Supporting Information

Ni-catalyzed reductive cross-couplings of diaryl disulfides with aryl bromides for biaryl synthesis through C-S bond cleavage

Xuan-Qi Zhang,[a] Cai-Yu He,[a] Shuang-Feng Song,[a] Xue-Qiang Chu,[a] Hao Xu,*[,a] Xiaocong Zhou,*[a,b] Weidong Rao,[c] and Zhi-Liang Shen*[,a]

[a] Technical Institute of Fluorochemistry (TIF), School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, China. E-mail: xuhao@njtech.edu.cn, ias_zlshen@njtech.edu.cn

[b] College of Biological, Chemical Science and Engineering, Jiaxing University, 118 Jiahang Road, Jiaxing 314001, China. E-mail: xczhou@zjxu.edu.cn

[c] Jiangsu Provincial Key Lab for the Chemistry and Utilization of Agro-Forest Biomass, College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, China

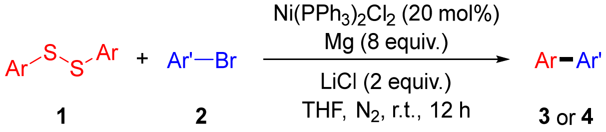
Table of Contents

General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Analytical thin layer chromatography (TLC) was performed using silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm). Flash chromatography was performed using Merck silica gel (200-300 mesh) for column chromatography with freshly distilled solvents. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Avance or Jeol 400 MHz spectrometers. Tetramethylsilane (TMS) served as internal standard for ^{1}H, ^{19}F, and ^{13}C NMR analysis. High resolution mass spectra (HRMS) were obtained on a Waters Q-TOF Premier Spectrometer (ESI or EI Source).

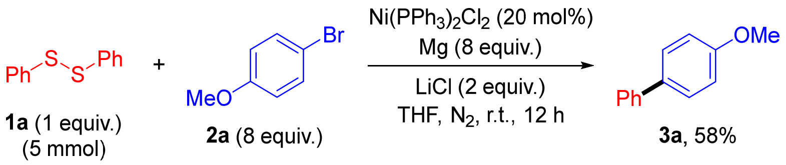
Experimental procedure

1. Typical procedure for the cross-coupling reactions of diaryl disulfides with aryl bromides.



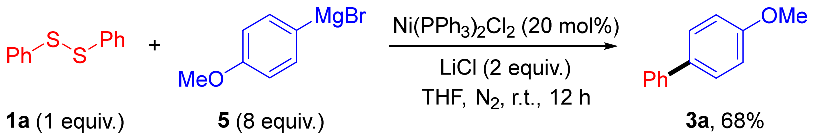
To an oven-dried Schlenk tube equipped with a magnetic stir bar was added magnesium turnings (97.2 mg, 4 mmol, 8 equiv.) and LiCl (42.3 mg, 1 mmol, 2 equiv.). Then the mixture was dried under reduced pressure with a heat gun (320 °C) for 3 min. After cooling down to room temperature, dry THF (2 mL) was added and the Schlenk tube was backfilled with nitrogen for three times. Then diaryl disulfide (0.5 mmol, 1 equiv.) and $Ni(PPh_3)_2Cl_2$ (65.4 mg, 0.1 mmol, 20 mol%) were added into the tube, followed by the addition of aryl bromide **2** (4 mmol, 8 equiv.). The reaction mixture was stirred at room temperature for 12 h before quenching with saturated NH_4Cl solution (2 mL) and water (20 mL) and extracting with EtOAc (20 mL x 3). The organic layers were combined, washed with brine, and dried over anhydrous Na_2SO_4. The extracts were concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to yield the product **3** or **4**.

2. Scale-up reaction.



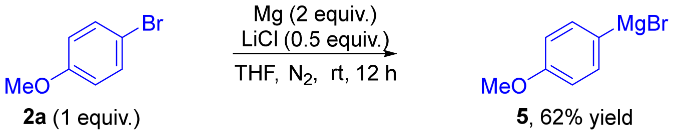
To an oven-dried Schlenk tube equipped with a magnetic stir bar was added magnesium turnings (0.9724 g, 40 mmol, 8 equiv.) and LiCl (0.4239 g, 10 mmol, 2 equiv.). Then the mixture was dried under reduced pressure with a heat gun (320 °C) for 3 min. After cooling down to room temperature, dry THF (10 mL) was added and the Schlenk tube was backfilled with nitrogen for three times. Then 1,2-diphenyldisulfane **1a** (1.09 g, 5 mmol, 1 equiv.) and $Ni(PPh_3)_2Cl_2$ (0.6542 g, 1 mmol, 20 mol%) were added into the tube, followed by the addition of 1-bromo-4-methoxybenzene **2a** (7.48 g, 40 mmol, 8 equiv.). The reaction mixture was stirred at room temperature for 12 h before quenching with saturated NH_4Cl solution (20 mL) and water (80 mL) and extracting with EtOAc (80 mL x 3). The organic layers were combined, washed with brine, and dried over Na_2SO_4. The extracts were concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to yield the product **3a** in 58% yield (1.06 g).

3. Direct cross-coupling using Grignard reagent 5 as substrate.



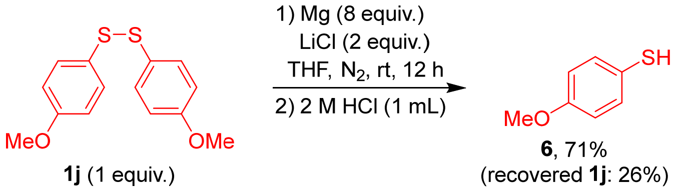
To a Schlenk tube equipped with a magnetic stir bar was added LiCl (42.3 mg, 1 mmol, 2 equiv.), which was dried under reduced pressure with a heat gun (320 °C) for 3 min. After cooling down, 1,2-diphenyldisulfane **1a** (109.2 mg, 0.5 mmol, 1 equiv.) and $Ni(PPh_3)_2Cl_2$ (65.4 mg, 0.1 mmol, 20 mol%) were added, and the Schlenk tube was backfilled with nitrogen for three times. Then arylmagnesium bromide **5** (8 mL, 4 mmol, 0.5 M in THF) was added into the tube by syringe. The reaction mixture was stirred at room temperature for 12 h before quenching with saturated NH_4Cl solution (2 mL) and water (20 mL) and extracting with EtOAc (20 mL x 3). The organic layers were combined, washed with brine, and dried over Na_2SO_4. The extracts were concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to yield the product **3a** in 68% yield (124.8 mg).

4. Formation of arylmagnesium reagent 5 via Mg insertion into 2a in the presence of LiCl



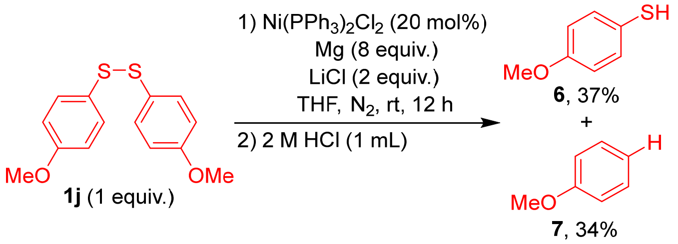
To an oven-dried Schlenk tube equipped with a magnetic stir bar was added magnesium turnings (48.6 mg, 2 mmol) and LiCl (21.2 mg, 0.5 mmol). Then the mixture was dried under reduced pressure with a heat gun (320 °C) for 3 min. After cooling down to room temperature, dry THF (2 mL) was added and the Schlenk tube was backfilled with nitrogen for three times. Then aryl bromide **2a** (187.0 mg, 1 mmol) was added into the tube. The reaction mixture was stirred at room temperature for 12 h. After that, the yield of the obtained arylmagnesium reagent was determined to be 62% by titrating with iodine (in anhydrous THF).

5. Reaction of 1j in the absence of aryl bromide and nickel catalyst



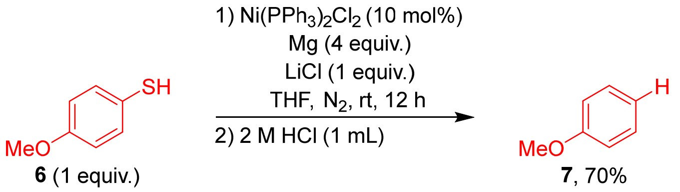
To an oven-dried Schlenk tube equipped with a magnetic stir bar was added magnesium turnings (97.2 mg, 4 mmol, 8 equiv.) and LiCl (42.3 mg, 1 mmol, 2 equiv.). Then the mixture was dried under reduced pressure with a heat gun (320 °C) for 3 min. After cooling down to room temperature, dry THF (2 mL) was added and the Schlenk tube was backfilled with nitrogen for three times. Then diaryl disulfide **1j** (139 mg, 0.5 mmol, 1 equiv.) was added into the tube. The reaction mixture was stirred at room temperature for 12 h before quenching with aqueous hydrochloric acid (2 mmol, 1 mL, 2 M in water) and water (20 mL) followed by extracting with EtOAc (20 mL x 3). The organic layers were combined, washed with brine, and dried over Na_2SO_4. The extracts were concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to give the product **6** in 71% yield (99.5 mg).

6. Reaction of 1j in the absence of aryl bromide



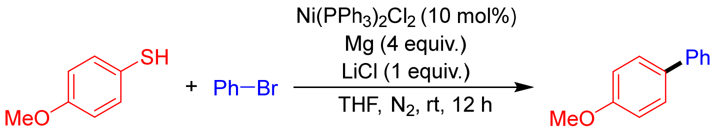
To an oven-dried Schlenk tube equipped with a magnetic stir bar was added magnesium turnings (97.2 mg, 4 mmol, 8 equiv.) and LiCl (42.3 mg, 1 mmol, 2 equiv.). Then the mixture was dried under reduced pressure with a heat gun (320 °C) for 3 min. After cooling down to room temperature, dry THF (2 mL) was added and the Schlenk tube was backfilled with nitrogen for three times. Then aryl disulfide **1j** (139 mg, 0.5 mmol, 1 equiv.) and $Ni(PPh_3)_2Cl_2$ (65.4 mg, 0.1 mmol, 20 mol%) were added into the tube. The reaction mixture was stirred at room temperature for 12 h before quenching with aqueous hydrochloric acid (2 mmol, 1 mL, 2 M in water) and water (20 mL) followed by extracting with EtOAc (20 mL x 3). The organic layers were combined, washed with brine, and dried over Na_2SO_4. The extracts were concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to the product **6** in 37% yield (51.8 mg) and product **7** in 34% yield (34.8 mg).

7. Reaction of benzenethiol 6 in the absence of aryl bromide



To an oven-dried Schlenk tube equipped with a magnetic stir bar was added magnesium turnings (48.6 mg, 2 mmol, 4 equiv.) and LiCl (21.2 mg, 0.5 mmol, 1 equiv.). Then the mixture was dried under reduced pressure with a heat gun (320 °C) for 3 min. After cooling down to room temperature, dry THF (2 mL) was added and the Schlenk tube was backfilled with nitrogen for three times. Then benzenethiol **6** (70.1 mg, 0.5 mmol, 1 equiv.) and $Ni(PPh_3)_2Cl_2$ (32.7 mg, 0.05 mmol, 10 mol%) were added into the tube. The reaction mixture was stirred at room temperature for 12 h before quenching with aqueous hydrochloric acid (2 mmol, 1 mL, 2 M in water) and water (20 mL) followed by extracting with EtOAc (20 mL x 3). The organic layers were combined, washed with brine, and dried over Na_2SO_4. The extracts were concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to the product **7** in 70% yield (37.8 mg).

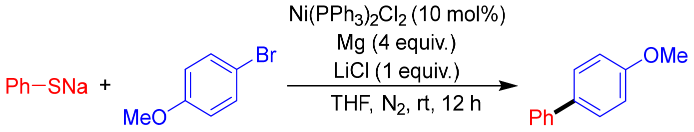
8. Cross-coupling of benzenethiol 6 with 2t



6 (1 equiv.) **2t** (4 equiv.) **3a**, 55% yield

To an oven-dried Schlenk tube equipped with a magnetic stir bar was added magnesium turnings (48.6 mg, 2 mmol, 4 equiv.) and LiCl (21.2 mg, 0.5 mmol, 1 equiv.). Then the mixture was dried under reduced pressure with a heat gun (320 °C) for 3 min. After cooling down to room temperature, dry THF (2 mL) was added and the Schlenk tube was backfilled with nitrogen for three times. Then benzenethiol **6** (70.1 mg, 0.5 mmol, 1 equiv.) and $Ni(PPh_3)_2Cl_2$ (32.7 mg, 0.05 mmol, 10 mol%) were added into the tube, followed by the addition of aryl bromide **2t** (314 mg, 2 mmol, 4 equiv.). The reaction mixture was stirred at room temperature for 12 h before quenching with saturated NH_4Cl solution (2 mL) and water (20 mL) and extracting with EtOAc (20 mL x 3). The organic layers were combined, washed with brine, and dried over anhydrous Na_2SO_4. The extracts were concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to yield the product **3a** in 55% yield (50.7 mg).

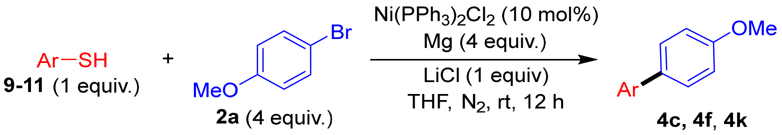
9. Cross-coupling of sodium thiophenolate 8 with 2a



8 (1 equiv.) **2a** (4 equiv.) **3a**, 61% yield

To an oven-dried Schlenk tube equipped with a magnetic stir bar was added magnesium turnings (48.6 mg, 2 mmol, 4 equiv.) and LiCl (21.2 mg, 0.5 mmol, 1 equiv.). Then the mixture was dried under reduced pressure with a heat gun (320 °C) for 3 min. After cooling down to room temperature, dry THF (2 mL) was added and the Schlenk tube was backfilled with nitrogen for three times. Then sodium thiophenolate **8** (66.1 mg, 0.5 mmol, 1 equiv.) and $Ni(PPh_3)_2Cl_2$ (32.7 mg, 0.05 mmol, 10 mol%) were added into the tube, followed by the addition of aryl bromide **2a** (374.1 mg, 2 mmol, 4 equiv.). The reaction mixture was stirred at room temperature for 12 h before quenching with saturated NH_4Cl solution (2 mL) and water (20 mL) and extracting with EtOAc (20 mL x 3). The organic layers were combined, washed with brine, and dried over anhydrous Na_2SO_4. The extracts were concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to yield the product **3a** in 61% yield (55.9 mg).

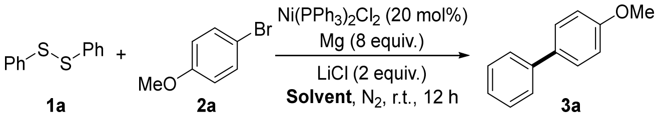
10. Cross-coupling of aryl thiols 9-11 with 2a



To an oven-dried Schlenk tube equipped with a magnetic stir bar was added magnesium turnings (48.6 mg, 2 mmol, 4 equiv.) and LiCl (21.2 mg, 0.5 mmol, 1 equiv.). Then the mixture was dried under reduced pressure with a heat gun (320 °C) for 3 min. After cooling down to room temperature, dry THF (2 mL) was added and the Schlenk tube was backfilled with nitrogen for three times. Then aryl thiols **9-11** (0.5 mmol, 1 equiv.) and $Ni(PPh_3)_2Cl_2$ (32.7 mg, 0.05 mmol, 10 mol%) were added into the tube, followed by the addition of aryl bromide **2a** (374.0 mg, 2 mmol, 4 equiv.). The reaction mixture was stirred at room temperature for 12 h before quenching with saturated NH_4Cl solution (2 mL) and water (20 mL) and extracting with EtOAc (20 mL x 3). The organic layers were combined, washed with brine, and dried over anhydrous Na_2SO_4. The extracts were concentrated under reduced pressure to afford the crude product, which was further purified through silica gel column chromatography (using EtOAc/petroleum ether as eluents) to yield the product **4** (**4c**: 52.4 mg, 52% yield; **4f**: 72 mg, 73% yield; **4k**: 76 mg, 65% yield).

Optimization of reaction conditions

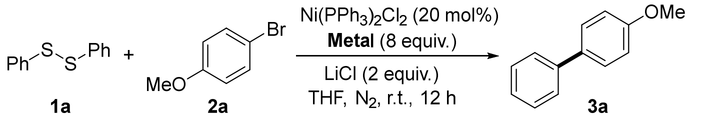
Table S1. Optimization of reaction conditions by using different solvents[a]



Entry	Solvent	Yield (%)[b]
1	**THF**	**80 (77)**[c]
2	DME	0
3	1,4-dioxane	0
4	2-MeTHF	0
5	^{t}BuOMe	0
6	DMA	0
7	^{i}Pr$_2$O	0
8	tetrahydropyran	0
9	DMF	0

[a] Conditions: 1,2-diphenyldisulfane **1a** (0.5 mmol, 1 equiv.), 1-bromo-4-methoxybenzene **2a** (4 mmol), $Ni(PPh_3)_2Cl_2$ (20 mol%, 0.1 mmol), magnesium turnings (4 mmol), LiCl (1 mmol), solvent (2 mL), room temperature, 12 h, nitrogen atmosphere. [b] NMR yield. [c] Isolated yield.

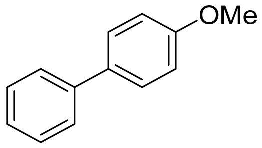
Table S2. Optimization of reaction conditions by using different metals[a]



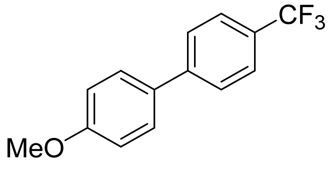
Entry	Metal	Yield (%)[b]
1	**Mg**	**80 (77)**[c]
2	Fe	<5
3	Mn	<5
4	Zn	<5
5	Al	<5
6	Pb	<5
7	Bi	<5
8	In	<5

[a] Conditions: 1,2-diphenyldisulfane **1a** (0.5 mmol, 1 equiv.), 1-bromo-4-methoxybenzene **2a** (4 mmol), $Ni(PPh_3)_2Cl_2$ (20 mol%, 0.1 mmol), metal (4 mmol), LiCl (1 mmol), THF (2 mL), room temperature, 12 h, nitrogen atmosphere. [b] NMR yield. [c] Isolated yield.

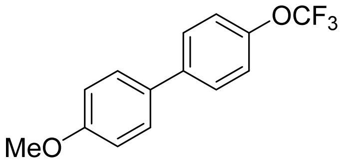
Characterization data of products



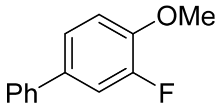
4-Methoxy-1,1'-biphenyl (3a)[1]: 141.8 mg, 77% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 7.67–7.53 (m, 4H), 7.51–7.42 (m, 2H), 7.39–7.31 (m, 1H), 7.07–6.98 (m, 2H), 3.88 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*)**: δ 159.1, 140.7, 133.7, 128.7, 128.1, 126.7, 126.6, 114.1, 55.3 ppm. **IR (KBr, neat):** ν = 2360, 2341, 1844, 1653, 1559, 1540, 1507, 1457, 1089, 803, 668 cm^{-1}. **HRMS (m/z):** calcd for $C_{13}H_{13}O$ $[M+H]^+$ 185.0961, found: 185.0965.



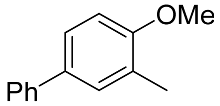
4-Methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (3b)[1]: 123.5 mg, 49% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 7.49–7.42 (m, 4H), 7.16–7.11 (m, 2H), 6.98–6.94 (m, 2H), 3.85 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*)**: δ 160.6, 144.8, 136.7, 127.3 (q, J = 32.3 Hz), 126.3, 125.6 (q, J = 3.6 Hz), 125.5 (q, J = 270.3 Hz), 121.6, 115.4, 55.4 ppm. **^{19}F NMR (376 MHz, Chloroform-*d*):** δ -62.23 (s, 3F) ppm. **IR (KBr, neat):** ν = 3649, 2977, 1922, 1603, 1494, 1329, 1112, 831, 742, 532 cm^{-1}. **HRMS (m/z):** calcd for $C_{14}H_{12}F_3O$ $[M+H]^+$ 253.0835, found: 253.0832.



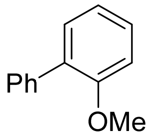
4-Methoxy-4'-(trifluoromethoxy)-1,1'-biphenyl (3c)[1]: 152.7 mg, 57% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 7.58–7.53 (m, 2H), 7.52–7.48 (m, 2H), 7.29–7.24 (m, 2H), 7.02–6.97 (m, 2H), 3.86 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*)**: δ 159.4, 148.2, 139.6, 132.3, 128.1, 127.9, 121.8 (q, J = 255.3 Hz), 121.2, 114.3, 55.3 ppm. **^{19}F NMR (376 MHz, Chloroform-*d*)**: δ -57.82 (s, 3F) ppm. **IR (KBr, neat):** ν = 2967, 1608, 1499, 1291, 1157, 1035, 828, 715, 508 cm^{-1}. **HRMS (m/z):** calcd for $C_{14}H_{12}F_3O_2$ [M+H]$^+$ 269.0784, found: 269.0784.



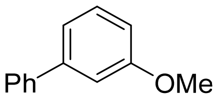
3-Fluoro-4-methoxy-1,1'-biphenyl (3d)[1]: 103.0 mg, 51% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.58–7.51 (m, 2H), 7.43 (dd, J = 8.5, 6.9 Hz, 2H), 7.37–7.29 (m, 3H), 7.03 (t, J = 8.7 Hz, 1H), 3.94 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** δ 153.7 (d, J = 243.5 Hz), 147.0 (d, J = 10.8 Hz), 139.7 (d, J = 2.2 Hz), 134.4 (d, J = 6.5 Hz), 128.8, 127.2, 126.6, 122.6 (d, J = 3.4 Hz), 114.8 (d, J = 18.8 Hz), 113.6 (d, J = 2.5 Hz), 56.3 ppm. **^{19}F NMR (376 MHz, Chloroform-*d*)**: δ -135.25 (s, 1F) ppm. **IR (KBr, neat):** ν = 2927, 1608, 1506, 1463, 1282, 1136, 1042, 806, 763, 561 cm^{-1}. **HRMS (m/z):** calcd for $C_{13}H_{12}FO$ [M+H]$^+$ 203.0867, found: 203.0864.



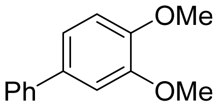
4-Methoxy-3-methyl-1,1'-biphenyl (3e)[1]: 145.2 mg, 73% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 7.75–7.66 (m, 2H), 7.59–7.50 (m, 4H), 7.47–7.39 (m, 1H), 7.00 (d, J = 8.0 Hz, 1H), 3.97 (s, 3H), 2.45 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*)**: δ 157.3, 141.0, 133.2, 129.4, 128.6, 126.7, 126.5, 126.4, 125.3, 110.1, 55.2, 16.4 ppm. **IR (KBr, neat):** ν = 3413, 2969, 1608, 1490, 1243, 1135, 1023, 763, 699 cm^{-1}. **HRMS (m/z):** calcd for $C_{14}H_{15}O$ [M+H]$^+$ 199.1117, found: 199.1119.



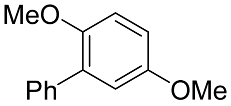
2-Methoxy-1,1'-biphenyl (3f)[1]: 75.5 mg, 41% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.63–7.55 (m, 2H), 7.51–7.41 (m, 2H), 7.40–7.33 (m, 3H), 7.13–7.00 (m, 2H), 3.85 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** δ 156.4, 138.5, 130.9, 130.6, 129.5, 128.6, 128.0, 126.9, 120.8, 111.1, 55.5 ppm. **IR (KBr, neat):** ν = 3413, 1617, 1483, 1400, 1237, 1028, 755, 699, 613 cm^{-1}. **HRMS (m/z):** calcd for $C_{13}H_{13}O$ [M+H]$^+$ 185.0961, found: 185.0963.



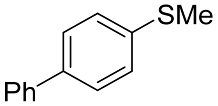
3-Methoxy-1,1'-biphenyl (3g)[1]: 127.5 mg, 69% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.70–7.61 (m, 2H), 7.49 (dd, J = 8.5, 6.8 Hz, 2H), 7.40 (td, J = 7.7, 3.5 Hz, 2H), 7.25–7.16 (m, 2H), 6.95 (ddd, J = 8.2, 2.6, 0.9 Hz, 1H), 3.90 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** δ 159.8, 142.7, 141.0, 129.7, 128.7, 127.4, 127.2, 119.6, 112.8, 112.6, 55.2 ppm. **IR (KBr, neat):** ν = 3329, 1613, 1477, 1302, 1239, 1207, 1057, 759, 699 cm^{-1}. **HRMS (m/z):** calcd for $C_{13}H_{13}O$ [M+H]$^+$ 185.0961, found: 185.0963.



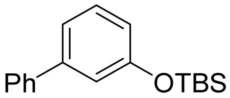
3,4-Dimethoxy-1,1'-biphenyl (3h)[2]: 125.9 mg, 59% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.60–7.56 (m, 2H), 7.48–7.41 (m, 2H), 7.37–7.30 (m, 1H), 7.20–7.10 (m, 2H), 6.96 (d, J = 8.2 Hz, 1H), 3.96 (s, 3H), 3.94 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** δ 149.0, 148.5, 140.9, 134.1, 128.6, 126.76, 126.75, 119.3, 111.3, 110.3, 55.9, 55.8 ppm. **IR (KBr, neat):** ν = 3321, 2965, 2844, 1523, 1211, 1141, 1023, 762, 591 cm^{-1}. **HRMS (m/z):** calcd for $C_{14}H_{15}O_2$ [M+H]$^+$ 215.1067, found: 215.1069.



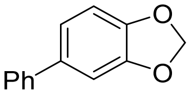
2,5-Dimethoxy-1,1'-biphenyl (3i)[3]: 148.4 mg, 69% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.55–7.52 (m, 2H), 7.44–7.39 (m, 2H), 7.36–7.31 (m, 1H), 7.25 (s, 2H), 6.94–6.84 (m, 1H), 3.81 (s, 3H), 3.76 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** δ 153.6, 150.7, 138.3, 131.5, 129.4, 128.0, 127.1, 116.6, 113.0, 112.5, 56.2, 55.7 ppm. **IR (KBr, neat):** ν = 3124, 2983, 2824, 1616, 1514, 1295, 1054, 835, 518 cm^{-1}. **HRMS (m/z):** calcd for $C_{14}H_{15}O_2$ [M+H]$^+$ 215.1067, found: 215.1069.



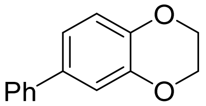
[1,1'-Biphenyl]-4-yl(methyl)sulfane (3j)[4]: 92.8 mg, 46% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 7.59–7.51 (m, 4H), 7.46–7.41 (m, 2H), 7.36–7.31 (m, 3H), 2.53 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*)**: δ 140.5, 138.0, 137.5, 128.8, 127.5, 127.2, 126.9, 126.8, 15.7 ppm. **IR (KBr, neat):** ν = 3511, 2917, 1648, 1479, 1098, 823, 754, 543 cm^{-1}. **HRMS (m/z):** calcd for $C_{13}H_{13}S$ [M+H]$^+$ 201.0732, found: 201.0729.



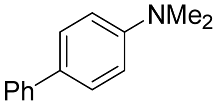
([1,1'-Biphenyl]-3-yloxy)(*tert*-butyl)dimethylsilane (3k)[4]: 119.5 mg, 42% yield. Yellow oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.64–7.60 (m, 2H), 7.56–7.52 (m, 2H), 7.51–7.45 (m, 2H), 7.40–7.33 (m, 1H), 7.03–6.96 (m, 2H), 1.10 (s, 9H), 0.32 (s, 6H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** *δ* 156.0, 142.7, 141.0, 129.6, 128.7, 127.3, 127.1, 120.2, 118.92, 118.89, 25.7, 18.2, -4.4 ppm. **IR (KBr, neat):** *ν* = 3325, 2971, 2833, 2765, 1599, 1497, 1259, 927, 762 cm^{-1}. **HRMS (m/z):** calcd for $C_{18}H_{25}OSi$ $[M+H]^+$ 285.1669, found: 285.1673.



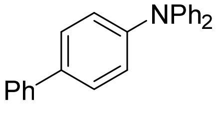
5-Phenylbenzo[*d*][1,3]dioxole (3l)[1]: 111.0 mg, 56% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: *δ* 7.58–7.51 (m, 2H), 7.43 (ddd, *J* = 7.8, 6.9, 1.2 Hz, 2H), 7.37–7.30 (m, 1H), 7.13–7.05 (m, 2H), 6.91 (dd, *J* = 7.9, 0.6 Hz, 1H), 6.02 (s, 2H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** *δ* 148.0, 147.0, 140.9, 135.5, 128.7, 126.9, 126.8, 120.6, 108.5, 107.6, 101.1 ppm. **IR (KBr, neat):** *ν* = 2351, 2138, 1620, 1514, 1485, 1231, 1043, 944, 762 cm^{-1}. **HRMS (m/z):** calcd for $C_{13}H_{11}O_2$ $[M+H]^+$ 199.2285, found: 199.2286.



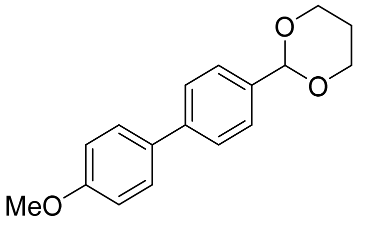
6-Phenyl-2,3-dihydrobenzo[*b*][1,4]dioxine (3m)[1]: 108.2 mg, 51% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** *δ* 7.62–7.56 (m, 2H), 7.48–7.42 (m, 2H), 7.38–7.31 (m, 1H), 7.20–7.12 (m, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 4.31 (s, 4H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** *δ* 143.6, 143.1, 140.5, 134.7, 128.7, 126.8, 126.7, 120.1, 117.5, 115.8, 64.3 ppm. **IR (KBr, neat):** *ν* = 2925, 2850, 1576, 1311, 1240, 1078, 904, 816, 697 cm^{-1}. **HRMS (m/z):** calcd for $C_{14}H_{13}O_2$ $[M+H]^+$ 213.0910, found: 213.0915.



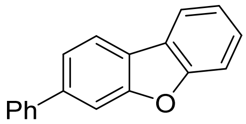
***N,N*-Dimethyl-[1,1'-biphenyl]-4-amine (3n)[1]:** 102.6 mg, 52% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** *δ* 7.66–7.54 (m, 4H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.38–7.29 (m, 1H), 6.92–6.82 (m, 2H), 3.04 (s, 6H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** *δ* 149.9, 141.2, 129.2, 128.6, 127.7, 126.2, 125.9, 112.7, 40.5 ppm. **IR (KBr, neat):** *ν* = 2937, 2856, 1612, 1494, 1355, 1237, 1068, 829, 765 cm^{-1}. **HRMS (m/z):** calcd for $C_{14}H_{16}N$ $[M+H]^+$ 198.1277, found: 198.1278.



