Supporting Information

Cobalt-Catalyzed Defluorosilylation of Aryl Fluorides *via* Grignard Reagent Formation

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1. Materials and Methods

Diethyl ether, toluene, and THF were distilled from deep purple sodium benzophenone ketyl. Acetonitrile was dried over P_2O_5 and vacuum-distilled. Cyclohexane was dried using CaH_2 and vacuum-distilled. DMF was used from a solvent purification system. Most substrates and all other chemicals were purchased from commercial sources and used as received. All deuterated solvents were purchased from Aldrich and Cambridge Isotope Laboratories. Ligands (**L1** = mesityl[3-(mesitylamino)-1-methyl-2-butenylidene]amine, **L2** = 2,4-bis-(2,6-diisopropylphenylimido)pentyl, **L3** = 2,2,6,6-tetramethyl-3,5-bis-(2,6-diisopropylphenylimido)heptane) were prepared by the method reported in the literature. Thin-layer chromatography was carried out on pre-coated with 0.25 mm silica gel plates (Merck Silica Gel 60 F254) and analyzed using ninhydrin as TLC stain or UV light. GC/MS analysis was performed on an Agilent 7890B GC model equipped with an Agilent 5977A Mass Spectrometer operating under ionization by electron impact (EI) to collect the mass spectrometry data. NMR spectra were recorded on a Bruker DRX 500 spectrometer operating at 500 MHz for ^1H, 126 MHz for ^{13}C and 203 MHz for ^{31}P acquisitions at room temperature. Chemical shifts were referenced to the residual proton solvent peak of $CDCl_3$ (^1H: 7.26 ppm, ^{13}C: 77.16 ppm), CD_3CN (^1H: 1.94 ppm, ^{13}C: 1.32 ppm) and $(CD_3)_2SO$ (^1H: 2.05 ppm, ^{13}C: 39.52 ppm). Signals are listed in ppm, and multiplicity identified as s = singlet, br = broad, d = doublet, t = triplet, q = quartet, quin = quintet, sep = septet, m = multiplet; coupling constants in Hz; integration. For HRMS analysis, two types of mass analyzer were used; magenetic sector-electric sector double focusing mass analyzer and Q-TOF mass spectrometer.

2. Experimental Data

2.1 Reaction optimization described in Table 1

General procedure for the reaction optimization

The reactions were carried out under nitrogen atmosphere using oven-dried glassware and magnetic bars in a glove box. 4-Fluorotoluene (44.1 mg, 0.4 mmol), cobalt(II), ligand, and reductant were added to a 4 mL vial. The solvent (0.5 mL) was added and subsequently, the mixture was stirred for 12 h at 25 °C. After the reaction, the reaction mixture was filtered through a pad of Celite. Volatiles in the filtrate were removed under vacuum. Subsequently, water (10 mL) and ethyl acetate, dichloromethane, or acidic methanol (20 mL) were added to the crude residue and the solution was shaken vigorously. The mixture was filtered through a pad of Celite again. Additional organic solvent (3 × 10 mL) and water (3 × 5 mL) were poured to the Celite to assure collecting all products. The organic layer was extracted and dried over by anhydrous Na_2SO_4. Known amount of dodecane (68.1 mg) was added to the solution and 0.1 mL of the mixture was filtered through Silica gel. Additional ethyl acetate (1.5 mL) was poured to the silica gel to assure collecting all products. The solution was measured for GC-MS spectroscopy.

2.2 Cobalt-catalyzed C–F bond silylation of the substrates described in Figure 2

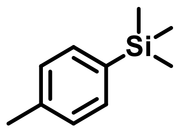
General procedure A

All the reactions were carried out under an inert atmosphere with stirring using oven-dried glassware and magnetic bars in a glove box unless otherwise noted.

Setup procedure: Cobalt(II) acetylacetonate (10.3 mg, 0.04 mmol (0.1 eq)), the corresponding ligand, **L1** (13.4 mg, 0.04 mmol (0.1 eq)), aryl fluoride (0.4 mmol (1 eq)) and magnesium (19.4 mg, 0.8 mmol (2 eq)) were added to a 4 mL vial. Then dried THF (0.5 mL) and chlorotrimethylsilane (152.3 µL, 1.2 mmol (3 eq)) or chlorotriethoxysilane (235.6 µL, 1.2 mmol (3 eq)) were added. The mixture solution was stirred at 25 °C.

Workup procedure: After the reaction, the reaction mixture was filtered through a pad of Celite. Volatiles in the filtrate were removed under vacuum. Subsequently, water (10 mL) and ethyl acetate (EA), or dichloromethane (20 mL) were added to the crude residue and the solution was shaken vigorously. The mixture was filtered through a pad of Celite again. The additional organic solvent (3 × 10 mL) and water (3 × 5 mL) were poured to the Celite to assure collecting all products. The organic layer was extracted and dried over by anhydrous Na_2SO_4. The solution was concentrated under vacuum. The purification of the residues was conducted using preparative TLC, column chromatography, or recrystallization.

Trimethyl(*p*-tolyl)silane (2a)

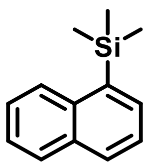


Time (h)	Mg (eq)	TMSCl (eq)	$Co(acac)_2$ (eq)	Ligand (eq)	Solvent (mL)
12	2	3	0.1	0.2	0.5

General procedure A: After the workup procedure, dodecane (68.1 mg) and ethyl acetate were added to the concentrated residue. The solution was filtered through Silica gel. Additional ethyl acetate (1.5 mL) was poured to the silica gel to assure collecting all products. The solution was measured for GC-MS spectroscopy and the yield was 99%. The product was purified by column chromatography (Hexane 100%) to afford **2a** (31.7 mg, 48%) as a colorless oil.

^{1}H NMR (500 Hz, $CDCl_3$) δ 7.43 (d, *J* = 6.60 Hz, 2H), 7.19 (d, *J* = 7.35 Hz, 2H), 0.26 (d, *J* = 1.45 Hz, 9H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 138.6, 136.8, 133.4, 128.6, 21.4, –1.1. These spectroscopic data are consistent with those previously reported in the literature.[1]

Trimethyl(naphthalen-1-yl)silane (2b)

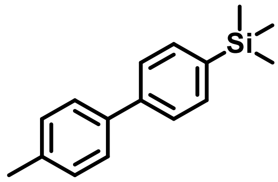


Time (h)	Mg (eq)	TMSCl (eq)	$Co(acac)_2$ (eq)	Ligand (eq)	Solvent (mL)
14	1.5	3	0.1	0.1	0.5

General procedure A: After the workup procedure, the product was purified by column chromatography (Hexane 100%) to afford **2b** (65.0 mg, 81%) as colorless oil.

^{1}H NMR (500 Hz, $CDCl_3$) δ 8.10 (d, *J* = 8.68 Hz, 1H)), 7.88-7.84 (m, 2H), 7.70 (dd, *J* = 1.15, 6.75 Hz, 1H), 7.53-7.44 (m, 3H), 0.47 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 138.2, 136.9, 133.4, 133.2, 129.7, 129.1, 128.1, 125.6, 125.3, 125.1, 0.3. These spectroscopic data are consistent with those previously reported in the literature.[2]

Trimethyl(4'-methyl-[1,1'-biphenyl]-4-yl)silane (2c)



1) **General procedure A**

Time (h)	Mg (eq)	TMSCl (eq)	Co(acac)$_2$ (eq)	Ligand (eq)	Solvent (mL)
5	2	3	0.1	0.1	0.5

After the workup procedure, the product was purified by column chromatography (Hexane 100%) to afford **2c** (91.4 mg, 95%) as white solid.

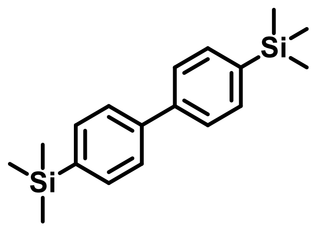
2) **Large-scale reaction / General procedure A**

Time (h)	Mg (eq)	TMSCl (eq)	Co(acac)$_2$ (eq)	Ligand (eq)	Solvent (mL)
5	2	3	0.1	0.1	0.5

Cobalt(II) acetylacetonate (138.1 mg, 0.537 mmol (0.1 eq)), the corresponding ligand, **L1** (179.6 mg, 0.537 mmol (0.1 eq)), aryl fluoride (1.0 g, 5.37 mmol (1 eq)) and magnesium (261.1 mg, 10.74 mmol (2 eq)) were added to a 20 mL vial. Then dried THF (5 mL) and chlorotrimethylsilane (2044.6 μL, 16.11 mmol (3 eq)) were added. The mixture solution was stirred at 25 °C. After the workup procedure, the product was purified by column chromatography (Hexane 100%) to afford **2c** (1.2058 g, 93%) as white solid.

^{1}H NMR (500 Hz, CD_3CN) δ 7.55 (d, *J* = 8.16 Hz, 4H), 7.28 (d, *J* = 7.86 Hz, 4H), 2.37 (s, 3H), 0.28 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 141.6, 138.9, 138.3, 137.1, 133.8, 129.5, 127.0, 126.3, 21.1, –1.1. These spectroscopic data are consistent with those previously reported in the literature.[3]

4,4'-Bis(trimethylsilyl)-1,1'-biphenyl (2d)

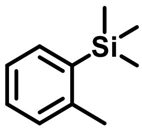


Time (h)	Mg (eq)	TMSCl (eq)	Co(acac)$_2$ (eq)	Ligand (eq)	Solvent (mL)
17	6	4	0.1	0.1	0.5

General procedure A: After the workup procedure, the product was purified by column chromatography (Hexane 100%) to afford **2d** (114.5 mg, 96%) as white solid.

^{1}H NMR (500 Hz, $CDCl_3$) δ 7.62-7.58 (m, 8H), 0.31 (s, 18H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 141.6, 139.3, 133.8, 126.5, –1.1. These spectroscopic data are consistent with those previously reported in the literature.[4]

Trimethyl(*o*-tolyl)silane (2e)

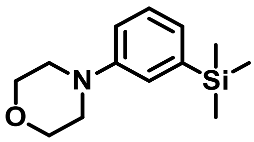


Time (h)	Mg (eq)	TMSCl (eq)	Co(acac)$_2$ (eq)	Ligand (eq)	Solvent (mL)
48	2	3	0.1	0.2	0.5

General procedure A: After the workup procedure, the product was purified by preparative TLC (Hexanes 100%) to afford **2e** (38.8 mg, 59%) as a colorless oil.

^{1}H NMR (500 Hz, CD_3CN) δ 7.46 (d, J = 6.40, 1H), 7.26 (td, J = 1.45, 7.30, 1H), 7.17-7.15 (m, 2H), 2.44 (s, 3H), 0.31 (s, 9H). ^{13}C NMR (126 Hz, CD_3CN) δ 143.5, 138.1, 134.3, 129.7, 129.2, 124.9, 2.2, –1.1. These spectroscopic data are consistent with those previously reported in the literature.[2]

4-(3-(Trimethylsilyl)phenyl)morpholine (2f)

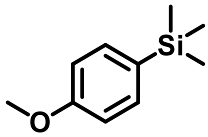


Time (h)	Mg (eq)	TMSCl (eq)	Co(acac)$_2$ (eq)	Ligand (eq)	Solvent (mL)
16	2	3	0.1	0.1	0.5

General procedure A: After the workup procedure, the product was purified by column chromatography (Hexanes:EA=40:1) to afford **2f** (78.1 mg, 83%) as a pale brown liquid.

^{1}H NMR (500 Hz, $CDCl_3$) δ 7.30 (t, J = 7.43 Hz, 1H), 7.10-7.06 (m, 2H), 6.92 (d, J = 8.65, 1H), 3.88 (s, 4H), 3.18 (s, 4H), 0.27 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 150.7, 141.4, 128.6, 125.2, 120.8, 116.3, 67.0, 49.6, –1.1. HRMS (FAB) m/z: [M] Calcd for $C_{13}H_{21}NOSi$ 235.1392; found 235.1391. Magenetic sector-electric sector double focusing mass analyzer was used.

(4-Methoxyphenyl)trimethylsilane (2g)

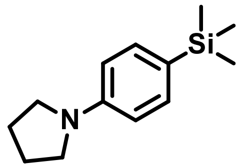


Time (h)	Mg (eq)	TMSCl (eq)	Co(acac)$_2$ (eq)	Ligand (eq)	Solvent (mL)
3	2	3	0.1	0.2	0.5

General procedure A: After the workup procedure, the product was purified by column chromatography (Hexanes 100%) to afford **2g** (64.5 mg, 89%) as a colorless oil.

^{1}H NMR (500 Hz, $CDCl_3$) δ 7.47 (d, *J* = 7.84 Hz, 2H), 6.93 (d, *J* = 7.85 Hz, 2H), 3.83 (s, 3H), 0.26 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 160.3, 134.7, 131.3, 113.5, 55.0, –0.9. These spectroscopic data are consistent with those previously reported in the literature.[2]

1-(4-(Trimethylsilyl)phenyl)pyrrolidine (2h)

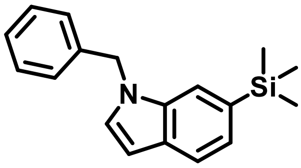


Time (h)	Mg (eq)	TMSCl (eq)	Co(acac)$_2$ (eq)	Ligand (eq)	Solvent (mL)
10	2.5	3.5	0.1	0.2	0.5

General procedure A: After the workup procedure, the product was purified by column chromatography (Hexanes: EA=10:1) to afford **2h** (70%) and 1-phenylpyrrolidine (hydrodefluorinated product, 28%) as pale yellow oil (78.0 mg). Hydrodefluorinated and defluorosilylated products could not be isolated.

^{1}H NMR of the mixture (500 Hz, $CDCl_3$) δ 7.46 (d, *J* = 8.42 Hz, 2H), 7.30 (t, *J* = 7.92 Hz, 2H'), 6.73 (t, *J* = 7.26 Hz, 1H'), 6.65 (d, *J* = 8.37 Hz, 2H+2H'), 3.37-3.34 (m, 4H+4H'), 2.08-2.04 (m, 4H+4H'), 0.31 (s, 9H). Proton signal from hydrodefluorinated and defluorosilylated products were indicated as H' and H, respectively. ^{13}C NMR of the mixture (126 Hz, $CDCl_3$) δ 148.3, 134.4, 129.1, 124.2, 115.4, 111.6, 111.3, 47.4, 25.5, –0.8. HRMS (FAB) m/z: [M] Calcd for $C_{13}H_{21}NSi$ 219.1443; found 219.1441. Magenetic sector-electric sector double focusing mass analyzer was used.

1-Benzyl-6-(trimethylsilyl)-1H-indoledioxaborolane (2i)

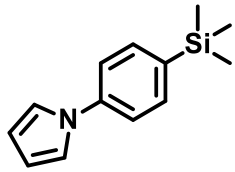


Time (h)	Mg (eq)	TMSCl (eq)	Co(acac)$_2$ (eq)	Ligand (eq)	Solvent (mL)
17	2	3	0.1	0.1	0.5

General procedure A: After the workup procedure, the product was purified by column chromatography (Hexanes 100%) to afford **2i** (109.8 mg, 98%) as pale yellow solid.

^{1}H NMR (500 Hz, CD_3CN) δ 7.58 (dd, *J* = 0.70, 7.85 Hz, 1H), 7.53 (d, *J* = 0.70 Hz, 1H), 7.32-7.29 (m, 3H), 7.27-7.24 (m, 1H), 7.19 (td, *J* = 0.87, 7.80 Hz, 3H), 6.48 (s, 1H), 5.40 (s, 2H), 0.24 (s, 9H). ^{13}C NMR (126 Hz, CD_3CN) δ 138.4, 136.1, 131.9, 129.5, 129.0, 128.6, 127.5, 127.1, 123.8, 120.2, 115.0, 101.0, 49.5, –1.7. HRMS (FAB) m/z: [M] Calcd for $C_{18}H_{21}NSi$ 279.1443; found 279.1441. Magenetic sector-electric sector double focusing mass analyzer was used.

1-(4-(Trimethylsilyl)phenyl)-1H-pyrrole (2j)

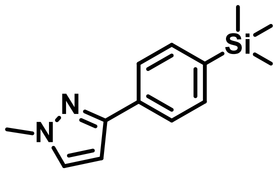


Time (h)	Mg (eq)	TMSCl (eq)	$Co(acac)_2$ (eq)	Ligand (eq)	Solvent (mL)
17	2	3	0.1	0.1	0.5

General procedure A: After the workup procedure, the product was purified by column chromatography (Hexanes: EA=20:1) to afford **2j** (82.4 mg, 96%) as white solid.

^{1}H NMR (500 Hz, $CDCl_3$) δ 7.57 (d, J = 8.40 Hz, 2H), 7.39 (d, J = 8.40 Hz, 2H), 7.11 (t, J = 2.18 Hz, 2H), 6.35 (t, J = 4.35 Hz, 2H), 0.30 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 141.1, 137.6, 134.6, 119.8, 119.2, 110.4, –1.1. HRMS (FAB) m/z: [M] Calcd for $C_{13}H_{17}NSi$ 215.1130; found 215.1128. Magenetic sector-electric sector double focusing mass analyzer was used.

1-Methyl-3-(4-(trimethylsilyl)phenyl)-1H-pyrazole (2k)

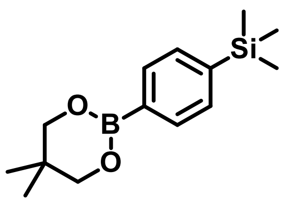


Time (h)	Mg (eq)	TMSCl (eq)	$Co(acac)_2$ (eq)	Ligand (eq)	Solvent (mL)
20	2	3	0.1	0.1	0.5

General procedure A: After the workup procedure, the product was purified by column chromatography (Hexanes: EA=5:1) to afford **2k** (82.5 mg, 90%) as a yellow oil.

^{1}H NMR (500 Hz, $CDCl_3$) δ 7.77 (d, J = 8.15 Hz, 2H), 7.54 (d, J = 8.17 Hz, 2H), 7.37 (d, J = 2.25 Hz, 1H), 6.55 (d, J = 2.27 Hz, 1H), 3.95 (s, 3H), 0.28 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 151.6, 139.6, 133.9, 133.6, 131.3, 124.8, 102.9, 39.1, –1.1. HRMS (FAB) m/z: [M] Calcd for $C_{13}H_{18}N_2Si$ 230.1239; found 230.1237. Magenetic sector-electric sector double focusing mass analyzer was used.

(4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)trimethylsilane (2l)

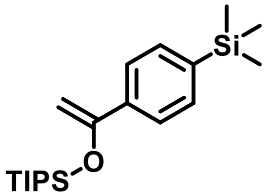


Time (h)	Mg (eq)	TMSCl (eq)	$Co(acac)_2$ (eq)	Ligand (eq)	Solvent (mL)
48	2	3	0.1	0.25	0.5

General procedure A: After the workup procedure, the product was purified by column chromatography (Hexanes:Et_2O=10:1) to afford **2l** (77.2 mg, 74%) as pale brown solid.

^{1}H NMR (500 Hz, $CDCl_3$) δ 7.79 (d, J = 7.69 Hz, 2H), 7.53 (d, J = 7.83 Hz, 2H), 3.78 (s, 4H), 1.03 (s, 6H), 0.27 (s, 8H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 143.3, 136.0, 135.9, 133.0, 132.5, 114.7, 114.5, 72.3, 31.9, 21.9, –1.2. These spectroscopic data are consistent with those previously reported in the literature.[2]

Triisopropyl((1-(4-(trimethylsilyl)phenyl)vinyl)oxy)silane (2m)

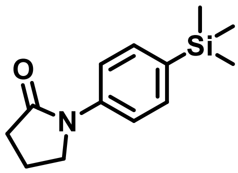


Time (h)	Mg (eq)	TMSCl (eq)	$Co(acac)_2$ (eq)	Ligand (eq)	Solvent (mL)
24	2	3	0.1	0.1	0.5

General procedure A: After the workup procedure, the product was purified by column chromatography (Hexane 100%) to afford **2m** (80.9 mg, 58%) as a colorless oil.

^{1}H NMR (500 Hz, $CDCl_3$) δ 7.65 (d, J = 7.56 Hz, 2H), 7.51 (d, J = 7.52 Hz, 2H), 4.89 (s, 1H), 4.42 (s, 1H), 1.37-1.27 (m, 3H), 1.15 (d, J = 7.36 Hz, 18H), 0.28 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 159.1, 140.4, 138.3, 133.1, 124.5, 89.9, 18.1, 12.8, –1.1. HRMS (FAB) m/z: [M] Calcd for $C_{20}H_{36}OSi_2$ 348.2305; found 348.2306. Magenetic sector-electric sector double focusing mass analyzer was used.

1-(4-(Trimethylsilyl)phenyl)pyrrolidin-2-one (2n)

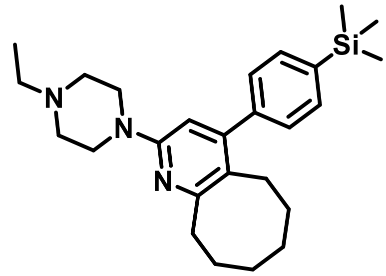


Time (h)	Mg (eq)	TMSCl (eq)	$Co(acac)_2$ (eq)	Ligand (eq)	Solvent (mL)
6	2	3	0.2	0.4	0.5

General procedure A: After the workup procedure, the product was purified by column chromatography (Hexanes:EA=4:1) to afford **2n** (35.2 mg, 38%) as yellow solid.

^{1}H NMR (500 Hz, $CDCl_3$) δ 3.89 (t, J = 6.90 Hz, 2H), 2.61 (t, J = 8.00 Hz, 2H), 2.16 (quin, J = 7.47 Hz, 2H), 0.25 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 174.3, 139.9, 136.3, 133.9, 119.2, 48.7, 32.8, 18.1, –1.1. These spectroscopic data are consistent with those previously reported in the literature.[5]

2-(4-Ethylpiperazin-1-yl)-4-(4-trimethylsilyl)phenyl)-5,6,7,8,9,10-hexahydrocycloocta[*b*] pyridine (2o)

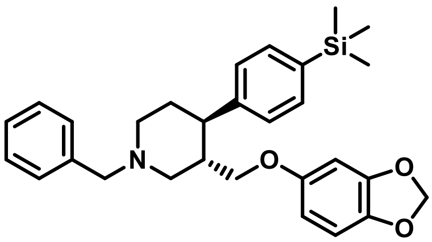


Time (h)	Mg (eq)	TMSCl (eq)	$Co(acac)_2$ (eq)	Ligand (eq)	Solvent (mL)
24	2	3	0.1	0.1	0.3

General procedure A: The reaction was conducted on a 0.15 mmol scale (The amount of other reactants was also reduced with the same ratio). After the workup procedure, the product was purified by column chromatography (Hexanes:EA=1:9) to afford **2o** (58.9 mg, 93%) as a yellow oil.

^{1}H NMR (500 Hz, CD_3CN) δ 7.60 (d, *J* = 8.10 Hz, 2H), 7.27 (d, *J* = 8.09 Hz, 2H), 6.34 (s, 1H), 3.50 (s, 4H), 2.86-2.84 (m, 2H), 2.60-2.48 (m, 8H), 1.76-1.71 (m, 2H), 1.44-1.33 (m, 6H), 1.10 (t, *J* = 7.18 Hz, 3H), 0.29 (s, 9H). ^{13}C NMR (126 Hz, CD_3CN) δ 159.5, 157.2, 151.5, 141.8, 139.2, 133.1, 127.9, 122.4, 105.8, 52.2, 51.9, 44.8, 35.0, 31.3, 30.5, 26.2, 26.2, 25.6, 11.0, –2.1. HRMS (ESI) m/z: [M + H]+ Calcd for $C_{26}H_{40}N_3Si$ 422.2986; found 422.2987. Q-TOF mass spectrometer was used.

3-((benzo[1,3]dioxol-5-yloxy)methyl)-1-benzyl-4-(4-(trimethylsilyl)phenyl)piperidine (2p)

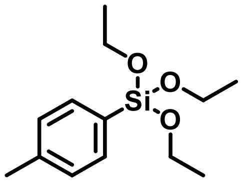


Time (h)	Mg (eq)	TMSCl (eq)	$Co(acac)_2$ (eq)	Ligand (eq)	Solvent (mL)
24	2	3	0.2	0.2	0.5

General procedure A: The reaction was conducted on a 0.2 mmol scale (The amount of other reactants was also reduced with the same ratio.). After the workup procedure, the product was purified by column chromatography (Hexanes:EA=9:1) to afford **2p** (22.8 mg, 24%) as a yellow oil.

^{1}H NMR (500 Hz, $CDCl_3$) δ 7.45-7.31 (m, 7H), 7.20 (d, *J* = 7.90 Hz, 2H), 6.61 (d, *J* = 8.46 Hz, 1H), 6.32 (d, *J* = 2.45 Hz, 1H), 6.11 (dd, *J* = 2.50, 8.56 Hz, 1H), 5.87 (s, 2H), 3.75-3.57 (m, 3H), 3.49-3.45 (m, 1H), 3.34 (br, 1H), 3.09 (br, 1H), 2.51 (br, 1H), 2.26-1.83 (m, 5H), 0.24 (s, 9H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 154.4, 148.1, 141.6, 138.5, 133.9, 133.7, 129.6, 128.7, 128.4, 127.0, 126.8, 107.8, 105.7, 101.1, 98.0, 69.5, 63.0, 57.2, 53.6, 44.4, 41.4, 33.7, –1.1. HRMS (FAB) m/z: [M + H]+ Calcd for $C_{29}H_{36}NO_3Si$ 474.2464; found 474.2461. Magenetic sector-electric sector double focusing mass analyzer was used.

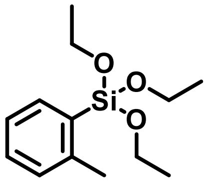
Triethoxy(*p*-tolyl)silane (2q)



General procedure A: The reaction time was 12 hours. After the workup procedure, the product was purified by column chromatography (Hexanes 100%) to afford **2q** (50.8 mg, 50%) as a colorless oil.

^{1}H NMR (500 Hz, $CDCl_3$) δ 7.57 (d, *J* = 7.90 Hz, 2H), 7.20 (d, *J* = 7.50 Hz, 2H), 3.86 (q, *J* = 7.00 Hz, 6H), 2.36 (s, 3H), 1.24 (t, *J* = 7.00 Hz, 9H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 140.3, 134.9, 128.7, 127.3, 58.7, 21.6, 18.2. These spectroscopic data are consistent with those previously reported in the literature.[6]

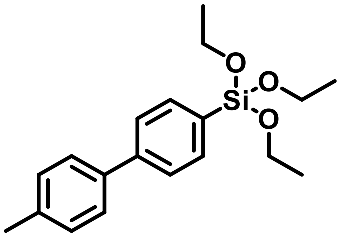
Triethoxy(*o*-tolyl)silane (2r)



General procedure A: The reaction time was 25 hours and 20 mol% of **L1** was used. After the workup procedure, the product was purified by column chromatography (Hexanes:EA=20:1) to afford **2r** (77.6 mg, 68%) as a colorless oil.

^{1}H NMR (500 Hz, $CDCl_3$) δ 7.75 (dd, *J* = 1.74, 8.13 Hz, 1H), 7.33 (td, *J* = 1.50, 7.69 Hz, 1H), 7.20-7.17 (m, 2H), 3.88 (q, *J* = 7.00 Hz, 6H), 2.53 (s, 3H), 1.27 (t, *J* = 7.01 Hz, 9H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 144.5, 136.5, 130.5, 129.9, 129.7, 124.7, 58.5, 22.4, 18.2. These spectroscopic data are consistent with those previously reported in the literature.[6]

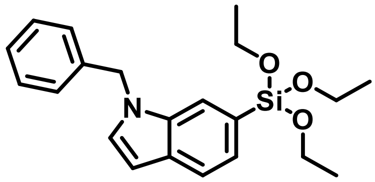
Triethoxy(4'-methyl-[1,1'-biphenyl]-4-yl)silane (2s)



General procedure A: The reaction time was 16 hours. After the workup procedure, the product was purified by column chromatography (Hexanes:EA=50:1) to afford **2s** (100.5 mg, 76%) as a colorless oil.

^{1}H NMR (500 Hz, CD_3CN) δ 7.68 (qd, *J* = 1.94, 7.68 Hz, 4H), 7.56 (d, *J* = 8.15 Hz, 2H), 7.29 (dd, *J* = 0.58, 8.43 Hz, 2H), 3.87 (q, *J* = 6.99 Hz, 6H), 2.38 (s, 3H), 1.22 (t, *J* = 7.00 Hz, 9H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 142.9, 138.1, 137.4, 135.3, 129.5, 129.2, 127.0, 126.4, 58.8, 21.1, 18.3. HRMS (ESI) m/z: [M + Na]+ Calcd for $C_{19}H_{26}O_3SiNa$ 353.1543; found 353.1544. Q-TOF mass spectrometer was used.

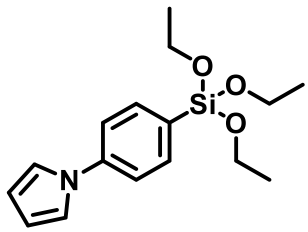
1-Benzyl-6-(triethoxysilyl)-1H-indole (2t)



1) **General procedure A**: The reaction time was 24 hours and 0.2 mmol of the starting material was used (The amount of other reactants was also reduced with the same ratio.). After the workup procedure, the product was purified by column chromatography (Hexanes:EA=15:1) to afford **2t** (58.2 mg, 79%) as a yellow oil.
2) **Large scale reaction / General procedure A:** Cobalt(II) acetylacetonate (54.0 mg, 0.21 mmol (0.1 eq)), the corresponding ligand, **L1** (70.2 mg, 0.21 mmol (0.1 eq)), aryl fluoride (473.1 mg, 2.1 mmol (1 eq)) and magnesium (102.1 mg, 4.2 mmol (2 eq)) were added to a 20 mL vial. Then dried THF (2 mL) and chlorotriethoxysilane (1237.1 μL, 6.3 mmol (3 eq)) were added. The mixture solution was stirred at 25 °C. After workup procedure, the product was purified by column chromatography (Hexanes:Ethyl acetate=15:1) to afford **2s** (490.1 mg, 63%) as a yellow oil.

^{1}H NMR (500 Hz, $CDCl_3$) δ 7.63 (dd, *J* = 0.78, 7.86 Hz, 1H), 7.59 (d, *J* = 0.81 Hz, 1H), 7.40 (d, *J* = 3.12 Hz, 1H), 7.31-7.23 (m, 4H), 7.17-7.15 (m, 2H), 6.53 (dd, *J* = 0.82, 3.12 Hz, 2H), 3.79 (q, *J* = 6.99 Hz, 6H), 1.16 (t, *J* = 7.00 Hz, 9H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 138.2, 135.7, 130.7, 130.1, 128.6, 127.5, 126.9, 124.7, 122.5, 120.5, 116.8, 101.1, 58.4, 49.8, 17.6. HRMS (ESI) m/z: [M + Na]+ Calcd for $C_{21}H_{27}NO_3SiNa$ 392.1652; found 392.1654. Q-TOF mass spectrometer was used.

Triethoxy(4'-methyl-[1,1'-biphenyl]-4-yl)silane (2u)



General procedure A: The reaction time was 20 hours. After the workup procedure, the product was purified by column chromatography (Hexanes:EA=20:1) to afford **2u** (49.4 mg, 40%) as a pale yellow oil.

^{1}H NMR (500 Hz, $CDCl_3$) δ 7.75 (d, *J* = 8.46 Hz, 2H), 7.43 (d, *J* = 8.48 Hz, 2H), 7.14 (t, *J* = 2.20 Hz, 2H), 3.91 (q, *J* = 7.00 Hz, 6H), 1.28 (t, *J* = 7.00 Hz, 9H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 142.3, 136.3, 128.0, 119.6, 119.1, 110.7, 58.8, 18.3. HRMS (ESI) m/z: [M + Na]+ Calcd for $C_{16}H_{23}NO_3SiNa$ 328.1339; found 328.1341. Q-TOF mass spectrometer was used.

General procedure B

All the reactions were carried out under inert atmosphere with stirring using oven-dried glassware and magnetic bars in a glove box unless otherwise noted.

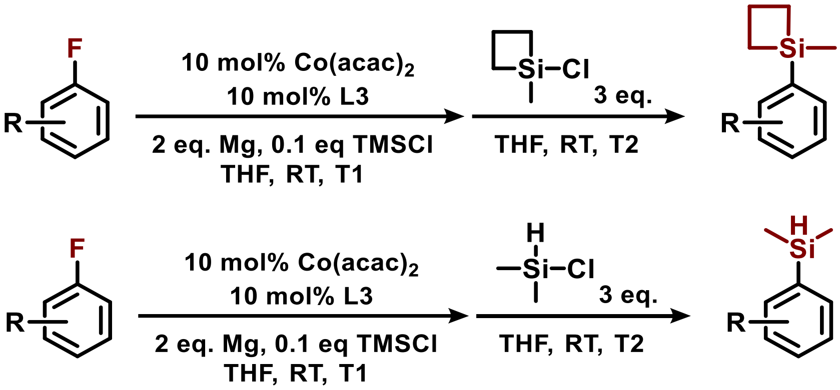
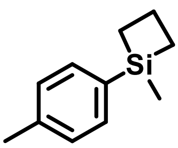


Figure S1. Defluorosilylation with 1-chloro-1-methylsilacyclobutane or chlorodimethylsilane.

Setup procedure: Cobalt(II) acetylacetonate (10.3 mg, 0.04 mmol (0.1 eq)), the corresponding ligand, **L1** (13.4 mg, 0.04 mmol (0.1 eq)), aryl fluoride (0.4 mmol (1 eq)) and magnesium (19.4 mg, 0.8 mmol (2 eq)) were added to a 4 mL vial. Then dried THF (0.5 mL) and chlorotrimethylsilane (4.65 µL, 0.04 mmol (0.1 eq)) were added. After several hours (T1) with stirring at 25°C, 1-Chloro-1-methylsilacyclobutane (147.0 µL, 1.2 mmol (3 eq)) or chlorodimethylsilane (133.3 µL, 1.2 mmol (3 eq)) was added and the mixture solution was stirred at 25 °C for several hours (T2).

Workup procedure: After the reaction, the reaction mixture was filtered through a pad of Celite. Volatiles in the filtrate were removed under vacuum. Subsequently, water (10 mL) and dichloromethane, or ethyl acetate (20 mL) were added to the crude residue and the solution was shaken vigorously. The mixture was filtered through a pad of Celite again. Additional organic solvent (3 × 10 mL) and water (3 × 5 mL) were poured to the Celite to assure collecting all products. The organic layer was extracted and dried over by anhydrous Na_2SO_4. The solution was concentrated under vacuum. The purification of the residues was conducted using preparative TLC, column chromatography, or recrystallization.

1-Methyl-1-(*p*-tolyl)siletane (2v)

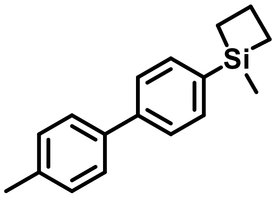


T1 (h)	T2 (h)
5	5

General procedure B: 20 mol% of Co(acac)$_2$ and **L1** were used. After the workup procedure, dibromomethane (5.0 mg) and $CDCl_3$ were added to the concentrated residue. The $CDCl_3$ solution was measured for ^{1}H NMR spectroscopy and the yield was 47% (see ^{1}H and ^{13}C NMR spectra). The product was purified by column chromatography (Hexanes 100%) to afford **2v** (25.2 mg, 36%) as a colorless oil.

^{1}H NMR (500 Hz, $CDCl_3$) δ 7.53 (d, *J* = 7.45 Hz, 2H), 7.23 (d, *J* = 7.45 Hz, 2H), 2.37 (s, 3H), 2.18 (quin, *J* = 8.23 Hz, 2H), 1.31-1.25 (m, 2H), 1.19-1.12 (m, 2H), 0.54 (s, 3H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 139.4, 135.1, 133.6, 128.8, 21.5, 18.2, 14.5, –1.7. HRMS (FAB) m/z: [M] Calcd for $C_{11}H_{16}Si$ 176.1021; found 176.1019. Magenetic sector-electric sector double focusing mass analyzer was used.

1-Methyl-1-(4'-methyl-[1,1'-biphenyl]-4-yl)siletane (2w)



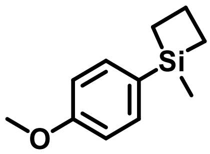
T1 (h)	T2 (h)
1	12

.

General procedure B: The reaction was conducted on a 0.1 mmol scale (The amount of other reactants was also reduced with the same ratio.). After the workup procedure, the product was purified by column chromatography (Hexanes 100%) to afford **2w** (10.9 mg, 43%) as white solid.

^{1}H NMR (500 Hz, CD_3CN) δ 7.74-7.72 (m, 2H), 7.68-7.66 (m, 2H), 7.29 (dd, *J* = 0.55, 8.39 Hz, 2H), 2.38 (s, 3H), 2.25-2.17 (m, 2H), 1.34-1.28 (m, 2H), 1.24-1.17 (m, 2H), 0.58 (s, 3H). ^{13}C NMR (126 Hz, CD_3CN) δ141.9, 137.7, 137.6, 137.0, 134.1, 129.6, 126.8, 126.3, 20.1, 17.8, 13.9, –2.7. HRMS (FAB) m/z: [M] Calcd for $C_{17}H_{20}Si$ 252.1334; found 252.1335. Magenetic sector-electric sector double focusing mass analyzer was used.

1-(4-Methoxyphenyl)-1-methylsiletane (2x)



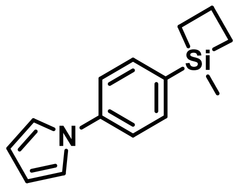
T1 (h)	T2 (h)
3	5

.

General procedure B: 20 mol% of $Co(acac)_2$ and **L1** were used. After the workup procedure, the product was purified by column chromatography (Hexanes:EA=80:1) to afford **2x** (25.8 mg, 34%) as a pale yellow oil.

^{1}H NMR (500 Hz, $CDCl_3$) δ 7.56 (d, *J* = 8.10 Hz, 2H), 6.95 (d, *J* = 8.10 Hz, 2H), 3.83 (s, 3H), 2.17 (quin, *J* = 8.13 Hz, 2H), 1.31-1.24 (m, 2H), 1.18-1.12 (m, 2H), 0.54 (s, 3H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 160.8, 135.0, 129.6, 113.7, 55.1, 18.1, 14.6, –1.8. These spectroscopic data are consistent with those previously reported in the literature.[7]

1-Methyl-1-(*p*-tolyl)siletane (2y)



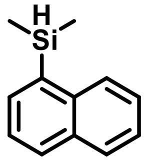
T1 (h)	T2 (h)
3	5

.

General procedure B: 20 mol% of $Co(acac)_2$ and **L1** were used. After the workup procedure, the product was purified by column chromatography (Hexanes:EA=60:1) to afford **2y** (37.2 mg, 41%) as a pale yellow oil.

^{1}H NMR (500 Hz, $CDCl_3$) δ 7.68 (d, *J* = 8.10 Hz, 2H), 7.43 (d, *J* = 8.08 Hz, 2H), 7.13 (s, 2H), 6.36 (s, 2H), 2.21 (quin, *J* = 8.28 Hz, 2H), 1.34-1.28 (m, 2H), 1.23-1.17 (m, 2H), 0.58 (s, 3H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 141.6, 135.7, 134.9, 119.8, 119.2, 110.6, 18.3, 14.5, –1.7. HRMS (FAB) m/z: [M] Calcd for $C_{14}H_{17}NSi$ 227.1130; found 227.1133 Magenetic sector-electric sector double focusing mass analyzer was used.

1-Dimethylsilyl-naphthalene (2z)



T1 (h)	T2 (h)
22	22

Large scale reaction / General procedure B: Cobalt(II) acetylacetonate (51.4 mg, 0.2 mmol (0.1 eq)), the corresponding ligand, L1 (66.9 mg, 0.2 mmol (0.1 eq)), aryl fluoride (292.3 mg, 2.0 mmol (1 eq)) and magnesium (97.2 mg, 4.0 mmol (2 eq)) were added to a 20 mL vial. Then dried THF (2 mL) and chlorotrimethylsilane (25.4 µL, 0.2 mmol (0.1 eq)) were added. After 22 hours (T1) with stirring at 25°C, chlorodimethylsilane (666.3 µL, 6.0 mmol (3 eq)) was added and the mixture solution was stirred at 25 °C for 22 hours (T2). After the workup procedure, the product was purified by column chromatography (Hexanes 100%) to afford **2z** (193.8 mg, 52%) as a colorless oil.

