Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Materials

Imidazo[1,5-*a*]pyridin-3-ylidenes as π-Accepting Carbene Ligands: Substituent Effects on Properties of N-Heterocyclic Carbenes

Yuma Koto, Fumitoshi Shibahara,* Toshiaki Murai*

Department of Chemistry and Biomolecular Science, Faculty of Engineering, Gifu University, Yanagido, Gifu, Gifu 501-1193, Japan

General remarks

The infrared (IR) spectra were obtained on JASCO FT/IR 410 spectrometer and PerkinElmer Spectrum 400 FT-IR/FT-FIR Spectrometer. ^{1}H, ^{13}C, ^{19}F and ^{77}Se NMR spectra were recorded in $CDCl_3$ or DMSO-d_6. Chemical shifts of ^{1}H and ^{13}C are reported in δ, and are referenced to tetramethylsilane (δ = 0), $CDCl_3$ and DMSO-d_6 as internal standards, respectively. ^{19}F chemical shifts are expressed in δ relative to the external standard CF_3COOH (δ = –76.55). ^{77}Se chemical shifts are expressed in δ relative to the external standard PhSeSePh (δ = 463). Mass spectra (MS) and high-resolution mass spectra (HRMS) were obtained by ionizing samples via electron ionization (EI) or fast atom bombardment ionization (FAB) in positive mode using a magnetic sector analyzer. Elemental analysis was performed by Organic Elemental Microanalysis Laboratory, Kyoto University. Preparative recycling gel permeation chromatography (GPC) was carried out using $CHCl_3$ as the eluent. The molecular weight distribution of the polymers was measured by size exclusion chromatography (SEC) using THF as the eluent at 40 ºC on Tosoh HLC-8020 SEC system equipped with Tosoh TSK gel columns (G2000HXL and G4000HXL) and Tosoh UV-8010 UV detector (254 nm). The number average molecular weight (M_n) and the polydispersity (M_w/M_n) of the polymers were calculated from SEC eluograms based on polystylene calibration.

Materials

Unless otherwise stated, all compounds were obtained from common commercial suppliers and used as received. Diphenyliodonium tetrafluoroborate,[S1] 1-ethynyl-2,3,4,5,6-pentafluorobenzene[S2] were prepared according to literature procedures. All solvents were purified by distillation over the drying agents indicated and were transferred under argon: CH_2Cl_2 (P_2O_5), toluene (Na), 1,4-dioxane (Na), MeCN, DMF (CaH_2), Et_3N (CaH_2), $^{i}Pr_2NEt$ (CaH_2). Et_2O (dehydrated) and THF (dehydrated) were purchased from Kanto Chemical Co. and used without further purification. Column chromatography was performed on silica gel 60N (spherical, neutral, 40–50 mm) from Kanto Chemical Co., Ltd. All manipulations were carried out under an argon atmosphere unless otherwise noted.

1-Bromoimidazo[1,5-*a*]pyridine (2Br)

Prepared according to literature procedure.[S3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60 (dd, *J* = 7.1, 6.3 Hz, 1H, Ar), 6.77 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.36 (d, *J* = 9.3 Hz, 1H, Ar), 7.89 (d, *J* = 7.1 Hz, 1H, Ar), 8.04 (s, 1H, Ar).

1-Iodoimidazo[1,5-*a*]pyridine (2I)

To a solution of imidazo[1,5-*a*]pyridine (590 mg, 5.0 mmol, 1.0 equiv) in THF (25 mL) was added I_2 (1.3 g, 5.0 mmol, 1.0 equiv) at room temperature under Ar atmosphere. The resulting mixture was stirred under reflux for 1 h and then cooled to room temperature. The reaction mixture was quenched with saturated $Na_2S_2O_3$ aq, neutralized with $NaHCO_3$ aq, and extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, filtrated, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 4/1) to give 1-iodoimidazo[1,5-*a*]pyridine (420 mg, 34%) as a brownish syrup. R_f = 0.35 (*n*-hexane/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61 (dd, *J* = 7.1, 6.3 Hz, 1H, Ar), 6.76 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.32 (d, *J* = 9.3 Hz, 1H, Ar), 7.91 (d, *J* = 7.1 Hz, 1H, Ar), 8.12 (s, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 72.3, 113.6, 118.5, 120.4, 122.6, 129.2, 132.3 (Ar); IR (KBr) 3074, 2929, 2360, 1929, 1749, 1629, 1559, 1523, 1506, 1430, 1356, 1324, 1305, 1292, 1260, 1237, 1174, 1139, 998, 973, 911, 827, 804, 757, 743, 649, 561 cm^{-1}; MS (EI): *m/z*: 244 $[M]^+$; HRMS (EI): *m/z* calcd for $C_7H_5IN_2$: 243.9497 $[M]^+$; found: 243.9512.

General procedure for the synthesis of 1-aryimidazo[1,5-*a*]pyridines

A flame dried and argon-flushed 2-neck flask equipped with refluxing condenser and dropping funnel was charged with 1-bromoimidazo[1,5-*a*]pyridine (1.0 equiv), Ni(dppe)Cl_2 (5.0 mol%) and anhydrous THF (0.50 M). The mixture was cooled to 0 ºC, and Grignard reagent (THF solution, 3.0 equiv) was added dropwise via dropping funnel. After the addition, the reaction mixture was stirred under reflux for indicated time and then cooled to room temperature. The reaction mixture was quenched with saturated NH_4Cl aq., extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, filtrated, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel to give 1-arylimidazo[1,5-*a*]pyridine.

1-(2-Methoxyphenyl)imidazo[1,5-*a*]pyridine (3a)

5.0 mmol scale; 0.46 M of (2-methoxyphenyl)magnesium bromide was used; Reflux for 20 h; Pinkish solid; 61% yield; R_f = 0.30 (*n*-hexane/EtOAc = 1/1); m.p. 155-158 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H, OMe), 6.56 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 6.70 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.02 (d, *J* = 8.3 Hz, 1H, Ar), 7.07 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 7.32 (dd, *J* = 8.3, 6.3 Hz, 1H, Ar), 7.55 (d, *J* = 9.3 Hz, 1H, Ar), 7.70 (d, *J* = 7.3 Hz, 1H, Ar), 7.90 (d, *J* = 7.3 Hz, 1H, Ar), 8.23 (s, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4 (OMe), 111.1, 112.8, 118.7, 120.4, 120.9, 122.1, 123.8, 127.4, 128.2, 131.1, 156.3 (Ar); IR (KBr) 3112, 3083, 3029, 2937, 2833, 1935, 1891, 1807, 1780, 1632, 1598, 1577, 1555, 1529, 1519, 1492, 1462, 1430, 1411, 1335, 1323, 1306, 1273, 1244, 1179, 1155, 1092, 1047, 1021, 1001, 970, 931, 913, 849, 837, 794, 779, 754, 741, 720, 689, 678, 614, 594, 571, 541, 516 cm^{-1}; MS (EI): *m/z* 224 $[M]^+$; HRMS (EI) *m/z* calcd for $C_{14}H_{12}N_2O$ 224.0950 $[M]^+$; found: 224.0955.

1-(4-Methoxyphenyl)imidazo[1,5-*a*]pyridine (3b)

1.7 mmol scale; 0.40 M of (4-methoxyphenyl)magnesium bromide was used; Reflux for 3 h; Yellow solid; 69% yield; R_f = 0.30 (*n*-hexane/EtOAc = 1/1); m.p. 100-101 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H, OMe), 6.58 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 6.75 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.01 (d, *J* = 8.8 Hz, 2H, Ar), 7.75 (d, *J* = 9.3 Hz, 1H, Ar), 7.81 (d, *J* = 8.8 Hz, 2H, Ar), 7.87 (d, *J* = 7.3 Hz, 1H, Ar), 8.23 (s, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3 (OMe), 112.9, 114.2, 118.9, 119.4, 122.4, 125.8, 127.1, 127.6, 131.3, 158.4 (Ar), A peak was not observed; IR (KBr) 3114, 3003, 2924, 2840, 1900, 1628, 1609, 1574, 1538, 1517, 1503, 1455, 1413, 1328, 1309, 1286, 1249, 1221, 1177, 1129, 1105, 1127, 1102, 971, 915, 836, 776, 751, 729, 679, 663, 634, 579, 531, 515 cm^{-1}; MS (EI): *m/z*: 224 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{14}H_{12}N_2O$ 224.0950 $[M]^+$; found 224.0947.

1-Phenylimidazo[1,5-*a*]pyridine (3c)

3.3 mmol scale; 0.70 M of phenylmagnesium bromide was used; Reflux for 1 h; Yellow solid; 62% yield; R_f = 0.50 (*n*-hexane/EtOAc = 1/1); m.p. 97-99 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 6.79 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.30 (dd, *J* = 7.8, 7.3 Hz, 1H, Ar), 7.47 (t, *J* = 7.8 Hz, 2H, Ar) 7.82 (d, *J* = 9.3 Hz, 1H, Ar), 7.89 (d, *J* = 7.3 Hz, 2H, Ar), 7.95 (d, *J* = 7.3 Hz, 1H, Ar), 8.21 (s, 1H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.0, 118.9, 120.0, 122.6, 126.42, 126.44, 127.5, 128.8 (2C), 131.4, 135.1

(Ar); IR (KBr): 3114, 3076, 3033, 1765, 1631, 1600, 1572, 1538, 1515, 1490, 1454, 1444, 1415, 1330, 1304, 1238, 1221, 1156, 1134, 1121, 1070, 1002, 964, 912, 829, 769, 755, 722, 700, 676, 614, 586, 566, 518 cm^{-1}; MS (EI): *m/z*: 194 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{13}H_{10}N_2$ 194.0844 $[M]^+$; found: 194.0822.

1-(4-Trifluoromethylphenyl)imidazo[1,5-*a*]pyridine (3d)

1.9 mmol scale; 0.20M of 4-trifluoromethylphenylmagnesium bromide and 10 mol% of Ni(dppp)Cl_2 was used; Reflux for 1 h; Pale yellow solid; 17% yield; R_f = 0.35 (*n*-hexane/EtOAc = 1/1); m.p. 109-112 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.62 (dd, *J* = 6.8, 6.1 Hz, 1H, Ar), 6.85 (dd, *J* = 9.5, 6.8 Hz, 1H, Ar), 7.67 (d, *J* = 8.1 Hz, 2H, Ar), 7.79 (d, *J* = 9.5 Hz, 1H, Ar), 7.95 (d, *J* = 6.1 Hz, 1H, Ar), 7.97 (d, *J* = 8.1Hz, 2H, Ar), 8.17 (s, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.3, 118.5, 121.2, 122.9, 124.4 (q, $^1J_{C–F}$ = 272.1 Hz, CF_3), 125.7 (q, $^3J_{C–F}$ = 3.3 Hz, *C*HCCF$_3$), 126.1, 127.3, 127.9 (Ar), 128.0 (q, $^2J_{C–F}$ = 33.1 Hz, *C*HCF$_3$), 129.7, 138.4 (Ar); ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.7; IR (KBr) 3099, 1615, 1525, 1504, 1459, 1409, 1325, 1247, 1187, 1165, 1101, 1067, 1006, 969, 915, 844,821, 803, 752, 738, 704, 676, 630, 593, 566 cm^{-1}; MS (EI): *m/z*: 262 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{14}H_9F_3N_2$ 262.0718, $[M]^+$; found 262.0717.

1-Pentafluorophenylimidazo[1,5-*a*]pyridine (3e)

A flame dried and argon-flushed 2-neck flask equipped with refluxing condenser and dropping funnel was charged with CuBr (1.2 g, 4.0 equiv) and anhydrous THF (4.0 mL). pentafluorophenylmagnesium bromide (0.45 M in Et_2O, 1.7 equiv) was added dropwise at room temperature and stirred for 1 h. The solution of 1-bromoimidazo[1,5-*a*]pyridine (390 mg, 2.0 mmol, 1.0 equiv) in anhydrous toluene (2.0 mL) and anhydrous 1,4-dioxane (2.0 mL) was added dropwise via dropping funnel to the reaction mixture. After the addition, the reaction mixture was stirred at 90 ºC for 12 h and then cooled to room temperature. The reaction mixture was quenched with saturated NH_4Cl aq, extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, filtrated, and concentrated *in vacuo*. The residue was purified by GPC to give 1-(pentafluorophenyl)imidazo[1,5-*a*]pyridine in 5.4% yield as a pale yellow solid. R_f = 0.35 (*n*-hexane/EtOAc = 1/1); m.p. 135-136 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (d, *J* = 6.8 Hz, 1H, Ar), 6.90 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.37 (d, *J* = 9.3 Hz, 1H, Ar), 8.01 (d, *J* = 6.8 Hz, 1H, Ar), 8.30 (s, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.8 (td, $J_{C–F}$ = 16.5,

4.1 Hz), 113.4, 116.9, 118.0 (t, J_{C-F} = 3.3 Hz), 121.4, 122.6, 128.6, 129.3, 137.9 (dm, J_{C-F} = 249.8 Hz), 140.3 (dm, J_{C-F} = 253.1 Hz), 144.52 (dm, J_{C-F} = 248.9 Hz) (Ar). ^{19}F NMR (376 MHz, $CDCl_3$) δ –162.8 (ddd, *J* = 22.9, 21.4, 7.6 Hz, 2F), –156.4 (t, *J* = 21.4 Hz, 1F), –141.3 (dd, *J* = 22.9, 7.6 Hz, 2F); IR (KBr) 3112, 2924, 2853, 1921, 1542, 1529, 1492, 1450, 1338, 1308, 1244, 1104, 1028, 1004, 980, 821, 804, 745, 733, 672, 426 cm^{-1}; MS (EI): *m/z*: 284 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{13}H_5F_5N_2$ 284.0373 $[M]^+$; found 284.0380.

1-(4-Methoxyphenyl)ethynyl) imidazo[1,5-*a*]pyridine (3f)

Prepared according to literature procedure.[S3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H, OMe), 6.67 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 6.83-6.92 (m, 3H, Ar), 7.53 (d, *J* = 8.8 Hz, 1H, Ar), 7.66 (d, *J* = 9.3 Hz, 1H, Ar), 7.96 (d, *J* = 7.3 Hz, 1H, Ar), 8.13 (s, 1H, Ar).

1-(Phenylethynyl)imidazo[1,5-*a*]pyridine (3g)

Prepared according to literature procedure.[S3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.63 (t, *J* = 6.6 Hz, 1H, Ar), 6.85 (dd, *J* = 9.0, 6.6 Hz, 1H, Ar), 7.30-7.38 (m, 3H, Ar), 7.58 (d, *J* = 8.3 Hz, 2H, Ar), 7.64 (d, *J* = 9.0 Hz, 1H, Ar), 7.92 (d, *J* = 7.0 Hz, 1H, Ar), 8.06 (s, 1H, Ar).

1-((4-Trifluoromethylphenyl)ethynyl)imidazo[1,5-*a*]pyridine (3h)

Prepared according to literature procedure.[S3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (dd, *J* = 6.8, 6.3 Hz, 1H, Ar), 6.96 (dd, *J* = 8.3, 6.3 Hz, 1H, Ar), 7.61 (d, *J* = 8.3 Hz, 2H, Ar), 7.66-7.71 (dm 3H, Ar), 8.02 (d, *J* = 6.8 Hz, 1H, Ar), 8.23 (s, 1H, Ar).

1-((Pentafluorophenyl)ethynyl)imidazo[1,5-*a*]pyridine (3i)

To a solution of 1-iodoimidazo[1,5-*a*]pyridine (240 mg, 1.0 mmol, 1.0 equiv), $Pd(PPh_3)Cl_2$ (70 mg, 0.10 mmol, 10 mol%), CuI (19 mg, 0.10 mmol, 10 mol%) and 1-ethynyl-2,3,4,5,6-pentafluorobenzene (250 mg, 1.3 equiv) in Et_3N (3.0 mL) under argon atmosphere was stirred at 80 ºC for 20 h. The reaction mixture was concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (*n*-hexane/EtOAc = 2/1) to give 1-((pentafluorophenyl)ethynyl)imidazo[1,5-*a*]pyridine in 73% yield as a yellow solid. R_f = 0.35 (*n*-hexane/EtOAc = 1/1); m.p. 176-179 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (dd, *J* = 7.1, 6.6 Hz, 1H; Ar), 6.99 (dd, *J* = 9.3, 6.6 Hz, 1H; Ar), 7.66 (d, *J* = 9.3 Hz, 1H; Ar), 8.01 (d, *J* = 7.1 Hz, 1H; Ar), 8.15 (s, 1H; Ar). ^{13}C NMR (100 MHz, $CDCl_3$) δ 76.3 (q, J_{C-F} = 4.1 Hz, CC), 95.3 (q, J_{C-F} = 3.3 Hz, CC), 100.7

(td, J_{C-F} = 18.2, 4.1 Hz), 112.8, 114.1, 118.1, 122.4, 123.0, 128.2, 134.4, 137.4 (dm, J_{C-F} = 250.6 Hz), 141.0 (dm, J_{C-F} = 256.4 Hz), 146.5 ppm (dm, J_{C-F} = 253.1 Hz) (Ar); ^{19}F NMR (376 MHz, $CDCl_3$) δ –158.5 (m, 2F), –150.2 (t, *J*=20.6 Hz, 1F), –132.7 ppm (m, 2F); IR (KBr) 3104, 2924, 2854, 2360, 2239, 2211, 1632, 1570, 1537, 1508, 1496, 1467, 1442, 1358, 1338, 1299, 1237, 1134, 1062, 1031, 984, 957, 915, 784, 755, 701, 666, 596, 571, 523 cm^{-1}; MS (EI): *m/z*: 308 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{15}H_5F_5N_2$ 308.0373 $[M]^+$; found 308.0380.

General procedure for the synthesis of imidazo[1,5-*a*]pyridinium salts

To a solution of a 1-substitutedimidazo[1,5-*a*]pyridine (1.0 equiv) in anhydrous THF (1.0 M) was added MeI (5.0 equiv) at room temperature under an Ar atmosphere and the mixture was stirred under reflux for overnight. Then the reaction mixture was cooled to room temperature. To this was added Et_2O (2.0 mL) and stirred at 0 ºC. The precipitate formed was filtered, washed with cold Et_2O and dried *in vacuo* to afford an imidazo[1,5-*a*]pyridinium salt.

1-(2-Methoxyphenyl)-2-methylimidazo[1,5-*a*]pyridinium iodide (4a)

1.0 mmol scale; Colorless powder; 88% yield; R_f = 0.35 (CH_2Cl_2/MeOH = 10/1); mp 220-221 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H, OMe), 4.07 (s, 3H, NMe), 7.03 (t, *J* = 6.8 Hz, 1H, Ar), 7.11 (m, 2H, Ar), 7.15 (dd, *J* = 7.3, 1.0 Hz, 1H, Ar), 7.32 (d, *J* = 7.8 Hz, 2H, Ar), 7.60 (dd, *J* = 7.3, 2.0 Hz, 1H, Ar), 8.96 (d, *J* = 6.8 Hz, 1H, Ar) 11.17 (s, 1H, Ar); ^{13}C NMR (100 MHz, DMSO-d_6) δ 35.2 (NMe), 55.8 (OMe), 112.4, 112.8, 117.7, 117.8, 121.2, 121.8, 124.3, 124.9, 127.1, 127.3, 132.7, 132.9, 157.7 (Ar); IR (KBr) 3050, 3003, 2925, 2850, 1650, 1604, 1582, 1545, 1493, 1469, 1443, 1406, 1326, 1277, 1246, 1191, 1164, 1145, 1115, 1052, 1015, 945, 837, 780, 760, 742, 725, 694, 655, 573, 557, 530 cm^{-1}; MS (FAB): *m/z*: 239 $[M–I]^+$; HRMS (FAB): *m/z* calcd for $C_{15}H_{15}N_2O$ 239.1179 $[M–I]^+$; found 239.1181.

1-(4-Methoxyphenyl)-2-methylimidazo[1,5-*a*]pyridinium iodide (4b)

0.50 mmol scale; Colorless powder; 94% yield; R_f = 0.30 (CH_2Cl_2/MeOH = 10/1); m.p. 173-174 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3H, OMe), 4.20 (s, 3H, NMe), 7.07 (dd, *J* = 7.3, 6.8 Hz, 1H, Ar), 7.13 (d, *J* = 8.8 Hz, 2H, Ar), 7.14 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.42 (d, *J* = 8.8 Hz, 2H, Ar), 7.47 (d, *J* = 9.3 Hz, 1H, Ar), 8.93 (d, *J* = 7.3 Hz, 1H, Ar),

11.16 (s, 1H, Ar); ^{13}C NMR (100 MHz, DMSO-d_6) δ 35.3 (NMe), 55.5 (OMe), 114.9, 116.6, 117.6, 117.7, 124.1, 124.5, 124.7, 126.5, 126.6, 131.8, 160.6 (Ar); IR (KBr) 3156, 3006, 2956, 2931, 2831, 1646, 1609, 1577, 1550, 1510, 1462, 1444, 1428, 1395, 1358, 1333, 1308, 1293, 1243, 1217, 1180, 1119, 1041, 1017, 941, 864, 844, 814, 795, 763, 727, 682, 649, 625, 584, 568, 516 cm^{-1}; MS (FAB): *m/z*: 239 [*M*–I]$^+$; HRMS (FAB): *m/z* calcd for $C_{15}H_{15}N_2O$ 239.1179 [*M*–I]$^+$; found 239.1174.

2-Methyl-1-phenylimidazo[1,5-*a*]pyridinium iodide (4c)

0.50 mmol scale; Hygroscopic brownish solid; 90% yield; R_f = 0.30 (CH_2Cl_2/MeOH = 10/1); m.p. 84-86 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.09 (s, 3H, NMe), 7.22-7.30 (m, 2H, Ar), 7.63-7.72 (m, 6H, Ar), 8.67 (d, *J* = 6.8 Hz, 1H, Ar), 9.84 ppm (s, 1H, Ar); ^{13}C NMR (100 MHz, DMSO-d_6) δ 35.5 (NMe), 117.5, 117.8, 124.2, 124.4, 124.7, 125.2, 126.7, 127.1, 129.4, 130.2 ppm (Ar); IR (KBr) 3106, 3020, 2998, 2958, 1950, 1650, 1551, 1508, 1489, 1440, 1412, 1331, 1289, 1243, 1194, 1158, 1114, 1064, 1026, 1001, 956, 922, 789, 749, 691, 632, 585, 553, 524 cm^{-1}; MS (FAB): *m/z*: 209 [*M*–I]$^+$; HRMS (FAB): *m/z* calcd for $C_{14}H_{13}N_2$ 209.1073 [*M*–I]$^+$; found 209.1088.

2-Methyl-1-(4-(trifluoromethyl)phenyl)imidazo[1,5-*a*]pyridinium iodide (4d)

0.76 mmol scale, Off-white powder; 84% yield; R_f = 0.20 (CH_2Cl_2/MeOH = 10/1); m.p. 173-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 (s, 3H, NMe), 7.14 (dd, *J* = 7.1, 6.6 Hz, 1H, Ar), 7.25 (dd, *J* = 9.3, 6.6 Hz, 1H, Ar), 7.50 (d, *J* = 9.3 Hz, 1H, Ar), 7.72 (d, *J* = 8.1 Hz, 2H, Ar), 7.91 (d, *J* = 8.1 Hz, 2H, Ar), 9.00 (d, *J* = 7.1 Hz, 1H, Ar), 11.26 (s, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.7 (NMe), 116.9, 118.0, 123.4 (Ar), 123.4 (q, $^1J_{C–F}$ = 272.9 Hz, CF_3), 124.4, 126.0 (Ar), 126.7 (q, $^3J_{C–F}$ = 3.3 Hz, *C*HCCF$_3$), 127.6, 127.91, 127.93, 131.1 (Ar), 132.6 (q, $^2J_{C–F}$ = 33.1 Hz, *C*HCF$_3$). ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.5; IR (KBr) 3114, 3048, 2352, 1651, 1615, 1550, 1507, 1456, 1413, 1325, 1222, 1195, 1168, 1124, 1069, 1035, 1014, 955, 850, 786, 762, 742, 707, 651, 609, 581, 560, 531, 513 cm^{-1}; MS (FAB): *m/z*: 277 [*M*–I]$^+$; HRMS (FAB): *m/z* calcd for $C_{15}H_{12}F_3N_2$ 277.0947 [*M*–I]$^+$; Found 277.0939.

2-Methyl-1-(pentafluorophenyl)imidazo[1,5-*a*]pyridinium iodide (4e)

0.4 mmol scale; Brownish powder; 82% yield; R_f = 0.40 (CH_2Cl_2/MeOH = 10/1); m.p. 117-118 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.27 (s, 3H, NMe), 7.22-7.26 (m, 1H, Ar),

7.38-7.39 (m, 2H, Ar), 9.19 (d, J = 7.3, 1H, Ar), 11.68 (s, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.8 (NMe), 99.6 (td, $J_{C–F}$ = 17.4, 4.1 Hz), 109.2, 116.5, 118.2, 125.0, 127.5, 129.4, 129.7, 138.3 (dm, $J_{C–F}$ = 258.9 Hz), 143.6 (dm, $J_{C–F}$ = 261.3 Hz), 145.0 (dm, $J_{C–F}$ = 253.0 Hz) (Ar); ^{19}F NMR (376 MHz, $CDCl_3$) δ –153.4 (m, 2F), –141.3 (t, J = 21.4 Hz, 1F), –131.7 (m, 2F); IR (KBr) 3116, 3077, 3035, 3000, 1664, 1577, 1555, 1525, 1497, 1470, 1310, 1269, 1184, 1152, 1069, 1043, 987, 953, 876, 822, 769, 748, 649, 624, 426 cm^{-1}; MS (FAB): *m/z*: 299 [*M*–I]$^+$; HRMS (FAB): *m/z* calcd for $C_{14}H_8F_5N_2$ 299.0602 [*M*–I]$^+$; found 299.0596.

1-((4-Methoxyphenyl)ethynyl)-2-methylimidazo[1,5-*a*]pyridinium iodide (4f)

0.79 mmol scale, Brownish yellow powder; 70% yield; R_f = 0.20 (CH_2Cl_2/MeOH = 10/1); m.p. 218-220 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (s, 3H, OMe), 4.34 (s, 3H, NMe), 6.96 (d, J = 9.0 Hz, 2H, Ar), 7.14 (dd, J = 7.2, 6.7 Hz, 1H, Ar), 7.31 (dd, J = 9.4, 6.7 Hz, 1H, Ar), 7.56 (d, J = 9.0 Hz, 2H, Ar), 7.73 (d, J = 9.4 Hz, 1H, Ar), 9.09 (d, J = 7.2 Hz, 1H, Ar), 11.26 (s, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.0 (OMe), 55.5 (NMe), 70.9 (CC), 103.7 (CC), 109.5, 111.9, 114.5, 117.6, 118.3, 125.1, 126.3, 127.2, 131.1, 133.7, 162.3 (Ar); IR (KBr) 3111, 3030, 3000, 2960, 2545, 2360, 2217, 1651, 1603, 1553, 1509, 1464, 1442, 1416, 1371, 1333, 1288, 1253, 1198, 1173, 1142, 1115, 1023, 955, 876, 835, 799, 761, 634, 583, 548, 530, 512 cm^{-1}; MS (FAB): *m/z*: 263 [*M*–I]$^+$; HRMS (FAB): *m/z* calcd for $C_{17}H_{15}N_2O$ 263.1179 [*M*–I]$^+$; found 263.1179.

2-Methyl-1-(phenylethynyl)imidazo[1,5-*a*]pyridinium iodide (4g)

1.3 mmol scale; Brownish yellow powder; 82% yield; R_f = 0.20 (CH_2Cl_2/MeOH = 10/1); m.p. 219-221 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.21 (s, 3H, NMe), 7.31 (t, J = 6.8 Hz, 1H, Ar), 7.47 (dd, J = 9.3, 6.8 Hz, 1H, Ar), 7.51-7.54 (m, 3H, Ar), 7.75-7.77 (m, 2H, Ar), 8.04 (d, J = 9.3 Hz, 1H, Ar), 8.73 (d, J = 6.8 Hz, 1H, Ar), 9.81 (s, 1H, Ar); ^{13}C NMR (100 MHz, DMSO-d_6) δ 35.6 (NMe), 73.6, (CC), 101.6 (CC), 107.8, 117.6, 118.3, 120.5, 125.4, 127.1, 128.2, 129.1, 130.3, 131.5, 131.7 (Ar); IR (KBr) 3106, 3021, 2998, 2958, 1950, 1650, 1551, 1508, 1489, 1440, 1412, 2331, 1289, 1243, 1194, 1158, 1141, 1114, 1068, 1026, 100, 955, 922, 789, 749, 691, 633, 585, 553, 524 cm^{-1}; MS (FAB): *m/z*: 233 [*M*–I]$^+$; HRMS (FAB): *m/z* calcd for $C_{16}H_{13}N_2$ 233.1073 [*M*–I]$^+$; found 233.1071.

2-Methyl-1-((4-trifluoromethylphenyl)ethynyl)imidazo[1,5-*a*]pyridinium iodide (4h)

1.0 mmol scale; Brownish yellow powder; 91% yield; R_f = 0.20 (CH_2Cl_2/MeOH = 10/1); m.p. 227-228 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.39 (s, 3H, NMe), 7.20 (dd, *J* = 7.3, 6.8 Hz, 1H, Ar), 7.39 (dd, *J* = 9.3, 6.8 Hz, 1H, Ar), 7.71-7.78 (m, 5H, Ar), 9.14 (d, *J* = 7.3 Hz, 1H, Ar), 11.35 (s, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.7 (NMe), 76.1, 100.1 (CC), 107.2, 117.6, 118.4 (Ar), 124.0 (q, $^1J_{C–F}$ = 272.1 Hz, CF_3), 124.9, 125.6 (Ar), 125.9 (q, $^3J_{C–F}$ = 3.3 Hz, *C*HCCF_3), 127.6, 128.7(Ar), 129.7 (q, $^2J_{C–F}$ = 32.3 Hz, *C*CF_3), 132.1, 132.3 (Ar); ^{19}F NMR (376 MHz, $CDCl_3$) δ –59.4; IR (KBr) 3122, 3063, 3033, 2360, 2216, 1928, 1652, 1610, 1552, 1505, 1460, 1439, 1405, 1391, 1320, 1284, 1173, 1127, 1108, 1062, 1014, 994, 957, 876, 842, 833, 748, 688, 624, 593, 546, 518 cm^{-1}; MS (FAB): *m/z*: 301 [*M*–I]$^+$; HRMS (FAB): *m/z* calcd for $C_{17}H_{12}F_3N_2$ 301.0947 [*M*–I]$^+$; found 301.0939.

2-Methyl-1-((pentafluorophenyl)ethynyl)imidazo[1,5-*a*]pyridinium iodide (4i)

0.50 mmol scale; Yellow powder; 90% yield; R_f = 0.15 (CH_2Cl_2/MeOH = 10/1); m.p. 183-185 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.38 (s, 3H, NMe), 7.24 (dd, *J* = 7.3, 6.8 Hz, 1H, Ar), 7.46 (dd, *J* = 9.3, 6.8 Hz, 1H, Ar), 7.77 (d, *J* = 9.3 Hz, 1H, Ar), 9.23 (d, *J* = 7.3 Hz, 1H, Ar), 11.52 (s, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.6 (NMe), 83.9 (CC), 86.9 (CC), 98.0 (td, $J_{C–F}$ = 17.9, 3.8 Hz), 106.9, 116.9, 118.5, 125.7, 128.1, 128.7, 131.8 (dd, $J_{C–F}$ = 280.0, 13.2 Hz), 132.5, 137.7 (dm, $J_{C–F}$ = 257.5 Hz), 142.6 (dm, $J_{C–F}$ = 261.2 Hz), 146.8 (dm, $J_{C–F}$ = 255.6 Hz) (Ar); ^{19}F NMR (376 MHz, $CDCl_3$) δ –155.8 (m, 2F), –143.9 (t, *J*=20.6 Hz, 1F), –130.6 (m, 2F); IR (KBr) 3114, 3026, 2219, 1646, 1556, 1522, 1497, 1444, 1399, 1362, 1331, 1273, 1187, 1147, 1132, 1106, 11341, 986, 939, 867, 786, 761, 712, 629, 565 cm^{-1}; MS (FAB): *m/z*: 323 [*M*–I]$^+$; HRMS (FAB) : *m/z* calcd for $C_{16}H_8F_5N_2$ 323,0602 [*M*–I]$^+$; found 323.0608.

1,2-Diphenylimidazo[1,5-*a*]pyridinium tetrafluoroborate (4j)

A screw-capped reaction tube was charged with 1-phenylimidazo[1,5-*a*]pyridine (97 mg, 0.50 mmol, 1.0 equiv), diphenyliodonium tetrafluoroborate (280 mg, 0.75 mmol, 1.5 equiv), $Cu(OAc)_2 \cdot H_2O$ (4.9 mg, 0.025 mmol, 5.0 mol%) and anhydrous DMF (2 mL). The resulting mixture was stirred at 100 ºC for 4 h. After cooled down to room temperature, the solvent was removed *in vacuo*. The residue was purified by flash column chromatography on silica gel to give 1,2-diphenylimidazo[1,5-*a*]pyridinium

tetrafluoroborate in 85% yield as a brownish yellow solid. R_f = 0.20 (CH_2Cl_2/acetone = 5/1); m.p. 229-231 ºC; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.33-7.40 (m, 4H, Ar), 7.46-7.49 (m, 3H, Ar), 7.54-7.63 (m, 5H, Ar), 7.83 (d, *J* = 9.3 Hz, 1H, Ar), 8.65 (d, *J* = 7.8 Hz, 1H, Ar), 10.19 (s, 1H, Ar); ^{13}C NMR (100 MHz, DMSO-d_6) δ 117.9, 118.6, 124.1, 124.4, 124.8, 125.7, 126.7, 126.9, 127.6, 129.1, 129.8, 129.9, 130.2, 130.8, 133.9 (Ar); IR (KBr) 3141, 3086, 1654, 1595, 1547, 1500, 1063, 770, 700 cm^{-1}; MS (FAB): *m/z*: 271 [*M*–BF_4]$^+$; HRMS (FAB): *m/z* calcd for $C_{19}H_{15}N_2$ 271.1230 [*M*–BF_4]$^+$; found 271.1237.

General procedure for the synthesis of Ag(L)I complexes

To a solution of imidazo[1,5-*a*]pyridinium salt (1.0 equiv) in anhydrous CH_2Cl_2 (0.10 M) was added Ag_2O (0.90 equiv) at room temperature under an argon atmosphere and the mixture was stirred in darkness at room temperature for 2 h. Then the reaction mixture was filtrated and filtrate or residue was concentrated/dried *in vacuo*. At this point, formation of Ag(L)I complex (L = NHC) was comfirmed by ^{1}H NMR, The product was used for next reaction without further purification.

Iodo(1-(2-methoxyphenyl)-2-methylimidazo[1,5-*a*]pyridin-3-ylidene)silver (I) (S1a)

Soluble in CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H, OMe), 3.92 (s, 3H, NMe), 6.67 (dd, *J* = 7.1, 6.3 Hz, 1H, Ar), 6.82 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.08 (d, *J* = 8.3, 1H, Ar), 7.12 (t, *J* = 7.3 Hz, 1H, Ar), 7.14 (d, *J* = 9.3 Hz, 1H, Ar), 7.29 (d, *J* = 7.3 Hz, 1H, Ar), 7.53 (dd, *J* = 8.3, 7.3 Hz, 1H, Ar), 8.25 (d, *J* = 7.1 Hz, 1H, Ar). Other characteritic data were not collected due to low solubility.

Iodo(1-(4-methoxyphenyl)-2-methylimidazo[1,5-*a*]pyridin-3-ylidene)silver (I) (S1b)

Soluble in CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (s, 3H, OMe), 4.06 (s, 3H, NMe), 6.61 (dd, *J* = 7.1, 6.3 Hz, 1H, Ar), 6.79 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.05 (d, *J* = 8.8 Hz, 2H, Ar), 7.19 (d, *J* = 9.3 Hz, 1H, Ar), 7.33 (d, *J* = 8.8 Hz, 2H, Ar), 8.50 (d, *J* = 7.1 Hz, 1H, Ar). Other characteritic data were not collected due to low solubility.

Iodo(2-methyl-1-phenylimidazo[1,5-*a*]pyridin-3-ylidene)silver (I) (S1c)

Soluble in CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.03 (s, 3H, NMe), 6.56 (t, *J* = 7.8 Hz, 1H, Ar), 6.76 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.17 (d, *J* = 9.3 Hz, 1H, Ar), 7.35 (d, *J* = 6.8 Hz, 2H, Ar), 7.42-7.49 (m, 3H, Ar), 8.44 (d, *J* = 6.8, 1H, Ar). Other characteritic data

were not collected due to low solubulity.

Iodo(2-methyl-1-(4-(trifluoromethyl)phenyl)imidazo[1,5-*a*]pyridin-3-ylidene)silver (I) (S1d)

Insoluble in CH_2Cl_2. ^1H NMR (400 MHz, $CDCl_3$) δ 4.00 (s, 3H, NMe), 6.69 (dd, *J* = 7.2, 6.3 Hz, 1H, Ar), 6.90 (dd, *J* = 9.4, 6.3 Hz, 1H, Ar), 7.22 (d, *J* = 9.4 Hz, 1H, Ar), 7.52 (d, *J* = 8.1 Hz, 2H, Ar), 7.77 (d, *J* = 8.1 Hz, 2H, Ar), 8.22 (d, *J* = 7.1 Hz, 1H, Ar). Other characteritic data were not collected due to low solubulity.

Iodo(2-methyl-1-(pentafluorphenyl)imidazo[1,5-*a*]pyridin-3-ylidene)silver (I) (S1e)

Soluble in CH_2Cl_2. ^1H NMR (400 MHz, $CDCl_3$) δ 4.08 (s, 3H, NMe), 6.81 (dd, *J* = 7.3, 5.9 Hz, 1H, Ar), 7.05 (dd, *J* = 9.3, 5.9 Hz, 1H; Ar), 7.10 (d, *J* = 9.3 Hz, 1H, Ar), 8.69 (d, *J* = 7.3 Hz, 1H, Ar). Other characteritic data were not collected due to low solubulity.

Iodo(1-((4-methoxyphenyl)ethynyl)-2-methylimidazo[1,5-*a*]pyridin-3-ylidene)silver (I) (S1f)

Insoluble in CH_2Cl_2. ^1H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H, OMe), 4.16 (s, 3H, NMe), 6.76 (t, *J* = 7.3 Hz, 1H, Ar), 6.94 (d, *J* = 8.8 Hz, 2H, Ar), 7.03 (dd, *J* = 9.3, 6.8 Hz, 1H, Ar), 7.50 (d, *J* = 8.8 Hz, 2H, Ar), 7.51 (t, *J* = 9.3 Hz, 1H, Ar), 8.30 (d, *J* = 7.3 Hz, 1H, Ar). Other characteritic data were not collected due to low solubulity.

Iodo(2-methyl-1-(phenylethnyl)imidazo[1,5-*a*]pyridin-3-ylidene)silver (I) (S1g)

Insoluble in CH_2Cl_2. ^1H NMR (400 MHz, $CDCl_3$) δ 4.18 (s, 3H, NMe), 6.79 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 7.07 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.42-7.43 (m, 3H, Ar), 7.52-7.58 (m, 3H, Ar), 8.33 (d, *J* = 7.3 Hz, 1H, Ar). Other characteritic data were not collected due to low solubulity.

Iodo(2-methyl-1-((4-(trifluoromethyl)phenyl)ethynyl)imidazo[1,5-*a*]pyridin-3-yliden e)silver (I) (S1h)

Insoluble in CH_2Cl_2. ^1H NMR (400 MHz, $CDCl_3$) δ 4.20 (s, 3H, NMe), 6.83 (dd, *J* = 7.3, 6.3 Hz, 1H), 7.13 (dd, *J* = 9.3, 6.3 Hz, 1H), 7.56 (d, *J* = 9.3 Hz, 1H, Ar), 7.67 (s, 4H, Ar), 8.36 (br s, 1H, Ar). Other characteritic data were not collected due to low solubulity.

Iodo(2-methyl-1-((pentafluorophenyl)ethynyl)imidazo[1,5-*a*]pyridin-3-ylidene)silver (I) (S1i)

Insoluble in CH_2Cl_2. ^1H NMR (400 MHz, $CDCl_3$) δ 4.19 (s, 3H, NMe), 6.89 (dd, *J* = 7.2, 6.7 Hz, 1H, Ar), 7.21 (dd, *J* = 9.0, 6.7 Hz, 1H, Ar), 7.58 (d, *J* = 9.0 Hz, 1H, Ar), 8.38 (d, *J* = 7.2 Hz, 1H, Ar). Other characteritic data were not collected due to low solubulity.

General procedure for the synthesis of Rh(cod)(L)Cl complexes

To a solution or slurry of Ag(L)I (L = NHC) in anhyrous CH_2Cl_2 (0.25 M) was added $[Rh(cod)Cl]_2$ (0.50 equiv) at room temperature under an argon atmosphere and the mixture was stirred in darkness at room temperature for 4 h. The reaction mixture was filtrated through celite plug and filtrate was evaporated *in vacuo*. The residue was purified by flash column chromatography on silica gel to give Rh(cod)(L)Cl complexes.

Chloro(1,5-cyclooctadiene)(1-(2-methoxyphenyl)-2-methylimidazo[1,5-*a*]pyridin-3-ylidene)rhodium (I) (5a)

0.20 mmol scale, Yellow solid; 85% yield (over 2 steps); R_f = 0.38 (*n*-hexane/EtOAc = 2/1); m.p. 106-110 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 1.96-2.04 (m, 4H, CH_2(cod)), 2.39-2.54 (m, 4H, CH_2(cod)), 3.36-3.44 (m, 2H, CH(cod)), 3.81 (s, 3H, OMe), 4.14 (s, 3H, NMe), 5.09-5.13 (m, 2H, CH(cod)), 6.53 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 6.65 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 6.95 (d, *J* = 9.27 Hz, 1H, Ar), 7.02 (d, *J* = 8.3 Hz, 1H, Ar), 7.06 (t, *J* = 7.3 Hz, 1H, Ar), 7.26 (d, *J* = 7.3 Hz, 1H, Ar), 7.45 (t, *J* = 8.3 Hz, 1H, Ar), 8.91 (d, *J* = 7.3 Hz, 1H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.8 (CH_2(cod)), 29.2 (CH_2(cod)), 32.8 (CH_2(cod)), 33.3 (CH_2(cod)), 36.9 (NMe), 55.4 (OMe), 68.2 (d, $^1J_{C-Rh}$ = 14.9 Hz, CH(cod)), 68.7 (d, $^1J_{C-Rh}$ = 14.1 Hz, CH(cod)), 98.8 (d, $^1J_{C-Rh}$ = 6.6 Hz, CH(cod)), 99.2 (d, $^1J_{C-Rh}$ =6.6 Hz, CH(cod)), 111.0, 112.4, 116.6, 117.3, 121.0, 121.6, 128.2, 129.2, 131.0, 132.1, 132.4, 157.7 (Ar), 172.2 (d, $^1J_{C-Rh}$ = 52.9 Hz, N_2C); IR (KBr) 2933, 2875, 2829, 1493, 1462, 1342, 1246, 1020, 753, 729 cm^{-1}; MS (FAB): *m/z*: 484 $[M]^+$; HRMS (FAB): *m/z* calcd for $C_{23}H_{26}ClN_2ORh$ 484.0789 $[M]^+$; found 484.0779.

Chloro(1,5-cyclooctadiene)(1-(4-methoxyphenyl)-2-methylimidazo[1,5-*a*]pyridin-3-ylidene)rhodium (I) (5b)

0.20 mmol scale, Yellow solid; 74% yield (over 2 steps); R_f = 0.43 (*n*-hexane/EtOAc, 2:1); m.p. 148-155 ºC (decomposed); ^1H NMR (400 MHz, $CDCl_3$) δ 1.95-2.06 (m, 4H,

CH_2(cod)), 2.39-2.53 (m, 4H, CH_2(cod)), 3.35-3.42 (m, 2H, CH(cod)), 3.88 (s, 3H, OMe), 4.26 (s, 3H, NMe), 5.09-5.19 (m, 2H, CH(cod)), 6.54 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 6.68 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.02 (d, *J* = 8.8 Hz, 2H, Ar), 7.06 (d, *J* = 9.3 Hz, 1H, Ar), 7.30 (d, *J* = 8.8 Hz, 2H, Ar), 8.91 (d, *J* = 7.3 Hz, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.8 (CH_2(cod)), 29.2 (CH_2(cod)), 32.8 (CH_2(cod)), 33.2 (CH_2(cod)), 37.2 (NMe), 55.4 (OMe), 68.2 (d, $^1J_{C–Rh}$ = 14.9 Hz, CH(cod)), 68.6 (d, $^1J_{C–Rh}$ = 14.9 Hz, CH(cod)), 99.0 (d, $^1J_{C–Rh}$ = 6.6 Hz, CH(cod)), 99.3 (d, $^1J_{C–Rh}$ = 7.4 Hz, CH(cod)), 112.7, 114.5, 117.3, 120.1, 121.8, 124.3, 128.2, 128.7, 131.1, 159.9, 172.5 (d, $^1J_{C–Rh}$ = 52.1 Hz, N_2C); IR (KBr) 2931, 2874, 2830, 1610, 1512, 1343, 1288, 1249, 1177, 1024, 833, 747 cm^{-1}; MS (FAB): *m/z*: 484 $[M]^+$; HRMS (FAB): *m/z* calcd for $C_{23}H_{26}ClN_2ORh$ 484.0789 $[M]^+$; found 484.0788.

Chloro(1,5-cyclooctadiene)(2-methyl-1-phenylimidazo[1,5-*a*]pyridin-3-ylidene)rhodium (I) (5c)

0.20 mmol scale; Yellow solid; quantitative yield (over 2 steps); R_f = 0.25 (*n*-hexane/EtOAc = 2/1); m.p. 157-162 ºC (decomposed); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.92-1.97 (m, 4H, CH_2(cod)), 2.35-2.46 (m, 4H, CH_2(cod)), 3.29-3.34 (m, 2H, CH(cod)), 4.24 (s, 3H, NMe), 5.05-5.10 (m, 2H, CH(cod)), 6.50 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 6.65 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.05 (d, *J* = 9.3 Hz, 1H, Ar), 7.32 (d, *J* = 7.3 Hz, 2H, Ar), 7.38 (t, *J* = 7.3 Hz, 1H, Ar), 7.44 (t, *J* = 7.3 Hz, 2H, Ar), 8.88 (d, *J* = 7.3 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.9 (CH_2(cod)), 29.3 (CH_2(cod)), 33.0 (CH_2(cod)), 33.3 (CH_2(cod)), 37.5 (NMe), 68.4 (d, $^1J_{C–Rh}$ = 14.1 Hz, CH(cod)), 68.8 (d, $^1J_{C–Rh}$ = 15.1 Hz, CH(cod)), 99.3 (d, $^1J_{C–Rh}$ = 6.5 Hz, CH(cod)), 99.6 (d, $^1J_{C–Rh}$ = 7.5 Hz, CH(cod)), 112.9, 117.3, 122.4, 124.5, 128.1, 128.5, 128.8, 129.0, 129.1, 129.7 (Ar), 173.4 (d, $^1J_{C–Rh}$ = 51.7 Hz, N_2C); IR (KBr) 2990, 2930, 2876, 2832, 1646, 1457, 1373, 1345, 1311, 1254, 949, 761, 751, 704 cm^{-1}; MS (FAB): *m/z*: 454 $[M]^+$; HRMS (FAB): *m/z* calcd for $C_{22}H_{24}ClN_2Rh$ 454.0683 $[M]^+$ Found 454.0679.

