

Supporting Information

Rh(NHC)-Catalyzed O-Arylation of Aryl Bromides

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General Methods. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F₂₅₄ plates. Visualization on TLC was achieved by the use of UV light (254 nm). Flash column chromatography was undertaken on silica gel (60 F₂₅₄ 400-630 mesh). ¹H NMR was recorded on FT AM 400 (400 MHz) or FT AM 300 (300 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). ¹³C NMR was recorded on FT AM 400 (100 MHz) and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d*. Infrared (IR) spectra were recorded neat in 0.5 mm path length using a sodium chloride cell. Frequencies are given in reciprocal centimeters (cm⁻¹) and only selected absorbance is reported. High resolution mass spectra were obtained from the Korea Basic Science Institute (Daegu) by using EI method. Unless otherwise stated, all commercial reagents and solvents were used without additional purification.

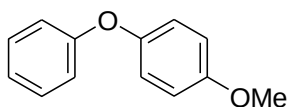
Experimental Procedures:

Preparation of Rh(cod)(NHC)Br. To a N₂ purged round bottom flask was added lithium *tert*-butoxide (235 mg, 2.95 mmol), [Rh(cod)Cl]₂ (600 mg, 1.22 mmol), and THF (20 mL). The mixture was vigorously stirred at room temperature for 30 min under nitrogen atmosphere. A solution of NHC ligand (2.44 mmol) in THF (5 mL) was then added to the Rh-containing solution via a cannula. The resulting solution was stirred for additional 5 h at room temperature under nitrogen atmosphere. Solvent was removed *in vacuo*, and the desired product was isolated by silica gel column chromatography.

Rh(cod)(*i*Pr₂-bimy)Br. 1,3-Diisopropylbenzimidazolium bromide (2.44 mmol) was used for the preparation of the title compound which was isolated by a column chromatography on silica gel (EtOAc/*n*-Hex, 1:3) as a light yellow crystalline solid (89%); ¹H NMR (400 MHz, CDCl₃) δ 7.49 (2H, m), 7.14 (2H, m), 6.36 (1H, m), 5.15 (2H, s), 3.49 (2H, s), 2.40 (4H, m), 2.00 (4H, m), 1.76 (2H, d, *J* = 7.1 Hz), 1.67 (2H, d, *J* = 6.9 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 194.1 (Rh-C, d, *J* = 48.9 Hz), 133.7, 121.4, 112.0, 98.6 (Rh-C, d, *J* = 6.0 Hz), 68.8 (Rh-C, d, *J* = 14.5 Hz), 53.7, 32.6, 28.9, 21.4, 20.6.

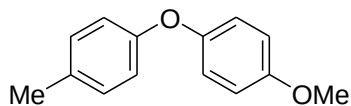
Experimental Procedure for the Optimization of Rh-Catalyzed O-Arylation Reaction (Table 1). To an oven-dried screwed vial were added bromobenzene (31 mg, 0.2 mmol), 4-methoxyphenol (37 mg, 0.3 mmol), sodium *tert*-butoxide (38 mg, 0.4 mmol), metal catalyst (indicated mol %), NHC ligand (indicated equiv if necessary), AgPF₆ (indicated equiv if necessary), and toluene (0.2 mL). The mixture was vigorously stirred at 100 °C and diluted with diethyl ether. The crude reaction mixture was filtered through a pad of silica gel and organic solvents were removed *in vacuo*.

Experimental Procedure for the O-Arylation of Aryl Bromides with Various Phenols (Table 2). To an oven-dried screwed vial were added bromoarenes (0.2 mmol), phenol (0.3 mmol), sodium *tert*-butoxide (38 mg, 0.4 mmol), Rh₂(OAc)₄ (3.2 mg, 3 mol %), *N,N*- dicyclohexylbenzimidazolium hexafluorophosphate (8 mg, 10 mol %), AgPF₆ (5 mg, 10 mol %) and toluene (0.2 mL). The mixture was vigorously stirred at 100 °C for 24 h and diluted with ethyl acetate. The crude reaction mixture was filtered through a pad of silica gel, and then organic solvents were removed *in vacuo* followed by silica gel column chromatography (ethyl acetate/*n*-hexane).



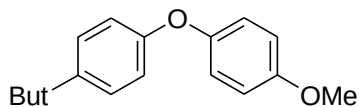
1-Methoxy-4-phenoxybenzene (3a, Table 2).¹

The title compound was purified by silica gel column chromatography (EtOAc/*n*-Hx, 1:10) as a colorless oil (36 mg, 90%); ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.26 (2H, m), 6.98-6.96 (1H, m), 6.94-6.92 (4H, m), 6.88-6.86 (2H, m), 3.79 (3H, s); ¹³C NMR (100 MHz, CDCl₃) δ 158.4, 155.8, 150.0, 129.5, 122.3, 120.8, 117.5, 114.8, 55.6.



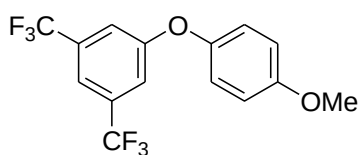
4-Methyl-4'-methoxy-diphenylether (3b, Table 2).²

The title compound was purified by silica gel column chromatography (EtOAc/*n*-Hx, 1:10) as a white solid (21 mg, 50%); ¹H NMR (400 MHz, CDCl₃) δ 7.14 (2H, d, *J* = 8.3 Hz), 7.00 (2H, d, *J* = 9.1 Hz), 6.91 (4H, m), 3.83 (3H, s), 2.36 (3H, s); ¹³C NMR (100 MHz, CDCl₃) δ 156.0, 155.6, 150.7, 132.0, 130.0, 120.2, 117.7, 114.7, 55.6, 20.5.



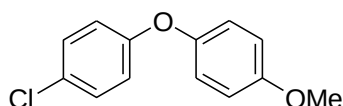
1-(4-*tert*-Butylphenoxy)-4-methoxybenzene (3c, Table 2).³

The title compound was purified by silica gel column chromatography (EtOAc/*n*-Hx, 1:10) as a colorless oil (25 mg, 50%); ¹H NMR (400 MHz, CDCl₃) δ 7.30 (2H, d, *J* = 8.7 Hz), 6.97 (2H, d, *J* = 9.0 Hz), 6.87 (4H, m), 3.78 (3H, s), 1.30 (9H, s); ¹³C NMR (100 MHz, CDCl₃) δ 156.0, 155.7, 150.5, 145.2, 126.3, 120.5, 117.1, 114.7, 55.6, 34.2, 31.4.



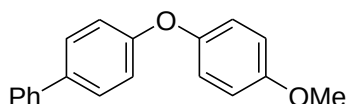
1-(4-Methoxyphenoxy)-3,5-bis(trifluoromethyl)benzene (3d, Table 2).

The title compound was purified by silica gel column chromatography (EtOAc/*n*-Hx, 1:10) as a colorless oil (49 mg, 74%); ¹H NMR (400 MHz, CDCl₃) δ 7.55 (1H, s), 7.35 (2H, m), 7.06-7.03 (2H, m), 7.00-6.97 (2H, m), 3.87 (3H, s); ¹³C NMR (100 MHz, CDCl₃) δ 159.7, 157.0, 147.9, 133.5 (q, ²*J*_{C-F} = 33.4 Hz), 127.0 (q, ¹*J*_{C-F} = 271.0 Hz), 121.4, 116.9, 115.6 (q, ³*J*_{C-F} = 3.6 Hz), 115.5, 55.6; IR (Film) ν 2840, 1616, 1506, 1374, 1278, 1187, 1133, 951, 838, 681 cm⁻¹; HRMS (EI+) *m/z* calcd. for C₁₅H₁₀F₆O₂ [M]⁺: 336.0587, found: 336.0585.



1-(4-Chlorophenoxy)-4-methoxybenzene (3e, Table 2).³

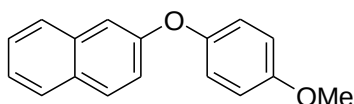
The title compound was purified by silica gel column chromatography (EtOAc/*n*-Hx, 1:10) as a white solid (39 mg, 83%); ¹H NMR (400 MHz, CDCl₃) δ 7.23 (2H, d, *J* = 8.8 Hz), 6.95 (2H, m), 6.88 (4H, m), 3.78 (3H, s); ¹³C NMR (100 MHz, CDCl₃) δ 157.2, 156.1, 149.7, 129.5, 127.3, 120.8, 118.7, 114.9, 55.6.



4-(4-Methoxyphenoxy)biphenyl (3f, Table 2).

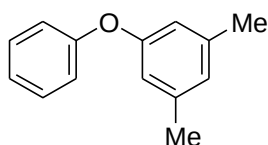
The title compound was purified by silica gel column chromatography (EtOAc/*n*-Hx, 1:10) as a

white solid (33 mg, 60%); m.p. 110-112 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.57-7.48 (4H, m), 7.42-7.38 (2H, m), 7.31-7.28 (1H, m), 7.03-6.97 (4H, m), 6.91-6.87 (2H, m), 3.80 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 158.1, 156.0, 150.0, 140.6, 135.5, 128.7, 128.2, 126.8, 126.8, 120.9, 117.7, 114.9, 55.6; IR (Film) ν 2837, 1509, 1407, 1315, 1246, 1103, 1034, 835, 769, 692 cm^{-1} ; HRMS (EI+) m/z calcd. for $\text{C}_{19}\text{H}_{16}\text{O}_2$ $[\text{M}]^+$: 276.1147, found: 276.1147.



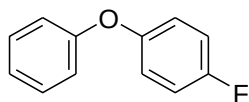
2-(4-Methoxyphenoxy)naphthalene (3g, Table 2).³

The title compound was purified by silica gel column chromatography (EtOAc/*n*-Hex, 1:10) as a white solid (40 mg, 80%); ^1H NMR (400 MHz, CDCl_3) δ 7.80 (2H, d, J = 9.0 Hz), 7.66 (1H, d, J = 8.0 Hz), 7.42 (2H, m), 7.26 (1H, m), 7.18 (1H, m), 7.06 (2H, d, J = 8.9 Hz), 6.92 (2H, d, J = 9.0 Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 156.4, 156.0, 140.0, 134.3, 129.7, 127.6, 126.9, 126.4, 124.3, 121.0, 119.3, 114.9, 112.2, 55.6.



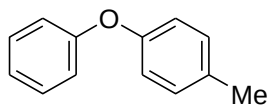
3,5-Dimethylphenyl phenyl ether (3h, Table 2).³

The title compound was purified by silica gel column chromatography (EtOAc/*n*-Hex, 1:10) as a colorless oil (30 mg, 75%); ^1H NMR (400 MHz, CDCl_3) δ 7.34 (2H, m), 7.10 (1H, m), 7.01 (2H, m), 6.74 (1H, s), 6.65 (1H, s), 2.28 (6H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 157.4, 157.1, 139.5, 129.6, 124.9, 122.9, 118.8, 116.5, 21.2.



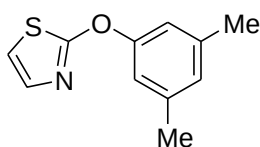
1-Fluoro-4-phenoxybenzene (3i, Table 2).⁴

The title compound was purified by silica gel column chromatography (EtOAc/*n*-Hex, 1:10) as a yellow oil (14 mg, 38%); ^1H NMR (400 MHz, CDCl_3) δ 7.32 (2H, m), 7.01 (7H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 160.0, 157.6, 152.8, 129.7, 123.1, 120.5, 118.2, 116.3.



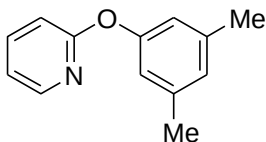
4-Methyl-diphenylether (3j, Table 2).²

The title compound was purified by silica gel column chromatography (EtOAc/*n*-Hx, 1:10) as a colorless oil (25 mg, 70%); ¹H NMR (400 MHz, CDCl₃) δ 7.32 (2H, t, *J* = 7.5 Hz), 7.13 (2H, d, *J* = 8.1 Hz), 7.05 (1H, m), 6.98 (2H, d, *J* = 7.7 Hz), 6.92 (2H, d, *J* = 8.3 Hz), 2.32 (3H, s); ¹³C NMR (100 MHz, CDCl₃) δ 157.8, 154.7, 132.8, 130.2, 129.6, 122.7, 119.1, 118.3, 20.6.



2-(3,5-Dimethylphenoxy)thiazole (3k, Table 2).

The title compound was purified by silica gel column chromatography (EtOAc/*n*-Hx, 1:10) as a colorless oil (29 mg, 70%); ¹H NMR (400 MHz, CDCl₃) δ 7.23 (1H, d, *J* = 3.7 Hz), 6.86 (3H, s), 6.77 (1H, d, *J* = 3.8 Hz), 2.31 (6H, s); ¹³C NMR (100 MHz, CDCl₃) δ 155.4, 139.8, 137.6, 127.5, 117.7, 112.6, 21.2; IR (Film) ν 2919, 1617, 1593, 1516, 1460, 1291, 1222, 1132, 940, 850 cm⁻¹; HRMS (EI+) *m/z* calcd. for C₁₁H₁₁NOS [M]⁺: 205.0561, found: 205.0561.

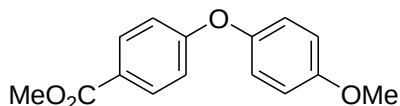


2-(3,5-Dimethyl-phenoxy)-pyridine (3l, Table 2).⁵

The title compound was purified by silica gel column chromatography (EtOAc/*n*-Hx, 1:10) as a pale yellow solid (32 mg, 80%); ¹H NMR (400 MHz, CDCl₃) δ 8.19 (1H, d, *J* = 1.9 Hz), 7.64-7.62 (1H, m), 6.96-6.94 (1H, m), 6.86 (2H, t, *J* = 7.6 Hz), 6.73 (2H, s), 2.30 (6H, s); ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 154.0, 147.8, 139.4, 139.2, 126.4, 118.7, 118.1, 111.4, 21.2.

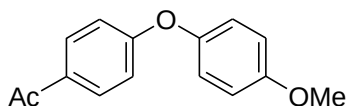
Experimental Procedure for the O-Arylation using Cs₂CO₃ as a Mild Base (Table 3). To an oven-dried screwed vial were added bromoarene (0.2 mmol), phenols (0.3 mmol), cesium carbonate (130 mg, 0.4 mmol), Rh(cod)(*i*Pr-bimy)Br (4.5 mg, 5 mol %), AgSbF₆ (7 mg, 10 mol %), toluene (0.2 mL), and Et₃N (0.2 mL). The mixture was vigorously stirred at 100 °C for 24 h and diluted with ethyl acetate. The crude reaction mixture was filtered through a pad of

silica gel and organic solvents were removed *in vacuo*, and then it was purified by silica gel column chromatography (ethyl acetate/*n*-hexane).



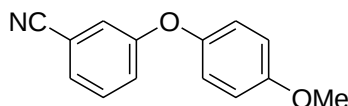
Methyl 4-(4-methoxyphenoxy)benzoate (3m, Table 3).⁶

The title compound was purified by silica gel column chromatography (EtOAc/*n*-Hx, 1:10) as a white solid (46 mg, 90%); ¹H NMR (400 MHz, CDCl₃) δ 7.96 (2H, d, *J* = 8.8 Hz), 7.00 (2H, d, *J* = 9.0 Hz), 6.91-6.88 (4H, m), 3.86 (3H, s), 3.80 (3H, s); ¹³C NMR (100 MHz, CDCl₃) δ 166.6, 162.7, 156.6, 148.5, 131.5, 123.8, 121.6, 116.2, 115.0, 55.6, 51.9.



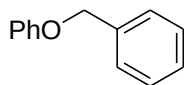
1-[4-(4-Methoxy-phenoxy)-phenyl]-ethanone (3n, Table 3).⁷

The title compound was purified by silica gel column chromatography (EtOAc/*n*-Hx, 1:5) as a colorless oil (41 mg, 85%); ¹H NMR (400 MHz, CDCl₃) δ 7.90 (2H, d, *J* = 8.8 Hz), 7.00 (2H, d, *J* = 9.0 Hz), 6.92-6.88 (4H, m), 3.80 (3H, s), 2.55 (3H, s); ¹³C NMR (100 MHz, CDCl₃) δ 196.6, 162.9, 156.6, 148.4, 131.3, 130.5, 121.6, 116.3, 115.0, 55.6, 26.3.



