Synthesis, characterization, catalytic and biological application of half-sandwich ruthenium complexes bearing hemilabile (κ^2–*C*,*S*)-thioether-functionalised NHC ligands.

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Supporting Information

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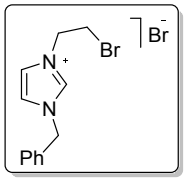
1 GENERAL REMARKS

All manipulations were carried out under an inert atmosphere of argon using standard Schlenk techniques unless stated otherwise. Reagents were purchased from commercial chemical suppliers (mainly Acros, Aldrich, Alfa Aesar, TCI Europe and Strem) and used without further purification. Solvents were dried and degassed according to standard procedures.1-2-Dichlorobenzene (ODCB) solvent was either distilled under argon in presence of $CaCl_2$ and store under activated 4 Å molecular sieves or purchase dry from Aldrich. Benzylamine was distilled from CaH_2 under a nitrogen atmosphere, and then stored over 3Å molecular sieves for 2 days. 3-aminobenzylamine was sublimed under vacuum at room temperature for 12 h. ^{1}H, ^{13}C [1] and ^{19}F nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 300 spectrometer and a Bruker Avance III HD - 500 MHz, VT NMR experiments were conducted with a Bruker Avance III – 600 MHz. ^{13}C assignments were confirmed when necessary with the use of DEPT 135 experiments. ^{1}H and ^{13}C-NMR spectra were referenced using the residual solvent peak ($CDCl_3$: δ H = 7.26 ppm; δ C = 77.16 ppm) at 295K. Chemical shifts δ are given in ppm whereas coupling constants *J* are stated in Hertz (Hz). The following abbreviations are used to classify the multiplicity of the observed signals: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, dd = doublet from doublet, dt = doublet from triplet, m = complex multiplet or broad signal. Positive mode electrospray ionization mass spectra (ESI-MS) were recorded on microTOF, Bruker Daltonics. All manipulations were conducted under an argon atmosphere unless otherwise stated. GC-MS analyses were performed using a GC-MS Agilent 7890A-5975C with EI detector; the GC contains Agilent HP-5ms (dimethylsiloxane, 5%phenyl), #19091S-433, 30x0.25x0.32 I.D column. GC measurements were conducted using the following method: 45 °C hold for the first 2.25 min, ramp to 300 °C at 40 °C/min and hold for 8 min.

2 SYNTHESIS OF IMIDAZOLIUM SALTS

1-benzyl-3-(2-bromoethyl)-1H-imidazol-3-ium bromide (Precursor):



Precursor was synthesized according to the procedure reported in literature and all data correspond to previously reported material.[2] A mixture of 1-

benzylimidazole (3 g, 0.037 mmol) and 1,2-dibromobutane (40 mL, excess) was heated overnight at 85 °C. After this time a white solid is formed in the solution. Then the excess of 1,2-dibromobutane was distilled of under reduced pressure, and the solid residue was taken in 40 mL of CH_2Cl_2. The resulting suspension was filtered over Celite and the solvent was removed *under vaccuo* to give off-white solid.Yield: 98%. ^{1}H NMR (300MHz, DMSO) : δ 9.4 (s, 1H, CH_{imid}), 7.87 (m, 2H, CH_{imid}), 7.4 (m, 5H, CH_{benz}), 5.48 (s, 2H, CH_2), 4.64 (t, *J*=6 Hz, 2H, NCH_2), 3.96 (t, *J*=6 Hz, 2H, CH_2Br) ppm.

S-functionalized imidazolium (a-l)

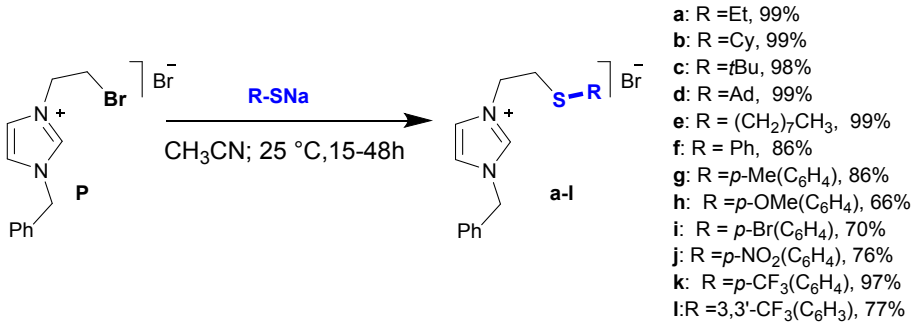


Figure S1. Imidazolium synthesis

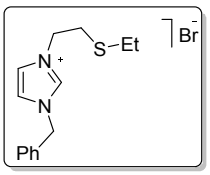
Procedure A:

1-benzyl-3-(2-bromoethyl)-1*H*-imidazol-3-ium bromide (1 equiv) was dissolved in dry acetonitrile. Then a slight excess of the appropriate thiolate salts (1.5 equiv) was added, and the resulting mixture was stirred for 15-48 hours at ambient temperature under argon. After this time, the solvent is removed *under vaccuo*. The solid residue was suspended in CH_2Cl_2 (15 mL) and filtered over celite. Finally the resulting solution is concentrated to 1-2 mL and pass through a silica plug. First elution is conducted with DCM (to eradicate the remaining trace of unreacted thiol) and the resulting filtrate is removed, then the second elution use a mixture of DCM/MeOH (90/10), then the resulting filtrate is concentrate under reduce pressure to afford the resulting compound in orange sticky oil.

Procedure B:

Appropriate thiol (1.50 equiv) was dissolved in dry acetonitrile. Sodium hydroxide (1.50 equiv) in water was added, and the resulting mixture was stirred for 30 min at ambient temperature. Then, the bromine precursor (1 equiv) was added, and the resulting mixture was stirred at room temperature for 15-48 h. After this time, the solvent was removed under reduced pressure. The solid residue was suspended in dichloromethane and filtered over celite. Finally the resulting solution is concentrated to 1-2 mL and pass through a silica plug. First elution is conducted with DCM (to eradicate the remaining trace of unreacted thiol) and the resulting filtrate is removed, then the second elution use a mixture of DCM/MeOH (90/10), then the resulting filtrate is concentrate under reduce pressure to afford the resulting compound in orange sticky oil.

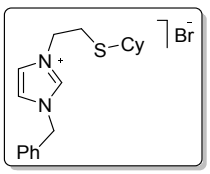
1-benzyl-3-(2-(ethylthio)ethyl)-1*H*-imidazol-3-ium bromide (a)



This imidazolium was synthesized according to the procedure reported in literature and all data correspond to previously reported material.[3]

Procedure A 1-benzyl-3-(2-bromoethyl)-1*H*-imidazol-3-ium bromide (2 g, 5.8 mmol, 1 equiv) was dissolved into a solution of sodium ethanethiolate (0.5 g, 5.8 mmol, 1 equiv) and dry acetonitrile (70 mL). Yield: 99%. ^{1}H NMR (300MHz, DMSO) : δ 9.34 (s, 1H, CH_{imid}), 7.84 (s, 1H, CH_{imid}), 7.83 (s, 1H, CH_{imid}), 7.42 (m, 5H, CH_{benz}), 5.46 (s, 2H, CH_2), 4.37 (t, J = 6 Hz, 2H, NCH_2), 2.98 (t, J = 6 Hz, 2H, CH_2S), 2.5 (t, J = 7 Hz, 2H, CH_2), 1.14 (t, J = 7 Hz, 3H, CH_3) ppm.

1-benzyl-3-(2-(cyclohexylthio)ethyl)-1*H*-imidazol-3-ium bromide (b)

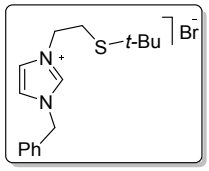


This imidazolium was synthesized according to the procedure reported in

literature and all data correspond to previously reported material.[3]

Procedure B cyclohexanethiol (0.1 g, 0.86 mmol, 1.5 equiv), dry acetonitrile (7 mL), sodium hydroxide (37 mg, 0.9 mmol, 1.5 equiv) and 1-benzyl-3-(2-bromoethyl)-1*H*-imidazol-3-ium bromide (0.2g, 0.58 mmol, 1 equiv). Yield: 99%. ^{1}H NMR (300MHz, DMSO) : δ 9.34 (s, 1H, CH_{imid}), 7.84 (s, 1H, CH_{imid}), 7.83 (s, 1H, CH_{imid}), 5.45 (s, 2H, $PhCH_2$), 4.35 (t, J = 7 Hz, 2H, NCH_2), 2.99 (t, J = 7 Hz, 2H, CH_2S), 2.64 (m, 1H, SCH), 1.86-1.1 (m, 10H, CH_2) ppm.

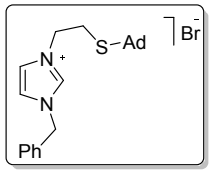
1-benzyl-3-(2-(tert-butylthio)ethyl)-1H-imidazol-3-ium bromide (c)



This imidazolium was synthesized according to the procedure reported in literature and all data correspond to previously reported material.[3]

1-benzyl-3-(2-bromoethyl)-1*H*-imidazol-3-ium bromide (2 g, 5.8 mmol, 1 equiv) was dissolved into a solution of sodium 2-methylpropane-2-thiolate (0.972 g, 8.66 mmol, 1.5 equiv) and dry acetonitrile (60 mL). Yield: 98%. ^{1}H NMR (300MHz, $CDCl_3$) : δ 10.79 (s, 1H, CH_{imid}), 7.45-7.39 (m, 6H, CH_{imid}, CH_{benz}), 7.2 (s, 1H, CH_{imid}), 5.56 (s, 2H, CH_2), 4.57 (t, J = 6 Hz, 2H, NCH_2), 3.09 (t, J = 6 Hz, 2H, CH_2S), 1.28 (s, 9H, CH_3) ppm.

3-(2-(((1*R*,3*s*)-adamantan-1-yl)thio)ethyl)-1-benzyl-1*H*-imidazol-3-ium bromide (d)

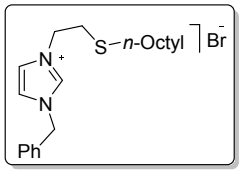


This imidazolium was synthesized according to the procedure reported in literature and all data correspond to previously reported material.[3]

(3s,5s,7s)-Adamantane-1-thiol (0.73 g, 4.34 mmol, 1.5 equiv) was dissolved into

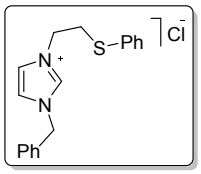
a solution of sodium hydroxide (0.17g, 4.34 mmol, 1.5 equiv) and dry acetnonitrile (30 mL) was added, and the resulting mixture was stirred for 30 minutes at ambient temperature under argon. Then 1-benzyl-3-(2-bromoethyl)-1*H*-imidazol-3-ium bromide (1 g, 2.9 mmol, 1 equiv) was added, and stirring was continued for 48 hours at ambient temperature under argon. After this time, the volatiles were removed under reduced pressure. The solid residue was suspended in CH_2Cl_2 (15 ml) and filtered. The solvent was removed under reduced pressure. Yield: 99%. ^{1}H NMR (300MHz, $CDCl_3$) : δ 10.75 (s, 1H, CH_{imid}), 7.45-7.39 (m, 6H, CH_{benz}, CH_{imid}), 7.11 (s, 1H, CH_{imid}), 5.56 (s, 2H, $PhCH_2$), 4.56 (t, *J* = 6 Hz, 2H, NCH_2), 3.07 (t, *J* = 6 Hz, 2H, CH_2S), 2-1.6 (m, 15H, H_{Ad}) ppm.

1-benzyl-3-(2-(octylthio)ethyl)-1*H*-imidazol-3-ium bromide (e)



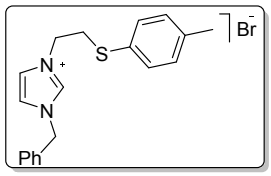
Procedure B: octane-1-thiol (0.32 g, 2.2 mmol, 1.4 equiv), sodium hydroxide (87 mg, 2.2 mmol, 1.4 equiv), dry acetonitrile (7 mL) and 1-benzyl-3-(2-bromoethyl)-1*H*-imidazol-3-ium bromide (0.5 g, 1.4 mmol, 1 equiv). Yield: 99%. ^{1}H NMR (300MHz, $CDCl_3$) : δ 10.74 (s, 1H, CH_{imid}), 7.47-7.38 (m, 6H, CH_{imid} , CH_{benz}), 7.16 (m, 1H, CH_{imid}), 5.54 (s, 2H, $PhCH_2$), 4.60 (t, *J* = 6 Hz, 2H, NCH_2), 3.04 (t, *J* = 6 Hz, 2H, CH_2S), 2.55 (t, *J* = 7 Hz, *2H*, SCH_2), 1.53 (m, 2H, CH_2), 1.35-1.17 (m, 10H, CH_2), 0.87 (t, *J* = 7 Hz, 3H, CH_3) ppm. ^{13}C NMR (75MHz, $CDCl_3$) : δ 137.6 (CH_{imid}), 133 (C_{benz}), 129.6 (CH_{benz}), 129.57 (2xCH_{benz}), 129 (2xCH_{benz}), 122.9 (CH_{imid}), 121.5 (CH_{imid}), 53.6 ($PhCH_2$), 49.6 (NCH_2), 32.5 (CH_2S), 32.4 (SCH_2), 31.9 (CH_2), 29. 6 (CH_2), 29.3 (2xCH_2), 28.8 (CH_2), 22.7 (CH_2), 14.2 (CH_3). FTIR: ν max(pure, diamond orbit)/cm^{-1}: 2918s, 2850m, 1554s, 1464s, 1365w, 1175m, 1143vs, 1085w, 745s, 716vs, 640vs, 475m. MS (ESI): m/z, calcd for $[C_{20}H_{31}N_2S]^+$ calculated 331.22, found 331.22.

1-benzyl-3-(2-(phenylthio)ethyl)-1H-imidazol-3-ium chloride (f)



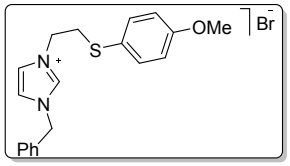
This imidazolium was synthesized according to the procedure reported in literature and all data correspond to previously reported material.[4] Benzylimidazole (1.43 g, 9.06 mmol, 1 equiv) and 2-chloroethyl phenyl sulfide (1.34 ml, 9.06 mmol, 1 equiv). Yield: 99% ^{1}H NMR (300MHz, DMSO) : δ 9.32 (m, 1H, CH_{imid}), 7.81 (m, 1H, CH_{imid}), 7.77 (m, 1H, H_{imid}), 7.43-7.23 (m, 10H, CH_{benz}), 5.4 (s, 2H, CH_2), 4,39 (t, *J* =7 Hz, 2H, NCH_2), 3.5 (t, *J* =7 Hz, 2H, SCH_2) ppm.

1-benzyl-3-(2-(*p*-tolylthio)ethyl)-1*H*-imidazol-3-ium bromide (g)



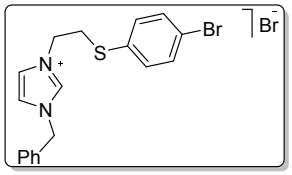
Procedure B: 4-methylbenzenethiol (0.27 g, 2.2 mmol, 1.4 equiv), sodium hydroxide (87 mg, 2.2 mmol, 1.4 equiv), dried acetonitrile (7 mL) and 1-benzyl-3-(2-bromoethyl)-1*H*-imidazol-3-ium bromide (0.5 g, 1.4 mmol, 1 equiv). Yield: 86%. ^{1}H NMR (300MHz, $CDCl_3$) : δ 10.92 (s, 1H, CH_{imid}), 7.43 (m, 5H, CH_{benz}), 7.25 (m, 2H, CH_{aro}), 7.22 (m, 1H, CH_{imid}), 7.11 (m, 2H, CH_{aro}), 6.99 (m, 2H, CH_{imid}), 5.49 (s, 2H, $PhCH_2$), 4.53 (t, *J* = 6 Hz, 2H, NCH_2), 3.47 (t, *J* = 6 Hz, 2H, CH_2S) ppm. ^{13}C NMR (75MHz, $CDCl_3$) : δ 137.8 (CH_{imid}), 137.4 (C_{benz}), 132.9 (C_{Ar}), 131.2 ($2xCH_{benz}$), 130.4 ($2xCH_{benz}$), 129.7 (C_{Ar}), 129.6 ($2xCH_{Ar}$), 129.5 (CH_{benz}), 129.2 ($2xCH_{Ar}$), 123 (CH_{imid}), 121.5 (CH_{imid}), 53.6 ($PhCH_2$), 49.3 (NCH_2), 35.1 (SCH_2), 21.2 ($PhCH_3$) ppm. FTIR: ν max(pure, diamond orbit)/cm^{-1}: 2950m, 1552m, 1493m, 1452m, 1404m, 1173m, 1148s, 842w, 815s, 747s, 718vs, 635s, 502s, 475m. MS (ESI): m/z, calcd for $[C_{19}H_{21}N_2S]^+$ calculated 309.14, found 309.14.

1-benzyl-3-(2-((4-bromophenyl)thio)ethyl)-1*H*-imidazol-3-ium bromide (h)



Procedure B: 4-bromobenzenethiol (0.41 g, 2.2 mmol, 1.6 equiv), sodium hydroxide (87 mg, 2.2 mmol, 1.6 equiv), dried acetonitrile (7 mL) and 1-benzyl-3-(2-bromoethyl)-1*H*-imidazol-3-ium bromide (0.5 g, 1.4 mmol, 1 equiv). Yield:70%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.75 (s, 1H, CH_{imid}), 7.47-7.38 (m, 5H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.29 (t, *J* = 1.7 Hz, 1H, CH_{imid}), 7.08 (t, *J* = 1.7 Hz, 1H, CH_{imid}), 6.84 (d, *J* = 8.8 Hz, 2H), 5.53 (s, 2H, $PhCH_2$), 4.49 (t, *J* = 6.2Hz, 2H, NCH_2), 3.79 (s, 3H, OMe), 3.38 (m, 2H, t, *J* = 5.9 Hz, SCH_2) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.82 (*C*-OMe), 137.54 (CH_{imid}), 134.09 ($2xCH_{Ar}$), 132.82(C_{Benz}), 129.73 (CH_{benz}), 129.63 ($2xCH_{benz}$), 129.19 ($2xCH_{benz}$), 123.31 (C-S), 122.84 (CH_{imid}), 121.46 (CH_{imid}), 115.30 ($2xCH_{Ar}$),, 55.57 (OMe)., 53.58 ($PhCH_2$), 49.32 (NCH_2), 36.23(CH_2-S) ppm. FTIR: ν max(pure, diamond orbit)/cm^{-1}: 1589m, 1552m, 1493s, 1246s, 1176s, 1147s, 1029s, 824s, 720s, 638s, 529m, 474m. MS (ESI): m/z, $[M]^+$ 325.14 (81), 139.0 (100).

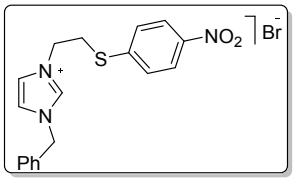
1-benzyl-3-(2-((4-bromophenyl)thio)ethyl)-1*H*-imidazol-3-ium bromide (i)



Procedure B: 4-bromobenzenethiol (0.41 g, 2.2 mmol, 1.6 equiv), sodium hydroxide (87 mg, 2.2 mmol, 1.6 equiv), dried acetonitrile (7 mL) and 1-benzyl-3-(2-bromoethyl)-1*H*-imidazol-3-ium bromide (0.5 g, 1.4 mmol, 1 equiv). Yield:70%. ^{1}H NMR (300MHz, $CDCl_3$) : δ 10.97 (s, 1H, CH_{imid}), 7.42 (m, 5H, CH_{benz}), 7.39 (m, 2H, CH_{aro}), 7.25 (m, 2H, CH_{Ar}), 7.22 (m, 1H, CH_{imid}), 6.98 (m, 2H, CH_{imid}), 5.49 (s, 2H, $PhCH_2$), 4.62 (t, *J* = 6 Hz, 2H, NCH_2), 3.57 (t, *J* = 6 Hz, 2H, CH_2S) ppm. ^{13}C NMR (75MHz, $CDCl_3$) : δ 138.1 (CH_{imid}), 132.8 (S-C_{Ar}), 132.6 (2 x CH_{Ar}), 131.9 (2 x CH_{Ar}), 129.8 (CH_{benz}), 129.7 (2 x CH_{benz}), 129.2 (2 x CH_{benz}), 123 (CH_{imid}), 121.4 (Br-C_{Ar}), 121.2 (CH_{imid}), 53.7 ($PhCH_2$),

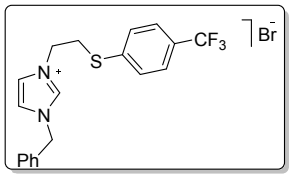
49.6 (NCH_2), 34.5 (SCH_2) ppm. FTIR: ν max(pure, diamond orbit)/cm^{-1}: 3000br, 1552s, 1457s, 1148s, 1088m, 818vs, 750s, 718vs, 635vs, 506s, 485m. MS (ESI): m/z, calcd for $[C_{18}H_{18}N_2SBr]^+$ calculated 373.04, found 373.04.

1-benzyl-3-(2-((4-nitrophenyl)thio)ethyl)-1*H*-imidazol-3-ium bromide (j)



Procedure B: 4-nitrobenzenethiol (0.33g, 2 mmol, 1.4 equiv), sodium hydroxide (85 mg, 2 mmol, 1.4 equiv), dried acetonitrile (7 mL) and 1-benzyl-3-(2-bromoethyl)-1*H*-imidazol-3-ium bromide (0.5 g, 1.4 mmol, 1 equiv). Yield: 76%. ^{1}H NMR (300HMz, $CDCl_3$) : δ 10.99 (s, 1H, CH_{imid}), 8.11 (m, 2H, CH_{aro}), 7.47 (m, 2H, CH_{Ar}), 7.4 (m, 5H, CH_{benz}), 7.32 (m, 1H, CH_{imid}), 7 (m, 2H, CH_{imid}), 5.44 (s, 2H, $PhCH_2$), 4.71 (t, *J* = 6 Hz, 2H, NCH_2), 3.78 (t, *J* = 6 Hz, 2H, CH_2S) ppm. ^{13}C NMR (75MHz, $CDCl_3$) : δ 153.05 (CH_{imid}) 145.88 (NO_2-CH_{Ar}), 145.53 (S-C_{Ar}), 136.74 (C_{Ar}), 131.5 (C_{benz}), 128.94 (2 x CH_{benz}), 128.05 (CH_{benz}), 128.00 (2 x CH_{benz}), 126.7 (2 x CH_{Ar}), 124.2 (2 x CH_{Ar}), 110.99 (CH_{imid}), 110.45 (CH_{imid}), 47.3 ($PhCH_2$), 43.5 (NCH_2), 31.0 (SCH_2).ppm. FTIR: ν max(pure, diamond orbit)/cm^{-1}: 2980br, 1596m, 1554m, 1515vs, 1450m, 1340vs, 1170m, 1105m, 852s, 837s, 718vs, 635vs, 523m. MS (ESI): m/z, calcd for $[C_{18}H_{18}N_3O_2S]^+$ calculated 340.11, found 340.11.

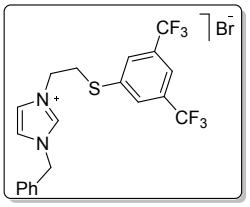
1-benzyl-3-(2-((4-(trifluoromethyl)phenyl)thio)ethyl)-1H-imidazol-3-ium bromide (k)



Procedure B: 4-(trifluoromethyl)benzenethiol (0.154 g, 0.86 mmol, 1.5 equiv), sodium hydroxide (35 mg, 086 mmol, 1.5 equiv), dried acetonitrile (8 mL) and 1-benzyl-3-(2-bromoethyl)-1*H*-imidazol-3-ium bromide (0.2 g, 0.577 mmol, 1 equiv). Yield: 97%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.06 (s, 1H, CH_{imid}), 7.53 (d, *J* = 8.4 Hz, 2H), 7.49-7.36 (m, 7H), 7.20 (t, *J* = 1.7 Hz, 1H, CH_{imid}), 6.93 (t, *J* = 1.7 Hz, 1H, CH_{imid}), 5.43 (s, 2H, $PhCH_2$), 4.66 (t, *J* =6.1 Hz, 2H, NCH_2), 3.70

(m, 2H, t, J = 6. Hz, SCH_2) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.05 (*C*-S), 137.72 (CH_{imid}), 132.54 (C_{benz}), 129.85(CH_{benz}), 129.69 ($2xCH_{Ar}$), 129.13 ($2xCH_{benz}$), 128.85 ($2xCH_{benz}$), 128.80 (q, $^2J_{CF}$ = 32.7 Hz, C_{Ar}), 126.27 (q, $^3J_{CF}$ = 3.7 Hz, $2xCH_{Ar}$), 123.98 (d, $^1J_{CF}$ = 272.0 Hz, CF_3), 123.16 (CH_{imid}), 121.23 (CH_{imid}), 53.74 ($PhCH_2$), 49.50 (NCH_2), 33.23 (SCH_2) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.57 ppm. FTIR: ν max(pure, diamond orbit)/cm^{-1}: 1604m, 1557m, 1497w, 1401w, 1326s, 11154s, 1120s, 1107s, 1091s, 1060s, 1011m, 833m, 711s, 646ms, 591w, 472wm. MS (ESI): m/z, $[M]^+$ 363.11 (100), 205.03 (18).

1-benzyl-3-(2-((3,5-bis(trifluoromethyl)phenyl)thio)ethyl)-1H-imidazol-3-ium bromide (l)



Procedure B: 3,5-bis(trifluoromethyl) benzene thiol (0.213 g, 0.86 mmol, 1.5 equiv), sodium hydroxide (35 mg, 086 mmol, 1.5 equiv), dried acetonitrile (8 mL) and 1-benzyl-3-(2-bromoethyl)-1*H*-imidazol-3-ium bromide (0.2 g, 0.577 mmol, 1 equiv)Yield:77%. ^1H NMR (300 MHz, $CDCl_3$) δ 10.86 (s, 1H), 7.71 (s, 3H), 7.41 (s, J = 13.7 Hz, 5H), 7.37 (s, 1H), 7.09 (s, 1H), 5.48 (s, 2H), 4.75 (t, J = 6.2 Hz, 2H, NCH_2), 3.75 (t, J = 6.1 Hz, 2H, SCH_2) ppm. . ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.06 (*C*-S), 138.03 (CH_{imid}), 132.75 (q, $^2J_{CF}$ = 33.6 Hz, C_{Ar}), 132.39 (C_{benz}), 129.92 (s), 129.73 (CH_{benz}), 129.12 ($2xCH_{benz}$), 128.91 ($2xCH_{benz}$), 128.78 (m, $2xCH_{Ar}$), 122.97 (CH_{imid}), 122.90 (q, $^1J_{CF}$ = 272.0 Hz, 2 x CF_3), 121.34 (CH_{imid}), 53.92 ($PhCH_2$), 49.17 (NCH_2), 33.98 (SCH_2). ppm ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.94 ppm. FTIR: ν max(pure, diamond orbit)/cm^{-1}: 1551w, 1349m, 1276s, 1168m, 1119s, 879m, 843m, 819m, 711s, 696ms, 679, 472wm. MS (ESI): m/z, $[M]^+$ 431.10 (100).

3 SYNTHESIS OF [(NHC)Ru(*p*-cym)Cl][PF_6] COMPLEXES

General procedure

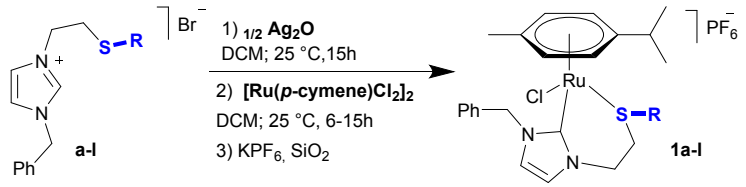
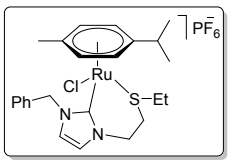


Figure S2. Ruthenium NHCs complexes synthesis

A solution of appropriate imidazolium (2 equiv) in CH_2Cl_2 was treated with a slight excess of Ag_2O (1.3 equiv). The resulting suspension was stirred in the dark (flask wrapped with aluminum foil) for 15 h under argon to generate the silver carbene intermediate. After this time, the solution was filtered over a pad of celite to remove residual solids and concentrated to 2-4 mL. This silver solution is then added to a solution of [$RuCl_2(\eta^6$-*p*-cymene)]$_2$ (1 equiv) in CH_2Cl_2. A precipitate is directly formed and the resulting red mixture is stirred for 5 h in the dark, at room temperature, under argon. After this time, the solution is filtered through celite and concentrate to 2-4mL, and then excess of KPF_6 was added and the solution stirred for 15 min. Finally, the solution is deposited on a silica column for chromatographic separation using a DCM/Acetone (1/1). Filtrate containing the complex is evaporated to dryness and retaken in DCM. The resulting suspension was filtered over Celite and the solvent was removed *under vaccuo* to give desired compound as red to orange solids.

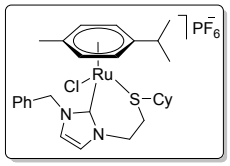
Complex 1a :



The general procedure was used with imidazolium **a** (0.1 g, 2 equiv), Ag_2O (0.035 g, 1.3 equiv) and [Ru(*p*-cym)$Cl_2)_2$] (0.089 g, 1 equiv). Yield: 90% (135mg). ^{1}H NMR (400MHz, $CDCl_3$) : δ 7.30-7.43 (m, 5H), 7.19 (d, *J* = 2 Hz, 1H, CH_{imid}), 6.90 (d, *J* = 2 Hz, 1H, CH_{imid}), 5.77 (d, *J* = 6 Hz, 1H, CH_{cym}), 5.68 (d, *J* = 15 Hz, 1H, NCH_2), 5.59 (d, *J* = 6 Hz, 1H, CH_{cym}), 5.52 (d, *J* = 6 Hz, 1H, CH_{cym}), 5.38-5.46 (m, 2H, NCH_2 + CH_{cym}), 4.47-4.55 (m, 1H, NCH_2), 3.75 (t, *J* = 13 Hz, 1H, NCH_2), 3.26 (br, 1H, SCH_2), 2.90 (br, 1H, SCH_2CH_3), 2.70-2.82 (m, 1H, $CHMe_2$), 2.46 (br, 1H, SCH_2CH_3), 2.09 (br, 1H, SCH_2), 2.04 (s, 3H, CH_{3cym}),

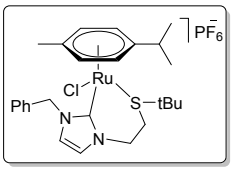
1.20-1.34 (m, 6H, 2 x CH_3) and 1.14 (d, J = 7 Hz, 3H, CH_{3cym}) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8 (Ru-*C*), 136.2 (C_{Ar}), 129.3 (2 x CH_{Ar}), 128.67 (CH_{Ar}), 128.08 (2 x CH_{Ar}), 124.3 (CH_{imid}), 123.1 (CH_{imid}), 113.5 (C_{cym}), C_{cym} around 100 ppm not observed, 89.62 and 88.57 (4 x CH_{cym}), 54.4 (NCH_2), 48.5 (NCH_2CH_2), 32.1 (SCH_2), 30.81 ($CHMe_2$), 30.17 (SCH_2CH_3), 23.8 (CH_{3cym}), 20.9 (CH_{3cym}), 18.2 (CH_{3cym}) and 12.4 (CH_3CH_2S) ppm. FTIR: ν max(pure, diamond orbit)/cm^{-1}: 1456w, 1418w, 1238w, 1160w, 1052w, 1032w, 831s, 724m, 692m, 555s. HRMS (ESI): m/z calcd for $[C_{24}H_{32}ClN_2RuS]^+$ calculated 517.0994, found 517.1015.

Complex 1b :



The general procedure was used with imidazolium **b** (0.1 g, 2 equiv), Ag_2O (0.037 g, 1.3 equiv) and [Ru(*p*-cym)$Cl_2)_2$] (0.080 g, 1 equiv). Yield: 60% (112 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.28 (m, 1H), 7.18 (d, J = 2.0 Hz, 1H, CH_{imid}), 6.89 (d, J = 2.0 Hz, 1H, CH_{imid}), 5.77-5.58 (m, 3H, $PhCH_2$, CH_{cym}), 5.58-5.35 (m, 3H, $PhCH_2$, CH_{cym}), 4.60-4.47 (m, 1H, NCH_2), 3.81-3.60 (m, 1H, NCH_2), 3.32-3.11 (m, 2H, CH_2S + CH_{cym}), 2.68 (m, 1H, CH_{3cym}), 2.21-2.18 (m, 1H, CH_2S) 2.12 (s, 3H,CH_{3cym}), 1.79 (m,3H, CH_{2Cy}), 1.50-1.23 (m, 7H, CH_{2Cy}), 1.21 (d, J = 6.9 Hz, 1H), 1.09 (d, J = 6.9 Hz, 1H) ppm. ^{13}C NMR (400MHz, $CDCl_3$) : 168.3 (Ru-C), 136.1 (C_{benz}), 129.4 (2xCH_{benz}), 128.7 (CH_{benz}), 128 (2xCH_{benz}), 124.3 (CH_{imid}), 123.1 (CH_{imid}), 111.8 (C_{cym}), 104.3 (C_{cym}), 90 (CH_{cym}), 89.4 (CH_{cym}), 88.7 (CH_{cym}), 87.5 (CH_{cym}), 54.5 ($PhCH_2$), 48.3 (NCH_2), 44.6 (CH_2S), 44.3 (CH_{Cy}), 31.5 (CH_{2Cy}), 30.7 ($CH(CH_3)_2$), 30.3 (CH_{2Cy}), 29.4 (CH_{2Cy}), 25.7 (CH_{2Cy}), 25.6(CH_{2Cy}), 23.9 ($CH(CH_3)_2$), 21.3 ($CH(CH_3)_2$), 18.1 (CH_3) ppm. FTIR: ν max(pure, diamond orbit)/cm^{-1}: 3000br, 1447m, 1406m, 1236m, 1053m, 912m, 832vs, 723vs, 643w. HRMS (ESI): m/z calcd for $[C_{28}H_{39}ClN_2RuS\text{-}H]^+$ calculated 571.1566, found 571.1514.

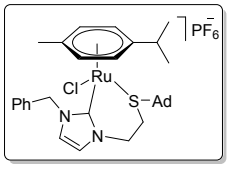
Complex 1c :



The general procedure was used with imidazolium **c** (0.1g, 2 equiv), Ag_2O (0.033 g, 1 equiv) and [Ru(*p*-cym)$Cl_2)_2$] (0.086 g, 1 equiv). Yield: 82% (159 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.14 (m, $CH_{benz,}$ 5H) overlap with $CDCl_3$ pick, 6.90 (d,

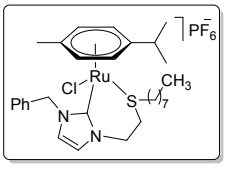
J = 1.9 Hz, 1H, CH_{imid}), 5.77-5.59 (m, 3H, $PhCH_2$, CH_{cym}), 5.44- 5.32 (m, 3H, $PhCH_2$, CH_{cym}), 4.59 (d, J = 15.2 Hz, 1H, NCH_2), 3.78-3.57 (m, 1H, NCH_2), 3.09 (dd, J = 11.8, 3.5 Hz, 1H, CH_2S), 2.71 (dt, J = 13.7, 6.8 Hz, 1H, $CH_{cym}(CH_2)_2$), 2.39 (t, J = 12.1 Hz, 1H, CH_2S), 2.09 (s, 3H, CH_{3cym}), 1.46 (s, 9H, S*t*-Bu), 1.20 (d, J = 6.9 Hz, 3H, CH_{3cym}), 1.09 (d, J = 6.8 Hz, 3H, CH_{3cym}) ppm. ^{13}C NMR (400MHz, $CDCl_3$) : 168.1 (Ru-C), 136.4 (C_{benz}), 129.3 ($2xCH_{benz}$), 128.56 (CH_{benz}), 127.9 ($2xCH_{benz}$), 124.5 (CH_{imid}), 123.4 (CH_{imid}), 113.5 (C_{cym}), 104 (C_{cym}), 90 (CH_{cym}), 89.7 (CH_{cym}), 89 (CH_{cym}), 87.7 (CH_{cym}), 54.3 ($PhCH_2$), 52.2 (S-*C* $(CH_3)_3$), 48.3 (NCH_2), 30.7 ($CH(CH_3)_2$), 29.6 ($3xCH_3$), 27.6 (CH_2S), 23.6 ($CH(CH_3)_2$), 21.2 ($CH(CH_3)_2$), 18.0 (CH_3) ppm. FTIR: ν max(pure, diamond orbit)/cm^{-1}: 1456m, 1406m, 1366w, 1236m, 1161m, 1057w, 1032w, 728s, 694s. HRMS (ESI): m/z calcd for $[C_{30}H_{44}ClN_2RuS]^+$ calculated 545.1331, found 545.1329.

Complex 1d :



The general procedure was used with imidazolium **d** (0.1g, 2 equiv), Ag_2O (0.027 g, 1 equiv) and $[Ru(p\text{-cym})Cl_2)_2]$ (0.071 g, 1 equiv). Yield: 45% (115 mg). ^1H NMR (400MHz, $CDCl_3$) : δ 7.46-7.27 (m, 5H, CH_{benz}), 7.24 (d, J = 1.9 Hz, CH_{imd}), 6.95 (d, J = 1.9 Hz, 1H, CH_{imid}), 5.71-5.59 (m, 3H, CH_{cym} + $PhCH_2$), 5.48-5.30 (m, 3H, CH_{cym} + $PhCH_2$), 4.63-4.60 (m, 1H, NCH_2), 3.83-3.72 (m, 1H, NCH_2), 3.03 (dd, J = 11.6, 3.3 Hz, 1H, CH_2S), 2.76 (m, 1H, $C_{cym}H(CH_2)_2$), 2.45 (m, 1H, CH_2S), 2.11 (m, 12H, CH_{3cym} + CH_{2Ad}), 1.76-1.62 (m, 6H, CH_3, CH_{Ad}), 1.22 (d, J = 7Hz, 3H, $C_{cym}H(CH_2)_2$), 1.14 (d, J= 7Hz, 3H, $C_{cym}H(CH_2)_2$) ppm. ^{13}C NMR (400MHz, $CDCl_3$) : 165 (Ru-C), 136.3 (C_{benz}), 129.3 ($2xCH_{benz}$), 128.5 (CH_{benz}), 127.7 ($2xCH_{benz}$), 124.4 (CH_{imid}), 123.2 (CH_{imid}), 113.4 (C_{cym}), undetected (C_{cym}), 96 (CH_{cym}), 89.7 (CH_{cym}), 88.8 (CH_{cym}), 87.2 (CH_{cym}), 54.9 ($PhCH_2$), 48.2 (SC_{Ad}), 41.4 (NCH_2), 35.9 (CH_{2Ad}), 30.4 (CH_2C_{Ad}), 30.3 (CH_2C_{Ad}), 24.8 ($CH(CH_3)_2$), 23.4 (CH_2S), 21.2 ($CH(CH_3)_2$), 17.9 (CH_3) ppm. FTIR: ν max(pure, diamond orbit)/cm^{-1}: 2908m, 2852m, 1455m 1408m, 1231m, 1034s, 832vs, 694vs, 575w. MS (ESI): m/z, calcd for $[C_{32}H_{43}ClN_2RuS]^+$ calculated 624.21, found 623.18.

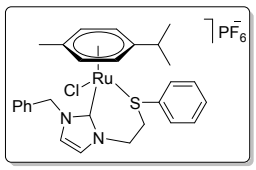
Complex 1e :



The general procedure was used with imidazolium **e** (0.1g, 2 equiv), Ag_2O (0.028 g, 1 equiv) and $[Ru(p\text{-cym})Cl_2)_2]$ (0.074 g, 1 equiv). Yield: 64% (116 mg). ^1H NMR (400MHz, $CDCl_3$) : δ

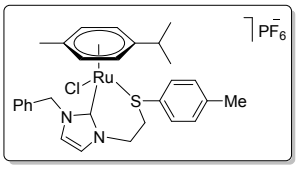
7.43-7.31 (m, 5H, CH_{benz}), 7.20 (d, J = 1.8 Hz, 1H, CH_{imd}), 6.92 (d, J = 1.7 Hz, 1H, CH_{imid}), 5.77 (d, J = 6.0 Hz, 1H, CH_{cym}), 5.67 (d, J = 14.9 Hz, 1H, CH_{cym}), 5.52 (s, 2H, $PhCH_2$), 5.48-5.40 (m, 2H, CH_{cym}), 4.52 (d, J = 15.9 Hz, 1H, NCH_2), 3.79 (t (br), J = 13.5 Hz, 1H, NCH_2), 3.28 (br, 1H, CH_2S), 2.96- 2.72 (m, 2H), 2.36 (br, 1H, CH_2S), 2.04 (s, 3H, CH_{3cym}), 1.71 (br, 1H, CH_2), 1.48-1.19 (m, 14H, CH_{3cym} + CH_2), 1.24 (d, J = 7Hz, 3H, $C_{cym}H(CH_2)_2$), 1.16 (d, J = 6.8 Hz, 3H, CH_{3cym}), 0.88 (t, J = 6.7 Hz, 3H, CH_3) ppm. ^{13}C NMR (400MHz, $CDCl_3$) : 168.9 (Ru-C), 136.2 (C_{benz}), 129.4 (2xCH_{benz}), 128.7 (CH_{benz}), 128.0 (2xCH_{benz}), 124.3 (CH_{imid}), 123.1 (CH_{imid}), 113.9 (C_{cym}), 104.9 (C_{cym}), 90.3 (CH_{cym}), 89.4 (CH_{cym}), 88.8 (CH_{cym}), 87.1 (CH_{cym}), 54.5 ($PhCH_2$), 48.7 (NCH_2), 32.6 (CH_2S), 31.9 (CH_2), 30.81 (CH), 29.22 (CH_2), 29.19 (CH_2), 28,7 (CH_2 x 2) 27,4 (CH_2S), 23.8 ($CH(CH_3)_2$), 22.8 (CH_2CH_3), 21.1 ($CH(CH_3)_2$), 18.2 (CH_3), 14.2 (CH_2CH_3) ppm. FTIR: ν max(pure, diamond orbit)/cm^{-1}: 2950m, 2800m, 1457m, 1406m, 1231m, 1073m, 832vs, 720vs, 575w. HRMS (ESI): m/z calcd for $[C_{30}H_{44}ClN_2RuS]^+$ calculated 601.1957, found 601.1956.

Complex 1f :



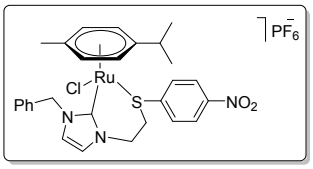
The general procedure was used with imidazolium **f** (0.1 g, 2 equiv), Ag_2O (0.038 g, 1.3 equiv) and [Ru(*p*-cym)$Cl_2)_2$] (0.078 g, 1 equiv). Yield: 73% (132 mg). ^1H NMR (400MHz, $CDCl_3$) : δ ^1H NMR (400 MHz, $CDCl_3$) δ 7.60-7.45 (m, 5H), 7.44-7.35 (m, 3H), 7.33-7.27 (m, 3H), 6.99 (d, J = 2 Hz, 1H, CH_{imid}), 5.68 (d, J = 15 Hz, 1H, NCH_2), 5.50 (d, J = 15 Hz, 1H, NCH_2), 5.44 (d, J = 6 Hz, 1H, CH_{cym}), 5.29 (d, J = 6 Hz, 1H, CH_{cym}), 5.12 (d, J = 5.5 Hz, 1H, CH_{cym}), 5.05 (br, 1H, CH_{cym}), 4.77 (dt, J = 15, 3 Hz, 1H, NCH_2), 4.28 (t, J = 13 Hz, 1H, NCH_2), 3.53 (d, J = 14 Hz, 1H, SCH_2), 2.93-2.73 (m, 2H, SCH_2 + $CHMe_2$), 1.97 (s, 3H, CH_3), 1.19 (d, J = 7 Hz, 3H, CH_3) and 1.03 (d, J = 7 Hz, 3H, CH_3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4 (Ru-*C*), 136.2 (C_{Bn}), not observed (S-C_{Ar}), 130.8 (2 x CH_{Ar}), 130.3 (CH_{Ar}), 130.2 (2 x CH_{Ar}), 129.4 (2 x CH_{Ar}), 128.8 (CH_{Ar}), 127.96 (2 x CH_{Ar}), 124.1 (CH_{imid}), 123.7 (CH_{imid}), 115.7 (C_{cym}), 101.4 (C_{cym}), 90.9, 89.9, 87.7 and 84.3 (4 x CH_{cym}), 54.6 (N-CH_2), 50.6 (N-CH_2CH_2), 35.5 (S-CH_2), 30.7 ($CHMe_2$), 23.9 (CH_3), 20.4 (CH_3), and 18.2 (CH_3) ppm. FTIR: ν max(pure, diamond orbit)/cm^{-1}: 3000w, 1456m, 1237m, 1152m, 1082m, 832s, 721s, 686m, 555s. HRMS (ESI): m/z calcd for $[C_{28}H_{32}ClN_2RuS]^+$ calculated 565.1035, found 565.1016.

Complex 1g :



The general procedure was used with imidazolium **g** (0.1 g, 2 equiv), Ag_2O (0.037 g, 1.3 equiv) and [Ru(*p*-cym)$Cl_2)_2$] (0.074 g, 1 equiv). Yield: 95% (167 mg). ^{1}H NMR (400MHz, $CDCl_3$) : δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.47 (m, 11H), 6.96 (d, *J* = 2 Hz, 1H, CH_{imid}), 5.69 (d, *J* = 15 Hz, 1H, NCH_2), 5.48 (d, *J* = 15 Hz, 1H, NCH_2), 5.42 (d, *J* = 6.2 Hz, 1H, CH_{cym}), 5.24 (d, *J* = 5 Hz, 1H, CH_{cym}), 5.16 (d, *J* = 6 Hz, 1H, CH_{cym}), 5.04 (br, 1H, CH_{cym}), 4.74 (d, *J* = 15 Hz, 1H, NCH_2), 4.24 (t, *J* = 14 Hz, 1H, NCH_2), 3.44 (d, *J* = 14 Hz, 1H, SCH_2), 2.71-2.90 (m, 2H, SCH_2 + C*H*Me_2), 2.38 (s, 3H, CH_3), 1.95 (s, 3H, CH_{3cym}), 1.19 (d, *J* = 7 Hz, 1H, CH_{3cym}) and 1.03 (d, *J* = 7 Hz, 1H, CH_{3cym}) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3 (Ru-*C*), 141.3 (C_{Ar}-Me), 136.2 (C_{Bn}), 130.87 (2 x CH_{Ar}), 130.21 (2 x CH_{Ar}), 129.30 (2 x CH_{Ar}), 128.71 (CH_{Ar}), 128.08 (2 x CH_{Ar}), 124.1 (CH_{imid}), 123.6 (CH_{imid}), 115.5 (C_{cym}), 101.2 (C_{cym}), 90.9, 89.9, 87.8 and 84.4 (4 x CH_{cym}), 54.6 (N-CH_2), 50.5 (N-CH_2CH_2), 35.7 (S-CH_2), 30.7 (*C*HMe_2), 23.9 (CH_{3cym}), 21.5 (CH_3), 20.3 (CH_{3cym}) and 18.2 (CH_{3cym}) ppm; not observed (S-C_{Ar}). FTIR: ν max(pure, diamond orbit)/cm^{-1}: 1456m, 1419m, 1236m, 1151w, 1050w, 832s, 727m, 693m, 555s. HRMS (ESI): m/z calcd for $[C_{29}H_{34}ClN_2RuS]^+$ calculated 579.1205, found 579.1173.

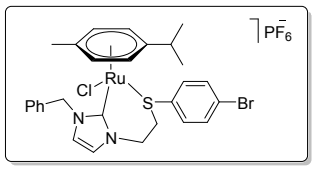
Complex 1h :



The general procedure was used with imidazolium **h** (0.1 g, 2 equiv), Ag_2O (0.034 g, 1.3 equiv) and [Ru(*p*-cym)$Cl_2)_2$] (0.069 g, 1 equiv). Yield: 96% (165 mg). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.19 (d, *J* = 9 Hz, 2H), 7.42-7.36 (m, 5H), 7.30 (d, *J* = 2 Hz, 1H, CH_{imid}), 7.28- 7.21 (m, 2H), 7.04 (d, *J* = 2 Hz, 1H, CH_{imid}), 5.69 (d, *J* = 15 Hz, 1H, NCH_2), 5.60-5.57 (m, 2H, CH_{cym}), 5.42 (d, *J* = 6 Hz, 1H, CH_{cym}), 5.38 (d, *J* = 6 Hz, 1H, CH_{cym}), 5.33 (d, *J* = 15 Hz, 1H, NCH_2), 4.70 (dt, *J* = 15, 3 Hz, 1H, NCH_2), 4.10-4.00 (m, 1H, NCH_2), 3.66 (dt, *J* = 13, 2 Hz, 1H, SCH_2), 2.89-2.72 (m, 2H, SCH_2 + C*H*Me_2), 2.03 (s, 3H, CH_{3cym}), 1.22 (d, *J* = 7 Hz, 3H, CH_{3cym}) and 1.08 (d, *J* = 7 Hz, 3H, CH_{3cym}) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 169.4 (Ru-*C*), 149.1 (C_{Ar}-NO_2), 136.6 (C_{Bn}), 132.6 (2 x $CH_{Ar\text{-}NO2}$), 129.8 (2 x CH_{Ar}), 129.3 (CH_{Ar}), 128.4 (2 x CH_{Ar}), 124.7 (CH_{imid}), 124.5 (2 x $CH_{Ar\text{-}NO2}$), 124.3 (CH_{imid}), 116.0 (C_{cym}), 103.7 (C_{cym}), 91.21,

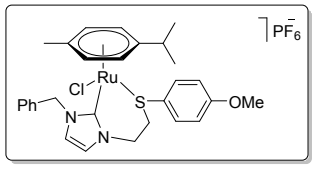
89.6, 89.2 and 86.3 (4 x CH_{cym}), 55.0 (N-CH_2), 49.5 (N-CH_2CH_2), 35.5(S-CH_2), 31.5 ($CHMe_2$), 23.8 (CH_{3cym}), 21.2 (CH_{3cym}) and 18.7 (CH_{3cym}) ppm; not observed (S-C_{Ar}). FTIR: ν max(pure, diamond orbit)/cm^{-1}: 1517m, 1454w, 1416w, 1344m, 1229w, 1214w, 1153w, 1055w, 831s, 721s, 690m, 555s. HRMS (ESI): m/z calcd for $[C_{28}H_{31}ClN_2RuS]^+$ calculated 610.0810, found 610.0867.

Complex 1i :



The general procedure was used with imidazolium **i** (0.1 g, 2 equiv), Ag_2O (0.025 g, 1.3 equiv) and [Ru(*p*-cym)$Cl_2)_2$] (0.064 g, 1 equiv). Yield: 97% (160 mg). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.59 (d, *J* = 8 Hz, 2H), 7.46-7.36 (m, 3H), 7.31-7.28 (m, 3H, CH_{Ar} + CH_{imid}), 7.22 (br, 2H), 7.04 (d, *J* = 2 Hz, 1H, CH_{imid}), 5.73 (d, *J* = 15 Hz, 1H, NCH_2), 5.52 (d, *J* = 6 Hz, 1H, CH_{cym}), 5.39 (d, *J* = 15 Hz, 1H, NCH_2), 5.28 (d, *J* = 5 Hz, 1H, CH_{cym}), other CH_{cym} signals are overlap by solvent peak, 4.69 (dt, *J* = 15, 3 Hz, 1H, NCH_2), 4.08 (t, *J* = 14 Hz, 1H, NCH_2), 3.54 (dt, *J* = 14, 3 Hz, 1H, SCH_2), 2.83-2.75 (m, 2H, SCH_2 + CHMe$_2$), 2.01 (s, 3H, CH_{3cym}), 1.23 (d, *J* = 7 Hz, 3H) and 1.07 (d, *J* = 7 Hz, 3H, CH_{3cym}) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 169.8 (Ru-*C*), 136.7 (C_{Ar}), 133.2 (2 x CH_{Ar}), 132.9 (S-C_{Ar}), 129.7 (2 x CH_{Ar}), 129.2 (CH_{Ar}), 128.4 (2 x CH_{Ar}), 125.5 (2 x CH_{Ar} ou C-Br), 124.6 (CH_{imid}), 124.1 (CH_{imid}), 115.8 (C_{cym}), 103.0 (C_{cym}), 91.1, 90.1, 88.9 and 85.8 (4 x CH_{cym}), 55.0 (N-CH_2), other N-CH_2 signal overlap by solvent peak, 36.0 (S-CH_2), 31.4 (CH_{3cym}), 23.9 (CH_{cym}), 20.9 (CH_{3cym}), 18.7 (CH_{3cym}) ppm; signal (Br-$C_{Ar\ ou}$ CH_{Ar}) not observed. FTIR: ν max(pure, diamond orbit)/cm^{-1}: 1455w, 1419w, 1405w, 1419w, 1234w, 1151w, 1070w, 1007m, 834s, 728m, 693m, 555s. HRMS (ESI): m/z calcd for $[C_{28}H_{31}BrClN_2RuS]^+$ calculated 645.0069, found 645.0108.

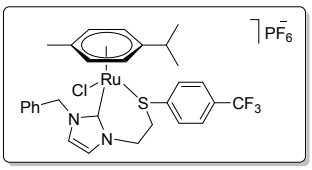
Complex 1j :



The general procedure was used with imidazolium **j** (0.1 g, 2 equiv), Ag_2O (0.035 g, 1.2 equiv) and [Ru(*p*-cym)$Cl_2)_2$] (0.076 g, 1 equiv). Yield: 87% (159 mg). ^{1}H NMR (500MHz, $CDCl_3$) : δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53-7.35 (m, 5H), 7.33-7.28 (m, 2H), 7.26 (overlap by $CDCl_3$, 2H), 7.02 (d, *J*

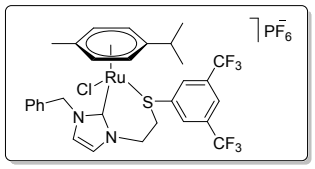
= 7.8 Hz, 1H, CH_{imid}), 6.99 (d, *J* = 2.0 Hz, 1H, CH_{imid}), 5.67 (d, *J* = 15.1 Hz, 1H, NCH_2), 5.52 (d, *J* = 15.1 Hz, 1H, NCH_2), 5.44 (d, *J* = 6.2 Hz, 1H, CH_{cym}), 5.31 (d, *J* = 5.3 Hz, 1H, CH_{cym}), 5.19-4.98 (m broad, 2H, CH_{cym}), 4.77-4.68 (m, 1H, NCH_2), 4.29 (t, *J* = 12.8 Hz, 1H, NCH_2), 3.85 (s, 2H, OCH_3), 3.46 (d, *J* = 13.9 Hz, 1H, SCH_2), 2.86-2.75 (m, 2H, NCH_2 + $CHMe_2$), 1.97 (s, 3H, CH_{3cym}), 1.20 (d, *J* = 7.0 Hz, 3H, CH_{3cym}), 1.04 (d, *J* = 6.8 Hz, 2H, CH_{3cym}) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.84 (Ru-*C*), 161.52 (O-C_{Ar}), 136.25 (2 x CH_{Ar}), 132.17 (C_{Bn}), 129.40 (2 x CH_{Ar}), 128.80 (CH_{Ar}), 127.87 (2 x CH_{Ar}), 124.01(CH_{imid}), 123.65 (CH_{imid}), 115.67 (2 x CH_{Ar}), 115.47 (C_{cym}), 101.18 (C_{cym}), 91.09, 90.21, 87.58 and 84.10 (4 x CH_{cym}), 55.76 (OCH_3), 54.66 (N-CH_2), 50.64 (N-CH_2CH_2), 36.40 (S-CH_2), 30.76 ($CHMe_2$), 23.96 (CH_{3cym}), 20.3 (CH_{3cym}), and 18.2 (CH_{3cym}) ppm; not observed (S-C_{Ar}). FTIR: ν max(pure, diamond orbit)/cm^{-1}: 1495m, 1456m, 1417w, 1251m, 1177w, 1025w, 829s, 725m, 693m, 555s. HRMS (ESI): m/z calcd for $[C_{29}H_{34}ClN_2ORuS]^+$ calculated 595.1122, found 595.1119.

Complex 1k :



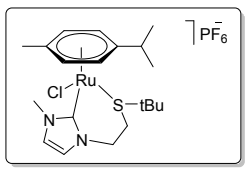
The general procedure was used with imidazolium **k** (0.05 g, 2 equiv), Ag_2O (0.016 g, 1.3 equiv) and [Ru(*p*-cym)$Cl_2)_2$] (0.033 g, 1 equiv). Yield: 88% (73 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H, CH_{Ar}), 7.303-7.58 (m, 5H, CH_{Ar}), 7.27 aromatic proton overlap with $CDCl_3$ pick, 7.32 (d, *J* = 2.0 Hz, 1H, CH_{imid}), 7.03 (d, *J* = 2.0 Hz, 1H, CH_{imid}), 5.67 (d, *J* = 15.1 Hz, 1H, NCH_2), 5.53 (d, *J* = 6.2 Hz, 1H, CH_{cym}), 5.48 (d, *J* = 15.1 Hz, 1H, NCH_2), 5.45 (d, *J* = 5.7 Hz, 1H, CH_{cym}), 5.34 (br, 1H, CH_{cym}), 5.17 (d, *J* = 5.7 Hz, 1H, CH_{cym}), 4.77 (dt, *J* = 15.2, 3.0 Hz, 1H, NCH_2), 4.24 (t, *J* = 13.1 Hz, 1H, NCH_2), 3.66 (dt, *J* = 13.4, 2.3 Hz, 1H, SCH_2), 2.73-2.92 (m, 2H, $SCH_2 + CHMe_2$), 2.02 (s, 3H, CH_3), 1.22 (d, *J* = 7.0 Hz, 3H, CH_3), 1.07 (d, *J* = 6.8 Hz, 3H, CH_3).ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.35 (C-Ru), 136.08 (C_{Bn}), 132.54 (q, $^2J_{C-F}$ = 30.9 Hz, C_{Ar}) 131.42 (2 x CH_{Ar}), 129.46 (2 x CH_{Ar}), 128.95 (CH_{Ar}), 127.78 (2 x CH_{Ar}), 126.71 (d, $^3J_{C-F}$ = 3.7 Hz, 2 x CH_{Ar}), 124.21 (CH_{imid}), 123.85 (CH_{imid}), 123.49 (q, $^1J_{C-F}$ = 271.0 Hz, CF_3), 115.87 (C_{cym}), 102.40 (C_{cym}), 90.59 (CH_{cym}), 90.07 (CH_{cym}), 87.80 (CH_{cym}), 84.73 (CH_{cym}), 54.60 (N-CH_2), 50.03 (N-CH_2CH_2), 35.53 ($CHMe_2$), 30.85 (S-CH_2), 23.68 (CH_3), 20.78 (CH_3), 18.29 (CH_3) ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.06 (CF_3), -72.32 (d, J_{P-F} = 713 Hz, PF_6) ppm FTIR: ν max(pure, diamond orbit)/cm^{-1}: 142w, 1324m, 1235m, 1167m, 1127m, 1062m, 827s, 730s, 692m, 555s. HRMS (ESI): m/z calcd for $[C_{29}H_{31}ClF_3N_2RuS]^+$ calculated 633.0891, found 633.0873.