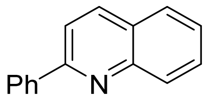
***N,N*-Diphenyl-[1,1'-biphenyl]-4-amine (3o)[1]:** 160.7 mg, 50% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** *δ* 7.68–7.62 (m, 2H), 7.58–7.53 (m, 2H), 7.48 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.41–7.29 (m, 5H), 7.25–7.18 (m, 6H), 7.14–7.06 (m, 2H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** *δ* 147.6, 147.1, 140.6, 135.1, 129.2, 128.7, 127.7, 126.8, 126.6, 124.4, 123.9, 122.9 ppm. **IR (KBr, neat):** *ν* = 2560, 2371, 1606, 1504, 1386, 1253, 1034, 860, 690 cm^{-1}. **HRMS (m/z):** calcd for $C_{24}H_{20}N$ $[M+H]^+$ 322.1590, found: 322.1593.



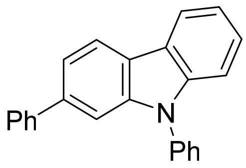
2-(4'-Methoxy-[1,1'-biphenyl]-4-yl)-1,3-dioxane (3p): 139.8 mg, 52% yield. Yellow solid. **^{1}H NMR (400 MHz, Chloroform-*d*)**: δ 7.57–7.51 (m, 6H), 7.00–6.95 (m, 2H), 5.55 (s, 1H), 4.29 (ddd, J = 12.3, 4.9, 1.5 Hz, 2H), 4.06–3.98 (m, 2H), 3.85 (s, 3H), 2.32–2.18 (m, 1H), 1.50–1.43 (m, 1H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*)**: δ 159.2, 141.2, 137.1, 133.4, 128.2, 126.6, 126.3, 114.1, 101.5, 67.4, 55.3, 25.7 ppm. **IR (KBr, neat):** ν = 2960, 1603, 1500, 1376, 1250, 1160, 988, 820, 523 cm^{-1}. **HRMS (m/z):** calcd for $C_{17}H_{19}O_3$ [M+H]$^+$ 271.1329, found: 271.1332.



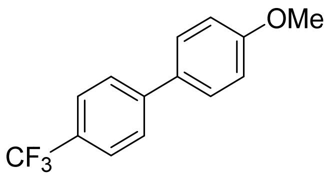
3-Phenyldibenzo[*b,d*]furan (3q)[1]: 112.4 mg, 46% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 8.19 (d, J = 1.9 Hz, 1H), 8.05–8.01 (m, 1H), 7.75–7.71 (m, 3H), 7.68–7.63 (m, 2H), 7.57–7.50 (m, 3H), 7.46–7.39 (m, 2H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*)**: 156.5, 155.6, 141.2, 136.3, 128.8, 127.4, 127.2, 127.0, 126.5, 124.6, 124.2, 122.7, 120.6, 119.1, 111.7 ppm. **IR (KBr, neat):** ν = 2375, 2168, 1472, 1265, 1129, 1028, 893, 758, 696 cm^{-1}. **HRMS (m/z):** calcd for $C_{18}H_{13}O$ [M+H]$^+$ 245.0961, found: 245.0957.



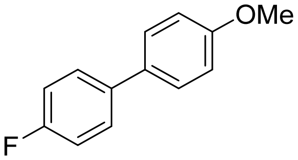
2-Phenylquinoline (3r)[4]: 93.3 mg, 45% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 8.85 (dd, J = 8.6, 1.9 Hz, 2H), 8.37–8.20 (m, 4H), 7.87 (dd, J = 8.2, 1.5 Hz, 2H), 7.75 (tdd, J = 7.3, 3.5, 1.8 Hz, 2H), 7.61–7.54 (m, 1H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** δ 156.1, 147.9, 136.7, 136.5, 133.6, 131.3, 129.9, 129.5, 128.7, 128.4, 127.6, 126.9, 119.4 ppm. **IR (KBr, neat):** ν = 3370, 2681, 1597, 1426, 1331, 1165, 1084, 913, 832 cm^{-1}. **HRMS (m/z):** calcd for $C_{15}H_{12}N$ [M+H]$^+$ 206.0964, found: 206.0969.



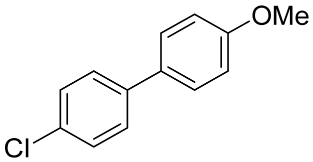
2,9-Diphenyl-9*H*-carbazole (3s)[5]: 120.5 mg, 38% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 8.27–8.21 (m, 2H), 7.73–7.69 (m, 2H), 7.69–7.64 (m, 5H), 7.61 (dd, J = 8.1, 1.5 Hz, 1H), 7.55–7.46 (m, 5H), 7.42–7.34 (m, 2H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** δ 141.6, 141.4, 140.2, 137.6, 133.1, 129.9, 129.2, 128.8, 127.6, 127.5, 127.2, 125.9, 123.1, 122.4, 120.4, 120.3, 120.1, 120.0, 109.7, 108.6 ppm. **IR (KBr, neat):** ν = 3280, 2425, 2361, 1604, 1415, 1229, 1082, 806, 704 cm^{-1}. **HRMS (m/z):** calcd for $C_{24}H_{18}N$ [M+H]$^+$ 320.1434, found: 320.1440.



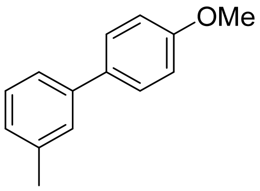
4-Methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (4b)[4]: 88.3 mg, 35% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** *δ* 7.71–7.62 (m, 4H), 7.59–7.52 (m, 2H), 7.05–6.97 (m, 2H), 3.87 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** *δ* 159.8, 144.3, 132.1, 128.8 (q, *J* = 32.5 Hz), 128.3, 126.8, 125.7 (q, *J* = 3.9 Hz), 124.9 (q, *J* = 270.2 Hz), 114.4, 55.3 ppm. **^{19}F NMR (376 MHz, Chloroform-*d*):** *δ* -62.16 (s, 3F) ppm. **IR (KBr, neat):** *ν* = 3350, 2761, 2243, 1605, 1405, 1340, 1278, 1184, 708 cm^{-1}. **HRMS (m/z):** calcd for $C_{14}H_{12}F_3O$ [M+H]$^+$ 253.0835, found: 253.0838.



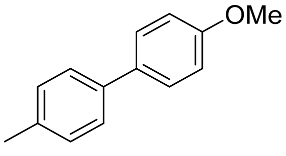
4-Fluoro-4'-methoxy-1,1'-biphenyl (4c)[4]: 89.0 mg, 44% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** *δ* 7.49 (ddt, *J* = 8.7, 7.1, 2.6 Hz, 4H), 7.18–7.05 (m, 2H), 7.03–6.94 (m, 2H), 3.86 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** δ 162.0 (d, *J* = 243.6 Hz), 159.0, 136.8 (d, *J* = 3.3 Hz), 132.7, 128.1 (d, *J* = 7.9 Hz), 127.9, 115.5 (d, *J* = 21.2 Hz), 114.2, 55.2 ppm. **^{19}F NMR (376 MHz, Chloroform-*d*):** *δ* -116.55 (s, 1F) ppm. **IR (KBr, neat):** *ν* = 3250, 2895, 1562, 1463, 1327, 1288, 1075, 828, 761 cm^{-1}. **HRMS (m/z):** calcd for $C_{13}H_{12}FO$ [M+H]$^+$ 203.0867, found: 203.0869.



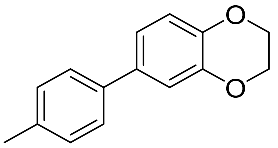
4-Chloro-4'-methoxy-1,1'-biphenyl (4d)[6]: 144.2 mg, 66% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** *δ* 7.52–7.45 (m, 4H), 7.41–7.36 (m, 2H), 7.02–6.96 (m, 2H), 3.86 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** *δ* 159.3, 139.2, 132.6, 132.4, 128.8, 128.0, 127.9, 114.3, 55.3 ppm. **IR (KBr, neat):** *ν* = 2962, 2839, 1605, 1484, 1037, 811, 736, 498 cm^{-1}. **HRMS (m/z):** calcd for $C_{13}H_{12}OCl$ [M+H]$^+$ 219.6875, found: 219.6872.



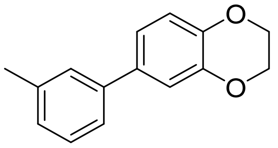
4'-Methoxy-3-methyl-1,1'-biphenyl (4e)[7]: 156.6 mg, 79% yield. Yellow solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** *δ* 7.57–7.52 (m, 2H), 7.42–7.30 (m, 3H), 7.19–7.12 (m, 1H), 7.04–6.96 (m, 2H), 3.87 (s, 3H), 2.44 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** *δ* 159.0, 140.7, 138.2, 133.8, 128.6, 128.1, 127.5, 127.4, 123.8, 114.0, 55.2, 21.5 ppm. **IR (KBr, neat):** *ν* = 3145, 2980, 1608, 1522, 1486, 1297, 1186, 843, 693 cm^{-1}. **HRMS (m/z):** calcd for $C_{14}H_{15}O$ [M+H]$^+$ 199.1117, found: 199.1120.



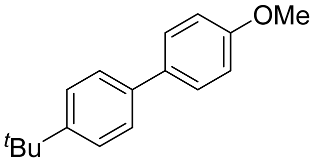
4-Methoxy-4'-methyl-1,1'-biphenyl (4f)[1]: 162.6 mg, 82% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.59–7.54 (m, 2H), 7.53–7.48 (m, 2H), 7.31–7.26 (m, 2H), 7.05–6.99 (m, 2H), 3.88 (s, 3H), 2.44 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** δ 158.9, 137.9, 136.3, 133.7, 129.4, 127.9, 126.5, 114.1, 55.3, 21.0 ppm. **IR (KBr, neat):** ν = 3360, 2870, 1610, 1502, 1290, 1188, 1044, 848, 697 cm^{-1}. **HRMS (m/z):** calcd for $C_{14}H_{15}O$ [M+H]$^+$ 199.1117, found: 199.1121.



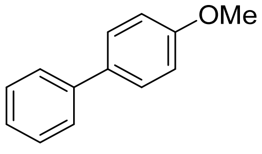
6-(*p*-Tolyl)-2,3-dihydrobenzo[*b*][1,4]dioxine (4g)[8]: 168.9 mg, 74% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.42–7.34 (m, 3H), 7.20–7.12 (m, 3H), 6.99 (dd, J = 8.4, 3.8 Hz, 1H), 4.31 (s, 4H), 2.46 (d, J = 0.7 Hz, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** δ 143.6, 142.9, 137.7, 136.5, 134.8, 129.4, 126.6, 119.9, 117.5, 115.6, 64.4, 64.3, 21.0 ppm. **IR (KBr, neat):** ν = 3320, 2925, 1594, 1493, 1319, 1248, 1077, 902, 797 cm^{-1}. **HRMS (m/z):** calcd for $C_{15}H_{15}O_2$ [M+H]$^+$ 227.1067, found: 227.1065.



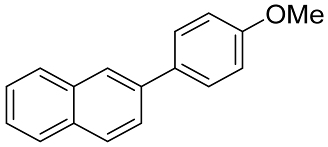
6-(*m*-Tolyl)-2,3-dihydrobenzo[*b*][1,4]dioxine (4h): 168.3 mg, 74% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.44–7.33 (m, 3H), 7.21–7.11 (m, 3H), 6.99 (dd, J = 8.3, 3.8 Hz, 1H), 4.31 (s, 4H), 2.46 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** δ 143.6, 143.1, 140.5, 138.2, 134.9, 128.6, 127.5, 126.7, 123.8, 120.1, 117.4, 115.8, 64.4, 64.3, 21.5 ppm. **IR (KBr, neat):** ν = 3310, 2878, 1588, 1492, 1313, 1252, 1073, 895, 789 cm^{-1}. **HRMS (m/z):** calcd for $C_{15}H_{15}O_2$ [M+H]$^+$ 227.1067, found: 227.1062.



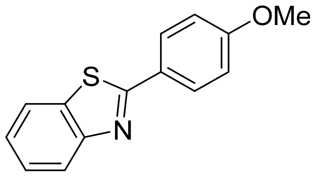
4-(*tert*-Butyl)-4'-methoxy-1,1'-biphenyl (4i)[1]: 132.2 mg, 55% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.55 (dd, J = 8.7, 1.5 Hz, 4H), 7.49 (dd, J = 8.3, 1.4 Hz, 2H), 7.03–6.99 (m, 2H), 3.88 (s, 3H), 1.41 (s, 9H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** δ 158.9, 149.5, 137.9, 133.6, 128.0, 126.3, 125.6, 114.1, 55.3, 34.4, 31.3 ppm. **IR (KBr, neat):** ν = 3329, 2931, 2876, 1609, 1507, 1397, 1295, 1197, 829 cm^{-1}. **HRMS (m/z):** calcd for $C_{17}H_{21}O$ [M+H]$^+$ 241.1587, found: 241.1590.



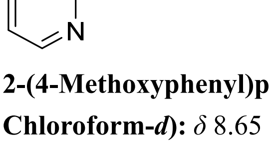
4-Methoxy-1,1'-biphenyl (4j)[1]: 104.9 mg, 57% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.61–7.53 (m, 4H), 7.47–7.40 (m, 2H), 7.35–7.29 (m, 1H), 7.03–6.97 (m, 2H), 3.87 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** δ 159.1, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3 ppm. **IR (KBr, neat):** ν = 3032, 2835, 1605, 1487, 1270, 1034, 833, 759, 571, 490 cm^{-1}. **HRMS (m/z):** calcd for $C_{13}H_{13}O$ [M+H]$^{+}$ 185.0961, found: 185.0960.



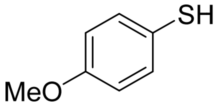
2-(4-Methoxyphenyl)naphthalene (4k)[3]: 100.7 mg, 43% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 8.01 (d, *J* = 1.8 Hz, 1H), 7.96–7.84 (m, 3H), 7.74 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.71–7.66 (m, 2H), 7.55–7.44 (m, 2H), 7.10–7.01 (m, 2H), 3.89 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** δ 159.2, 138.1, 133.7, 133.6, 132.3, 128.4, 128.3, 128.0, 127.6, 126.2, 125.6, 125.4, 125.0, 114.3, 55.3 ppm. **IR (KBr, neat):** ν = 2950, 2368, 1911, 1618, 1498, 1285, 1189, 816, 660 cm^{-1}. **HRMS (m/z):** calcd for $C_{17}H_{15}O$ [M+H]$^{+}$ 235.1117, found: 235.1119.



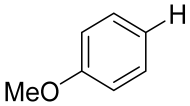
2-(4-Methoxyphenyl)benzo[*d*]thiazole (4l)[9]: 113.4 mg, 47% yield. Yellow solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.60–7.56 (m, 2H), 7.55 (d, *J* = 2.1 Hz, 1H), 7.47–7.40 (m, 2H), 7.35–7.30 (m, 1H), 7.03–6.96 (m, 2H), 3.87 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** δ 167.9, 161.9, 154.2, 134.8, 129.1, 126.4, 126.2, 124.8, 122.8, 121.5, 114.3, 55.4 ppm. **IR (KBr, neat):** ν = 3612, 2835, 1605, 1285, 1172, 833, 759, 553, 511 cm^{-1}. **HRMS (m/z):** calcd for $C_{14}H_{12}NOS$ [M+H]$^{+}$ 242.0634, found: 242.0638.



2-(4-Methoxyphenyl)pyridine (4m)[3]: 75.9 mg, 41% yield. White solid. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 8.65 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.98–7.93 (m, 2H), 7.75–7.63 (m, 2H), 7.17 (ddd, *J* = 7.1, 4.9, 1.4 Hz, 1H), 7.05–6.96 (m, 2H), 3.86 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** δ 160.4, 157.0, 149.5, 136.7, 131.9, 128.1, 121.4, 119.8, 114.1, 55.3 ppm. **IR (KBr, neat):** ν = 3260, 2825, 1618, 1529, 1431, 1256, 1187, 838, 787 cm^{-1}. **HRMS (m/z):** calcd for $C_{12}H_{12}NO$ [M+H]$^{+}$ 186.0913, found: 186.0908.



4-Methoxybenzenethiol (6): 99.5 mg, 71% yield. Colorless oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.31–7.25 (m, 2H), 6.85–6.79 (m, 2H), 3.79 (s, 3H), 3.40 (s, 1H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** δ 158.3, 132.2, 119.7, 114.6, 55.2 ppm.



Anisole (7): 37.8 mg, 70% yield. Colorless oil. **^{1}H NMR (400 MHz, Chloroform-*d*):** δ 7.40–7.34 (m, 2H), 7.06–6.96 (m, 3H), 3.86 (s, 3H) ppm. **^{13}C NMR (100 MHz, Chloroform-*d*):** δ 159.5, 129.4, 120.6, 113.8, 55.0 ppm.

References

[1] N.-N. Ma, J.-A. Ren, X. Liu, X.-Q. Chu, W. Rao and Z.-L. Shen, Nickel-Catalyzed Direct Cross-Coupling of Aryl Sulfonium Salt with Aryl Bromide. *Org. Lett.*, 2022, **24**, 1953-1957.

[2] W.-X. Li, B.-W. Yang, X. Ying, Z.-W. Zhang, X.-Q. Chu, X. Zhou, M. Ma and Z.-L. Shen, Nickel-Catalyzed Direct Cross-Coupling of Diaryl Sulfoxide with Aryl Bromide. *J. Org. Chem.*, 2022, **87**, 11899-11908.

[3] N.-N. Ma, X.-B. Hu, Y.-S. Wu, Y.-W. Zheng, M. Ma, X.-Q. Chu, H. Xu, H. Luo and Z.-L. Shen, Nickel-Catalyzed Direct Cross-Coupling of Aryl Thioether with Aryl Bromide. *Org. Lett.*, 2023, **25**, 1771-1775.

[4] J.-H. Na, X. Liu, J.-W. Jing, J. Wang, X.-Q. Chu, M. Ma, H. Xu, X. Zhou and Z.-L. Shen, Nickel-Catalyzed Direct Cross-Coupling of Aryl Fluorosulfates with Aryl Bromides. *Org. Lett.*, 2023, **25**, 2318-2322.

[5] W. Kong, C. Fu and S. Ma, Efficient Synthesis of Carbazoles via $PtCl_2$-Catalyzed RT Cyclization of 1-(Indol-2-yl)-2,3-allenols: Scope and Mechanism. *Org. Biomol. Chem.*, 2012, **10**, 2164-2173.

[6] C. Zhang, N.-N. Ma, Z.-L. Yu, C. Shen, X. Zhou, X.-Q. Chu, W. Rao and Z.-L. Shen, Palladium-Catalyzed Direct Reductive Cross-Coupling of Aryltrimethylammonium Salts with Aryl Bromides. *Org. Chem. Front.*, 2021, **8**, 4865-4870.

[7] P. Tian and R. Tong, In-water Oxidative Suzuki Coupling of Arenes and Arylboronic Acids Using H_2O_2 as a Terminal Oxidant. *Green Chem.*, 2023, **25**, 1345-1350.

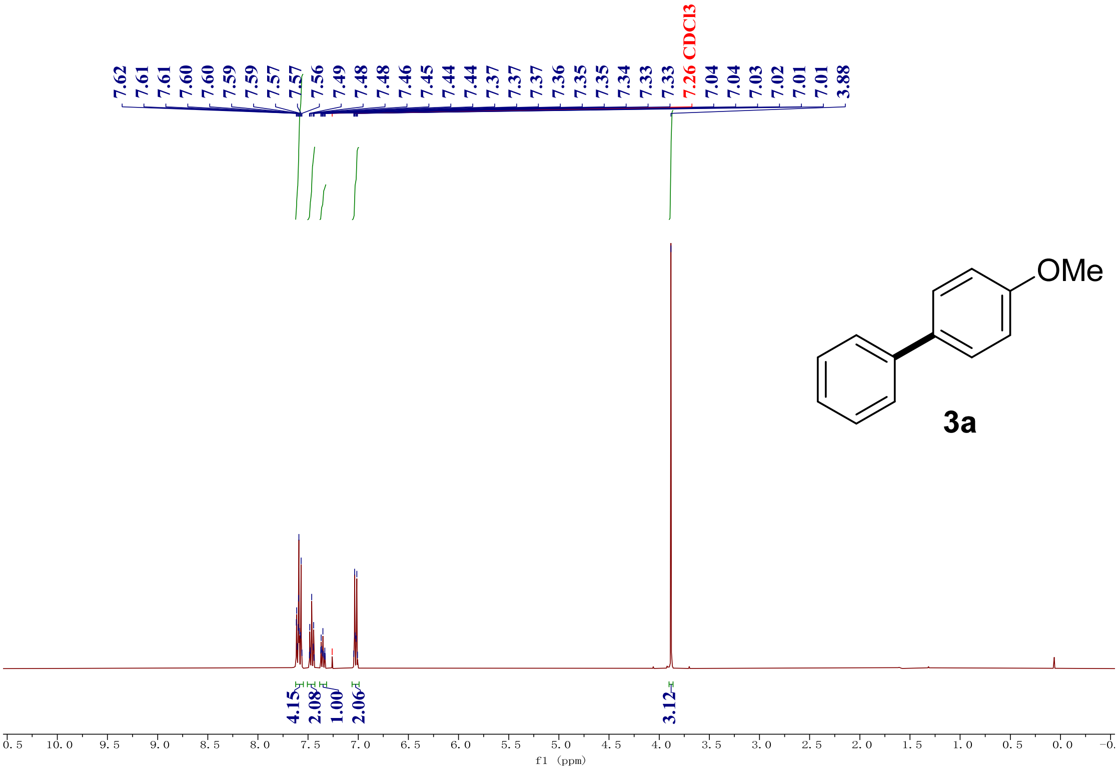
[8] Q.-Q. Fu, Y. Liang, X.-X. Sun, X.-Q. Chu, H. Xu, X. Zhou, W. Rao and Z.-L. Shen, Palladium-Catalyzed Cross-Electrophile Couplings of Aryl Thianthrenium Salts with Aryl Bromides via C–S Bond Activation. *Org. Lett.*, 2024, **26**, 8577–8582.

[9] F. Shibahara, E. Yamaguchi and T. Murai, Direct Multiple C–H bond Arylation Reaction of

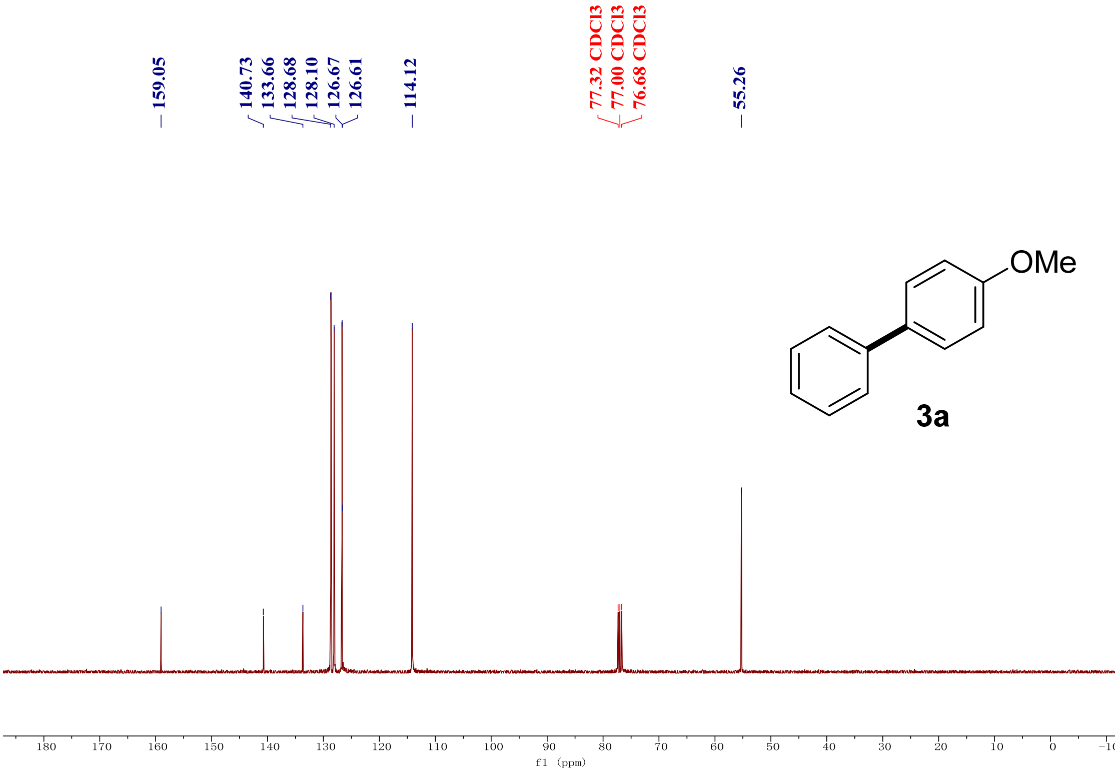
Heteroarenes Catalyzed by Cationic Palladium Complex Bearing 1,10-Phenanthroline. *Chem. Commun.*, 2010, **46**, 2471-2473.

^1H, ^{13}C, and ^{19}F NMR spectra of products

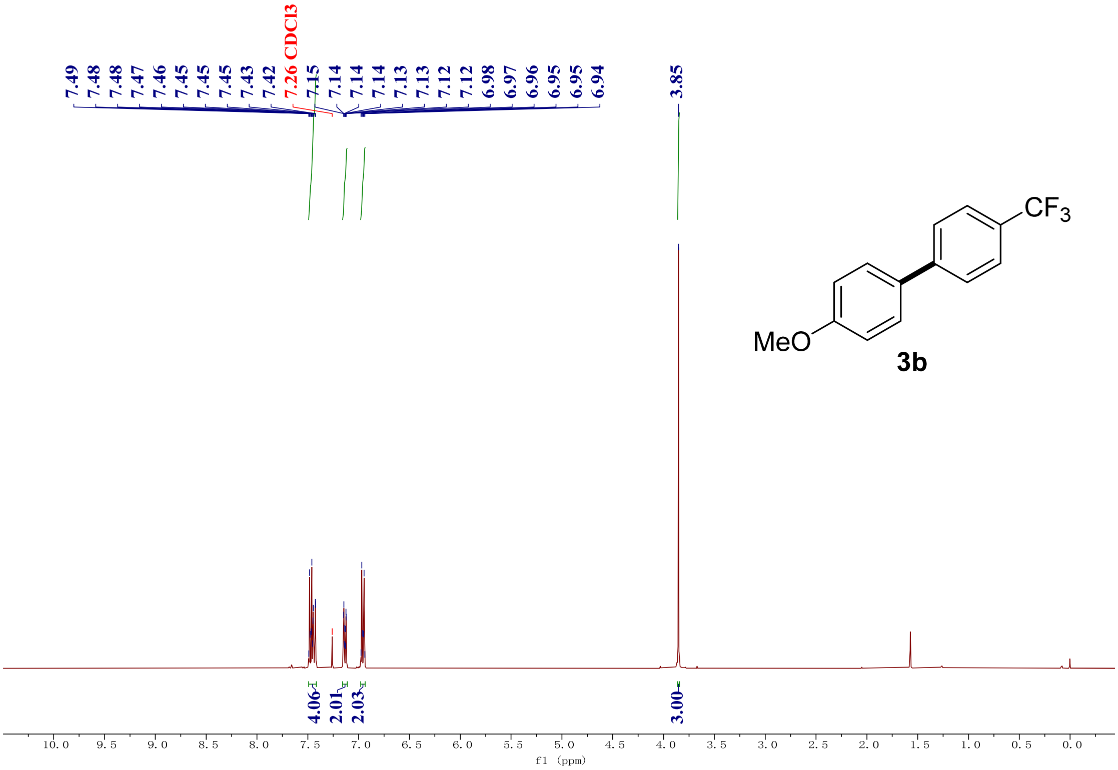
^1H NMR spectrum of 3a (400 MHz, $CDCl_3$)



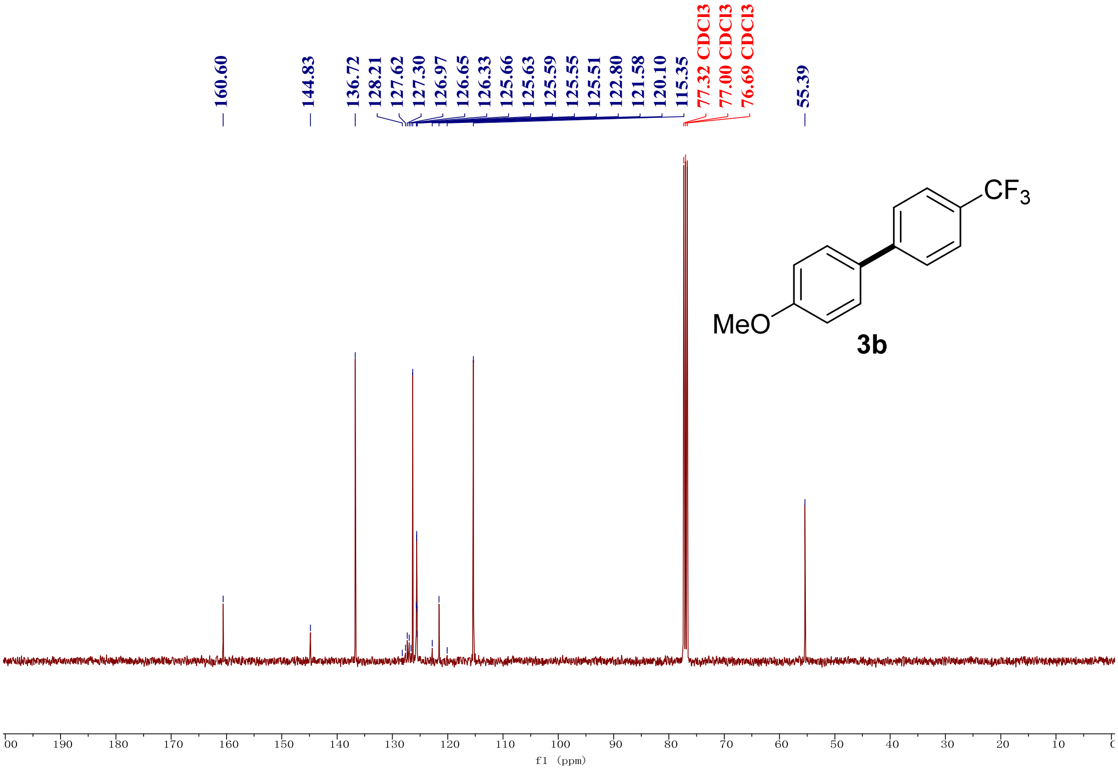
^{13}C NMR spectrum of 3a (100 MHz, $CDCl_3$)



