Supplementary Information (SI) for Chemical Science.

Electronic supporting information for:

Reversible addition of ethene to gallium(I) monomers and dimers

*Ryan J. Schwamm, Malavika A. Bhide, Gary S. Nichol and Michael J. Cowley**

School of Chemistry, The University of Edinburgh, Joseph Black Building, David Brewster Road, Edinburgh EH9 3FJ, UK.

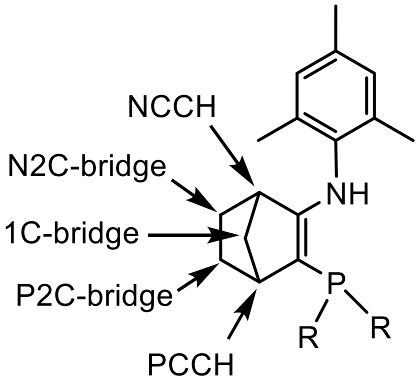
Contents

S1 Experimental

S1.1 General

All manipulations were carried out under an argon atmosphere using standard Schlenk or glovebox techniques unless stated. Reactions were carried out in glass Schlenk tubes, which were dried for 16 hours at 110 °C before use. Solvents were obtained from an Inert solvent purification system and stored over 4 Å molecular sieves. C_6D_6 and d_8-toluene were dried over a potassium mirror then vacuum distilled. NMR spectra were recorded on Bruker PRO500 MHz (^{7}Li at 194.3 MHz, ^{31}P at 202.4 MHz and ^{11}B at 160.4 MHz) or AVA500 MHz spectrometers (^{1}H at 500.0 MHz, ^{13}C at 125.7 Hz). Variable temperature NMR spectra were recorded in C_7D_8 at the temperature specified and on an AVA 400 MHz spectrometer (^{1}H at 400.0 MHz and ^{31}P at 161.9 MHz). ^{1}H and ^{13}C spectra were referenced to residual solvent signals. ^{31}P NMR spectra were referenced to an external standard of 85% H_3PO_4 in H_2O. Elemental Analysis was performed by Elemental Microanalysis Ltd. *N*-bicyclo[2.2.1]hept-2-ylidene-2,4,6-trimethyl-benzenamine, Mes_2PCl / Br (2 : 3)[1], **HL**$^{\mathbf{Mes/}t\mathbf{Bu}}$ [2] and GaCp* [3] were synthesised according to literature procedure. All other reagents were purchased from commercial suppliers and used without further purification.

Key for NMR spectroscopic assignment of ligand resonances:



S1.2 Synthetic procedures

Synthesis of HL$^{\mathrm{Mes/Mes}}$

A solution of ^{n}BuLi in hexane (2.7 mL of a 2.5 M solution, 6.83 mmol) was added dropwise to a stirring solution of *N*-bicyclo[2.2.1]hept-2-ylidene-2,4,6-trimethyl-benzenamine (1.55 g, 6.83 mmol) in THF (30 mL) which was cooled to -78 °C. After addition was complete, the suspension was allowed to warm to room temperature and stirred for 2 hours. The solution was cooled to -78 °C and a solution of $\mathrm{Mes_2PCl}$/ $\mathrm{Mes_2PBr}$ (ratio 2:3, 2.19 g, 6.83 mmol) in THF (10 mL) was added dropwise. The resulting orange solution was stirred at -78 °C for 2 hours then allowed to warm to room temperature and stirred overnight to give a dark orange solution. The volatile components were removed under reduced pressure to give an oily residue, which was extracted with pentane (40 mL) and filtered. The volatile components of the yellow filtrate were removed under reduced pressure to give **HL$^{\mathrm{Mes/Mes}}$** as an off-white solid. The solid was washed with cold pentane (10 mL) and dried under reduced pressure. Yield 2.99 g, 78%.

^{1}H NMR (500 MHz, 298 K, C_6D_6): δ 6.85 (s, 1H, $\mathrm{NC_6}H_2$), 6.78 (s, 1H, $\mathrm{NC_6}H_2$), 6.75 (s, 2H, $\mathrm{PC_6}H_2$), 6.69 (d, $^4J_{\mathrm{HP}}$ = 3.0 Hz, 2H, $\mathrm{PC_6}H_2$), 4.45 (d, $^2J_{\mathrm{HP}}$ = 2.8 Hz, 1H, $\mathrm{PC}H$), 2.77 (br, 6H, *o-Me*$^{\mathrm{P}}$), 2.61 (br, 6H, *o-Me*$^{\mathrm{P}}$), 2.57 (s, 1H, $\mathrm{NCC}H$), 2.22 (d, $^4J_{\mathrm{HP}}$ = 2.4 Hz, 6H, *o-Me*$^{\mathrm{N}}$), 2.20 (s, 3H, *p-Me*$^{\mathrm{N}}$), 2.11 (m, 1H, ½ $\mathrm{C}H_2^{\mathrm{1C\text{-}bridge}}$), 2.07 (s, 3H, *p-Me*$^{\mathrm{P}}$), 2.05 (s, 3H, *p-Me*$^{\mathrm{P}}$), 1.99 (m, 1H, $\mathrm{PCC}H$), 1.30 – 1.13 (m, 4H, $\mathrm{C}H_2^{\mathrm{N2C\text{-}bridge}}$ and $\mathrm{CH_2}^{\mathrm{P2C\text{-}bridge}}$), 0.90 (dm, $^2J_{\mathrm{HP}}$ = 3.0 Hz, 1H, ½ $\mathrm{C}H_2^{\mathrm{1C\text{-}bridge}}$).

^{13}C NMR: δ 182.2 (d, J_{CP} = 7.1 Hz, N*C*CH), 148.0 (d, J_{CP} = 2.3 Hz, *p*-NC_6H$_2$), 144.7 (br, *i*-PC_6H$_2$), 142.3 (d, J_{CP} = 14.7 Hz, *i*-PC_6H$_2$), 138.7 (s, *p*-PC_6H$_2$), 136.7 (s, *p*-PC_6H$_2$), 133.2 (d, J_{CP} = 24.4 Hz, *o*-PC_6H$_2$), 132.5 (d, J_{CP} = 31.9 Hz, *o*-PC_6H$_2$), 131.6 (s, *i*-NC_6H$_2$), 131.2 (br, *m*-PC_6H$_2$), 130.2 (br, *m*-PC_6H$_2$), 129.1 (*m*-NC_6H$_2$), 128.8 (*m*-NC_6H$_2$), 126.3 (d, J_{CP} = 2.8 Hz, *o*-NC_6H$_2$), 125.8 (d, J_{PC} = 2.1 Hz, *o*-NC_6H$_2$), 45.2 (d, J_{PC} = 26.9 Hz, P*C*H), 43.2 (s, NC*C*H), 40.7 (d, J_{CP} = 5.9 Hz, PC*C*H), 36.4 (d, J_{PC} = 4.4 Hz, $C\mathrm{H_2}^{\mathrm{1C\text{-}bridge}}$), 30.9 (s, $C\mathrm{H_2}^{\mathrm{N2C\text{-}bridge}}$), 24.8 (d, J_{PC} = 2.5 Hz, $C\mathrm{H_2}^{\mathrm{P2C\text{-}bridge}}$), 23.8 (d, J_{PC} = 14.1 Hz, *o-Me*$^{\mathrm{P}}$), 22.9 (d, J_{PC} = 16.1 Hz, *o-Me*$^{\mathrm{P}}$), 20.9 (d, J_{PC} = 5.7 Hz, *p-Me*$^{\mathrm{N}}$), 20.7 (s, *o-Me*$^{\mathrm{N}}$), 18.8 (s, *p-Me*$^{\mathrm{N}}$), 18.6 (d, J_{PC} = 4.7 Hz, *p-Me*$^{\mathrm{N}}$).

^{31}P NMR: δ -16.4.

Synthesis of L$^{\mathrm{Mes}/t\mathrm{Bu}}$Li(OEt$_2$)

A solution of ^{n}BuLi in hexane (1.6 mL of a 2.5 M solution, 4.04 mmol) was added dropwise to a stirring solution of **A** (1.50 g, 4.04 mmol) in $\mathrm{Et_2O}$ (50 mL) which was cooled to 0 °C. The resulting suspension was stirred at 0 °C for 30 minutes before allowing to warm to room temperature giving a pale yellow solution. The solution was stirred overnight at room temperature then the volatile components were removed *in vacuo* to give **1** as a pale yellow solid. Yield 1.45 g, 79 %.

^{1}H NMR: δ 6.97(s, 1H, $NC_6\mathit{H_2}$) , 6.94 (br, 1H, $NC_6\mathit{H_2}$), 3.26 (s, 1H, NCC*H*), 3.00 (q, J_{HH} = 7.0 Hz, 4H, $OC\mathit{H_2}$), 2.31 - 2.20 (m, 10H, *o-Me*^{N}, *p-Me*^{N} and PCC*H*), 1.93 (br, 1H, ½ $C\mathit{H_2}^{1C\text{-bridge}}$), 1.80 (br, 1H, ½ $C\mathit{H_2}^{N2C\text{-bridge}}$), 1.72 (br, 1H, ½ $C\mathit{H_2}^{N2C\text{-bridge}}$), 1.53 (br, 1H, ½ $C\mathit{H_2}^{P2C\text{-bridge}}$), 1.35 (m, 11H, $PC\mathit{Me_3}$, ½ $C\mathit{H_2}^{P2C\text{-bridge}}$ and ½ $C\mathit{H_2}^{1C\text{-bridge}}$), 1.34 (d, $^3J_{HP}$ = 13.4 Hz, 9H, $PC\mathit{Me_3}$), 0.90 (t, J_{HH} = 7.0 Hz, 6H, $OCH_2C\mathit{H_3}$),

^{13}C{^{1}H} NMR: Reliable data unable to be obtained due to the poor solubility of **1**.

^{31}P NMR: δ 10.1 (br).

^{7}Li NMR: δ -1.25 (br).

Synthesis of L$^{Mes/Mes}$Li(OEt$_2$)

A solution of ^{n}BuLi in hexane (4.0 mL of a 2.5 M solution, 10.1 mmol) was added dropwise to a stirring solution of **B** (5.06 g, 10.1 mmol) in Et_2O (70 mL) which was cooled to 0 °C. The resulting suspension was stirred at 0 °C for 30 minutes and then allowed to warm to room temperature to give a clear orange solution. The solution was stirred overnight at room temperature overnight. Removal of the volatile components were removed *in vacuo* gave **2** as a yellow solid. Yield 5.56 g, 95 %.

^{1}H NMR (500 MHz, 298 K, C_6D_6): δ 6.98 (br, 2H, $NC_6\mathit{H_2}$), 6.81 (br, 2H, $PC_6\mathit{H_2}$), 6.77 (br, 2H, $PC_6\mathit{H_2}$), 3.10 (br, 1H, NCC*H*), 2.94 (q, *J* = 7.0 Hz, 4H, $OC\mathit{H_2}$), 2.78 (br, 1H, PCC*H*), 2.57 (br, 3H, *o-Me*^{N}), 2.46 – 2.39 (br, 15H, *o-Me*^{N} and *o-Me*^{P}), 2.31 (s, 3H, *o-Me*^{N}), 2.16 (s, 3H, *o-Me*^{P}), 2.14 (s, 3H, *p-Me*^{P}), 1.87 (br, 1H, ½ $C\mathit{H_2}^{1C\text{-bridge}}$), 1.51 (br, 1H, ½ $C\mathit{H_2}^{N2C\text{-bridge}}$), 1.43 (br, 1H, ½ $C\mathit{H_2}^{P2C\text{-bridge}}$), 1.34 (br, 1H, ½ $C\mathit{H_2}^{P2C\text{-bridge}}$), 1.21 (br, 1H, ½ $C\mathit{H_2}^{1C\text{-bridge}}$), 0.79 (m, 5H, ½ $C\mathit{H_2}^{N2C\text{-bridge}}$ and $OCH_2C\mathit{H_3}$).

^{13}C{^{1}H} NMR: δ 181.5 (br, N*C*CH), 152.6 (br, *p*-NC_6H$_2$), 141.3 (br, *i*-P*C*$_6$H$_2$), 140.1 (d, J_{CP} = 12.6 Hz, *i*-P*C*$_6$H$_2$), 136.8 (s, *p*-N*C*$_6$H$_2$), 135.9 (br, *p*-P*C*$_6$H$_2$), 135.8 (s, *o*-N*C*$_6$H$_2$), 133.5 (d, J_{CP} = 12.6 Hz, *o*-P*C*$_6$H$_2$), 132.2 (br, *o*-P*C*$_6$H$_2$), 130.4 (s, *m*-P*C*$_6$H$_2$), 130.0 (br, *m*-P*C*$_6$H$_2$), 129.2 (*m*-N*C*$_6$H$_2$), 128.9 (*m*-N*C*$_6$H$_2$), 77.0 (br, P*C*CH), 66.2 (s, O*C*H$_2$), 47.5 (s, NC*C*H), 44.8 (d, J_{PC} = 10.6 Hz, PC*C*H), 43.7 (br, *C*H$_2^{1C\text{-bridge}}$), 30.7 (s, *C*H$_2^{N2C\text{-bridge}}$), 28.4 (s, *C*H$_2^{P2C\text{-bridge}}$), 23.7 (d, J_{PC} = 15.7 Hz, *C*H$_2^{P2C\text{-bridge}}$), 22.6 (br, *p-Me*^{N}), 22.6 (d, J_{PC} = 16.1 Hz, *o-Me*^{P}), 21.1 (d, J_{PC} = 2.8 Hz, *p-Me*^{P}), 20.3 (s, *p-Me*^{N}), 19.9 (br, *p-Me*^{P}), 14.7 (s, $OCH_2C\mathit{H_3}$).

^{31}P NMR: δ -53.9 (br).

^{7}Li NMR: δ -2.37 (br).

Synthesis of [$L^{Mes/tBu}$Ga]$_2$ (1)

A solution of $L^{Mes/tBu}Li(OEt_2)$ (1.40 g, 3.70 mmol) in toluene (30 mL) was added dropwise to a stirring solution of GaCp* (0.75 g, 3.70 mmol) in toluene (30 mL). The resulting orange solution was heated to 80 °C and stirred for 3 hours resulting in the formation of an orange precipitate and red solution. Hot filtration of the suspension at 80 °C gave a clear red solution. Upon cooling to room temperature, the solution deposited **1** as an orange precipitate, which was isolated by filtration and dried *in vacuo*. A second crop of **1** was obtained by further extraction of the orange residue and hot filtration and removal of the volatile components under reduced pressure. Yield (combined) 1.23 g, 74 %.

^{1}H NMR (500 MHz, 298 K, C_6D_6): δ 6.84 (s, 2H, C_6H_2), 3.02 (br s, 1H, NCC*H*), 2.50 (s, 3H, *o-Me*^{N}), 2.44 (br m, 1H, PCC*H*), 2.40 (s, 3H, *o-Me*^{N}), 2.25 (s, 3H, *p-Me*^{N}), 1.75 – 1.65 (m, 2H, ½ $CH_2^{N2C\text{-bridge}}$ and ½ $CH_2^{1C\text{-bridge}}$), 1.60 – 1.55 (m, 1H, ½ $CH_2^{N2C\text{-bridge}}$) 1.48 – 1.41 (m, 1H, ½ $CH_2^{P2C\text{-bridge}}$), 1.34 (m, 1H, ½ $CH_2^{P2C\text{-bridge}}$), 1.23 (d, $^3J_{HP}$ = 13.4 Hz, 9H, $PCMe_3$), 1.20 (m, 1H, ½ $CH_2^{1C\text{-bridge}}$), 1.18 (d, $^3J_{HP}$ = 13.4 Hz, 9H, $PCMe_3$).

^{13}C{^{1}H} NMR: δ 182.1 (d, J_{CP} = 27.4 Hz, N*C*CH), 145.6 (d, J_{CP} = 3.7 Hz, *i*-NC_6H_2), 135.9 (s, *o*-C_6H_2), 135.0 (s, *o*-C_6H_2), 132.6 (s, *p*-C_6H_2), 129.3 (s, *m*-C_6H_2), 129.0 (s, *m*-C_6H_2), 82.8 (d, J_{CP} = 31.4 Hz, P*C*CH), 49.3 (d J_{CP} = 11.4 Hz, $CH_2^{1C\text{-bridge}}$), 45.0 (d, J_{CP} = 5.5 Hz, NC*C*H), 44.0 (d, J_{CP} = 11.4 Hz, PC*C*H), 35.3 (d, J_{CP} = 8.1 Hz, P*C*Me$_3$), 34.5 (d, J_{CP} = 8.0 Hz, P*C*Me$_3$), 30.9 (d, J_{CP} = 6.1 Hz, $PCMe_3$), 30.4 (d, J_{CP} = 5.0 Hz, $PCMe_3$), 30.3 (s, $CH_2^{N2C\text{-bridge}}$), 25.6 (s, $CH_2^{P2C\text{-bridge}}$), 21.0 (s, *p-Me*^{N}), 20.2 (s, *o-Me*^{N}), 19.6 (s, *o-Me*^{N}).

^{31}P NMR: δ 26.0 (br).

Elemental Analysis: Anal. Calc'd for $C_{54}H_{81}Ga_2N_2P_2$ ([**3**.C_6H_7], *972.67*): C, 67.92; H, 8.50; N, 2.88. Found: C, 67.93; H, 8.42; N, 2.83.