^{1}H NMR (500 Hz, $CDCl_3$) δ 8.14 (d, J = 8.21 Hz, 1H), 7.91-7.88 (m, 2H), 7.75 (dd, J = 6.73, 1.25 Hz, 1H), 7.57-7.47 (m, 3H), 4.89 (sep, J = 3.78 Hz, 1H), 0.52 (d, J = 3.79 Hz, 6H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 137.0, 135.7, 133.7, 133.2, 130.0, 129.0, 127.6, 125.6, 125.6, 125.2, –3.2. These spectroscopic data are consistent with those previously reported in the literature.[8]

2.3 Halogen containing substrates (Cl or Br)

All the reactions were carried out under an inert atmosphere with stirring using oven-dried glassware and magnetic bars in a glove box unless otherwise noted.

4-Chloro-4'-fluorobiphenyl (82.7 mg, 0.4 mmol (1 eq)), cobalt(II) acetylacetonate (10.3 mg, 0.04 mmol (0.1 eq)), the corresponding ligand, **L1** (13.4 mg, 0.04 mmol (0.1 eq)), and magnesium (19.4 mg, 0.8 mmol (2 eq)) were added to a 4 mL vial. Then dried THF (0.5 mL) and chlorotrimethylsilane (101.5 μL, 0.8 mmol (2 eq)) were added. The mixture solution was stirred at 25 °C for 26 hours.

After the reaction, the reaction mixture was filtered through a pad of Celite. Volatiles in the filtrate were removed under vacuum. Subsequently, water (10 mL) and ethyl acetate, or dichloromethane (20 mL) were added to the crude residue and the solution was shaken vigorously. The mixture was filtered through a pad of Celite again. The additional organic solvent (3 × 10 mL) and water (3 × 5 mL) were poured to the Celite to assure collecting all products. The organic layer was extracted and dried over by anhydrous Na_2SO_4. The solution was concentrated under vacuum and GC-MS spectrum was measured.

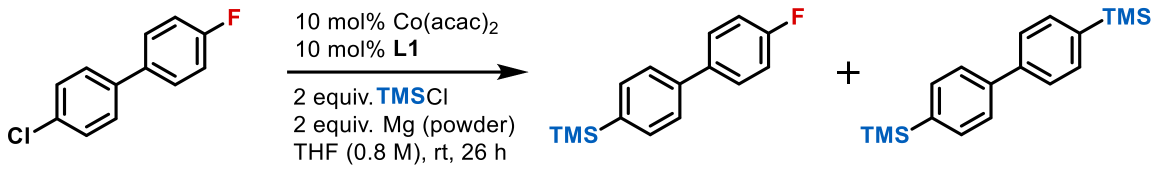


Figure S2. Dehalosilylation of 4-chloro-4'-fluorobiphenyl.

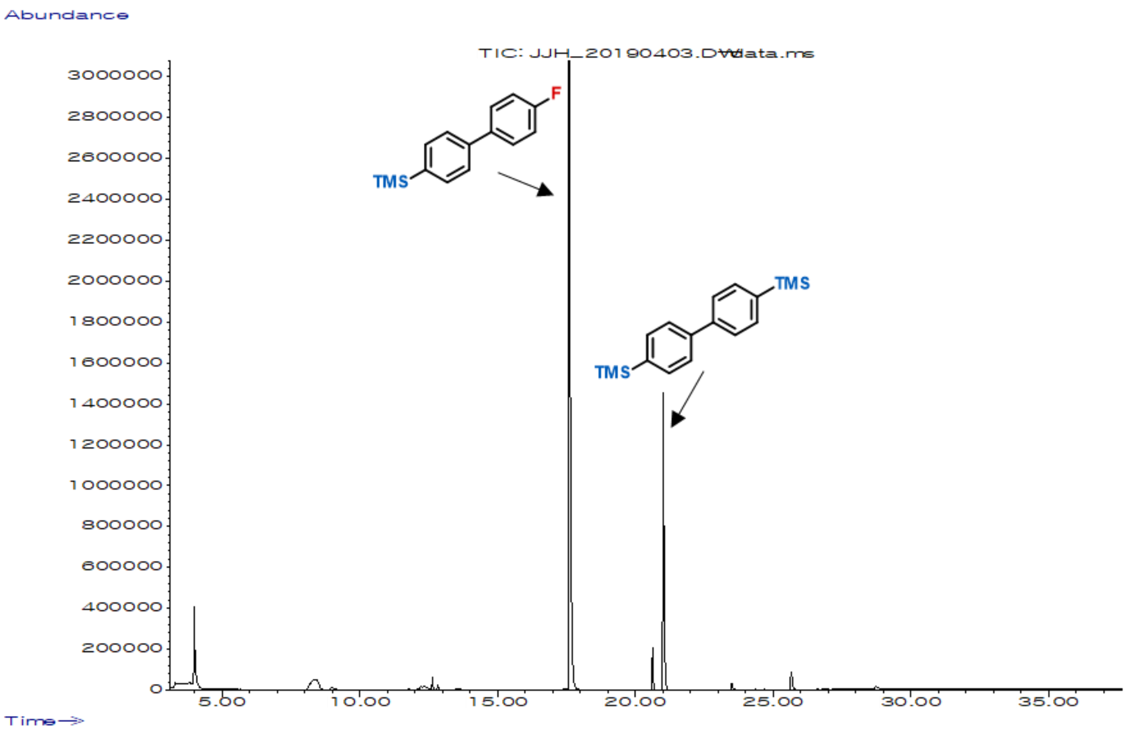


Figure S3. GC-MS spectrum after dehalosilylation of 4-chloro-4'-fluorobiphenyl (**Figure S2**).

All C(sp^2)–Cl bonds are activated and some C(sp^2)–F bonds remain intact.

Simple aryl bromide (4-bromotoluene) was also used for dehalosilylation.

Cobalt(II) acetylacetonate (10.3 mg, 0.04 mmol (0.1 eq)), the corresponding ligand, **L1** (13.4 mg, 0.04 mmol (0.1 eq)), and magnesium (19.4 mg, 0.8 mmol (2 eq)) were added to a 4 mL vial. Then dried THF (0.5 mL) and 4-bromotoluene (49.22 μL, 0.4 mmol (1 eq)) were added. Lastly, chlorotrimethylsilane (152.3 μL, 1.2 mmol (3 eq)) was added and the mixture solution was stirred at 25 °C.

After the reaction, ethyl acetate (5 mL) and water (5 mL) were added to the reaction mixture and it was filtered through a pad of Celite. The additional organic solvent (3 × 10 mL) and water (3 × 5 mL) were poured to the Celite to assure collecting all products. The organic layer was extracted and dried over by anhydrous Na_2SO_4. The known amount of dodecane (68.1 mg) was added to the solution and 0.1 mL of the mixture was filtered through Silica gel. Additional ethyl acetate (1.5 mL) was poured to the silica gel to assure collecting all products. The solution was measured for GC-MS spectroscopy.

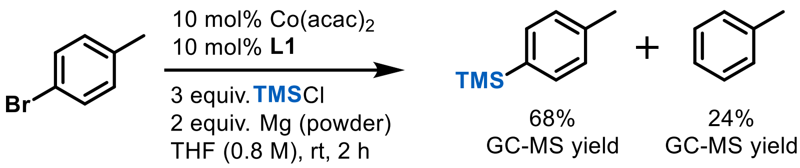


Figure S4. Dehalosilylation of 4-bromotoluene.

Compared to 4-fluorotoluene, the reaction time for a full conversion was short, but dehalohydrogenation was observed. Elongated reaction time could not increase the yields of the silylated product.

3. Mechanistic study described in Figure 3

3.1 Reactions without stoichiometric equivalents of TMSCl

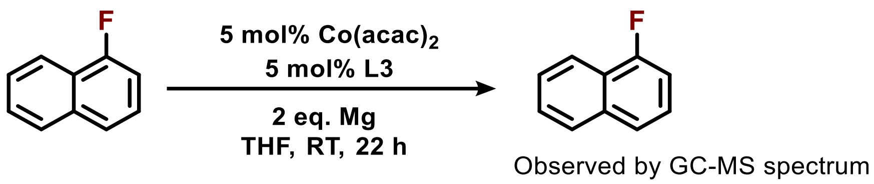


Figure S5. Reaction without TMSCl.

The reaction was carried out under inert atmosphere with stirring using oven-dried glassware and magnetic bars in a glove box. Cobalt(II) acetylacetonate (5.1 mg, 0.02 mmol (0.05 eq)), the corresponding ligand, **L1** (6.7 mg, 0.02 mmol (0.05 eq)), and magnesium (19.4 mg, 0.8 mmol (2 eq)) were added to a 4 mL vial. Then dried THF (0.5 mL) and 1-fluoronaphthalene (51.6 µL, 0.4 mmol (1 eq)) were added. The mixture solution was stirred at 25 °C for 22 hours.

After the reaction, the reaction mixture was filtered through a pad of Celite. Subsequently, water (10 mL) and dichloromethane (20 mL) were added to the crude residue and the solution was shaken vigorously. The mixture was filtered through a pad of Celite again. Additional organic solvent (3 × 10 mL) and water (3 × 5 mL) were poured to the Celite to assure collecting all products. The organic layer was extracted and dried over by anhydrous Na_2SO_4. The known amount of dodecane (68.1 mg) was added to the solution and 0.1 mL of the mixture was filtered through Silica gel. Additional ethyl acetate (1.5 mL) was poured to the silica gel to assure collecting all products. The solution was measured for GC-MS spectroscopy.

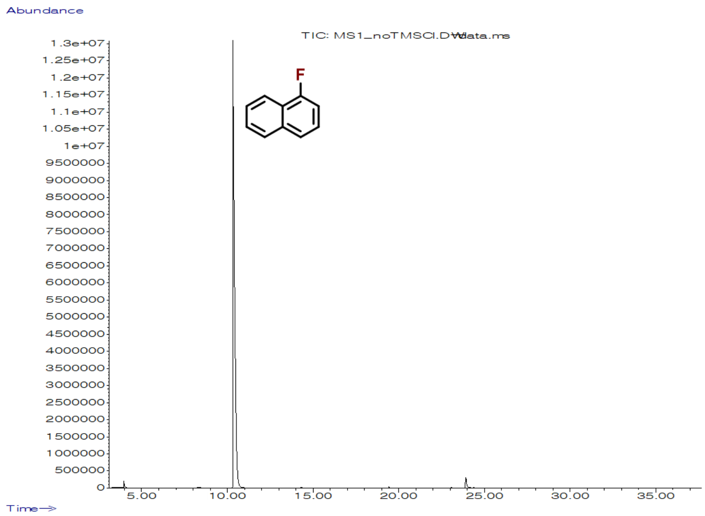


Figure S6. GC-MS spectrum after the reaction without TMSCl (**Figure S5**).

Without TMSCl, C–F bond activation was not observed, as the starting material remained.

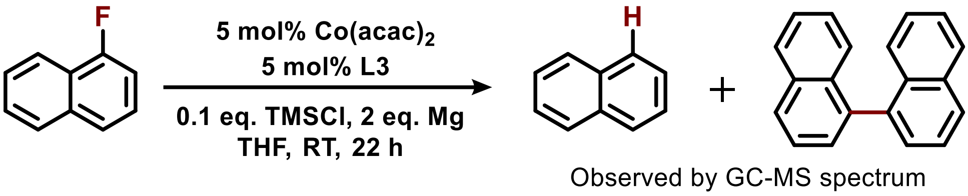


Figure S7. Reaction with a catalytic amount of TMSCl.

The reaction was carried out under inert atmosphere with stirring using oven-dried glassware and magnetic bars in a glove box. Cobalt(II) acetylacetonate (5.1 mg, 0.02 mmol (0.05 eq)), the corresponding ligand, **L1** (6.7 mg, 0.02 mmol (0.05 eq)), and magnesium (19.4 mg, 0.8 mmol (2 eq)) were added to a 4 mL vial. Then dried THF (0.5 mL), chlorotrimethylsilane (5.08 µL, 0.04 mmol (0.1 eq)) and 1-fluoronaphthalene (51.6 µL, 0.4 mmol (1 eq)) were added. The mixture solution was stirred at 25 °C for 22 hours.

After the reaction, the reaction mixture was filtered through a pad of Celite. Subsequently, water (10 mL) and dichloromethane (20 mL) were added to the crude residue and the solution was shaken vigorously. The mixture was filtered through a pad of Celite again. Additional organic solvent (3 × 10 mL) and water (3 × 5 mL) were poured to the Celite to assure collecting all products. The organic layer was extracted and dried over by anhydrous Na_2SO_4. 0.1 mL of the solution was filtered through Silica gel. Additional ethyl acetate (1.5 mL) was poured to the silica gel to assure collecting all products. The solution was measured for GC-MS spectroscopy.

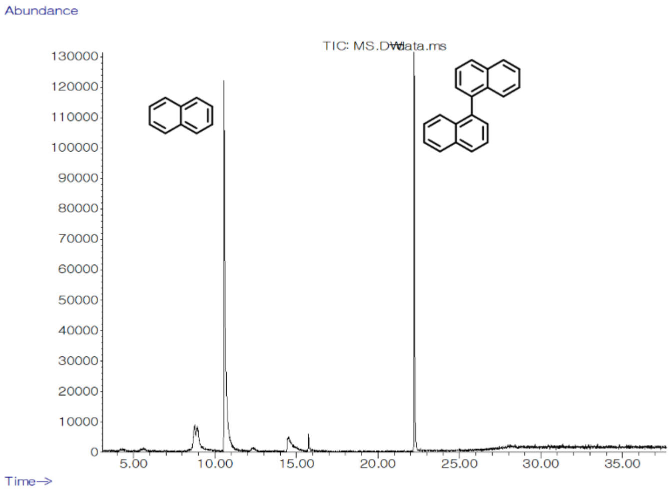


Figure S8. GC-MS spectrum after the reaction with a catalytic amount of TMSCl (**Figure S7**).

All C–F bonds were cleavage and converted to C–H or C–C bonds to form naphthalene or 1,1’-binaphthalene with a catalytic amount of TMSCl.

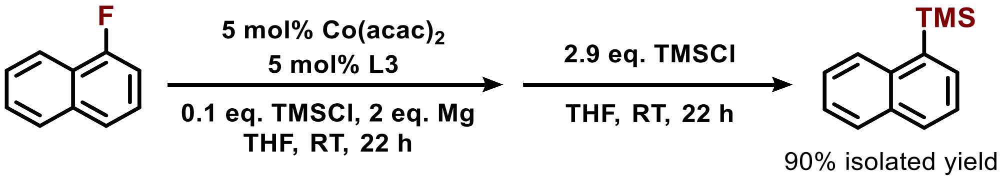


Figure S9. Addition of TMSCl to the reaction intermediate (**Figure 3a**. (1)).

The reaction was carried out under inert atmosphere with stirring using oven-dried glassware and magnetic bars in a glove box. Cobalt(II) acetylacetonate (5.1 mg, 0.02 mmol (0.05 eq)), the corresponding ligand, **L1** (6.7 mg, 0.02 mmol (0.05 eq)), and magnesium (19.4 mg, 0.8 mmol (2 eq)) were added to a 4 mL vial. Then dried THF (0.5 mL), chlorotrimethylsilane (5.08 µL, 0.04 mmol (0.1 eq)) and 1-fluoronaphthalene (51.6 µL, 0.4 mmol (1 eq)) were added. The mixture solution was stirred at 25 °C for 22 hours. After 22 hours, additional chlorotrimethylsilane (134.9 µL, 1.16 mmol (2.9 eq)) was added under inert condition. The mixture was stirred at 25 °C for 22 hours.

After the reaction, the reaction mixture was filtered through a pad of Celite. Subsequently, water (10 mL) and dichloromethane (20 mL) were added to the crude residue and the solution was shaken vigorously. The mixture was filtered through a pad of Celite again. Additional organic solvent (3 × 10 mL) and water (3 × 5 mL) were poured to the Celite to assure collecting all products. The organic layer was extracted and dried over by anhydrous Na_2SO_4. The solution was evaporated at 0 °C to prevent evaporation of naphthalene moieties, and the product was purified by column chromatography (Hexanes 100%) to afford **2e** (72.1 mg, 90%) as a colorless oil.

Defluorosilylation was successfully achieved and it indicates that stoichiometric equivalents of intermediates containing magnesium were formed.

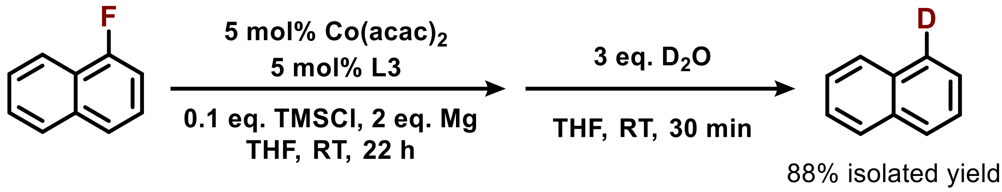


Figure S10. Addition of D_2O to the reaction intermediate (**Figure 3a**. (2)).

The reaction was carried out under inert atmosphere with stirring using oven-dried glassware and magnetic bars in a glove box. Cobalt(II) acetylacetonate (5.1 mg, 0.02 mmol (0.05 eq)), the corresponding ligand, **L1** (6.7 mg, 0.02 mmol (0.05 eq)), and magnesium (19.4 mg, 0.8 mmol (2 eq)) were added to a 4 mL vial. Then dried THF (0.5 mL), chlorotrimethylsilane (5.08 μL, 0.04 mmol (0.1 eq)) and 1-fluoronaphthalene (51.6 μL, 0.4 mmol (1 eq)) were added. The mixture solution was stirred at 25 °C for 22 hours. After 22 hours, D_2O (24.0 μL, 1.2 mmol (3 eq)) was added to capture the intermediate.

After the reaction, the reaction mixture was filtered through a pad of Celite. Subsequently, water (10 mL) and dichloromethane (20 mL) were added to the crude residue and the solution was shaken vigorously. The mixture was filtered through a pad of Celite again. Additional organic solvent (3 × 10 mL) and water (3 × 5 mL) were poured to the Celite to assure collecting all products. The organic layer was extracted and dried over by anhydrous Na_2SO_4. The solution was evaporated at 0 °C to prevent evaporation of naphthalene moieties, and the product was purified by column chromatography (Hexanes 100%) to afford 1-deuteronaphthalene (45.4 mg, 88%) with a trace amount of **2e** as white solid.

^{1}H NMR (500 Hz, $CDCl_3$) δ 7.87-7.84 (m, 4H), 7.48 (d, J = 3.95 Hz, 3H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 127.9, 127.8, 125.8, 125.7. These spectroscopic data are consistent with those previously reported in the literature.[9] The NMR spectra are provided in the NMR data section.

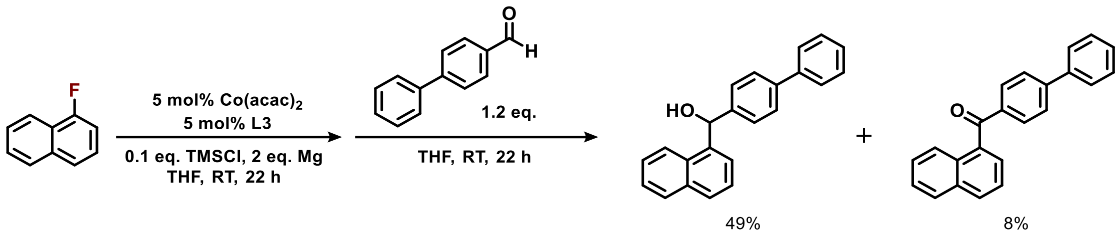


Figure S11. Addition of 4-phenylbenzaldehyde to the reaction intermediate (**Figure 3a**. (3)).

The reaction was carried out under inert atmosphere with stirring using oven-dried glassware and magnetic bars in a glove box. Cobalt(II) acetylacetonate (5.1 mg, 0.02 mmol (0.05 eq)), the corresponding ligand, **L1** (6.7 mg, 0.02 mmol (0.05 eq)), and magnesium (19.4 mg, 0.8 mmol (2 eq)) were added to a 4 mL vial. Then dried THF (0.5 mL), chlorotrimethylsilane (5.08 μL, 0.04 mmol (0.1 eq)) and 1-fluoronaphthalene (51.6 μL, 0.4 mmol (1 eq)) were added. The mixture solution was stirred at 25 °C for 22 hours. After 22 hours, additional 4-phenylbenzaldehyde (87.5 mg, 0.48 mmol (1.2 eq)) was added under inert condition. The mixture was stirred at 25 °C for 22 hours.

After the reaction, the reaction mixture was filtered through a pad of Celite. Subsequently, water (10 mL) and ethyl acetate (20 mL) were added to the crude residue and the solution was shaken vigorously. The mixture was filtered through a pad of Celite again. Additional organic solvent (3 × 10 mL) and water (3 × 5 mL) were poured to the Celite to assure collecting all products. The organic layer was extracted and dried over by anhydrous Na_2SO_4. The product was purified by column chromatography (gradient, Hexanes:EA=30:1 to 10:1) to afford the mixture of α-1-naphthalenyl-[1,1'-biphenyl]-4-methanol (49%) and [1,1'-biphenyl]-4-yl-1-naphthalenyl-methanone (8%) as white solid (70.7 mg). Alcohol and ketone could not be separated.

^{1}H NMR of the mixture (500 Hz, $CDCl_3$) δ 8.10-8.08 (m, 1H+1H'), 7.89-7.88 (m, 1H+1H'), 7.84 (d, J = 8.24 Hz, 1H+1H'), 7.70 (d, J = 7.11 Hz, 1H+1H'), 7.57-7.41 (m, 11H+11H'), 7.35-7.32 (m, 1H+1H'), 6.61 (s, 1H), 2.34 (s, 1H). Proton signals from alcohol and ketone were indicated as H and H', respectively. ^{13}C NMR of the mixture (126 Hz, $CDCl_3$) δ 142.2, 140.8, 140.6, 138.8, 134.0, 130.7, 128.8, 128.7, 128.6, 127.5, 127.3, 127.1, 126.2, 125.7, 125.7, 124.7, 124.0, 73.5. These spectroscopic data are consistent with those previously reported in the literature.[10] The NMR spectra are provided in the NMR data section.

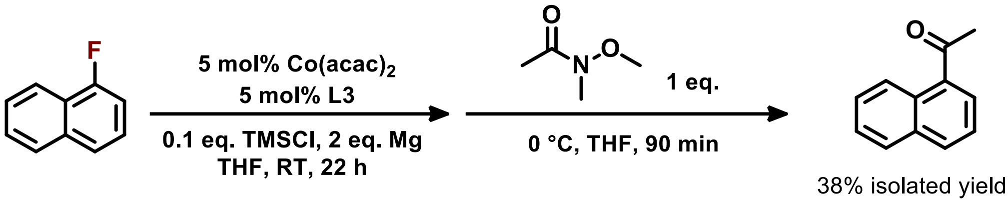


Figure S12. Addition of *N*-methoxy-*N*-methylacetamide to the reaction intermediate (**Figure 3a**. (4)).

The reaction was carried out under inert atmosphere with stirring using oven-dried glassware and magnetic bars in a glove box. Cobalt(II) acetylacetonate (5.1 mg, 0.02 mmol (0.05 eq)), the corresponding ligand, **L1** (6.7 mg, 0.02 mmol (0.05 eq)), and magnesium (19.4 mg, 0.8 mmol (2 eq)) were added to a 4 mL vial. Then dried THF (0.5 mL), chlorotrimethylsilane (5.08 μL, 0.04 mmol (0.1 eq)) and 1-fluoronaphthalene (51.6 μL, 0.4 mmol (1 eq)) were added. The mixture solution was stirred at 25 °C for 22 hours. After 22 hours, residue solid was filtrated and Weinreb amide, *N*-methoxy-*N*-methylacetamide (42.5 μL, 0.4 mmol (1 eq)) was added under inert condition. The mixture was stirred at 0 °C for 90 minutes.

After the reaction, a cold saturated NH_4Cl aqueous solution (2 mL) was added. Subsequently, ethyl acetate (10 mL) was added to the crude residue and the solution was shaken vigorously. The organic layer was extracted and washed with brine. It was dried over by anhydrous Na_2SO_4 and the product was purified by column chromatography (Hexanes:Ethyl acetate=9:1) to afford 1-(1-naphthalenyl)-ethanone (25.6 mg, 38%) as yellow oil.

^{1}H NMR (500 Hz, $CDCl_3$) δ 8.74 (d, *J* = 8.66 Hz, 1H), 8.00 (d, *J* = 8.20 Hz, 1H), 7.95 (dd, *J* = 7.20, 1.00 Hz, 1H), 7.88 (d, *J* = 8.15 Hz, 1H), 7.63-7.59 (m, 1H), 7.56-7.49 (m, 2H), 2.76 (s, 3H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 201.8, 135.6, 134.0, 133.0, 130.2, 128.6, 128.4, 128.1, 126.4, 126.0, 124.3, 30.0. These spectroscopic data are consistent with those previously reported in the literature.[11] The NMR spectra are provided in the NMR data section.

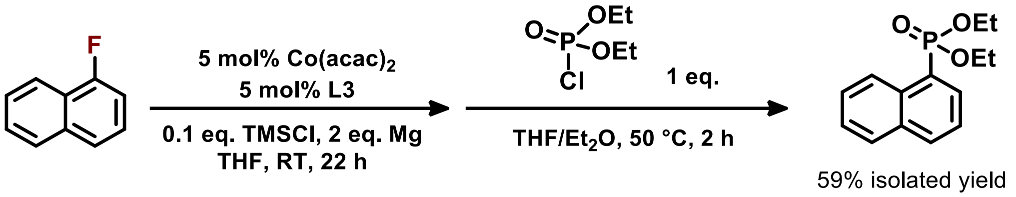


Figure S13. Addition of diethyl chlorophophate to the reaction intermediate (**Figure 3a**. (5)).

The reaction was carried out under inert atmosphere with stirring using oven-dried glassware and magnetic bars in a glove box. Cobalt(II) acetylacetonate (5.1 mg, 0.02 mmol (0.05 eq)), the corresponding ligand, **L1** (6.7 mg, 0.02 mmol (0.05 eq)), and magnesium (19.4 mg, 0.8 mmol (2 eq)) were added to a 4 mL vial. Then dried THF (0.5 mL), chlorotrimethylsilane (5.08 µL, 0.04 mmol (0.1 eq)) and 1-fluoronaphthalene (51.6 µL, 0.4 mmol (1 eq)) were added. The mixture solution was stirred at 25 °C for 22 hours. After 22 hours, the residual solid was filtrated and diethyl chlorophophate (57.9 µL, 0.4 mmol (1 eq)) and diethyl ether (1mL) were added under inert condition. The mixture was stirred at 50 °C for 2 hours. Heating block was used for heating.

After the reaction, the reaction mixture was cooled to room temperature and cold 10% HCl aqueous solution (1 mL) was added. Subsequently, diethyl ether (10 mL) was added to the crude residue and the solution was shaken vigorously. The organic layer was extracted and dried over by anhydrous Na_2SO_4. The product was purified by column chromatography (Hexanes:EA=2:1) to afford 1-diethoxyphosphorylnaphthalene (62.2 mg, 59%) as a yellow oil.

^{1}H NMR (500 Hz, $CDCl_3$) δ 8.52 (d, *J* = 8.50 Hz, 1H), 8.25 (ddd, *J* = 1.20, 7.05, 16.31, 1H), 8.04 (d, *J* = 8.20 Hz, 1H), 7.90 (d, *J* = 8.10 Hz, 1H), 7.63-7.59 (m, 1H), 7.57-7.51 (m, 2H), 4.25-4.17 (m, 2H), 4.12-4.04 (m, 2H), 1.31 (t, *J* = 7.05 Hz, 6H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 134.6 (d, *J* = 8.92 Hz), 133.6, 132.7 (d, *J* = 10.77 Hz), 128.8, 127.4, 126.7, 126.3, 125.4, 124.5 (d, *J* = 16.54 Hz), 124.0, 62.2 (d, *J* = 4.58 Hz), 16.3 (d, *J* = 6.03 Hz). ^{31}P NMR (203 MHz, $CDCl_3$) δ 19.20. These spectroscopic data are consistent with those previously reported in the literature.[12] The NMR spectra are provided in the NMR data section.

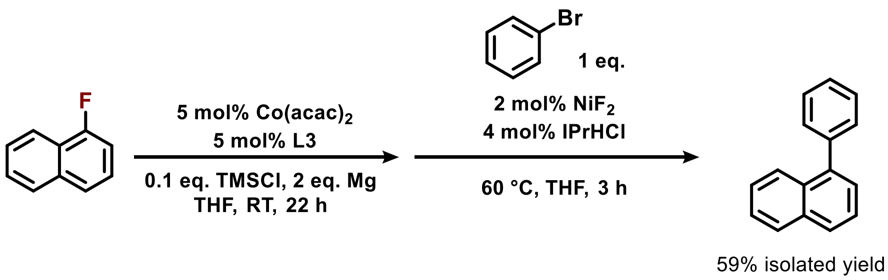


Figure S14. Nickel catalyzed Kumada coupling of the reaction intermediate with aryl bromides (**Figure 3a**. (6)).

The reaction was carried out under inert atmosphere with stirring using oven-dried glassware and magnetic bars in a glove box. Cobalt(II) acetylacetonate (5.1 mg, 0.02 mmol (0.05 eq)), the corresponding ligand, **L1** (6.7 mg, 0.02 mmol (0.05 eq)), and magnesium (19.4 mg, 0.8 mmol (2 eq)) were added to a 4 mL vial. Then dried THF (0.5 mL), chlorotrimethylsilane (5.08 µL, 0.04 mmol (0.1 eq)) and 1-fluoronaphthalene (51.6 µL, 0.4 mmol (1 eq)) were added. The mixture solution was stirred at 25 °C for 22 hours. After 22 hours, residue solid was filtrated and nickel(II) fluoride (0.8 mg, 0.008 mmol (0.02 eq)) and 1,3-Bis-(2,6-diisopropylphenyl)imidazolinium chloride (IPrHCl, 6.8 mg, 0.016 mmol (0.04 eq)) were added under inert condition. The mixture was stirred at room temperature for 5 minutes and bromobenzene (41.9 µL, 0.4 mmol (1 eq)) was added and the mixture was stirred at 60 °C for 3 hours. Heating block was used for heating.

After the reaction, the reaction mixture was filtered through a pad of Celite. Subsequently, water (10 mL) and dichloromethane (20 mL) were added to the crude residue and the solution was shaken vigorously. The mixture was filtered through a pad of Celite again. Additional organic solvent (3 × 10 mL) and water (3 × 5 mL) were poured to the Celite to assure collecting all products. The organic layer was extracted and dried over by anhydrous Na_2SO_4. The product was purified by column chromatography (Hexanes 100%) to afford 1-phenyl-naphthalene (48.5 mg, 59%) as a colorless oil.

^{1}H NMR (500 Hz, $CDCl_3$) δ 7.93 (d, J = 9.46 Hz, 2H), 7.88 (d, J = 7.80 Hz, 1H), 7.57-7.44 (m, 9H). ^{13}C NMR (126 Hz, $CDCl_3$) δ 140.8, 140.3, 133.8, 131.7, 130.1, 128.3, 127.6, 127.2, 126.9, 126.1, 126.0, 125.8, 125.4. These spectroscopic data are consistent with those previously reported in the literature.[13] The NMR spectra are provided in the NMR data section.

Evidence for the formation of fluorotrimethylsilane

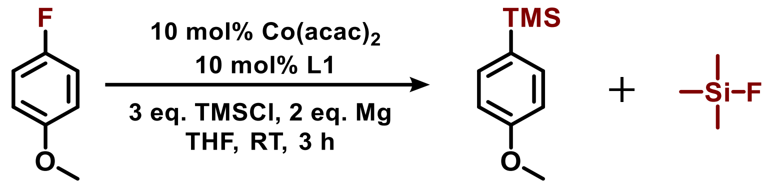


Figure S15. Defluorosilylation of 4-fluoroanisole to detect fluorotrimethylsilane.

The reaction was carried out under inert atmosphere with stirring using oven-dried glassware and magnetic bars in a glove box. Cobalt(II) acetylacetonate (10.3 mg, 0.04 mmol (0.1 eq)), the corresponding ligand, **L1** (13.4 mg, 0.04 mmol (0.1 eq)), and magnesium (19.4 mg, 0.8 mmol (2 eq)) were added to a 4 mL vial. Then dried THF (0.5 mL), chlorotrimethylsilane (152.3 µL, 1.2 mmol (3 eq)), and 4-fluoroanisole (45.3 µL, 0.4 mmol (1 eq)) were added and the mixture was stirred at room temperature for 3 hours. After the reaction, the reaction mixture and a J-Young NMR tube with $CDCl_3$ (50 µL) were cooled to −15 °C. 200 µL of the reaction mixture was transferred to the J-Young NMR tube and subsequently, ^{19}F-NMR data was obtained. The residue reaction mixture was warmed to room temperature and the headspace (gas phase) was used for GC-MS measurement. Fluorotrimethylsilane was observed from ^{19}F NMR and GC-MS spectrum.

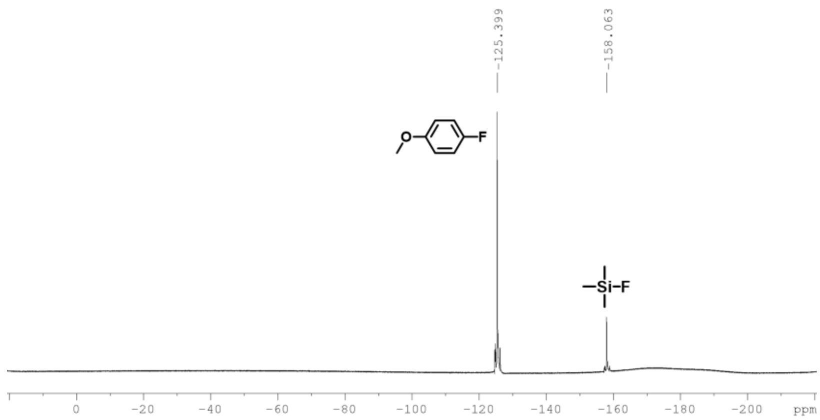


Figure S16. Crude ^{19}F NMR spectrum after defluorosilylation of 4-fluoroanisole.

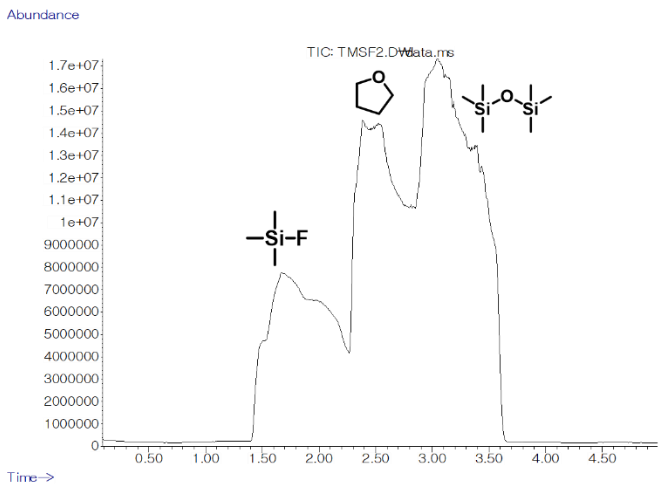


Figure S17. GC-MS spectrum of headspace (gas phase) after defluorosilylation of 4-fluoroanisole.

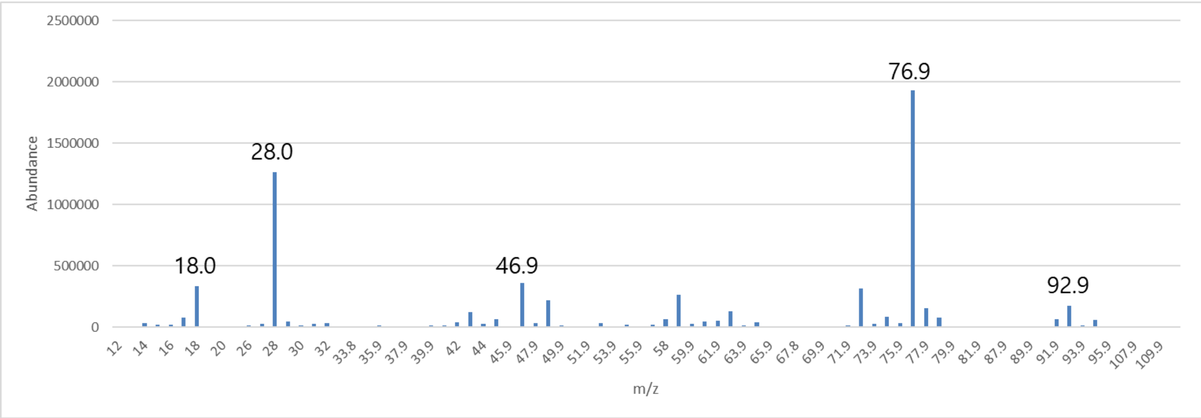


Figure S18. Observed MS spectrum of fluorotrimethylsilane.

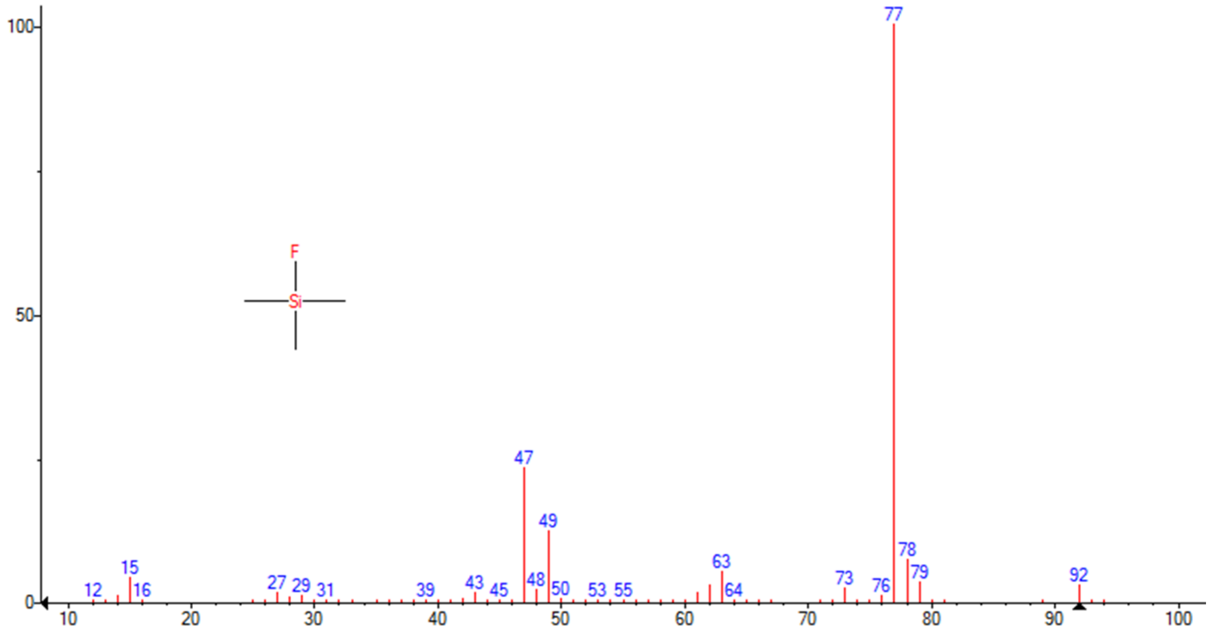


Figure S19. Theoretical MS spectrum of fluorotrimethylsilane.