Complex 1l :



The general procedure was used with imidazolium **l** (0.028 g, 2 equiv), Ag_2O (0.008 g, 1.3 equiv) and [Ru(*p*-cym)$Cl_2)_2$] (0.016 g, 1 equiv). Yield: 90% (40 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.41-7.35 (m, 4H), 7.32 (s, 2H), 7.25-7.22 (m, 2H, CH_{imid} + CH_{Ar}), 7.01 (d, *J* = 2.0 Hz, 1H, CH_{imid}), 5.93 (d, *J* = 6.0 Hz, 1H, CH_{cym}), 5.73-5.63 (m, 3H, 2 x CH_{cym} + CH_{2Bn}), 5.45 (dd, *J* = 6.2, 1.0 Hz, 1H, $CH_{cym,}$), 5.33 (d, *J* = 14.8 Hz, 1H, CH_{2Bn}), 4.75 (dt, *J* = 15.4, 3.0 Hz, 1H, NCH_2), 4.08 (ddd, *J* = 15.3, 12.7, 2.5 Hz, 1H, NCH_2), 3.86 (dt, *J* = 13.0, 2.6 Hz, 1H, SCH_2), 2.86 (dt, *J* = 13.8, 6.9 Hz, 1H, CH_{cym}), 2.72 (td, *J* = 12.9, 3.3 Hz, 1H, SCH_2), 2.06 (s, 3H, CH_3), 1.25 (d, *J* = 7.0 Hz, 3H, CH_3), 1.15 (d, *J* = 6.9 Hz, 3H, CH_3) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.02 (Ru-*C*), 135.82 (S-C_{Ar}), 132.55 (C_{Ar}), 132.14 (q, $^2J_{CF}$ = 34.0 Hz, 2 x *C*-CF_3), 132.09 (CH_{Ar}), 129.37 (2 x CH_{Ar}), 128.88 (CH_{Ar}), 128.02 (2 x CH_{Ar}), 124.43 (CH_{imid}), 123.96 (CH_{imid}), 122.62 (q, $^1J_{CF}$ = 274.3 Hz, 2 x CF_3), 115.99 (C_{cym}), 103.87 (C_{cym}), 92.36 (CH_{cym}), 89.57 (CH_{cym}), 87.81 (CH_{cym}), 85.24 (CH_{cym}), 54.44 (N-*C*H_2), 48.75 (N-*C*H_2CH_2), 36.34 (S-*C*H_2), 30.97 (CH_{cym}), 23.21 (CH_3), 21.43 (CH_3), 18.47 (CH_3).ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.98 (CF_3), -72.34 (d, J_{P-F} = 713 Hz, PF_6) ppm. FTIR: ν max(pure, diamond orbit)/cm^{-1}: 1406w, 1351m, 1276s, 1236w, 1182m, 1133s, 1096m, 829s, 726m, 695m, 680m, 556s. HRMS (ESI): m/z calcd for $[C_{30}H_{30}ClF_6N_2RuS]^+$ calculated 701.0765, found 701.0717.

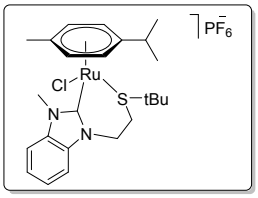
Complex 4 :



The general procedure was used with appropriate imidazolium (0.1 g, 2 equiv), Ag_2O (0.051 g, 1.3 equiv) and [Ru(*p*-cym)$Cl_2)_2$] (0.104 g, 1 equiv). Yield: 82% (180 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 2.0 Hz, 1H, CH_{imid}), 7.12 (d, *J* = 2.0 Hz, 1H, CH_{imid}), 5.80-5.72 (m, 2H, CH_{cym}), 5.50 (dd, *J* = 6.1, 1.3 Hz, 1H, CH_{cym}), 5.42 (dd, *J* = 6.2, 1.2 Hz, 1H, CH_{cym}), 4.57 (ddd, *J* = 15.2, 4.1, 2.4 Hz, 1H, NCH_2), 3.95 (s, 1H, NCH_3), 3.70 (ddd, *J* = 15.0, 12.5, 1.3 Hz, 1H, NCH_2), 3.08 (ddd, *J* = 11.9, 4.1, 1.4 Hz, 1H, SCH_2), 2.79 – 2.69 (m, 1H, CH_{cym}), 2.36 (td, *J* = 12.3, 2.4 Hz, 1H, NCH_2), 2.14 (s, 1H, CH_{3cym}), 1.43 (s, 9H, S-tBu), 1.25 (d, *J* = 6.9 Hz, 3H, , CH_{3cym}), 1.10 (d, *J* = 6.9 Hz, 3H, CH_{3cym}) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.16 (Ru-*C*), 124.50 (CH_{imid}), 124.19 (CH_{imid}), 113.23 (C_{cym}), 104.87 (C_{cym}), 90.54 (CH_{cym}), 89.67

(CH_{cym}), 88.88 (CH_{cym}), 87.21 (CH_{cym}), 52.21 (C_{tBu}), 48.24 (N-*C*H_2), 38.82 (N-*C*H_3), 30.67 (CH_{cym}), 29.63 (CH_{3tBu}), 27.57 (S-*C*H_2), 23.60 (CH_{3cym}), 21.19 (CH_{3cym}), 18.16 (CH_{3cym}) ppm. FTIR: ν max(pure, diamond orbit)/cm^{-1}: 2961w, 1462m, 1240m, 1161m, 1083m, 872s, 732s, 687m, 567s. HRMS (ESI): m/z calcd for $[C_{20}H_{32}ClN_2RuS]^+$ calculated 469.1018, found 469.1000.

Complex 5 :



The general procedure was used with appropriate benzimidazolium (0.1 g, 2 equiv), Ag_2O (0.051 g, 1.3 equiv) and [Ru(*p*-cym)$Cl_2)_2$] (0.104 g, 1 equiv). Yield: 82% (180 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.53 (m, 1H, $CH_{Benzimid}$), 7.51-7.46 (m, 1H, $CH_{Benzimid}$), 7.43-7.36 (m, 2H, $CH_{Benzimid}$), 5.86 (d, *J* = 6.1 Hz, 1H, CH_{cym}), 5.81 (d, *J* = 6.1 Hz, 1H, CH_{cym}), 5.66 (d, *J* = 6.0 Hz, 1H, CH_{cym}), 5.55 (d, *J* = 6.1 Hz, 1H, CH_{cym}), 5.01-5.04 (m, 1H, NC*H*$_2$), 4.15 (s, 3H, NC*H*$_3$), 3.87-3.77 (m, 1H, NC*H*$_2$), 3.29 (dd, *J* = 11.9, 3.6 Hz, 1H, SC*H*$_2$), 2.88-2.77 (m, 1H, CH_{cym}), 2.33 (dd, *J* = 12.0, 10.1 Hz, 1H, SC*H*$_2$), 2.13 (s, 3H, CH_{3cym}), 1.41 (s, 9H, S-*t*Bu), 1.26 (d, *J* = 6.9 Hz, 3H, CH_{3cym}), 1.08 (d, *J* = 6.9 Hz, 3H, CH_{3cym}) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.12 (Ru-*C*), 135.64 (C_{Ar}), 134.16 (C_{Ar}), 124.38 (CH_{Ar}), 124.27 (CH_{Ar}), 114.76 (C_{cym}), 110.65 (CH_{Ar}), 110.10 (CH_{Ar}), 105.46 (C_{cym}), 90.99 (CH_{cym}), 90.02 (CH_{cym}), 89.85 (CH_{cym}), 88.17 (CH_{cym}), 52.50 (C_{tBu}), 44.03 (N-*C*H_2), 35.79 (N-*C*H_3), 30.69 (CH_{cym}), 29.56 (CH_{3tBu}), 27.49 (S-*C*H_2), 23.40 (CH_{3cym}), 21.42 (CH_{3cym}), 18.27(CH_{3cym}) ppm. FTIR: ν max(pure, diamond orbit)/cm^{-1}: 2930w, 1456m, 1396m, 1203m, 1162m, 1092w, 830s, 745s, 556s. HRMS (ESI): m/z calcd for $[C_{24}H_{34}ClN_2RuS]^+$ calculated 519.1172, found 519.1154.

4 VARIABLE TEMPERATURE H[1]-NMR EXPERIMENTS

Procedure:
In a NMR tube 5 mg of complex **1c** were dissolved in the desired deuterated solvent. Then variable temperature NMR experiments were conducted on a Spectromètre Bruker Avance III – 600 MHz. Then one ^{1}H NMR spectra were recorded every ±10 °C.

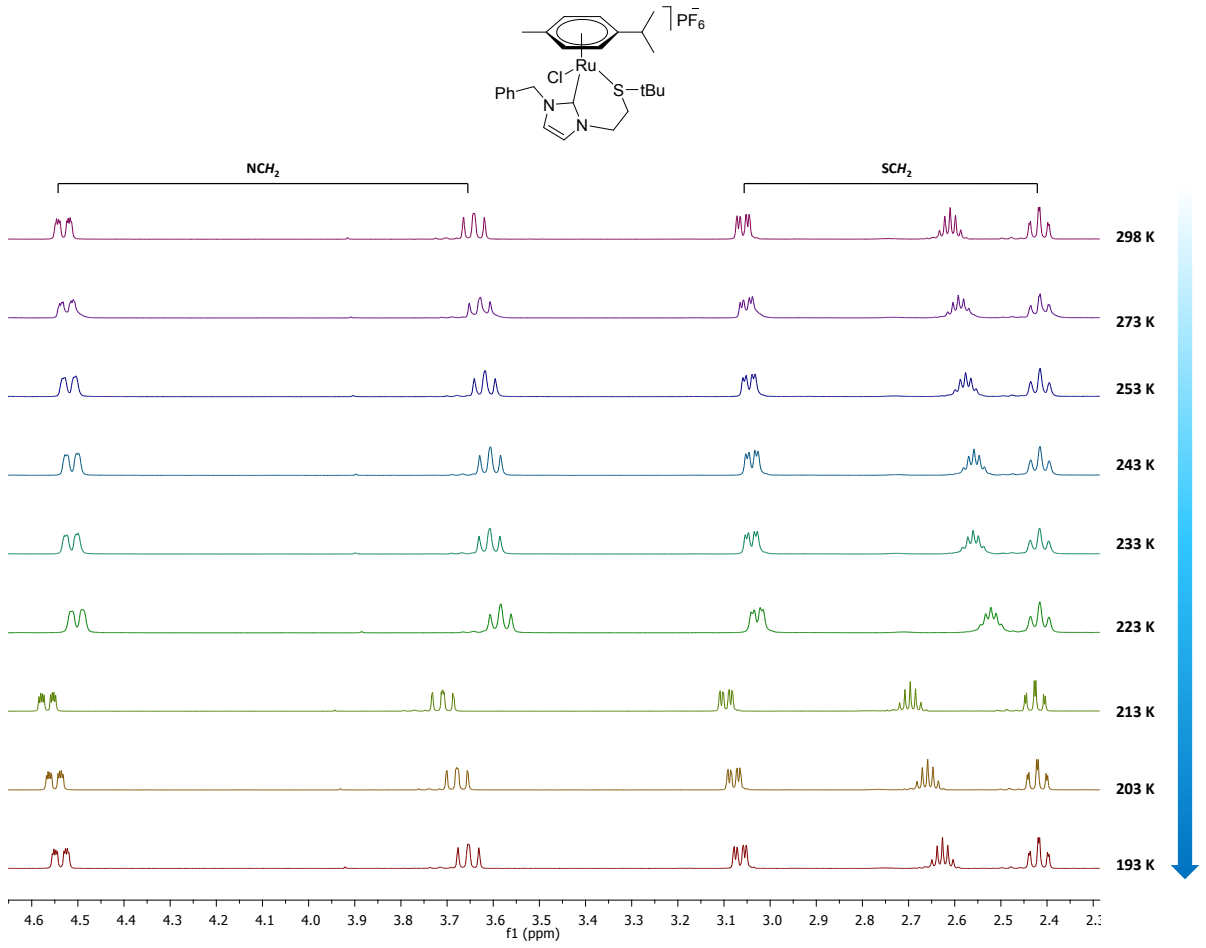


Figure S3. Variable temperature (VT) ^{1}H-NMR spectra of complex **1c** in Dichloromethane-d_2, expanded spectra in between 2.2-4.8 ppm (with lowering the temperature)

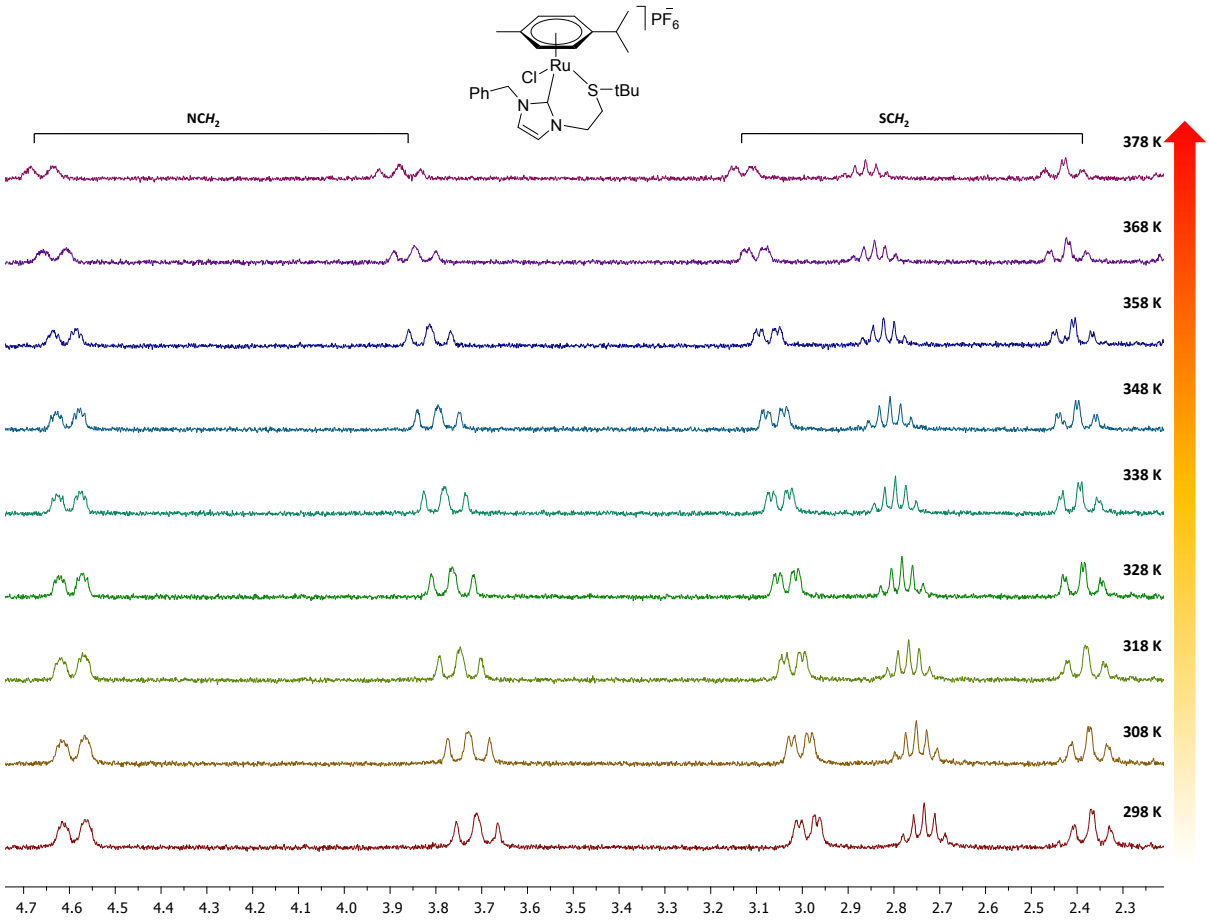


Figure S4. Variable temperature (VT) ^{1}H-NMR spectra of complex **1c** in 1,2-Dichlorobenzene-d_4, expanded spectra in between 2.2-4.8 ppm (with rising the temperature).

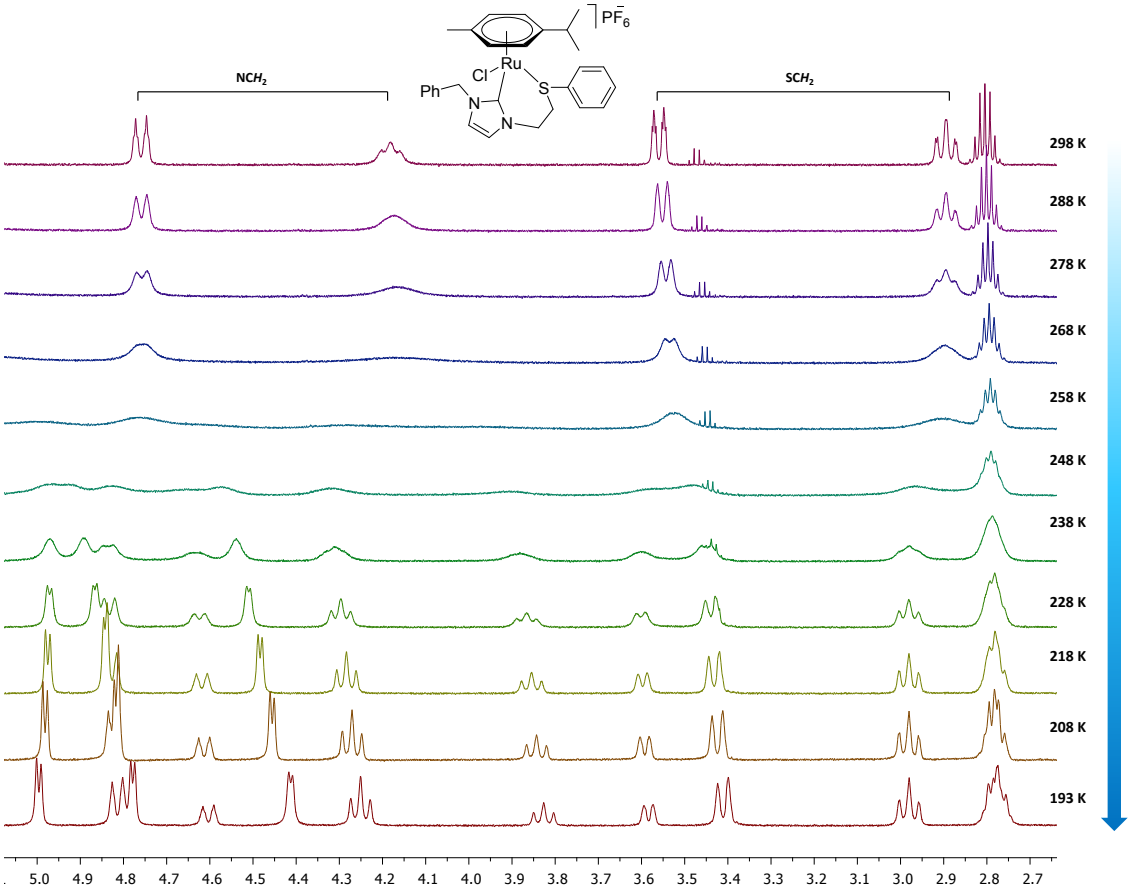


Figure S5. Variable temperature (VT) ^{1}H-NMR spectra of complex **1f** in Dichloromethane-d_2, expanded spectra in between 2.6-5.2 ppm (with lowering the temperature).

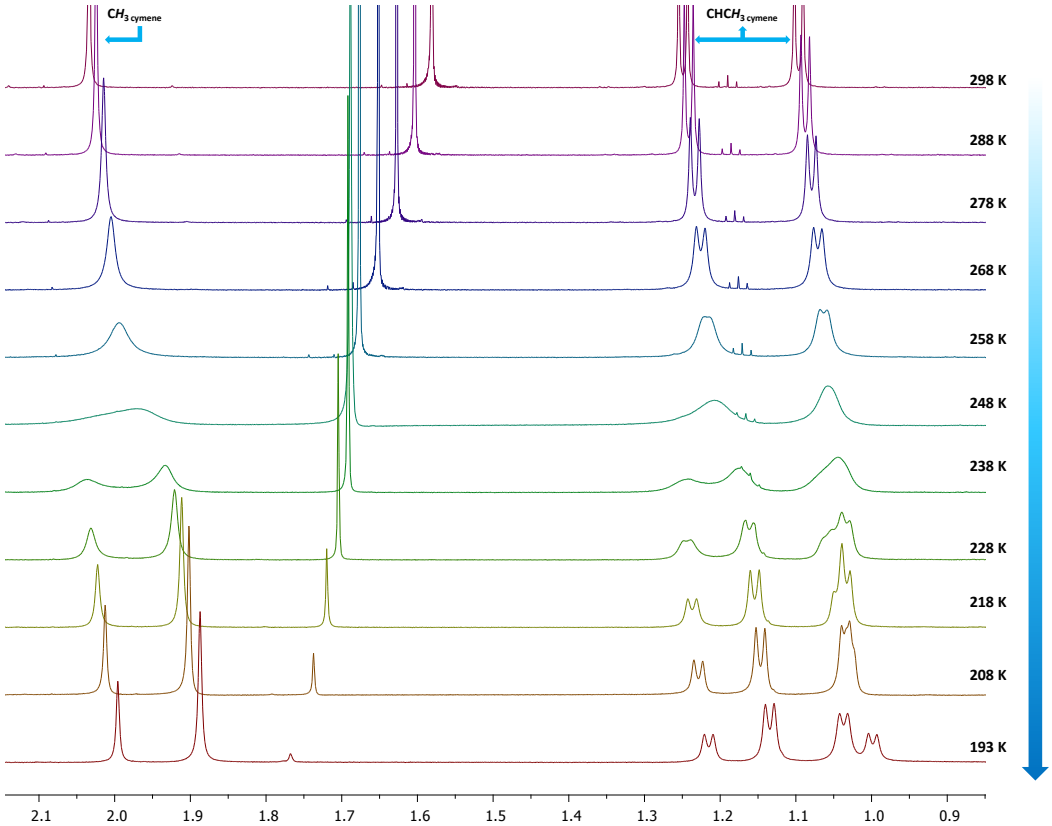


Figure S6. Variable temperature (VT) ^{1}H-NMR spectra of complex **1f** in Dichloromethane-d_2, expanded spectra in between 0.9 -2.2 ppm (with lowering the temperature).

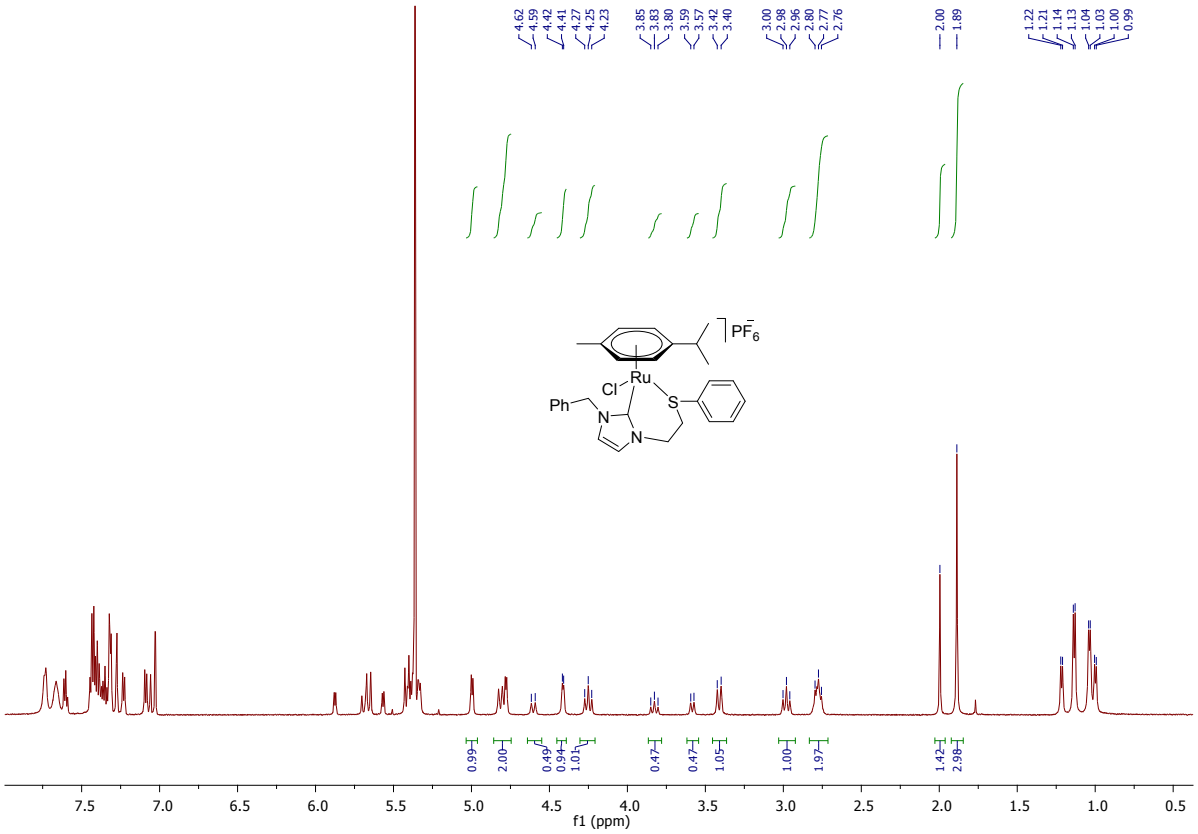


Figure S7. ^{1}H-NMR spectra of complex **1f** in Dichloromethane-d_2, recorded at 193 K.

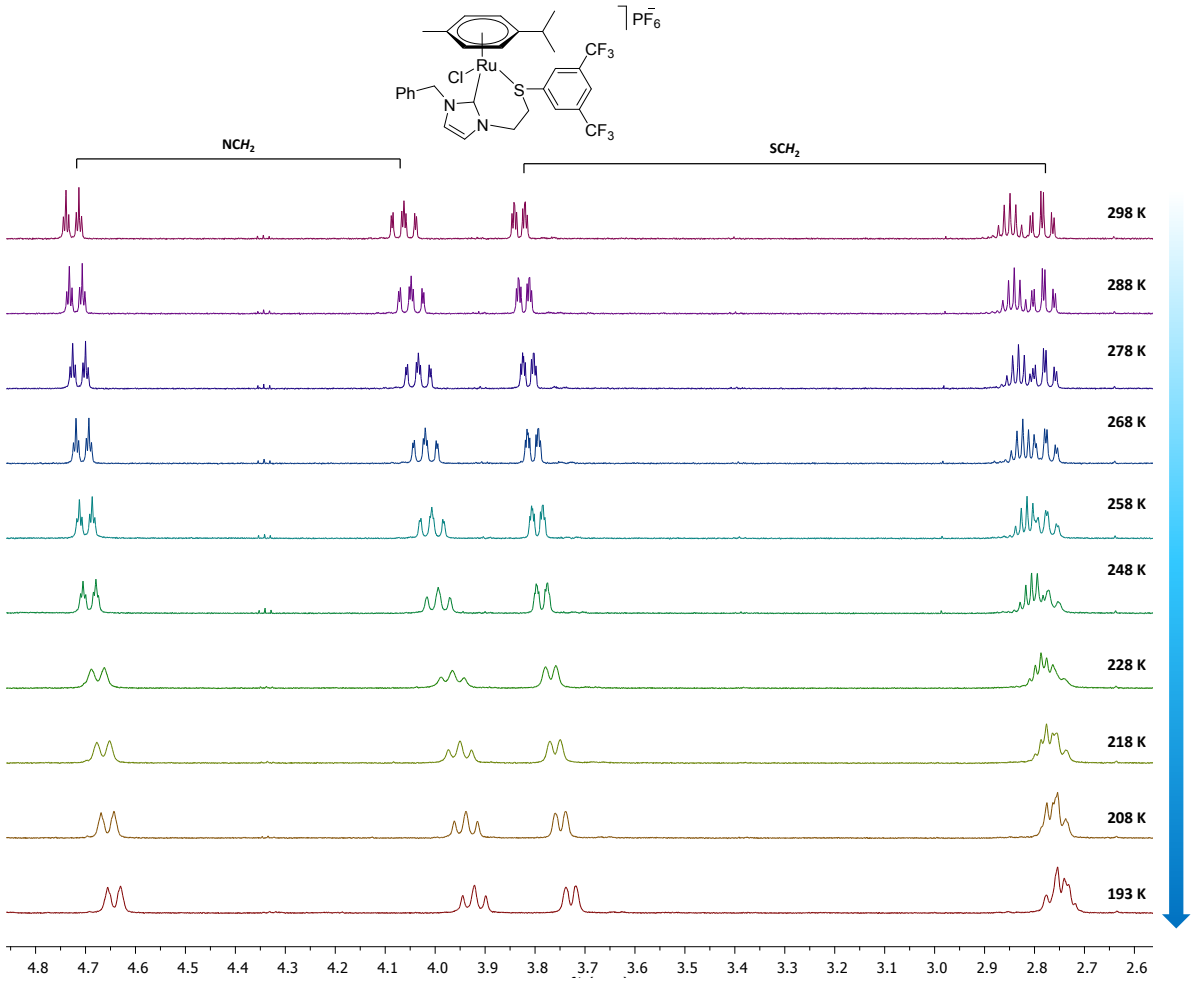


Figure S8. Variable temperature (VT) ^{1}H-NMR spectra of complex **1l** in Dichloromethane-d_2, expanded spectra in between 2.5 -4.9 ppm (with lowering the temperature).

5 GENERAL PROCEDURE FOR AMINE DEHYDROGENATION CATALYSED BY [Ru(*NHC*)Cl][PF_6]

The amine (0.2 mmol) was added into an 10 mL oven-dried schlenck tube under argon containing a solution of complex **1c** (2.5 mol%, 0.0025 mmol) in dry 1,2-dichlorobenzene (0.2 mL). The schlenck tube was then capped with a Rotilabo®-stoppers made of natural rubber, and the schlenck valve is opened to the Schlenk line, and then heated to 110 °C.

After 24-48 h, a 0.005 mL aliquot was diluted with 1 mL Toluene, and the product(s) ratio was determined by GC-MS analysis. After cooling to ambient temperature, the product is purified by silica gel chromatography (h : 10 cm; Ø :1 cm) using first 60 mL of pentane (to remove the 1,2-dichlorobenzene) followed by either a pentane:diethyl ether (80:20) or (90:10) mixture to afford the corresponding nitrile as the isolated product in 30-80% yield. The identity of the nitrile product was confirmed by comparison to the reported NMR spectra of known compounds and by GC-MS analysis. Benzylamine derivatives always generated a mixture of nitrile and imine. The latter is hydrolysed into benzaldehyde derivatives during the purification on column chromatography. Unfortunately, those by-products are difficult to separate from the desired products(very close retention value), which lower the isolated yields.

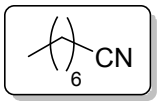
Most of the present prepared nitriles are commercially available and they are identified with authentic nitrile compounds.

6 DATAS OF NITRILES COMPOUNDS

Hexanenitrile(6):

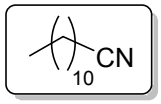
Any attempts to purify the product by chromatography gave the compound with a significant amount of ODCB solvent.

Octanenitrile (7): Colorless oil : 80% (20 mg)



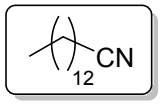
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.33 (t, *J* = 7.1 Hz, 2H), 1.59-1.72 (m, 2H), 1.39-1.50 (m, 2H), 1.20-1.37 (m, 6H), 0.88 (d, *J* = 6.9 Hz, 2H) ppm. Spectroscopic data are consistent with those reported in the literature.[5]

Dodecanenitrile (8): Yellowish oil : 65% (23 mg)



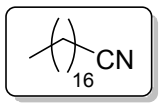
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.33 (t, *J* = 7.1 Hz, 2H), 1.57-1.72 (m, 2H), 1.39-1.49 (m, 2H), 1.20-1.37 (s, 14H), 0.88 (t, *J* = 6.7 Hz, 3H) ppm. Spectroscopic data are consistent with those reported in the literature.[6]

Tetradecanenitrile (9): Colorless oil : 71% (30 mg)



^{1}H NMR (300 MHz, $CDCl_3$) δ 2.33 (t, *J* = 7.1 Hz, 2H), 1.57-1.72 (m, 2H), 1.38-1.51 (m, 2H), 1.26 (s, 18H), 0.88 (t, *J* = 6.6 Hz, 3H) ppm. Spectroscopic data are consistent with those reported in the literature.[5]

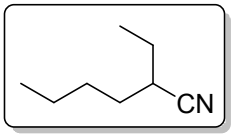
Stearonitrile (10): soft white solid 50% (26 mg)



^{1}H NMR (300 MHz, $CDCl_3$) δ 2.33 (t, *J* = 7.1 Hz, 2H), 1.57-1.73 (m, 2H), 1.36-1.51 (m, 2H), 1.23-1.30 (br, 32H), 0.88 (t, *J* = 6.6 Hz, 3H) ppm. Spectroscopic

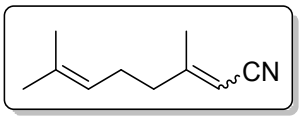
data are consistent with those reported in the literature.[7]

2-ethylhexanenitrile (11): colorless oil (7.5 mg, 30 %), as a purification on SiO_2 (Et_2O : pentane = 30:70).



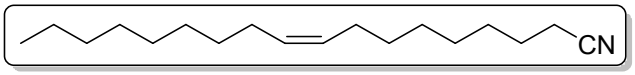
^{1}H NMR (300 MHz, $CDCl_3$) δ 2.53-2.38 (m, 1H), 1.71-1.19 (m, 8H), 1.08 (t, *J* = 7.4 Hz, 1H), 0.92 (t, *J* = 7.1 Hz, 1H). Spectroscopic data are consistent with those reported in the literature.[8]

Geranylnitrile (12): colorless oil (17 mg, 56 %) , *E*/*Z*= 6/1, as a purification on SiO_2 (Et_2O : pentane = 20:80).



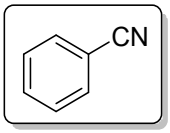
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.10 (d, *J* = 1.0 Hz, CH minor + Major , 1.12 H), 5.00-5.04 (m, CH minor + Major 1,13 H), 2.39-2.47 (m, CH_2 minor, 0.39 H), 2.09-2.25 (m, 4H, CH_2 Major), 2.05 (s, CH_3 Major, 3H), 1.91 (d, *J* = 1.4 Hz, CH_3 minor, 0.39H), 1.69 (s, CH_3 minor + Major, 3.55 H), 1.60 (s, CH_3 minor + Major, 3.32 H) ppm. Spectroscopic data are consistent with those reported in the literature.[9]

Oleonitrile/9-Octadecenenitrile (13). Yellowish oil (32 mg, 60%)



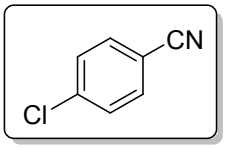
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.24-5.46 (m, 2H), 2.33 (t, *J* = 7.1 Hz, 2H), 1.92-2.06 (m, 4H), 1.61-1.70 (m, 2H), 1.23-1.37 (m, 20 H), 0.88 (t, *J* = 6.6 Hz, 3H) ppm. Spectroscopic data are consistent with those reported in the literature.[5]

Benzonitrile (2): colorless oil 50% (10 mg)



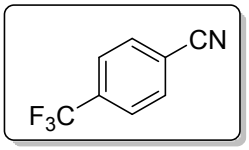
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57-7.70 (m, 3H), 7.45-7.52 (m, 2H). Spectroscopic data are consistent with those reported in the literature.[9a]

p-Chlorobenzonitrile (14): White solid 37% (10 mg);



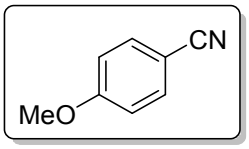
^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.61 (d, *J* = 8.5 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H) ppm. Spectroscopic data are consistent with those reported in the literature.[5]

4-(Trifluoromethyl)benzonitrile (15): Colorless oil 30% (10 mg)



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.3 Hz, 1H) ppm. ^{19}F NMR ($CDCl_3$) δ -63.53 ppm. Spectroscopic data are consistent with those reported in the literature.[10]

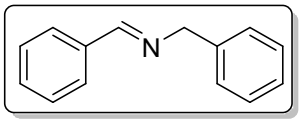
p-Methoxybenzonitrile (16): White solid 45% (12 mg);



^{1}H NMR (300 MHz, $CDCl_3$) : δ 7.59 (d, *J* = 8.9 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 3.86 (s, 3H). Spectroscopic data are consistent with those reported in the

literature.[5]

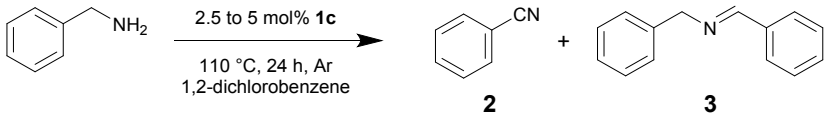
***N*-(Phenylmethylene)benzenemethanamine (3):** light yellow oil (4 mg, 15%)

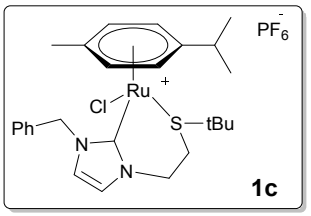


^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.81 (m, 2H), 7.48-7.39 (m, 3H), 7.40-7.33 (m, 4H), 7.30 (m, 1H), 4.85 (s, 2H) ppm. Spectroscopic data are consistent with those reported in the literature.[11]

7 OPTIMISATION CONDITIONS

Table S1 Evaluation of benzylamine oxidation under varying conditions.[a]





Entry	Additive (10%)	Solvent	Volume mL	T (C °)	Conv. (%)[b]	Selectivity (%)[b] 2	3
1		Neat	-	110	65%	22	78
2		ODCB	0.2	110	5%<[c]		
3		ODCB	1	110	70	44	56
4		tol[d]	0.2	110	80	35	65
5		CH_3CN	0.2	110	5		
6		*i*-PrOH	0.2	110	0	-	-
7		Anisole	0.2	110	100[e]	54	46
8		Anisole[g]	0.2	110	72[e]	50	50
9		ODCB[g]	0.2	110	90	58	42
10		ODCB[g]	0.2	130	100	55	45
11	KOH	ODCB[g]	0.2	110	90	50	50
12	*t*BuOK	ODCB[g]	0.2	110	100	56	44
13	Cs_2CO_3	ODCB[g]	0.2	110	100	68	32
14	K_2CO_3	ODCB[g]	0.2	110	95	63	37
15	CsCl	ODCB[g]	0.2	110	95	56	44
16	CsOAc	ODCB[g]	0.2	110	84	37	63

17	HMTA (5%)	ODCB	0.2	110	100[h]	70	30	

[a] Reaction conditions: benzylamine (0.2 mmol), 5 mol% [Ru], 24h, open vessel under argon atmosphere; [b] Conversion and selectivity were determined by ^{1}H RMN, internal reference hexadecane; [c] Closed system under argon atmosphere; [d] catalyst is not soluble; [e] presence of aldehyde, imine/aldehyde ratio 1/1.5, [g] 2.5mol% [Ru]; [h] presence of aldehyde (5%), amide (5%) and new imine (4%).

8 REPRESENTATIVE ^{1}H NMR SPECTRA OF CRUDE REACTION MIXTURES:

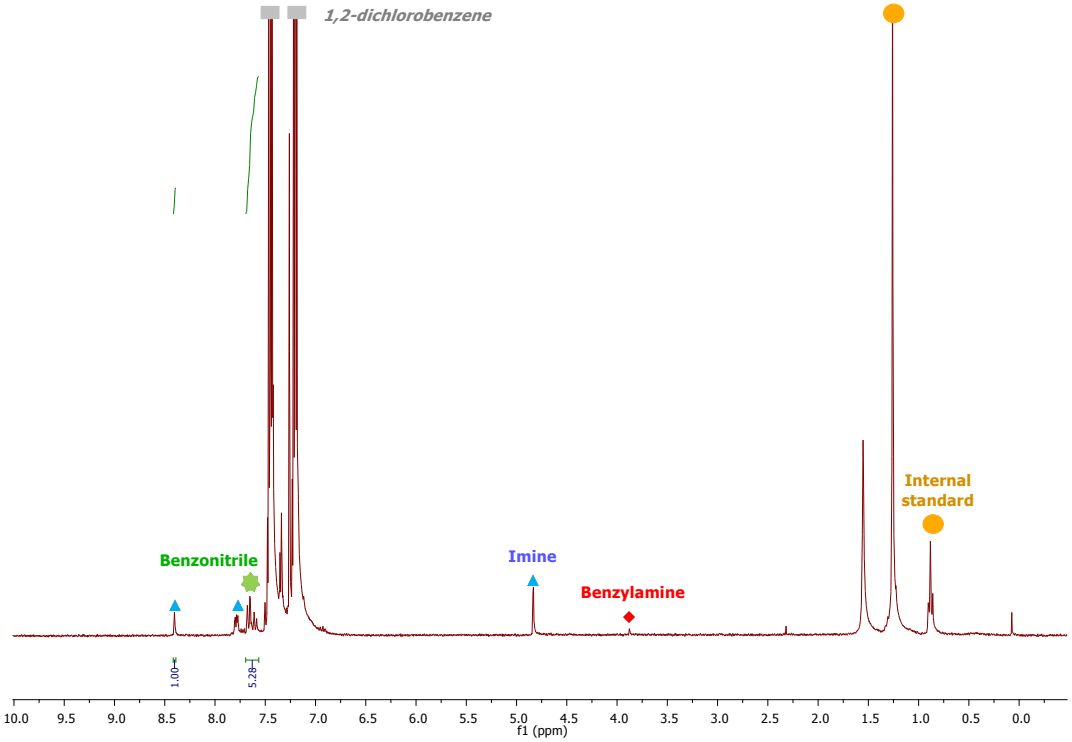


Figure S9. ^{1}H-NMR spectra of the crude reaction mixture after 26h for benzylamine substrate, (2.5 mol% of **1c**, conv 98%)

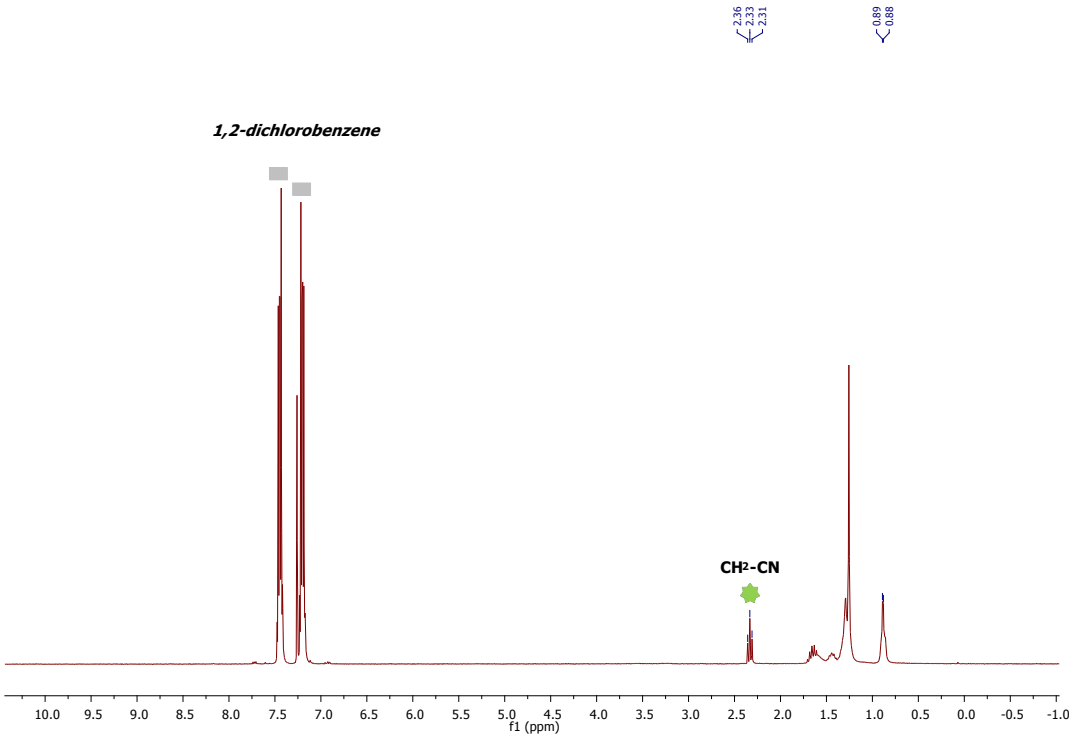


Figure S10. ^{1}H-NMR spectra of the crude reaction mixture after 30h for *n*-octylamine substrate (2.5 mol% of complex **1c**, 100%conv).

9 REPRESENTATIVE GC CHROMATOGRAM OF BENZYLAMINE DEHYDROGENATION

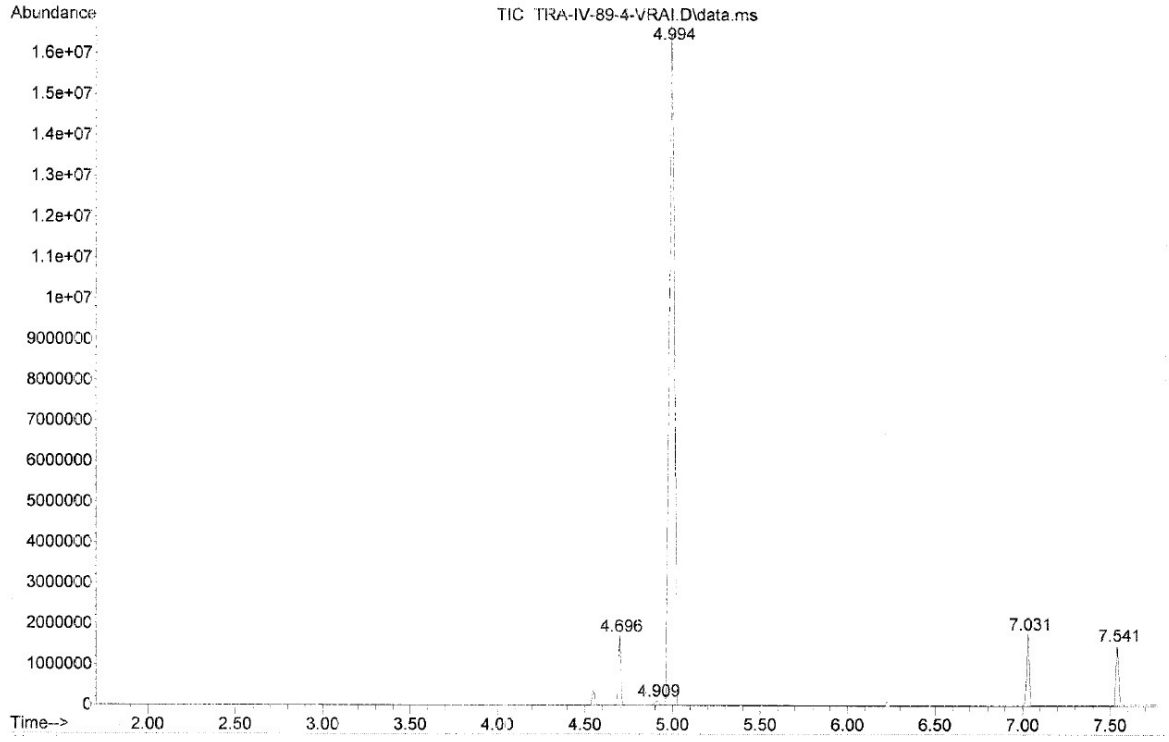


Figure S11. Representative GC chromatogram of benzylamine dehydrogenation catalysed by $[Ru(p\text{-cym})Cl_2]_2$. : benzonitrile (4.69 min), benzylamine (4.90 min), 1,2-dichlorobenzene (4.94 min) and. hexadecane (**Std**, 7.0 min) and benzylidenebenzylamine (7.5 min).

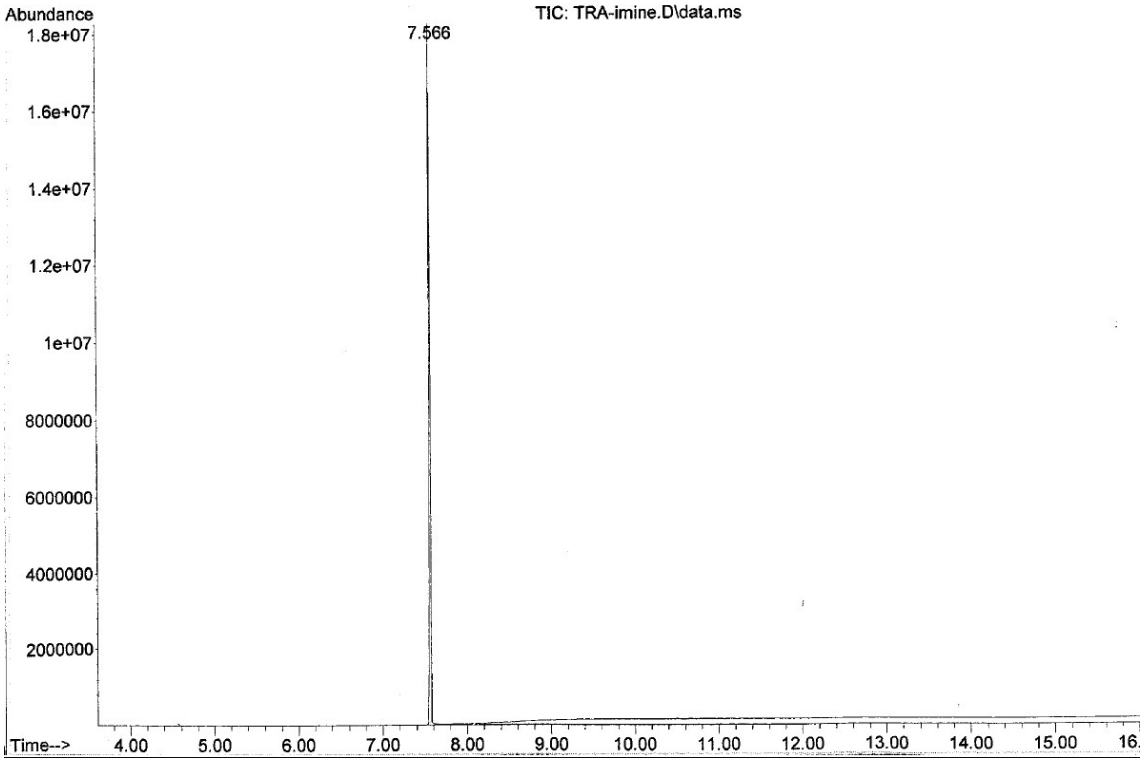


Figure S12. GC chromatogram of pure benzylidenebenzylamine product (7.5 min).

10 EVALUATION OF THE LABILITY OF THE THIOETHER MOIETY AND THE ROBUSTNESS OF THE COMPLEX 1C

Procedure:

Benzylamine (2.0 equiv, 28.4 mmol) was added dropwise to a Schleck tube containing a solution of complex **1c** (1 equiv 14.49 mmol) in dry 1,2-dichlorobenzene (ODCB, 0.1 mL) under argon. The solution was heated at 110 °C and ^{1}H NMR spectra of aliquots were the recorded over time. Addition of extra benzylamine (8.0 equiv, 115.92 mmol) to the ODCB solution was done after 18 hours, the system was again put at 110 °C and ^{1}H NMR spectra of aliquots were the recorded over time at room temperature.

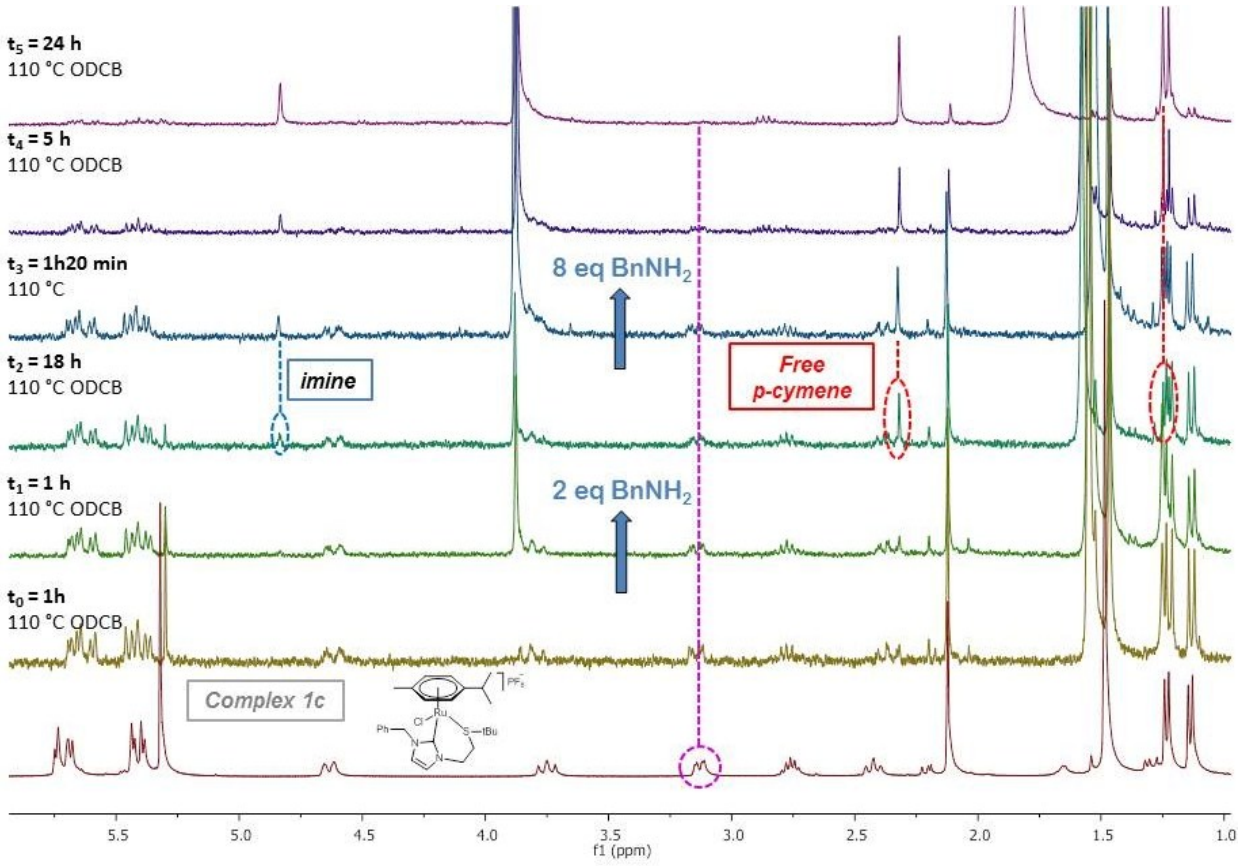


Figure S13. ^{1}H-NMR spectra of lability experiment between the benzylamine and complex **1c**

Procedure:

Complex **1c** (5 mg) was put into a NMR tube and dissolves in a 1/1 mixture of dmso-d_6/D_2O (0.5 mL in total). ^{1}H NMR spectra were the recorded over time at room temperature

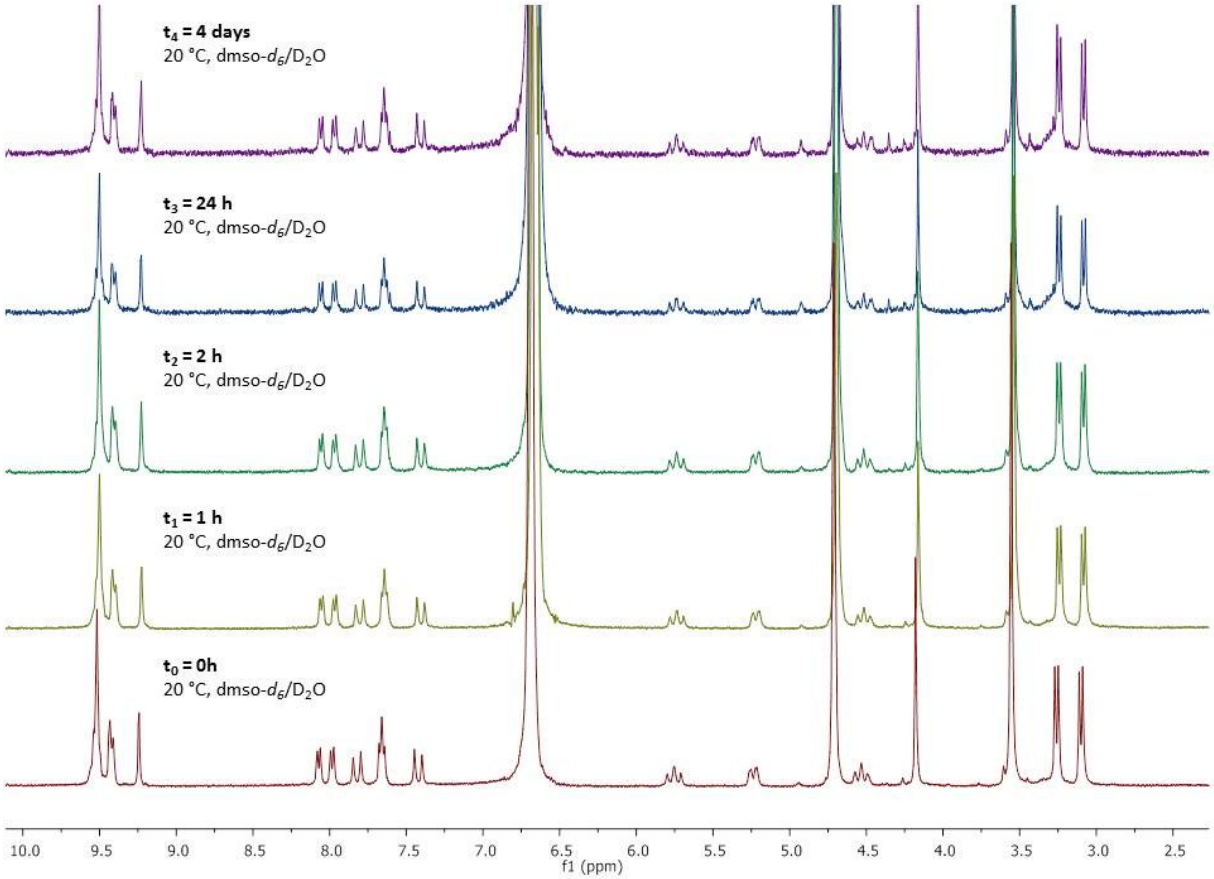


Figure S14. ^{1}H-NMR spectra of complex **1c** stability in a 1/1 mixture of dmso-d_6/D_2O

11 GAS PHASE CALCULATIONS WITH SOLVENT

DFT calculations were run with Gaussian 09.[12] Ru, S and Cl centers were described with the Stuttgart RECPs[13] and associated basis sets with additional *f*-polarization function for Ru (ζ = 1.235) and *d*-polarization functions for S (ζ = 0.503) and Cl (ζ = 0.640),[14] and 6-31G** basis sets[15] were used for all other atoms. Initial B3PW91[16] optimizations were performed with all stationary points being fully characterized via analytical frequency calculations as either minima (all positive eigenvalues) or transition states (one negative eigenvalue). IRC calculations and subsequent geometry optimizations were used to confirm the minima linked by each transition state. Single point solvent calculations at the SCRF method[17] (dicholomethane) were run at the M06L/def2TZVP level of theory.[18]

All energies are ΔH solvent corrected energies in kcal·mol^{-1}. In all figures hydrogens atoms have been removed for clarity except for $CH(CH_3)_2$ and CH_3 on the *p*-cymene substituent, the substituent in the sulphur atom and the aryl moiety of the carbene.