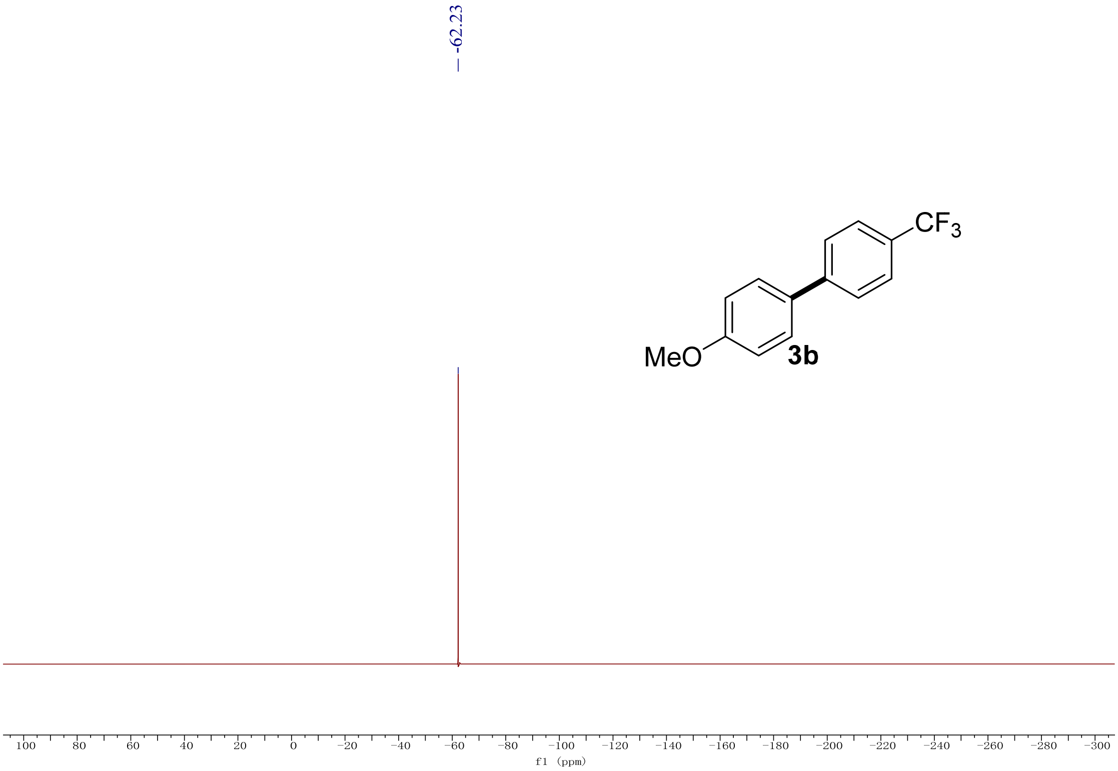
^{1}H NMR spectrum of 3b (400 MHz, CDCl$_3$)



^{13}C NMR spectrum of 3b (100 MHz, CDCl$_3$)

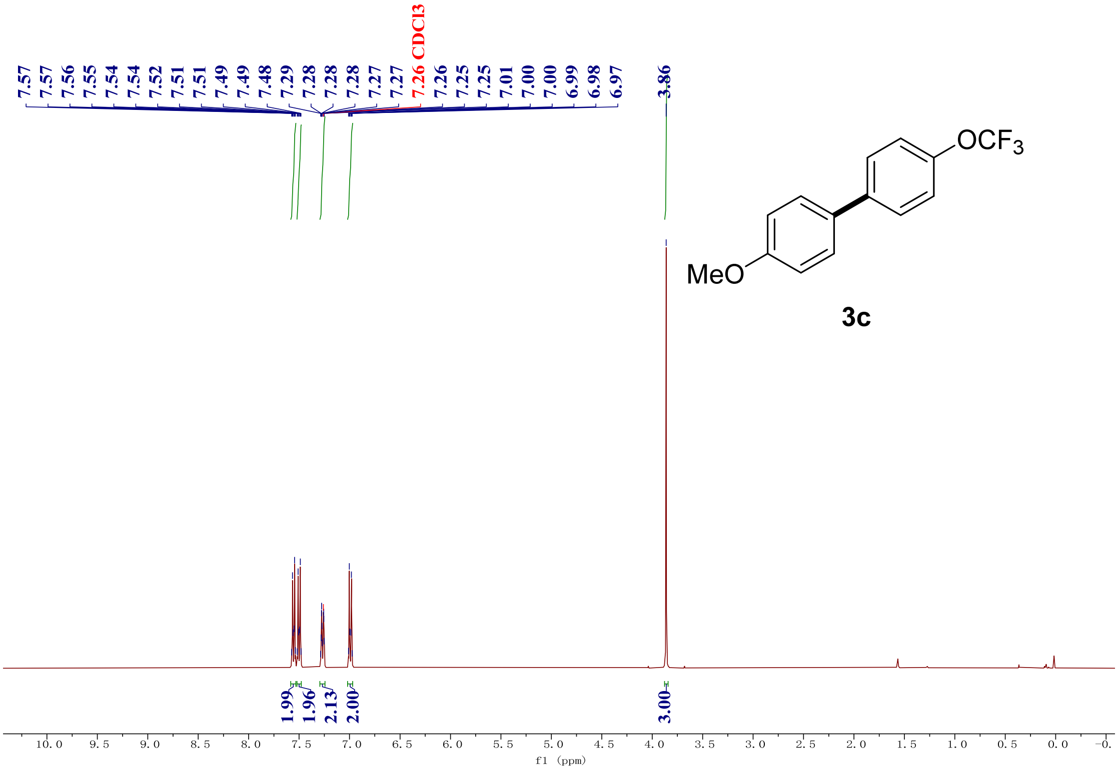


^{19}F NMR spectrum of 3b (376 MHz, $CDCl_3$)



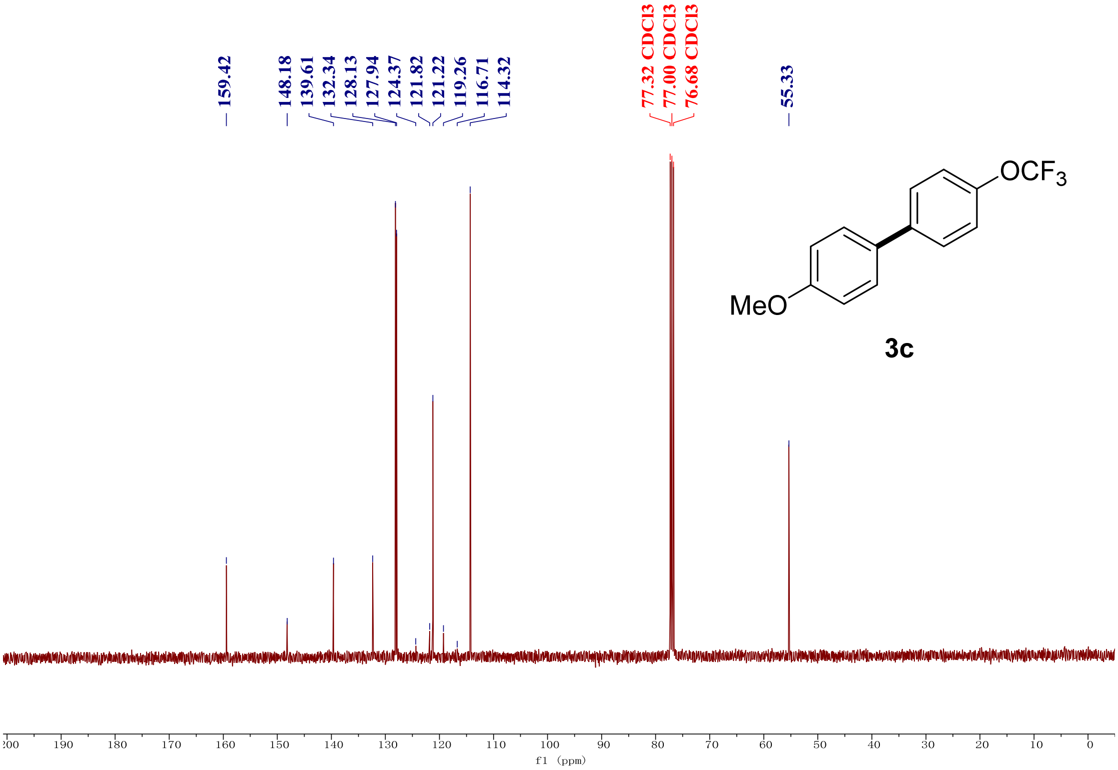
3b

^{1}H NMR spectrum of 3c (400 MHz, $CDCl_3$)

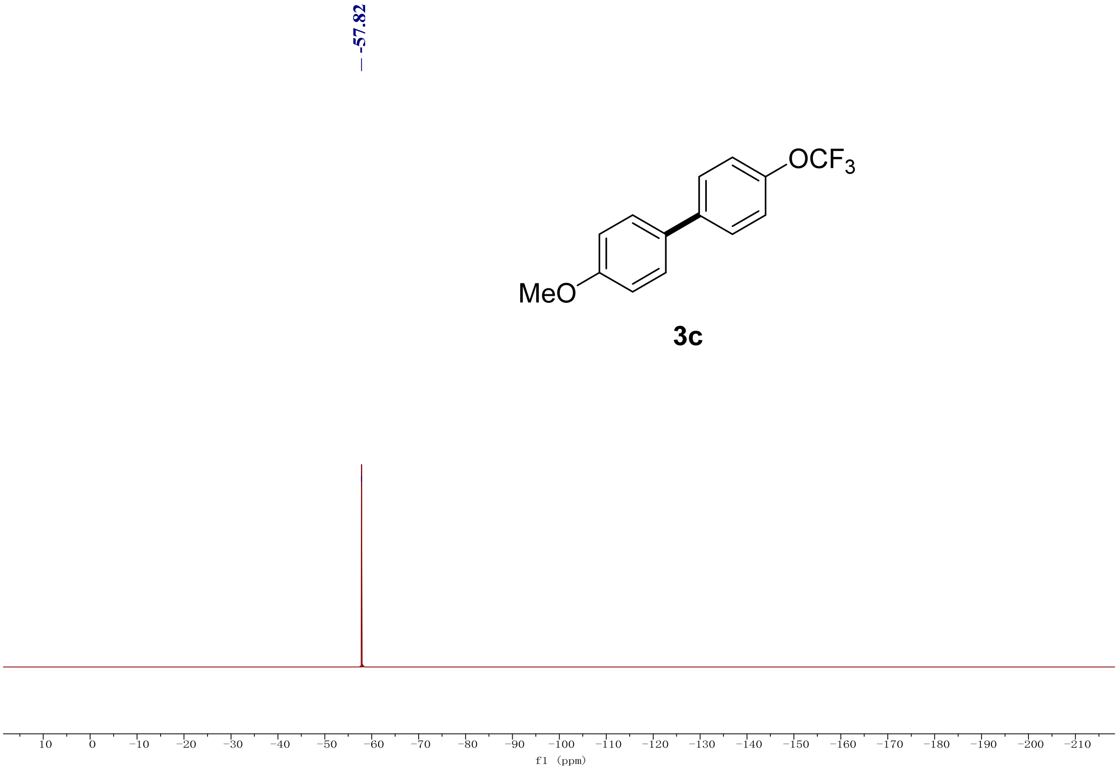


3c

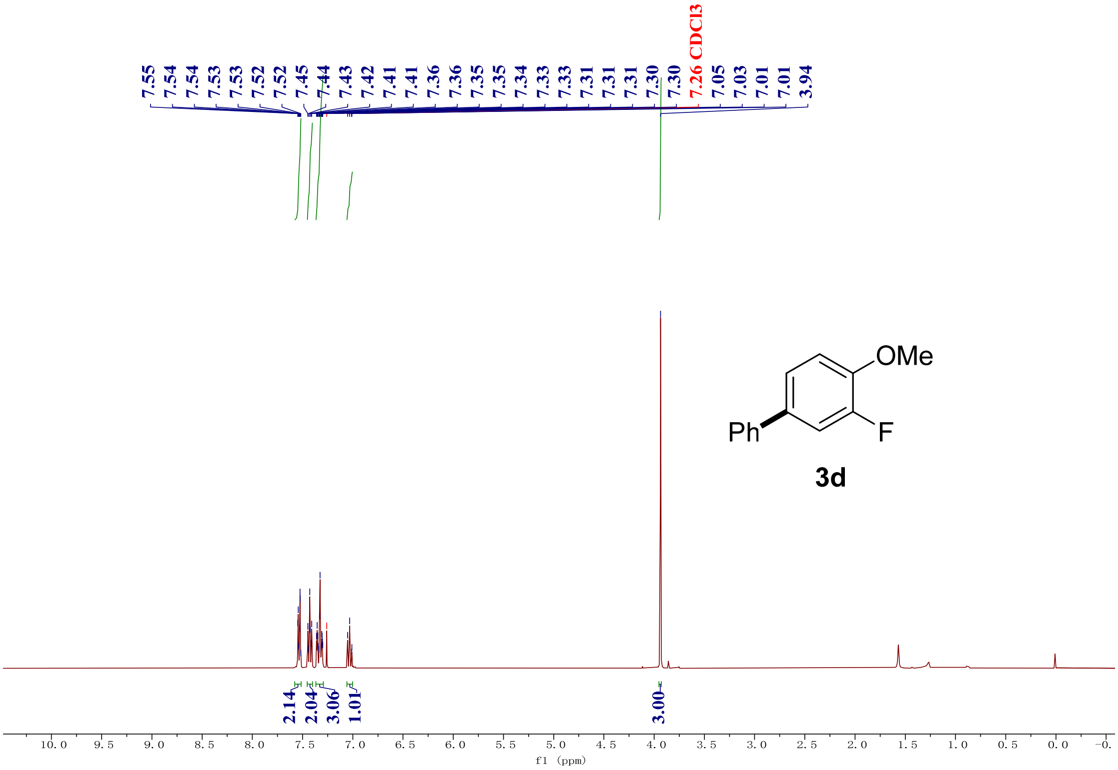
^{13}C NMR spectrum of 3c (100 MHz, CDCl$_3$)



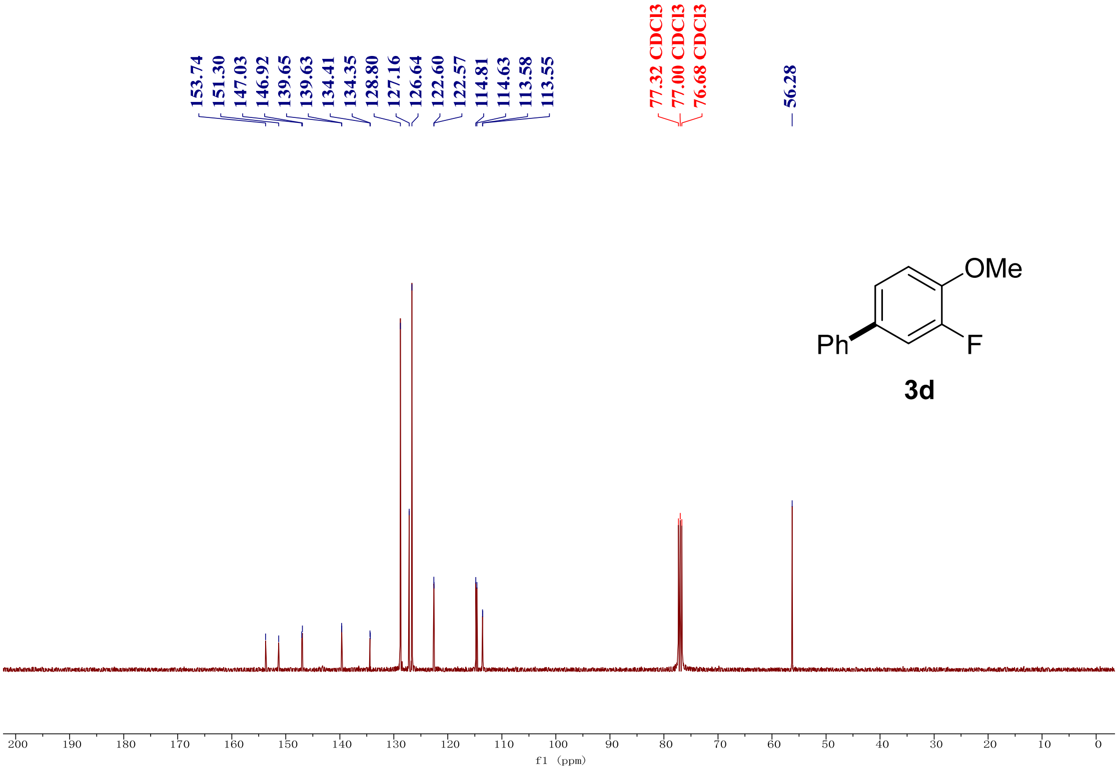
^{19}F NMR spectrum of 3c (376 MHz, CDCl$_3$)



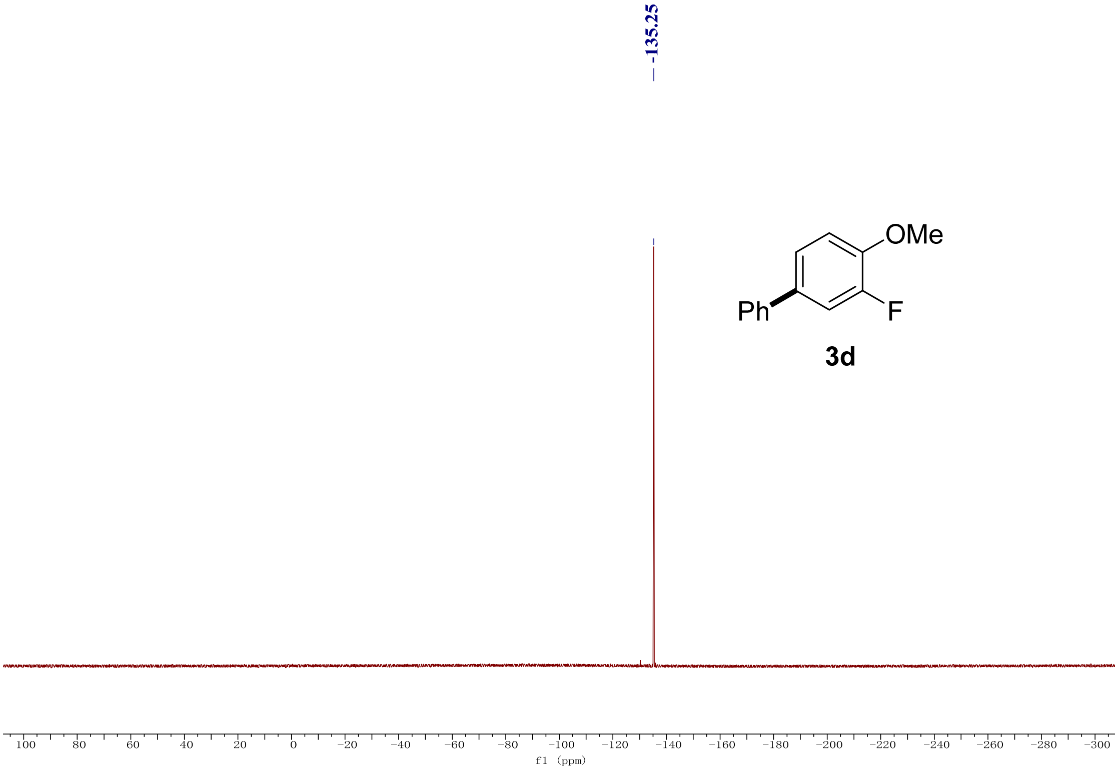
^{1}H NMR spectrum of 3d (400 MHz, $CDCl_3$)



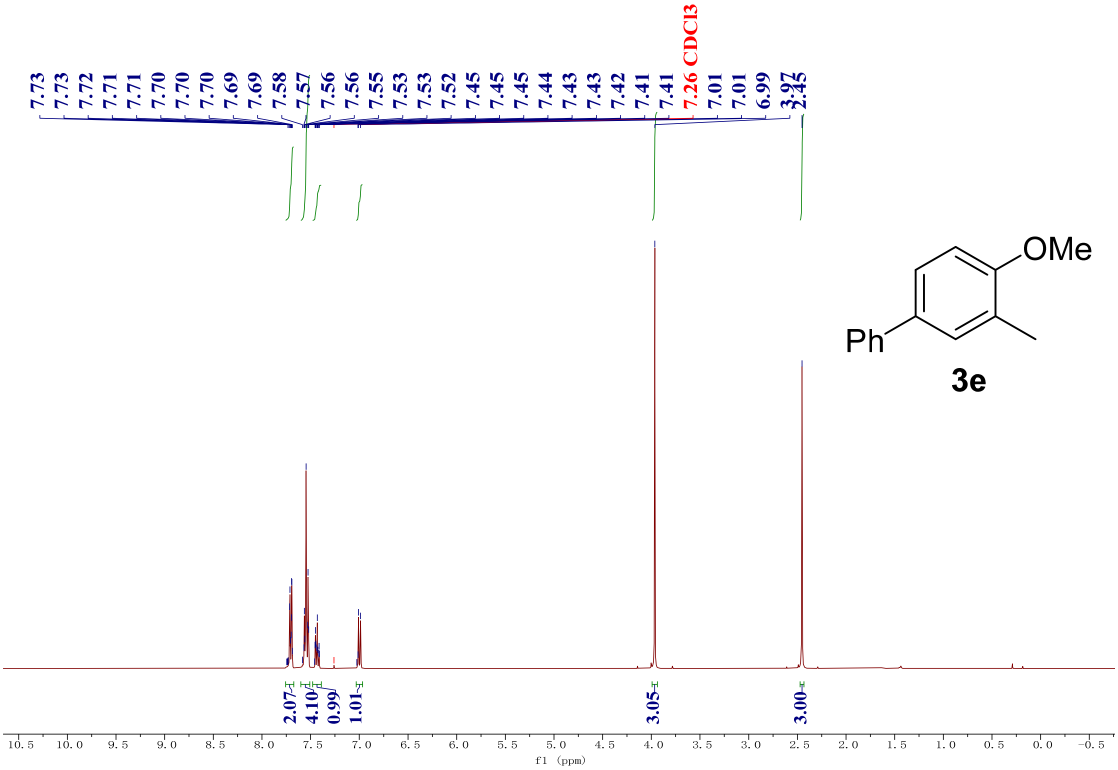
^{13}C NMR spectrum of 3d (100 MHz, $CDCl_3$)



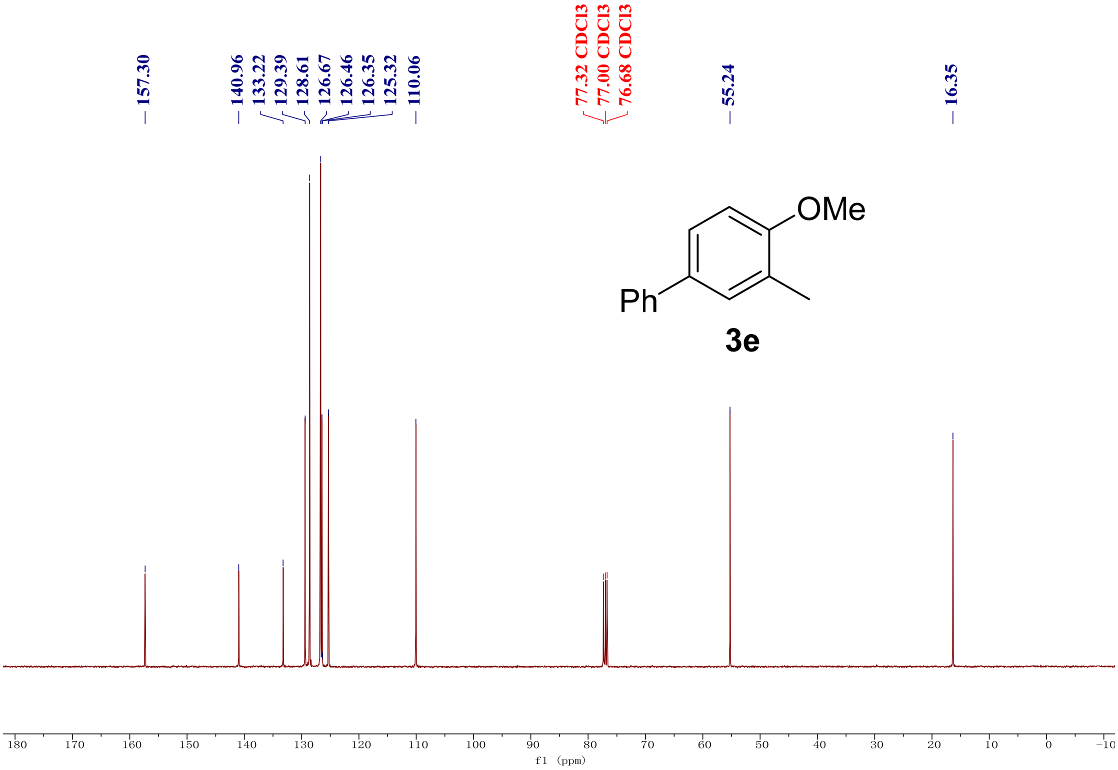
^{19}F NMR spectrum of 3d (376 MHz, CDCl$_3$)



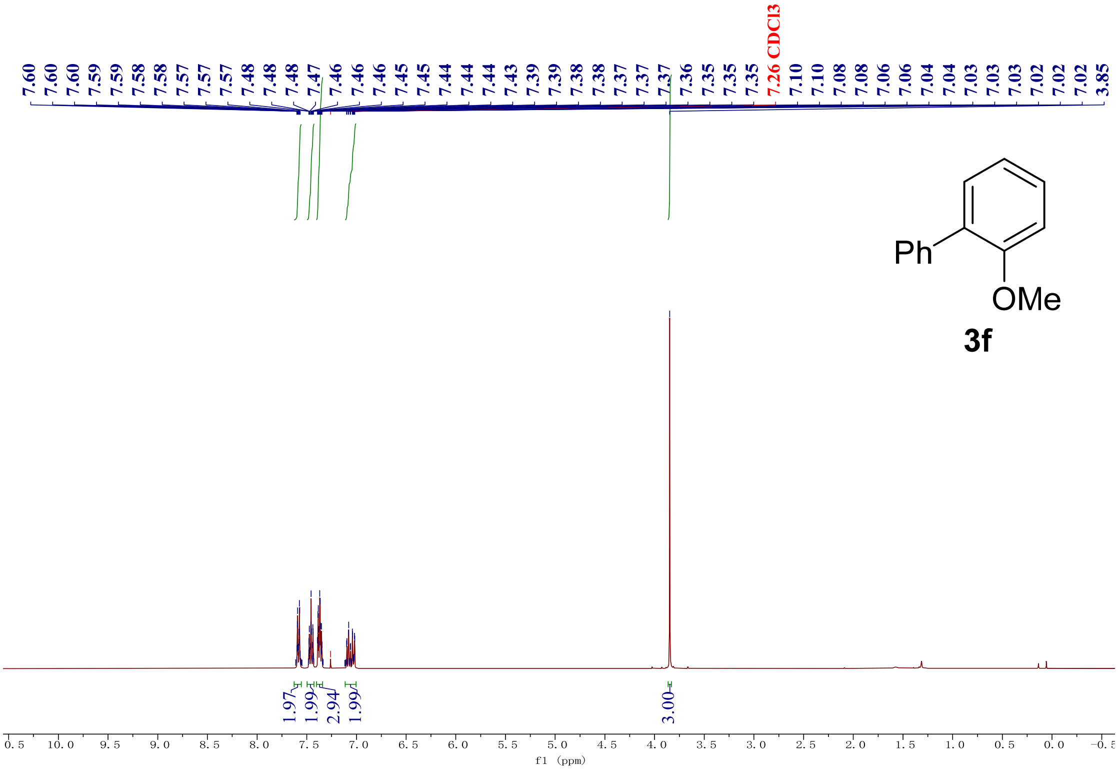
^{1}H NMR spectrum of 3e (400 MHz, CDCl$_3$)



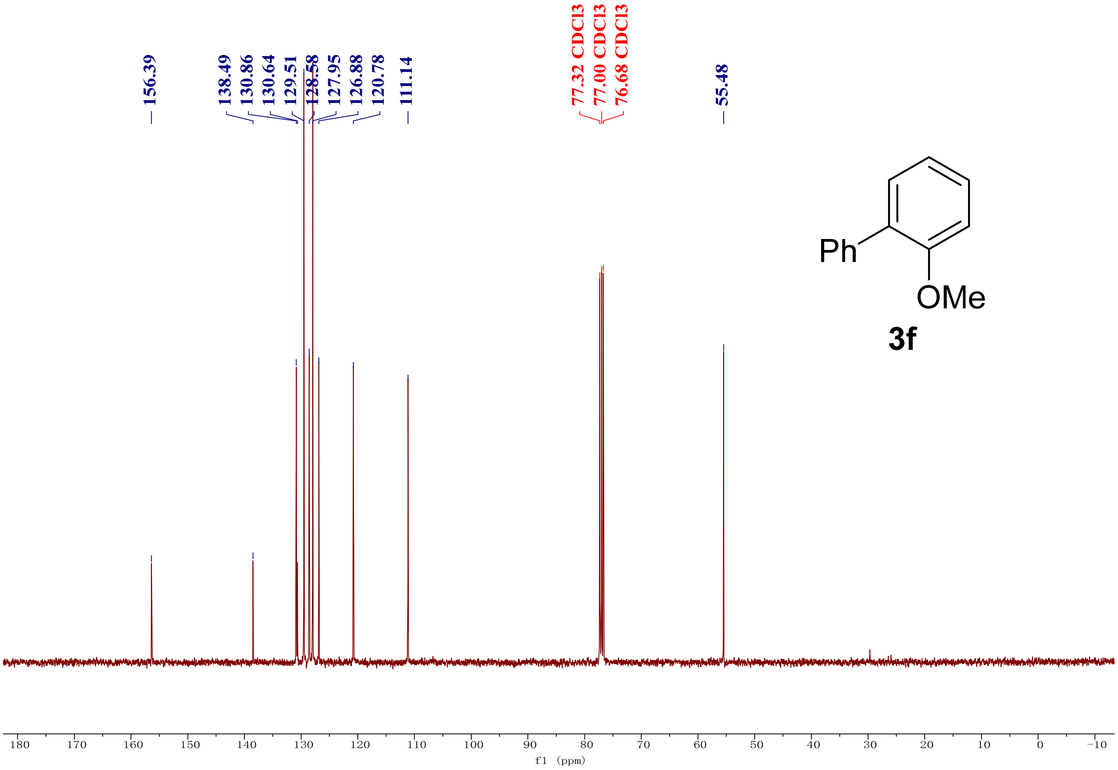
^{13}C NMR spectrum of 3e (100 MHz, CDCl$_3$)



