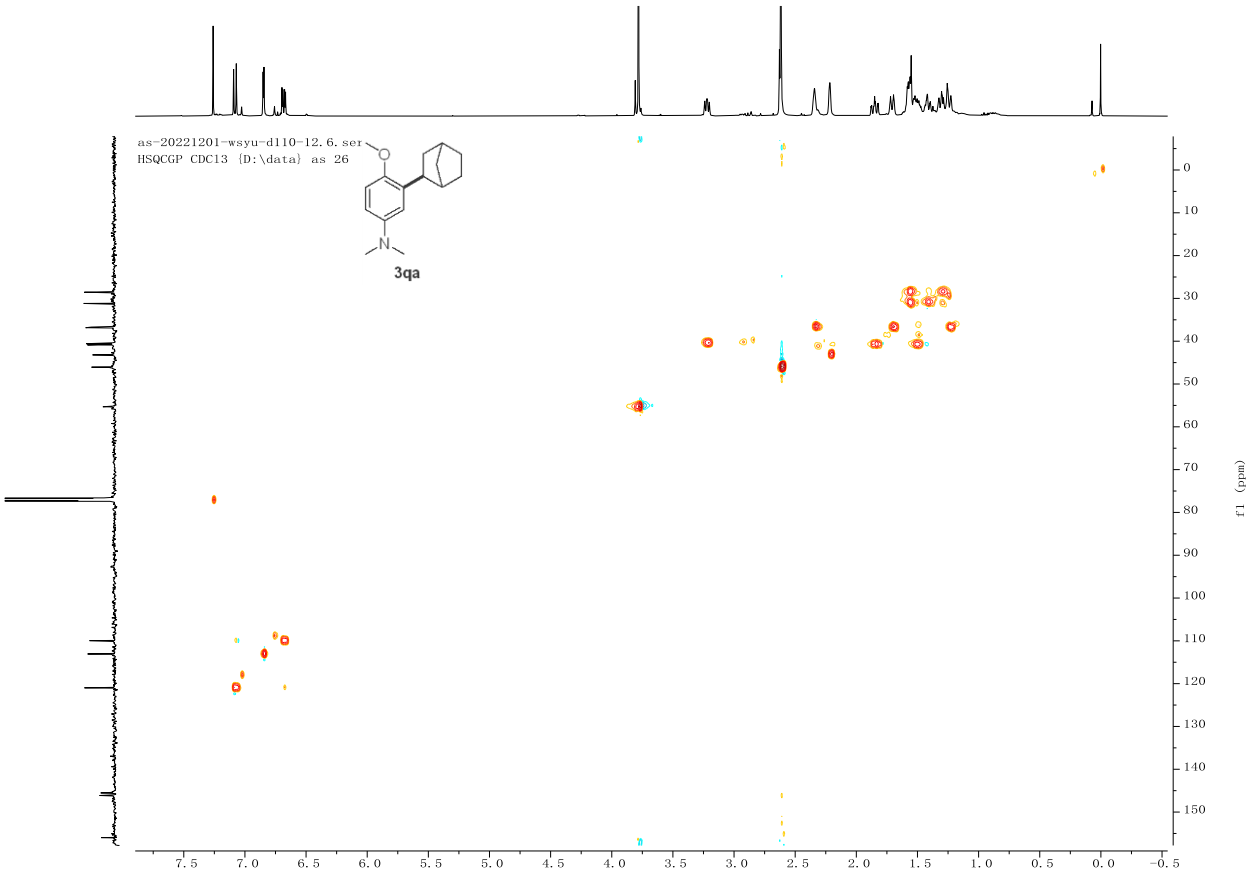

Figure S105. 2D ^{1}H-^{13}C HSQC NMR spectrum of **3qa** in $CDCl_3$.

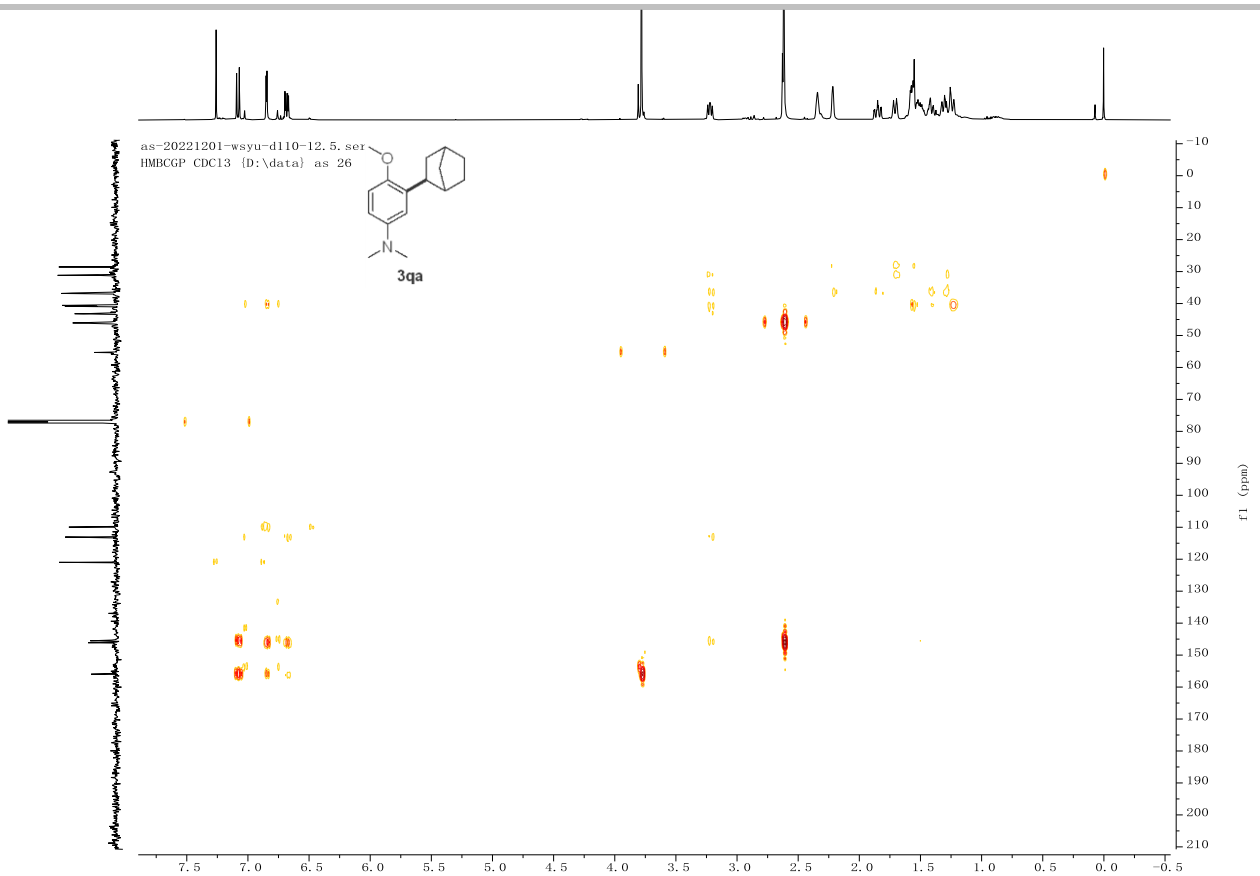

Figure S106. 2D ^{1}H-^{13}C HMBC NMR spectrum of **3qa** in $CDCl_3$.

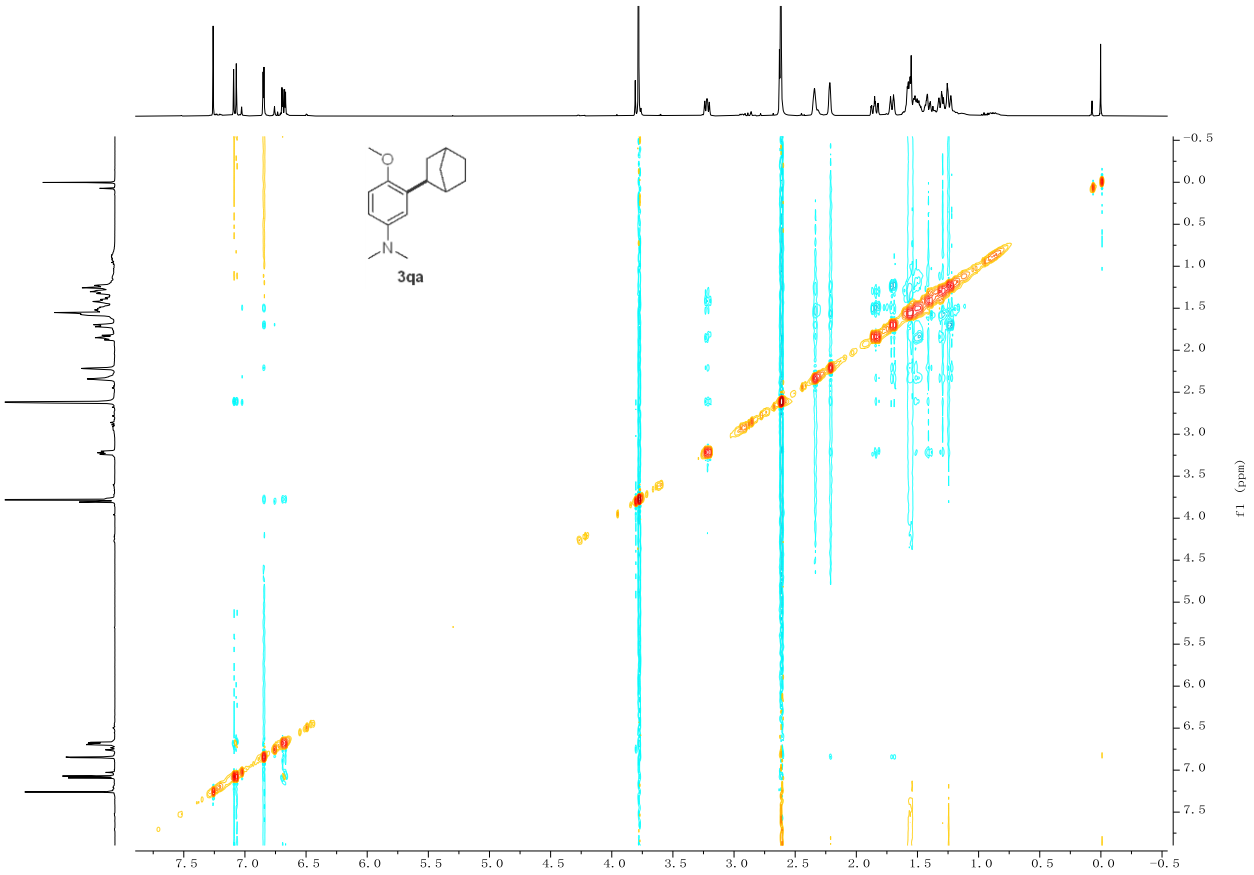

Figure S107. 2D NOESY NMR spectrum of **3qa** in $CDCl_3$.

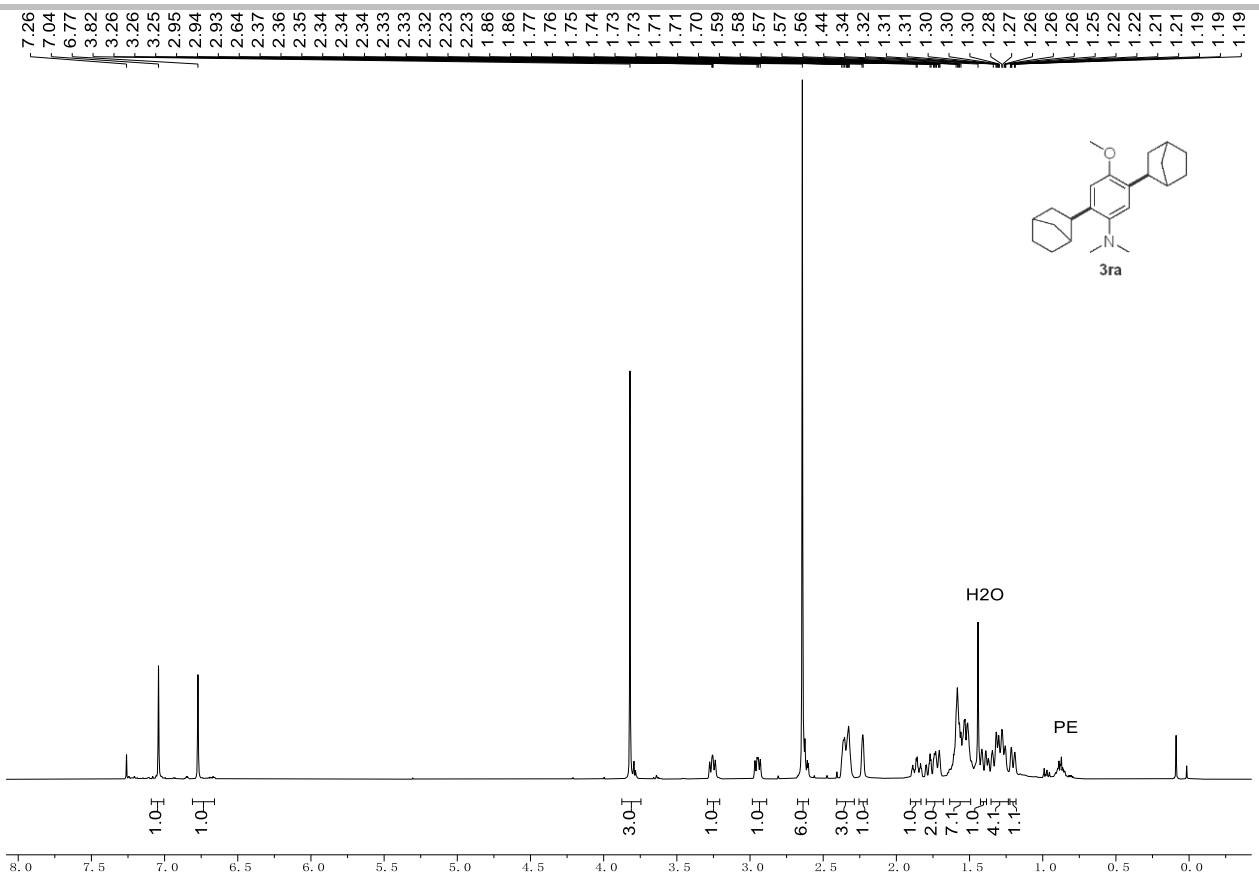

Figure S108. ^{1}H NMR spectrum (400 MHz) of **3ra** in $CDCl_3$.

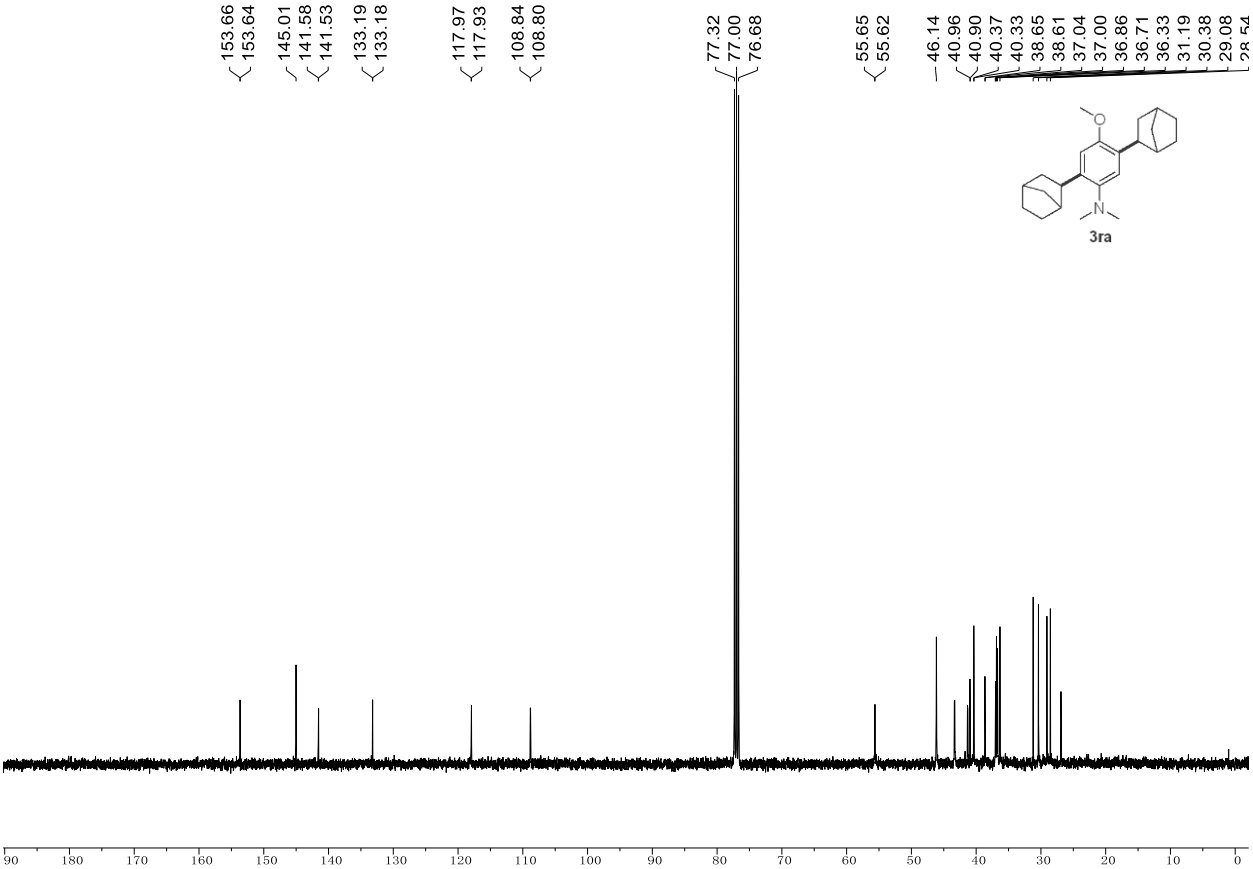

Figure S109. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3ra** in $CDCl_3$.

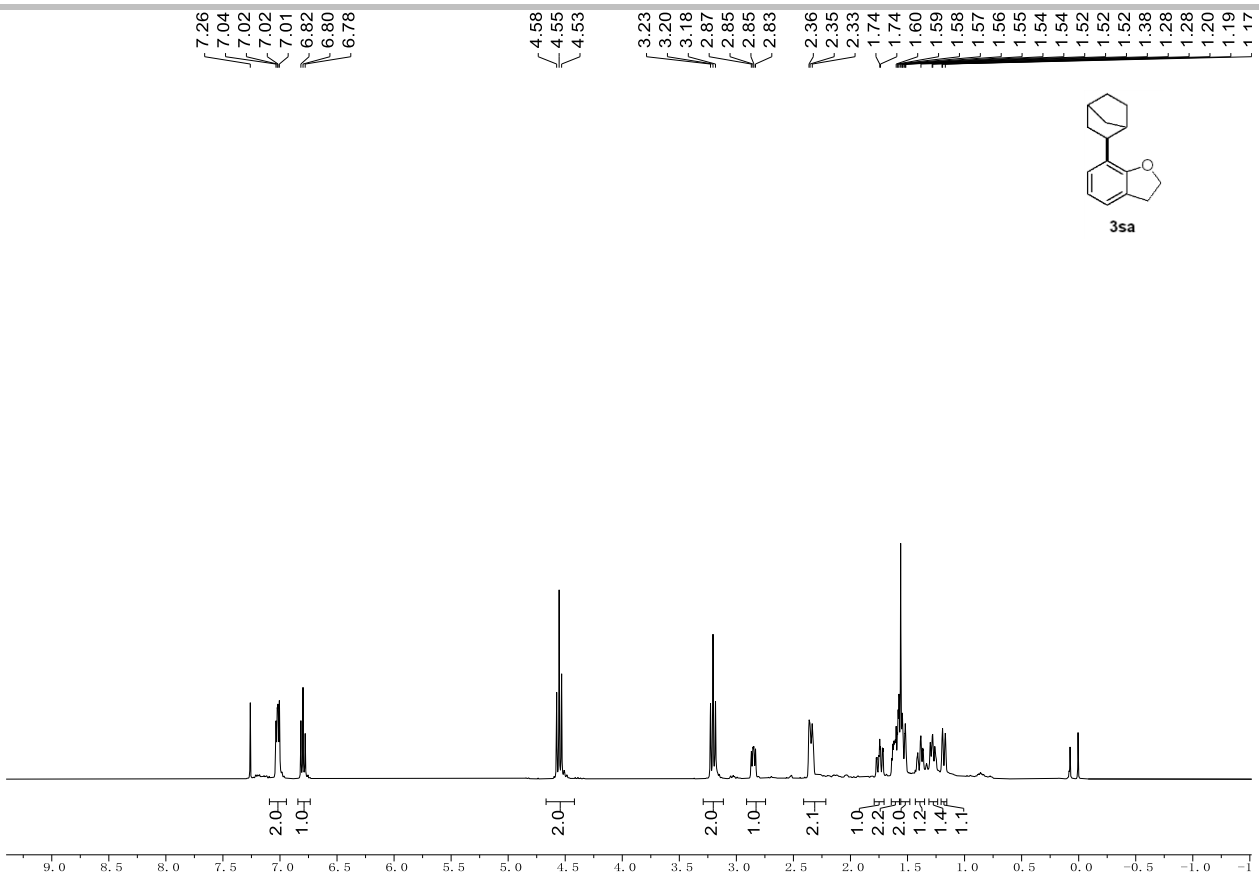

Figure S110. ^{1}H NMR spectrum (400 MHz) of **3sa** in $CDCl_3$.

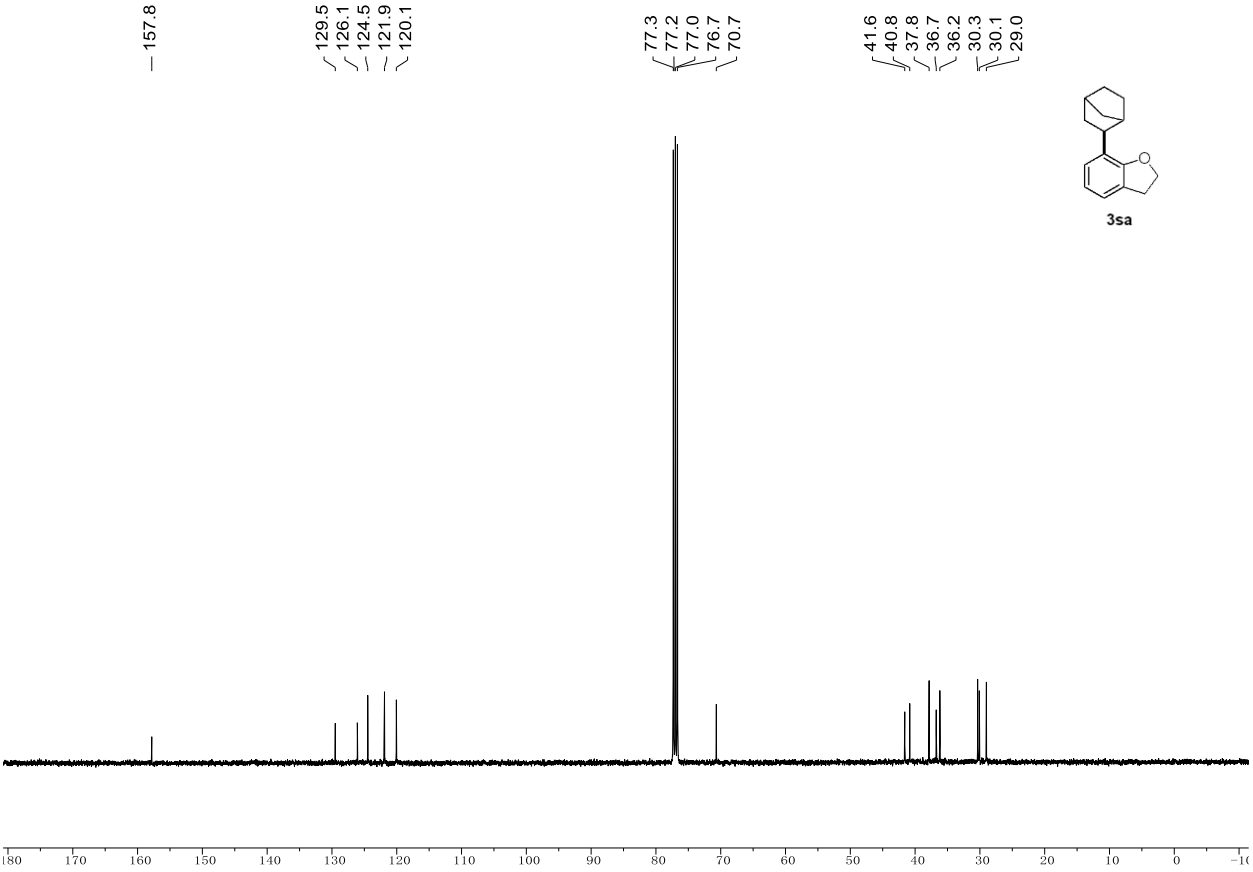

Figure S111. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3sa** in $CDCl_3$.

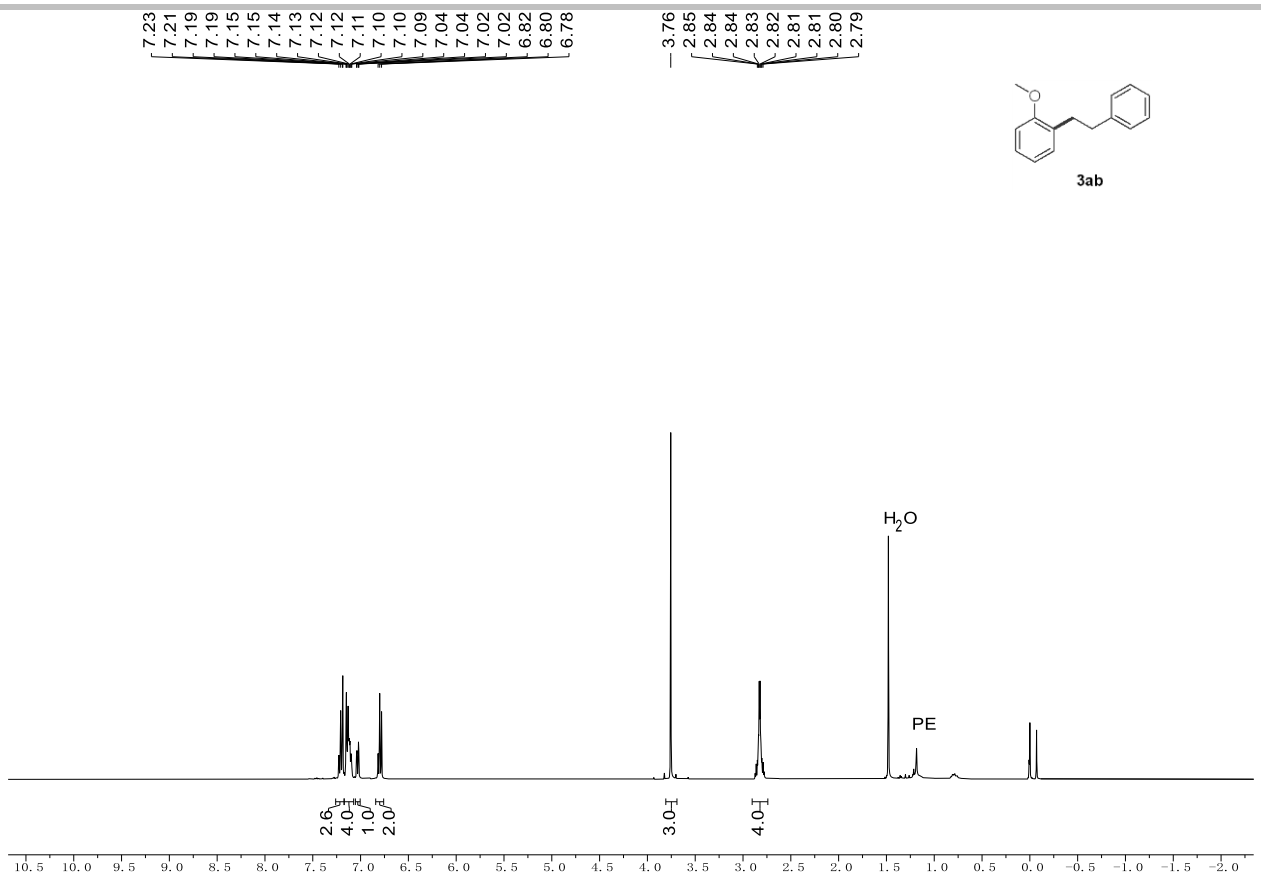

Figure S112. ^{1}H NMR spectrum (400 MHz) of **3ab** in $CDCl_3$.

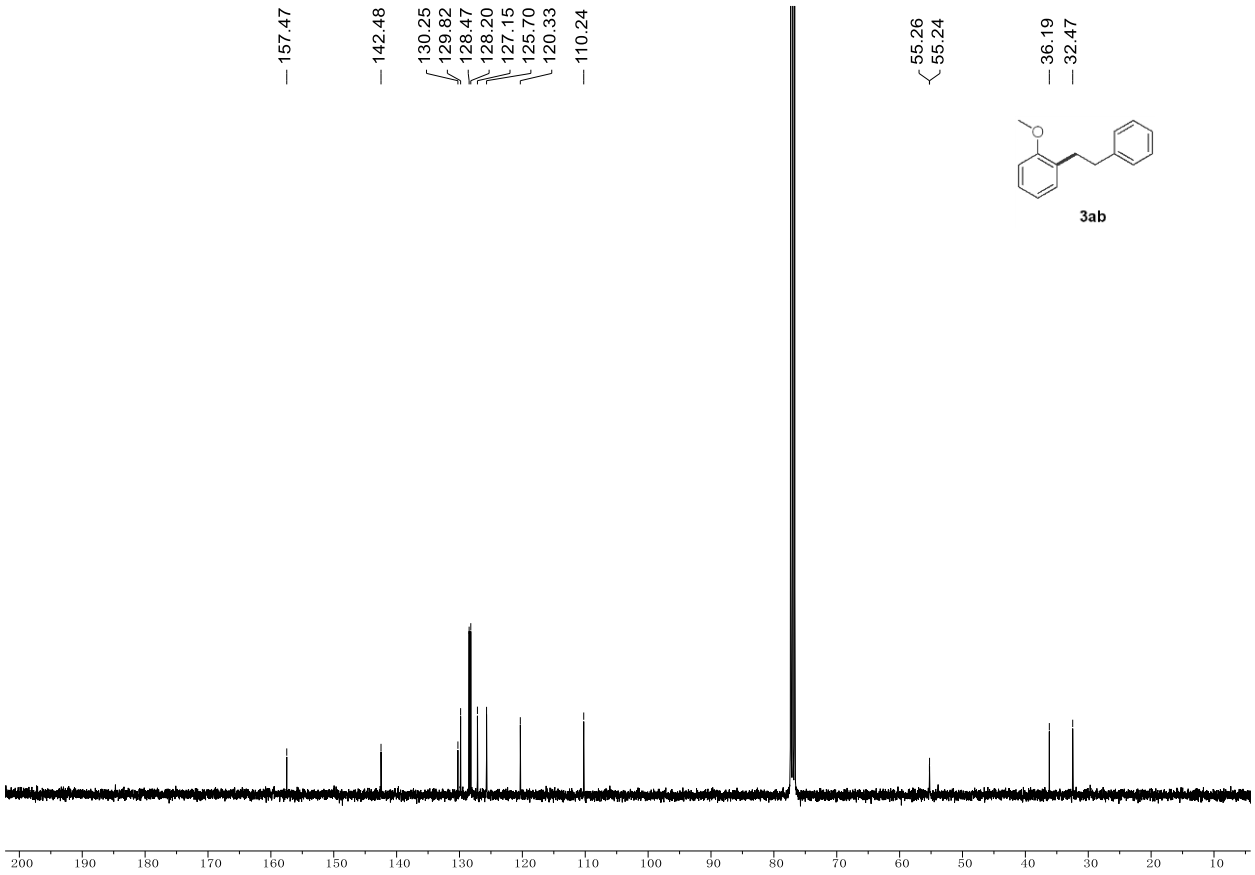

Figure S113. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3ab** in $CDCl_3$.

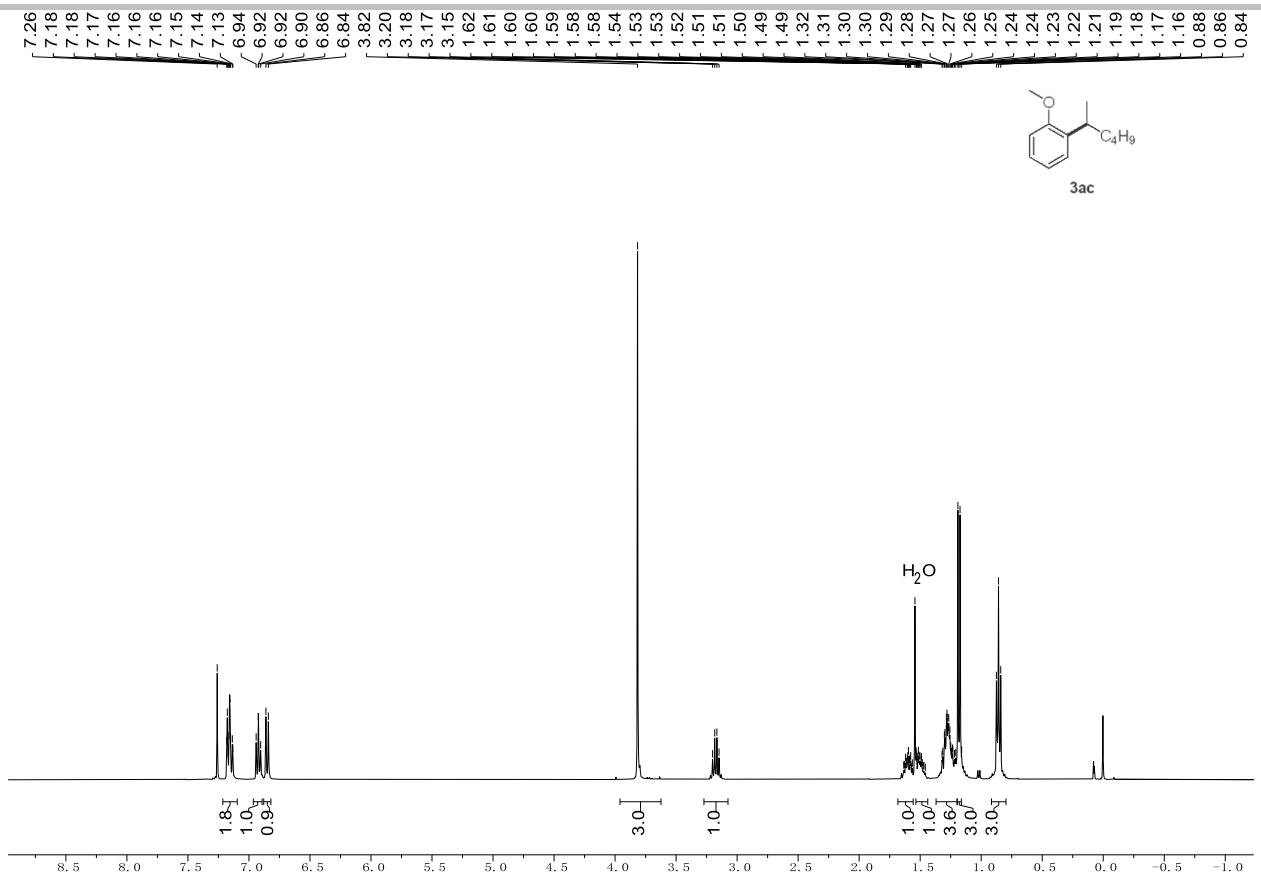

Figure S114. ^{1}H NMR spectrum (400 MHz) of **3ac** in $CDCl_3$.

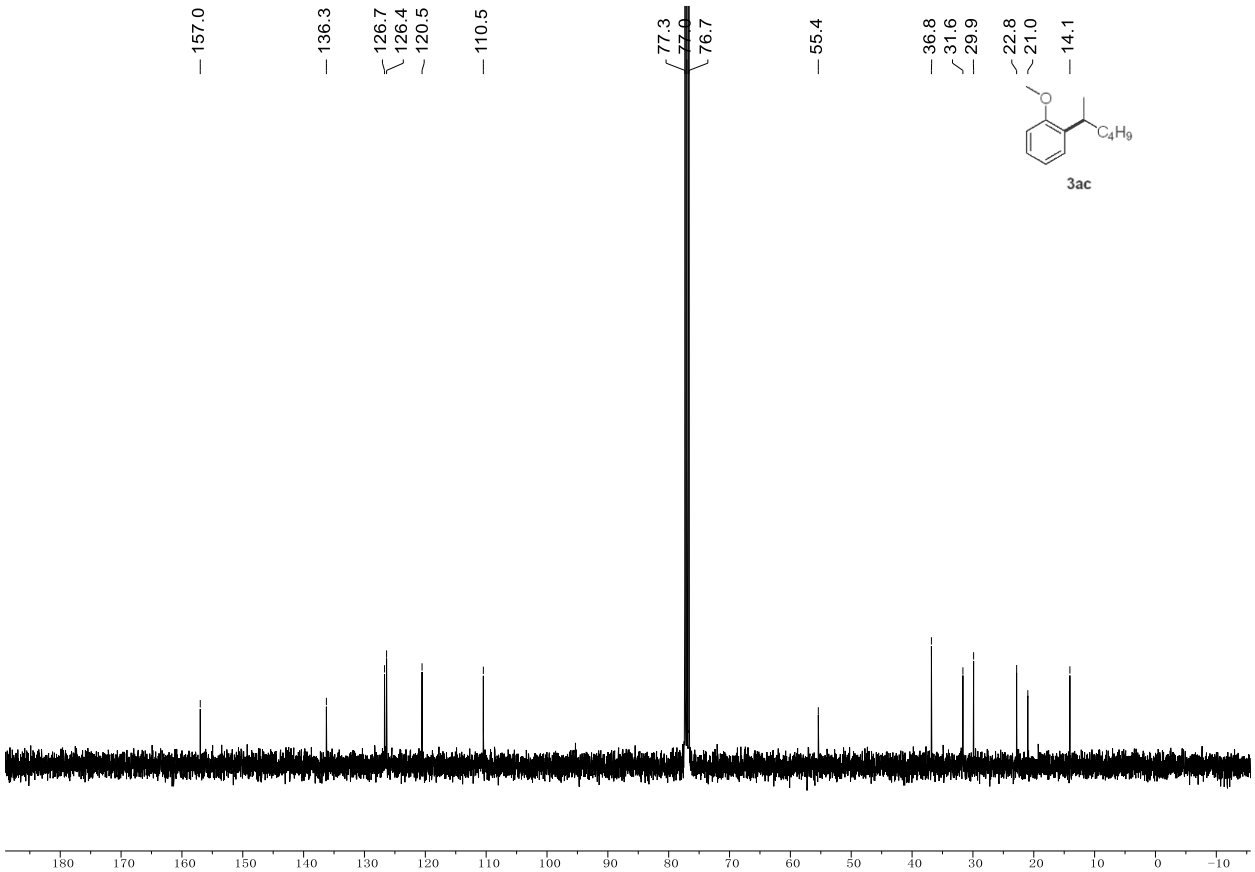

Figure S115. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3ac** in $CDCl_3$.

