Electronic Supplementary Information for

Abnormal oxazol-4-ylidene and thiazol-4-ylidene rhodium complexes: synthesis, structure, and property

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General Information:

Unless otherwise stated, all reactions and manipulations were performed using standard Schlenk techniques. All solvents were purified by distillation using standard methods. Commercially available reagents were used without further purification. NMR spectra were recorded by using a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (^{1}H NMR $CDCl_3$: 7.26 ppm ; ^{13}C NMR $CDCl_3$: 77.0 ppm). Mass spectra were recorded on the HP-5989 instrument by EI/ESI methods. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. X-ray diffraction analysis was performed by using a Bruker Smart-1000 X-ray diffractometer.

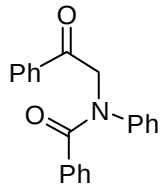
1-Phenyl-2-(phenylamino)ethanone (**1**) has been previously reported, and its spectra were consistent with that of the published data.[1]

Preparation and characterization

Preparation of *N*-aryl-amidoacetophenones 2a-2c:

In general, *N*-aryl-amidoacetophenones **2a-2c** were prepared following a literature method.[1]

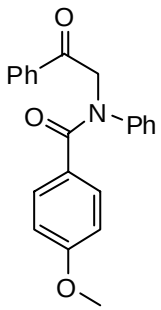
***N*-Phenyl-amidoacetophenones (2a)**[1]



Aminoketone **1** (0.8 g, 2.83 mmol) and Benzoyl chloride (0.8 g, 5.66 mmol) were dissolved in dried DCE (15 mL), and refluxed for 12 h. After filtration, the solvent was evaporated, and the residue was purified by flash chromatography (hexane/EtOAc 10/1) to afford **2a** as a white solid (0.85 g, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 (d, *J* = 7.2 Hz, 2 H, Ar*H*), 7.58 (t, *J* = 7.4 Hz, 1 H, Ar*H*), 7.47 (t, *J* = 7.6 Hz, 2 H, Ar*H*), 7.40 (d, *J* = 7.2 Hz, 2 H, Ar*H*), 7.22-7.26 (m, 1 H, Ar*H*), 7.15-7.21 (m, 6 H, Ar*H*), 7.09-7.13 (m, 1 H, Ar*H*), 5.34 (s, 2 H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.4 (N*C*O), 170.6 (*C*OCH_2), 144.0, 135.2, 135.1, 133.5, 129.7, 129.0, 128.8, 128.7, 127.9, 127.6, 127.4, 126.7, 57.0 (*C*H_2).

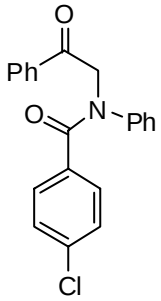
1 F. J. Lakner, M. A. Parker, B. Rogovoy, A. Khvat and A. Ivachtchenko, *Synthesis*, 2009, **12**, 1987.

_N_-4-methoxylphenyl-amidoacetophenones (2b)



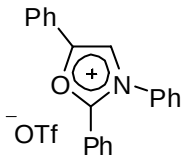
Aminoketone **1** (3.0 g, 14.2 mmol) and 4-methoxylbenzoyl chloride (1.2 g, 7.1 mmol) were dissolved in dried DCE (30 mL), and refluxed for 12 h. After filtration, the solvent was evaporated, and the residue was purified by flash chromatography (hexane/EtOAc 4/1) to afford **2a** as a white solid (2.31 g, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 (d, J = 7.2 Hz, 2 H, Ar*H*), 7.58 (t, J = 7.4 Hz, 1 H, Ar*H*), 7.47 (t, J = 7.6 Hz, 2 H, Ar*H*), 7.36 (d, J = 9.2 Hz, 2 H, Ar*H*), 7.21-7.24 (m, 1 H, Ar*H*), 7.17-7.20 (m, 3 H, Ar*H*), 7.11-7.15 (m, 1 H, Ar*H*), 6.67 (d, J = 9.2 Hz, 2 H, Ar*H*), 5.32 (s, 2 H, CH_2), 3.73 (s, 3 H, OCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.6 (N*C*O), 170.0 (*C*OCH$_2$), 160.7, 144.4, 135.1, 133.4, 131.0, 129.0, 128.6, 127.9, 127.3, 127.1, 126.5, 112.8, 57.1 (*C*H$_2$), 55.0 (O*C*H$_3$).

_N_-4-chlorophenyl-amidoacetophenones (2c)



Aminoketone **1** (3.0 g, 14.2 mmol) and 4-chlorobenzoyl chloride (1.2 g, 7.1 mmol) were dissolved in dried DCE (30 mL), and refluxed for 12 h. After filtration, the solvent was evaporated, and the residue was purified by flash chromatography (hexane/EtOAc 4/1) to afford **2a** as a white solid (2.20 g, 91%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00 (d, J = 7.6 Hz, 2 H, Ar*H*), 7.59 (t, J = 7.4 Hz, 1 H, Ar*H*), 7.48 (t, J = 7.6 Hz, 2 H, Ar*H*), 7.34 (d, J = 8.4 Hz, 2 H, Ar*H*), 7.21-7.24 (m, 2 H, Ar*H*), 7.14-7.17 (m, 5 H, Ar*H*), 5.33 (s, 2 H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.0 (N*C*O), 169.3 (CH$_2$*C*O), 143.6, 135.7, 134.8, 133.5, 133.5, 130.2, 129.1, 128.6, 127.8, 127.8, 127.3, 126.8, 57.0 (*C*H$_2$).

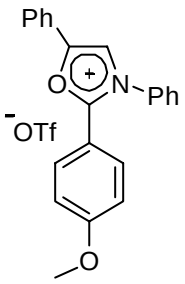
2,3,5-Triphenyloxazolium trifluoromethanesulfonate (3a)



2a (0.16 g, 0.51 mmol) was dissolved in dried CH_2Cl_2 (5 mL), and Et_3N (0.112 g, 1.12 mmol) was added at 0 °C. Tf_2O (0.32 g, 1.12 mmol) was added carefully over 5 mins at -40 °C. The solution was warmed to room temperature and stirred for 10 h and concentrated in vacuo. The resulting residue was purified by chromatography on silica gel (CH_2Cl_2/EtOH=30:1) to give **33** as a white powder (0.20 g, 88%). Mp: 176-178 °C. ^{1}H NMR (DMSO, 400 MHz): δ 9.15 (s, 1 H, CH_{oxa}), 8.07 (d, J = 6.8 Hz, 2 H, Ar*H*), 7.82-7.85 (m, 2 H, Ar*H*), 7.74-7.79 (m, 6 H, Ar*H*), 7.67-7.71 (m, 2 H, Ar*H*), 7.59-7.65 (m, 3 H, Ar*H*). ^{13}C NMR (DMSO, 100 MHz): δ 159.1 (N*C*O), 151.5, 134.6, 133.6, 131.9, 131.3, 130.6, 129.7, 129.6, 129.3, 125.8, 124.9, 124.0, 120.6

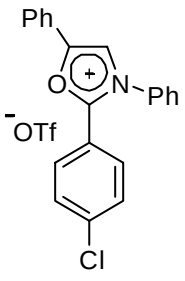
(q, *J*(C,F) = 315 Hz), 120.2, 120.2. IR (CH_2Cl_2): ν (cm^{-1}) 1638.19, 1545.14, 1491.21, 1463.43, 1449.90, 1403.19, 1258.19, 1222.69, 1170.25, 1150.13, 1029.37, 759.49, 732.51, 688.64, 658.86. MS: m/z calculated for $C_{21}H_{16}NO$ $(M\text{-}OTf)^+$ 298.1226, found 298.1228.

3,5-Diphenyl-2-(4-methoxyl)phenyloxazolium trifluoromethanesulfonate (3b)



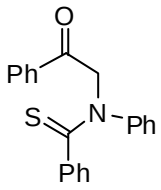
2b (0.79 g, 2.29 mmol) was dissolved in dried CH_2Cl_2 (20 mL), and Et_3N (0.463 g, 4.58 mmol) was added at 0 °C. Tf_2O (1.29 g, 4.58 mmol) was added carefully over 5 mins at -40 °C. The solution was warmed to room temperature and stirred for 10 h and concentrated in vacuo. The resulting residue was purified by chromatography on silica gel (CH_2Cl_2/EtOH=30:1) to give **33** as a white powder (1.0 g, 88%). Mp: 168-170 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.14 (s, 1 H, CH_{oxa}), 7.82-7.84 (m, 2 H, Ar*H*), 7.65 (d, *J* = 7.6 Hz, 2 H, Ar*H*), 7.52-7.61 (m, 5 H, Ar*H*), 7.41-7.42 (m, 3 H, Ar*H*), 6.91 (d, *J* = 8.8 Hz, 2 H, Ar*H*) , 3.81 (s, 3 H, OCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.0 (N*C*O), 158.9, 152.6, 133.2, 131.9, 131.9, 131.2, 130.8, 129.1, 125.5, 125.4, 123.5, 120.5 (q, *J*(C,F) = 292 Hz), 118.6, 115.2, 110.9, 55.8 (O*C*H$_3$). IR (CH_2Cl_2): ν (cm^{-1}) 1604.21, 1505.17, 1488.78, 1434.45, 1403.41, 1259.16, 1223.45, 1151.90, 1029.74, 840.02, 763.28, 738.70, 692.00. MS: m/z calculated for $C_{22}H_{18}NO_2$ $(M\text{-}OTf)^+$ 328.1332, found 328.1331.

3,5-Diphenyl-2-(4-chloride)phenyloxazolium trifluoromethanesulfonate (3c)



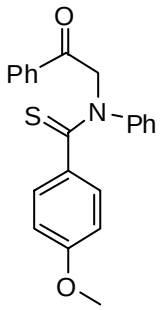
2c (0.48 g, 1.37 mmol) was dissolved in dried CH_2Cl_2 (10 mL), and Et_3N (0.277 g, 2.74 mmol) was added at 0 °C. Tf_2O (0.77 g, 2.74 mmol) was added carefully over 5 mins at -40 °C. The solution was warmed to room temperature and stirred for 10 h and concentrated in vacuo. The resulting residue was purified by chromatography on silica gel (CH_2Cl_2/EtOH=30:1) to give **3c** as a white powder (0.61 g, 89%). Mp: 217-219 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.13 (s, 1 H, CH_{oxa}), 8.05 (d, *J* = 7.6 Hz, 2 H, Ar*H*), 7.76-7.79 (m, 5 H, Ar*H*), 7.72 (s, 4 H, Ar*H*), 7.64-7.68 (m, 2 H, Ar*H*). ^{13}C NMR (DMSO, 100 MHz): δ 163.7 (N*C*O), 158.4, 151.8, 139.8, 131.5, 130.8, 129.7, 129.6, 129.1, 128.5, 125.7, 125.0, 121.3, 120.8 (q, *J*(C,F) = 298 Hz), 119.1, 114.1. IR (CH_2Cl_2): ν (cm^{-1}) 1634.25, 1600.72, 1491.84, 1268.43, 1257.34, 1157.17, 1033.81, 832.11, 732.16, 689.23, 670.59, 663.52. MS: m/z calculated for $C_{21}H_{15}ClNO$ $(M\text{-}OTf)^+$ 332.0837, found 332.0833.

_N_-(2-oxo-2-phenylethyl)-_N_-phenylbenzothioamide (4a)



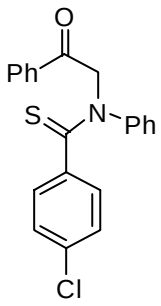
To a solution of **2a** (1.80 g, 5.7 mmol) in dried toluene (30mL) was added Lawesson's Reagent (1.3 g, 3.14 mmol) at room temperature. The resulting mixture was refluxed for 6 h, and then concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane : EtOAc = 8:1) to give **4a** as yellow solid (0.72 g, 40%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04 (d, J = 7.2 Hz, 2 H, Ar*H*), 7.61 (t, J = 7.4 Hz, 1 H, Ar*H*), 7.51 (t, J = 7.8 Hz, 2 H, Ar*H*), 7.33-7.35 (m, 2 H, Ar*H*), 7.16-7.23 (m, 4 H, Ar*H*), 7.08-7.12 (m, 4 H, Ar*H*), 5.89 (s, 2 H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 203.2 (N*C*S), 191.5 (*C*OCH_2), 145.7, 142.8, 135.0, 133.5, 128.8, 128.6, 128.3, 127.8, 127.6, 127.3, 127.2, 126.6, 63.2 (*C*H_2).

4-methoxy-_N_-(2-oxo-2-phenylethyl)-_N_-phenylbenzothioamide (4b)



To a solution of **2b** (0.8 g, 2.3 mmol) in dried toluene (15mL) was added Lawesson's Reagent (0.51 g, 1.27 mmol) at room temperature. The resulting mixture was refluxed for 6 h, and then concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane : EtOAc = 8:1) to give **4b** as yellow solid (0.28 g, 35%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (d, J = 7.6 Hz, 2 H, Ar*H*), 7.60 (t, J = 7.6 Hz, 1 H, Ar*H*), 7.49 (t, J = 7.6 Hz, 2 H, Ar*H*), 7.33 (d, J = 8.8 Hz, 2 H, Ar*H*), 7.20 (d, J = 4.4 Hz, 4 H, Ar*H*), 7.09-7.14 (m, 1 H, Ar*H*), 6.61 (d, J = 8.8 Hz, 2 H, Ar*H*), 5.89 (s, 2 H, CH_2), 3.70 (s, 3 H, OCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 203.1 (N*C*S), 191.9 (*C*OCH_2), 159.9, 146.4, 135.4, 135.2, 133.6, 129.9, 129.0, 128.7, 127.9, 127.0, 126.6, 112.7, 63.6 (*C*H_2), 55.1 (O*C*H_3).

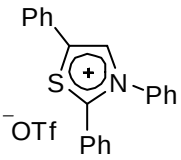
4-chloro-N-(2-oxo-2-phenylethyl)-N-phenylbenzothioamide (4c)



To a solution of **2c** (0.37 g, 1.06 mmol) in dried toluene (10mL) was added Lawesson's Reagent (0.23 g, 0.58 mmol) at room temperature. The resulting mixture was refluxed for 6 h, and then concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane : EtOAc = 8:1) to give **4b** as yellow solid (0.18 g, 49%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03 (d, J = 7.6 Hz, 2 H, Ar*H*), 7.61 (t, J = 7.4 Hz, 1 H, Ar*H*), 7.50 (t, J = 7.6 Hz, 2 H, Ar*H*), 7.29 (d, J = 8.4 Hz, 2 H, Ar*H*), 7.19-7.24 (m, 4 H, Ar*H*), 7.13-7.16 (m, 1 H, Ar*H*), 7.09 (d, J = 8.8 Hz, 2 H, Ar*H*), 5.87 (s, 2 H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 201.8 (N*C*S), 191.5 (*C*OCH_2), 145.7, 141.3, 135.1, 134.4, 133.7,

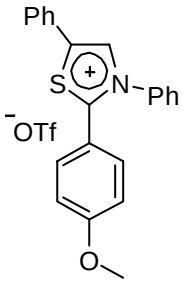
129.2, 128.8, 127.9, 127.7, 127.5, 126.6, 63.3 (CH_2).

2,3,5-Triphenylthiazolium trifluoromethanesulfonate (5a)



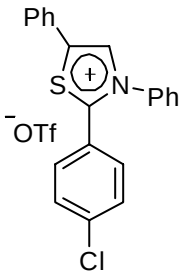
4a (0.15 g, 0.453 mmol) was dissolved in dried CH_2Cl_2 (5 mL), and Et_3N (0.091 g, 0.906 mmol) was added at 0 °C. Tf_2O (0.256 g, 2.74 mmol) was added carefully over 5 mins at -40 °C. The solution was warmed to room temperature and stirred for 10 h and concentrated in vacuo. The resulting residue was purified by chromatography on silica gel (CH_2Cl_2/EtOH=30:1) to give **5a** as a white powder (0.187 g, 89%). Mp: 185-187 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.39 (s, 1 H, CH_{thiaz}), 7.74-7.77 (m, 2 H, Ar*H*), 7.64-7.66 (m, 2 H, Ar*H*), 7.49-7.56 (m, 9 H, Ar*H*), 7.43 (t, *J* = 7.6 Hz, 2 H, Ar*H*). ^{13}C NMR (DMSO, 100 MHz): δ 168.6 (N*C*S), 139.8, 136.9, 135.5, 133.0, 131.2, 130.9, 129.9, 129.9, 129.7, 129.2, 127.1, 126.6, 126.3, 124.9, 120.6 (q, *J*(C,F) = 320 Hz). IR (CH_2Cl_2): ν (cm^{-1}) 1561.22, 1489.20, 1456.12, 1275.10, 1257.24, 1222.21, 1169.10, 1150.39, 1029.46, 758.88, 708.60, 688.33. MS: m/z calculated for $C_{21}H_{16}NS$ $(M\text{-}OTf)^+$ 314.0998, found 314.1002.

3,5-Diphenyl-2-(4-methoxyl)phenylthiazolium trifluoromethanesulfonate (5b)



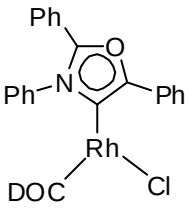
4b (0.185 g, 0.512 mmol) was dissolved in dried CH_2Cl_2 (5 mL), and Et_3N (0.104 g, 1.024 mmol) was added at 0 °C. Tf_2O (0.288 g, 1.024 mmol) was added carefully over 5 mins at -40 °C. The solution was warmed to room temperature and stirred for 10 h and concentrated in vacuo. The resulting residue was purified by chromatography on silica gel (CH_2Cl_2/EtOH=30:1) to give **5b** as a white powder (0.19 g, 75%). Mp: 148-150 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.23 (s, 1 H, CH_{thiaz}), 7.67-7.70 (m, 2 H, Ar*H*), 7.56 (d, *J* = 7.6 Hz, 2 H, Ar*H*), 7.47-7.51 (m, 3 H, Ar*H*), 7.37-7.42 (m, 3 H, Ar*H*), 7.36 (d, *J* = 9.2 Hz, 2 H, Ar*H*), 6.84 (d, *J* = 8.8 Hz, 2 H, Ar*H*) 3.78 (s, 3 H, OCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.8 (N*C*S), 163.7, 140.3, 136.7, 133.6, 131.8, 131.3, 130.9, 130.4, 129.5, 127.1, 126.7, 125.8, 120.7 (q, *J*(C,F) = 318 Hz), 116.5, 115.1, 55.6(OCH_3). IR (CH_2Cl_2): ν (cm^{-1}) 160.43, 1491.79, 1452.57, 1261.29, 1223.20, 1181.39, 1152.55, 1029.81, 835.19, 761.67, 691.44. MS: m/z calculated for $C_{22}H_{18}NOS$ $(M\text{-}OTf)^+$ 344.1104, found 344.1110.

3,5-Diphenyl-2-(4-chloride)phenylthiazolium trifluoromethanesulfonate (5c)



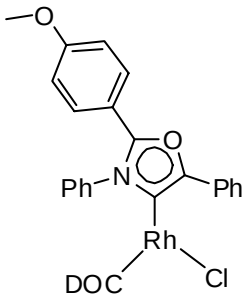
4c (0.436 g, 1.19 mmol) was dissolved in dried CH_2Cl_2 (5 mL), and Et_3N (0.242 g, 2.38 mmol) was added at 0 °C. Tf_2O (0.671 g, 2.38 mmol) was added carefully over 5 mins at -40 °C. The solution was warmed to room temperature and stirred for 10 h and concentrated in vacuo. The resulting residue was purified by chromatography on silica gel (CH_2Cl_2/EtOH=30:1) to give **5c** as a white powder (0.47 g, 80%). Mp: 185-187 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.26 (s, 1 H, C*H*$_{thiaz}$), 7.68-7.71 (m, 2 H, Ar*H*), 7.62 (d, *J* = 7.2 Hz, 2 H, Ar*H*), 7.51-7.53 (m, 2 H, Ar*H*), 7.43-7.50 (m, 6 H, Ar*H*), 7.36 (d, *J* = 8.4 Hz, 2 H, Ar*H*). ^{13}C NMR (DMSO, 100 MHz): δ 167.3 (N*C*S), 140.2, 138.1, 136.7, 135.5, 131.8, 131.2, 130.9, 130.0, 129.8, 129.4, 127.0, 126.6, 126.2, 123.7, 120.6 (q, *J*(C,F) = 320 Hz). IR (CH_2Cl_2): ν (cm^{-1}) 1591.57, 1490.57, 1451.61, 1257.52, 1222.83, 1150.46, 1093.47, 1028.95, 1002.49, 829.85, 761.26, 745.40, 691.03. MS: m/z calculated for $C_{21}H_{15}ClNS$ $(M\text{-}OTf)^+$ 348.0608, found 348.0605.