UV-Vis (Et_2O solution, 298K): λ_{max} 501 nm (ε = 9847 L mol^{-1} cm^{-1}).

Synthesis of $L^{Mes/Mes}$Ga: (2)

A solution of $L^{Mes/Mes}Li(OEt_2)$ (2.20 g, 3.83 mmol) in toluene (30 mL) was added dropwise to a stirring solution of GaCp* (0.78 g, 3.83 mmol) in toluene (30 mL). The resulting dark yellow solution was heated to 80 °C and stirred for 3 hours resulting in the formation of a dark orange solution and colourless precipitate. Filtration of the suspension gave a clear dark orange solution. Removal of the volatile components under reduced pressure gave a dark residue. Extraction of the residue into toluene (5 mL) and storage at -30 °C overnight gave dark red-purple crystals of **$L^{Mes/Mes}$Ga…GaL$^{Mes/Mes}$**. Yield 0.98 g, 45 %. Recrystallisation of the crystals by storage of a concentrated pentane solution at -30 °C gave yellow crystals of **2**.

^{1}H NMR (500 MHz, 298 K, C$_6$D$_6$): δ 6.93 (s, 1H, NC$_6H_2$), 6.90 (s, 1H, NC$_6H_2$), 6.71 (s, 4H, PC$_6H_2$), 2.97 (br, 1H, NCCH), 2.54 (br, 6H, *o-Me*$^{\mathrm{P}}$), 2.43 (s, 3H, *p-Me*$^{\mathrm{N}}$), 2.36 (br, 7H, *o-Me*$^{\mathrm{P}}$ and PCCH), 2.24 (s, 3H, *o-Me*$^{\mathrm{N}}$), 2.22 (s, 3H, *o-Me*$^{\mathrm{N}}$), 2.07 (s, 3H, *p-Me*$^{\mathrm{P}}$), 2.05 (s, 3H, *p-Me*$^{\mathrm{P}}$), 1.83 (m, 1H, ½ C$H_2^{\text{1C-bridge}}$), 1.38 – 1.30 (m, 2H, ½ C$H_2^{\text{N2C-bridge}}$ and ½ C$H_2^{\text{P2C-bridge}}$), 1.23 – 1.14 (m, 2H, ½ C$H_2^{\text{1C-bridge}}$ and ½ C$H_2^{\text{P2C-bridge}}$), 0.66 (m, 1H, ½ C$H_2^{\text{N2C-bridge}}$).

^{13}C{^{1}H} NMR: δ 180.1 (d, J_{PC} = 41.1 Hz, N*C*CH), 143.6 (d, J_{PC} = 3.3 Hz, *i*-N*C*$_6$H$_2$), 142.2 (d, J_{PC} = 10.7 Hz, *i*-P*C*$_6$H$_2$), 141.9 (d, J_{PC} = 11.4 Hz, *i*-P*C*$_6$H$_2$), 138.7 (d, J_{PC} = 2.3 Hz, *p*-P*C*$_6$H$_2$), 135.6 (s, N*C*$_6$H$_2$), 132.9 (d, J_{PC} = 12.6 Hz, *o*-P*C*$_6$H$_2$), 130.9 (d, J_{PC} = 5.7 Hz, *m*-P*C*$_6$H$_2$), 130.5 (s, N*C*$_6$H$_2$), 130.4 (s, N*C*$_6$H$_2$), 130.1 (d, J_{PC} = 7.0 Hz, *m*-P*C*$_6$H$_2$), 129.6 (s, *m*-N*C*$_6$H$_2$), 127.2 (d, J_{PC} = 2.7 Hz, *p*-P*C*$_6$H$_2$), 88.4 (d, J_{PC} = 28.6 Hz, P*C*CH), 46.9 (d, $^1J_{\mathrm{PC}}$ = 5.9 Hz, NC*C*H), 46.6 (s, *C*H$_2^{\text{1C-bridge}}$), 44.9 (d, J_{PC} = 14.2 Hz, PC*C*H), 29.4 (s, *C*H$_2^{\text{N2C-bridge}}$), 27.7 (d, J_{PC} = 2.2 Hz, *C*H$_2^{\text{P2C-bridge}}$), 23.9 (br, *o-Me*$^{\mathrm{P}}$), 22.8 (d, J_{PC} = 7.4 Hz, *o-Me*$^{\mathrm{P}}$), 21.0 (s, *o-Me*$^{\mathrm{N}}$), 21.0 (s, *p-Me*$^{\mathrm{N}}$), 20.9 (s, *p-Me*$^{\mathrm{P}}$), 20.0 (s, *o-Me*$^{\mathrm{N}}$)

^{31}P NMR: δ -38.7.

UV-Vis (Et$_2$O solution, 298K): λ_{max} 440 nm (ε = 2081 L mol^{-1} cm^{-1}). **UV-Vis** (Et$_2$O solution, 223K): λ_{max} 510 nm ($\varepsilon_{\mathrm{minimium}}$ = 3256 L mol^{-1} cm^{-1}), 414 nm ($\varepsilon_{\mathrm{minimum}}$ = 6014 L mol^{-1} cm^{-1}).

Elemental Analysis: Anal. Calc'd for C$_{54}$H$_{51}$BF$_{15}$GaNP: C, 72.35; H, 7.32; N, 2.48. Found: C, 73.18; H, 7.71; N, 2.10.

Synthesis of L$^{\mathrm{Mes}/t\mathrm{Bu}}$Ga-B(C$_6F_5$)$_3$ (3)

Toluene (20 mL) was added to a Schlenk tube charged with **1** (0.100 g, 0.113 mmol) and B(C$_6$F$_5$)$_3$.Et$_2$O (0.132, 0.226 mmol), resulting in an immediate colour change from orange to a yellow suspension. The resulting suspension was stirred for 12 hours at room temperature, giving a clear pale-yellow solution. Removal of the volatile components *in vacuo* gave **3** as a pale-yellow powder which was washed with 5 mL of pentane and dried *in vacuo*. Yield 0.172 g, 67 %. Pale yellow crystals suitable for analysis using single crystal X-ray diffraction were obtained by slow evaporation of a concentrated pentane solution.

^{1}H NMR (500 MHz, 298 K, C$_6$D$_6$): δ 6.64 (s, 2H, C$_6H_2$), 2.64 (br m, 1H, NCCH), 2.19 (s, 4H, *o-Me*$^{\mathrm{N}}$ and PCCH), 2.00 (s, 3H, *o-Me*$^{\mathrm{N}}$), 1.90 (s, 3H, *p-Me*$^{\mathrm{N}}$), 1.48 – 1.41 (m, 1H, ½ C$H_2^{\text{N2C-bridge}}$), 1.36 – 1.30 (m, 1H, ½ C$H_2^{\text{1C-bridge}}$), 1.26 – 1.19 (m, 2H, ½ C$H_2^{\text{N2C-bridge}}$ and ½ C$H_2^{\text{P2C-bridge}}$) 1.09 (d, $^3J_{\mathrm{HP}}$ = 15.6 Hz, 9H, PCMe_3), 0.92 (m, 11H, PCMe_3, ½ C$H_2^{\text{1C-bridge}}$ and ½ C$H_2^{\text{P2C-bridge}}$)

^{13}C{^{1}H} NMR: δ 185.9 (d, J_{CP} = 14.9 Hz, N*C*CH), 149.1 (m, BC$_6$F$_5$) , 147.2 (m, BC$_6$F$_5$), 141.7 (d, 3.7 Hz, *i*-N*C*$_6$H$_2$), 138.4 (m, BC$_6$F$_5$), 136.4 (m, BC$_6$F$_5$), 136.4 (s, *o-C*$_6$H$_2$), 134.2 (s, *o-C*$_6$H$_2$), 133.3 (s, *p*-C_6H_2), 129.3 (s, *m*-C_6H_2), 129.2 (s, *m*-C_6H_2), 82.8 (d, J_{CP} = 45.9 Hz, P*C*CH), 49.0 (d J_{CP} = 3.9 Hz, $CH_2^{1C\text{-bridge}}$), 44.9 (d, J_{CP} = 1.7 Hz, NC*C*H), 44.0 (d, J_{CP} = 8.5 Hz, PC*C*H), 37.6 (d, J_{CP} = 21.4 Hz, P*C*Me$_3$), 36.5 (d, J_{CP} = 19.8 Hz, P*C*Me$_3$), 29.3 (d, J_{CP} = 3.9 Hz, PC*Me$_3$*), 29.0 (d, J_{CP} = 3.8 Hz, PC*Me$_3$*), 29.1 (s, $CH_2^{N2C\text{-bridge}}$), 24.9 (s, $CH_2^{P2C\text{-bridge}}$), 20.7 (s, *p-Me*^{N}), 19.3 (s, *o-Me*^{N}), 18.2 (s, *o-Me*^{N}).

^{31}P NMR: δ 15.3 (d, J_{PF} = 32 Hz).

^{11}B NMR: δ -19.0.

^{19}F NMR: δ -130.3 (d, *J* = 25.0 Hz), -158.5 (t, *J* = 20.7 Hz), -163.6 (td, *J* = 25.0 and 8.1 Hz).

Elemental Analysis: Anal. Calc'd for $C_{54}H_{51}BF_{15}GaNP$ ([**5**.$(C_6H_7)_2$], *1136.53*): C, 59.18; H, 4.72; N, 1.23. Found: C, 59.26; H, 5.02; N, 1.18.

Synthesis of $L^{Mes/Mes}Ga\text{-}B(C_6F_5)_3$ (4)

Toluene (20 mL) was added to a J. Youngs NMR tube charged with **2** (0.030 g, 0.53 mmol) and $B(C_6F_5)_3.Et_2O$ (0.311 g, 0.053 mmol), resulting in an immediate colour change from red to yellow. The resulting pale-yellow solution was stirred overnight at room temperature, followed by removal of the volatile components *in vacuo* to obtain **6** as a bright yellow powder. Yield 0.502 g, 88 %. Yellow crystals suitable for analysis using single crystal X-ray diffraction were obtained by slow evaporation of a concentrated toluene solution.

^{1}H NMR (500 MHz, 298 K, C_6D_6): δ 6.73 (s, 2H, NC$_6$*H$_2$* and PC$_6$*H$_2$*), 6.67 (s, 1H, NC$_6$*H$_2$*), 6.48 (br, 3H, PC$_6$*H$_2$*), 2.86 (s, 1H, NCC*H*), 2.69 (br, 3H, *o-Me*^{P}), 2.42 (br, 3H, *o-Me*^{P}), 2.30 (s, 1H, PCC*H*), 2.23 (s, 3H, *p-Me*^{N}), 2.16 (s, 3H, *o-Me*^{N}), 2.15 (s, 3H, *o-Me*^{N}) 2.00 (s, 3H, *p-Me*^{P}), 1.88 (s, 3H, *p-Me*^{P}), 1.75 (br, 6H, *o-Me*^{P}), 1.56 (m, 1H, ½ C$H_2^{1C\text{-bridge}}$), 1.12 – 1.08 (m, 2H, ½ C$H_2^{N2C\text{-bridge}}$ and ½ C$H_2^{P2C\text{-bridge}}$), 0.93 – 0.89 (m, 2H, ½ C$H_2^{1C\text{-bridge}}$ and ½ C$H_2^{P2C\text{-bridge}}$), 0.25 (m, 1H, ½ C$H_2^{N2C\text{-bridge}}$).

^{13}C{^{1}H} NMR: δ 181.0 (d, J_{PC} = 21.3 Hz, N*C*CH), 149.2 (m, BC_6F_5) , 147.3 (m, BC_6F_5), 141.6 (d, J_{PC} = 4.5 Hz, *i*-NC_6H_2), 141.3 (d, J_{PC} = 2.7 Hz, *o*-PC_6H_2), 141.1 (d, J_{PC} = 2.5 Hz, *o*-PC_6H_2), 138.2 (m, BC_6F_5), 136.3 (m, BC_6F_5), 135.9 (s, *p*-PC_6H_2), 135.2 (s, NC_6H_2), 133.8 (s, *m*-PC_6H_2), 129.7 (d, J_{PC} = 10.0 Hz, *m*-PC_6H_2), 125.6 (d, J_{PC} = 52.7 Hz, *i*-PC_6H_2), 122.2 (d, J_{PC} = 50.4 Hz, *i*-PC_6H_2), 87.0 (d, J_{PC} = 49.9 Hz, P*C*CH), 46.3 (s, $CH_2^{1C\text{-bridge}}$), 45.8 (d, $^1J_{PC}$ = 5.7 Hz, NC*C*H), 44.5 (d, J_{PC} = 9.9 Hz, PC*C*H), 28.1 (s, $CH_2^{N2C\text{-bridge}}$), 27.0 (s, $CH_2^{P2C\text{-bridge}}$), 22.7 (s, *o-Me*^{P}), 22.4 (s, *o-Me*^{P}), 22.3 (s, *o-Me*^{P}), 20.8 (s, *p-Me*^{N}), 20.7* (m, *p-Me*^{P} and *o-Me*^{N}), 19.8 (s, *p-Me*^{P}), 18.8 (s, *o-Me*^{N}). *overlapping resonances

^{31}P NMR: δ -47.2 (br).

^{11}B NMR: δ -18.2.

^{19}F NMR: δ 130.1 (d, *J* = 25.0 Hz), -158.8 (t, *J* = 20.7 Hz), -163.7 (td, *J* = 25.0 and 8.1 Hz).

Elemental Analysis: Anal. Calc'd for $C_{52}H_{41}BF_{15}GaNP$ (**6**, *1076.39*): C, 58.02; H, 3.84; N, 1.30. Found: C, 57.69; H, 3.91; N, 1.24.

Synthesis of $[L^{Mes/tBu}Ga]_2[B(C_6F_5)_4]_2 \cdot 2PhF$ (5)

A solution of digallene **1** (44 mg, 0.05 mmol) in fluorobenzene was added to a solution of $[Ph_3C][B(C_6F_5)_4]$ (94 mg, 0.1 mmol) in fluorobenzene. Upon mixing and stirring, the solution turned brown and then green. After 5 minutes, green needles precipitated out of the solution. The supernatant was decanted and the green needles (**7**) were dried under reduced pressure (yield = 56.6 mg, 51%).

NMR data could not be obtained due to the insolubility of **7**.

Elemental Analysis: Anal. Calc'd: C, 51.46; H, 3.30; N, 1.25. Found: C, 51.55; H, 1.90; N, 1.09.

Synthesis of $[L^{Mes/tBu}Ga]_2(CH_2CH_2)$ (6)

Toluene (30 mL) was added to a 100 mL J. Youngs ampoule charged with **1** (0.402 g, 0.46 mmol). The suspension was freeze-pump-thaw degassed three times and the atmosphere was replaced by gaseous ethene (1 bar). The suspension was stirred at room temperature for 3 hours followed by removal of the volatile components *in vacuo*. The colourless solid was extracted with pentane (30 mL), concentrated to 10 mL and then stored at -30 °C overnight to give colourless crystals of **5** (crop 1, 0.103 g). A second crop of colourless crystals of **5** was obtained by further concentration of the mother liquor and storage at -30 °C (crop 2, 0.207 g). Combined Yield 0.311 g, 74 %. Due to the presence of multiple diastereomers and overlapping resonances, the complete assignment of the $^{1}H\{^{13}C\}$ and ^{31}C NMR spectra of **5** was impractical.

^{1}H NMR (500 MHz, 298 K, C_6D_6): *Major isomer:* δ 6.89 - 6.86 (m, 4H, C_6H_2), 3.03 (s, 2H, NCC*H*), 2.49 (s, 2H, PCC*H*), 2.42 (s, 6H, o-Me^{N}), 2.27 (s, 6H, o-Me^{N}, 2.26 (s, 6H, p-Me^{N}), 1.71 – 1.63 (m, 4H, ½ $CH_2^{1C\text{-bridge}}$ and ½ $CH_2^{P2C\text{-bridge}}$),* 1.62 – 1.55 (m, 4H, ½ $CH_2^{P2C\text{-bridge}}$), 1.42 – 1.29* (m, 4H, $CH_2^{N2C\text{-bridge}}$), 1.28 - 1.12* (4H, ½ $CH_2^{1C\text{-bridge}}$ and GaCH_2), 1.08 (t, $^3J_{HP}$ = 15.6 and 1.0 Hz, 18H, PCMe_3), 1.00 (dd $^3J_{HP}$ = 15.6 and 2.1 Hz, 18H, PCMe_3).

