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Supporting Information

Cyclometallated Ruthenium(II) Complexes with ditopic Thienyl-NHC Ligands: Syntheses and Alkyne Annulations

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General Considerations.

Unless otherwise noted, all operations were performed without taking precautions to exclude air and moisture. Chemicals were purchased and used as received without further purification. ^{1}H and $^{13}C\{^{1}H\}$ NMR chemical shifts for were recorded in parts per million (ppm) and were internally referenced to the residual solvent signals relative to tetramethylsilane.

X-ray data were collected with a Bruker AXS SMART APEX diffractometer, using Mo Kα radiation at 100(2) K, with the SMART suite of programs.[1] Data were processed and corrected for Lorentz and polarization effects with SAINT[2] and for absorption effects with SADABS.[3] Structural solution and refinement were carried out with the SHELXTL suite of programs.[4] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All hydrogen atoms were placed at calculated positions. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model.

Synthesis of ligand precursors 3–8

1-(thiophen-2-yl)imidazole (1). Under nitrogen, CuI (1.52 g, 8 mmol, 20 mol%), L-proline (0.93 g, 16 mmol, 40 mol%) and DMSO (20 mL) were added to a 100 mL Schlenk tube. The resulting suspension was stirred at ambient temperature for 10 min Then imidazole (2.68 g, 40 mmol), 2-bromothiophene (6.52 g, 40 mmol), K_2CO_3 (16.6 g, 120 mmol) and DMSO (30 mL) were added. The mixture was stirred at 120 °C for 72 h before it was cooled to ambient temperature. DMSO was removed by vacuum distillation, and dichloromethane (100 mL) was added. The organic solution was washed with diluted

aqueous ammonia (3 × 30 mL), dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate, v/v = 3:1) to give **1** (4.80 g, 31 mmol, 78%) as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (s, 1 H, NCHN), 6.93–6.85 (m, 3 H, Ar–H), 6.72 (s, 2 H, Ar–H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 138.6 (NCHN), 136.6. 129.8, 126.1, 121.5, 119.6, 118.5 (Ar–C). MS (ESI): *m/z* 151 $[M + H]^+$.

1-(thiophen-2-yl)benzimidazole (2). Compound **2** was prepared in analogy to **1** from benzimidazole (4.72 g, 40 mmol) and 2-bromothiophene (6.52 g, 40 mmol). It was isolated as colorless oil (5.7 g, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (s, 1 H, NCHN), 7.91–7.89 (m, 1 H, Ar–H), 7.60–7.57 (m, 1 H, Ar–H), 7.41–7.35 (m, 2 H, Ar–H), 7.33–7.30 (m, 1 H, Ar–H). 7.18–7.16 (m, 1 H, Ar–H), 7.14–7.11 (m, 1 H, Ar–H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 143.5 (NCHN), 143.1, 136.9, 134.6, 126.4, 124.0, 123.3, 123.1, 121.8, 120.5, 110.5 (Ar–C). MS (ESI): *m/z* 201 $[M + H]^+$.

3-benzyl-1-(thiophen-2-yl)imidazolium Bromide (3). Compound **1** (750 mg, 5 mmol) was suspended in an excess of benzyl bromide (10 mL), and the mixture was heated at 120 °C for 24 h. After cooling to ambient temperature, the mixture was poured into ethyl acetate (50 mL). The precipitation was collected and further washed by diethyl ether (30 mL). Compound **3** was obtained as yellow solid (1.03 g, 4.1 mmol, 83%). Excess benzyl bromide was recycled by removing the solvents from filtrate. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.76 (s, 1 H, NCHN), 7.84 (s, 1 H, Ar–H), 7.64 (s, 1 H, Ar–H), 7.56 (s, 2 H, Ar–H), 7.43 (s, 1 H, Ar–H), 7.61–7.09 (m, 4 H), 6.77 (s, 1 H, Ar–H), 5.68 (s, 2 H, CH_2). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 135.5 (NCHN), 134.6, 133.0, 129.3, 129.1, 126.8, 124.6, 123.4, 122.5, 122.4 (Ar–C), 52.9 (CH_2). MS (ESI): *m/z* 241 $[M - Br]^+$.

3-isopropyl-1-(thiophen-2-yl)imidazolium Bromide (4). Compound **4** was prepared in analogy to **3** from **1** (5 mmol) and excess of 2-bromopropane (10 mL). After the reaction finished, the mixture was poured into ethyl acetate (50 mL). The precipitation was collected and further washed by diethyl ether (30 mL) to give compound **4** as yellow solid (704 mg, 3.7 mmol, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.82 (s, 1 H, NCHN), 8.00 (s, 1 H, Ar–H), 7.72 (s, 2 H, Ar–H), 7.30–7.25 (m, 1 H, Ar–H), 6.99–6.96 (m, 1 H, Ar–H), 5.26–5.18 (m, 1 H, $(CH_3)_2CH$), 1.94 (d, 6 H, 3J(H,H) = 7 Hz (CH3)2CH). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 135.3 (NCHN), 134.8, 127.0, 124.5, 122.9, 122.6, 121.6 (Ar–C), 54.1($CH(CH_3)_2$), 23.1 (($CH_3)_2CH$). MS (ESI): *m/z* 193 $[M - Br]^+$.

3-benzhydryl-1-(thiophen-2-yl)imidazolium Bromide (5). Compound **5** was prepared in analogy to **3** from **1** (5 mmol) and excess benzhydryl bromide (10 mL), which was liquefied by warming the bottle in a warm water bath. After the reaction finished, **5** was isolated as yellow solid (967 mg, 3.1 mmol, 61%), and benzhydryl bromide was recycled by evaporating the washings. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.63 (s, 1 H, NCHN), 7.96 (m, 1 H, Ar–H), 7.88 (s, 1 H, Ph_2CH), 7.67–7.64 (m, 1 H, Ar–H), 7.36 (s, 11 H, Ar–H), 7.24–7.21 (m, 1 H, Ar–H), 6.95–6.92 (m, 1 H, Ar–H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 136.5 (NCHN), 136.0, 134.5, 129.3, 129.2, 128.4, 127.1, 124.7, 123.2, 122.9, 122.1 (Ar–C), 66.7 (Ph_2CHN). MS (ESI): *m/z* 317 $[M - Br]^+$.

3-benzyl-1-(thiophen-2-yl)benzimidazolium Bromide (6). Compound **6** was prepared in analogy to **3** from benzimidazole **2** (1.0 g, 5 mmol) and excess of benzyl bromide (10 mL). After the reaction finished, **6** was isolated as gray solid (1.66 g, 4.8 mmol, 95%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.45 (s, 1 H, NCHN), 8.01–7.98 (m, 1 H, Ar–H), 7.90–7.84 (m, 2 H, Ar–H), 7.74–7.64 (m, 5 H, Ar–H), 7.47–7.31 (m, 4 H, Ar–H), 5.86 (s,

2 H, CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-d_6): δ 144.4 (NCN), 133.8, 132.7. 132.4, 130.0, 129.3, 129.2, 128.9, 128.3, 128.2, 127.6, 127.1, 126.9, 114.7, 113.8 (Ar–C), 50.7 (CH_2). MS (ESI): *m/z* 291 $[M - Br]^+$.

3-isopropyl-1-(thiophen-2-yl)benzimidazolium Bromide (7). Compound **7** was prepared in analogy to **3** from **2** (5 mmol) and excess of 2-bromopropane (10 mL) to give compound **7** as yellow solid (924 mg, 3.8 mmol, 76%). ^1H NMR (300 MHz, $CDCl_3$): δ 11.33 (s, 1 H, NCN), 7.97–7.94 (m, 2 H, Ar–H), 7.87–7.84 (m, 1 H, Ar–H), 7.76–7.70 (m, 2 H, Ar–H), 7.51–7.48 (m, 1 H, Ar–H), 7.21–7.18 (m, 1 H, Ar–H), 5.46–5.39 (m, 1 H, $(CH_3)_2CH$), 1.95 (d, 6 H, ^3J(H,H) = 7 Hz $(CH_3)_2CH$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 141.9 (NCHN), 132.4, 131.7, 130.1, 128.0, 127.7, 126.7, 126.3, 114.2, 113.8 (Ar–C), 53.2 ($(CH_3)_2CH$), 21.9 ($(CH_3)_2CH$). MS (ESI): *m/z* 243 $[M - Br]^+$.

3-benzhydryl-1-(thiophen-2-yl)benzimidazolium bromide (8). Compound **8** was prepared in analogy to **3** from **2** (5 mmol) and excess of benzhydryl bromide (10 mL), which was liquefied by warming the bottle in a warm water bath. After the reaction finished, **8** was isolated as yellow solid (1.17 g, 3.2 mmol, 64%). ^1H NMR (300 MHz, $CDCl_3$): δ 11.17 (s, 1 H, NCHN), 8.14 (s, 1 H, $CHPh_2$), 7.89 (s, 1 H, Ar–H), 7.77–7.76 (m, 1 H, Ar–H), 7.59–7.53 (m, 5 H, Ar–H), 7.45–7.38 (m, 8 H, Ar–H), 7.18–7.15 (m, 2 H, Ar–H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 143.0 (NCHN), 135.1, 132.7, 131.4, 130.7, 129.8, 129.2, 128.7, 128.3, 128.1, 128.0, 127.6, 126.9, 126.8 (Ar–C), 66.7 ($NCPh_2$). MS (ESI): *m/z* 367 $[M - Br]^+$.

Syntheses of complexes 9–14.

Synthesis of complexes 9a and 9b. In an aluminum wrapped flask, precursor **3** (128 mg, 0.4 mmol) was dissolved in dichloromethane (30 mL) before silver oxide was added (50 mg, 0.2 mmol). After stirring for about 2 h, [Ru(*p*-cymene)Cl_2]$_2$ (121 mg, 0.2 mmol) was added, and the reaction mixture was stirred for 24 h. The resulting yellow suspension was filtered over Celite, and the solvent of the filtrate was removed *in vacuo*. The residue was purified by column chromatography using an eluent gradient (neutral alumina, dichloromethane:methanol v/v = 100:0 to 50:1) to afford a mixture of complexes **9a (**84 mg, 16 mmol, 41%) and **9b** (110 mg, 20 mmol, 50%) as yellow solids. Complex **9a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, 1 H, ^3J(H,H) = 5 Hz, Ar–H), 7.42–7.34 (m, 5 H, Ar–H), 7.20 (d, 1 H, ^3J(H,H) = 2 Hz, Ar–H), 6.98 (d, 1 H, ^3J(H,H) = 5 Hz, Ar–H), 6.85 (d, 1 H, ^3J(H,H) = 2 Hz, Ar–H), 5.73 (s, 2 H, NCH_2Ph), 5.71 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H), 5.52 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H), 5.28 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H), 4.94 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H), 2.17–2.10 (m, 1 H, $(CH_3)_2CH$Ar), 2.02 (s, 1 H, CH_3Ar), 0.87 (d, 3 H, ^3J(H,H) = 7 Hz, $(CH_3)_2$CHAr), 0.67 (d, 3 H, ^3J(H,H) = 7 Hz, $(CH_3)_2$CHAr). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 188.9 (NCN), 155.7, 137.1, 136.2, 129.1, 128.1, 127.1, 120.3, 116.5, 115.7, 104.4, 99.0, 91.1, 89.0, 85.8, 82.3 (Ar–C), 54.2 (CH_2Ph), 30.9 (Ar$CH(CH_3)_2$), 22.9, 21.5 (($CH_3)_2$CHAr), 18.8 (CH_3Ar). HRMS (ESI), *m/z* calcd. for $C_{24}H_{26}ClN_2RuS$ $[M + H]^+$: 511.0544. Found: 511.0546. Complex **9b :** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43–7.41 (m, 2 H, Ar–H), 7.40 (d, 1 H, ^3J(H,H) = 5 Hz, Ar–H), 7.37–7.35 (m, 3 H, Ar–H), 7.21 (1 H, ^3J(H,H) = 2 Hz, Ar–H), 7.00 (d, 1 H, ^3J(H,H) = 5 Hz, Ar–H), 6.85 (d, 1 H, ^3J(H,H) = 2 Hz, Ar–H), 5.74 (d, 1 H, ^3J(H,H) = 17 Hz, NCH_2Ph), 5.67 (d, 1 H, ^3J(H,H) = 17 Hz, NCH_2Ph), 5.65 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H),

5.47 (d, 1 H, ^{3}J(H,H) = 6 Hz, Ar–H), 5.28 (d, 1 H, ^{3}J(H,H) = 6 Hz, Ar–H), 4.94 (d, 1 H, ^{3}J(H,H) = 6 Hz, Ar–H), 2.24–2.18 (m, 1 H, $(CH_3)_2CH$Ar), 2.11 (s, 1 H, CH_3Ar), 0.91 (d, 3 H, ^{3}J(H,H) = 7 Hz, $((CH_3)_2$CHAr), 0.70 (d, 3 H, ^{3}J(H,H) = 7 Hz, $(CH_3)_2$CHAr). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): 188.4 (NCN), 154.8, 137.1, 136.5, 134.8, 129.0, 128.0, 127.0, 120.4, 116.5, 115.7, 103.4, 100.2, 90.6, 88.7, 85.8, 82.3 (Ar–C), 54.2 (NCH_2Ph), 31.0 (Ar$CH(CH_3)_2$), 22.9, 21.5($(CH_3)_2$CHAr), 19.5 (CH_3Ar). HRMS (ESI), *m/z* calcd. for $C_{24}H_{26}BrN_2RuS$ $[M + H]^+$: 555.0044. Found: 555.0041.

Synthesis of complex 9c. An excess of LiI (2 mmol) was added to a solution of **9a** (102 mg, 0.2 mmol) in acetonitrile (5 mL). The resulting solution was stirred at ambient temperature for 24 h. After solvent evaporation, the crude product was dissolved in dichloromethane (20 mL) and washed with water (10 mL × 3). The organic phase was dried over Na_2SO_4 and concentrated to give **9c** as yellow solid (114 mg, 0.19 mmol, 95%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.41 (m, 2 H, Ar–H), 7.41 (d, 1 H, ^{3}J(H,H) = 5 Hz, Ar–H), 7.38–7.35 (m, 3 H, Ar–H), 7.21 (d, 1 H, ^{3}J(H,H) = 2 Hz, Ar–H), 6.99 (d, 1 H, ^{3}J(H,H) = 5 Hz, Ar–H), 6.85 (d, 1 H, ^{3}J(H,H) = 2 Hz, Ar–H), 5.75 (d, 1 H, ^{3}J(H,H) = 16 Hz, NCH_2Ph), 5.68 (d, 1 H, ^{3}J(H,H) = 16 Hz, NCH_2Ph), 5.65 (d, 1 H, ^{3}J(H,H) = 6 Hz, Ar–H), 5.47 (d, 1 H, ^{3}J(H,H) = 6 Hz, Ar–H), 5.28 (d, 1 H, ^{3}J(H,H) = 6 Hz, Ar–H), 4.94 (d, 1 H, ^{3}J(H,H) = 6 Hz, Ar–H), 2.23–2.19 (m, 1 H, $(CH_3)_2CH$Ar), 2.11 (s, 1 H, CH_3Ar), 0.90 (d, 3 H, ^{3}J(H,H) = 7 Hz, $(CH_3)_2$CHAr), 0.70 (d, 3 H, ^{3}J(H,H) = 7 Hz, $(CH_3)_2$CHAr). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): 188.3 (NCN), 154.9, 137.2, 136.5, 134.9, 129.1, 128.1, 127.2, 120.5, 116.6, 115.7, 103.5, 100.3, 90.7, 88.8, 85.9, 82.3 (Ar–H), 54.2 (CH_2Ph), 31.2 (Ar$CH(CH_3)_2$), 23.1, 21.6 ($(CH_3)_2$CHAr), 19.6 (CH_3Ar). HRMS (ESI), *m/z* calcd. for $C_{24}H_{26}IN_2RuS$ $[M + H]^+$: 651.9983, Found: 651.9980.