2,3,5-Triphenyloxazol-4-ylidene rhodium(I) cyclooctadiene chloride (6a)



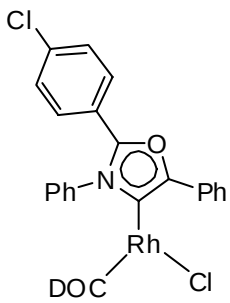
KHMDS (1.0 M in hexane, 0.246 mL, 0.246 mmol) was added dropwise to a solution of **3a** (0.10 g, 0.224 mmol) and $[(COD)RhCl]_2$ (0.055 g, 0.112 mmol) in THF (5 mL) at -78 °C. After 30 mins, the mixture was warmed to room temperature and stirred for 5 h. The solvent was evacuated in vacuo and the residue was purified by column chromatography on silica gel (PE/EtOAc = 2:1) to give the product **6a** as a yellow powder (59 mg, 49%). Mp: 204-206 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.79 (d, *J* = 7.0 Hz, 2 H, Ar*H*), 7.99 (s, 2 H, Ar*H*), 7.58-7.62 (m, 3 H, Ar*H*), 7.46-7.51 (m, 5 H, Ar*H*), 7.32-7.39 (m, 3 H, Ar*H*), 4.91-4.95 (m, 1 H, CH_2CH), 4.82-4.86 (m, 1 H, CH_2CH), 3.23 (s, 1 H, CH_2CH), 2.66-2.70 (m, 1 H, CH_2CH), 2.29-2.34 (m, 2 H, CH_2), 1.67-1.79 (m, 4 H, CH_2), 1.38-1.48 (m, 2 H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.3 (d, $J_{C\text{-}Rh}$ = 46.3 Hz, C=Rh), 157.5, 152.2, 152.2, 138.7, 132.5, 130.0, 129.3, 129.1, 129.1, 128.3, 128.3, 127.8, 125.2, 121.6, 96.5 (d, $J_{C\text{-}Rh}$ = 7.5 Hz, *C*H, COD), 95.2 (d, $J_{C\text{-}Rh}$ = 6.9 Hz, *C*H, COD), 69.3 (d, $J_{C\text{-}Rh}$ = 15.5 Hz, *C*H, COD), 67.2 (d, $J_{C\text{-}Rh}$ = 14.4 Hz, *C*H, COD), 33.2 (CH_2), 31.3 (CH_2), 29.0 (CH_2), 28.5 (CH_2). MS: m/z calculated for $C_{29}H_{27}NORh$ $(M\text{-}Cl)^+$ 508.1148, found 508.1141.

3,5-Diphenyl-2-(4-methoxy)phenyloxazol-4-ylidene rhodium(I) cyclooctadiene chloride (6b)



KHMDS (1.0 M in hexane, 0.46 mL, 0.46 mmol) was added dropwise to a solution of **3b** (0.2 g, 0.42 mmol) and $[(COD)RhCl]_2$ (0.104 g, 0.21 mmol) in THF (5 mL) at -78 °C. After 30 mins, the mixture was warmed to room temperature and stirred for 5 h. The solvent was evacuated in vacuo and the residue was purified by column chromatography on silica gel (PE/EtOAc = 2:1) to give the product **6b** as a yellow powder (135 mg, 56%). Mp: 230-232 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.76 (d, *J* = 7.8 Hz, 2 H, Ar*H*), 7.98 (s, 2 H, Ar*H*), 7.62 (s, 3 H, Ar*H*), 7.48 (t, *J* = 7.6 Hz, 2 H, Ar*H*), 7.42 (d, *J* = 9.2 Hz, 2 H, Ar*H*), 7.33 (t, *J* = 7.4 Hz, 1 H, Ar*H*), 6.86 (d, *J* = 8.8 Hz, 2 H, Ar*H*), 4.89-4.94 (m, 1 H, CH_2CH), 4.80-4.84 (m, 1 H, CH_2CH), 3.82 (s, 3 H, OCH_3), 3.23 (s, 1 H, CH_2CH), 2.68-2.70 (m, 1 H, CH_2CH), 2.30-2.35 (m, 2 H, CH_2), 1.68-1.77 (m, 4 H, CH_2), 1.38-1.48 (m, 2 H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ162.8, 158.3 (d, $J_{C\text{-}Rh}$ = 46.7 Hz, C=Rh), 157.7, 151.4, 151.3, 138.9, 130.3, 129.9, 129.3, 128.3, 127.5, 125.1, 114.7, 113.8, 96.4 (d, $J_{C\text{-}Rh}$ = 8.2 Hz, *C*H, COD), 95.1 (d, $J_{C\text{-}Rh}$ = 7.1 Hz, *C*H, COD), 69.3 (d, $J_{C\text{-}Rh}$ = 15.4 Hz, *C*H, COD), 67.1 (d, $J_{C\text{-}Rh}$ = 14.2 Hz, *C*H, COD), 55.5 (OCH_3), 33.2 (CH_2), 31.4 (CH_2), 29.0 (CH_2), 28.5 (CH_2). MS: m/z calculated for $C_{30}H_{29}NO_2Rh$ $(M\text{-}Cl)^+$ 538.1253, found 538.1251.

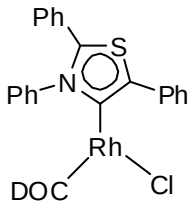
3,5-Diphenyl-2-(4-chloride)phenyloxazol-4-ylidene rhodium(I) cyclooctadiene chloride (6c)



KHMDS (1.0 M in hexane, 0.23 mL, 0.23 mmol) was added dropwise to a solution of **3c** (0.1 g, 0.21 mmol) and $[(COD)RhCl]_2$ (0.051 g, 0.105 mmol) in THF (5 mL) at -78 °C. After 30 mins, the mixture was warmed to room temperature and stirred for 5 h. The solvent was evacuated in vacuo and the residue was purified by column chromatography on silica gel (PE/EtOAc = 2:1) to give the product **6c** as a yellow powder (85 mg, 71%). Mp: 203-205 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.78 (d, *J* = 8.0 Hz, 2 H, Ar*H*), 7.97 (s, 2 H, Ar*H*), 7.63 (s, 3 H, Ar*H*), 7.50 (t, *J* = 7.8 Hz, 2 H, Ar*H*), 7.34-7.41 (m, 5 H, Ar*H*), 4.93 (s, 1 H, CH_2CH), 4.81-4.86 (m, 1 H, CH_2CH), 3.22 (s, 1 H, CH_2CH), 2.66-2.69 (m, 1 H, CH_2CH), 2.27-2.35 (m, 2 H, CH_2), 1.68-1.79 (m, 4 H, CH_2), 1.36-1.51 (m, 2 H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.9 (d, $J_{C\text{-}Rh}$ = 46.9 Hz, C-Rh), 156.5, 152.5, 152.5, 139.1, 138.5, 130.2, 129.6, 129.4, 129.4, 128.9, 128.4, 127.9, 125.3, 120.0, 96.7 (d, $J_{C\text{-}Rh}$ = 7.3 Hz, *C*H, COD), 95.4 (d, $J_{C\text{-}Rh}$ = 7.6 Hz, *C*H, COD), 69.3 (d, $J_{C\text{-}Rh}$ = 14.3 Hz, *C*H, COD), 67.3 (d,

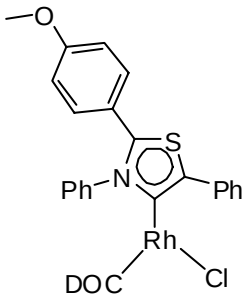
$J_{C\text{-}Rh}$ = 14.8 Hz, *C*H, COD), 33.2 (*C*H_2), 31.4 (*C*H_2), 29.0 (*C*H_2), 28.5 (*C*H_2). MS: m/z calculated for $C_{29}H_{26}ClNORh$ $(M\text{-}Cl)^+$ 542.0758, found 542.0750.

2,3,5-Triphenylthiazol-4-ylidene rhodium(I) cyclooctadiene chloride (7a)



KHMDS (1.0 M in hexane, 0.12 mL, 0.12 mmol) was added dropwise to a solution of **5a** (0.05 g, 0.108 mmol) and $[(COD)RhCl]_2$ (0.027 g, 0.054 mmol) in THF (5 mL) at -78 °C. After 30 mins, the mixture was warmed to room temperature and stirred for 5 h. The solvent was evacuated in vacuo and the residue was purified by column chromatography on silica gel (PE/EtOAc = 2:1) to give the product **7a** as a red powder (30 mg, 50%). Mp: 202-204 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.05 (s, 1 H, Ar*H*), 8.72 (d, *J* = 7.2 Hz, 2 H, Ar*H*), 7.72 (s, 1 H, Ar*H*), 7.41-7.53 (m, 3 H, Ar*H*), 7.39 (t, *J* = 7.0 Hz, 2 H, Ar*H*), 7.24-7.33 (m, 5 H, Ar*H*), 6.89 (s, 1 H, Ar*H*), 4.83-4.88 (m, 1 H, CH_2CH), 4.72-4.77 (m, 1 H, CH_2CH), 2.88-2.92 (m, 1 H, CH_2CH), 2.47-2.49 (m, 1 H, CH_2CH), 2.08-2.15 (m, 1 H, CH_2), 1.95-2.05 (m, 1 H, CH_2), 1.52-1.65 (m, 4 H, CH_2), 1.25-1.35 (m, 2 H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 187.0 (d, $J_{C\text{-}Rh}$ = 44.9 Hz, C=Rh), 165.2, 165.2, 142.1, 133.5, 133.5, 133.5, 131.0, 129.2, 129.0, 128.7, 128.3, 127.9, 127.4, 95.5 (d, $J_{C\text{-}Rh}$ = 7.1 Hz, *C*H, COD), 94.6 (d, $J_{C\text{-}Rh}$ = 6.6 Hz, *C*H, COD), 69.7 (d, $J_{C\text{-}Rh}$ = 14.9 Hz, *C*H, COD), 66.4 (d, $J_{C\text{-}Rh}$ = 15.2 Hz, *C*H, COD), 33.2 (*C*H_2), 30.7 (*C*H_2), 29.1 (*C*H_2), 27.8 (*C*H_2). MS: m/z calculated for $C_{29}H_{27}ClNRhS$ $(M)^+$ 559.0608, found 559.0611.

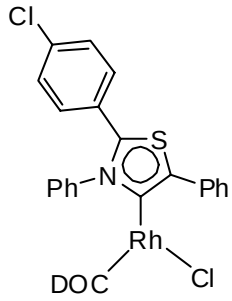
3,5-Diphenyl-2-(4-methoxy)phenylthiazol-4-ylidene rhodium(I) cyclooctadiene chloride (7b)



KHMDS (1.0 M in hexane, 0.11 mL, 0.11 mmol) was added dropwise to a solution of **5b** (0.1 g, 0.2 mmol) and $[(COD)RhCl]_2$ (0.05 g, 0.1 mmol) in THF (5 mL) at -78 °C. After 30 mins, the mixture was warmed to room temperature and stirred for 5 h. The solvent was evacuated in vacuo and the residue was purified by column chromatography on silica gel (PE/EtOAc = 2:1) to give the product **7a** as a red powder (55 mg, 46%). Mp: 186-188 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.02 (s, 1 H, Ar*H*), 8.69 (d, *J* = 7.2 Hz, 2 H, Ar*H*), 7.69 (s, 1 H, Ar*H*), 7.48-7.54 (m, 3 H, Ar*H*), 7.37 (t, *J* = 7.4 Hz, 1 H, Ar*H*), 7.29 (s, 1 H, Ar*H*), 7.18 (d, *J* = 9.2 Hz, 2 H, Ar*H*), 6.90 (s, 1 H, Ar*H*), 6.80 (d, *J* = 8.8 Hz, 2 H, Ar*H*), 4.81-4.86 (m, 1 H, CH_2CH), 4.70-4.75 (m, 1 H, CH_2CH), 3.79 (s, 3 H, OCH_3), 2.86-2.90 (m, 1 H, CH_2CH), 2.44-2.49 (m, 1 H, CH_2CH), 2.07-2.15 (m, 1 H, CH_2), 1.97-2.02 (m, 1 H,

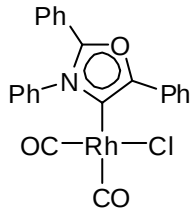
CH_2), 1.51-1.64 (m, 4 H, CH_2), 1.25-1.34 (m, 2 H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 186.0 (d, $J_{C\text{-}Rh}$ = 44.4 Hz, C=Rh), 165.5, 165.5, 161.6, 142.2, 133.6, 132.2, 132.2, 130.8, 129.0, 128.5, 128.2, 127.6, 119.5, 114.4, 95.3 (d, J = 7.3 Hz, *C*H, COD), 94.3 (d, $J_{C\text{-}Rh}$ = 6.7 Hz, *C*H, COD), 69.6 (d, $J_{C\text{-}Rh}$ = 15.1 Hz, *C*H, COD), 66.3 (d, $J_{C\text{-}Rh}$ = 15.2 Hz, *C*H, COD), 55.3 (O*C*H$_3$), 33.2 (*C*H$_2$), 30.6 (*C*H$_2$), 29.0 (*C*H$_2$), 27.8 (*C*H$_2$). MS: m/z calculated for $C_{30}H_{29}ClNORhS$ $(M)^+$ 589.0713, found 589.0714.

3,5-Diphenyl-2-(4-chloride)phenylthiazol-ylidene rhodium(I) cyclooctadiene chloride (7c)



KHMDS (1.0 M in hexane, 0.11 mL, 0.11 mmol) was added dropwise to a solution of **5c** (0.1 g, 0.2 mmol) and $[(COD)RhCl]_2$ (0.05 g, 0.1 mmol) in THF (5 mL) at -78 °C. After 30 mins, the mixture was warmed to room temperature and stirred for 5 h. The solvent was evacuated in vacuo and the residue was purified by column chromatography on silica gel (PE/EtOAc = 2:1) to give the product **7c** as a red powder (60 mg, 50%). Mp: 208-210 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.03 (s, 1 H, Ar*H*), 8.70 (d, J = 7.2 Hz, 2 H, Ar*H*), 7.42 (s, 1 H, Ar*H*), 7.50-7.56 (m, 3 H, Ar*H*), 7.42 (t, J = 7.4 Hz, 1 H, Ar*H*), 7.27-7.31 (m, 3 H, Ar*H*), 7.19 (d, J = 8.8 Hz, 2 H, Ar*H*), 6.88 (s, 1 H, Ar*H*), 4.83-4.88 (m, 1 H, CH_2CH), 4.72-4.77 (m, 1 H, CH_2CH), 2.89 (t, J = 7.2 Hz, 1 H, CH_2CH), 2.45-2.49 (m, 1 H, CH_2CH), 2.08-2.17 (m, 1 H, CH_2CH), 1.94-2.04 (m, 1 H, CH_2), 1.52-1.63 (m, 4 H, CH_2), 1.26-1.36 (m, 2 H, CH_2). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 187.7 (d, $J_{C\text{-}Rh}$ = 45.1 Hz, C=Rh), 163.6, 163.6, 141.8, 137.6, 133.8, 133.8, 133.3, 130.3, 129.4, 129.4, 128.7, 128.3, 128.1, 125.8, 95.7 (d, $J_{C\text{-}Rh}$ = 7.5 Hz, *C*H, COD), 94.7 (d, $J_{C\text{-}Rh}$ = 7.8 Hz, *C*H, COD), 69.7 (d, $J_{C\text{-}Rh}$ = 14.7 Hz, *C*H, COD), 66.5 (d, $J_{C\text{-}Rh}$ = 14.3 Hz, *C*H, COD), 33.2 (*C*H$_2$), 30.7 (*C*H$_2$), 29.0 (*C*H$_2$), 27.8 (*C*H$_2$). MS: m/z calculated for $C_{29}H_{26}Cl_2NRhS$ $(M)^+$ 593.0218, found 593.0219.

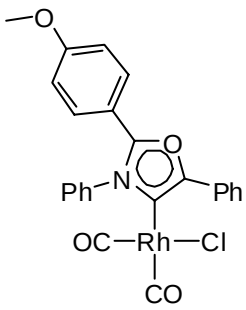
2,3,5-Triphenyloxazol-4-ylidene rhodium(I) biscarbonyl chloride (8a)



Rh complex **6a** (37 mg, 0.068 mmol) was dissolved in dried CH_2Cl_2 (5 mL) and carbon monoxide was bubbled through the solution for 1h at room temperature. A color change from yellow to pale yellow was observed during this time. The solvent was evacuated in vacuo and the residue was purified by column chromatography on silica gel (PE/EtOAc = 3:1) to give the product **8a** as a yellow powder (25mg, 75%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.45 (d, J = 7.2 Hz, 2 H, Ar*H*), 7.53-7.66 (m, 6 H, Ar*H*), 7.48 (t, J = 8.4 Hz, 4 H, Ar*H*),

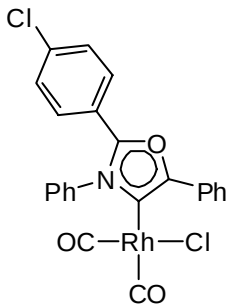
7.40 (t, J = 7.6 Hz, 3 H, Ar*H*). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 185.6 (d, $J_{C\text{-}Rh}$ = 54.2 Hz, Rh-CO), 183.1 (d, $J_{C\text{-}Rh}$ = 75.5 Hz, Rh-CO), 158.0, 155.0, 155.0, 151.4 (d, $J_{C\text{-}Rh}$ = 39.5 Hz, Rh=C), 138.2, 133.2, 130.8, 130.0, 129.4, 129.0, 128.5, 128.5, 128.1, 125.8, 121.2. IR (CH_2Cl_2): ν (cm^{-1}) 2067.01 (CO), 1988.82 (CO).

3,5-Diphenyl-2-(4-methoxy)phenyloxazol-4-ylidene rhodium(I) biscarbonyl chloride (8b)



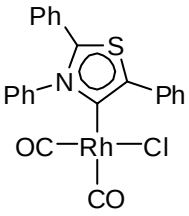
Rh complex **6b** (68 mg, 0.118 mol) was dissolved in dried CH_2Cl_2 (5 mL) and carbon monoxide was bubbled through the solution for 1h at room temperature. A color change from yellow to pale yellow was observed during this time. The solvent was evacuated in vacuo and the residue was purified by column chromatography on silica gel (PE/EtOAc = 3:1) to give the product **8b** as a yellow powder (55mg, 89%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.43 (d, J = 8.4 Hz, 2 H, Ar*H*), 7.59-7.64 (m, 5 H, Ar*H*), 7.41-7.48 (m, 4 H, Ar*H*), 7.38 (t, J = 7.4 Hz, 1 H, Ar*H*), 6.89 (d, J = 8.8 Hz, 2 H, Ar*H*), 3.84 (s, 3 H, OCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 185.8 (d, $J_{C\text{-}Rh}$ = 54.1 Hz, Rh-CO), 183.2 (d, $J_{C\text{-}Rh}$ = 74.7 Hz, Rh-CO), 163.4, 158.1, 154.0, 154.0, 150.5 (d, $J_{C\text{-}Rh}$ = 39.4 Hz, Rh=C), 138.4, 130.7, 130.5, 130.0, 128.7, 128.5, 128.3, 125.6, 114.7, 113.3, 55.6 (O*C*H_3). IR (CH_2Cl_2): ν (cm^{-1}) 2064.94 (CO), 1985.79 (CO).

3,5-Diphenyl-2-(4- chloride)phenyloxazol-4-ylidene rhodium(I) biscarbonyl chloride (8c)



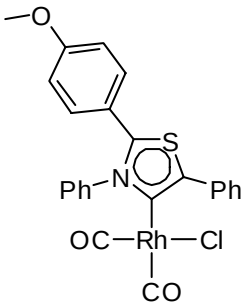
Rh complex **6c** (62 mg, 0.107 mol) was dissolved in dried CH_2Cl_2 (5 mL) and carbon monoxide was bubbled through the solution for 1h at room temperature. A color change from yellow to pale yellow was observed during this time. The solvent was evacuated in vacuo and the residue was purified by column chromatography on silica gel (PE/EtOAc = 3:1) to give the product **8c** as a yellow powder (48mg, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.44 (d, J = 7.2 Hz, 2 H, Ar*H*), 7.60-7.63 (m, 5 H, Ar*H*), 7.48 (t, J = 7.4 Hz, 2 H, Ar*H*), 7.37-7.44 (m, 5 H, Ar*H*). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 185.5 (d, $J_{C\text{-}Rh}$ = 54.3 Hz, Rh-CO), 183.0 (d, $J_{C\text{-}Rh}$ = 75 Hz, Rh-CO), 157.0, 155.2, 155.2, 151.8 (d, $J_{C\text{-}Rh}$ = 39.9 Hz, Rh=C), 139.9, 137.9, 131.0, 130.2, 129.8, 129.6, 129.1, 128.5, 127.8, 125.8, 119.5. IR (CH_2Cl_2): ν (cm^{-1}) 2065.97 (CO), 1986.25 (CO).