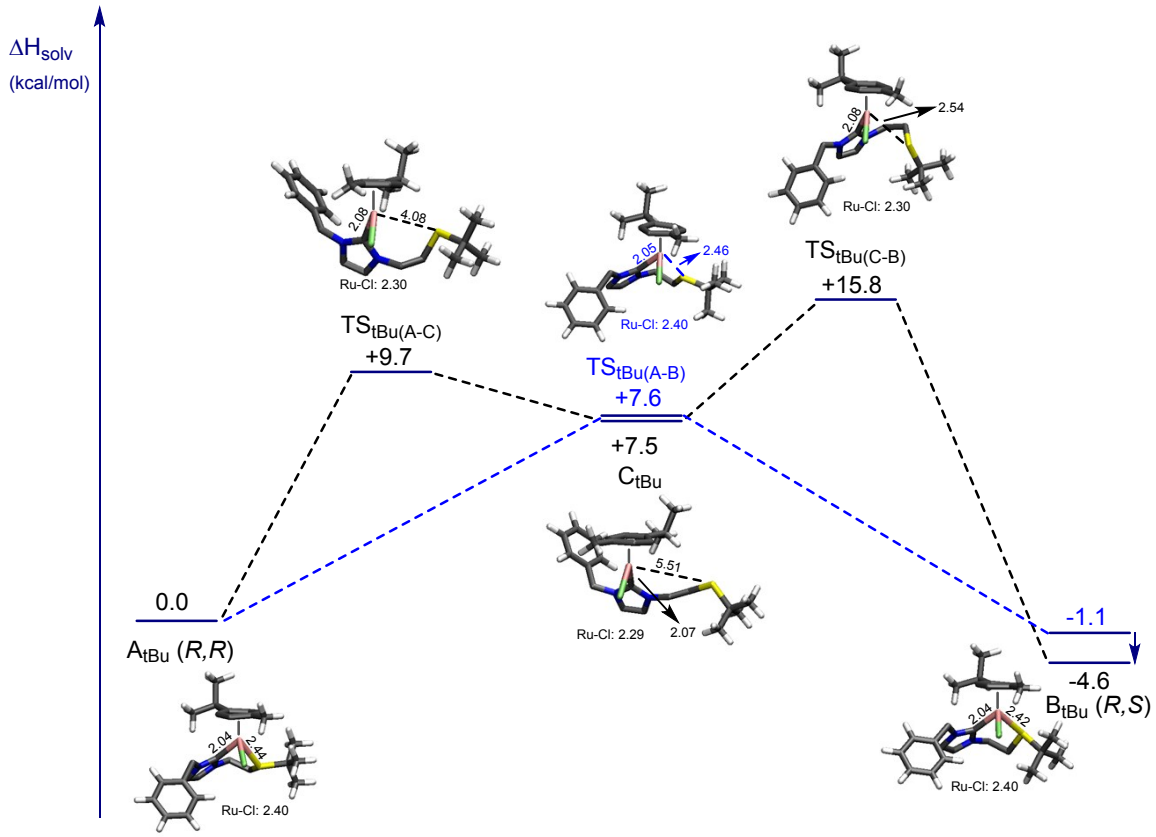


Figure S15. Reaction energy profiles computed for direct inversion of the sulphur atom (in blue) and for the coordination-discoordination of the Ru─S bond (in black) of complex 1c. The ΔH solvent corrected energies are given in kcal·mol-1.

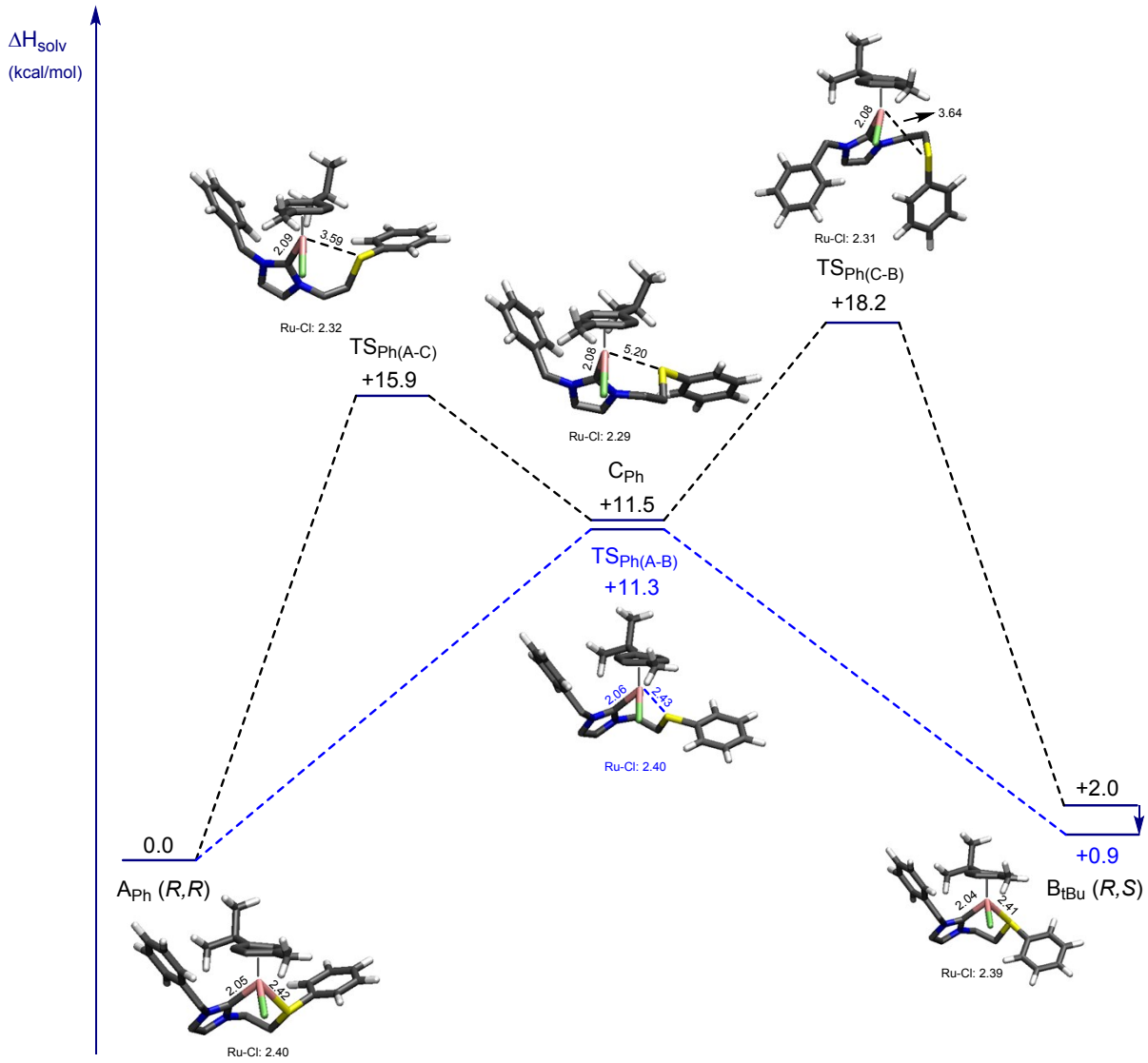


Figure S16. Reaction energy profiles computed for direct inversion of the sulphur atom (in blue) and for the coordination-discoordination of the Ru─S bond (in black) of complex **1l**. The ΔH solvent corrected energies are given in kcal·mol-1.

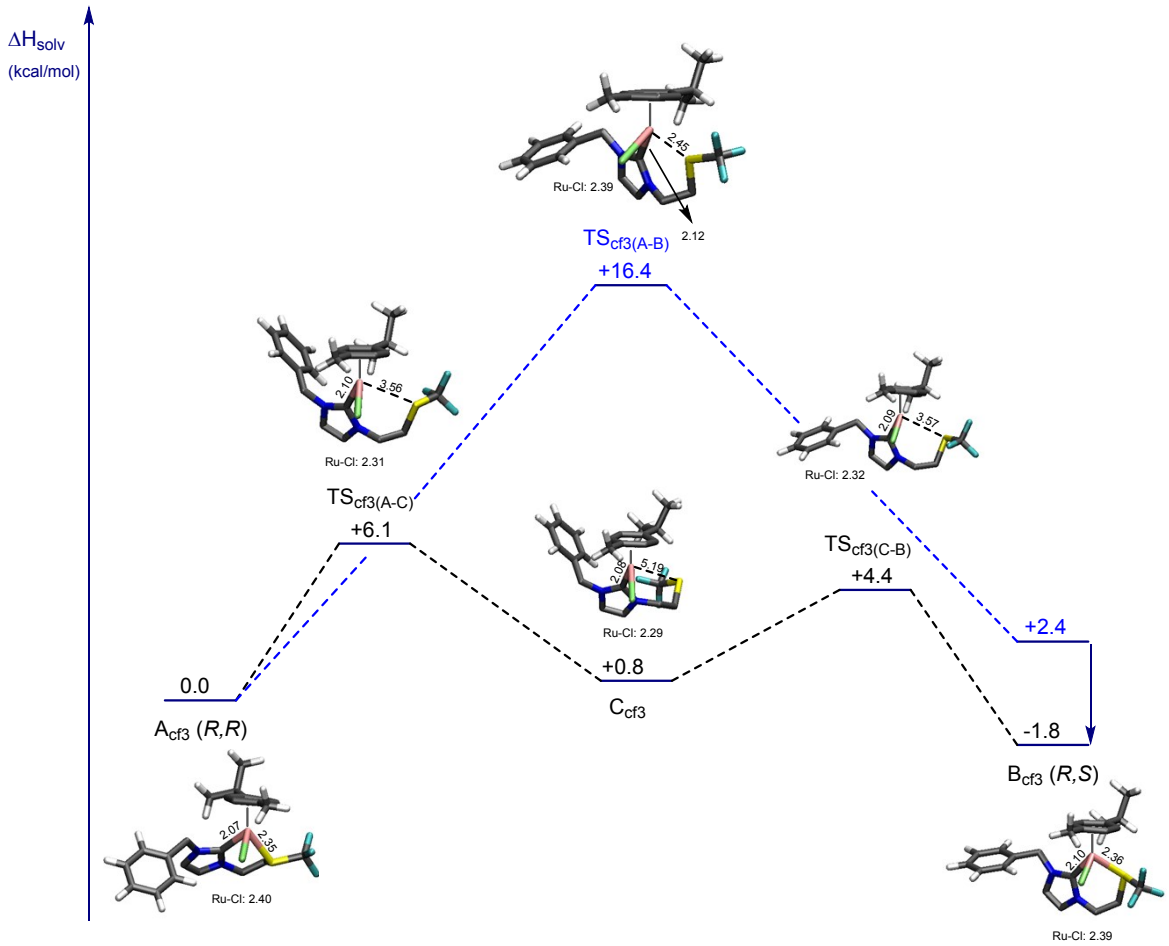


Figure S17. Reaction energy profiles computed for direct inversion of the sulphur atom (in blue) and for the coordination-discoordination of the Ru─S bond (in black) with S-CF_3 thioether group. The ΔH solvent corrected energies are given in kcal·mol-1.

Atomic coordinates of the optimized species

Table S2. Atomic coordinates of the optimized species derived from complex **1c**.[a]

1c - R_{Ru}/R_S	**1c - R_{Ru}/S_S**
E (SCF) = -1241.70497 E (SCF; solvent = DCM) = -2075.59121564 Zero-point correction = 0.569576 Thermal correction to Enthalpy = 0.603008 Thermal correction to Gibbs Free Energy = 0.50843	E (SCF) = -1241.71176 E (SCF; solvent = DCM) = -2075.59379153 Zero-point correction = 0.570827 Thermal correction to Enthalpy = 0.603810 Thermal correction to Gibbs Free Energy = 0.51108
C -0.662910 0.359059 -0.905269 C -2.586036 0.583000 -2.066481 H -3.652055 0.682936 -2.194810 C -1.584667 0.481553 -2.972543	C -0.567055 0.314072 -0.967959 C -2.540250 0.473883 -2.063544 H -3.610703 0.563464 -2.155223 C -1.574323 0.325690 -2.999009

H	-1.601190	0.489281	-4.051274	H	-1.631438	0.272756	-4.075004
C	-2.784939	0.663075	0.433032	C	-2.654142	0.649794	0.430514
H	-2.167655	0.239331	1.226577	H	-2.026322	0.225561	1.214871
H	-2.920371	1.735815	0.611206	H	-2.771675	1.725937	0.600072
C	-4.126173	-0.022761	0.368022	C	-4.007464	-0.015566	0.411392
C	-5.300102	0.728611	0.257620	C	-5.172315	0.751223	0.309857
H	-5.246105	1.815034	0.222782	H	-5.103019	1.835653	0.249706
C	-6.542033	0.095777	0.204810	C	-6.424320	0.136477	0.296355
H	-7.448444	0.688688	0.124952	H	-7.323230	0.741417	0.222300
C	-6.615934	-1.294242	0.259936	C	-6.517946	-1.250785	0.382433
H	-7.582044	-1.789002	0.221819	H	-7.491946	-1.731226	0.374210
C	-5.447616	-2.049984	0.372167	C	-5.358989	-2.021874	0.487434
H	-5.504402	-3.133428	0.425303	H	-5.430982	-3.102921	0.565043
C	-4.207641	-1.419804	0.427647	C	-4.109136	-1.409408	0.503804
H	-3.297470	-2.005294	0.528010	H	-3.205794	-2.006413	0.597590
C	0.920199	0.259609	-2.819495	C	0.908266	0.039901	-2.969676
H	1.540820	1.023474	-2.346684	H	1.566162	0.885400	-2.743619
H	0.844135	0.496096	-3.884394	H	0.725412	0.047635	-4.047156
C	1.560498	-1.108335	-2.642428	C	1.553374	-1.279005	-2.578157
H	2.613421	-1.048712	-2.928619	H	2.370548	-1.512370	-3.265132
H	1.067889	-1.856667	-3.268145	H	0.812295	-2.080156	-2.608783
C	3.025773	-2.605340	-0.613647	C	2.612269	-2.956948	-0.438887
C	3.052597	-3.750535	-1.630890	C	3.021954	-2.920098	1.032132
H	3.151091	-3.396039	-2.661284	H	2.189850	-2.615759	1.670612
H	2.156604	-4.373066	-1.557350	H	3.876135	-2.253903	1.194519
H	3.921531	-4.384510	-1.423027	H	3.332295	-3.927141	1.330817
C	4.254677	-1.714832	-0.755750	C	1.410072	-3.867627	-0.664781
H	5.152895	-2.320070	-0.589189	H	1.665279	-4.866005	-0.290763
H	4.257514	-0.909375	-0.019549	H	1.170609	-3.983916	-1.725832
H	4.348701	-1.276928	-1.754215	H	0.529599	-3.514674	-0.126834
C	2.901104	-3.165345	0.804390	C	3.797511	-3.375195	-1.313787
H	2.017498	-3.800111	0.909686	H	4.664873	-2.725427	-1.166057
H	2.834917	-2.371968	1.552715	H	3.546349	-3.389867	-2.378596
H	3.787727	-3.769872	1.023903	H	4.088085	-4.395359	-1.038708
C	1.628648	0.589539	2.665415	C	1.554543	0.757392	2.650316
C	2.689472	0.596640	1.753589	C	2.665047	0.838624	1.800104
H	3.550100	-0.038096	1.935679	H	3.554767	0.257356	2.018672
C	2.630101	1.388403	0.560711	C	2.610138	1.618421	0.601614
H	3.458598	1.349502	-0.140666	H	3.465521	1.604647	-0.068339
C	1.572737	2.298733	0.315456	C	1.500043	2.434647	0.272759
C	0.466409	2.244974	1.222036	C	0.360947	2.324200	1.132532
H	-0.416571	2.843919	1.028997	H	-0.548755	2.861184	0.888073
C	0.472688	1.382530	2.336860	C	0.372365	1.482324	2.262783
H	-0.404962	1.320648	2.971828	H	-0.527408	1.375854	2.860283
C	1.629950	-0.261817	3.895452	C	1.544908	-0.090637	3.882840
H	2.557961	-0.829062	3.991188	H	0.738659	-0.829318	3.824140
H	0.790037	-0.964047	3.864457	H	1.371267	0.535477	4.764594
H	1.516667	0.367132	4.784851	H	2.492287	-0.616634	4.014781
C	1.691936	3.339582	-0.781497	C	1.592750	3.429543	-0.867924
H	2.265650	2.885303	-1.600997	H	2.210941	2.964482	-1.648044
C	2.526882	4.516247	-0.241290	C	2.342761	4.678237	-0.367877
H	2.018341	5.004156	0.596996	H	1.783336	5.175676	0.431599
H	2.673172	5.264684	-1.025782	H	2.468120	5.394690	-1.185111
H	3.512355	4.190814	0.104526	H	3.335360	4.429216	0.018703

C	0.359606	3.841488	-1.340640	C	0.249060	3.821521	-1.484323
H	-0.282892	3.027002	-1.686339	H	-0.330186	2.951910	-1.806853
H	0.543568	4.507825	-2.188029	H	0.416574	4.457212	-2.358264
H	-0.193908	4.424185	-0.596554	H	-0.361209	4.403067	-0.784781
N	-2.008403	0.506884	-0.812069	N	-1.913324	0.463414	-0.831951
N	-0.414656	0.348960	-2.246631	N	-0.375294	0.233342	-2.313726
S	1.398497	-1.688794	-0.903069	S	2.266787	-1.139710	-0.898612
Ru	0.781437	0.182785	0.529939	Ru	0.871795	0.275436	0.484213
Cl	-0.518369	-1.585721	1.511225	Cl	-0.331723	-1.603026	1.369354

1c - intermediate	**1c – TS-inversion**
E (SCF) = -1241.67804 E (SCF; solvent = DCM) = -2075.57076100 Zero-point correction = 0.567333 Thermal correction to Enthalpy = 0.600013 Thermal correction to Gibbs Free Energy = 0.50386	E (SCF) = -1241.69261 E (SCF; solvent = DCM) = -2075.57651265 Zero-point correction = 0.567933 Thermal correction to Enthalpy = 0.600372 Thermal correction to Gibbs Free Energy = 0.50745

C	0.310426	-0.627292	-1.101776	C	-0.620485	0.287337	-0.945110
C	0.339835	-2.639288	-2.118172	C	-2.550510	0.293564	-2.119752
H	0.781295	-3.499555	-2.597041	H	-3.619288	0.333904	-2.256322
C	-0.953598	-2.337207	-1.851568	C	-1.543315	0.130416	-3.008637
H	-1.859588	-2.884214	-2.058415	H	-1.557054	0.012242	-4.080938
C	2.549676	-1.493464	-1.816647	C	-2.757932	0.643129	0.354968
H	2.789252	-0.458844	-2.076748	H	-2.142213	0.293845	1.185045
H	2.802365	-2.099981	-2.693313	H	-2.906059	1.725506	0.440751
C	3.356530	-1.944429	-0.616733	C	-4.091838	-0.059811	0.343642
C	4.670264	-1.479352	-0.481443	C	-5.272332	0.665529	0.156172
H	5.079414	-0.792990	-1.220712	H	-5.228793	1.744496	0.020973
C	5.467376	-1.904945	0.579519	C	-6.507380	0.017257	0.152997
H	6.486566	-1.540292	0.668593	H	-7.419030	0.590469	0.012261
C	4.958796	-2.799852	1.520883	C	-6.567852	-1.362523	0.335389
H	5.579223	-3.133710	2.347037	H	-7.528616	-1.869032	0.335978
C	3.653867	-3.271631	1.388784	C	-5.393003	-2.092227	0.525066
H	3.255747	-3.979425	2.110218	H	-5.439371	-3.166782	0.676993
C	2.856799	-2.848971	0.323979	C	-4.159936	-1.446253	0.531136
H	1.844531	-3.232230	0.227121	H	-3.244448	-2.010153	0.689780
C	-2.163122	-0.366389	-0.849874	C	0.954964	0.021116	-2.878093
H	-2.706273	-0.086831	-1.757370	H	1.570456	0.848142	-2.514828
H	-1.826427	0.560850	-0.379248	H	0.834941	0.141969	-3.957901
C	-3.059953	-1.147053	0.109699	C	1.643980	-1.305744	-2.591775
H	-2.464120	-1.562960	0.927327	H	2.622802	-1.307358	-3.079290
H	-3.554415	-1.986441	-0.387399	H	1.048579	-2.141662	-2.968520
C	-5.915294	-0.469217	-0.040404	C	2.969412	-2.914542	-0.413327
C	-5.763876	-0.273681	-1.548209	C	2.309874	-4.166547	-0.989874
C	-6.358068	-1.893845	0.293228	H	2.211457	-4.116253	-2.078546
C	-6.908866	0.546604	0.533495	H	1.322196	-4.331221	-0.553034
C	2.318637	2.845128	0.246079	H	2.939540	-5.034533	-0.762364
C	1.020585	3.253487	0.581116	C	4.347301	-2.668145	-1.021675
H	0.637386	4.197248	0.206878	H	4.995251	-3.521089	-0.788217
C	0.135340	2.352270	1.250444	H	4.813484	-1.767046	-0.614335
H	-0.901802	2.646979	1.390419	H	4.311353	-2.582480	-2.111893

C	0.568886	1.098152	1.784931	C	3.034201	-2.982214	1.110385
C	1.868839	0.677712	1.425236	H	2.039718	-3.071570	1.554310
H	2.213086	-0.320434	1.670969	H	3.530883	-2.103717	1.531368
C	2.690195	1.499229	0.600526	H	3.623002	-3.862202	1.391256
H	3.641133	1.101732	0.258922	C	1.503029	0.925015	2.667341
C	3.243439	3.708021	-0.555130	C	2.608604	0.908835	1.808429
H	2.698671	4.476202	-1.106799	H	3.477367	0.311816	2.064368
H	3.822806	3.116227	-1.268026	C	2.577577	1.603844	0.556428
H	3.950188	4.204557	0.120181	H	3.430458	1.515515	-0.110363
C	-0.366597	0.296943	2.665420	C	1.501026	2.444940	0.182107
H	-1.377528	0.415332	2.252031	C	0.352035	2.409951	1.033705
C	-0.369564	0.926300	4.071227	H	-0.545098	2.947794	0.747614
H	0.618991	0.851380	4.536391	C	0.334591	1.638670	2.218651
H	-1.084861	0.402407	4.711728	H	-0.572014	1.590888	2.813231
H	-0.654145	1.982424	4.046009	C	1.472232	0.164380	3.954778
C	-0.040770	-1.193994	2.736173	H	2.409648	-0.367349	4.128589
H	0.013003	-1.650237	1.742962	H	0.654852	-0.563981	3.937919
H	-0.814531	-1.713734	3.308247	H	1.302972	0.851522	4.790633
H	0.910487	-1.375262	3.247596	C	1.628230	3.374932	-1.008678
N	1.101338	-1.581354	-1.654150	H	2.243736	2.857345	-1.757205
N	-0.953082	-1.101770	-1.228660	C	2.405498	4.628700	-0.565684
S	-4.325551	-0.059169	0.860457	H	1.852718	5.181586	0.201370
Cl	0.590664	1.914066	-2.616789	H	2.556380	5.298148	-1.417740
Ru	0.858263	1.262297	-0.441639	H	3.387864	4.374733	-0.156827
H	-7.897093	0.375258	0.093544	C	0.301078	3.767384	-1.659597
H	-7.004176	0.445627	1.619227	H	-0.296297	2.896889	-1.944871
H	-6.609998	1.573904	0.304185	H	0.492762	4.354819	-2.561860
H	-7.321698	-2.102707	-0.186217	H	-0.301974	4.396815	-0.996395
H	-5.647896	-2.643730	-0.071094	N	-1.971929	0.387826	-0.867627
H	-6.473783	-2.029246	1.371708	N	-0.368117	0.133235	-2.277443
H	-6.727003	-0.452016	-2.040750	S	1.831748	-1.453012	-0.786795
H	-5.442587	0.743624	-1.788777	Ru	0.789229	0.330480	0.544699
H	-5.048728	-0.979971	-1.984211	Cl	-0.435306	-1.467901	1.556030

1c – TS1-decoordination	**1c – TS2-coordination**
E (SCF) = -1241.67303 E (SCF; solvent = DCM) = -2075.56683994 Zero-point correction = 0.568026 Thermal correction to Enthalpy = 0.599577 Thermal correction to Gibbs Free Energy = 0.50875	E (SCF) = -1241.66375 E (SCF; solvent = DCM) = -2075.55792303 Zero-point correction = 0.567551 Thermal correction to Enthalpy = 0.600329 Thermal correction to Gibbs Free Energy = 0.50554

C	0.405545	-0.634366	-1.343551	C	0.294194	-0.146003	-0.838048
C	1.474310	-2.350483	-2.358387	C	2.220733	0.175249	-1.975939
H	2.318766	-2.895324	-2.751102	H	3.270418	0.054496	-2.190809
C	0.148962	-2.620637	-2.391027	C	1.266416	0.923767	-2.573326
H	-0.390580	-3.455696	-2.810219	H	1.321262	1.584961	-3.423590
C	2.889688	-0.420991	-1.674364	C	2.340733	-1.455833	-0.094931
H	2.649734	0.640672	-1.592948	H	1.759673	-1.593013	0.816813
H	3.355277	-0.553270	-2.658194	H	2.355775	-2.403123	-0.644796
C	3.858452	-0.844151	-0.588846	C	3.752115	-1.026847	0.219571
C	4.959570	-0.015122	-0.336950	C	4.833275	-1.722721	-0.329354

H	5.083252	0.907689	-0.900927
C	5.910861	-0.369605	0.615760
H	6.760207	0.282210	0.797872
C	5.774794	-1.560268	1.330302
H	6.517302	-1.839400	2.071661
C	4.684947	-2.391023	1.082581
H	4.575588	-3.323209	1.629218
C	3.730744	-2.036774	0.126656
H	2.887665	-2.696542	-0.055803
C	-1.953321	-1.436482	-1.794501
H	-2.274555	-1.808529	-2.772673
H	-2.197193	-0.374455	-1.763049
C	-2.664438	-2.214478	-0.678213
H	-2.035884	-3.036283	-0.322983
H	-3.575576	-2.671604	-1.072171
C	-4.912664	-0.761662	0.483969
C	-5.073795	-0.036221	-0.851228
C	-5.797199	-2.006978	0.550717
C	-5.239838	0.179860	1.647581
C	0.634153	3.187746	0.316475
C	-0.608188	2.900132	0.905383
H	-1.451331	3.561194	0.733907
C	-0.815132	1.653942	1.564229
H	-1.818525	1.391724	1.885941
C	0.240957	0.727257	1.824338
C	1.481750	1.004199	1.208804
H	2.290870	0.283458	1.259131
C	1.652571	2.176506	0.413725
H	2.596934	2.336768	-0.097601
C	0.866981	4.432194	-0.481680
H	-0.070737	4.851631	-0.850060
H	1.516123	4.238214	-1.338766
H	1.356278	5.181140	0.152313
C	-0.005687	-0.462592	2.726091
H	-1.069329	-0.712164	2.637883
C	0.257743	-0.022109	4.178353
H	1.310336	0.242589	4.325895
H	0.016387	-0.839358	4.864390
H	-0.351527	0.842525	4.459127
C	0.801894	-1.708862	2.370754
H	0.632967	-2.012210	1.333269
H	0.500160	-2.537279	3.017974
H	1.877064	-1.561496	2.514411
N	1.616894	-1.134200	-1.716240
N	-0.493674	-1.556698	-1.784069
S	-3.123186	-1.231031	0.792958
Cl	-0.844867	1.886886	-2.412809
Ru	-0.028330	1.160041	-0.383541
H	-6.293362	0.473873	1.591845
H	-5.080599	-0.305175	2.616050
H	-4.637642	1.093391	1.607994
H	-6.847215	-1.718310	0.424686
H	-5.566495	-2.724322	-0.243275
H	-5.692940	-2.515980	1.512521
H	4.653356	-2.571367	-0.986244
C	6.142482	-1.344592	-0.032179
H	6.974814	-1.895634	-0.459920
C	6.378036	-0.263513	0.813994
H	7.396503	0.031947	1.048388
C	5.302917	0.435942	1.365182
H	5.484608	1.274084	2.031843
C	3.995838	0.057391	1.072491
H	3.158633	0.594555	1.509613
C	-1.154085	1.335496	-2.338371
H	-1.765082	0.566111	-2.824035
H	-0.845719	2.025003	-3.125505
C	-2.032928	2.091817	-1.320662
H	-2.816770	1.428822	-0.952093
H	-2.549449	2.894626	-1.856163
C	-0.643430	4.455724	-0.239165
C	0.095560	4.884543	1.032777
H	0.943957	4.226891	1.243990
H	-0.568166	4.884345	1.903060
H	0.476594	5.903344	0.903628
C	0.315711	4.416394	-1.426826
H	0.740448	5.414440	-1.586788
H	-0.198499	4.137140	-2.352674
H	1.140301	3.719671	-1.252861
C	-1.824033	5.386683	-0.513850
H	-2.502692	5.429829	0.342009
H	-2.398342	5.078893	-1.394162
H	-1.454100	6.400080	-0.710320
C	-2.788734	-1.252403	2.007855
C	-3.195507	-0.681396	0.758992
H	-3.775839	0.237506	0.775388
C	-2.888605	-1.284758	-0.492799
H	-3.273460	-0.846275	-1.407698
C	-2.014624	-2.394126	-0.565526
C	-1.453612	-2.848772	0.669754
H	-0.692295	-3.620974	0.661834
C	-1.897692	-2.335048	1.931468
H	-1.423837	-2.699096	2.837899
C	-3.178142	-0.627759	3.312920
H	-2.416598	-0.800117	4.076079
H	-4.122098	-1.060611	3.663415
H	-3.319697	0.450617	3.207662
C	-1.715521	-3.039757	-1.902301
H	-1.736428	-2.239495	-2.653906
C	-2.856165	-4.022550	-2.226406
H	-2.891583	-4.837285	-1.495546
H	-2.696256	-4.464971	-3.213891
H	-3.832759	-3.529493	-2.231005
C	-0.356962	-3.733634	-1.986413
H	0.459289	-3.054076	-1.728280
H	-0.188519	-4.087591	-3.007055
H	-0.303734	-4.610543	-1.332578
N	1.614411	-0.468538	-0.917820
N	0.088429	0.714334	-1.876872

H	-6.112975	0.293828	-0.965164	S	-1.274077	2.743954	0.197204
H	-4.429626	0.846083	-0.910958	Ru	-1.049369	-0.763571	0.632130
H	-4.853059	-0.686667	-1.703621	Cl	0.390945	0.002931	2.260511

Table S3. Atomic coordinates of the optimized species derived from complex **1f**.[a]

1f - R_{Ru}/R_S	**1f - R_{Ru}/S_S**
E (SCF) = -1315.46298 E (SCF; solvent = DCM) = -2149.40486696 Zero-point correction = 0.537952 Thermal correction to Enthalpy = 0.570433 Thermal correction to Gibbs Free Energy = 0.47665	E (SCF) = -1315.46449 E (SCF; solvent = DCM) = -2149.40230088 Zero-point correction = 0.537463 Thermal correction to Enthalpy = 0.569237 Thermal correction to Gibbs Free Energy = 0.47760
C -0.736205 1.399971 -0.531482	C 0.439685 -0.668721 1.218337
C -2.300650 2.998669 -0.878560	C 1.551751 -2.152348 2.519285
H -3.254384 3.394797 -1.190540	H 2.223205 -2.969784 2.730936
C -1.211497 3.614179 -0.363453	C 0.785952 -1.398768 3.341014
H -1.025110 4.651329 -0.132221	H 0.656902 -1.423407 4.411824
C -2.939760 0.686287 -1.538338	C 1.979532 -2.315225 0.075511
H -2.342915 -0.104500 -1.996479	H 1.296789 -2.199238 -0.768372
H -3.451412 1.198333 -2.361345	H 2.026366 -3.389918 0.285788
C -3.957207 0.126382 -0.565764	C 3.363762 -1.792617 -0.249293
C -4.624310 -1.052570 -0.923218	C 3.881483 -2.059575 -1.523541
H -4.385864 -1.540790 -1.866252	H 3.280080 -2.610883 -2.243953
C -5.601526 -1.596578 -0.092896	C 5.163485 -1.641018 -1.871980
H -6.111302 -2.509318 -0.387344	H 5.550536 -1.858960 -2.863143
C -5.924427 -0.970931 1.111339	C 5.947721 -0.946087 -0.951090
H -6.686171 -1.393551 1.759495	H 6.947525 -0.619955 -1.221229
C -5.268776 0.203841 1.472897	C 5.442581 -0.680292 0.319693
H -5.521967 0.703654 2.403662	H 6.050752 -0.149458 1.046708
C -4.292798 0.752214 0.638470	C 4.159060 -1.103269 0.670914
H -3.796275 1.672670 0.933083	H 3.783483 -0.893178 1.668742
C 1.078276 2.877466 0.331851	C -0.854060 0.461897 3.037359
H 1.253514 2.269136 1.223168	H -0.535926 1.475496 2.772300
H 1.126445 3.929198 0.628319	H -0.845443 0.391286 4.127745
C 2.118681 2.601775 -0.741123	C -2.253697 0.174146 2.520428
H 3.108956 2.948326 -0.437458	H -3.001289 0.731808 3.090579
H 1.847943 3.105688 -1.673029	H -2.476882 -0.892592 2.581639
C 0.207867 -2.682232 -0.524276	C -0.031462 0.955982 -2.604362
C 1.355912 -2.285301 0.174337	C -0.794373 1.946971 -1.967762
H 2.330210 -2.648087 -0.135809	H -1.765856 2.220054 -2.366608
C 1.266675 -1.336303 1.242085	C -0.333639 2.542828 -0.753016
H 2.184482 -1.009959 1.722341	H -0.977138 3.260075 -0.249951
C 0.029889 -0.842427 1.723694	C 0.938169 2.262471 -0.192939
C -1.130031 -1.216930 0.974944	C 1.686334 1.223808 -0.827380
H -2.098021 -0.793899 1.221749	H 2.623293 0.886590 -0.396878
C -1.041801 -2.083264 -0.136831	C 1.204175 0.566325 -1.980414

H	-1.939172	-2.308271	-0.702967	H	1.785604	-0.243826	-2.407012
C	0.264166	-3.628273	-1.681568	C	-0.497010	0.269634	-3.849148
H	1.288115	-3.942110	-1.892787	H	-1.483104	0.622182	-4.156738
H	-0.143254	-3.151055	-2.578371	H	-0.553220	-0.810828	-3.684932
H	-0.334608	-4.518807	-1.461813	H	0.211507	0.459887	-4.662652
C	-0.023842	-0.048343	3.013962	C	1.465860	3.102665	0.953829
H	0.915376	0.518854	3.078190	H	0.597753	3.385695	1.565346
C	-0.049556	-1.036162	4.194772	C	2.067558	4.398097	0.378940
H	-0.959821	-1.644811	4.172991	H	2.931412	4.178996	-0.257744
H	-0.032690	-0.491706	5.143699	H	2.405347	5.049979	1.190095
H	0.809710	-1.713117	4.176957	H	1.339292	4.953284	-0.219633
C	-1.189101	0.936636	3.110369	C	2.477289	2.391507	1.853291
H	-1.211032	1.631264	2.265953	H	2.083640	1.453971	2.256629
H	-1.102414	1.522543	4.030055	H	2.740203	3.038367	2.695270
H	-2.153084	0.419422	3.150068	H	3.406666	2.168884	1.319142
N	-1.999931	1.651706	-0.973157	N	1.334786	-1.696862	1.231236
N	-0.269293	2.622519	-0.152190	N	0.118409	-0.495729	2.531561
S	2.273793	0.820882	-1.178519	S	-2.383949	0.735674	0.778893
Cl	-0.055087	-0.392788	-2.852260	Cl	-1.082392	-1.752217	-1.139131
Ru	0.292235	-0.367815	-0.472268	Ru	-0.303176	0.374099	-0.376597
C	3.734410	0.331518	-0.242327	C	-3.840308	-0.159932	0.220544
C	4.060250	0.811260	1.030305	C	-4.857081	0.619575	-0.338884
C	5.233155	0.379322	1.648690	C	-6.025574	0.003631	-0.784616
C	6.069063	-0.537932	1.011656	C	-6.176944	-1.376197	-0.660342
C	5.738068	-1.016971	-0.254784	C	-5.158373	-2.145072	-0.096664
C	4.576403	-0.578499	-0.889838	C	-3.979955	-1.544774	0.339905
H	3.418069	1.520453	1.543556	H	-4.741515	1.697178	-0.412412
H	5.491896	0.761379	2.631881	H	-6.819447	0.605832	-1.215911
H	6.980990	-0.869931	1.498171	H	-7.090519	-1.854100	-1.001031
H	6.393543	-1.717928	-0.762793	H	-5.273797	-3.220995	-0.006886
H	4.334301	-0.922480	-1.891671	H	-3.176521	-2.151602	0.740278

1f - intermediate	**1f – TS-inversion**
E (SCF) = -1315.43132 E (SCF; solvent = DCM) = -2149.38107347 Zero-point correction = 0.536866 Thermal correction to Enthalpy = 0.568386 Thermal correction to Gibbs Free Energy = 0.47498	E (SCF) = -1315.44528 E (SCF; solvent = DCM) = -2149.38465656 Zero-point correction = 0.537095 Thermal correction to Enthalpy = 0.568302 Thermal correction to Gibbs Free Energy = 0.47777

C	-0.530391	0.061435	-1.316581	C	-0.620881	1.029447	-0.992877
C	-0.001136	1.779112	-2.675948	C	-1.844029	2.104792	-2.563276
H	-0.166433	2.691164	-3.228130	H	-2.599399	2.205789	-3.326852
C	1.100277	1.000066	-2.559108	C	-0.959936	3.000310	-2.066780
H	2.082512	1.110487	-2.988299	H	-0.791157	4.038367	-2.307047
C	-2.363930	1.684505	-1.850288	C	-2.412127	-0.289134	-2.180848
H	-3.022253	0.813188	-1.802361	H	-1.746937	-1.143318	-2.038489
H	-2.562650	2.169540	-2.812558	H	-2.651260	-0.257555	-3.249730
C	-2.657721	2.639651	-0.712128	C	-3.682550	-0.429674	-1.368164
C	-3.988674	2.810842	-0.311965	C	-4.275198	-1.696569	-1.289782
H	-4.778988	2.248353	-0.806117	H	-3.805887	-2.541646	-1.789823
C	-4.314735	3.713447	0.698128	C	-5.467241	-1.881697	-0.592983

H	-5.351909	3.839450	0.994764	H	-5.915677	-2.869821	-0.545552
C	-3.312033	4.455099	1.322937	C	-6.083086	-0.802021	0.040316
H	-3.564601	5.159717	2.109495	H	-7.012671	-0.944769	0.582990
C	-1.986018	4.293274	0.926019	C	-5.502373	0.462095	-0.035814
H	-1.200840	4.874494	1.400801	H	-5.981964	1.310785	0.443789
C	-1.659327	3.392252	-0.088381	C	-4.310585	0.649107	-0.738817
H	-0.621961	3.281092	-0.391780	H	-3.875874	1.643385	-0.797465
C	1.598538	-1.222847	-1.472349	C	0.826406	2.968308	-0.316177
H	1.473221	-1.915695	-2.311963	H	0.635203	2.759070	0.739622
H	1.192842	-1.710304	-0.580767	H	0.739097	4.047322	-0.466867
C	3.076254	-0.916982	-1.284850	C	2.230838	2.515028	-0.689937
H	3.510615	-0.454530	-2.176403	H	2.961869	3.046118	-0.075199
H	3.593467	-1.867195	-1.126769	H	2.444333	2.690326	-1.747470
C	-3.411035	-2.147431	0.851113	C	0.029855	-2.465335	1.242546
C	-2.300221	-2.926942	1.200873	C	0.986348	-1.701863	1.927088
H	-2.311453	-3.996498	1.017804	H	1.985817	-2.096981	2.075828
C	-1.084733	-2.297724	1.614395	C	0.683516	-0.368580	2.349301
H	-0.202879	-2.915658	1.763790	H	1.469644	0.219414	2.814593
C	-0.992521	-0.897120	1.891762	C	-0.607850	0.202437	2.220107
C	-2.103589	-0.110731	1.513884	C	-1.550407	-0.555422	1.461671
H	-2.050333	0.971268	1.556056	H	-2.518897	-0.132281	1.216691
C	-3.251602	-0.717401	0.926934	C	-1.231759	-1.837759	0.950633
H	-4.047654	-0.076133	0.560462	H	-1.964641	-2.361471	0.346561
C	-4.664494	-2.748046	0.294601	C	0.320115	-3.845481	0.745934
H	-4.489252	-3.753179	-0.092688	H	1.353381	-4.134451	0.946203
H	-5.073367	-2.134569	-0.512198	H	0.148604	-3.903643	-0.332907
H	-5.420399	-2.809466	1.086257	H	-0.345192	-4.560865	1.242000
C	0.261744	-0.341079	2.531370	C	-0.942266	1.508150	2.913754
H	1.118294	-0.840988	2.059370	H	-0.026274	2.115692	2.911000
C	0.254644	-0.726020	4.022845	C	-1.290719	1.208514	4.383345
H	-0.584151	-0.254600	4.545824	H	-2.189435	0.586381	4.451490
H	1.180355	-0.387362	4.496740	H	-1.485557	2.140324	4.922667
H	0.179804	-1.807968	4.168964	H	-0.477806	0.685061	4.895171
C	0.441693	1.164743	2.356925	C	-2.059931	2.312504	2.248768
H	0.431276	1.457728	1.303630	H	-1.856841	2.505878	1.191392
H	1.406098	1.467121	2.773072	H	-2.173417	3.275738	2.754396
H	-0.333515	1.730524	2.885026	H	-3.024035	1.798391	2.319836
N	-0.991970	1.189680	-1.910212	N	-1.629322	0.911479	-1.897798
N	0.759897	-0.046324	-1.721525	N	-0.223533	2.331169	-1.104471
S	3.355399	0.171065	0.171086	S	2.310569	0.725927	-0.341804
Cl	-1.853370	-2.447194	-2.227807	Cl	0.627778	-1.613734	-1.831069
Ru	-1.597088	-1.353292	-0.234255	Ru	0.231195	-0.410126	0.206989
C	5.149229	0.220812	0.191202	C	4.009198	0.187393	-0.342169
C	5.879295	-0.817262	0.780698	C	4.871924	0.551947	0.697843
C	7.270618	-0.752487	0.812365	C	6.193139	0.112253	0.669740
C	7.933091	0.349072	0.270652	C	6.637008	-0.704177	-0.371740
C	7.204520	1.388909	-0.305017	C	5.764860	-1.078900	-1.393188
C	5.812594	1.327967	-0.347491	C	4.444975	-0.630122	-1.390302
H	5.358185	-1.664366	1.217493	H	4.513856	1.170150	1.515763
H	7.836873	-1.559024	1.269032	H	6.872504	0.398309	1.467192
H	9.017466	0.398992	0.302543	H	7.666059	-1.050807	-0.384387
H	7.718723	2.250232	-0.721409	H	6.111693	-1.715921	-2.201266
H	5.238181	2.136080	-0.790579	H	3.753474	-0.910576	-2.177850

1f – TS1-decoordination	**1f – TS2-coordination**
E (SCF) = -1315.42492 E (SCF; solvent = DCM) = -2149.37406906 Zero-point correction = 0.537011 Thermal correction to Enthalpy = 0.568657 Thermal correction to Gibbs Free Energy = 0.47480	E (SCF) = -1315.41893 E (SCF; solvent = DCM) = -2149.37277779 Zero-point correction = 0.538107 Thermal correction to Enthalpy = 0.570941 Thermal correction to Gibbs Free Energy = 0.47408
C 0.792246 -0.422805 1.541314 C 1.651507 0.862813 3.197605 H 2.401997 1.449514 3.704194 C 0.407321 0.492254 3.576052 H -0.148012 0.703177 4.476807 C 3.194415 0.311791 1.336728 H 3.229047 -0.538025 0.655108 H 3.915020 0.090687 2.133205 C 3.593287 1.593355 0.633180 C 4.744940 1.565374 -0.164577 H 5.303403 0.637906 -0.277732 C 5.195178 2.718517 -0.801022 H 6.090937 2.681007 -1.413849 C 4.500499 3.918819 -0.646744 H 4.852601 4.820204 -1.139048 C 3.356760 3.954666 0.146538 H 2.813498 4.886175 0.276665 C 2.903863 2.798227 0.784924 H 2.010247 2.843814 1.400262 C -1.359909 -1.033322 2.753540 H -1.433606 -1.239238 3.824912 H -1.259465 -2.002595 2.259862 C -2.611130 -0.290412 2.298874 H -2.526842 0.783632 2.483318 H -3.475018 -0.671824 2.849851 C 1.494296 -2.564854 -1.930495 C 0.110195 -2.517175 -2.186011 H -0.447143 -3.439039 -2.314044 C -0.586986 -1.284441 -2.087750 H -1.670406 -1.295150 -2.159069 C 0.067939 -0.028976 -1.891103 C 1.451750 -0.080235 -1.615153 H 1.990077 0.823070 -1.348572 C 2.139135 -1.330952 -1.579452 H 3.192959 -1.355121 -1.320258 C 2.253356 -3.854446 -1.925158 H 1.601607 -4.699281 -1.696555 H 3.063249 -3.837433 -1.192535 H 2.693570 -4.013956 -2.916810 C -0.722298 1.255694 -2.007989 H -1.753201 1.020570 -1.718482 C -0.729561 1.682295 -3.487627 H 0.279898 1.932785 -3.831047 H -1.359152 2.567611 -3.616726	C -0.042250 0.209680 0.746972 C 1.476670 1.486150 1.829897 H 2.004038 2.393154 2.078310 C 1.644998 0.212096 2.247319 H 2.352630 -0.214285 2.940592 C -0.066336 2.704760 0.289265 H -0.630053 2.398716 -0.592237 H -0.755179 3.175589 0.999001 C 1.029776 3.673911 -0.078225 C 1.175543 4.869667 0.631632 H 0.497053 5.098532 1.451095 C 2.177523 5.777716 0.289480 H 2.278465 6.705916 0.844135 C 3.042579 5.493168 -0.764582 H 3.821765 6.199949 -1.034468 C 2.901771 4.301656 -1.478197 H 3.568857 4.082555 -2.307017 C 1.900598 3.395883 -1.139503 H 1.783186 2.473924 -1.702320 C 0.603820 -1.989579 1.906153 H -0.173643 -2.123036 2.668607 H 1.556848 -2.243373 2.374796 C 0.352017 -2.985517 0.776958 H -0.697288 -2.989532 0.476205 H 0.570150 -3.980123 1.179431 C -3.208077 -1.099622 -1.935526 C -2.902484 -2.011868 -0.883292 H -2.607748 -3.025765 -1.142471 C -2.972767 -1.645405 0.492622 H -2.777263 -2.392117 1.256077 C -3.226675 -0.310180 0.879158 C -3.347850 0.647223 -0.176254 H -3.425697 1.703137 0.058205 C -3.394890 0.244000 -1.549615 H -3.455551 1.011660 -2.315272 C -3.175583 -1.513574 -3.375463 H -2.773018 -0.716307 -4.004357 H -4.190427 -1.743938 -3.718792 H -2.560351 -2.404869 -3.518200 C -3.365057 0.039234 2.346293 H -2.703988 -0.641033 2.899399 C -4.815129 -0.265048 2.769372 H -5.521760 0.381097 2.238136 H -4.935626 -0.083963 3.841338

H	-1.122590	0.894138	-4.137145	H	-5.090121	-1.304770	2.569146
C	-0.229112	2.384238	-1.106582	C	-2.983192	1.473315	2.710097
H	-0.211984	2.073029	-0.057910	H	-1.959186	1.710597	2.410523
H	-0.898346	3.244689	-1.197211	H	-3.052265	1.605040	3.793353
H	0.773544	2.727663	-1.379850	H	-3.661880	2.204579	2.258400
N	1.873330	0.297948	1.955663	N	0.447983	1.468319	0.910003
N	-0.100592	-0.305719	2.567768	N	0.707034	-0.562835	1.584452
S	-2.885244	-0.599748	0.513340	S	1.244372	-2.723438	-0.792114
Cl	0.494745	-3.399718	1.106547	Ru	-1.525870	-0.361916	-0.602280
Ru	0.509062	-1.507321	-0.229066	Cl	-0.218747	0.480662	-2.306329
C	-4.175841	0.580485	0.120041	C	2.951790	-2.681870	-0.242211
C	-5.417045	0.092604	-0.302326	C	3.693729	-1.510214	-0.420975
C	-6.427387	0.986581	-0.655700	C	5.039420	-1.481640	-0.054884
C	-6.208655	2.360613	-0.574560	C	5.639556	-2.610802	0.499572
C	-4.971885	2.845931	-0.148097	C	4.897872	-3.779815	0.674998
C	-3.950179	1.960710	0.187381	C	3.558801	-3.824139	0.293013
H	-5.589486	-0.978748	-0.343053	H	3.217092	-0.634237	-0.850292
H	-7.390387	0.605473	-0.982529	H	5.617418	-0.573901	-0.202843
H	-7.000687	3.053678	-0.841854	H	6.686934	-2.585209	0.785418
H	-4.799106	3.916555	-0.085589	H	5.367805	-4.666572	1.090534
H	-2.981059	2.338627	0.500824	H	2.993673	-4.746841	0.391682

Table S4. Atomic coordinates of the optimized species derived from complex $\mathbf{1}_{CF3}$.[a]

$\mathbf{1}_{CF3}$ - R_{Ru}/R_S			$\mathbf{1}_{CF3}$ - R_{Ru}/S_S		
E (SCF) = -1421.38935 E (SCF; solvent = DCM) = -2255.41977218 Zero-point correction = 0.461518 Thermal correction to Enthalpy = 0.492176 Thermal correction to Gibbs Free Energy = 0.40310			E (SCF) = -1421.38714 E (SCF; solvent = DCM) = -2255.41815166 Zero-point correction = 0.463165 Thermal correction to Enthalpy = 0.494394 Thermal correction to Gibbs Free Energy = 0.40361		
C	-0.660212	0.209757 -1.000439	C	-0.710108	-0.817737 -0.654481
C	-2.618713	0.658386 -2.046500	C	-2.594159	-1.610375 -1.654451
H	-3.675764	0.860809 -2.112303	H	-3.633862	-1.604621 -1.938290
C	-1.681082	0.504874 -3.005636	C	-1.620019	-2.521481 -1.858108
H	-1.754926	0.549570 -4.081239	H	-1.636446	-3.473077 -2.365744
C	-2.724170	0.515878 0.445248	C	-2.847214	0.559519 -0.495415
H	-2.123587	-0.049076 1.158475	H	-2.348160	0.976559 0.372366
H	-2.792310	1.560374 0.767804	H	-2.848086	1.307916 -1.295405
C	-4.106636	-0.076405 0.332915	C	-4.264219	0.181695 -0.139141
C	-5.234079	0.750283 0.346967	C	-5.333784	0.663447 -0.898207
H	-5.114753	1.827822 0.442818	H	-5.143211	1.298800 -1.760525
C	-6.512854	0.201458 0.251458	C	-6.646246	0.340574 -0.552565
H	-7.383161	0.850756 0.269190	H	-7.470860	0.722997 -1.146628
C	-6.669415	-1.178283 0.139116	C	-6.895104	-0.470234 0.552137
H	-7.664244	-1.608019 0.067357	H	-7.916139	-0.722287 0.822647
C	-5.547463	-2.008917 0.127116	C	-5.830693	-0.956964 1.313469
H	-5.669063	-3.085446 0.049572	H	-6.022749	-1.587158 2.176821
C	-4.270702	-1.463299 0.225598	C	-4.521512	-0.631600 0.972156

H	-3.396092	-2.108911	0.228788	H	-3.695295	-1.015454	1.566829
C	0.655683	-0.193571	-3.178311	C	0.740178	-2.819713	-1.199167
H	0.779845	0.545836	-3.976211	H	0.538779	-3.759147	-1.720195
H	0.388662	-1.146859	-3.647734	H	0.979824	-3.044478	-0.157556
C	1.984560	-0.346335	-2.466826	C	1.884850	-2.106398	-1.888607
H	2.382114	0.603894	-2.108373	H	1.598718	-1.737325	-2.876888
H	2.691486	-0.805265	-3.163410	H	2.756005	-2.755051	-2.004519
C	3.508762	-1.825224	-0.668390	C	3.749273	-1.456981	0.061253
F	3.998373	-2.593309	-1.638889	F	3.384229	-2.617222	0.587369
F	4.266194	-0.722044	-0.592430	F	4.787227	-1.674628	-0.752825
F	3.571477	-2.472632	0.488670	F	4.126195	-0.621947	1.026373
C	1.322381	0.151282	2.751060	C	0.541628	1.556033	2.341466
C	2.459884	0.342103	1.956526	C	1.889614	1.558103	1.877193
H	3.335507	-0.276182	2.121719	H	2.683057	1.207944	2.527429
C	2.454160	1.282849	0.876232	C	2.187022	1.973887	0.564842
H	3.340651	1.370519	0.256723	H	3.222028	1.942444	0.232646
C	1.357281	2.140941	0.625108	C	1.183436	2.379179	-0.369320
C	0.190199	1.919742	1.422716	C	-0.152523	2.298771	0.083211
H	-0.708497	2.489917	1.218452	H	-0.954893	2.561641	-0.595408
C	0.157527	0.932899	2.427786	C	-0.468101	1.928306	1.427987
H	-0.762672	0.753473	2.974293	H	-1.495632	1.936784	1.774211
C	1.270787	-0.864807	3.847584	C	0.217524	1.155754	3.744799
H	2.196398	-1.440578	3.903019	H	0.851113	0.329269	4.071801
H	0.440691	-1.558389	3.681119	H	-0.825200	0.850303	3.845484
H	1.113860	-0.364765	4.809535	H	0.394206	2.012876	4.406038
C	1.481331	3.270693	-0.378736	C	1.582459	2.893606	-1.737245
H	2.107502	2.898607	-1.202151	H	2.468148	2.320044	-2.043338
C	2.234451	4.438368	0.285049	C	2.003741	4.369053	-1.618642
H	1.664952	4.840465	1.129707	H	1.159869	4.994860	-1.309325
H	2.382333	5.248508	-0.434984	H	2.359124	4.736612	-2.585646
H	3.216834	4.131690	0.655779	H	2.810134	4.506167	-0.891678
C	0.153462	3.750872	-0.966344	C	0.506955	2.708602	-2.808155
H	-0.423384	2.935535	-1.412157	H	0.154842	1.672808	-2.854797
H	0.344195	4.493107	-1.746412	H	0.911781	2.972736	-3.788816
H	-0.468115	4.242762	-0.210192	H	-0.355993	3.361376	-2.636063
N	-1.986472	0.468932	-0.833963	N	-2.032271	-0.585894	-0.917733
N	-0.486687	0.226062	-2.359166	N	-0.484740	-2.033465	-1.242253
S	1.731314	-1.467033	-1.040581	S	2.415333	-0.631629	-0.945395
Ru	0.720317	-0.029345	0.520003	Ru	0.722384	0.290276	0.416143
Cl	-0.487447	-2.026518	1.062939	Cl	0.608877	-1.598247	1.880716

1_{CF3} - intermediate	**1_{CF3} – TS-inversion**
E (SCF) = -1421.36889 E (SCF; solvent = DCM) = -2255.41125092 Zero-point correction = 0.461426 Thermal correction to Enthalpy = 0.491555 Thermal correction to Gibbs Free Energy = 0.40175	E (SCF) = -1421.36134 E (SCF; solvent = DCM) = -2255.39418834 Zero-point correction = 0.461739 Thermal correction to Enthalpy = 0.492795 Thermal correction to Gibbs Free Energy = 0.40102
C 0.076836 -0.225252 -1.277706 C 1.075321 1.122499 -2.786381 H 1.173155 1.978001 -3.436414	C -0.750318 -0.855971 -0.521566 C -2.550859 -1.611777 -1.688019 H -3.547753 -1.567461 -2.095522