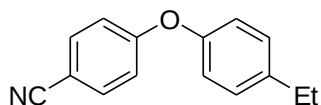
3-(4-Methoxyphenoxy)benzonitrile (3o, Table 3).

The title compound was purified by silica gel column chromatography (EtOAc/*n*-Hx, 1:10) as a white solid (34 mg, 77%); m.p. 55-57 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.33 (1H, m), 7.29-7.26 (1H, m), 7.16-7.13 (1H, m), 7.11-7.10 (1H, m), 6.97-6.94 (2H, m), 6.92-6.89 (2H, m), 3.80 (3H, s); ¹³C NMR (100 MHz, CDCl₃) δ 159.1, 156.7, 148.3, 130.4, 125.7, 121.7, 121.4, 119.9, 118.3, 115.1, 113.3, 55.6; IR (Film) ν 2836, 2232, 1578, 1505, 1480, 1321, 1241, 1204, 1104, 944 cm⁻¹; HRMS (EI+) *m/z* calcd. for C₁₄H₁₁NO₂ [M]⁺: 225.0791, found: 225.0790.



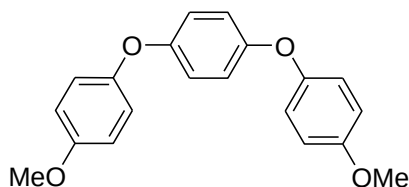
Benzyl phenyl ether (3p, Table 3).⁸

To an oven-dried screwed vial were added bromoarene (0.3 mmol), phenols (0.2 mmol), cesium carbonate (130 mg, 0.4 mmol), Rh(cod)(iPr-bimy)Br (4.5 mg, 5 mol %), AgSbF₆ (7 mg, 10 mol %), toluene (0.2 mL), and Et₃N (0.2 mL). The title compound was purified by silica gel column chromatography (EtOAc/*n*-Hex, 1:10) as a white solid (22 mg, 60%); ¹H NMR (400 MHz, CDCl₃) δ 7.43-7.41 (2H, m), 7.37-7.30 (2H, m), 7.28-7.23 (3H, m), 6.98-6.95 (3H, m), 5.05 (2H, s); ¹³C NMR (100 MHz, CDCl₃) δ 158.7, 137.0, 129.4, 128.5, 127.9, 127.4, 120.9, 114.8, 69.8.



4-(4-Ethylphenoxy)benzonitrile (3q, Table 3).

The title compound was purified by silica gel column chromatography (EtOAc/*n*-Hex, 1:10) as a pale yellow oil (31 mg, 70%); ¹H NMR (400 MHz, CDCl₃) δ 7.57-7.54 (2H, m), 7.23-7.20 (2H, m), 6.98-6.94 (4H, m), 2.67 (2H, q, *J* = 7.6), 1.25 (3H, m, *J* = 7.5 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 162.0, 152.4, 141.2, 134.0, 129.4, 120.3, 118.9, 117.5, 105.4, 28.2, 15.6; IR (Film) ν 2966, 2872, 2226, 1597, 1499, 1455, 1416, 1286, 1249, 1201, 874, 835, 544 cm⁻¹; HRMS (EI+) *m/z* calcd. for C₁₅H₁₃NO [M]⁺: 208.0757, found: 223.0997.

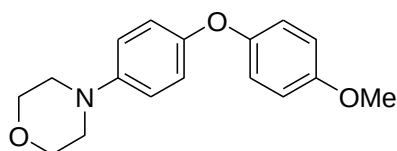


1,4-Bis(4-methoxyphenoxy)benzene (3r, Table 3).

To an oven-dried screwed vial were added bromoarene (0.2 mmol), phenols (0.6 mmol), cesium carbonate (260 mg, 0.8 mmol), Rh(cod)(iPr-bimy)Br (9.0 mg, 5 mol %), AgSbF₆ (14 mg, 10 mol %), toluene (0.4 mL), and Et₃N (0.4 mL). The title compound was purified by silica gel column chromatography (EtOAc/*n*-Hex, 1:10) as a white solid (32 mg, 50%); m.p. 130-132 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.96-6.94 (4H, m), 6.88 (4H, s), 6.87-6.83 (4H, m), 3.77 (6H, s); ¹³C NMR (100 MHz, CDCl₃) δ 155.6, 153.3, 150.9, 120.0, 119.1, 114.7, 55.6; IR (Film) ν 2966, 2838, 1877, 1511, 1301, 1245, 1192, 1180, 1154, 1032, 842, 831, 588 cm⁻¹; HRMS (EI+) *m/z* calcd. for C₂₀H₁₈O₄ [M]⁺: 322.1205, found: 322.1205.

Experimental Procedure for Tandem C-O, C-N Bond Formations (Scheme 2). To an oven-dried screwed vial were added 4-bromochlorobenzene (76 mg, 0.4 mmol), 4-

methoxyphenol (74 mg, 0.6 mmol), cesium carbonate (260 mg, 0.8 mmol), Rh(cod)(iPr-bimy)br (9 mg, 5 mol %), AgSbF₆ (14 mg, 10 mol %), Et₃N (0.4 mL) and toluene (0.4 mL). The mixture was vigorously stirred at 100 °C for 24 h and diluted with diethyl ether. The crude reaction mixture was filtered through a pad of silica gel and organic solvents were removed *in vacuo*, and then it was purified by silica gel column chromatography (EtOAc/*n*-Hx, 1:10). After this purification procedure, product **3e** was obtained as a white solid (70 mg, 75%). To an oven-dried screwed vial were added **3e**, morpholine (78 mg, 0.9 mmol), cesium carbonate (195 mg, 0.6 mmol), Rh(cod)(iPr)Cl (2.4 mg, 2 mol %), AgBF₄ (2.3 mg, 4 mol %), and 1,2-dimethoxyethane (0.3 mL). The mixture was vigorously stirred at 90 °C for 12 h and diluted with diethyl ether. The crude reaction mixture was filtered through a pad of silica gel and organic solvents were removed *in vacuo*, and then it was purified by silica gel column chromatography (EtOAc/*n*-Hx, 1:2). After this purification procedure, desired product was obtained as a white solid (48 mg, 57%).



4-(4-(4-Methoxyphenoxy)phenyl)morpholine (Scheme 2).

m.p. 81-83 °C; ¹H NMR (400 MHz, CDCl₃) δ 6.91-6.81 (8H, m), 3.85 (4H, m), 3.77 (3H, s), 3.08 (4H, m); ¹³C NMR (100 MHz, CDCl₃) δ 155.3, 151.6, 151.3, 147.1, 119.6, 119.1, 117.3, 114.6, 66.9, 55.6, 50.2; IR (Film) ν 3044, 2968, 2824, 1589, 1497, 1497, 1215, 1199, 1118, 92, 824 cm⁻¹; HRMS (EI⁺) m/z calcd. for C₁₇H₁₉NO₃ [M]⁺: 285.1361, found: 285.1365.

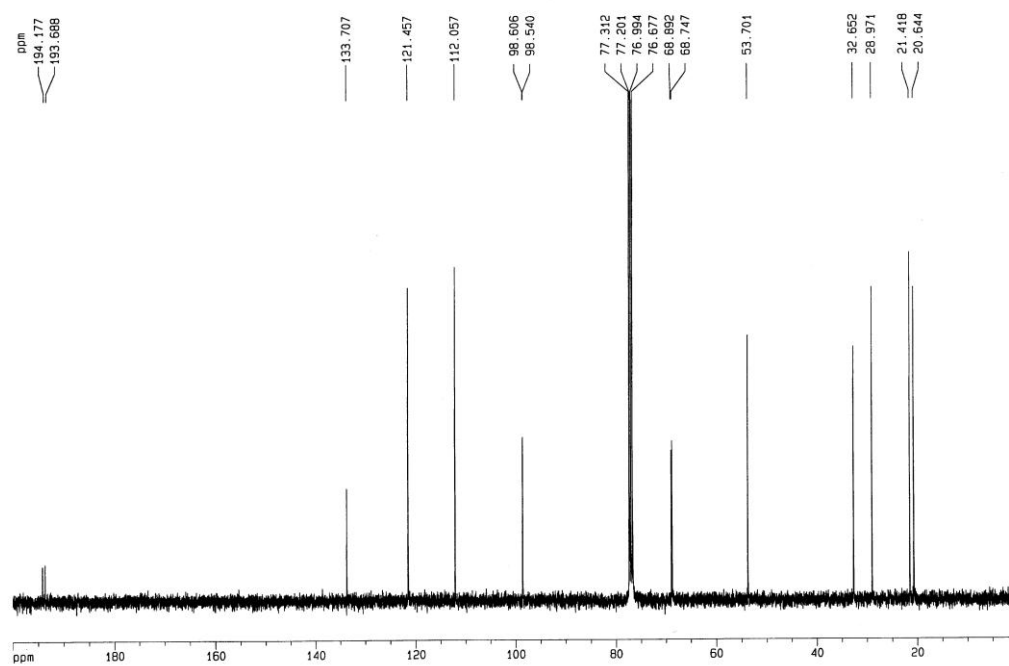
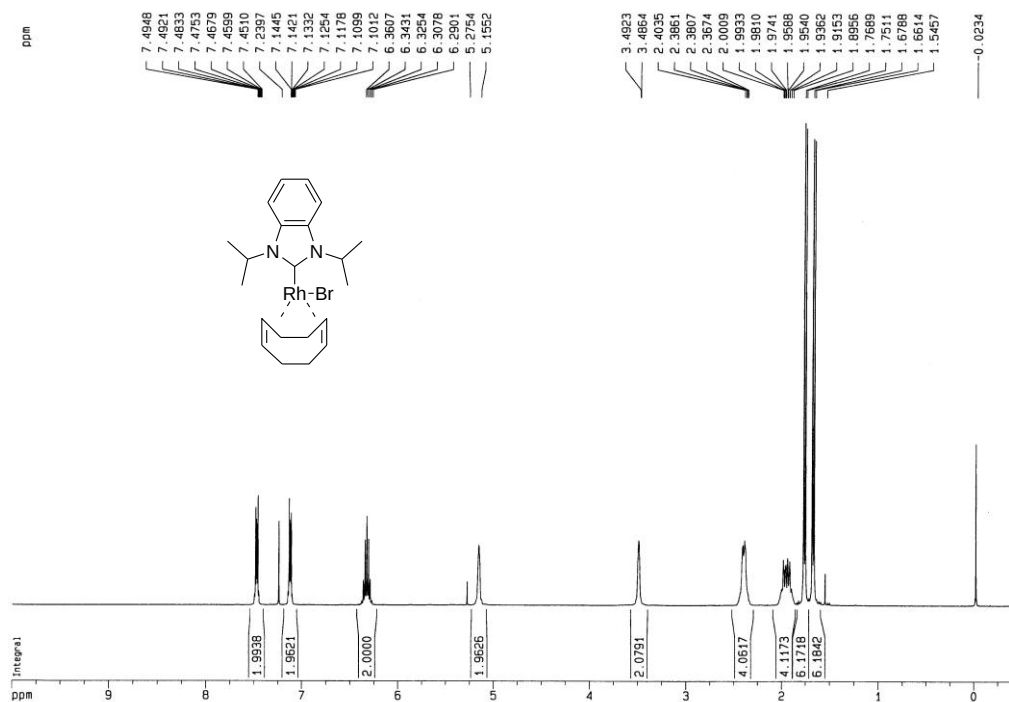
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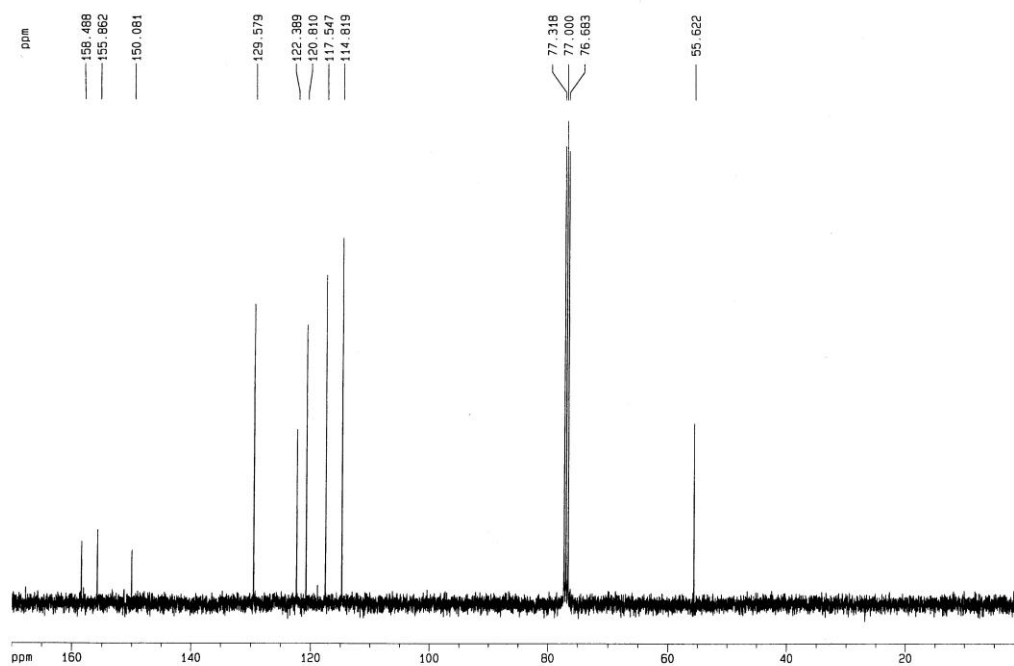
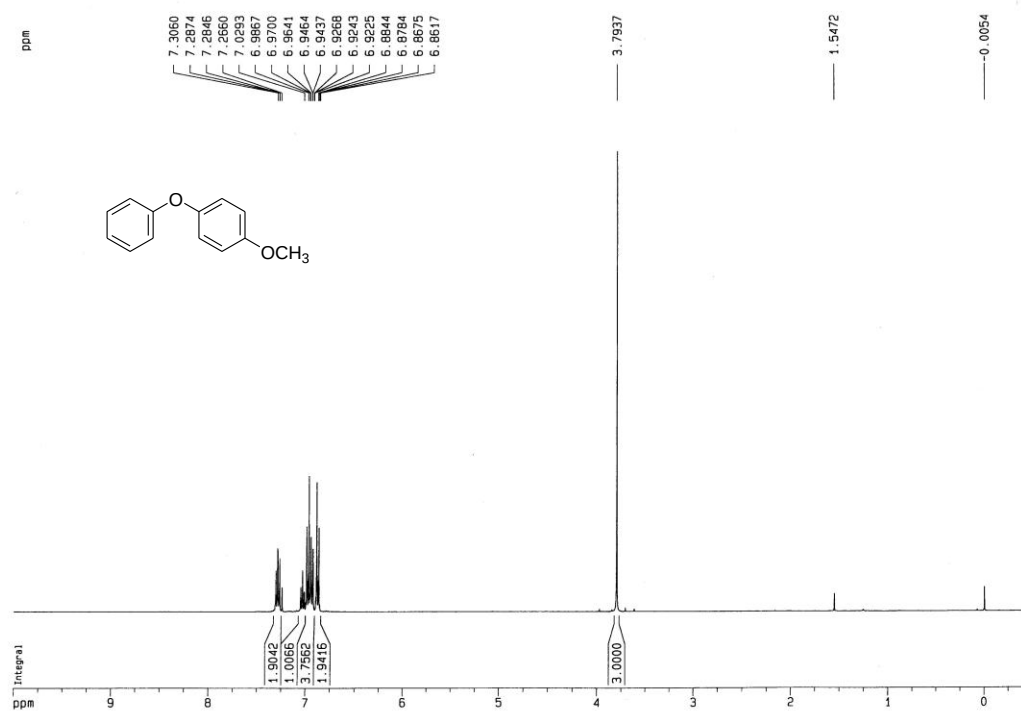
Appendix I