Synthesis of complex 10. Complex **10** was synthesized in analogy to **9a** from **4** (109 mg, 0.4 mmol), Ag_2O (50 mg, 0.2 mmol) and [Ru(*p*-cymene)Cl_2]$_2$ (121 mg, 0.2 mmol). The product was obtained as yellow solid (118 mg, 0.25 mmol, 62%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, 1 H, ^3J(H,H) = 5 Hz, Ar–H), 7.21 (d, 1 H, ^3J(H,H) = 2 Hz, Ar–H), 7.01 (d, 1 H, ^3J(H,H) = 2 Hz, Ar–H), 6.98 (d, 1 H, ^3J(H,H) = 5 Hz, Ar–H), 5.68 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H), 5.61 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H), 5.40 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H), 5.39–5.32 (m, 1 H, $(CH_3)_2CHN$), 5.32 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H), 2.22–2.18 (m, 1 H, $(CH_3)_2CHAr$), 2.06 (s, 1 H, CH_3Ar), 1.70 (d, 3 H, ^3J(H,H) = 7 Hz, $(CH_3)_2CHN$), 1.58 (d, 3 H, ^3J(H,H) = 7 Hz, $(CH_3)_2CHN$), 0.92 (d, 3 H, ^3J(H,H) = 7 Hz, $(CH_3)_2CHAr$), 0.78 (d, 3 H, ^3J(H,H) = 7 Hz, $(CH_3)_2CHAr$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 186.5 (NCN), 155.2, 136.2, 135.1, 116.3, 115.7, 103.9, 99.2, 90.3, 89.2, 85.3, 83.4 (Ar–C), 52.4 ($(CH_3)_2CHN$), 31.1 ($ArCH(CH_3)_2$), 24.5 ($(CH_3)_2CHN$), 23.8, 22.8 ($(CH_3)_2CHAr$), 18.9 (CH_3Ar). HRMS (ESI), *m/z* calcd. for $C_{20}H_{26}ClN_2RuS$ $[M + H]^+$: 463.0535. Found: 463.0545.

Synthesis of complex 11. Complex **11** was synthesized in analogy to **9a** from **5** (159 mg, 0.4 mmol), Ag_2O (50 mg, 0.2 mmol) and [Ru(*p*-cymene)Cl_2]$_2$ (121 mg, 0.2 mmol). The product was obtained as yellow solid (130 mg, 0.22 mmol, 54%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (s, 1 H Ph_2CH), 7.54–7.51 (m, 2 H, Ar–H), 7.48 (d, 1 H, ^3J(H,H) = 5 Hz, Ar–H), 7.47–7.46 (m, 1 H, Ar–H), 7.41–7.39 (m, 2 H, Ar–H), 7.35–7.32 (m, 5 H, Ar–H), 7.19 (d, 1 H, ^3J(H,H) = 2 Hz, Ar–H), 7.01 (d, 1 H, ^3J(H,H) = 5 Hz, Ar–H), 6.71 (d, 1 H, ^3J(H,H) = 2 Hz, Ar–H), 5.72 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H), 5.53 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H), 5.16 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H), 4.56 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H), 2.02–1.99 (m, 4 H, CH_3Ar & $(CH_3)_2CHAr$), 0.84 (d, 3 H, ^3J(H,H) = 7 Hz, $(CH_3)_2CHAr$),

0.57 (d, 3 H, ^{3}J(H,H) = 7 Hz, (CH_3)$_2$CHAr). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 189.6 (NCN), 155.7, 140.7, 139.5, 136.3, 135.1, 130.2, 129.1, 128.8, 128.5, 128.1, 126.9, 119.7, 116.6, 115.6, 91.7, 89.4, 84.8, 82.0 (Ar–C), 67.5 (Ph_2CH), 30.8 (Ar*C*H(CH$_3$)$_2$), 22.8, 21.5((*C*H$_3$)$_2$CHAr), 18.3 (CH_3Ar). HRMS (ESI), *m/z* calcd. $C_{30}H_{30}ClN_2RuS$ [M + H]$^+$: 587.0853. Found: 587.0860.

Synthesis of complex 12. Compound **12** was synthesized in analogy to **9a** from **6** (149 mg, 0.4 mmol), Ag_2O (50 mg, 0.2 mmol) and [Ru(*p*-cymene)Cl_2]$_2$ (121 mg, 0.2 mmol). The product was obtained as yellow solid (131 mg, 0.24 mmol, 61%).^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, 1 H, ^{3}J(H,H) = 8 Hz, Ar–H), 7.51 (d, 1 H, ^{3}J(H,H) = 5 Hz, Ar–H), 7.46–7.43 (m, 1 H, Ar–H), 7.45 (d, 1 H, ^{3}J(H,H) = 8 Hz, Ar–H), 7.40–7.31 (m, 4 H, Ar–H), 7.21–7.19 (m, 2 H, Ar–H), 7.16 (d, 1 H, ^{3}J(H,H) = 5 Hz, Ar–H), 6.32 (d, 2 H, ^{3}J(H,H) = 17 Hz, CH_2Ph), 5.88 (d, 2 H, ^{3}J(H,H) = 17 Hz, CH_2Ph), 5.81 (d, 1 H, ^{3}J(H,H) = 6 Hz, Ar–H), 5.55 (d, 1 H, ^{3}J(H,H) = 6 Hz, Ar–H), 5.33 (d, 1 H, ^{3}J(H,H) = 6 Hz, Ar–H), 4.88 (d, 1 H, ^{3}J(H,H) = 6 Hz, Ar–H), 2.25–2.19 (m, 1 H, ArC*H*(CH$_3$)$_2$), 2.15 (s, 1 H, CH_3Ar), 0.91 (d, 3 H, ^{3}J(H,H) = 7 Hz, (C*H*$_3$)2CHAr), 0.66 (d, 3 H, ^{3}J(H,H) = 7 Hz, (C*H*$_3$)$_2$CHAr). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 202.6 (NCN), 153.7, 137.0, 135.9, 133.8, 130.5, 129.4, 127.9, 125.9, 123.1, 123.2, 122.4, 117.0, 110.8, 110.6, 104.8, 101.2, 92.6, 90.0, 86.9, 82.4 (Ar–C), 52.0 (CH_2Ph), 31.4 (Ar*C*H(CH$_3$)$_2$), 23.1, 21.4 ((*C*H$_3$)$_2$CHAr), 19.6 (CH_3Ar). HRMS (ESI), *m/z* calcd. for $C_{28}H_{27}ClN_2RuS$ [M + H]$^+$: 561.0708. Found: 561.0703.

Synthesis of complex 13. Compound **13** was synthesized in analogy to **9a** from **7** (129 mg, 0.4 mmol), Ag_2O (50 mg, 0.2 mmol) and [Ru(*p*-cymene)Cl_2]$_2$ (121 mg, 0.2 mmol). The product was obtained as yellow solid (132 mg, 0.24 mmol, 59%).^{1}H NMR (500 MHz,

$CDCl_3$): δ 7.75 (d, 1 H, ^3J(H,H) = 8 Hz, Ar–H), 7.65 (d, 1 H, ^3J(H,H) = 8 Hz, Ar–H), 7.55 (d, 1 H, ^3J(H,H) = 5 Hz, Ar–H), 7.31 (t, 1 H, ^3J(H,H) = 7 Hz), 7.25 (t, 1 H, ^3J(H,H) = 7 Hz, Ar–H), 7.12 (d, 1 H, ^3J(H,H) = 5 Hz, Ar–H), 6.05–6.00 (m, 1 H, $(CH_3)_2CHN$), 5.78 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H), 5.70 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H), 5.49 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H), 5.43 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H), 2.28–2.20 (m, 1 H, $(CH_3)_2CHAr$), 2.08 (m, 3 H, CH_3Ar), 1.99 (d, 3 H, ^3J(H,H) = 7 Hz, $(CH_3)_2CHN$), 1.79 (d, 3 H, ^3J(H,H) = 7 Hz, $(CH_3)_2CHN$), 0.93 (d, 3 H, ^3J(H,H) = 7 Hz, $(CH_3)_2CHAr$), 0.80 (d, 3 H, ^3J(H,H) = 7 Hz, $(CH_3)_2CHAr$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 200.8 (NCN), 154.3, 135.5, 134.1, 132.4, 131.3, 122.8, 121.7, 116.7, 112.0, 111.1, 104.4, 100.87, 91.4, 90.9, 86.2, 84.6 (Ar–C), 54.1 ($(CH_3)_2CHN$), 31.2 ($ArCH(CH_3)_2$), 22.6, 22.2 ($(CH_3)_2CHN$), 22.1, 21.7 ($(CH_3)_2CHAr$), 19.9 (CH_3Ar). HRMS (ESI), *m/z* calcd. for $C_{24}H_{28}ClN_2RuS$ $[M + H]^+$: 513.0705. Found: 513.0702.

Synthesis of complex 14. Compound **14** was synthesized in analogy to **9a** from **8** (178 mg, 0.4 mmol), Ag_2O (50 mg, 0.2 mmol) and $[Ru(p\text{-cymene})Cl_2]_2$ (121 mg, 0.2 mmol). The product was obtained as yellow solid (130 mg, 0.21 mmol, 51%).^1H NMR (500 MHz, $CDCl_3$): δ 8.31 (s, 1 H, Ph_2CH), 7.76 (d, 1 H, ^3J(H,H) = 8 Hz, Ar–H), 7.58 (d, 1 H, ^3J(H,H) = 5 Hz, Ar–H), 7.55–7.48 (m, 7 H, Ar–H), 7.29 (m, 1 H, Ar–H), 7.22 (t, 1 H, ^3J(H,H) = 8 Hz, Ar–H), 7.16 (d, 1 H, ^3J(H,H) = 5 Hz, Ar–H), 6.94 (t, 1 H, ^3J(H,H) = 8 Hz, Ar–H), 6.84 (d, 1 H, ^3J(H,H) = 8 Hz, Ar–H), 5.82 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H), 5.63 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H), 5.30 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H), 4.76 (d, 1 H, ^3J(H,H) = 6 Hz, Ar–H), 2.03 (s, 1 H, CH_3Ar), 2.00–1.95 (m, 1 H, $ArCH(CH_3)_2$), 0.78 (d, 3 H, ^3J(H,H) = 7 Hz, $(CH_3)_2CHAr$), 0.53 (d, 3 H, ^3J(H,H) = 7 Hz, $(CH_3)_2CHAr$). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 203.3 (NCN), 154.6, 139.2, 138.1, 135.6, 134.1, 134.0, 130.8,

130.2, 129.2, 128.5, 128.3, 128.1, 127.2, 122.8, 122.0, 117.1, 113.1, 110.8, 106.4, 93.2, 90.5, 85.6, 83.4 (Ar–C), 68.0 ($CHPh_2$), 30.8 (Ar*C*H(CH_3)$_2$), 22.7, 21.7 ((*C*H$_3$)$_2$CHN), 19.0 (CH_3Ar). HRMS (ESI), *m/z* calcd. for $C_{34}H_{32}ClN_2RuS$ $[M + H]^+$: 637.1021. Found: 637.1018.

Synthesis of compounds 15–18.

Synthesis of compound 15. A mixture of complex 12 (56 mg, 0.1 mmol), KPF_6 (92 mg, 0.5 mmol) and diphenyl acetylene (53.4 mg, 0.3 mmol) were weighed in a Schlenk tube equipped with a stir bar. Dry methanol (3.0 mL) was added, and the mixture was stirred at 80°C under an N_2 atmosphere for 12 h. Solvent was removed under reduced pressure after the system was cooling down to room temperature and the residue was purified by flash column chromatography with CH_2Cl_2/CH_3OH (v/v = 100:1, alumina) to afford **15** as yellow solid (52 mg, 0.085 mmol, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.70–8.67 (m, 2H, Ar–H), 7.95–7.89 (m, 4H, Ar–H), 7.32–7.16 (m, 13H, Ar–H), 6.75–6.72 (m, 2H, Ar–H), 5.58 (s, 1H, NCH_2Ph). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 148.9, 140.7, 138.6, 134.6, 133.9, 131.4, 131.0, 130.6, 130.0, 129.2, 129.1, 128.8, 128.7, 128.4, 127.9, 126.4, 125.8, 125.3, 123.7, 121.0, 114.8, 113.8 (Ar–C), 50.1 (NCH_2Ph). ^{31}P{1H} NMR (158 MHz, $CDCl_3$): δ –143.6 (sept, ^2J(P,F) = 712 Hz, PF_6). HRMS (ESI), *m/z* calcd. for $C_{34}H_{23}N_2S$ $[M - PF_6]^+$: 476.1582. Found: 467. 1580.

Synthesis of compound 16. Compound **16** was synthesized in analogy to **15** from **12** (56 mg, 0.1 mmol), KPF_6 (92 mg, 0.5 mmol) and octyne (33 mg, 0.3 mmol). The product was obtained as yellow solid (39 mg, 0.071 mmol, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.49 (s, 1H, Ar–H), 7.84–7.68 (m, 6H, Ar–H), 7.41–7.15 (m, 4H, Ar–H), 6.15 (s, 1H,

NCH_2Ph), 3.21–3.19 (m, 2H, $ArCH_2CH_2CH_3$), 3.16–3.16 (m, 2H, $ArCH_2CH_2CH_3$), 3.10–2.97 (m, 2H, $ArCH_2$), 1.86–1.73 (m, 4H, $CH_3CH_2CH_2Ar$), 1.20–1.15 (m, 3H, $CH_3CH_2CH_2Ar$), 1.10–1.06 (m, 3H, $CH_3CH_2CH_2Ar$). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 150.1, 142.1, 134.4, 134.1, 130.1, 129.8, 129.6, 128.5, 126.1, 125.0, 124.0, 122.1, 119.7, 114.3, 112.9 (Ar–C), 50.4 (NCH_2Ph), 33.1, 28.7, 25.1, 24.3, 14.6, 13.9 (Alkyl–C). $^{31}P\{1H\}$ NMR (158 MHz, $CDCl_3$): δ –143.8 (sept, ^2J(P,F) = 712 Hz, PF_6). HRMS (ESI), *m/z* calcd. for $C_{26}H_{27}N_2S$ $[M - PF_6]^+$: 399.1895. Found: 399.1891.

Synthesis of compound 17. Compound **17** was synthesized in analogy to **15** from **12** (56 mg, 0.1 mmol), KPF_6 (92 mg, 0.5 mmol) and phenyl acetylene (31 mg, 0.3 mmol). The product was obtained as yellow solid (40 mg, 0.074 mmol, 74%). ^1H NMR (500 MHz, $CDCl_3$): δ 8.52–8.50 (m, 1H, Ar–H), 8.30 (s, 1H, Ar–H), 7.81–7.78 (m, 2H, Ar–H), 7.73–7.61 (m, 3H, Ar–H), 7.47–7.44 (m, 1H, Ar–H), 7.39–7.31 (m, 4H, Ar–H), 7.22–7.16 (m, 3H, Ar–H), 6.56–6.64 (m, 2H, Ar–H), 5.45 (s, 2H, NCH_2Ph). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): δ 140.2, 138.9, 136.3, 133.5, 133.4, 132.8, 129.9, 129.8, 129.7, 129.6, 128.9, 128.8, 128.1, 126.3, 126.1, 125.2, 124.7, 123.4, 122.8, 114.7, 113.1 (Ar–C), 49.7 (NCH_2Ph). $^{31}P\{1H\}$ NMR (202.4 MHz, $CDCl_3$): δ –144.3 (sept, ^2J(P,F) = 712 Hz, PF_6). HRMS (ESI), *m/z* calcd. for $C_{26}H_{19}N_2S$ $[M - PF_6]^+$: 391.1263. Found: 391.1261.

Synthesis of compound 18. Compound **18** was synthesized in analogy to **15** from **12** (56 mg, 0.1 mmol), KPF_6 (92 mg, 0.5 mmol) and trimethylsilyl acetylene (31 mg, 0.3 mmol). The product was obtained as yellow solid (30 mg, 0.064 mmol, 64%). ^1H NMR (500 MHz, CD_3CN): δ 8.73 (d, 1H, ^2J(H,H) = 10 Hz, Ar–H), 8.59 (d, 1H, ^2J(H,H) = 10 Hz, Ar–H), 8.09–7.98 (m, 2H, Ar–H), 7.98–7.90 (m, 3H, Ar–H), 7.82–7.18 (m, 1H, Ar–H), 7.40 (s, 2H, NCH_2Ph). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$): δ 135.1, 133.7, 130.1,

129.6, 129.1, 128.8, 127.2, 125.9, 124.9, 123.7, 114.9, 112.8, 106.2 (Ar–C), 48.3 (NCH_2Ph). $^{31}P\{1H\}$ NMR (202.4 MHz, $CDCl_3$): δ –144.2 (sept, $^2J(P,F)$ = 712 Hz, PF_6). HRMS (ESI), *m/z* calcd. for $C_{26}H_{19}N_2S$ $[M - PF_6]^+$: 315.0950. Found: 315.0950.