4. Synthetic methods described in Figure 4

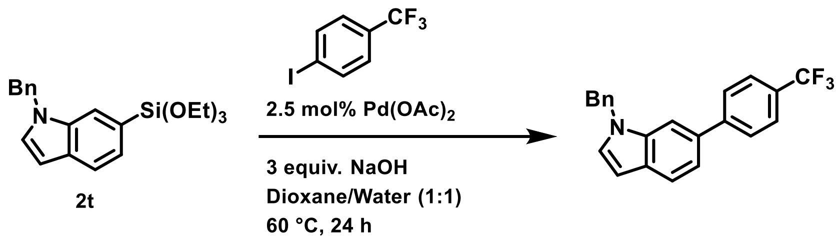


Figure S20. C–C bond coupling reaction of the aryl silane (**Figure 4**. (a)).

Organosilane, **2t** (37.0 mg, 0.1 mmol), 4-iodobenzotrifluoride (14.70 μL, 0.1 mmol (1 eq)), palladium(II) acetate (0.8 mg, 0.0025 mmol (2.5 mol%)), sodium hydroxide (12.0 mg, 0.3 mmol (3 eq)) were added to a 4 mL vial. Then dioxane (0.5 mL) and water (0.5 mL) were added. The mixture was refluxed at 60 °C for 24 hours. Heating block was used for heating.

After the reaction, ethyl acetate (5 mL) and water (5 mL) were added and the solution was shaken vigorously. The organic layer was extracted and dried over by anhydrous Na_2SO_4. The solution was concentrated under vacuum and the product was purified by column chromatography (gradient, Hexanes 100% to Ethyl acetate 100%) to afford 1-benzyl-6-(4-(trifluoromethyl)phenyl)-1*H*-indole (24.2 mg, 69%) as a yellow solid.

^{1}H NMR (500 Hz, CD_3CN) δ 7.83-7.81 (m, 2H), 7.74-7.68 (m, 4H), 7.41-7.39 (m, 2H), 7.33-7.21 (m, 5H), 6.57 (dd, J = 0.82, 3.14 Hz, 1H), 5.46 (s, 2H). ^{13}C NMR (126 Hz, CD_3CN) δ 146.0, 138.2, 136.7, 132.8, 130.2, 129.0, 128.7, 128.0, 127.8, 127.6, 127.0, 125.6, 125.6, 121.3, 118.9, 108.8, 101.3, 49.6. HRMS (ESI) m/z: [M + H]+ Calcd for $C_{22}H_{17}F_3N$ 352.1308; found 352.1310. Q-TOF mass spectrometer was used. The NMR spectra are provided in the NMR data section.

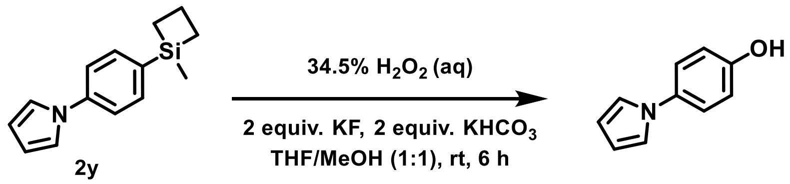


Figure S21. Oxidation of the aryl silane (**Figure 4**. (b)).

Organosilane, **2y** (22.7 mg, 0.1 mmol) was dissolved in 1 mL of THF/MeOH. Potassium fluoride (11.6 mg, 0.2 mmol (2 eq)), potassium bicarbonate (20.0 mg, 0.2 mmol (2 eq)) and hydrogen peroxide (34.5% in H_2O_2, 0.4 mL) were added. The mixture was stirred at room temperature for 6 hours.

After the reaction, ethyl acetate (2 mL) was added and the mixture was shaken vigorously. The organic layer was extracted and washed with 1.0 M Na_2SO_3 aqueous solution and brine. The organic phase was dried over by anhydrous Na_2SO_4 and the product was purified by column chromatography (Hexanes:EA=10:1) to afford 4-(1H-pyrrol-1-yl)-phenol (12.9 mg, 81%) as pale brown solid.

^{1}H NMR (500 Hz, d^6-DMSO) δ 9.48 (s, 1H), 7.33 (d, J = 8.81 Hz, 2H), 7.16 (t, J = 2.15 Hz, 2H), 6.82 (d, J = 8.76 Hz, 2H), 6.19 (t, J = 2.10 Hz, 2H). ^{13}C NMR (126 Hz, d^6-DMSO) δ 155.7, 132.8, 121.7, 119.6, 116.4, 110.03. These spectroscopic data are consistent with those previously reported in the literature.[14] The NMR spectra are provided in the NMR data section.

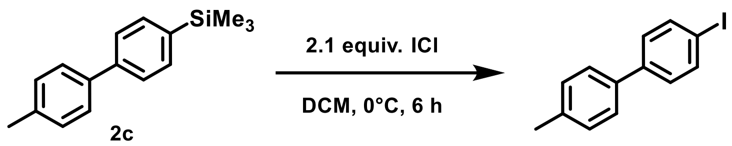


Figure S22. Iodination of the aryl silane (**Figure 4**. (c))

Organosilane, **2c** (96.2 mg, 0.4 mmol) was dissolved in dichloromethane (1 mL). Iodine chloride (44.0 µL, 0.84 mmol (2.1 eq)) was added and the mixture was cooled to 0 °C and stirred for 6 hours.

After the reaction, 40% Na_2SO_3 aqueous solution was added to the reaction mixture upon which the red solution turns yellow. The organic layer was extracted and washed with aqueous 10% HCl solution and brine. The organic phase was dried over by Na_2SO_4 and the product was purified by column chromatography (Hexanes 100%) to afford 4-iodo-4'-methylbiphenyl (64.4 mg, 55%) as white solid.

^{1}H NMR (500 Hz, CD_3CN) δ 7.79 (d, J = 8.54 Hz, 2H), 7.52 (d, J = 8.16 Hz, 2H), 7.41 (d, J = 8.53 Hz, 2H), 7.28 (d, J = 7.90 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (126 Hz, CD_3CN) δ 140.5, 137.9, 137.9, 136.7, 129.6, 128.8, 126.6, 92.0, 20.1. These spectroscopic data are consistent with those previously reported in the literature.[15] The NMR spectra are provided in the NMR data section.

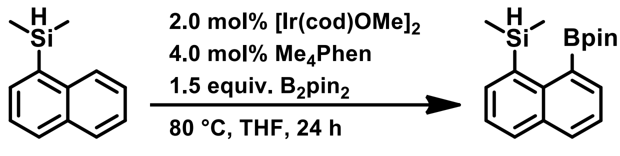


Figure S23. Hydrosilane group as a directing group for dehydroborylation (**Figure 4**. (d)).

Iridium catalyst, $[Ir(cod)OMe]_2$ (5.3 mg, 2.0 mol%), Me_4Phen (3.8 mg, 4.0 mol%), B_2pin_2 (152.4 mg, 1.5 eq) and a magnetic bar were added to a 4 mL vial under inert condition. THF (0.5 mL) was added to the vial and the solution was stirred at room temperature for 5 minutes. After 5 minutes, organosilane, **2z** (74.5 mg, 0.4 mmol) was added to the reaction mixture and it was stirred at 80 °C for 24 hours. Heating block was used for heating.

After the reaction, all volatiles were evaporated under vacuum and water (5 mL) and ethyl acetate (5 mL) were added. The organic layer was separated and dried over by Na_2SO_4. The solvent was evaporated and CH_2Br_2 (8.9 mg) and $CDCl_3$ were added for the measurement of ^{1}H NMR spectrum. ^{1}H NMR yield was 58% and the NMR spectrum was provided in the NMR data section. The spectroscopic data are consistent with the previously reported in the literature.[8]

5. Density function theory calculations

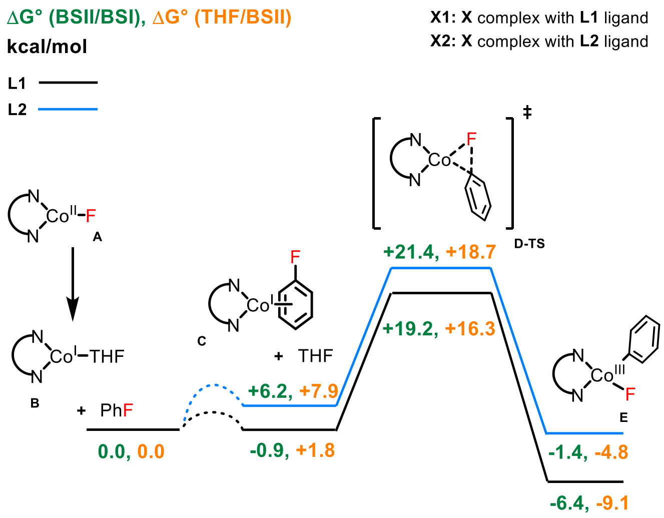


Figure S24. Schematic C−F bond activation and relative free energies (kcal/mol) computed at the B3PW91/BS I//BS II, SMD level in the gas and solution (THF) phase.

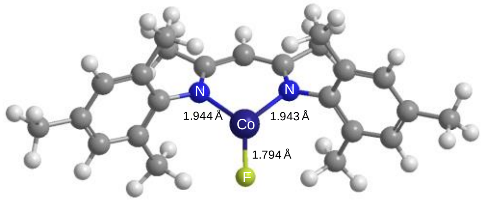
To elucidate a feasible mechanism as well as the origin of ligand dependence, a theoretical study was carried out using the Gaussian 16 program[16] package at the B3PW91/BSI//BSII, SMD level in the gas and solution (THF) phase to obtain an energy profile for the cobalt catalysis (see Supporting Information for details of the calculation).[17] The mechanistic study on cobalt-catalyzed C−F bond activation of aryl fluoride was intensively studied by the Holland group. Inspired by the experimental data provided by the group, we investigated further the effect of the supporting beta-diketiminate ligands, which plays a critical role in the successful catalytic performance. **Figure S24** summarizes structural and free energy data for the proposed pathway (a concerted mechanism) suggested by the Holland group. The DFT data clearly demonstrated that **L1** is more effective than **L2**, as the activation energy with **L1** is lower by 2.2 and 2.4 kcal/mol in the gas phase and THF solution, respectively, compared with one with **L2**. The detailed analysis of the transition states for both **D1-TS** and **D2-TS** indicates that the steric factor could affect the efficacy of the catalyst. For example, Co−C and C−F bond distances in the transition states show a significant difference, which induces stronger sigma bonding contribution of Co in **D1-TS** (Co−C and C−F bond: 2.055 Å and 1.594 Å for **D1-TS** vs 2.101 Å and 1.574 Å for **D2-TS**) while Co−F bond distances are almost the same (See the Supporting Information). We assumed that the electronic effect is less important in this catalysis because there are negligible metric differences in other cobalt complexes coordinating to small molecules such as **A** and **B**.

The DFT calculations were performed using Gaussian16[16] at the clusters at Korea Institute of Science and Technology Information (KISTI) computational resource. Geometry optimizations of all compounds were carried out using the atomic coordinates from energy minimized structures. The nature of all stationary points calculated from full optimizations was confirmed *via* frequency analysis, which revealed zero imaginary frequency for the ground state. All geometries were optimized using the B3PW91[17] under standard convergence criteria with the following basis sets, which include SDD quasirelativistic pseudopotentials on Co (10), with their associated basis sets (Co: (8s7p6d)/[6s5p3d])[18] augmented by polarization functions (Co: f, 2.780),[19] and 6-31G(d,p)[20] on H, C, N and O. For all BS I-optimized geometries, single-point energy calculations were performed with BS II, in which SDD pseudopotentials are used for Co (10) with the associated SDD basis set augmented by (2f1g) functions[21] and for the other atoms described by 6-311G+(2d,p) basis sets.[22] Solvation energies were computed on BS I, gas phase-optimized geometries using SMD model of Cramer and Truhlar.[23]

However, due to the expensive computational cost to calculate Gibbs free energies ($G°_{gas}$) of all the compounds at B3PW91/BSII level, their $G°_{gas}$ (BSII/BSI) values were combined with thermochemical corrections calculated *via* frequency analyses at B3PW91/BSI level in gas phase without scaling to produce improved estimates in the text and schemes ($G°_{gas}$ (BSII/BSI) = $G°_{gas}$ (BSI) + ($E°_{gas}$ (BSII) - $E°_{gas}$ (BSI)). The $G°_{THF}$ (BSII) values were calculated in a similar way ($G°_{THF}$ (BSII) = $G°_{gas}$ (BSI) + ($E°_{THF}$ (BSII) - $E°_{gas}$ (BSI)). The transition state was confirmed by one substantial imaginary frequency. *Energy unit provided below is hatree.*

Optimized Structures

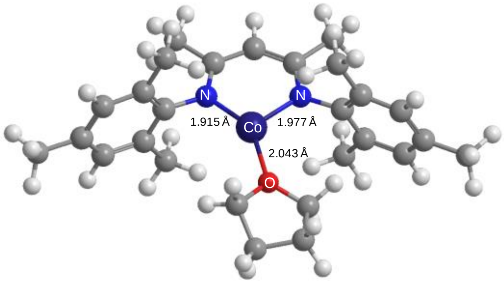
A1 (E°$_{BSI}$ = -1264.1475101, G°$_{BSI}$ = -1263.711168; E°$_{THF(BSII)}$ = -1249.212796, G°$_{THF(BSII)}$ = -1248.776454; E°$_{BSII}$ = -1249.1690363, G°$_{BSII}$ = -1248.732694; spin muliplicity=4)



F	3.56128299	5.048491044	-0.744593352	H	3.302747407	-0.769941242	-1.445906511
C	4.611389948	0.856230111	-1.769475223	H	5.378717733	0.555029032	-3.761499743
C	3.523321966	0.241087015	-1.125213975	H	4.902453863	-0.941040515	-2.929072048
C	2.720842266	0.733154421	-0.080843456	H	6.40534151	-0.10225296	-2.500550124
C	5.361201495	0.039731651	-2.795917177	H	1.876463073	-0.399637926	1.554600098
C	1.683159938	-0.201263156	0.495812066	H	1.671403976	-1.152576756	-0.038006235
C	6.180047934	2.632984086	-2.143757963	H	0.685952373	0.246672296	0.440668582
C	6.056453337	3.432734198	-3.295146286	H	7.119795252	4.591117163	-4.749072479
C	7.214025935	3.974819038	-3.857042315	H	9.537904244	2.825878667	-1.685744883
C	8.478617098	3.760540138	-3.30603223	H	-0.795623028	4.055373606	2.299385422
C	8.565167647	2.988052592	-2.146341284	H	2.113039738	2.342182545	4.936378876
C	7.43780465	2.4222855	-1.548093093	H	4.119639763	2.819216728	-4.05597363
C	2.047525861	2.367129124	1.542818567	H	4.810770569	4.243207924	-4.849606124
C	0.85658795	3.088993326	1.338824073	H	4.120645725	4.374943115	-3.224950561
C	0.130118796	3.504951526	2.45605677	H	10.11431673	3.652277903	-4.713088971
C	0.557243184	3.244674577	3.759537584	H	10.50607946	4.503709193	-3.218097315
C	1.754333647	2.54712376	3.929402035	H	9.500435413	5.284610724	-4.447503442
C	2.515481823	2.107760764	2.844453576	H	7.238452597	0.589997674	-0.395712117
C	4.70626806	3.72895409	-3.890616736	H	6.95012611	2.055956765	0.523178836
C	9.712834846	4.332723554	-3.951772034	H	8.603949732	1.613121697	0.068944212
C	7.566795537	1.628446015	-0.275576777	H	-0.613913857	3.869169953	-0.022815173
C	0.386810147	3.430035009	-0.049815572	H	0.354087256	2.551354564	-0.70247504
C	-0.23058241	3.736280517	4.945098517	H	1.059867676	4.157048441	-0.520678079
C	3.819944046	1.390555414	3.068280411	H	-0.040258965	3.127291539	5.833658479
N	5.007519504	2.106270577	-1.520048671	H	-1.306576783	3.718102601	4.74676064
N	2.831975475	1.966331721	0.418085041	H	0.035428676	4.770745602	5.194966765
Co	3.925864926	3.316854658	-0.451138935	H	4.047061473	1.32177705	4.135189641

H	4.649070769	1.913420711	2.578127294	H	3.813608923	0.373466636	2.660781065

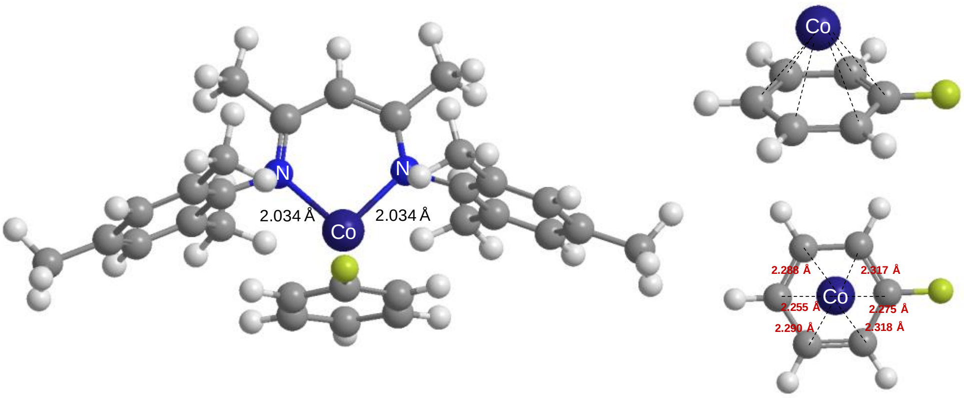
B1 (E°$_{BSI}$ = -1381.416655, G°$_{BSI}$ = -1380.907599; E°$_{THF(BSII)}$ = -1381.740451, G°$_{THF(BSII)}$ = -1381.231396; E°$_{BSII}$ = -1381.712831, G°$_{BSII}$ = -1381.203775; spin muliplicity=3)



C	4.109476597	7.706579116	0.119353169	C	1.772911781	2.54891666	1.407244949
C	5.429924852	6.085642048	-1.013725588	C	0.460711386	2.770155147	0.940106424
C	5.103744786	7.571822309	-1.03723736	C	-0.495924643	3.276190177	1.822941339
C	3.294244052	6.42838748	-0.014857341	C	-0.196047306	3.571795751	3.154274152
O	4.216343754	5.442551998	-0.541754928	C	1.113868193	3.358782448	3.589674837
H	3.486957219	8.602640681	0.054900234	C	2.103898543	2.855186581	2.743970674
H	4.637428626	7.725820638	1.079026082	C	4.055171739	3.020320145	-4.140801425
H	5.679374013	5.66025948	-1.986605917	C	8.644063507	4.944971838	-4.98728757
H	6.233291414	5.853713763	-0.306089084	C	7.607635606	2.770261592	-0.551029817
H	4.627814769	7.845642306	-1.985235304	C	0.104416803	2.487409917	-0.493684784
H	5.995850044	8.191220985	-0.913921956	C	-1.255866839	4.080224797	4.096468175
H	2.89754407	6.04783583	0.929774327	C	3.509632866	2.656069118	3.239738395
H	2.469277143	6.542744098	-0.727897002	N	4.934741687	2.291699695	-1.490029945
C	4.861971575	0.964380769	-1.398050708	N	2.78657682	2.105385922	0.515717104
C	3.985712203	0.2834492	-0.527941495	Co	3.717849091	3.46305483	-0.462572374
C	3.016855389	0.7985884	0.346763572	H	4.047736539	-0.798487834	-0.563549359
C	5.74139208	0.106047091	-2.284657423	H	5.527121254	0.29025335	-3.343275705
C	2.190173629	-0.200465914	1.127791614	H	5.585727709	-0.955634255	-2.084474006
C	5.864766764	2.884905397	-2.378781269	H	6.802745176	0.332289854	-2.139849611
C	5.454975354	3.297876921	-3.663660189	H	2.280278014	-0.031336798	2.206159734
C	6.364179198	3.973909397	-4.481142708	H	2.50283722	-1.223633524	0.911703923
C	7.670503657	4.251254222	-4.070494064	H	1.1254691	-0.1076517	0.887969263
C	8.050671452	3.83992443	-2.790805358	H	6.040451996	4.289402692	-5.471976496
C	7.17502915	3.166114691	-1.936672578	H	9.059930838	4.05379144	-2.441642392

H	-1.507063704	3.44557405	1.455670655	H	8.589269718	3.188781123	-0.310953904
H	1.376668515	3.592493581	4.620414023	H	-0.928021761	2.778983144	-0.706177207
H	3.859859128	1.944859599	-4.220178173	H	0.214199265	1.426122073	-0.743203741
H	3.878555948	3.468710695	-5.122610241	H	0.770580044	3.02919107	-1.176559953
H	3.312055647	3.412013054	-3.436477394	H	-1.757856646	3.254532557	4.616674715
H	9.195031512	4.223659124	-5.604022715	H	-2.028685683	4.6440373	3.564874734
H	9.385861698	5.520532464	-4.424800188	H	-0.83054866	4.733750864	4.864584216
H	8.133906802	5.630230085	-5.671454284	H	3.624330826	3.033701406	4.259766483
H	7.671453272	1.682177485	-0.435131706	H	4.228412527	3.167177077	2.587982989
H	6.882650028	3.110243891	0.197098353	H	3.798902659	1.598966186	3.236629128

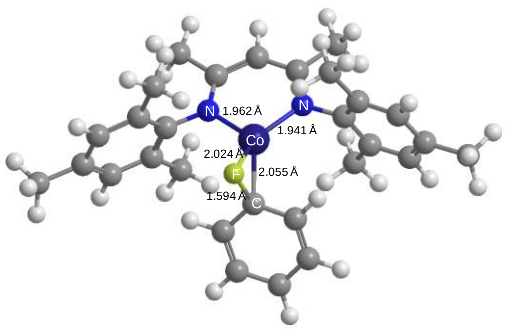
C1 (E°$_{BSI}$ = -1480.40882, G°$_{BSI}$ = -1479.920973; E°$_{THF(BSII)}$ = -1480.763272, G°$_{THF(BSII)}$ = -1480.275425; E°$_{BSII}$ = -1480.738774, G°$_{BSII}$ = -1480.250927; spin muliplicity=3)



Co	22.88293335	51.03078198	9.262135128	C	23.83972057	47.76908296	7.711521172
C	25.46123864	51.98377892	7.386972739	C	21.34631522	53.48860755	6.693148257
C	24.91256896	54.39676044	7.25862518	C	25.15802804	46.72840072	9.940773832
C	22.68055058	53.95540508	8.792656434	N	23.4875665	52.82073436	8.508464922
C	21.60289322	54.2838842	7.945059476	C	20.97973788	56.11638574	9.439620524
C	25.89673372	49.0226279	10.67886648	C	20.09160433	57.28823696	9.766895854
C	26.50628959	49.75642131	7.092075357	C	24.50702606	48.63555745	8.601318958
C	24.57661476	53.00674882	7.761586078	C	25.17446397	48.10919489	9.725243957
C	20.77439891	55.35598176	8.285975504	N	24.44121773	50.04182073	8.407528973
C	24.50485324	45.85024444	9.073918966	C	23.12192447	48.31593646	6.506735007
C	24.52960741	44.36230035	9.307431407	C	25.3988943	50.6117603	7.675186538
C	22.052906	55.77138433	10.26341616	C	22.90858104	54.70832723	9.961804774

C	23.85125203	46.39541894	7.966235263
C	24.05997775	54.37255984	10.87113334
H	26.30281843	52.29465022	6.779166932
H	24.11103452	54.79375753	6.627122194
H	25.83614489	54.39000184	6.677246233
H	25.03084471	55.10226007	8.087138469
H	26.20721721	48.48506612	11.57940806
H	25.26630638	49.86975171	10.96915688
H	26.79581055	49.45555127	10.22451208
H	27.05158922	49.22195859	7.876407606
H	27.21767303	50.36564673	6.531875742
H	26.10370257	48.99160373	6.419936268
H	19.94369006	55.60402796	7.627008862
H	23.61336362	43.88394452	8.947740736
H	24.63904885	44.12462713	10.36988543
H	25.36881776	43.89025587	8.781257384
H	22.23433906	56.34761464	11.1695119
H	20.45251271	53.84977546	6.176846155
H	21.21185241	52.42456686	6.915050252
H	22.18674225	53.54895319	5.992888017
H	25.67431239	46.32915893	10.81256602
H	20.05135604	57.47258363	10.84472037
H	19.06820664	57.1275325	9.414052569
H	20.45599763	58.20875107	9.293776057
H	23.80621828	48.83203976	5.824367976
H	22.36406382	49.05343658	6.79188186
H	22.63089951	47.51472282	5.947405404
H	23.33353636	45.73191359	7.275154126
H	24.08384445	53.30194571	11.10043826
H	23.99909045	54.93530665	11.80704577
H	25.02562999	54.60444318	10.40654428
C	20.67962184	51.55728498	9.747112989
C	20.73260416	50.2991822	9.129250347
F	20.00185015	50.09133547	8.01902535
C	21.47404807	49.23299451	9.659256914
C	22.25073635	49.46379517	10.80780865
C	22.26888003	50.73779077	11.41201356
C	21.46208483	51.77234695	10.89490758
H	20.09144126	52.35447788	9.309706843
H	21.48561761	48.27442152	9.155471767
H	22.87110426	48.66368271	11.19375331
H	22.88731415	50.91612043	12.28472505
H	21.47275923	52.75633686	11.34842246

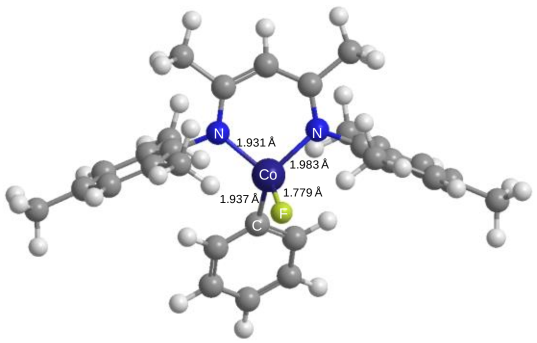
D1-TS ($E°_{BSI}$ = -1480.375332, $G°_{BSI}$ = -1479.892034; $E°_{THF(BSII)}$ = -1480.735637, $G°_{THF(BSII)}$ = -1480.252339; $E°_{BSII}$ = -1480.702137, $G°_{BSII}$ = -1480.218839; the only imaginary frequency = -278.7957 cm^{-1}; spin muliplicity=3)



C	3.909645269	7.10102915	-1.495000868
C	4.685876697	6.030984007	-1.071675142
C	4.290224828	5.333472085	0.088335597
C	3.265560663	5.832082571	0.920332532

C	2.505413195	6.902470574	0.462999315	H	1.675221295	7.254733927	1.069484584
C	2.811060627	7.538243829	-0.744232162	H	2.222551892	8.386260511	-1.079780451
F	5.508054814	4.713537991	0.908468792	H	3.452951701	-0.670044072	-1.263631999
C	4.761021784	0.95734752	-1.570327451	H	5.46545012	0.61513673	-3.589867995
C	3.6631333	0.342226759	-0.93932539	H	5.06883926	-0.862664513	-2.693789667
C	2.79074986	0.849591644	0.038385195	H	6.556325602	0.040640489	-2.343022912
C	5.497947956	0.136617416	-2.606219622	H	1.739951722	-0.231265316	1.586831364
C	1.679353411	-0.063170264	0.506659999	H	1.725311344	-1.029144045	0.001616366
C	6.274511126	2.74403105	-2.031786372	H	0.697413207	0.381697963	0.316629814
C	6.03536368	3.398441385	-3.256373258	H	6.925994353	4.489979516	-4.871888293
C	7.112409655	3.984942529	-3.925661168	H	9.618892979	3.27234546	-1.771200847
C	8.412170763	3.947118833	-3.417125832	H	-1.002011665	4.133246115	1.850849886
C	8.616366184	3.305508637	-2.193985429	H	1.616946841	2.717726637	4.931387862
C	7.572470643	2.704925087	-1.487762433	H	4.197123139	2.508512473	-3.997348444
C	1.960290596	2.499812911	1.558848446	H	4.647380639	4.033270662	-4.772450508
C	0.778643446	3.157778194	1.166488864	H	3.974748066	4.021576238	-3.13310354
C	-0.088031804	3.626655905	2.155793902	H	10.0574998	3.815888475	-4.812039728
C	0.185580252	3.473809407	3.516641284	H	10.32031929	4.959843099	-3.495478823
C	1.375205566	2.837624288	3.876799642	H	9.226067913	5.37198129	-4.824019786
C	2.271429117	2.348180524	2.923930992	H	7.459352417	1.010368984	-0.140898562
C	4.643487858	3.49309534	-3.821902941	H	7.321848827	2.574756194	0.650009986
C	9.561714506	4.558366692	-4.174232996	H	8.898269015	2.024066157	0.064546776
C	7.828912064	2.040911787	-0.162085795	H	-0.498670335	3.869695588	-0.411388922
C	0.47249702	3.382935856	-0.289102281	H	0.457214642	2.448302132	-0.859398936
C	-0.782324579	3.959620485	4.563284167	H	1.232973116	4.022142938	-0.751802112
C	3.552615168	1.682783368	3.350570827	H	-1.500206221	3.175557262	4.834764475
N	5.18474331	2.191712512	-1.298356004	H	-1.359737351	4.81827584	4.207824343
N	2.893825678	2.068921297	0.57182387	H	-0.265276369	4.256788166	5.480638221
Co	4.334286615	3.279349412	0.095695129	H	3.613342669	1.616848113	4.440036112
H	4.174058306	7.611870768	-2.417405612	H	4.430427019	2.238622941	2.998888563
H	5.551993449	5.69823515	-1.63468319	H	3.645278376	0.670470176	2.943119587
H	3.047151683	5.354551173	1.870663978				

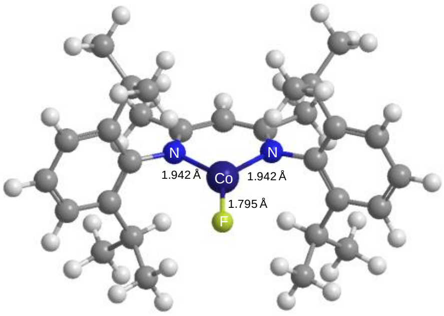
E1 (E°$_{BSI}$ = -1480.417598, G°$_{BSI}$ = -1479.931997; E°$_{THF(BSII)}$ = -1480.778426, G°$_{THF(BSII)}$ = -1480.292825; E°$_{BSII}$ = -1480.745176, G°$_{BSII}$ = -1480.259575; spin muliplicity=3)



C	4.874931035	7.063933958	-1.35728346	C	0.479157935	3.022758354	-0.333371217
C	5.133563884	5.722999652	-1.060163077	C	-0.866837301	3.946598328	4.436580827
C	4.180899236	4.991181632	-0.358549363	C	3.608908114	1.830917461	3.483070069
C	3.004132436	5.582888483	0.092712544	N	5.164846561	2.192781577	-1.290685917
C	2.756863014	6.924745856	-0.213378498	N	2.998615944	2.005174458	0.651634352
C	3.687406836	7.662522887	-0.941036544	Co	4.538943896	3.185458237	0.243371345
F	5.478493959	3.674323296	1.673147008	H	5.613484868	7.638204084	-1.910756376
C	4.747753905	0.948511694	-1.567334102	H	6.068134617	5.272882627	-1.378790945
C	3.718849851	0.292528384	-0.882910596	H	2.284621885	5.027026193	0.686393728
C	2.880979626	0.783927003	0.1351318	H	1.835490381	7.388127791	0.130188854
C	5.447910988	0.166869512	-2.656608743	H	3.493164907	8.706022533	-1.173416077
C	1.821954552	-0.157625798	0.662681037	H	3.525487609	-0.726088956	-1.196657059
C	6.17438242	2.773662795	-2.115698074	H	5.324911619	0.639550301	-3.635118469
C	5.826253224	3.361298174	-3.348099576	H	5.059040474	-0.85082907	-2.713393951
C	6.834549764	3.947923928	-4.114884098	H	6.524672377	0.121392704	-2.465518764
C	8.164949553	3.981450295	-3.691023874	H	1.917710536	-0.272911521	1.74674738
C	8.474677143	3.405275971	-2.457661933	H	1.90629718	-1.140707348	0.196994552
C	7.503845173	2.80348243	-1.652898891	H	0.8149383	0.227349685	0.478630311
C	2.022872048	2.442472632	1.600844617	H	6.568009242	4.400752695	-5.0679959
C	0.797614761	2.963645092	1.138129468	H	9.504569601	3.420727653	-2.106376292
C	-0.125651052	3.434349384	2.075264407	H	-1.07122126	3.838254305	1.718071859
C	0.129330857	3.402508936	3.44692777	H	1.566308359	2.829293394	4.938424224
C	1.348691886	2.872726626	3.87293176	H	3.955723113	2.405266845	-3.913143647
C	2.30809292	2.393054089	2.978770771	H	4.316602533	3.904395807	-4.779172535
C	4.395388152	3.403157672	-3.81112399	H	3.775291081	3.948712189	-3.091667207
C	9.227337991	4.649601451	-4.523369617	H	8.992512598	4.596892165	-5.59058205
C	7.876720749	2.201792759	-0.324488571	H	10.20680248	4.187464064	-4.368845348

H	9.324635611	5.710990489	-4.263630945
H	7.573148057	1.151332121	-0.255275844
H	7.38913652	2.726674249	0.505466884
H	8.957676887	2.250975964	-0.169448631
H	-0.437136263	3.593289093	-0.506324626
H	0.332176168	2.026556845	-0.766867462
H	1.288312569	3.49364377	-0.900108888
H	-0.865973339	3.367646705	5.365246978
H	-1.882865649	3.934132384	4.031367633
H	-0.633571965	4.984920623	4.702742251
H	3.616057108	1.797908821	4.57577645
H	4.453543331	2.441295083	3.145595559
H	3.780257403	0.81291251	3.11460672

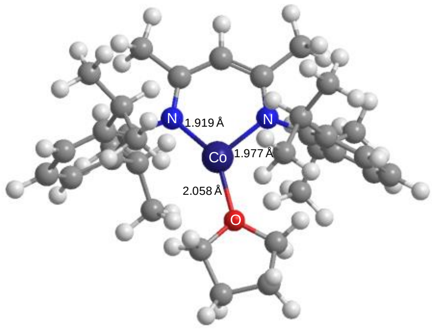
A2 ($E°_{BSI}$ = -1484.689735, $G°_{BSI}$ = -1484.12409; $E°_{THF(BSII)}$ = -1485.056847, $G°_{THF(BSII)}$ = -1484.491202; $E°_{BSII}$ = -1485.006556, $G°_{BSII}$ = -1484.440911; spin muliplicity=4)



F	4.134567314	4.680311063	-0.130911417
C	4.548250519	0.496623173	-1.822579282
C	3.462361341	-0.109739052	-1.167967182
C	2.659618375	0.391169709	-0.128909401
C	5.2469824	-0.306400206	-2.892830217
C	1.573193862	-0.511937912	0.402713571
C	6.115305848	2.276235637	-2.238583432
C	5.90236719	3.070757519	-3.387192788
C	7.013385907	3.649213477	-4.007319836
C	8.298154349	3.459782302	-3.513861565
C	8.48977935	2.687356384	-2.374724656
C	7.414066883	2.086510512	-1.715779933
C	1.971402205	2.04341549	1.480941365
C	0.80414758	2.784813759	1.191622615
C	0.036837344	3.255629987	2.260838427
C	0.404454453	3.012186158	3.578227117
C	1.563250753	2.293727582	3.846719534
C	2.366778736	1.800533734	2.815522774
C	4.510059543	3.345208476	-3.935482862
C	7.65932291	1.29928146	-0.437352644
C	0.387293389	3.1162826	-0.233459835
C	3.659305082	1.071772788	3.151166754
N	4.988239305	1.725881089	-1.544048797
N	2.812512114	1.604911649	0.405900326
Co	4.10188571	2.890952762	-0.267850697
C	4.389818596	3.009440439	-5.428092798
C	4.096652539	4.800634542	-3.664111945
C	8.745222462	0.227338446	-0.596606483
C	7.999351731	2.250213623	0.720677156
C	0.603289081	4.609049715	-0.529652577
C	-1.059213131	2.700838271	-0.533659549
C	4.715474276	2.063095699	3.663717968
C	3.456249573	-0.071857154	4.153359996
H	3.21701512	-1.109874742	-1.503865804
H	5.246001793	0.231982321	-3.845330456
H	4.765828961	-1.274856934	-3.035471539

H	6.296379114	-0.472365807	-2.630211414	H	3.078589709	4.982347125	-4.026877003
H	1.730645243	-0.725115683	1.464548357	H	8.828823085	-0.367413171	0.319310376
H	1.544965659	-1.456409357	-0.142206551	H	9.728880089	0.669004152	-0.788334024
H	0.59420353	-0.029699508	0.32392993	H	8.522829161	-0.455297399	-1.422962087
H	6.865903576	4.266455198	-4.889413507	H	8.933041261	2.788605156	0.524267961
H	9.147589174	3.920155507	-4.010778213	H	8.121237051	1.695222442	1.657383169
H	9.494618839	2.553889812	-1.983006949	H	7.215013729	3.000038849	0.866762174
H	-0.861809165	3.830836617	2.054951273	H	0.33794344	4.834486155	-1.568779925
H	-0.206022784	3.388796025	4.394247249	H	1.644582594	4.903628714	-0.368923539
H	1.855539494	2.118238693	4.878562685	H	-0.027021008	5.229855689	0.117113169
H	3.807972202	2.698179807	-3.39908703	H	-1.229352529	1.638981403	-0.327805421
H	6.72773156	0.786154496	-0.178001632	H	-1.29385614	2.882150047	-1.587980956
H	1.035658558	2.549452596	-0.909902465	H	-1.778056727	3.272930625	0.062656443
H	4.043977521	0.631830998	2.225483408	H	5.667275634	1.554762483	3.853309878
H	5.019033164	3.661672254	-6.043151352	H	4.391512521	2.531587015	4.59955662
H	3.356070273	3.143954329	-5.763945827	H	4.894602656	2.866509102	2.941746163
H	4.680956341	1.97497482	-5.637905265	H	4.393901939	-0.61841668	4.300614551
H	4.764261731	5.49821351	-4.1824686	H	2.701101291	-0.784754365	3.807216961
H	4.128270108	5.034337977	-2.595764755	H	3.13769865	0.297167005	5.134041242

B2 (E°$_{BSI}$ = -1617.20976, G°$_{BSI}$ = -1616.534604; E°$_{THF(BSII)}$ = -1617.58365, G°$_{THF(BSII)}$ = -1616.908494; E°$_{BSII}$ = -1617.555479, G°$_{BSII}$ = -1616.880323; spin muliplicity=3)

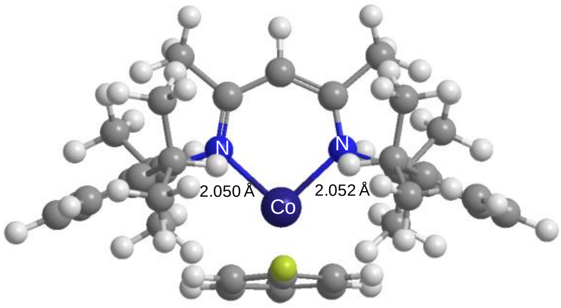


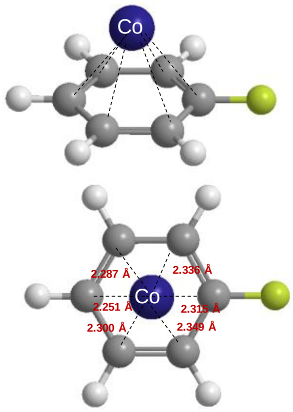
C	3.910608541	7.513950485	-0.079318837	H	3.197325895	8.33818558	-0.15990591
C	5.287962472	5.925878196	-1.183764446	H	4.514566502	7.67192925	0.820864489
C	4.810502827	7.364103457	-1.308683966	H	5.514024776	5.436794294	-2.132068216
C	3.218313144	6.1592492	-0.028040939	H	6.155562907	5.84110341	-0.521691824
O	4.178503101	5.21581146	-0.568104584	H	4.229804984	7.49822954	-2.227916005