Spectral Copies of ^1H and ^{13}C NMR of Compounds Obtained in this Study

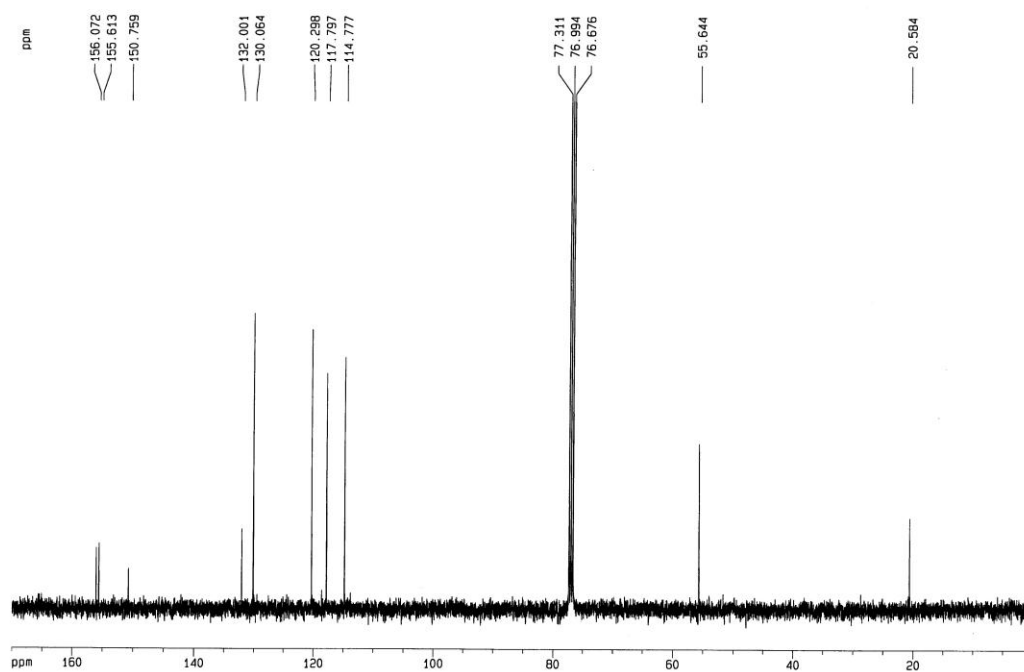
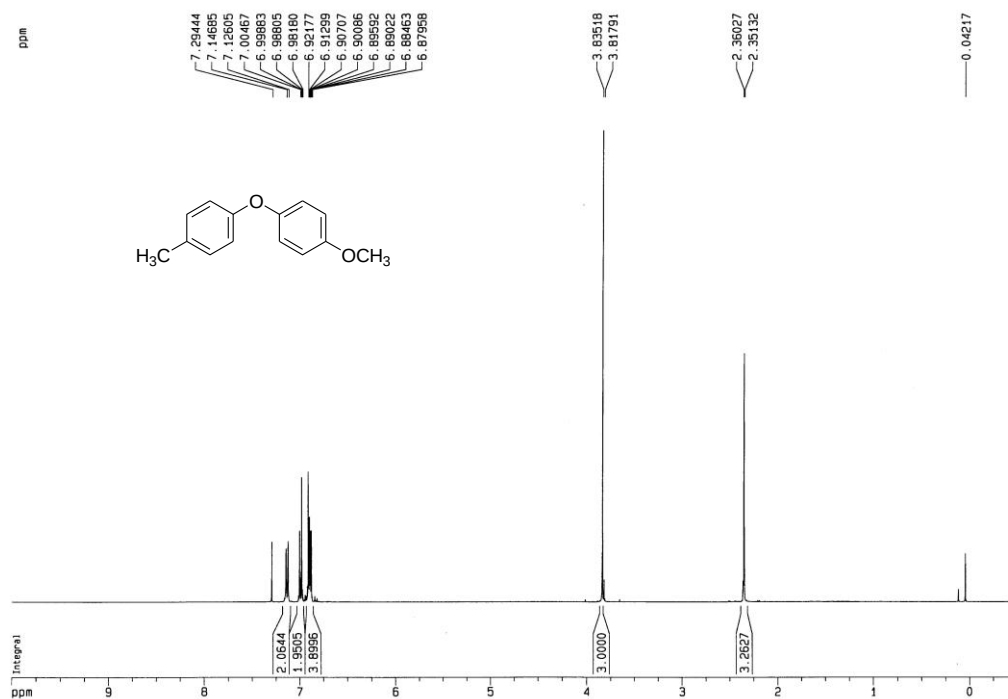
Rh(cod)(iPr-bimy)Br



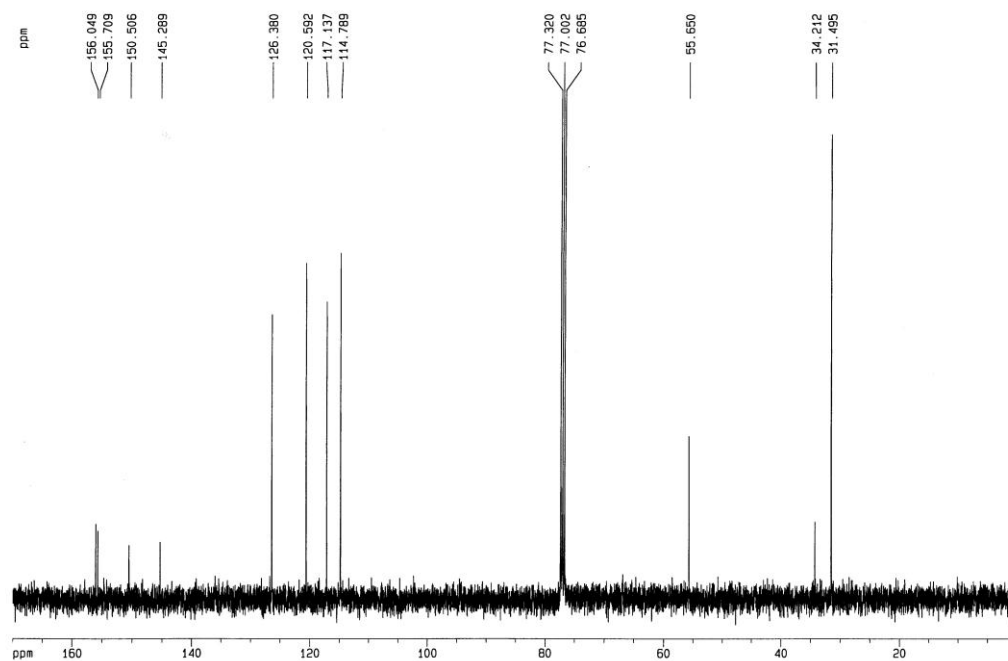
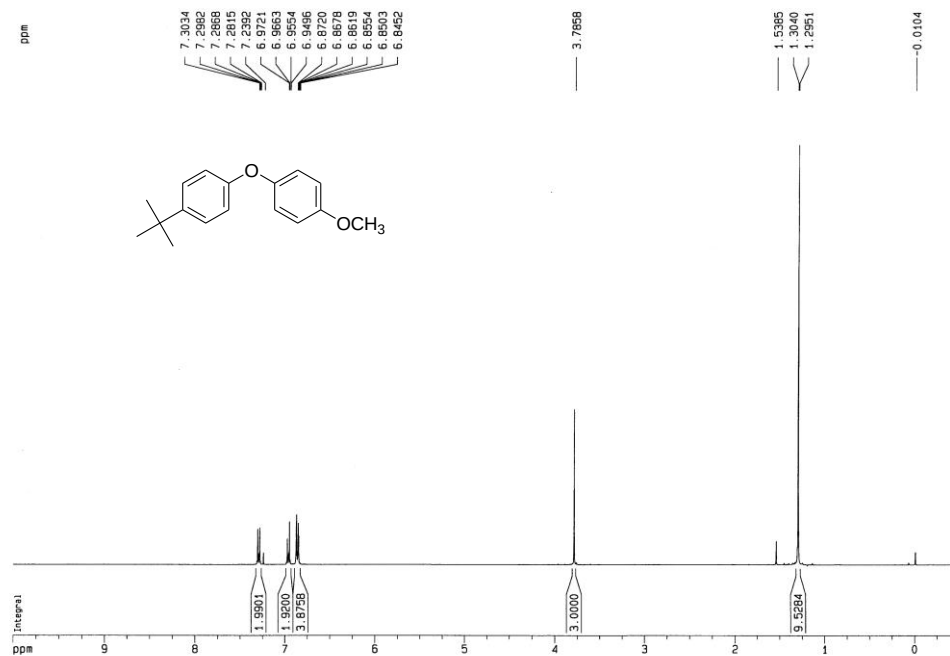
1-Methoxy-4-phenoxybenzene (3a, Table 2)



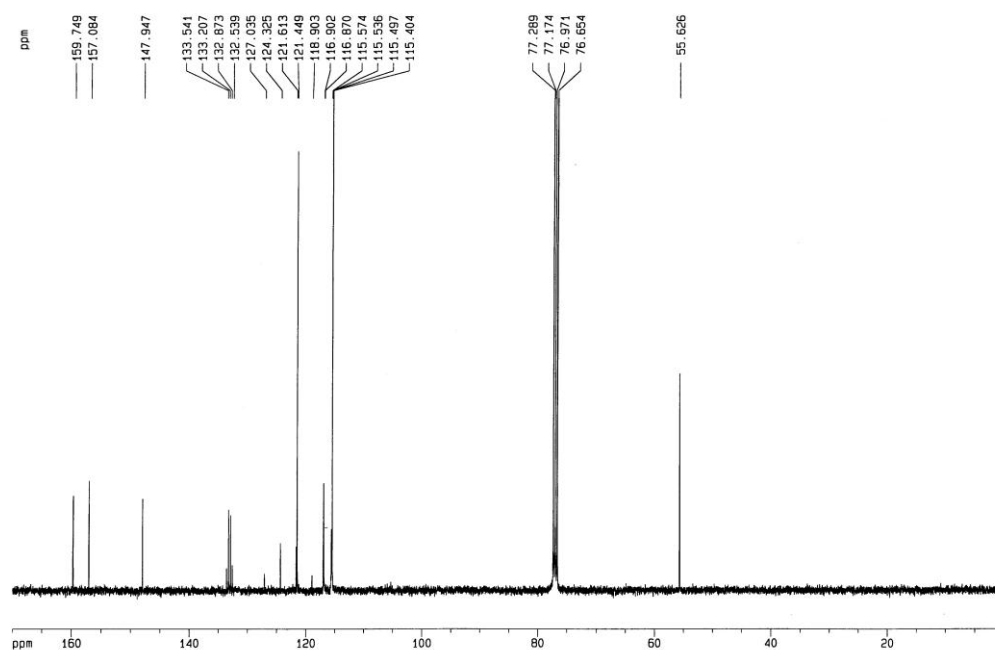
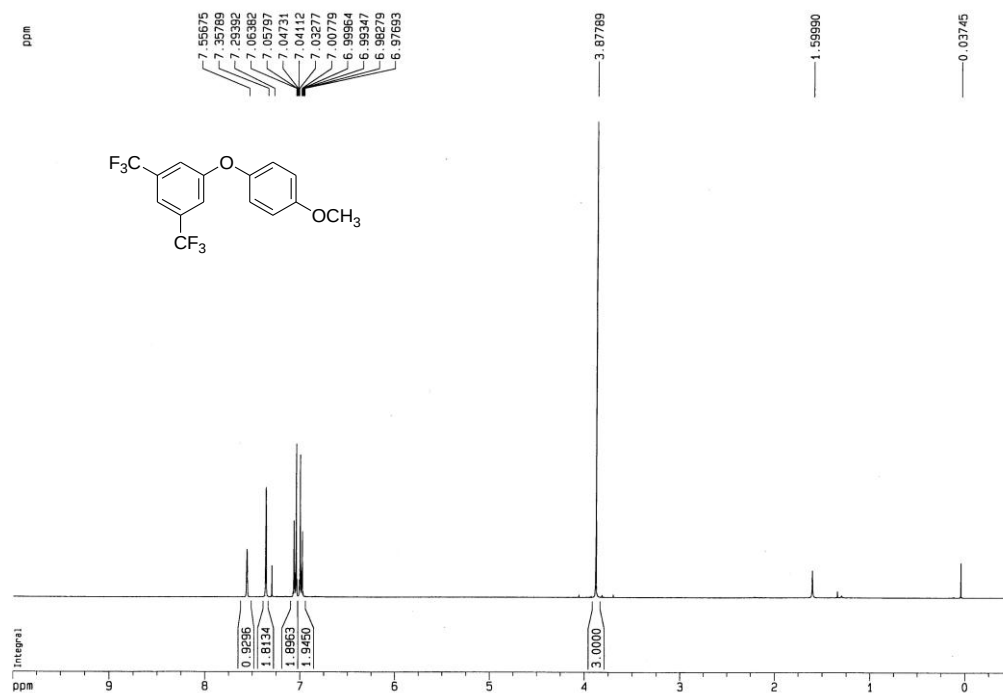
4-Methyl-4'-methoxy-diphenylether (**3b**, Table 2)



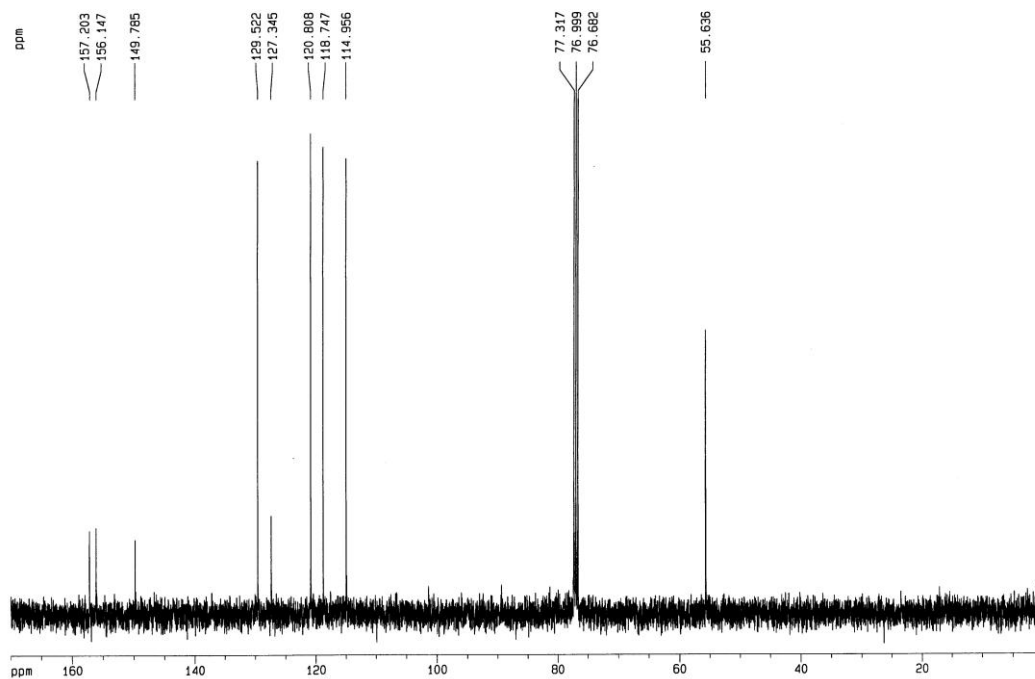
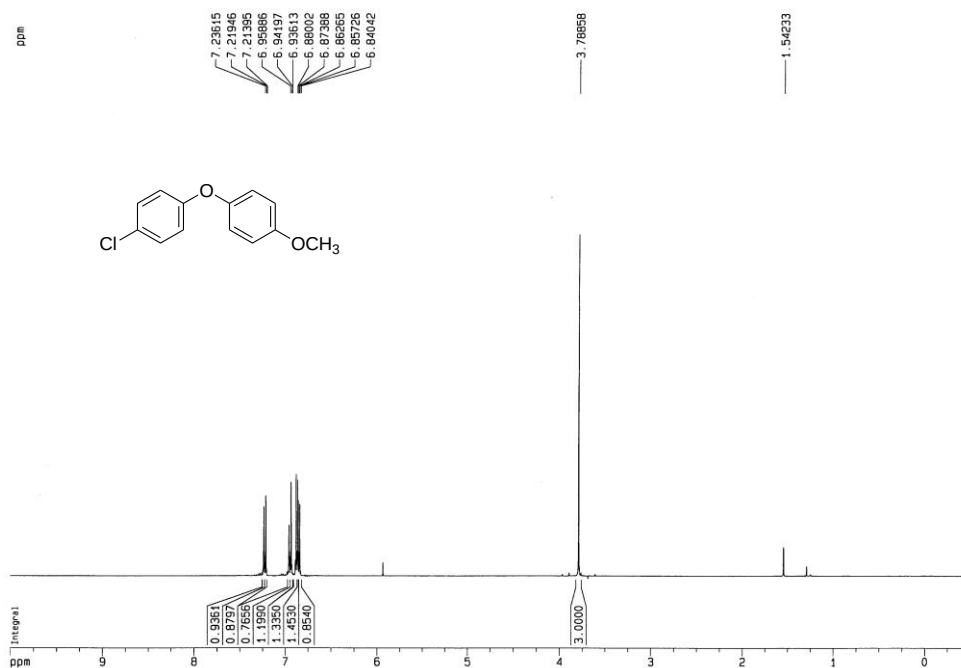
1-(4-*tert*-Butylphenoxy)-4-methoxybenzene (3c, Table 2)



