Supporting Information

Benoît Audic, Matthew Wodrich and Nicolai Cramer*

Laboratory of Asymmetric Catalysis and Synthesis, Institute of Chemical Sciences and Engineering,

Ecole Polytechnique Fédérale de Lausanne, BCH 4305, CH-1015 Lausanne, Switzerland

Contents

General Experimental

Experimental procedures, reagents and glassware

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware with magnetic stirring, unless otherwise indicated. Toluene and THF were purified by an Innovative Technology Solvent Delivery System. Chemicals were used as obtained from the suppliers. $[Rh(cod)OH]_2$,[1] $[Rh(cod)OMe]_2$,[1] $[Rh(cod)OAc]_2$,[2] were prepared according to the literature. Iridium precursors were prepared in a similar manner as Rhodium.[1-2]

Chromatography

Flash column chromatography was performed with Silicycle silica gel 60 (0.040-0.063 µm grade). Analytical thin-layer chromatography was performed with commercial glass plates coated with 0.25 mm silica gel (E. Merck, Kieselgel 60 F254). Compounds were visualized under UV-light at 254 nm and by dipping the plates in an aqueous potassium permanganate or vanillin solution followed by heating.

NMR Spectroscopy

Proton nuclear magnetic resonance (^{1}H NMR) data were acquired at 400 MHz on a Bruker AV400 spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to $CDCl_3$ (s, 7.260 ppm) or C_6D_6 (s, 7.160 ppm). Proton decoupled Carbon-13 nuclear magnetic resonance ($^{13}C\{^1H\}$ NMR) data were acquired at 101 MHz on a Bruker AV400 spectrometer. Chemical shifts are reported in ppm relative to $CDCl_3$ (77.160 ppm) or C_6D_6 (128.06 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. All NMR data were recorded at 298 K.

Infrared Spectroscopy

Infrared (IR) data were recorded on an Alpha-P Bruker FT-IR Spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}).

Mass Spectroscopy

HRMS measurements were performed by an Agilent Technologies 622 LC-MS TOF, Waters Xevo G2-S QTOF or Thermo Fisher LTQ Orbitrap ELITE ETD. High resolution mass are given in m/z.

Melting Points

Melting points were measured on a Büchi B-540 and are uncorrected.

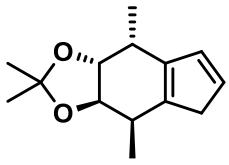
Optical rotations

Optical rotations were measured on a Polartronic M polarimeter using a 0.5 cm cell with a Na 589 nm filter.

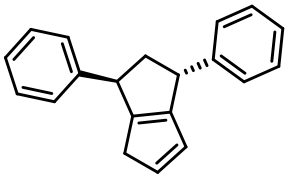
X-Ray analyses

X-ray analyses of compounds **1m**, **3a**, **3m** and **3o** were performed by Dr. R. Scopelliti and Dr. F.Fadaei Tirani at the EPF Lausanne

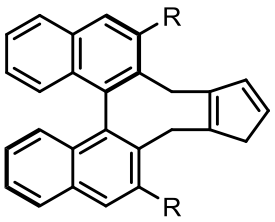
Precursors



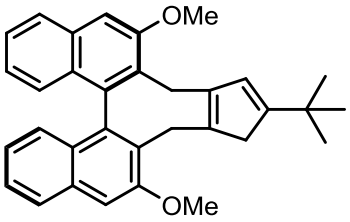
1a : Ref 3



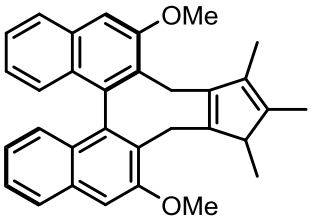
1f : Ref 7



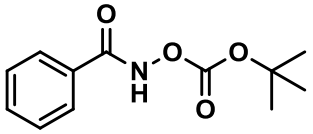
R = OMe 1g
O*i*Pr 1h
OTIPS 1i
Ph 1j
Ref 4



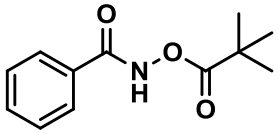
1k : Ref 9



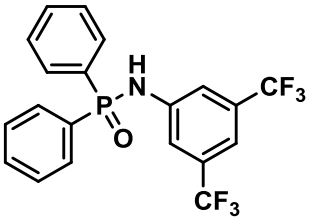
1l : Ref 6



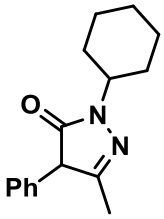
4 : Ref 3



7 : Ref 3



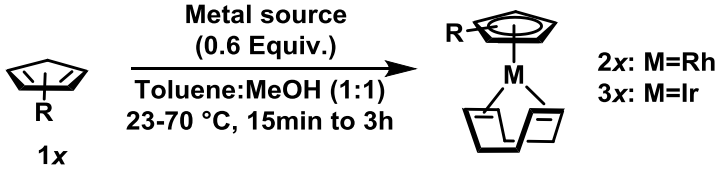
9 : Ref 11



11 : Ref 12

Experimental Procedures and Characterizations

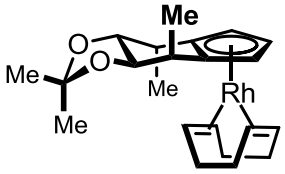
Synthesis of Metal Cp^X Complexes



Without any precautions from air and moisture, in a test tube were dissolved $[Rh(cod)OAc]_2$ (0.6 Equiv.), or $[Ir(cod)OMe]_2$, and corresponding cyclopentadienes **1** (1 Equiv.) in a mixture of MeOH/Toluene (1/1)

(C = 0.1 M) stirred at the preconized temperature for the indicated time. The solvents were evaporated *in vacuo*. The crude was filtrated on a pad of silica (or Celite) with the indicated eluent.

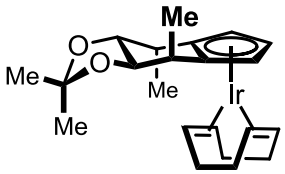
Complex (2a)



Reaction mixture stirred for 1 hour at 23 °C. The mixture was evaporated *in vacuo* and then filtrated on a pad of silica with toluene. 85% yield

Appearance : Yellow solid ; **^{1}H NMR** : (400 MHz, C_6D_6) δ 5.25 - 5.20 (m, 1H), 4.94 - 4.87 (m, 1H), 4.44 (dd, J = 10.0, 6.0 Hz, 1H), 4.18 (t, J = 2.1 Hz, 1H), 4.11 (td, J = 9.7, 6.2 Hz, 1H), 3.98 (ddt, J = 10.4, 4.5, 2.5 Hz, 2H), 3.62 (ddt, J = 9.3, 4.7, 2.5 Hz, 2H), 3.09 (p, J = 6.9 Hz, 1H), 2.53 (d, J = 6.9 Hz, 1H), 2.40 - 2.25 (m, 4H), 2.10 - 1.99 (m, 4H), 1.73 (d, J = 6.9 Hz, 3H), 1.63 (s, 3H), 1.55 (s, 3H), 1.26 (d, J = 7.2 Hz, 3H) ; **^{13}C NMR** : (101 MHz, C_6D_6) δ 111.29 (d, J = 4,4 Hz), 110.16, 111.29 (d, J = 4,4 Hz), 105.81, 86.79 (d, J = 4.1 Hz), 83.95 (d, J = 3.5 Hz), 82.69 (d, J = 4.1 Hz), 75.12, 74.76, 67.28, 67.13, 64.02, 63.89, 32.91 (d, J = 11.5 Hz), 30.81 (d, J = 15.9 Hz), 27.39 (d, J = 7.7 Hz), 21.39, 15.97 ; **IR (ATR)** : v = 2979, 2929, 2876, 2825, 1450, 1377, 1238, 1175, 1114, 1077, 1045, 860 cm^{-1} ; **HRMS (ESI)** : calculated for $[C_{22}H_{31}O_2Rh]$+: 430.1374, found: 430.1360 ; **$[\alpha]_D$** : -85.83 (c = 0.2, CH_2Cl_2) ; **m.p. :** 104-106 °C ; **R_f [Toluene]** : 0.37

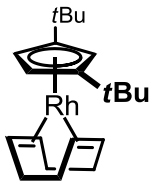
Complex (3a)



Reaction mixture stirred for 3 hours at 70 °C. The mixture was evaporated *in vacuo* and then filtrated on a pad of silica with toluene. 57% yield

Appearance : White powder ; **^{1}H NMR** : (400 MHz, C_6D_6) δ 4.79 (t, J = 2.6 Hz, 1H), 4.54 (dd, J = 2.7, 1.5 Hz, 1H), 4.04 (dd, J = 10.0, 5.9 Hz, 1H), 3.85 (t, J = 2.0 Hz, 1H), 3.73 (dd, J = 10.0, 6.8 Hz, 1H), 3.55 (td, J = 7.8, 2.6 Hz, 2H), 3.21 - 3.12 (m, 2H), 2.62 (p, J = 7.0 Hz, 1H), 2.31 - 2.21 (m, 1H), 2.05 - 1.91 (m, 4H), 1.80 - 1.67 (m, 4H), 1.33 (d, J = 7.0 Hz, 3H), 1.28 (s, 3H), 1.22 (s, 3H), 0.94 (d, J = 7.1 Hz, 3H) ; **^{13}C NMR** : (101 MHz, C_6D_6) δ 110.32, 105.48, 102.03, 81.87, 80.15, 78.12, 74.90, 74.41, 50.68, 47.46, 34.43, 30.34, 30.24, 27.33, 21.85, 16.39 ; **IR (ATR)** : v = 2965, 2929, 2882, 2827, 1450, 1377, 1367, 1231, 1173, 1113, 1077, 1044, 908, 859, 805, 793 cm^{-1} ; **HRMS (ESI)** : calculated for $[C_{22}H_{31}O_2Ir]$; $[M+H]^+$: 521.2026, found : 521.2032 ; **$[\alpha]_D$** : -83.33 (c = 0.1, $CHCl_3$) ; **m.p. :** 120-121 °C ; **R_f [Toluene]** : 0.50

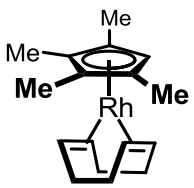
Complex (2b)



Reaction mixture heated for 3 hours at 70 °C. The crude mixture was evaporated and filtrated on Celite with toluene. 92% NMR yield

^{1}H NMR : (400 MHz, C_6D_6) δ 4.69 (t, J = 2.0 Hz, 1H), 4.59 (d, J = 2.0 Hz, 2H), 4.01 (dt, J = 5.9, 1.9 Hz, 4H), 2.32 – 2.22 (m, 4H), 2.01 (ddd, J = 9.0, 7.4, 1.6 Hz, 4H), 1.28 (s, 18H)

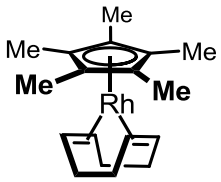
Complex (2c)



Reaction mixture heated for 3 hours at 70 °C. The crude mixture was evaporated and filtrated on Celite with toluene. 95% NMR yield

^{1}H NMR : (400 MHz, C_6D_6) δ 5.01 (s, 1H), 3.27 – 3.19 (m, 4H), 2.38 – 2.27 (m, 4H), 2.15 – 2.04 (m, 4H), 1.74 (s, 6H), 1.55 (s, 6H)

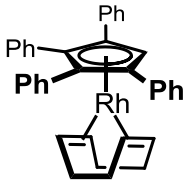
Complex (2d)



Reaction mixture heated for 3 hours at 70°C. The crude mixture was evaporated and filtrated on Celite with toluene. 91% NMR yield

^{1}H NMR : (400 MHz, C_6D_6) δ 3.10 (d, J = 3.9 Hz, 4H), 2.31 (tdd, J = 10.6, 9.0, 7.5, 4.1 Hz, 4H), 2.14 – 2.06 (m, 4H), 1.70 (s, 15H)

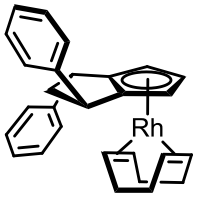
Complex (2e)



Reaction mixture heated for 24 hours at 70 °C. A slurry solution was observed, the crude mixture was filtrated to isolate the target complex 58% yield.

Appearance : Yellow powder ; **^{1}H NMR** : (400 MHz, C_6D_6) δ 7.37 – 7.31 (m, 4H), 7.31 – 7.26 (m, 4H), 7.05 (dd, J = 8.2, 6.6 Hz, 4H), 7.01 – 6.93 (m, 8H), 5.87 (s, 1H), 3.71 (d, J = 9.7 Hz, 4H), 2.38 – 2.17 (m, 4H), 1.91 (t, J = 8.1 Hz, 4H)

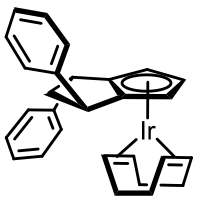
Complex (2f)



Reaction mixture stirred for 3 hours at 23 °C. The mixture was evaporated *in vacuo* and then purified by flash chromatography on silica with Pentane/toluene [8/1]. 84% yield

Appearance : Yellow gum ; **^{1}H NMR** : (400 MHz, C_6D_6) δ 7.80 - 7.74 (m, 2H), 7.28 (t, J = 7.6 Hz, 2H), 7.19-7.12 (m, 3H), 7.09 - 7.03 (m, 3H), 5.15 (dd, J = 2.6, 1.2 Hz, 1H), 4.69 (dt, J = 5.0, 2.4 Hz, 2H), 4.19 (t, J = 8.8 Hz, 1H), 3.82 (tddd, J = 11.3, 8.0, 6.0, 2.9 Hz, 4H), 3.55 (dd, J = 6.2, 2.6 Hz, 1H), 2.44 - 2.31 (m, 4H), 2.26 (dddd, J = 13.3, 11.2, 7.1, 4.7 Hz, 2H), 2.07 (dddd, J = 13.5, 11.4, 4.9, 2.5 Hz, 2H), 1.93 (dddd, J = 13.8, 10.9, 5.9, 3.2 Hz, 2H) ; **^{13}C NMR** : (101 MHz, C_6D_6) δ 145.3, 142.8, 128.8, 128.2, 127.9, 127.6, 126.7, 126.6, 118.2 (d, J = 4.0 Hz), 112.8 (d, J = 4.2 Hz), 88.5 (d, J = 4.3 Hz), 80.7 (d, J = 3.4 Hz), 80.3 (d, J = 3.6 Hz), 65.5 (d, J = 14.1 Hz), 65.4 (d, J = 14.0 Hz), 49.2, 43.3, 41.8, 33.5, 32.3 ; **IR (ATR)** : ν = 3058, 3024, 2987, 2959, 2927, 2864, 2823, 1602, 1493, 1448, 1323, 1239, 1153, 1077, 1031, 999, 961, 868, 753, 698 cm^{-1} ; **HRMS (ESI)** : calculated for $[C_{28}H_{29}Rh]^+$: 468.1319 , found: 468.1318 ; **$[\alpha]_D$** : -50.83 (c = 0.2, CH_2Cl_2) ; **R_f [Pentane/Toluene(4/1)]** : 0.5

Complex (3f)

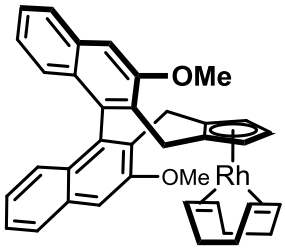


Reaction mixture stirred for 3 hours at 70 °C. The mixture was evaporated *in vacuo* and then purified by flash chromatography on silica with Pentane/toluene [8/1]. 87% yield

Appearance : White gum ; **^{1}H NMR** : (400 MHz, C_6D_6) δ 7.66 – 7.61 (m, 2H), 7.26 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.15 – 7.12 (m, 3H), 7.10 – 7.05 (m, 1H), 7.05 – 7.00 (m, 2H), 5.05 (t, *J* = 1.8 Hz, 1H), 4.63 (d, *J* = 1.7 Hz, 2H), 4.16 (dd, *J* = 10.3, 7.3 Hz, 1H), 3.73 (td, *J* = 7.5, 2.5 Hz, 2H), 3.69 – 3.59 (m, 3H), 2.44 – 2.31 (m, 3H), 2.31 – 2.19 (m, 3H), 2.05 (ddq, *J* = 10.9, 8.3, 2.7 Hz, 2H),

1.96 – 1.88 (m, 2H) ; **^{13}C NMR** : (101 MHz, C_6D_6) δ 144.85, 141.85, 128.80, 128.41, 127.64, 126.90, 126.72, 113.75, 108.51, 83.69, 76.16, 74.90, 49.14, 48.77, 42.68, 41.36, 34.84, 33.91 ; **IR (ATR)** : v = 2954, 2934, 2871, 2824, 2268, 1618, 1595, 1450, 1421, 1329, 1293, 1225, 1196, 1167, 1150, 1114, 1022, 946, 908, 863, 830, 811, 746, 645, 622 cm^{-1} ; **HRMS (ESI)** : calculated for $[C_{28}H_{30}Ir]$, $[M+H]^+$: 559.1971 , found: 559.1986 ; **$[\alpha]_D$** : 43.33 (c = 0.2, CH_2Cl_2) ; **R_f [Pentane/Toluene: 7/3]** : 0.76

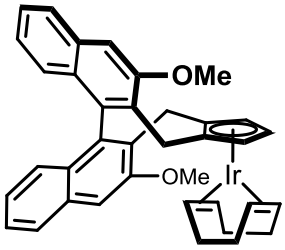
Complex (2g)



Reaction mixture stirred for 3 hours at 70 °C. The mixture was evaporated *in vacuo* and then filtrated on a pad of silica with toluene. 95% yield

Appearance : Yellow powder ; **^{1}H NMR** : (400 MHz, C_6D_6) δ 7.77 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.34 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.31 – 7.28 (m, 1H), 7.28 – 7.22 (m, 2H), 7.21 (s, 1H), 7.02 (s, 1H), 6.92 (dddd, *J* = 8.3, 6.8, 4.0, 1.3 Hz, 2H), 5.34 (t, *J* = 2.3 Hz, 1H), 4.68 (t, *J* = 2.6 Hz, 1H), 4.62 (t, *J* = 2.2 Hz, 1H), 4.33 (d, *J* = 14.5 Hz, 1H), 3.81 (td, *J* = 9.6, 3.7 Hz, 3H), 3.66 (s, 3H), 3.49 – 3.38 (m, 5H), 3.11 (dd, *J* = 14.5, 1.4 Hz, 1H), 2.85 (d, *J* = 13.3 Hz, 1H), 2.34 – 2.20 (m, 2H), 2.10 (dddd, *J* = 12.7, 10.1, 7.3, 5.1 Hz, 2H), 2.05 – 1.95 (m, 2H), 1.90 (ddd, *J* = 12.8, 6.6, 3.5 Hz, 2H) ; **^{13}C NMR** : (101 MHz, C_6D_6) δ 156.46, 155.78, 138.39, 136.75, 133.91 (d, *J* = 8.7 Hz), 130.03, 126.29, 126.08, 124.32 (d, *J* = 7.3 Hz), 106.36 (d, *J* = 4.0 Hz), 106.08, 105.48, 98.73 (d, *J* = 3.5 Hz), 88.22 (dd, *J* = 13.0, 3.9 Hz), 82.30 (d, *J* = 4.2 Hz), 78.56 (d, *J* = 13.9 Hz), 65.03 (d, *J* = 14.1 Hz), 64.17 (d, *J* = 14.0 Hz), 55.02 (d, *J* = 25.8 Hz), 33.34, 32.43, 26.08, 25.41 ; **IR (ATR)** : v = 2930, 2870, 2823, 2278, 1618, 1595, 1573, 1503, 1449, 1422, 1399, 1361, 1328, 1293, 1260, 1237, 1226, 1195, 1168, 1150, 1114, 1085, 1022, 946, 863, 830, 812, 766, 746 cm^{-1} ; **HRMS (ESI+)** : calculated for $[C_{37}H_{35}O_2Rh]^+$: 614.162, found: 614.1975 ; **$[\alpha]_D$** : -232.50 (c = 0.2, CH_2Cl_2) ; **m.p. :** 135-137 °C ; **R_f [Pentane/Toluene: 7/3]** : 0.29

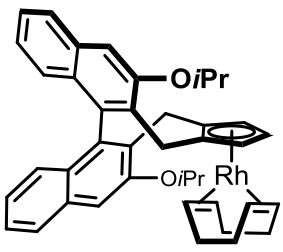
Complex (3g)



Reaction mixture stirred for 3 hours at 70 °C. The mixture was evaporated *in vacuo* and then filtrated on a pad of silica with toluene. 93% yield

Appearance : White solid ; **^{1}H NMR** : (400 MHz, C_6D_6) δ 7.79 – 7.74 (m, 1H), 7.74 – 7.69 (m, 1H), 7.31 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.30 – 7.22 (m, 3H), 7.19 (s, 1H), 7.02 (s, 1H), 6.92 (dtd, *J* = 8.1, 6.7, 1.3 Hz, 2H), 5.25 – 5.21 (m, 1H), 4.64 (t, *J* = 2.5 Hz, 1H), 4.54 (t, *J* = 2.0 Hz, 1H), 4.23 (d, *J* = 14.5 Hz, 1H), 3.77 – 3.68 (m, 3H), 3.65 (s, 3H), 3.43 (s, 3H), 3.32 (td, *J* = 7.6, 2.6 Hz, 2H), 3.11 (d, *J* = 14.5 Hz, 1H), 2.97 (d, *J* = 13.4 Hz, 1H), 2.20 (dddd, *J* = 12.1, 9.8, 7.0, 5.0 Hz, 2H), 2.11 – 2.01 (m, 2H), 1.94 (ddtd, *J* = 20.2, 12.0, 6.2, 5.3, 2.6 Hz, 4H) ; **^{13}C NMR** : (101 MHz, C_6D_6) δ 156.37, 155.74, 138.30, 136.82, 133.99 (d, *J* = 4.4 Hz), 130.17, 128.92, 127.38 (d, *J* = 5.7 Hz), 127.17, 126.36, 126.19, 124.34, 106.07, 105.48, 101.12, 94.65, 83.72, 83.29, 77.82, 55.13, 54.85, 48.48, 47.41, 34.68, 34.22, 25.55, 24.72 ; **IR (ATR)** : v = 3059, 3024, 2952, 2922, 2865, 2824, 1601, 1493, 1442, 1318, 1237, 1152, 1077, 1031, 1003, 909, 838, 797, 750, 697 cm^{-1} ; **HRMS (ESI)** : calculated for $[C_{37}H_{35}O_2Ir]$, $[M+H]^+$: 705.2339 , found: 705.2358 ; **$[\alpha]_D$** : -175.83 (c = 0.2, CH_2Cl_2) ; **m.p. :** 154-155 °C ; **R_f [Pentane/Toluene: 7/3]** : 0.50

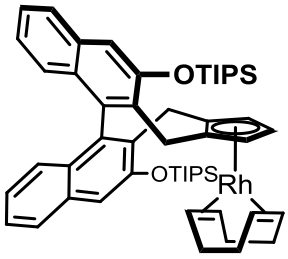
Complex (2h)



Reaction mixture stirred for 3 hours at 23 °C. The mixture was evaporated *in vacuo* and then filtrated on a pad of silica with toluene. 92% yield

Appearance : Yellow powder ; **^{1}H NMR** : (400 MHz, C_6D_6) δ 7.76 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.32 (s, 1H), 7.25 (ddd, *J* = 9.4, 6.1, 2.1 Hz, 3H), 7.12 (s, 1H), 6.88 (dddd, *J* = 15.4, 8.4, 6.8, 1.3 Hz, 2H), 5.36 (t, *J* = 2.2 Hz, 1H), 4.72 (t, *J* = 2.6 Hz, 1H), 4.68 (d, *J* = 2.1 Hz, 1H), 4.56 (hept, *J* = 6.0 Hz, 1H), 4.39 – 4.29 (m, 2H), 3.89 (d, *J* = 13.3 Hz, 1H), 3.83 (tt, *J* = 6.8, 3.0 Hz, 2H), 3.50 (tt, *J* = 6.3, 2.8 Hz, 2H), 3.14 (d, *J* = 14.3 Hz, 1H), 2.92 (d, *J* = 13.2 Hz, 1H), 2.33 – 2.15 (m, 4H), 2.04 – 1.85 (m, 4H), 1.46 (d, *J* = 6.1 Hz, 3H), 1.25 (d, *J* = 6.0 Hz, 3H), 1.16 (d, *J* = 5.9 Hz, 6H) ; **^{13}C NMR** : (101 MHz, C_6D_6) δ 154.58, 153.85, 138.52, 137.09, 134.04, 133.79, 130.69, 130.51, 127.49, 127.34, 127.01, 126.99, 126.18, 125.97, 124.33, 124.09, 109.00, 107.51, 107.10, 107.06, 98.65, 98.62, 88.43, 88.39, 88.11, 88.07, 82.04, 82.00, 78.63, 78.49, 70.75, 69.60, 65.34, 65.20, 64.16, 64.01, 33.14, 32.60, 30.93, 26.21, 25.75, 23.02, 22.15, 22.04, 21.26 ; **IR (ATR)** : v = 3060, 2973, 2928 2870, 2821, 2279, 1618, 1594, 1572, 1500, 1431, 1383, 1371, 1327, 1291, 1235, 1224, 1203, 1173, 1135, 1111, 1082, 1052, 1027, 997, 965, 944, 864, 831, 813, 768, 746 cm^{-1} ; **HRMS (ESI+)** : calculated for $[C_{41}H_{43}O_2Rh]^+$: 670.2318, found: 670.2308 ; **$[\alpha]_D$** : -211.67 (c = 0.2, CH_2Cl_2) ; **m.p. :** 132-134 °C ; **R_f [Pentane/Toluene: 7/3]** : 0.38

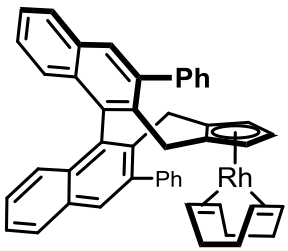
Complex (2i)



Reaction mixture stirred for 3 hours at 70 °C. The mixture was evaporated *in vacuo* and then filtrated on a pad of silica with toluene. 83% yield

Appearance : Yellow powder ; **^{1}H NMR** : (400 MHz, C_6D_6) δ 7.70 – 7.61 (m, 3H), 7.48 (s, 1H), 7.30 (d, J = 8.5 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 6.99 – 6.93 (m, 1H), 6.89 (dd, J = 8.5, 6.7 Hz, 1H), 5.55 (q, J = 4.5, 3.4 Hz, 1H), 4.85 (h, J = 2.6 Hz, 1H), 4.73 – 4.64 (m, 1H), 4.21 (dd, J = 14.2, 6.4 Hz, 1H), 3.97 (dd, J = 13.5, 9.9 Hz, 1H), 3.84 – 3.74 (m, 2H), 3.42 (tt, J = 7.4, 3.1 Hz, 2H), 3.02 (d, J = 14.2 Hz, 1H), 2.91 (d, J = 13.4 Hz, 1H), 2.38 (tt, J = 12.8, 5.5 Hz, 2H), 2.31 – 2.18 (m, 2H), 1.96 (ddd, J = 16.4, 7.6, 3.6 Hz, 2H), 1.87 (dq, J = 17.2, 7.1, 5.6 Hz, 2H), 1.43 (dt, J = 14.9, 7.5 Hz, 3H), 1.33 (dt, J = 14.1, 7.1 Hz, 4H), 1.24 (d, J = 7.3 Hz, 8H), 1.19 (dd, J = 7.5, 2.3 Hz, 16H), 1.14 (d, J = 7.3 Hz, 10H), 1.11 – 0.93 (m, 3H) ; **^{13}C NMR** : (101 MHz, C_6D_6) δ 153.03, 152.35, 138.47, 137.84, 133.97, 133.54, 132.41, 131.64, 128.85, 128.61, 127.20, 127.01, 126.25, 126.11, 124.79, 124.38, 115.62, 113.67, 106.88 (d, *J* = 3.9 Hz), 98.18 (d, *J* = 3.3 Hz), 89.06 (d, *J* = 3.8 Hz), 88.18 (d, *J* = 4.0 Hz), 82.05, 78.56 (d, *J* = 13.9 Hz), 65.41, 65.27, 64.77, 64.64, 33.21, 32.34, 26.86, 26.15, 18.48, 18.42, 18.38, 13.65, 13.30 ; **IR (ATR)** : v = 3059, 2942, 2864, 2823, 1592, 1462, 1428, 1329, 1240, 1224, 1171, 1113, 1052, 1014, 997, 957, 926, 881, 867, 812, 779, 763, 744, 728, 683 cm^{-1} ; **HRMS (ESI+)** : calculated for $[C_{53}H_{71}O_2Si_2Rh]^+$: 898.4048, found: 898.4040 ; **$[\alpha]_D$** : -116.83 (c = 0.2, CH_2Cl_2) ; **m.p. :** 118-122 °C ; **R_f [Pentane/Toluene: 7/3]** : 0.83

Complex (2j)

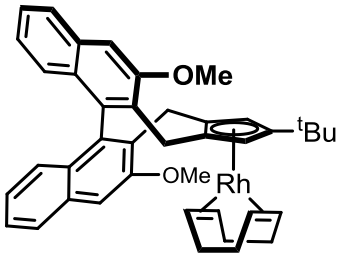


Reaction mixture stirred for 3 hours at 70 °C. The mixture was evaporated *in vacuo* and then filtrated on a pad of silica with toluene. 96% yield

Appearance : Yellow powder ; **^{1}H NMR** : (400 MHz, C_6D_6) δ 8.13 (s, 1H), 7.80 (d, J = 8.2 Hz, 1H), 7.77 (s, 1H), 7.67 (d, J = 8.5 Hz, 1H), 7.48 (td, J = 7.3, 1.3 Hz, 2H), 7.44 – 7.39 (m, 2H), 7.39 – 7.17 (m, 8H), 7.15 – 7.07 (m, 2H), 6.98 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 6.88 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 5.08 (p, J = 1.4 Hz, 1H), 4.70 (t, J = 2.1 Hz, 1H), 4.38 (t, J = 2.6 Hz, 1H), 4.03 (d, J = 14.7 Hz, 1H), 3.48 (tt, J = 7.8, 3.5 Hz, 2H), 3.38 (d, J = 13.9 Hz, 1H), 3.32 (d, J = 14.7 Hz, 1H), 3.18 (tt, J = 7.6, 2.5 Hz, 2H), 2.81 (d, J = 13.9 Hz, 1H), 2.27 – 2.17 (m, 2H), 2.00 (dddd, J = 14.3, 11.3, 8.1, 3.6 Hz, 2H), 1.89 – 1.81 (m, 2H), 1.54 – 1.46 (m, 2H) ; **^{13}C NMR** : (101 MHz, C_6D_6) δ 142.24, 142.02, 141.36, 140.72,

137.01, 136.65, 135.86, 134.97, 132.81, 132.63, 132.41, 132.32, 130.55, 130.11, 130.06, 128.50, 127.60, 127.47, 127.12, 127.05, 126.72, 126.58, 126.08, 125.98, 110.62 (d, *J* = 3.5 Hz), 96.24 (d, *J* = 3.8 Hz), 90.88 (d, *J* = 3.3 Hz), 87.24 (d, *J* = 4.1 Hz), 82.88 (d, *J* = 4.2 Hz), 78.56 (d, *J* = 14.0 Hz), 65.61, 65.47, 65.03, 64.89, 33.89, 30.67, 30.41, 29.54 ; **IR (ATR)** : v = 3050, 2921, 2859, 2824, 1588, 1492, 1470, 1445, 1415, 1357, 1322, 1231, 1203, 1181,1155, 1072, 1027, 1000, 959, 890, 870, 855, 810, 794, 763, 748, 729, 701, 645 cm^{-1} ; **HRMS (ESI+)** : calculated for $[C_{47}H_{39}Rh]^+$: 706.2107, found: 706.2085 ; **$[\alpha]_D$** : -170.00 (c = 0.1, CH_2Cl_2) ; **m.p. :** 134-138 °C ; **R_f [Pentane/Toluene: 7/3]** : 0.50

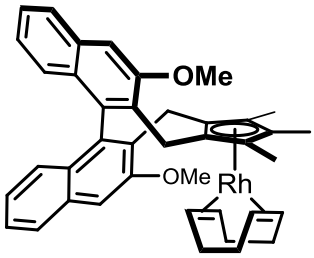
Complex (2k)



Reaction mixture stirred for 3 hours at 70 °C. The mixture was evaporated *in vacuo* and then filtrated on a pad of silica with toluene. 92% yield

Appearance : Yellow gum ; **^{1}H NMR** : (400 MHz, C_6D_6) δ 7.79 (dd, J = 8.3, 1.2 Hz, 1H), 7.72 – 7.64 (m, 1H), 7.33 (d, J = 1.0 Hz, 1H), 7.31 – 7.21 (m, 4H), 6.97 (d, J = 9.5 Hz, 1H), 6.92 (ddt, J = 8.3, 6.9, 1.3 Hz, 2H), 4.86 (d, J = 2.2 Hz, 1H), 4.43 (d, J = 2.2 Hz, 1H), 4.21 (d, J = 14.6 Hz, 1H), 4.02 (tt, J = 7.6, 2.8 Hz, 2H), 3.74 (d, J = 13.2 Hz, 1H), 3.67 (s, 3H), 3.48 (s, 3H), 3.38 (td, J = 7.5, 3.0 Hz, 2H), 3.09 (dd, J = 16.6, 13.9 Hz, 2H), 2.28 – 2.16 (m, 2H), 2.09 – 2.00 (m, 2H), 2.00 – 1.92 (m, 4H), 1.23 (s, 9H) ; **^{13}C NMR** : (101 MHz, C_6D_6) δ 155.94, 155.40, 138.07, 136.40, 133.53, 129.71, 129.14, 127.10, 126.98, 126.85, 126.74, 125.89, 125.57, 123.99, 123.99 – 115.54 (m), 106.06, 105.14, 104.58 (d, J = 4.1 Hz), 97.31 (d, J = 3.7 Hz), 85.15 (d, J = 3.8 Hz), 84.74 (d, J = 3.7 Hz), 66.18 (d, J = 14.0 Hz), 63.72 (d, J = 13.9 Hz), 54.89, 53.72, 54.46, 52.96, 32.56 (d, J = 8.4 Hz), 31.84, 31.04, 25.41, 25.24 ; **IR (ATR)** : v = 3061, 2957, 2924, 2865, 2822, 2279, 1618, 1596, 1449, 1421, 1326, 1294, 1260, 1224, 1196, 1163, 1112, 1077, 1021, 946, 863, 827, 810, 745, 623 cm^{-1} ; **HRMS (ESI+)** : calculated for $[C_{41}H_{43}O_2Rh]^+$: 670.2313 , found: 670.2318 ; **$[\alpha]_D$** : -131.67 (c = 0.1, CH_2Cl_2) ; **R_f [Pentane/Toluene: 7/3]** : 0.62

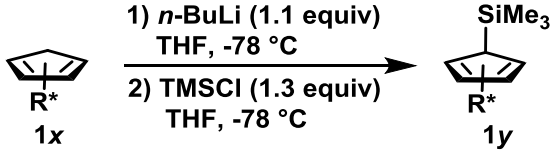
Complex (2l)



Reaction mixture stirred for 3 hours at 70 °C. The mixture was evaporated *in vacuo* and then filtrated on a pad of silica with toluene. 94% yield. Match the literature[6] :

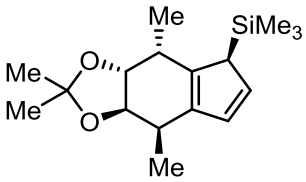
Appearance : White solid ; **^{1}H NMR** : (400 MHz, C_6D_6) δ7.79 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 9.3 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.36 (s, 1H), 6.99 (s, 1H), 6.95 (t, *J* = 7.9 Hz, 2H), 4.31 (d, *J* = 14.3 Hz, 1H), 3.77 (d, *J* = 13.6 Hz, 1H), 3.68 (s, 3H), 3.40 (s, 3H), 3.20 – 3.10 (m, 2H), 2.90 (d, *J* = 14.2, 1H), 2.85 – 2.77 (m, 2H), 2.73 (d, *J* = 13.6 Hz, 1H), 2.30 – 2.19 (m, 2H), 2.18 – 2.08 (m, 2H), 2.15 (3H, s), 2.06 – 1.95 (m, 4H), 1.78 (s, 3H), 1.46 (s, 3H)

Synthesis of Silylated Intermediates



In a flame dried RBF, the corresponding cyclopentadienes **1** (1 Equiv.) was dissolved into dry THF under nitrogen at -78 °C. *n*-BuLi (1.1 Equiv., 1.6M in Hexanes) was added dropwise. The reaction was stirred at the same temperature over 3 hours. The distilled chlorotrimethylsilane (1.3 Equiv.) was added dropwise at the same temperature and stirred over 2 hours. The reaction was quenched with water at -78 °C and slowly warm up to rt. The aqueous layer was extracted with Et_2O (3 times). The combined organic layers were dried over $MgSO_4$ and concentrated under vacuum to give a white foam. The product was purify by flash column chromatography on silica gel (Eluent : Pentane/EthylAcetate [50/1]).

