Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

for

Bulky bis(aryl)triazenides: just aspiring amidinates? A structural and spectroscopic study

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Experimental

General Synthetic Procedures

All manipulations were performed using conventional Schlenk or glovebox techniques under an atmosphere of high purity argon in flame-dried glassware. Diethyl ether, dimethoxyethane, THF, toluene and ^{n}hexane were dried over sodium wire and purged with nitrogen prior to distillation from sodium benzophenone ketyl. Benzene-d_6 (C_6D_6) was dried over sodium and freeze-thaw degassed prior to use. The yields given are not optimized. Infrared spectra were recorded as solutions in CH_2Cl_2 or as Nujol mulls using sodium chloride plates on a Nicolet Avatar 320 FTIR spectrophotometer. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopic characterizations were recorded on Bruker spectrometers (see below for MHz) at 298 K unless otherwise stated, with chemical shifts referenced to the residual ^{1}H and $^{13}C\{^{1}H\}$ resonances of benzene-d_6 (δ 7.16 and 128.06 ppm respectively) or THF-d_8 (δ 3.58 and 67.21 ppm respectively). Melting points were determined in sealed glass capillaries under argon and are uncorrected. Microanalyses were conducted at the Microanalytical unit of the Australian National University, Canberra, Australia or the Campbell Microanalytical Lab of the University of Otago, P.O. Box 56, Dunedin, New Zealand.

Starting Materials

$Dipp_2N_3H$,[S1] $[\{Rh(\mu\text{-}OEt)(COD)\}_2]$,[S2] $[\{Rh(\mu\text{-}Cl)(COD)\}_2]$,[S3] $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$,[S4] $[LiGaH_4]$,[S5] $[LiInH_4]$,[S6] $TlCl_3$,[S7] $[Sn(N\{SiMe_3\}_2)_2]$,[S8] IEt·HBr[S9] and $[(THF)SnCl_2\cdot W(CO)_5]$[S10] were prepared according to literature procedures. All other reagents were purchased from commercial vendors and used as received.

$[(\mu\text{-}N_3Dipp_2)Rh(\mu\text{-}CO)(CO)]_2$ (1).

^{n}BuLi (0.45 mL, 0.5 mmol, 1.19 M in hexane) was added dropwise a solution of $Dipp_2N_3H$ (183 mg, 0.5 mmol) in THF (20 mL) at ambient temperature, the resultant solution was stirred for a further 2 h. The solution was then added to a bright yellow solution of $[RhCl(CO)_2]_2$ (100 mg, 0.25 mmol) in THF (20 mL), immediately the colour changed to dark brown with the formation of a precipitate. The mixture was stirred for a further 12 h, the solvent was then removed *in vacuo*. The resultant solid was then extracted with hexane (40 mL). Concentration followed by slow cooling -25°C afforded orange blocks suitable for X-ray diffraction structure determination. Yield = 182 mg

(70%). ^{1}H NMR (400 MHz, C_6D_6) δ 1.25 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.32 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 3.96 (sept, $^{3}J_{HH}$ = 6.9 Hz, 4H, CH(CH$_3$)$_2$), 7.04-7.08 (m, 6H, *m*- and *p*-ArH). IR (CH_2Cl_2, cm^{-1}) 2020 m, 1814 sh s. Calc. for $C_{52}H_{64}Rh_2N_6O_4$: C, 59.89; H, 6.19; N, 8.06. Found: C, 60.81; H, 6.58; N, 8.17%.

In one preparation a few single crystals of [{Rh(μ-N_3Dipp$_2$)}$_2$(CO)$_2$(H_2NDipp)] were isolated and crystallographically characterized. No attempt at spectroscopic characterisation was undertaken.

[(Piso)Rh(CO)$_2$]

A cool (-78°C) solution of (DippN)$_2$C (190 mg, 0.52 mmol) in THF (20 mL) was treated with ^{t}BuLi (0.35 mL, 0.6 mmol, 1.7 M in pentane). The resultant pale yellow solution was stirred at -78 °C for 4 h, then allowed to slowly warm to room temperature overnight. The solution was then added to a yellow solution of [{Rh(CO)$_2$Cl}$_2$] (100 mg, 0.25 mmol) in THF (20 mL) at ambient temperature. The resultant yellow solution was stirred for a further 16 h, then the solvent was removed *in vacuo* and the residue was extracted with hexane (40 mL). Concentration to *ca*. 10 mL followed by slow cooling to -25°C afforded yellow crystals. Yield = 77 mg (27%), 156-157°C (dec.). ^{1}H NMR (400 MHz, C_6D_6) δ 0.82 (s, 9H, C(CH_3)$_3$), 1.35 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, CH_3), 1.51 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, CH_3), 3.89 (sept, $^{3}J_{HH}$ = 6.9 Hz, 4H, CH), 7.02 - 7.08 (m, 6H, ArH). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 22.4, 24.7 (CH$_3$), 28.9 (CH), 28.9 (CH$_3$), 44.4 (d, $^{3}J_{RhC}$ = 2.4 Hz, CMe$_3$), 123.7, 126.2 (ArCH), 142.9, 144.9 (ArC), 186.6 (d, $^{1}J_{RhC}$ = 69.0 Hz, CO), 188.8 (d, $^{2}J_{RhC}$ = 5.3 Hz, NCN). IR (Nujol, cm^{-1}) 2064 sh s, 1996 sh s; (DCM, cm^{-1}) 2063 sh s, 1992 sh s. Anal. Calc. for $C_{31}H_{43}RhO_2N_2$: C, 64.35; H, 7.49; N, 4.84. Found: C, 64.84; H, 7.43; N, 5.10%.

[(Giso)Rh(CO)$_2$]

^{n}BuLi (0.42 mL, 0.5 mmol, 1.19 M in hexane) was added dropwise a solution of GisoH (270 mg, 0.5 mmol) in THF (20 mL) at ambient temperature, the resultant solution was stirred for a further 12 h. The solution was then added to a bright yellow solution of [{Rh(CO)$_2$Cl}$_2$] (100 mg, 0.25 mmol) in THF (20 mL), immediately the colour changed to dark brown with the formation of a precipitate. The mixture was stirred for a further 12 h, the solvent was then removed *in vacuo*. The resultant solid was then extracted with hexane (40 mL). Concentration followed by slow cooling -25°C afforded yellow

crystals. Yield = 241 mg (69%), m.p. 194-198°C (dec.). ^{1}H NMR (400 MHz, C_6D_6) δ 0.65 - 0.80 (m, 6H, C*H*$_2$), 1.20 - 1.58 (m, 14H, C*H*$_2$), 1.42 (d, $^{3}J_{HH}$ = 6.8 Hz, 12H, C*H*$_3$), 1.69 (d, $^{3}J_{HH}$ = 6.8 Hz, 12H, C*H*$_3$), 3.52 (br t, 2H, NC*H*), 3.87 (sept, $^{3}J_{HH}$ = 6.8 Hz, 4H, C*H*), 7.06 - 7.13 (m, 6H, *m*- and *p*-Ar*H*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 22.9, 25.0 (CH_3), 25.8, 26.9 (CH_2), 28.6 (CH), 35.4 (CH_2), 57.5 (NCH), 124.0, 125.2 (ArCH), 142.9, 146.1 (ArC), 172.1 (d, $^{2}J_{RhC}$ = 5.9 Hz, CN_3), 187.5 (d, $^{1}J_{RhC}$ = 69.2 Hz, CO). IR (Nujol, cm^{-1}) 2050 sh s, 1979 sh s; (DCM, cm^{-1}) 2055 sh s, 1983 sh s. Anal. Calc. for $C_{39}H_{56}RhO_2N_3$: C, 66.75; H, 8.04; N, 5.99. Found: C, 67.07; H, 8.26; N, 6.01%.

[(Dipp$_2$N$_3$)Rh(COD)] (3)

A solution of [{Rh(μ-OEt)(COD)}$_2$] (80 mg, 0.17 mmol) in toluene (20 mL) was treated with a solution of Dipp$_2$N$_3$H (109 mg, 0.30 mmol) in toluene (10 mL) at ambient temperature. After 10 min, the colour of the mixture had changed from yellow to orange. After 4 h the solvent was removed *in vacuo* and the residue was extracted with hexane (40 mL). Concentration to insipient crystallisation, followed by cooling to -25°C afforded red prisms suitable for X-ray diffraction structure determination. Yield = 80 mg (46%), m.p. 190-192°C (dec.). ^{1}H NMR (400 MHz, C_6D_6) δ 1.41 (br m, 4H, C*H*$_2$-cod), 1.44 (d, $^{3}J_{HH}$ = 6.9 Hz, 24H, CH(C*H*$_3$)$_2$), 2.19 (br m, 4H, C*H*$_2$-cod), 3.86 (br s, 4H, C*H*-cod), 4.21 (sept, $^{3}J_{HH}$ = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 7.12-7.15 (m, 6H, *m*- and *p*-Ar*H*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 24.4 (CH(*C*H$_3$)$_2$), 28.2 (*C*H(CH$_3$)$_2$), 30.8 (*C*H$_2$-cod), 81.9 (d, $^{1}J_{RhC}$ = 12.3 Hz, =*C*H), 123.4, 127.0 (Ar*C*H), 143.0, 144.6 (Ar*C*). IR (Nujol, cm^{-1}) 1926 (w), 1860 (w), 1584 (w), 1356 (w), 1320 (w), 1253 (s, N=N), 1234 (w), 1176 (w), 1154 (w), 1104 (w), 1057 (w), 994 (w), 966 (w), 955 (m), 933 (w), 920 (w), 864 (w), 797 (s), 766 (w), 752 (s), 726 (w). Anal. Calc. for $C_{32}H_{46}RhN_3$: C, 66.77; H, 8.05; N, 7.30. Found: C, 67.36; H, 8.25; N, 7.51%.

[(Fiso)Rh(COD)] (4)

A solution of FisoH (182 mg, 0.50 mmol) in THF (20 mL) was treated with ^{n}BuLi (1.19 M in hexane, 0.45 mL, 0.50 mmol) at ambient temperature. The resultant colourless solution was stirred at ambient temperature for 12 h, then added to a yellow solution of [{Rh(μ-Cl)(COD)}$_2$] (125 mg, 0.25 mmol) in THF (20 mL). The resultant mixture was stirred for a further 16 h, over which time the colour of solution changed from yellow to gold. The solvent was removed *in vacuo* and the residue was extracted with hexane (60 mL). Concentration to insipient crystallisation (*ca*. 25 mL) followed by cooling to -

25°C afforded golden yellow prisms suitable for X-ray diffraction structure determination. Yield = 227 mg (79%), 186-187°C. ^{1}H NMR (400 MHz, C_6D_6) δ 1.30 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.46 (br m, 4H, CH_2-cod), 1.47 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 2.26 (br m, 4H, CH_2-cod), 3.81 (br m, 4H, C*H*-cod), 4.09 (sept, $^{3}J_{HH}$ = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 7.00-7.13 (m, 6H, *m*- and *p*-Ar*H*), 8.00 (d, $^{3}J_{RhH}$ = 2.3 Hz, 1H, NC*H*). ^{1}H NMR (400 MHz, THF-d_8) δ 1.20 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.39 (d, $^{3}J_{HH}$ = 6.9 Hz, 12H, CH(CH_3)$_2$), 1.67-1.74 (br m, 4H, CH_2-cod), 2.35-2.44 (br m, 4H, CH_2-cod), 3.71 (br s, 4H, C*H*-cod), 3.94 (sept, $^{3}J_{HH}$ = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 6.96-7.03 (m, 6H, *m*- and *p*-Ar*H*), 8.09 (d, $^{3}J_{RhH}$ = 2.3 Hz, 1H, NC*H*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 23.4, 25.7 (CH(*C*H$_3$)$_2$), 28.2 (*C*H(CH$_3$)$_2$), 31.1 (*C*H$_2$-cod), 78.7 (d, $^{1}J_{RhC}$ = 13.1 Hz, =*C*H), 123.3, 125.3 (Ar*C*H), 142.0, 144.6 (Ar*C*), 169.9 (d, $^{2}J_{RhC}$ = 5.1 Hz, N*C*N). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8) δ 23.3, 25.7 (CH(*C*H$_3$)$_2$), 28.4 (*C*H(CH$_3$)$_2$), 31.3 (*C*H$_2$-cod), 79.0 (d, $^{1}J_{RhC}$ = 13.0 Hz, =*C*H), 123.3, 125.2 (Ar*C*H), 142.3, 144.9 (Ar*C*), 170.9 (d, $^{2}J_{RhC}$ = 5.2 Hz, N*C*N). IR (Nujol, cm^{-1}) 1531 (br s, N=C), 1360 (m), 1321 (s), 1260 (s), 1193 (s), 1152 (w), 1100 (m), 1077 (w), 1057 (m), 1045 (w), 993 (w), 976 (w), 952 (s), 935 (w), 899 (w), 885 (w), 865 (m), 831 (w), 802 (sh s), 758 (s), 723 (w), 666 (w). Anal. Calc. for $C_{33}H_{47}RhN_2$: C, 68.97; H, 8.24; N, 4.87. Found: C, 69.14; H, 8.53; N, 4.74%.

In one preparation a few single crystals of [{Rh(COD)}$_2$(μ-Fiso)(μ-OH)] were isolated and crystallographically characterized. No attempt at spectroscopic characterisation was undertaken.

Attempted syntheses of [(L)Rh(CO)$_2$] complexes by carbonylation of 1,5-cod precursor complexes

A solution of **3** or **4** (ca. 0.10 mmol) in dichloromethane (2.0 mL) was sparged with CO(g) for 5 min. The colour of the solution changed from pale orange to dark red. The reaction mixture was then evaluated as soon as practicable (< 5 min) by IR spectroscopy.

3:

IR (CH_2Cl_2, cm^{-1}) 2084 (sh s, CO), 2028 (sh s, CO).

New Carbonyl stretches 24 h later: 2020 and 1814 cm^{-1}

4:

IR (CH_2Cl_2, cm^{-1}) 2078 (sh s, CO), 2011 (sh s, CO).

New Carbonyl stretches 24 h later: 2039, 1771 and 1656 cm^{-1}.

[Li(N_3Dipp$_2$)] (5)

A solution of [LiN($SiMe_3$)$_2$] (460 mg, 2.75 mmol) in toluene (10 mL) was added to a solution of $Dipp_2N_3H$ (1.00 g, 2.74 mmol) at ambient temperature. A colourless precipitate was immediately observed. The slurry was stirred for a further 12 h, whereupon the solvent was decanted and the precipitate washed with pentane (5×5 mL). Drying *in vacuo* afforded a pale brown powder. Yield = 895 mg (88%), m.p. > 360°C. ^{1}H NMR (250 MHz, THF-d_8) δ 1.12 (d, $^3J_{HH}$ = 6.9 Hz, 24H, CH(CH_3)$_2$), 3.51 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, CH(CH$_3$)$_2$), 6.83 (t, $^{AAB}J_{HH}$ = 7.6 Hz, 2H, *p*-ArH), 6.98 (d, $^{AAB}J_{HH}$ = 7.6 Hz, 4H, *m*-ArH). ^{13}C{^{1}H} NMR (63 MHz, THF-d_8) δ 24.6 (CH(*C*H$_3$)$_2$), 28.4 (*C*H(CH$_3$)$_2$), 122.8, 123.0 (Ar*C*H), 142.4, 150.0 (Ar*C*). IR (ATR, cm^{-1}) 3036 (w), 2937 (s), 2845 (w), 1447 (m), 1422 (m), 1371 (m), 1350 (m), 1315 (w), 1276 (s, N=N), 1244 (s, N=N), 1173 (m), 1150 (w), 1087 (w), 1050 (w), 1032 (w), 964 (w), 927 (w), 794 (m), 768 (m), 751 (s), 723 (w), 680 (w), 591 (w), 548 (w), 529 (m), 449 (w), 422 (m). Elemental analysis calculated (%) for $C_{24}H_{34}N_3Li$: C, 77.59; H, 9.22; N, 11.31. Found: C, 72.88; H, 9.60; N, 10.13. Unsatisfactory elemental analysis was repeatable obtained for this compound which presumably arises due to $DippNH_2$ impurities in the starting triazene as has been previously reported.[S1]

[Li(N_3Dipp$_2$)(THF)$_2$] (5-THF$_2$)

Extraction of **5** into THF. Then concentration to incipient crystallisation followed by cooling to -25°C afforded pale yellow square slabs suitable for X-ray diffraction structure determination. Yield = 330 mg (72%), m.p. 94-96°C (dec.). ^{1}H NMR (400 MHz, C_6D_6) δ 1.20 (m, 8H, *β*-CH_2 THF), 1.23 (d, $^3J_{HH}$ = 6.7 Hz, 24H, CH(CH_3)$_2$), 3.41 (m, 8H, *α*-CH_2 THF), 3.62 (sept, $^3J_{HH}$ = 6.7 Hz, 4H, CH(CH$_3$)$_2$), 7.05-7.17 (m, 6H, *m*- and *p*-ArH). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 24.6 (CH(*C*H$_3$)$_2$), 25.4 (*β*-*C*H$_2$ THF), 28.3 (*C*H(CH$_3$)$_2$), 68.4 (*α*-*C*H$_2$ THF), 123.3, 123.5 (Ar*C*H), 142.2, 148.9 (Ar*C*). IR (Nujol, cm^{-1}) 1587 (w), 1515 (w), 1361 (w), 1256 (br s, N=N), 1098 (m), 1044 (s), 971 (w), 935 (w), 894 (w), 837 (w), 799 (s), 770 (s), 755 (s), 723 (w), 666 (w). Samples repeatedly gave microanalyses low in carbon and hydrogen, presumably due to solvent loss. For example, elemental analysis calculated (%) for $C_{37}H_{52}N_3LiO_2$: C, 74.53; H, 9.77; N, 8.15. Found: C, 72.66; H, 8.78; N, 10.18%.

[Li(N_3Dipp$_2$)(OEt$_2$)$_2$] (5-(OEt$_2$)$_2$)

Extraction of **5** into diethyl ether. Then concentration to insipient crystallisation followed by cooling to -25°C afforded colourless prisms suitable for X-ray diffraction structure determination. Yield = 223 mg (65%), m.p. 98-99°C (dec.). ^{1}H NMR (400 MHz, C_6D_6) δ 0.95 (br s, 12H, CH_2CH_3), 1.33 (br s, 24H, $CH(CH_3)_2$), 3.26 (br s, 8H, OCH_2), 3.67 (br s, 4H, $CH(CH_3)_2$), 7.15-7.24 (m, 6H, *m*- and *p*-Ar*H*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 14.6 (CH_2CH_3), 24.7 ($CH(CH_3)_2$), 28.1 ($CH(CH_3)_2$), 65.6 (OCH_2), 123.2, 123.8 (Ar*C*H), 142.6, 148.5 (Ar*C*). IR (Nujol, cm^{-1}) 1589 (w), 1518 (m), 1416 (m), 1362 (w), 1328 (w), 1256 (s, N=N), 1218 (s), 1189 (s), 1097 (w), 1058 (s), 934 (w), 838 (w), 799 (s), 770 (m), 751 (s), 721 (w). Samples repeatedly gave microanalyses low in carbon and hydrogen, presumably due to solvent loss. For example, elemental analysis calculated (%) for $C_{32}H_{54}N_3LiO_2$: C, 73.95; H, 10.47; N, 8.08. Found: C, 72.64; H, 9.44; N, 10.68%.

[Na(N_3Dipp$_2$)] (6)

A solution of Na*O*^{t}Bu (482 mg, 5.02 mmol) in toluene (*ca*. 50 mL) was added to a solution of Dipp$_2N_3H$ (1.83 g, 5.00 mmol) also in toluene (*ca*. 15 mL). The resulting thick suspension was stirred for 2 h and then filtered. The precipitate was washed with *n*-hexane (3×10 mL) and then dried in vacuo at room temperature for overnight to afford a colourless powder. Yield = 1.82 g (94%), m.p. >250°C. ^{1}H NMR (300 MHz, THF-d_8) δ 1.10 (d, $^3J_{HH}$ = 6.9 Hz, 24H, $CH(CH_3)_2$), 3.55 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, $CH(CH_3)_2$), 6.76-6.81 (m, 2H, *p*-CH), 6.93-6.95 (m, 4H, *m*-C*H*). ^{13}C{^{1}H} NMR (75.5 MHz, THF-d_8) δ 24.3 ($CH(CH_3)_2$), 27.9 ($CH(CH_3)_2$), 122.1, 122.5 (Ar*C*H), 142.4, 151.8 (Ar*C*). IR (Nujol, cm^{-1}) 666 (sh, w), 723 (sh, w), 757 (sh, m), 777 (sh, m), 797 (sh, w), 934 (sh, w), 1057 (sh, w), 1096 (sh, w), 1186 (sh, w), 1232 (s, w), 1294 (br, s), 1336 (s, w), 1588 (sh, w). Elemental analysis calculated (%) for $C_{24}H_{34}N_3Na$: C, 74.38; H, 8.84; N, 10.84. Found: C, 70.20; H, 8.87; N, 10.03. Unsatisfactory elemental analysis was repeatable obtained for this compound which presumably arises due to DippNH_2 impurities in the starting triazene as has been previously reported.[S1]

[Na(N_3Dipp$_2$)] (6) by Desolvation of [Na(N_3Dipp$_2$)(THF)$_3$] (6-THF$_3$)

A solution of Dipp$_2N_3H$ (17.54 g, 47.98 mmol) and Na*O*^{t}Bu (4.62 mg, 48.1 mmol) in tetrahydrofuran (*ca*. 150 mL) was stirred for 18 hours at room temperature. The resulting cloudy solution was filtered and volatiles removed *in vacuo*. Coordinated

tetrahydrofuran was removed by drying *in vacuo* at room temperature for 6 hours. ^{n}Pentane (*ca*. 50 mL) was added to the resulting colourless solid and the suspension stirred for 30 mins, filtered, the solid washed with further ^{n}pentane (2×30 mL) and then dried *in vacuo* for 24 h to afford [Na(N_3Dipp_2)] as a pale yellow-brown powder. Yield = 14.3 g (77%).

[Na(N_3Dipp_2)$(THF)_3$] (6-THF_3)

A solution of $Dipp_2N_3H$ (2.92 g, 8.00 mmol) and NaO^{t}Bu (774 mg, 8.05 mmol) in tetrahydrofuran (*ca*. 50 mL) was stirred for 18 hours at room temperature. The resulting cloudy solution was filtered and concentrated *in vacuo* to the point of incipient crystallisation (*ca*. 10 mL) and then slowly cooled over several hours to -25°C. Storage at this temperature for 48 h afforded a crop of yellow orange blocks, which were isolated through decantation of the supernatant. Further concentration of the supernatant (*ca*. 5 mL) and storage at -25°C did not afford a second crop. Yield = 3.17 g (66%), m.p. 200-210°C (dec.). ^{1}H NMR (300 MHz, C_6D_6) δ 1.33 (d, $^{3}J_{HH}$ = 6.9 Hz, 24H, CH(CH_3)$_2$), 1.38 (s br, 12H, OCH_2CH_2), 3.46 (s br, 12H, OCH_2CH_2), 3.76 (sept, $^{3}J_{HH}$ = 6.8 Hz, 4H, CH(CH_3)$_2$), 7.10-7.15 (m, 2H, *p*-ArCH), 7.24-7.26 (m, 4H, *m*-ArCH). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6) δ 20.4 (CH(CH_3)$_2$), 25.3 (OCH_2CH_2), 27.6 ($CH(CH_3)_2$), 67.6 (OCH_2CH_2), 122.4, 122.5 (ArCH), 142.1, 150.7 (ArC). IR (Nujol, cm^{-1}) 723 (sh, w), 757 (sh, m), 777 (sh, m), 797 (sh, w), 916 (sh, w), 1055 (sh, w), 1074 (sh, w), 1097 (sh, w), 1187 (s, w), 1232 (sh, m), 1296 (br, s), 1357 (sh, w), 1435 (sh, w), 1367 (sh, m), 1376 (sh, m), 1586 (sh, s), 1694 (sh, w), 1784 (sh, w), 1838 (sh, w), 1892 (sh, w), 2472 (br, w), 2720 (br, w). Elemental analysis calculated (%) for $C_{36}H_{58}N_3NaO_3$: C, 71.60; H, 9.68; N, 6.96. Found: C, 71.77; H, 9.89; N, 9.60.

[Na(N_3Dipp_2)$(DME)_2$] (6-DME_2)

A solution of $Dipp_2N_3H$ (2.91 g, 7.96 mmol) and NaO^{t}Bu (770 mg, 8.01 mmol) in 1,2-dimethoxyethane (*ca*. 30 mL) was stirred for 18 hours at room temperature. The resulting cloudy solution was filtered and concentrated *in vacuo* to the point of incipient crystallisation (*ca*. 10 mL) and slowly cooled over two hours to -25°C. Storage at this temperature overnight afforded a crop of yellow blocks, which were isolated through decantation of the supernatant. Further concentration of the supernatant to the point of incipient crystallisation (*ca*. 3-4 mL) afforded a second crop of yellow-orange blocks of equivalent purity. Yield = 3.56 g (79%), m.p. 146-148°C (with dec.). ^{1}H NMR (300

MHz, C_6D_6) δ 1.33 (d, $^3J_{HH}$ = 6.8 Hz, 24H, CH(CH_3)$_2$), 2.97 (s, 8H, CH_3OCH_2), 2.99 (s, 12H, CH_3OCH_2), 3.76 (sept, $^3J_{HH}$ = 6.7 Hz, 4H, C*H*(CH_3)$_2$), 7.05-7.16 (m, 2H, *p*-ArCH), 7.18-7.30 (m, 4H, *m*-ArC*H*). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6) δ 24.7 (CH(*C*H_3)$_2$), 27.9 (*C*H(CH_3)$_2$), 58.8 (*C*H_3OCH_2), 71.1 (CH_3O*C*H_2), 122.6, 122.8 (Ar*C*H), 142.3, 151.1 (Ar*C*). IR (Nujol, cm^{-1}) 724 (sh, w), 553 (sh, s), 765 (sh, s), 797 (sh, w), 843 (sh, w), 863 (sh, s), 937 (sh, w), 1031 (sh, m), 1090 (br, s), 1130 (sh, s), 1225 (br, s), 1272 (br, s), 1357 (sh, m), 1367 (sh, m), 1376 (sh, m), 1586 (sh, s), 1694 (sh, w), 1784 (sh, w), 1838 (sh, w), 1892 (sh, w), 2472 (br, w), 2720 (br, w). Elemental analysis calculated (%) for $C_{32}H_{54}N_3NaO_4$: C, 67.69; H, 9.59; N, 7.40. Found: C, 67.51; H, 9.70; N, 7.54.

[Na(N$_3$Dipp$_2$)(15c5)] (6-15c5)

15-crown-5 (0.12 mL, 0.61 mmol) was added to a stirred suspension of **6** (201 mg, 0.52 mmol) in toluene (20 mL). The reaction mixture was stirred at ambient temperature for 2 hours then filtered. Concentration of the filtrate (approx. 10 mL), followed by standing the solution at 2°C overnight afforded large colourless/yellow needles. Yield = 107 mg (34%), m.p. 250°C (melts with dec.). ^{1}H NMR (400 MHz, C_6D_6) δ 1.40 (d, $^3J_{HH}$ = 6.9 Hz, 24H, CH_3), 2.89 (br s, 10H, OCH_2), 3.29 (br s, 10H, OCH_2), 4.00 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*(CH_3)$_2$), 7.20-7.30 (m, 2H, *p*-ArC*H*), 7.34-7.41 (m, 4H, *m*-ArC*H*). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6) δ 24.9 (*C*H_3), 27.3 (*C*H(CH_3)$_2$), 68.9 (O*C*H_2), 122.9, 123.0 (Ar*C*H), 143.5, 152.0 (Ar*C*). IR (Nujol) *v*/cm^{-1}: 754 (sh m), 800 (sh m), 861 (sh w), 947 (m), 1040 (w), 1120 (s), 1232 (m), 1273 (s) 1352 (sh m), 1585 (w), 3049 (w). Elemental analysis calculated (%) for $C_{34}H_{54}N_3NaO_5$: C, 67.19; H, 8.96; N, 6.91. Found: C, 67.32; H, 8.98; N, 6.93%.

[K(N$_3$Dipp$_2$)] (7)

A solution of KO^{t}Bu (567 mg, 5.05 mmol) in toluene (*ca*. 80 mL) was added to a solution of Dipp$_2$N$_3$H (1.831 g, 5.009 mmol) also in toluene (*ca*. 15 mL). A suspension gradually formed over 30 mins. After stirring for a further 2 h the solid was isolated by filtration, the filtrate was washed with *n*-hexane (2×10 mL) and then dried in vacuo at room temperature overnight to afford a pale pink, fine powder. Yield = 1.821 g (90%), m.p. >250°C. IR (Nujol, cm^{-1}) 727 (sh, w), 754 (sh, m), 781 (sh, m), 801 (sh, m) 934 (sh, s), 954 (sh, w), 969 (sh, w), 1057 (sh, w), 1097 (sh, m), 1159 (sh, w), 1186 (sh, w), 1235 (sh, m), 1293 (br, s), 1319 (sh, w), 1358 (sh, m). Elemental analysis calculated (%) for $C_{24}H_{34}N_3K$: C, 71.41; H, 8.49; N, 10.41. Found: C, 69.69; H, 8.92;

N, 10.09. Unsatisfactory elemental analysis was repeatable obtained for this compound which presumably arises due to $DippNH_2$ impurities in the starting triazene as has been previously reported.[S1]

[K(N_3Dipp_2)] (7) by Desolvation of [K(N_3Dipp_2)(THF)$_2$] (7-THF$_2$)

A solution of $Dipp_2N_3H$ (1.86 g, 5.08 mmol) and KO^{t}Bu (571 mg, 5.09 mmol) in tetrahydrofuran (*ca*. 20 mL) was stirred for 18 hours at room temperature. The resulting fine suspension was filtered and volatiles removed *in vacuo*. Coordinated tetrahydrofuran was removed by drying *in vacuo* at room temperature for 18 hours. ^{n}Pentane (*ca*. 30 mL) was added to the resulting colourless solid and the suspension stirred for 30 mins, filtered, the solid washed with further ^{n}pentane (2×5 mL) and then dried *in vacuo* for 4 h to afford [K(N_3Dipp_2)] as a colourless powder. Yield =1.79 g (87%).

[K(N_3Dipp_2)(THF)$_2$] (7-THF$_2$)

A solution of $Dipp_2N_3H$ (2.92 g, 7.99 mmol) and KO^{t}Bu (899 mg, 8.01 mmol) in THF (*ca*. 50 mL) was stirred for 18 h at room temperature. The resulting cloudy solution was filtered and concentrated *in vacuo* to the point of incipient crystallisation (*ca*. 8 mL) and slowly cooled over two hours to -25°C. Storage at this temperature for 2 h afforded a crop of colourless plates, which were isolated through decantation of the supernatant and briefly (*ca*. 10 s) dried *in vacuo*. Storage of the supernatant at -25°C overnight afforded a second crop of colourless plates, which were again isolated through decantation of the supernatant and dried as above. The supernatant was concentrated *in vacuo* to *ca*. 3 mL and stored at -25°C overnight to afford a third and final crop of colourless plates, which were isolated and dried as above. Yield = 2.67 g, (70%), m.p. 240-250°C (dec.). ^{1}H NMR (300 MHz, THF-d_8) δ 1.05 (d, $^3J_{HH}$ = 7.6 Hz, 24H, CH(CH_3)$_2$), 1.72 (OCH$_2$CH_2), 3.50 (sept, $^3J_{HH}$ = 7.0 Hz, 4H, CH(CH$_3$)$_2$), 3.72 (OCH_2CH$_2$), 6.69 (t, $^3J_{HH}$ = 7.6 Hz, 2H, *p*-CH), 6.97 (d, $^3J_{HH}$ = 7.6 Hz, 4H, *m*-CH). ^{13}C{^{1}H} NMR (75.5 MHz, THF-d_8) δ 24.7 (CH(*C*H$_3$)$_2$), 26.4 (OCH$_2$*C*H$_2$), 28.3 (*C*H(CH$_3$)$_2$), 68.2 (O*C*H$_2$CH$_2$), 121.5, 122.5 (Ar*C*H), 142.1, 153.1 (Ar*C*). IR (Nujol, cm^{-1}) 646 (sh, w), 666 (sh, w), 728 (sh, w), 757 (sh, s), 779 (sh, m), 804 (sh, s), 915 (br, w), 933 (sh, w), 952 (s, w), 1038 (sh, w), 1059 (sh, m), 1095 (sh, w), 1107 (sh, w), 1157 (sh, w), 1185 (sh, w), 1235 (sh, w), 1257 (sh, w), 1293 (sh, m), 1323 (sh, w), 1357 (sh,

m), 1430 (sh, m), 1585 (sh, w). Elemental analysis calculated (%) for $C_{28}H_{42}N_3KO$: C, 70.69; H, 8.90; N, 8.83. Found: C, 69.95; H, 9.39; N, 9.10.

[K(N$_3$Dipp$_2$)(DME)$_2$] (7-DME$_2$)

A solution of $Dipp_2N_3H$ (2.92 g, 7.99 mmol) and KO^{t}Bu (990 mg, 8.02 mmol) in 1,2-dimethoxyethane was stirred for 18 hours at room temperature. The resulting cloudy solution was filtered and concentrated *in vacuo* to the point of incipient crystallisation (*ca*. 5 mL) and slowly cooled over two hours to 5°C. Storage at this temperature overnight afforded a crop of yellow-orange blocks, which were isolated through decantation of the supernatant. Further concentration of the supernatant (*ca*. 5 mL) and storage at -25°C did afford a second crop, which could not be isolated due to the highly viscous nature of the supernatant. Yield = 1.30 g (28%), m.p. 230-240°C (dec.). ^{1}H NMR (300 MHz, C_6D_6) δ 1.35 (d, $^3J_{HH}$ = 6.9 Hz, 24H, CH(CH_3)$_2$), 3.06 (s, CH_3OCH$_2$), 3.25 (s, CH$_3$OCH_2), 3.75 (m br, 4H, CH(CH$_3$)$_2$), 7.11-7.14 (m, 2H, *p*-CH), 7.26-7.29 (m, 4H, *m*-CH). ^{1}H NMR (300 MHz, THF-d_8) δ 1.10 (d, $^3J_{HH}$ = 6.9 Hz, 24H, CH(CH_3)$_2$), 3.27 (s, 12H, CH_3OCH$_2$), 3.43 (s, 8H CH$_3$OCH_2), 3.90 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, CH(CH$_3$)$_2$), 6.71-6.76 (m, 2H, *p*-CH), 6.90-6.93 (m, 4H, *m*-CH). ^{13}C{^{1}H} NMR (75.5 MHz, THF-d_8) δ 24.7 CH(*C*H$_3$)$_2$, 28.3 (*C*H(CH$_3$)$_2$, 58.9 (*C*H$_3$OCH$_2$), 72.7 (CH$_3$O*C*H$_2$), 121.5, 122.5 (Ar*C*H), 142.1, 153.1 (Ar*C*). IR (Nujol, cm^{-1}) 723 (sh, w), 754 (sh, w), 762 (sh, w), 779 (sh, w), 803 (sh, w), 858 (sh, w), 936 (sh, w), 1032 (br, w), 1095 (sh, m), 1159 (sh, w), 1187 (sh, w), 1225 (br, m), 1269 (sh, m), 1293 (sh, m), 1358 (sh, w), 1586 (sh, s), 1694 (sh, w), 1784 (sh, w), 1838 (sh, w), 1892 (sh, w), 2472 (br, w), 2720 (br, w). Satisfactory elemental analysis was not obtained. For example, calculated (%) for $C_{32}H_{54}N_3KO_4$: C, 65.83; H, 9.32; N, 7.20. Found: C, 62.18; H, 9.10; N, 9.18.

[K(N$_3$Dipp$_2$)(18C6)] (7-18C6)

Toluene (20 mL) was added to a solid mixture of **7** (201 mg, 0.50 mmol) and 18-crown-6 (0.148 g, 0.56 mmol) forming a bright yellow solution. This was left to stir overnight. Concentration of the solution (approx. 12 mL) followed by standing the solution at -20°C overnight afforded yellow crystalline rods. Yield = 251 mg (76% over 2 crops), m.p. 281°C (melts with dec.). ^{1}H NMR (400 MHz, C_6D_6) δ 1.42 (d, $^3J_{HH}$ = 6.9 Hz, 24H, CH_3), 3.08 (s, 24H, OCH_2), 4.02 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, CH(CH$_3$)$_2$), 7.20-7.30 (m, 2H, *p*-ArCH), 7.34-7.41 (m, 4H, *m*-ArCH). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 24.9 (*C*H$_3$), 27.5 (*C*H(CH$_3$)$_2$), 69.8 (O*C*H$_2$), 122.1, 122.7 (Ar*C*H), 142.8, 153.4 (Ar*C*). IR (Nujol, cm^{-}

[1]) 754 (sh m), 768 (sh w), 797 (sh w), 839 (sh m), 964 (m), 1113 (s), 1178 (m), 1229 (sh m), 1274 (s), 1352 (sh m), 1585 (w), 2745 (w) 3050 (w). Elemental analysis calculated (%) for $C_{34}H_{58}KN_3O_6 \cdot 0.5C_7H_8$: C, 66.44; H, 8.75; N, 5.88. Found: C, 66.25; H, 8.92; N, 6.13%.

[Tl(N_3Dipp$_2$)] (8)

TlOEt (255 µL, 3.70 mmol) was added dropwise with stirring, to a solution of $Dipp_2N_3H$ (1.30 g, 3.60 mmol) in toluene (20 mL) at -20°C with immediate colour change from pale yellow to deep red. With the exclusion of light, the mixture was allowed to warm to ambient temperature and stirred for a further 24 h. The solvent was removed *in vacuo* and the red residue was extracted into hexane (60 mL). Concentration of the solution to *ca.* 15 mL *in vacuo* and standing at ambient temperature after light warming to dissolve precipitated solids afforded large red plates suitable for X-ray diffraction structure determination. Yield = 604 mg (29%); m.p. 203-205°C (dec.). ^{1}H NMR (300 MHz, C_6D_6) δ 1.23 (d, $^3J_{HH}$ = 6.9 Hz, 48H, CH(CH_3)$_2$), 3.56 (sept, $^3J_{HH}$ = 6.9 Hz, 8H, CH(CH$_3$)$_2$), 7.07 (t, $^{AAB}J_{HH}$ = 7.4 Hz, 4H, *p*-Ar*H*), 7.17 (d, $^{AAB}J_{HH}$ = 7.4 Hz, 8H, *m*-Ar*H*). ^{13}C NMR (76 MHz, C_6D_6) δ 24.8 (CH(*C*H$_3$)$_2$), 29.1 (*C*H(CH$_3$)$_2$), 123.4, 125.5 (Ar*C*H), 142.7, 148.7 (Ar*C*). Anal. Cal. for $C_{24}H_{34}N_3Tl$: C 50.67, H 6.02, N 7.39. Found: C, 49.73; H, 6.06; N, 7.25%.