Variable-temperature ^1H NMR spectral plot of complexes 9a and 9c

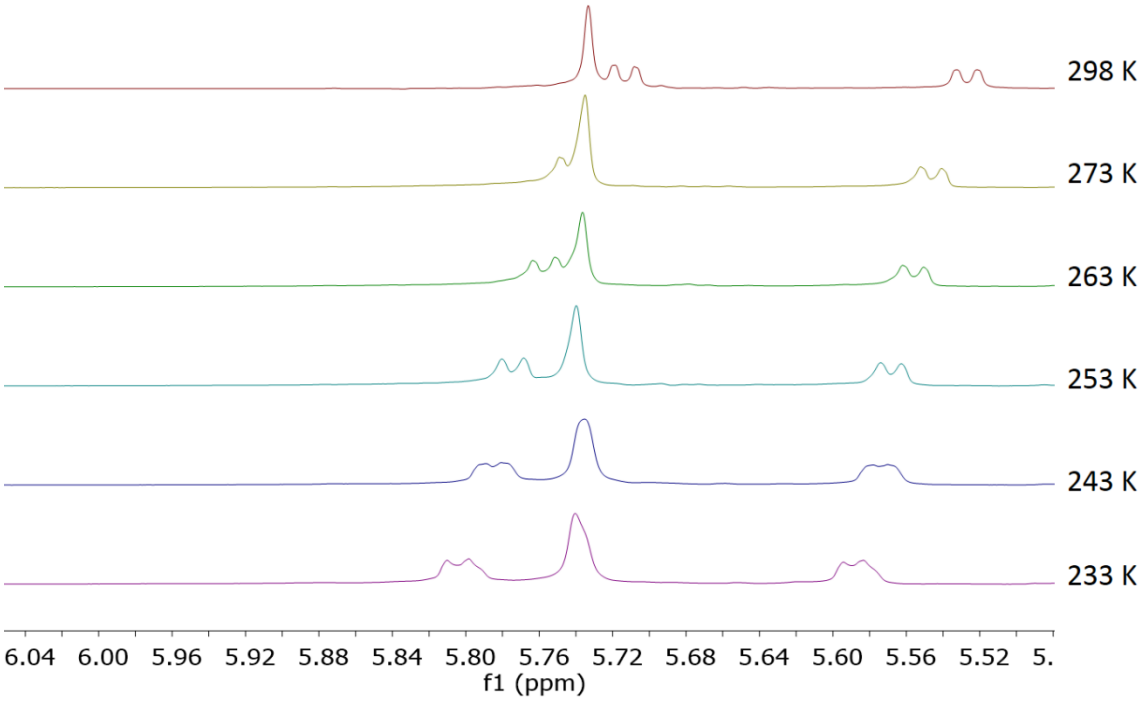


Figure S1 Section of the Variable-temperature ^1H NMR spectral plot of complex 9a in $CDCl_3$.

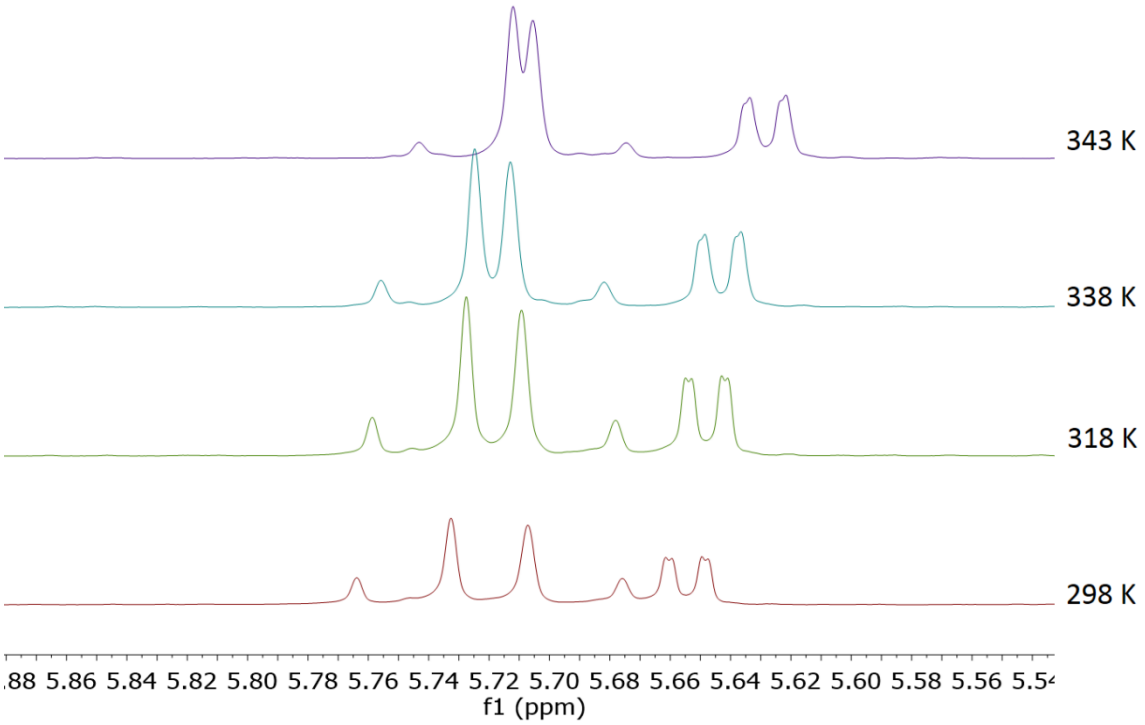
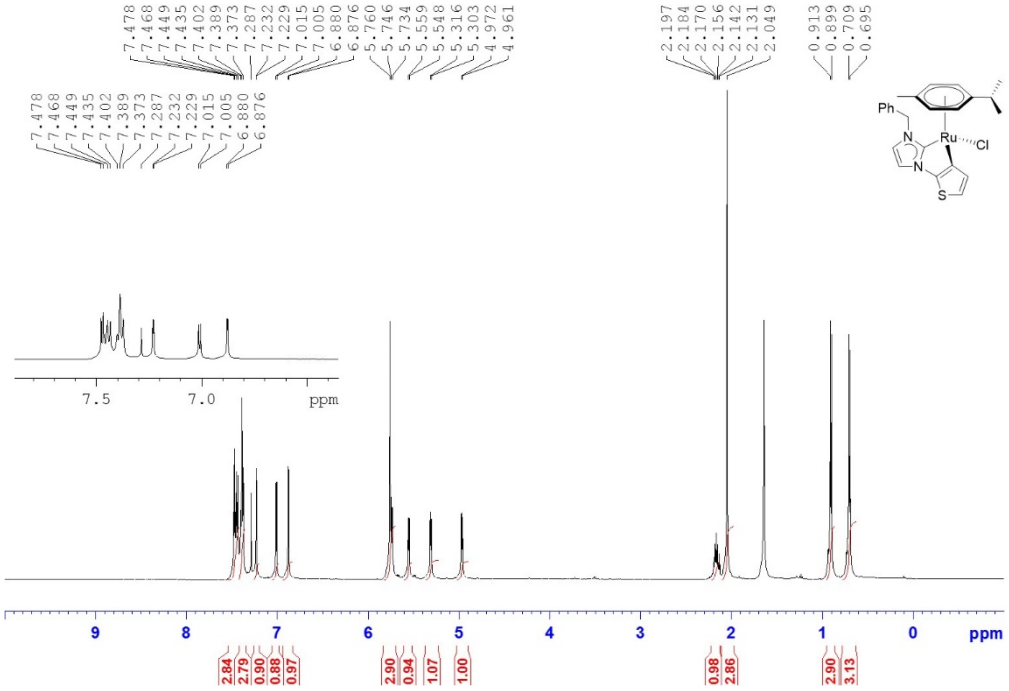


Figure S2 Section of the Variable-temperature ^{1}H NMR spectral plot of complex 9a in $CDCl_3$.

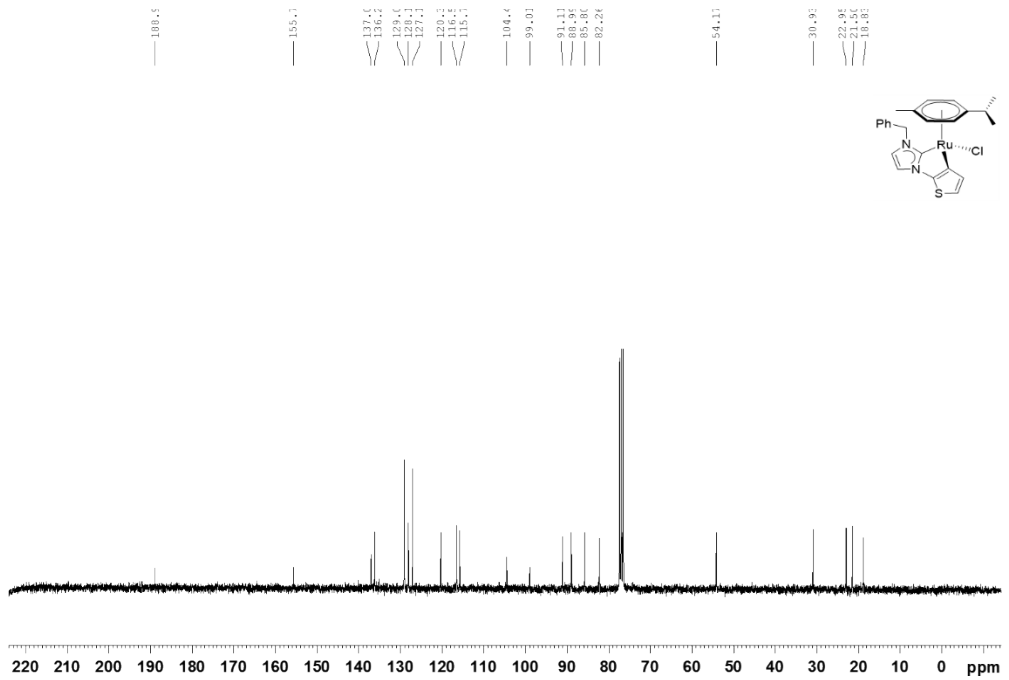
Selected crystal data for complex 9a, 9b, 11 and 12

	9a	**9b**	**11**	**12**
Formula	$C_{24}H_{25}ClN_2SRu$	$C_{24}H_{25}BrN_2RuS$	$C_{30}H_{29}ClN_2RuS$	$C_{28}H_{27}ClN_2RuS$
MW (g/mol)	514.04	554.50	586.13	560.09
crystal size (mm)	0.373 × 0.128 × 0.101	0.275 × 0.198 × 0.107	0.245 × 0.175 × 0.105	0.440 × 0.260 × 0.240
crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
space group	*P*-1	*P*-1	*P* 21/c	*P* 21/n
a (Å)	10.0366(4)	10.5184(5)	10.4555(4)	14.301(4)
b (Å)	10.6641(5)	10.8146(5)	15.1572(5)	11.104(3)
c (Å)	12.3895	10.8146(5)	16.4668(6)	15.932(5)
α (°)	70.891(2)	87.0400(10)	90	90
β (°)	84.601(2)	64.7810(10)	94.422(2)	108.464(6)
γ (°)	64.031(2)	69.9870	90	90
V (Å^3)	1124.59(9)	1105.18(9)kkj..	2601.83(16)	2399.7(12)
Z	2	2	4	4
$\rho_{calculated}$ (g/cm^3)	1.518	1.666	1.496	1.550
temperature (K)	100(2)	100(2)	180(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
θ (°)	2.242 to 30.547	2.289 to 30.216	2.371 to 33.141	2.276 to 27.500
no. of unique reflections	7557	24124	36821	16633
final *R* indices [I>2σ(I)]	*R1 = 0.0251, wR2 = 0.0631*	R1 = 0.0291, wR2 = 0.0534	R1 = 0.0336, wR2 = 0.0868	R1 = 0.0271, wR2 = 0.0641
R indices (all data)	*R1 = 0.0285, wR2 = 0.0649*	R1 = 0.0467, wR2 = 0.0570	R1 = 0.0415, wR2 = 0.0974	R1 = 0.0290, wR2 = 0.0651
Goodness-of-fit on F^2	1.074	1.074	1.088	1.064
Peak/hole (e.Å^{-3})	1.734 and -0.751	0.835 and -0.455	0.898 and -0.544	0.799 and -0.617

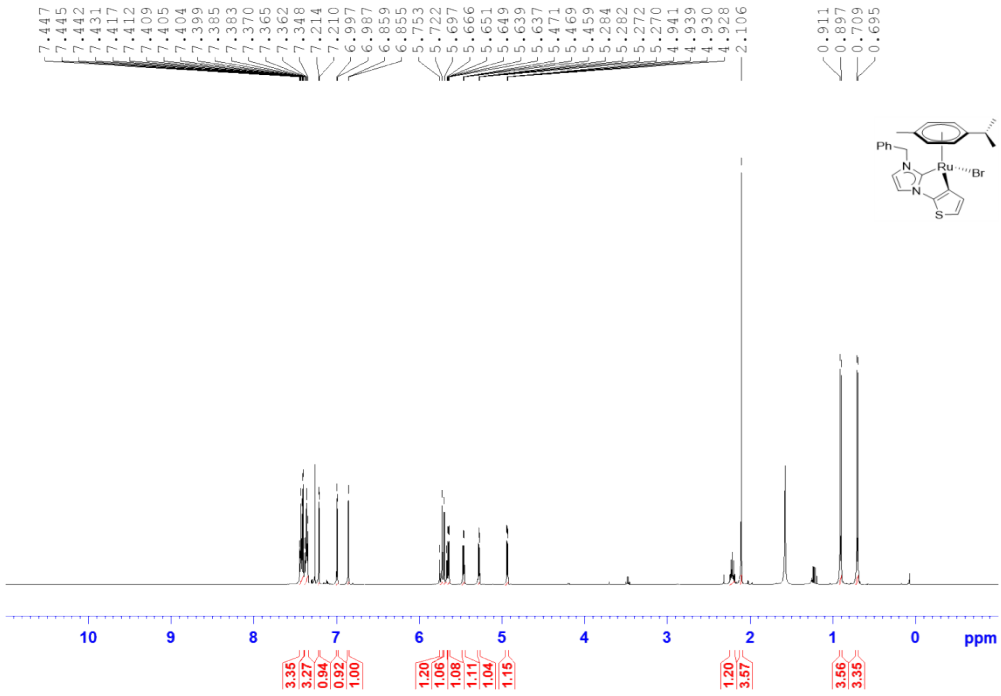
NMR Data of all complexes and compounds:



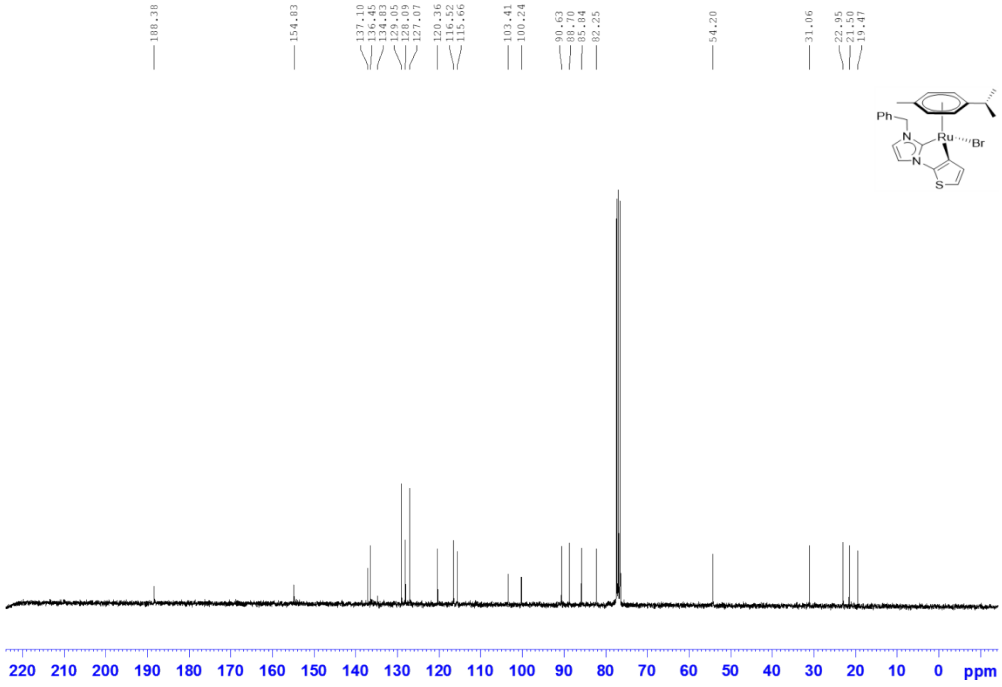
^{1}H NMR of **9a** (500 MHz, $CDCl_3$)