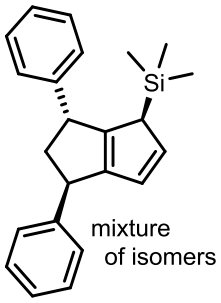
Intermediate (1m)



Mixture of isomers

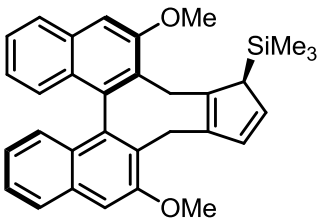
Appearance : Yellow solid ; **^{1}H NMR** : (400 MHz, Benzene-d6) δ 6.30 (q, J = 5.2 Hz, 2H), 4.15 (qd, J = 10.1, 5.6 Hz, 2H), 3.05 (h, J = 6.7 Hz, 2H), 1.50 (d, J = 12.9 Hz, 6H), 1.22 (dd, J = 22.0, 7.1 Hz, 6H), -0.15 (s, 9H) ; **^{13}C NMR** : (101 MHz, Benzene-d6) δ 143.2, 141.2, 133.6, 131.1, 109.6, 75.2, 74.9, 49.6, 33.7, 33.3, 27.5, 27.4, 15.3, 14.9, 13.8, -2.1 ; **IR (ATR)** : v = 2964, 2932, 2880, 1453, 1376, 1233, 1078, 1036, 833 cm^{-1} ; **HRMS (APPI+)** : calculated for $[C_{17}H_{28}O_2Si]^+$: 292.1859, found: 292.1853 ; **R_f [Pent/EtOAc (20/1)]** : 0.60

Intermediate (1n)



Appearance : Yellow gum ; **^{1}H NMR** : (400 MHz, Benzene-d6) δ 7.28 – 7.22 (m, 4H), 7.14 – 7.04 (m, 6H), 6.49 (dd, J = 5.1, 1.4 Hz, 0.7H), 6.42 (dt, J = 5.1, 1.1 Hz, 0.7H), 6.09 – 5.93 (m, 0.6H), 4.35 – 4.24 (m, 0.7H), 4.22 – 4.05 (m, 1.6H), 2.83 – 2.65 (m, 3H), -0.06 (d, J = 7.3 Hz, 9H) ; **^{13}C NMR** : (101 MHz, Benzene-d6) δ 155.50, 154.02, 149.18, 148.52, 139.09, 130.67, 130.60, 130.54, 129.01, 128.33, 128.25, 128.22, 53.89, 50.49, 48.61, 48.09, 0.23, -0.09. ; **IR (ATR)** : v = 3083, 3061, 3025, 2954, 2928, 2895, 2859, 1601, 1493, 1452, 1248, 1075, 1030, 991, 938, 862, 834, 753, 721, 698 cm^{-1} ; **HRMS (APPI+)** : calculated for $[C_{23}H_{26}Si]^+$: 330.1798, found: 330.1804 ; **R_f [Pentane/AcOEt (24/1)]** : 0.70

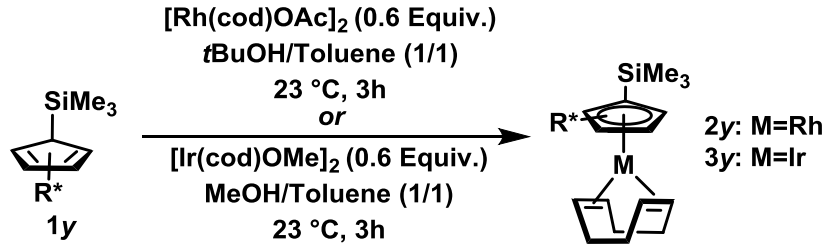
Intermediate (1o)



mixture of isomers

Appearance : White foam ; **^{1}H NMR** : (400 MHz, Benzene-d6) δ 7.75 (t, J = 8.9 Hz, 2H), 7.51 (dd, J = 12.2, 8.5 Hz, 2H), 7.29 (q, J = 8.5, 7.9 Hz, 2H), 7.07 (d, J = 4.0 Hz, 2H), 7.04 – 6.92 (m, 2H), 6.33 – 6.23 (m, 1H), 6.19 (s, 1H), 4.41 (d, J = 14.2 Hz, 1H), 4.32 (d, J = 13.8 Hz, 1H), 3.54 – 3.29 (m, 7H), 3.18 (d, J = 13.8 Hz, 1H), 3.09 (d, J = 6.3 Hz, 1H), -0.12 (s, 7H), -0.27 (s, 1H). ; **^{13}C NMR** : (101 MHz, Benzene-d6) δ 156.74, 155.85, 144.51, 139.95, 138.53, 138.32, 138.05, 134.24, 133.75, 129.97, 129.21, 128.97, 127.44, 127.18, 126.23, 126.07, 124.31, 106.02, 105.75, 105.54, 55.08, 46.82, 38.97, 29.16, -2.04 ; **IR (ATR)** : v = 3058, 2997, 2951, 2899, 2827, 1618, 1594, 1572, 1449, 1422, 1408, 1328, 1244, 1232, 1195, 1169, 1114, 1021, 963, 862, 826, 744 cm^{-1} ; **HRMS (ESI+)** : calculated for $[C_{32}H_{32}O_2Si]$; $[M+H]^+$: 477.2244, found: 477.2241 ; **R_f [Pentane/AcOEt 25/1]** : 0.26

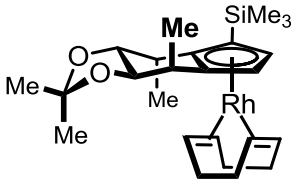
Synthesis of Metal Cp^{XTMS} Complexes



With Rhodium: Without any precautions from air and moisture, $[Rh(cod)OAc]_2$ (0.6 Equiv.) and corresponding cyclopentadienes **1*y*** (1 Equiv.) were dissolved in a mixture of *t*BuOH/Toluene (1/1) (C = 0.1 M) stirred at room temperature for 3 hours. The solvents were evaporated *in vacuo*. The crude was filtrated on a pad of silica with the indicated eluent.

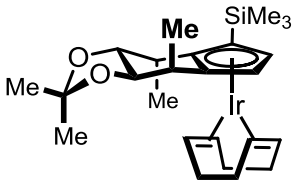
With Iridium: Without any precautions from air and moisture, $[Ir(cod)OMe]_2$ (0.6 Equiv.) and corresponding cyclopentadienes **1*y*** (1 Equiv.) were dissolved in a mixture of MeOH/Toluene (1/1) (C = 0.1 M) stirred at room temperature for 3 hours. The solvents were evaporated *in vacuo*. The crude was filtrated on a pad of silica with the indicated eluent.

Complex (2m)



Appearance : Yellow powder ; **^{1}H NMR** : 1H NMR (400 MHz, C_6D_6) δ 5.01 (dd, J = 2.9, 0.8 Hz, 1H), 4.96 (dd, J = 2.8, 0.7 Hz, 1H), 4.25 (dd, J = 10.0, 6.3 Hz, 1H), 4.11 (dd, J = 10.0, 6.1 Hz, 1H), 3.86 (tt, J = 7.6, 2.7 Hz, 2H), 3.68 (tt, J = 7.7, 2.9 Hz, 2H), 3.25 (p, J = 6.8 Hz, 1H), 2.67 - 2.58 (m, 1H), 2.31 - 2.13 (m, 4H), 2.02 - 1.92 (m, 2H), 1.92 - 1.82 (m, 2H), 1.72 (d, J = 6.9 Hz, 3H), 1.52 (s, 3H), 1.45 (s, 3H), 1.17 (d, J = 7.1 Hz, 3H), 0.14 (s, 9H) ; **^{13}C NMR** : (101 MHz, C_6D_6) δ 137.89, 129.33, 128.57, 125.70, 116.03 (d, J = 3.9 Hz), 110.34, 109.72 (d, J = 3.3 Hz), 92.12 (d, J = 4.4 Hz), 90.14 (d, J = 4.0 Hz), 86.41 (d, J = 3.8 Hz), 75.72, 74.49, 66.06 (d, J = 14.2 Hz), 64.69 (d, J = 14.0 Hz), 33.13, 32.49, 31.59, 31.18, 27.41 (d, J = 6.5 Hz), 20.97, 16.51, 0.62 ; **IR (ATR)** : ν = 2980, 2932, 2875, 2825, 1450, 1377, 1323, 1246, 1230, 1174, 1113, 1078, 1038, 915, 860, 831, 805, 755, 689, 635 cm^{-1} ; **HRMS (ESI)** : calculated for $[C_{25}H_{39}O_2RhSi]^+$: 502.1774, found: 502.1763 ; **$[\alpha]_D$** : -22.50 (c = 0.2, CH_2Cl_2) ; **m.p. :** 109-112 °C ; **R_f [Toluene]** : 0.55

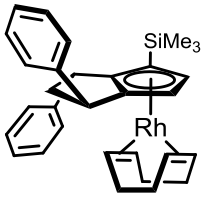
Complex (3m)



Appearance : White powder ; **^{1}H NMR** : (400 MHz, C_6D_6) δ 4.92 (d, J = 2.6 Hz, 1H), 4.89 (d, J = 2.6 Hz, 1H), 4.20 (dd, J = 10.0, 6.2 Hz, 1H), 4.07 (dd, J = 10.0, 6.2 Hz, 1H), 3.75 (td, J = 7.8, 2.7 Hz, 2H), 3.52 (td, J = 7.9, 2.8 Hz, 2H), 3.19 (p, J = 6.8 Hz, 1H), 2.69 - 2.58 (m, 1H), 2.25 - 2.09 (m, 4H), 1.91 (dddd, J = 24.0, 12.0, 6.3, 3.4 Hz, 4H), 1.66 (d, J = 6.9 Hz, 3H), 1.49 (s, 3H), 1.44 (s,

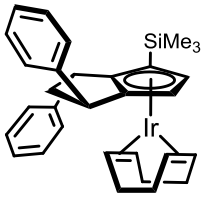
3H), 1.17 (d, J = 7.2 Hz, 3H), 0.11 (s, 9H) ; **^{13}C NMR** : (101 MHz, C_6D_6) δ 110.51, 110.06, 105.94, 87.11, 85.20, 82.14, 75.52, 74.16, 49.66, 48.05, 34.53, 34.09, 31.26, 30.55, 27.36, 21.51, 16.85 ; **IR (ATR)** : v = 2981, 2969, 2934, 2908, 2889, 2877, 2861, 2827, 1457, 1367, 1226, 1195, 1172, 1080, 1042, 911, 832, 753 cm^{-1} ; **HRMS (ESI)** : calculated for $[C_{25}H_{39}O_2IrSi]$; $[M+H]^+$: 593.2421, found: 593.2415 ; **$[\alpha]_D$** : 38.33 (c = 0.1, $CHCl_3$) ; **m.p. :** 122-124 °C ; **R_f [Toluene]** : 0.62

Complex (2n)



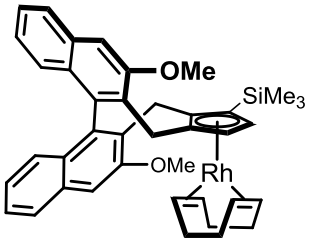
Appearance : Yellow gum ; **^{1}H NMR** : (400 MHz, C_6D_6) δ 7.95 – 7.90 (m, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 11.7 Hz, 4H), 7.10 – 7.02 (m, 2H), 5.28 (dd, *J* = 2.6, 1.0 Hz, 1H), 4.86 (d, *J* = 2.7 Hz, 1H), 4.19 – 4.11 (m, 1H), 3.96 (ddt, *J* = 8.2, 5.8, 2.7 Hz, 4H), 3.54 (t, *J* = 4.5 Hz, 1H), 2.55 – 2.29 (m, 6H), 2.12 (ddt, *J* = 11.0, 7.6, 2.6 Hz, 2H), 2.04 – 1.96 (m, 2H), -0.06 (s, 9H) ; **^{13}C NMR** : (101 MHz, C_6D_6) δ 145.49, 143.43, 129.68, 128.94, 127.73, 127.32, 126.72, 126.35 (d, *J* = 4.2 Hz), 115.79 (d, *J* = 4.1 Hz), 94.84 (d, *J* = 4.6 Hz), 88.12 (d, *J* = 3.3 Hz), 82.53 (d, *J* = 3.6 Hz), 66.27, 66.13, 65.71, 65.57, 51.39, 43.91, 43.06, 33.50, 32.48, 0.22 ; **IR (ATR)** : v = 3060, 3025 2952, 2926, 2864, 2825, 1602, 1494, 1450, 1323, 1246, 1153, 1108, 1077, 1031, 961, 868, 835, 777, 753, 698 cm^{-1} ; **HRMS (ESI)** : calculated for $[C_{31}H_{37}SiRh]^+$: 540.1714 , found: 540.1709 ; **$[\alpha]_D$** : 5.00 (c = 0.1, CH_2Cl_2) ; **R_f [Pentane/Toluene: 4/1]** : 0.68

Complex (3n)



Appearance : Yellow gum ; **^{1}H NMR** : (400 MHz, C_6D_6) δ 7.83 – 7.76 (m, 2H), 7.24 (t, J = 7.6 Hz, 3H), 7.12 – 7.05 (m, 5H), 5.11 (d, J = 2.5 Hz, 1H), 4.83 (d, J = 2.5 Hz, 1H), 4.13 (dd, J = 10.8, 6.9 Hz, 1H), 3.84 (dt, J = 7.1, 3.9 Hz, 2H), 3.78 (td, J = 7.7, 2.4 Hz, 2H), 3.60 (d, J = 7.9 Hz, 1H), 2.53 – 2.43 (m, 1H), 2.41 – 2.34 (m, 5H), 2.07 – 2.00 (m, 4H), -0.12 (s, 9H) ; **^{13}C NMR** : (101 MHz, C_6D_6) δ 144.98, 142.31, 129.76, 128.86, 127.94, 127.66, 127.43, 126.73, 120.57, 111.74, 89.80, 77.46, 50.75, 49.20, 43.35, 42.25, 34.42, 34.27, -0.10 ; **IR (ATR)** : v = 3060, 3025, 2953, 2924, 2865, 2826, 1602, 1494, 1453, 1441, 1318, 1246, 1152, 1110, 1076, 1030, 1003, 907, 875, 833, 752, 697 cm^{-1} ; **HRMS (ESI)** : calculated for $[C_{31}H_{37}SiIr]^+$: 631.2367 , found: 631.2368 ; **$[\alpha]_D$** : 16.67 (c = 0.1, CH_2Cl_2) ; **R_f [Pentane/Toluene: 9/1]** : 0.53

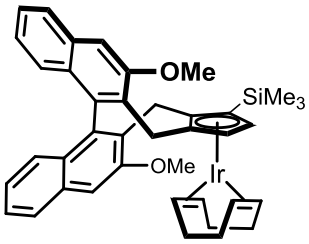
Complex (2o)



Appearance : Yellow powder ; **^{1}H NMR** : (400 MHz, C_6D_6) δ δ 7.75 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.69 - 7.65 (m, 1H), 7.34 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.29 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.24 (ddt, *J* = 8.1, 6.8, 1.2 Hz, 2H), 7.13 (s, 1H), 6.92 (dtd, *J* = 8.2, 6.8, 1.3 Hz, 3H), 5.57 (d, *J* = 2.6 Hz, 1H), 4.46 (d, *J* = 14.4 Hz, 1H), 4.36 (d, *J* = 2.6 Hz, 1H), 4.07 (d, *J* = 13.4 Hz, 1H), 3.76 (tt, *J* = 7.5, 3.3 Hz, 2H), 3.64 (s, 3H), 3.44 (ddt, *J* = 8.9, 6.3, 2.7 Hz, 2H), 3.40 (s, 3H), 3.23 (d, *J* = 14.4 Hz, 1H), 3.02 (d, *J* = 13.4 Hz, 1H), 2.24 (ddt, *J* = 13.5, 10.7, 6.8 Hz, 2H), 2.18 - 2.08 (m, 2H), 2.06 - 1.97 (m, 2H), 1.81 (dtd, *J* = 13.3, 6.8, 3.5 Hz, 2H), 0.23 (s, 9H) ; **^{13}C NMR** : (101 MHz, C_6D_6) δ 156.27, 155.76, 138.68, 136.55, 133.99, 133.85, 129.83, 127.56, 127.31, 127.25, 127.13, 126.37, 126.07, 124.38, 124.29, 110.91 (d, *J* = 3.7 Hz), 106.25, 105.29, 103.44 (d, *J* = 3.2 Hz), 94.49 (d, *J* = 3.5 Hz), 90.70 (d, *J* = 3.7 Hz), 87.07 (d, *J* = 4.8 Hz), 66.82, 66.68, 64.04, 63.90, 54.99, 54.39, 33.88, 31.85, 26.91, 25.96, 0.47 ; **IR (ATR)** : v = 3057, 2987, 2971, 2927, 2881, 2860, 2808, 1618, 1596, 1574, 1449, 1425, 1410, 1392, 1327, 1294, 1259, 1242, 1232, 1223,

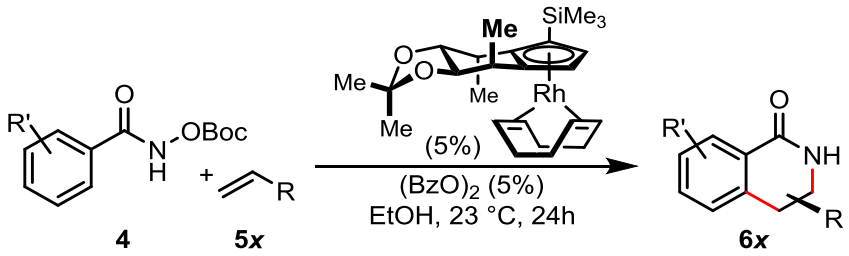
1198, 1163, 1151, 1115, 1089, 1021, 970, 894, 867, 826, 801, 768, 745, 679, 647, 625 cm^{-1} ; **HRMS (ESI+)** : calculated for $[C_{40}H_{43}O_2RhSi]^+$: 686.2082 , found: 686.2085 ; **$[\alpha]_D$** : -167.50 (c = 0.2, CH_2Cl_2) ; **m.p. :** >200 °C (Decomposition) ; **Rf [Pentane/Toluene: 1/1]** : 0.75

Complex (3o)



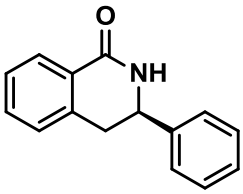
Appearance : White powder ; **^{1}H NMR** : (400 MHz, C_6D_6) δ 7.74 (dd, J = 8.2, 1.2 Hz, 1H), 7.67 (dd, J = 8.2, 1.2 Hz, 1H), 7.34 - 7.27 (m, 2H), 7.24 (ddd, J = 8.0, 6.8, 1.2 Hz, 2H), 7.12 (d, J = 6.8 Hz, 1H), 6.91 (m, 4H), 5.46 (d, J = 2.3 Hz, 1H), 4.41 (d, J = 14.4 Hz, 1H), 4.36 (d, J = 2.4 Hz, 1H), 3.97 (d, J = 13.5 Hz, 1H), 3.64 (s, 3H), 3.60 (td, J = 7.7, 3.2 Hz, 2H), 3.39 (d, J = 2.6 Hz, 3H), 3.38 - 3.32 (m, 2H), 3.10 (d, J = 13.4 Hz, 1H), 2.22 - 1.99 (m, 6H), 1.76 (dq, J = 10.6, 3.3, 2.9 Hz, 2H), 0.18 (s, 9H) ; **^{13}C NMR** : (101 MHz, C_6D_6) δ 156.23, 155.71, 138.56, 136.67, 134.04, 133.95, 129.79, 127.49, 127.35, 127.25, 127.18, 126.43, 126.17, 125.70, 124.37, 124.34, 106.27, 105.91, 105.31, 99.42, 88.95, 85.64, 82.61, 54.99, 54.38, 49.88, 47.43, 35.52, 33.29, 26.30, 25.31 ; **IR (ATR)** : v = 2955, 2907, 2887, 2863, 2813, 1619, 1596, 1450, 1423, 1328, 1294, 1260, 1233, 1197, 1163, 1115, 1021, 907, 827, 746, 647, 623 cm^{-1} ; **HRMS (ESI+)** : calculated for $[C_{40}H_{43}IrO_2Si]$; $[M+H]^+$: 777.2734, found: 777.2743 ; **$[\alpha]_D$** : -123.33 (c = 0.1, $CHCl_3$) ; **m.p. :** >200 °C (Decomposition) ; **R_f [Pentane/AcOEt (24/1)]** : 0.78

Representative Procedure for the Synthesis of Dihydroquinolinone



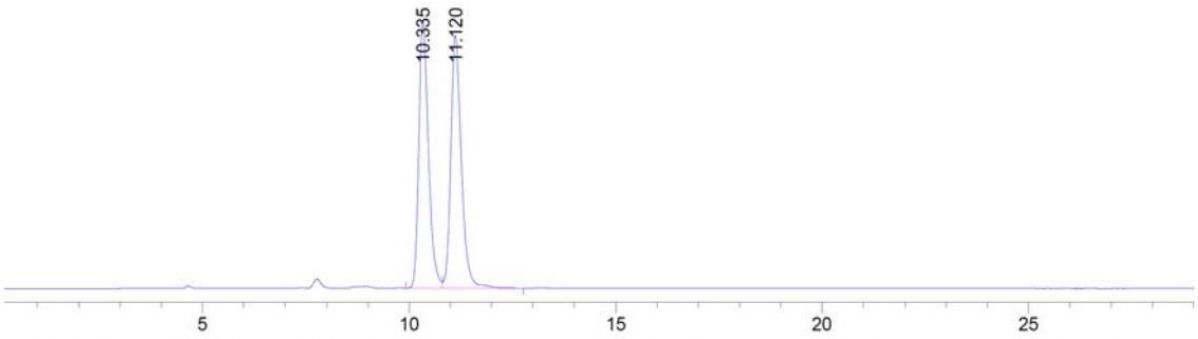
Prepared according to a modification of the procedure reported[3]. Without protection from oxygen or moisture, **4a** (5.0 mg, 10.00 µmol) and benzoic peroxyanhydride (2.4 mg, 10.00 µmol) were mixed and dissolved in ethanol (0.400 ml) and stirred for 10 min. Then, N-((tert-butoxycarbonyl)oxy)benzamide (47.5 mg, 0.2 mmol) was added to the mixture and stirred for 15 minutes before to add styrene (0.046 ml, 0.400 mmol). The reaction was stirred for 24 hours at 23 °C. The volatiles were evaporated in vacuo and the residue was purified on a silica gel (CH_2Cl_2:EtOAc (5:1)) giving 35.5 mg (80%, 91 : 9 er) of **6a** as colorless solid.

(R)-3-phenyl-3,4-dihydroisoquinolin-1(2H)-one (6a)

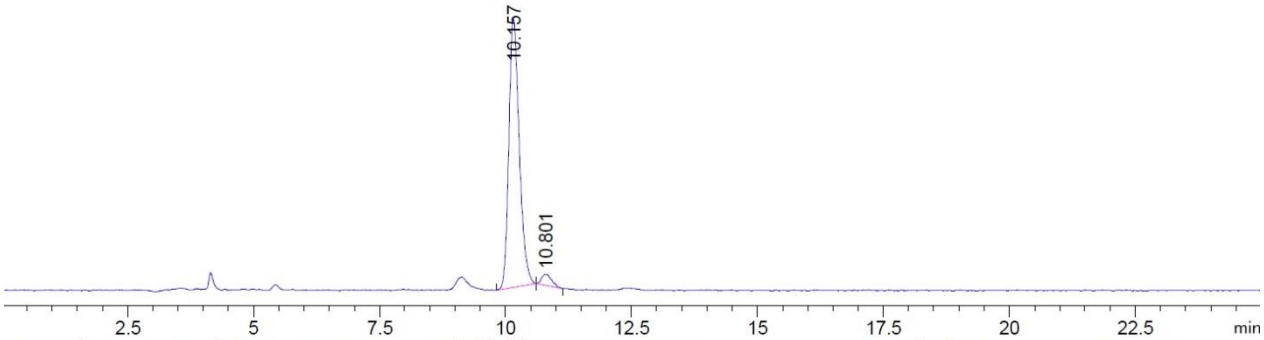


Prepared from styrene. Match the literature[3] :**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.43 – 7.29 (m, 6H), 7.19 (d, *J* = 7.5 Hz, 1H), 5.95 (s, 1H), 4.87 (ddd, *J* = 11.2, 4.7, 1.1 Hz, 1H), 3.22 (dd, *J* = 15.7, 11.2 Hz, 1H), 3.12 (dd, *J* = 15.7, 4.7 Hz, 1H) ; **HPLC separation** (Chiralpak

IA, 4.6x250 mm; 20% i-PrOH/hexane, 1.0 mL/min, 280 nm; tr (major) = 10.2 min, tr (minor) = 10.8 min), 96:4 er

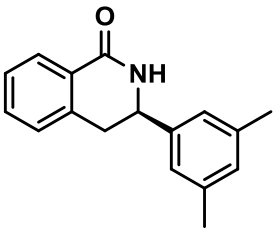


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.335	BV	0.2474	2183.00757	134.45552	49.1533
2	11.120	VB	0.2696	2258.21606	126.89674	50.8467



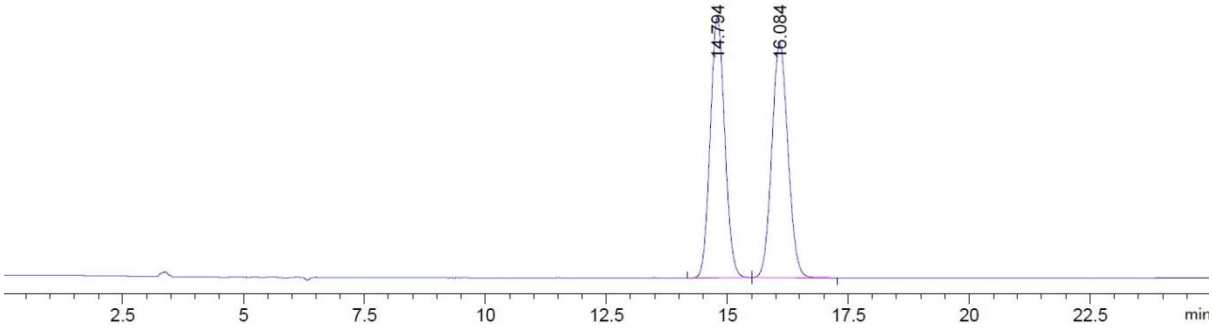
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.157	BB	0.2180	667.52710	46.36492	95.9722
2	10.801	BB	0.1963	28.01533	1.98982	4.0278

(R)-3-(3,5-dimethylphenyl)-3,4-dihydroisoquinolin-1(2H)-one (6b)

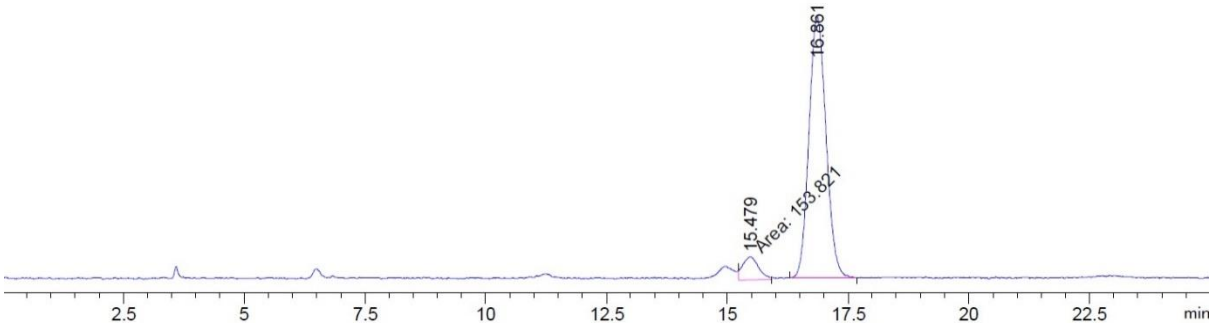


Prepared from 3,5-Dimethylstyrene. Match the literature[8] **Appearance :** White solid ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (dt, J = 7.5, 1.0 Hz, 1H), 7.57 (td, J = 7.5, 1.3 Hz, 1H), 7.53 – 7.45 (m, 1H), 7.39 (dd, J = 7.5, 1.0 Hz, 1H), 6.93 (s, 1H), 6.88 (s, 2H), 6.40 (s, 1H), 4.75 (dd, J = 9.9, 4.6 Hz, 1H), 3.21 (dd, J = 13.5, 4.6 Hz, 1H), 2.62 (dd, J = 13.4, 9.9 Hz, 1H), 2.32 (s, 6H) **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.44, 141.01, 138.78, 137.89, 132.58, 130.12, 128.47, 128.16, 127.41, 127.36, 124.30, 56.27, 37.71, 21.43 **IR (ATR)** : v = 3206, 3070, 3028, 2945, 2918, 2859, 1661, 1605, 1579, 1463, 1418, 1378, 1328, 1263, 1155, 1033, 907, 855, 837, 726, 701, 644 cm^{-1} ; **HRMS (ESI)** : calculated for $[C_{17}H_{17}NO+H]^+$: 252.1383 , found: 252.1383, **R_f [CH_2Cl_2/AcOEt: 5/1]** : 0.5, **HPLC separation** (Chiralpak

IA, 4.6x250 mm; 20% i-PrOH/hexane, 1.0 mL/min, 210 nm; tr (major) = 8.8 min, tr (minor) = 7.1 min), 92.5:7.5 er

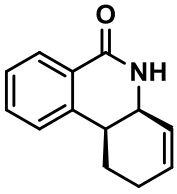


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.916	BB	0.3190	1722.71716	84.10281	50.0335
2	12.533	BB	0.3789	1720.40808	70.95335	49.9665