Chloro(1,5-cyclooctadiene)(2-methyl-1-(4-(trifluoromethyl)phenyl)imidazo[1,5-*a*]pyridin-3-ylidene)rhodium (I) (5d)

0.10 mmol scale; Pale yellow solid; 85% yield (over 2 steps); R_f = 0.20 (*n*-Hexane/EtOAc = 2/1); m.p. 174-178 ºC (decomposed); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.97-2.09 (m, 4H, CH_2(cod)), 2.40-2.54 (m, 4H, CH_2(cod)), 3.34-3.44 (m, 2H, CH(cod)),

4.35 (s, 3H, NMe), 5.12-5.21 (m, 2H, CH(cod)), 6.63 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 6.81 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.13 (d, *J* = 9.3 Hz, 1H, Ar), 7.39 (d, *J* = 8.3 Hz, 2H, Ar), 7.65 (d, *J* = 8.3 Hz, 2H, Ar), 8.38 (d, *J* = 7.3 Hz, 1H, Ar), 9.01 (s, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.8 (CH_2(cod)), 29.1 (CH_2(cod)), 32.8 (CH_2(cod)), 33.2 (CH_2(cod)), 37.5 (NMe), 68.4 (d, $^1J_{C–Rh}$ = 14.9 Hz, CH(cod)), 68.9 (d, $^1J_{C–Rh}$ = 14.9 Hz, CH(cod)), 99.6 (d, $^1J_{C–Rh}$ = 6.6 Hz, CH(cod)), 99.8 (d, $^1J_{C–Rh}$ = 7.4 Hz, CH(cod)), 113.1, 116.6, 122.8, 123.4, 123.8 (q, $^1J_{C–F}$ = 272.1 Hz, CF_3), 126.1 (q, $^3J_{C–F}$ = 3.3 Hz; *C*HCCF_3), 128.6, 129.4, 129.6, 130.4 (q, $^2J_{C–F}$ =33.1 Hz, *C*CF_3), 131.7, 175.0 (d, $^1J_{C–Rh}$ = 52.1 Hz, N_2C); ^{19}F NMR (376 MHz, $CDCl_3$) δ –59.1; IR (KBr) 2992, 2935, 2912, 2878, 2830, 1614, 1520, 1321, 1253, 1178, 1107, 1069, 843, 750, 740, 617 cm^{-1}; MS (FAB): *m/z*: 522 [*M*]$^+$; HRMS (FAB): *m/z* calcd for $C_{23}H_{23}ClF_3N_2Rh$ 522.0557 [*M*]$^+$; found 522.0552.

Chloro(1,5-cyclooctadiene)(2-methyl-1-(pentafluorophenyl))imidazo[1,5-*a*]pyridin-3-ylidene)rhodium (I) (5e)

0.089 mmol scale; Yellow solid; 79% yield (over 2 steps); R_f = 0.58 (*n*-hexane/EtOAc = 1/1); m.p. 159-164 ºC (decomposed); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.97-2.09 (m, 4H, CH_2(cod)), 2.44-2.54 (m, 4H, CH_2(cod)), 3.32-3.42 (m, 2H, CH(cod)), 4.27 (s, 3H, NMe), 5.13-5.24 (m, 2H, CH(cod)), 6.71 (dd, *J* = 7.3, 5.9 Hz, 1H, Ar), 6.93-6.94 (m, 2H, Ar), 9.07 (d, *J* = 7.3 Hz, 1H; Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.8 (CH_2(cod)), 29.1 (CH_2(cod)), 32.8 (CH_2(cod)), 33.1 (CH_2(cod)), 37.2 (NMe), 68.7 (d, $^1J_{C–Rh}$ = 14.1 Hz, CH(cod)), 69.0 (d, $^1J_{C–Rh}$ = 14.1 Hz, CH(cod)), 100.0 (d, $^1J_{C–Rh}$ = 6.6 Hz, CH(cod)), 100.1 (d, $^1J_{C–Rh}$ = 6.6 Hz, CH(cod)), 103.3 (td, $J_{C–F}$ = 18.2, 4.1 Hz), 108.0, 113.1, 116.3, 124.6, 129.1, 131.1, 138.0 (dm, $^1J_{C–F}$ = 253.9 Hz), 142.1 (dm, $^1J_{C–F}$ = 253.1 Hz), 144.6 (dm, $^1J_{C–F}$ = 250.6 Hz) (Ar), 177.4 (d, $^1J_{C–Rh}$ = 52.9 Hz; N_2C); ^{19}F NMR (376 MHz, $CDCl_3$) δ –156.5 (td, *J* = 22.1, 8.4 Hz, 1F), –155.7 (m, 1F), –146.7 (t, *J* = 21.4 Hz, 1F), –133.8 (dd, *J* = 23.7, 7.6 Hz, 1F), –131.9 (d, *J* = 22.9 Hz, 1F); IR (KBr) 2918, 2882, 2834, 1521, 1494, 1066, 990, 825, 741 cm^{-1}; MS (FAB): *m/z*: 509 [*M*–Cl]$^+$; HRMS (FAB): *m/z* calcd for $C_{22}H_{19}F_5N_2Rh$ 509.0523 [*M*–Cl]$^+$; found 509.0537.

Chloro(1,5-cyclooctadiene)(1-((4-methoxyphenyl)ethynyl)-2-methylimidazo[1,5-*a*] pyridin-3-ylidene)rhodium (I) (5f)

0.20 mmol, Yellow solid; 87% yield (over 2 steps); R_f = 0.40 (*n*-hexane/EtOAc = 2/1); m.p. 130-134 ºC (decomposed); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.99-2.07 (m, 4H,

CH_2(cod)), 2.41-2.50 (m, 4H, CH_2(cod)), 3.27-3.37 (m, 2H, CH(cod)), 3.85 (s, 3H, OMe), 4.37 (s, 3H, NMe), 5.13-5.17 (m, 2H, CH(cod)), 6.64 (dd, *J* = 7.1, 6.3 Hz, 1H, Ar), 6.88 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 6.91 (d, *J* = 8.8 Hz, 2H, Ar), 7.33 (d, *J* = 9.3 Hz, 1H, Ar), 7.47 (d, *J* = 8.8 Hz, 2H, Ar), 8.98 (d, *J* = 7.1 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.7 (CH_2(cod)), 29.1 (CH_2(cod)), 32.8 (CH_2(cod)), 33.1 (CH_2(cod)), 37.1 (NMe), 55.3 (OMe), 68.4 (d, $^1J_{C–Rh}$ = 14.9 Hz, CH(cod)), 68.8 (d, $^1J_{C–Rh}$ = 14.9 Hz, CH(cod)), 74.2 (CC), 99.6 (d, $^1J_{C–Rh}$ = 6.6 Hz, CH(cod)), 99.8 (d, $^1J_{C–Rh}$ = 6.6 Hz, CH(cod)), 100.7 (CC), 108.7, 113.3, 114.1 (2C), 117.5, 123.6, 129.1, 132.9, 133.5, 160.1 (Ar), 175.1 (d, $^1J_{C–Rh}$ = 52.1 Hz, N_2C); IR (KBr) 2932, 2869, 2826, 2200, 1603, 1508, 1307, 1247, 1177, 1028, 832, 755 cm^{-1}; MS (FAB): *m/z*: 508 [*M*]$^+$; HRMS (FAB): *m/z* calcd for $C_{25}H_{26}ClN_2ORh$ 508.0789 [*M*]$^+$; found 508.0798.

Chloro(1,5-cyclooctadiene)(2-methyl-1-(phenylethynyl)imidazo[1,5-*a*]pyridin-3-ylidene)rhodium (I) (5g)

0.20 mmol scale; Yellow solid; 96% yield (over 2 steps); R_f = 0.25 (*n*-hexane/EtOAc = 2/1); m.p. 137-144 ºC (decomposed); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.95-2.07 (m, 4H, CH_2(cod)), 2.41-2.54 (m, 4H, CH_2(cod)), 3.26-3.40 (m, 2H, CH(cod)), 4.39 (s, 3H, NMe), 5.13-5.18 (m, 2H, CH(cod)), 6.66 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 6.95 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.36 (d, *J* = 9.3 Hz, 1H, Ar), 7.38-7.42 (m, 3H, Ar), 7.50-7.55 (m, 2H, Ar), 8.99 (d, *J* = 7.3 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.8 (CH_2(cod)), 29.1 (CH_2(cod)), 32.8 (CH_2(cod)), 33.1 (CH_2(cod)), 37.1 (NMe), 68.5 (d, $^1J_{C–Rh}$ = 14.9 Hz, CH(cod)), 68.9 (d, $^1J_{C–Rh}$ = 14.1 Hz, CH(cod)), 75.7 (CC), 99.8 (d, $^1J_{C–Rh}$ = 6.6 Hz, CH(cod)), 100.0 (d, $^1J_{C–Rh}$ = 6.6 Hz, CH(cod)), 100.9 (CC), 108.3, 113.4, 117.5, 122.2, 123.9, 128.5, 128.8, 129.2, 131.2, 133.9 (Ar), 175.7 (d, $^1J_{C–Rh}$ = 52.1 Hz, N_2C); IR (KBr) 2932, 2870, 2824, 2196, 1517, 1490, 1430, 1336, 1304, 1252, 751, 690 cm^{-1}; MS (FAB): *m/z*: 478 [*M*]$^+$; HRMS (FAB): *m/z* calcd for $C_{24}H_{24}ClN_2Rh$ 484.0683 [*M*]$^+$; found 478.0688.

Chloro(1,5-cyclooctadiene)(2-methyl-1-((4-(trifluoromethyl)phenyl)ethynyl)imidazo[1,5-*a*]pyridin-3-ylidene)rhodium (I) (5h)

0.20 mmol scale, Yellows solid; 64% yield (over 2 steps); R_f = 0.20 (*n*-hexane/EtOAc = 2/1); m.p. 171-175 ºC (decomposed); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.00-2.05 (m, 4H, CH_2(cod)), 2.37-2.53 (m, 4H, CH(cod)), 3.29-3.38 (m, 2H, CH(cod)), 4.41 (s, 3H, NMe), 5.16-5.20 (m, 2H, CH(cod)), 6.70 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 6.97 (dd, *J* = 9.3, 6.3 Hz,

1H, Ar), 7.37 (d, *J* = 9.27 Hz, 1H, Ar), 7.61 (d, *J* = 8.8 Hz, 2H, Ar), 7.65 (d, *J* = 8.8 Hz, 2H, Ar), 9.04 (d, *J* = 7.3 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.8 (CH_2(cod)), 29.1 (CH_2(cod)), 32.8 (CH_2(cod)), 33.1 (CH_2(cod)), 37.2 (NMe), 68.6 (d, $^1J_{C–Rh}$ = 14.8 Hz, CH(cod)), 69.0 (d, $^1J_{C–Rh}$ = 14.0 Hz, CH(cod)), 78.2 (CC), 99.7 (CC), 100.0 (d, $^1J_{C–Rh}$ = 6.6 Hz, CH(cod)), 100.3 (d, $^1J_{C–Rh}$ = 6.6 Hz; CH(cod)), 107.7, 113.6, 117.3 (Ar), 123.8 (q, $^1J_{C–F}$ = 272.1 Hz, CF_3), 124.7 (Ar), 125.5 (q, $^3J_{C–F}$ = 3.3 Hz; *C*HCCF_3), 126.0, 129.5 (Ar), 130.3 (q, $^2J_{C–F}$ = 33.1 Hz; *C*CF_3), 131.2, 134.5, 176.8 (d, $^1J_{C–Rh}$ = 52.1 Hz, N_2C); ^{19}F NMR (376 MHz, $CDCl_3$) δ –62,7; IR (KBr) 2930, 2875, 2830, 2197, 1610, 1567, 1510, 1322, 1250, 1169, 1123, 1065, 835, 753 cm^{-1}; MS (FAB): *m/z*: 546 [*M*]$^+$; HRMS (FAB): *m/z* calcd for $C_{25}H_{23}ClF_3N_2Rh$ 546.0557 [*M*]$^+$; found 546.0573.

Chloro(1,5-cyclooctadiene)(2-methyl-1-((pentafluorophenyl)ethynyl)imidazo[1,5-*a*]pyridin-3-ylidene)rhodium (I) (5i)

0.20 mmol scale; Yellow solid; 87% yield (over 2 steps); R_f = 0.20 (*n*-hexane/EtOAc = 2/1); m.p. 162-172 ºC (decomposed); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.97-2.09 (m, 4H, CH_2(cod)), 2.42-2.53 (m, 4H, CH_2(cod)), 3.27-3.41 (m, 2H, CH(cod)), 4.40 (s, 3H, NMe), 5.15-5.23 (m, 2H, CH(cod)), 6.75 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 7.04 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.37 (d, *J* = 9.3 Hz, 1H, Ar), 9.09 (d, *J* = 7.3 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.7 (CH_2(cod)), 28.9 (CH_2(cod)), 32.8 (CH_2(cod)), 33.0 (CH_2(cod)), 37.1 (NMe), 68.6 (d, $^1J_{C–Rh}$ = 14.1 Hz, CH(cod)), 69.0 (d, $^1J_{C–Rh}$ = 14.1 Hz, CH(cod)), 85.3 (q, *J* = 4.1 Hz; CC), 88.1 (q, *J* = 3.3 Hz, CC), 99.6 (td, $J_{C–F}$ = 18.2, 4.1 Hz, Ar), 100.2 (d, $^1J_{C–Rh}$ = 6.6 Hz, CH(cod)), 100.4 (d, $^1J_{C–Rh}$ = 6.6 Hz, CH(cod)), 106.7, 113.8, 117.0, 125.6, 129.6, 135.2, 137.5 (dm, $^1J_{C–F}$ = 252.2 Hz), 141.3 (dm, $^1J_{C–F}$ = 258.0 Hz), 146.0 (dm, $^1J_{C–F}$ = 253.1 Hz) (Ar), 178.1 (d, $^1J_{C–Rh}$ = 52.1 Hz, N_2C). ^{19}F NMR (376 MHz, $CDCl_3$) δ –157.1 (m, 2F), –147.1 (t, *J* = 20.6 Hz, 1F), –132.0 (m, 2F); IR (KBr) 2928, 2870, 2823, 2212, 1514, 1498, 1287, 1241, 988, 759 cm^{-1}; MS (FAB): *m/z*: 568 [*M*]$^+$; HRMS (FAB): *m/z* calcd for $C_{24}H_{19}ClF_5N_2Rh$ 568.0212 [*M*]$^+$; Found 568.0217.

Chloro(1,5-cyclooctadiene)(1,2-diphenylimidazo[1,5-*a*]pyridin-3-ylidene)rhodium (I) (5j)

To a solution of 1,2-diphenylimidazo[1,5-*a*]pyridin-2-ium tetrafluoroborate (72 mg, 0.20 mmol, 1.0 equiv) and *t*-BuOK (25 mg, 0.22 mmol, 1.1 equiv) in anhydrous THF (4.0 mL) was added $[Rh(cod)Cl]_2$ (49 mg, 0.10 mmol, 0.50 equiv) at room temperature under an

argon atmosphere and the mixture was stirred at room temperature for 12 h. After stirring, the solvent was removed *in vacuo*. The residue was purified by flash column chromatography on silica gel to give Chloro(1,5-cyclooctadiene)(1,2-diphenylimidazo[1,5-*a*]pyridine-3-ylidene)rhodium (I) in 88% yield as a yellow solid. R_f = 0.43 (*n*-hexane/EtOAc = 2/1); m.p. 225-227 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35-1.52 (m, 2H, CH_2(cod)), 1.73-2.05 (m, 4H, CH_2(cod)), 2.27-2.36 (m, 1H, CH_2(cod)), 2.41-2.50 (m, 1H, CH_2(cod)), 2.54-2.59 (m, 1H, CH(cod)), 3.33-3.38 (m, 1H, CH(cod)), 4.97-5.02 (m, 1H, CH(cod)), 5.06-5.11 (m, 1H, CH(cod)), 6.63 (dd, *J* = 7.8, 6.3 Hz, 1H, Ar), 6.80 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.10 (d, *J* = 7.3 Hz, 2H, Ar), 7.26-7.31 (m, 5H, Ar), 7.44-7.48 (m, 3H, Ar), 7.81 (br s 1H, Ar), 9.08 (d, *J* = 7.3 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.2 (CH_2(cod)), 28.8 (CH_2(cod)), 31.3 (CH_2(cod)), 33.6 (CH_2(cod)), 68.2 (d, $^1J_{C–Rh}$ =14.1 Hz, CH(cod)), 68.6 (d, $^1J_{C–Rh}$ = 14.9 Hz, CH(cod)), 98.3 (d, $^1J_{C–Rh}$ = 9.1 Hz; CH(cod)), 98.4 (d, $^1J_{C–Rh}$ = 9.1 Hz, CH(cod)), 113.4, 117.4, 123.2, 124.0, 127.9, 128.05, 128.11, 128.3, 128.5, 128.7, 129.1, 129.3, 139.1 (Ar), 175.4 (d, $^1J_{C–Rh}$ = 52.1Hz, N_2C); A peak was not observed; IR (KBr) 2931, 2869, 2826, 1496, 1350, 1308, 764, 700 cm^{-1}; MS (FAB): *m/z*: 516 [*M*]$^+$; HRMS (FAB): *m/z* calcd for $C_{27}H_{26}ClN_2Rh$ 516.0840 [*M*]$^+$; found 516.0844.

General procedure for the synthesis of $Rh(CO)_2(L)Cl$ complexes

An argon-flushed 2-neck flask was charged with Rh(cod)(L)Cl complexes (L = NHC) (1.0 equiv) and anhydrus THF (0.050 M). CO was bubbled for 10 min and then the solvent was evaporated *in vacuo*. The remaining oil was washed with *n*-hexane to give $Rh(CO)_2(L)Cl$ complexes. Elemental analyses were carried out with lightly dried powder since the complexes were not so stable under low partial pressure of CO gas, thus some solvents were remaind in the samples.

Chlorodicarbonyl(1-(2-methoxyphenyl)-2-methylimidazo[1,5-*a*]pyridin-3-ylidene)rhodium (I) (6a)

0.16 mmols scale, Yellow solid; 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3,78 (s, 3H, OMe), 3.96 (s, 3H, NMe), 6.58 (dd, *J* = 7.2, 6.3 Hz, 1H, Ar), 6.75 (dd, *J* = 9.4, 6.3 Hz, 1H, Ar), 7.01-7.08 (m, 3H, Ar), 7.25 (d, *J* = 7.7 Hz, 1H, Ar), 7.47 (dd, *J* = 8.5, 7.7 Hz, 1H, Ar), 8.56 (d, *J* = 7.2 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.6 (NMe), 55.5 (OMe), 111.4, 113.6, 115.9, 117.5, 121.0, 122.3, 122.5, 127.8, 129.6, 131.6, 132.4, 158.0 (Ar),

163.5 (d, $^{1}J_{C-Rh}$ = 45.1 Hz, N_2C), 182.6 (d, $^{1}J_{C-Rh}$ = 74.3 Hz, CO), 185.3 (d, $^{1}J_{C-Rh}$ = 54.5 Hz, CO); IR (CH_2Cl_2) 2081.1, 2001.4 cm^{-1}; Anal. calcd for $C_{17}H_{14}ClN_2O_3Rh\cdot(C_6H_{14})_{0.4}(CH_2Cl_2)_{0.05}$ (%): C 49.56; H 4.21; N 5.94, found C 49.62; H 4.26; N 6.06.

Chlorodicarbonyl(1-(4-methoxyphenyl)-2-methylimidazo[1,5-*a*]pyridin-3-ylidene)rhodium (I) (6b)

0.15 mmol scale, Yellow solid; 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H, OMe), 4.03 (s, 3H, NMe), 6.57 (dd, *J* = 7.1, 6.3Hz, 1H, Ar), 6.74 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 6.99 (d, *J* = 8.8, 2H, Ar), 7.12 (d, *J* = 9.3 Hz, 1H, Ar), 7.29 (d, *J* = 8.8 Hz, 2H, Ar), 8.52 ppm (d, *J* = 7.1 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.8 (NMe), 55.5 (OMe), 113.9, 114.8, 117.4, 119.3, 122.6, 125.3, 127.8, 129.1, 131.5, 160.5 (Ar), 163.8 (d, $^{1}J_{C-Rh}$ = 44.2 Hz, N_2C), 182.6 (d, $^{1}J_{C-Rh}$ = 74.3 Hz, CO), 185.3 ppm (d, $^{1}J_{C-Rh}$ = 54.5 Hz, CO); IR (CH_2Cl_2) 2081.7, 2001.8 cm^{-1}; Anal. calcd for $C_{17}H_{14}ClN_2O_3Rh\cdot(C_6H_{14})_{0.35}(CH_2Cl_2)_{0.17}$ (%): C 48.50; H 4.06; N 5.87, found C 48.35; H 4.12; N 5.99.

Chlorodicarbonyl(2-methyl-1-phenylimidazo[1,5-*a*]pyridin-3-ylidene)rhodium (I) (6c)

0.13 mmol scale, Yellow solid; 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 (s, 3H, NMe), 6.67 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 6.85 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.24 (d, *J* = 9.3 Hz, 1H, Ar), 7.43 (d, *J* = 6.3 Hz, 2H, Ar), 7.48-7.57 (m, 3H, Ar), 8.62 (d, *J* = 7.3 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.9 (NMe), 114.0, 117.3, 123.0, 125.3, 127.3, 127.9, 128.7, 129.3, 129.4, 130.0, 164.4 (d, J_{C-Rh} = 44.7 Hz, N_2C), 182.6 (d, $^{1}J_{C-Rh}$ = 74.4 Hz, CO), 185.3 ppm (d, $^{1}J_{C-Rh}$ = 54.6 Hz, CO); IR (CH_2Cl_2) 2082.2, 2002.2 cm^{-1}; Anal. calcd for $C_{16}H_{12}ClN_2O_2Rh\cdot(C_6H_{14})_{0.2}(CH_2Cl_2)_{0.15}$ (%): C 48.17; H 3.52; N 6.48, found C 48.03; H 3.55; N 6.39.

Chlorodicarbonyl(2-methyl-1-(4-(trifluoromethyl)phenyl)imidazo[1,5-*a*]pyridin-3-ylidene)rhodium (I) (6d)

0.088 mmol scale, Yellow solid; 76% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.17 (s, 3H, NMe), 6.72 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 6.93 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.25 (d, *J* = 9.3 Hz, 1H, Ar), 7.59 (d, *J* = 8.3 Hz, 2H, Ar), 7.82 (d, *J* = 8.3 Hz, 2H, Ar), 8.66 (d, *J* = 7.3

Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.1 (NMe), 114.2, 116.7, 123.7 (q, $^1J_{C–F}$ = 272.1 Hz, CF_3), 124.1, 126.3 (q, $^3J_{C–Rh}$ = 3.3 Hz; *C*HCCF$_3$), 128.1, 128.7, 129.9, 130.2, 130.9, 131.2 (q, $^2J_{C–F}$ =33.1 Hz, *C*CF$_3$), 165.8 ppm (d, $^1J_{C–Rh}$ = 46.3 Hz, N_2C), 182.3 (d, $^1J_{C–Rh}$ = 73.6 Hz, CO), 185.0 ppm (d, $^1J_{C–Rh}$ = 53.8 Hz, CO); ^{19}F NMR (376 MHz, $CDCl_3$) δ –64.0; IR (CH_2Cl_2) 2083.5, 2003.4 cm^{-1}; Anal. calcd for $C_{17}H_{11}ClF_3N_2O_2Rh\cdot(C_6H_{14})_{0.5}(CH_2Cl_2)_{0.7}$ (%): C 43.38; H 3.41; N 4.89, found C 43.39; H 3.63; N 5.01.

Chlorodicarbonyl(2-methyl-1-(pentafluorophenyl)imidazo[1,5-*a*]pyridin-3-ylidene) rhodium (I) (6e)

0.070 mmol scale, Yellow solid; 89% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.11 (s, 3H, NMe), 6.80 (dd, *J* = 7.3, 5.9 Hz, 1H, Ar), 7.03-7.07 (m, 2H, Ar), 8.75 (d, *J* = 7.3 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.0 (NMe), 102.6 (td, $J_{C–F}$ =17.4, 4.1 Hz), 114.2, 116.2, 125.3, 128.72, 128.78, 131.5, 136.7 (dm, $^1J_{C–F}$ =253.9 Hz), 142.6 (dm, $^1J_{C–F}$ =259.7 Hz), 144.8 (dm, $^1J_{C–F}$ =251.5 Hz) (Ar), 168.2 (d, $^1J_{C–Rh}$ = 45.5 Hz, N_2C), 182.1 (d, $^1J_{C–Rh}$ = 73.6 Hz, CO), 184.9 ppm (d, $^1J_{C–Rh}$ = 54.6 Hz, CO). ^{19}F NMR (376 MHz, $CDCl_3$) δ –160.3 (br s, 2F), –150.0 (t, *J* = 21.4 Hz, 1F), –137.8 (br s, 1F), –136.7 (br s, 1F); IR (CH_2Cl_2) 2085.1, 2005.4 cm^{-1}; Anal. calcd for $C_{16}H_7ClF_5N_2O_2Rh\cdot(C_6H_{14})_{0.4}(CH_2Cl_2)_{1.7}$ (%): C 35.96; H 2.40; N 4.17, found C 35.98; H 2.59; N 4.17.

Chlorodicarbonyl(2-methyl-1-((4-methoxyphenyl)ethynyl)imidazo[1,5-*a*]pyridin-3-ylidene)rhodium (I) (6f)

0.18 mmol scale, Yellow solid; 98% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.86 (s, 3H, OMe), 4.24 (s, 3H, NMe), 6.72 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 6.93 (d, *J* = 9.0 Hz, 2H, Ar), 7.00 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.47 (d, *J* = 9.3 Hz, 1H, Ar), 7.50 (d, *J* = 9.0 Hz, 2H, Ar), 8.64 (d, *J* = 7.3 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.8 (NMe), 55.4 (OMe), 73.5 (CC), 101.3 (CC), 109.6, 113.6, 114.2, 114.4, 117.6, 124.2, 128.6, 133.1, 133.6, 160.4, 165.8 (d, $^1J_{C–Rh}$ = 45.5 Hz, N_2C), 182.2 (d, $^1J_{C–Rh}$ = 73.6 Hz, CO), 185.0 (d, $^1J_{C–Rh}$ = 54.6 Hz, CO); IR (CH_2Cl_2) 2083.7, 2004.2 cm^{-1}; Anal. calcd for $C_{19}H_{14}ClN_2O_3Rh\cdot(C_6H_{14})_{0.66}(CH_2Cl_2)_{0.6}$ (%): C 50.13; H 4.36; N 4.96, found C 50.10; H 4.13; N 4.82.

Chlorodicarbonyl(2-methyl-1-(phenylethynyl)imidazo[1,5-*a*]pyridin-3-ylidene)rhod

ium(I) (6g)

0.15 mmol scale, Yellow solid; 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 (s, 3H, NMe), 6.67 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 6.96 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.32-7.36 (m, 3H, Ar), 7.42 (d, *J* = 9.3 Hz, 1H, Ar), 7.48-7.50 (m, 2H, Ar), 8.59 (d, *J* = 7.3 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.9 (Me), 74.8 (CC), 101.4 (CC), 109.3, 114.5, 117.5, 121.7, 124.7, 128.6, 128.8, 129.3, 131.4, 133.9 (Ar), 166.3 (d, $^{1}J_{C–Rh}$ = 45.5 Hz, N_2C), 182.2 (d, $^{1}J_{C–Rh}$ = 73.6 Hz, CO), 185.0 (d, $^{1}J_{C–Rh}$ = 54.6 Hz, CO); IR (CH_2Cl_2) 2084.1, 2004.6 cm^{-1}; Anal. calcd for $C_{18}H_{12}ClN_2O_2Rh\cdot(C_6H_{14})_{0.4}(CH_2Cl_2)_{0.1}$ (%): C 52.43; H 3.82; N 5.97, found C 52.40; H 3.63; N 6.21.

Chlorodicarbonyl(2-methyl-1-((4-(trifluoromethyl)phenyl)ethynyl)imidazo[1,5-*a*]pyridin-3-ylidene)rhodium (I) (6h)

0.10 mmol scale, Yellow solid; 92% yield; ^{1}H NMR (400 MHz,) δ 4.28 (s, 3H, NMe), 6.79 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 7.09 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.51 (d, *J* = 9.3 1H, Ar), 7.67 (m, 4H, Ar), 8.71 (d, *J* = 7.3 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.9 (NMe), 67.9 (CC), 100.1 (CC), 108.5, 114.7, 117.3 (Ar), 123.7 (q, $^{1}J_{C–F}$ = 272.1 Hz, CF_3), 125.3 (Ar), 125.6 (q, $^{3}J_{C–F}$ = 4.1 Hz, *C*HCCF$_3$), 129.0 (Ar), 130.7 (q, $^{2}J_{C–F}$ = 33.1 Hz, *C*CF$_3$), 131.2, 131.4, 134.5 (Ar), 167.3 (d, $^{1}J_{C–Rh}$ = 45.5 Hz, N_2C), 182.1 (d, $^{1}J_{C–Rh}$ = 73.6 Hz, CO), 184.9 (d, $^{1}J_{C–Rh}$ = 54.6 Hz, CO); ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.8 (C*F*$_3$); IR (CH_2Cl_2) 2084.5, 2005.2 cm^{-1}; Anal. calcd for $C_{19}H_{11}ClF_3N_2O_2Rh\cdot(C_6H_{14})_{0.33}$ (%): C 48.17; H 3.01; N 5.36, found C 48.11; H 3.07; N 5.48.

Chlorodicarbonyl(2-methyl-1-((pentafluorophenyl)ethynyl)imidazo[1,5-*a*]pyridin-3-ylidene)rhodium (I) (6i)

0.17 mmol scale, Yellow solid; 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 (s, 3H, NMe), 6.83 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 7.16 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.52 (d, *J* = 9.3 Hz, 1H, Ar), 8.75 (d, *J* = 7.3 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.0 (NMe), 85.7 (q, *J* = 4.1 Hz; CC), 87.1 (q, *J* = 3.3 Hz; CC), 99.3 (td, $J_{C–F}$ = 18.2, 4.1 Hz), 107.6, 114.9, 117.1, 126.3, 129.3, 135.2, 137.8 (dm, $^{1}J_{C–Rh}$ = 250.6 Hz), 142.0 (dm, $^{1}J_{C–Rh}$ = 258.9 Hz), 146.4 (dm $^{1}J_{C–Rh}$ = 253.9 Hz) (Ar), 168.6 (d, $J_{C–Rh}$ = 45.5 Hz, N_2C), 182.0 (d, $J_{C–Rh}$ = 73.6 Hz, CO), 184.8 (d, $J_{C–Rh}$ = 54.6 Hz, CO); ^{19}F NMR (376 MHz, $CDCl_3$) δ –157.0 (m, 2F), –147.0 (t, *J* = 20.6 Hz, 1F), –132.0 (m, 2F); IR (CH_2Cl_2) 2085.9, 2006.2 cm^{-1}; Anal. calcd for $C_{18}H_7ClF_5N_2O_2Rh\cdot(C_6H_{14})_{0.33}$ (%): C 44.03; H 2.15; N 5.14, found C

43.83; H 2.10; N 5.21.

Chlorodicarbonyl(1,2-diphenylimidazo[1,5-*a*]pyridin-3-ylidene)rhodium (I) (6j)

0.18 mmol scale, Yellow solid; 91% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (dd, *J* = 7.2, 6.3 Hz, 1H, Ar), 6.95 (dd, *J* = 9.4, 6.3 Hz, 1H, Ar), 7.14-7.17 (m, 2H, Ar), 7.31-7.35 (m, 3H, Ar), 7.42 (d, *J* = 9.0 Hz, 1H, Ar), 7.44-7.51 (m, 5H, Ar), 8.81 ppm (d, *J* = 7.6 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.1, 117.4, 123.8, 125.0, 127.4, 128.1, 128.5, 128.7, 128.8, 129.0, 129.27, 129.31, 129.4, 138.4 (Ar), 166.0 (d, $^{1}J_{C–Rh}$ = 46.0 Hz; N_2C), 181.9 (d, $^{1}J_{C–Rh}$ = 75.2 Hz, CO), 185.3 (d, $^{1}J_{C–Rh}$ = 54.5 Hz, CO); IR (CH_2Cl_2) 2080.6, 2002.8 cm^{-1}; Anal. calcd for $C_{21}H_{14}ClN_2O_2Rh\cdot(C_6H_{14})_{0.33}(CH_2Cl_2)_{0.1}$ (%): C 55.26; H 3.78; N 5.58, found C 55.32; H 3.63; N 5.42.

Chlorodicarbonyl(1,2-dimethylimidazol-2-ylidene)rhodium (I) (10a)

Prepared according to literature procedure.[S2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 6H, Me), 6.94 (s, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.3 (Me), 122.7 (Ar), 174.5 (d, $^{1}J_{C–Rh}$ = 43.2 Hz; N_2C), 182.6 (d, $^{1}J_{C–Rh}$ = 74.2 Hz, CO), 185.5 (d, $^{1}J_{C–Rh}$ = 53.6 Hz, CO); IR (CH_2Cl_2) 2081.7, 2000.4 cm^{-1}.

General procedure for the synthesis of selenoureas

To a suspension of azolium salts (0.50 mmol, 1.0 equiv) and elemental selenium (1.0 mmol, 2.0 equiv) in anhydrous THF (4.0 mL) was added NaH (0.55 mmol, 1.1 equiv) at room temperature under an argon atmosphere and the mixture was stirred at room temperature for 3-5 h. After stirring, the solvent was removed *in vacuo*. The residue was purified by flash column chromatography on silica gel to give selenourea.

(4-methoxyphenyl)-2-methylimidazo[1,5-*a*]pyridine-3-selenone (13b)

Yellow solid; 77% yield; m.p. 150-152 ºC; R_f = 0.20 (*n*-Hexane/EtOAc, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.07 (s, 3H, OMe), 3.92 (s, 3H, NMe), 6.64 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 6.77 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.05 (d, *J* = 8.8 Hz, 2H, Ar), 7.15 (d, *J* = 9.3 Hz, 1H, Ar), 7.33 (d, *J* = 8.8 Hz, 1H, Ar), 8.52 (d, *J* = 7.3 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.7 (NMe), 55.7 (OMe), 113.7, 114.9, 117.2, 119.6, 122.66, 122.72, 126.2, 126.7, 131.4 (Ar), 145.4 (C=Se, $^{1}J_{C–Se}$ = 234.9 Hz), 160.4 (Ar); ^{77}Se NMR (76 MHz, $CDCl_3$) δ –9.8; IR (KBr) 1640.2, 1609.3, 1562.1, 1438.6, 1375.0, 1346.1, 1322.9,

1291.1, 1250.6, 1176.4, 1047.2, 1025.9, 831.2, 737.6 cm^{-1}; MS (EI): *m/z*: 318 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{15}H_{14}N_2OSe$ 318.0271 $[M]^+$; found 318.0280.

2-methy-1-phenylimidazo[1,5-*a*]pyridine-3-selenone (13c)

Yellow solid; 72% yield; m.p. 101-102 ºC; R_f = 0.30 (*n*-Hexane/EtOAc, 4:1). ^1H NMR (400 MHz, $CDCl_3$) δ 3.96 (s, 3H, Me), 6.66 (t, *J* = 6.8 Hz, 1H, Ar), 6.81 (dd *J* = 9.3, 6.3 Hz, 1H, Ar), 7.21 (d, *J* = 9.8 Hz, 1H, Ar), 7.42 (d *J* = 8.3 Hz, 2H, Ar), 7.49-7.57 (m, 3H, Ar), 8.55 (d, *J* =7.3 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.4 (Me), 113.4, 116.7, 122.3, 122.8, 126.0, 126.5, 127.2, 128.9, 129.0, 129.5 (Ar), 145.8 (C=Se, $^1J_{C–Se}$ = 234.9 Hz); ^{77}Se NMR (76 MHz, $CDCl_3$) δ –2.9; IR (KBr) 2922.6, 2853.2, 1642.1, 1597.7, 1515.6, 1498.4, 1468.5, 1450.2, 1432.9, 1380.8, 1349.0, 1325.8, 1313.3, 1251.6, 1080.9, 947.8, 761.7, 734.7, 702.0 cm^{-1}; MS (EI): *m/z*: 288 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{14}H_{12}N_2Se$ 288.0166 $[M]^+$; found 288.0162.

(4-trifluoromethylphenyl)-2-methylimidazo[1,5-*a*]pyridin-3-selenone (13d)

0.5 mmol scale; Yellow solid; 90% yield; m.p. 173-175 ºC; R_f = 0.33 (*n*-Hexane/EtOAc, 4:1); ^1H NMR (400 MHz, $CDCl_3$) δ 3.98 (s, 3H, NMe), 6.70 (dd, *J* = 7.3, 6.4 Hz, 1H, Ar), 6.88 (dd, *J* = 9.2, 6.4 Hz, 1H, Ar), 7.22 (d, *J* = 9.2 Hz, 1H, Ar), 7.56 (d, *J* = 8.2 Hz, 2H, Ar), 7.80 (d, *J* = 8.2 Hz, 1H, Ar), 8.58 (d, *J* = 7.3 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.7 (NMe), 113.7, 116.3, 120.6 (Ar), 123.6 (q, $^1J_{C–F}$ = 272.2 Hz, *C*F_3), 124.1 (Ar), 126.2 (q, $^3J_{C–F}$ = 3.8 Hz, *C*H=C–CF_3), 126.5, 127.2, 129.7 (Ar), 130.7 (q, $^2J_{C–F}$ = 32.6 Hz, *C*–CF_3), 131.2 (Ar), 147.7 (*C*=Se, $^1J_{C–Se}$ = 236.8Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.7 (C*F*$_3$); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 4.7 (C=*Se*); IR (KBr) 1614.1, 1518.7, 1377.9, 1313.3, 1247.7, 1169.6, 1133.0, 1112.7, 1069.3, 949.8, 838.9, 751.1, 737.6 cm^{-1}; MS (EI): *m/z*: 356 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{15}H_{11}F_3N_2Se$ 356.0040 $[M]^+$; found 356.0032.

1-((4-Methoxyphenyl)ethynyl)-2-methylimidazo[1,5-*a*]pyridin-3-selenone (13f)

0.5 mmol scale, KHMDS (1.1 equiv, 0.5 M toluene solution) was used instead of NaH; Yellow solid; 93% yield; m.p. 171-173 ºC; R_f = 0.40 (*n*-Hexane/EtOAc, 4:1); ^1H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H, OMe), 4.03 (s, 3H, NMe), 6.71 (dd, *J* = 7.2, 6.7 Hz, 1H, Ar), 6.91 (d, *J* = 9.0 Hz, 2H, Ar), 6.96 (dd, *J* = 9.4, 6.7 Hz, 1H, Ar), 7.42 (d, *J* = 9.4 Hz, 1H, Ar), 7.49 (d, *J* = 9.0 Hz, 2H, Ar), 8.55 (d, *J* = 7.2 Hz, 1H, Ar); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 35.2 (NMe), 55.3 (OMe), 74.1, 100.4 (CC), 106.1, 113.6, 113.9, 114.1, 117.2, 124.2, 126.8, 131.4, 132.8 (Ar), 147.0 (*C*=Se, $^1J_{C-Se}$ = 237.1 Hz); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 8.5 (C=Se); IR (KBr) 2934.2, 2837.7, 2200.4, 1603.5, 1507.1, 1377.9, 1316.2, 1287.3, 1247.7, 1122.4, 1027.9, 829.2, 811.9 cm^{-1}; MS (EI): *m/z*: 342 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{17}H_{14}N_2OSe$ 342.0271 $[M]^+$; found 342.0278.

2-methyl-1-(phenylethynyl)imidazo[1,5-*a*]pyridine-3-selenone (13g)

Orange solid; 92% yield; m.p. 122-124 ºC; R_f = 0.35 (*n*-Hexane/EtOAc, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (s, 3H, Me), 6.73 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 6.99 (dd, 9.3, 6.3 Hz, 1H, Ar), 7.39-7.42 (m, 3H, Ar), 7.45 (d, *J* = 9.3 Hz, 1H, Ar), 7.53-7.57 (m, 2H, Ar), 8.58 (d, *J* = 7.3 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.1 (Me), 75.4 (CC), 100.3 (CC), 105.5, 113.8, 117.0, 121.5, 124.4, 126.7, 128.3, 128.7, 130.9, 131.5 (Ar), 147.4 (C=Se, $^1J_{C-Se}$ = 238.7 Hz); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 13.5; IR (KBr) 1642.1, 1517.7, 1490.7, 1379.8, 1343.2, 1316.2, 1255.4, 971.9, 743.4, 687.5 cm^{-1}; MS (EI): *m/z*: 312 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{16}H_{12}N_2Se$ 312.0166 $[M]^+$; found 312.0156.

2-Methyl-1-((4-(trifluoromethyl)phenyl)ethynyl)imidazo[1,5-*a*]pyridine-2-selenone (13h)

Yellow solid; 58% yield; m.p. 192-194 ºC; R_f = 0.35 (*n*-Hexane/EtOAc, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.06 (s, 3H, Me), 6.77 (dd, *J* = 7.3, 6.3 Hz, 1H, Ar), 7.05 (dd, *J* = 9.3, 6.3 Hz, 1H, Ar), 7.47 (d, *J* = 9.3 Hz, 1H, Ar), 7.65 (s, 4H, Ar), 8.62 (d, *J* = 7.3 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.3 (Me), 78.1 (CC), 99.3 (CC), 105.1, 114.2, 117.1 (Ar), 123.7 (q, $^1J_{C-F}$ = 272.1 Hz, CF_3), 125.5 (q, $^3J_{C-F}$ = 4.1 Hz, *C*HCCF$_3$), 125.7 (q, $^4J_{C-F}$ = 1.7 Hz, *C*HCHCCF$_3$), 127.3 (Ar), 130.4 (q, $^2J_{C-F}$ = 33.1 Hz, *C*CF$_3$), 131.2, 132.6 (Ar), 148.6 (C=Se, $^1J_{C-Se}$ = 239.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.2 (C*F*$_3$); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 18.5; IR (KBr) 2194.6, 1610.3, 1566.0, 1518.7, 1509.0, 1314.3, 1251.6, 1171.5, 1125.3, 1103.1, 1061.6, 834.1, 741.5 cm^{-1}; MS (EI): *m/z*: 380 $[M]^+$; HRMS (EI): *m/z* calcd for $C_{17}H_{11}F_3N_2Se$ 380.0040 $[M]^+$; found 380.0051.

1,3-Dimesitylimidazole-2-selenone (14)

Prepared according to literature procedure.[S4] m.p. >300 ºC; R_f = 0.58 (*n*-Hexane/EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13 (s, 12H, Me), 2.34 (s, 6H, *p*-Me), 6.96 (s, 2H, Ar), 7.02 (s, 4H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$) d 17.9, 21.0 (Me), 120.1, 129.1, 134.1,

135.2, 139.2 (Ar), 157.3 (C=Se, $^1J_{C-Se}$ = 230.0 Hz); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 27.0.

1,3-Bis(2,6-diisopropylphenyl)imidazole-2-selenone (15)

Prepared according to literature procedure.[S5] m.p. >300 ºC; R_f = 0.41 (*n*-Hexane/EtOAc, 19:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (d, *J* = 6.8 Hz, 12H, CH(CH_3)$_2$), 1.34 (d, *J* = 6.8 Hz, 12H, CH(CH_3)$_2$), 2.69 (sept, *J* = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$), 7.01 (s, 2H, Ar), 7.30 (d, *J* = 7.8 Hz, 4H, Ar), 7.48 (t, *J* = 7.8 Hz, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.3, 24.2, 28.9 (^{i}Pr), 121.1, 124.4, 130.2, 134.4, 146.2 (Ar), 162.5 (C=Se, $^1J_{C-Se}$ = 234.1 Hz); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 90.0.

1,3-Dimethylbenzimidazole-2-selenone (16)

Prepared according to literature procedure.[S6] Beige solid; 80% yield; m.p. 174-175 ºC; R_f = 0.43 (*n*-Hexane/EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 6H, Me), 7.17-7.23 (m, 4H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.0 (Me), 109.2, 123.1, 133.1 (Ar), 166.4 (C=Se, $^1J_{C-Se}$ = 232.0 Hz); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 65.2; MS (EI): *m/z*: 226 [*M*]$^+$; HRMS (EI): *m/z* calcd for $C_9H_{10}N_2Se$ 226.0009 [*M*]$^+$; found 226.0004.

1,3-Dimethyl-1,2,4-triazole-3-selenone (17)

Beige solid; 89% yield; m.p. 80-82 ºC; R_f = 0.35 (*n*-Hexane/EtOAc, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (s, 3H, Me), 3.90 (s, 3H, Me), 7.87 (s, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.5, 38.3 (Me), 140.7 (Ar), 160.7 (C=Se, $^1J_{C-Se}$ = 241.5 Hz); ^{77}Se NMR (76 MHz, $CDCl_3$) δ 20.3; IR (KBr) 3107.7, 3042.2, 1719.2, 1546.6, 1475.3, 1351.9, 1224.6, 1136.8, 1058.7, 976.8, 863.0, 770.4, 632.5 cm^{-1}; MS (EI): *m/z*: 177 [*M*]$^+$; HRMS (EI): *m/z* calcd for $C_4H_7N_3Se$ 176.9805 [*M*]$^+$; found 176.9802.