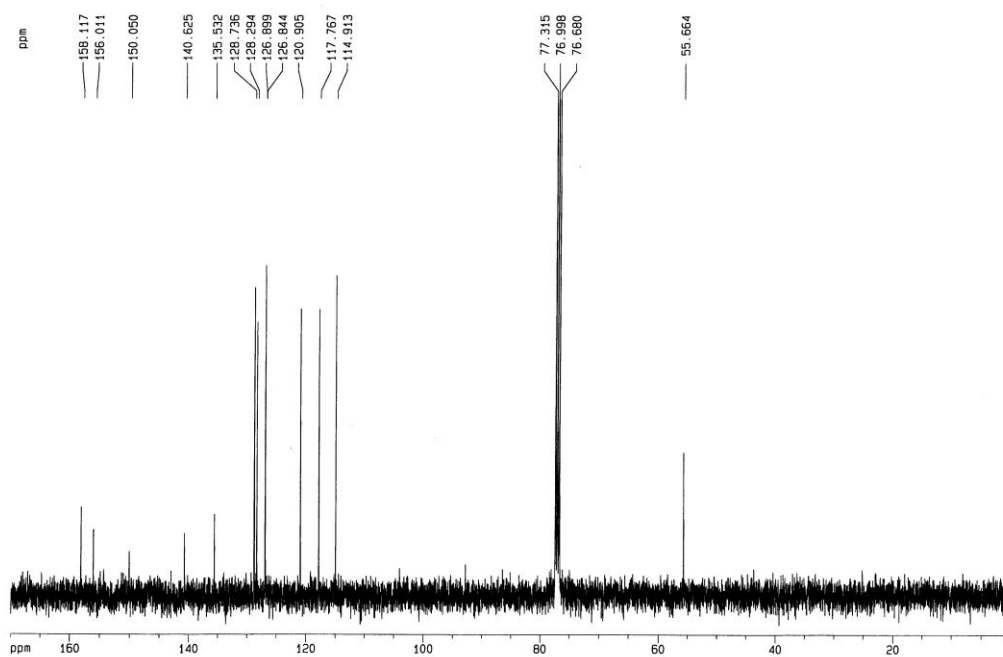
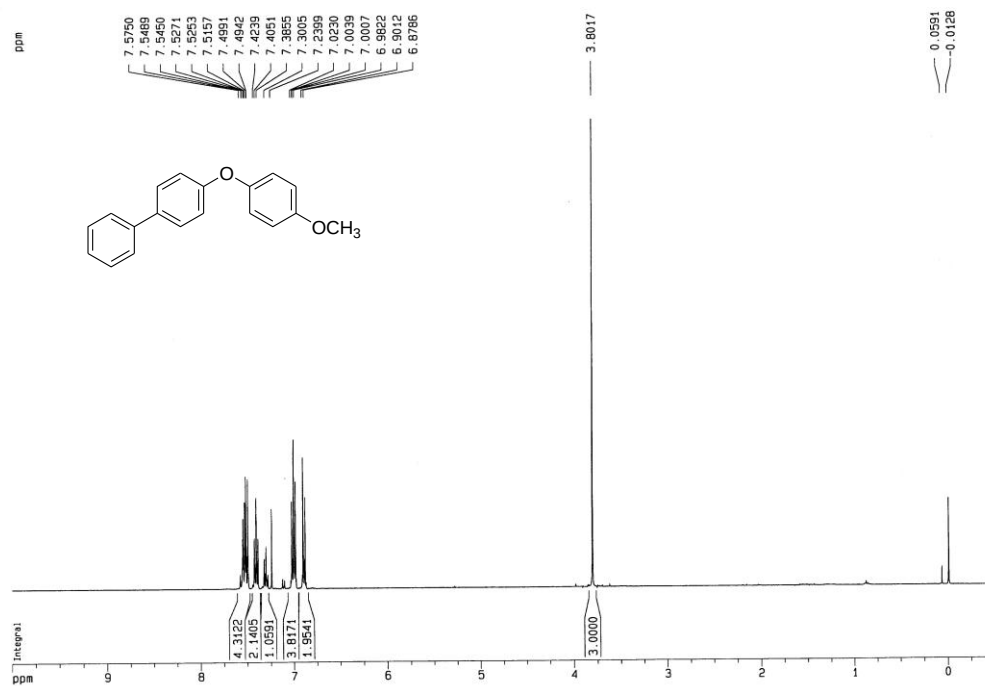
1-(4-Methoxyphenoxy)-3,5-bis(trifluoromethyl)benzene (3d, Table 2)



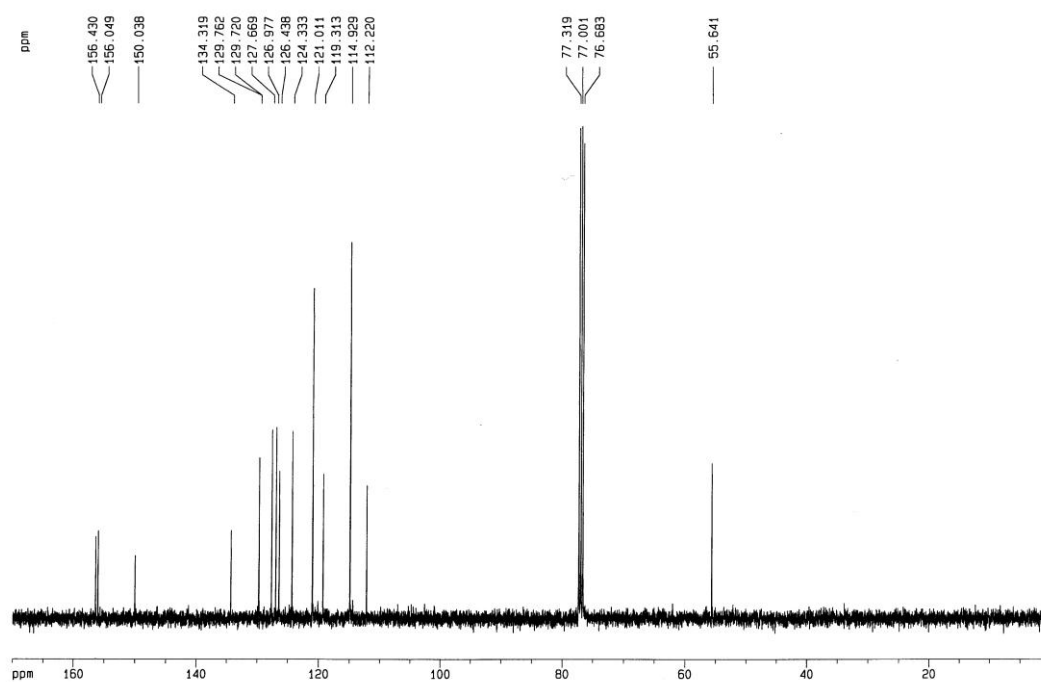
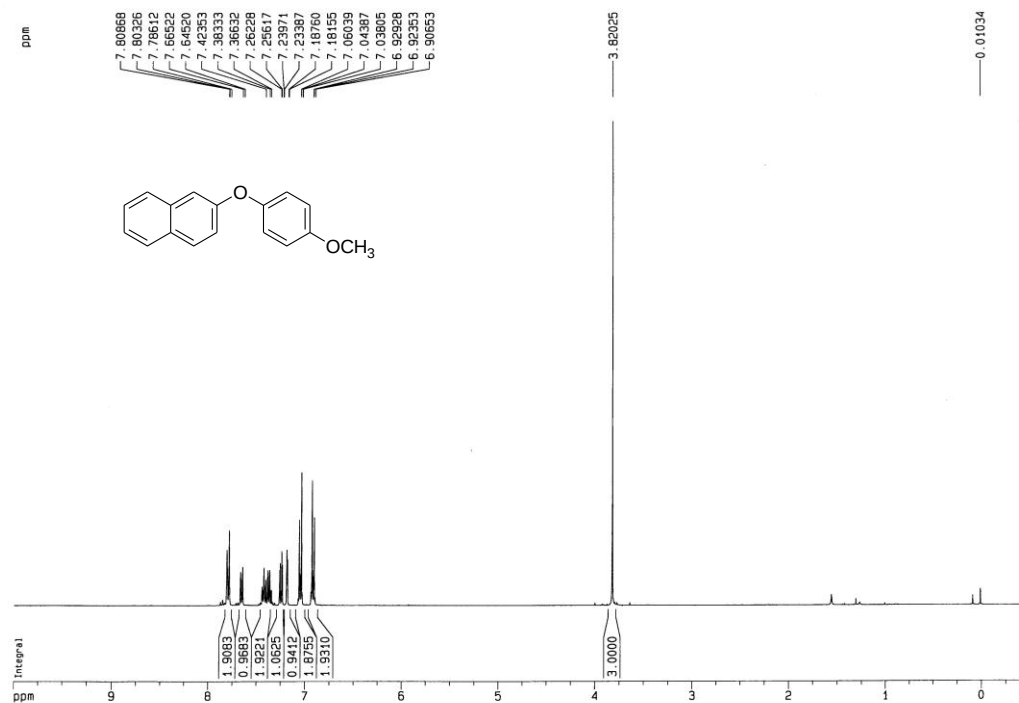
1-(4-Chlorophenoxy)-4-methoxybenzene (3e, Table 2)



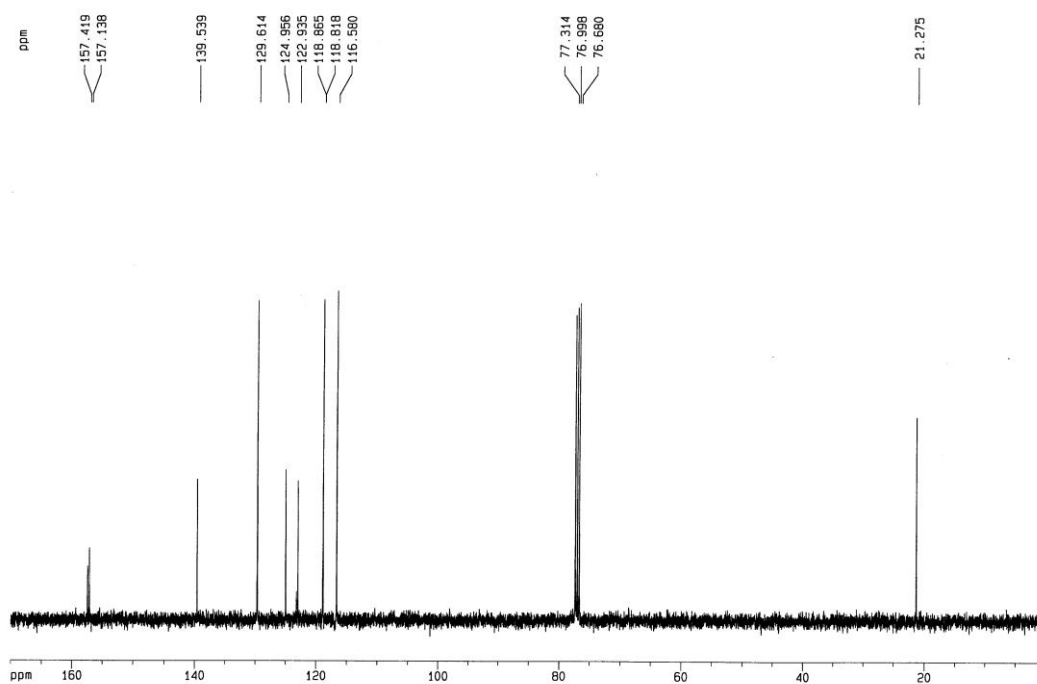
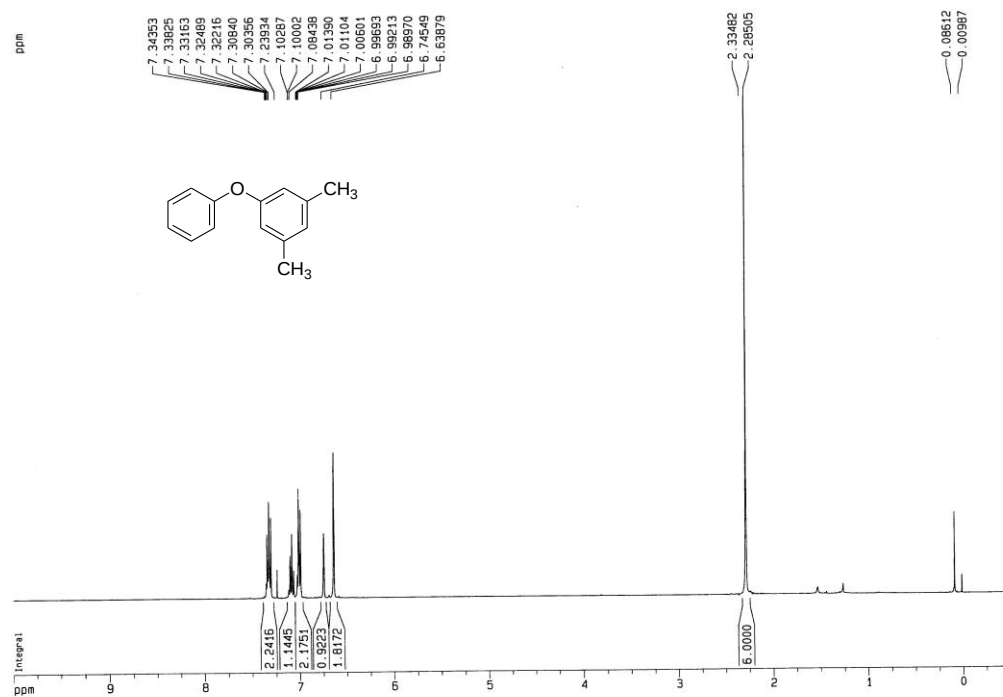
4-(4-Methoxyphenoxy)biphenyl (3f, Table 2)