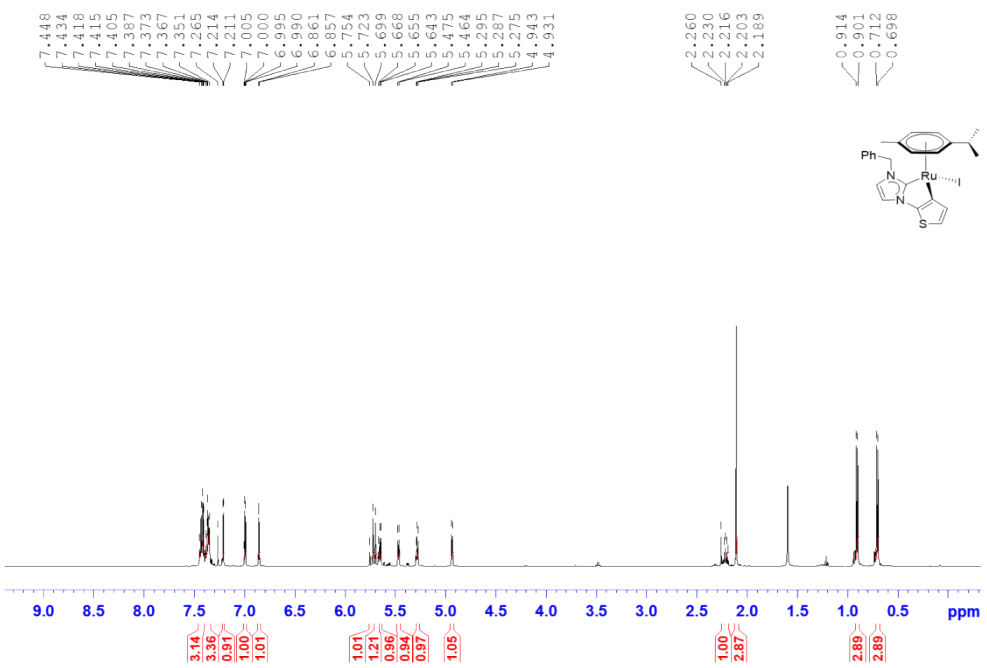
^{13}C{^{1}H} NMR of **9a** (125 MHz, $CDCl_3$)



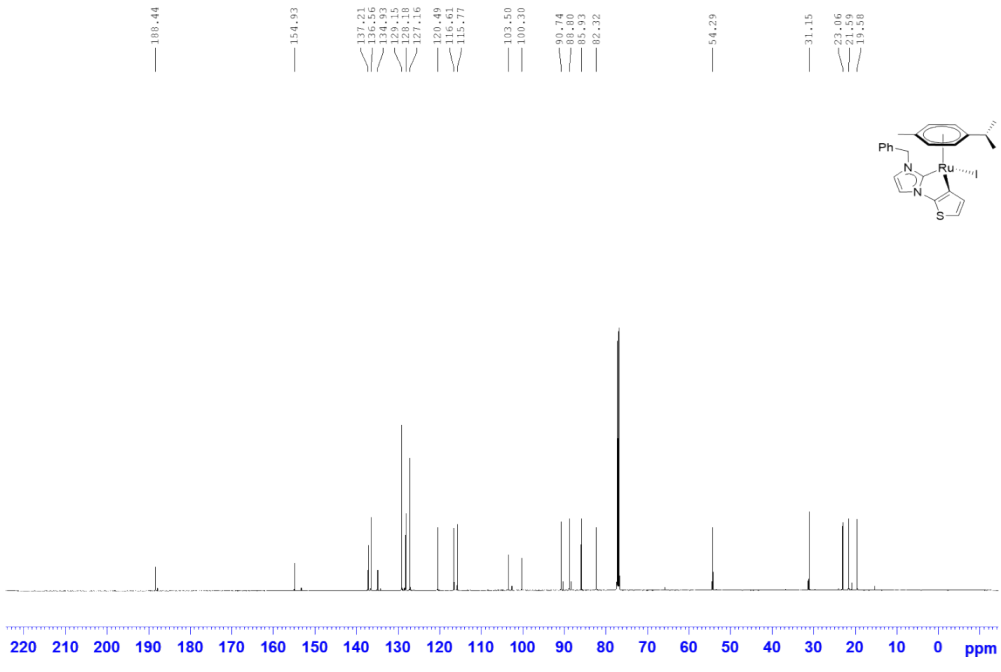
^{1}H NMR of **9b** (500 MHz, $CDCl_3$)



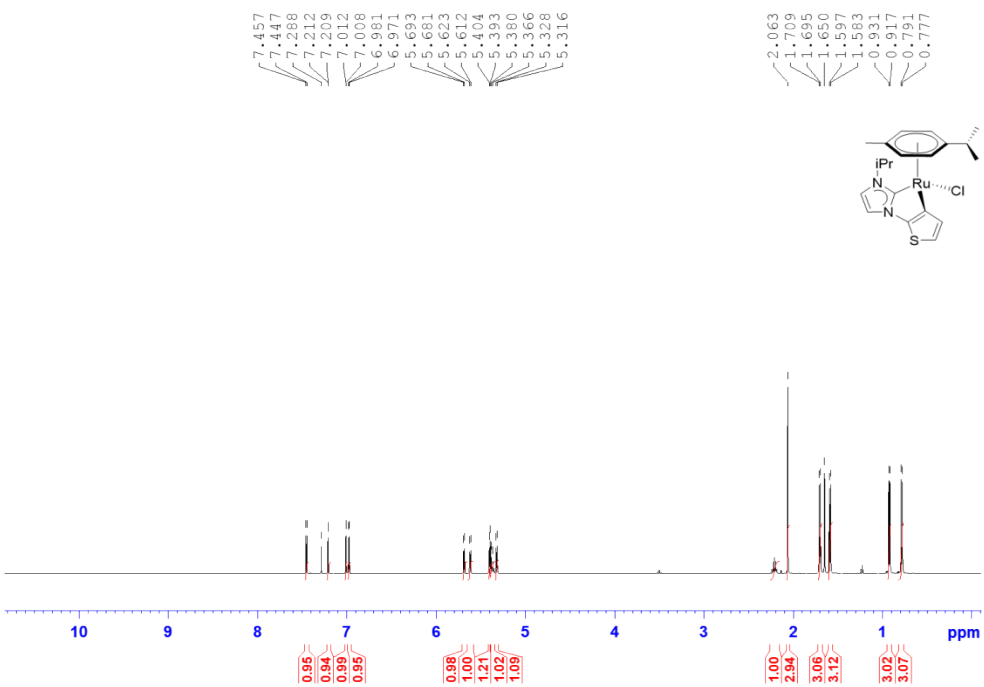
^{13}C NMR of **9b** (125 MHz, $CDCl_3$)



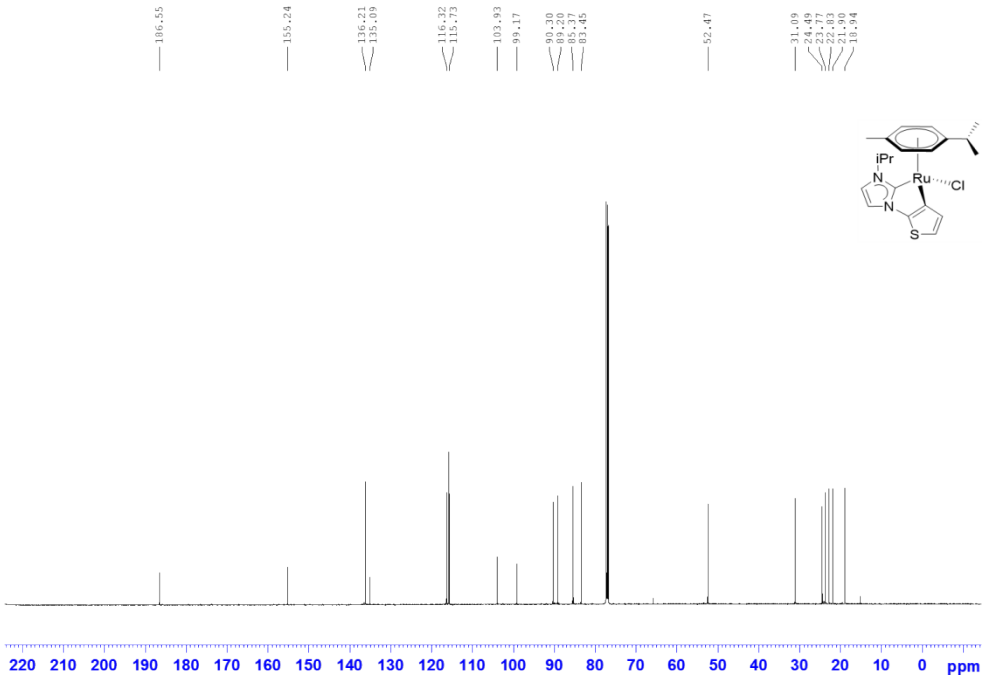
^{1}H NMR of **9c** (500 MHz, $CDCl_3$)



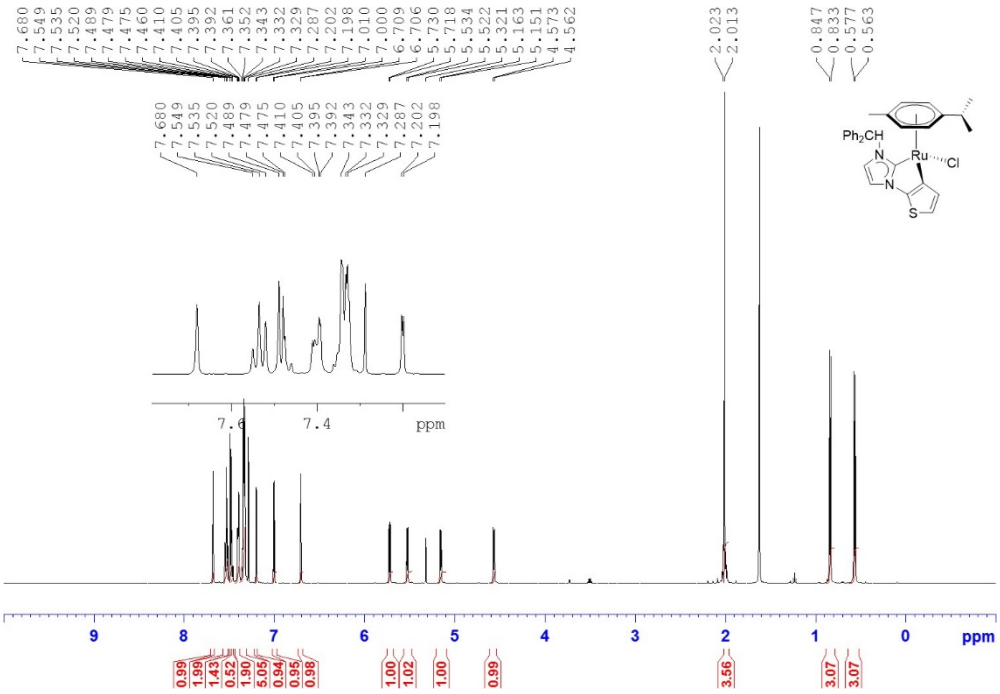
^{13}C NMR of **9b** (125 MHz, $CDCl_3$)



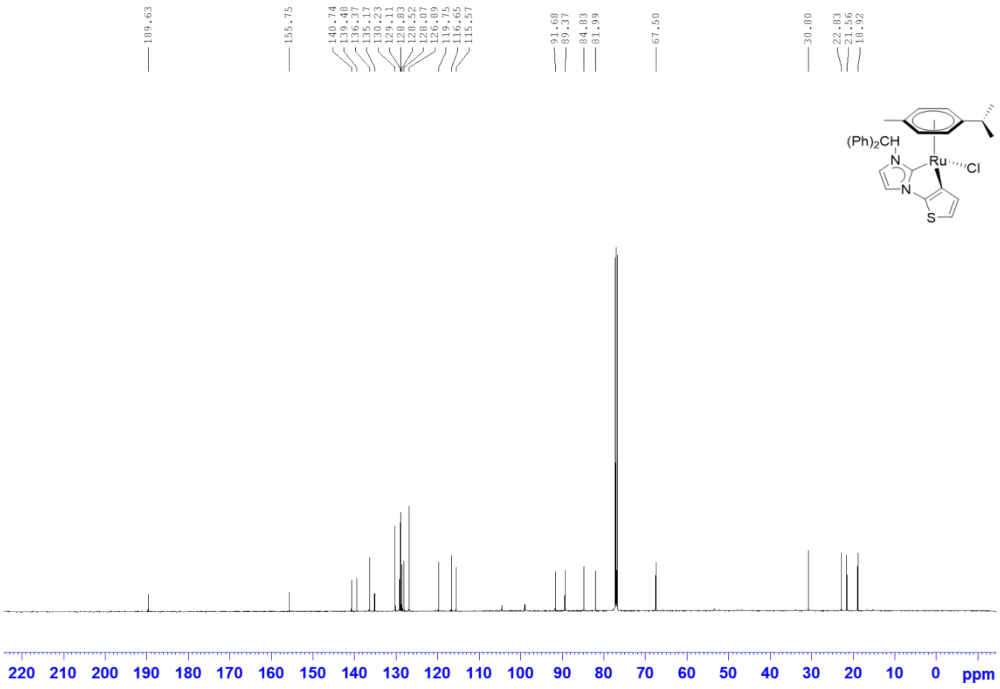
^{1}H NMR of **10** (500 MHz, $CDCl_3$)



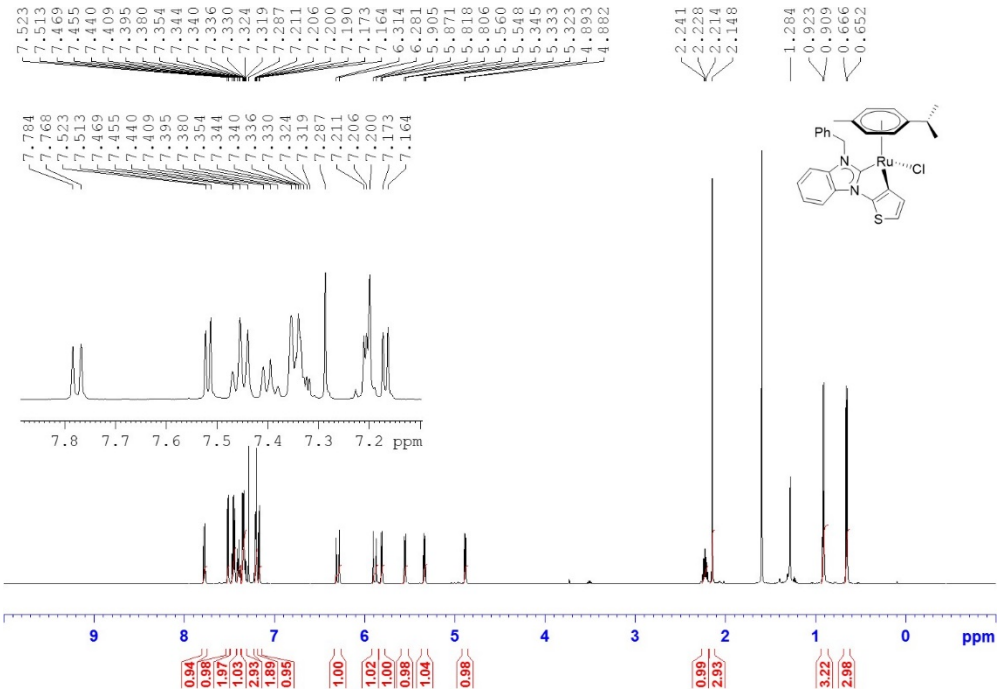
^{13}C NMR of **10** (125 MHz, $CDCl_3$)



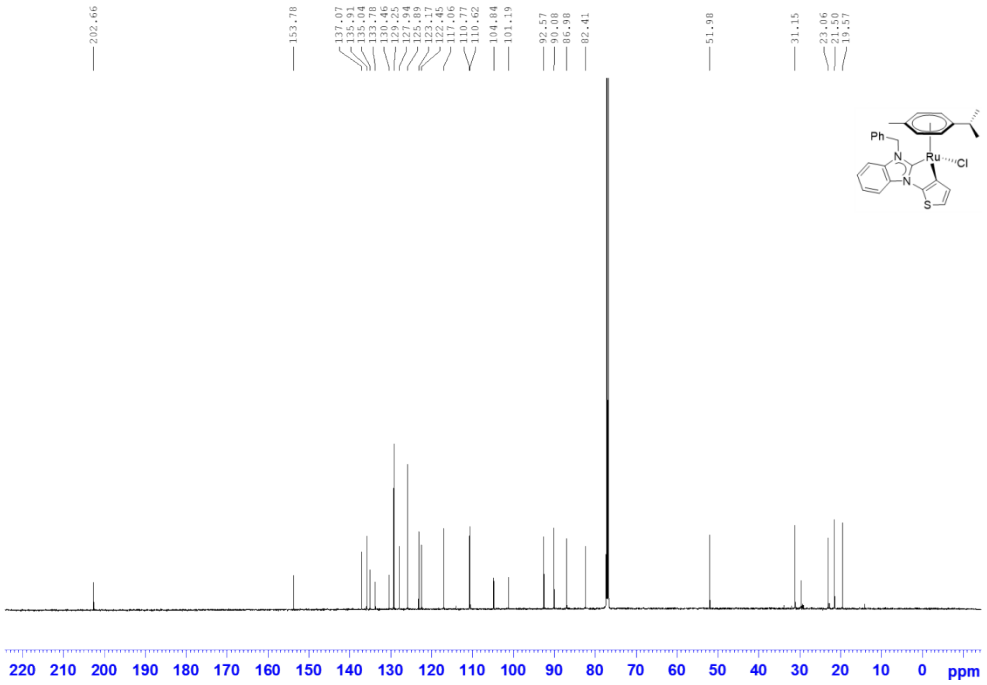
^{1}H NMR of **11** (500 MHz, $CDCl_3$)