2,3,5-Triphenylthiazol-4-ylidene rhodium(I) biscarbonyl chloride (9a)



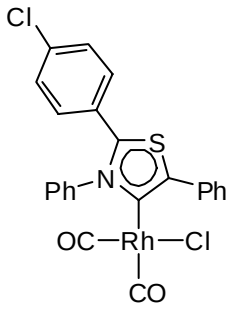
Rh complex **7a** (43 mg, 0.077 mol) was dissolved in dried CH_2Cl_2 (5 mL) and carbon monoxide was bubbled through the solution for 1h at room temperature. A color change from red to orange yellow was observed during this time. The solvent was evacuated in vacuo and the residue was purified by column chromatography on silica gel (PE/EtOAc = 3:1) to give the product **9a** as a yellow powder (38mg, 98%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.27 (d, *J* = 6.8 Hz, 2 H, Ar*H*), 7.99 (s, 1 H, Ar*H*), 7.42-7.49 (m, 7 H, Ar*H*), 7.34 (t, *J* = 16 Hz, 2 H, Ar*H*), 7.27 (d, *J* = 7.6 Hz, 2 H, Ar*H*), 7.20 (s, 1 H, Ar*H*). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 185.9 (d, $J_{C\text{-}Rh}$ = 53.3 Hz, Rh-CO), 183.2 (d, $J_{C\text{-}Rh}$ = 76.5 Hz, Rh-CO), 176.6 (d, $J_{C\text{-}Rh}$ = 38.2 Hz, Rh=C), 171.3, 166.6, 166.6, 141.4, 138.7, 138.7, 132.3, 131.7, 130.0, 129.2, 129.1, 128.9, 128.6, 126.9. IR (CH_2Cl_2): ν (cm^{-1}) 2060.96 (CO), 1981.06 (CO).

3,5-Diphenyl-2-(4-methoxy)phenylthiazol-4-ylidene rhodium(I) biscarbonyl chloride (9b)



Rh complex **7b** (52 mg, 0.088 mol) was dissolved in dried CH_2Cl_2 (5 mL) and carbon monoxide was bubbled through the solution for 1h at room temperature. A color change from yellow to pale yellow was observed during this time. The solvent was evacuated in vacuo and the residue was purified by column chromatography on silica gel (PE/EtOAc = 3:1) to give the product **9b** as a yellow powder (46 mg, 97%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.26 (d, *J* = 7.2 Hz, 2 H, Ar*H*), 8.00 (s, 1 H, Ar*H*), 7.38-7.55 (m, 7 H, Ar*H*), 7.20 (d, *J* = 9.2 Hz, 2 H, Ar*H*), 6.82 (d, *J* = 9.2 Hz, 2 H, Ar*H*), 3.80 (s, 3 H, OCH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 186.0 (d, $J_{C\text{-}Rh}$ = 54.5 Hz, Rh-CO), 183.2 (d, $J_{C\text{-}Rh}$ = 76.4 Hz, Rh-CO), 175.8 (d, $J_{C\text{-}Rh}$ = 37.9 Hz, Rh=C), 167.0, 167.0, 162.1, 141.6, 137.4, 137.3, 132.4, 130.9, 129.9, 128.9, 128.7, 128.6, 119.0, 114.7, 55.4 (O*C*H$_3$). IR (CH_2Cl_2): ν (cm^{-1}) 2061.47 (CO), 1981.71 (CO).

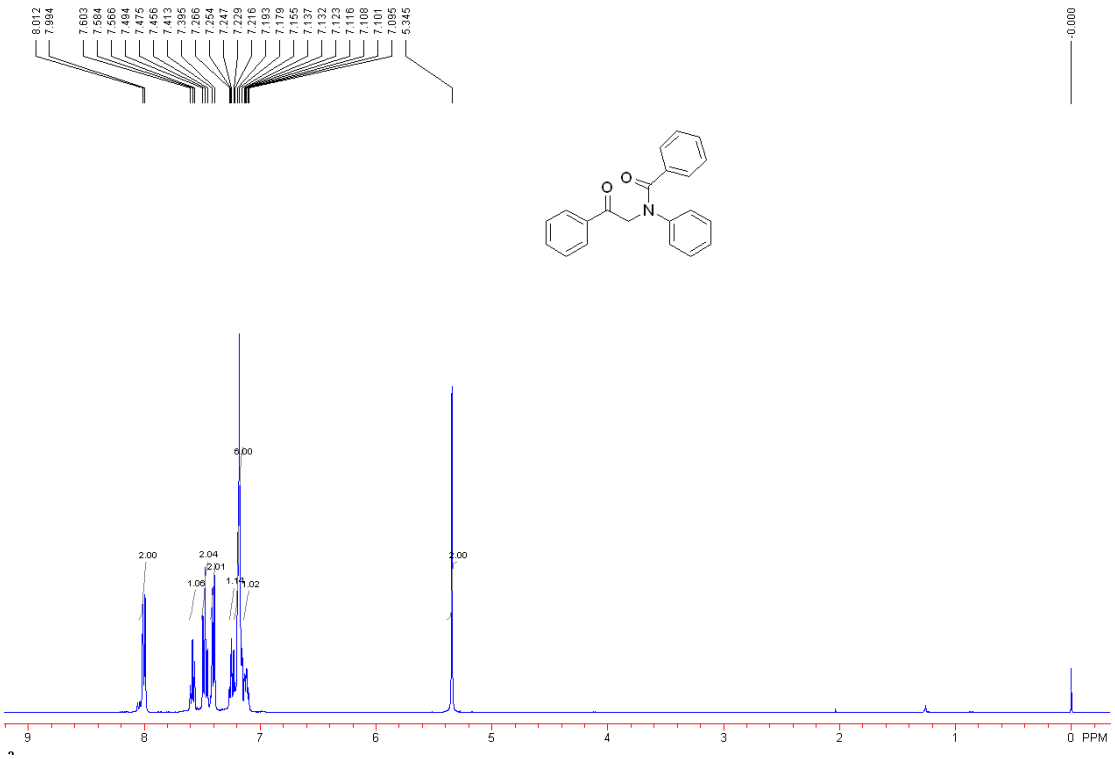
3,5-Diphenyl-2-(4- chloride)phenylthiazol-4-ylidene rhodium(I) biscarbonyl chloride (9c)

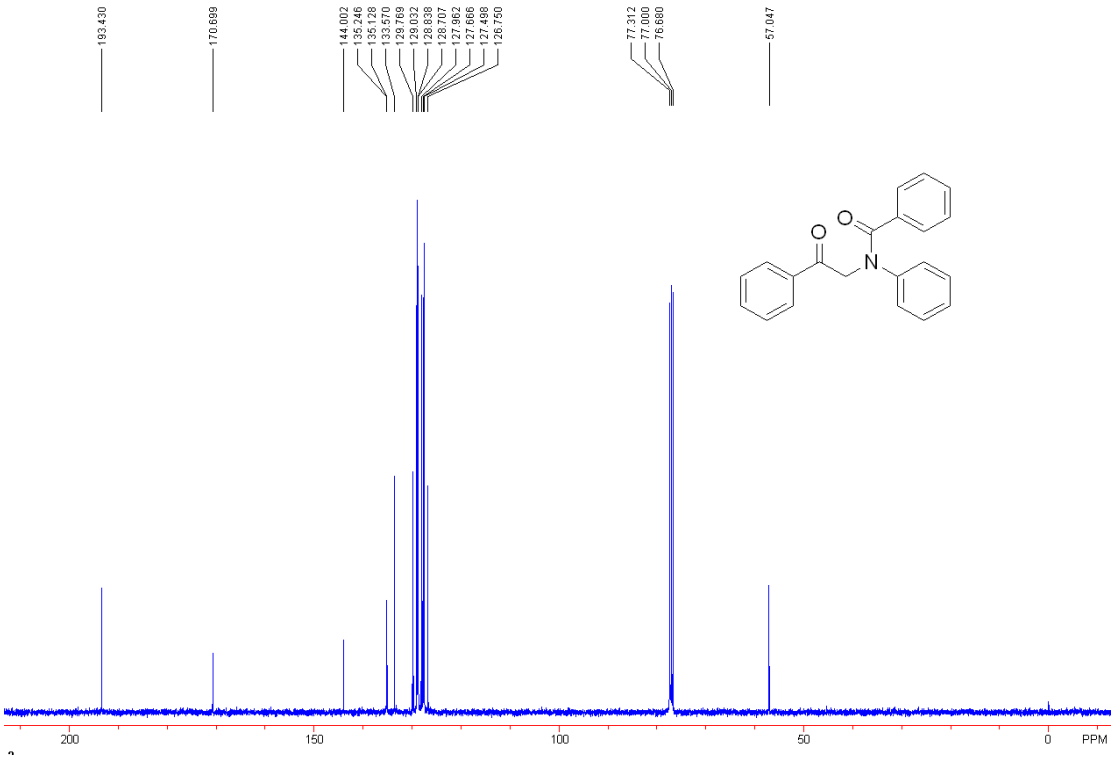


Rh complex **7c** (54 mg, 0.091 mmol) was dissolved in dried CH_2Cl_2 (5 mL) and carbon monoxide was bubbled through the solution for 1h at room temperature. A color change from red to orange yellow was observed during this time. The solvent was evacuated in vacuo and the residue was purified by column chromatography on silica gel (PE/EtOAc = 3:1) to give the product **9c** as a yellow powder (42mg, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.26 (d, *J* = 7.2 Hz, 2 H, Ar*H*), 7.99 (s, 1 H, Ar*H*), 7.42-7.53 (m, 7 H, Ar*H*), 7.33 (d, *J* = 8.4 Hz, 2 H, Ar*H*), 7.21 (d, *J* = 8.8 Hz, 2 H, Ar*H*). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 185.9 (d, $J_{C\text{-}Rh}$ = 53.6 Hz, Rh-CO), 183.1 (d, $J_{C\text{-}Rh}$ = 76.4 Hz, Rh-CO), 177.2 (d, $J_{C\text{-}Rh}$ = 39.2 Hz, Rh=C), 165.1, 165.1, 141.2, 139.0, 139.0, 138.3, 132.1, 130.3, 130.2, 129.6, 129.1, 129.1, 128.7, 125.2. IR (CH_2Cl_2): ν (cm^{-1}) 2061.95 (CO), 1981.92 (CO).

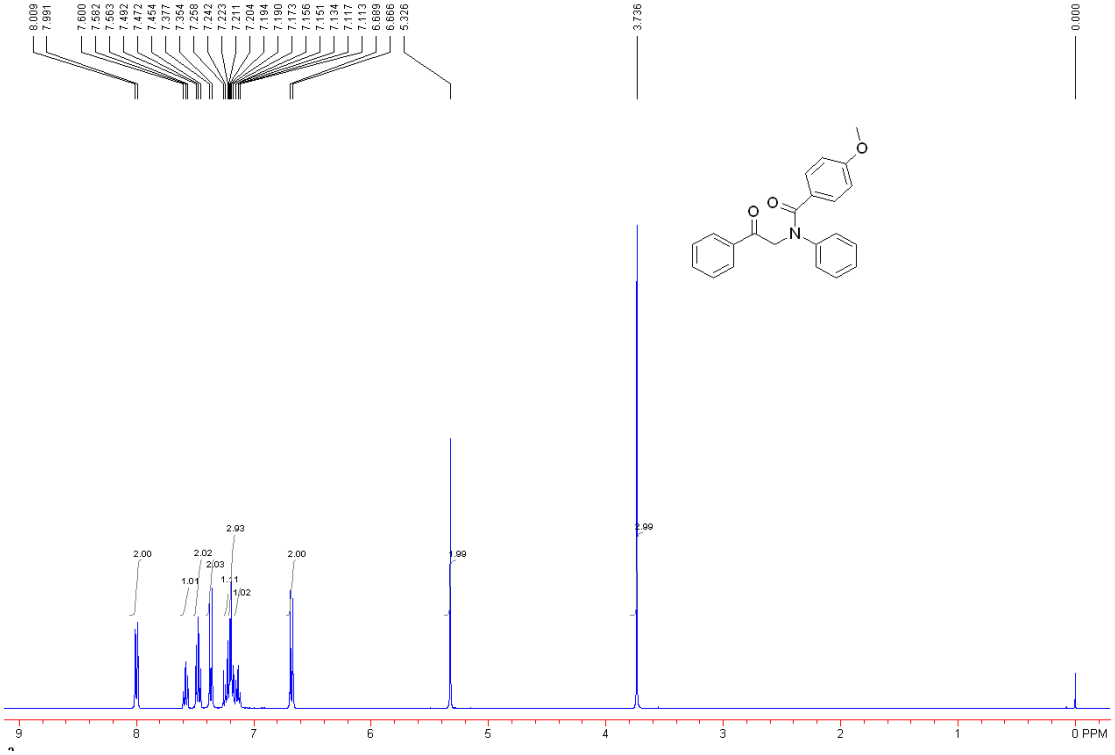
NMR Spectra:

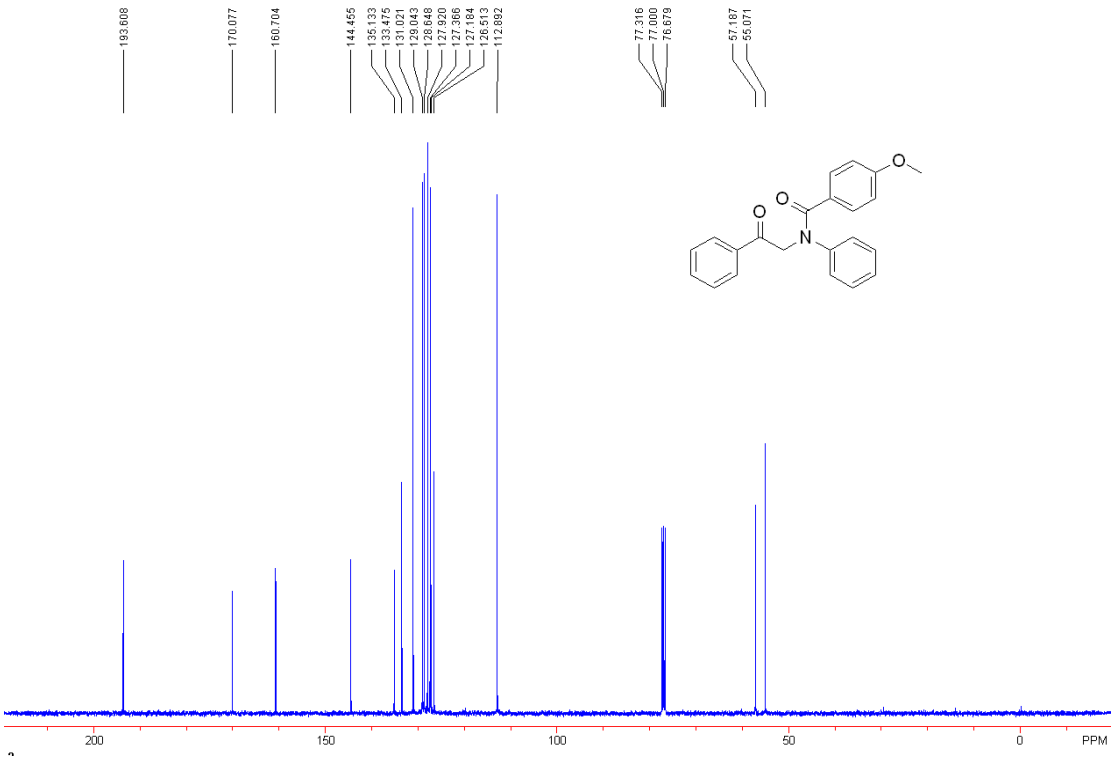
N-Phenyl-amidoacetophenones (2a)



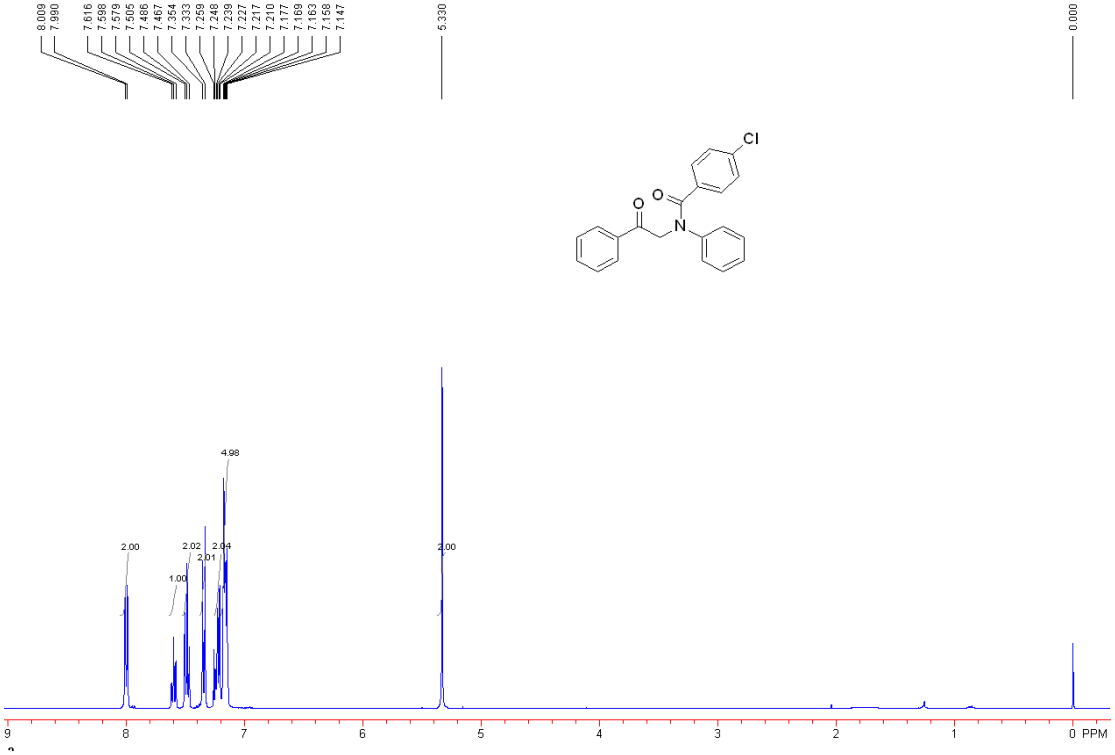


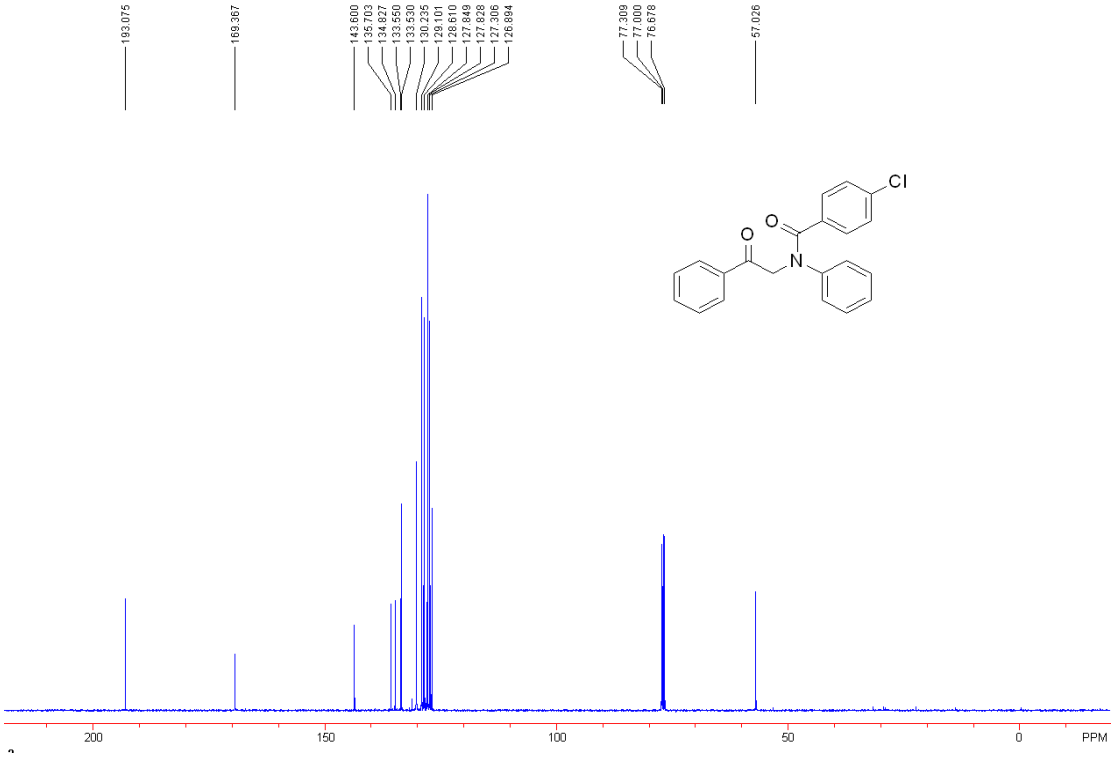
N-4-methoxylphenyl-amidoacetophenones (2b)



