Supporting Information for “Controlling Dinitrogen Functionalization at Rhenium through Alkali Metal Ion Pairing”

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General Considerations

All manipulations were carried out under a dry nitrogen atmosphere, either in an MBraun LabStar glovebox or on a Schlenk line using standard techniques. Toluene, diethyl ether, tetrahydrofuran, *n*-pentane, and *n*-hexane were dried by passage through a basic alumina column and were handled and stored under a dry nitrogen atmosphere in standard Strauss flasks or in the glovebox. Hexamethyldisiloxane (HMDSO) was dried over Na/benzophenone, distilled under N_2, and stored in the glovebox prior to use. Deuterated benzene was obtained commercially, dried over an appropriate reagent (Na/benzophenone), and distilled prior to storage in the glovebox over molecular sieves. Deuterated THF was obtained commercially and dried over molecular sieves in the glovebox prior to use. Celite was dried in a 150 ^{o}C oven for 24 hours prior to storage in the glovebox. Benzo-12-crown-4, tetraethylammonium chloride, tetramethylammonium fluoride, trimethylsilyl chloride, lithium hexamethyldisilazide, and zirconocene dichloride were obtained from commercial sources and stored in the glovebox. Carbon monoxide was obtained commercially and handled exclusively inside a fume hood. The reported compounds Na[Re(η^5-Cp)(BDI)][1] and 2,6-xylylisocyanide[2] were synthesized using known procedures. Unless noted otherwise, "room temperature" and "ambient temperature" both refer to approx. 23 ^{o}C. NMR spectroscopy data were obtained on Bruker AVB-400, AV-500 and AV-600 instruments. All ^{1}H and ^{13}C spectra were referenced to the residual peak of the solvent used. Select peak assignments were corroborated with ^{1}H-^{13}C HSQC experiments as necessary. Owing to the dynamic nature of organometallic salts containing alkali metal ions in solution, the collection of complete ^{13}C NMR data was not feasible for all compounds (though it was attempted in every case). FT-IR data were obtained using a Thermo Scientific Nicolet iS10 instrument, with the sample chamber under ambient atmosphere. FT-IR samples were prepared as Nujol mulls pressed between KBr plates in the glovebox.

Synthetic Procedures

Re(H)(η^5-$C_5H_4SiMe_3$)(BDI) (1)

In the glovebox, a solid mixture of Na[Re(η^5-Cp)(BDI)] (50 mg, 0.072 mmol) and benzo-12-crown-4 (32 mg, 0.14 mmol, 2 equiv) was dissolved in THF (6 mL) by magnetic stirring to give a dark maroon solution. Neat trimethylsilyl chloride (0.25 mL, 2 mmol) was added, and the solution immediately lightened. After stirring the reaction mixture for 1 hour, its volatile components were removed in vacuo. The tacky residue was triturated with hexane (2 x 1 mL), and then extracted with pentane (6 mL). These extracts were filtered through Celite, and then solid lithium hexamethyldisilazide (LiHMDS, 24 mg, 0.14 mmol, 2 equiv) was added to these extracts with gentle agitation, generating a fine white precipitate of (benzo-12-crown-4)LiHMDS.[3] After this precipitate settled (ca. 5 min) the extracts were again filtered through Celite. Concentration in vacuo led to the formation of pale yellow solids (residual LiHMDS), after which the solution was again filtered through Celite. The solution was concentrated in vacuo until crystals began to form, and this mixture was stored at -40 ^{o}C to yield crude **1** (30 mg, 50% crude yield based on 91% purity with 9% of **2** present by ^{1}H NMR). This crude material was recrystallized slowly from pentane at room temperature and washed with pentane (2 x 0.5 mL) to give analytically pure **1** (15.5 mg, 29%). m.p.: 152-158 ^{o}C melting with decomp. ^{1}H NMR (600 MHz, C_6D_6, 298 K): 7.08 (bs, 4H, BDI Ar), 6.97 (t, 2H, *J* = 7.6 Hz, BDI Ar), 6.38 (s, 1H, *H*C[MeC(NAr)]$_2$), 5.28 (s, 2H, C_5H_4-SiMe$_3$), 5.07 (s, 2H, C_5H_4-SiMe$_3$), 2.80 (s, 6H, HC[*Me*C(NAr)]$_2$), 1.12 (bd, 28H, *J* = 3.2 Hz, BDI C*H*(CH$_3$)$_2$ and CH(C*H$_3$*)$_2$), 0.22 (s, 9H, C_5H_4-Si*Me$_3$*), -28.52 (s, 1H, Re-*H*). ^{13}C NMR (151 MHz, C_6D_6, 298 K): 167.28 (HC[Me*C*(NAr)]$_2$), 159.10 (BDI Ar), 139.28 (BDI Ar), 125.16 (BDI Ar), 123.45 (BDI Ar), 106.22

(H*C*[MeC(NAr)]$_2$), 92.26 (*ipso*-*C*$_5$H$_4$-SiMe$_3$), 85.77 (*C*$_5$H$_4$-SiMe$_3$), 80.17 (*C*$_5$H$_4$-SiMe$_3$), 28.98 (BDI *C*H(Me)$_2$), 24.86 (BDI CH(*Me*)$_2$), 23.69 (HC[*Me*C(NAr)]$_2$), 2.00 (C$_5$H$_4$-Si*Me$_3$*). FT-IR (Nujol): 2029 cm^{-1} (Re-H). Anal. Calcd. for $ReC_{37}H_{55}N_2Si$ (**1**): C, 59.88; H, 7.47; N, 3.78 %. Found: C, 54.58; H, 7.29; N, 3.98. Despite our efforts we were unable to obtain a satisfactory elemental analysis of **1**, despite the high purity observed in the NMR spectra of recrystallized material.

Re(N=NSiMe$_3$)(η^5-Cp)(BDI) (2)

A solution of Na[Re(η^5-Cp)(BDI)] (150 mg, 0.22 mmol) in Et$_2$O (7 mL) was cooled in the cold well of the glovebox to -78 °C. Neat trimethylsilyl chloride (0.50 mL, 3.9 mmol) was then added to this stirring, cooled solution leading to a rapid color change to deep red. Stirring at -78 °C was continued for 15 minutes, at which time the reaction mixture was removed from the cold well and its volatile components were removed in vacuo. The dry residue was extracted with hexane (8 mL), and these extracts were filtered through Celite and concentrated in vacuo prior to storage at -40 °C. Compound **2** was isolated as red crystals in two crops (118 mg and 14 mg) of similar purity. Total yield: 132 mg, 79%. m.p.: 213-220 °C melting with decomp. ^{1}H NMR (600 MHz, C$_6$D$_6$, 298 K): 7.19-7.15 (m, 2H, BDI Ar), 7.05-7.02 (m, BDI Ar), 4.69 (s, 1H, *H*C[MeC(NAr)]$_2$), 4.38 (s, 5H, Cp), 3.60 (sept, 2H, *J* = 6.7 Hz, BDI C*H*(Me)$_2$), 3.08 (sept, 2H, *J* = 6.9 Hz, BDI C*H*(Me)$_2$), 1.58 (s, 6H, HC[*Me*C(NAr)]$_2$), 1.36 (d, 6H, *J* = 6.9 Hz, BDI CH(*Me*)$_2$), 1.28 (d, 6H, *J* = 6.6 Hz, BDI CH(*Me*)$_2$), 1.21 (d, 6H, *J* = 6.9 Hz, BDI CH(*Me*)$_2$), 1.10 (d, 6H, *J* = 6.7 Hz, BDI CH(*Me*)$_2$), 0.48 (s, 9H, Si(*C*H$_3$)$_3$). ^{13}C NMR (151 MHz, C$_6$D$_6$, 298 K): 164.01 (HC[Me*C*(NAr)]$_2$), 153.97 (BDI Ar), 142.37 (BDI Ar), 140.88 (BDI Ar), 125.73 (BDI Ar), 125.36 (BDI Ar), 123.25 (BDI Ar), 104.29 (H*C*[MeC(NAr)]$_2$), 89.06 (Cp), 28.64 (BDI *C*H(Me)$_2$), 27.42 (BDI *C*H(Me)$_2$), 25.39 (BDI CH(*Me*)$_2$), 25.37 (BDI CH(*Me*)$_2$), 24.26 (BDI CH(*Me*)$_2$), 23.88 (BDI CH(*Me*)$_2$), 22.48 (HC[*Me*C(NAr)]$_2$), 0.77 (Si(*C*H$_3$)$_3$). FT-IR (Nujol): 1617 cm^{-1} (ReN=NSiMe$_3$), 847 cm^{-1} (ReNN-SiMe$_3$). Anal. Calcd. for $ReC_{37}H_{55}N_4Si$ (**2**): C, 57.69; H, 7.20; N, 7.28 %. Found: C, 58.06; H, 7.01; N, 7.06 %.

[Na(b-12-c-4)$_2$][Re(η^5-Cp)(BDI)] (3)

Na[Re(η^5-Cp)(BDI)] (25 mg, 0.029 mmol) and benzo-12-crown-4 (13 mg, 0.058 mmol) were separately dissolved in 3 mL of Et$_2$O. The crown ether solution was then added by pipette to the rhenium solution and the reaction vial capped prior to swirling by hand to ensure complete mixing of the reagents. The reaction mixture was then allowed to sit at room temperature for 1 h at ambient temperature, over which time dark red-purple crystals formed. These crystals were isolated from their mother liquor and washed with 2 x 2 mL of Et$_2$O prior to the removal of residual volatiles in vacuo to yield **3** (30 mg, 91%). m.p.: 119-122 °C. ^{1}H NMR (600 MHz, THF-*d*8, 298 K): 7.12-7.08 (m, 4H, crown Ar), 6.99-6.95 (m, 4H, crown Ar), 6.07 (bs, 4H, BDI Ar), 5.90 (bs, 4H, BDI Ar and *H*C[MeC(NAr)]$_2$), 4.68 (bs, 2H, BDI C*H*(Me)$_2$), 4.47-3.96 (bs, 5H, Cp), 4.29-4.24 (m, 8H, crown), 3.72-3.68 (m, 8H, crown), 3.67 (s, 8H, crown), 0.85 (bs, 12H, BDI CH(*Me*)$_2$), 0.67 (bs, 6H, HC[*Me*C(NAr)]$_2$), -1.22 (bs, 12H, BDI CH(*Me*)$_2$). ^{13}C NMR (151 MHz, THF-*d*8, 298 K): 150.24 (crown Ar), 139.32 (BDI Ar), 124.20 (crown Ar), 119.14 (crown Ar), 113.07 (BDI), 71.08 (crown), 68.09 (crown), 28.48 (BDI), 27.91 (BDI), 26.25 (BDI). Anal. Calcd. for $ReC_{62}H_{88}N_2O_9Na$ (**3 •** Et$_2$O): C, 61.29; H, 7.31; N, 2.31 %. Found: C, 61.11; H, 7.20; N, 2.12 %.

Re(Me)(η^5-Cp)(BDI) (4)

THF (6 mL) was added to a solid mixture of Na[Re(η^5-Cp)(BDI)] (50 mg, 0.072 mmol) and tetramethylammonium fluoride (6.7 mg, 0.072 mmol) and the resulting suspension was set to stir at room temperature. After 2 h the volatile components of the reaction mixture were removed in vacuo and triturated with 2 mL of hexane. The dry residue was then extracted with pentane (10 mL), and these extracts were filtered through Celite. The filtered extracts were then stored at -40 ^oC to yield **4** as dark green crystals (28.5 mg, 58%). m.p.: 222-227 ^oC melting with decomp. ^1H NMR (600 MHz, C_6D_6, 298 K): 7.12 (d, 2H, *J* = 7.7 Hz, BDI Ar), 6.96 (t, 2H, *J* = 7.5 Hz, BDI Ar), 6.89 (d, 2H, *J* = 7.4 Hz, BDI Ar), 6.10 (s, 1H, *H*C[MeC(NAr)]$_2$), 5.46 (s, 5H, Cp), 3.69 (s, 3H, Re-C*H*$_3$), 3.29 (s, 6H, HC[*Me*C(NAr)]$_2$), 3.13 (sept, 2H, *J* = 6.7 Hz, BDI C*H*(Me)$_2$), 1.55 (sept, 2H, *J* = 6.8 Hz, BDI C*H*(Me)$_2$), 1.23 (d, 12H, *J* = 6.7 Hz, BDI CH(*Me*)$_2$), 1.06 (d, 6H, *J* = 6.7 Hz, BDI CH(*Me*)$_2$), 0.86 (d, 6H, *J* = 6.9 Hz, BDI CH(*Me*)$_2$). ^{13}C NMR (151 MHz, C_6D_6, 298 K): 169.06 (HC[Me*C*(NAr)]$_2$), 159.41 (BDI Ar), 140.02 (BDI Ar), 125.36 (BDI Ar), 124.54 (BDI Ar), 123.00 (BDI Ar), 111.75 (Re-*C*H$_3$), 107.74 (H*C*[MeC(NAr)]$_2$), 86.38 (Cp), 30.72 (BDI *C*H(Me)$_2$), 27.20 (BDI *C*H(Me)$_2$), 25.48 (BDI CH(*Me*)$_2$), 25.37 (BDI CH(*Me*)$_2$), 24.75 (BDI CH(*Me*)$_2$), 24.00 (BDI CH(*Me*)$_2$), 22.32 (HC[*Me*C(NAr)]$_2$). *The ^{13}C shift for the Re-CH_3 carbon was only observed in a ^1H-^{13}C HSQC experiment.* Anal. Calcd. for $ReC_{35}H_{49}N_2$ (**4**): C, 61.44; H, 7.22; N, 4.10 %. Found: C, 61.40; H, 7.20; N, 4.15 %.

$Cp_2Zr[(\mu-\eta^1:\eta^1-N=N)Re(\eta^5-Cp)(BDI)]_2$ (5)

A solution of Na[Re(η^5-Cp)(BDI)] (150 mg, 0.22 mmol) in THF (5 mL) was cooled in the cold well of the glovebox to -78 ^oC. Solid zirconocene dichloride (32 mg, 0.11 mmol) was added to this cooled, stirred solution, which changed to a purple-red color within minutes. After the reaction mixture was stirred for 30 minutes at -78 ^oC, its volatile components were removed in vacuo. The tacky dark residue was triturated with hexane (2 mL), and then was extracted with toluene (9 mL). The dark purple extracts were filtered through Celite, and then their volatile components were removed in vacuo to give a film-like oily residue. This residue dissolved and crystallized upon the addition of Et_2O (3 mL). After this mixture was allowed to sit at ambient temperature overnight, **5** was isolated as dark purple crystals (138 mg, 79%). m.p.: decomp. 172-180 ^oC with melting. ^1H NMR (600 MHz, C_6D_6, 298 K): 7.14-7.01 (m, 12H, BDI Ar), 6.55 (s, 10H, ZrCp$_2$) 4.88 (s, 2H, *H*C[MeC(NAr)]$_2$), 4.53 (s, 10H, ReCp), 3.77 (sept, 4H, *J* = 6.8 Hz, BDI C*H*(Me)$_2$), 3.24 (bs, 4H, BDI C*H*(Me)$_2$), 1.70 (s, 12H, HC[*Me*C(NAr)]$_2$), 1.43 (bd, 12H, *J* = 5.9 Hz, BDI CH(*Me*)$_2$), 1.27 (d, 12H, *J* = 6.9 Hz, BDI CH(*Me*)$_2$), 1.19 (d, 12H, *J* = 6.7 Hz, BDI CH(*Me*)$_2$), 1.15 (bd, 12H, *J* = 4.9 Hz, BDI CH(*Me*)$_2$).^{13}C NMR (151 MHz, C_6D_6, 298 K): 163.75 (HC[Me*C*(NAr)]$_2$), 153.17 (BDI Ar), 142.01 (BDI Ar), 140.95 (BDI Ar), 125.21 (BDI Ar), 124.69 (BDI Ar), 123.09 (BDI Ar), 111.40 (ZrCp$_2$), 104.56 (H*C*[MeC(NAr)]$_2$), 87.43 (ReCp), 28.07 (BDI *C*H(Me)$_2$), 26.92 (BDI *C*H(Me)$_2$), 25.07 (BDI CH(*Me*)$_2$), 25.05 (BDI CH(*Me*)$_2$), 24.27 (BDI CH(*Me*)$_2$), 22.18 (HC[*Me*C(NAr)]$_2$). FT-IR (Nujol): 1667 cm^{-1} (ReN=NZrCp$_2$). Anal. Calcd. for $Re_2C_{78}H_{102}N_8Zr$ (**11**): C, 57.98; H, 6.37; N, 6.94 %. Found: C, 57.96; H, 6.39; N, 6.85 %.

$[(Et_2O)Na(OC)Re(\eta^5-Cp)(BDI)]_2$ (6)

A solution of Na[Re(η^5-Cp)(BDI)] (200 mg, 0.29 mmol) in Et_2O (7 mL) was prepared in the glovebox and sealed inside a 50 mL Schlenk tube. This Schlenk tube was removed from the glovebox and the solution therein was degassed by a freeze-pump-thaw cycle on a Schlenk line. The headspace above the thawed solution was then replaced with ca. 1 atm of CO gas, leading to an immediate color change of the solution to a dark orange/green color. The flask was then sealed and allowed to sit at ambient temperature for 5 minutes, over which time green crystals precipitated from solution. The volatile components of the reaction mixture were then removed in vacuo, and the Schlenk tube was returned to the glovebox. The crystalline residue was washed with Et_2O (3 x 4 mL) to yield **6** as dark green crystals (159 mg, 69%). m.p.: slow decomp. above ca. 130 ^oC without melting. ^1H NMR (600 MHz, THF-*d*8, 298 K): 6.96 (bs, 4H, BDI Ar), 6.97 (d, 4H, *J* = 7.6 Hz, BDI Ar), 6.70 (bs, 4H, BDI Ar), 4.25 (bs, 2H, *H*C[MeC(NAr)]$_2$), 3.94 (bs, 4H, BDI C*H*(Me)$_2$), 3.41 (bs, 12H, Cp and BDI C*H*(Me)$_2$), 1.25 (bs, 24H, BDI CH(*Me*)$_2$) 1.15 (bs, 12H, HC[*Me*C(NAr)]$_2$), 1.09 (bs, 24H, BDI CH(*Me*)$_2$). ^{13}C NMR (151 MHz, THF-*d*8, 298 K): 155.27 (HC[Me*C*(NAr)]$_2$), 123.49 (BDI Ar), 28.57 (BDI *C*H(Me)$_2$), 24.80 (BDI CH(*Me*)$_2$), 24.72 (BDI CH(*Me*)$_2$). FT-IR (Nujol): 1639 cm^{-1} (CO). Anal. Calcd. for $Re_2C_{78}H_{112}N_4O_4Na_2$ (**6**): C, 58.97; H, 7.11; N, 3.53 %. Found: C, 59.17; H, 7.14; N, 3.53 %.

