Supporting Information

Nickel-catalyzed cross-electrophile coupling of aryl thiols with aryl bromides via C−S bond activation

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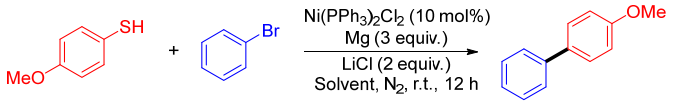
General information

Unless otherwise stated, all reagents (≥98% purity) 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).

Optimization of reaction conditions

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

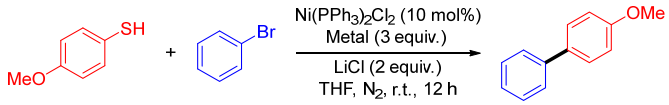


1a (1 equiv.) **2a** (3 equiv.) **3a**

Entry	Solvent	Yield (%)[b]
1	**THF**	**57**
2	DME	<5
3	1,4-dioxane	<5
4	2-MeTHF	<5
5	^{t}BuOMe	<5
6	CPME	<5
7	$^{i}Pr_2O$	<5
8	tetrahydropyran	<5
9	DMF	<5

[a] The reactions were performed at room temperature for 12 h under nitrogen atmosphere by using **1a** (0.6 mmol, 1 equiv.), **2a** (1.8 mmol), $Ni(PPh_3)_2Cl_2$ (10 mol%, 0.06 mmol), magnesium turnings (1.8 mmol), and LiCl (1.2 mmol) in solvent (2 mL). [b] Yields were determined by NMR analysis of crude reaction mixture after work-up by using 1,4-dimethoxybenzene as an internal standard.

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

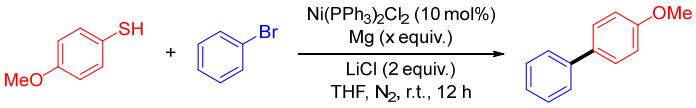


1a (1 equiv.) **2a** (3 equiv.) **3a**

Entry	Metal	Yield (%)[b]
1	**Mg**	**57**
2	Fe	<5
3	Mn	<5
4	Zn	<5
5	Al	<5
6	Pb	<5
7	Bi	<5
8	In	<5

[a] The reactions were performed at room temperature for 12 h under nitrogen atmosphere by using **1a** (0.6 mmol, 1 equiv.), **2a** (1.8 mmol), $Ni(PPh_3)_2Cl_2$ (10 mol%, 0.06 mmol), metal (1.8 mmol), and LiCl (1.2 mmol) in THF (2 mL). [b] Yields were determined by NMR analysis of crude reaction mixture after work-up by using 1,4-dimethoxybenzene as an internal standard.

Table S3. Optimization of reaction conditions by using different equivalents of **2a** and Mg turnings[a]



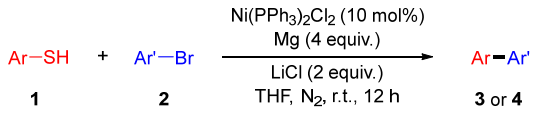
1a (1 equiv.) **2a** (x equiv.) **3a**

Entry	x	Yield (%)[b]
1	1	0
2	2	17
3	3	57
4	**4**	**76**

[a] The reactions were performed at room temperature for 12 h under nitrogen atmosphere by using **1a** (0.6 mmol, 1 equiv.), **2a** (x equiv.), $Ni(PPh_3)_2Cl_2$ (10 mol%, 0.06 mmol), magnesium turnings (x equiv.), and LiCl (1.2 mmol) in THF (2 mL). [b] Yields were determined by NMR analysis of crude reaction mixture after work-up by using 1,4-dimethoxybenzene as an internal standard.

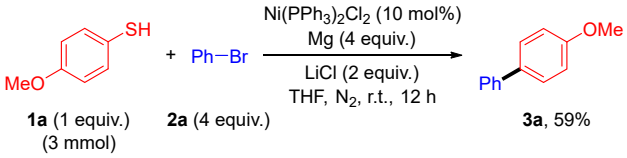
Experimental procedure

1. Typical procedures for the cross-coupling reaction of aryl thiols with aryl bromide.



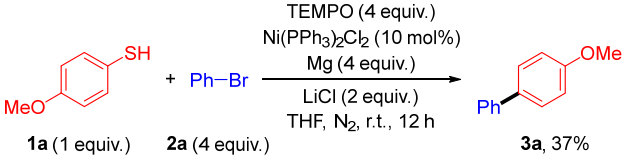
To an oven-dried Schlenk tube equipped with a magnetic stir bar was added magnesium turnings (58.3 mg, 2.4 mmol) and LiCl (50.9 mg, 1.2 mmol). Then the mixture was dried under reduced pressure with a heat gun (320 ºC) for 3 min. After cooling down to room temperature, dry THF (2 mL) was added and the Schlenk tube was backfilled with nitrogen for three times. Then aryl thiols (0.6 mmol) and $Ni(PPh_3)_2Cl_2$ (39.3 mg, 0.06 mmol) were added into the tube, followed by the addition of aryl bromide **2** (2.4 mmol). The reaction mixture was stirred at room temperature for 12 h before quenching with saturated NH_4Cl solution (2 mL) and extracting with EtOAc (20 mL × 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 **3** or **4**.

2. Scale-up reaction.



To an oven-dried Schlenk tube equipped with a magnetic stir bar was added magnesium turnings (291.7 mg, 12 mmol) and LiCl (254.3 mg, 6 mmol). Then the mixture was dried under reduced pressure with a heat gun (320 ºC) 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 4-methoxybenzenethiol **1a** (420.6 mg, 3 mmol) and $Ni(PPh_3)_2Cl_2$ (196.3 mg, 0.3 mmol) were added into the tube, followed by the addition of bromobenzene **2a** (1884.1 mg, 12 mmol). The reaction mixture was stirred at room temperature for 12 h before quenching with saturated NH_4Cl solution (20 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 59% yield (552.7 mg).

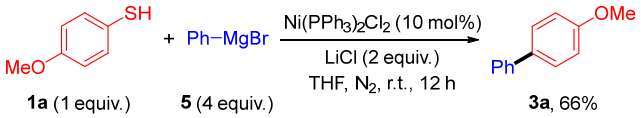
3. Radical-quenching experiment with TEMPO.



To an oven-dried Schlenk tube equipped with a magnetic stir bar was added magnesium turnings (58.3 mg, 2.4 mmol) and LiCl (50.9 mg, 1.2 mmol). Then the mixture was dried under reduced pressure with a heat gun (320 ºC) 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 4-methoxybenzenethiol **1a** (84.1 mg, 0.6 mmol), $Ni(PPh_3)_2Cl_2$ (39.3 mg, 0.06 mmol), TEMPO (375.0 mg, 2.4 mmol), and aryl bromide **2a** (376.8 mg, 2.4 mmol) were sequentially added into Schlenk tube. The reaction mixture was stirred at room temperature for 12 h before quenching with saturated NH_4Cl solution (2 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 37% yield (41.1 mg).

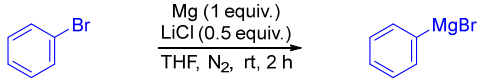
4. Cross-coupling of 4-methoxybenzenethiol (1a) with arylmagnesium reagent 5.



1a (1 equiv.) **5** (4 equiv.) **3a**, 66%

To a Schlenk tube equipped with a magnetic stir bar was added LiCl (50.9 mg, 1.2 mmol), which was dried under reduced pressure with a heat gun (320 °C) for 3 min. After cooling down, 4-methoxybenzenethiol **1a** (84.1 mg, 0.6 mmol) and $Ni(PPh_3)_2Cl_2$ (39.3 mg, 0.06 mmol) were added, and the Schlenk tube was backfilled with nitrogen for three times. Then arylmagnesium bromide **5** (2.4 mmol, 1 M in THF) were added into the tube. The reaction mixture was stirred at room temperature for 12 h before quenching with saturated NH_4Cl solution (2 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 66% yield (73.2 mg).

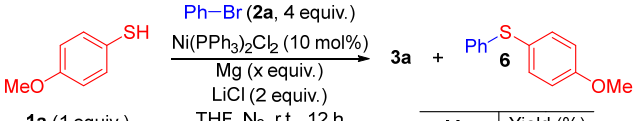
5. Formation of arylmagnesium 5 via Mg insertion into 2a in the presence of LiCl



2a (1 equiv.) **5**, 70% yield

To an oven-dried Schlenk tube equipped with a magnetic stir bar was added magnesium turnings (58.3 mg, 2.4 mmol) and LiCl (50.9 mg, 1.2 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** (376.8 mg, 2.4 mmol) were added into the tube. The reaction mixture was stirred at room temperature for 2 h. After that, the yield of the obtained arylmagnesium reagent was determined to be 70% by titrating with iodine (in anhydrous THF).

6. Cross-electrophile coupling in the absence or presence of Mg.

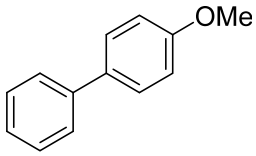


1a (1 equiv.)

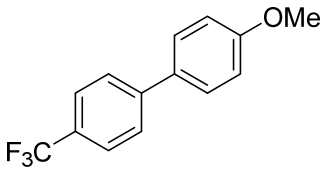
Mg (x equiv)	Yield (%)	
	3a	**6**
0	0	0
0.5	0	0
1.0	0	0

To an oven-dried Schlenk tube equipped with a magnetic stir bar was added magnesium turnings (0-1 mmol) and LiCl (50.9 mg, 1.2 mmol). Then the mixture was dried under reduced pressure with a heat gun (320 ºC) 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 4-methoxybenzenethiol **1a** (84.1 mg, 0.6 mmol) and $Ni(PPh_3)_2Cl_2$ (39.3 mg, 0.06 mmol) were added into the tube, followed by the addition of bromobenzene **2a** (376.8 mg, 2.4 mmol). The reaction mixture was stirred at room temperature for 12 h before quenching with saturated NH_4Cl solution (2 mL) and extracting with EtOAc (20 mL × 3). The organic layers were combined, washed with brine, and dried over Na_2SO_4. The extracts were concentrated under reduced pressure, and the residue obtained was subjected to crude ^1H NMR analysis which showed that no any thioether **6** and product **3a** was formed under the reaction conditions.

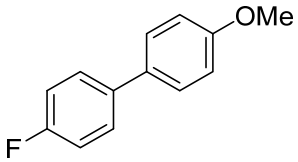
Characterization data of products



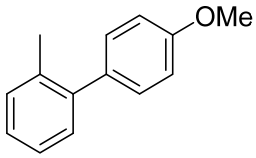
4-Methoxy-1,1'-biphenyl (3a):[1] This product was purified by silica gel column chromatography using petroleum ether as eluant. 86.5 mg, 78% yield. White solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.64–7.56 (m, 4H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.40–7.32 (m, 1H), 7.06–7.00 (m, 2H), 3.88 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.2, 140.9, 133.9, 128.9, 128.3, 126.84, 126.78, 114.3, 55.4 ppm. **IR (KBr, neat):** ν = 2965, 2840, 1613, 1524, 1495, 1258, 1027, 835, 761, 691 cm^{-1}. **HRMS (m/z):** calcd for $C_{13}H_{13}O$ $[M+H]^+$ 185.0961, found: 185.0959.



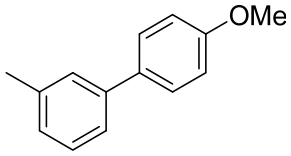
4-Methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (3b or 4b):[2] This product was purified by silica gel column chromatography using petroleum ether as eluant. 51.5 mg, 34% yield (for **3b**); 41.3 mg, 27% yield (for **4b**). White solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.66 (d, *J* = 1.3 Hz, 4H), 7.56–7.53 (m, 2H), 7.02–6.99 (m, 2H), 3.87 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.0, 144.4, 132.2, 128.9 (q, *J* = 32.2 Hz), 128.5, 127.0, 125.8 (q, *J* = 4.0 Hz), 124.2 (q, *J* = 269.6 Hz), 114.5, 55.4 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -62.19 (s, 3F) ppm. **IR (KBr, neat):** ν = 2965, 2840, 1607, 1508, 1325, 1127, 835, 704 cm^{-1}. **HRMS (m/z):** calcd for $C_{14}H_{12}F_3O$ $[M+H]^+$ 253.0835, found: 253.0831.



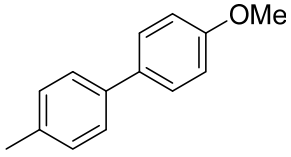
4-Fluoro-4'-methoxy-1,1'-biphenyl (3c or 4c):[1] This product was purified by silica gel column chromatography using petroleum ether as eluant. 78.3 mg, 65% yield (for **3c**); 58.3 mg, 48% yield (for **4c**). White solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.52–7.45 (m, 4H), 7.14–7.07 (m, 2H), 7.00–6.95 (m, 2H), 3.85 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.2 (d, J = 244.0 Hz), 159.2, 137.0 (d, J = 3.2 Hz), 132.9, 128.3 (d, J = 7.9 Hz), 128.2, 115.7 (d, J = 21.3 Hz), 114.3, 55.5 ppm. **^{19}F NMR (376 MHz, $CDCl_3$):** δ -116.62 (s, 1F) ppm. **IR (KBr, neat):** ν = 2968, 2837, 1610, 1501, 1287, 1239, 1162, 1034, 835, 761 cm^{-1}. **HRMS (m/z):** calcd for $C_{13}H_{12}FO$ $[M+H]^+$ 203.0867, found: 203.0869.



4'-Methoxy-2-methyl-1,1'-biphenyl (3d or 4d):[5] This product was purified by silica gel column chromatography using petroleum ether as eluant. 92.8 mg, 78% yield (for **3d**); 78.3 mg, 66% yield (for **4d**). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.30–7.22 (m, 6H), 7.00–6.94 (m, 2H), 3.87 (s, 3H), 2.30 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 158.6, 141.6, 135.6, 134.5, 130.42, 130.38, 130.0, 127.1, 125.9, 113.6, 55.4, 20.7 ppm. **IR (KBr, neat):** ν = 2959, 2834, 1610, 1517, 1485, 1245, 1171, 1043, 838, 758 cm^{-1}. **HRMS (m/z):** calcd for $C_{14}H_{15}O$ $[M+H]^+$ 199.1117, found: 199.1113.

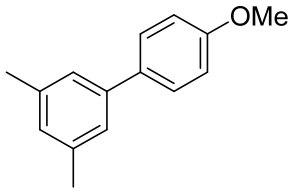


4'-Methoxy-3-methyl-1,1'-biphenyl (3e or 4e):[1] This product was purified by silica gel column chromatography using petroleum ether as eluant. 97.5 mg, 82% yield (for **3e**); 83.7 mg, 70% yield (for **4e**). White solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.64–7.59 (m, 2H), 7.45 (dt, J = 9.7, 1.7 Hz, 2H), 7.40 (t, J = 7.5 Hz, 1H), 7.22 (dd, J = 7.4, 1.9 Hz, 1H), 7.10–7.03 (m, 2H), 3.91 (s, 3H), 2.50 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.2, 140.9, 138.4, 134.0, 128.8, 128.3, 127.5, 126.8, 124.0, 114.2, 55.4, 21.7 ppm. **IR (KBr, neat):** ν = 2959, 2837, 1613, 1517, 1488, 1255, 1184, 1030, 835, 787, 701 cm^{-1}. **HRMS (m/z):** calcd for $C_{14}H_{15}O$ $[M+H]^+$ 199.1117, found: 199.1112.

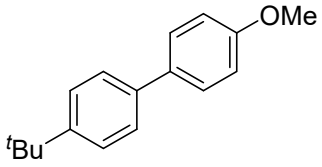


4-Methoxy-4'-methyl-1,1'-biphenyl (3f or 4f):[1] This product was purified by silica gel column chromatography using petroleum ether as eluant. 109.3 mg, 92% yield (for **3f**); 83.3 mg, 70%

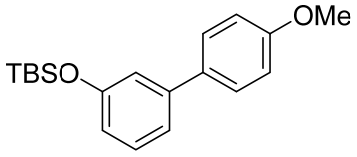
yield (for **4f**). White solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.60–7.56 (m, 2H), 7.54–7.50 (m, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.04–7.01 (m, 2H), 3.89 (s, 3H), 2.45 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.1, 138.1, 136.5, 133.9, 129.6, 128.1, 126.7, 114.3, 55.5, 21.2 ppm. **IR (KBr, neat):** ν = 2959, 2850, 1610, 1504, 1287, 1255, 1187, 1040, 813, 761 cm^{-1}. **HRMS (m/z):** calcd for $C_{14}H_{15}O$ $[M+H]^+$ 199.1117, found: 199.1120.



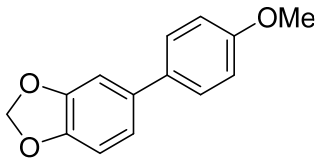
4'-Methoxy-3,5-dimethyl-1,1'-biphenyl (3g):[4] This product was purified by silica gel column chromatography using petroleum ether as eluant. 93.9 mg, 74% yield. Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.59–7.55 (m, 2H), 7.24 (s, 2H), 7.03–6.98 (m, 3H), 3.89 (s, 3H), 2.43 (s, 6H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.1, 140.9, 138.3, 134.1, 128.5, 128.3, 124.8, 114.2, 55.4, 21.5 ppm. **IR (KBr, neat):** ν = 2930, 2853, 1617, 1520, 1463, 1248, 1184, 1037, 825, 701 cm^{-1}. **HRMS (m/z):** calcd for $C_{15}H_{17}O$ $[M+H]^+$ 213.1274, found: 213.1279.



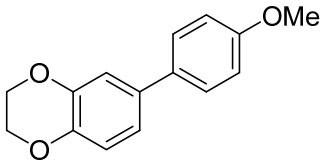
4-(*tert*-Butyl)-4'-methoxy-1,1'-biphenyl (3h or 4i):[4] This product was purified by silica gel column chromatography using petroleum ether as eluant. 88.9 mg, 62% yield (for **3h**); 91.0 mg, 63% yield (**4i**). White solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58–7.53 (m, 4H), 7.52–7.48 (m, 2H), 7.03–7.00 (m, 2H), 3.88 (s, 3H), 1.41 (s, 9H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.1, 149.7, 138.0, 133.7, 128.1, 126.5, 125.8, 114.3, 55.4, 34.6, 31.5 ppm. **IR (KBr, neat):** ν = 2962, 2869, 1607, 1498, 1258, 1203, 1187, 1037, 825 cm^{-1}. **HRMS (m/z):** calcd for $C_{17}H_{21}O$ $[M+H]^+$ 241.1587, found: 241.1582.



