Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Mesoionic Thiazol-5-ylidenes as Ligands for Transition Metal Complexes

*Daniel Mendoza-Espinosa, Gaël Ung, Bruno Donnadieu, Guy Bertrand**

UCR-CNRS Joint Research Chemistry Laboratory (UMI 2957), Department of Chemistry, University of California, Riverside, Riverside, CA 92521-0403 (USA)

Contents:

Synthesis, physical and spectroscopic data for all new compounds

General Considerations:

All manipulations related to the synthesis of thiazolium salts **3a-c** were performed under air. For compounds **4a-c** and metal complexes, all experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. Solvents were dried by standard methods and distilled under argon. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a Bruker 300 spectrometer at 25 °C. NMR multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *sept* = septet, *m* = multiplet, *b* = broad signal. N-phenylbenzothiamide (**1a**), N-mesitylbenzothiamide (**1b**), and N-(2,6-diisopropylphenyl)benzothiamide (**1c**) were prepared following the literature procedure,[1] while all other starting materials were purchased from commercial sources.

Synthesis and characterization

***2-Oxo-2-phenylethyl-N-phenylbenzimidothioate* (*2a*)**. Triethylamine (1.30 g, 12.9 mmol) was added dropwise to a solution of N-phenylbenzothiamide (**1a**) (2.50 g, 11.7 mmol) and phenacyl bromide (2.33 g, 11.7 mmol) in 100 mL of acetonitrile. The resulting solution was stirred for 20 h at room temperature. The final yellow solution was cooled down to 0 °C and 50 mL of diethyl ether (Et_2O) was added to precipitate the ammonium salt. The mixture was filtered and the filtrate dried under vacuum, and further extracted with a mixture of toluene/hexane (1:1). The suspension obtained was then filtered and the filtrate was vacuum dried to yield 2.95 g of **2a** as a yellow solid. Yield 76% (8.90 mmol). Mp: 80-82 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.69 (bs, 2 H, C*H*$_2$), 6.63 (bs, 2 H, Ar*H*), 6.94 (bs, 1 H, Ar*H*), 7.13 (bs, 2 H, Ar*H*), 7.19 (bm, 5 H, Ar*H*), 7.48 (bs, 2 H, Ar*H*), 7.59 (bs, 1 H, Ar*H*), 8.10 (bs, 2 H, Ar*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 38.2 (*C*H$_2$), 121.3 (*C*H$_{ar}$), 123.4 (*C*$_{ar}$), 127.3 (*C*$_{ar}$), 129.0 (*C*H$_{ar}$, two signals overlapping), 129.3

(*C*H_{ar}), 129.9 (*C*H_{ar}, three signals overlapping), 131.4 (*C*H_{ar}), 133.8 (*C*H_{ar}), 135.2 (C_{ar}), 149.5 (S*C*N), 191.4 (*C*=O).

2-Oxo-2-phenylethyl-N-(2,4,6-trimethylphenyl)benzimidothioate (2b). The procedure described for the preparation of compound **2a** was followed using in this case N-mesitylbenzothiamide (**1b**). After purification by column chromatography on silica gel (DCM/Hex 1:1), **2b** was obtained as a yellow oil. Yield 63% (2.75 g, 7.37 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.96 (bs, 6 H, *o*-CH_3), 2.18 (bs, 3 H, *p*-CH_3), 4.67 (bs, 2 H, CH_2), 6.73 (bs, 2 H, Ar*H*), 7.18-7.38 (bm, 4 H, Ar*H*), 7.45-7.60 (bm, 4 H, Ar*H*), 8.03 (bs, 2 H, Ar*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.3 (*o*-*C*H_3), 20.8 (*p*-*C*H_3), 38.5 (*C*H_2), 126.5 (C_{ar}), 127.4 (C_{ar}), 128.5 (*C*H_{ar}), 128.7 (*C*H_{ar}, two signals overlapping), 128.8 (*C*H_{ar}, two signals overlapping), 129.4 (C_{ar}), 130.3 (*C*H_{ar}), 131.4 (C_{ar}), 133.5 (*C*H_{ar}), 135.4 (C_{ar}), 145.2 (S*C*N), 194.0 (*C*=O).

2-Oxo-2-phenylethyl-N-(2,6-diisopropylphenyl)benzimidothioate (2c). The procedure described for the preparation of compound **2a** was followed using in this case N-(2,6-diisopropylphenyl) benzothiamide (**1c**). After purification by column chromatography on silica gel (DCM/Hex 1:1), **2c** was obtained as a yellowish oil. Yield 55% (2.67 g, 6.43 mmol). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.04 (bs, 6 H, CH(CH_3)$_2$), 1.17 (bs, 6 H, CH(CH_3)$_2$), 2.91 (bs, 2 H, C*H*(CH$_3$)$_2$), 4.57 (bs, 2 H, CH_2), 7.08 (bs, 4 H, CH$_{ar}$), 7.27-7.35 (bs, 3 H, C*H*$_{ar}$), 7.43-7.49 (bs, 4 H, C*H*$_{ar}$), 8.01-8.04 (bs, 2 H, C*H*$_{ar}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 22.6, 23.4 (CH(*C*H_3)$_2$), 28.4 (*C*H(CH$_3$)$_2$), 38.6 (*C*H_2), 123.1 (*C*H_{ar}), 123.9 (*C*H_{ar}), 124.0 (C_{ar}), 126.9 (C_{ar}), 127.8 (*C*H_{ar}), 128.4 (*C*H_{ar}, two signals overlapping), 128.7 (*C*H_{ar}), 130.2 (*C*H_{ar}), 131.5 (C_{ar}), 133.5 (*C*H_{ar}), 136.9 (C_{ar}), 145.1 (S*C*N), 193.5 (*C*=O).

2,3,4-Triphenylthiazolium bromide (3a). Hydrobromic acid (47% in H_2O, 10 mL, 88.9 mmol) was added slowly to a pre-cooled (0 °C) toluene (50 mL) solution of **2a** (1.00 g, 3.02 mmol) in acetic anhydride (8.7 g, 85.2 mmol). The resulting yellow mixture was heated at 90 °C for 48 h. The reaction mixture was quenched with 50 mL of water, and the aqueous layer was extracted with 100 mL of dichloromethane (DCM). The organic layer was washed twice with water (50 mL), dried over $MgSO_4$, filtered, and evaporated under vacuum to yield the crude product as a yellow solid. **3a** was obtained as a white solid after washing the crude material with Et_2O (3 x 50 mL). Yield 60% (0.720 g, 1.82 mmol). Mp: 222-224 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.23 (d, *J* = 7.6 Hz, 2 H, Ar*H*), 7.28 (d, *J* = 7.2 Hz, 2 H, Ar*H*), 7.32-7.36 (m, 6 H, Ar*H*), 7.46 (t, *J* = 7.4 Hz, 1 H, Ar*H*), 7.51-7.54 (m, 4 H, Ar*H*), 8.64 (s, 1 H, CH_{thiaz}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 125.1 (*C*H$_{thiaz}$), 126.9 (*C*$_{ar}$), 127.7 (*C*$_{ar}$), 128.2 (*C*H$_{ar}$), 128.8 (*C*H$_{ar}$), 129.4 (*C*H$_{ar}$), 129.9 (*C*H$_{ar}$), 130.5 (*C*H$_{ar}$), 130.6 (*C*H$_{ar}$, two signals overlapping), 131.1 (*C*H$_{ar}$), 133.0 (*C*H$_{ar}$), 135.9 (*C*$_{ar}$), 153.1 (N*C*C), 172.9 (N*C*S).

3-(2,4,6-Trimethylphenyl)-2,4-diphenylthiazolium bromide (3b). The procedure described for the preparation of salt **3a** was followed using in this case **2b**. **3b** was obtained as a white solid after washing the crude material with Et_2O (3 x 50 mL). Single crystals were obtained by the slow evaporation of a concentrated acetone solution of **3b**. Yield 44% (0.579 g, 1.33 mmol). Mp: > 273 °C (decomp). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.83 (s, 6 H, *o*-CH_3), 2.28 (s, 3 H, *p*-CH_3), 6.88 (s, 2 H, Ar*H*), 7.10 (d, *J* = 7.4 Hz, 2 H, Ar*H*), 7.24-7.30 (m, 4 H, Ar*H*), 7.35-7.39 (m, 3 H, Ar*H*), 7.55 (t, *J* = 7.4 Hz, 1 H, Ar*H*), 9.10 (s, 1 H, CH_{thiaz}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.0 (*o*-*C*H_3), 21.3 (*p*-*C*H_3), 125.7 (*C*$_{ar}$), 126.9 (*C*$_{ar}$), 128.6 (*C*H$_{thiaz}$), 129.0 (*C*H$_{ar}$, two signals overlapping), 130.0 (*C*H$_{ar}$), 130.6 (*C*H$_{ar}$), 131.1 (*C*H$_{ar}$), 131.6 (*C*$_{ar}$), 133.8 (*C*H$_{ar}$), 134.2 (*C*H$_{ar}$), 142.4 (*C*$_{ar}$), 148.0 (N*C*C), 170.4 (N*C*S).

3-(2,6-Diisopropylphenyl)-2,4-diphenylthiazolium bromide (3c). The procedure described for the preparation of salt **3a** was followed using in this case **2c**. **3c** was obtained as a white solid after washing the crude material with Et_2O (3 x 50 mL). Yield 42% (0.606 g, 1.27 mmol). Mp: 246-248 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.71 (d, *J* = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 0.74 (d, *J* = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 2.16 (sept, *J* = 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$), 7.11 (d, *J* = 7.4 Hz, 2 H, Ar*H*), 7.22-7.28 (m, 6 H, Ar*H*), 7.35 (d, *J* = 7.6 Hz, 2 H, Ar*H*), 7.38 (d, *J* = 7.9 Hz, 2 H, Ar*H*), 7.56 (t, *J* = 7.4 Hz, 1 H, Ar*H*), 9.20 (s, 1 H, C*H*$_{thiaz}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 23.6, 23.7 (CH(*C*H$_3$)$_2$), 29.0 (*C*H(CH$_3$)$_2$), 126.1 (*C*$_{ar}$), 126.4 (*C*H$_{ar}$), 127.1 (*C*$_{ar}$), 127.8 (*C*H$_{thiaz}$), 129.1 (*C*H$_{ar}$), 129.4 (*C*H$_{ar}$), 129.7 (*C*H$_{ar}$), 130.0 (*C*H$_{ar}$), 131.1 (*C*H$_{ar}$), 133.1 (*C*H$_{ar}$), 134.0 (*C*H$_{ar}$), 144.6 (*C*$_{ar}$), 148.8 (N*C*C), 171.0 (N*C*S).

2,3,4-Triphenylthiazolium trifluoromethanesulfonate (4a). DCM (15 mL) was added at room temperature to a Schlenk flask charged with silver trifluoromethanesulfonate (0.326 g, 1.27 mmol) and the thiazolium salt **3a** (0.500 g, 1.27 mmol). The reaction mixture was stirred for 4 h. After cannula filtration, the supernatant was dried under vacuum yielding the crude product as a pale yellow solid. **4a** was obtained as a white solid after washing the crude material with Et_2O (3 x 10 mL). Yield 93% (0.547 g, 1.18 mmol). Mp: 182-184 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.20-7.24 (m, 2 H, Ar*H*), 7.26-7.34 (m, 10 H, Ar*H*), 7.42-7.45 (m, 3 H, Ar*H*), 8.13 (s, 1 H, C*H*$_{thiaz}$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 120.9 (q, *J*(C,F) = 319 Hz), 121.9 (*C*H$_{thiaz}$), 125.7 (*C*$_{ar}$), 127.5 (*C*$_{ar}$), 128.0 (*C*H$_{ar}$), 128.7 (*C*H$_{ar}$), 129.4 (*C*H$_{ar}$), 130.0 (*C*H$_{ar}$), 130.3 (*C*H$_{ar}$, two signals overlapping), 130.6 (*C*H$_{ar}$), 131.1 (*C*H$_{ar}$), 132.9 (*C*H$_{ar}$), 135.5 (*C*$_{ar}$), 150.4 (N*C*C), 172.1 (N*C*S). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −79.5.

3-(2,4,6-Trimethylphenyl)-2,4-diphenylthiazolium trifluoromethanesulfonate (4b). The procedure described for the preparation of salt **4a** was followed using in this case **3b**. **4b** was obtained as a white solid after washing the crude material with Et_2O (3 x 10 mL). Yield 87% (0.559 g, 1.10 mmol). Mp: 166-168 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.85 (s, 6 H, *o*-CH_3), 2.29 (s, 3 H, *p*-CH_3), 6.91 (s, 2 H, Ar*H*), 7.13 (d, *J* = 7.4 Hz, 2 H, Ar*H*), 7.27-7.32 (m, 4 H, Ar*H*), 7.38-7.45 (m, 3 H, Ar*H*), 7.59 (t, *J* = 7.4 Hz, 1 H, Ar*H*), 8.60 (s, 1 H, CH_{thiaz}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.0 (*o*-CH_3), 21.3 (*p*-CH_3), 120.8 (q, *J*(C,F) = 318 Hz), 124.2 (CH_{thiaz}), 125.5 (C_{ar}), 126.7 (C_{ar}), 129.2 (CH_{ar}, two signals overlapping), 130.1 (CH_{ar}), 130.7 (CH_{ar}), 131.3 (CH_{ar}), 131.8 (C_{ar}), 134.1 (CH_{ar}), 134.3 (CH_{ar}), 142.6 (C_{ar}), 149.7 (N*C*C), 171.7 (N*C*S). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −77.2.

3-(2,6-Diisopropylphenyl)-2,4-diphenylthiazolium trifluoromethanesulfonate (4c). The procedure described for the preparation of salt **4a** was followed using in this case **3c**. **4c** was obtained as a white solid after washing the crude material with Et_2O (3 x 10 mL). Yield 90% (0.625 g, 1.14 mmol). Mp: 188-190 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.75 (d, *J* = 6.9 Hz, 6 H, CH(CH_3)$_2$), 0.77 (d, *J* = 6.9 Hz, 6 H, CH(CH_3)$_2$), 2.21 (sept, *J* = 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$), 7.16 (d, *J* = 7.6 Hz, 2 H, Ar*H*), 7.26-7.32 (m, 6 H, Ar*H*), 7.41-7.45 (m, 3 H, Ar*H*), 7.57-7.65 (m, 2 H, Ar*H*), 8.78 (s, 1 H, CH_{thiaz}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 23.7, 23.8 (CH(*C*H$_3$)$_2$), 29.1 (*C*H(CH$_3$)$_2$), 121.0 (q, *J*(C,F) = 318 Hz), 123.9 (CH_{thiaz}), 126.0 (C_{ar}), 126.5 (CH_{ar}), 127.0 (C_{ar}), 129.3 (CH_{ar}), 129.6 (CH_{ar}), 129.8 (CH_{ar}), 130.2 (CH_{ar}), 131.3 (CH_{ar}), 133.2 (CH_{ar}), 134.4 (CH_{ar}), 144.8 (C_{ar}), 150.5 (N*C*C), 172.4 (N*C*S). ^{19}F NMR ($CDCl_3$, 282 MHz): δ −76.9.

2,3,4-Triphenylthiazol-5-ylidene gold(I) chloride (5a). THF (12 mL) was added at −78 °C to a Schlenk flask charged with thiazolium **4a** (0.200 g, 0.431 mmol), LiHMDS (0.075 g, 0.450

mmol) and (THT)AuCl (0.138 g, 0.430 mmol). The reaction mixture was stirred for 16 h. The solvent was removed under vacuum and the residue was washed with hexane (10 mL) and extracted with DCM (10 mL). The final light yellow solution was dried under vacuum to yield the crude product as a pale yellow solid. **5a** was obtained after recrystallization from a mixture of chloroform/hexane (1:1). Yield 71% (0.167 g, 0.306 mmol). Mp: 276-278 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.05 (d, *J* = 7.4 Hz, 2 H, Ar*H*), 7.16-7.23 (m, 5 H, Ar*H*), 7.24-7.26 (m, 2 H, Ar*H*), 7.29-7.35 (m, 5 H, Ar*H*), 7.44 (t, *J* = 7.0 Hz, 1 H, Ar*H*). No ^{13}C NMR spectrum is available due to limited solubility of the title product.