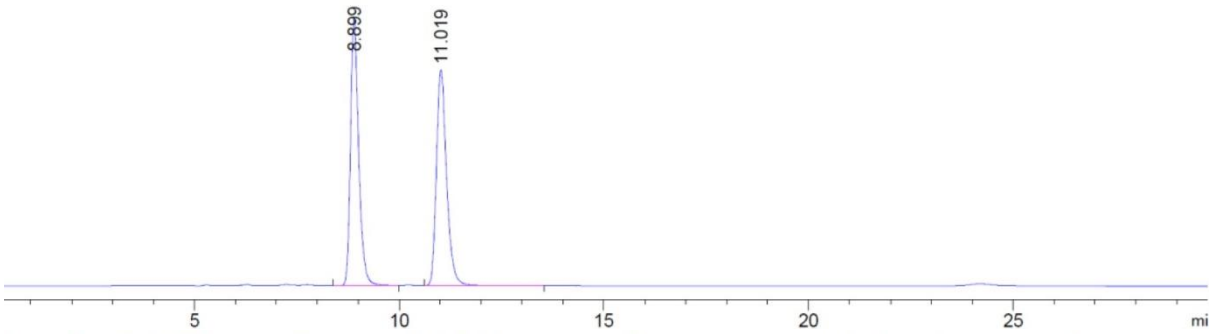


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.479	FM	0.3795	153.82111	6.75557	7.5099
2	16.861	BB	0.3871	1894.40991	76.96962	92.4901

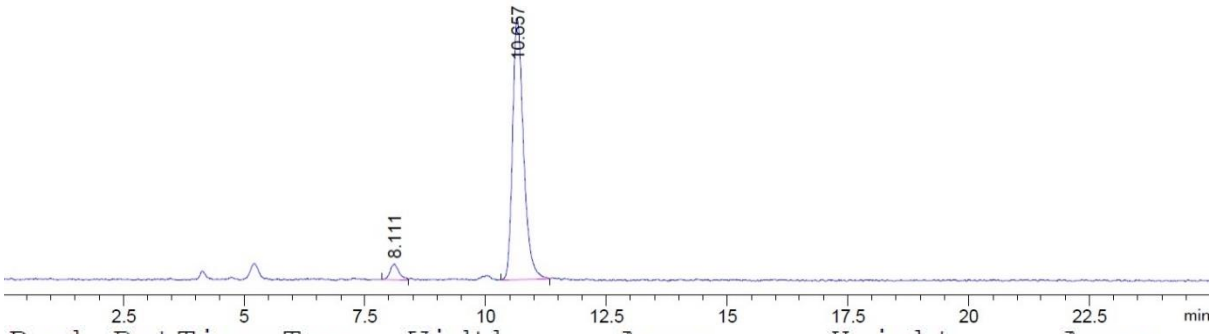
(4aS,10bS)-1,4a,5,10b-tetrahydrophenanthridin-6(2H)-one (6c)



Prepared from 1,3-Cyclohexadiene. Match the literature[3]: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (dd, J = 7.8, 1.5 Hz, 1H), 7.48 (td, J = 7.5, 1.5 Hz, 1H), 7.35 (td, J = 7.6, 1.3 Hz, 1H), 7.27 – 7.23 (m, 1H), 6.13 (s, 1H), 6.03 (dt, J = 9.9, 3.7 Hz, 1H), 5.80 (ddt, J = 9.6, 4.6, 2.2 Hz, 1H), 4.27 (t, J = 4.9 Hz, 1H), 2.94 (dt, J = 12.2, 4.0 Hz, 1H), 2.21 (tt, J = 7.2, 2.8 Hz, 2H), 2.07 – 1.90 (m, 1H), 1.69 (dq, J = 13.1, 3.9 Hz, 1H) ; **HPLC separation** (Chiralpak IA, 4.6x250 mm; 20% i-PrOH/hexane, 1.0 mL/min, 210 nm; tr (major) = 8.1 min, tr (minor) = 10.6 min), 95:5 er

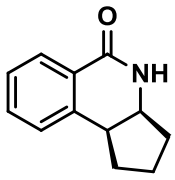


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.899	BB	0.2128	2182.71362	156.42065	49.9355
2	11.019	BB	0.2633	2188.35620	126.82656	50.0645

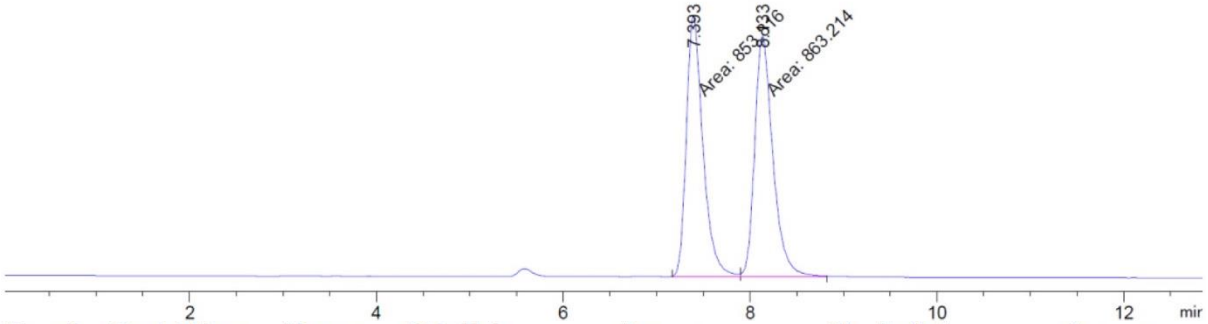


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.111	BV	0.1712	49.20351	3.79724	4.6719
2	10.657	BB	0.2394	1003.97882	63.87860	95.3281

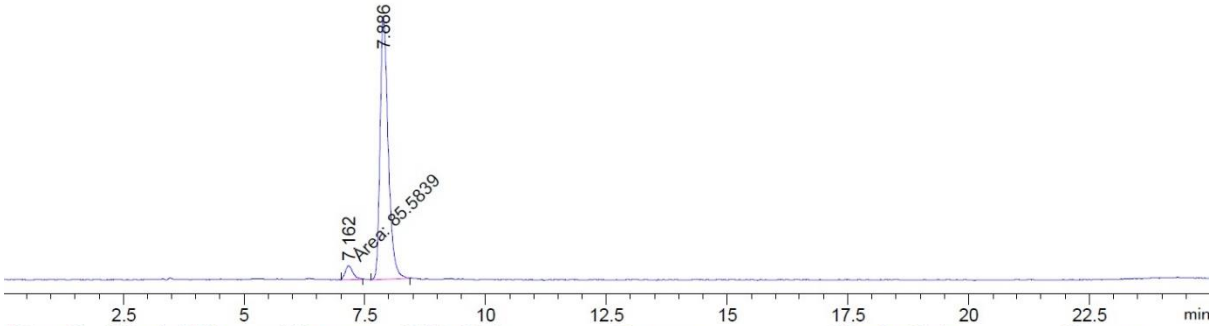
(3aS,9bS)-1,2,3,3a,4,9b-hexahydro-5H-cyclopenta[c]isoquinolin-5-one (6d)



Prepared from Cyclopentene. Match the literature[3]: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (dd, J = 7.8, 1.4 Hz, 1H), 7.44 (td, J = 7.4, 1.5 Hz, 1H), 7.33 (td, J = 7.5, 1.3 Hz, 1H), 7.21 (dd, J = 7.6, 1.2 Hz, 1H), 6.08 (s, 1H), 4.19 (td, J = 5.4, 1.5 Hz, 1H), 3.10 (td, J = 8.7, 5.0 Hz, 1H), 2.21 – 1.99 (m, 2H), 1.99 – 1.71 (m, 4H) ; **HPLC separation** (Chiralpak IA, 4.6x250 mm; 20% i-PrOH/hexane, 1.0 mL/min, 254 nm; tr (major) = 7.9 min, tr (minor) = 7.2 min), 95:5 er

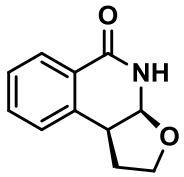


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.393	MF	0.2070	853.81592	68.74513	49.7263
2	8.133	MF	0.2264	863.21393	63.55803	50.2737

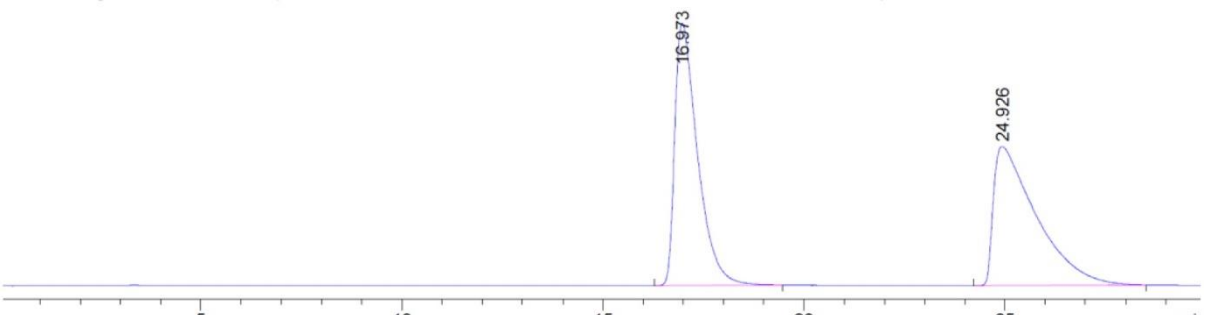


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.162	MM	0.1897	85.58395	7.51990	4.9538
2	7.886	BV	0.1792	1642.04895	139.65758	95.0462

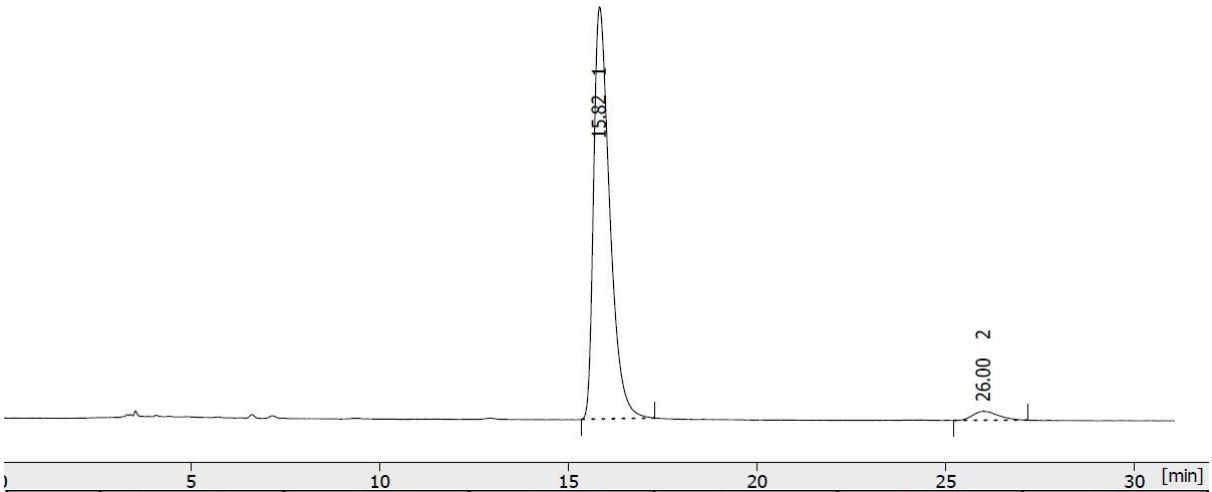
(3aS,9bS)-1,3a,4,9b-tetrahydrofuro[2,3-c]isoquinolin-5(2H)-one (6e)



Prepared from 2,3-dihydrofurane. Match the literature[3] : **^{1}H NMR** (400 MHz, $CDCl_3$) : δ 8.16 (dd, J = 7.6, 1.5 Hz, 1H), 7.56 (td, J = 7.4, 1.5 Hz, 1H), 7.53 – 7.43 (m, 2H), 7.02 (s, 1H), 4.83 (d, J = 4.6 Hz, 1H), 4.35 (q, J = 5.2, 3.7 Hz, 1H), 4.11 – 3.96 (m, 2H), 2.43 (dtd, J = 18.1, 8.9, 5.6 Hz, 1H), 2.20 (dddd, J = 13.1, 6.5, 3.8, 2.1 Hz, 1H) ; **HPLC separation** (Chiralpak AYH, 4.6 x 250 mm; 20% i-PrOH / hexane, 1.0 mL/min, 254 nm; tr (minor) = 26.0 min, tr (major) = 15.8 min), 97 : 3 e.r.

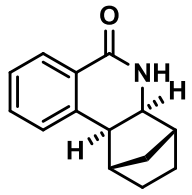


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.973	BB	0.5896	3392.78711	86.13158	50.0005
2	24.926	BB	1.0111	3392.72461	45.75384	49.9995

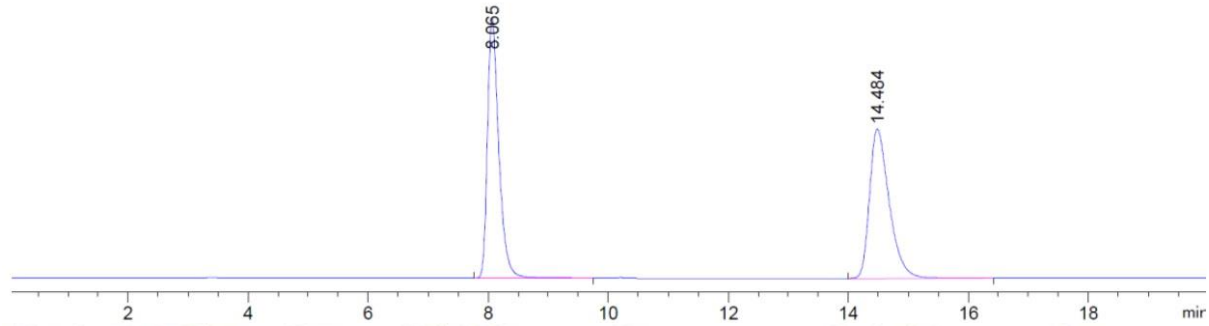


	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	15.821	2004.600	67.544	96.7	97.9	0.45
2	25.999	69.420	1.476	3.3	2.1	0.74
	Total	2074.020	69.020	100.0	100.0	

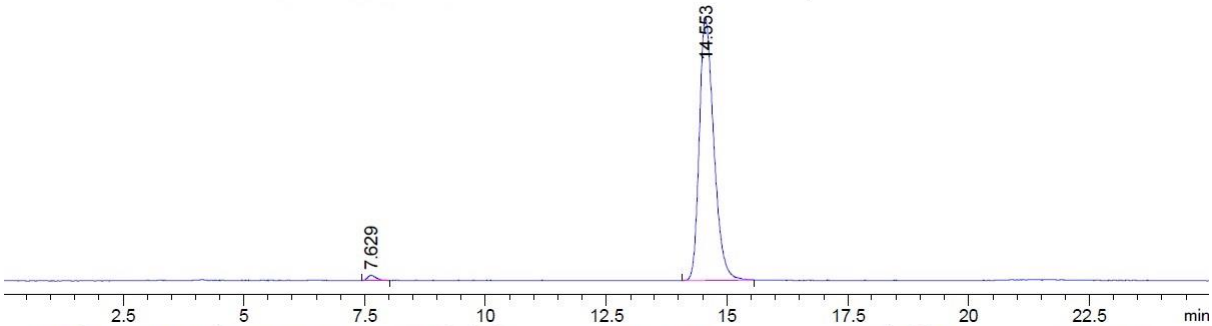
(1S,4R,4aS,10bS)-1,3,4,4a,5,10b-hexahydro-1,4-methanophenanthridin-6(2H)-one (6f)



Prepared from norbornene. Matched the literature[9]: **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.11 (dd, J = 7.8, 1.5 Hz, 1H), 7.48 (td, J = 7.5, 1.5 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.24 (d, J = 7.7 Hz, 1H), 6.14 (s, 1H), 3.83 (dt, J = 8.8, 1.8 Hz, 1H), 3.15 (d, J = 8.8 Hz, 1H), 2.41 – 2.31 (m, 1H), 2.28 – 2.20 (m, 1H), 1.75 – 1.60 (m, 3H), 1.60 – 1.49 (m, 1H), 1.46 – 1.30 (m, 1H), 1.25 – 1.16 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm) = 163.6, 140.3, 132.3, 128.4, 127.3, 126.3, 125.8, 58.3, 47.8, 46.3, 44.1, 32.4, 30.1, 25.7; **IR (ATR)** : v = 3185, 3039, 2955, 2872, 1665, 1602, 1578, 1491, 1473, 1419, 1341, 1288, 856, 792, 754, 716 cm-1; **HRMS (ESI)** calculated for $[C_{14}H_{16}NO+H]^+$: 214.1226, found: 214.1226; **Rf:** 0.32 (CH_2Cl_2:EtOAc, 1:1); **HPLC separation** (Chiralpak IA, 4.6 x 250 mm 20% i-PrOH / hexane, 1.0 mL/min, 254 nm; tr (minor) = 7.6 min, tr (major) = 14.5 min), 1 : 99 e.r.

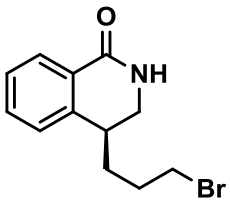


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.065	BB	0.1990	5434.98682	414.52432	50.0157
2	14.484	BB	0.3457	5431.58105	238.49257	49.9843

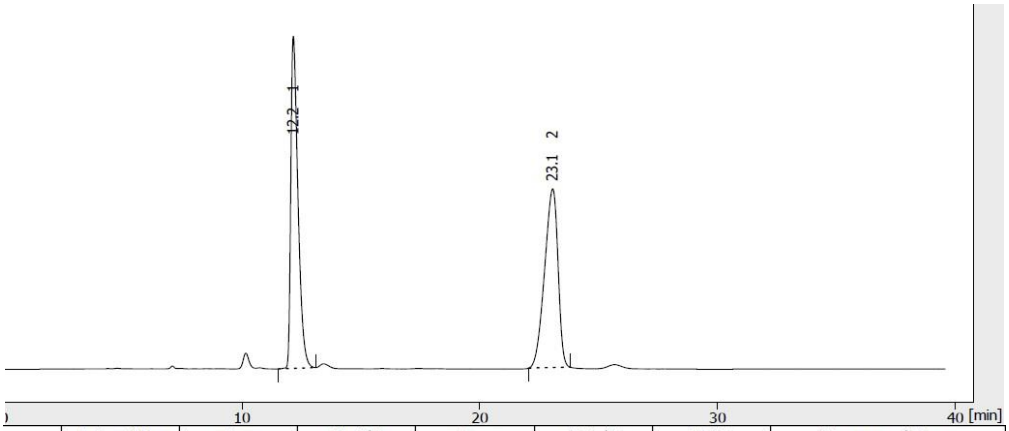


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.629	BB	0.1742	40.51275	3.18970	1.2017
2	14.553	BB	0.3220	3330.72900	159.23604	98.7983

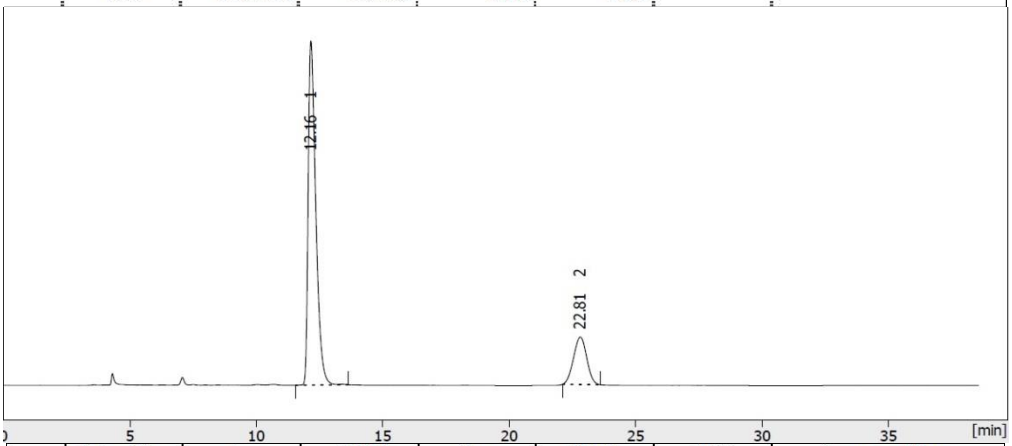
(S)-4-(3-bromopropyl)-3,4-dihydroisoquinolin-1(2H)-one (6g)



Prepared from 5-Bromo-1-Pentene. Match the literature[9]: **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.08 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.48 (td, *J* = 7.5, 1.5 Hz, 1H), 7.38 (td, *J* = 7.6, 1.3 Hz, 1H), 7.20 (dd, *J* = 7.6, 1.1 Hz, 1H), 6.17 (s, 1H), 3.83 – 3.69 (m, 1H), 3.48 – 3.31 (m, 3H), 2.97 – 2.83 (m, 1H), 2.07 – 1.78 (m, 4H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ (ppm) = 166.1, 142.2, 132.5, 128.4, 127.5, 127.1, 123.1, 44.3, 37.2, 33.1, 32.0, 30.4; **IR (ATR):** v = 3221, 3073, 2930, 2867, 1664, 1604, 1575, 1475, 1460, 1406, 1334, 1295, 1249, 1058, 759, 720 cm-1; **HRMS (ESI)** calculated for $[C_{12}H_{15}BrNO+H]^+$: 268.0332, found: 268.0336; ***R*f**: 0.15 (CH_2Cl_2:EtOAc, 5:1); **HPLC separation** (Chiralpak AYH, 4.6 x 250 mm; 20% *i*-PrOH / hexane, 1.0 mL/min, 254 nm; tr (major) = 12.2 min, tr (minor) = 23.0 min), 81 : 19 e.r

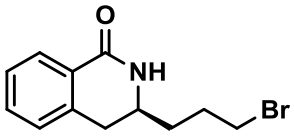


	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	12.159	7753.279	370.021	49.9	65.0	0.32	
2	23.064	7799.556	199.212	50.1	35.0	0.62	
	Total	15552.835	569.233	100.0	100.0		

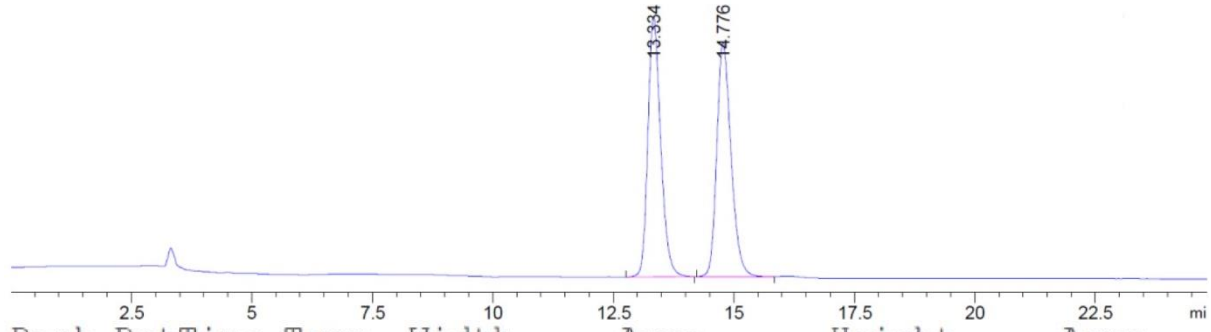


	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	12.156	7078.266	338.746	80.7	87.9	0.32	
2	22.809	1696.056	46.746	19.3	12.1	0.57	
	Total	8774.322	385.492	100.0	100.0		

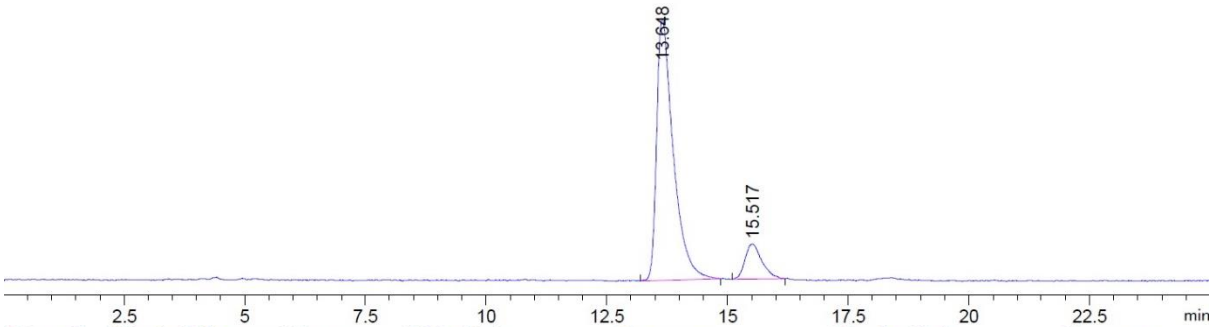
(S)-3-(3-bromopropyl)-3,4-dihydroisoquinolin-1(2H)-one (6g')



Prepared from 5-Bromo-1-Pentene. Match the literature[9]: **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 8.05 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.45 (td, *J* = 7.5, 1.5 Hz, 1H), 7.38 – 7.32 (m, 1H), 7.22 – 7.15 (m, 1H), 6.59 (s, 1H), 3.79 – 3.70 (m, 1H), 3.49 – 3.38 (m, 2H), 3.03 (dd, *J* = 15.5, 4.6 Hz, 1H), 2.84 (dd, *J* = 15.5, 9.6 Hz, 1H), 2.10 – 1.91 (m, 2H), 1.82 – 1.75 (m, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ (ppm) = 166.2, 137.7, 132.4, 128.4, 128.0, 127.5, 127.2, 50.6, 34.0, 33.8, 32.9, 28.6; **IR (ATR):** v = 3204, 3074, 2939, 1665, 1605, 1577, 1465, 1400, 1338, 1305, 746 cm-1; **HRMS (ESI)** calculated for $[C12H15BrNO+H]^+$: 268.0332, found: 268.0335; ***R*f**: 0.18 (CH_2Cl_2:EtOAc, 5:1); HPLC separation (Chiralpak IB, 4.6 x 250 mm; 10% *i*- PrOH / hexane, 1.0 mL/min, 254 nm; tr (minor) = 15.5 min, tr (major) = 13.6 min), 88 : 12 e.r.



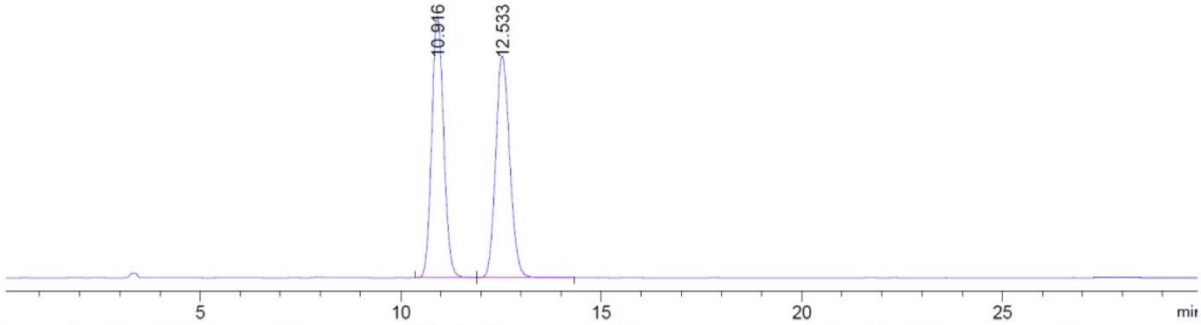
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.334	BB	0.2843	724.07184	39.05124	50.0728
2	14.776	BB	0.3158	721.96582	35.12806	49.9272



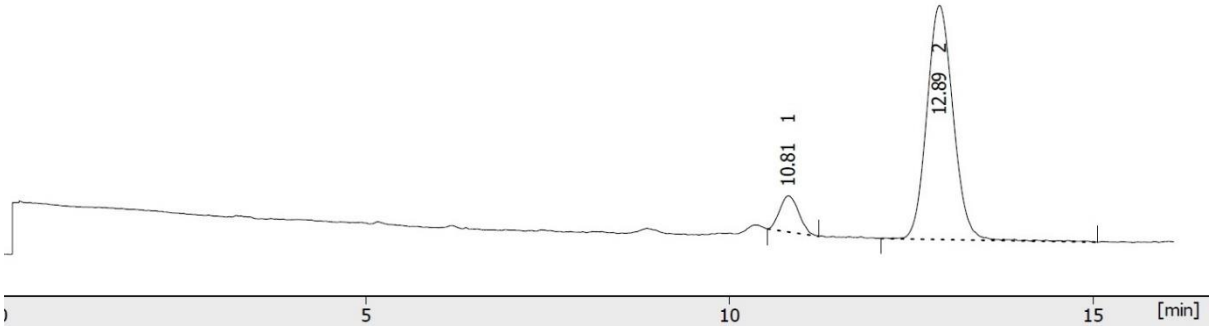
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.648	BB	0.3455	1816.76660	75.83101	87.9985
2	15.517	BB	0.3044	247.77527	10.23618	12.0015

(S)-4-(trimethylsilyl)-3,4-dihydroisoquinolin-1(2H)-one (6h)

Prepared from vinyltrimethylsilane. Match the literature[3] : **^{1}H NMR** δ 8.03 (dd, J = 7.8, 1.5 Hz, 1H), 7.39 (td, J = 7.5, 1.5 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.04 (d, J = 7.6 Hz, 1H), 3.91 (dd, J = 12.0, 4.8 Hz, 1H), 3.54 (ddd, J = 12.0, 5.3, 1.4 Hz, 1H), 2.35 (d, J = 4.7 Hz, 1H), 0.02 (s, 9H) ; **HPLC separation** (Chiralpak OZH, 4.6 x 250 mm; 10% *i*-PrOH / hexane, 1.0 mL/min, 254 nm; t_r (minor) = 10.8 min, t_r (major) = 12.9 min), 90 : 10 e.r.