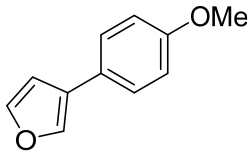
***tert*-Butyl((4'-methoxy-[1,1'-biphenyl]-3-yl)oxy)dimethylsilane (3i):**[6] This product was purified by silica gel column chromatography using petroleum ether as eluant. 91.4 mg, 48% yield. White solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58–7.54 (m, 2H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.20 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.09 (t, *J* = 2.1 Hz, 1H), 7.04–6.98 (m, 2H), 6.87–6.82 (m, 1H), 3.88 (s, 3H), 1.06 (s, 9H), 0.29 (s, 6H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.3, 156.1, 142.4, 133.6, 129.7, 128.2, 120.0, 118.6, 118.4, 114.3, 55.4, 25.9, 18.4, -4.2 ppm. **IR (KBr, neat):** ν = 2959, 2856, 1604, 1482, 1264, 1213, 1046, 938, 697 cm^{-1}. **HRMS (m/z):** calcd for $C_{19}H_{27}O_2Si$ $[M+H]^+$ 315.1775, found: 315.1779.



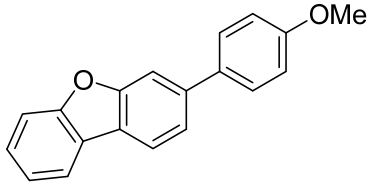
5-(4-Methoxyphenyl)benzo[*d*][1,3]dioxole (3j):[7] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 200:1). 97.7 mg, 71% yield. White solid. **^{1}H NMR (400 MHz, DMSO-d_6):** δ 7.50–7.44 (m, 2H), 7.14 (d, J = 1.8 Hz, 1H), 7.02 (dd, J = 8.1, 1.9 Hz, 1H), 6.95–6.88 (m, 3H), 6.00 (s, 2H), 3.72 (s, 3H) ppm. **^{13}C NMR (100 MHz, DMSO-d_6):** δ 159.1, 148.5, 146.8, 134.8, 132.9, 128.0, 120.1, 114.7, 109.1, 107.3, 101.6, 55.6 ppm. **IR (KBr, neat):** ν = 2962, 2840, 1613, 1479, 1437, 1242, 1037, 931, 809, 768, 697 cm^{-1}. **HRMS (m/z):** calcd for $C_{14}H_{13}O_3$ $[M+H]^+$ 229.0859, found: 229.0858.



6-(4-Methoxyphenyl)-2,3-dihydrobenzo[*b*][1,4]dioxine (3k):[8] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 200:1). 96.9 mg, 67% yield. White solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48–7.44 (m, 2H), 7.08–7.02 (m, 2H), 6.97–6.89 (m, 3H), 4.29 (s, 4H), 3.84 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 158.9, 143.7, 142.8, 134.6, 133.3, 127.9, 119.9, 117.6, 115.5, 114.2, 64.6, 55.5 ppm. **IR (KBr, neat):** ν = 2930, 2834, 1607, 1498, 1312, 1248, 1072, 1030, 896, 806, 694 cm^{-1}. **HRMS (m/z):** calcd for $C_{15}H_{15}O_3$ $[M+H]^+$ 243.1016, found: 243.1014.

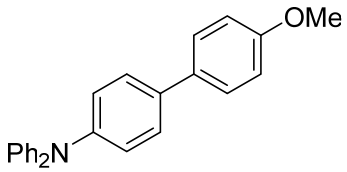


2-(4-Methoxyphenyl)furan (3l):[9] This product was purified by silica gel column chromatography using petroleum ether as eluant. 53.3 mg, 51% yield. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.79–7.70 (m, 1H), 7.46 (ddd, J = 7.5, 3.2, 1.2 Hz, 1H), 7.42–7.39 (m, 3H), 6.86–6.83 (m, 2H), 3.79 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.0, 132.8, 132.4, 132.3, 128.7, 128.6, 128.5, 114.7, 55.4 ppm. **IR (KBr, neat):** ν = 2965, 2927, 2850, 1594, 1492, 1261, 1104, 1034, 806 cm^{-1}. **HRMS (m/z):** calcd for $C_{11}H_{11}O_2$ $[M+H]^+$ 175.0754, found: 175.0756.

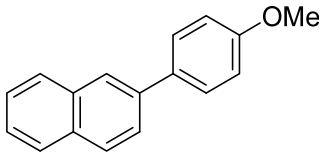


3-(4-Methoxyphenyl)dibenzo[*b*,*d*]furan (3m):[10] This product was purified by silica gel column chromatography using petroleum ether as eluant. 121.5 mg, 74% yield. White solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.12 (dd, J = 1.9, 0.7 Hz, 1H), 8.01 (ddd, J = 7.7, 1.4, 0.6 Hz, 1H), 7.66–

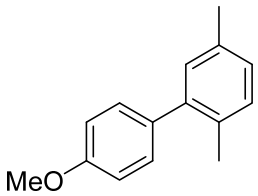
7.60 (m, 5H), 7.51 (ddd, J = 8.3, 7.3, 1.4 Hz, 1H), 7.39 (td, J = 7.5, 1.0 Hz, 1H), 7.08–7.03 (m, 2H), 3.89 (s, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 159.1, 156.7, 155.5, 136.1, 133.9, 128.5, 127.3, 126.4, 124.7, 124.4, 122.8, 120.8, 118.7, 114.3, 111.81, 111.76, 55.4 ppm. **IR (KBr, neat):** ν = 2959, 2840, 1604, 1479, 1280, 1207, 1037, 813, 745, 723 cm^{-1}. **HRMS (m/z):** calcd for $C_{19}H_{15}O_2$ $[M+H]^+$ 275.1067, found: 275.1071.



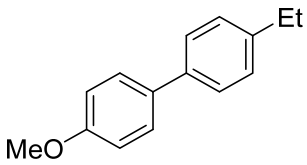
4'-Methoxy-*N*,*N*-diphenyl-[1,1'-biphenyl]-4-amine (3n):[11] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 200:1). 208.0 mg, 99% yield. White solid. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.53–7.50 (m, 2H), 7.48–7.46 (m, 2H), 7.45–7.42 (m, 2H), 7.31–7.27 (m, 5H), 7.16–7.12 (m, 5H), 6.99–6.96 (m, 2H), 3.86 (s, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 147.9, 146.7, 135.1, 133.4, 129.4, 127.8, 127.5, 127.4, 124.42, 124.36, 122.9, 114.3, 55.5 ppm. **IR (KBr, neat):** ν = 3058, 1738, 1585, 1495, 1328, 1277, 1181, 822, 752, 701 cm^{-1}. **HRMS (m/z):** calcd for $C_{25}H_{22}NO$ $[M+H]^+$ 352.1696, found: 352.1692.



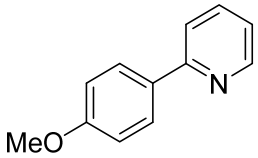
2-(4-Methoxyphenyl)naphthalene (3o or 4l):[11] This product was purified by silica gel column chromatography using petroleum ether as eluant. 92.9 mg, 66% yield (for **3o**); 108.7 mg, 77% yield (for **4l**). White solid. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.53–7.50 (m, 1H), 7.48–7.46 (m, 3H), 7.45–7.42 (m, 1H), 7.31–7.27 (m, 2H), 7.16–7.12 (m, 2H), 6.99–6.96 (m, 2H), 3.86 (s, 3H). **^{13}C NMR (100 MHz, CDCl$_3$):** δ 159.3, 138.2, 135.4, 133.8, 132.4, 128.6, 128.5, 128.2, 127.7, 126.4, 125.8, 125.6, 125.1, 114.4, 55.5 ppm. **IR (KBr, neat):** ν = 2962, 2920, 2846, 1607, 1501, 1248, 1184, 1034, 819, 768 cm^{-1}. **HRMS (m/z):** calcd for $C_{17}H_{15}O$ $[M+H]^+$ 235.1117, found: 235.1116.



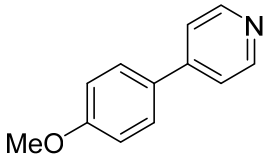
4'-Methoxy-2,5-dimethyl-1,1'-biphenyl (4g):[2] This product was purified by silica gel column chromatography using petroleum ether as eluant. 110.2 mg, 87% yield. White solid. **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.31–7.21 (m, 2H), 7.18–7.14 (m, 1H), 7.07 (d, J = 6.7 Hz, 2H), 6.98–6.93 (m, 2H), 3.86 (s, 3H), 2.35 (s, 3H), 2.25 (s, 3H) ppm. **^{13}C NMR (100 MHz, CDCl$_3$):** δ 158.5, 141.5, 135.3, 134.6, 132.4, 130.8, 130.4, 127.8, 113.5, 55.4, 21.1, 20.2 ppm. **IR (KBr, neat):** ν = 2930, 2834, 1613, 1514, 1498, 1175, 1027, 832, 765, 697 cm^{-1}. **HRMS (m/z):** calcd for $C_{15}H_{17}O$ $[M+H]^+$ 213.1274, found: 213.1279.



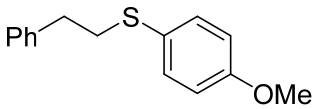
4-Ethyl-4'-methoxy-1,1'-biphenyl (4h):[12] This product was purified by silica gel column chromatography using petroleum ether as eluant. 61.3 mg, 48% yield. Slightly yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.53–7.50 (m, 2H), 7.49–7.45 (m, 2H), 7.24 (d, *J* = 4.1 Hz, 2H), 6.98–6.94 (m, 2H), 3.84 (s, 3H), 2.68 (q, *J* = 7.6 Hz, 2H), 1.26 (t, *J* = 7.6 Hz, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.0, 142.9, 138.3, 133.9, 128.4, 128.1, 126.8, 114.3, 55.5, 28.6, 15.8 ppm. **IR (KBr, neat):** ν = 2930, 2843, 1607, 1508, 1283, 1251, 1181, 1037, 816, 749 cm^{-1}. **HRMS (m/z):** calcd for $C_{15}H_{17}O$ $[M+H]^+$ 212.1274, found: 212.1279.



2-(4-Methoxyphenyl)pyridine (4j):[3] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 20:1). 45.0 mg, 41% yield. Pale yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.65 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.98–7.91 (m, 2H), 7.74–7.62 (m, 2H), 7.16 (ddd, *J* = 7.1, 4.8, 1.5 Hz, 1H), 7.02–6.96 (m, 2H), 3.85 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.5, 157.2, 149.6, 136.8, 132.1, 128.3, 121.5, 120.0, 114.2, 55.4 ppm. **IR (KBr, neat):** ν = 3003, 2840, 1613, 1517, 1466, 1434, 1178, 1021, 845, 777 cm^{-1}. **HRMS (m/z):** calcd for $C_{12}H_{12}NO$ $[M+H]^+$ 186.0913, found: 186.0910.



4-(4-Methoxyphenyl)pyridine (4k):[3] This product was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluant (petroleum ether/EtOAc = 10:1). 85.5 mg, 77% yield. Colorless solid. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.62 (s, 2H), 7.62–7.56 (m, 2H), 7.49–7.45 (m, 2H), 7.03–6.98 (m, 2H), 3.86 (s, 3H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.6, 150.2, 148.0, 130.4, 128.3, 121.3, 114.6, 55.5 ppm. **IR (KBr, neat):** ν = 2968, 2846, 1607, 1485, 1290, 1258, 1226, 1191, 1037, 813 cm^{-1}. **HRMS (m/z):** calcd for $C_{12}H_{12}NO$ $[M+H]^+$ 186.0913, found: 186.0917.



(4-Methoxyphenyl)(phenethyl)sulfane (3q'):[13] This product was purified by silica gel column chromatography using petroleum ether as eluant. 106.8 mg, 73% yield. Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.40–7.36 (m, 2H), 7.29 (tt, *J* = 6.9, 1.0 Hz, 2H), 7.23–7.16 (m, 3H), 6.89–6.85 (m, 2H), 3.81 (s, 3H), 3.09-3.05 (m, 2H), 2.87 (dd, *J* = 9.3, 6.4 Hz, 2H) ppm. **^{13}C NMR (100**

MHz, $CDCl_3$): δ 159.0, 140.5, 133.4, 128.62, 128.57, 126.5, 126.4, 114.7, 55.4, 37.3, 36.0 ppm. The characterization data of this compound is in accord with the reported ones.[13]

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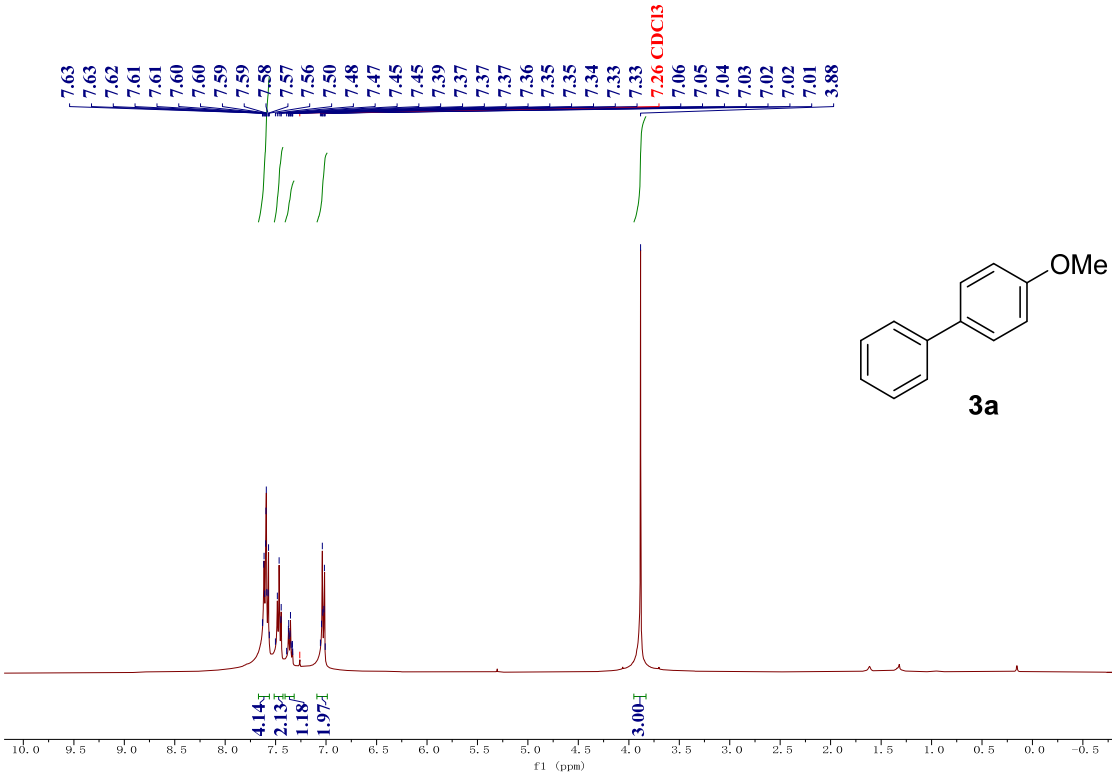
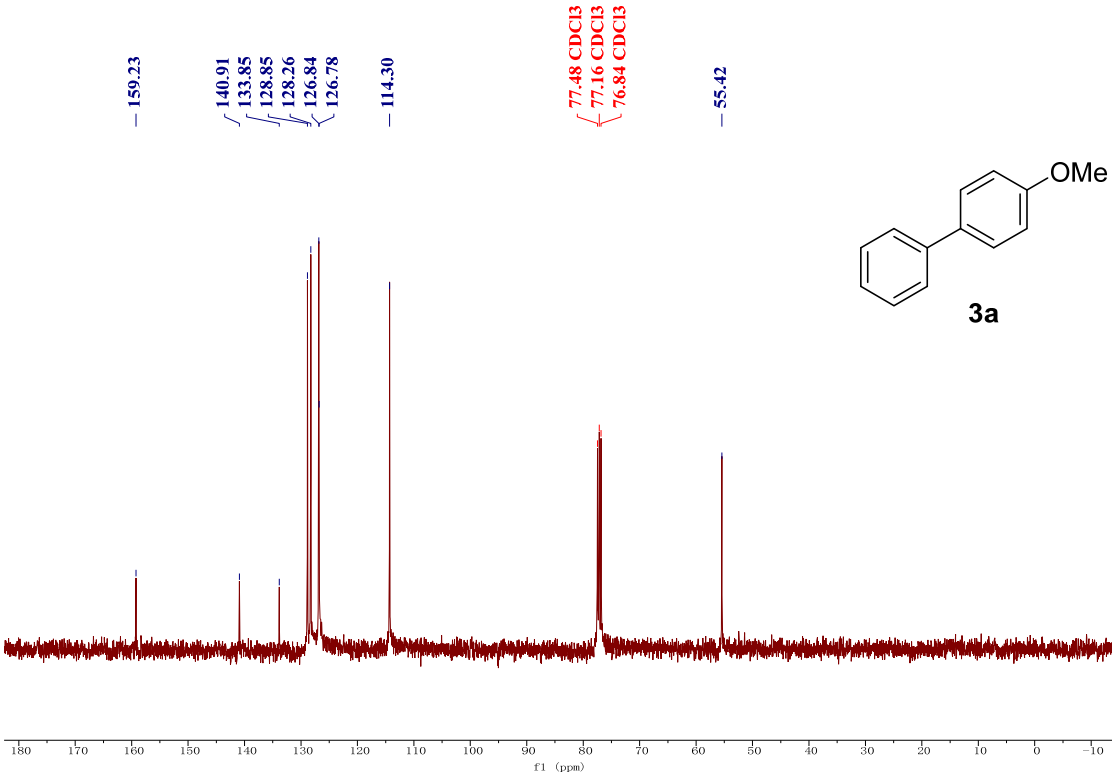
^{1}H, ^{13}C, and ^{19}F NMR spectra of products