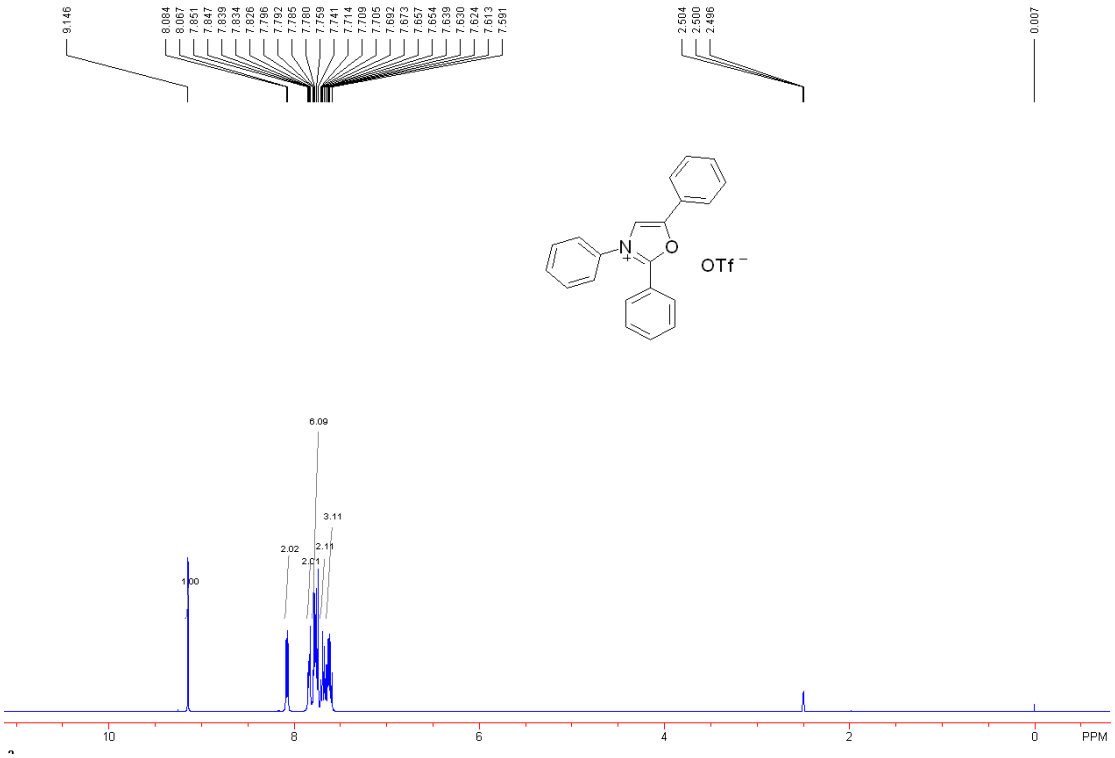


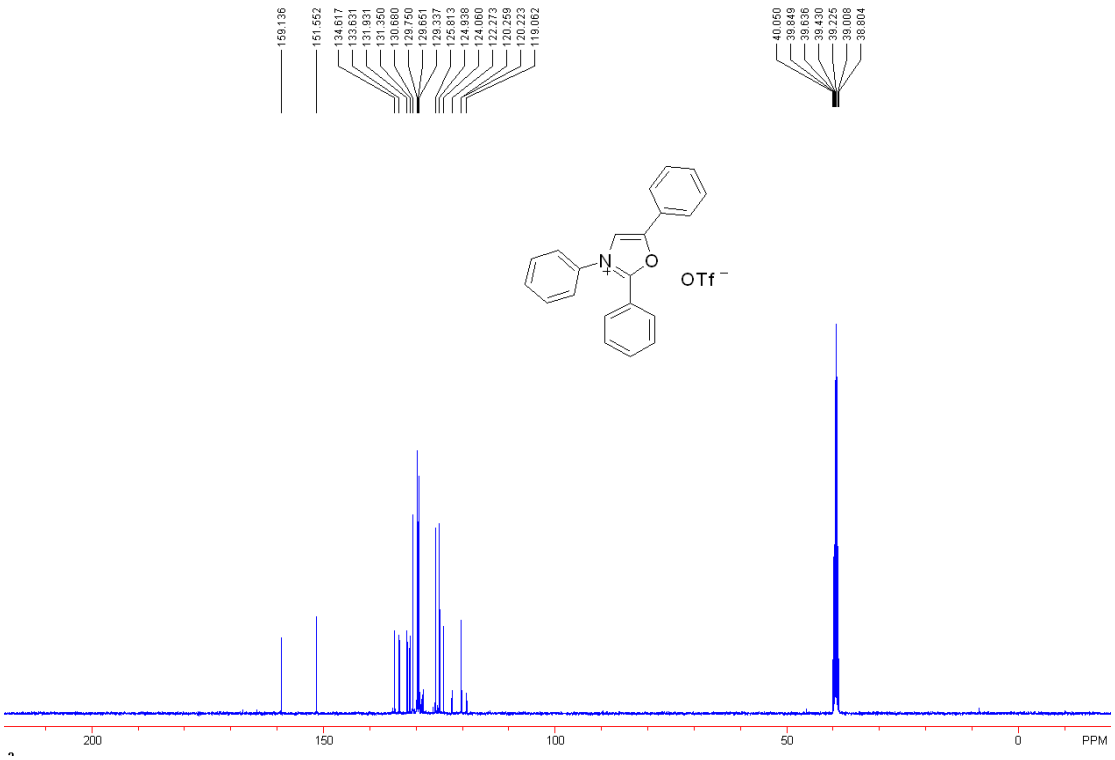
N-4-chlorophenyl-amidoacetophenones (2c)



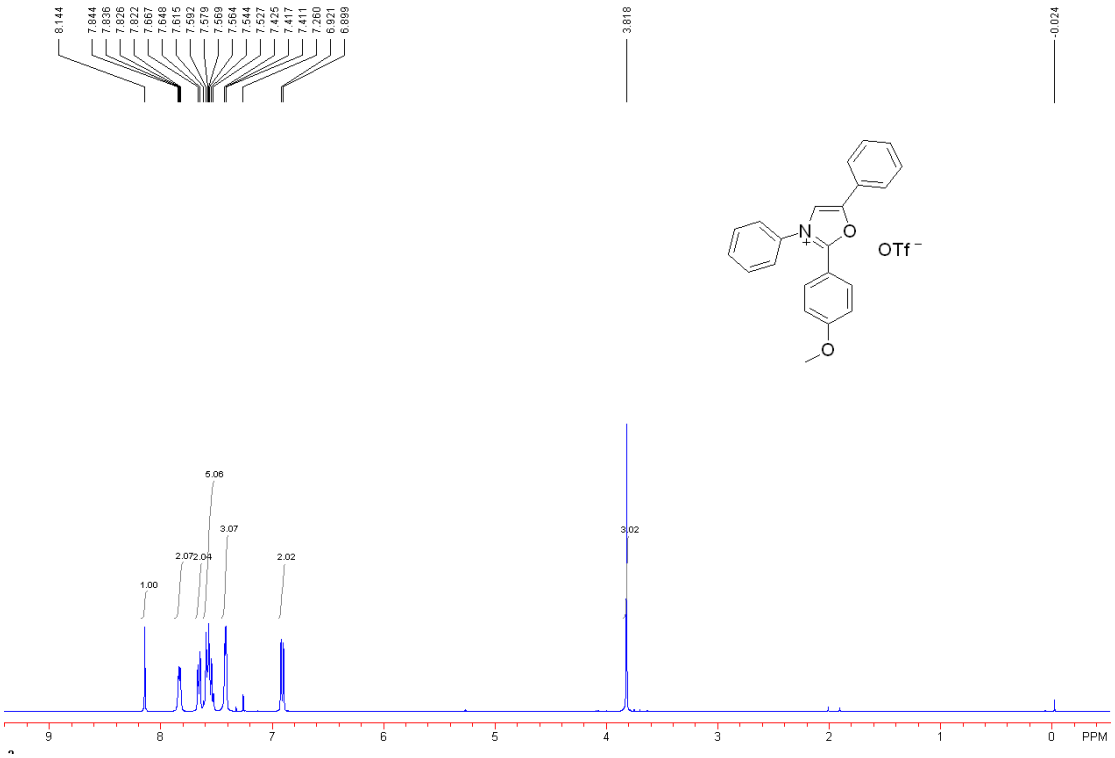


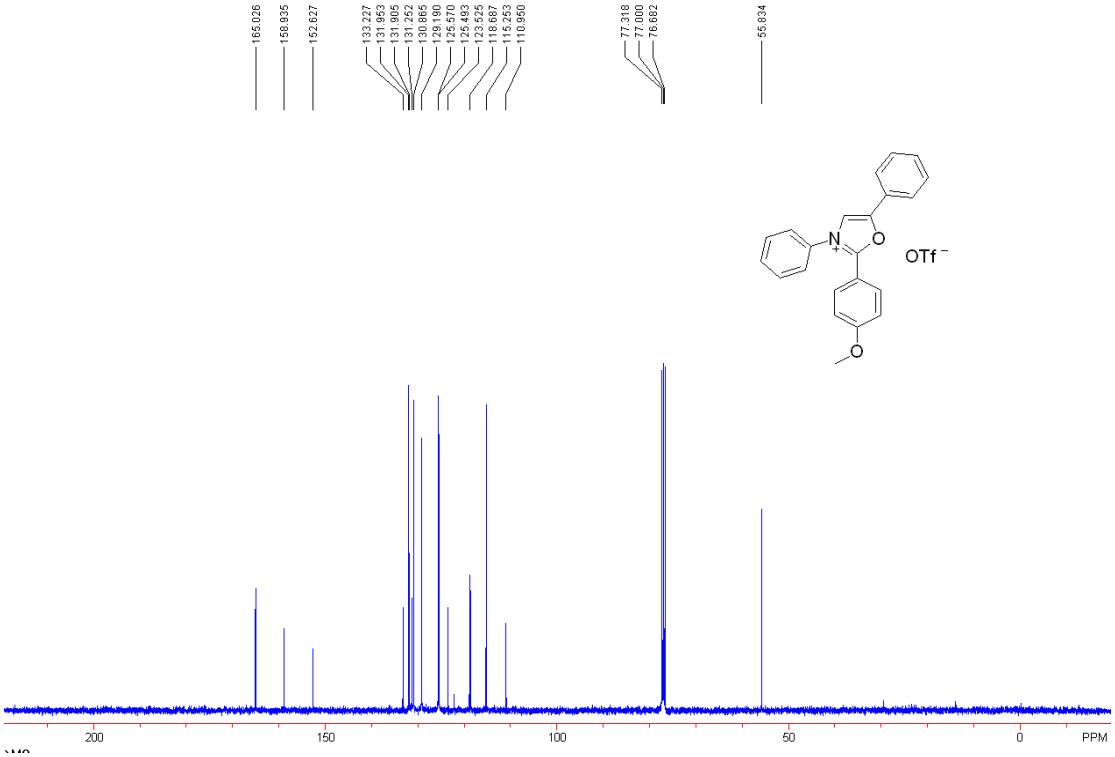
2,3,5-Triphenyloxazolium trifluoromethanesulfonate (3a)



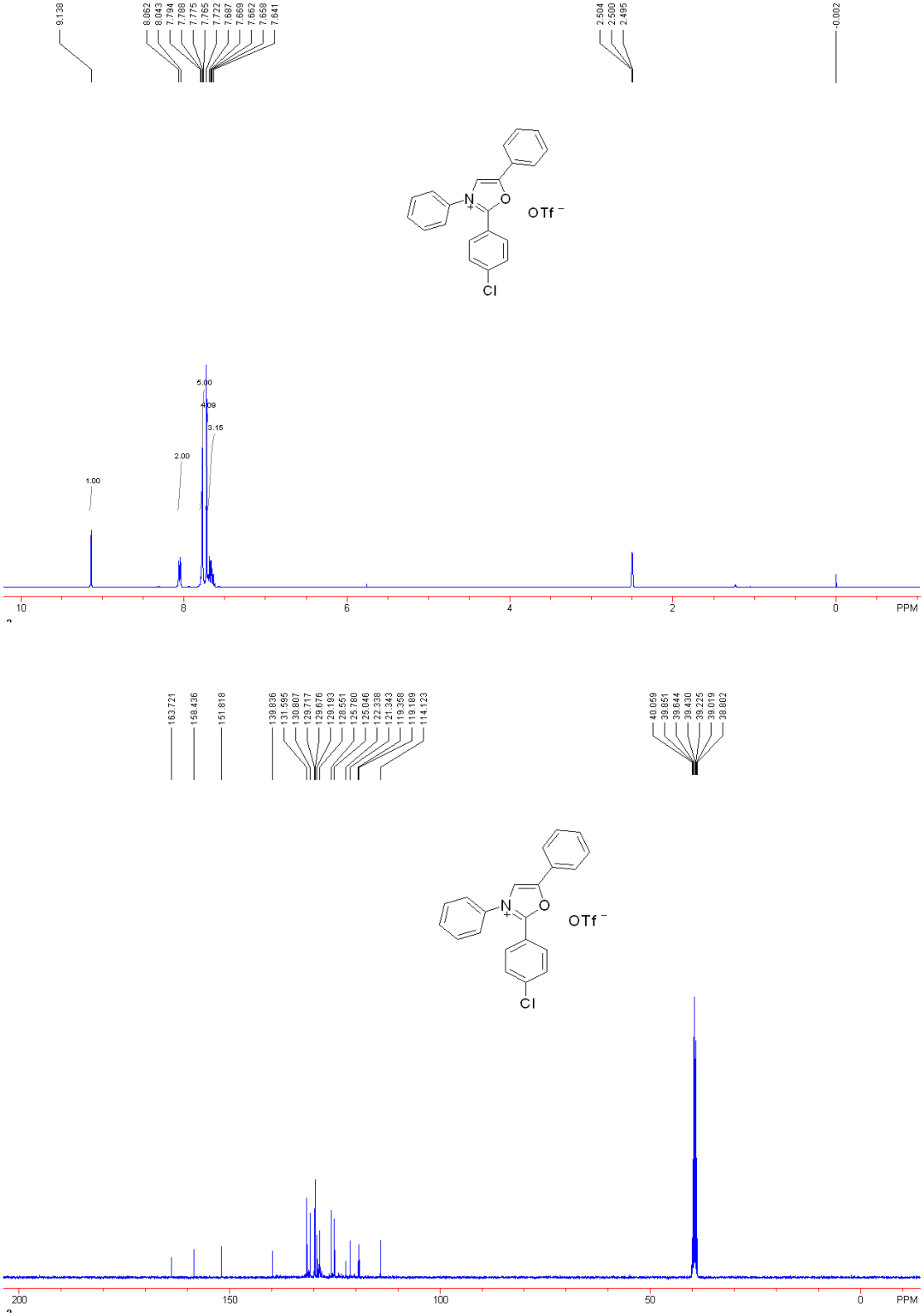


3,5-Diphenyl-2-(4-methoxyl)phenyloxazolium trifluoromethanesulfonate (3b)

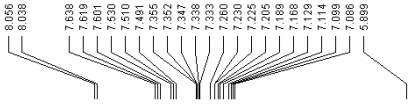


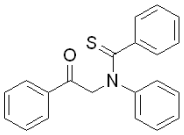


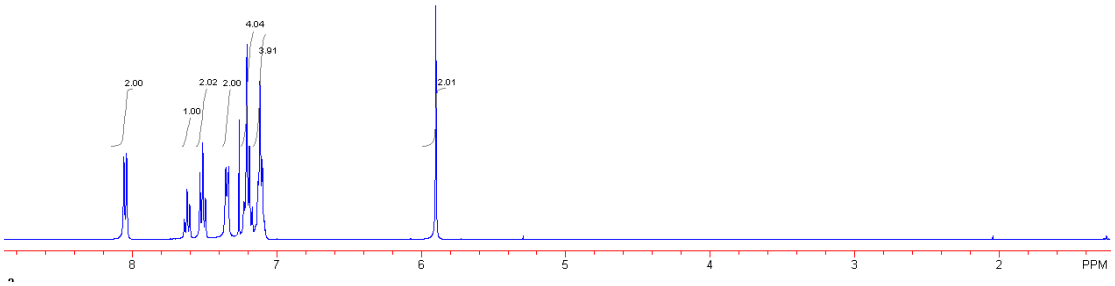
3,5-Diphenyl-2-(4-chloride)phenyloxazolium trifluoromethanesulfonate (3c)

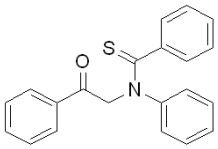


_N_-(2-oxo-2-phenylethyl)-_N_-phenylbenzothioamide (4a)