3-(2,4,6-Trimethylphenyl)-2,4-diphenylthiazol-5-ylidene gold(I) chloride (5b). THF (12 mL) was added at −78 °C to a Schlenk flask charged with thiazolium **4b** (0.218 g, 0.431 mmol), LiHMDS (0.075 g, 0.450 mmol) and (THT)AuCl (0.138 g, 0.430 mmol). The reaction mixture was stirred for 16 h. The solvent was removed under vacuum and the residue was washed with hexane (10 mL) and extracted with DCM (10 mL). The final light yellow solution was dried under vacuum to yield the crude product as a pale yellow solid. **5b** was obtained after recrystallization from a mixture of chloroform/hexane (1:1). Yield 79% (0.200 g, 0.340 mmol). Mp: 303-305 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.66 (s, 6 H, *o*-CH_3), 2.06 (s, 3 H, *p*-CH_3), 6.69 (s, 2 H, Ar*H*), 6.99-7.05 (m, 5 H, Ar*H*), 7.12 (d, *J* = 7.4 Hz, 2 H, Ar*H*), 7.22 (d, *J* = 7.4 Hz, 2 H, Ar*H*), 7.35 (t, *J* = 7.4 Hz, 1 H, Ar*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 16.4 (*o*-*C*H_3), 19.6 (*p*-*C*H_3), 125.2 (C_{ar}), 126.6 (*C*H_{ar}), 127.0 (*C*H_{ar}), 127.8 (C_{ar}), 128.2 (*C*H_{ar}), 128.4 (*C*H_{ar}), 128.6 (*C*H_{ar}), 130.5 (C_{ar}), 131.0 (*C*H_{ar}), 132.4 (C_{ar}), 132.6 (C_{ar}), 139.5 (*C*H_{ar}), 149.5 (Au=*C*), 150.1 (N*C*C), 170.3 (N*C*S).

3-(2,6-Diisopropylphenyl)-2,4-diphenylthiazol-5-ylidene gold(I) chloride (5c). THF (12 mL) was added at −78 °C to a Schlenk flask charged with thiazolium **4c** (0.236 g, 0.431 mmol), LiHMDS (0.075 g, 0.450 mmol) and (THT)AuCl (0.138 g, 0.430 mmol). The reaction mixture was stirred for 16 h. The solvent was removed under vacuum and the residue was washed with hexane (10 mL) and extracted with DCM (10 mL). The final light yellow solution was dried under vacuum to yield the crude product as a pale yellow solid. **5c** was obtained after recrystallization from a mixture of chloroform/hexane (1:1). Yield 90% (0.244 g, 0.388 mmol). Mp: 138-140 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.56 (d, *J* = 6.7 Hz, 6 H, CH(CH_3)$_2$), 0.68 (d, *J* = 6.7 Hz, 6 H, CH(CH_3)$_2$), 2.14 (sept, *J* = 6.7 Hz, 2 H, C*H*(CH$_3$)$_2$), 7.01-7.09 (m, 7 H, Ar*H*), 7.17-7.22 (t, *J* = 7.6 Hz, 2 H, Ar*H*), 7.26-7.34 (m, 3 H, Ar*H*), 7.39 (t, *J* = 7.6 Hz, 1 H, Ar*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 23.7, 24.0 (CH(*C*H$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 126.0 (*C*H$_{ar}$), 127.4 (*C*$_{ar}$), 128.1 (*C*H$_{ar}$), 129.0 (*C*H$_{ar}$), 129.2 (*C*$_{ar}$), 129.8 (*C*H$_{ar}$), 130.6 (*C*H$_{ar}$), 131.7 (*C*$_{ar}$), 132.2 (*C*H$_{ar}$), 132.6 (*C*H$_{ar}$), 133.0 (*C*$_{ar}$), 144.7 (*C*H$_{ar}$), 151.4 (Au=*C*), 152.3 (N*C*C), 170.6 (N*C*S).

2,3,4-Triphenylthiazol-5-ylidene palladium(II) allyl chloride (6a). THF (12 mL) was added at −78 °C to a Schlenk flask charged with thiazolium **4a** (0.200 g, 0.431 mmol), LiHMDS (0.075 g, 0.450 mmol) and [Pd(allyl)Cl]$_2$ (0.079 g, 0.216 mmol). The reaction mixture was stirred for 16 h. The solvent was removed under vacuum and the residue was washed with hexane (10 mL) and extracted with DCM (10 mL). The final yellow solution was dried under vacuum to yield the crude product as a yellow solid. **6a** was obtained after washing the crude material with Et_2O (3 x 5 mL). Yield 58% (0.124 g, 0.250 mmol). Mp: 220-222 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.44 (b, 1 H, CH(CH_2)$_2$), 3.04 (b, 1 H, CH(CH_2)$_2$), 3.45 (d, *J* = 7.2 Hz, 1 H, CH(CH_2)$_2$), 4.11 (b, 1 H, CH(CH_2)$_2$), 5.11 (pentet, *J* = 6.9 Hz, 1 H, C*H*(CH$_2$)$_2$), 6.88 (d, *J* = 6.9 Hz, 2 H, Ar*H*), 7.03-7.07 (m, 3 H, Ar*H*), 7.15-7.19 (m, 4 H, Ar*H*), 7.22-7.26 (m, 4 H, Ar*H*), 7.38 (d, *J* = 7.4 Hz, 2 H,

Ar*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 59.9, 65.9 (CH(*C*H_2)$_2$), 117.7 (*C*H(CH$_2$)$_2$), 125.6 (*C*$_{ar}$), 127.4 (*C*H$_{ar}$), 127.6 (*C*H$_{ar}$), 127.7 (*C*H$_{ar}$) 128.3 (*C*H$_{ar}$), 128.6 (*C*H$_{ar}$), 129.1 (*C*H$_{ar}$), 129.3 (*C*H$_{ar}$), 130.3 (*C*$_{ar}$), 131.5 (*C*H$_{ar}$), 134.0 (*C*$_{ar}$), 136.9 (*C*H$_{ar}$), 149.2 (N*C*C), 159.2 (Pd=*C*), 172.4 (N*C*S).

3-(2,4,6-Trimethylphenyl)-2,4-diphenylthiazol-5-ylidene palladium(II) allyl chloride (6b). THF (12 mL) was added at −78 °C to a Schlenk flask charged with thiazolium **4b** (0.218 g, 0.431 mmol), LiHMDS (0.075 g, 0.450 mmol) and [Pd(allyl)Cl]$_2$ (0.079 g, 0.216 mmol). The reaction mixture was stirred for 16 h. The solvent was removed under vacuum and the residue was washed with hexane (10 mL) and extracted with DCM (10 mL). The final yellow solution was dried under vacuum to yield the crude product as a yellow solid. **6b** was obtained after washing the crude material with Et_2O (3 x 5 mL). Yield 51% (0.118 g, 0.220 mmol). Mp: 198-200 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.56 (s, 6 H, *o*-CH_3), 2.05 (s, 3 H, *p*-CH_3), 2.29 (d, *J* = 13.1 Hz, 1 H, CH(C*H*$_2$)$_2$), 2.84 (b, 1 H, CH(C*H*$_2$)$_2$), 3.24 (d, *J* = 7.1 Hz, 1 H, CH(C*H*$_2$)$_2$), 3.90 (b, 1 H, CH(C*H*$_2$)$_2$), 4.97 (pentet, *J* = 6.8 Hz, 1 H, C*H*(CH$_2$)$_2$), 6.62 (s, 2 H, Ar*H*), 6.77-6.84 (m, 2 H, Ar*H*), 6.96-7.00 (m, 3 H, Ar*H*), 7.11-7.18 (m, 4 H, Ar*H*), 7.27 (t, *J* = 7.4 Hz, 1 H, Ar*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 17.9 (*o*-*C*H_3), 21.1 (*p*-*C*H_3), 59.9, 67.9 (CH(*C*H_2)$_2$), 117.5 (*C*H(CH$_2$)$_2$), 126.9 (C$_{ar}$), 127.6 (*C*H$_{ar}$), 127.8 (*C*H$_{ar}$), 128.6 (*C*$_{ar}$), 129.1 (*C*$_{ar}$), 129.4 (*C*H$_{ar}$), 130.0 (*C*H$_{ar}$), 130.2 (*C*H$_{ar}$), 130.7 (*C*H$_{ar}$), 131.4 (*C*$_{ar}$), 133.7 (*C*$_{ar}$), 141.0 (*C*H$_{ar}$), 149.1 (N*C*C), 156.0 (Pd=*C*), 171.8 (N*C*S).

3-(2,6-Diisopropylphenyl)-2,4-diphenylthiazol-5-ylidene palladium(II) allyl chloride (6c). THF (12 mL) was added at −78 °C to a Schlenk flask charged with thiazolium **4c** (0.236 g, 0.431 mmol), LiHMDS (0.075 g, 0.450 mmol) and [Pd(allyl)Cl]$_2$ (0.079 g, 0.216 mmol). The reaction mixture was stirred for 16 h. The solvent was removed under vacuum and the residue was

washed with hexane (10 mL) and extracted with DCM (10 mL). The final yellow solution was dried under vacuum to yield the crude product as a yellow solid. **6c** was obtained after washing the crude material with Et_2O (3 x 5 mL). Yield 53% (0.133 g, 0.228 mmol). Mp: 212-214 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.58 (d, *J* = 6.7 Hz, 6 H, CH(C*H*$_3$)$_2$), 0.62 (d, *J* = 6.7 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.97 (sept, *J* = 6.7 Hz, 2 H, C*H*(CH$_3$)$_2$), 2.25 (b, 1 H, CH(C*H*$_2$)$_2$), 2.39 (b, 1 H, CH(C*H*$_2$)$_2$), 3.04 (d, *J* = 11.5 Hz, 1 H, CH(C*H*$_2$)$_2$), 4.03 (b, 1 H, CH(C*H*$_2$)$_2$), 5.02 (pentet, *J* = 6.9 Hz, 1 H, C*H*(CH$_2$)$_2$), 7.03-7.09 (m, 4 H, Ar*H*), 7.12-7.18 (m, 4 H, Ar*H*), 7.26-7.31 (m, 4 H, Ar*H*), 7.42 (t, *J* = 7.6 Hz, 1 H, Ar*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 23.6, 23.9 (CH(*C*H$_3$)$_2$), 28.4 (*C*H(CH$_3$)$_2$), 51.8, 69.9 (CH(*C*H$_2$)$_2$), 113.8 (*C*H(CH$_2$)$_2$), 125.6 (*C*H$_{ar}$), 125.7 (*C*$_{ar}$), 127.1 (*C*H$_{ar}$), 127.8 (*C*$_{ar}$), 128.4 (*C*H$_{ar}$), 128.5 (*C*H$_{ar}$), 129.2 (*C*H$_{ar}$), 130.9 (*C*$_{ar}$), 131.4 (*C*H$_{ar}$), 131.6 (*C*H$_{ar}$), 133.5 (*C*$_{ar}$), 144.5 (*C*H$_{ar}$), 150.8 (N*C*C), 159.5 (Pd=*C*), 171.8 (N*C*S).

2,3,4-Triphenylthiazol-5-ylidene rhodium(I) biscarbonyl chloride (7a). THF (12 mL) was added at −78 °C to a Schlenk flask charged with thiazolium salt **4a** (0.200 g, 0.431 mmol), LiHMDS (0.075 g, 0.450 mmol) and $[Rh(COD)Cl]_2$ (0.106 g, 0.216 mmol). The reaction mixture was stirred for 16 h. The solvent was removed under vacuum and the residue was washed with hexane (10 mL) and extracted with DCM (12 mL). Carbon monoxide was bubbled for 30 minutes into the resulting dark red extract, and the final orange solution was dried under vacuum to yield the crude product as an orange solid. **7a** was obtained as an orange-yellow solid after washing the crude material with Et_2O (3 x 5 mL). Yield 45% (0.098 g, 0.193 mmol). Mp: 238-240 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.00 (d, *J* = 7.4 Hz, 2 H, Ar*H*), 7.16 (d, *J* = 7.6 Hz, 2 H, Ar*H*), 7.19-7.24 (m, 3 H, Ar*H*), 7.28-7.35 (m, 8 H, Ar*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 127.6 (C$_{ar}$), 127.7 (*C*H$_{ar}$), 127.9 (*C*H$_{ar}$), 128.5 (*C*H$_{ar}$, two signals overlapping), 129.3 (*C*H$_{ar}$), 129.4 (*C*H$_{ar}$), 129.9 (*C*H$_{ar}$), 130.4 (*C*$_{ar}$), 132.1 (*C*H$_{ar}$), 133.2 (*C*$_{ar}$), 137.2 (*C*H$_{ar}$), 150.9 (N*C*C), 157.8 (d,

J = 37.1 Hz, Rh=*C*), 172.4 (N*C*S), 183.3 (d, *J* = 76.3 Hz, Rh-*C*O), 185.9 (d, *J* = 55.6 Hz, Rh-*C*O). IR (C_6H_6): *v* = 2070.8, 1996.0 (CO).

3-(2,4,6-Trimethylphenyl)-2,4-diphenylthiazol-5-ylidene rhodium(I) biscarbonyl chloride (7b). THF (12 mL) was added at −78 °C to a Schlenk flask charged with thiazolium salt **4b** (0.218 g, 0.431 mmol), LiHMDS (0.075 g, 0.450 mmol) and $[Rd(COD)Cl]_2$ (0.106 g, 0.216 mmol). The reaction mixture was stirred for 16 h. The solvent was removed under vacuum and the residue was washed with hexane (10 mL) and extracted with DCM (12 mL). Carbon monoxide was bubbled for 30 minutes into the resulting dark red extract, and the final orange solution was dried under vacuum to yield the crude product as an orange solid. **7b** was obtained as an orange-yellow solid after washing the crude material with Et_2O (3 x 5 mL). Yield 41% (0.098 g, 0.177 mmol). Mp: 218-220 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.83 (s, 6 H, *o*-CH_3), 2.24 (s, 3 H, *p*-CH_3), 6.80 (s, 2 H, Ar*H*), 7.15 (d, *J* = 7.9 Hz, 2 H, Ar*H*), 7.22 (d, *J* = 7.4 Hz, 2 H, Ar*H*), 7.28-7.35 (m, 5 H, Ar*H*), 7.44 (t, *J* = 6.9 Hz, 1 H, Ar*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 18.2 (*o*-*C*H_3), 21.3 (*p*-*C*H_3), 127.5 (C_{ar}), 127.7 (*C*H_{ar}), 128.3 (*C*H_{ar}), 128.5 (*C*H_{ar}), 129.3 (C_{ar}), 129.5 (*C*H_{ar}), 130.0 (*C*H_{ar}), 131.6 (*C*H_{ar}), 132.0 (C_{ar}), 132.7 (C_{ar}), 134.3 (C_{ar}), 140.9 (*C*H_{ar}), 150.5 (N*C*C), 158.6 (d, *J* = 40.1 Hz, Rh=*C*), 171.6 (N*C*S), 183.3 (d, *J* = 79.5 Hz, Rh-*C*O), 185.6 (d, *J* = 57.6 Hz, Rh-*C*O). IR (C_6H_6): *v* = 2071.9, 1998.1 (CO).