H	5.641790214	8.073668911	-1.324339187	H	5.534638041	0.142608066	-3.433587915
H	2.950009746	5.830622197	0.979261588	H	5.459817343	-1.192635766	-2.26847876
H	2.322676733	6.135750114	-0.659453867	H	6.753628141	0.014039896	-2.178238023
C	4.827440466	0.716341254	-1.472051317	H	2.287016502	-0.309296401	2.163926643
C	3.955862641	0.026922102	-0.603857835	H	2.522736709	-1.497348691	0.866730138
C	3.016767537	0.531069718	0.30908392	H	1.13532323	-0.394848669	0.843396155
C	5.688060265	-0.131661087	-2.384795757	H	6.043483632	4.282618902	-5.386475912
C	2.200109327	-0.477994421	1.085738226	H	8.341426446	4.717399086	-4.580616861
C	5.861483379	2.660649813	-2.393689386	H	9.074316686	3.79917154	-2.406560229
C	5.448307582	3.156257543	-3.654245197	H	-1.461505165	3.199216629	1.584877834
C	6.356571313	3.895191826	-4.419582747	H	-0.805827035	3.771169805	3.897800169
C	7.650407693	4.139504963	-3.972831648	H	1.516994185	3.378067256	4.649794201
C	8.057481107	3.620684402	-2.747435722	H	3.539683326	2.25203292	-3.469389435
C	7.190291073	2.873742624	-1.946252958	H	6.940944367	1.591330892	-0.270202594
C	1.816267874	2.279978531	1.437504364	H	0.853003402	1.599641516	-0.884927295
C	0.482679732	2.486957491	1.008307994	H	4.163009607	1.8706142	2.463558948
C	-0.437943468	3.028808584	1.909741816	H	3.038691673	1.961892533	-5.865663808
C	-0.074026673	3.353102879	3.211776083	H	4.625835232	1.263485329	-5.505176089
C	1.233259408	3.130709668	3.629456301	H	4.510612903	2.824086165	-6.325097552
C	2.192358074	2.594640941	2.766030878	H	2.215998015	4.011815609	-4.620130179
C	4.044170738	2.908608707	-4.18524624	H	3.69450485	4.928972822	-4.94721259
C	7.673722812	2.32992085	-0.60817091	H	3.156071502	4.67905312	-3.275551688
C	0.044666357	2.166874921	-0.413422091	H	9.28284771	1.142492359	0.237680664
C	3.614986738	2.381120668	3.261120461	H	9.842199449	2.323251399	-0.94611203
N	4.918648533	2.045447305	-1.529229031	H	9.027230534	0.853461837	-1.491598097
N	2.806956578	1.83737923	0.513089194	H	8.071950056	3.025830397	1.418032361
Co	3.733630726	3.20923118	-0.457493224	H	6.724037959	3.853672335	0.625879622
C	4.059514686	2.199075337	-5.546199098	H	8.398534846	4.239012576	0.169016058
C	3.232433912	4.209063864	-4.261487304	H	-0.442851196	3.219462585	-2.26042675
C	9.031653201	1.623634176	-0.71376277	H	0.79223535	4.021382525	-1.275643546
C	7.719386709	3.429481735	0.462093408	H	-0.913877367	4.094038131	-0.791870624
C	-0.142525679	3.451844268	-1.232349457	H	-1.445094375	1.012252954	-1.49420158
C	-1.222919645	1.303856365	-0.461852521	H	-2.098464571	1.840430489	-0.079924284
C	4.321189661	3.720674005	3.51326141	H	-1.112026648	0.39021072	0.130663446
C	3.669689921	1.495920031	4.513457632	H	5.35254672	3.560028089	3.846976903
H	4.001537081	-1.054431011	-0.66838169	H	3.806178211	4.304952975	4.28457239

H	4.353927718	4.32119297	2.598231271
H	4.709498073	1.297278719	4.795950786
H	3.176172489	0.533236019	4.347422616
H	3.182400948	1.972925608	5.371178556

C2 (E°$_{BSI}$ = -1716.192097, G°$_{BSI}$ = -1715.536292; E°$_{THF(BSII)}$ = -1716.598607, G°$_{THF(BSII)}$ = -1715.942802; E°$_{BSII}$ = -1716.57194, G°$_{BSII}$ = -1715.916135; spin muliplicity=3)

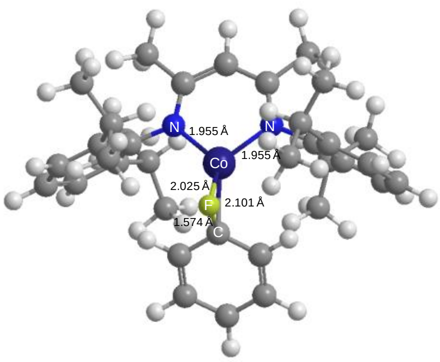




Co	22.95276409	51.05267029	9.160244286
C	25.58841446	52.03045666	7.409251721
C	25.14853522	54.44502173	7.338637992
C	22.75048826	54.00525844	8.733055185
C	21.62041048	54.25901762	7.911241378
C	26.2272991	48.9270284	10.5159731
C	26.72928882	49.86988296	7.167373039
C	24.70238997	53.05779784	7.765657175
C	20.76454334	55.31049663	8.25109842
C	24.53292141	45.87379962	8.990249553
C	22.11268082	55.85764907	10.15955887
C	23.85150932	47.80181229	7.67199982
C	21.3560201	53.42614551	6.662089573
C	25.27978741	46.7020077	9.817424688
N	23.57276807	52.87596039	8.450842225
C	20.99611688	56.10239369	9.371332468
C	24.60413166	48.64308615	8.533660838
C	25.33992643	48.08438759	9.606972589
N	24.54802132	50.05479609	8.346109708
C	23.09988336	48.37567346	6.476376323
C	25.53292334	50.65455361	7.675924852
C	23.00816183	54.82482814	9.859028364
C	23.83485202	46.42661247	7.921219326
C	24.2458973	54.65000297	10.73163224
C	25.7592273	48.91729995	11.97806839
C	27.69359549	48.46999784	10.44663663
C	19.86981164	53.27246411	6.317691772
C	22.10043109	53.98957642	5.440621217
C	24.00354475	48.47432326	5.236596708
C	21.82735508	47.6029543	6.109850058
C	23.9039401	54.27181184	12.17968879
C	25.11652808	55.91715471	10.72783364
H	26.46090981	52.35280617	6.850147064
H	24.32840718	55.16280073	7.304268081
H	25.62584507	54.40553961	6.356018063
H	25.89626495	54.82618196	8.042927583
H	26.17468885	49.96143032	10.16270989
H	27.56953933	49.98592667	7.860836207
H	27.05686531	50.25987914	6.200147333
H	26.52595792	48.80326647	7.067668949

H	19.89802339	55.5148336	7.62909547
H	24.50214863	44.80243287	9.168942261
H	22.3025504	56.48849218	11.02484738
H	21.76201458	52.42614334	6.857037964
H	25.8396711	46.26682292	10.64196889
H	20.31485138	56.91147845	9.62024089
H	22.80792802	49.39745053	6.747784769
H	23.2639334	45.77348106	7.267797072
H	24.83463878	53.82974868	10.30960748
H	26.43297106	49.51830192	12.59893265
H	25.74879964	47.90184309	12.38975675
H	24.75442224	49.33337222	12.08240938
H	28.33670619	49.15743616	11.00730818
H	28.05872741	48.42463487	9.417265715
H	27.82018817	47.47300794	10.88320767
H	19.75190118	52.54548936	5.50789309
H	19.4306733	54.2137681	5.968705623
H	19.27404868	52.9202729	7.164886957
H	23.18145633	53.99765886	5.590752217
H	21.77827932	55.01577126	5.22937129
H	21.89223333	53.38150194	4.553067653
H	24.37591323	47.48451374	4.948278594
H	24.86406315	49.12284702	5.410156579
H	23.44385636	48.88401896	4.388211068
H	22.05389181	46.61726068	5.688208957
H	21.26688692	48.15475728	5.348569292
H	21.16178675	47.45521623	6.965277419
H	24.81855051	54.1752114	12.77530563
H	23.37261587	53.31865926	12.23334892
H	23.27831995	55.03436499	12.65701167
H	26.05844858	55.73707124	11.25780458
H	24.6106625	56.74838768	11.23158607
H	25.35399388	56.24618803	9.712798406
C	20.71319124	51.55600229	9.595844403
C	20.77076797	50.29933055	8.978937255
F	20.04621025	50.0885172	7.867194007
C	21.50677013	49.23621649	9.518718751
C	22.26612738	49.46531561	10.67689201
C	22.2757002	50.73712496	11.28394549
C	21.47768738	51.77096503	10.75394853
H	20.12655266	52.35336644	9.159478089
H	21.52258123	48.27487056	9.022790928
H	22.87511813	48.66119818	11.07164349
H	22.87733118	50.9133952	12.16862469
H	21.47400826	52.75390495	11.20890068

D2-TS ($E°_{BSI}$ = -1716.165681, $G°_{BSI}$ = -1715.516003; $E°_{THF(BSII)}$ = -1716.575293, $G°_{THF(BSII)}$ = -1715.925616; $E°_{BSII}$ = -1716.541606, $G°_{BSII}$ = -1715.891928; the only imaginary frequency = -291.2949 cm^{-1}; spin muliplicity=3)

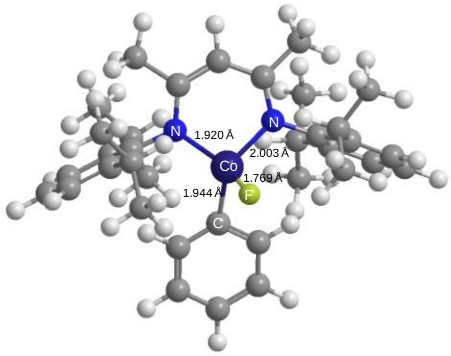


C	4.772135201	7.01446883	-0.960704292
C	5.247935562	5.789763141	-0.511183753

C	4.476748032	5.074174755	0.429856622	C	3.148172057	0.338338119	4.231161973
C	3.368920963	5.675467985	1.065152302	H	5.329153711	7.546394211	-1.727434165
C	2.921392268	6.901887723	0.591927911	H	6.16562334	5.36227438	-0.902830593
C	3.60657596	7.575437986	-0.425897163	H	2.857433655	5.161184703	1.872720474
F	5.351035951	4.205184683	1.409372937	H	2.034627448	7.345932897	1.036398423
C	4.722829984	0.716743677	-1.579688226	H	3.257088319	8.542776759	-0.772357699
C	3.654600134	0.091927979	-0.910446742	H	3.454800821	-0.926802922	-1.222364516
C	2.766790821	0.599809086	0.055403199	H	5.216150403	-1.160543752	-2.517638394
C	5.396941296	-0.093967997	-2.66364052	H	6.473973562	0.084831402	-2.691416284
C	1.641567732	-0.317919245	0.477460044	H	5.001191208	0.179803837	-3.64770395
C	6.198850448	2.544836413	-2.087255126	H	0.720234107	-0.064864674	-0.058251724
C	5.917783808	3.166363004	-3.327750042	H	1.425226518	-0.226929576	1.544144605
C	6.956226119	3.821427177	-3.995534452	H	1.884113123	-1.357655946	0.250336158
C	8.243170885	3.864309896	-3.472432627	H	6.750391082	4.308870704	-4.94510198
C	8.509686309	3.23886005	-2.260637197	H	9.035667014	4.378427372	-4.009318825
C	7.507063943	2.574316854	-1.547562817	H	9.519020787	3.262502328	-1.857840962
C	1.882140344	2.286284276	1.521911837	H	-1.146980803	3.831942699	1.658043635
C	0.667909985	2.84981584	1.061298	H	-0.629419667	3.798158519	4.073309338
C	-0.215141165	3.389371795	2.00068407	H	1.480151765	2.783692507	4.86589456
C	0.072311983	3.373927409	3.360419925	H	3.893085308	2.509876384	-3.334332393
C	1.261284304	2.806050237	3.801404489	H	6.927706295	1.501261908	0.193682298
C	2.183370832	2.257415891	2.904675851	H	1.056622283	2.331775511	-0.96646555
C	4.526517268	3.159299781	-3.946241244	H	4.072790679	1.337672957	2.582936179
C	7.859624123	1.87992629	-0.239337757	H	5.075113918	3.253338154	-6.064254327
C	0.303632788	2.904058854	-0.416102113	H	3.507107073	2.506976197	-5.752278056
C	3.457091429	1.620657507	3.443313262	H	5.000474283	1.609710784	-5.426312603
N	5.141469565	1.957834552	-1.326087438	H	4.480653631	5.261841889	-4.532389594
N	2.855120695	1.82150593	0.584295889	H	3.840886567	4.959882537	-2.912457316
Co	4.347131282	2.998613325	0.126336016	H	2.881855397	4.528452612	-4.341170752
C	4.531672141	2.5973485	-5.375505367	H	8.989096956	0.156513085	0.462981956
C	3.896126051	4.559001542	-3.927692397	H	9.738766623	0.985456771	-0.908745333
C	8.779851968	0.673398394	-0.48004545	H	8.329533994	-0.049813557	-1.166692939
C	8.487476495	2.841072953	0.779219347	H	9.443628648	3.239706169	0.422592838
C	0.344612505	4.342406292	-0.951151877	H	8.682654537	2.318490124	1.722115233
C	-1.06590008	2.269393867	-0.698856865	H	7.825698924	3.683956554	0.99274904
C	4.277722892	2.594093589	4.300307879	H	0.116371728	4.360188344	-2.022716175

H	1.327353127	4.796798078	-0.802030887	H	3.732261898	2.899240164	5.200131515
H	-0.394525918	4.972230543	-0.442926663	H	4.540742652	3.494501931	3.739913921
H	-1.135409172	1.25100496	-0.303971733	H	4.075346698	-0.133845954	4.57416138
H	-1.250542507	2.228714336	-1.777777325	H	2.605088712	-0.391071192	3.622618152
H	-1.879647496	2.850275525	-0.251187277	H	2.537231106	0.553701343	5.114946683
H	5.208062788	2.117454453	4.628183536				

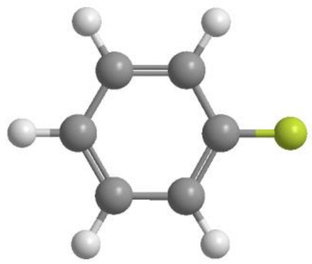
E2 (E°$_{BSI}$ = -1716.20395, G°$_{BSI}$ = -1715.550958; E°$_{THF(BSII)}$ = -1716.616099, G°$_{THF(BSII)}$ = -1715.963106; E°$_{BSII}$ = -1716.581138, G°$_{BSII}$ = -1715.928145; spin muliplicity=3)



C	5.157182124	6.892865829	-1.259055899	C	7.405991898	2.706877574	-1.816004415
C	5.303336445	5.51251511	-1.08411051	C	1.974995303	2.325875017	1.578426102
C	4.403544214	4.830361182	-0.272032254	C	0.856806036	2.994520012	1.018325439
C	3.391337586	5.515232735	0.40160082	C	-0.098101727	3.529793313	1.886381834
C	3.251980775	6.893021392	0.21580117	C	0.041163854	3.42865522	3.266077978
C	4.132388142	7.581983613	-0.616371126	C	1.146528558	2.778878432	3.797300766
F	5.286848582	3.386705134	1.815362544	C	2.13055414	2.214822982	2.977895948
C	4.762011297	0.691675551	-1.453749336	C	4.160536158	2.871420038	-3.931732355
C	3.777596622	0.035795856	-0.717549942	C	7.937609142	2.212530863	-0.477681422
C	2.896562245	0.560698261	0.252482843	C	0.659983563	3.106064685	-0.489012284
C	5.46493868	-0.126841162	-2.512261262	C	3.298307801	1.487685376	3.628936383
C	1.875486219	-0.410688606	0.79985951	N	5.125391464	1.978543135	-1.279978824
C	6.054610618	2.553140626	-2.205091445	N	2.970777859	1.810328124	0.684375713
C	5.606110832	3.007819451	-3.469292477	Co	4.550504007	2.967031087	0.262896961
C	6.529493789	3.627931042	-4.315324179	C	4.050002049	2.171527899	-5.295144203
C	7.858439244	3.793811565	-3.943420763	C	3.455181789	4.234929946	-3.987367915
C	8.286737569	3.330750935	-2.705957161	C	9.005428731	1.124180453	-0.664096528

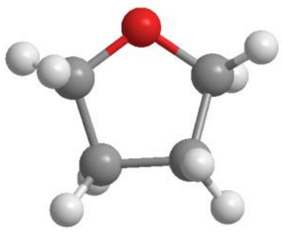
C	8.479989786	3.364193068	0.380413932
C	0.115204472	4.469033912	-0.932712835
C	-0.253808612	1.987280157	-1.015291694
C	4.113176119	2.414878644	4.541036198
C	2.819417494	0.254541607	4.411525222
H	5.856781383	7.423397207	-1.899932485
H	6.113574867	4.99699602	-1.587544147
H	2.716165298	4.996516416	1.075928045
H	2.459469412	7.4236516	0.737459829
H	4.026206565	8.654588768	-0.753644444
H	3.630119228	-1.010203399	-0.960148746
H	5.175289245	0.194109069	-3.51653739
H	5.215286119	-1.183693317	-2.407340432
H	6.549544735	-0.009537647	-2.444799789
H	2.360580016	-1.064897316	1.532999679
H	1.486670472	-1.049961404	0.003222971
H	1.045543896	0.092060752	1.296046536
H	6.197990898	3.992992735	-5.2837086
H	8.557921495	4.280709054	-4.617376858
H	9.327490266	3.455301277	-2.419016172
H	-0.965413082	4.037285278	1.474579935
H	-0.711102165	3.855541884	3.923720552
H	1.25258473	2.700995577	4.87600701
H	3.627318034	2.259397664	-3.19775564
H	7.104210371	1.762907609	0.070812512
H	1.643721756	2.980268917	-0.954377766
H	3.968024809	1.148438792	2.833040093
H	4.473765268	2.784778537	-6.097618137
H	2.998383895	1.99310628	-5.543391435
H	4.568140713	1.207605835	-5.313160257
H	3.943525834	4.900199935	-4.708331579
H	3.464295951	4.731247058	-3.014811721
H	2.413287299	4.110747366	-4.303037581
H	9.332265049	0.743495159	0.309401283
H	9.889655287	1.513275264	-1.180867818
H	8.627987846	0.277503188	-1.246428191
H	9.33090993	3.856962318	-0.103415502
H	8.820783482	2.984311518	1.34901345
H	7.709863176	4.114951556	0.573222852
H	0.110782965	4.527288776	-2.026127525
H	0.728313552	5.291795714	-0.556901304
H	-0.916283749	4.628616095	-0.599953102
H	0.144935001	0.993546754	-0.797457234
H	-0.374924924	2.069253467	-2.10118322
H	-1.248616123	2.054285474	-0.560285034
H	4.9568107	1.86599662	4.974229983
H	3.507033075	2.795156479	5.371174062
H	4.51237644	3.256289525	3.973230404
H	3.676620006	-0.303488406	4.803788415
H	2.226923689	-0.424685499	3.791345876
H	2.197445423	0.544188397	5.265883086

Fluorobenezene ($E°_{BSI}$ = -331.3647235, $G°_{BSI}$ = -331.300834; $E°_{THF}$ = -331.4679556, $G°_{THF}$ = -331.4040661; $E°_{BSII}$ = -331.460261, $G°_{BSII}$ = -331.3963715)



F	0.008130824	0.00153074	-2.276032325	C	-1.215321699	-0.001009933	-0.264678324
C	0.002929947	0.00118406	-0.931029027	H	2.142891577	0.003342058	-0.821558399
C	1.216864538	0.001522104	-0.256442131	H	2.143289903	0.001089824	1.680569679
C	1.202795039	0.000368672	1.137124714	H	-0.010023474	-0.002067783	2.917861785
C	-0.006294517	-0.001463263	1.83212849	H	-2.154623581	-0.003850349	1.666117917
C	-1.210466761	-0.002380214	1.129041921	H	-2.137751122	-0.001618967	-0.835573919

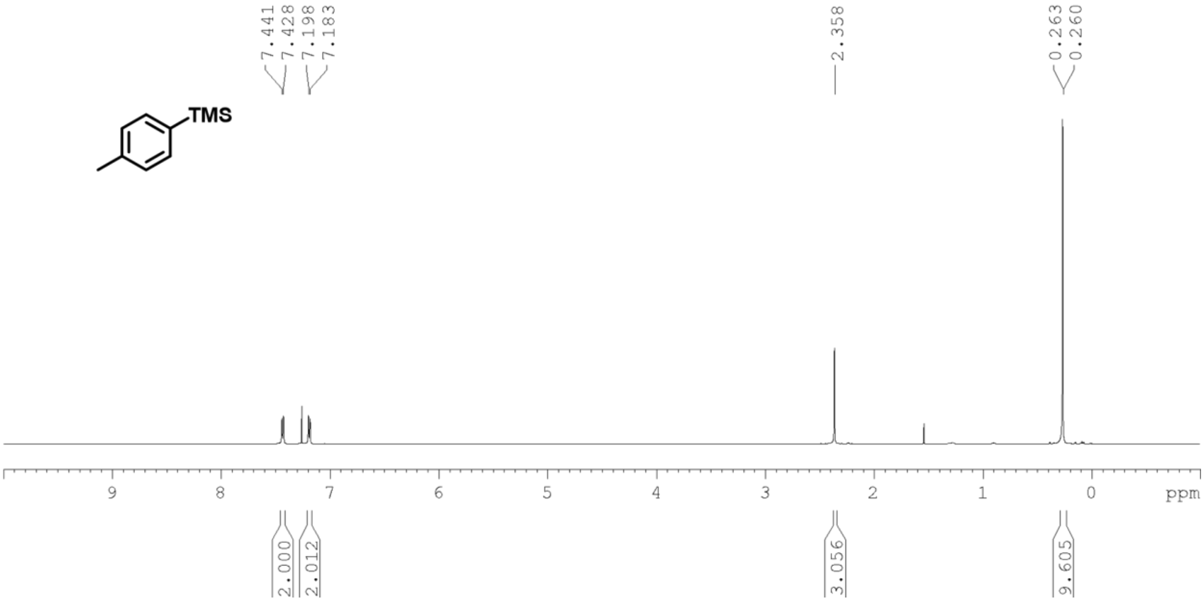
THF ($E°_{BSI}$ = -232.3763006, $G°_{BSI}$ = -232.287711; $E°_{THF}$ = -232.4457172, $G°_{THF}$ = -232.3571276; $E°_{BSII}$ = -232.4393032, $G°_{BSII}$ = -232.3507136)



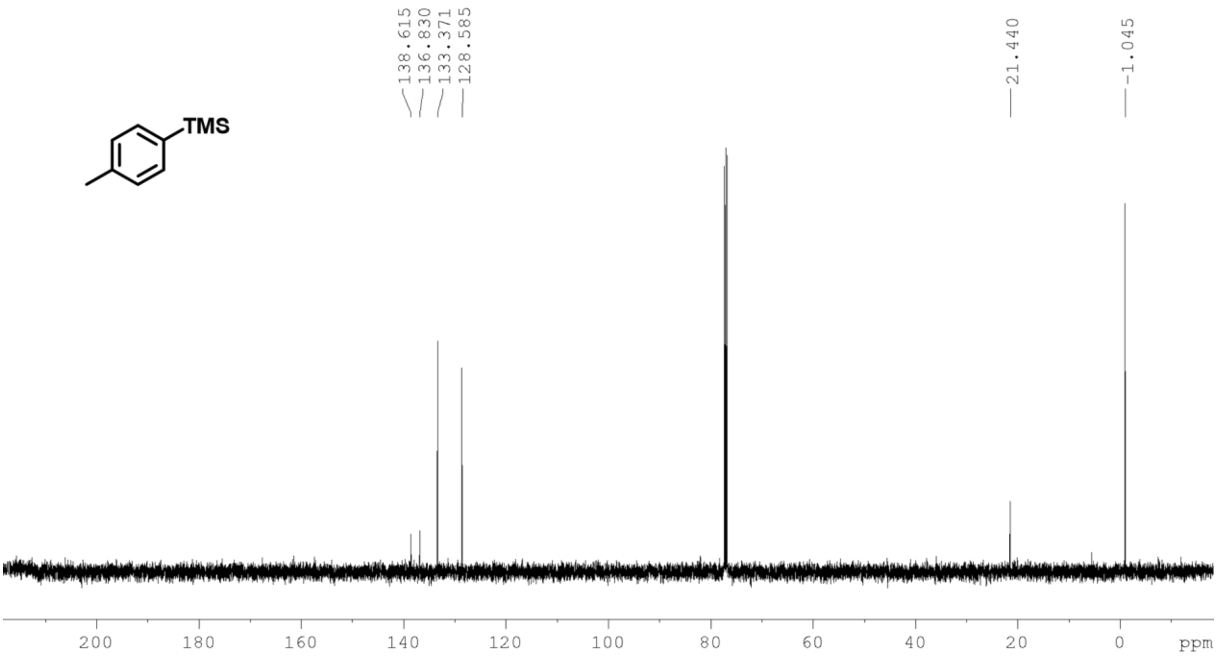
C	-6.908589263	-0.155755014	-0.264273481
C	-7.538451157	-0.161527204	1.127979555
C	-9.009478203	-0.415751323	0.792473804
C	-9.166575886	0.385289126	-0.499378055
O	-7.901506108	0.346963737	-1.154413757
H	-6.620480181	-1.173849128	-0.569658223
H	-6.017779117	0.479733825	-0.331415479
H	-7.42138028	0.817994682	1.605621908
H	-7.102128938	-0.915410129	1.789243947
H	-9.700583539	-0.096664079	1.577674684
H	-9.177687117	-1.482431384	0.604784291
H	-9.438849655	1.430263895	-0.283320609
H	-9.927020556	-0.027606005	-1.172527584

6. ^{1}H and ^{13}C NMR spectra

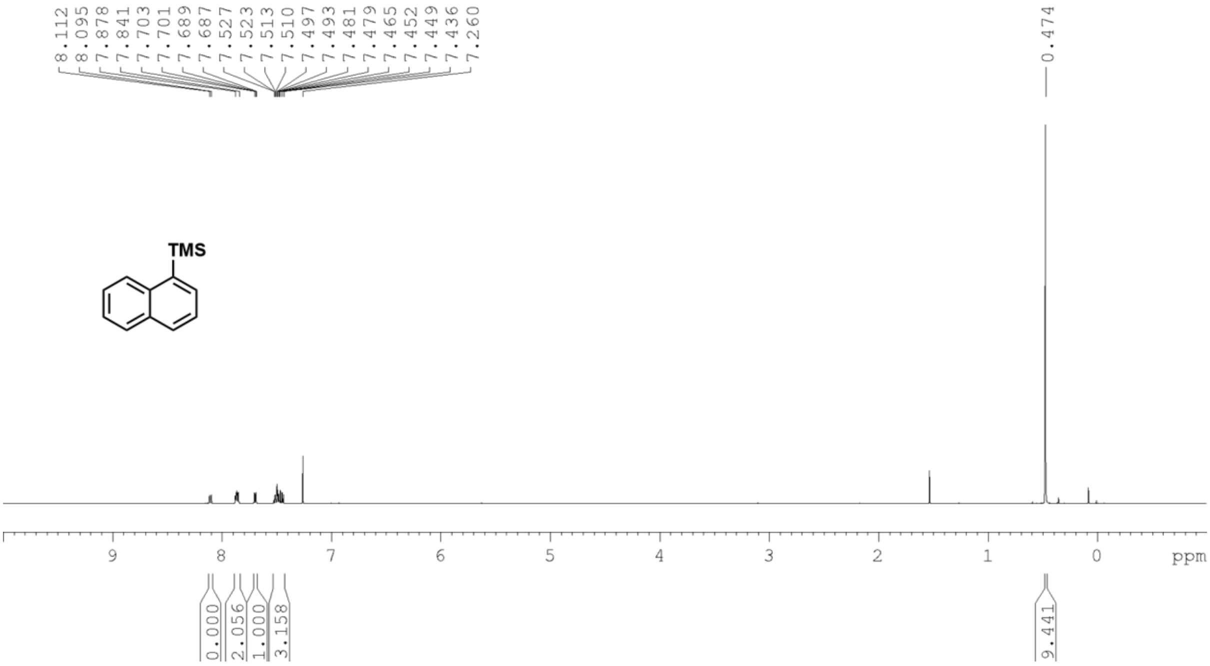
^{1}H NMR (500 Hz, $CDCl_3$) spectrum of **2a**



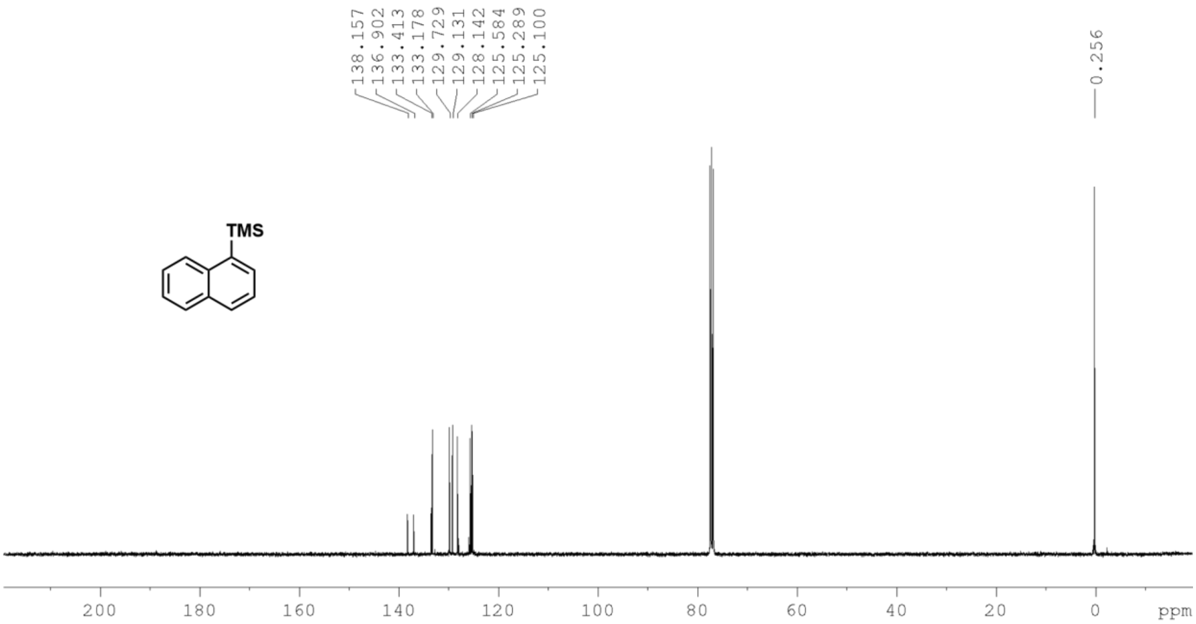
^{13}C NMR (126 Hz, $CDCl_3$) spectrum of **2a**



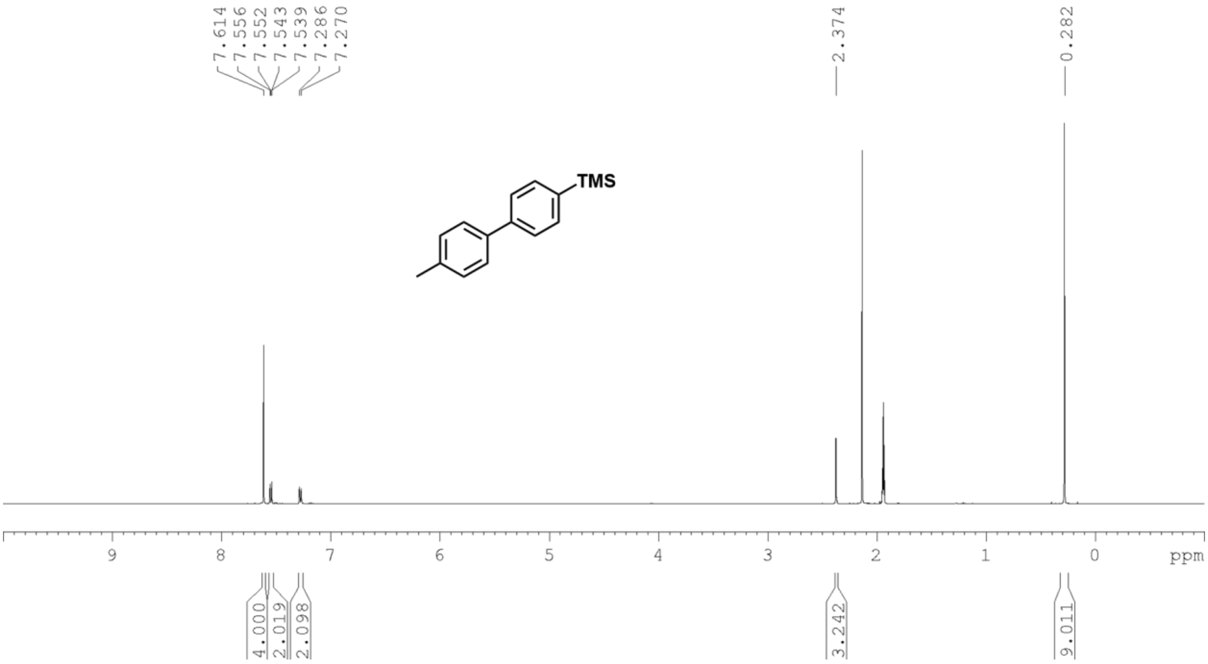
^{1}H NMR (500 Hz, $CDCl_3$) spectrum of **2b**



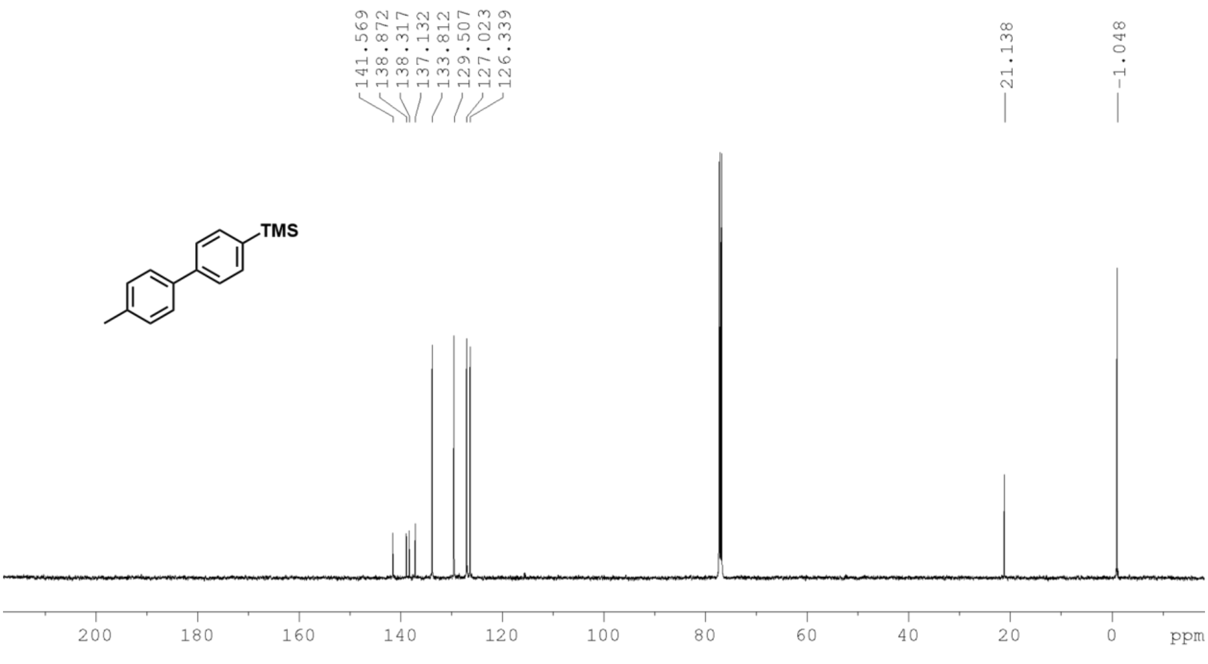
^{13}C NMR (126 Hz, $CDCl_3$) spectrum of **2b**



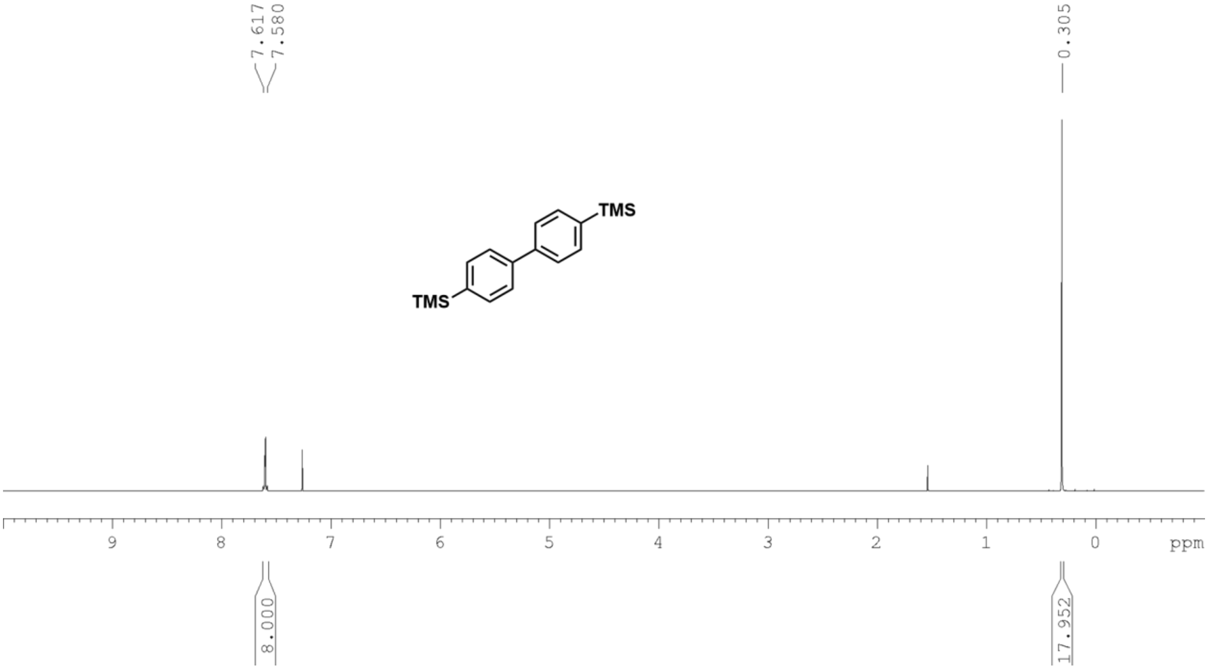
^{1}H NMR (500 Hz, CD_3CN) spectrum of **2c**



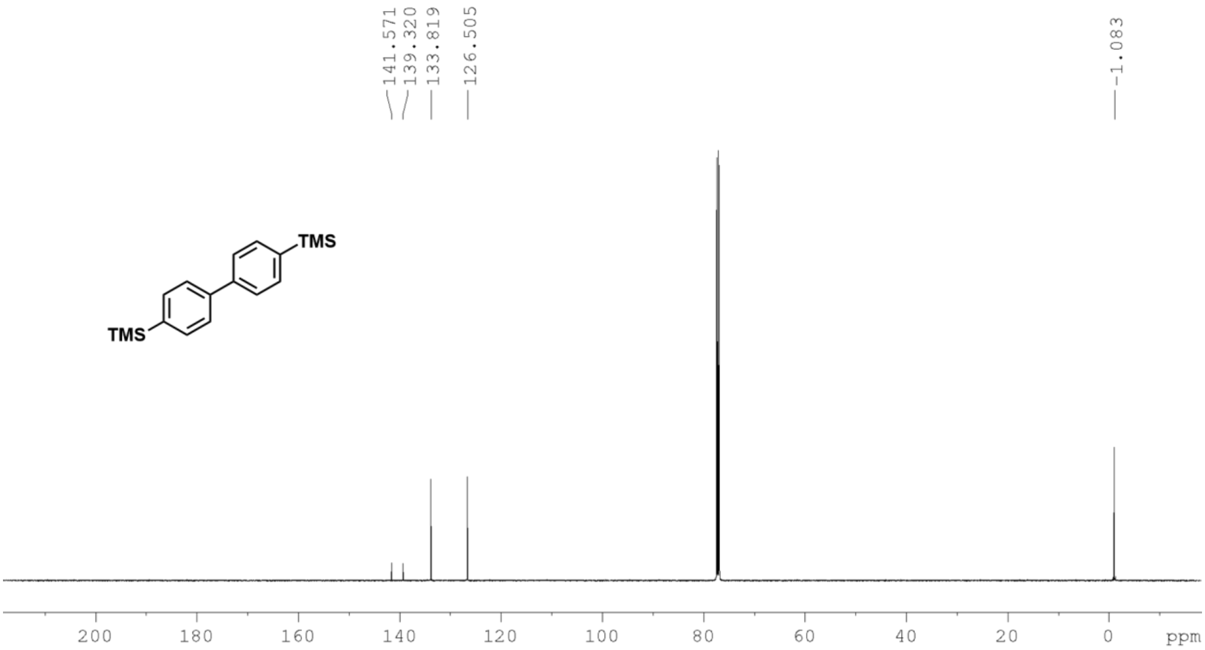
^{13}C NMR (126 Hz, $CDCl_3$) spectrum of **2c**