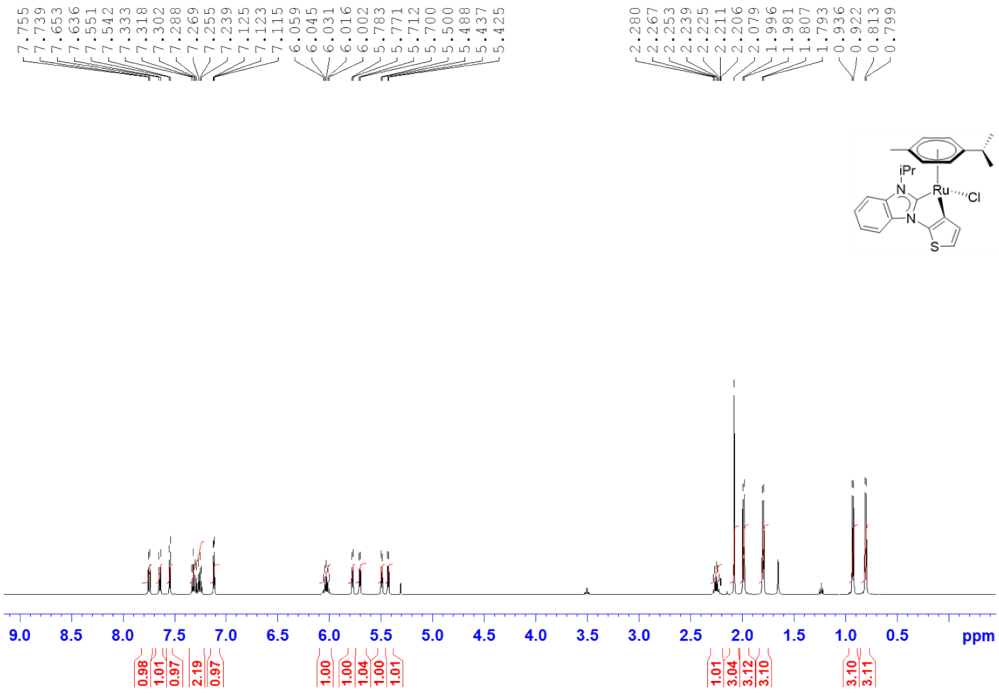
^{13}C NMR of **11** (125 MHz, $CDCl_3$)



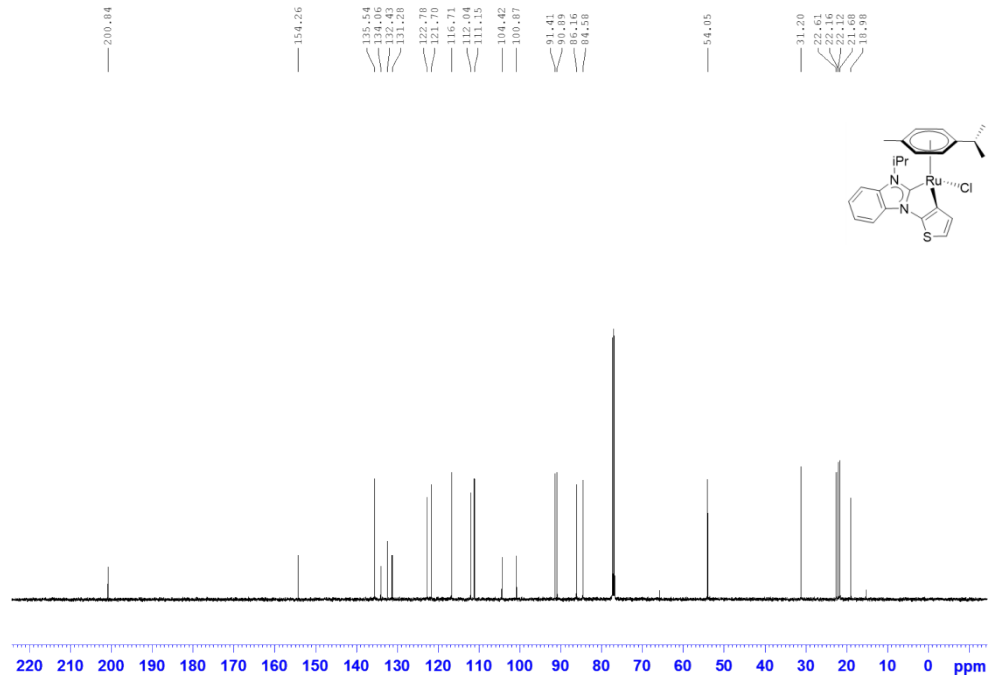
^{1}H NMR of **12** (500 MHz, $CDCl_3$)



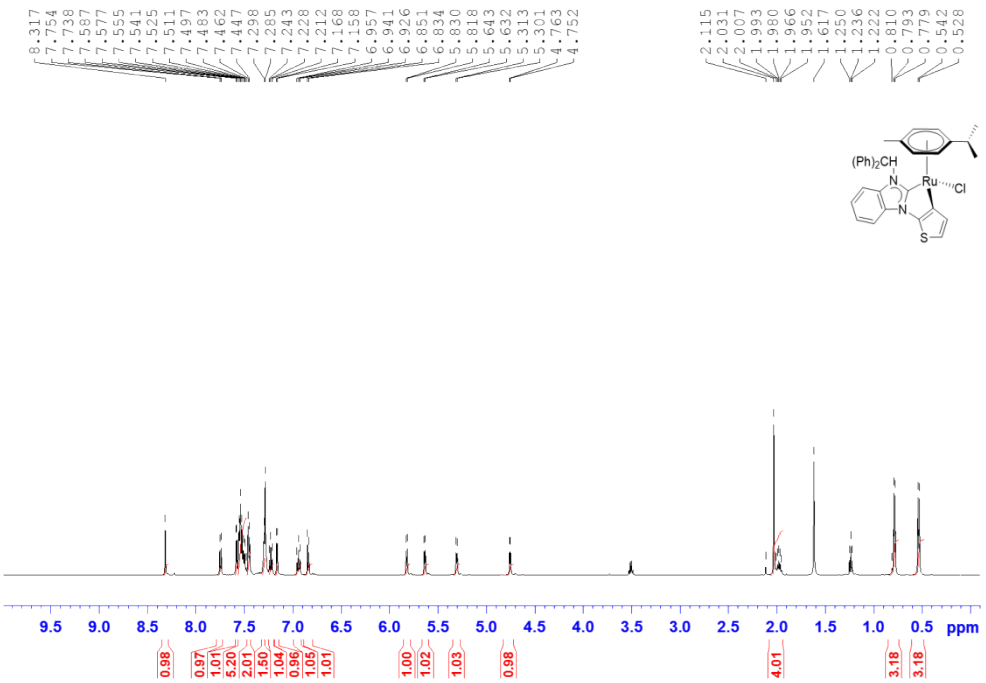
^{13}C NMR of **12** (125 MHz, $CDCl_3$)



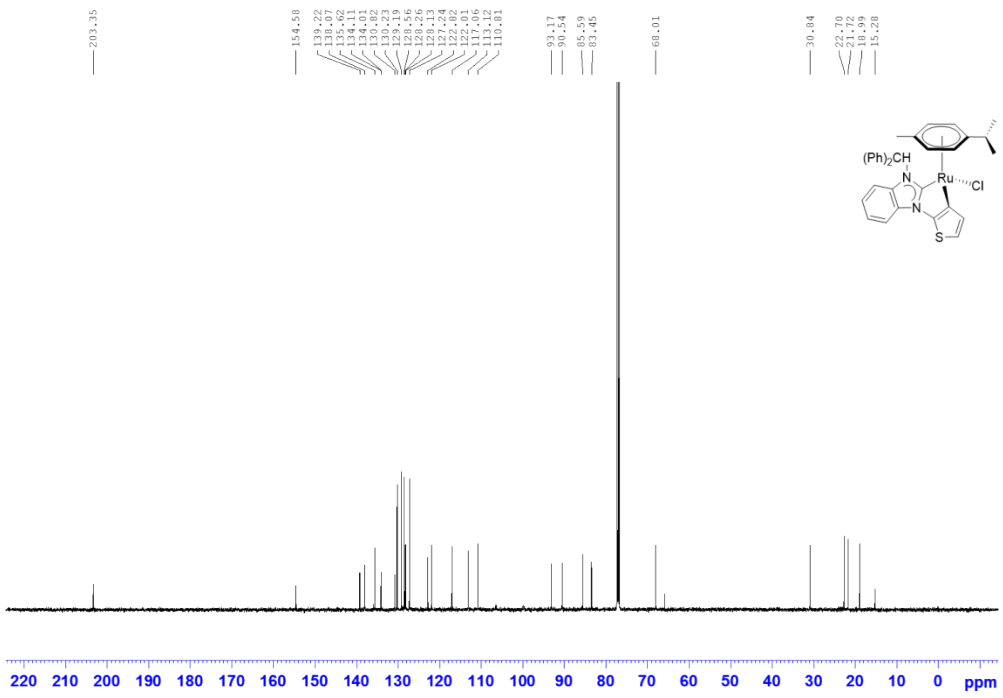
^{1}H NMR of **13** (500 MHz, $CDCl_3$)



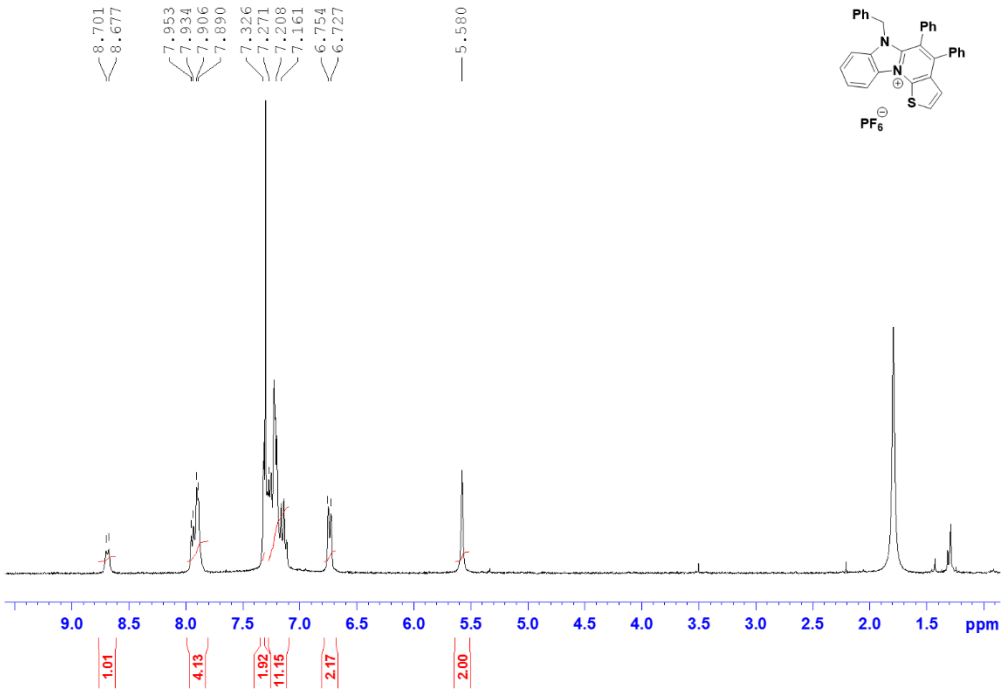
^{13}C NMR of **13** (125 MHz, $CDCl_3$)



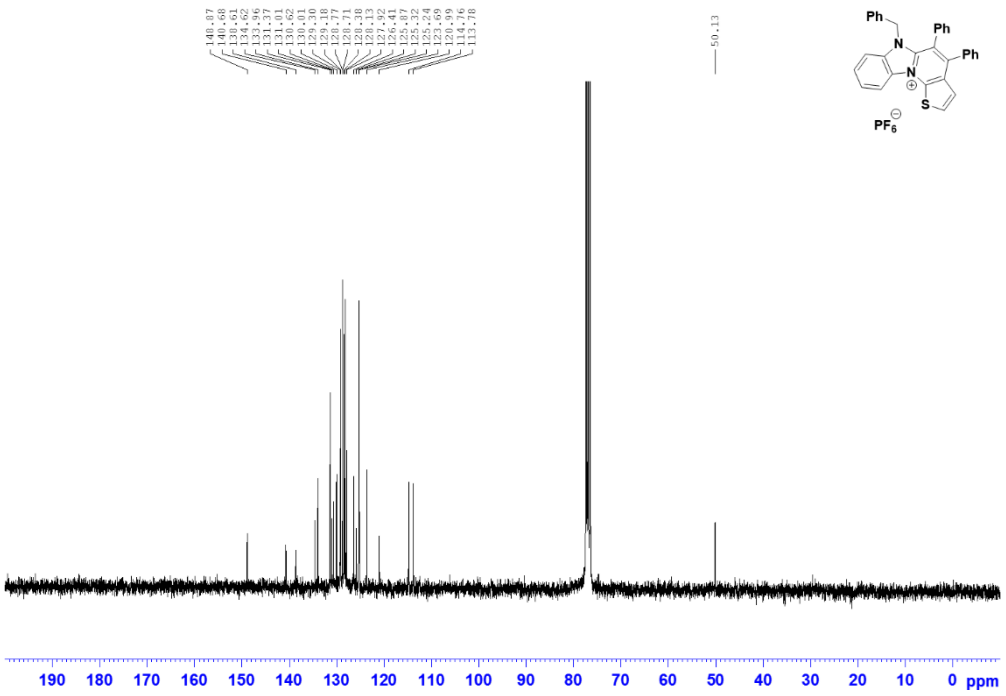
^{1}H NMR of **14** (500 MHz, $CDCl_3$)



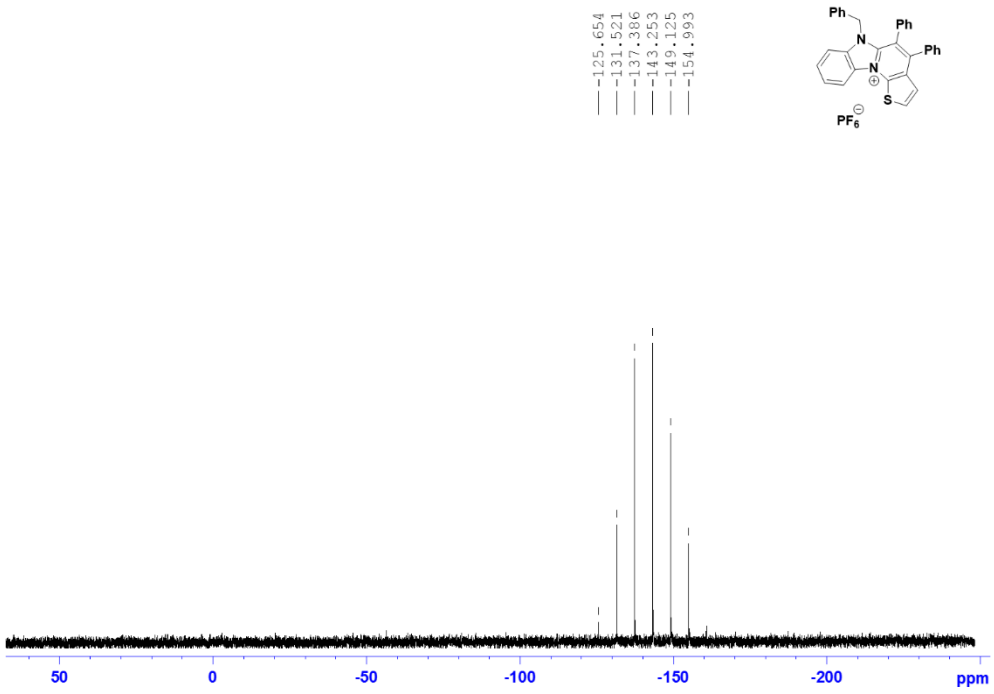
^{13}C NMR of **14** (125 MHz, $CDCl_3$)