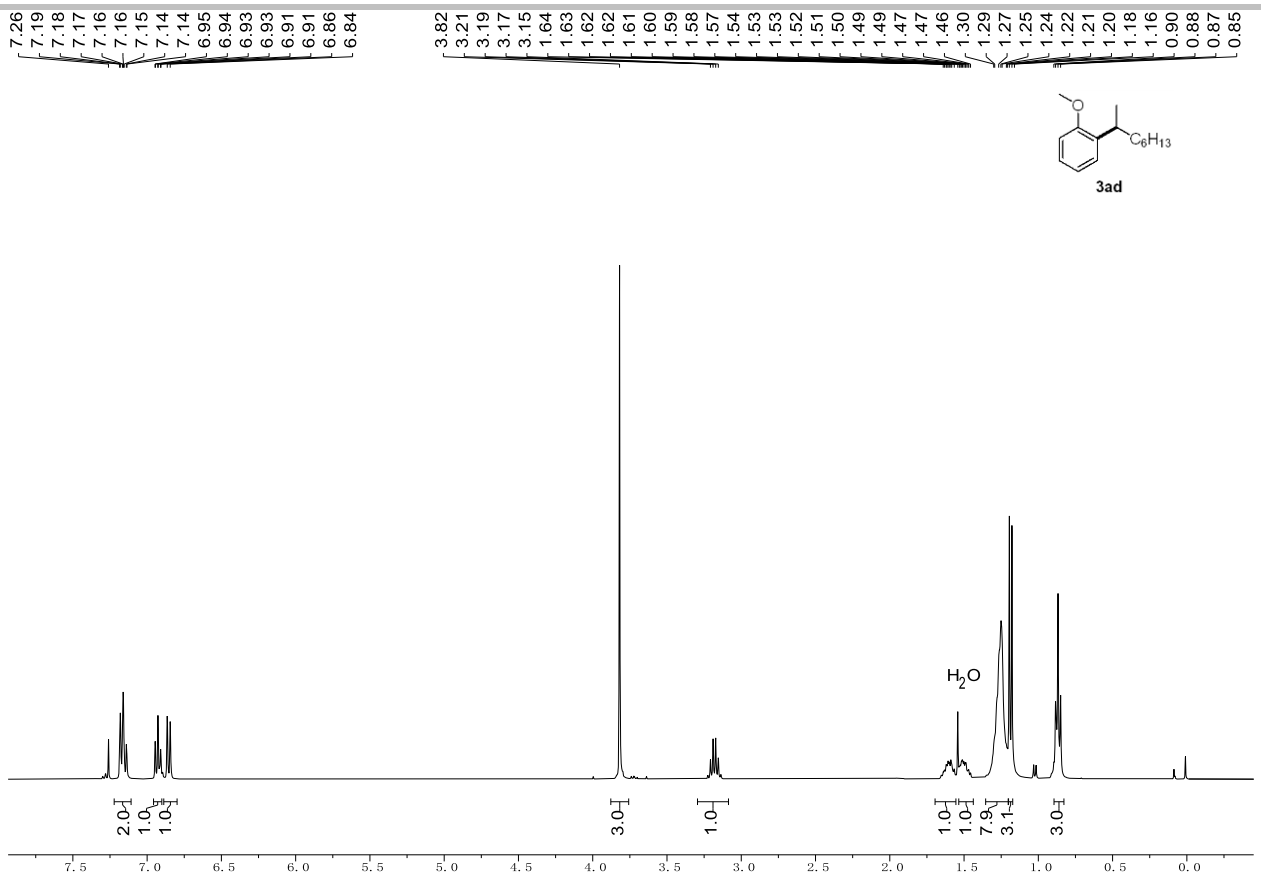

Figure S116. ^{1}H NMR spectrum (400 MHz) of **3ad** in $CDCl_3$.

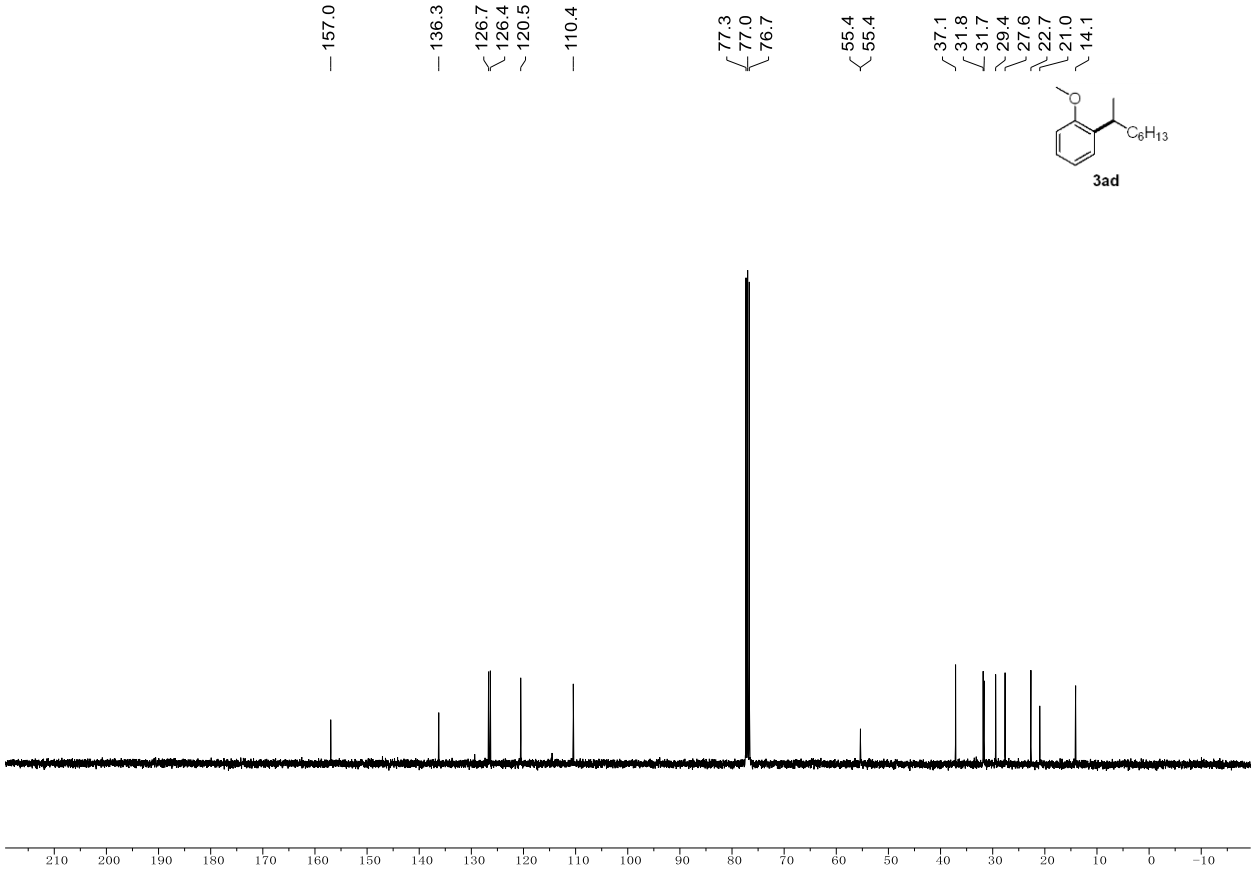

Figure S117. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3ad** in $CDCl_3$.

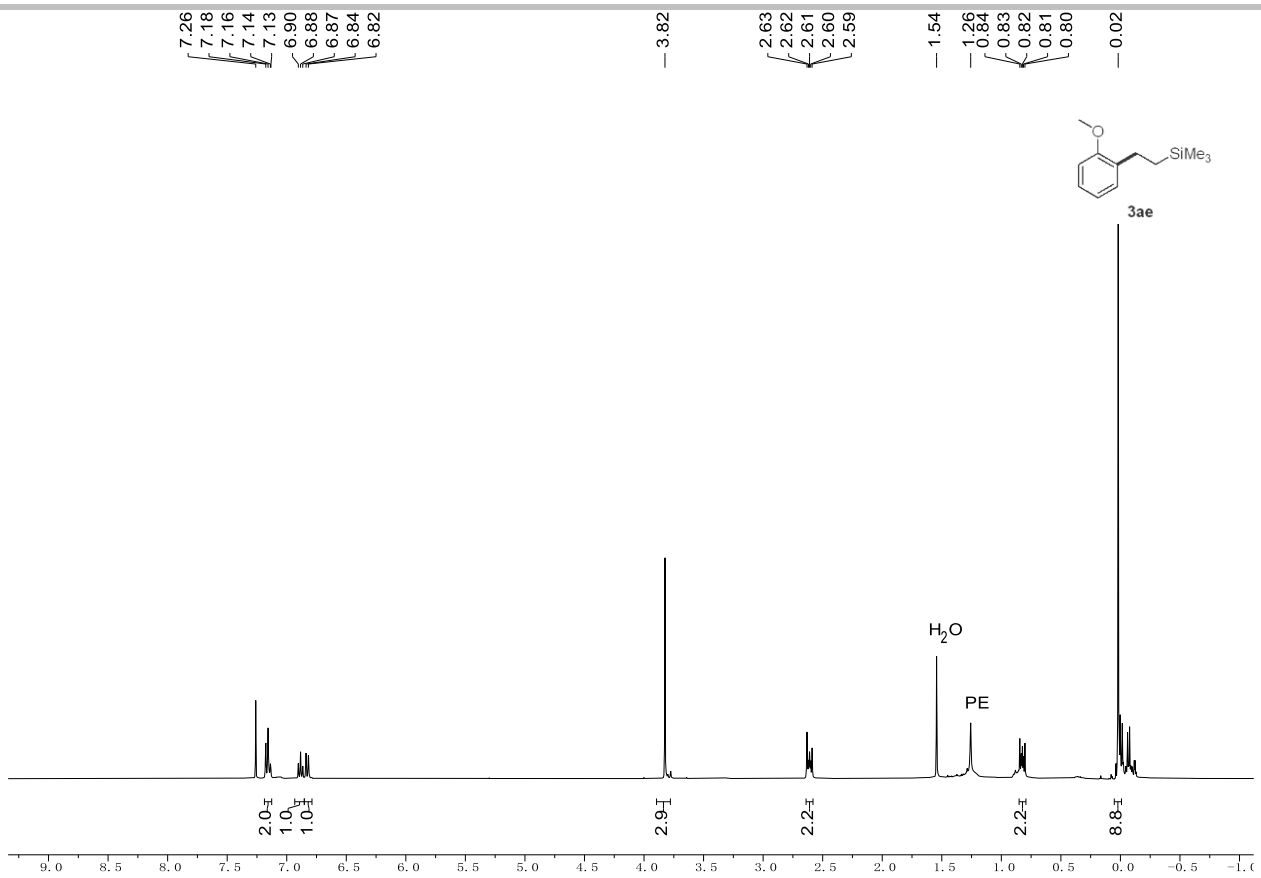

Figure S118. ^{1}H NMR spectrum (400 MHz) of **3ae** in $CDCl_3$.

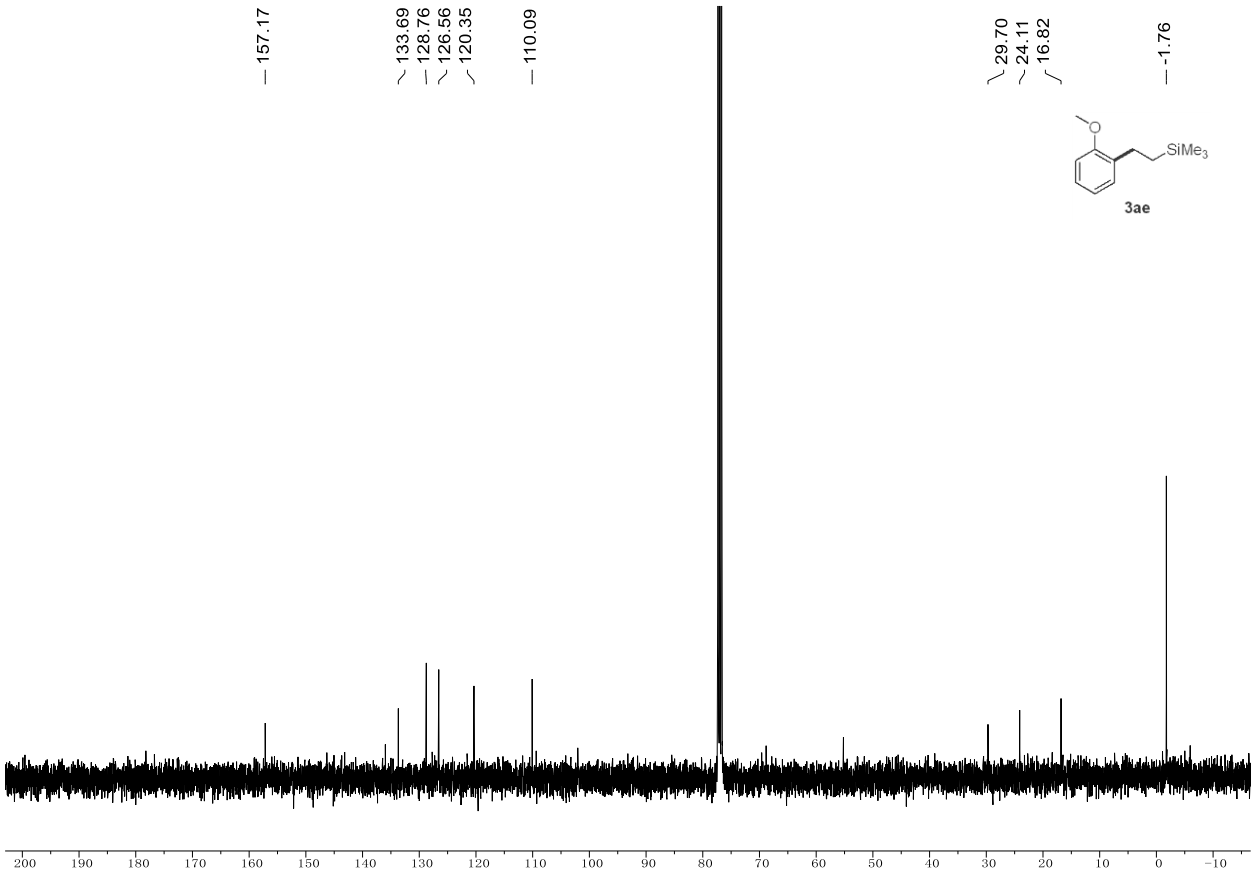

Figure S119. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **3ae** in $CDCl_3$.

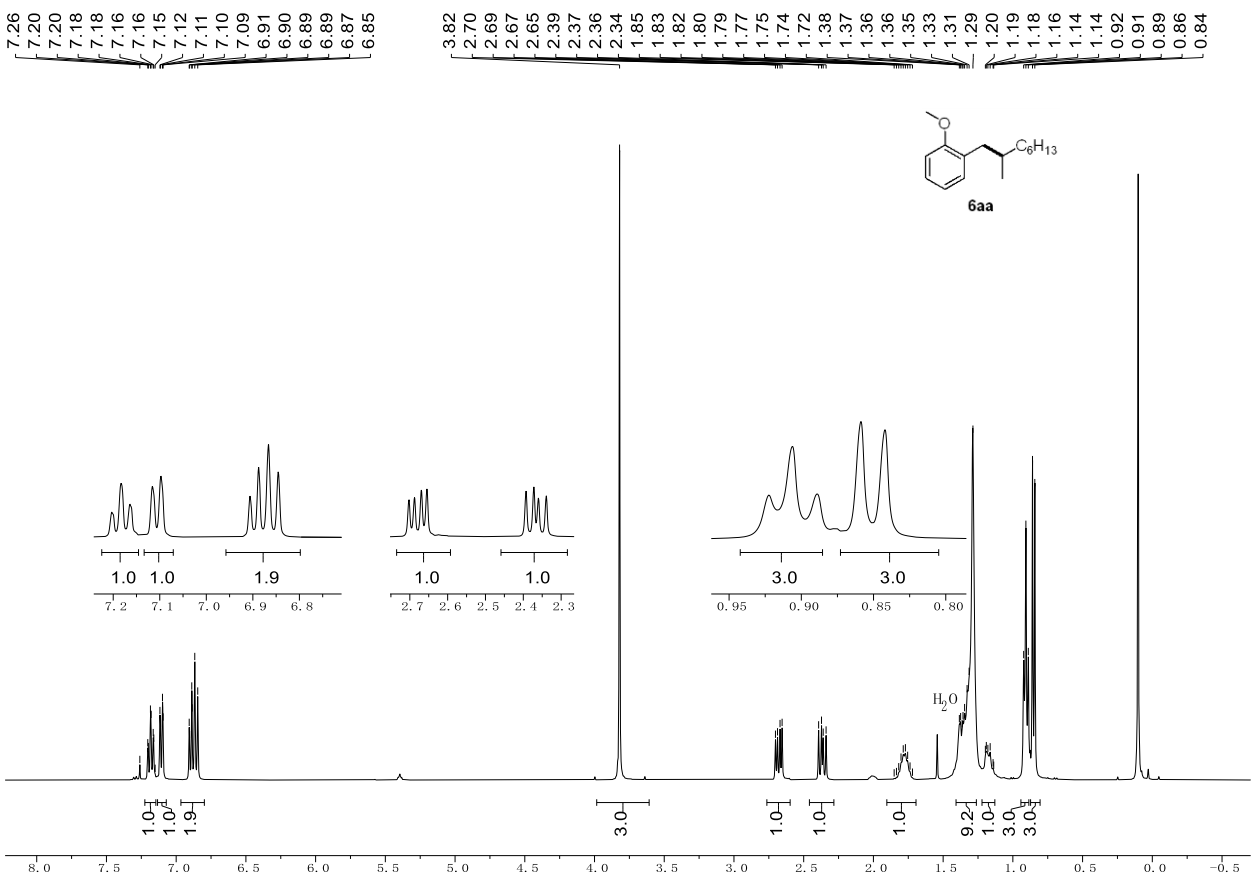

Figure S120. ^{1}H NMR spectrum (400 MHz) of **6aa** in $CDCl_3$.

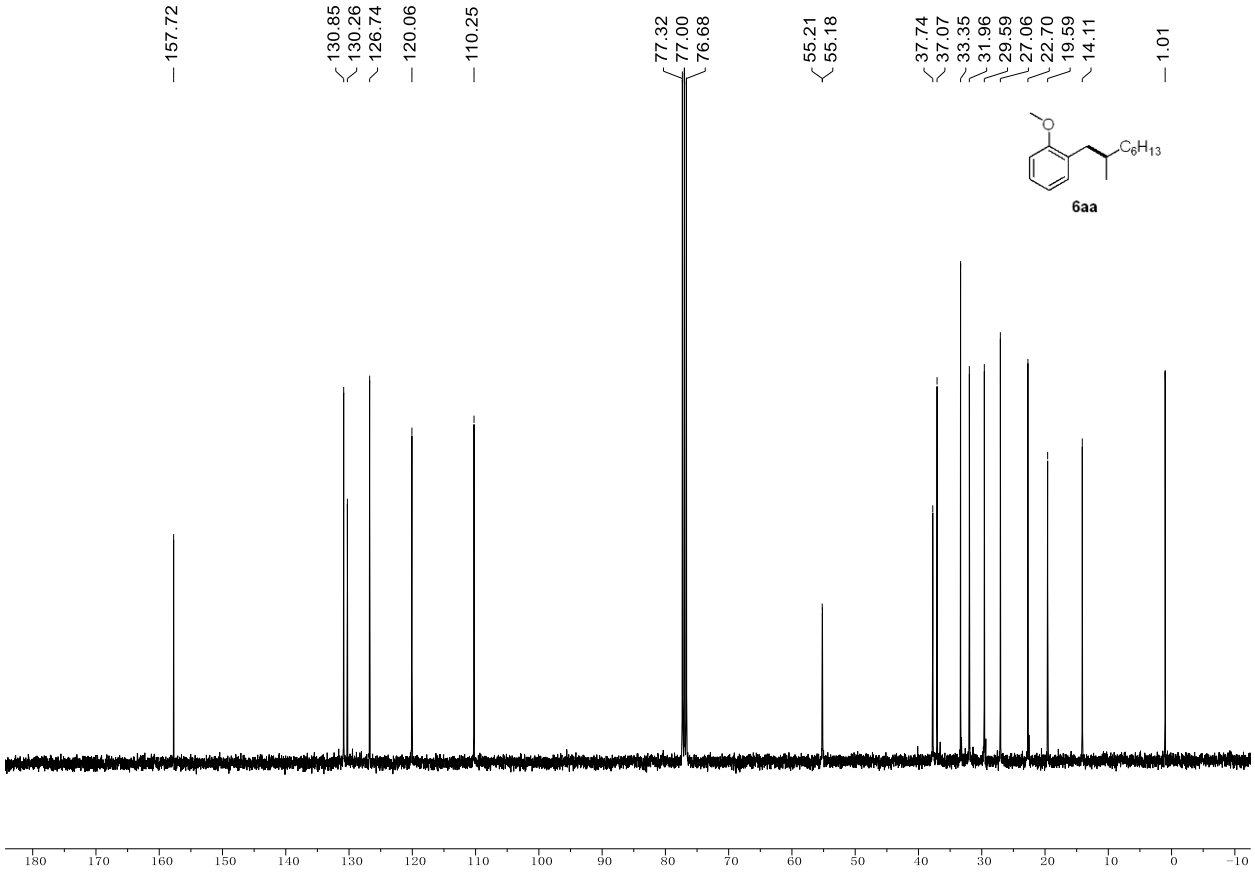

Figure S121. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6aa** in $CDCl_3$.

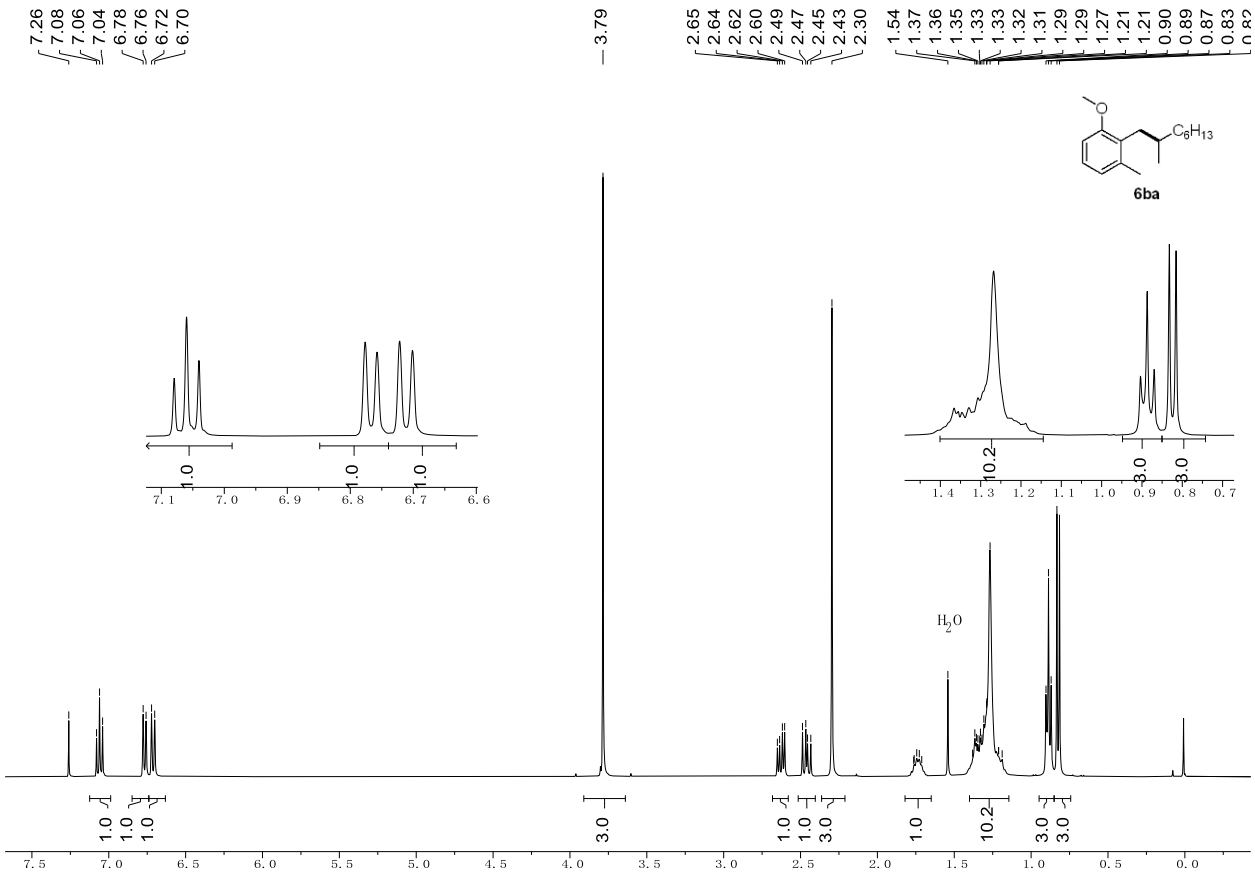

Figure S122. ^{1}H NMR spectrum (400 MHz) of **6ba** in $CDCl_3$.

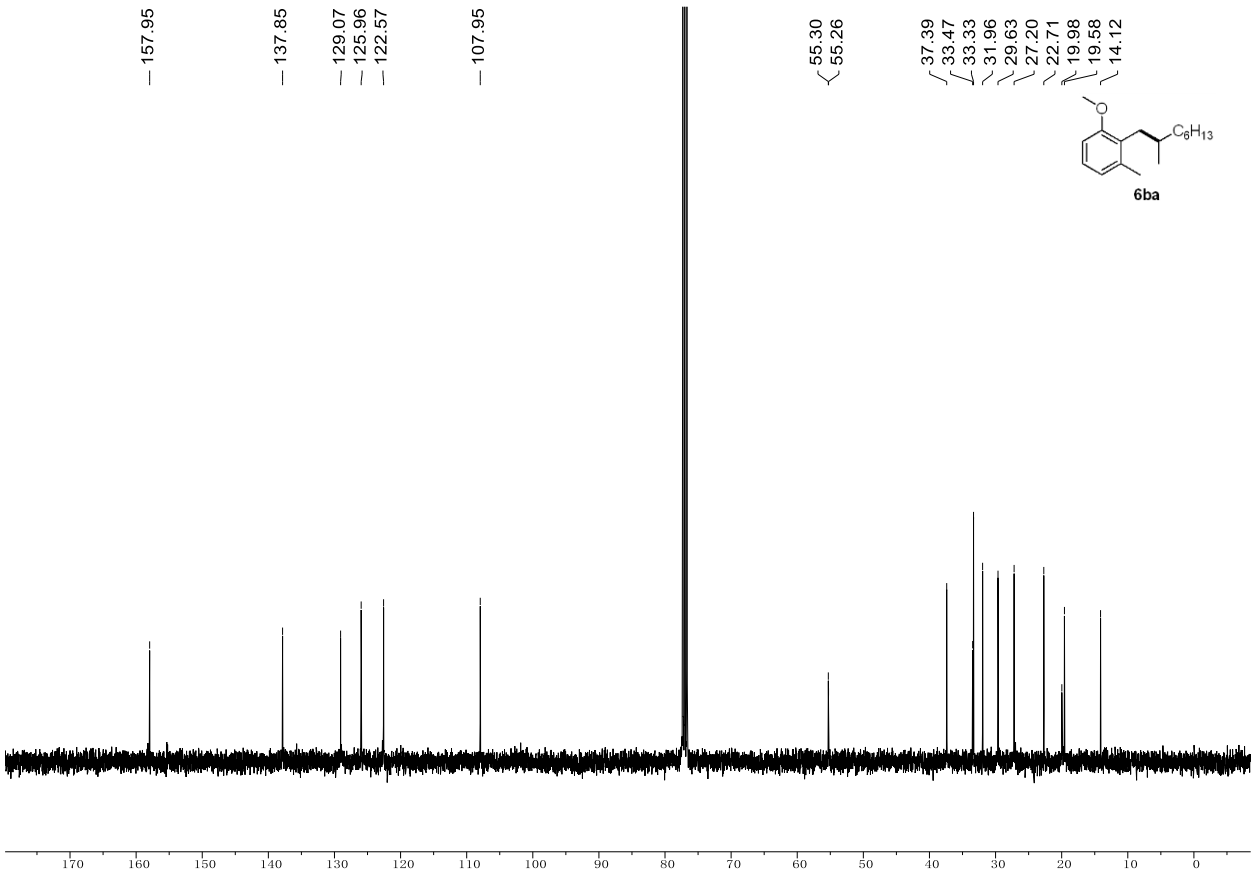

Figure S123. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6ba** in $CDCl_3$.

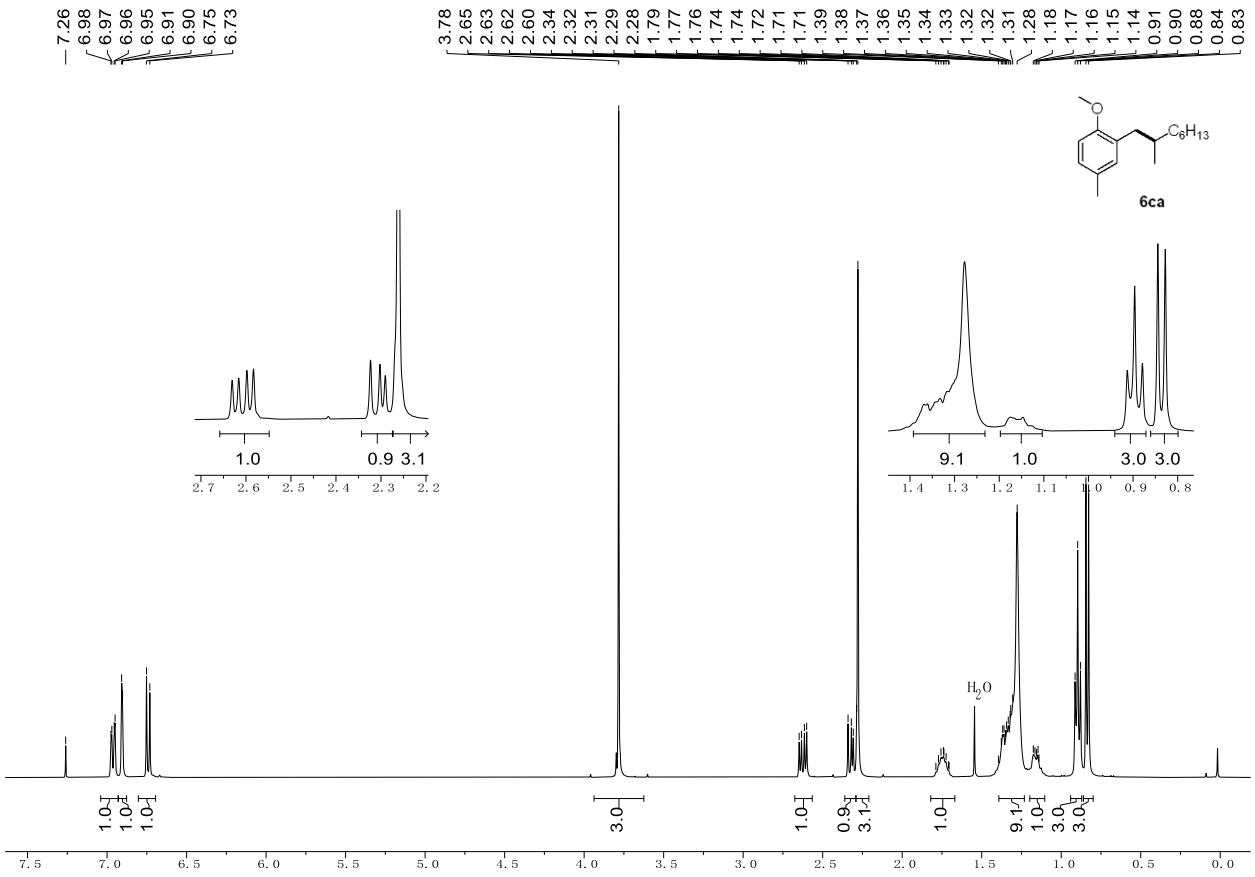

Figure S124. ^{1}H NMR spectrum (400 MHz) of **6ca** in $CDCl_3$.

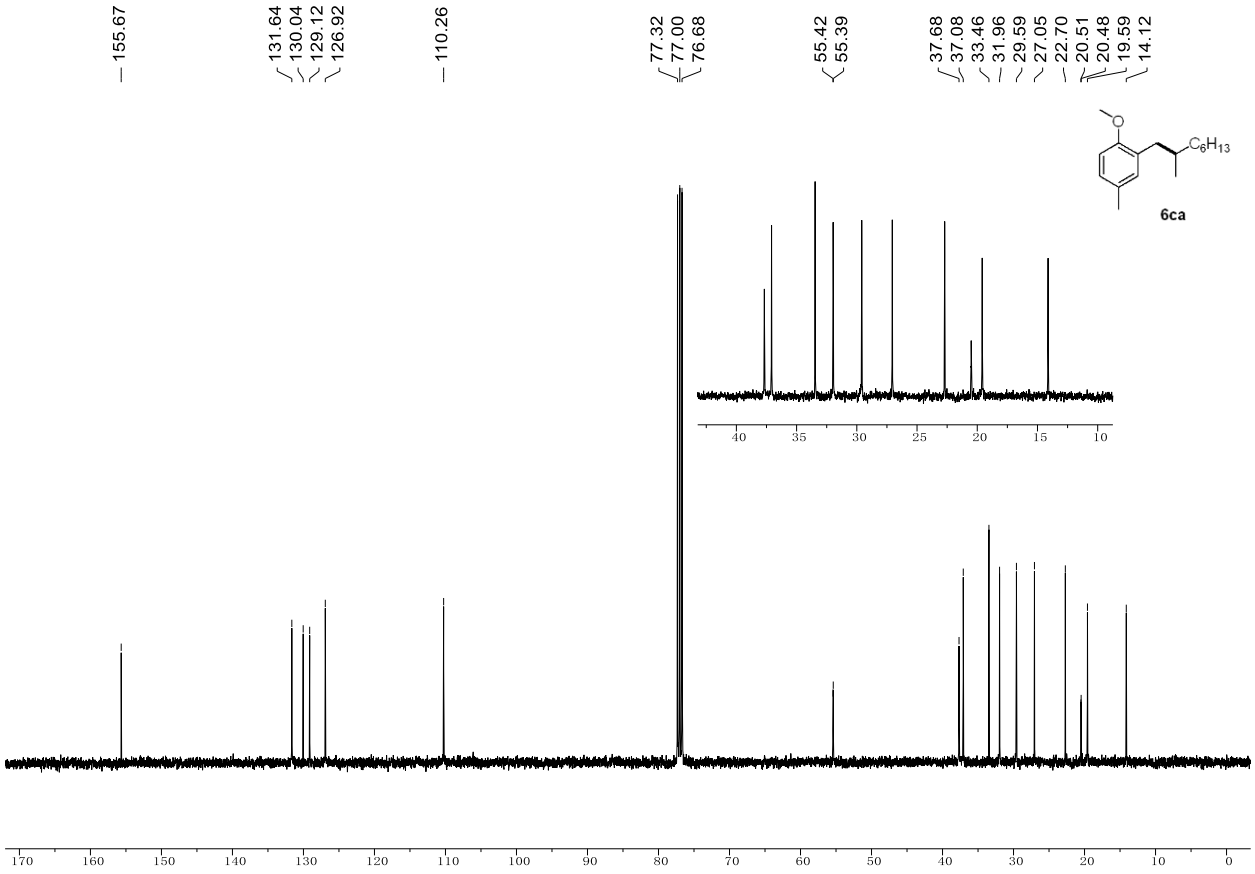

Figure S125. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6ca** in $CDCl_3$.

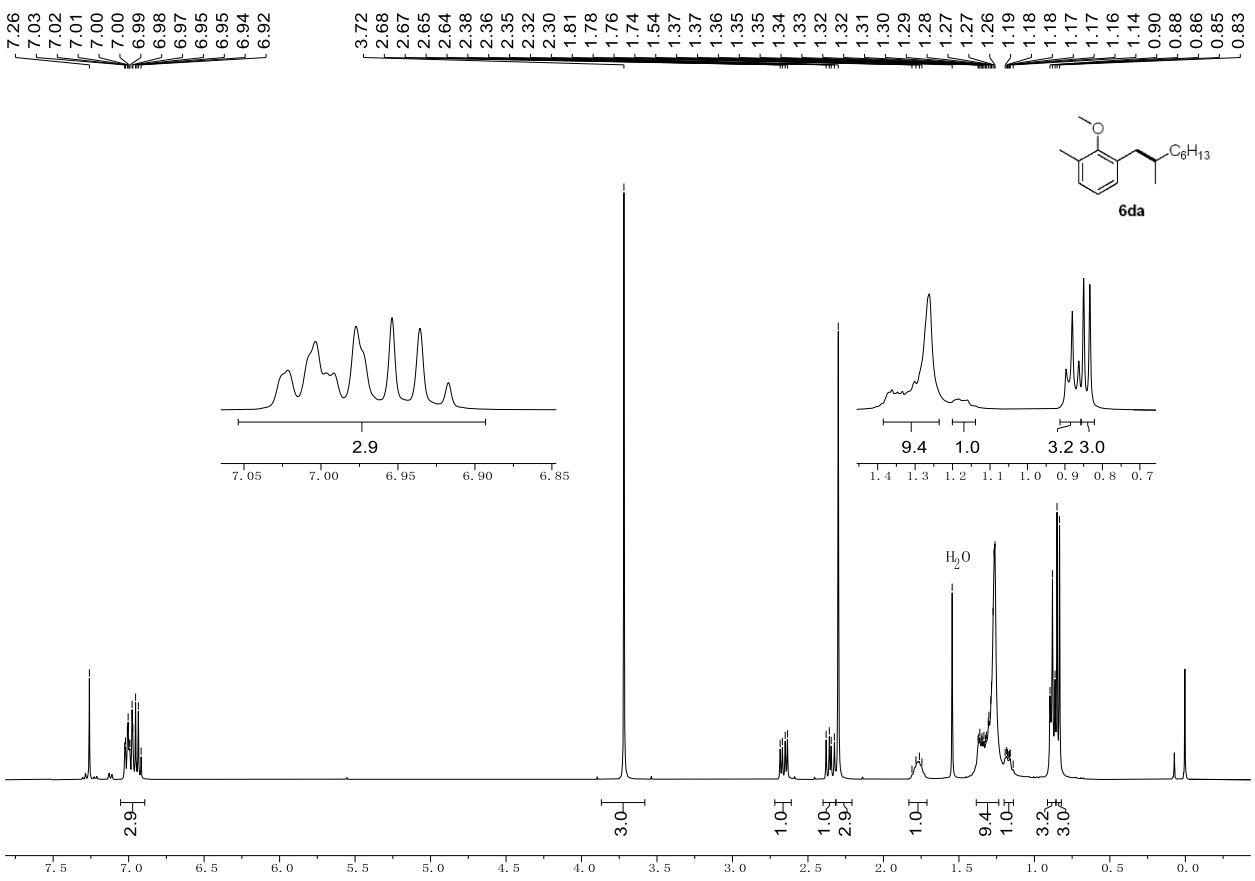

Figure S126. ^{1}H NMR spectrum (400 MHz) of **6da** in $CDCl_3$.