C	1.919989	0.094112	-2.541359
H	2.900465	-0.110950	-2.939388
C	-1.223030	1.775830	-2.057757
H	-2.104558	1.133882	-1.980308
H	-1.246743	2.208634	-3.063980
C	-1.264099	2.874930	-1.016411
C	-2.487507	3.511457	-0.773132
H	-3.378057	3.199838	-1.316381
C	-2.571528	4.558492	0.141808
H	-3.525829	5.046469	0.316957
C	-1.431776	4.980981	0.826589
H	-1.495019	5.798406	1.538434
C	-0.210782	4.354627	0.585282
H	0.682821	4.685141	1.106776
C	-0.124563	3.307061	-0.333486
H	0.835164	2.831831	-0.515321
C	1.793816	-2.033459	-1.212063
H	1.634523	-2.724823	-2.047937
H	1.164485	-2.374179	-0.386368
C	3.263237	-2.077443	-0.810434
H	3.928926	-1.668165	-1.573061
H	3.544493	-3.128251	-0.694467
C	4.286695	0.329831	0.266912
F	5.078724	0.263881	-0.811551
F	3.294670	1.191137	-0.034139
F	4.974171	0.845401	1.284590
C	-3.481175	-1.302752	0.652545
C	-2.725529	-2.343620	1.215377
H	-3.042265	-3.373008	1.084767
C	-1.444336	-2.067701	1.776155
H	-0.821769	-2.901804	2.089765
C	-0.958629	-0.736413	1.985234
C	-1.714137	0.306942	1.407961
H	-1.336884	1.323204	1.406956
C	-2.907427	0.017834	0.688236
H	-3.417793	0.830518	0.180311
C	-4.772831	-1.555764	-0.061033
H	-4.846883	-2.589975	-0.401575
H	-4.885554	-0.897587	-0.925990
H	-5.606826	-1.356708	0.622430
C	0.299944	-0.524151	2.799038
H	1.022750	-1.288580	2.484658
C	-0.040468	-0.777698	4.280369
H	-0.764442	-0.042726	4.647459
H	0.864857	-0.690665	4.887866
H	-0.458160	-1.775835	4.444086
C	0.946894	0.845615	2.616284
H	1.202755	1.042455	1.572896
H	1.871155	0.892146	3.198739
H	0.299112	1.651417	2.977901
N	-0.046791	0.913531	-2.005486
N	1.298465	-0.718088	-1.610232
S	3.693932	-1.308764	0.794572
Cl	-1.668496	-2.501470	-2.049100
C	-1.625702	-2.592272	-1.704175
H	-1.649037	-3.577018	-2.143939
C	-2.844428	0.592754	-0.611440
H	-2.367842	1.057965	0.245483
H	-2.841291	1.295474	-1.451567
C	-4.262005	0.210196	-0.259863
C	-5.324408	0.608841	-1.074945
H	-5.130139	1.190583	-1.973651
C	-6.635708	0.272066	-0.738008
H	-7.455715	0.589383	-1.375238
C	-6.889219	-0.468523	0.413941
H	-7.909367	-0.731213	0.677644
C	-5.831280	-0.869930	1.232063
H	-6.027714	-1.443595	2.133065
C	-4.523201	-0.531390	0.899531
H	-3.701252	-0.846675	1.539034
C	0.503995	-3.078124	-0.575376
H	0.218246	-4.051680	-0.979475
H	0.497691	-3.141771	0.516771
C	1.895750	-2.735563	-1.078966
H	1.927451	-2.589188	-2.160839
H	2.593369	-3.521636	-0.781536
C	4.169834	-1.198825	-0.135303
F	4.633740	-2.381833	0.258159
F	4.716846	-0.913661	-1.318451
F	4.535354	-0.260862	0.742039
C	0.604975	1.936531	2.180126
C	1.922317	1.806682	1.686736
H	2.732504	1.564854	2.365579
C	2.173705	1.894332	0.291398
H	3.187242	1.722026	-0.058155
C	1.166548	2.174856	-0.672814
C	-0.153118	2.259237	-0.167214
H	-0.970111	2.414703	-0.860280
C	-0.438920	2.132425	1.226068
H	-1.458655	2.212282	1.587207
C	0.305395	1.833172	3.640844
H	1.027428	1.192906	4.150070
H	-0.693312	1.430696	3.816875
H	0.358711	2.836789	4.080675
C	1.532006	2.371854	-2.128978
H	2.387696	1.712753	-2.326501
C	1.997686	3.822710	-2.342924
H	1.183244	4.529342	-2.150322
H	2.327499	3.963759	-3.376331
H	2.832817	4.083206	-1.685549
C	0.415969	1.996768	-3.104458
H	0.042914	0.984583	-2.919218
H	0.792425	2.036078	-4.130200
H	-0.425454	2.696714	-3.050340
N	-2.013597	-0.571106	-0.954872
N	-0.539492	-2.134105	-0.980695
S	2.346907	-1.214119	-0.205307
Ru	0.622200	0.343123	0.559748

Ru -1.401174 -1.202752 -0.182489	Cl 0.052067 -1.211292 2.286798

1_{CF3} – TS1-decoordination	**1_{CF3} – TS2-coordination**
E (SCF) = -1421.35962 E (SCF; solvent = DCM) = -2255.40282726 Zero-point correction = 0.461319 Thermal correction to Enthalpy = 0.491655 Thermal correction to Gibbs Free Energy = 0.40141	E (SCF) = -1421.36623 E (SCF; solvent = DCM) = -2255.40574357 Zero-point correction = 0.461955 Thermal correction to Enthalpy = 0.491908 Thermal correction to Gibbs Free Energy = 0.40413
C -0.324941 0.203050 1.586924 C -1.383105 -1.090410 3.119077 H -2.227149 -1.550912 3.608669 C -0.064901 -1.107379 3.418027 H 0.470504 -1.597613 4.216368 C -2.844505 0.129226 1.534129 H -2.697224 1.054440 0.977693 H -3.421739 0.400942 2.426001 C -3.618966 -0.885033 0.716882 C -4.792916 -0.449803 0.087438 H -5.106967 0.588027 0.183136 C -5.574649 -1.337446 -0.646219 H -6.482999 -0.985577 -1.126203 C -5.194856 -2.675504 -0.758810 H -5.805839 -3.369974 -1.327307 C -4.031574 -3.115671 -0.133186 H -3.732093 -4.156827 -0.210514 C -3.245616 -2.225776 0.602331 H -2.341316 -2.586107 1.083536 C 1.979136 0.058246 2.664428 H 2.169769 0.024817 3.740294 H 2.097823 1.101024 2.361917 C 2.975284 -0.860988 1.964360 H 2.626935 -1.896318 1.956795 H 3.936689 -0.810356 2.480467 C 3.921692 -1.810520 -0.468670 F 5.087867 -2.134355 0.090106 F 3.105493 -2.868219 -0.337279 F 4.112855 -1.584927 -1.774859 C -0.711116 2.939422 -1.482741 C 0.590047 2.602733 -1.906547 H 1.350249 3.373031 -1.980731 C 0.955776 1.240607 -2.052744 H 1.995437 1.002954 -2.258172 C 0.023470 0.162203 -1.935727 C -1.276821 0.499126 -1.501639 H -2.003011 -0.279419 -1.293080 C -1.618853 1.856700 -1.228114 H -2.608511 2.092646 -0.849735 C -1.115741 4.356006 -1.220328 H -0.255362 4.975941 -0.963093 H -1.842078 4.419518 -0.407006	C 0.721712 -0.880049 0.172429 C 2.351903 -2.120675 1.138774 H 3.322986 -2.309490 1.567890 C 1.331797 -2.957188 0.839707 H 1.230996 -4.022695 0.977564 C 2.882275 0.286825 0.778921 H 2.463725 1.033463 0.106008 H 2.879172 0.688398 1.797836 C 4.288445 -0.066676 0.360140 C 5.334597 -0.013937 1.284786 H 5.134739 0.277423 2.313813 C 6.637191 -0.324351 0.893316 H 7.444704 -0.276776 1.617739 C 6.898367 -0.692947 -0.424109 H 7.911890 -0.934383 -0.730184 C 5.856961 -0.748011 -1.352557 H 6.059592 -1.030798 -2.381327 C 4.558141 -0.434572 -0.964278 H 3.750046 -0.478328 -1.691491 C -0.840957 -2.816037 -0.342088 H -0.537063 -3.803346 -0.704352 H -1.140531 -2.232965 -1.213032 C -1.989157 -2.981689 0.645043 H -1.650961 -3.405471 1.594842 H -2.744931 -3.658602 0.238737 C -4.122961 -1.391278 -0.191127 F -3.635584 -1.379236 -1.440223 F -4.942885 -2.437697 -0.091650 F -4.829768 -0.267091 -0.004933 C -0.551574 2.670130 -1.635297 C -1.845040 2.323416 -1.207164 H -2.647127 2.235535 -1.932429 C -2.072295 1.917649 0.137872 H -3.058018 1.549076 0.403692 C -1.071814 1.990292 1.152065 C 0.232190 2.303058 0.712091 H 1.053526 2.284443 1.417975 C 0.503500 2.568963 -0.666022 H 1.524715 2.751493 -0.988075 C -0.254128 3.020807 -3.058536 H -0.982184 2.577741 -3.739968 H 0.741958 2.683523 -3.352476

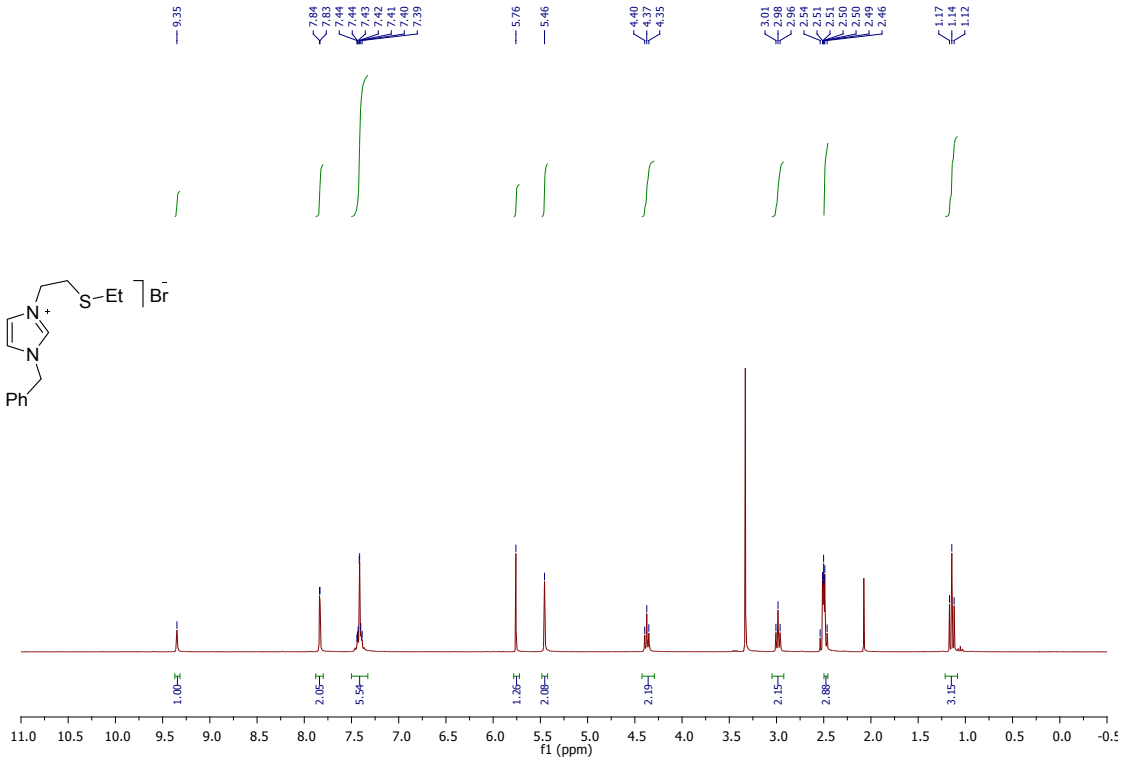
H	-1.580846	4.766964	-2.124472
C	0.451267	-1.241562	-2.302632
H	1.533316	-1.294044	-2.143556
C	0.189467	-1.442969	-3.807112
H	-0.882081	-1.400313	-4.029236
H	0.560247	-2.423286	-4.120165
H	0.692739	-0.684362	-4.414336
C	-0.201712	-2.343062	-1.471674
H	-0.036529	-2.185523	-0.402105
H	0.231298	-3.310202	-1.741245
H	-1.279495	-2.409811	-1.649172
N	-1.527065	-0.288168	2.003358
N	0.569329	-0.300242	2.491091
S	3.212213	-0.293258	0.240310
Cl	0.815481	3.023611	1.464293
Ru	0.109378	1.433415	-0.060461

H	-0.292684	4.111075	-3.170599
C	-1.429219	1.745354	2.602296
H	-2.267609	1.038742	2.606983
C	-1.928956	3.067542	3.213132
H	-1.132926	3.819637	3.227837
H	-2.255937	2.902959	4.243919
H	-2.774473	3.480068	2.654492
C	-0.297753	1.142831	3.435246
H	0.098800	0.230888	2.978048
H	-0.668530	0.887114	4.431591
H	0.526579	1.850602	3.577759
N	1.967704	-0.862957	0.720415
N	0.351247	-2.195908	0.232103
S	-2.814803	-1.408622	1.076694
Ru	-0.447069	0.676734	-0.596201
Cl	-0.235319	-0.410362	-2.637133

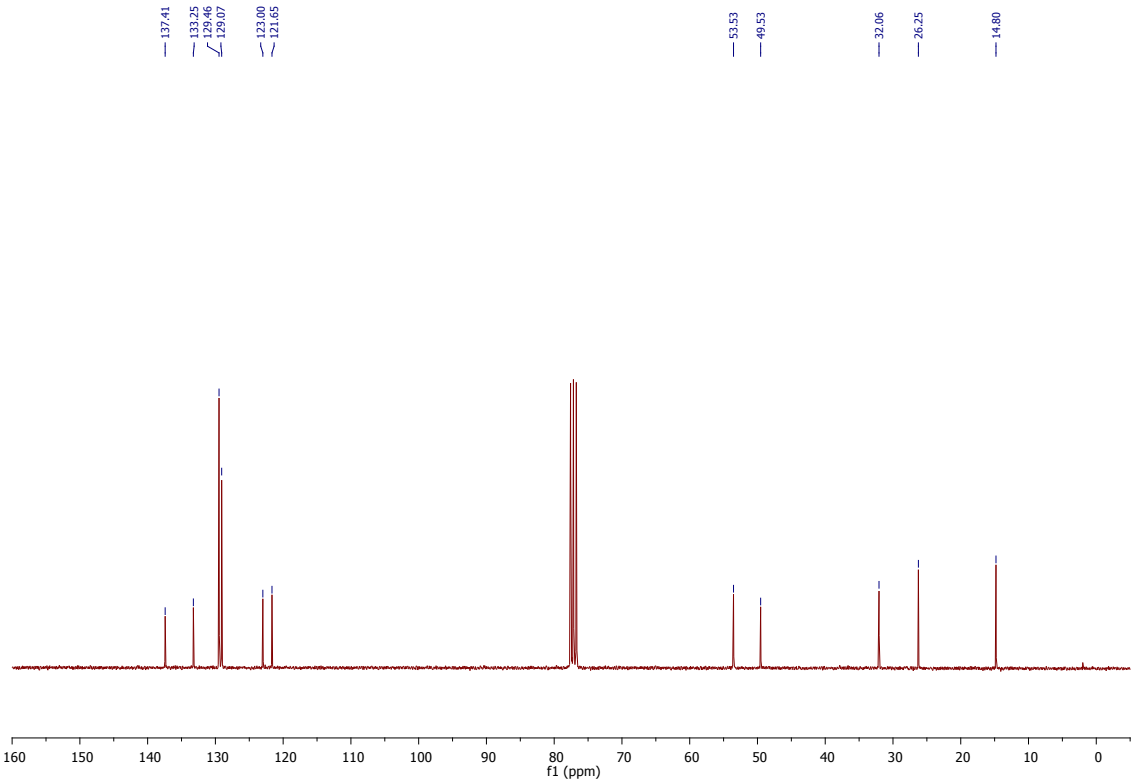
12 ^{1}H, ^{19}F and ^{13}C NMR SPECTRA OF ALL COMPOUNDS.

S-Et (a)

^{1}H NMR (300 MHz) DMSO-d_6

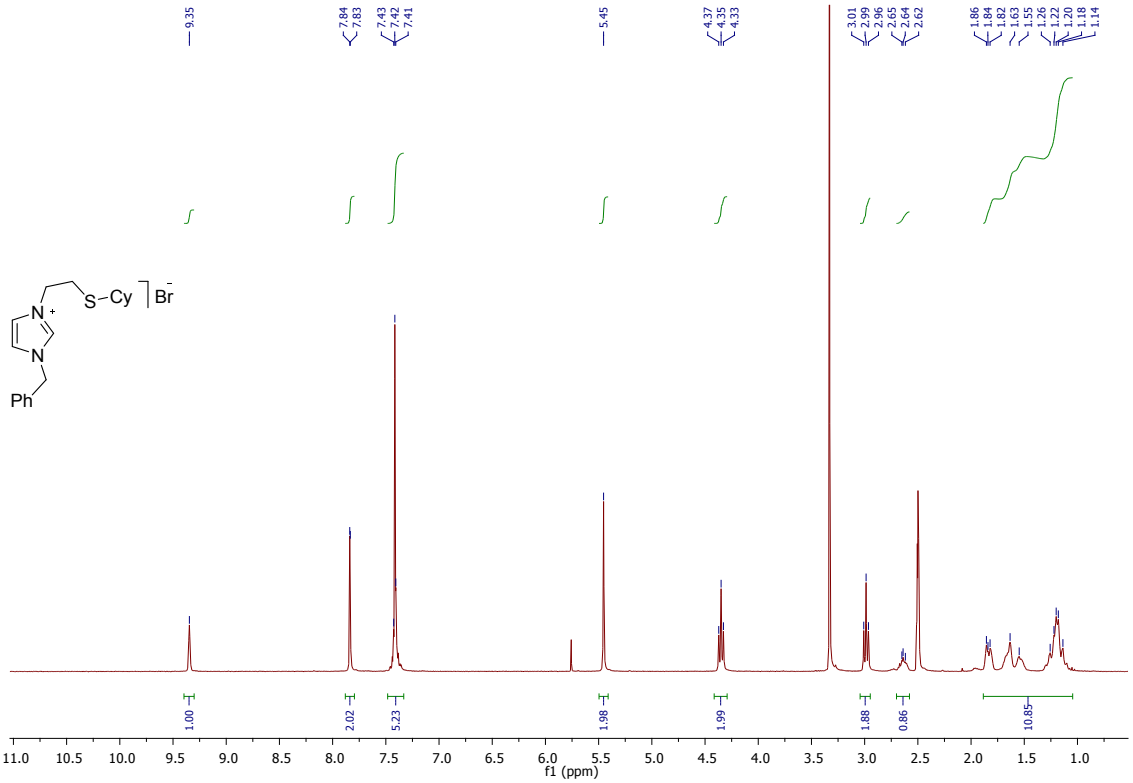


^{13}C NMR (75 MHz) $CDCl_3$

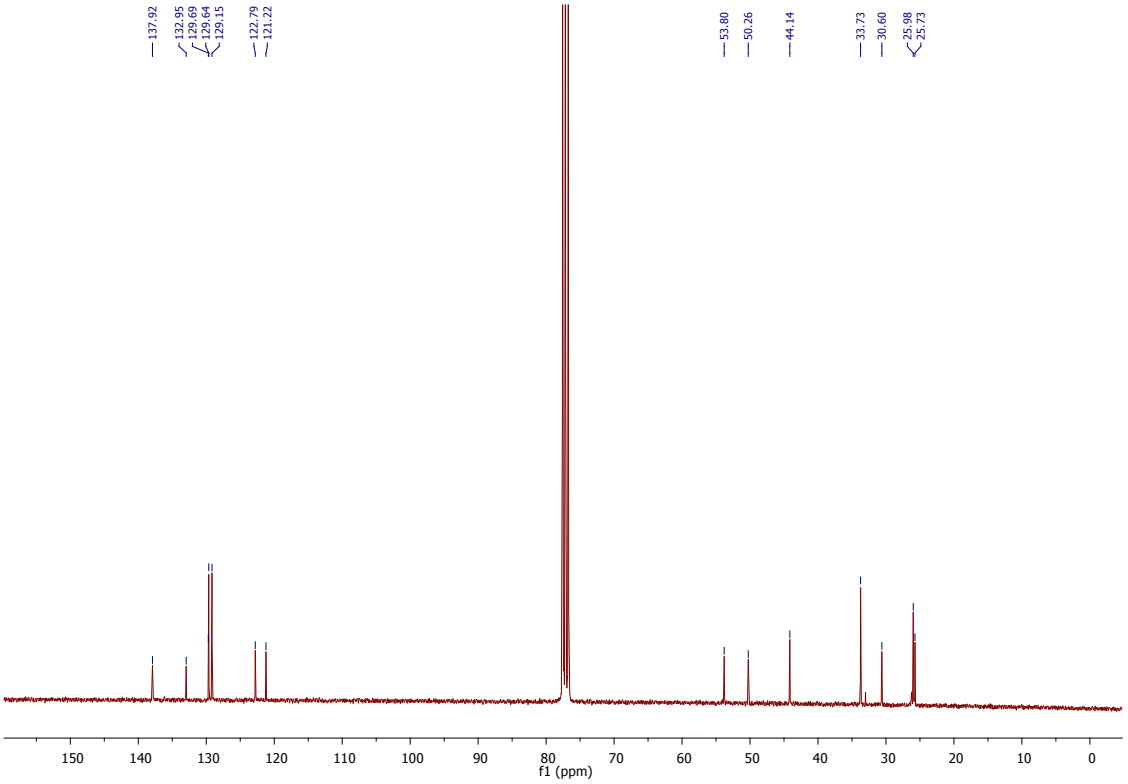


S-Cy (b)

^{1}H NMR (300 MHz) DMSO-d_6

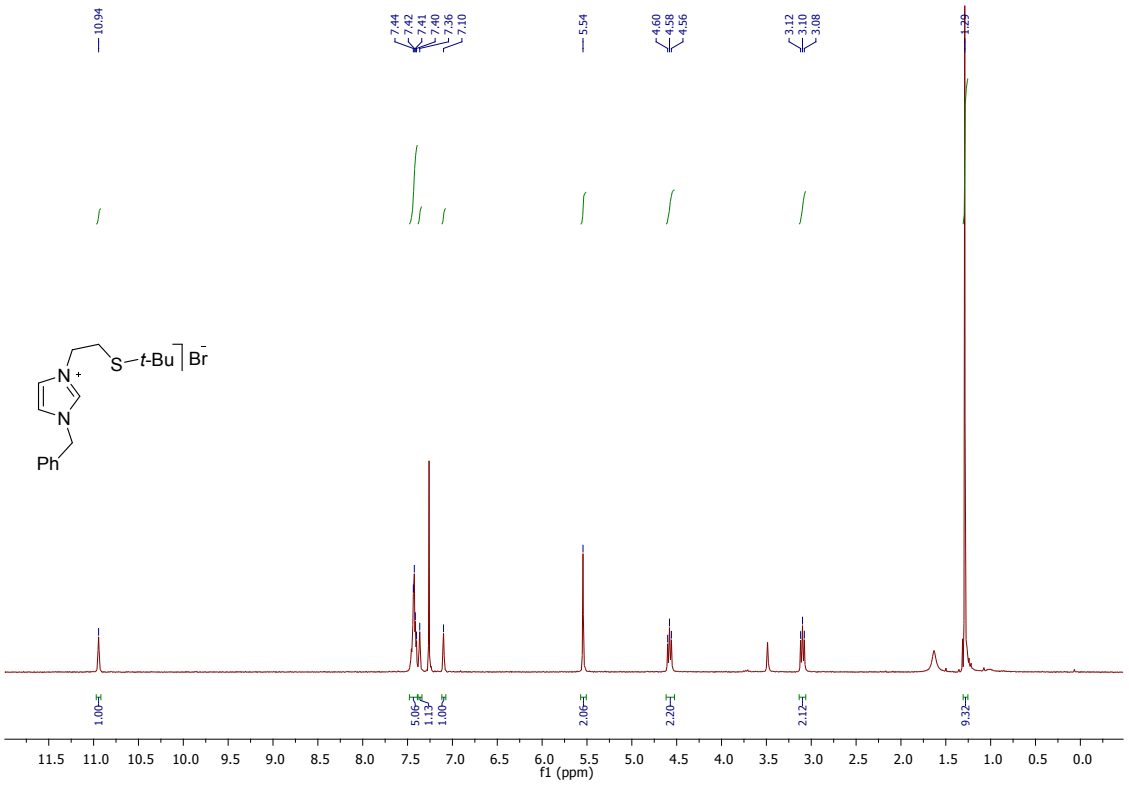


^{13}C NMR (75 MHz) $CDCl_3$

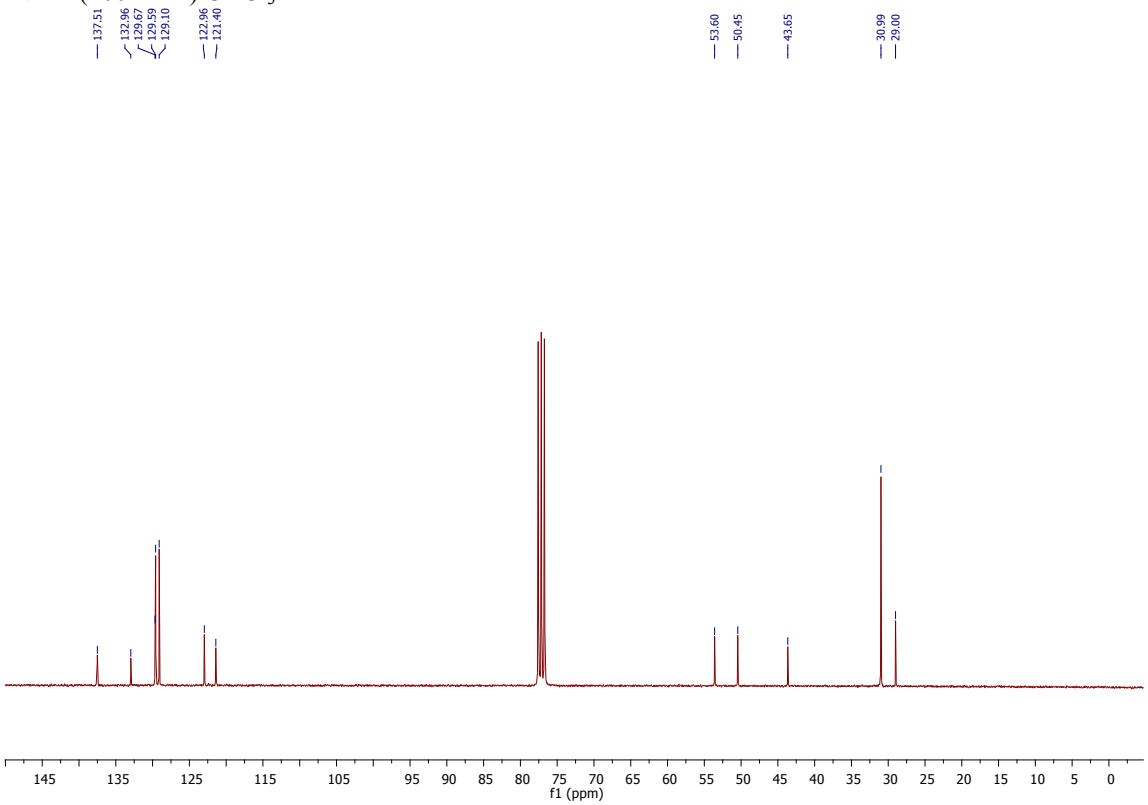


S-tBu (c)

^{1}H NMR (300 MHz) $CDCl_3$

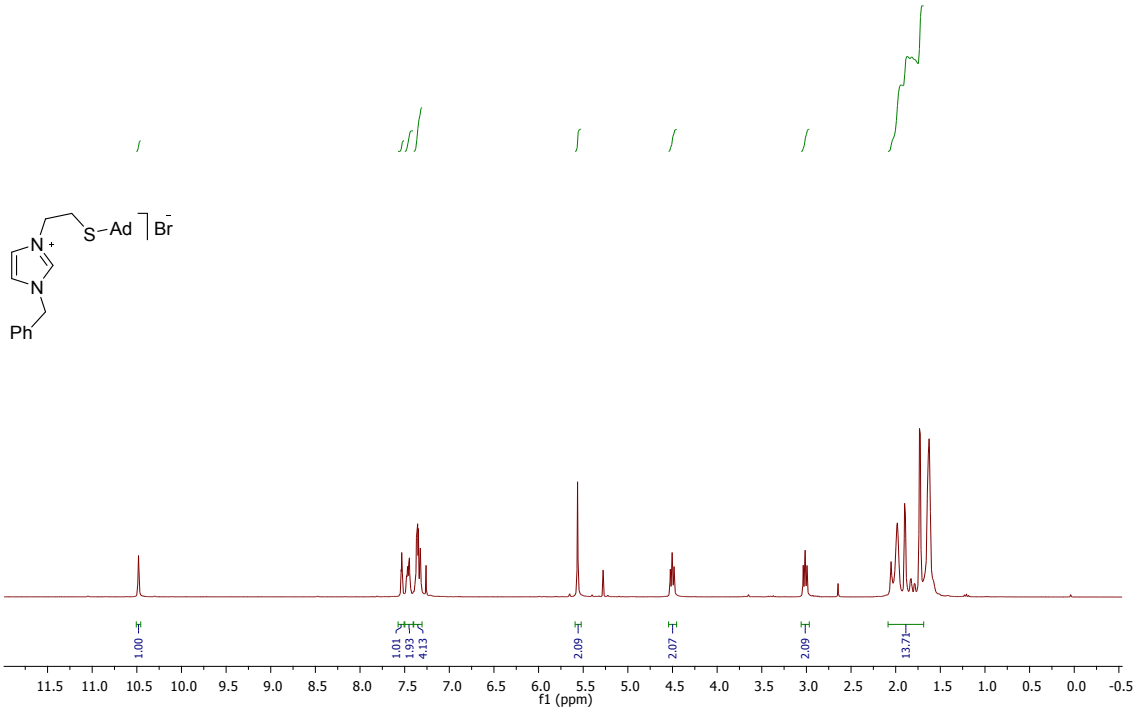


^{13}C NMR (100 MHz) $CDCl_3$

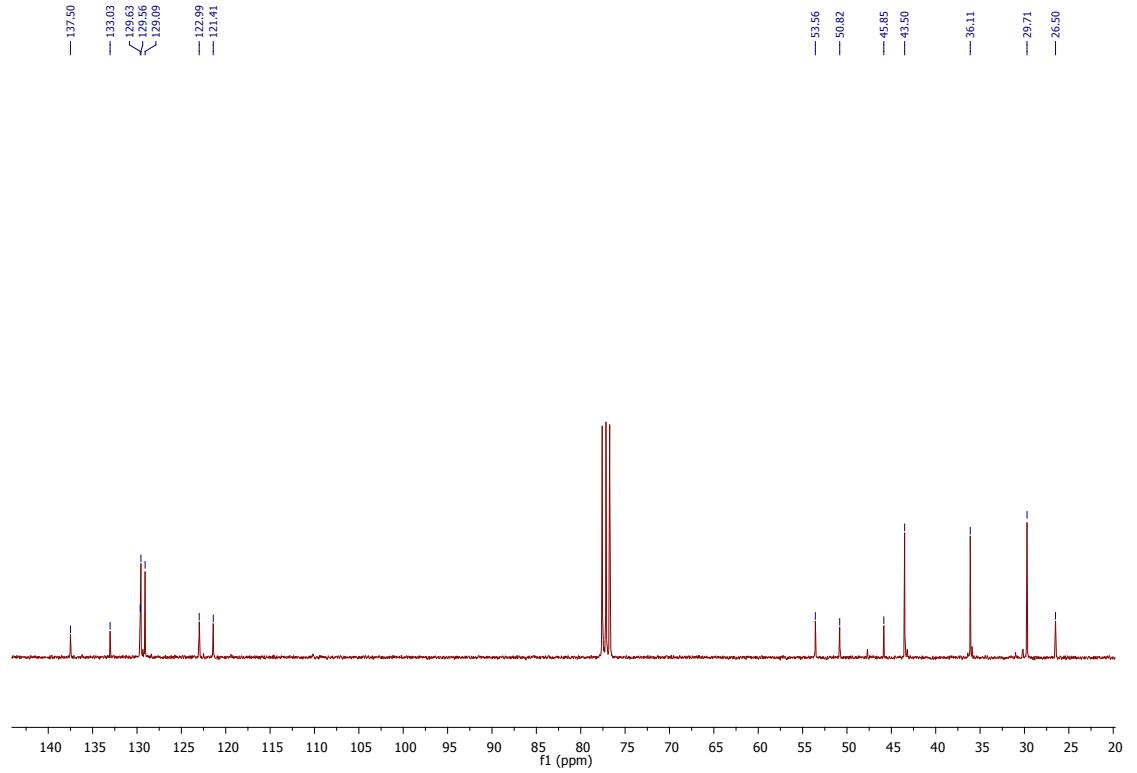


S-Ad (d)

^{1}H NMR (300 MHz) $CDCl_3$

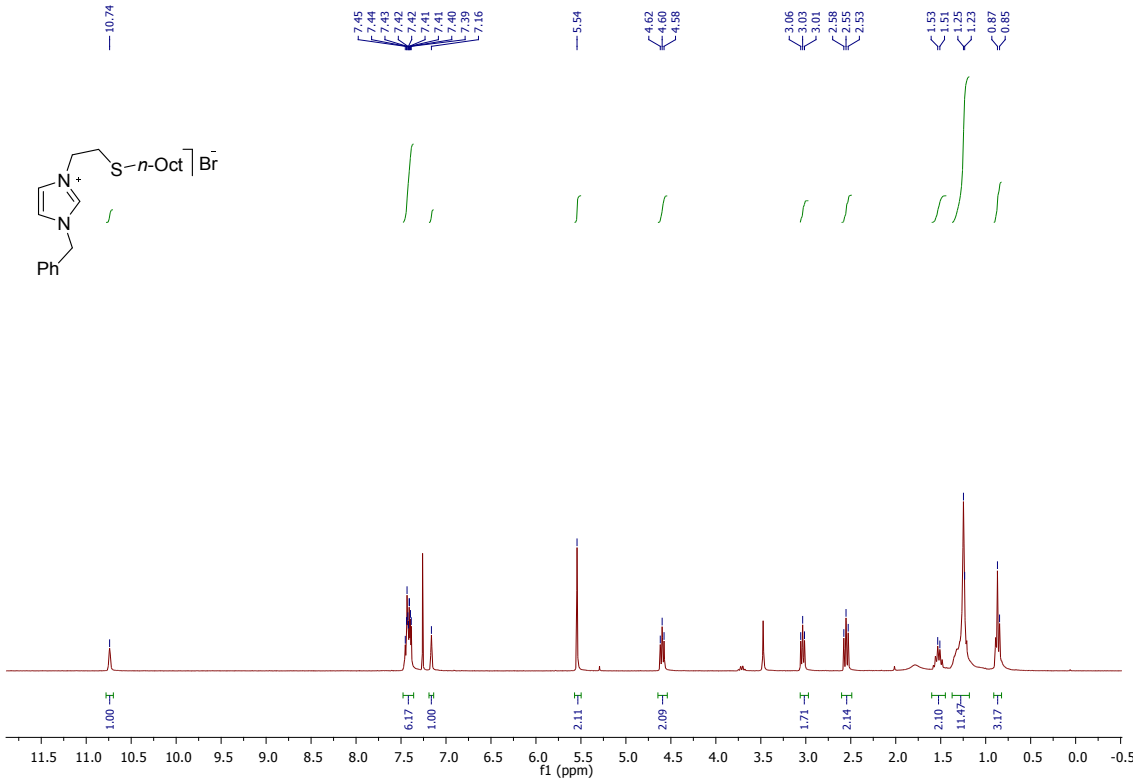


^{13}C NMR (75 MHz) $CDCl_3$

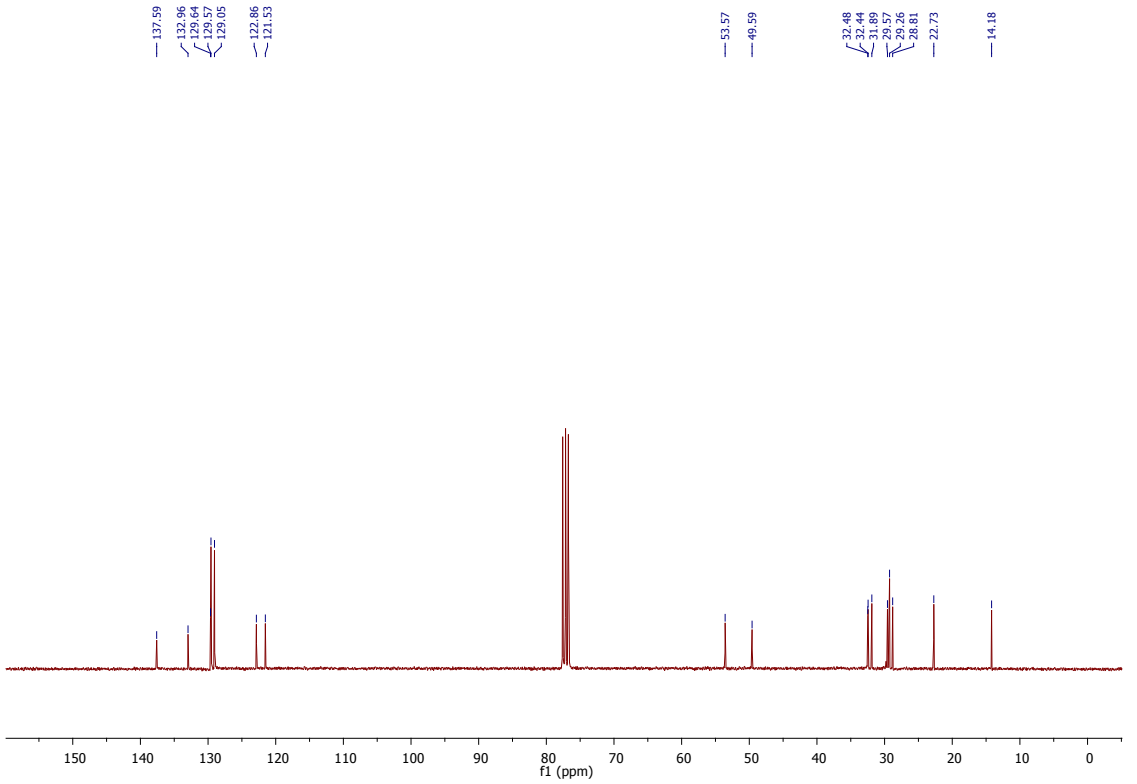


S-Oct (e)

^{1}H NMR (300 MHz) $CDCl_3$

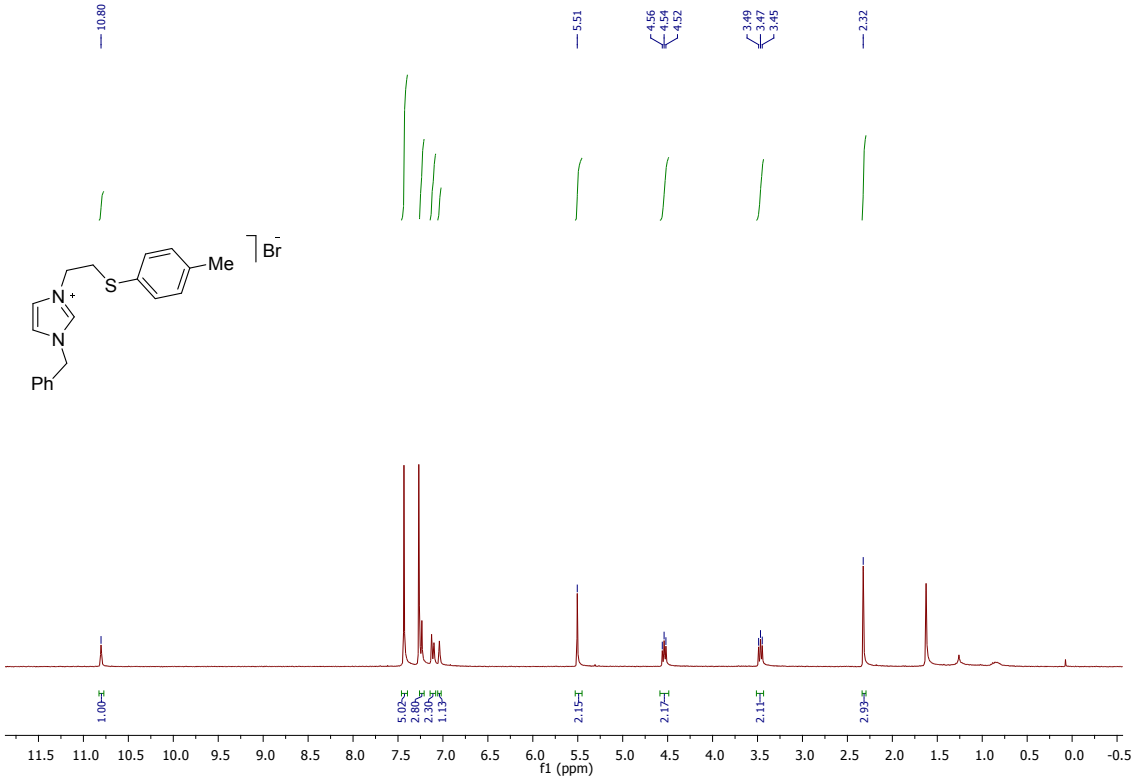


^{13}C NMR (75 MHz) $CDCl_3$

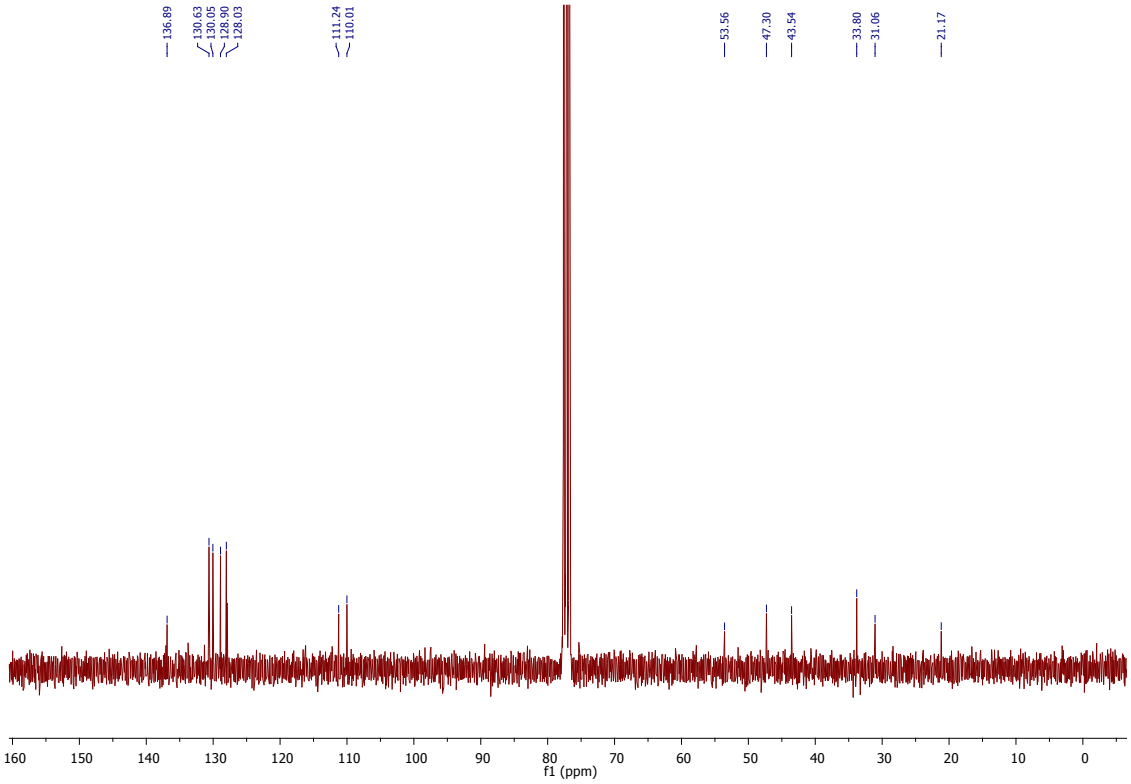


S-p-Me (g)

^{1}H NMR (300 MHz) $CDCl_3$

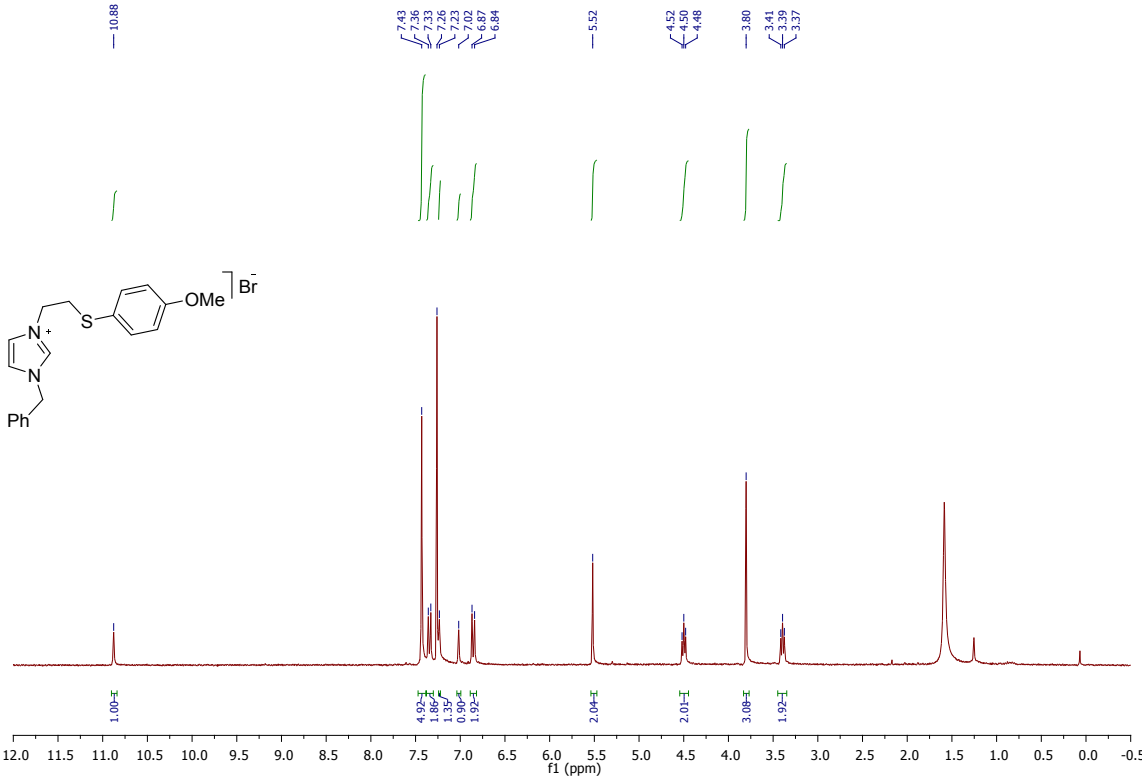


^{13}C NMR (75 MHz) $CDCl_3$

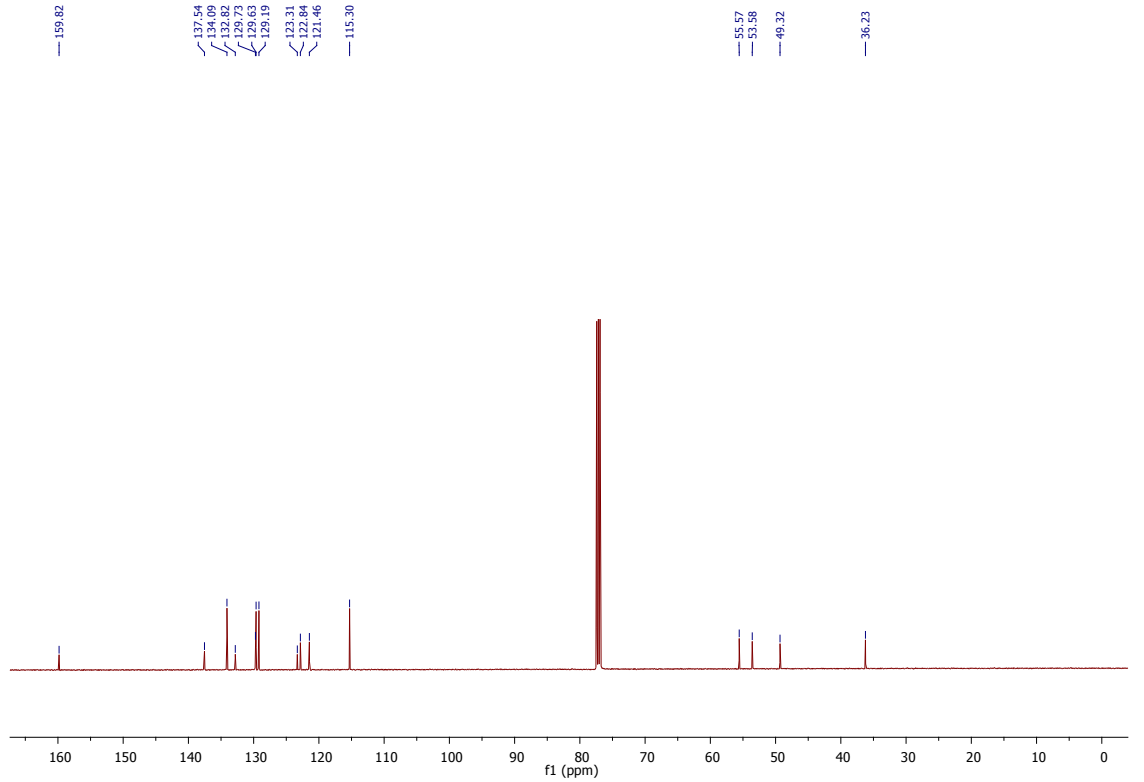


p-OMe imidazoium (h)

^{1}H NMR (300 MHz) $CDCl_3$

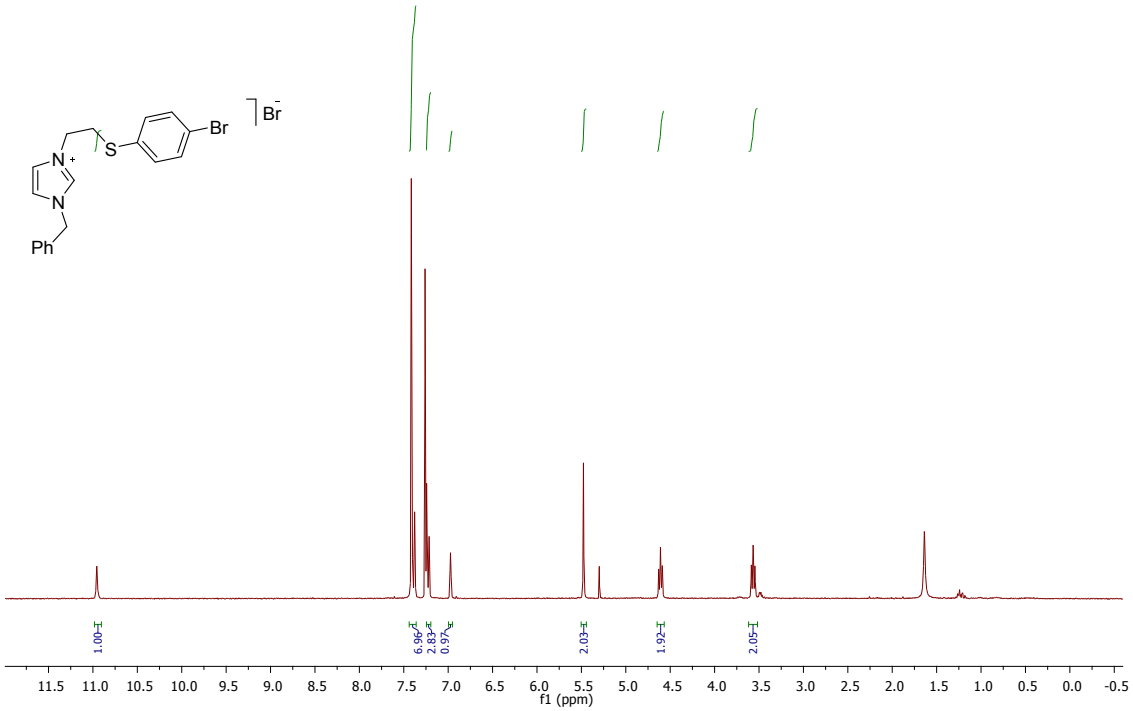


^{13}C NMR (125 MHz) $CDCl_3$

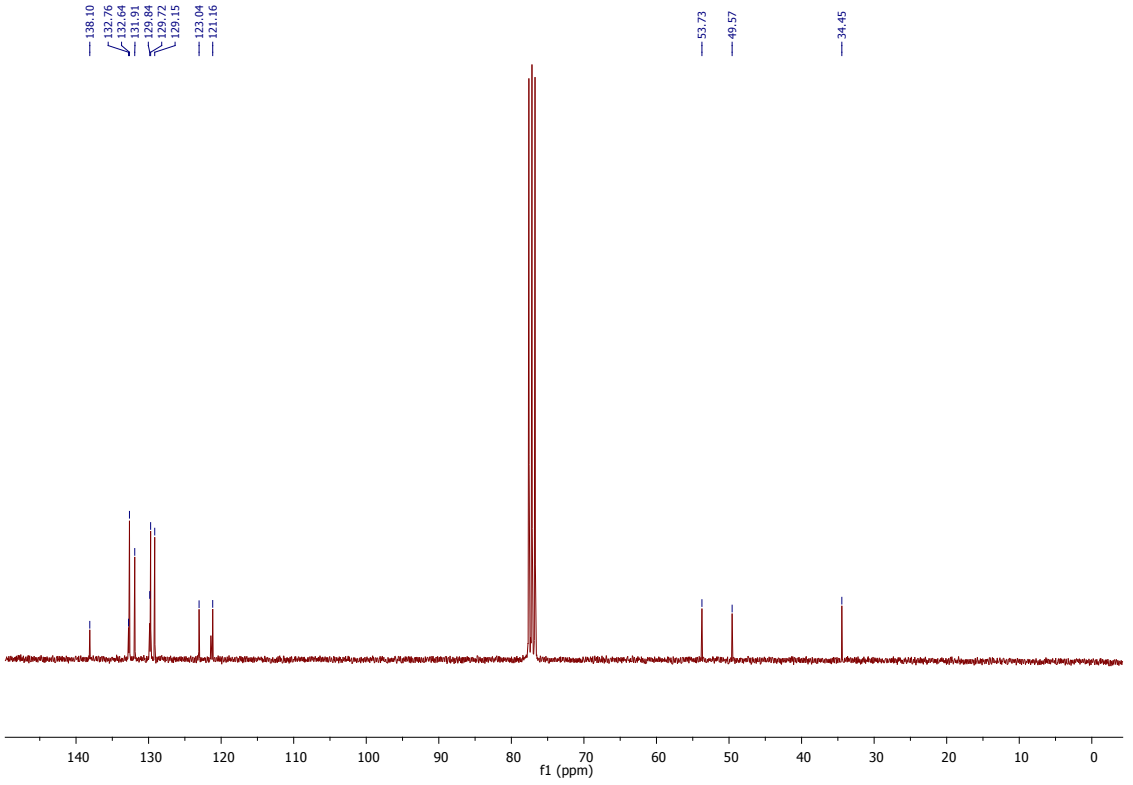


S-p-Br (i)

^{1}H NMR (300 MHz) $CDCl_3$

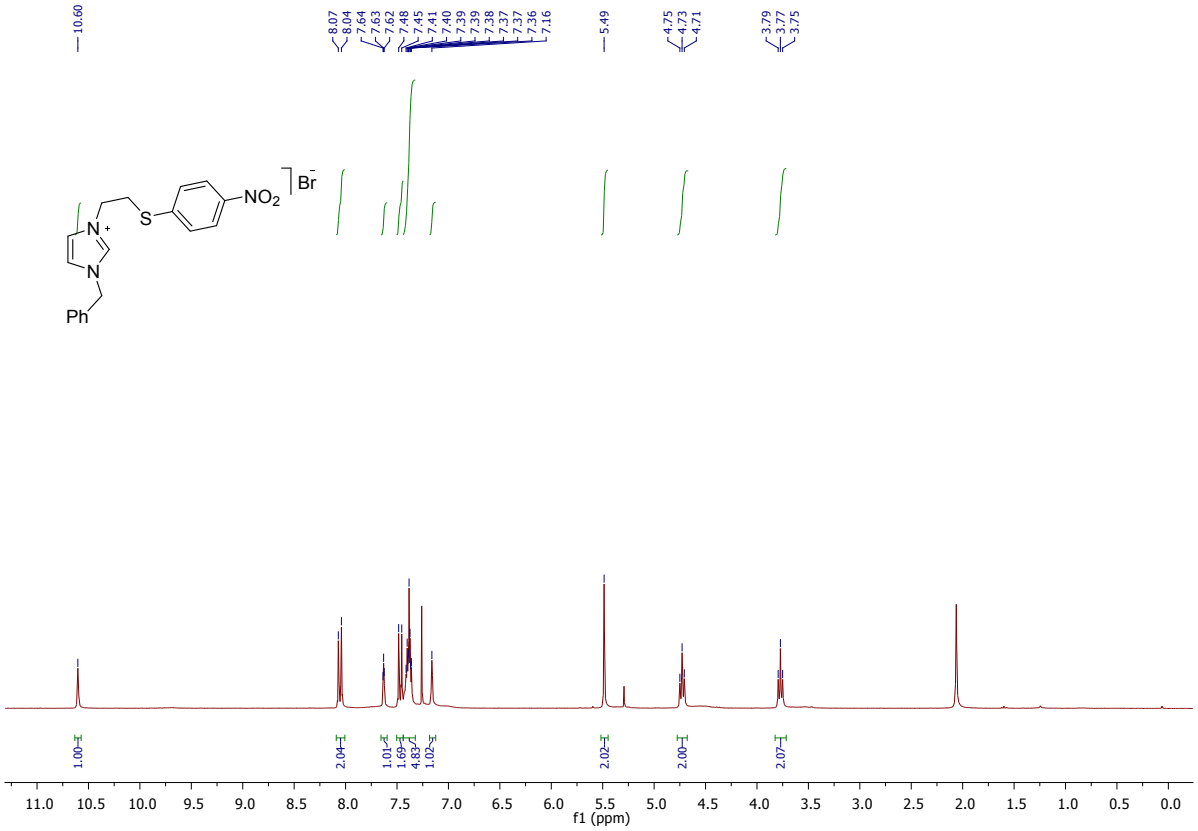


^{13}C NMR (75 MHz) $CDCl_3$

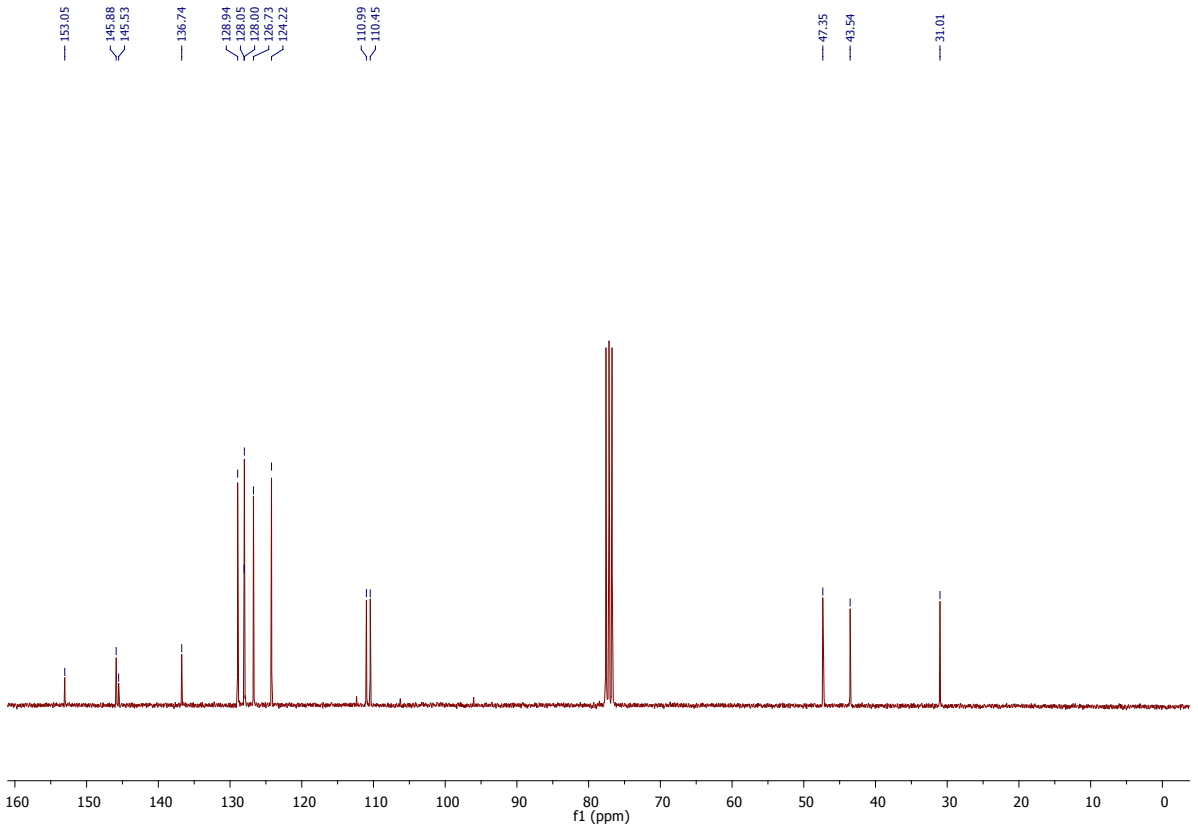


S-p-NO_2 (j)