[InCl(N_3Dipp$_2$)$_2$] (9)

Method A: Cold (-78°C) toluene (30 mL) was added to a mixture of **5** (296 mg, 0.81 mmol) and InCl (122 mg, 0.81 mmol). The resultant slurry was allowed to warm to ambient temperature overnight. The colourless supernatant solution was then isolated from a large amount of grey precipitate by filtration. The solvent was removed *in vacuo* and the colourless residue was extracted with hexane (80 mL). The volume of the solution was reduced to *ca.* 40 mL *in vacuo*, and the obtained precipitate was redissolved by slight warming. Storage at ambient temperature overnight afforded large colourless cubes over two crops. Yield = 207 mg (42%).

Method B: Cold (-78°C) toluene (20 mL) was added to a mixture of **5** (180 mg, 0.50 mmol) and In[$InCl_4$] (90 mg, 0.25 mmol). The resultant light brown slurry was allowed to warm to ambient temperature over 8 h leading to the formation of a black precipitate. The mixture was then filtered and the toluene removed *in vacuo*. The resultant pale-yellow powder was then extracted with hexane (40 mL), concentrated to *ca*. 10 mL,

placement at -25°C afforded a crop of colourless cubes suitable for X-ray diffraction structure determination. Yield = 78 mg (35%), m.p. 103-105 °C (dec.). ^{1}H NMR (400 MHz, C_6D_6) δ 1.06 (br d, $^{3}J_{HH}$ = 6.7 Hz, 24H, CH(CH_3)$_2$), 1.15 (br d, $^{3}J_{HH}$ = 6.7 Hz, 24H, CH(CH_3)$_2$), 3.43 (sept, $^{3}J_{HH}$ = 6.7 Hz, 8H, CH(CH$_3$)$_2$), 7.01-7.12 (m, 12H, *m*- and *p*-Ar*H*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 23.6, 24.3 (CH(*C*H$_3$)$_2$), 28.9 (*C*H(CH$_3$)$_2$), 124.0, 128.2 (Ar*C*H), 139.8, 144.9 (Ar*C*). Elemental analysis calculated (%) for $C_{48}H_{68}InClN_6$: C, 65.56; H, 7.89; N, 9.56. Found: C, 63.91; H, 8.09; N, 8.51%.

[InI(N$_3$Dipp$_2$)$_2$] (10)

Cold (-78°C) THF (25 mL) was added to a mixture of Dipp$_2$N$_3$H (366 mg, 1.0 mmol), [NaN(SiMe$_3$)$_2$] (184 mg, 1.0 mmol) and InI (240 mg, 1.0 mmol). The resultant slurry was allowed to warm to ambient temperature overnight. The colourless supernatant was then filtered to remove a large amount of grey precipitate. The solvent was removed *in vacuo* and the colourless residue was extracted with hexane (40 mL). The volume of the solution was reduced to *ca*. 20 mL under vacuum, and the obtained precipitate was redissolved by slight warming. Storage at ambient temperature overnight afforded large colourless cubes suitable for X-ray diffraction structure determination. Yield = 48 mg (13%), m.p. 206-210°C (dec.). ^{1}H NMR (250 MHz, C_6D_6) δ 1.06 (d, $^{3}J_{HH}$ = 6.7 Hz, 24H, CH(CH_3)$_2$), 1.16 (d, $^{3}J_{HH}$ = 6.7 Hz, 24H, CH(CH_3)$_2$), 3.43 (sept, $^{3}J_{HH}$ = 6.7 Hz, 8H, CH(CH$_3$)$_2$), 7.03-7.14 (m, 12H, *m*- and *p*-Ar*H*). ^{13}C{^{1}H} NMR (63 MHz, C_6D_6) δ 23.7, 24.8 (CH(*C*H$_3$)$_2$), 29.1 (*C*H(CH$_3$)$_2$), 124.0, 128.2 (Ar*C*H), 140.2, 144.9 (Ar*C*). Elemental analysis calculated (%) for $C_{48}H_{68}InIN_6$: C, 59.38; H, 7.06; N, 8.66. Found: C, 59.60; H, 7.18; N, 8.55%.

[{GaI(N$_3$Dipp$_2$)}$_2$] (11)

Cold (-78°C) toluene (30 mL) was added to a mixture of **7** (300 mg, 0.75 mmol) and "GaI" (300 mg, 1.53 mmol). The resultant light brown slurry was allowed to warm to ambient temperature over 4 h leading to the formation of a black precipitate. After a further 4 h, the mixture was filtered and the filtrate dried *in vacuo*. The resultant pale-yellow solid was recrystallised from the minimum amount of hexane at -25°C, which afforded colourless prisms suitable for X-ray diffraction structure determination. Yield = 180 mg (42%), m.p. 176-182°C (dec.). ^{1}H NMR (300 MHz, C_6D_6) δ 1.14 (d, $^{3}J_{HH}$ = 6.7 Hz, 24H, CH(CH_3)$_2$), 1.29 (d, $^{3}J_{HH}$ = 6.7 Hz, 24H, CH(CH_3)$_2$), 3.74 (sept, $^{3}J_{HH}$ = 6.7 Hz, 8H, CH(CH$_3$)$_2$), 7.03-7.11 (m, 12H, *m*- and *p*-Ar*H*). ^{13}C{^{1}H} NMR (76 MHz, C_6D_6)

δ 24.6, 25.3 (CH(CH$_3$)$_2$), 29.2 (CH(CH$_3$)$_2$), 124.2, 128.7 (ArCH), 138.8, 145.5 (ArC). Elemental analysis calculated (%) for $C_{48}H_{68}Ga_2I_2N_6 \cdot C_6H_{14}$: C, 53.67; H, 6.84; N, 6.95. Found: C, 54.79; H, 7.42; N, 6.71%.

[GaI(N$_3$Dipp$_2$)$_2$] (12)

Cold (-78°C) toluene (30 mL) was added to a mixture of **7** (200 mg, 0.50 mmol) and "GaI" (120 mg, 0.61 mmol). The resultant light brown slurry was allowed to warm to ambient temperature over 4 h leading to the formation of a black precipitate. After a further 4 h, the mixture was filtered and the filtrate dried *in vacuo*. The resultant brown solid was recrystallised from the minimum amount of hexane at -25°C, which afforded pale yellow blocks. Yield = 88 mg (48%), m.p. 188-192°C (dec.). ^{1}H NMR (300 MHz, C_6D_6) δ 1.06 (d, $^3J_{HH}$ = 6.7 Hz, 24H, CH(CH_3)$_2$), 1.13 (d, $^3J_{HH}$ = 6.7 Hz, 24H, CH(CH_3)$_2$), 3.40 (sept, $^3J_{HH}$ = 6.7 Hz, 8H, CH(CH$_3$)$_2$), 7.03-7.11 (m, 12H, *m*- and *p*-ArH). ^{13}C{^{1}H} NMR (76 MHz, C_6D_6) δ 23.7, 24.3 (CH(CH$_3$)$_2$), 29.2 (CH(CH$_3$)$_2$), 123.9, 124.2 (ArCH), 144.6, 145.6 (ArC). Elemental analysis calculated (%) for $C_{48}H_{68}GaIN_6$: C, 62.28; H, 7.40; N, 9.08. Found: C, 62.69; H, 7.53; N, 8.99%.

[GaCl(N$_3$Dipp$_2$)$_2$] (13)

Cold (-78°C) toluene (20 mL) was added to a mixture of **5** (180 mg, 0.50 mmol) and Ga[GaCl$_4$] (70 mg, 0.25 mmol). The resultant light brown slurry was allowed to warm to ambient temperature over 8 h leading to the formation of a black precipitate. The mixture was filtered and the filtrate dried *in vacuo*. The resultant pale-yellow solid was then extracted with hexane (40 mL), concentrated to *ca*. 10 mL, placement at -25°C overnight afforded a crop of colourless crystals suitable for X-ray diffraction structure determination. Yield = 55 mg (26%). ^{1}H NMR (400 MHz, C_6D_6) δ 1.04 (d, $^3J_{HH}$ = 6.7 Hz, 24H, CH(CH_3)$_2$), 1.13 (d, $^3J_{HH}$ = 6.7 Hz, 24H, CH(CH_3)$_2$), 3.46 (sept, $^3J_{HH}$ = 6.7 Hz, 8H, CH(CH$_3$)$_2$), 7.04-7.12 (m, 12H, *m*- and *p*-ArH). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 23.8, 24.4 (CH(CH_3)$_2$), 28.9 (CH(CH$_3$)$_2$), 124.1, 128.5 (ArCH), 139.3, 145.4 (ArC). Elemental analysis calculated (%) for $C_{48}H_{68}GaClN_6$: C, 69.10; H, 8.22; N, 10.07. Found: C, 68.99; H, 8.23; N, 10.06%.

[GaH(N$_3$Dipp$_2$)$_2$] (14)

A solution of Dipp$_2$N$_3$H (645 mg, 1.76 mmol) in diethyl ether (10 mL) was added dropwise to a cool (-10°C) solution of LiGaH$_4$ (ca. 0.88 mmol) in diethyl ether (30 mL).

Gas evolution was observed immediately. After 2 h, the reaction was allowed to warm to ambient temperature. The solvent was removed *in vacuo* and the colourless residue was extracted with warm hexane (100 mL). Concentration *in vacuo* followed by cooling to -25°C afforded colourless cubes suitable for X-ray diffraction structure determination. Yield = 130 mg (19%), m.p. 190-210°C (dec.). ^{1}H NMR (400 MHz, C_6D_6) δ 1.06 (d, $^{3}J_{HH}$ = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 1.12 (d, $^{3}J_{HH}$ = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 3.40 (sept, $^{3}J_{HH}$ = 6.8 Hz, 8H, C*H*(CH$_3$)$_2$), 6.59 (br s, 1H, Ga-*H*), 7.04-7.15 (m, 12H, Ar*H*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 23.7, 24.3 (CH(*C*H$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 123.9, 127.7 (Ar*C*H), 140.6, 144.6 (Ar*C*). IR (Nujol, cm^{-1}) 1912 (sh s, Ga-H). Elemental analysis calculated (%) for $C_{48}H_{69}GaN_6$: C, 72.08; H, 8.70; N, 10.51. Found: C, 72.52; H, 8.77; N, 10.51%.

[InH(N$_3$Dipp$_2$)$_2$] (15)

A solution of Dipp$_2$N$_3$H (760 mg, 2.0 mmol) in diethyl ether (30 mL) was added dropwise to a solution of LiInH$_4$ (ca. 1.0 mmol) in diethyl ether (40 mL) at -78°C. The reaction mixture was allowed to slowly warm to ambient temperature over 6 h. The mixture was filtered and the solvent removed *in vacuo*. The resultant colourless residue was extracted into hexane (40 mL). Concentration *in vacuo* followed by cooling to -25°C afforded colourless cubes suitable for X-ray diffraction structure determination. Yield = 380 mg (45%); m.p. 164-172°C (dec.). ^{1}H NMR (400 MHz, C_6D_6) δ 1.06 (d, $^{3}J_{HH}$ = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 1.14 (d, $^{3}J_{HH}$ = 6.8 Hz, 24H, CH(C*H*$_3$)$_2$), 3.39 (sept, $^{3}J_{HH}$ = 6.8 Hz, 8H, C*H*(CH$_3$)$_2$), 7.04-7.15 (m, 12H, *m*- and *p*-Ar*H*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 23.5, 24.4 (CH(*C*H$_3$)$_2$), 28.8 (*C*H(CH$_3$)$_2$), 123.8, 127.4 (Ar*C*H), 141.3, 144.2 (Ar*C*). IR (Nujol, cm^{-1}) 1747 (sh s, In-H). Elemental analysis calculated (%) for $C_{48}H_{69}InN_6$: C, 68.23; H, 8.23; N, 9.95. Found: C, 67.96; H, 8.27; N, 9.91%.

[TlCl(N$_3$Dipp$_2$)$_2$] (16)

A solution of **5-(OEt$_2$)$_2$** (180 mg, 0.50 mmol) in diethyl ether (20 mL) was added dropwise to a suspension of TlCl$_3$ (90 mg, 0.25 mmol) in diethyl ether (20 mL). Upon complete addition, the solution changed colour from pale yellow to bright orange with the formation of a colourless precipitate. The reaction mixture was filtered after 12 h and the solvent removed *in vacuo*. The resulting orange residue was then extracted into hexane (2×30 mL), concentrated and cooled to ambient temperature to afford a crop of orange cubes suitable for X-ray diffraction structure determination. Yield = 110

mg (45%), 147-148°C (dec.).^{1}H NMR (400 MHz, C_6D_6) δ 1.12 (d, $^{3}J_{HH}$ = 6.8 Hz, 48H, CH(CH_3)$_2$), 3.52 (overlapping sept, $^{3}J_{HH}$ = 6.8 Hz, 8H, CH(CH$_3$)$_2$), 7.00-7.14 (m, 12H, *m*- and *p*-Ar*H*). ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ 23.7, 23.9 (CH(*C*H$_3$)$_2$) 28.8, 29.0 (*C*H(CH$_3$)$_2$), 123.7, 124.1, 128.8 (Ar*C*H), 140.1, 140.4, 145.2, 145.6 (Ar*C*). IR (Nujol, cm^{-1}) 3062 (m), 1587 (m), 1324 (br s), 1256 (m, N=N), 1183 (s), 1098 (m), 1058 (m), 832 (w), 799 (s), 770 (s), 754 (s), 727 (s), 665 (w), 623 (w). Elemental analysis calculated (%) for $C_{48}H_{68}TlClN_6$: C, 59.50; H, 7.07; N, 8.67. Found: C, 59.77; H, 7.13; N, 8.72%.

[TlBr(N$_3$Dipp$_2$)$_2$] (17)

Bromine (300 µL, 5.8 mmol) was added dropwise to a stirred suspension of TlBr (298 mg, 1.05 mmol) in THF (20 mL). The resultant red solution was stirred for 1 h at which point no residual solid was evident. The solvent and excess bromine were removed *in vacuo* to afford a viscous pale brown oil that was redissolved in THF (30 mL). A solution of **5-THF$_2$** (770 mg, 2.07 mmol) in THF (10 mL), was then added at ambient temperature. The reaction mixture changed colour from brown to red with the formation of a colourless precipitate. After 12 h, the solvent was removed *in vacuo* and the residue extracted with toluene (2×20 mL). Drying *in vacuo* followed by extraction of the red solid into hexane (30 mL) concentration *in vacuo* and cooling to -25°C, afforded a small number of orange cubes suitable for X-ray diffraction structure determination and characterisation by NMR spectroscopy. ^{1}H NMR (300 MHz, C_6D_6) δ 1.12 (d, $^{3}J_{HH}$ = 6.8 Hz, 48H, CH(CH_3)$_2$), 3.51 (sept, $^{3}J_{HH}$ = 6.8 Hz, 8H, CH(CH$_3$)$_2$), 6.97-7.14 (m, 12H, *m*- and *p*-Ar*H*). ^{13}C{^{1}H} NMR (76 MHz, C_6D_6) δ 23.8, 24.1 (CH(*C*H$_3$)$_2$), 28.8, 28.9 (*C*H(CH$_3$)$_2$), 123.6, 124.2, 128.8 (Ar*C*H), 140.1, 140.6, 145.2, 145.7 (Ar*C*). Insufficient material was available for elemental analysis to be conducted.

[TlCl(Fiso)$_2$] (18)

A solution of [NaFiso] (364 mg, 0.94 mmol) in THF (8 mL) was added to a solution of $TlCl_3$ (150 mg, 0.48 mmol) in THF (5 mL) and allowed to stir for 1 hour, resulting in a bright orange cloudy solution. THF was removed *in vacuo* and the orange residue was extracted into toluene (15 mL). The mixture was filtered, concentrated to incipient crystallization (approx. 5 mL) and allowed to stand at -20°C overnight, affording small orange cubes for X-ray diffraction structure determination. Yield = 274 mg (60%). ^{1}H NMR (600 MHz, C_6D_6) δ 1.11 (br s, 48H, CH_3), 3.50 (br m, 8H, CH(CH$_3$)$_2$), 6.95-7.13

(m, 12H, ArC*H*), 8.25 (d, $^{3}J_{TlH}$ = 2044 Hz, 2H, NC*H*N). $^{13}C\{^{1}H\}$ NMR (150 MHz, C_6D_6) δ 23.6 (*C*H_3), 28.1 (*C*H(CH_3)$_2$), 123.4, 126.5 (Ar*C*H), 139.4, 140.2 (Ar*C*), 157.0 (N*C*HN).

[Ge(N_3Dipp$_2$)$_2$] (19)

THF (10 mL) was added to a solid mixture of **7** (133 mg, 0.33 mmol) and [$GeCl_2$(Dioxane)] (41 mg, 0.18 mmol) and stirred for 30 mins. THF was removed *in vacuo* and the colourless residue was extracted into hexane (20 mL). Filtration followed by concentrated to incipient crystallization (approx. 5 mL) and slow cooling to -20°C afforded colourless blocks suitable for X-ray diffraction structure determination. Yield = 891 mg (63%). ^{1}H NMR (400 MHz, C_6D_6) δ 1.09 (d, $^{3}J_{HH}$ = 6.8 Hz, 24H, C*H*$_3$), 1.13 (d, $^{3}J_{HH}$ = 6.8 Hz, 24H, C*H*$_3$), 3.41 (sept, $^{3}J_{HH}$ = 6.8 Hz, 8H, C*H*(CH_3)$_2$), 7.06-7.13 (m, 12H, ArC*H*). $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6) δ 23.9, 25.3 (*C*H_3), 29.3 (*C*H(CH_3)$_2$), 123.9 (Ar*C*H), 141.6, 144.8 (Ar*C*).

[Sn(N_3Dipp$_2$)$_2$] (20)

Et_2O (10 mL) was added to a solid mixture of **7** (100 mg, 0.25 mmol) and $SnCl_2$ (47 mg, 0.25 mmol) and stirred for 30 mins, resulting in a cloudy yellow solution. Filtration followed by concentrated to incipient crystallization (approx. 5 mL) and slow cooling to -20°C afforded yellow blocks suitable for X-ray diffraction structure determination. Yield = 89 mg (42%). ^{1}H NMR (400 MHz, C_6D_6) δ 1.12 (d, $^{3}J_{HH}$ = 6.9 Hz, 48H, C*H*$_3$), 3.42 (sept, $^{3}J_{HH}$ = 6.9 Hz, 8H, C*H*(CH_3)$_2$), 7.08 (m, 12H, ArC*H*). $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6) δ 24.5 (br d, *C*H_3), 29.2 (m, $^{4}J_{SnC}$ = 15.4 Hz, *C*H(CH_3)$_2$), 123.8, 127.3 (Ar*C*H), 142.6, 144.2 (Ar*C*).

[SnBr(N_3Dipp$_2$)(IEt)] (21)

A solution of [Sn(N{$SiMe_3$}$_2$)$_2$] (228 mg, 0.52 mmol) in Et_2O (15 mL) was added to solid IEt·HBr (106 mg, 0.52 mmol) and allowed to stir for 3 hours, during which time the coloured solution slowly became a colourless suspension. A solution of $Dipp_2N_3H$ (189 mg, 0.517 mmol) in Et_2O (5 mL) was then added dropwise and allowed to stir for a further 1 hour. Filtration followed by slow cooling to -20°C afforded large yellow blocks suitable for X-ray diffraction structure determination. Yield = 163 mg (46%). ^{1}H NMR (400 MHz, C_6D_6) δ 0.90 (t, $^{3}J_{HH}$ = 6.9 Hz, 6H, CH_2CH_3), 1.27 (d, $^{3}J_{HH}$ = 6.9 Hz, 24H, C*H*$_3$), 3.53 (sept, $^{3}J_{HH}$ = 6.9 Hz, 4H, C*H*(CH_3)$_2$), 3.92 (br s, 4H, CH_2CH_3), 5.88 (s, 2H,

NC*H*), 7.20 (br s, 6H, ArC*H*). $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6) δ 15.9 (CH_2CH_3), 24.9 (CH_3), 28.9 ($CH(CH_3)_2$), 45.3 (CH_2CH_3), 120.2 (NCH), 123.5, 126.7 (ArCH), 143.6, 144.8 (ArC), 178.7 (SnC).

Attempted synthesis of $[SnCl(N_3Dipp_2)\cdot W(CO)_5]$

A solution of **7** (120 mg, 0.297 mmol) in THF (8 mL) was added dropwise to a solution of $[(THF)_2SnCl_2\cdot W(CO)_5]$ (175 mg, 0.299 mmol) in THF (8 mL) at room temperature and was stirred overnight, resulting in a white precipitate. THF was removed *in vacuo* and the residue was extracted into toluene (15 mL). The resulting brown mixture was filtered, the filtrate concentrated *in vacuo* (3 mL) and cooled to -20°C, affording yellow crystals suitable for X-ray diffraction structure determination. Further standing of the filtrate for a prolonged period (several weeks) also resulted in the co-crystallisation of colourless crystals of the KCl included product, $\{W(CO)_5(\mu\text{-}CO)K(\mu\text{-}Cl)_2Sn(N_3Dipp_2)\}_n$. Further characterisation was frustrated by the formation of a sticky brown residue from which the crystals could not be separated.

X-ray Crystallography

General details

Crystalline samples were mounted on MiTeGen micromounts in type NVH immersion oil. Data for **9** and **10** were collected on an Oxford Xcalibur^{TM}2 diffractometer with an Enhance (Mo) X-ray Source (λ = 0.71073 Å) and Sapphire2 CCD at 112(2) K. Data for all other samples were collected on a Bruker Kappa Apex II diffractometer with a Bruker Quazar Multilayer Optics $Mo_{K\alpha}$ X-ray micro source (λ = 0.71073 Å) and a Bruker APEX-II CCD at 150(2) K or 180(2) K (**8**). Corrections for absorption was carried out using CrysAlisPro[S11] or SADABS.[S12] The structures were solved with SHELXT[S13] and refined with SHELXL[S14] using the interface OLEX2.[S15] Hydrogen atoms were refined in calculated positions (riding model) for all compounds excepting hydrides in **14** and **15** which were located in the difference map and refined isotropically. A summary of crystallographic data can be found in the tables below.

Further Comments on Individual Structures

Compound 1: Checkcif alerts are observed for elevated Hirshfeld Test Diff between the Rh atoms and the carbon atoms of the bridging CO moiety. Attempts to model these carbon atoms as disordered over multiple sites was unsuccessful.

Compound 2: Data at high Bragg angles ($\theta > 20.8°$) was weak and not employed in refinement. The resultant structure is of poor quality and is included as confirmation of atom connectivity.

Compound 6(THF)$_3$: Single crystals rapidly degraded upon inspection likely due to desolvation. Data collected was weak and the quality of this structure is poor. X-ray diffraction data for this compound has been included as confirmation of connectivity and for provision of unit cell parameters only.

Compound 6(DME)$_2$: Single crystals rapidly degraded upon inspection likely due to desolvation. Data was weak and the quality of this structure is poor.

Compound 7(THF): The compound forms a 1D polymer composed of approximately half $KL_2K(THF)_2$ polymers and $KL_2K(THF)_1$ polymers. The second molecule of THF

lies on a special position in the cell. The former exhibit the anticipated N,Ar coordination and to the KL_2 units. The latter exhibit two distinct isomeric forms of the triazenide, each modelled as disordered over two sites, one as per the THF_2 species, and the other pi-coordinating but with rotation of the NDipp group to enable N,N' chelation of the 'cationic' K (anionic K = that in the pi bound unit).

Compound 8: Refined as an inversion twin.

Compound 10: The final Fourier difference map revealed notable peaks of electron density proximal to indium atom and diametrically opposed across the atom at ca.1.00 Å, these are of each of magnitude ca. 2 e $Å^{-3}$. In addition, a positive residual density (ca. 2 e $Å^{-3}$) on the indium was observed. Twinning was investigated, but twin scale factors refine to zero for all sensible twin laws. The locations of the electron densities are such that a chemically sensible disorder model could not be generated. These are therefore attributed to Fourier truncation errors.

Compound 11: Data was weak and incomplete (92% to θ = 25°). The quality of this structure is poor and is included as confirmation of connectivity and for provision of unit cell parameters only.

The X-ray crystal structures of compounds **19** and **20** were recently reported by Johnson.[S16] The structure of **19** reported herein is superior to that reported by Johnson, whilst the structure of **20** reported herein is inferior to that reported by Johnson.

Compound 21: The asymmetric unit contains four unique molecules.

Compound $[(Dipp_2N_3)SnCl{\cdot}W(CO)_5]{\cdot}KCl$: The Fourier difference map revealed large peaks of electron density proximal to W2 and Sn2. Twinning was investigated, but a suitable twin law was not found. W2 and Sn2 were modelled as disordered over two sites, with occupancies refining to 0.78/0.22. Residual peaks of electron density are noted proximate to these atoms. Attempts to extend this disorder model to other atoms of the fragment was not attempted.

Compound $[Rh_2(CO)_2(N_3Dipp_2)_2(H_2NDipp_2)]$: 1.5 hexane molecules were modelled in per asymmetric unit, with the aid of the FragmentDB module. Several Checkcif level A and B alerts are associated with these solvent molecules.

Molecular Structures

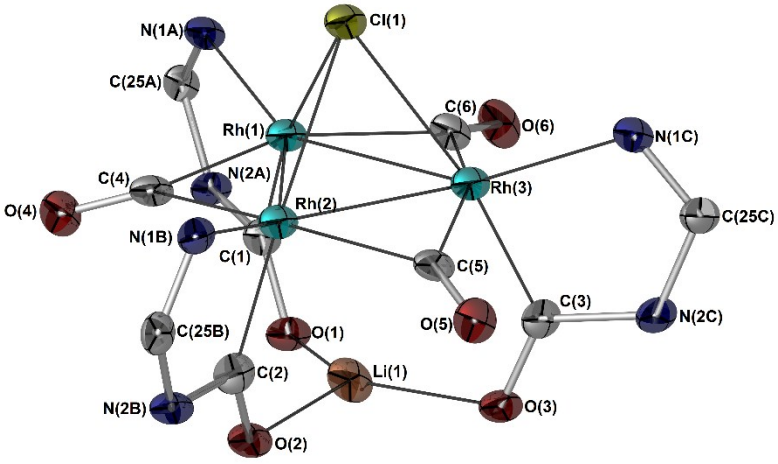

Figure S1. Molecular structure (50% displacement ellipsoids) of **2**. All Dipp groups and hydrogen atoms removed for clarity.

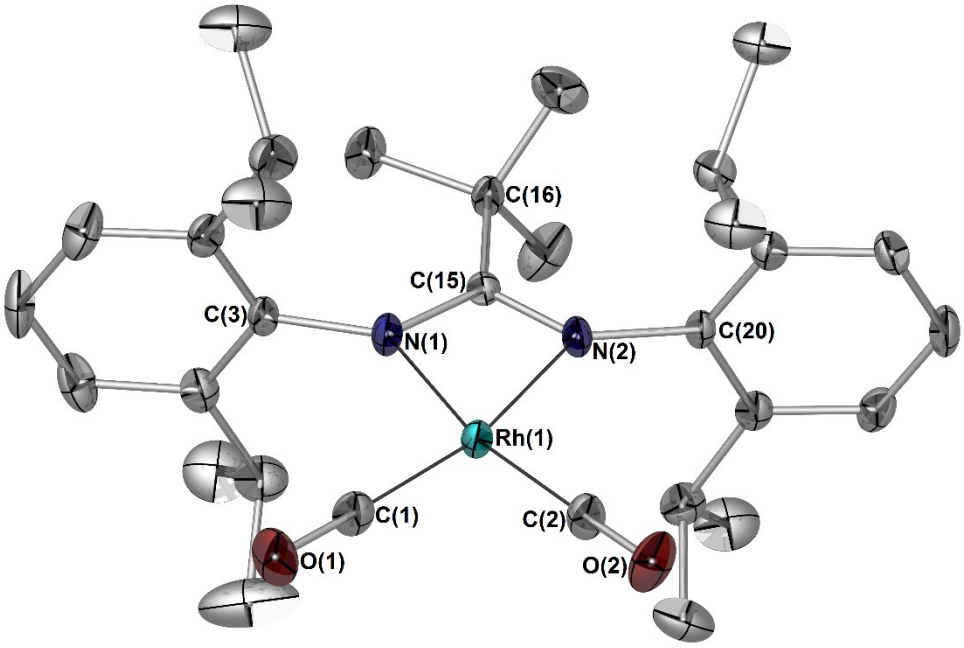

Figure S2. Molecular structure (50% displacement ellipsoids) of **[(Piso)Rh(CO)$_2$]**. All hydrogen atoms removed for clarity.

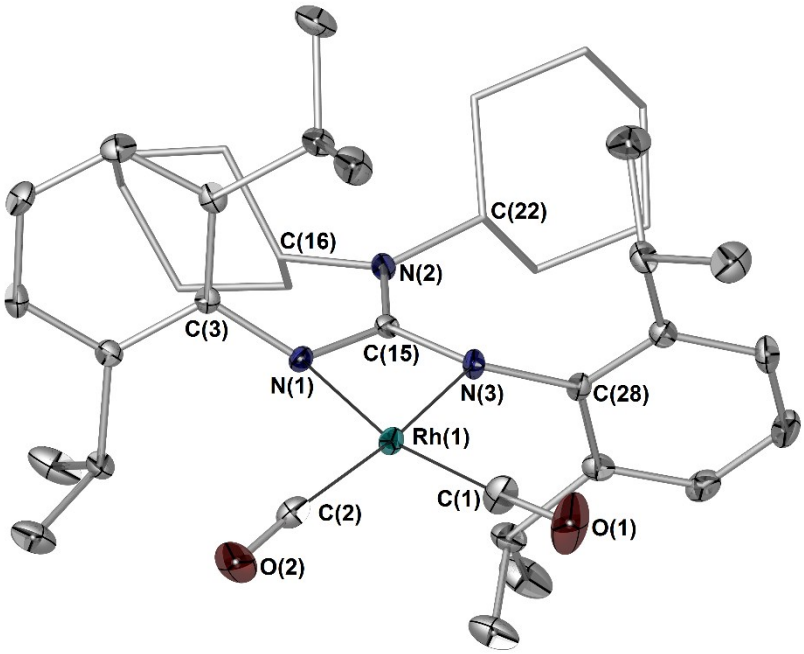

Figure S3. Molecular structure (50% displacement ellipsoids) of **[(Giso)Rh(CO)$_2$]**. All hydrogen atoms removed and cyclohexyl groups depicted as wireframes for clarity.

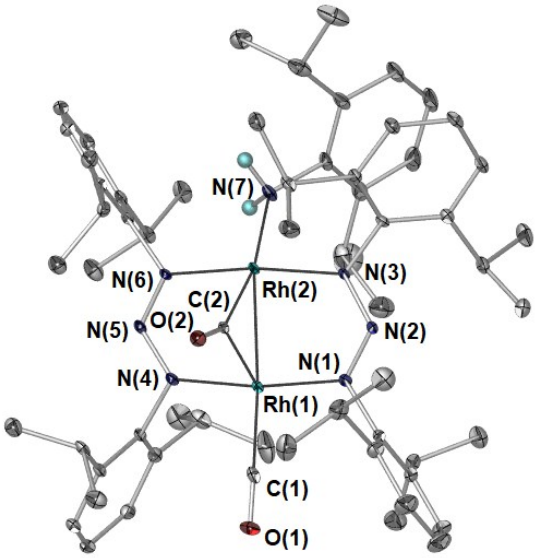

Figure S4. Molecular structure (25% displacement ellipsoids) of [{Rh(μ-N_3Dipp_2)}$_2$(μ-CO)(CO)(H_2NDipp)]. All hydrogen atoms excepting those on the aniline removed for clarity.

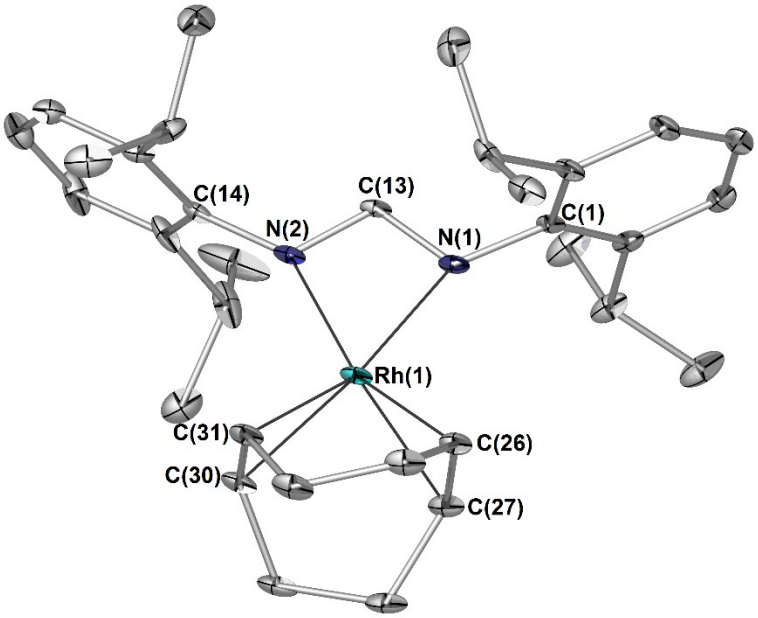

Figure S5. Molecular structure (20% displacement ellipsoids) of **4**. All hydrogen atoms removed for clarity.

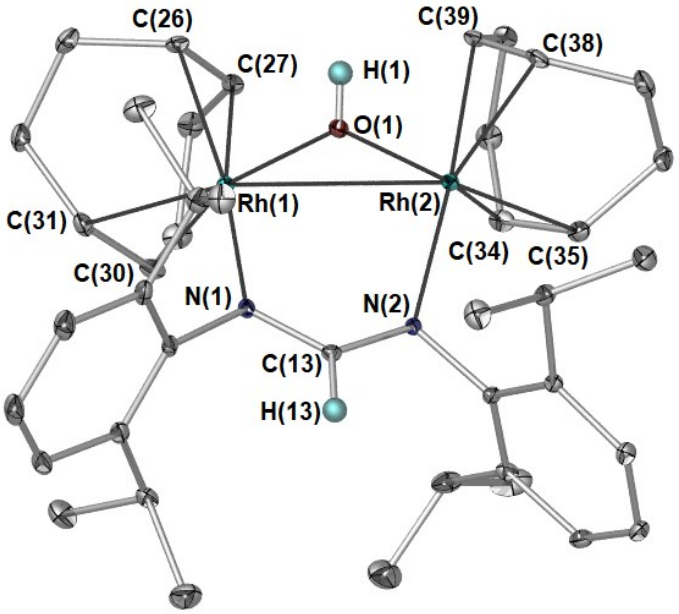

Figure S6. Molecular structure (25% displacement ellipsoids) of [{Rh(COD)}$_2$(μ-Fiso)(μ-OH)]. All hydrogen atoms excepting that on the formamidinate donor set and the OH removed for clarity.

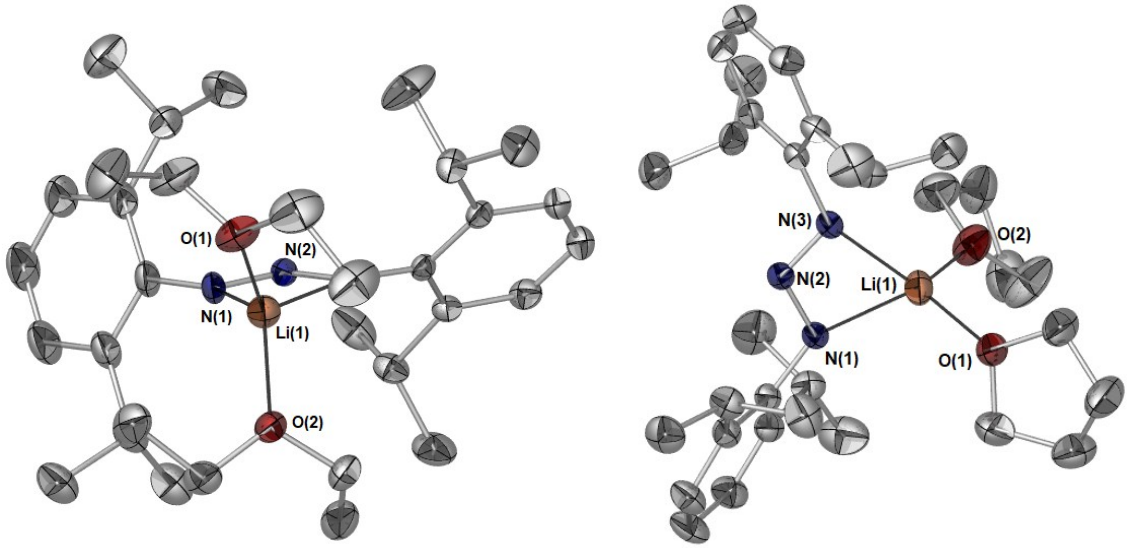

Figure S7. Molecular structures (50% displacement ellipsoids) of **5-(OEt_2)** (left) and **5-THF_2** (right). All hydrogen atoms and minor disorder components removed for clarity.