General procedure for Rh-catalyzed polymerization of phenylacetylene

To a solution of Rh catalyst **6c** or **6c'** (10 μmol, 1.0 mol%) in CH_2Cl_2 (1.0 mL) was added phenylacetylene (102 mg, 1.0 mmol) at room temperature under an argon atmosphere. The resulting mixture was stirred at room temperature. After the time indicated in Table 5, two portions of trifluoroacetic acid were added to the reaction mixture to deactivate the catalyst. Then, methanol (5 mL) was added to the reaction mixture. Precipitate was filtered, washed with methanol (5 mL x 3), and dried *in vacuo* to afford polyphenylacetylene. The molecular weight and polydispersity of polymers were

determind by SEC (polystylene standards, THF as eluent). The *cis*-content in polyphenylacetylene (%-*cis*) was determined by ^{1}H NMR spectroscopy using following equation: %-*cis* = 100 x ($A_{5.84}$ x 6)/(A_{total}) where $A_{5.84}$ is the area of the vinylic proton at 5.84 ppm, and A_{total} is the total area of all the signals of the polyene.[S7]

Cationic Rh complex **6c'** was prepared by adding an $AgPF_6$ (2.5 mg, 10 μmol) to a solution of **6c** (4.5 mg, 10 μmol) in CH_2Cl_2 (2 mL) under an argon atmosphere and stirred in darkness at room temperature for 1 h. After stirring, the reaction mixture was filtered through Celite pad and the solvent was distilled under reduced pressure.

X-ray diffraction analysis

The X-ray diffraction analyses of **6b**, **6c**, **6e**, **6g**, **6h** and **13b** was carried out on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochlomates Mo-Ka radiation (l = 0.71069 Å). Reflection data were collected at 123-193 K using a Rigaku XR-TCS-2-050 temperature controller. The structure was solved by direct methods and refined by full-matrix least-squares procedures (SHELXL-97 and SHELXS-97)[S8] using Yadokari-XG 2009[S9]. The crystal was cut from the grown crystals and was attached to the tip of a MiTeGen MicroMount™. Crystal data and measurement descriptions are summarized in Table S1-S36.

Table S1. Crystal data and structure refinement for **6b**.

Empirical formula	$C_{17}H_{14}ClN_2O_3Rh$	
Formula weight	432.66	
Temperature	193(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	*P* $2_1/n$	
Unit cell dimensions	a = 11.611(3) Å	α = 90°.
	b = 7.436(2) Å	β = 95.124(4)°.
	c = 20.143(6) Å	γ = 90°.
Volume	1732.3(8) $Å^3$	
Z	4	
Density (calculated)	1.659 Mg/m^3	
Absorption coefficient	1.157 mm^{-1}	
F(000)	864	
Crystal size	0.42 x 0.28 x 0.14 mm^3	
Theta range for data collection	1.95 to 27.50°.	
Index ranges	-13<=*h*<=15, -6<=*k*<=9, -26<=*l*<=26	
Reflections collected	12913	
Independent reflections	3927 [R(int) = 0.0376]	
Completeness to theta = 27.50°	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.851 and 0.512	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3927 / 0 / 219	
Goodness-of-fit on F^2	1.113	
Final *R* indices [I>2sigma(I)]	*R*1 = 0.0368, *wR*2 = 0.1014	
R indices (all data)	*R*1 = 0.0459, *wR*2 = 0.1267	
Largest diff. peak and hole	1.056 and -1.100 e.$Å^{-3}$	

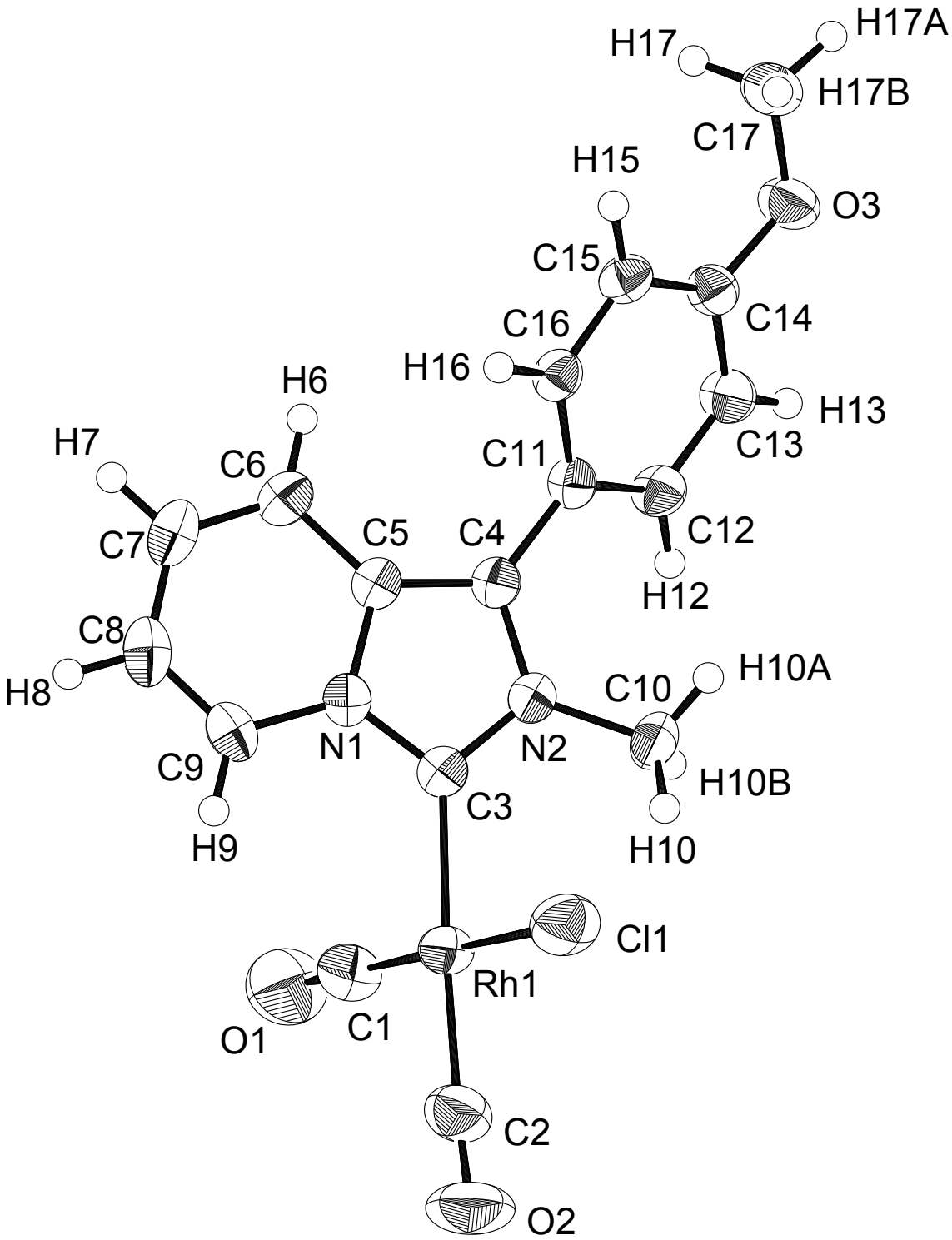


Figure S1. ORTEP drawing of **6b** with thermal ellipsoids at 50% probability.

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **6b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	1953(1)	-2335(1)	4783(1)	61(1)
Rh(1)	2816(1)	491(1)	4669(1)	42(1)
O(1)	4020(3)	3971(5)	4531(2)	86(1)
O(2)	3786(3)	-177(6)	6094(2)	90(1)
O(3)	-3641(2)	1755(4)	1362(1)	50(1)
N(1)	2585(2)	873(3)	3138(1)	35(1)
N(2)	907(2)	885(4)	3493(1)	36(1)
C(1)	3541(3)	2658(6)	4585(2)	58(1)
C(2)	3454(4)	126(6)	5565(2)	60(1)
C(3)	2046(3)	773(4)	3709(2)	37(1)
C(4)	714(2)	1067(4)	2807(2)	34(1)
C(5)	1797(2)	1059(4)	2575(2)	33(1)
C(6)	2231(3)	1252(4)	1942(2)	41(1)
C(7)	3395(3)	1215(5)	1906(2)	49(1)
C(8)	4170(3)	980(5)	2486(2)	48(1)
C(9)	3771(3)	802(4)	3081(2)	43(1)
C(10)	2(3)	765(5)	3963(2)	47(1)
C(11)	-419(2)	1224(4)	2426(2)	33(1)
C(12)	-1293(2)	2337(4)	2634(2)	38(1)
C(13)	-2343(3)	2475(5)	2265(2)	41(1)
C(14)	-2556(2)	1533(4)	1675(2)	36(1)
C(15)	-1698(3)	455(4)	1449(2)	36(1)
C(16)	-651(3)	307(4)	1828(2)	34(1)
C(17)	-3890(3)	973(6)	725(2)	52(1)

Table S3. Bond lengths [Å] and angles [°] for **6b**.

Cl(1)-Rh(1)	2.3484(11)
Rh(1)-C(1)	1.833(4)
Rh(1)-C(2)	1.907(5)
Rh(1)-C(3)	2.067(4)
O(1)-C(1)	1.134(5)
O(2)-C(2)	1.124(6)
O(3)-C(14)	1.368(4)
O(3)-C(17)	1.416(4)
N(1)-C(3)	1.361(4)
N(1)-C(9)	1.393(4)
N(1)-C(5)	1.398(4)
N(2)-C(3)	1.357(4)
N(2)-C(4)	1.387(4)
N(2)-C(10)	1.478(4)
C(4)-C(5)	1.379(4)
C(4)-C(11)	1.468(4)
C(5)-C(6)	1.421(4)
C(6)-C(7)	1.359(5)
C(6)-H(6)	0.9500
C(7)-C(8)	1.420(6)
C(7)-H(7)	0.9500
C(8)-C(9)	1.329(5)
C(8)-H(8)	0.9500
C(9)-H(9)	0.9500
C(10)-H(10)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(11)-C(16)	1.389(4)
C(11)-C(12)	1.402(4)
C(12)-C(13)	1.375(4)
C(12)-H(12)	0.9500

C(13)-C(14)	1.382(4)
C(13)-H(13)	0.9500
C(14)-C(15)	1.387(4)
C(15)-C(16)	1.381(5)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(17)-H(17)	0.9800
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800

C(1)-Rh(1)-C(2)	94.0(2)
C(1)-Rh(1)-C(3)	89.36(16)
C(2)-Rh(1)-C(3)	176.43(16)
C(1)-Rh(1)-Cl(1)	177.91(13)
C(2)-Rh(1)-Cl(1)	85.03(15)
C(3)-Rh(1)-Cl(1)	91.66(9)
C(14)-O(3)-C(17)	118.3(2)
C(3)-N(1)-C(9)	126.9(3)
C(3)-N(1)-C(5)	111.9(3)
C(9)-N(1)-C(5)	121.2(3)
C(3)-N(2)-C(4)	113.0(2)
C(3)-N(2)-C(10)	121.3(3)
C(4)-N(2)-C(10)	125.6(3)
O(1)-C(1)-Rh(1)	177.9(4)
O(2)-C(2)-Rh(1)	175.8(5)
N(2)-C(3)-N(1)	103.5(3)
N(2)-C(3)-Rh(1)	129.3(2)
N(1)-C(3)-Rh(1)	127.1(2)
C(5)-C(4)-N(2)	105.4(3)
C(5)-C(4)-C(11)	128.6(3)
N(2)-C(4)-C(11)	125.9(2)
C(4)-C(5)-N(1)	106.1(3)
C(4)-C(5)-C(6)	135.3(3)

N(1)-C(5)-C(6)	118.6(3)
C(7)-C(6)-C(5)	118.7(3)
C(7)-C(6)-H(6)	120.7
C(5)-C(6)-H(6)	120.7
C(6)-C(7)-C(8)	121.2(3)
C(6)-C(7)-H(7)	119.4
C(8)-C(7)-H(7)	119.4
C(9)-C(8)-C(7)	120.5(3)
C(9)-C(8)-H(8)	119.7
C(7)-C(8)-H(8)	119.7
C(8)-C(9)-N(1)	119.8(3)
C(8)-C(9)-H(9)	120.1
N(1)-C(9)-H(9)	120.1
N(2)-C(10)-H(10)	109.5
N(2)-C(10)-H(10A)	109.5
H(10)-C(10)-H(10A)	109.5
N(2)-C(10)-H(10B)	109.5
H(10)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(16)-C(11)-C(12)	117.4(3)
C(16)-C(11)-C(4)	120.6(2)
C(12)-C(11)-C(4)	121.9(3)
C(13)-C(12)-C(11)	120.8(3)
C(13)-C(12)-H(12)	119.6
C(11)-C(12)-H(12)	119.6
C(12)-C(13)-C(14)	120.6(3)
C(12)-C(13)-H(13)	119.7
C(14)-C(13)-H(13)	119.7
O(3)-C(14)-C(13)	114.9(3)
O(3)-C(14)-C(15)	125.3(3)
C(13)-C(14)-C(15)	119.8(3)
C(16)-C(15)-C(14)	119.2(3)
C(16)-C(15)-H(15)	120.4

C(14)-C(15)-H(15)	120.4
C(15)-C(16)-C(11)	122.2(3)
C(15)-C(16)-H(16)	118.9
C(11)-C(16)-H(16)	118.9
O(3)-C(17)-H(17)	109.5
O(3)-C(17)-H(17A)	109.5
H(17)-C(17)-H(17A)	109.5
O(3)-C(17)-H(17B)	109.5
H(17)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **6b**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	73(1)	59(1)	51(1)	13(1)	0(1)	-11(1)
Rh(1)	39(1)	53(1)	34(1)	-1(1)	-1(1)	2(1)
O(1)	98(2)	76(2)	84(3)	-4(2)	2(2)	-32(2)
O(2)	84(2)	133(3)	47(2)	-2(2)	-21(2)	29(2)
O(3)	38(1)	67(2)	44(2)	-11(1)	-6(1)	12(1)
N(1)	33(1)	34(1)	38(2)	2(1)	5(1)	0(1)
N(2)	34(1)	41(1)	33(2)	2(1)	6(1)	0(1)
C(1)	53(2)	70(3)	49(2)	-7(2)	-2(2)	-5(2)
C(2)	49(2)	78(3)	52(3)	-5(2)	-6(2)	12(2)
C(3)	37(2)	39(2)	35(2)	1(1)	4(1)	-1(1)
C(4)	34(1)	33(1)	35(2)	1(1)	5(1)	0(1)
C(5)	36(1)	30(1)	35(2)	1(1)	6(1)	1(1)
C(6)	48(2)	40(2)	36(2)	3(1)	8(1)	2(1)
C(7)	51(2)	49(2)	51(2)	1(2)	23(2)	2(2)
C(8)	38(2)	45(2)	64(3)	-2(2)	17(2)	0(1)
C(9)	31(2)	45(2)	53(2)	0(2)	1(1)	1(1)
C(10)	39(2)	65(2)	38(2)	7(2)	13(2)	3(2)
C(11)	33(1)	31(1)	36(2)	1(1)	5(1)	2(1)
C(12)	41(2)	36(2)	36(2)	-8(1)	4(1)	4(1)
C(13)	39(2)	43(2)	41(2)	-7(1)	3(1)	10(1)
C(14)	34(1)	36(2)	37(2)	2(1)	1(1)	5(1)
C(15)	42(2)	35(2)	31(2)	-2(1)	5(1)	4(1)
C(16)	36(2)	33(2)	35(2)	1(1)	7(1)	5(1)
C(17)	45(2)	64(2)	44(2)	-6(2)	-5(2)	0(2)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **6b**.

	x	y	z	U(eq)
H(6)	1719	1404	1551	49
H(7)	3695	1348	1485	59
H(8)	4980	951	2448	58
H(9)	4294	627	3466	52
H(10)	283	28	4347	70
H(10A)	-693	213	3738	70
H(10B)	-184	1974	4114	70
H(12)	-1157	3004	3036	45
H(13)	-2928	3225	2416	50
H(15)	-1830	-175	1039	43
H(16)	-69	-446	1675	41
H(17)	-3365	1467	416	77
H(17A)	-4691	1243	560	77
H(17B)	-3786	-333	757	77

Table S6. Torsion angles [°] for **6b**.

C(2)-Rh(1)-C(1)-O(1)	78(12)
C(3)-Rh(1)-C(1)-O(1)	-103(12)
Cl(1)-Rh(1)-C(1)-O(1)	16(15)
C(1)-Rh(1)-C(2)-O(2)	172(5)
C(3)-Rh(1)-C(2)-O(2)	12(7)
Cl(1)-Rh(1)-C(2)-O(2)	-10(5)
C(4)-N(2)-C(3)-N(1)	-0.5(3)
C(10)-N(2)-C(3)-N(1)	177.9(3)
C(4)-N(2)-C(3)-Rh(1)	-180.0(2)
C(10)-N(2)-C(3)-Rh(1)	-1.6(4)
C(9)-N(1)-C(3)-N(2)	-179.3(3)
C(5)-N(1)-C(3)-N(2)	0.5(3)
C(9)-N(1)-C(3)-Rh(1)	0.2(4)
C(5)-N(1)-C(3)-Rh(1)	179.9(2)
C(1)-Rh(1)-C(3)-N(2)	-118.3(3)
C(2)-Rh(1)-C(3)-N(2)	42(2)
Cl(1)-Rh(1)-C(3)-N(2)	63.6(3)
C(1)-Rh(1)-C(3)-N(1)	62.4(3)
C(2)-Rh(1)-C(3)-N(1)	-138(2)
Cl(1)-Rh(1)-C(3)-N(1)	-115.8(3)
C(3)-N(2)-C(4)-C(5)	0.3(4)
C(10)-N(2)-C(4)-C(5)	-178.0(3)
C(3)-N(2)-C(4)-C(11)	-179.9(3)
C(10)-N(2)-C(4)-C(11)	1.8(5)
N(2)-C(4)-C(5)-N(1)	0.0(3)
C(11)-C(4)-C(5)-N(1)	-179.8(3)
N(2)-C(4)-C(5)-C(6)	-177.4(4)
C(11)-C(4)-C(5)-C(6)	2.8(6)
C(3)-N(1)-C(5)-C(4)	-0.3(3)
C(9)-N(1)-C(5)-C(4)	179.5(3)
C(3)-N(1)-C(5)-C(6)	177.6(3)

C(9)-N(1)-C(5)-C(6)	-2.6(4)
C(4)-C(5)-C(6)-C(7)	178.3(3)
N(1)-C(5)-C(6)-C(7)	1.2(5)
C(5)-C(6)-C(7)-C(8)	0.3(5)
C(6)-C(7)-C(8)-C(9)	-0.4(6)
C(7)-C(8)-C(9)-N(1)	-1.0(5)
C(3)-N(1)-C(9)-C(8)	-177.7(3)
C(5)-N(1)-C(9)-C(8)	2.5(5)
C(5)-C(4)-C(11)-C(16)	41.7(5)
N(2)-C(4)-C(11)-C(16)	-138.1(3)
C(5)-C(4)-C(11)-C(12)	-136.3(3)
N(2)-C(4)-C(11)-C(12)	44.0(5)
C(16)-C(11)-C(12)-C(13)	1.4(5)
C(4)-C(11)-C(12)-C(13)	179.3(3)
C(11)-C(12)-C(13)-C(14)	-0.7(5)
C(17)-O(3)-C(14)-C(13)	174.1(3)
C(17)-O(3)-C(14)-C(15)	-6.5(5)
C(12)-C(13)-C(14)-O(3)	178.7(3)
C(12)-C(13)-C(14)-C(15)	-0.8(5)
O(3)-C(14)-C(15)-C(16)	-177.8(3)
C(13)-C(14)-C(15)-C(16)	1.5(5)
C(14)-C(15)-C(16)-C(11)	-0.9(5)
C(12)-C(11)-C(16)-C(15)	-0.6(4)
C(4)-C(11)-C(16)-C(15)	-178.6(3)

Symmetry transformations used to generate equivalent atoms:

Table S7. Crystal data and structure refinement for **6c**.

Empirical formula	$C_{16}H_{12}ClN_2O_2Rh$	
Formula weight	402.64	
Temperature	193(2) K	
Wavelength	0.71075 Å	
Crystal system	Monoclinic	
Space group	*P* 2_1/*a*	
Unit cell dimensions	a = 7.875(2) Å	α = 90°.
	b = 16.458(4) Å	β = 100.553(3)°.
	c = 12.568(3) Å	γ = 90°.
Volume	1601.3(7) $Å^3$	
Z	4	
Density (calculated)	1.670 Mg/m^3	
Absorption coefficient	1.240 mm^{-1}	
F(000)	800	
Crystal size	0.37 x 0.14 x 0.02 mm^3	
Theta range for data collection	1.65 to 27.50°.	
Index ranges	-10<=*h*<=9, -21<=*k*<=15, -15<=*l*<=16	
Reflections collected	13157	
Independent reflections	3679 [R(int) = 0.0456]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Integration	
Max. and min. transmission	0.968 and 0.741	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3679 / 0 / 200	
Goodness-of-fit on F^2	1.089	
Final R indices [I>2sigma(I)]	*R*1 = 0.0420, *wR*2 = 0.0827	
R indices (all data)	*R*1 = 0.0579, *wR*2 = 0.0896	
Largest diff. peak and hole	0.769 and -0.416 e.$Å^{-3}$	

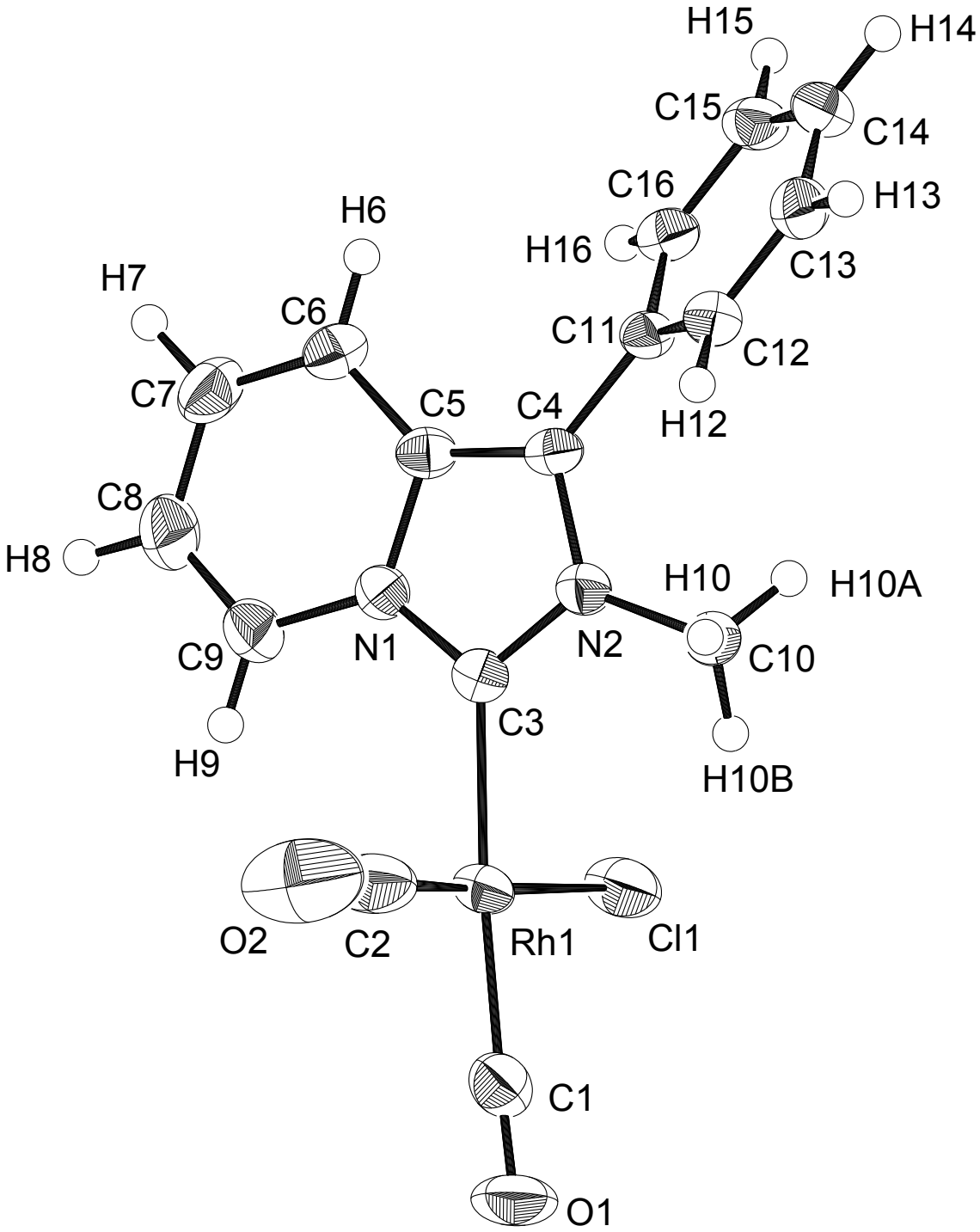


Figure S2. ORTEP drawing of **6c** with thermal ellipsoids at 50% probability.

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh(1)	9916(1)	4592(1)	2854(1)	34(1)
Cl(1)	7256(1)	5042(1)	3215(1)	49(1)
O(1)	8822(4)	2840(1)	3031(3)	60(1)
O(2)	13335(5)	4083(2)	2429(4)	100(2)
N(1)	11446(4)	6316(2)	3314(2)	31(1)
N(2)	9893(4)	6245(2)	1730(2)	31(1)
C(1)	9232(5)	3494(2)	2996(3)	42(1)
C(2)	12021(6)	4278(2)	2575(4)	60(1)
C(3)	10512(5)	5790(2)	2610(3)	32(1)
C(4)	10406(4)	7056(2)	1869(3)	29(1)
C(5)	11388(4)	7107(2)	2877(3)	30(1)
C(6)	12318(5)	7733(2)	3509(3)	37(1)
C(7)	13221(5)	7556(2)	4495(3)	45(1)
C(8)	13251(6)	6751(2)	4917(3)	51(1)
C(9)	12381(5)	6146(2)	4341(3)	41(1)
C(10)	8754(5)	5911(2)	784(3)	38(1)
C(11)	9932(4)	7690(2)	1047(3)	28(1)
C(12)	10054(4)	7563(2)	-33(3)	34(1)
C(13)	9597(5)	8170(2)	-790(3)	40(1)
C(14)	9032(5)	8923(2)	-484(3)	42(1)
C(15)	8944(5)	9055(2)	583(3)	38(1)
C(16)	9385(5)	8450(2)	1355(3)	34(1)

Table S9. Bond lengths [Å] and angles [°] for **6c**.

Rh(1)-C(2)	1.830(5)
Rh(1)-C(1)	1.903(4)
Rh(1)-C(3)	2.064(3)
Rh(1)-Cl(1)	2.3435(12)
O(1)-C(1)	1.128(4)
O(2)-C(2)	1.130(5)
N(1)-C(3)	1.354(4)
N(1)-C(9)	1.391(4)
N(1)-C(5)	1.411(4)
N(2)-C(3)	1.350(4)
N(2)-C(4)	1.396(4)
N(2)-C(10)	1.459(4)
C(4)-C(5)	1.361(5)
C(4)-C(11)	1.468(4)
C(5)-C(6)	1.420(5)
C(6)-C(7)	1.343(5)
C(7)-C(8)	1.426(5)
C(8)-C(9)	1.343(5)
C(11)-C(12)	1.394(5)
C(11)-C(16)	1.400(4)
C(12)-C(13)	1.381(5)
C(13)-C(14)	1.393(5)
C(14)-C(15)	1.372(6)
C(15)-C(16)	1.390(5)
C(2)-Rh(1)-C(1)	91.84(18)
C(2)-Rh(1)-C(3)	90.15(16)
C(1)-Rh(1)-C(3)	175.95(15)
C(2)-Rh(1)-Cl(1)	177.94(13)
C(1)-Rh(1)-Cl(1)	90.19(13)
C(3)-Rh(1)-Cl(1)	87.84(10)

C(3)-N(1)-C(9)	127.6(3)
C(3)-N(1)-C(5)	111.1(3)
C(9)-N(1)-C(5)	121.3(3)
C(3)-N(2)-C(4)	112.0(3)
C(3)-N(2)-C(10)	122.3(3)
C(4)-N(2)-C(10)	125.6(3)
O(1)-C(1)-Rh(1)	176.8(4)
O(2)-C(2)-Rh(1)	178.4(5)
N(2)-C(3)-N(1)	104.6(3)
N(2)-C(3)-Rh(1)	126.4(3)
N(1)-C(3)-Rh(1)	128.6(3)
C(5)-C(4)-N(2)	106.1(3)
C(5)-C(4)-C(11)	129.7(3)
N(2)-C(4)-C(11)	124.2(3)
C(4)-C(5)-N(1)	106.1(3)
C(4)-C(5)-C(6)	135.5(3)
N(1)-C(5)-C(6)	118.3(3)
C(7)-C(6)-C(5)	119.4(3)
C(6)-C(7)-C(8)	121.0(4)
C(9)-C(8)-C(7)	121.0(4)
C(8)-C(9)-N(1)	118.9(3)
C(12)-C(11)-C(16)	118.9(3)
C(12)-C(11)-C(4)	121.6(3)
C(16)-C(11)-C(4)	119.4(3)
C(13)-C(12)-C(11)	120.4(3)
C(12)-C(13)-C(14)	120.6(4)
C(15)-C(14)-C(13)	119.1(3)
C(14)-C(15)-C(16)	121.2(3)
C(15)-C(16)-C(11)	119.8(4)

Symmetry transformations used to generate equivalent atoms:

Table S10. Anisotropic displacement parameters ($Å^2$ x 10^3) for **6c**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh(1)	40(1)	24(1)	38(1)	5(1)	5(1)	2(1)
Cl(1)	47(1)	38(1)	66(1)	12(1)	17(1)	5(1)
O(1)	84(2)	26(1)	67(2)	4(1)	9(2)	-9(1)
O(2)	77(3)	63(2)	176(5)	-4(2)	66(3)	9(2)
N(1)	33(2)	32(1)	27(2)	3(1)	4(1)	-2(1)
N(2)	35(2)	25(1)	32(2)	0(1)	2(1)	0(1)
C(1)	47(2)	37(2)	38(2)	1(2)	3(2)	6(2)
C(2)	56(3)	33(2)	94(4)	7(2)	24(3)	3(2)
C(3)	33(2)	30(2)	32(2)	3(1)	5(2)	-1(1)
C(4)	30(2)	23(1)	35(2)	1(1)	9(2)	-3(1)
C(5)	34(2)	28(2)	29(2)	1(1)	11(2)	-2(1)
C(6)	38(2)	34(2)	39(2)	-2(2)	11(2)	-8(2)
C(7)	49(2)	48(2)	38(2)	-8(2)	3(2)	-15(2)
C(8)	53(3)	61(3)	34(2)	5(2)	-5(2)	-3(2)
C(9)	43(2)	43(2)	34(2)	8(2)	3(2)	1(2)
C(10)	41(2)	28(2)	42(2)	1(2)	-5(2)	-3(1)
C(11)	26(2)	26(2)	33(2)	5(1)	7(2)	-3(1)
C(12)	35(2)	30(2)	37(2)	1(1)	4(2)	0(1)
C(13)	42(2)	42(2)	32(2)	2(2)	1(2)	-6(2)
C(14)	40(2)	33(2)	50(3)	12(2)	4(2)	1(2)
C(15)	34(2)	26(2)	56(3)	3(2)	11(2)	2(1)
C(16)	34(2)	30(2)	41(2)	-1(2)	10(2)	-4(1)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x10^3) for **6c**.

	x	y	z	U(eq)
H(6)	12300	8272	3238	44
H(7)	13851	7973	4917	54
H(8)	13897	6641	5618	61
H(9)	12403	5612	4629	49
H(10)	9447	5722	260	58
H(10A)	7951	6333	451	58
H(10B)	8100	5455	1006	58
H(12)	10455	7056	-250	41
H(13)	9668	8074	-1525	47
H(14)	8712	9338	-1006	50
H(15)	8575	9569	797	46
H(16)	9315	8551	2090	41

Table S12. Torsion angles [°] for **6c**.

C(2)-Rh(1)-C(1)-O(1)	-70(7)
C(3)-Rh(1)-C(1)-O(1)	49(8)
Cl(1)-Rh(1)-C(1)-O(1)	110(7)
C(1)-Rh(1)-C(2)-O(2)	-84(13)
C(3)-Rh(1)-C(2)-O(2)	99(13)
Cl(1)-Rh(1)-C(2)-O(2)	86(14)
C(4)-N(2)-C(3)-N(1)	-0.6(4)
C(10)-N(2)-C(3)-N(1)	-177.8(3)
C(4)-N(2)-C(3)-Rh(1)	173.5(2)
C(10)-N(2)-C(3)-Rh(1)	-3.7(5)
C(9)-N(1)-C(3)-N(2)	-178.7(3)
C(5)-N(1)-C(3)-N(2)	0.9(4)
C(9)-N(1)-C(3)-Rh(1)	7.3(6)
C(5)-N(1)-C(3)-Rh(1)	-173.1(3)
C(2)-Rh(1)-C(3)-N(2)	104.6(4)
C(1)-Rh(1)-C(3)-N(2)	-15(2)
Cl(1)-Rh(1)-C(3)-N(2)	-75.9(3)
C(2)-Rh(1)-C(3)-N(1)	-82.7(4)
C(1)-Rh(1)-C(3)-N(1)	158(2)
Cl(1)-Rh(1)-C(3)-N(1)	96.8(3)
C(3)-N(2)-C(4)-C(5)	0.1(4)
C(10)-N(2)-C(4)-C(5)	177.2(3)
C(3)-N(2)-C(4)-C(11)	179.8(3)
C(10)-N(2)-C(4)-C(11)	-3.1(5)
N(2)-C(4)-C(5)-N(1)	0.4(4)
C(11)-C(4)-C(5)-N(1)	-179.2(3)
N(2)-C(4)-C(5)-C(6)	178.6(4)
C(11)-C(4)-C(5)-C(6)	-1.0(7)
C(3)-N(1)-C(5)-C(4)	-0.8(4)
C(9)-N(1)-C(5)-C(4)	178.8(3)
C(3)-N(1)-C(5)-C(6)	-179.4(3)

C(9)-N(1)-C(5)-C(6)	0.2(5)
C(4)-C(5)-C(6)-C(7)	-177.8(4)
N(1)-C(5)-C(6)-C(7)	0.2(5)
C(5)-C(6)-C(7)-C(8)	-0.5(6)
C(6)-C(7)-C(8)-C(9)	0.2(7)
C(7)-C(8)-C(9)-N(1)	0.3(6)
C(3)-N(1)-C(9)-C(8)	179.1(4)
C(5)-N(1)-C(9)-C(8)	-0.5(5)
C(5)-C(4)-C(11)-C(12)	133.6(4)
N(2)-C(4)-C(11)-C(12)	-46.0(5)
C(5)-C(4)-C(11)-C(16)	-44.8(5)
N(2)-C(4)-C(11)-C(16)	135.7(3)
C(16)-C(11)-C(12)-C(13)	-1.8(5)
C(4)-C(11)-C(12)-C(13)	179.9(3)
C(11)-C(12)-C(13)-C(14)	1.0(6)
C(12)-C(13)-C(14)-C(15)	0.4(6)
C(13)-C(14)-C(15)-C(16)	-0.9(6)
C(14)-C(15)-C(16)-C(11)	0.1(5)
C(12)-C(11)-C(16)-C(15)	1.2(5)
C(4)-C(11)-C(16)-C(15)	179.6(3)

Symmetry transformations used to generate equivalent atoms:

Table S13. Crystal data and structure refinement for **6e**.

Empirical formula	$C_{16}H_7ClF_5N_2O_2Rh$	
Formula weight	492.60	
Temperature	123(2) K	
Wavelength	0.71075 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.436(3) Å	α = 82.159(8)°.
	b = 12.000(3) Å	β = 89.752(9)°.
	c = 14.960(4) Å	γ = 66.314(6)°.
Volume	1697.0(7) $Å^3$	
Z	4	
Density (calculated)	1.928 Mg/m^3	
Absorption coefficient	1.230 mm^{-1}	
F(000)	960	
Crystal size	0.29 x 0.17 x 0.14 mm^3	
Theta range for data collection	1.87 to 27.50°.	
Index ranges	-13<=*h*<=12, -15<=*k*<=11, -19<=*l*<=19	
Reflections collected	13809	
Independent reflections	7738 [R(int) = 0.0392]	
Completeness to theta = 27.50°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.676	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7738 / 0 / 489	
Goodness-of-fit on F^2	0.875	
Final R indices [I>2sigma(I)]	*R1* = 0.0296, *wR2* = 0.0571	
R indices (all data)	*R1* = 0.0393, *wR2* = 0.0596	
Largest diff. peak and hole	0.743 and -0.881 $e.Å^{-3}$	

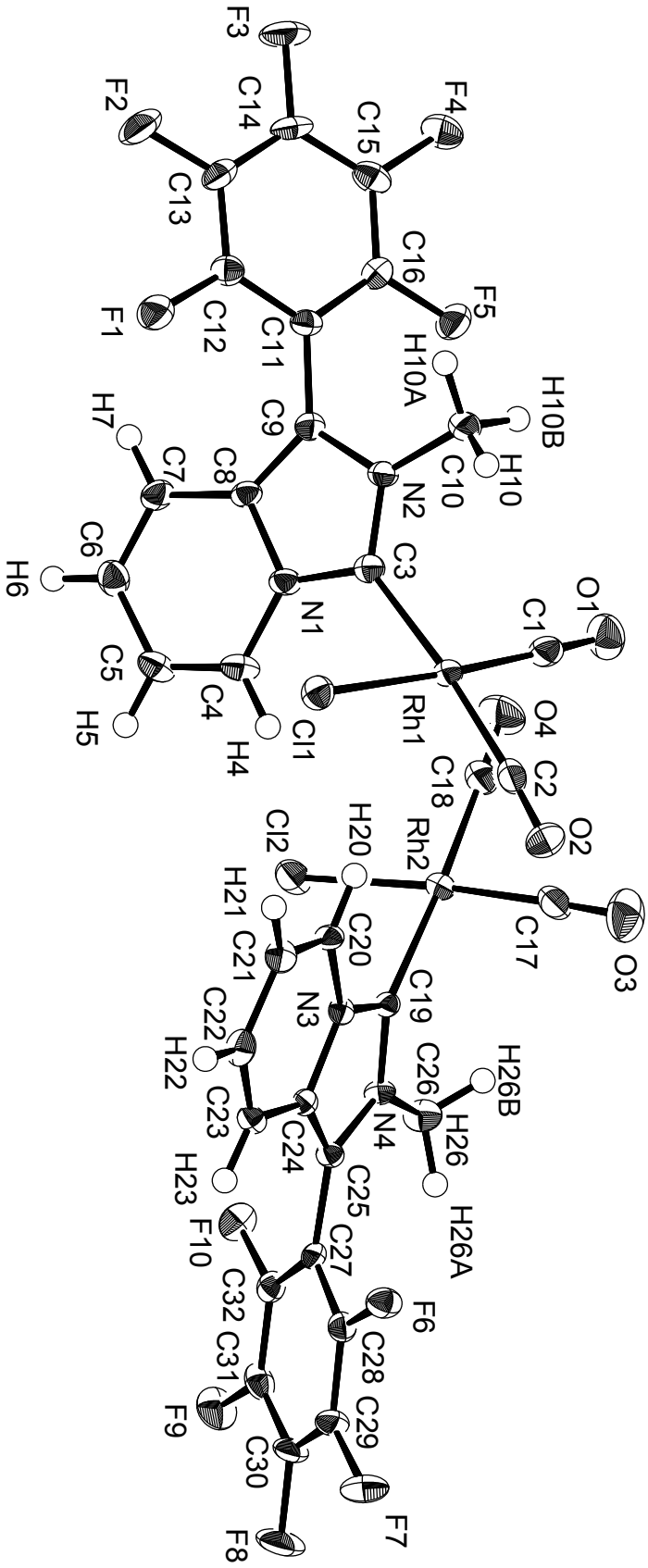


Figure S3. ORTEP drawing of **6e** with thermal ellipsoids at 50% probability.

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **6e**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh(1)	4725(1)	2588(1)	3103(1)	18(1)
Rh(2)	2704(1)	6255(1)	1977(1)	17(1)
Cl(1)	3628(1)	1449(1)	2520(1)	23(1)
Cl(2)	333(1)	6939(1)	2309(1)	30(1)
F(1)	1695(2)	554(2)	6390(1)	32(1)
F(2)	1799(2)	-219(2)	8164(1)	38(1)
F(3)	3407(2)	275(2)	9332(1)	39(1)
F(4)	4800(2)	1682(2)	8721(1)	35(1)
F(5)	4555(2)	2613(2)	6950(1)	31(1)
F(6)	2020(2)	6609(2)	-2455(1)	23(1)
F(7)	937(2)	8288(2)	-3934(1)	34(1)
F(8)	-1347(2)	10402(2)	-3823(1)	40(1)
F(9)	-2528(2)	10817(2)	-2221(1)	33(1)
F(10)	-1438(2)	9163(2)	-726(1)	25(1)
O(1)	6032(2)	4005(2)	3957(2)	37(1)
O(2)	6084(2)	2701(2)	1309(1)	32(1)
O(3)	5623(2)	5531(2)	1412(2)	45(1)
O(4)	3300(2)	6470(2)	3918(2)	41(1)
N(1)	2194(2)	3088(2)	4271(2)	18(1)
N(2)	4067(2)	1975(2)	5080(2)	18(1)
N(3)	1992(2)	5299(2)	306(2)	14(1)
N(4)	1476(2)	7230(2)	48(2)	15(1)
C(1)	5544(3)	3459(3)	3621(2)	24(1)
C(2)	5622(3)	2648(3)	1993(2)	23(1)
C(3)	3615(3)	2560(3)	4239(2)	18(1)
C(4)	1216(3)	3845(3)	3585(2)	24(1)
C(5)	-154(3)	4279(3)	3743(2)	25(1)
C(6)	-614(3)	3963(3)	4606(2)	24(1)

C(7)	314(3)	3267(3)	5284(2)	21(1)
C(8)	1769(3)	2812(3)	5140(2)	18(1)
C(9)	2976(3)	2106(3)	5646(2)	19(1)
C(10)	5566(3)	1211(3)	5348(2)	25(1)
C(11)	3151(3)	1585(3)	6608(2)	18(1)
C(12)	2464(3)	858(3)	6945(2)	20(1)
C(13)	2527(3)	441(3)	7857(2)	24(1)
C(14)	3324(3)	699(3)	8447(2)	24(1)
C(15)	4034(3)	1413(3)	8136(2)	24(1)
C(16)	3919(3)	1860(3)	7236(2)	21(1)
C(17)	4507(3)	5800(3)	1643(2)	25(1)
C(18)	3123(3)	6368(3)	3200(2)	26(1)
C(19)	2069(3)	6246(3)	684(2)	14(1)
C(20)	2469(3)	4069(3)	707(2)	17(1)
C(21)	2289(3)	3257(3)	237(2)	20(1)
C(22)	1588(3)	3645(3)	-634(2)	21(1)
C(23)	1119(3)	4832(3)	-1028(2)	16(1)
C(24)	1336(3)	5702(3)	-558(2)	14(1)
C(25)	1011(3)	6940(3)	-723(2)	15(1)
C(26)	1387(3)	8442(3)	189(2)	23(1)
C(27)	353(3)	7838(3)	-1535(2)	16(1)
C(28)	889(3)	7647(3)	-2376(2)	18(1)
C(29)	338(3)	8502(3)	-3142(2)	23(1)
C(30)	-801(3)	9569(3)	-3089(2)	26(1)
C(31)	-1391(3)	9789(3)	-2268(2)	23(1)
C(32)	-809(3)	8922(3)	-1517(2)	19(1)

Table S15. Bond lengths [Å] and angles [°] for **6e**.