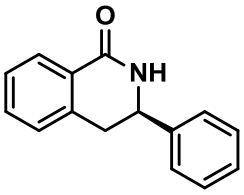
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.916	BB	0.3190	1722.71716	84.10281	50.0335
2	12.533	BB	0.3789	1720.40808	70.95335	49.9665



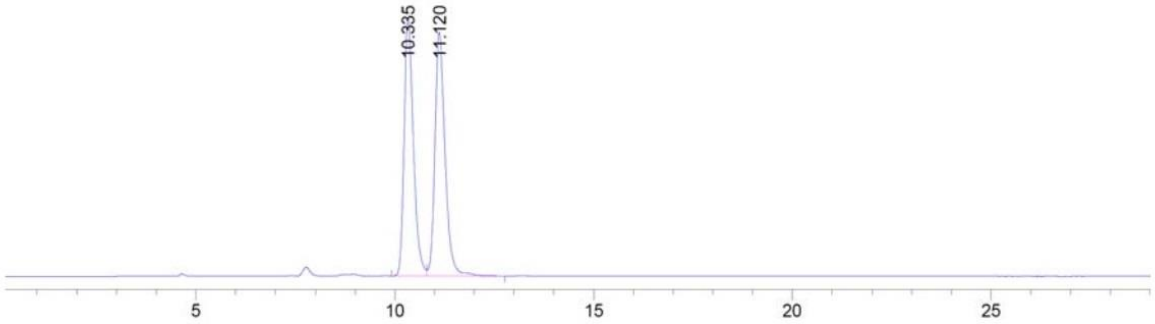
	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]
1	10.808	24.024	1.321	10.0	13.4	0.29
2	12.891	215.901	8.552	90.0	86.6	0.39
	Total	239.925	9.872	100.0	100.0	

C-H Transformations using *in-situ* Cp^X complexes

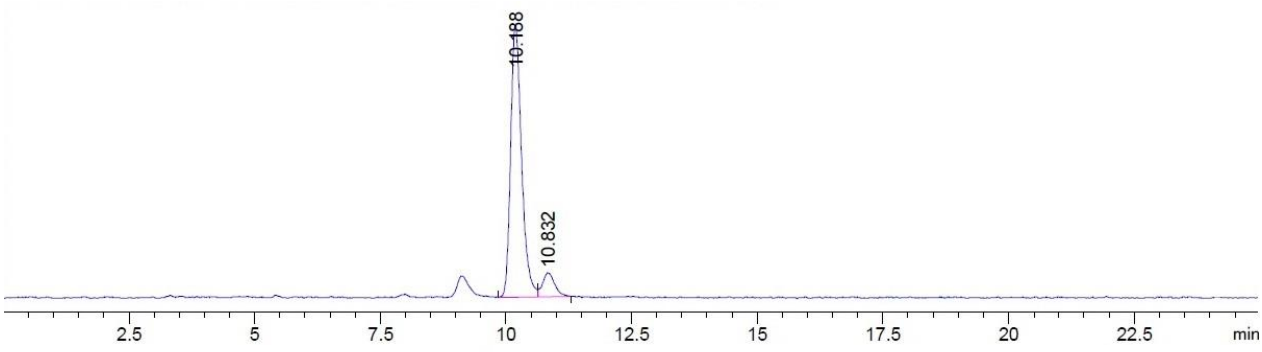
(R)-3-phenyl-3,4-dihydroisoquinolin-1(2H)-one (6a)



Prepared according to a modification of the procedure reported[3]. Without protection from oxygen or moisture, $[Rh(cod)OAc]_2$ (1.6 mg, 3.0 µmol) and Cp ligand **1a** (2.8 mg, 5.0 µmol) were mixed in EtOH (0.1 mL) over 1 hour. Dibenzoylperoxide (1.5 mg, 6.0 µmol) was added to the solution and stirred at the same temperature for 15 minutes. N-((tert-butoxycarbonyl)oxy)benzamide **4** (71 mg, 0.30 mmol) was added to the mixture and stirred for 30 minutes, followed by styrene (69.0 µL, 0.60 mmol, 2.00 equiv.) and the reaction was stirred for 16 hours at 23°C. The volatiles were evaporated in vacuo and the residue was purified on a silica gel (CH_2Cl_2:EtOAc 5:1) giving 55 mg (82%, 91 : 9 er) of **6a** as colorless solid. Match the literature[3] : **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.47 (td, *J* = 7.5, 1.5 Hz, 1H), 7.43 – 7.29 (m, 6H), 7.19 (d, *J* = 7.5 Hz, 1H), 5.95 (s, 1H), 4.87 (ddd, *J* = 11.2, 4.7, 1.1 Hz, 1H), 3.22 (dd, *J* = 15.7, 11.2 Hz, 1H), 3.12 (dd, *J* = 15.7, 4.7 Hz, 1H) ; **HPLC separation** (Chiralpak IA, 4.6x250 mm; 20% i-PrOH/hexane, 1.0 mL/min, 280 nm; tr (major) = 10.2 min, tr (minor) = 10.8 min), 91:9 er

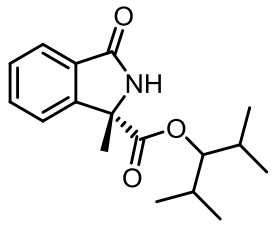


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.335	BV	0.2474	2183.00757	134.45552	49.1533
2	11.120	VB	0.2696	2258.21606	126.89674	50.8467

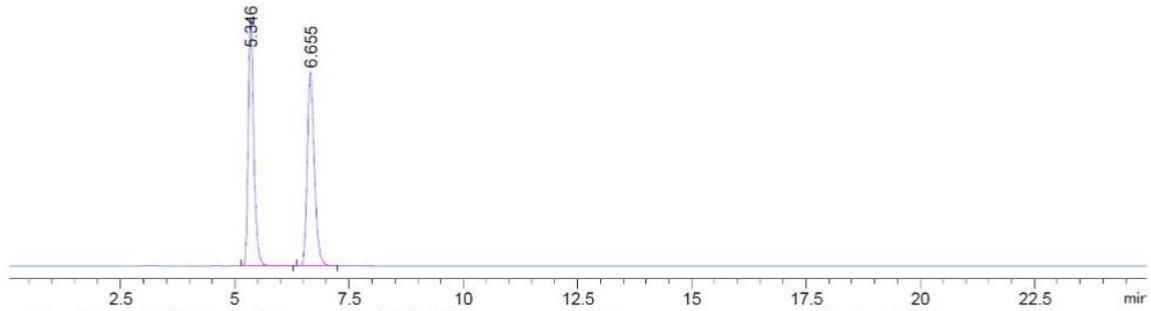


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.188	BV	0.2319	645.71008	42.82944	90.9906
2	10.832	VB	0.2367	63.93441	3.75352	9.0094

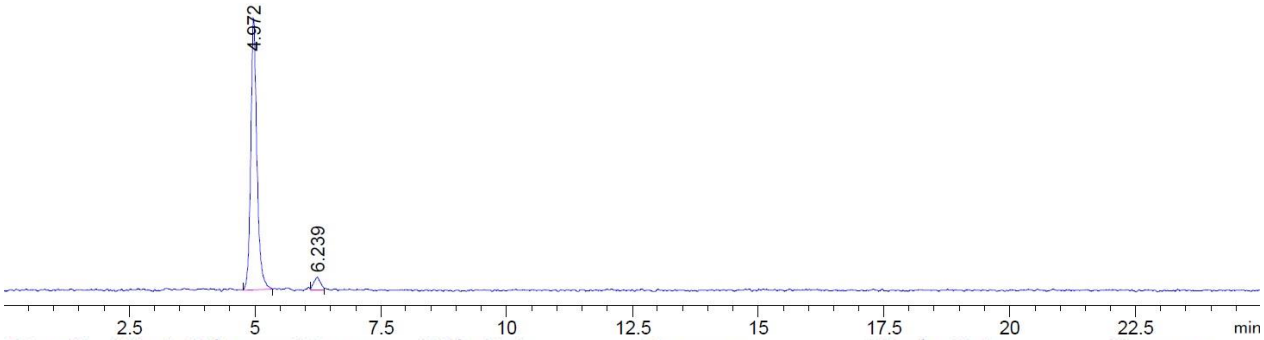
(S)-2,4-Dimethylpentan-3-yl 1-methyl-3-oxoisoindoline-1-carboxylate (8)



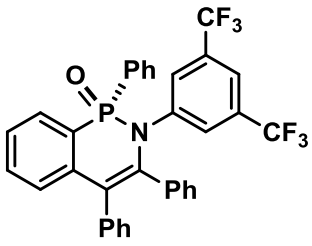
Prepared according to a modification of the procedure reported.[10] A solution of ligand **1h** (4.5 mg, 5.00 µmol) and [Rh(cod)OAc]2 was stirred in MeOH (0.1 mL) at 35 °C over 90 minutes. Dibenzoylperoxide (1.20 mg, 5.00 µmol) and N-(pivaloyloxy)benzamide **7** (22.0 mg, 0.10 mol) in CH_3CN (0.9 mL) was stirred for 15 minutes at 35°C. Then, 2,4-dimethylpentan-3-yl 2-diazopropanoate (20.0 mg, 0.10 mmol) was added and the solution was stirred at 35°C for 16 h. The volatiles were removed in vacuo and the residue was purified by chromatography on silica gel with a gradient elution (hexane/EtOAc 5:1 -> 3:1) affording 23.0 mg (79 %) of **8** as colorless foam. NMR matches the literature.[10] **HPLC separation** (Chiralpak IA, 4.6x250 mm; 20% i-PrOH/hexane, 1.0 mL/min, 280 nm; tr (major) = 5.0 min, tr (minor) = 6.2 min), 95:5 er



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.346	BB	0.1289	2566.02441	302.63095	50.0853
2	6.655	BB	0.1645	2557.28491	235.87741	49.9147

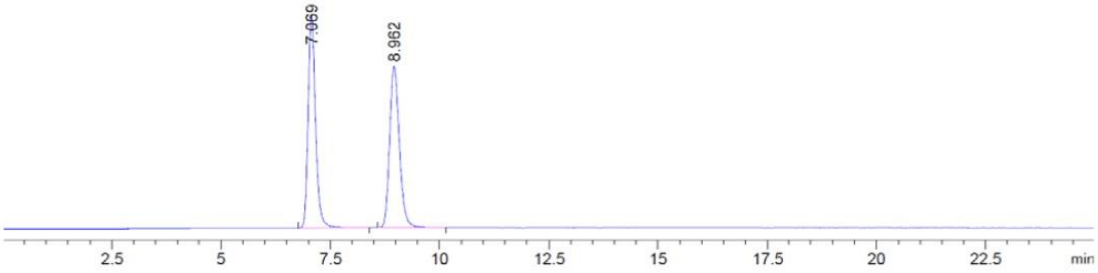


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.972	VB	0.1251	1340.55042	157.85005	94.8147
2	6.239	VV	0.1278	73.31349	7.65038	5.1853

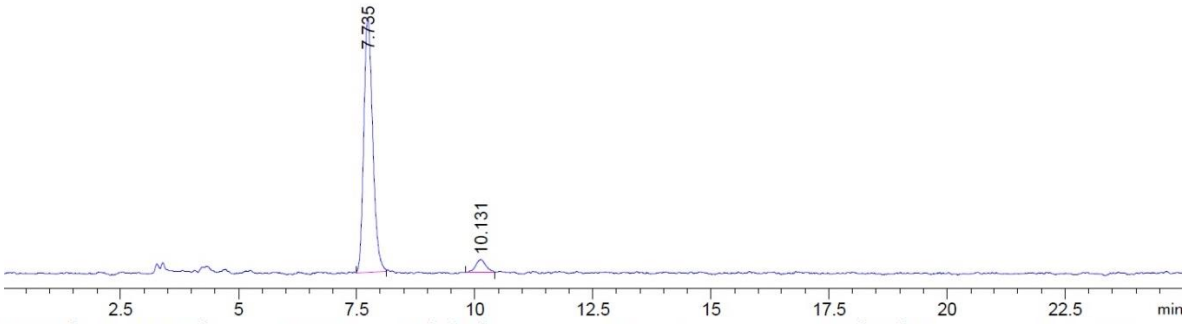


(R)-2-(3,5-bis(trifluoromethyl)phenyl)-1,3,4-triphenyl-2H-benzo[c][1,2]azaphosphinine 1-oxide (10)

Prepared according to a modification of the procedure reported.[11] Without protection from oxygen or moisture, $[Rh(cod)OBz]_2$ (1.7 mg, 2.5 µmol) and Cp ligand **1g** (2.0 mg, 5.0 µmol) were weighed into a microwave tube equipped with a magnetic stir bar. tBuOH (400 µL) was added and the mixture stirred at 90 °C for 1 hour. The mixture was cooled down to 23 °C, then dibenzoylperoxide (1.2 mg, 5.0 µmol) was added to the solution and stirred at the same temperature for 15 minutes. To the solution were added **9** (42.9 mg, 0.1 mmol, 1.0 equiv.), diphenylacetylene (26.7 mg, 0.15 mmol, 1.5 equiv.), K_2CO_3 (13.8 mg, 0.1 mmol, 1.0 equiv.), Ag_2CO_3 (55.1 mg, 0.2 mmol, 2.0 equiv.) and the tube sealed. The reaction mixture was stirred at 90°C for 16 hours. After cooling down to 23 °C, the mixture was filtered over a pad of celite (washing with EtOAc), the volatiles removed under reduced pressure and the crude purified by column chromatography on silica gel (hexane:EtOAc 10:1 to 6:1), yielding 45.8 mg of **10** with 94.5:5.5 er. Match the literature[11] **^{1}H NMR** (400MHz, $CDCl_3$) δ =7.73 (dd,J=13.0,7.1,2H), 7.59 (ddd,J=14.4,7.7,1.4,1H), 7.50 (t,J=7.8,1H), 7.45 (s,2H), 7.42 (dd, J=7.4, 1.7, 1H), 7.39–7.31(m, 3H), 7.31–7.15 (m, 7H), 7.03–6.96 (m,2H), 6.93–6.79 (m,3H) ppm **HPLC separation** (Chiralpak ID, 4.6x250 mm; 10% i-PrOH/hexane, 1.0 mL/min, 280 nm; tr (major) = 7.7 min, tr (minor) = 10.1 min), 94.5:5.5 er

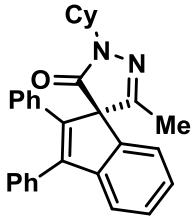


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.069	BB	0.1794	2328.44312	197.66333	50.0325
2	8.962	BB	0.2395	2325.41406	149.46860	49.9675

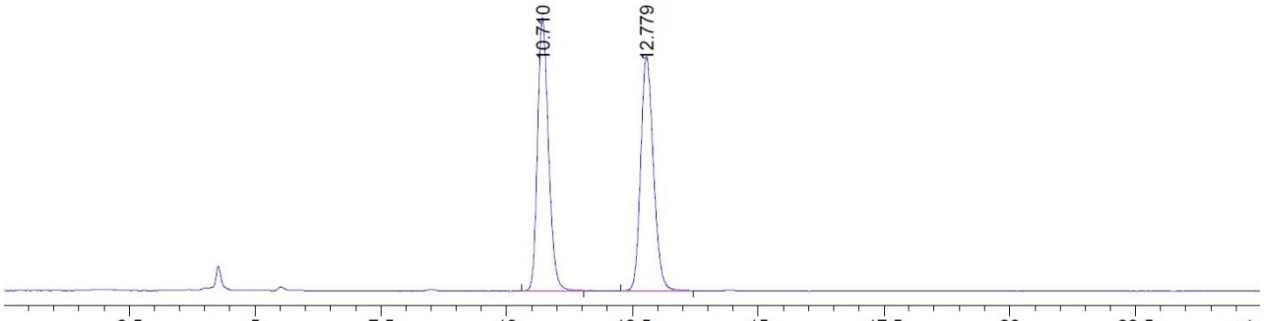


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.735	VV	0.2081	2546.34277	192.71953	94.4381
2	10.131	MM	0.2561	149.96538	9.75775	5.5619

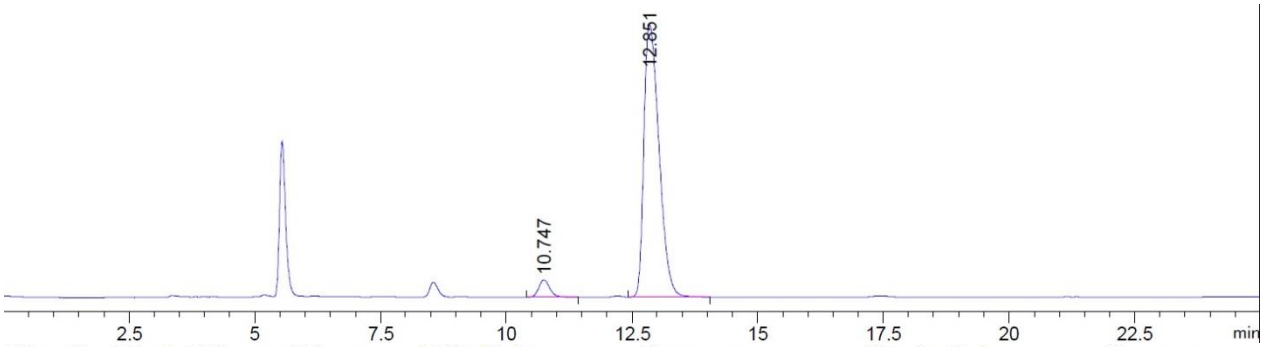
(S)-1'-cyclohexyl-3'-methyl-2,3-diphenylspiro[indene-1,4'-pyrazol]-5'(1'H)-one (12)



Prepared according to a modification of the procedure reported.[12]To a Schlenk tube, $[Rh(C_2H_4)_2OAc]_2$ (1.4 mg, 3.30 µmol) and **1g** (2.022 mg, 5.00 µmol) were dissolved in *t*AmylOH (0.200 mL) and heated at 80°C over 1 hour. Then, the catalyst solution was added to a solution of anhydrous $Cu(OAc)_2$ (36 mg, 0.2 mmol), **11** (0.038 g, 0.150 mmol) and 1,2-diphenylethyne (18 mg, 0.1 mmol) in *t*AmylOH (0.200 ml). The resulting mixture was stirred at 80 °C for 2 hours. The reaction was quenched with 25% ammonia aqueous solution, and the aqueous layer was extracted with DCM (25 mL).The combined organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuo. Purification of the residue by silica gel column chromatography gave **12** (32 mg, 0.074 mmol, 74.0 % yield). Match the literature[12] : **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 7H), 7.27 – 7.22 (m, 1H), 7.15 (qd, J = 4.1, 1.6 Hz, 3H), 7.10 – 7.02 (m, 3H), 4.15 (tt, J = 10.9, 4.4 Hz, 1H), 2.02 – 1.79 (m, 4H), 1.72 (s, 6H), 1.48 – 1.31 (m, 2H), 1.31 – 1.15 (m, 1H) ; **HPLC separation** (Chiralpak IA, 4.6x250 mm; 5% i-PrOH/hexane, 1.0 mL/min, 254 nm; tr (major) = 12.8 min, tr (minor) = 10.7 min, 95.5 : 4.5 er

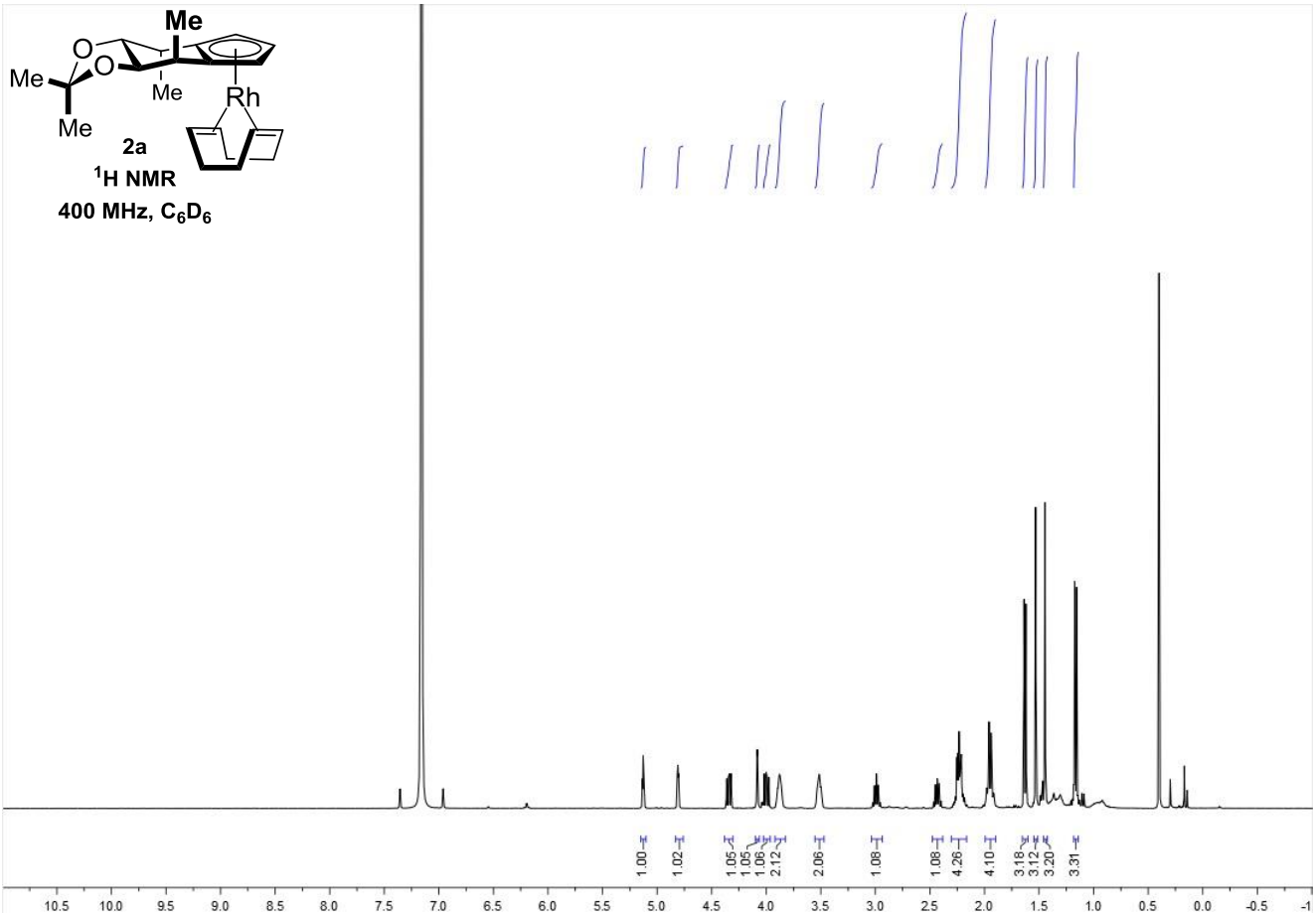


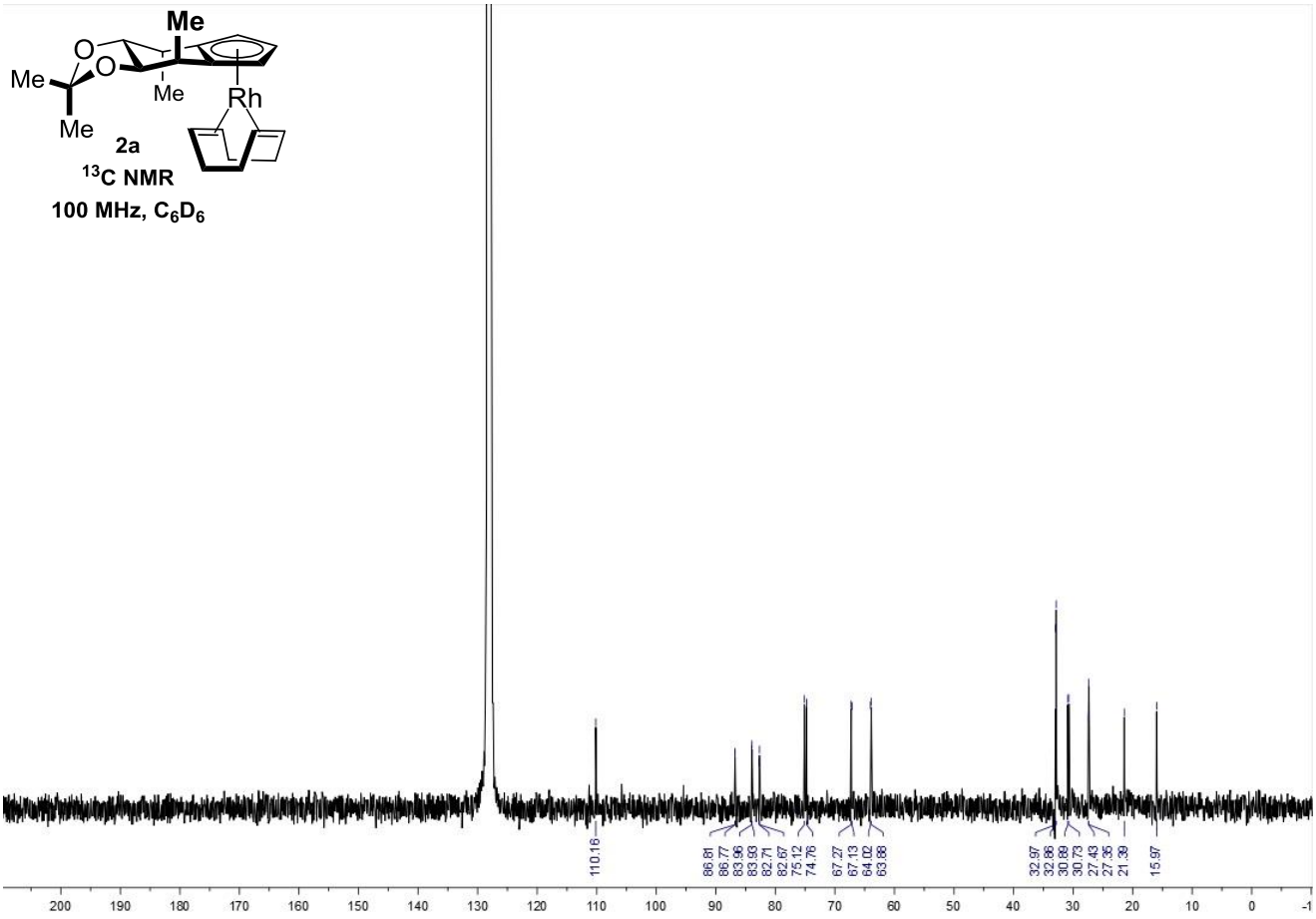
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.710	BB	0.2330	3902.18555	257.27853	50.0002
2	12.779	BB	0.2741	3902.15405	220.89023	49.9998

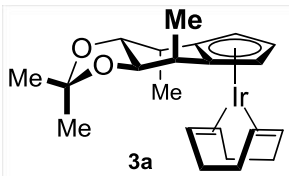


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.747	BB	0.2376	856.18982	55.61585	4.4668
2	12.851	VV	0.3328	1.83117e4	872.67200	95.5332