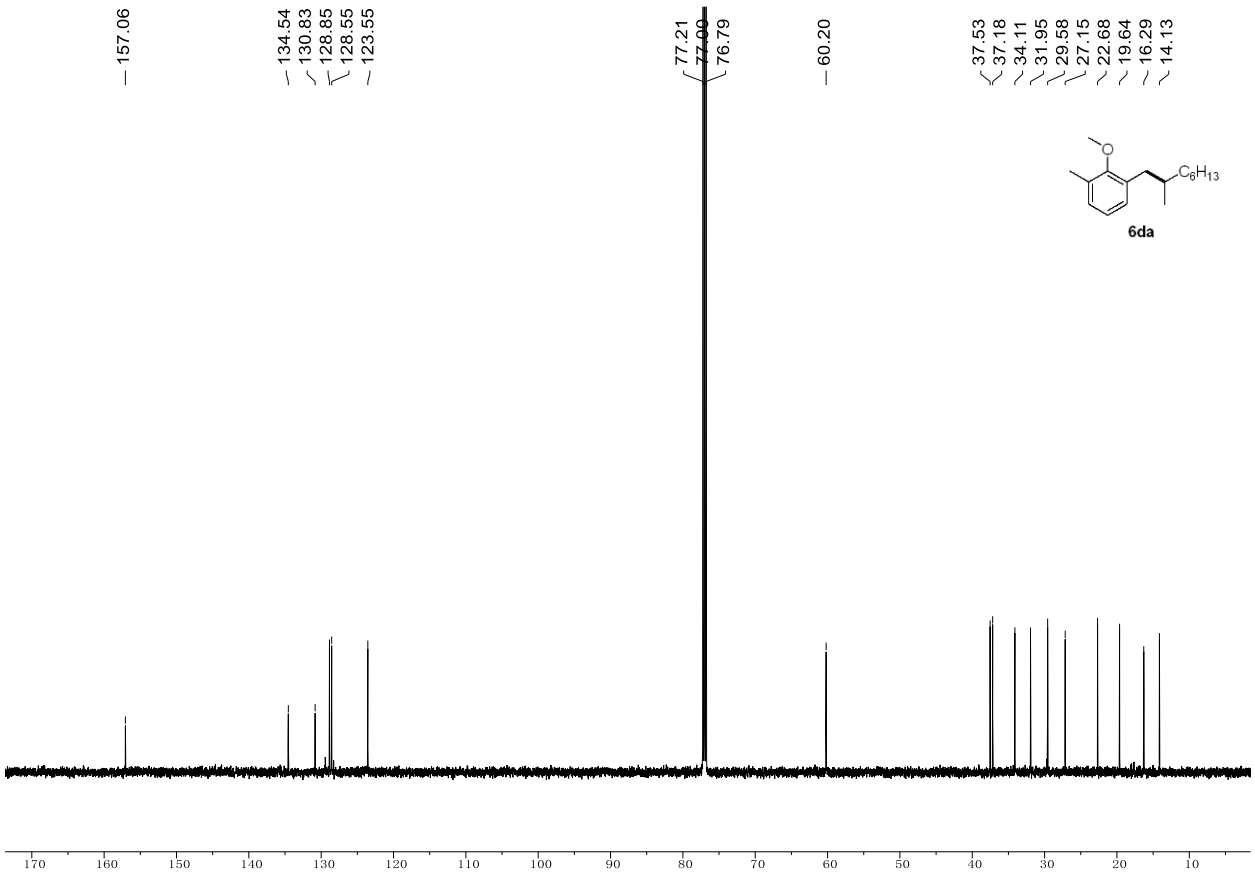

Figure S127. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6da** in $CDCl_3$.

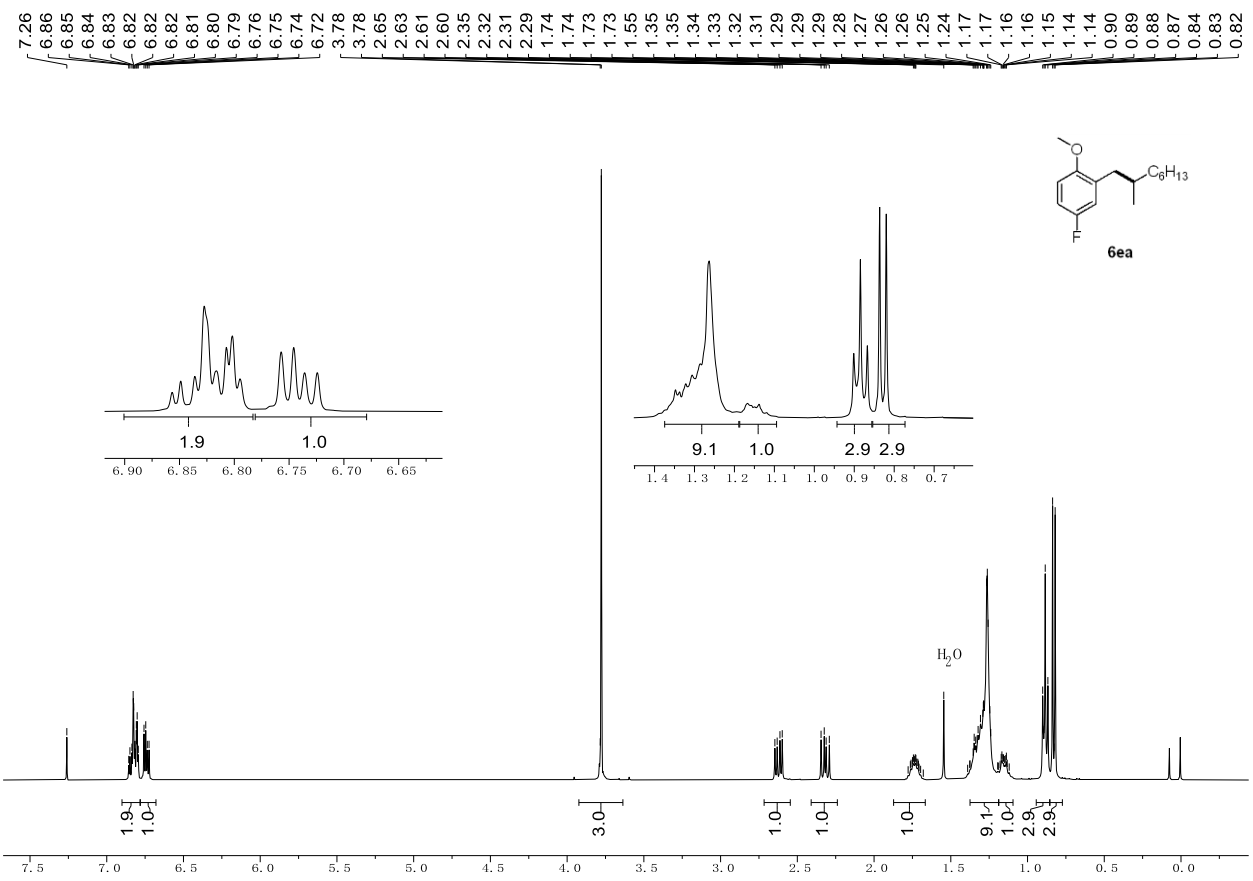

Figure S128. ^{1}H NMR spectrum (400 MHz) of **6ea** in $CDCl_3$.

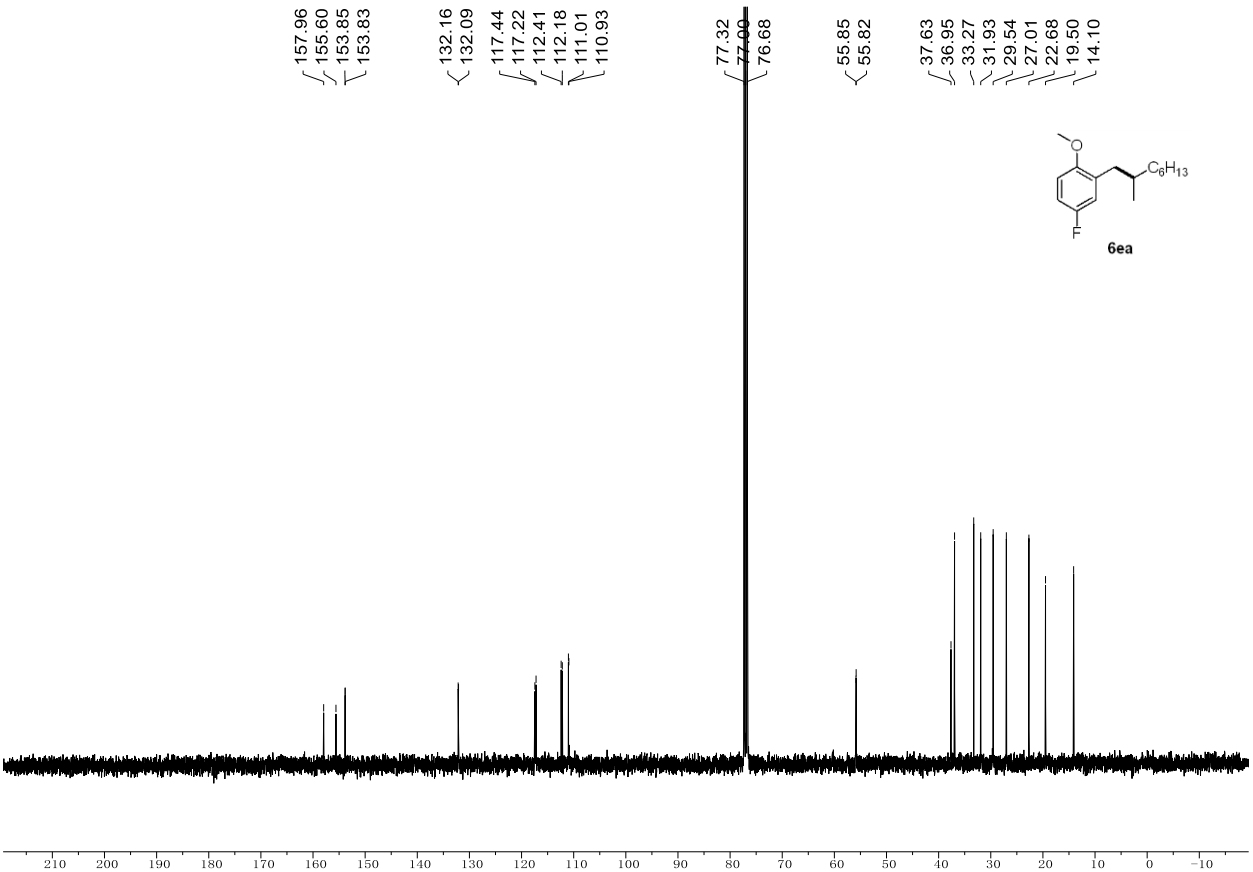

Figure S129. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6ea** in $CDCl_3$.

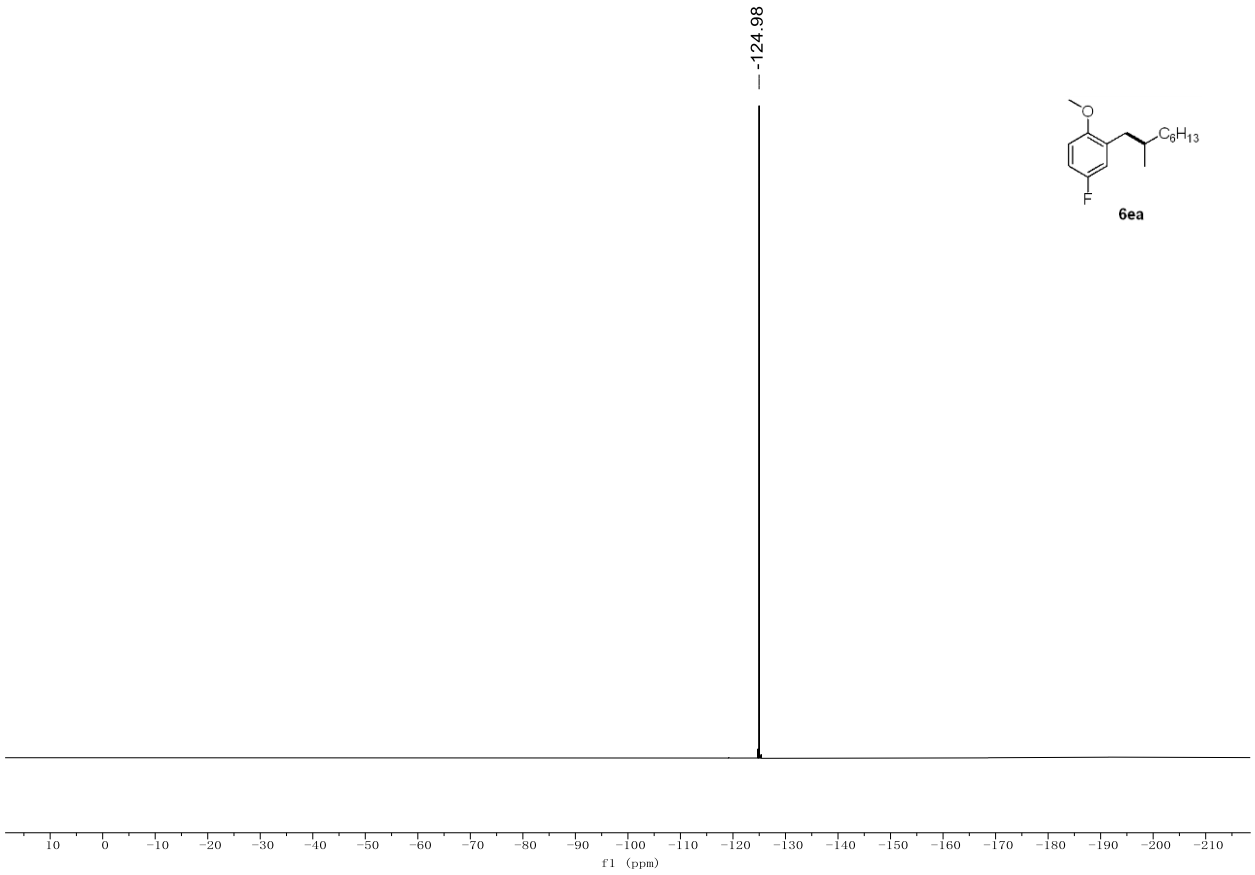

Figure S130. $^{19}F\{^{1}H\}$ NMR spectrum (377 MHz) of **6ea** in $CDCl_3$.

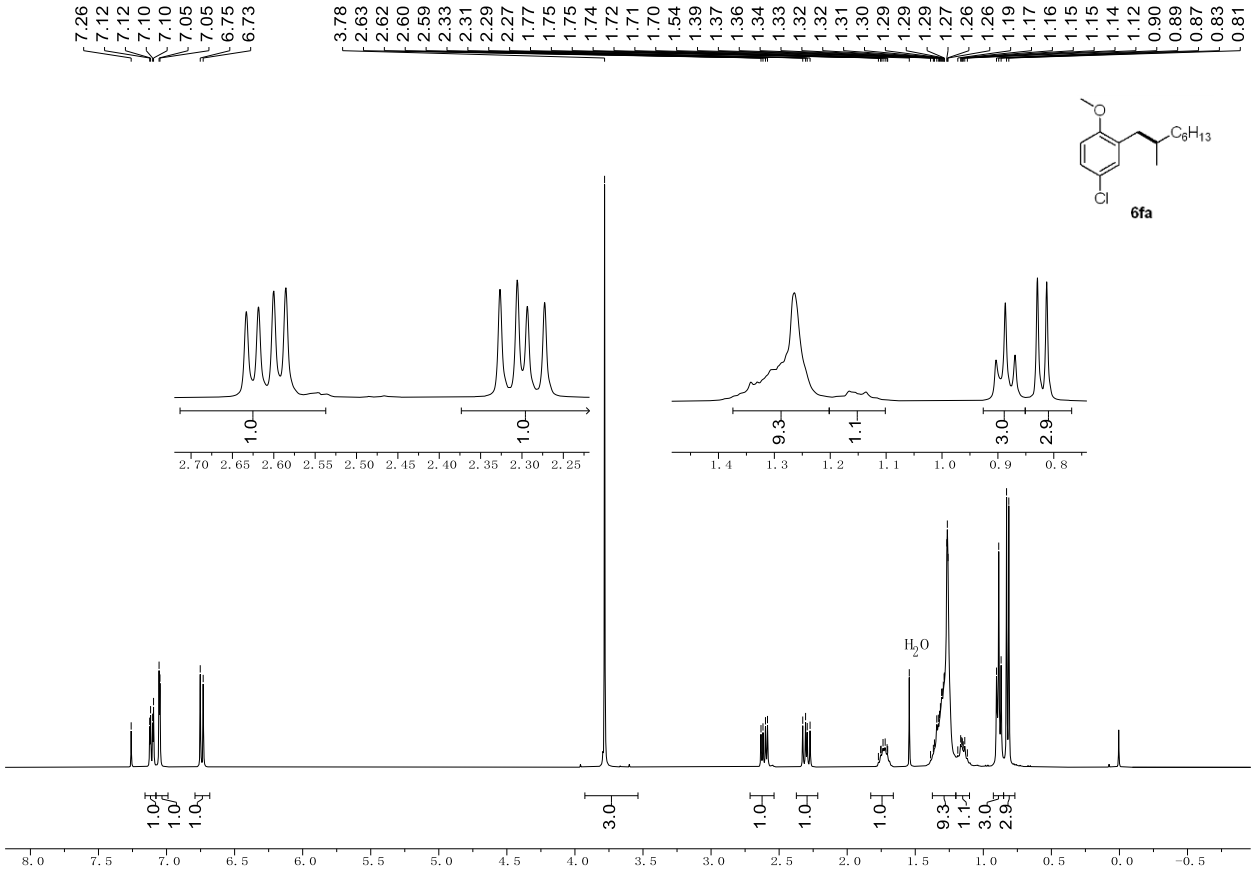

Figure S131. ^{1}H NMR spectrum (400 MHz) of **6fa** in $CDCl_3$.

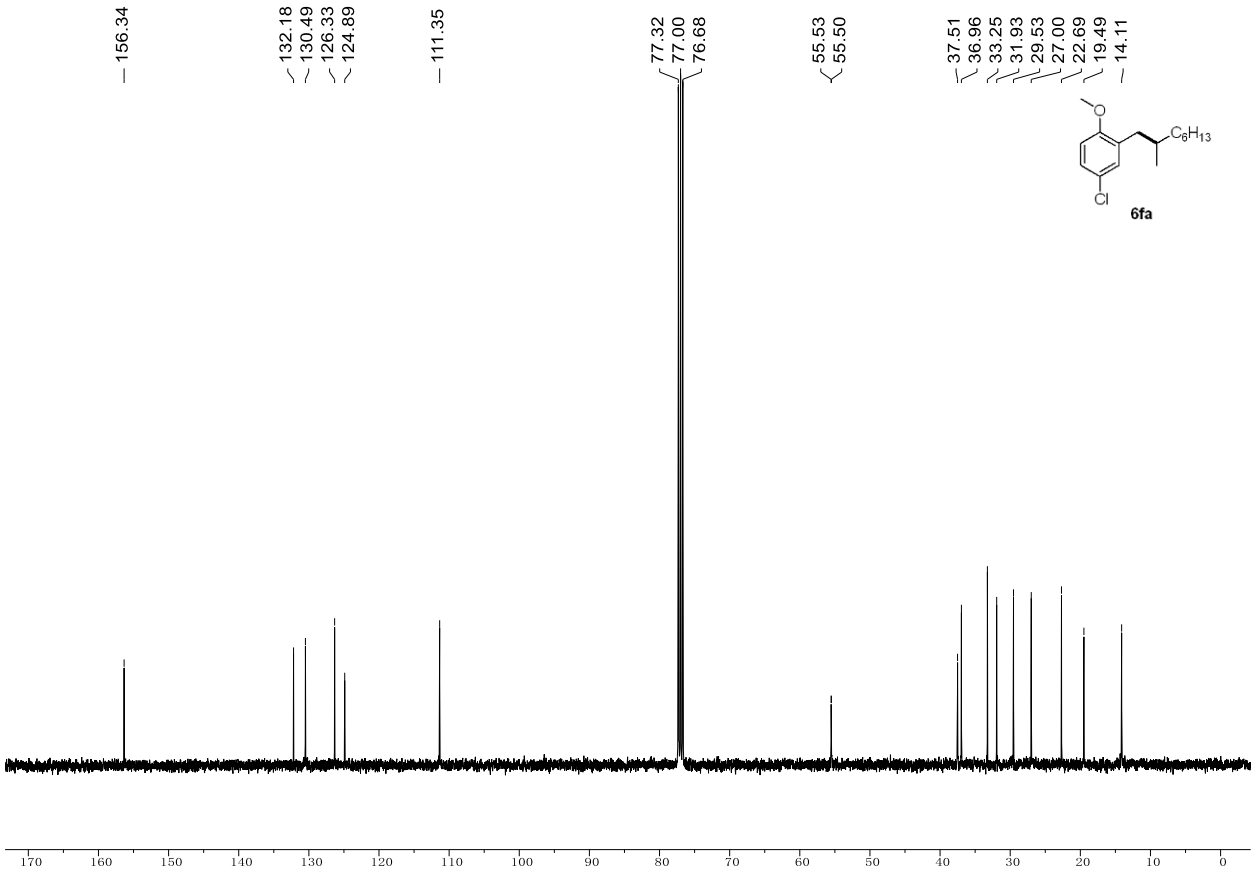

Figure S132. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6fa** in $CDCl_3$.

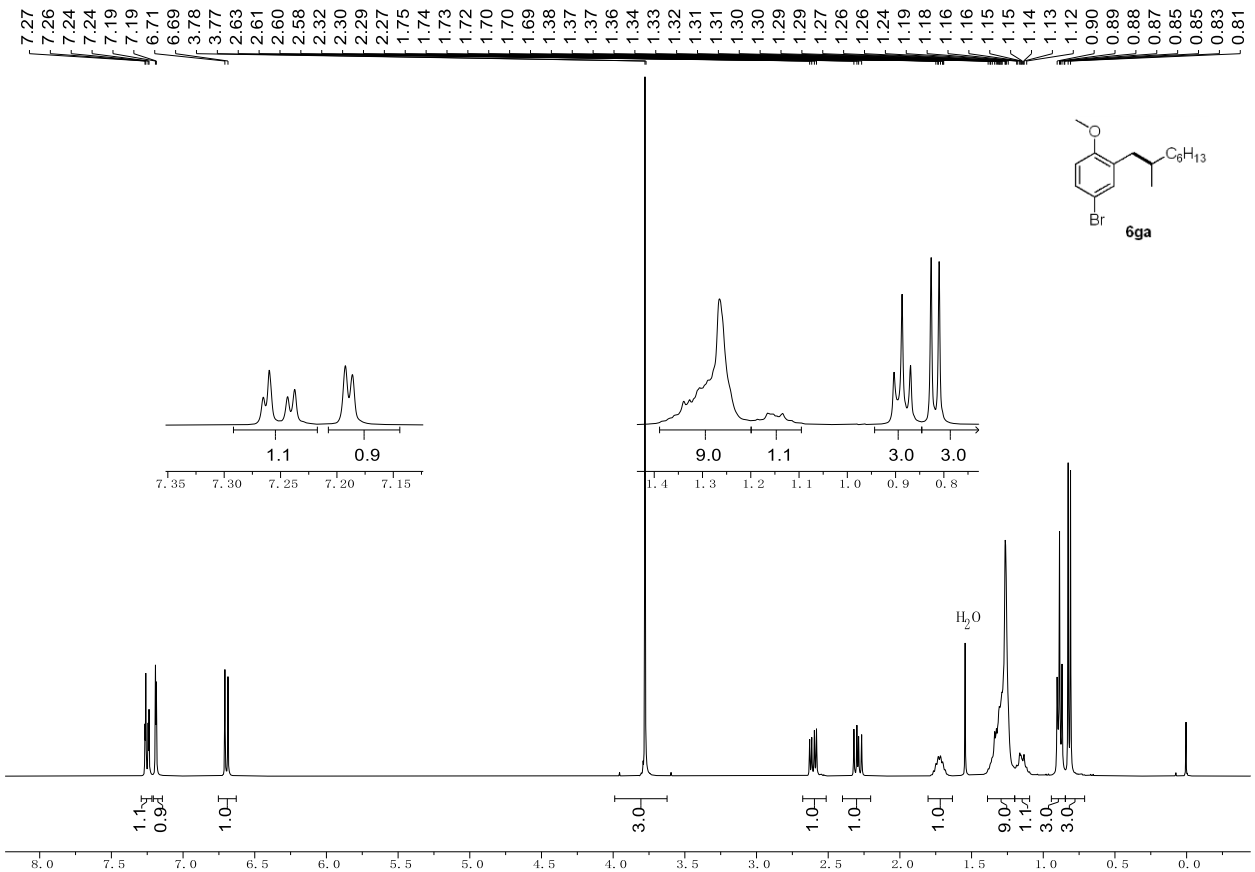

Figure S133. ^{1}H NMR spectrum (400 MHz) of **6ga** in $CDCl_3$.

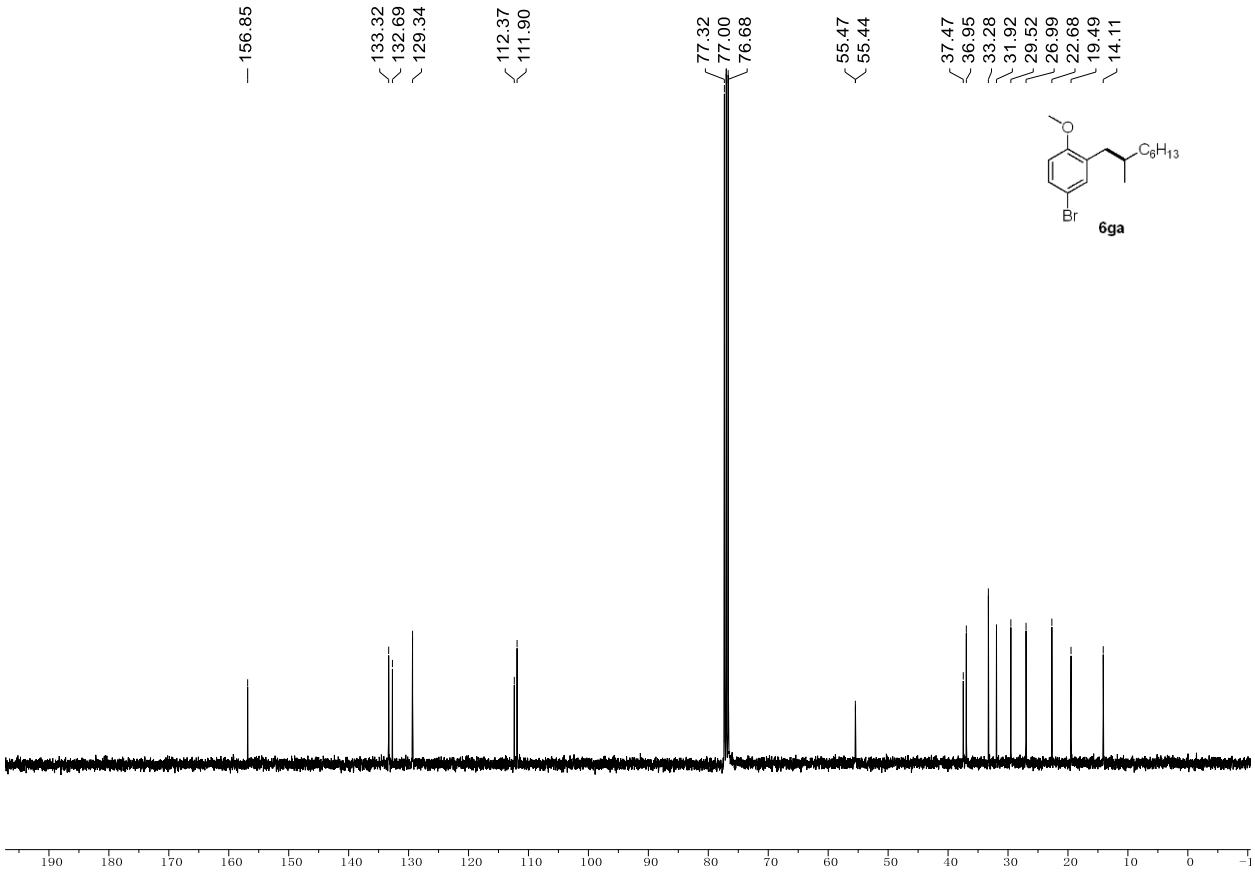

Figure S134. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6ga** in $CDCl_3$.

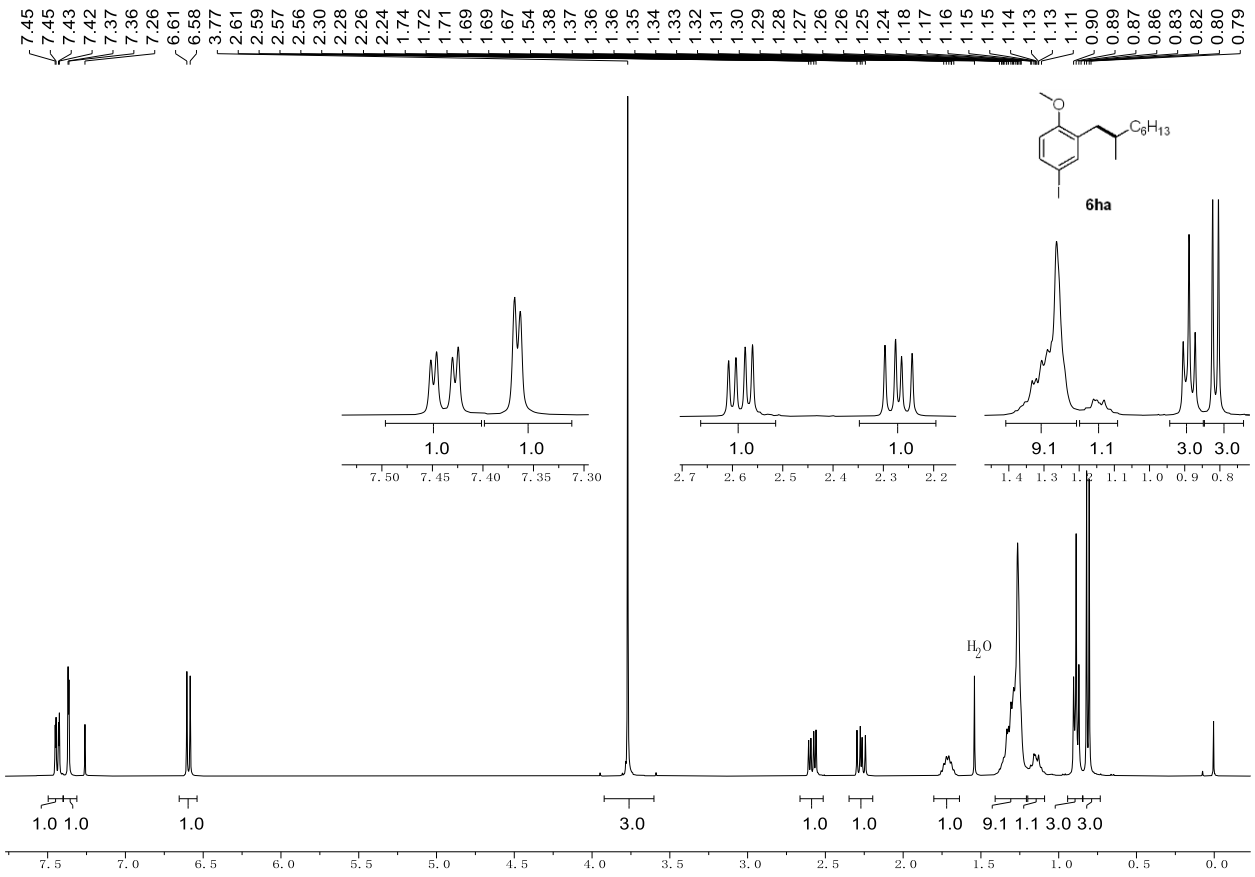

Figure S135. ^{1}H NMR spectrum (400 MHz) of **6ha** in $CDCl_3$.

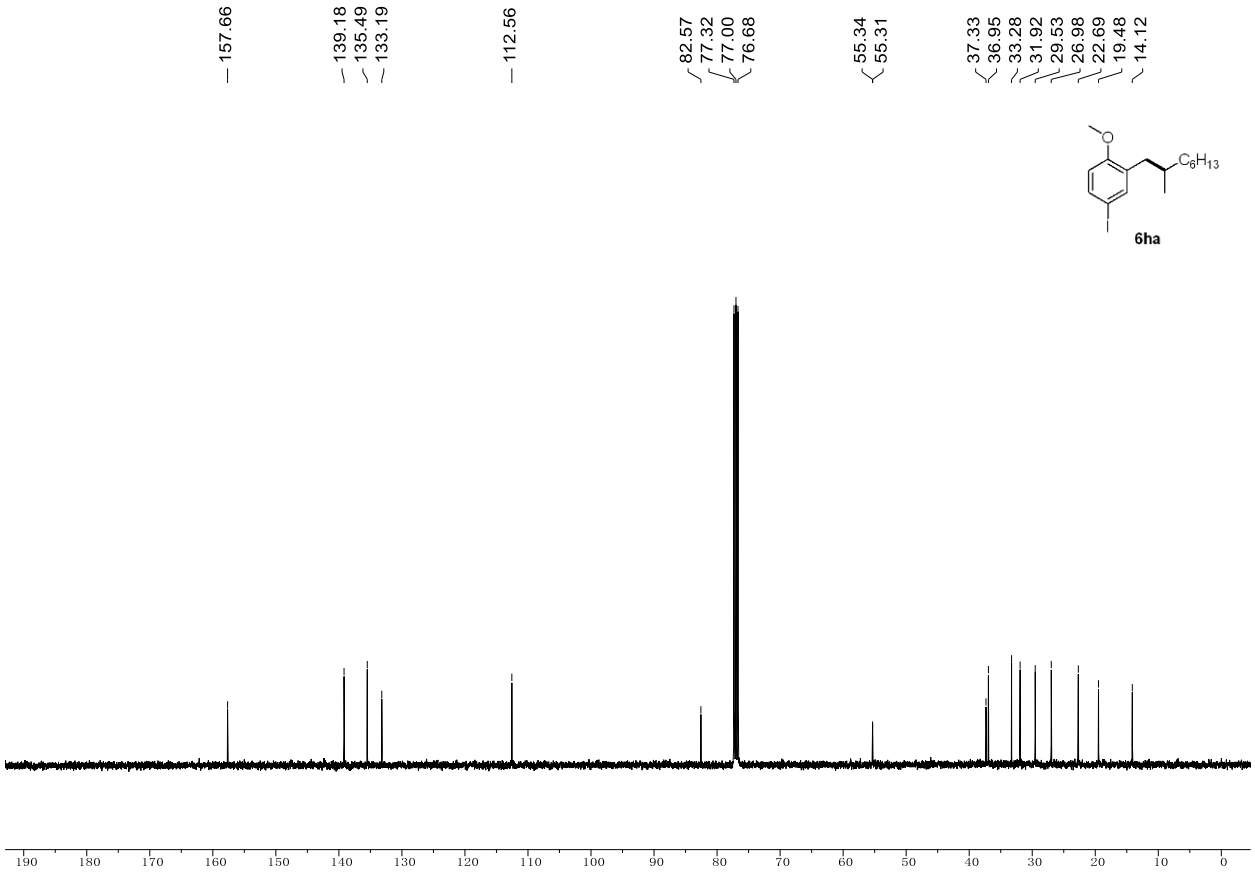

Figure S136. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6ha** in $CDCl_3$.

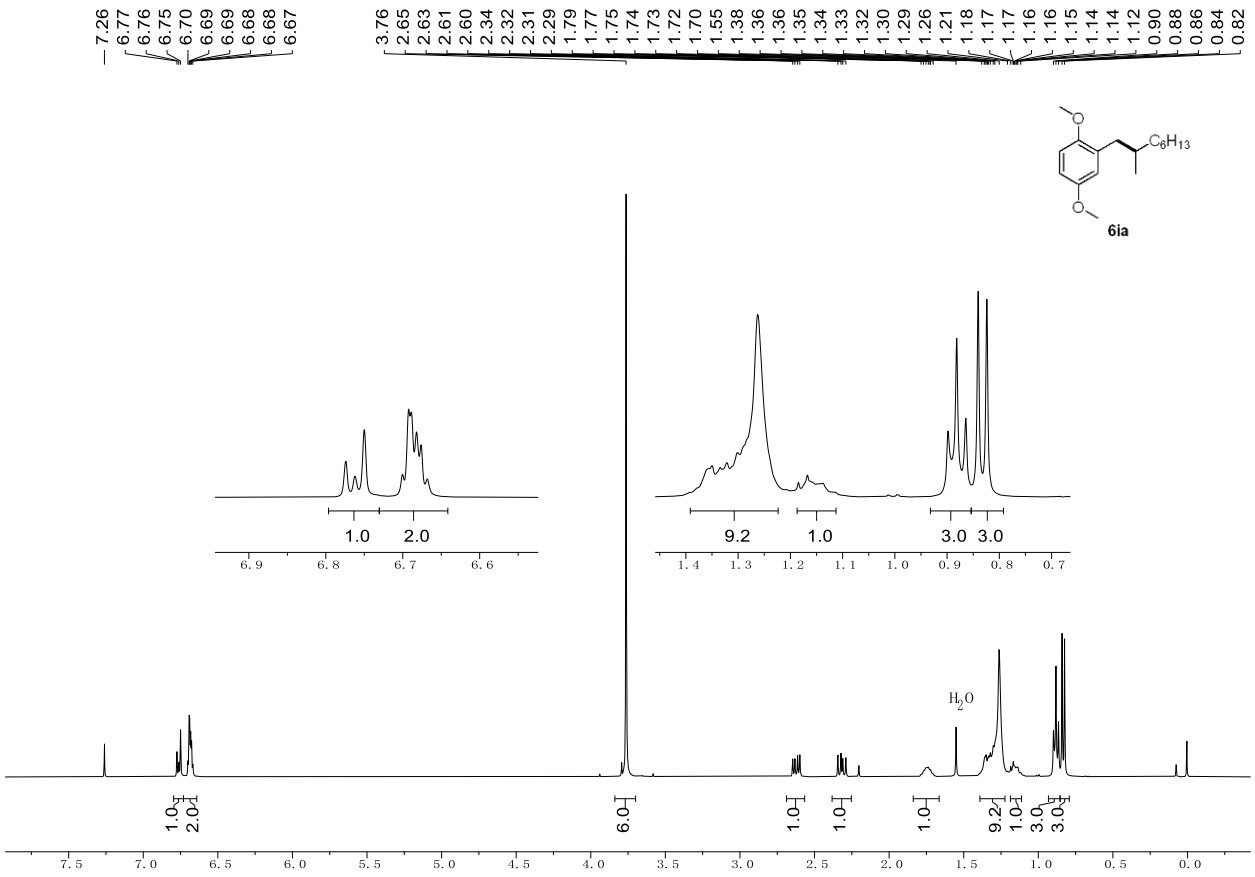

Figure S137. ^{1}H NMR spectrum (400 MHz) of **6ia** in $CDCl_3$.