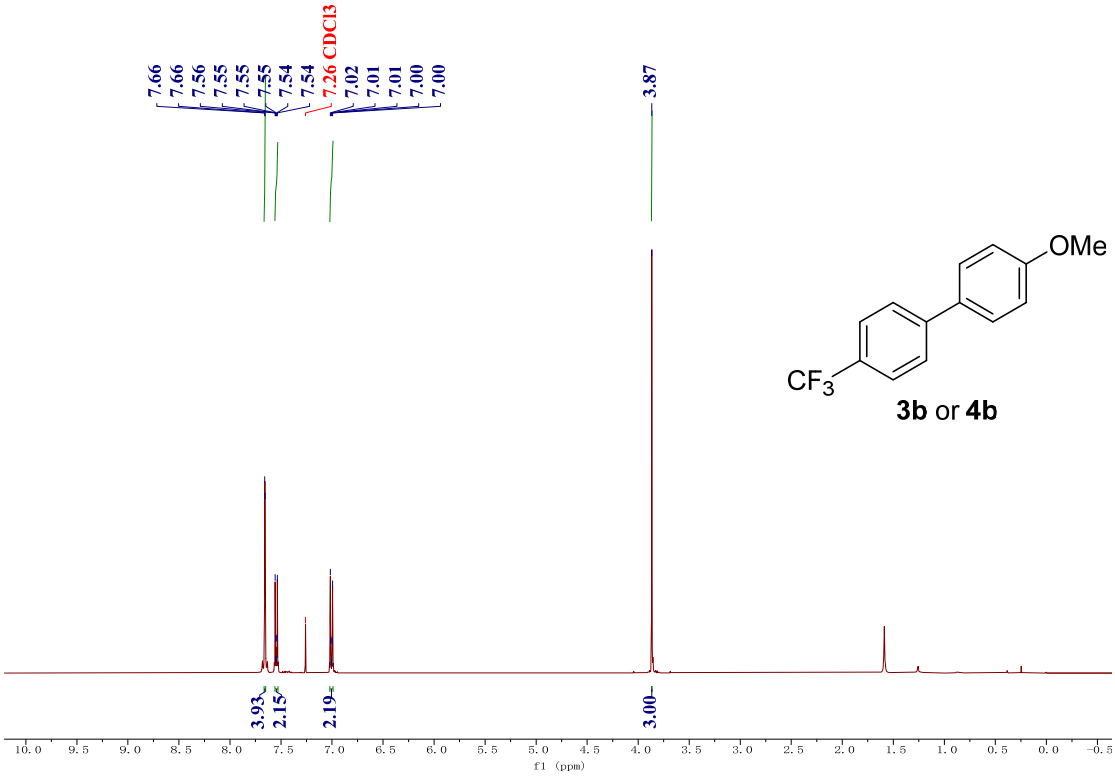
^{1}H NMR spectrum of 3a (400 MHz, $CDCl_3$)



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



^{1}H NMR spectrum of 3b or 4b (400 MHz, $CDCl_3$)



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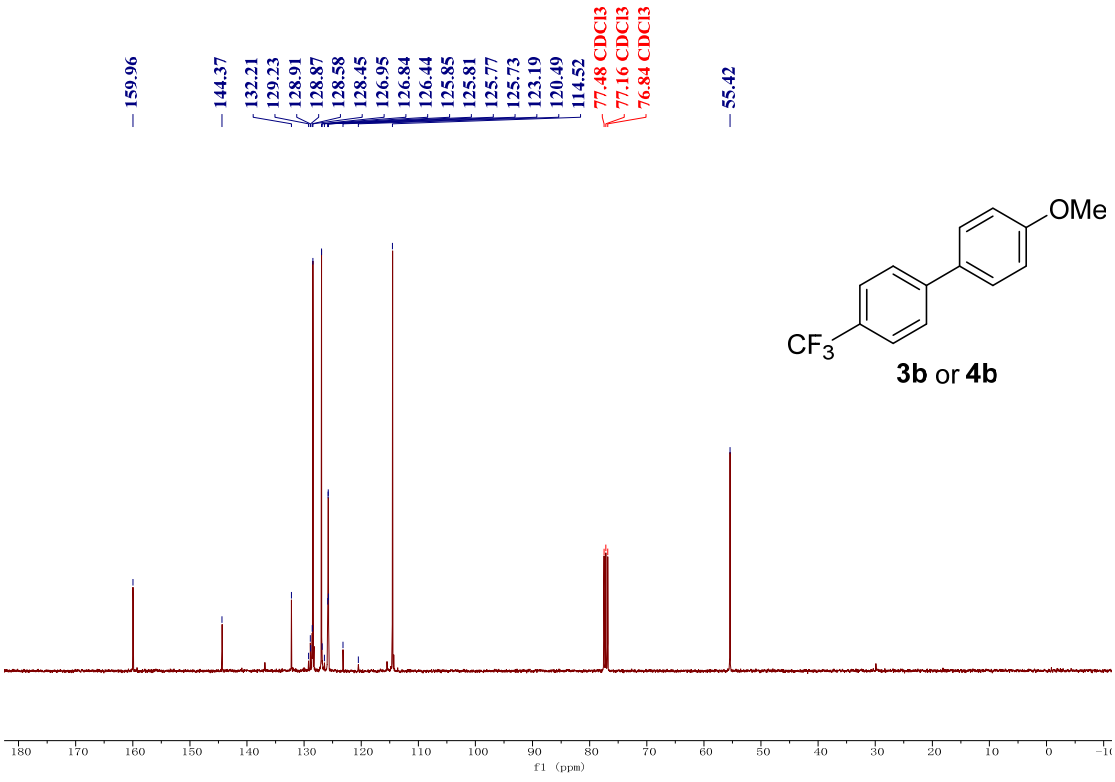
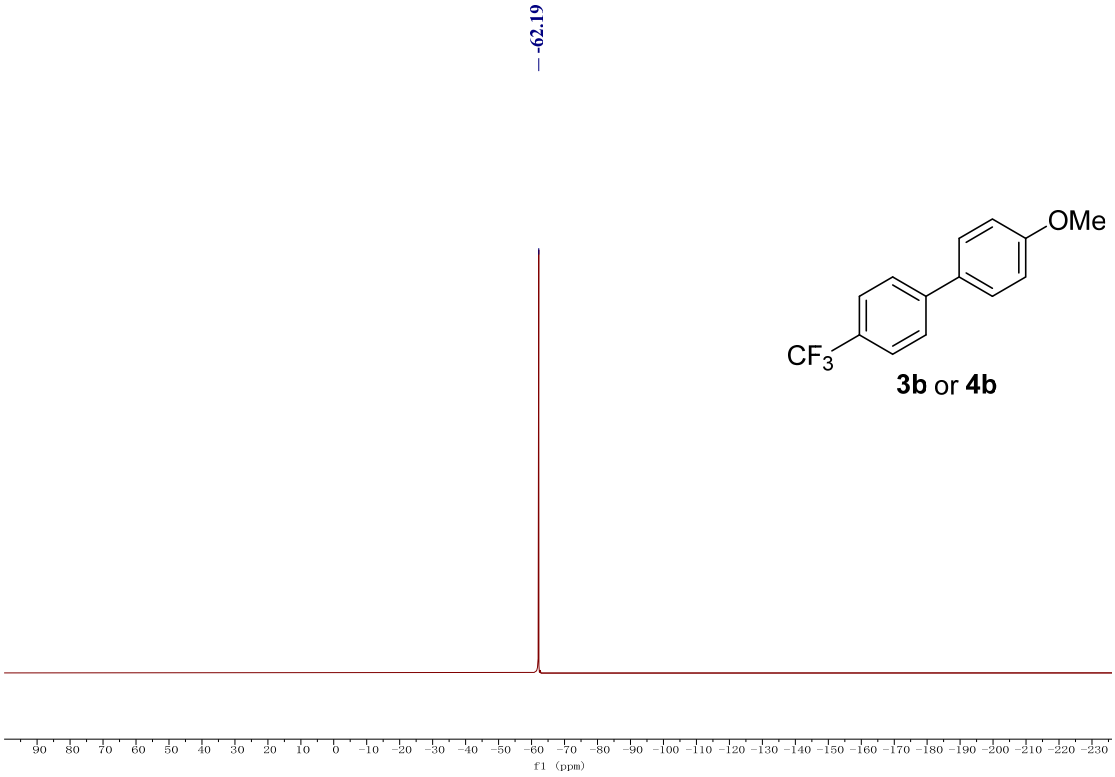
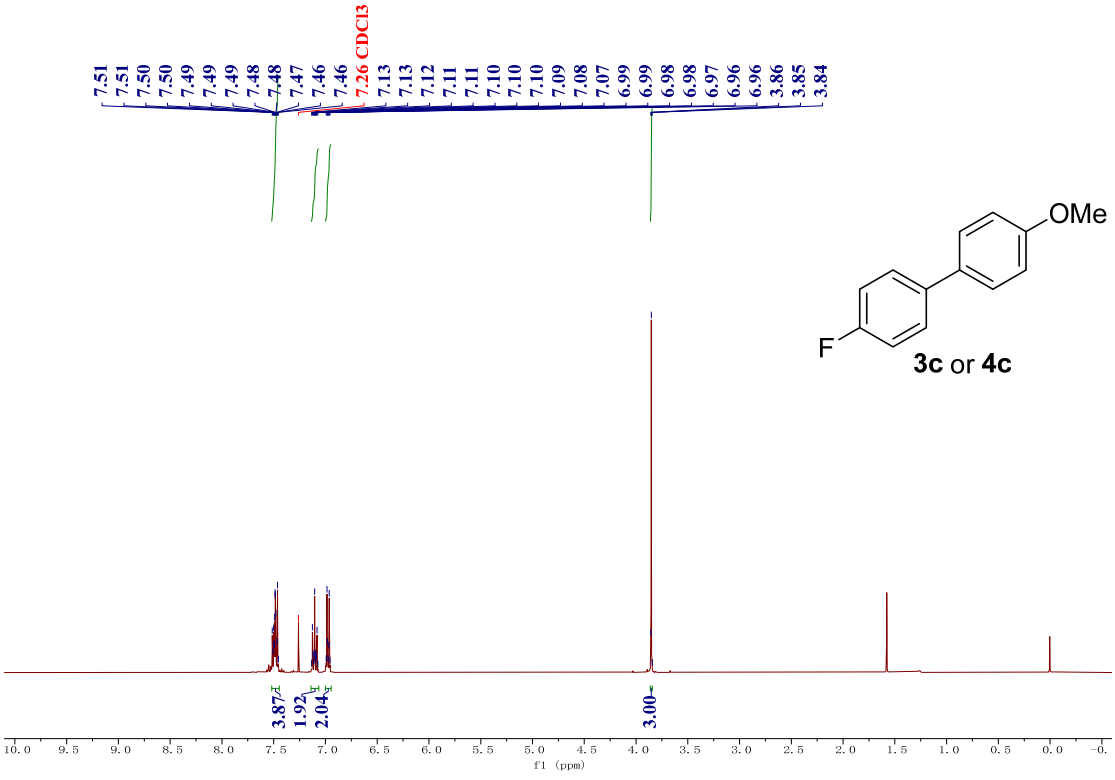


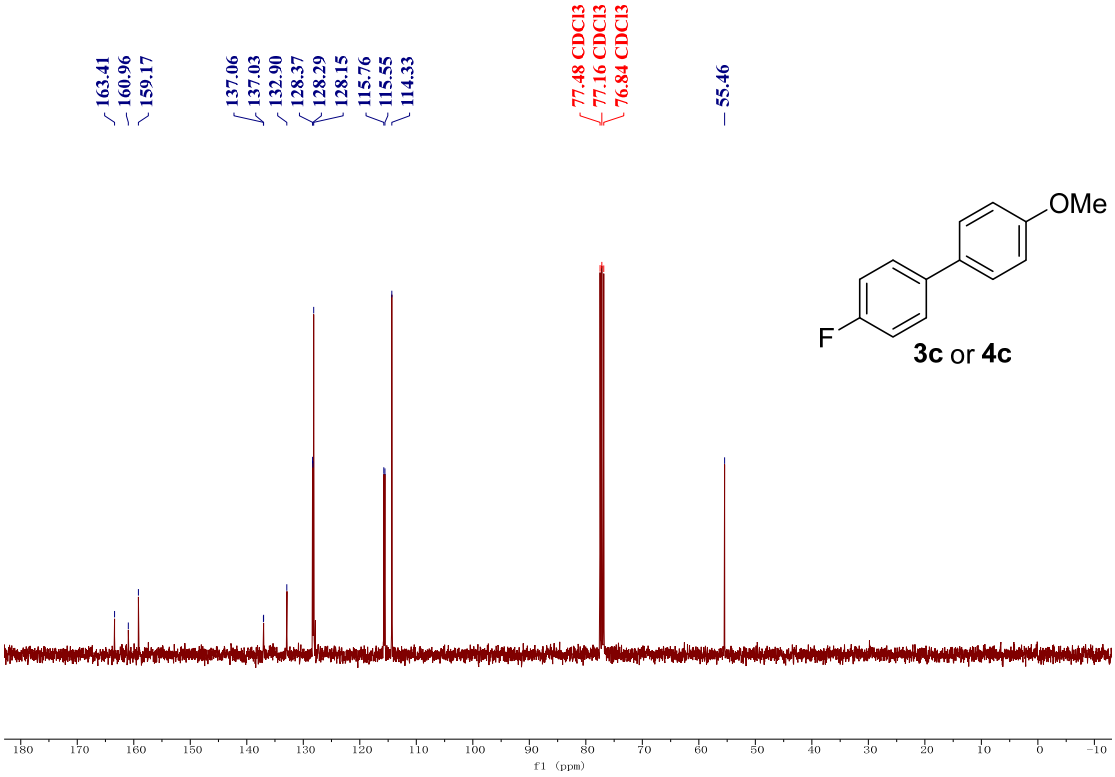
^{19}F NMR spectrum of 3b or 4b (376 MHz, $CDCl_3$)



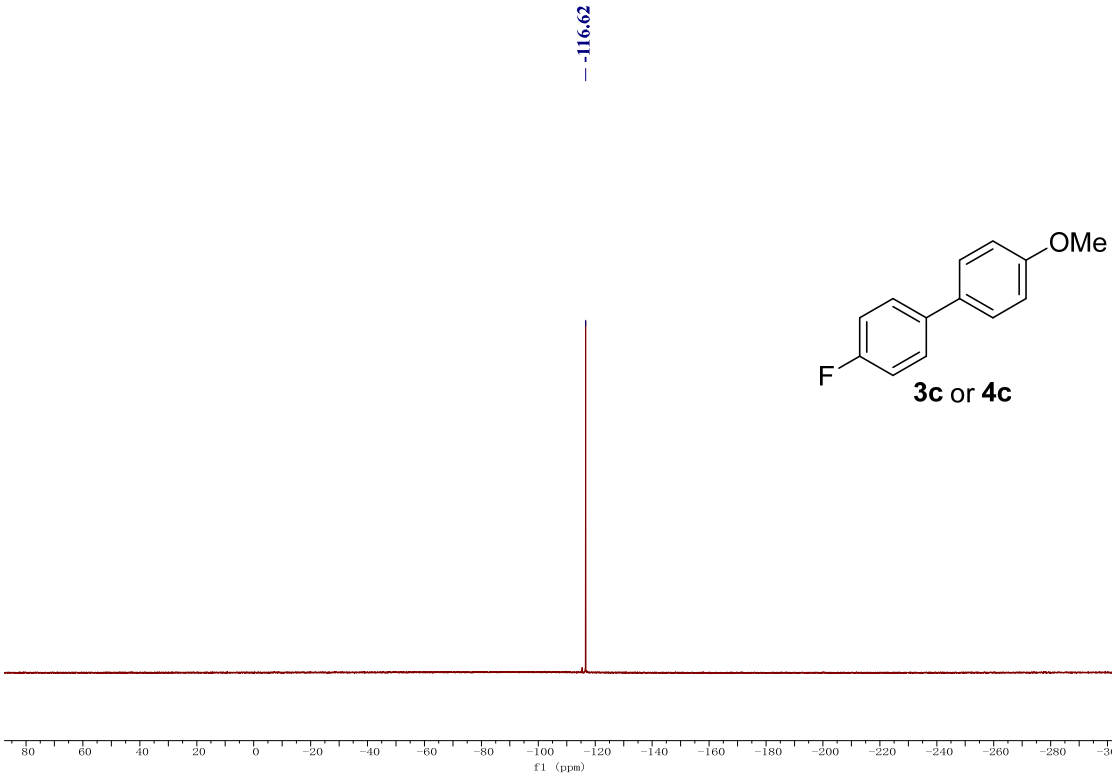
^{1}H NMR spectrum of 3c or 4c (400 MHz, $CDCl_3$)



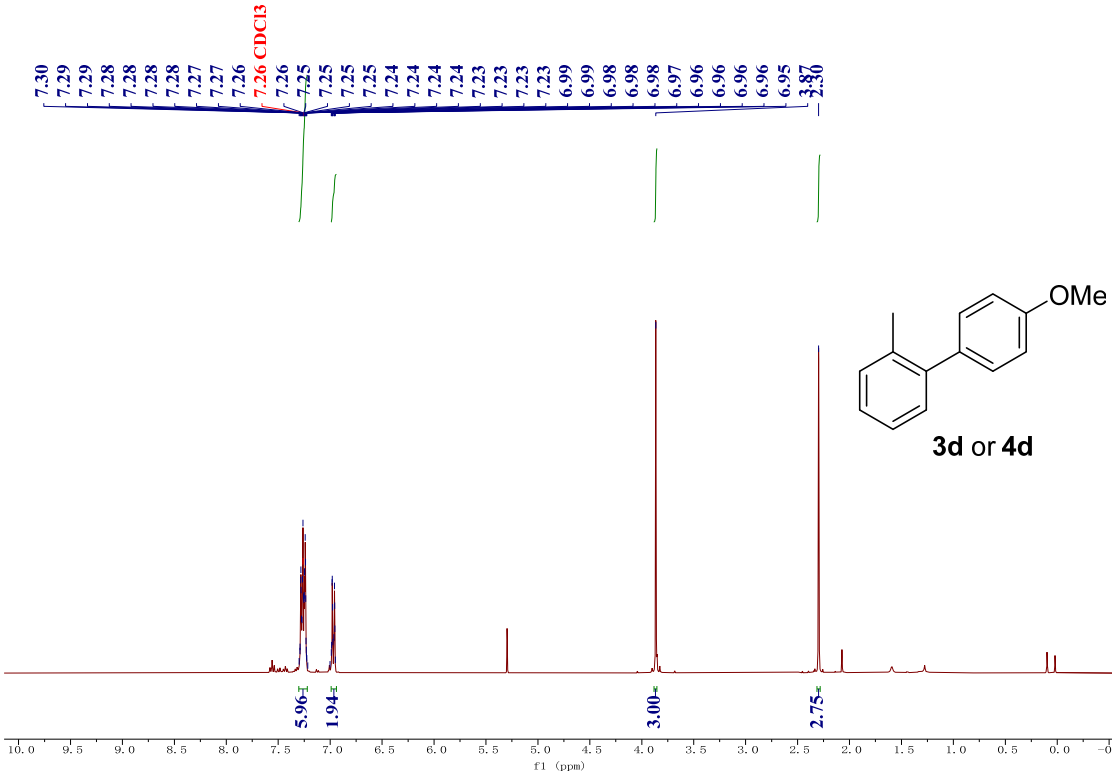
^{13}C NMR spectrum of 3c or 4c (100 MHz, $CDCl_3$)