Minor isomer: δ 6.85 – 6.82 (m, 2H, C_6H_2), 2.94 (s, 2H, NCC*H*), 2.40 (s, 2H, PCC*H*), 2.38 (s, 3H, o-Me^{N}), 2.34 (s, 6H, o-Me^{N}), 2.34 (s, 3H, o-Me^{N}), 2.31 (s, 3H, p-Me^{N}), 2.30 (s, 3H, p-Me^{N}), 1.79 – 1.71* (m, CH_2, 4H, ½ $CH_2^{1C\text{-bridge}}$ and ½ $CH_2^{P2C\text{-bridge}}$), 1.69 – 1.64 (m, 4H, $CH_2^{N2C\text{-bridge}}$), 1.47 (m, 2H, ½ $CH_2^{P2C\text{-bridge}}$) 1.28 – 1.17 (m, 38H, PCMe_3 and ½ $CH_2^{1C\text{-bridge}}$). *overlapping resonances

^{31}C{^{1}H} NMR: δ 181.5 – 181.1 (m, N*C*CH), 145.9 – 145.1 (N*C*$_6$H$_2$), 136.3 – 135.4 (m, *o-C*$_6$H$_2$), 133.0 – 132.7 (m, *p-C*$_6$H$_2$), 129.6 – 128.8 (m, *m-C*$_6$H$_2$), 79.2 – 78.4 (m, P*C*CH), 49.3 (m, *C*H$_2^{\text{1C-bridge}}$), 48.7 – 48.6 (m, *C*H$_2^{\text{1C-bridge}}$), 44.5 (m, NC*C*H), 44.2 – 44.0 (m, NC*C*H and PC*C*H), 36.7 – 36.0 (m, P*C*Me$_3$), 34.4 – 33.9 (m, P*C*Me$_3$), 30.7 (m, PC*Me$_3$*), 30.4 (m, PC*Me$_3$*), 30.2 – 29.5 (m, PC*Me$_3$* and *C*H$_2^{\text{N2C-bridge}}$), 25.6 (m, *C*H$_2^{\text{P2C-bridge}}$), 21.1 (m, *Me*$^{\text{N}}$), 20.5 (m, *Me*$^{\text{N}}$), 20.1 (m, *Me*$^{\text{N}}$), 19.2 (m, *Me*$^{\text{N}}$), 19.1 (m, *Me*$^{\text{N}}$), 19.0 (m, *Me*$^{\text{N}}$), 18.6 (br m, Ga*C*H$_2$), 18.1 (br m, Ga*C*H$_2$), 17.2 (br m, Ga*C*H$_2$).

^{31}P NMR: δ 17.9 (d, J_{PP} = 17.1 Hz, isomer C), 17.7 (s, isomer A or B), 17.6 (d, J_{PP} = 17.1 Hz, isomer C), 17.6 (s, isomer A or B).

Elemental Analysis: Anal. Calc'd for $C_{56}H_{90}Ga_2N_2P_2$ (**7**, *908.58*): C, 66.10; H, 8.65; N, 3.08. Found: C, 66.25; H, 8.95; N, 3.06.

Synthesis of [L$^{\text{Mes/Mes}}$Ga]$_2$(CH$_2$CH$_2$) (7)

Toluene (10 mL) was added to a 100 mL J. Youngs ampoule tube charged with **2** (0.290 g, 0.51 mmol). The resulting red solution was freeze-pump-thaw degassed three times and the atmosphere was replaced by gaseous ethene (1 bar). The solution was stirred at room temperature for 3 hours resulting in the immediate loss of colour. Removal of the volatile components *in vacuo* gave a colourless oily solid which was extracted with pentane (15 mL), filtered and concentrated to 10 mL resulting in the formation of **6** as colourless needles at room temperature. Yield 0.210 g, 71 %.

^{1}H NMR (500 MHz, 298 K, C$_6$D$_6$): δ 6.88 (br s, 2H, PC$_6$*H$_2$*), 6.85 (s, 2H, NC$_6$*H$_2$*), 6.79 (s, 2H, NC$_6$*H$_2$*), 6.66 (s, 4H, PC$_6$*H$_2$*), 6.51 (br s, 2H, PC$_6$*H$_2$*) , 3.02 (s, 2H, NCC*H*), 2.98 (s, 6H, *o-Me*$^{\text{P}}$), 2.74 (s, 12H, *o-Me*$^{\text{N}}$), 2.56 (s, 2H, PCC*H*), 2.22 (s, 6H, *p-Me*$^{\text{N}}$), 2.07 (s, 12H, *o-Me*$^{\text{P}}$), 1.97 (s, 12H, *o-Me*$^{\text{P}}$), 1.73 (d, 2H, ½ C*H$_2$*$^{\text{1C-bridge}}$), 1.40 – 1.34 (m, 7H, *p-Me*$^{\text{P}}$ and C*H$_2$*$^{\text{P2C-bridge}}$), 1.30 (br, 5H, *p-Me*$^{\text{P}}$ and ½ C*H$_2$*$^{\text{N2C-bridge}}$), 1.10 (d, 2H, ½ C*H$_2$*$^{\text{1C-bridge}}$), 0.71 – 0.67 (m, 2H, C*H$_2$*$^{\text{N2C-bridge}}$), 0.38 (m, 2H, GaC*H$_2$*), -0.15 (m, 2H, GaC*H$_2$*).

^{13}C{^{1}H} NMR: δ 178.2 (d, J_{PC} = 30.8 Hz, N*C*CH), 144.5 (d, J_{PC} = 4.0 Hz, *i*-N*C*$_6$H$_2$), 140.8 (br, P*C*$_6$H$_2$), 138.7 (s, P*C*$_6$H$_2$), 137.7 (s, P*C*$_6$H$_2$), 135.9 (s, N*C*$_6$H$_2$), 134.1 (s, N*C*$_6$H$_2$), 133.0 (s, P*C*$_6$H$_2$), 130.7 (br, P*C*$_6$H$_2$), 130.1 (br, N*C*$_6$H$_2$), 129.7 (s, N*C*$_6$H$_2$), 129.6 (s, P*C*$_6$H$_2$), 129.3 (s, *i*-P*C*$_6$H$_2$), 128.9 (d, N*C*$_6$H$_2$), 128.6 (d, N*C*$_6$H$_2$), 81.8 (d, J_{PC} = 46.1 Hz, P*C*CH), 46.6 (s, *C*H$_2^{\text{1C-bridge}}$), 45.6 (s, NC*C*H), 44.5 (d, J_{PC} = 9.9 Hz, PC*C*H), 29.5 (s, *C*H$_2^{\text{N2C-bridge}}$), 27.9 (s, *C*H$_2^{\text{P2C-bridge}}$), 26.2 (s, *o-Me*$^{\text{P}}$), 23.4 (br, *o-Me*$^{\text{P}}$), 22.6* (br, *o-Me*$^{\text{P}}$), 21.6 (s, *o-Me*$^{\text{N}}$), 21.0 (s, *o-Me*$^{\text{P}}$), 20.9 (s, *o-Me*$^{\text{P}}$), 20.8 (s, Ga*C*H$_2$), 19.2 (s, *p-Me*$^{\text{N}}$).

^{31}P NMR: δ -40.0 (s).

Elemental Analysis: Anal. Calc’d for $C_{70}H_{86}Ga_2N_2P_2$ (**8**, *1156.87*): C, 72.68; H, 7.49; N, 2.42. Found: C, 72.74; H, 7.53; N, 2.34.

S1.3 Crystallographic methods

Single crystal X-ray diffraction data for compounds **1** – **7** were collected using MoK$_{\alpha}$ on either a Bruker APEX-II CCD diffractometer, Rigaku Oxford Diffraction Xcalibur diffractometer or Rigaku Oxford Diffraction SuperNova diffractometer. The crystals were maintained at the specified temperature during data collections. All structures were solved with the ShelXT (Sheldrick, 2015) solution program using dual methods and by using Olex2 1.5-beta (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F2.

Compound 1: An orange block-shaped-shaped crystal with dimensions 0.15 × 0.09 × 0.08 mm^3 was mounted on a MITIGEN holder in Paratone oil. Data were collected using a Bruker APEX-II CCD diffractometer equipped with an Oxford Cryosystems Cryostream low-temperature device operating at T = 100.00 K. There is a half molecule of 1 and C_6D_6 in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 0.5. The twinned diffraction pattern was deconvoluted with cell now and SAINT. Twin la [1 0 0 0 -1 0 -0.11767 0 -1] and refined twin scale factor 0.4338(11). Part of the molecule, including the Ga(1) and P(1) sites, was modelled as disordered consistent with peaks in a difference map. Displacement ellipsoid and geometric restraints were used.

Compounds 2 and L$^{\text{Mes/Mes}}$Ga…GaL$^{\text{Mes/Mes}}$: Two distinct sets of crystals were obtained from either a concentrated pentane solution (**4**) or toluene solution (**L$^{\text{Mes/Mes}}$Ga…GaL$^{\text{Mes/Mes}}$**).

2: A single clear yellow block-shaped crystal with dimensions 0.23 x 0.18 x 0.12 mm^3 was mounted on a MITIGEN holder in Paratone oil. Data were collected using a Rigaku Oxford Diffraction Xcalibur diffractometer equipped with an Oxford Cryosystems Cryostream 700+ low-temperature device operating at T = 120.00 K. There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

L$^{\text{Mes/Mes}}$Ga…GaL$^{\text{Mes/Mes}}$: A single clear red needle-shaped crystal with dimensions 0.52 x 0.09 x 0.07 mm^3 was mounted on a MITIGEN holder in Paratone oil. Data were collected using a Rigaku Oxford Diffraction Xcalibur diffractometer equipped with an Oxford Cryosystems Cryostream 700+ low-temperature device operating at T = 120.00 K. There is a single molecule of **L$^{\text{Mes/Mes}}$Ga…GaL$^{\text{Mes/Mes}}$** and a single molecule of toluene in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1. A single molecule of toluene is incorporated into the unit cell which was modelled as disordered over two sites, consistent with peaks in a Fourier map. The fragment database in Olex2 was used to generate the model for both disorder components.

Compound 3: A single pale yellow block-shaped crystal with dimensions 0.32 x 0.20 x 0.07 mm^3 was mounted on a MITIGEN holder in Paratone oil. Data were collected using a Rigaku Oxford Diffraction SuperNova Dual, Cu at home/near, Altlas diffractometer equipped with an Oxford Cryosystems Cryostream 700+ low-temperature device operating at T = 120.01 K. There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 8 and Z' is 1.

Compound 4: A single clear colourless block-shaped crystal with dimensions 0.28 x 0.22 x 0.13 mm^3 was mounted on a MITIGEN holder in Paratone oil. Data were collected using a Rigaku Oxford Diffraction Xcalibur diffractometer equipped with an Oxford Cryosystems Cryostream 700+ low-temperature device operating at T = 120.01 K. There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1. Disorder in the norbornene backbone was modelled based on peaks in a difference map and refined using distance similarity and displacement ellipsoid similarity restraints.

Compound 5: A clear light green needle-shaped-shaped crystal with dimensions 0.18 × 0.03 × 0.02 mm^3 was mounted on a mitegen tip in Paratone oil.. Data were collected using a XtaLAB Synergy R, HyPix-Arc 100 diffractometer equipped with an Oxford Cryosystems Cryostream 1000 low-temperature device operating at T = 100.00(10) K.

Data were measured using w scans with Cu K_a radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro 1.171.43.143a (Rigaku OD, 2024). The maximum resolution that was achieved was $Q = 50.432^{\circ}$ (1.00 Å).

The unit cell was refined using CrysAlisPro 1.171.43.143a (Rigaku OD, 2024) on 2694 reflections, 16% of the observed reflections.

Compound 6: A single clear colourless block-shaped crystal with dimensions 0.31 × 0.22 × 0.16mm^3 was mounted on a MITIGEN holder in Paratone oil. Data were collected using a Rigaku Oxford Diffraction Xcalibur diffractometer equipped with an Oxford Cryosystems Cryostream 700+ low-temperature device operating at T = 120.01 K. There is a single molecule of **5** and a single molecule of C_6D_6 in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1. Refined as a 2-component inversion twin. The Flack parameter was refined to 0.490(12). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in None.

Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

Compound 7: A single clear colourless rod-shaped crystal with dimensions 0.05 x 0.30 x 0.0 mm^3 was mounted on a MITIGEN holder in Paratone oil. Data were collected using a Rigaku Oxford Diffraction Xcalibur diffractometer equipped with an Oxford Cryosystems Cryostream 700+ low-temperature device operating at T = 120.01 K. There is a single molecule of **6** in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1. Four large residual Q-peaks (4.0, 3.2, 2.0 and 1.5) were assumed to correspond to disordered Ga and P atoms which were unable to be modelled to provide a sensible structure. Refined as a 2-component inversion twin. The Flack parameter was refined to 0.47(2). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 0.484(10).

Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

Table S1. Crystallographic parameters for compounds **1 – 7** and **L$^{\mathbf{Mes/Mes}}$Ga…GaL$^{\mathbf{Mes/Mes}}$**.

Compound	1	**2**	**$L^{Mes/Mes}$Ga…Ga$L^{Mes/Mes}$**	3	**4**	**6**	**7**
Formula	$C_{54}H_{74}D_6Ga_2N_2P_2$	$C_{34}H_{41}GaNP$	$C_{75}H_{90}Ga_2N_2P_2$	$C_{45}H_{40}BF_{15}GaNP$	$C_{52}H_{41}BF_{15}GaNP$	$C_{56}H_{78}D_6Ga_2N_2P_2$	$C_{70}H_{86}N_2P_2Ga_2$
$D_{calc.}$/ g cm^{-3}	1.247	1.257	1.247	1.558	1.551	1.245	1.269
□/mm^{-1}	1.146	0.999	0.922	0.790	0.732	1.114	1.906
Formula Weight	964.61	564.37	1220.86	991.28	1076.36	992.66	1156.78
Colour	orange	clear yellow	clear red	pale yellow	clear colourless	colourless	colourless
Shape	block-shaped	block-shaped	needle-shaped	block-shaped	block-shaped	block-shaped	rod-shaped
Size/mm^3	0.15×0.09×0.08	0.23×0.18×0.12	0.52×0.09×0.07	0.32×0.20×0.07	0.28×0.22×0.13	0.31×0.22×0.16	0.30×0.05×0.04
***T*/K**	100.00	120.00(10)	120.00(10)	120.01(10)	120.01(11)	120.01(10)	100.01(10)
Crystal System	monoclinic	triclinic	triclinic	orthorhombic	monoclinic	orthorhombic	orthorhombic
Space Group	$P2_1/n$	P-1	P-1	$Pbca$	$P2_1/c$	$Pna2_1$	$Pca2_1$
***a*/Å**	13.2842(7)	9.8258(3)	12.0391(3)	15.4213(2)	14.3929(5)	28.6854(12)	14.02530(10)
***b*/Å**	14.0429(7)	10.6897(4)	12.1205(3)	17.2470(3)	14.7735(5)	8.5990(3)	16.50370(10)
***c*/Å**	13.7970(7)	15.1671(6)	22.5729(6)	31.7812(5)	21.6915(6)	21.4708(10)	26.14870(10)
***α*/°**	90	80.922(3)	91.413(2)	90	90	90	90
***β*/°**	93.272(2)	76.755(3)	96.822(2)	90	92.238(3)	90	90
***γ*/°**	90	75.256(3)	96.004(2)	90	90	90	90
V/Å^3	2569.6(2)	1491.24(10)	3250.28(14)	8452.9(2)	4608.8(3)	5296.1(4)	6052.62(6)
Z	2	2	2	8	4	4	4
Z'	0.5	1	1	1	1	1	1
Wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	1.54184
Radiation type	MoK□	Mo K_a	Mo K_a	Mo K_a	Mo K_a	Mo K_a	Cu K_a
Q_{min}/°	2.192	3.233	3.383	3.320	3.256	3.325	3.380
Q_{max}/°	26.461	29.303	26.371	27.484	29.270	30.568	76.012
Measured Refl's.	119020	32783	53072	119571	42048	29105	126586
Indep't Refl's	8531	7290	13265	9662	10782	8872	11105
Refl's I≥2σ(I)	7584	6256	10443	7971	8101	7592	10449
R_{int}	0.0550	0.0406	0.0565	0.0717	0.0469	0.0577	0.0791

Parameters	424	343	805	614	698	652	703
Restraints	98	0	272	66	83	100	1
Largest Peak	0.339	0.413	0.611	0.545	0.713	0.579	4.008
Deepest Hole	-0.388	-0.335	-0.540	-0.359	-0.584	-0.576	-0.850
GooF	1.171	0.929	1.043	1.074	1.043	1.081	1.038
wR_2 (all data)	0.1164	0.1278	0.1089	0.0936	0.0978	0.0828	0.1722
wR_2	0.1116	0.1193	0.1008	0.0877	0.0882	0.0763	0.1673
R_1 (all data)	0.0630	0.0492	0.0690	0.0526	0.0780	0.0588	0.0705
R_1	0.0528	0.0391	0.0485	0.0396	0.0504	0.0446	0.0673
Flack Parameter						0.490(12)	0.47(2)
Hooft Parameter							0.484(10)

Compound	**5**
Formula	$C_{108}H_{84}B_2F_{42}Ga_2N_2P_2$
***$D_{calc.}$*/ g cm^{-3}**	1.546
***m*/mm^{-1}**	2.039
Formula Weight	2430.77
Colour	clear light green
Shape	needle-shaped
Size/mm^3	0.18×0.03×0.02
***T*/K**	100.00(10)
Crystal System	monoclinic
Space Group	$P2_1/c$
***a*/Å**	13.8266(9)
***b*/Å**	24.9376(12)
***c*/Å**	16.2676(7)
***a*/°**	90
***b*/°**	111.413(6)
***g*/°**	90
V/Å^3	5221.9(5)
Z	2
Z'	0.5
Wavelength/Å	1.54184
Radiation type	Cu K_a
Q_{min}/°	3.414
Q_{max}/°	50.432
Measured Refl's.	17135
Indep't Refl's	5425
Refl's I≥2 *s*(I)	3570
R_{int}	0.1052
Parameters	785
Restraints	331
Largest Peak	0.764
Deepest Hole	-0.474
GooF	1.051
wR_2 (all data)	0.2159
wR_2	0.1922
R_1 (all data)	0.1186
R_1	0.0754

S1.4 Computational methods

Electronic structure calculations were performed using the Gaussian 16 program package.[4] Calculations were performed at the BP86/Def2SVP level. Structures were optimized using crystal structures as starting points where available. Comparison of the metric parameters for **1** indicates that optimization at the BP86-D3/Def2SVP level gives excellent agreement with their experimentally determined geometries (Table S2). The electronic structure analysis of **1** has been performed on isomer **1B** which is the major component in the crystal structure. Single point energy calculations were performed on the optimized geometries at the BP86-D3/Def2SVP level of theory. Frequency calculations were performed at the same level of theory to confirm the nature of optimized stationary points, with true minima and transition states revealing no or exactly one imaginary eigenmode, respectively. The connectivity of transition states was further established by small displacement of the imaginary mode (corresponding to the reaction coordinate) in forward and backward direction. In dimeric structures **1**, **$L^{Mes/Mes}$Ga…GaL$^{Mes/Mes}$** and [**2**]$_2$, Ga-Ga bond dissociation energies were calculated both with and without Grimme's dispersion correction (Empirical Dispersion = D3) and the basis-set superposition error (BSSE) was corrected with the counterpoise method by Boys and Simon.[5] Natural Bond Orbital (NBO) analysis was performed on the optimized structures using the NBO6.0 program at the BP86/Def2SVP level of theory. Time-dependent (TD-)DFT calculations were carried out at the SMD-BP86-D3/Def2SVP level of theory, employing toluene as the solvent (ε = 2.3741).