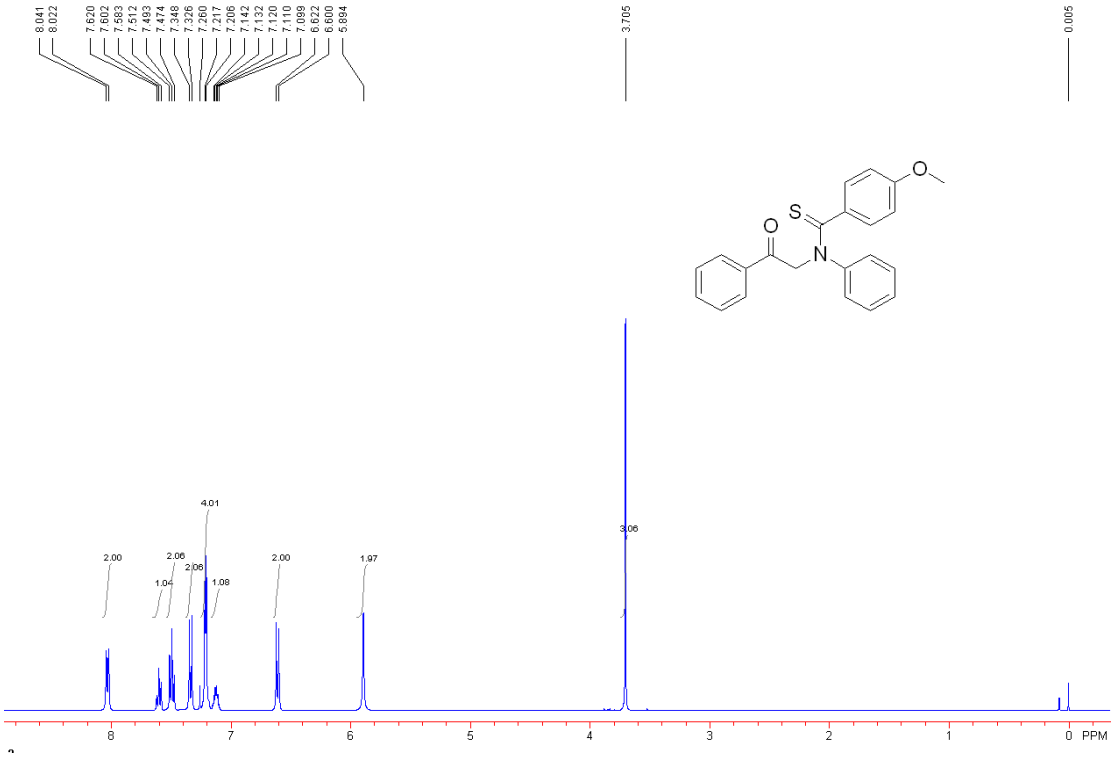


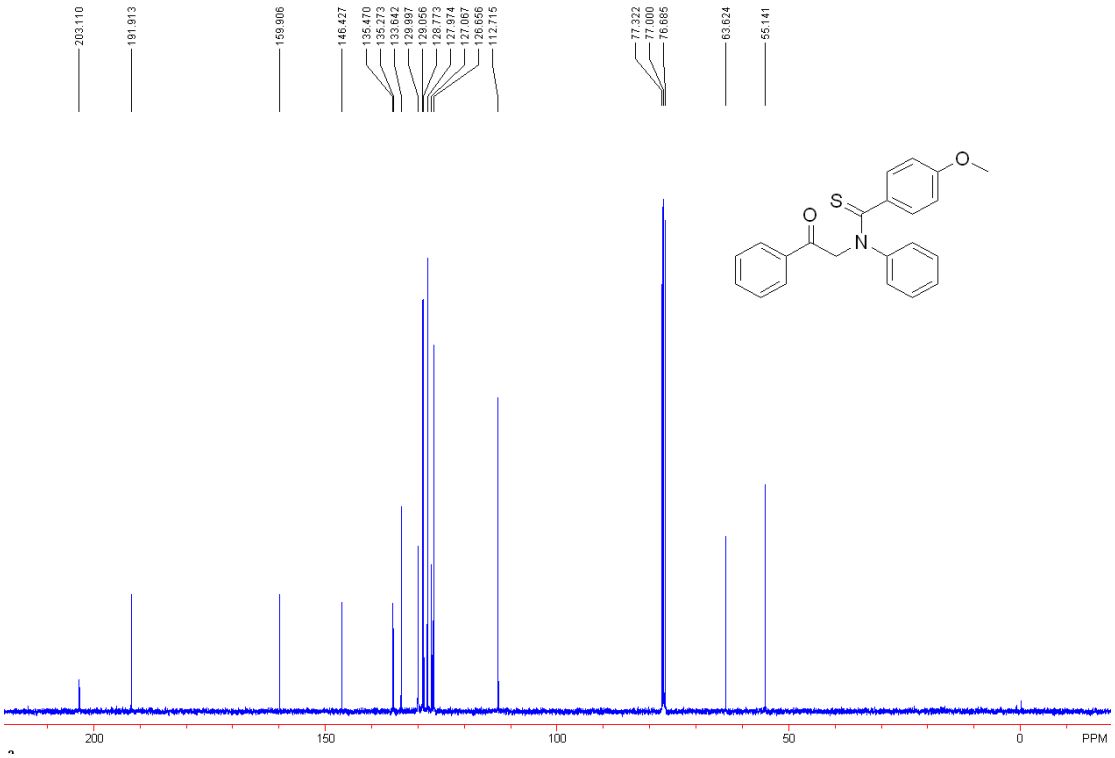




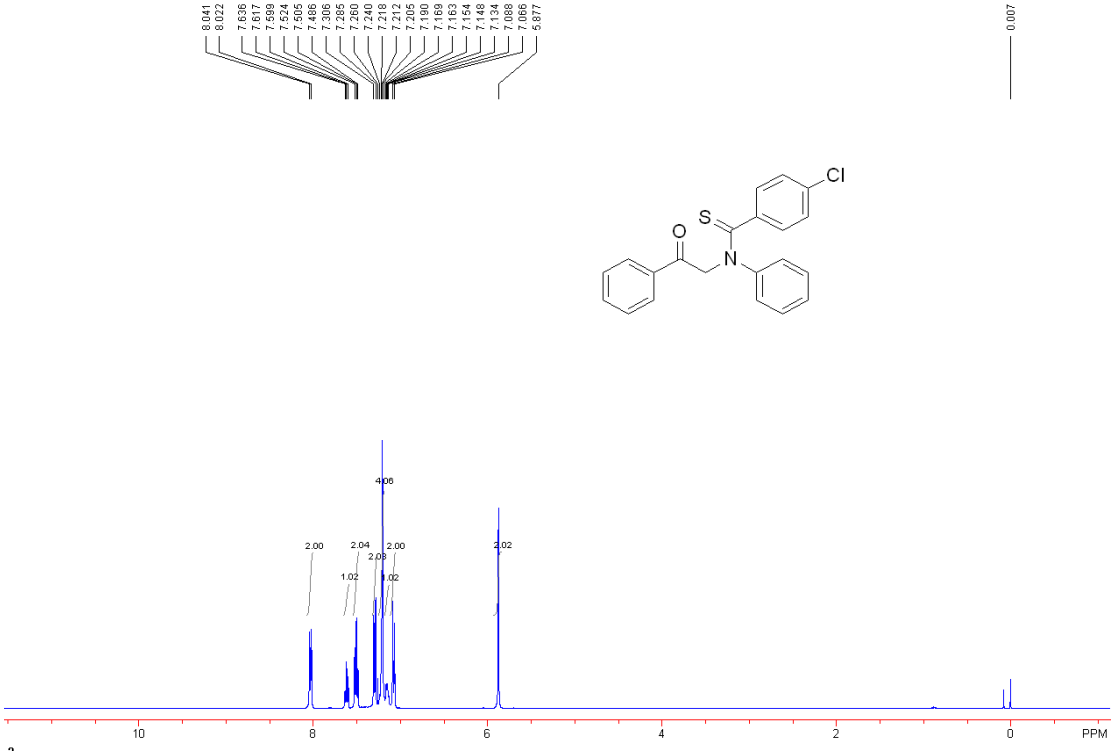


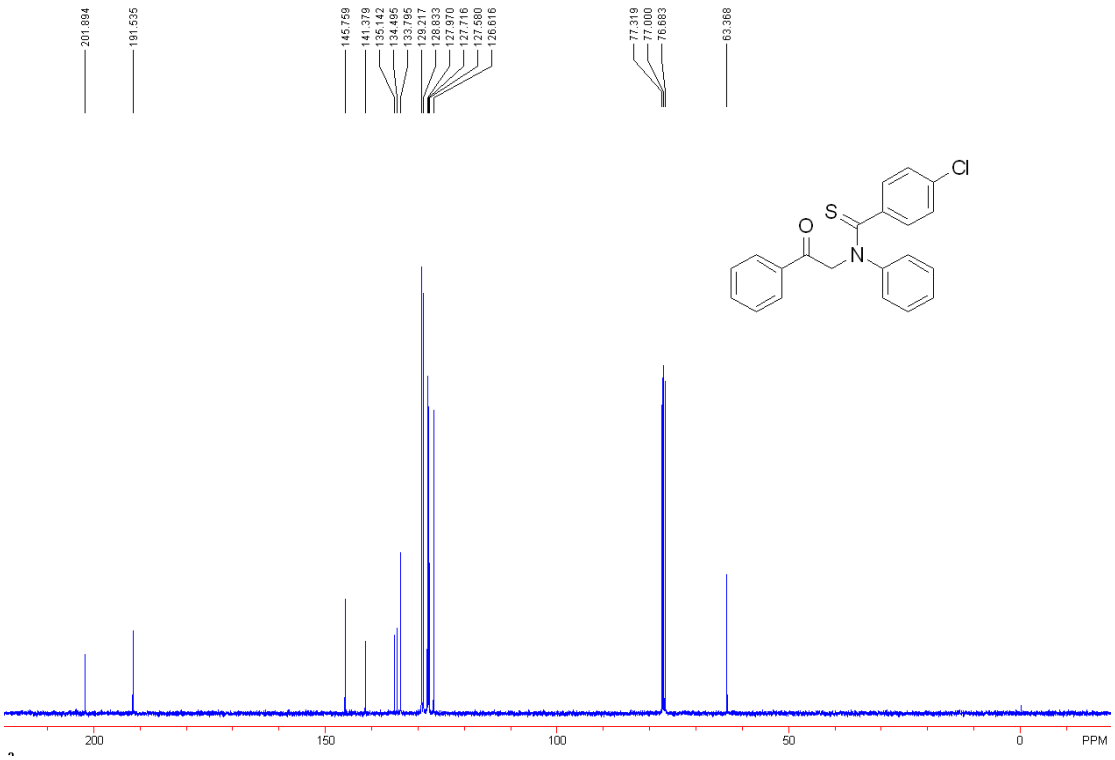
4-methoxy-*N*-(2-oxo-2-phenylethyl)-*N*-phenylbenzothioamide (4b)



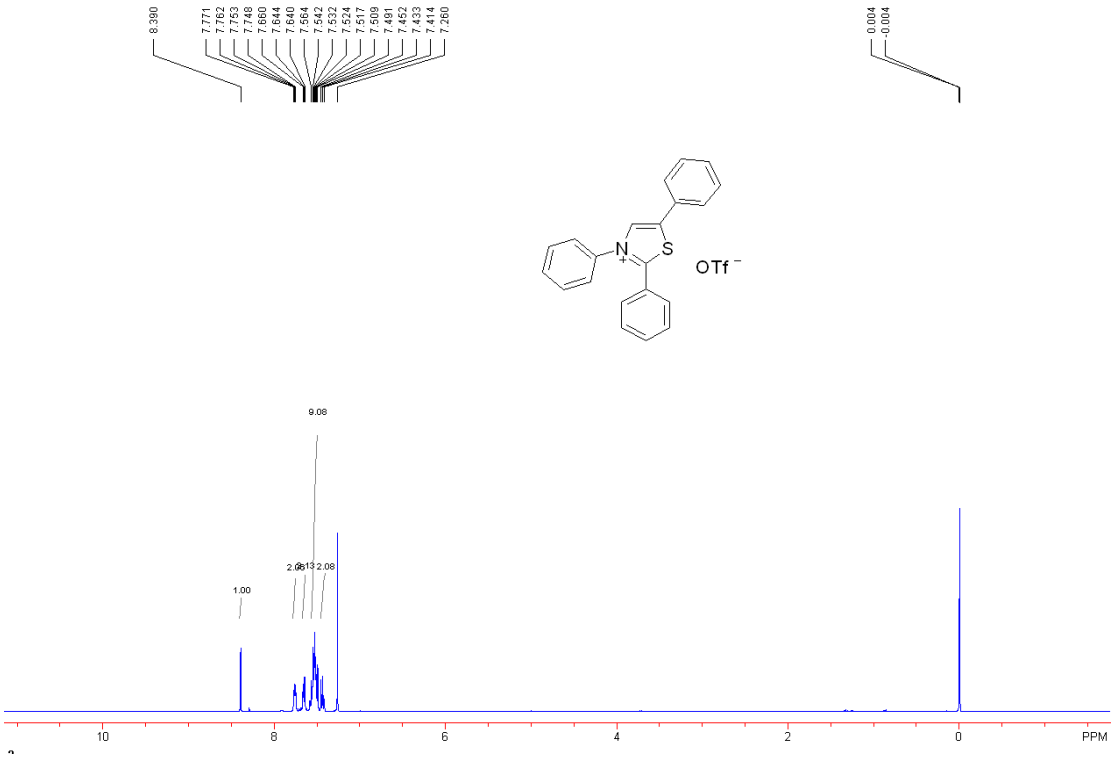


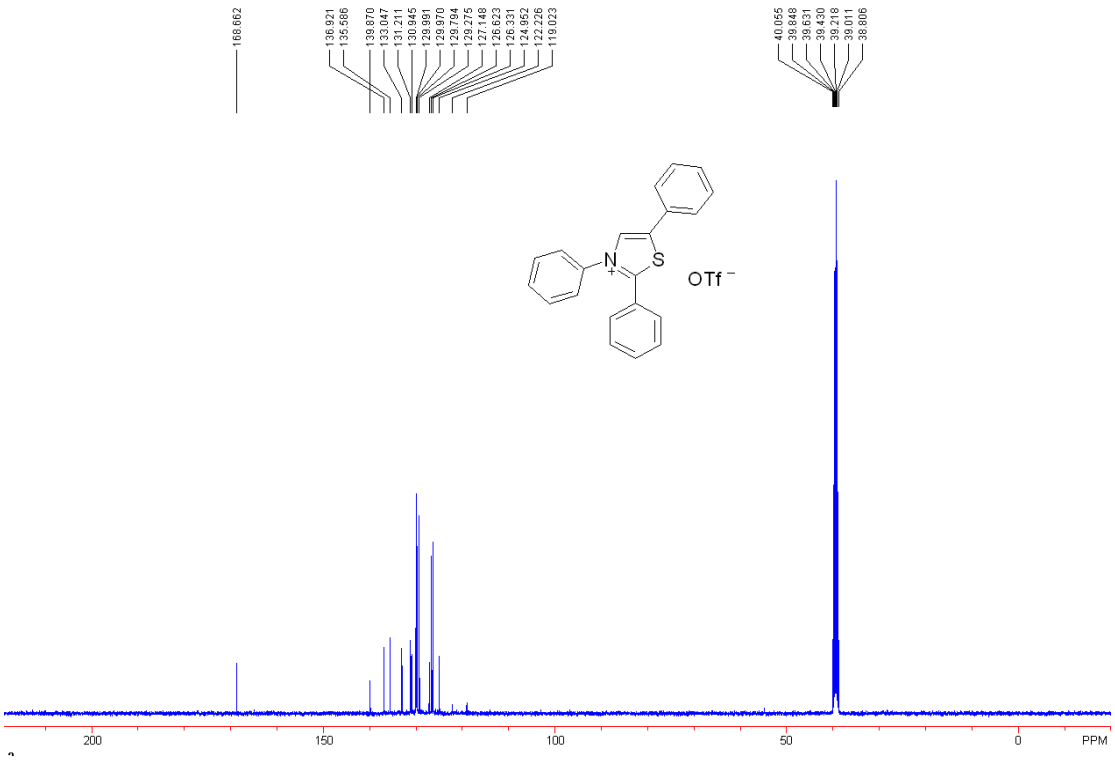
4-chloro-*N*-(2-oxo-2-phenylethyl)-*N*-phenylbenzothioamide (4c)



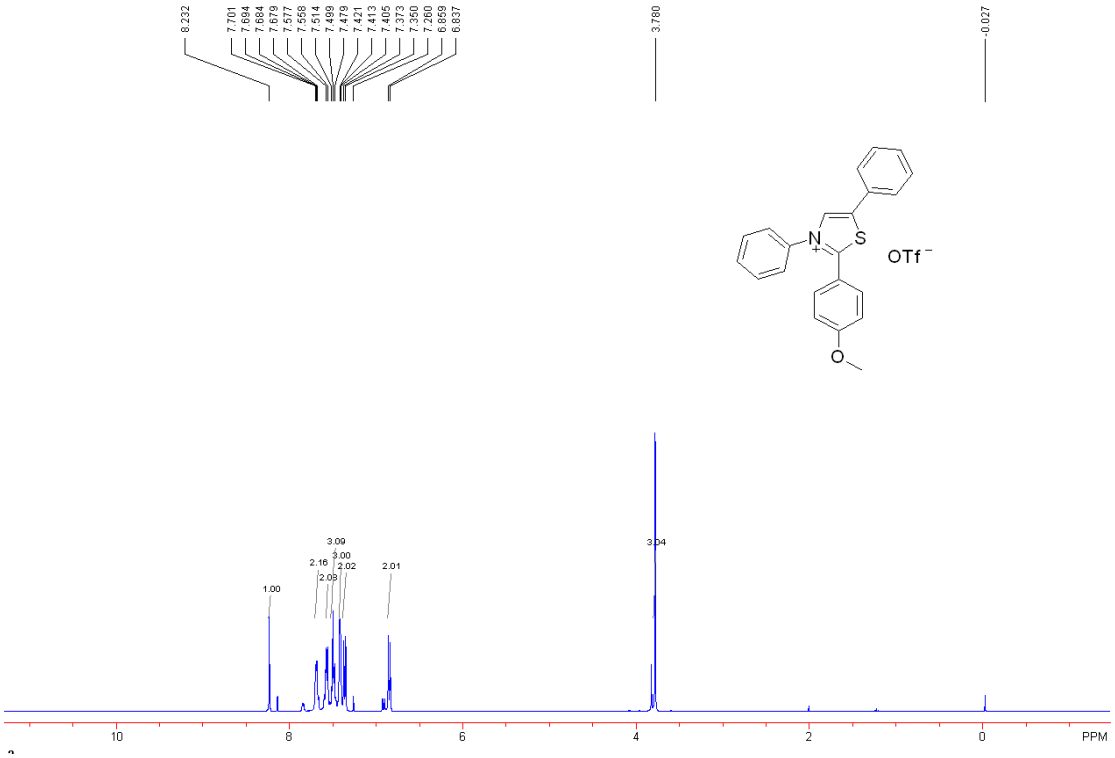


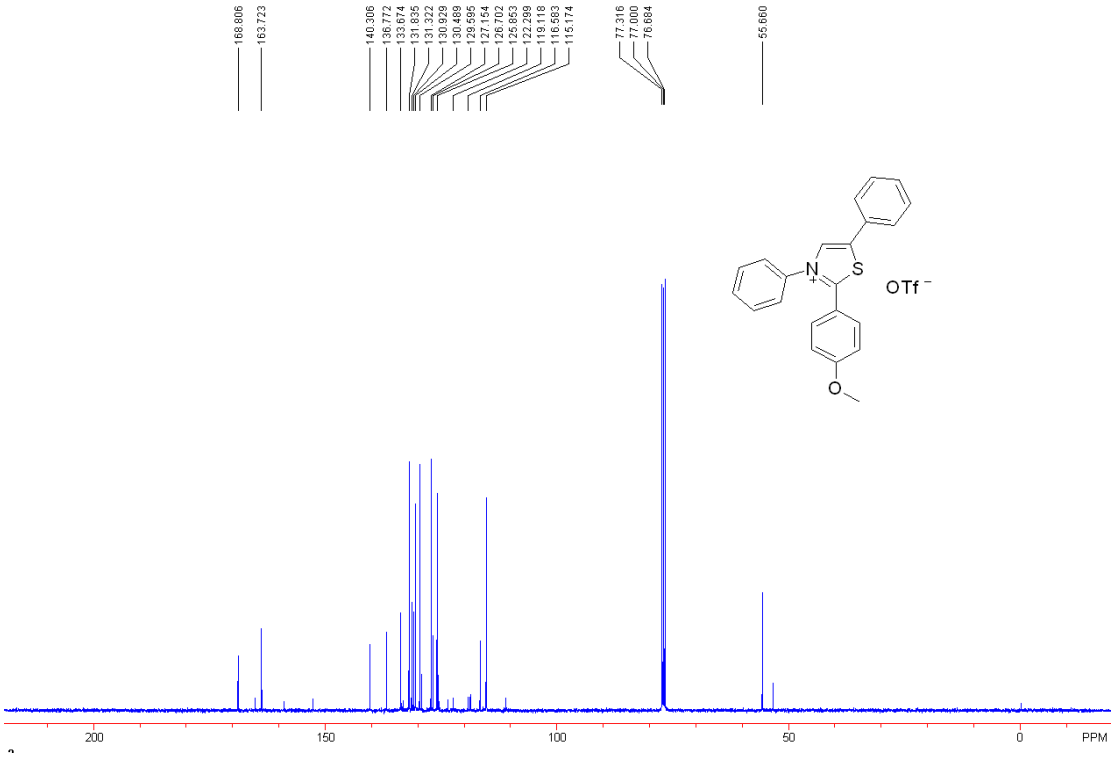
2,3,5-Triphenylthiazolium trifluoromethanesulfonate (5a)



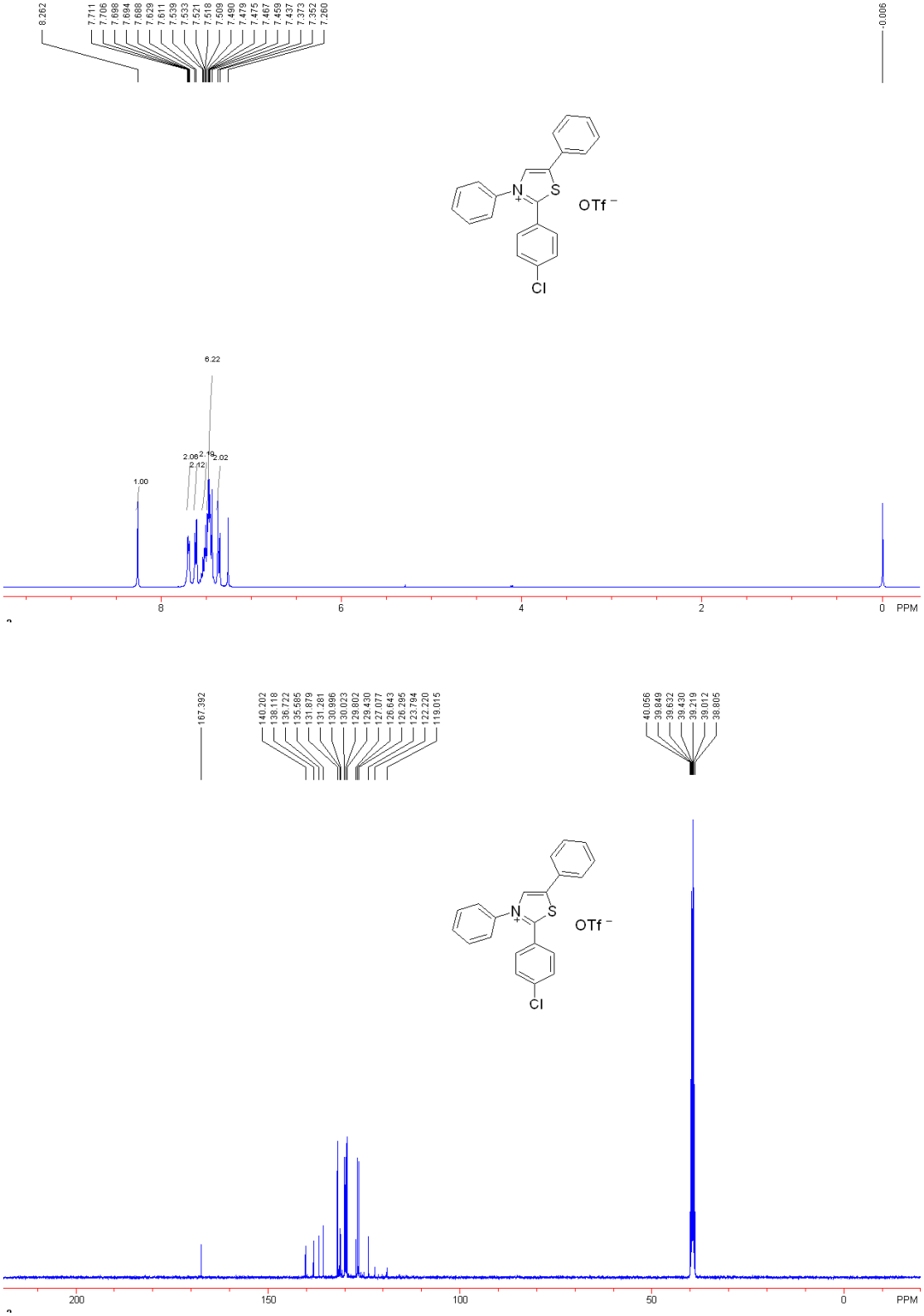


3,5-Diphenyl-2-(4-methoxyl)phenylthiazolium trifluoromethanesulfonate (5b)