3-(2,6-Diisopropylphenyl)-2,4-diphenylthiazol-5-ylidene rhodium(I) biscarbonyl chloride (7c). THF (12 mL) was added at −78 °C to a Schlenk flask charged with the thiazolium salt **4c** (0.236 g, 0.431 mmol), LiHMDS (0.075 g, 0.450 mmol) and $[Rd(COD)Cl]_2$ (0.106 g, 0.216 mmol). The reaction mixture was stirred for 16 h. The solvent was removed under vacuum and the residue was washed with hexane (10 mL) and extracted with DCM (12 mL). Carbon monoxide was

bubbled for 30 minutes into the resulting dark red extract, and the final orange solution was dried under vacuum to yield the crude product as an orange solid. **7c** was obtained as an orange-yellow solid after washing the crude material with Et_2O (3 x 5 mL). Yield 47% (0.120 g, 0.202 mmol). Mp: 270-272 ^{o}C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.68 (d, *J* = 6.4 Hz, 6 H, CH(C*H*$_3$)$_2$), 0.78 (d, *J* = 6.4 Hz, 6 H, CH(C*H*$_3$)$_2$), 2.27 (sept, *J* = 6.4 Hz, 2 H, C*H*(CH$_3$)$_2$), 7.08-7.20 (m, 6 H, Ar*H*), 7.21-7.28 (m, 4 H, Ar*H*), 7.40 (d, *J* = 7.4 Hz, 2 H, Ar*H*), 7.50 (t, *J* = 7.4 Hz, 1 H, Ar*H*). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 23.7, 24.0 (CH(*C*H$_3$)$_2$), 28.7 (*C*H(CH$_3$)$_2$), 125.8 (*C*H$_{ar}$), 127.5 (*C*H$_{ar}$), 128.4 (*C*$_{ar}$), 128.8 (*C*H$_{ar}$), 129.3 (*C*H$_{ar}$), 129.5 (*C*H$_{ar}$), 131.4 (*C*$_{ar}$), 132.0 (*C*H$_{ar}$), 132.2 (*C*H$_{ar}$), 132.5 (*C*$_{ar}$), 133.1 (*C*$_{ar}$), 144.6 (*C*H$_{ar}$), 151.9 (N*C*C), 157.7 (d, *J* = 37.7 Hz, Rh=*C*), 172.7 (N*C*S), 183.2 (d, *J* = 76.1 Hz, Rh-*C*O), 186.0 (d, *J* = 54.6 Hz, Rh-*C*O). IR (C_6H_6): *v* = 2069.7, 1996.9 (CO).

Crystal Structure Determination of Compounds 3b and 5b.

The Bruker X8-APEX[2] X-ray diffraction instrument with Mo-radiation was used for data collection. All data frames [with exception of **5b** (200 K)] were collected at low temperatures (T = 100 K) using an ω, φ-scan mode (0.3^{o} ω-scan width, hemisphere of reflections) and integrated using a Bruker SAINTPLUS software package.[3] The intensity data were corrected for Lorentzian polarization. Absorption corrections were performed using the SADABS program.[4] The SIR97[5] software was used for direct methods solution and phase determination, and Bruker SHELXTL[6] for structure refinement and difference Fourier maps. Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms of three compounds were refined by means of a full matrix least-squares procedure on F^2.

Table S1. Crystallographic Data and Summary of Data Collection and Structure Refinement

	3b	**5b**
Formula	$C_{27}H_{30}BrNO_2S$	$C_{24}H_{21}AuClNS$
Fw	512.49	587.89
cryst syst	Monoclinic	Monoclinic
space group	$P2_1/c$	$C2/c$
Size (mm^3)	0.32 x 0.17 x 0.10	0.27 x 0.17 x 0.10
T, K	100(2)	200(2)
a, Å	9.4960(14)	18.170(4)
b, Å	28.054(4)	9.7695(15)
c, Å	9.6399(14)	24.734(4)
α, deg	90	90
β, deg	104.693(2)	99.134(3)
γ, deg	90	90
V, $Å^3$	2484.1(6)	4334.9(12)
Z	4	8
d_{calcd} $g\cdot cm^{-3}$	1.370	1.802
μ, mm^{-1}	1.763	7.016
Refl collected	20859	11994
T_{min}/T_{max}	0.714	0.468
N_{measd}	6277	4607
[R_{int}]	[0.0276]	[0.0501]
R [I>2sigma(I)]	0.0319	0.0648
R_w[I>2sigma(I)]	0.0887	0.2058
GOF	1.120	1.174
Largest diff peak/hole[$e\cdot Å^{-3}$]	0.476/-0.361	2.279/-2.230

^{1}H-NMR and ^{13}C-NMR Spectra

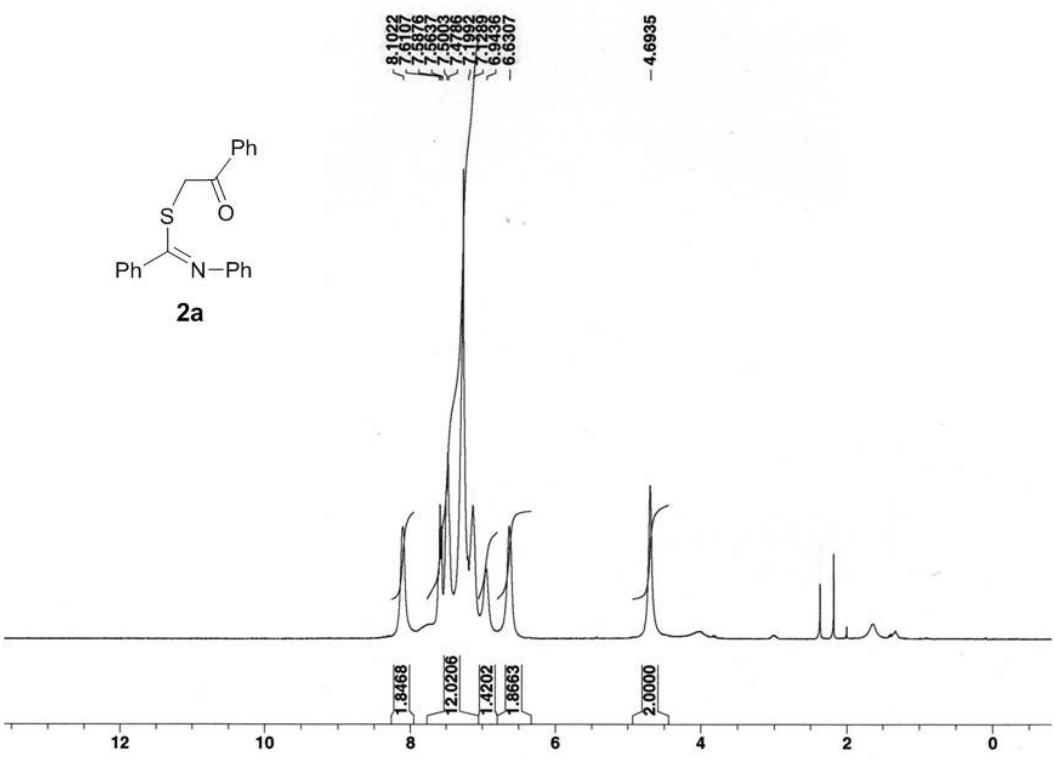

Figure S1. ^{1}H NMR spectrum of **2a** in $CDCl_3$.

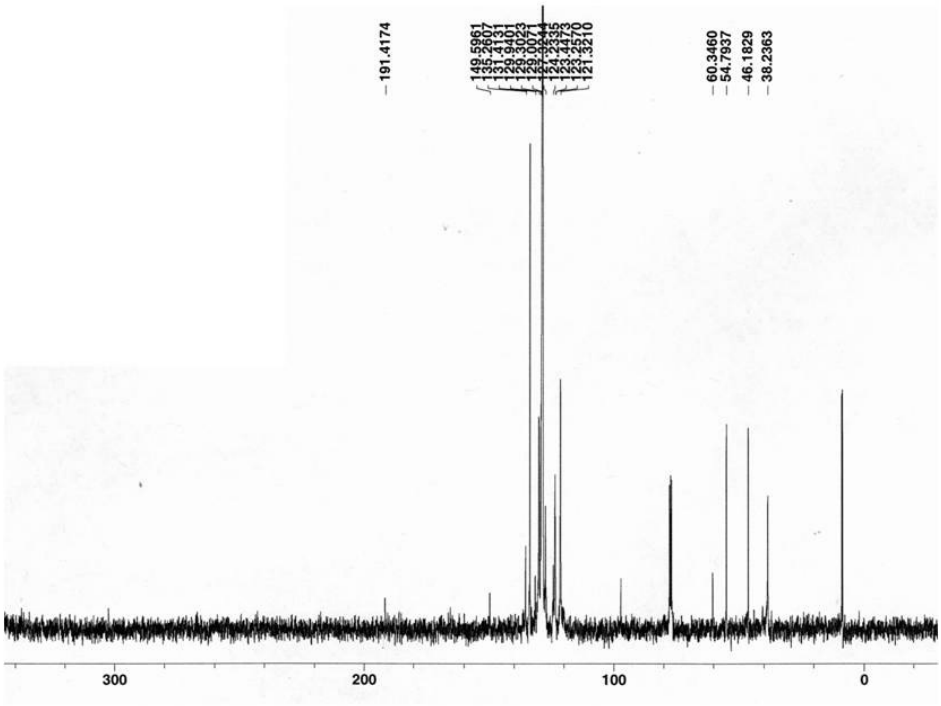

Figure S2. ^{13}C-NMR spectrum of **2a** in $CDCl_3$.

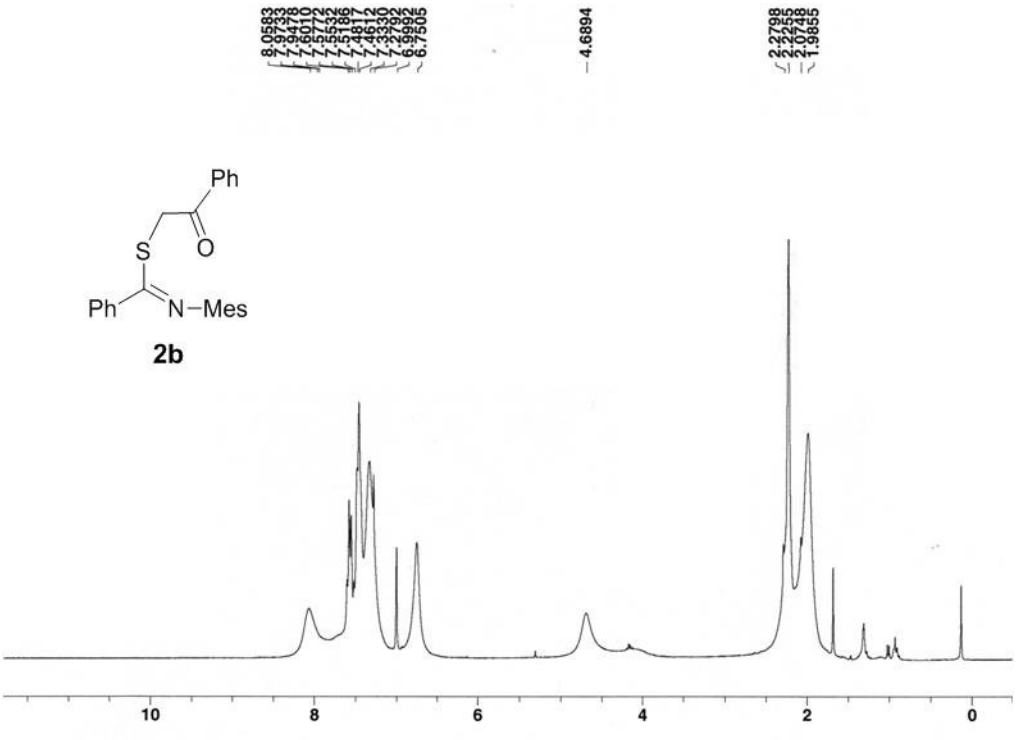

Figure S3. ^{1}H-NMR spectrum of **2b** in $CDCl_3$.

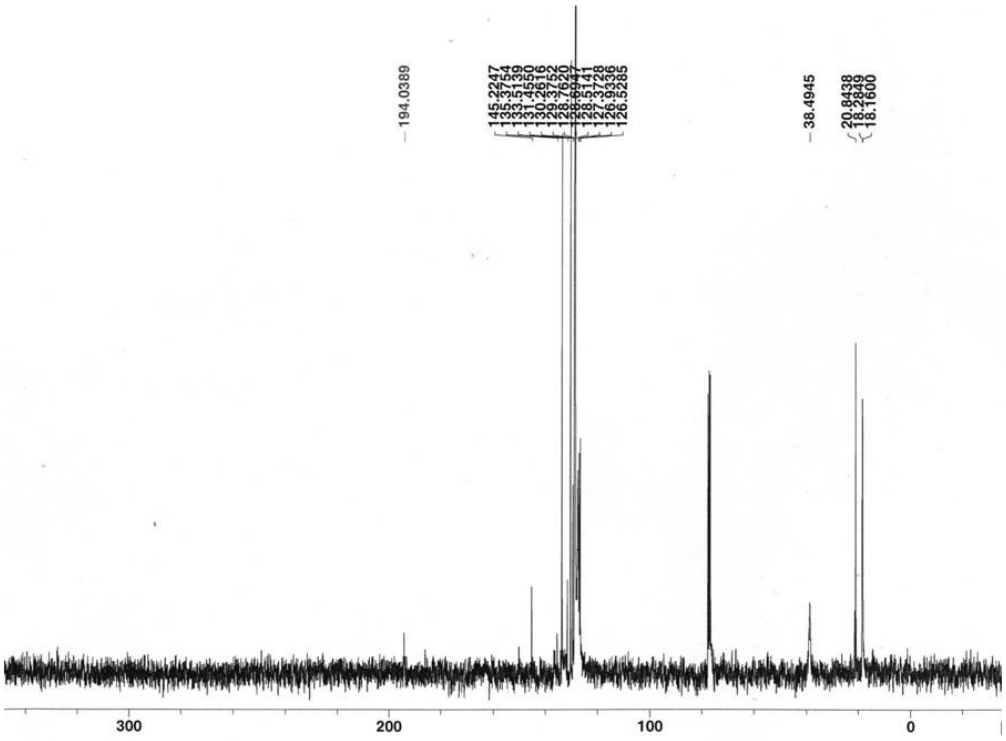

Figure S4. ^{13}C-NMR spectrum of **2b** in $CDCl_3$.

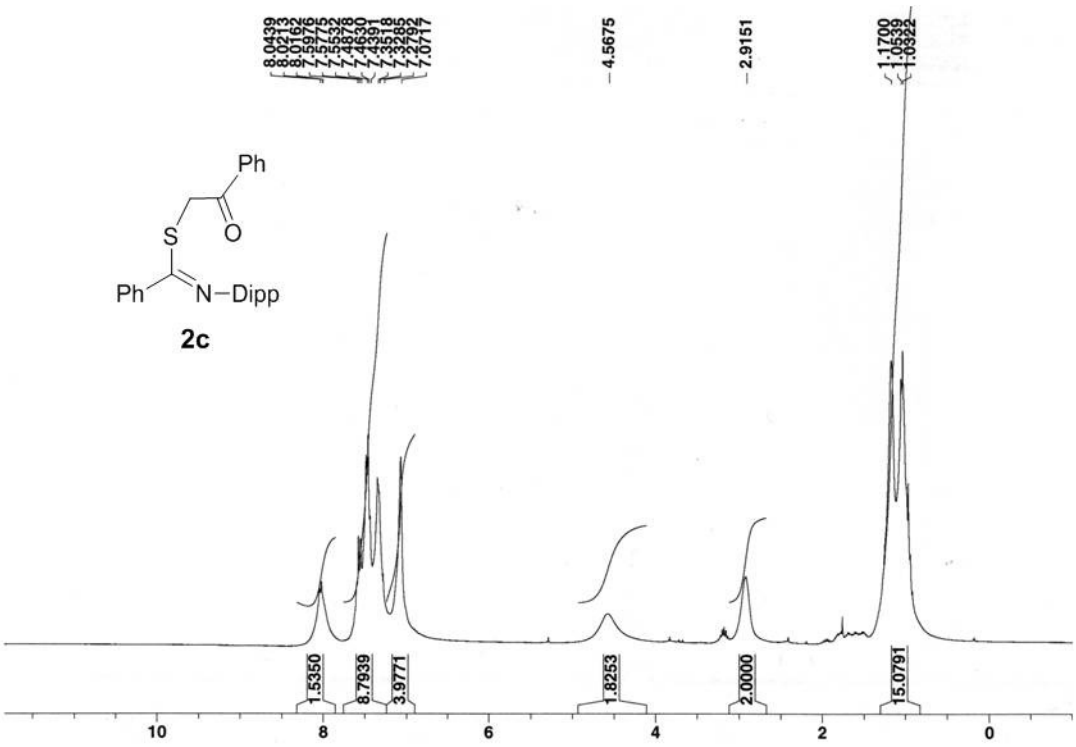

Figure S5. ^{1}H-NMR spectrum of **2c** in $CDCl_3$.