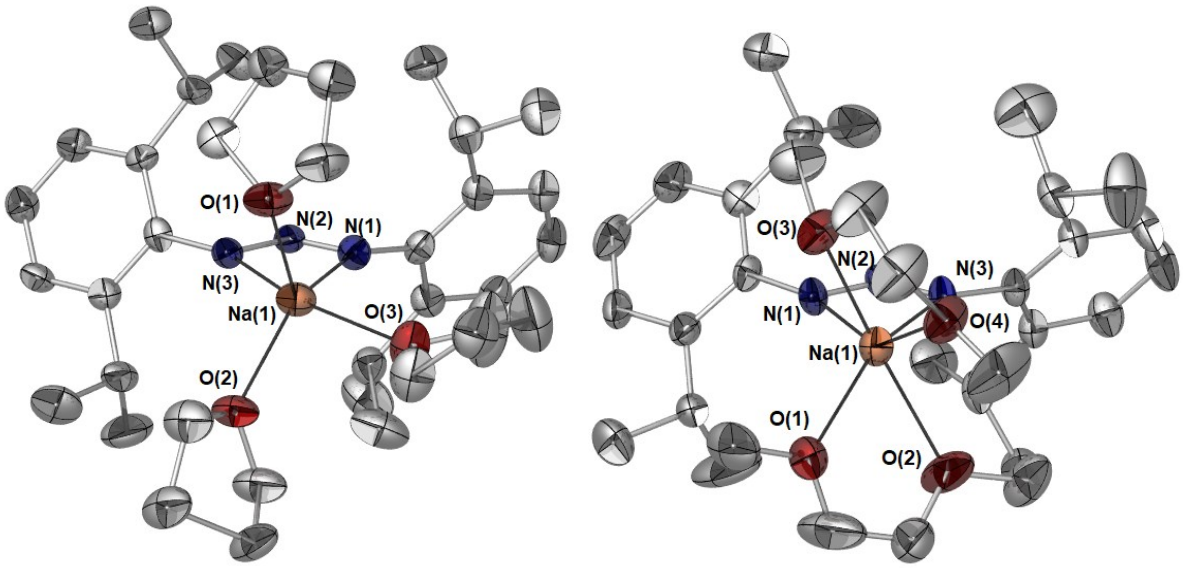

Figure S8. Molecular structures (50% displacement ellipsoids) of **6-THF_3** (left) and **6-DME_2** (right). All hydrogen atoms and minor disorder components removed for clarity.

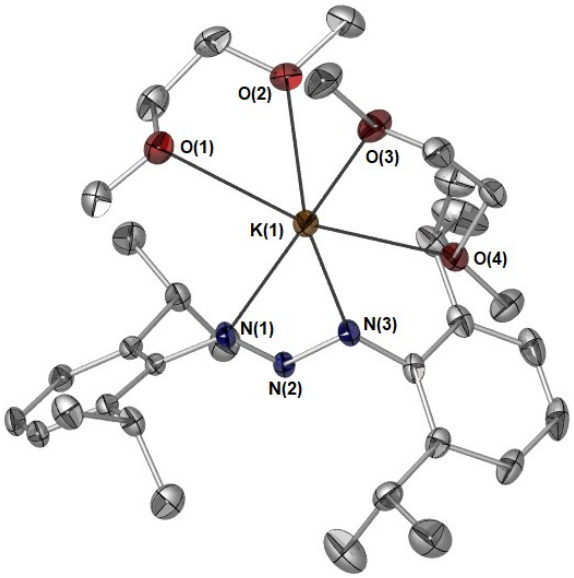

Figure S9. Molecular structure (50% displacement ellipsoids) of **7-DME$_2$**. All hydrogen atoms and minor disorder components removed for clarity.

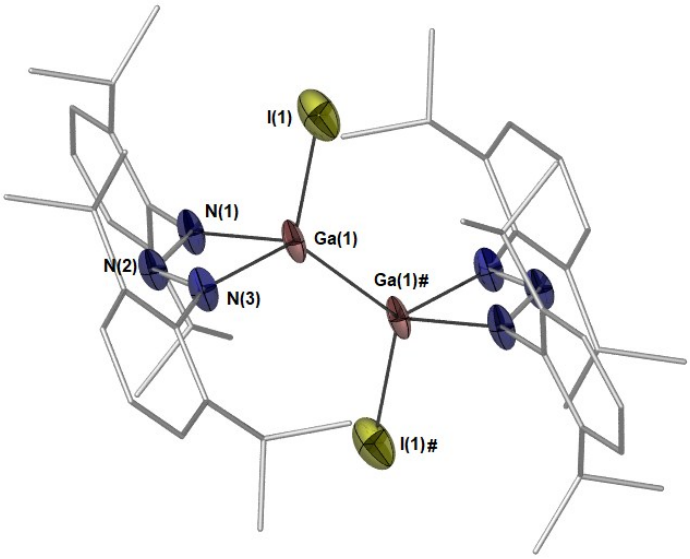

Figure S10. Molecular structure (50% displacement ellipsoids) of **9**. All hydrogen atoms and minor disorder components removed for clarity. Dipp groups depicted as wireframes for clarity. Symmetry operation to produce # atoms: 1-x,-y,1-z.

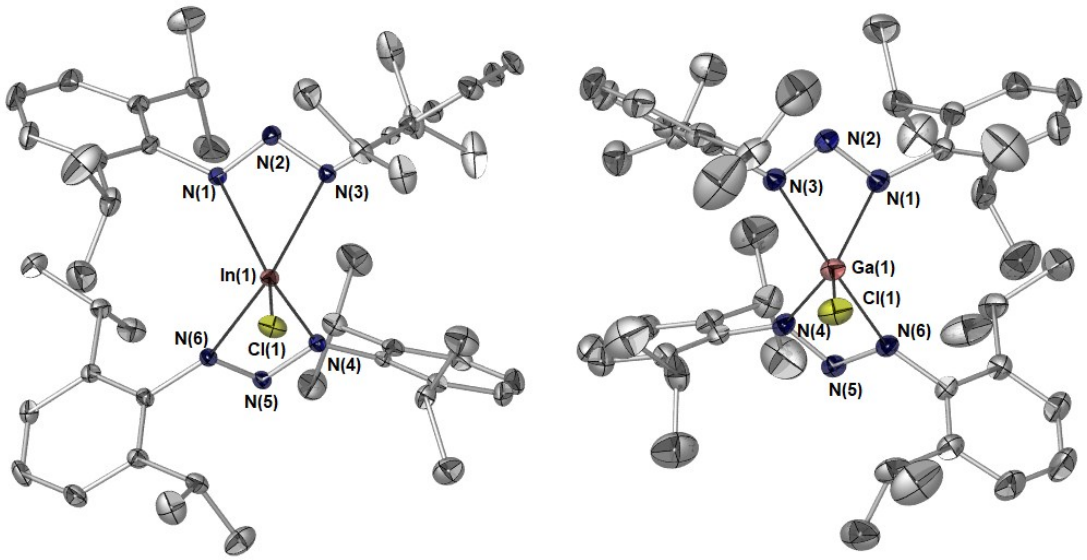

Figure S11. Molecular structure (50% displacement ellipsoids) of **9** (left) and **13** (right). All hydrogen atoms and minor disorder components removed for clarity.

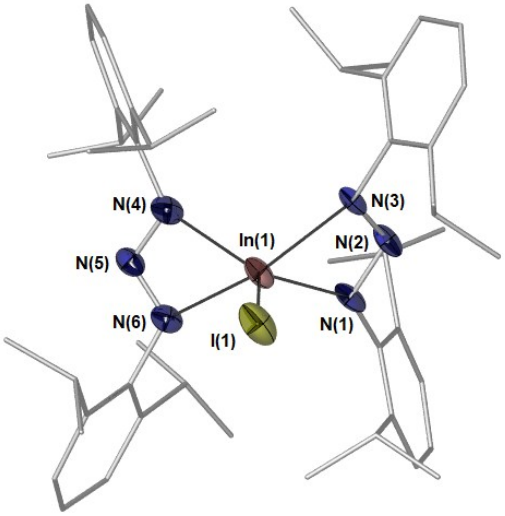

Figure S12. Molecular structure (50% displacement ellipsoids) of **10**. All hydrogen atoms and minor disorder components removed for clarity. Dipp groups depicted as wireframes for clarity.

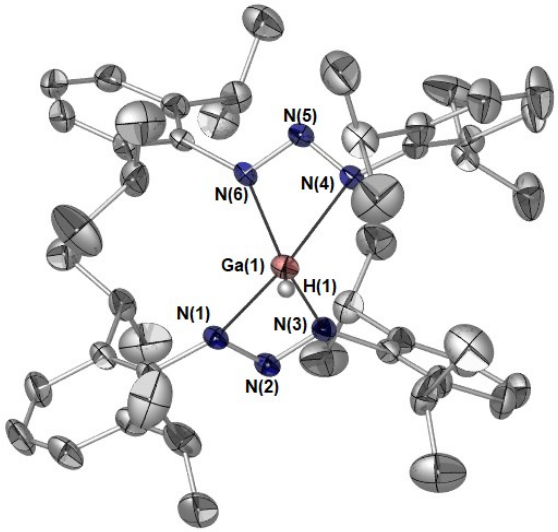

Figure S13. Molecular structure (50% displacement ellipsoids) of **14**. All hydrogen atoms and minor disorder components removed for clarity.

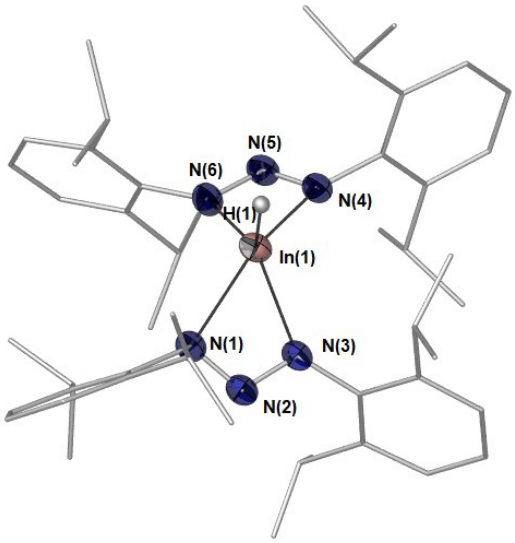

Figure S14. Molecular structure (50% displacement ellipsoids) of **15**. All hydrogen atoms and minor disorder components removed for clarity. Dipp groups depicted as wireframes for clarity.

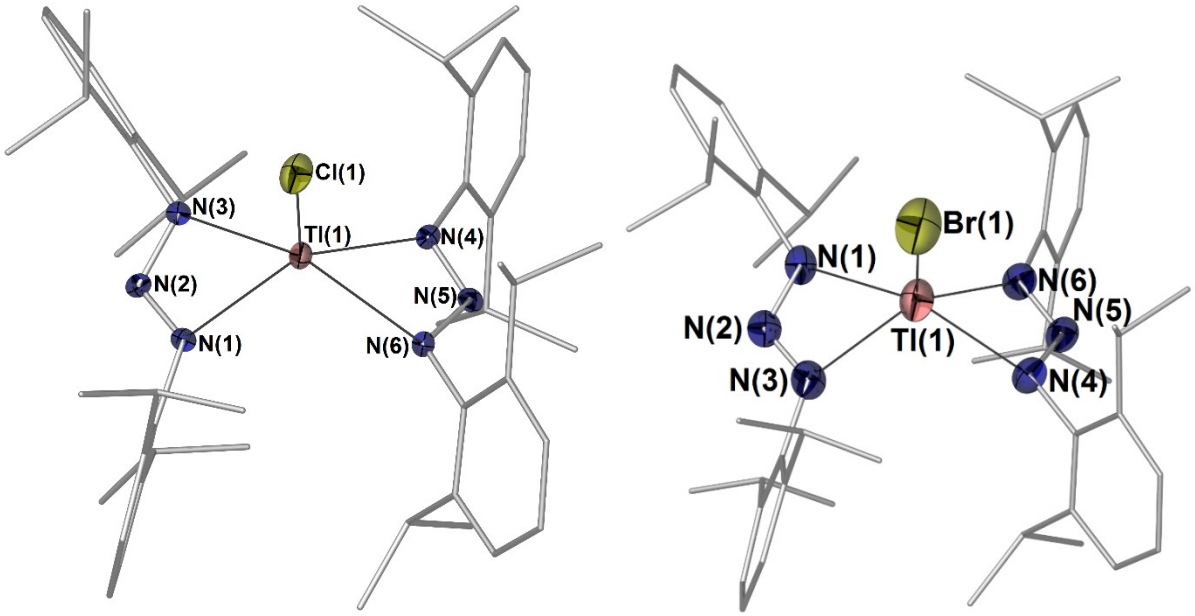

Figure S15. Molecular structure (50% displacement ellipsoids) of **16** (left) and **17** (right). All hydrogen atoms and minor disorder components removed for clarity. Dipp groups depicted as wireframes for clarity.

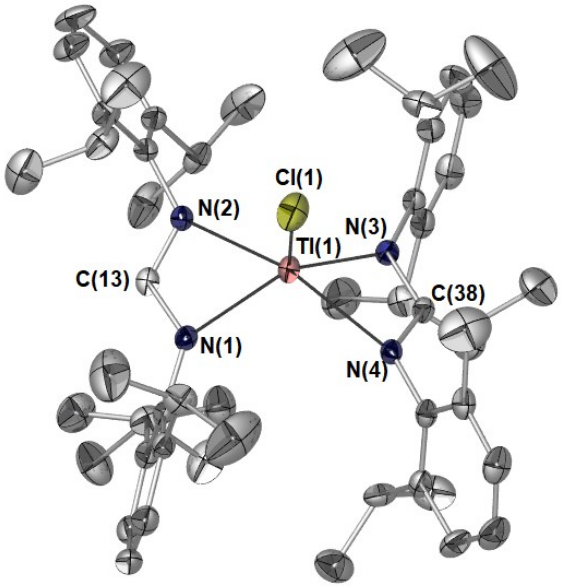

Figure S16. Molecular structure (50% displacement ellipsoids) of **18**. All hydrogen atoms removed for clarity.

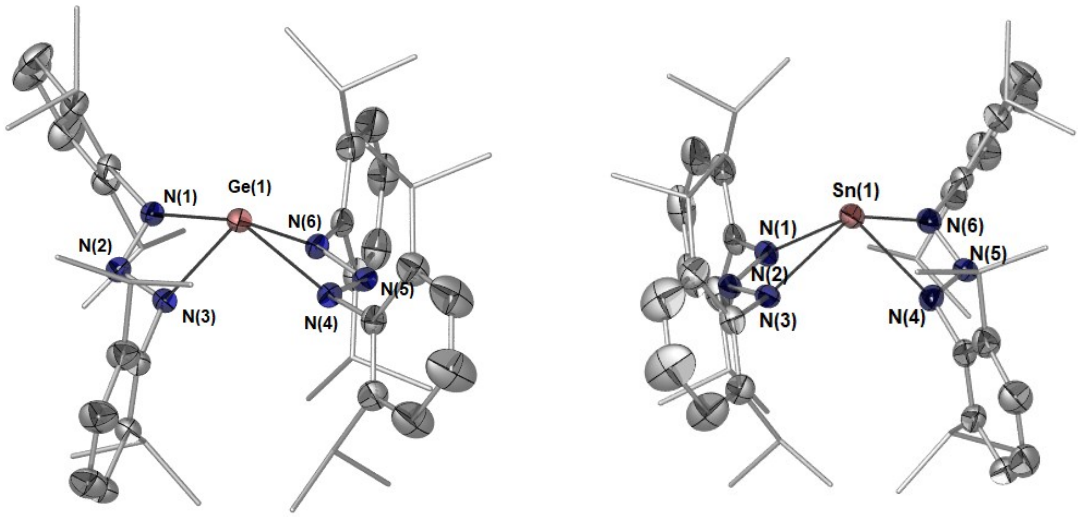

Figure S17. Molecular structure (50% displacement ellipsoids) of **19** (left) and **20** (right). All hydrogen atoms and minor disorder components removed for clarity. Isopropyl groups depicted as wireframes for clarity.

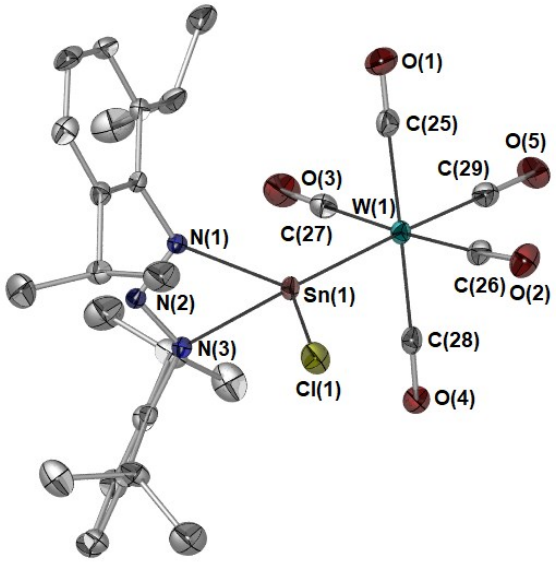

Figure S18. Molecular structure (50% displacement ellipsoids) of $[SnCl(N_3Dipp_2)\cdot W(CO)_5]$. All hydrogen atoms and minor disorder components removed for clarity. Atoms with a # suffix are symmetry generated.

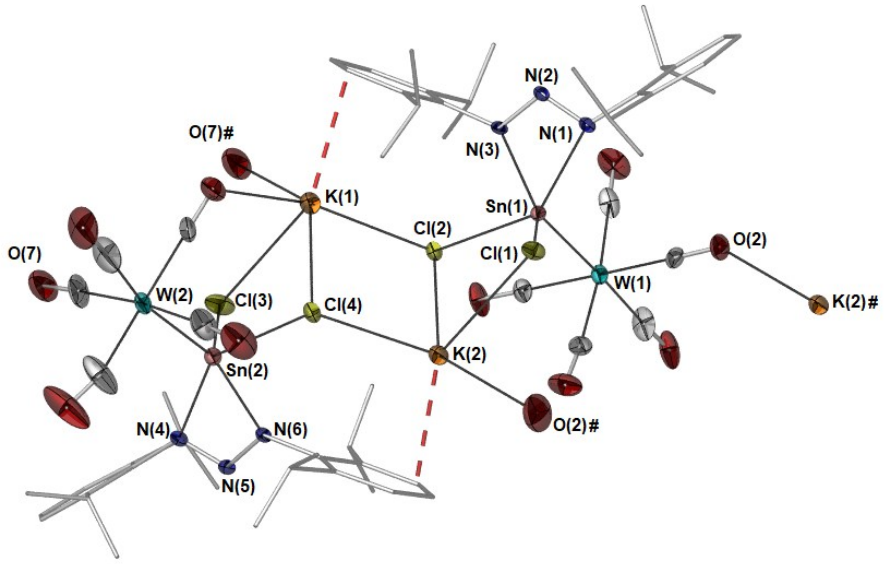

Figure S19. Molecular structure (25% displacement ellipsoids) of $\{W(CO)_5(\mu\text{-}CO)K(\mu\text{-}Cl)_2Sn(N_3Dipp_2)\}_n$. All hydrogen atoms and minor disorder components removed for clarity. Atoms with a # suffix are symmetry generated.

	1	**2**	**[(Piso)Rh(CO)$_2$]**	**[(Giso)Rh(CO)$_2$]**	**3**	**4**
empirical formula	$C_{52}H_{68}N_6O_4Rh_2$	$C_{81}H_{105}N_6ClLiO_2Rh_2$	$C_{31}H_{43}N_2O_2Rh$	$C_{39}H_{56}N_3O_2Rh$	$C_{32}H_{46}N_3Rh$	$C_{32}H_{46}N_3Rh$
formula weight	1046.94	1609.82	578.58	701.77	575.63	574.63
crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic	triclinic
space group	*P*-1	*C*2/*c*	*P*-1	$P2_1/n$	*C*2/*c*	*P*-1
***a* (Å)**	13.2722(5)	34.876(3)	10.2807(4)	9.4904(4)	17.0526(8)	10.5092(6)
***b* (Å)**	13.4363(5)	26.438(3	10.9865(4)	18.2900(8)	8.8969(3)	11.2966(6)
***c* (Å)**	15.3662(7)	22.979(2)	14.6713(5)	20.8209	18.8292(8)	14.1488(7)
***α* (deg)**	81.307(2)	90	70.800(11)	90	90	93.648(2)
***β* (deg)**	74.676(2)	115.098(5)	79.7465(13)	99.416(2)	93.738(2)	102.187(2)
***γ* (deg)**	77.317(2)	90	74.6877(15)	90	90	113.466(2)
***V* (Å^3)**	2565.68(18)	19187(3)	1502.48(10)	3565.4(2)	2850.6(2)	1485.51(14)
Z	2	8	2	4	4	2
***ρ*(calcd) (g cm^{-3})**	1.355	1.115	1.279	1.307	1.341	1.285
***μ* (mm^{-1})**	0.691	0.582	0.596	0.516	0.624	0.589
***F*(000)**	1088	6688	608	1488	1216	608
reflections collected	39793	128648	21909	27965	20172	22600
unique reflections	11201	17113	5884	7766	3153	6536
R_{int}	0.0623	0.1887	0.0424	0.0431	0.0311	0.0676
R_1 [$I > 2\sigma(I)$]	0.0409	0.0706	0.0242	0.0280	0.0186	0.0460
wR_2 (all data)	0.0887	0.2245	0.0625	0.0689	0.0479	0.1134
GooF	1.041	0.960	1.055	1.036	1.119	1.059
largest peak and hole (e Å^{-3})	0.80 / -0.66	0.83 / -0.90	0.64 / -0.26	0.41 / -0.52	0.34 / -0.32	0.62 / -1.51
CCDC no.	1971987	1971988	1976265	1976266	1971989	1971990

	$[Rh_2(CO)_2(N_3Dipp_2)_2(H_2NDipp_2)]$	$[\{Rh(COD)\}_2(Fiso)(OH)]$	$5\text{-}(OEt_2)_2$	$5\text{-}THF_2$	$6\text{-}THF_3$	$6\text{-}DME_2$
empirical formula	$C_{71}H_{115}N_7O_2Rh_2$	$C_{41}H_{60}N_2ORh_2$	$C_{32}H_{54}LiN_3O_2$	$C_{32}H_{50}LiN_3O_2$	$C_{36}H_{58}NaN_3O_3$	$C_{32}H_{54}NaN_3O_4$
formula weight	1304.51	802.73	519.72	515.69	603.84	567.77
crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	*P*-1	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$
***a* (Å)**	13.5047(12)	15.7881(19)	16.5557(5)	18.8789(9)	10.105(3)	20.0231(15)
***b* (Å)**	14.7204(12)	13.8759(18)	11.0635(3)	18.6075(9)	14.969(5)	10.9042(8)
***c* (Å)**	18.3174(17)	17.064(2)	18.9451(6)	19.5150(8)	24.904(7))	33.135(3)
***α* (deg)**	85.510(4)	90	90	90	90	90
***β* (deg)**	76.563(4)	90.921(5)	104.915(1)	111.03(2)	99.173(16)	105.340(4)
***γ* (deg)**	84.116(4)	90	90	90	90	90
***V* (Å^3)**	3517.5(5)	3727.9(8)	3353.15(17)	6397.4(5)	3719.0(19)	6976.8(4)
Z	2	4	4	8	4	8
***ρ*(calcd) (g cm^{-3})**	1.232	1.426	1.029	1.071	1.078	1.081
***μ* (mm^{-1})**	0.516	0.916	0.063	0.066	0.078	0.081
***F*(000)**	1392	1672	1144	2256	1320	2480
reflections collected	48305	54865	39776	78234	21513	51336
unique reflections	15295	8211	7364	14123	6603	12438
R_{int}	0.0597	0.0310	0.0601	0.0923	0.1513	0.1518
R_1 [$I > 2\sigma(I)$]	0.0437	0.0237	0.0613	0.0621	0.0835	0.0780
wR_2 (all data)	0.1008	0.0581	0.1900	0.0917	0.2975	0.2454
GooF	1.025	1.031	1.030	1.034	0.914	0.978
largest peak and hole (e Å^{-3})	0.90 / -0.79	1.46 / -0.36	0.62 / -0.31	0.42 / -0.27	0.37 / -0.27	0.31 / -0.30
CCDC no.	1971991	1971992	1971993	1971994	1971995	1971996

	6-15C5	**7-THF$_{1.5}$**	**7-DME$_2$**	**7-18C6**	**8**	**9**	**10**
empirical formula	$C_{41}H_{62}NaN_3O_5$	$C_{57.5}H_{84}K_2N_6O_{1.5}$	$C_{32}H_{54}KN_3O_4$	$C_{39.5}H_{62}KN_3O_6$	$C_{48}H_{68}Tl_2N_6$	$C_{48}H_{68}ClInN_6$	$C_{48}H_{68}IInN_6$
formula weight	669.92	961.50	583.88	714.02	1137.82	879.35	968.78
crystal system	monoclinic	triclinic	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/n$	P-1	$P2_1/n$	P-1	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
***a* (Å)**	14.0109(15)	13.1068(9)	14.2751(5)	8.9780(6)	13.5767(5)	14.5014(4)	14.375(3)
***b* (Å)**	16.0444(13)	14.9847(10)	15.4085(5)	10.6630(9)	20.2026(7)	16.4263(4)	16.586(3)
***c* (Å)**	18.2255(18)	15.9757(11)	16.3889(6)	21.8772(19)	35.6666(11)	21.0903(6)	21.259(4)
***α* (deg)**	90	96.92394)	90	80.650(4)	90	90	90
***β* (deg)**	86.298(4)	110.851(3)	108.583(1)	85.194(4)	90	109.584(3)	109.19(3)
***γ* (deg)**	90	98.577(3)	90	79.586(4)	90	90	90
***V* (Å^3)**	4088.5(7)	2847.7(3)	3416.9(2)	2029.3(3)	9782.8(6)	4733.2(2)	4786.8(19)
Z	4	2	4	2	8	4	4
***ρ*(calcd) (g cm^{-3})**	1.137	1.121	1.135	1.169	1.545	1.234	1.344
***μ* (mm^{-1})**	0.083	0.209	0.192	0.177	6.617	0.593	1.176
***F*(000)**	1520	1042	1272	774	4480	1856	1992
reflections collected	33867	42503	41517	33912	45357	59913	28650
unique reflections	9014	12220	6705	8950	21417	10392	9062
R_{int}	0.1501	0.0492	0.0535	0.0628	0.0339	0.0386	0.1254
R_1 [$I > 2\sigma(I)$]	0.0703	0.0612	0.0422	0.0490	0.0379	0.0275	0.0905
wR_2 (all data)	0.1868	0.1725	0.1088	0.1260	0.0615	0.0669	0.2658
GooF	0.960	1.033	1.033	1.042	1.023	1.049	1.039
largest peak and hole (e Å^{-3})	0.25 / -0.30	0.52 / -0.32	0.44 / -0.31	0.33 / -0.27	1.00 / -1.67	0.72 / -0.43	2.53 / -1.78
CCDC no.	1971997	1971998	1971999	1972000	1972001	1972002	1972003

	11	**13**	**14**	**15**	**16**	**17**
empirical formula	$C_{48}H_{68}I_2Ga_2N_6$	$C_{48}H_{68}ClGaN_6$	$C_{48}H_{69}GaN_6$	$C_{48}H_{69}InN_6$	$C_{48}H_{68}ClTlN_6$	$C_{48}H_{68}BrTlN_6$
formula weight	1122.32	834.25	799.81	844.91	968.90	1013.36
crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	*P*-1	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
***a* (Å)**	10.764(3)	14.315(3)	14.6502(6)	14.667(5)	14.6044(6)	14.570(3)
***b* (Å)**	11.169(3)	16.444(3)	16.1245(6)	16.510(6)	16.5465(9)	16.835(3)
***c* (Å)**	12.729(5)	21.068(4)	20.9328(8)	21.164(6)	21.0726(11)	21.235(4)
***α* (deg)**	96.760(17)	90	90	90	90	90
***β* (deg)**	114.864(10)	109.614(9)	110.465(2)	109.752(11)	109.055(2)	108.21(3)
***γ* (deg)**	105.707(12)	90	90	90	90	90
***V* (Å^3)**	1288.8(7)	4671.6(17)	4632.8(3)	4823(3)	4813.2(4)	4947.6(19)
Z	1	4	4	4	4	4
***ρ*(calcd) (g cm^{-3})**	1.446	1.186	1.147	1.163	1.337	1.360
***μ* (mm^{-1})**	2.279	0.684	0.631	0.526	3.448	4.108
***F*(000)**	566	1784	1720	1792	1984	2056
reflections collected	11588	39262	39795	46764	86173	33377
unique reflections	4243	10285	10201	10632	10514	10694
R_{int}	0.1085	0.0913	0.0568	0.0498	0.0631	0.0610
R_1 [$I > 2\sigma(I)$]	0.0890	0.0544	0.0571	0.0330	0.0244	0.0591
wR_2 (all data)	0.2382	0.1359	0.1675	0.0935	0.0532	0.1559
GooF	1.060	1.022	1.046	1.026	1.042	1.041
largest peak and hole (e Å^{-3})	1.94 / -1.73	0.70 / -0.45	1.77 / -0.53	0.48 / -0.34	0.60 / -0.68	0.80 / -1.09
CCDC no.	1972004	1972005	1972006	1972007	1972008	1972009

	18	**19**	**20**	**21**	**[(Dipp$_2$N$_3$)SnCl·W(CO)$_5$]**	**[(Dipp$_2$N$_3$)SnCl·W(CO)$_5$]·KCl**
empirical formula	$C_{50}H_{70}ClTlN_4$	$C_{48}H_{68}GeN_6$	$C_{48}H_{68}SnN_6$	$C_{31}H_{46}BrSnN_5$	$C_{29}H_{34}ClN_3O_5SnW$	$C_{29}H_{34}Cl_2N_3O_5KSnW$
formula weight	966.92	801.67	847.77	687.33	842.58	917.13
crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	P-1	P-1	P-1
***a* (Å)**	14.5473(4)	14.737(3)	14.6665(5)	17.1551(13)	10.6676(7)	13.3890(7)
***b* (Å)**	16.5705(6)	15.884(4)	16.3711(7)	21.1932(16)	11.0404(7)	16.2162(8)
***c* (Å)**	21.2327(8)	20.901(5)	20.8400(8)	21.6061(17)	15.4465(11)	18.0413(9)
***α* (deg)**	90	90	90	87.943(2)	73.901(3)	113.6900(10)
***β* (deg)**	109.137(1)	110.220(7)	110.247(2)	68.502(2)	71.850(3)	93.105(2)
***γ* (deg)**	90	90	90	69.655(2)	72.069(3)	91.697(2)
***V* (Å^3)**	4835.4(3)	4591.3(18)	4694.6(3)	6815.6(9)	1611.28(19)	3568.6(3)
Z	4	4	4	8	2	4
***ρ*(calcd) (g cm^{-3})**	1.328	1.160	1.199	1.340	1.737	1.707
***μ* (mm^{-1})**	3.431	0.705	0.581	1.948	4.464	4.225
***F*(000)**	1984	1720	1792	2816	820	1784
reflections collected	42717	75551	32593	132490	24732	62536
unique reflections	10671	9441	9410	27861	6965	14648
R_{int}	0.0590	0.0696	0.0574	0.0447	0.0279	0.0508
R_1 [$I > 2\sigma(I)$]	0.0281	0.0390	0.0454	0.0391	0.0153	0.0561
wR_2 (all data)	0.0697	0.1038	0.1317	0.0981	0.0351	0.1591
GooF	1.040	1.038	1.051	1.101	1.063	1.069
largest peak and hole (e Å^{-3})	0.55 / -0.63	0.62 / -0.47	0.66 / -1.32	1.57 / -0.80	0.68 / -0.48	3.72 / -3.90
CCDC no.	1972010	1972011	-	1972012	1972013	1972014

In Situ IR Spectra

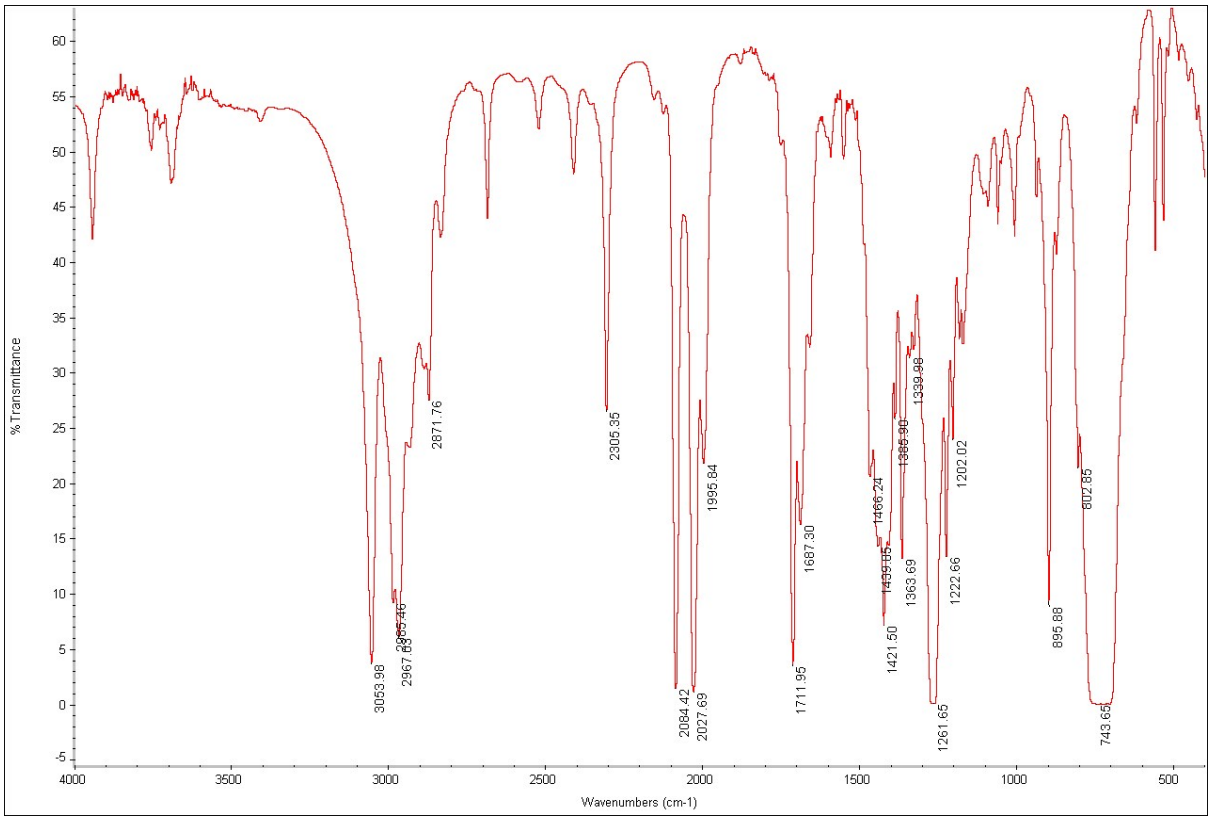

Figure S20. Solution (CH_2Cl_2) IR spectrum of **3** treated with CO.

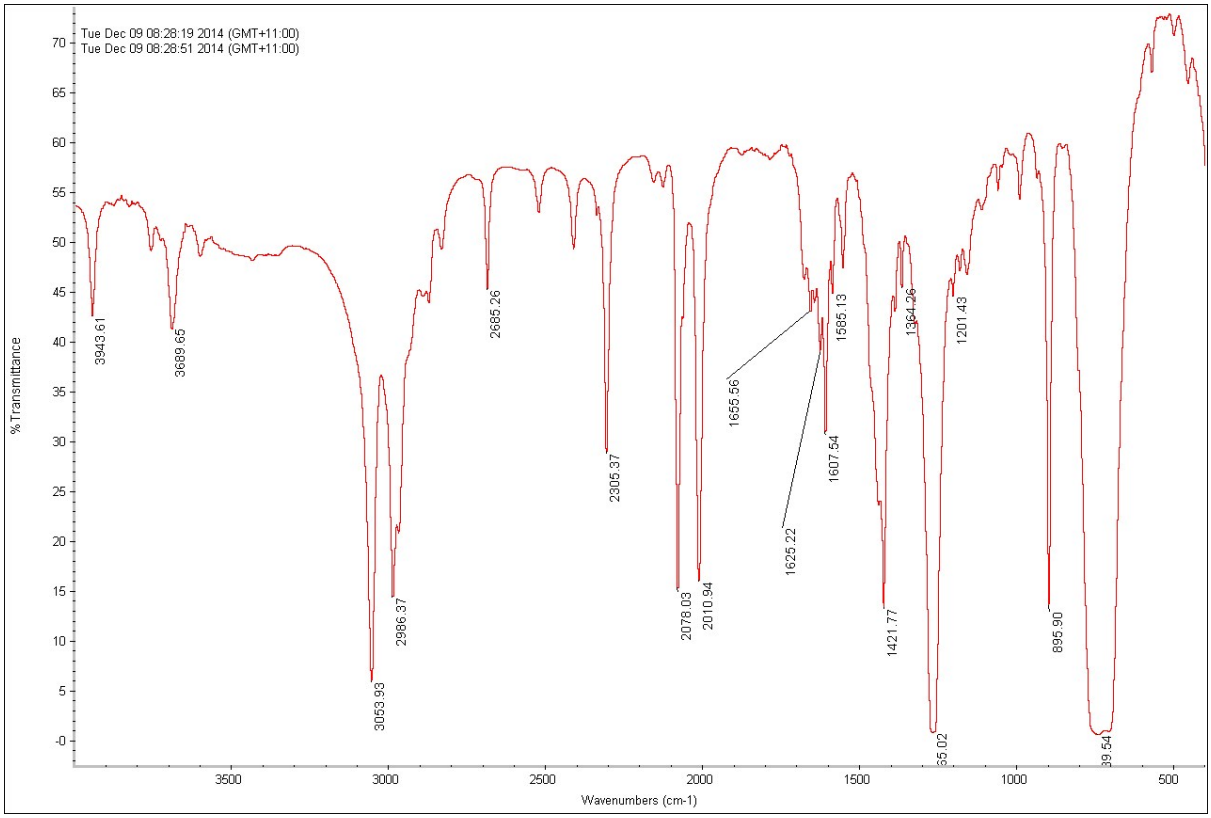

Figure S21. Solution (CH_2Cl_2) IR spectrum of **4** treated with CO.