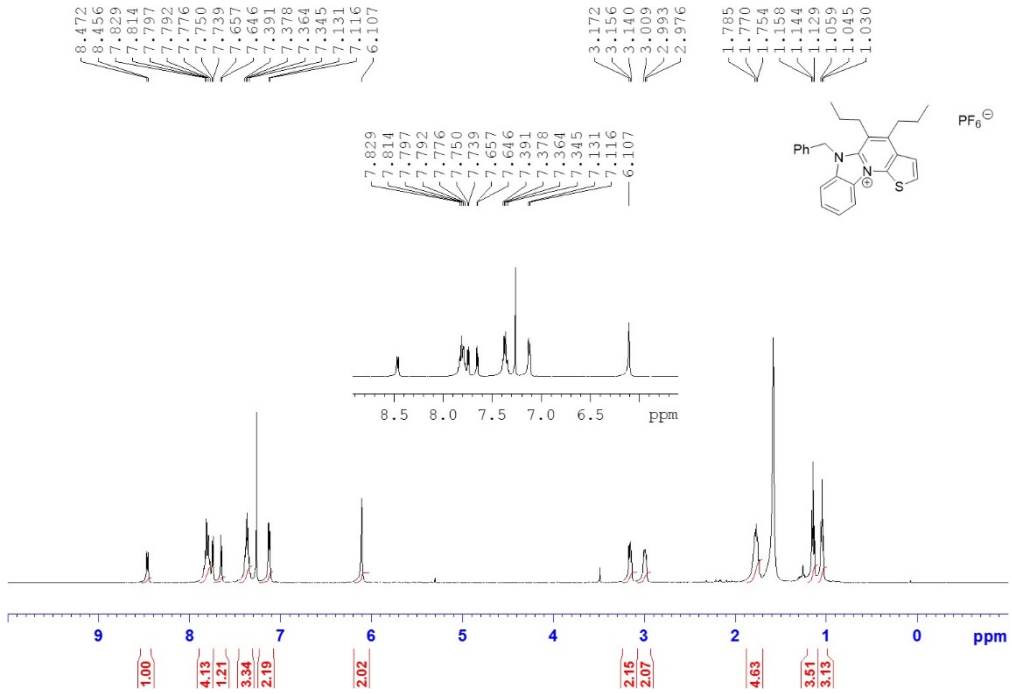
^{1}H NMR of **15** (300 MHz, $CDCl_3$)



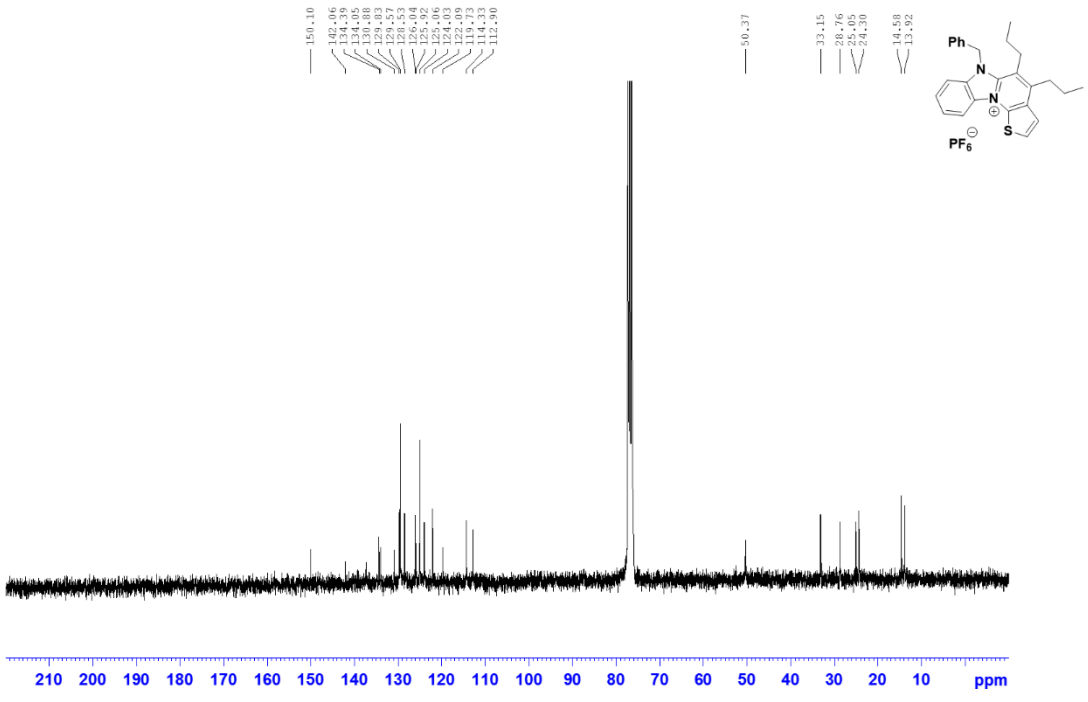
^{13}C {^{1}H} NMR of **15** (75.5 MHz, $CDCl_3$)



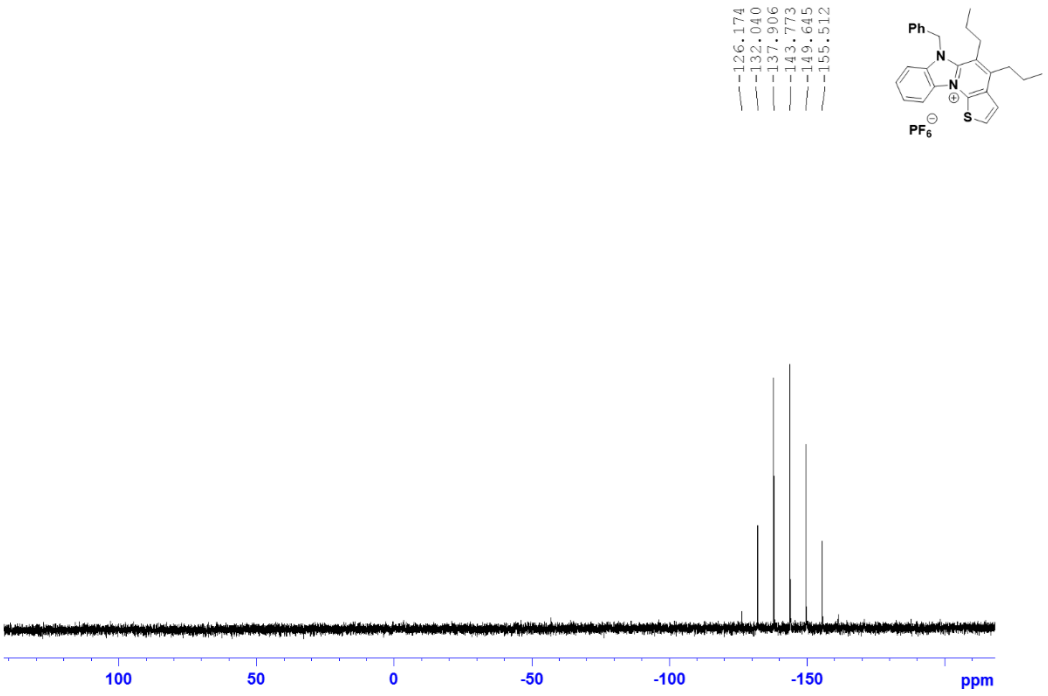
$^{31}P\{^{1}H\}$ NMR of **15** (158 MHz, $CDCl_3$)



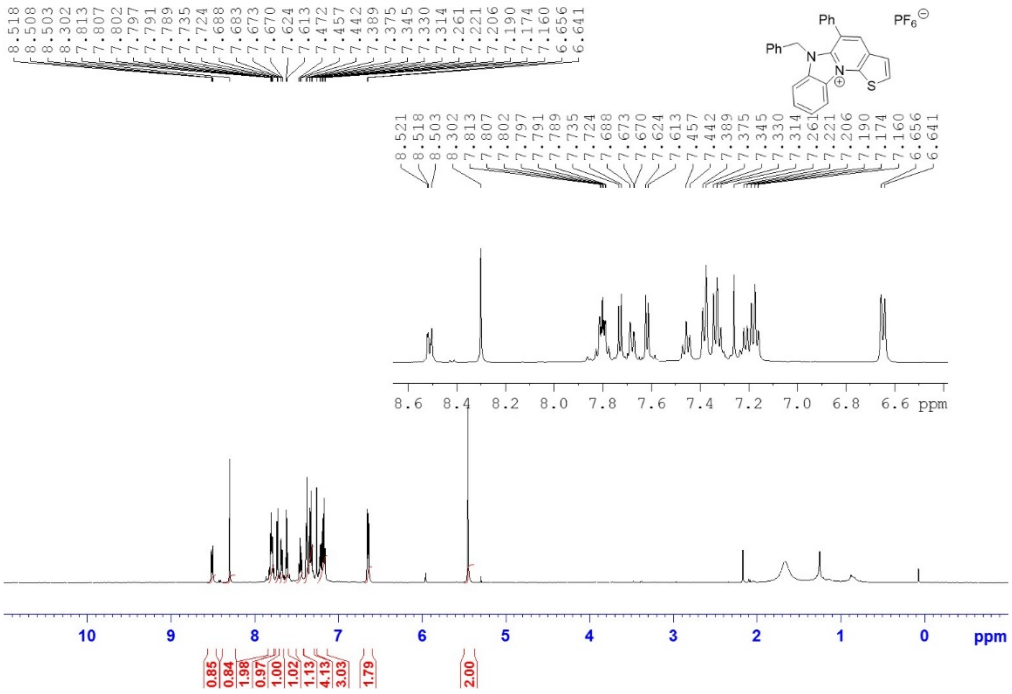
^{1}H NMR of **16** (300 MHz, $CDCl_3$)



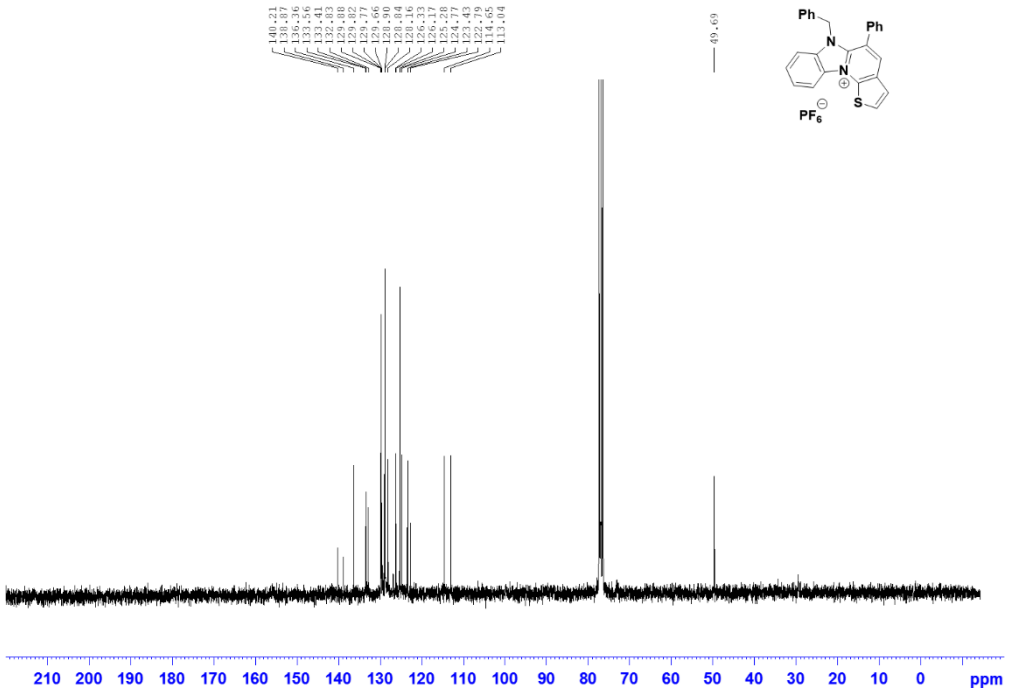
^{13}C {^{1}H} NMR of **16** (75.5 MHz, $CDCl_3$)



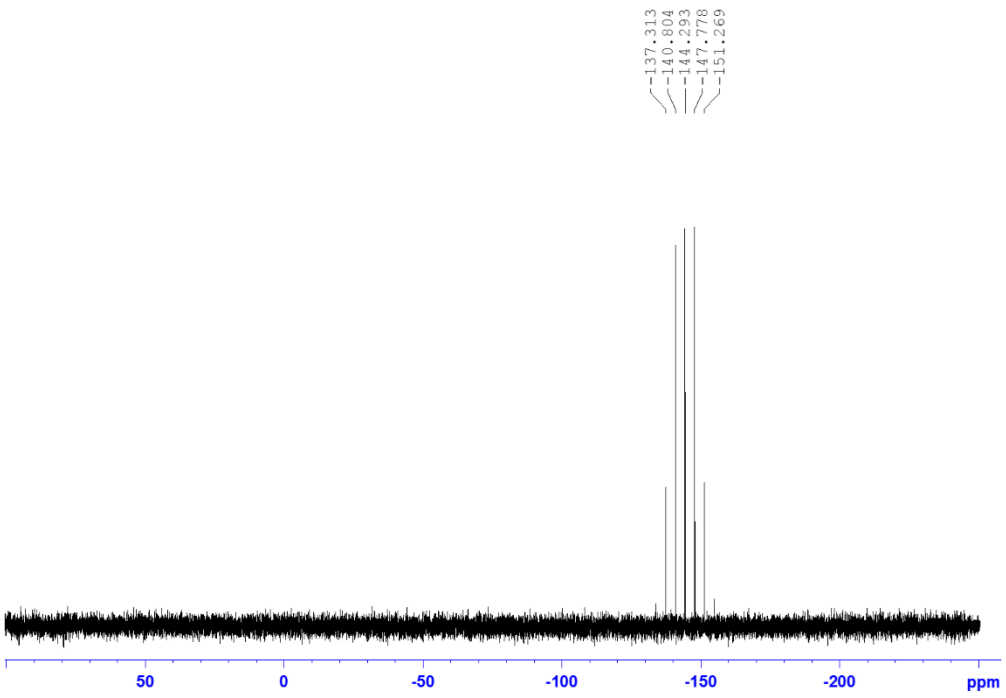
$^{31}P\{^{1}H\}$ NMR of **16** (158 MHz, $CDCl_3$)



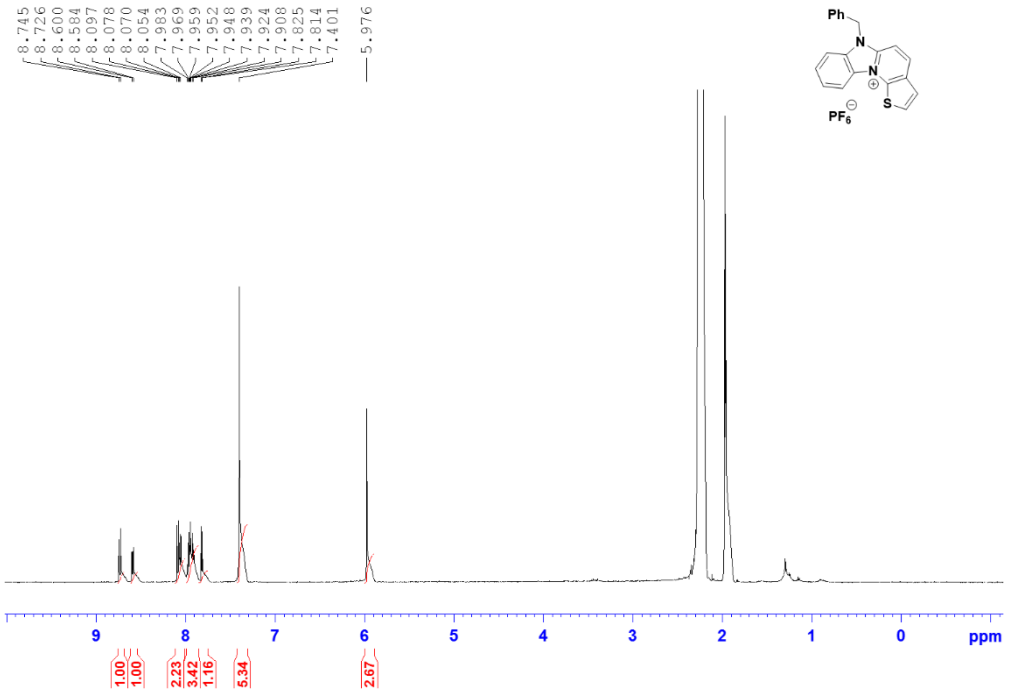
^{1}H NMR of **17** (500 MHz, $CDCl_3$)