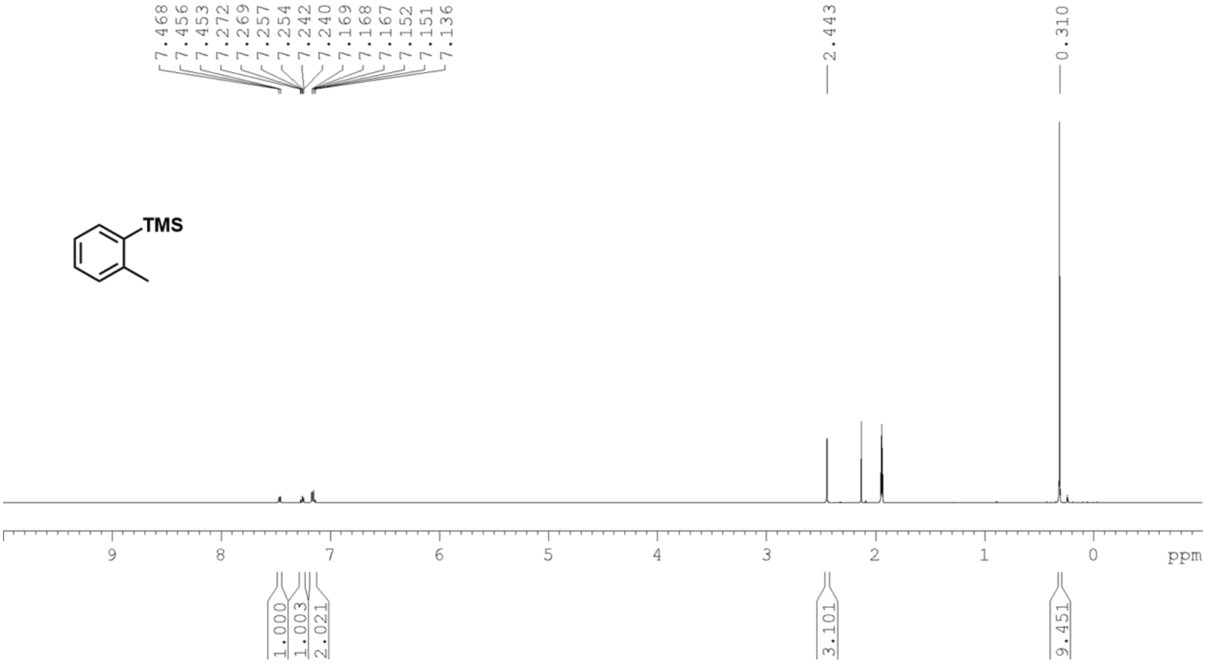
^{1}H NMR (500 Hz, $CDCl_3$) spectrum of **2d**



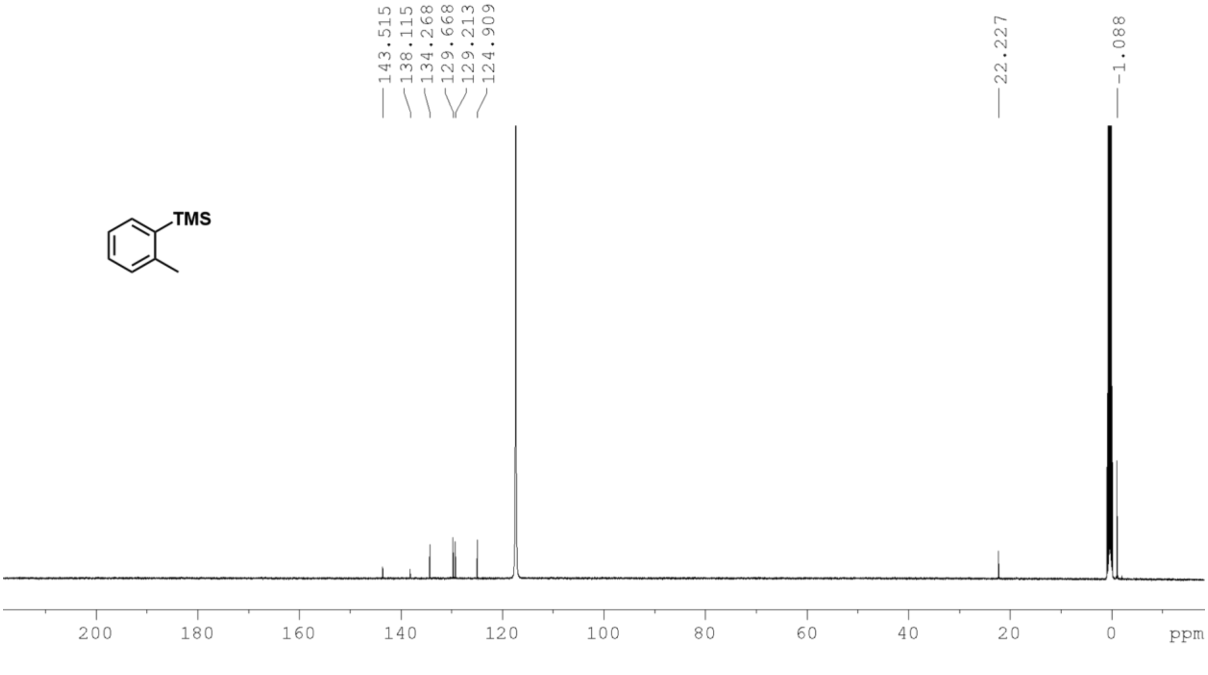
^{13}C NMR (126 Hz, $CDCl_3$) spectrum of **2d**



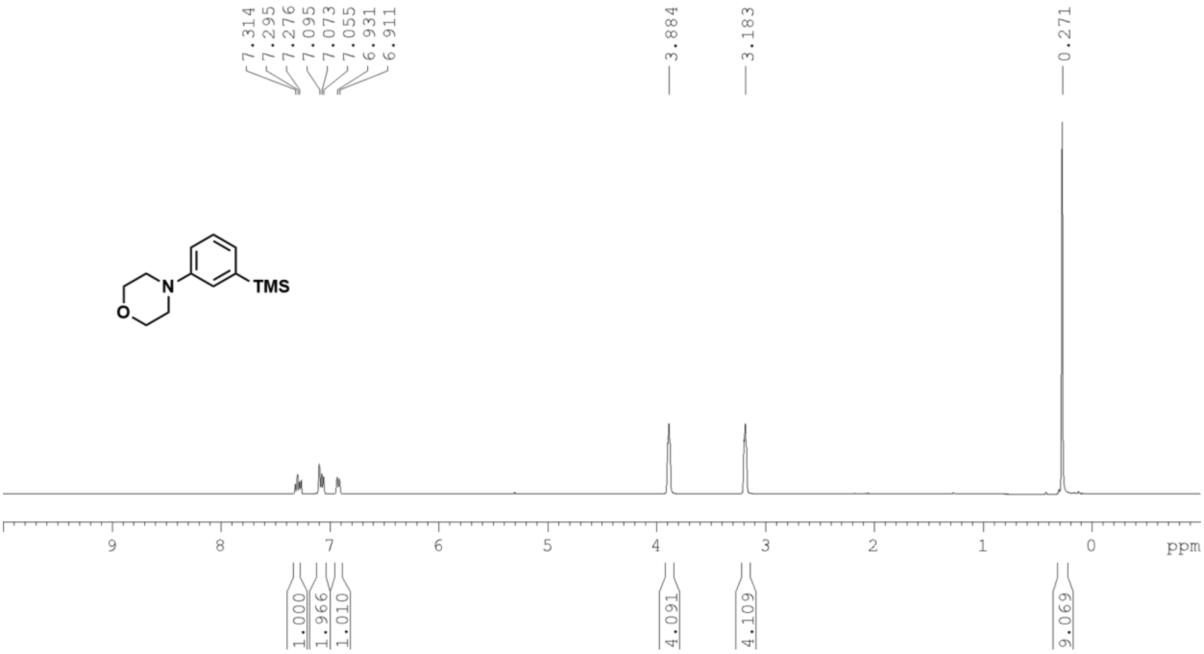
^{1}H NMR (500 Hz, CD_3CN) spectrum of **2e**



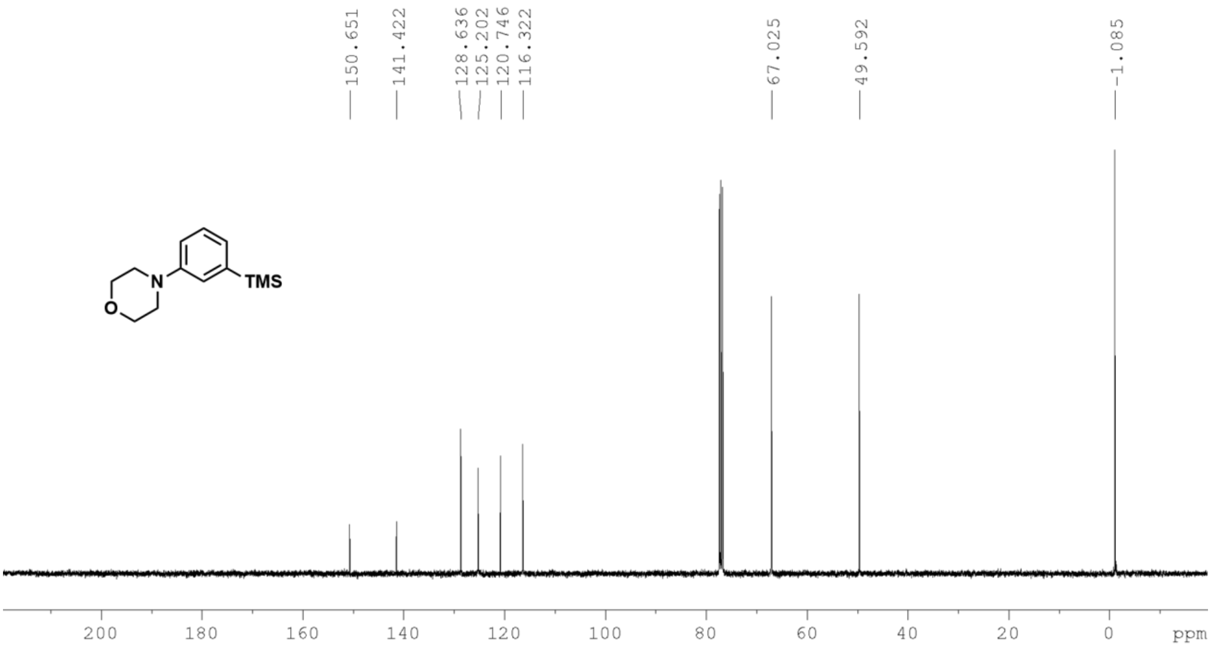
^{13}C NMR (126 Hz, CD_3CN) spectrum of **2e**



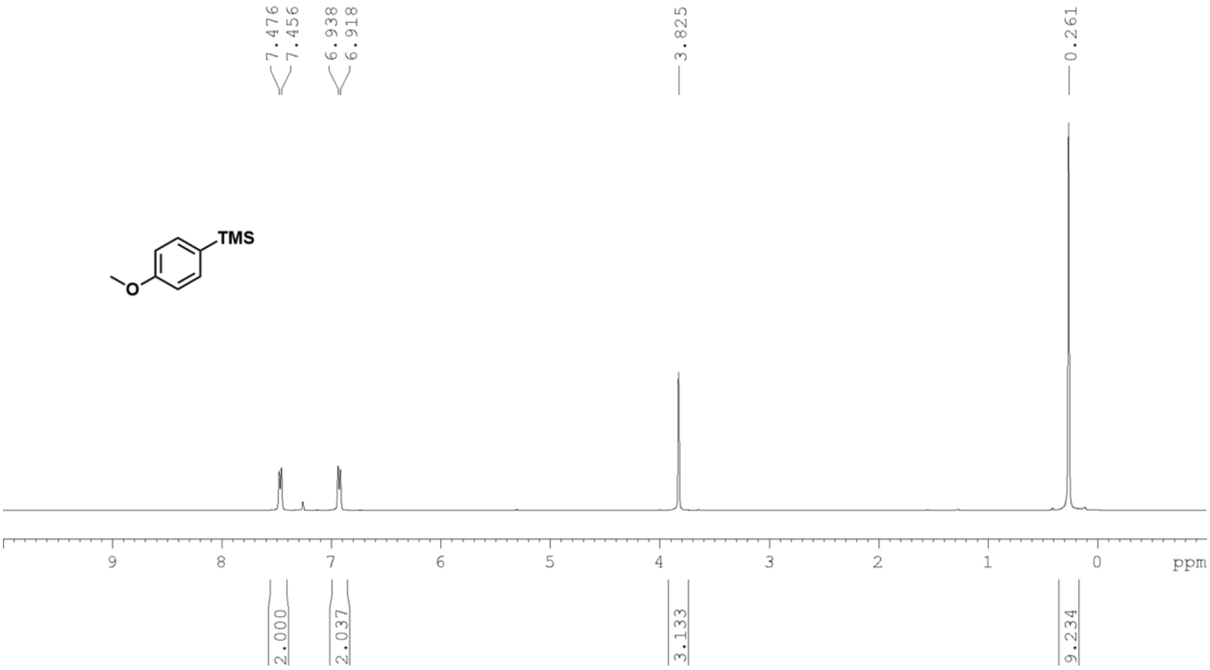
[1]H NMR (500 Hz, $CDCl_3$) spectrum of **2f**



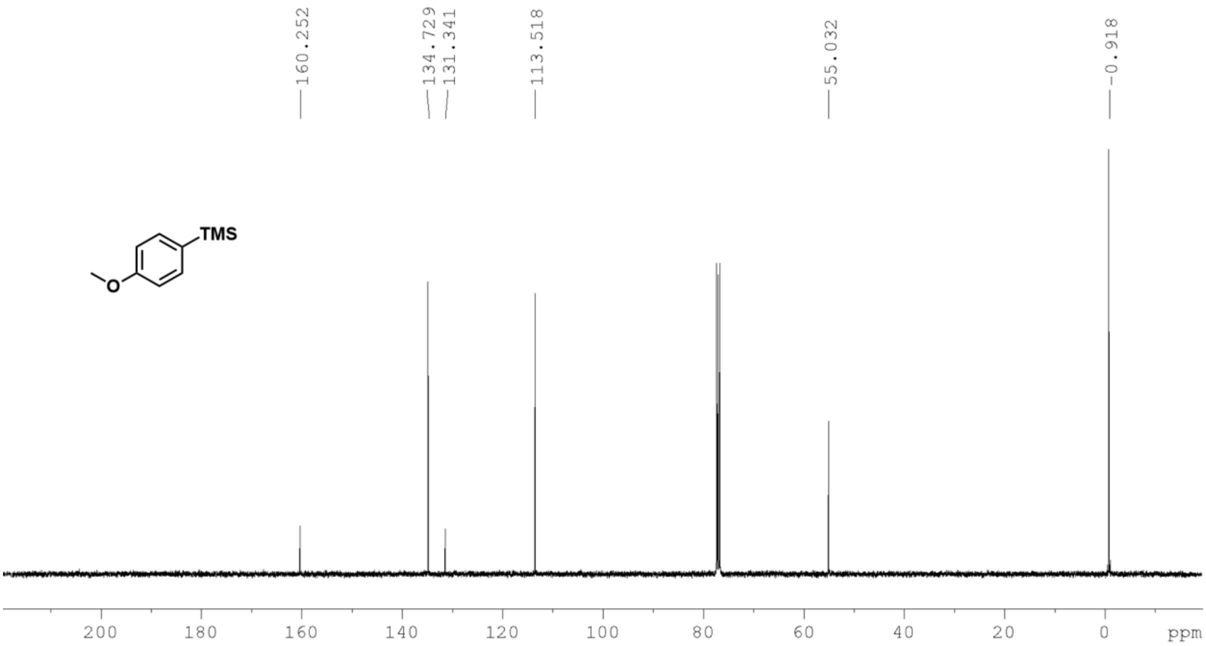
[13]C NMR (126 Hz, $CDCl_3$) spectrum of **2f**



[1]H NMR (500 Hz, $CDCl_3$) spectrum of **2g**

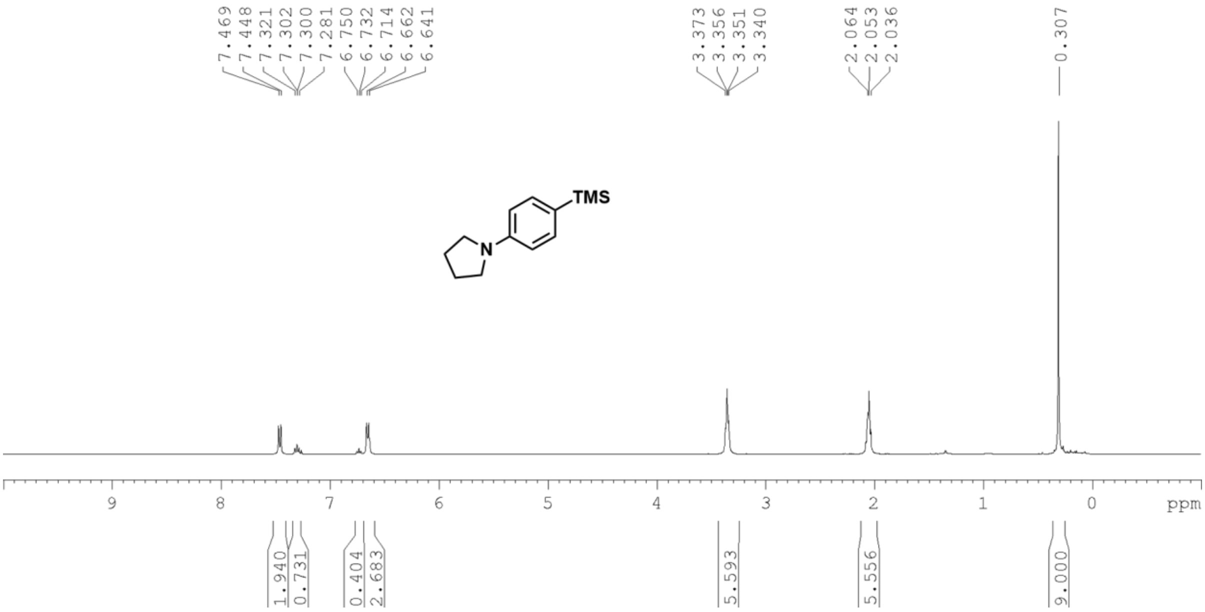


[13]C NMR (126 Hz, $CDCl_3$) spectrum of **2g**



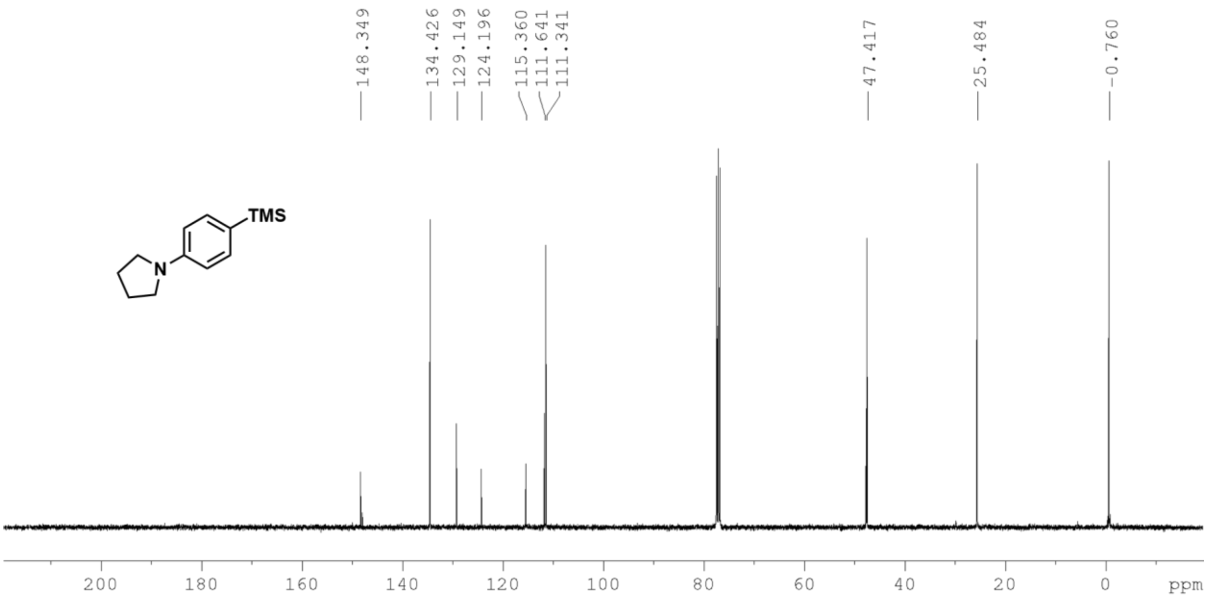
[1]H NMR (500 Hz, $CDCl_3$) spectrum of **2h**

(mixture of 1-(4-(trimethylsilyl)phenyl)pyrrolidine and 1-phenylpyrrolidine)

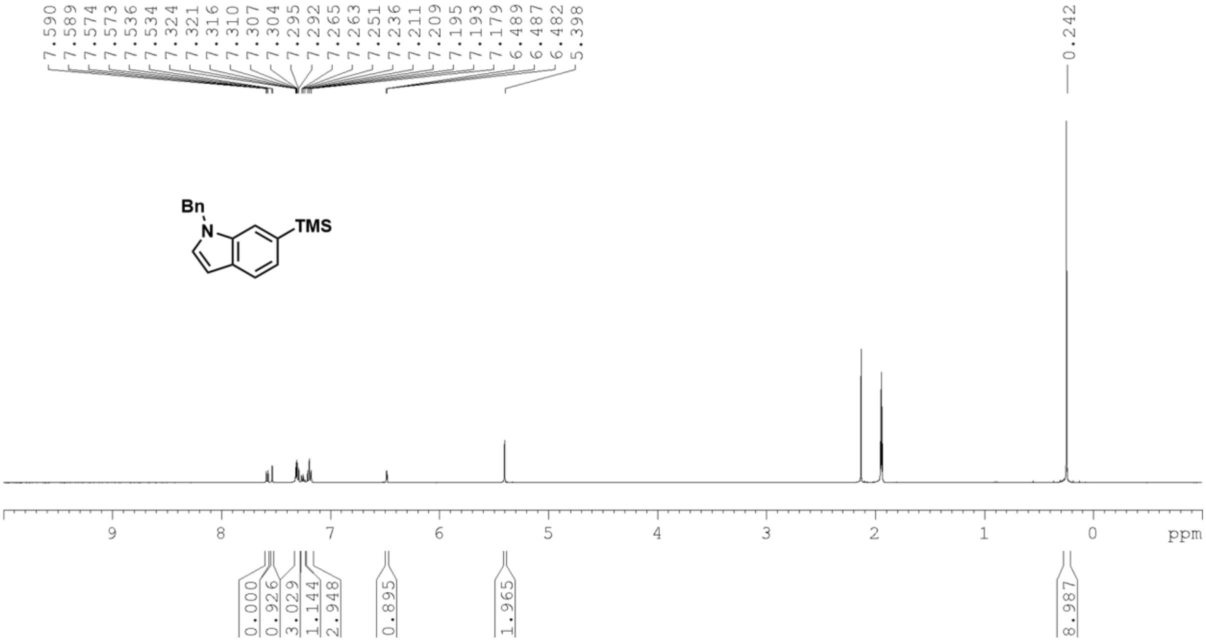


[13]C NMR (126 Hz, $CDCl_3$) spectrum of **2h**

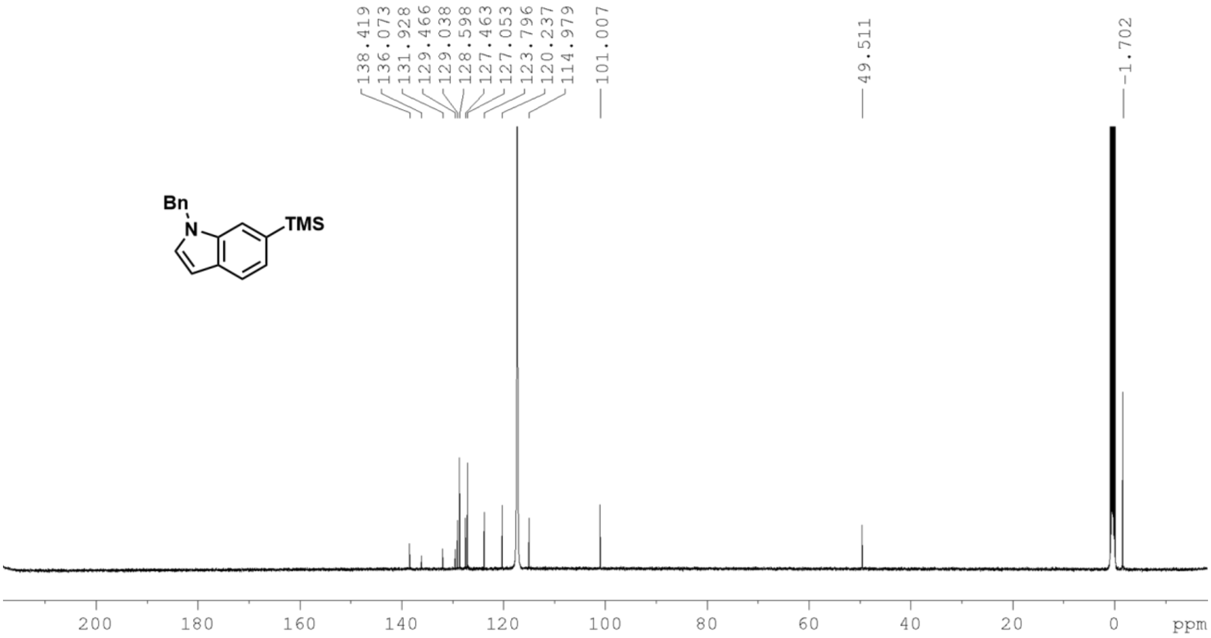
(mixture of 1-(4-(trimethylsilyl)phenyl)pyrrolidine and 1-phenylpyrrolidine)



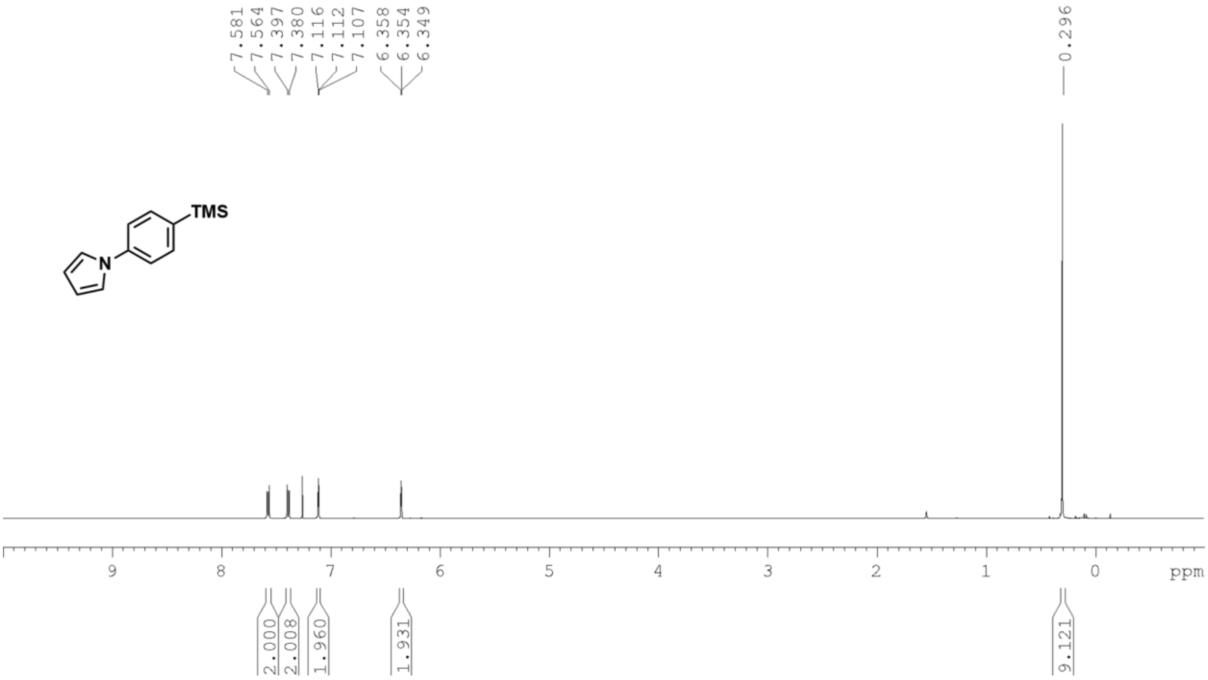
^{1}H NMR (500 Hz, CD_3CN) spectrum of **2i**



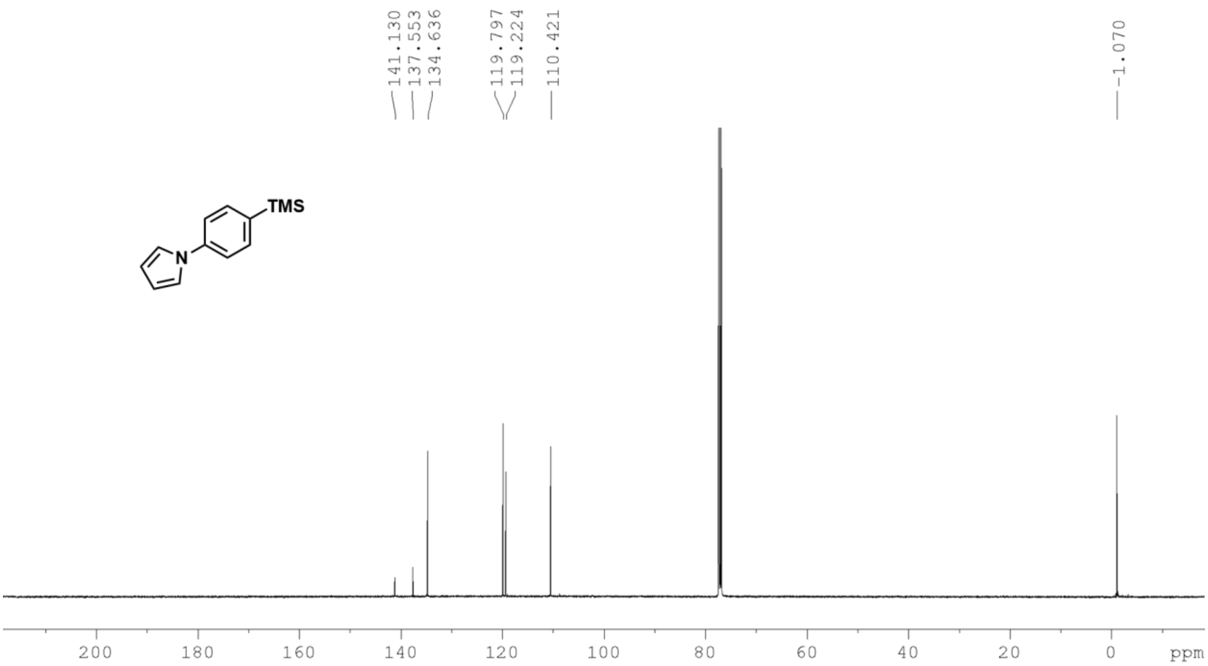
^{13}C NMR (126 Hz, CD_3CN) spectrum of **2i**



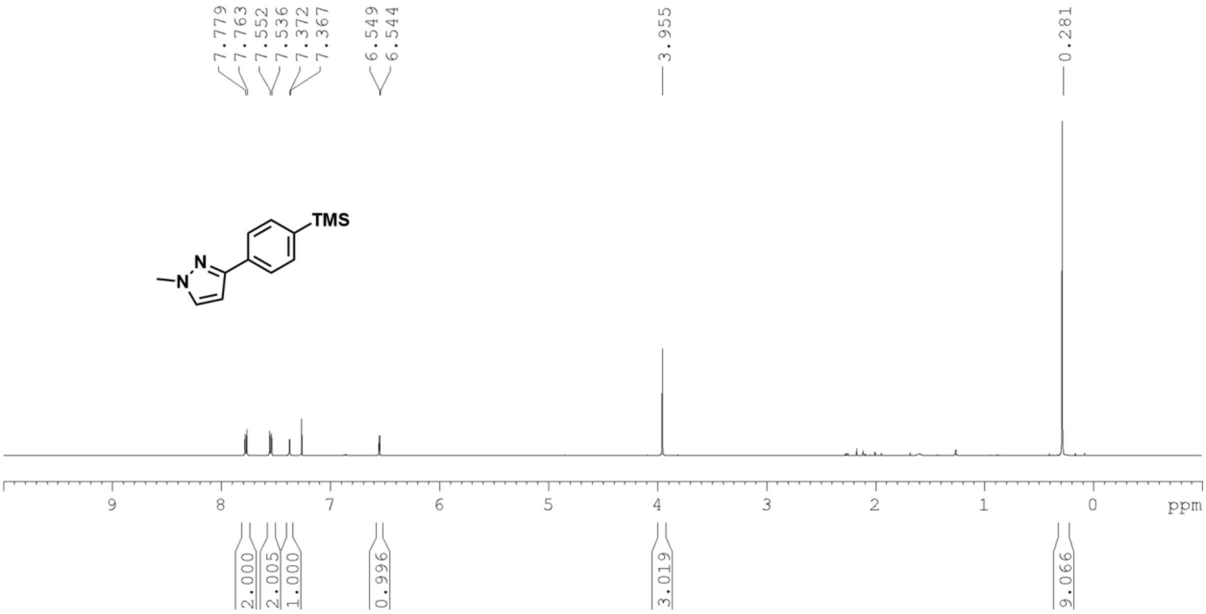
[1]H NMR (500 Hz, $CDCl_3$) spectrum of **2j**



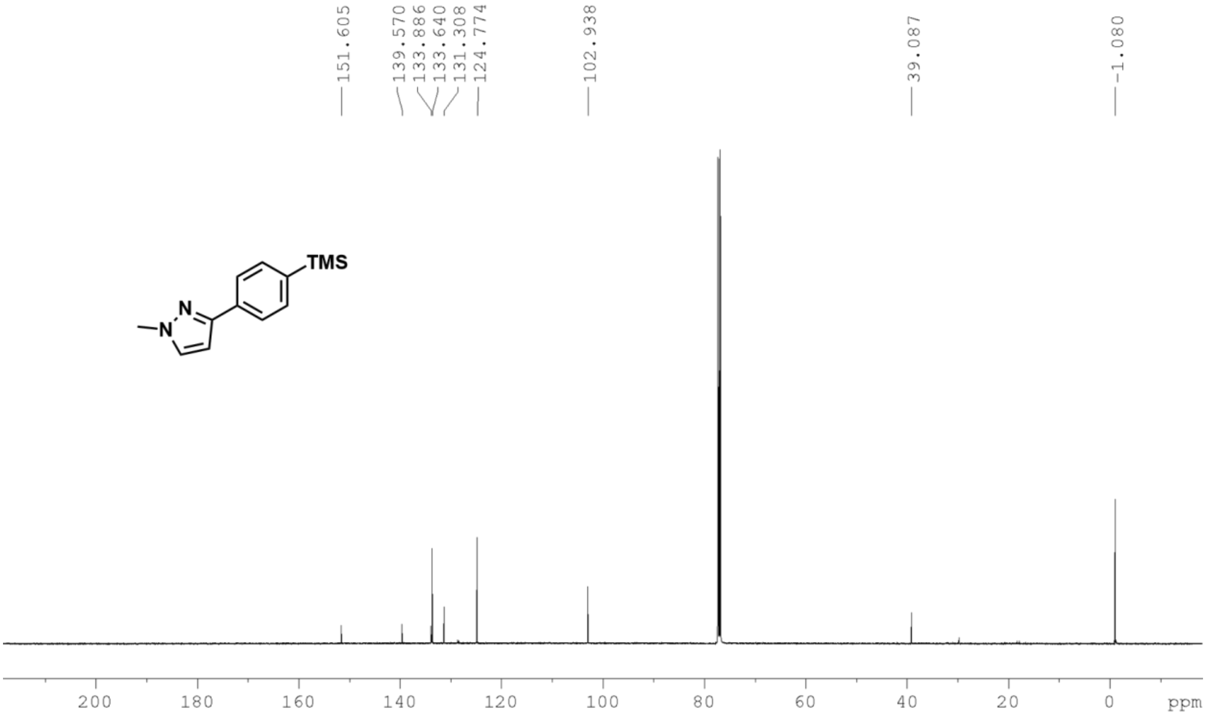
[13]C NMR (126 Hz, $CDCl_3$) spectrum of **2j**



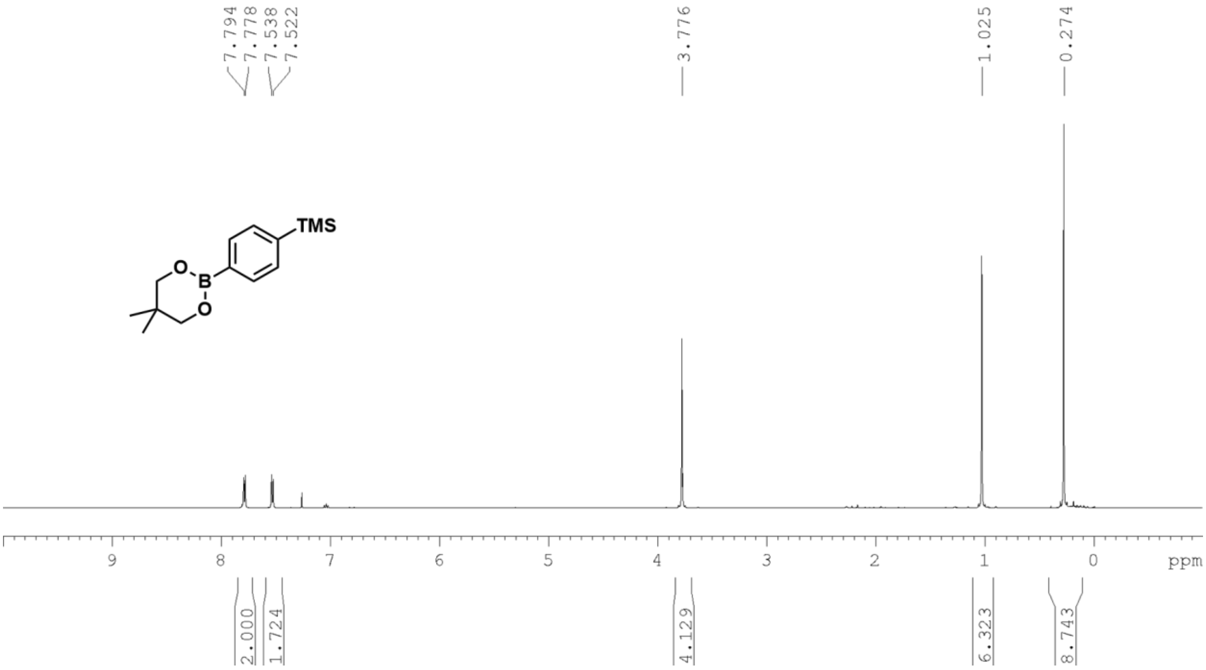
^{1}H NMR (500 Hz, $CDCl_3$) spectrum of **2k**