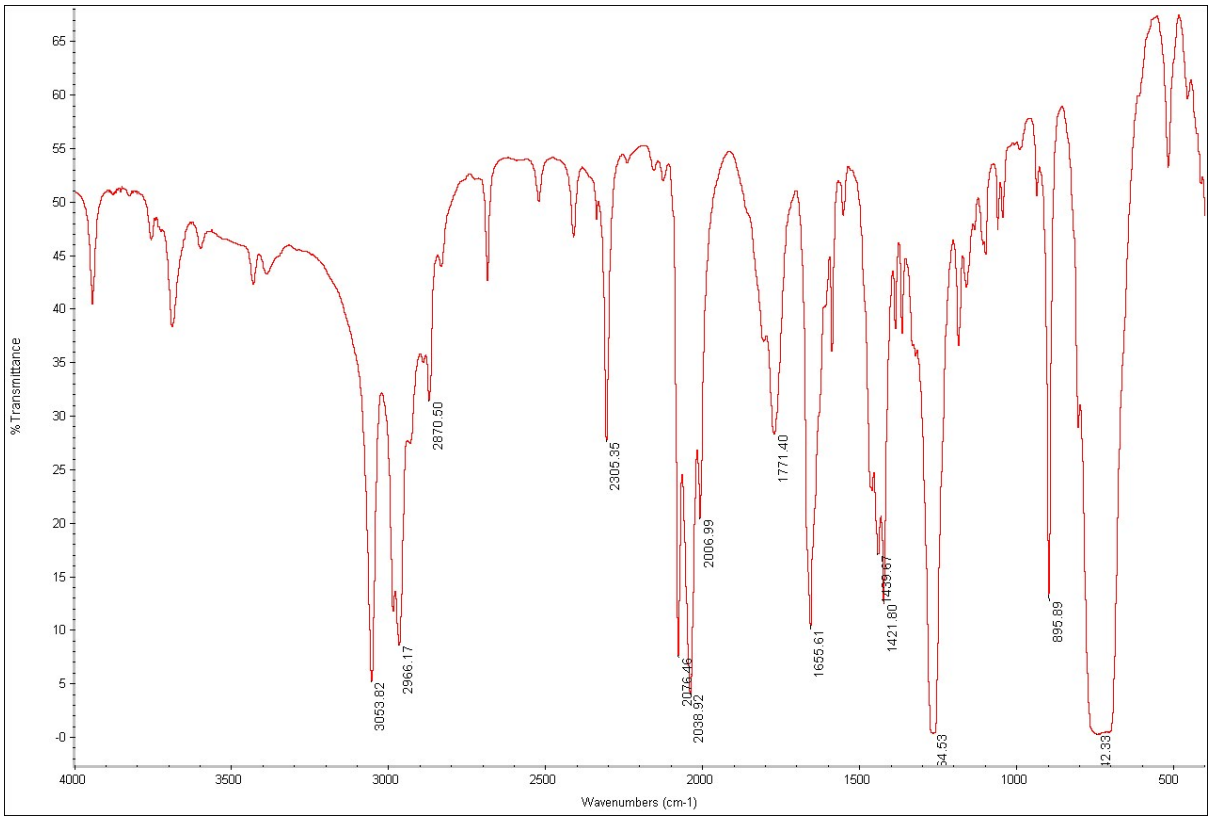

Figure S22. Solution (CH_2Cl_2) IR spectrum of **4** treated with CO and aged for 24 h at room temperature.

NMR Spectra

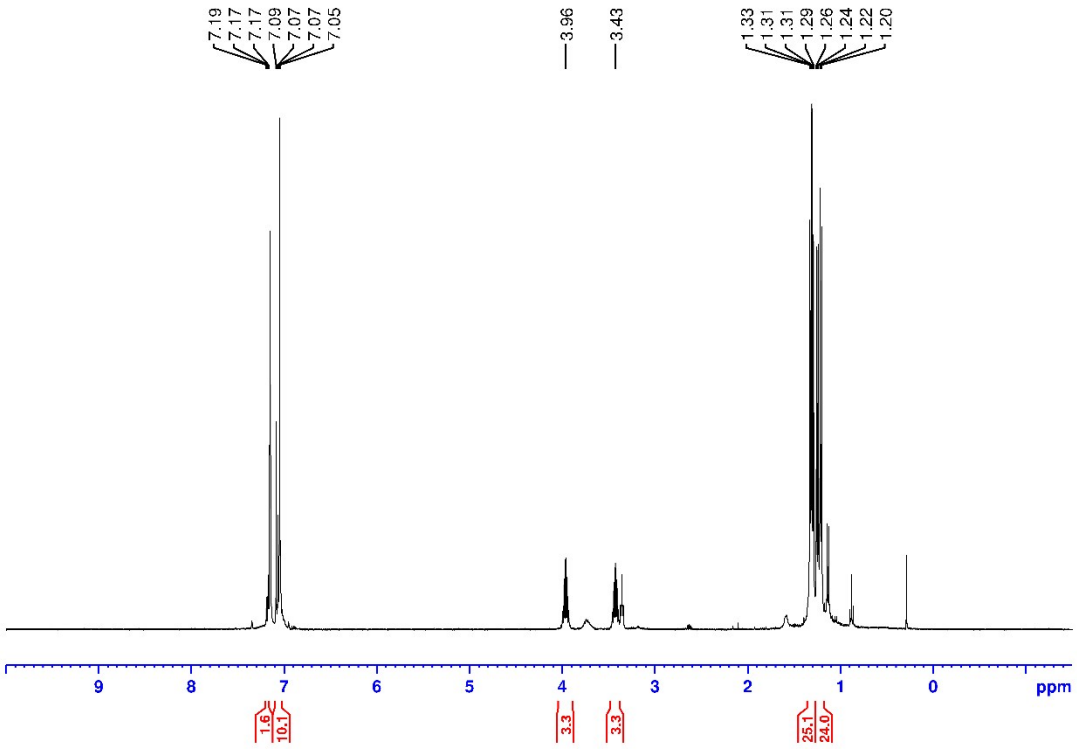

Figure S23. ^{1}H NMR spectrum of **1**.

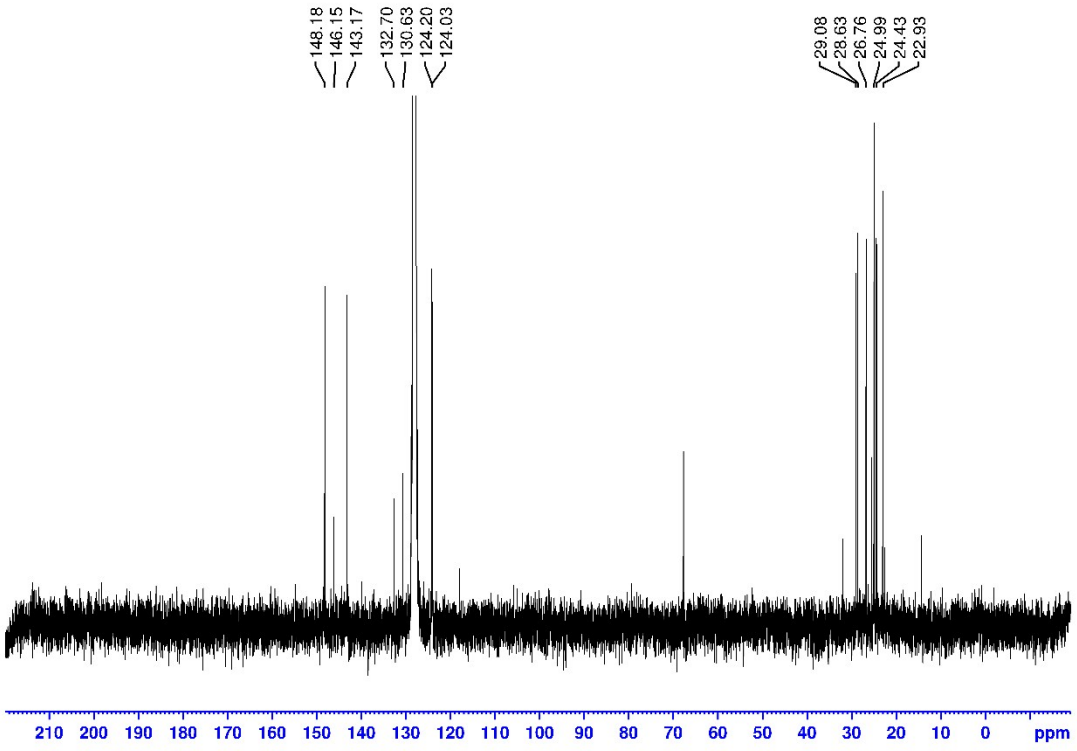

Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of **1**.

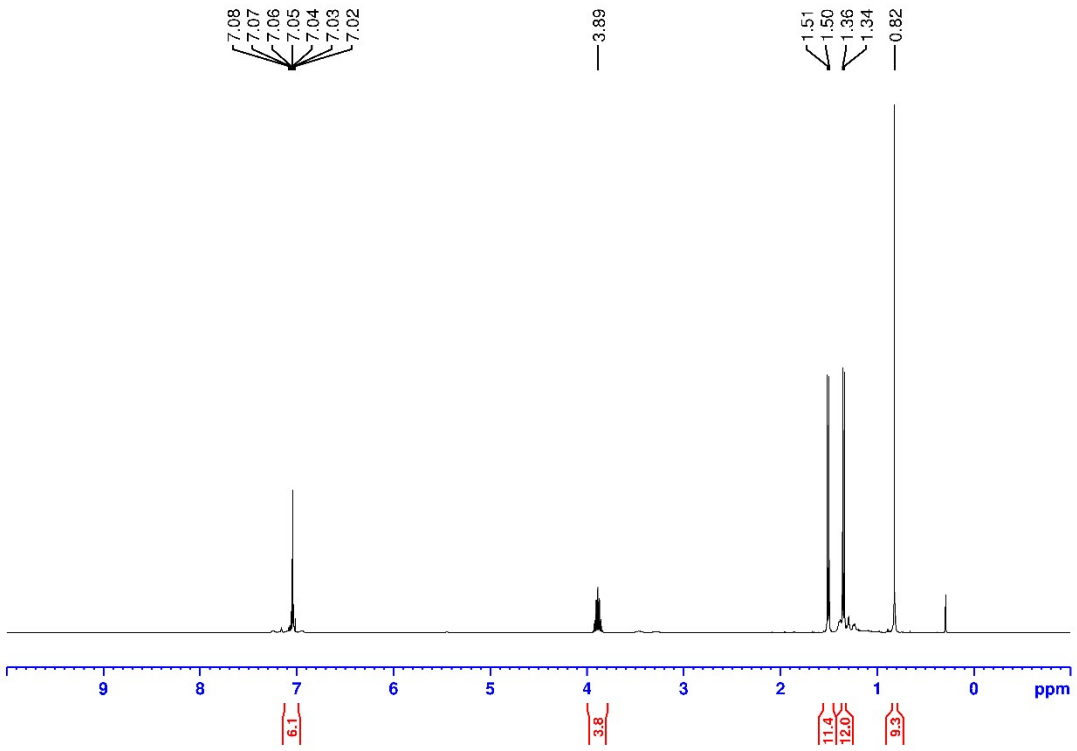

Figure S25. ^{1}H NMR spectrum of **[(Piso)Rh(CO)$_2$]**.

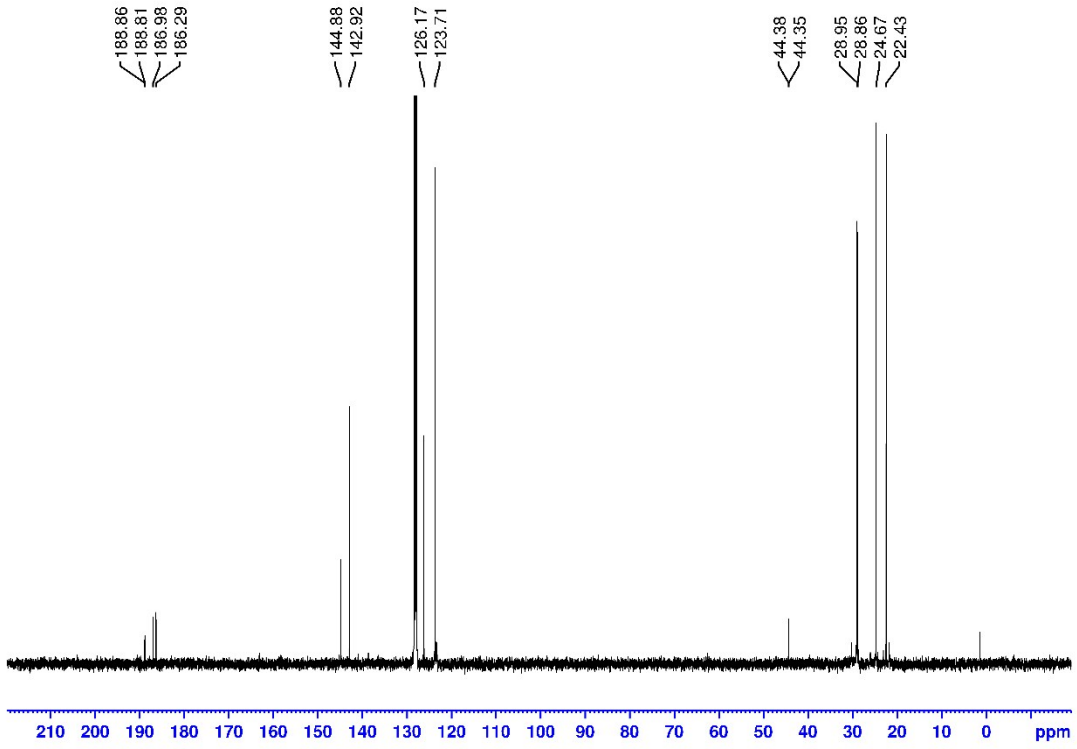

Figure S26. ^{13}C{^{1}H} NMR spectrum of **[(Piso)Rh(CO)$_2$]**.

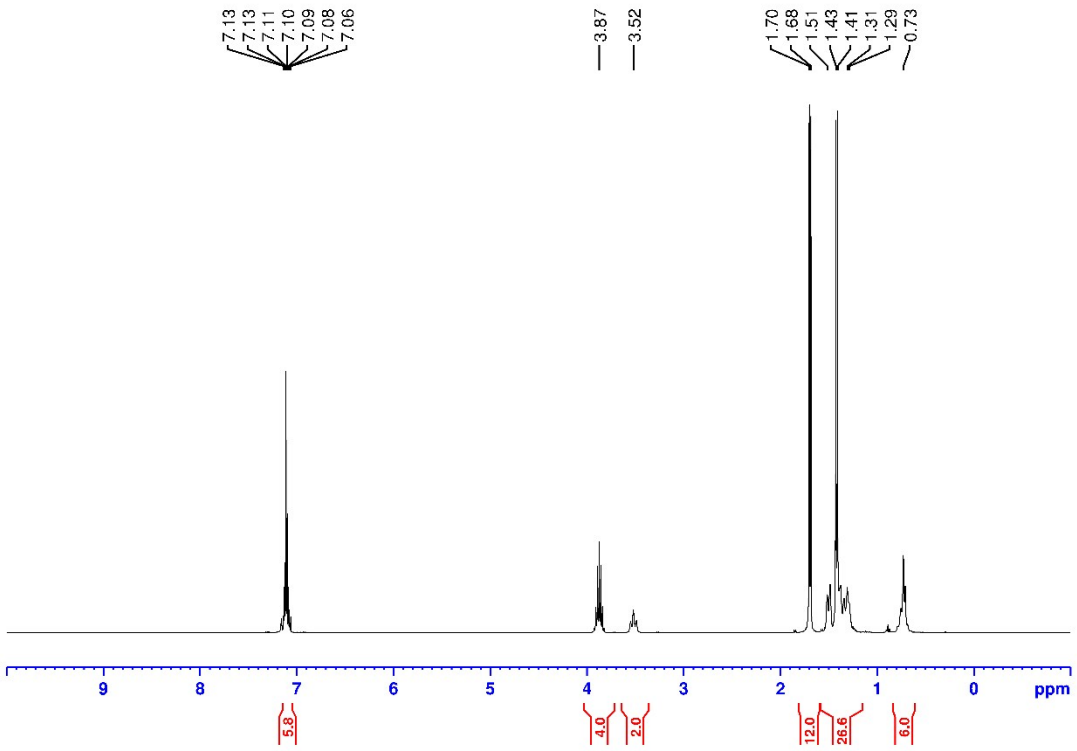

Figure S27. ^{1}H NMR spectrum of **[(Giso)Rh(CO)$_2$]**.

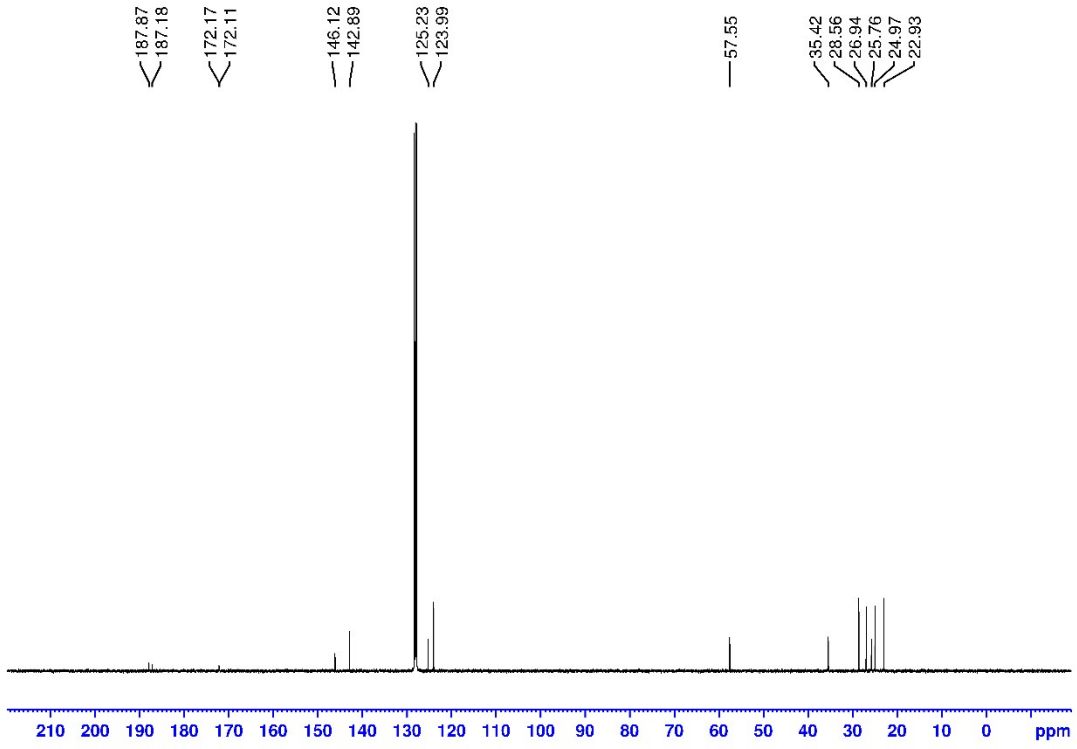

Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of **[(Giso)Rh(CO)$_2$]**.

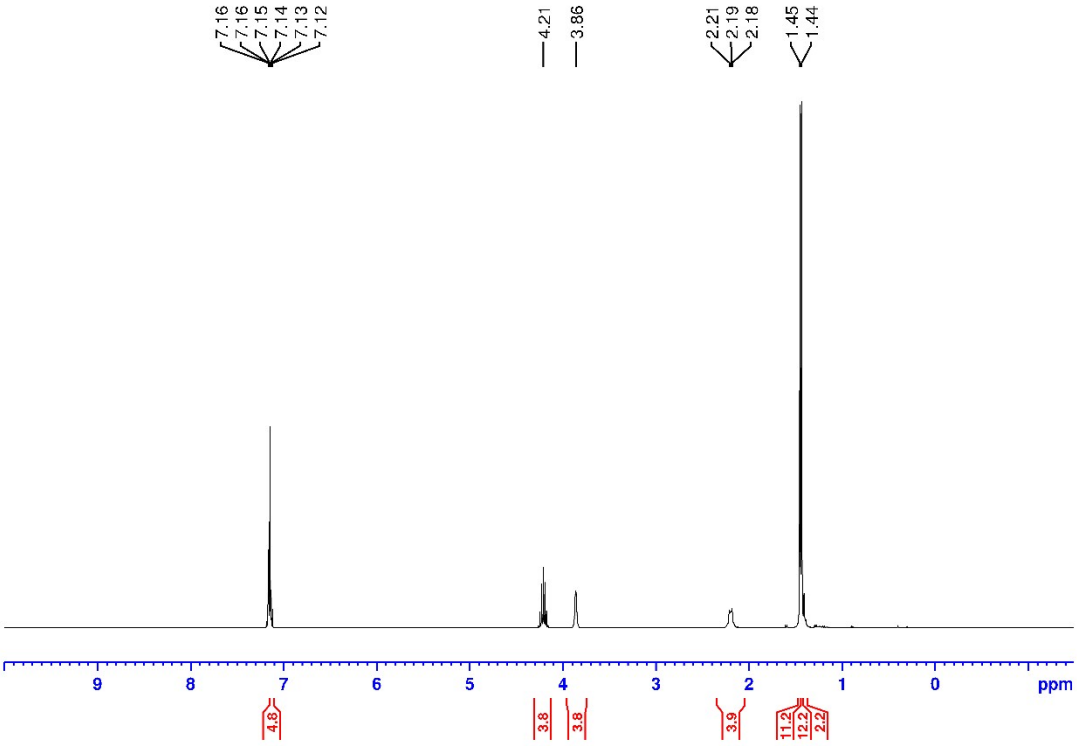

Figure S29. ^{1}H NMR spectrum of **3**.

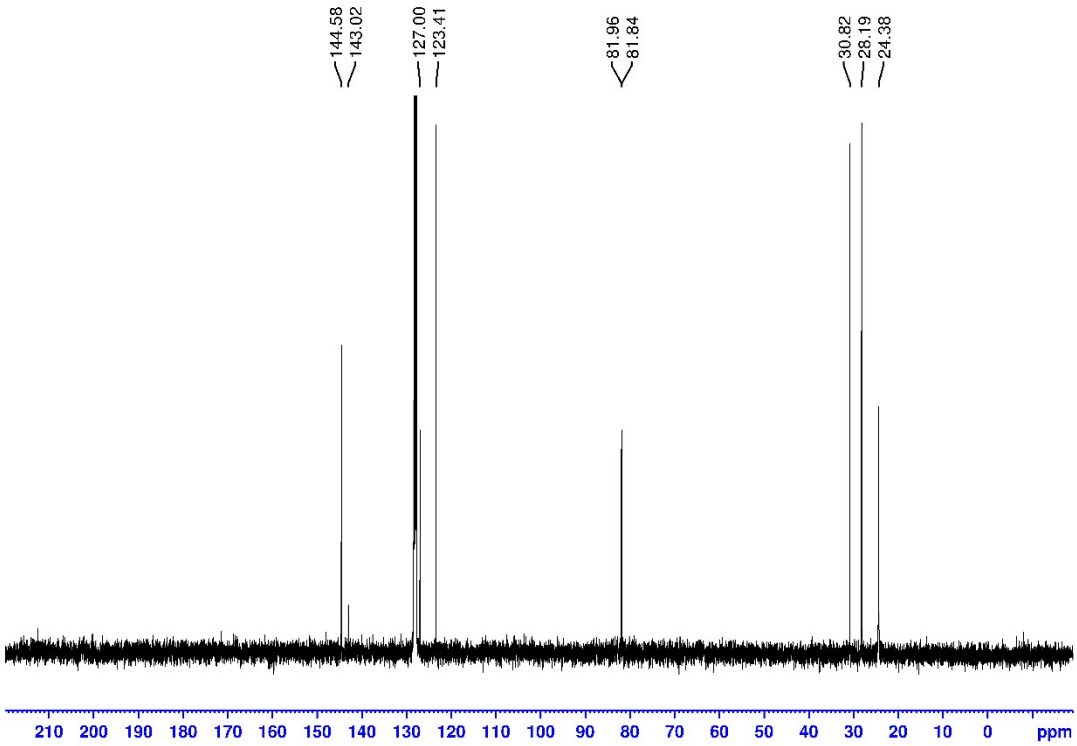

Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of **3**.

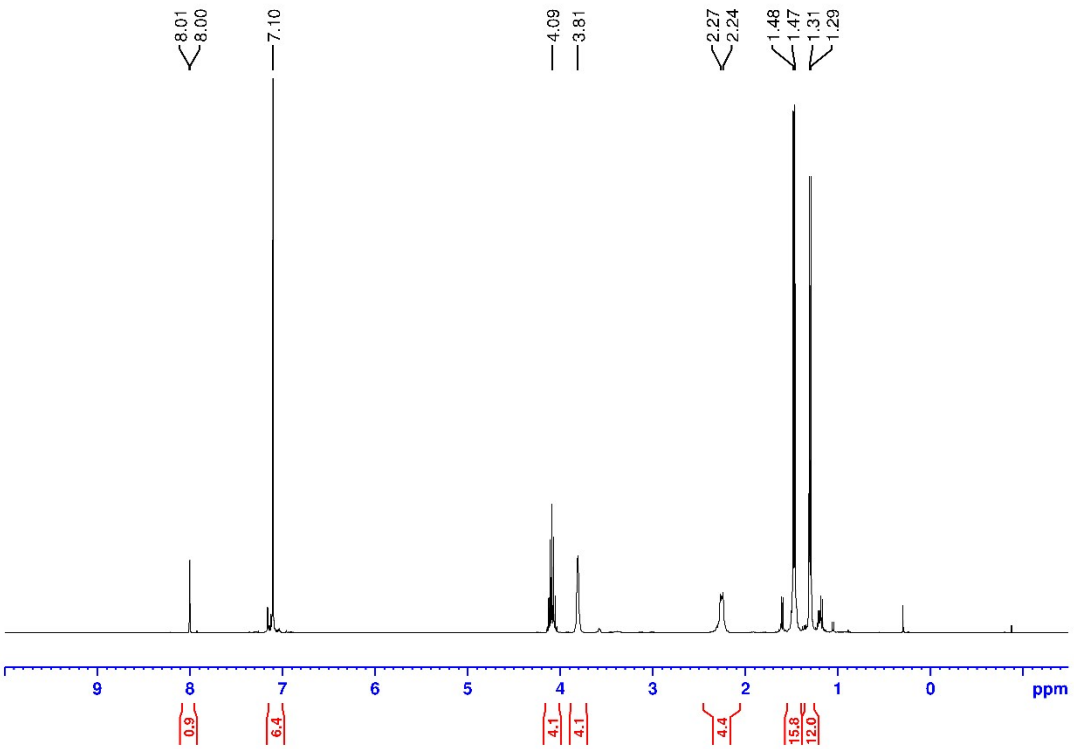

Figure S31. ^{1}H NMR spectrum of **4**.

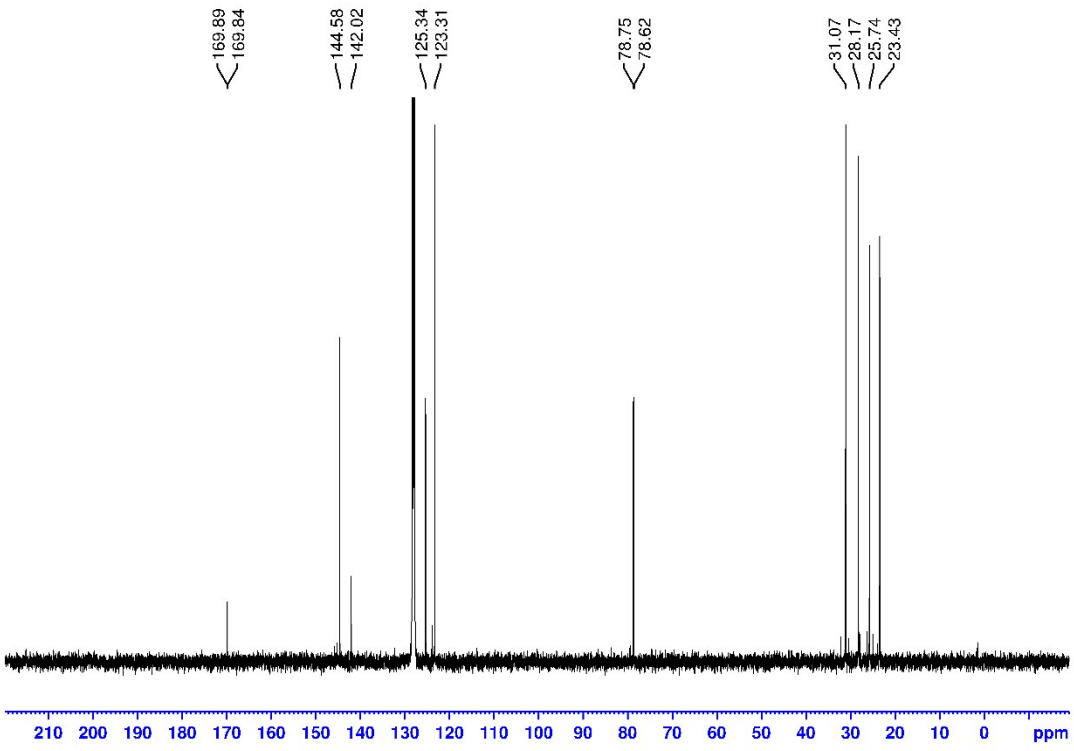

Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of **4**.

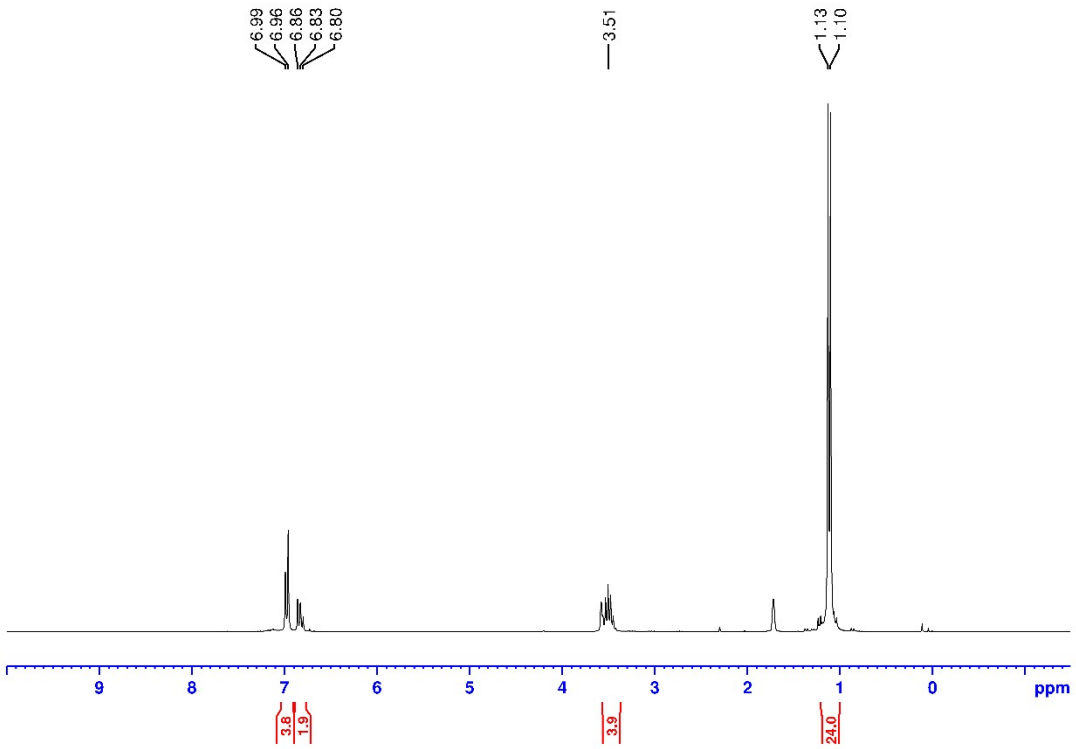

Figure S33. ^{1}H NMR spectrum of **5**.

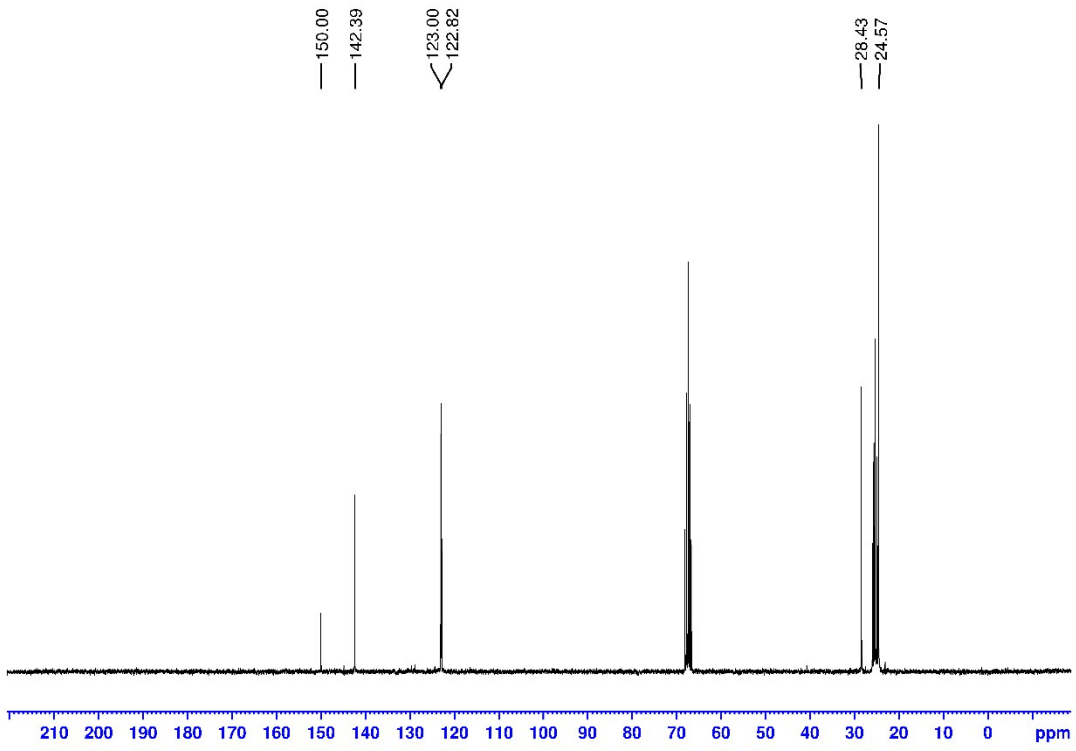

Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum of **5**.

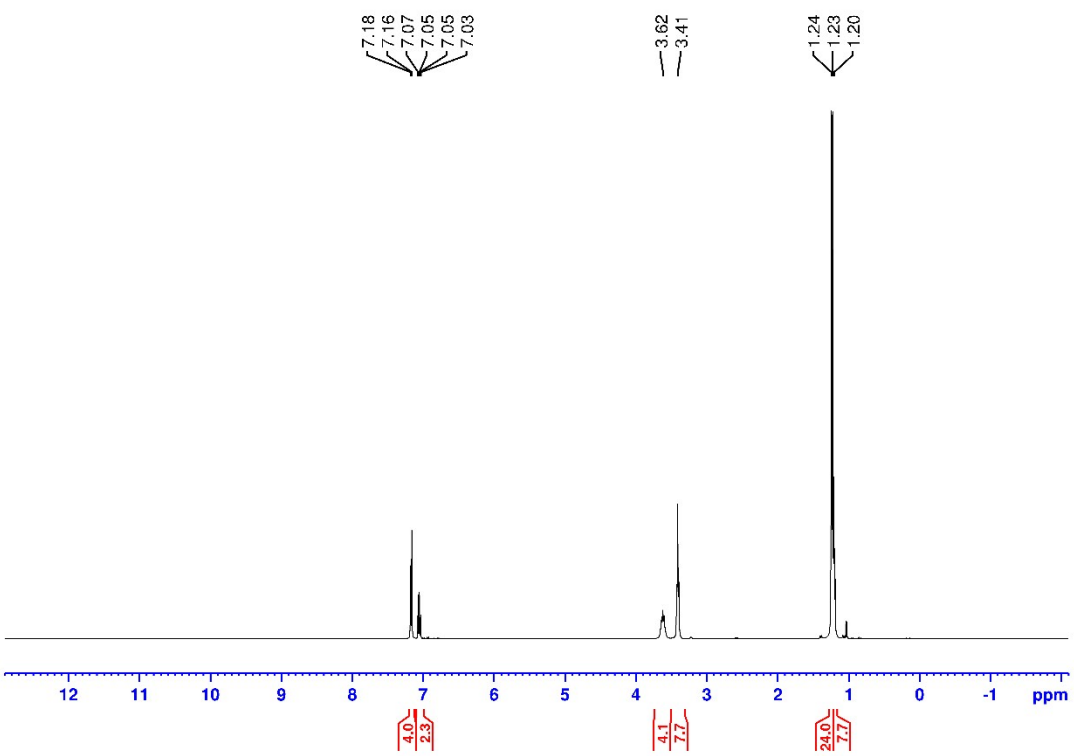

Figure S35. ^{1}H NMR spectrum of **5-THF$_2$**.

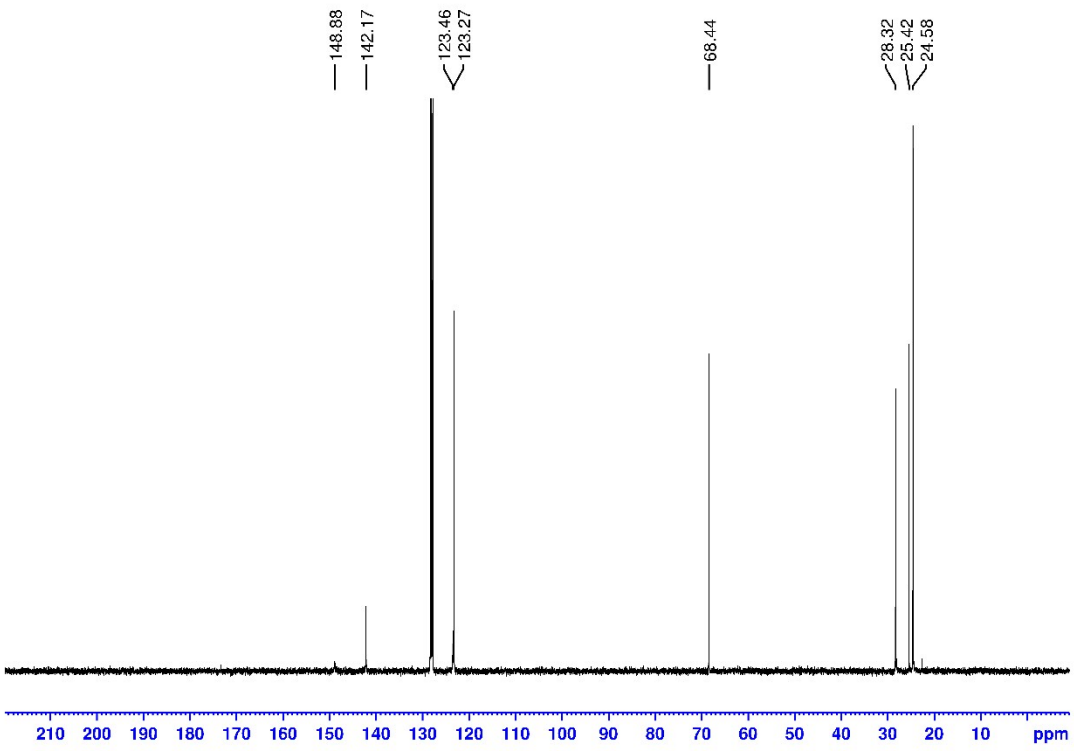

Figure S36. ^{13}C{^{1}H} NMR spectrum of **5-THF$_2$**.