(Et$_2$O)Na(XylNC)Re(η^5-Cp)(BDI) (7)

Na[Re(η^5-Cp)(BDI)] (50 mg, 0.072 mmol) and 2,6-xylylisocyanide (9.5 mg, 0.072 mmol) were separately dissolved in Et$_2$O (4 mL), and the isocyanide solution was then added slowly to the stirred rhenium solution to give a dark, brown/orange solution. After the reaction mixture was stirred at room temperature for 15 minutes, it was filtered through Celite, concentrated in vacuo, and stored at -40 ^{o}C. Compound **7** was isolated as dark brown crystals in two crops (39 mg and 3 mg) of similar purity. Total yield: 42 mg, 65%. m.p.: 211-216 ^{o}C. ^{1}H NMR (600 MHz, THF-*d*8, 298 K): 6.89 (d, 2H, *J* = 7.3 Hz, BDI Ar), 6.87 (d, 2H, *J* = 7.5 Hz, XylNC Ar), 6.76 (d, 2H, *J* = 6.4 Hz, BDI Ar), 6.65 (t, 2H, *J* = 7.5 Hz, BDI Ar), 6.36 (t, 1H, *J* = 7.2 Hz, XylNC Ar), 4.15 (bs, 2H, BDI C*H*(Me)$_2$), 3.40 (bs, 5H, Cp), 2.44 (bs, 6H, XylNC Me), 1.25 (bs, 6H, BDI CH(*Me*)$_2$), 1.09 (bs, 6H, BDI CH(*Me*)$_2$), 0.93 (bd, 6H, *J* = 5.3 Hz, BDI CH(*Me*)$_2$), 0.78 (bd, 6H, *J* = 4.2 Hz, BDI CH(*Me*)$_2$). ^{13}C NMR (151 MHz, THF-*d*8, 298 K): 144.54 (XylNC Ar), 124.87 (XylNC Ar), 122.99 (BDI Ar), 122.31 (BDI Ar), 115.35 (XylNC Ar), 100.97 (XylNC Ar), 80.86 (Cp), 28.70 (BDI *C*H(Me)$_2$), 27.37 (XylNC Me), 25.93 (XylNC Me), 25.01 (BDI CH(*Me*)$_2$), 24.49 (BDI CH(*Me*)$_2$), 23.30 (BDI CH(*Me*)$_2$). FT-IR (Nujol): 1560 cm^{-1} (XylNC). Elemental analyses on crystalline **7** were low in C and H, despite multiple attempts on separate batches of highly crystalline material. These low values may be attributed to the loss of Et$_2$O upon exposure of the crystalline product to high vacuum. We believe the other data provided supports our structural assignment of this **7**, and is also indicative of its bulk purity.

[(b-12-c-4)$_2$Na]{Na[(OC)Re(η^5-Cp)(BDI)]$_2$} (8)

THF (5 mL) was added to a solid mixture of **6** (50 mg, 0.063 mmol) and benzo-12-crown-4 (28.2 mg, 0.126 mmol), giving a homogeneous, dark brown/green solution. After the reaction mixture was stirred for 5 minutes at ambient temperature, its volatile components were removed in vacuo to give an oily residue. Et$_2$O (5 mL) was added to this residue, giving a heterogeneous mixture that was set to stir. A green microcrystalline powder formed, which was isolated after 30 minutes of stirring to give **8** (50 mg, 84%). m.p.: decomp. above 100 ^{o}C to form **12** without melting. ^{1}H NMR (600 MHz, THF-*d*8, 298 K): 7.11-7.07 (m, 4H, crown Ar), 6.98 (bs, 4H, BDI Ar), 6.98-6.94 (m, 4H, crown Ar), 6.91 (dd, 4H, *J* = 7.5, 0.7 Hz, BDI Ar), 6.70 (t, 4H, *J* = 7.5 Hz, BDI Ar), 4.33-4.27 (m, 8H, crown), 3.92 (bs, 4H, BDI C*H*(Me)$_2$), 3.82-3.77 (m, 8H, crown), 3.73 (s, 8H, crown), 3.40 (bs, 10H, Cp), 1.27 (bs, 12H, BDI CH(*Me*)$_2$) 1.14 (bs, 12H, BDI CH(*Me*)$_2$), 1.08 (bs, 24H, BDI CH(*Me*)$_2$), 1.50-0.50 (bs, 12H, HC[*Me*C(NAr)]$_2$). ^{13}C NMR (151 MHz, THF-*d*8, 298 K): 155.21 (HC[Me*C*(NAr)]$_2$), 150.82 (crown Ar), 123.82 (crown Ar), 123.36 (BDI Ar), 122.65 (BDI Ar), 118.95 (crown Ar), 71.68 (crown), 69.65 (crown), 68.83 (crown), 28.56 (BDI *C*H(kkMe)$_2$), 24.83 (BDI CH(*Me*)$_2$), 24.68 (BDI CH(*Me*)$_2$). FT-IR (Nujol): 1667 cm^{-1} (CO). Anal. Calcd. for $Re_2C_{98}H_{134}N_4O_{11}Na_2$ (**8** • Et$_2$O): C, 59.96; H, 6.89; N, 2.86 %. Found: C, 59.66; H, 6.87; N, 2.99 %.

[(b-12-c-4)$_2$Na][(XylNC)Re(η^5-Cp)(BDI)] (9)

Na[Re(η^5-Cp)(BDI)] (25 mg, 0.036 mmol) was dissolved in Et$_2$O (2 mL) and set to stir. Separately, 2,6-xylylisocyanide (4.7 mg, 0.036 mmol) was dissolved in Et$_2$O (3 mL) and this solution was added to the stirring rhenium solution, leading to a dark orange/brown solution (indicating the formation of **7**). After this mixture was stirred for 5 minutes at room temperature, benzo-12-crown-4 (16.2 mg, 0.072 mmol) was dissolved in Et$_2$O (3 mL) and added to the reaction mixture. After being stirred for 15 minutes, the reaction mixture was filtered through Celite and allowed to sit at room temperature for 4 hours, leading to the formation of dark brown crystals. These crystals of **9** (29 mg) were collected, and the mother liquor was stored at -40 °C to yield an additional crop of material of similar purity (8.5 mg). Total yield: 37.5 mg, 82%. m.p.: 169-173 °C. ^{1}H NMR (600 MHz, THF-*d*8, 298 K): 7.15-7.10 (m, 4H, crown Ar), 7.04-6.99 (m, 4H, crown Ar), 6.90 (d, 2H, *J* = 6.3 Hz, BDI Ar), 6.86 (d, 2H, *J* = 7.5 Hz, XylNC Ar), 6.75 (d, 2H, *J* = 5.3 Hz, BDI Ar), 6.63 (t, 2H, *J* = 7.5 Hz, BDI Ar), 6.35 (t, 1H, *J* = 7.2 Hz, XylNC Ar), 4.32-4.26 (m, 8H, crown), 4.15 (bs, 2H, BDI C*H*(Me)$_2$), 3.72-3.67 (m, 8H, crown), 3.66 (s, 8H, crown), 3.34 (bs, 7H, Cp and BDI C*H*(Me)$_2$), 2.44 (bs, 6H, XylNC Me), 1.24 (bs, 6H, BDI CH(*Me*)$_2$), 1.10 (bs, 6H, BDI CH(*Me*)$_2$), 0.96 (bs, 6H, HC[*Me*C(NAr)]$_2$)), 0.91 (bs, 6H, BDI CH(*Me*)$_2$), 0.78 (bs, 6H, BDI CH(*Me*)$_2$). ^{13}C NMR (151 MHz, THF-*d*8, 298 K): 150.03 (crown Ar), 144.26 (XylNC Ar), 124.40 (crown Ar), 122.84 (BDI Ar), 122.35 (BDI Ar), 119.16 (crown Ar), 114.91 (XylNC Ar), 81.31 (Cp), 70.80 (crown), 28.73 (BDI *C*H(Me)$_2$), 27.20 (XylNC Me), 26.09 (XylNC Me), 25.01 (BDI CH(*Me*)$_2$), 24.57 (BDI CH(*Me*)$_2$), 24.49 (BDI CH(*Me*)$_2$), 23.39 (BDI CH(*Me*)$_2$). FT-IR (Nujol): 1695 cm^{-1} (XylNC). Anal. Calcd. for ReC$_{71}$H$_{97}$N$_3$O$_9$Na (**9** • Et$_2$O): C, 63.35; H, 7.27; N, 3.12 %. Found: C, 63.34; H, 7.15; N, 3.13 %.

Re(COSiMe$_3$)(η^5-Cp)(BDI) (10)

Compound **6** (75 mg, 0.094 mmol) was suspended in Et$_2$O (5 mL), and this suspension was set to stir. Neat trimethylsilyl chloride (0.10 mL, 0.79 mmol, 8.4 equiv) was then added, leading to a homogenous purple/red solution almost immediately. The reaction mixture was stirred at room temperature for 15 minutes, then its volatile components were removed in vacuo. The dry residue was extracted with pentane (12 mL), and these extracts were filtered through Celite and concentrated in vacuo. Storage of the concentrated extracts at -40 °C led to the formation of red crystals of **10** (48 mg, 66%). m.p.: 221-227 °C. ^{1}H NMR (600 MHz, C$_6$D$_6$, 298 K): 7.16 (dd, 2H, *J* = 1.7 Hz, BDI Ar), 7.09 (dd, 2H, *J* = 7.7, 1.7 Hz, BDI Ar), 7.05 (t, 2H, *J* = 7.6 Hz, BDI Ar), 4.60 (s, 1H, *H*C[MeC(NAr)]$_2$), 4.43 (s, 5H, Cp), 3.84 (sept, 2H, *J* = 6.8 Hz, BDI C*H*(Me)$_2$), 3.35 (sept, 2H, *J* = 6.8 Hz, BDI C*H*(Me)$_2$), 1.51 (s, 6H, HC[*Me*C(NAr)]$_2$), 1.34 (d, 6H, *J* = 6.9 Hz, BDI CH(*Me*)$_2$), 1.34 (d, 6H, *J* = 6.9 Hz, BDI CH(*Me*)$_2$), 1.28 (d, 6H, *J* = 6.8 Hz, BDI CH(*Me*)$_2$), 1.15 (d, 6H, *J* = 6.8 Hz, BDI CH(*Me*)$_2$), 0.47 (s, 9H, Si(*C*H$_3$)$_3$).^{13}C NMR (151 MHz, C$_6$D$_6$, 298 K): 164.34 (HC[Me*C*(NAr)]$_2$), 153.73 (BDI Ar), 142.53 (BDI Ar), 141.03 (BDI Ar), 125.59 (BDI Ar), 125.44 (BDI Ar), 123.27 (BDI Ar), 104.14 (H*C*[MeC(NAr)]$_2$), 86.02 (Cp), 28.67 (BDI *C*H(Me)$_2$), 27.69 (BDI *C*H(Me)$_2$), 25.52 (BDI CH(*Me*)$_2$), 25.16 (BDI CH(*Me*)$_2$), 24.34 (BDI CH(*Me*)$_2$), 24.01 (BDI CH(*Me*)$_2$), 22.22 (HC[*Me*C(NAr)]$_2$), 0.62 (Si(*C*H$_3$)$_3$). FT-IR (Nujol): 1408 cm^{-1} (ReC-OSiMe$_3$), 848 cm^{-1} (ReCO-SiMe$_3$). Anal. Calcd. for ReC$_{38}$H$_{55}$N$_2$OSi (**10**): C, 59.25; H, 7.20; N, 3.64 %. Found: C, 59.42; H, 7.06; N, 3.42 %.

Cp$_2$Zr[(μ-η^1:η^1-OC)Re(η^5-Cp)(BDI)]$_2$ (11)

Compound **6** (75 mg, 0.094 mmol) was dissolved in THF (6 mL), and this solution was set to stir. Solid zirconocene dichloride (14 mg, 0.047 mmol) was added, leading to an immediate color change from dark green to dark red/orange. After the reaction mixture was stirred for 15 minutes at room temperature, its volatile components were removed in vacuo. The residue was extracted with toluene (5 mL), and these extracts were filtered through Celite before their volatile components were removed in vacuo. The resulting crystalline residue was washed with Et$_2$O (2 x 1 mL) and the residual solvent was removed in vacuo. Compound **11** was isolated as dark orange/brown crystals (57 mg, 75%). m.p.: 238-242 °C. ^{1}H NMR (600 MHz, C$_6$D$_6$, 298 K): 7.15-7.11 (m, 8H, BDI Ar), 7.08 (t, 4 H, *J* = 7.5 Hz, BDI Ar), 6.77 (s, 10H, ZrCp$_2$) 4.68 (s, 2H, *H*C[MeC(NAr)]$_2$), 4.59 (s, 10H, ReCp), 4.08 (sept, 4H, *J* = 6.9 Hz, BDI C*H*(Me)$_2$), 3.44 (sept, 4H, *J* = 6.8 Hz, BDI C*H*(Me)$_2$), 1.55 (s, 12H, HC[*Me*C(NAr)]$_2$), 1.44-1.36 (m, 24H, BDI CH(*Me*)$_2$), 1.23 (bd, 12H, *J* = 6.3 Hz, BDI CH(*Me*)$_2$), 1.20 (d, 12H, *J* = 6.7 Hz, BDI CH(*Me*)$_2$).^{13}C NMR (151 MHz, C$_6$D$_6$, 298 K): 163.96 (HC[Me*C*(NAr)]$_2$), 153.09 (BDI Ar), 142.13 (BDI Ar), 140.84 (BDI Ar), 125.04 (BDI Ar), 124.90 (BDI Ar), 123.15 (BDI Ar), 115.64 (ZrCp$_2$), 104.18 (H*C*[MeC(NAr)]$_2$), 84.89 (ReCp), 28.18 (BDI *C*H(Me)$_2$), 27.24 (BDI *C*H(Me)$_2$), 25.13 (BDI

CH(Me)$_2$), 24.76 (BDI CH(Me)$_2$), 24.70 (BDI CH(Me)$_2$), 24.26 (BDI CH(Me)$_2$), 22.09 (HC[MeC(NAr)]$_2$). FT-IR (Nujol): 1410 cm^{-1} (ReC-OZrCp$_2$). Anal. Calcd. for $Re_2C_{80}H_{102}N_4O_2Zr$ (**11**): C, 59.46; H, 6.37; N, 3.47 %. Found: C, 59.37; H, 6.33; N, 3.37 %.

NMR Spectra

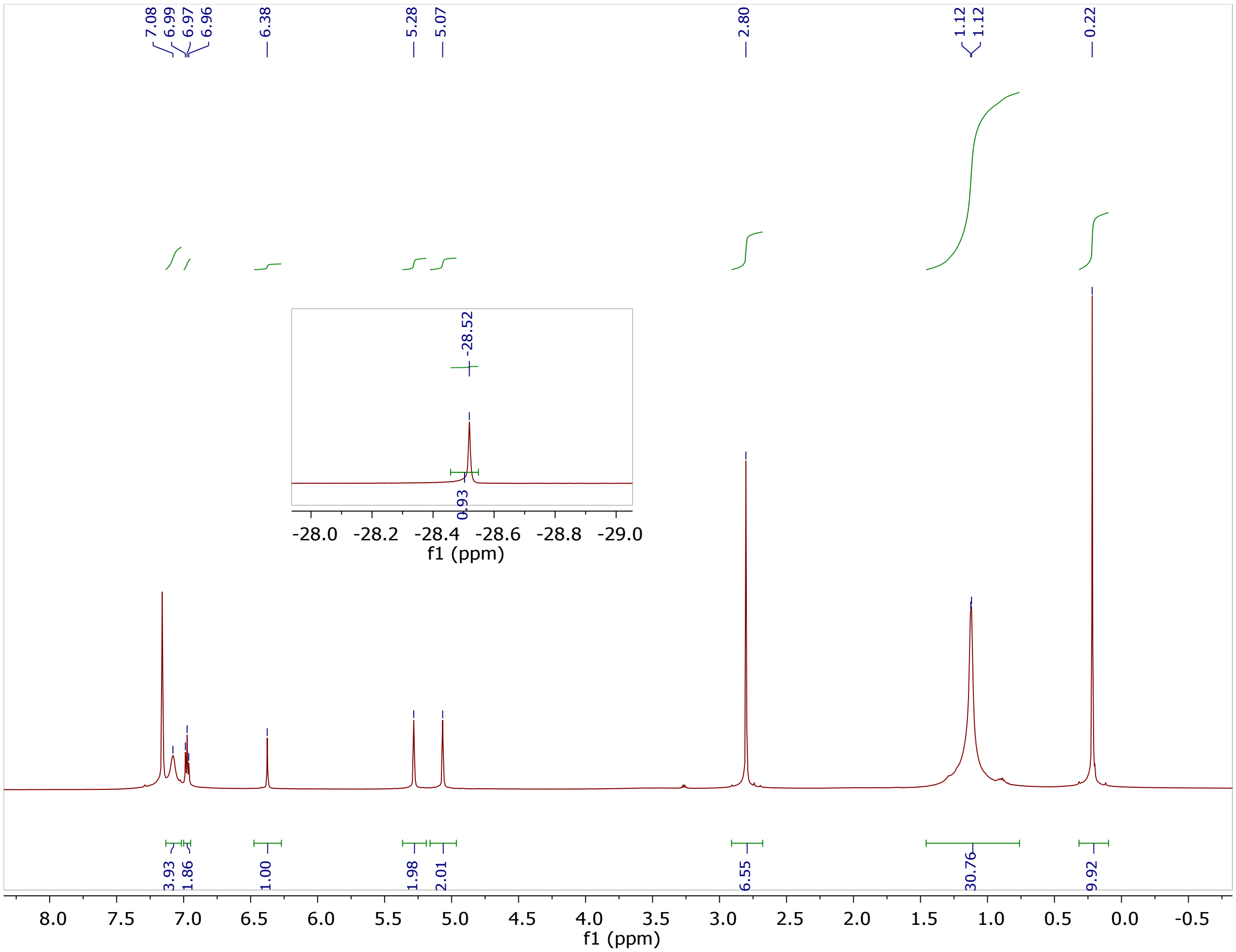

Figure S1. ^1H NMR Spectrum of **1** in C_6D_6.