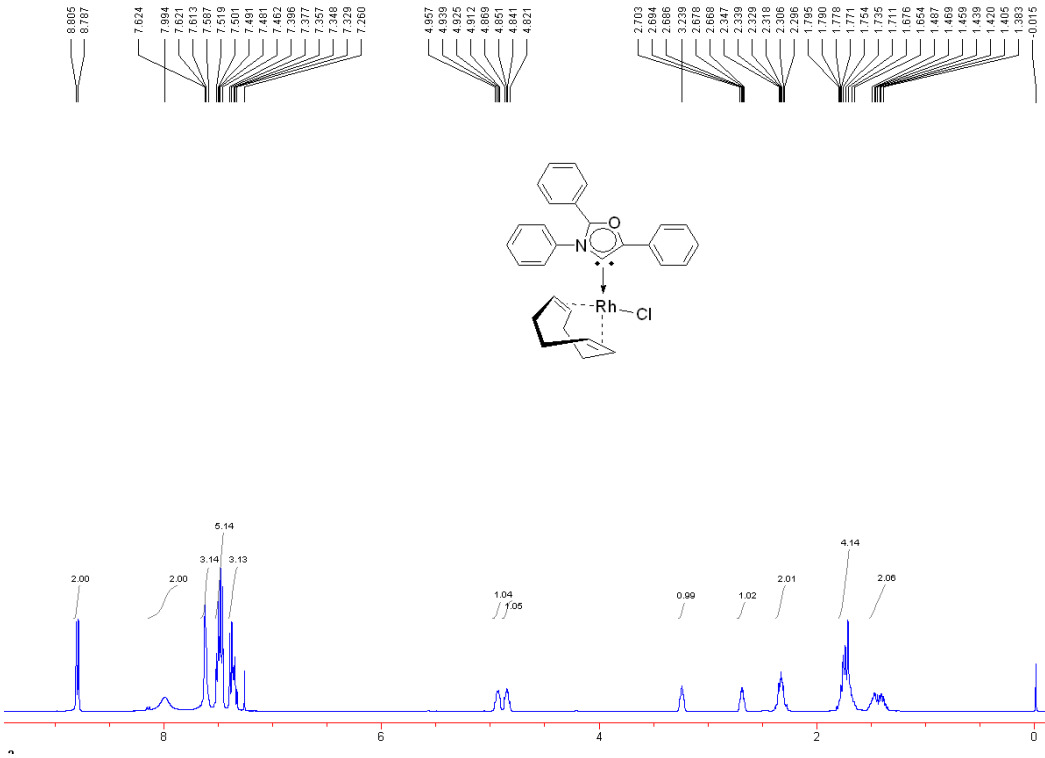


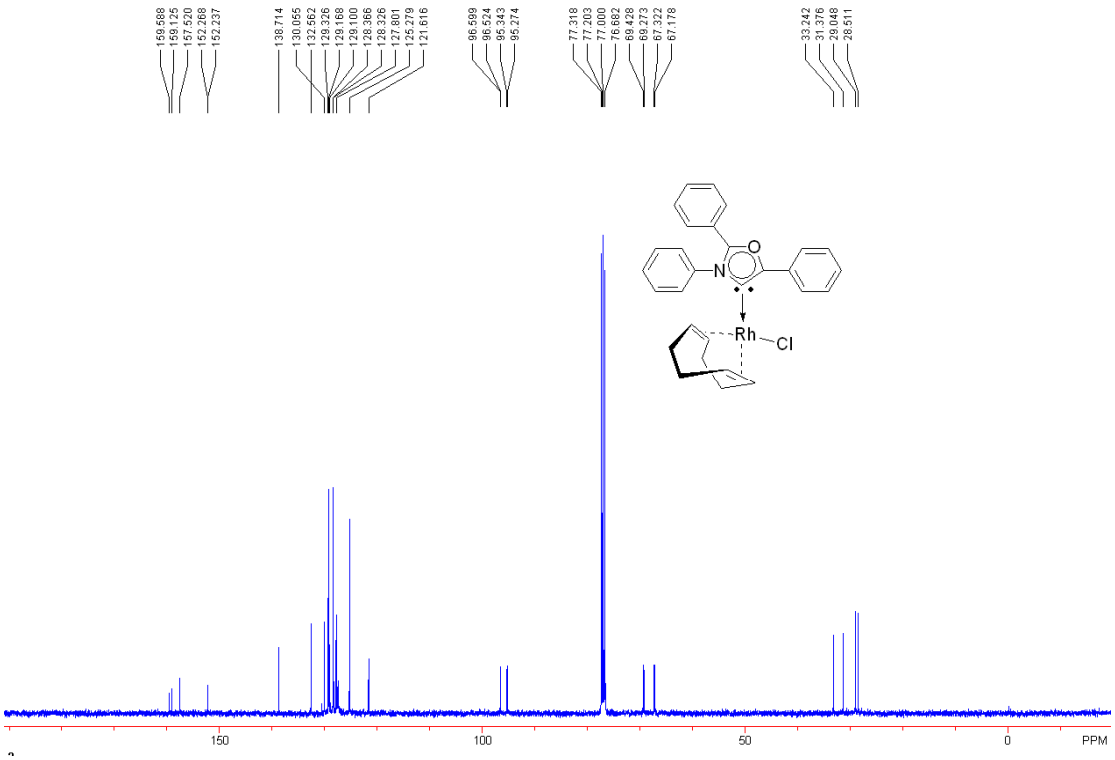


3,5-Diphenyl-2-(4-chloride)phenylthiazolium trifluoromethanesulfonate (5c)

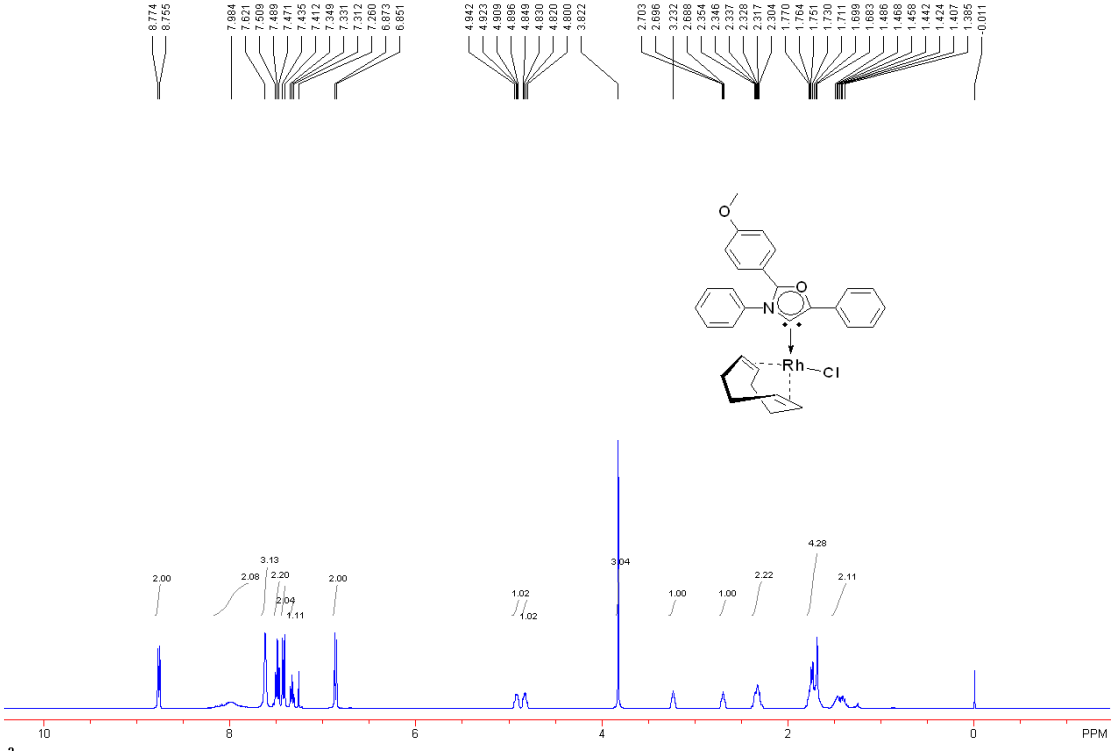


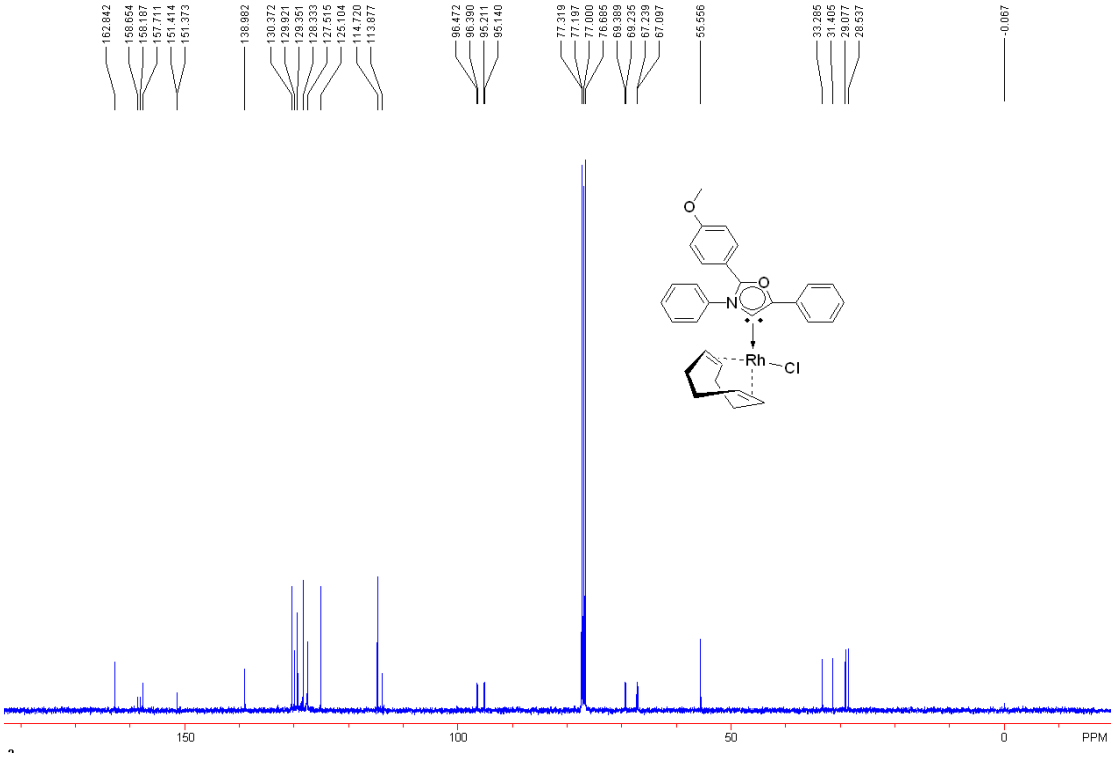
2,3,5-Triphenyloxazol-4-ylidene rhodium(I) cyclooctadiene chloride (6a)



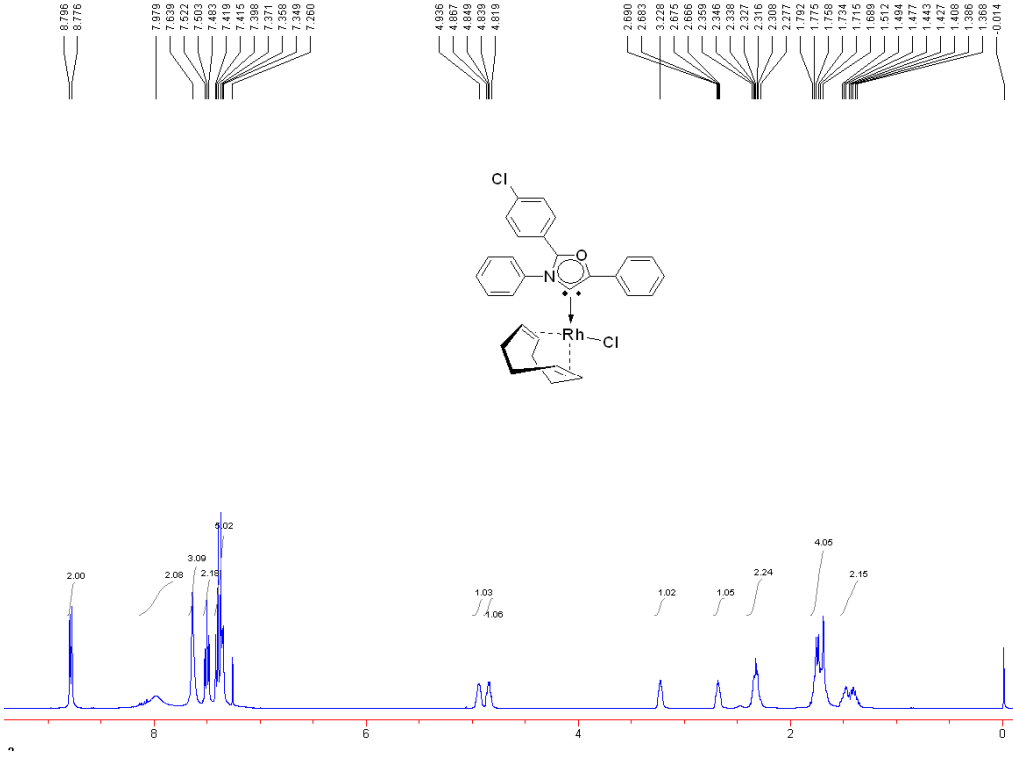


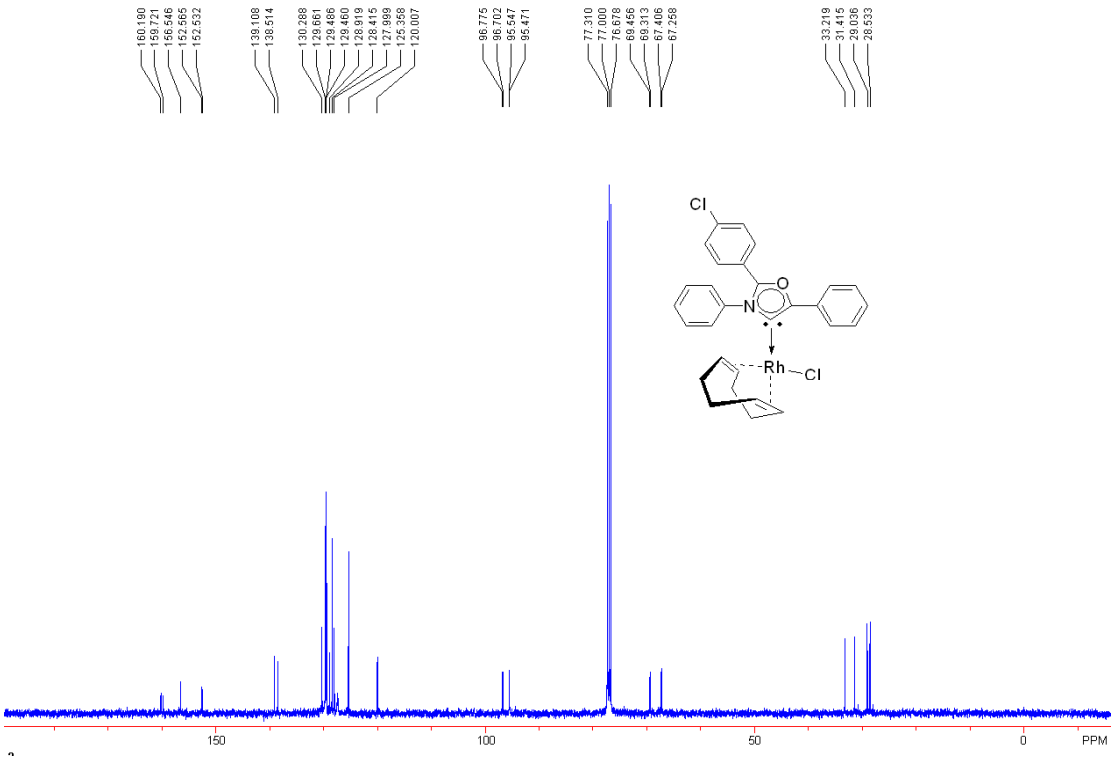
3,5-Diphenyl-2-(4-methoxy)phenyloxazol-4-ylidene rhodium(I) cyclooctadiene chloride (6b)



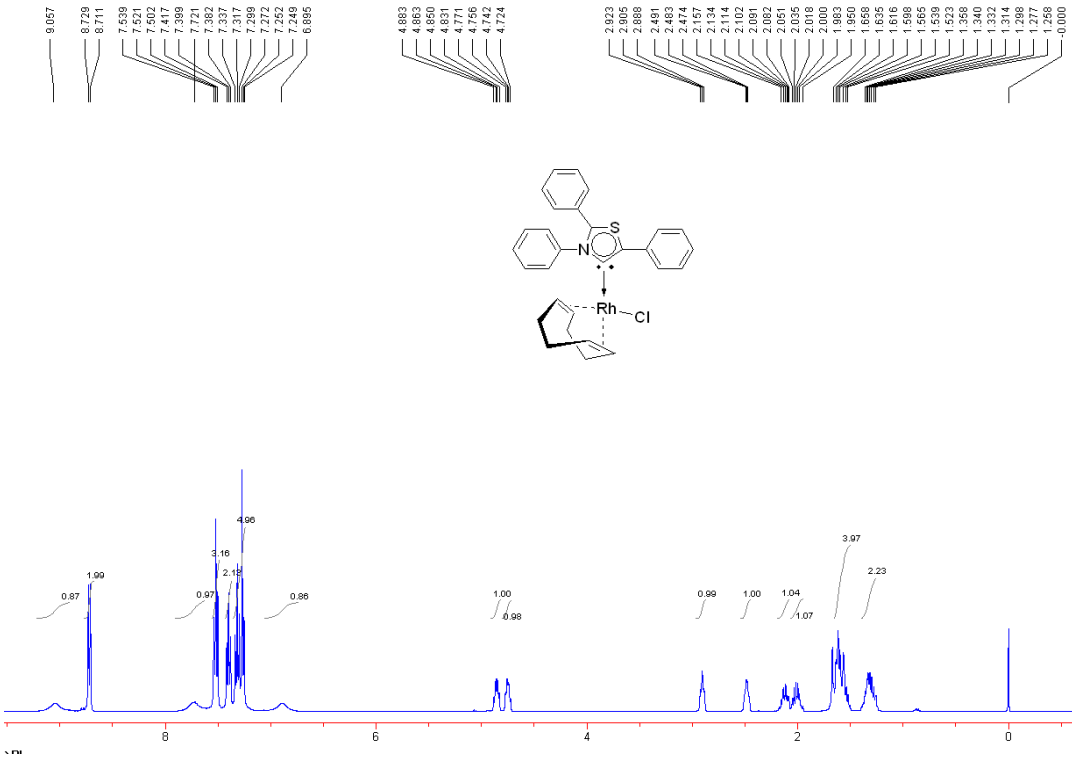


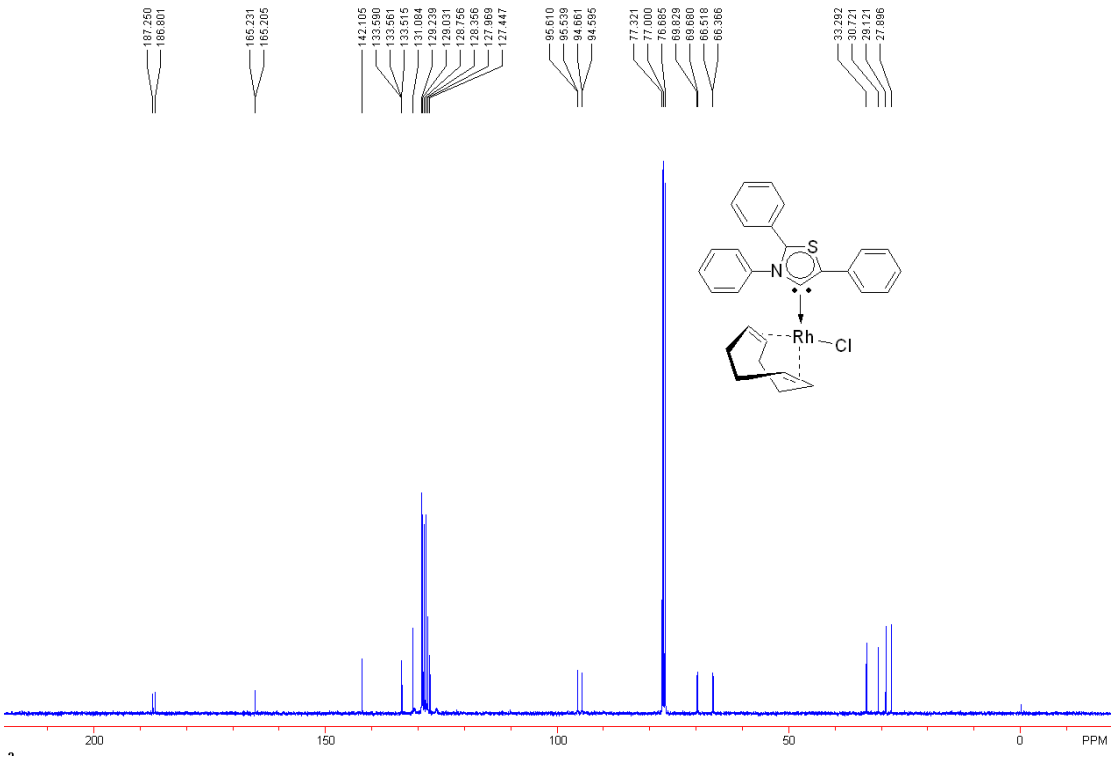
3,5-Diphenyl-2-(4-chloride)phenyloxazol-4-ylidene rhodium(I) cyclooctadiene chloride (6c)