^{1}H NMR (300 MHz) $CDCl_3$

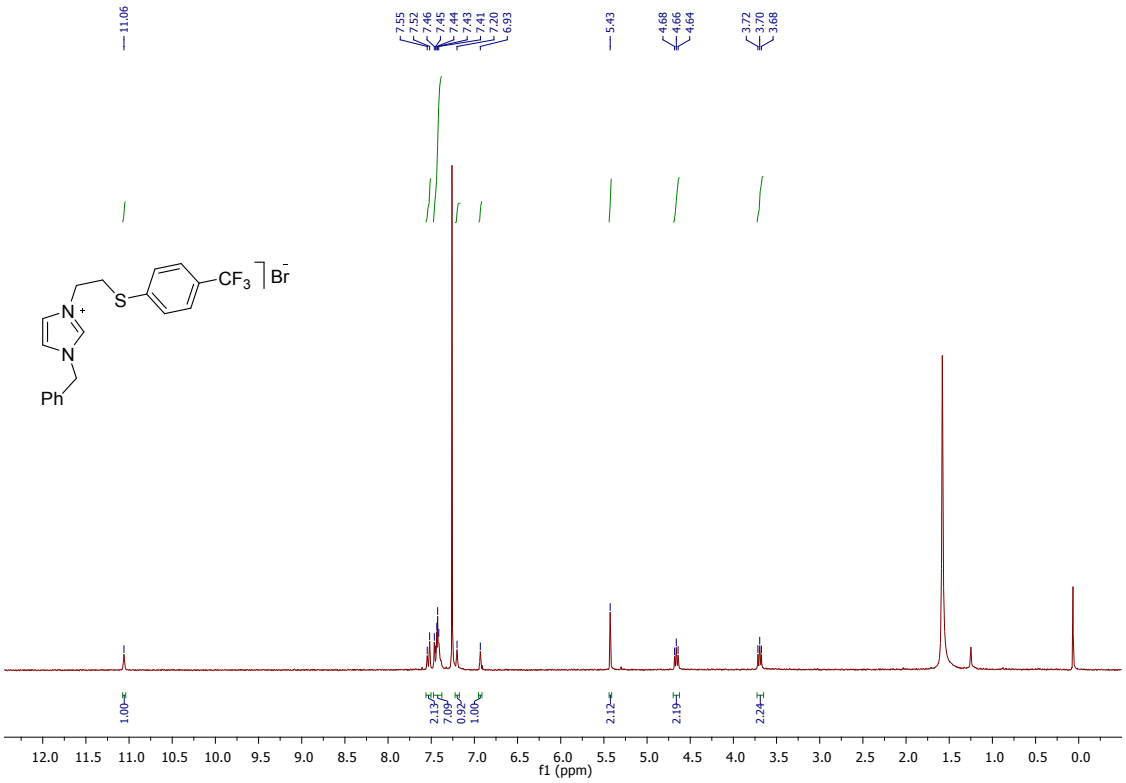


^{13}C NMR (75 MHz) $CDCl_3$

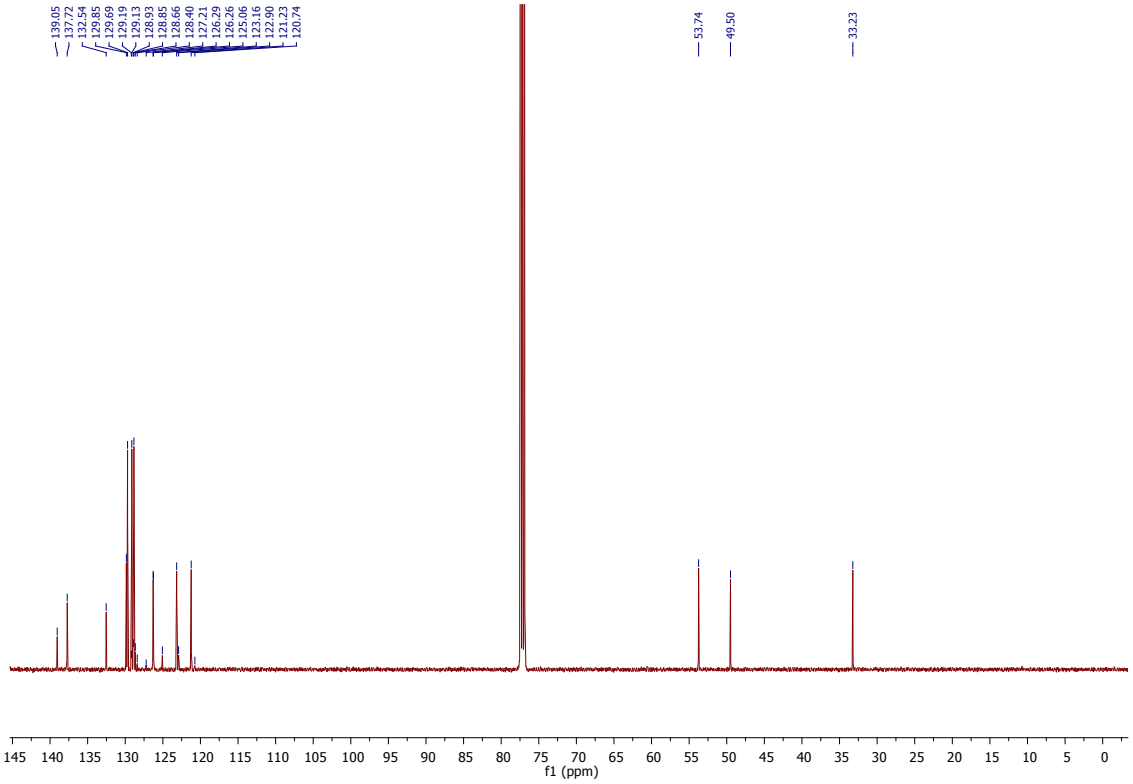


p-CF_3 imidazoium (k)

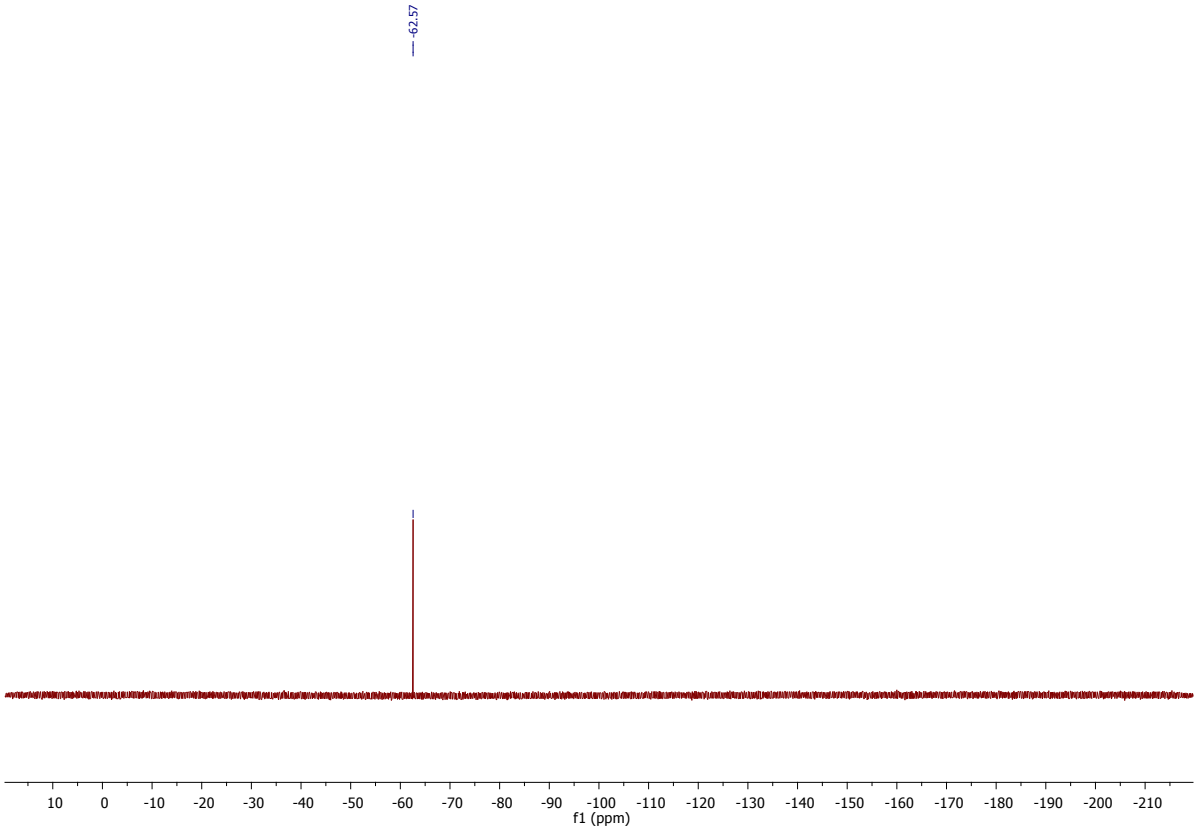
^{1}H NMR (300 MHz) $CDCl_3$



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

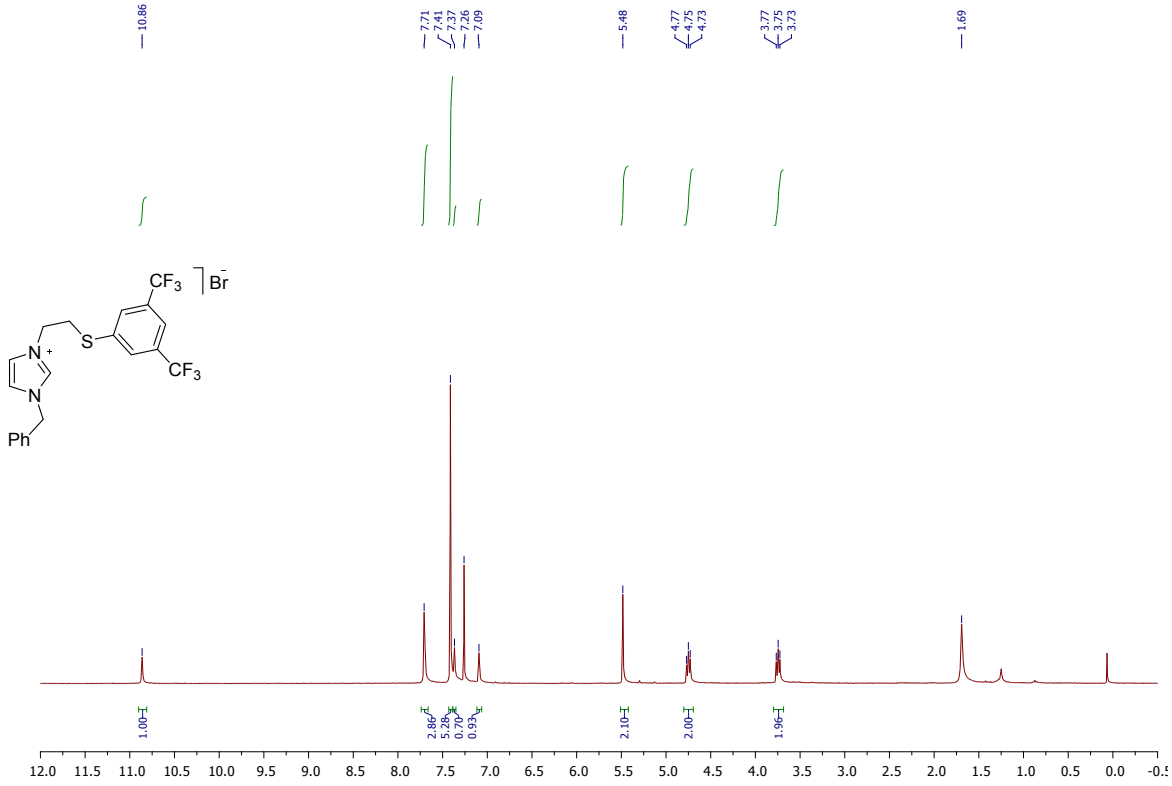


^{19}F NMR (300 MHz) $CDCl_3$

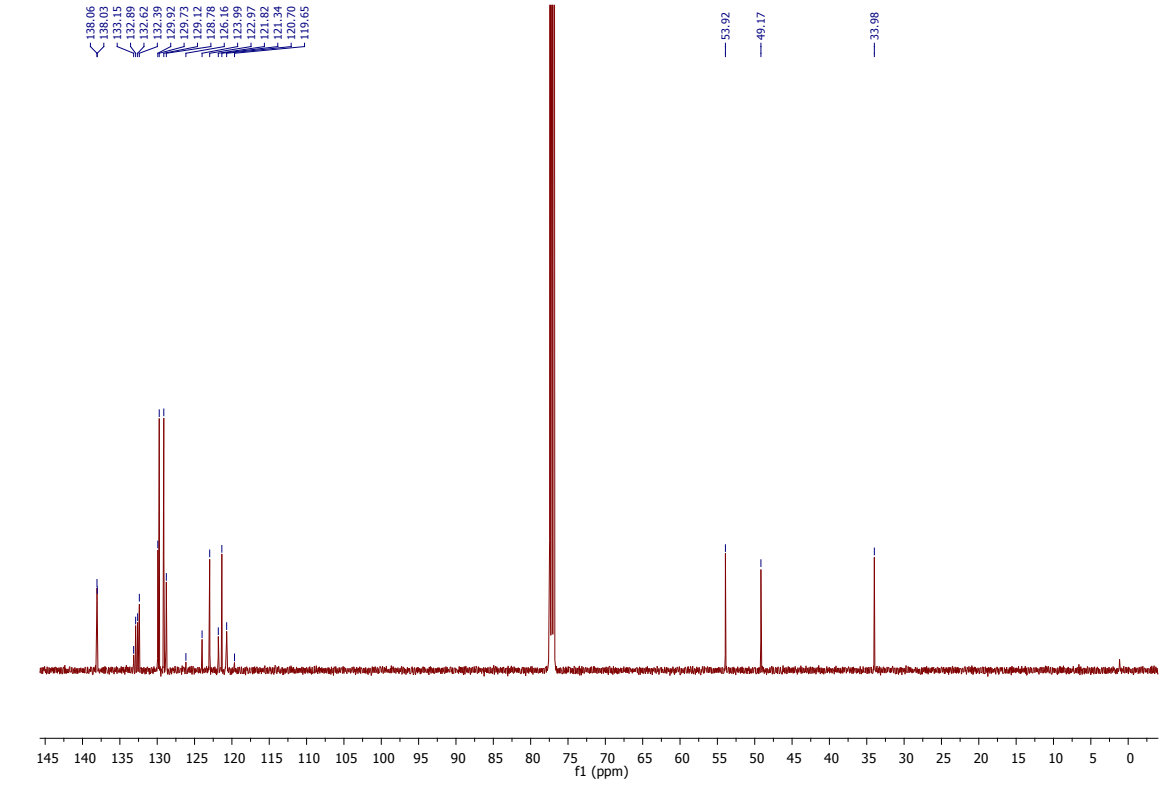


3,5-CF_3 imidazoium (l)

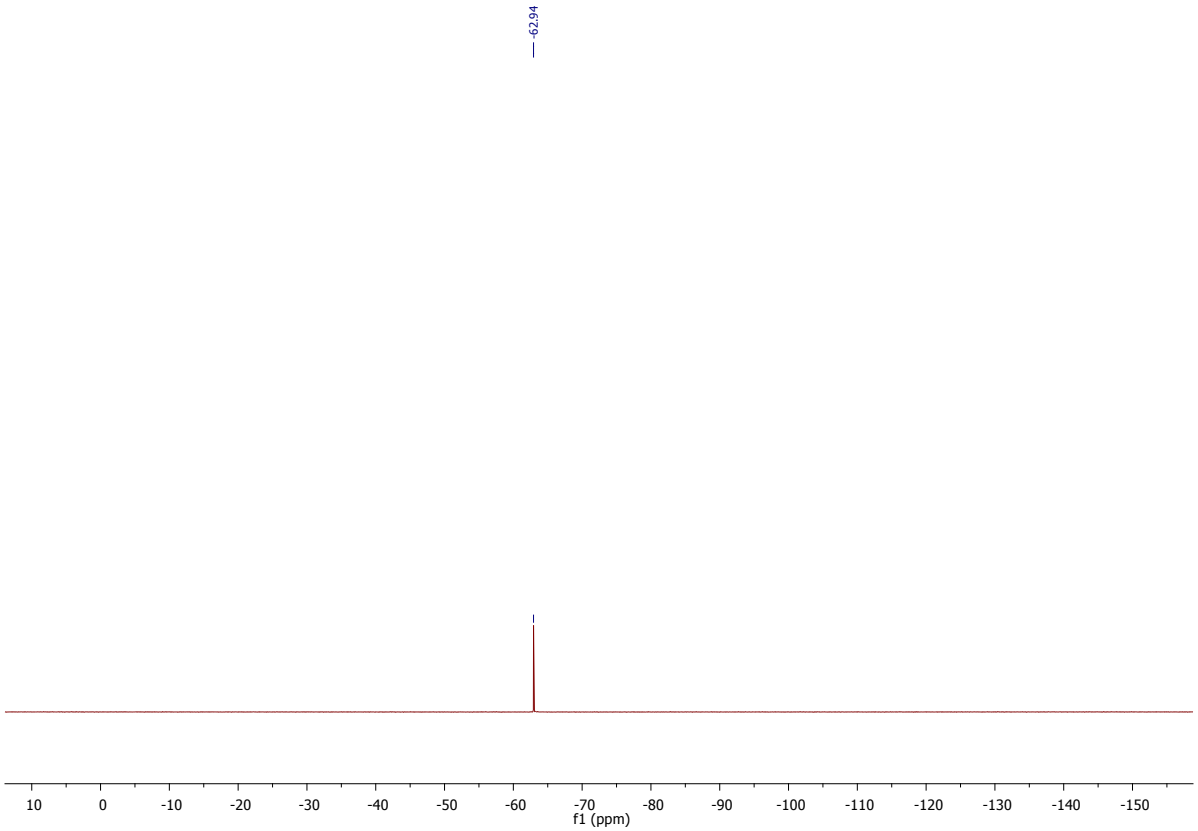
^{1}H NMR (300 MHz) $CDCl_3$



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

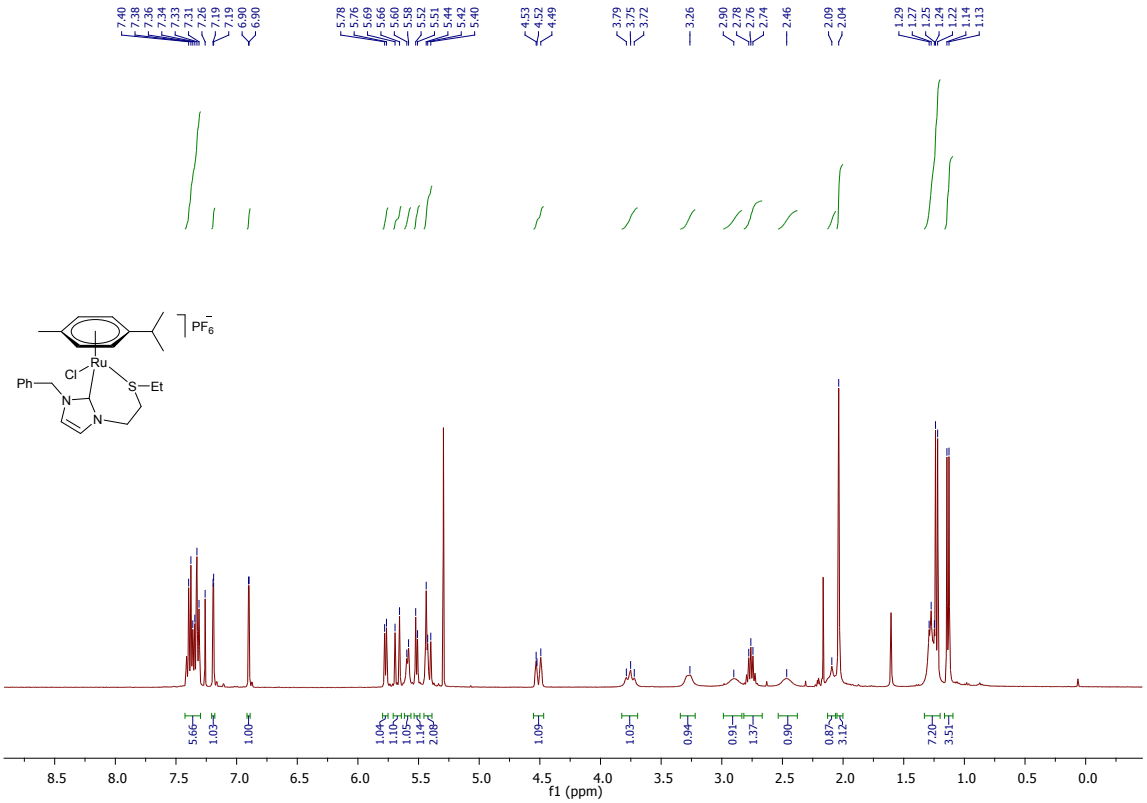


^{19}F NMR (300 MHz) $CDCl_3$

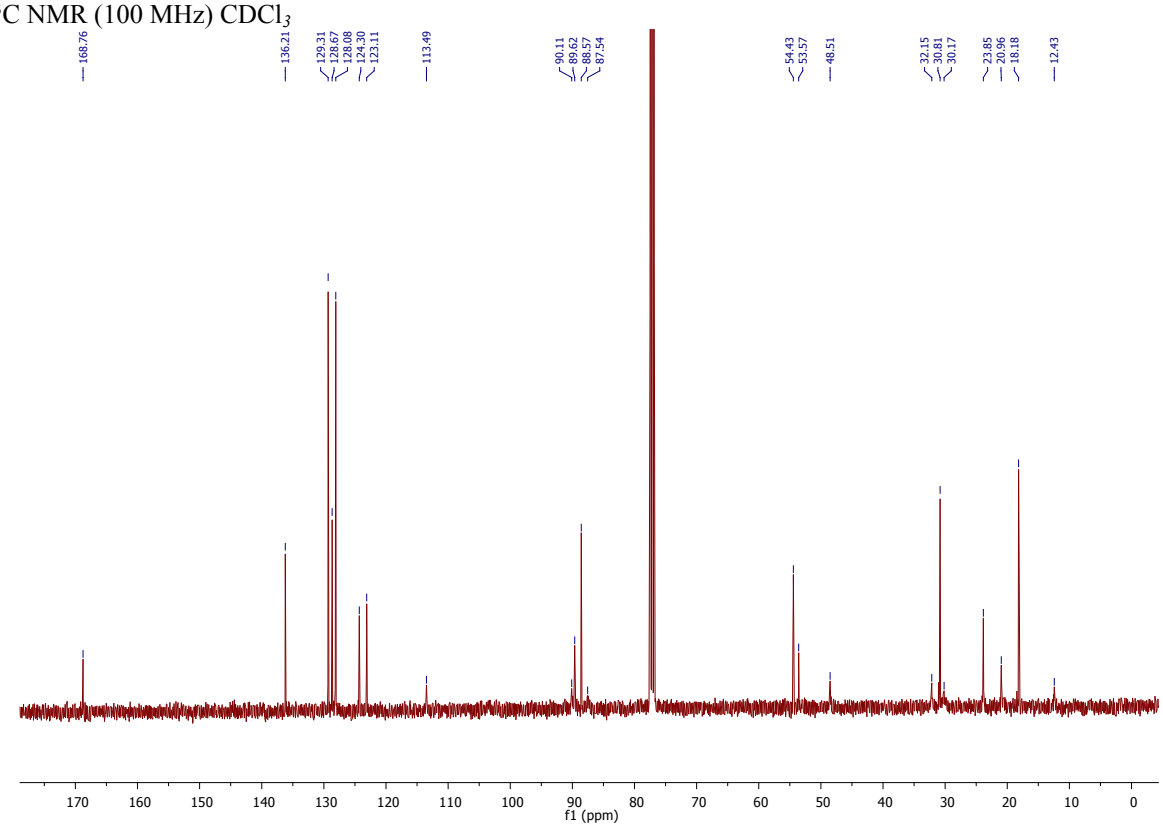


Ru SEt (1a)

^{1}H NMR (400 MHz) $CDCl_3$

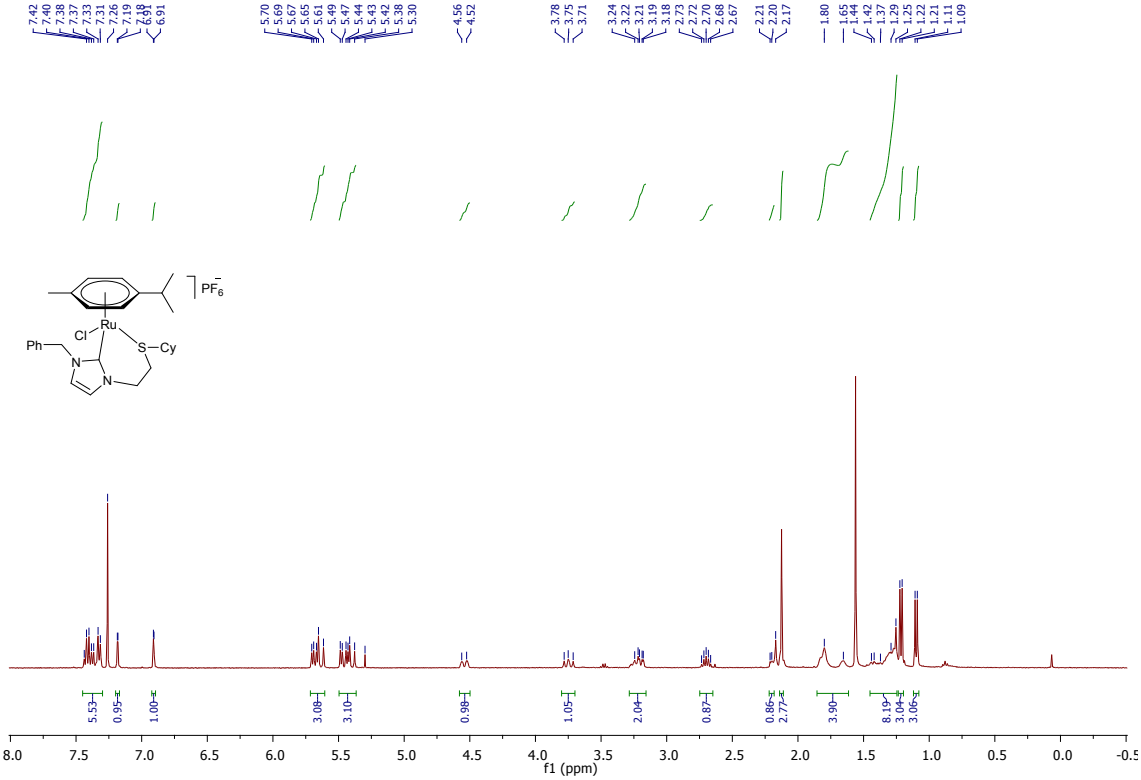


^{13}C NMR (100 MHz) $CDCl_3$

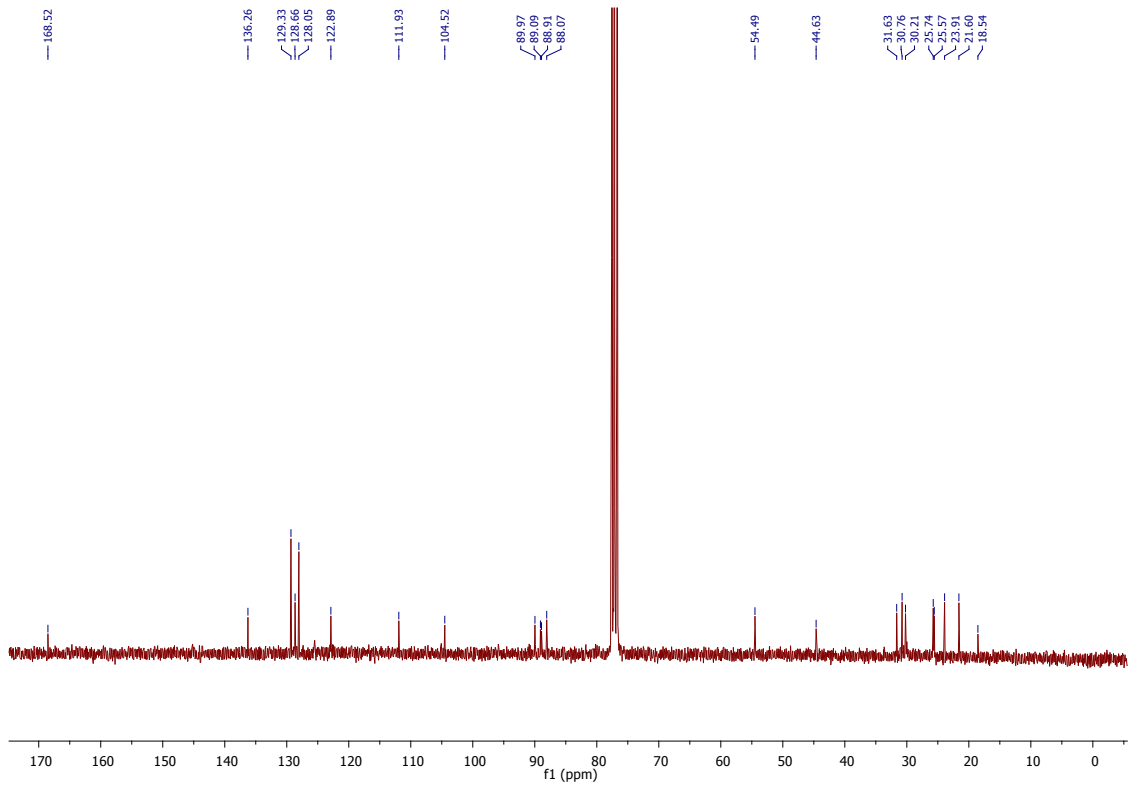


Ru SCy (1b)

^{1}H NMR (400 MHz) $CDCl_3$

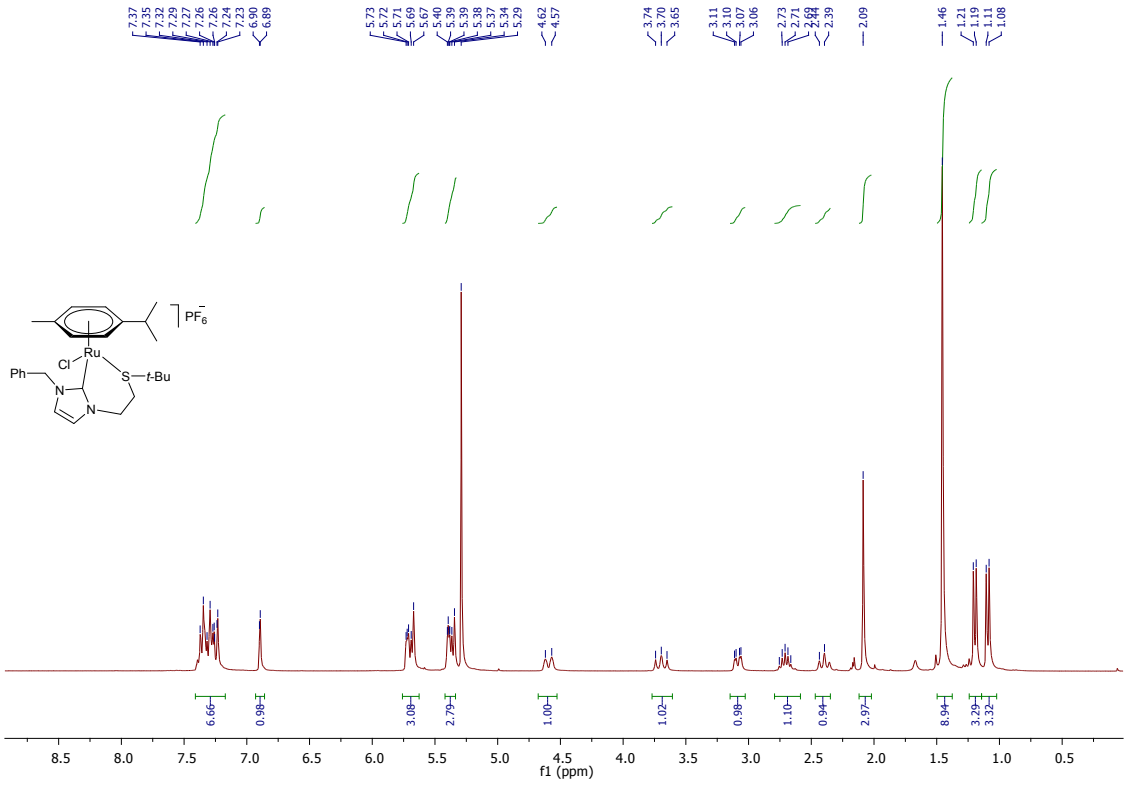


^{13}C NMR (100 MHz) $CDCl_3$

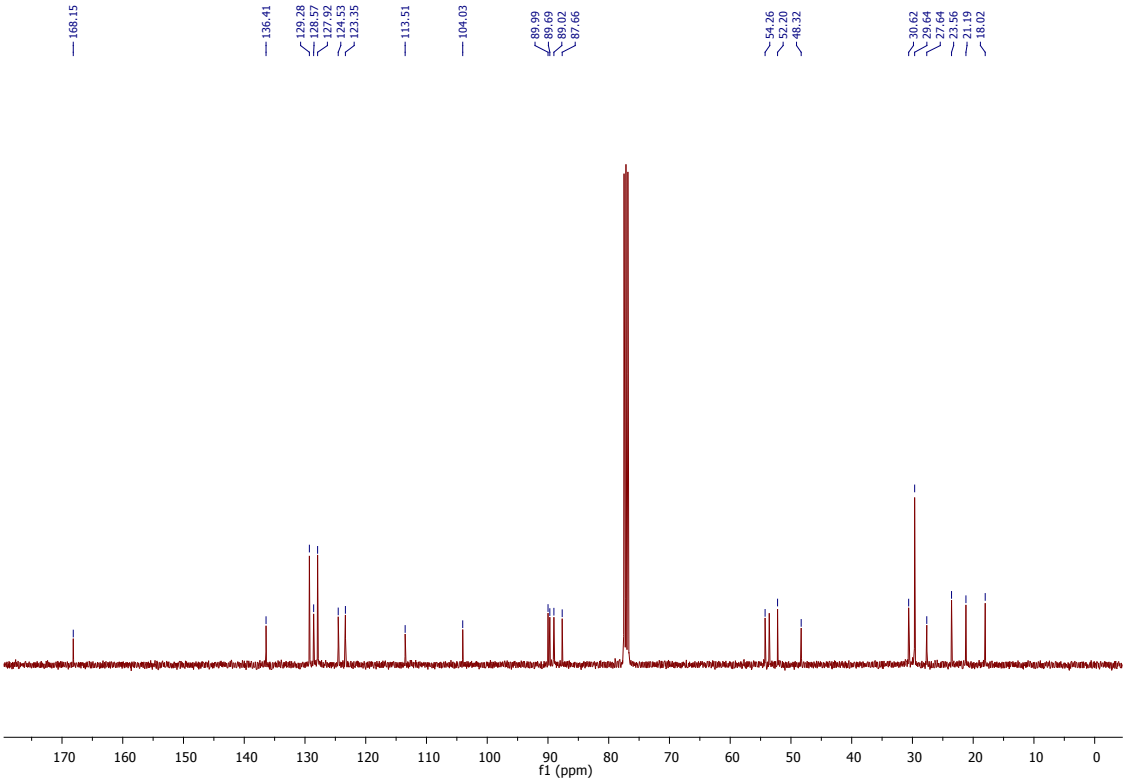


Ru StBu (1c)

^{1}H NMR (400 MHz) $CDCl_3$

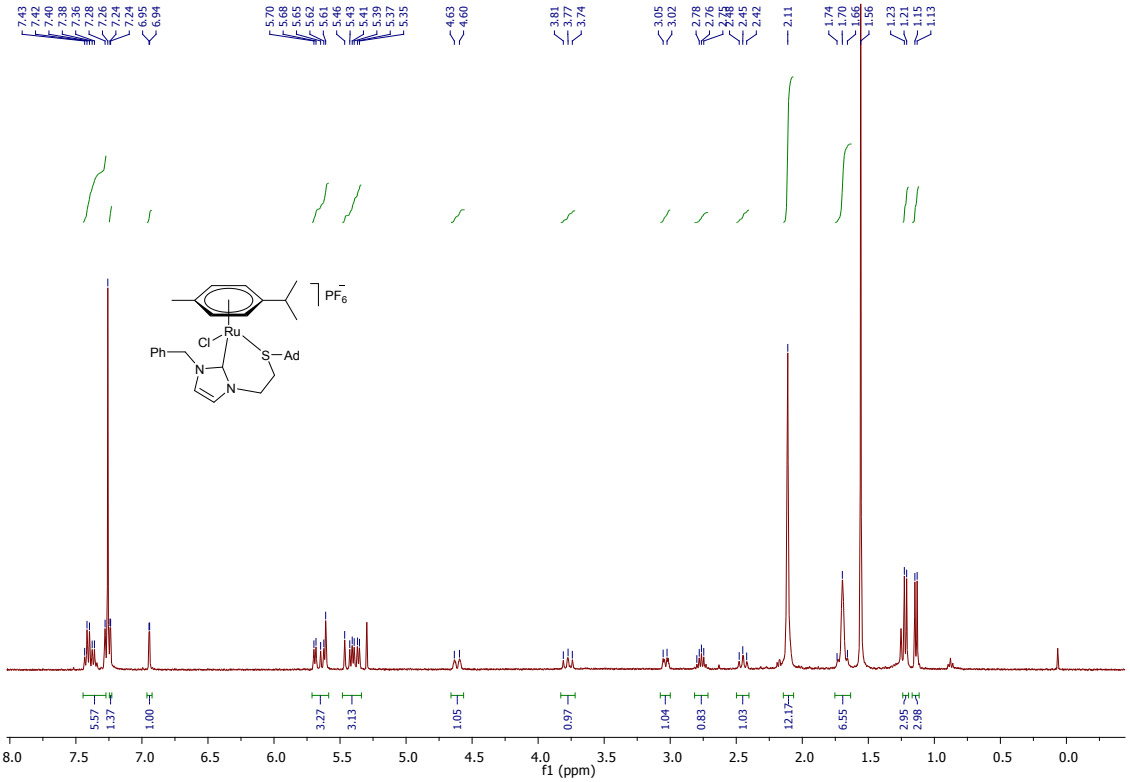


^{13}C NMR (100 MHz) $CDCl_3$

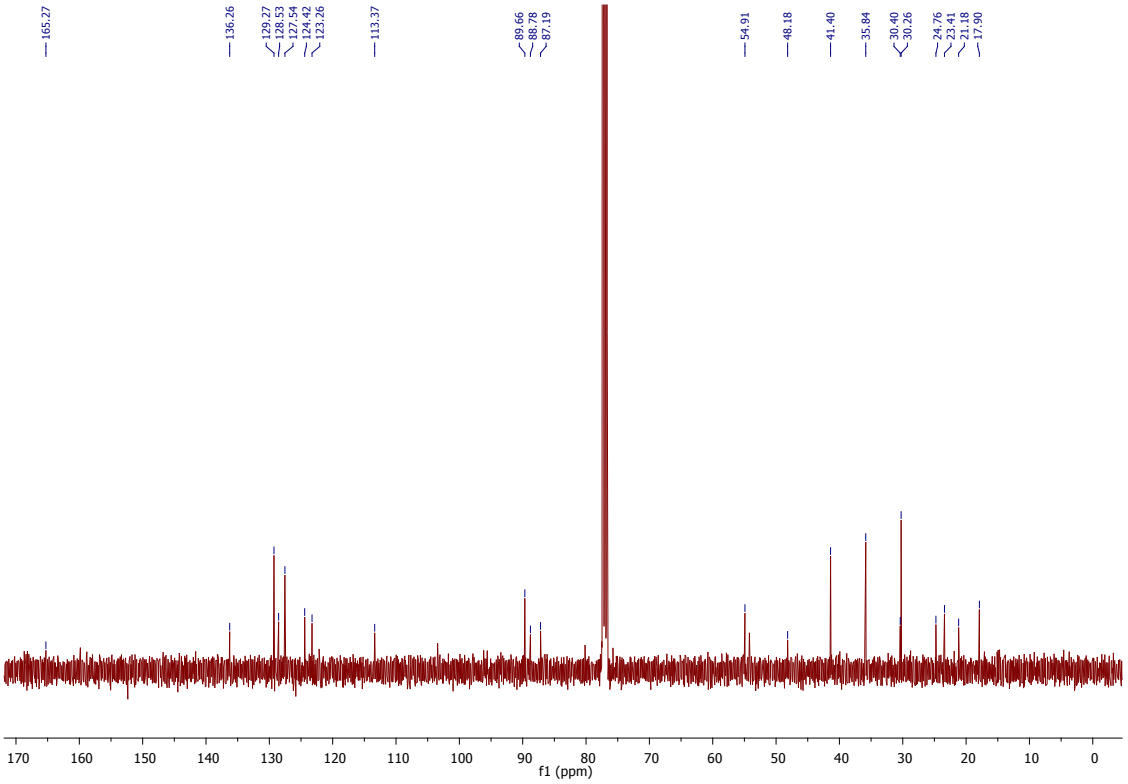


Ru StAd (1d)

^{1}H NMR (400 MHz) $CDCl_3$

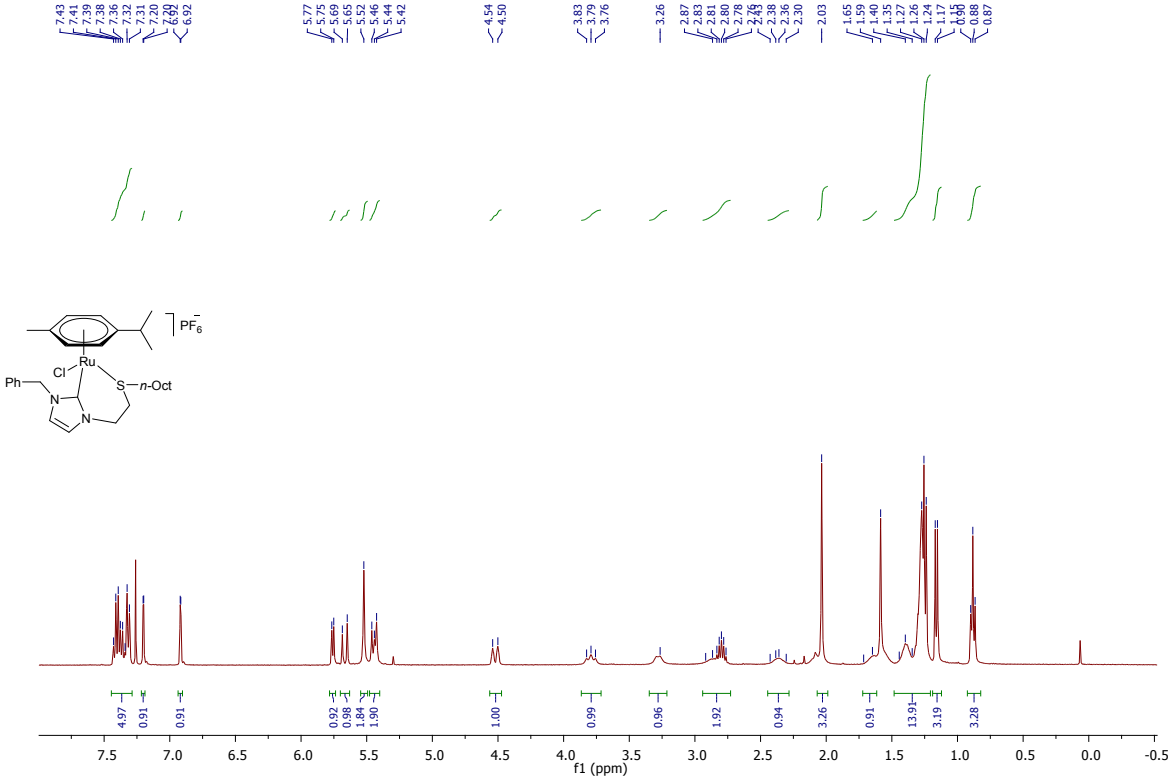


^{13}C NMR (100 MHz) $CDCl_3$

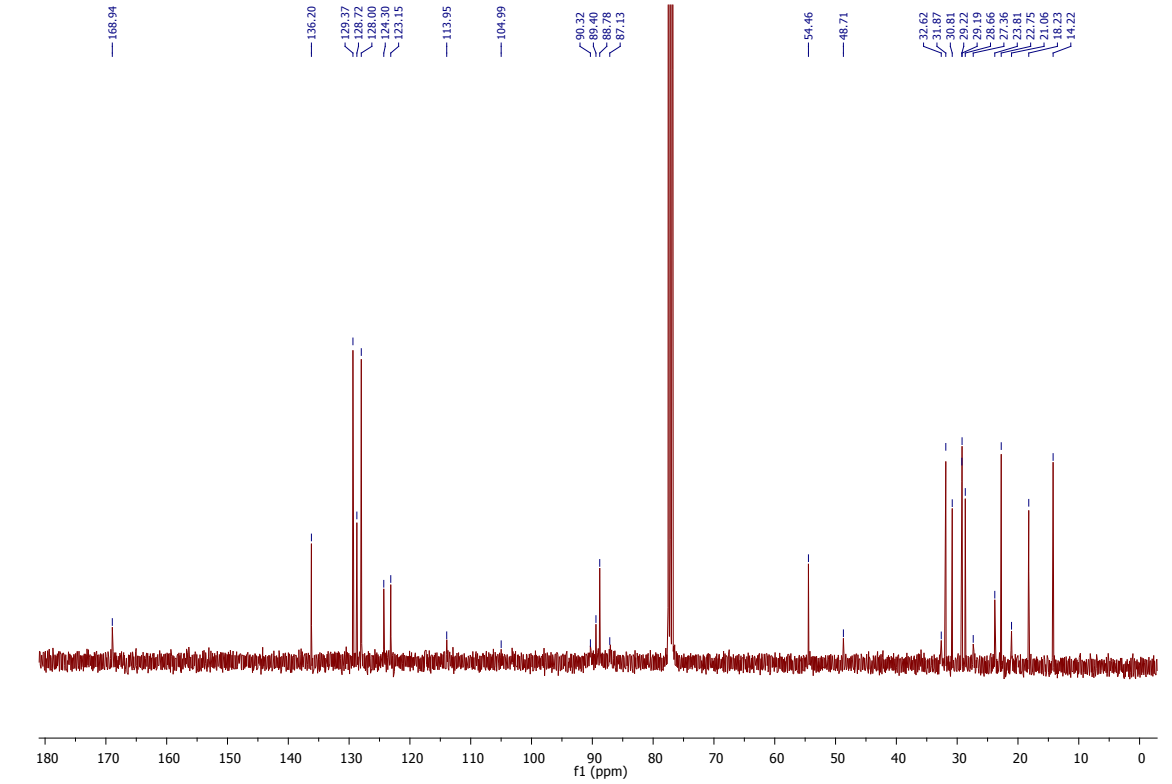


Ru S-*n*-Oct (1e)

^{1}H NMR (400 MHz) $CDCl_3$

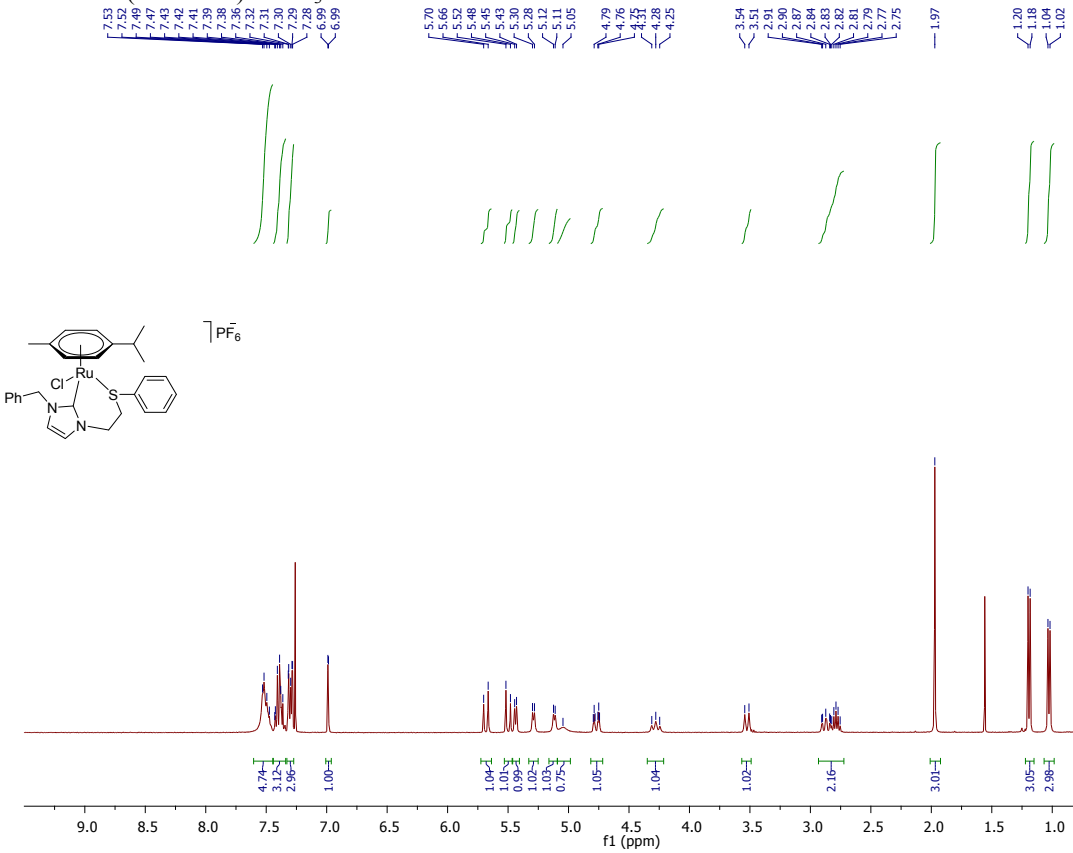


^{13}C NMR (100 MHz) $CDCl_3$

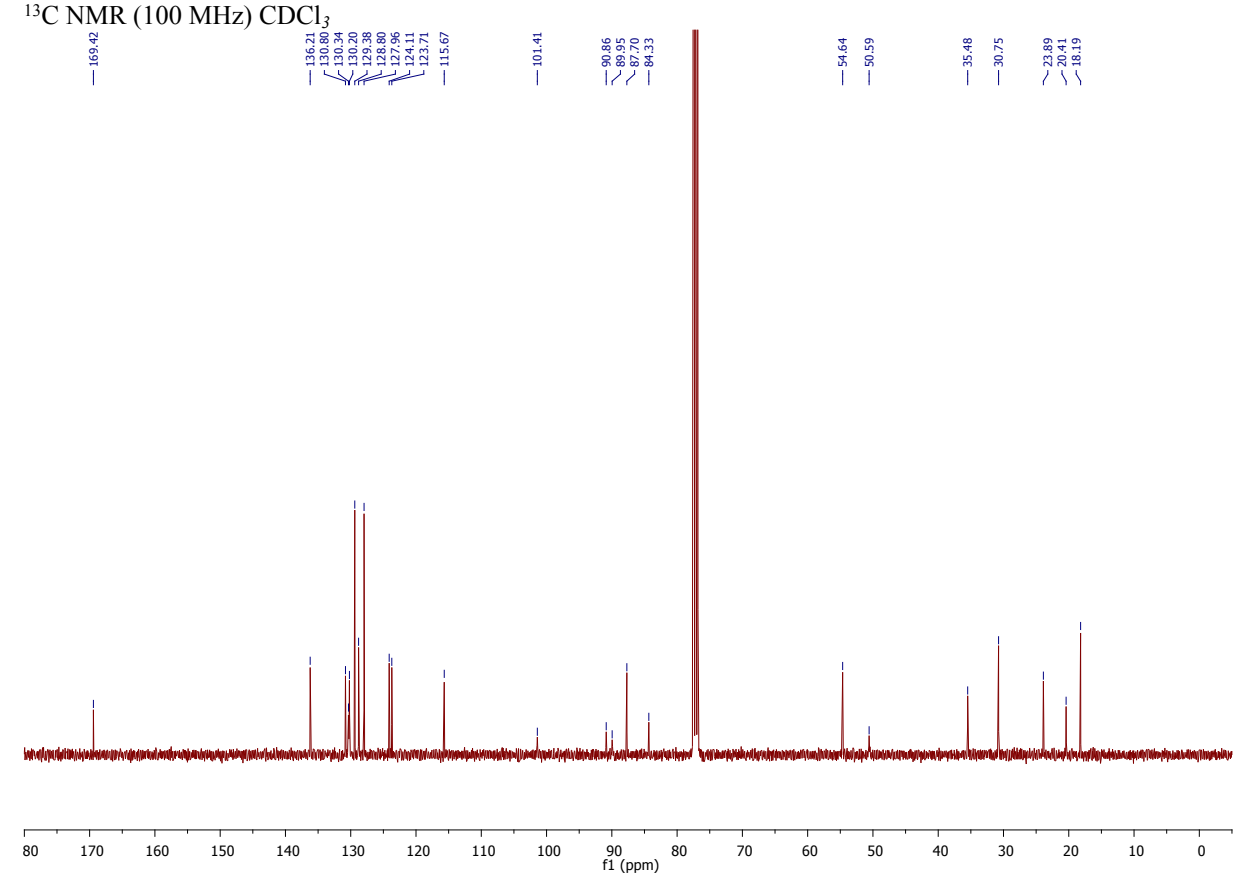


Ru S-*Ph* (1l)