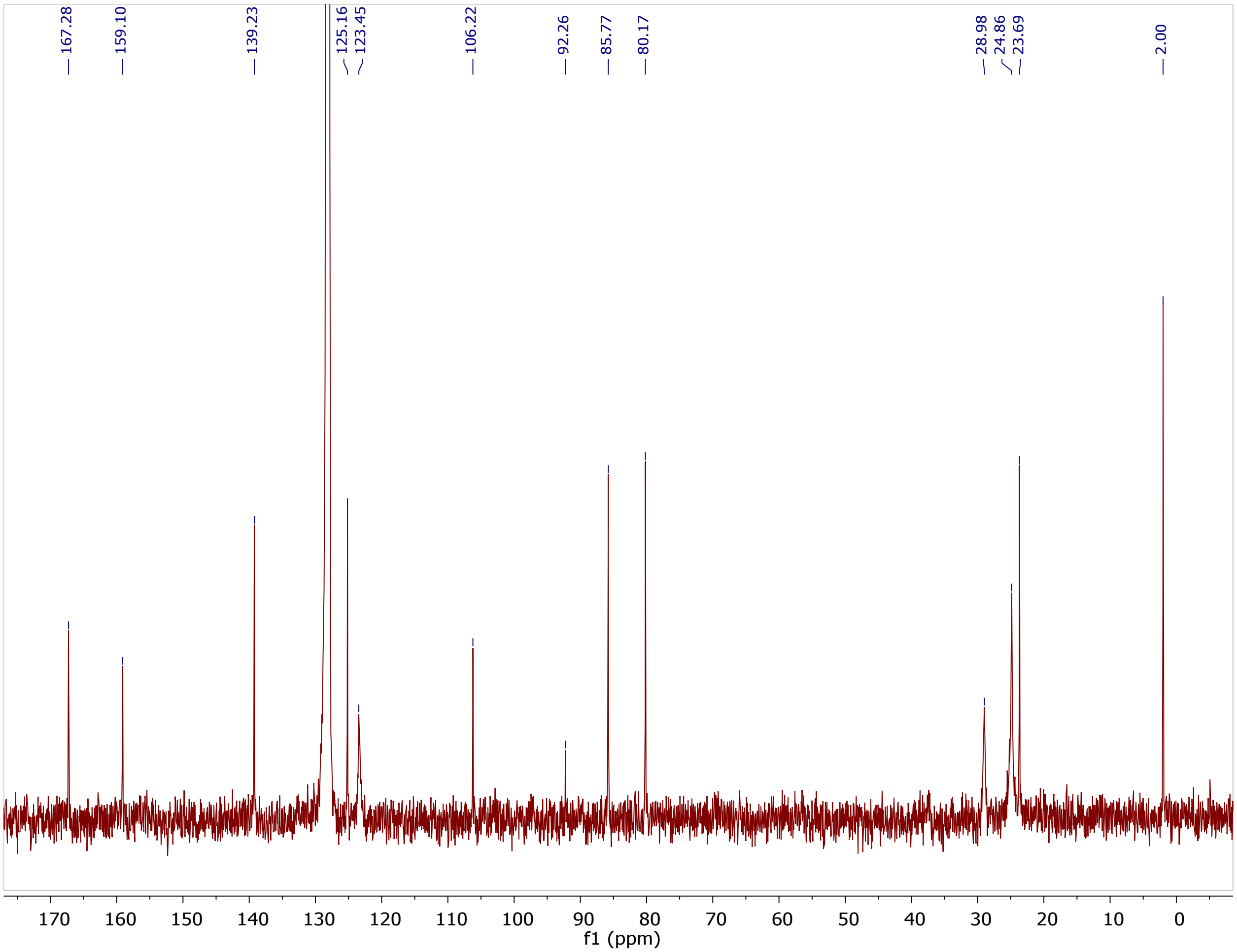

Figure S2. ^{13}C NMR Spectrum of **1** in C_6D_6.

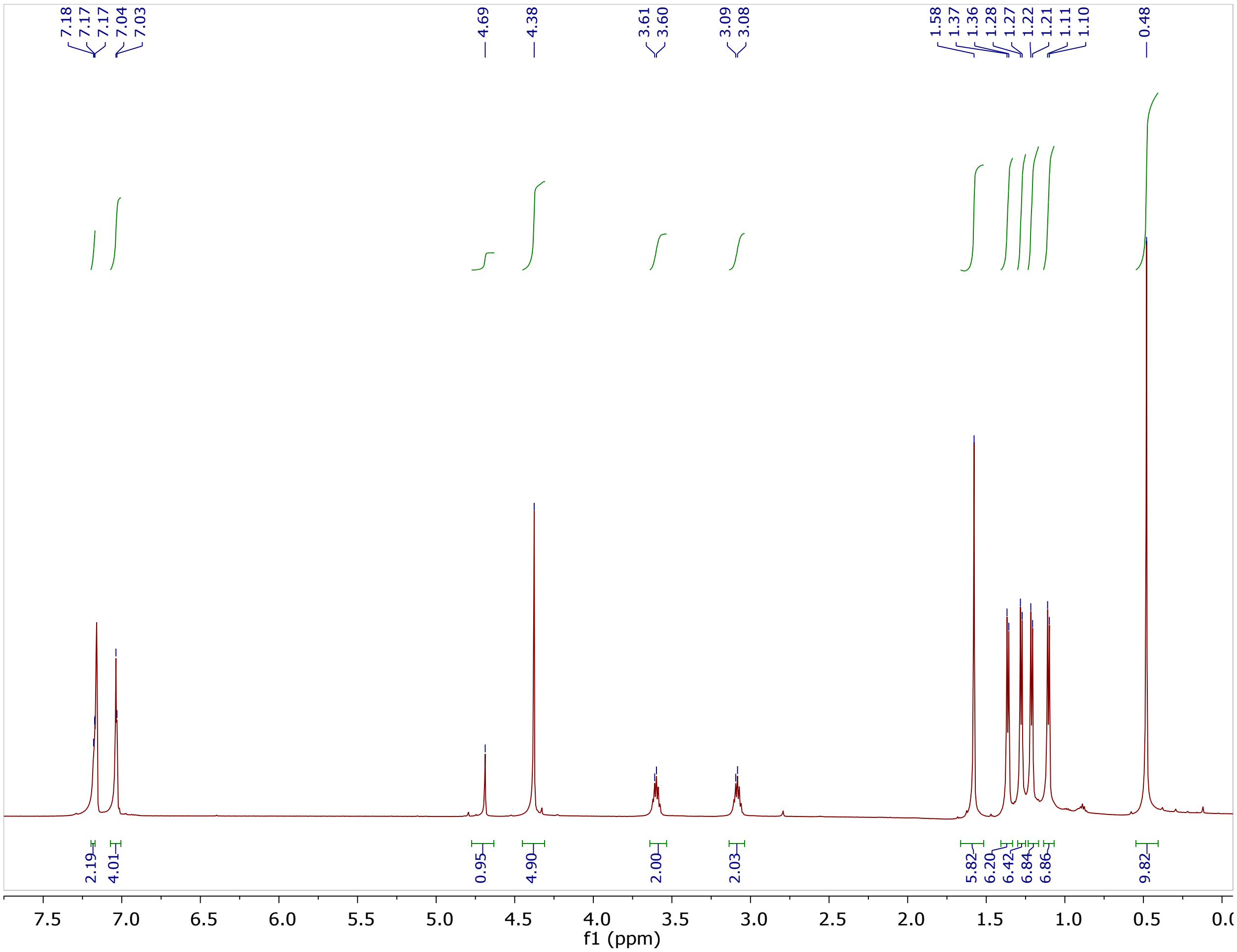

Figure S3. ^{1}H NMR Spectrum of **2** in C_6D_6.

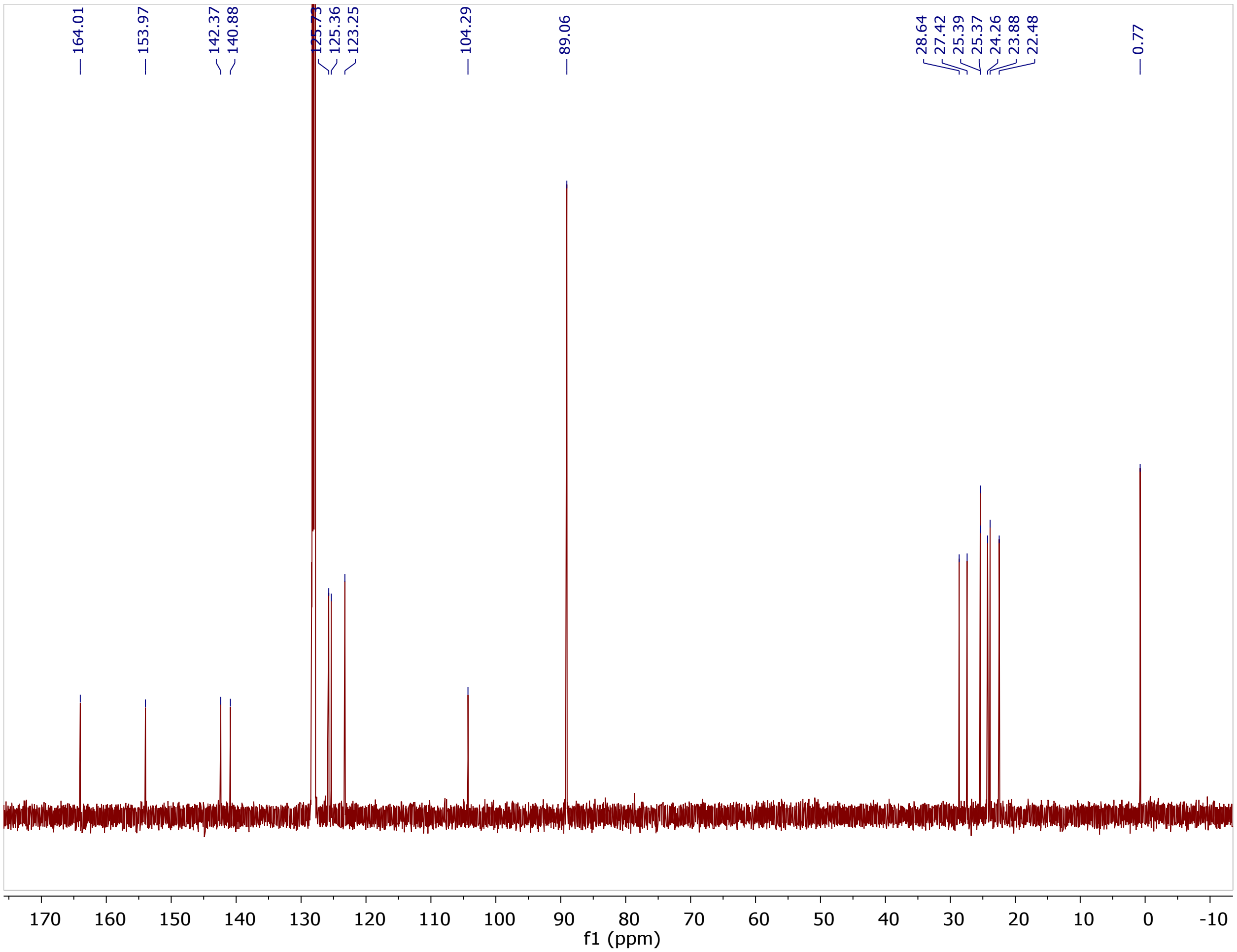

Figure S4. ^{13}C NMR Spectrum of **2** in C_6D_6.

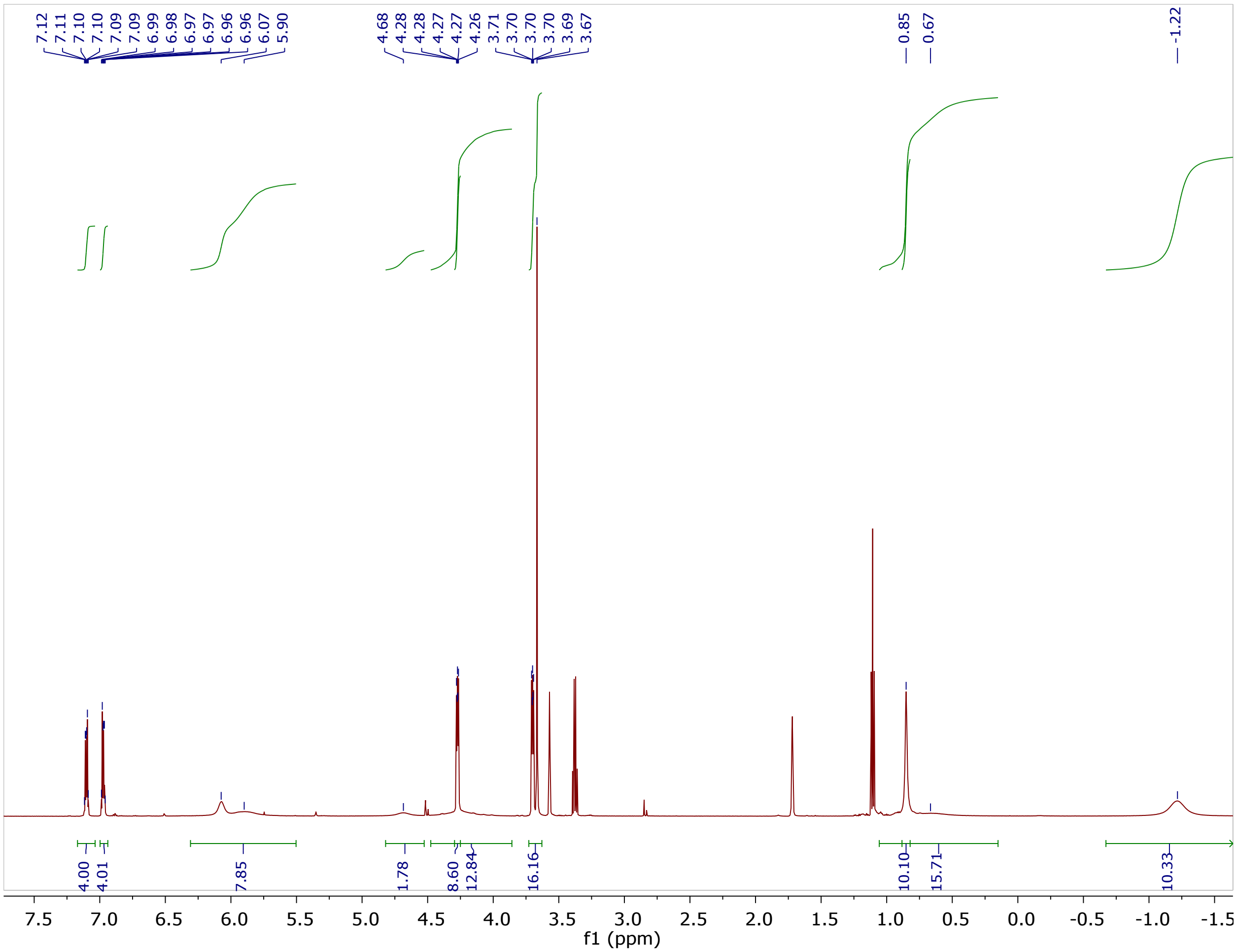

Figure S5. ^{1}H NMR Spectrum of **3** in THF-*d*8.

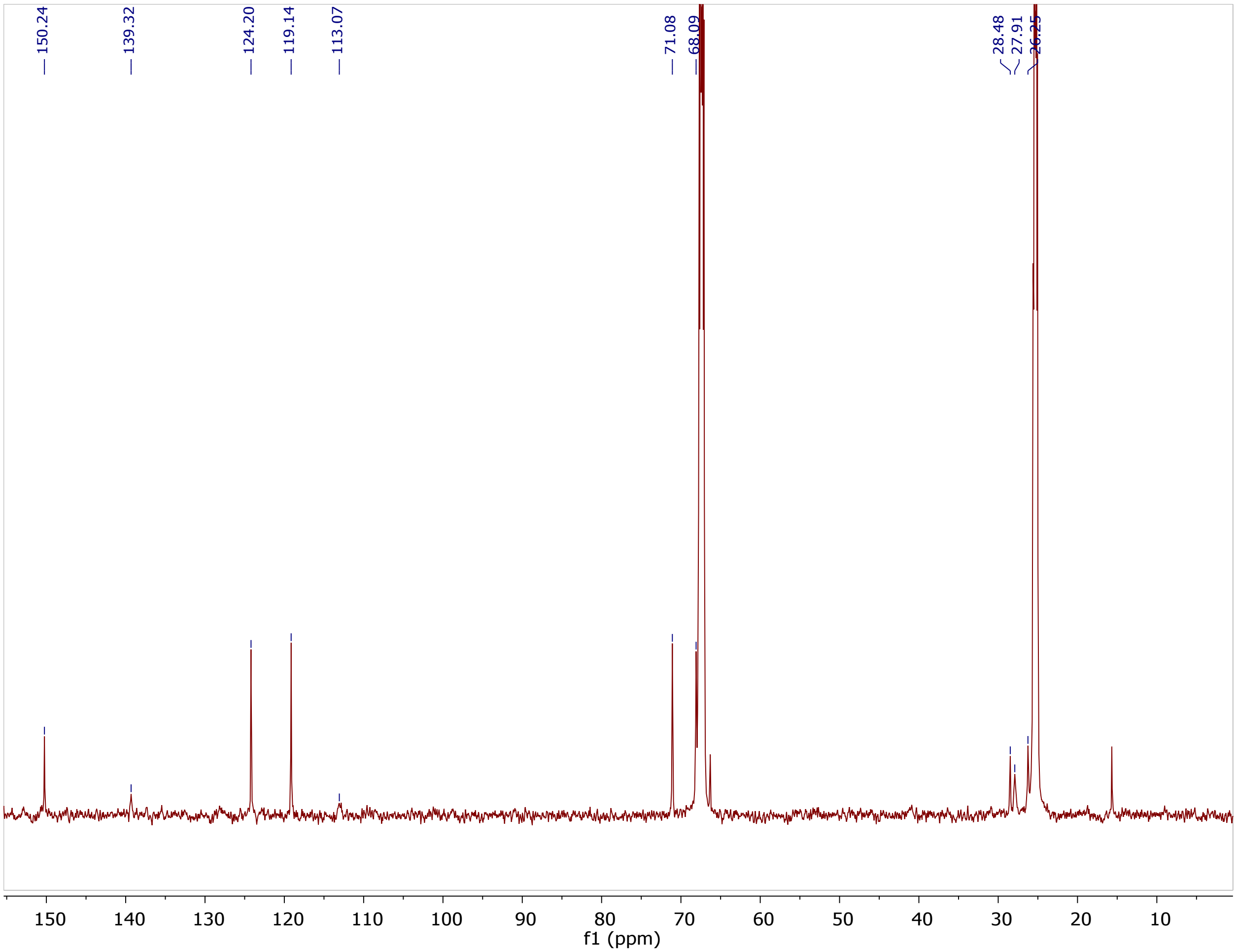

Figure S6. ^{13}C NMR Spectrum of **3** in THF-*d*8. A line broadening filter of 10 Hz has been applied to distinguish select, broad peaks.