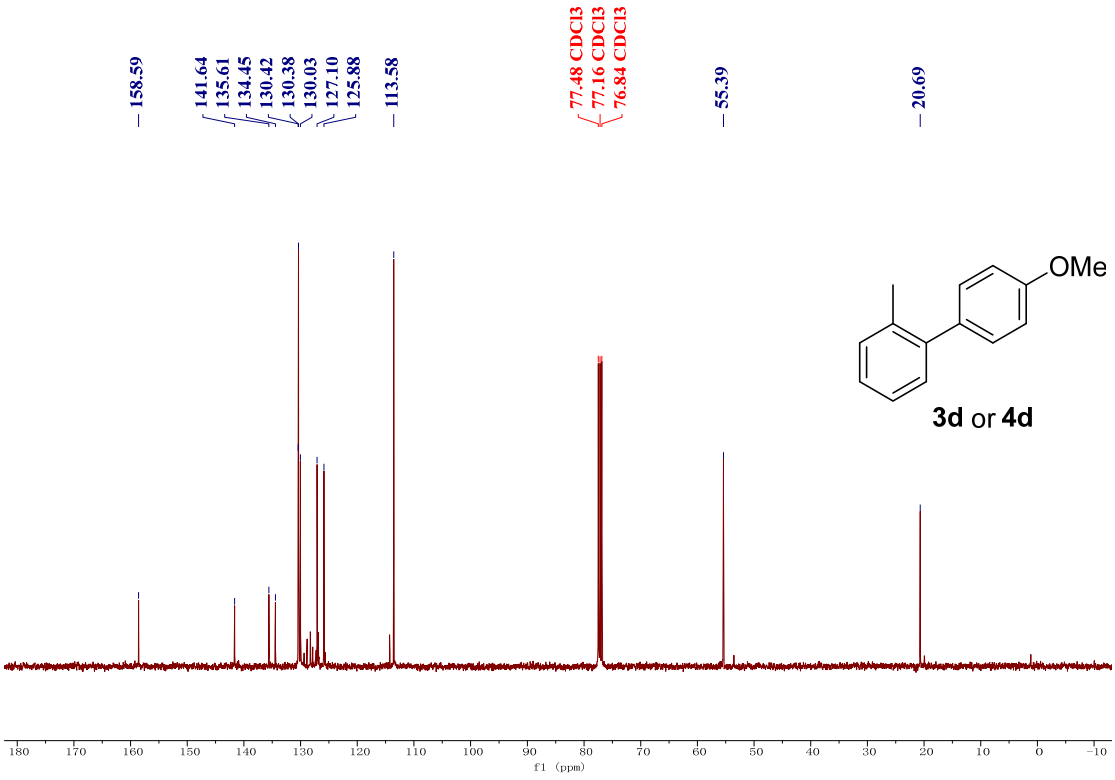
^{19}F NMR spectrum of 3c or 4c (376 MHz, $CDCl_3$)



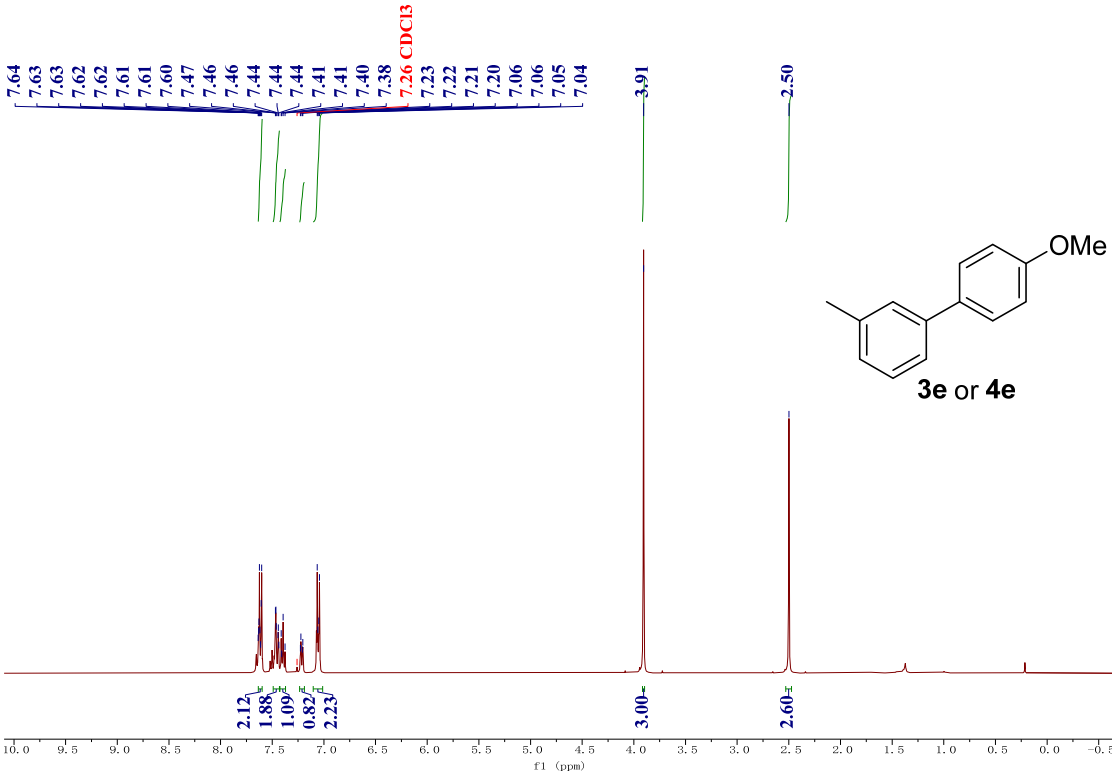
^{1}H NMR spectrum of 3d or 4d (400 MHz, $CDCl_3$)



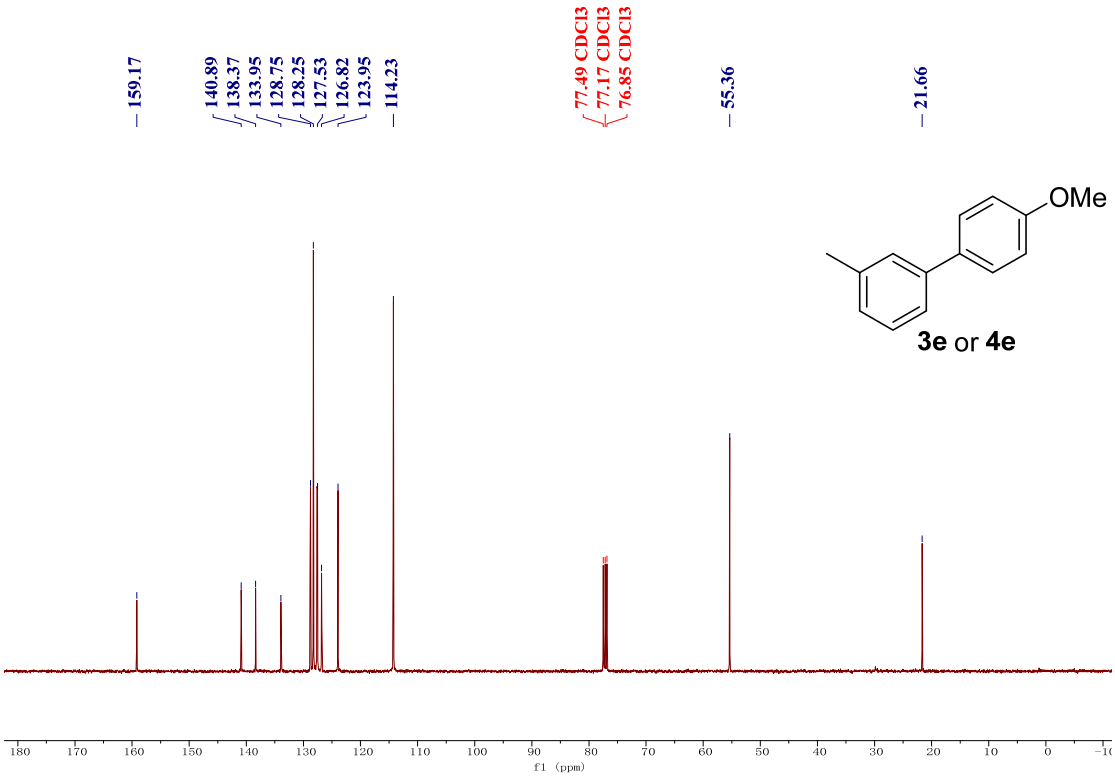
^{13}C NMR spectrum of 3d or 4d (100 MHz, $CDCl_3$)



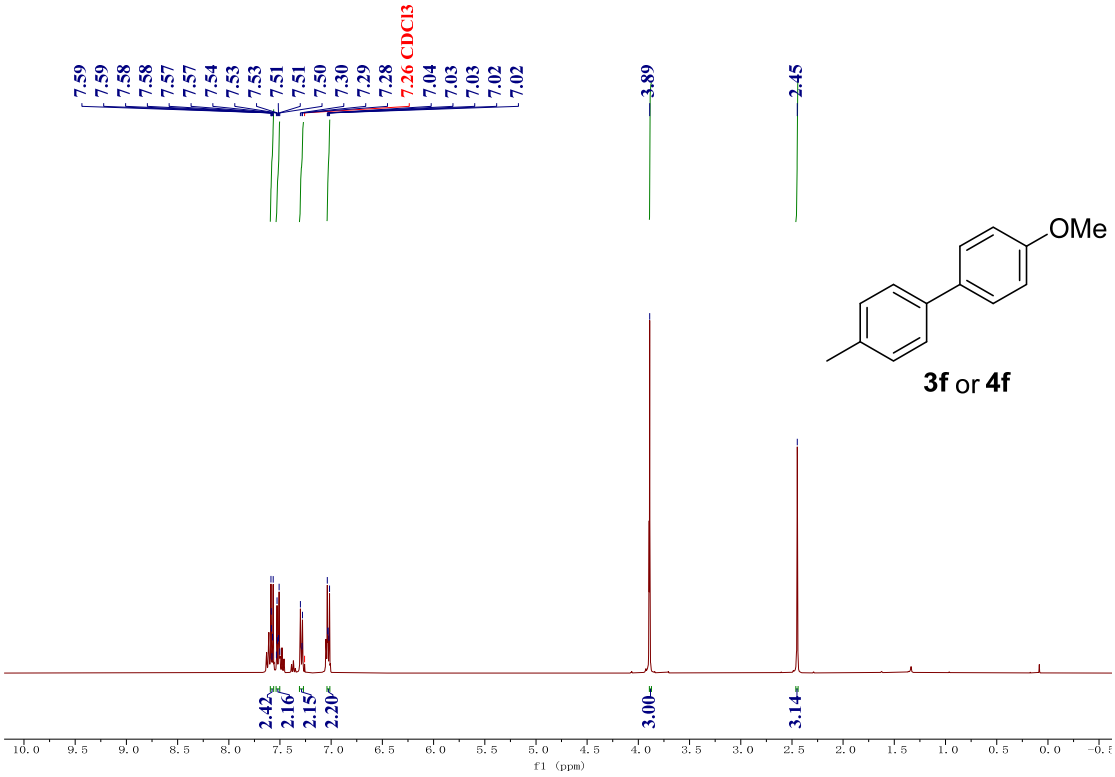
^{1}H NMR spectrum of 3e or 4e (400 MHz, $CDCl_3$)



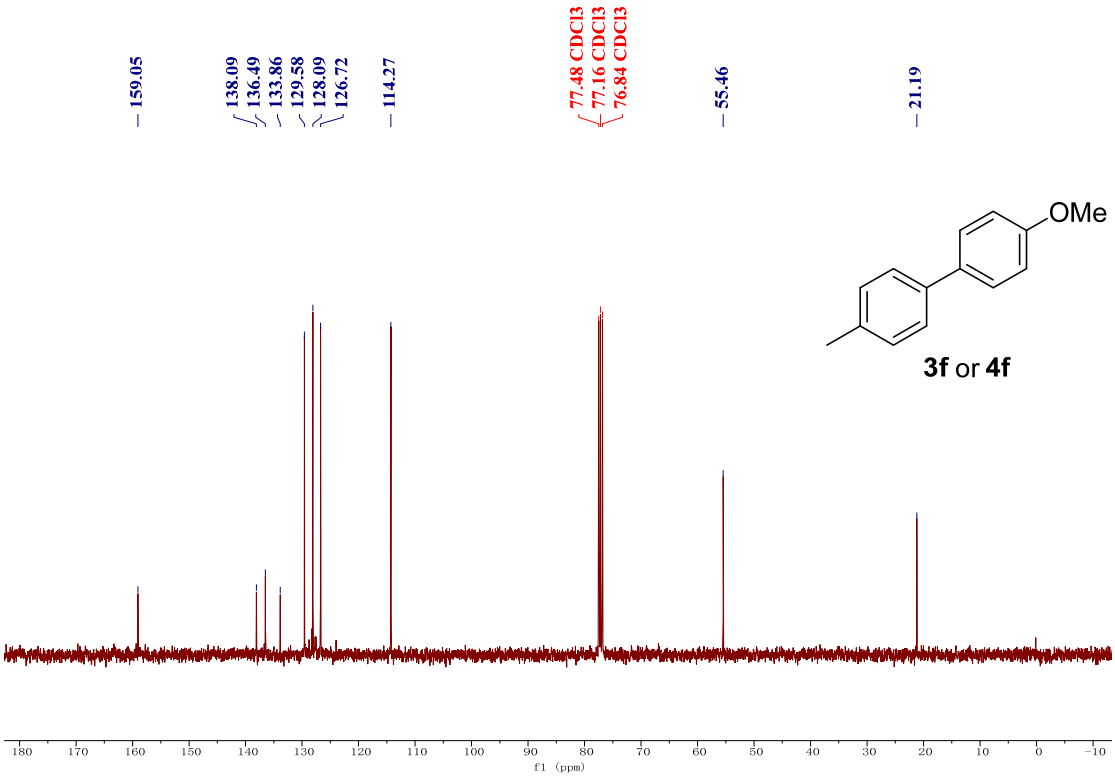
^{13}C NMR spectrum of 3e or 4e (100 MHz, $CDCl_3$)



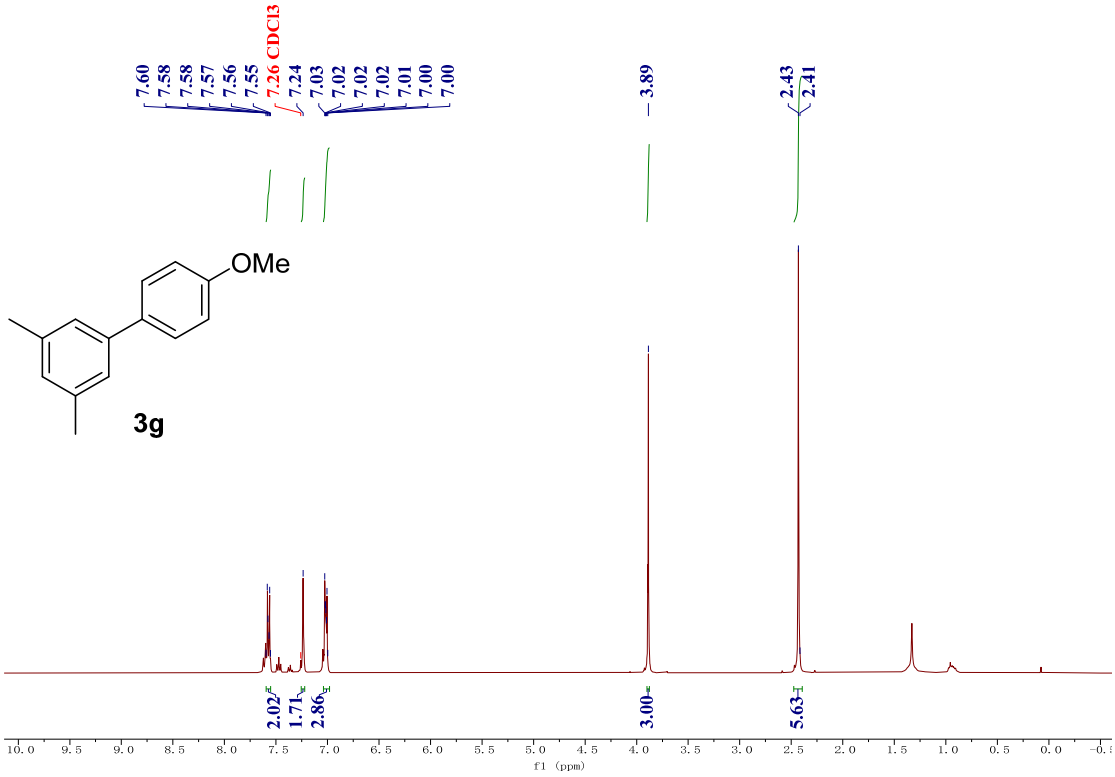
^{1}H NMR spectrum of 3f or 4f (400 MHz, $CDCl_3$)