Images were rendered using Chemcraft 1.8.

Optimized geometries for **1**, **1^M, 2, $L^{Mes/Mes}$Ga…GaL$^{Mes/Mes}$**, [**2**]$_2$, [Me_2NGaMe_3]$_2$ and **5** are supplied as .xyz files.

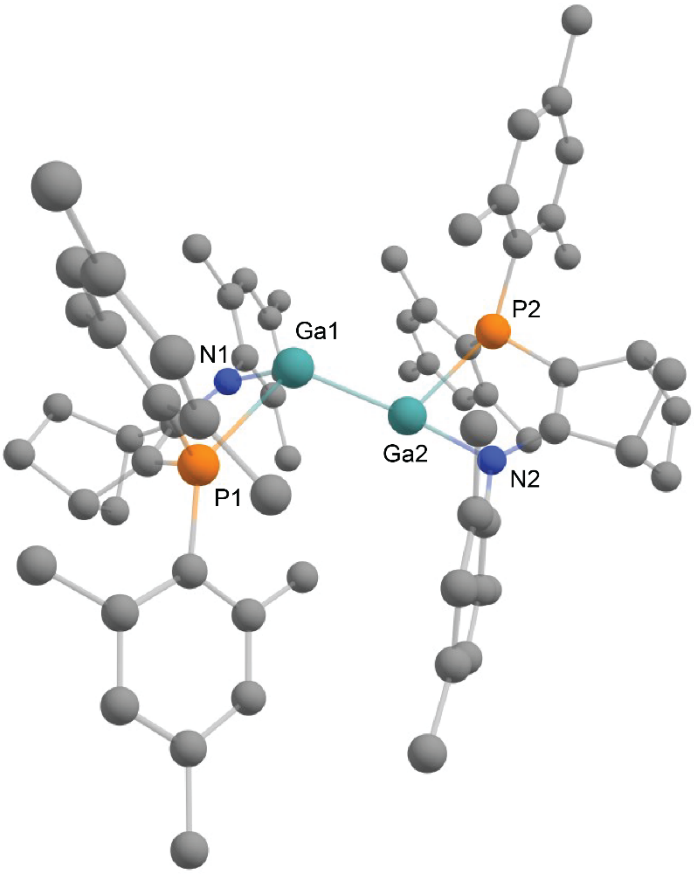


Figure S1. Computationally identified dimeric structure [**2**]$_2$.

Table S2. Comparison of experimental and computational metric parameters of **1B** using different basis-set and functionals.

Basis-set / Functional	**X-ray structure**	**BP86-D3/Def2SVP**	**BP86/ Def2SVP (no disp)**	**M062X-D3/Def2SVP**	**M062X / Def2SVP (no dispersion)**	**M062X-D3/ 6-31G**	**wB97XD-D3/ Def2SVP**
Ga-Ga / Å	2.4796(12), 2.468(3)	2.483	2.604	2.560	2.564	2.587	2.502
Ga-P / Å	2.513(6), 2.472(16)	2.529	2.606	2.573	2.576	2.582	2.524
Ga-N / Å	2.002(3), 2.096(3)	2.035	2.057	2.012	2.012	2.016	2.005
P-Ga-N / °	82.7(2), 82.8(4)	82.9	82.3	81.7	81.7	81.2	82.6
Θ / °	55.6	58.28	53.72	57.05	56.90	58.25	56.56

Table S3. Differences between diastereoisomers of **1** at BP86/Def2SVP-D3

	X-ray structure (B)	**1A**	**1B**	**1C**	**1D**	**1E**	**1F**
Ga-Ga / Å	2.4796(12), 2.468(3)	2.482	2.483	2.485	2.483	2.501	2.484
Ga-P / Å	2.513(6), 2.472(16)	2.534	2.529	2.540	2.549	2.558	2.544
Ga-N / Å	2.002(3), 2.096(3)	2.029	2.035	2.032	2.031	2.031	2.035
P-Ga-N / °	82.7(2), 82.8(4)	82.3	82.9	83.1	82.8	82.6	82.7
ΔE	—	+2.2	0	-2.1	14.5	4.5	14.6

Table S4. Summary of experimentally and computationally determined bond parameters for **1** / **1**^{M} and **2** / **L**$^{Mes/Mes}$**Ga…GaL**$^{Mes/Mes}$ / [**2**]$_2$.

Bond	**1 (XRD)**	**1**	**1**^{M}	**L**$^{Mes/Mes}$**Ga…GaL**$^{Mes/Mes}$ **(XRD)**	**2 (XRD)**	**L**$^{Mes/Mes}$**Ga…GaL**$^{Mes/Mes}$	[**2**]$_2$	**2**
Ga-Ga / Å	2.4796(12), 2.468(3)	2.483	—	2.8565(6)	—	3.119	2.612	—
Ga-P / Å	2.513(6), 2.472(16)	2.529	2.718	2.7283(8) 2.6491(8)	2.709(1)	2.764, 2.762	2.585	2.734
Ga-N / Å	2.002(3), 2.096(3)	2.035	2.070	2.040(2) 1.994(2)	1.962(2)	2.138, 2.085	2.054	2.074
P-Ga-N / °	82.7(2), 82.8(4)	82.9	77.9	78.4(1) 80.2(7)	78.9(1)	77.5, 77.6	82.2	78.1
Θ / °	55.6	58.28	—	78.37 / 30.79	—	87.8 / 43.1	60.9 / 48.63	—
T / °	0	0	—	81.9	—	72.5	30.8	—

Table S5. Ga-Ga bond dissociation energies for **1**, **$L^{Mes/Mes}$Ga…GaL$^{Mes/Mes}$** and [**2**]$_2$ with and without counterpoise correction for basis-set superposition error (BSSE), in kcal mol^{-1}.

	1B	**1B***	**$L^{Mes/Mes}$Ga… GaL$^{Mes/Mes}$**	**$L^{Mes/Mes}$Ga… GaL$^{Mes/Mes}$ ***	[**2**]$_2$	[**2**]$_2$ *
BDE / kcal mol^{-1} (Uncorrected)	-42.1	-14.9	-38.9	-5.5	-34.2	-8.2
BDE / kcal mol- (BSSE-corrected)	-37.5	-10.3	-33.2	-3.1	-29.3	-5.7
BSSE / kcal mol^{-1}	4.6	4.5	5.8	2.4	4.9	2.5

* = without D3 dispersion correction

Table S6. Bond enthalpies, free energies and BSSE correction in hartrees for **1B**, **$L^{Mes/Mes}$Ga…GaL$^{Mes/Mes}$** and [**2**]$_2$, and their monomers, with and without dispersion correction.

	1B	**1B***	**$L^{Mes/Mes}$Ga…GaL$^{Mes/Mes}$**
Enthalpy	-6513.171898	-6513.171898	-7279.434506
Free energy	-6513.337283	-6513.337283	-7279.636254
BSSE correction	0.007415082498	0.007415082600	0.009156837128
Enthalpy (monomer)	-3256.558386	-3256.558386	-3639.689902
Free energy (monomer)	-3256.653886	-3256.653886	-3639.806546
	$L^{Mes/Mes}$Ga…GaL$^{Mes/Mes}$ (no dispersion)	[**2**]$_2$	[**2**]$_2$ *
Enthalpy	-7279.434506	-7279.416463	-7279.416463
Free energy	-7279.636254	-7279.619390	-7279.619390
BSSE correction	0.003813216103	0.008220942	0.004057164288
Enthalpy (monomer)	-3639.689902	-3639.689902	-3639.689902
Free energy (monomer)	-3639.806546	-3639.806546	-3639.806546

* = without D3 dispersion correction

Table S7. Calculated ΔH and ΔG for the dissociation process RLGa=GaLR → 2 RLGa: for **1**, **2** and the model system $[Me_2NGaPMe_3]_2$ in which the Ga-Ga bond distance is fixed at the experimentally-determined distance for compounds **1** and **2**.

(model) compound	**ΔH / kcal mol^{-1}**	**ΔG / kcal mol^{-1}**
1	30.06	13.92
2	17.92	-1.21
$[Me_2NGaPMe_3]_2$ ($d_{Ga\text{-}Ga}$ = **1**)	13.71	0.76
$[Me_2NGaPMe_3]_2$ ($d_{Ga\text{-}Ga}$ = **2**)	14.67	1.98

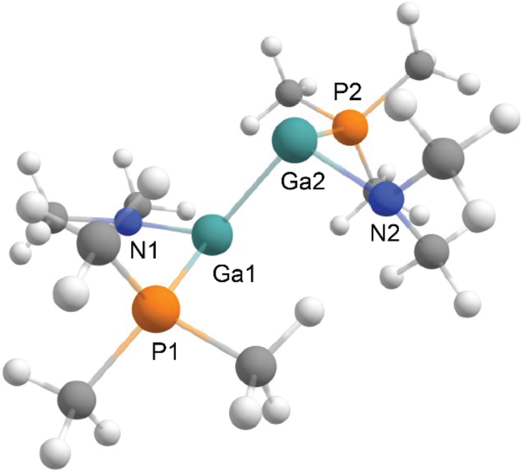


Figure S2. Optimized structure of the minimal model $[Me_2NGaMe_3]_2$ showing trans-bent geometry (bond length fixed 2.483 Å).

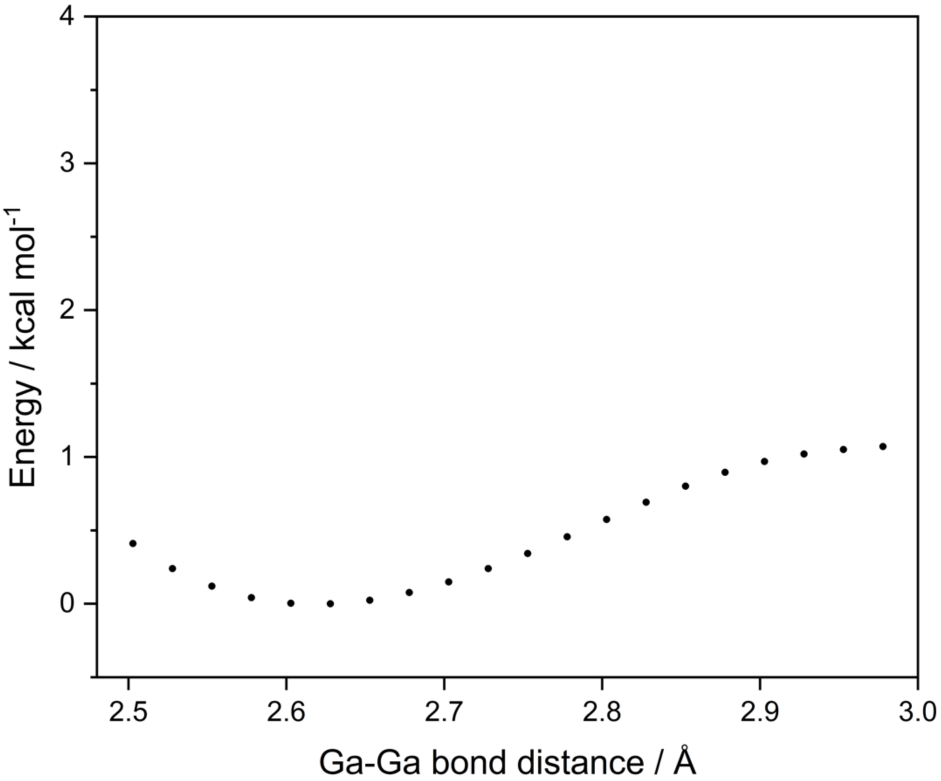


Figure S3. Plot of the relaxed potential energy surface scan as the Ga-Ga bond distance is varied in the minimal model $[Me_2NGaPMe_3]_2$.

Table S8. Results from time-dependent DFT (TD-DFT) calculations

	Wavelength [nm]	**MO contributions**	**F (oscillator strength)**
1	586.55	HOMO-2 → LUMO HOMO → LUMO	0.2266
	501.99	HOMO-2 → LUMO HOMO → LUMO HOMO → LUMO+1	0.1331
$L^{Mes/Mes}$Ga…Ga$L^{Mes/Mes}$	618.94	HOMO → LUMO HOMO → LUMO+1	0.0578
	580.34	HOMO → LUMO+1	0.0112
	519.46	HOMO-1 → LUMO HOMO → LUMO+2	0.0666
[**2**]$_2$	643.95	HOMO-1 → LUMO HOMO → LUMO	0.0136
	593.09	HOMO-2→LUMO HOMO→LUMO	0.0390
	569.00	HOMO-2→LUMO HOMO-1→LUMO HOMO→LUMO	0.2092

S1.5 Frontier molecular orbitals of 1 and [2]$_2$

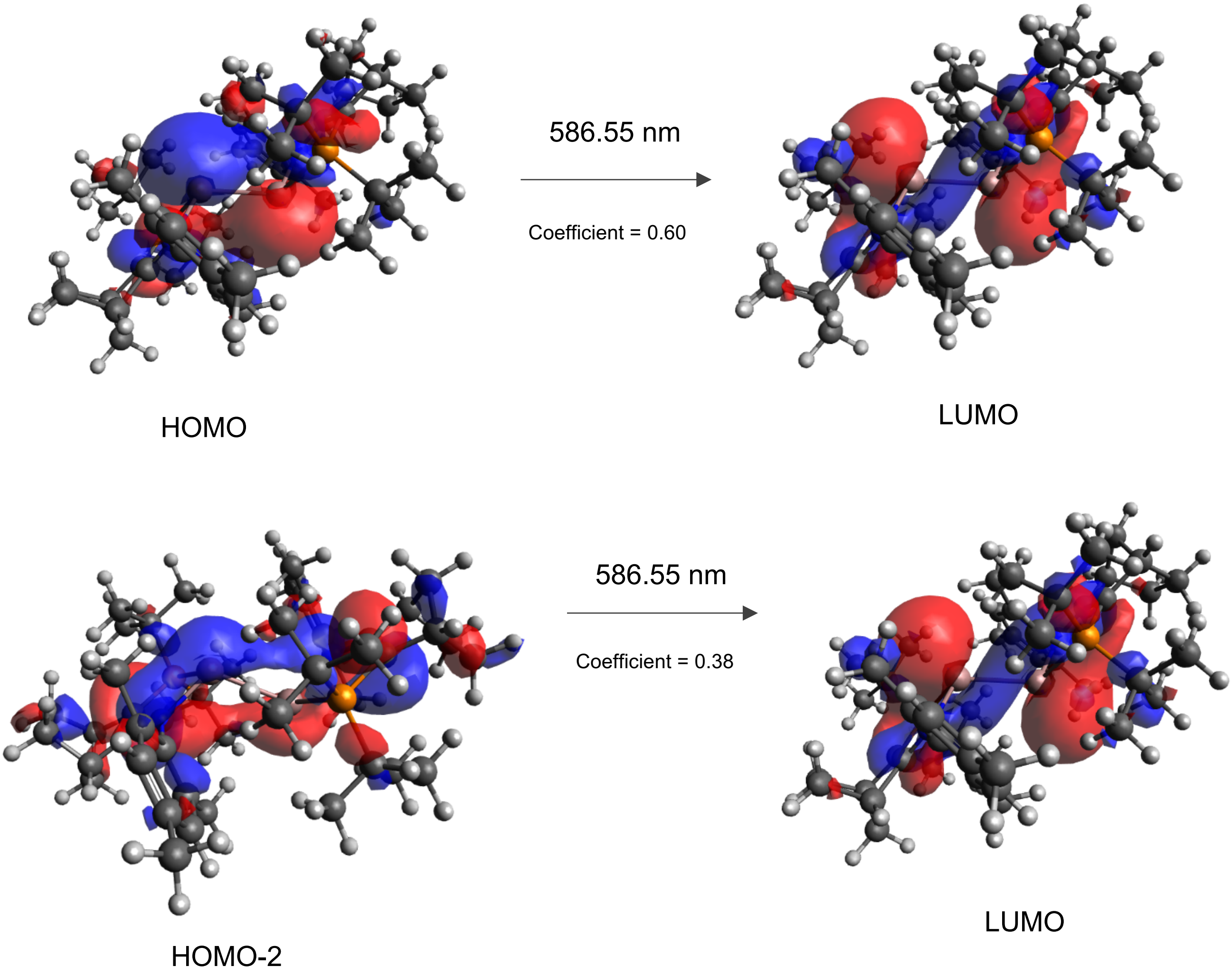


Figure S4a. Frontier molecular orbitals of **1** showing the dominant transition.