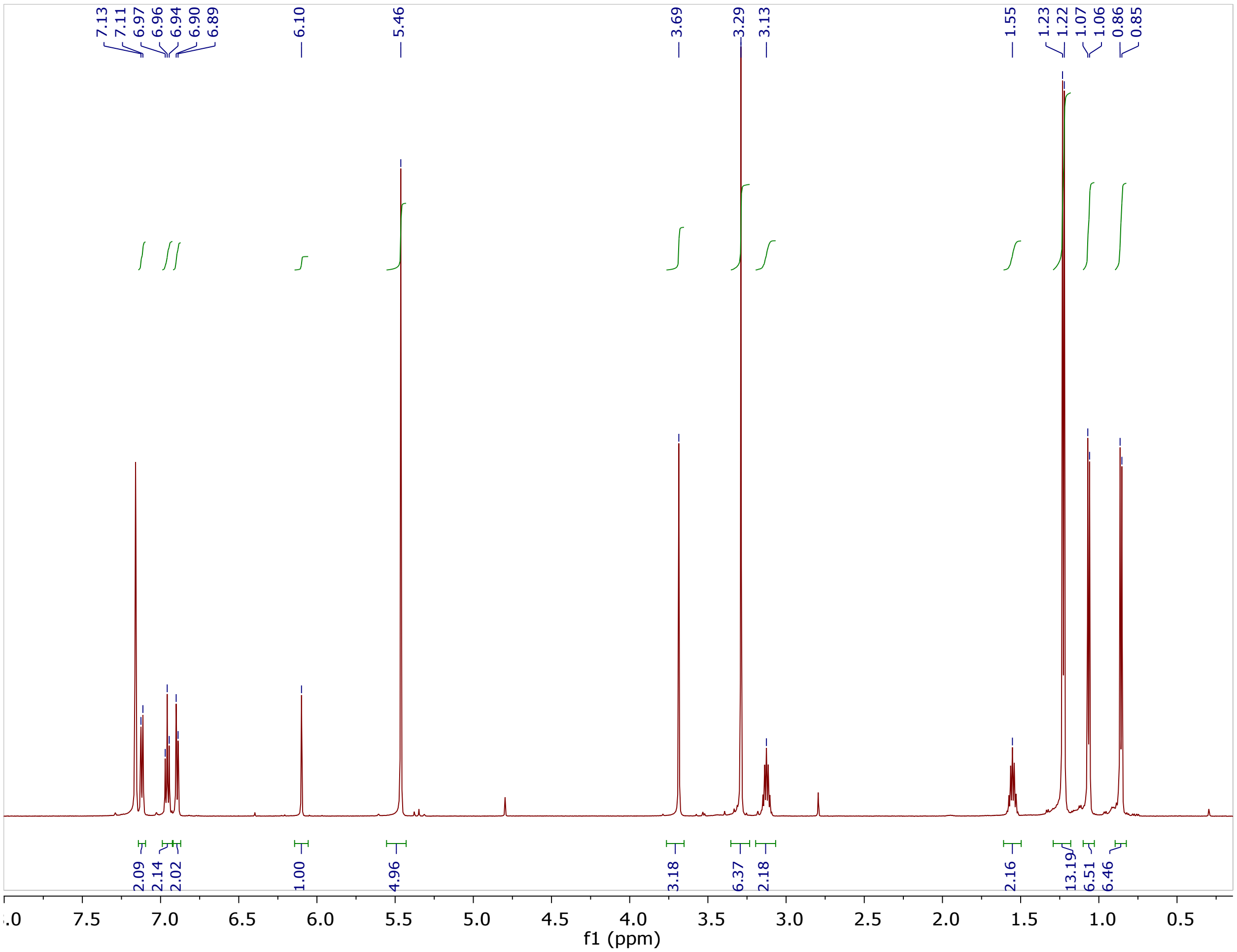

Figure S7. ^{1}H NMR Spectrum of **4** in C_6D_6.

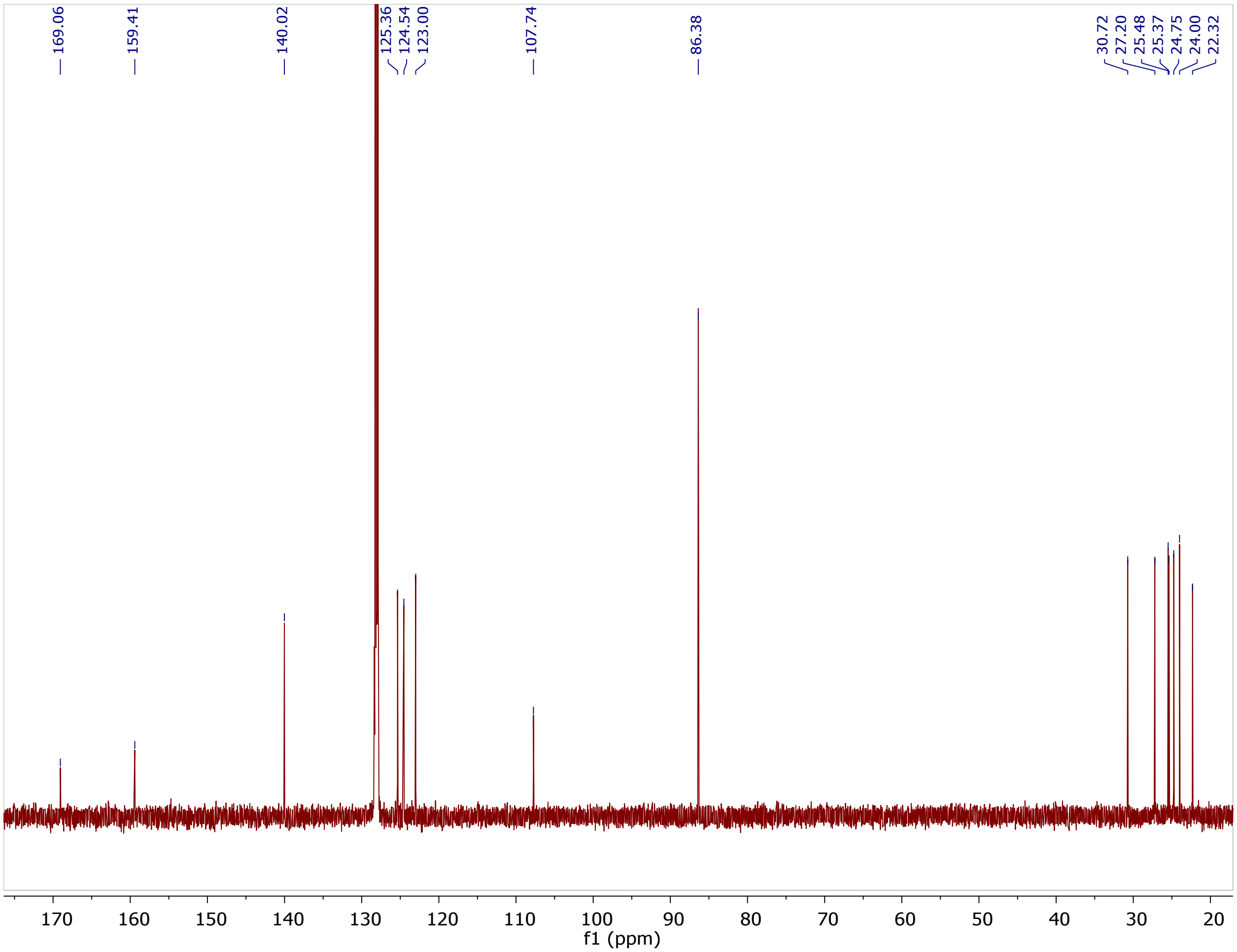

Figure S8. ^{13}C NMR Spectrum of **4** in C_6D_6.

Figure S9. ^{1}H-^{13}C HSQC NMR Spectrum of **4** in C_6D_6. The peak corresponding to the Re-methyl group is marked.

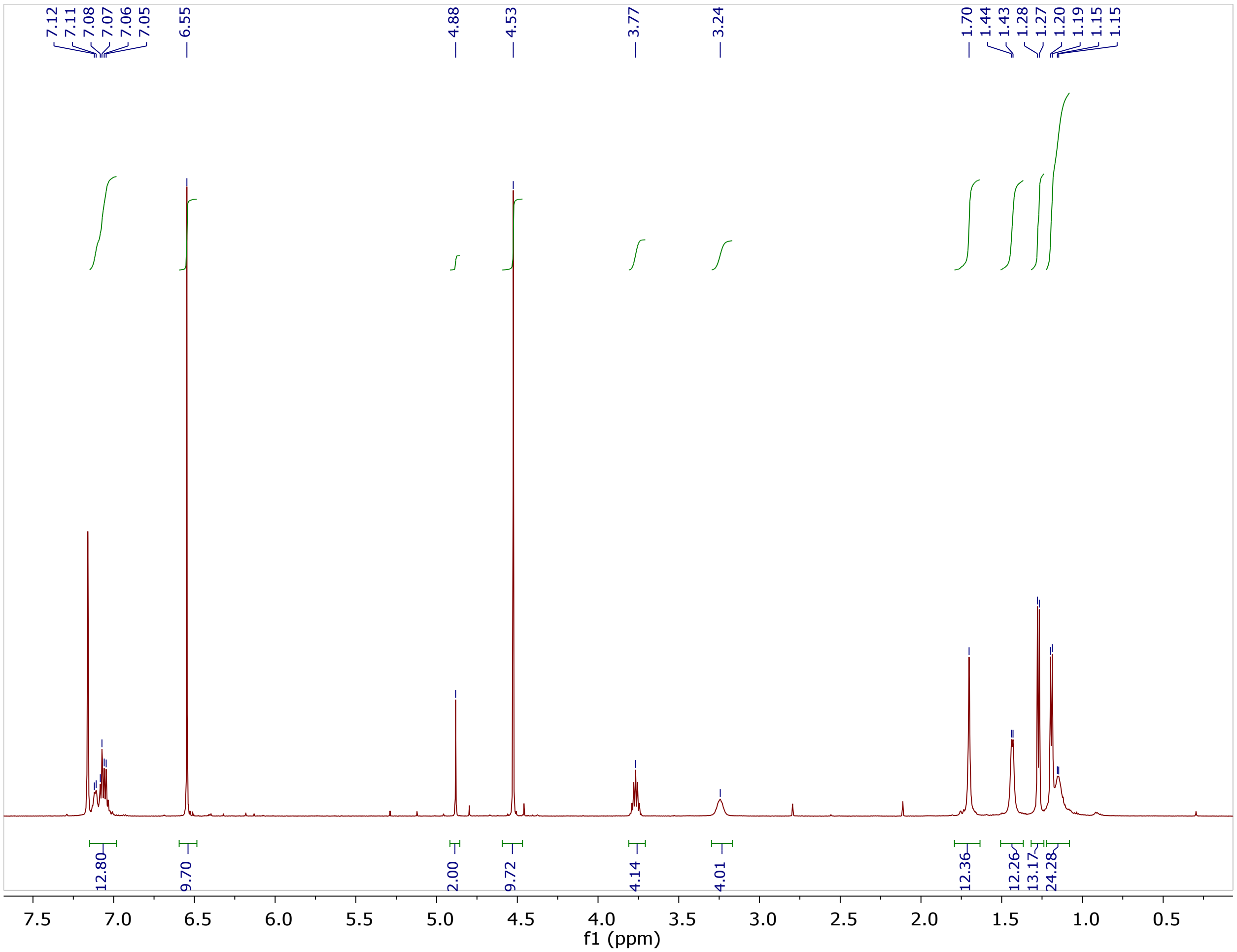

Figure S10. ^{1}H NMR Spectrum of **5** in C_6D_6.

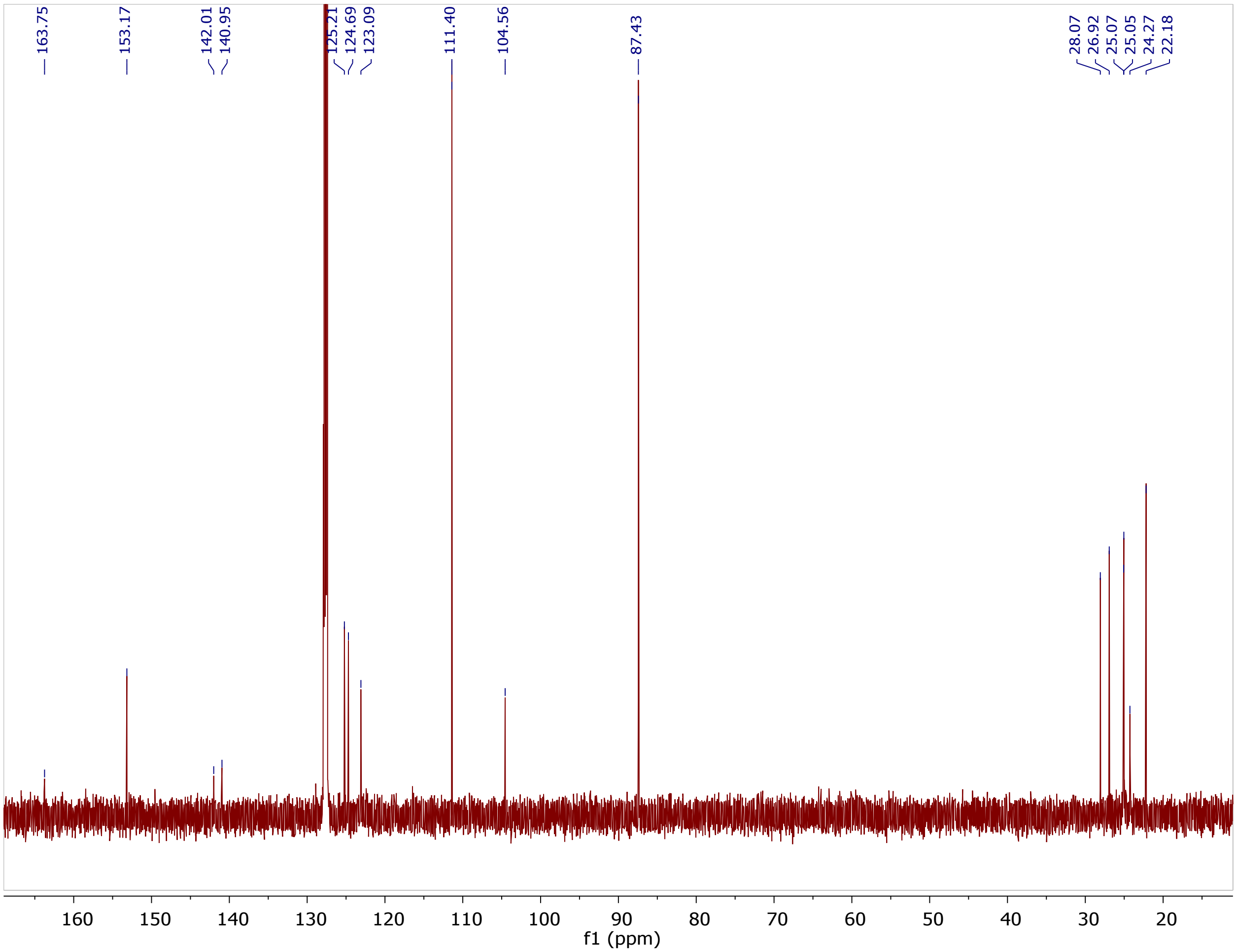

Figure S11. ^{13}C NMR Spectrum of **5** in C_6D_6.

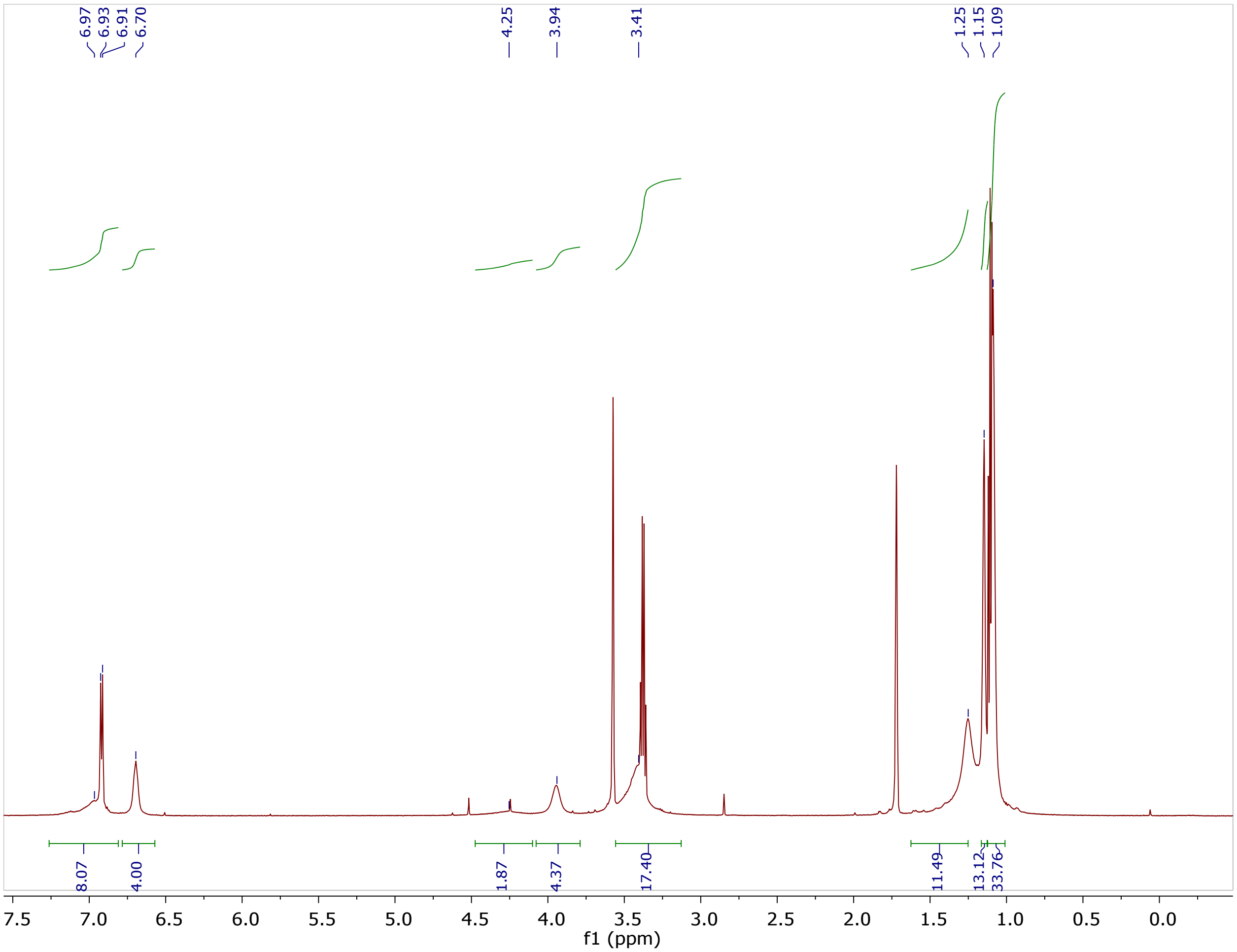

Figure S12. ^{1}H NMR Spectrum of **6** in THF-*d*8.