^{1}H NMR (400 MHz) $CDCl_3$

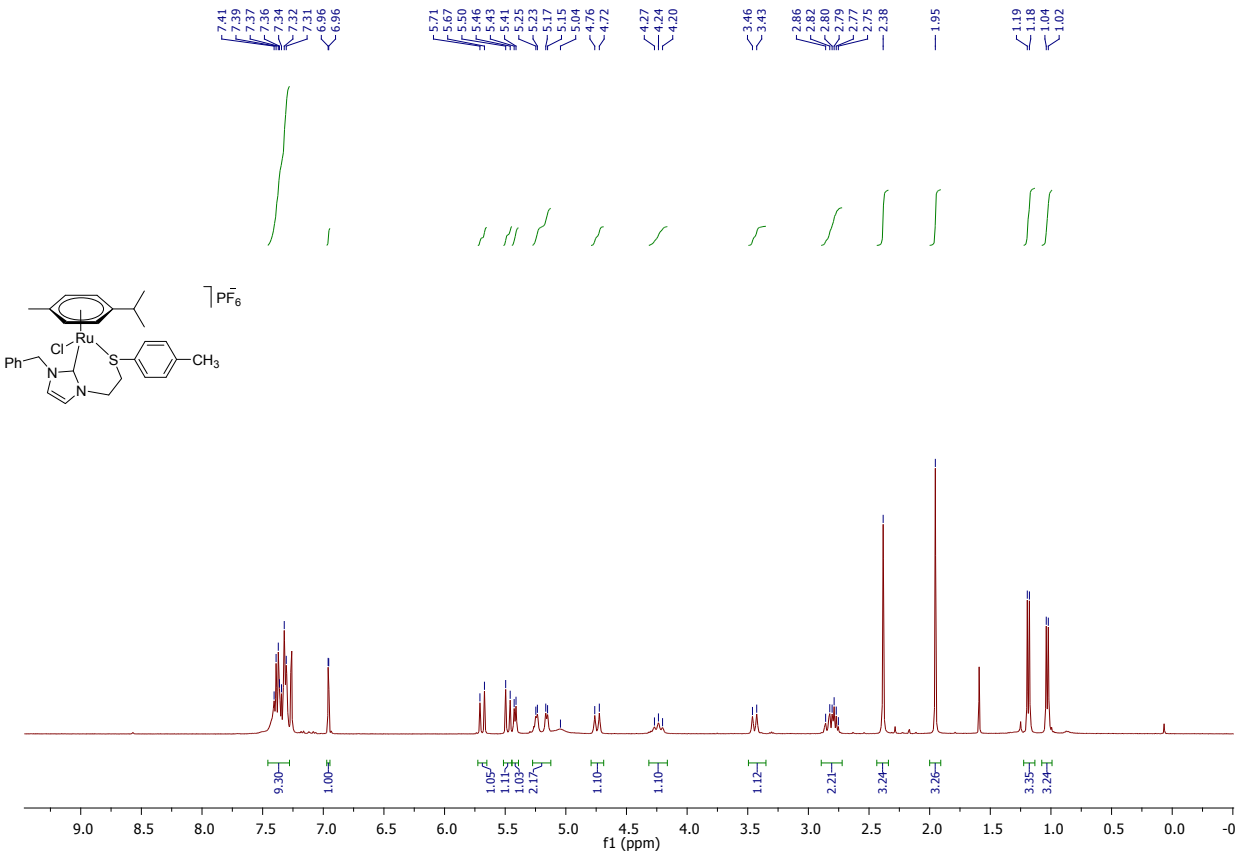


^{13}C NMR (100 MHz) $CDCl_3$

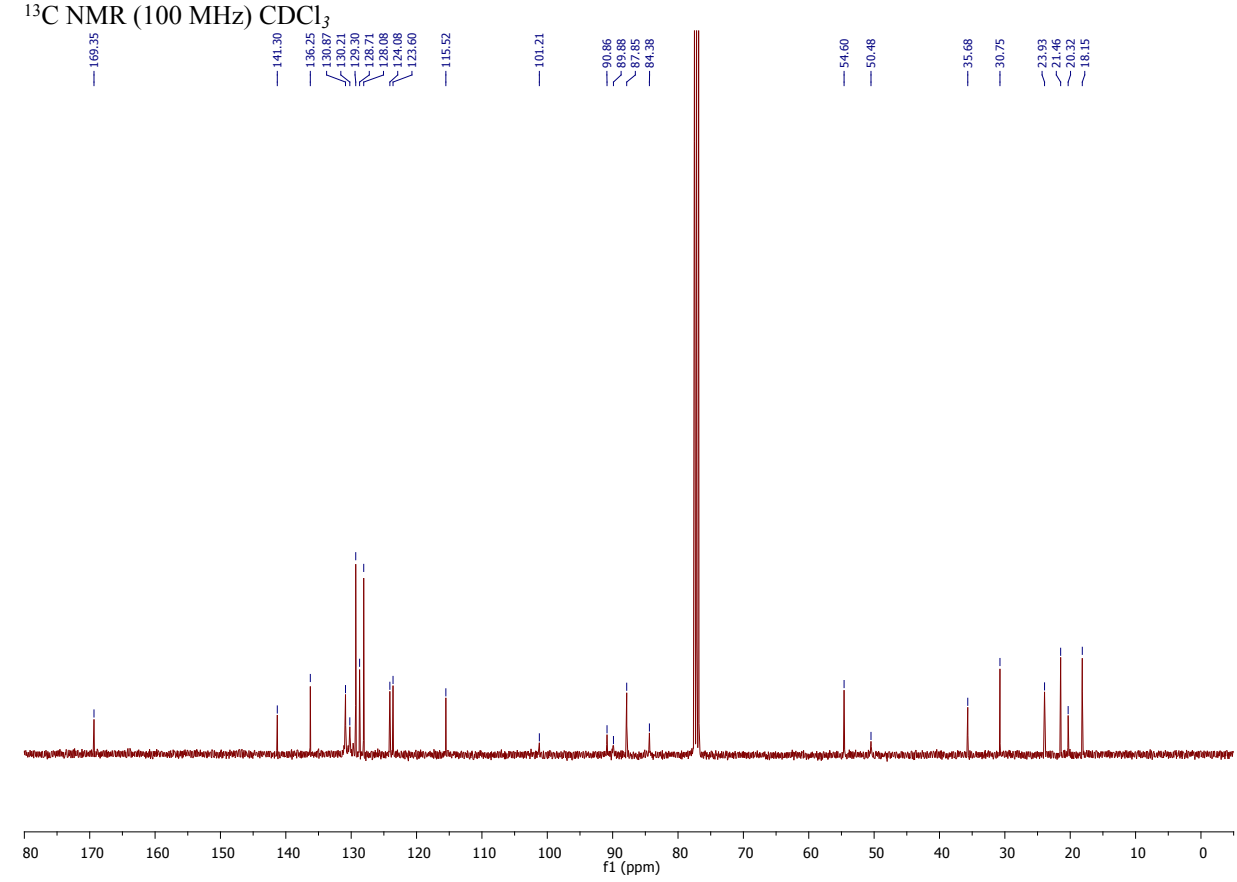


Ru S-*Ph* (1l)

^{1}H NMR (400 MHz) $CDCl_3$

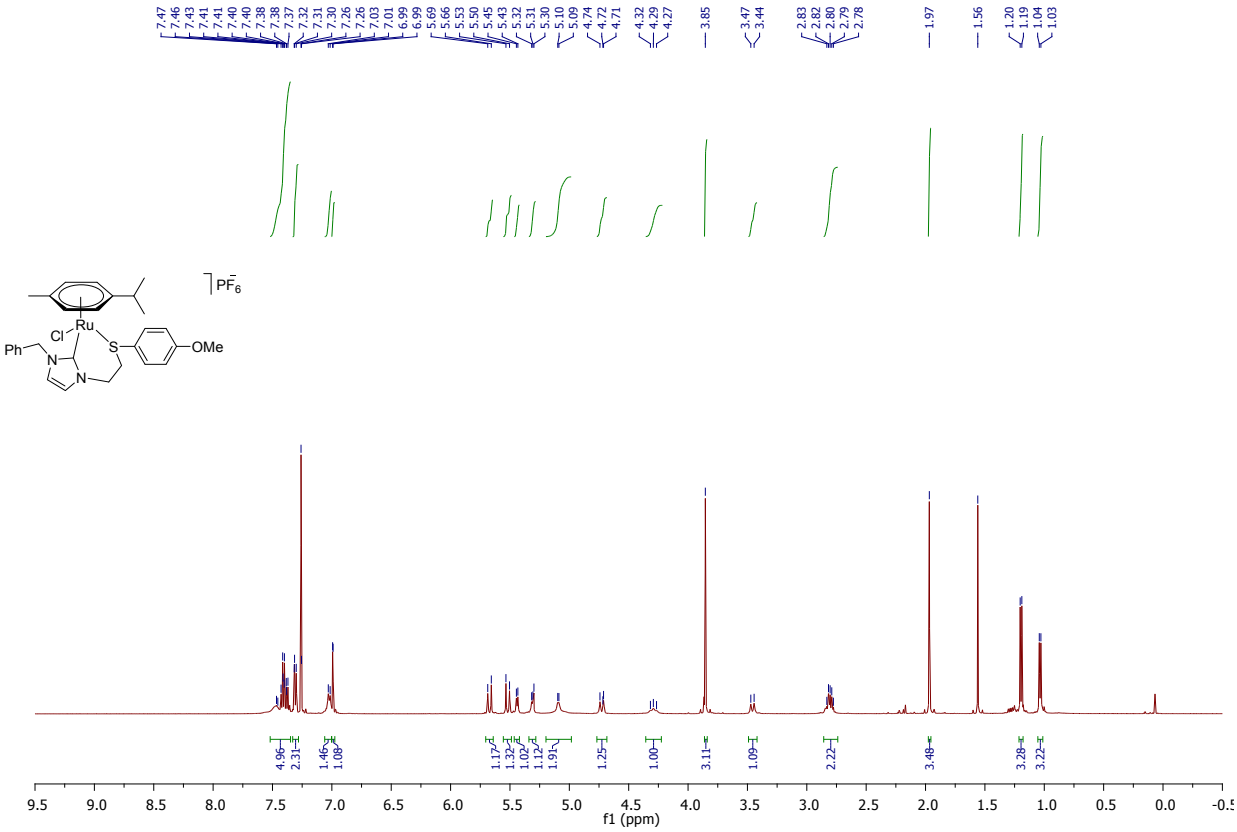


^{13}C NMR (100 MHz) $CDCl_3$

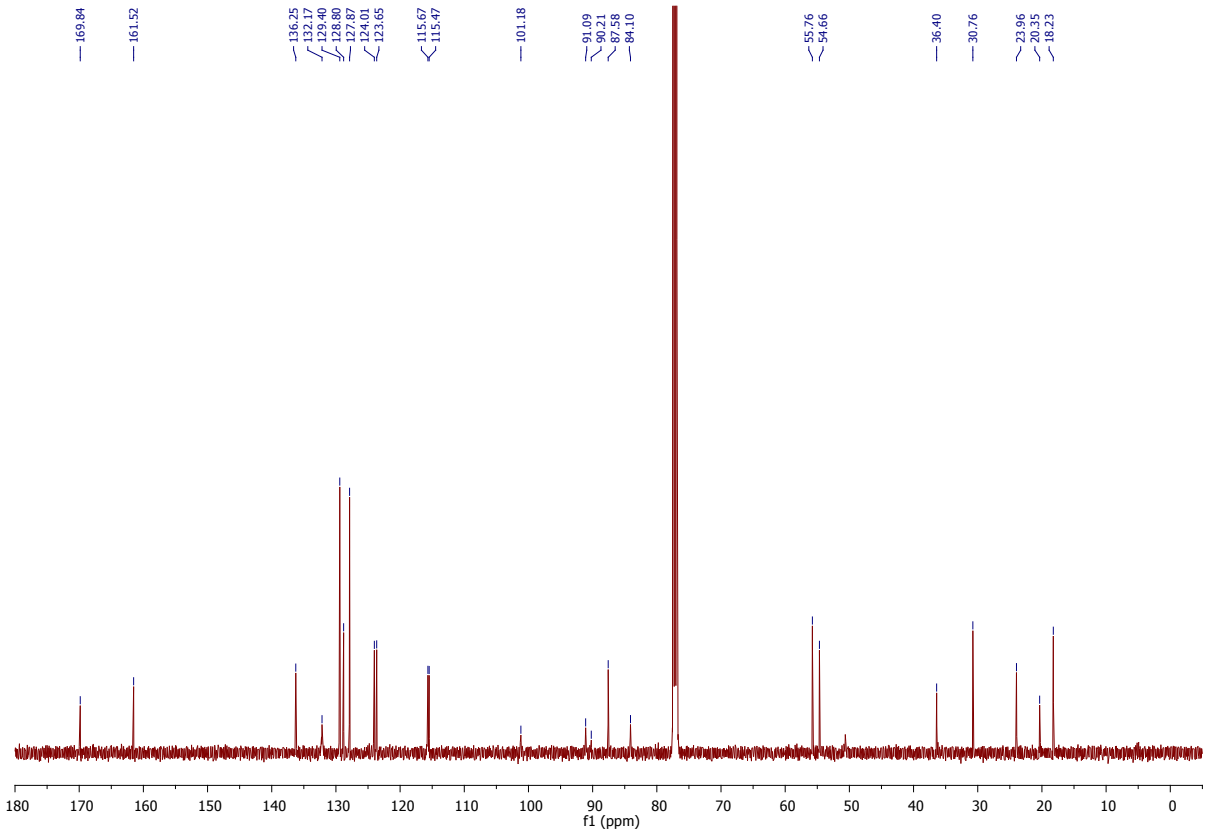


Ru S-*p-OMe* (1h)

^{1}H NMR (400 MHz) $CDCl_3$

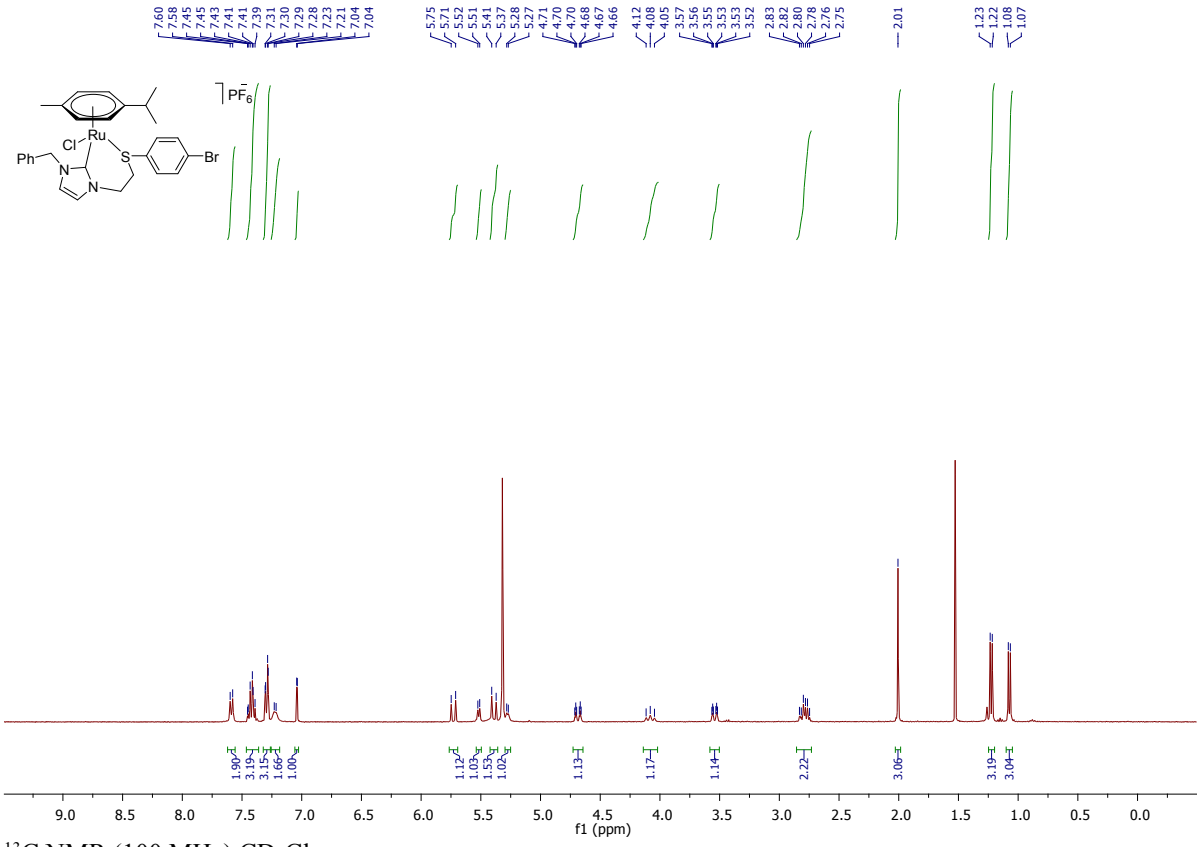


^{13}C NMR (100 MHz) $CDCl_3$

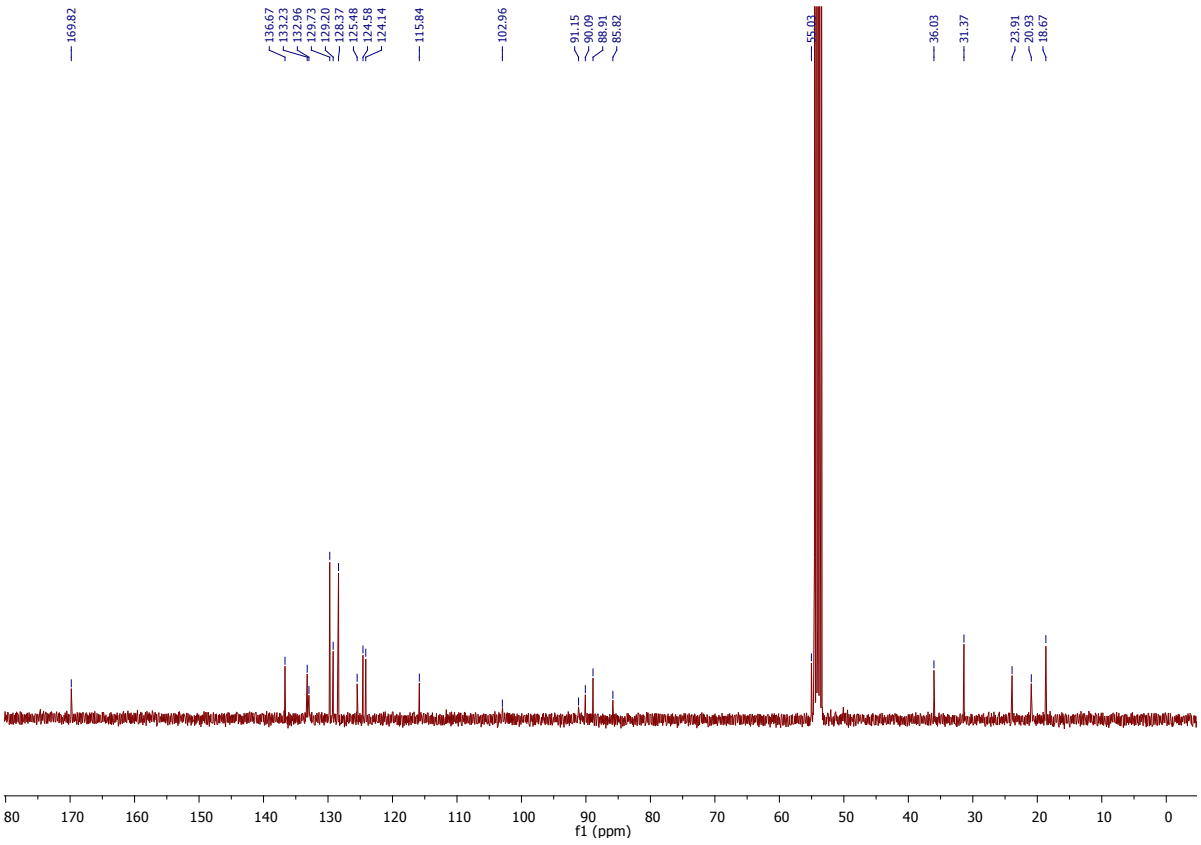


Ru S-*p-Br* (1i)

^{1}H NMR (400 MHz) CD_2Cl_2

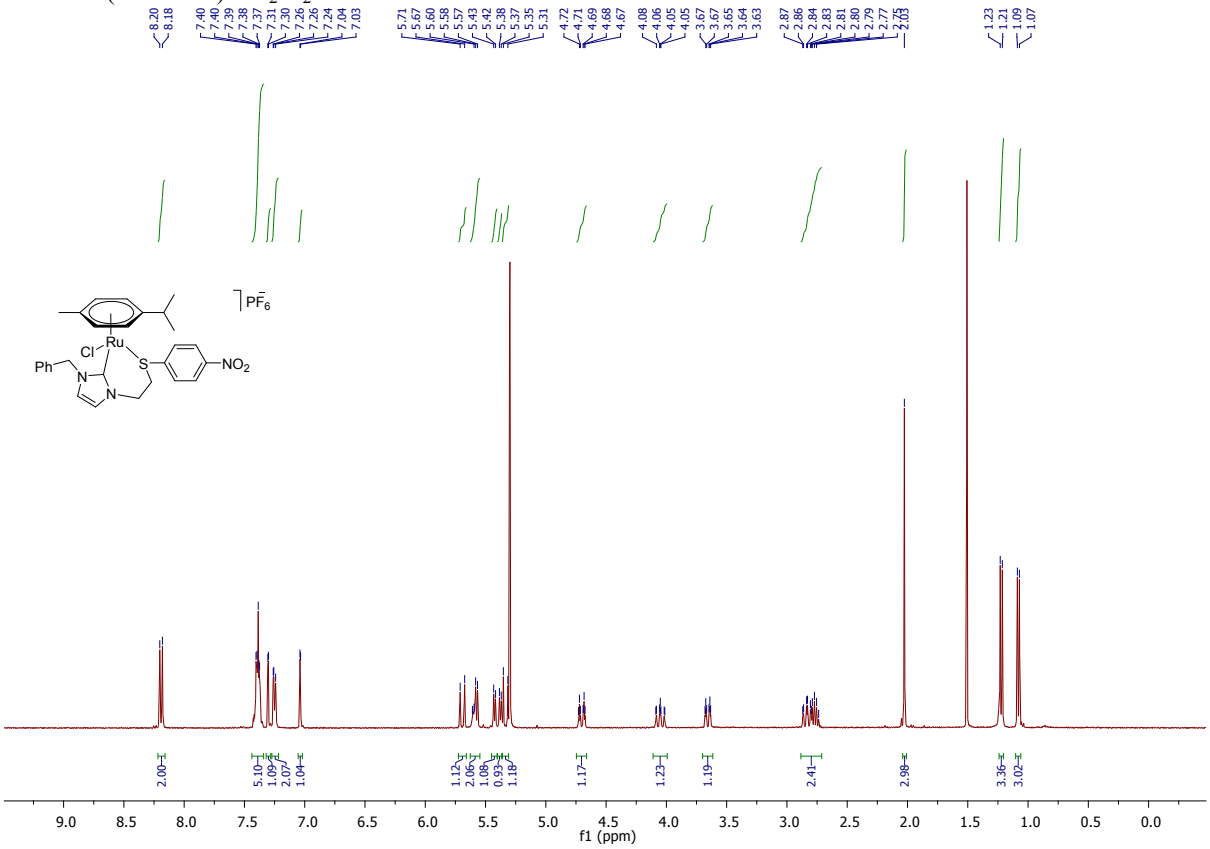


^{13}C NMR (100 MHz) CD_2Cl_2

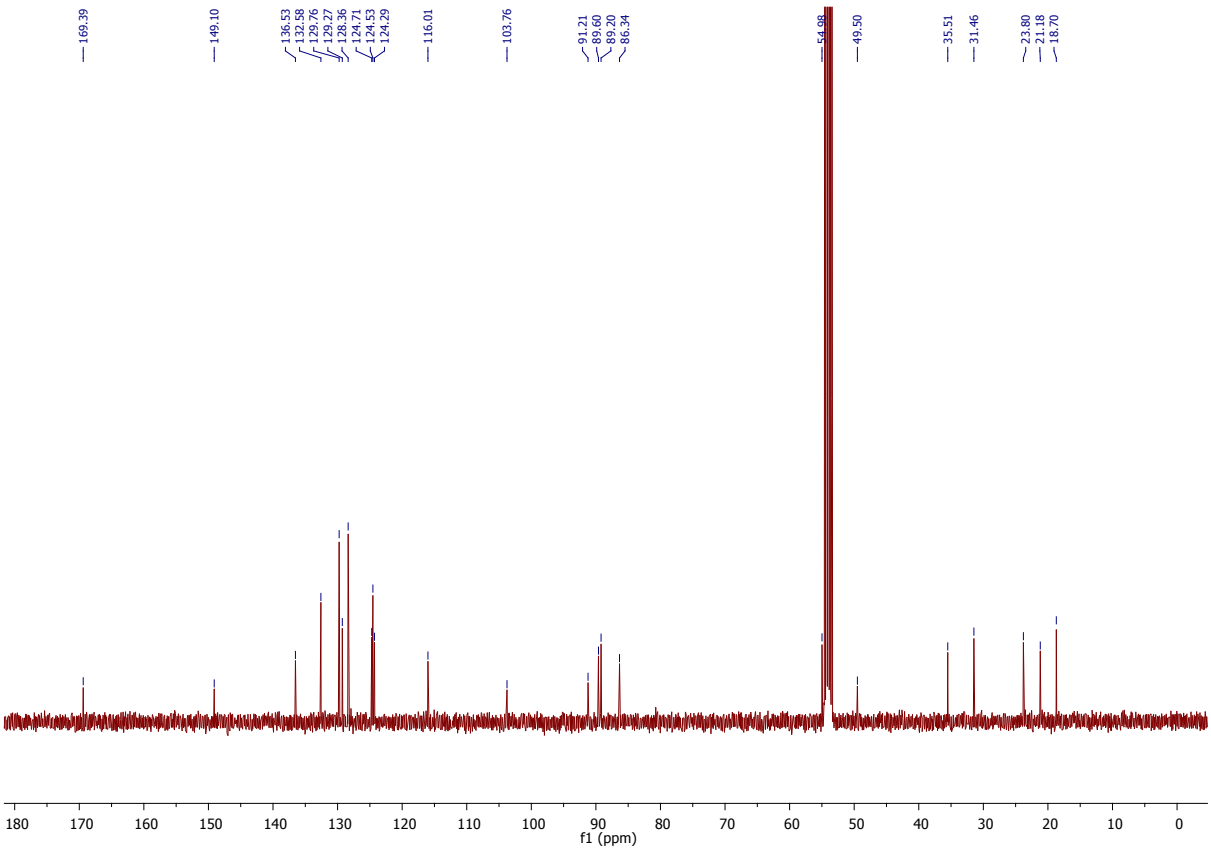


Ru S-*p*-NO_2 (1j)

^{1}H NMR (400 MHz) CD_2Cl_2

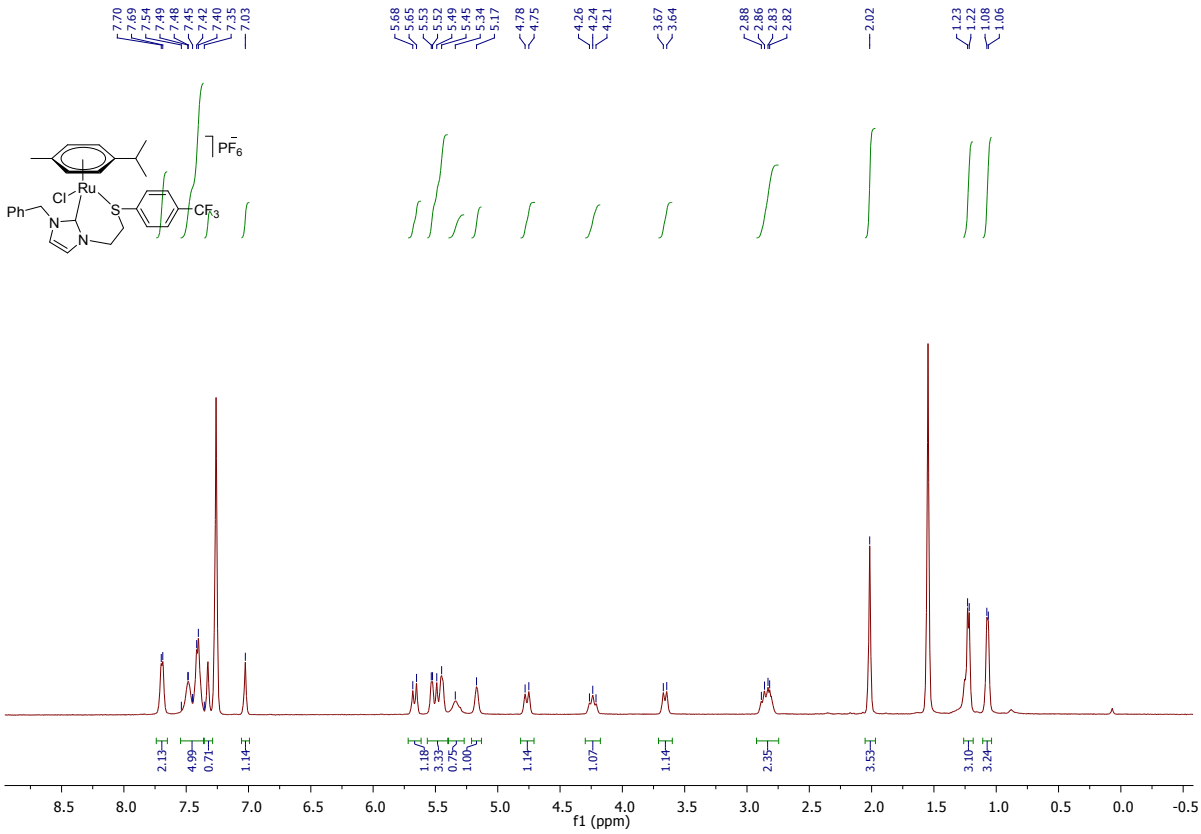


^{13}C NMR (100 MHz) CD_2Cl_2

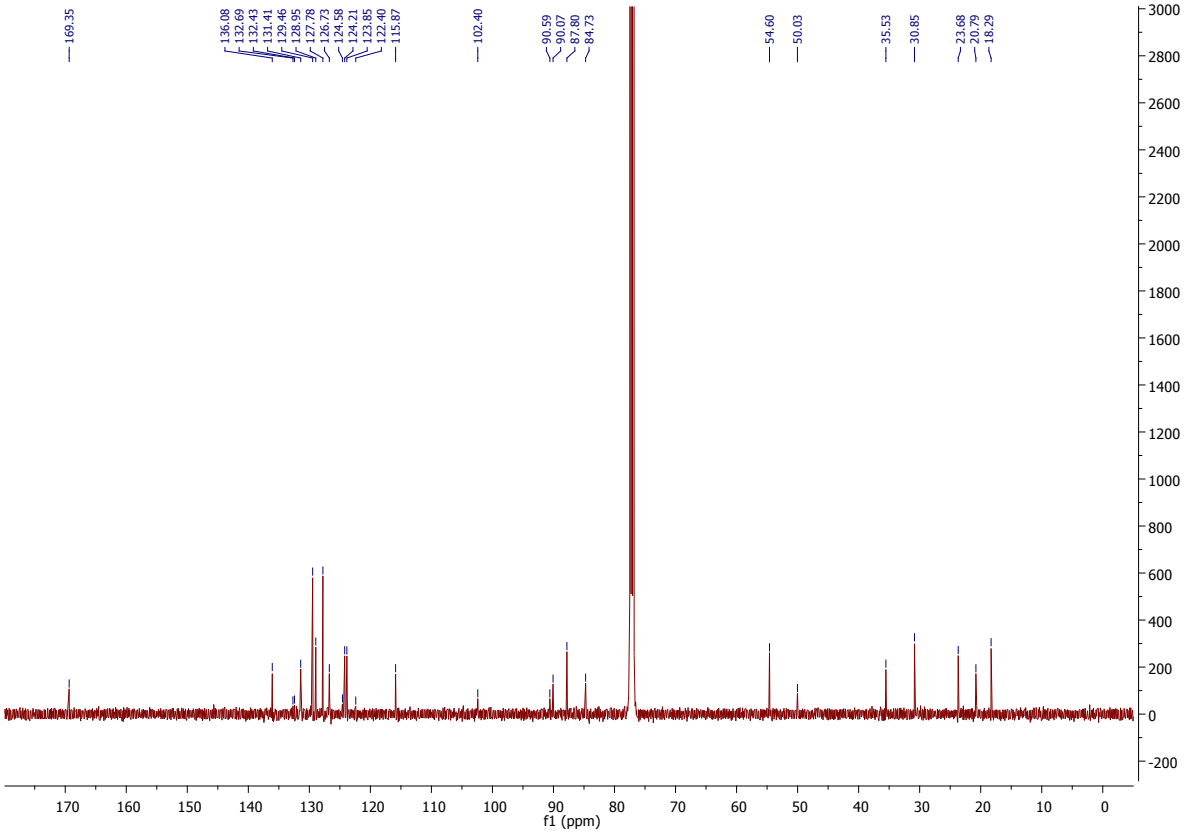


Ru S-*p*-CF_3 (1k)

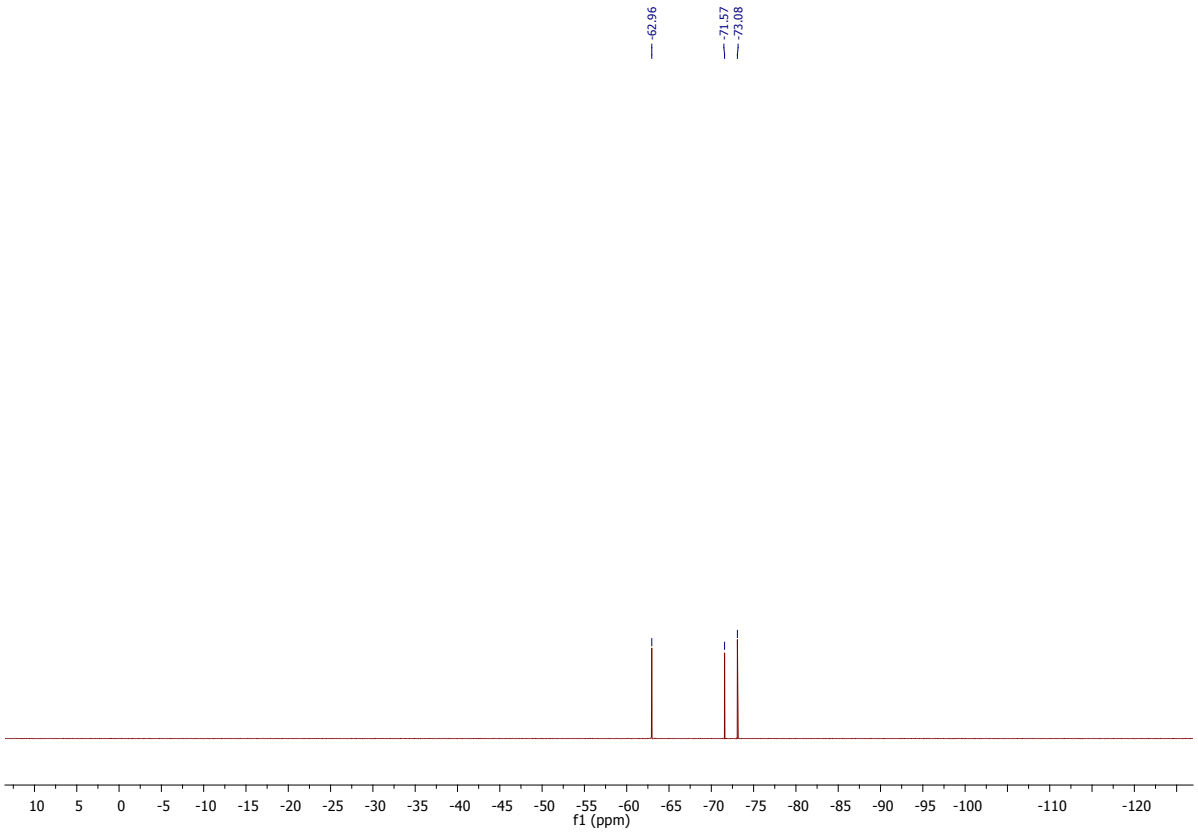
^{1}H NMR (500 MHz) $CDCl_3$



^{13}C NMR (126 MHz) CD_2Cl_2

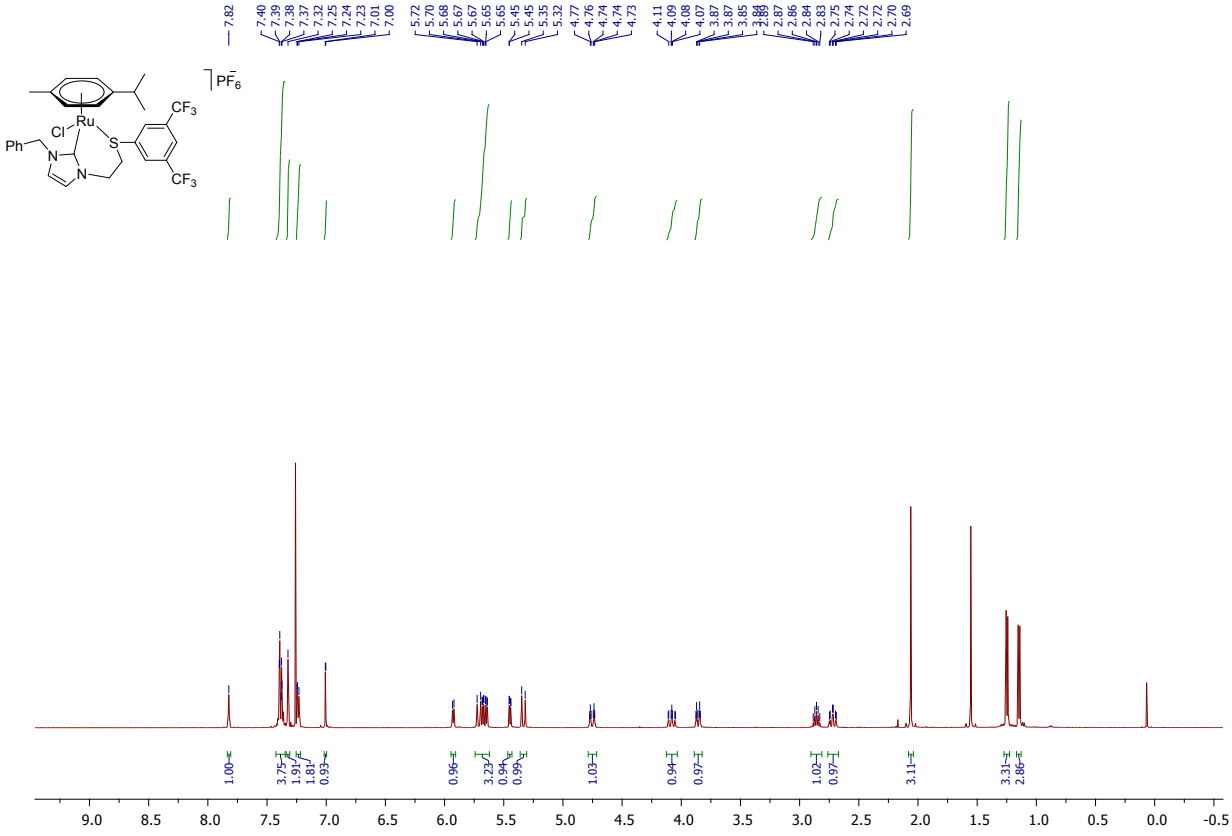


^{19}F NMR (471 MHz) $CDCl_3$

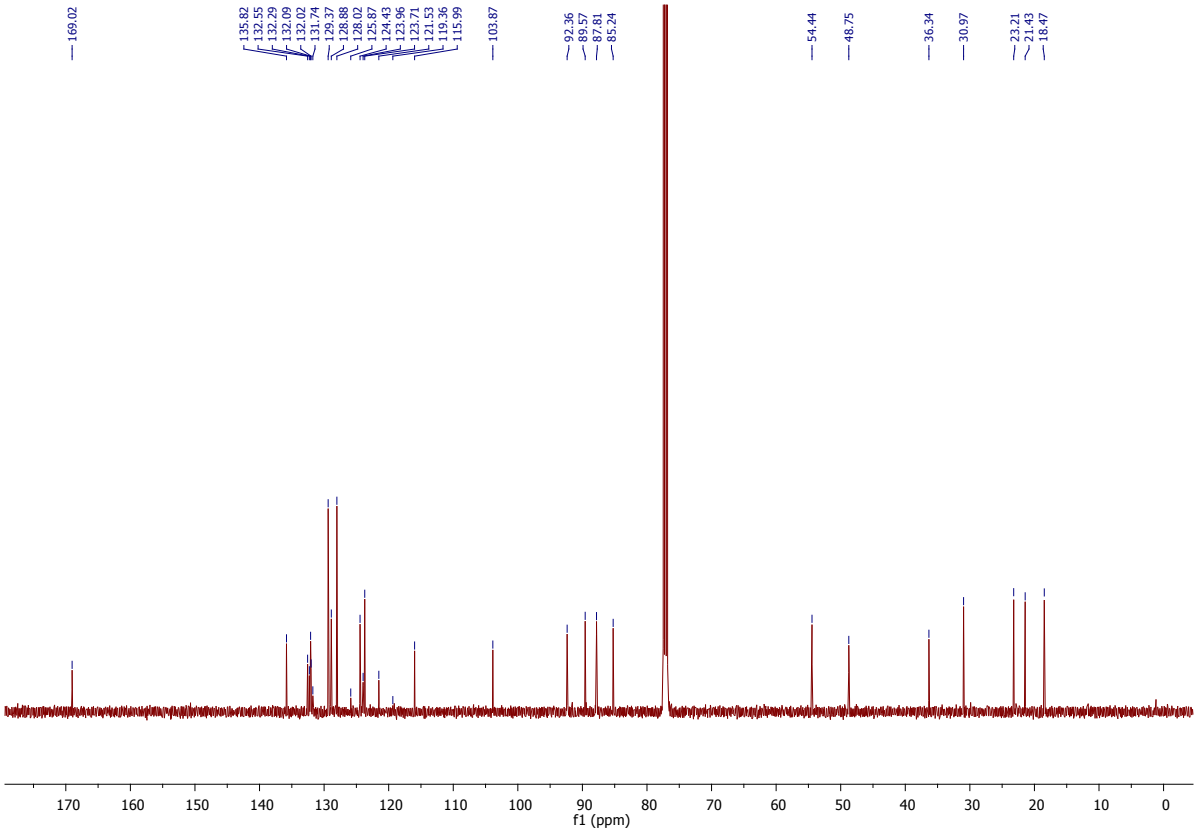

-62.96
-71.57
-73.08
10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -110 -120
f1 (ppm)

Ru S-*3,5-CF$_3$* (1l)

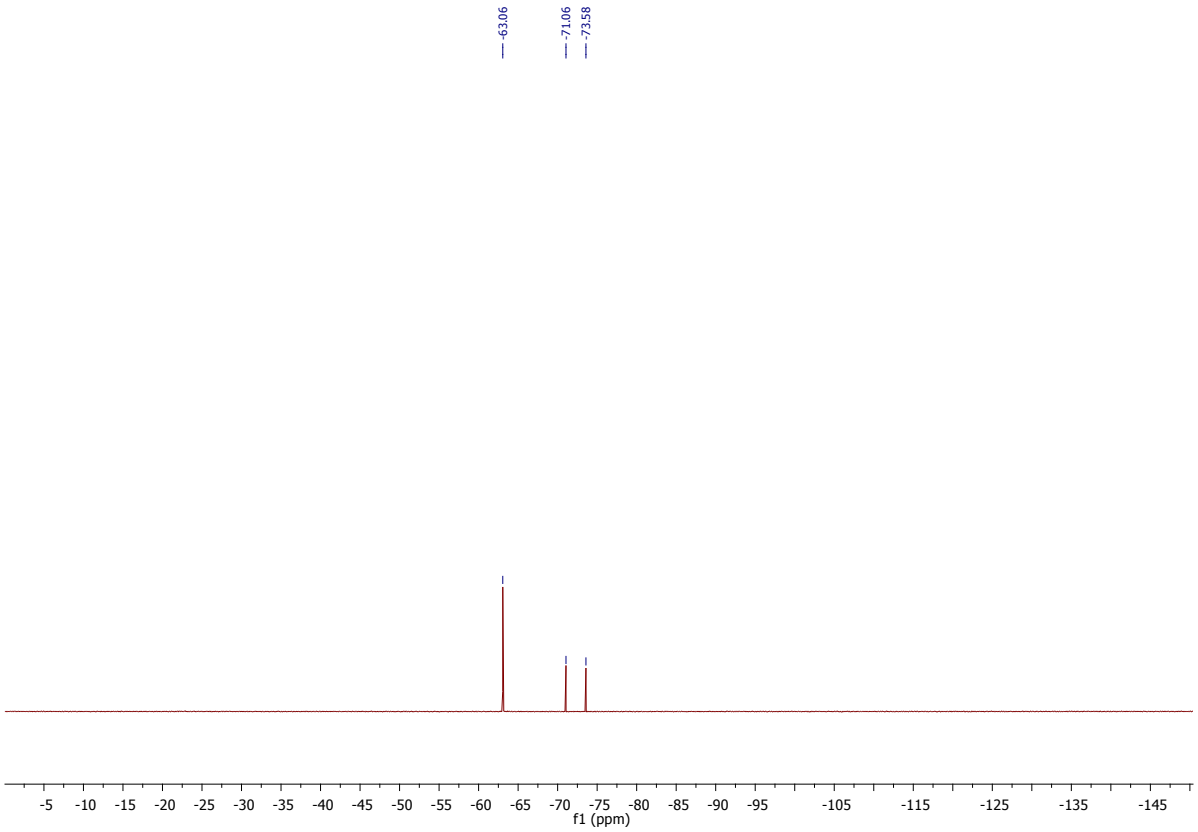
^{1}H NMR (400 MHz) $CDCl_3$



^{13}C NMR (100 MHz) $CDCl_3$

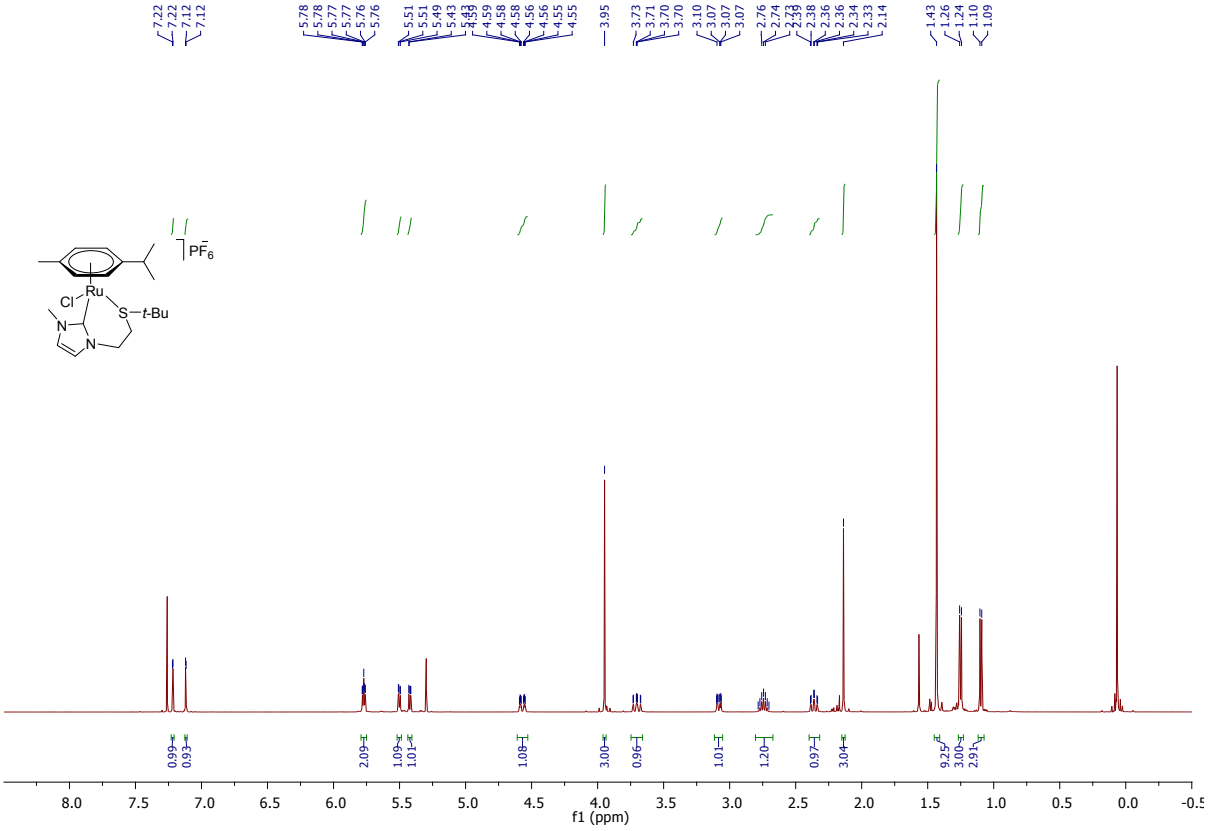


^{19}F NMR (282 MHz) $CDCl_3$

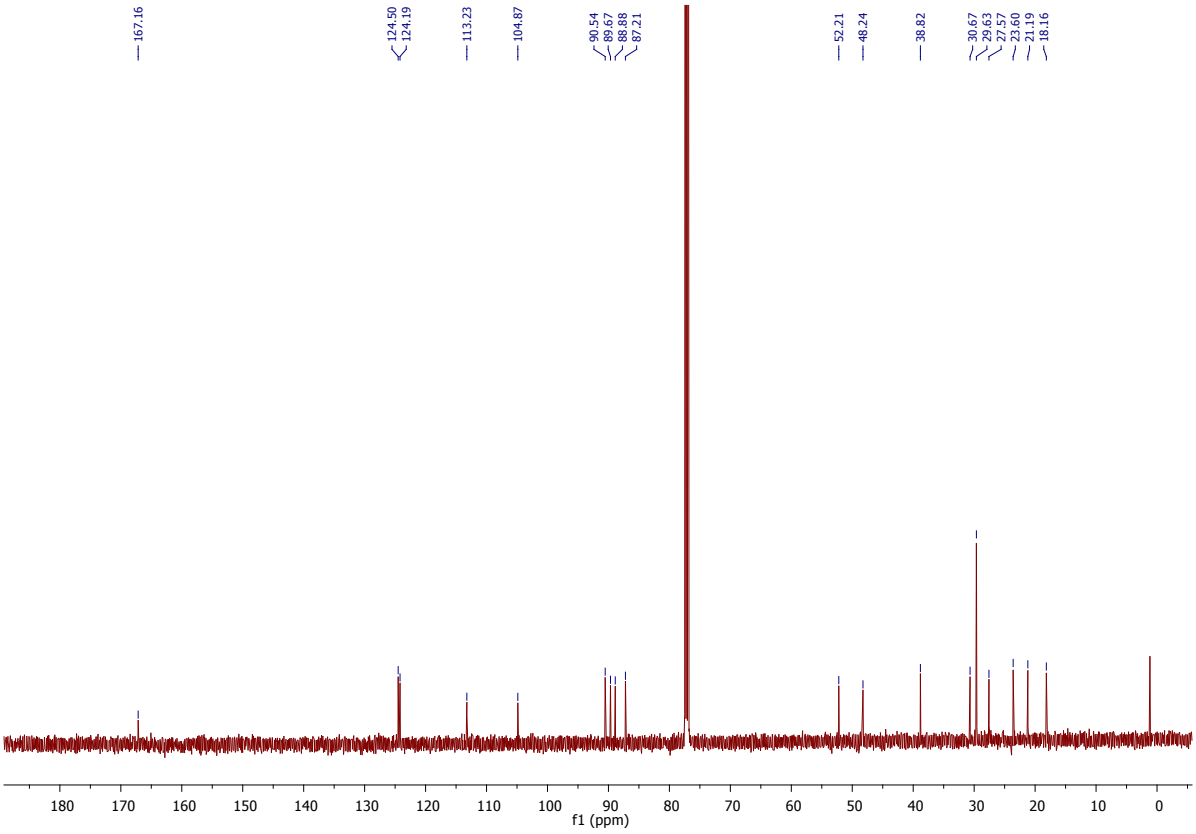


Ru Benzimidazole (4)

^{1}H NMR (500 MHz) $CDCl_3$

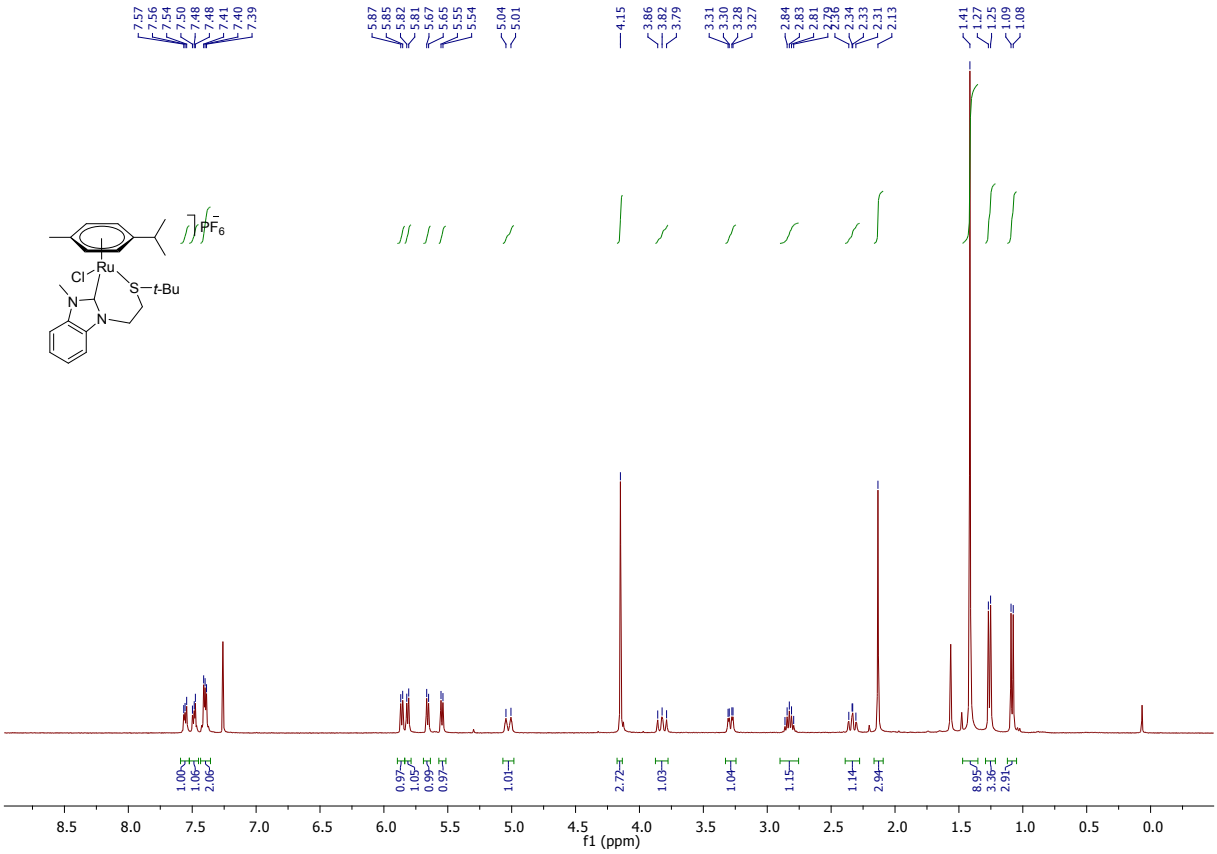


^{13}C NMR (100 MHz) $CDCl_3$

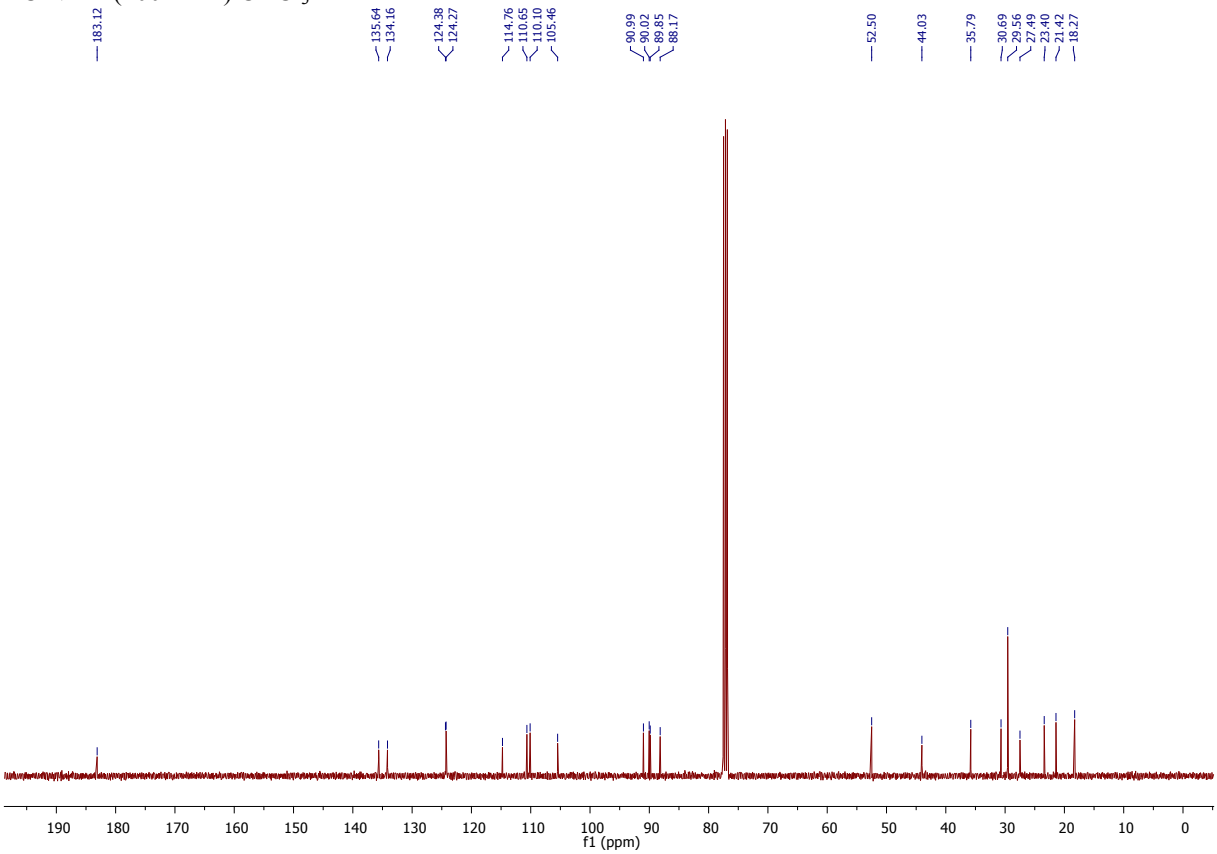


Ru Benzimidazole (5)

^{1}H NMR (400 MHz) $CDCl_3$

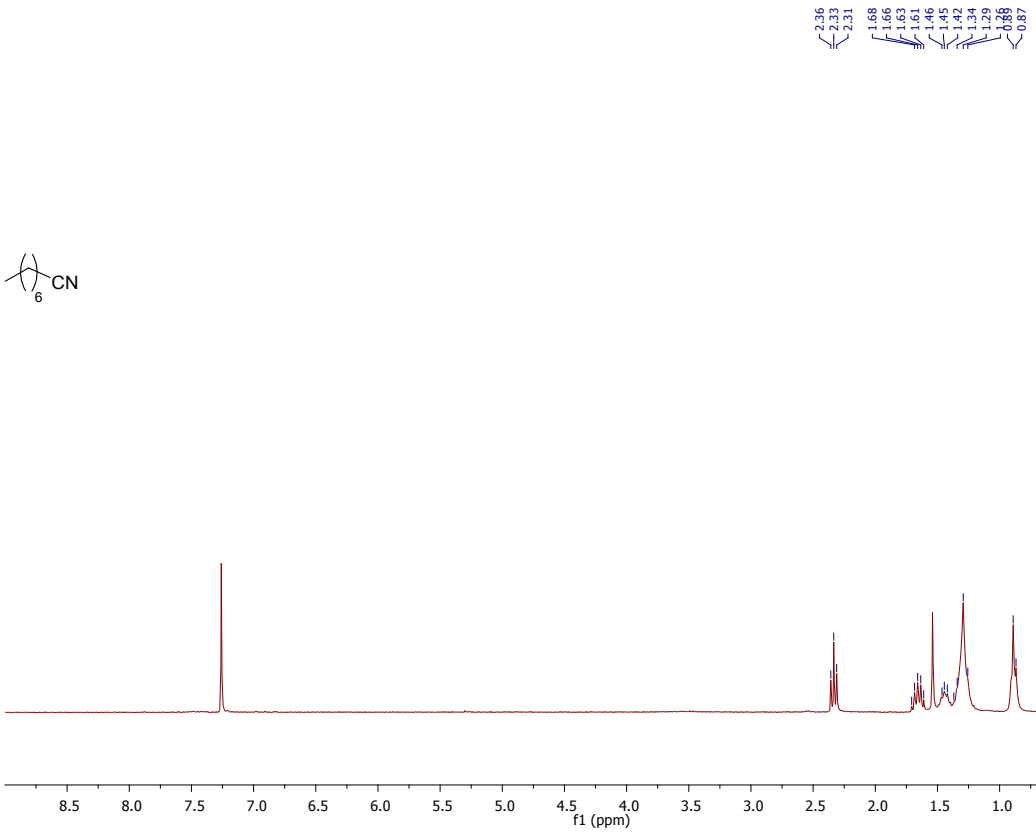


^{13}C NMR (100 MHz) $CDCl_3$



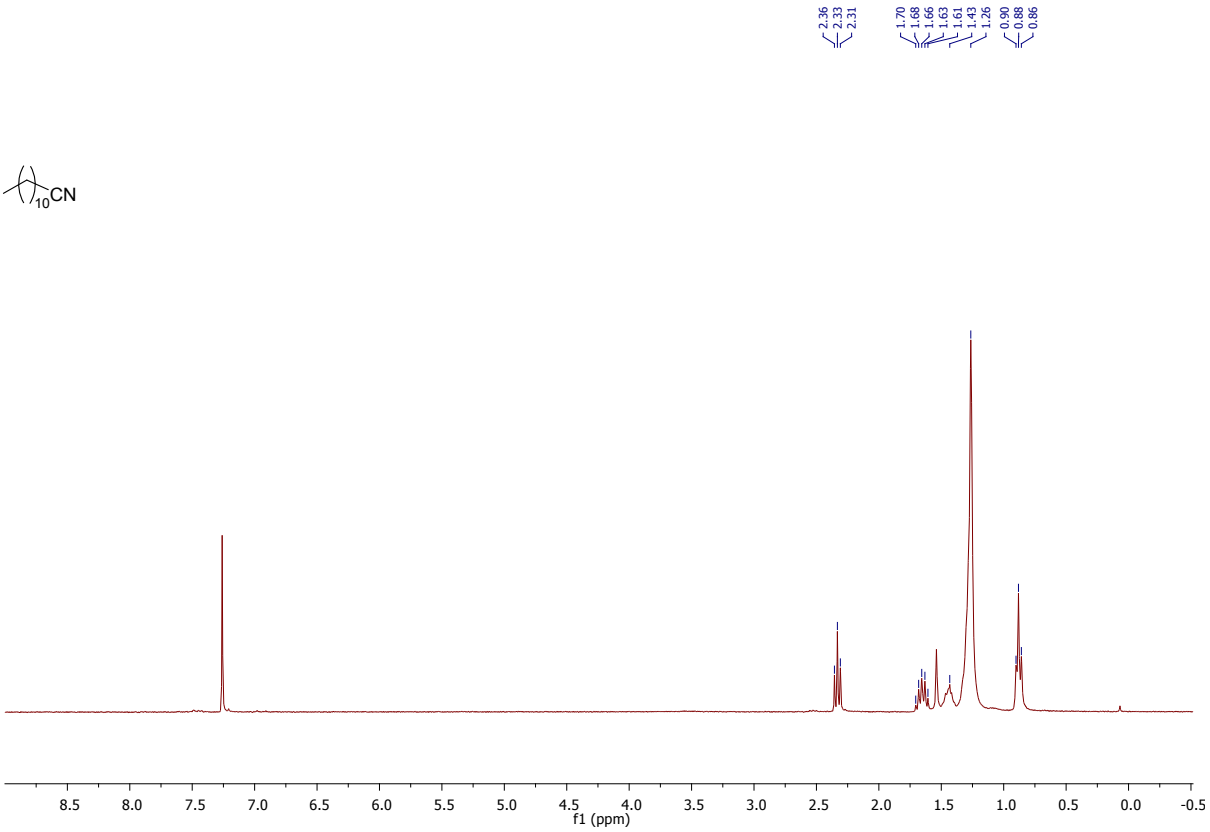
Octanenitrile (7)

^{1}H NMR (300 MHz) $CDCl_3$



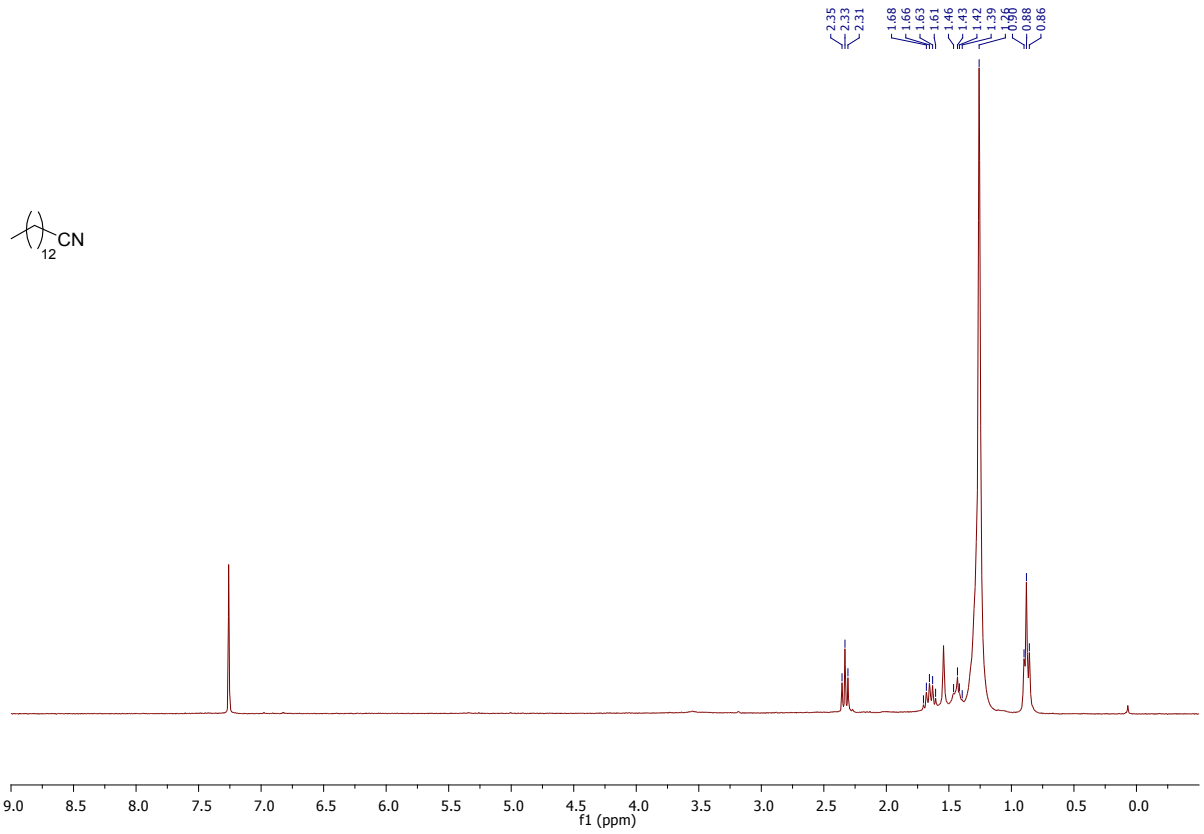
Dodecanenitrile (8).