Rh(1)-C(1)	1.835(3)
Rh(1)-C(2)	1.909(3)
Rh(1)-C(3)	2.057(3)
Rh(1)-Cl(1)	2.3520(8)
Rh(2)-C(17)	1.825(3)
Rh(2)-C(18)	1.918(3)
Rh(2)-C(19)	2.050(3)
Rh(2)-Cl(2)	2.3484(9)
F(1)-C(12)	1.338(3)
F(2)-C(13)	1.341(3)
F(3)-C(14)	1.341(3)
F(4)-C(15)	1.342(3)
F(5)-C(16)	1.347(3)
F(6)-C(28)	1.348(3)
F(7)-C(29)	1.344(3)
F(8)-C(30)	1.334(3)
F(9)-C(31)	1.335(3)
F(10)-C(32)	1.359(3)
O(1)-C(1)	1.141(3)
O(2)-C(2)	1.134(3)
O(3)-C(17)	1.142(3)
O(4)-C(18)	1.123(3)
N(1)-C(3)	1.363(3)
N(1)-C(4)	1.389(4)
N(1)-C(8)	1.412(3)
N(2)-C(3)	1.339(3)
N(2)-C(9)	1.387(3)
N(2)-C(10)	1.484(3)
N(3)-C(19)	1.366(3)
N(3)-C(24)	1.395(3)
N(3)-C(20)	1.399(3)

N(4)-C(19)	1.339(3)
N(4)-C(25)	1.393(3)
N(4)-C(26)	1.464(3)
C(4)-C(5)	1.343(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.430(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.339(4)
C(6)-H(6)	0.9500
C(7)-C(8)	1.418(4)
C(7)-H(7)	0.9500
C(8)-C(9)	1.361(4)
C(9)-C(11)	1.469(4)
C(10)-H(10)	0.9800
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(11)-C(12)	1.382(3)
C(11)-C(16)	1.393(4)
C(12)-C(13)	1.379(4)
C(13)-C(14)	1.362(4)
C(14)-C(15)	1.378(4)
C(15)-C(16)	1.366(4)
C(20)-C(21)	1.347(4)
C(20)-H(20)	0.9500
C(21)-C(22)	1.421(4)
C(21)-H(21)	0.9500
C(22)-C(23)	1.353(4)
C(22)-H(22)	0.9500
C(23)-C(24)	1.423(4)
C(23)-H(23)	0.9500
C(24)-C(25)	1.371(4)
C(25)-C(27)	1.470(4)
C(26)-H(26)	0.9800

C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(27)-C(32)	1.381(4)
C(27)-C(28)	1.385(4)
C(28)-C(29)	1.381(4)
C(29)-C(30)	1.365(4)
C(30)-C(31)	1.382(4)
C(31)-C(32)	1.375(4)

C(1)-Rh(1)-C(2)	93.66(12)
C(1)-Rh(1)-C(3)	89.48(12)
C(2)-Rh(1)-C(3)	175.50(12)
C(1)-Rh(1)-Cl(1)	176.74(9)
C(2)-Rh(1)-Cl(1)	89.56(9)
C(3)-Rh(1)-Cl(1)	87.33(8)
C(17)-Rh(2)-C(18)	94.75(13)
C(17)-Rh(2)-C(19)	90.12(12)
C(18)-Rh(2)-C(19)	174.67(12)
C(17)-Rh(2)-Cl(2)	175.91(10)
C(18)-Rh(2)-Cl(2)	88.19(9)
C(19)-Rh(2)-Cl(2)	86.84(7)
C(3)-N(1)-C(4)	127.9(2)
C(3)-N(1)-C(8)	111.2(2)
C(4)-N(1)-C(8)	120.8(2)
C(3)-N(2)-C(9)	112.5(2)
C(3)-N(2)-C(10)	123.0(2)
C(9)-N(2)-C(10)	124.3(2)
C(19)-N(3)-C(24)	111.5(2)
C(19)-N(3)-C(20)	126.6(2)
C(24)-N(3)-C(20)	121.9(2)
C(19)-N(4)-C(25)	112.3(2)
C(19)-N(4)-C(26)	121.1(2)
C(25)-N(4)-C(26)	126.6(2)

O(1)-C(1)-Rh(1)	178.5(3)
O(2)-C(2)-Rh(1)	176.1(3)
N(2)-C(3)-N(1)	104.3(2)
N(2)-C(3)-Rh(1)	129.8(2)
N(1)-C(3)-Rh(1)	125.8(2)
C(5)-C(4)-N(1)	119.4(3)
C(5)-C(4)-H(4)	120.3
N(1)-C(4)-H(4)	120.3
C(4)-C(5)-C(6)	120.7(3)
C(4)-C(5)-H(5)	119.6
C(6)-C(5)-H(5)	119.6
C(7)-C(6)-C(5)	120.7(3)
C(7)-C(6)-H(6)	119.6
C(5)-C(6)-H(6)	119.6
C(6)-C(7)-C(8)	119.7(3)
C(6)-C(7)-H(7)	120.1
C(8)-C(7)-H(7)	120.1
C(9)-C(8)-N(1)	105.4(2)
C(9)-C(8)-C(7)	136.1(3)
N(1)-C(8)-C(7)	118.4(3)
C(8)-C(9)-N(2)	106.6(2)
C(8)-C(9)-C(11)	128.6(3)
N(2)-C(9)-C(11)	124.8(3)
N(2)-C(10)-H(10)	109.5
N(2)-C(10)-H(10A)	109.5
H(10)-C(10)-H(10A)	109.5
N(2)-C(10)-H(10B)	109.5
H(10)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(12)-C(11)-C(16)	116.3(3)
C(12)-C(11)-C(9)	120.8(3)
C(16)-C(11)-C(9)	122.7(2)
F(1)-C(12)-C(13)	118.0(2)

F(1)-C(12)-C(11)	120.4(3)
C(13)-C(12)-C(11)	121.6(3)
F(2)-C(13)-C(14)	119.8(3)
F(2)-C(13)-C(12)	119.9(3)
C(14)-C(13)-C(12)	120.3(2)
F(3)-C(14)-C(13)	120.4(2)
F(3)-C(14)-C(15)	119.8(3)
C(13)-C(14)-C(15)	119.8(3)
F(4)-C(15)-C(16)	121.0(2)
F(4)-C(15)-C(14)	119.7(3)
C(16)-C(15)-C(14)	119.3(3)
F(5)-C(16)-C(15)	118.6(3)
F(5)-C(16)-C(11)	118.8(2)
C(15)-C(16)-C(11)	122.6(2)
O(3)-C(17)-Rh(2)	178.2(3)
O(4)-C(18)-Rh(2)	176.5(3)
N(4)-C(19)-N(3)	104.3(2)
N(4)-C(19)-Rh(2)	126.3(2)
N(3)-C(19)-Rh(2)	129.03(19)
C(21)-C(20)-N(3)	118.6(3)
C(21)-C(20)-H(20)	120.7
N(3)-C(20)-H(20)	120.7
C(20)-C(21)-C(22)	120.9(3)
C(20)-C(21)-H(21)	119.6
C(22)-C(21)-H(21)	119.6
C(23)-C(22)-C(21)	121.1(3)
C(23)-C(22)-H(22)	119.4
C(21)-C(22)-H(22)	119.4
C(22)-C(23)-C(24)	119.1(3)
C(22)-C(23)-H(23)	120.4
C(24)-C(23)-H(23)	120.4
C(25)-C(24)-N(3)	105.8(2)
C(25)-C(24)-C(23)	135.8(3)

N(3)-C(24)-C(23)	118.4(2)
C(24)-C(25)-N(4)	106.1(2)
C(24)-C(25)-C(27)	130.1(3)
N(4)-C(25)-C(27)	123.8(3)
N(4)-C(26)-H(26)	109.5
N(4)-C(26)-H(26A)	109.5
H(26)-C(26)-H(26A)	109.5
N(4)-C(26)-H(26B)	109.5
H(26)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(32)-C(27)-C(28)	115.5(3)
C(32)-C(27)-C(25)	123.3(3)
C(28)-C(27)-C(25)	121.2(3)
F(6)-C(28)-C(29)	118.0(3)
F(6)-C(28)-C(27)	119.4(3)
C(29)-C(28)-C(27)	122.6(3)
F(7)-C(29)-C(30)	120.3(3)
F(7)-C(29)-C(28)	119.9(3)
C(30)-C(29)-C(28)	119.8(3)
F(8)-C(30)-C(29)	120.5(3)
F(8)-C(30)-C(31)	119.8(3)
C(29)-C(30)-C(31)	119.8(3)
F(9)-C(31)-C(32)	121.3(3)
F(9)-C(31)-C(30)	119.7(3)
C(32)-C(31)-C(30)	118.9(3)
F(10)-C(32)-C(31)	117.1(3)
F(10)-C(32)-C(27)	119.5(3)
C(31)-C(32)-C(27)	123.4(3)

Symmetry transformations used to generate equivalent atoms:

Table S16. Anisotropic displacement parameters ($Å^2$ x 10^3) for **6e**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh(1)	18(1)	22(1)	14(1)	-1(1)	2(1)	-8(1)
Rh(2)	18(1)	18(1)	15(1)	-1(1)	-2(1)	-6(1)
Cl(1)	26(1)	24(1)	23(1)	-5(1)	2(1)	-13(1)
Cl(2)	19(1)	50(1)	17(1)	-7(1)	3(1)	-9(1)
F(1)	40(1)	37(1)	26(1)	0(1)	-1(1)	-25(1)
F(2)	48(1)	39(1)	32(1)	6(1)	9(1)	-27(1)
F(3)	49(1)	46(1)	14(1)	6(1)	3(1)	-15(1)
F(4)	40(1)	51(1)	17(1)	-7(1)	-3(1)	-22(1)
F(5)	40(1)	40(1)	26(1)	-1(1)	2(1)	-29(1)
F(6)	22(1)	24(1)	18(1)	-3(1)	3(1)	-5(1)
F(7)	48(1)	39(1)	14(1)	1(1)	2(1)	-16(1)
F(8)	45(1)	37(1)	27(1)	16(1)	-18(1)	-12(1)
F(9)	24(1)	18(1)	48(1)	1(1)	-6(1)	0(1)
F(10)	25(1)	21(1)	28(1)	-8(1)	9(1)	-7(1)
O(1)	36(1)	50(2)	33(2)	-17(1)	4(1)	-24(1)
O(2)	32(1)	47(2)	19(1)	-5(1)	9(1)	-18(1)
O(3)	23(1)	43(2)	63(2)	-8(1)	8(1)	-9(1)
O(4)	48(2)	58(2)	21(1)	-11(1)	-4(1)	-24(2)
N(1)	22(1)	22(2)	12(1)	-3(1)	1(1)	-9(1)
N(2)	17(1)	20(1)	14(1)	1(1)	0(1)	-6(1)
N(3)	12(1)	11(1)	17(1)	-2(1)	1(1)	-3(1)
N(4)	19(1)	11(1)	13(1)	-2(1)	1(1)	-5(1)
C(1)	23(2)	30(2)	17(2)	-2(2)	5(1)	-9(2)
C(2)	18(2)	21(2)	29(2)	-1(2)	-4(1)	-8(2)
C(3)	20(2)	18(2)	17(2)	-2(1)	1(1)	-8(1)
C(4)	29(2)	24(2)	14(2)	-1(1)	-1(1)	-7(2)
C(5)	25(2)	28(2)	17(2)	-3(1)	-5(1)	-7(2)
C(6)	23(2)	30(2)	23(2)	-8(2)	1(1)	-12(2)
C(7)	25(2)	27(2)	15(2)	-6(1)	6(1)	-13(2)

C(8)	24(2)	20(2)	12(2)	-3(1)	1(1)	-12(1)
C(9)	21(2)	23(2)	15(2)	-2(1)	1(1)	-11(1)
C(10)	18(2)	29(2)	22(2)	4(2)	-1(1)	-6(2)
C(11)	19(2)	17(2)	15(2)	0(1)	0(1)	-4(1)
C(12)	23(2)	22(2)	17(2)	-4(1)	1(1)	-9(2)
C(13)	24(2)	19(2)	25(2)	3(1)	7(1)	-8(2)
C(14)	29(2)	19(2)	13(2)	3(1)	6(1)	-2(2)
C(15)	26(2)	25(2)	18(2)	-6(1)	-2(1)	-5(2)
C(16)	21(2)	21(2)	21(2)	-3(1)	4(1)	-10(2)
C(17)	23(2)	26(2)	26(2)	0(2)	-7(1)	-10(2)
C(18)	20(2)	30(2)	24(2)	-2(2)	-2(1)	-8(2)
C(19)	13(1)	16(2)	13(2)	-1(1)	2(1)	-5(1)
C(20)	16(1)	15(2)	17(2)	3(1)	0(1)	-4(1)
C(21)	18(2)	13(2)	27(2)	-1(1)	1(1)	-4(1)
C(22)	22(2)	22(2)	25(2)	-9(1)	5(1)	-11(2)
C(23)	15(1)	21(2)	12(2)	-6(1)	2(1)	-5(1)
C(24)	11(1)	18(2)	13(2)	-4(1)	4(1)	-5(1)
C(25)	16(1)	18(2)	12(2)	-3(1)	1(1)	-6(1)
C(26)	32(2)	15(2)	22(2)	-4(1)	1(1)	-10(2)
C(27)	18(2)	18(2)	15(2)	0(1)	0(1)	-12(1)
C(28)	17(2)	18(2)	20(2)	-2(1)	0(1)	-8(1)
C(29)	28(2)	31(2)	12(2)	-1(1)	-2(1)	-15(2)
C(30)	30(2)	25(2)	22(2)	11(2)	-12(1)	-14(2)
C(31)	16(2)	15(2)	33(2)	-1(2)	-5(1)	-4(1)
C(32)	20(2)	18(2)	21(2)	-3(1)	2(1)	-11(1)

Table S17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x10^3) for **6e**.

	x	y	z	U(eq)
H(4)	1513	4054	3009	28
H(5)	-826	4801	3277	30
H(6)	-1588	4251	4698	29
H(7)	0	3080	5859	26
H(10)	6061	891	4819	37
H(10A)	5643	523	5811	37
H(10B)	5985	1715	5590	37
H(20)	2911	3812	1297	21
H(21)	2634	2413	492	24
H(22)	1447	3060	-945	26
H(23)	652	5082	-1611	20
H(26)	556	8846	522	34
H(26A)	1319	8945	-397	34
H(26B)	2228	8345	538	34

Table S18. Torsion angles [°] for **6e**.

C(2)-Rh(1)-C(1)-O(1)	166(12)
C(3)-Rh(1)-C(1)-O(1)	-11(12)
Cl(1)-Rh(1)-C(1)-O(1)	-23(13)
C(1)-Rh(1)-C(2)-O(2)	-135(4)
C(3)-Rh(1)-C(2)-O(2)	-1(5)
Cl(1)-Rh(1)-C(2)-O(2)	46(4)
C(9)-N(2)-C(3)-N(1)	0.5(3)
C(10)-N(2)-C(3)-N(1)	176.8(2)
C(9)-N(2)-C(3)-Rh(1)	-175.2(2)
C(10)-N(2)-C(3)-Rh(1)	1.2(4)
C(4)-N(1)-C(3)-N(2)	177.1(3)
C(8)-N(1)-C(3)-N(2)	-0.6(3)
C(4)-N(1)-C(3)-Rh(1)	-7.0(4)
C(8)-N(1)-C(3)-Rh(1)	175.23(19)
C(1)-Rh(1)-C(3)-N(2)	-68.3(3)
C(2)-Rh(1)-C(3)-N(2)	157.3(14)
Cl(1)-Rh(1)-C(3)-N(2)	111.0(3)
C(1)-Rh(1)-C(3)-N(1)	116.9(3)
C(2)-Rh(1)-C(3)-N(1)	-17.5(17)
Cl(1)-Rh(1)-C(3)-N(1)	-63.8(2)
C(3)-N(1)-C(4)-C(5)	179.8(3)
C(8)-N(1)-C(4)-C(5)	-2.6(4)
N(1)-C(4)-C(5)-C(6)	-0.4(5)
C(4)-C(5)-C(6)-C(7)	2.6(5)
C(5)-C(6)-C(7)-C(8)	-1.6(5)
C(3)-N(1)-C(8)-C(9)	0.6(3)
C(4)-N(1)-C(8)-C(9)	-177.4(3)
C(3)-N(1)-C(8)-C(7)	-178.5(3)
C(4)-N(1)-C(8)-C(7)	3.6(4)
C(6)-C(7)-C(8)-C(9)	179.9(3)
C(6)-C(7)-C(8)-N(1)	-1.4(4)

N(1)-C(8)-C(9)-N(2)	-0.3(3)
C(7)-C(8)-C(9)-N(2)	178.5(3)
N(1)-C(8)-C(9)-C(11)	178.5(3)
C(7)-C(8)-C(9)-C(11)	-2.7(6)
C(3)-N(2)-C(9)-C(8)	-0.1(3)
C(10)-N(2)-C(9)-C(8)	-176.4(3)
C(3)-N(2)-C(9)-C(11)	-179.0(3)
C(10)-N(2)-C(9)-C(11)	4.7(5)
C(8)-C(9)-C(11)-C(12)	54.8(4)
N(2)-C(9)-C(11)-C(12)	-126.6(3)
C(8)-C(9)-C(11)-C(16)	-120.4(4)
N(2)-C(9)-C(11)-C(16)	58.2(4)
C(16)-C(11)-C(12)-F(1)	179.6(3)
C(9)-C(11)-C(12)-F(1)	4.2(4)
C(16)-C(11)-C(12)-C(13)	0.7(4)
C(9)-C(11)-C(12)-C(13)	-174.8(3)
F(1)-C(12)-C(13)-F(2)	-1.8(4)
C(11)-C(12)-C(13)-F(2)	177.2(3)
F(1)-C(12)-C(13)-C(14)	178.3(3)
C(11)-C(12)-C(13)-C(14)	-2.7(5)
F(2)-C(13)-C(14)-F(3)	1.3(4)
C(12)-C(13)-C(14)-F(3)	-178.8(3)
F(2)-C(13)-C(14)-C(15)	-177.8(3)
C(12)-C(13)-C(14)-C(15)	2.1(5)
F(3)-C(14)-C(15)-F(4)	-0.2(4)
C(13)-C(14)-C(15)-F(4)	178.9(3)
F(3)-C(14)-C(15)-C(16)	-178.7(3)
C(13)-C(14)-C(15)-C(16)	0.4(5)
F(4)-C(15)-C(16)-F(5)	-2.2(4)
C(14)-C(15)-C(16)-F(5)	176.3(3)
F(4)-C(15)-C(16)-C(11)	179.0(3)
C(14)-C(15)-C(16)-C(11)	-2.5(5)
C(12)-C(11)-C(16)-F(5)	-176.9(3)

C(9)-C(11)-C(16)-F(5)	-1.5(4)
C(12)-C(11)-C(16)-C(15)	1.9(4)
C(9)-C(11)-C(16)-C(15)	177.3(3)
C(18)-Rh(2)-C(17)-O(3)	-147(10)
C(19)-Rh(2)-C(17)-O(3)	30(10)
Cl(2)-Rh(2)-C(17)-O(3)	-12(11)
C(17)-Rh(2)-C(18)-O(4)	159(5)
C(19)-Rh(2)-C(18)-O(4)	3(5)
Cl(2)-Rh(2)-C(18)-O(4)	-18(5)
C(25)-N(4)-C(19)-N(3)	0.6(3)
C(26)-N(4)-C(19)-N(3)	-178.5(2)
C(25)-N(4)-C(19)-Rh(2)	-172.71(17)
C(26)-N(4)-C(19)-Rh(2)	8.3(3)
C(24)-N(3)-C(19)-N(4)	-0.7(3)
C(20)-N(3)-C(19)-N(4)	-179.8(2)
C(24)-N(3)-C(19)-Rh(2)	172.27(17)
C(20)-N(3)-C(19)-Rh(2)	-6.8(4)
C(17)-Rh(2)-C(19)-N(4)	-99.3(2)
C(18)-Rh(2)-C(19)-N(4)	56.8(12)
Cl(2)-Rh(2)-C(19)-N(4)	78.0(2)
C(17)-Rh(2)-C(19)-N(3)	89.1(2)
C(18)-Rh(2)-C(19)-N(3)	-114.7(11)
Cl(2)-Rh(2)-C(19)-N(3)	-93.6(2)
C(19)-N(3)-C(20)-C(21)	179.1(2)
C(24)-N(3)-C(20)-C(21)	0.2(4)
N(3)-C(20)-C(21)-C(22)	-2.0(4)
C(20)-C(21)-C(22)-C(23)	2.0(4)
C(21)-C(22)-C(23)-C(24)	0.1(4)
C(19)-N(3)-C(24)-C(25)	0.6(3)
C(20)-N(3)-C(24)-C(25)	179.7(2)
C(19)-N(3)-C(24)-C(23)	-177.3(2)
C(20)-N(3)-C(24)-C(23)	1.8(3)
C(22)-C(23)-C(24)-C(25)	-179.0(3)

C(22)-C(23)-C(24)-N(3)	-1.9(4)
N(3)-C(24)-C(25)-N(4)	-0.3(3)
C(23)-C(24)-C(25)-N(4)	177.1(3)
N(3)-C(24)-C(25)-C(27)	177.8(2)
C(23)-C(24)-C(25)-C(27)	-4.8(5)
C(19)-N(4)-C(25)-C(24)	-0.2(3)
C(26)-N(4)-C(25)-C(24)	178.8(2)
C(19)-N(4)-C(25)-C(27)	-178.4(2)
C(26)-N(4)-C(25)-C(27)	0.6(4)
C(24)-C(25)-C(27)-C(32)	127.2(3)
N(4)-C(25)-C(27)-C(32)	-55.1(4)
C(24)-C(25)-C(27)-C(28)	-53.8(4)
N(4)-C(25)-C(27)-C(28)	124.0(3)
C(32)-C(27)-C(28)-F(6)	-179.7(2)
C(25)-C(27)-C(28)-F(6)	1.2(4)
C(32)-C(27)-C(28)-C(29)	2.4(4)
C(25)-C(27)-C(28)-C(29)	-176.7(2)
F(6)-C(28)-C(29)-F(7)	-0.6(4)
C(27)-C(28)-C(29)-F(7)	177.3(2)
F(6)-C(28)-C(29)-C(30)	-179.5(2)
C(27)-C(28)-C(29)-C(30)	-1.6(4)
F(7)-C(29)-C(30)-F(8)	1.2(4)
C(28)-C(29)-C(30)-F(8)	-179.9(2)
F(7)-C(29)-C(30)-C(31)	-178.7(2)
C(28)-C(29)-C(30)-C(31)	0.2(4)
F(8)-C(30)-C(31)-F(9)	2.0(4)
C(29)-C(30)-C(31)-F(9)	-178.1(2)
F(8)-C(30)-C(31)-C(32)	-179.7(2)
C(29)-C(30)-C(31)-C(32)	0.2(4)
F(9)-C(31)-C(32)-F(10)	-0.4(4)
C(30)-C(31)-C(32)-F(10)	-178.7(2)
F(9)-C(31)-C(32)-C(27)	179.0(2)
C(30)-C(31)-C(32)-C(27)	0.7(4)

C(28)-C(27)-C(32)-F(10)	177.4(2)
C(25)-C(27)-C(32)-F(10)	-3.5(4)
C(28)-C(27)-C(32)-C(31)	-2.0(4)
C(25)-C(27)-C(32)-C(31)	177.1(3)

Symmetry transformations used to generate equivalent atoms:

Table S19. Crystal data and structure refinement for **6g**.

Empirical formula	$C_{18}H_{12}ClN_2O_2Rh$	
Formula weight	426.66	
Temperature	193(2) K	
Wavelength	0.71075 Å	
Crystal system	Triclinic	
Space group	*P* -1	
Unit cell dimensions	a = 7.0475(15) Å	α = 95.006(2)°.
	b = 9.2569(18) Å	β = 104.3135(19)°.
	c = 14.015(3) Å	γ = 101.011(3)°.
Volume	860.9(3) $Å^3$	
Z	2	
Density (calculated)	1.646 Mg/m^3	
Absorption coefficient	1.158 mm^{-1}	
F(000)	424	
Crystal size	1.50 x 1.00 x 0.50 mm^3	
Theta range for data collection	2.26 to 27.50°.	
Index ranges	-5<=*h*<=9, -11<=*k*<=12, -18<=*l*<=17	
Reflections collected	6785	
Independent reflections	3874 [R(int) = 0.0225]	
Completeness to theta = 27.50°	98.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.561 and 0.371	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3874 / 0 / 218	
Goodness-of-fit on F^2	1.009	
Final R indices [I>2sigma(I)]	*R*1 = 0.0283, *wR*2 = 0.0716	
R indices (all data)	*R*1 = 0.0308, *wR*2 = 0.0727	
Largest diff. peak and hole	0.503 and -0.933 $e.Å^{-3}$	

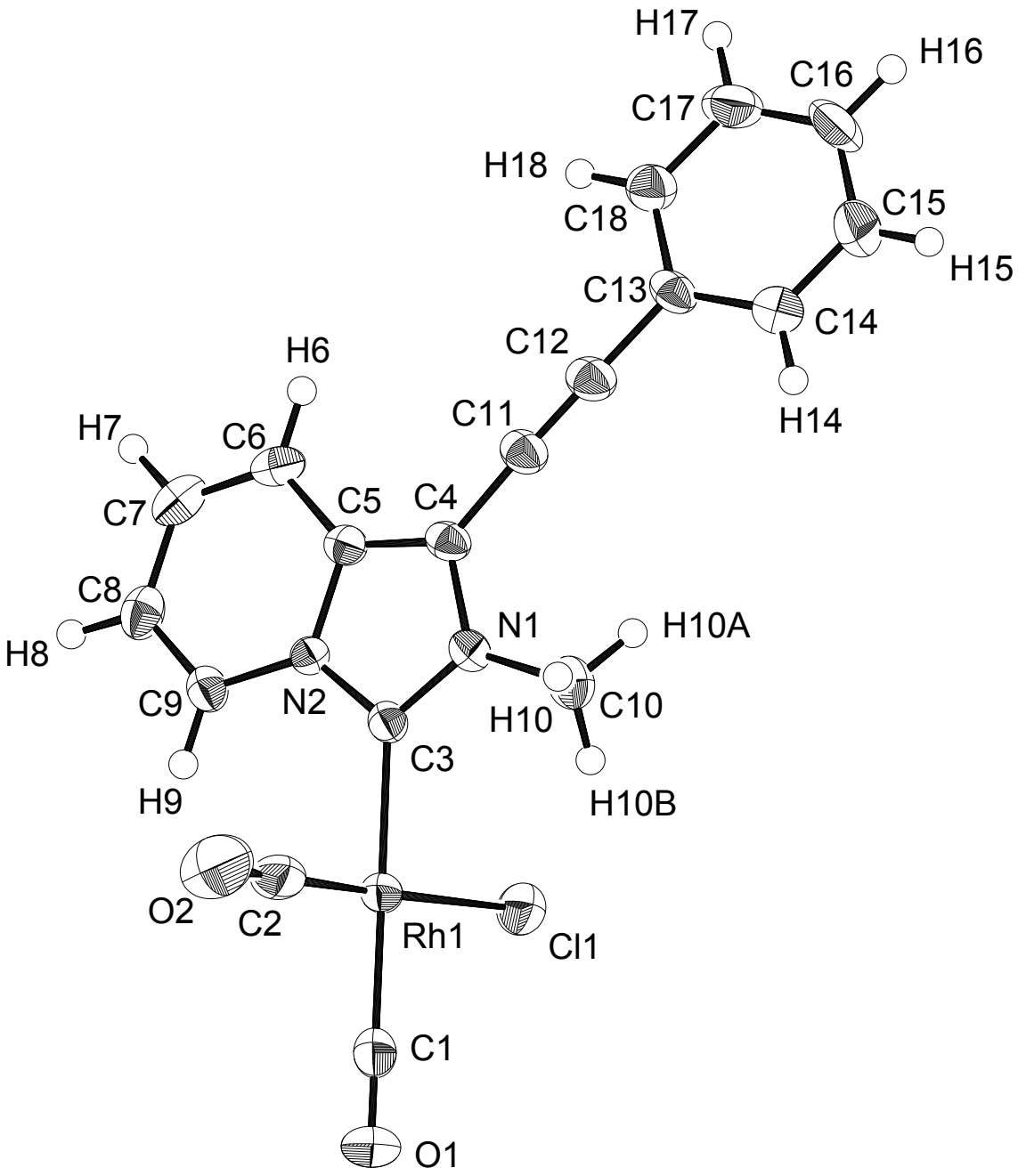


Figure S4. ORTEP drawing of **6g** with thermal ellipsoids at 50% probability.

Table S20. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **6g**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh(1)	8418(1)	6092(1)	7254(1)	30(1)
Cl(1)	11511(1)	6138(1)	8405(1)	43(1)
O(1)	9584(3)	4015(2)	5807(2)	58(1)
O(2)	4426(4)	5948(3)	5895(2)	75(1)
N(1)	7451(3)	7427(2)	9128(1)	28(1)
N(2)	7940(2)	9086(2)	8189(1)	24(1)
C(1)	9128(4)	4772(3)	6340(2)	39(1)
C(2)	5956(4)	6015(3)	6402(2)	45(1)
C(3)	7835(3)	7597(2)	8248(2)	26(1)
C(4)	7353(3)	8761(2)	9643(2)	28(1)
C(5)	7683(3)	9823(2)	9040(2)	26(1)
C(6)	7857(3)	11386(2)	9129(2)	34(1)
C(7)	8192(4)	12090(2)	8365(2)	39(1)
C(8)	8356(3)	11294(2)	7487(2)	36(1)
C(9)	8257(3)	9825(2)	7407(2)	29(1)
C(10)	7168(4)	6006(2)	9511(2)	43(1)
C(11)	7080(3)	8894(2)	10608(2)	32(1)
C(12)	6930(3)	8990(3)	11437(2)	35(1)
C(13)	6878(3)	9149(3)	12455(2)	32(1)
C(14)	6742(4)	7919(3)	12959(2)	43(1)
C(15)	6775(5)	8080(3)	13944(2)	56(1)
C(16)	6947(5)	9476(4)	14452(2)	58(1)
C(17)	7069(4)	10698(3)	13957(2)	50(1)
C(18)	7033(4)	10549(3)	12968(2)	38(1)

Table S21. Bond lengths [Å] and angles [°] for **6g**.

Rh(1)-C(2)	1.832(3)
Rh(1)-C(1)	1.914(3)
Rh(1)-C(3)	2.052(2)
Rh(1)-Cl(1)	2.3600(8)
O(1)-C(1)	1.125(3)
O(2)-C(2)	1.122(4)
N(1)-C(3)	1.343(3)
N(1)-C(4)	1.398(3)
N(1)-C(10)	1.460(3)
N(2)-C(3)	1.376(2)
N(2)-C(9)	1.383(3)
N(2)-C(5)	1.391(3)
C(4)-C(5)	1.375(3)
C(4)-C(11)	1.410(3)
C(5)-C(6)	1.420(3)
C(6)-C(7)	1.347(3)
C(7)-C(8)	1.420(3)
C(8)-C(9)	1.342(3)
C(11)-C(12)	1.190(3)
C(12)-C(13)	1.432(3)
C(13)-C(14)	1.392(3)
C(13)-C(18)	1.397(3)
C(14)-C(15)	1.369(4)
C(15)-C(16)	1.388(4)
C(16)-C(17)	1.377(4)
C(17)-C(18)	1.376(4)
C(2)-Rh(1)-C(1)	93.03(11)
C(2)-Rh(1)-C(3)	89.47(10)
C(1)-Rh(1)-C(3)	176.27(9)
C(2)-Rh(1)-Cl(1)	177.30(9)
C(1)-Rh(1)-Cl(1)	88.15(8)

C(3)-Rh(1)-Cl(1)	89.47(6)
C(3)-N(1)-C(4)	112.65(17)
C(3)-N(1)-C(10)	123.93(19)
C(4)-N(1)-C(10)	123.42(19)
C(3)-N(2)-C(9)	126.92(18)
C(3)-N(2)-C(5)	111.52(17)
C(9)-N(2)-C(5)	121.56(17)
O(1)-C(1)-Rh(1)	178.6(2)
O(2)-C(2)-Rh(1)	178.2(3)
N(1)-C(3)-N(2)	103.89(18)
N(1)-C(3)-Rh(1)	129.59(15)
N(2)-C(3)-Rh(1)	126.27(15)
C(5)-C(4)-N(1)	105.68(18)
C(5)-C(4)-C(11)	130.6(2)
N(1)-C(4)-C(11)	123.65(19)
C(4)-C(5)-N(2)	106.22(17)
C(4)-C(5)-C(6)	134.7(2)
N(2)-C(5)-C(6)	119.05(19)
C(7)-C(6)-C(5)	118.5(2)
C(6)-C(7)-C(8)	121.0(2)
C(9)-C(8)-C(7)	121.0(2)
C(8)-C(9)-N(2)	118.8(2)
C(12)-C(11)-C(4)	177.1(2)
C(11)-C(12)-C(13)	176.5(2)
C(14)-C(13)-C(18)	118.9(2)
C(14)-C(13)-C(12)	120.5(2)
C(18)-C(13)-C(12)	120.5(2)
C(15)-C(14)-C(13)	120.5(2)
C(14)-C(15)-C(16)	120.3(3)
C(17)-C(16)-C(15)	119.6(3)
C(18)-C(17)-C(16)	120.6(2)
C(17)-C(18)-C(13)	120.0(2)

Symmetry transformations used to generate equivalent atoms:

Table S22. Anisotropic displacement parameters ($Å^2$ x 10^3) for **6g**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh(1)	40(1)	25(1)	25(1)	3(1)	10(1)	10(1)
Cl(1)	45(1)	45(1)	39(1)	7(1)	6(1)	18(1)
O(1)	86(2)	55(1)	42(1)	-1(1)	24(1)	37(1)
O(2)	66(2)	77(1)	64(2)	-17(1)	-16(1)	30(1)
N(1)	31(1)	31(1)	25(1)	5(1)	10(1)	7(1)
N(2)	23(1)	25(1)	23(1)	4(1)	7(1)	7(1)
C(1)	54(2)	35(1)	31(1)	9(1)	10(1)	15(1)
C(2)	58(2)	38(1)	35(2)	-8(1)	5(1)	16(1)
C(3)	28(1)	27(1)	23(1)	5(1)	8(1)	6(1)
C(4)	23(1)	35(1)	25(1)	1(1)	8(1)	8(1)
C(5)	20(1)	33(1)	24(1)	1(1)	3(1)	8(1)
C(6)	28(1)	32(1)	39(1)	-6(1)	7(1)	10(1)
C(7)	35(1)	28(1)	56(2)	6(1)	10(1)	10(1)
C(8)	34(1)	34(1)	44(1)	16(1)	13(1)	9(1)
C(9)	28(1)	34(1)	26(1)	8(1)	8(1)	7(1)
C(10)	59(2)	36(1)	42(2)	17(1)	26(1)	10(1)
C(11)	27(1)	43(1)	29(1)	4(1)	10(1)	11(1)
C(12)	29(1)	46(1)	32(1)	3(1)	10(1)	12(1)
C(13)	26(1)	48(1)	25(1)	5(1)	11(1)	10(1)
C(14)	52(2)	44(1)	37(2)	6(1)	16(1)	18(1)
C(15)	73(2)	69(2)	42(2)	24(1)	27(2)	33(2)
C(16)	70(2)	94(2)	23(1)	10(1)	18(1)	38(2)
C(17)	56(2)	58(2)	36(2)	-10(1)	9(1)	24(1)
C(18)	38(1)	43(1)	36(1)	4(1)	12(1)	13(1)

Table S23. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **6g**.

	x	y	z	U(eq)
H(6)	7739	11922	9713	40
H(7)	8321	13137	8415	47
H(8)	8538	11809	6948	43
H(9)	8403	9303	6825	35
H(10)	5747	5501	9283	64
H(10A)	7592	6180	10239	64
H(10B)	7974	5383	9266	64
H(14)	6624	6960	12617	52
H(15)	6681	7234	14281	67
H(16)	6980	9587	15136	70
H(17)	7179	11652	14303	60
H(18)	7114	11398	12633	46

Table S24. Torsion angles [°] for **6g**.

C(2)-Rh(1)-C(1)-O(1)	137(9)
C(3)-Rh(1)-C(1)-O(1)	5(10)
Cl(1)-Rh(1)-C(1)-O(1)	-46(9)
C(1)-Rh(1)-C(2)-O(2)	110(8)
C(3)-Rh(1)-C(2)-O(2)	-73(8)
Cl(1)-Rh(1)-C(2)-O(2)	-5(9)
C(4)-N(1)-C(3)-N(2)	-1.4(2)
C(10)-N(1)-C(3)-N(2)	178.68(19)
C(4)-N(1)-C(3)-Rh(1)	173.20(15)
C(10)-N(1)-C(3)-Rh(1)	-6.8(3)
C(9)-N(2)-C(3)-N(1)	-178.21(19)
C(5)-N(2)-C(3)-N(1)	1.8(2)
C(9)-N(2)-C(3)-Rh(1)	7.0(3)
C(5)-N(2)-C(3)-Rh(1)	-172.99(14)
C(2)-Rh(1)-C(3)-N(1)	109.2(2)
C(1)-Rh(1)-C(3)-N(1)	-118.7(13)
Cl(1)-Rh(1)-C(3)-N(1)	-68.30(19)
C(2)-Rh(1)-C(3)-N(2)	-77.3(2)
C(1)-Rh(1)-C(3)-N(2)	54.8(14)
Cl(1)-Rh(1)-C(3)-N(2)	105.15(18)
C(3)-N(1)-C(4)-C(5)	0.4(2)
C(10)-N(1)-C(4)-C(5)	-179.6(2)
C(3)-N(1)-C(4)-C(11)	-176.3(2)
C(10)-N(1)-C(4)-C(11)	3.6(3)
N(1)-C(4)-C(5)-N(2)	0.7(2)
C(11)-C(4)-C(5)-N(2)	177.1(2)
N(1)-C(4)-C(5)-C(6)	-177.1(2)
C(11)-C(4)-C(5)-C(6)	-0.6(4)
C(3)-N(2)-C(5)-C(4)	-1.6(2)
C(9)-N(2)-C(5)-C(4)	178.42(18)
C(3)-N(2)-C(5)-C(6)	176.60(19)

C(9)-N(2)-C(5)-C(6)	-3.4(3)
C(4)-C(5)-C(6)-C(7)	180.0(2)
N(2)-C(5)-C(6)-C(7)	2.4(3)
C(5)-C(6)-C(7)-C(8)	0.4(3)
C(6)-C(7)-C(8)-C(9)	-2.5(4)
C(7)-C(8)-C(9)-N(2)	1.6(3)
C(3)-N(2)-C(9)-C(8)	-178.7(2)
C(5)-N(2)-C(9)-C(8)	1.3(3)
C(5)-C(4)-C(11)-C(12)	-112(5)
N(1)-C(4)-C(11)-C(12)	64(5)
C(4)-C(11)-C(12)-C(13)	41(8)
C(11)-C(12)-C(13)-C(14)	-108(4)
C(11)-C(12)-C(13)-C(18)	70(4)
C(18)-C(13)-C(14)-C(15)	-0.5(4)
C(12)-C(13)-C(14)-C(15)	177.3(2)
C(13)-C(14)-C(15)-C(16)	0.0(4)
C(14)-C(15)-C(16)-C(17)	0.5(5)
C(15)-C(16)-C(17)-C(18)	-0.4(5)
C(16)-C(17)-C(18)-C(13)	-0.2(4)
C(14)-C(13)-C(18)-C(17)	0.6(4)
C(12)-C(13)-C(18)-C(17)	-177.2(2)

Symmetry transformations used to generate equivalent atoms:

Table S25. Crystal data and structure refinement for **6h**.

Empirical formula	$C_{19}H_{11}ClF_3N_2O_2Rh$	
Formula weight	494.66	
Temperature	123(2) K	
Wavelength	0.71075 Å	
Crystal system	Triclinic	
Space group	*P* -1	
Unit cell dimensions	a = 7.168(4) Å	α = 76.479(14)°.
	b = 9.002(5) Å	β = 80.476(18)°.
	c = 15.020(8) Å	γ = 81.147(16)°.
Volume	922.6(8) $Å^3$	
Z	2	
Density (calculated)	1.781 Mg/m^3	
Absorption coefficient	1.117 mm^{-1}	
F(000)	488	
Crystal size	0.29 x 0.23 x 0.20 mm^3	
Theta range for data collection	1.41 to 27.50°.	
Index ranges	-9<=*h*<=9, -7<=*k*<=11, -18<=*l*<=19	
Reflections collected	7286	
Independent reflections	4171 [R(int) = 0.0396]	
Completeness to theta = 27.50°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.727	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4171 / 0 / 254	
Goodness-of-fit on F^2	1.010	
Final R indices [I>2sigma(I)]	*R*1 = 0.0446, *wR*2 = 0.1025	
R indices (all data)	*R*1 = 0.0556, *wR*2 = 0.1097	
Largest diff. peak and hole	1.171 and -0.931 e.$Å^{-3}$	

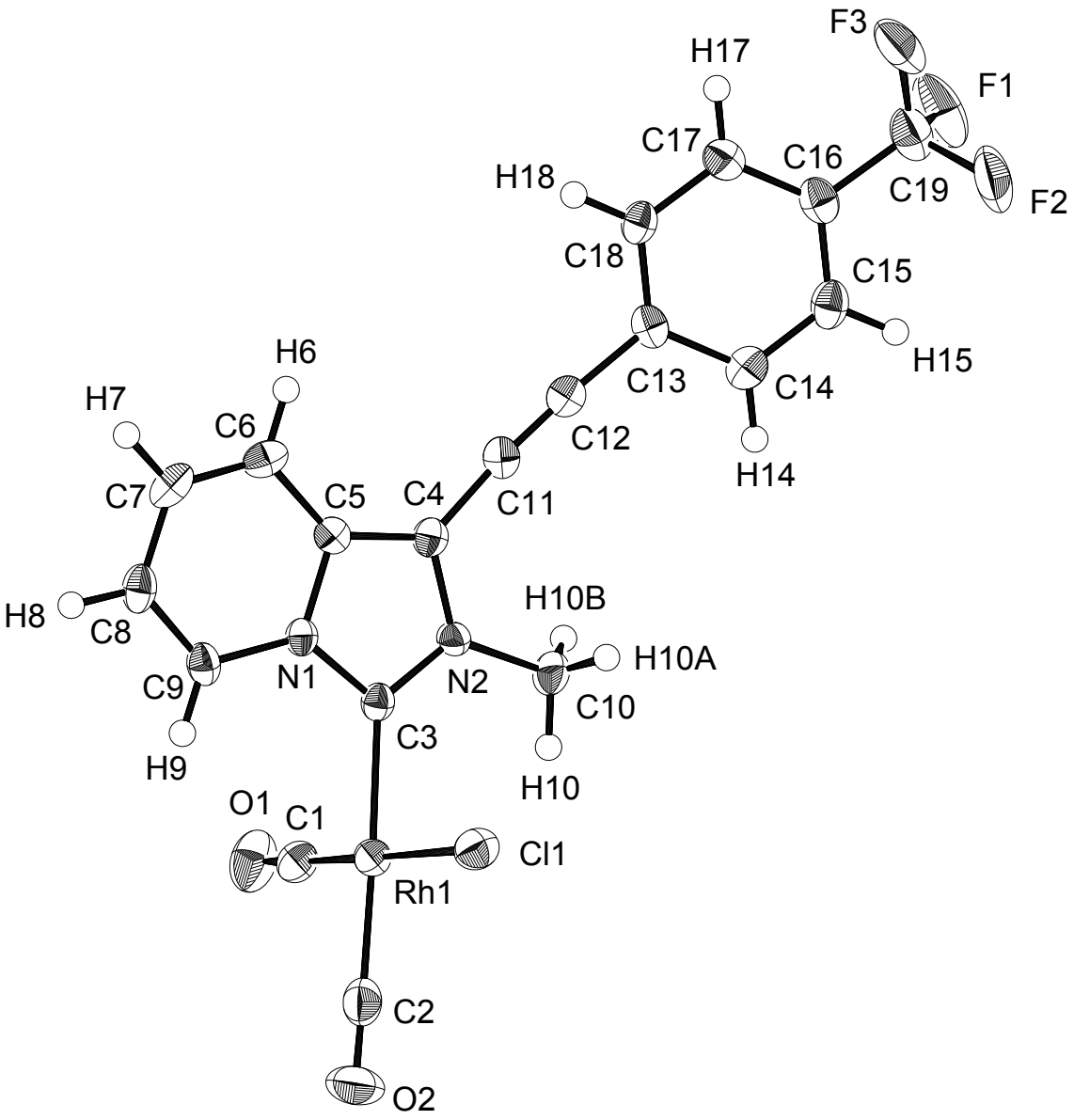


Figure S5. ORTEP drawing of **6h** with thermal ellipsoids at 50% probability.

Table S26. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **6h**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Rh(1)	5810(1)	8898(1)	7266(1)	27(1)
Cl(1)	7871(2)	8879(1)	8348(1)	34(1)
F(1)	-4516(4)	6751(4)	14890(2)	69(1)
F(2)	-1828(4)	7164(4)	15162(2)	63(1)
F(3)	-2520(5)	4866(4)	15440(2)	62(1)
O(1)	3022(5)	8983(4)	6003(2)	51(1)
O(2)	8252(5)	11018(4)	5839(2)	54(1)
N(1)	4598(4)	5762(3)	8265(2)	22(1)
N(2)	3220(4)	7454(3)	9017(2)	23(1)
C(1)	4129(6)	8951(5)	6466(3)	35(1)
C(2)	7315(7)	10263(5)	6361(3)	37(1)
C(3)	4375(5)	7320(4)	8236(3)	23(1)
C(4)	2744(5)	6055(4)	9550(3)	25(1)
C(5)	3640(5)	4952(4)	9074(3)	22(1)
C(6)	3798(5)	3330(4)	9238(3)	27(1)
C(7)	4810(6)	2612(5)	8593(3)	32(1)
C(8)	5669(5)	3462(5)	7749(3)	30(1)
C(9)	5604(5)	5014(5)	7589(3)	27(1)
C(10)	2500(6)	8935(4)	9273(3)	32(1)
C(11)	1626(5)	5912(5)	10430(3)	26(1)
C(12)	754(5)	5886(5)	11169(3)	28(1)
C(13)	-186(5)	5917(5)	12087(3)	25(1)
C(14)	-474(5)	7340(5)	12359(3)	31(1)
C(15)	-1276(6)	7401(5)	13244(3)	33(1)
C(16)	-1811(5)	6089(5)	13869(3)	31(1)
C(17)	-1530(5)	4691(5)	13604(3)	32(1)
C(18)	-724(5)	4608(5)	12710(3)	28(1)
C(19)	-2658(6)	6198(6)	14834(3)	43(1)

Table S27. Bond lengths [Å] and angles [°] for **6h**.