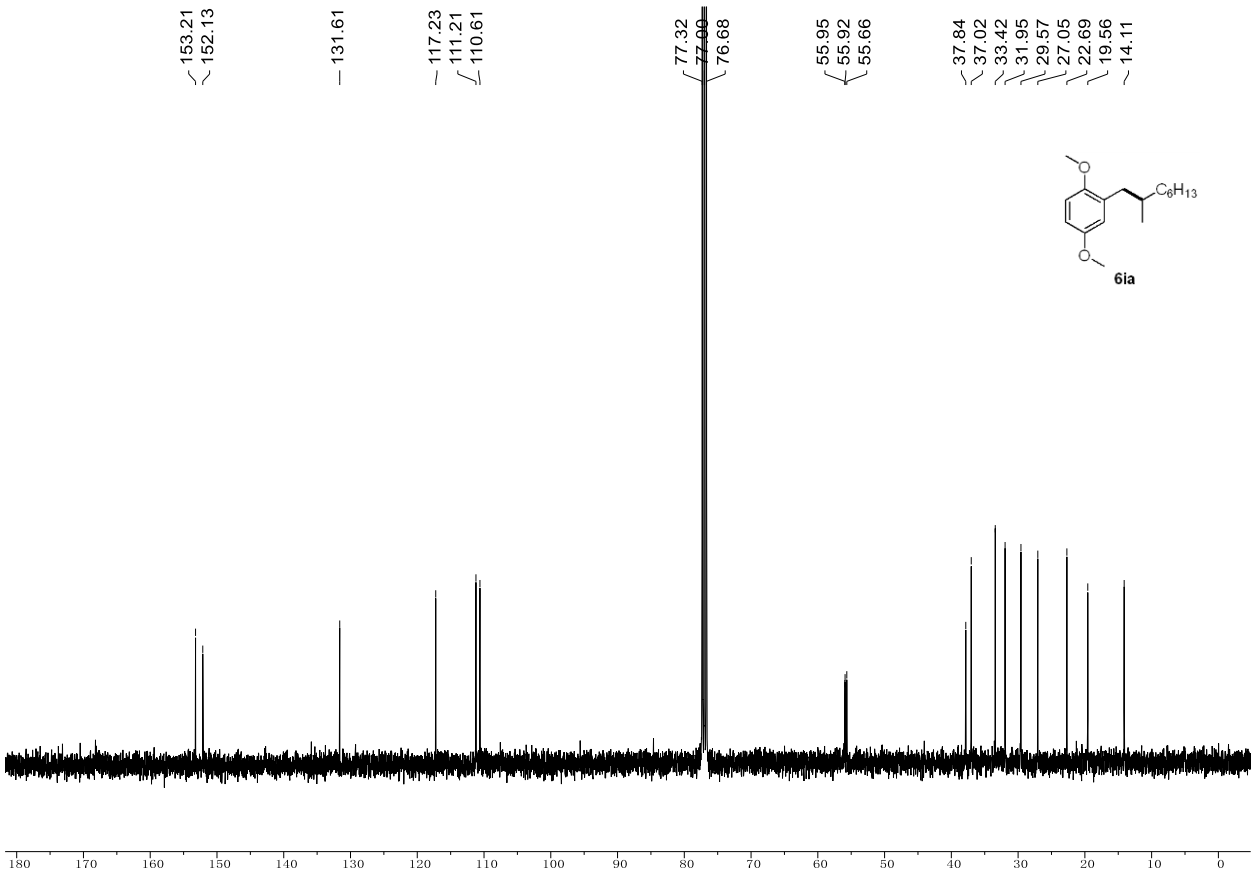

Figure S138. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6ia** in $CDCl_3$.

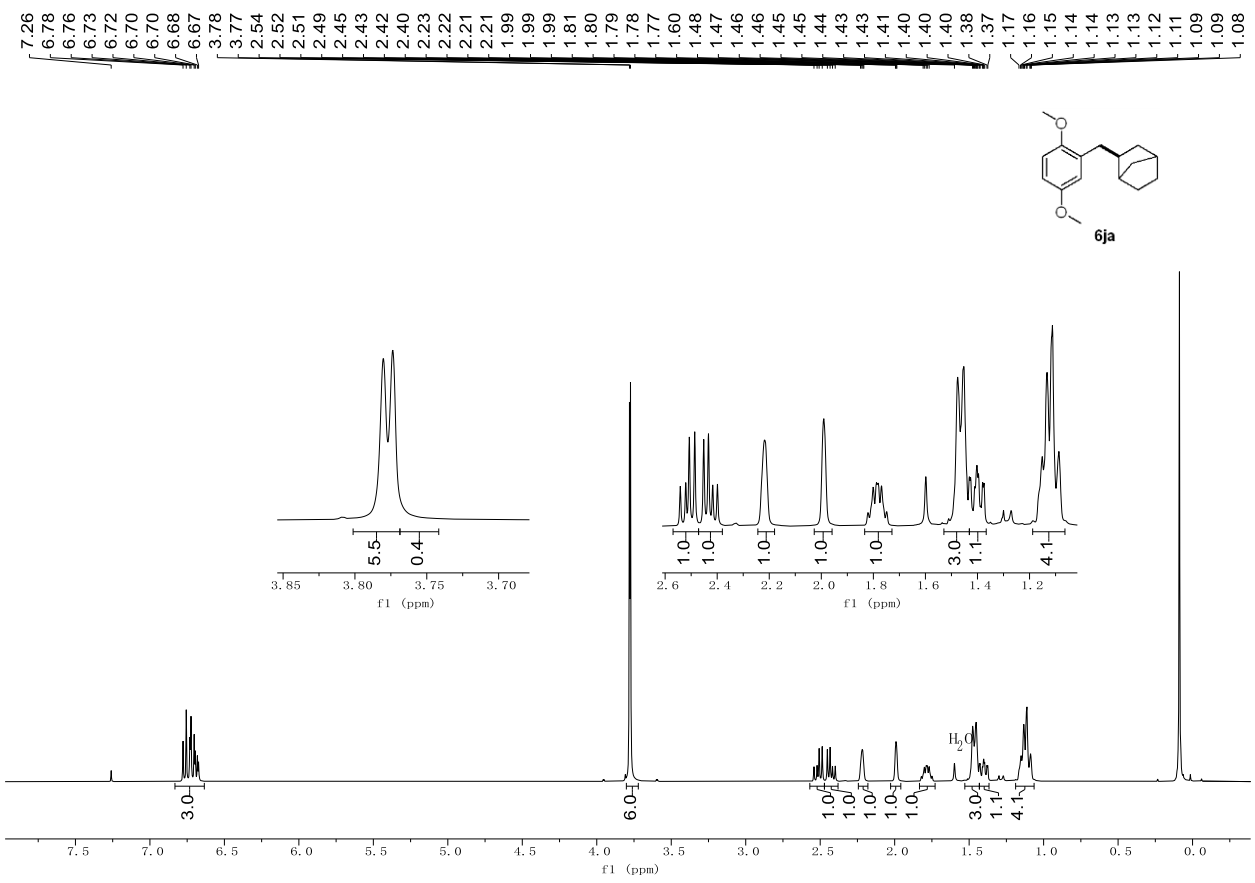

Figure S139. ^{1}H NMR spectrum (400 MHz) of **6ja** in $CDCl_3$.

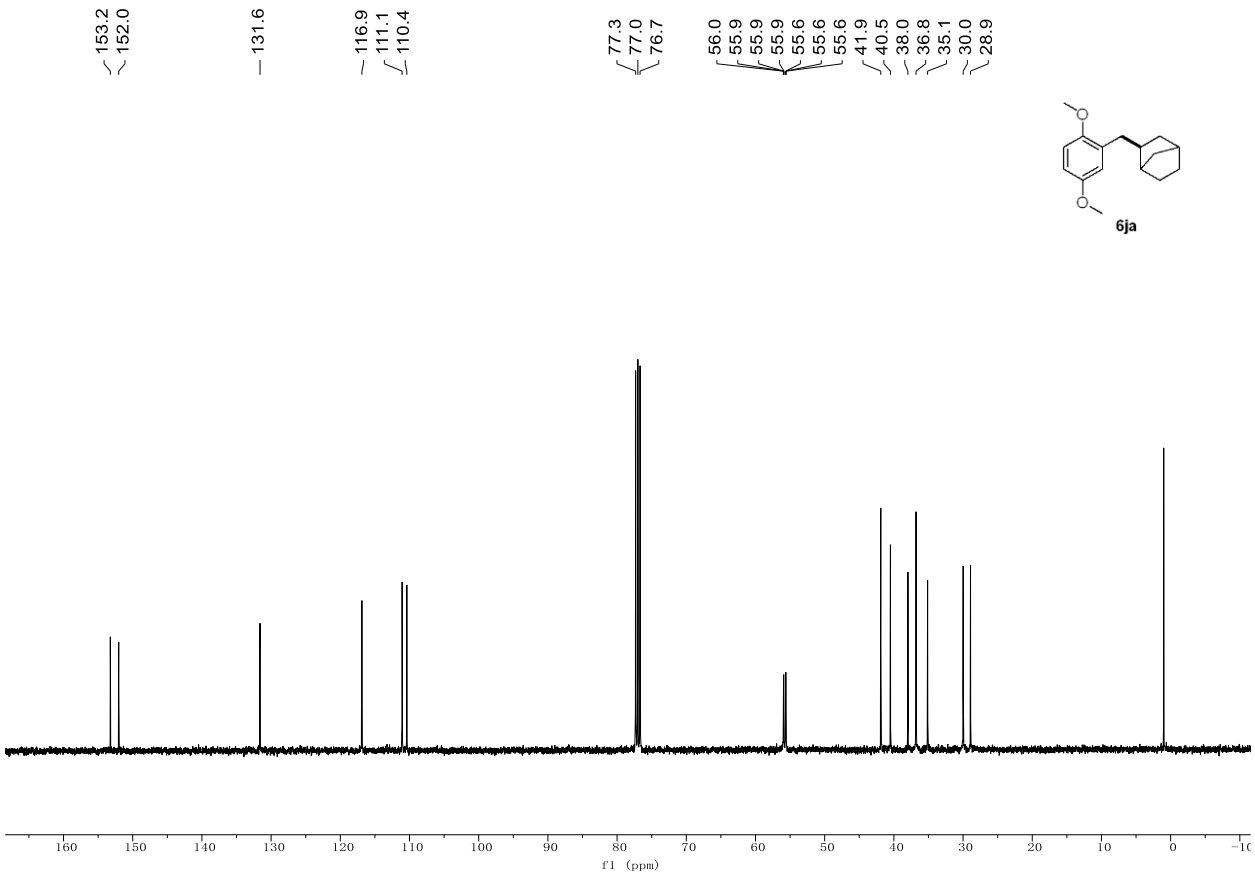

Figure S140. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6ja** in $CDCl_3$.

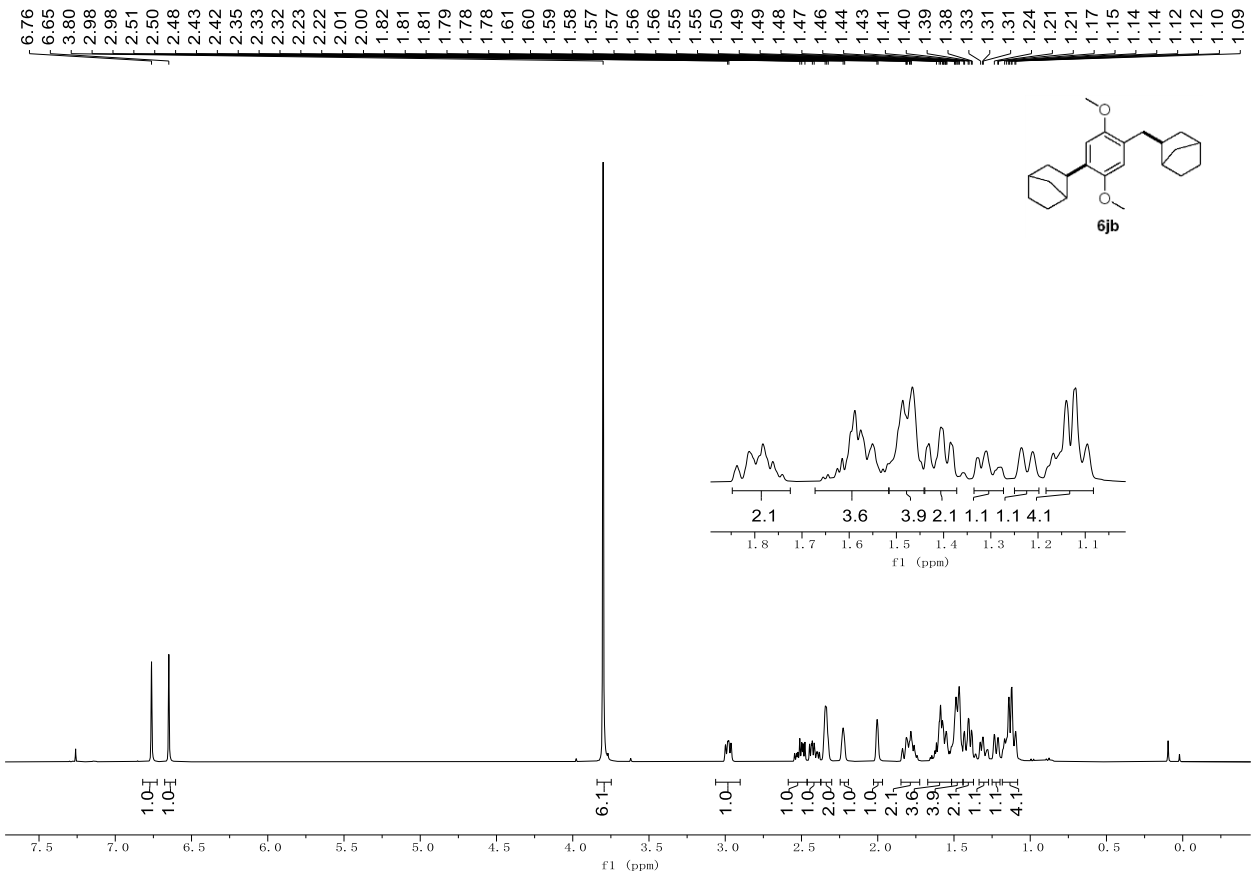

Figure S141. ^{1}H NMR spectrum (400 MHz) of **6jb** in $CDCl_3$.

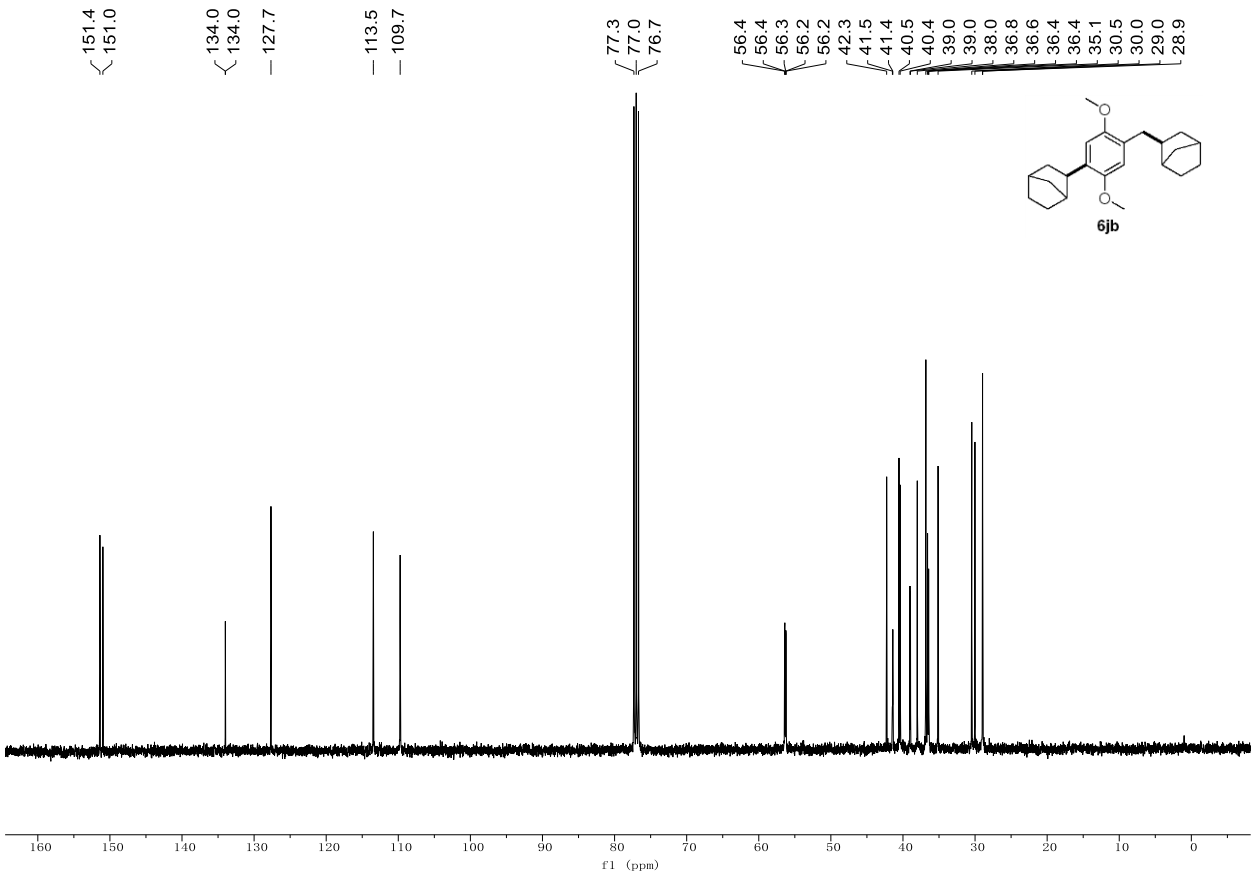

Figure S142. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6jb** in $CDCl_3$.

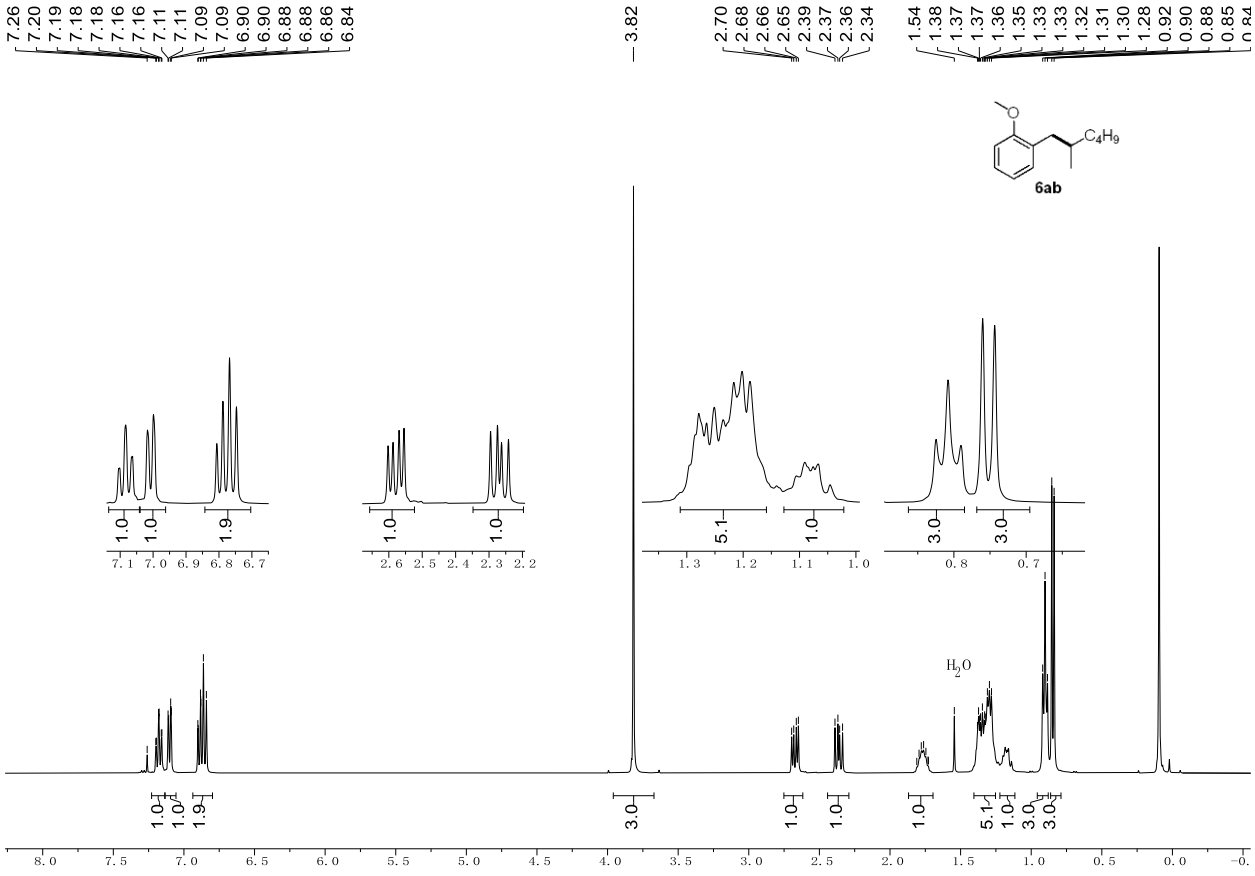

Figure S143. ^{1}H NMR spectrum (400 MHz) of **6ab** in $CDCl_3$.

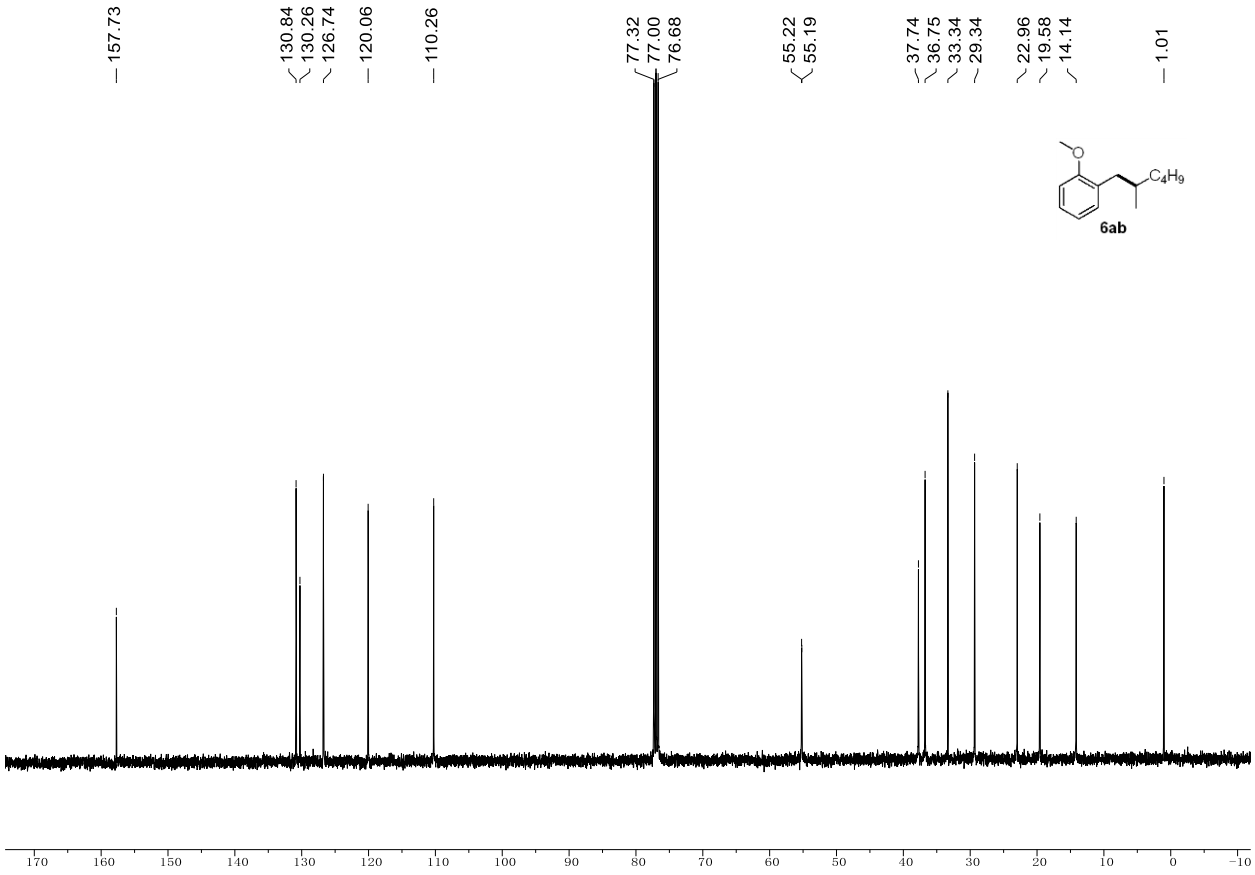

Figure S144. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6ab** in $CDCl_3$.

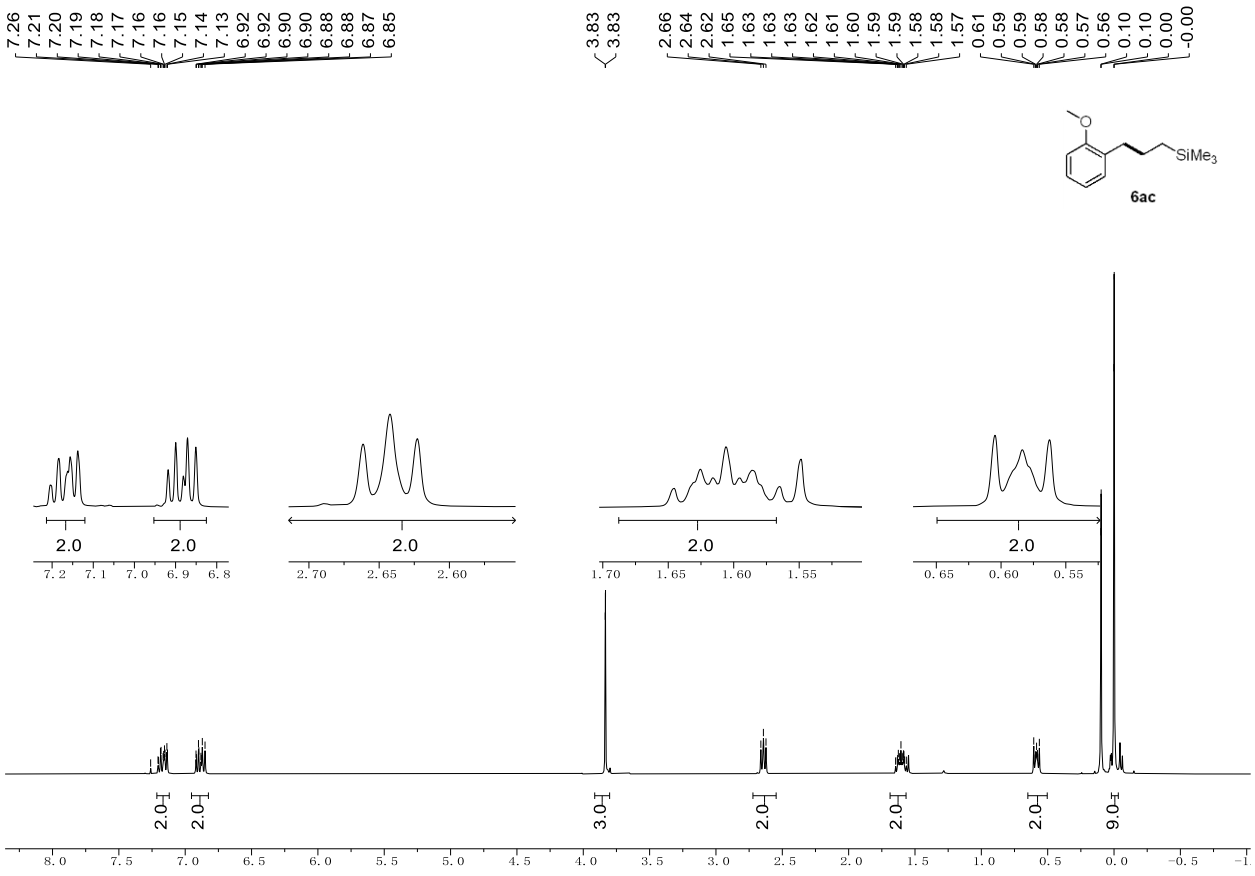

Figure S145. ^{1}H NMR spectrum (400 MHz) of **6ac** in $CDCl_3$.

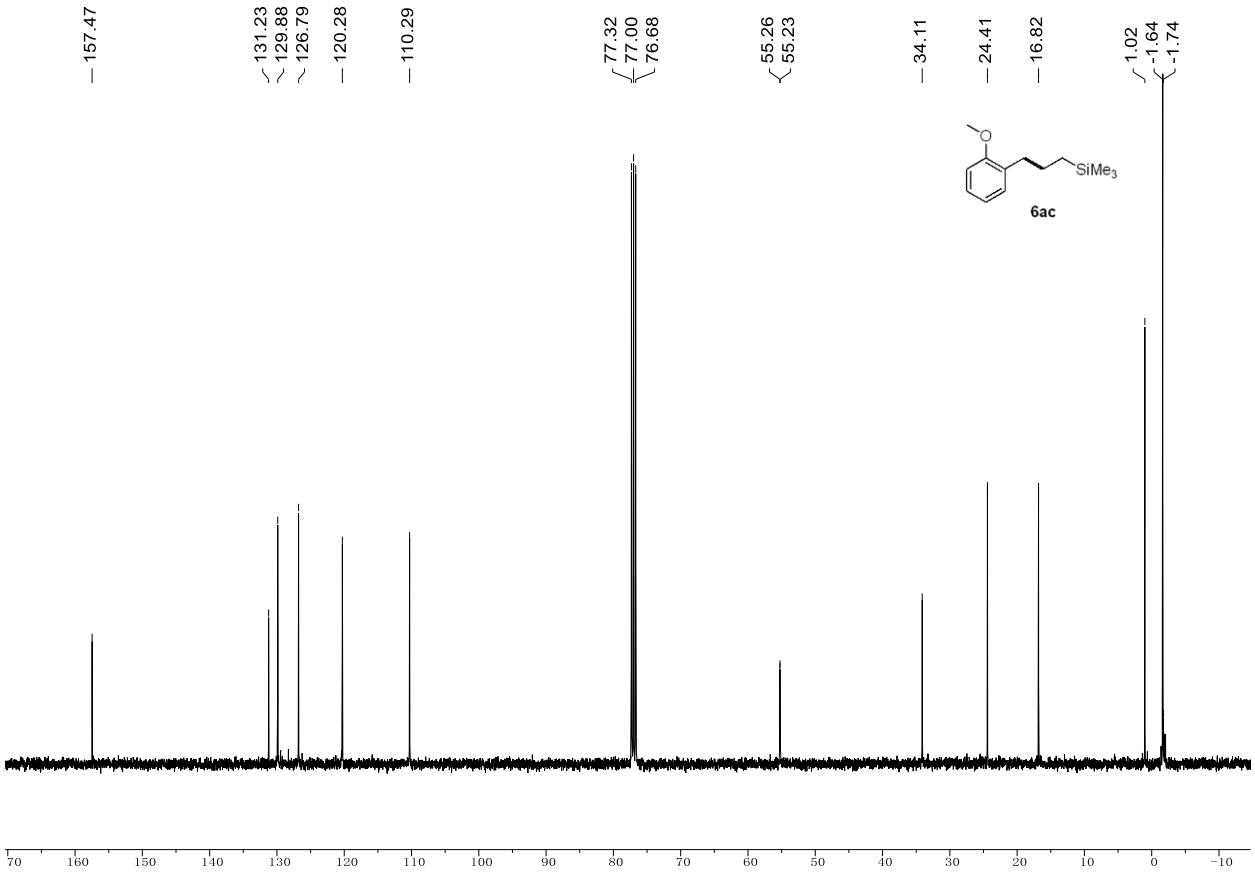

Figure S146. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6ac** in $CDCl_3$.

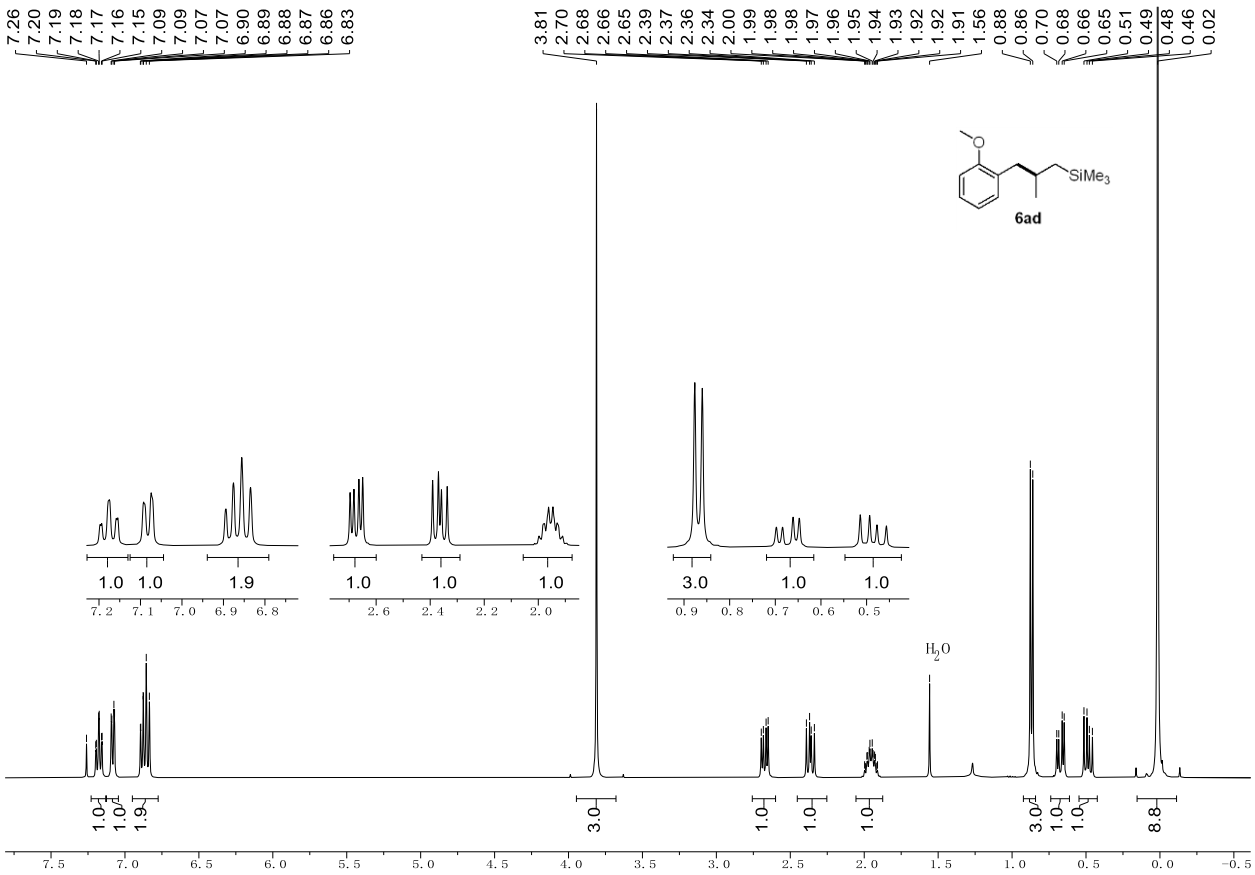

Figure S147. ^{1}H NMR spectrum (400 MHz) of **6ad** in $CDCl_3$.