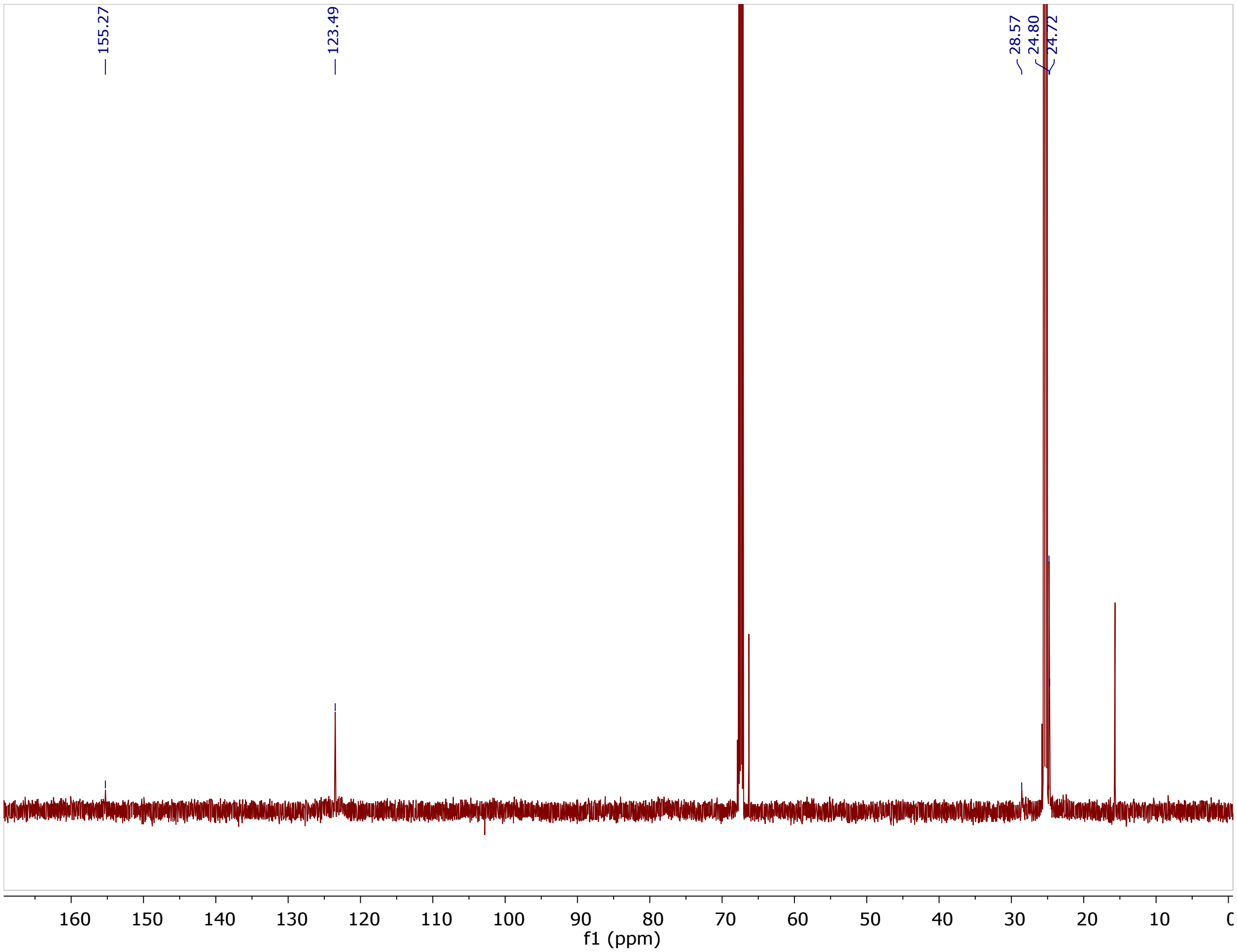

Figure S13. ^{13}C NMR Spectrum of **6** in THF-*d*8.

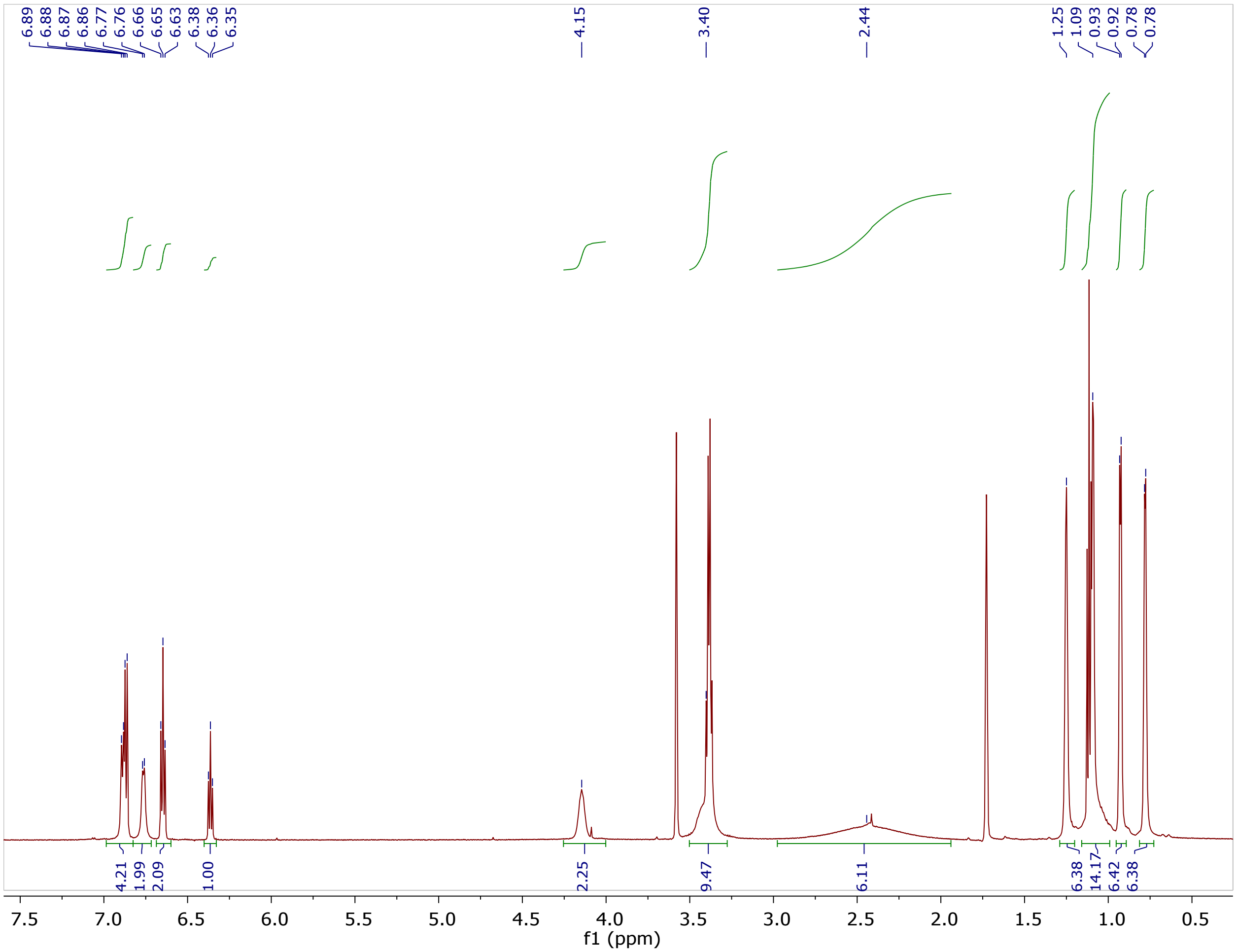

Figure S14. ^{1}H NMR Spectrum of **7** in THF-*d*8.

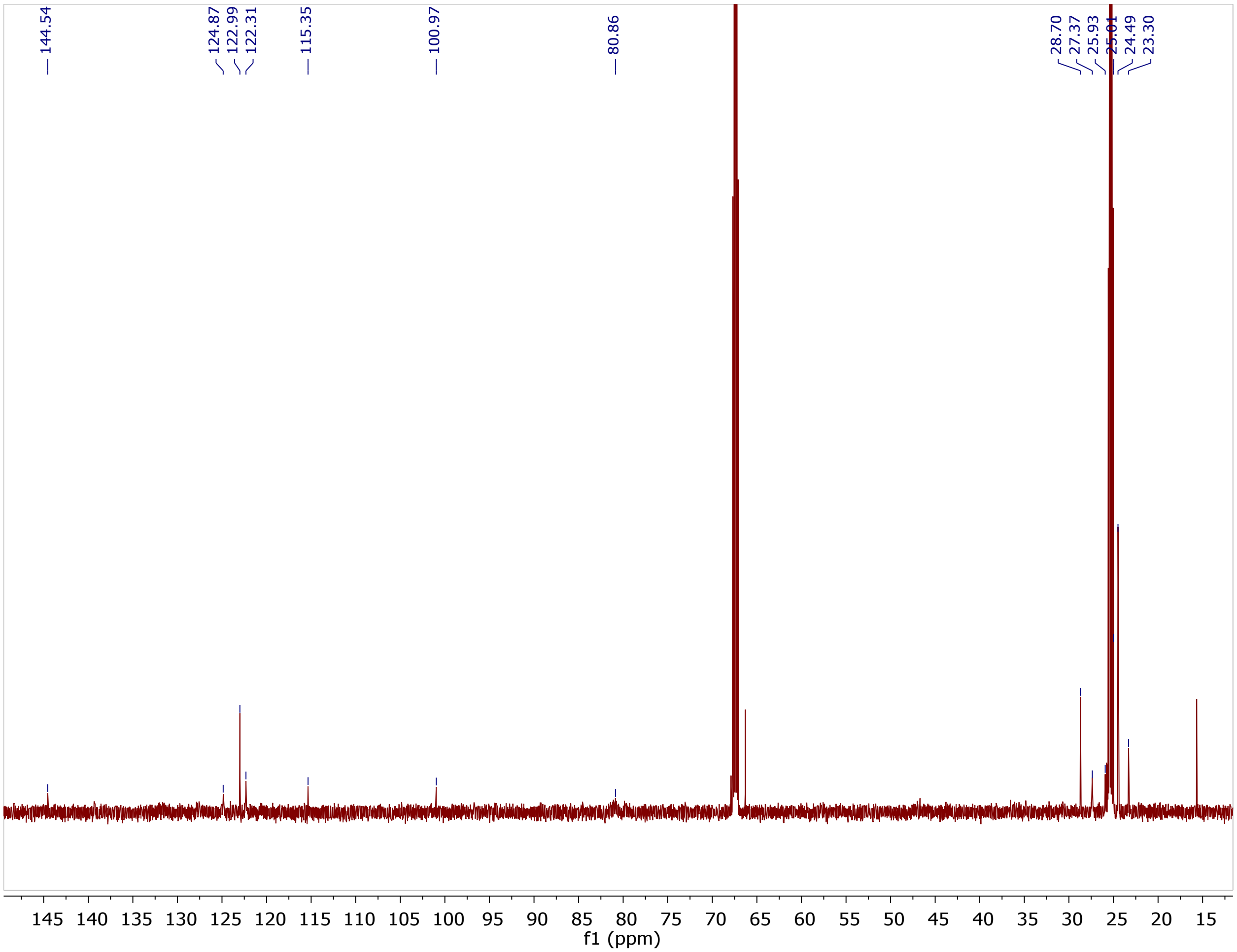

Figure S15. ^{13}C NMR Spectrum of **7** in THF-*d*8.

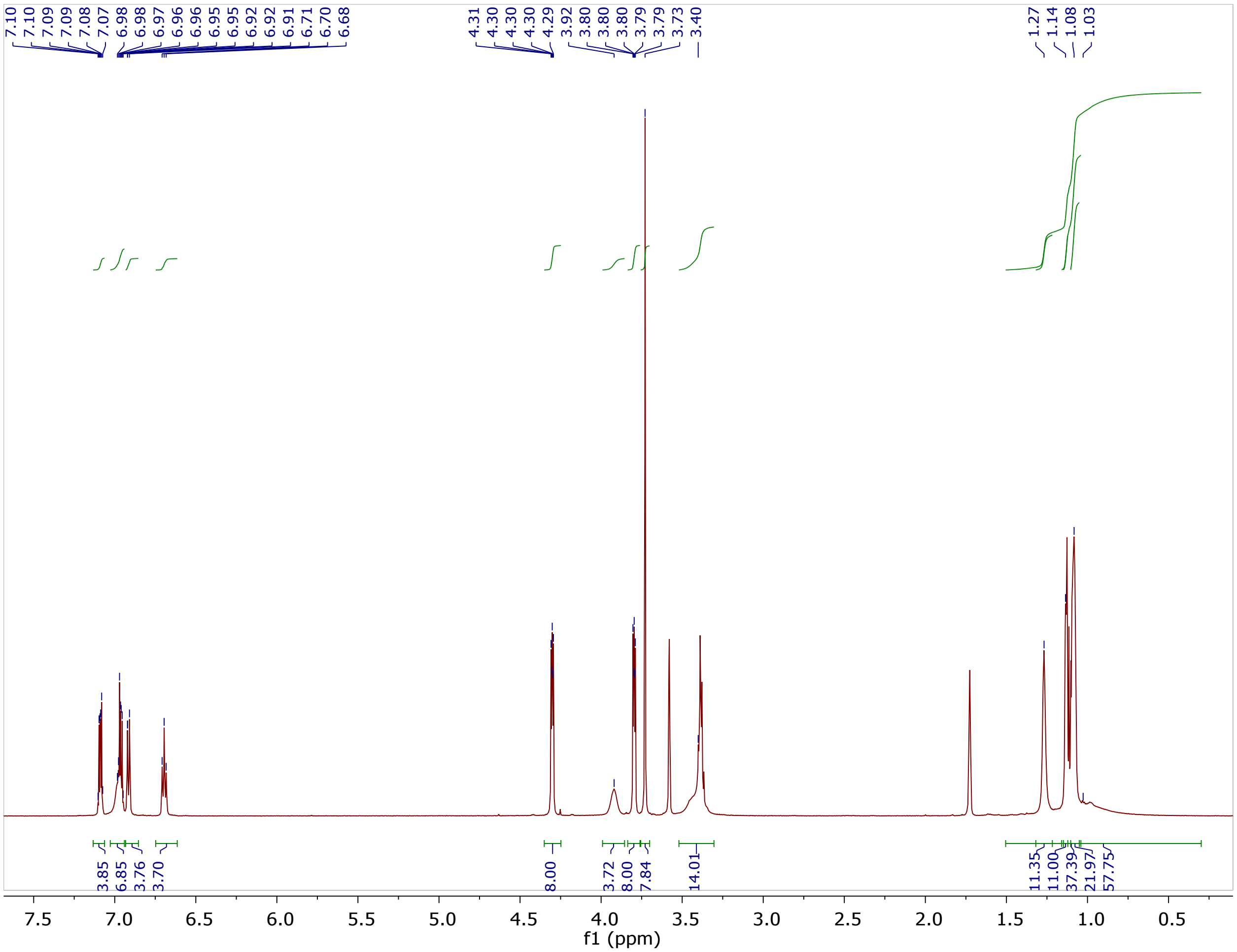

Figure S16. ^{1}H NMR Spectrum of **8** in THF-*d*8.

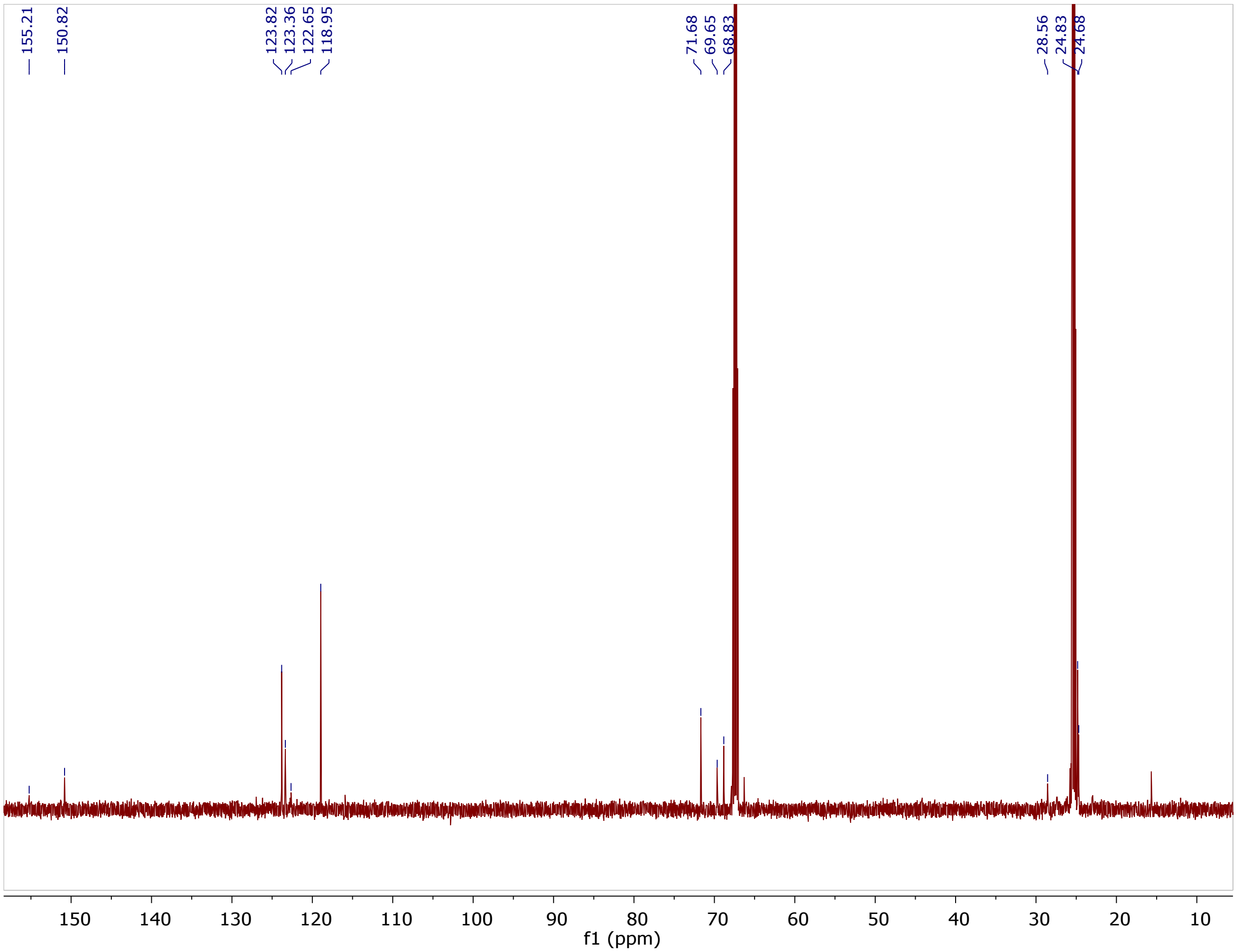

Figure S17. ^{13}C NMR Spectrum of **8** in THF-*d*8.