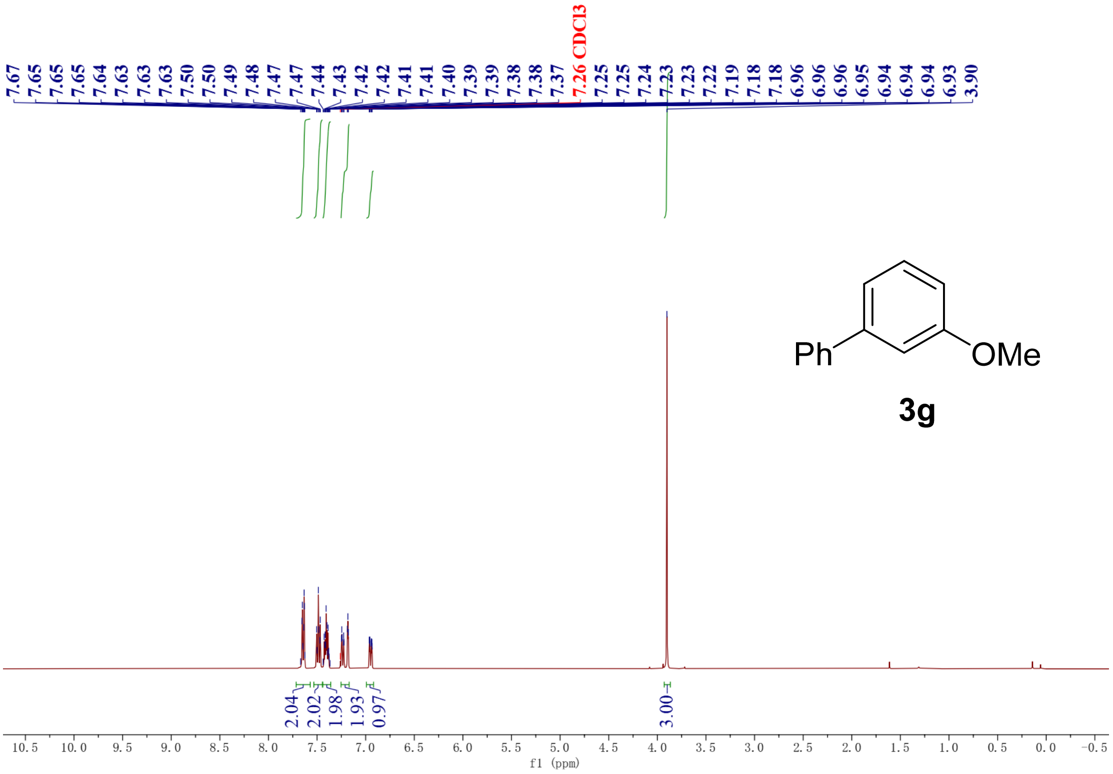
^{1}H NMR spectrum of 3f (400 MHz, CDCl$_3$)



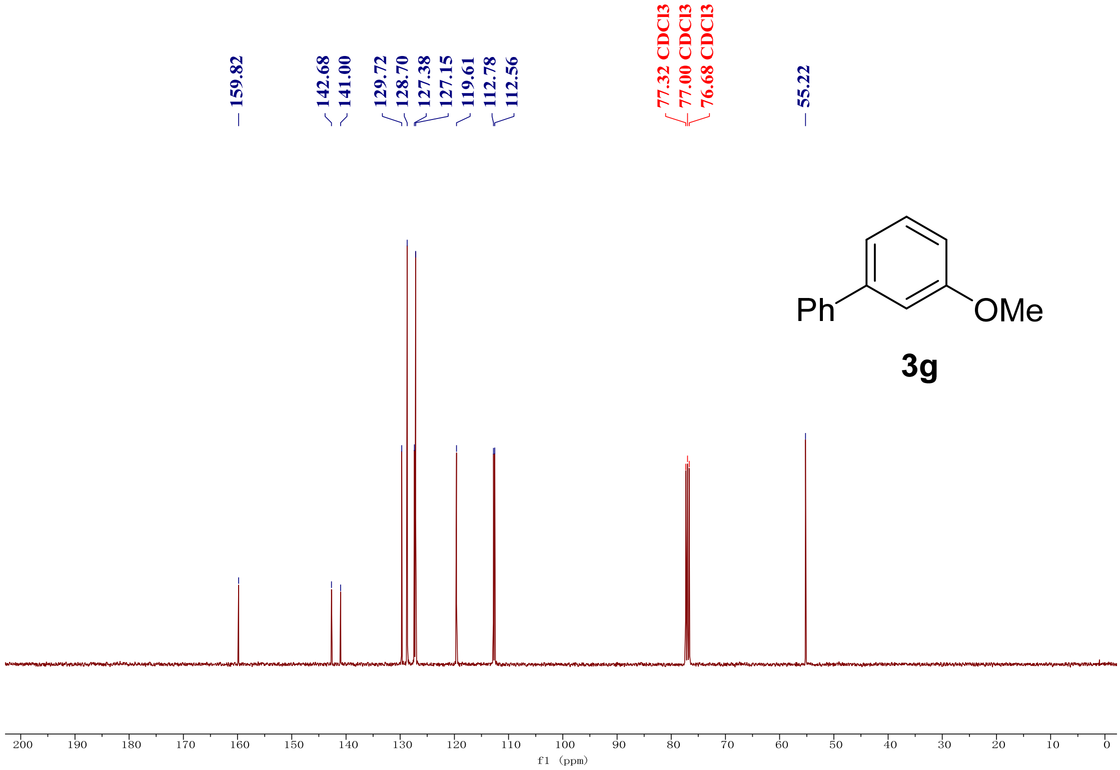
^{13}C NMR spectrum of 3f (100 MHz, CDCl$_3$)



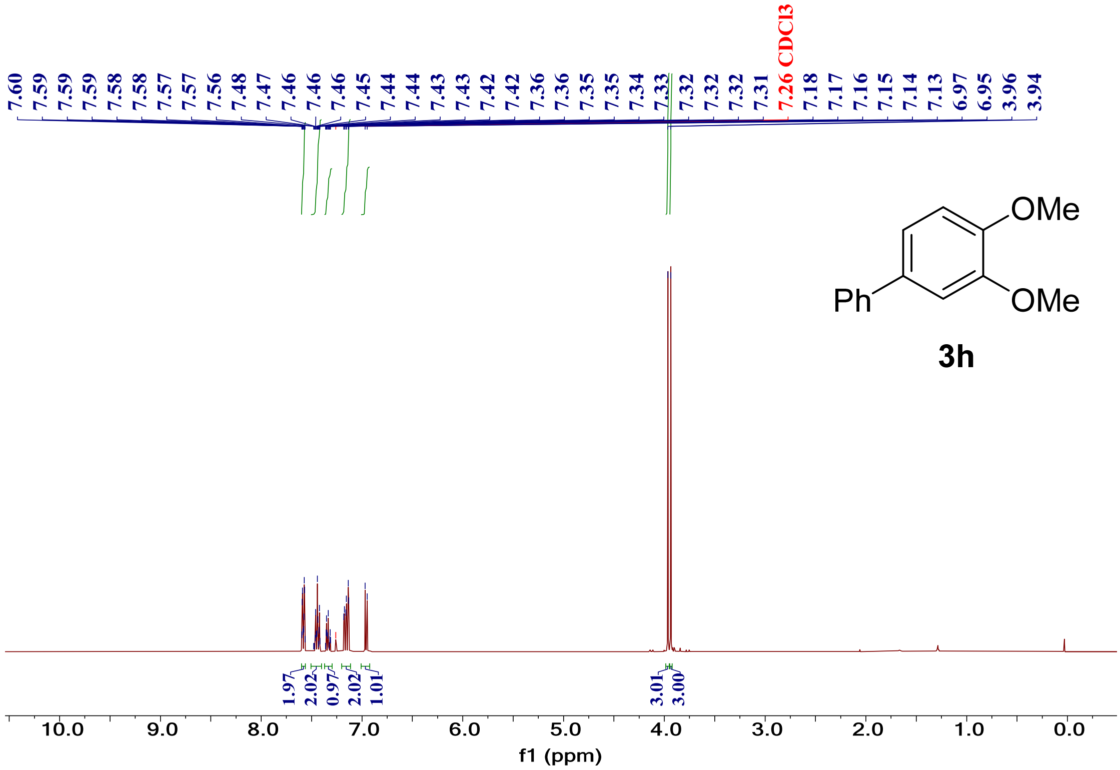
^{1}H NMR spectrum of 3g (400 MHz, CDCl$_3$)



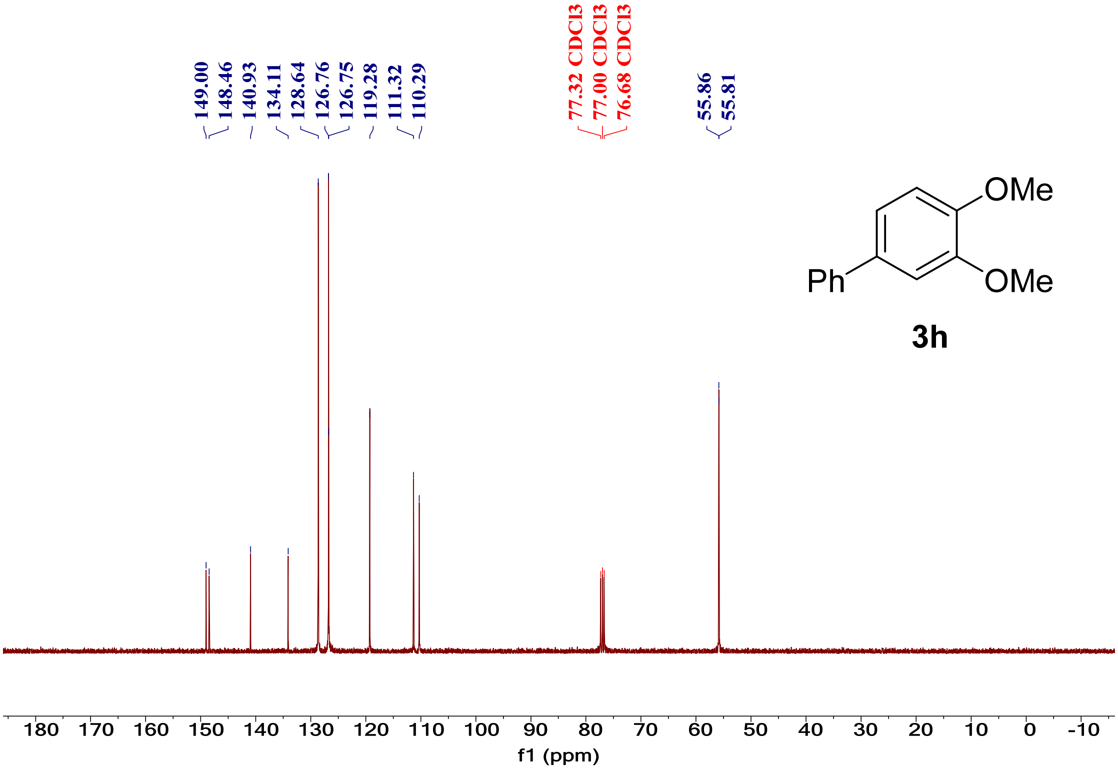
^{13}C NMR spectrum of 3g (100 MHz, CDCl$_3$)



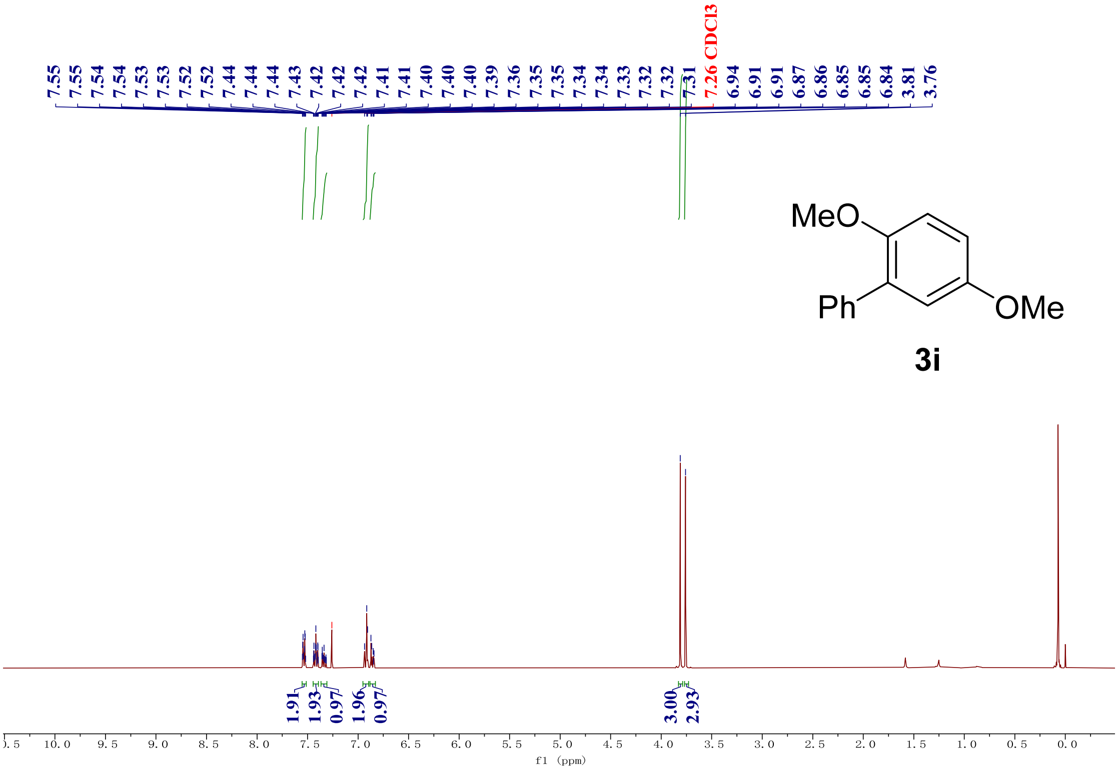
^{1}H NMR spectrum of 3h (400 MHz, CDCl$_3$)



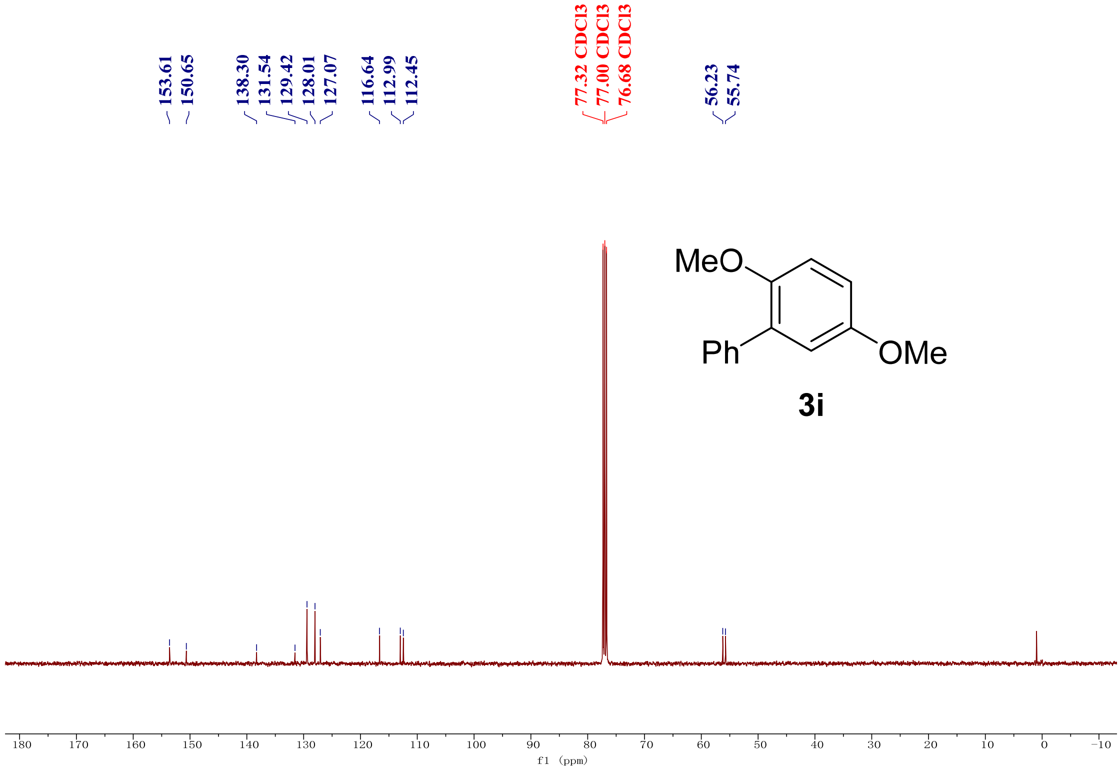
^{13}C NMR spectrum of 3h (100 MHz, $CDCl_3$)



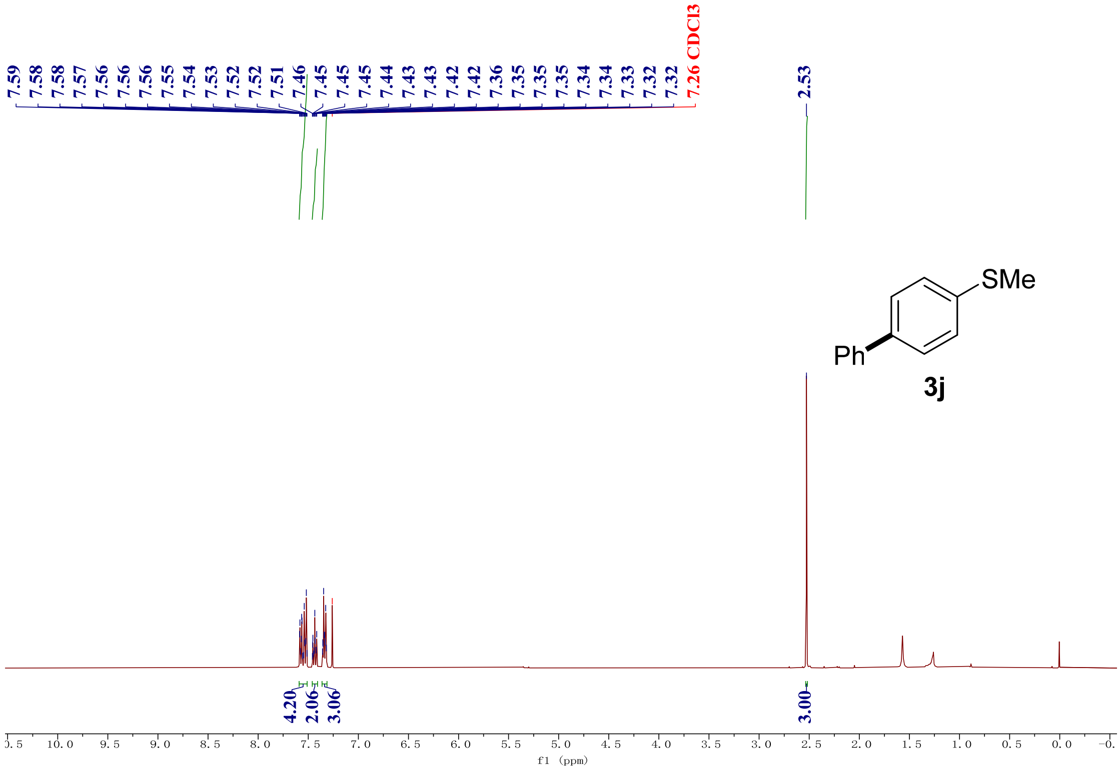
^{1}H NMR spectrum of 3i (400 MHz, $CDCl_3$)



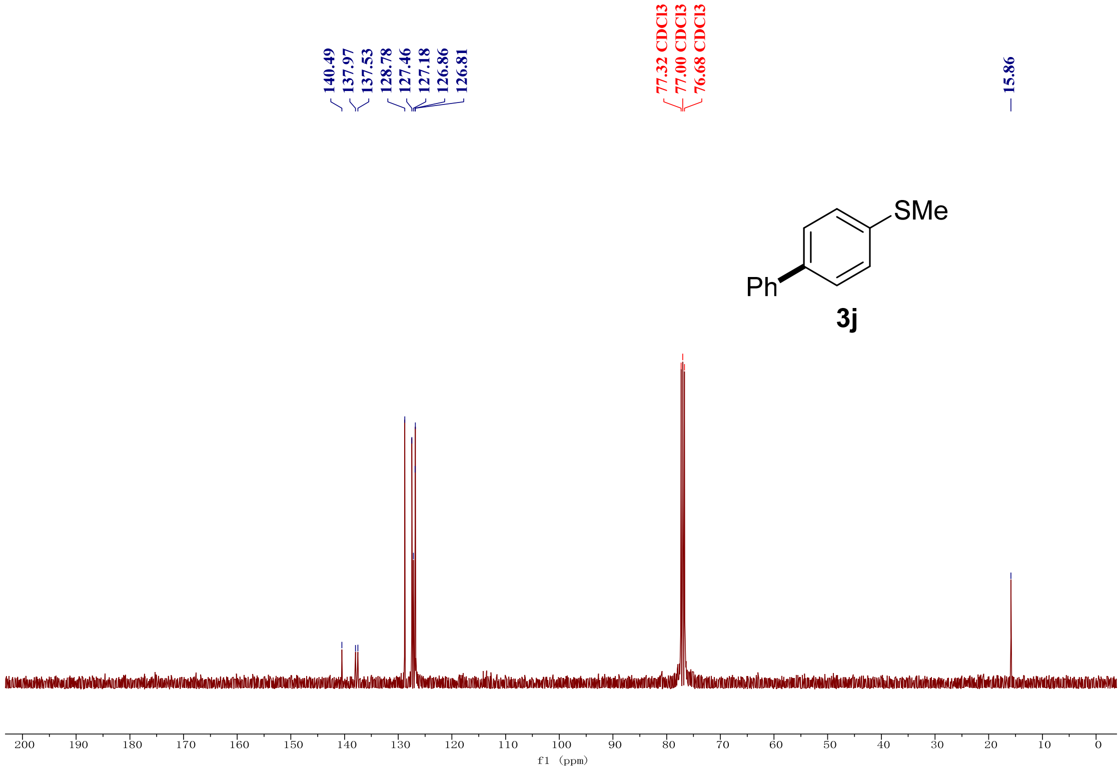
^{13}C NMR spectrum of 3i (100 MHz, CDCl$_3$)



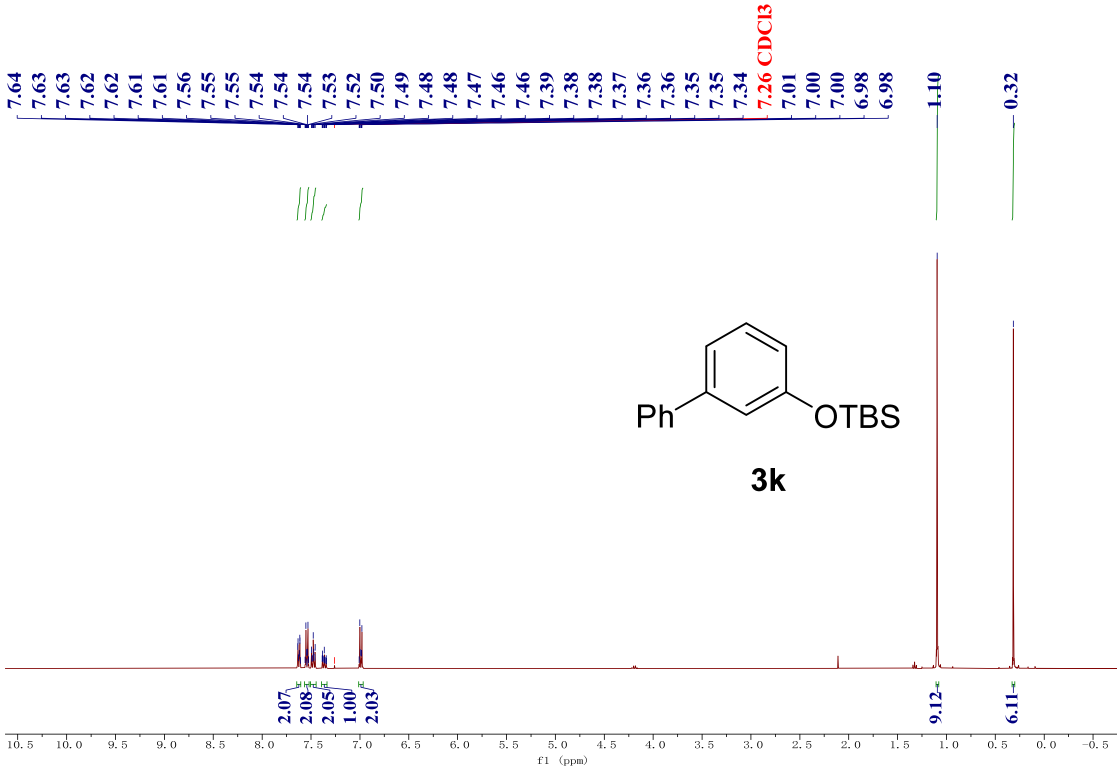
^{1}H NMR spectrum of 3j (400 MHz, CDCl$_3$)



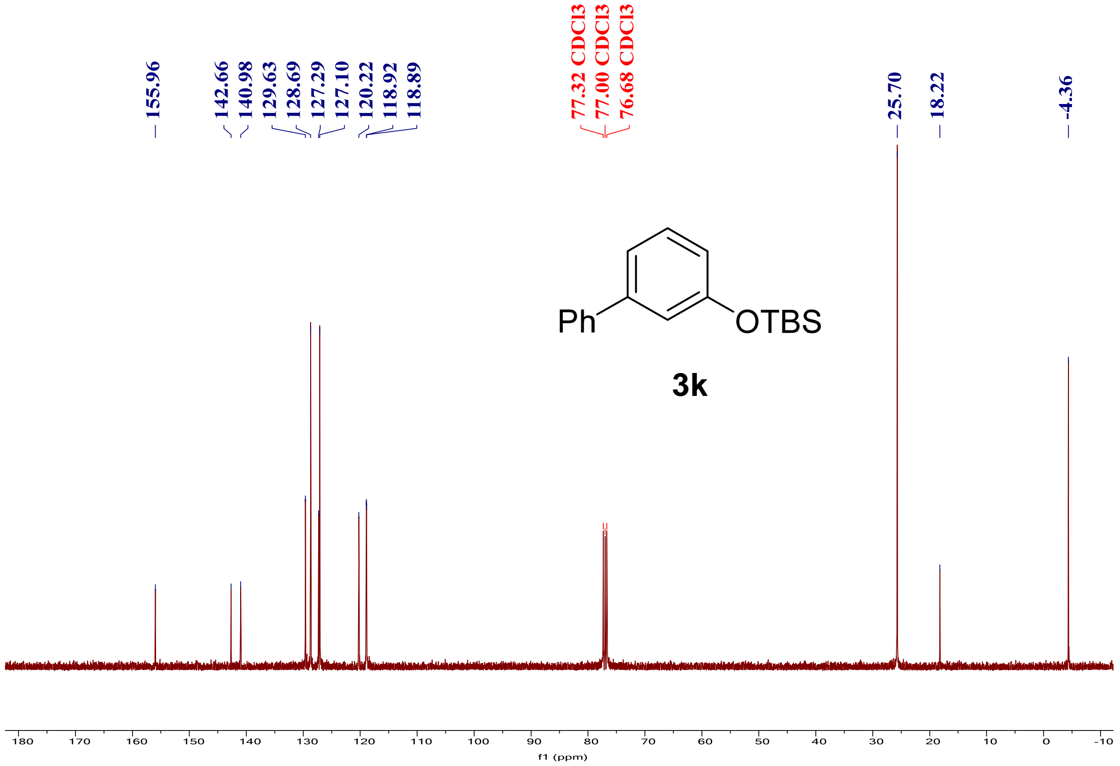
^{13}C NMR spectrum of 3j (100 MHz, CDCl$_3$)



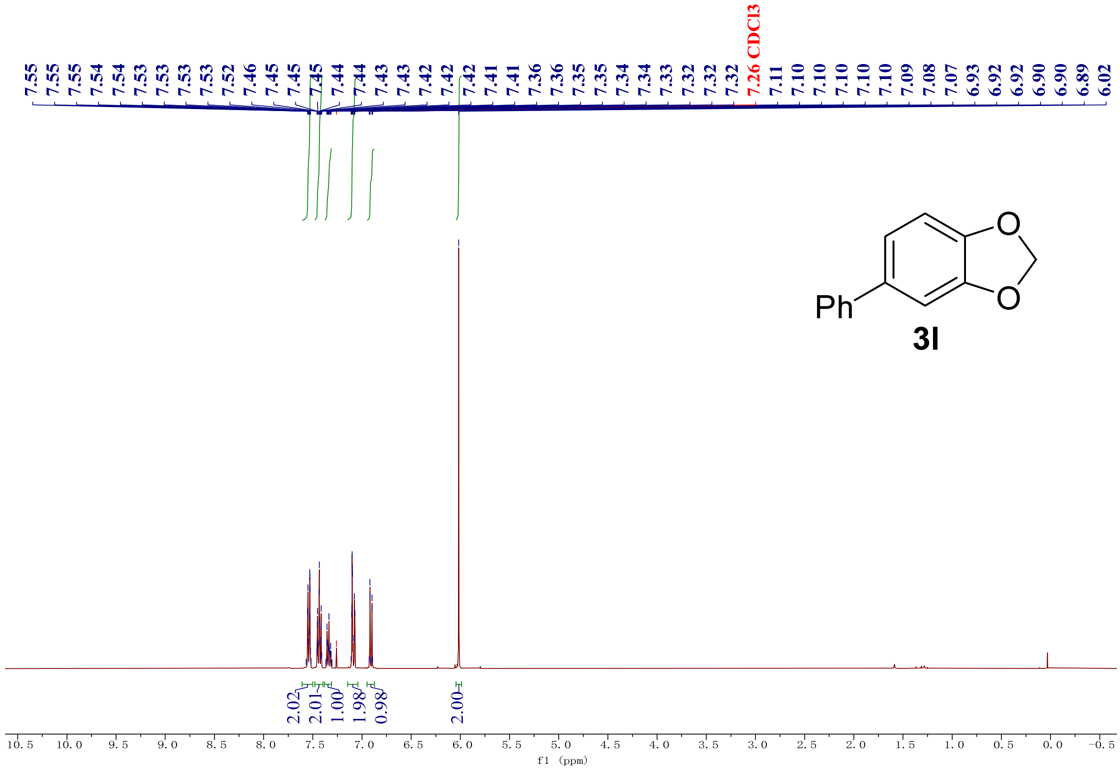
^{1}H NMR spectrum of 3k (400 MHz, CDCl$_3$)