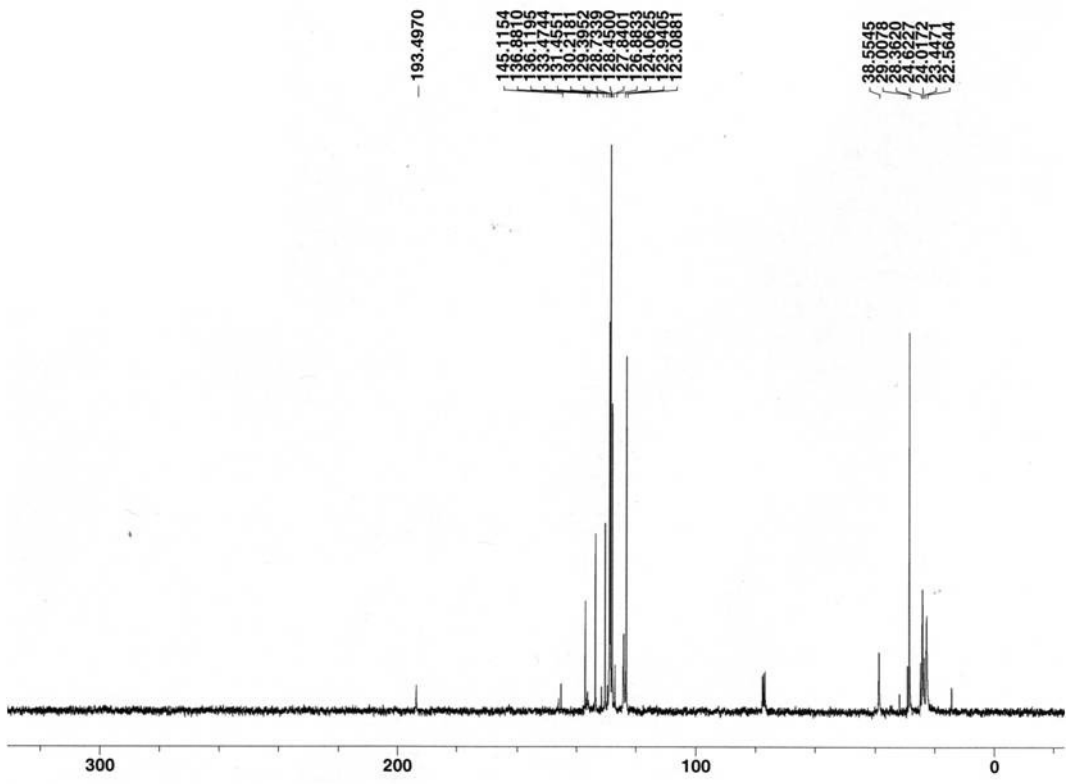

Figure S6. ^{13}C-NMR spectrum of **2c** in $CDCl_3$.

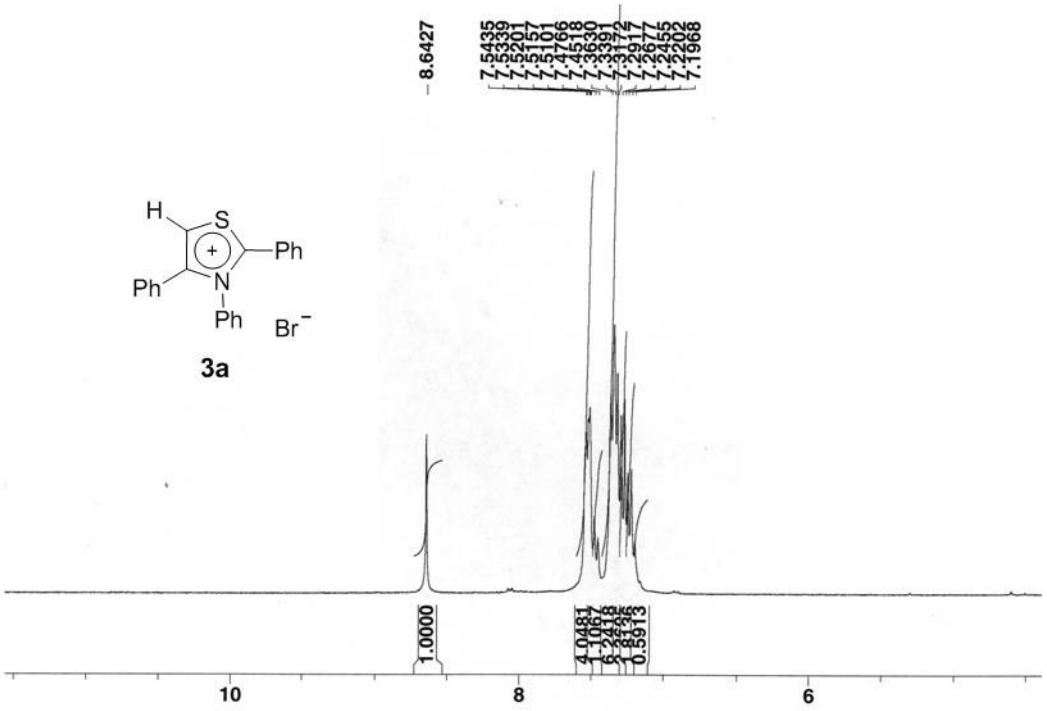

Figure S7. ^{1}H-NMR spectrum of **3a** in $CDCl_3$.

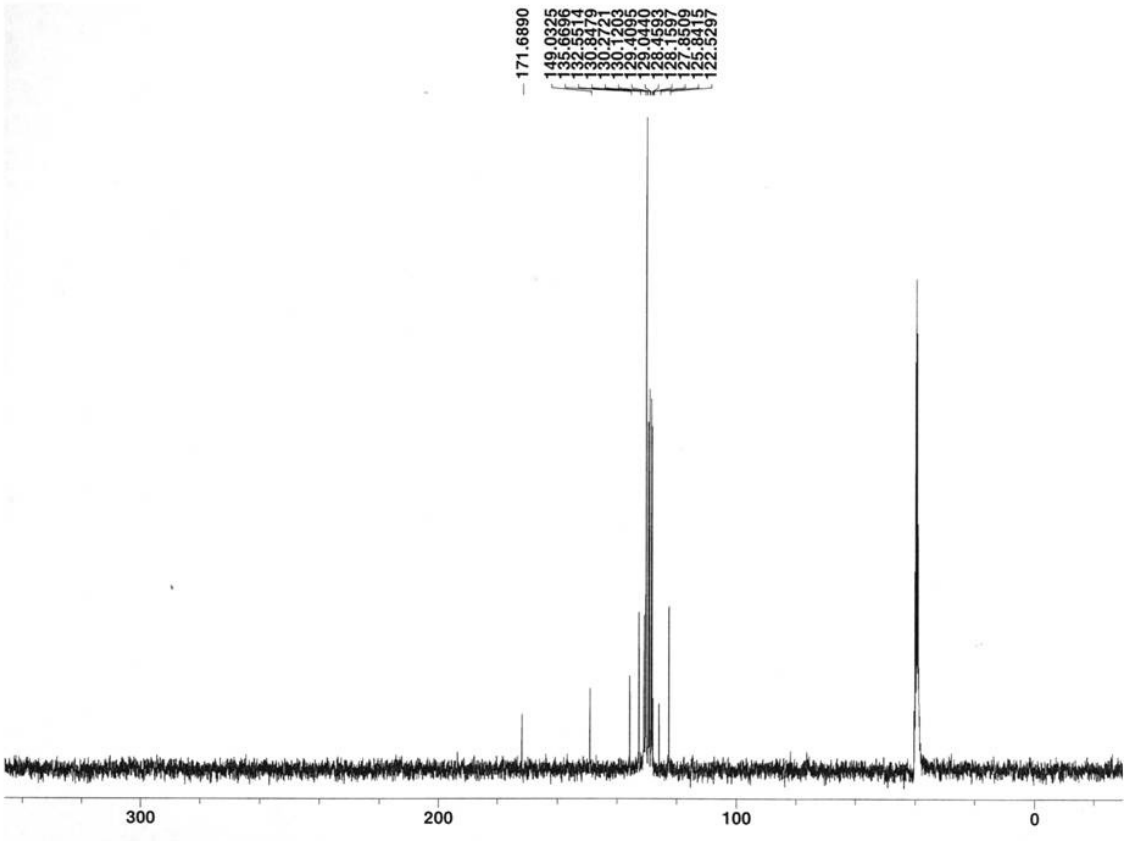

Figure S8. ^{13}C-NMR spectrum of **3a** in DMSO-d_6.

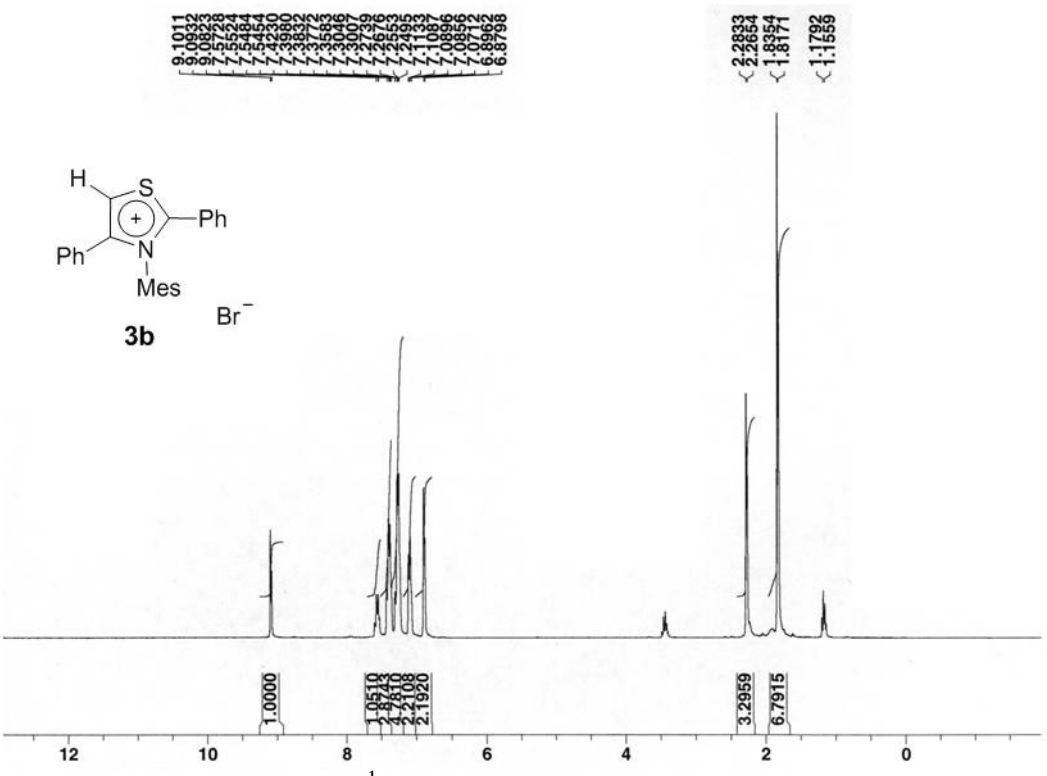

Figure S9. ^{1}H-NMR spectrum of **3b** in $CDCl_3$.

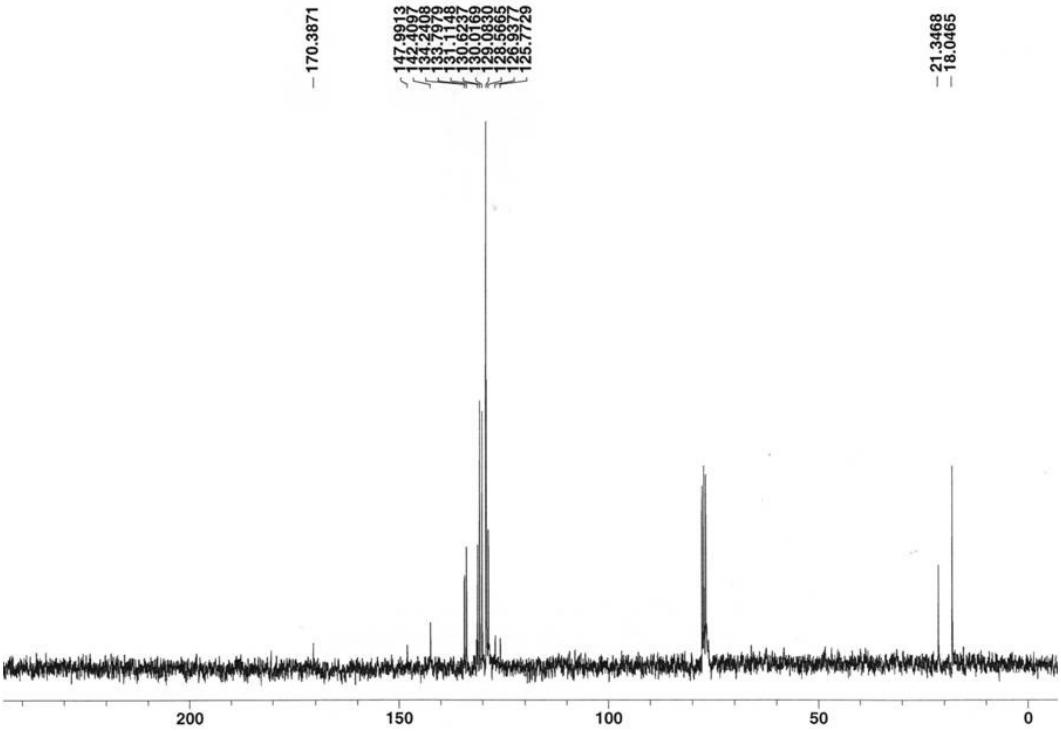

Figure S10. ^{13}C-NMR spectrum of **3b** in $CDCl_3$.

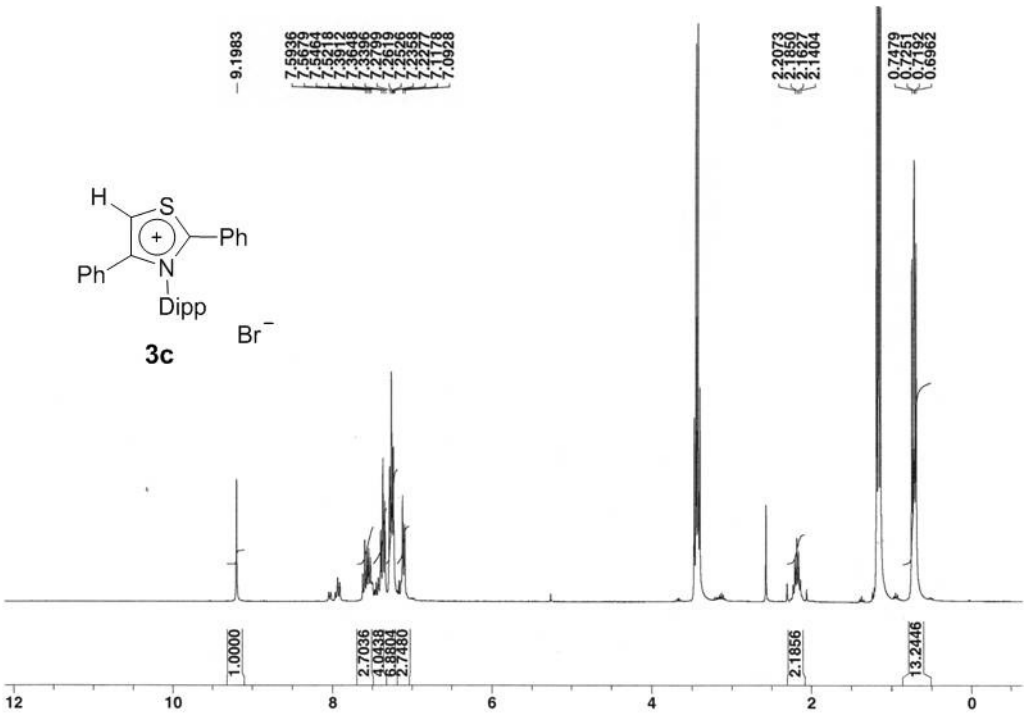

Figure S11. ^{1}H-NMR spectrum of **3c** in $CDCl_3$.