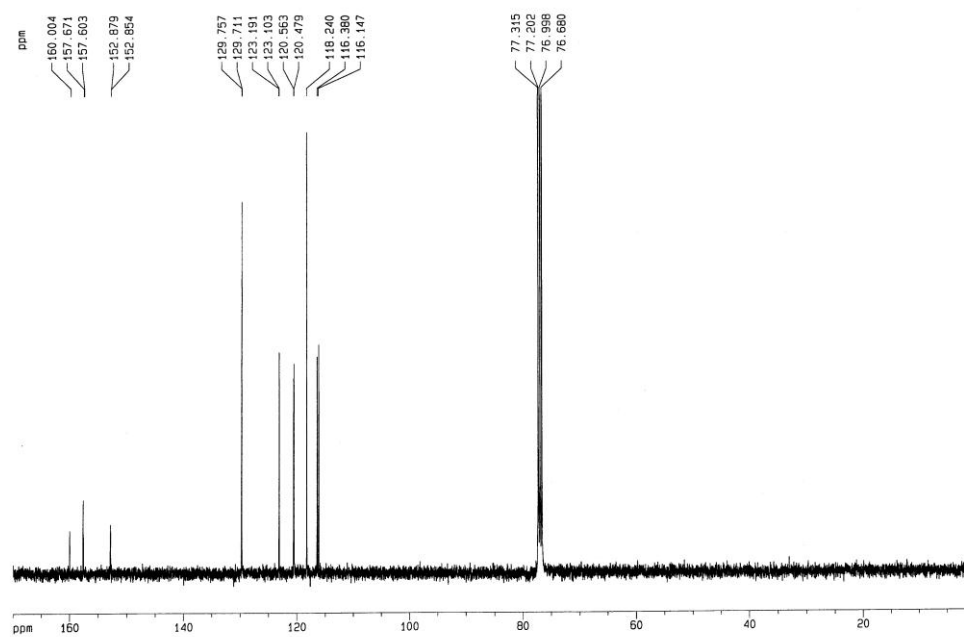
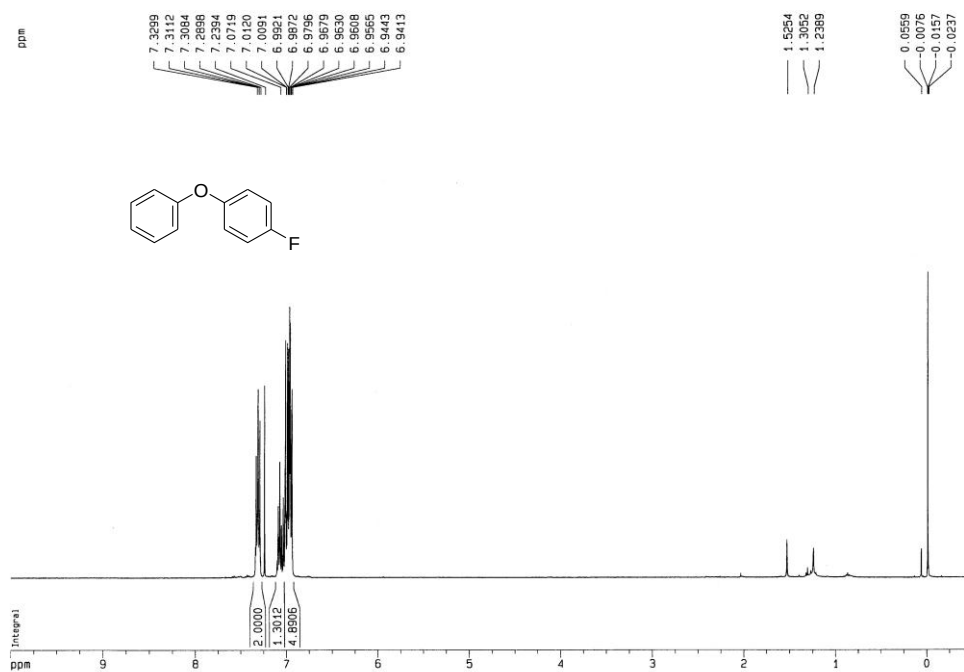
2-(4-Methoxyphenoxy)naphthalene (3g, Table 2)



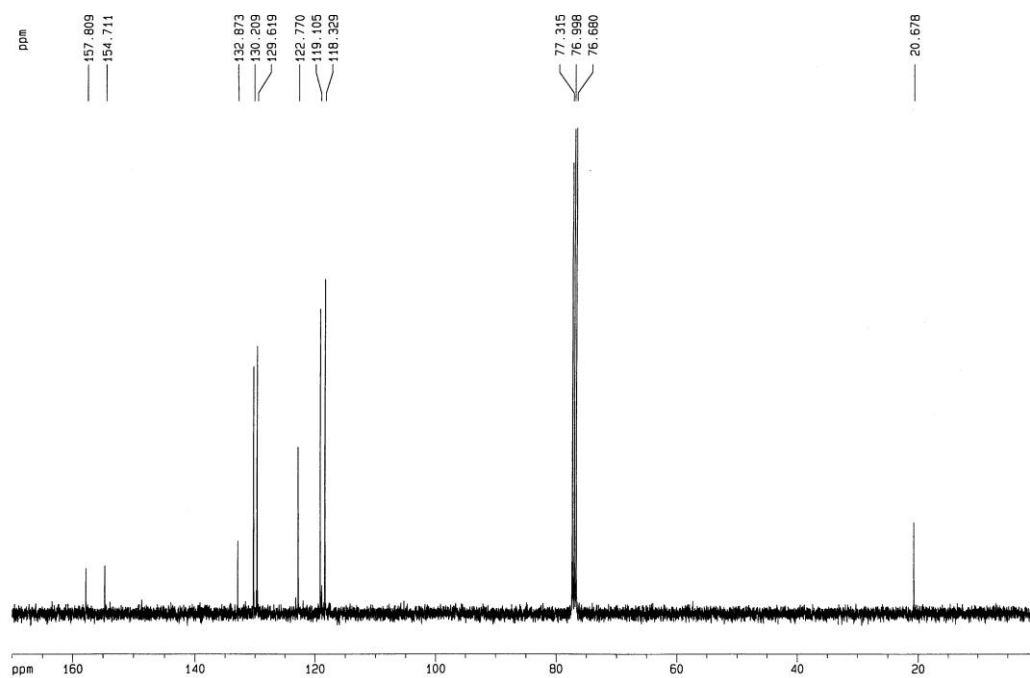
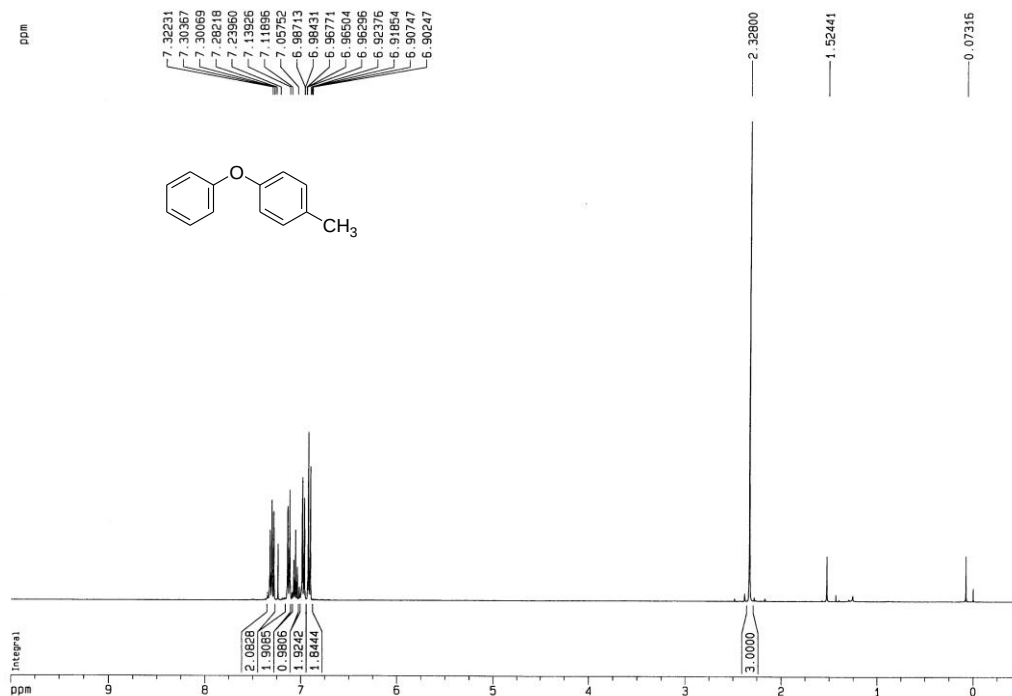
3, 5-Dimethylphenyl phenyl ether (3h, Table 2)



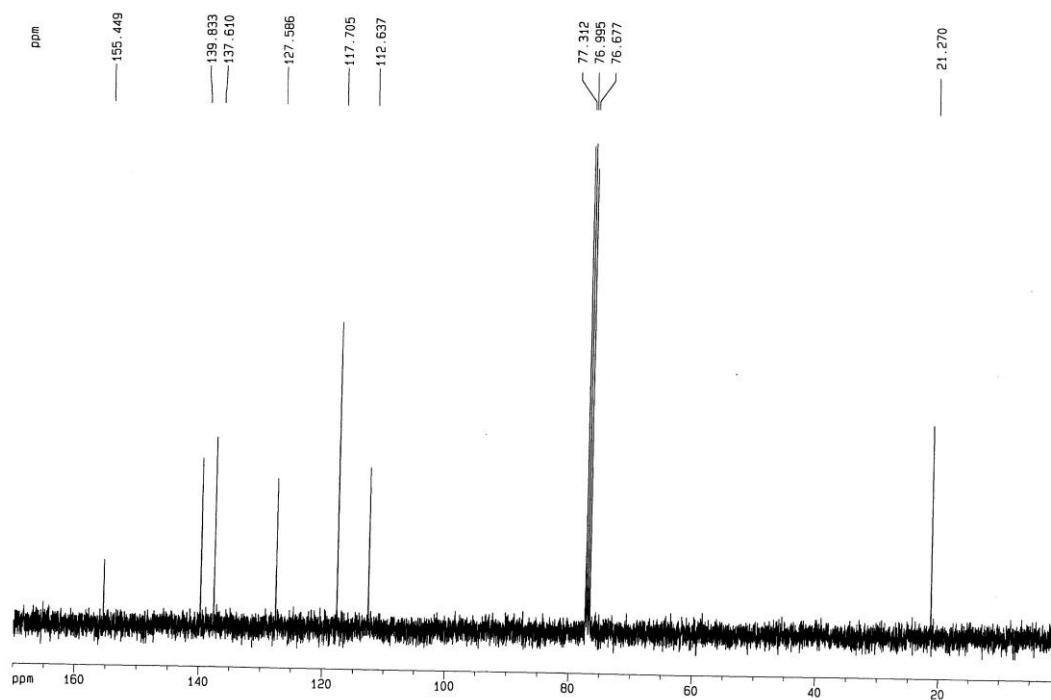
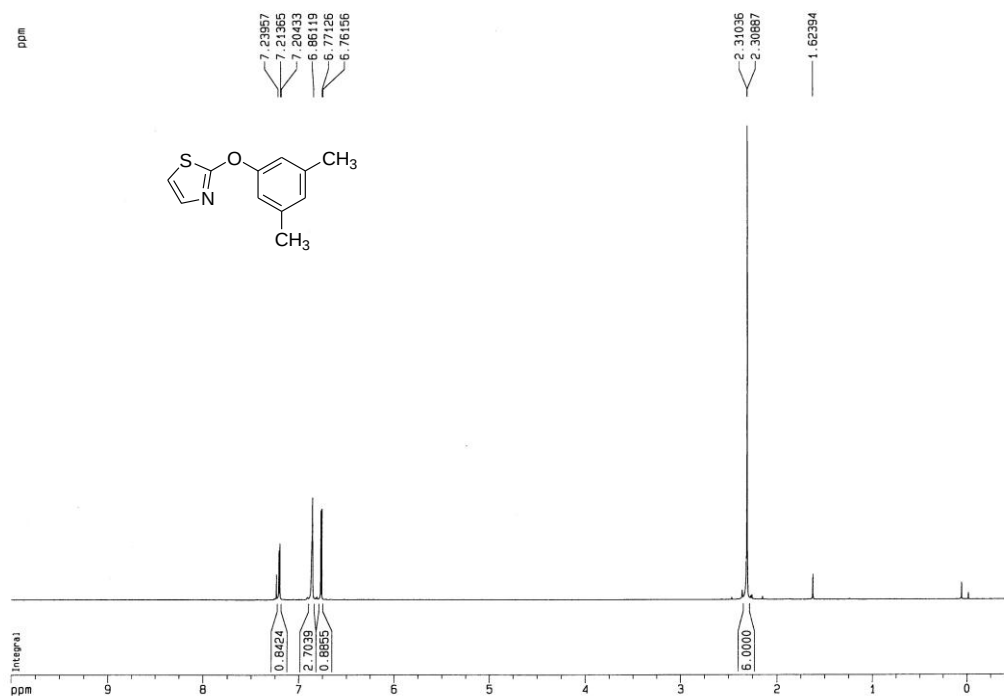
1-Fluoro-4-phenoxybenzene (3i, Table 2)



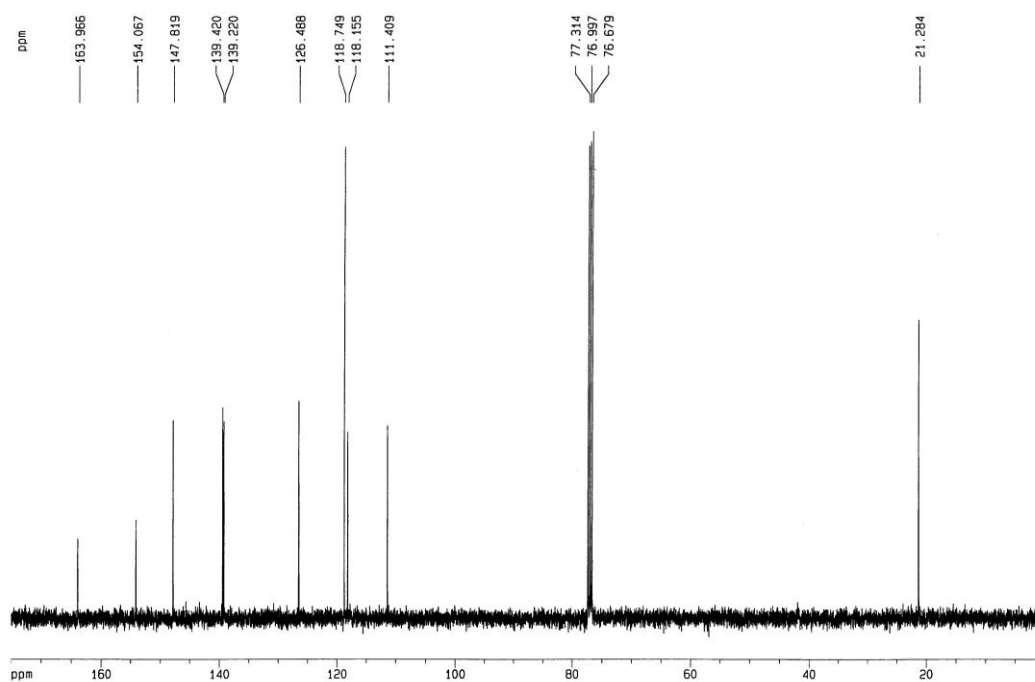
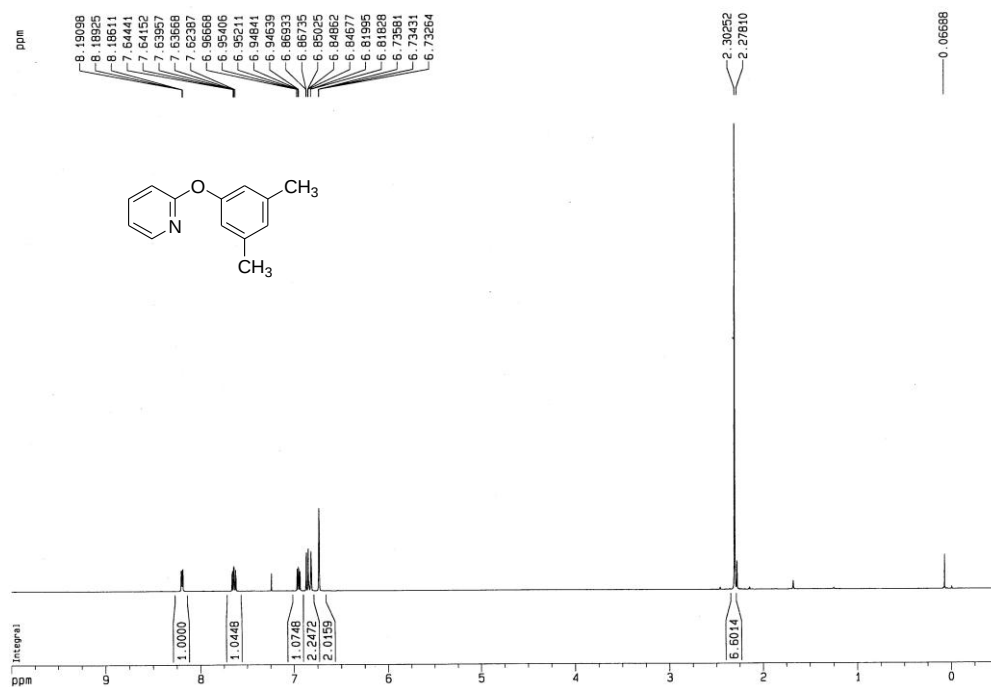
4-Methyl-diphenylether (3j, Table 2)