Rh(1)-C(1)	1.826(4)
Rh(1)-C(2)	1.913(5)
Rh(1)-C(3)	2.046(4)
Rh(1)-Cl(1)	2.3660(13)
F(1)-C(19)	1.345(5)
F(2)-C(19)	1.344(5)
F(3)-C(19)	1.326(6)
O(1)-C(1)	1.131(5)
O(2)-C(2)	1.116(6)
N(1)-C(3)	1.378(5)
N(1)-C(9)	1.389(5)
N(1)-C(5)	1.394(5)
N(2)-C(3)	1.338(5)
N(2)-C(4)	1.383(5)
N(2)-C(10)	1.467(5)
C(4)-C(5)	1.376(5)
C(4)-C(11)	1.417(5)
C(5)-C(6)	1.413(5)
C(6)-C(7)	1.342(6)
C(7)-C(8)	1.416(6)
C(8)-C(9)	1.356(5)
C(11)-C(12)	1.177(6)
C(12)-C(13)	1.436(5)
C(13)-C(18)	1.384(6)
C(13)-C(14)	1.409(5)
C(14)-C(15)	1.369(6)
C(15)-C(16)	1.388(6)
C(16)-C(17)	1.383(6)
C(16)-C(19)	1.495(6)
C(17)-C(18)	1.386(5)

C(1)-Rh(1)-C(2)	92.17(19)
C(1)-Rh(1)-C(3)	89.90(17)
C(2)-Rh(1)-C(3)	175.76(16)
C(1)-Rh(1)-Cl(1)	177.32(14)
C(2)-Rh(1)-Cl(1)	89.11(12)
C(3)-Rh(1)-Cl(1)	88.98(10)
C(3)-N(1)-C(9)	126.9(4)
C(3)-N(1)-C(5)	111.9(3)
C(9)-N(1)-C(5)	121.3(3)
C(3)-N(2)-C(4)	113.0(3)
C(3)-N(2)-C(10)	123.5(3)
C(4)-N(2)-C(10)	123.4(3)
O(1)-C(1)-Rh(1)	176.9(4)
O(2)-C(2)-Rh(1)	177.3(4)
N(2)-C(3)-N(1)	103.5(3)
N(2)-C(3)-Rh(1)	131.2(3)
N(1)-C(3)-Rh(1)	125.0(3)
C(5)-C(4)-N(2)	106.4(3)
C(5)-C(4)-C(11)	130.7(4)
N(2)-C(4)-C(11)	122.8(3)
C(4)-C(5)-N(1)	105.2(3)
C(4)-C(5)-C(6)	135.4(4)
N(1)-C(5)-C(6)	119.4(4)
C(7)-C(6)-C(5)	119.0(4)
C(6)-C(7)-C(8)	120.8(4)
C(9)-C(8)-C(7)	121.4(4)
C(8)-C(9)-N(1)	118.0(4)
C(12)-C(11)-C(4)	175.0(4)
C(11)-C(12)-C(13)	175.2(4)
C(18)-C(13)-C(14)	120.1(4)
C(18)-C(13)-C(12)	122.6(4)
C(14)-C(13)-C(12)	117.3(4)
C(15)-C(14)-C(13)	119.0(4)

C(14)-C(15)-C(16)	120.9(4)
C(17)-C(16)-C(15)	120.1(4)
C(17)-C(16)-C(19)	120.5(4)
C(15)-C(16)-C(19)	119.3(4)
C(16)-C(17)-C(18)	119.7(4)
C(13)-C(18)-C(17)	120.1(4)
F(3)-C(19)-F(2)	105.9(4)
F(3)-C(19)-F(1)	106.8(4)
F(2)-C(19)-F(1)	105.3(4)
F(3)-C(19)-C(16)	113.8(4)
F(2)-C(19)-C(16)	112.4(4)
F(1)-C(19)-C(16)	112.1(4)

Symmetry transformations used to generate equivalent atoms:

Table S28. Anisotropic displacement parameters ($Å^2$ x 10^3) for **6h**. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Rh(1)	32(1)	23(1)	25(1)	-5(1)	-2(1)	-2(1)
Cl(1)	36(1)	33(1)	35(1)	-4(1)	-8(1)	-8(1)
F(1)	37(2)	113(3)	55(2)	-40(2)	10(1)	11(2)
F(2)	68(2)	90(3)	44(2)	-44(2)	3(2)	-16(2)
F(3)	79(2)	76(2)	26(2)	-12(2)	6(2)	-10(2)
O(1)	64(2)	42(2)	54(2)	-16(2)	-29(2)	6(2)
O(2)	64(2)	64(2)	36(2)	2(2)	0(2)	-36(2)
N(1)	22(2)	21(2)	24(2)	-8(1)	-2(1)	1(1)
N(2)	25(2)	20(2)	21(2)	-4(1)	0(1)	-1(1)
C(1)	46(3)	19(2)	35(2)	-4(2)	-3(2)	3(2)
C(2)	45(3)	34(3)	33(2)	-12(2)	-9(2)	-3(2)
C(3)	21(2)	24(2)	25(2)	-9(2)	-3(2)	-1(2)
C(4)	25(2)	24(2)	26(2)	-7(2)	-5(2)	-1(2)
C(5)	18(2)	26(2)	23(2)	-5(2)	-5(2)	-2(2)
C(6)	23(2)	26(2)	34(2)	0(2)	-12(2)	-6(2)
C(7)	28(2)	22(2)	50(3)	-9(2)	-11(2)	-3(2)
C(8)	25(2)	31(2)	38(2)	-18(2)	-5(2)	4(2)
C(9)	23(2)	32(2)	27(2)	-14(2)	-1(2)	-1(2)
C(10)	33(2)	25(2)	38(2)	-13(2)	0(2)	1(2)
C(11)	21(2)	30(2)	28(2)	-10(2)	-5(2)	-1(2)
C(12)	25(2)	27(2)	31(2)	-7(2)	-6(2)	-2(2)
C(13)	15(2)	34(2)	26(2)	-10(2)	-4(2)	2(2)
C(14)	27(2)	28(2)	37(2)	-8(2)	-7(2)	-1(2)
C(15)	28(2)	33(2)	40(3)	-17(2)	-5(2)	2(2)
C(16)	22(2)	42(3)	30(2)	-13(2)	-3(2)	-1(2)
C(17)	30(2)	35(2)	29(2)	-6(2)	-2(2)	-5(2)
C(18)	27(2)	25(2)	33(2)	-11(2)	-5(2)	1(2)
C(19)	36(2)	58(3)	38(3)	-21(3)	0(2)	-6(2)

Table S29. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **6h**.

	x	y	z	U(eq)
H(6)	3197	2757	9797	33
H(7)	4952	1520	8704	39
H(8)	6303	2935	7285	36
H(9)	6229	5574	7032	32
H(10)	2916	9775	8769	48
H(10A)	3000	8979	9834	48
H(10B)	1105	9041	9387	48
H(14)	-116	8244	11934	37
H(15)	-1469	8356	13434	39
H(17)	-1887	3791	14033	38
H(18)	-540	3651	12524	33

Table S30. Torsion angles [°] for **6h**.

C(2)-Rh(1)-C(1)-O(1)	-142(7)
C(3)-Rh(1)-C(1)-O(1)	42(7)
Cl(1)-Rh(1)-C(1)-O(1)	-24(9)
C(1)-Rh(1)-C(2)-O(2)	-128(8)
C(3)-Rh(1)-C(2)-O(2)	-9(9)
Cl(1)-Rh(1)-C(2)-O(2)	55(8)
C(4)-N(2)-C(3)-N(1)	1.7(4)
C(10)-N(2)-C(3)-N(1)	-177.2(3)
C(4)-N(2)-C(3)-Rh(1)	-171.4(2)
C(10)-N(2)-C(3)-Rh(1)	9.8(5)
C(9)-N(1)-C(3)-N(2)	176.8(3)
C(5)-N(1)-C(3)-N(2)	-2.2(4)
C(9)-N(1)-C(3)-Rh(1)	-9.6(5)
C(5)-N(1)-C(3)-Rh(1)	171.5(2)
C(1)-Rh(1)-C(3)-N(2)	-106.6(3)
C(2)-Rh(1)-C(3)-N(2)	134.2(18)
Cl(1)-Rh(1)-C(3)-N(2)	70.9(3)
C(1)-Rh(1)-C(3)-N(1)	81.6(3)
C(2)-Rh(1)-C(3)-N(1)	-38(2)
Cl(1)-Rh(1)-C(3)-N(1)	-100.8(3)
C(3)-N(2)-C(4)-C(5)	-0.6(4)
C(10)-N(2)-C(4)-C(5)	178.2(3)
C(3)-N(2)-C(4)-C(11)	176.3(3)
C(10)-N(2)-C(4)-C(11)	-4.9(5)
N(2)-C(4)-C(5)-N(1)	-0.7(3)
C(11)-C(4)-C(5)-N(1)	-177.3(3)
N(2)-C(4)-C(5)-C(6)	177.5(3)
C(11)-C(4)-C(5)-C(6)	1.0(6)
C(3)-N(1)-C(5)-C(4)	1.8(4)
C(9)-N(1)-C(5)-C(4)	-177.2(3)
C(3)-N(1)-C(5)-C(6)	-176.8(3)

C(9)-N(1)-C(5)-C(6)	4.2(4)
C(4)-C(5)-C(6)-C(7)	179.3(4)
N(1)-C(5)-C(6)-C(7)	-2.6(5)
C(5)-C(6)-C(7)-C(8)	-1.6(5)
C(6)-C(7)-C(8)-C(9)	4.4(5)
C(7)-C(8)-C(9)-N(1)	-2.7(5)
C(3)-N(1)-C(9)-C(8)	179.6(3)
C(5)-N(1)-C(9)-C(8)	-1.6(5)
C(5)-C(4)-C(11)-C(12)	145(4)
N(2)-C(4)-C(11)-C(12)	-31(5)
C(4)-C(11)-C(12)-C(13)	-26(9)
C(11)-C(12)-C(13)-C(18)	-126(5)
C(11)-C(12)-C(13)-C(14)	51(5)
C(18)-C(13)-C(14)-C(15)	0.4(5)
C(12)-C(13)-C(14)-C(15)	-176.7(3)
C(13)-C(14)-C(15)-C(16)	-0.3(5)
C(14)-C(15)-C(16)-C(17)	0.3(6)
C(14)-C(15)-C(16)-C(19)	179.2(4)
C(15)-C(16)-C(17)-C(18)	-0.4(6)
C(19)-C(16)-C(17)-C(18)	-179.3(4)
C(14)-C(13)-C(18)-C(17)	-0.6(5)
C(12)-C(13)-C(18)-C(17)	176.3(3)
C(16)-C(17)-C(18)-C(13)	0.6(5)
C(17)-C(16)-C(19)-F(3)	20.4(5)
C(15)-C(16)-C(19)-F(3)	-158.4(4)
C(17)-C(16)-C(19)-F(2)	140.8(4)
C(15)-C(16)-C(19)-F(2)	-38.1(5)
C(17)-C(16)-C(19)-F(1)	-100.9(5)
C(15)-C(16)-C(19)-F(1)	80.2(5)

Symmetry transformations used to generate equivalent atoms:

Table S31. Crystal data and structure refinement for **13b**.

Empirical formula	$C_{15}H_{14}N_2OSe$	
Formula weight	317.24	
Temperature	193(2) K	
Wavelength	0.71075 Å	
Crystal system	Triclinic	
Space group	*P* -1	
Unit cell dimensions	a = 8.144(2) Å	α = 97.961(2)°.
	b = 9.039(3) Å	β = 106.050(4)°.
	c = 9.707(3) Å	γ = 95.085(3)°.
Volume	674.0(3) $Å^3$	
Z	2	
Density (calculated)	1.563 Mg/m^3	
Absorption coefficient	2.778 mm^{-1}	
F(000)	320	
Crystal size	0.51 x 0.31 x 0.31 mm^3	
Theta range for data collection	2.22 to 27.50°.	
Index ranges	-6<=*h*<=10, -11<=*k*<=10, -12<=*l*<=12	
Reflections collected	5428	
Independent reflections	3060 [R(int) = 0.0268]	
Completeness to theta = 27.50°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4797 and 0.3315	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3060 / 0 / 174	
Goodness-of-fit on F^2	1.000	
Final R indices [I>2sigma(I)]	*R*1 = 0.0330, *wR*2 = 0.0817	
R indices (all data)	*R*1 = 0.0367, *wR*2 = 0.0828	
Largest diff. peak and hole	0.843 and -0.745 e.$Å^{-3}$	

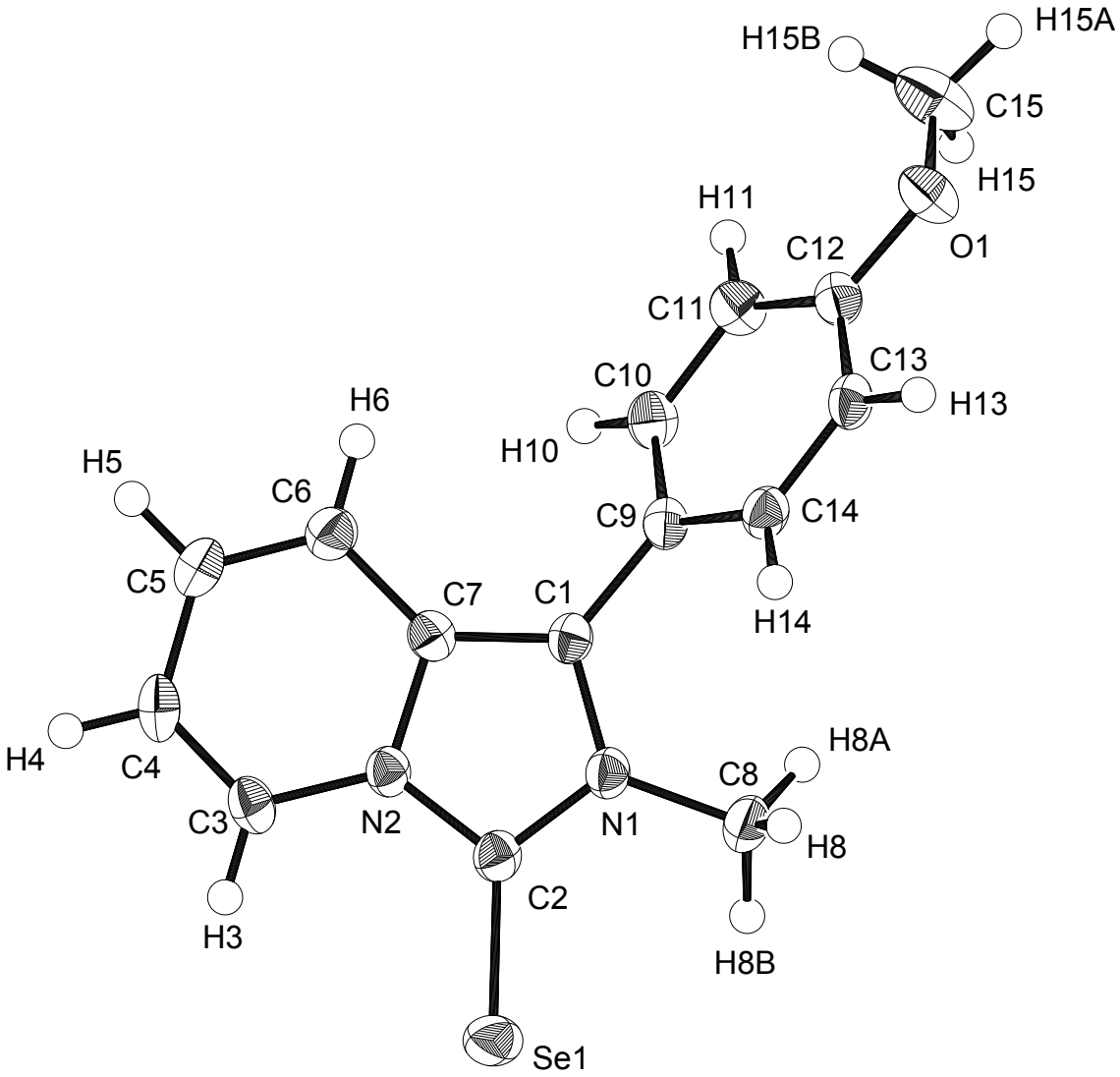


Figure S6. ORTEP drawing of **13b** with thermal ellipsoids at 50% probability.

Table S32. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **13b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3828(3)	11553(2)	8145(2)	24(1)
N(1)	4323(2)	10358(2)	7365(2)	25(1)
C(2)	5938(3)	10078(2)	8065(2)	25(1)
N(2)	6455(2)	11111(2)	9323(2)	23(1)
C(3)	8026(3)	11334(3)	10400(3)	28(1)
C(4)	8350(3)	12462(3)	11510(3)	32(1)
C(5)	7070(3)	13452(3)	11612(3)	33(1)
C(6)	5526(3)	13234(3)	10585(3)	29(1)
C(7)	5169(3)	12046(2)	9385(2)	24(1)
Se(1)	7177(1)	8647(1)	7476(1)	35(1)
C(8)	3232(3)	9414(3)	6023(3)	33(1)
C(9)	2224(3)	12211(2)	7623(2)	24(1)
C(10)	1225(3)	12560(3)	8536(3)	28(1)
C(11)	-257(3)	13244(3)	8081(3)	30(1)
C(12)	-743(3)	13578(2)	6683(3)	26(1)
C(13)	266(3)	13252(2)	5761(3)	26(1)
C(14)	1734(3)	12574(2)	6222(2)	26(1)
O(1)	-2174(2)	14235(2)	6109(2)	36(1)
C(15)	-3385(3)	14371(4)	6914(4)	51(1)

Table S33. Bond lengths [Å] and angles [°] for **13b**.

C(1)-C(7)	1.371(3)
C(1)-N(1)	1.386(3)
C(1)-C(9)	1.474(3)
N(1)-C(2)	1.366(3)
N(1)-C(8)	1.460(3)
C(2)-N(2)	1.368(3)
C(2)-Se(1)	1.834(2)
N(2)-C(3)	1.388(3)
N(2)-C(7)	1.412(3)
C(3)-C(4)	1.327(3)
C(4)-C(5)	1.447(3)
C(5)-C(6)	1.350(3)
C(6)-C(7)	1.416(3)
C(9)-C(10)	1.383(3)
C(9)-C(14)	1.401(3)
C(10)-C(11)	1.396(3)
C(11)-C(12)	1.388(3)
C(12)-O(1)	1.370(3)
C(12)-C(13)	1.393(3)
C(13)-C(14)	1.384(3)
O(1)-C(15)	1.421(3)
C(7)-C(1)-N(1)	106.58(18)
C(7)-C(1)-C(9)	128.5(2)
N(1)-C(1)-C(9)	124.71(19)
C(2)-N(1)-C(1)	111.66(18)
C(2)-N(1)-C(8)	122.90(19)
C(1)-N(1)-C(8)	125.26(18)
N(1)-C(2)-N(2)	104.87(19)
N(1)-C(2)-Se(1)	128.48(17)
N(2)-C(2)-Se(1)	126.65(17)

C(2)-N(2)-C(3)	127.97(19)
C(2)-N(2)-C(7)	110.38(18)
C(3)-N(2)-C(7)	121.58(19)
C(4)-C(3)-N(2)	119.8(2)
C(3)-C(4)-C(5)	120.4(2)
C(6)-C(5)-C(4)	120.5(2)
C(5)-C(6)-C(7)	119.8(2)
C(1)-C(7)-N(2)	106.50(19)
C(1)-C(7)-C(6)	135.5(2)
N(2)-C(7)-C(6)	118.0(2)
C(10)-C(9)-C(14)	118.7(2)
C(10)-C(9)-C(1)	120.6(2)
C(14)-C(9)-C(1)	120.61(19)
C(9)-C(10)-C(11)	121.3(2)
C(12)-C(11)-C(10)	119.4(2)
O(1)-C(12)-C(11)	124.8(2)
O(1)-C(12)-C(13)	115.4(2)
C(11)-C(12)-C(13)	119.8(2)
C(14)-C(13)-C(12)	120.4(2)
C(13)-C(14)-C(9)	120.4(2)
C(12)-O(1)-C(15)	117.42(19)

Symmetry transformations used to generate equivalent atoms:

Table S34. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **13b**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	25(1)	26(1)	19(1)	4(1)	5(1)	3(1)
N(1)	26(1)	26(1)	20(1)	3(1)	3(1)	3(1)
C(2)	30(1)	26(1)	19(1)	6(1)	6(1)	5(1)
N(2)	24(1)	27(1)	18(1)	5(1)	5(1)	4(1)
C(3)	24(1)	37(1)	23(1)	10(1)	4(1)	5(1)
C(4)	26(1)	42(1)	21(1)	6(1)	0(1)	-3(1)
C(5)	36(1)	32(1)	26(1)	-3(1)	5(1)	-1(1)
C(6)	30(1)	30(1)	27(1)	3(1)	9(1)	4(1)
C(7)	24(1)	26(1)	22(1)	7(1)	7(1)	4(1)
Se(1)	43(1)	40(1)	26(1)	6(1)	11(1)	18(1)
C(8)	36(1)	31(1)	24(1)	-1(1)	1(1)	3(1)
C(9)	24(1)	24(1)	22(1)	4(1)	3(1)	1(1)
C(10)	31(1)	33(1)	21(1)	9(1)	7(1)	4(1)
C(11)	29(1)	35(1)	29(1)	9(1)	13(1)	5(1)
C(12)	26(1)	26(1)	26(1)	6(1)	4(1)	2(1)
C(13)	29(1)	29(1)	18(1)	4(1)	2(1)	2(1)
C(14)	28(1)	30(1)	20(1)	2(1)	6(1)	3(1)
O(1)	30(1)	44(1)	38(1)	15(1)	10(1)	14(1)
C(15)	40(1)	64(2)	63(2)	28(2)	24(2)	25(1)

Table S35. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3)
for **13b**.

	x	y	z	U(eq)
H(3)	8866	10681	10344	33
H(4)	9430	12621	12243	38
H(5)	7318	14261	12407	40
H(6)	4682	13874	10668	35
H(8)	3390	9840	5186	49
H(8A)	2022	9378	6011	49
H(8B)	3552	8393	5971	49
H(10)	1555	12330	9493	34
H(11)	-928	13479	8722	36
H(13)	-55	13497	4810	32
H(14)	2414	12354	5586	31
H(15)	-3802	13370	7057	77
H(15A)	-4358	14829	6378	77
H(15B)	-2829	15008	7862	77

Table S36. Torsion angles [°] for **13b**.

C(7)-C(1)-N(1)-C(2)	-0.3(2)
C(9)-C(1)-N(1)-C(2)	174.59(19)
C(7)-C(1)-N(1)-C(8)	174.94(19)
C(9)-C(1)-N(1)-C(8)	-10.2(3)
C(1)-N(1)-C(2)-N(2)	0.8(2)
C(8)-N(1)-C(2)-N(2)	-174.54(18)
C(1)-N(1)-C(2)-Se(1)	-179.01(15)
C(8)-N(1)-C(2)-Se(1)	5.7(3)
N(1)-C(2)-N(2)-C(3)	-177.93(18)
Se(1)-C(2)-N(2)-C(3)	1.9(3)
N(1)-C(2)-N(2)-C(7)	-1.0(2)
Se(1)-C(2)-N(2)-C(7)	178.78(14)
C(2)-N(2)-C(3)-C(4)	175.6(2)
C(7)-N(2)-C(3)-C(4)	-1.0(3)
N(2)-C(3)-C(4)-C(5)	0.7(3)
C(3)-C(4)-C(5)-C(6)	0.5(3)
C(4)-C(5)-C(6)-C(7)	-1.3(3)
N(1)-C(1)-C(7)-N(2)	-0.4(2)
C(9)-C(1)-C(7)-N(2)	-174.98(19)
N(1)-C(1)-C(7)-C(6)	176.9(2)
C(9)-C(1)-C(7)-C(6)	2.3(4)
C(2)-N(2)-C(7)-C(1)	0.9(2)
C(3)-N(2)-C(7)-C(1)	178.03(18)
C(2)-N(2)-C(7)-C(6)	-176.94(17)
C(3)-N(2)-C(7)-C(6)	0.2(3)
C(5)-C(6)-C(7)-C(1)	-176.1(2)
C(5)-C(6)-C(7)-N(2)	0.9(3)
C(7)-C(1)-C(9)-C(10)	-50.3(3)
N(1)-C(1)-C(9)-C(10)	136.0(2)
C(7)-C(1)-C(9)-C(14)	126.0(2)
N(1)-C(1)-C(9)-C(14)	-47.7(3)

C(14)-C(9)-C(10)-C(11)	0.8(3)
C(1)-C(9)-C(10)-C(11)	177.2(2)
C(9)-C(10)-C(11)-C(12)	0.1(3)
C(10)-C(11)-C(12)-O(1)	179.5(2)
C(10)-C(11)-C(12)-C(13)	-1.1(3)
O(1)-C(12)-C(13)-C(14)	-179.41(19)
C(11)-C(12)-C(13)-C(14)	1.1(3)
C(12)-C(13)-C(14)-C(9)	-0.1(3)
C(10)-C(9)-C(14)-C(13)	-0.8(3)
C(1)-C(9)-C(14)-C(13)	-177.18(19)
C(11)-C(12)-O(1)-C(15)	-10.2(3)
C(13)-C(12)-O(1)-C(15)	170.3(2)

Symmetry transformations used to generate equivalent atoms:

Discussion of Polymerization of phenylacetylene with complexes 5b-d

The monomer consumption in the polymerization of phenylacetylene with **5b**-**d** was monitored. As a result, electron-deficient catalyst **5d** exhibited the highest activity among **5b**-**5d**, even though conversion at 12h was the almost same (Figure S7). The results of polymerization of phenylacetylene with **5b**-**d** are summarized in Table S37-40.

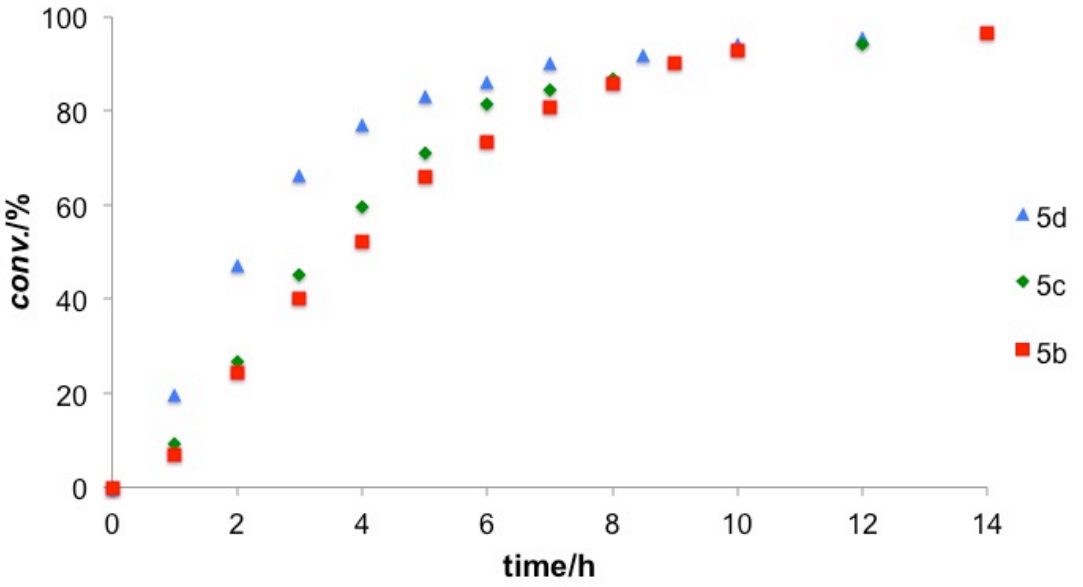


Figure S7 Time dependences of substrate conversion on polymerization of phenylacetylene with **5b**-**d**

Table S37. Time dependences of **5b**

Time (h)	1	2	3	4	5	6	7	8	12	18	24
conv. (%)	9	27	45	60	71	82	84	87	94	97	98

Table S38. Time dependences of **5c**

Time (h)	1	2	3	4	5	6	7	8	9	10	14	24
conv. (%)	7	24	40	52	66	73	81	86	90	93	97	98

Table S39. Time dependences of **5d**

Time (h)	1	2	3	4	5	6	7	8.5	10	12	24
conv. (%)	20	47	66	77	83	86	90	92	94	95	98

General procedure for polymerization of phenylacetylene in Figure S7

To a solution of Rh catalyst **5b**-**d** (10 μmol, 1.0 mol%) in CH_2Cl_2 (1.0 mL) was added phenylacetylene (102 mg, 1.0 mmol) and mesitylene (120 mg, 1.0 mmol) at room temperature under an argon atmosphere. The resulting mixture was stirred at room temperature. The conversion of the substrate at each reaction time was determined by GC analysis using mesitylene as internal standard.

Table S40. Result of polymerization of phenylacetylene by **5b**-**d** after 12 h[a]

Rh complex	yield[b]	%-*cis*[c]	M_n[d] [g/mol]	PDI (M_w/M_n)
5b	87%	89%	27000	1.94
5c	93%	92%	20600	1.80
5d	81%	93%	22300	1.85

[a] Reaction conditions: Phenylacetylene (1.0 mmol), Rh complex (10 μmol), and CH_2Cl_2 (1.0 mL), rt, 12 h. [b] Yields based on MeOH-insoluble product. [c] The percentage of *cis*-content in polyphenylacetylene was determined by ^{1}H NMR. [d] The molecular weight was determined by SEC (PS standards, eluent THF)

References

S1) M. Bielawski, D. Aili and B. Olofsson, *J. Org. Chem.*, 2008, **73**, 4602–4607.

S2) T. X. Neenan and G. M. Whitesides, *J. Org. Chem.*, 1988, **53**, 2489–2496.

S3) F. Shibahara, Y. Dohke and T. Murai, *J. Org. Chem.*, 2012, **77**, 5381–5388.

S4) D. M. Khramov, V. M. Lynch and C. W. Bielawski, *Organometallics*, 2007, **26**, 6042–6049.

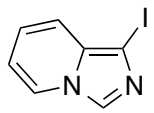
S5) D. J. Nelson, A. Collado, S. Manzini, S. Meiri1es, A. M. Z. Slawin, D. B. Cordes and S. P. Nolan, *Organometallics*, 2014, **33**, 2048–2058.

S6) A. Liske, K. Varlinden, H. Buhl, K. Schaper and C. Ganter, *Organometallics*, 2013, **32**, 5269-5272.

S7) (a) A. Furlani, C. Napoletano, M. V. Russo, A. Camus and N. Marsich, *J. Polym. Sci., Part A: Polym. Chem.*, 1989, **27**, 75–86. (b) A. Furlani, C. Napoletano, M. V. Russo and W. Feast, *J. Polym. Bull.*, 1986, **16**, 311–317.

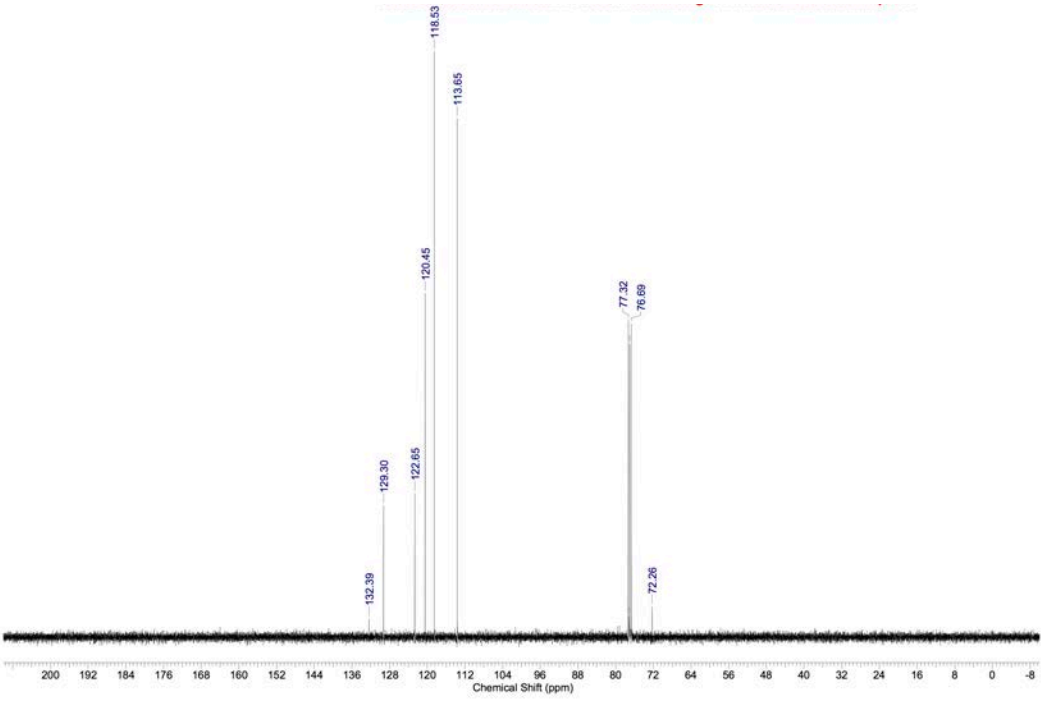
S8) G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112–122.

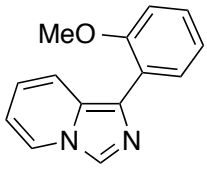
S9) Yadokari-XG, Software for Crystal Structure Analyses, K. Wakita (2001); Release of Software (Yadokari-XG 2009) for Crystal Structure Analyses, C. Kabuto, S. Akine, T. Nemoto, and E. Kwon, *J. Cryst. Soc. Jpn.*, 2009, **51**, 218-224.


I
N
N

2l

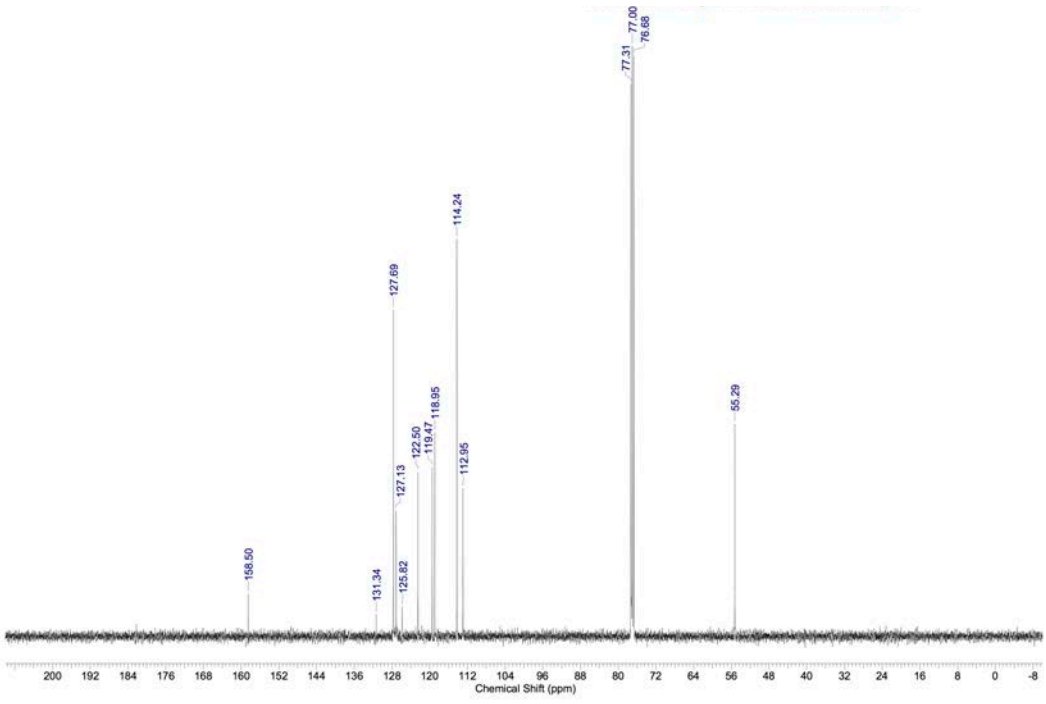
8.11
7.91
7.89
7.32
7.30
6.80
6.79
6.78
6.60
6.59
7.26
-0.01
1.00 1.02 1.02 1.06 1.04
Chemical Shift (ppm)

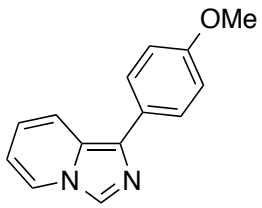

118.53
113.65
120.45
129.30
122.65
132.39
77.32
76.69
72.26
Chemical Shift (ppm)


MeO
N
N

3a

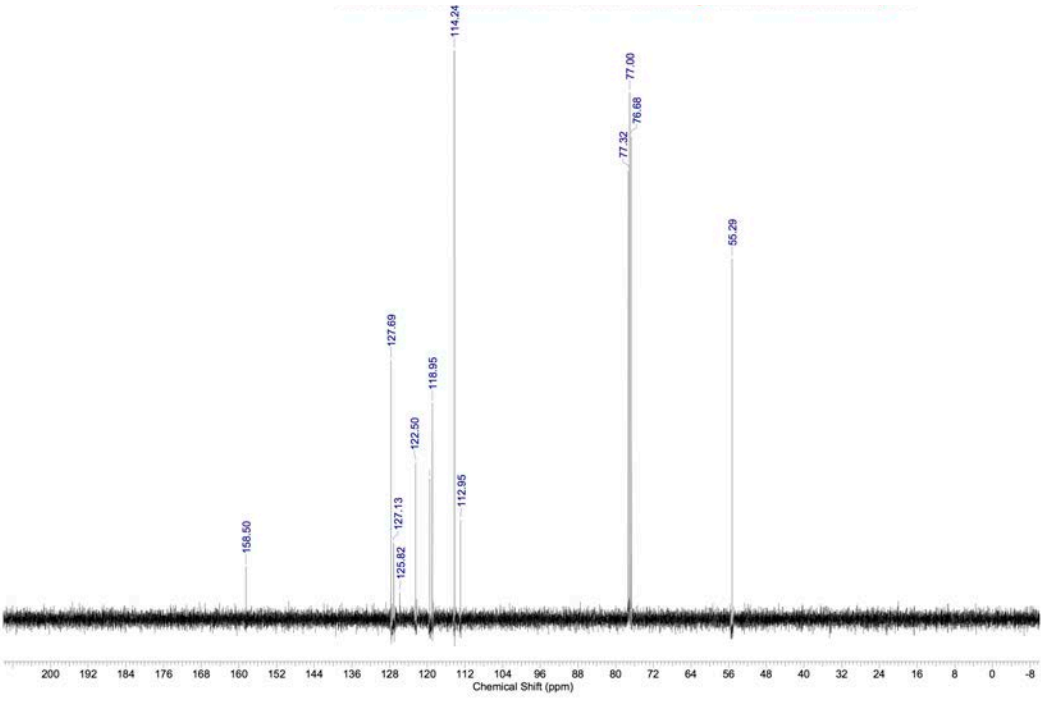
3.87
8.23
7.91
7.89
7.72
7.71
7.70
7.69
7.54
7.26
7.07
7.03
7.01
6.70
6.54
6.56
6.54
1.00 0.93 0.97 0.91 0.98 0.96 0.97 0.95 0.92
3.06
Chemical Shift (ppm)

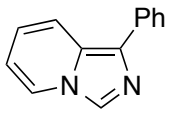

77.31
77.00
76.68
114.24
127.69
55.29
118.95
122.50
119.47
127.13
112.95
158.50
131.34
125.82
Chemical Shift (ppm)


OMe
N
N

3b

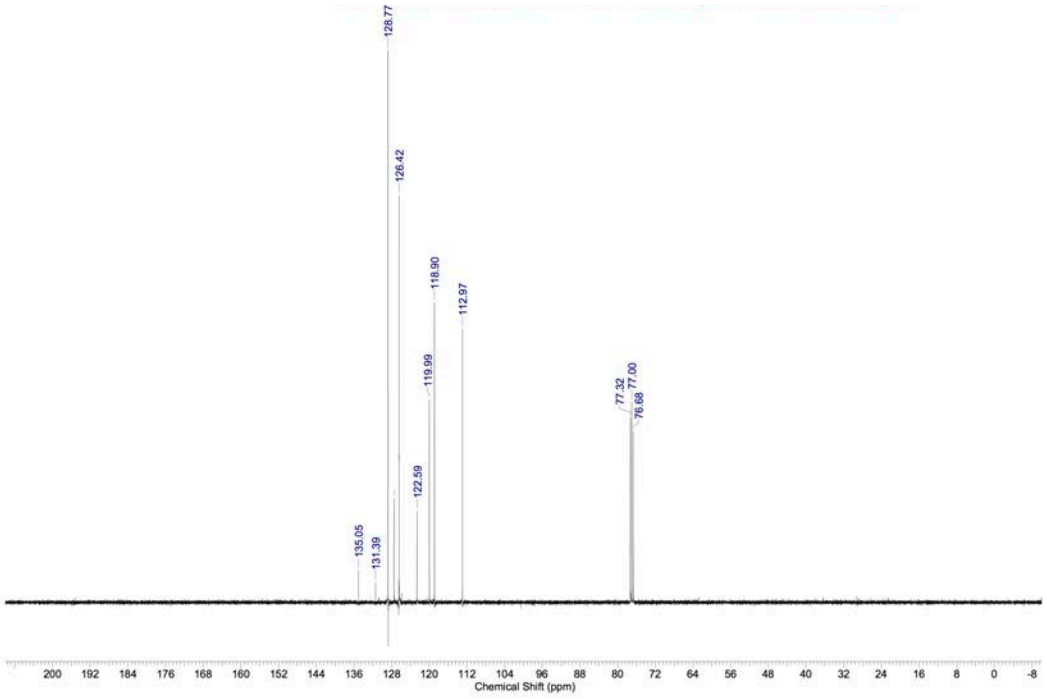
3.86
7.26
8.22
7.94
7.82
7.79
7.76
7.74
7.02
7.00
6.75
6.73
6.58
6.56
1.01 1.04 2.11 2.07 1.04 1.00 3.38
Chemical Shift (ppm)

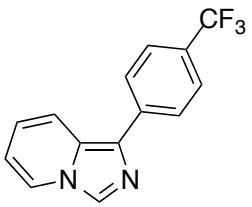

114.24
77.00
76.68
77.32
55.29
127.69
118.95
122.50
112.95
127.13
125.82
158.50
Chemical Shift (ppm)


Ph
N
N

3c

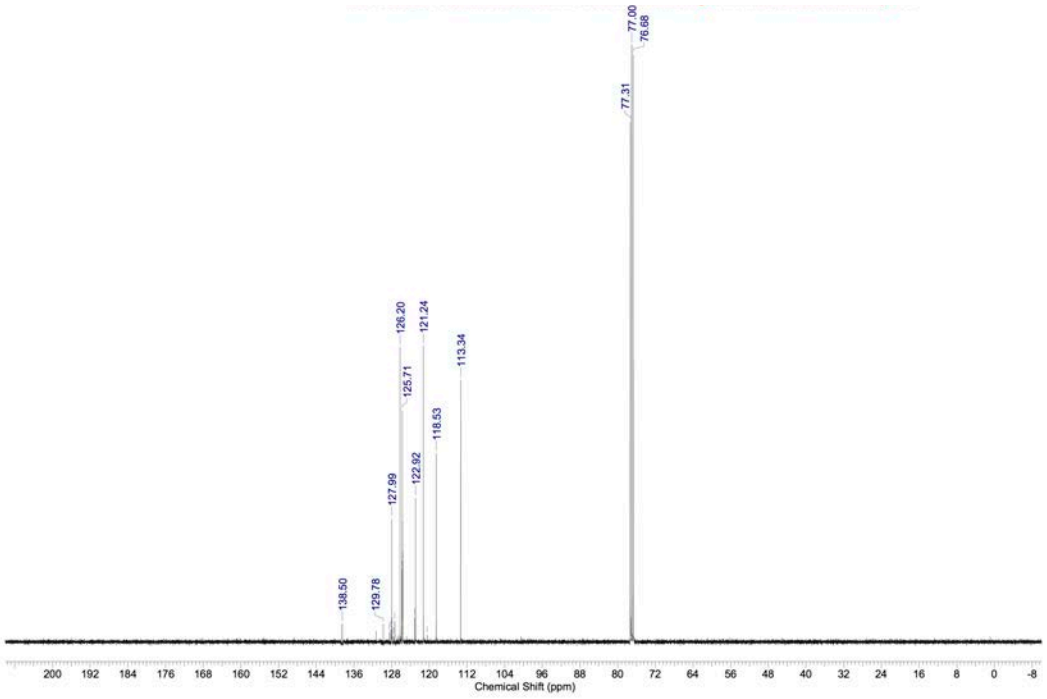
7.26
8.21
7.90
7.88
7.88
7.46
7.44
7.94
7.48
7.82
7.80
7.29
6.81
6.79
6.79
6.60
6.58
-0.01
1.00 0.98 1.98 1.01 2.04 0.98 0.99 0.97
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

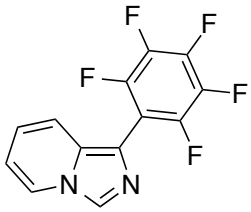

128.77
126.42
118.90
112.97
119.99
77.32
77.00
76.68
122.59
135.05
131.39
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)


CF3
N
N

3d

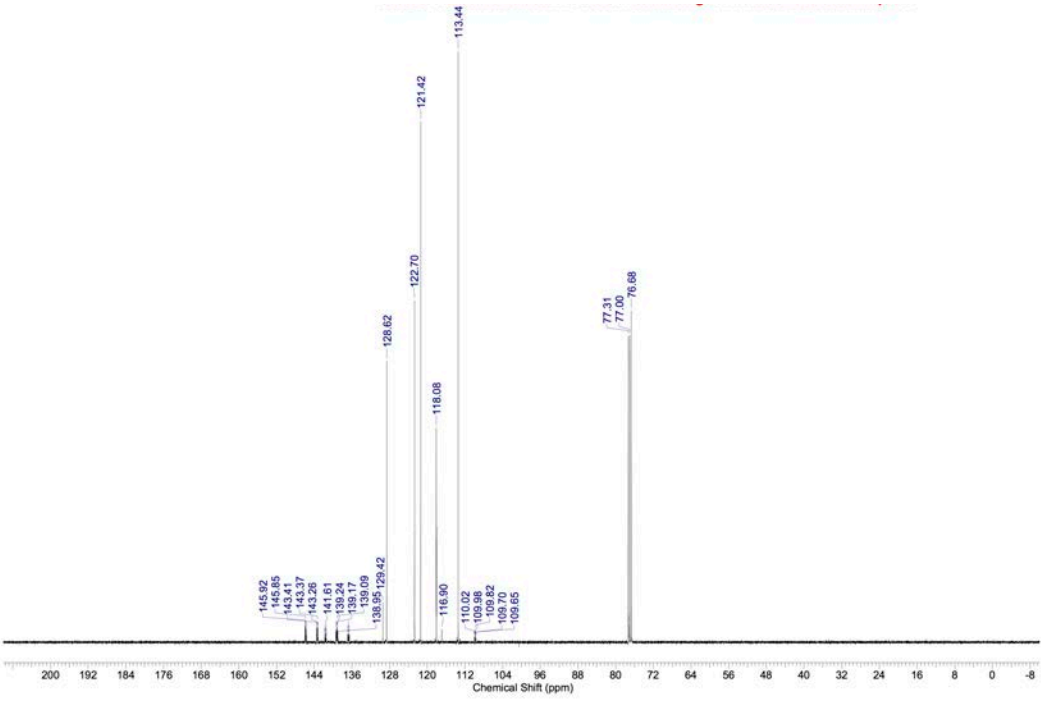
7.26
8.25
8.00
8.02
7.99
7.71
7.69
7.81
6.91
6.89
6.89
6.66
6.65
6.65
1.00 3.21 1.05 2.12 1.08 1.03
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

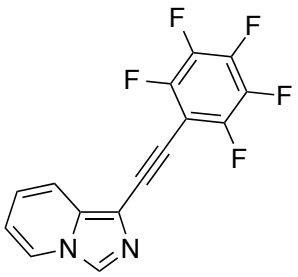

77.00
76.68
77.31
126.20
121.24
125.71
113.34
118.53
122.92
127.99
138.50
129.78
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)


F
F
F
F
F
N
N

3e

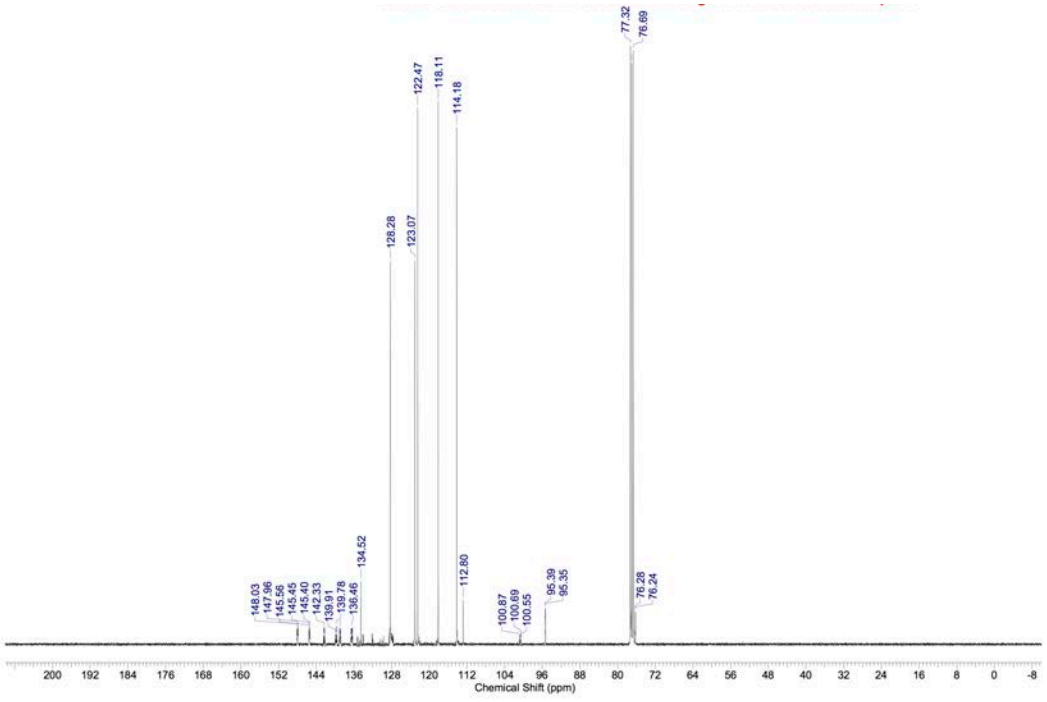
8.29
8.01
7.99
7.37
7.35
7.26
6.91
6.89
6.71
6.69
6.68
1.00 1.01 0.99 1.03 1.00
Chemical Shift (ppm)