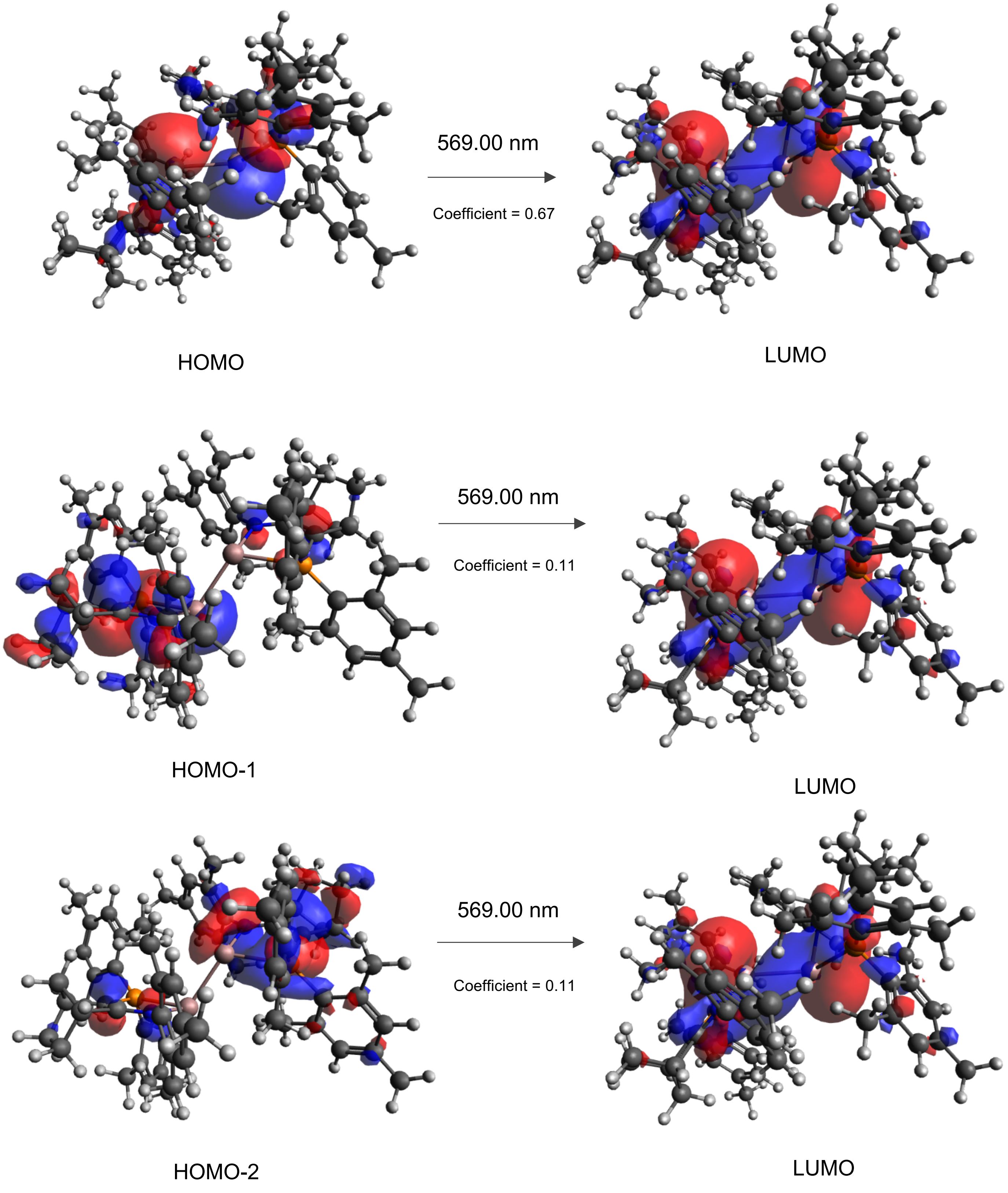


Figure S4b. Frontier molecular orbitals of [**2**]$_2$ showing the dominant transition.

S1.6 Spectral data

1.6.1 NMR spectra

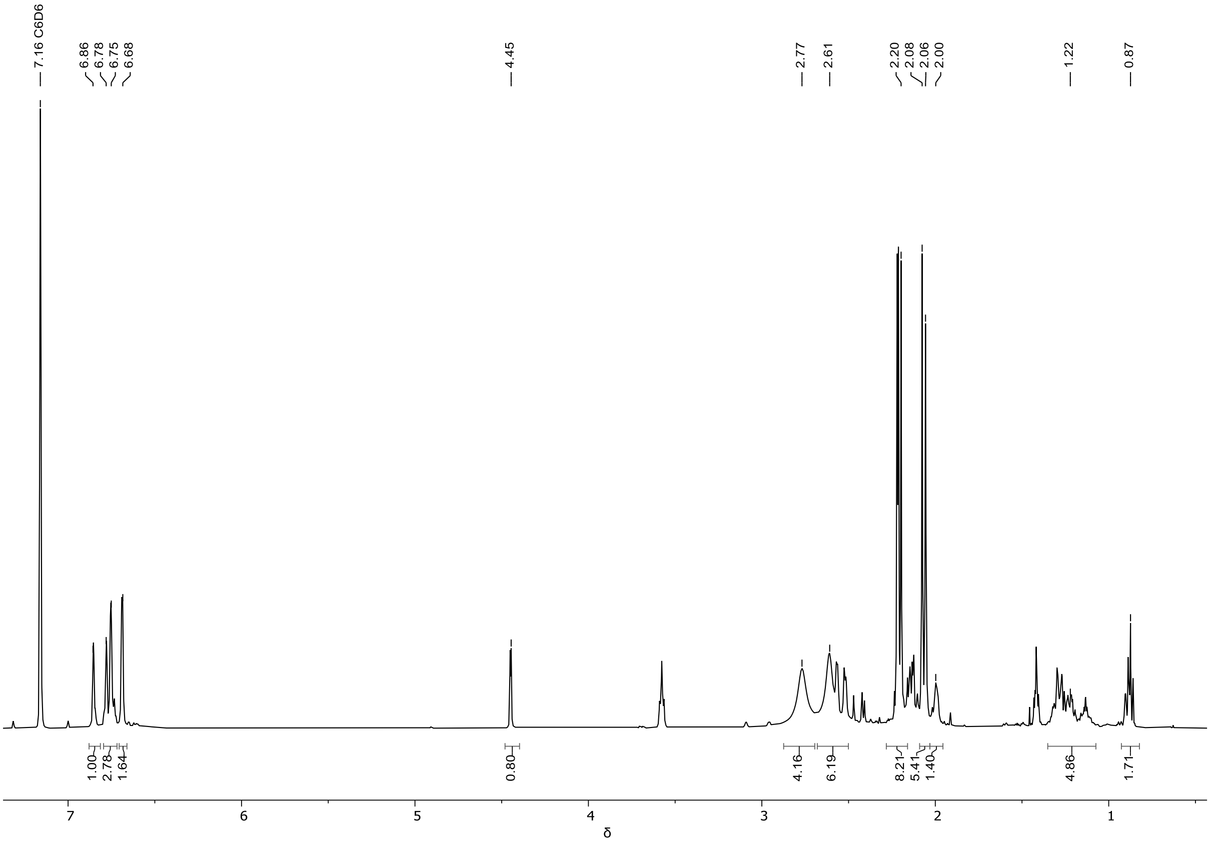


Figure S5. ^{1}H NMR spectrum of HL$^{Mes/Mes}$.

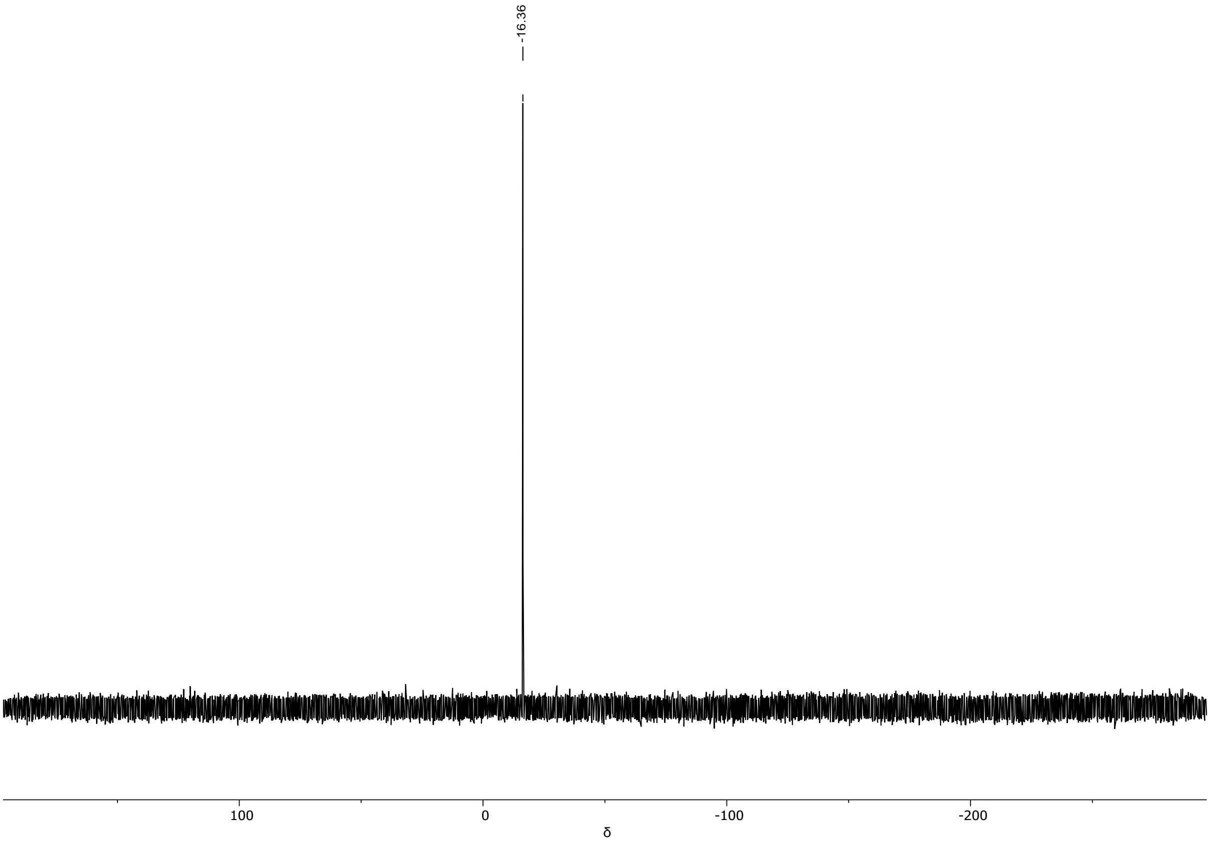


Figure S6. $^{31}P\{^1H\}$ NMR spectrum of $HL^{Mes/Mes}$.

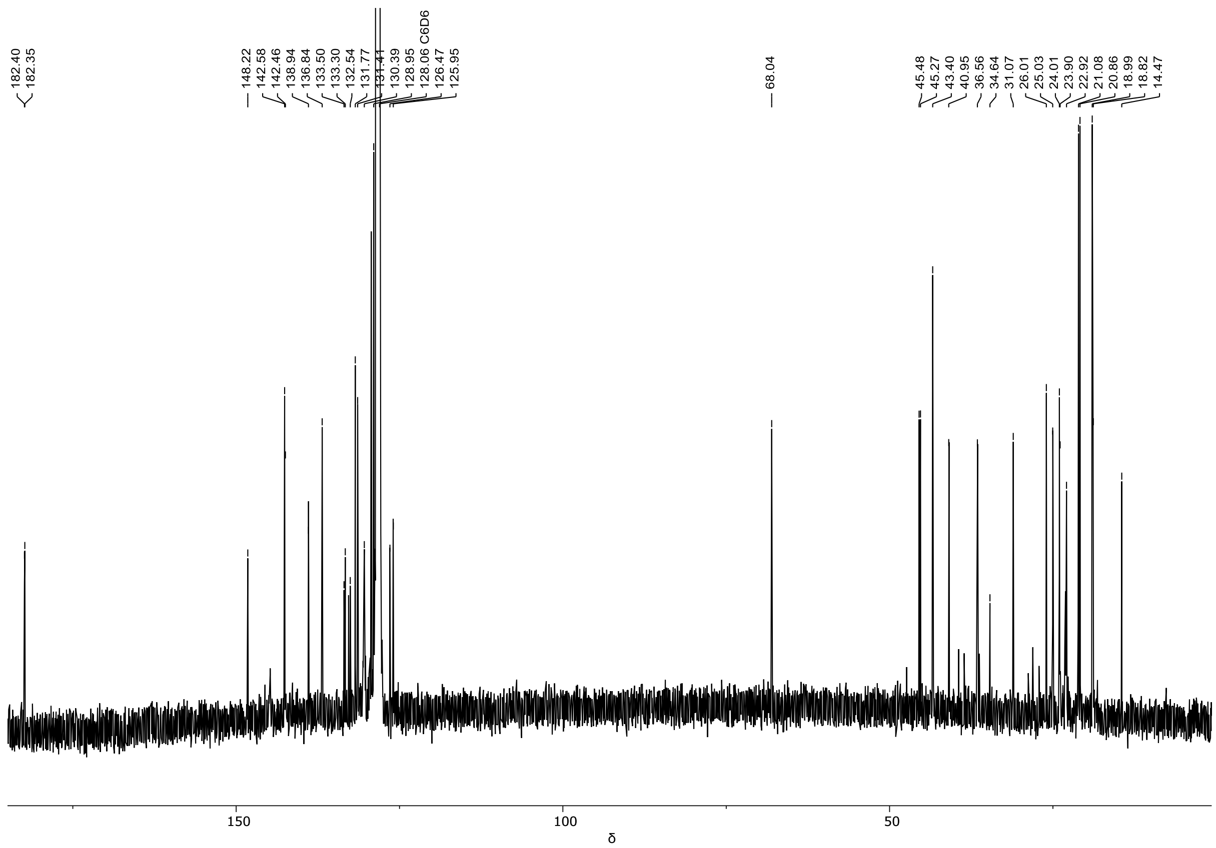


Figure S7. $^{13}C\{^1H\}$ NMR spectrum of $HL^{Mes/Mes}H$.

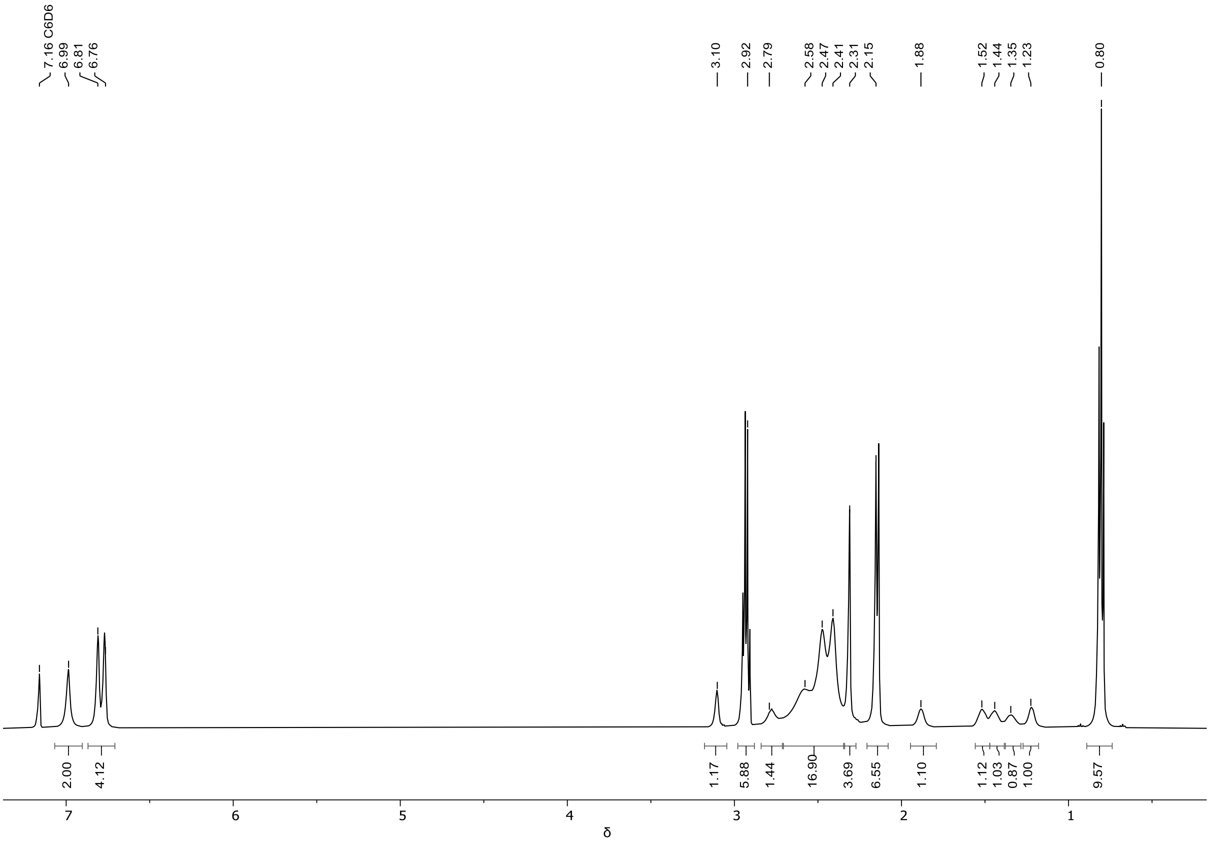


Figure S8. ^{1}H NMR spectrum of L$^{Mes/Mes}$ Li(OEt$_2$).