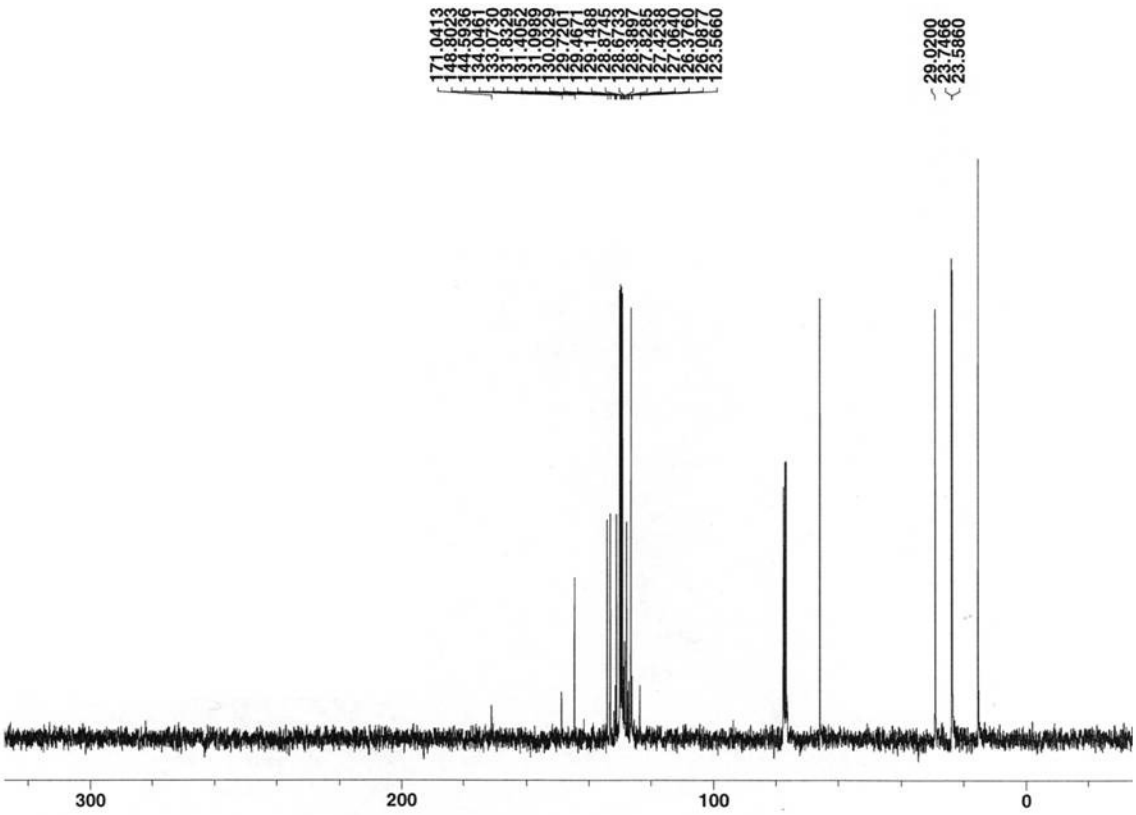

Figure S12. ^{13}C-NMR spectrum of **3c** in $CDCl_3$.

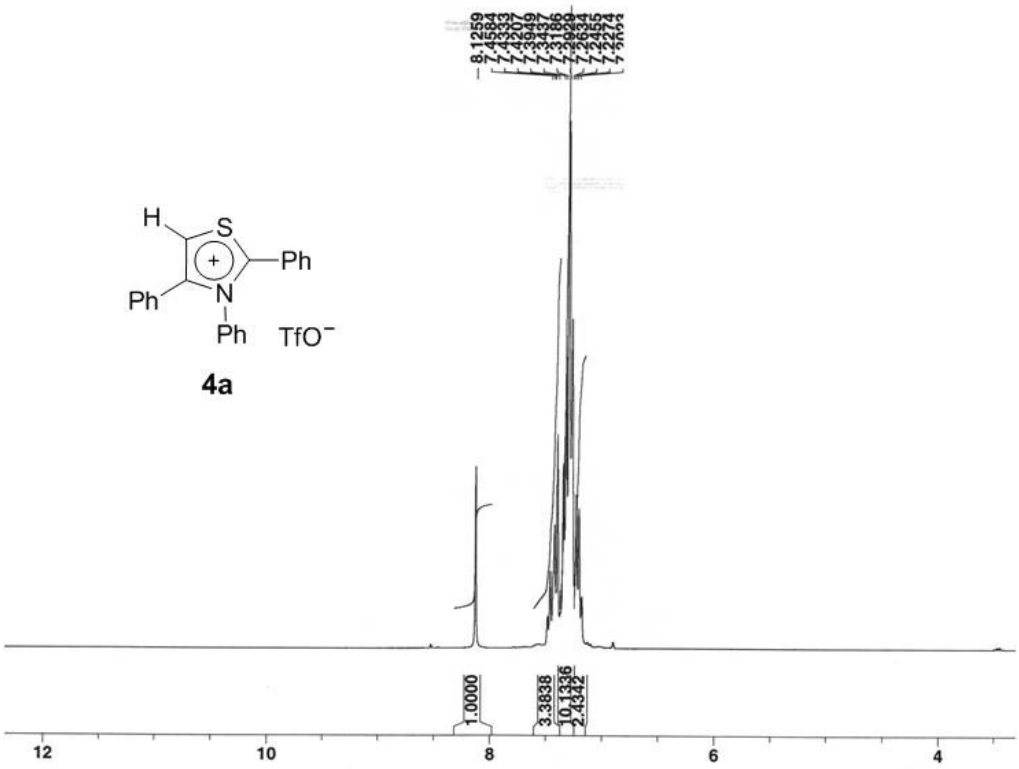

Figure S13. ^{1}H-NMR spectrum of **4a** in $CDCl_3$.

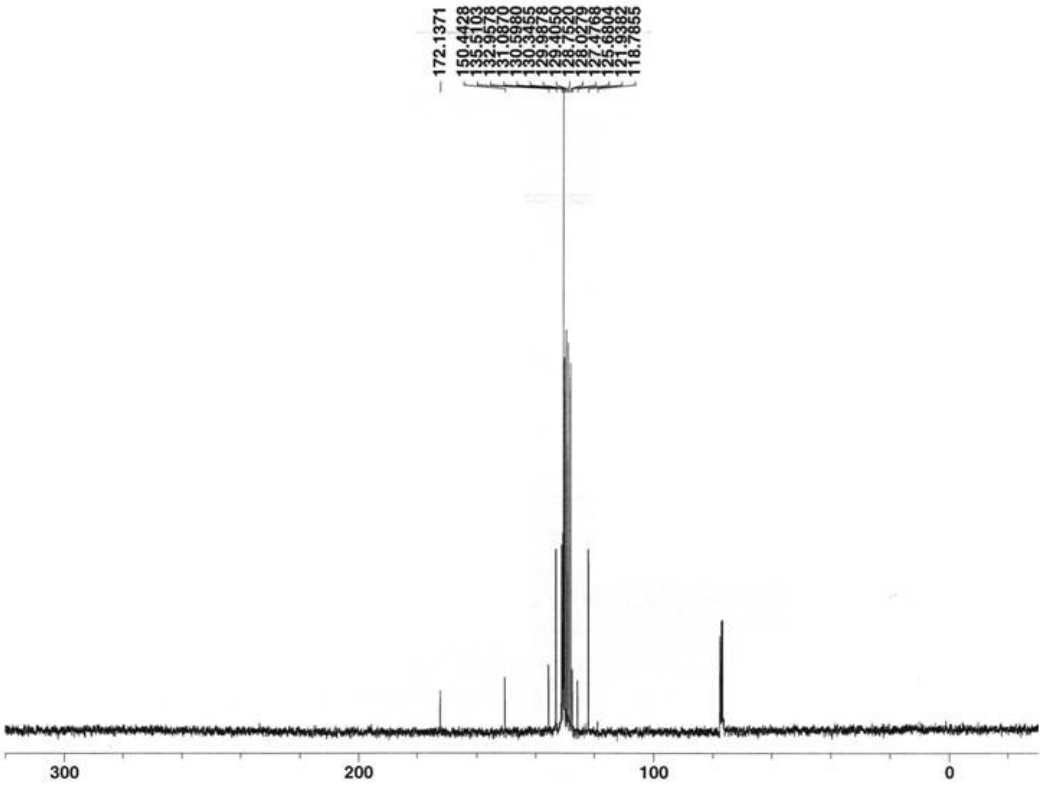

Figure S14. ^{13}C-NMR spectrum of **4a** in $CDCl_3$.

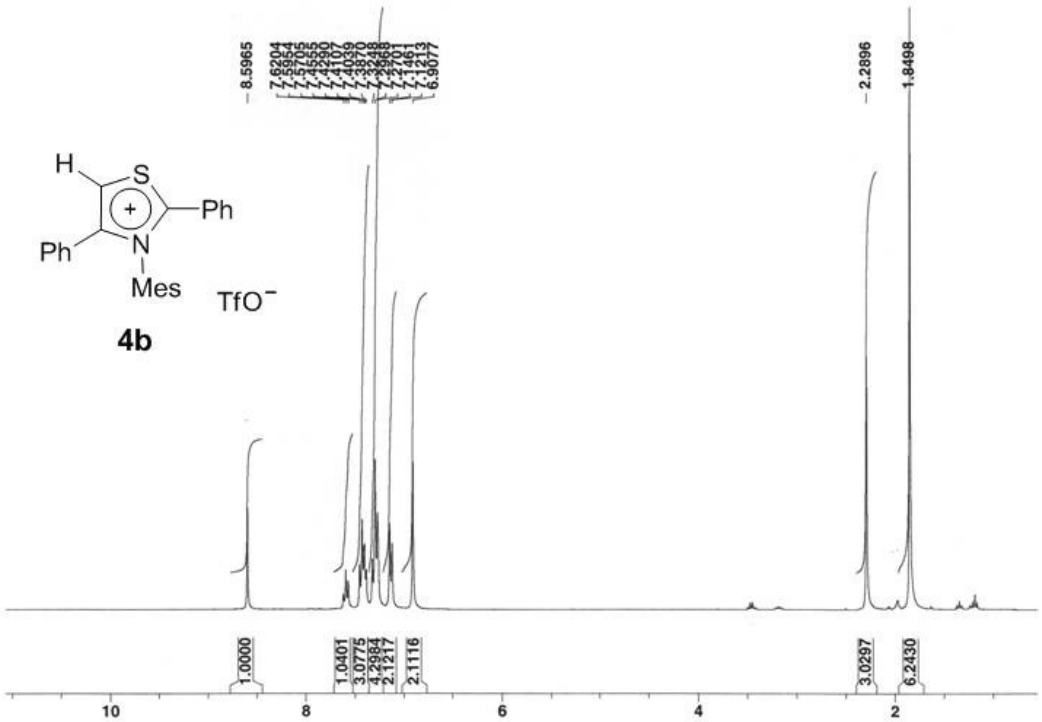

Figure S15. ^{1}H-NMR spectrum of **4b** in $CDCl_3$.

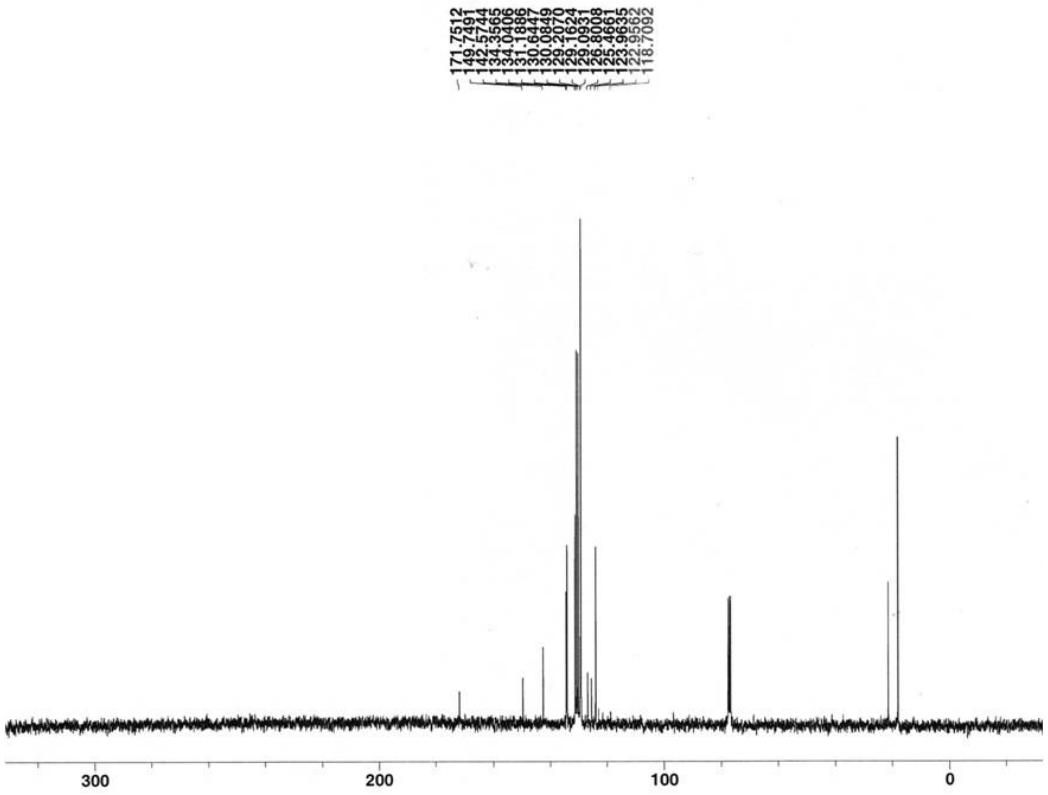

Figure S16. ^{13}C-NMR spectrum of **4b** in $CDCl_3$.

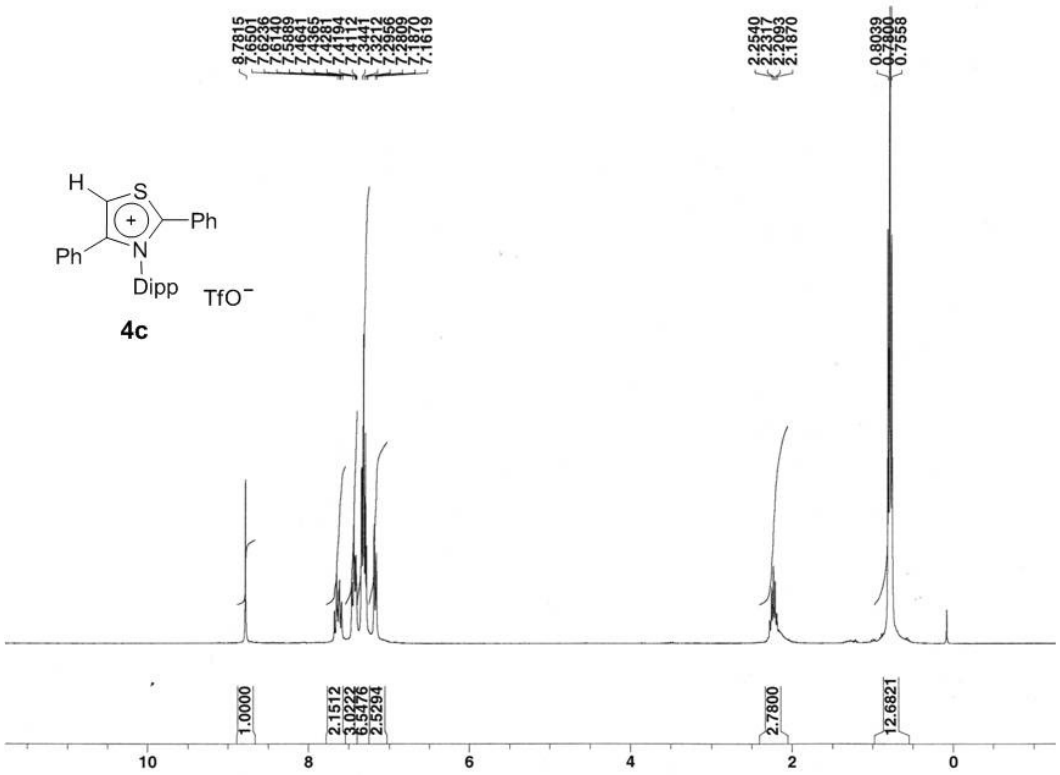

Figure S17. ^{1}H-NMR spectrum of **4c** in $CDCl_3$.