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



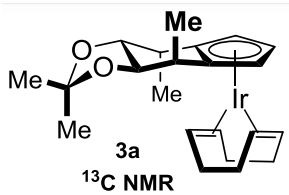




3a

^{1}H NMR

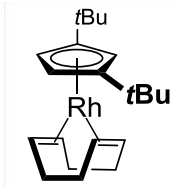
400 MHz, C_6D_6



3a

^{13}C NMR

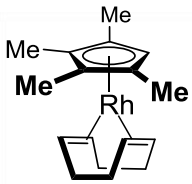
100 MHz, C_6D_6



2b

^{1}H NMR

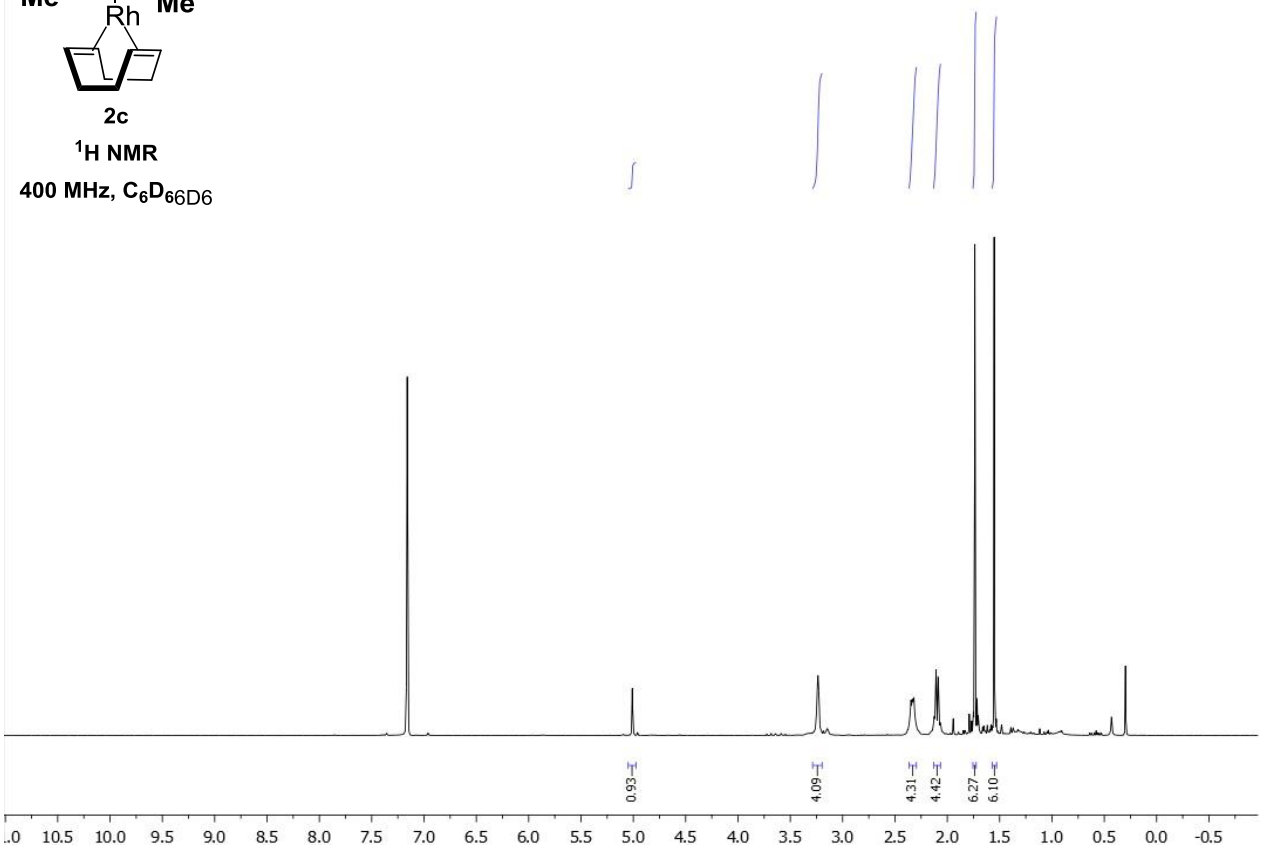
400 MHz, C_6D_6

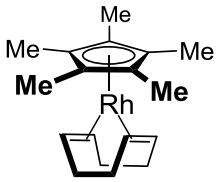


2c

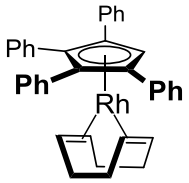
^{1}H NMR

400 MHz, $C_6D_{66}D6$

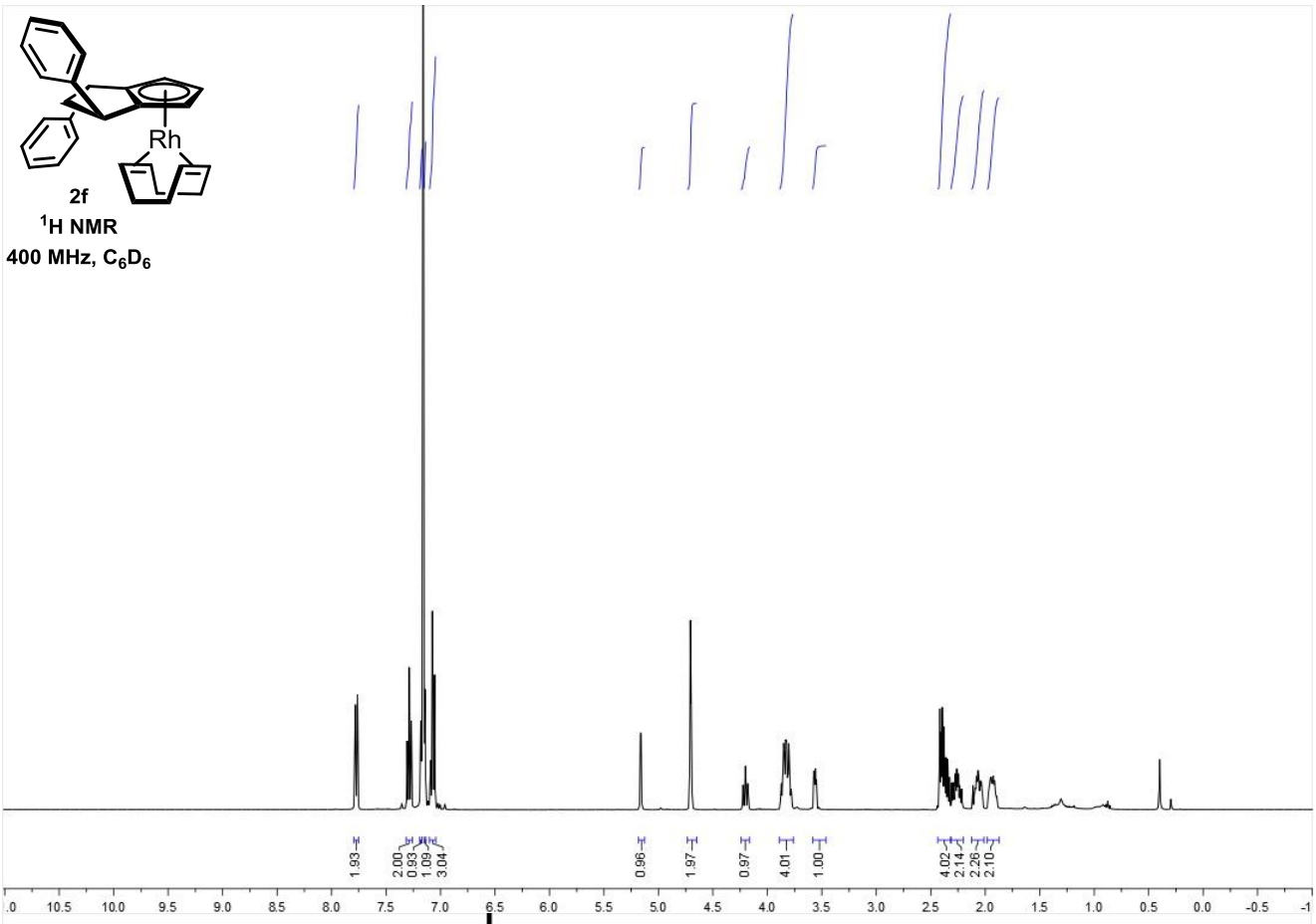


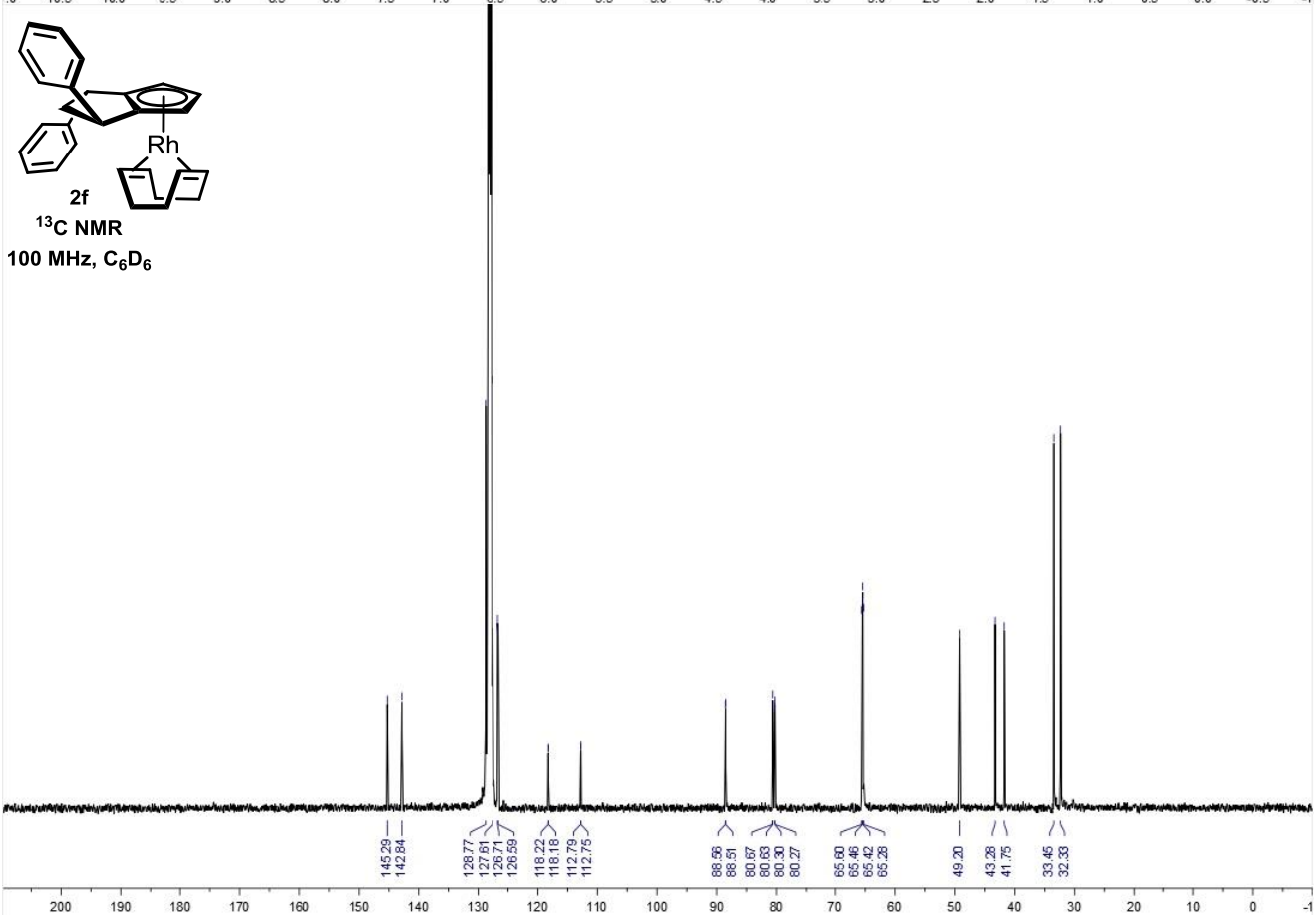


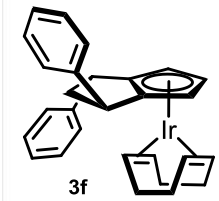
2d
^{1}H NMR
400 MHz, C_6D_6



2e
^{1}H NMR
400 MHz, C_6D_6


Rh
2f
1H NMR
400 MHz, C6D6

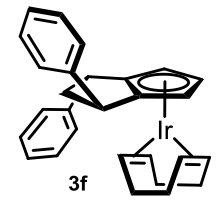

Rh
2f
13C NMR
100 MHz, C6D6



3f

^{1}H NMR

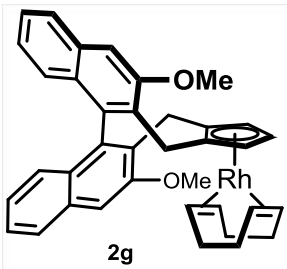
400 MHz, C_6D_6



3f

^{13}C NMR

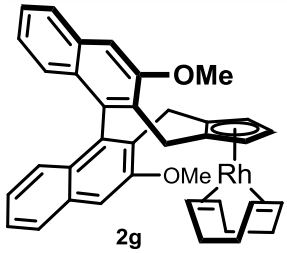
100 MHz, C_6D_6



2g

^{1}H NMR

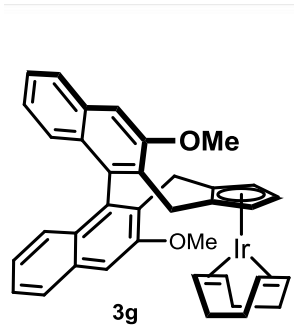
400 MHz, C_6D_6



2g

^{13}C NMR

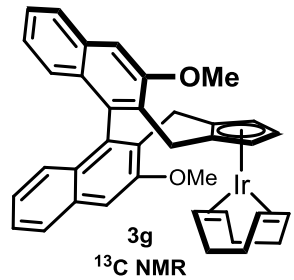
100 MHz, C_6D_6



3g

^{1}H NMR

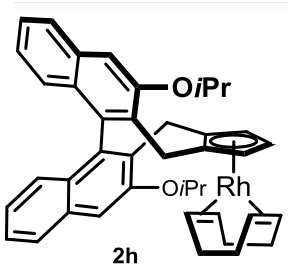
400 MHz, C_6D_6



3g

^{13}C NMR

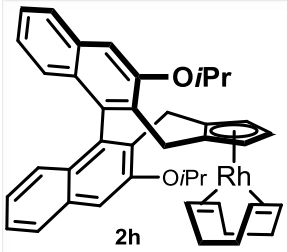
100 MHz, C_6D_6



2h

^{1}H NMR

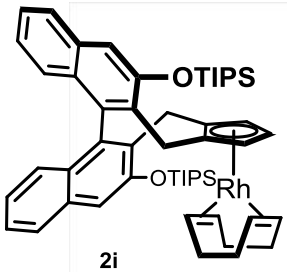
400 MHz, C_6D_6



2h

^{13}C NMR

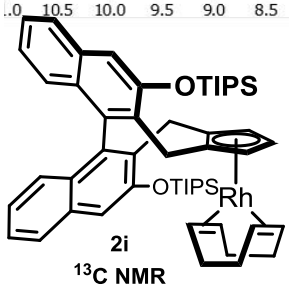
100 MHz, C_6D_6



2i

^{1}H NMR

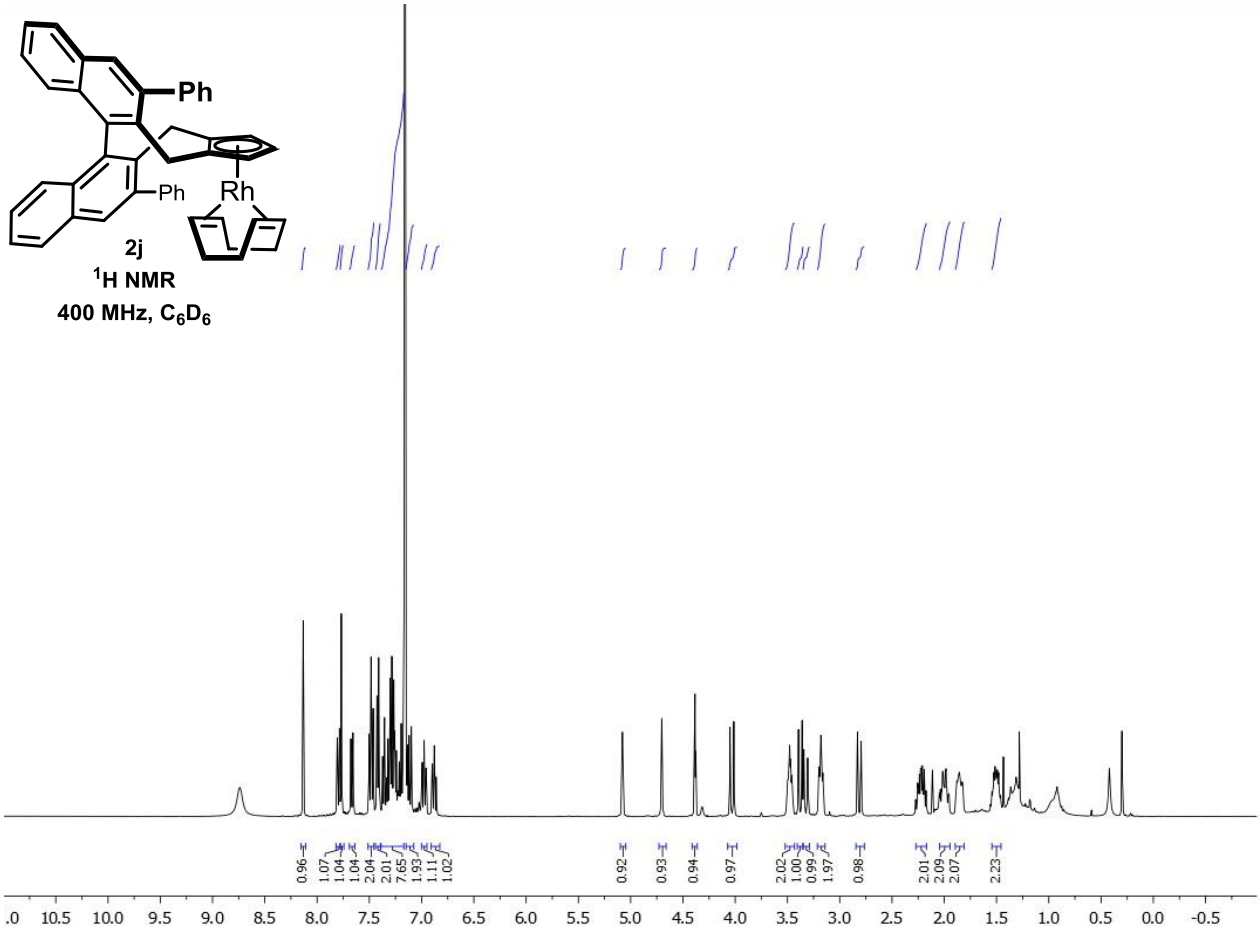
400 MHz, C_6D_6

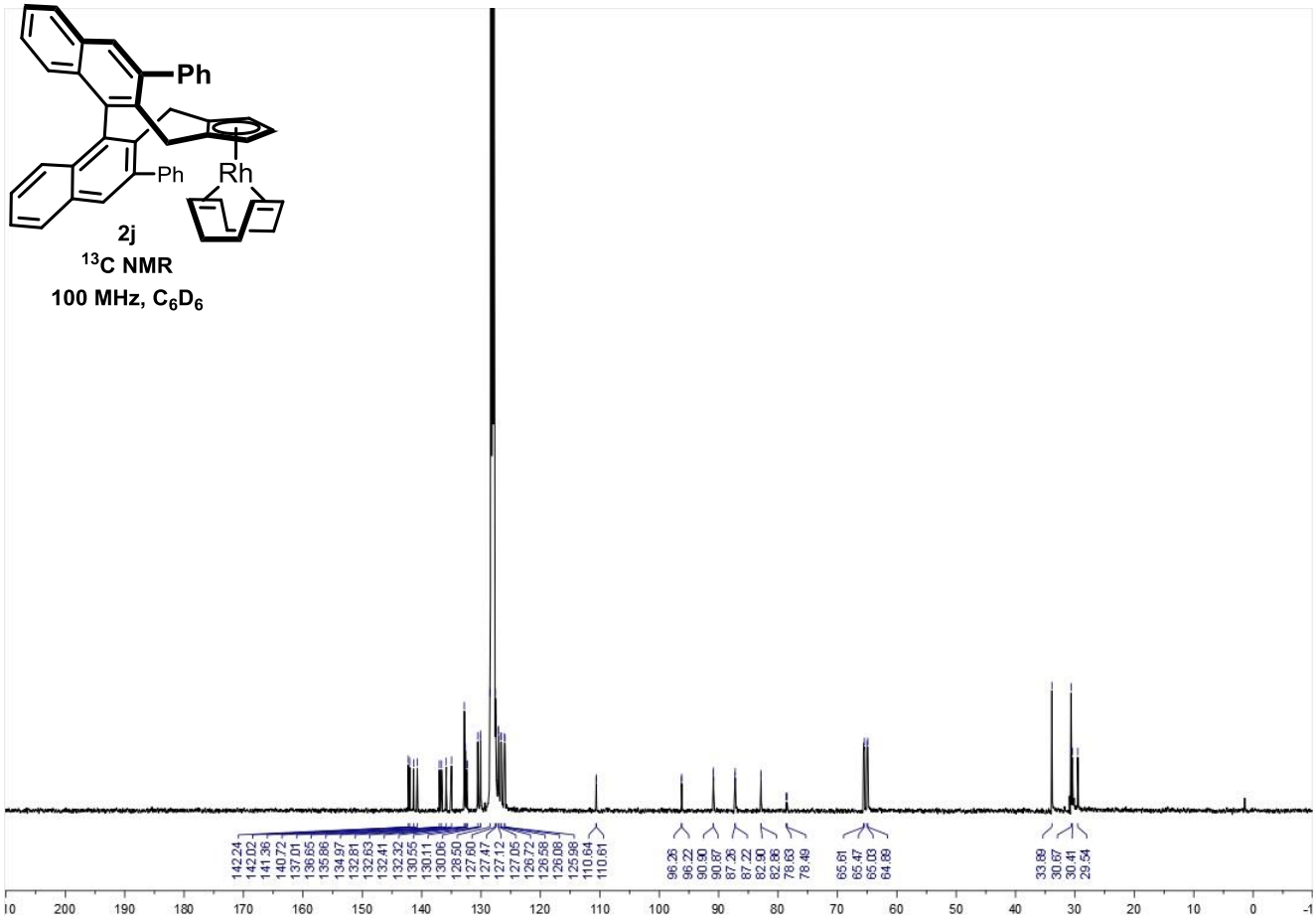


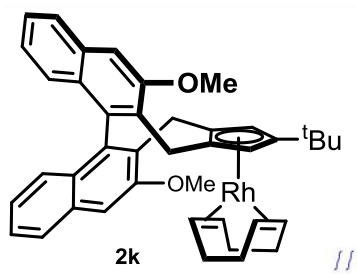
2i

^{13}C NMR

100 MHz, C_6D_6


Ph
Ph
Rh
2j
^{1}H NMR
400 MHz, C_6D_6

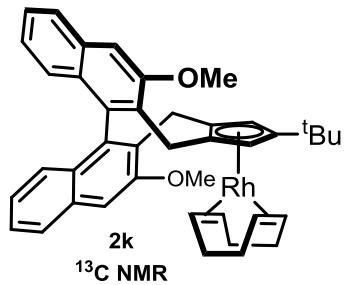

Ph
Ph
Rh
2j
^{13}C NMR
100 MHz, C_6D_6



2k

^{1}H NMR

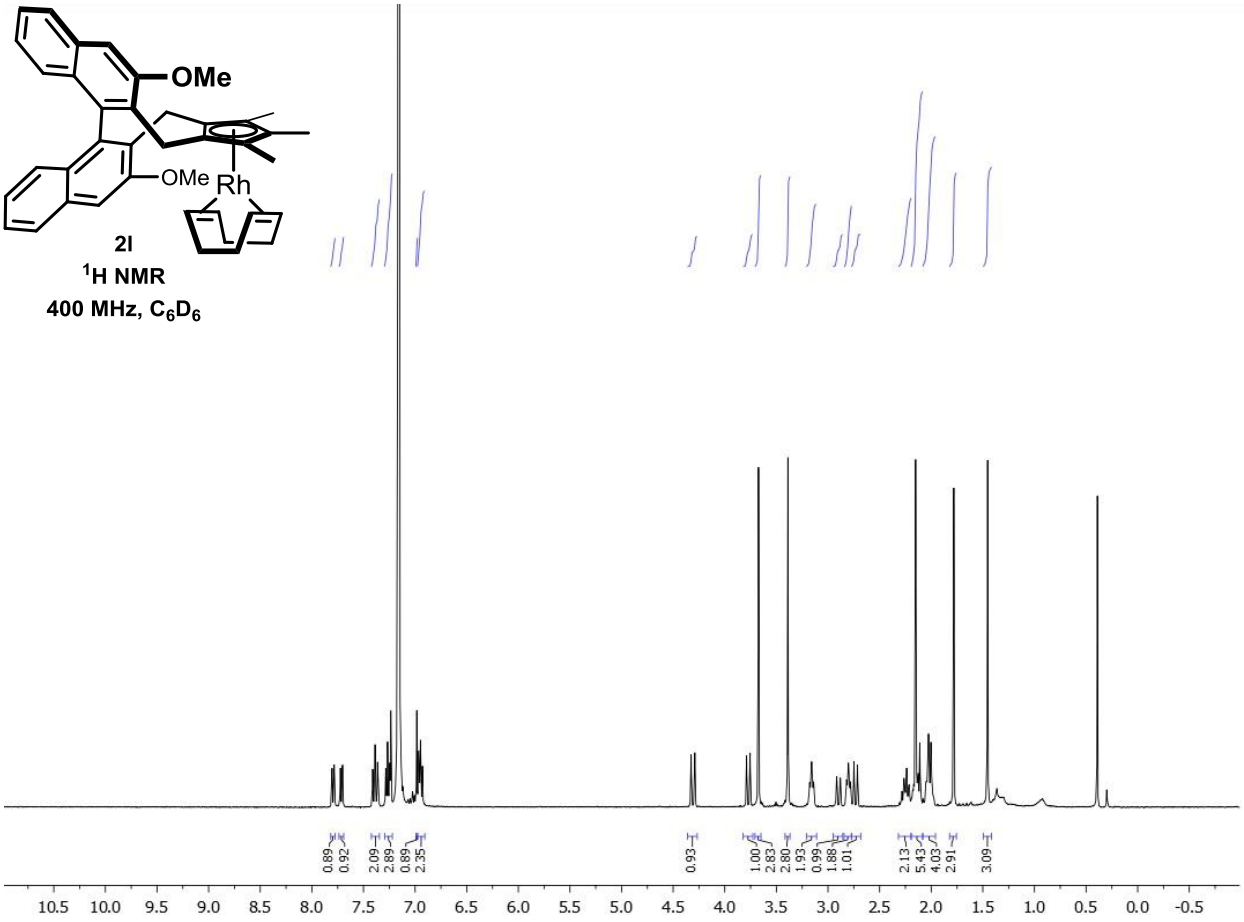
400 MHz, C_6D_6

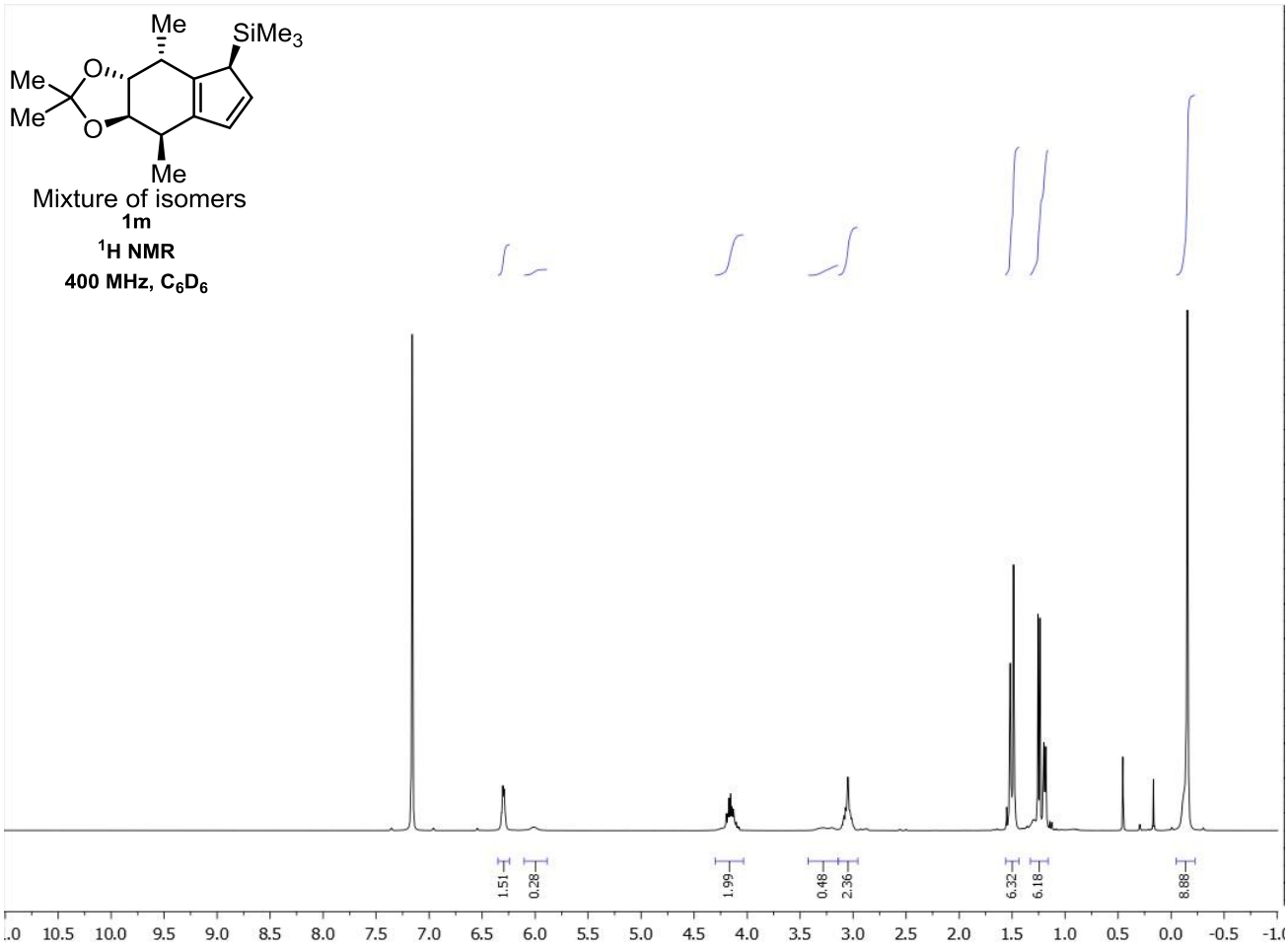


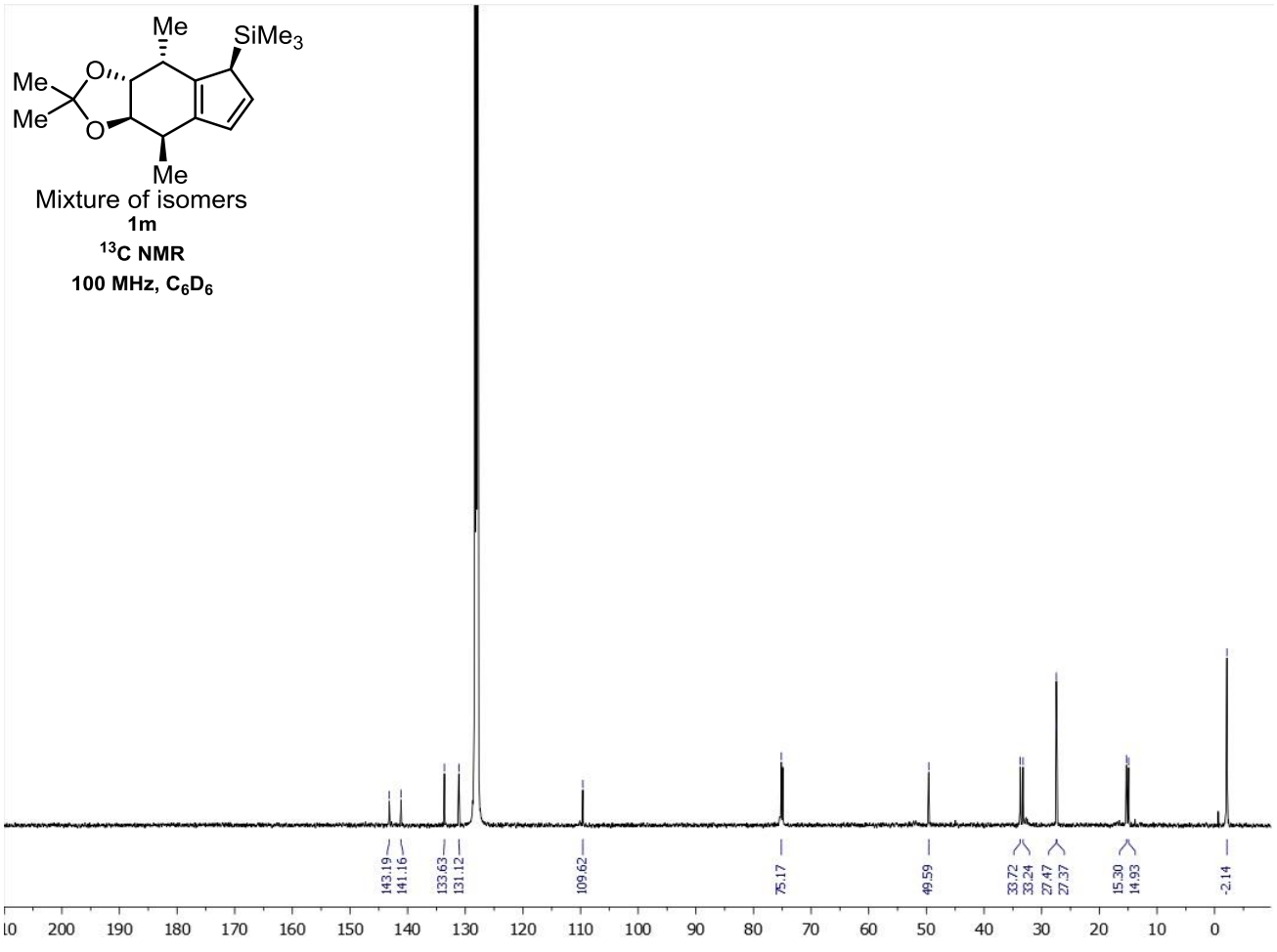
2k

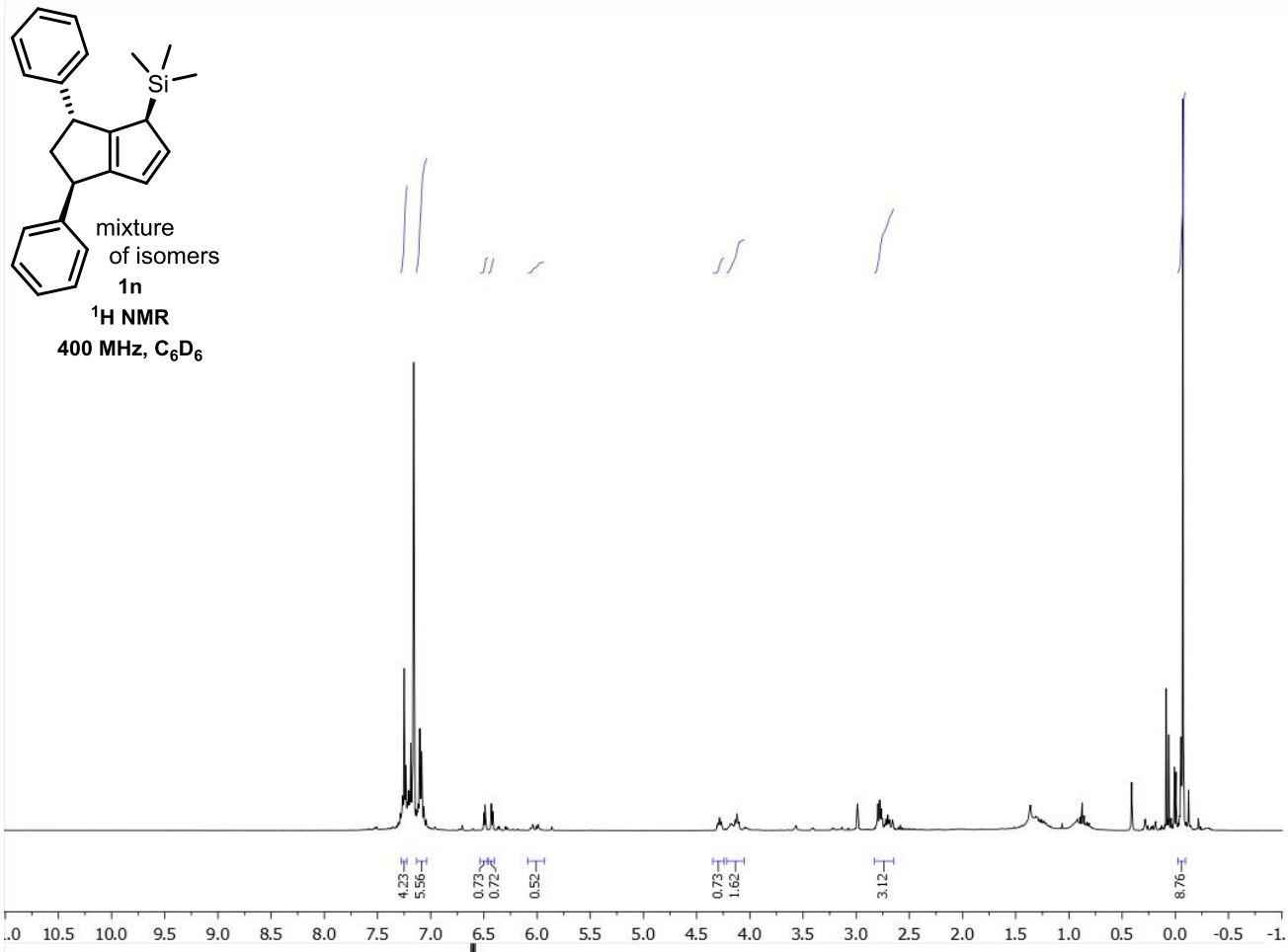
^{13}C NMR

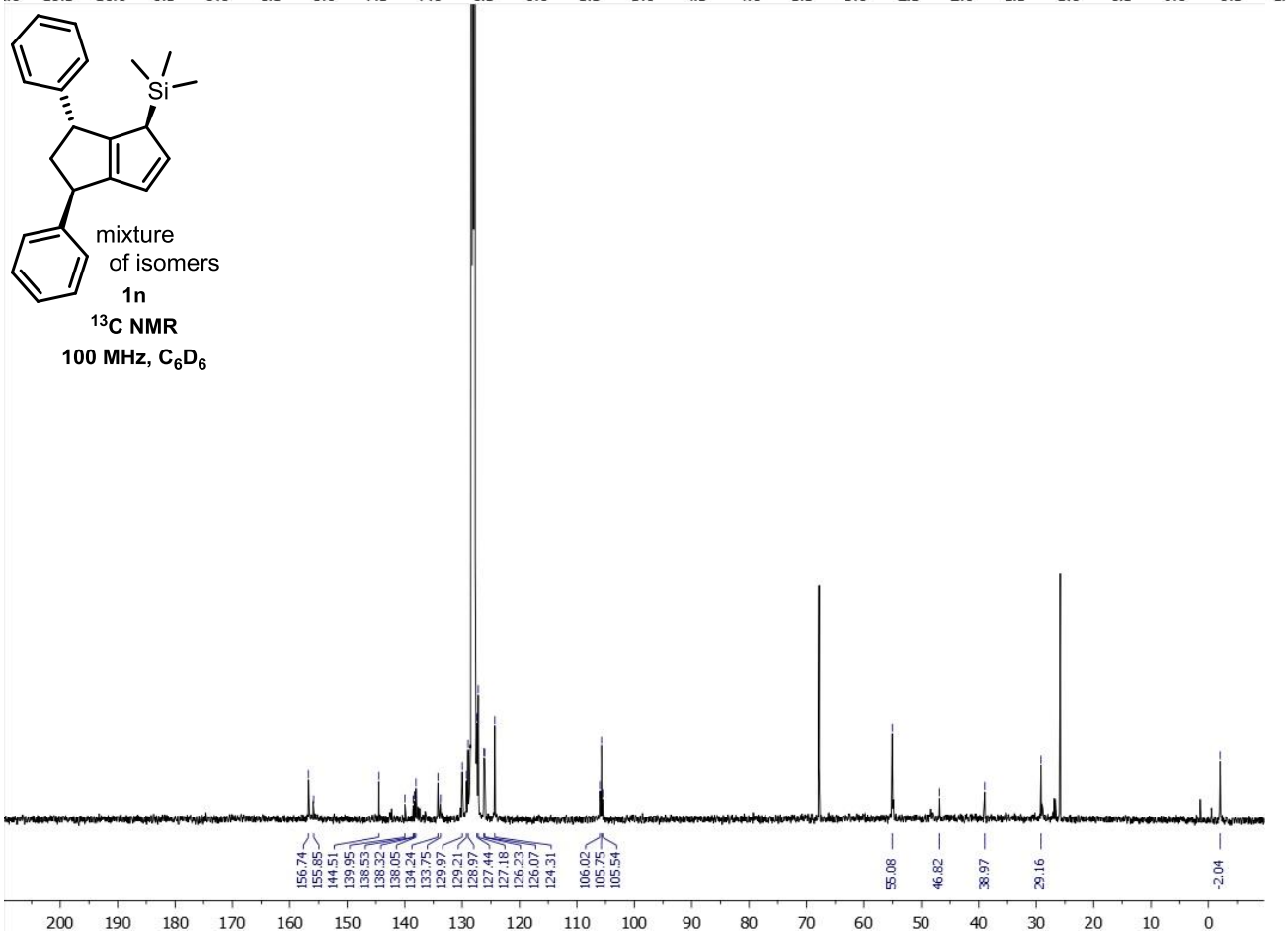
100 MHz, C_6D_6

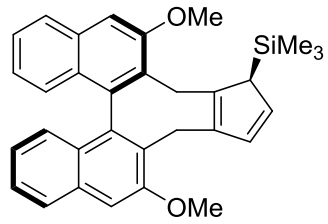

OMe
OMe
Rh
2l
^{1}H NMR
400 MHz, C_6D_6
0.89
0.92
2.09
2.89
0.89
2.35
0.93
1.00
2.83
2.80
1.93
0.99
1.88
1.01
2.13
5.43
4.03
2.91
3.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


Me
SiMe3
Me
Me
O
O
Me
Mixture of isomers
1m
1H NMR
400 MHz, C6D6
1.51
0.28
1.99
0.48
2.36
6.32
6.18
8.88


Me
SiMe3
Me
Me
O
O
Me
Mixture of isomers
1m
13C NMR
100 MHz, C6D6
143.19
141.16
133.63
131.12
109.62
75.17
49.59
33.72
33.24
27.47
27.37
15.30
14.93
-2.14


Si
mixture
of isomers
1n
1H NMR
400 MHz, C6D6
4.23
5.56
0.73
0.72
0.52
0.73
1.62
3.12
8.76