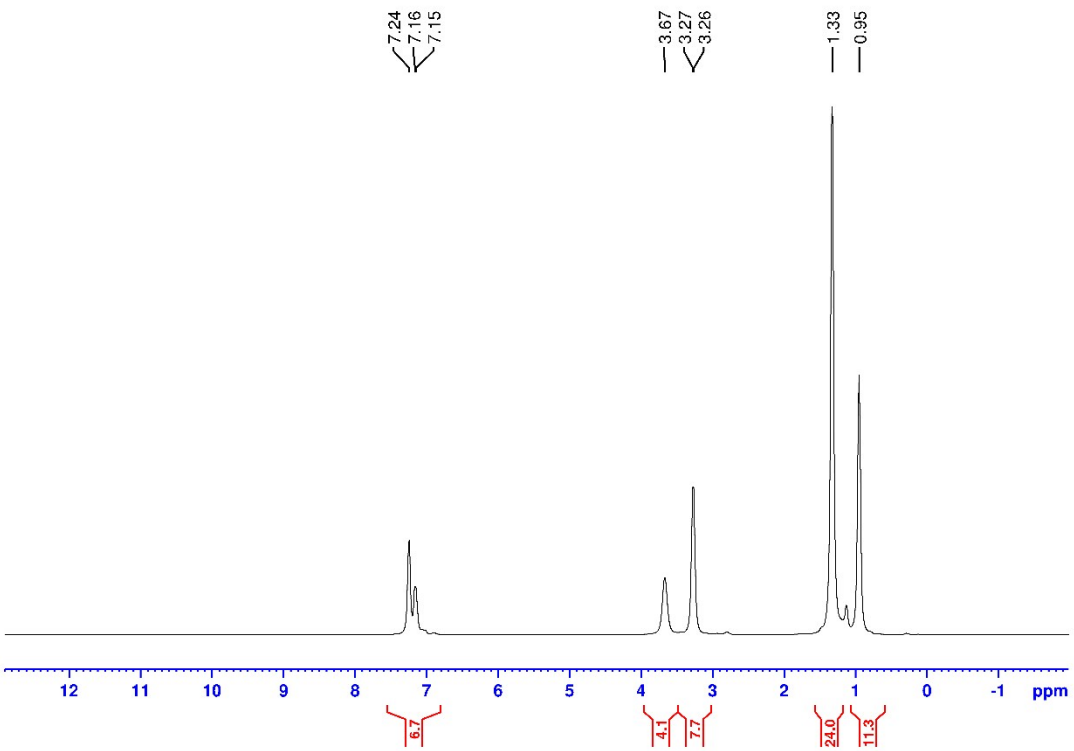

Figure S37. ^{1}H NMR spectrum of **5-$(OEt_2)_2$**.

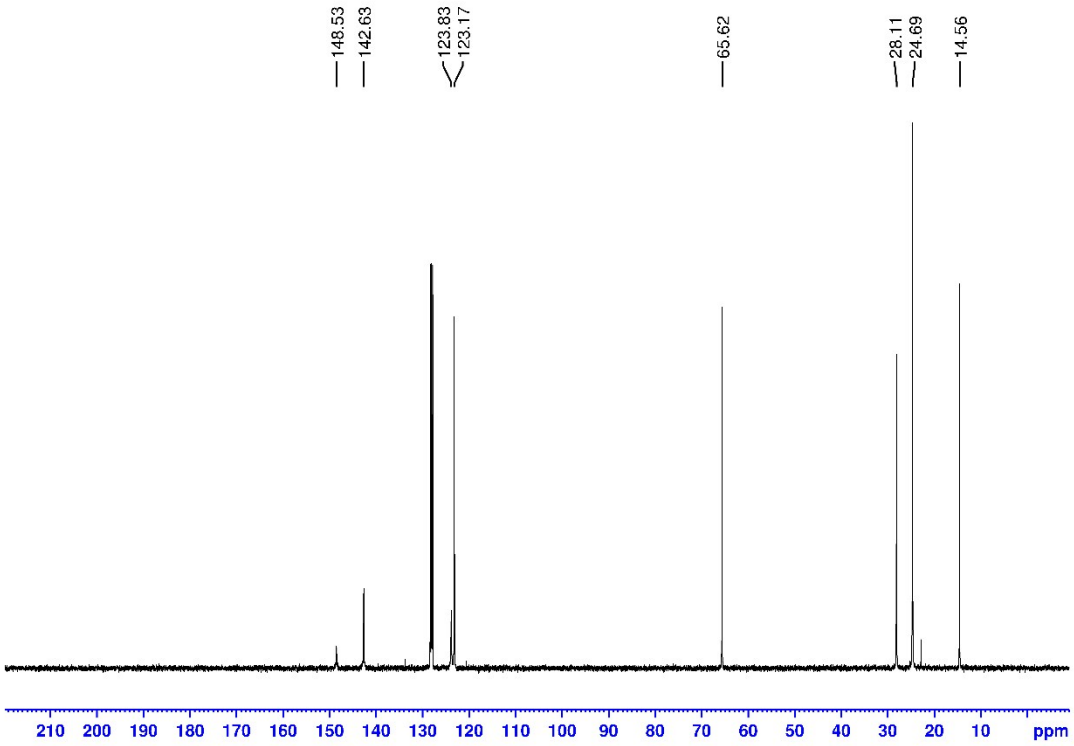

Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of **5-$(OEt_2)_2$**.

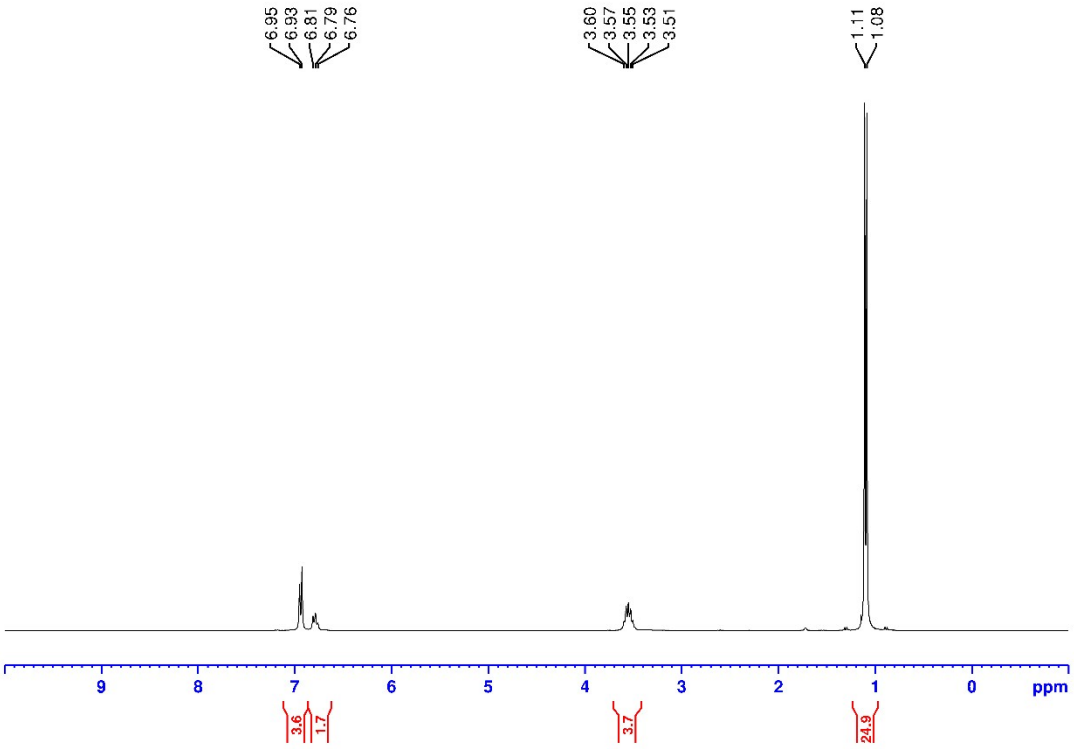

Figure S39. ^{1}H NMR spectrum of **6**.

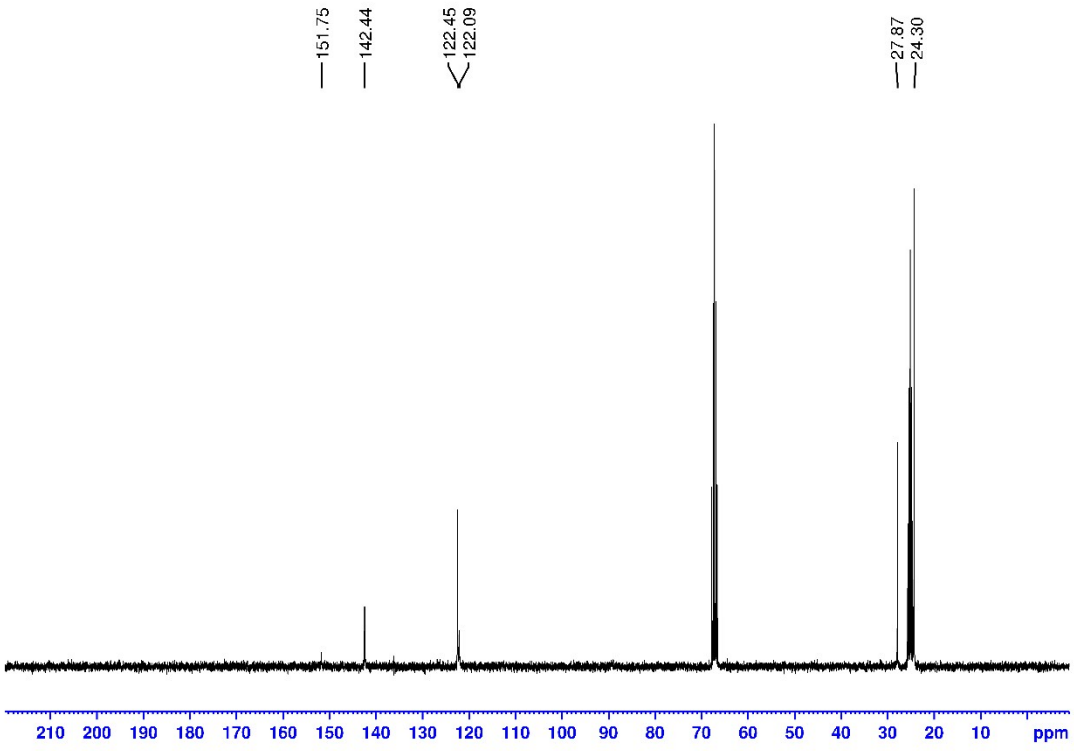

Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum of **6**.

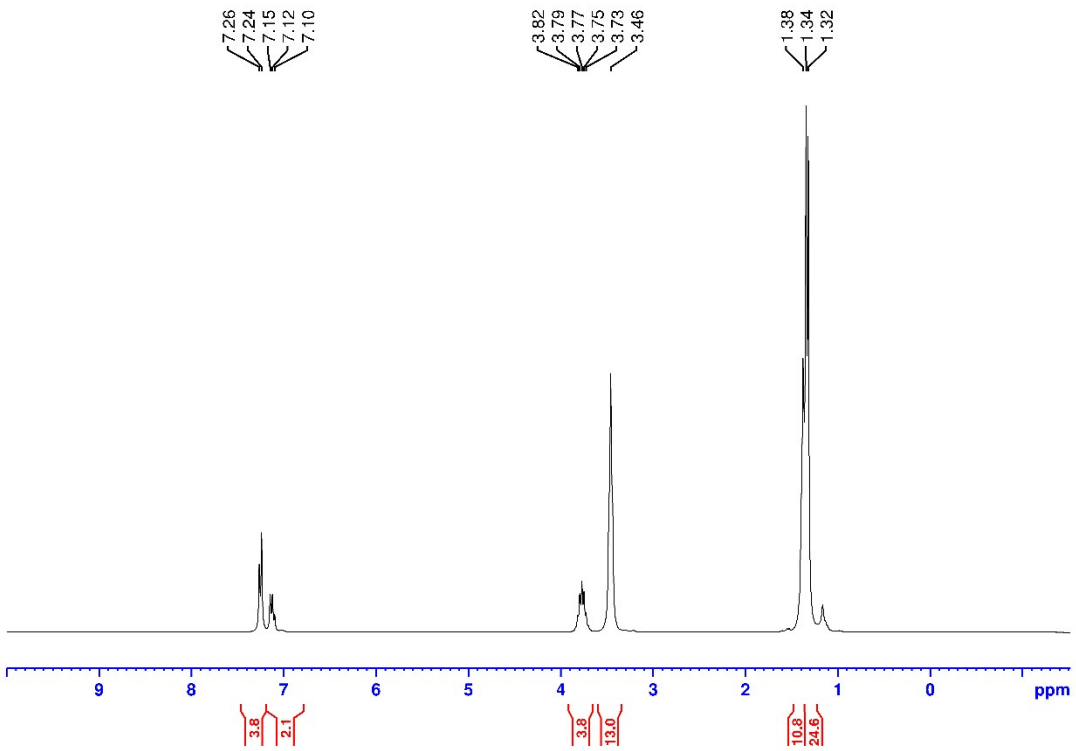

Figure S41. ^{1}H NMR spectrum of **6-THF$_3$**.

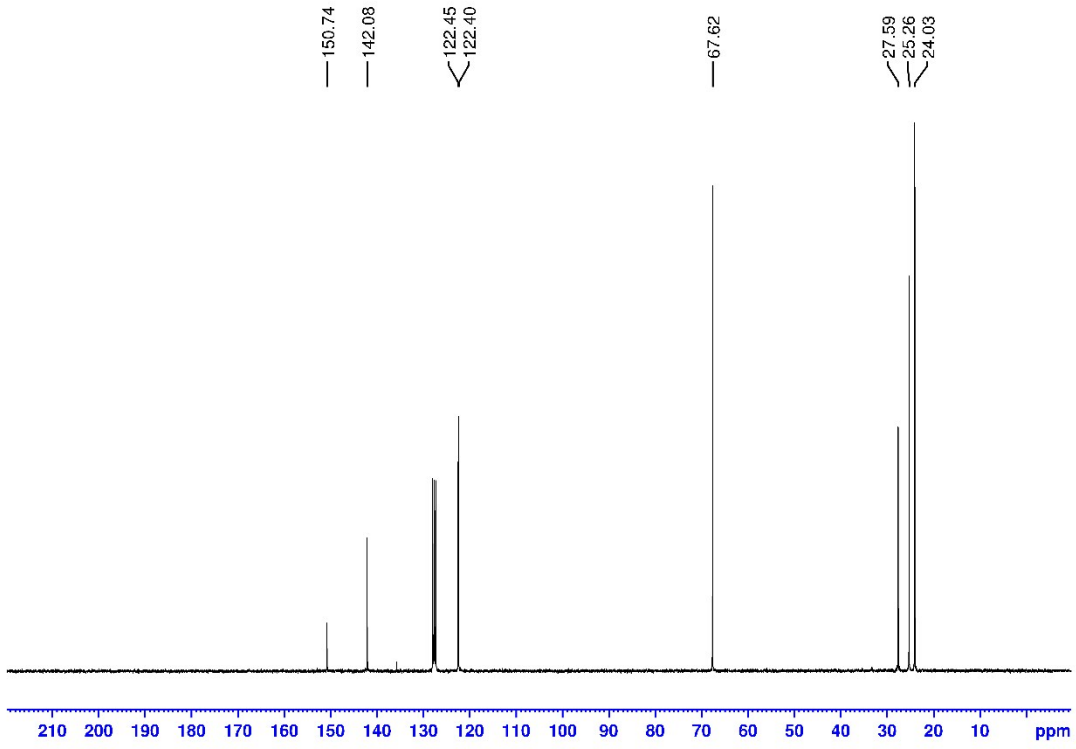

Figure S42. ^{13}C{^{1}H} NMR spectrum of **6-THF$_3$**.

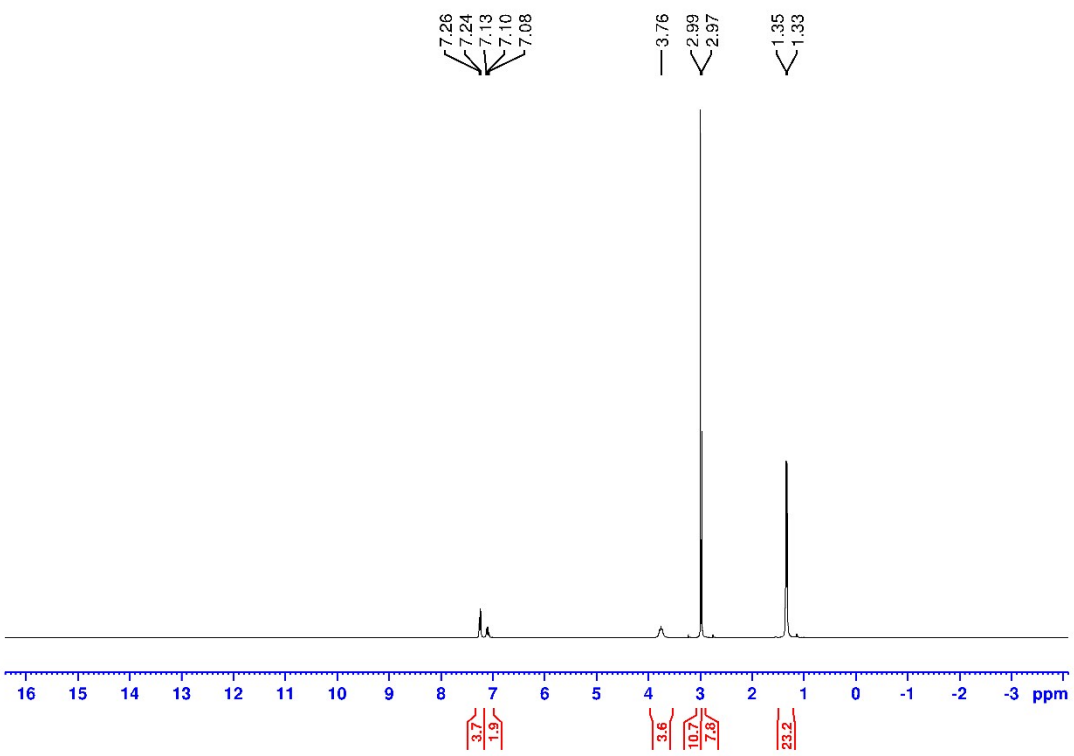

Figure S43. ^{1}H NMR spectrum of **6-DME$_2$**.

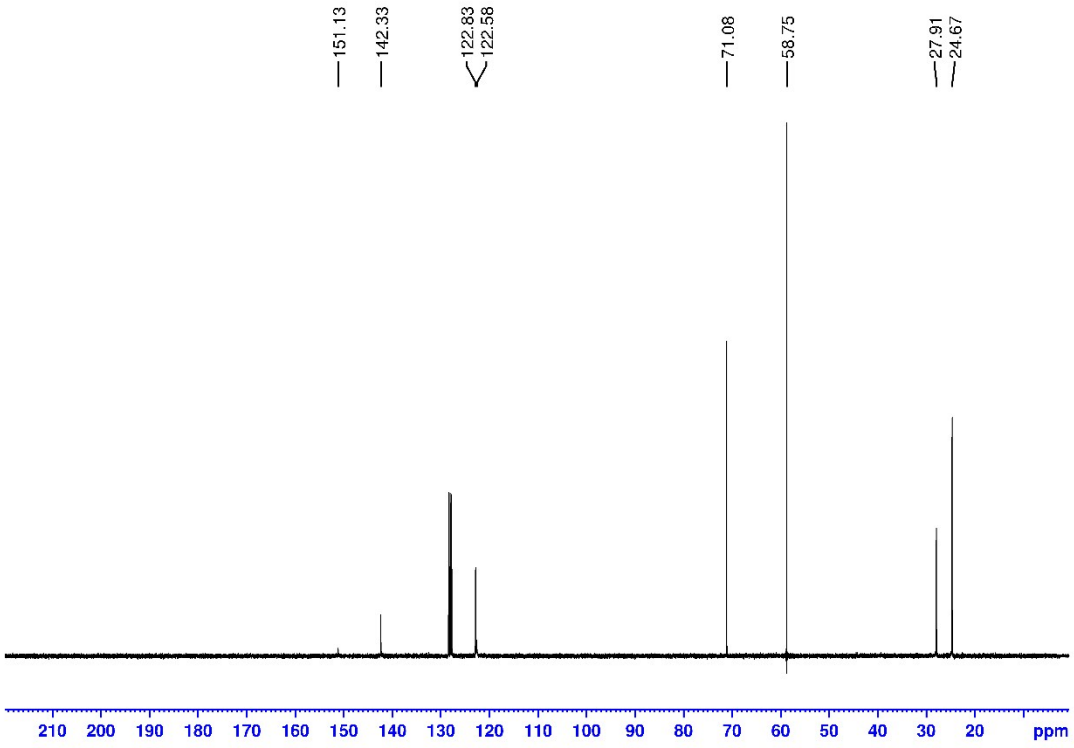

Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum of **6-DME$_2$**.

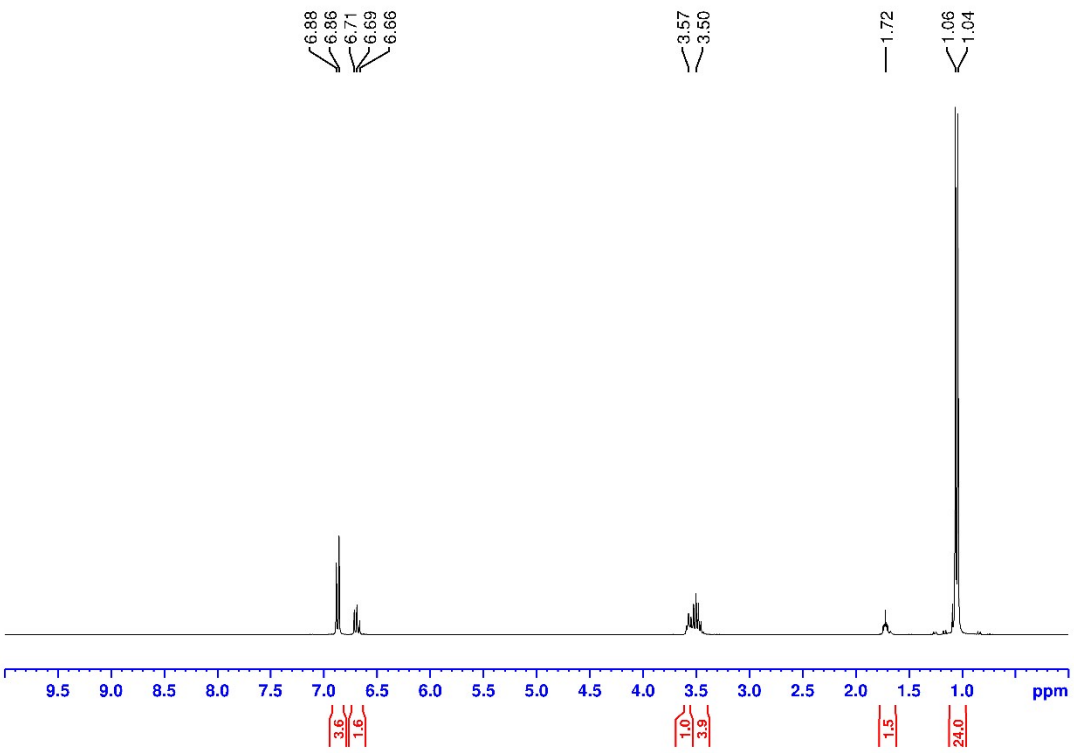

Figure S45. ^{1}H NMR spectrum of **7-THF**.

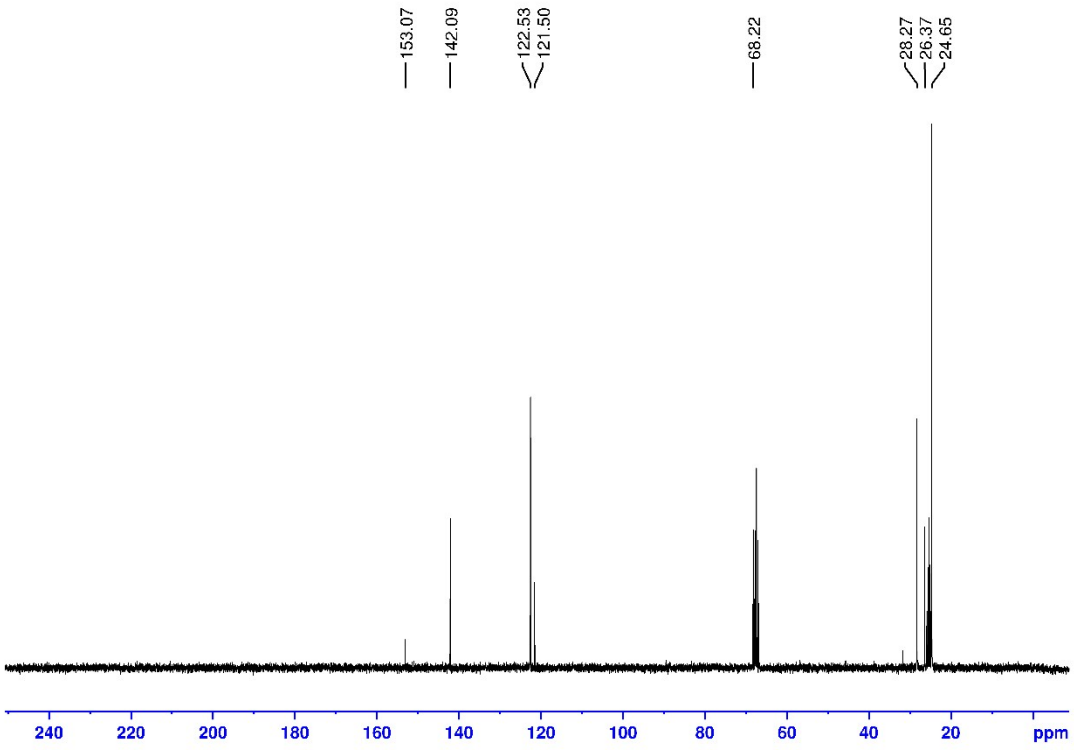

Figure S46. ^{13}C{^{1}H} NMR spectrum of **7-THF**.

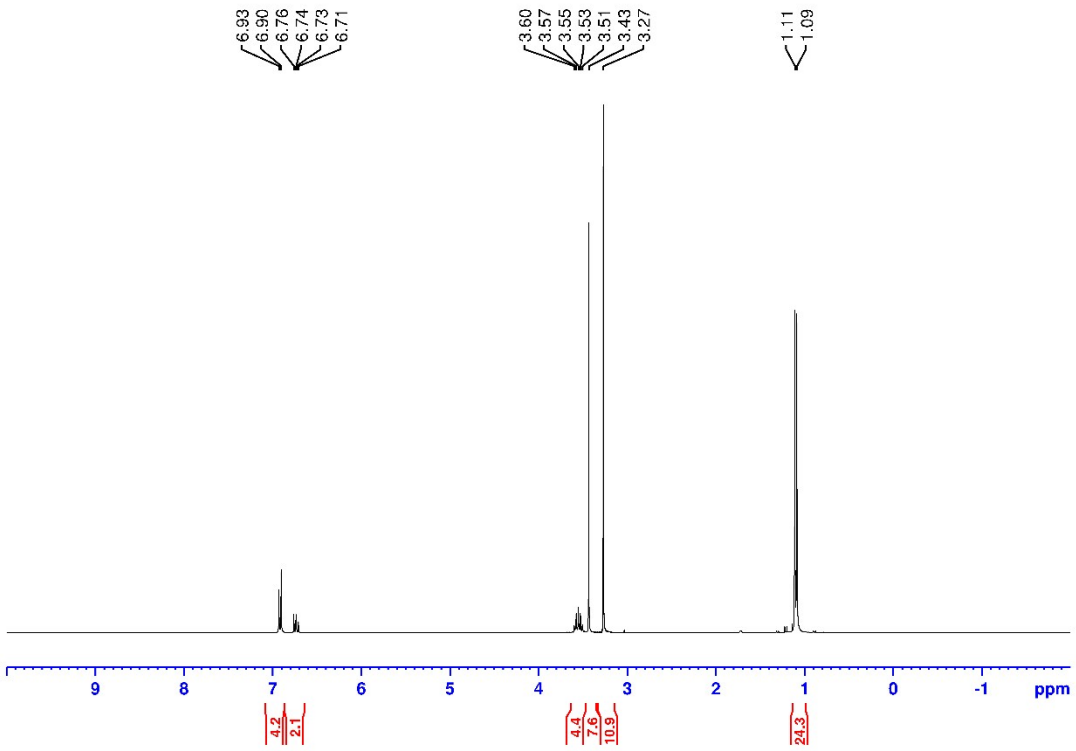

Figure S47. ^{1}H NMR spectrum of **7-DME$_2$**.

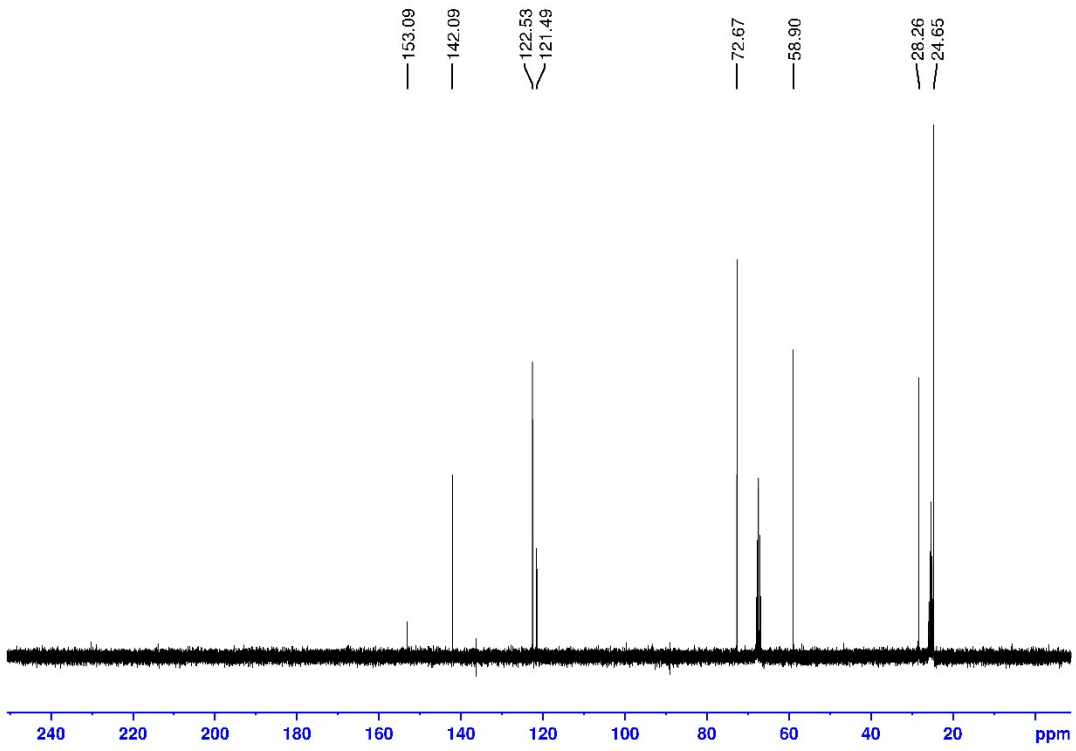

Figure S48. ^{13}C{^{1}H} NMR spectrum of **7-DME$_2$**.

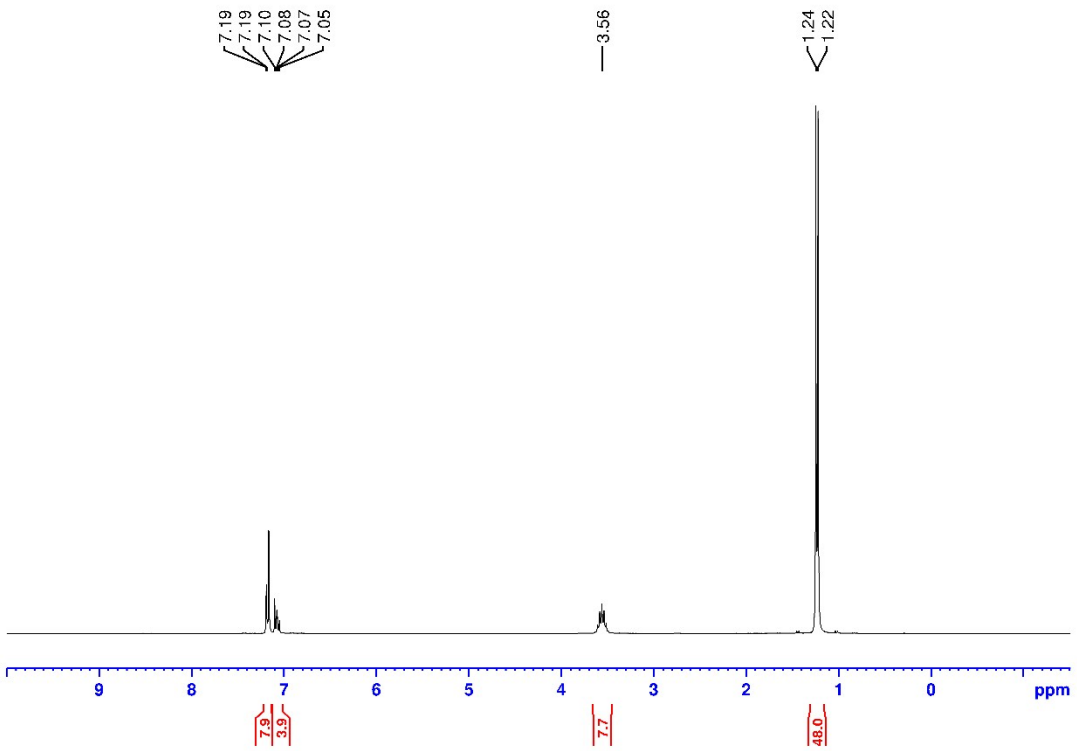

Figure S49. ^{1}H NMR spectrum of **8**.

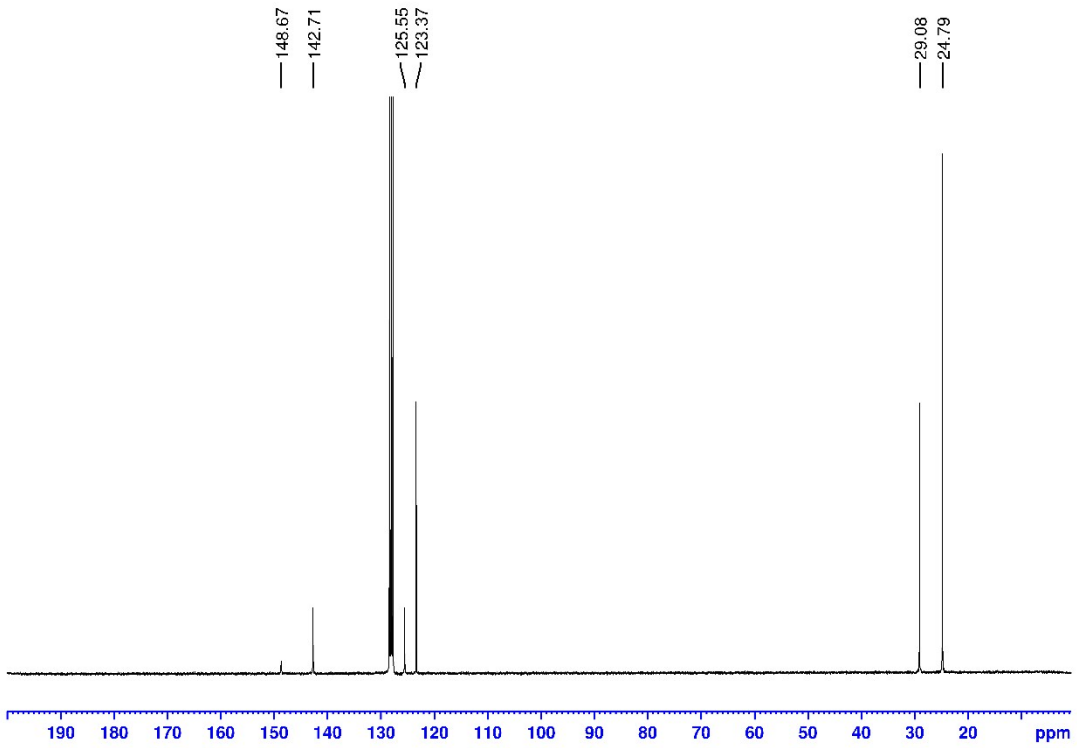

Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum of **8**.