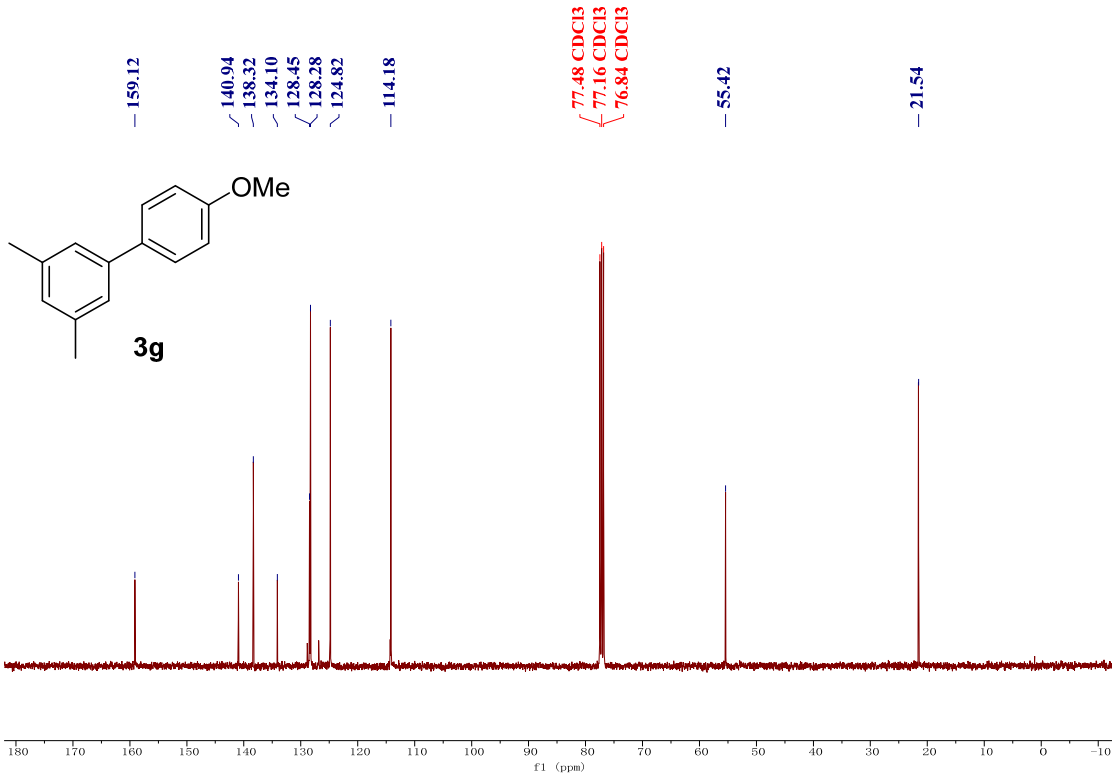
^{13}C NMR spectrum of 3f or 4f (100 MHz, $CDCl_3$)



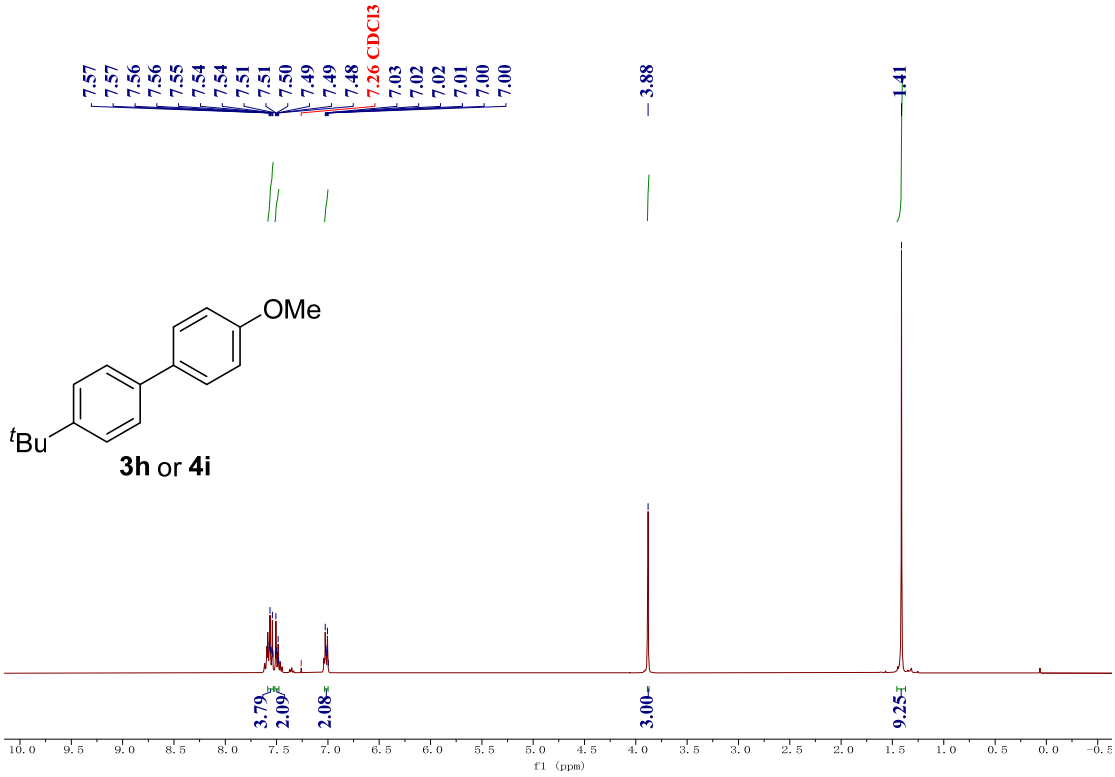
^{1}H NMR spectrum of 3g (400 MHz, $CDCl_3$)



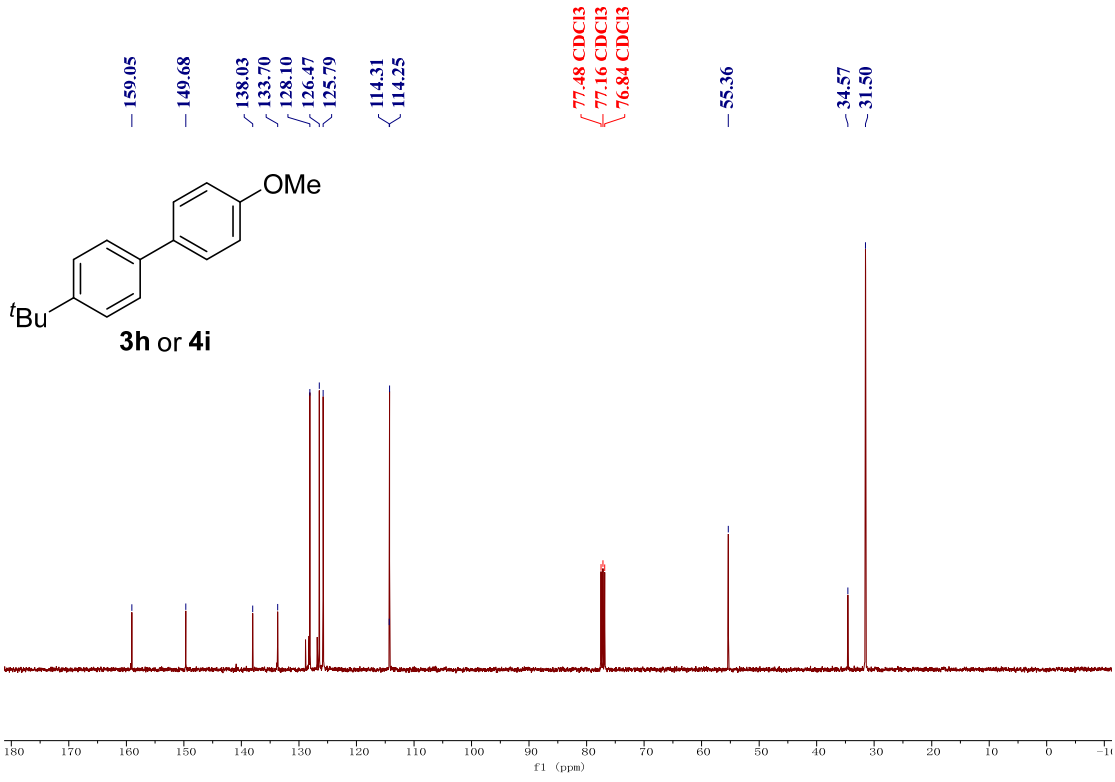
^{13}C NMR spectrum of 3g (100 MHz, $CDCl_3$)



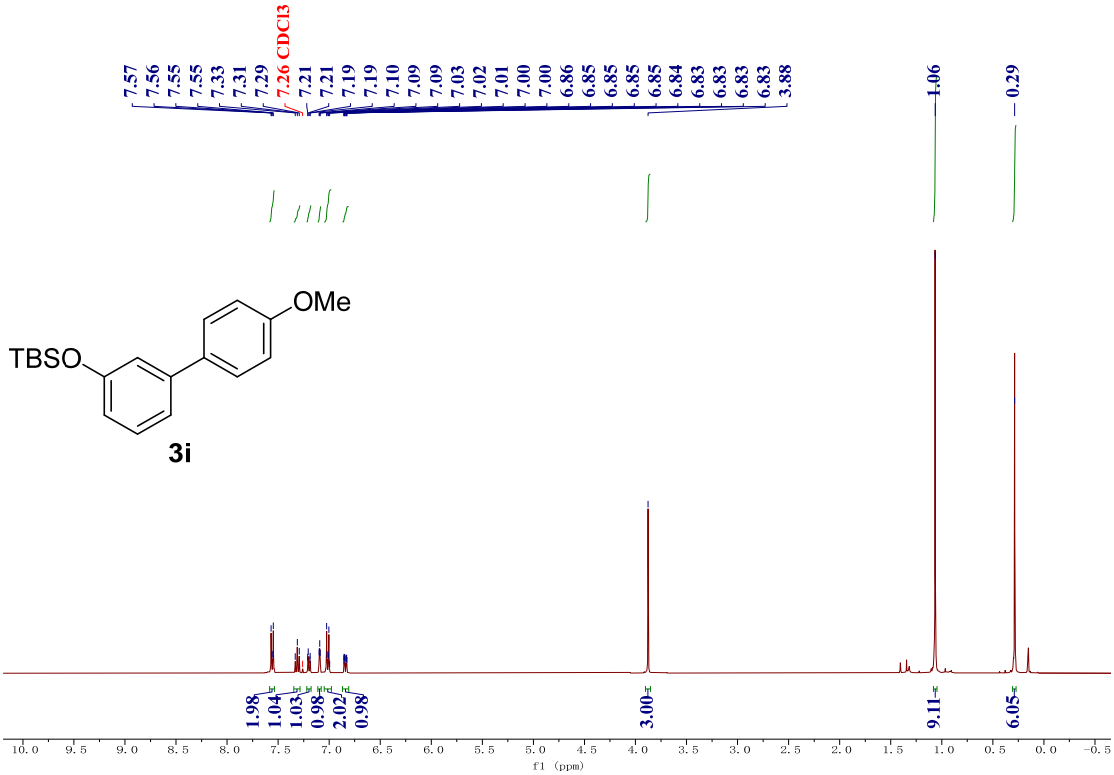
^{1}H NMR spectrum of 3h or 4i (400 MHz, $CDCl_3$)



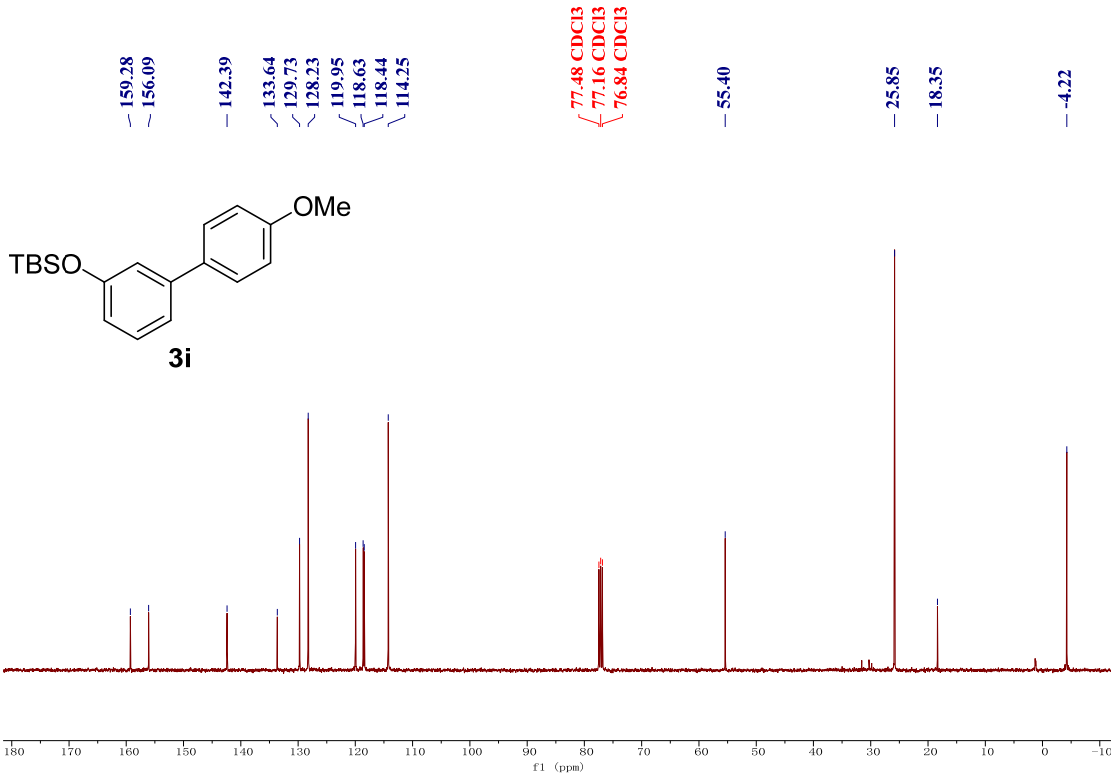
^{13}C NMR spectrum of 3h or 4i (100 MHz, $CDCl_3$)



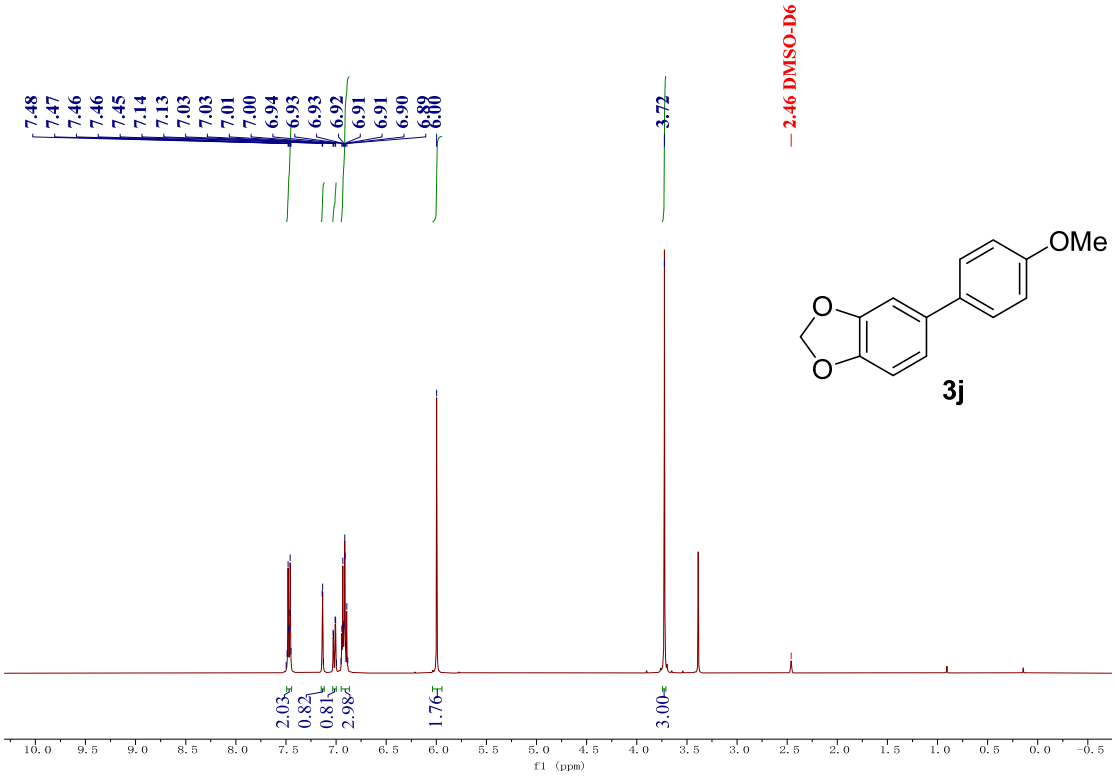
^{1}H NMR spectrum of 3i (400 MHz, $CDCl_3$)



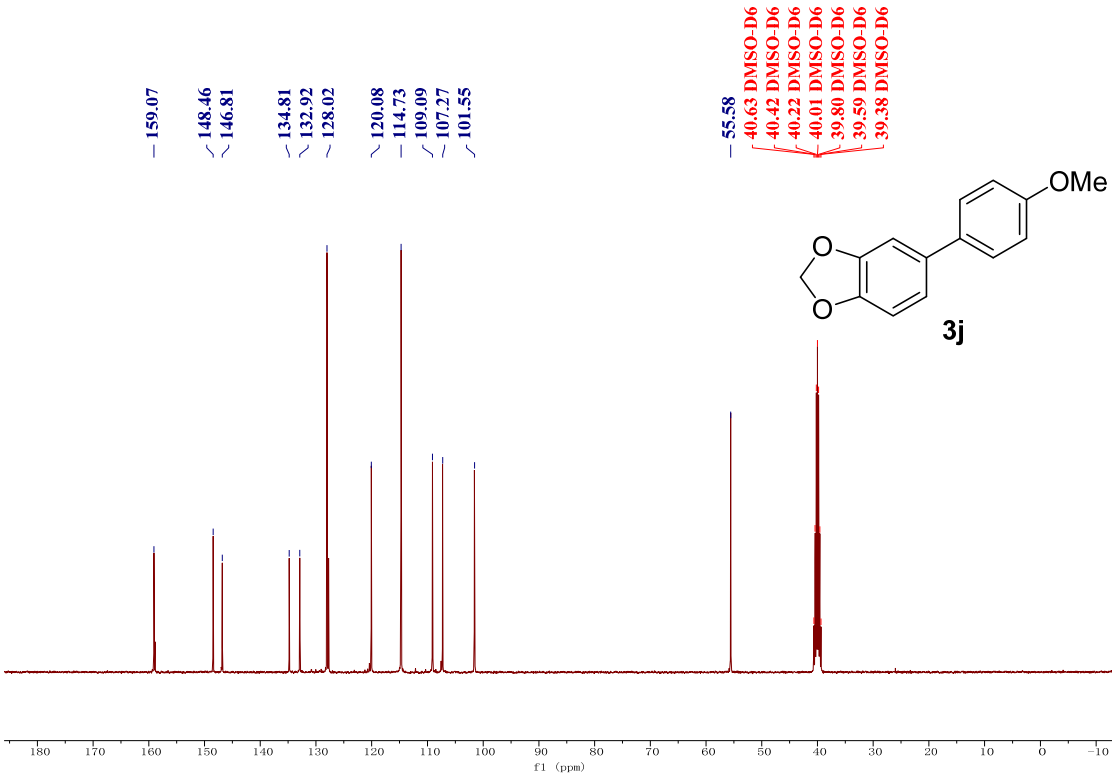
^{13}C NMR spectrum of 3i (100 MHz, $CDCl_3$)