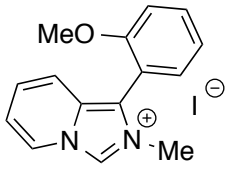

145.92
143.65
143.41
143.37
143.26
141.61
139.24
139.17
139.09
138.95
129.42
128.62
122.70
121.42
118.08
116.90
113.44
110.02
109.98
109.82
109.70
109.65
77.31
77.00
76.68
Chemical Shift (ppm)


F
F
F
F
F
N
N

3i

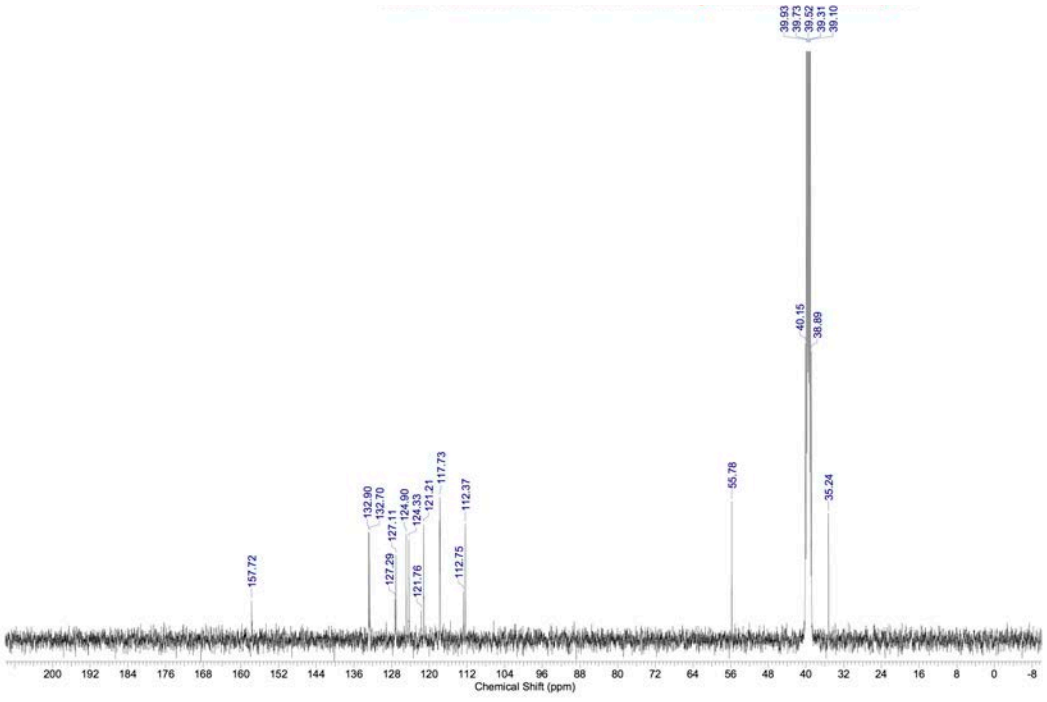
7.26
8.14
8.02
8.00
8.00
7.67
7.65
7.01
7.00
6.97
6.97
6.74
6.73
6.72
-0.01
1.00 1.02 1.08
1.01 0.99
Chemical Shift (ppm)

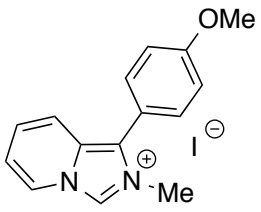

77.32
76.69
122.47
118.11
114.18
128.28
123.07
134.52
112.80
148.03
147.96
145.56
145.45
145.40
142.33
139.91
139.78
136.46
100.67
100.62
100.55
95.39
95.35
76.28
76.24
Chemical Shift (ppm)


MeO
I
N
N
Me

4a

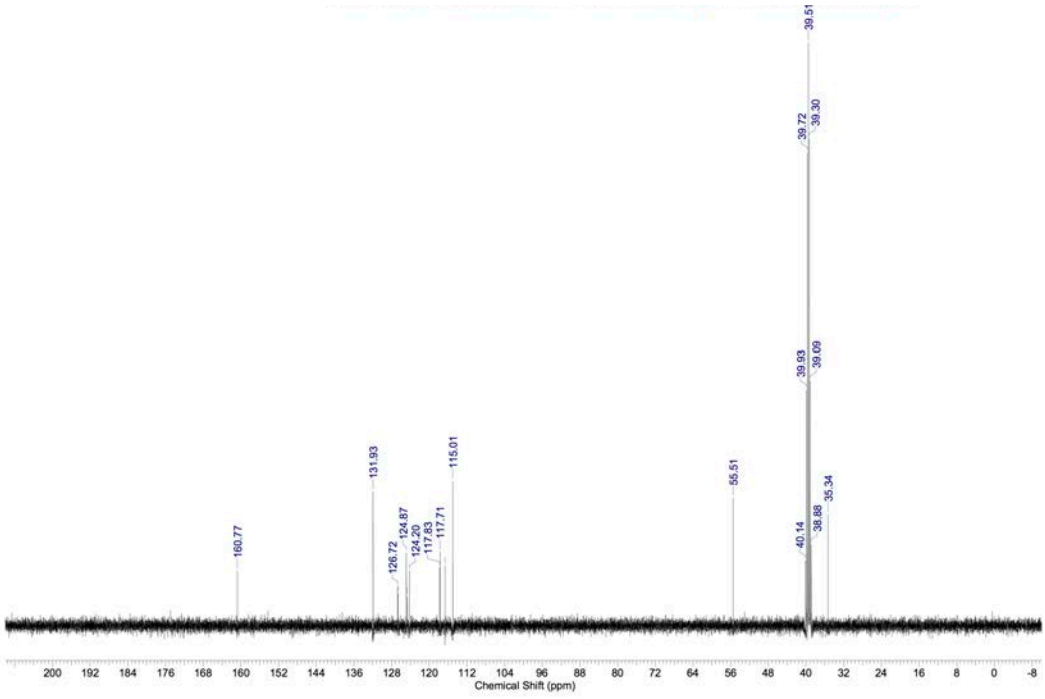
11.25
8.99
8.97
7.63
7.62
7.37
7.35
7.35
7.34
7.18
7.14
7.13
7.10
7.12
7.05
7.26
4.08
3.85
-0.01
1.00
1.04
1.02
2.13
3.25
1.04
3.22
3.30
Chemical Shift (ppm)

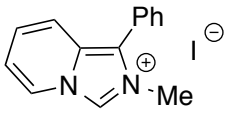

39.93
39.73
39.52
39.31
39.10
40.15
38.89
157.72
132.90
132.70
127.29
127.11
124.90
124.53
121.76
121.21
117.73
112.75
112.37
55.78
35.24
Chemical Shift (ppm)


OMe
I
N
N
Me

4b

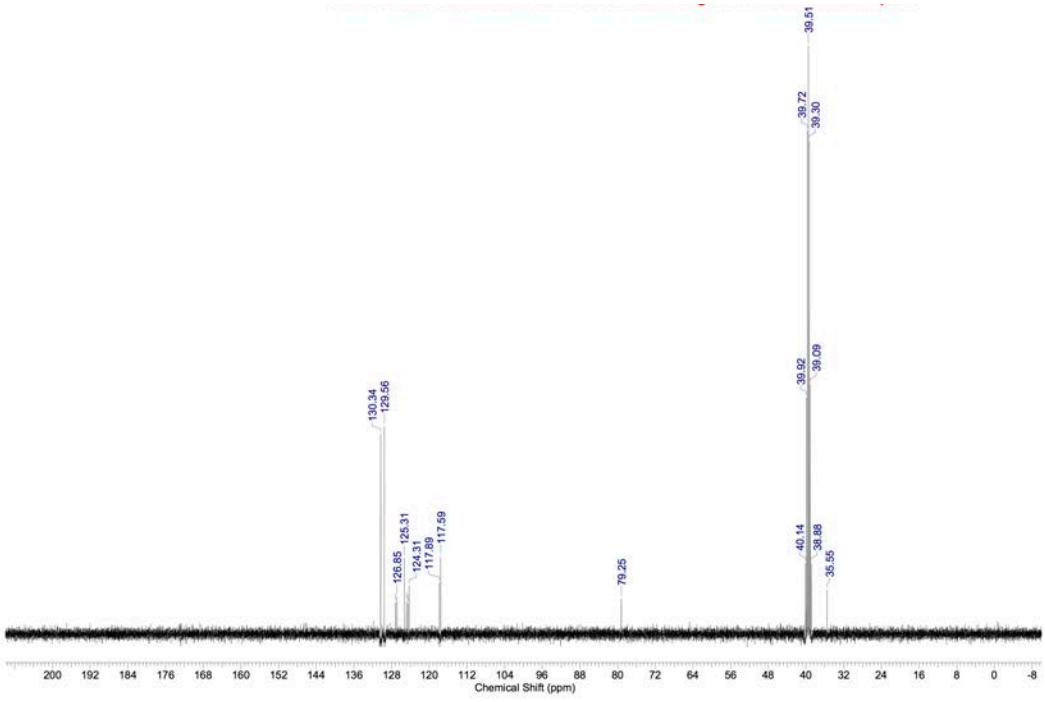
9.79
8.65
8.65
8.64
8.63
7.64
7.63
7.61
7.23
7.23
7.22
7.20
4.05
3.87
3.34
2.50
2.50
1.00
1.01
3.08
4.19
3.09
3.15
Chemical Shift (ppm)

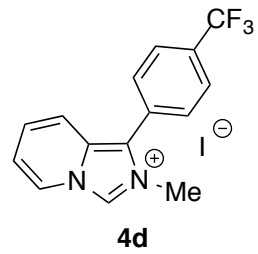

160.77
131.93
126.72
124.87
124.20
117.83
117.71
115.01
55.51
39.51
39.72
39.30
39.93
39.09
40.14
38.88
35.34
Chemical Shift (ppm)


Ph
I
N
N
Me

4c

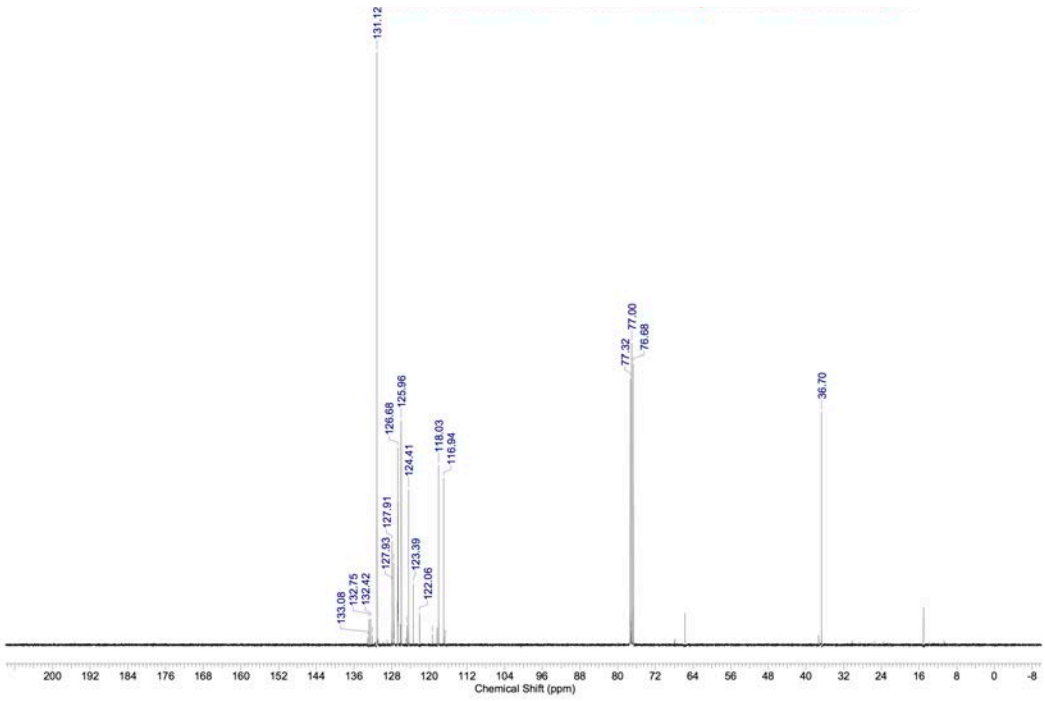
3.35
4.09
9.83
8.68
8.68
8.65
8.65
8.32
8.66
7.69
7.71
7.70
7.67
7.71
7.65
7.64
7.28
7.26
7.25
7.23
2.50
2.50
2.50
2.51
1.00
1.01
0.65
6.26
2.12
2.99
Chemical Shift (ppm)

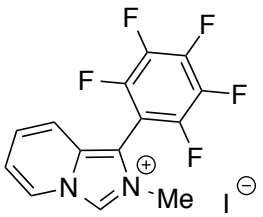

39.51
39.72
39.30
39.92
39.09
130.34
129.56
125.31
126.85
124.31
117.89
117.59
79.25
40.14
38.88
35.55
Chemical Shift (ppm)


CF3
I
N
N
Me

4d

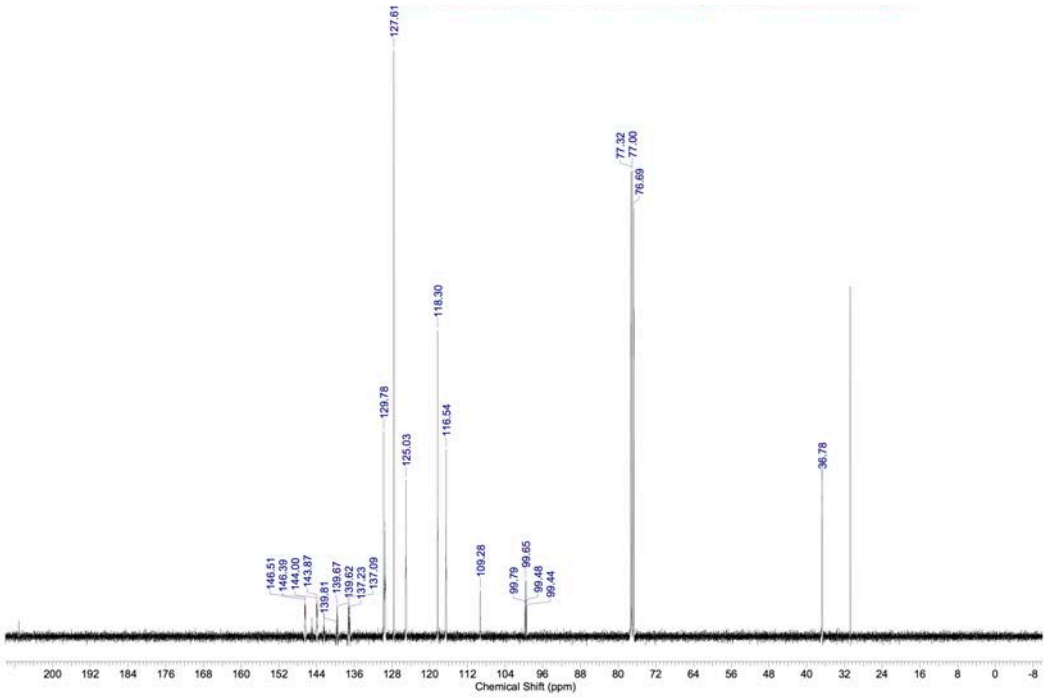
11.35
9.15
9.13
7.78
7.75
7.73
7.72
7.41
7.39
7.26
7.20
7.19
7.18
4.38
-0.01
1.00
0.98
5.25
1.05
0.96
3.20
Chemical Shift (ppm)

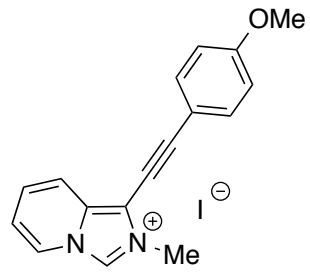

131.12
133.08
132.75
132.42
127.93
127.91
126.68
125.96
124.41
123.39
122.06
118.03
116.94
77.32
77.00
76.68
36.70
Chemical Shift (ppm)


F
F
F
F
F
N
N
Me
I

4e

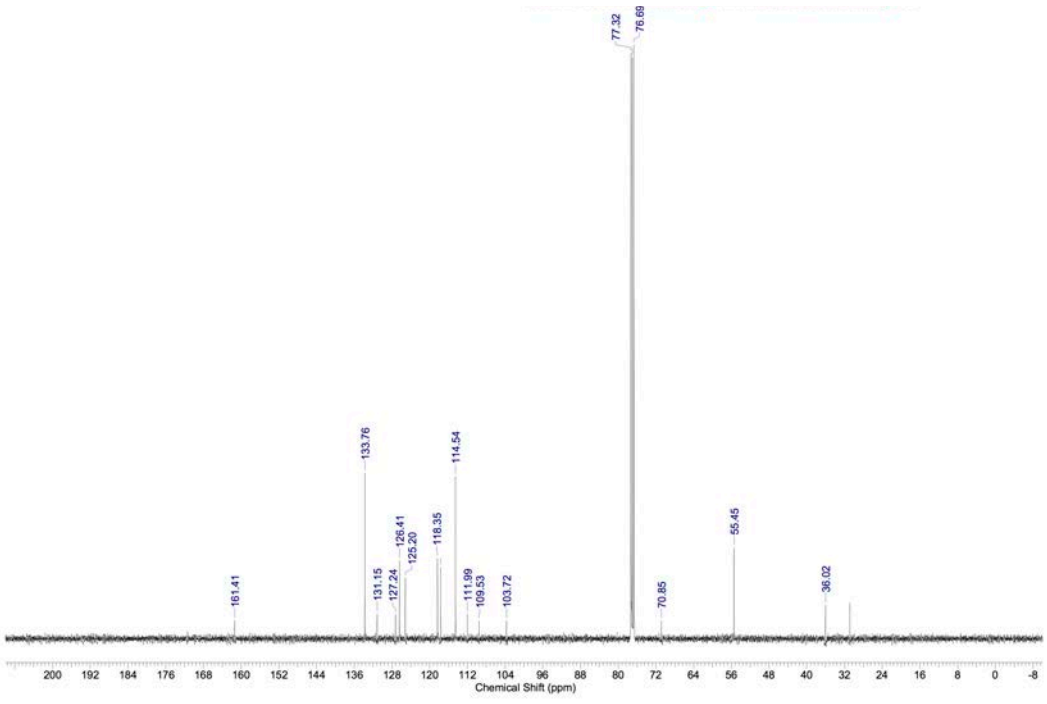
7.26
4.26
11.68
7.38
7.39
9.19
9.17
7.25
7.23
7.23
7.22
7.22
1.00
1.01
1.96
1.00
3.03
Chemical Shift (ppm)

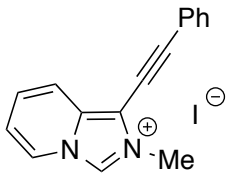

127.61
77.32
77.00
76.69
118.30
129.78
116.54
125.03
36.78
146.51
146.39
144.00
143.87
139.81
139.67
139.62
137.73
137.09
109.28
99.79
99.65
99.48
99.44
Chemical Shift (ppm)


OMe
I
N
N
Me

4f

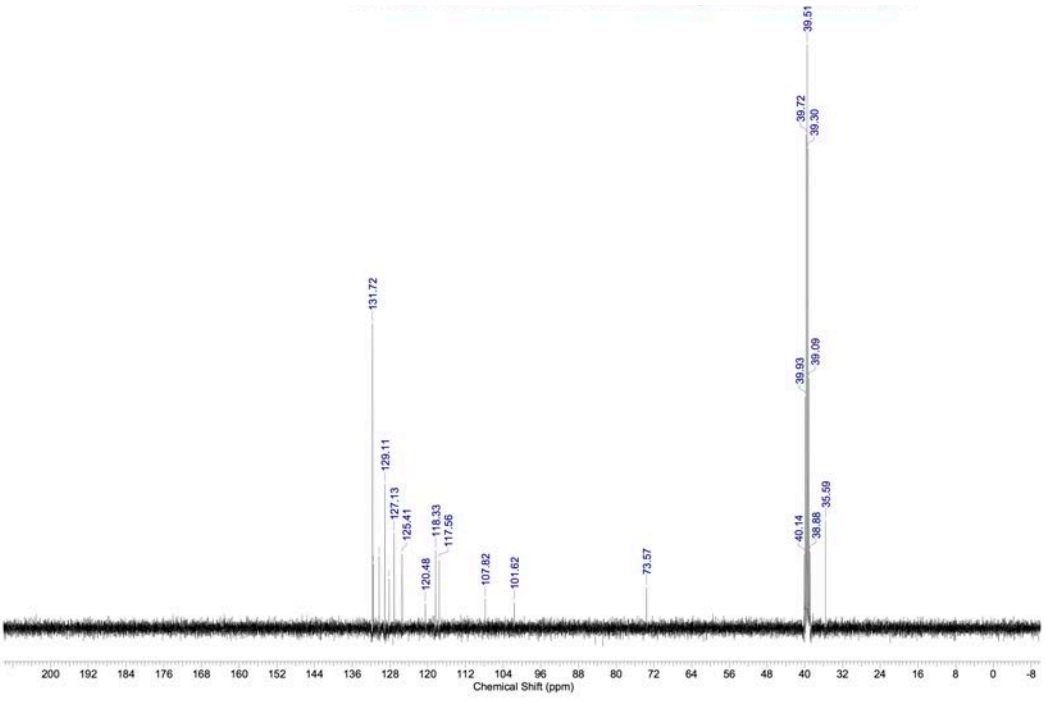
3.34
4.05
3.87
9.79
8.65
8.65
8.64
8.63
7.64
7.63
7.61
7.23
7.23
7.22
7.20
2.50
2.50
1.00
1.01
3.08
4.19
3.09
3.15
Chemical Shift (ppm)

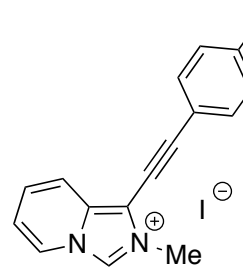

77.32
76.69
133.76
114.54
126.41
125.20
118.35
55.45
131.15
127.24
111.99
109.53
103.72
161.41
70.85
36.02
Chemical Shift (ppm)


Ph
I
N
N
Me

4g

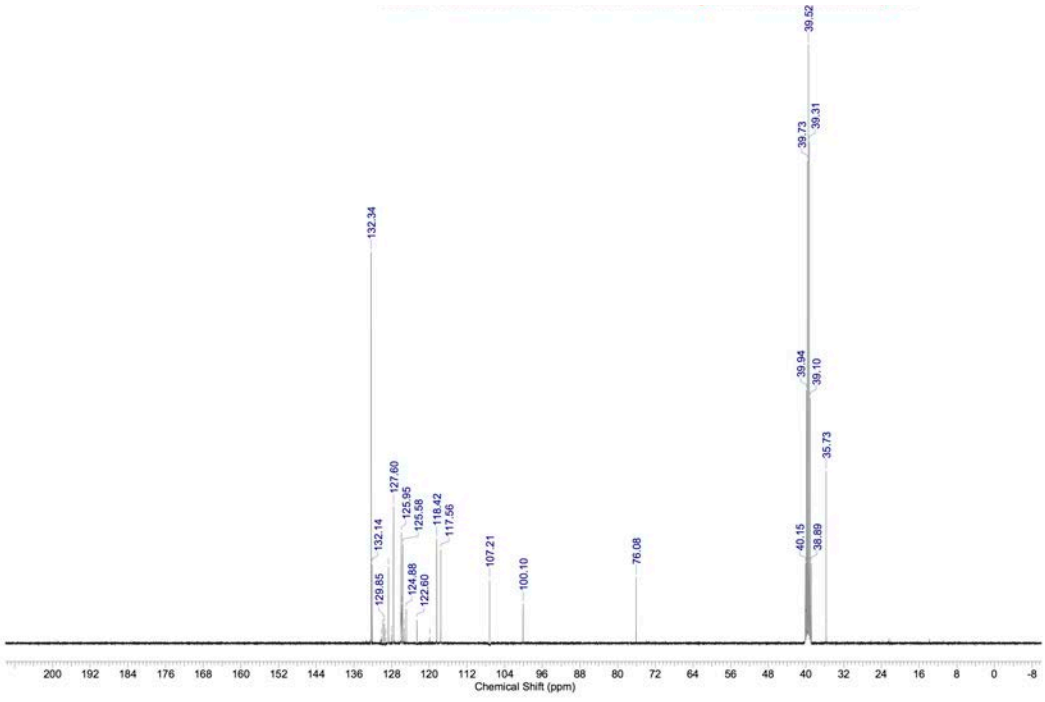
3.35
4.21
9.81
8.73
8.72
8.72
8.05
8.03
7.77
7.77
7.75
7.54
7.54
7.53
7.48
7.45
7.31
7.29
2.50
2.50
2.50
1.00
0.99
0.96
2.60
4.43
1.06
3.25
Chemical Shift (ppm)

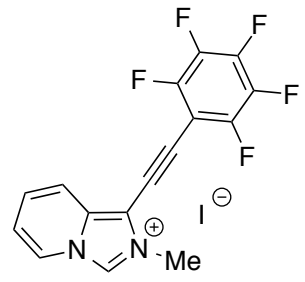

39.51
39.72
39.30
131.72
39.93
39.09
129.11
127.13
125.41
118.33
117.56
120.48
107.82
101.62
73.57
40.14
38.88
35.59
Chemical Shift (ppm)


CF3
I
N
N
Me

4h

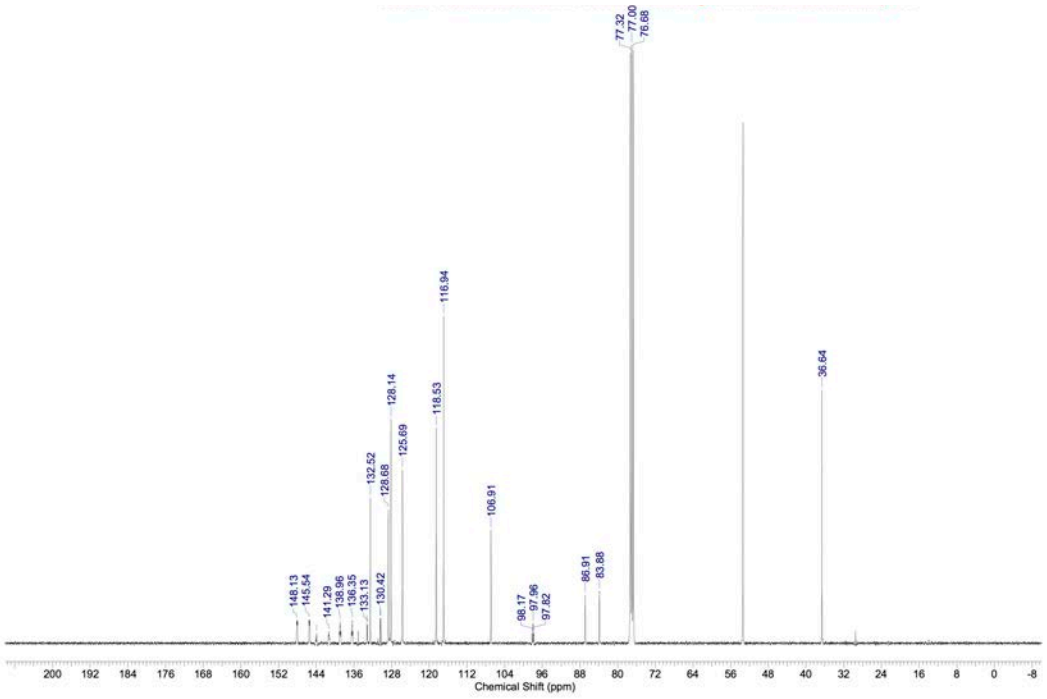
11.36
9.16
9.14
7.79
7.76
7.74
7.73
7.42
7.40
7.27
7.21
7.19
7.19
4.39
0.00
1.00
0.98
5.25
1.05
0.96
3.20
Chemical Shift (ppm)

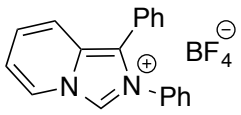

132.34
132.14
129.85
127.60
125.95
125.58
124.88
122.60
118.42
117.56
107.21
100.10
76.08
39.52
39.73
39.31
39.94
39.10
40.15
38.89
35.73
Chemical Shift (ppm)


F
F
F
F
F
I
N
N
Me

4i

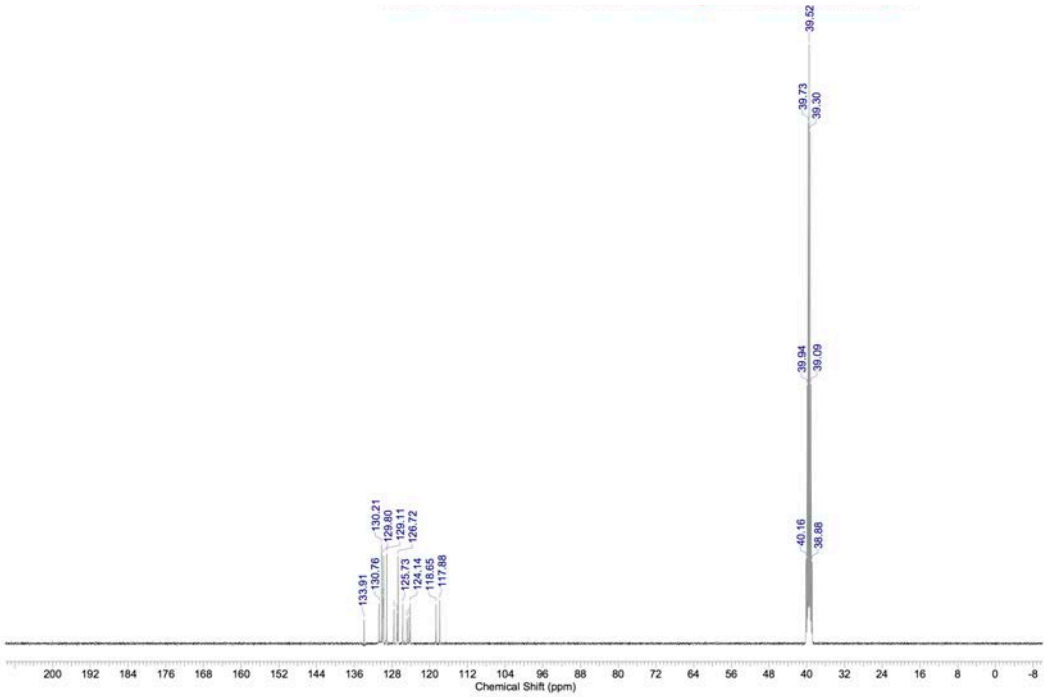
7.26
4.38
11.52
9.24
9.22
7.78
7.75
7.48
7.46
7.26
7.24
7.22
7.22
1.00
1.01
1.04
1.04
0.98
3.06
Chemical Shift (ppm)

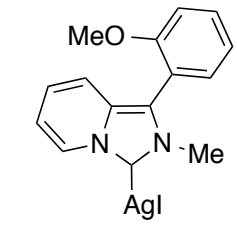

77.32
77.00
76.68
116.94
36.64
128.14
118.53
125.69
132.52
128.68
106.91
148.13
145.54
141.29
138.96
136.35
133.13
130.42
98.17
97.96
97.82
86.91
83.88
Chemical Shift (ppm)


Ph
BF4
N
N
Ph

4j

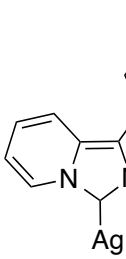
10.19
8.65
8.64
7.83
7.61
7.59
7.56
7.56
7.48
7.47
7.36
7.36
7.34
2.51
2.50
2.50
2.49
1.00
1.04
1.03
5.66
3.36
4.43
Chemical Shift (ppm)


39.52
39.73
39.30
39.94
39.09
40.16
38.88
133.91
130.76
130.21
129.80
129.11
126.72
125.73
124.14
118.65
117.88
Chemical Shift (ppm)


MeO
N
N
Me
AgI

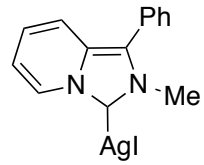
S1a

3.82
7.26
3.96
3.96
7.09
7.07
7.05
7.28
7.28
7.53
7.52
7.51
6.78
6.76
6.61
6.59
8.49
8.47
8.46
8.44
0.95
1.05 1.41 3.55 1.09 1.07
3.41 3.70
Chemical Shift (ppm)


OMe
N
N
Me
AgI

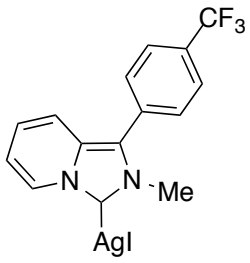
S1b

4.07
3.87
7.30
7.28
7.26
7.03
7.01
7.11
6.74
6.72
6.70
6.52
6.50
8.65
8.63
1.00
1.99 1.07 2.10 1.03 1.05
3.03 3.18
Chemical Shift (ppm)


Ph
N
N
Me
AgI

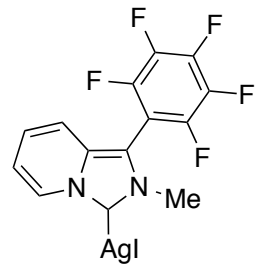
S1c

7.26
4.10
8.52
8.50
7.56
7.56
7.54
7.52
7.42
7.26
6.84
7.23
6.83
6.80
6.63
6.61
1.00
3.15
2.05
2.05
1.07
1.06
3.26
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


CF3
N
N
Me
AgI

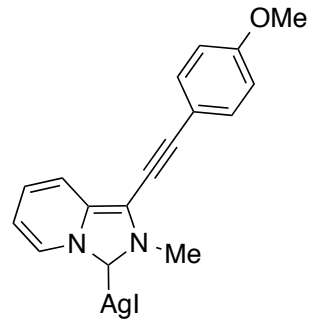
S1d

7.26
4.08
8.35
8.33
7.85
7.83
7.60
7.58
7.30
6.98
6.96
6.95
6.94
6.77
6.75
6.74
1.00
2.27
2.40
1.06
1.08
1.01
3.70
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


F
F
F
F
F
N
N
Me
AgI

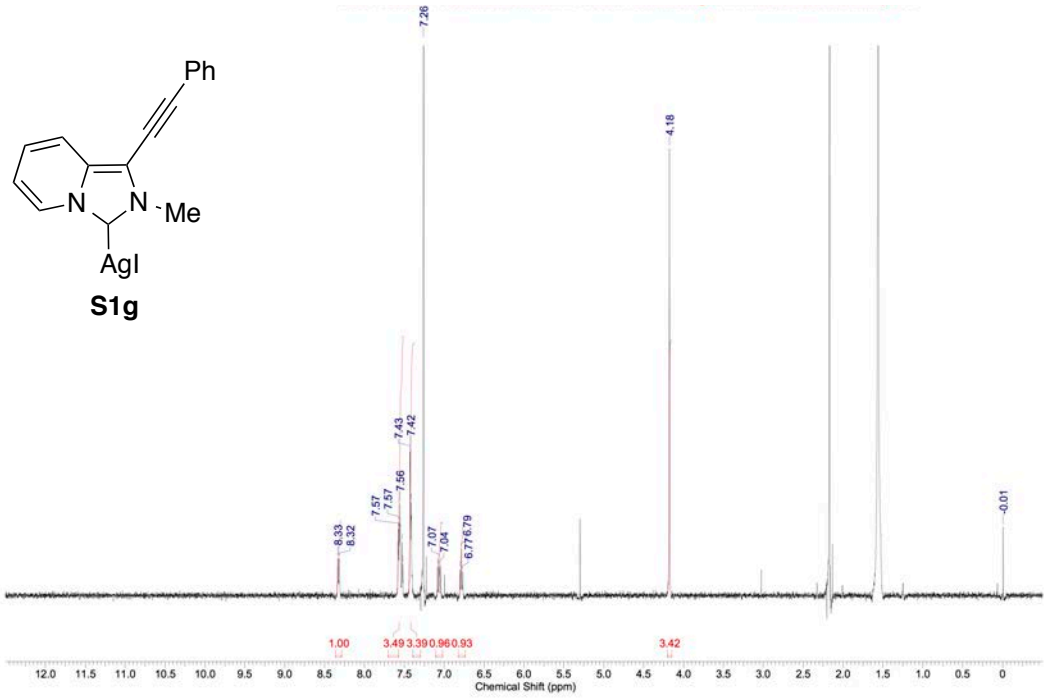
S1e

4.07
7.26
8.69
8.67
7.08
7.06
7.05
6.80
7.10
7.04
6.81
6.79
1.00
1.99
0.97
2.87
Chemical Shift (ppm)

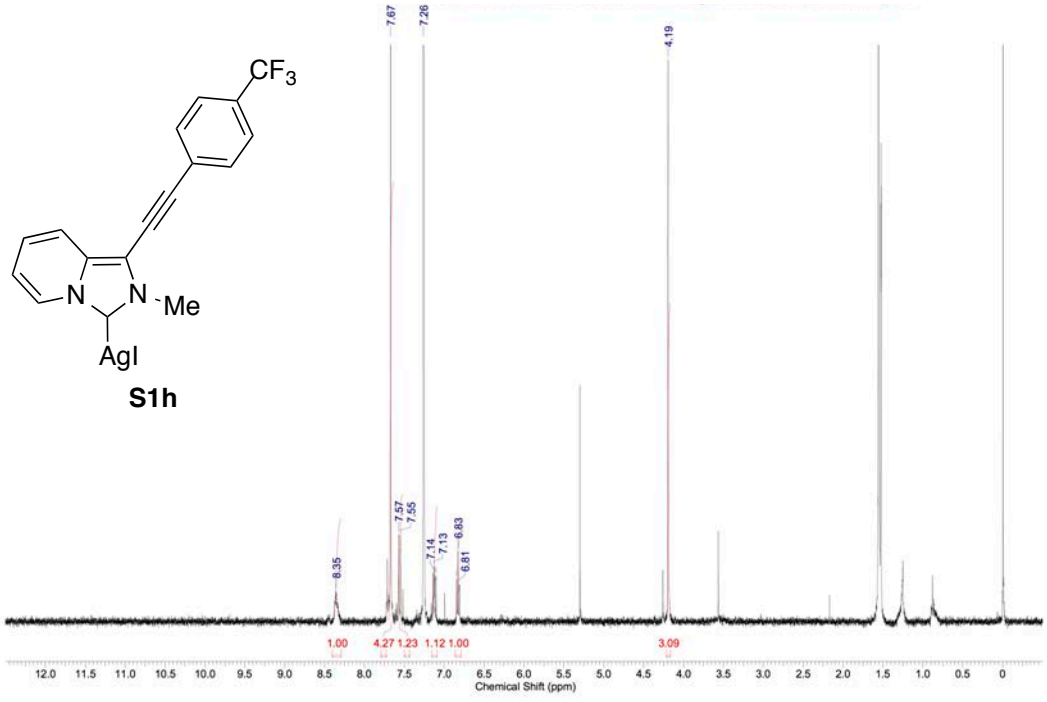

OMe
N
N
Me
AgI

S1f

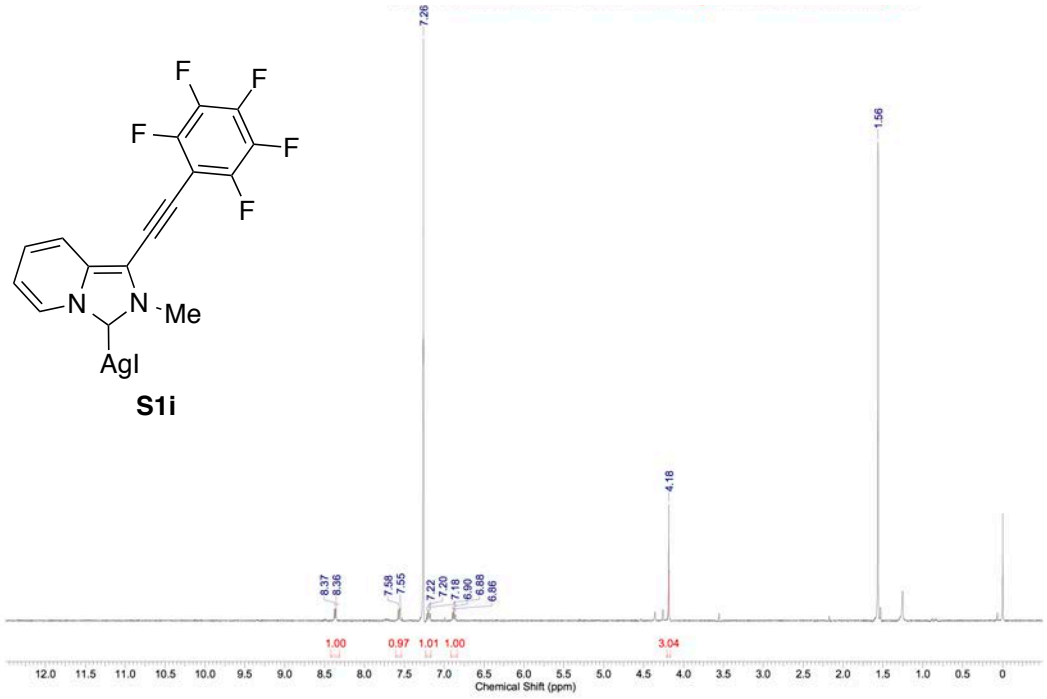
7.26
3.86
4.15
7.52
7.49
6.94
6.92
8.31
8.29
7.53
7.03
6.76
6.74
1.00
3.30
1.15
2.26
1.04
3.04
3.20
Chemical Shift (ppm)


Ph
N
N
Me
AgI
7.26
4.18
7.43
7.42
7.57
7.57
7.56
8.33
8.32
7.07
7.04
6.77
6.79
-0.01
1.00
3.49
3.39
0.96
0.93
3.42
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

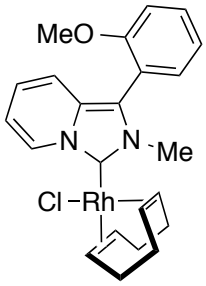
S1g


CF3
N
N
Me
AgI
7.67
7.26
4.19
7.57
7.55
7.14
7.13
6.83
6.81
8.35
1.00
4.27
1.23
1.12
1.00
3.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

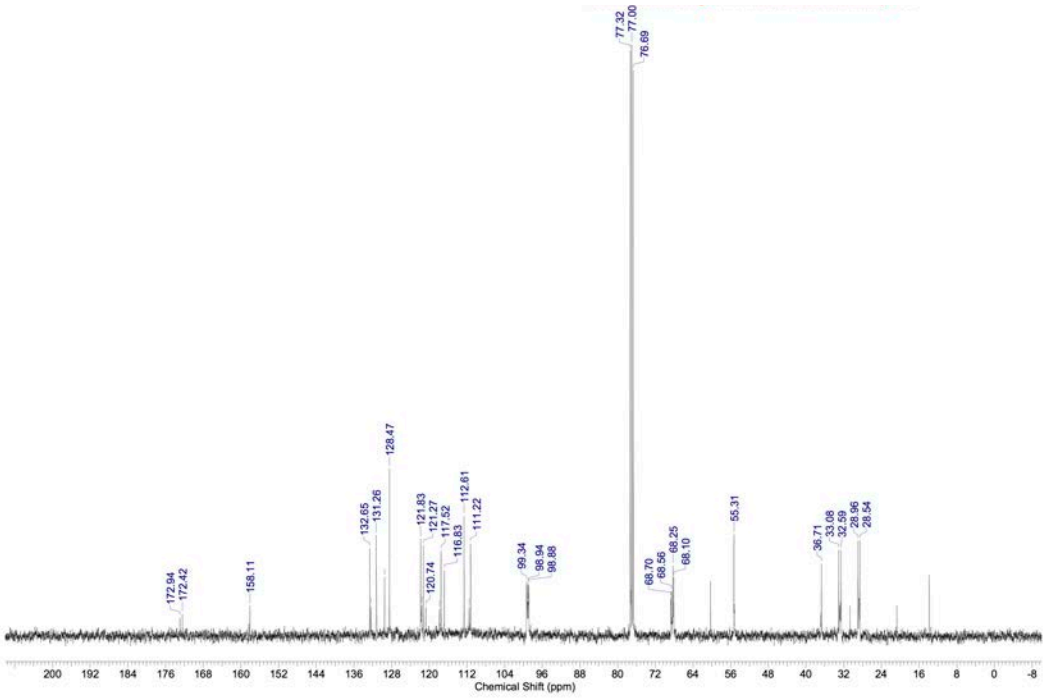
S1h

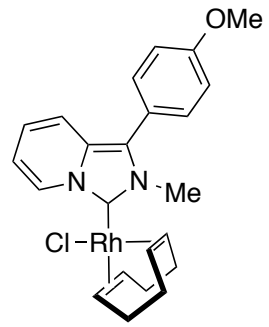

F
F
F
F
F
N
N
Me
AgI
7.26
1.56
4.18
8.37
8.36
7.58
7.55
7.22
7.20
7.18
6.90
6.88
6.86
1.00
0.97
1.01
1.00
3.04
Chemical Shift (ppm)