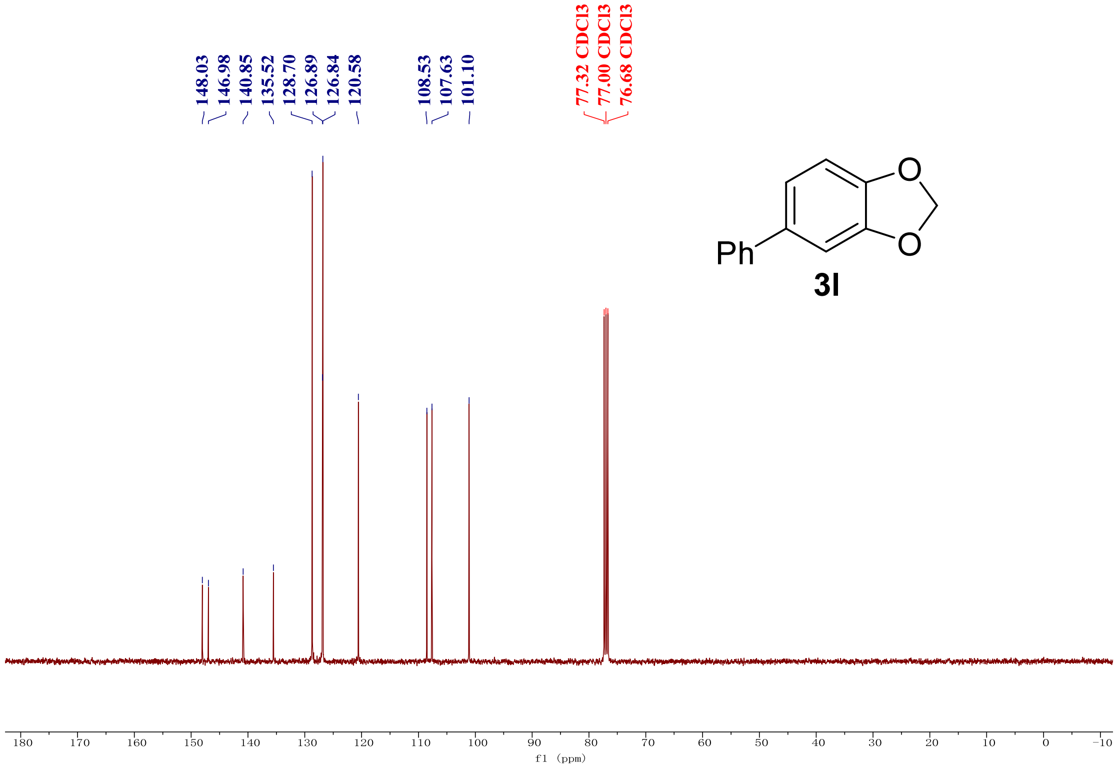
^{13}C NMR spectrum of 3k (100 MHz, CDCl$_3$)



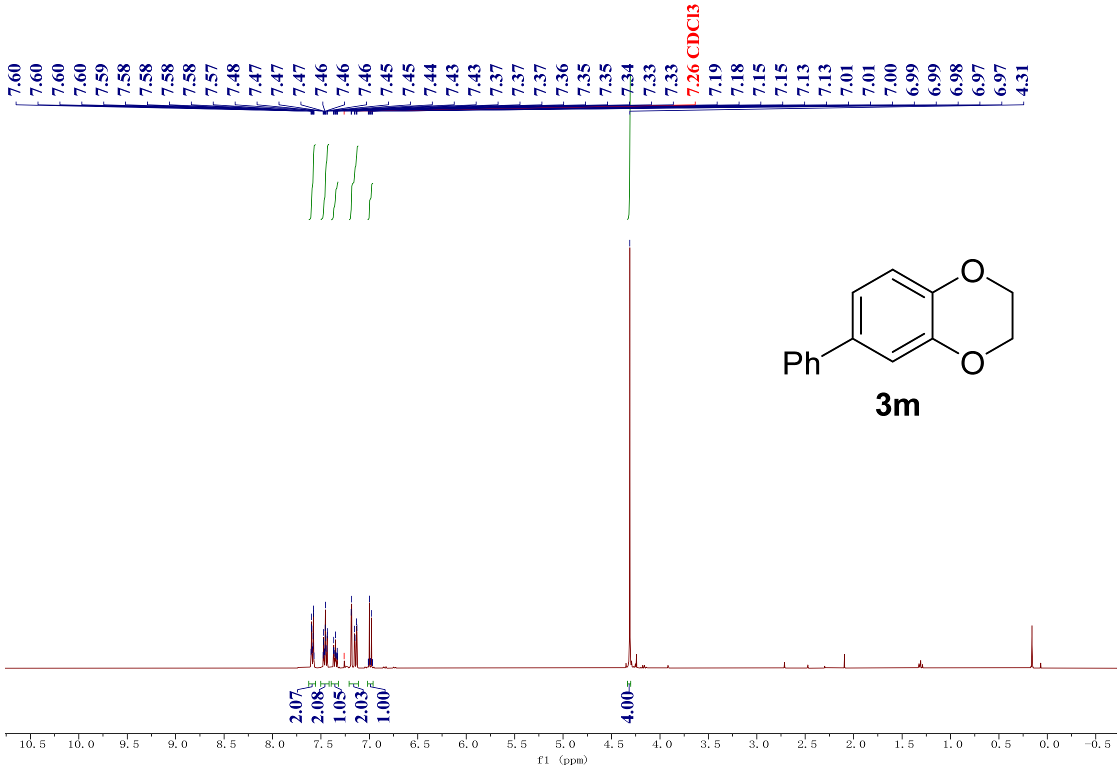
^{1}H NMR spectrum of 3l (400 MHz, CDCl$_3$)



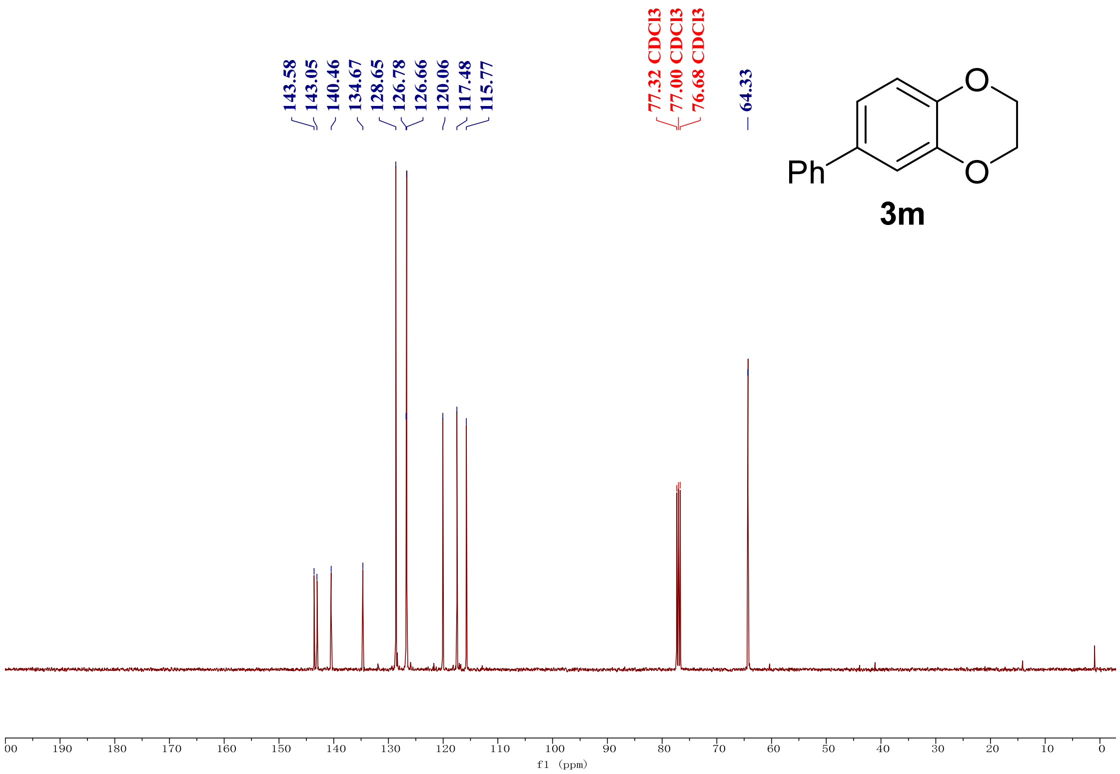
^{13}C NMR spectrum of 3l (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of 3m (400 MHz, $CDCl_3$)

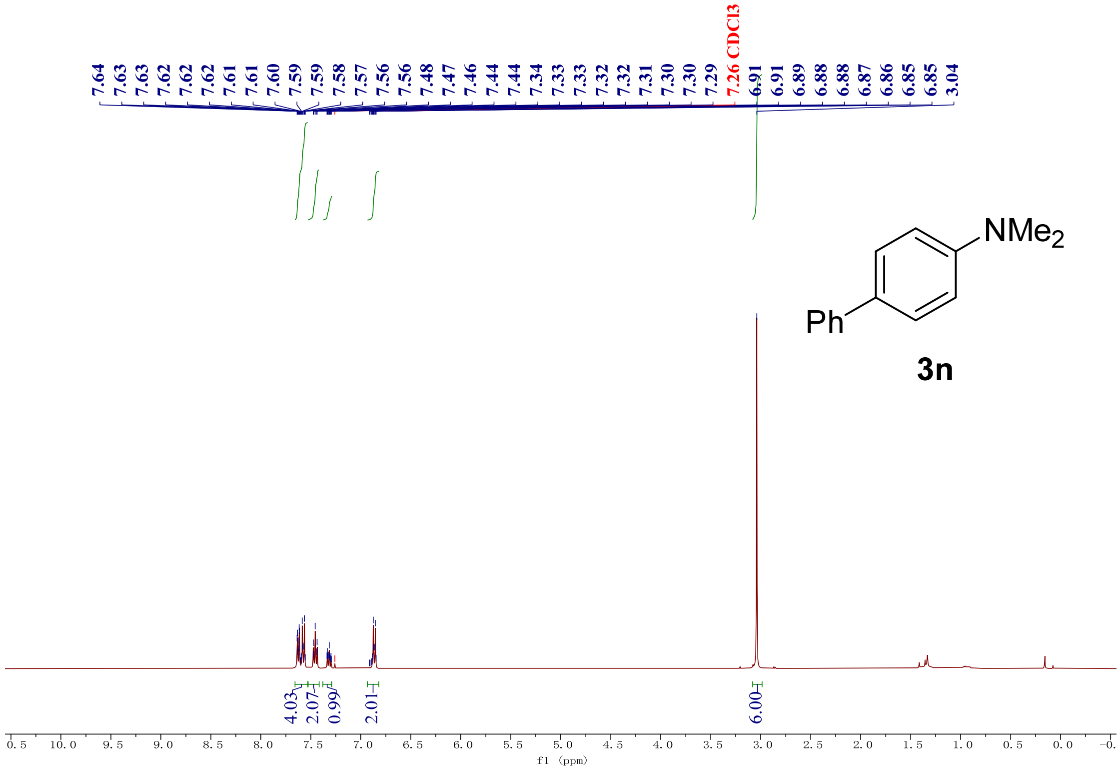


^{13}C NMR spectrum of 3m (100 MHz, CDCl$_3$)



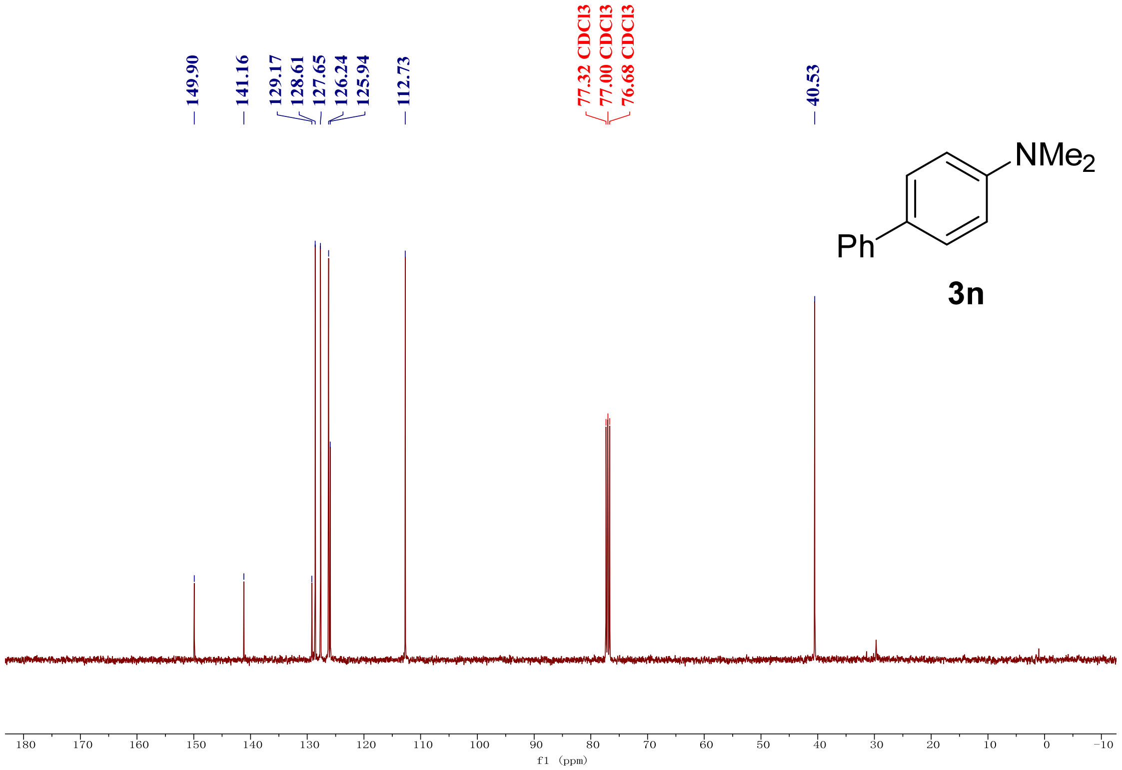
3m

^{1}H NMR spectrum of 3n (400 MHz, CDCl$_3$)

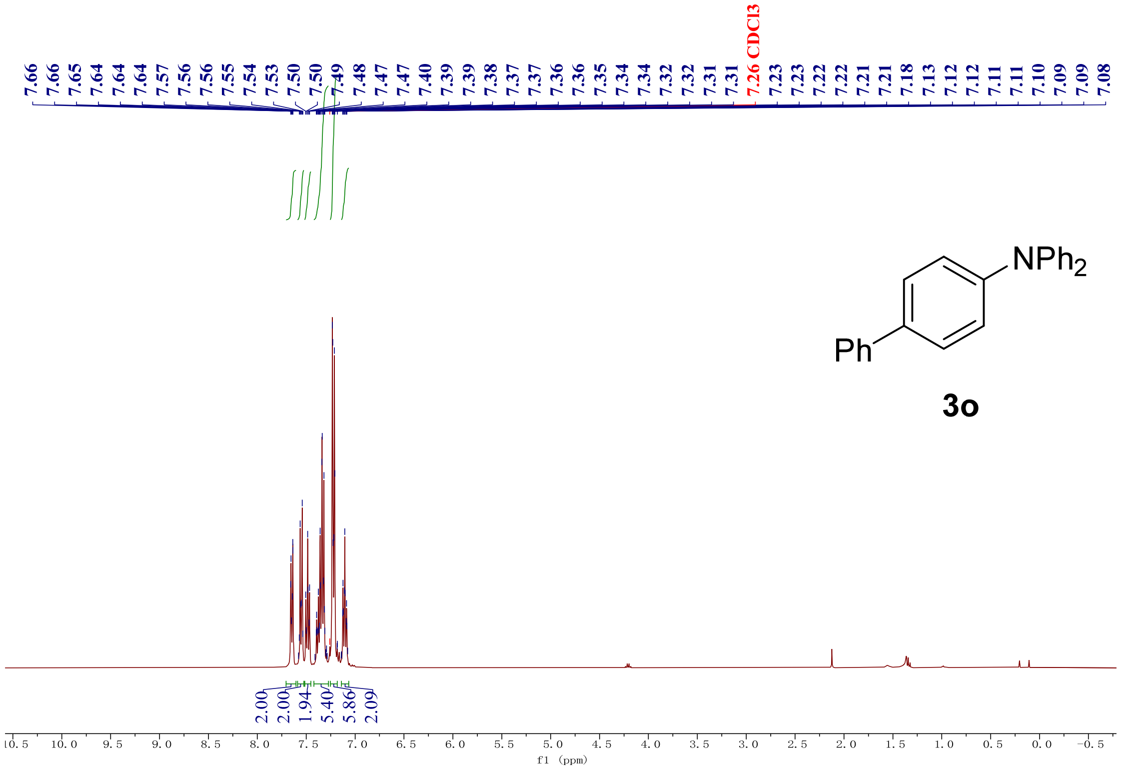


3n

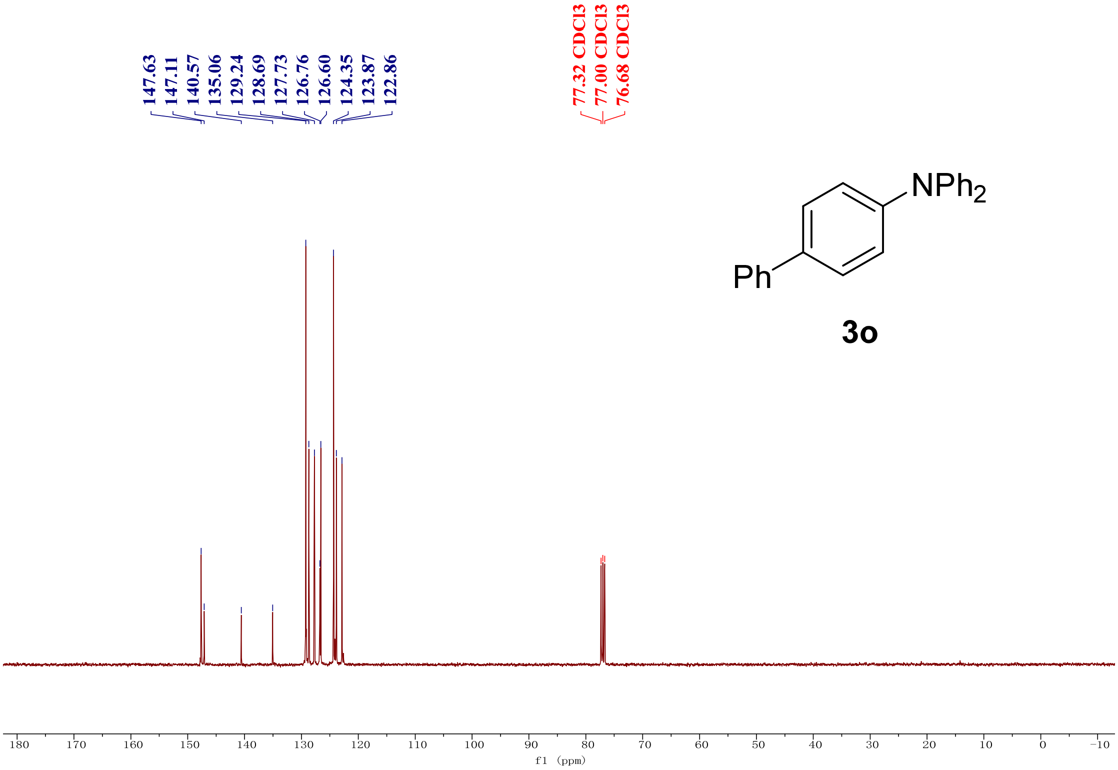
^{13}C NMR spectrum of 3n (100 MHz, $CDCl_3$)



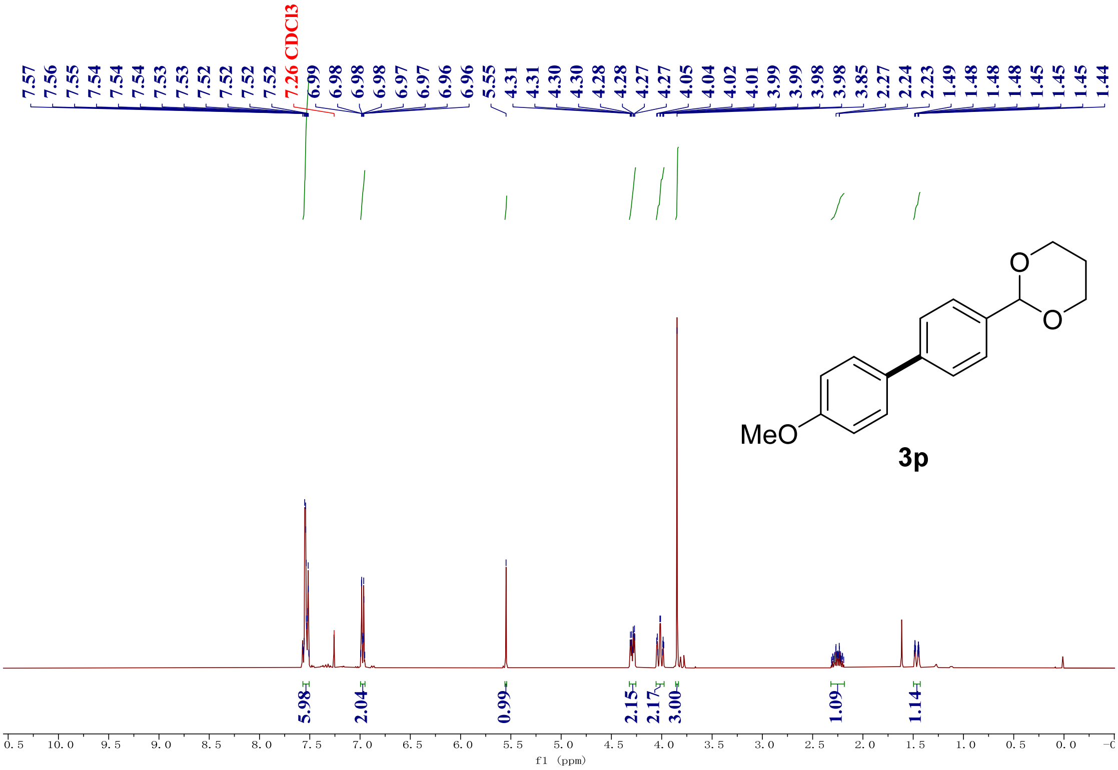
^{1}H NMR spectrum of 3o (400 MHz, $CDCl_3$)



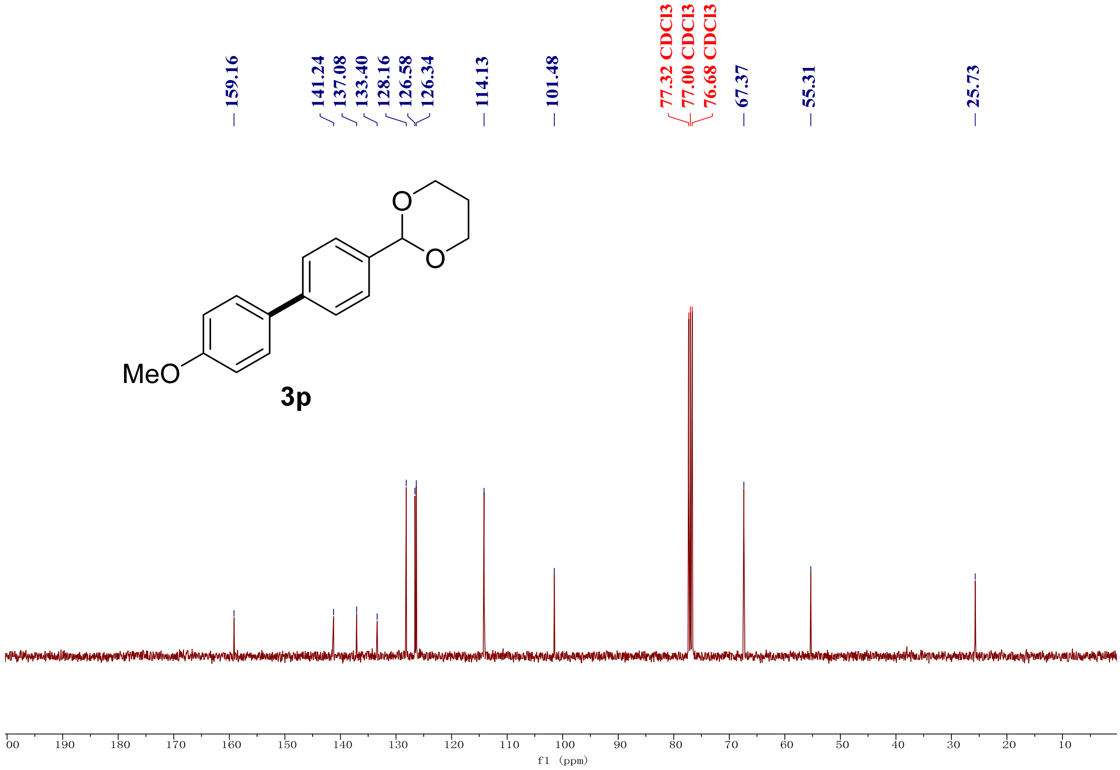
^{13}C NMR spectrum of 3o (100 MHz, $CDCl_3$)



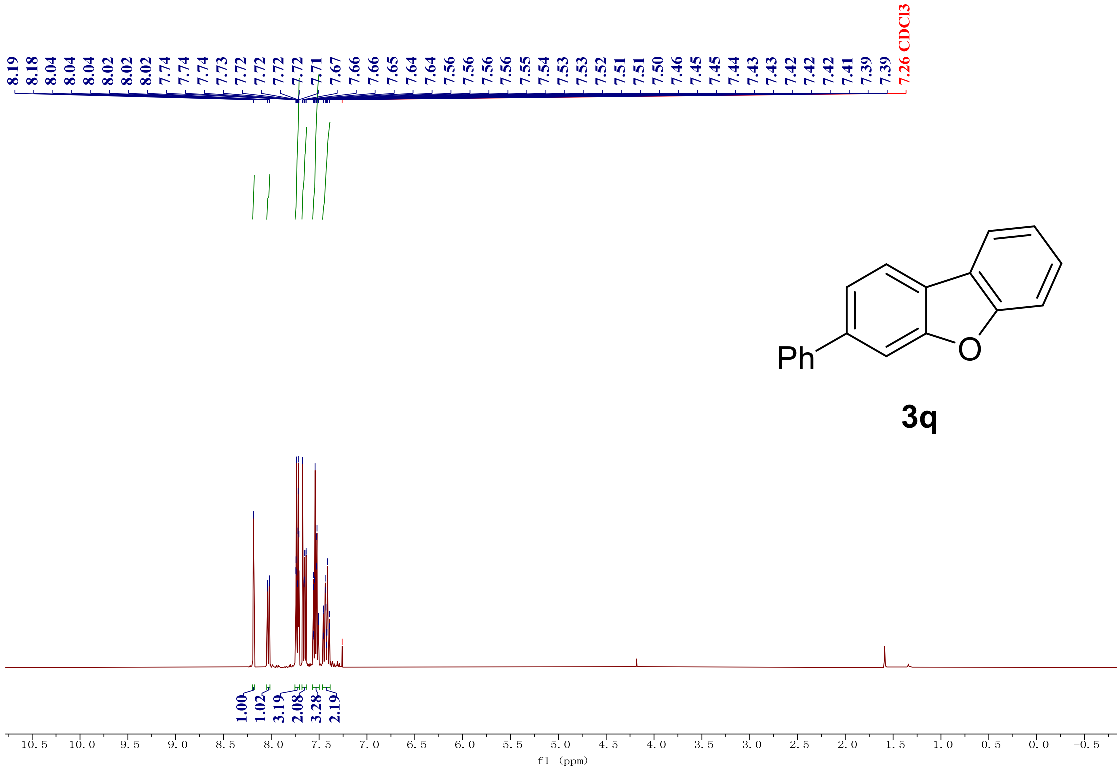
^{1}H NMR spectrum of 3p (400 MHz, $CDCl_3$)



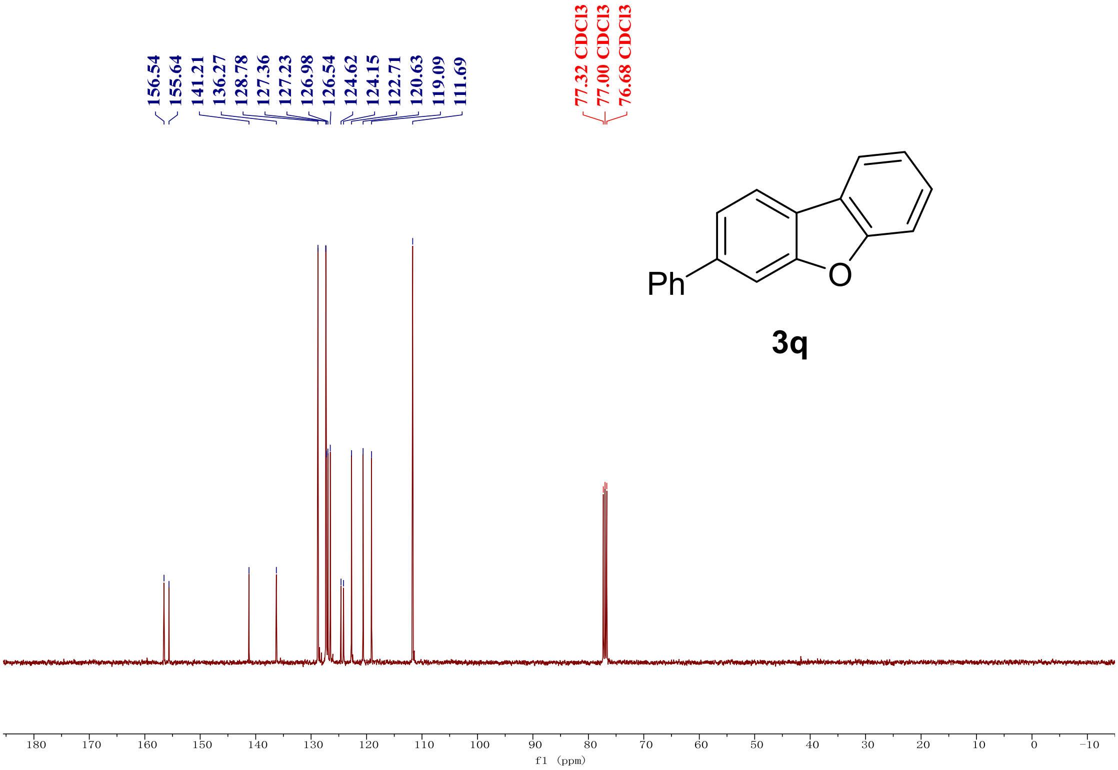
^{13}C NMR spectrum of 3p (100 MHz, CDCl$_3$)



^{1}H NMR spectrum of 3q (400 MHz, CDCl$_3$)