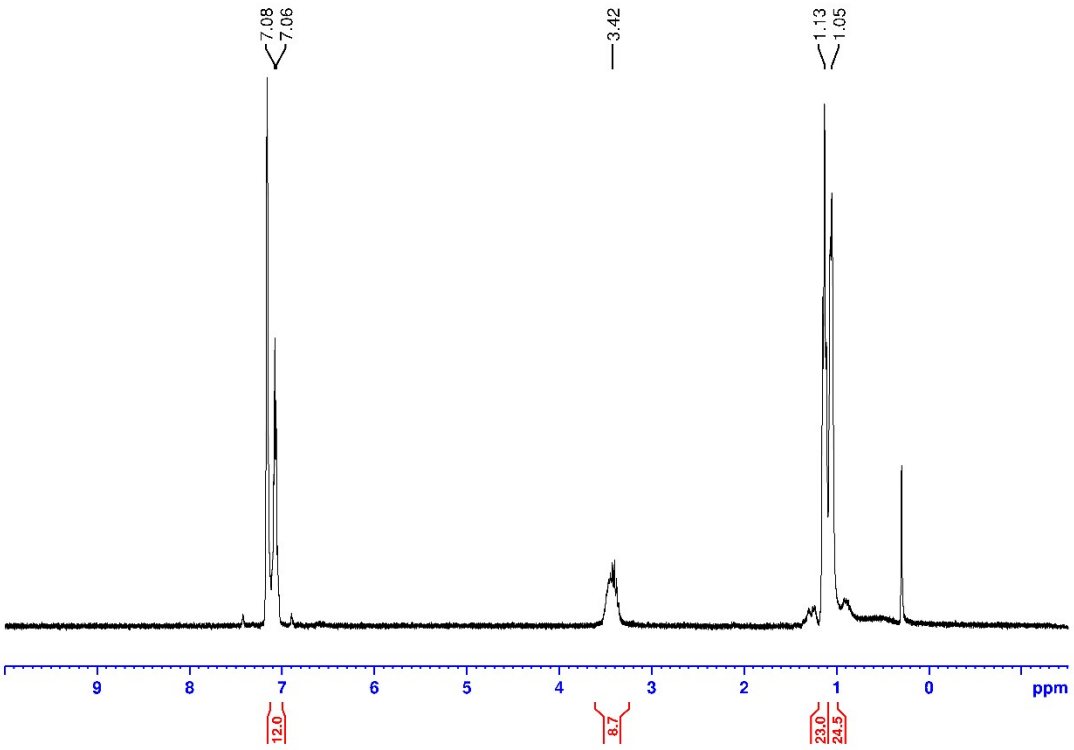

Figure S51. ^{1}H NMR spectrum of **9**.

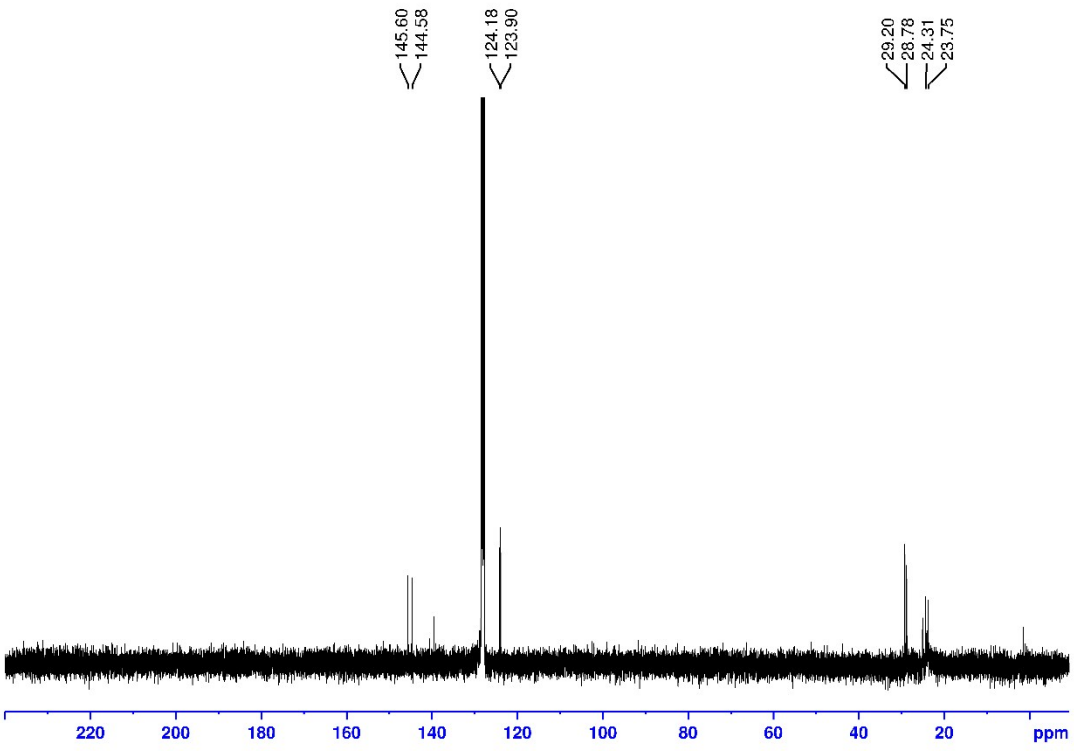

Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of **9**.

Figure S53. ^{1}H NMR spectrum of **11**.

Figure S54. $^{13}C\{^{1}H\}$ NMR spectrum of **11**.

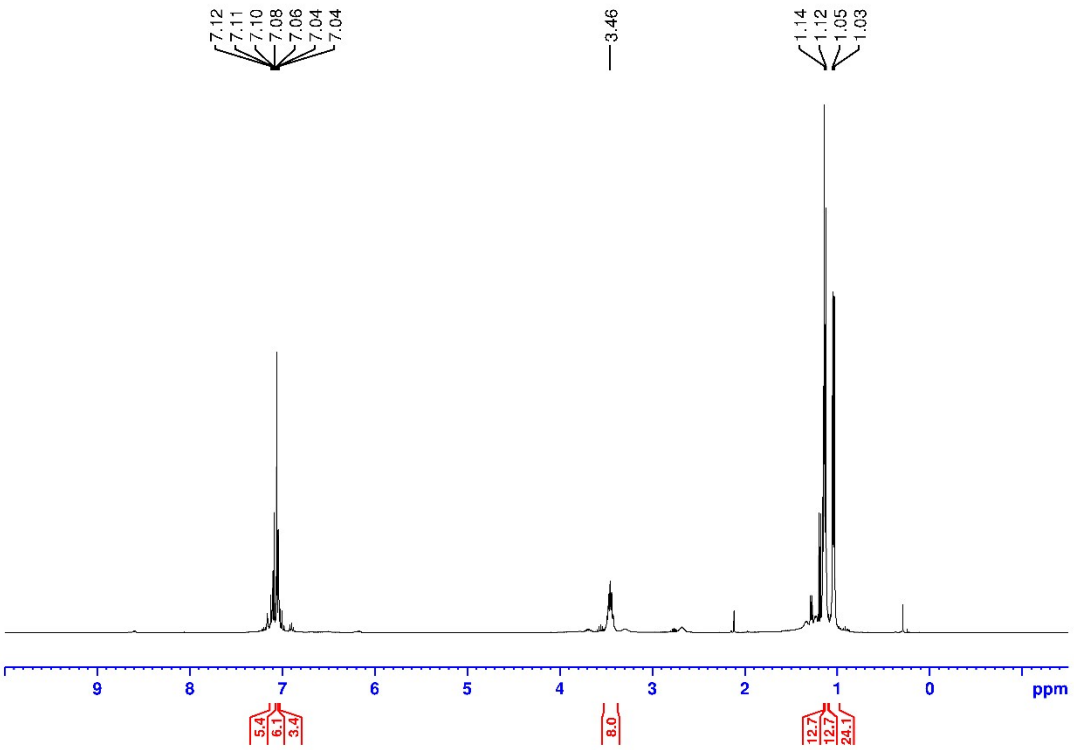

Figure S55. ^{1}H NMR spectrum of **10**.

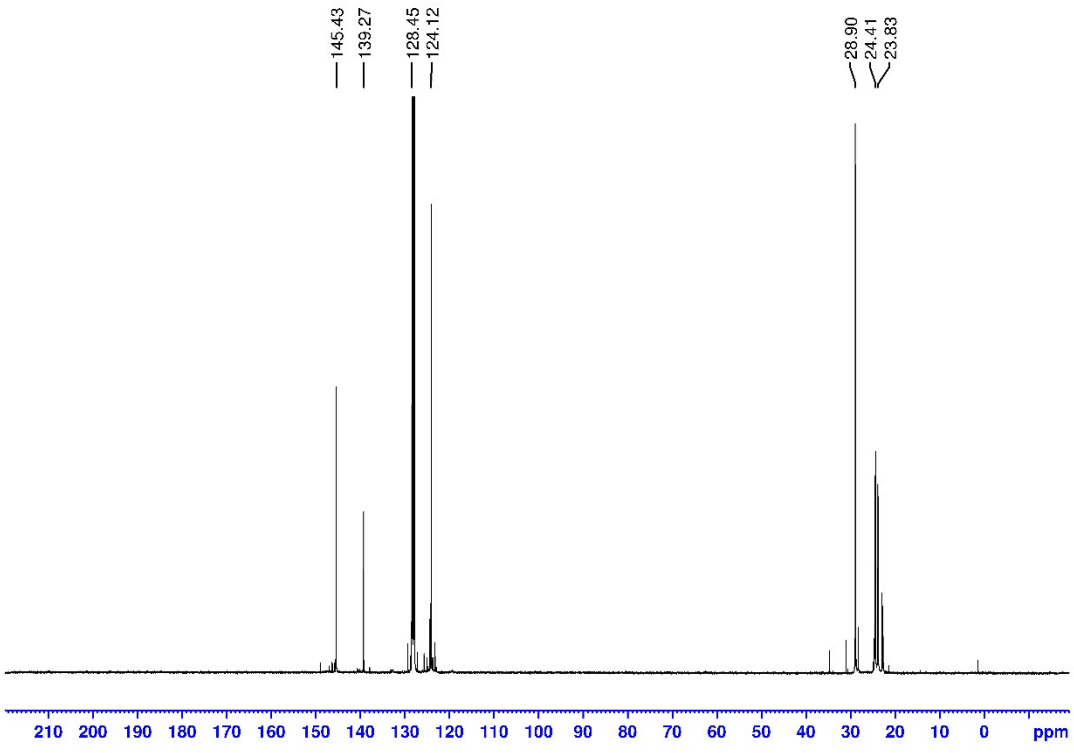

Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum of **10**.

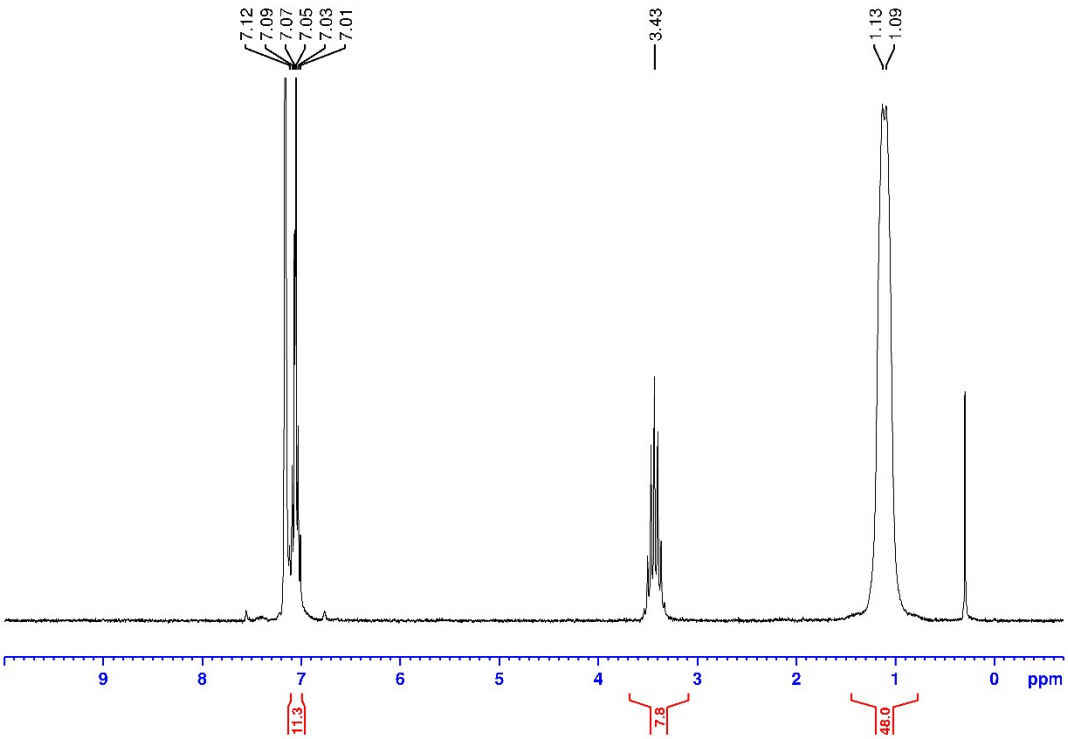

Figure S57. ^{1}H NMR spectrum of **11**.

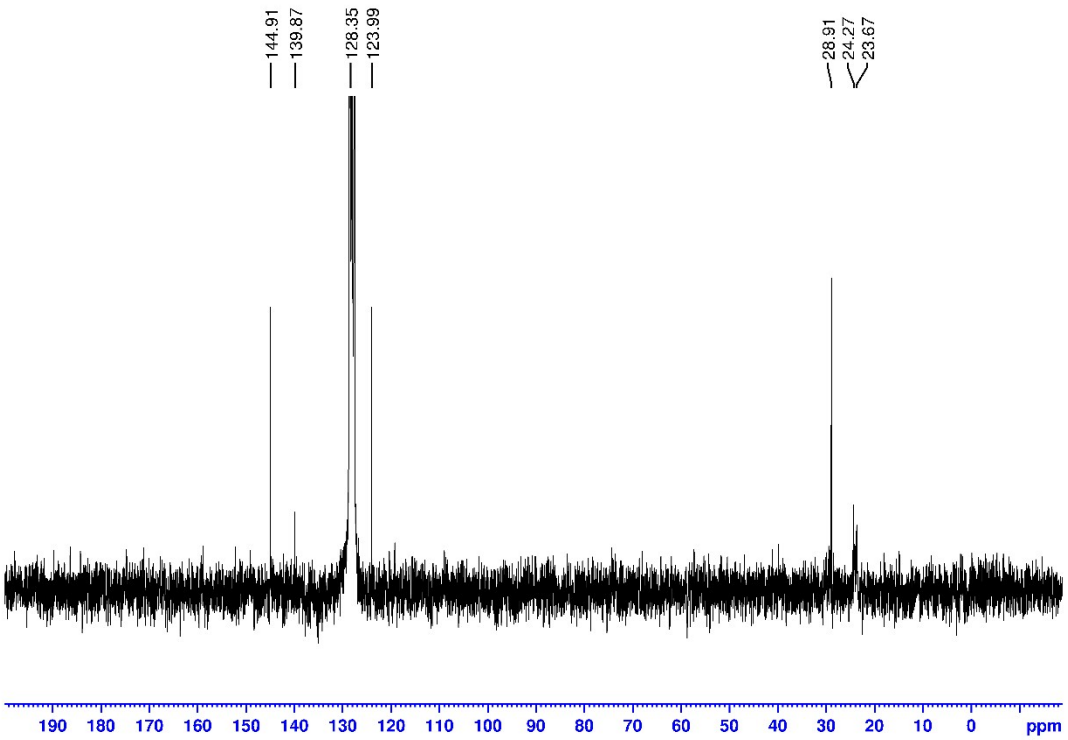

Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum of **11**.

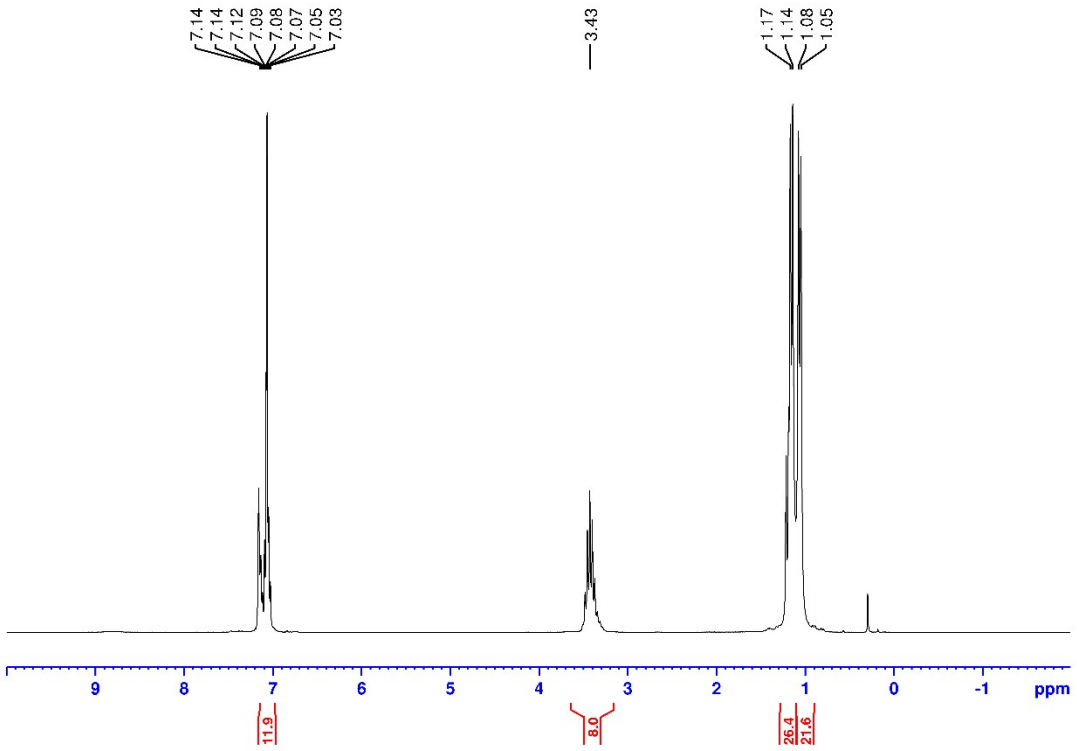

Figure S59. ^{1}H NMR spectrum of **13**.

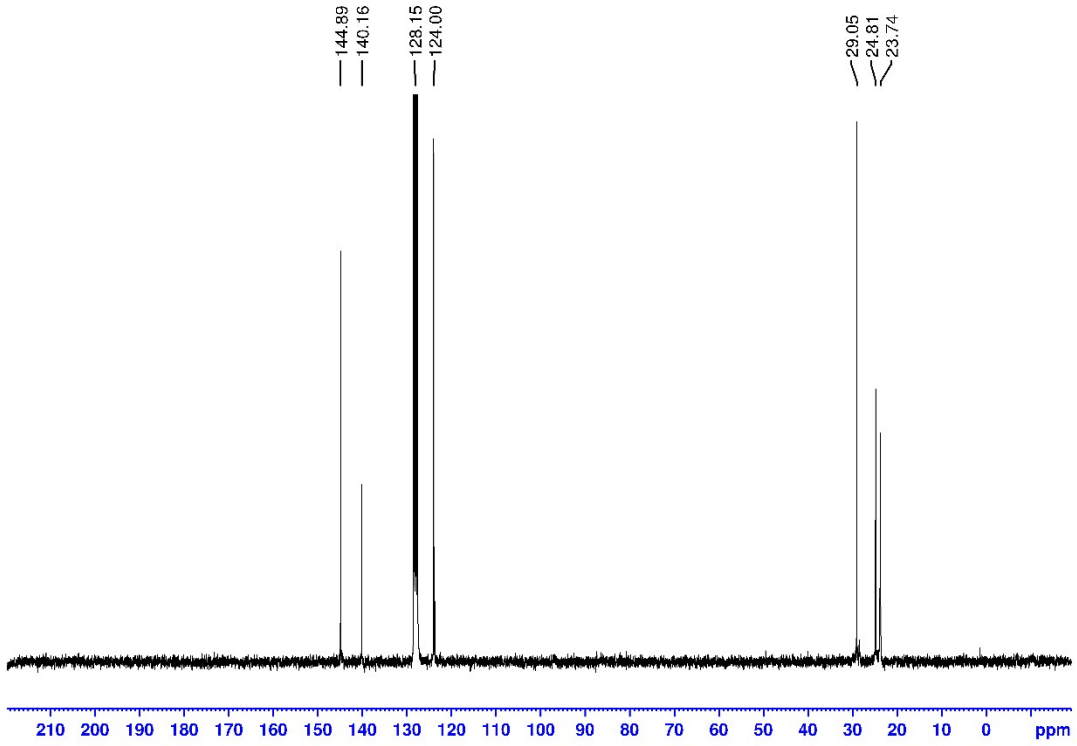

Figure S60. $^{13}C\{^{1}H\}$ NMR spectrum of **13**.

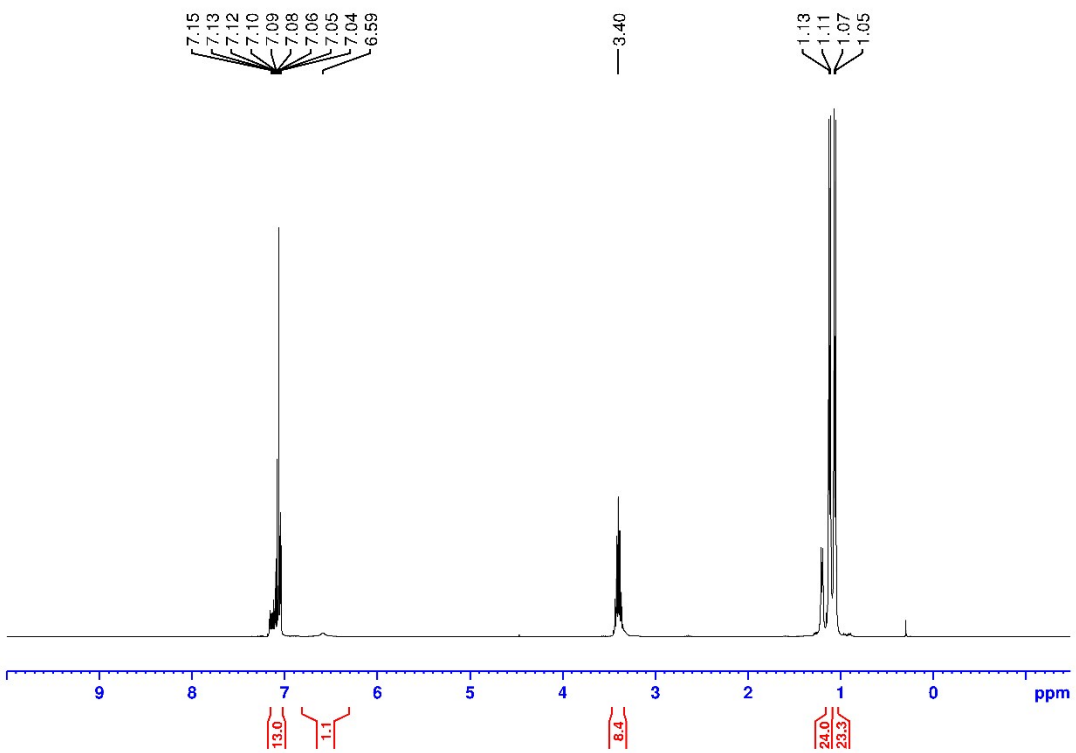

Figure S61. ^{1}H NMR spectrum of **14**.

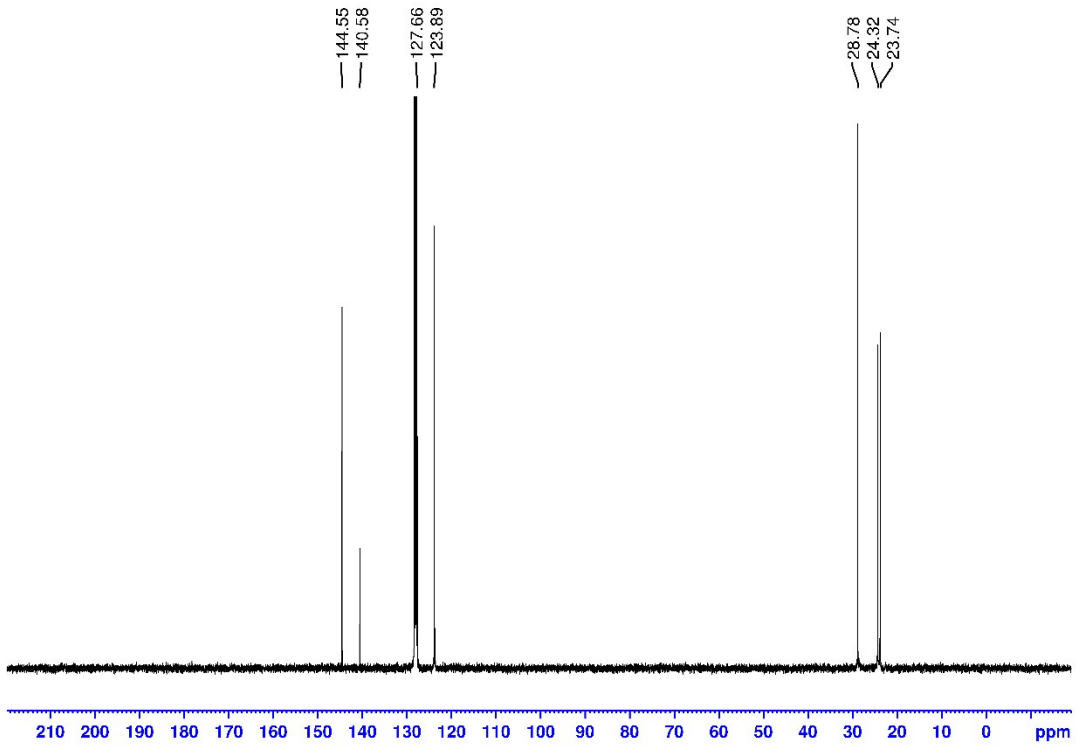

Figure S62. $^{13}C\{^{1}H\}$ NMR spectrum of **14**.

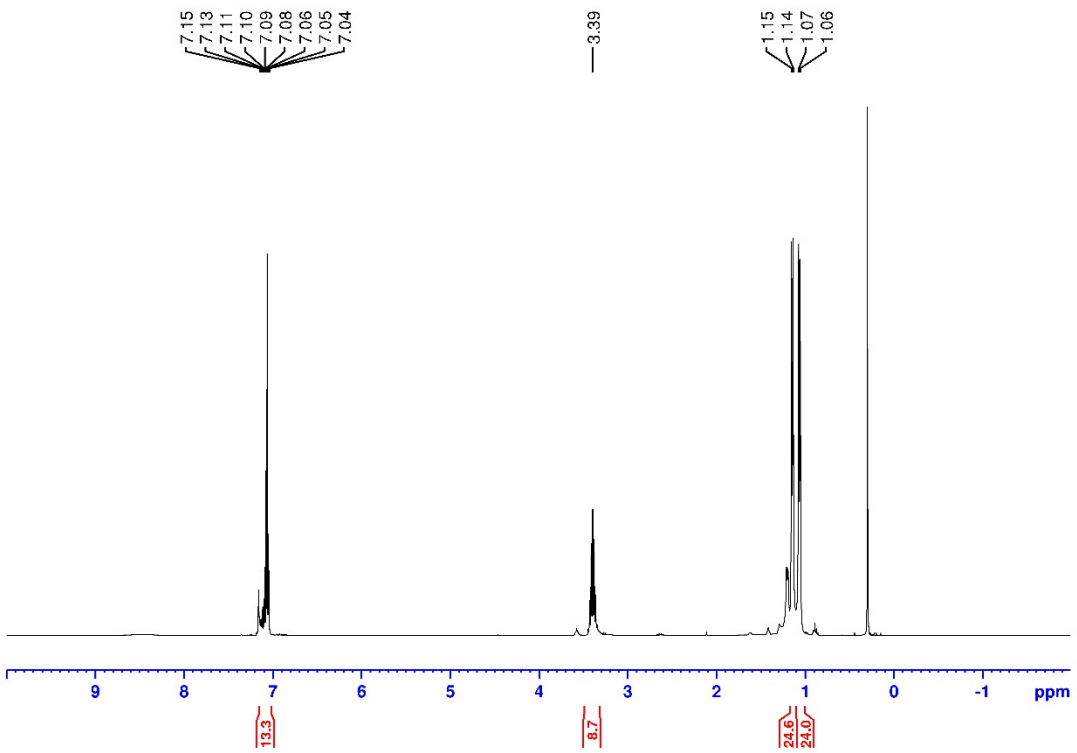

Figure S63. ^{1}H NMR spectrum of **15**.

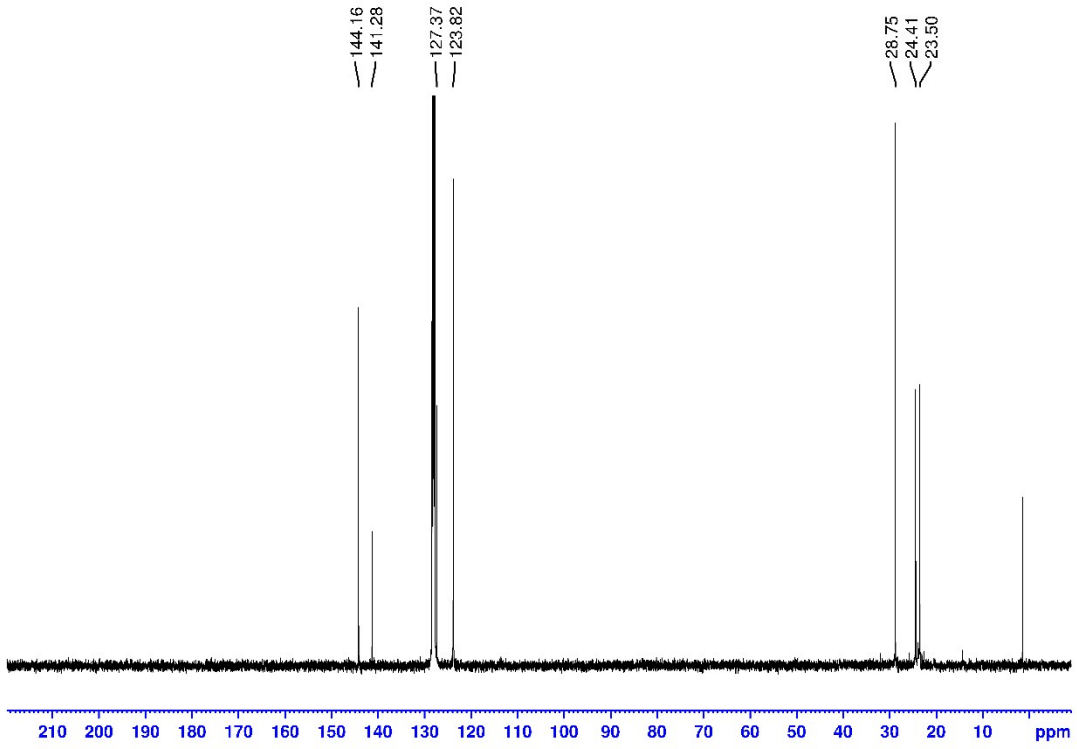

Figure S64. $^{13}C\{^{1}H\}$ NMR spectrum of **15**.

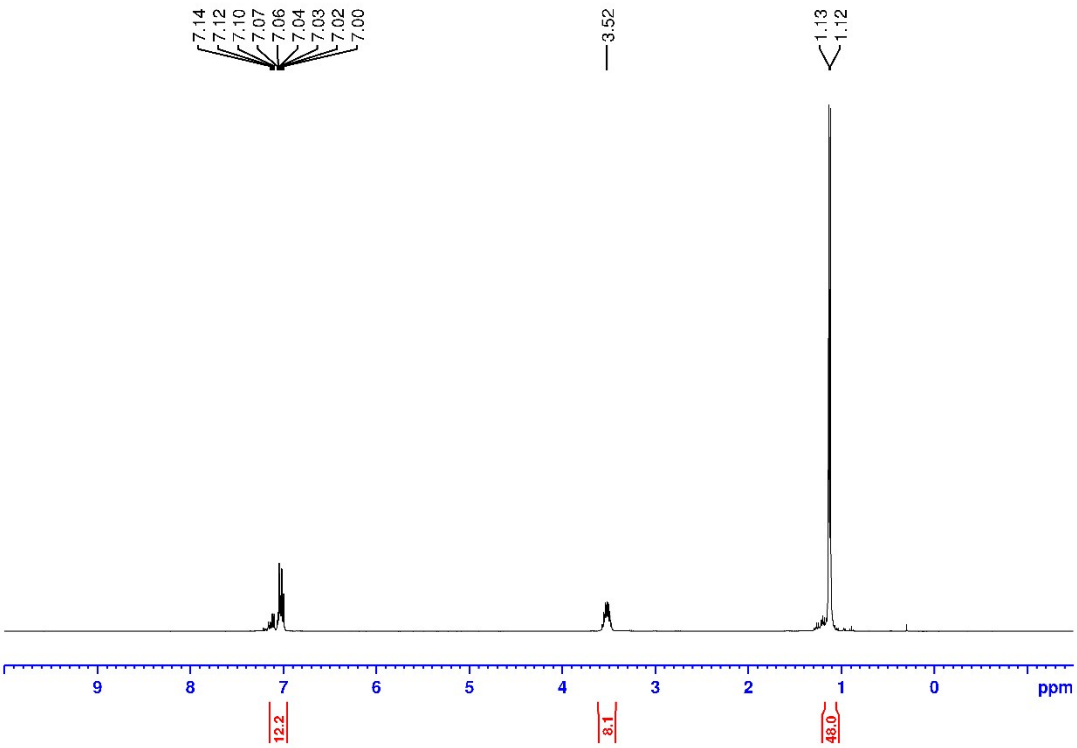

Figure S65. ^{1}H NMR spectrum of **16**.

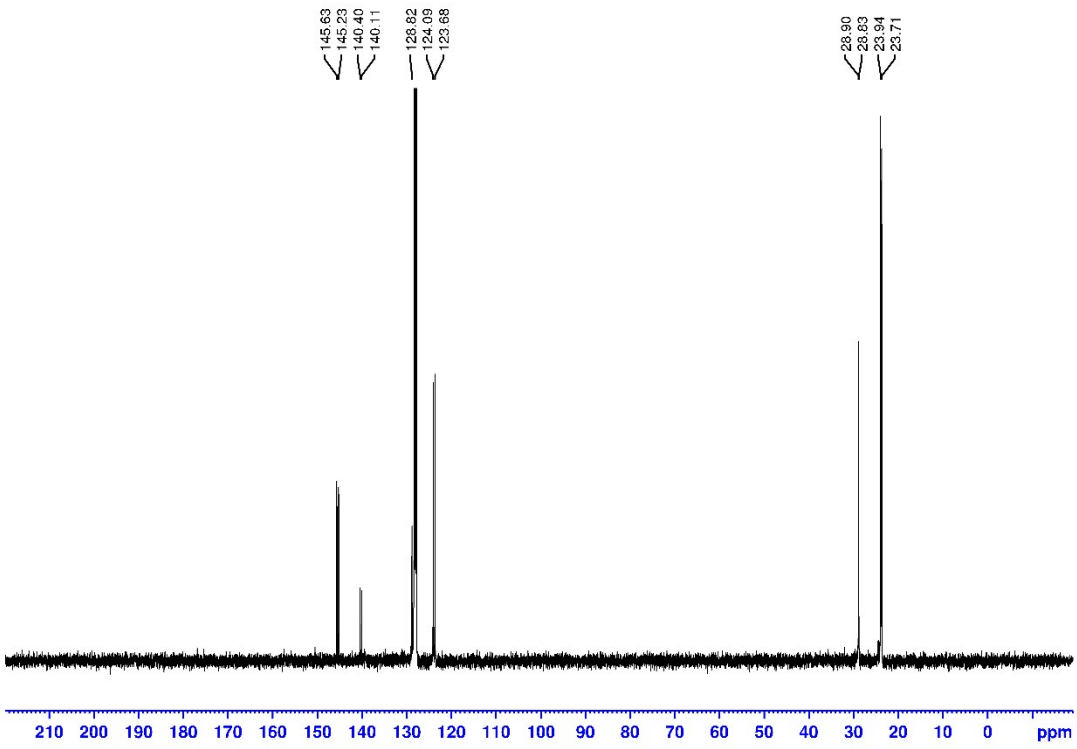

Figure S66. $^{13}C\{^{1}H\}$ NMR spectrum of **16**.

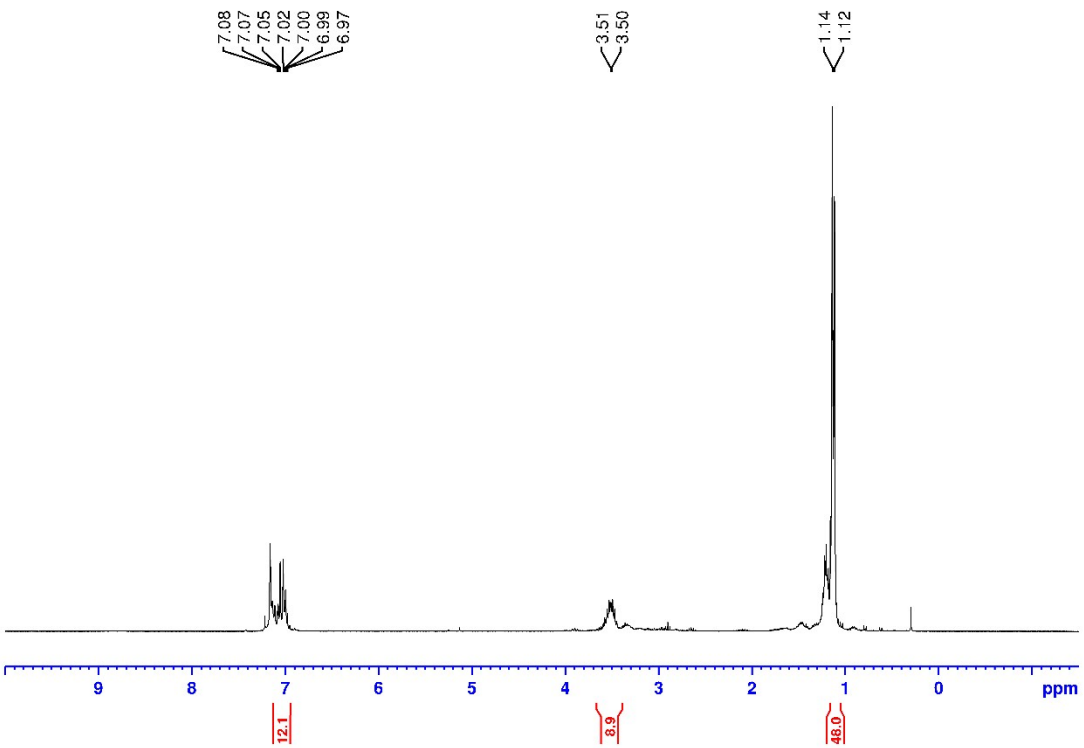

Figure S67. ^{1}H NMR spectrum of **17**.