Si
mixture
of isomers
1n
13C NMR
100 MHz, C6D6
156.74
155.85
144.51
139.95
138.53
138.32
138.05
134.24
133.75
129.97
129.21
128.97
127.44
127.18
126.23
126.07
124.31
106.02
105.75
105.54
55.08
46.82
38.97
29.16
-2.04

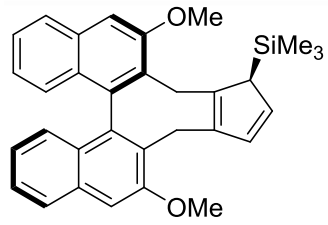


mixture of isomers

1o

^{1}H NMR

400 MHz, C_6D_6

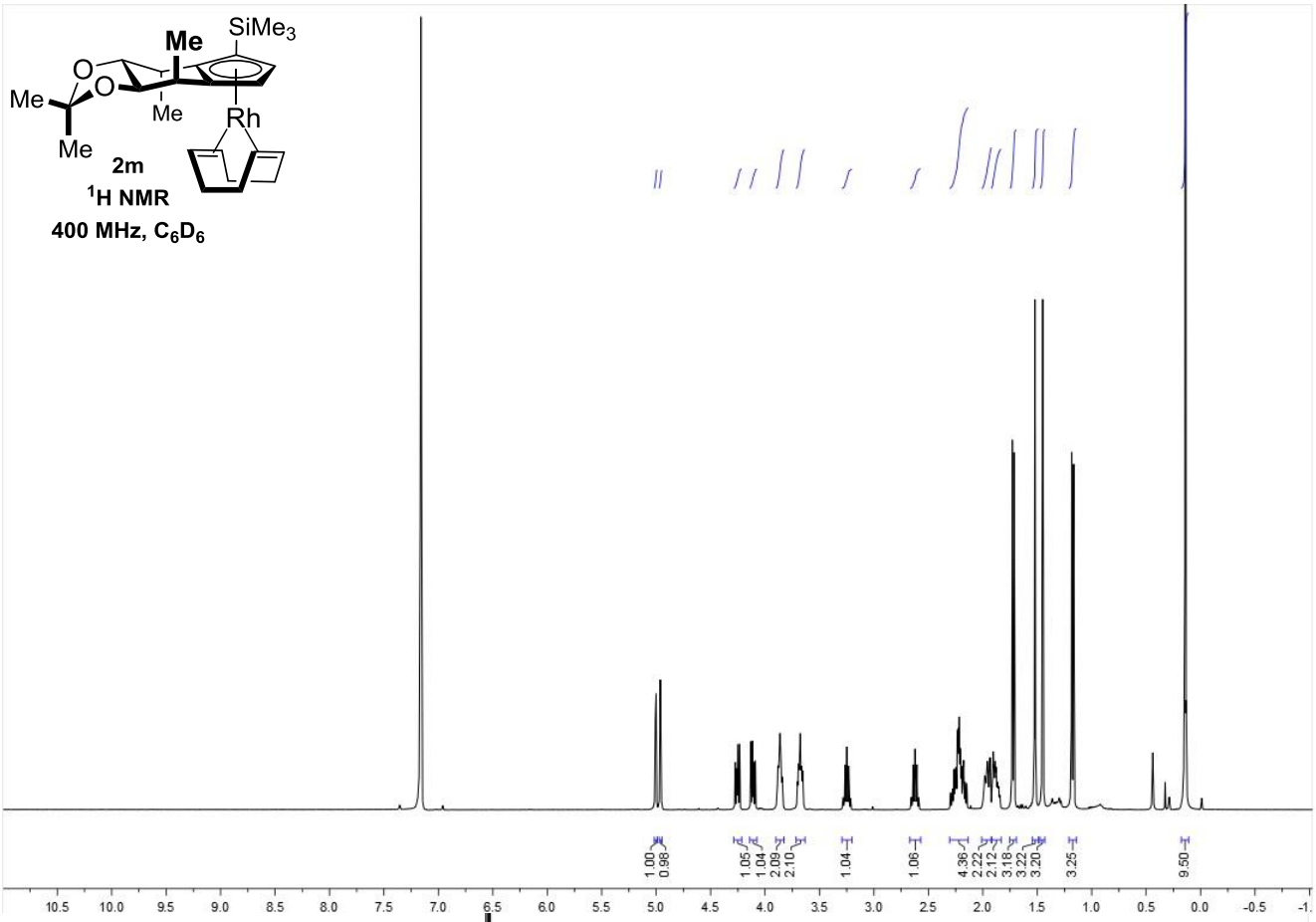


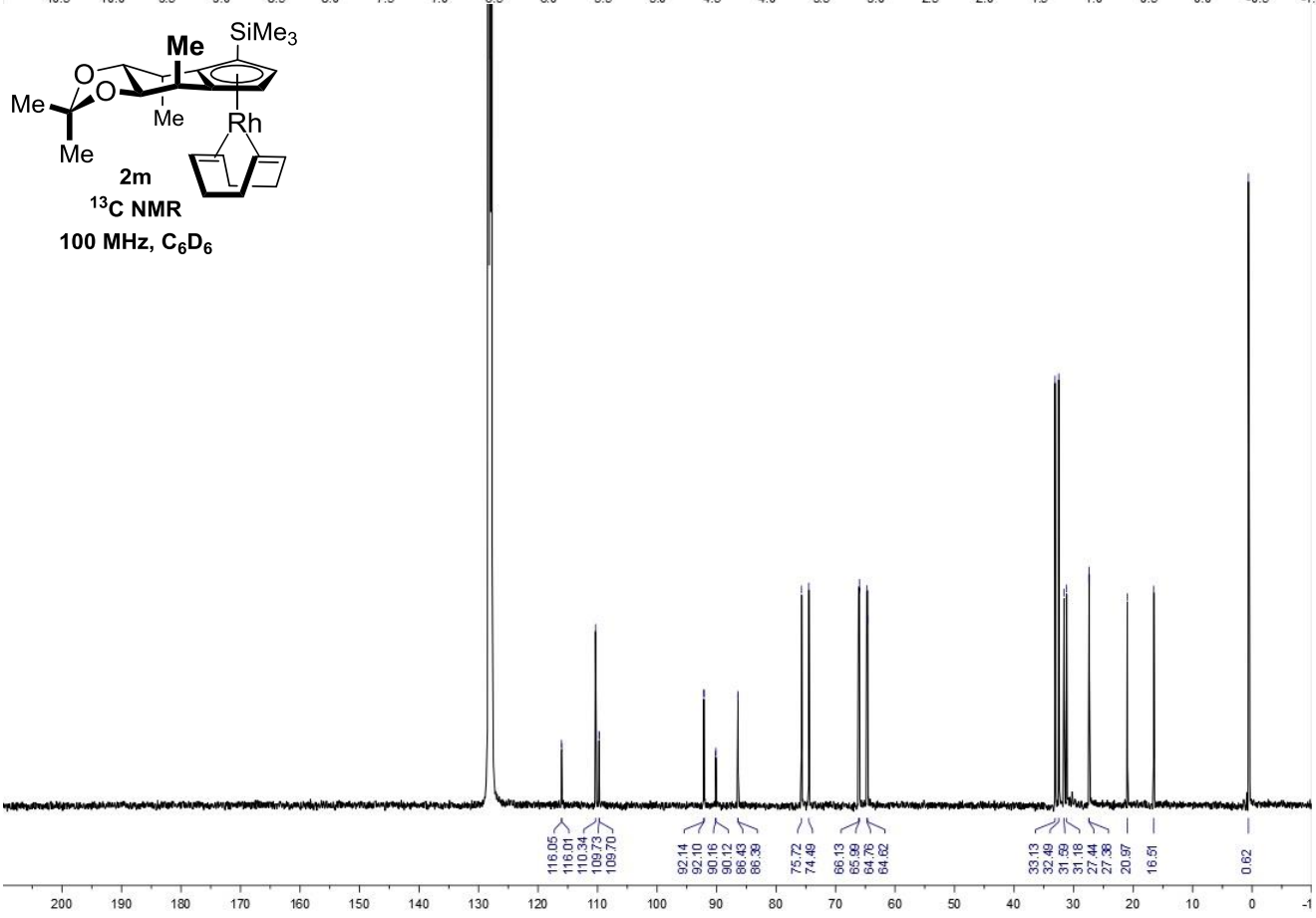
mixture of isomers

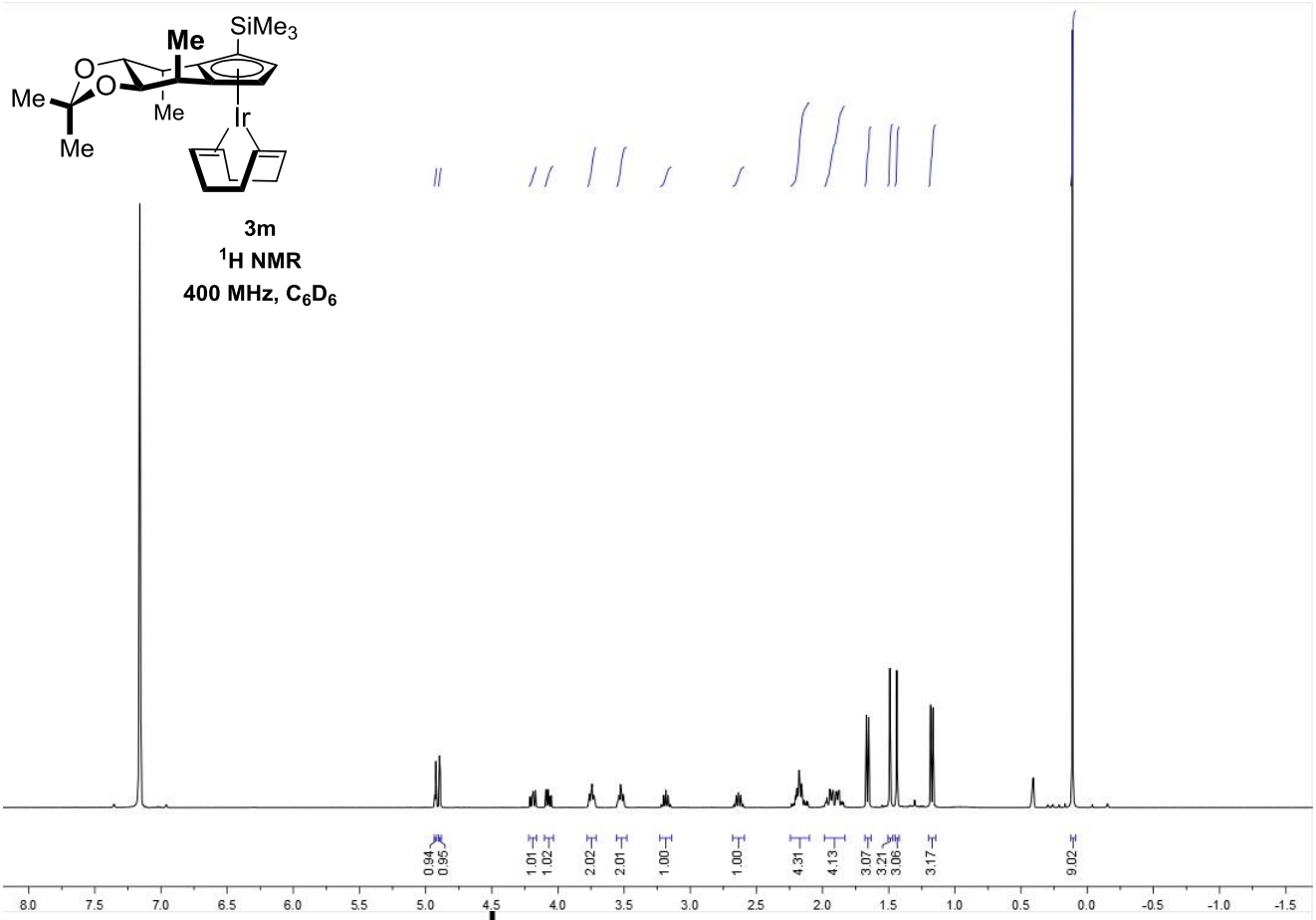
1o

^{13}C NMR

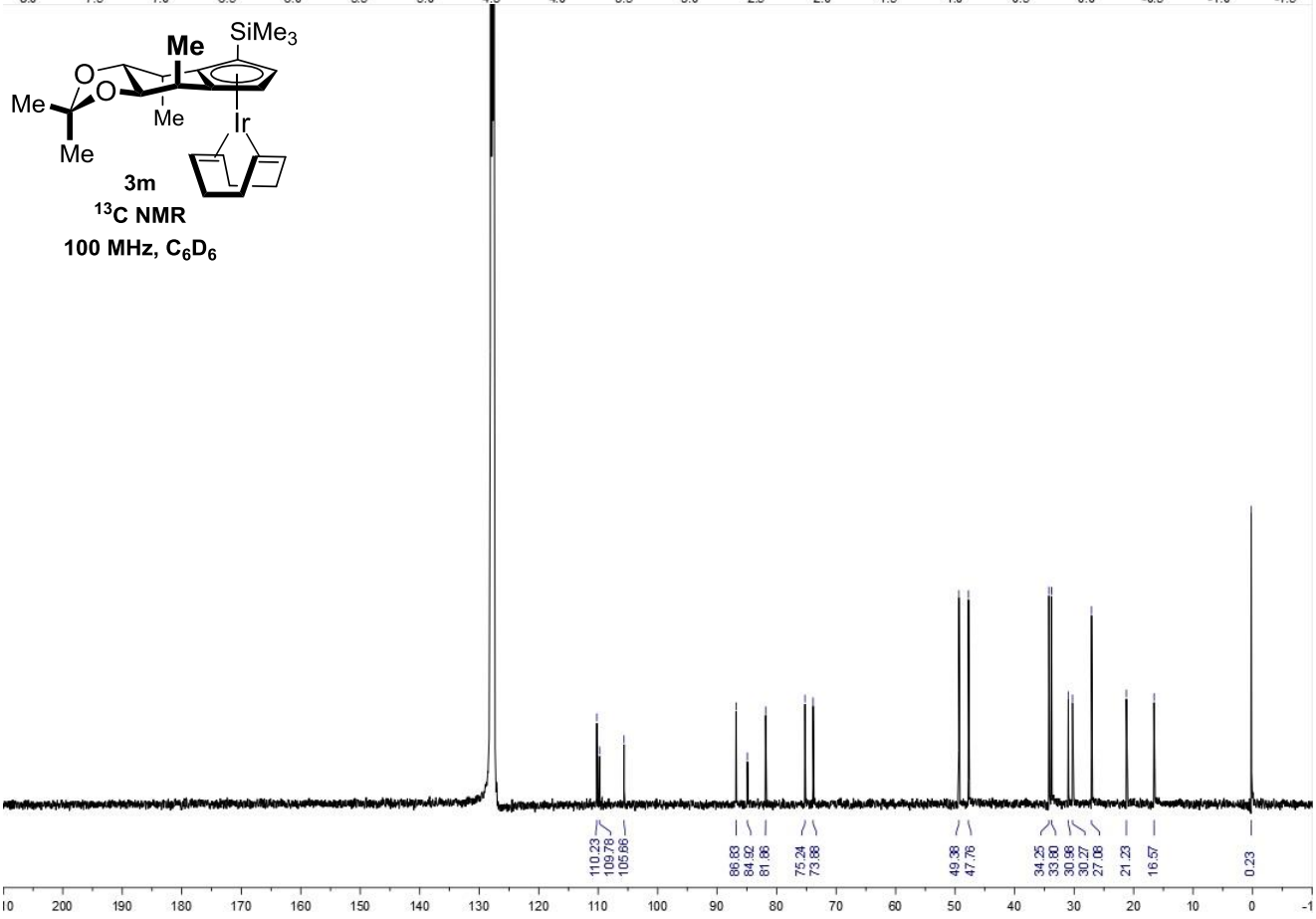
100 MHz, C_6D_6


Me
SiMe3
O
O
Me
Me
Me
Rh
2m
1H NMR
400 MHz, C6D6

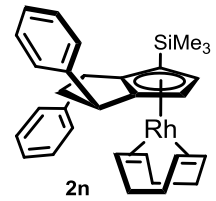

Me
SiMe3
O
O
Me
Me
Me
Rh
2m
13C NMR
100 MHz, C6D6



3m
^{1}H NMR
400 MHz, C_6D_6



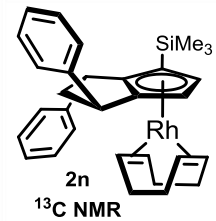
3m
^{13}C NMR
100 MHz, C_6D_6



2n

^{1}H NMR

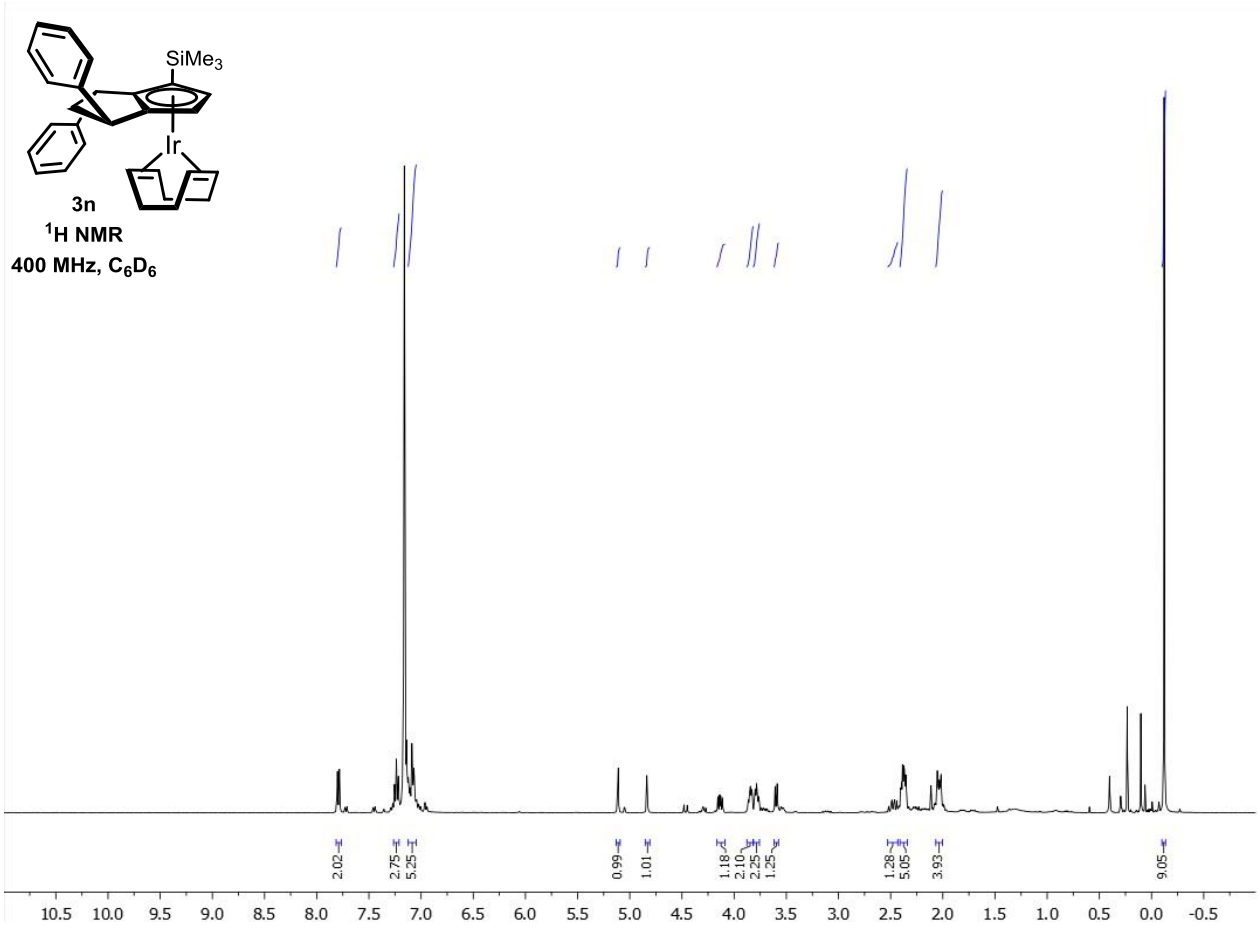
400 MHz, C_6D_6

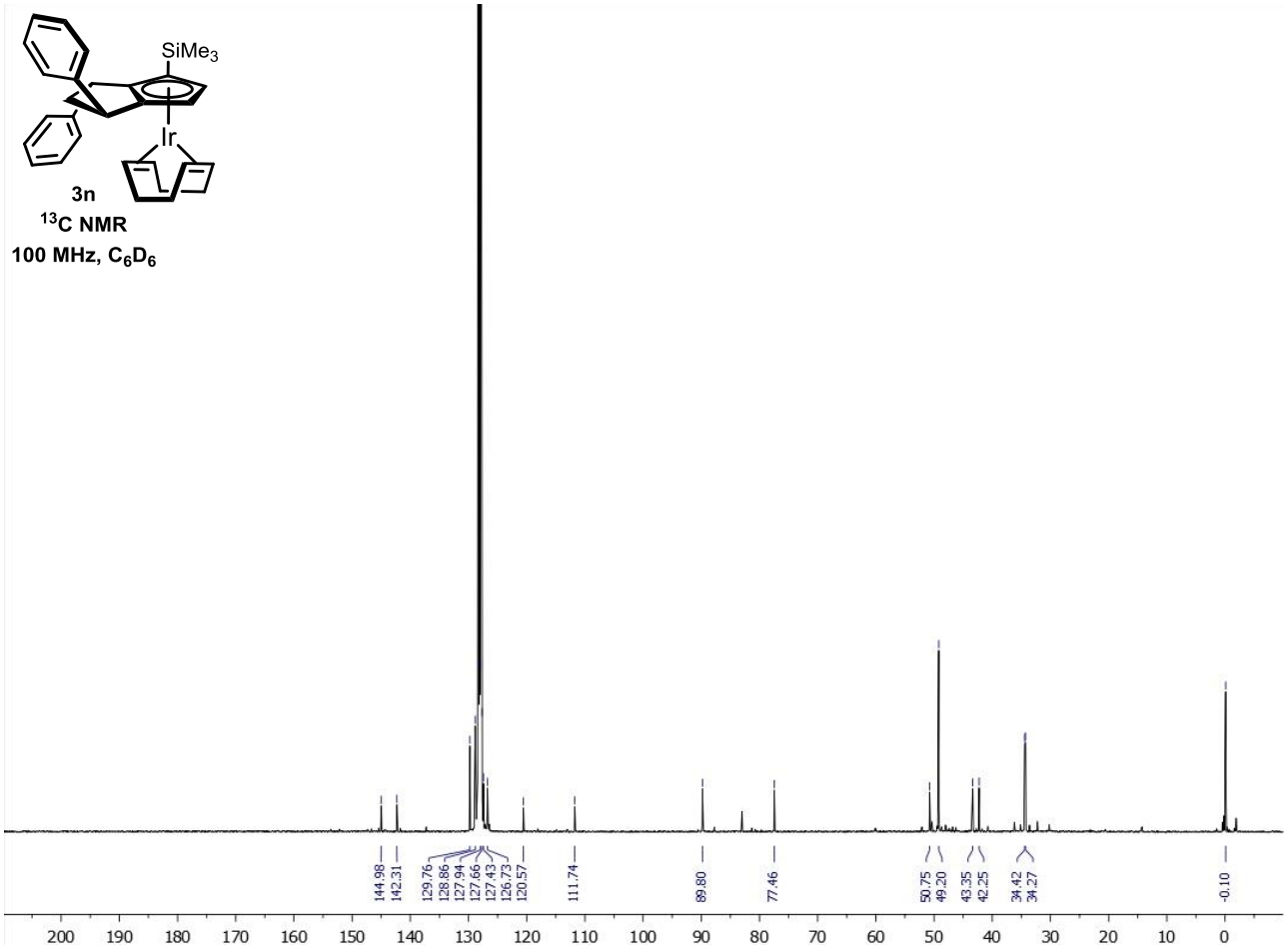


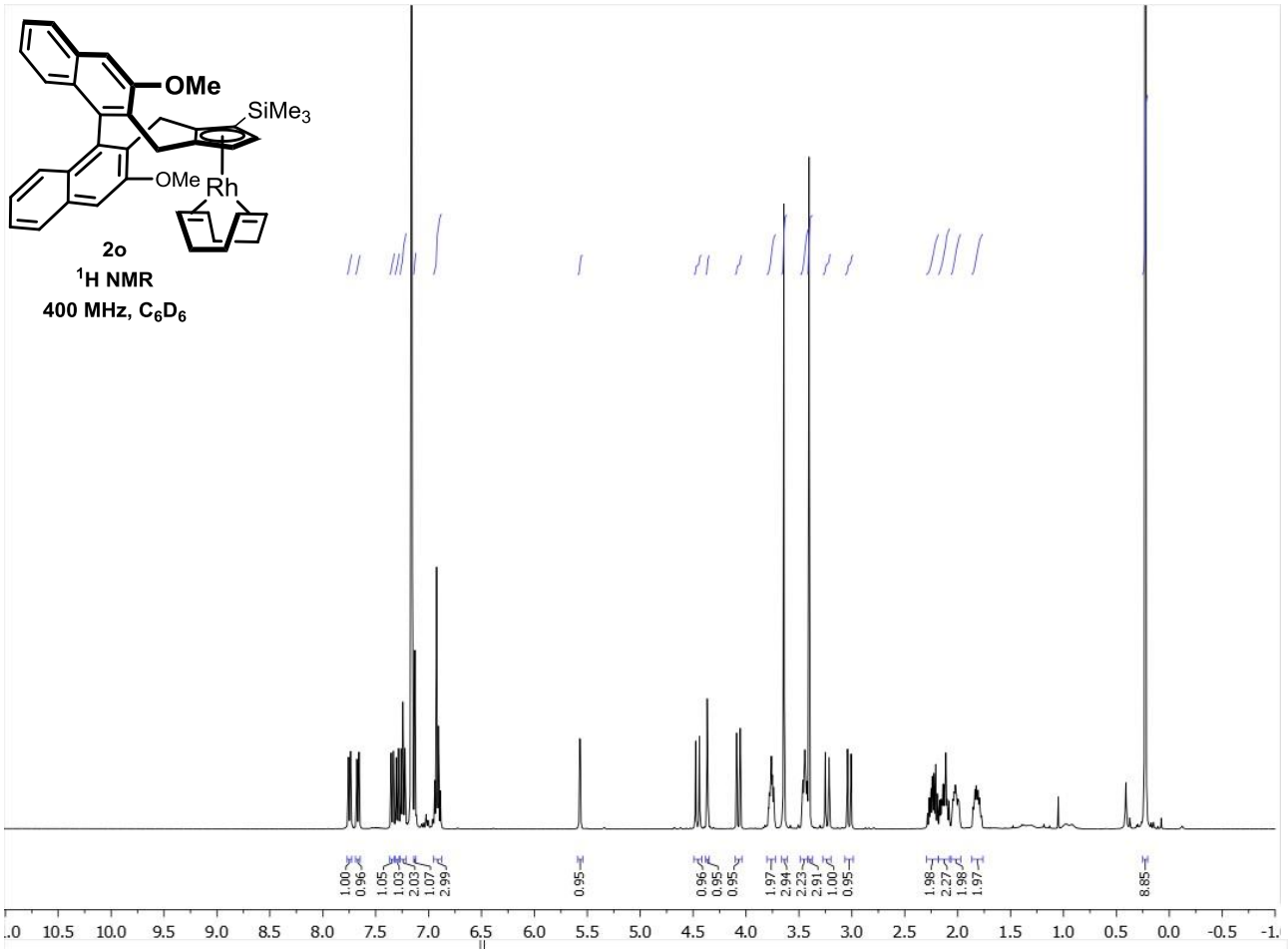
2n

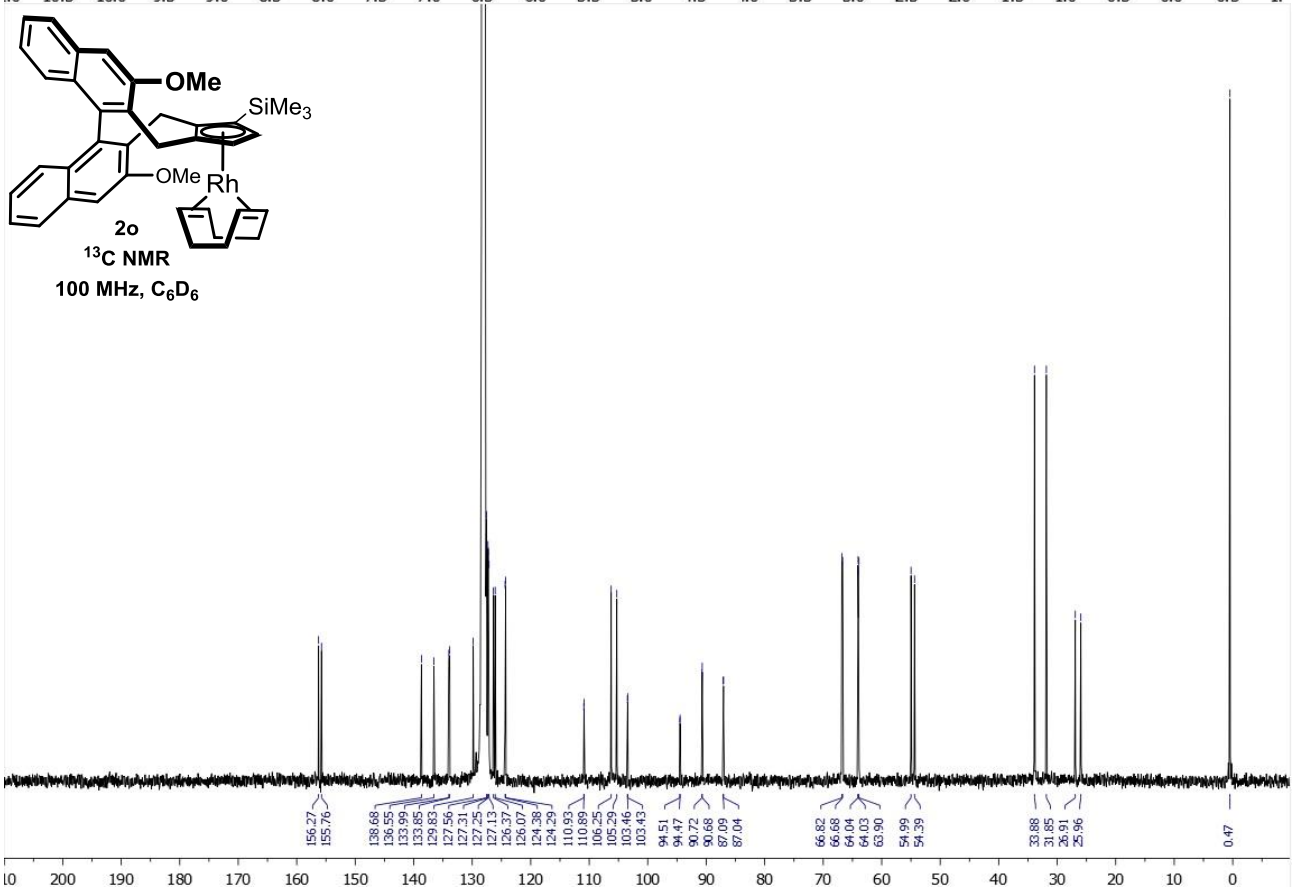
^{13}C NMR

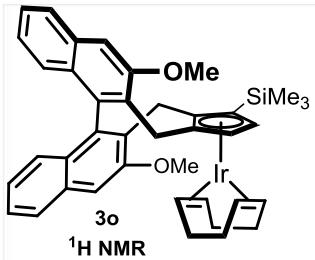
100 MHz, C_6D_6


SiMe3
Ir
3n
1H NMR
400 MHz, C6D6
2.02
2.75
5.25
0.99
1.01
1.18
2.10
2.25
1.25
1.28
5.05
3.93
9.05
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 0.0 -0.5


SiMe3
Ir
3n
13C NMR
100 MHz, C6D6
144.98
142.31
129.76
128.86
127.94
127.66
127.43
126.73
120.57
111.74
89.80
77.46
50.75
49.20
43.35
42.25
34.42
34.27
-0.10
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