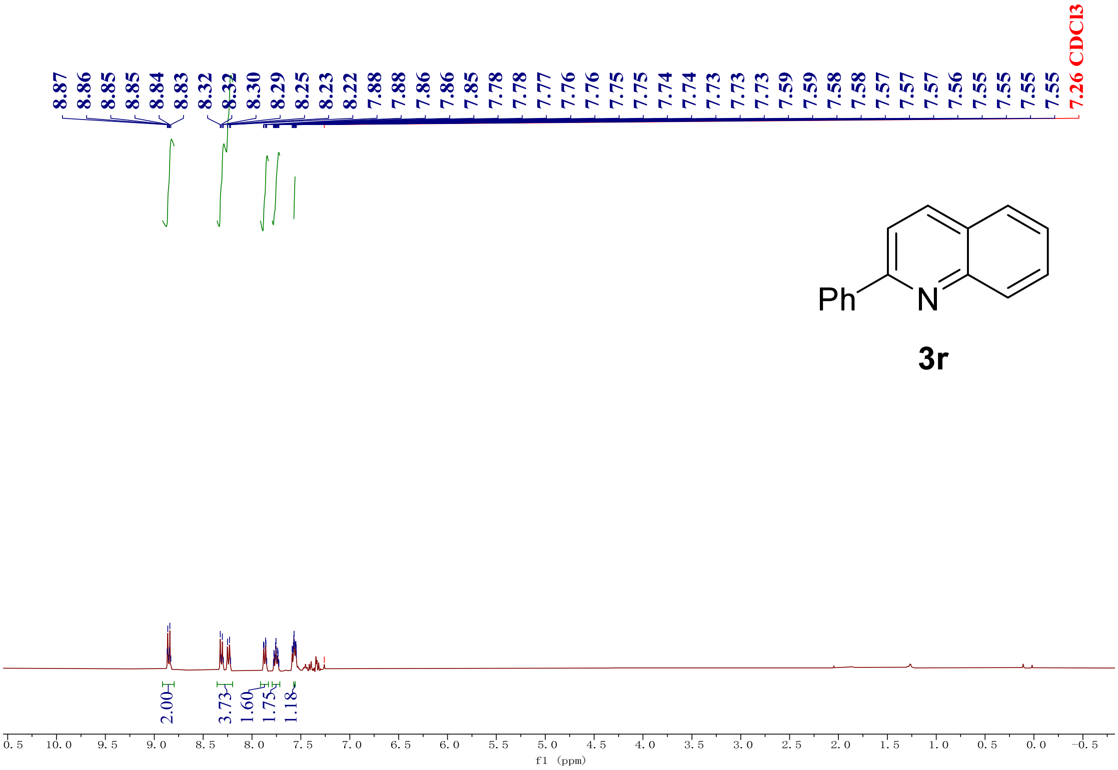


^{13}C NMR spectrum of 3q (100 MHz, CDCl$_3$)



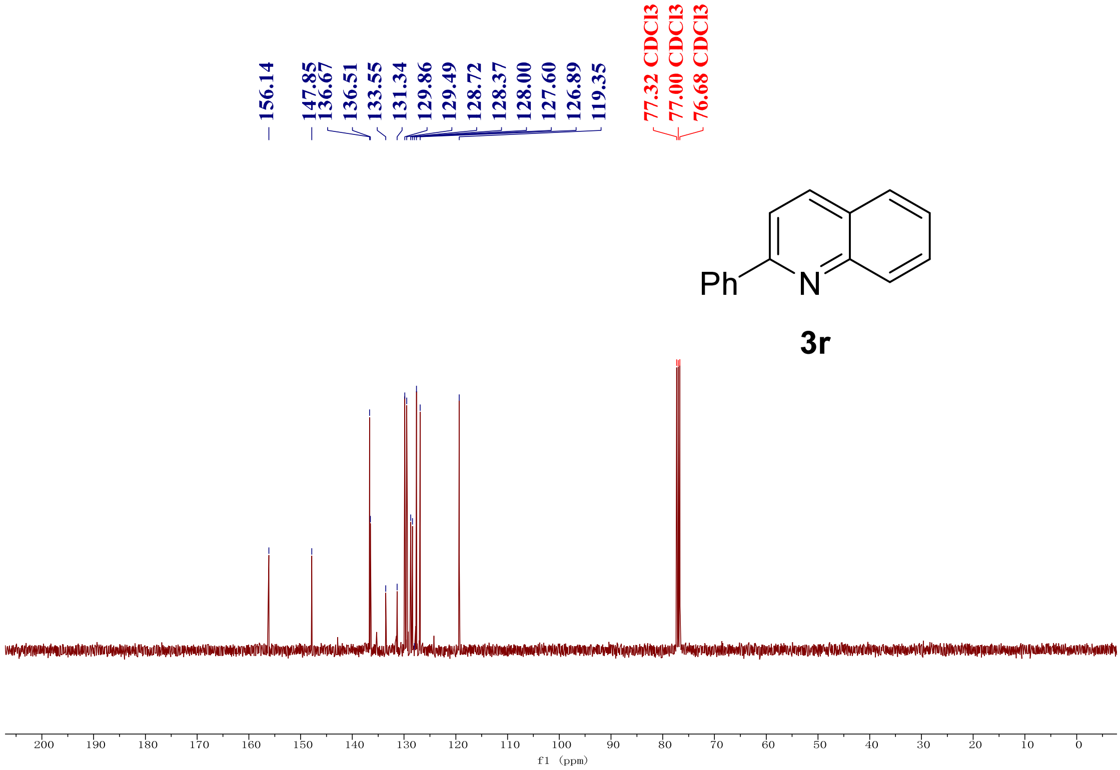
3q

^{1}H NMR spectrum of 3r (400 MHz, CDCl$_3$)

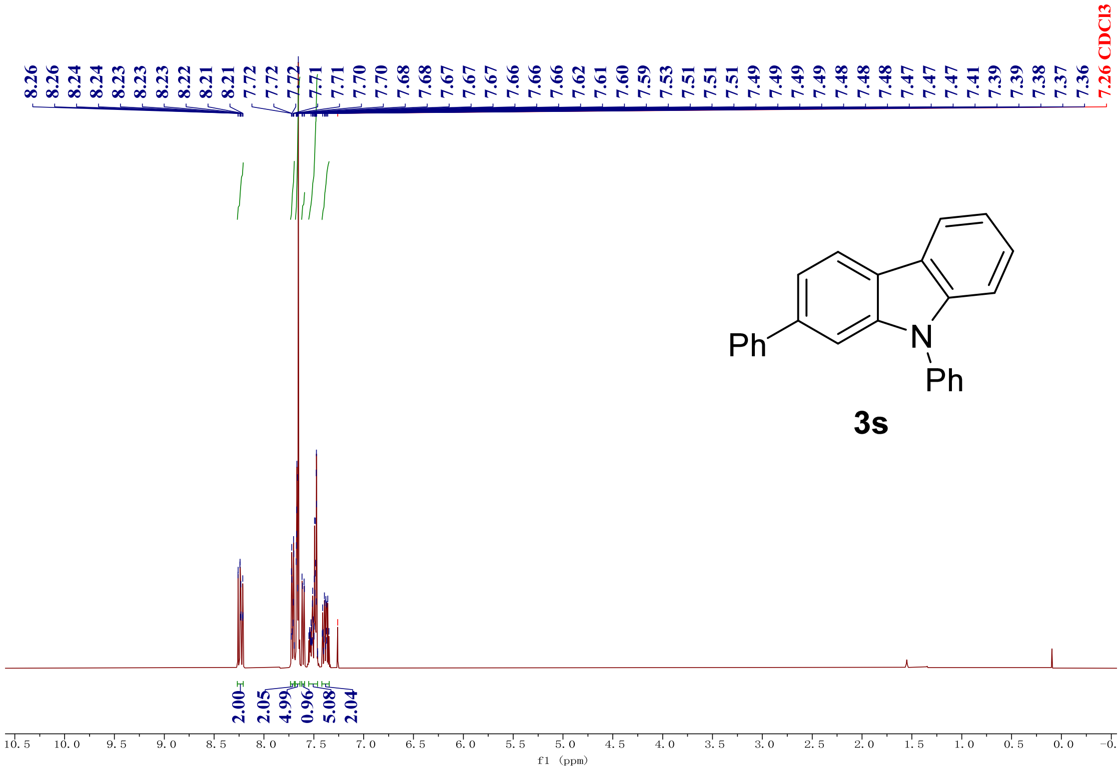


3r

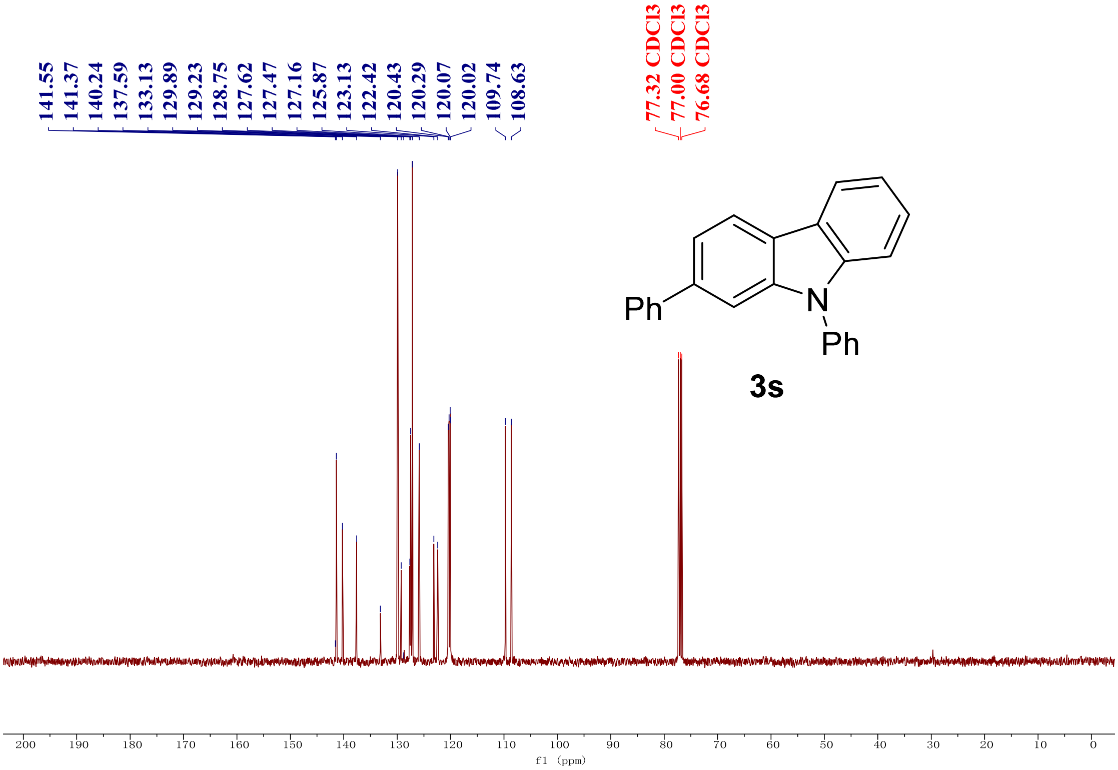
^{13}C NMR spectrum of 3r (100 MHz, CDCl$_3$)



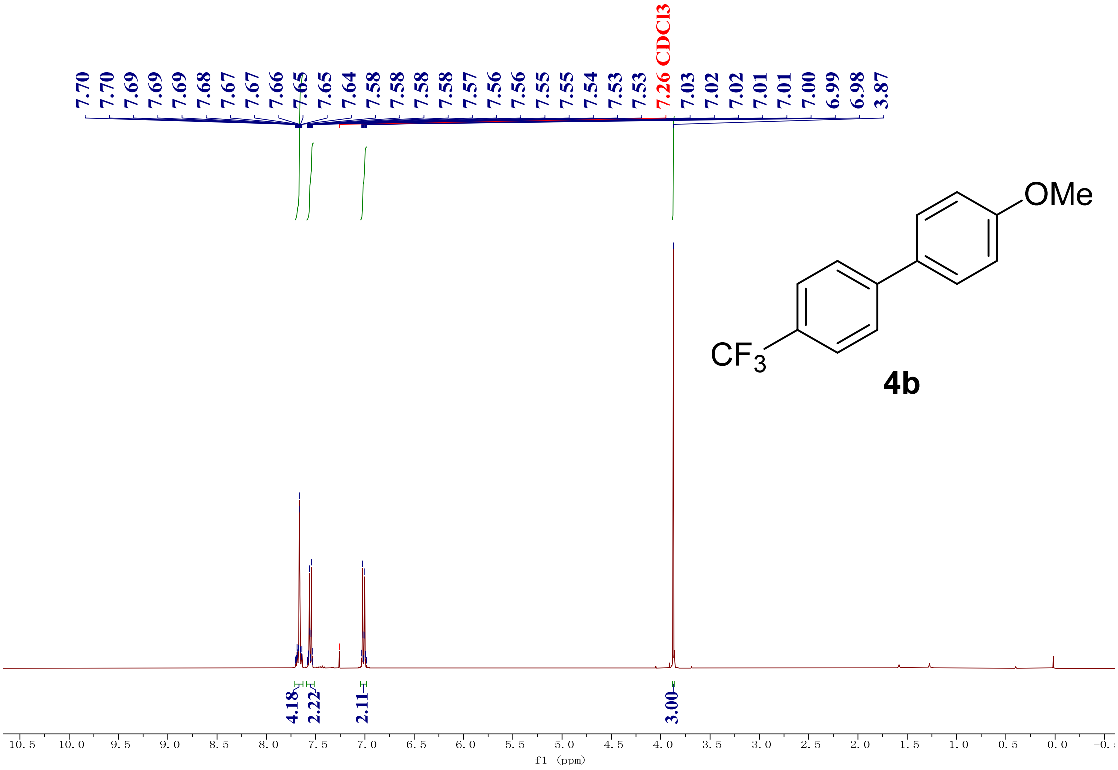
^{1}H NMR spectrum of 3s (400 MHz, CDCl$_3$)



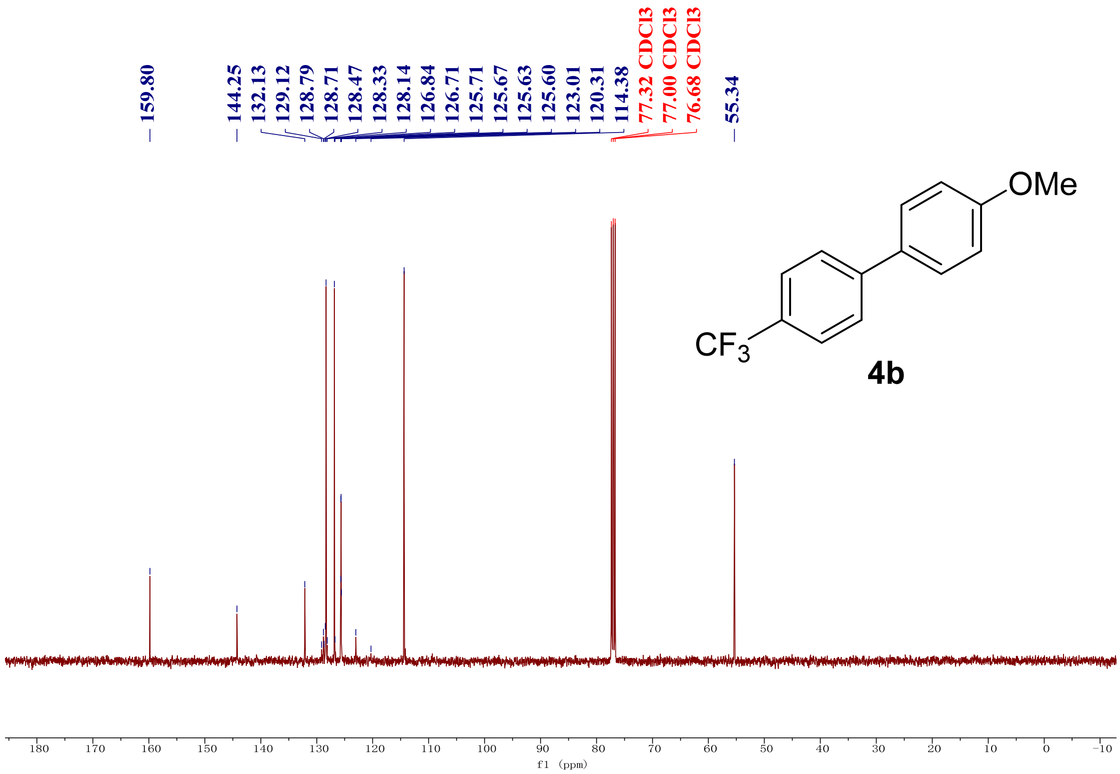
^{13}C NMR spectrum of 3s (100 MHz, CDCl$_3$)



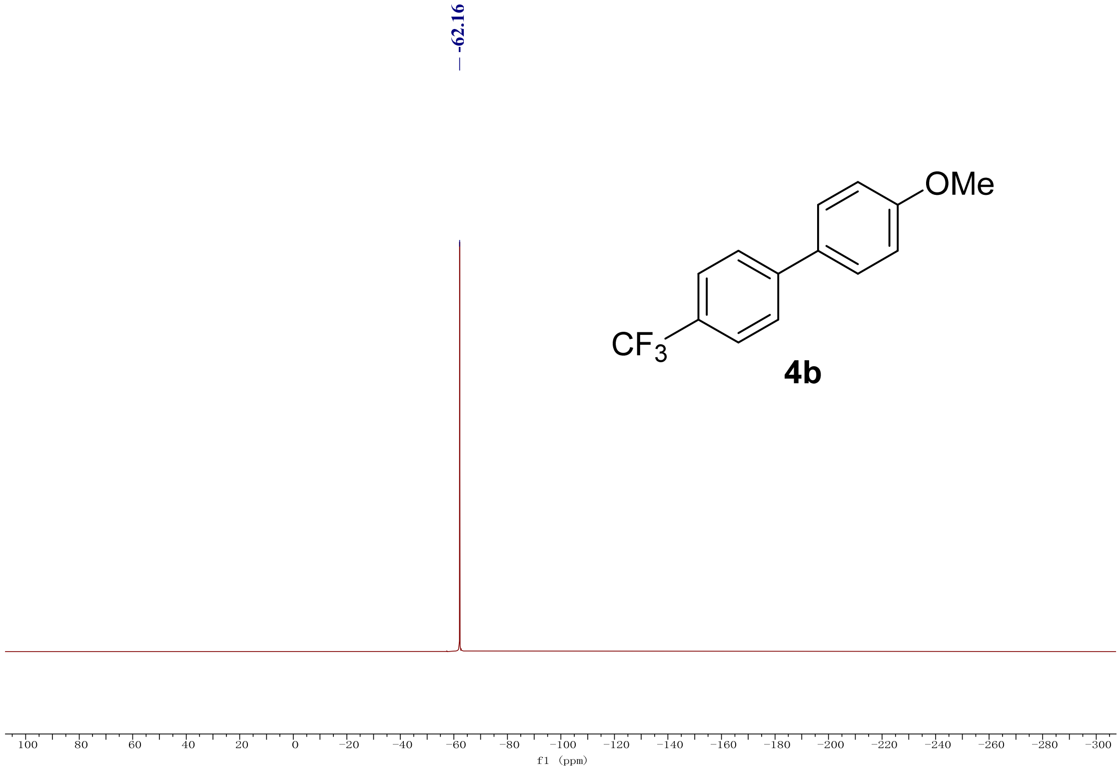
^{1}H NMR spectrum of 4b (400 MHz, CDCl$_3$)



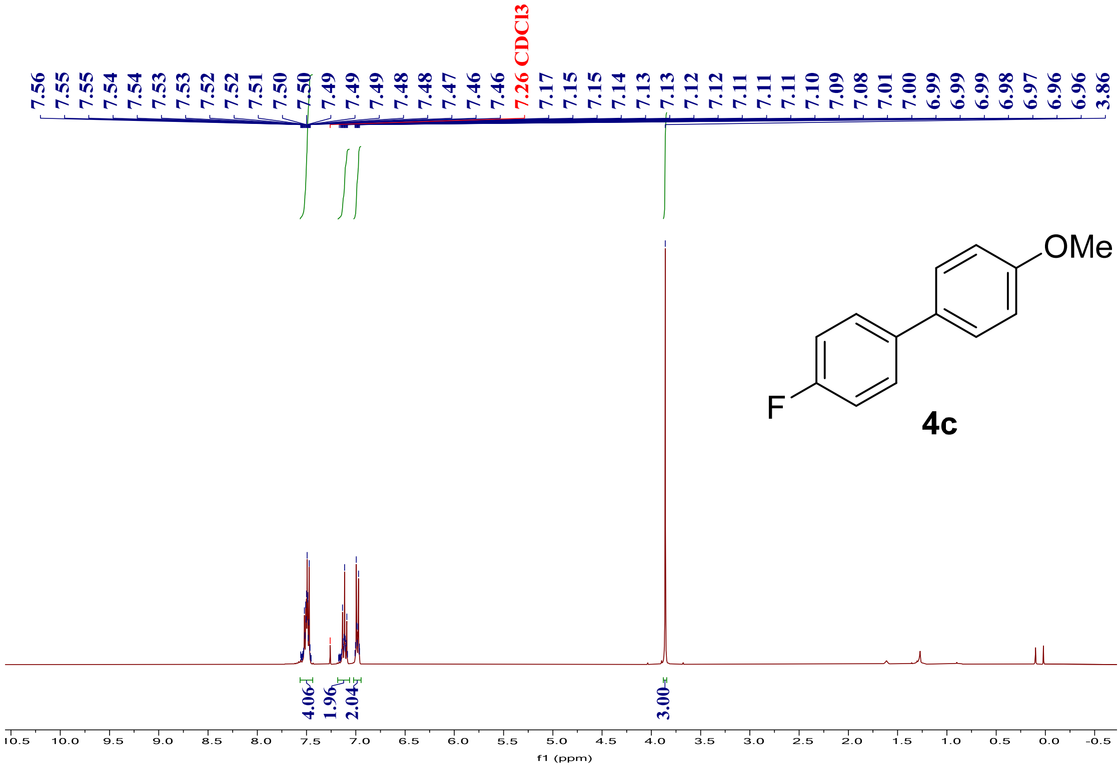
^{13}C NMR spectrum of 4b (100 MHz, CDCl$_3$)



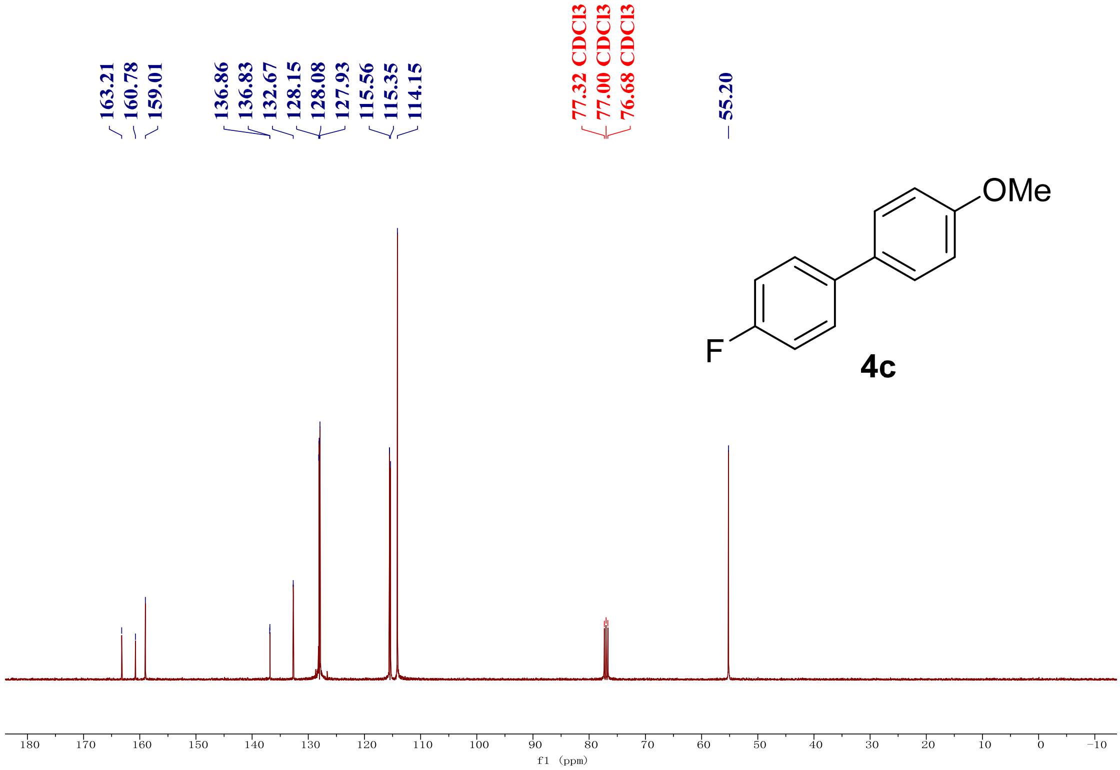
^{19}F NMR spectrum of 4b (376 MHz, CDCl$_3$)



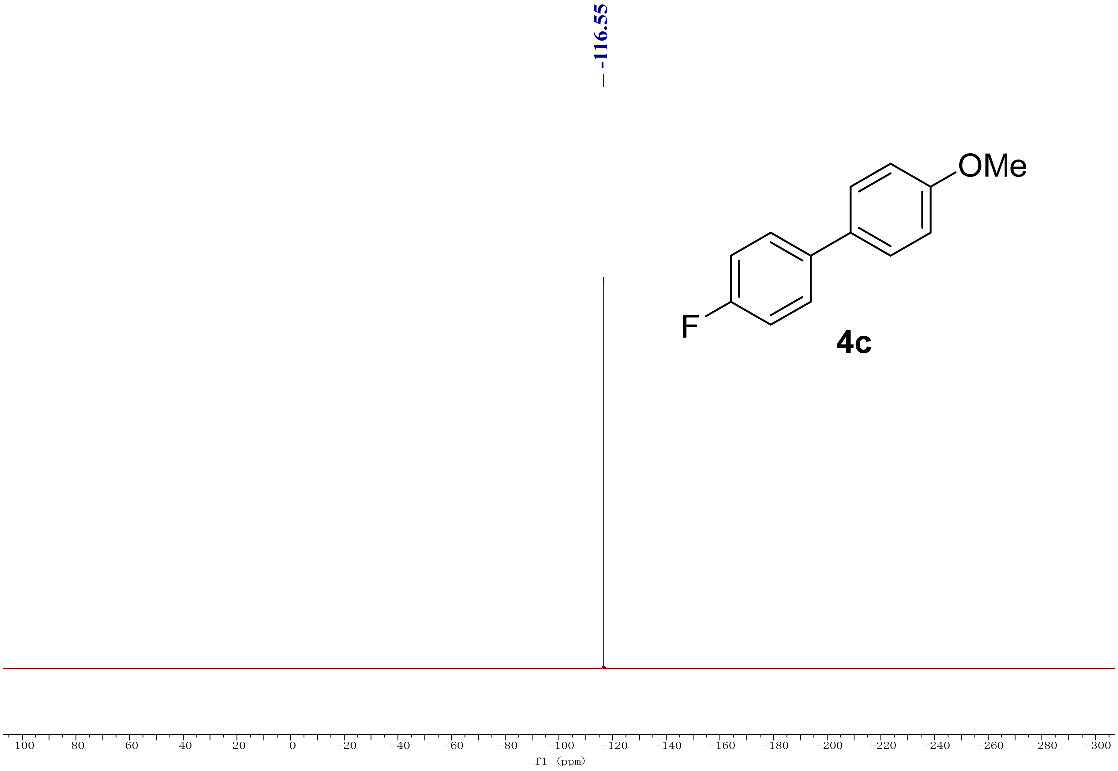
^{1}H NMR spectrum of 4c (400 MHz, $CDCl_3$)



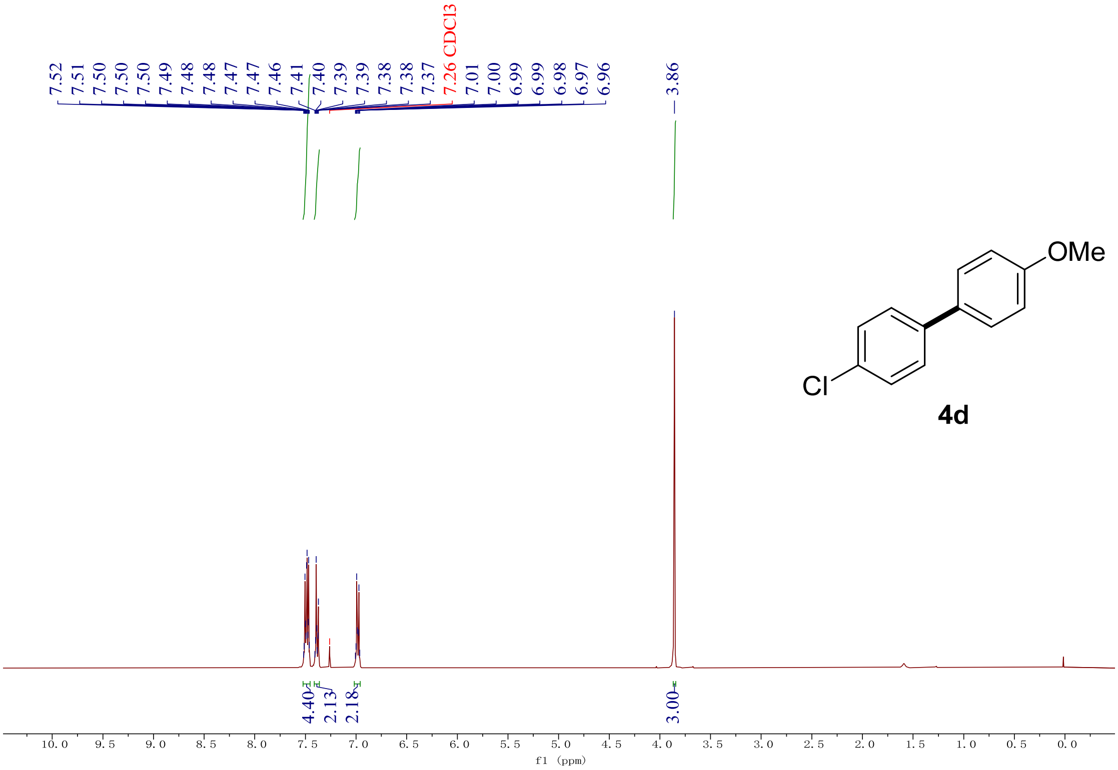
^{13}C NMR spectrum of 4c (100 MHz, $CDCl_3$)