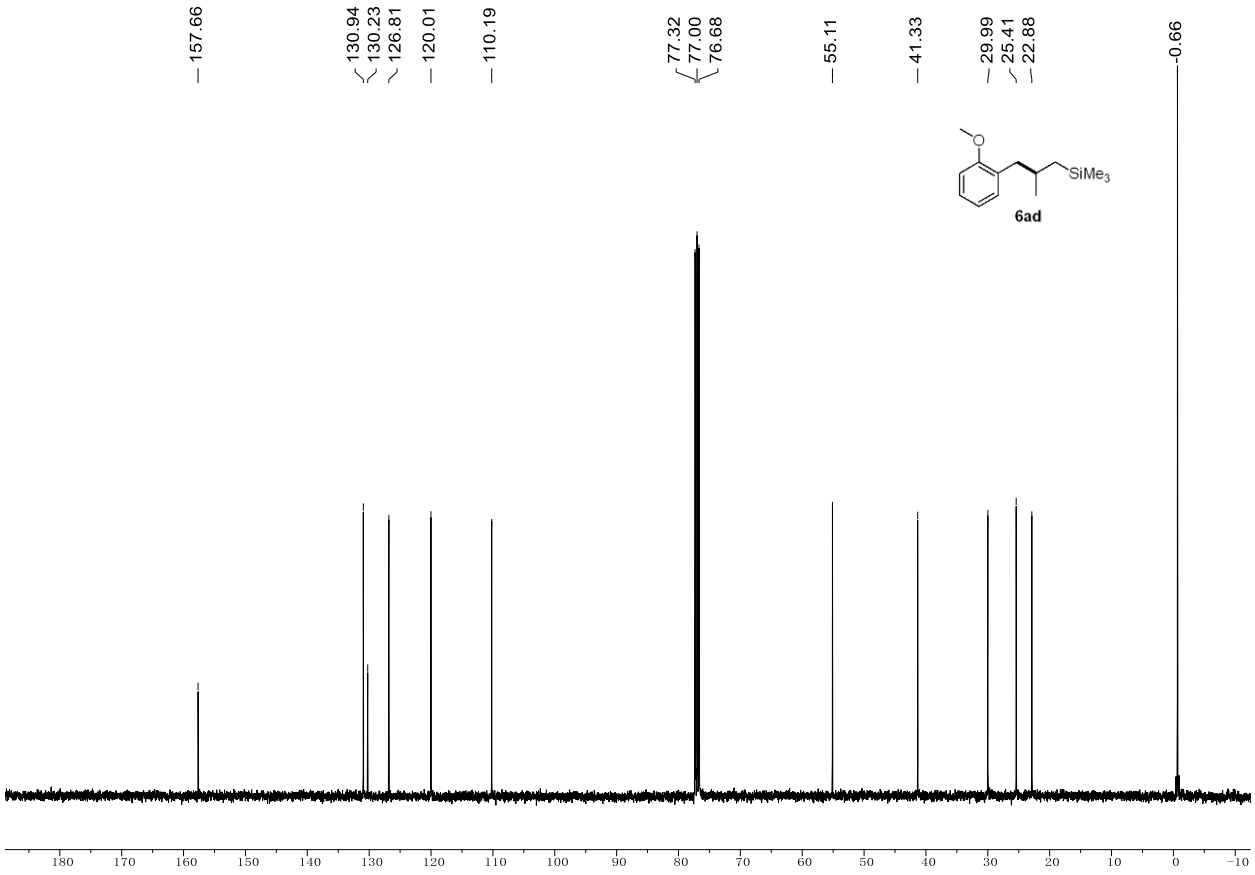

Figure S148. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6ad** in $CDCl_3$.

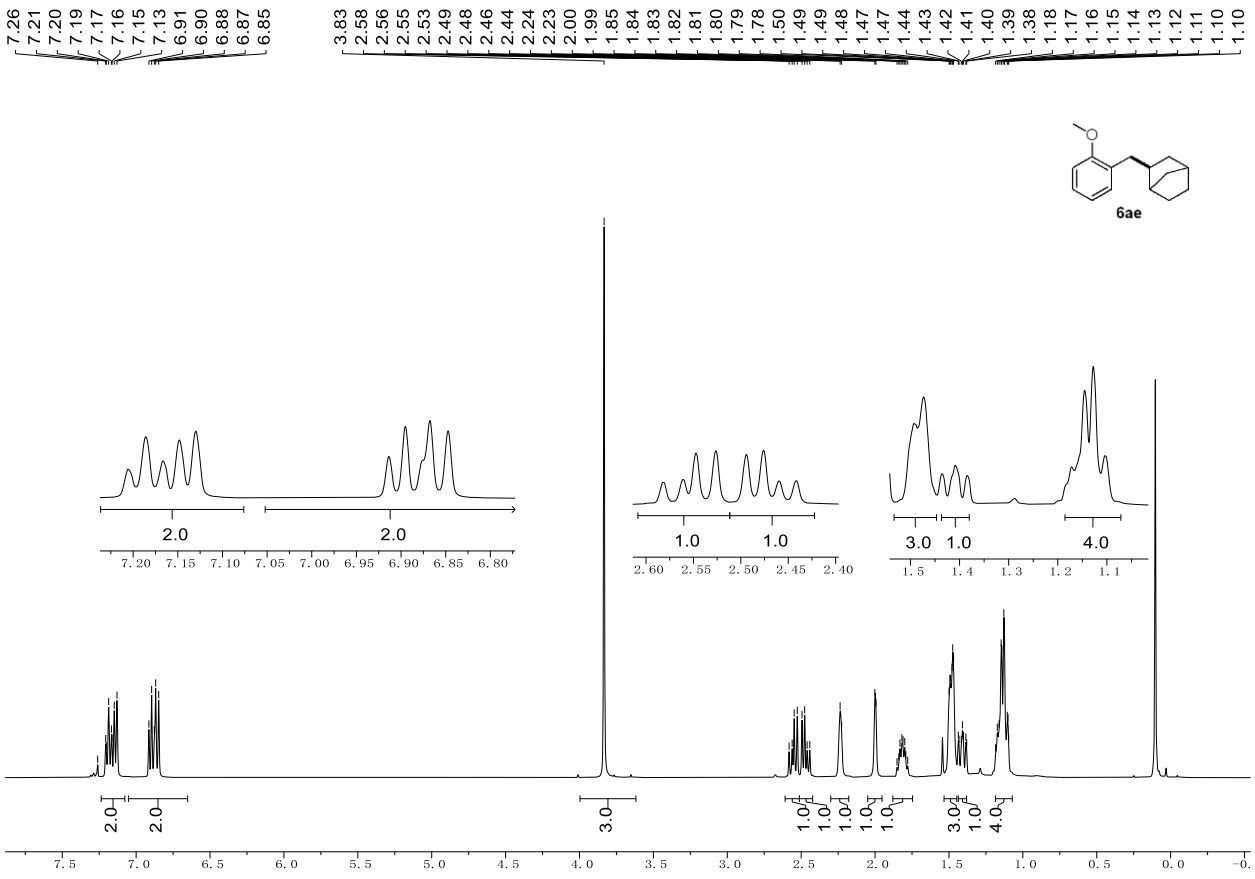

Figure S149. ^{1}H NMR spectrum (400 MHz) of **6ae** in $CDCl_3$.

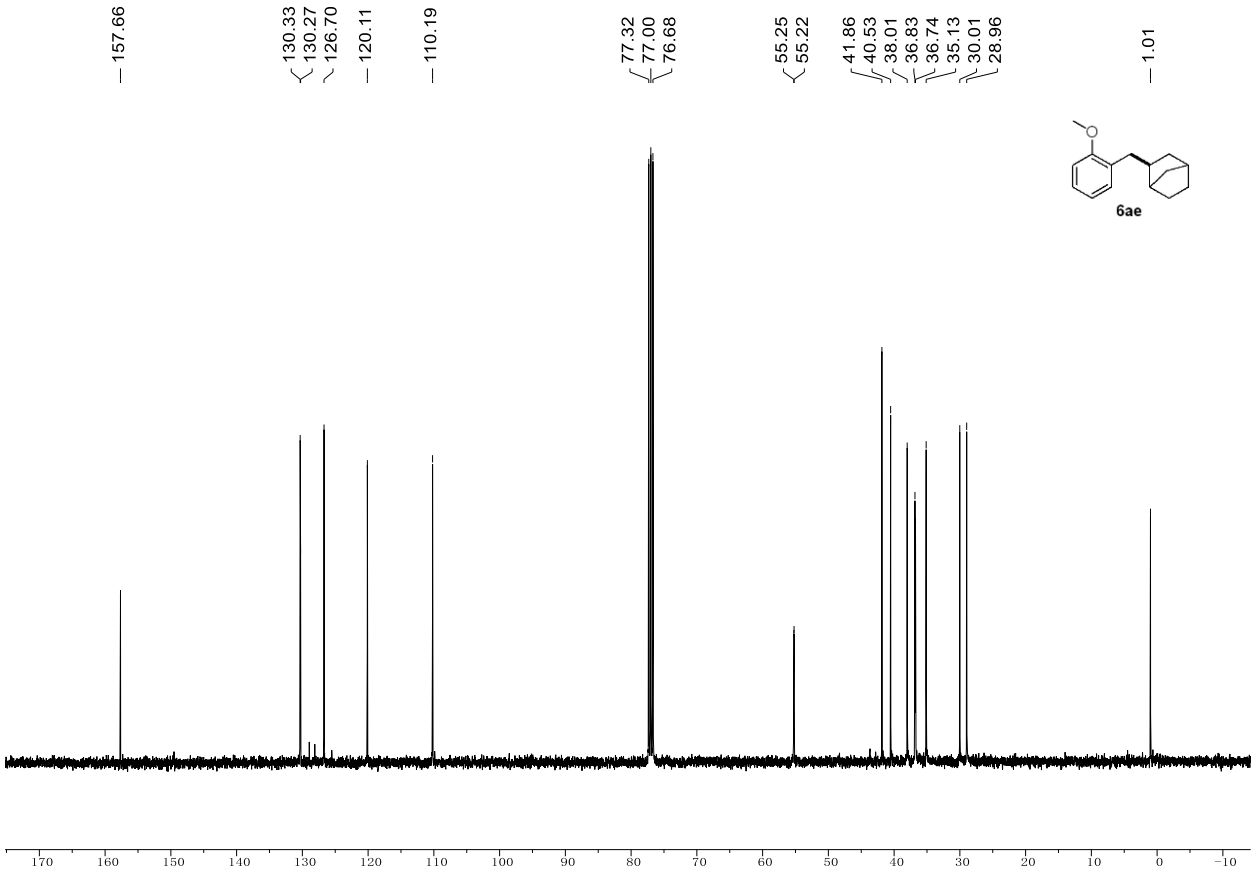

Figure S150. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6ae** in $CDCl_3$.

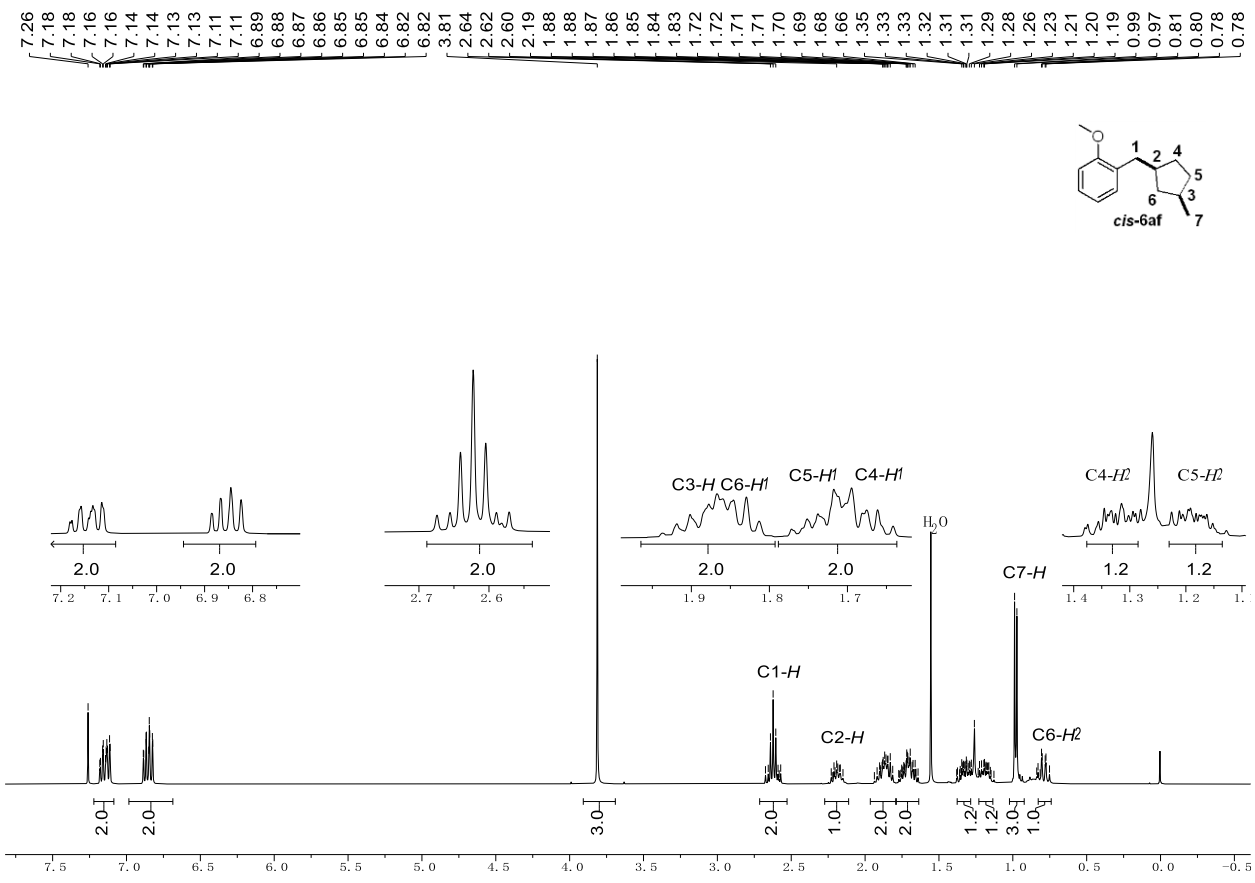

Figure S151. ^{1}H NMR spectrum (400 MHz) of *cis*-**6af** in $CDCl_3$.

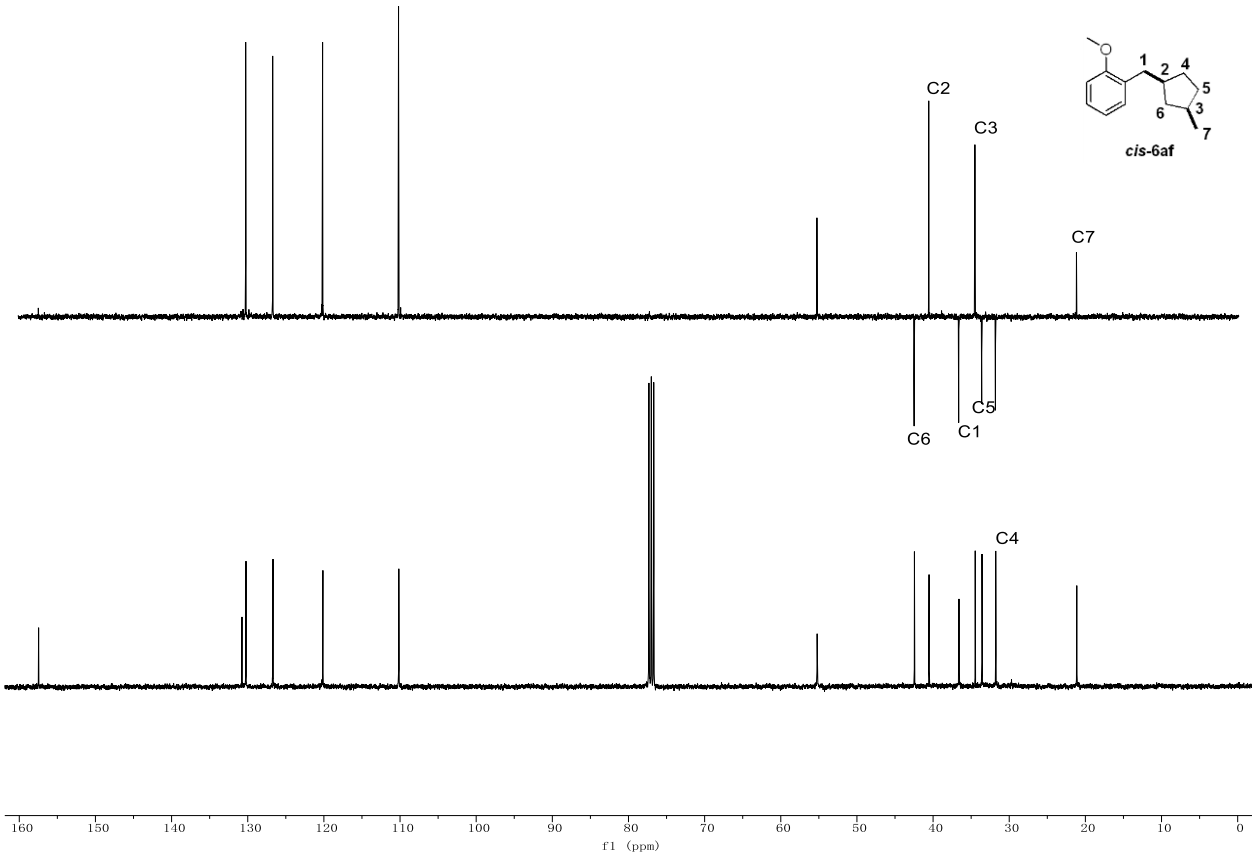

Figure S152. ^{135}Dept, $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of *cis*-**6af** in $CDCl_3$.

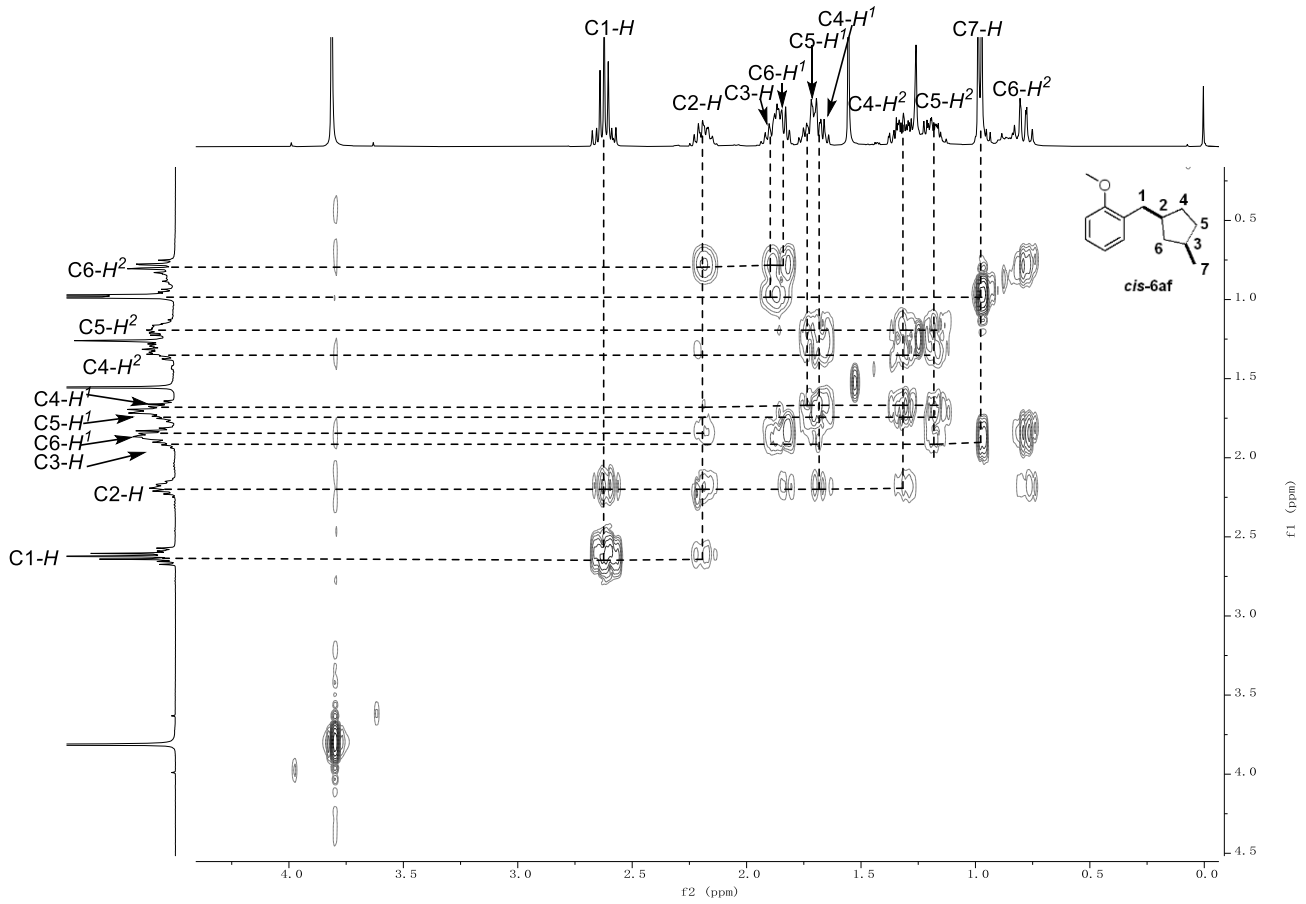

Figure S153. 2D ^{1}H-^{1}H COSY NMR spectrum of *cis*-**6af** in $CDCl_3$.

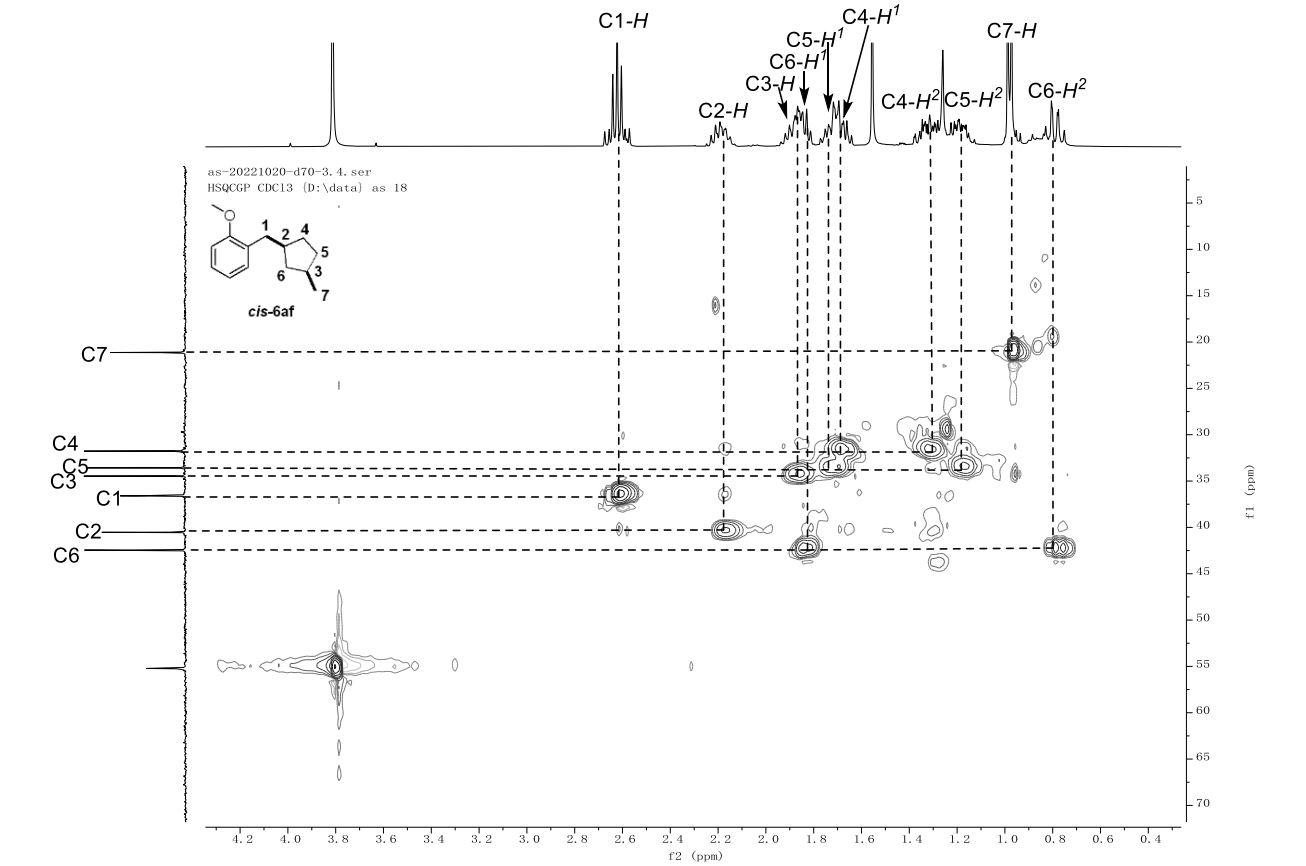

Figure S154. 2D ^{1}H-^{13}C HSQC NMR spectrum of *cis*-**6af** in $CDCl_3$.

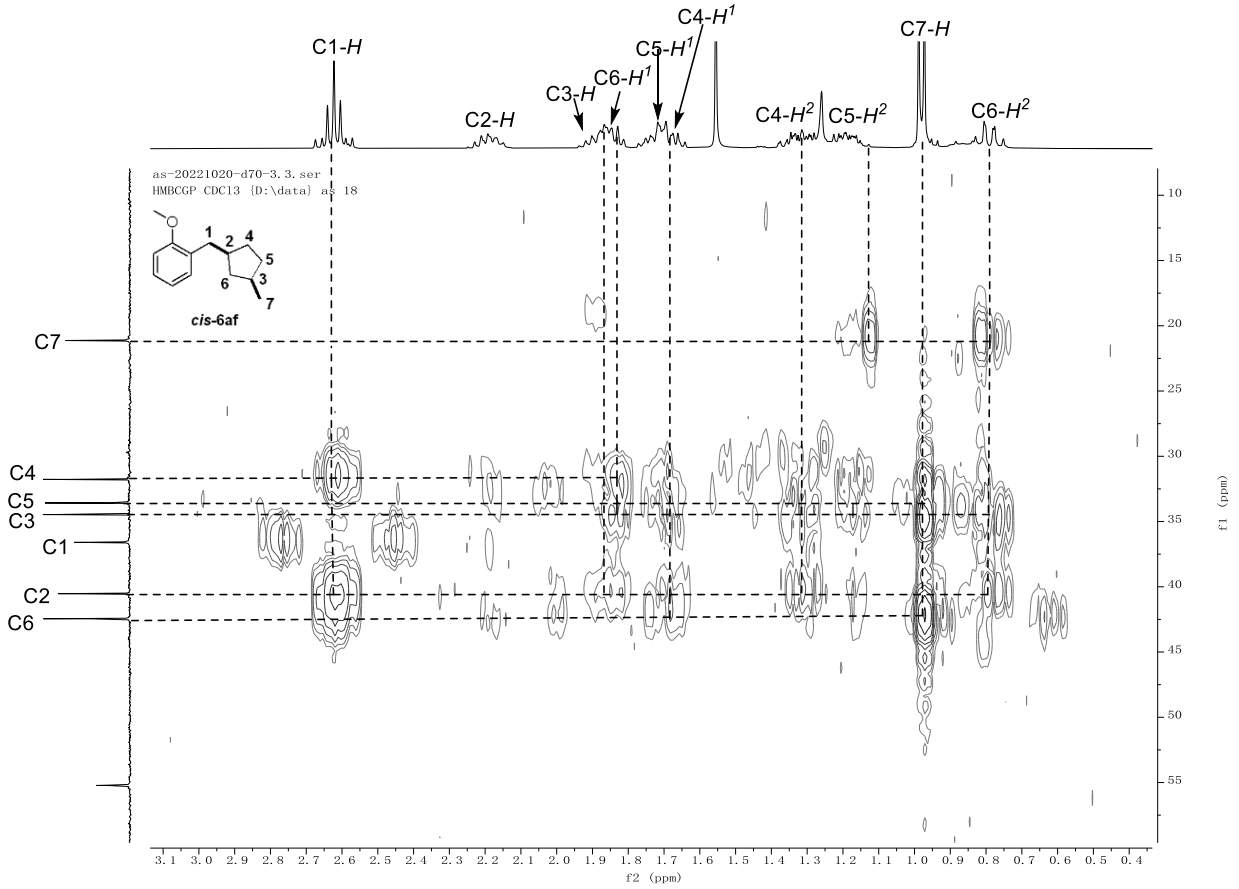

Figure S155. 2D ^{1}H-^{13}C HMBC NMR spectrum of *cis*-**6af** in $CDCl_3$.

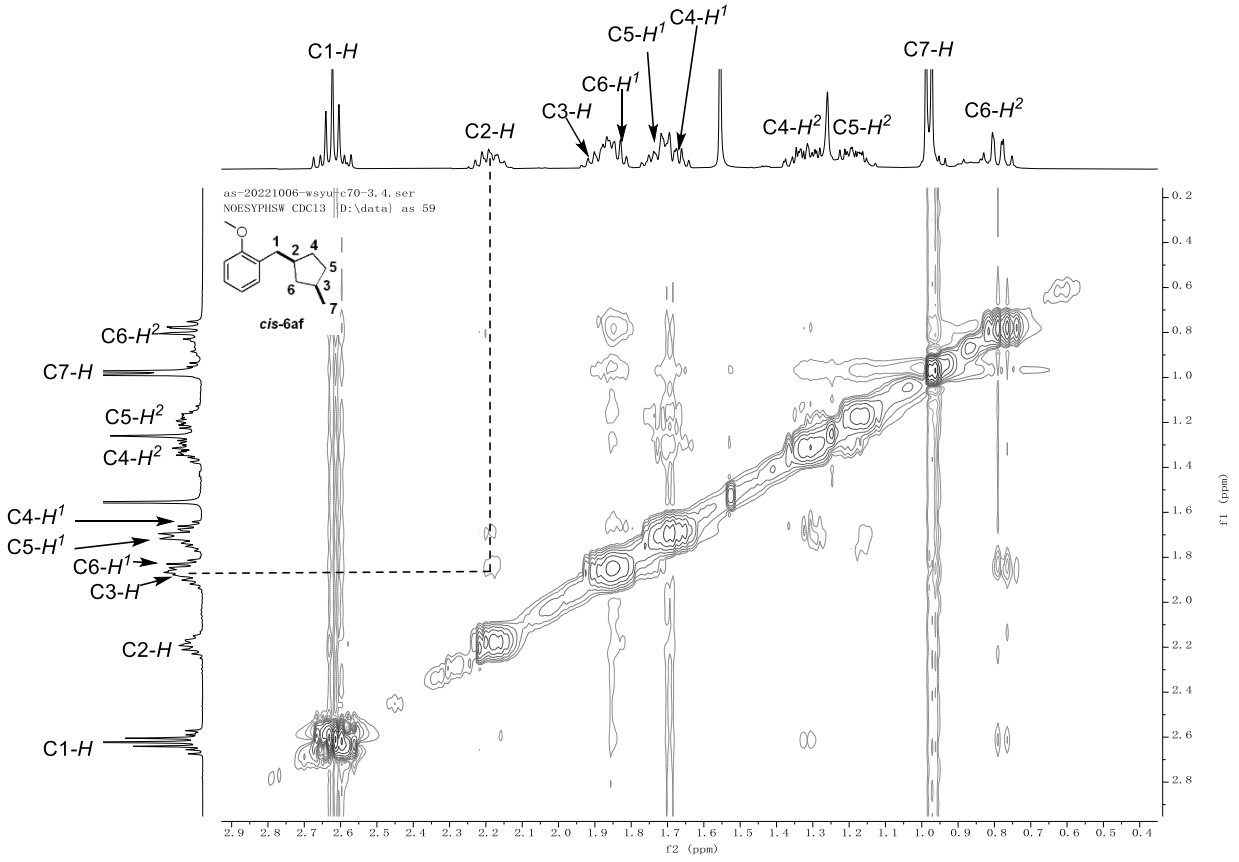

Figure S156. 2D NOESY NMR spectrum of *cis*-**6af** in $CDCl_3$.

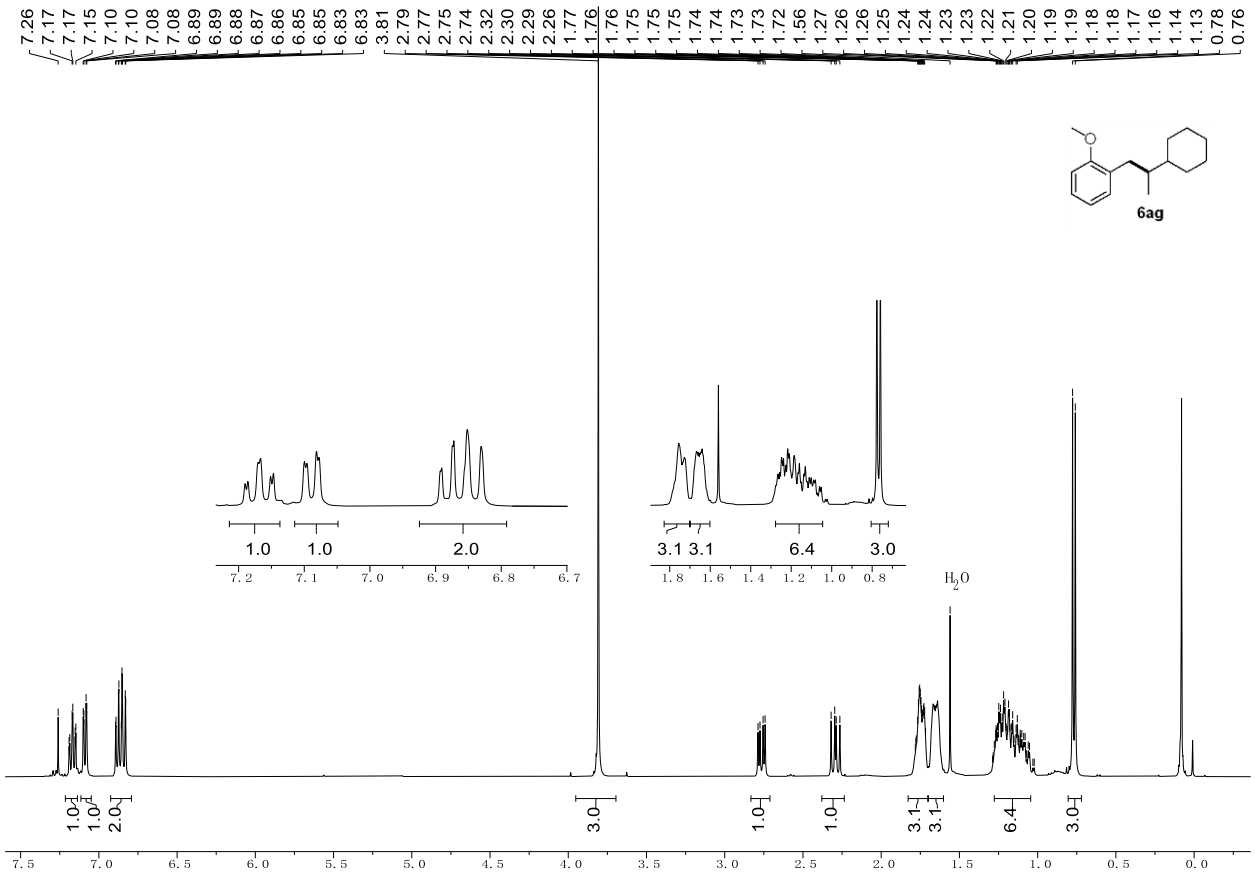

Figure S157. ^{1}H NMR spectrum (400 MHz) of **6ag** in $CDCl_3$.

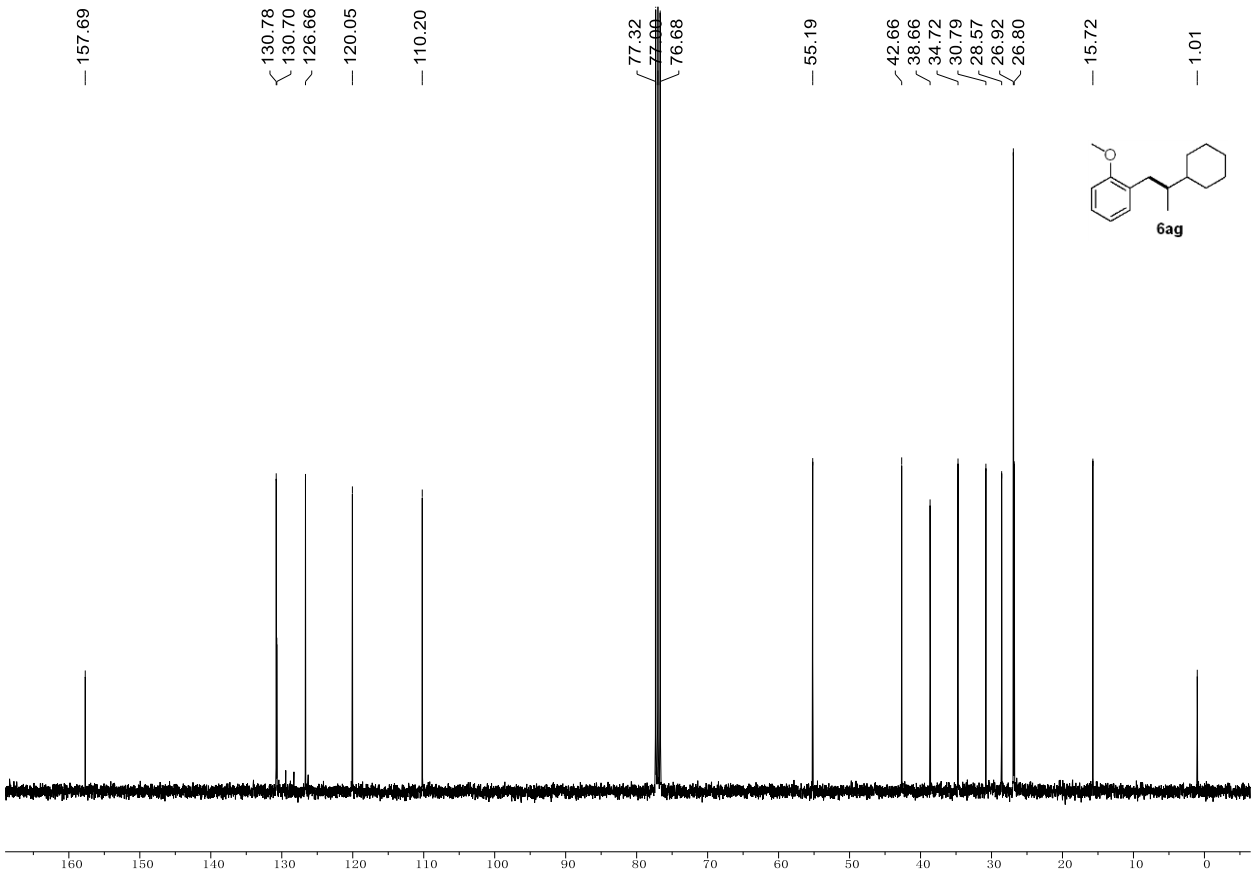

Figure S158. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6ag** in $CDCl_3$.