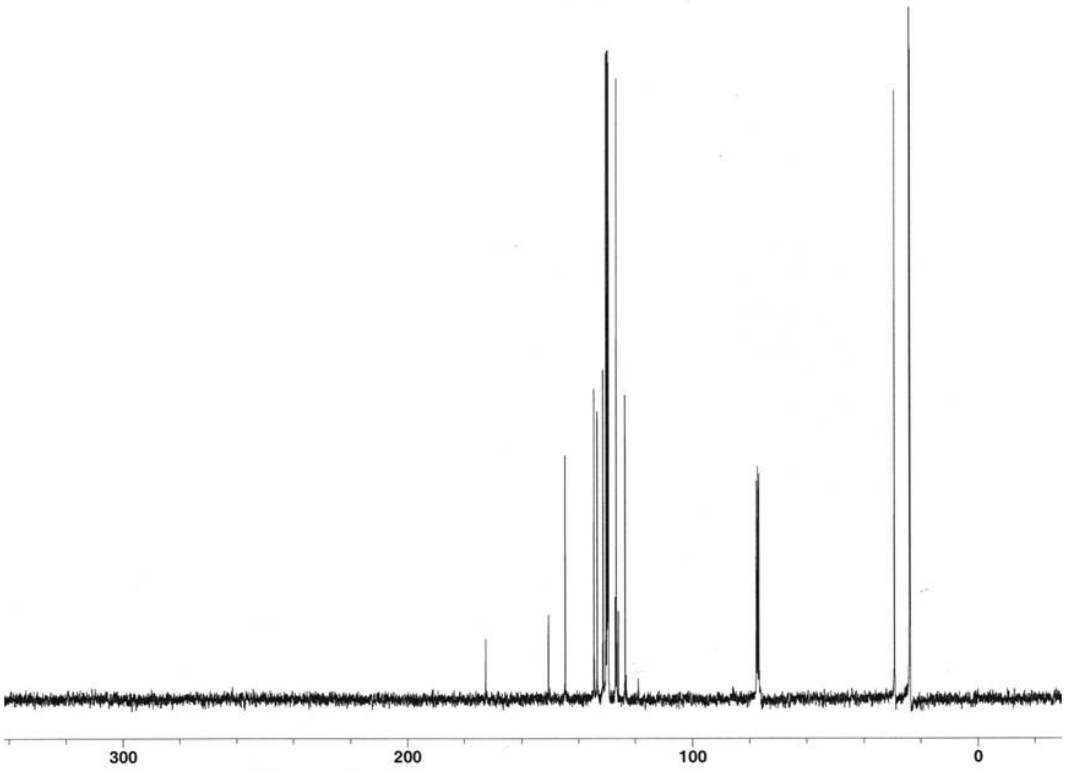

Figure S18. ^{13}C-NMR spectrum of **4c** in $CDCl_3$.

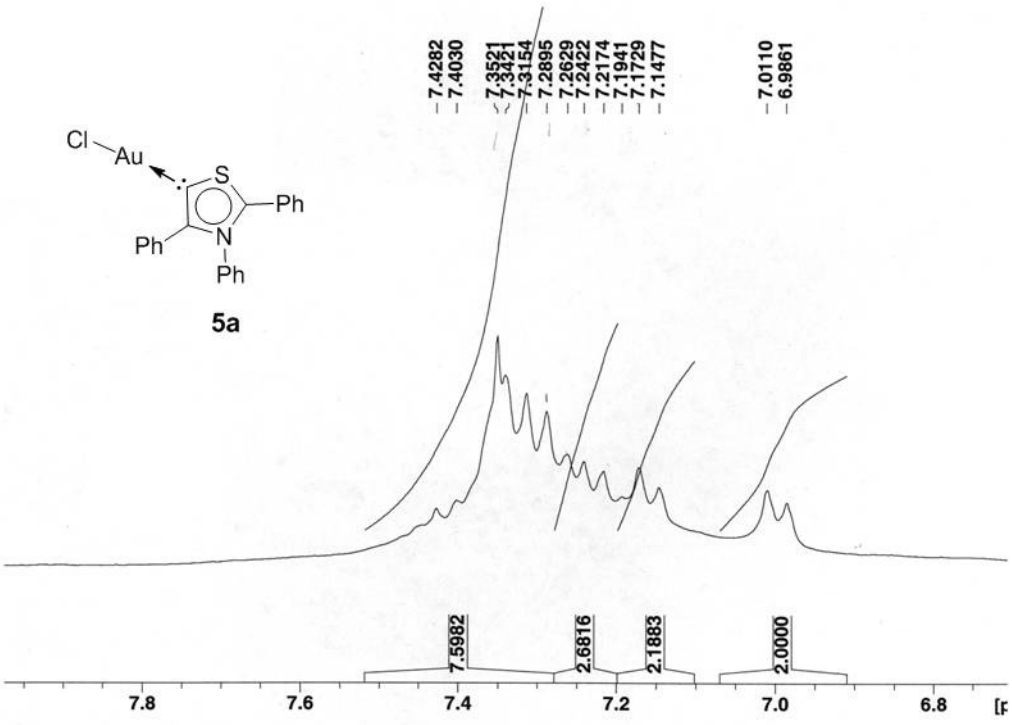

Figure S19. ^{1}H-NMR spectrum of **5a** in $CDCl_3$.

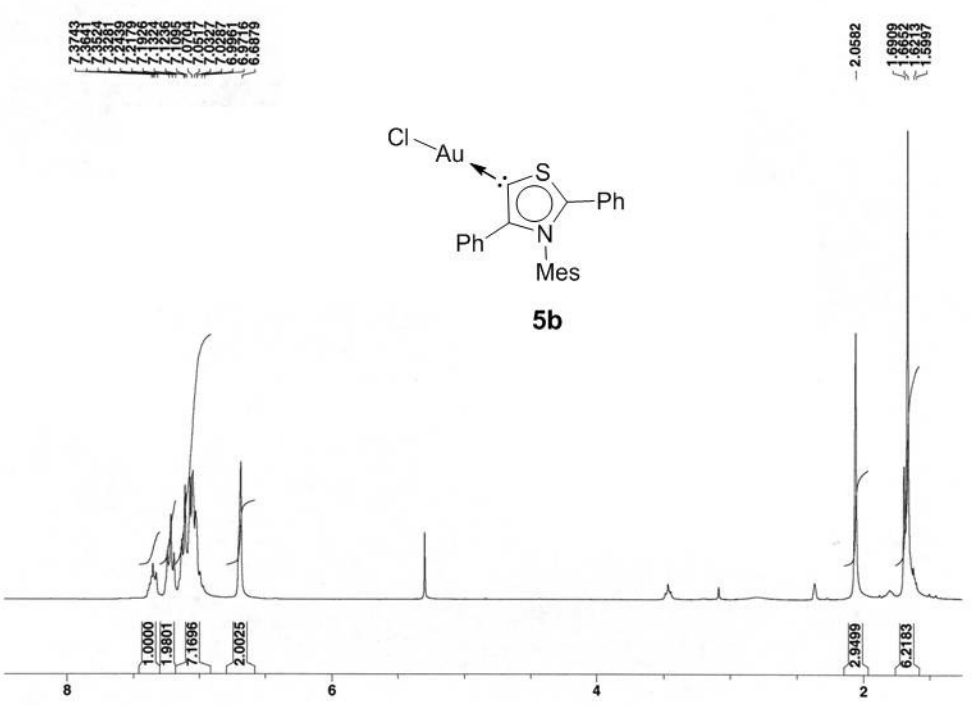

Figure S20. ^{1}H-NMR spectrum of **5b** in $CDCl_3$.

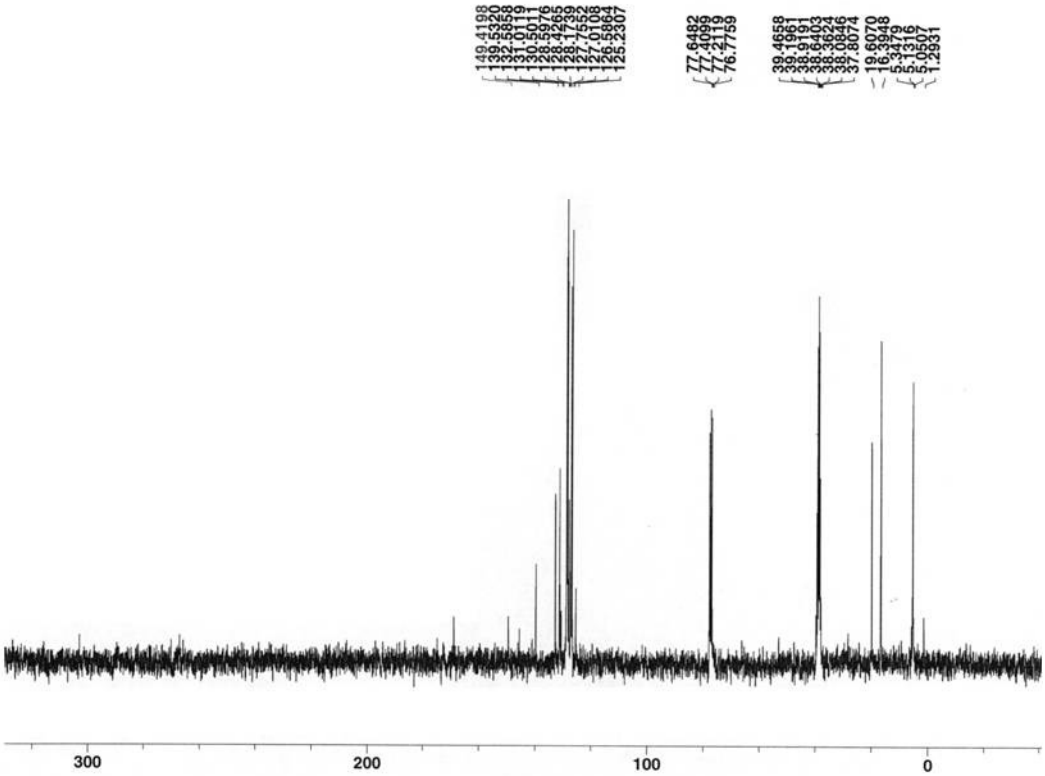

Figure S21. ^{13}C-NMR spectrum of **5b** in $CDCl_3$.

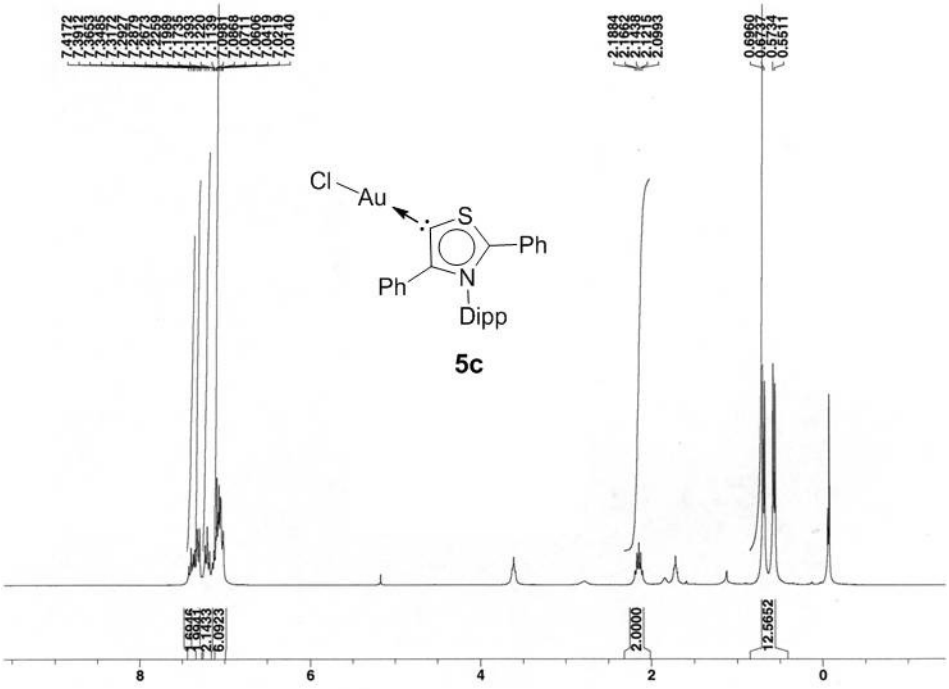

Figure S22. ^{1}H-NMR spectrum of **5c** in $CDCl_3$.

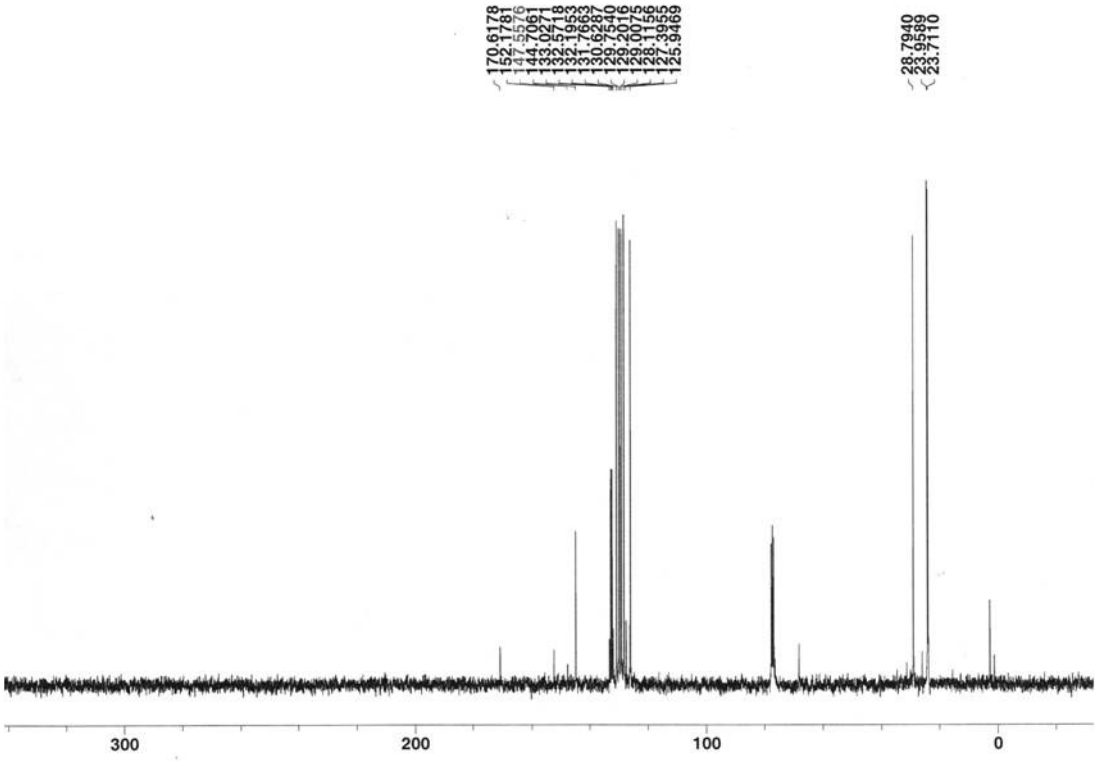

Figure S23. ^{13}C-NMR spectrum of **5c** in $CDCl_3$.