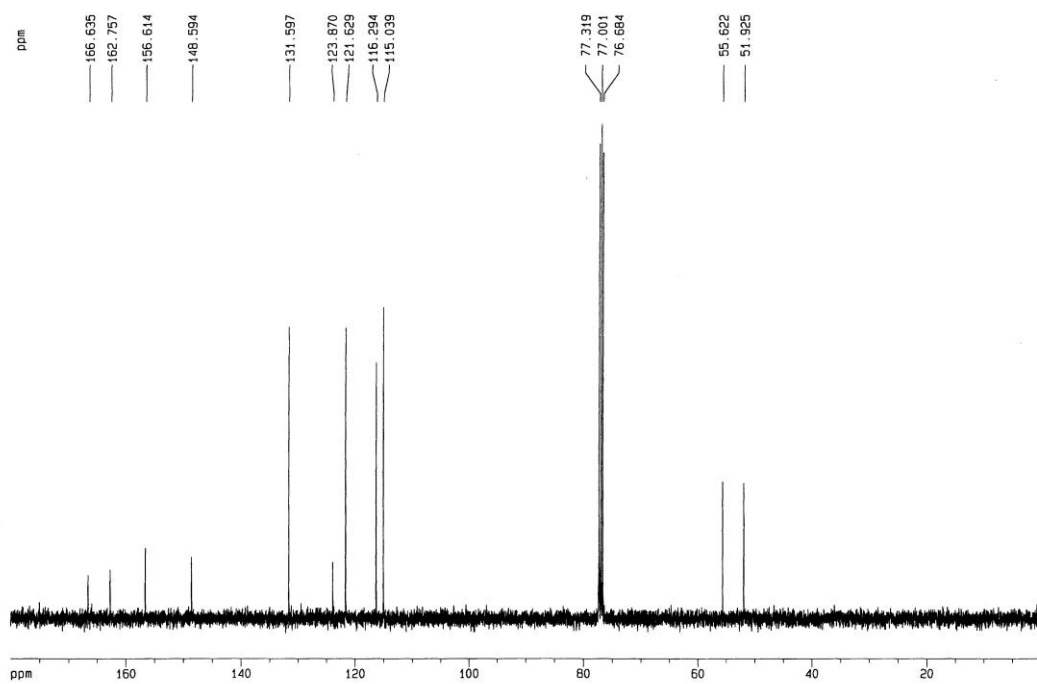
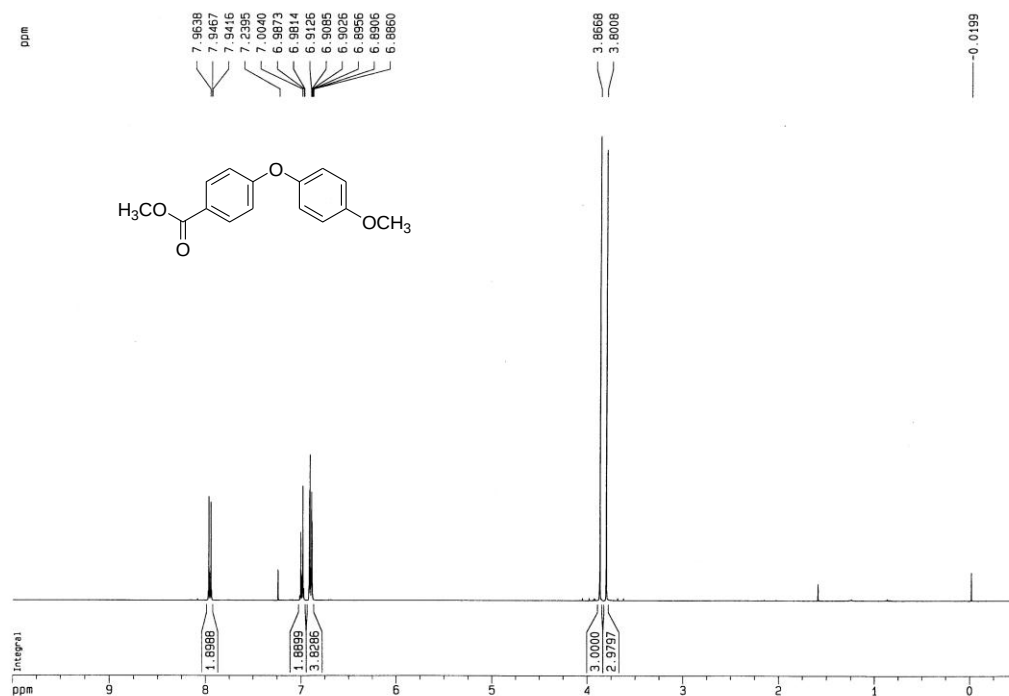
2-(3,5-Dimethylphenoxy)thiazole (3k, Table 2)



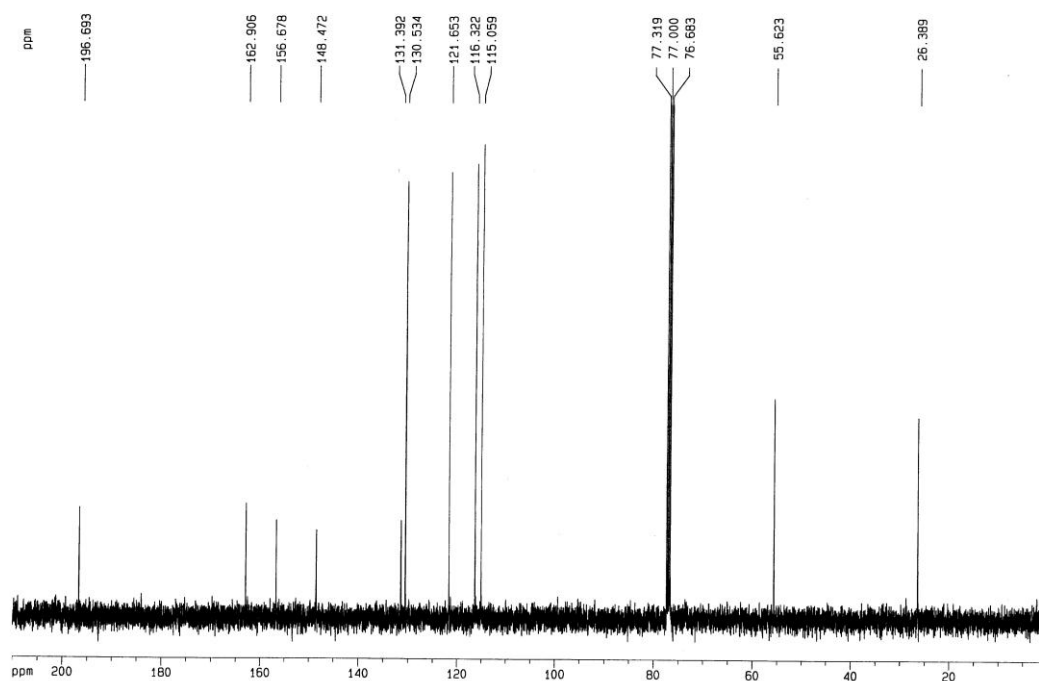
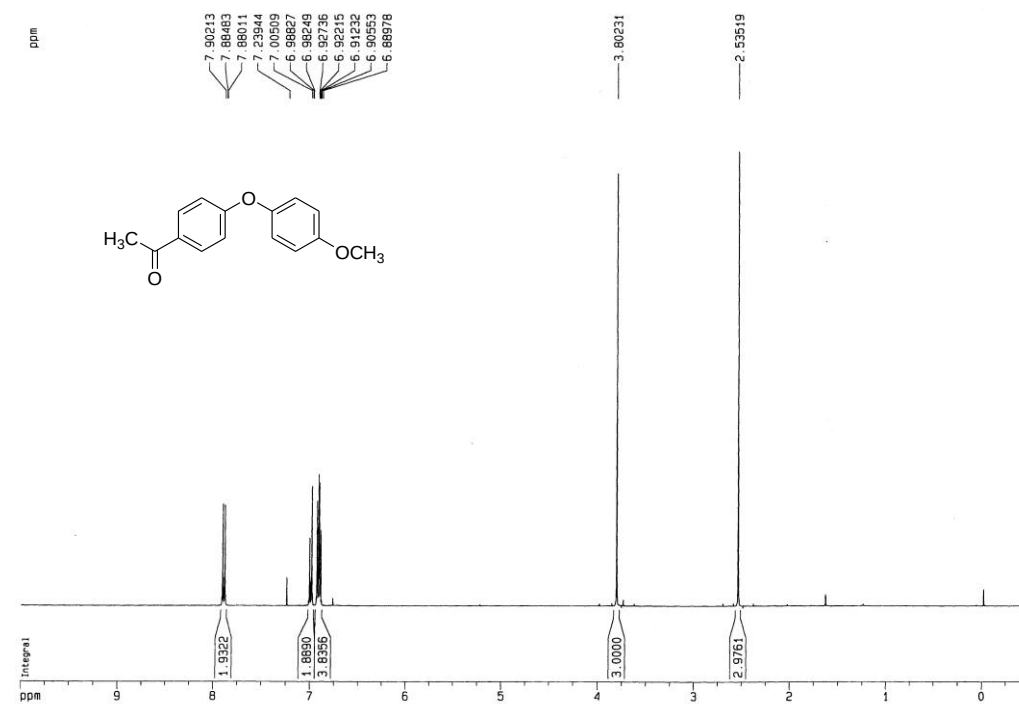
2-(3,5-Dimethyl-phenoxy)-pyridine (3l, Table 2)



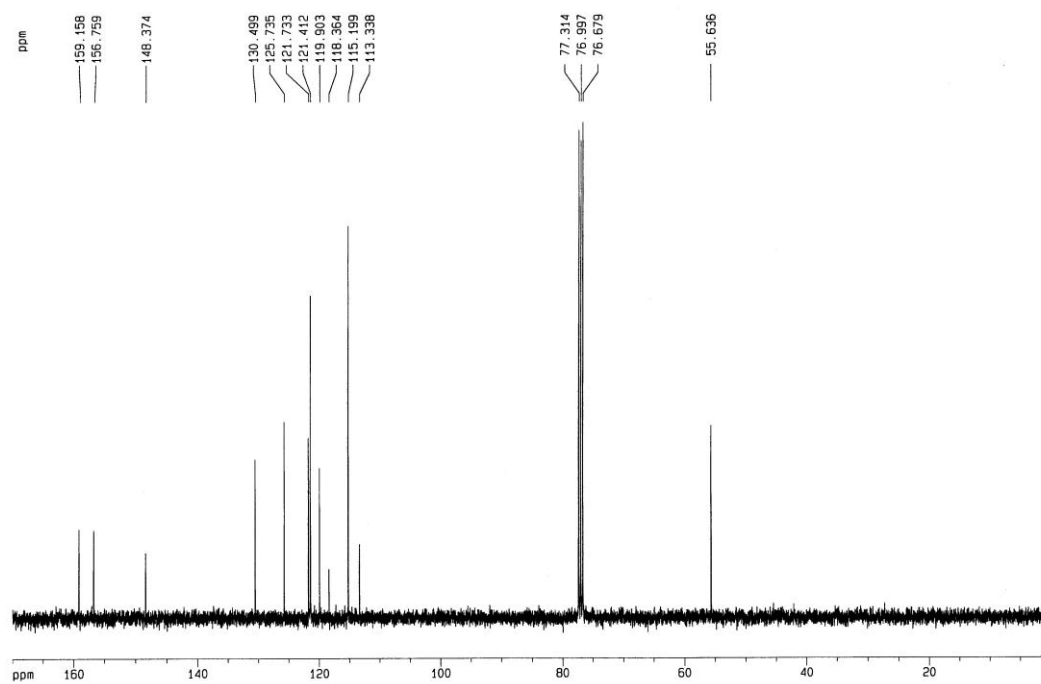
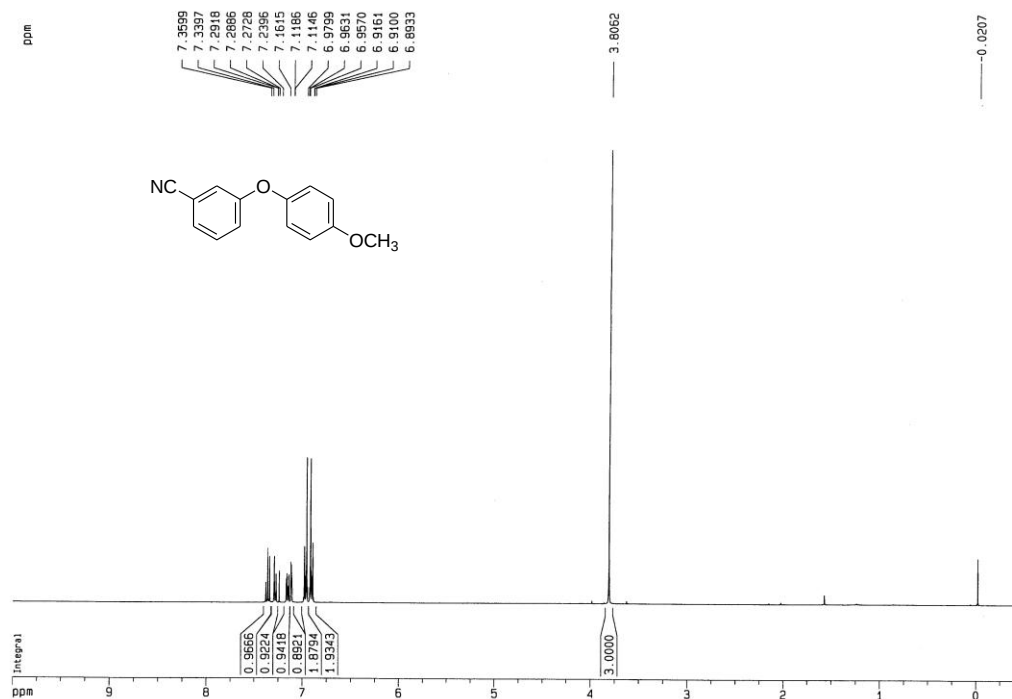
Methyl 4-(4-methoxyphenoxy)benzoate (3m, Table 3)