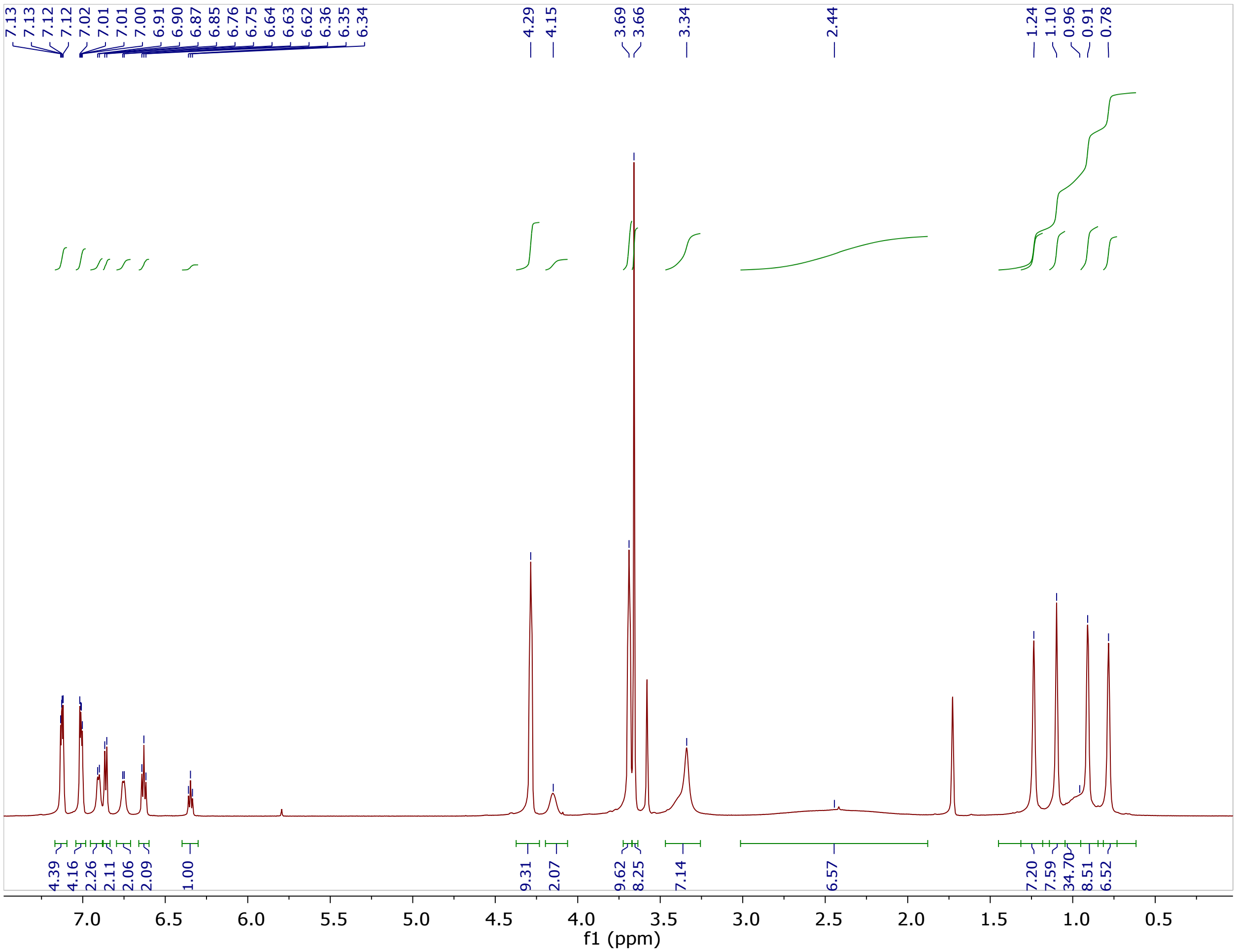

Figure S18. ^{1}H NMR Spectrum of **9** in THF-*d*8.

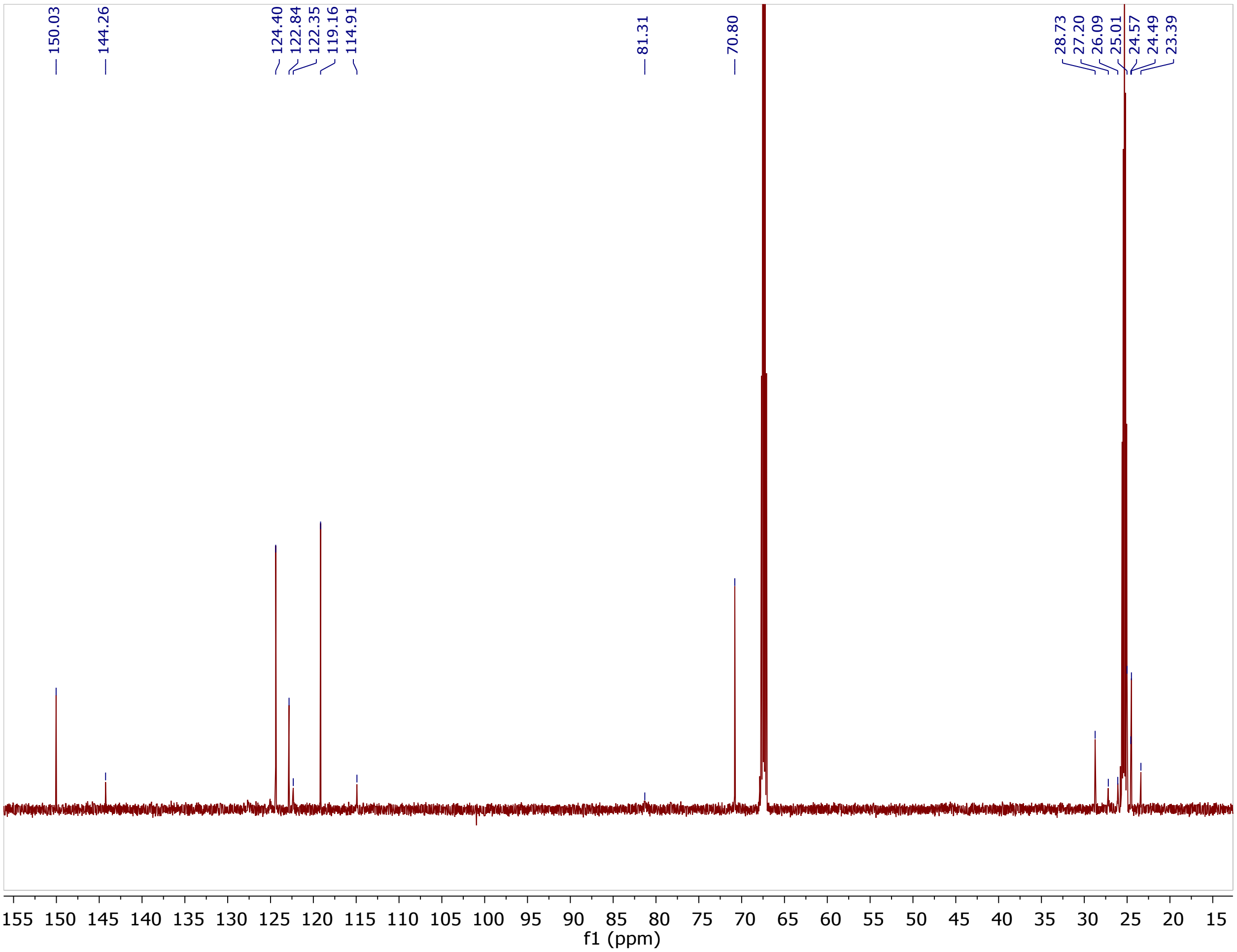

Figure S19. ^{13}C NMR Spectrum of **9** in THF-*d*8.

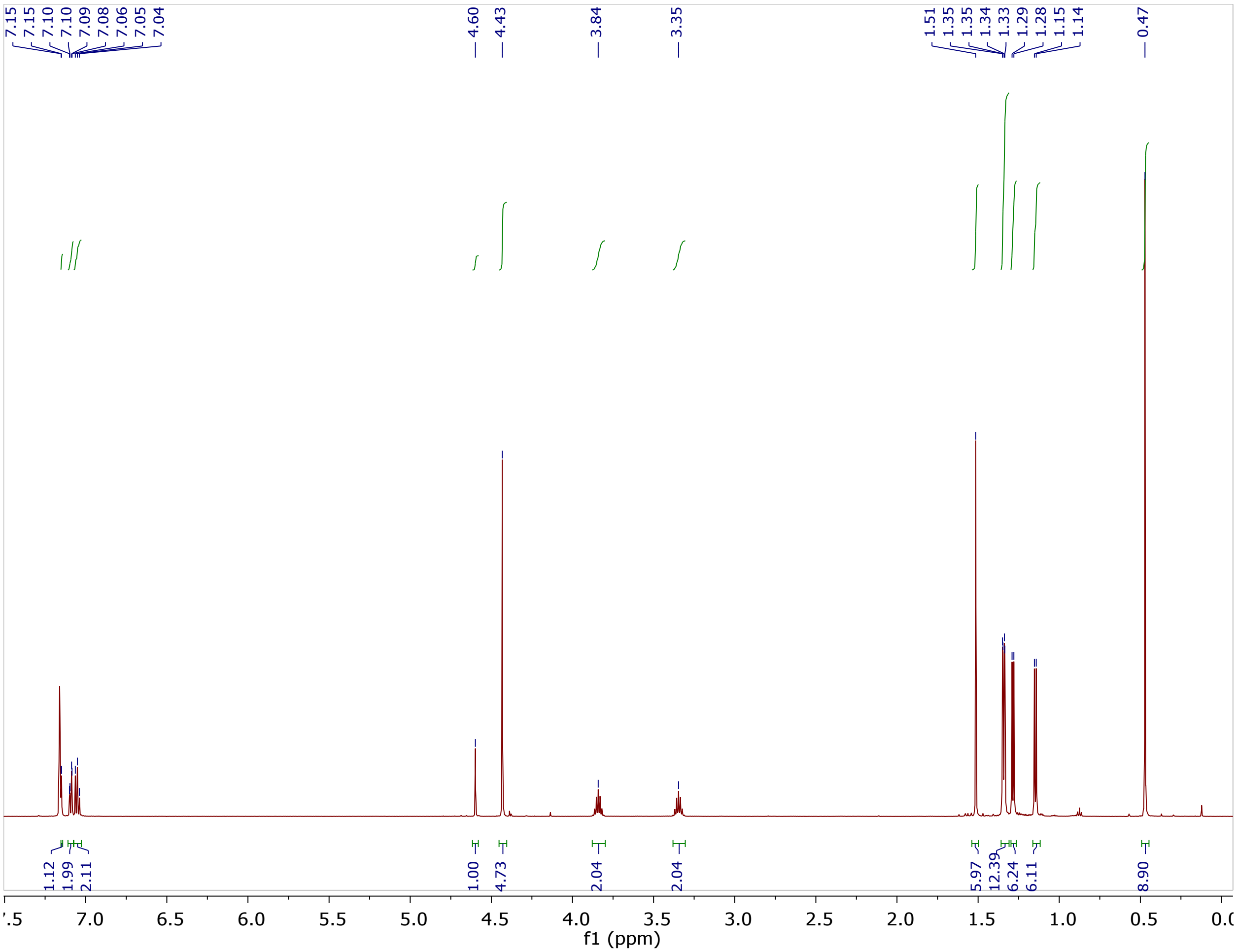

Figure S20. ^{1}H NMR Spectrum of **10** in C_6D_6.

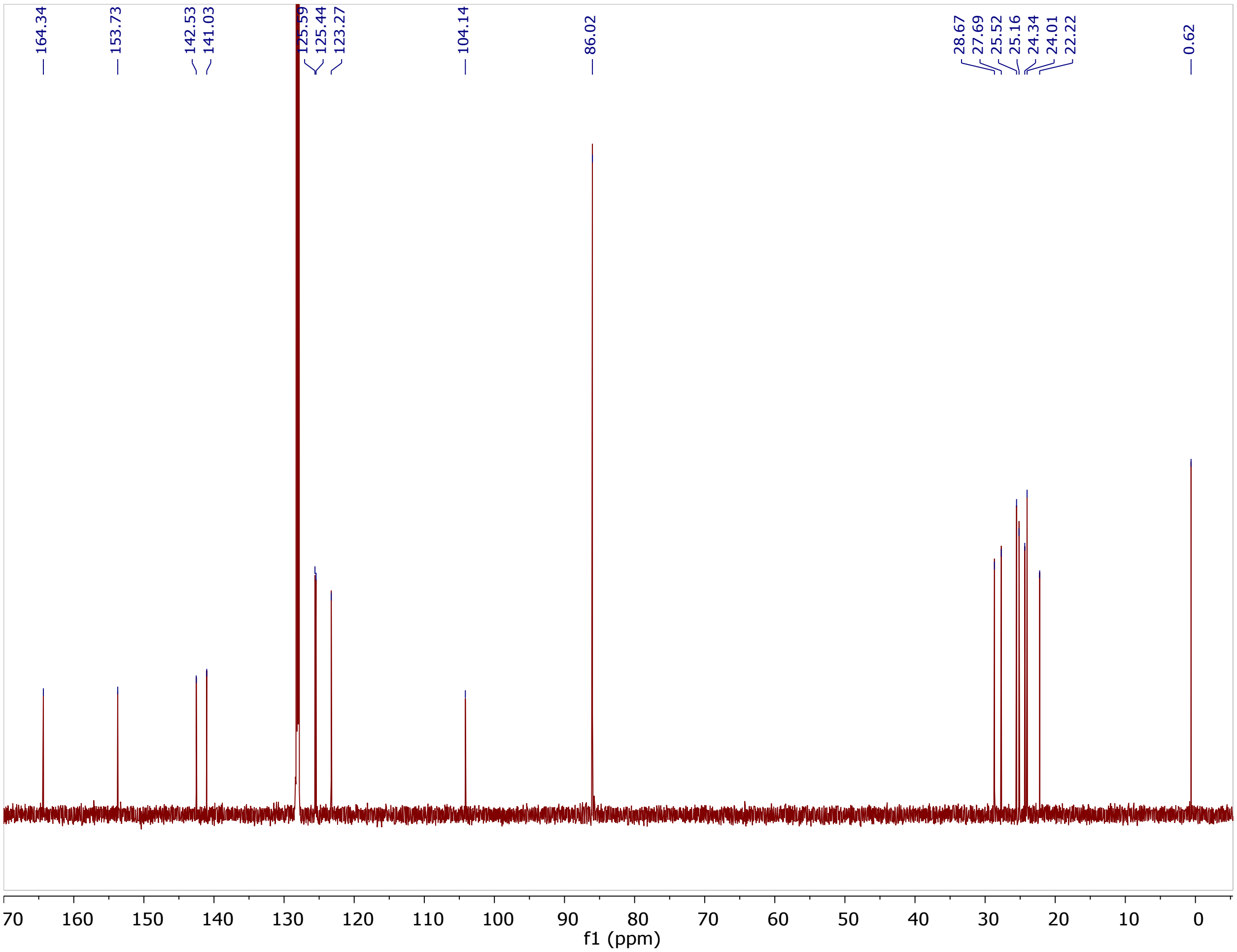

Figure S21. ^{13}C NMR Spectrum of **10** in C_6D_6.

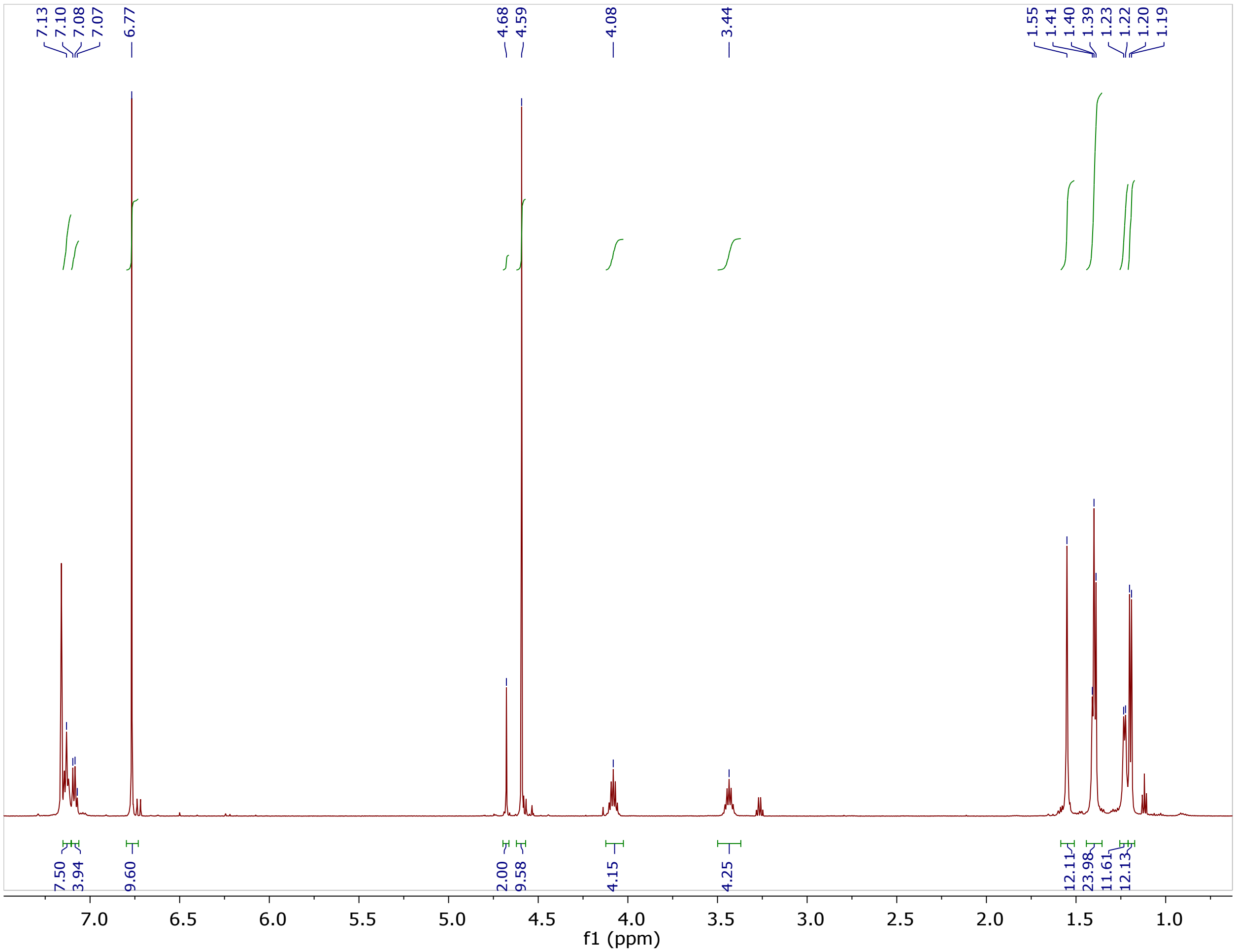

Figure S22. ^{1}H NMR Spectrum of **11** in C_6D_6.