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



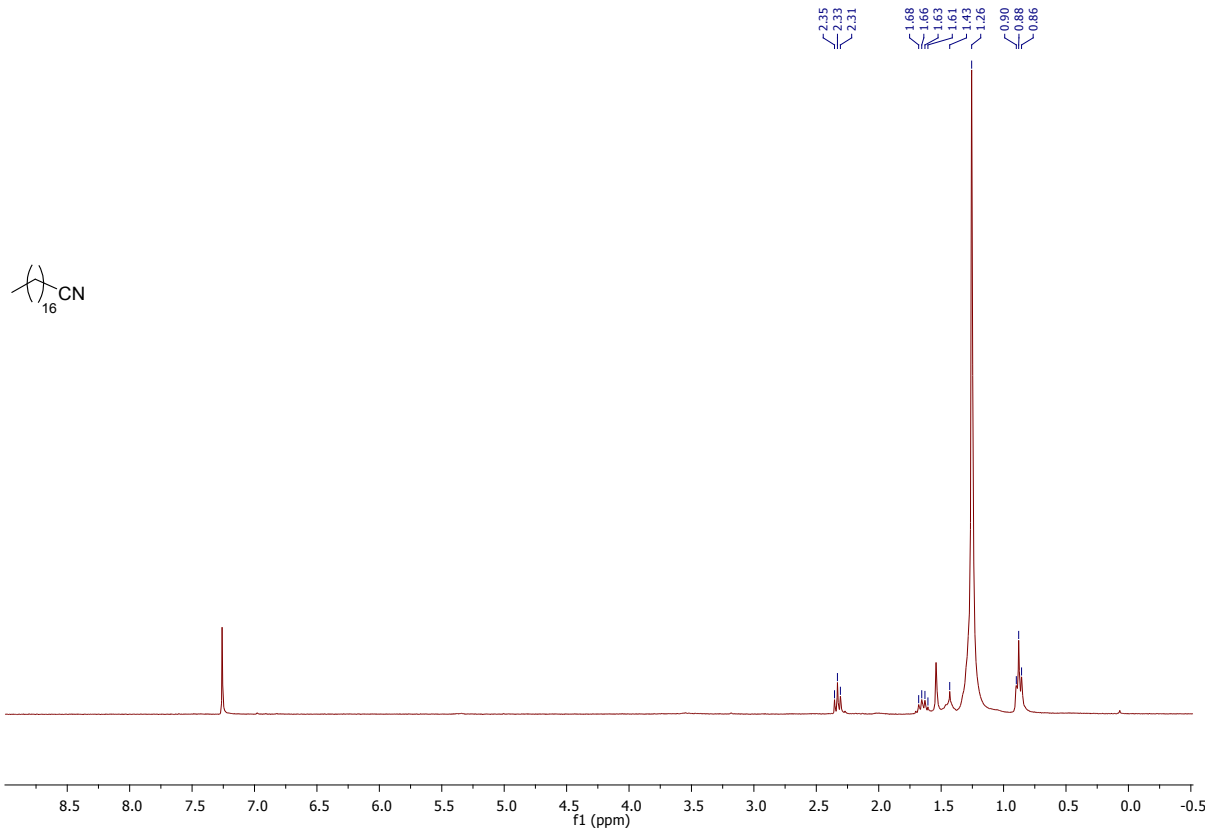
Tetradecanenitrile (9)

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



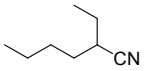
Stearonitrile (10)

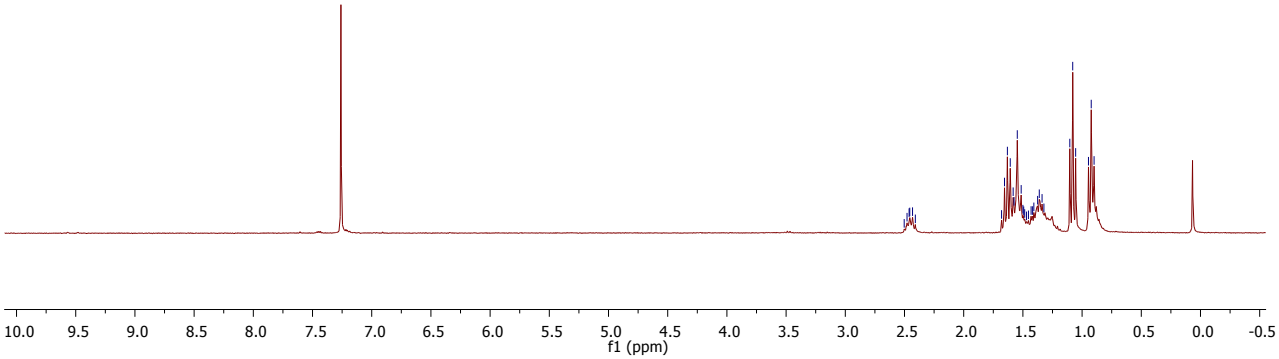
^{1}H NMR (300 MHz) $CDCl_3$



2-ethylhexanenitrile (11)

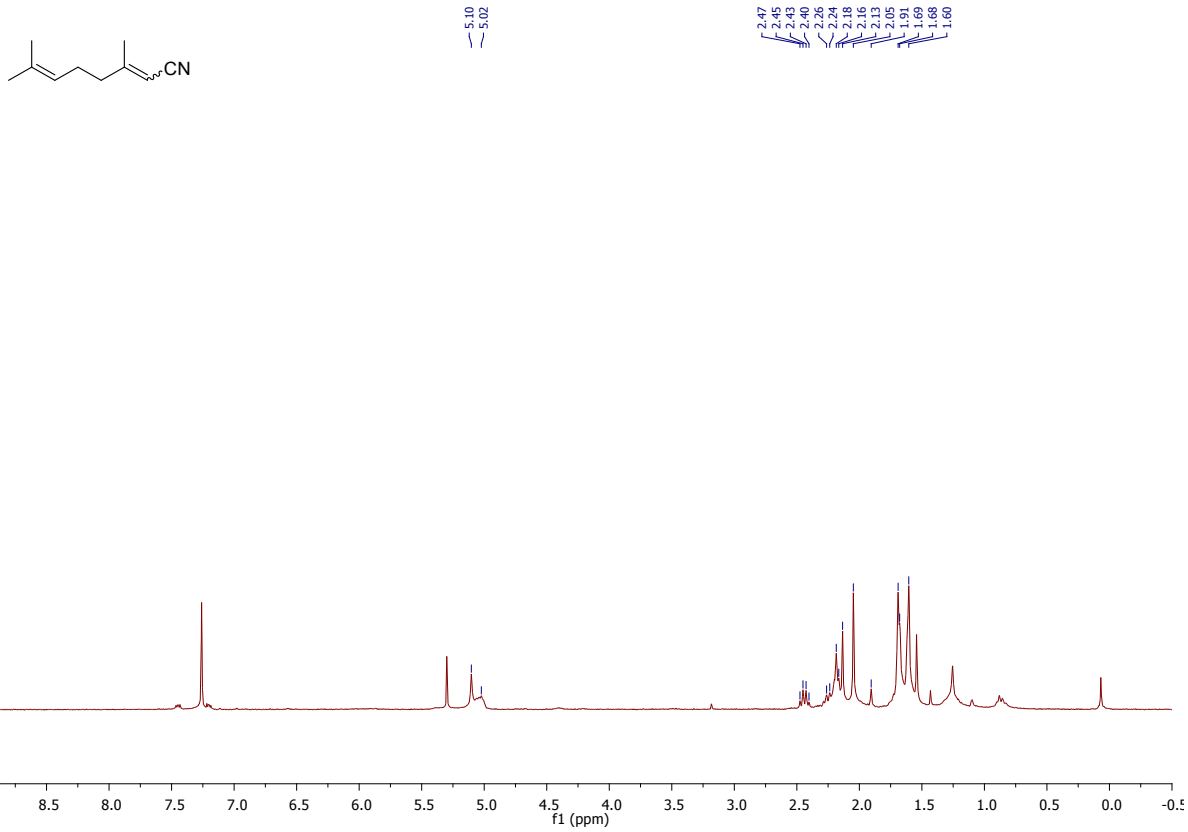
^{1}H NMR (300 MHz) $CDCl_3$





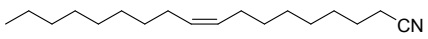
Geranylnitrile (12):

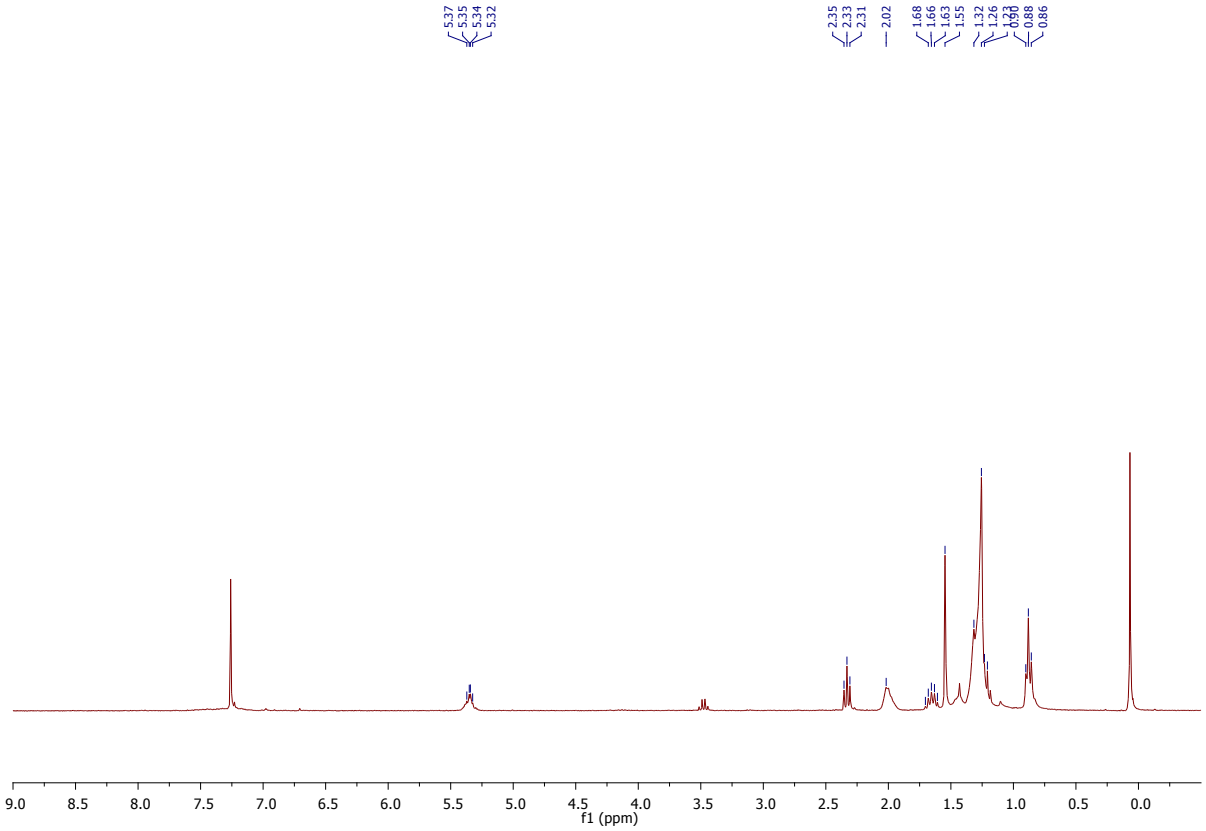
^{1}H NMR (300 MHz) $CDCl_3$



Oleonitrile (13)

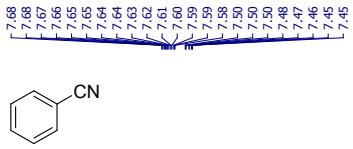
^{1}H NMR (400 MHz) $CDCl_3$

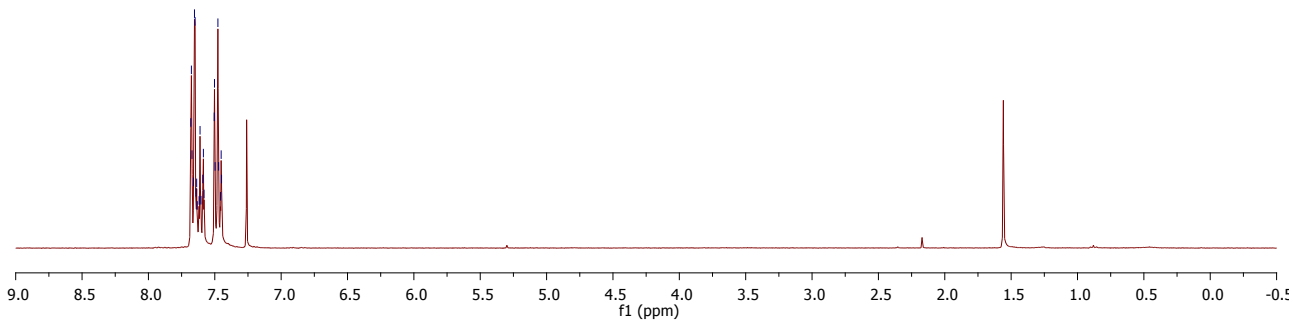




Benzonitrile (2)

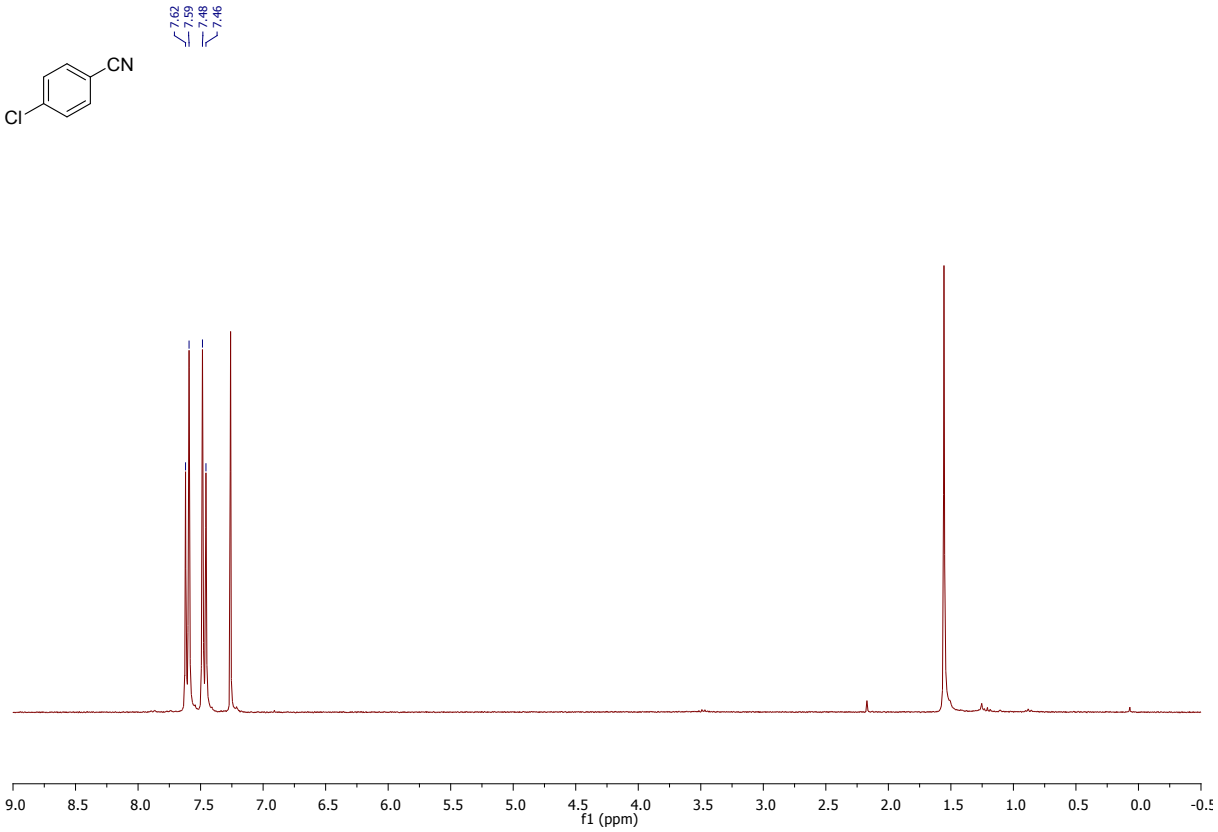
^{1}H NMR (300 MHz) $CDCl_3$





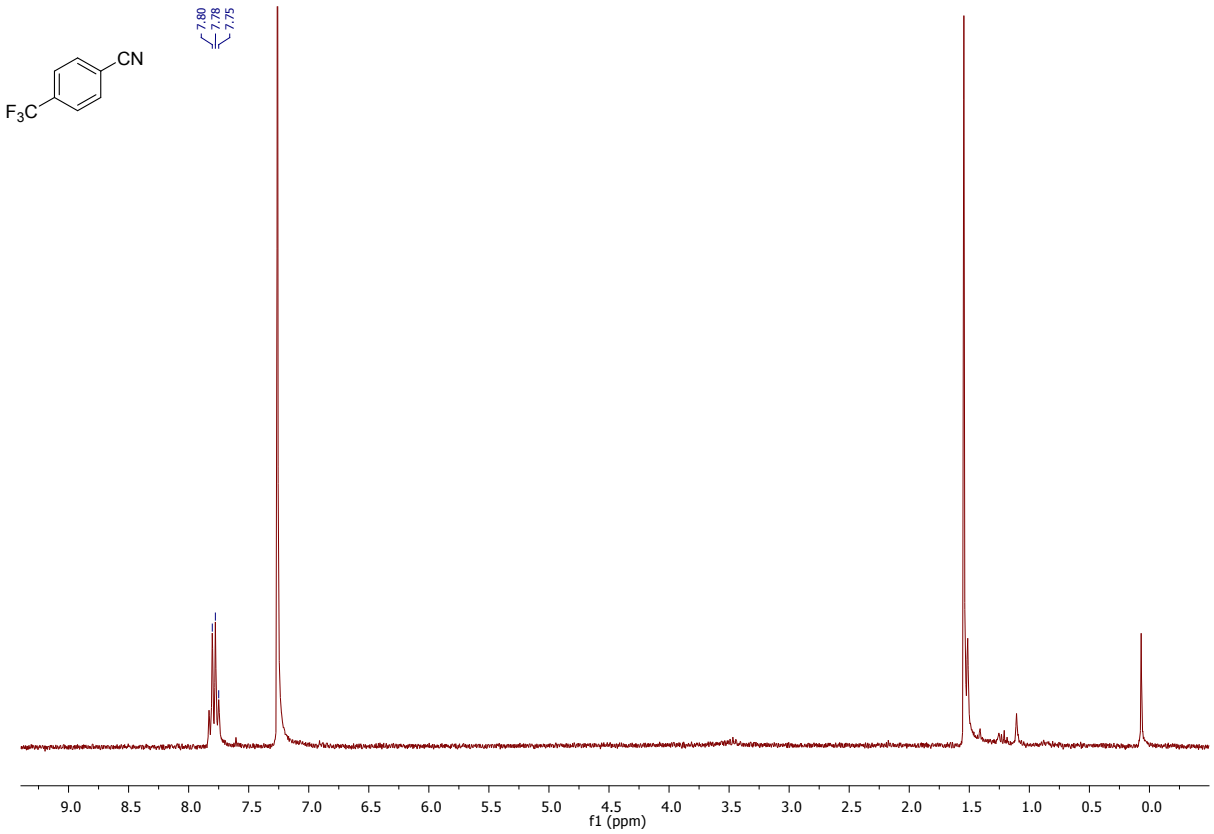
4-Chlorobenzonitrile (14)

^{1}H NMR (300 MHz) $CDCl_3$

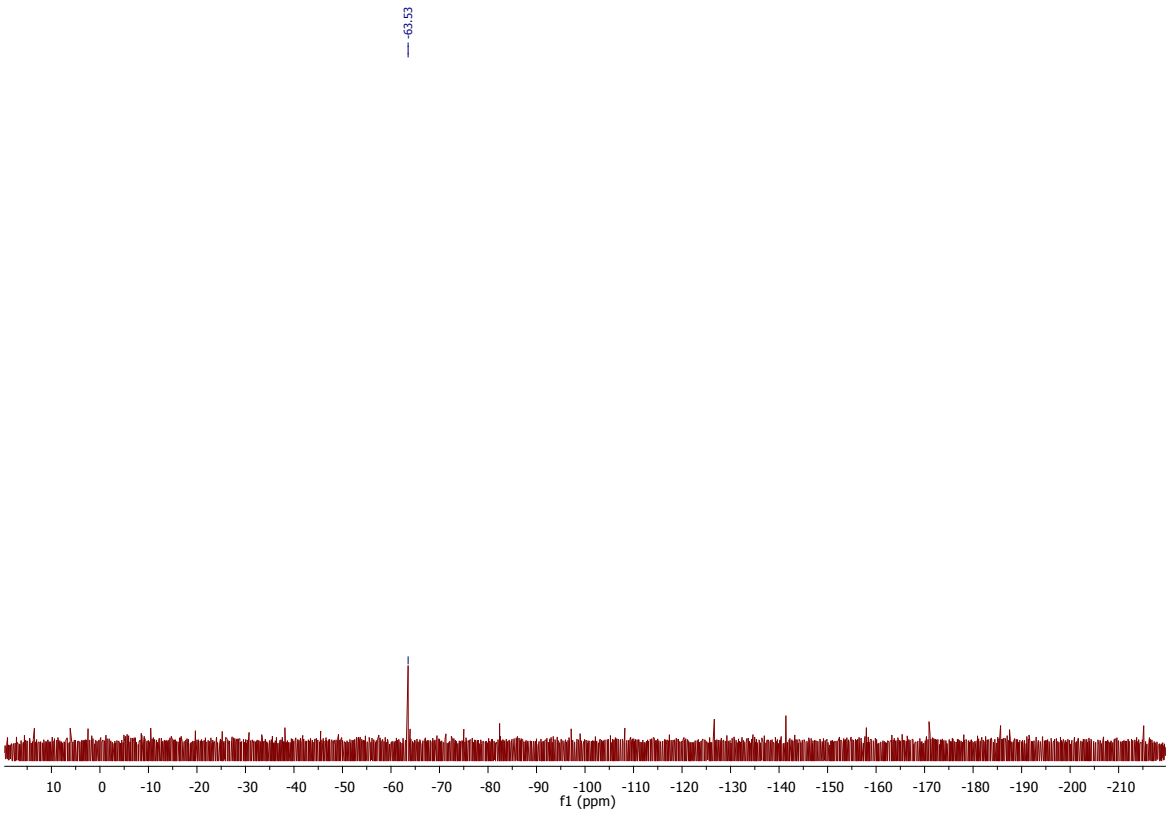


4-(Trifluoromethyl)benzonitrile (15)

^{1}H NMR (300 MHz) $CDCl_3$

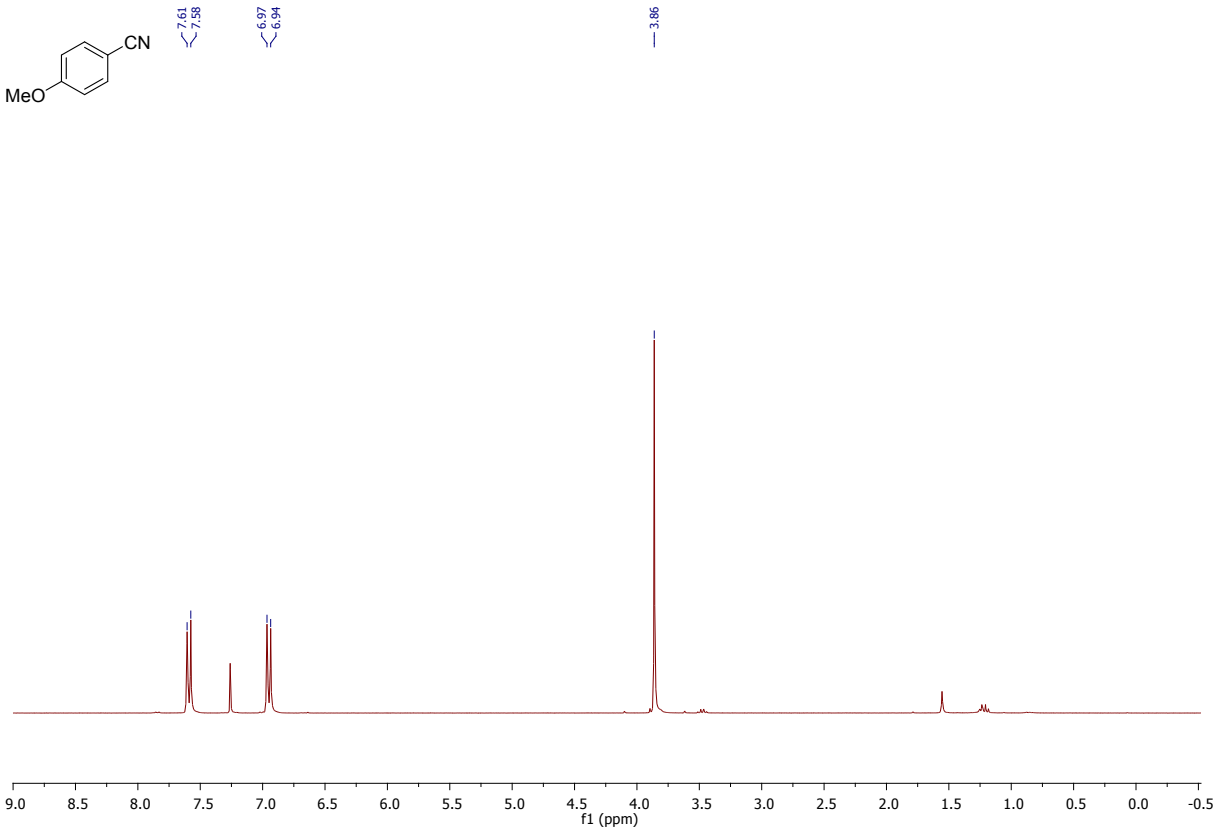


^{19}F NMR (300 MHz) $CDCl_3$



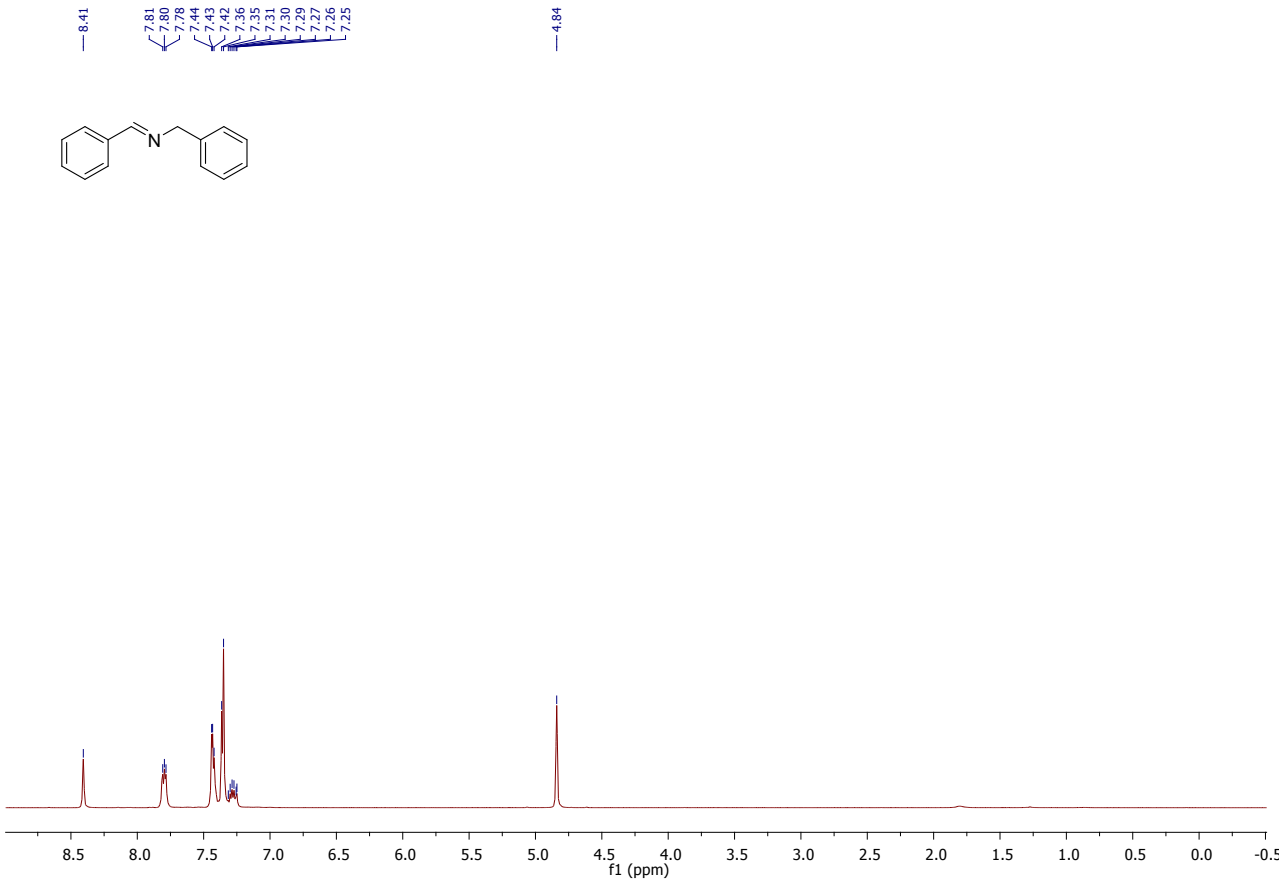
4-Methoxybenzonitrile (16)

^{1}H NMR (300 MHz) $CDCl_3$



N-Benzylidenebenzylamine (3)

^{1}H NMR (300 MHz) $CDCl_3$



13 INHIBITION OF CELL PROLIFERATION

Samples were prepared by dissolution of the compounds in DMSO (except for Cisplatin that was dissolved in water since it rapidly decomposes in DMSO) at stock concentrations of 10 mM. MCF7, CT116 and PC3 cell lines were maintained as monolayers in RPMI 1640 medium supplemented with 10% fetal calf serum, in the presence of penicilline, streptomycine and fungizone in 75cm^2 flask under 5%CO_2, while MRC5 were grown in complete D-MEM medium. Cells were plated in 96-well tissue culture plates in 200µl complete medium at a density of 1000-2500 cells per well and treated 24h later with 2µl of compounds using a Biomek 3000 automation workstation (Beckman-Coulter). Controls received the same volume of the appropriate vehicle (DMSO, EtOH or water, 1% final volume). After 72h exposure, MTS reagent (CellTiter 96® Aqueous One, Promega) was added and incubated for 3h at 37°C: the absorbance was monitored at 90nm and results expressed as the inhibition of cell proliferation calculated as the ratio [(1-(OD490 reated/OD490 control))×100] in triplicate experiments after subtraction of the blank without cells. Positive controls (cells incubated with a reference drug at its IC50 concentration) were routinely added to check the responsiveness of cells. For IC50 determination [50% inhibition of cell proliferation], cells were incubated for 72 h following the same protocol with compound concentrations ranged 5nM to 100µM in separate duplicate experiments. At these concentrations, no interference with Pt complexes was noticed at 490nm. Values are given as means ± SD from at least three independent experiments performed in triplicate.

14 X-RAY DATA AND TABLES

Complex 1c

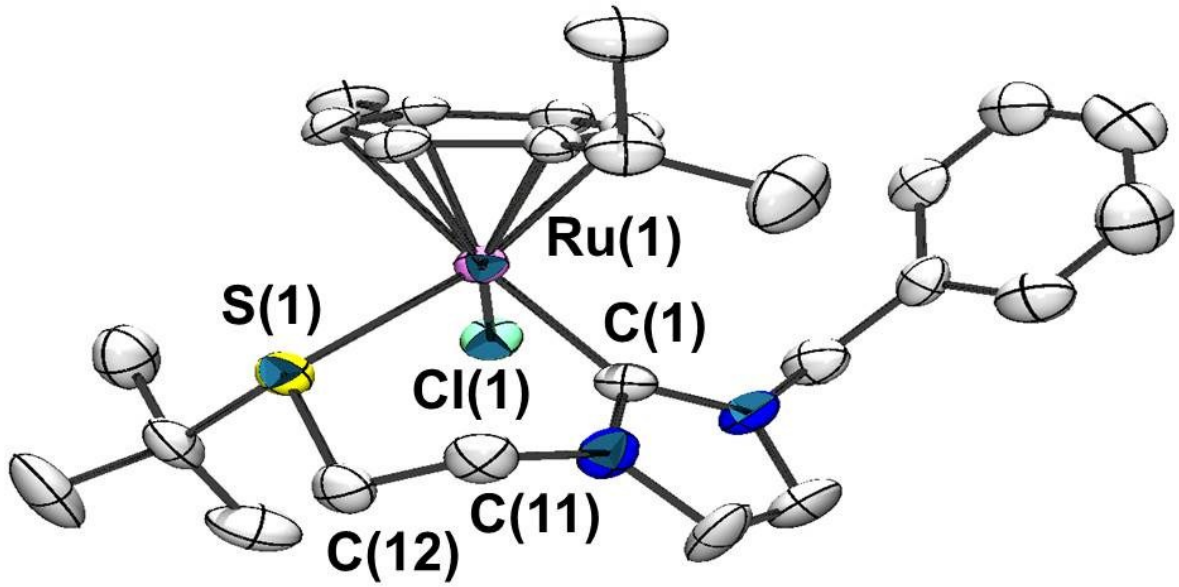


Table S5. Crystal data and structure refinement for sblta150414, **complex 1c**.

Identification code	sblta150414
Empirical formula	C26 H36 Cl F6 N2 P Ru S
Formula weight	690.12
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 2/c
Unit cell dimensions	a = 18.3465(10) A alpha = 90 deg. b = 9.5046(3) A beta = 115.491(2) deg. c = 18.6302(12) A gamma = 90 deg.

Volume	2932.4(3) A^3
Z, Calculated density	4, 1.563 Mg/m^3
Absorption coefficient	0.809 mm^-1
F(000)	1408
Crystal size	0.36 x 0.10 x 0.06 mm
Theta range for data collection	1.230 to 27.456 deg.
Limiting indices	-23<=h<=22, -9<=k<=12, -24<=l<=24
Reflections collected / unique	26064 / 6703 [R(int) = 0.1396]
Completeness to theta = 25.242	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.90401 and 0.81264
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6703 / 0 / 351
Goodness-of-fit on F^2	1.059
Final R indices [I>2sigma(I)]	R1 = 0.0646, wR2 = 0.1395
R indices (all data)	R1 = 0.1620, wR2 = 0.2089
Extinction coefficient	n/a
Largest diff. peak and hole	0.928 and -1.970 e.A^-3

Table S6. Bond lengths [A] and angles [deg] for sblta150414, **complex 1c**

C(1)-N(1)	1.360(9)
C(1)-N(2)	1.373(9)
C(1)-Ru(1)	2.075(7)
C(2)-C(3)	1.334(11)
C(2)-N(1)	1.389(9)
C(2)-H(2)	0.9500
C(3)-N(2)	1.393(9)

C(3)-H(3)	0.9500
C(4)-N(1)	1.460(9)
C(4)-C(5)	1.497(10)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.400(10)
C(5)-C(10)	1.408(11)
C(6)-C(7)	1.373(11)
C(6)-H(6)	0.9500
C(7)-C(8)	1.365(12)
C(7)-H(7)	0.9500
C(8)-C(9)	1.374(13)
C(8)-H(8)	0.9500
C(9)-C(10)	1.372(12)
C(9)-H(9)	0.9500
C(10)-H(10)	0.9500
C(11)-N(2)	1.455(9)
C(11)-C(12)	1.508(10)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-S(1)	1.810(7)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.510(11)
C(13)-C(15)	1.517(11)
C(13)-C(16)	1.520(10)
C(13)-S(1)	1.875(8)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(17)-C(18)	1.407(9)
C(17)-C(22)	1.416(10)
C(17)-C(23)	1.506(10)
C(17)-Ru(1)	2.283(7)
C(18)-C(19)	1.425(9)
C(18)-Ru(1)	2.244(6)
C(18)-H(18)	0.9500
C(19)-C(20)	1.427(9)
C(19)-Ru(1)	2.183(6)
C(19)-H(19)	0.9500

C(20)-C(21)	1.433(9)
C(20)-C(24)	1.514(9)
C(20)-Ru(1)	2.237(7)
C(21)-C(22)	1.399(10)
C(21)-Ru(1)	2.224(7)
C(21)-H(21)	0.9500
C(22)-Ru(1)	2.207(7)
C(22)-H(22)	0.9500
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-C(25)	1.528(10)
C(24)-C(26)	1.545(11)
C(24)-H(24)	1.0000
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800
F(1)-P(1)	1.594(5)
F(2)-P(1)	1.584(5)
F(3)-P(1)	1.580(5)
F(4)-P(2)	1.578(5)
F(5)-P(2)	1.541(7)
F(6)-P(2)	1.525(9)
F(7)-P(2)	1.501(9)
P(1)-F(3)#1	1.580(5)
P(1)-F(2)#1	1.584(5)
P(1)-F(1)#1	1.594(5)
P(2)-F(5)#2	1.541(7)
P(2)-F(4)#2	1.578(5)
S(1)-Ru(1)	2.3982(18)
Cl(1)-Ru(1)	2.4068(18)

N(1)-C(1)-N(2)	105.0(6)
N(1)-C(1)-Ru(1)	131.0(5)
N(2)-C(1)-Ru(1)	124.0(5)
C(3)-C(2)-N(1)	109.3(7)
C(3)-C(2)-H(2)	125.4
N(1)-C(2)-H(2)	125.4
C(2)-C(3)-N(2)	105.6(6)
C(2)-C(3)-H(3)	127.2
N(2)-C(3)-H(3)	127.2
N(1)-C(4)-C(5)	114.3(6)
N(1)-C(4)-H(4A)	108.7

C(5)-C(4)-H(4A) 108.7
N(1)-C(4)-H(4B) 108.7
C(5)-C(4)-H(4B) 108.7
H(4A)-C(4)-H(4B) 107.6
C(6)-C(5)-C(10) 116.4(7)
C(6)-C(5)-C(4) 120.4(7)
C(10)-C(5)-C(4) 123.3(7)
C(7)-C(6)-C(5) 120.8(8)
C(7)-C(6)-H(6) 119.6
C(5)-C(6)-H(6) 119.6
C(8)-C(7)-C(6) 122.1(8)
C(8)-C(7)-H(7) 118.9
C(6)-C(7)-H(7) 118.9
C(7)-C(8)-C(9) 118.2(9)
C(7)-C(8)-H(8) 120.9
C(9)-C(8)-H(8) 120.9
C(10)-C(9)-C(8) 121.2(9)
C(10)-C(9)-H(9) 119.4
C(8)-C(9)-H(9) 119.4
C(9)-C(10)-C(5) 121.3(8)
C(9)-C(10)-H(10) 119.3
C(5)-C(10)-H(10) 119.3
N(2)-C(11)-C(12) 111.1(6)
N(2)-C(11)-H(11A) 109.4
C(12)-C(11)-H(11A) 109.4
N(2)-C(11)-H(11B) 109.4
C(12)-C(11)-H(11B) 109.4
H(11A)-C(11)-H(11B) 108.0
C(11)-C(12)-S(1) 110.0(5)
C(11)-C(12)-H(12A) 109.7
S(1)-C(12)-H(12A) 109.7
C(11)-C(12)-H(12B) 109.7
S(1)-C(12)-H(12B) 109.7
H(12A)-C(12)-H(12B) 108.2
C(14)-C(13)-C(15) 111.0(7)
C(14)-C(13)-C(16) 112.5(7)
C(15)-C(13)-C(16) 110.4(7)
C(14)-C(13)-S(1) 112.8(6)
C(15)-C(13)-S(1) 105.1(6)
C(16)-C(13)-S(1) 104.6(5)
C(13)-C(14)-H(14A) 109.5
C(13)-C(14)-H(14B) 109.5
H(14A)-C(14)-H(14B) 109.5
C(13)-C(14)-H(14C) 109.5
H(14A)-C(14)-H(14C) 109.5
H(14B)-C(14)-H(14C) 109.5

C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(13)-C(16)-H(16A)	109.5
C(13)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(13)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(18)-C(17)-C(22)	118.0(7)
C(18)-C(17)-C(23)	120.6(7)
C(22)-C(17)-C(23)	121.2(6)
C(18)-C(17)-Ru(1)	70.4(4)
C(22)-C(17)-Ru(1)	68.7(4)
C(23)-C(17)-Ru(1)	128.2(5)
C(17)-C(18)-C(19)	120.2(6)
C(17)-C(18)-Ru(1)	73.4(4)
C(19)-C(18)-Ru(1)	68.9(4)
C(17)-C(18)-H(18)	119.9
C(19)-C(18)-H(18)	119.9
Ru(1)-C(18)-H(18)	130.3
C(18)-C(19)-C(20)	122.1(6)
C(18)-C(19)-Ru(1)	73.6(4)
C(20)-C(19)-Ru(1)	73.2(4)
C(18)-C(19)-H(19)	118.9
C(20)-C(19)-H(19)	118.9
Ru(1)-C(19)-H(19)	126.2
C(19)-C(20)-C(21)	116.3(6)
C(19)-C(20)-C(24)	119.3(6)
C(21)-C(20)-C(24)	124.2(6)
C(19)-C(20)-Ru(1)	69.1(4)
C(21)-C(20)-Ru(1)	70.8(4)
C(24)-C(20)-Ru(1)	133.6(5)
C(22)-C(21)-C(20)	121.1(7)
C(22)-C(21)-Ru(1)	71.0(4)
C(20)-C(21)-Ru(1)	71.8(4)
C(22)-C(21)-H(21)	119.5
C(20)-C(21)-H(21)	119.5
Ru(1)-C(21)-H(21)	130.5
C(21)-C(22)-C(17)	122.0(6)
C(21)-C(22)-Ru(1)	72.2(4)
C(17)-C(22)-Ru(1)	74.5(4)
C(21)-C(22)-H(22)	119.0

C(17)-C(22)-H(22)	119.0
Ru(1)-C(22)-H(22)	126.2
C(17)-C(23)-H(23A)	109.5
C(17)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(17)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(20)-C(24)-C(25)	108.9(6)
C(20)-C(24)-C(26)	114.0(6)
C(25)-C(24)-C(26)	110.2(7)
C(20)-C(24)-H(24)	107.8
C(25)-C(24)-H(24)	107.8
C(26)-C(24)-H(24)	107.8
C(24)-C(25)-H(25A)	109.5
C(24)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(24)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(24)-C(26)-H(26A)	109.5
C(24)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(24)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(1)-N(1)-C(2)	109.2(6)
C(1)-N(1)-C(4)	127.1(6)
C(2)-N(1)-C(4)	123.7(6)
C(1)-N(2)-C(3)	110.8(6)
C(1)-N(2)-C(11)	126.2(6)
C(3)-N(2)-C(11)	122.7(6)
F(3)-P(1)-F(3)#1	90.1(4)
F(3)-P(1)-F(2)	90.0(3)
F(3)#1-P(1)-F(2)	90.8(3)
F(3)-P(1)-F(2)#1	90.8(3)
F(3)#1-P(1)-F(2)#1	90.0(3)
F(2)-P(1)-F(2)#1	178.9(4)
F(3)-P(1)-F(1)#1	179.1(3)
F(3)#1-P(1)-F(1)#1	89.8(3)
F(2)-P(1)-F(1)#1	91.0(3)
F(2)#1-P(1)-F(1)#1	88.3(3)
F(3)-P(1)-F(1)	89.8(3)
F(3)#1-P(1)-F(1)	179.1(3)
F(2)-P(1)-F(1)	88.3(3)
F(2)#1-P(1)-F(1)	91.0(3)

F(1)#1-P(1)-F(1)	90.4(4)
F(7)-P(2)-F(6)	180.0
F(7)-P(2)-F(5)#2	90.4(4)
F(6)-P(2)-F(5)#2	89.6(4)
F(7)-P(2)-F(5)	90.4(4)
F(6)-P(2)-F(5)	89.6(4)
F(5)#2-P(2)-F(5)	179.2(8)
F(7)-P(2)-F(4)	90.2(2)
F(6)-P(2)-F(4)	89.8(2)
F(5)#2-P(2)-F(4)	93.3(3)
F(5)-P(2)-F(4)	86.7(3)
F(7)-P(2)-F(4)#2	90.2(2)
F(6)-P(2)-F(4)#2	89.8(2)
F(5)#2-P(2)-F(4)#2	86.7(3)
F(5)-P(2)-F(4)#2	93.3(3)
F(4)-P(2)-F(4)#2	179.7(5)
C(12)-S(1)-C(13)	101.0(4)
C(12)-S(1)-Ru(1)	111.5(2)
C(13)-S(1)-Ru(1)	121.1(2)
C(1)-Ru(1)-C(19)	121.5(3)
C(1)-Ru(1)-C(22)	119.2(3)
C(19)-Ru(1)-C(22)	78.9(3)
C(1)-Ru(1)-C(21)	94.7(3)
C(19)-Ru(1)-C(21)	66.9(3)
C(22)-Ru(1)-C(21)	36.8(3)
C(1)-Ru(1)-C(20)	94.7(3)
C(19)-Ru(1)-C(20)	37.6(2)
C(22)-Ru(1)-C(20)	67.4(3)
C(21)-Ru(1)-C(20)	37.5(2)
C(1)-Ru(1)-C(18)	159.0(3)
C(19)-Ru(1)-C(18)	37.5(2)
C(22)-Ru(1)-C(18)	65.9(3)
C(21)-Ru(1)-C(18)	78.3(3)
C(20)-Ru(1)-C(18)	67.7(3)
C(1)-Ru(1)-C(17)	155.6(3)
C(19)-Ru(1)-C(17)	66.7(3)
C(22)-Ru(1)-C(17)	36.7(3)
C(21)-Ru(1)-C(17)	66.2(3)
C(20)-Ru(1)-C(17)	79.6(3)
C(18)-Ru(1)-C(17)	36.2(2)
C(1)-Ru(1)-S(1)	90.3(2)
C(19)-Ru(1)-S(1)	84.77(19)
C(22)-Ru(1)-S(1)	150.50(19)
C(21)-Ru(1)-S(1)	149.39(18)
C(20)-Ru(1)-S(1)	112.07(17)
C(18)-Ru(1)-S(1)	86.26(18)

C(17)-Ru(1)-S(1)	113.96(19)
C(1)-Ru(1)-Cl(1)	86.8(2)
C(19)-Ru(1)-Cl(1)	151.65(19)
C(22)-Ru(1)-Cl(1)	88.0(2)
C(21)-Ru(1)-Cl(1)	115.13(18)
C(20)-Ru(1)-Cl(1)	152.59(17)
C(18)-Ru(1)-Cl(1)	114.13(19)
C(17)-Ru(1)-Cl(1)	87.82(19)
S(1)-Ru(1)-Cl(1)	95.27(7)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+3/2 #2 -x+2,y,-z+1/2

Table S7. Torsion angles [deg] for sblta150414.; **complex 1c**

N(1)-C(2)-C(3)-N(2)	-1.5(11)
N(1)-C(4)-C(5)-C(6)	-131.8(7)
N(1)-C(4)-C(5)-C(10)	49.3(9)
C(10)-C(5)-C(6)-C(7)	-2.1(10)
C(4)-C(5)-C(6)-C(7)	178.9(6)
C(5)-C(6)-C(7)-C(8)	1.4(11)
C(6)-C(7)-C(8)-C(9)	-0.2(12)
C(7)-C(8)-C(9)-C(10)	-0.3(13)
C(8)-C(9)-C(10)-C(5)	-0.4(13)
C(6)-C(5)-C(10)-C(9)	1.6(11)
C(4)-C(5)-C(10)-C(9)	-179.5(7)
N(2)-C(11)-C(12)-S(1)	-75.2(7)
C(22)-C(17)-C(18)-C(19)	1.3(10)
C(23)-C(17)-C(18)-C(19)	176.1(6)
Ru(1)-C(17)-C(18)-C(19)	52.6(6)
C(22)-C(17)-C(18)-Ru(1)	-51.3(6)
C(23)-C(17)-C(18)-Ru(1)	123.5(6)
C(17)-C(18)-C(19)-C(20)	2.7(10)
Ru(1)-C(18)-C(19)-C(20)	57.3(6)
C(17)-C(18)-C(19)-Ru(1)	-54.6(6)
C(18)-C(19)-C(20)-C(21)	-3.1(10)
Ru(1)-C(19)-C(20)-C(21)	54.4(5)
C(18)-C(19)-C(20)-C(24)	173.3(6)
Ru(1)-C(19)-C(20)-C(24)	-129.3(6)
C(18)-C(19)-C(20)-Ru(1)	-57.5(6)
C(19)-C(20)-C(21)-C(22)	-0.4(10)
C(24)-C(20)-C(21)-C(22)	-176.6(6)
Ru(1)-C(20)-C(21)-C(22)	53.1(6)
C(19)-C(20)-C(21)-Ru(1)	-53.6(5)

C(24)-C(20)-C(21)-Ru(1)	130.3(6)
C(20)-C(21)-C(22)-C(17)	4.4(11)
Ru(1)-C(21)-C(22)-C(17)	57.9(6)
C(20)-C(21)-C(22)-Ru(1)	-53.5(6)
C(18)-C(17)-C(22)-C(21)	-4.8(10)
C(23)-C(17)-C(22)-C(21)	-179.6(7)
Ru(1)-C(17)-C(22)-C(21)	-56.9(6)
C(18)-C(17)-C(22)-Ru(1)	52.0(6)
C(23)-C(17)-C(22)-Ru(1)	-122.7(6)
C(19)-C(20)-C(24)-C(25)	-77.9(8)
C(21)-C(20)-C(24)-C(25)	98.2(8)
Ru(1)-C(20)-C(24)-C(25)	-166.2(6)
C(19)-C(20)-C(24)-C(26)	158.6(7)
C(21)-C(20)-C(24)-C(26)	-25.4(10)
Ru(1)-C(20)-C(24)-C(26)	70.3(9)
N(2)-C(1)-N(1)-C(2)	2.8(9)
Ru(1)-C(1)-N(1)-C(2)	-174.9(6)
N(2)-C(1)-N(1)-C(4)	-176.2(7)
Ru(1)-C(1)-N(1)-C(4)	6.0(12)
C(3)-C(2)-N(1)-C(1)	-0.9(11)
C(3)-C(2)-N(1)-C(4)	178.2(8)
C(5)-C(4)-N(1)-C(1)	91.7(9)
C(5)-C(4)-N(1)-C(2)	-87.2(9)
N(1)-C(1)-N(2)-C(3)	-3.8(9)
Ru(1)-C(1)-N(2)-C(3)	174.1(6)
N(1)-C(1)-N(2)-C(11)	-177.4(7)
Ru(1)-C(1)-N(2)-C(11)	0.6(10)
C(2)-C(3)-N(2)-C(1)	3.4(11)
C(2)-C(3)-N(2)-C(11)	177.2(8)
C(12)-C(11)-N(2)-C(1)	65.2(10)
C(12)-C(11)-N(2)-C(3)	-107.6(8)
C(11)-C(12)-S(1)-C(13)	160.6(5)
C(11)-C(12)-S(1)-Ru(1)	30.6(6)
C(14)-C(13)-S(1)-C(12)	-56.3(6)
C(15)-C(13)-S(1)-C(12)	64.8(6)
C(16)-C(13)-S(1)-C(12)	-178.9(5)
C(14)-C(13)-S(1)-Ru(1)	67.2(6)
C(15)-C(13)-S(1)-Ru(1)	-171.7(5)
C(16)-C(13)-S(1)-Ru(1)	-55.4(6)