S1i

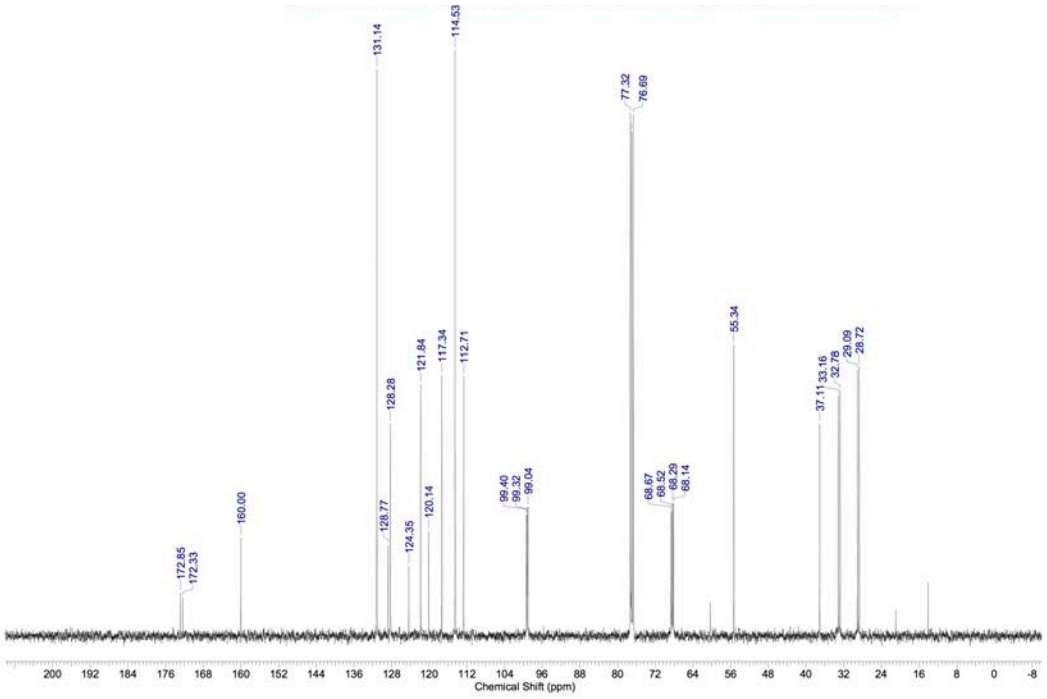


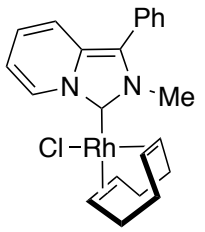
5a





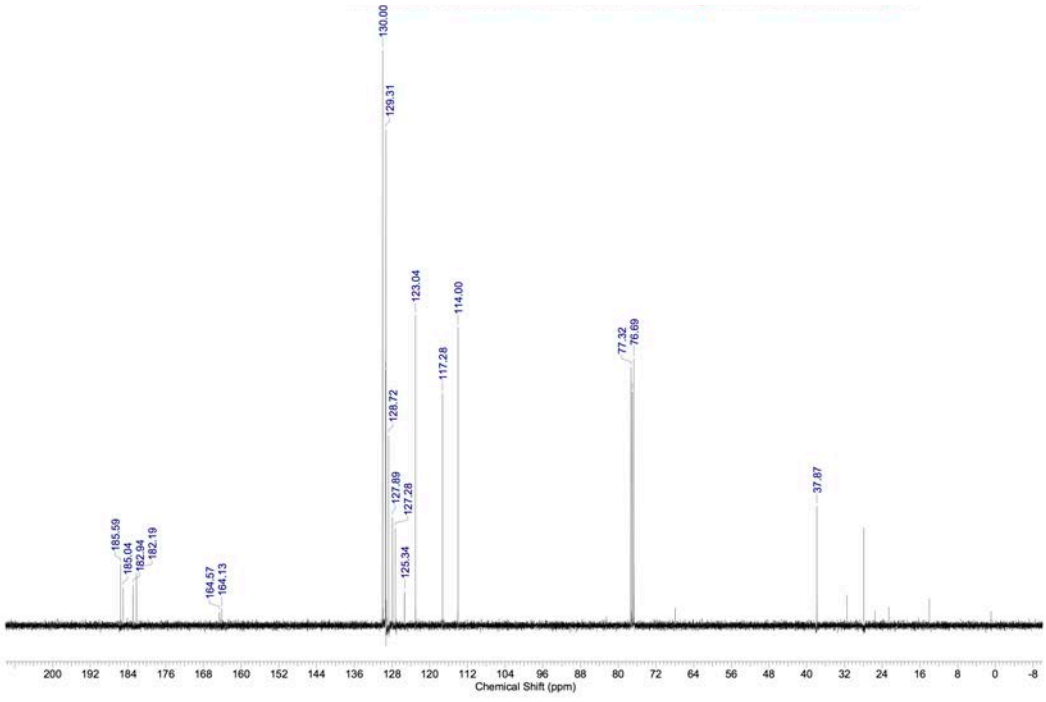
5b

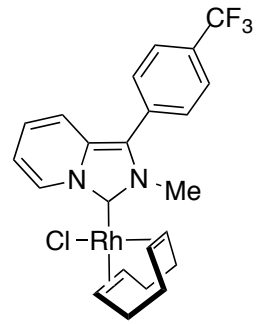



Ph
N
N
Me
Cl
Rh

5c

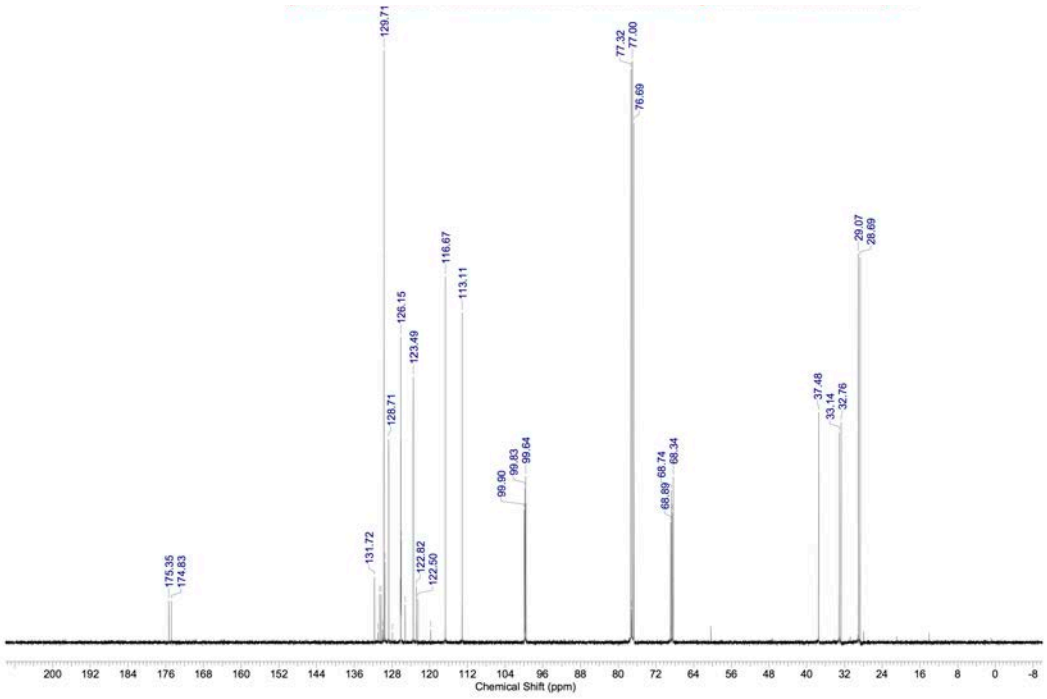
4.31
8.96
8.94
7.52
7.51
7.39
7.38
7.27
7.13
7.11
6.72
6.72
6.57
6.56
5.17
5.15
5.14
5.12
5.11
3.43
3.41
3.37
3.36
2.53
2.52
2.51
2.51
2.50
2.49
2.48
2.46
2.08
1.96
2.05
2.02
1.99
0.00
1.00
2.12
1.06
1.99
0.99
1.02
1.01
2.05
3.09
2.09
4.38
4.36
Chemical Shift (ppm)

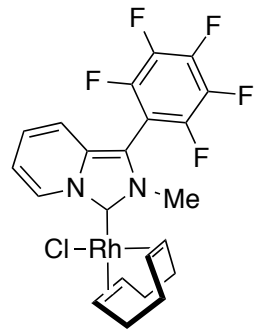

130.00
129.31
123.04
114.00
117.28
77.32
76.69
128.72
127.89
127.28
125.34
37.87
185.59
185.04
182.94
182.19
164.57
164.13
Chemical Shift (ppm)


CF3
N
N
Me
Cl
Rh

5d

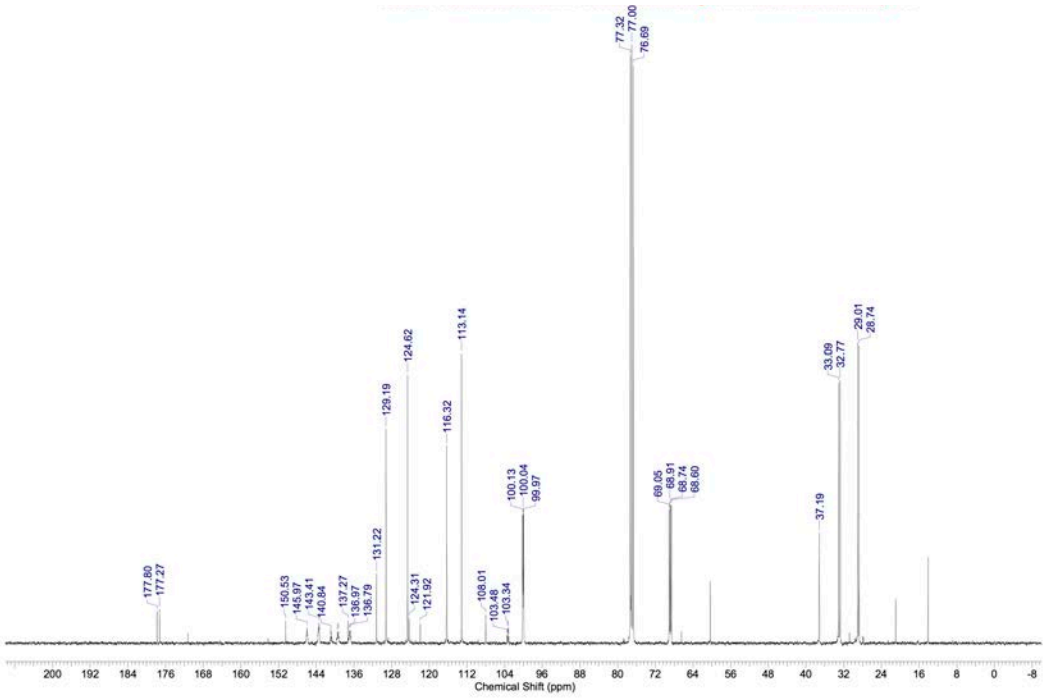
4.34
7.26
9.00
8.99
7.78
7.76
7.53
7.51
7.15
7.12
6.83
6.81
6.80
6.63
6.61
6.61
5.19
5.16
5.14
5.12
3.44
3.42
3.40
3.38
3.36
2.57
2.54
2.53
2.51
2.49
2.47
2.40
2.08
1.97
2.04
2.02
2.00
1.00
1.97
2.04
0.96
1.02
1.03
2.02
3.01
2.03
4.09
4.21
Chemical Shift (ppm)

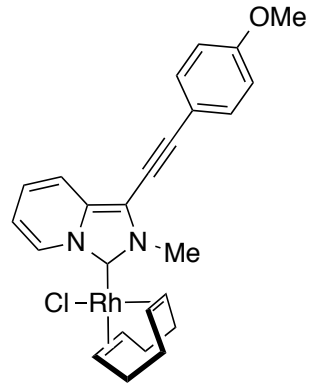

129.71
77.32
77.00
76.69
116.67
113.11
126.15
123.49
128.71
99.90
99.83
99.64
68.74
68.34
68.89
37.48
33.14
32.76
29.07
28.69
131.72
122.82
122.50
175.35
174.83
Chemical Shift (ppm)


F
F
F
F
F
N
N
Me
Cl
Rh

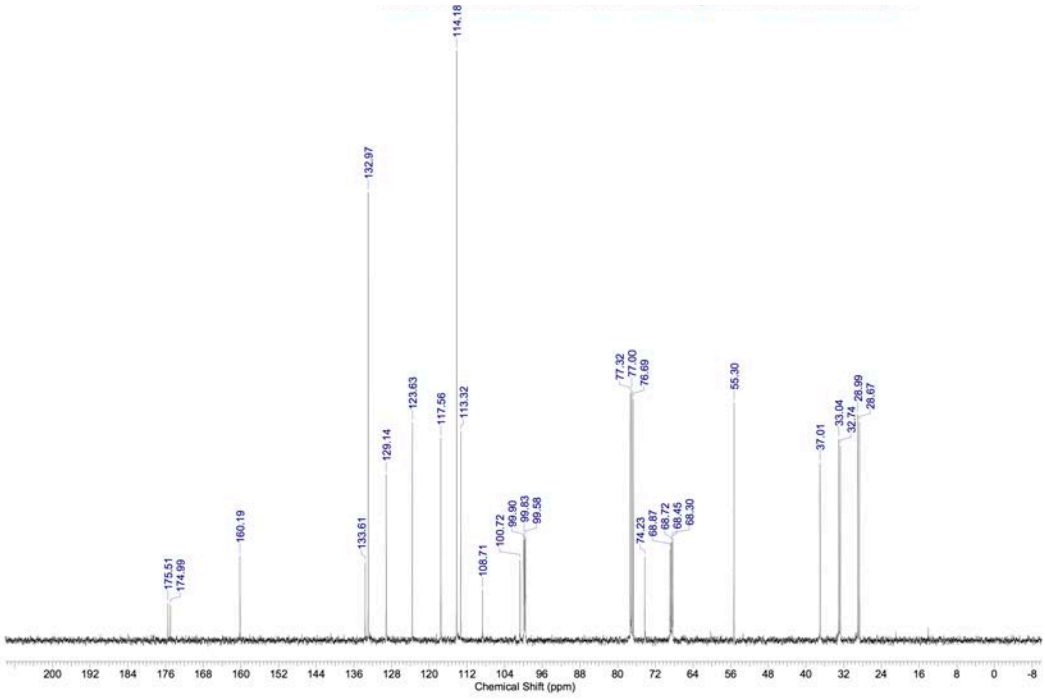
5e

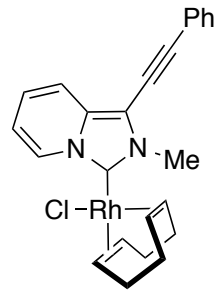
4.25
2.03
2.03
7.26
6.93
6.91
2.02
2.00
9.06
9.04
6.70
6.72
6.69
6.68
5.17
5.15
5.13
3.37
3.35
3.33
3.33
3.38
2.50
2.48
2.52
2.46
2.55
2.40
2.05
2.04
2.07
1.96
1.00
1.96
1.04
2.06
3.07
2.12
4.31
5.23
Chemical Shift (ppm)


77.32
77.00
76.69
113.14
124.62
129.19
116.32
131.22
100.13
100.04
99.97
69.05
68.91
68.74
68.60
33.09
32.77
29.01
28.74
37.19
177.80
177.27
150.53
145.97
143.41
140.84
137.27
136.97
136.79
124.31
121.92
108.01
103.48
103.34
Chemical Shift (ppm)



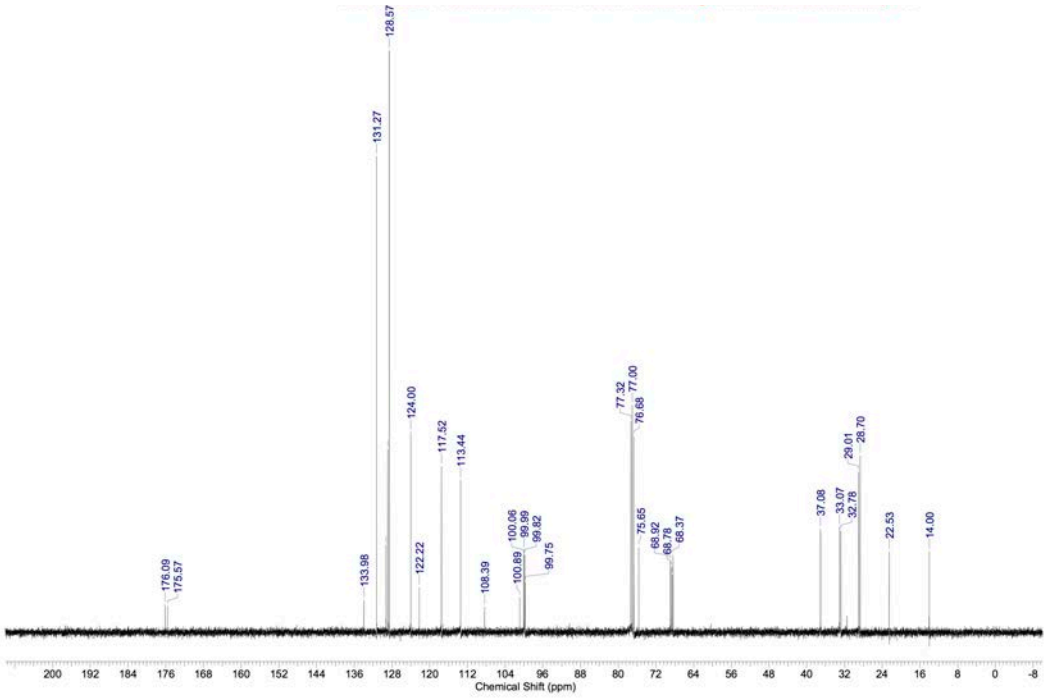
5f

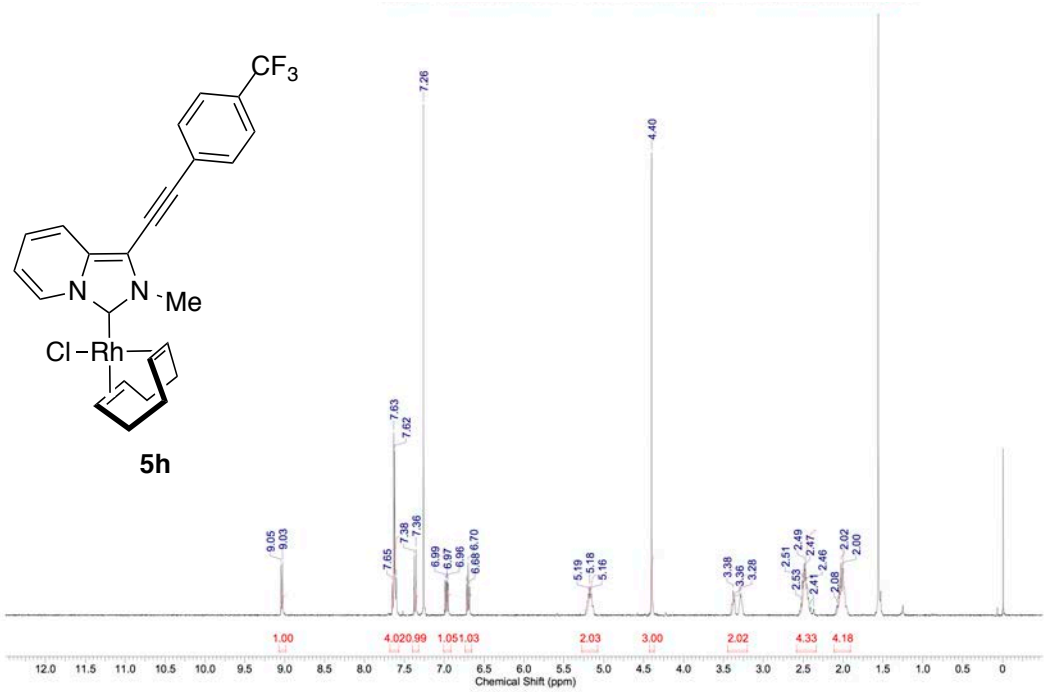



Ph
N
N
Me
Cl
Rh

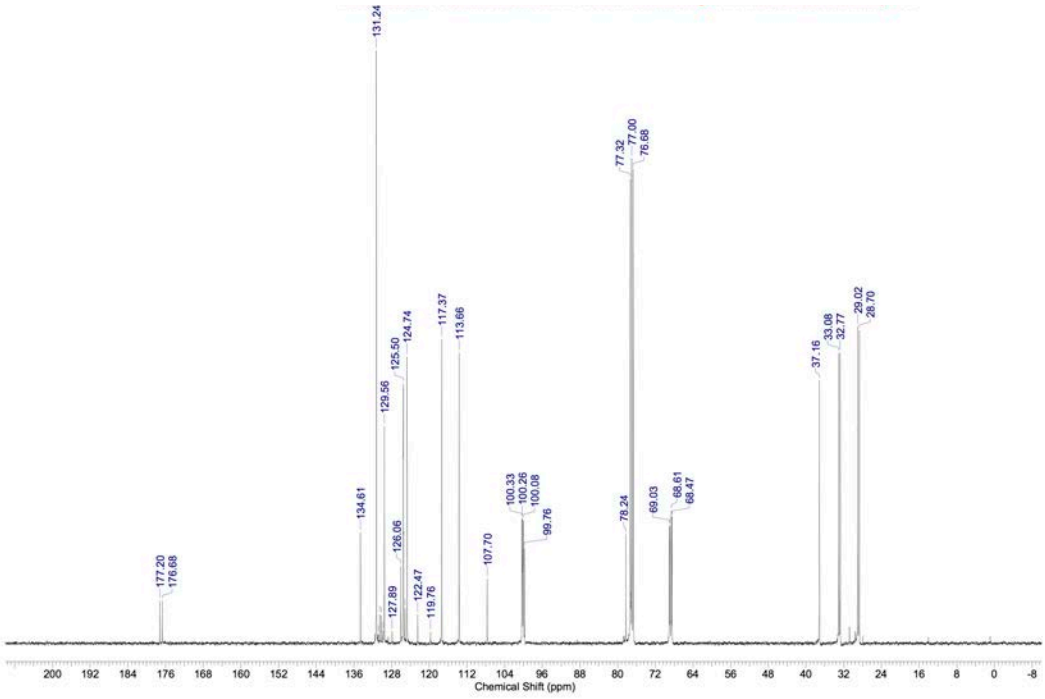
5g

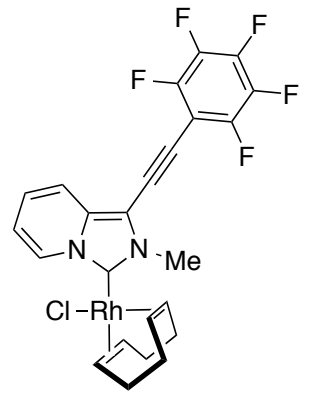
4.38
9.00
8.98
7.52
7.51
7.53
7.37
7.37
7.38
7.35
7.33
7.26
6.90
6.65
6.63
5.17
5.16
5.14
5.12
3.38
3.37
3.35
3.28
3.27
3.25
2.51
2.50
2.47
2.46
2.44
2.40
2.06
2.03
2.01
1.98
1.94
1.00
1.96
3.87
1.04
1.02
2.04
3.06
2.05
4.18
4.36
Chemical Shift (ppm)


128.57
131.27
124.00
117.52
113.44
77.32
77.00
76.68
75.65
69.92
68.78
68.37
37.08
33.07
32.78
29.01
28.70
22.53
14.00
176.09
175.97
133.98
122.22
108.39
100.89
100.06
99.99
99.82
99.75
Chemical Shift (ppm)


CF3
N
N
Me
Cl
Rh
7.26
4.40
7.63
7.62
9.05
9.03
7.65
7.38
7.36
6.99
6.97
6.96
6.68
6.70
5.19
5.18
5.16
3.38
3.35
3.28
2.51
2.49
2.47
2.46
2.41
2.08
2.02
2.00
1.00
4.02
0.99
1.05
1.03
2.03
3.00
2.02
4.33
4.18
Chemical Shift (ppm)

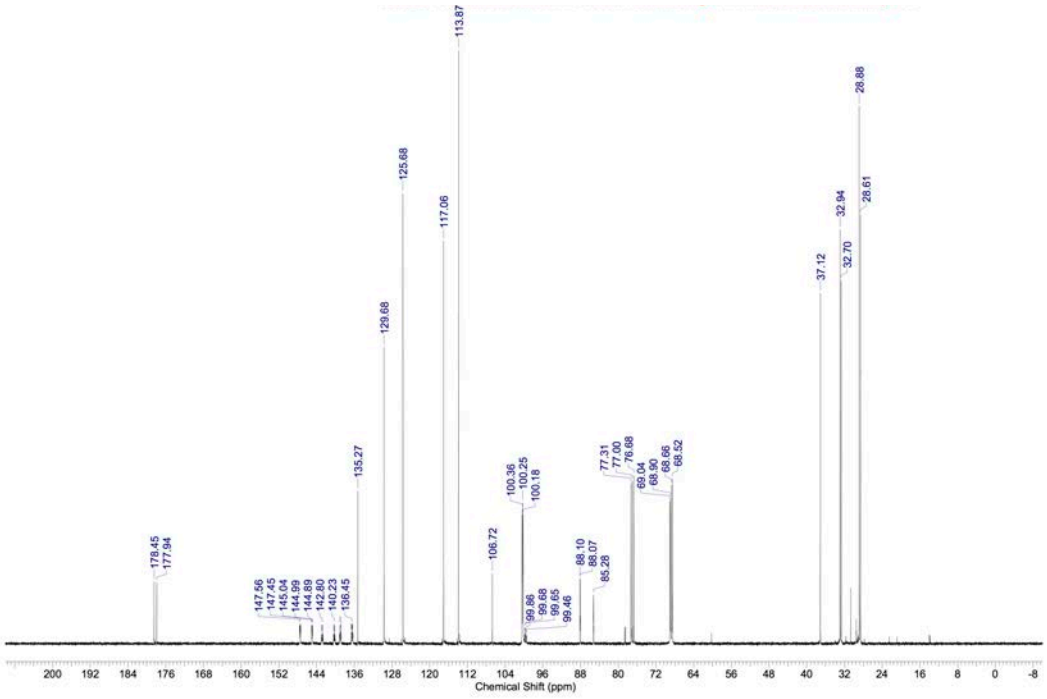
5h

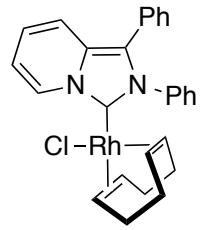

131.24
77.32
77.00
76.68
117.37
113.66
124.74
125.50
129.56
134.61
126.06
127.89
122.47
119.76
107.70
100.33
100.26
100.08
99.76
78.24
69.03
68.61
68.47
37.16
33.08
32.77
29.02
28.70
177.20
176.68
Chemical Shift (ppm)


F
F
F
F
F
N
N
Me
Cl
Rh

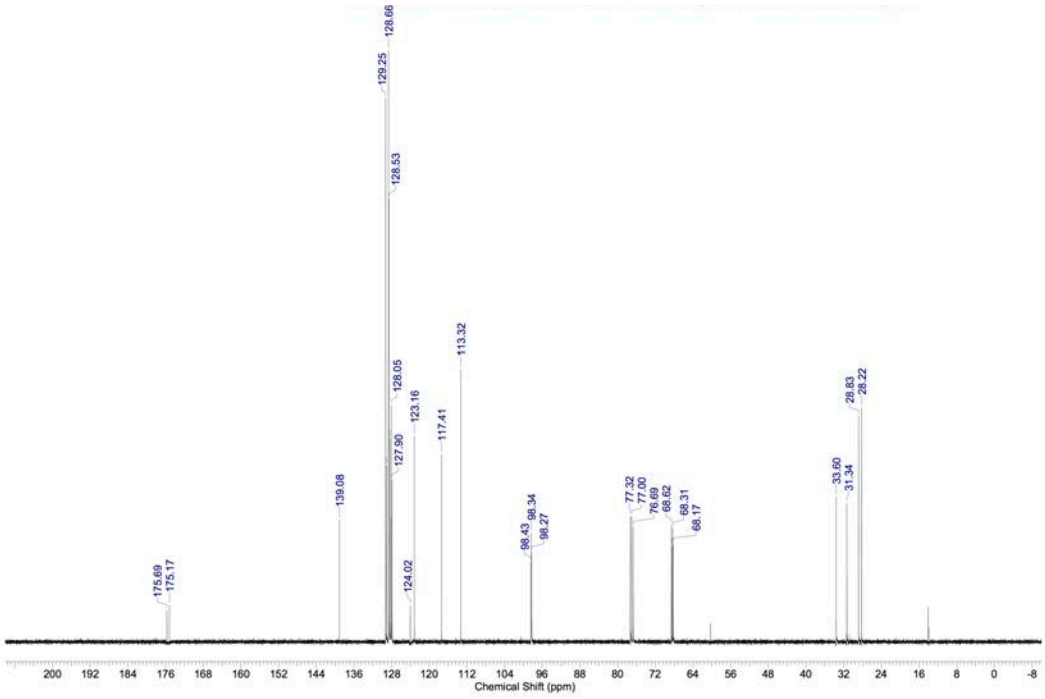
5i

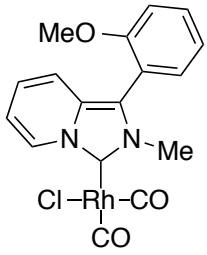
7.26
4.40
9.09
9.07
7.38
7.36
7.05
7.04
7.02
6.75
6.73
6.73
5.19
5.17
3.40
3.38
3.37
3.29
3.28
2.53
2.51
2.50
2.48
2.47
2.46
2.04
2.03
2.00
1.97
1.00
0.99
1.05
1.07
2.10
3.03
2.08
4.45
4.33
Chemical Shift (ppm)


113.87
125.68
117.06
129.68
135.27
28.88
32.94
28.61
32.70
37.12
77.31
77.00
76.68
69.04
68.90
68.66
68.52
100.36
100.25
100.18
106.72
88.10
88.07
85.28
178.45
177.94
147.56
147.45
145.04
144.99
144.89
142.80
142.23
138.45
99.86
99.68
99.65
99.46
Chemical Shift (ppm)



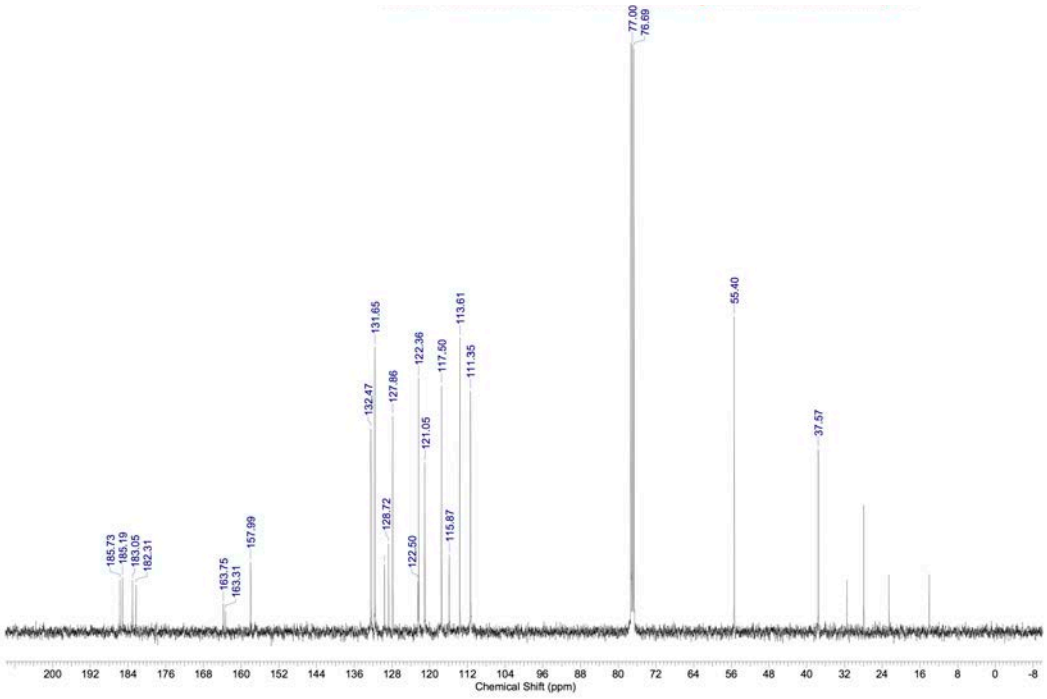
5j

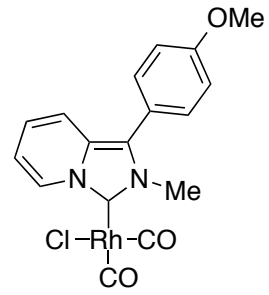



MeO
N
N
Me
Cl
Rh
CO
CO

6a

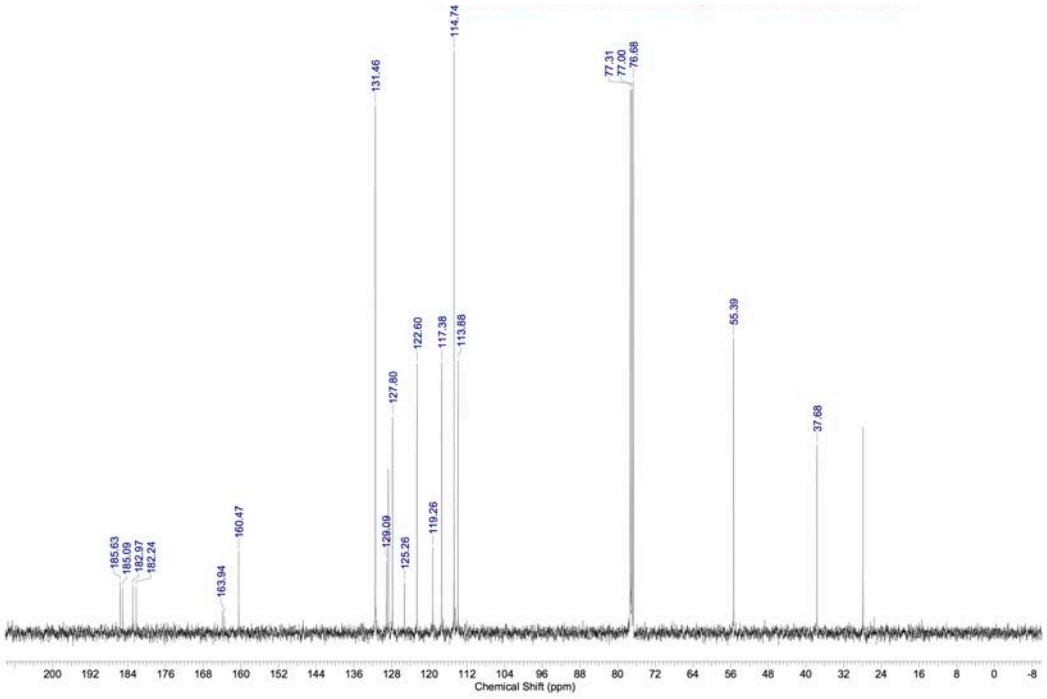
4.00
3.82
8.62
8.60
7.52
7.51
7.30
7.29
7.28
7.26
7.10
7.07
7.07
7.05
6.81
6.79
6.62
6.61
1.00
1.18
1.10
3.51
1.16
1.16
3.32
3.59
Chemical Shift (ppm)

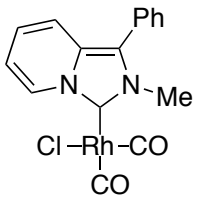

77.00
76.69
55.40
37.57
131.65
132.47
127.86
122.36
121.05
117.50
113.61
111.35
128.72
122.50
115.87
157.99
163.75
163.31
165.73
165.19
183.05
182.31
Chemical Shift (ppm)


OMe
N
N
Me
Cl
Rh
CO
CO

6b

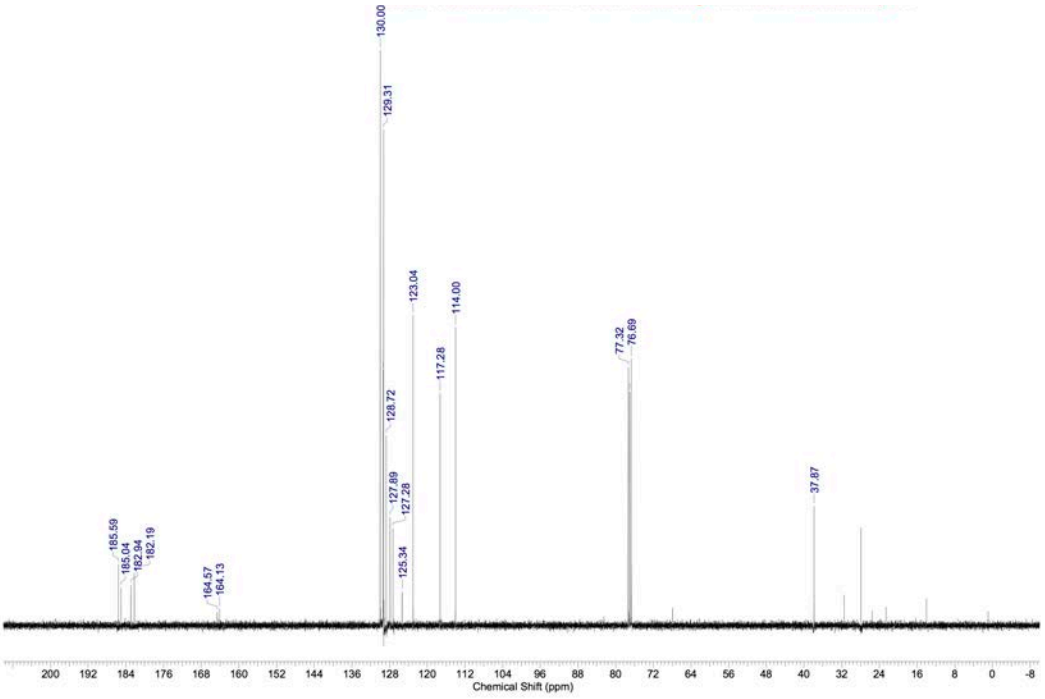
7.26
4.10
3.89
7.36
7.34
7.07
7.05
8.60
8.58
7.37
7.18
6.83
6.82
6.79
6.64
6.63
1.00
2.09
0.92
2.27
1.04
1.07
3.09
3.50
Chemical Shift (ppm)

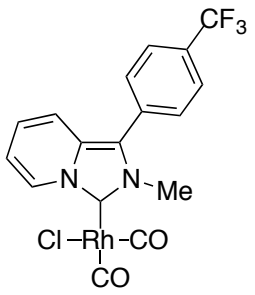

114.74
131.46
77.31
77.00
76.68
55.39
122.60
117.38
113.88
127.80
37.68
160.47
129.09
119.26
125.26
185.63
185.09
182.97
182.24
163.94
Chemical Shift (ppm)


Ph
N
N
Me
Cl
Rh
CO
CO

6c

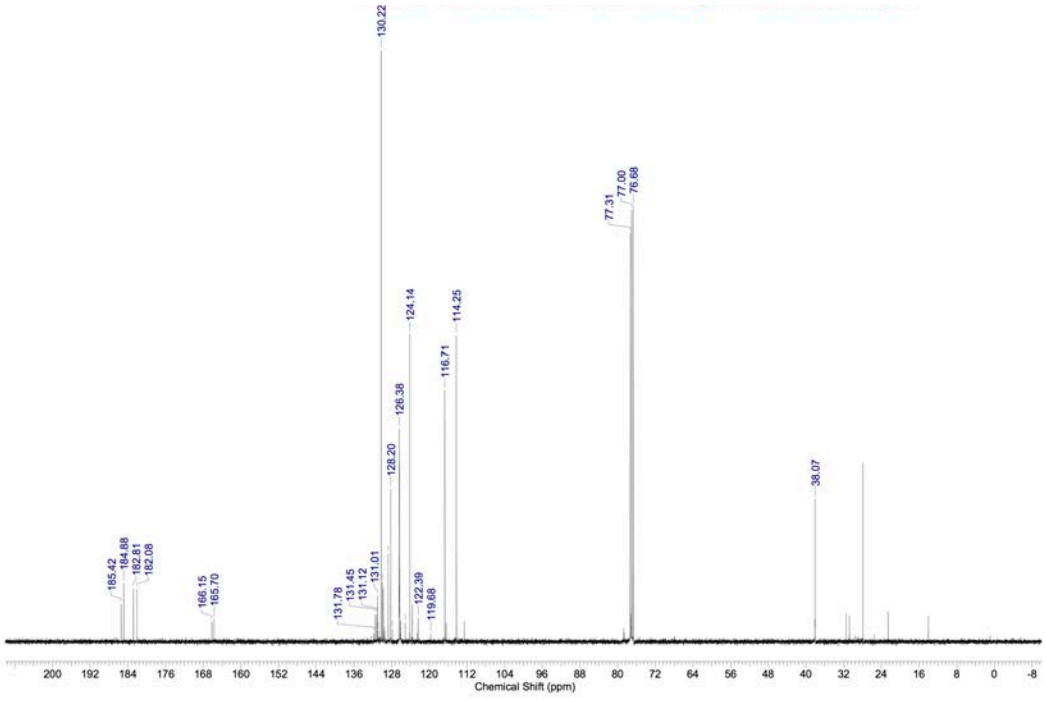
4.14
7.26
7.55
7.53
7.45
7.42
7.35
7.23
8.63
8.61
7.57
7.57
7.22
6.86
6.85
6.66
6.65
6.64
1.00
3.65
2.31
1.09
1.15
1.14
3.42
Chemical Shift (ppm)

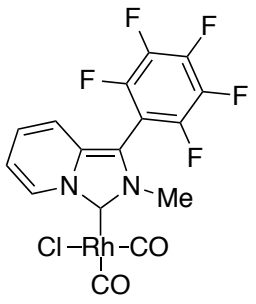

130.00
129.31
123.04
114.00
117.28
77.32
76.69
128.72
127.89
127.28
125.34
37.87
185.59
185.04
182.94
182.19
164.57
164.13
Chemical Shift (ppm)


CF3
N
N
Me
Cl
Rh
CO
CO

6d

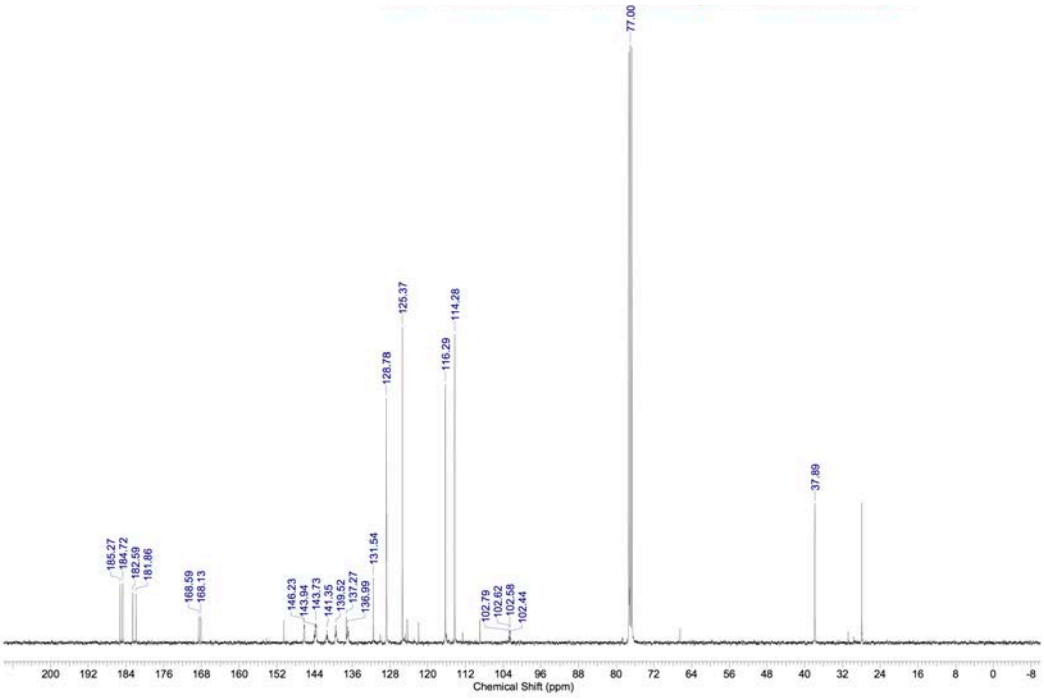
4.17
8.67
8.65
7.83
7.81
7.60
7.58
7.26
7.24
7.24
6.93
6.70
6.72
1.01
2.60
2.46
0.95
1.18
1.18
3.47
Chemical Shift (ppm)

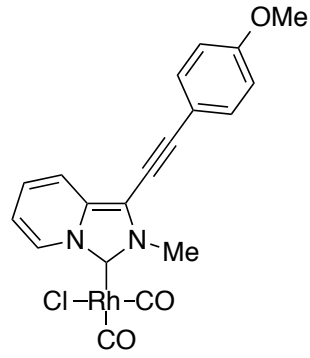

130.22
77.31
77.00
76.68
124.14
114.25
116.71
126.38
128.20
38.07
185.42
184.88
183.81
182.08
166.15
165.70
131.78
131.45
131.12
131.01
122.39
119.68
Chemical Shift (ppm)


F
F
F
F
F
N
N
Me
Cl–Rh–CO
CO

6e

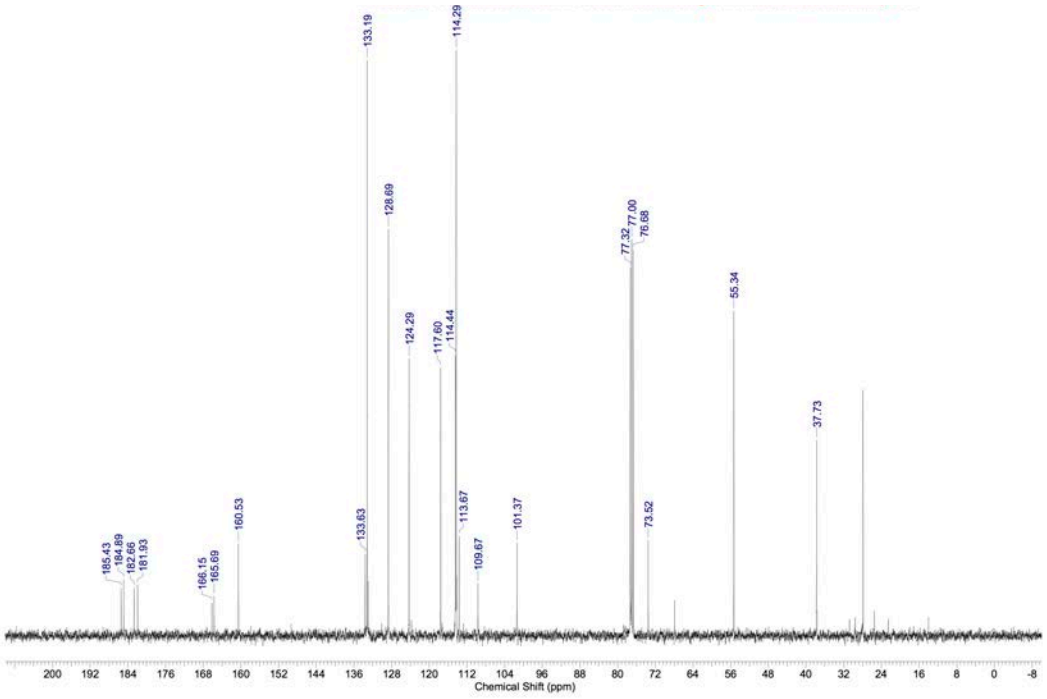
7.26
4.11
7.07
8.76
8.74
7.05
7.05
6.82
6.80
6.78
6.78
1.00
2.42
1.18
3.44
Chemical Shift (ppm)

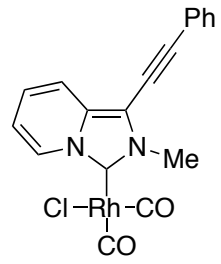

77.00
125.37
114.26
116.29
128.78
37.89
131.54
185.27
184.72
182.59
181.86
168.59
168.13
146.23
143.94
141.73
141.35
139.52
137.27
136.99
102.79
102.62
102.58
102.44
Chemical Shift (ppm)