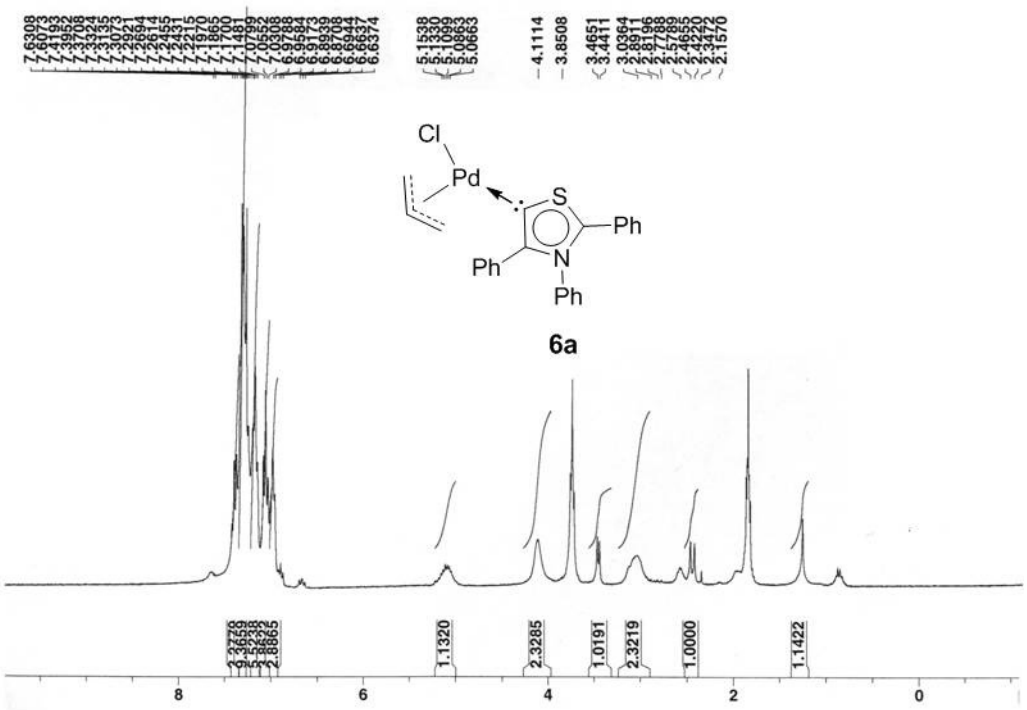

Figure S24. ^{1}H-NMR spectrum of **6a** in $CDCl_3$.

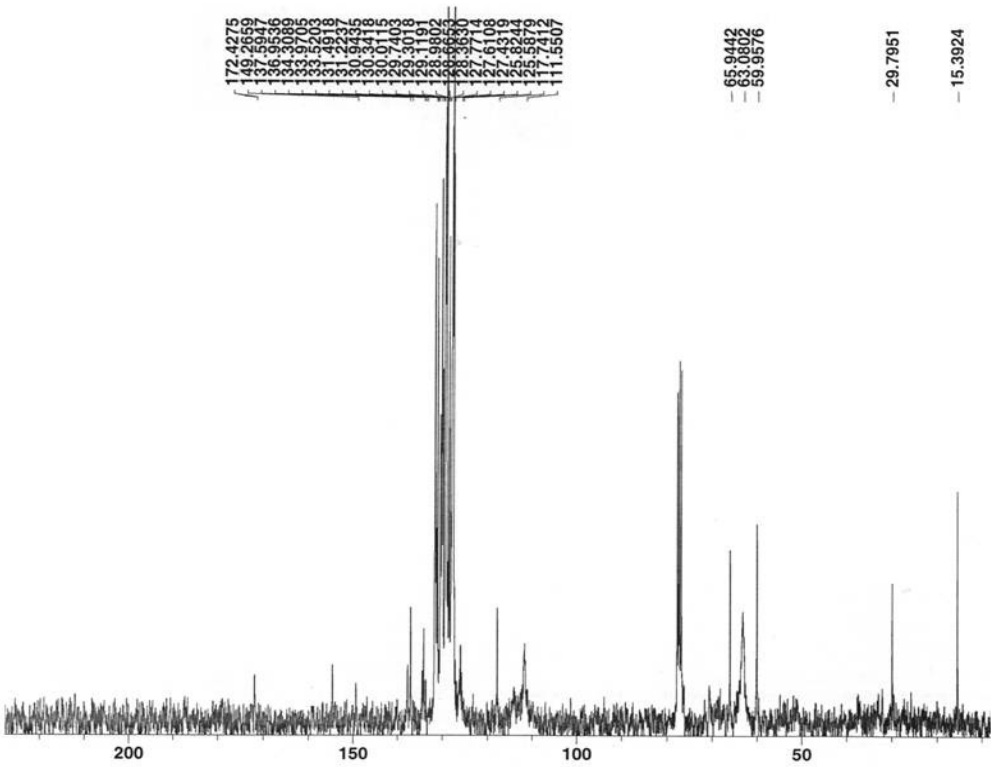

Figure S25. ^{13}C-NMR spectrum of **6a** in $CDCl_3$.

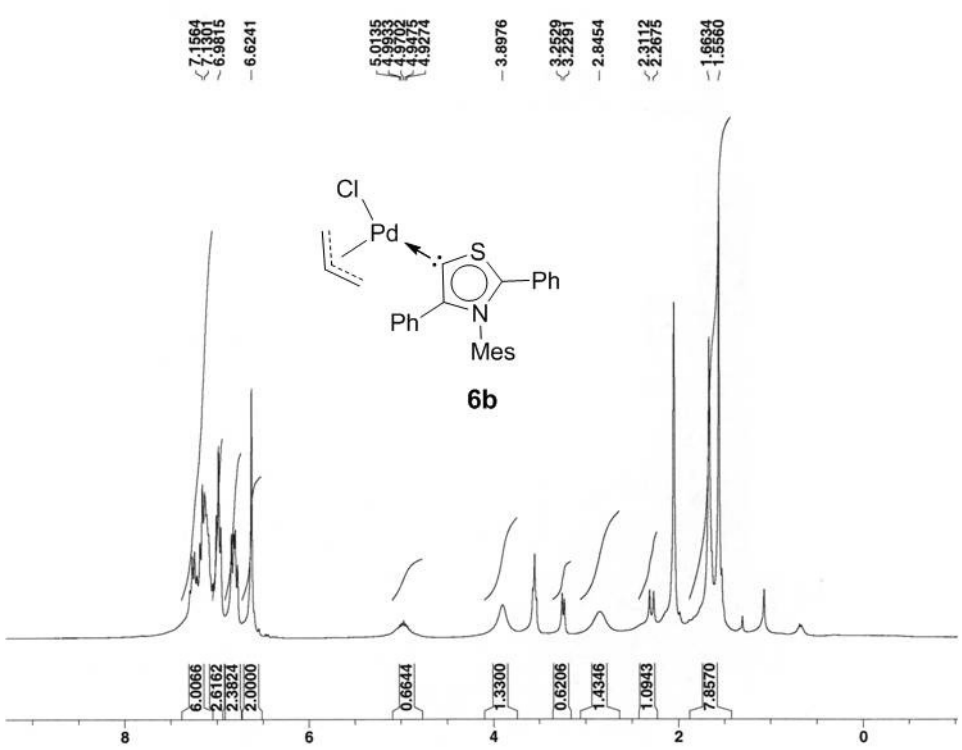

Figure S26. ^{1}H-NMR spectrum of **6b** in $CDCl_3$.

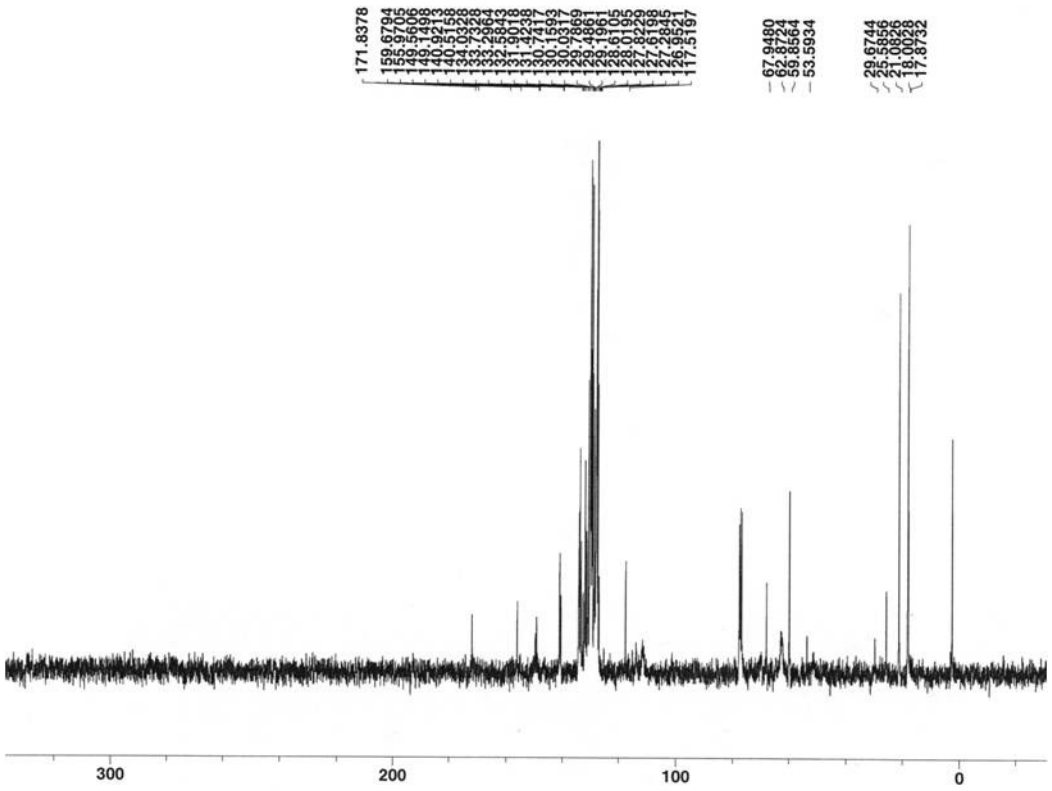

Figure S27. ^{13}C-NMR spectrum of **6b** in $CDCl_3$.

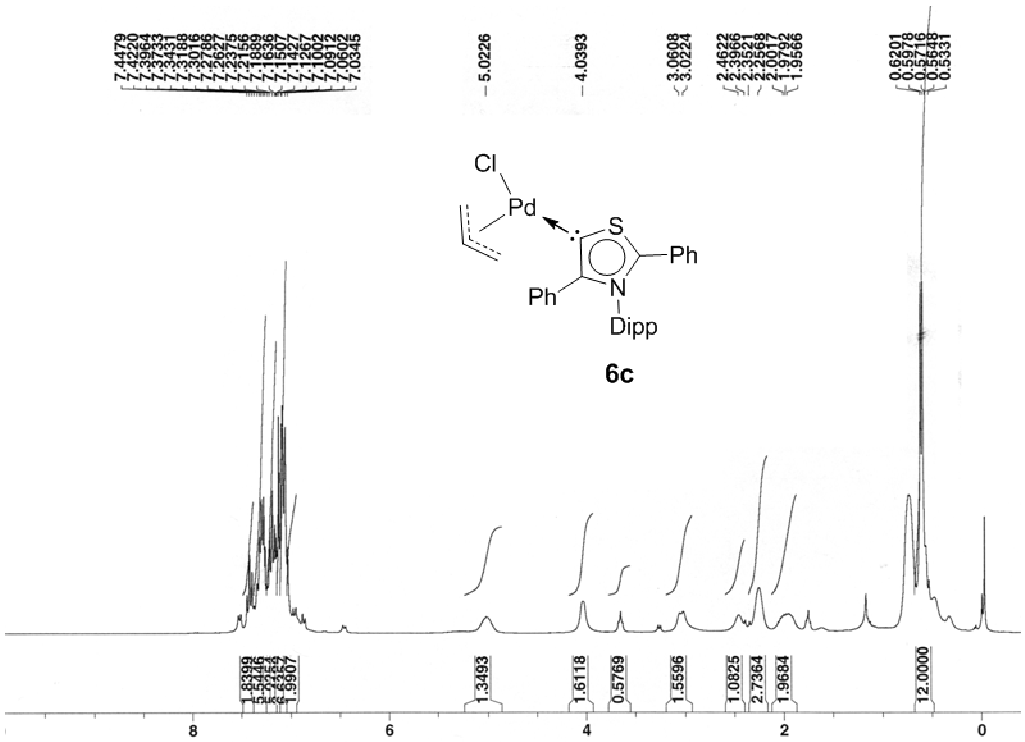

Figure S28. ^{1}H-NMR spectrum of **6c** in $CDCl_3$.

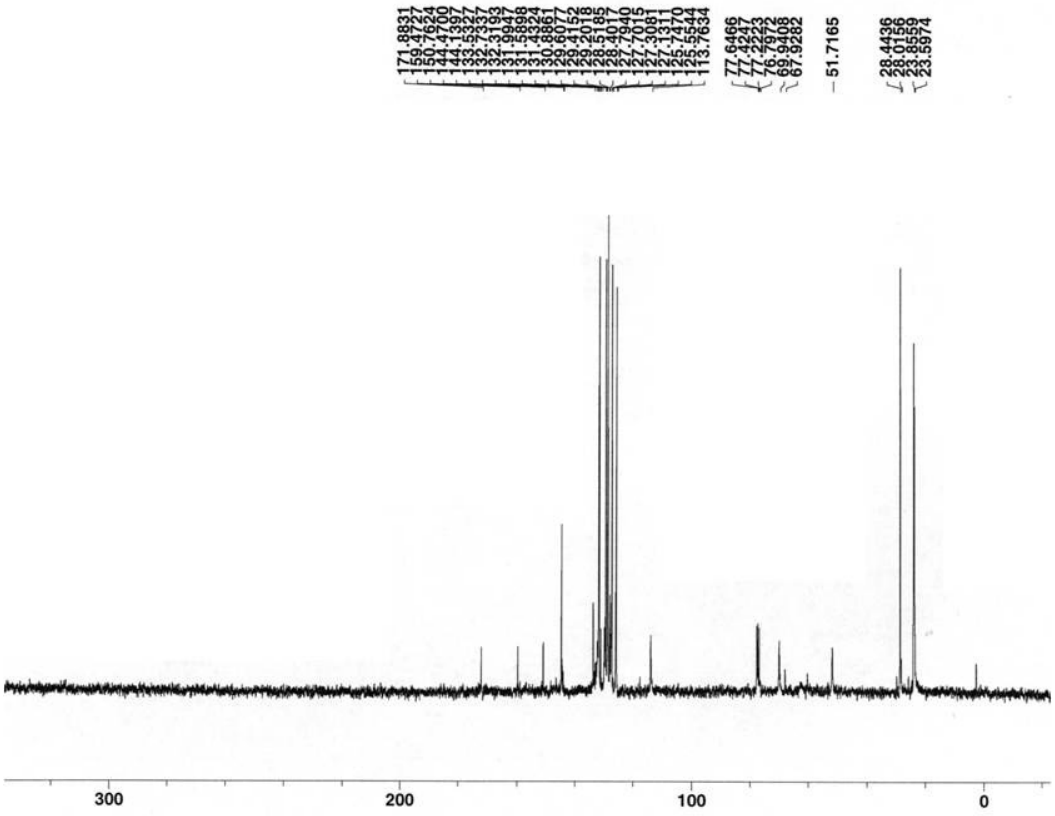

Figure S29. ^{13}C-NMR spectrum of **6c** in $CDCl_3$.