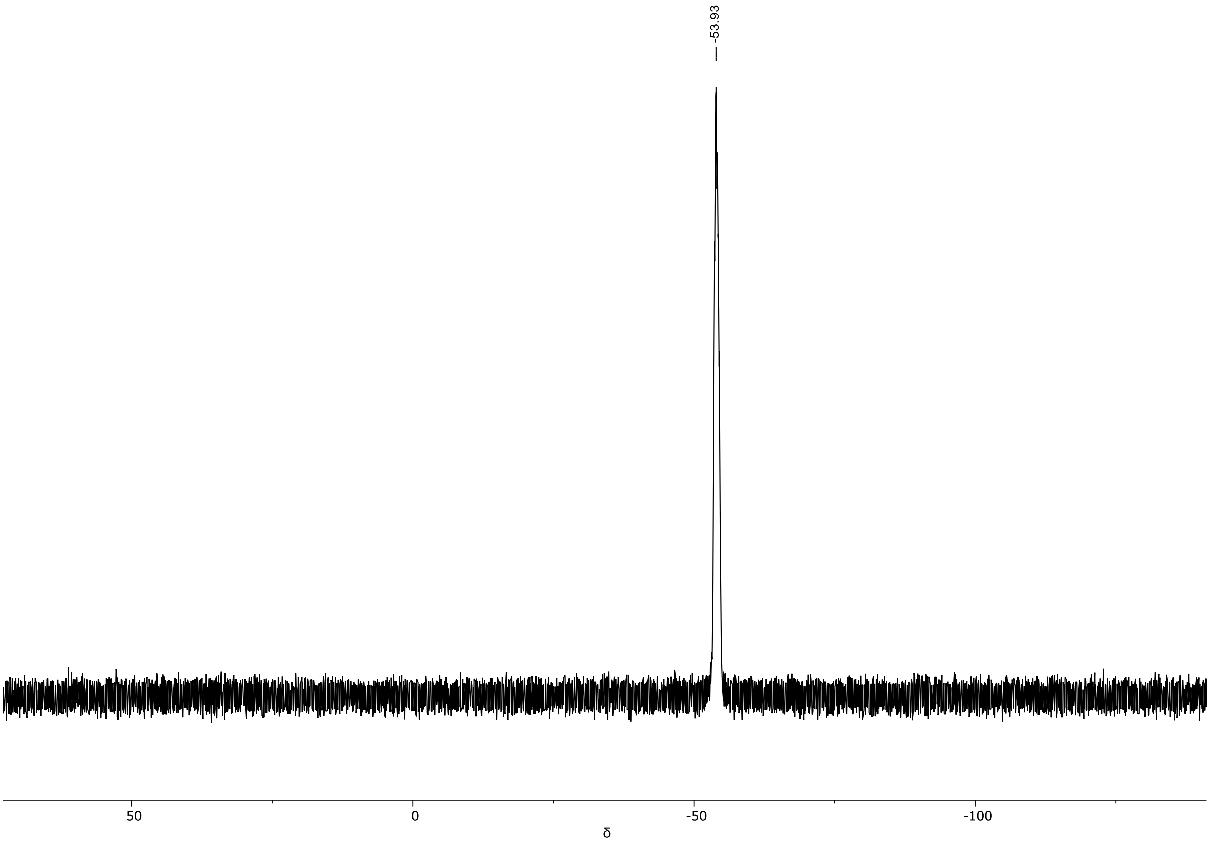


Figure S9. ^{31}P{^{1}H} NMR spectrum of L$^{Mes/Mes}$ Li(OEt$_2$).

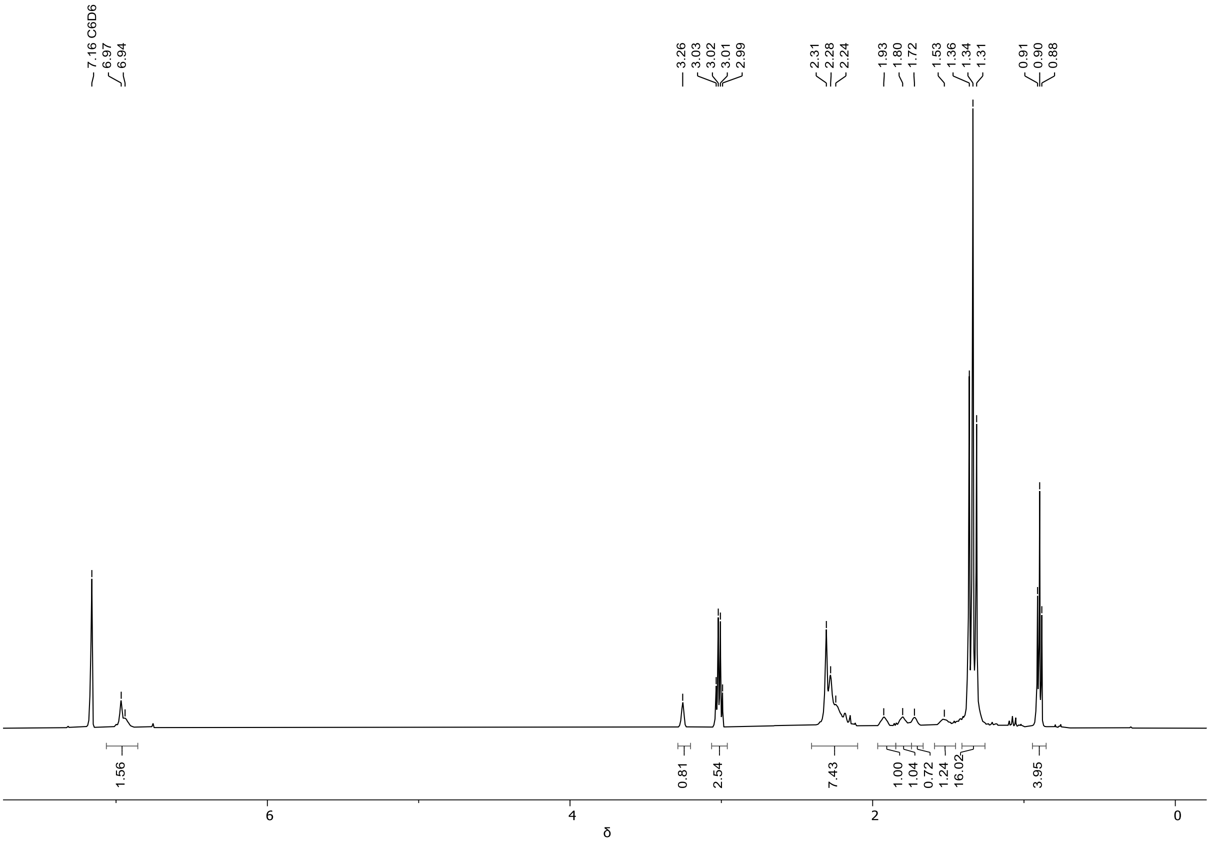


Figure S10. ^{1}H NMR spectrum of $L^{Mes/tBu}Li(OEt_2)$.

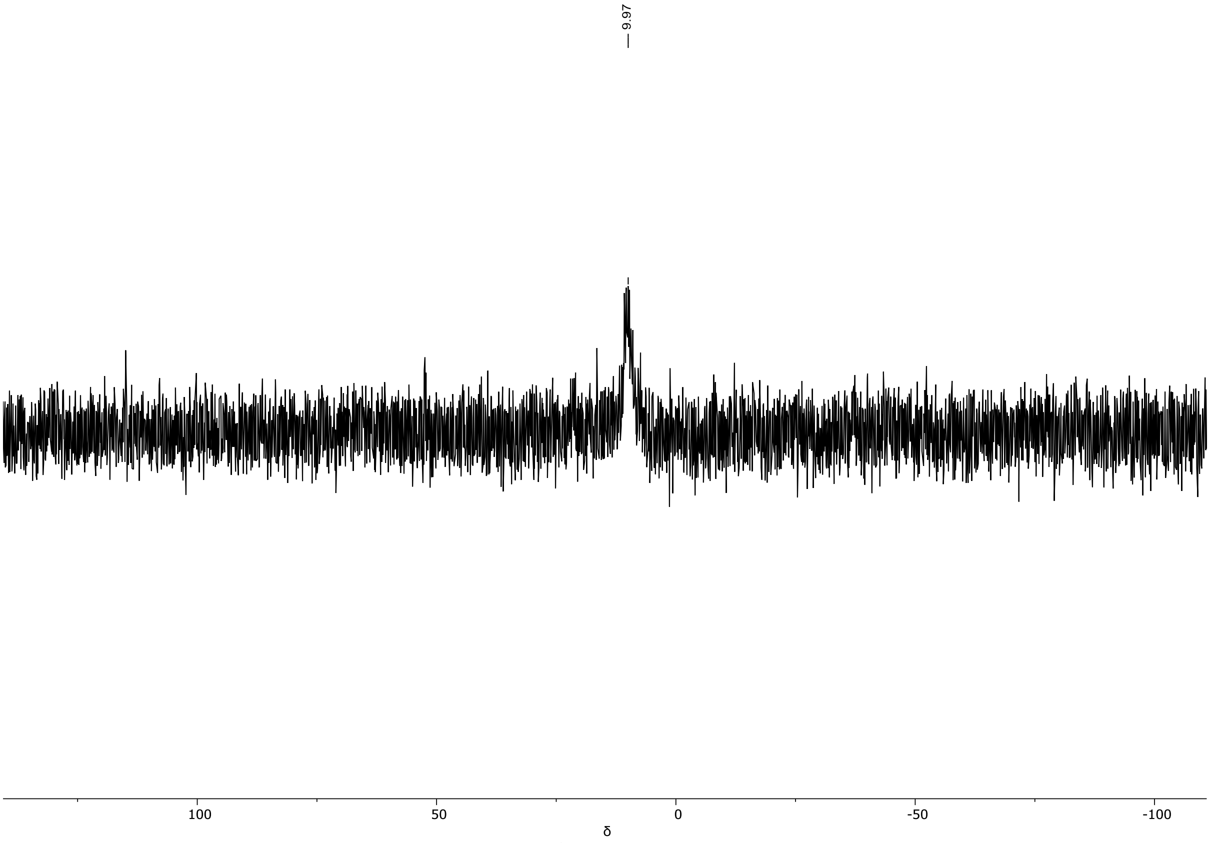


Figure S11. $^{31}P\{^1H\}$ NMR spectrum of $L^{Mes/tBu}Li(OEt_2)$

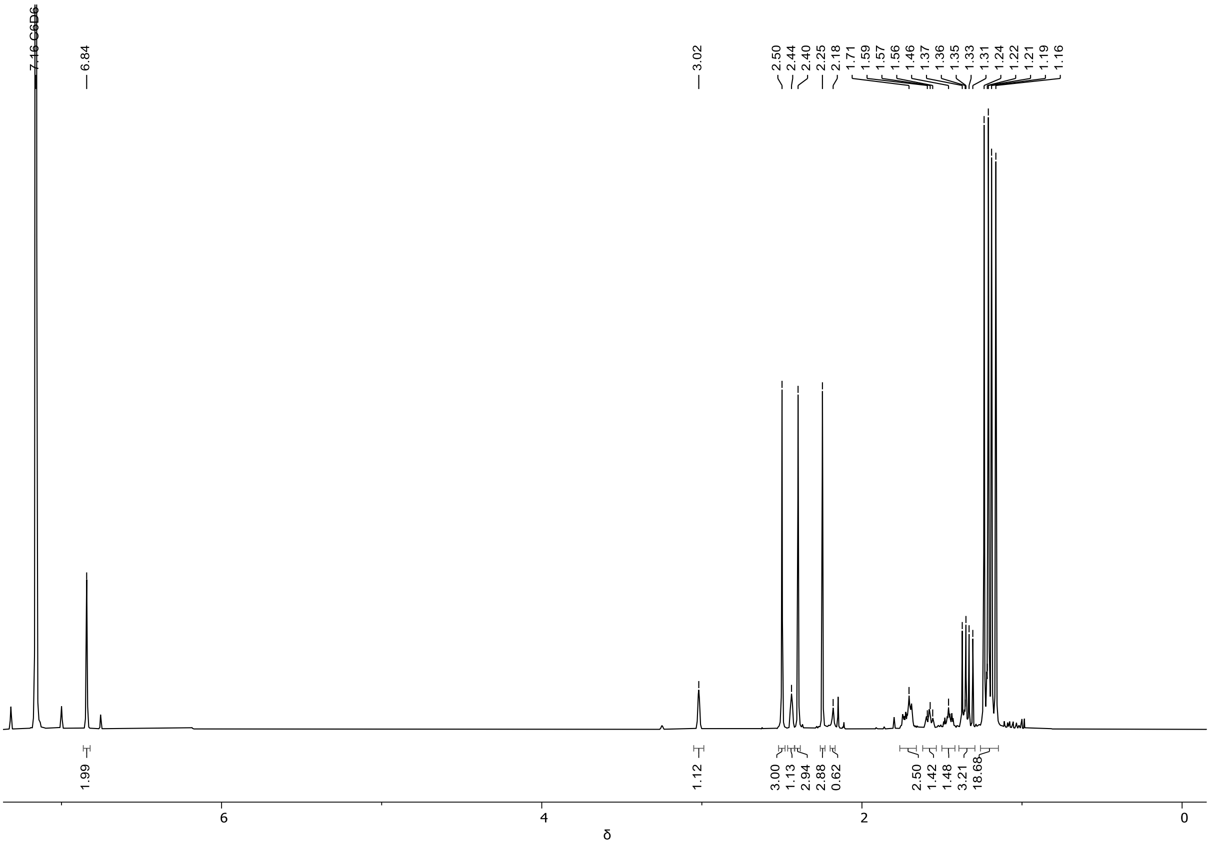


Figure S12. ^{1}H NMR spectrum of **1**.

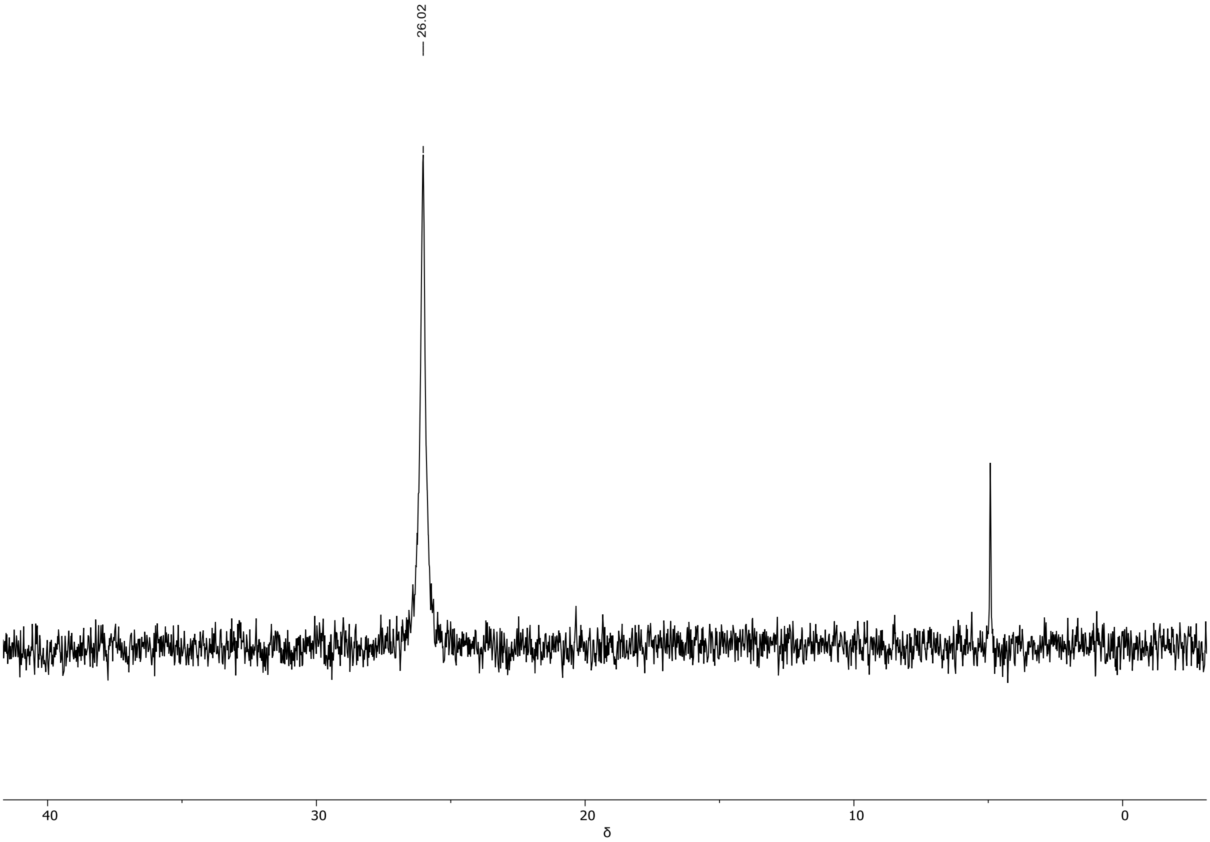


Figure S13. ^{31}P{^{1}H} NMR spectrum of **1**. (Peak at 4.90 ppm is a known impurity.)