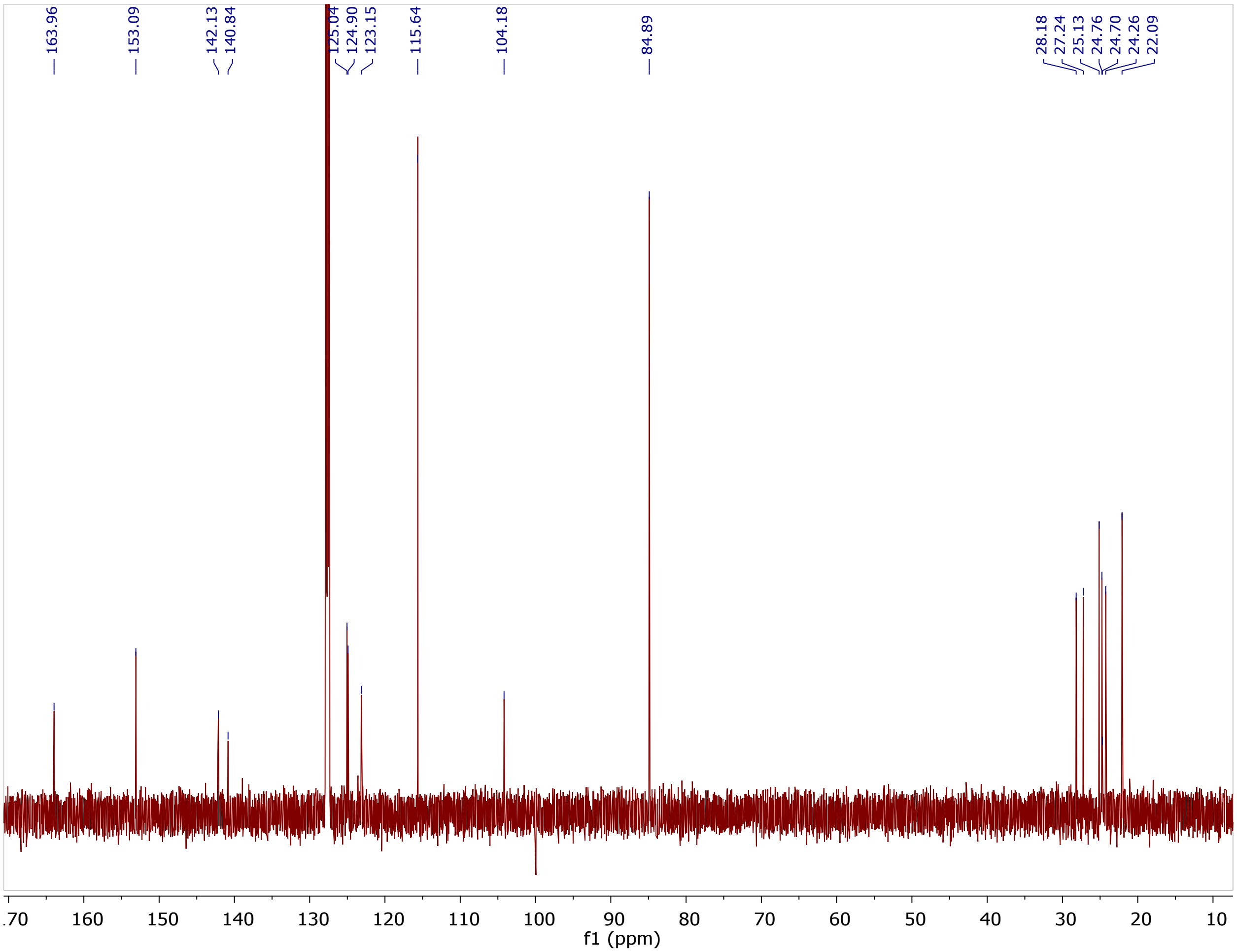

Figure S23. ^{13}C NMR Spectrum of **11** in C_6D_6.

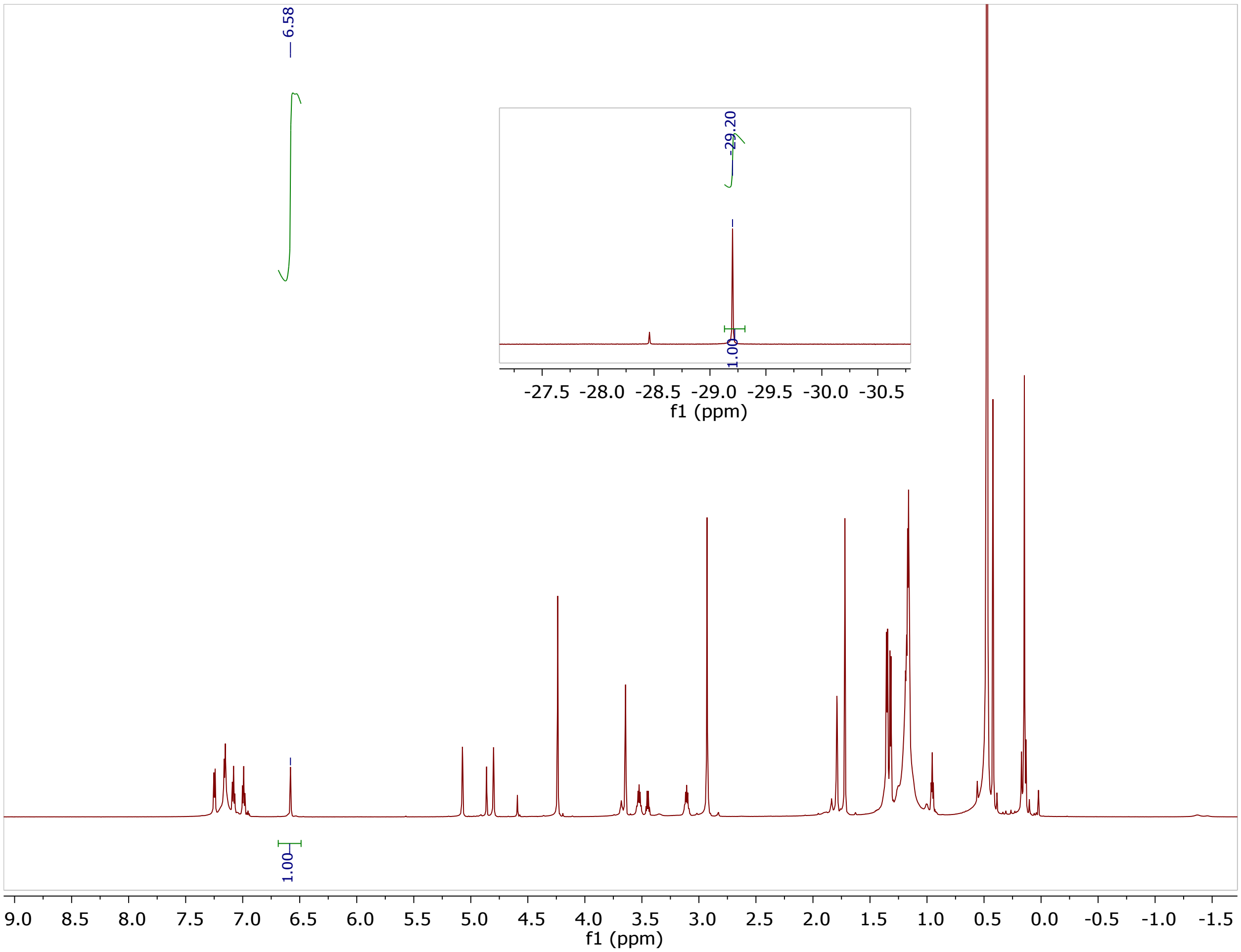

Figure S24. ^{1}H NMR spectrum of **1** and **2** generated from Na[Re(η^5-Cp)(BDI)] and excess Me_3SiCl in THF-d_8. The NMR tube used in this experiment was silylated using a reported procedure.[4]

Crystallographic Tables and Information

X-ray diffraction data were collected at CheXray, UC Berkeley (**5**, **11**) and the Advanced Light Source (ALS) beamline 12.2.1, Lawrence Berkeley National Laboratory (**1**, **2**, **3**, **4**, **6**, **7**, **8**, **9**, **10**). At CheXray, measurements for **5** and **11** were taken at CheXray using a Bruker APEX-II Quazar diffractometer equipped with a micro-focus Mo K_α X-ray source and a Bruker APEX-II CCD detector, with data analyzed and reduced using either the Bruker APEX2 or APEX3 software package, and solutions and refinements conducted using WinGX (SHELXT and SHELXL-2014).[5-7] Measurements for **1**, **2**, **3**, **4**, **6**, **7**, **8**, **9**, and **10** were taken using the ALS beam line 12.2.1, using a monochromated beam of 17 keV (0.7288 Å) synchrotron radiation and a Bruker D8 diffractometer equipped with a Bruker PHOTON II CPAD detector. Diffraction data collected at the ALS were analyzed and reduced using the Bruker APEX3 software package, and the structures were solved and refined using SHELXT and SHELXL-2014 as implemented by WinGX. All structures were collected at 100 K in a stream of dry nitrogen. The crystals analyzed for compounds **4** and **10** were found to be two-component twins, and were corrected for absorption using TWINABS and refined using the HKL5 protocol. The crystal of **7** that was analyzed was found to be an inversion twin in $P2_1$ with a domain ratio of ca. 0.63:0.37. A solution for **7** could be obtained in $P2_1/c$ and $P2_1/n$, but these models contained large amounts of random peaks of residual electron density, did not yield a stable anisotropic refinement, and did not give refinement metrics in line with the general high quality of the data (wR2 was >40% despite no signs of non-merohedral twinning and R(int) below 7%). All structures have been deposited to the Cambridge Crystallographic Data Centre (CCDC), with deposition numbers 1943017 (**1**), 1943018 (**2**), 1943019 (**3**), 1943020 (**4**), 1943021 (**5**), 1943022 (**6**), 1943023 (**7**), 1943024 (**8**), 1943025 (**9**), 1943026 (**10**), 1943027 (**11**).

Table S1. Crystallographic details and refinement metrics.

	1	**2**	**3 • Et_2O**	**4**	**5 • *n*-hexane**
Chemical formula	$C_{37}H_{55}N_2ReSi$	$C_{37}H_{55}N_4ReSi$	$C_{62}H_{88}N_2O_9ReNa$	$C_{35}H_{49}N_2Re$	$C_{90}H_{130}N_8Re_2Zr$
Formula weight	742.12	770.14	1214.53	683.96	1787.63
Color, habit	Green, block	Red, shard	Red, plate	Orange, block	Purple, lath
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	P-1	Pnma	$P2_1/n$	$P2_1/m$	C2/c
a (Å)	11.2050(6)	17.4379(8)	18.2169(14)	9.9082(4)	40.420(6)
b (Å)	11.6532(6)	19.7759(10)	13.5751(10)	21.1364(9)	9.9942(12)
c (Å)	15.7734(7)	10.2741(5)	23.0882(16)	14.5809(6)	28.451(4)
α (°)	99.762(2)	90	90	90	90
β (°)	97.186(2)	90	92.707(3)	91.647(2)	134.070(4)
γ (°)	118.544(2)	90	90	90	90
V (Å^3)	1731.79(15)	3543.0(3)	5703.3(7)	3052.3(2)	8258(2)
Z	2	4	4	4	4
Density (Mg m^{-3})	1.423	1.444	1.414	1.488	1.438
F(000)	760	1576	2528	1392	3664
Radiation Type	Synchrotron	Synchrotron	Synchrotron	Synchrotron	MoK_α
μ (mm^{-1})	3.779	3.699	2.325	4.242	3.097
Crystal size (mm^3)	0.080 x 0.030 x 0.030	0.150 x 0.080 x 0.045	0.055 x 0.030 x 0.015	0.060 x 0.045 x 0.040	0.160 x 0.040 x 0.020
Meas. Refl.	15553	43583	76152	92771	35861
Indep. Refl.	6207	3350	10579	7228	7556
R(int)	0.0377	0.0678	0.0792	0.1118	0.0629
Completeness to arcsin(0.6*λ)	98.0%	100.0%	100.0%	100.0%	99.9%
Final R indices [I > 2σ(I)]	R = 0.0247 R_w = 0.0672	R = 0.0419 R_w = 0.1045	R = 0.0299 R_w = 0.0720	R = 0.0460 R_w = 0.1051	R = 0.0386 R_w = 0.0814
Goodness-of-fit	1.024	1.302	1.028	1.214	1.034
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.701, -1.199	2.341, -3.334	1.713, -0.908	2.163, -2.132	1.750, -1.145
Flack parameter	n/a	n/a	n/a	n/a	n/a

	6	**7**	**8 • Et_2O**	**9 • 2 Et_2O**	**10 • 0.5 *n*-hexane**
Chemical formula	$C_{78}H_{112}N_4O_4Re_2Na_2$	$C_{47}H_{65}N_3OReNa$	$C_{98}H_{134}N_4O_{11}Re_2Na_2$	$C_{75}H_{107}N_3O_{10}ReNa$	$C_{41}H_{62}N_2OReSi$
Formula weight	1588.09	897.21	1962.46	1419.82	813.21
Color, habit	Orange, plate	Orange, lath	Orange, block	Orange, block	Red, shard
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Triclinic	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space group	P-1	$P2_1$	Pccn	P-1	$P2_1/c$
a (Å)	12.1197(6)	12.2440(6)	26.7486(11)	14.4071(7)	22.3061(13)
b (Å)	12.6219(6)	19.7563(10)	14.7414(6)	16.3244(8)	10.3851(6)
c (Å)	12.7468(6)	17.8939(9)	23.3350(10)	17.5429(9)	17.2124(10)
α (°)	83.6242(18)	90	90	86.467(2)	90
β (°)	71.6180(17)	92.124(2)	90	70.184(2)	105.885(2)
γ (°)	80.2046(17)	90	90	65.348(2)	90
V ($Å^3$)	1820.02(15)	4325.5(4)	9201.3(7)	3512.4(3)	3835.0(4)
Z	1	4	4	2	4
Density (Mg m^{-3})	1.449	1.378	1.417	1.342	1.408
F(000)	812	1848	4040	1488	1676
Radiation Type	Synchrotron	Synchrotron	Synchrotron	Synchrotron	Synchrotron
μ (mm^{-1})	3.466	3.024	2.857	1.900	3.422
Crystal size (mm^3)	0.115 x 0.110 x 0.010	0.125 x 0.035 x 0.015	0.135 x 0.115 x 0.080	0.100 x 0.060 x 0.045	0.145 x 0.070 x 0.030
Meas. Refl.	28643	56677	138595	50320	84815
Indep. Refl.	8383	17653	10596	14502	8844
R(int)	0.0415	0.0637	0.0613	0.0429	0.0588
Completeness to arcsin(0.6*λ)	99.9%	99.9%	99.9%	99.9%	100.0%
Final R indices [I > 2σ(I)]	R = 0.0207 R_w = 0.0496	R = 0.0357 R_w = 0.0911	R = 0.0235 R_w = 0.0523	R = 0.0250 R_w = 0.0590	R = 0.0343 R_w = 0.0694
Goodness-of-fit	1.023	1.020	1.053	1.072	1.076
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.538, -0.658	1.277, -2.662	0.556, -1.253	1.275, -0.601	1.384, -1.436
Flack parameter	n/a	0.369(7)	n/a	n/a	n/a

	11
Chemical formula	$C_{80}H_{102}N_4O_2Re_2$ Zr
Formula weight	1615.27
Color, habit	Orange, block
Temperature (K)	100(2)
Crystal system	Monoclinic
Space group	C2/c
a (Å)	38.4204(19)
b (Å)	10.5896(5)
c (Å)	18.2368(8)
α (°)	90
β (°)	108.020(2)
γ (°)	90
V (Å^3)	7055.8(6)
Z	4
Density (Mg m^{-3})	1.521
F(000)	3264
Radiation Type	MoK$_\alpha$
μ (mm^{-1})	3.617
Crystal size (mm^3)	0.300 x 0.250 x 0.080
Meas. Refl.	40509
Indep. Refl.	7233
R(int)	0.0475
Completeness to arcsin(0.6*λ)	100.0%
Final R indices [I > 2σ(I)]	R = 0.0233 R$_w$ = 0.0474
Goodness-of-fit	1.029
Δρ$_{max}$, Δρ$_{min}$ (e Å^{-3})	0.568, -0.492
Flack parameter	n/a

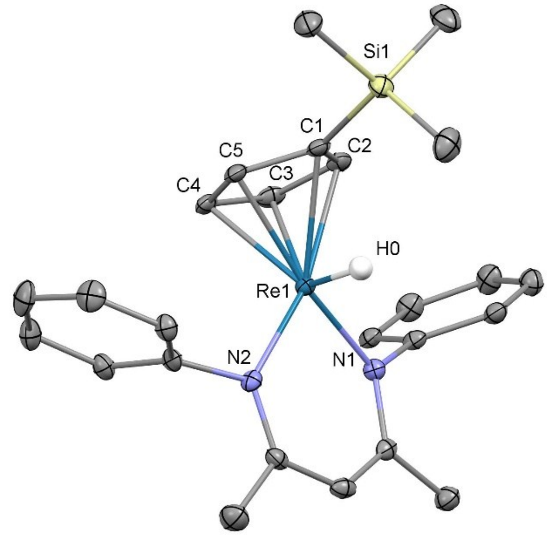

Figure S25. X-ray crystal structure of **1** with 50% probability ellipsoids. BDI isopropyl groups and hydrogen atoms, except for the metal hydride, have been omitted for clarity. Selected bond distances (Å): Re1-N1 = 2.014(2), Re1-N2 = 2.023(2), Re1-H0 = 1.43(4), Re1-Cp(centroid) = 1.899(2).

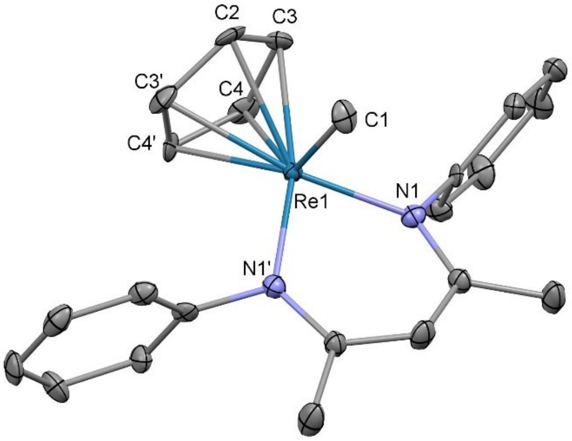

Figure S26. X-ray crystal structure of one of the two half units of **4** in the ASU with 50% probability ellipsoids, extended to show the whole molecule. BDI isopropyl groups and hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Re1-C1 = 2.126(9) and 2.156(10), Re1-N1 = 2.028(5) and 2.038(5), Re1-Cp(centroid) = 1.896(3) and 1.895(3).