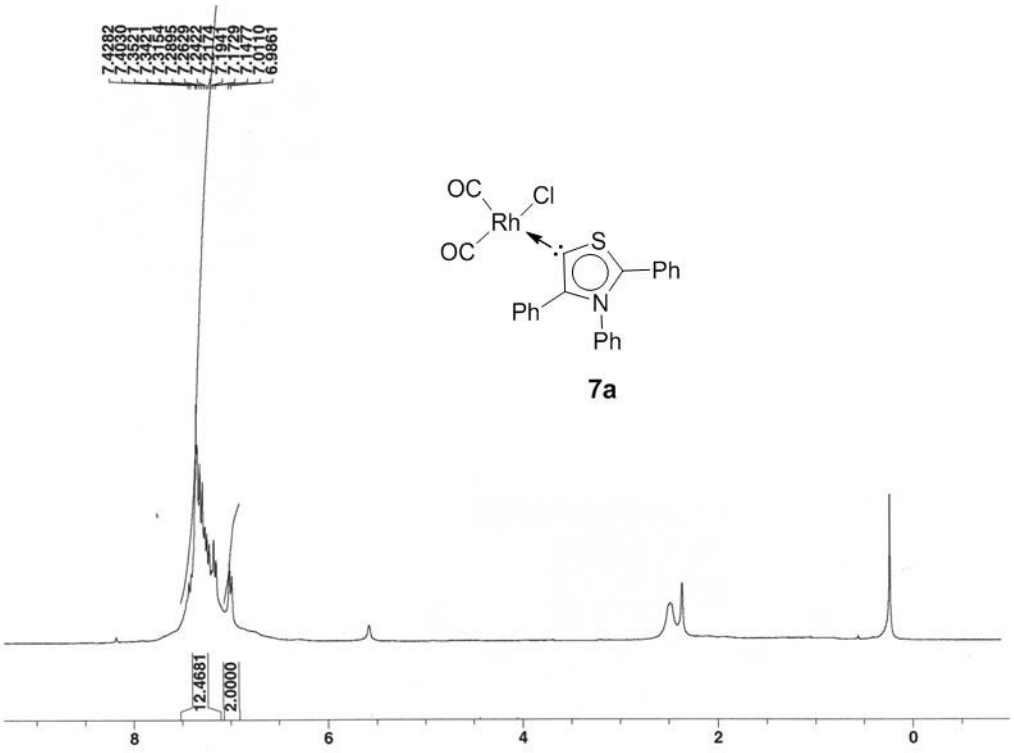

Figure S30. ^{1}H-NMR spectrum of **7a** in $CDCl_3$.

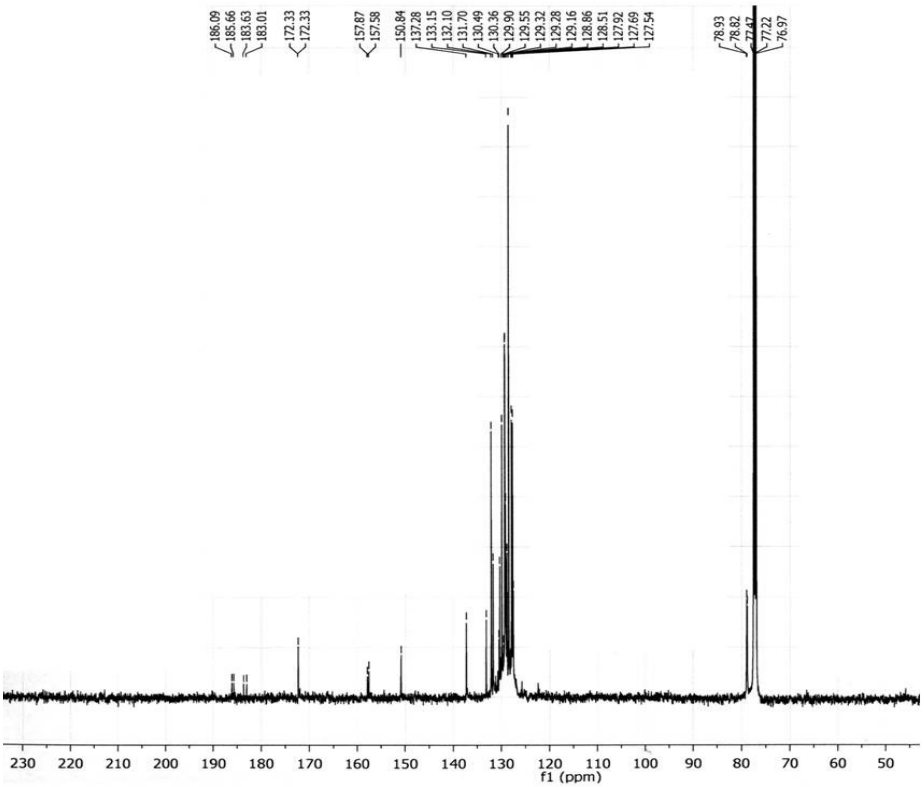

Figure S31. ^{13}C-NMR spectrum of **7a** in $CDCl_3$

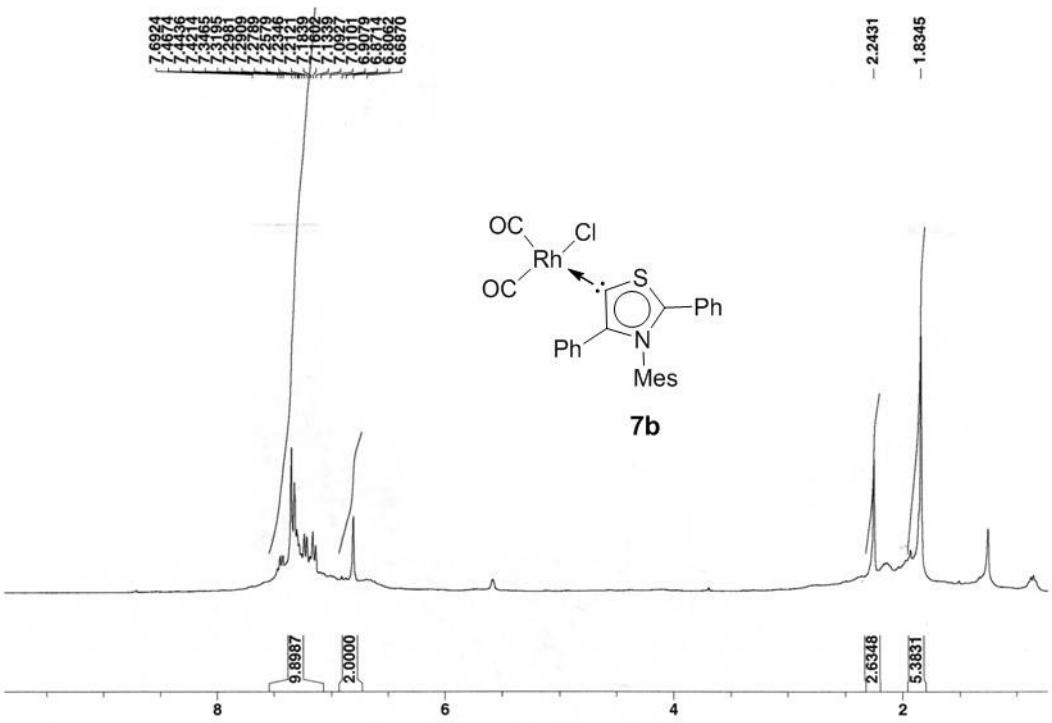

Figure S32. ^{1}H-NMR spectrum of **7b** in $CDCl_3$.

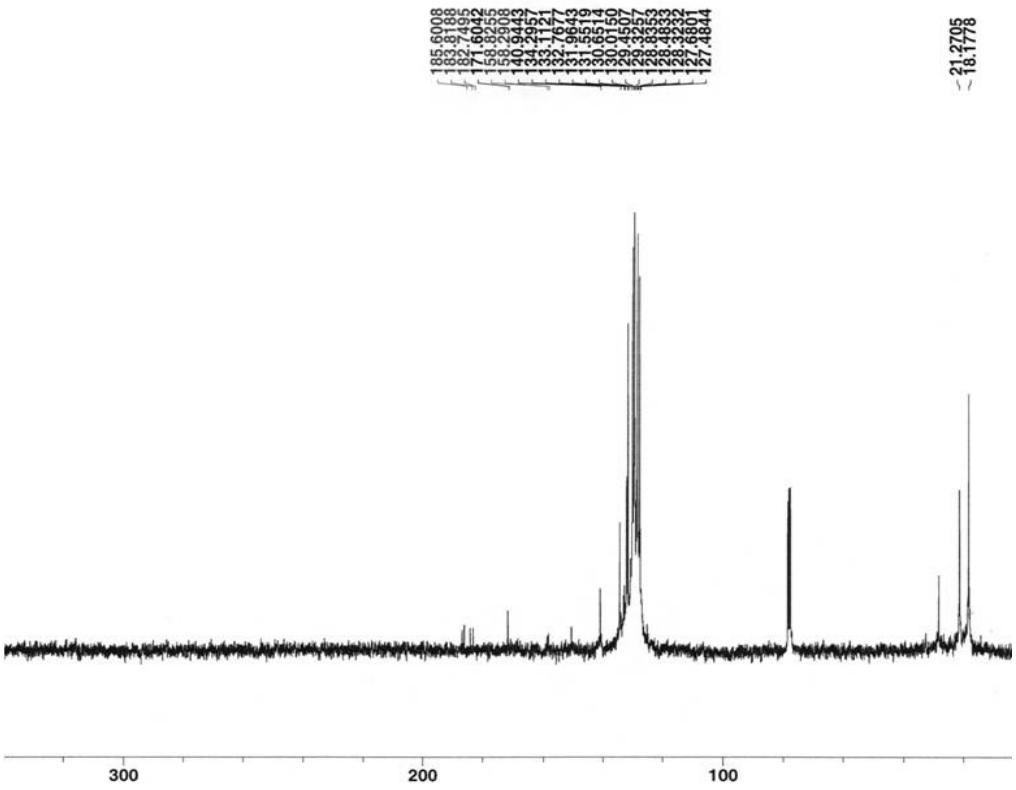

Figure S33. ^{13}C-NMR spectrum of **7b** in $CDCl_3$.

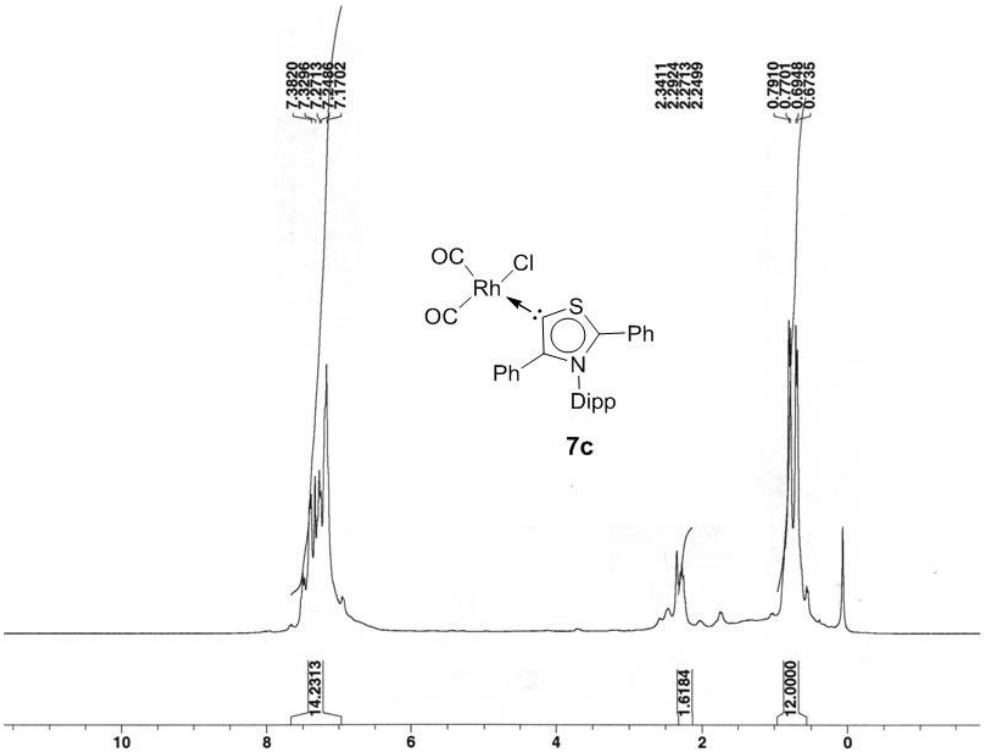

Figure S34. ^{1}H-NMR spectrum of **7c** in $CDCl_3$.

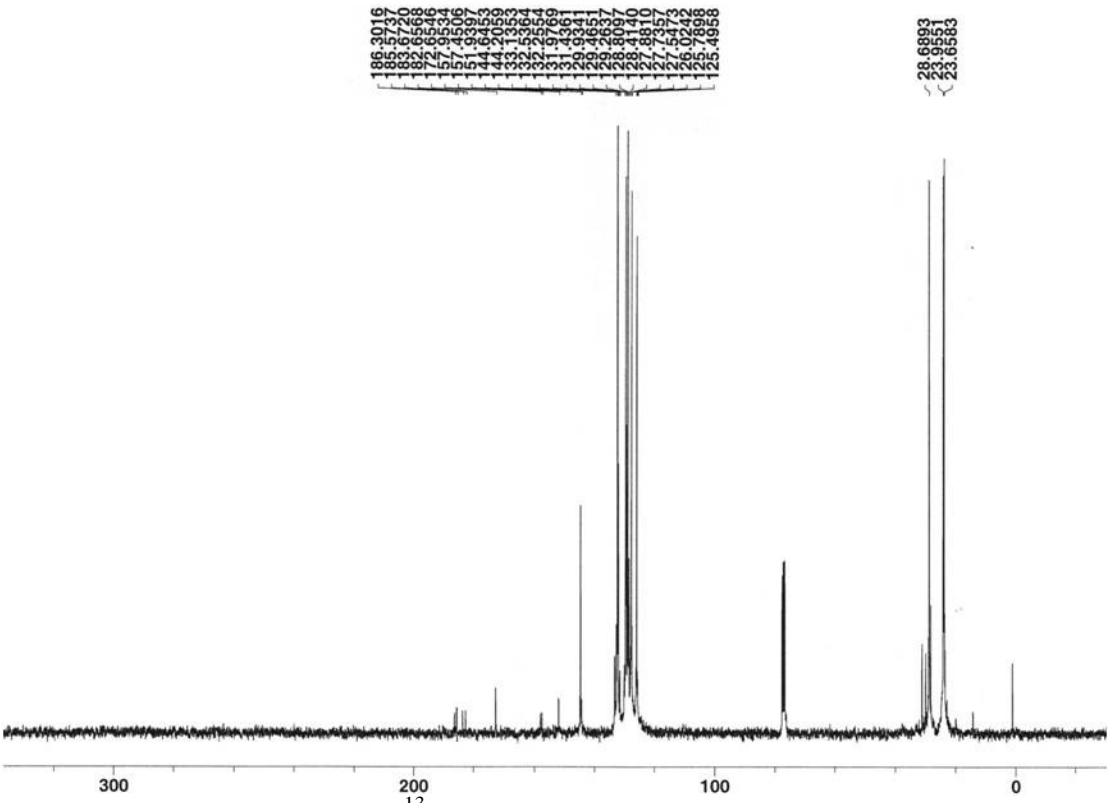

Figure S35. ^{13}C-NMR spectrum of **7c** in $CDCl_3$.

References:

1 K. Serdonds, T. Verduyckt, D. Vanderghinste, P. Borghgraef, J. Cleynhens, F. Van Leuven, H. Kung, G. Bormans, A. Verbruggen, *Eur. J. Med. Chem.,* 2009, **44**, 1415.

2 APEX 2 Version 5.1, Bruker **2009**. Bruker AXS Inc. Madison, Wisconsin, U.S.A.

3 Bruker **2009**. SAINT Version V7.60A. Bruker AXS Inc. Madison, Wisconsin, U.S.A.

4 Bruker **2008**. SADABS, Version 2008/1. Bruker Analytical X-Ray System, Inc., Madison, Wisconsin, U.S.A.

5 A. Altomare, M. C. Burla, M. Carnalli, M. Carascano, G. Giacovazzo, C. Guagliardi, A. G. G. Moliterni, G. Polidori, G. R. Spagan, SIR 97 *J. Appl. Cryst.,* 1999, **32**, 115.

6 Bruker **2003**. SHELXTL Software Version 6.14, Dec, Bruker Analytical X-Ray System, Inc., Madison, Wisconsin, U.S.A.