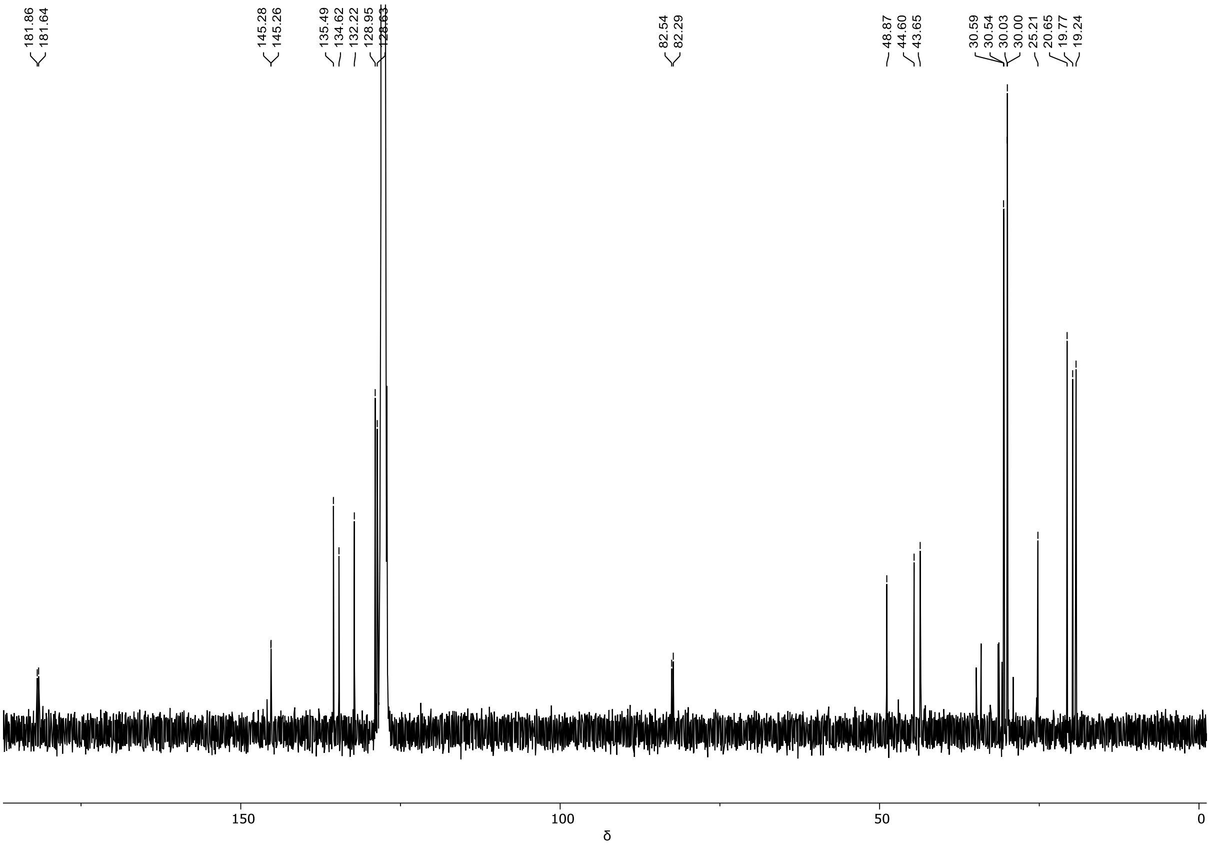


Figure S14. $^{13}C\{^1H\}$ NMR spectrum of **1**.

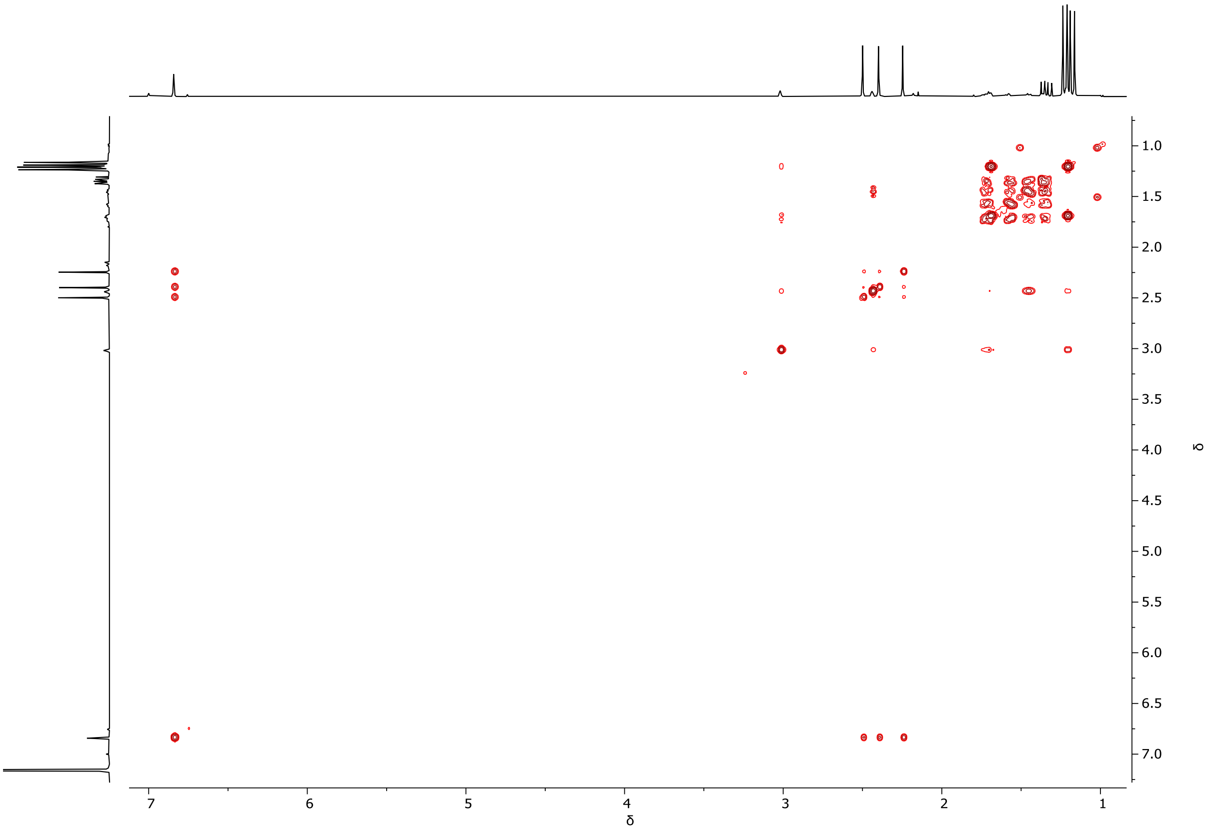


Figure S15. COSY NMR spectrum of **1**.

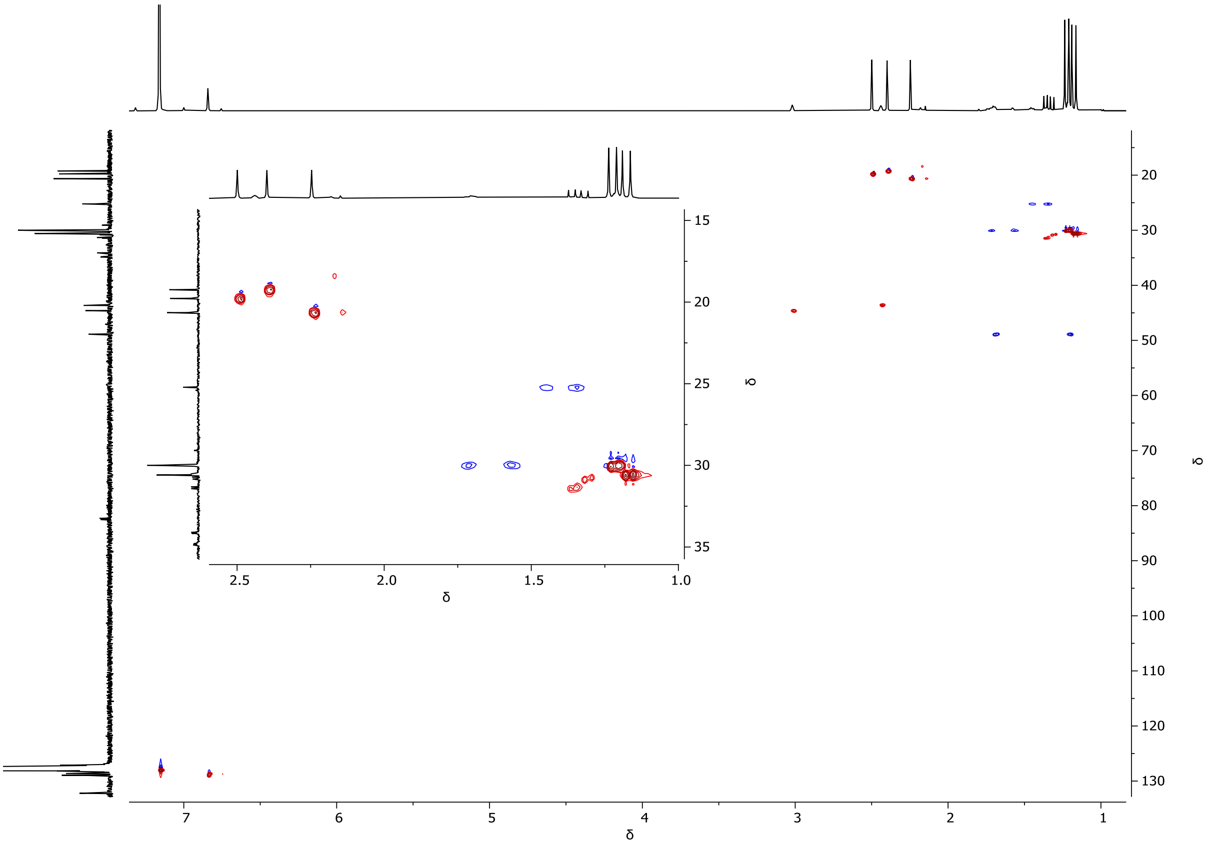


Figure S16. HSQC NMR spectrum of **1**.

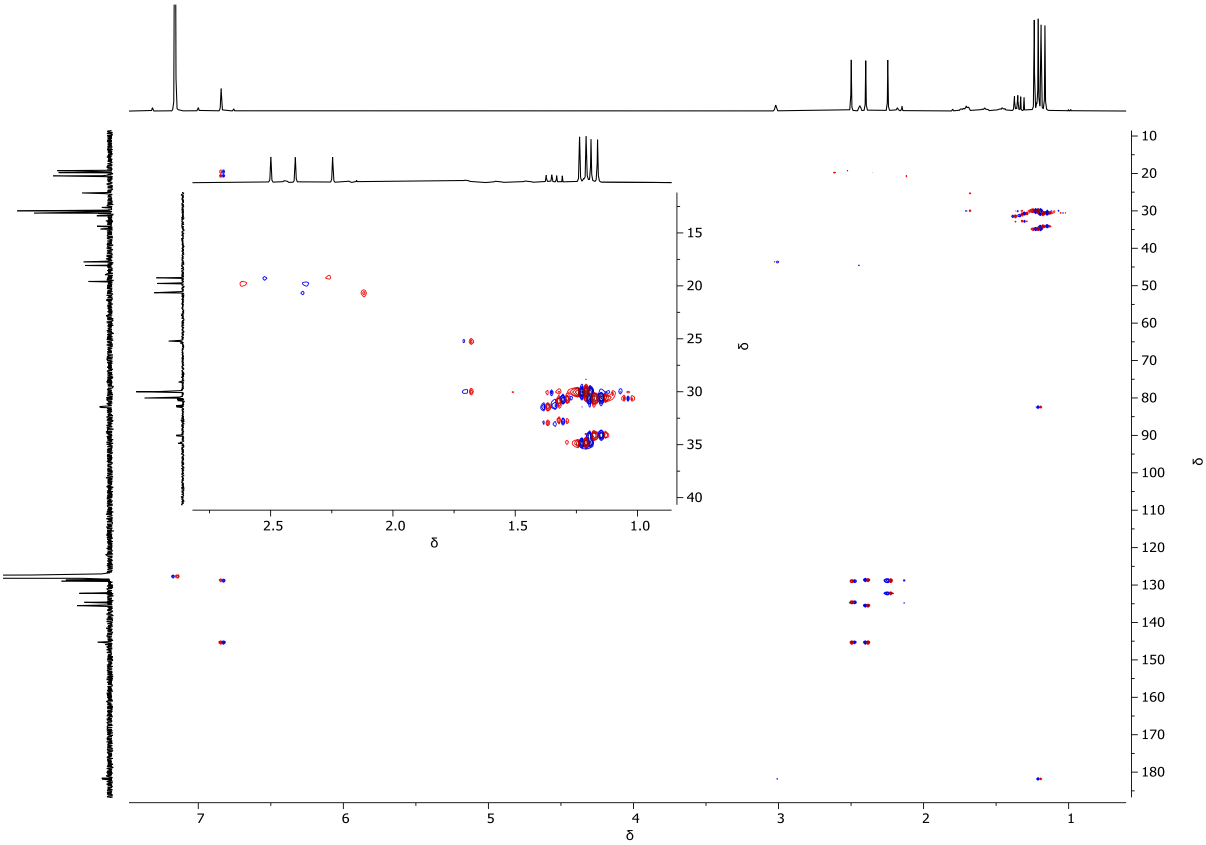


Figure S17. HMBC NMR spectrum of **1**.

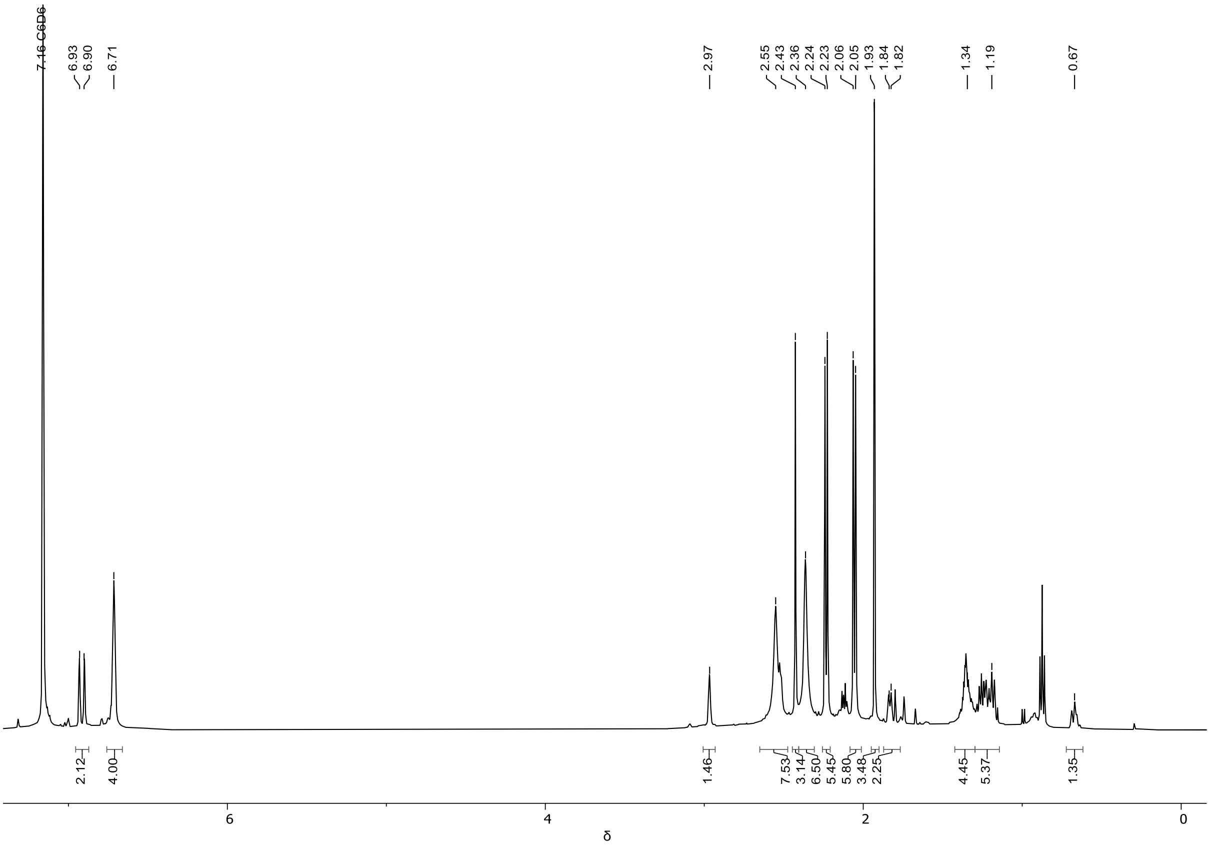


Figure S18. ^{1}H NMR spectrum of **2**.