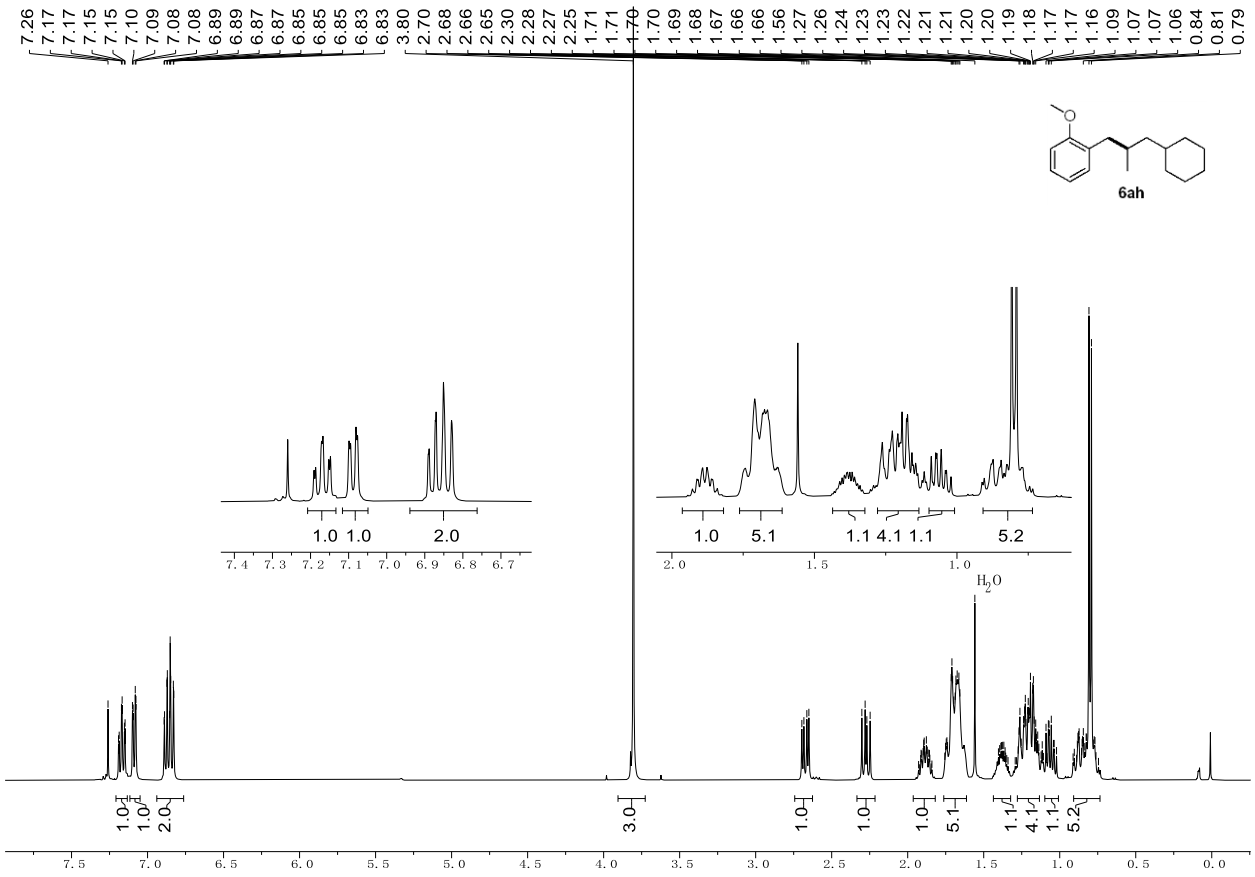

Figure S159. ^{1}H NMR spectrum (400 MHz) of **6ah** in $CDCl_3$.

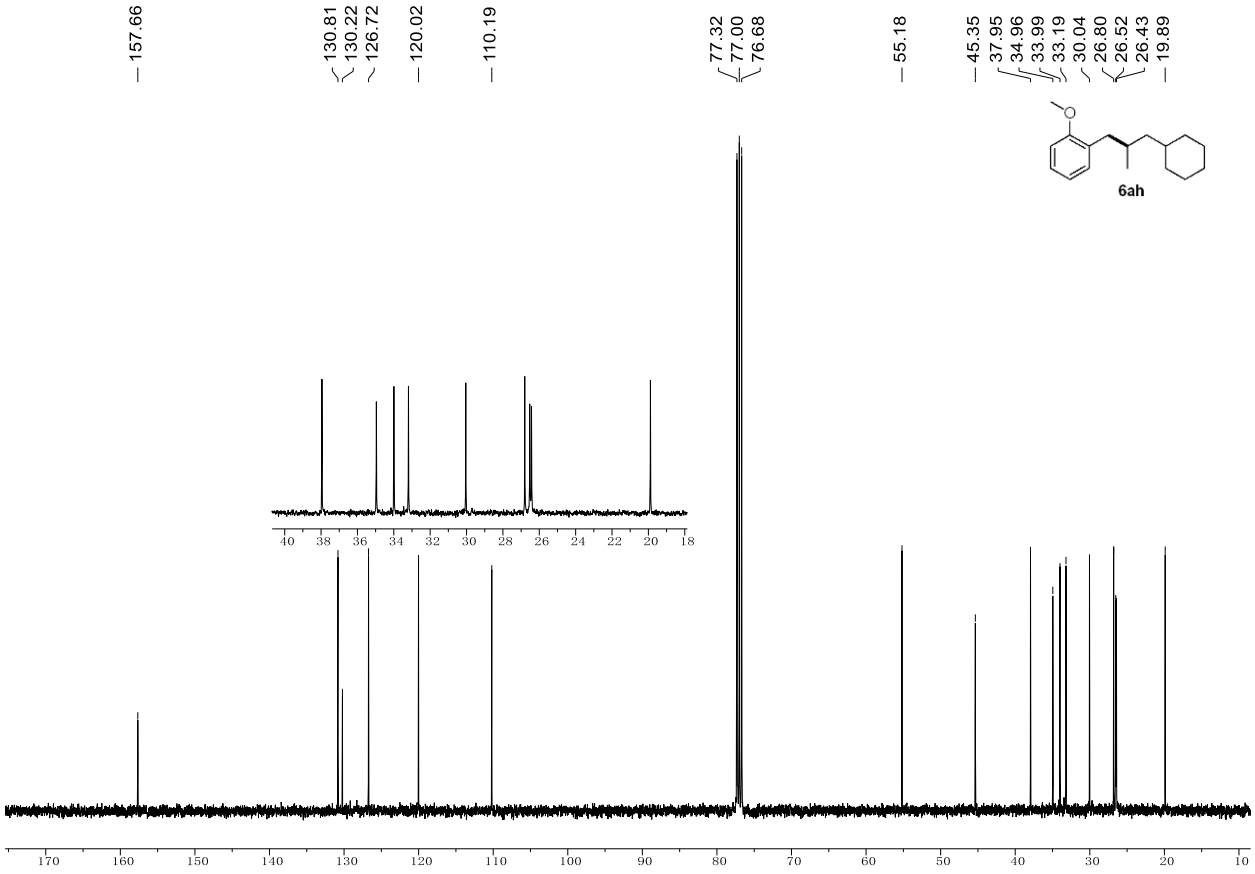

Figure S160. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6ah** in $CDCl_3$.

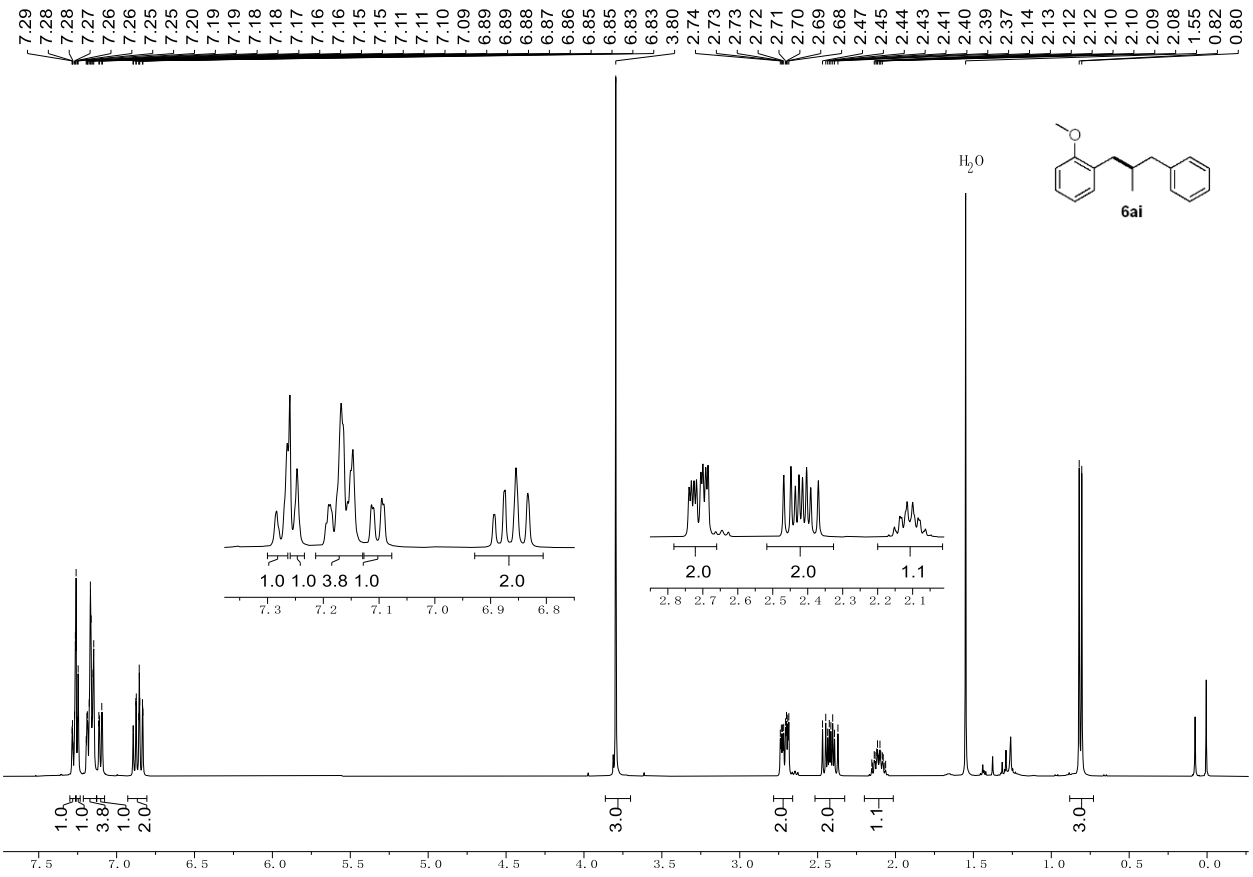

Figure S161. ^{1}H NMR spectrum (400 MHz) of **6ai** in $CDCl_3$.

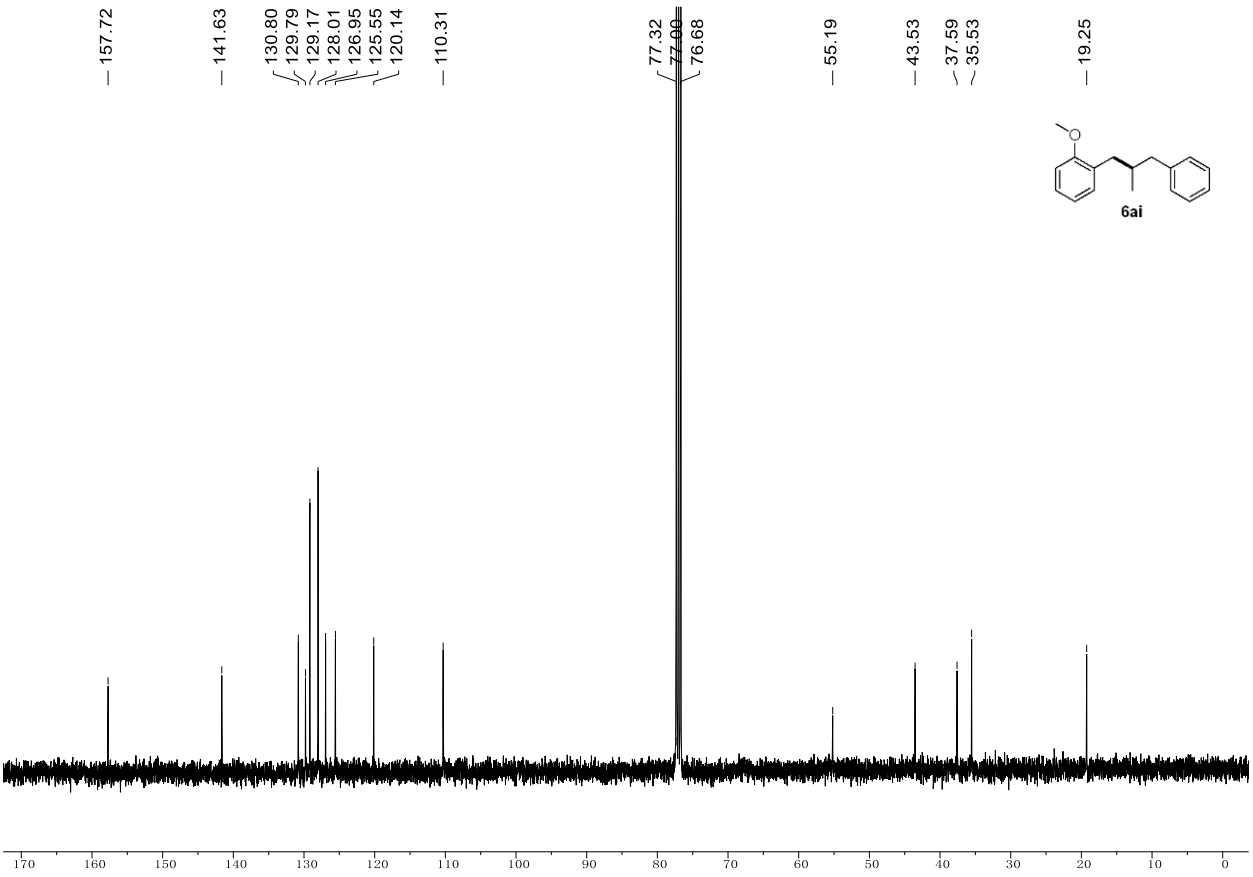

Figure S162. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6ai** in $CDCl_3$.

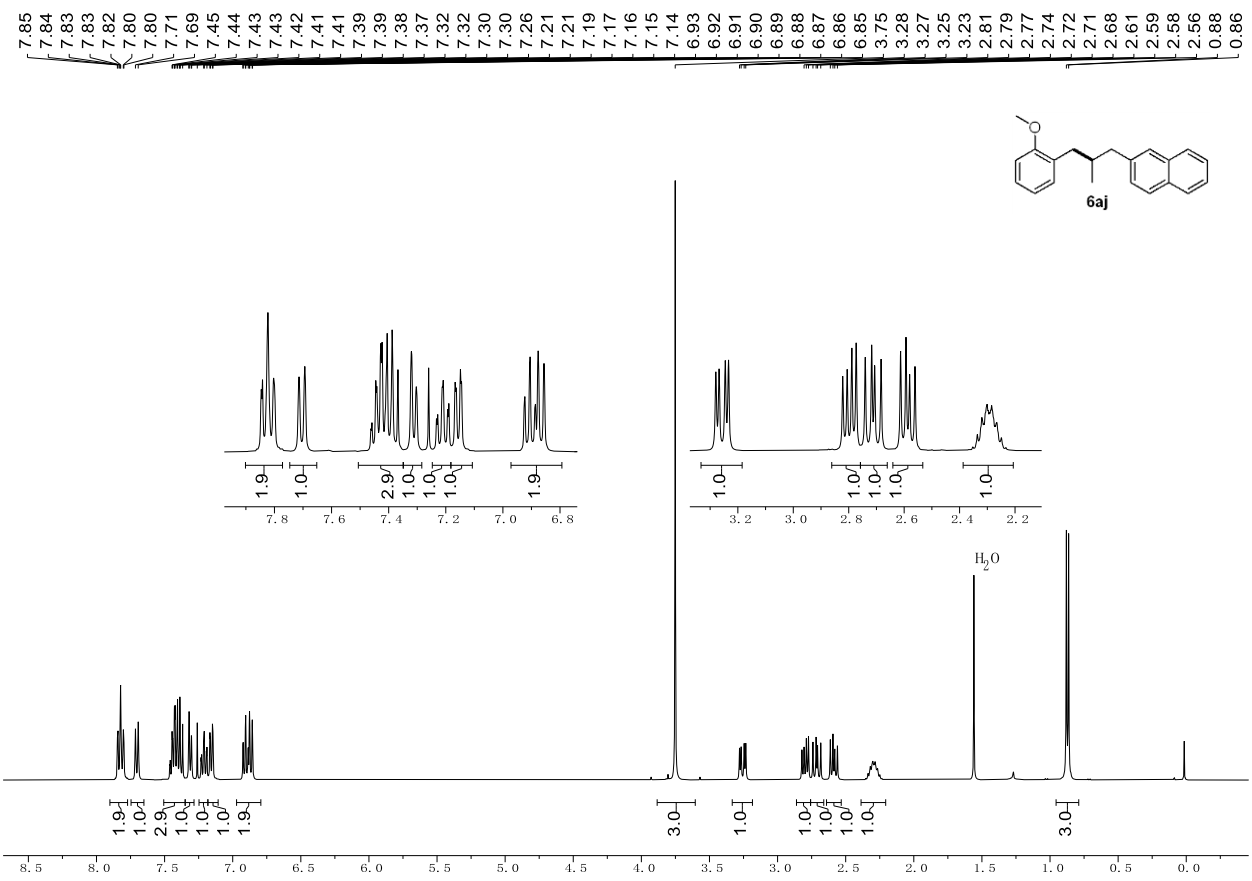

Figure S163. ^{1}H NMR spectrum (400 MHz) of **6aj** in $CDCl_3$.

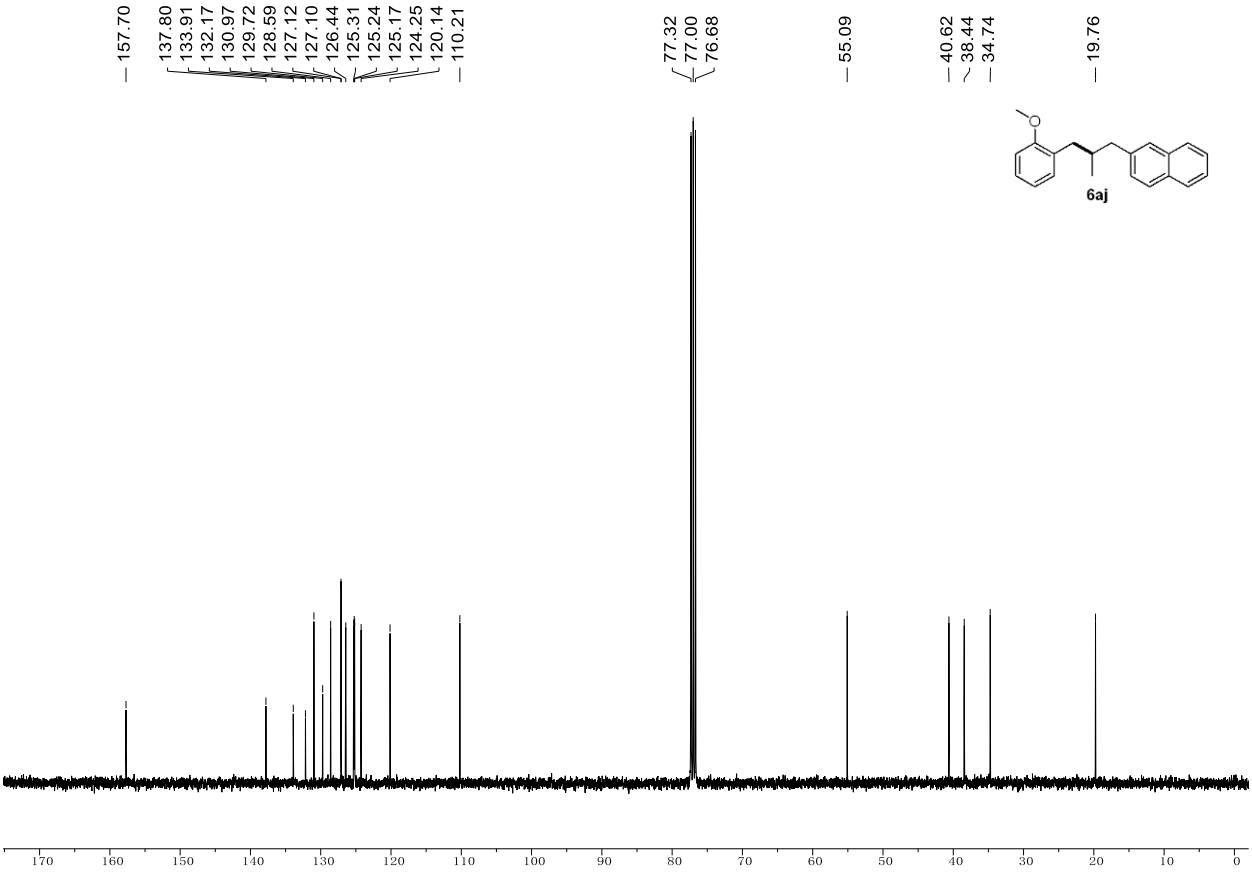

Figure S164. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6aj** in $CDCl_3$.

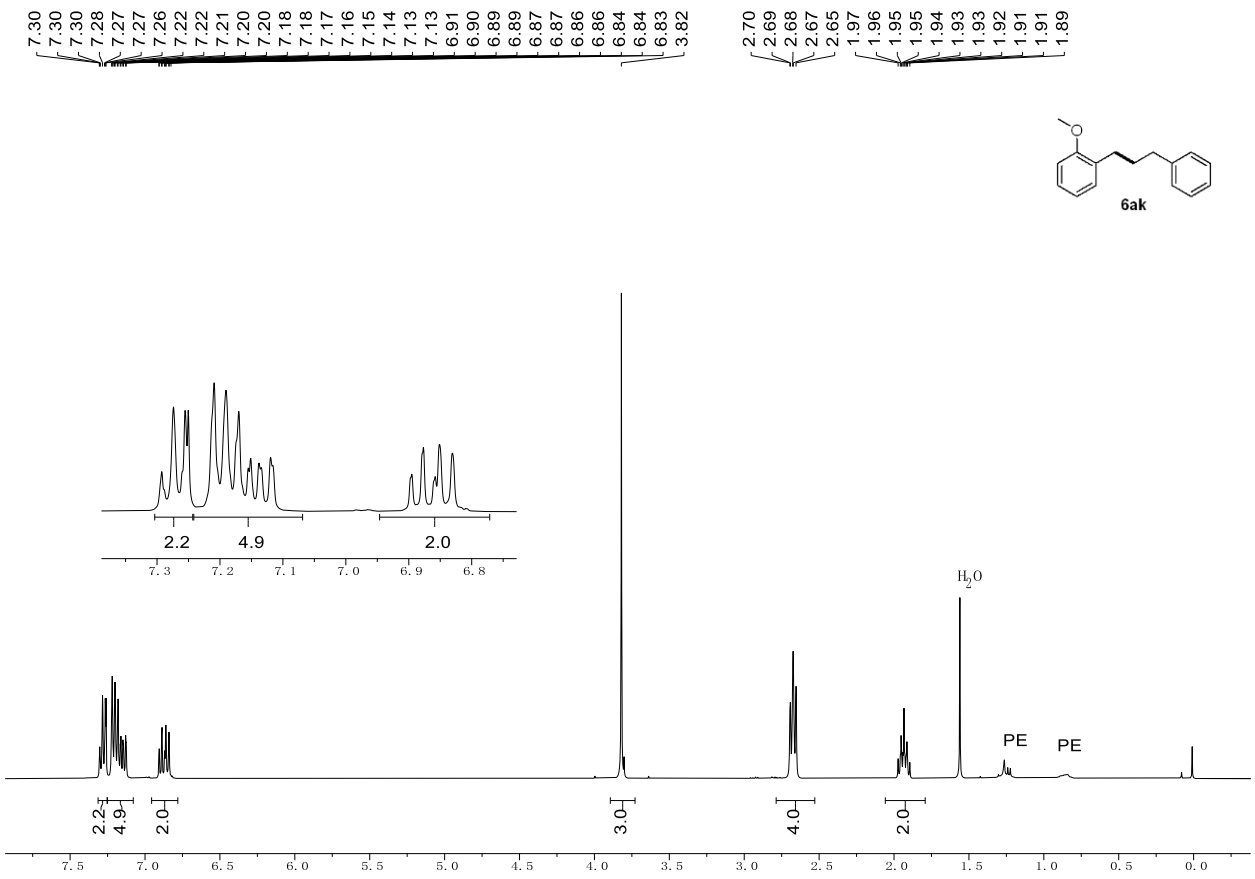

Figure S165. ^{1}H NMR spectrum (400 MHz) of **6ak** in $CDCl_3$.

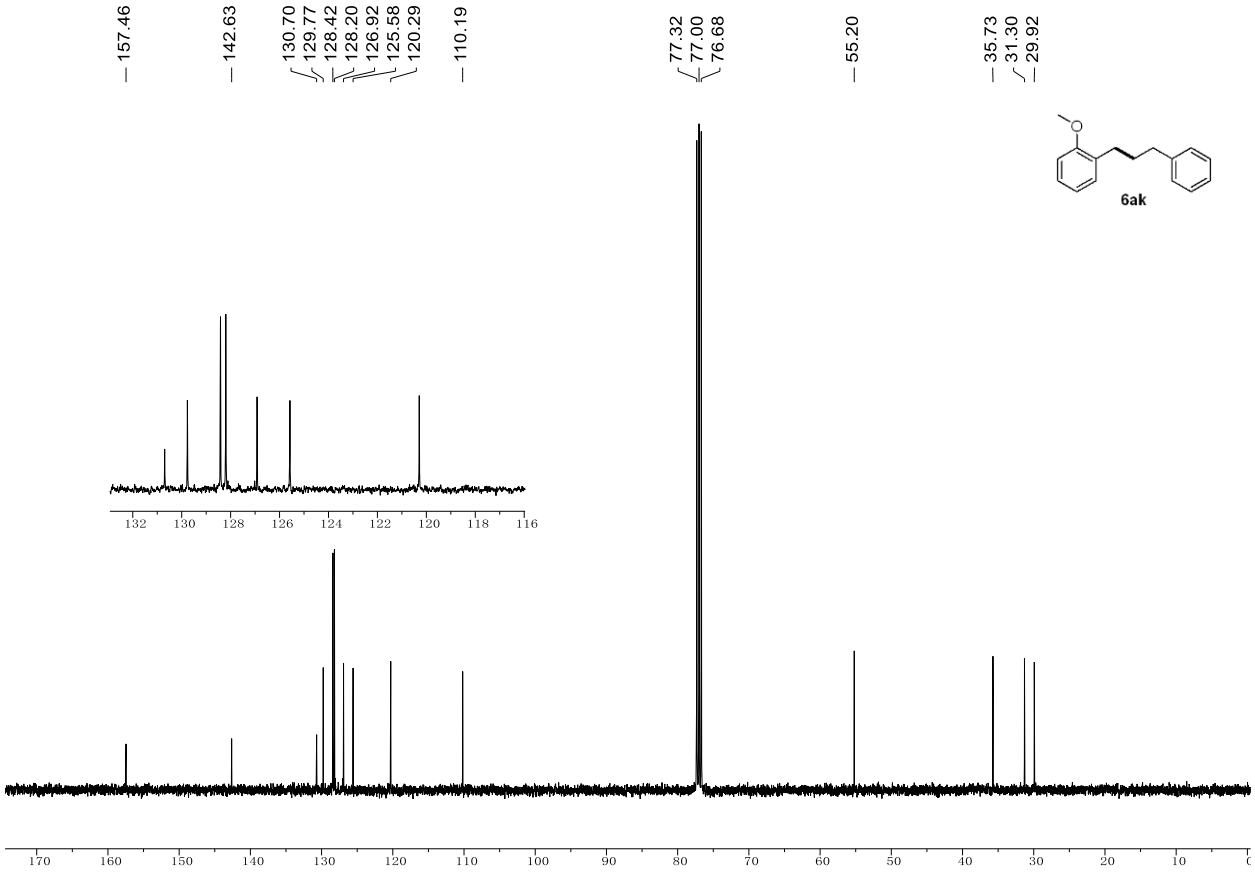

Figure S166. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6ak** in $CDCl_3$.

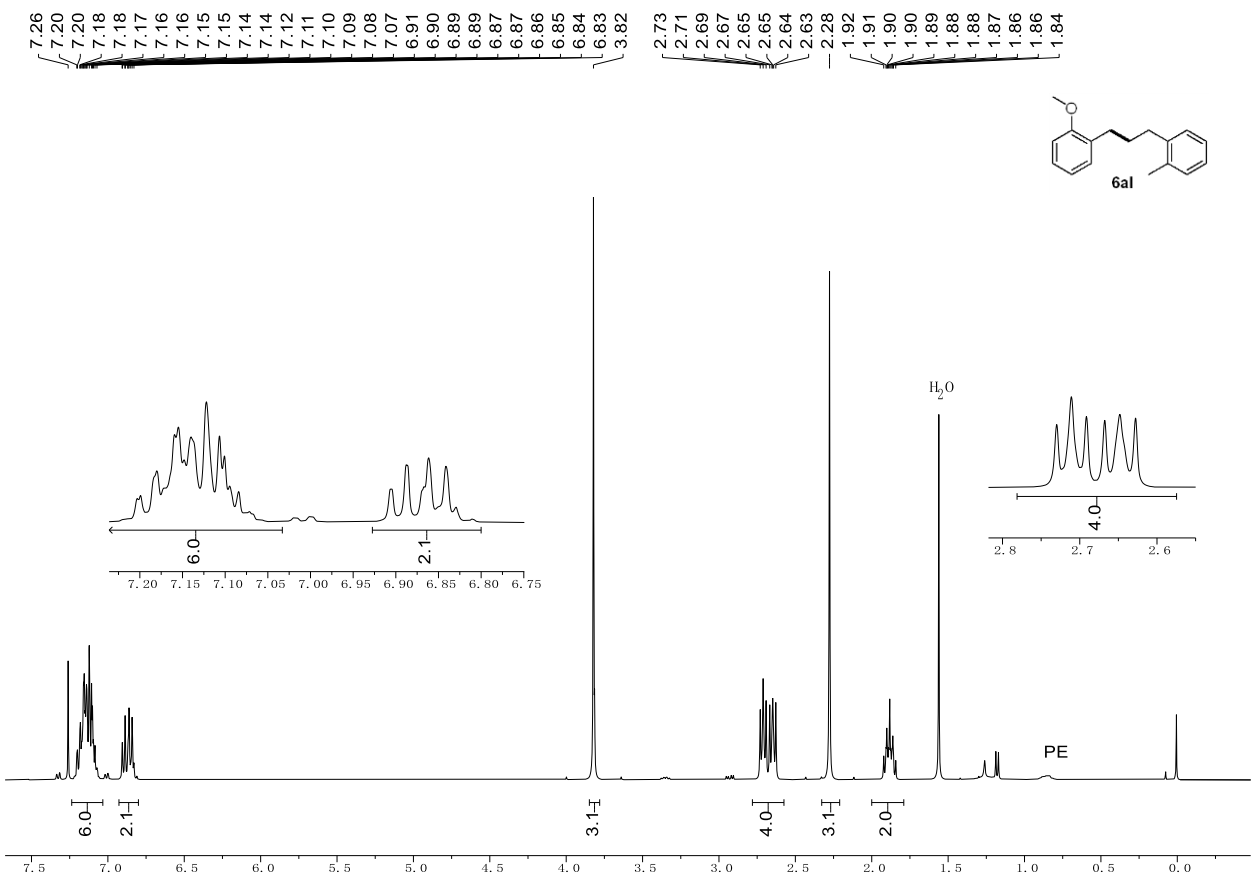

Figure S167. ^{1}H NMR spectrum (400 MHz) of **6al** in $CDCl_3$.

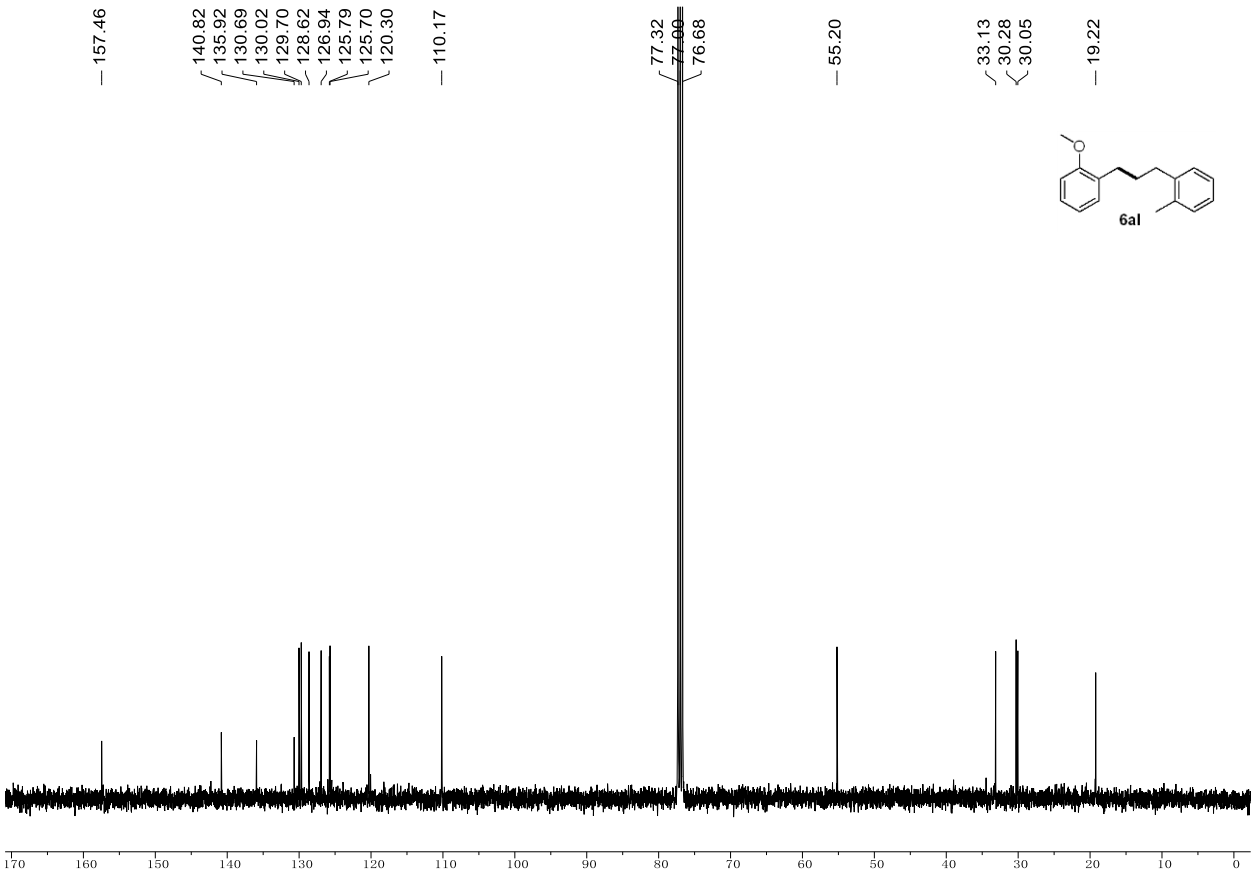

Figure S168. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6al** in $CDCl_3$.

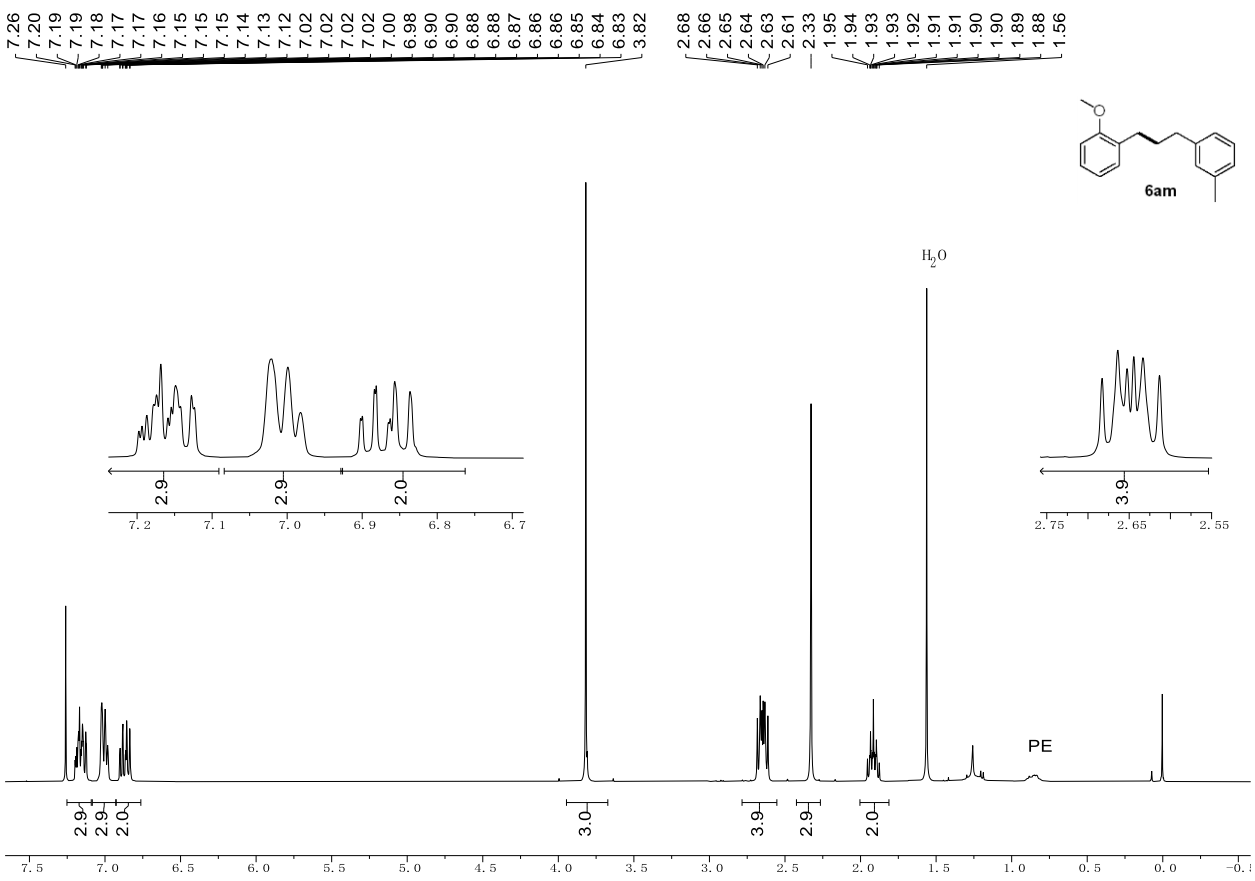

Figure S169. ^{1}H NMR spectrum (400 MHz) of **6am** in $CDCl_3$.