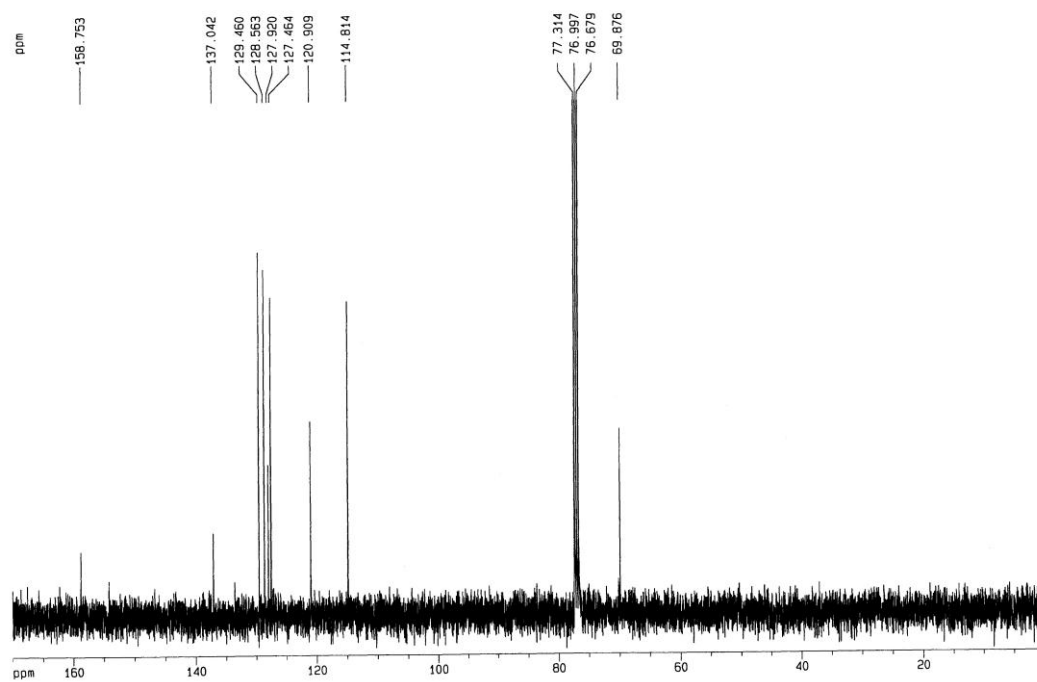
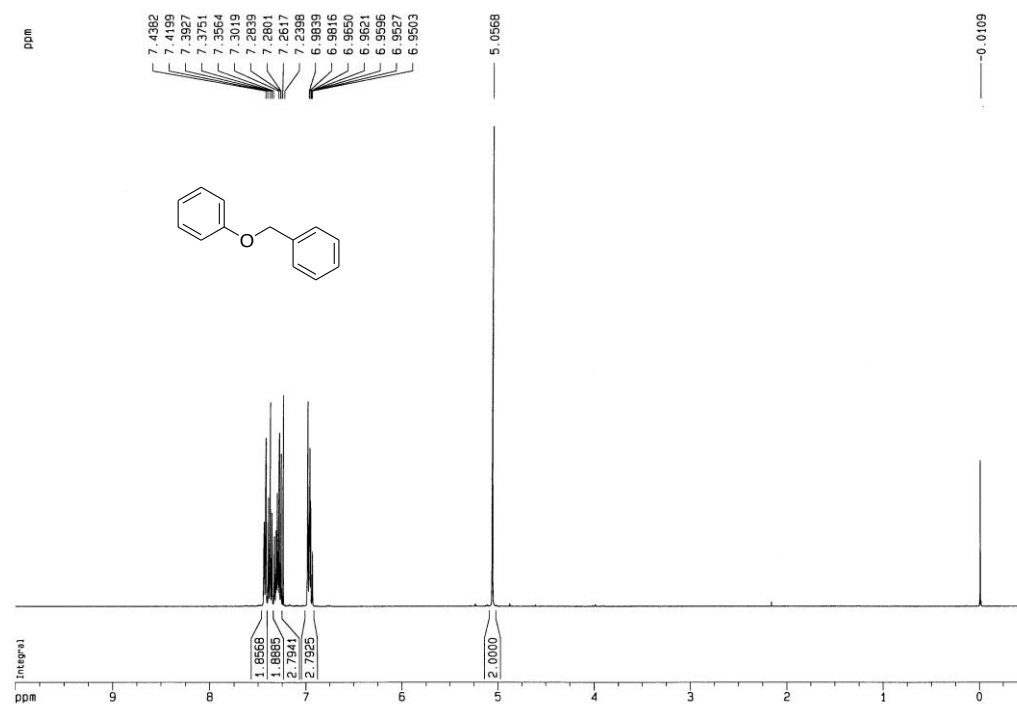
1-[4-(4-Methoxy-phenoxy)-phenyl]-ethanone (3n, Table 3)



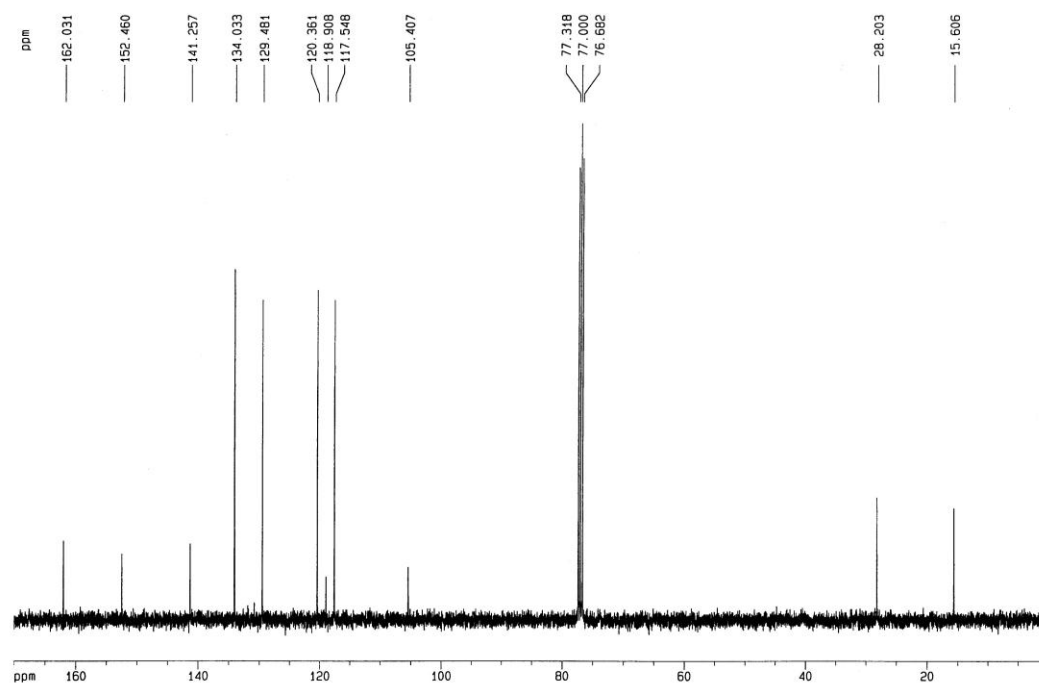
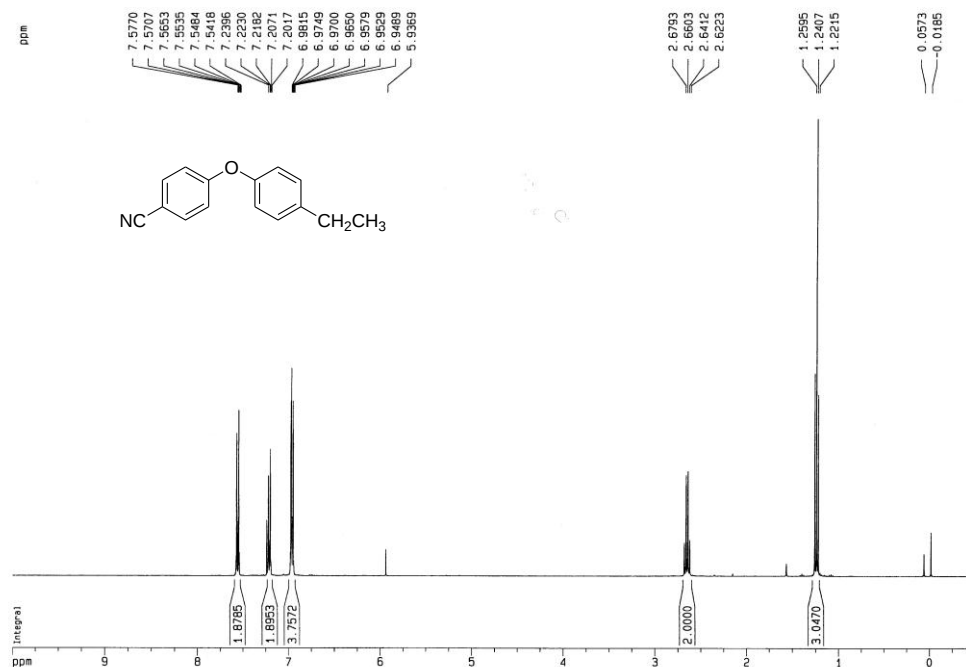
3-(4-Methoxyphenoxy)benzonitrile (**3o**, Table 3)



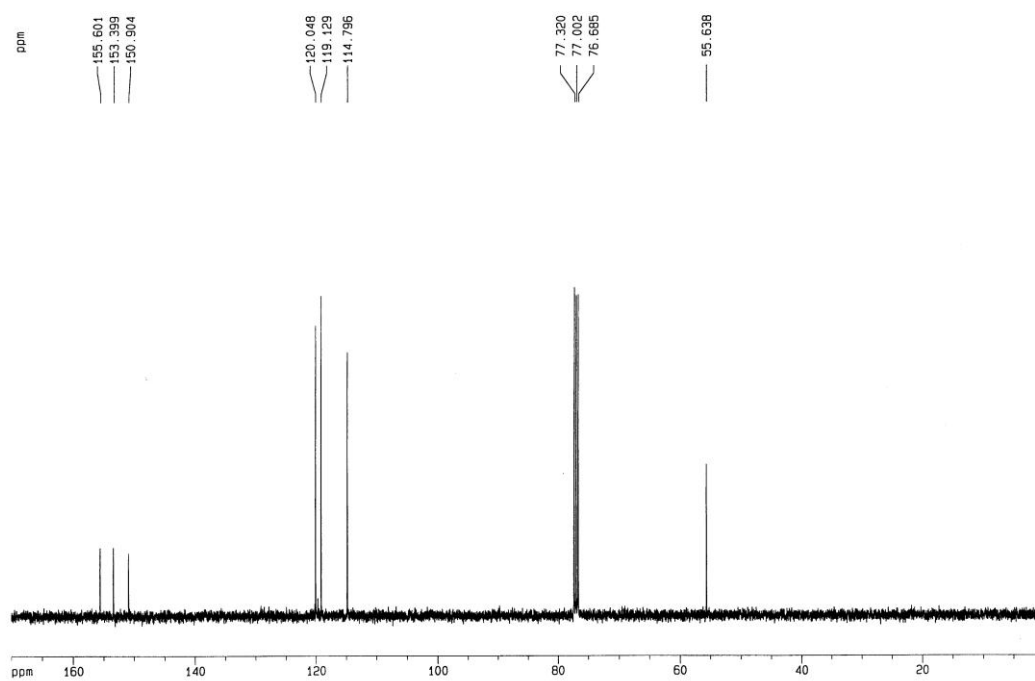
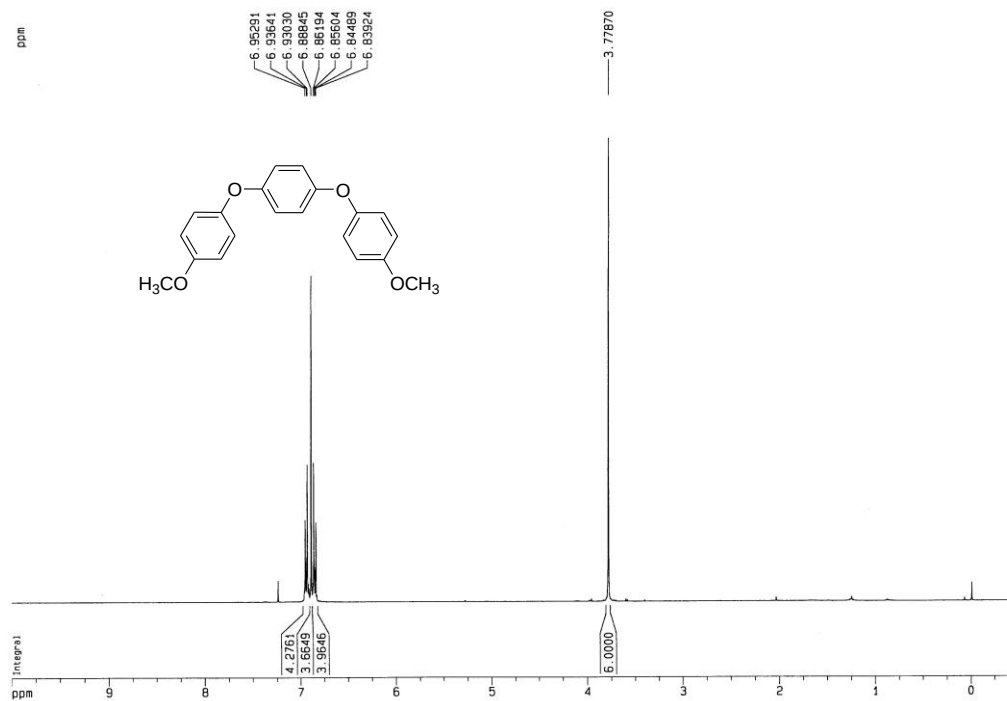
Benzyl phenyl ether (3p, Table 3)



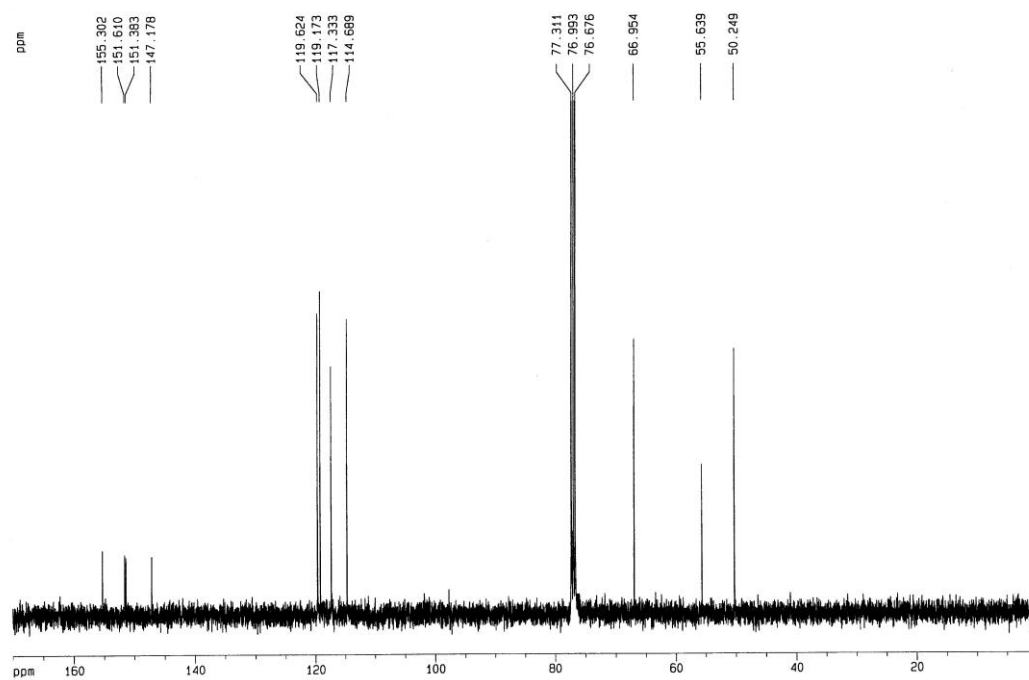
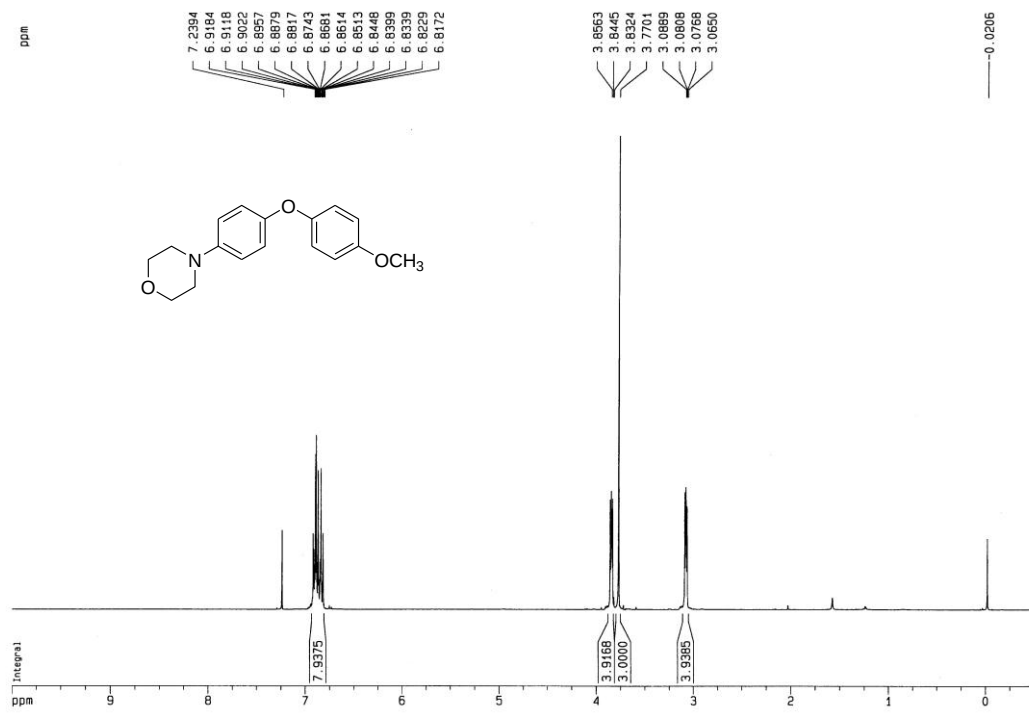
4-(4-Ethylphenoxy)benzonitrile (3q, Table 3)