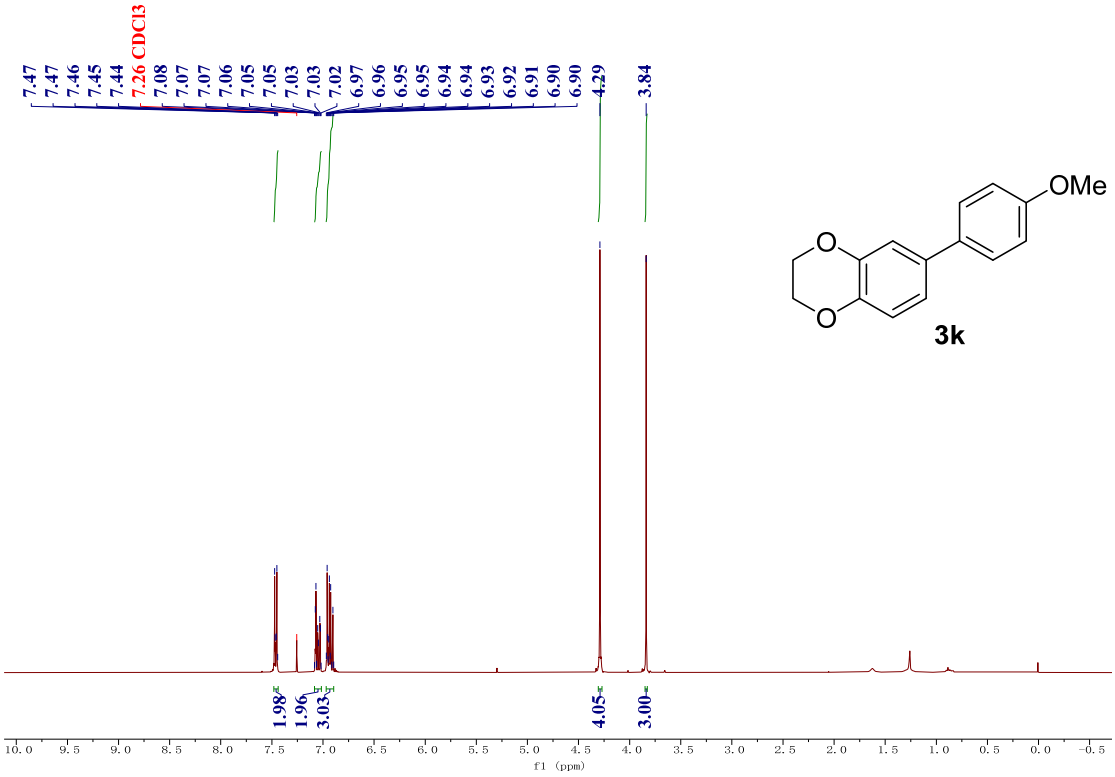
^{1}H NMR spectrum of 3j (400 MHz, DMSO-d_6)



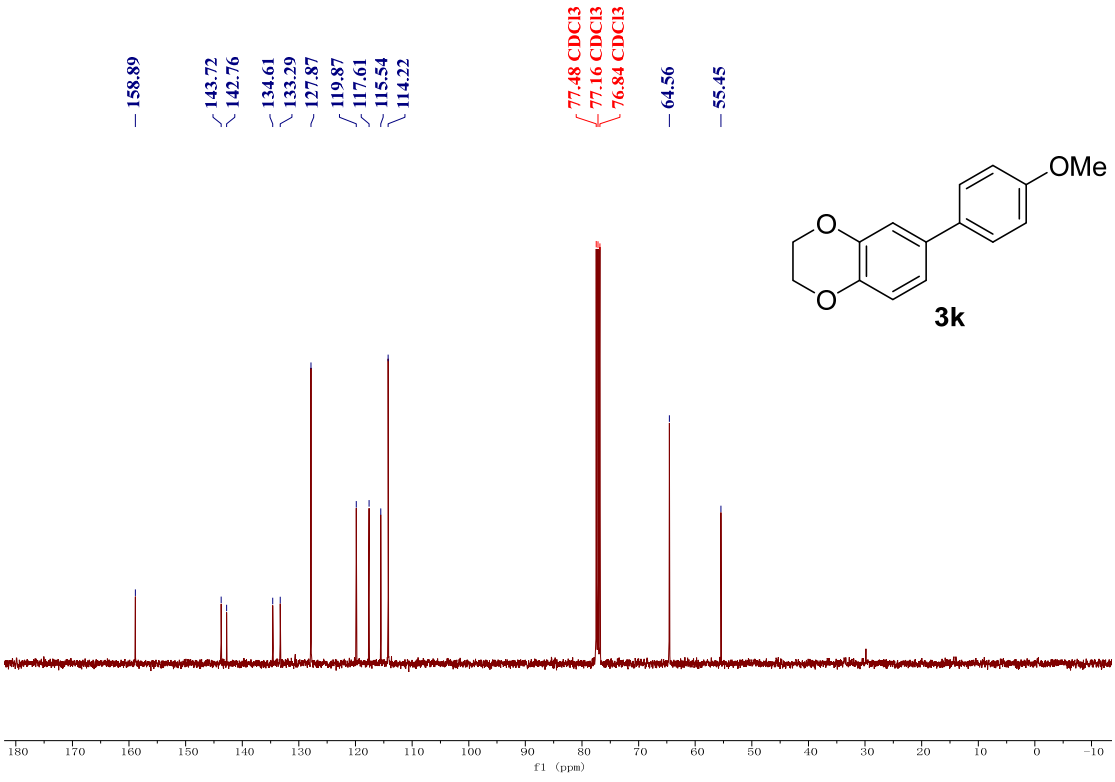
^{13}C NMR spectrum of 3j (100 MHz, DMSO-d_6)



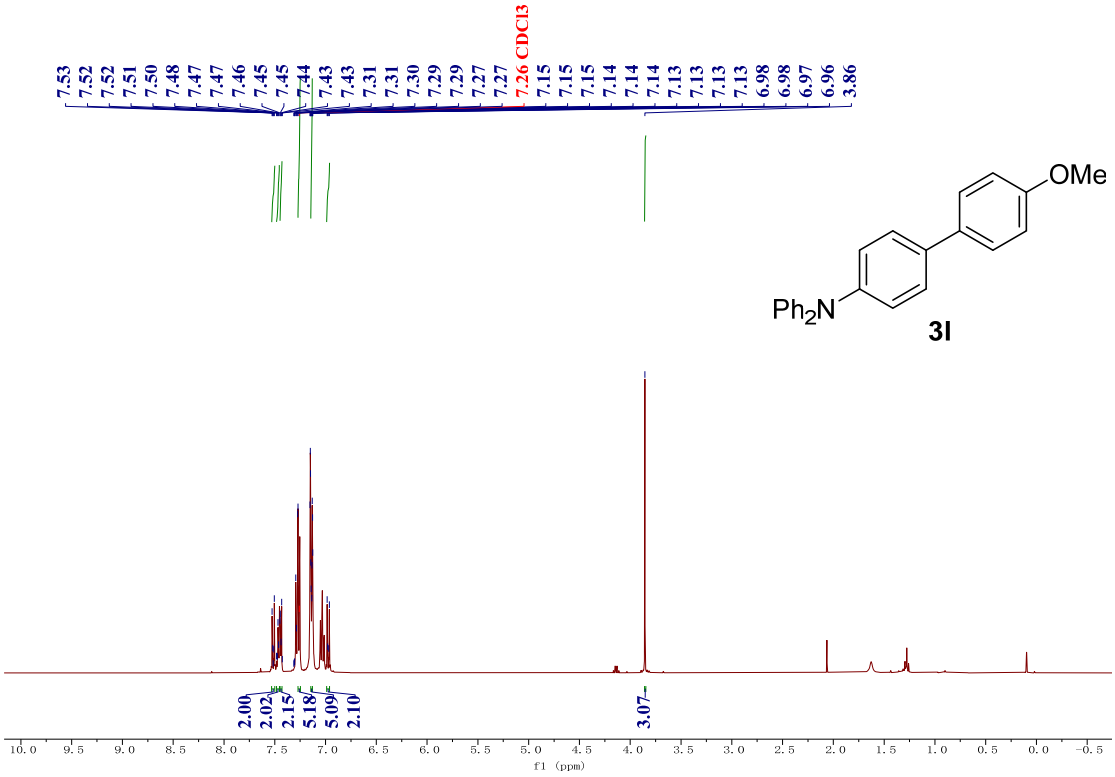
^{1}H NMR spectrum of 3k (400 MHz, $CDCl_3$)



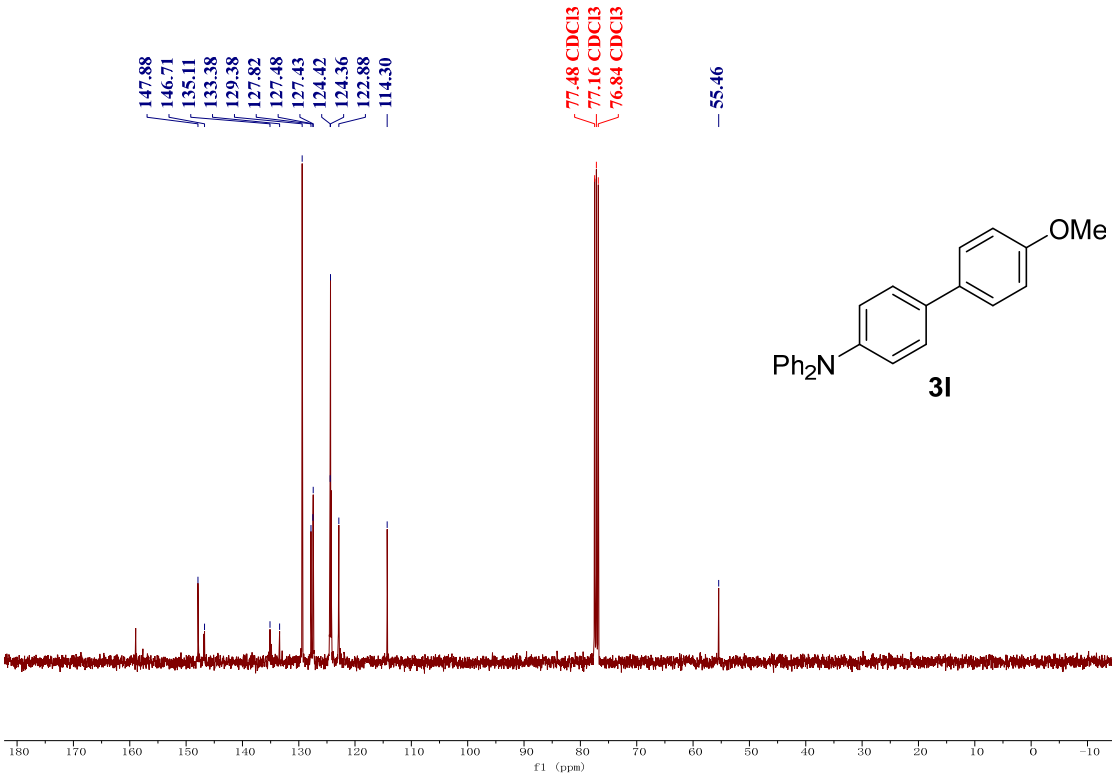
^{13}C NMR spectrum of 3k (100 MHz, $CDCl_3$)



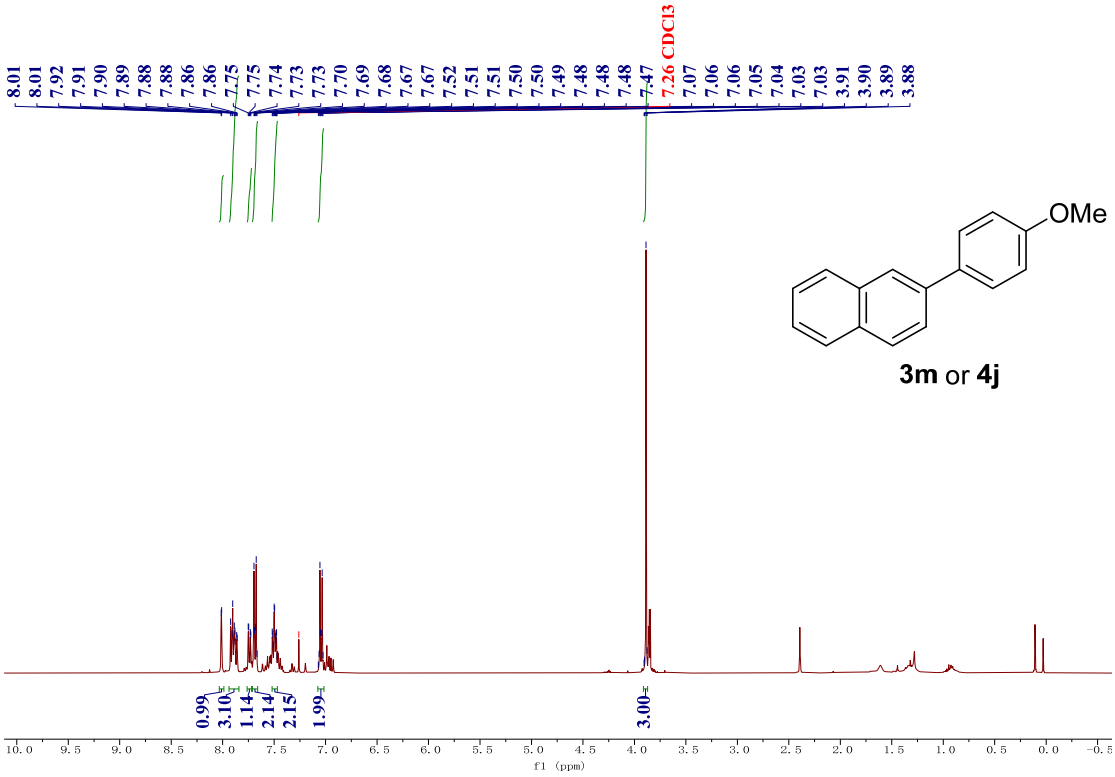
^{1}H NMR spectrum of 3l (400 MHz, $CDCl_3$)



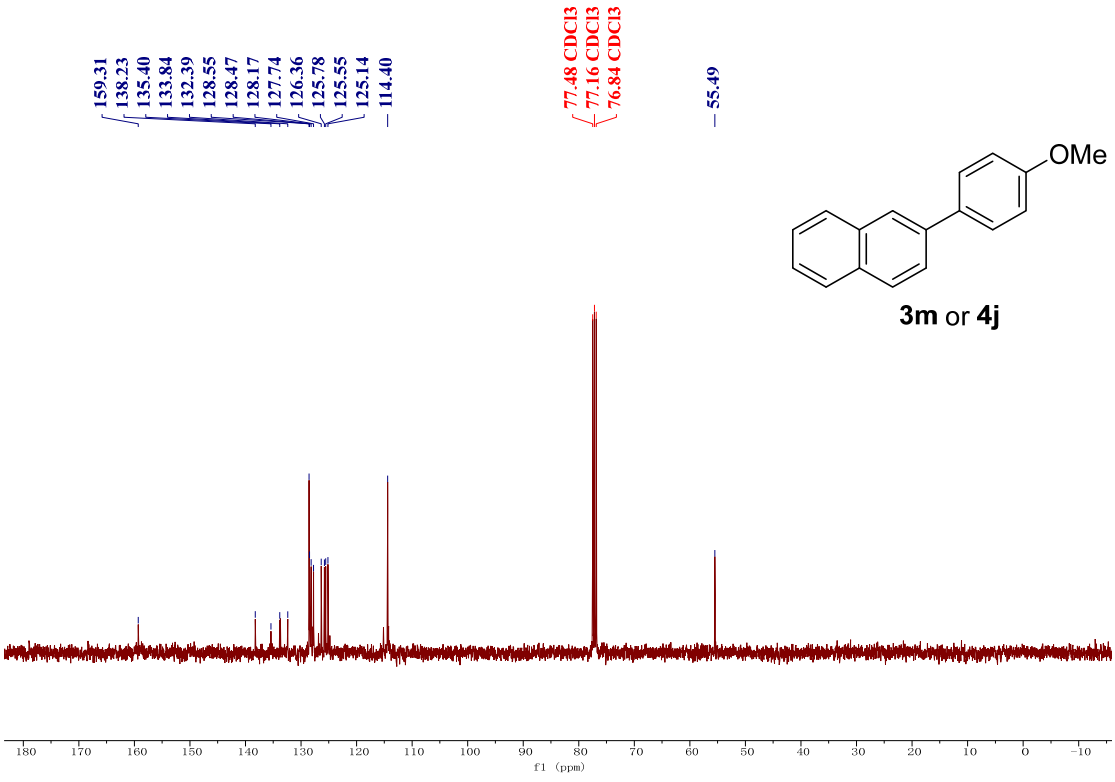
^{13}C NMR spectrum of 3l (100 MHz, $CDCl_3$)