OMe
SiMe3
OMe
Rh
2o
1H NMR
400 MHz, C6D6

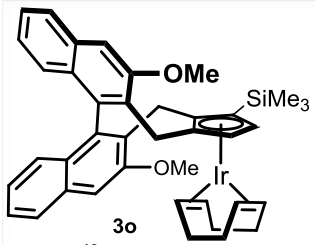

OMe
SiMe3
OMe
Rh
2o
13C NMR
100 MHz, C6D6



3o

^{1}H NMR

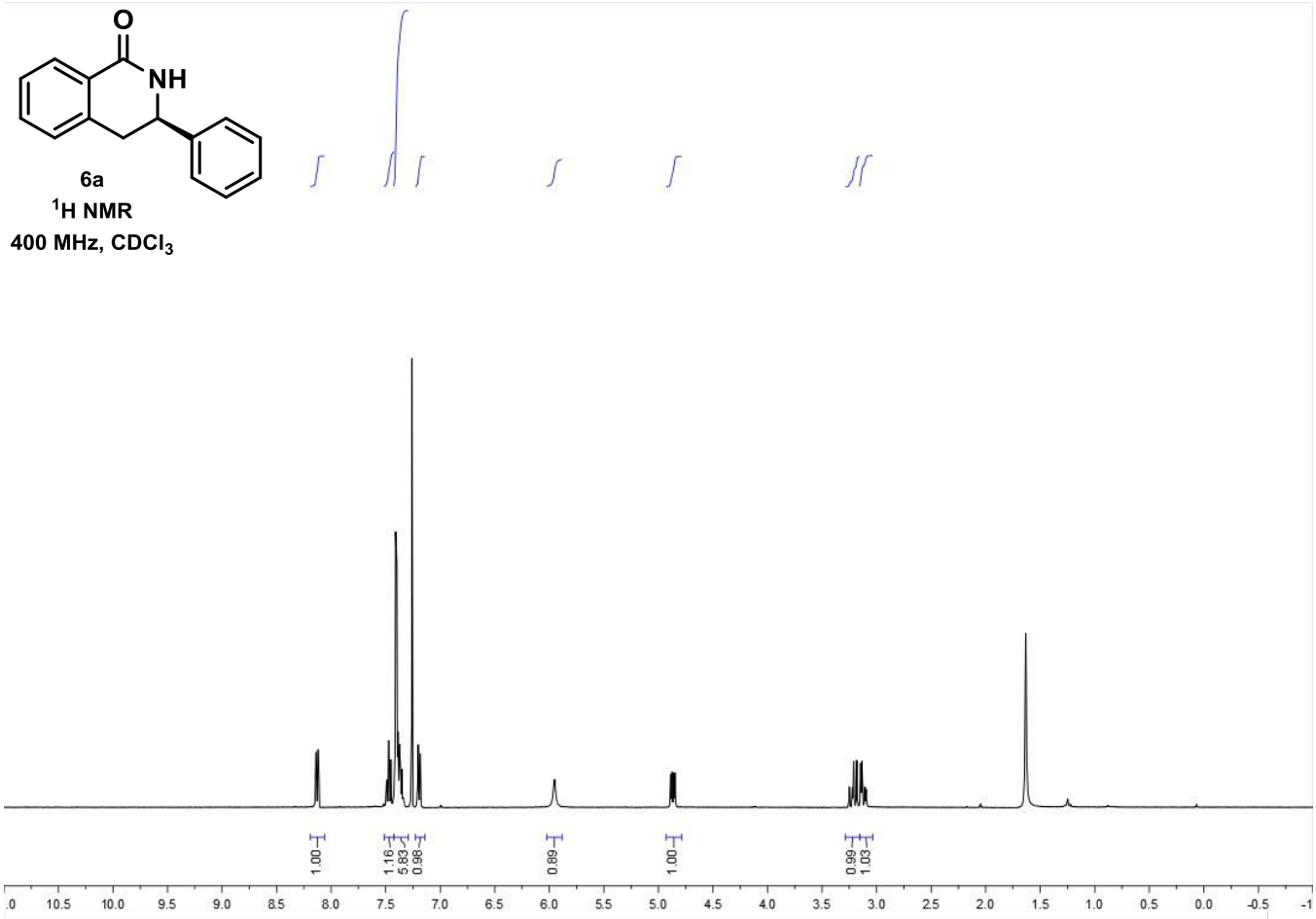
400 MHz, C_6D_6

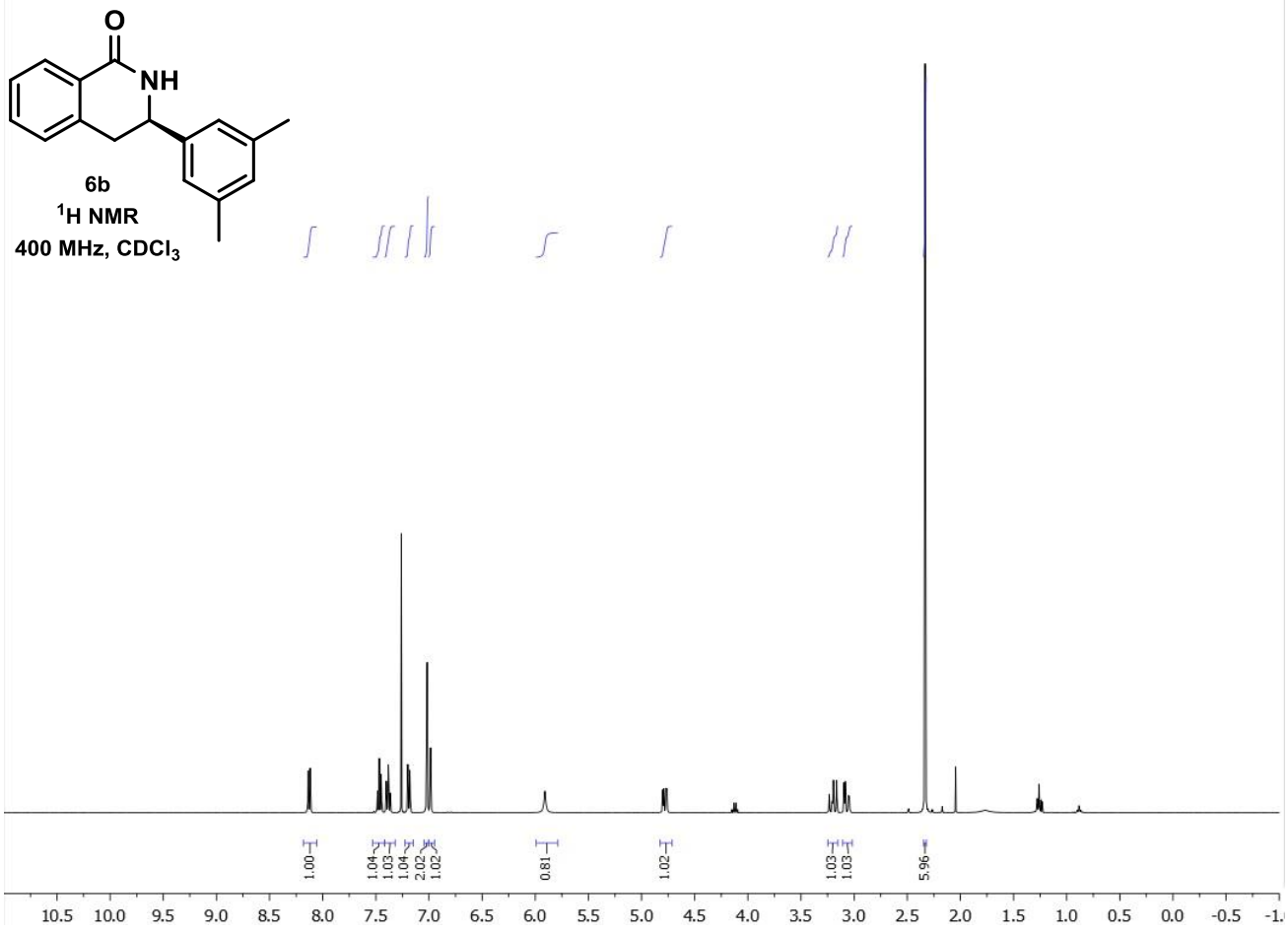


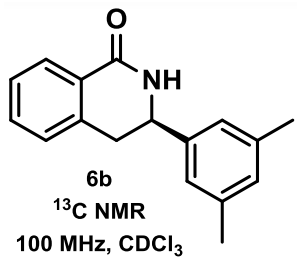
3o

^{13}C NMR

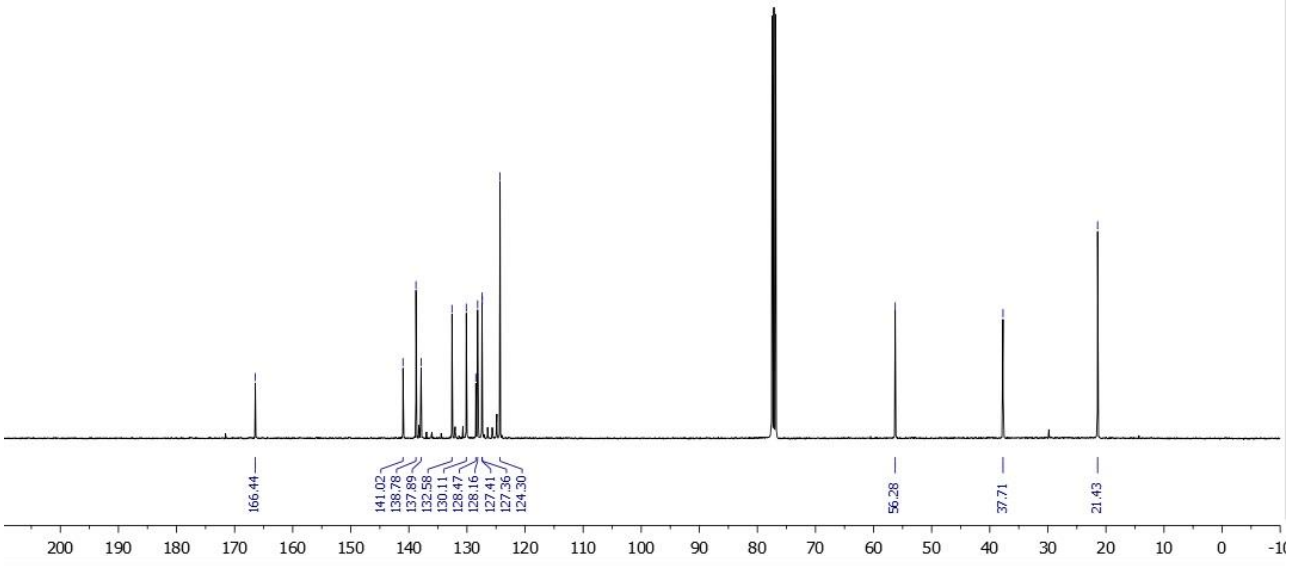
100 MHz, C_6D_6

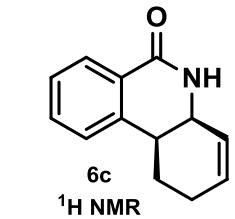

O
NH
6a
1H NMR
400 MHz, CDCl3
1.00
1.16
5.83
0.98
0.89
1.00
0.99
1.03


O
NH
6b
1H NMR
400 MHz, CDCl3
1.00
1.04
1.03
1.04
2.02
1.02
0.81
1.02
1.03
1.03
5.96

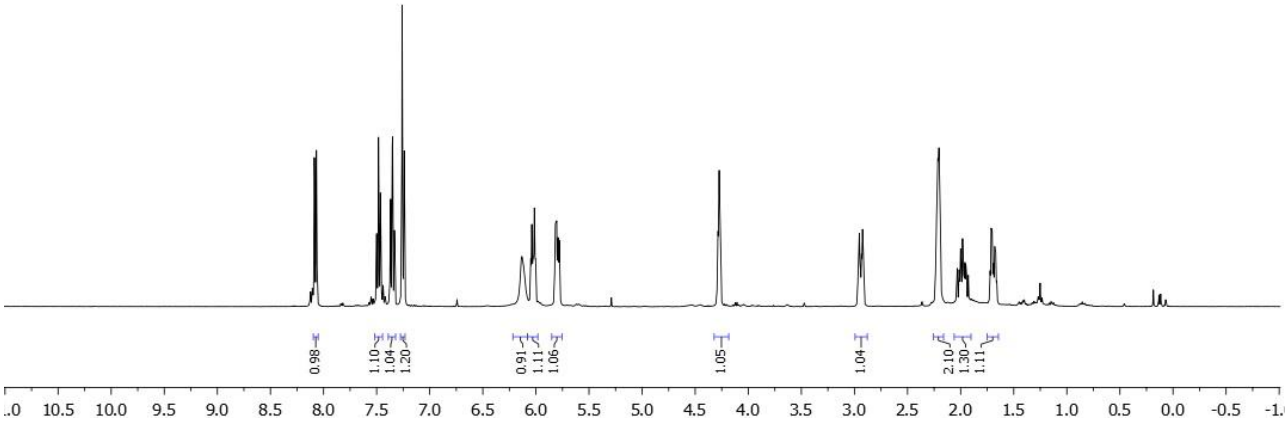


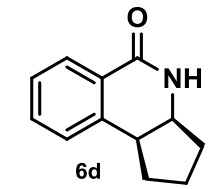
6b
^{13}C NMR
100 MHz, $CDCl_3$





6c
^{1}H NMR
400 MHz, $CDCl_3$

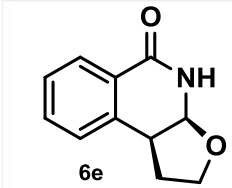




6d

^{1}H NMR

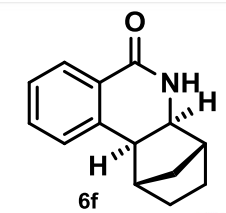
400 MHz, $CDCl_3$



6e

^{1}H NMR

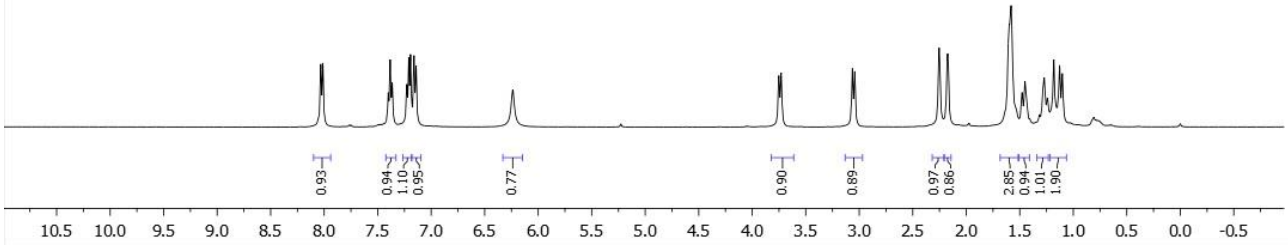
400 MHz, $CDCl_3$

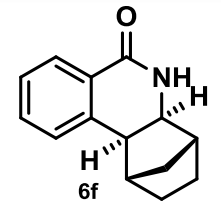


6f

^{1}H NMR

400 MHz, $CDCl_3$

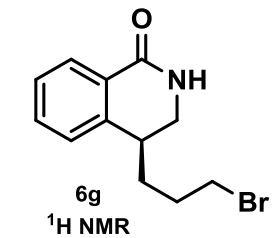




6f

^{13}C NMR

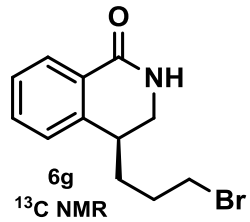
100 MHz, $CDCl_3$



6g

^{1}H NMR

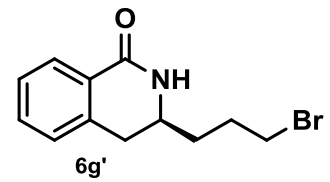
400 MHz, $CDCl_3$



6g

^{13}C NMR

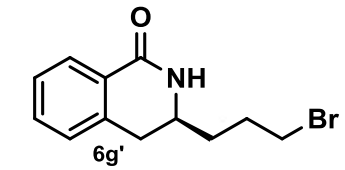
100 MHz, $CDCl_3$



6g'

^{1}H NMR

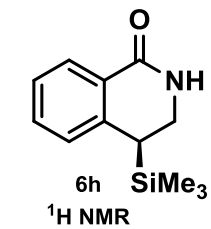
400 MHz, $CDCl_3$



6g'

^{13}C NMR

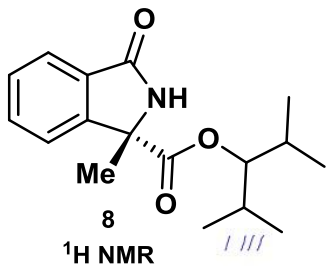
100 MHz, $CDCl_3$



6h

^{1}H NMR

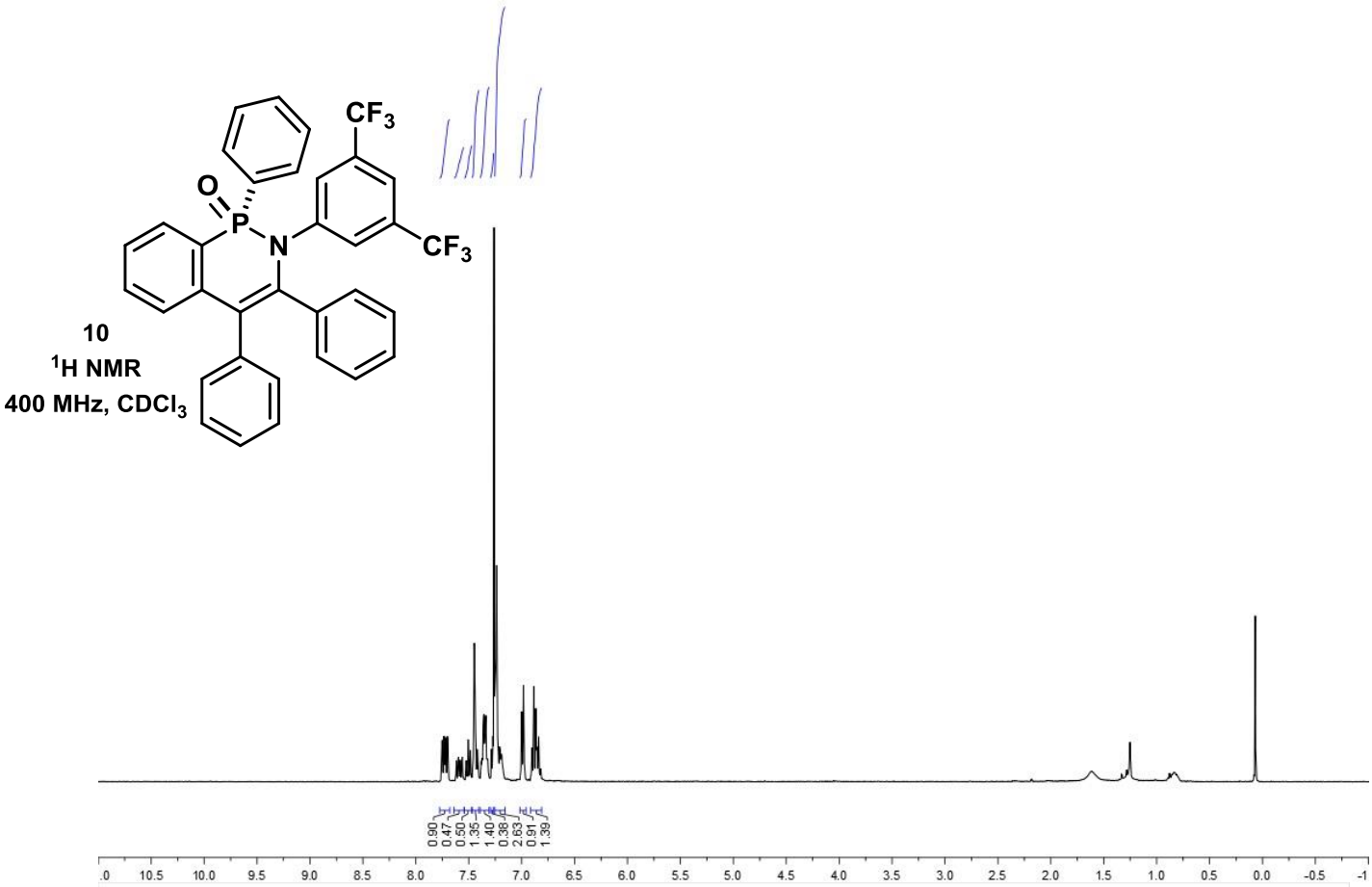
400 MHz, $CDCl_3$

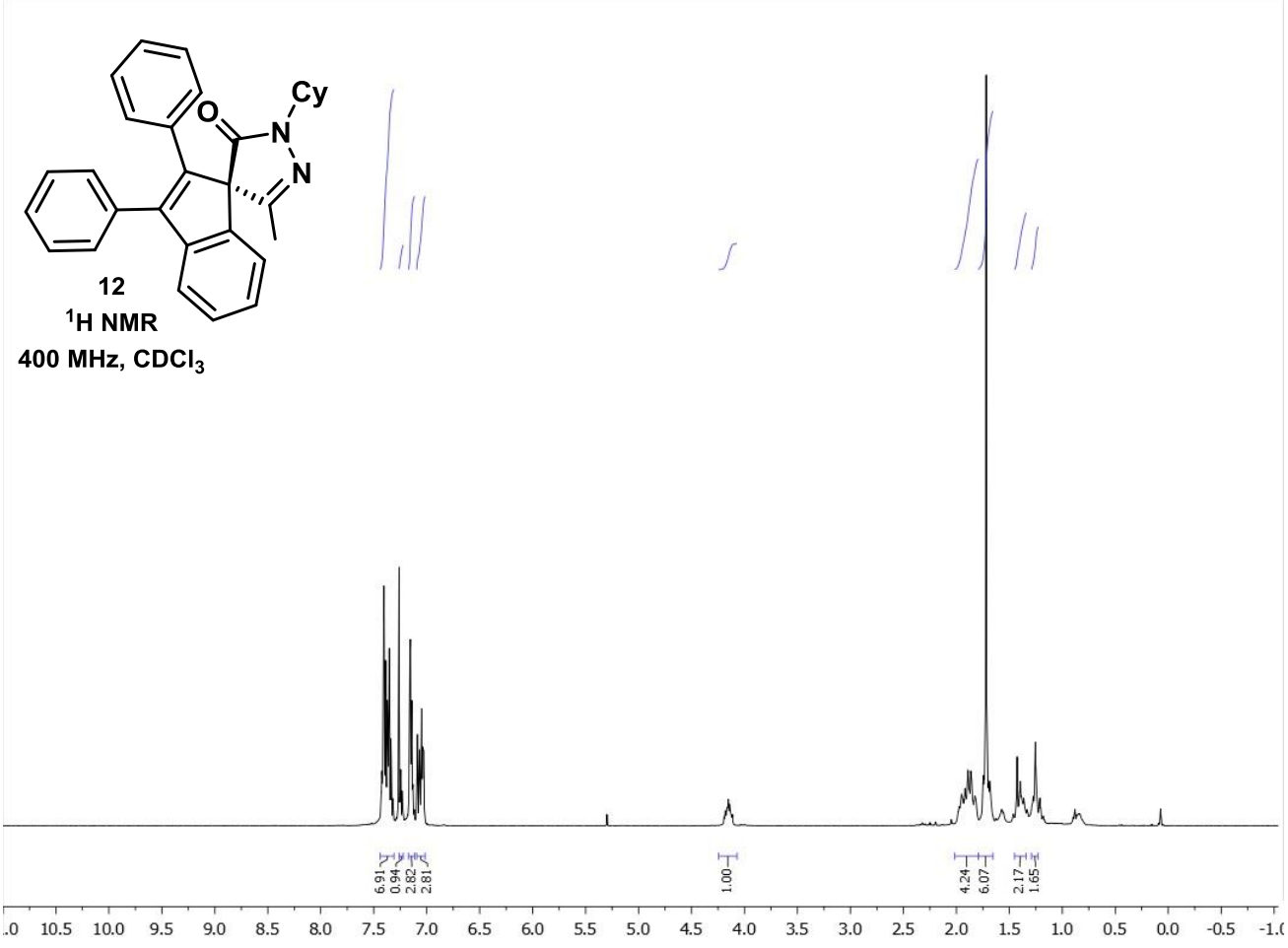


8

^{1}H NMR

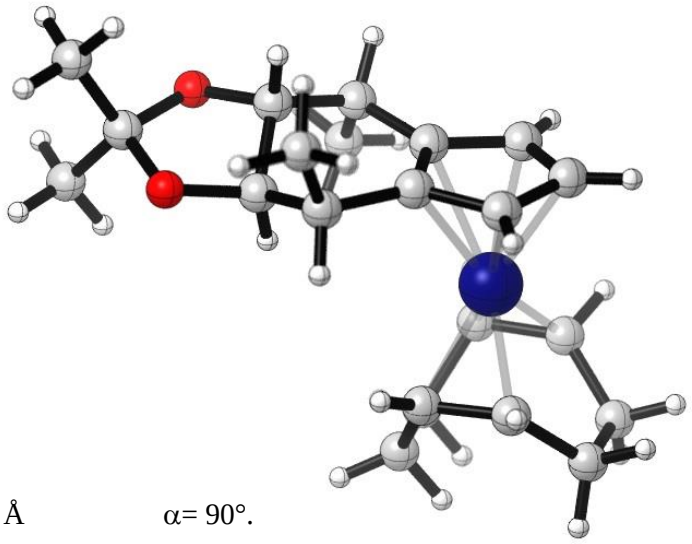
400 MHz, $CDCl_3$


CF3
CF3
O
P
N
10
1H NMR
400 MHz, CDCl3
0.90
0.47
0.50
1.35
1.40
0.38
2.63
0.91
1.39


Cy
O
N
N
12
1H NMR
400 MHz, CDCl3
6.91
0.94
2.82
2.81
1.00
4.24
6.07
2.17
1.65

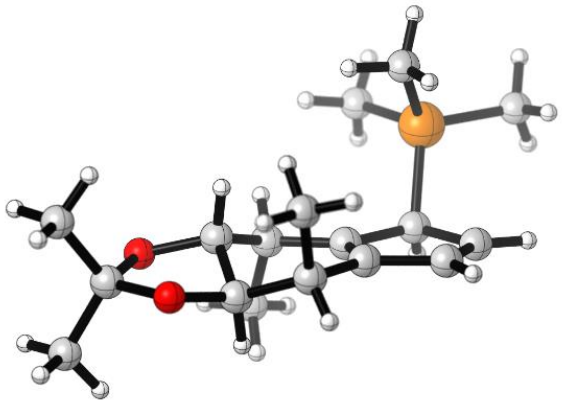
X-Ray Crystallographic Data

Crystal data and structure refinement for (3a)



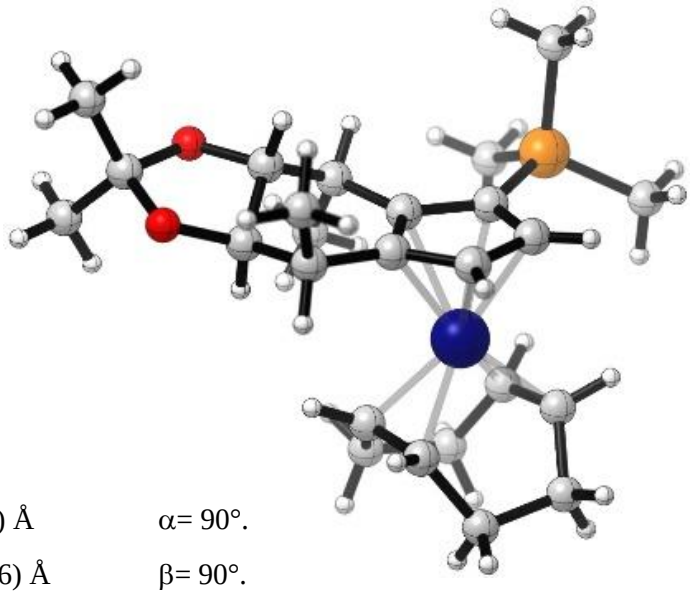
Empirical formula	$C_{22}H_{31}IrO_2$	
Formula weight	519.67	
Temperature	100.00(10) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*I*2	
Unit cell dimensions	a = 10.8334(2) Å	α= 90°.
	b = 8.23239(14) Å	β= 98.0838(17)°.
	c = 22.2298(4) Å	γ = 90°.
Volume	1962.86(6) Å^3	
Z	4	
Density (calculated)	1.759 Mg/m^3	
Absorption coefficient	6.814 mm^{-1}	
F(000)	1024	
Crystal size	0.597 x 0.179 x 0.139 mm^3	
Theta range for data collection	2.642 to 32.878°.	
Index ranges	$-16 \le h \le 15$, $-12 \le k \le 12$, $-33 \le l \le 33$	
Reflections collected	20184	
Independent reflections	6792 [R_{int} = 0.0416]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Analytical	
Max. and min. transmission	0.474 and 0.055	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6792 / 147 / 266	
Goodness-of-fit on F^2	1.042	
Final R indices [I > 2σ(I)]	R_1 = 0.0235, wR_2 = 0.0488	
R indices (all data)	R_1 = 0.0247, wR_2 = 0.0497	
Absolute structure parameter	-0.008(8)	
Largest diff. peak and hole	0.806 and -0.894 e.Å^{-3}	

Crystal data and structure refinement for (1m)



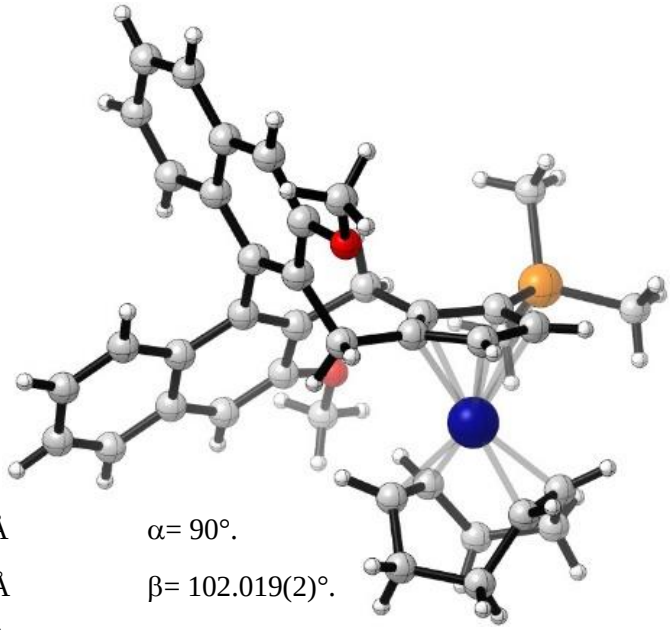
Empirical formula	$C_{17}H_{28}O_2Si$	
Formula weight	292.48	
Temperature	100.01(10) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.53335(13) Å	α= 90°.
	b = 10.27117(14) Å	β= 90°.
	c = 22.6089(3) Å	γ = 90°.
Volume	1749.39(4) Å^3	
Z	4	
Density (calculated)	1.111 Mg/m^3	
Absorption coefficient	1.172 mm^{-1}	
F(000)	640	
Crystal size	0.545 x 0.119 x 0.079 mm^3	
θ range for data collection	3.910 to 73.574°.	
Index ranges	$-9 \leq h \leq 8$, $-12 \leq k \leq 12$, $-28 \leq l \leq 28$	
Reflections collected	28192	
Independent reflections	3520 [R_{int} = 0.0236]	
Completeness to θ = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.512	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3520 / 0 / 293	
Goodness-of-fit on F^2	1.058	
Final R indices [I>2σ(I)]	R_1 = 0.0223, wR_2 = 0.0567	
R indices (all data)	R_1 = 0.0225, wR_2 = 0.0569	
Absolute structure parameter	-0.006(6)	
Largest diff. peak and hole	0.182 and -0.156 e.Å^{-3}	

Crystal data and structure refinement for (3m)



Empirical formula	$C_{25}H_{39}IrO_2Si$	
Formula weight	591.85	
Temperature	100.01(10) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.70304(11) Å	α= 90°.
	b = 11.49824(16) Å	β= 90°.
	c = 26.9058(4) Å	γ = 90°.
Volume	2383.08(6) $Å^3$	
Z	4	
Density (calculated)	1.650 Mg/m^3	
Absorption coefficient	5.671 mm^{-1}	
F(000)	1184	
Crystal size	0.829 x 0.186 x 0.151 mm^3	
θ range for data collection	2.750 to 32.981°.	
Index ranges	$-11 \le h \le 11$, $-17 \le k \le 16$, $-40 \le l \le 41$	
Reflections collected	51991	
Independent reflections	8448 [R_{int} = 0.0458]	
Completeness to θ = 25.242°	99.9 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.963 and 0.145	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8448 / 0 / 270	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2σ(I)]	R_1 = 0.0205, wR_2 = 0.0366	
R indices (all data)	R_1 = 0.0223, wR_2 = 0.0374	
Absolute structure parameter	-0.014(3)	
Extinction coefficient	0.00045(6)	
Largest diff. peak and hole	0.643 and -0.944 $e.Å^{-3}$	

Crystal data and structure refinement for (3o)



Empirical formula	$C_{40}H_{43}IrO_2Si$	
Formula weight	776.03	
Temperature	100.00(10) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 10.1531(2) Å	α= 90°.
	b = 14.0965(3) Å	β= 102.019(2)°.
	c = 23.1228(6) Å	γ = 90°.
Volume	3236.86(14) $Å^3$	
Z	4	
Density (calculated)	1.592 Mg/m^3	
Absorption coefficient	4.197 mm^{-1}	
F(000)	1560	
Crystal size	0.883 x 0.593 x 0.118 mm^3	
θ range for data collection	2.517 to 29.700°.	
Index ranges	$-13 \leq h \leq 14$, $-19 \leq k \leq 19$, $-31 \leq l \leq 31$	
Reflections collected	54468	
Independent reflections	16010 [R_{int} = 0.0663]	
Completeness to θ = 25.242°	99.8 %	
Absorption correction	Gaussian	
Max. and min. transmission	1.000 and 0.028	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	16010 / 493 / 803	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2σ(I)]	R_1 = 0.0409, wR_2 = 0.0881	
R indices (all data)	R_1 = 0.0448, wR_2 = 0.0912	
Absolute structure parameter	-0.007(5)	
Largest diff. peak and hole	1.649 and -1.516 e.$Å^{-3}$	

Computational Details

The geometries of all species were optimized at the M06[13,14]/def2-SVP[15] level in implicit methanol solvent using the SMD solvation model.[16] Each geometry optimizations were performed in Gaussian09[17] and used the "ultrafine" integration grid to remove known problems with grid size involving the Minnesota family of density functionals.[18] Refined energy estimates were obtained through single point computations on the M06 optimized geometries with a density-dependent dispersion correction (-dDsC)[19-22] appended to the PBE0 functional[23,24] (PBE0-dDsC) using the TZ2P basis set as implemented in ADF.[25,26] Final reported free energies include PBE0-dDsC electronic energies, M06 free energy corrections obtained using the rigid-rotor harmonic oscillator proposed by Grimme[27] and implemented in the "Goodvibes" program of Paton and Funes-Ardoiz,[28] and PBE0-dDsC solvation corrections (in methanol) obtained from COSMO-RS.[29] All structures were confirmed as either minima or transition states by inspection of the number of imaginary frequencies (zero for minima, one for transition states).