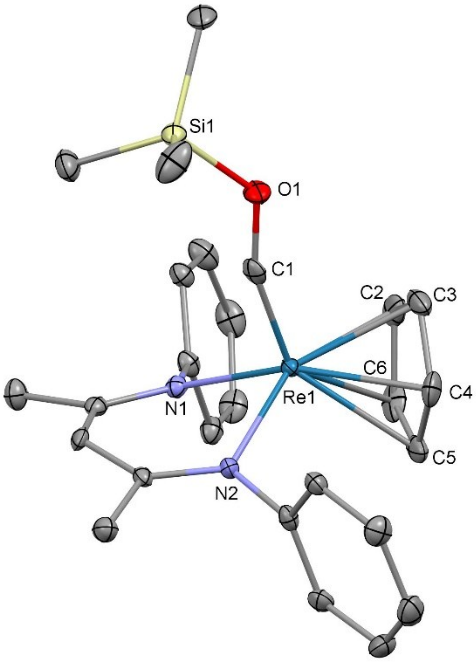

Figure S27. X-ray crystal structure of **10** with 50% probability ellipsoids. BDI isopropyl groups, hydrogen atoms, and solvent have been omitted for clarity. Selected bond distances (Å) and angles (°): Re1-C1 = 1.776(4), Re1-N1 = 2.147(3), Re1-N2 = 2.143(3), Re1-Cp(centroid) = 1.930(2), C1-O1 = 1.301(5), O1-Si1 = 1.704(3), Re1-C1-O1 = 159.2(3), C1-O1-Si1 = 128.5(3).

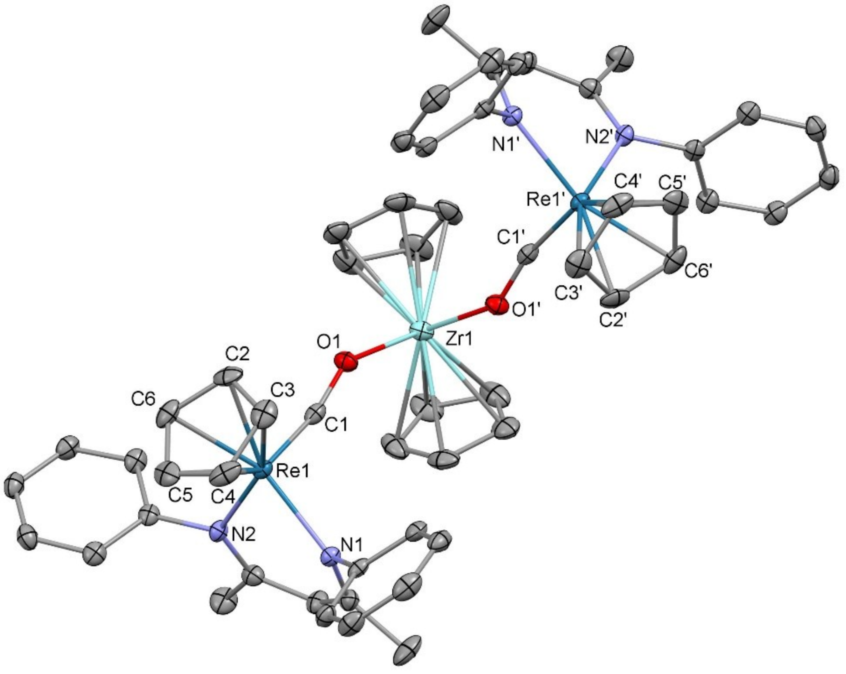

Figure S28. X-ray crystal structure of **11** with 50% probability ellipsoids. BDI isopropyl group and hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Re1-C1 = 1.785(3), Re1-N1 = 2.157(2), Re1-N2 = 2.149(2), Re1-Cp(centroid) = 1.933(2) , C1-O1 = 1.279(3), O1-Zr1 = 2.050(2), Re1-C1-O1 = 164.5(2) , C1-O1-Zr1 = 144.3(2).

FT-IR Spectra

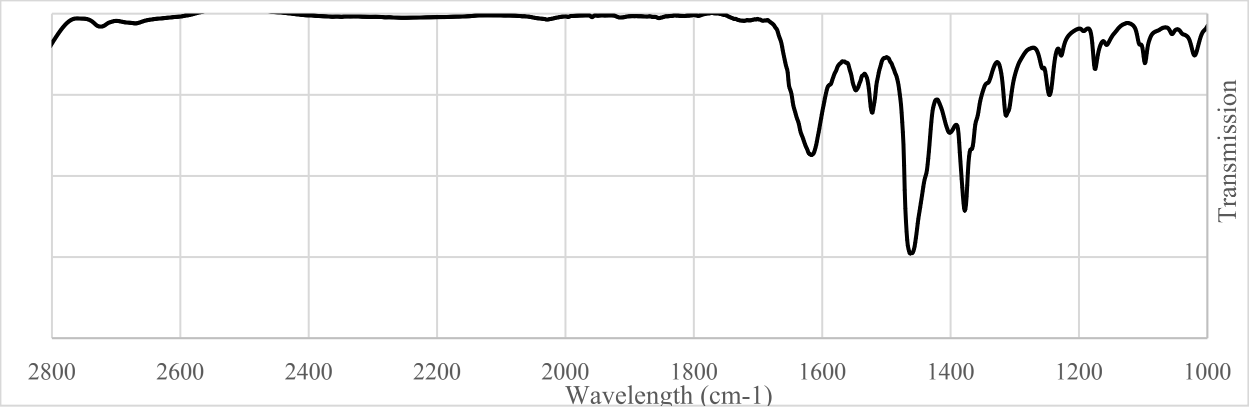

Figure S29. FT-IR absorbance spectrum of **2** (Nujol/KBr).

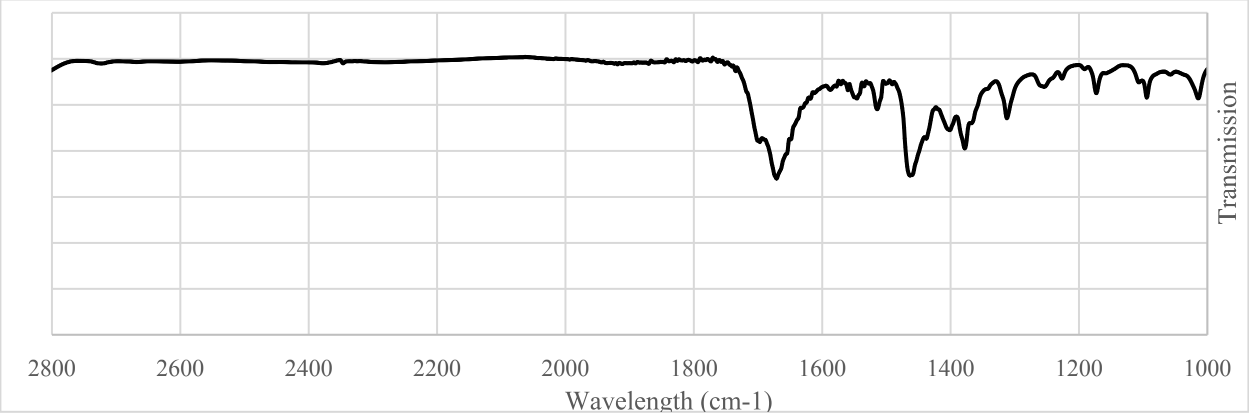

Figure S30. FT-IR absorbance spectrum of **5** (Nujol/KBr).

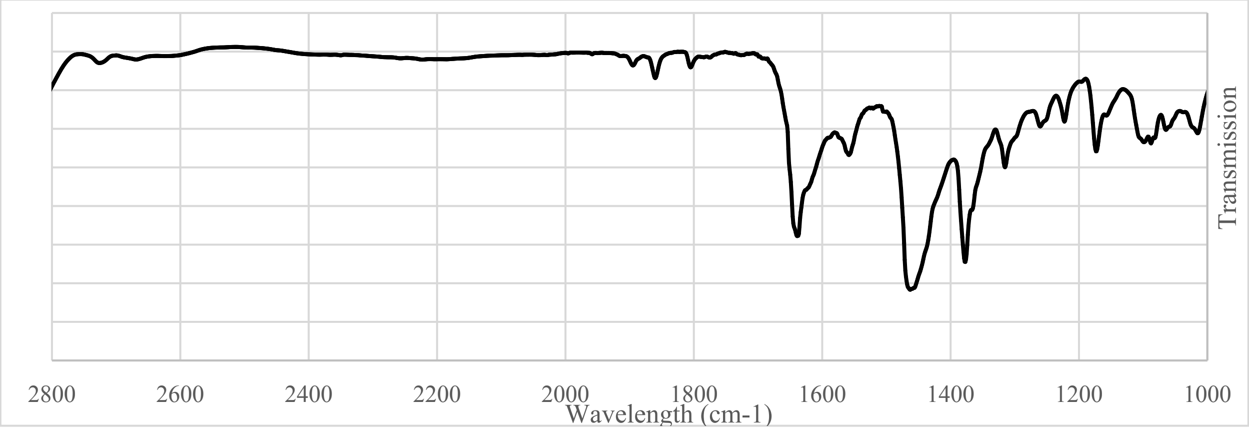

Figure S31. FT-IR absorbance spectrum of **6** (Nujol/KBr).

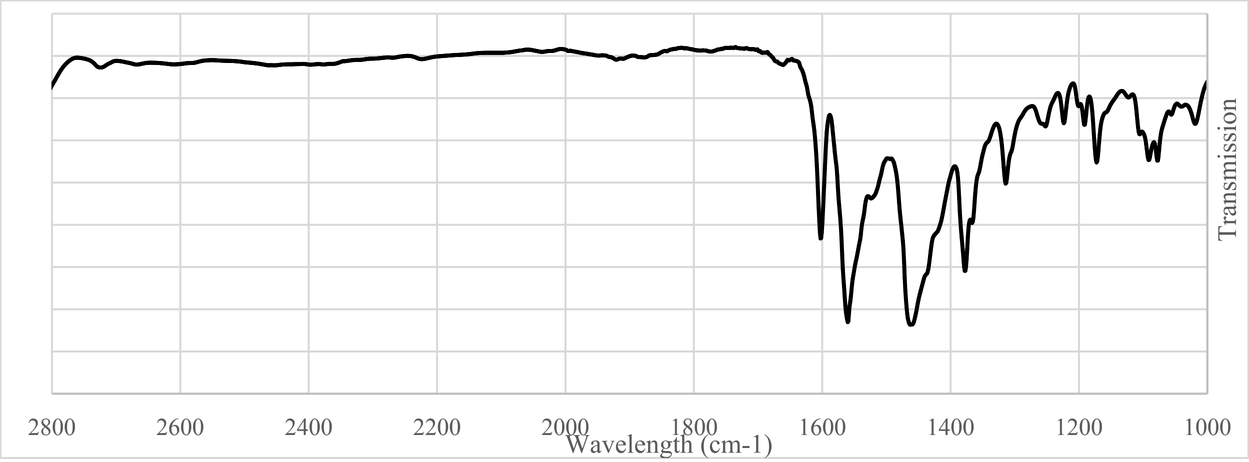

Figure S32. FT-IR absorbance spectrum of **7** (Nujol/KBr).

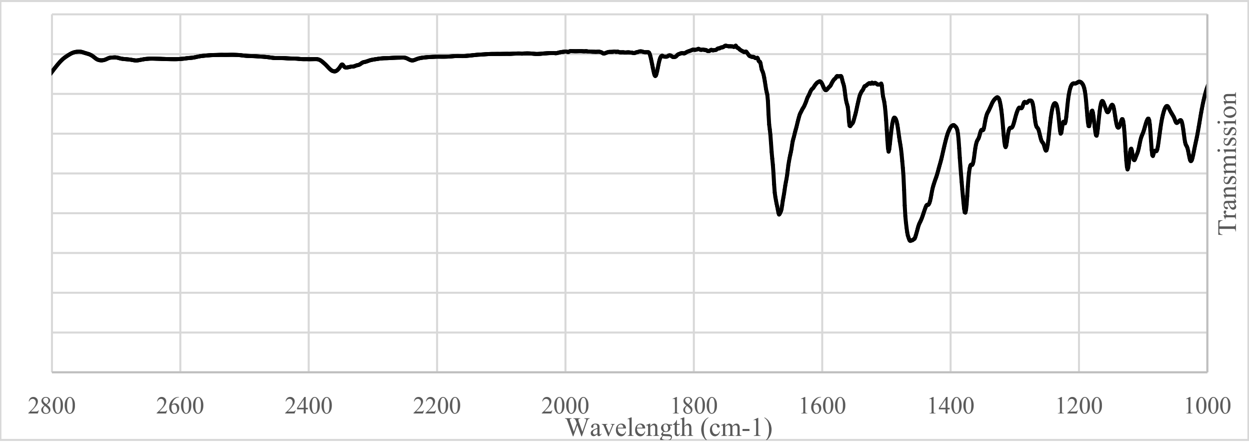

Figure S33. FT-IR absorbance spectrum of **8** (Nujol/KBr).

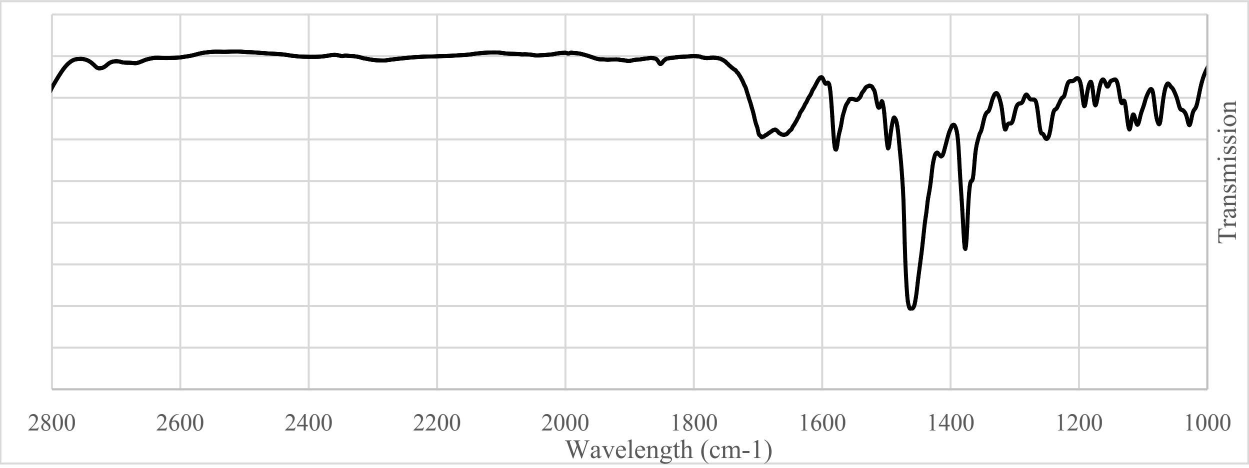

Figure S34. FT-IR absorbance spectrum of **9** (Nujol/KBr).

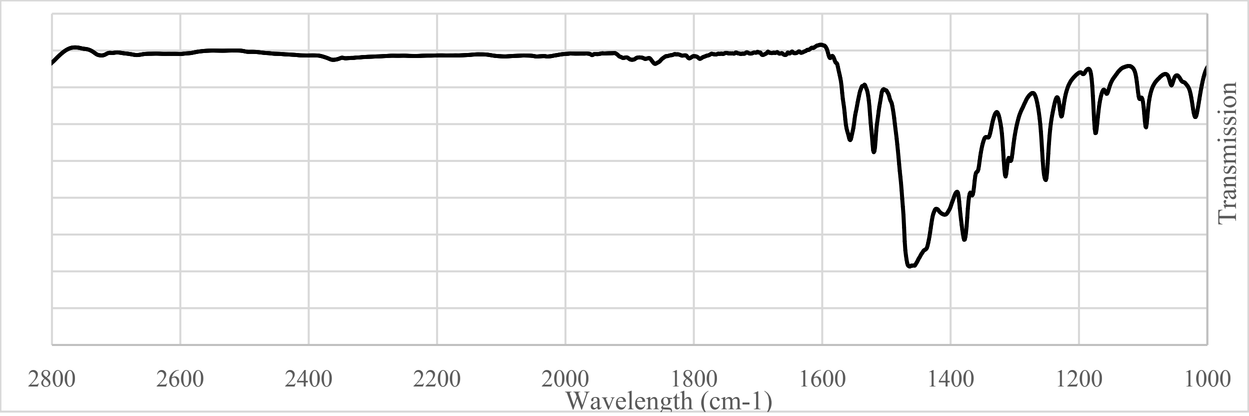

Figure S35. FT-IR absorbance spectrum of **10** (Nujol/KBr).

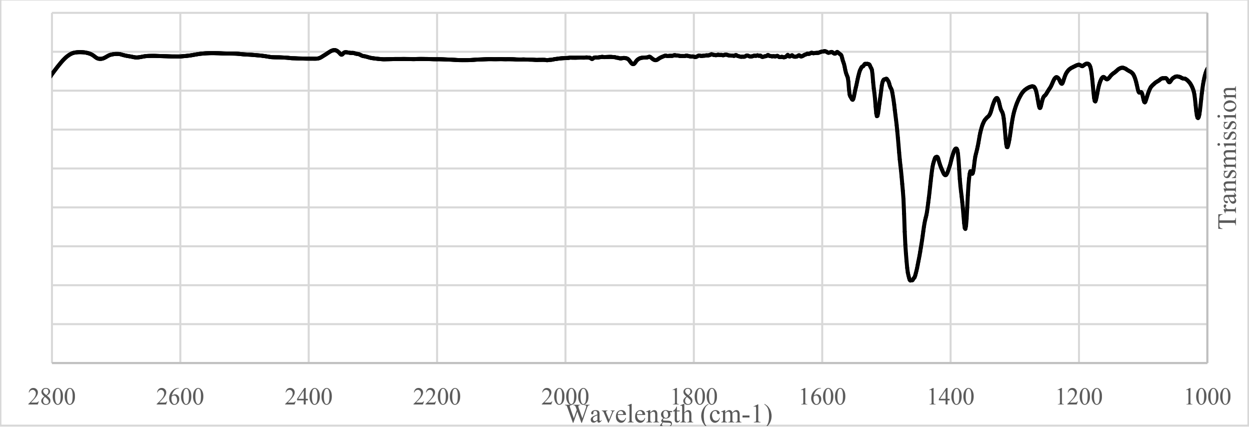

Figure S36. FT-IR absorbance spectrum of **11** (Nujol/KBr).

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