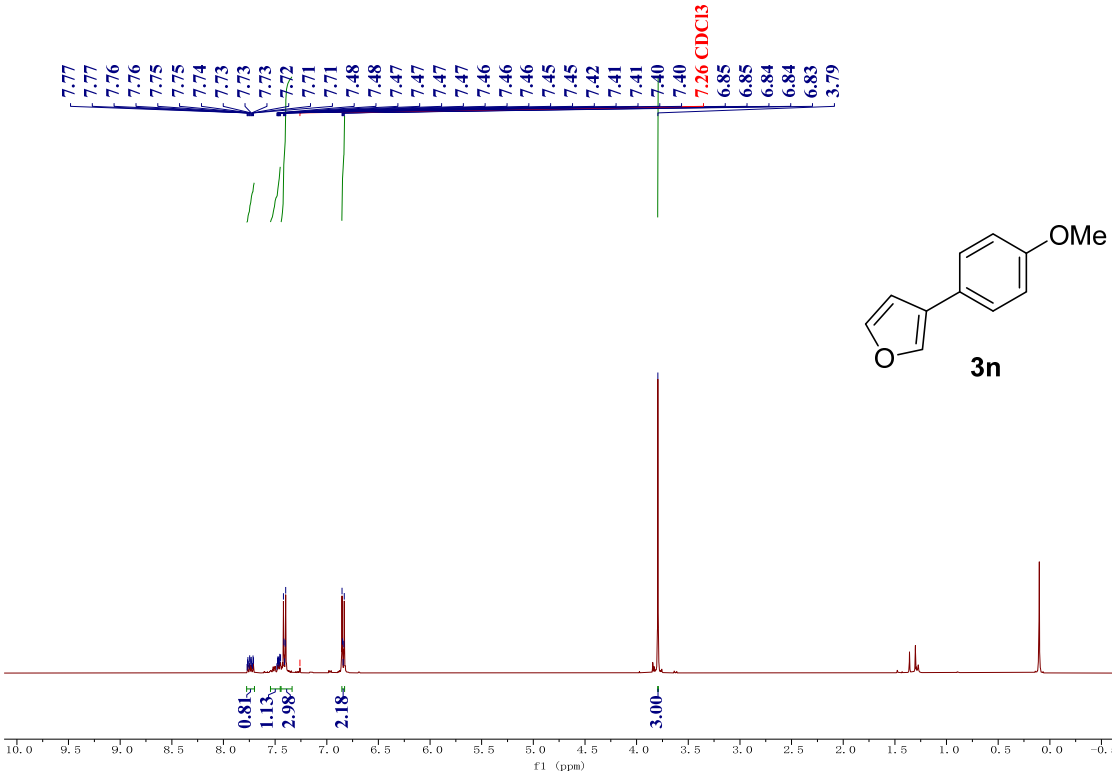
^{1}H NMR spectrum of 3m or 4j (400 MHz, $CDCl_3$)



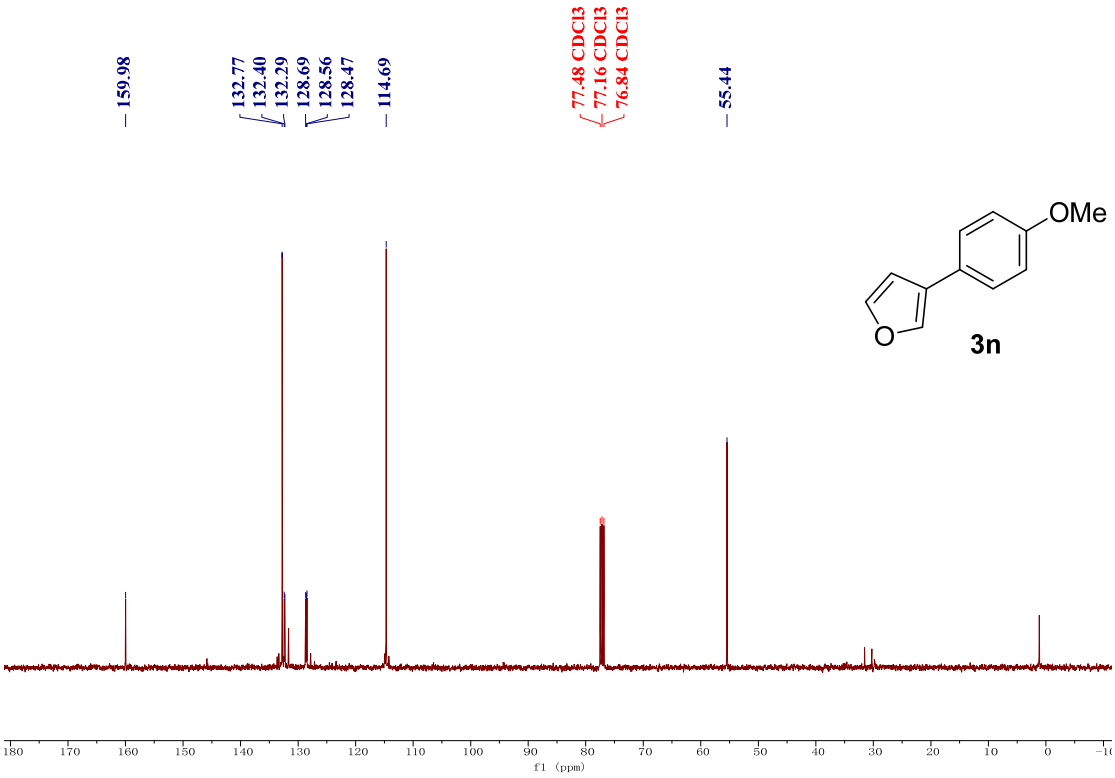
^{13}C NMR spectrum of 3m or 4j (100 MHz, $CDCl_3$)



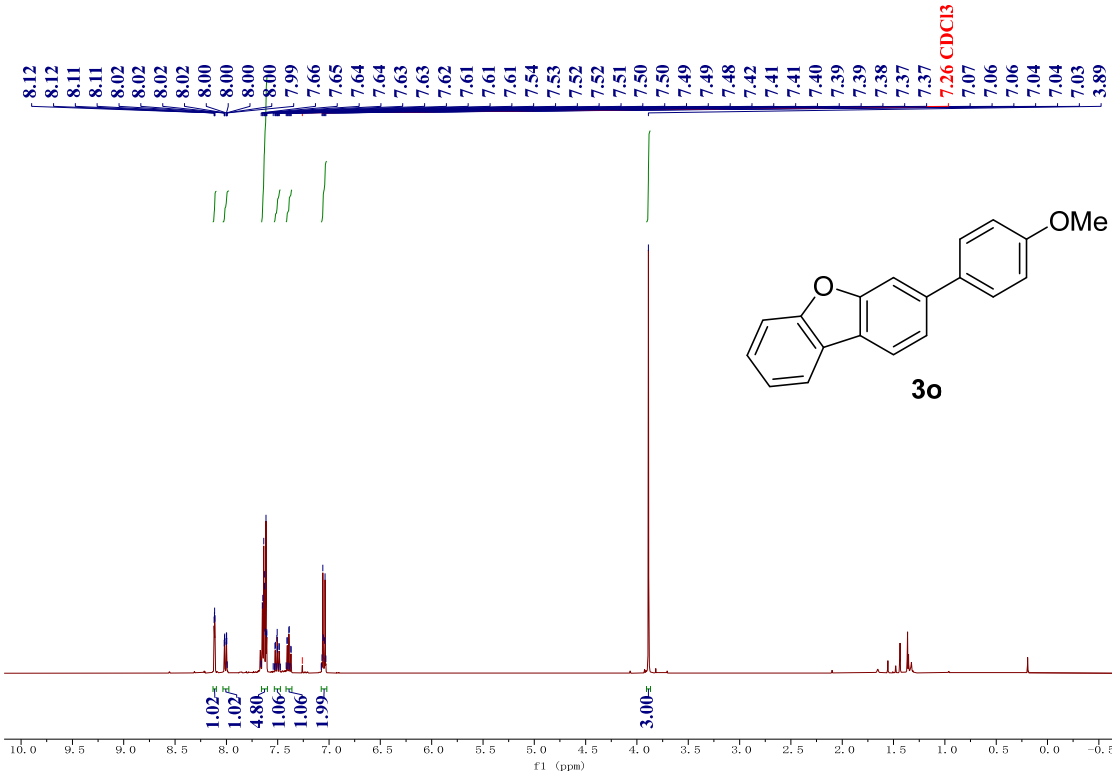
^{1}H NMR spectrum of 3n (400 MHz, $CDCl_3$)



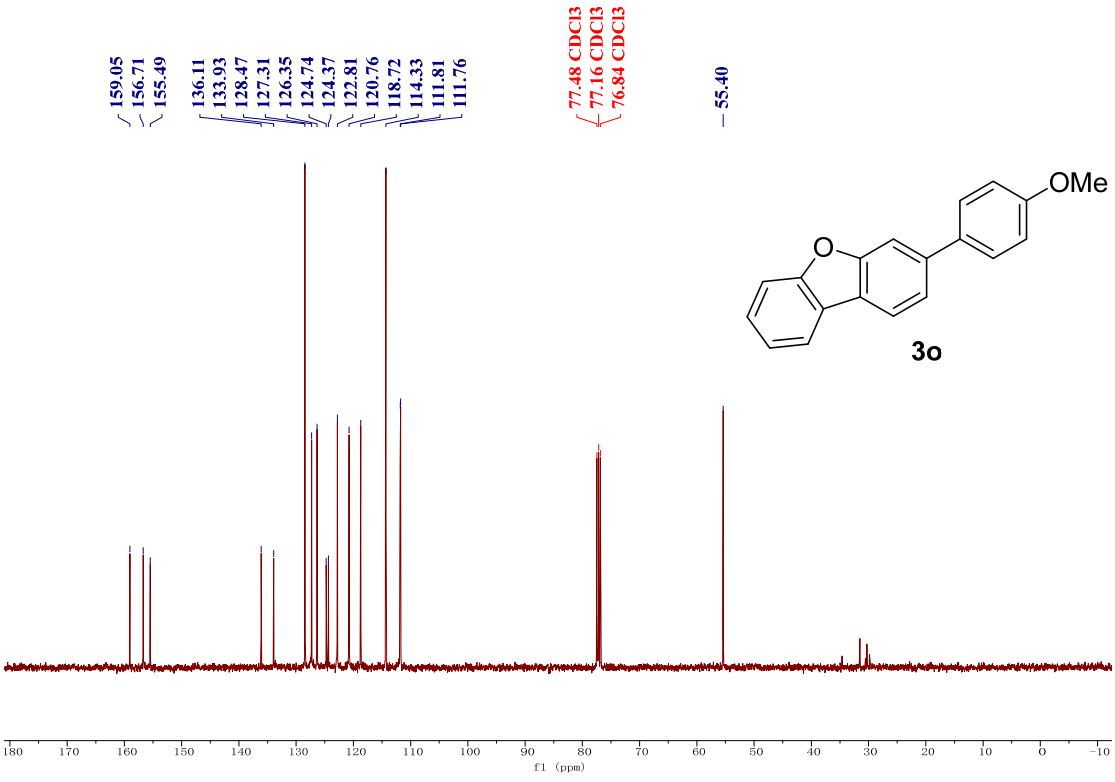
^{13}C NMR spectrum of 3n (100 MHz, $CDCl_3$)



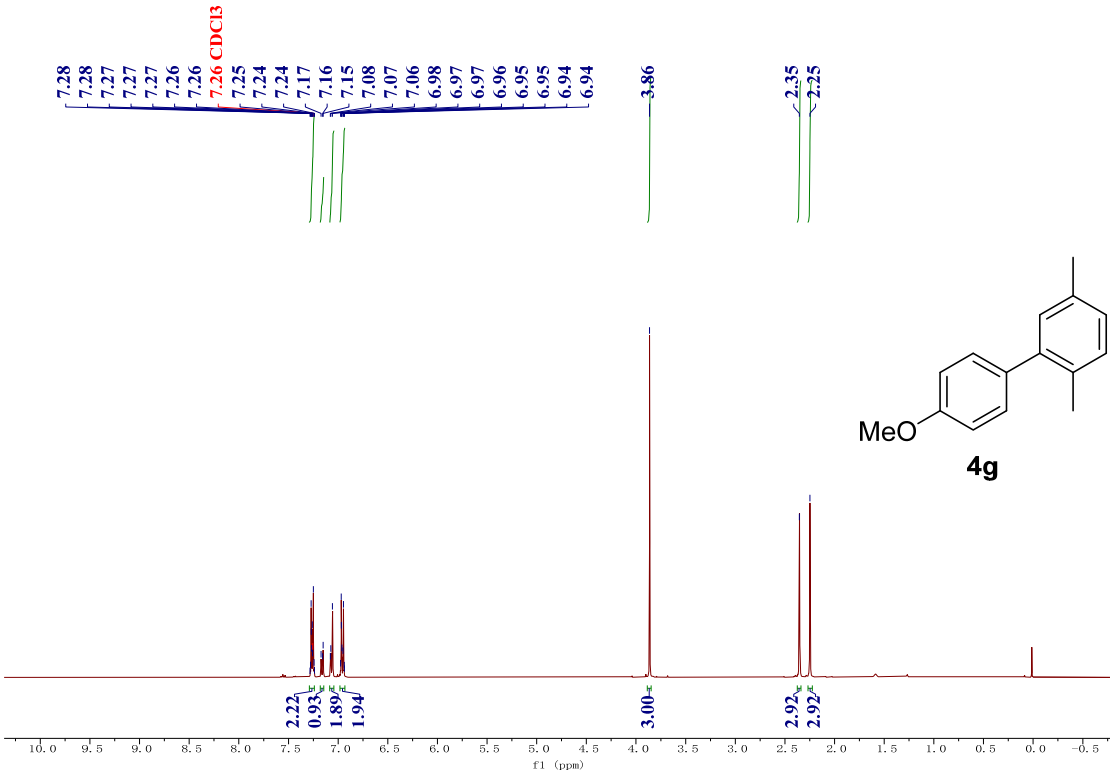
^{1}H NMR spectrum of 3o (400 MHz, $CDCl_3$)



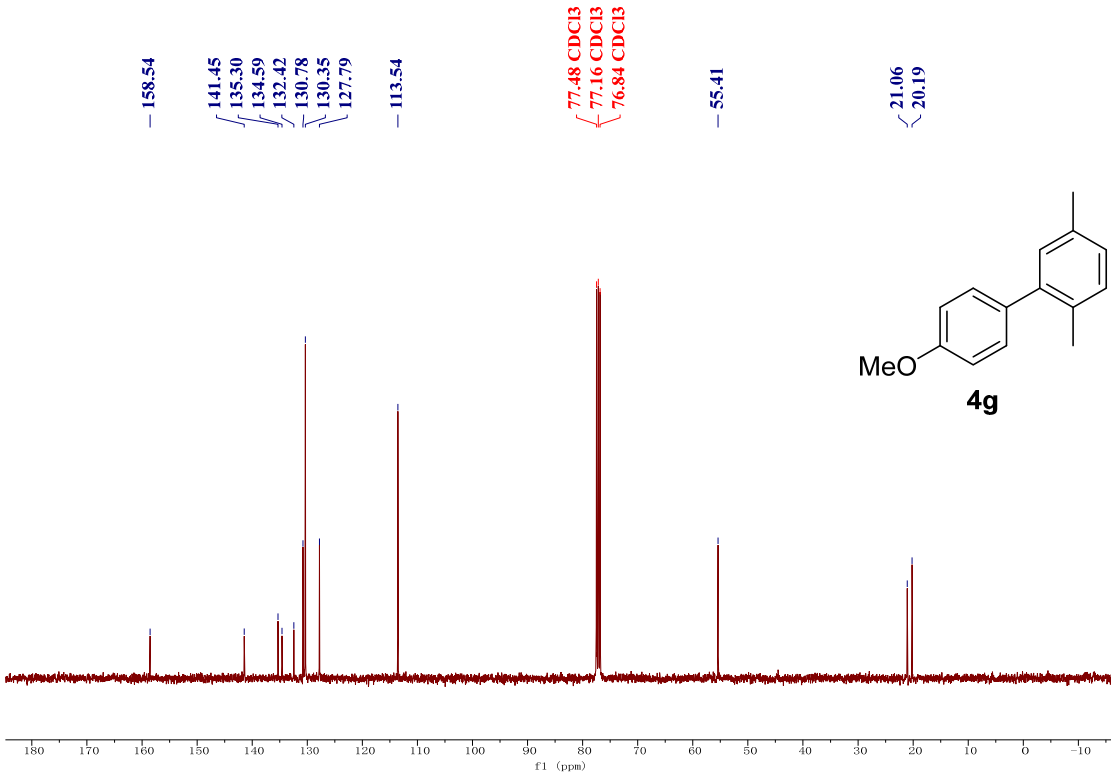
^{13}C NMR spectrum of 3o (100 MHz, $CDCl_3$)



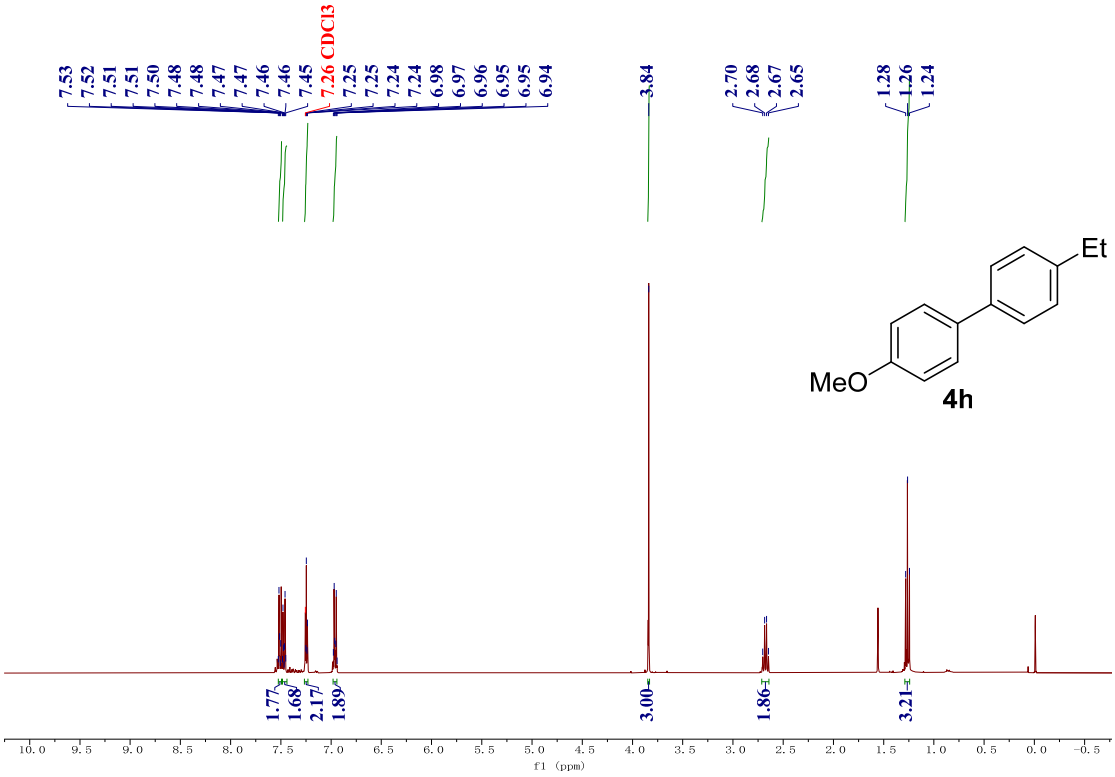
^{1}H NMR spectrum of 4g (400 MHz, $CDCl_3$)