Table S1. Computed electronic energies, free energy corrections and solvation energies for relevant species. Values in hartree. Free energies reported in the manuscript include PBE0-dDsC/TZ2P electronic energies, the free energy correction (determined using the rigid-rotor harmonic oscillator, see computational details), and COSMO-RS solvation energies.

	M06/def2-SVP Electronic Energy	**Free Energy Correction**	**PBE0-dDsC/TZ2P Electronic Energy**	**COSMO-RS Solvation Energy**
Methanol	-115.568506	0.028256	-1.376639	-0.008332
Acetic Acid	-228.802073	0.033941	-2.150562	-0.013522
Cp* Precursor	-390.091292	0.191122	-6.583055	-0.007237
$[Rh(COD)OAc]_2$, 2 MeOH	-1532.018061	0.511077	-17.714368	-0.030084
Int1	-765.994163	0.242240	-8.846723	-0.017645
A(TS1)	-765.979455	0.241253	-8.825916	-0.017906
A(INT2)	-650.393767	0.192029	-7.418881	-0.024182
A(INT3)	-1040.502995	0.411003	-14.030623	-0.028757
A(TS2)	-1040.467463	0.405538	-14.008738	-0.017471
A(Prod)	-1040.524346	0.411304	-14.072150	-0.017374
B(TS1)	-765.965277	0.238749	-8.782566	-0.045060
B(TS2)	-765.966644	0.236701	-8.800694	-0.026686
B(Int2)	-537.143077	0.184760	-6.633340	-0.017312
B(Int3)	-927.245457	0.400769	-13.235869	-0.017973
B(TS3)	-927.227327	0.397346	-13.229686	-0.015461
B(Prod)	-927.289644	0.403560	-13.297280	-0.014755

Optimized Cartesian Coordinates (M06/def2-SVP)

6
Methanol

O	-0.75537	-1.09598	-0.62007
H	-0.88709	-0.21169	-0.25325
C	-0.65596	-1.99957	0.44927
H	-0.50555	-3.00901	0.03477
H	-1.56932	-2.03208	1.07390
H	0.20073	-1.78622	1.11714

8
Acetic Acid

H	-1.44817	0.99851	-1.32276
O	-1.16261	0.20327	-0.83645
C	-0.01387	0.47574	-0.21506
O	0.52493	1.55738	-0.29167
C	0.49224	-0.69085	0.55848
H	-0.24698	-0.97698	1.32276
H	1.44817	-0.44662	1.03709
H	0.61457	-1.55738	-0.10929

26
Cp* Precursor Olefin

C	2.18453	1.20009	1.51384
C	3.56924	1.69278	1.91419
H	3.56690	2.78849	2.05563
H	4.32192	1.45220	1.14520
H	3.90595	1.23036	2.85682
C	1.66920	1.80979	0.23778
C	2.44614	1.75715	-1.02825
H	1.86707	2.11785	-1.89292
H	3.36365	2.37362	-0.97402
H	2.78461	0.73019	-1.25715
C	0.46511	2.38430	0.48259
C	-0.42721	3.10333	-0.46825
H	-1.42738	2.63710	-0.52162
H	-0.59574	4.15034	-0.15777
H	-0.01755	3.12649	-1.48984
C	0.11867	2.19951	1.90824
C	-1.14758	2.71881	2.49497
H	-2.03464	2.30921	1.97929
H	-1.24393	2.47455	3.56411
H	-1.22090	3.81732	2.40066
C	1.11365	1.51351	2.52407
C	1.23634	1.11194	3.94989
H	0.30916	1.28722	4.51794
H	2.04175	1.66818	4.46634
H	1.49398	0.04199	4.05197
H	2.23808	0.09566	1.38368

68
[Rh(COD)OAc]2, 2MeOH

C	0.48499	0.85984	-2.05045
H	1.46624	1.32168	-1.85860
C	-0.63133	1.46369	-1.43691
H	-0.43058	2.33394	-0.79502
C	-2.04795	1.34411	-1.96092
H	-2.03105	1.21520	-3.05695
H	-2.58509	2.28983	-1.78204
C	-2.79480	0.19438	-1.28540
H	-3.25823	0.55856	-0.35111
H	-3.63450	-0.16399	-1.91400
C	-1.88657	-0.94932	-0.91653
H	-2.25260	-1.56711	-0.08311
C	-0.89220	-1.51969	-1.73809
H	-0.57247	-2.54087	-1.47785
C	-0.65166	-1.09713	-3.17535
H	-1.60213	-0.75764	-3.62268
H	-0.34774	-1.97511	-3.77010
C	0.42059	-0.01044	-3.27999
H	1.40908	-0.48334	-3.40796
H	0.27134	0.61079	-4.18548
C	2.30591	1.35357	1.04582
C	2.81814	2.43323	1.95024
H	2.01753	3.09495	2.30546
H	3.59347	3.02005	1.43592
H	3.30037	1.95318	2.81817
C	0.76100	-1.80033	2.14791
C	0.37082	-2.11763	3.55969
H	-0.18020	-1.25661	3.97197
H	1.24248	-2.33240	4.19226
H	-0.32010	-2.97441	3.57260
C	3.68877	-1.21927	-2.02916
H	3.34784	-0.24137	-2.40321
C	3.36427	-2.41494	-2.90507
H	4.29292	-2.96693	-3.13167
H	2.98954	-2.06432	-3.88154
C	2.32621	-3.33431	-2.25691
H	1.31458	-3.01400	-2.56034
H	2.42950	-4.37425	-2.62568
C	2.38270	-3.30111	-0.75056
H	1.43660	-3.54854	-0.24383
C	3.56160	-3.42842	0.01181
H	3.44359	-3.73430	1.06185
C	4.93236	-3.66162	-0.59014
H	4.83349	-4.21511	-1.53984
H	5.51612	-4.31802	0.07518
C	5.68023	-2.34516	-0.79907
H	6.23158	-2.08627	0.12173
H	6.45078	-2.44261	-1.58987
C	4.75536	-1.19705	-1.10761
H	5.15396	-0.20832	-0.83695
O	-0.16914	-1.62682	1.31610
O	1.98679	-1.71479	1.87027
O	1.06310	1.15325	0.99307
O	3.16437	0.69399	0.40052
Rh	2.95413	-1.40231	-0.05060
Rh	-0.01579	-0.22023	-0.31536
O	4.53613	-1.14385	2.81144
H	3.61450	-1.39320	2.59898
C	4.76322	-1.39124	4.17363
H	4.09942	-0.79670	4.83027
H	4.63597	-2.45759	4.44240
H	5.80113	-1.11363	4.41784
O	-1.39704	1.04925	2.37114
H	-0.49585	0.99875	2.00113
C	-1.76508	2.40333	2.37860
H	-1.04642	3.03519	2.93460
H	-1.87051	2.82683	1.35974
H	-2.74357	2.50250	2.87560

34
Int1
Rh 0.63675 -0.66748 -2.20529
C -0.59947 1.97583 -1.29425
C -0.89560 3.43199 -1.52899
C 1.91101 -2.25403 -1.67904
C 0.99990 -2.70685 -2.65304
C 1.23091 -0.41594 -4.19296
C 2.31089 -0.08666 -3.34728
C 3.35032 -1.87943 -1.92367
C 1.36604 -2.93723 -4.10579
C 1.07467 -1.70305 -4.96124
C 3.52135 -0.97664 -3.14496
H -1.11402 3.95284 -0.58678
H -0.05718 3.92071 -2.04710
H -1.77500 3.51481 -2.18868
H 1.68406 -2.50446 -0.63185
H 0.11790 -3.25550 -2.28834
H 0.63721 0.42397 -4.58388
H 2.46075 0.98254 -3.13628
H 3.98159 -2.78687 -2.00326
H 3.70827 -1.34785 -1.02473
H 2.42853 -3.22635 -4.17925
H 0.79971 -3.79881 -4.49471
H 1.70345 -1.69201 -5.87384
H 0.03165 -1.74629 -5.32050
H 4.42047 -0.35162 -3.02104
H 3.70088 -1.57343 -4.05566
O -0.09650 1.35123 -2.28479
O -0.87403 1.46747 -0.18812
O -0.77328 -1.10022 -0.60463
H -0.88069 -0.16109 -0.27083
C -0.64821 -2.02049 0.45434
H -1.56905 -2.03769 1.06243
H -0.50329 -3.03091 0.04194
H 0.20195 -1.78415 1.11851

34
A(TS1)
Rh -0.01669 -0.22458 0.02503
C -2.51116 -1.11009 -0.04136
C -3.84831 -1.76974 0.01663
C 1.22133 0.73093 -1.38109
C 1.33654 1.41067 -0.15616
C 1.43050 -0.88573 1.34894
C 1.57852 -1.56325 0.10950
C 2.22200 -0.25066 -1.93599
C 2.53202 1.30270 0.76708
C 2.29995 0.24080 1.84276
C 2.68060 -1.26777 -0.88939
H -4.17582 -2.02330 -1.00358
H -3.83128 -2.67681 0.63507
H -4.58411 -1.05774 0.42208
H 0.52740 1.15643 -2.12380
H 0.71251 2.30756 -0.02939
H 0.89317 -1.42988 2.14229
H 1.13686 -2.56941 0.04550
H 3.08517 0.28173 -2.38215
H 1.73535 -0.78170 -2.77220
H 3.44111 1.08355 0.18177
H 2.71551 2.27978 1.24231
H 3.25858 -0.14777 2.24004
H 1.78423 0.70016 2.70409
H 2.98348 -2.20200 -1.38857
H 3.57961 -0.91166 -0.35787
O -1.53876 -1.61011 0.60975
O -2.35412 -0.06270 -0.72817
O -1.87924 2.27284 0.74682
H -2.13093 1.38549 0.43078
C -1.97602 3.12348 -0.36615
H -3.00558 3.17426 -0.77030
H -1.68849 4.14258 -0.06168
H -1.30460 2.82660 -1.19656

28
A(Int2)

Rh	2.09853	-0.42156	0.27913
C	0.14217	-2.41232	-0.38099
C	-0.60882	-3.71220	-0.27167
C	2.99140	1.24357	-0.65217
C	3.29599	1.28742	0.71770
C	3.79671	-1.40607	0.89746
C	3.72680	-1.40792	-0.52684
C	3.91650	0.78207	-1.74958
C	4.65373	0.93085	1.28729
C	4.70087	-0.53256	1.72764
C	4.60451	-0.54110	-1.41065
H	-1.39812	-3.78484	-1.03206
H	0.09453	-4.55121	-0.39655
H	-1.04946	-3.81527	0.73221
H	2.13997	1.85662	-0.98844
H	2.65702	1.92449	1.34777
H	3.47300	-2.33153	1.39837
H	3.34536	-2.33014	-0.99228
H	4.65700	1.56784	-1.99785
H	3.30517	0.65039	-2.65918
H	5.43717	1.14437	0.54008
H	4.87699	1.58669	2.14419
H	5.73787	-0.92336	1.71822
H	4.36334	-0.61187	2.77566
H	4.84147	-1.08366	-2.33978
H	5.57474	-0.36789	-0.91351
O	1.04459	-2.23064	0.51300
O	-0.10786	-1.60456	-1.28726

54
A(Int3)

O	1.48273	-1.12957	0.35735
Rh	-0.40914	-0.56767	-0.43640
C	2.42373	-1.22057	-0.50240
C	-1.79223	-0.39893	-2.01866
C	-2.50043	-0.20670	-0.82208
C	-1.19026	-2.26083	0.48287
C	-0.70064	-2.61986	-0.80017
C	-1.76571	-1.65739	-2.84689
C	-3.40035	-1.23929	-0.17419
C	-2.63901	-2.08323	0.84890
C	-1.58780	-2.91032	-1.99290
H	-1.49417	0.51152	-2.56182
H	-2.70921	0.83414	-0.54971
H	-0.52706	-2.47543	1.33569
H	0.29796	-3.07978	-0.82695
H	-2.67279	-1.72185	-3.48043
H	-0.91649	-1.57338	-3.54832
H	-3.86166	-1.87595	-0.94854
H	-4.23999	-0.72690	0.32373
H	-3.12461	-3.06803	1.00009
H	-2.67046	-1.58386	1.83354
H	-1.13857	-3.71258	-2.59999
H	-2.56127	-3.30424	-1.65444
C	-0.33346	1.82657	1.06453
C	0.79102	1.50437	1.96011
C	1.66468	2.15044	-0.10468
C	1.95712	1.69677	1.29605
C	0.15618	2.15343	-0.17584
C	2.26488	3.51689	-0.42504
H	2.09232	1.41473	-0.81832
C	3.34699	1.46019	1.76274
C	0.58273	0.96200	3.32963
C	-1.72061	1.98131	1.58568
C	-0.56514	2.78902	-1.31464
O	2.32033	-0.89178	-1.69679
C	3.71828	-1.80929	-0.00190
H	3.85412	-1.66120	1.07930
H	3.69963	-2.89616	-0.19044
H	4.57337	-1.39385	-0.55486
H	2.05405	3.82288	-1.46267
H	1.85846	4.29090	0.25006
H	3.36073	3.50321	-0.30492
H	-0.43688	3.88837	-1.30411
H	-0.17654	2.44443	-2.28927
H	-1.64937	2.59689	-1.29248
H	-1.72764	2.73678	2.39257
H	-2.42829	2.32555	0.81759
H	-2.11516	1.05164	2.03186
H	1.53264	0.78224	3.85600
H	-0.02379	1.63580	3.96018
H	0.03528	0.00017	3.29100
H	3.93730	0.92467	0.99704
H	3.88743	2.40677	1.95267
H	3.38649	0.87209	2.69360

54
A(TS2)
O 0.72824 1.42254 -1.08762
Rh -0.68096 0.02582 -0.06561
C 1.30508 2.27011 -0.36926
C -2.04186 -0.39637 1.47572
C -2.30683 -1.26345 0.39410
C -2.08327 0.74303 -1.50540
C -2.08782 1.63204 -0.41761
C -2.83268 0.83480 1.83560
C -3.49017 -1.11433 -0.54366
C -3.12710 -0.30409 -1.78652
C -3.18357 1.69386 0.62284
H -1.48095 -0.81440 2.32161
H -1.91831 -2.28589 0.48114
H -1.46822 1.02507 -2.37296
H -1.47346 2.53837 -0.51772
H -3.73919 0.55335 2.40884
H -2.21454 1.42768 2.53354
H -4.33772 -0.65520 -0.00603
H -3.84270 -2.11417 -0.84505
H -4.02765 0.15470 -2.24175
H -2.71855 -0.98068 -2.55778
H -3.32923 2.73913 0.94055
H -4.14553 1.38309 0.18090
C 1.17240 -1.83999 -0.46928
C 2.34967 -1.19982 -0.92349
C 1.98385 -0.48161 1.24416
C 2.88208 -0.43811 0.12508
C 0.91074 -1.43184 0.87453
C 2.39268 -0.28308 2.68200
H 1.58797 0.82244 1.01479
C 4.07595 0.44309 -0.00271
C 2.87186 -1.21497 -2.32050
C 0.42700 -2.86959 -1.25541
C 0.40377 -2.38921 1.91771
O 1.52203 2.08928 0.87515
C 1.74848 3.56477 -0.97098
H 1.91344 3.46222 -2.05240
H 0.94705 4.30751 -0.81904
H 2.65311 3.94244 -0.47402
H 1.53505 0.02692 3.30529
H 2.81035 -1.19986 3.13913
H 3.15570 0.50724 2.78190
H 1.20789 -3.10025 2.19224
H 0.10860 -1.89232 2.85580
H -0.44856 -3.00074 1.58262
H 1.08894 -3.70862 -1.53906
H -0.41706 -3.29878 -0.69446
H 0.02292 -2.46491 -2.20168
H 3.97306 -1.15772 -2.35151
H 2.57666 -2.12501 -2.86846
H 2.49833 -0.35358 -2.90946
H 4.27936 1.01437 0.91641
H 4.98361 -0.14476 -0.22914
H 3.97208 1.16778 -0.83377

54
A(Prod)

O	2.45839	-2.61101	1.13065
Rh	-0.40943	0.48454	0.04835
C	2.51228	-2.75328	-0.07357
C	-1.40231	-0.97700	-1.17068
C	-2.34084	-0.02114	-0.70662
C	-1.35206	-0.02536	1.87558
C	-0.55946	-1.12981	1.46773
C	-1.32822	-2.38321	-0.61757
C	-3.35590	-0.34413	0.37541
C	-2.85370	0.07454	1.75401
C	-1.14592	-2.41637	0.90447
H	-1.05296	-0.87169	-2.21085
H	-2.63288	0.77399	-1.40881
H	-0.93019	0.60562	2.67278
H	0.40299	-1.24462	1.98792
H	-2.22641	-2.96098	-0.91892
H	-0.48076	-2.89619	-1.10066
H	-3.58845	-1.42381	0.35541
H	-4.31006	0.16310	0.15474
H	-3.35752	-0.50036	2.55870
H	-3.12714	1.13085	1.93253
H	-0.48695	-3.25847	1.17850
H	-2.10719	-2.62930	1.40846
C	-0.10548	2.71732	0.07377
C	0.91562	2.08848	0.86093
C	1.25231	1.41943	-1.32433
C	1.78937	1.33979	-0.02039
C	0.05263	2.23344	-1.26321
C	1.82316	0.87192	-2.58739
H	1.28266	-1.32157	-0.44062
C	3.06865	0.71186	0.41657
C	1.19963	2.31718	2.30602
C	-1.14122	3.67765	0.55303
C	-0.74126	2.64558	-2.45525
O	1.84007	-1.98434	-0.92479
C	3.31587	-3.79636	-0.77031
H	3.93933	-4.34289	-0.05244
H	2.63649	-4.49946	-1.27791
H	3.94352	-3.33718	-1.54880
H	1.07499	0.31281	-3.17519
H	2.18724	1.68401	-3.24321
H	2.67062	0.19485	-2.40252
H	-0.22531	3.44276	-3.02176
H	-0.89693	1.81040	-3.15872
H	-1.73156	3.03982	-2.17713
H	-0.84399	4.72913	0.38317
H	-2.10726	3.53177	0.04032
H	-1.32651	3.57077	1.63453
H	2.00787	3.05906	2.44225
H	0.31986	2.69668	2.84932
H	1.53125	1.39285	2.80902
H	3.54356	0.13173	-0.38978
H	3.79619	1.48062	0.73623
H	2.93374	0.03422	1.27717

34
B(TS1)

Rh	0.65116	-0.81495	-2.80979
C	-1.26983	2.45435	-0.80838
C	-0.95253	3.88483	-0.44165
C	1.88456	-2.04111	-1.70227
C	1.11761	-2.82588	-2.61165
C	1.49954	-1.09328	-4.70401
C	2.44454	-0.46489	-3.87038
C	3.33734	-1.67859	-1.86896
C	1.69190	-3.46008	-3.86456
C	1.50246	-2.55328	-5.08099
C	3.64614	-1.17042	-3.27698
H	-0.08227	4.24270	-1.01395
H	-1.81004	4.54968	-0.61658
H	-0.67093	3.93321	0.62310
H	1.53455	-2.01668	-0.65868
H	0.22715	-3.32394	-2.19713
H	0.91343	-0.43927	-5.36915
H	2.51028	0.63205	-3.93411
H	3.98531	-2.53434	-1.59443
H	3.56275	-0.88596	-1.13462
H	2.75871	-3.69307	-3.70454
H	1.20069	-4.42993	-4.04206
H	2.26752	-2.75655	-5.85586
H	0.53117	-2.77513	-5.55527
H	4.50185	-0.47716	-3.24526
H	3.95853	-1.99722	-3.93728
O	-2.42395	2.13436	-1.12904
O	-0.28535	1.64019	-0.74627
O	-0.86744	-0.71959	-1.31679
H	-0.71740	0.28044	-1.05360
C	-1.00269	-1.49188	-0.14822
H	-1.98771	-1.31209	0.31806
H	-0.94011	-2.56426	-0.39341
H	-0.22495	-1.25593	0.60115

34
B(TS2)

Rh	0.40964	-0.87625	-3.33087
C	-0.94007	2.14758	-0.22683
C	-0.27657	3.32158	0.42111
C	1.68143	-1.41572	-1.80394
C	1.13899	-2.58477	-2.41294
C	1.49110	-1.62885	-4.97594
C	2.24275	-0.60761	-4.36908
C	3.07243	-0.87854	-2.01847
C	1.92686	-3.49698	-3.33590
C	1.73700	-3.10769	-4.80346
C	3.45822	-0.84980	-3.49794
H	0.10424	4.00909	-0.35011
H	-0.97497	3.85217	1.08084
H	0.59522	2.98029	1.00150
H	1.21847	-1.09618	-0.85716
H	0.30272	-3.06546	-1.88344
H	0.90096	-1.35323	-5.86436
H	2.16247	0.39646	-4.81349
H	3.80929	-1.44870	-1.41822
H	3.08983	0.14924	-1.61363
H	2.99396	-3.47619	-3.05467
H	1.60259	-4.53896	-3.18372
H	2.59778	-3.43935	-5.41743
H	0.85958	-3.63975	-5.21041
H	4.20215	-0.05581	-3.67353
H	3.95383	-1.78935	-3.79577
O	-2.09508	1.82061	0.00267
O	-0.16151	1.50161	-1.05894
O	-1.17532	-0.51251	-2.06939
H	-0.66407	0.65963	-1.50152
C	-1.59046	-1.32384	-1.01580
H	-2.48761	-0.89601	-0.52558
H	-1.86904	-2.34265	-1.35084
H	-0.82489	-1.43774	-0.21629

26
B(Int2)

Rh	-1.62562	0.14415	-0.00133
O	0.01592	1.27759	-0.13269
C	0.10455	2.64019	-0.33085
C	-2.87448	1.49476	-0.92988
C	-3.00197	1.61130	0.48615
C	-3.08291	-1.11517	0.88815
C	-3.19614	-1.20992	-0.51044
C	-3.87022	0.81752	-1.83732
C	-4.20698	1.11419	1.26425
C	-3.98926	-0.30794	1.78528
C	-4.30442	-0.55060	-1.30769
H	-0.58562	3.24158	0.30484
H	1.12487	3.01039	-0.09045
H	-0.08787	2.95807	-1.38182
H	-2.25656	2.25561	-1.43148
H	-2.44878	2.43844	0.95794
H	-2.51733	-1.91286	1.39618
H	-2.70235	-2.06815	-0.99145
H	-4.74392	1.47555	-2.01825
H	-3.38535	0.69301	-2.82153
H	-5.10802	1.16940	0.62883
H	-4.40253	1.79381	2.10960
H	-4.95730	-0.82392	1.94461
H	-3.51183	-0.26024	2.77969
H	-4.59273	-1.20079	-2.14991
H	-5.21085	-0.46060	-0.68437

52
B(Int3)
O 1.71967 -1.66431 -0.05744
Rh -0.04329 -0.88141 -0.63861
C 2.06216 -2.99218 0.08441
C -1.41090 0.11757 -1.90903
C -2.01657 -0.05257 -0.65124
C -1.10048 -2.63153 -0.33350
C -0.70908 -2.53806 -1.70030
C -1.69346 -0.71949 -3.13268
C -3.09131 -1.08308 -0.36786
C -2.48905 -2.37250 0.19147
C -1.67030 -2.21838 -2.82974
H 3.16431 -3.10791 0.17350
H 1.76805 -3.64177 -0.77216
H 1.63669 -3.47409 0.99519
H -0.96692 1.10343 -2.11851
H -1.98769 0.80746 0.03539
H -0.49571 -3.28984 0.30827
H 0.18347 -3.11149 -1.99373
H -2.65254 -0.42420 -3.60344
H -0.91403 -0.48780 -3.87950
H -3.66934 -1.28429 -1.28620
H -3.81822 -0.67064 0.35088
H -3.14671 -3.24376 -0.00217
H -2.41458 -2.29585 1.29053
H -1.37248 -2.77604 -3.73242
H -2.67896 -2.58740 -2.57483
C 0.44767 2.34029 0.47639
C 0.10405 2.16671 1.90437
C 2.17934 1.17929 1.51781
C 1.10808 1.49633 2.52429
C 1.64796 1.74812 0.22980
C 3.55078 1.72898 1.89447
H 2.26338 0.07653 1.41097
C 1.23408 1.10344 3.95201
C -1.16227 2.68842 2.48942
C -0.38744 3.15377 -0.44925
C 2.43555 1.71528 -1.03263
H 4.30824 1.48251 1.13206
H 3.51870 2.82886 1.99596
H 3.90314 1.31039 2.85187
H 3.27475 2.43712 -1.01592
H 2.88931 0.72150 -1.19655
H 1.82477 1.95504 -1.91851
H -0.43990 4.20336 -0.10623
H 0.01475 3.16972 -1.47422
H -1.43335 2.80074 -0.49698
H -1.24839 2.46469 3.56396
H -1.24447 3.78419 2.37394
H -2.05077 2.26114 1.98958
H 1.49021 0.03344 4.05689
H 2.04354 1.66041 4.46097
H 0.30932 1.28173 4.52293

52
B(TS3)

O	-0.52742	1.93763	0.20851
Rh	0.57463	0.15661	-0.02558
C	-0.50803	2.77103	1.32236
C	1.76285	-1.16977	-1.16397
C	1.75259	-1.62707	0.16599
C	2.09582	0.89591	1.24534
C	2.36981	1.30879	-0.07537
C	2.88675	-0.41490	-1.82677
C	2.92077	-1.48000	1.12035
C	2.77942	-0.22677	1.97820
C	3.44717	0.70374	-0.94983
H	-1.37193	3.46753	1.29774
H	0.39619	3.41239	1.36160
H	-0.56571	2.22156	2.28712
H	1.09372	-1.67798	-1.87166
H	1.06911	-2.44993	0.40635
H	1.62313	1.63403	1.90729
H	2.05879	2.32854	-0.34430
H	3.68723	-1.11091	-2.14882
H	2.48386	0.02200	-2.75798
H	3.86968	-1.47037	0.55715
H	2.97466	-2.36952	1.76930
H	3.75980	0.10595	2.37446
H	2.16601	-0.46097	2.86701
H	3.88465	1.48919	-1.58721
H	4.27660	0.33699	-0.32146
C	-1.44388	-1.27894	-0.41816
C	-1.93966	-1.18901	0.96161
C	-2.72929	0.64638	-0.20904
C	-2.74275	-0.07798	1.07164
C	-1.97882	-0.18975	-1.12563
C	-3.87181	1.52040	-0.66578
H	-1.74532	1.41355	0.02221
C	-3.46253	0.42712	2.27400
C	-1.60414	-2.19063	2.01692
C	-1.11866	-2.59707	-1.05963
C	-1.86520	0.08695	-2.58270
H	-3.60198	2.10916	-1.55870
H	-4.77776	0.93907	-0.92284
H	-4.16432	2.24667	0.11211
H	-2.82568	-0.08197	-3.10649
H	-1.59632	1.14244	-2.77013
H	-1.10583	-0.54107	-3.07576
H	-2.02940	-3.22510	-1.08721
H	-0.78736	-2.49025	-2.10446
H	-0.36050	-3.19204	-0.52676
H	-2.13002	-1.98678	2.96316
H	-1.87729	-3.21767	1.71166
H	-0.52247	-2.21450	2.24823
H	-3.17967	1.46793	2.51752
H	-4.55784	0.44015	2.11941
H	-3.26703	-0.18304	3.17006

52
B(Prod)
O 2.54912 -0.41307 -1.80447
Rh -0.32465 0.08115 0.18317
C 3.80648 -0.62519 -1.22204
C -0.44825 -1.84835 -0.73556
C -1.53491 -1.67191 0.15994
C 0.04362 -0.58837 2.15810
C 1.14630 -0.97794 1.35300
C 0.73939 -2.73530 -0.43491
C -1.61743 -2.37604 1.50350
C -1.06425 -1.50228 2.62669
C 1.38073 -2.41695 0.91786
H 4.14731 0.23118 -0.60843
H 4.54481 -0.76305 -2.02841
H 3.84195 -1.53333 -0.58855
H -0.66481 -1.72026 -1.80884
H -2.50232 -1.39696 -0.28632
H 0.19692 0.28899 2.80481
H 2.05312 -0.35892 1.45272
H 0.45154 -3.80555 -0.49571
H 1.48402 -2.58481 -1.23428
H -1.08034 -3.33976 1.45385
H -2.66624 -2.64010 1.71961
H -0.73762 -2.11578 3.49225
H -1.87561 -0.85782 3.01302
H 2.46601 -2.61177 0.86955
H 1.00546 -3.10061 1.70084
C -1.60175 1.41764 -1.05294
C -1.63245 1.91311 0.29127
C 0.54077 2.13471 -0.55808
C -0.28823 2.27892 0.62296
C -0.26769 1.60755 -1.58930
C 1.96308 2.57217 -0.63495
H 1.88589 -0.26811 -1.09971
C 0.17809 2.90229 1.89392
C -2.83112 2.00923 1.17359
C -2.77181 0.97175 -1.86151
C 0.09925 1.36206 -3.01223
H 2.47265 2.17654 -1.52628
H 2.04098 3.67480 -0.66898
H 2.53999 2.25009 0.24910
H -0.37868 2.10407 -3.67829
H 1.18515 1.42051 -3.17722
H -0.23631 0.37091 -3.36261
H -3.12852 1.78068 -2.52539
H -2.52208 0.11730 -2.51291
H -3.62396 0.67512 -1.22975
H -2.55640 1.97781 2.24090
H -3.39124 2.94949 1.01538
H -3.53921 1.18221 0.99548
H 1.17915 2.54356 2.18771
H 0.25411 4.00071 1.79423
H -0.50729 2.70246 2.73272

References

[1] R. Uson, L. A. Oro, J. A. Cabeza, H. E. Bryndza, M. P. Stepro, in *Inorg. Synth.*, John Wiley & Sons, Inc., **2007**, pp. 126-130.

[2] K. Shibata, S. Natsui, N. Chatani *Org. Lett.*, **2017**, *19*, 2234–2237

[3] B. Ye, N. Cramer, *Science* **2012**, *338*, 504-506

[4] B. Ye, N. Cramer, *J. Am. Chem. Soc.* **2013**, *135*, 636-639

[5] Y. Sun, N. Cramer, *Chem. Sci.* **2018**, *9*, 2981-2985

[6] G. Smits, B. Audic, M. D. Wodrich, C. Corminboeuf, N. Cramer, *Chem. Sci.* **2017**, *8*, 7174-7179

[7] S.-G. Wang, S.-H. Park, N. Cramer, *Angew. Chem. Int. Ed.* **2018**, *57*, 5459-5462

[8] S. Miaskiewicz, J. H. Reed, P. A. Donets, C. C. Oliveira and N. Cramer, *Angew. Chem. Int. Ed.*, **2018**, *57*, 4039-4042

[9] B. Ye, PhD thesis, Ecole Polytechnique Fédérale de Lausanne, 2015

[10] B. Ye, N. Cramer, *Angew. Chem. Int. Ed.* **2014**, *53*, 7896-7899

[11] Y. Sun, N. Cramer, *Angew. Chem. Int. Ed.* **2017**, *56*, 364-367

[12] J. Zheng, S-B. Wang, C. Zheng, S-L. You, *Angew. Chem. Int. Ed.* **2017**, *56*, 4540 –4544

[13] Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008**, *41*, 157-167.

[14] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215-241.

[15] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.

[16] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378-6396**.**

[17] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09* (Gaussian, Inc., Wallingford CT, 2009).

[18] S. E. Wheeler, K. N. Houk, *J. Chem. Theory Comput.* **2010**, *6*, 395-404.

[19] S. N. Steinmann, C. Corminboeuf, *J. Chem. Theory Comput.* **2010**, *6*, 1990-2001.

[20] S. N. Steinmann, C. Corminboeuf, *Chimia* **2011**, *65*, 240-244.

[21] S. N. Steinmann, C. Corminboeuf, *J. Chem. Phys.* **2011**, *134*, 044117.

[22] S. N. Steinmann, C. Corminboeuf, *J. Chem. Theory Comput.* **2011**, *7*, 3567-3577.

[23] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.

[24] C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158-6170.

[25] C. Fonseca Guerra, J. G. Snijders, G. te Velde, E. J. Baerends, *Theor. Chem. Acc.* **1998**, *99*, 391-403.

[26] G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders, T. Ziegler, *J. Comput. Chem.* **2001**, *22*, 931-967.

[27] S. Grimme, *Chem. Eur. J.* **2012**, *18*, 9955-9964.

[28] I. Funes-Ardoiz, R. S. Paton. **2016**. Goodvibes: Goodvibes v1.0.2. https://doi.org/10.5281/zenodo.595246.

[29] A. Klamt, *WIREs Comput. Mol. Sci.* **2011**, *1*, 699-709.