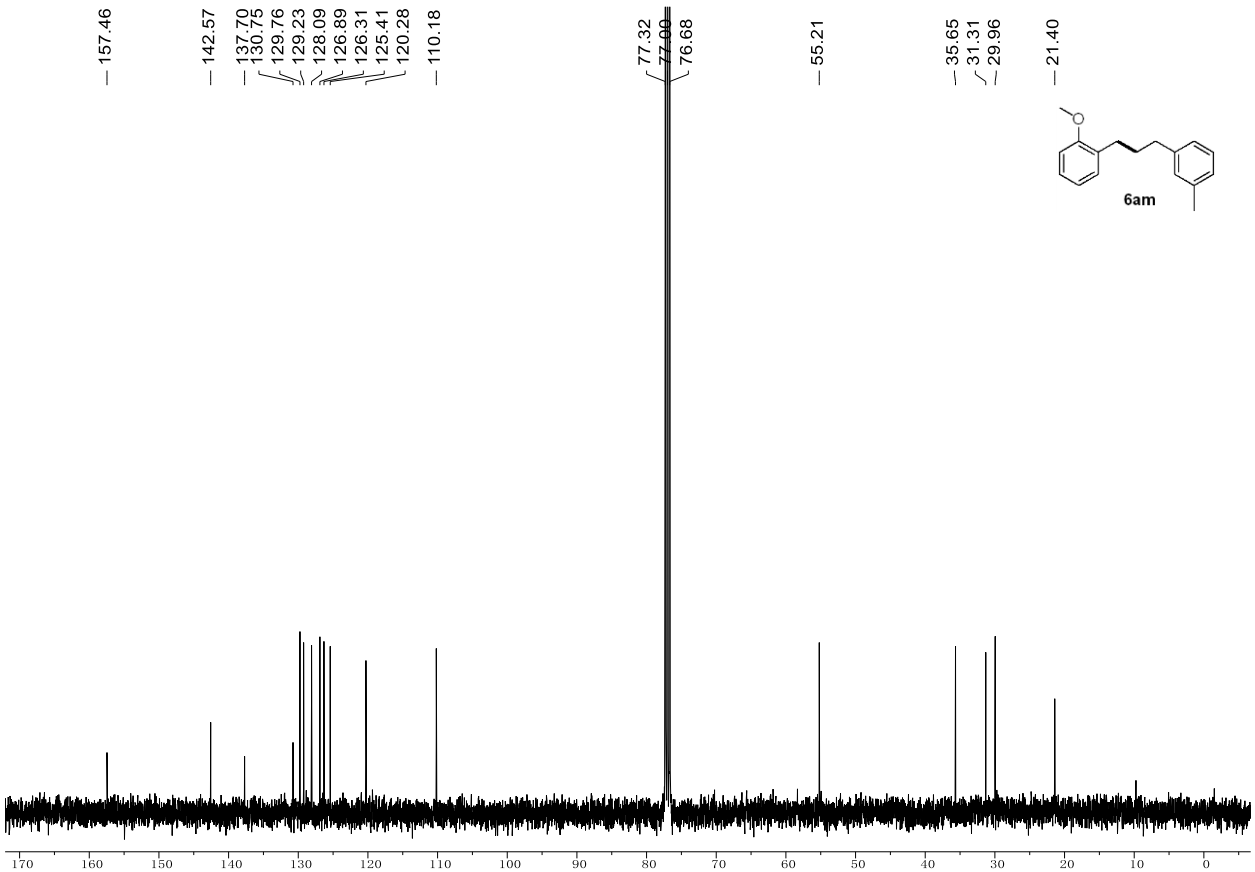

Figure S170. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6am** in $CDCl_3$.

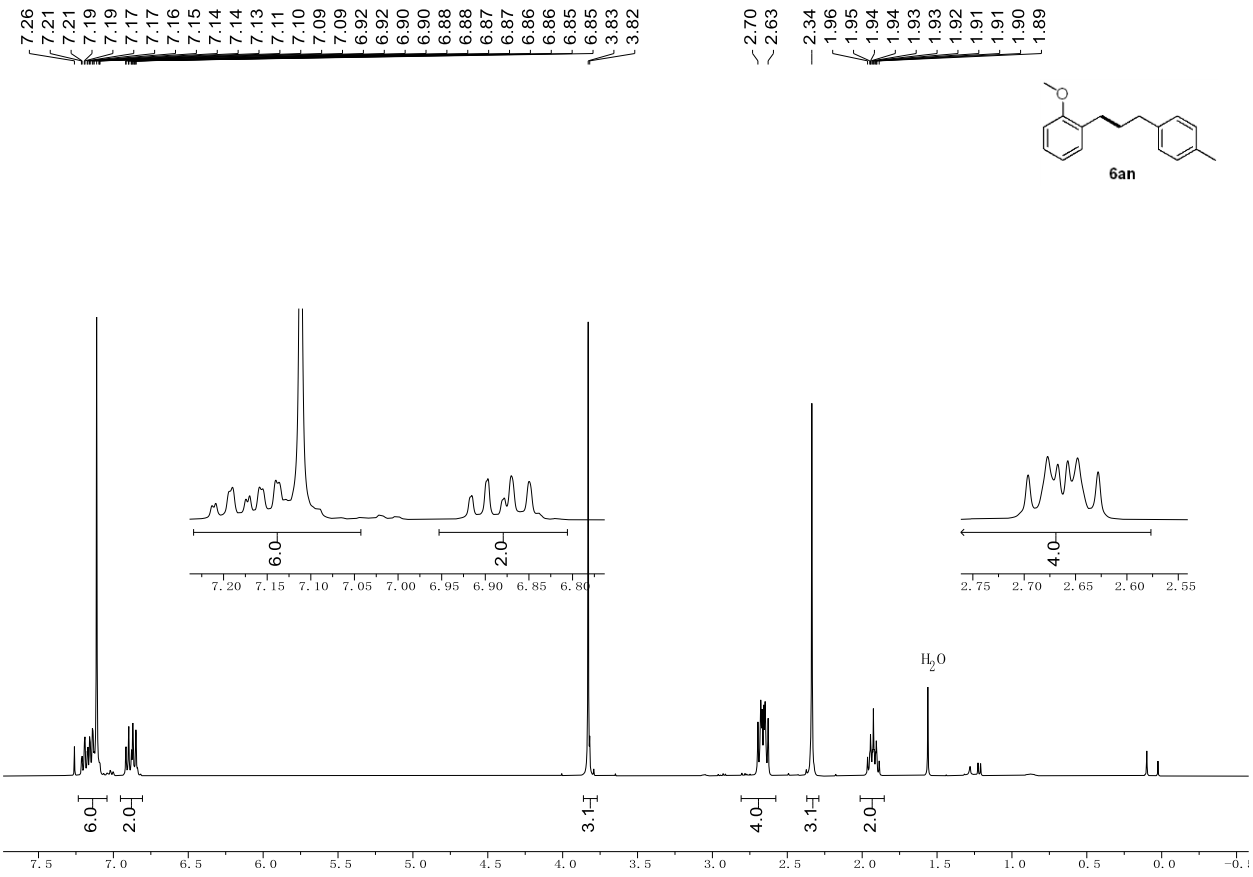

Figure S171. ^{1}H NMR spectrum (400 MHz) of **6an** in $CDCl_3$.

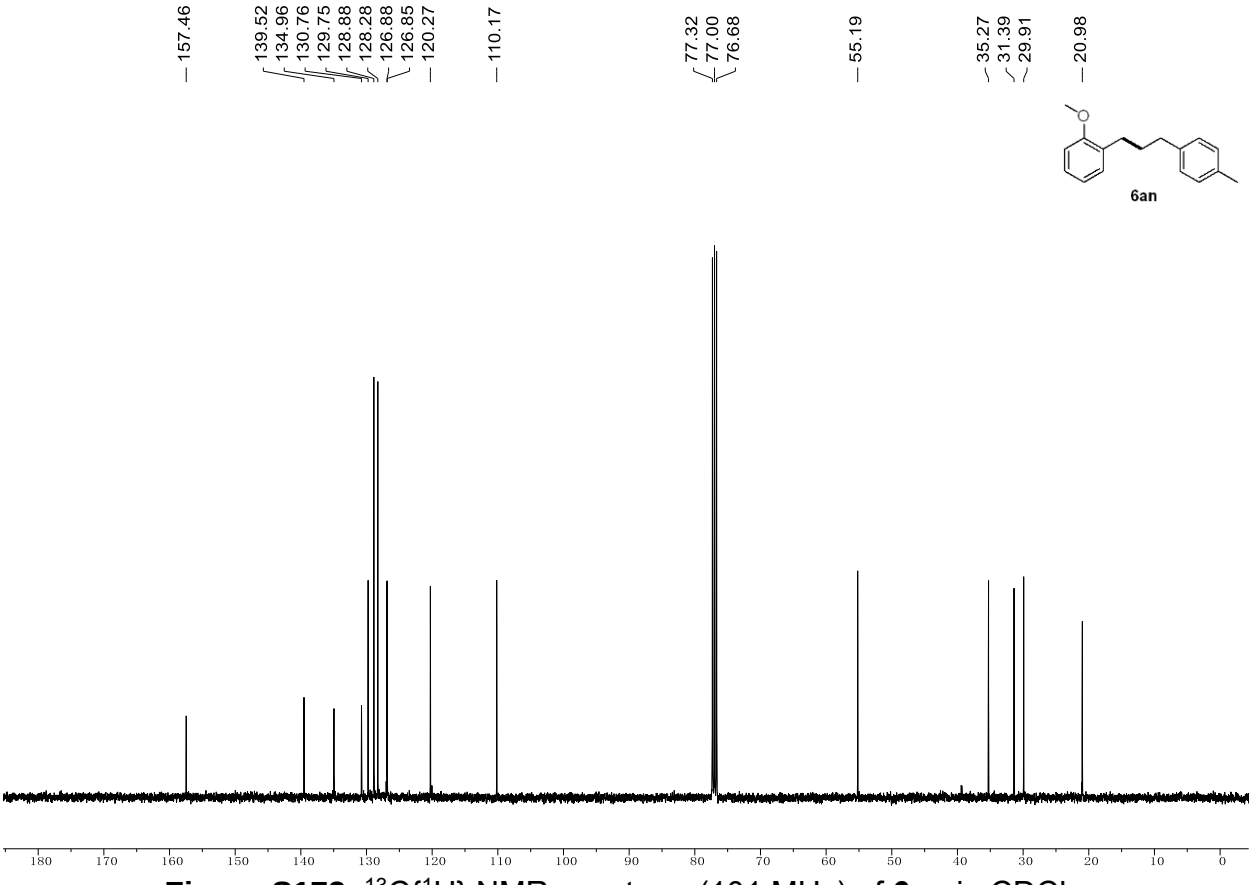

Figure S172. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6an** in $CDCl_3$.

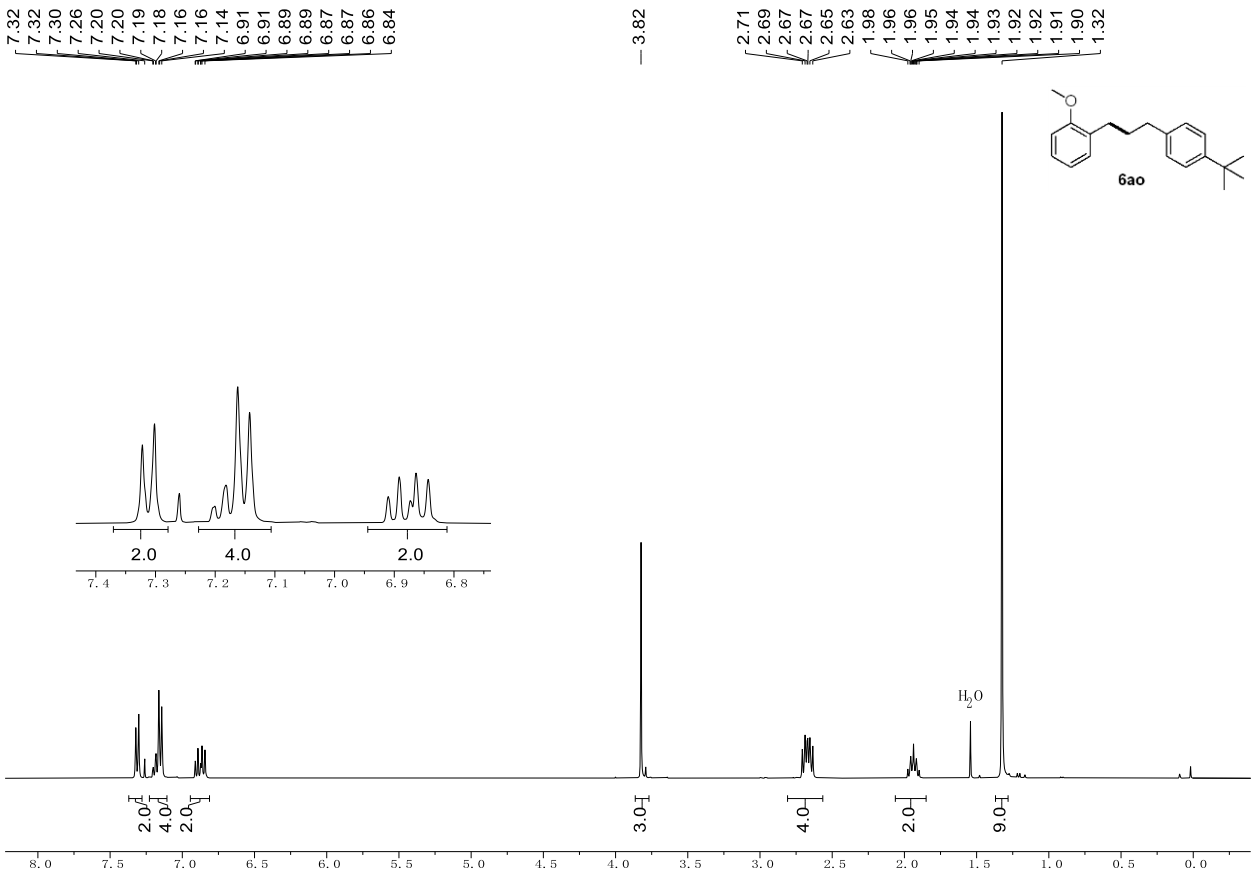

Figure S173. ^{1}H NMR spectrum (400 MHz) of **6ao** in $CDCl_3$.

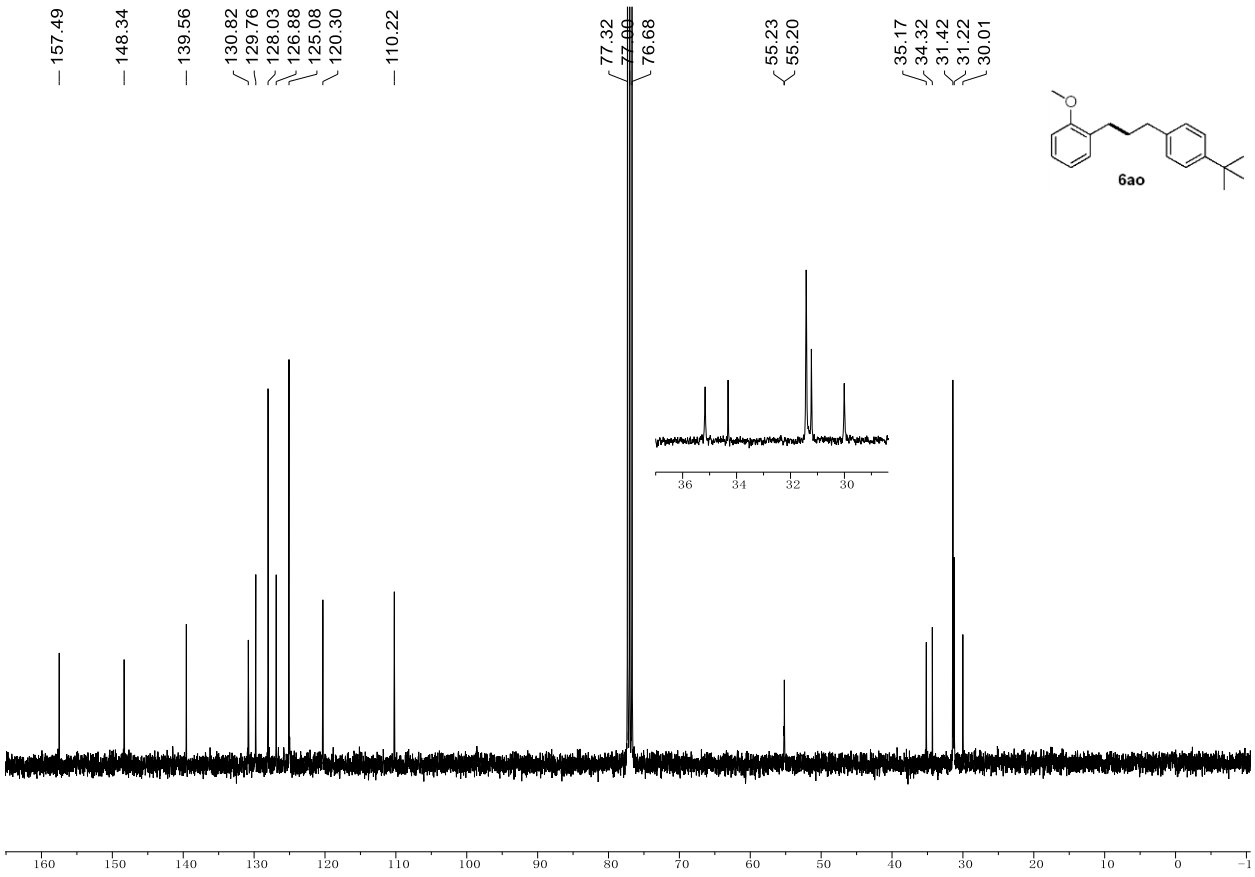

Figure S174. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6ao** in $CDCl_3$.

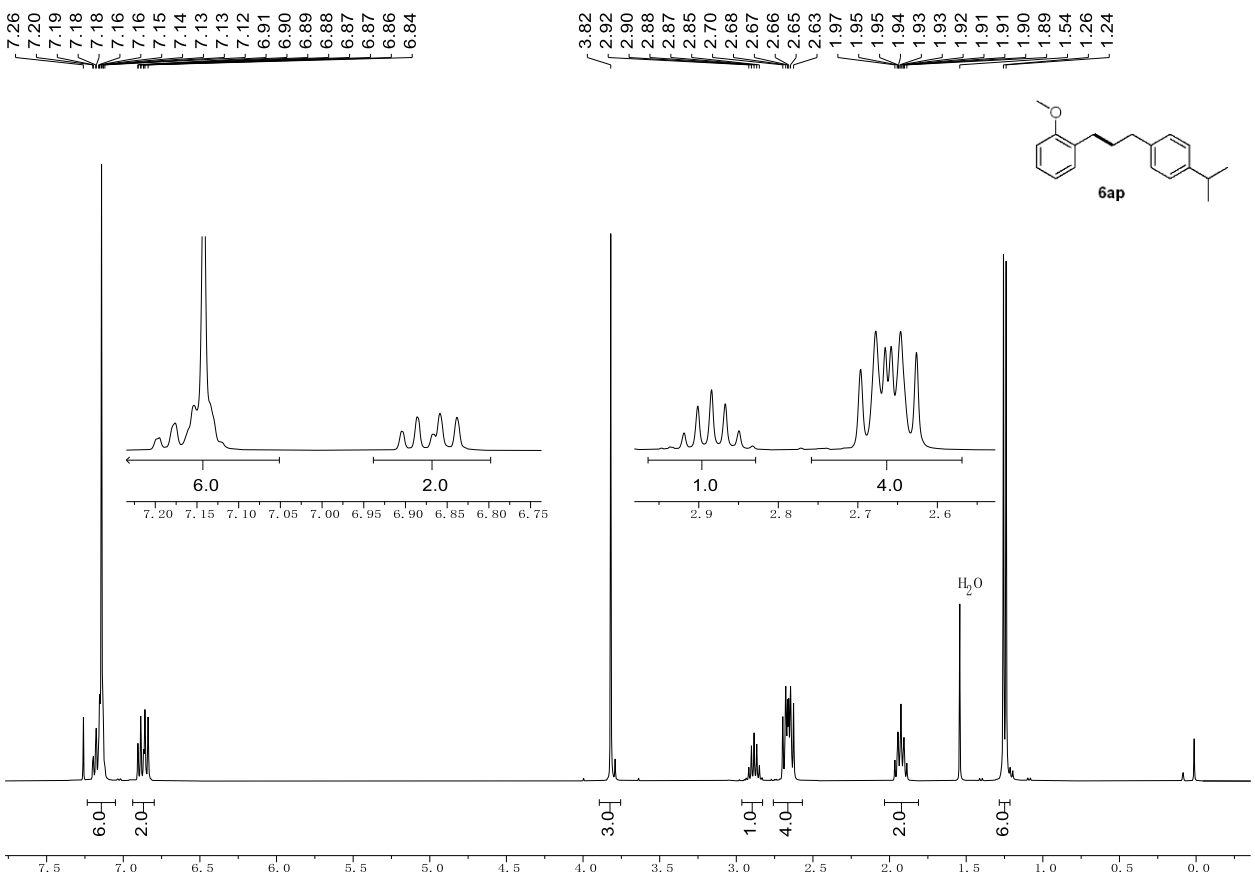

Figure S175. ^{1}H NMR spectrum (400 MHz) of **6ap** in $CDCl_3$.

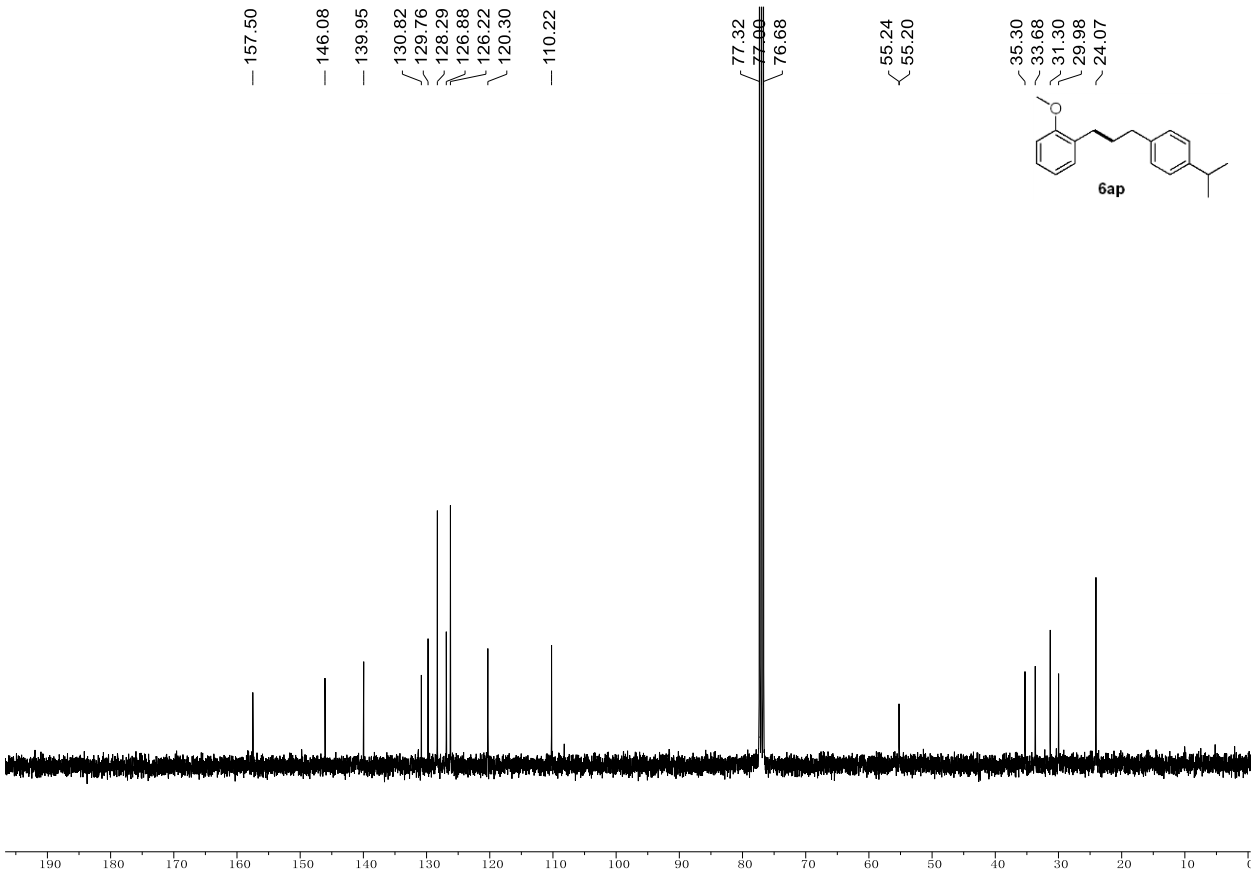

Figure S176. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6ap** in $CDCl_3$.

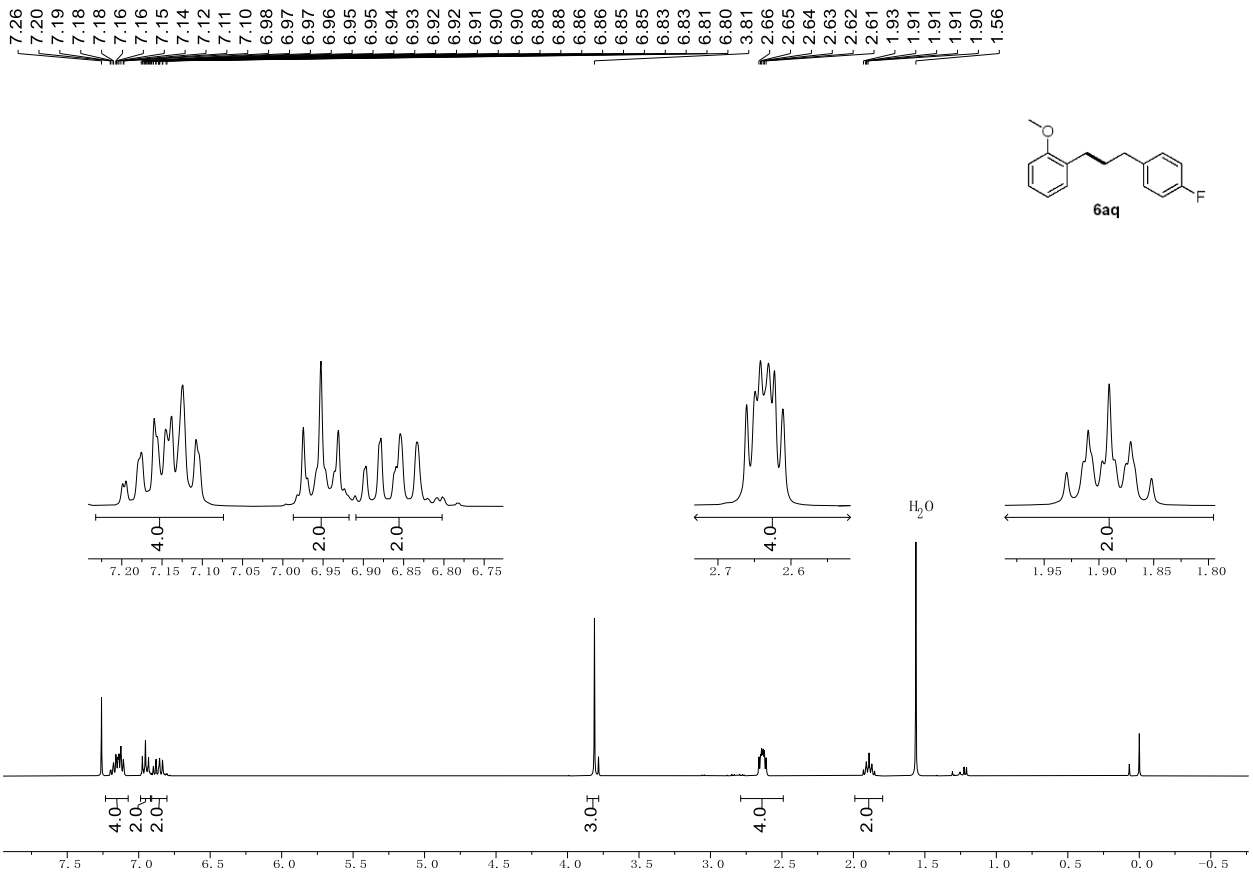

Figure S177. ^{1}H NMR spectrum (400 MHz) of **6aq** in $CDCl_3$.

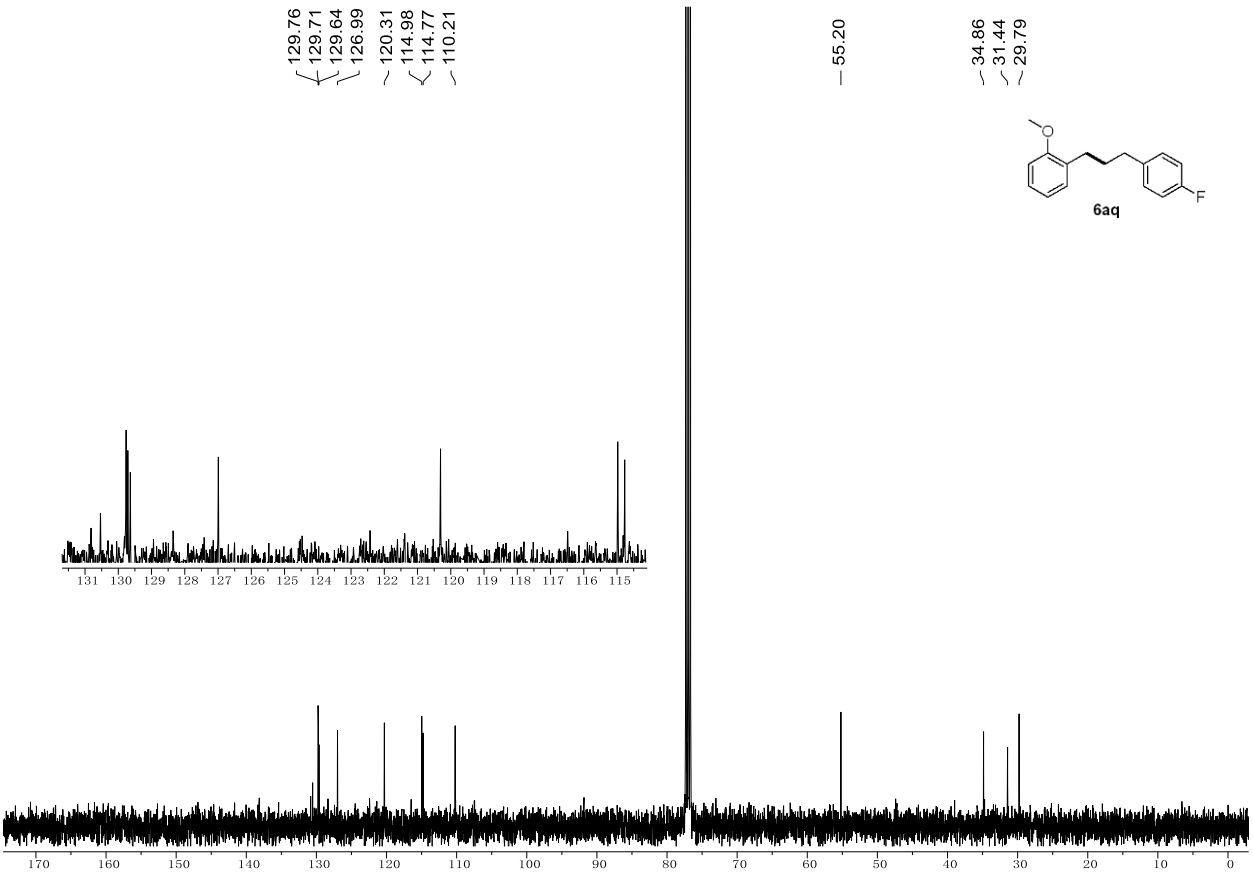

Figure S178. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6aq** in $CDCl_3$.

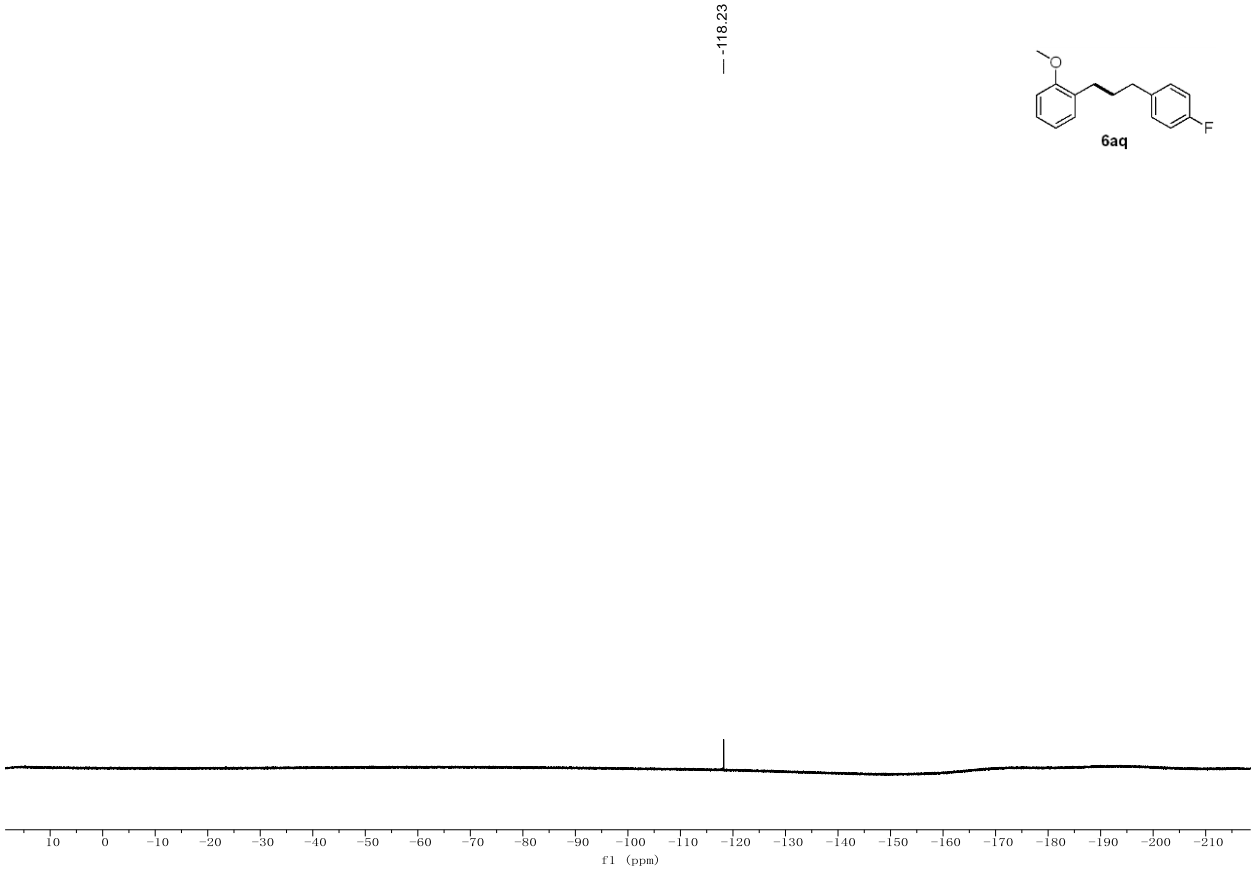

Figure S179. $^{19}F\{^{1}H\}$ NMR spectrum (377 MHz) of **6aq** in $CDCl_3$.

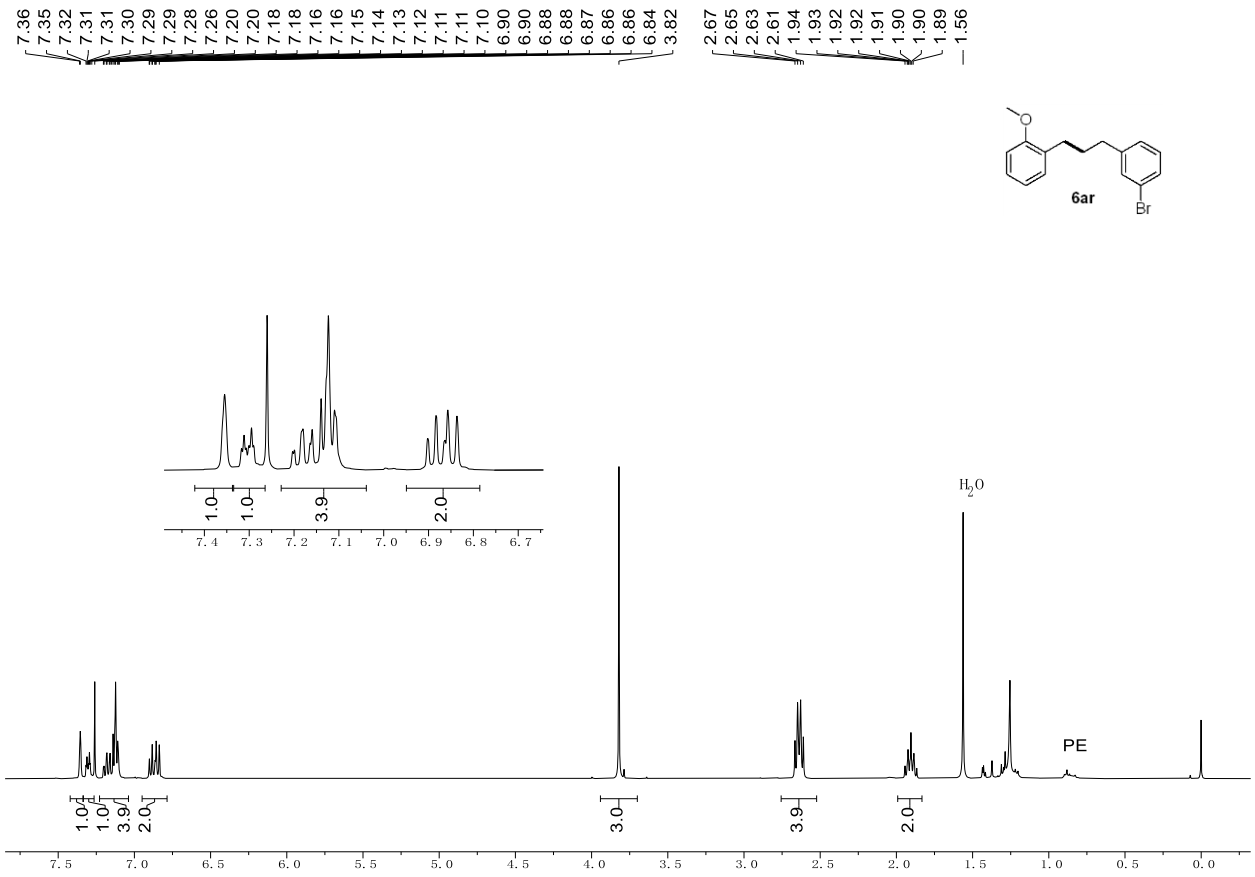

Figure S180. ^{1}H NMR spectrum (400 MHz) of **6ar** in $CDCl_3$.