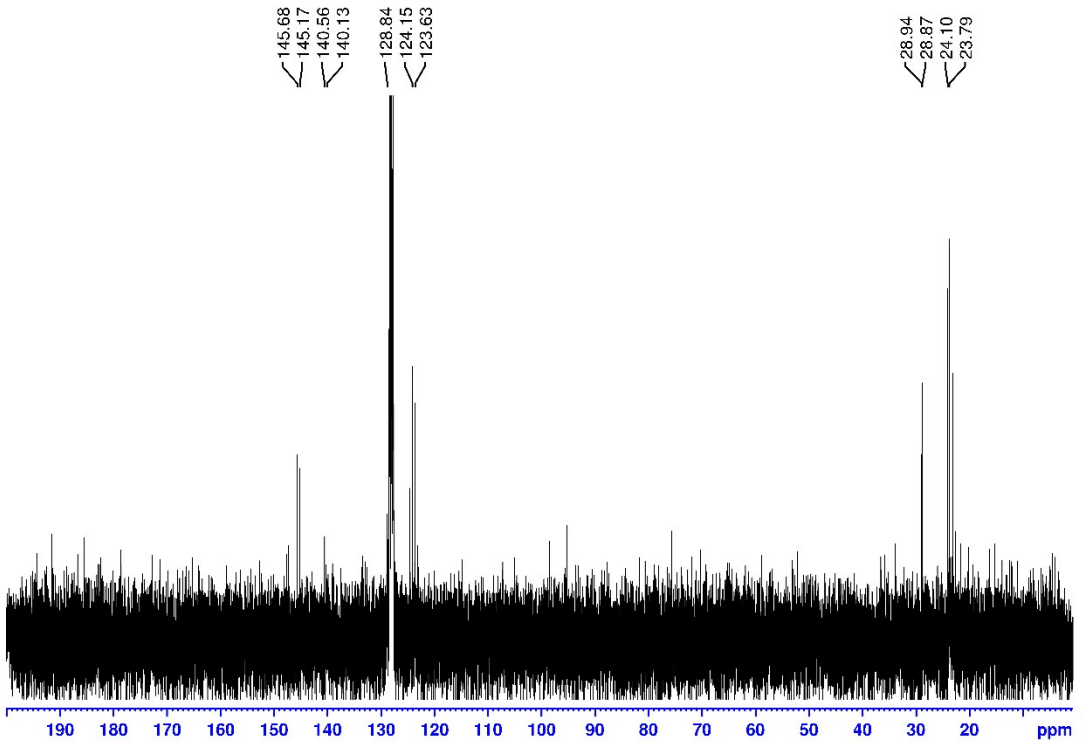

Figure S68. ^{13}C{^{1}H} NMR spectrum of **17**.

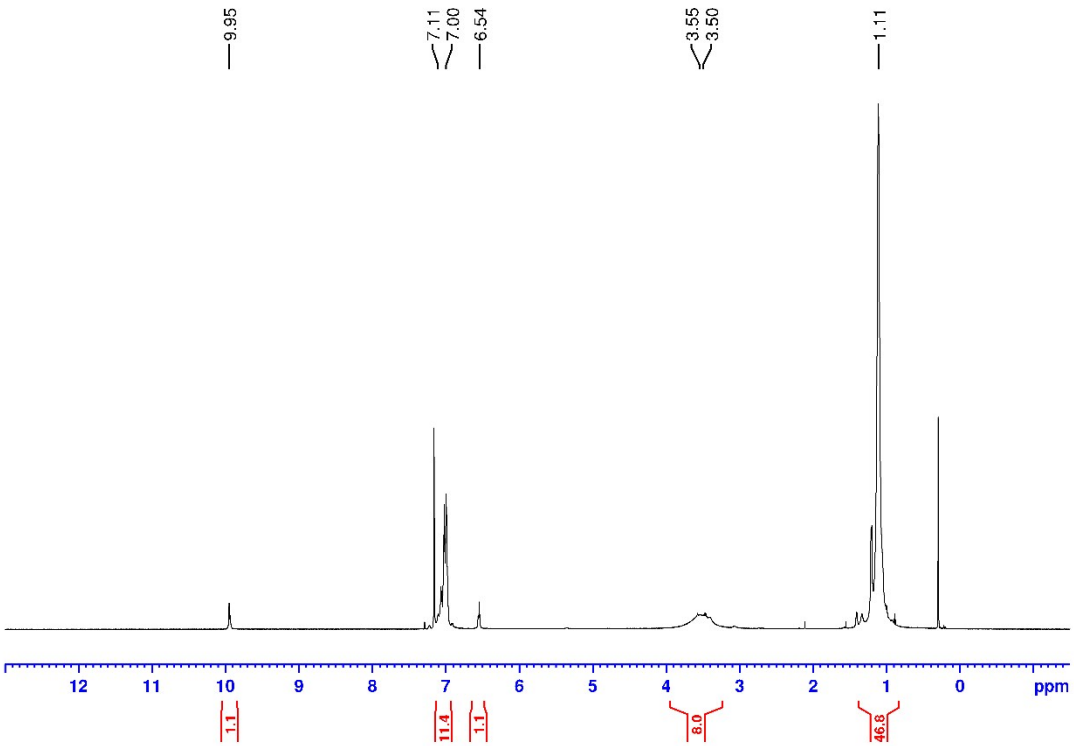

Figure S69. ^{1}H NMR spectrum of **18**.

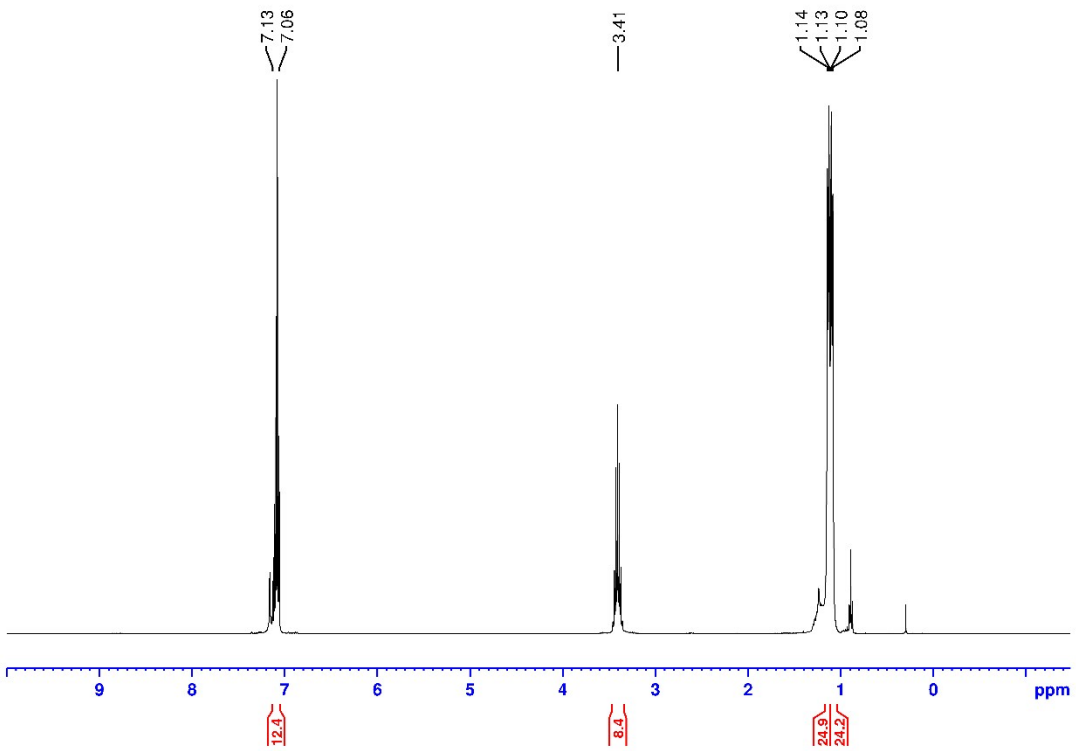

Figure S70. ^{1}H NMR spectrum of **19**.

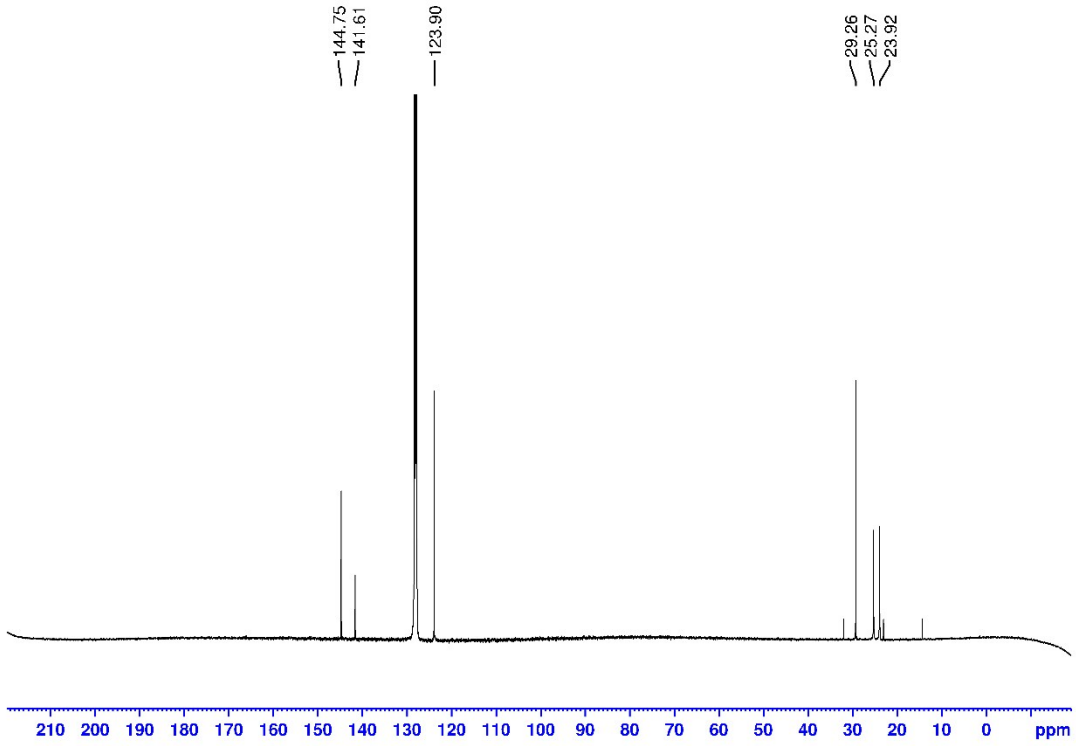

Figure S71. $^{13}C\{^{1}H\}$ NMR spectrum of **19**.

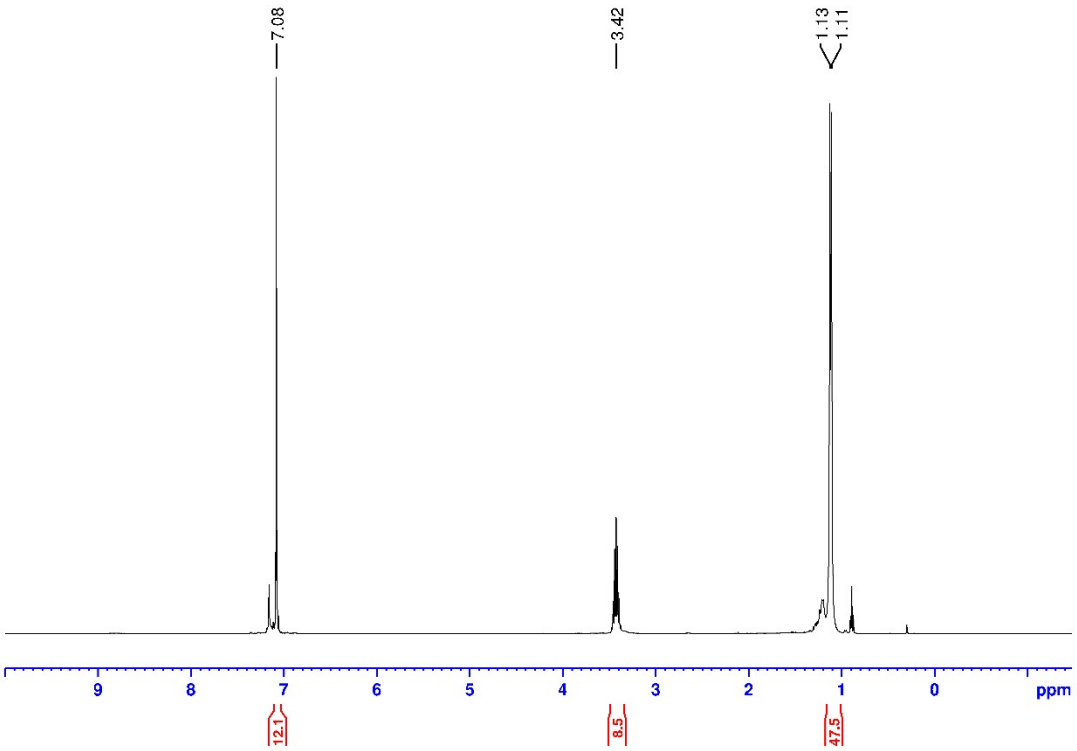

Figure S72. ^{1}H NMR spectrum of **20**.

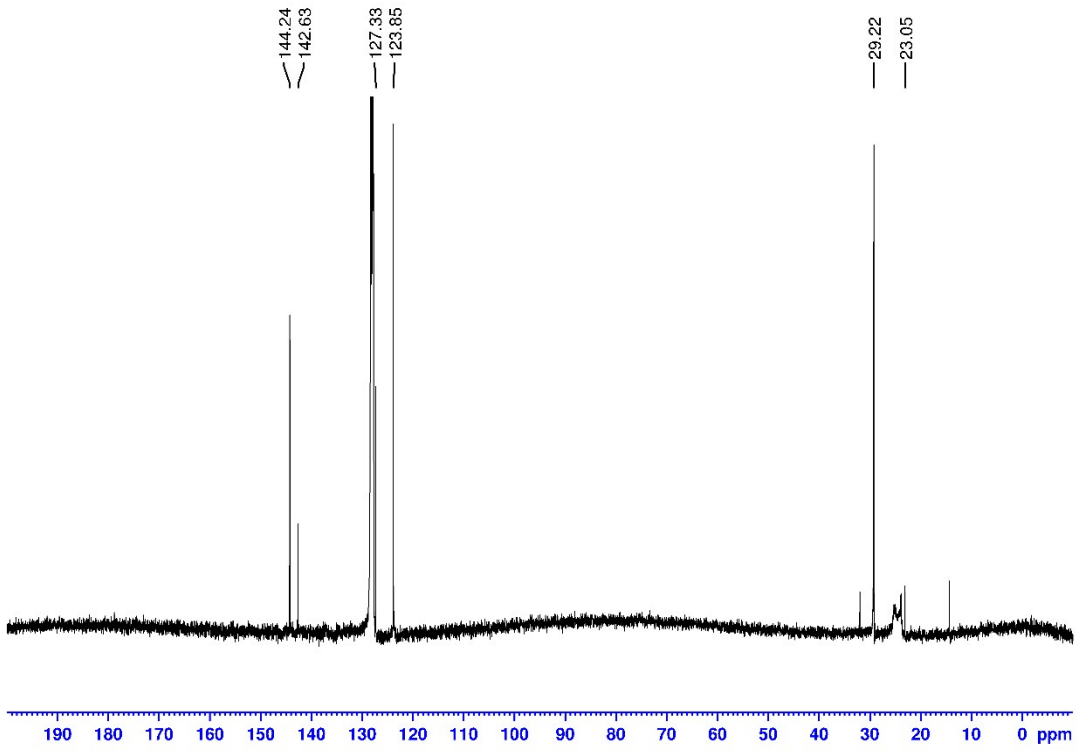

Figure S73. $^{13}C\{^{1}H\}$ NMR spectrum of **20**.

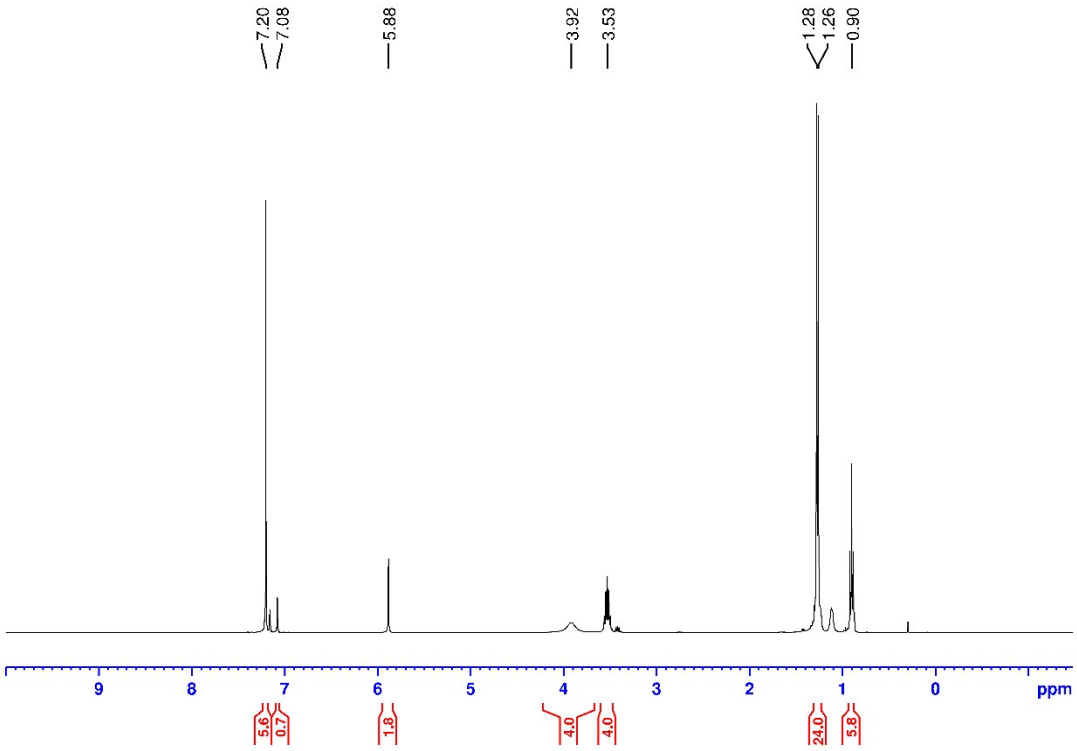

Figure S74. ^{1}H NMR spectrum of **21**.

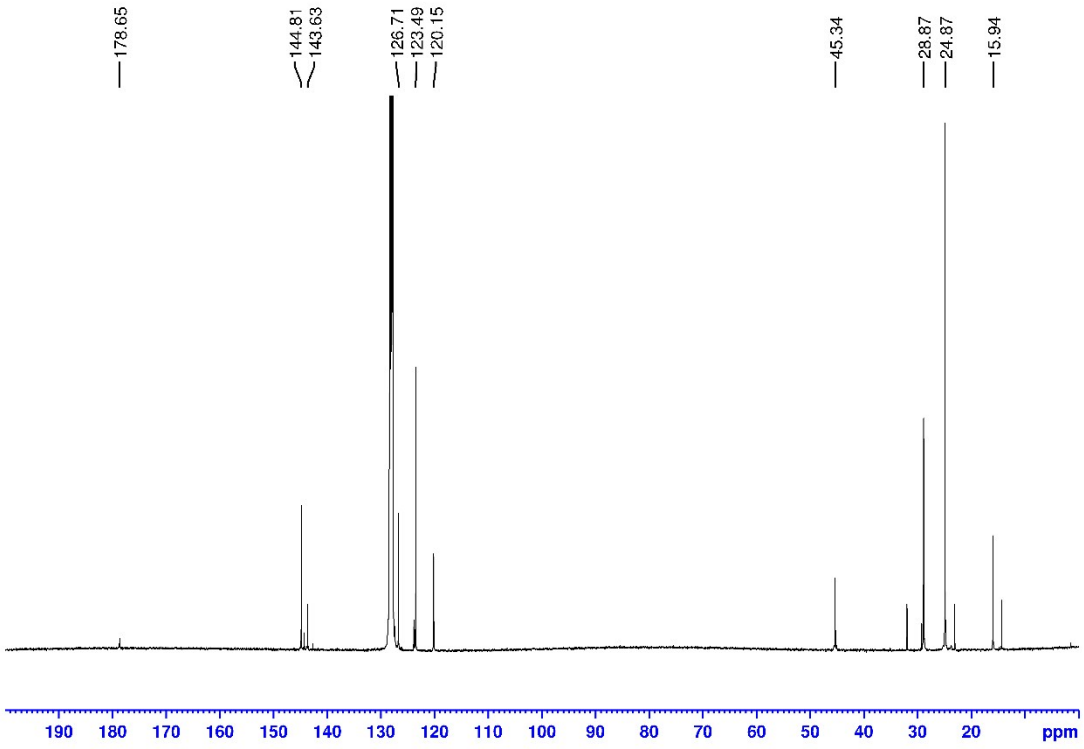

Figure S75. $^{13}C\{^{1}H\}$ NMR spectrum of **21**.

Computational Studies

General details

Gaussian 16 (Revision B.01)[S17] was used to fully optimize all the structures reported in this paper at the BP86[S18] level of density functional theory (DFT). For structure optimizations the def2-TZVP[S19] basis set was chosen and empirical dispersion correction (GD3) were employed.[S20] NBO calculations were performed using the NBO 7.0 program,[S21] using the optimized geometries.

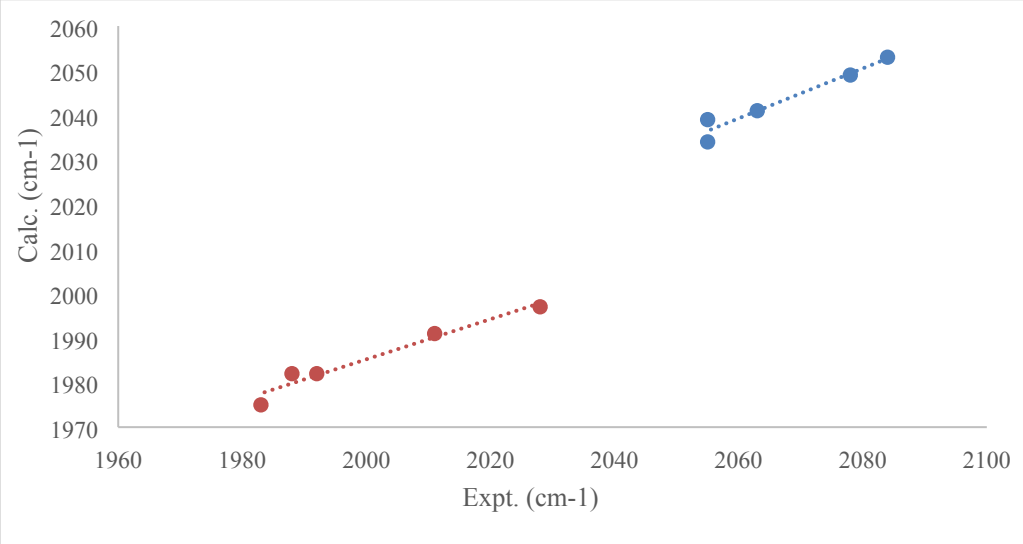

Figure S76. Calculated and experimental rhodium carbonyl stretching frequencies for [(L)Rh(CO)$_2$].

	$N_3Dipp_2^-$	$Fiso^-$	$Piso^-$	$Giso^-$	$^{Dipp}nacnac^-$
NPA Charge (N)	-0.352	-0.559	-0.554	-0.590	-0.487
NPA Charge (X)	-0.099	0.208	0.539	0.566	-
E_{HOMO} **/eV**	-0.740	-0.938	-0.967	-1.211	-0.768
E_{LUMO} **/eV**	1.592	2.137	2.018	2.025	1.953
$E_{HOMO-LUMO}$ **/eV**	2.332	3.075	2.985	3.236	2.721

Table S1. Selected theoretical parameters associated with free monoanionic *N*,*N*'-ligands.

Molecular Orbital Diagrams

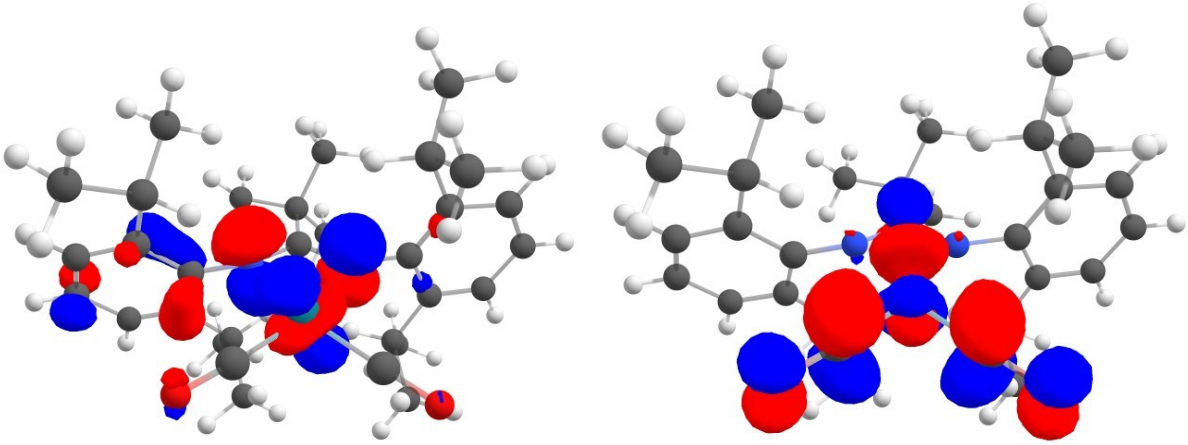

Figure S77. Orbital diagrams for **[(Piso)Rh(CO)$_2$]**: HOMO (left), LUMO (right).

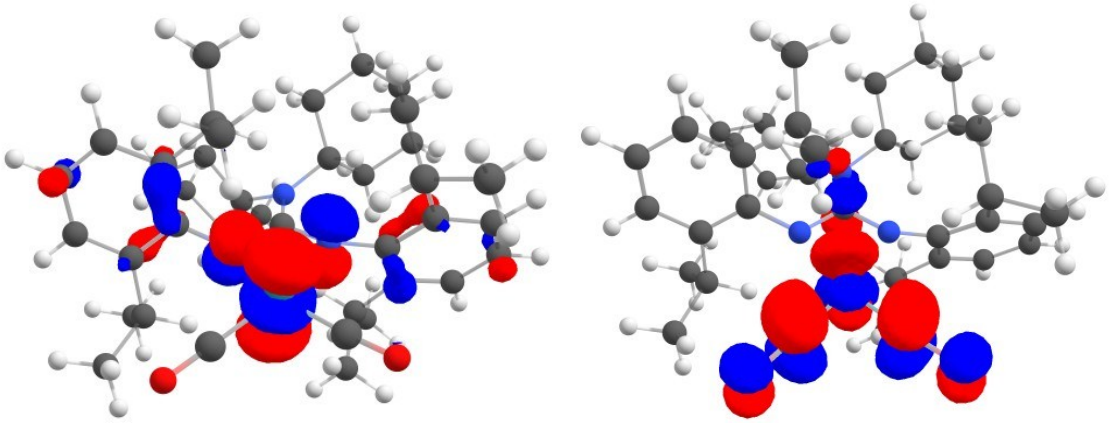

Figure S78. Orbital diagrams for **[(Giso)Rh(CO)$_2$]**: HOMO (left), LUMO (right).

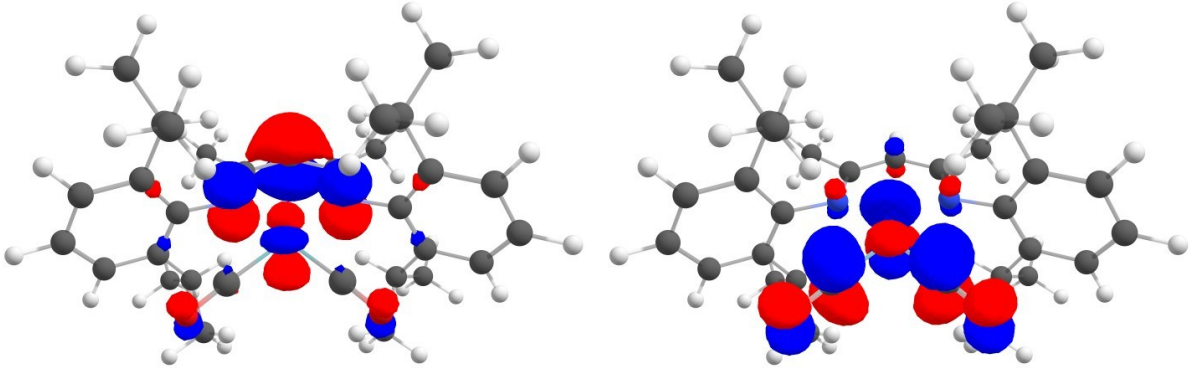

Figure S79. Orbital diagrams for **[(^{Dipp}nacnac)Rh(CO)$_2$]**: HOMO (left), LUMO (right).

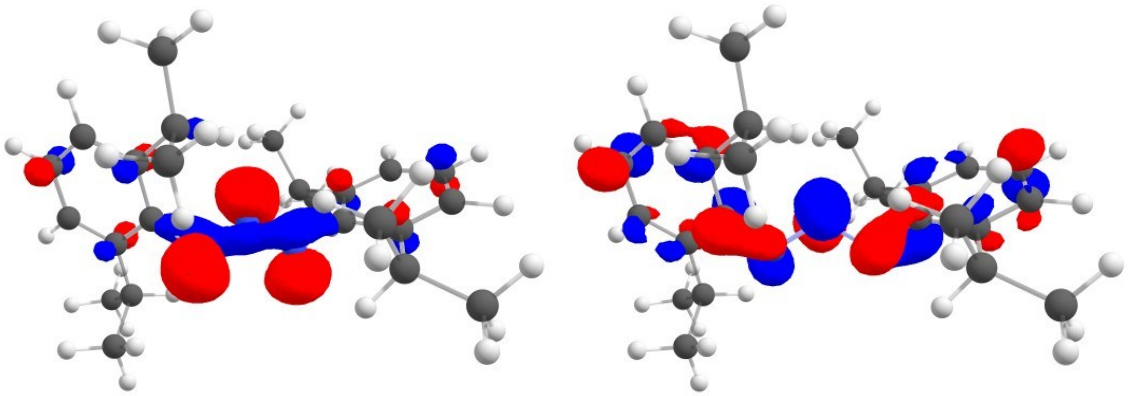

Figure S80. Orbital diagrams for $\mathbf{N_3Dipp_2}^{\bullet-}$: HOMO (left), LUMO (right).

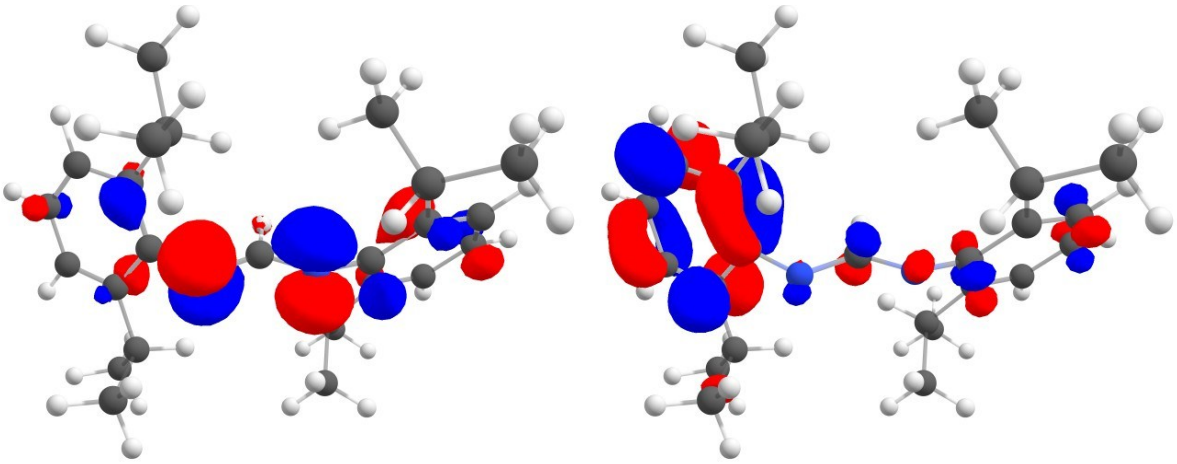

Figure S81. Orbital diagrams for $\mathbf{Fiso}^{\bullet-}$: HOMO (left), LUMO (right).

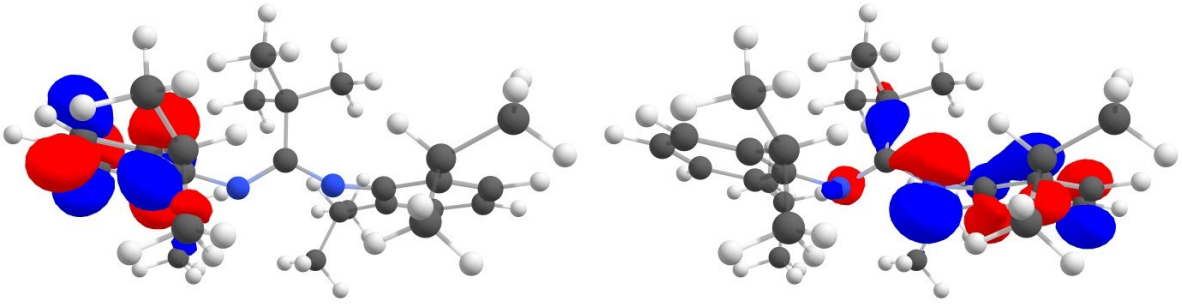

Figure S82. Orbital diagrams for $\mathbf{Piso}^{\bullet-}$: HOMO (left), LUMO (right).

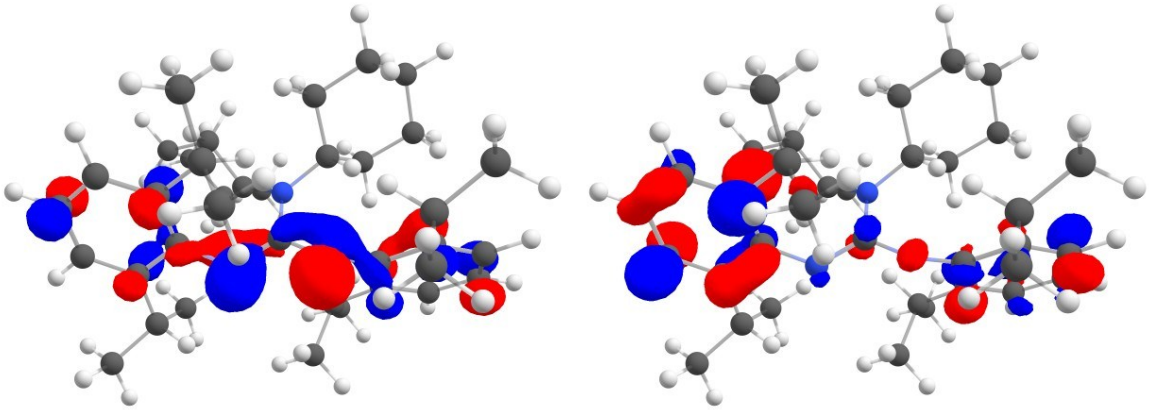

Figure S83. Orbital diagrams for **Giso**$^{-}$: HOMO (left), LUMO (right).

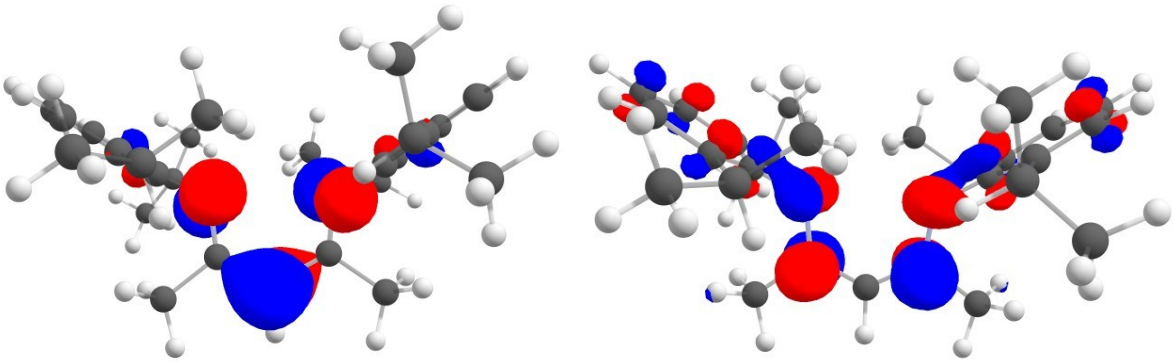

Figure S84. Orbital diagrams for ^{Dipp}**nacnac**$^{-}$: HOMO (left), LUMO (right).