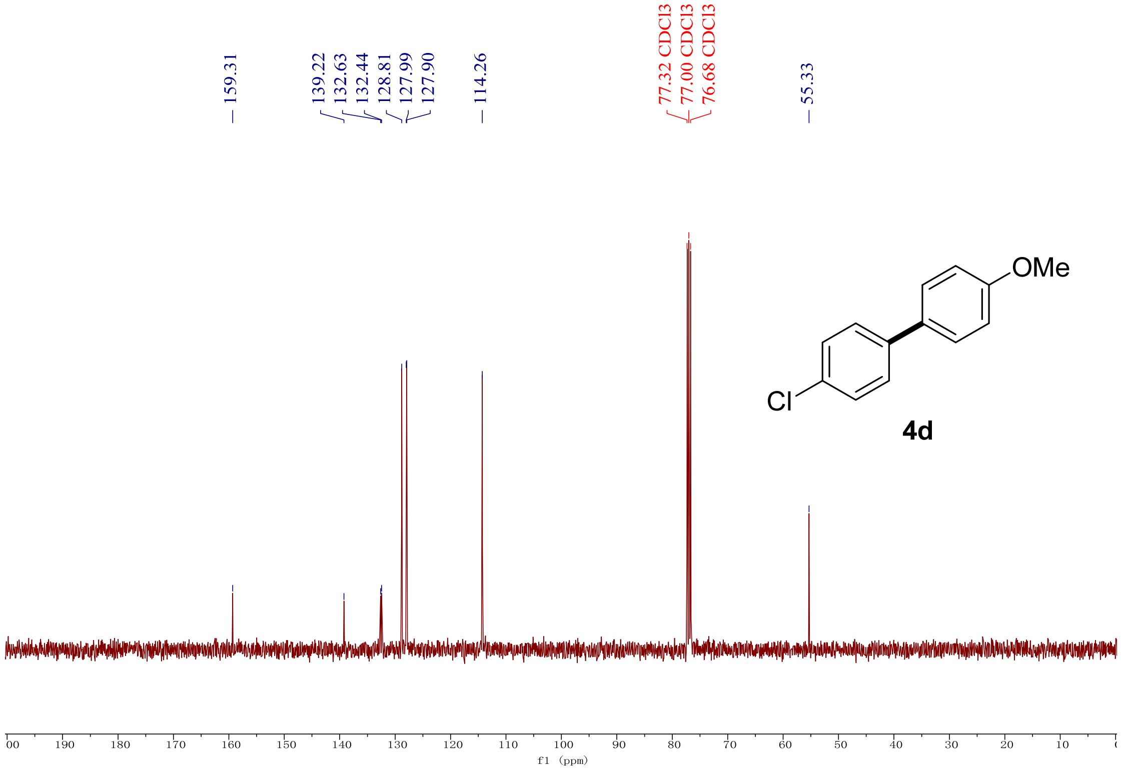
^{19}F NMR spectrum of 4c (376 MHz, $CDCl_3$)



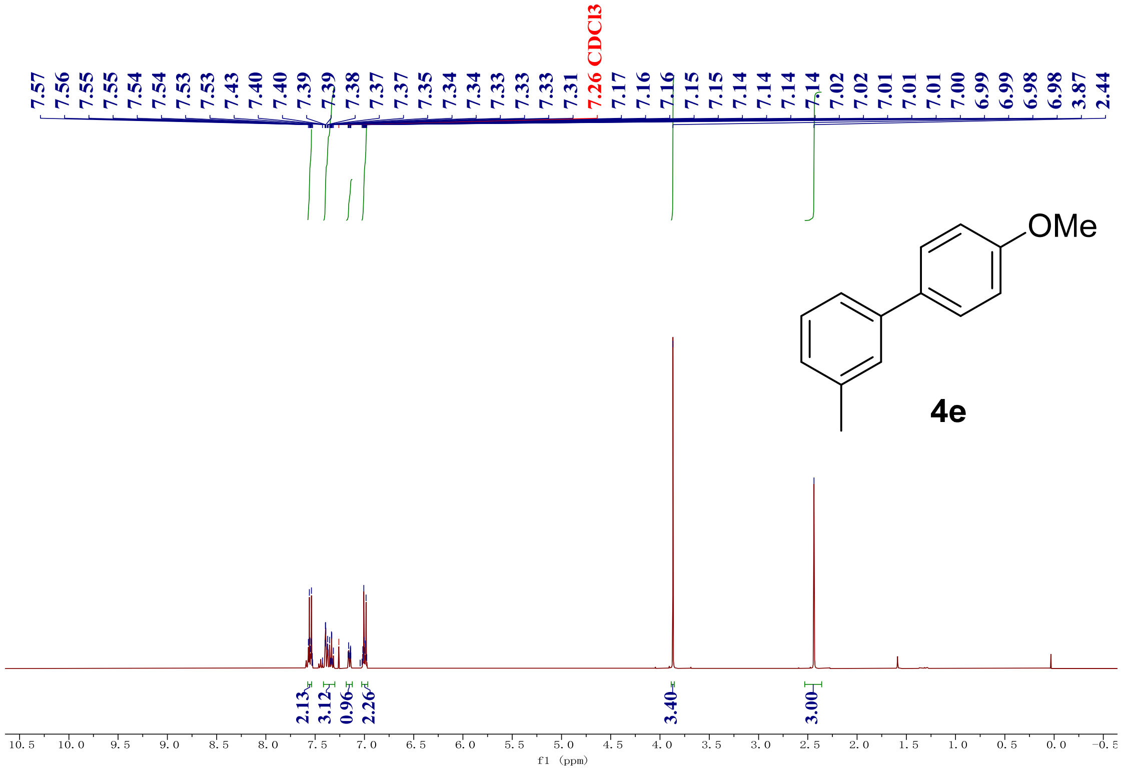
^{1}H NMR spectrum of 4d (400 MHz, $CDCl_3$)



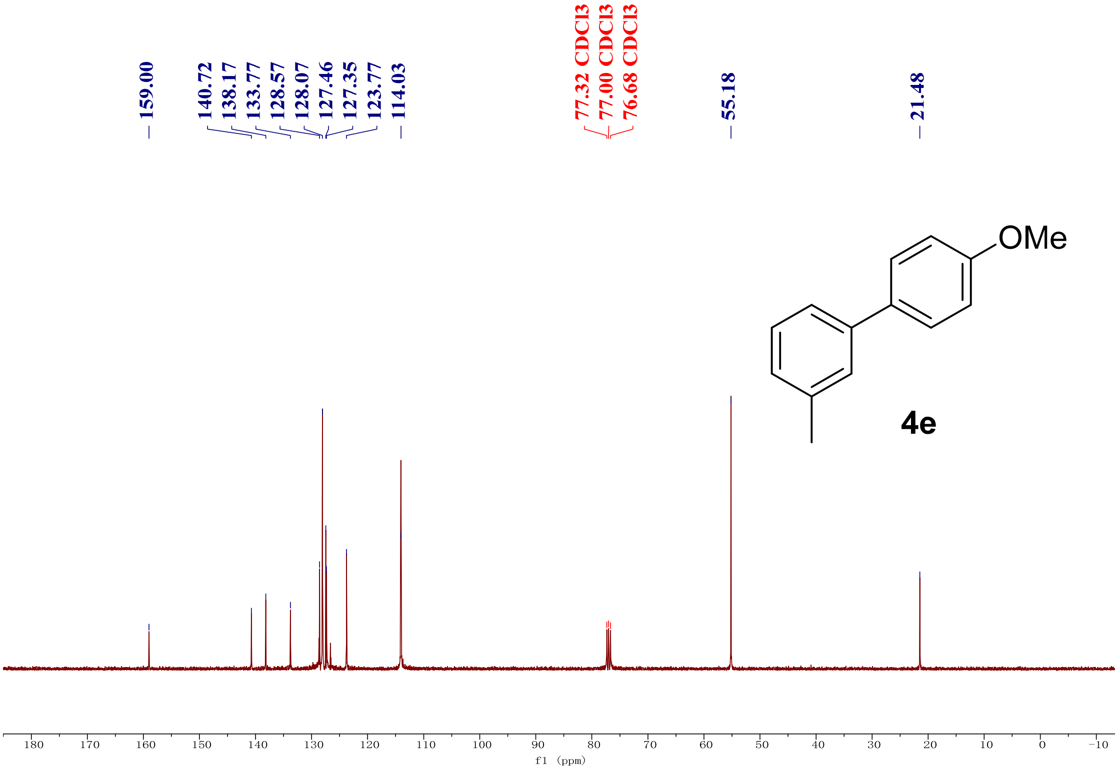
^{13}C NMR spectrum of 4d (100 MHz, $CDCl_3$)



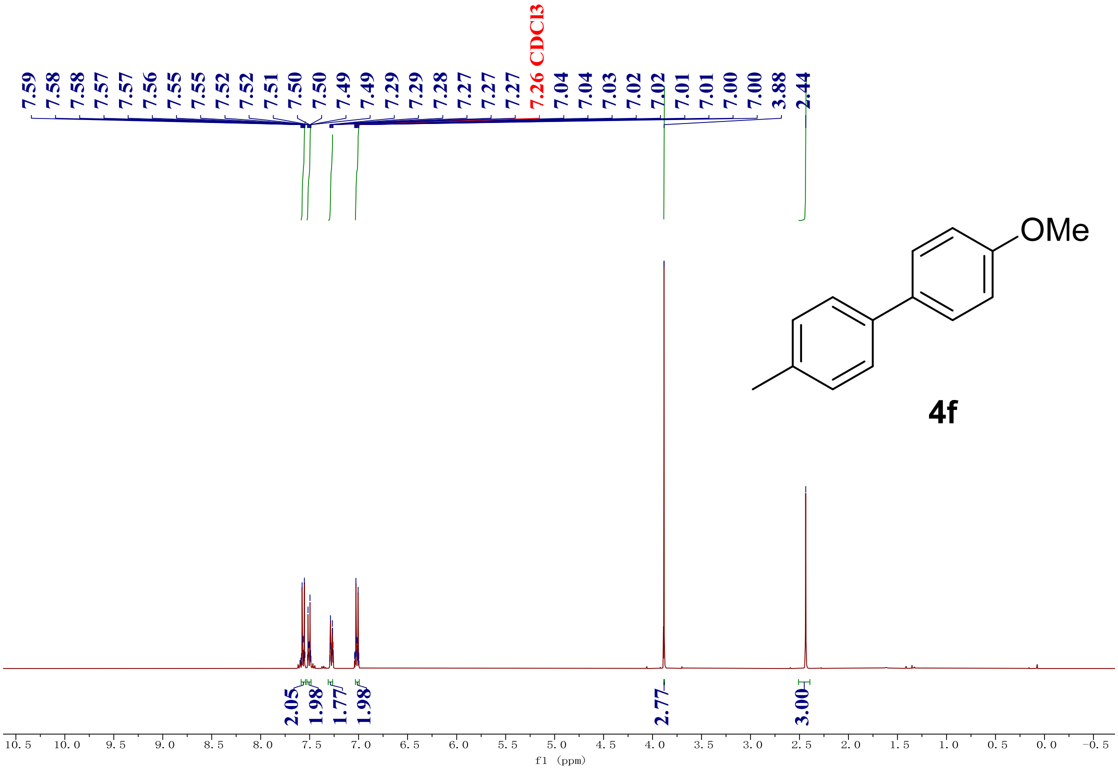
^{1}H NMR spectrum of 4e (400 MHz, $CDCl_3$)



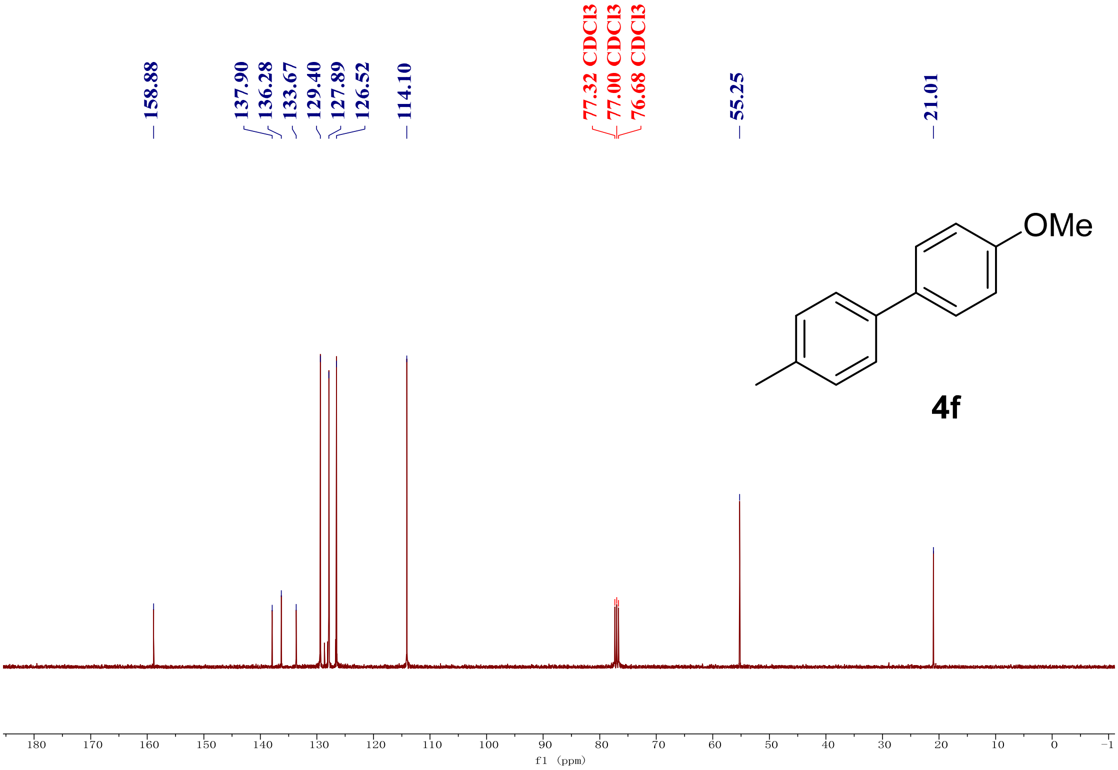
^{13}C NMR spectrum of 4e (100 MHz, CDCl$_3$)



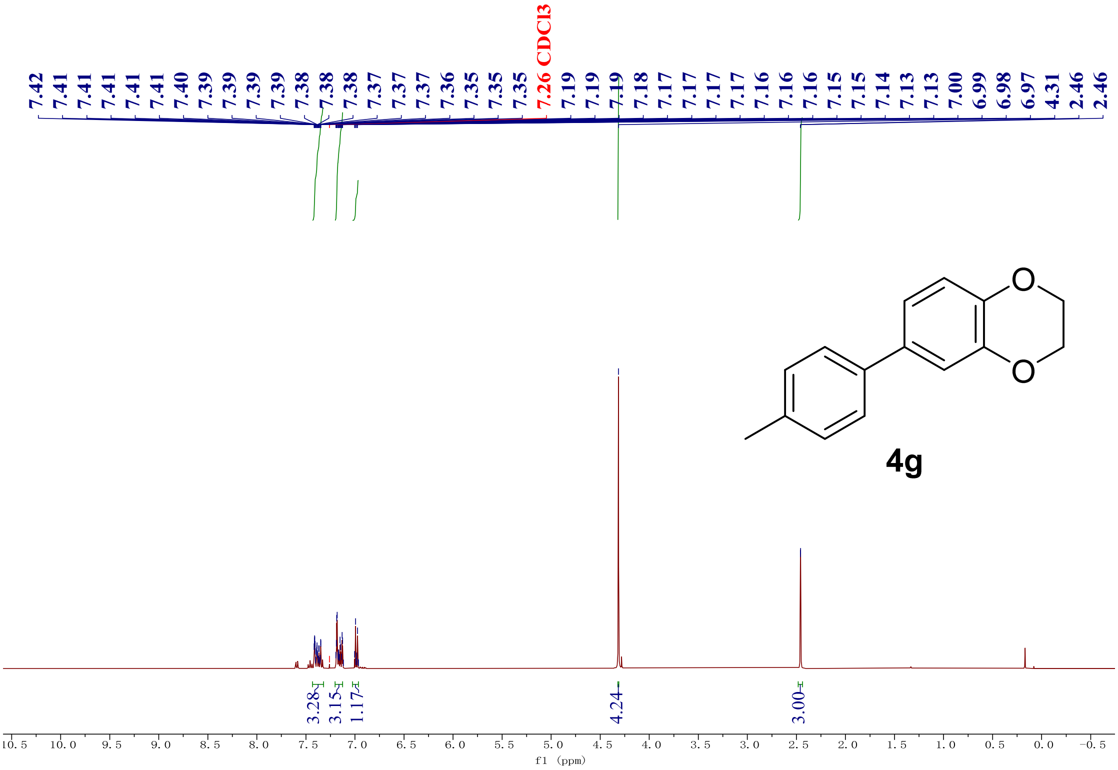
^{1}H NMR spectrum of 4f (400 MHz, CDCl$_3$)



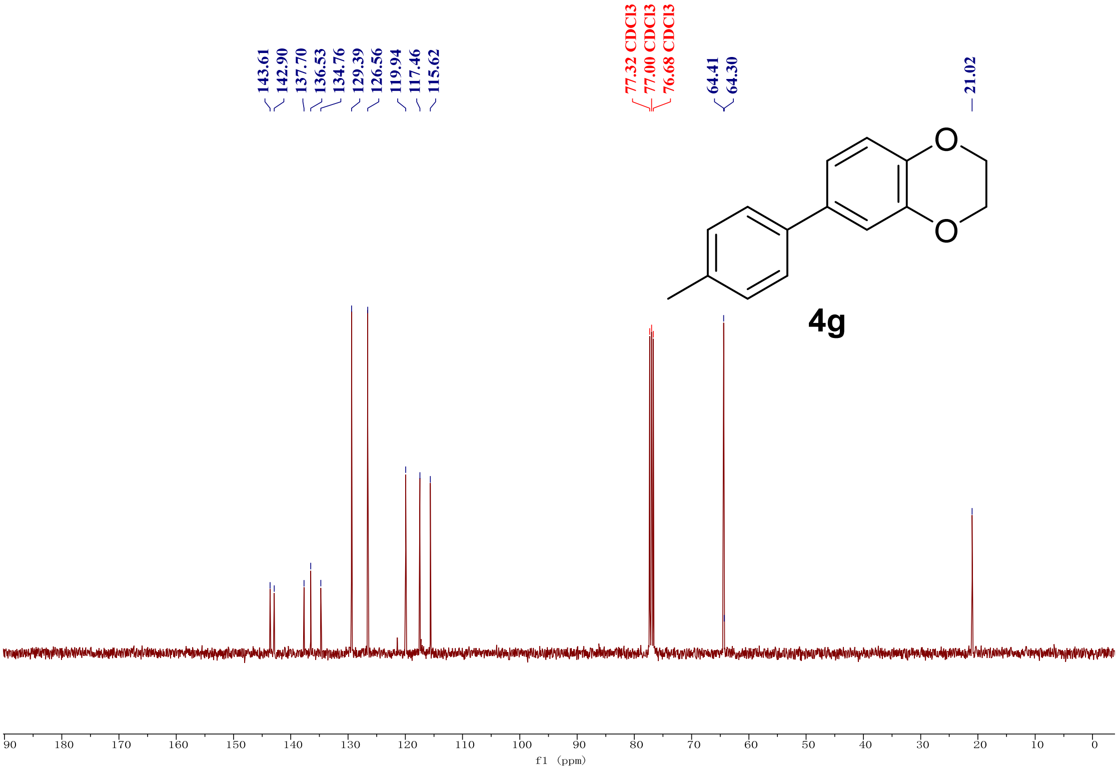
^{13}C NMR spectrum of 4f (100 MHz, $CDCl_3$)



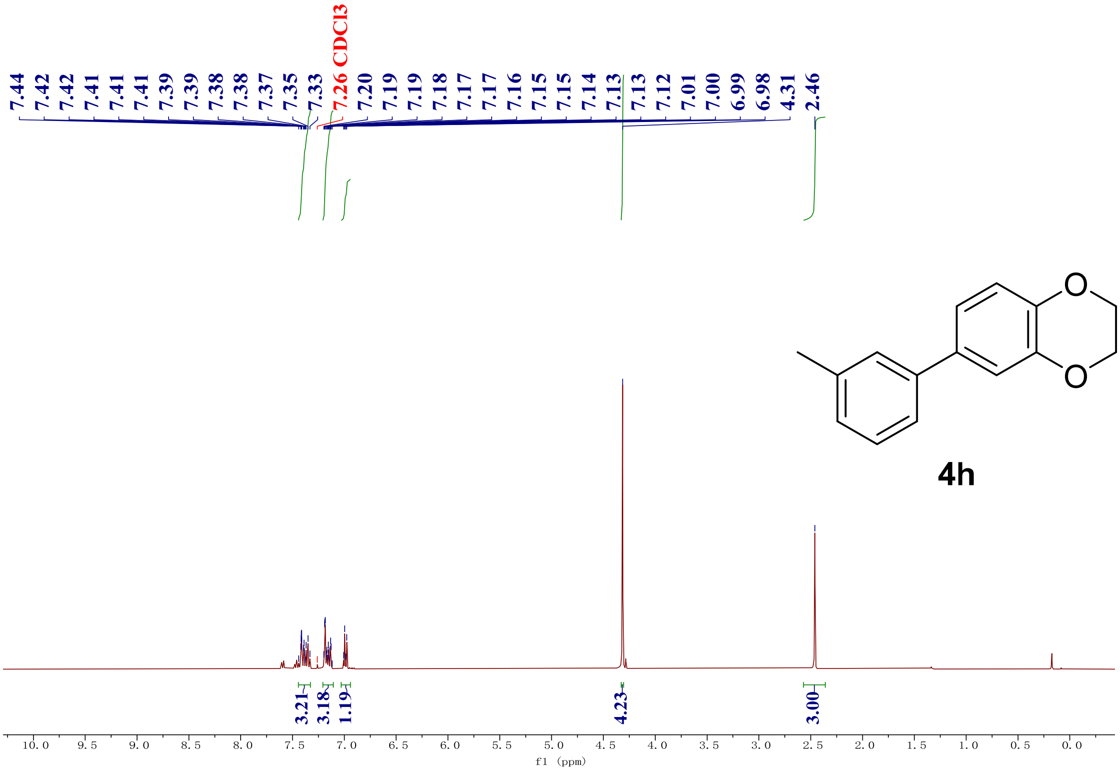
^{1}H NMR spectrum of 4g (400 MHz, $CDCl_3$)



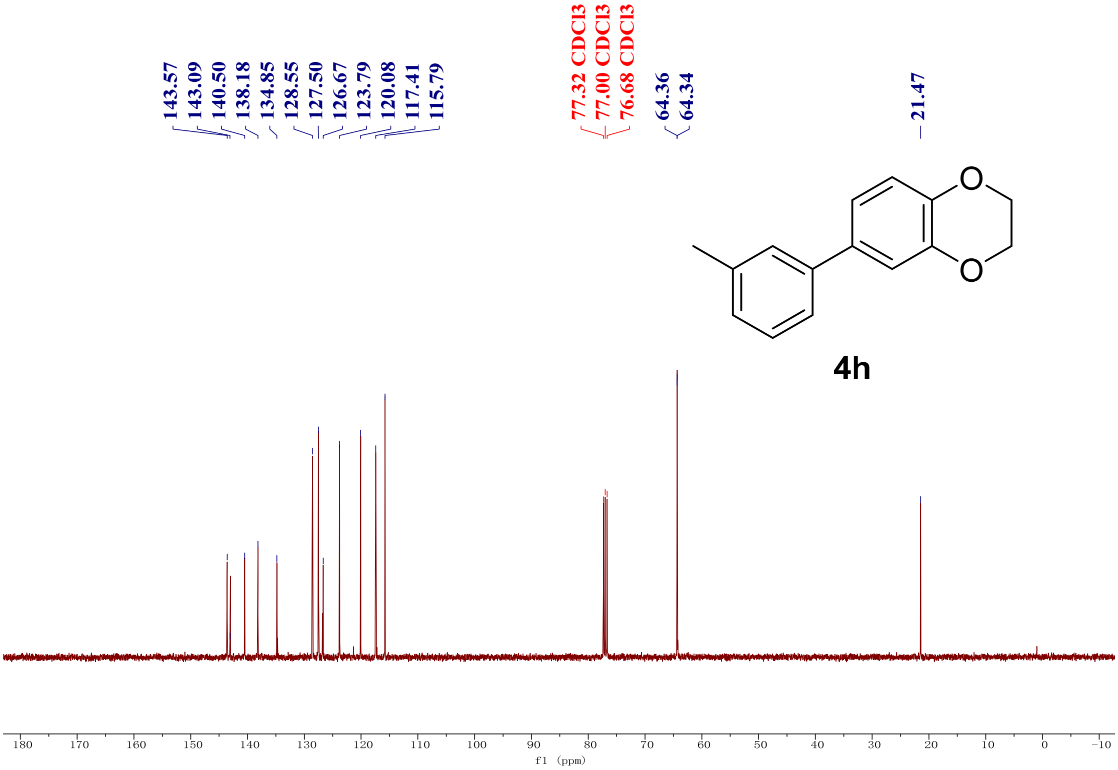
^{13}C NMR spectrum of 4g (100 MHz, CDCl$_3$)



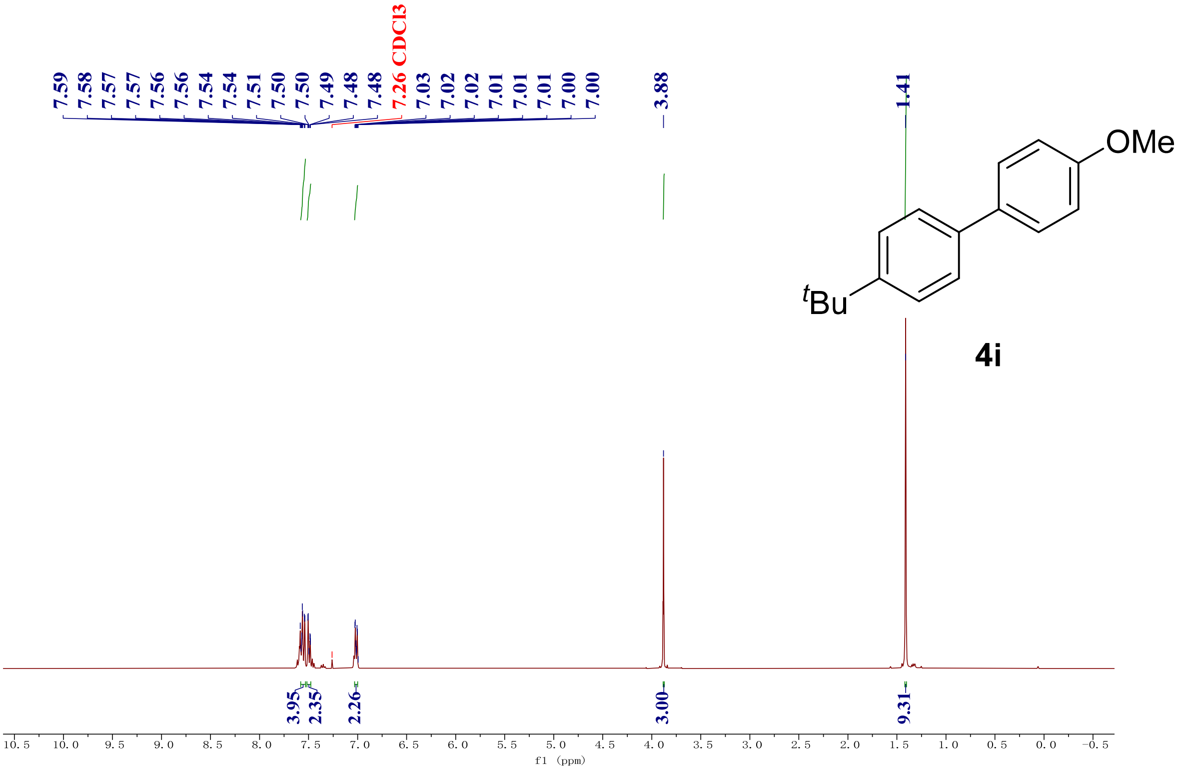
^{1}H NMR spectrum of 4h (400 MHz, CDCl$_3$)



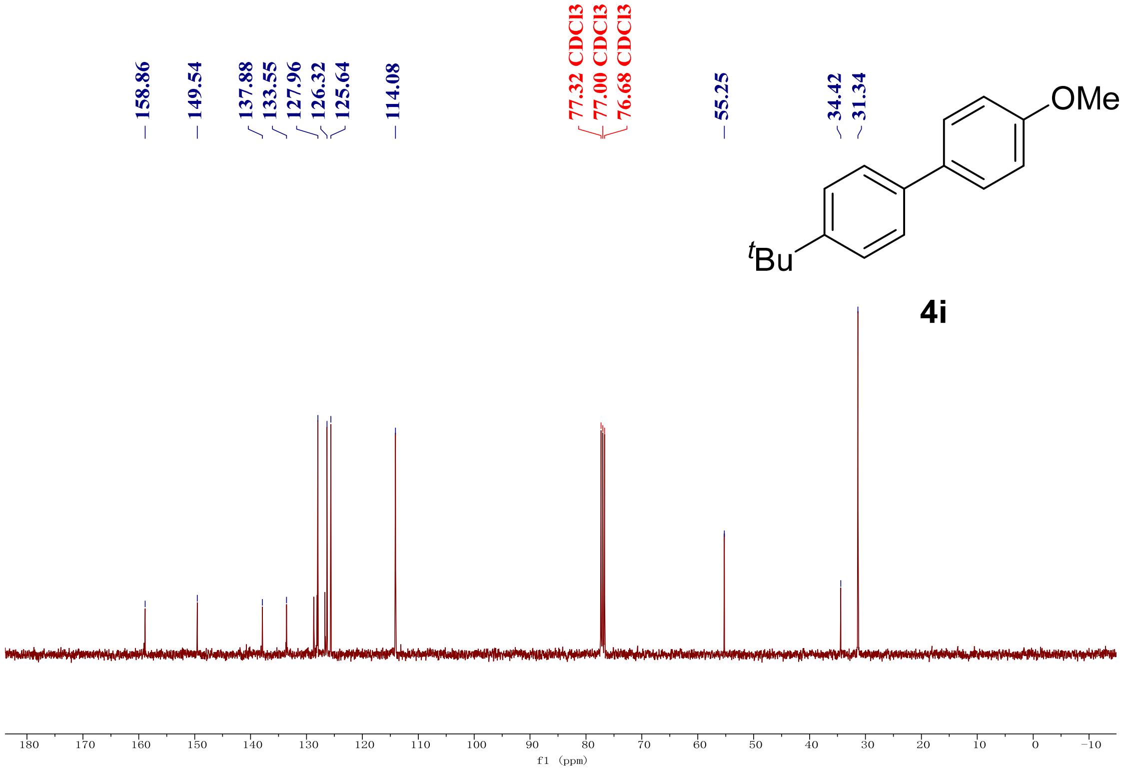
^{13}C NMR spectrum of 4h (100 MHz, $CDCl_3$)