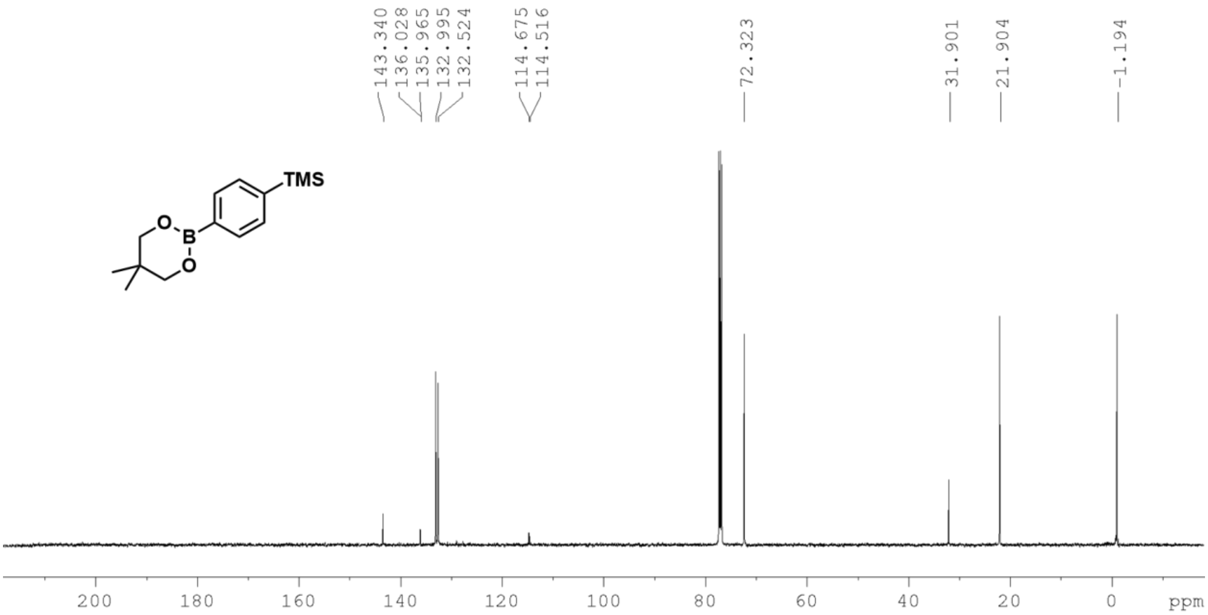
^{13}C NMR (126 Hz, $CDCl_3$) spectrum of **2k**



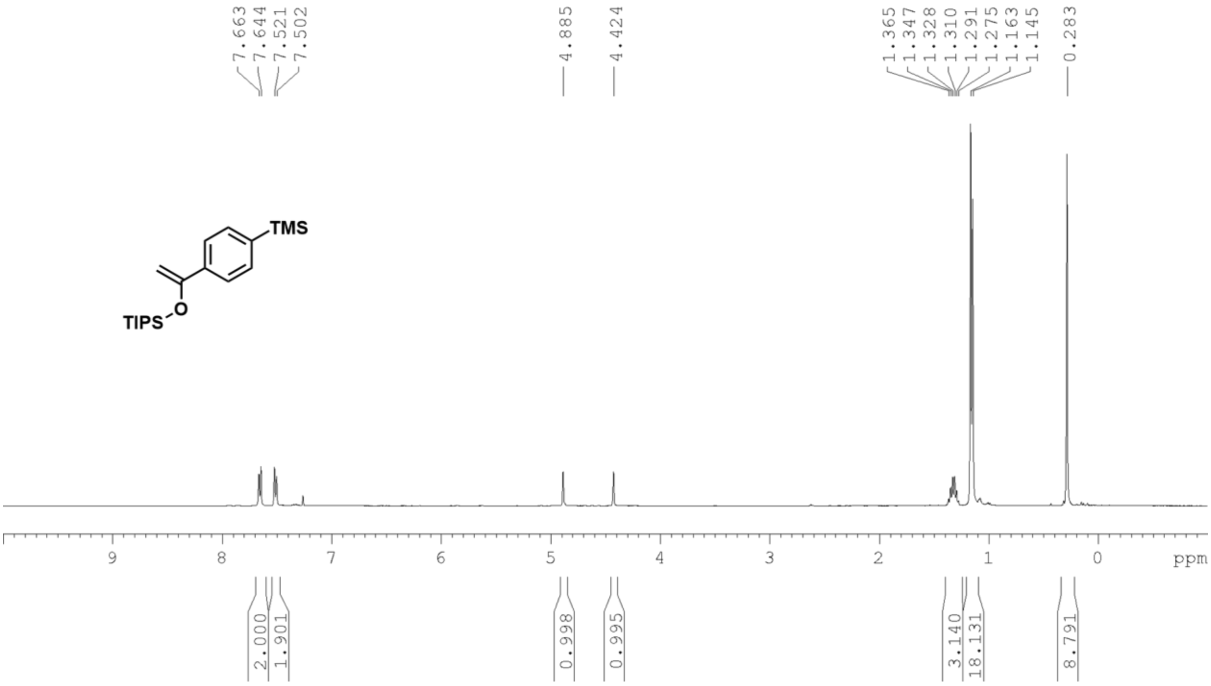
[1]H NMR (500 Hz, $CDCl_3$) spectrum of **2l**



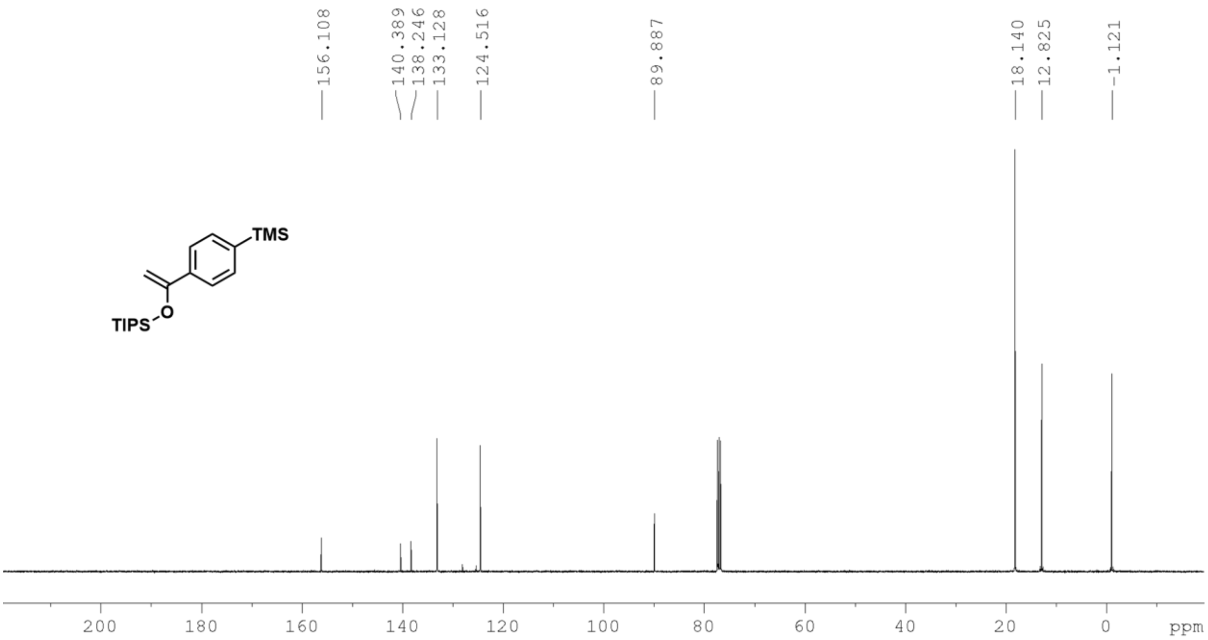
[13]C NMR (126 Hz, $CDCl_3$) spectrum of **2l**



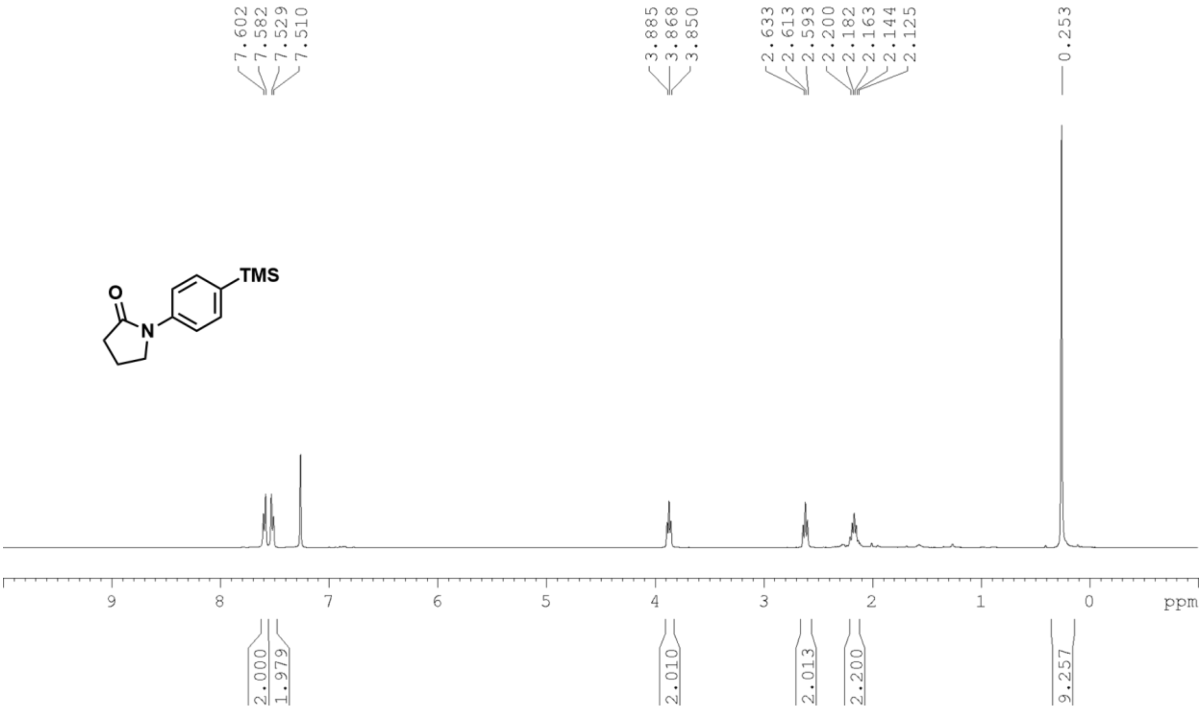
[1]H NMR (500 Hz, $CDCl_3$) spectrum of **2m**



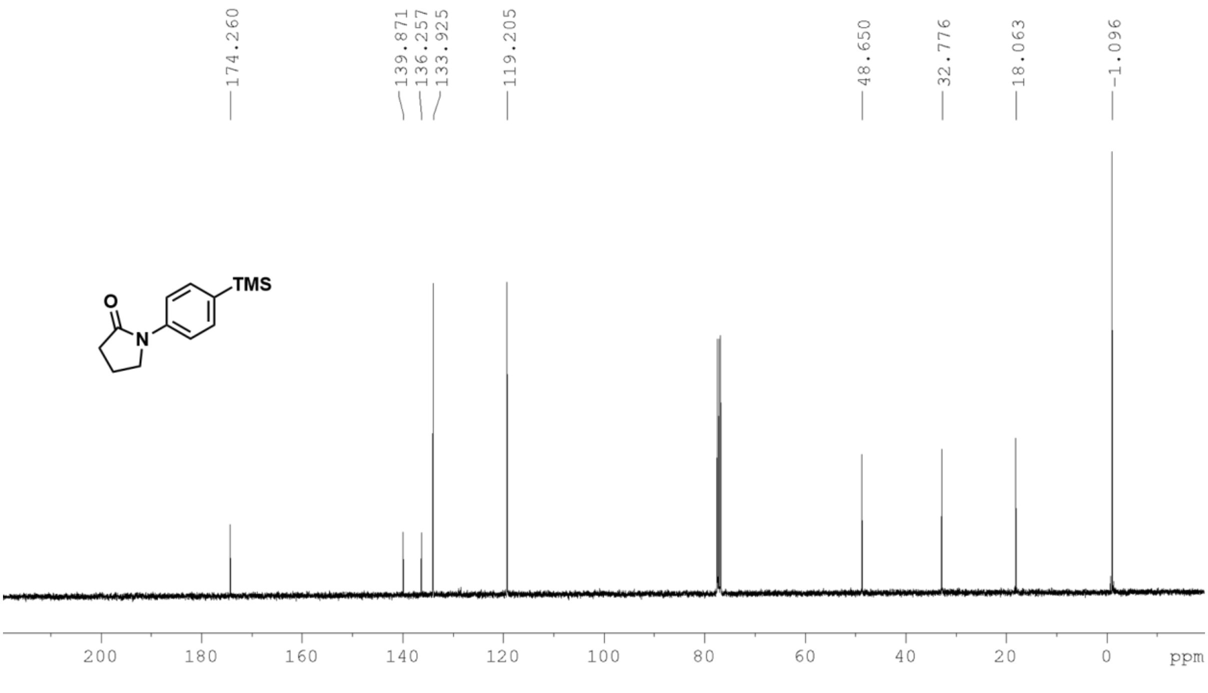
[13]C NMR (126 Hz, $CDCl_3$) spectrum of **2m**



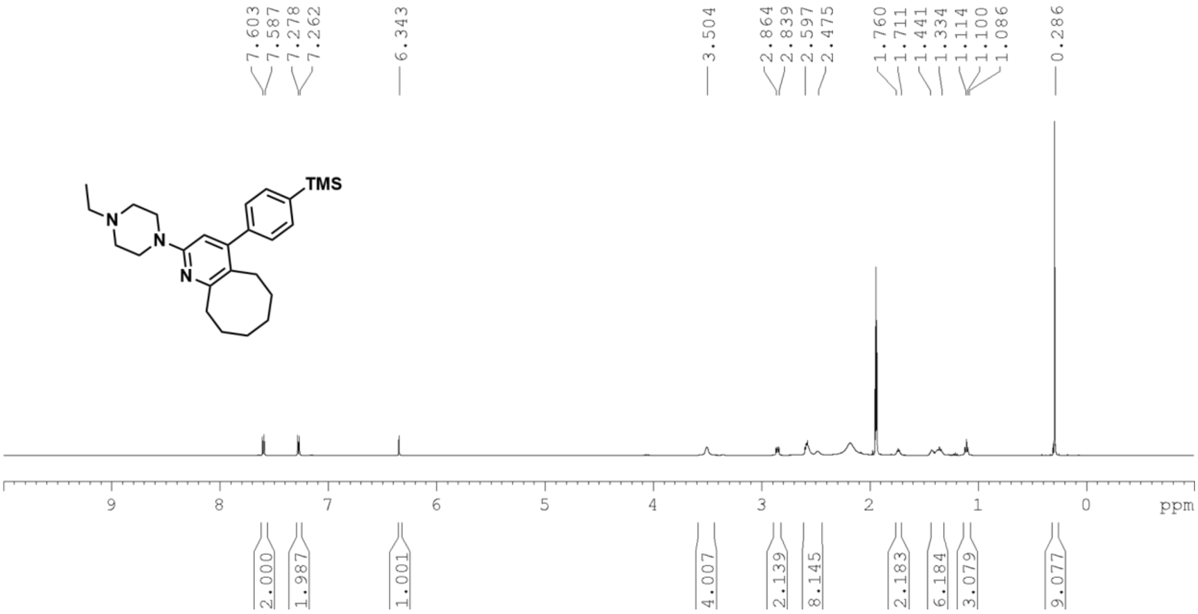
^{1}H NMR (500 Hz, $CDCl_3$) spectrum of **2n**



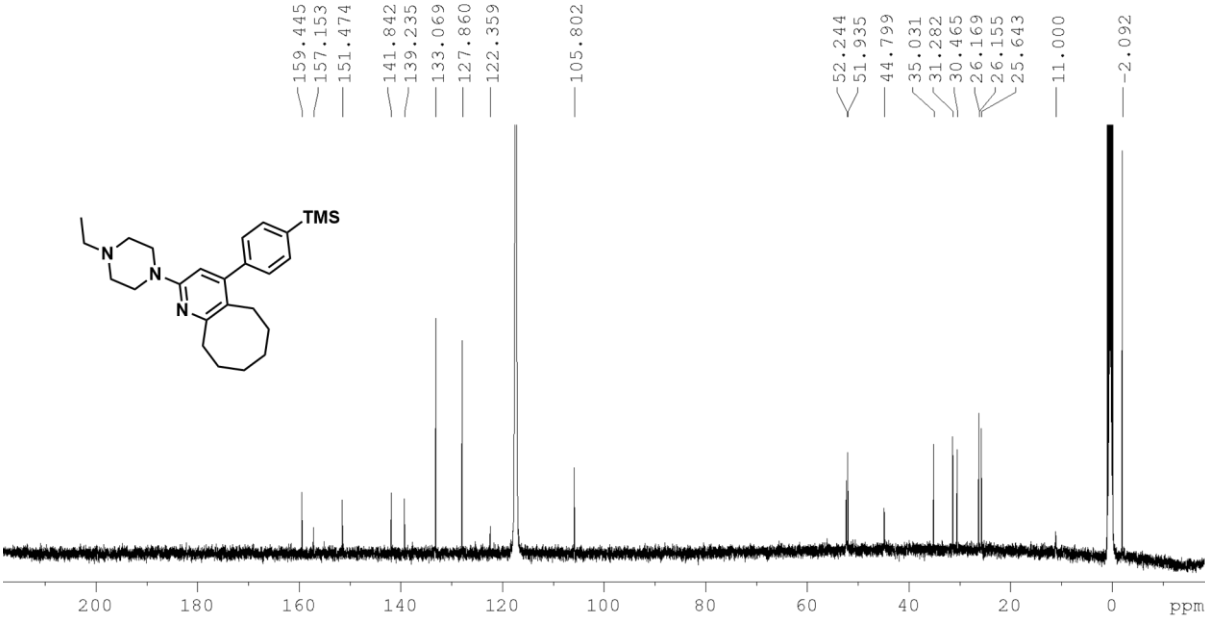
^{13}C NMR (126 Hz, $CDCl_3$) spectrum of **2n**



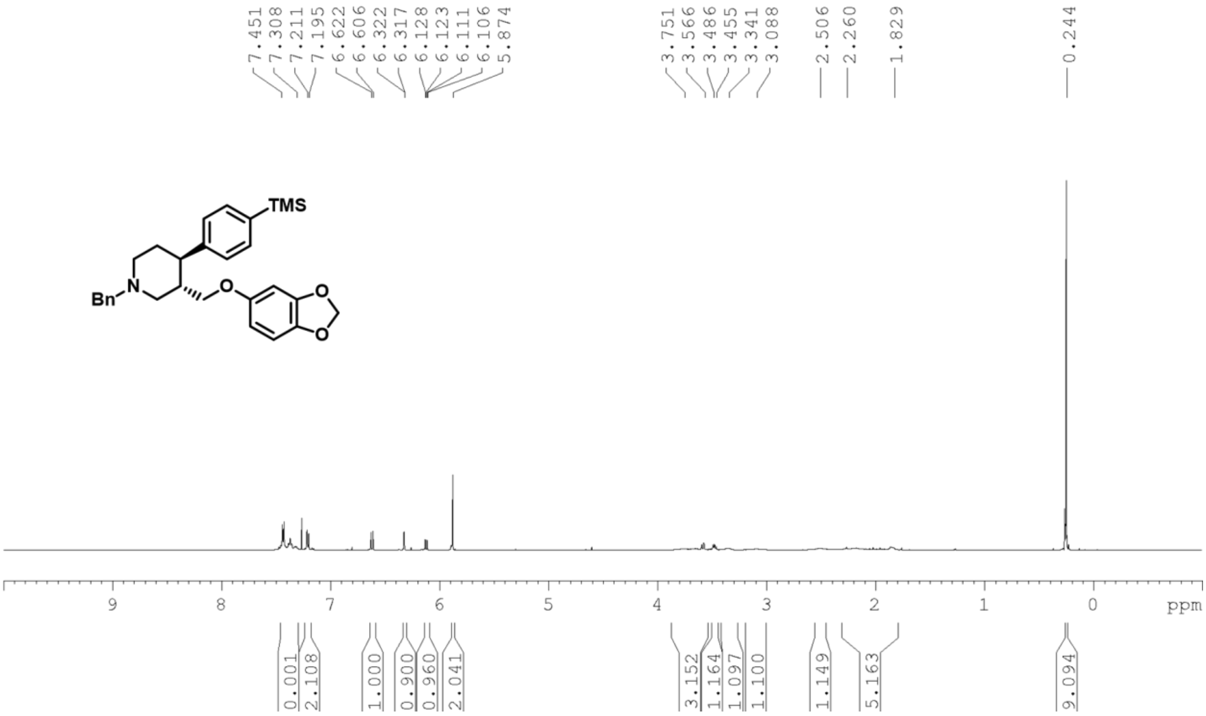
^{1}H NMR (500 Hz, CD_3CN) spectrum of **2o**



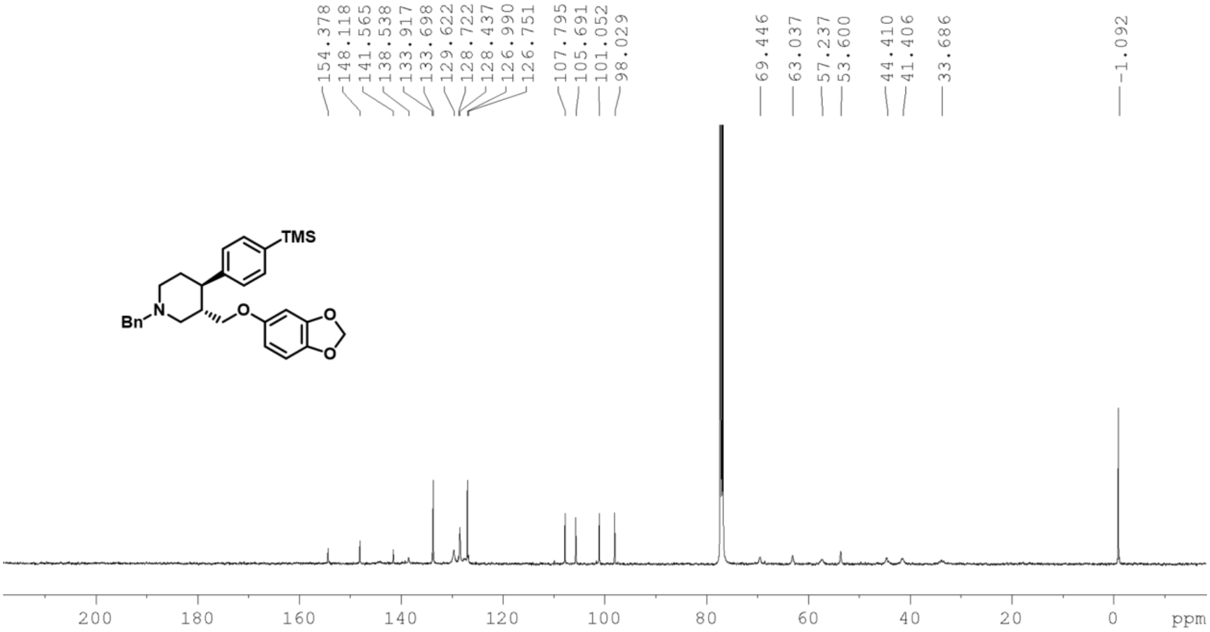
^{13}C NMR (126 Hz, CD_3CN) spectrum of **2o**



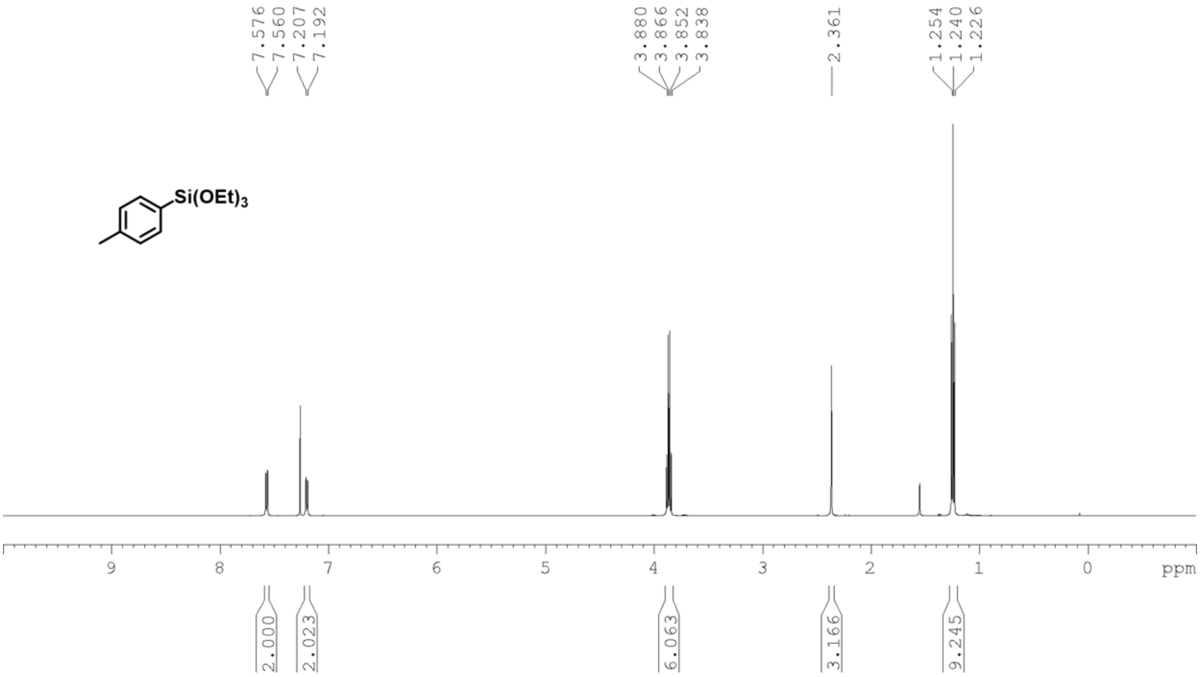
[1]H NMR (500 Hz, $CDCl_3$) spectrum of **2p**



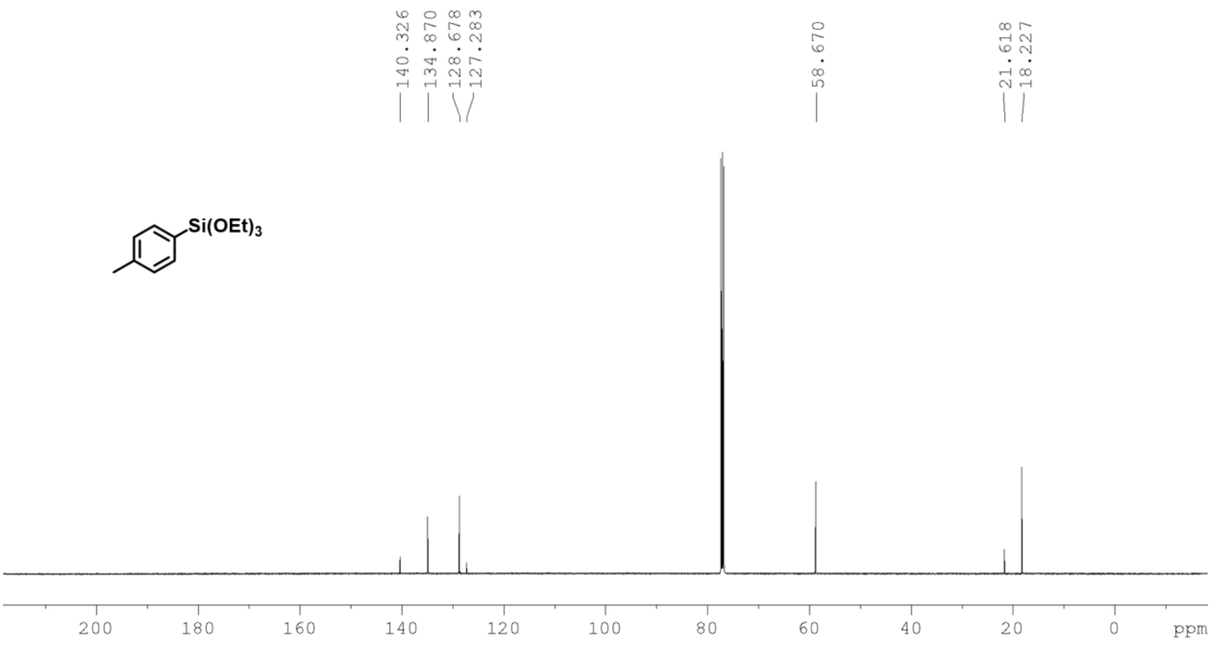
[13]C NMR (126 Hz, $CDCl_3$) spectrum of **2p**



[1]H NMR (500 Hz, $CDCl_3$) spectrum of **2q**



[13]C NMR (126 Hz, $CDCl_3$) spectrum of **2q**



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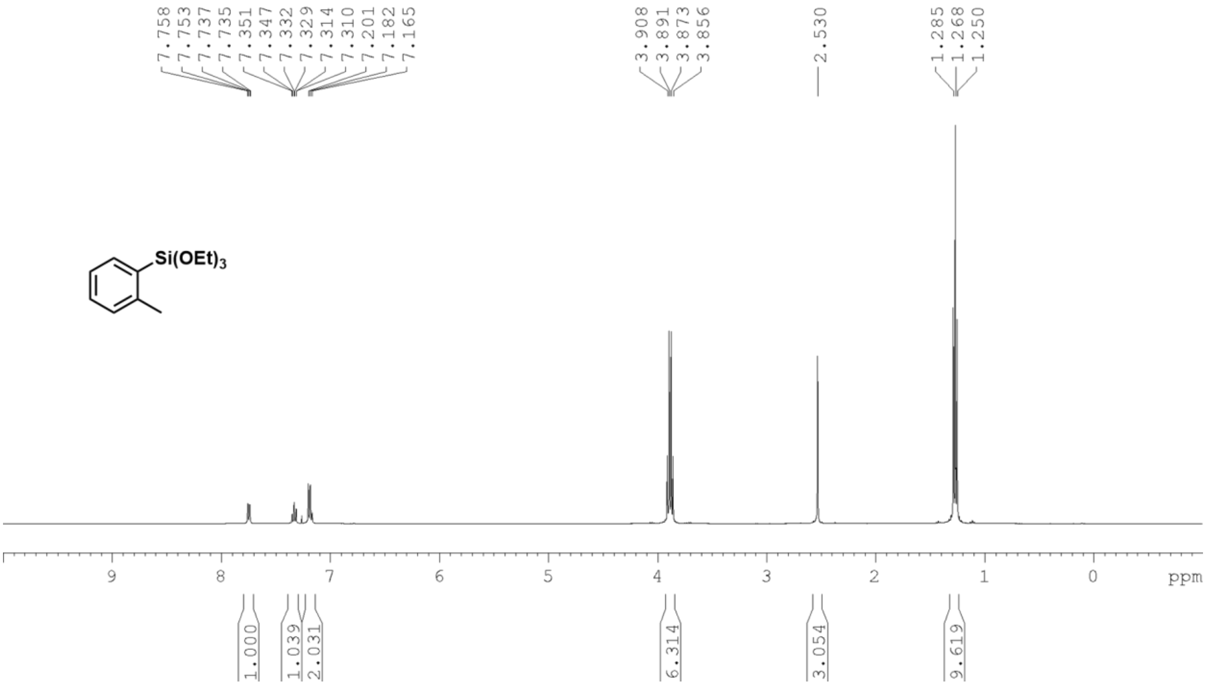
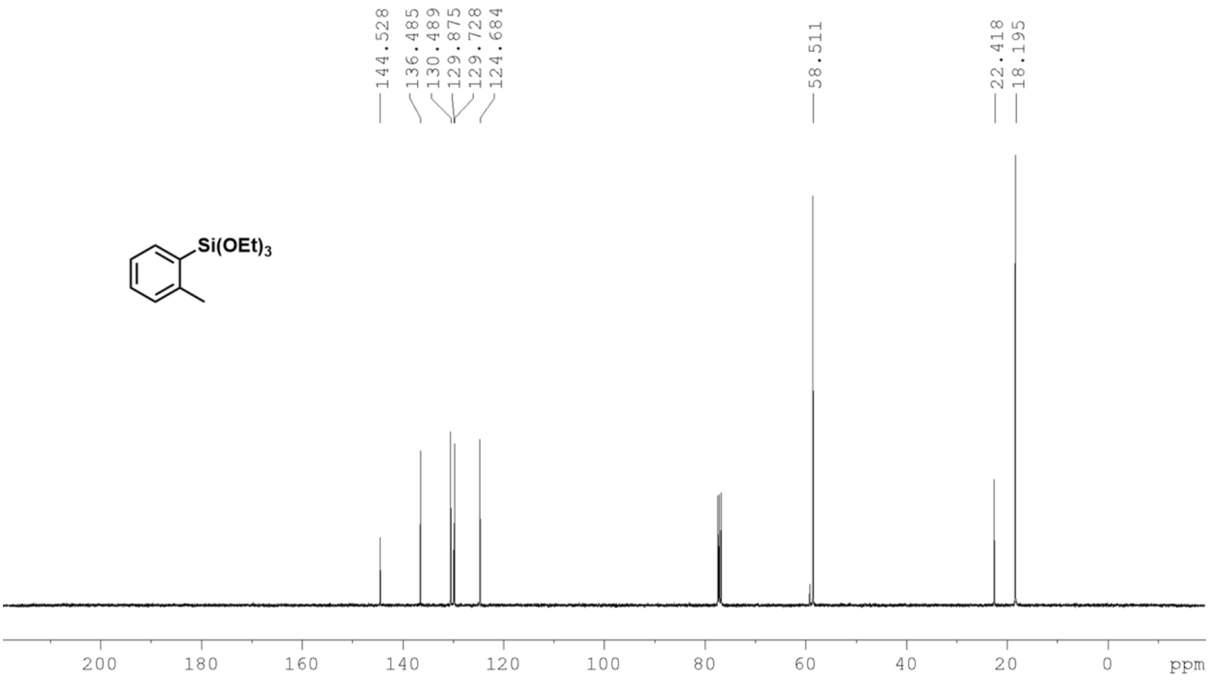
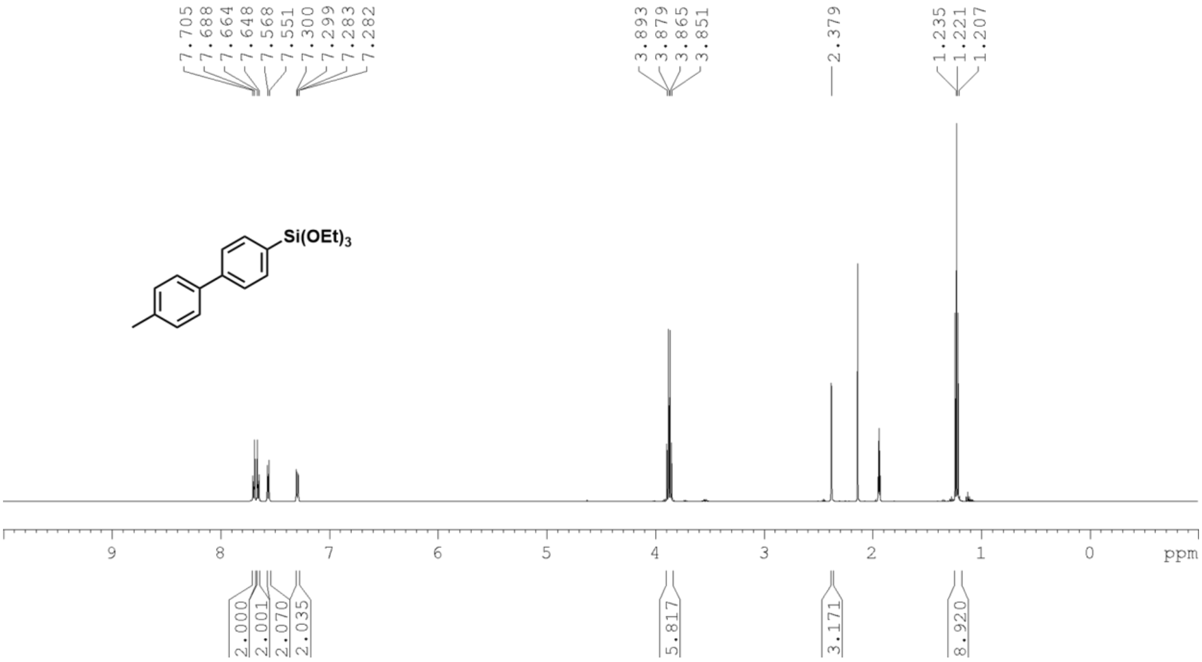


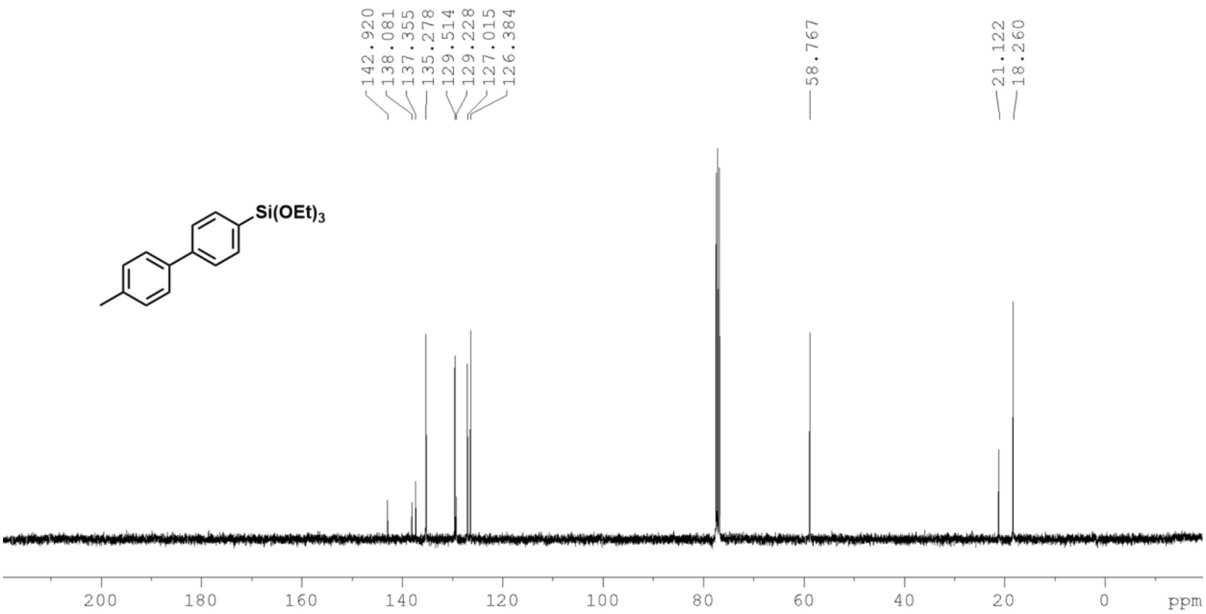
^{13}C NMR (126 Hz, $CDCl_3$) spectrum of **2r**