Complex 1i

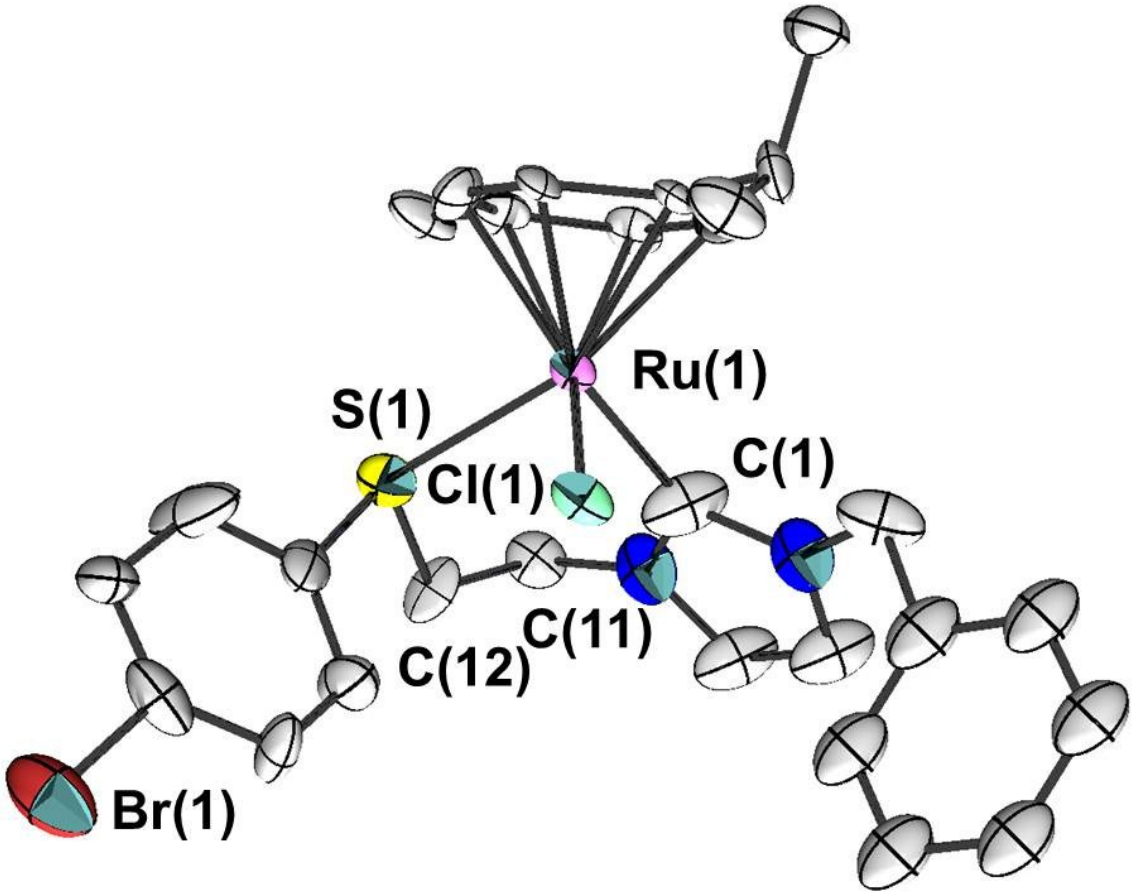


Table S8. Crystal data and structure refinement for sblta151104, **complex 1i**

Identification code	sblta151104
Empirical formula	C28 H31 Br Cl F6 N2 P Ru S
Formula weight	789.01
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P c
Unit cell dimensions	a = 10.3883(10) A alpha = 90 deg. b = 19.6463(19) A beta = 95.526(2) deg. c = 14.7966(14) A gamma = 90 deg.
Volume	3005.8(5) A^3

Z, Calculated density	4, 1.744 Mg/m^3
Absorption coefficient	2.122 mm^-1
F(000)	1576
Crystal size	0.250 x 0.120 x 0.100 mm
Theta range for data collection	1.728 to 28.040 deg.
Limiting indices	-13<=h<=13, -25<=k<=25, -19<=l<=19
Reflections collected / unique	35513 / 13689 [R(int) = 0.0593]
Completeness to theta = 25.242	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6500
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13689 / 2 / 664
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0734, wR2 = 0.1693
R indices (all data)	R1 = 0.1122, wR2 = 0.1906
Absolute structure parameter	0.55(2)
Extinction coefficient	n/a
Largest diff. peak and hole	4.796 and -1.394 e.A^-3

Table S9. Bond lengths [A] and angles [deg] for sblta151104, **complex 1i**

C(1)-N(1)	1.315(19)
C(1)-N(2)	1.354(17)
C(1)-Ru(1)	2.050(15)
C(2)-C(3)	1.35(2)
C(2)-N(1)	1.411(18)
C(2)-H(2)	0.9500

C(3)-N(2)	1.361(19)
C(3)-H(3)	0.9500
C(4)-N(1)	1.473(17)
C(4)-C(5)	1.511(19)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.393(19)
C(5)-C(10)	1.41(2)
C(6)-C(7)	1.41(2)
C(6)-H(6)	0.9500
C(7)-C(8)	1.38(3)
C(7)-H(7)	0.9500
C(8)-C(9)	1.36(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.37(2)
C(9)-H(9)	0.9500
C(10)-H(10)	0.9500
C(11)-N(2)	1.491(19)
C(11)-C(12)	1.52(2)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-S(1)	1.809(15)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(18)	1.37(2)
C(13)-C(14)	1.402(18)
C(13)-S(1)	1.775(14)
C(14)-C(15)	1.385(19)
C(14)-H(14)	0.9500
C(15)-C(16)	1.35(2)
C(15)-H(15)	0.9500
C(16)-C(17)	1.40(2)
C(16)-Br(1)	1.893(14)
C(17)-C(18)	1.40(2)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(19)-C(24)	1.41(2)
C(19)-C(20)	1.46(2)
C(19)-C(25)	1.50(2)
C(19)-Ru(1)	2.274(16)
C(20)-C(21)	1.37(2)
C(20)-Ru(1)	2.225(18)
C(20)-H(20)	0.9500
C(21)-C(22)	1.43(2)
C(21)-Ru(1)	2.215(16)
C(21)-H(21)	0.9500

C(22)-C(23)	1.43(2)
C(22)-C(26)	1.510(19)
C(22)-Ru(1)	2.236(13)
C(23)-C(24)	1.40(2)
C(23)-Ru(1)	2.184(13)
C(23)-H(23)	0.9500
C(24)-Ru(1)	2.236(15)
C(24)-H(24)	0.9500
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-C(27)	1.48(2)
C(26)-C(28)	1.515(17)
C(26)-H(26)	1.0000
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-N(3)	1.4200
C(29)-N(4)	1.4200
C(29)-Ru(2)	2.054(8)
N(3)-C(30)	1.4200
N(3)-C(32)	1.45(2)
C(30)-C(31)	1.4200
C(30)-H(30)	0.9500
C(31)-N(4)	1.4200
C(31)-H(31)	0.9500
N(4)-C(39)	1.40(2)
C(32)-C(33)	1.52(2)
C(32)-H(32A)	0.9900
C(32)-H(32B)	0.9900
C(33)-C(34)	1.3900
C(33)-C(38)	1.3900
C(34)-C(35)	1.3900
C(34)-H(34)	0.9500
C(35)-C(36)	1.3900
C(35)-H(35)	0.9500
C(36)-C(37)	1.3900
C(36)-H(36)	0.9500
C(37)-C(38)	1.3900
C(37)-H(37)	0.9500
C(38)-H(38)	0.9500
C(39)-C(40)	1.44(2)
C(39)-H(39A)	0.9900

C(39)-H(39B)	0.9900
C(40)-S(2)	1.758(16)
C(40)-H(40A)	0.9900
C(40)-H(40B)	0.9900
C(41)-C(46)	1.38(3)
C(41)-C(42)	1.41(3)
C(41)-S(2)	1.72(2)
C(42)-C(43)	1.38(2)
C(42)-H(42)	0.9500
C(43)-C(44)	1.35(3)
C(43)-H(43)	0.9500
C(44)-C(45)	1.37(3)
C(44)-Br(2)	1.893(19)
C(45)-C(46)	1.49(3)
C(45)-H(45)	0.9500
C(46)-H(46)	0.9500
C(47)-C(52)	1.39(3)
C(47)-C(48)	1.45(2)
C(47)-C(53)	1.50(2)
C(47)-Ru(2)	2.265(15)
C(48)-C(49)	1.40(2)
C(48)-Ru(2)	2.198(14)
C(48)-H(48)	0.9500
C(49)-C(50)	1.40(2)
C(49)-Ru(2)	2.216(16)
C(49)-H(49)	0.9500
C(50)-C(51)	1.43(2)
C(50)-C(54)	1.52(2)
C(50)-Ru(2)	2.283(15)
C(51)-C(52)	1.39(2)
C(51)-Ru(2)	2.243(15)
C(51)-H(51)	0.9500
C(52)-Ru(2)	2.222(18)
C(52)-H(52)	0.9500
C(53)-H(53A)	0.9800
C(53)-H(53B)	0.9800
C(53)-H(53C)	0.9800
C(54)-C(55)	1.48(2)
C(54)-C(56)	1.54(2)
C(54)-H(54)	1.0000
C(55)-H(55A)	0.9800
C(55)-H(55B)	0.9800
C(55)-H(55C)	0.9800
C(56)-H(56A)	0.9800
C(56)-H(56B)	0.9800
C(56)-H(56C)	0.9800

F(1)-P(1)	1.596(11)
F(2)-P(1)	1.575(11)
F(3)-P(1)	1.609(10)
F(4)-P(1)	1.567(12)
F(5)-P(1)	1.588(12)
F(6)-P(1)	1.599(11)
F(7)-P(2)	1.570(13)
F(8)-P(2)	1.513(13)
F(9)-P(2)	1.591(11)
F(10)-P(2)	1.566(13)
F(11)-P(2)	1.589(13)
F(12)-P(2)	1.597(10)
S(1)-Ru(1)	2.384(3)
S(2)-Ru(2)	2.401(5)
Cl(1)-Ru(1)	2.395(3)
Cl(2)-Ru(2)	2.392(4)

N(1)-C(1)-N(2)	103.9(12)
N(1)-C(1)-Ru(1)	130.3(10)
N(2)-C(1)-Ru(1)	125.1(11)
C(3)-C(2)-N(1)	104.5(12)
C(3)-C(2)-H(2)	127.7
N(1)-C(2)-H(2)	127.7
C(2)-C(3)-N(2)	106.9(12)
C(2)-C(3)-H(3)	126.5
N(2)-C(3)-H(3)	126.5
N(1)-C(4)-C(5)	113.0(12)
N(1)-C(4)-H(4A)	109.0
C(5)-C(4)-H(4A)	109.0
N(1)-C(4)-H(4B)	109.0
C(5)-C(4)-H(4B)	109.0
H(4A)-C(4)-H(4B)	107.8
C(6)-C(5)-C(10)	118.6(13)
C(6)-C(5)-C(4)	120.4(13)
C(10)-C(5)-C(4)	120.8(13)
C(5)-C(6)-C(7)	120.0(14)
C(5)-C(6)-H(6)	120.0
C(7)-C(6)-H(6)	120.0
C(8)-C(7)-C(6)	120.2(16)
C(8)-C(7)-H(7)	119.9
C(6)-C(7)-H(7)	119.9
C(9)-C(8)-C(7)	118.9(16)
C(9)-C(8)-H(8)	120.5
C(7)-C(8)-H(8)	120.5
C(8)-C(9)-C(10)	122.3(17)
C(8)-C(9)-H(9)	118.8

C(10)-C(9)-H(9)	118.8
C(9)-C(10)-C(5)	119.3(15)
C(9)-C(10)-H(10)	120.3
C(5)-C(10)-H(10)	120.3
N(2)-C(11)-C(12)	110.2(11)
N(2)-C(11)-H(11A)	109.6
C(12)-C(11)-H(11A)	109.6
N(2)-C(11)-H(11B)	109.6
C(12)-C(11)-H(11B)	109.6
H(11A)-C(11)-H(11B)	108.1
C(11)-C(12)-S(1)	108.0(11)
C(11)-C(12)-H(12A)	110.1
S(1)-C(12)-H(12A)	110.1
C(11)-C(12)-H(12B)	110.1
S(1)-C(12)-H(12B)	110.1
H(12A)-C(12)-H(12B)	108.4
C(18)-C(13)-C(14)	120.4(13)
C(18)-C(13)-S(1)	116.3(10)
C(14)-C(13)-S(1)	123.2(11)
C(15)-C(14)-C(13)	118.9(13)
C(15)-C(14)-H(14)	120.5
C(13)-C(14)-H(14)	120.5
C(16)-C(15)-C(14)	120.3(13)
C(16)-C(15)-H(15)	119.9
C(14)-C(15)-H(15)	119.9
C(15)-C(16)-C(17)	122.3(13)
C(15)-C(16)-Br(1)	119.3(11)
C(17)-C(16)-Br(1)	118.2(12)
C(18)-C(17)-C(16)	117.4(14)
C(18)-C(17)-H(17)	121.3
C(16)-C(17)-H(17)	121.3
C(13)-C(18)-C(17)	120.6(14)
C(13)-C(18)-H(18)	119.7
C(17)-C(18)-H(18)	119.7
C(24)-C(19)-C(20)	115.5(14)
C(24)-C(19)-C(25)	123.5(16)
C(20)-C(19)-C(25)	121.0(15)
C(24)-C(19)-Ru(1)	70.4(9)
C(20)-C(19)-Ru(1)	69.3(9)
C(25)-C(19)-Ru(1)	129.2(11)
C(21)-C(20)-C(19)	121.2(14)
C(21)-C(20)-Ru(1)	71.6(10)
C(19)-C(20)-Ru(1)	72.8(9)
C(21)-C(20)-H(20)	119.4
C(19)-C(20)-H(20)	119.4
Ru(1)-C(20)-H(20)	128.5

C(20)-C(21)-C(22)	123.3(15)
C(20)-C(21)-Ru(1)	72.4(10)
C(22)-C(21)-Ru(1)	72.1(8)
C(20)-C(21)-H(21)	118.4
C(22)-C(21)-H(21)	118.4
Ru(1)-C(21)-H(21)	129.9
C(21)-C(22)-C(23)	115.5(13)
C(21)-C(22)-C(26)	124.4(14)
C(23)-C(22)-C(26)	119.9(13)
C(21)-C(22)-Ru(1)	70.5(8)
C(23)-C(22)-Ru(1)	69.2(8)
C(26)-C(22)-Ru(1)	133.2(10)
C(24)-C(23)-C(22)	121.6(13)
C(24)-C(23)-Ru(1)	73.5(8)
C(22)-C(23)-Ru(1)	73.1(8)
C(24)-C(23)-H(23)	119.2
C(22)-C(23)-H(23)	119.2
Ru(1)-C(23)-H(23)	126.0
C(23)-C(24)-C(19)	122.7(14)
C(23)-C(24)-Ru(1)	69.5(8)
C(19)-C(24)-Ru(1)	73.3(9)
C(23)-C(24)-H(24)	118.6
C(19)-C(24)-H(24)	118.6
Ru(1)-C(24)-H(24)	131.7
C(19)-C(25)-H(25A)	109.5
C(19)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(19)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(27)-C(26)-C(22)	114.2(12)
C(27)-C(26)-C(28)	109.5(12)
C(22)-C(26)-C(28)	107.1(11)
C(27)-C(26)-H(26)	108.6
C(22)-C(26)-H(26)	108.6
C(28)-C(26)-H(26)	108.6
C(26)-C(27)-H(27A)	109.5
C(26)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(26)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(26)-C(28)-H(28A)	109.5
C(26)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(26)-C(28)-H(28C)	109.5

H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
N(3)-C(29)-N(4)	108.0
N(3)-C(29)-Ru(2)	129.0(2)
N(4)-C(29)-Ru(2)	122.6(2)
C(30)-N(3)-C(29)	108.0
C(30)-N(3)-C(32)	124.7(10)
C(29)-N(3)-C(32)	127.3(10)
N(3)-C(30)-C(31)	108.0
N(3)-C(30)-H(30)	126.0
C(31)-C(30)-H(30)	126.0
N(4)-C(31)-C(30)	108.0
N(4)-C(31)-H(31)	126.0
C(30)-C(31)-H(31)	126.0
C(39)-N(4)-C(31)	123.7(8)
C(39)-N(4)-C(29)	127.9(8)
C(31)-N(4)-C(29)	108.0
N(3)-C(32)-C(33)	113.0(14)
N(3)-C(32)-H(32A)	109.0
C(33)-C(32)-H(32A)	109.0
N(3)-C(32)-H(32B)	109.0
C(33)-C(32)-H(32B)	109.0
H(32A)-C(32)-H(32B)	107.8
C(34)-C(33)-C(38)	120.0
C(34)-C(33)-C(32)	115.0(11)
C(38)-C(33)-C(32)	124.9(11)
C(35)-C(34)-C(33)	120.0
C(35)-C(34)-H(34)	120.0
C(33)-C(34)-H(34)	120.0
C(34)-C(35)-C(36)	120.0
C(34)-C(35)-H(35)	120.0
C(36)-C(35)-H(35)	120.0
C(35)-C(36)-C(37)	120.0
C(35)-C(36)-H(36)	120.0
C(37)-C(36)-H(36)	120.0
C(38)-C(37)-C(36)	120.0
C(38)-C(37)-H(37)	120.0
C(36)-C(37)-H(37)	120.0
C(37)-C(38)-C(33)	120.0
C(37)-C(38)-H(38)	120.0
C(33)-C(38)-H(38)	120.0
N(4)-C(39)-C(40)	112.0(13)
N(4)-C(39)-H(39A)	109.2
C(40)-C(39)-H(39A)	109.2
N(4)-C(39)-H(39B)	109.2
C(40)-C(39)-H(39B)	109.2

H(39A)-C(39)-H(39B)	107.9
C(39)-C(40)-S(2)	116.9(15)
C(39)-C(40)-H(40A)	108.1
S(2)-C(40)-H(40A)	108.1
C(39)-C(40)-H(40B)	108.1
S(2)-C(40)-H(40B)	108.1
H(40A)-C(40)-H(40B)	107.3
C(46)-C(41)-C(42)	116.0(19)
C(46)-C(41)-S(2)	117.7(16)
C(42)-C(41)-S(2)	125.7(15)
C(43)-C(42)-C(41)	121.7(18)
C(43)-C(42)-H(42)	119.2
C(41)-C(42)-H(42)	119.2
C(44)-C(43)-C(42)	120.6(17)
C(44)-C(43)-H(43)	119.7
C(42)-C(43)-H(43)	119.7
C(43)-C(44)-C(45)	123.8(18)
C(43)-C(44)-Br(2)	119.7(16)
C(45)-C(44)-Br(2)	116.4(16)
C(44)-C(45)-C(46)	114.2(18)
C(44)-C(45)-H(45)	122.9
C(46)-C(45)-H(45)	122.9
C(41)-C(46)-C(45)	123.1(19)
C(41)-C(46)-H(46)	118.5
C(45)-C(46)-H(46)	118.5
C(52)-C(47)-C(48)	115.7(15)
C(52)-C(47)-C(53)	124.5(17)
C(48)-C(47)-C(53)	119.8(16)
C(52)-C(47)-Ru(2)	70.3(10)
C(48)-C(47)-Ru(2)	68.6(8)
C(53)-C(47)-Ru(2)	131.7(13)
C(49)-C(48)-C(47)	121.5(15)
C(49)-C(48)-Ru(2)	72.2(9)
C(47)-C(48)-Ru(2)	73.6(8)
C(49)-C(48)-H(48)	119.3
C(47)-C(48)-H(48)	119.3
Ru(2)-C(48)-H(48)	127.0
C(50)-C(49)-C(48)	121.7(15)
C(50)-C(49)-Ru(2)	74.6(9)
C(48)-C(49)-Ru(2)	70.8(9)
C(50)-C(49)-H(49)	119.2
C(48)-C(49)-H(49)	119.2
Ru(2)-C(49)-H(49)	127.6
C(49)-C(50)-C(51)	116.8(14)
C(49)-C(50)-C(54)	120.6(14)
C(51)-C(50)-C(54)	122.4(14)

C(49)-C(50)-Ru(2)	69.3(9)
C(51)-C(50)-Ru(2)	70.1(8)
C(54)-C(50)-Ru(2)	135.6(11)
C(52)-C(51)-C(50)	121.5(16)
C(52)-C(51)-Ru(2)	71.0(10)
C(50)-C(51)-Ru(2)	73.2(9)
C(52)-C(51)-H(51)	119.3
C(50)-C(51)-H(51)	119.3
Ru(2)-C(51)-H(51)	129.0
C(51)-C(52)-C(47)	122.8(17)
C(51)-C(52)-Ru(2)	72.7(10)
C(47)-C(52)-Ru(2)	73.6(10)
C(51)-C(52)-H(52)	118.6
C(47)-C(52)-H(52)	118.6
Ru(2)-C(52)-H(52)	127.3
C(47)-C(53)-H(53A)	109.5
C(47)-C(53)-H(53B)	109.5
H(53A)-C(53)-H(53B)	109.5
C(47)-C(53)-H(53C)	109.5
H(53A)-C(53)-H(53C)	109.5
H(53B)-C(53)-H(53C)	109.5
C(55)-C(54)-C(50)	108.0(15)
C(55)-C(54)-C(56)	110.6(15)
C(50)-C(54)-C(56)	115.3(13)
C(55)-C(54)-H(54)	107.6
C(50)-C(54)-H(54)	107.6
C(56)-C(54)-H(54)	107.6
C(54)-C(55)-H(55A)	109.5
C(54)-C(55)-H(55B)	109.5
H(55A)-C(55)-H(55B)	109.5
C(54)-C(55)-H(55C)	109.5
H(55A)-C(55)-H(55C)	109.5
H(55B)-C(55)-H(55C)	109.5
C(54)-C(56)-H(56A)	109.5
C(54)-C(56)-H(56B)	109.5
H(56A)-C(56)-H(56B)	109.5
C(54)-C(56)-H(56C)	109.5
H(56A)-C(56)-H(56C)	109.5
H(56B)-C(56)-H(56C)	109.5
C(1)-N(1)-C(2)	112.4(12)
C(1)-N(1)-C(4)	126.8(12)
C(2)-N(1)-C(4)	120.7(12)
C(1)-N(2)-C(3)	112.2(12)
C(1)-N(2)-C(11)	123.4(13)
C(3)-N(2)-C(11)	124.2(12)
F(4)-P(1)-F(2)	90.9(8)

F(4)-P(1)-F(5)	89.8(8)
F(2)-P(1)-F(5)	179.0(8)
F(4)-P(1)-F(1)	177.1(8)
F(2)-P(1)-F(1)	91.7(8)
F(5)-P(1)-F(1)	87.6(7)
F(4)-P(1)-F(6)	89.9(7)
F(2)-P(1)-F(6)	91.4(7)
F(5)-P(1)-F(6)	89.3(7)
F(1)-P(1)-F(6)	91.3(7)
F(4)-P(1)-F(3)	88.8(7)
F(2)-P(1)-F(3)	90.2(6)
F(5)-P(1)-F(3)	89.2(6)
F(1)-P(1)-F(3)	89.9(6)
F(6)-P(1)-F(3)	178.0(7)
F(8)-P(2)-F(10)	91.7(10)
F(8)-P(2)-F(7)	92.2(10)
F(10)-P(2)-F(7)	175.8(10)
F(8)-P(2)-F(11)	179.4(11)
F(10)-P(2)-F(11)	88.0(9)
F(7)-P(2)-F(11)	88.1(9)
F(8)-P(2)-F(9)	87.6(9)
F(10)-P(2)-F(9)	87.9(7)
F(7)-P(2)-F(9)	90.6(7)
F(11)-P(2)-F(9)	92.9(9)
F(8)-P(2)-F(12)	92.3(8)
F(10)-P(2)-F(12)	91.9(8)
F(7)-P(2)-F(12)	89.5(7)
F(11)-P(2)-F(12)	87.2(8)
F(9)-P(2)-F(12)	179.8(8)
C(13)-S(1)-C(12)	102.8(7)
C(13)-S(1)-Ru(1)	112.0(4)
C(12)-S(1)-Ru(1)	111.1(5)
C(41)-S(2)-C(40)	104.8(9)
C(41)-S(2)-Ru(2)	115.2(6)
C(40)-S(2)-Ru(2)	108.5(7)
C(1)-Ru(1)-C(23)	114.5(5)
C(1)-Ru(1)-C(21)	98.0(6)
C(23)-Ru(1)-C(21)	66.6(6)
C(1)-Ru(1)-C(20)	125.4(6)
C(23)-Ru(1)-C(20)	78.8(6)
C(21)-Ru(1)-C(20)	36.0(6)
C(1)-Ru(1)-C(24)	150.8(5)
C(23)-Ru(1)-C(24)	37.0(5)
C(21)-Ru(1)-C(24)	77.4(6)
C(20)-Ru(1)-C(24)	65.9(6)
C(1)-Ru(1)-C(22)	91.5(6)

C(23)-Ru(1)-C(22)	37.7(6)
C(21)-Ru(1)-C(22)	37.4(5)
C(20)-Ru(1)-C(22)	67.1(5)
C(24)-Ru(1)-C(22)	67.2(6)
C(1)-Ru(1)-C(19)	163.3(6)
C(23)-Ru(1)-C(19)	67.2(6)
C(21)-Ru(1)-C(19)	66.8(6)
C(20)-Ru(1)-C(19)	37.9(6)
C(24)-Ru(1)-C(19)	36.3(6)
C(22)-Ru(1)-C(19)	80.5(5)
C(1)-Ru(1)-S(1)	89.1(4)
C(23)-Ru(1)-S(1)	90.3(4)
C(21)-Ru(1)-S(1)	156.8(4)
C(20)-Ru(1)-S(1)	145.4(4)
C(24)-Ru(1)-S(1)	85.7(4)
C(22)-Ru(1)-S(1)	120.9(4)
C(19)-Ru(1)-S(1)	107.6(4)
C(1)-Ru(1)-Cl(1)	87.6(4)
C(23)-Ru(1)-Cl(1)	157.9(4)
C(21)-Ru(1)-Cl(1)	111.0(4)
C(20)-Ru(1)-Cl(1)	87.5(4)
C(24)-Ru(1)-Cl(1)	121.2(4)
C(22)-Ru(1)-Cl(1)	147.8(4)
C(19)-Ru(1)-Cl(1)	91.4(4)
S(1)-Ru(1)-Cl(1)	91.23(12)
C(29)-Ru(2)-C(48)	91.7(5)
C(29)-Ru(2)-C(49)	91.3(5)
C(48)-Ru(2)-C(49)	37.0(6)
C(29)-Ru(2)-C(52)	154.8(5)
C(48)-Ru(2)-C(52)	65.9(7)
C(49)-Ru(2)-C(52)	77.7(7)
C(29)-Ru(2)-C(51)	153.3(5)
C(48)-Ru(2)-C(51)	77.4(6)
C(49)-Ru(2)-C(51)	65.3(6)
C(52)-Ru(2)-C(51)	36.3(6)
C(29)-Ru(2)-C(47)	118.7(5)
C(48)-Ru(2)-C(47)	37.8(6)
C(49)-Ru(2)-C(47)	67.3(6)
C(52)-Ru(2)-C(47)	36.2(6)
C(51)-Ru(2)-C(47)	65.7(6)
C(29)-Ru(2)-C(50)	116.6(5)
C(48)-Ru(2)-C(50)	66.1(6)
C(49)-Ru(2)-C(50)	36.2(5)
C(52)-Ru(2)-C(50)	66.1(6)
C(51)-Ru(2)-C(50)	36.7(6)
C(47)-Ru(2)-C(50)	78.9(6)

C(29)-Ru(2)-Cl(2)	87.1(2)
C(48)-Ru(2)-Cl(2)	156.4(5)
C(49)-Ru(2)-Cl(2)	119.5(4)
C(52)-Ru(2)-Cl(2)	118.0(5)
C(51)-Ru(2)-Cl(2)	93.3(4)
C(47)-Ru(2)-Cl(2)	153.9(5)
C(50)-Ru(2)-Cl(2)	93.5(4)
C(29)-Ru(2)-S(2)	91.5(3)
C(48)-Ru(2)-S(2)	113.5(5)
C(49)-Ru(2)-S(2)	150.5(4)
C(52)-Ru(2)-S(2)	87.6(5)
C(51)-Ru(2)-S(2)	115.2(4)
C(47)-Ru(2)-S(2)	85.7(5)
C(50)-Ru(2)-S(2)	151.8(4)
Cl(2)-Ru(2)-S(2)	90.04(15)

Table S10. Torsion angles [deg] for sblta151104, **complex 1i**

N(1)-C(2)-C(3)-N(2)	-0.3(16)
N(1)-C(4)-C(5)-C(6)	-136.2(13)
N(1)-C(4)-C(5)-C(10)	48.1(17)
C(10)-C(5)-C(6)-C(7)	-2(2)
C(4)-C(5)-C(6)-C(7)	-177.5(13)
C(5)-C(6)-C(7)-C(8)	4(2)
C(6)-C(7)-C(8)-C(9)	-8(2)
C(7)-C(8)-C(9)-C(10)	9(3)
C(8)-C(9)-C(10)-C(5)	-7(2)
C(6)-C(5)-C(10)-C(9)	3(2)
C(4)-C(5)-C(10)-C(9)	178.6(13)
N(2)-C(11)-C(12)-S(1)	-78.3(14)
C(18)-C(13)-C(14)-C(15)	2(2)
S(1)-C(13)-C(14)-C(15)	-178.6(11)
C(13)-C(14)-C(15)-C(16)	-1(2)
C(14)-C(15)-C(16)-C(17)	1(3)
C(14)-C(15)-C(16)-Br(1)	176.5(11)
C(15)-C(16)-C(17)-C(18)	-2(3)
Br(1)-C(16)-C(17)-C(18)	-177.3(12)
C(14)-C(13)-C(18)-C(17)	-2(2)
S(1)-C(13)-C(18)-C(17)	177.7(12)
C(16)-C(17)-C(18)-C(13)	3(2)
C(24)-C(19)-C(20)-C(21)	0(2)
C(25)-C(19)-C(20)-C(21)	-179.0(16)
Ru(1)-C(19)-C(20)-C(21)	-55.0(15)
C(24)-C(19)-C(20)-Ru(1)	54.6(12)

C(25)-C(19)-C(20)-Ru(1)	-124.1(15)
C(19)-C(20)-C(21)-C(22)	2(3)
Ru(1)-C(20)-C(21)-C(22)	-53.6(14)
C(19)-C(20)-C(21)-Ru(1)	55.5(15)
C(20)-C(21)-C(22)-C(23)	0(2)
Ru(1)-C(21)-C(22)-C(23)	-54.0(11)
C(20)-C(21)-C(22)-C(26)	-176.7(15)
Ru(1)-C(21)-C(22)-C(26)	129.6(14)
C(20)-C(21)-C(22)-Ru(1)	53.7(15)
C(21)-C(22)-C(23)-C(24)	-3(2)
C(26)-C(22)-C(23)-C(24)	173.6(14)
Ru(1)-C(22)-C(23)-C(24)	-57.7(13)
C(21)-C(22)-C(23)-Ru(1)	54.7(11)
C(26)-C(22)-C(23)-Ru(1)	-128.8(13)
C(22)-C(23)-C(24)-C(19)	5(2)
Ru(1)-C(23)-C(24)-C(19)	-52.7(14)
C(22)-C(23)-C(24)-Ru(1)	57.5(12)
C(20)-C(19)-C(24)-C(23)	-3(2)
C(25)-C(19)-C(24)-C(23)	175.7(16)
Ru(1)-C(19)-C(24)-C(23)	51.1(14)
C(20)-C(19)-C(24)-Ru(1)	-54.1(13)
C(25)-C(19)-C(24)-Ru(1)	124.6(16)
C(21)-C(22)-C(26)-C(27)	-32(2)
C(23)-C(22)-C(26)-C(27)	151.3(14)
Ru(1)-C(22)-C(26)-C(27)	63(2)
C(21)-C(22)-C(26)-C(28)	88.9(16)
C(23)-C(22)-C(26)-C(28)	-87.3(15)
Ru(1)-C(22)-C(26)-C(28)	-176.0(10)
N(4)-C(29)-N(3)-C(30)	0.0
Ru(2)-C(29)-N(3)-C(30)	173.1(3)
N(4)-C(29)-N(3)-C(32)	-178.4(10)
Ru(2)-C(29)-N(3)-C(32)	-5.3(9)
C(29)-N(3)-C(30)-C(31)	0.0
C(32)-N(3)-C(30)-C(31)	178.4(10)
N(3)-C(30)-C(31)-N(4)	0.0
C(30)-C(31)-N(4)-C(39)	-172.8(9)
C(30)-C(31)-N(4)-C(29)	0.0
N(3)-C(29)-N(4)-C(39)	172.5(10)
Ru(2)-C(29)-N(4)-C(39)	-1.2(9)
N(3)-C(29)-N(4)-C(31)	0.0
Ru(2)-C(29)-N(4)-C(31)	-173.6(3)
C(30)-N(3)-C(32)-C(33)	-49.8(18)
C(29)-N(3)-C(32)-C(33)	128.3(12)
N(3)-C(32)-C(33)-C(34)	154.9(12)
N(3)-C(32)-C(33)-C(38)	-29(2)
C(38)-C(33)-C(34)-C(35)	0.0

C(32)-C(33)-C(34)-C(35)	176.6(14)
C(33)-C(34)-C(35)-C(36)	0.0
C(34)-C(35)-C(36)-C(37)	0.0
C(35)-C(36)-C(37)-C(38)	0.0
C(36)-C(37)-C(38)-C(33)	0.0
C(34)-C(33)-C(38)-C(37)	0.0
C(32)-C(33)-C(38)-C(37)	-176.3(15)
C(31)-N(4)-C(39)-C(40)	112.3(13)
C(29)-N(4)-C(39)-C(40)	-59.0(18)
N(4)-C(39)-C(40)-S(2)	72.7(18)
C(46)-C(41)-C(42)-C(43)	4(3)
S(2)-C(41)-C(42)-C(43)	174.5(16)
C(41)-C(42)-C(43)-C(44)	2(3)
C(42)-C(43)-C(44)-C(45)	-2(3)
C(42)-C(43)-C(44)-Br(2)	176.9(16)
C(43)-C(44)-C(45)-C(46)	-3(3)
Br(2)-C(44)-C(45)-C(46)	178.1(17)
C(42)-C(41)-C(46)-C(45)	-9(3)
S(2)-C(41)-C(46)-C(45)	179.3(19)
C(44)-C(45)-C(46)-C(41)	9(4)
C(52)-C(47)-C(48)-C(49)	-3(2)
C(53)-C(47)-C(48)-C(49)	176.8(16)
Ru(2)-C(47)-C(48)-C(49)	-56.4(14)
C(52)-C(47)-C(48)-Ru(2)	53.7(14)
C(53)-C(47)-C(48)-Ru(2)	-126.8(16)
C(47)-C(48)-C(49)-C(50)	0(2)
Ru(2)-C(48)-C(49)-C(50)	-56.9(14)
C(47)-C(48)-C(49)-Ru(2)	57.0(14)
C(48)-C(49)-C(50)-C(51)	2(2)
Ru(2)-C(49)-C(50)-C(51)	-53.3(12)
C(48)-C(49)-C(50)-C(54)	-173.3(15)
Ru(2)-C(49)-C(50)-C(54)	131.6(14)
C(48)-C(49)-C(50)-Ru(2)	55.2(14)
C(49)-C(50)-C(51)-C(52)	-1(2)
C(54)-C(50)-C(51)-C(52)	173.6(16)
Ru(2)-C(50)-C(51)-C(52)	-54.3(14)
C(49)-C(50)-C(51)-Ru(2)	52.8(12)
C(54)-C(50)-C(51)-Ru(2)	-132.1(14)
C(50)-C(51)-C(52)-C(47)	-1(3)
Ru(2)-C(51)-C(52)-C(47)	-56.4(16)
C(50)-C(51)-C(52)-Ru(2)	55.3(14)
C(48)-C(47)-C(52)-C(51)	3(3)
C(53)-C(47)-C(52)-C(51)	-176.3(16)
Ru(2)-C(47)-C(52)-C(51)	56.0(16)
C(48)-C(47)-C(52)-Ru(2)	-52.9(13)
C(53)-C(47)-C(52)-Ru(2)	127.7(17)

C(49)-C(50)-C(54)-C(55)	83.1(19)
C(51)-C(50)-C(54)-C(55)	-91.8(18)
Ru(2)-C(50)-C(54)-C(55)	174.0(13)
C(49)-C(50)-C(54)-C(56)	-152.7(16)
C(51)-C(50)-C(54)-C(56)	32(2)
Ru(2)-C(50)-C(54)-C(56)	-62(2)
N(2)-C(1)-N(1)-C(2)	3.0(16)
Ru(1)-C(1)-N(1)-C(2)	173.2(11)
N(2)-C(1)-N(1)-C(4)	-173.6(13)
Ru(1)-C(1)-N(1)-C(4)	-3(2)
C(3)-C(2)-N(1)-C(1)	-1.8(17)
C(3)-C(2)-N(1)-C(4)	175.0(13)
C(5)-C(4)-N(1)-C(1)	-136.3(14)
C(5)-C(4)-N(1)-C(2)	47.3(17)
N(1)-C(1)-N(2)-C(3)	-3.2(16)
Ru(1)-C(1)-N(2)-C(3)	-174.1(10)
N(1)-C(1)-N(2)-C(11)	-177.6(12)
Ru(1)-C(1)-N(2)-C(11)	11.5(19)
C(2)-C(3)-N(2)-C(1)	2.2(17)
C(2)-C(3)-N(2)-C(11)	176.5(12)
C(12)-C(11)-N(2)-C(1)	60.8(18)
C(12)-C(11)-N(2)-C(3)	-112.9(15)
C(18)-C(13)-S(1)-C(12)	139.8(11)
C(14)-C(13)-S(1)-C(12)	-40.0(13)
C(18)-C(13)-S(1)-Ru(1)	-100.7(10)
C(14)-C(13)-S(1)-Ru(1)	79.4(12)
C(11)-C(12)-S(1)-C(13)	153.4(10)
C(11)-C(12)-S(1)-Ru(1)	33.4(11)
C(46)-C(41)-S(2)-C(40)	-141.2(18)
C(42)-C(41)-S(2)-C(40)	48.3(18)
C(46)-C(41)-S(2)-Ru(2)	99.7(18)
C(42)-C(41)-S(2)-Ru(2)	-70.8(17)
C(39)-C(40)-S(2)-C(41)	-154.4(14)
C(39)-C(40)-S(2)-Ru(2)	-30.9(15)

Complex 1j

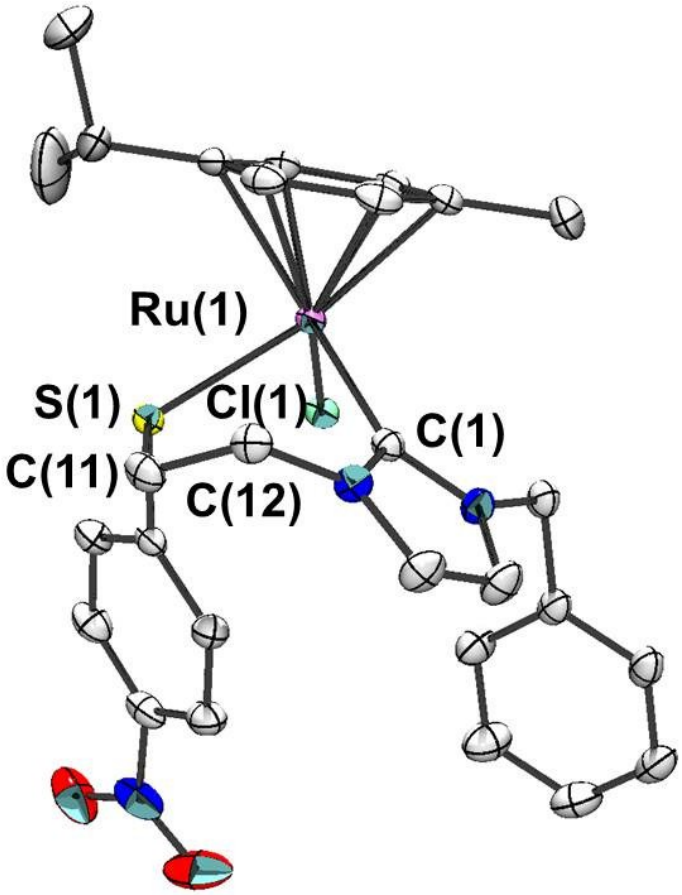


Table S11. Crystal data and structure refinement for sblta151118, **complex 1j**

Identification code	sblta151118
Empirical formula	C28 H31 Cl F6 N3 O2 P Ru S
Formula weight	755.11
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 8.9199(7) A alpha = 81.652(2) deg. b = 11.3270(9) A beta = 84.987(2) deg. c = 15.5712(13) A gamma = 73.995(2) deg.
Volume	1494.4(2) A^3

Z, Calculated density	2, 1.678 Mg/m^3
Absorption coefficient	0.808 mm^-1
F(000)	764
Crystal size	0.350 x 0.300 x 0.250 mm
Theta range for data collection	1.323 to 30.977 deg.
Limiting indices	-12<=h<=12, -16<=k<=16, -22<=l<=22
Reflections collected / unique	35892 / 9480 [R(int) = 0.0183]
Completeness to theta = 25.242	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7462 and 0.7149
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9480 / 0 / 391
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0247, wR2 = 0.0599
R indices (all data)	R1 = 0.0288, wR2 = 0.0625
Extinction coefficient	n/a
Largest diff. peak and hole	0.694 and -0.631 e.A^-3

Table S12. Bond lengths [A] and angles [deg] for sblta151118, **complex 1j**

C(1)-N(1)	1.3573(17)
C(1)-N(2)	1.3636(18)
C(1)-Ru(1)	2.0592(14)
C(2)-C(3)	1.349(2)
C(2)-N(1)	1.3906(19)
C(2)-H(2)	0.9500
C(3)-N(2)	1.3837(19)
C(3)-H(3)	0.9500

C(4)-N(1)	1.4795(19)
C(4)-C(5)	1.517(2)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.391(2)
C(5)-C(10)	1.396(2)
C(6)-C(7)	1.394(2)
C(6)-H(6)	0.9500
C(7)-C(8)	1.394(3)
C(7)-H(7)	0.9500
C(8)-C(9)	1.379(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.395(2)
C(9)-H(9)	0.9500
C(10)-H(10)	0.9500
C(11)-N(2)	1.4643(18)
C(11)-C(12)	1.518(2)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-S(1)	1.8280(16)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-C(14)	1.390(2)
C(13)-C(18)	1.393(2)
C(13)-S(1)	1.7863(14)
C(14)-C(15)	1.391(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.379(2)
C(15)-H(15)	0.9500
C(16)-C(17)	1.383(3)
C(16)-N(3)	1.473(2)
C(17)-C(18)	1.392(2)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(19)-C(20)	1.400(2)
C(19)-C(24)	1.429(2)
C(19)-C(25)	1.505(2)
C(19)-Ru(1)	2.2322(14)
C(20)-C(21)	1.429(2)
C(20)-Ru(1)	2.2149(14)
C(20)-H(20)	0.9500
C(21)-C(22)	1.396(2)
C(21)-Ru(1)	2.2611(14)
C(21)-H(21)	0.9500
C(22)-C(23)	1.438(2)
C(22)-C(26)	1.514(2)

C(22)-Ru(1)	2.2808(14)
C(23)-C(24)	1.403(2)
C(23)-Ru(1)	2.2056(14)
C(23)-H(23)	0.9500
C(24)-Ru(1)	2.1884(15)
C(24)-H(24)	0.9500
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-C(27)	1.523(4)
C(26)-C(28)	1.524(3)
C(26)-H(26)	1.0000
C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
N(3)-O(2)	1.222(2)
N(3)-O(1)	1.226(2)
F(1)-P(1)	1.5912(15)
F(2)-P(1)	1.6009(13)
F(3)-P(1)	1.5708(13)
F(4)-P(1)	1.5910(15)
F(5)-P(1)	1.5908(14)
F(6)-P(1)	1.6029(12)
S(1)-Ru(1)	2.3891(4)
Cl(1)-Ru(1)	2.4061(4)

N(1)-C(1)-N(2)	104.07(11)
N(1)-C(1)-Ru(1)	133.84(10)
N(2)-C(1)-Ru(1)	122.06(10)
C(3)-C(2)-N(1)	106.93(13)
C(3)-C(2)-H(2)	126.5
N(1)-C(2)-H(2)	126.5
C(2)-C(3)-N(2)	106.43(13)
C(2)-C(3)-H(3)	126.8
N(2)-C(3)-H(3)	126.8
N(1)-C(4)-C(5)	111.07(12)
N(1)-C(4)-H(4A)	109.4
C(5)-C(4)-H(4A)	109.4
N(1)-C(4)-H(4B)	109.4
C(5)-C(4)-H(4B)	109.4
H(4A)-C(4)-H(4B)	108.0
C(6)-C(5)-C(10)	119.13(15)
C(6)-C(5)-C(4)	121.14(13)

C(10)-C(5)-C(4)	119.73(14)
C(5)-C(6)-C(7)	120.33(15)
C(5)-C(6)-H(6)	119.8
C(7)-C(6)-H(6)	119.8
C(6)-C(7)-C(8)	120.04(18)
C(6)-C(7)-H(7)	120.0
C(8)-C(7)-H(7)	120.0
C(9)-C(8)-C(7)	119.92(16)
C(9)-C(8)-H(8)	120.0
C(7)-C(8)-H(8)	120.0
C(8)-C(9)-C(10)	120.11(15)
C(8)-C(9)-H(9)	119.9
C(10)-C(9)-H(9)	119.9
C(9)-C(10)-C(5)	120.47(16)
C(9)-C(10)-H(10)	119.8
C(5)-C(10)-H(10)	119.8
N(2)-C(11)-C(12)	112.19(12)
N(2)-C(11)-H(11A)	109.2
C(12)-C(11)-H(11A)	109.2
N(2)-C(11)-H(11B)	109.2
C(12)-C(11)-H(11B)	109.2
H(11A)-C(11)-H(11B)	107.9
C(11)-C(12)-S(1)	113.42(10)
C(11)-C(12)-H(12A)	108.9
S(1)-C(12)-H(12A)	108.9
C(11)-C(12)-H(12B)	108.9
S(1)-C(12)-H(12B)	108.9
H(12A)-C(12)-H(12B)	107.7
C(14)-C(13)-C(18)	121.08(13)
C(14)-C(13)-S(1)	115.46(11)
C(18)-C(13)-S(1)	123.43(12)
C(13)-C(14)-C(15)	119.59(15)
C(13)-C(14)-H(14)	120.2
C(15)-C(14)-H(14)	120.2
C(16)-C(15)-C(14)	118.52(15)
C(16)-C(15)-H(15)	120.7
C(14)-C(15)-H(15)	120.7
C(15)-C(16)-C(17)	122.91(14)
C(15)-C(16)-N(3)	118.33(16)
C(17)-C(16)-N(3)	118.76(16)
C(16)-C(17)-C(18)	118.42(15)
C(16)-C(17)-H(17)	120.8
C(18)-C(17)-H(17)	120.8
C(17)-C(18)-C(13)	119.42(15)
C(17)-C(18)-H(18)	120.3
C(13)-C(18)-H(18)	120.3

C(20)-C(19)-C(24)	117.15(14)
C(20)-C(19)-C(25)	121.36(15)
C(24)-C(19)-C(25)	121.49(16)
C(20)-C(19)-Ru(1)	70.98(8)
C(24)-C(19)-Ru(1)	69.49(8)
C(25)-C(19)-Ru(1)	129.70(11)
C(19)-C(20)-C(21)	122.18(14)
C(19)-C(20)-Ru(1)	72.32(8)
C(21)-C(20)-Ru(1)	73.15(8)
C(19)-C(20)-H(20)	118.9
C(21)-C(20)-H(20)	118.9
Ru(1)-C(20)-H(20)	127.9
C(22)-C(21)-C(20)	120.67(14)
C(22)-C(21)-Ru(1)	72.87(8)
C(20)-C(21)-Ru(1)	69.64(8)
C(22)-C(21)-H(21)	119.7
C(20)-C(21)-H(21)	119.7
Ru(1)-C(21)-H(21)	130.5
C(21)-C(22)-C(23)	117.61(14)
C(21)-C(22)-C(26)	123.84(16)
C(23)-C(22)-C(26)	118.53(15)
C(21)-C(22)-Ru(1)	71.33(8)
C(23)-C(22)-Ru(1)	68.49(8)
C(26)-C(22)-Ru(1)	129.93(10)
C(24)-C(23)-C(22)	121.32(14)
C(24)-C(23)-Ru(1)	70.72(8)
C(22)-C(23)-Ru(1)	74.17(8)
C(24)-C(23)-H(23)	119.3
C(22)-C(23)-H(23)	119.3
Ru(1)-C(23)-H(23)	128.0
C(23)-C(24)-C(19)	121.02(14)
C(23)-C(24)-Ru(1)	72.05(9)
C(19)-C(24)-Ru(1)	72.81(8)
C(23)-C(24)-H(24)	119.5
C(19)-C(24)-H(24)	119.5
Ru(1)-C(24)-H(24)	127.8
C(19)-C(25)-H(25A)	109.5
C(19)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(19)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(22)-C(26)-C(27)	113.77(18)
C(22)-C(26)-C(28)	107.95(18)
C(27)-C(26)-C(28)	113.4(3)
C(22)-C(26)-H(26)	107.1

C(27)-C(26)-H(26)	107.1
C(28)-C(26)-H(26)	107.1
C(26)-C(27)-H(27A)	109.5
C(26)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(26)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(26)-C(28)-H(28A)	109.5
C(26)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(26)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(1)-N(1)-C(2)	111.05(12)
C(1)-N(1)-C(4)	127.37(12)
C(2)-N(1)-C(4)	121.58(12)
C(1)-N(2)-C(3)	111.51(12)
C(1)-N(2)-C(11)	124.93(12)
C(3)-N(2)-C(11)	123.52(12)
O(2)-N(3)-O(1)	123.88(16)
O(2)-N(3)-C(16)	118.41(17)
O(1)-N(3)-C(16)	117.71(17)
F(3)-P(1)-F(5)	90.47(9)
F(3)-P(1)-F(4)	91.05(9)
F(5)-P(1)-F(4)	178.32(10)
F(3)-P(1)-F(1)	91.88(9)
F(5)-P(1)-F(1)	88.08(10)
F(4)-P(1)-F(1)	92.57(11)
F(3)-P(1)-F(2)	89.69(8)
F(5)-P(1)-F(2)	89.49(8)
F(4)-P(1)-F(2)	89.82(10)
F(1)-P(1)-F(2)	177.13(10)
F(3)-P(1)-F(6)	179.05(8)
F(5)-P(1)-F(6)	90.23(8)
F(4)-P(1)-F(6)	88.23(9)
F(1)-P(1)-F(6)	88.79(8)
F(2)-P(1)-F(6)	89.68(7)
C(13)-S(1)-C(12)	101.75(7)
C(13)-S(1)-Ru(1)	110.25(5)
C(12)-S(1)-Ru(1)	109.47(5)
C(1)-Ru(1)-C(24)	90.24(6)
C(1)-Ru(1)-C(23)	112.89(6)
C(24)-Ru(1)-C(23)	37.23(6)
C(1)-Ru(1)-C(20)	124.88(5)
C(24)-Ru(1)-C(20)	66.50(6)

C(23)-Ru(1)-C(20)	78.32(5)
C(1)-Ru(1)-C(19)	95.41(5)
C(24)-Ru(1)-C(19)	37.70(6)
C(23)-Ru(1)-C(19)	67.48(6)
C(20)-Ru(1)-C(19)	36.70(6)
C(1)-Ru(1)-C(21)	161.74(5)
C(24)-Ru(1)-C(21)	78.45(6)
C(23)-Ru(1)-C(21)	65.72(6)
C(20)-Ru(1)-C(21)	37.21(5)
C(19)-Ru(1)-C(21)	66.89(5)
C(1)-Ru(1)-C(22)	149.45(6)
C(24)-Ru(1)-C(22)	67.26(6)
C(23)-Ru(1)-C(22)	37.34(6)
C(20)-Ru(1)-C(22)	66.16(5)
C(19)-Ru(1)-C(22)	79.52(5)
C(21)-Ru(1)-C(22)	35.79(5)
C(1)-Ru(1)-S(1)	84.62(4)
C(24)-Ru(1)-S(1)	122.08(4)
C(23)-Ru(1)-S(1)	93.74(4)
C(20)-Ru(1)-S(1)	150.33(4)
C(19)-Ru(1)-S(1)	159.70(4)
C(21)-Ru(1)-S(1)	113.52(4)
C(22)-Ru(1)-S(1)	90.13(4)
C(1)-Ru(1)-Cl(1)	92.16(4)
C(24)-Ru(1)-Cl(1)	150.14(4)
C(23)-Ru(1)-Cl(1)	154.94(5)
C(20)-Ru(1)-Cl(1)	88.05(4)
C(19)-Ru(1)-Cl(1)	112.48(4)
C(21)-Ru(1)-Cl(1)	90.75(4)
C(22)-Ru(1)-Cl(1)	117.74(4)
S(1)-Ru(1)-Cl(1)	87.773(12)

Table S13. Torsion angles [deg] for sblta151118, **complex 1j**

N(1)-C(2)-C(3)-N(2)	0.87(19)
N(1)-C(4)-C(5)-C(6)	-81.74(18)
N(1)-C(4)-C(5)-C(10)	97.56(16)
C(10)-C(5)-C(6)-C(7)	-0.4(2)
C(4)-C(5)-C(6)-C(7)	178.95(16)
C(5)-C(6)-C(7)-C(8)	0.5(3)
C(6)-C(7)-C(8)-C(9)	-0.4(3)
C(7)-C(8)-C(9)-C(10)	0.1(3)
C(8)-C(9)-C(10)-C(5)	0.0(2)
C(6)-C(5)-C(10)-C(9)	0.1(2)
C(4)-C(5)-C(10)-C(9)	-179.22(14)

N(2)-C(11)-C(12)-S(1)	56.38(15)
C(18)-C(13)-C(14)-C(15)	-1.8(2)
S(1)-C(13)-C(14)-C(15)	-179.94(12)
C(13)-C(14)-C(15)-C(16)	-0.3(2)
C(14)-C(15)-C(16)-C(17)	2.1(2)
C(14)-C(15)-C(16)-N(3)	-176.68(14)
C(15)-C(16)-C(17)-C(18)	-1.8(2)
N(3)-C(16)-C(17)-C(18)	176.94(14)
C(16)-C(17)-C(18)-C(13)	-0.3(2)
C(14)-C(13)-C(18)-C(17)	2.1(2)
S(1)-C(13)-C(18)-C(17)	-179.94(12)
C(24)-C(19)-C(20)-C(21)	-2.3(2)
C(25)-C(19)-C(20)-C(21)	178.52(14)
Ru(1)-C(19)-C(20)-C(21)	-55.95(12)
C(24)-C(19)-C(20)-Ru(1)	53.60(11)
C(25)-C(19)-C(20)-Ru(1)	-125.53(14)
C(19)-C(20)-C(21)-C(22)	1.4(2)
Ru(1)-C(20)-C(21)-C(22)	-54.17(12)
C(19)-C(20)-C(21)-Ru(1)	55.57(12)
C(20)-C(21)-C(22)-C(23)	0.5(2)
Ru(1)-C(21)-C(22)-C(23)	-52.17(11)
C(20)-C(21)-C(22)-C(26)	178.79(14)
Ru(1)-C(21)-C(22)-C(26)	126.10(14)
C(20)-C(21)-C(22)-Ru(1)	52.69(12)
C(21)-C(22)-C(23)-C(24)	-1.4(2)
C(26)-C(22)-C(23)-C(24)	-179.77(14)
Ru(1)-C(22)-C(23)-C(24)	-54.95(12)
C(21)-C(22)-C(23)-Ru(1)	53.54(12)
C(26)-C(22)-C(23)-Ru(1)	-124.82(13)
C(22)-C(23)-C(24)-C(19)	0.4(2)
Ru(1)-C(23)-C(24)-C(19)	-56.13(12)
C(22)-C(23)-C(24)-Ru(1)	56.55(13)
C(20)-C(19)-C(24)-C(23)	1.4(2)
C(25)-C(19)-C(24)-C(23)	-179.43(14)
Ru(1)-C(19)-C(24)-C(23)	55.77(12)
C(20)-C(19)-C(24)-Ru(1)	-54.34(11)
C(25)-C(19)-C(24)-Ru(1)	124.80(14)
C(21)-C(22)-C(26)-C(27)	-18.8(2)
C(23)-C(22)-C(26)-C(27)	159.44(18)
Ru(1)-C(22)-C(26)-C(27)	74.6(2)
C(21)-C(22)-C(26)-C(28)	108.0(3)
C(23)-C(22)-C(26)-C(28)	-73.7(3)
Ru(1)-C(22)-C(26)-C(28)	-158.6(2)
N(2)-C(1)-N(1)-C(2)	0.24(16)
Ru(1)-C(1)-N(1)-C(2)	-177.67(12)
N(2)-C(1)-N(1)-C(4)	-179.17(13)

Ru(1)-C(1)-N(1)-C(4)	2.9(2)
C(3)-C(2)-N(1)-C(1)	-0.72(19)
C(3)-C(2)-N(1)-C(4)	178.73(14)
C(5)-C(4)-N(1)-C(1)	128.12(15)
C(5)-C(4)-N(1)-C(2)	-51.24(19)
N(1)-C(1)-N(2)-C(3)	0.33(16)
Ru(1)-C(1)-N(2)-C(3)	178.54(11)
N(1)-C(1)-N(2)-C(11)	178.21(13)
Ru(1)-C(1)-N(2)-C(11)	-3.57(19)
C(2)-C(3)-N(2)-C(1)	-0.77(19)
C(2)-C(3)-N(2)-C(11)	-178.70(14)
C(12)-C(11)-N(2)-C(1)	-66.04(18)
C(12)-C(11)-N(2)-C(3)	111.60(16)
C(15)-C(16)-N(3)-O(2)	-168.58(16)
C(17)-C(16)-N(3)-O(2)	12.6(2)
C(15)-C(16)-N(3)-O(1)	11.4(2)
C(17)-C(16)-N(3)-O(1)	-167.44(15)
C(14)-C(13)-S(1)-C(12)	-142.68(12)
C(18)-C(13)-S(1)-C(12)	39.22(14)
C(14)-C(13)-S(1)-Ru(1)	101.24(11)
C(18)-C(13)-S(1)-Ru(1)	-76.86(13)
C(11)-C(12)-S(1)-C(13)	-114.55(11)
C(11)-C(12)-S(1)-Ru(1)	2.10(12)

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