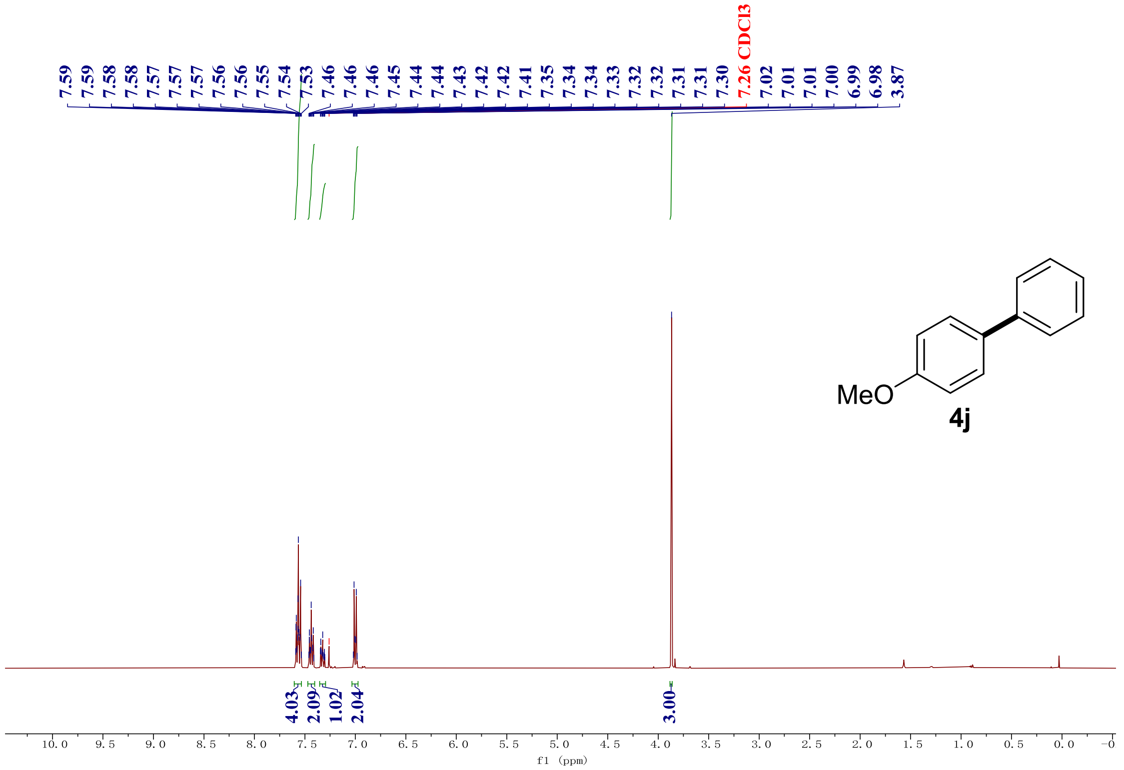
^{1}H NMR spectrum of 4i (400 MHz, $CDCl_3$)



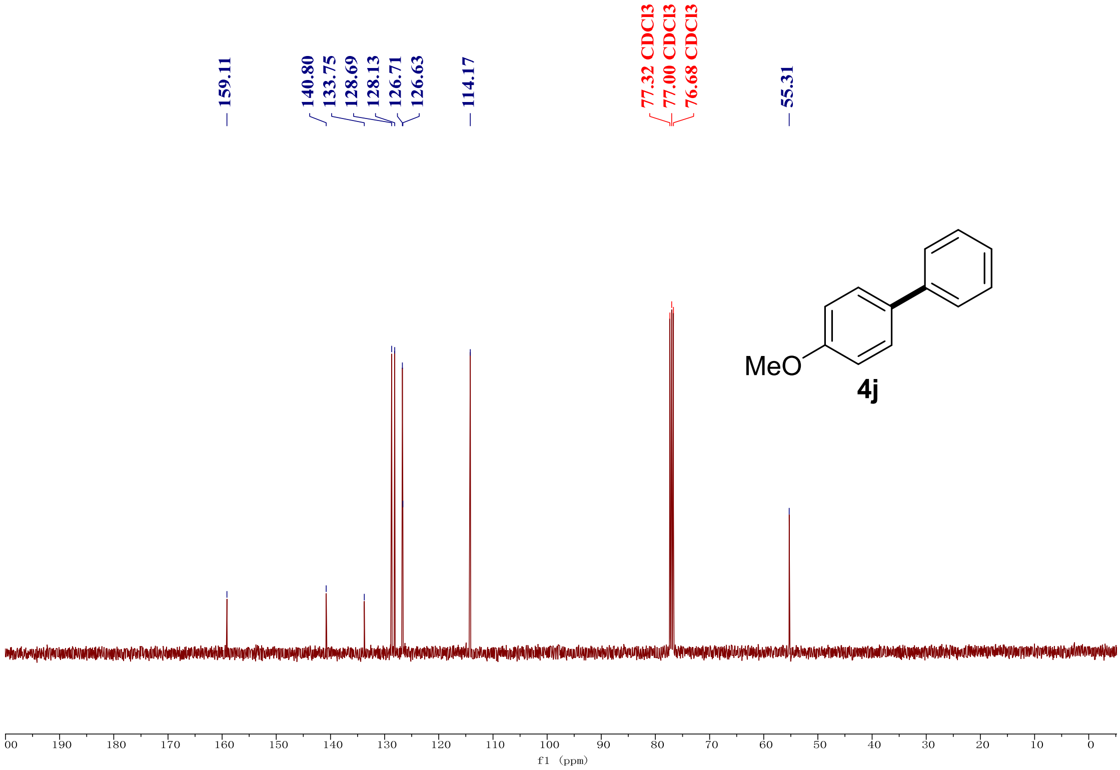
^{13}C NMR spectrum of 4i (100 MHz, CDCl$_3$)



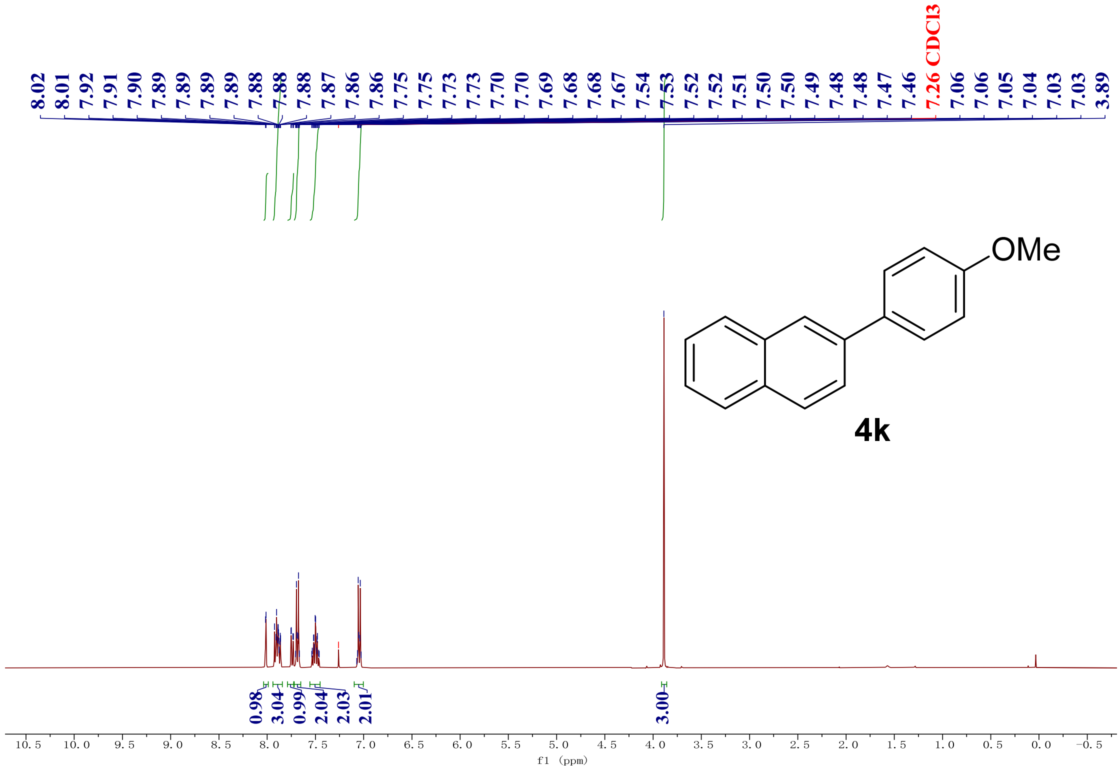
^{1}H NMR spectrum of 4j (400 MHz, CDCl$_3$)



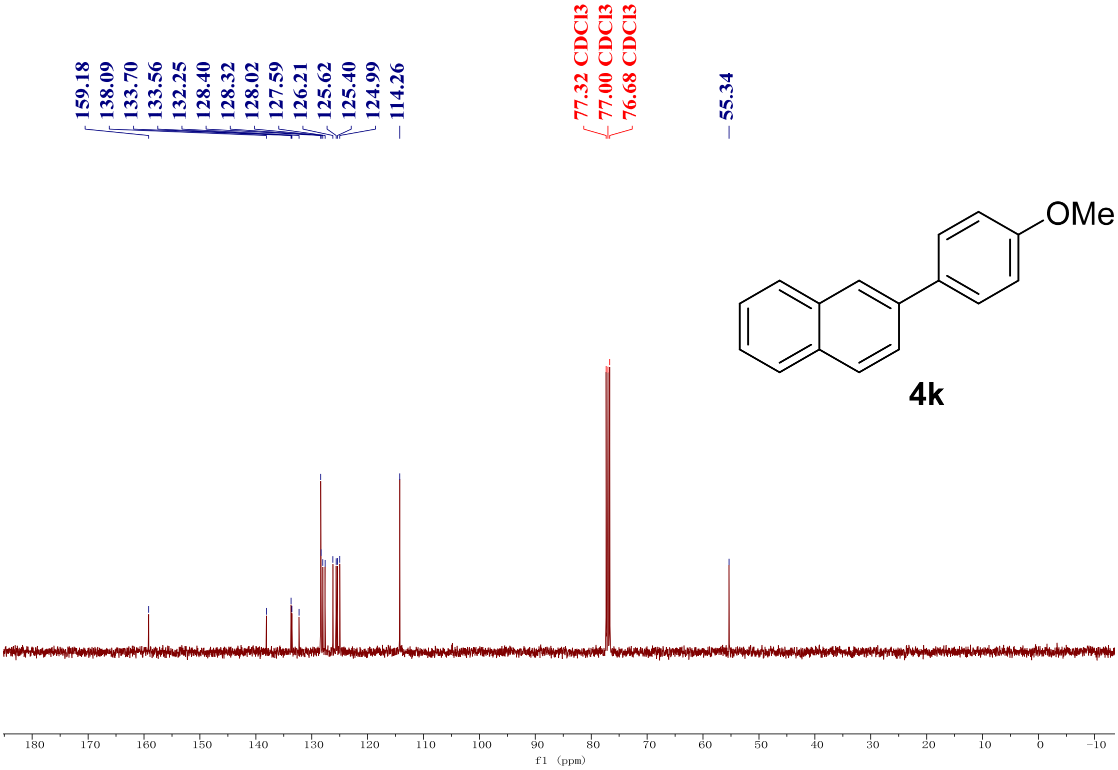
^{13}C NMR spectrum of 4j (100 MHz, CDCl$_3$)



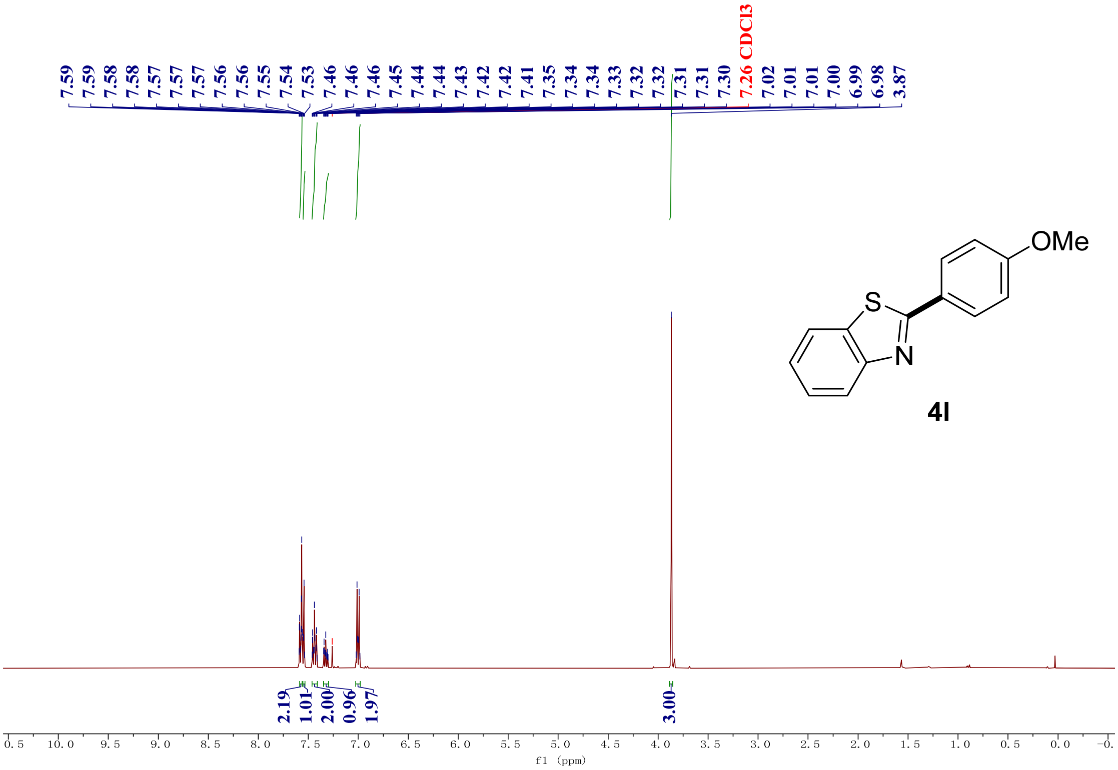
^{1}H NMR spectrum of 4k (400 MHz, CDCl$_3$)



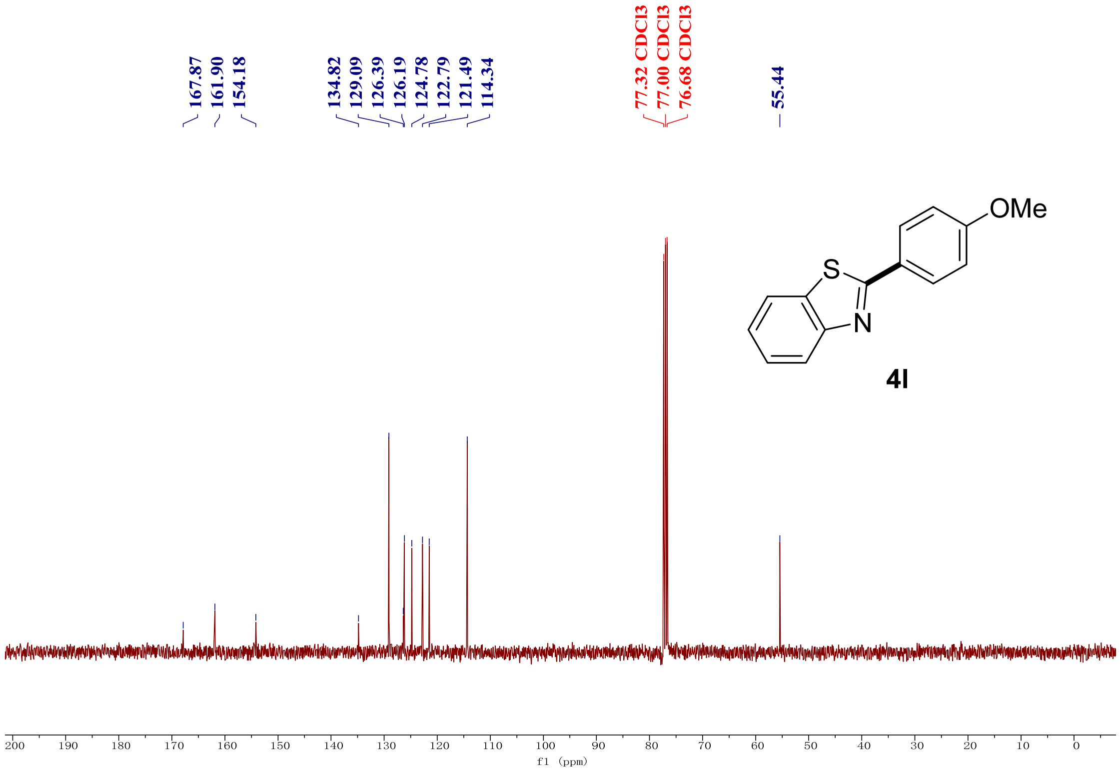
^{13}C NMR spectrum of 4k (100 MHz, CDCl$_3$)



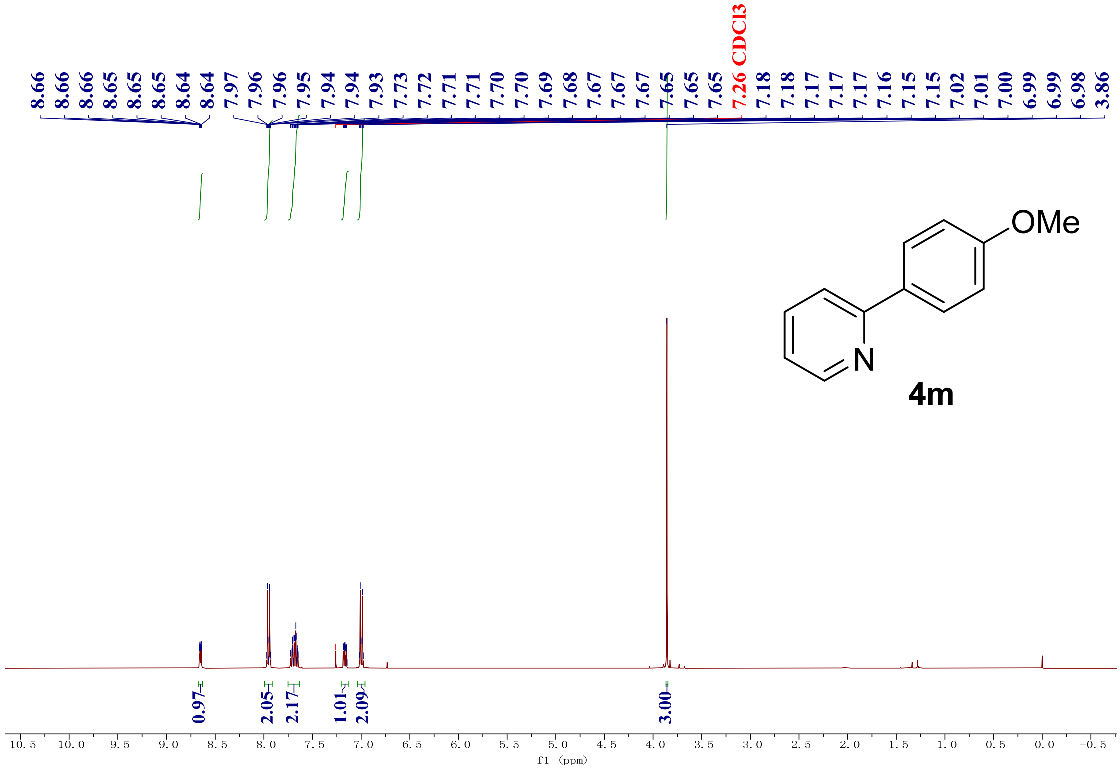
^{1}H NMR spectrum of 4l (400 MHz, CDCl$_3$)



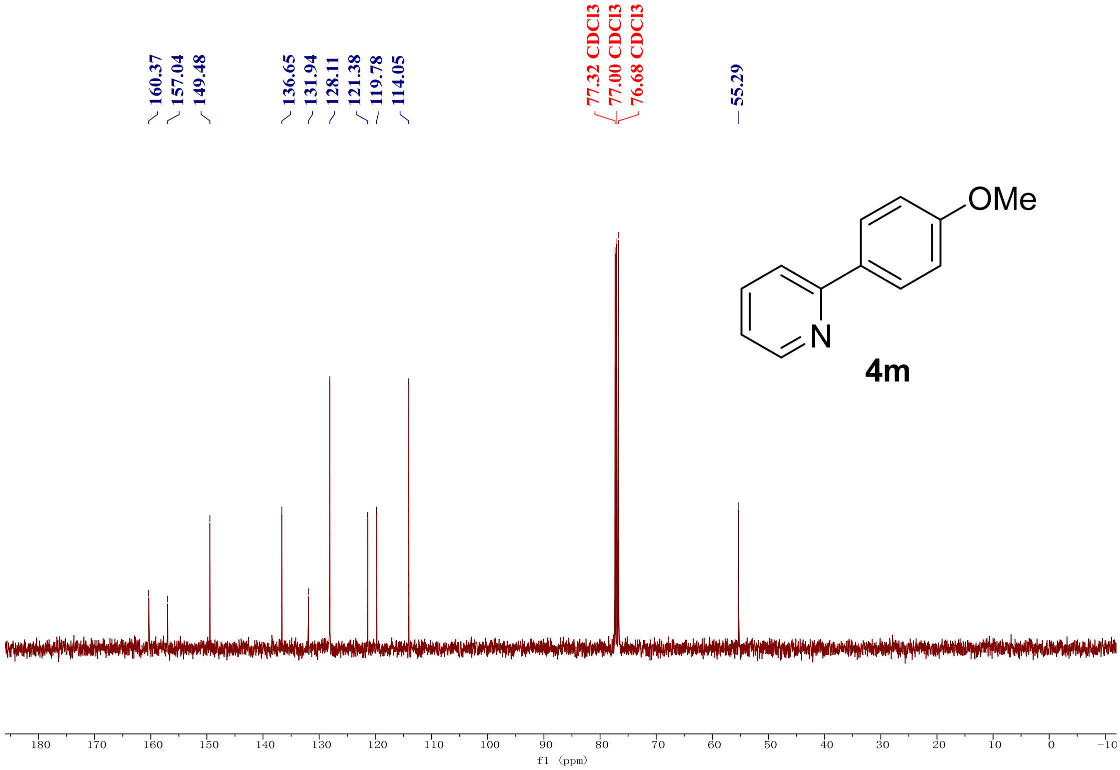
^{13}C NMR spectrum of 4l (100 MHz, CDCl$_3$)



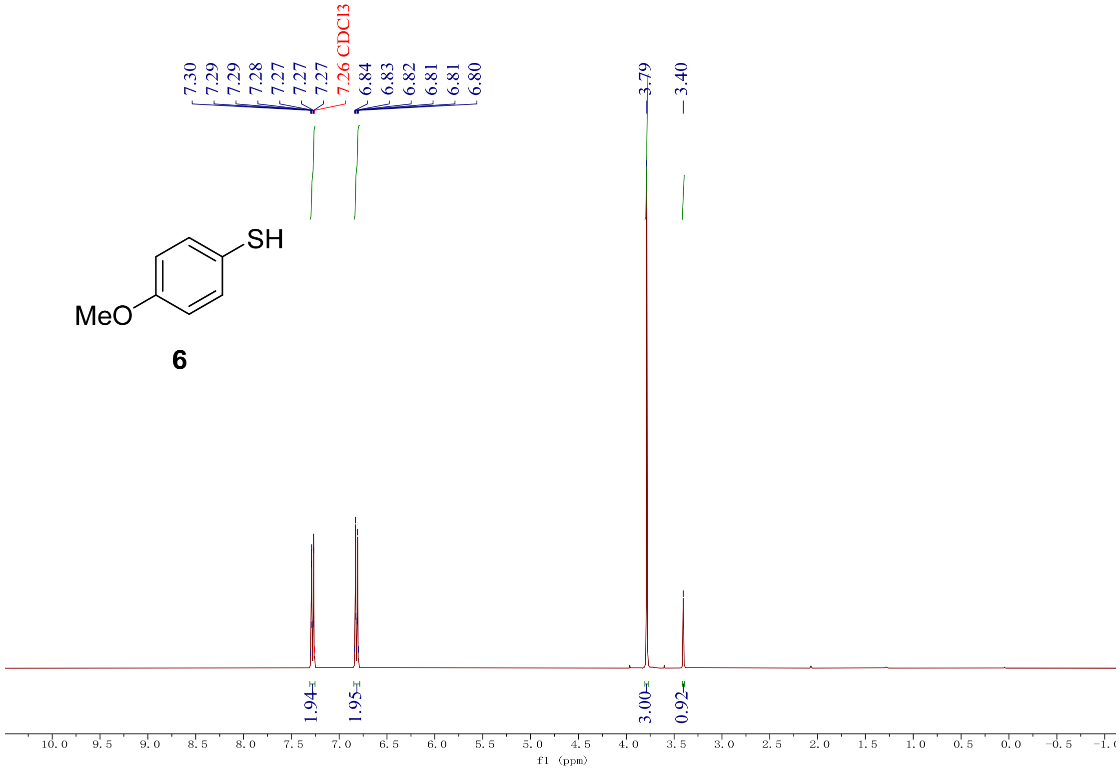
^{1}H NMR spectrum of 4m (400 MHz, CDCl$_3$)



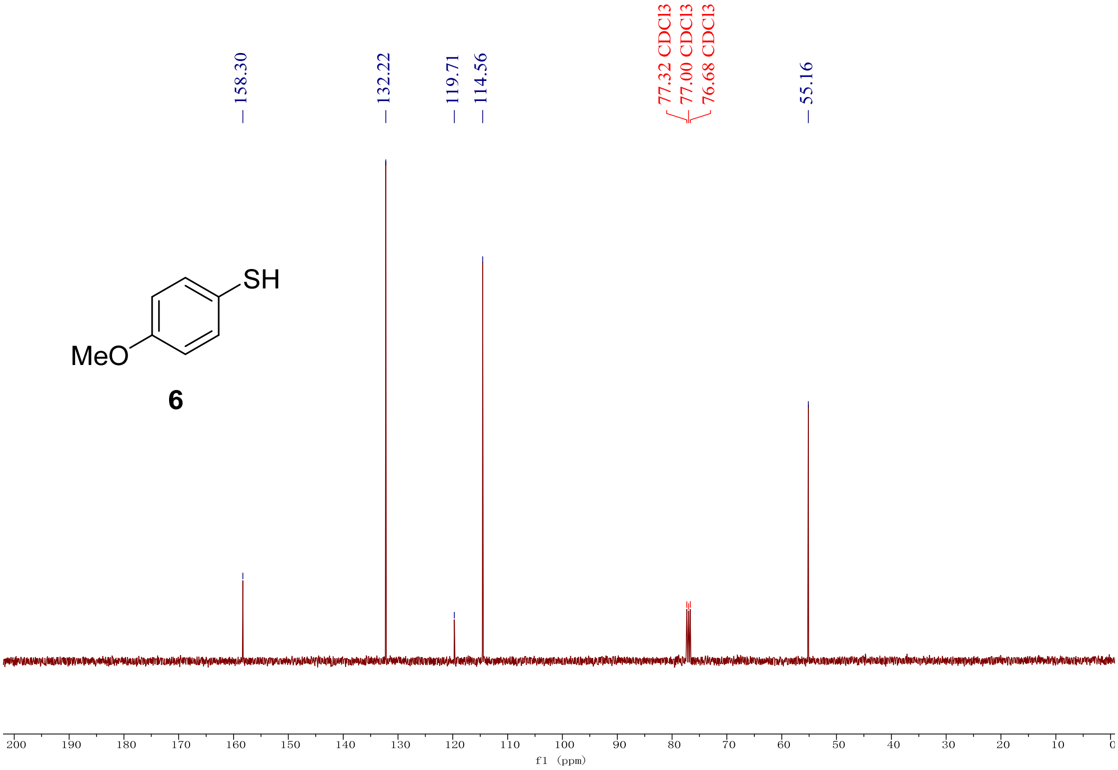
^{13}C NMR spectrum of 4m (100 MHz, $CDCl_3$)



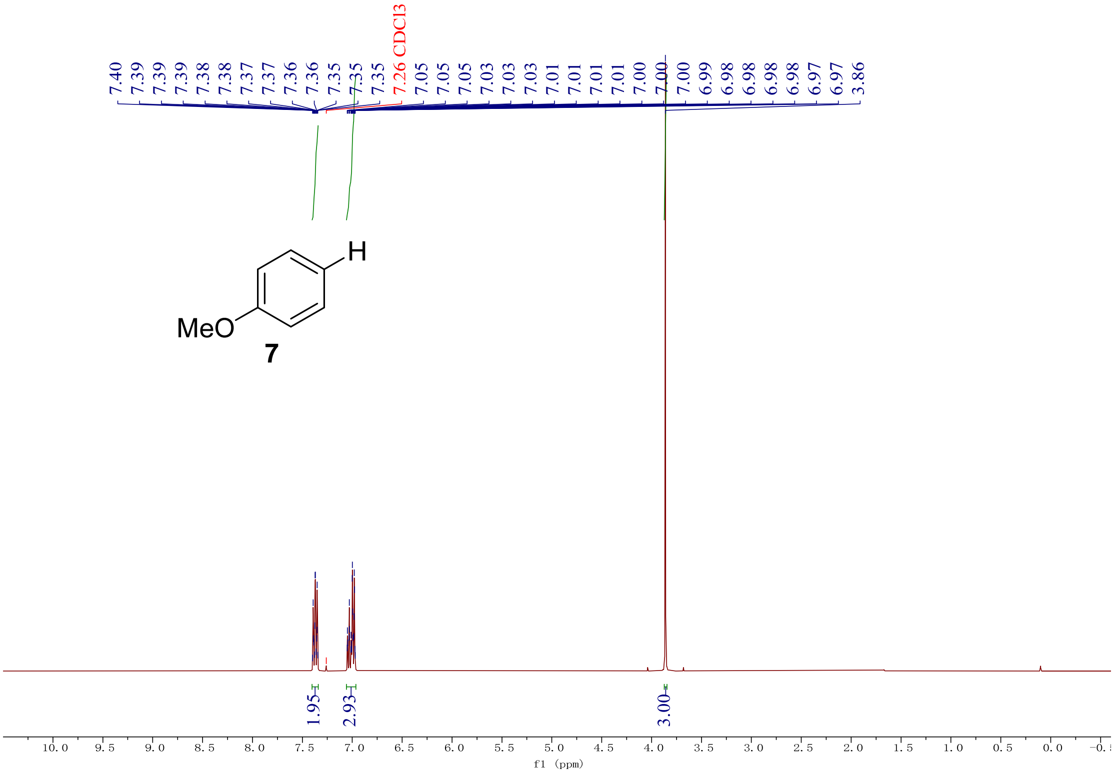
^{1}H NMR spectrum of 6 (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of 6 (100 MHz, CDCl$_3$)



^{1}H NMR spectrum of 7 (400 MHz, CDCl$_3$)



^{13}C NMR spectrum of 7 (100 MHz, $CDCl_3$)