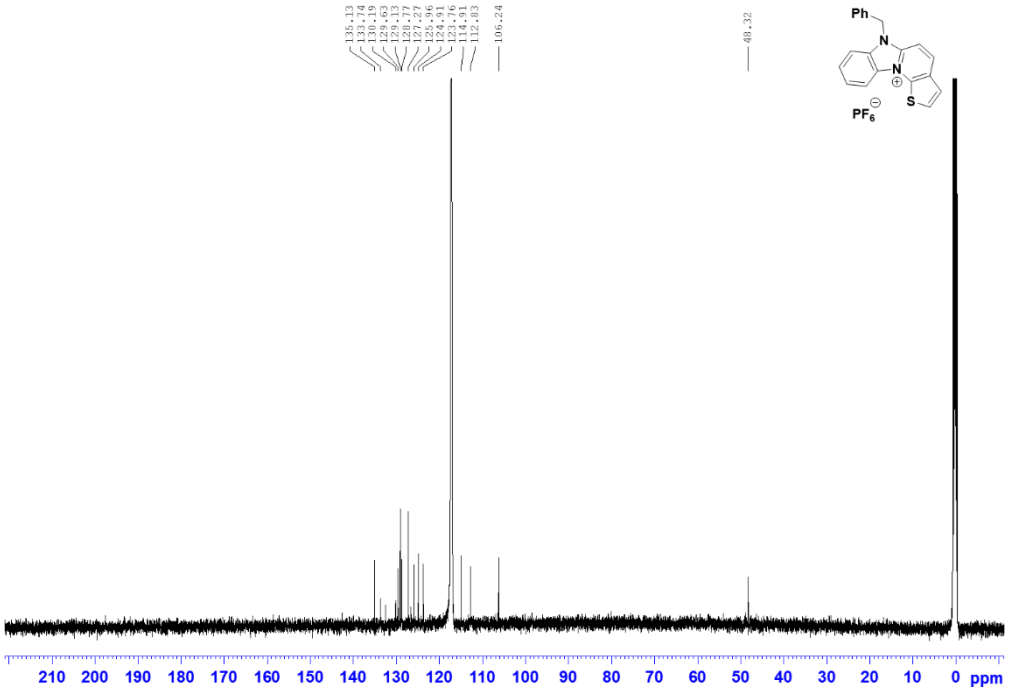
^{13}C {^{1}H} NMR of **17** (125 MHz, $CDCl_3$)



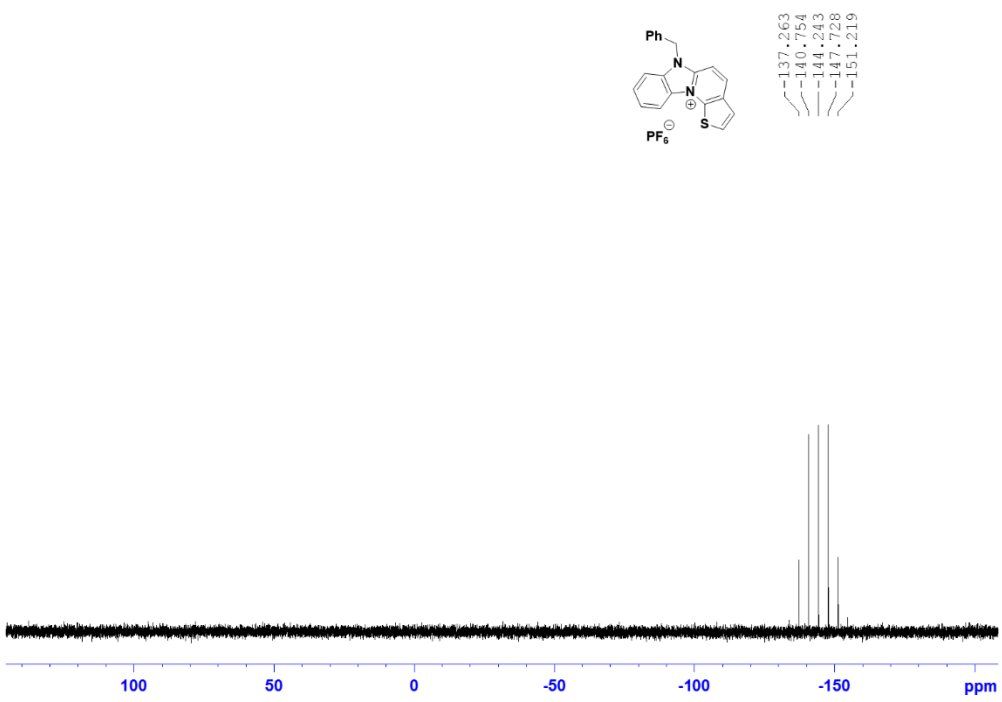
$^{31}P\{^{1}H\}$ NMR of **17** (202.4 MHz, $CDCl_3$)



^{1}H NMR of **18** (500 MHz, CD_3CN)

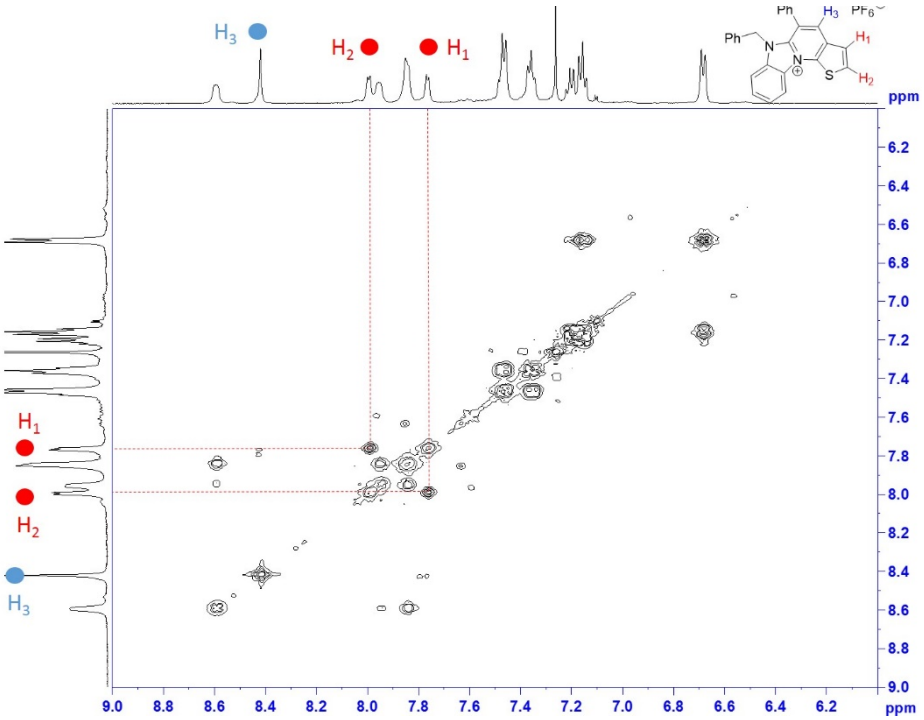


^{13}C {^{1}H} NMR of **18** (125 MHz, CD_3CN)

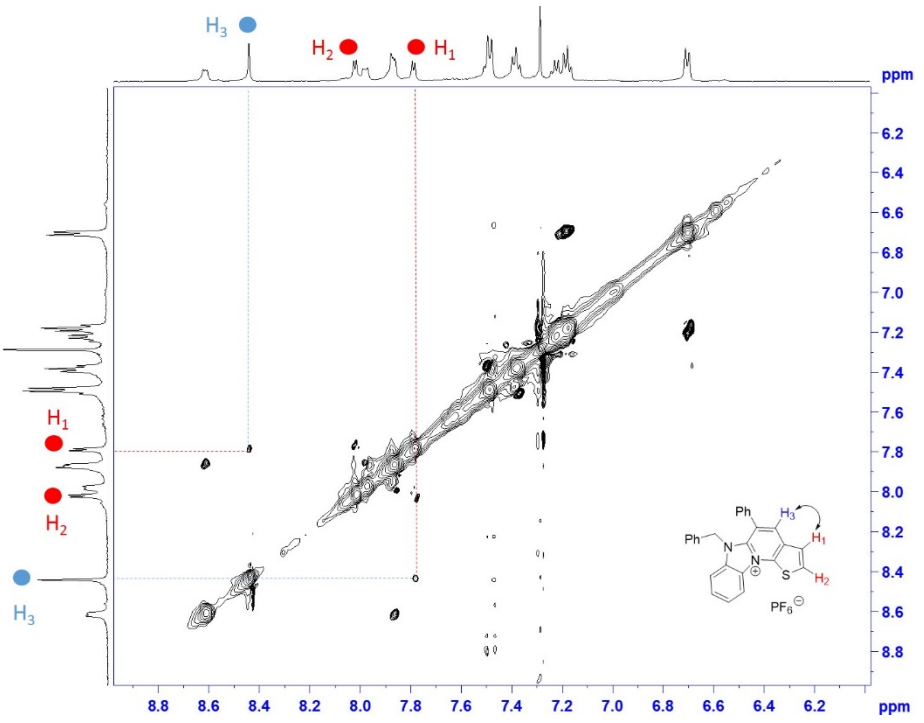


$^{31}P\{^{1}H\}$ NMR of **18**(202.4 MHz, CD_3CN)

2D NMR spectra of 17



2D COSY spectrum of **17** ($CDCl_3$, 500 MHz)



2D NOESY spectrum of **17** (CDCl3, 500 MHz)

^{1}H NMR monitoring of the C-H activation step:

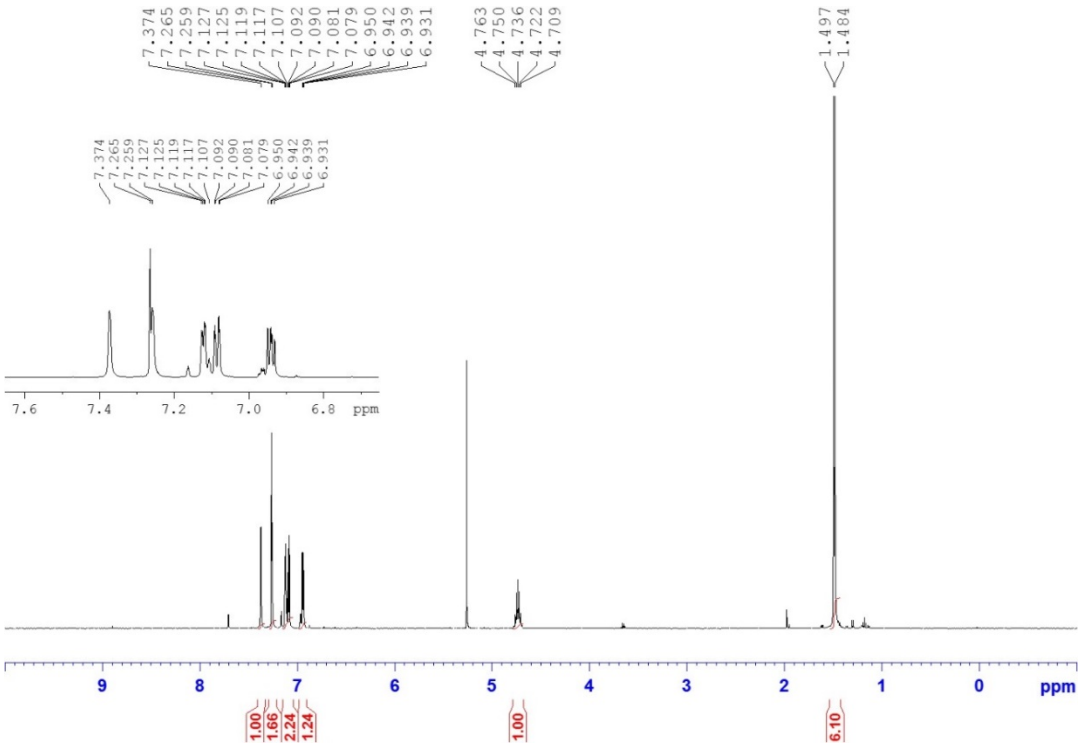


Fig. S1 ^{1}H NMR spectrum of the silver-NHC species **I** ($CDCl_3$, 500 MHz)

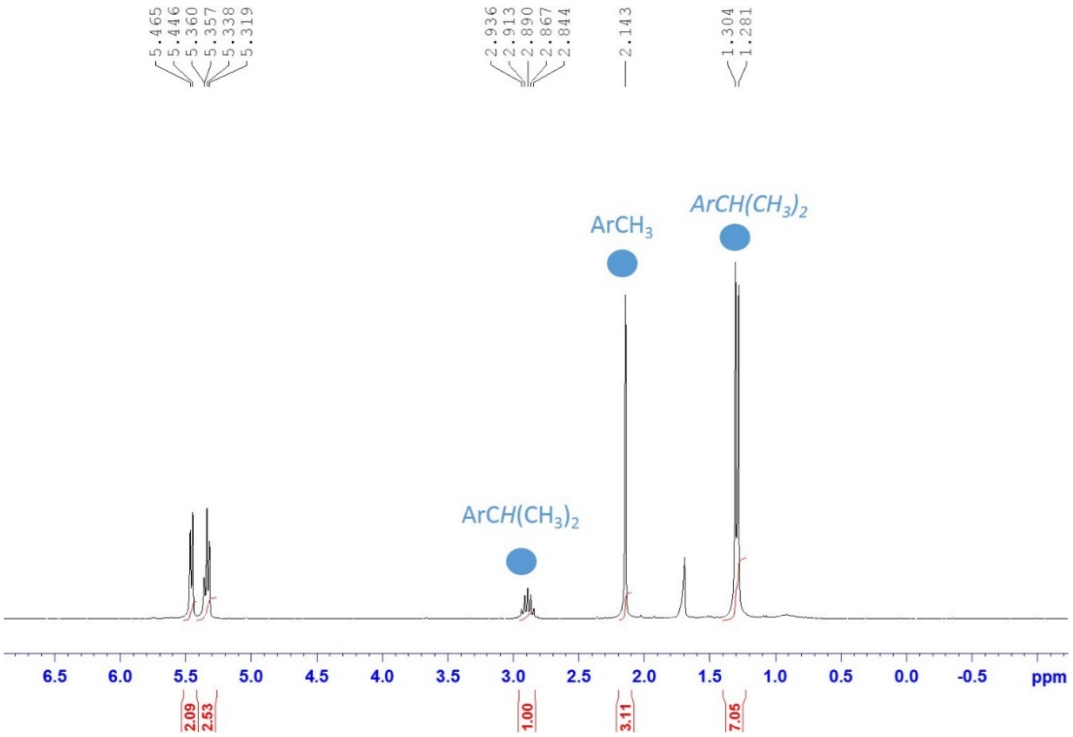


Fig. S2 ^{1}H NMR spectrum of the $[RuCl_2(p\text{-cymene})]_2$ ($CDCl_3$, 500 MHz)

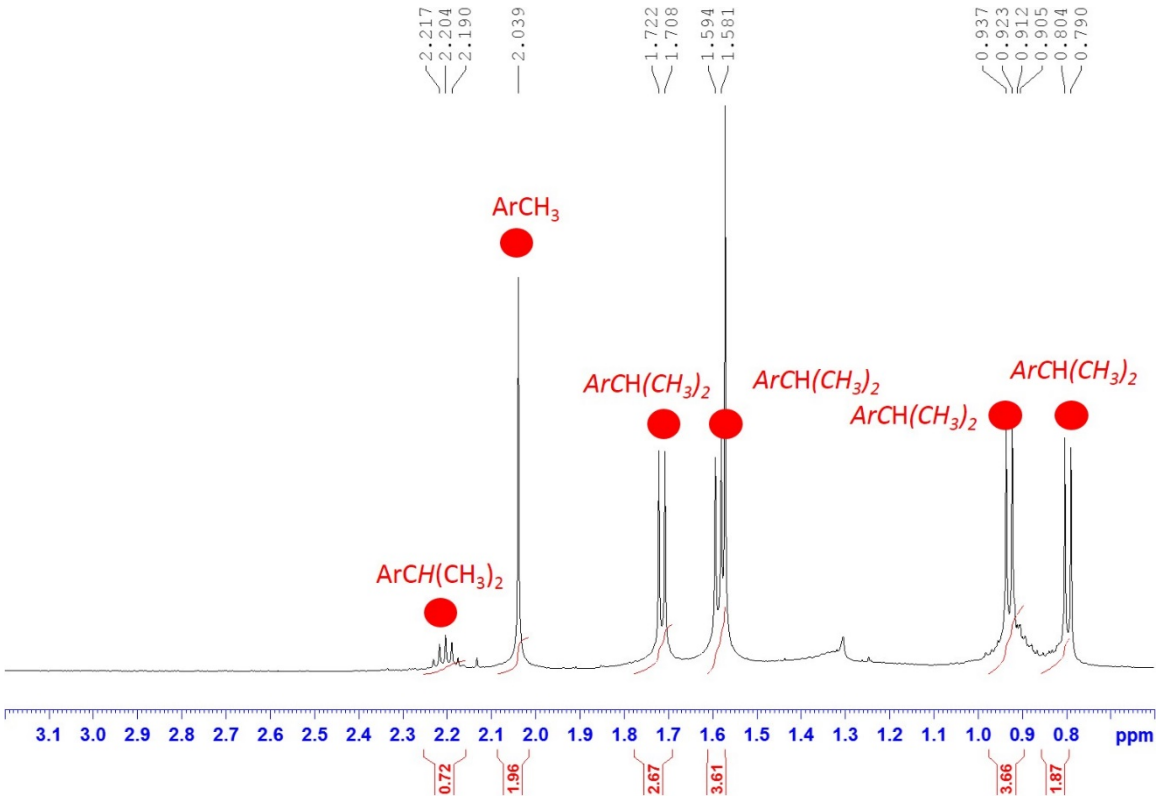


Fig. S3. Section of the ^{1}H NMR spectrum of complex **10** (CD_2Cl_2, 500 MHz)