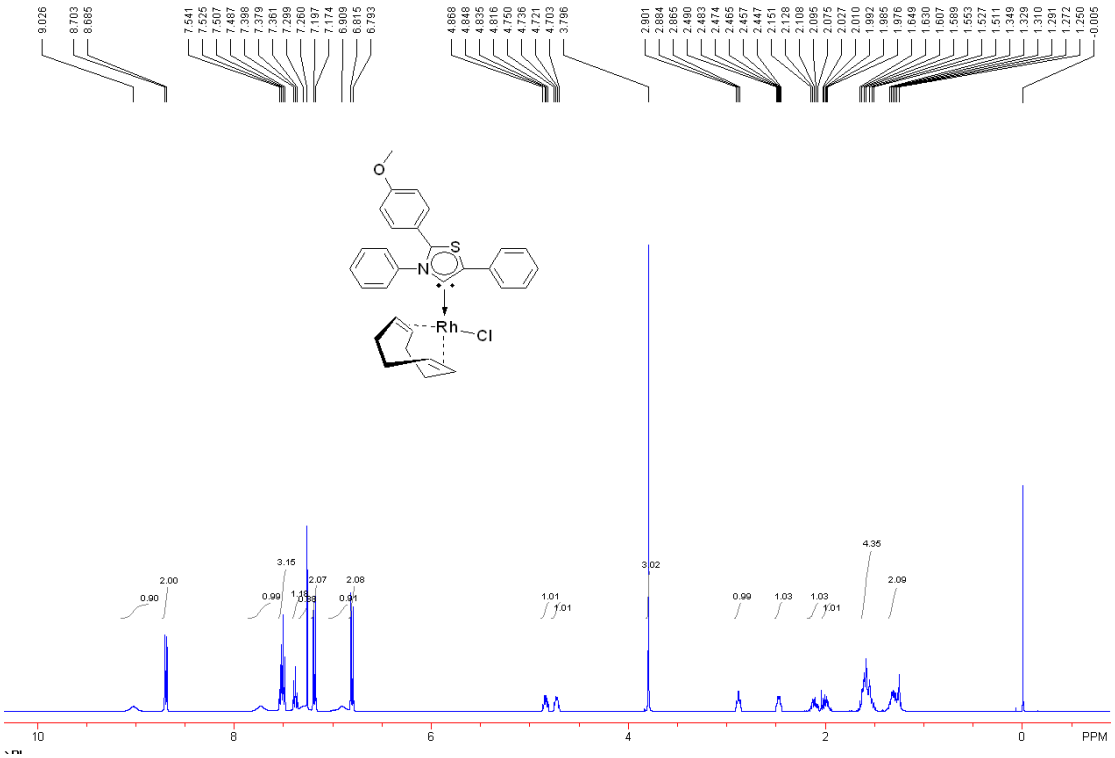


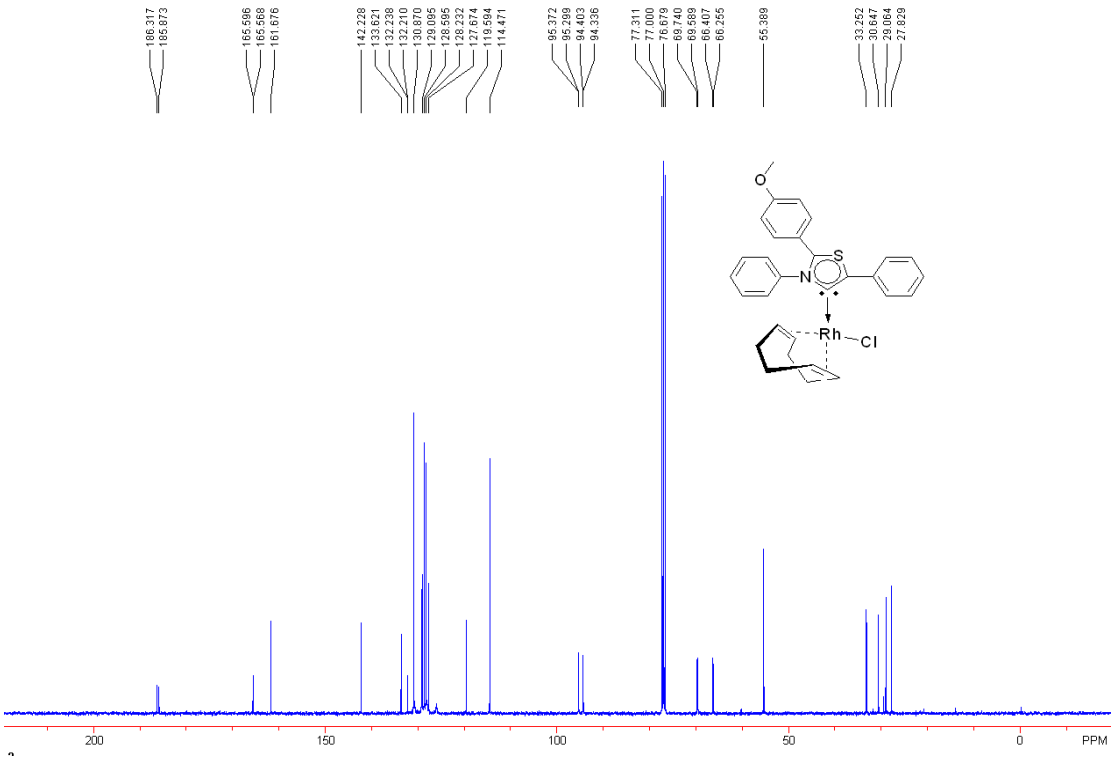
2,3,5-Triphenylthiazol-4-ylidene rhodium(I) cyclooctadiene chloride (7a)



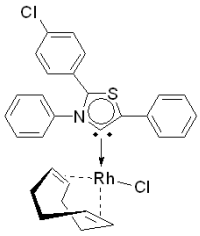


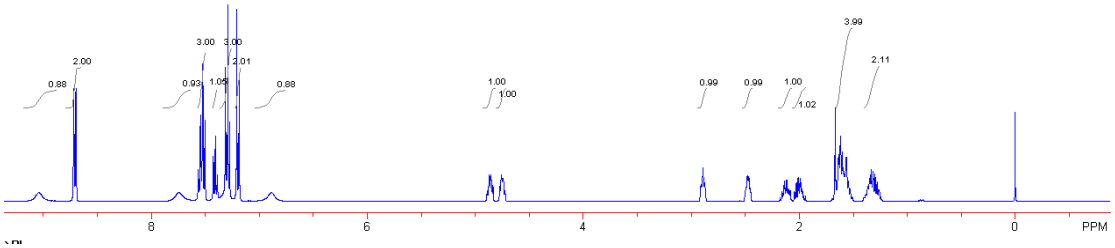
3,5-Diphenyl-2-(4-methoxy)phenylthiazol-4-ylidene rhodium(I) cyclooctadiene chloride (7b)

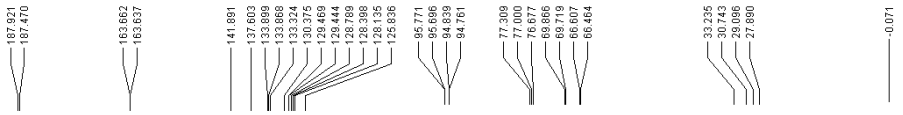


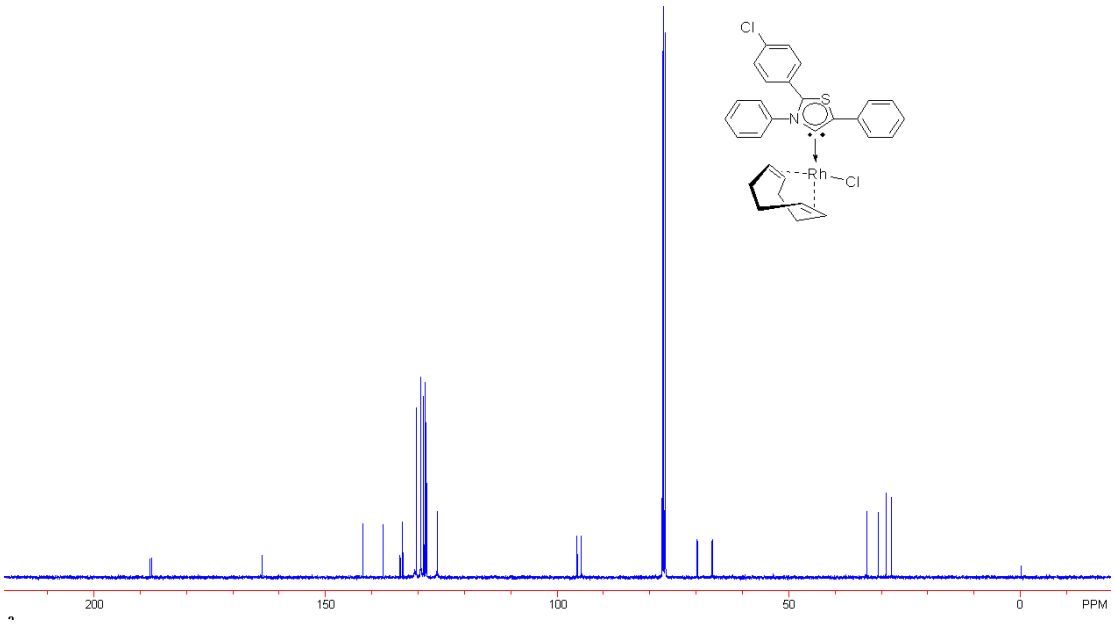


3,5-Diphenyl-2-(4-chloride)phenylthiazol-ylidene rhodium(I) cyclooctadiene chloride (7c)

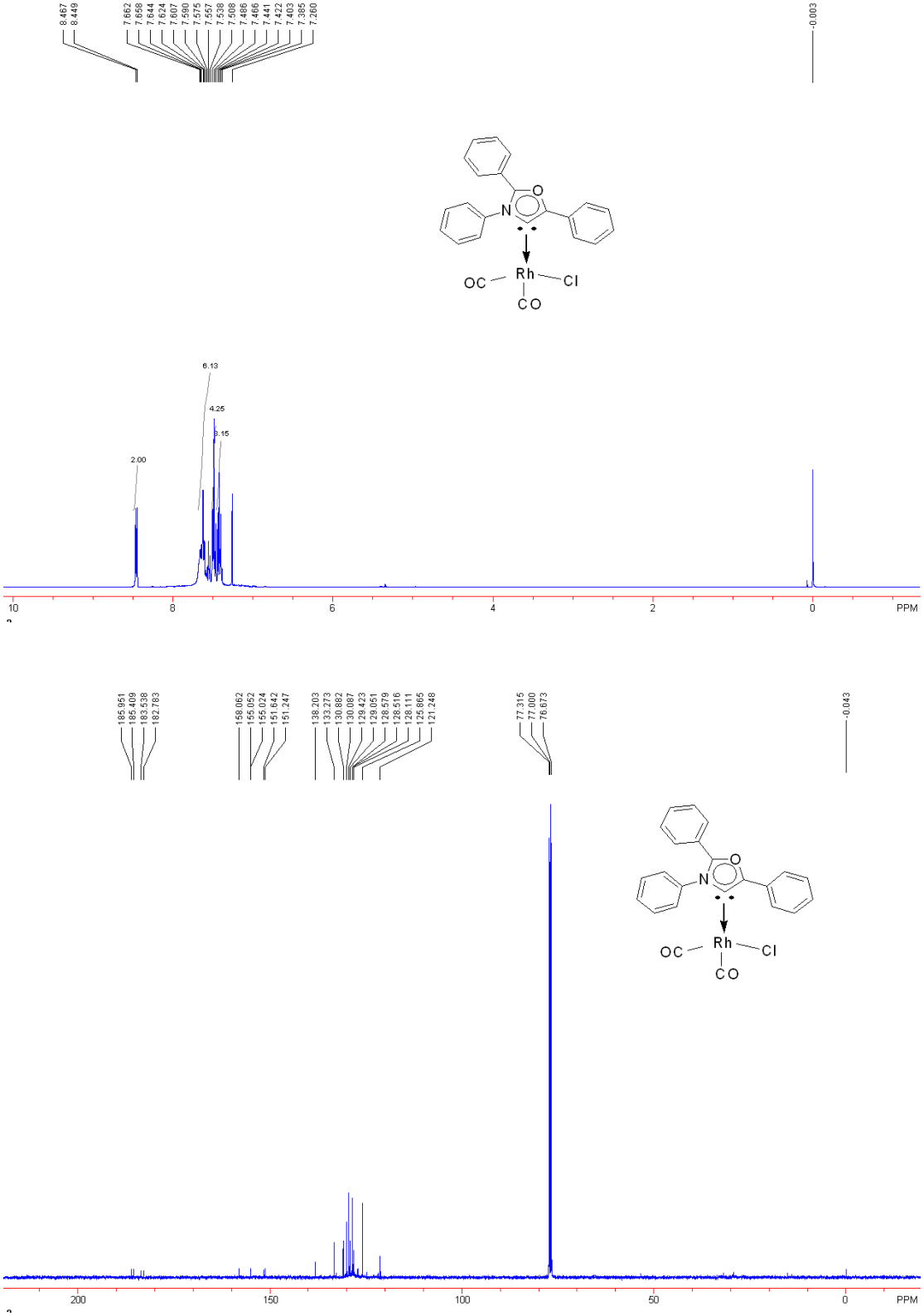




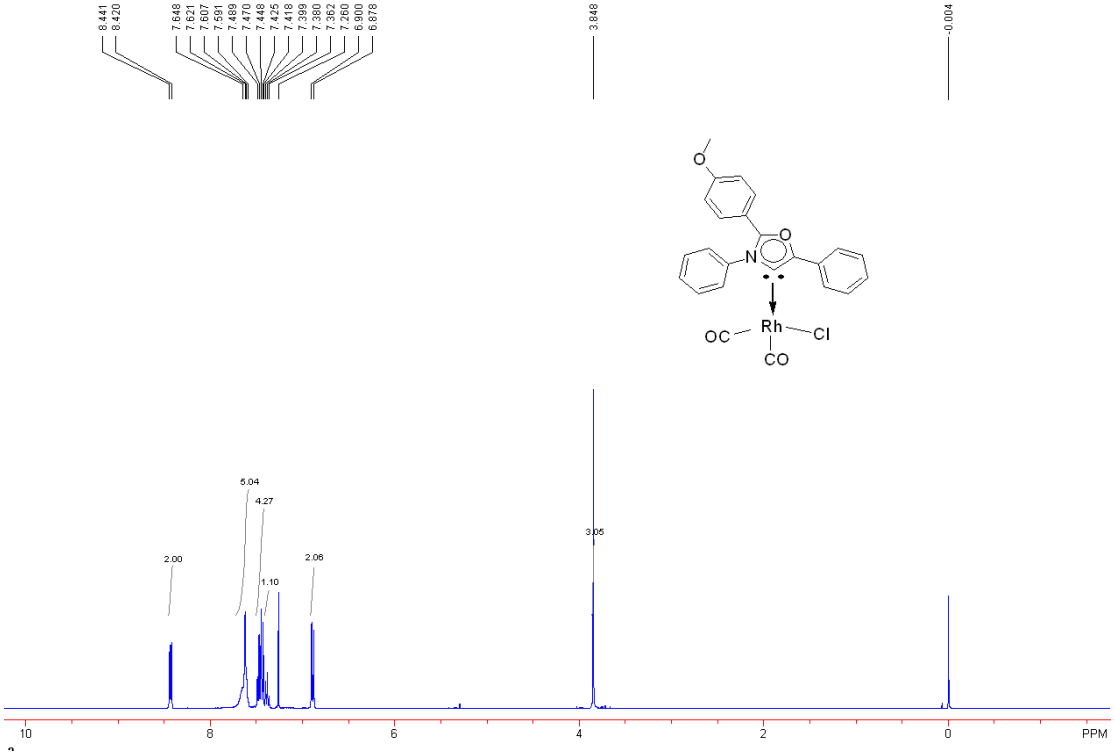


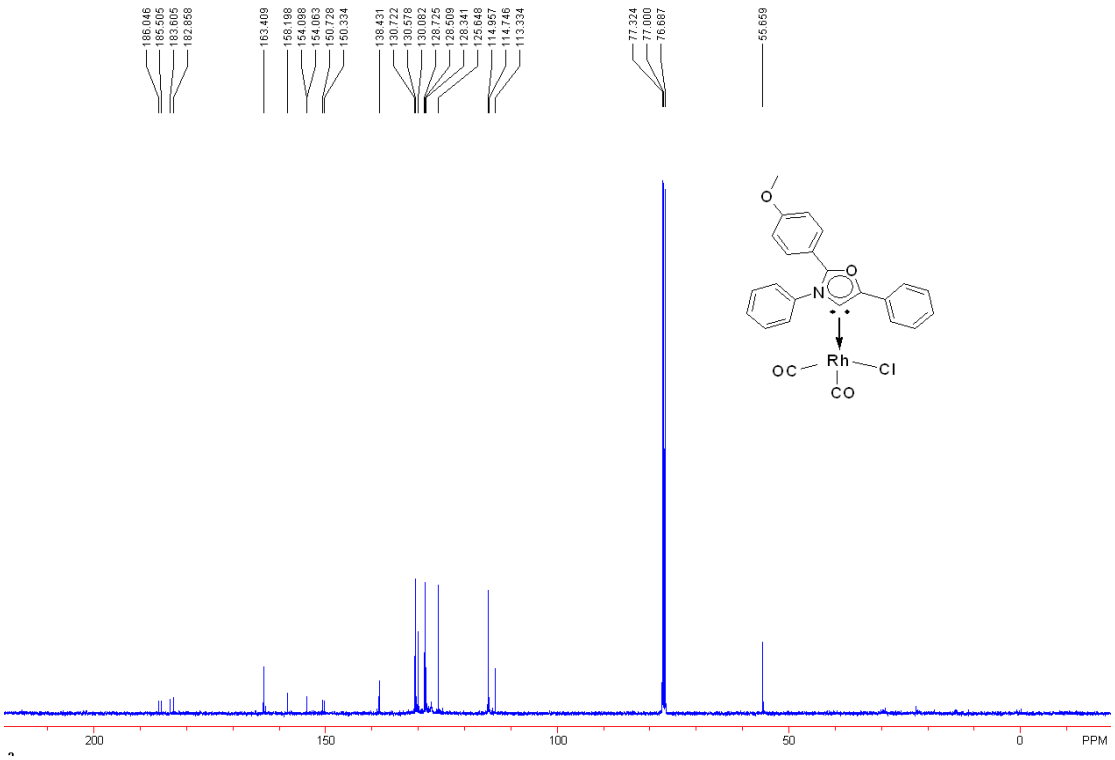


2,3,5-Triphenyloxazol-4-ylidene rhodium(I) biscarbonyl chloride (8a)

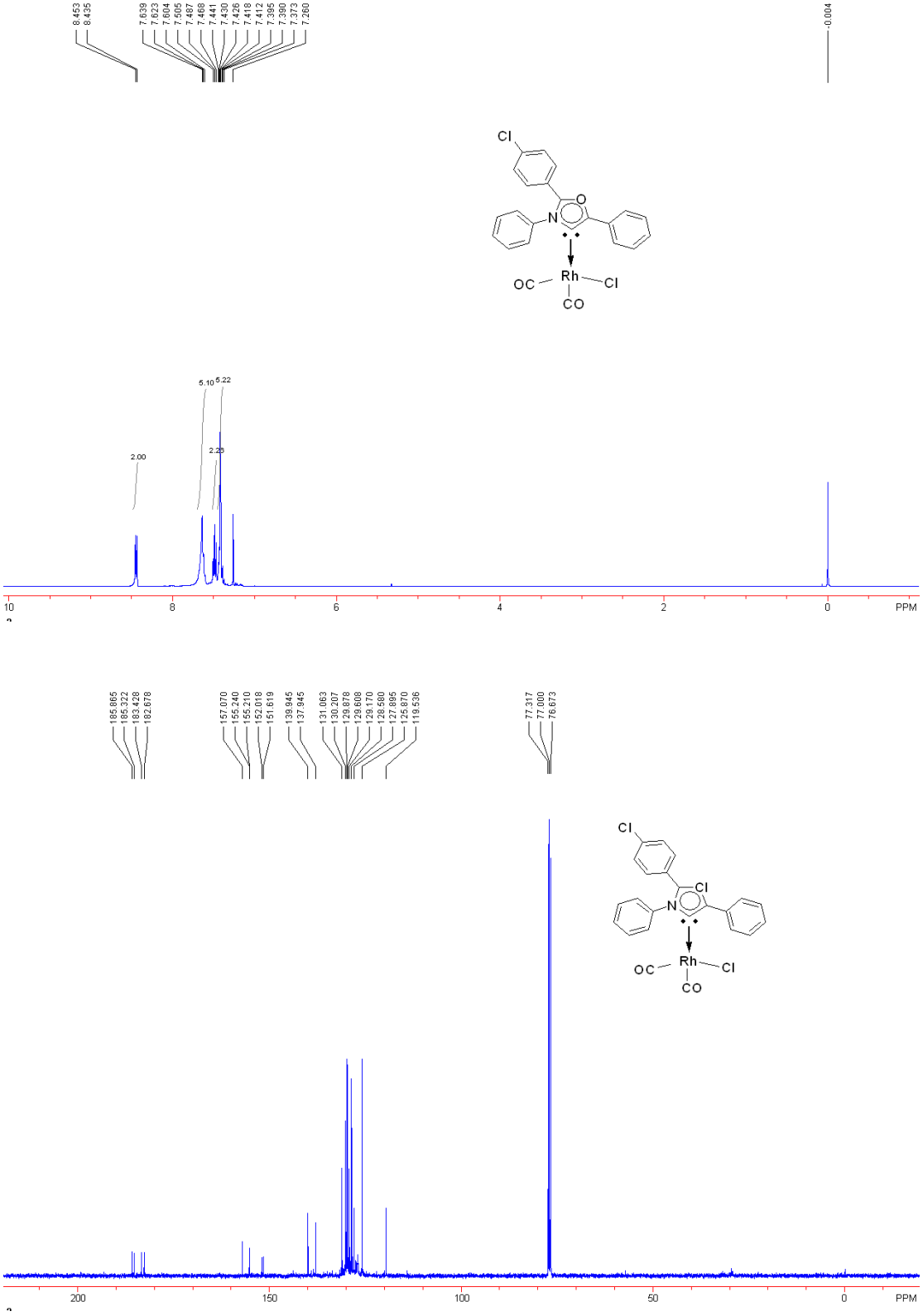


3,5-Diphenyl-2-(4-methoxy)phenyloxazol-4-ylidene rhodium(I) biscarbonyl chloride (8b)