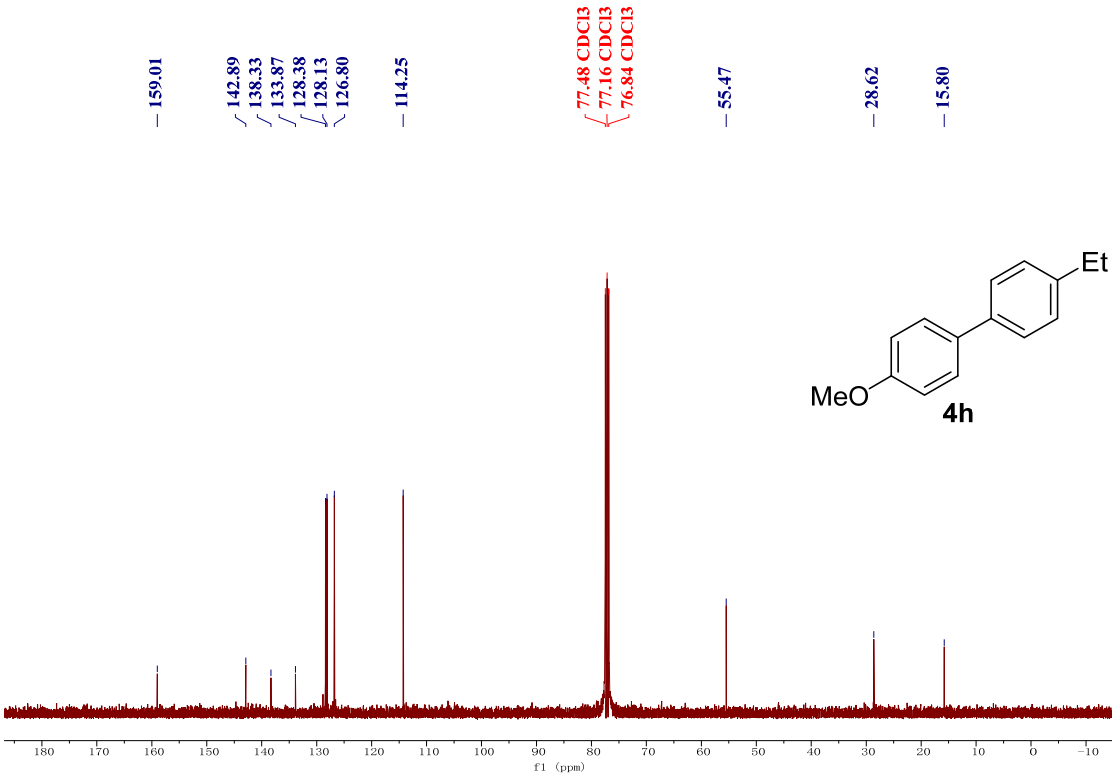
^{13}C NMR spectrum of 4g (100 MHz, $CDCl_3$)



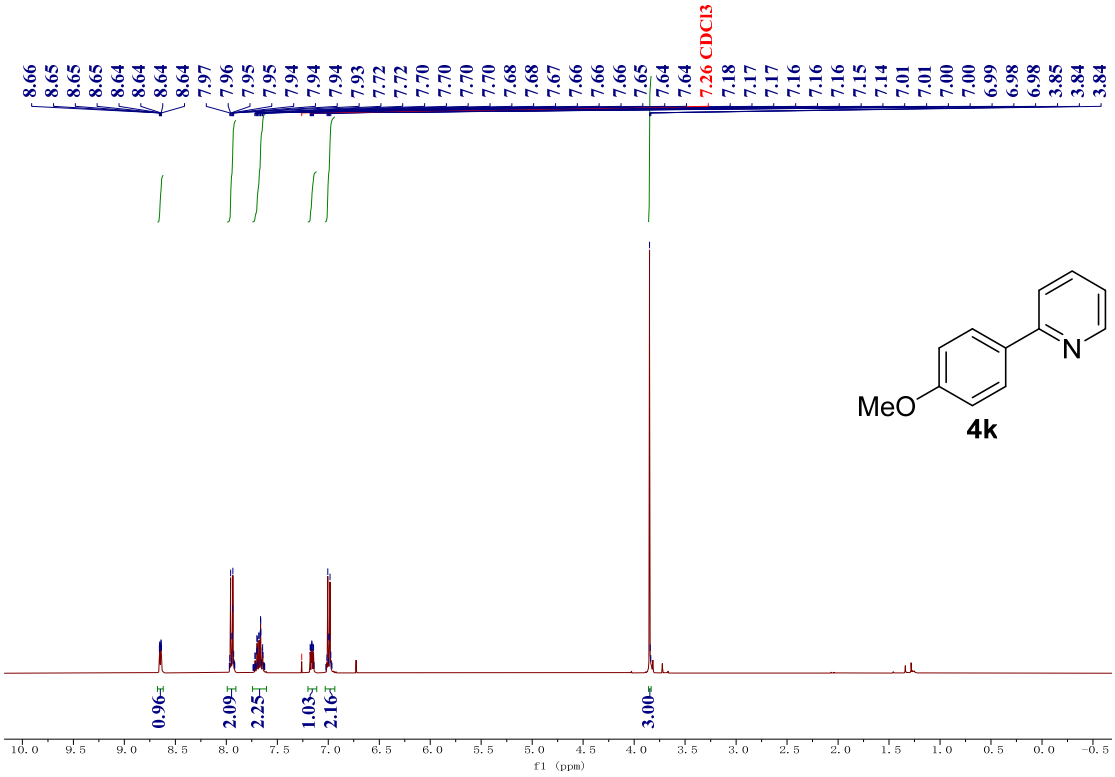
^{1}H NMR spectrum of 4h (400 MHz, $CDCl_3$)



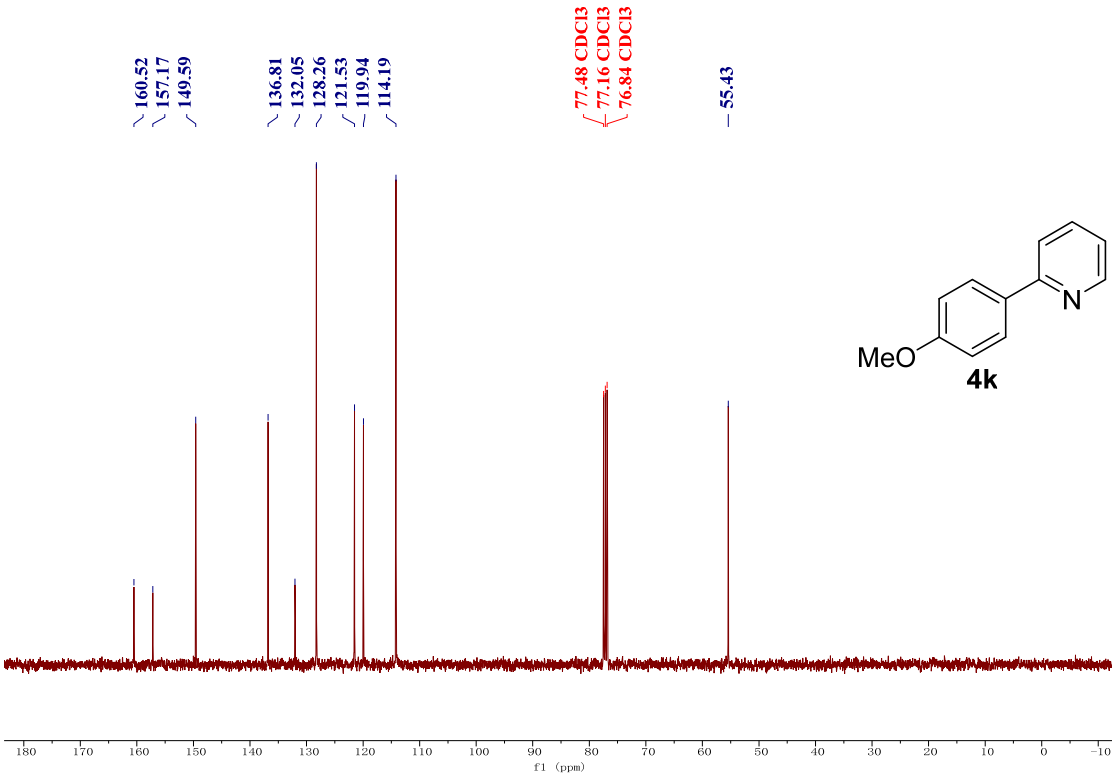
^{13}C NMR spectrum of 4h (100 MHz, $CDCl_3$)



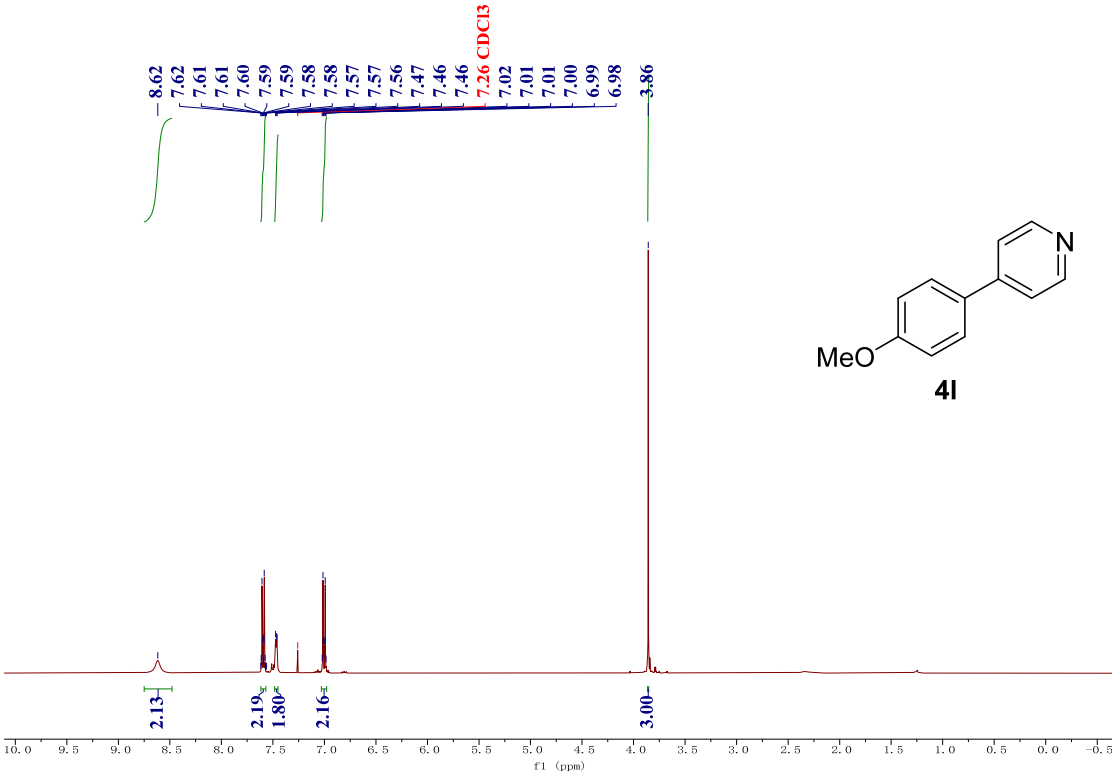
^{1}H NMR spectrum of 4k (400 MHz, $CDCl_3$)



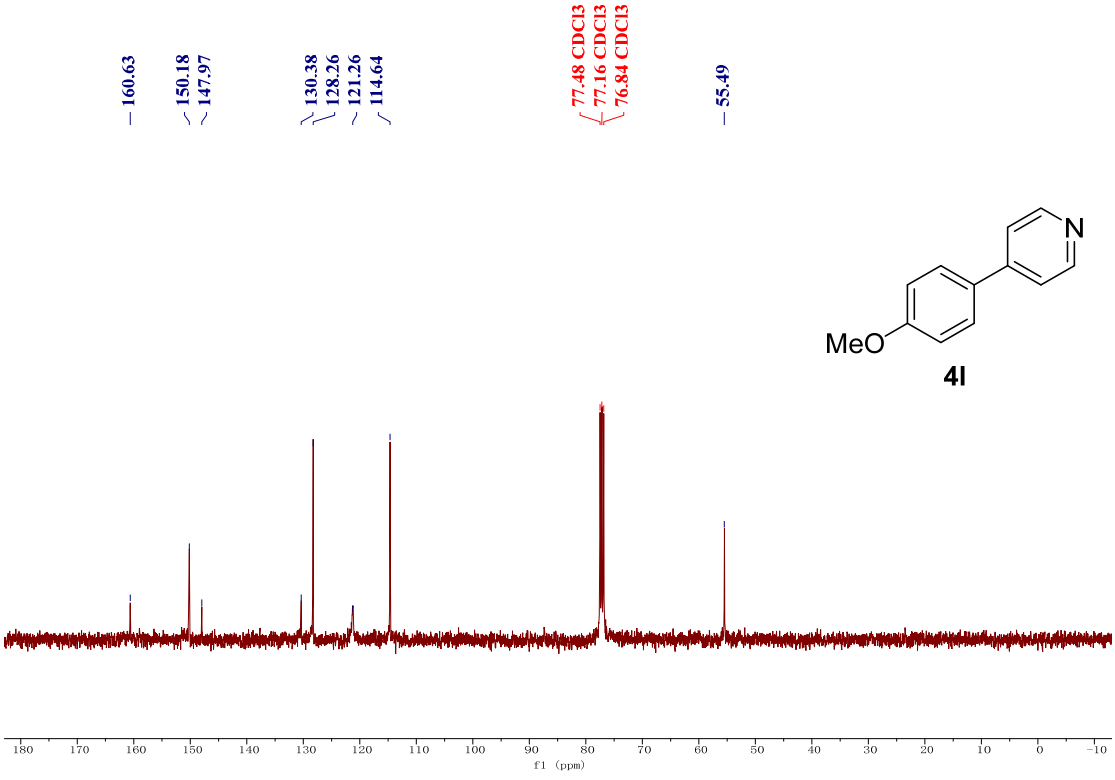
^{13}C NMR spectrum of 4k (100 MHz, $CDCl_3$)



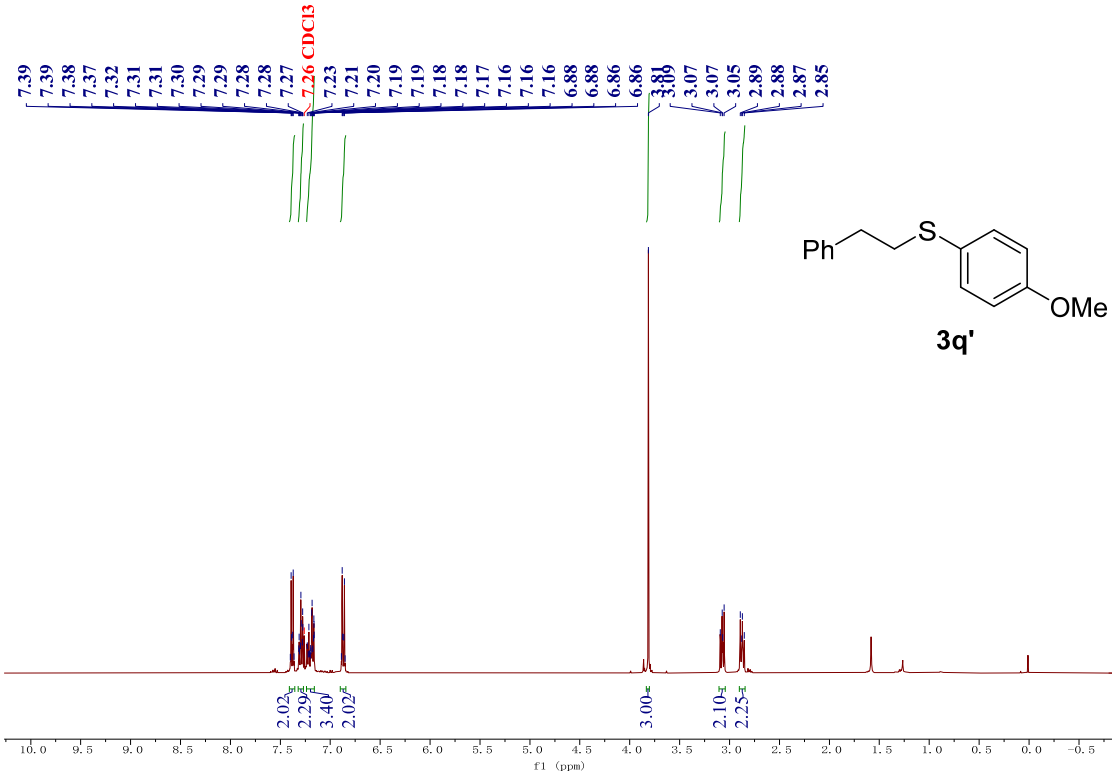
^{1}H NMR spectrum of 4l (400 MHz, $CDCl_3$)



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



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



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