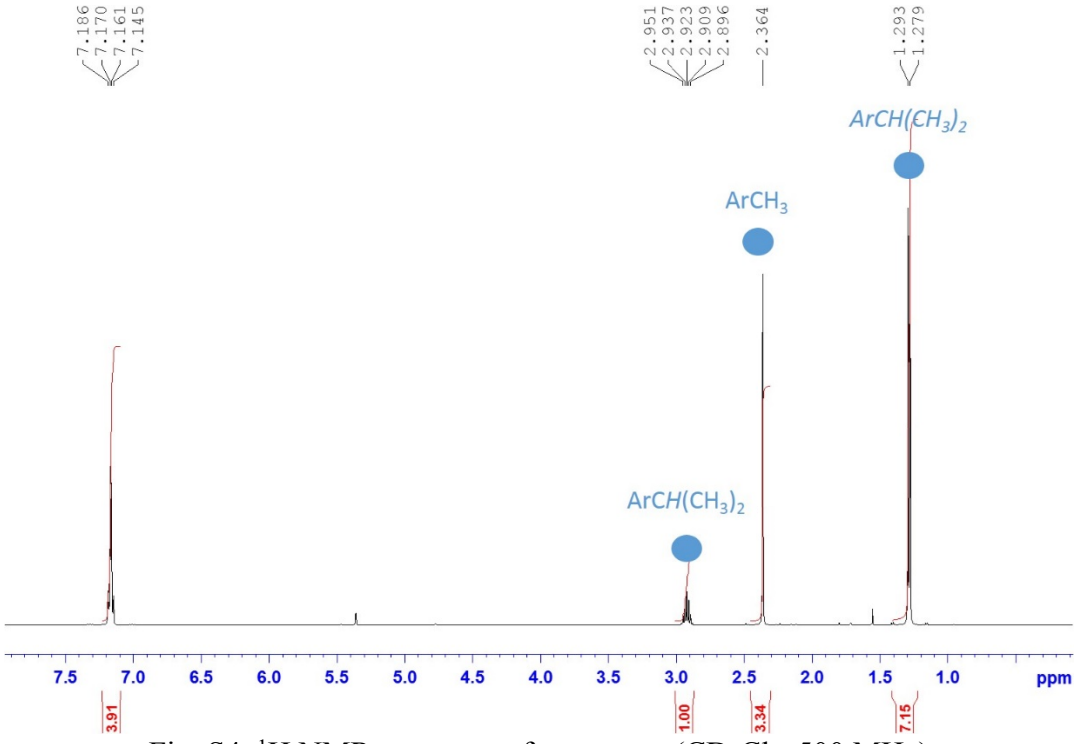


Fig. S4. ^{1}H NMR spectrum of *p*-cymene (CD_2Cl_2, 500 MHz)

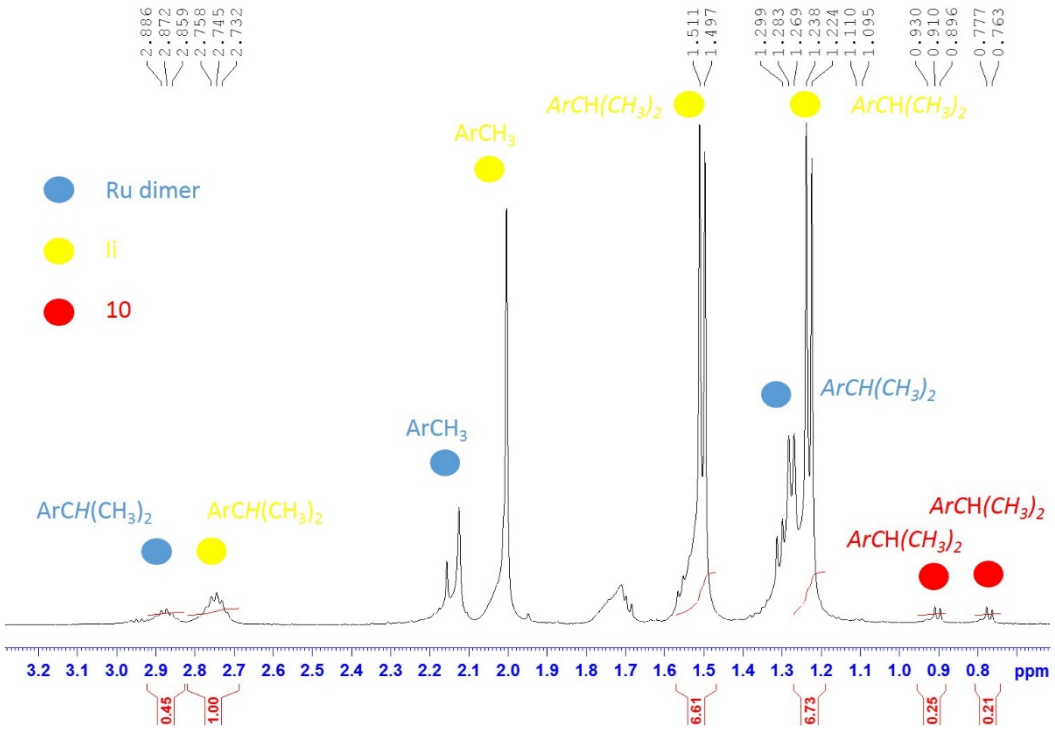


Fig. S5. Section of the ^{1}H NMR spectrum of the reaction at 10 min (CD_2Cl_2, 500 MHz)

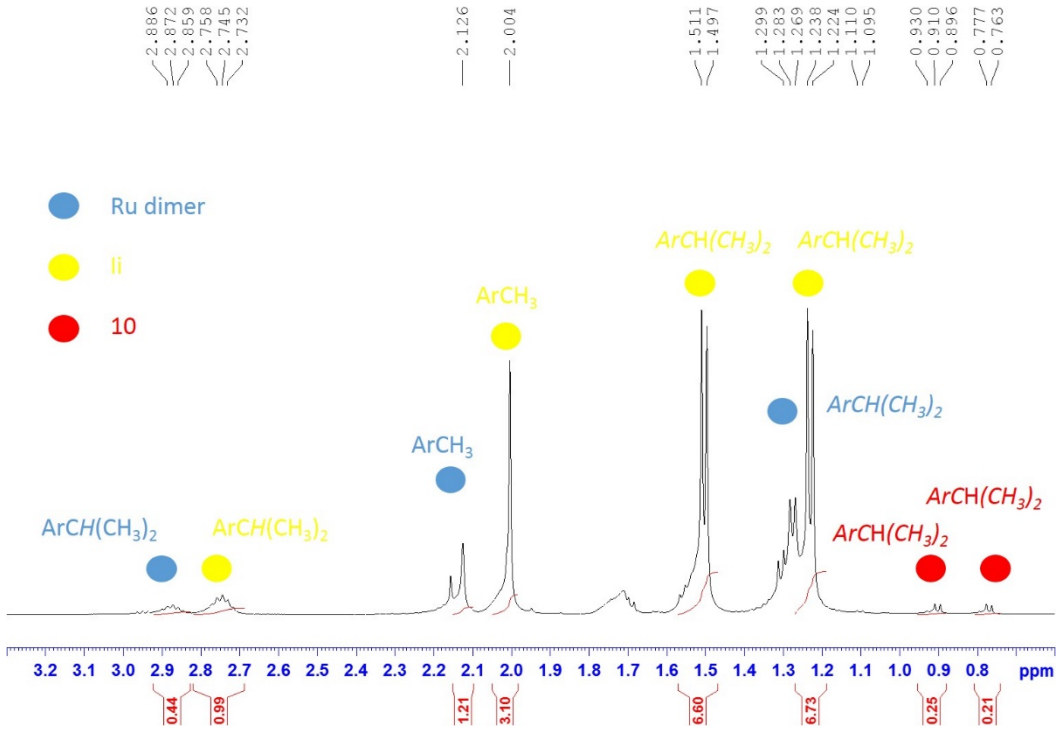


Fig. S6. Section of the ^{1}H NMR spectrum of the reaction at 1.5 h (CD_2Cl_2, 500 MHz)

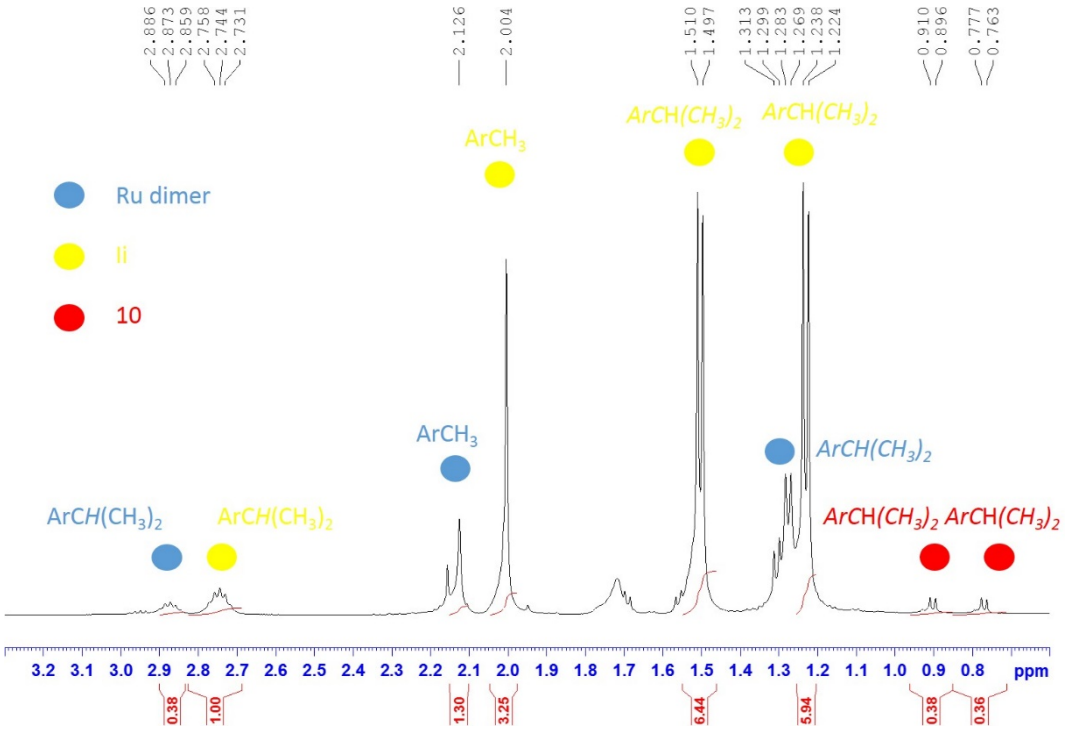


Fig. S7. Section of the ^{1}H NMR spectrum of the reaction at 4 h (CD_2Cl_2, 500 MHz)

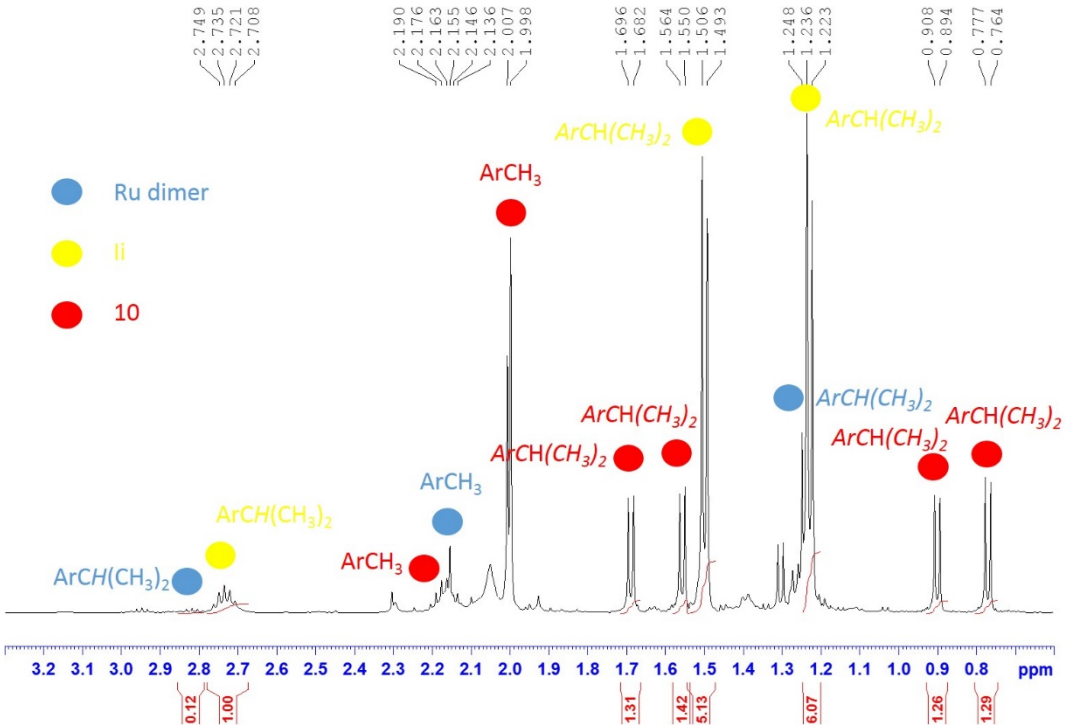


Fig. S8. Section of the ^{1}H NMR spectrum of the reaction 3 h after adding Ag_2O (CD_2Cl_2, 500 MHz)

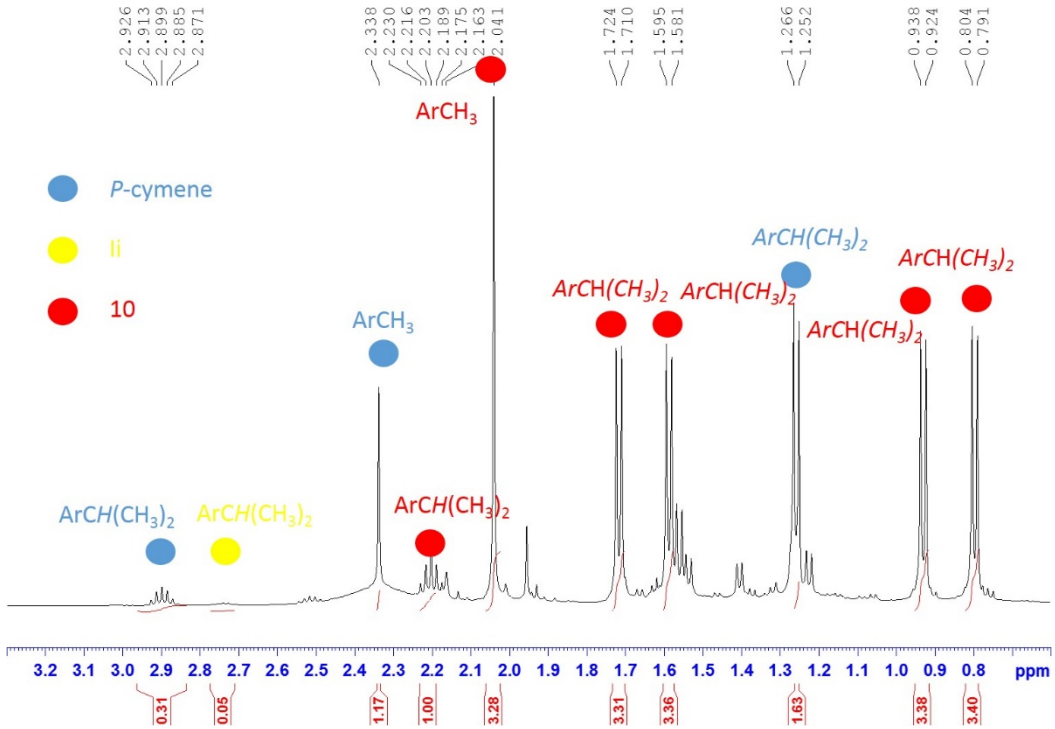


Fig. S9. Section of the ^{1}H NMR spectrum of the reaction 7 h after adding Ag_2O (CD_2Cl_2, 500 MHz)

References

(1) SMART version 5.628; Bruker AXS Inc., Madison, WI, 2001.

(2) SAINT+ version 6.22a; Bruker AXS Inc., Madison, WI, 2001.

(3) Sheldrick, G. W. SADABS version 2.10; University of Göttingen, Germany.

(4) SHELXTL version 6.14; Bruker AXS Inc., Madison, WI, 2000.