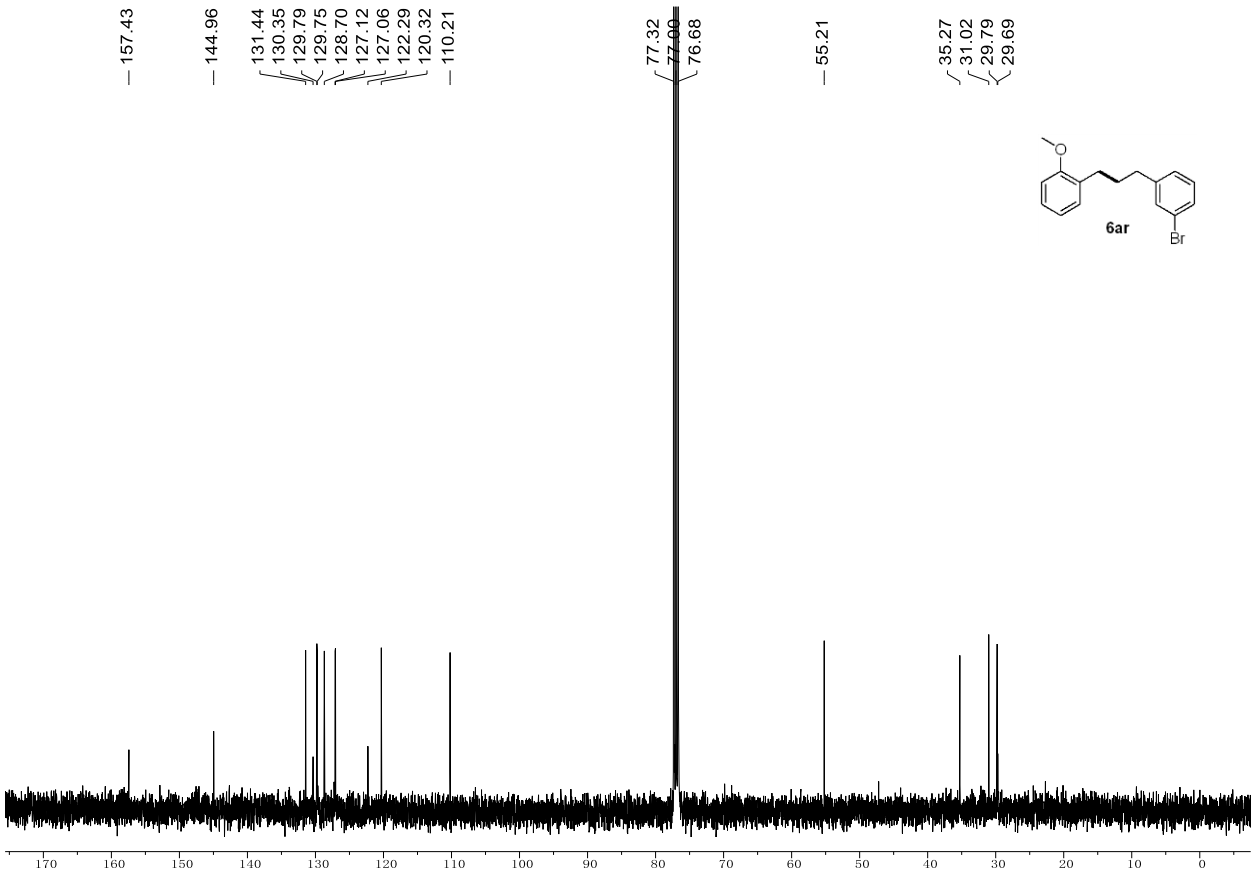

Figure S181. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6ar** in $CDCl_3$.

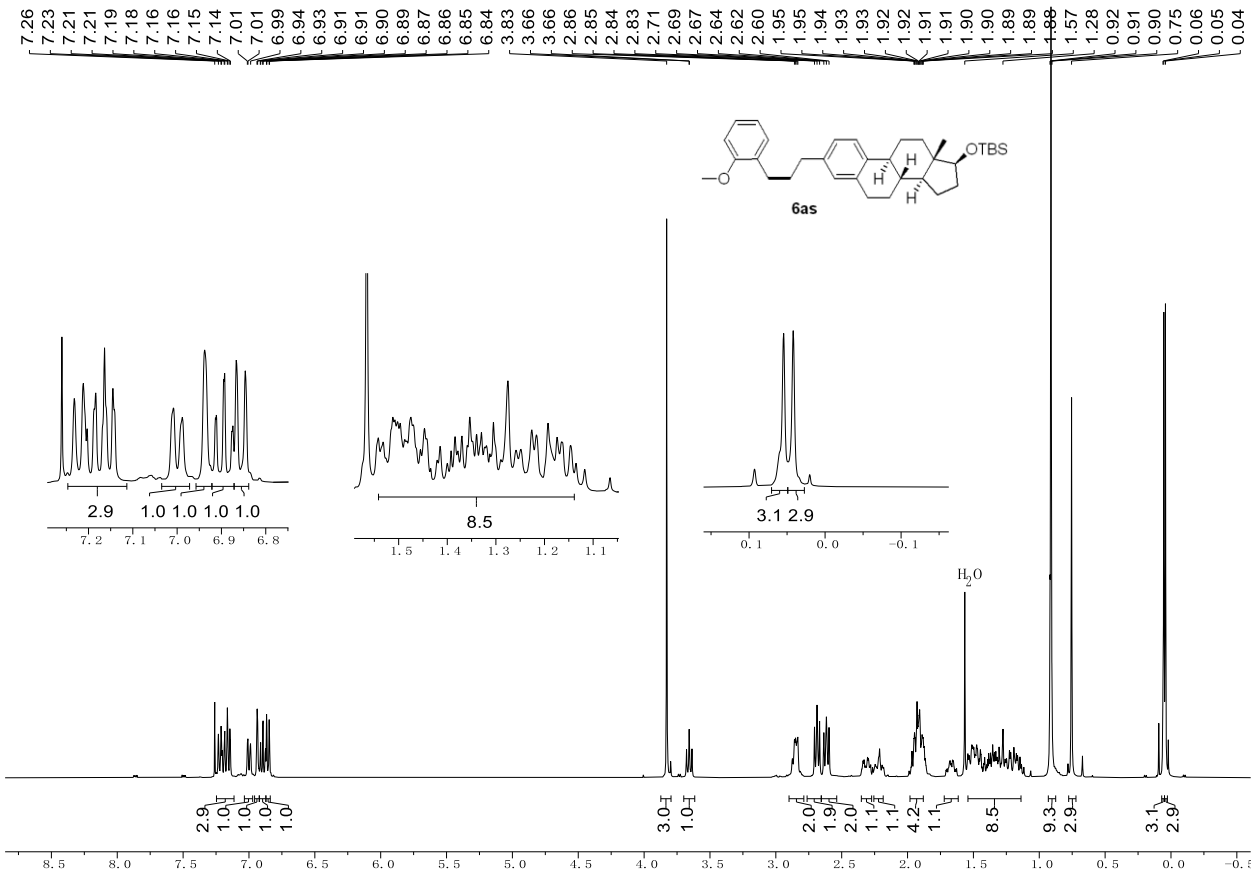

Figure S182. ^{1}H NMR spectrum (400 MHz) of **6as** in $CDCl_3$.

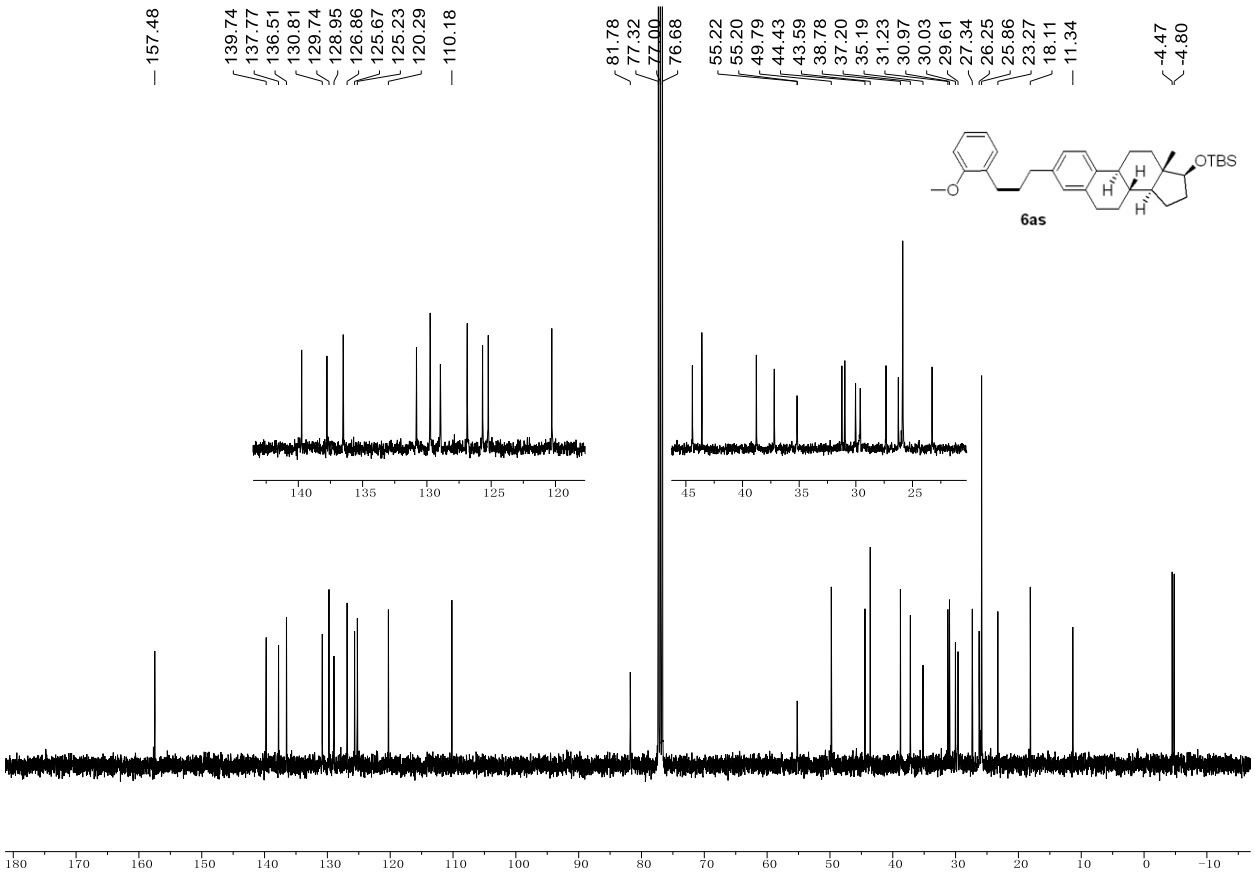

Figure S183. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **6as** in $CDCl_3$.

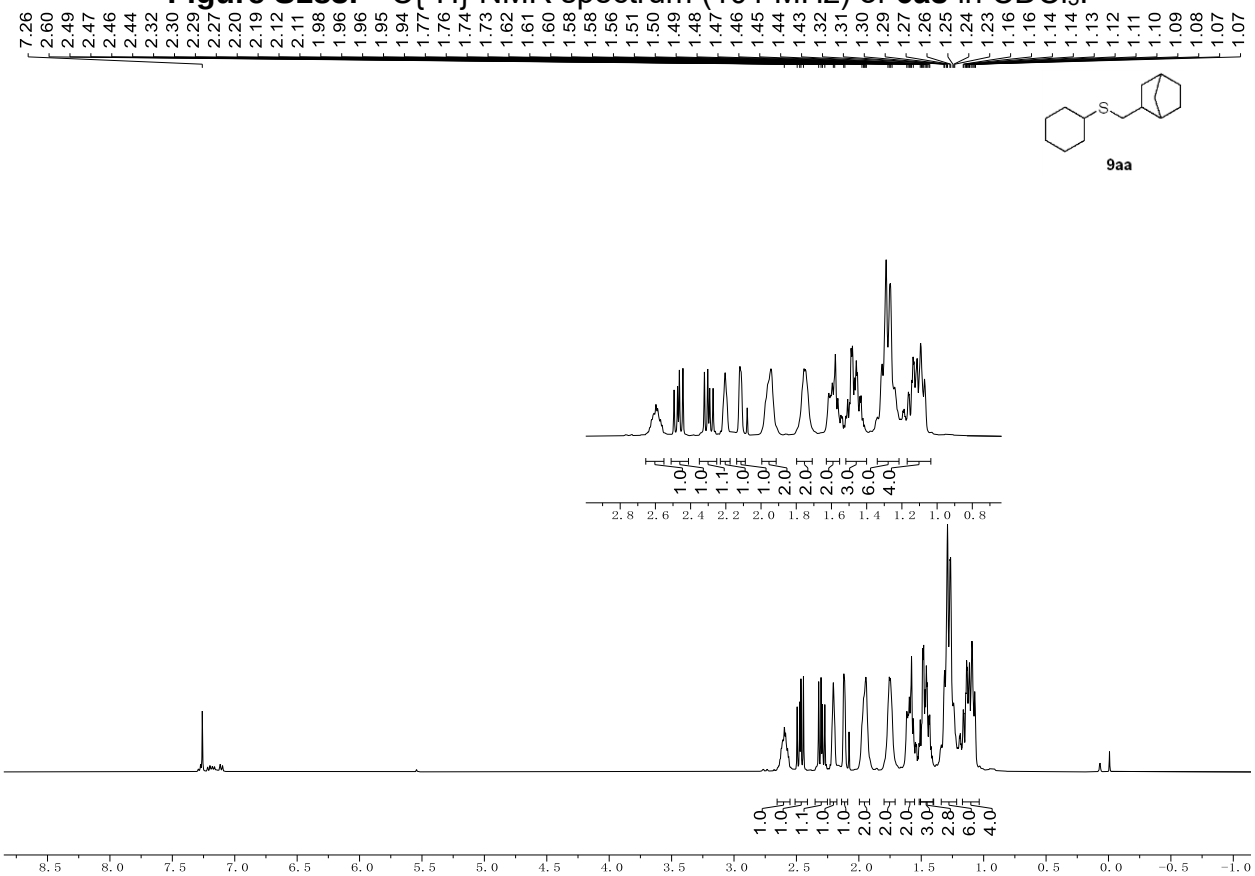

Figure S184. ^{1}H NMR spectrum (400 MHz) of **9aa** in $CDCl_3$.

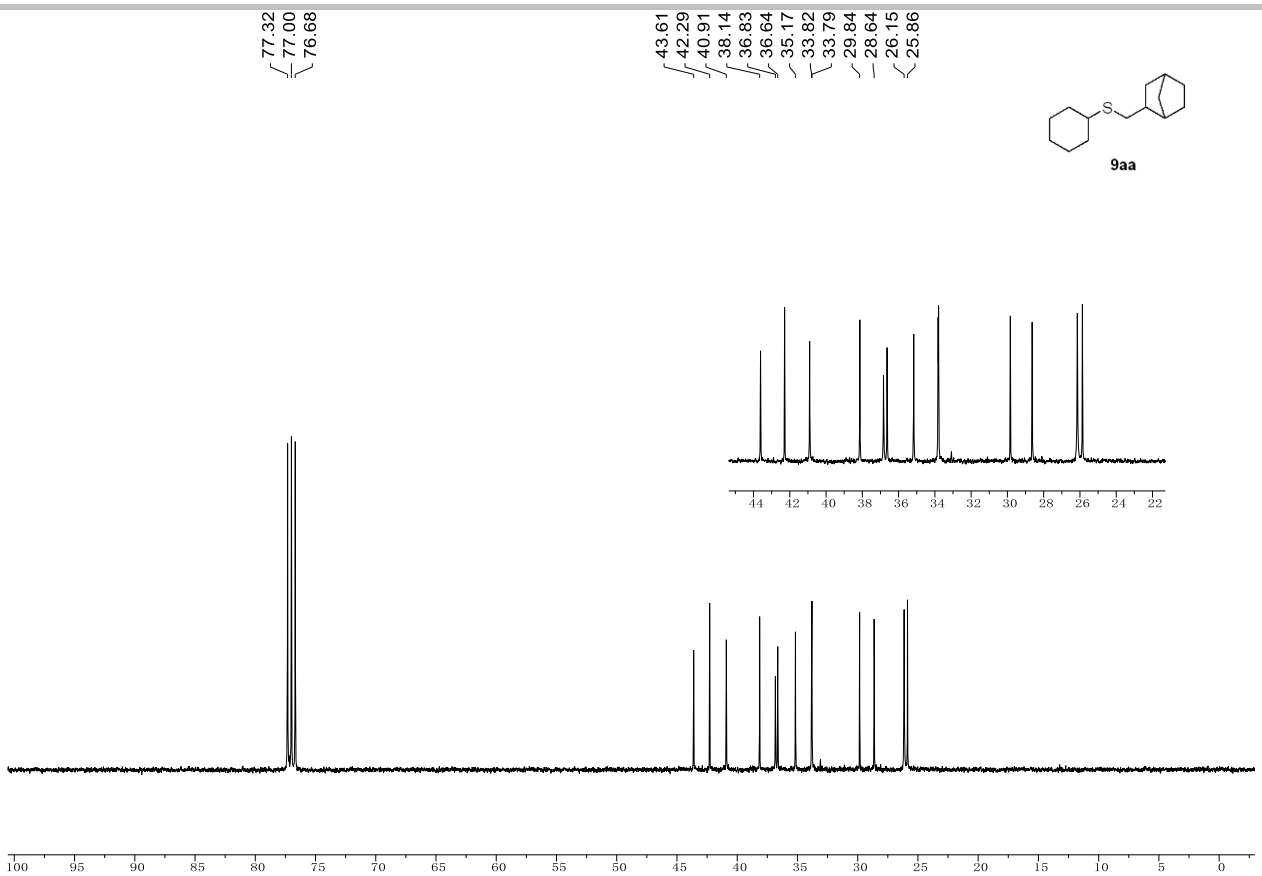

Figure S185. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **9aa** in $CDCl_3$.

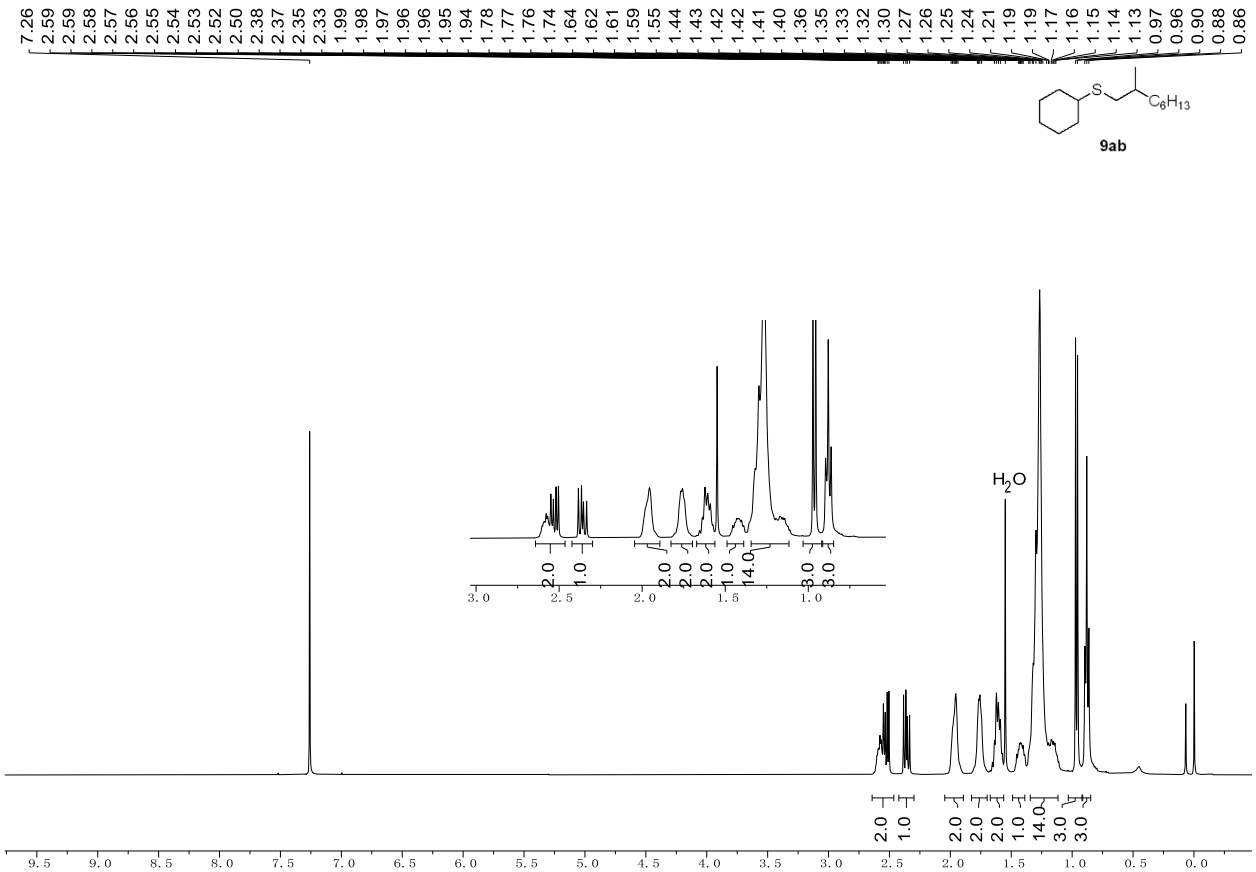

Figure S186. ^{1}H NMR spectrum (400 MHz) of **9ab** in $CDCl_3$.

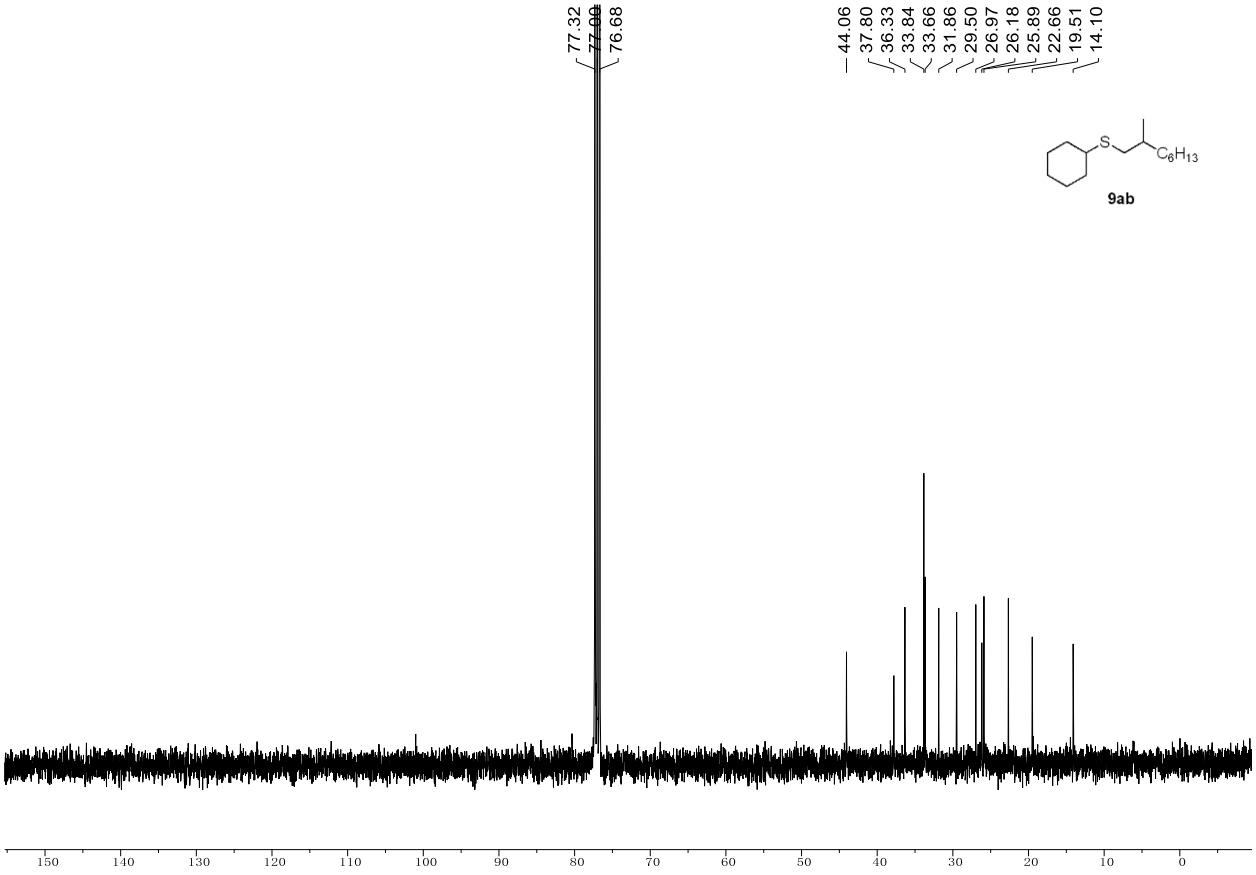

Figure S187. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **9ab** in $CDCl_3$.

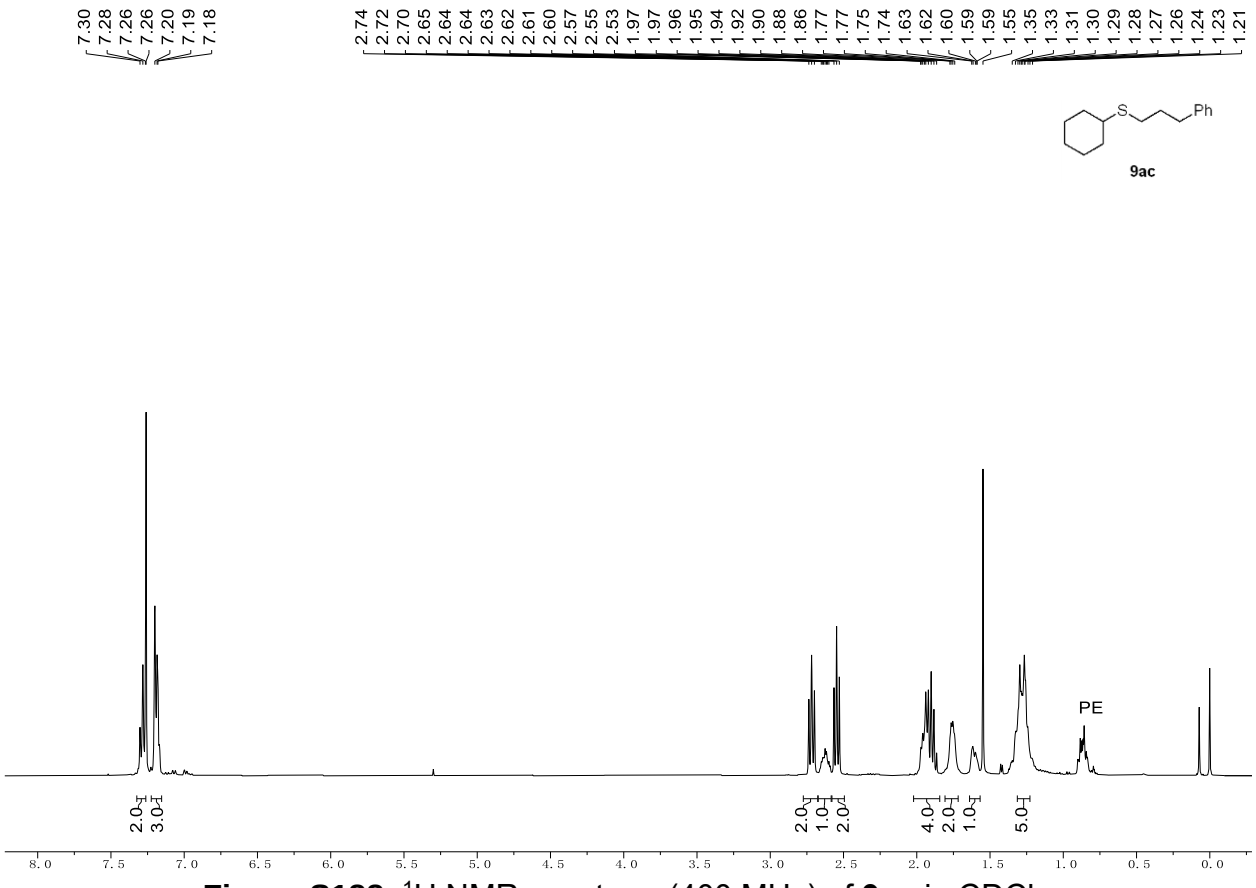

Figure S188. ^{1}H NMR spectrum (400 MHz) of **9ac** in $CDCl_3$.

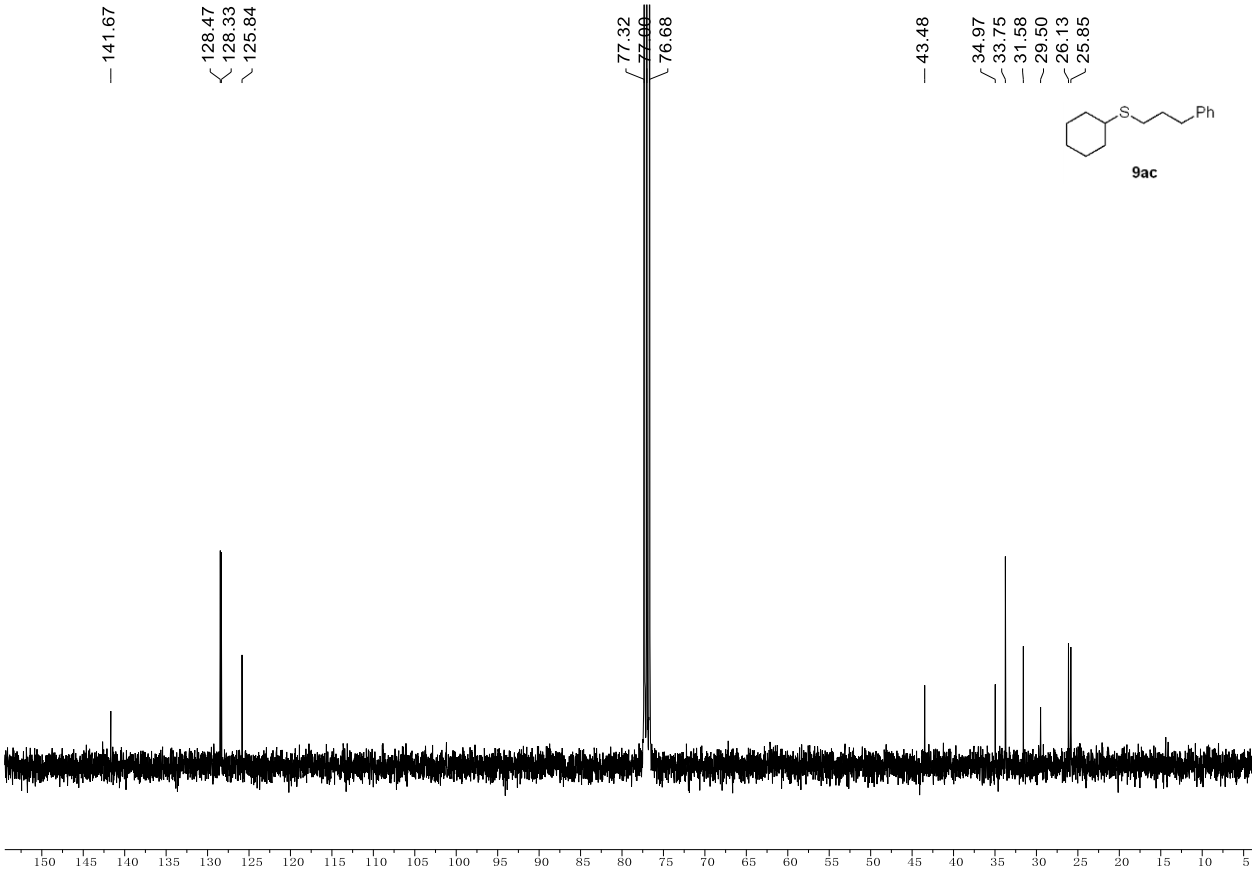

Figure S189. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **9ac** in $CDCl_3$.

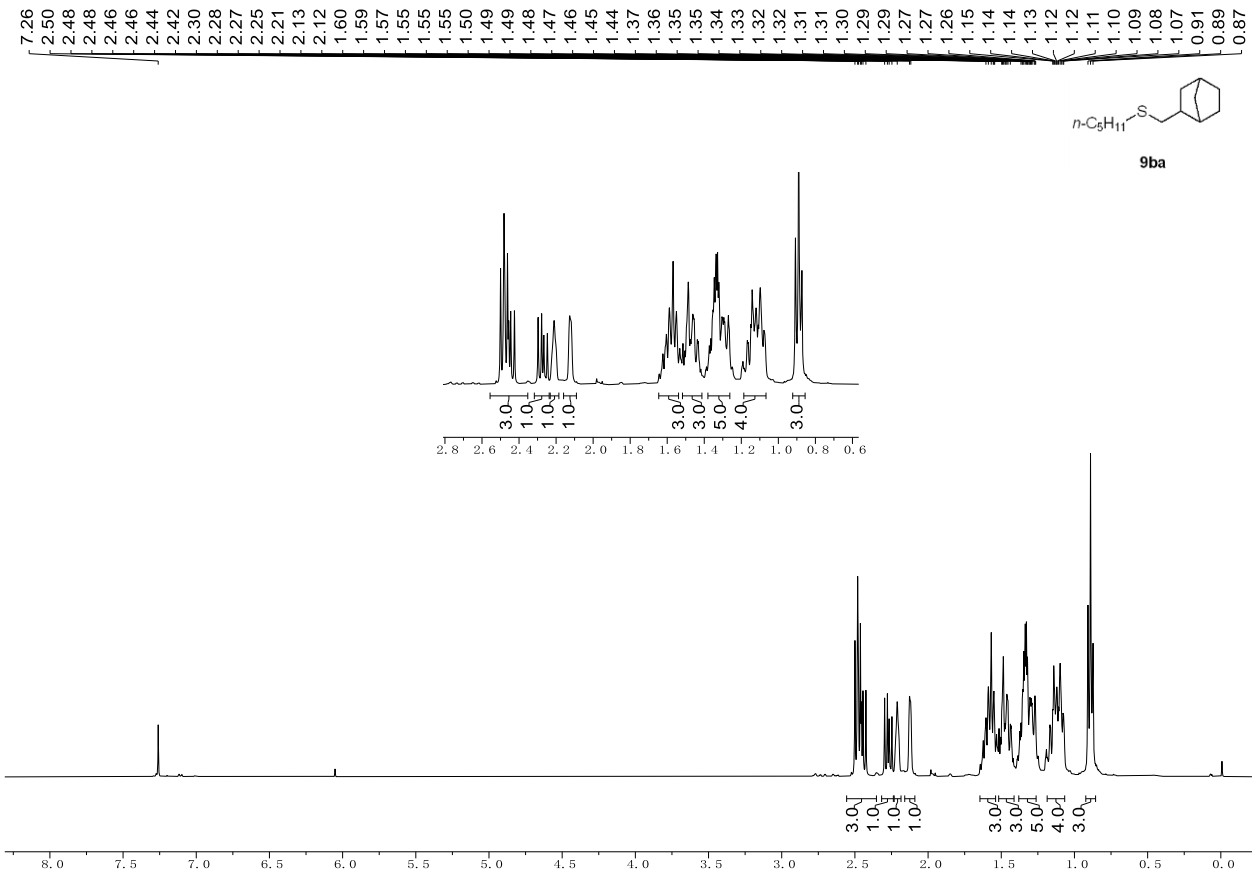

Figure S190. ^{1}H NMR spectrum (400 MHz) of **9ba** in $CDCl_3$.

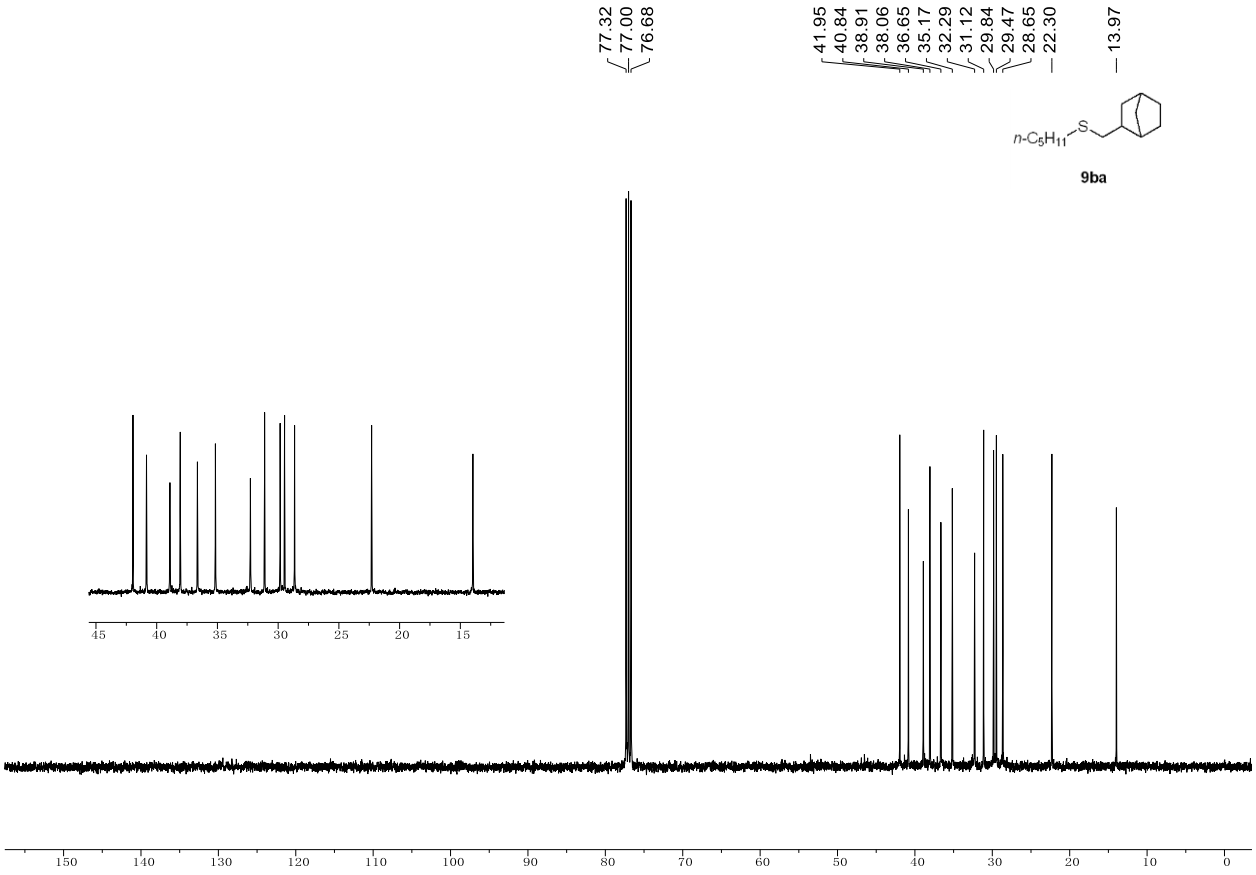

Figure S191. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz) of **9ba** in $CDCl_3$.