Coordinates

[($Dipp_2N_3$)$Rh(CO)_2$]

0 1

Rh	-0.00001600	0.00027800	1.61007900
N	1.04158300	-0.04627900	-0.18705300
C	1.33726900	-0.03597700	2.90238600
O	2.20716800	-0.05111600	3.66098600
N	-1.04167300	0.04600500	-0.18708100
O	-2.20678900	0.05262800	3.66142700
C	-1.33709700	0.03712900	2.90259800
C	2.33127500	-0.30576900	-0.70530000
C	-4.64321800	-0.36855900	-0.87059500
H	-5.44212600	-1.08616100	-0.67914000
C	-2.60166800	1.51910200	-1.38736400
C	-2.44601700	-2.95323100	-0.81306600
H	-3.22602700	-3.18635900	-1.55460500
H	-2.12922700	-3.89333700	-0.33596700
H	-1.58419300	-2.52990800	-1.34769100
C	-2.33133300	0.30545200	-0.70542300
C	-3.34191200	-0.64578100	-0.43396700
C	-3.91656700	1.73679400	-1.81706500
H	-4.16287000	2.65588100	-2.34968900
C	2.60168800	-1.51960100	-1.38688500
C	-2.98562000	-1.96296900	0.23844700
H	-2.15690200	-1.76486800	0.94100500
C	1.51738500	-2.57908500	-1.56180500
H	0.59619800	-2.05979500	-1.86770700
C	-1.51732800	2.57851100	-1.56250300
H	-0.59615300	2.05912800	-1.86827900
C	-4.92816900	0.80822400	-1.56218800
H	-5.94591300	1.00670600	-1.90441200
C	3.34178400	0.64561400	-0.43413300
C	3.91660600	-1.73734000	-1.81650400
H	4.16296900	-2.65656300	-2.34886500
C	2.98541100	1.96303100	0.23778500
H	2.15643100	1.76524000	0.94011900
C	4.64311600	0.36833900	-0.87065600
H	5.44197000	1.08606100	-0.67942000
C	-1.24046000	3.27722000	-0.21651400
H	-2.15335800	3.76654000	0.15699400
H	-0.45849300	4.04251600	-0.33229000
H	-0.90086200	2.56221900	0.54979200
C	4.92815200	-0.80863800	-1.56187900
H	5.94591400	-1.00716400	-1.90402300
C	-4.13305000	-2.58422600	1.04480800
H	-4.55342200	-1.86773700	1.76573800
H	-3.76781500	-3.45868700	1.60356600
H	-4.94954300	-2.93418800	0.39417200

C	-1.82453400	3.61473400	-2.65125600
H	-2.06117800	3.13621100	-3.61318900
H	-0.94935200	4.26432600	-2.80001700
H	-2.66884400	4.26511400	-2.37318700
C	1.82464100	-3.61552900	-2.65033400
H	2.06126500	-3.13720600	-3.61237200
H	0.94949100	-4.26519500	-2.79895600
H	2.66898100	-4.26580800	-2.37212000
C	2.44627600	2.95302700	-0.81421800
H	2.12946300	3.89333100	-0.33752600
H	1.58456700	2.52963800	-1.34898200
H	3.22654900	3.18580800	-1.55558900
C	4.13264400	2.58438500	1.04435500
H	4.55265900	1.86805400	1.76564900
H	3.76733400	3.45906700	1.60271700
H	4.94941600	2.93403300	0.39390200
C	1.24051700	-3.27752700	-0.21567600
H	2.15342200	-3.76674800	0.15793900
H	0.45857100	-4.04286700	-0.33131000
H	0.90088900	-2.56238400	0.55048100
N	-0.00003400	-0.00022200	-0.98842000

[(Fiso)Rh(CO)$_2$]

0 1

Rh	0.00000500	0.00020600	1.55271000
N	1.10085600	-0.01640600	-0.23947100
C	1.33201100	0.00045100	2.84156300
O	2.19256600	0.01090100	3.61284400
N	-1.10084000	0.01638900	-0.23947400
C	0.00000800	-0.00009000	-0.98123700
O	-2.19260800	-0.00989600	3.61278800
C	-1.33202700	0.00037700	2.84153300
C	2.41562600	-0.22777900	-0.69907300
C	-4.68111400	-0.58908800	-0.90876300
H	-5.42831000	-1.37104000	-0.76597400
C	-2.78257100	1.46895800	-1.28033100
C	-2.25675300	-3.01311900	-0.96788700
H	-2.99077300	-3.27905100	-1.74457500
H	-1.86743400	-3.94332600	-0.52602600
H	-1.42054700	-2.49187200	-1.45468400
C	-2.41561800	0.22759500	-0.69912900
C	-3.36126500	-0.80640600	-0.49549800
C	-4.11294600	1.62899500	-1.68967300
H	-4.42691200	2.56806600	-2.14701500
C	2.78252600	-1.46926800	-1.28003800
C	-2.91192200	-2.12749700	0.11106700
H	-2.12702000	-1.89517100	0.85220100
C	1.77843800	-2.61526600	-1.37028500
H	0.80886200	-2.19659300	-1.68347600
C	-1.77852800	2.61497500	-1.37078000
H	-0.80897800	2.19630200	-1.68404900
C	-5.05407500	0.61383000	-1.50905400
H	-6.08576200	0.76516600	-1.83306000
C	3.36131300	0.80622800	-0.49565500
C	4.11288300	-1.62941900	-1.68939800
H	4.42680400	-2.56858100	-2.14658500
C	2.91202600	2.12744100	0.11068300
H	2.12716700	1.89526200	0.85190900
C	4.68114500	0.58878700	-0.90890700
H	5.42837300	1.37073900	-0.76628100
C	-1.56705300	3.24764800	0.01866500
H	-2.51275300	3.66721100	0.39506300
H	-0.82335000	4.05741800	-0.03438600
H	-1.20759900	2.50576900	0.74843500
C	5.05405000	-0.61425300	-1.50899000
H	6.08572300	-0.76568200	-1.83300000
C	-4.02476700	-2.89110800	0.84021400
H	-4.52790200	-2.25682000	1.58469800
H	-3.60159400	-3.76211100	1.36238300
H	-4.78738500	-3.27081200	0.14229300
C	-2.14315300	3.68970600	-2.40334300

H	-2.33613900	3.25389200	-3.39500300
H	-1.31557200	4.40799100	-2.49978400
H	-3.03487300	4.26043900	-2.10077200
C	2.14291600	-3.69007800	-2.40281500
H	2.33577900	-3.25434100	-3.39453300
H	1.31531300	-4.40835800	-2.49909600
H	3.03466700	-4.26079900	-2.10031500
C	2.25680200	3.01286800	-0.96839800
H	1.86753000	3.94316600	-0.52668700
H	1.42055400	2.49154500	-1.45504100
H	2.99077800	3.27864000	-1.74518300
C	4.02492500	2.89117800	0.83961600
H	4.52810600	2.25702600	1.58418500
H	3.60179100	3.76227900	1.36165200
H	4.78749900	3.27074900	0.14157500
C	1.56711100	-3.24785200	0.01922300
H	2.51285200	-3.66739200	0.39554600
H	0.82340500	-4.05762700	-0.03370100
H	1.20773200	-2.50593300	0.74898800
H	0.00000600	-0.00023200	-2.08398000

[(Piso)Rh(CO)$_2$]

0 1

Rh	-0.10339900	-0.78449700	-1.41435400
N	-1.11475400	-0.13846600	0.29277800
C	-1.51226600	-1.36406800	-2.47900100
O	-2.42834600	-1.71573900	-3.09079100
N	1.04983500	-0.06659000	0.16005800
C	0.00162800	0.24663100	0.94024700
O	1.91934200	-1.46507300	-3.54478700
C	1.13370200	-1.21826300	-2.73237300
C	-2.45458900	0.28754000	0.38321400
C	0.09234600	0.80005400	2.37683100
C	4.58795500	-0.90333500	0.90587800
H	5.18465900	-1.74438500	1.26471100
C	3.08120400	1.26426000	-0.06943700
C	3.03264000	-3.03544500	2.40077800
H	4.08386900	-3.35095700	2.31585800
H	2.43969600	-3.93586100	2.62161800
H	2.95479900	-2.35522400	3.26100800
C	2.44395000	0.06614800	0.34454300
C	3.19736600	-1.04207000	0.80471600
C	4.47356700	1.35099500	0.05013800
H	4.98150100	2.26744100	-0.25652200
C	-3.44903200	-0.70652300	0.55524500
C	2.53082600	-2.37843700	1.10476300
H	1.45147700	-2.19316000	1.21229900
C	-3.04420000	-2.16785400	0.69089000
H	-2.15469400	-2.31078800	0.05164700
C	2.28414900	2.40058600	-0.69652500
H	1.23283800	2.26820600	-0.40346800
C	5.22446500	0.28336100	0.54354400
H	6.30917000	0.37175000	0.63132100
C	-2.80360000	1.64558600	0.16501500
C	-4.79009400	-0.30559300	0.59240900
H	-5.57239300	-1.05228600	0.73576700
C	-1.74170000	2.67719200	-0.19174000
H	-0.79963800	2.36562100	0.28182400
C	-4.15787400	1.99512100	0.21542300
H	-4.44995100	3.03562300	0.06319100
C	2.33799900	2.29727000	-2.23241500
H	3.37614900	2.37488000	-2.59079400
H	1.74968800	3.10352500	-2.69707600
H	1.92728900	1.33886500	-2.57873500
C	-5.14537800	1.03527600	0.44278100
H	-6.19564900	1.33078700	0.48257300
C	2.71322300	-3.33476300	-0.08984900
H	2.29355200	-2.90522200	-1.00970600
H	2.20655200	-4.29370900	0.09946200
H	3.78132200	-3.53724600	-0.26524000

C	2.72676700	3.79545800	-0.22974800
H	2.74711900	3.86962900	0.86698600
H	2.03109700	4.55767300	-0.61278400
H	3.72902600	4.05349000	-0.60476900
C	-2.60699000	-2.49658400	2.13066300
H	-1.75398500	-1.87484300	2.43415800
H	-2.30338900	-3.55170000	2.21401300
H	-3.43227700	-2.31877100	2.83797600
C	-2.04328900	4.09142900	0.32186700
H	-1.17382000	4.74466900	0.15307500
H	-2.26873400	4.09145300	1.39901600
H	-2.89731200	4.54583800	-0.20312100
C	-1.48799100	2.67949100	-1.71056500
H	-1.15076300	1.68751700	-2.05540300
H	-0.70677500	3.40993900	-1.97269400
H	-2.40753900	2.93972900	-2.25680900
C	-4.11958500	-3.15123100	0.21023900
H	-4.99490200	-3.16331700	0.87862400
H	-3.71139100	-4.17280400	0.19288200
H	-4.46558100	-2.90348700	-0.80394400
C	-1.28674000	1.07674300	3.00523800
H	-1.94840600	0.20253100	2.97374300
H	-1.80830900	1.90861200	2.51729100
H	-1.13408000	1.34814200	4.06084200
C	0.92043800	2.10228300	2.43394900
H	0.94692400	2.45712900	3.47556100
H	0.47277100	2.89796200	1.82211000
H	1.95426900	1.94533600	2.10455300
C	0.80967000	-0.27082600	3.23556500
H	0.30090900	-1.24371500	3.17973600
H	0.81181200	0.05457900	4.28682800
H	1.85111200	-0.40177400	2.91939400

[(Giso)Rh(CO)$_2$]

0 1

Rh	0.04365200	-2.42579100	-0.24241200
N	-1.10918300	-0.68934700	-0.09309100
C	1.43807000	-3.64493300	-0.34750500
N	-0.06896800	1.50759400	0.00643700
N	1.08262900	-0.63160400	-0.15365200
O	-1.95362100	-4.68236900	-0.27723200
C	2.37485800	-0.32468200	-0.62708900
C	-3.56652100	-0.20739800	2.67334900
H	-3.59317000	-0.04699800	3.75236300
C	2.58001000	0.17441200	-1.93966500
O	2.35066600	-4.35545300	-0.39604000
C	-2.32370400	-0.52617500	0.61845500
C	1.12509200	2.21957100	0.52994500
H	1.79457400	1.40802000	0.84241200
C	1.93053900	3.05976000	-0.47702800
H	1.39086400	3.98643700	-0.72394900
H	2.07413300	2.50061900	-1.40766000
C	-0.02718800	0.13507500	-0.07200600
C	-2.33018700	-0.32628700	2.02666700
C	-1.30785600	2.19748200	-0.43762600
H	-1.90066700	1.39834000	-0.90669700
C	4.76111900	-0.33118500	-0.22682200
H	5.61742100	-0.54474500	0.41485200
C	-1.19260000	-3.80960100	-0.27868600
C	3.46919900	-0.63573300	0.22000100
C	-4.74794200	-0.52519400	0.59614500
H	-5.68993100	-0.60979700	0.04924300
C	-3.53832600	-0.65178600	-0.09932300
C	4.97315500	0.23778100	-1.48277800
H	5.98616600	0.48105000	-1.80927300
C	3.89175900	0.46479200	-2.33542900
H	4.07574700	0.86888600	-3.33202000
C	-1.06064800	3.25360900	-1.53048900
H	-0.40695400	2.84357900	-2.31540800
H	-0.54094500	4.12124900	-1.09393000
C	-1.03665800	-0.30009300	2.83392500
H	-0.23950000	0.09360400	2.18758300
C	-4.76912500	-0.29364400	1.96948000
H	-5.72013800	-0.19350400	2.49630200
C	0.85494200	3.05707400	1.79292200
H	0.24936200	2.48109200	2.50737500
H	0.27759500	3.95745500	1.52729800
C	3.23453700	-1.30144300	1.57229400
H	2.30609100	-1.88839400	1.48239000
C	3.09170000	4.22845900	1.43829200
H	2.63013200	5.20111400	1.18739400
H	4.06394000	4.45340100	1.90538800

C	-3.34598300	4.25748000	-1.03800600
H	-2.92611200	5.19073900	-0.62003100
H	-4.31937300	4.52224400	-1.48121100
C	-2.39643000	3.72852000	-2.12381900
H	-2.20877200	4.50685600	-2.88088500
H	-2.87521700	2.88906700	-2.65622000
C	2.18763900	3.48461600	2.43287500
H	1.98885400	4.11252000	3.31615700
H	2.71382400	2.58710900	2.79850500
C	-1.09470600	0.61254700	4.06815900
H	-1.47462900	1.61441600	3.81689100
H	-0.08741800	0.72305200	4.49769300
H	-1.73925800	0.19584600	4.85722700
C	-0.62365800	-1.72804100	3.23608100
H	-1.39317800	-2.18761700	3.87552500
H	0.32895400	-1.71358000	3.78821600
H	-0.48716100	-2.36383900	2.34481600
C	3.28659000	3.42299300	0.14520100
H	3.84429300	2.49251900	0.35322600
H	3.89037100	3.99411800	-0.57750300
C	-3.54777900	-0.94595900	-1.59334400
H	-2.49681900	-0.97668500	-1.92066300
C	-4.26992500	0.14719100	-2.39927900
H	-5.33374800	0.21308500	-2.12231900
H	-4.21816100	-0.07029900	-3.47725500
H	-3.82221200	1.13553400	-2.22964300
C	1.62023600	1.35912600	-4.00995700
H	1.89027300	2.34076500	-3.59185900
H	0.69308100	1.47998000	-4.58992700
H	2.40896600	1.06481600	-4.71934300
C	-3.53086000	3.24216300	0.09961400
H	-4.06558000	2.34964400	-0.26769400
H	-4.15719000	3.67050400	0.89790100
C	1.41387600	0.30284600	-2.91478800
H	0.52336000	0.60431200	-2.34301500
C	2.98711800	-0.27350800	2.69101000
H	3.83503300	0.42410200	2.77679200
H	2.86030100	-0.78042100	3.66017200
H	2.07577400	0.31082800	2.50284300
C	4.35720000	-2.27222600	1.96615700
H	4.56722200	-2.98760700	1.15804100
H	4.06172300	-2.84212400	2.85981000
H	5.29288800	-1.74561600	2.21129900
C	-2.17753200	2.80433900	0.67866700
H	-2.32382000	2.07311700	1.48308500
H	-1.67198000	3.68066500	1.11289600
C	-4.17941000	-2.32076100	-1.88170500
H	-3.68979900	-3.11973100	-1.31120700
H	-4.10086200	-2.56430400	-2.95254400
H	-5.24781700	-2.32575900	-1.61361600

C	1.10957400	-1.07111400	-3.54508000
H	1.97841300	-1.43159800	-4.11729000
H	0.24776100	-1.00301800	-4.22695900
H	0.87016800	-1.81881400	-2.77162000

[(^{Dipp}nacnac)Rh(CO)$_2$]

0 1

Rh	0.00009000	-0.08985900	-0.69021500
C	-1.27220600	-0.10218200	-2.05456600
C	1.27268000	-0.10217900	-2.05433100
C	-2.80324900	0.01619600	0.28782200
C	-3.36619000	1.28231400	0.00981400
C	-2.61818700	2.57291300	0.32128900
H	-1.73494900	2.30897800	0.92215100
C	-3.50362700	-1.18167300	0.02311800
C	-5.32249700	0.15111900	-0.89736100
H	-6.30165400	0.20312200	-1.37746800
C	2.90489900	-2.54441900	0.34735400
H	2.00235200	-2.37546100	0.95385400
C	3.36594500	1.28245900	0.00982500
C	-1.26156500	-0.05416700	2.10565600
C	2.47577500	-0.02214800	3.00865600
H	2.17897000	-0.03301200	4.06389200
H	3.07939500	0.87807200	2.81930100
H	3.13222000	-0.88337100	2.81552400
C	-0.00007500	-0.07230600	2.71957900
H	-0.00013100	-0.07791800	3.80807000
C	2.80328900	0.01627400	0.28803900
C	-2.90450000	-2.54456200	0.34701700
H	-2.00163500	-2.37548300	0.95300400
C	4.76448800	-1.08668300	-0.58042800
H	5.31590500	-2.00011200	-0.81383400
C	1.26148300	-0.05405400	2.10578000
C	3.50392000	-1.18148300	0.02350900
C	-4.62965800	1.32292800	-0.59372200
H	-5.07560200	2.28976800	-0.83715500
C	-4.76420300	-1.08705100	-0.58083900
H	-5.31545400	-2.00056500	-0.81431500
C	4.62940000	1.32326400	-0.59373400
H	5.07511300	2.29016900	-0.83734200
C	2.61761800	2.57293200	0.32099300
H	1.73435200	2.30888800	0.92176400
C	3.47234900	3.54796800	1.14977100
H	4.33622900	3.91853700	0.57682000
C	-3.47317300	3.54767500	1.15010100
H	-2.87480200	4.42219300	1.44796800
H	-4.33704100	3.91822900	0.57712500
H	-3.85896800	3.06904000	2.06279400
C	5.32251000	0.15156400	-0.89715700
H	6.30162500	0.20370100	-1.37733300
C	-2.46211700	-3.27671300	-0.93335900
H	-2.04917500	-4.26769700	-0.68893200
C	-2.47594700	-0.02294300	3.00844200
H	-2.17919400	-0.03283300	4.06370100

H	-3.13126800	-0.88514800	2.81580800
H	-3.08072300	0.87635400	2.81848900
C	-2.10711900	3.24449800	-0.96649700
H	-1.57133200	4.17694800	-0.73038600
H	-2.94204000	3.48917600	-1.64139800
H	-1.41349500	2.58270300	-1.50490000
C	3.86889100	-3.41568900	1.17211700
H	3.37002300	-4.34534900	1.48561200
C	-3.86815700	-3.41553300	1.17249400
H	-3.36932200	-4.34527700	1.48580200
H	-4.75856800	-3.69865500	0.59037600
C	2.10657100	3.24426700	-0.96692000
H	1.57032900	4.17649100	-0.73094300
H	1.41335700	2.58216100	-1.50547200
C	2.46176500	-3.27610300	-0.93302700
H	1.68526900	-2.70643000	-1.46318400
H	2.04891400	-4.26715700	-0.68873000
H	3.31132100	-3.41750400	-1.61899900
N	-1.44960700	-0.05214200	0.77960200
N	1.44964500	-0.05232000	0.77975900
O	2.01523700	-0.10016800	-2.94040800
O	-2.01458500	-0.10005800	-2.94080100
H	4.75886700	-3.69898300	0.58942100
H	-4.21419200	-2.89055200	2.07563100
H	4.21559100	-2.89087500	2.07509800
H	2.87381700	4.42244700	1.44743300
H	3.85814000	3.06954800	2.06257700
H	2.94153500	3.48930600	-1.64163500
H	-3.31206000	-3.41835900	-1.61880100
H	-1.68590900	-2.70730400	-1.46418300

$[N_3Dipp_2]^-$

-1 1

N	-1.11032800	0.00882800	0.96740300
N	1.07766500	-0.18350500	0.92065600
C	-2.26089700	0.42541400	0.30152700
C	4.59298400	0.23058100	-0.11514400
H	5.48693800	0.74994300	0.23892800
C	2.29781100	-1.11190600	-1.05968000
C	4.33327000	2.31913000	1.96108700
H	5.35970900	1.93188300	2.07490300
H	4.12529300	2.94748500	2.84218700
H	4.31246000	2.96122400	1.06686100
C	2.21743000	-0.29646700	0.11481400
C	3.39164800	0.36409100	0.58726600
C	3.52473100	-1.20698000	-1.72892500
H	3.59915700	-1.82630900	-2.62559300
C	-2.34886300	1.54017000	-0.59406200
C	3.30039100	1.18758000	1.86611600
H	2.29326000	1.63621700	1.87423700
C	-1.14871000	2.42546000	-0.91691600
H	-0.39459500	2.24781500	-0.13696000
C	1.10830200	-1.97191200	-1.48986800
H	0.21009400	-1.34086200	-1.42831500
C	4.66802600	-0.54157400	-1.27725300
H	5.60963300	-0.62805800	-1.82557200
C	-3.45664100	-0.29240900	0.63182900
C	-3.59139200	1.84497500	-1.16858800
H	-3.65905800	2.68550600	-1.86520800
C	-3.34446300	-1.48635600	1.56962100
H	-2.56759700	-1.22226000	2.30703400
C	-4.66975400	0.06499200	0.04247500
H	-5.57492200	-0.49648600	0.28700600
C	0.92477800	-3.12834200	-0.48680500
H	1.81822700	-3.77501100	-0.47954700
H	0.05111800	-3.74555900	-0.75355700
H	0.77268000	-2.73534500	0.52933000
C	-4.74703200	1.12150300	-0.87264700
H	-5.70084900	1.38603800	-1.33620800
C	3.38381500	0.26619100	3.09954800
H	2.57745300	-0.47923900	3.05833800
H	3.28001400	0.84478100	4.03344100
H	4.35513300	-0.25599800	3.12302100
C	1.19457600	-2.50985100	-2.92314700
H	1.35195300	-1.69872100	-3.65124700
H	0.25571700	-3.02385800	-3.18307300
H	2.01167100	-3.24101200	-3.04542700
C	-0.50181700	2.03124300	-2.25712200
H	-0.15386400	0.99079000	-2.20710300
H	0.36482700	2.67566700	-2.48232400

H	-1.22836000	2.12817200	-3.08181900
C	-2.82171100	-2.71526700	0.79927400
H	-2.67036200	-3.57380700	1.47547900
H	-1.86076200	-2.48235600	0.32129900
H	-3.53974800	-3.01288700	0.01660500
C	-4.64019900	-1.82668100	2.31796100
H	-5.04876000	-0.94664800	2.83874300
H	-4.44903500	-2.61215500	3.06690000
H	-5.42108600	-2.20995600	1.63959100
C	-1.48975400	3.92782500	-0.89780200
H	-2.14671100	4.21715200	-1.73424800
H	-0.56755700	4.52478900	-0.98802200
H	-1.99440700	4.20931700	0.03909100
N	-0.01831700	0.06057600	0.25049400

[Fiso]$^-$

-1 1

N	-1.19806100	0.00385900	0.79017900
N	1.13893300	-0.07434200	0.78210600
C	-0.03111000	-0.03980500	0.16999600
C	-2.34741700	0.35485200	0.11602600
C	4.56137800	0.36761200	-0.52733700
H	5.34189900	1.13271900	-0.54970200
C	2.55946400	-1.61473300	-0.51843400
C	3.88012300	3.15978000	0.17889200
H	4.94376600	3.05543500	0.45161200
H	3.52817100	4.11319700	0.60469400
H	3.81876300	3.22879500	-0.91841800
C	2.30294700	-0.34243900	0.08862500
C	3.32888100	0.65430300	0.06642600
C	3.81062200	-1.85222000	-1.10158900
H	4.01609300	-2.82249800	-1.56036600
C	-2.49827400	1.61620400	-0.55347100
C	3.03567100	1.99822200	0.71873700
H	1.97407800	2.21854200	0.51077500
C	-1.36491600	2.64194900	-0.49572600
H	-0.42577200	2.13172300	-0.76067700
C	1.49854400	-2.70996800	-0.43379400
H	0.53121100	-2.25573600	-0.69923400
C	4.81275500	-0.87747900	-1.11244200
H	5.77927200	-1.08495100	-1.57874400
C	-3.47058900	-0.52889800	0.18201800
C	-3.72512300	1.92180700	-1.15618700
H	-3.84886000	2.87754700	-1.67112300
C	-3.27929700	-1.86031500	0.89083900
H	-2.57115800	-1.65941200	1.71409300
C	-4.67516300	-0.17332000	-0.42960900
H	-5.52621200	-0.85864400	-0.38614800
C	1.36247900	-3.21752900	1.01535900
H	2.30379300	-3.68917000	1.34310600
H	0.55236500	-3.96133600	1.09291400
H	1.13236500	-2.37989800	1.68921900
C	-4.81062900	1.04097900	-1.11023000
H	-5.75554900	1.30437500	-1.59221400
C	3.16900600	1.89073000	2.25118700
H	2.50032900	1.10362600	2.62611500
H	2.89890800	2.84274300	2.73898700
H	4.20761100	1.64250100	2.52747900
C	1.71471800	-3.88219700	-1.39846300
H	1.82384700	-3.53878700	-2.43917900
H	0.85341900	-4.56716100	-1.35161800
H	2.61301700	-4.46631300	-1.13748500
C	-1.51819400	3.81421200	-1.47293900
H	-1.64621800	3.46695300	-2.51030500

H	-0.62116800	4.45222500	-1.43403300
H	-2.38316000	4.44900900	-1.21782600
C	-2.59226800	-2.87461100	-0.04502300
H	-2.37474500	-3.81968600	0.48100700
H	-1.64315800	-2.46592300	-0.41785700
H	-3.23751200	-3.09946100	-0.91073100
C	-4.56643900	-2.45337700	1.47884000
H	-5.08570000	-1.72707400	2.12310200
H	-4.33397400	-3.34587400	2.08221800
H	-5.27125900	-2.76936400	0.69124400
C	-1.19052800	3.16017900	0.94637900
H	-2.10283600	3.68484100	1.27538600
H	-0.34241000	3.86215600	1.00891300
H	-0.99938900	2.32109400	1.63072500
H	-0.03577400	-0.04645100	-0.95042300

[Piso]$^-$

-1 1

N	1.19570900	-0.28584000	-0.32503300
N	-1.05296900	0.02707700	-0.44066100
C	0.04243900	-0.07091600	0.29292300
C	2.46194600	0.17828900	-0.20000800
C	-0.02451600	-0.02339300	1.87587800
C	-4.67572900	0.56762300	0.01184800
H	-5.39075900	1.39399600	0.06028200
C	-2.86318400	-1.57522800	-0.16655900
C	-3.55482900	3.33430400	0.43822400
H	-4.60165300	3.44170000	0.10902500
H	-3.07136400	4.31661800	0.31224200
H	-3.56201200	3.08858200	1.51128700
C	-2.37054600	-0.22639300	-0.19176800
C	-3.31605900	0.84852200	-0.14831300
C	-4.23158200	-1.80227700	0.00268500
H	-4.60410700	-2.82959000	0.03713800
C	2.77399800	1.58307300	-0.21834400
C	-2.80703200	2.26451900	-0.36718200
H	-1.75206800	2.27182700	-0.05077500
C	1.62947500	2.58386100	-0.30852800
H	0.84121000	2.25159700	0.38837200
C	-1.88522600	-2.70747600	-0.45542100
H	-0.92289800	-2.45047400	0.01023300
C	-5.14429800	-0.74613900	0.11383600
H	-6.20902700	-0.94660300	0.25498500
C	3.54556700	-0.76469700	-0.18312100
C	4.11203400	1.98505400	-0.21732800
H	4.34997800	3.05204000	-0.23230900
C	3.18903300	-2.24256000	-0.17173400
H	2.30440500	-2.34020000	0.48560300
C	4.86367700	-0.30623500	-0.18622400
H	5.68432000	-1.02861700	-0.16405100
C	-1.61383900	-2.78060600	-1.97209500
H	-2.53885100	-3.03002200	-2.51793200
H	-0.85491000	-3.54771400	-2.19818600
H	-1.23776700	-1.81082500	-2.32797900
C	5.16426500	1.06118200	-0.20033700
H	6.20204400	1.40261700	-0.19550300
C	-2.81361700	2.58865700	-1.87370800
H	-2.20917100	1.84934200	-2.41834600
H	-2.39203200	3.58930700	-2.06832600
H	-3.84245400	2.56220700	-2.26967000
C	-2.31359900	-4.07100200	0.09859200
H	-2.52432300	-4.01636400	1.17827600
H	-1.51401300	-4.81203400	-0.05945500
H	-3.21708600	-4.45412300	-0.40415000
C	2.00366900	4.01369700	0.10077100

H	2.46580300	4.04227100	1.10022700
H	1.10307500	4.64787300	0.11827000
H	2.71058300	4.46945300	-0.61213600
C	4.29222000	-3.15614100	0.37674500
H	3.92200700	-4.19050700	0.46392100
H	4.63388200	-2.82597600	1.37027000
H	5.16997500	-3.18022300	-0.29050500
C	2.74196300	-2.70810200	-1.57331300
H	1.91380700	-2.07946200	-1.92914500
H	2.40083100	-3.75738400	-1.55292500
H	3.58130900	-2.63114500	-2.28441300
C	0.99715400	2.56631600	-1.71462500
H	1.74171400	2.87274800	-2.46784300
H	0.14072400	3.25811900	-1.76693700
H	0.63285200	1.55816100	-1.95729000
C	1.36210000	0.16385900	2.51736300
H	1.83023600	1.11541300	2.23139300
H	2.05591700	-0.63977200	2.23588300
H	1.25321300	0.15362300	3.61557200
C	-0.59534900	-1.36215000	2.39203200
H	-0.58527200	-1.36813700	3.49589000
H	0.01834400	-2.20752900	2.04393000
H	-1.63069800	-1.51979800	2.06141100
C	-0.93711300	1.12109500	2.35643500
H	-0.58397800	2.09601800	1.98610600
H	-0.93447400	1.16106900	3.45929900
H	-1.97462500	0.98285000	2.02577000

[Giso]$^-$

-1 1

N	1.11955700	0.33599500	-1.33259800
N	0.02483400	-0.24902200	0.72487000
N	-1.16727800	0.36590300	-1.28653600
C	-2.34265800	-0.32063000	-1.20891900
C	3.51375200	2.86230200	-0.04527400
H	3.52739600	3.85478600	0.41230200
C	-2.42831300	-1.75653100	-1.22777600
C	2.27047000	0.95274000	-0.93275500
C	-1.15584100	-0.02727300	1.56777500
H	-1.84944200	0.50746300	0.90684700
C	-1.92427300	-1.28224200	2.03551200
H	-1.36056900	-1.80506200	2.82620400
H	-2.04738600	-1.97560600	1.19433100
C	-0.01396700	0.15990000	-0.65933600
C	2.28611100	2.26057800	-0.33712800
C	1.25480900	-0.87226900	1.23280300
H	1.86639300	-0.99696400	0.32986700
C	-4.78993200	-0.22212900	-1.17257700
H	-5.71485100	0.36075500	-1.18208700
C	-3.56149100	0.43689300	-1.26070800
C	4.72121700	0.96493800	-0.91466900
H	5.67215700	0.46782400	-1.12430400
C	3.52333500	0.31624600	-1.22270700
C	-4.86620700	-1.61586200	-1.07859500
H	-5.83417500	-2.11528300	-0.99455700
C	-3.68486300	-2.36376600	-1.14209700
H	-3.75281000	-3.45428000	-1.12510500
C	1.09534400	-2.29667700	1.80629700
H	0.44498000	-2.89764500	1.15290700
H	0.61486500	-2.26181800	2.79895700
C	0.96434200	2.98253100	-0.10287200
H	0.25576100	2.24564900	0.30555400
C	4.73242200	2.22997600	-0.31842000
H	5.67759600	2.72014700	-0.07358700
C	-0.92908900	0.90266300	2.77922300
H	-0.35009100	1.78647000	2.46887200
H	-0.33536400	0.38217700	3.54976300
C	-3.46031500	1.94496600	-1.45094200
H	-2.57896300	2.09582900	-2.10002100
C	-3.13863000	0.10655200	3.76550600
H	-2.65291100	-0.42609200	4.60531800
H	-4.12596700	0.43753100	4.13119400
C	3.40970700	-2.11510500	2.84014000
H	3.01222400	-2.13111200	3.87290000
H	4.41359100	-2.57190100	2.88175100
C	2.48175900	-2.94884400	1.94234200
H	2.38530600	-3.97477000	2.33748600

H	2.93317200	-3.03715100	0.93716100
C	-2.27981100	1.32280200	3.38393600
H	-2.11709400	1.96809100	4.26441200
H	-2.82661800	1.93116600	2.64371100
C	1.03677600	4.12629000	0.91565600
H	1.47309500	3.79080000	1.87013900
H	0.02417800	4.51023700	1.11707600
H	1.64057800	4.97117400	0.54503100
C	0.37015700	3.47073400	-1.43885200
H	1.04201400	4.20901700	-1.90769600
H	-0.61273800	3.94237500	-1.27693100
H	0.22909800	2.62250100	-2.12290400
C	-3.29568800	-0.86651100	2.58651900
H	-3.87094300	-0.39143600	1.77173400
H	-3.86939200	-1.75559800	2.89763200
C	3.48566800	-1.05753400	-1.87368500
H	2.60121600	-1.57476400	-1.45810500
C	4.71810700	-1.92489000	-1.59031600
H	5.62505200	-1.51945300	-2.06870000
H	4.56772900	-2.94188400	-1.98688000
H	4.91427000	-2.00281100	-0.50912800
C	-1.29250500	-4.05843200	-1.06766100
H	-1.68179400	-4.20591500	-0.04734900
H	-0.30941700	-4.55113700	-1.13143800
H	-1.96708700	-4.57972700	-1.76691800
C	3.50039900	-0.65865300	2.35995700
H	4.00758400	-0.61339700	1.38052100
H	4.11400600	-0.06308900	3.05648300
C	-1.15176500	-2.57080600	-1.41035800
H	-0.39685700	-2.16082200	-0.72304900
C	-3.15946500	2.69154800	-0.13816100
H	-3.94763700	2.49855700	0.60826900
H	-3.10416200	3.78030900	-0.30672400
H	-2.19481600	2.37026000	0.27681300
C	-4.68698500	2.56176300	-2.13872600
H	-4.94128600	2.02388700	-3.06480200
H	-4.48932400	3.61551200	-2.39348100
H	-5.57575700	2.54679300	-1.48550400
C	2.10668100	-0.03118200	2.20853200
H	2.19213500	0.99650500	1.83115100
H	1.61957600	0.01156600	3.19736700
C	3.22886300	-0.93038100	-3.38828200
H	2.30451300	-0.36139900	-3.55933400
H	3.11884000	-1.92302400	-3.85703400
H	4.06797400	-0.40686200	-3.87590200
C	-0.59286400	-2.38832600	-2.83643500
H	-1.30103700	-2.79090400	-3.57980400
H	0.36900500	-2.91569000	-2.94668400
H	-0.41716100	-1.32419400	-3.04557100

[^{Dipp}nacnac]$^{-}$

-1 1

C	2.62614500	-0.20728200	-0.05859300
C	3.00609500	-1.54809500	-0.39728300
C	2.09501300	-2.69246200	0.03117100
H	1.79201400	-2.50223100	1.07519300
C	3.42033800	0.87688200	-0.53289900
C	4.94701000	-0.69015500	-1.60942800
H	5.84533200	-0.87877600	-2.20237800
C	-2.09435900	2.69258700	0.03178000
H	-1.79084800	2.50151400	1.07550300
C	-3.42073200	-0.87621100	-0.53274000
C	1.26645400	-0.07645700	1.90069000
C	-2.48683200	0.25314500	2.80129200
H	-2.21281700	0.30012500	3.86457400
H	-3.19534800	-0.57757100	2.65098300
H	-3.02997300	1.17487600	2.53610400
C	-0.00012900	-0.00179700	2.53329400
H	-0.00035400	-0.00264500	3.62455700
C	-2.62602300	0.20767200	-0.05873200
C	3.00943600	2.30578000	-0.21020000
H	2.07034500	2.23592300	0.36147900
C	-4.15769500	1.75846300	-1.16008500
H	-4.45406700	2.77793300	-1.41909800
C	-1.26649900	0.07416700	1.90030100
C	-3.00579500	1.54860800	-0.39692100
C	4.15773800	-1.75745400	-1.16097100
H	4.45423500	-2.77679000	-1.42039800
C	4.56355000	0.61530100	-1.29633300
H	5.17243300	1.45412000	-1.64953100
C	-4.56421400	-0.61416700	-1.29564800
H	-5.17346900	-1.45274900	-1.64875700
C	-3.00995600	-2.30534400	-0.21089900
H	-2.07152100	-2.23598500	0.36189200
C	-4.05397500	-3.01952300	0.66567800
H	-5.01512400	-3.12305300	0.13480000
C	2.76033100	-4.07426400	-0.00800600
H	2.08017800	-4.83073800	0.41436500
H	2.99111500	-4.38501900	-1.04054100
H	3.69868800	-4.09399700	0.56903700
C	-4.94742000	0.69143700	-1.60839100
H	-5.84596600	0.88038000	-2.20090400
C	2.72053900	3.11373600	-1.48706300
H	2.36539200	4.12787000	-1.23989300
C	2.48653700	-0.25635300	2.80188100
H	2.21185700	-0.30828200	3.86476300
H	3.19307700	0.57678200	2.65553600
H	3.03219500	-1.17559000	2.53332600
C	0.79657500	-2.68774900	-0.80363600

H	0.12262200	-3.49622000	-0.47616800
H	1.02855900	-2.84553700	-1.86999800
H	0.26668400	-1.73115800	-0.68410200
C	-2.75953500	4.07449600	-0.00611000
H	-2.07907900	4.83059400	0.41644600
C	4.05265600	3.01861800	0.66843900
H	3.71027500	4.02933500	0.94721200
H	5.01450700	3.12213700	0.13882100
C	-2.71939700	-3.11168600	-1.48843600
H	-2.36469900	-4.12619100	-1.24215800
H	-1.94361100	-2.61646400	-2.08940700
C	-0.79637900	2.68827900	-0.80376000
H	-0.26643600	1.73164600	-0.68492600
H	-0.12226400	3.49661400	-0.47629600
H	-1.02897600	2.84656400	-1.86991100
N	1.43893900	0.02433200	0.59960600
N	-1.43848300	-0.02410200	0.59897200
H	-2.99079400	4.38599300	-1.03831800
H	4.24109700	2.45207900	1.59286400
H	-3.69760700	4.09394000	0.57140600
H	-3.71141800	-4.03034600	0.94382700
H	-4.24384100	-2.45405800	1.59047400
H	-3.62368600	-3.21131000	-2.11185500
H	3.62561400	3.21440200	-2.10917200
H	1.94562100	2.61922900	-2.08975400

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