[1]H NMR (500 Hz, CD_3CN) spectrum of **2s**



[13]C NMR (126 Hz, $CDCl_3$) spectrum of **2s**



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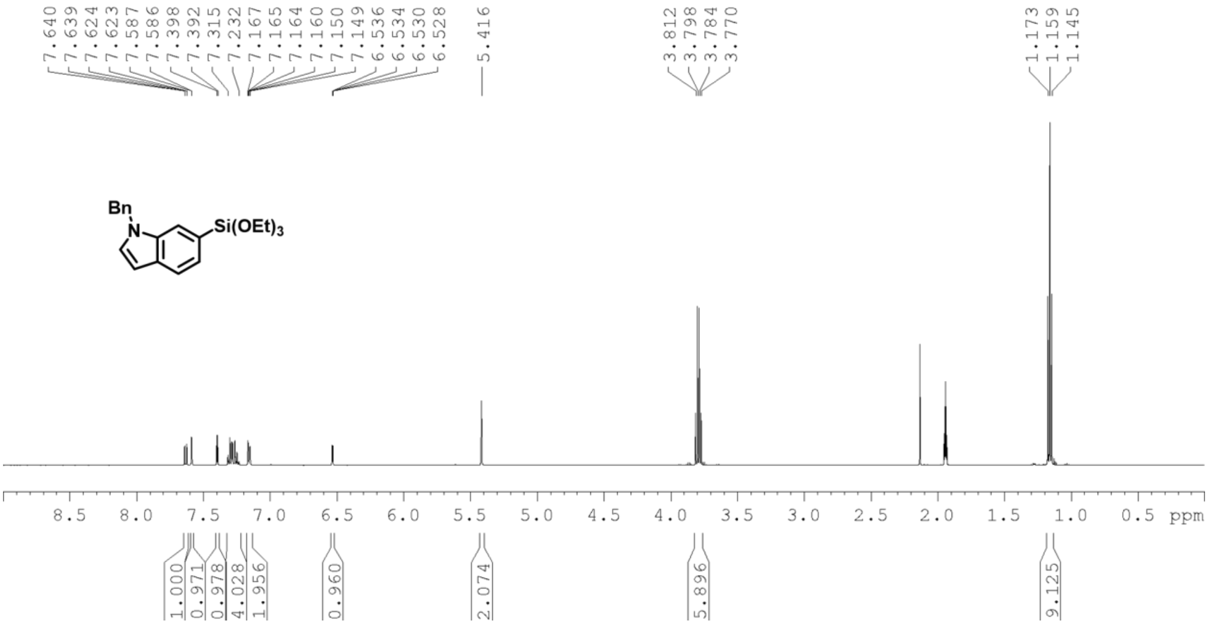
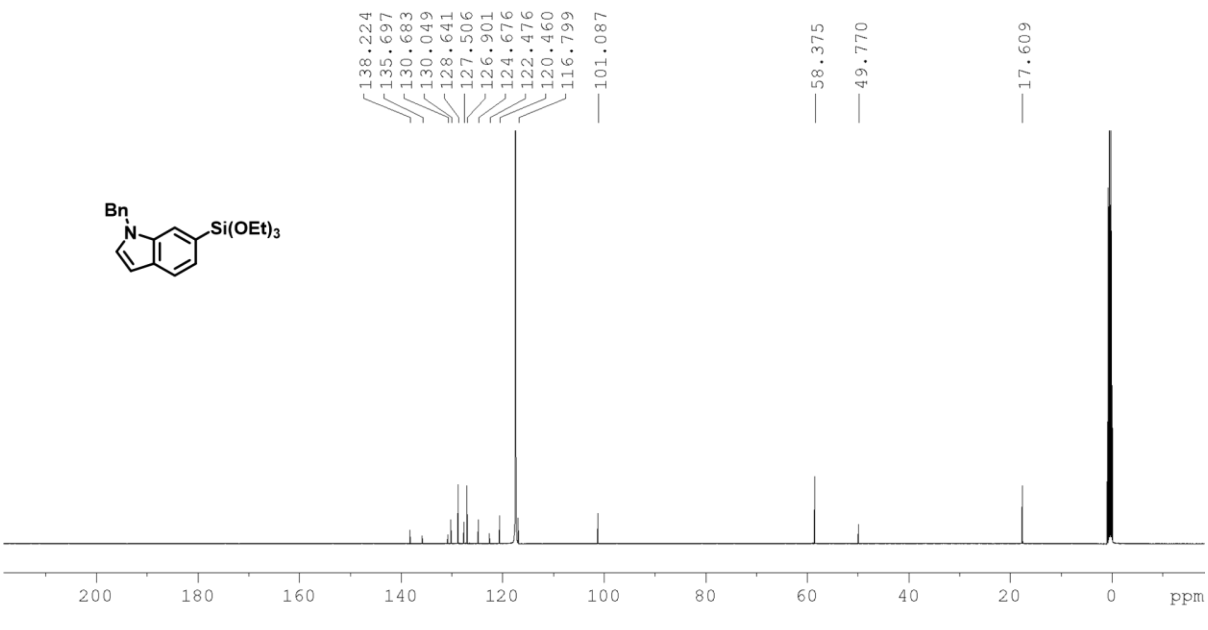
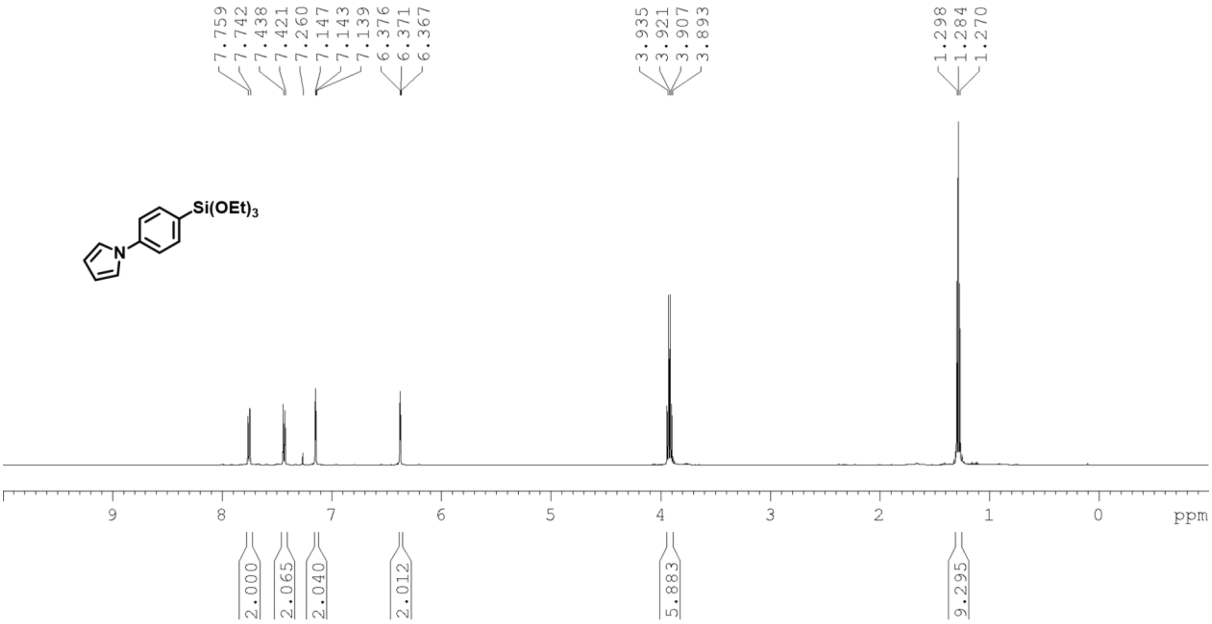


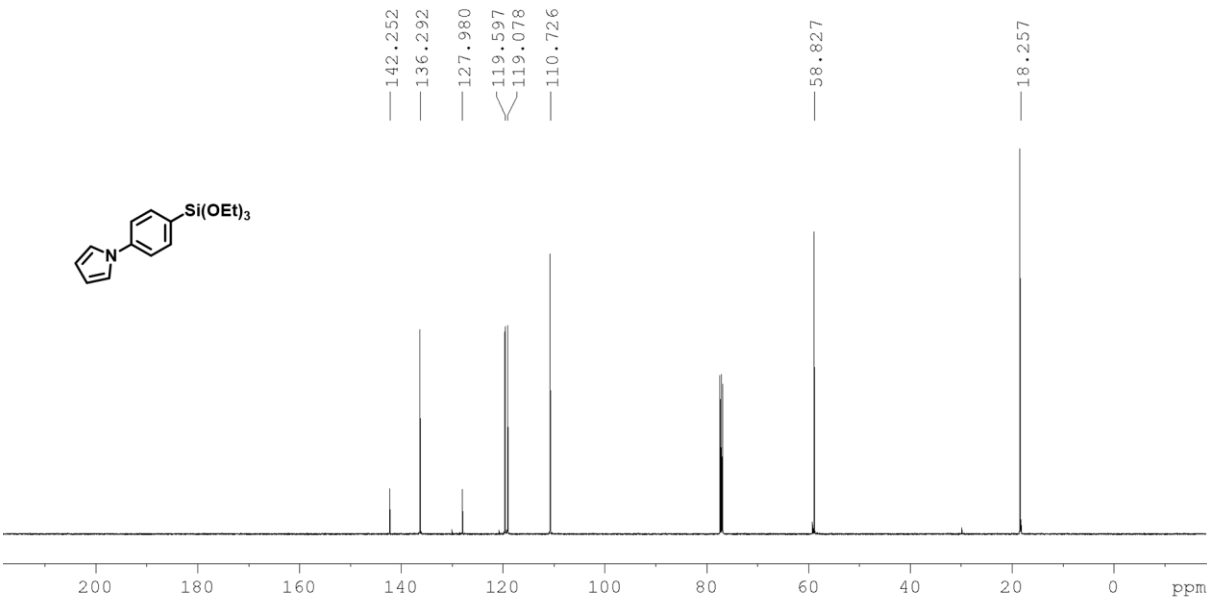
^{13}C NMR (126 Hz, $CDCl_3$) spectrum of **2t**



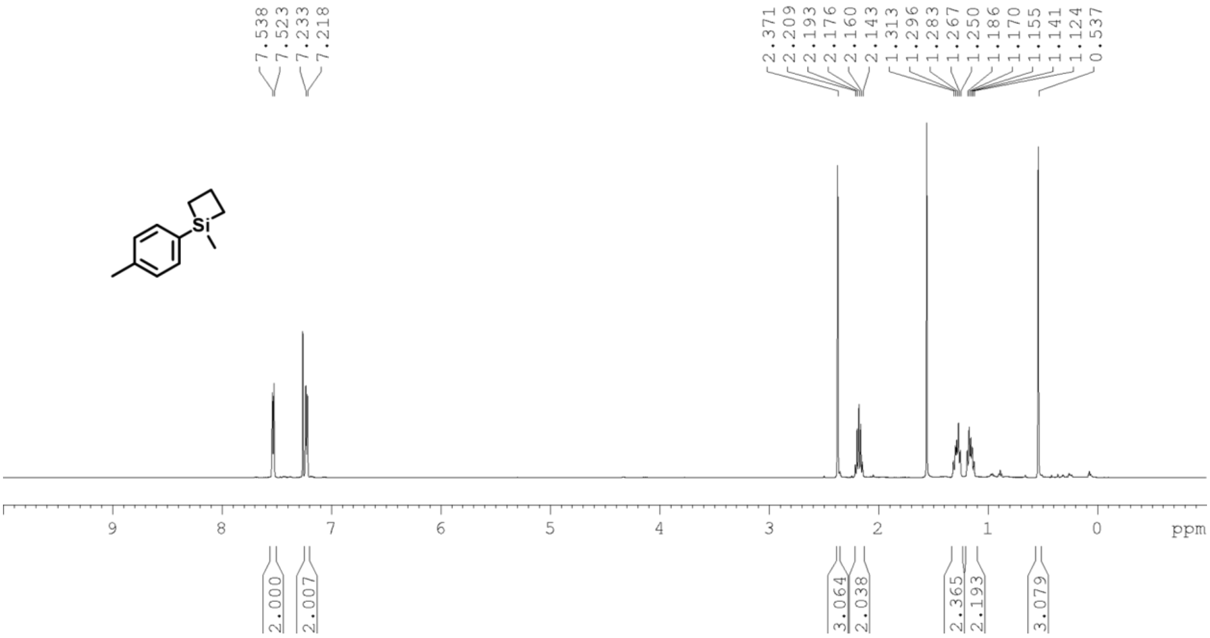
^{1}H NMR (500 Hz, $CDCl_3$) spectrum of **2u**



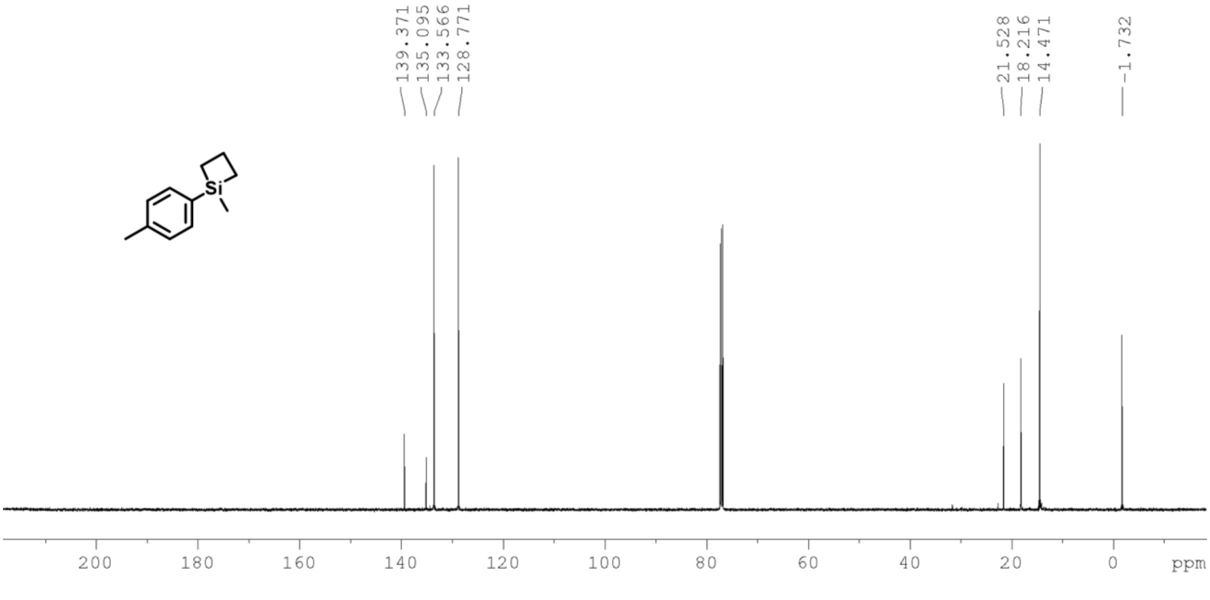
^{13}C NMR (126 Hz, $CDCl_3$) spectrum of **2u**



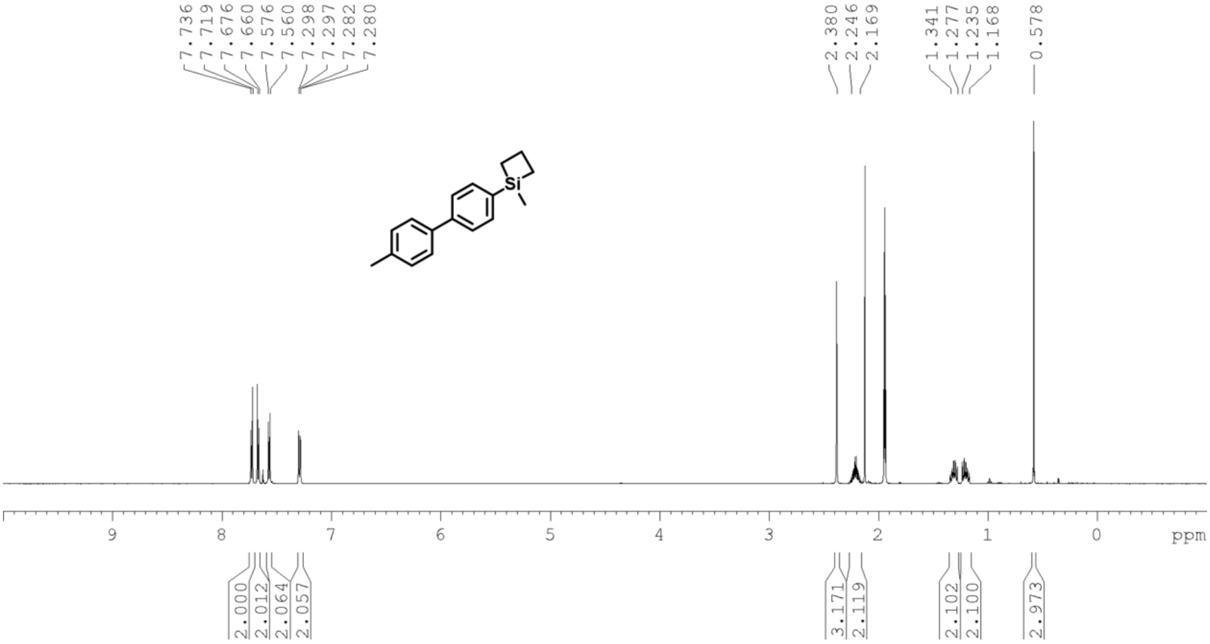
[1]H NMR (500 Hz, $CDCl_3$) spectrum of **2v**



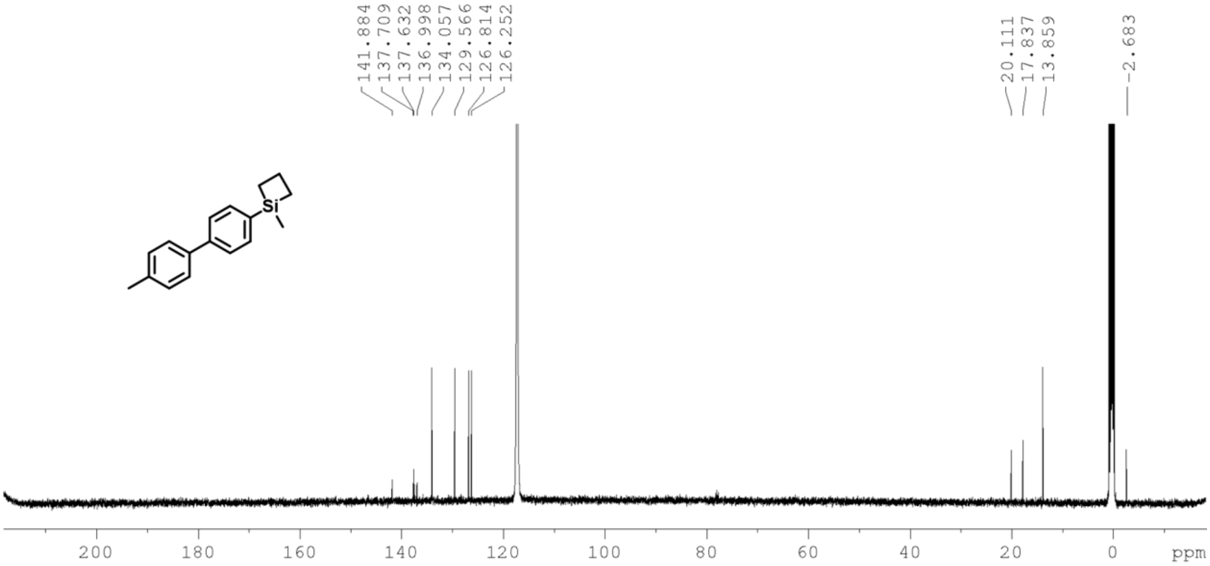
[13]C NMR (126 Hz, $CDCl_3$) spectrum of **2v**



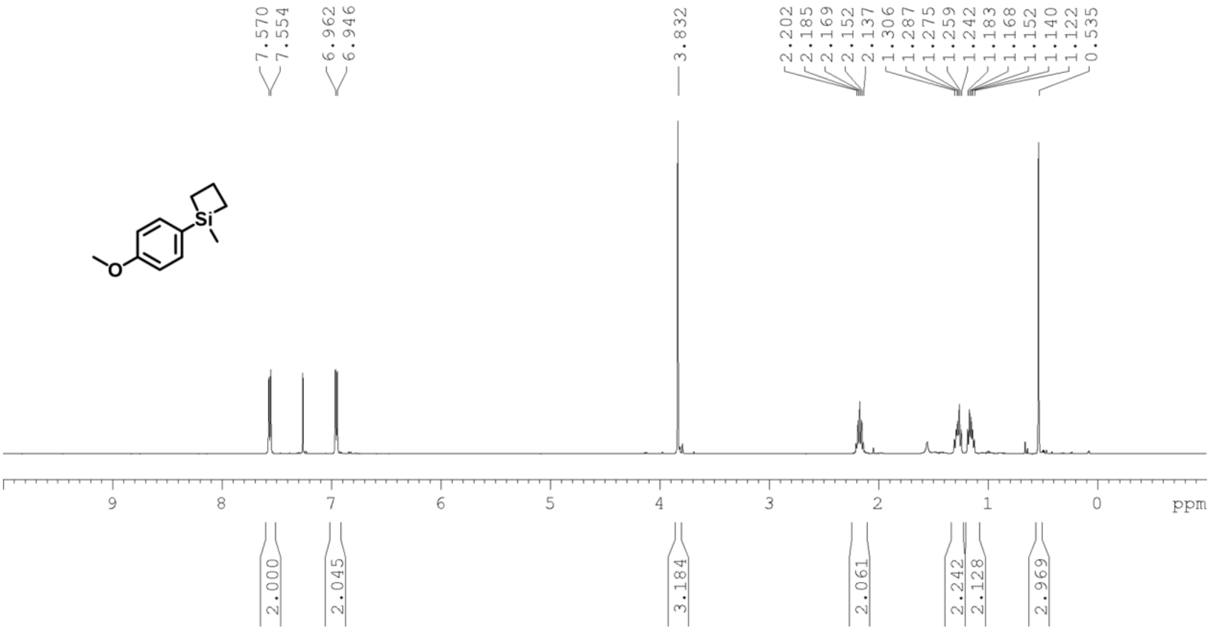
^{1}H NMR (500 Hz, CD_3CN) spectrum of **2w**



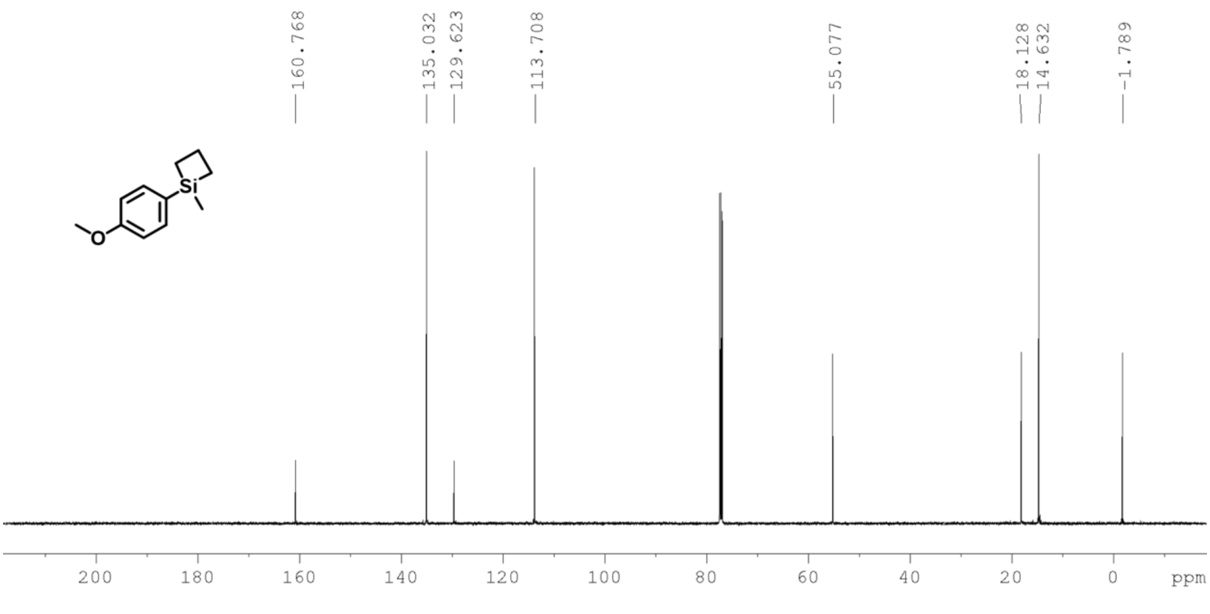
^{13}C NMR (126 Hz, CD_3CN) spectrum of **2w**



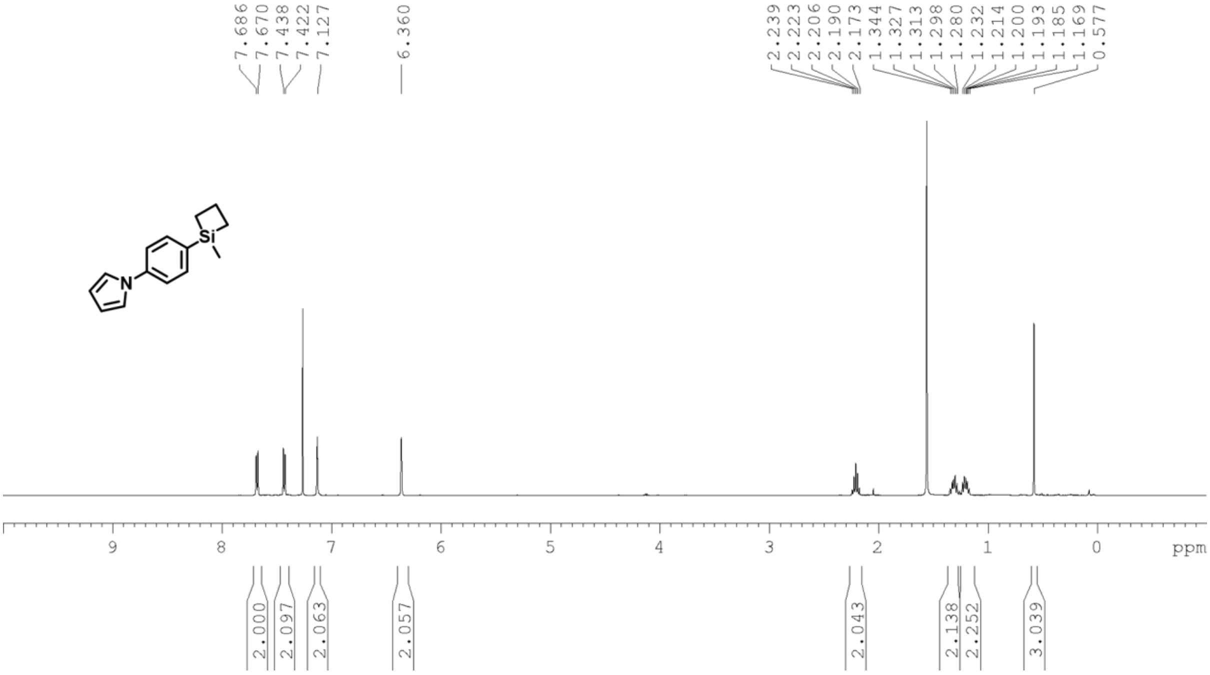
[1]H NMR (500 Hz, $CDCl_3$) spectrum of **2x**



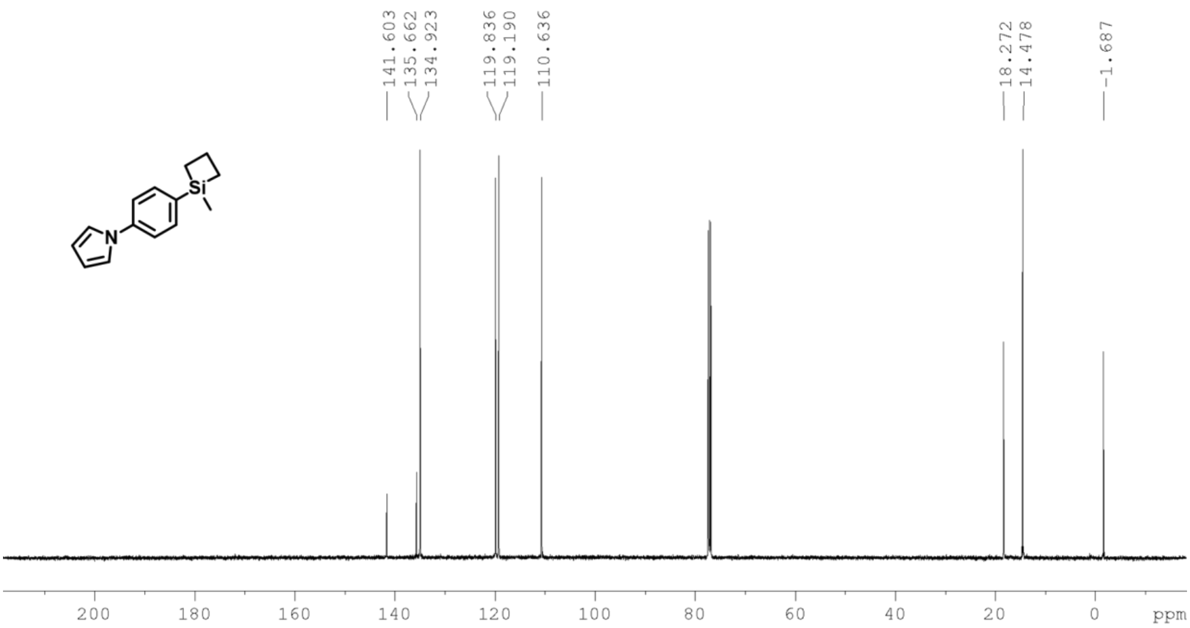
[13]C NMR (126 Hz, $CDCl_3$) spectrum of **2x**



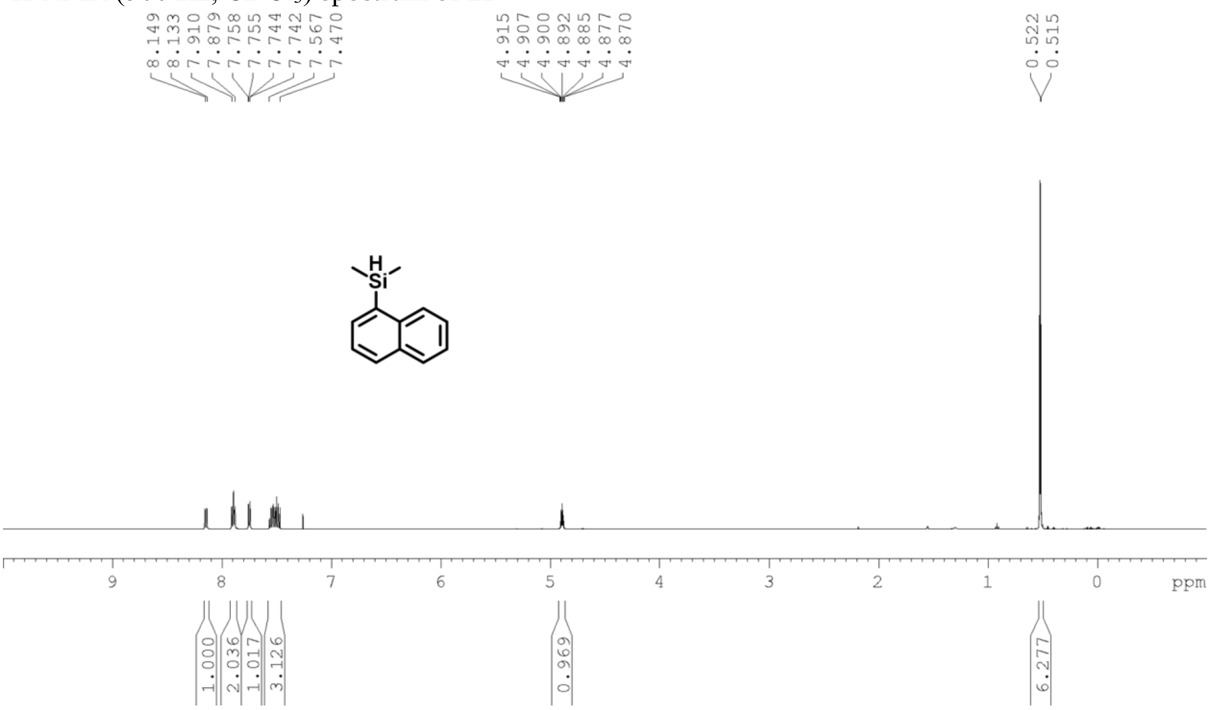
[1]H NMR (500 Hz, $CDCl_3$) spectrum of **2y**



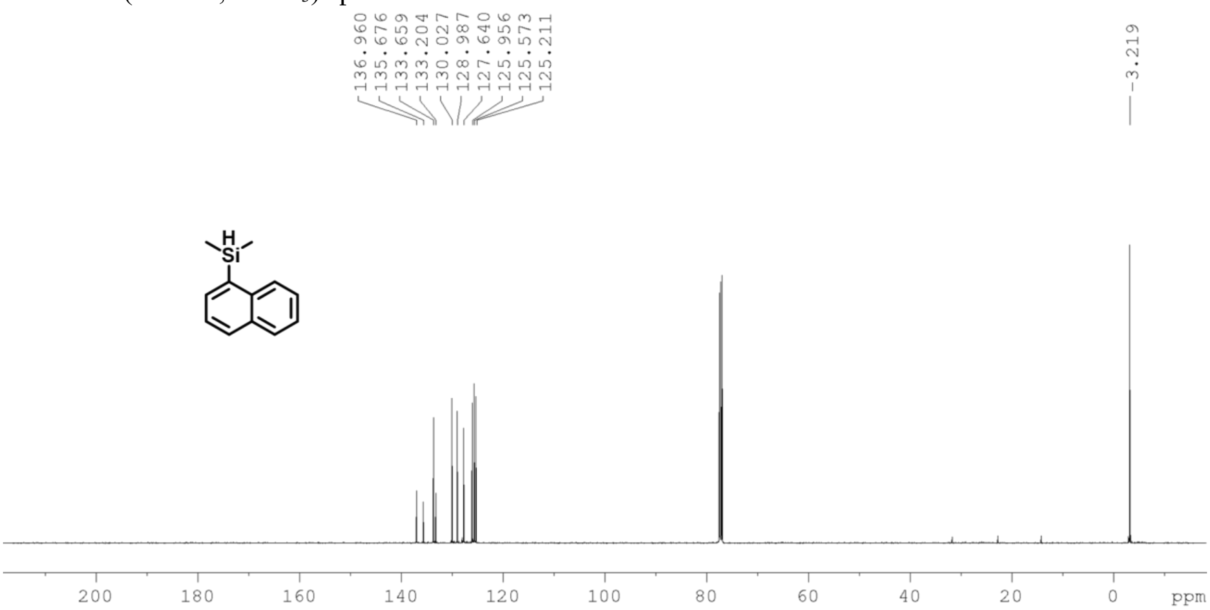
[13]C NMR (126 Hz, $CDCl_3$) spectrum of **2y**



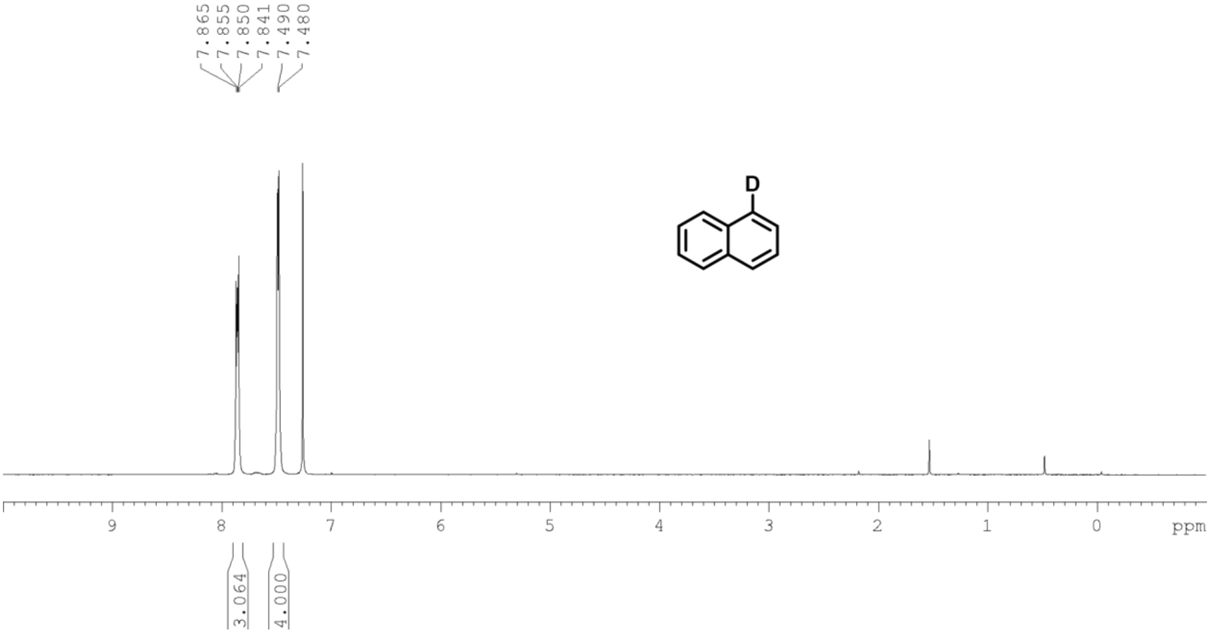
^{1}H NMR (500 Hz, $CDCl_3$) spectrum of **2z**



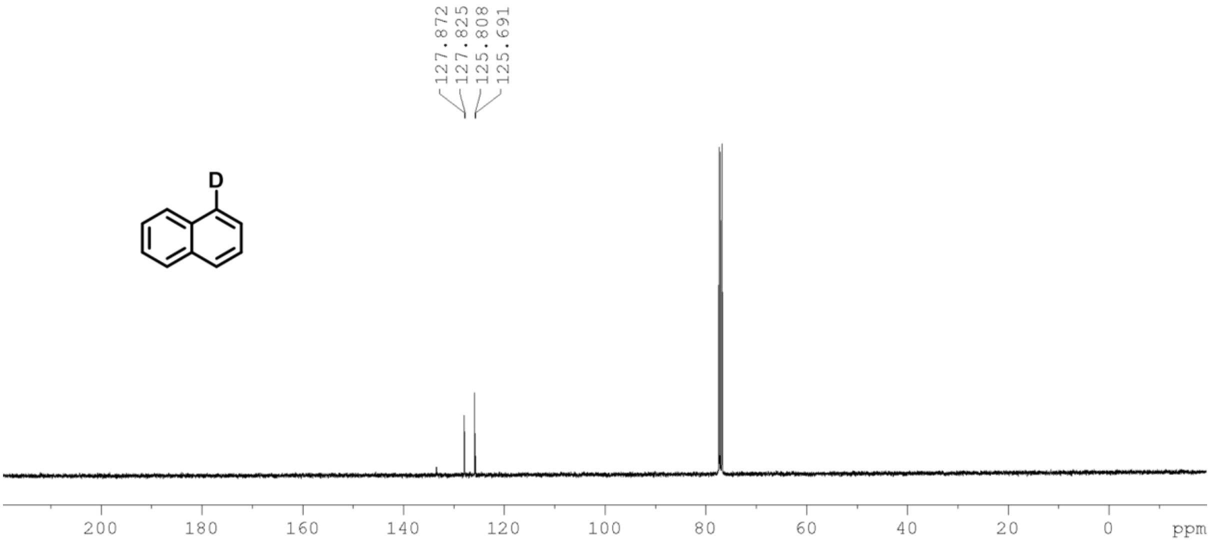
^{13}C NMR (126 Hz, $CDCl_3$) spectrum of **2z**