1,4-Bis(4-methoxyphenoxy)benzene (3r, Table 3)



4-(4-(4-Methoxyphenoxy)phenyl)morpholine (Scheme 1)



Appendix II

X-Ray Crystallographic Data of a Rh(cod)(*i*Pr₂-bimy)Br Complex

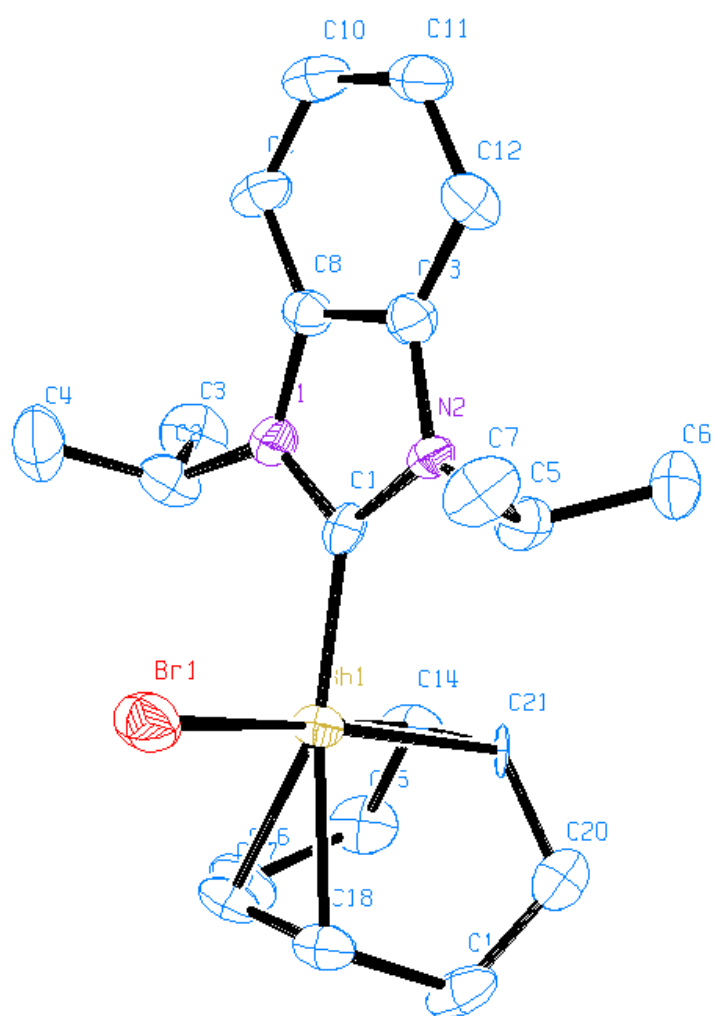


Table S1. Crystal data and structure refinement for Rh(cod)(iPr₂-bimy)Br.

Identification code	Rh
Empirical formula	C ₂₁ H ₃₀ Br N ₂ Rh
Formula weight	493.29
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 9.7809(4) Å α = 90°. b = 15.4141(6) Å β = 97.7140(10)° c = 13.4965(5) Å γ = 90°.
Volume	2016.37(14) Å ³
Z	4
Density (calculated)	1.625 Mg/m ³
Absorption coefficient	2.835 mm ⁻¹
F(000)	1000
Crystal size	0.38 x 0.22 x 0.19 mm ³
Theta range for data collection	2.02 to 28.28°
Index ranges	-12 ≤ h ≤ 13, -19 ≤ k ≤ 20, -17 ≤ l ≤ 8
Reflections collected	14800
Independent reflections	4988 [R(int) = 0.0742]
Completeness to theta = 28.28°	99.8 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4988 / 6 / 224
Goodness-of-fit on F ²	1.174
Final R indices [I > 2σ(I)]	R1 = 0.0500, wR2 = 0.1108
R indices (all data)	R1 = 0.0958, wR2 = 0.1846
Largest diff. peak and hole	1.936 and -2.733 e.Å ⁻³

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Rh(cod)(*i*Pr₂-bimy)Br. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh(1)	8326(1)	1738(1)	634(1)	25(1)
Br(1)	9084(1)	1368(1)	2440(1)	42(1)
C(1)	9189(7)	2920(5)	867(5)	22(1)
N(1)	8508(6)	3629(4)	1140(5)	27(1)
C(2)	7065(8)	3597(5)	1338(7)	36(2)
C(3)	6152(9)	4239(6)	688(7)	47(2)
N(2)	10518(6)	3168(3)	828(4)	22(1)
C(4)	6976(10)	3687(7)	2435(7)	51(2)
C(5)	11584(7)	2541(5)	627(6)	30(2)
C(6)	12295(8)	2824(6)	-275(6)	38(2)
C(7)	12599(9)	2389(6)	1563(6)	41(2)
C(8)	9413(7)	4333(4)	1313(5)	25(1)
C(9)	9227(8)	5177(5)	1632(5)	32(2)
C(10)	10385(9)	5708(5)	1745(6)	36(2)
C(11)	11678(9)	5423(5)	1539(6)	36(2)
C(12)	11846(8)	4587(5)	1202(6)	34(2)
C(13)	10701(8)	4045(5)	1093(5)	28(2)
C(14)	7265(8)	2124(5)	-770(5)	30(1)
C(15)	5889(9)	1657(6)	-1058(6)	41(2)
C(16)	5455(8)	1179(6)	-170(7)	43(2)
C(17)	6628(8)	802(5)	534(6)	33(2)
C(18)	7758(8)	361(5)	278(5)	30(1)
C(19)	7974(9)	163(5)	-817(6)	40(2)
C(20)	8788(9)	874(6)	-1258(6)	39(2)
C(21)	8514(7)	1766(4)	-901(4)	20(1)

Table S3. Bond lengths [Å] and angles [°] for Rh(cod)(iPr₂-bimy)Br.

C(2)-C(4)	1.501(13)
Rh(1)-C(1)	2.015(7)
Rh(1)-C(21)	2.104(6)
Rh(1)-C(14)	2.120(7)
Rh(1)-C(17)	2.190(7)
Rh(1)-C(18)	2.230(7)
Rh(1)-Br(1)	2.5164(10)
C(1)-N(1)	1.356(9)
C(1)-N(2)	1.363(8)
N(1)-C(8)	1.400(9)
N(1)-C(2)	1.472(10)
C(2)-C(3)	1.529(11)
N(2)-C(13)	1.402(9)
N(2)-C(5)	1.474(8)
C(5)-C(7)	1.516(10)
C(5)-C(6)	1.544(11)
C(8)-C(9)	1.390(10)
C(8)-C(13)	1.405(10)
C(9)-C(10)	1.390(11)
C(10)-C(11)	1.401(12)
C(11)-C(12)	1.384(11)
C(12)-C(13)	1.389(10)
C(14)-C(21)	1.374(10)
C(14)-C(15)	1.529(11)
C(15)-C(16)	1.516(12)
C(16)-C(17)	1.504(11)
C(17)-C(18)	1.381(11)
C(18)-C(19)	1.550(11)
C(19)-C(20)	1.522(12)
C(20)-C(21)	1.493(10)
C(1)-Rh(1)-C(21)	92.6(3)
C(1)-Rh(1)-C(14)	91.7(3)

C(21)-Rh(1)-C(14)	38.0(3)
C(1)-Rh(1)-C(17)	154.6(3)
C(21)-Rh(1)-C(17)	96.8(3)
C(14)-Rh(1)-C(17)	81.6(3)
C(1)-Rh(1)-C(18)	168.9(3)
C(21)-Rh(1)-C(18)	81.9(3)
C(14)-Rh(1)-C(18)	89.8(3)
C(17)-Rh(1)-C(18)	36.4(3)
C(1)-Rh(1)-Br(1)	89.49(17)
C(21)-Rh(1)-Br(1)	154.83(18)
C(14)-Rh(1)-Br(1)	167.1(2)
C(17)-Rh(1)-Br(1)	91.9(2)
C(18)-Rh(1)-Br(1)	91.46(18)
N(1)-C(1)-N(2)	106.8(6)
N(1)-C(1)-Rh(1)	124.1(5)
N(2)-C(1)-Rh(1)	129.0(5)
C(1)-N(1)-C(8)	110.4(6)
C(1)-N(1)-C(2)	122.7(6)
C(8)-N(1)-C(2)	126.5(6)
N(1)-C(2)-C(4)	111.1(7)
N(1)-C(2)-C(3)	112.0(7)
C(4)-C(2)-C(3)	113.6(8)
C(1)-N(2)-C(13)	110.5(6)
C(1)-N(2)-C(5)	121.6(6)
C(13)-N(2)-C(5)	127.6(6)
N(2)-C(5)-C(7)	110.4(6)
N(2)-C(5)-C(6)	111.4(6)
C(7)-C(5)-C(6)	112.7(7)
C(9)-C(8)-N(1)	132.2(7)
C(9)-C(8)-C(13)	121.3(7)
N(1)-C(8)-C(13)	106.5(6)
C(10)-C(9)-C(8)	116.5(7)
C(9)-C(10)-C(11)	122.5(7)
C(12)-C(11)-C(10)	120.5(7)
C(11)-C(12)-C(13)	117.7(8)

C(12)-C(13)-N(2)	132.8(7)
C(12)-C(13)-C(8)	121.4(7)
N(2)-C(13)-C(8)	105.7(6)
C(21)-C(14)-C(15)	123.0(7)
C(21)-C(14)-Rh(1)	70.4(4)
C(15)-C(14)-Rh(1)	113.8(5)
C(16)-C(15)-C(14)	111.0(6)
C(17)-C(16)-C(15)	114.5(7)
C(18)-C(17)-C(16)	126.9(8)
C(18)-C(17)-Rh(1)	73.4(4)
C(16)-C(17)-Rh(1)	107.1(5)
C(17)-C(18)-C(19)	123.5(7)
C(17)-C(18)-Rh(1)	70.2(4)
C(19)-C(18)-Rh(1)	109.3(5)
C(20)-C(19)-C(18)	112.2(6)
C(21)-C(20)-C(19)	114.2(7)
C(14)-C(21)-C(20)	127.8(7)
C(14)-C(21)-Rh(1)	71.6(4)
C(20)-C(21)-Rh(1)	110.0(5)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Rh(cod)(iPr₂-bimy)Br. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(4)	52(5)	55(6)	50(6)	7(5)	24(4)	2(5)
Rh(1)	27(1)	20(1)	28(1)	1(1)	2(1)	-2(1)
Br(1)	56(1)	37(1)	32(1)	4(1)	0(1)	-11(1)
C(1)	26(3)	31(4)	10(3)	-3(3)	-2(2)	1(3)
N(1)	27(3)	25(3)	30(3)	-3(3)	7(2)	1(2)
C(2)	28(4)	30(4)	49(5)	6(4)	4(3)	-2(3)
C(3)	32(4)	49(5)	58(6)	4(5)	0(4)	6(4)
N(2)	25(3)	18(3)	24(3)	-5(2)	5(2)	0(2)
C(5)	24(3)	26(4)	42(4)	-4(3)	6(3)	6(3)
C(6)	33(4)	47(5)	37(4)	-1(4)	13(3)	2(4)
C(7)	46(5)	39(5)	36(4)	-2(4)	-7(4)	13(4)
C(8)	26(3)	24(3)	24(3)	2(3)	1(3)	-3(3)
C(9)	44(4)	21(3)	29(4)	-3(3)	-2(3)	4(3)
C(10)	48(5)	22(4)	36(4)	-3(3)	-5(4)	-2(3)
C(11)	45(5)	29(4)	31(4)	0(3)	-2(3)	-11(3)
C(12)	29(4)	32(4)	42(5)	5(3)	7(3)	-4(3)
C(13)	31(4)	26(4)	26(4)	2(3)	4(3)	-1(3)
C(14)	41(3)	23(2)	22(2)	5(2)	-10(2)	-6(2)
C(15)	39(4)	43(5)	37(5)	3(4)	-13(4)	-1(4)
C(16)	25(4)	42(5)	63(6)	9(4)	5(4)	-10(3)
C(17)	30(4)	27(4)	43(5)	4(3)	2(3)	-13(3)
C(18)	41(3)	23(2)	22(2)	5(2)	-10(2)	-6(2)
C(19)	57(5)	30(4)	29(4)	-12(3)	-8(4)	5(4)
C(20)	39(4)	42(5)	35(4)	-7(4)	5(3)	4(4)
C(21)	24(3)	31(3)	8(2)	1(2)	12(2)	1(2)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for Rh(cod)(iPr₂-bimy)Br.

	x	y	z	U(eq)
H(2)	6714	3004	1140	43
H(3A)	6445	4833	868	70
H(3B)	5189	4160	796	70
H(3C)	6237	4135	-18	70
H(4A)	7547	3240	2806	76
H(4B)	6015	3617	2553	76
H(4C)	7308	4262	2664	76
H(5)	11109	1977	447	36
H(6A)	11594	2939	-850	57
H(6B)	12908	2360	-445	57
H(6C)	12835	3351	-104	57
H(7A)	13087	2930	1758	62
H(7B)	13266	1943	1430	62
H(7C)	12100	2194	2105	62
H(9)	8353	5381	1765	38
H(10)	10298	6287	1972	44
H(11)	12444	5807	1631	43
H(12)	12715	4390	1051	41
H(14)	7216	2767	-870	36
H(15A)	5171	2085	-1308	49
H(15B)	5979	1239	-1602	49
H(16A)	4934	1584	209	52
H(16B)	4821	703	-420	52
H(17)	6367	630	1198	40
H(18)	8171	-73	782	36
H(19A)	8471	-395	-838	48
H(19B)	7063	100	-1230	48
H(20A)	9785	748	-1091	46
H(20B)	8546	859	-1996	46
H(21)	9198	2204	-1073	24