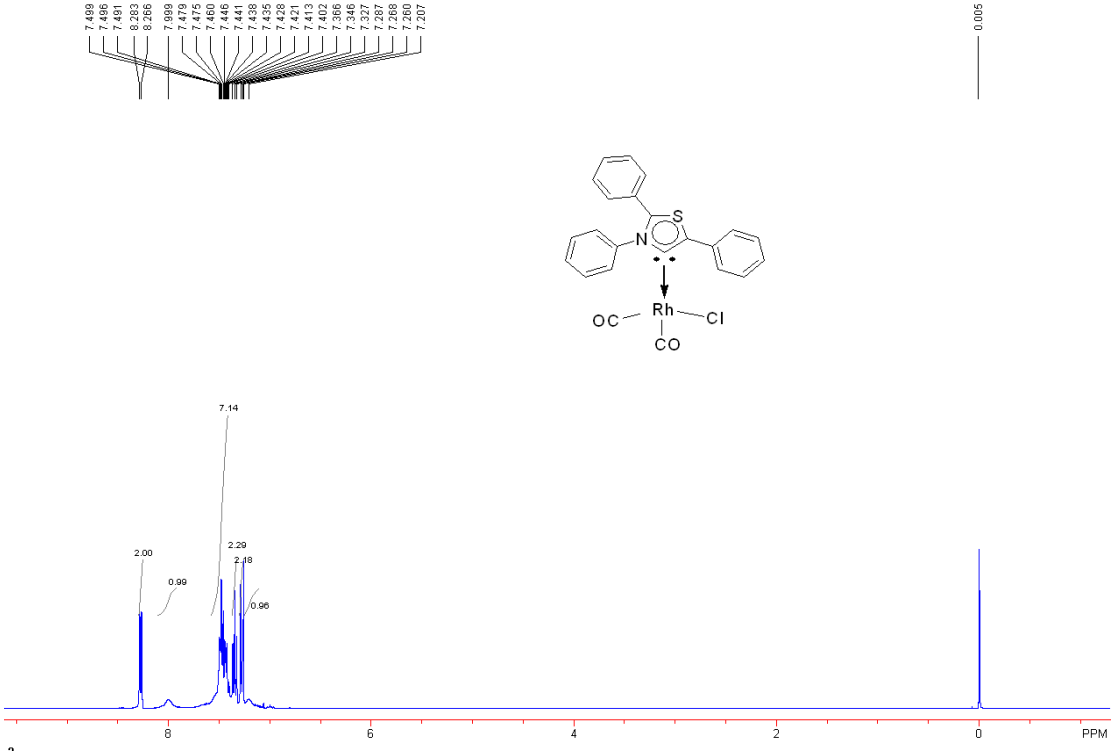


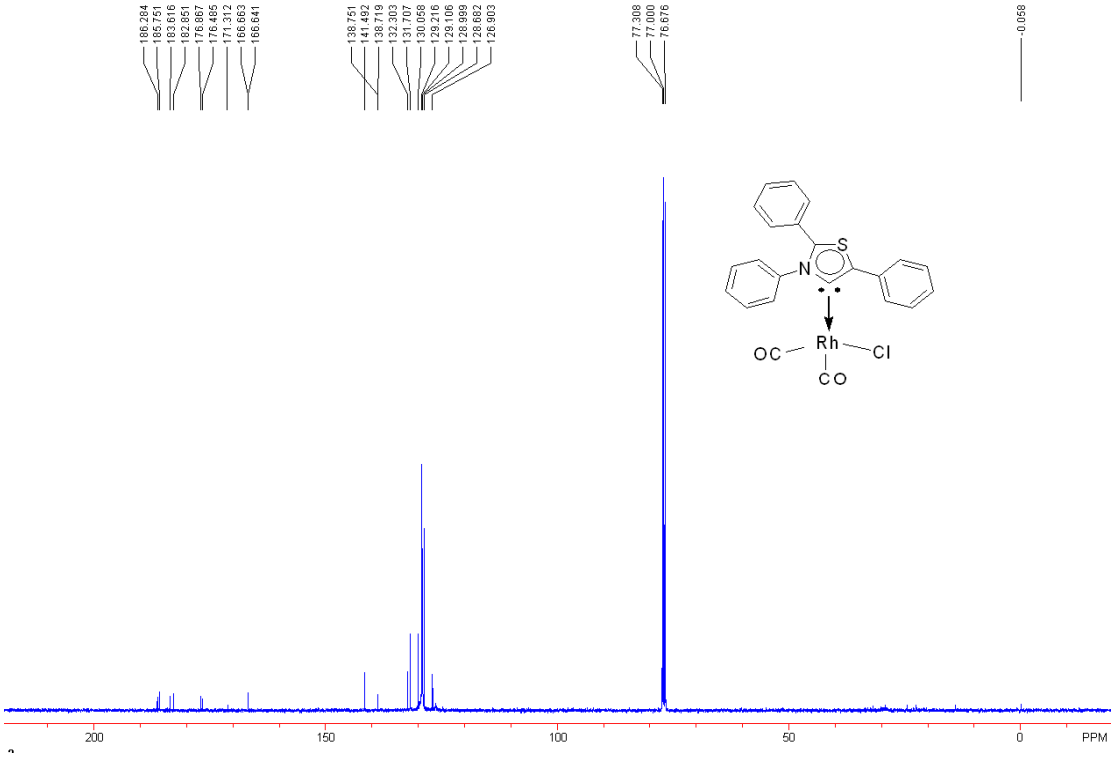


3,5-Diphenyl-2-(4- chloride)phenyloxazol-4-ylidene rhodium(I) biscarbonyl chloride (8c)

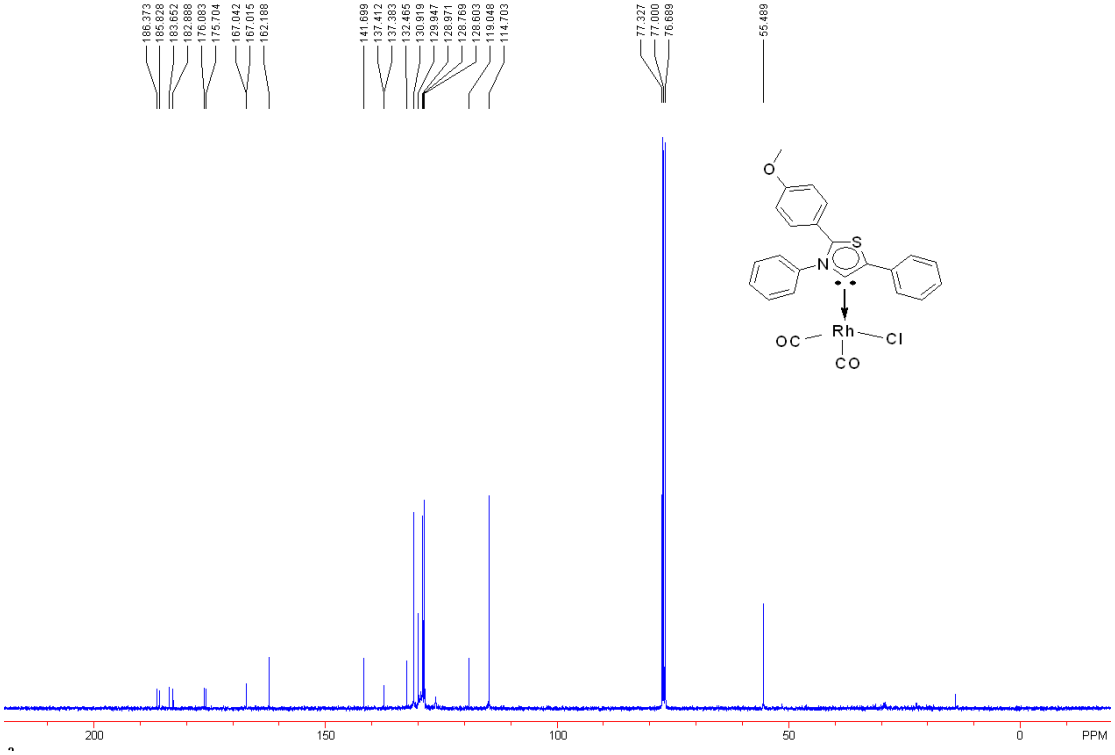


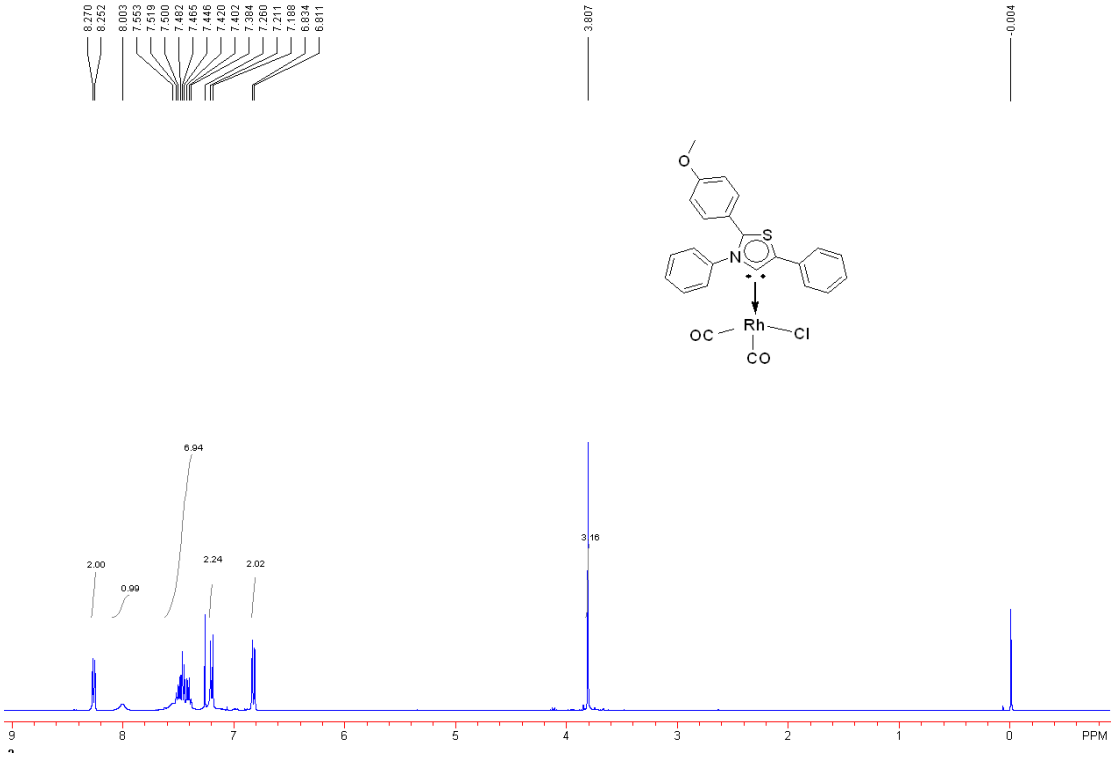
2,3,5-Triphenylthiazol-4-ylidene rhodium(I) biscarbonyl chloride (9a)



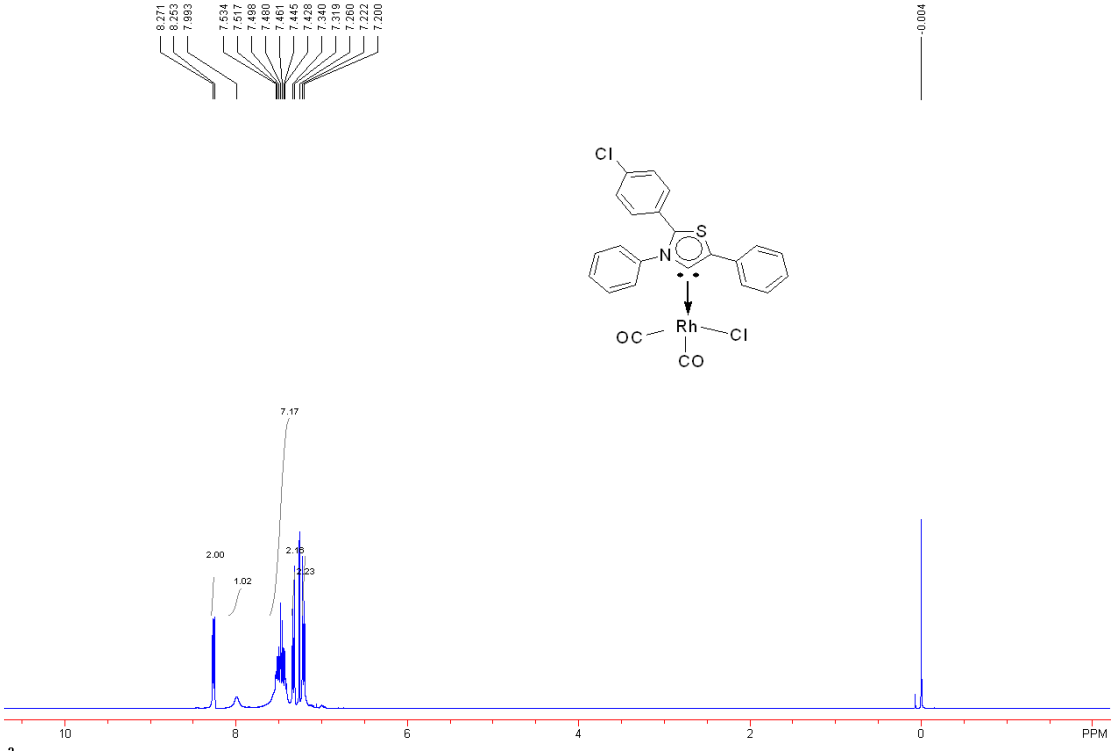


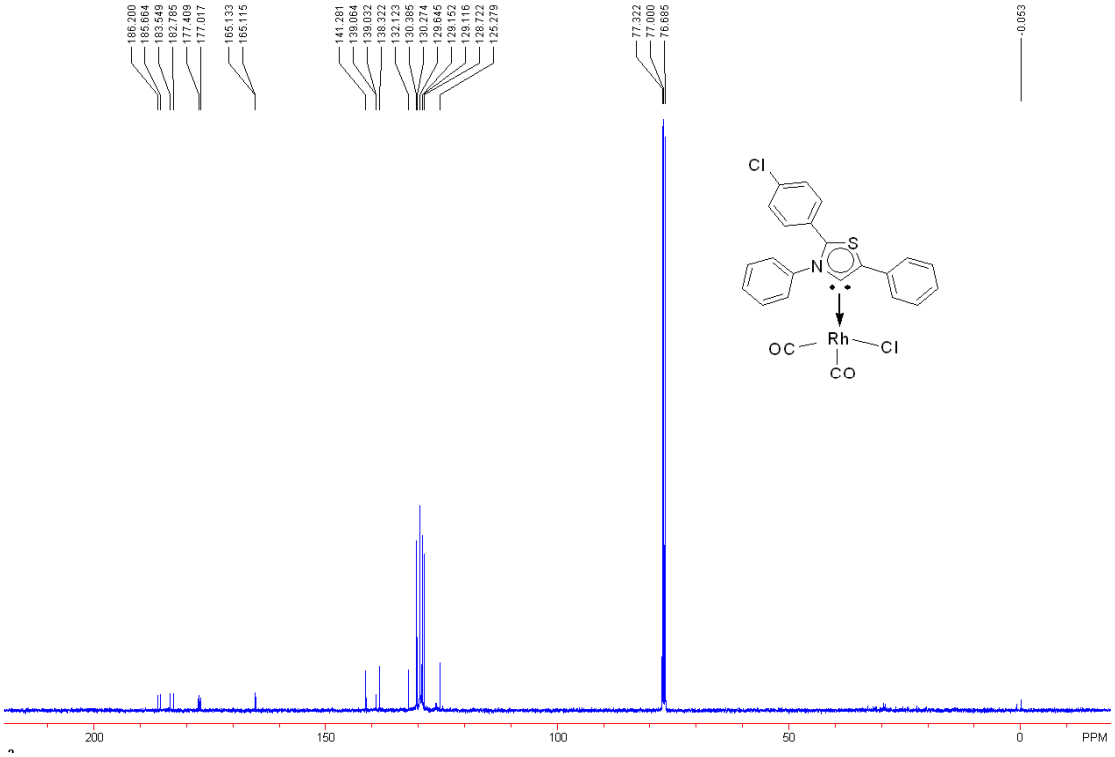
3,5-Diphenyl-2-(4-methoxy)phenylthiazol-4-ylidene rhodium(I) biscarbonyl chloride (9b)





3,5-Diphenyl-2-(4- chloride)phenylthiazol-4-ylidene rhodium(I) biscarbonyl chloride (9c)





X-Ray Crystallography.

Crystallographic measurements were made on a Bruker Smart Apex 100 CCD area detector using graphite monochromated Mo-Kαradiation ($\lambda_{\text{Mo-K}\alpha}$ = 0.71073 Å). The structures were solved by directed methods (SHELXS-97) and refined on F^2 by full-matrix least squares (SHELX-97) using all unique data. All the calculations were carried out with the SHELXTL18 program.[3]

Key details of the crystal and structure refinement data are summarized in Table S1. Further crystallographic details may be found in the respective CIF files, which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK. The CCDC reference numbers for **5a**, **5b**, **6a**, and **7a** were assigned as 887373, 887374, 885472, and 885473, respectively.

2. G. M. Sheldrick, SHELL-97, Program for crystal structure refinement, University of Göttingen: Göttingen, Germany, 1997.

Table S1. Crystal Data, Data Collection, and Structure Refinement for **5a**, **5b**, **6a**, and **7a**

	5a	**5b**	**6a**	**7a**
Identification code	a20614a	a20614b	a20325b	a20606b
Formula	$C_{22}H_{16}F_3NO_3S_2$	$C_{23}H_{18}F_3NO_4S_2$	$C_{29}H_{27}ClNORh$	$C_{30}H_{29}Cl_3NRhS$
Formula weight	463.48	493.50	543.88	644.86
T, K	293(2)	293(2)	293(2)	293(2)
crystal system	Monoclinic	Triclinic	Orthorhombic	Triclinic
space group	P2(1)/c	P-1	Pbca	P-1
a, Å	9.645(3)	7.594(6)	11.671(7)	7.677(9)
b, Å	14.571(5)	10.726(9)	19.299(12)	12.049(15)
c, Å	15.150(5)	15.412(12)	21.860(14)	16.55(2)
α, deg	90	106.631(9)	90	109.144(15)
β, deg	101.947(5)	98.221(10)	90	96.378(14)
γ, deg	90	103.331(10)	90	97.420(15)
Volume, Å ^{3}	2083.1(13)	1140.7(16)	4924(5)	1415(3)
Z	4	2	8	2
D_{calc}, Mg / m^3	1.478	1.437	1.467	1.514
absorption coefficient, mm^{-1}	0.307	0.288	0.824	0.981
F(000)	952	508	2224	656
crystal size, mm	0.20 x 0.20 x 0.18	0.32 x 0.25 x 0.22	0.12 x 0.09 x 0.08	0.63 x 0.54 x 0.45
2θ range, deg	1.96 to 26.00	1.41 to 25.01	1.86 to 27.01	1.82 to 25.01
reflections collected /unique	9226 / 4056 [R(int) = 0.0333]	4714 / 3924 [R(int) = 0.0665]	22379 / 5336 [R(int) = 0.0507]	5816 / 4862 [R(int) = 0.0381]
data / restraints / parameters	4056 / 0 / 280	3924 / 1 / 304	5336 / 1 / 315	4862 / 0 / 342
goodness of fit on F^2	1.056	1.161	0.901	1.095
final R indices [I >2σ(I)][a]	R1 = 0.0509, wR2 = 0.1502	R1 = 0.0978, wR2 = 0.2606	R1 = 0.0316, wR2 = 0.0671	R1 = 0.0471, wR2 = 0.1195
R indices (all data)	R1 = 0.0692, wR2 = 0.1624	R1 = 0.1077, wR2 = 0.2740	R1 = 0.0608, wR2 = 0.0742	R1 = 0.0501, wR2 = 0.1219
lgst diff peak and hole, e/Å^3	0.427 and -0.463	0.955 and -0.877	0.464 and -0.489	0.728 and -1.245