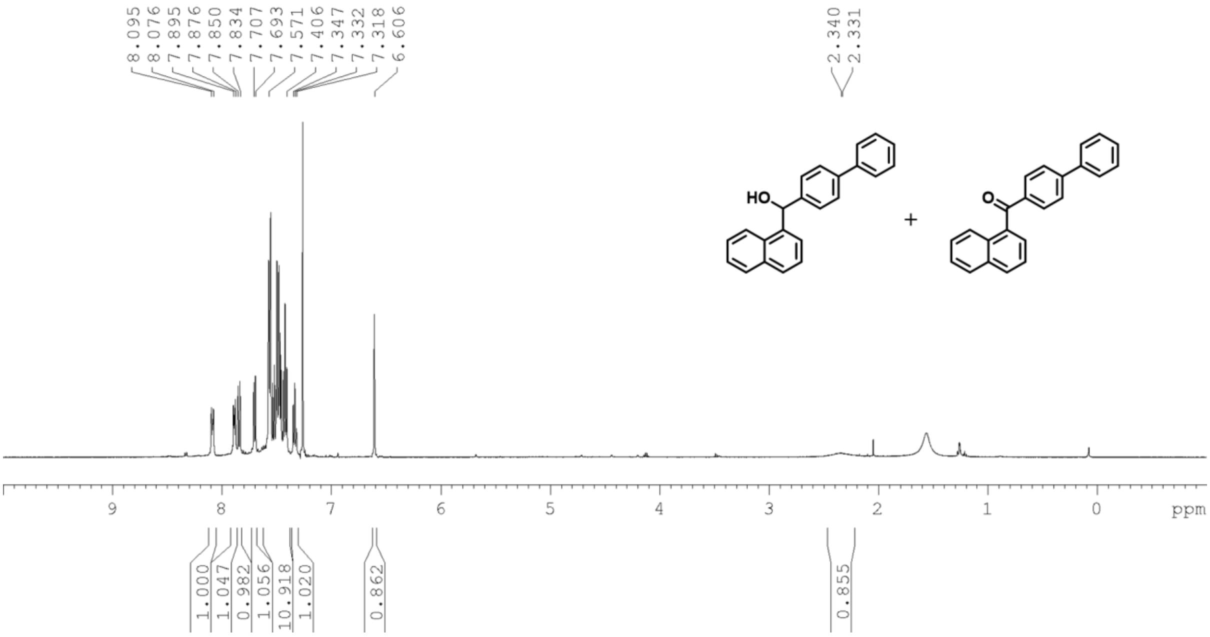
[1]H NMR (500 Hz, $CDCl_3$) spectrum of **1-deuteronaphthalene**



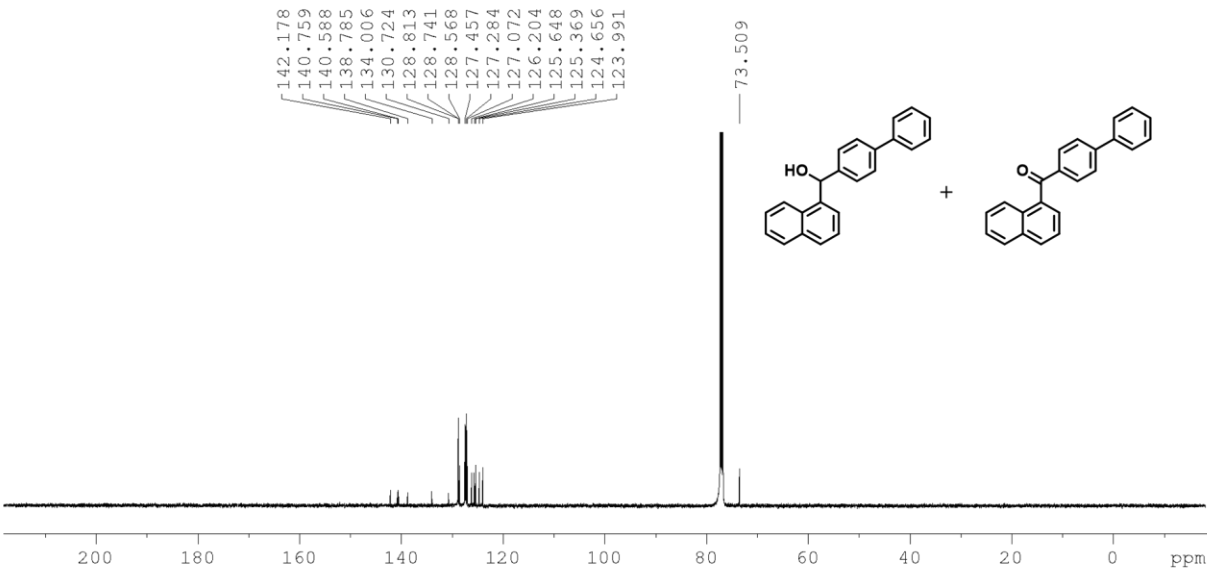
[13]C NMR (126 Hz, $CDCl_3$) spectrum of **1-deuteronaphthalene**



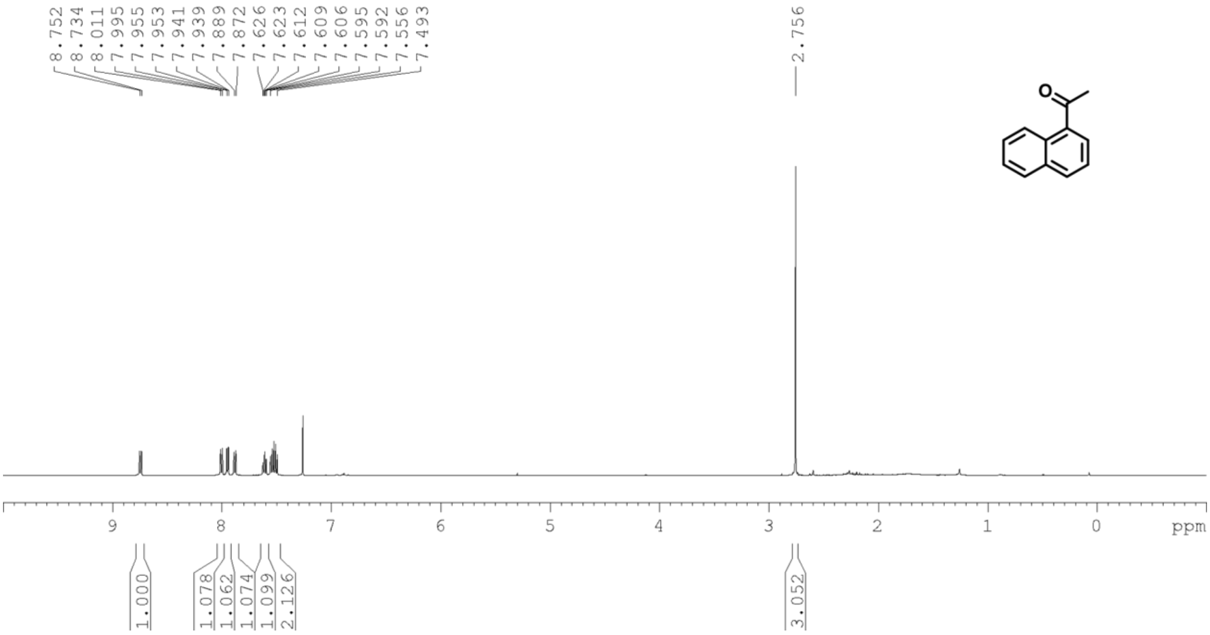
[1]H NMR (500 Hz, $CDCl_3$) spectrum of **α-1-naphthalenyl-[1,1'-biphenyl]-4-methanol (49%)** and **[1,1'-biphenyl]-4-yl-1-naphthalenyl-methanone (8%)**



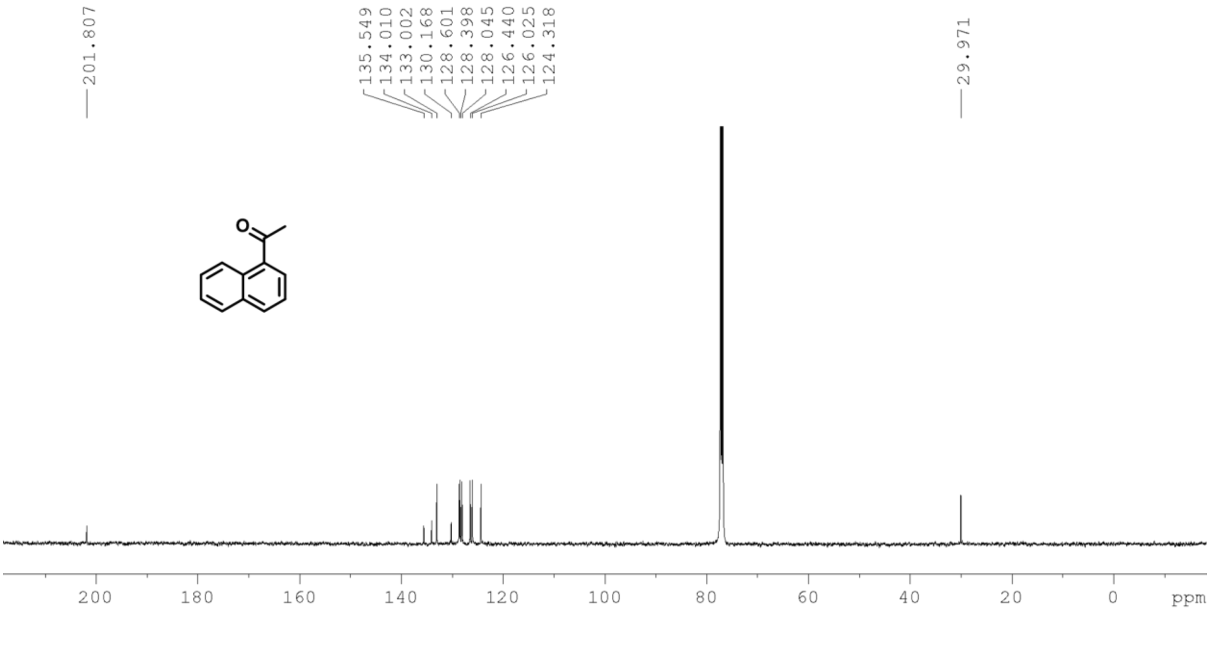
[13]C NMR (126 Hz, $CDCl_3$) spectrum of **α-1-naphthalenyl-[1,1'-biphenyl]-4-methanol (49%)** and **[1,1'-biphenyl]-4-yl-1-naphthalenyl-methanone (8%)**



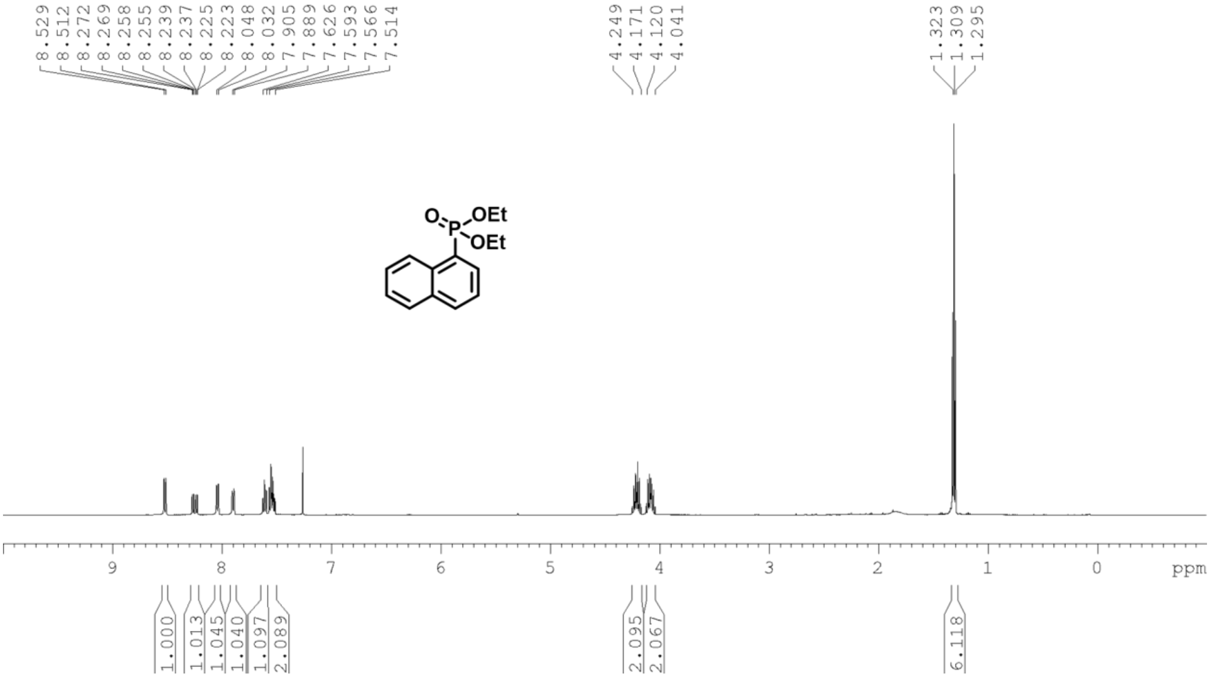
^{1}H NMR (500 Hz, $CDCl_3$) spectrum of **1-(1-naphthalenyl)-ethanone**



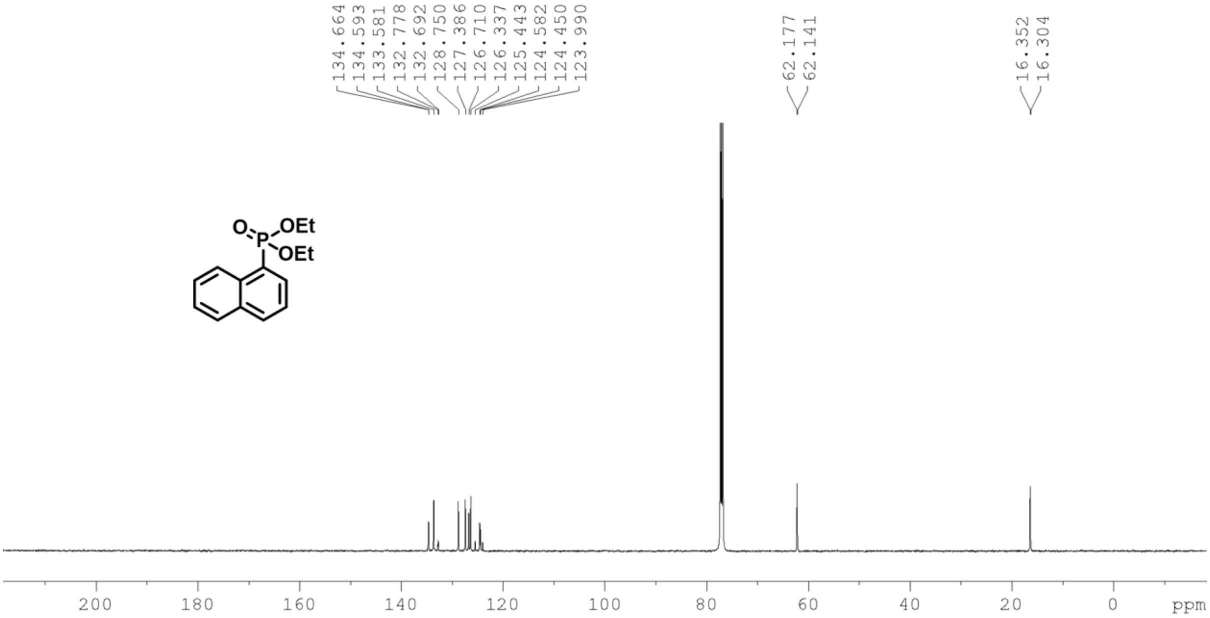
^{13}C NMR (126 Hz, $CDCl_3$) spectrum of **1-(1-naphthalenyl)-ethanone**



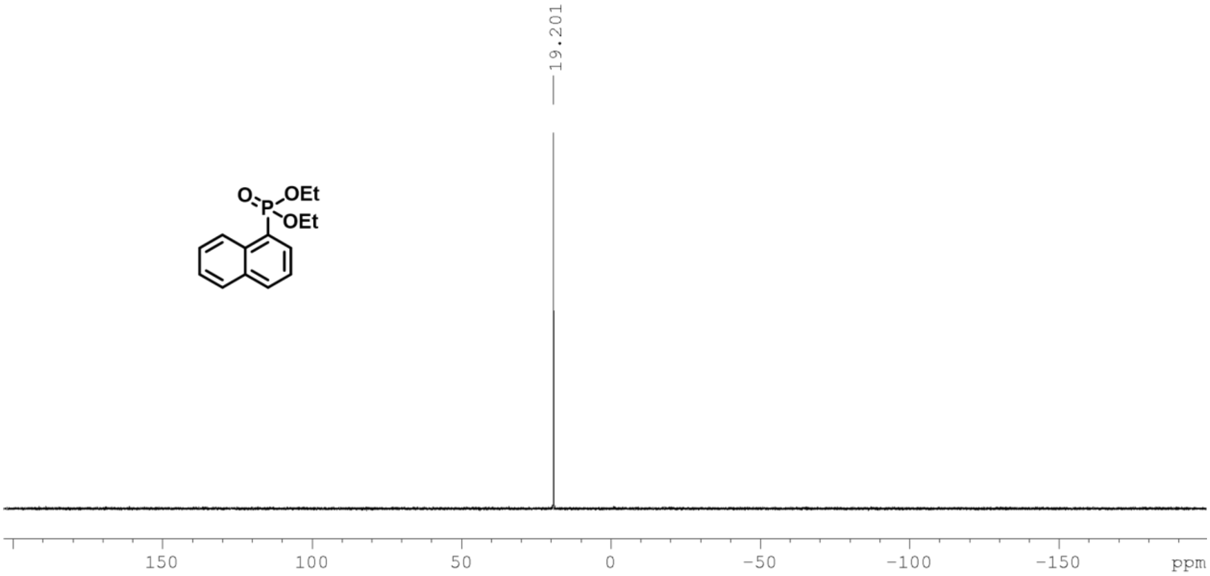
^{1}H NMR (500 Hz, $CDCl_3$) spectrum of **1-diethoxyphosphorylnaphthalene**



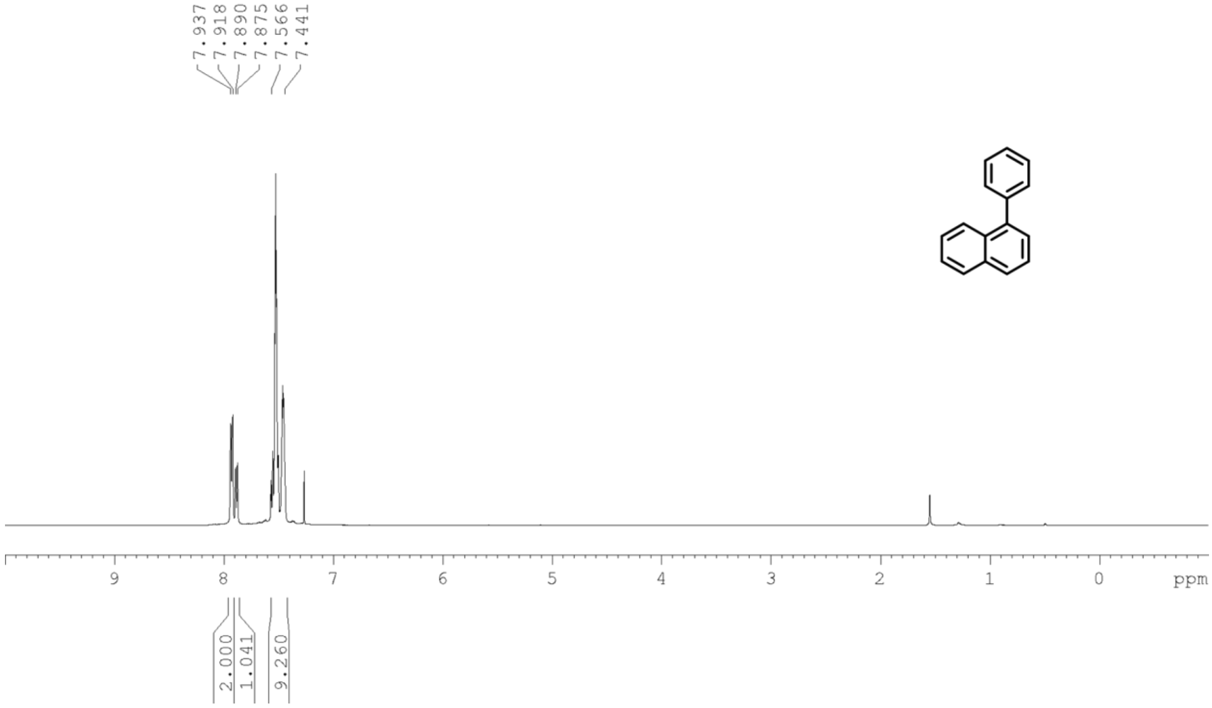
^{13}C NMR (126 Hz, $CDCl_3$) spectrum of **1-diethoxyphosphorylnaphthalene**



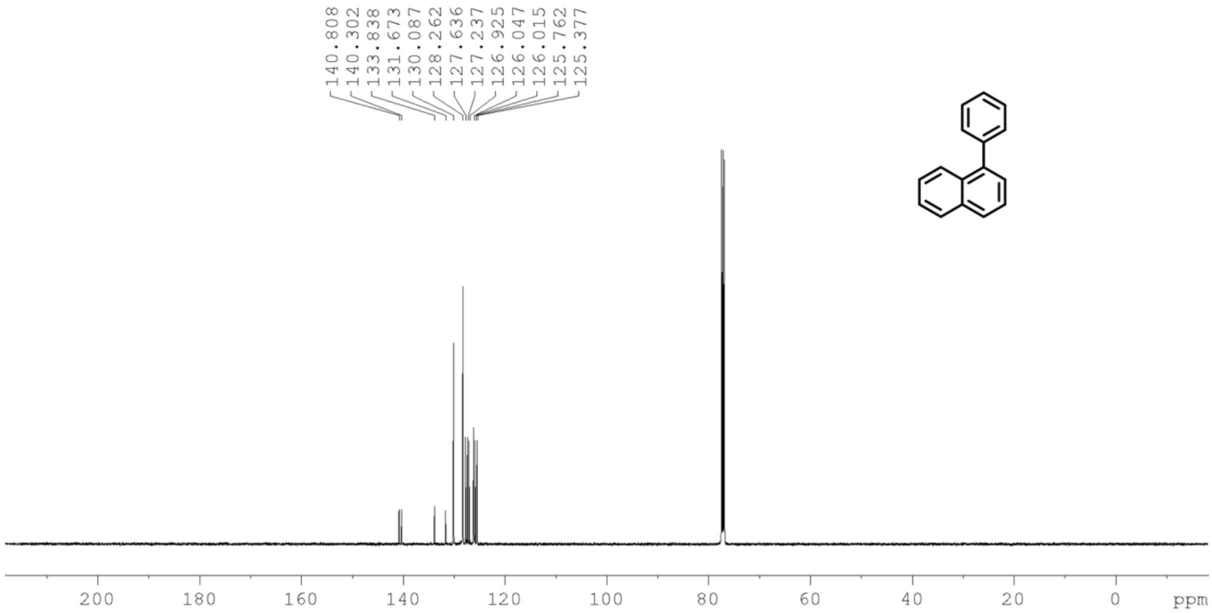
^{31}P NMR (203 Hz, $CDCl_3$) spectrum of **1-diethoxyphosphorylnaphthalene**



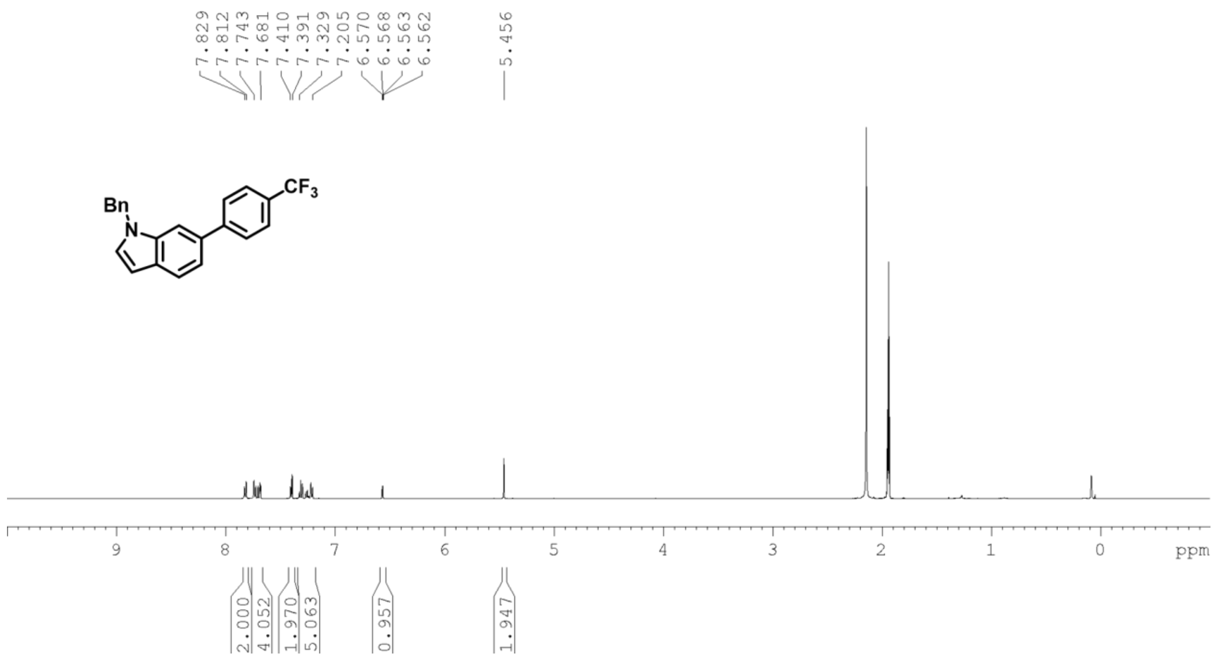
^{1}H NMR (500 Hz, $CDCl_3$) spectrum of **1-phenyl-naphthalene**



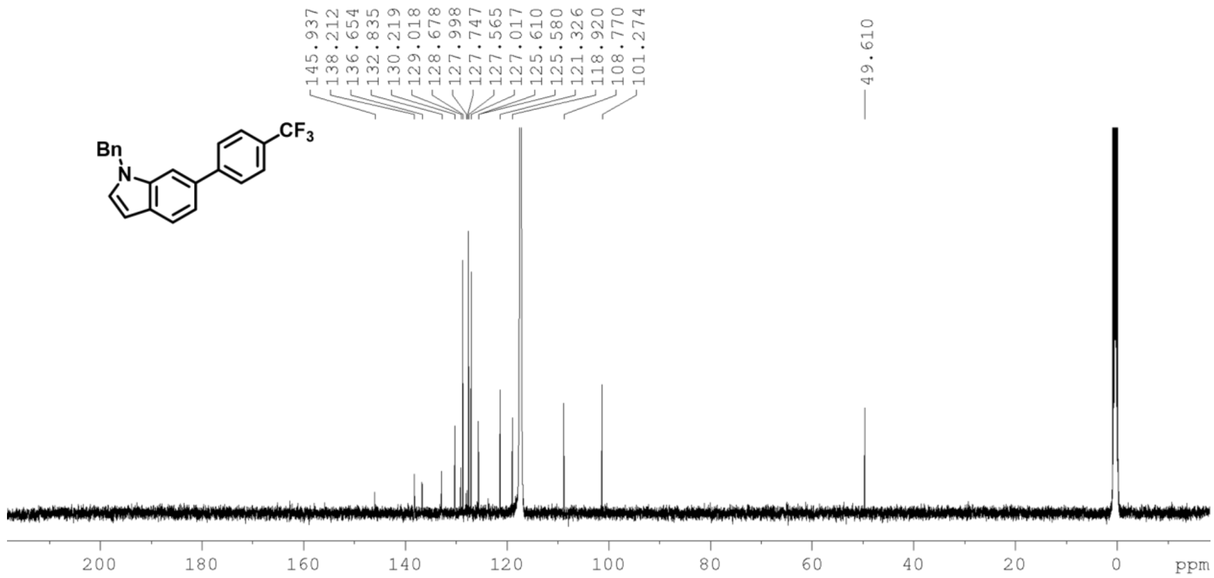
^{13}C NMR (126 Hz, $CDCl_3$) spectrum of **1-phenyl-naphthalene**



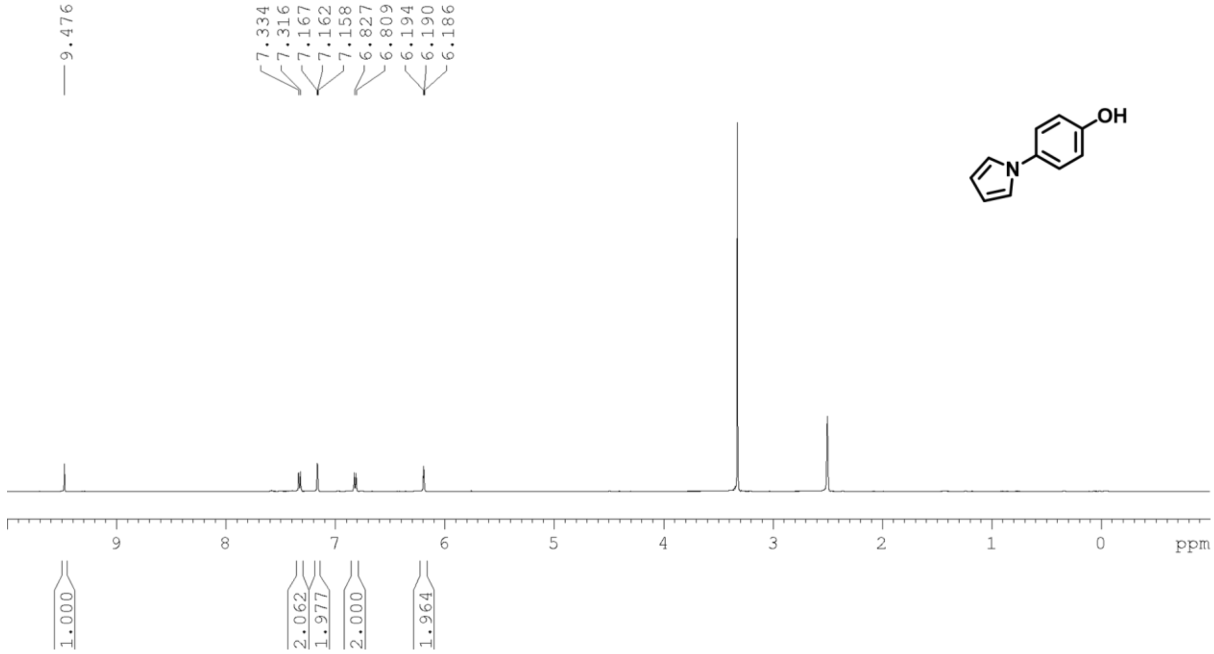
[1]H NMR (500 Hz, CD_3CN) spectrum of **1-benzyl-6-(4-(trifluoromethyl)phenyl)-1*H*-indol**



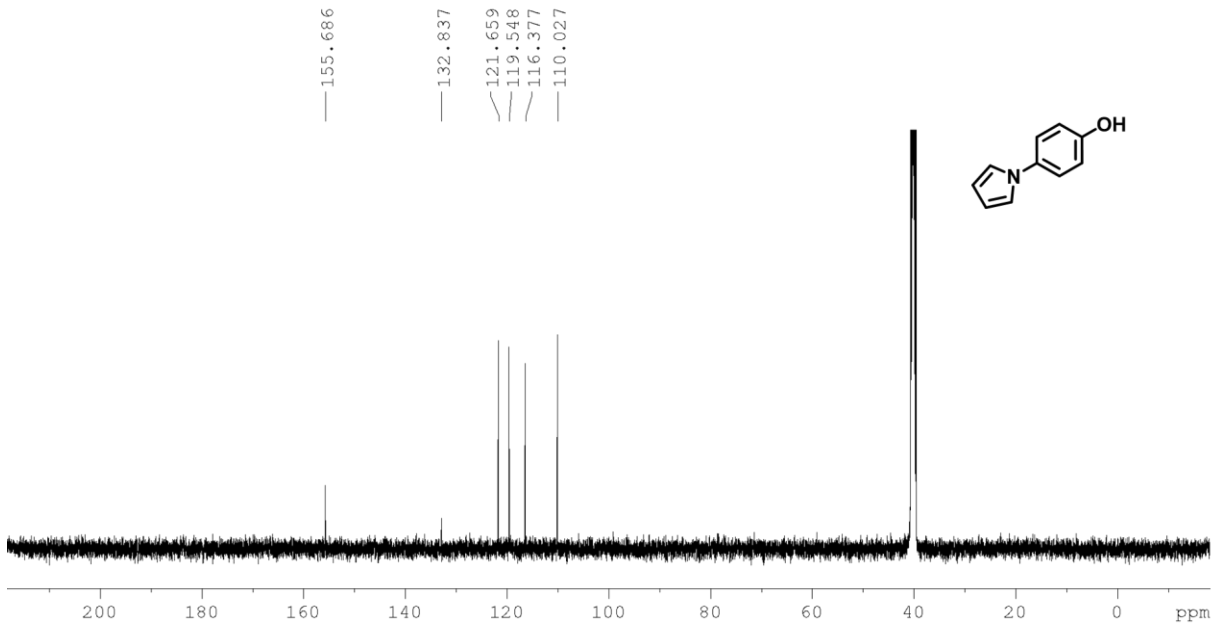
[13]C NMR (126 Hz, CD_3CN) spectrum of **1-benzyl-6-(4-(trifluoromethyl)phenyl)-1*H*-indole**



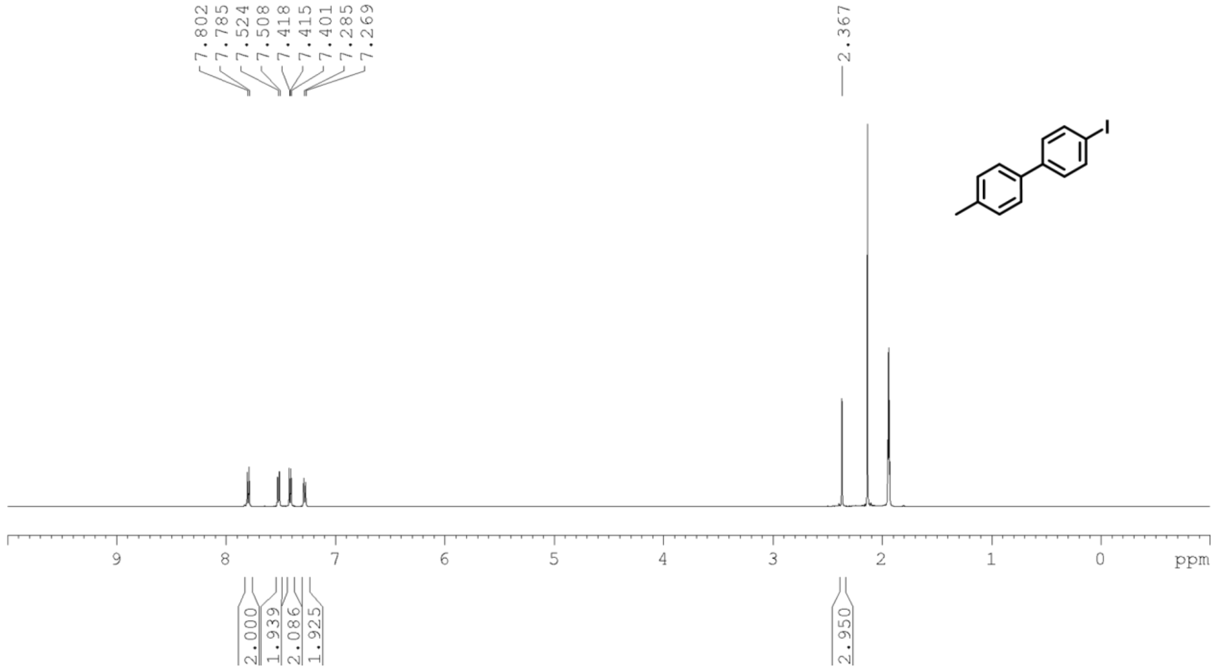
^{1}H NMR (500 Hz, d^{6}-DMSO) spectrum of **4-(1H-pyrrol-1-yl)-phenol**



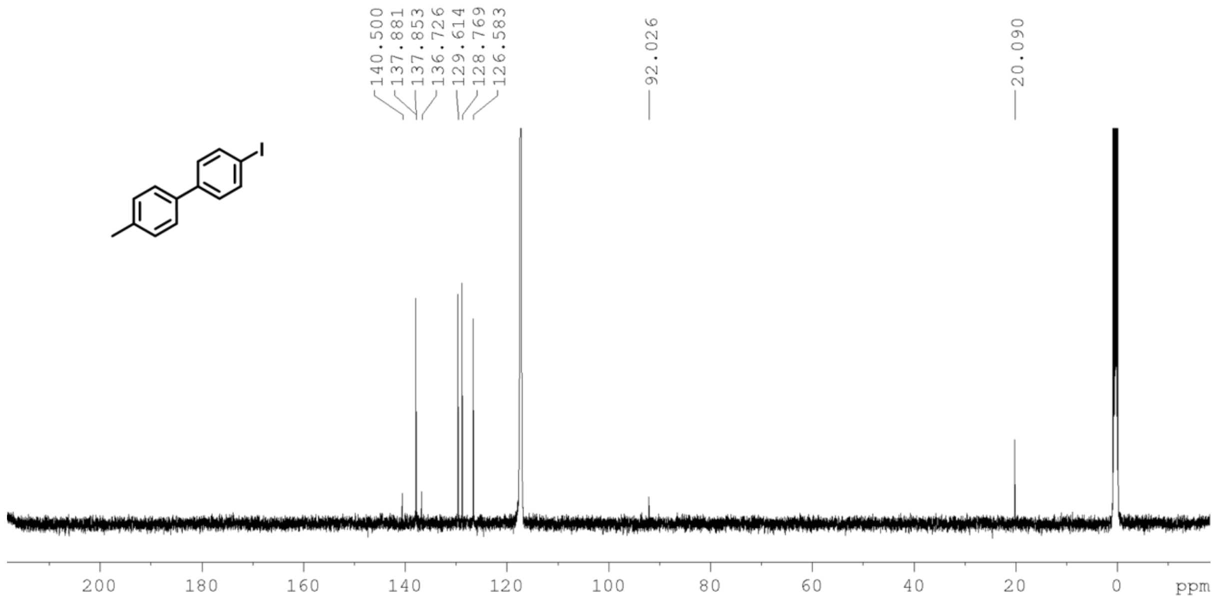
^{13}C NMR (126 Hz, d^{6}-DMSO) spectrum of **4-(1H-pyrrol-1-yl)-phenol**



[1]H NMR (500 Hz, CD_3CN) spectrum of **4-iodo-4'-methylbiphenyl**

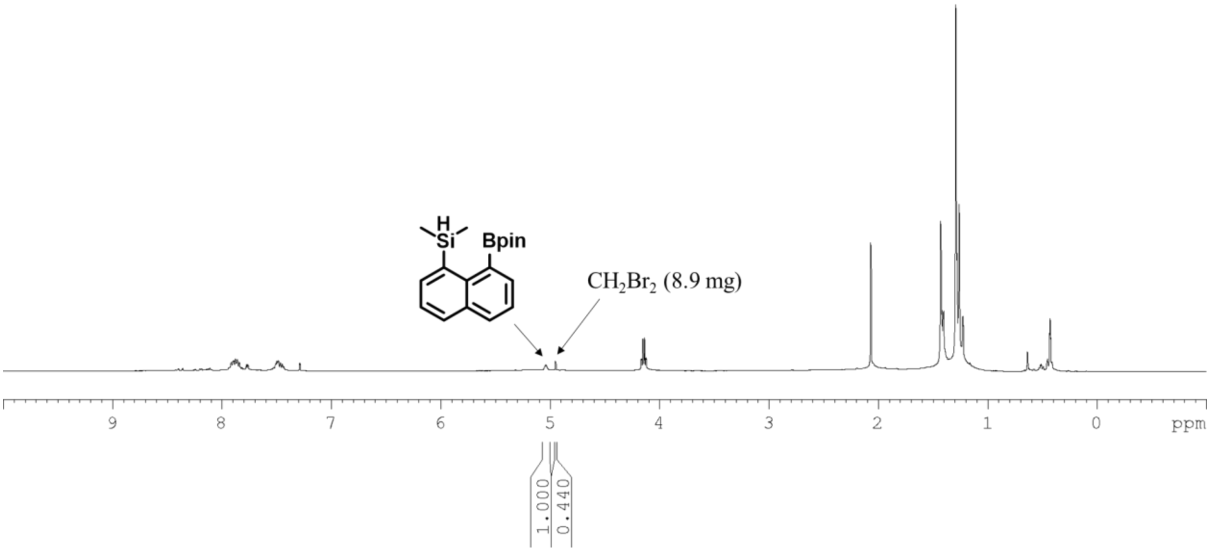


[13]C NMR (126 Hz, CD_3CN) spectrum of **4-iodo-4'-methylbiphenyl**



[1]H NMR (500 Hz, $CDCl_3$) spectrum for [1]H NMR yield of

dmethyl(8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-1-yl)silane



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