OMe
N
N
Me
Cl–Rh–CO
CO

6f

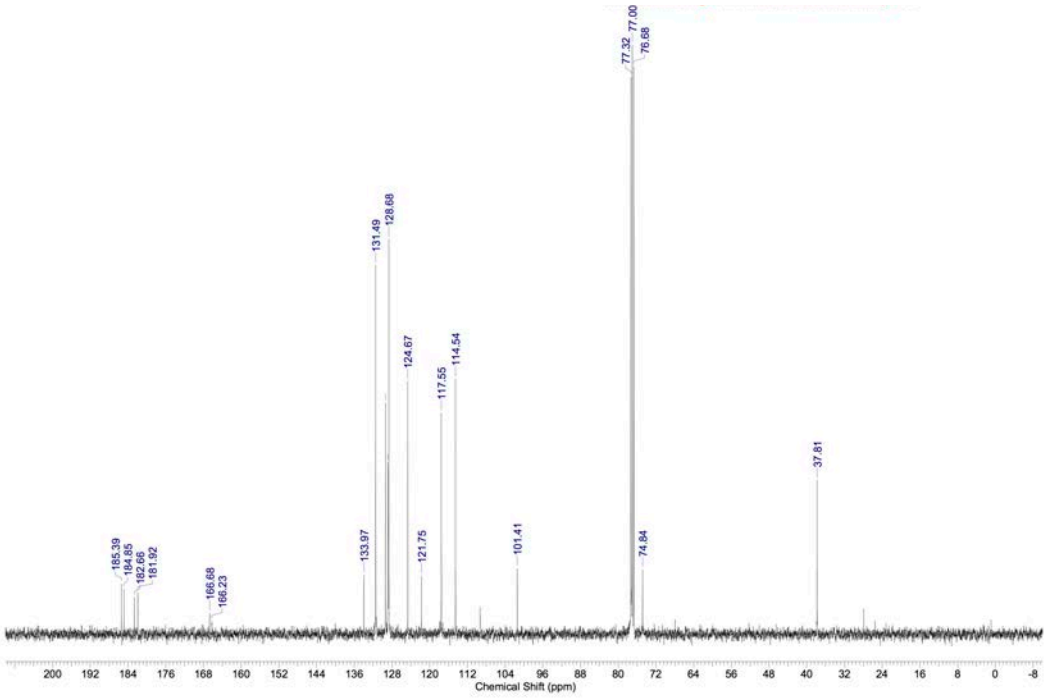
3.85
4.23
7.50
7.48
6.93
6.91
8.64
8.62
7.47
7.45
7.26
6.98
6.73
6.71
6.70
7.51
7.51
1.00
3.35
1.09
2.47
1.09
3.14
3.50
Chemical Shift (ppm)

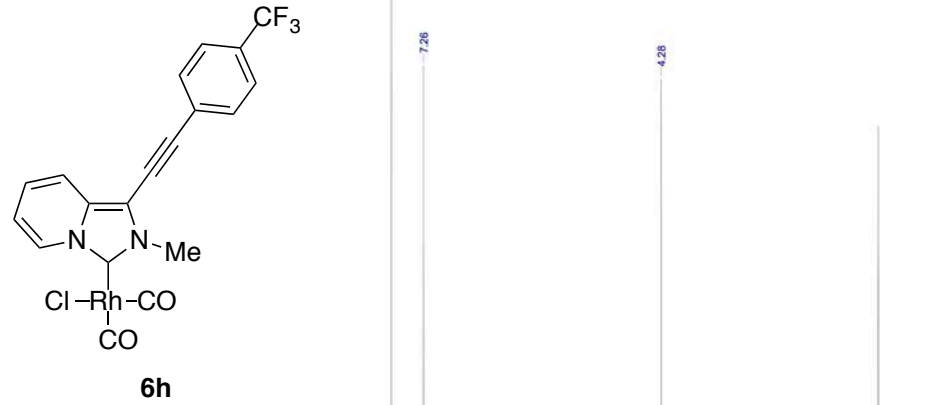

133.19
114.29
128.69
77.32
77.00
76.68
55.34
124.29
117.60
114.44
37.73
185.43
184.89
182.66
181.93
166.15
165.69
160.53
133.63
113.67
101.37
73.52
109.67
Chemical Shift (ppm)


Ph
N
N
Me
Cl
Rh
CO
CO

6g

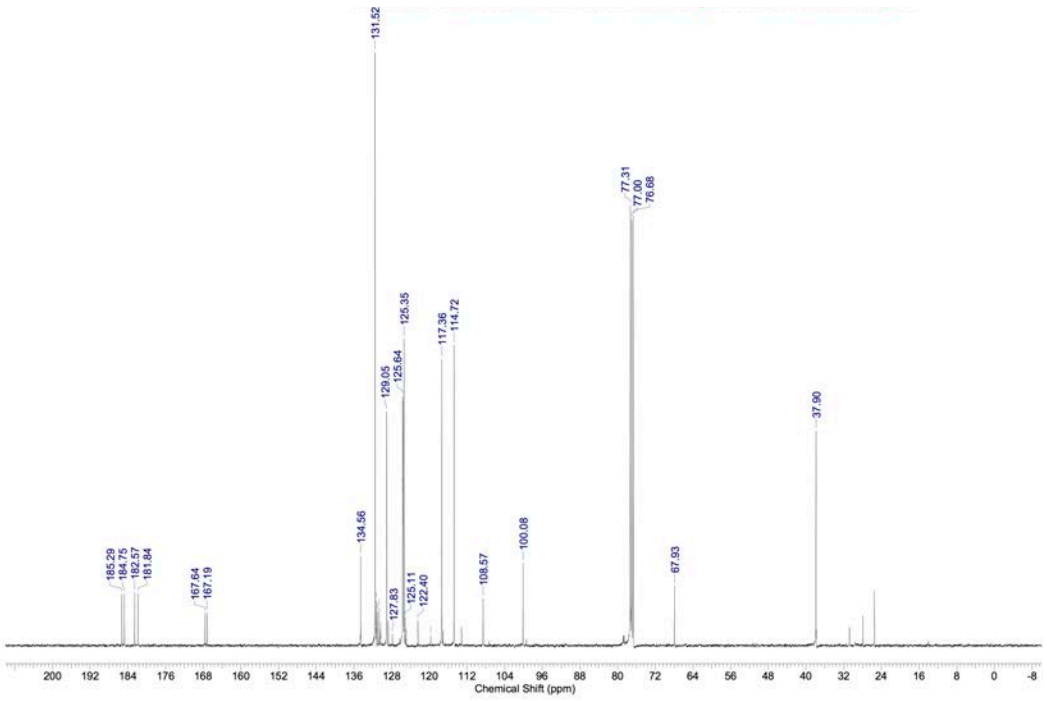
4.26
7.26
7.42
7.56
7.57
7.57
8.68
8.66
7.05
7.04
7.02
6.73
6.75
6.73
1.00
2.40
1.09
3.51
1.16
1.13
3.36
Chemical Shift (ppm)

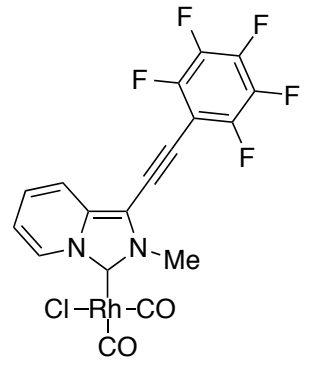

77.32
77.00
76.68
131.49
128.68
124.67
117.55
114.54
37.81
185.39
184.85
182.66
181.92
166.68
166.23
133.97
121.75
101.41
74.84
Chemical Shift (ppm)


CF3
N
N
Me
Cl
Rh
CO
CO

6h

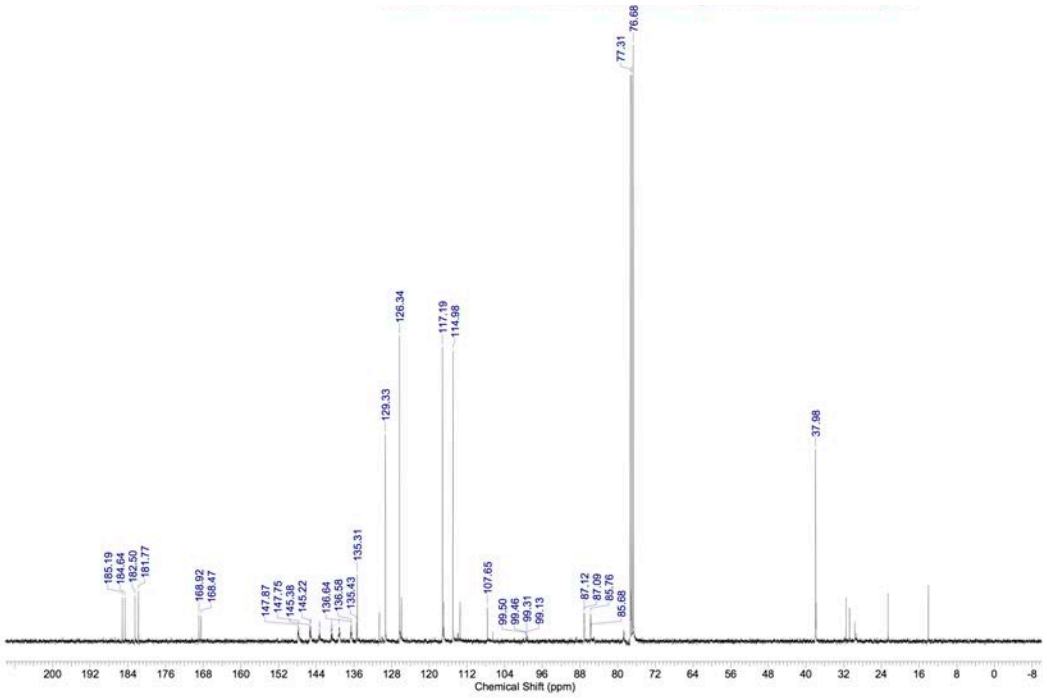
7.66
7.26
4.28
8.71
8.69
7.52
7.50
7.11
7.09
6.79
6.77
6.77
1.00
4.70
1.04
1.13
1.12
3.26
Chemical Shift (ppm)

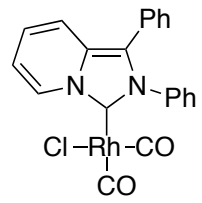

131.52
77.31
77.00
76.68
125.35
117.36
114.72
129.05
125.64
37.90
134.56
100.08
185.29
184.75
182.57
181.84
167.64
167.19
127.83
125.11
122.40
108.57
67.93
Chemical Shift (ppm)


F
F
F
F
F
N
N
Me
Cl–Rh–CO
CO

6i

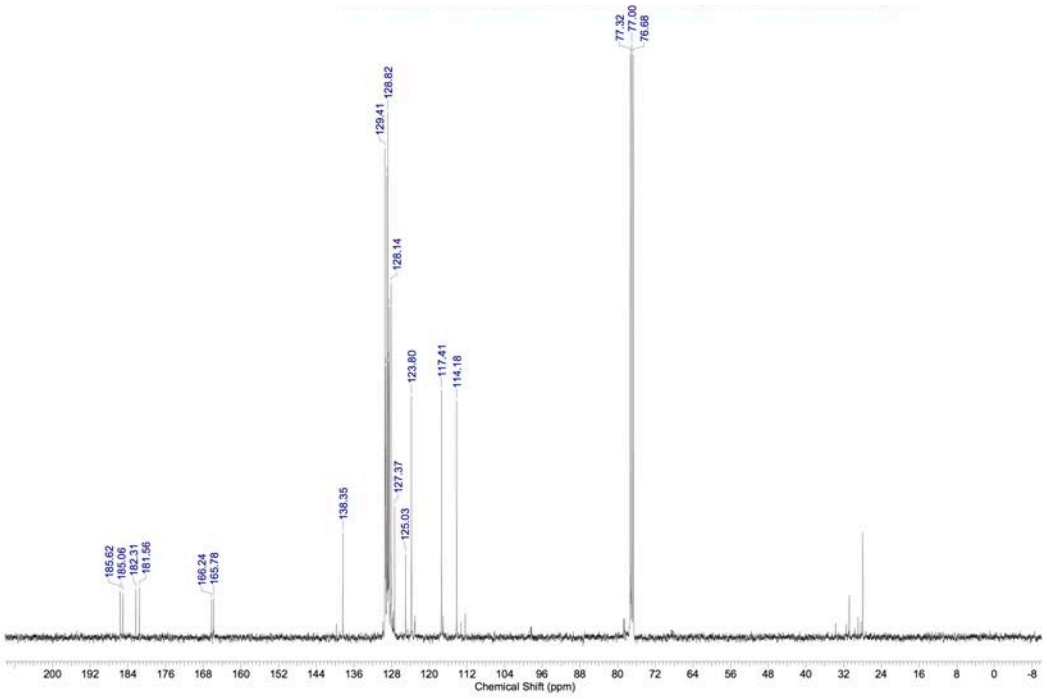
7.26
4.28
8.76
8.74
7.52
7.50
7.16
7.14
6.83
6.81
1.00
1.11
1.21
1.15
3.31
Chemical Shift (ppm)

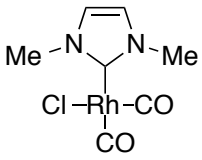

77.31
76.68
126.34
117.19
114.98
129.33
37.98
185.19
184.64
182.50
181.77
168.92
168.47
147.87
147.75
145.38
145.22
136.64
136.58
135.43
135.31
107.65
99.50
99.46
99.31
99.13
87.12
87.09
85.76
85.68
Chemical Shift (ppm)


Ph
N
N
Ph
Cl
Rh
CO
CO

6j

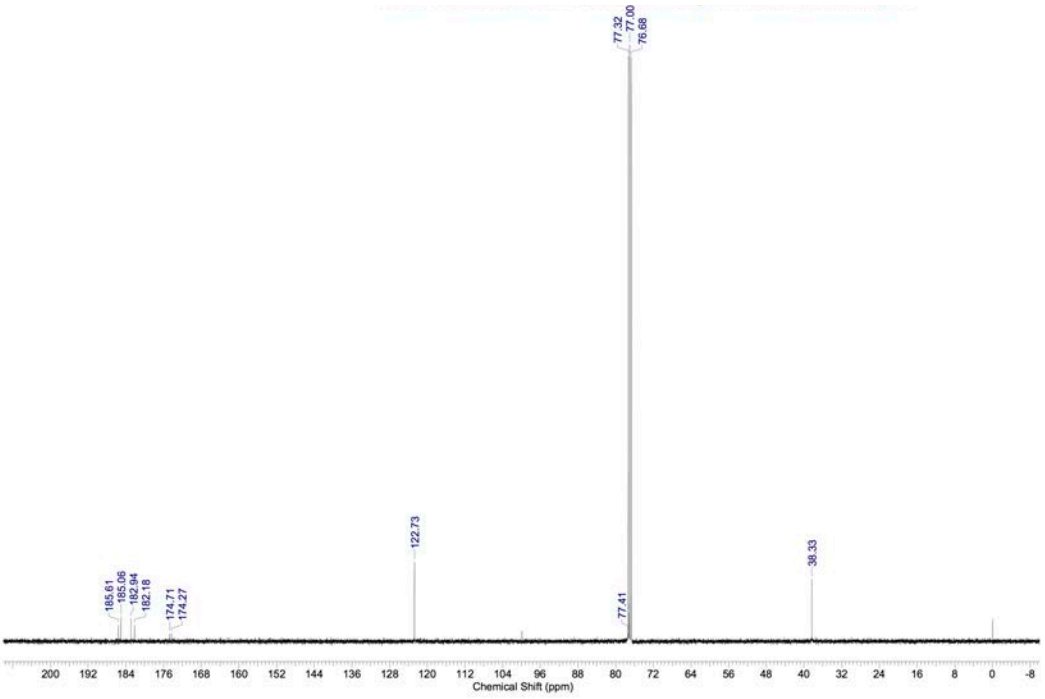
7.26
7.31
7.45
7.32
7.16
7.15
7.14
6.72
8.81
8.79
7.48
6.94
6.74
6.71
6.70
1.00
6.89 3.55 2.37 1.13 1.10
Chemical Shift (ppm)

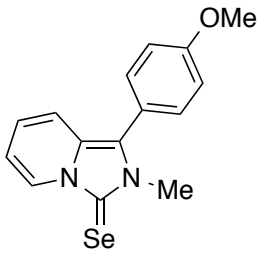

77.32
77.00
76.68
129.41
128.62
128.14
123.80
117.41
114.18
138.35
127.37
125.03
195.62
195.06
182.31
181.56
166.24
165.78
Chemical Shift (ppm)


Me
N
N
Me
Cl
Rh
CO
CO

10a

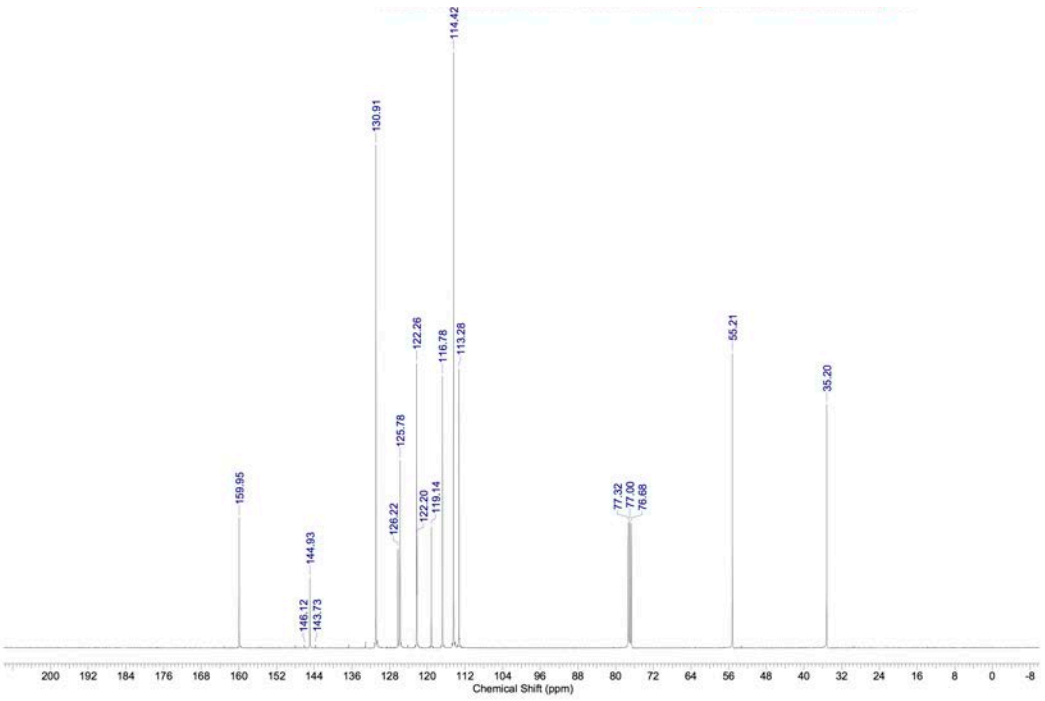
3.91
6.94
7.26
1.58
2.00
6.20
Chemical Shift (ppm)

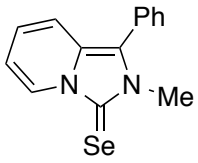

77.32
77.00
76.68
122.73
38.33
77.41
165.61
165.06
183.04
182.18
174.71
174.27
Chemical Shift (ppm)


OMe
N
N
Me
Se

13b

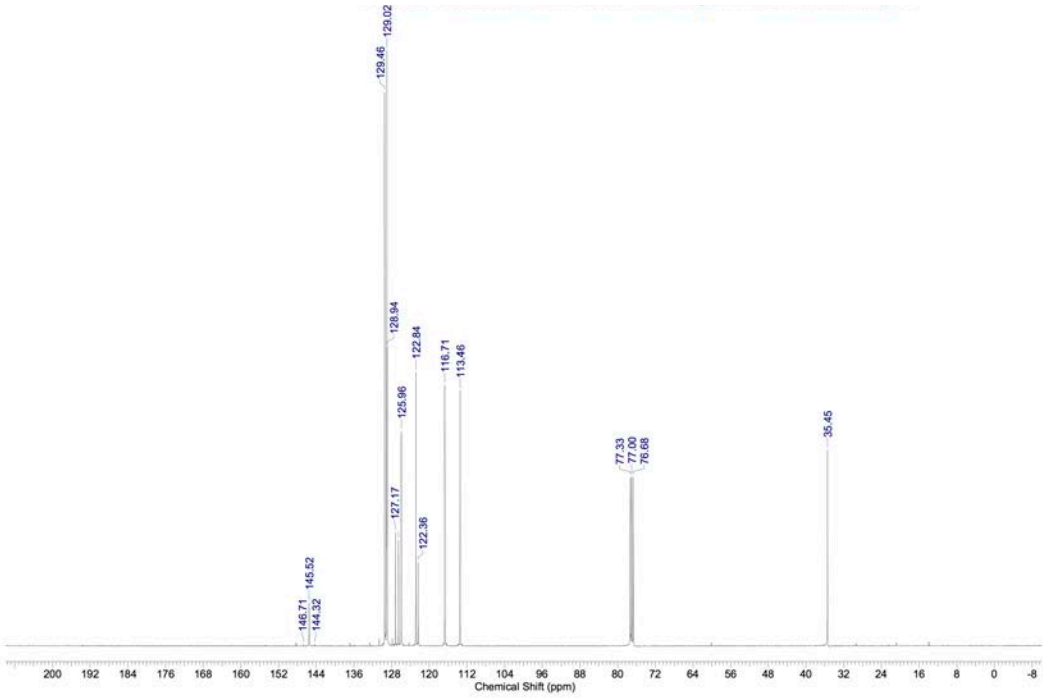
3.89
3.92
7.26
7.06
7.34
7.32
7.04
8.53
8.51
7.14
6.79
6.77
6.62
6.64
1.00
2.08
1.04
2.07
1.04
1.04
3.26
3.19
Chemical Shift (ppm)

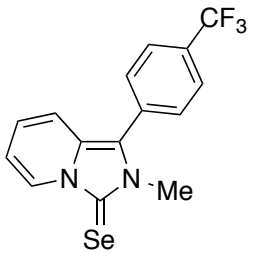

114.42
130.91
122.26
116.78
113.28
125.78
55.21
35.20
159.95
126.22
122.20
119.14
144.93
146.12
143.73
77.32
77.00
76.68
Chemical Shift (ppm)


Ph
N
N
Me
Se

13b

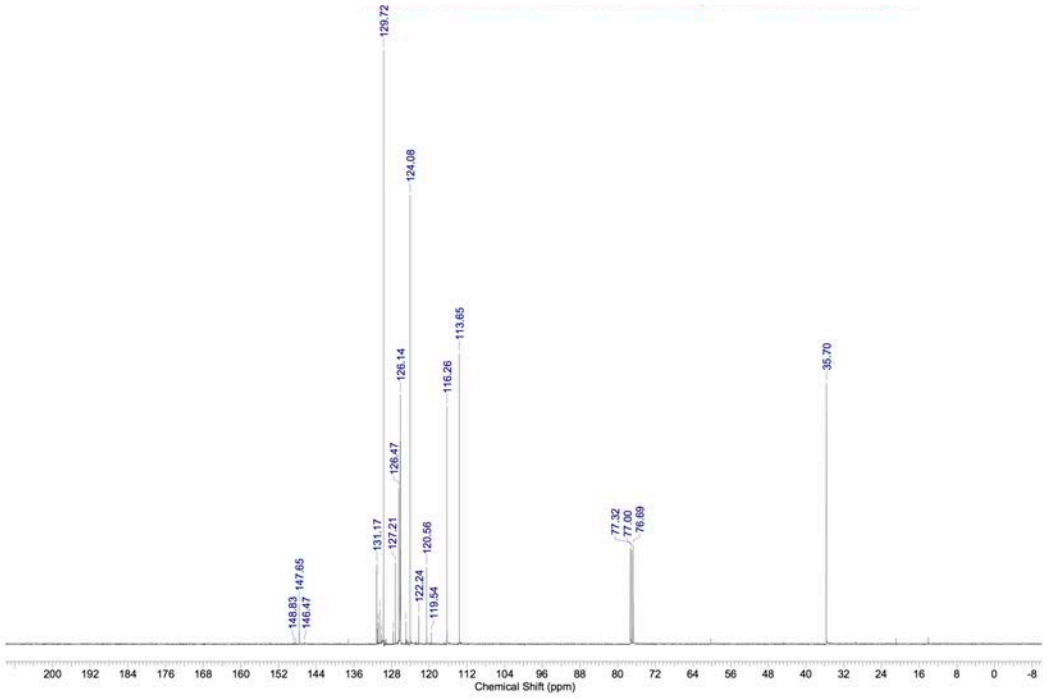
3.96
7.26
7.55
7.53
7.43
7.41
7.22
7.20
6.83
6.81
6.66
6.65
8.55
8.54
7.56
1.00
3.11
1.98
1.06
0.98
0.99
2.99
Chemical Shift (ppm)

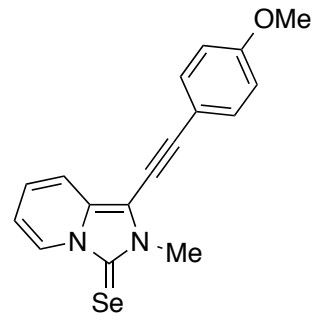

129.02
129.46
128.94
122.84
116.71
113.46
125.96
127.17
122.36
77.33
77.00
76.68
35.45
146.71
145.52
144.32
Chemical Shift (ppm)


CF3
N
N
Me
Se

13b

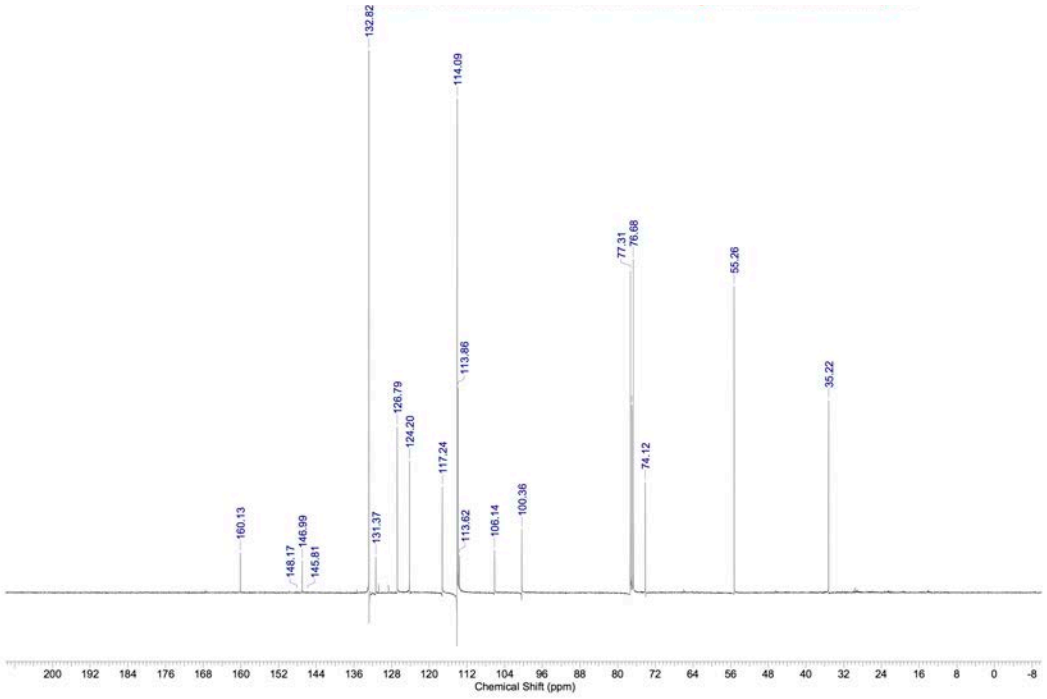
3.98
7.26
7.82
7.79
7.57
7.55
7.21
6.90
6.89
6.88
6.86
6.85
6.72
6.70
8.60
8.59
8.58
1.00
2.04
2.09
1.00
1.04
1.02
3.03
Chemical Shift (ppm)

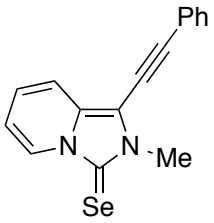

129.72
124.08
126.14
126.47
113.65
116.26
35.70
131.17
127.21
120.56
122.24
119.54
147.65
148.63
146.47
77.32
77.00
76.69
Chemical Shift (ppm)


OMe
N
N
Me
Se

13f

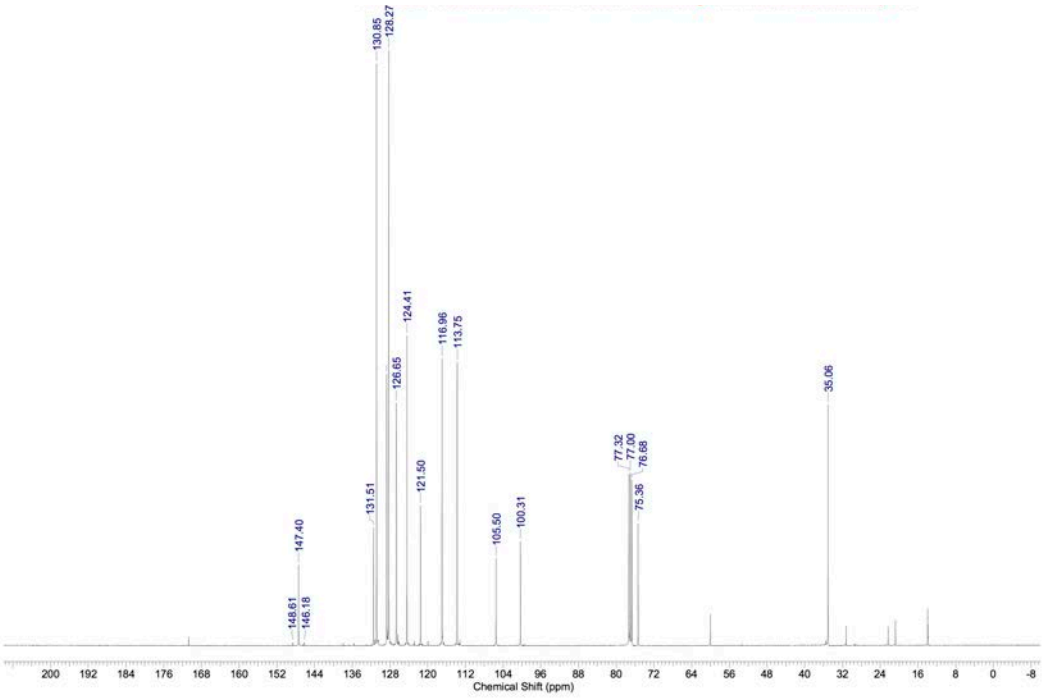
4.03
3.85
7.26
7.51
7.48
6.93
6.91
8.57
8.55
8.54
7.41
6.95
6.94
6.73
6.71
6.71
6.70
6.69
7.51
1.00
2.25
1.03
3.40
1.08
3.09
3.15
Chemical Shift (ppm)

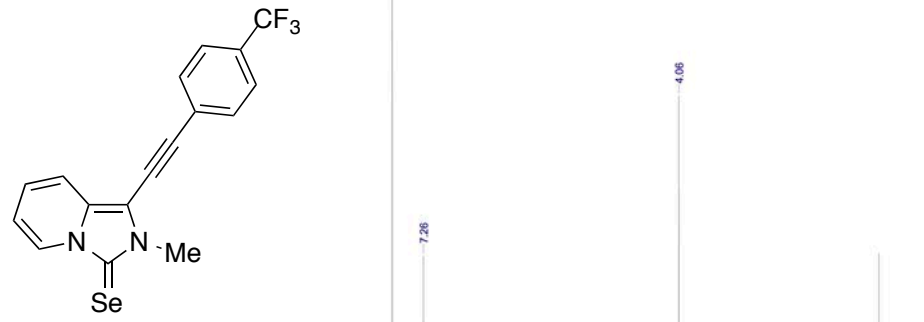

132.82
114.09
77.31
76.68
55.26
113.86
35.22
126.79
124.20
74.12
117.24
160.13
131.37
113.62
106.14
100.36
148.17
146.99
145.81
Chemical Shift (ppm)


Ph
N
N
Me
Se

13g

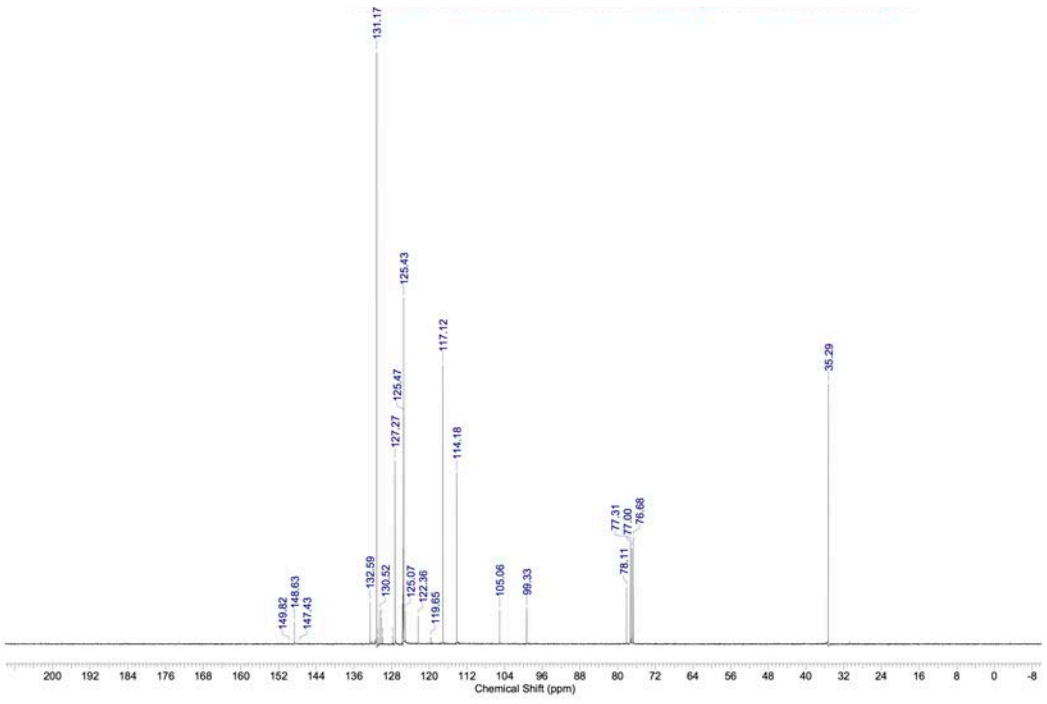
4.05
8.59
8.57
7.57
7.56
7.55
7.54
7.41
7.40
7.26
7.01
6.99
6.97
6.73
6.71
6.71
1.00
2.24
1.10
3.44
1.16
1.12
3.16
Chemical Shift (ppm)

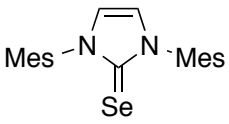

130.65
128.27
124.41
116.96
113.75
126.65
121.50
131.51
147.40
148.61
146.18
105.50
100.31
77.32
77.00
76.68
75.36
35.06
Chemical Shift (ppm)


CF3
N
N
Me
Se

13h

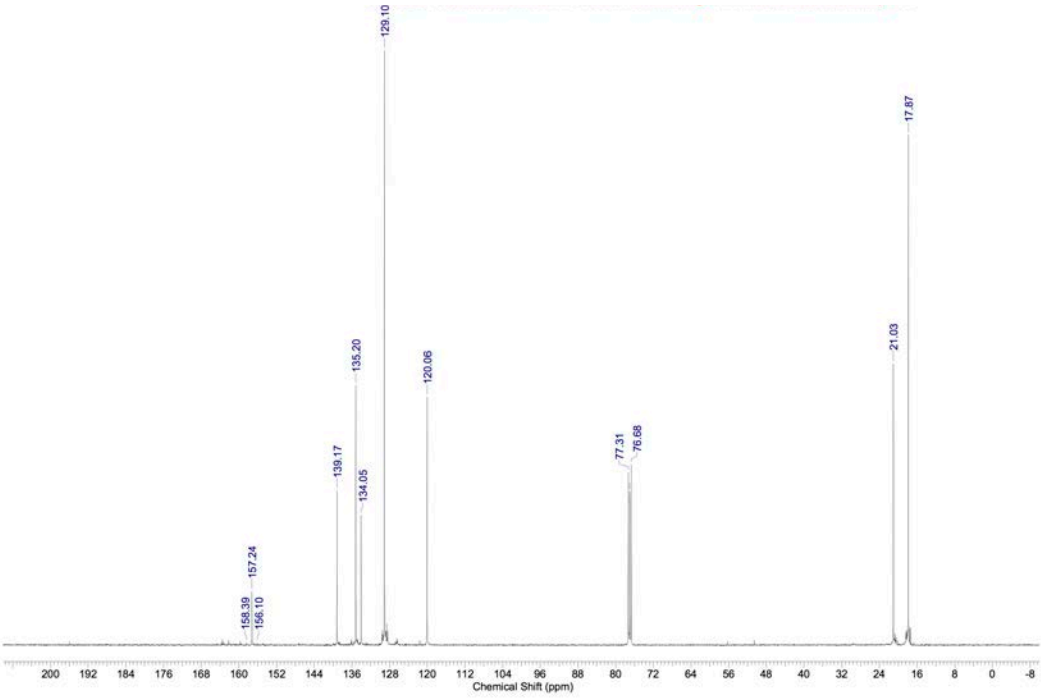
7.65
4.06
7.26
8.62
8.61
7.48
7.45
7.07
7.05
7.05
6.77
6.75
1.00
4.25
1.10
1.05
1.04
3.17
Chemical Shift (ppm)

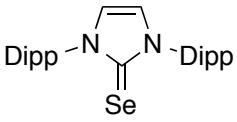

131.17
125.43
117.12
35.29
125.47
127.27
114.18
77.31
77.00
76.68
78.11
132.59
130.52
125.07
122.36
119.65
105.06
99.33
149.82
148.63
147.43
Chemical Shift (ppm)


Mes
N
N
Mes
Se

14

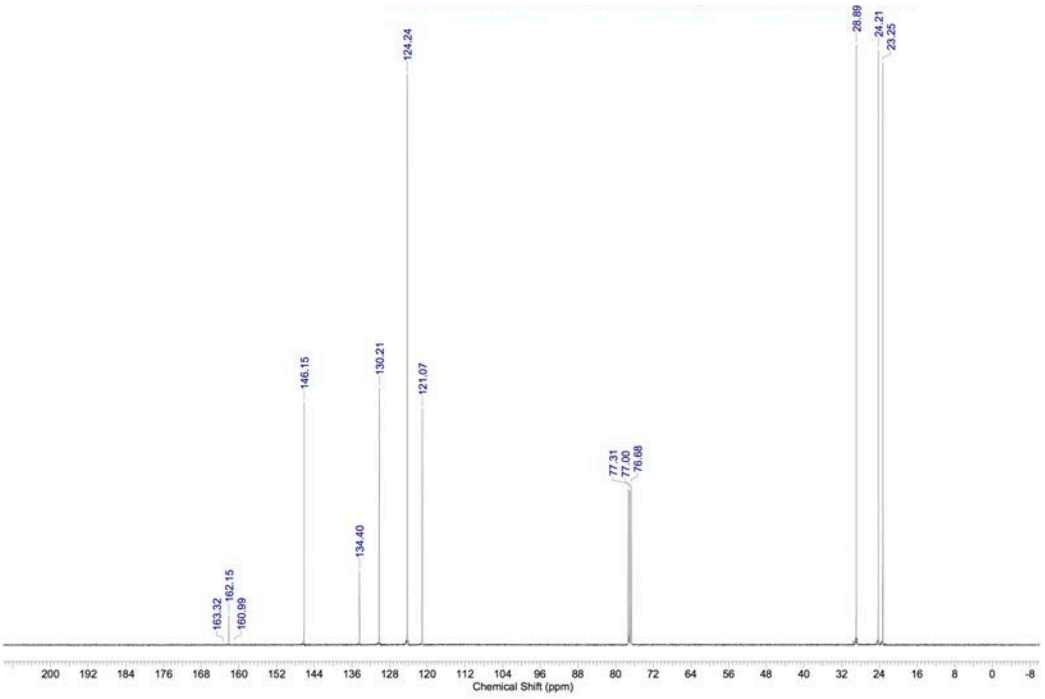
2.14
2.36
7.03
6.97
7.26
4.00 2.27
6.24 13.46
Chemical Shift (ppm)

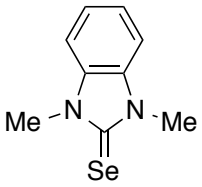

129.10
17.87
135.20
120.06
21.03
139.17
134.05
77.31
76.68
158.39
157.24
156.10
Chemical Shift (ppm)


Dipp
N
N
Dipp
Se

15

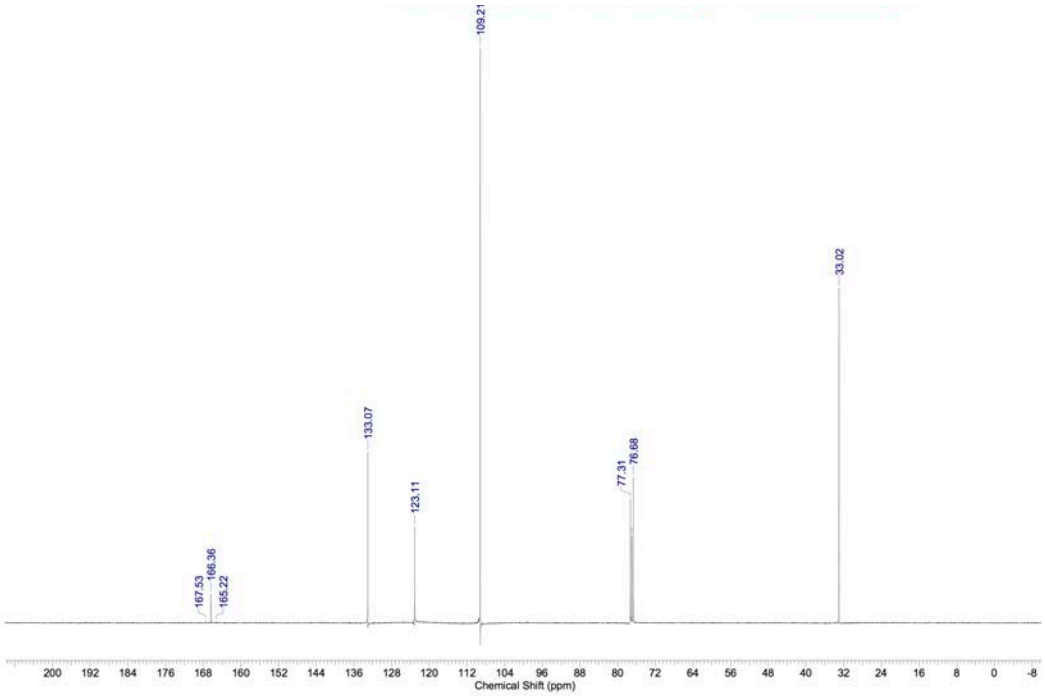
1.34
1.20
1.19
7.31
7.26
7.01
7.50
7.48
2.70
2.68
2.66
2.73
2.72
2.65
2.63
2.00 4.42 1.91
4.13
13.88 13.52
Chemical Shift (ppm)

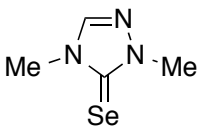

28.89
24.21
23.25
124.24
146.15
130.21
121.07
77.31
77.00
76.68
134.40
163.32
162.15
160.99
Chemical Shift (ppm)


Me
N
N
Me
Se

16

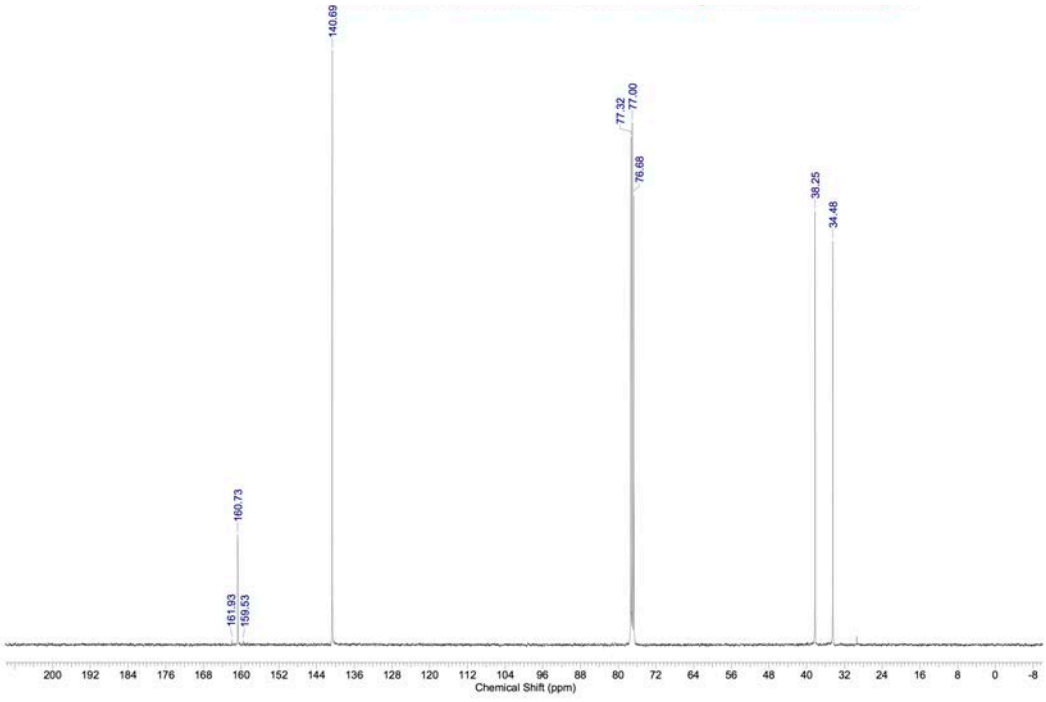
3.62
7.20
7.19
7.26
7.23
7.21
7.21
7.19
7.18
7.17
4.00
6.38
Chemical Shift (ppm)


109.21
33.02
133.07
123.11
77.31
76.68
167.53
166.36
165.22
Chemical Shift (ppm)


Me
N
N
N
Me
Se

17

3.90
3.69
7.87
7.26
1.00
3.29
3.44
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


140.69
77.32
77.00
76.68
38.25
34.48
160.73
161.93
159.53
200 192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0 -8
Chemical Shift (ppm)