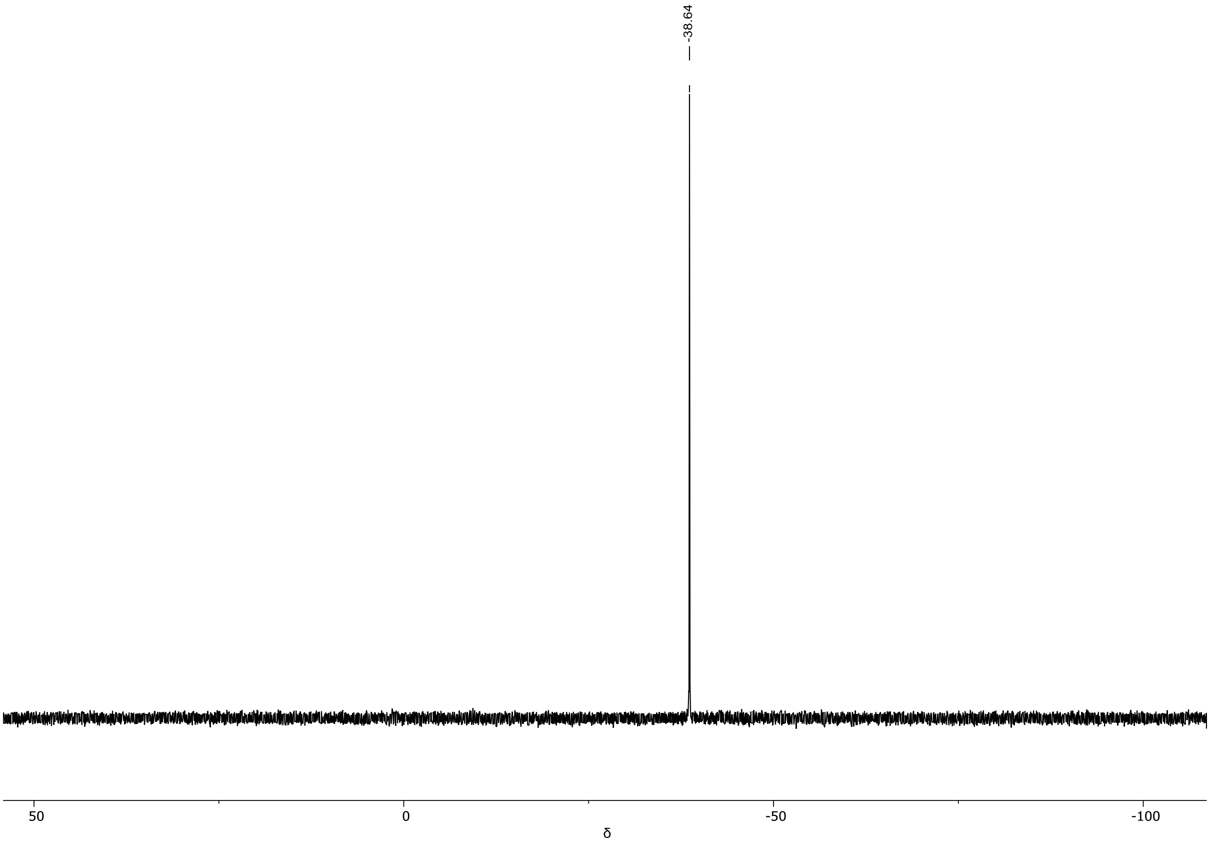


Figure S19. ^{31}P{^{1}H} NMR spectrum of **2**.

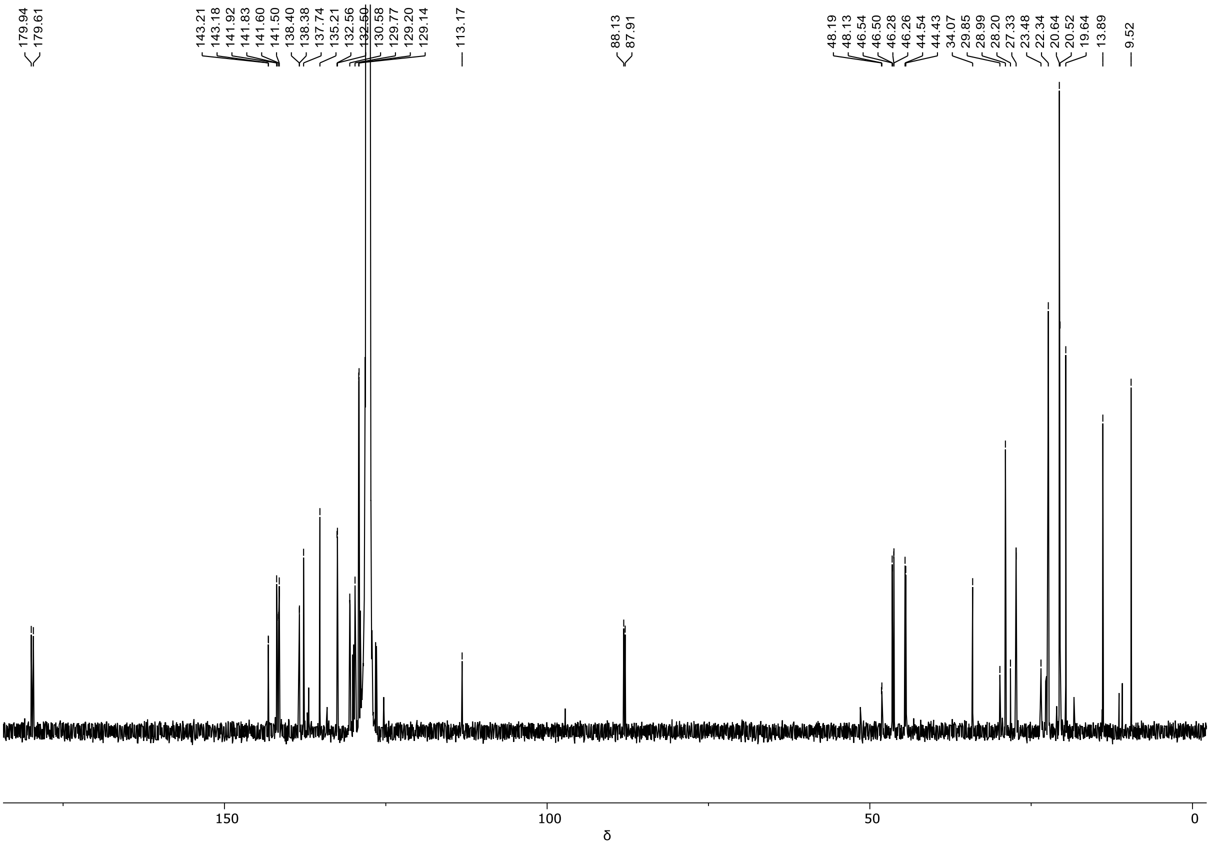


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of **2**.

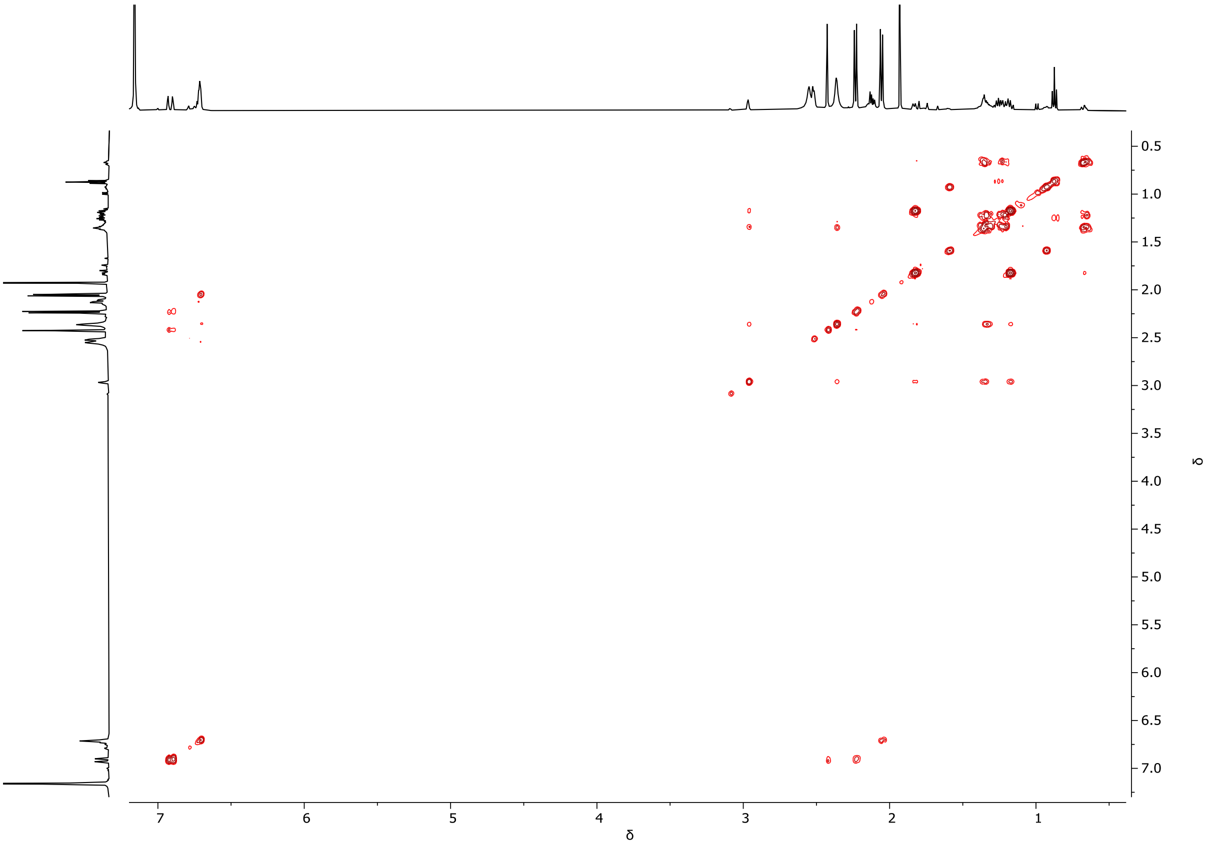


Figure S21. COSY NMR spectrum of **2**.

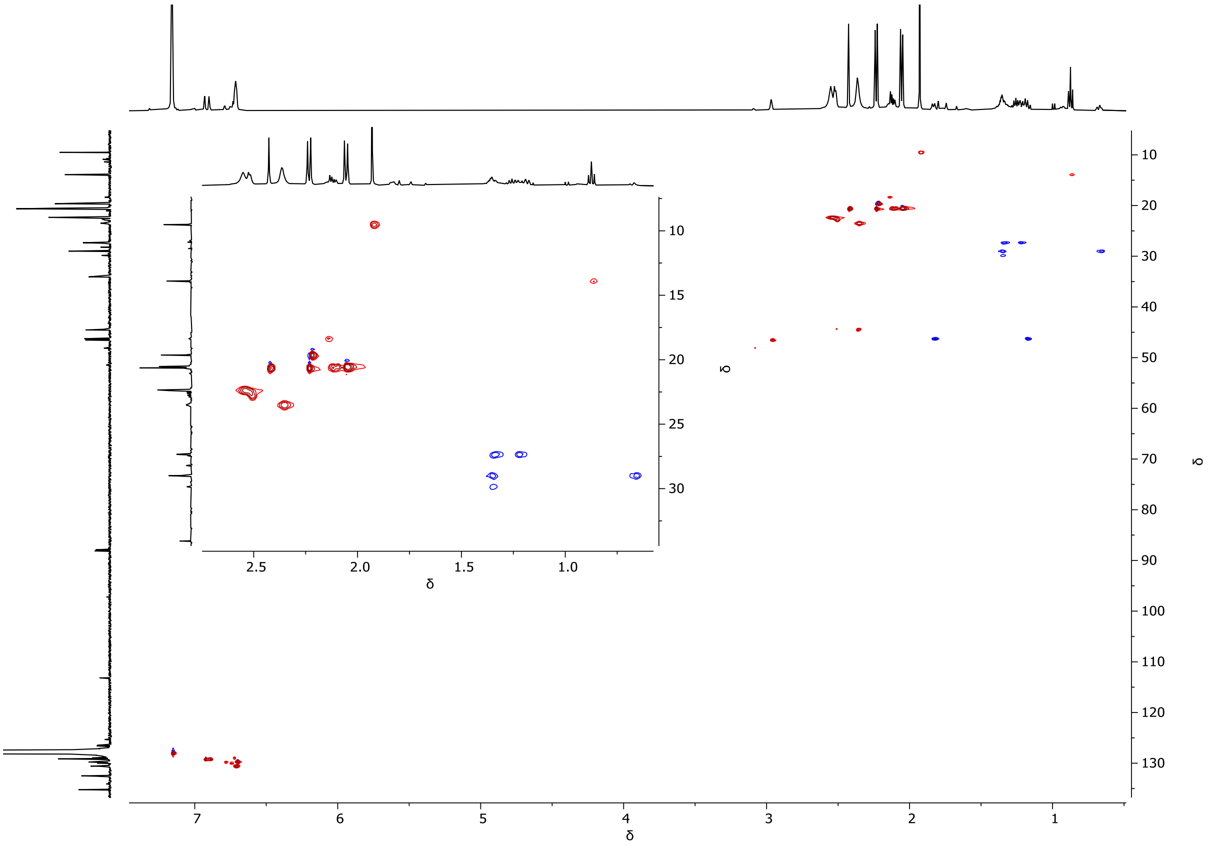


Figure S22. HSQC NMR spectrum of **2**.

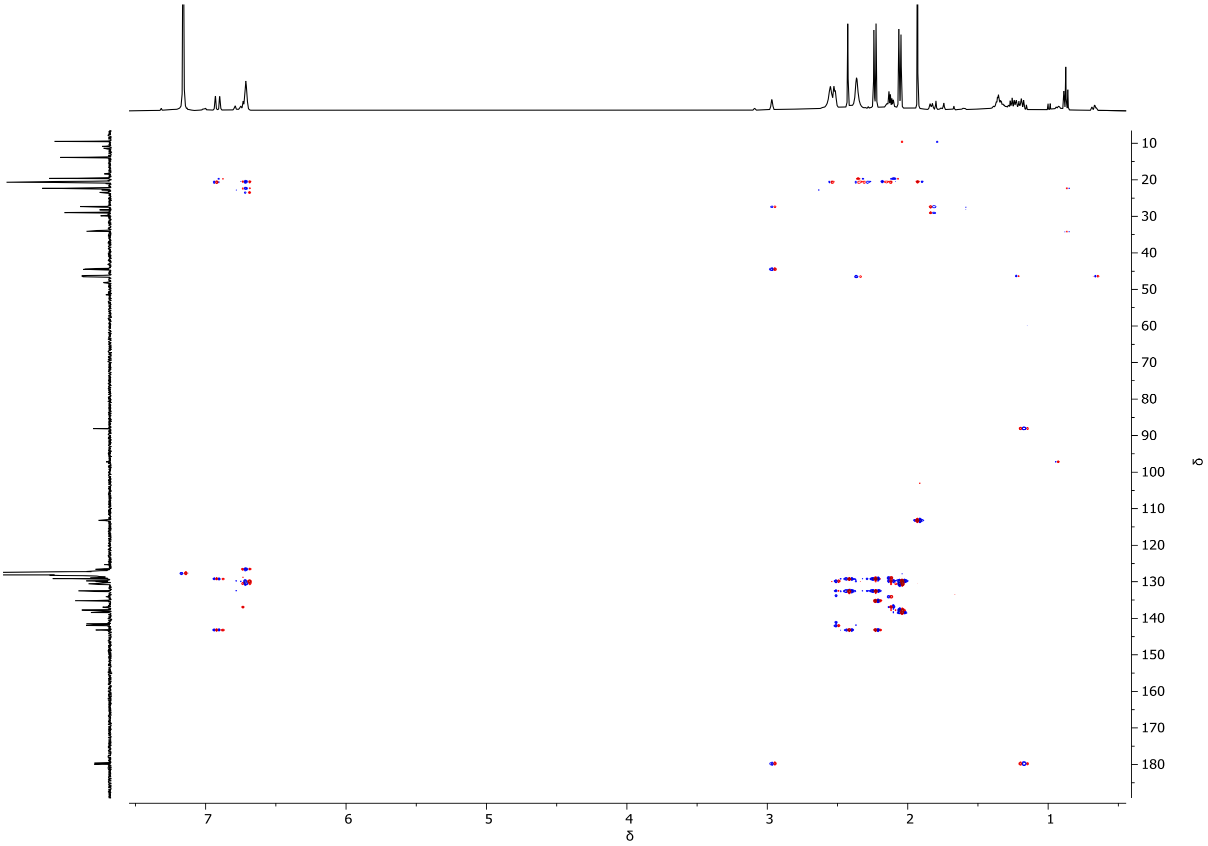


Figure S23. HMBC NMR spectrum of **2**.

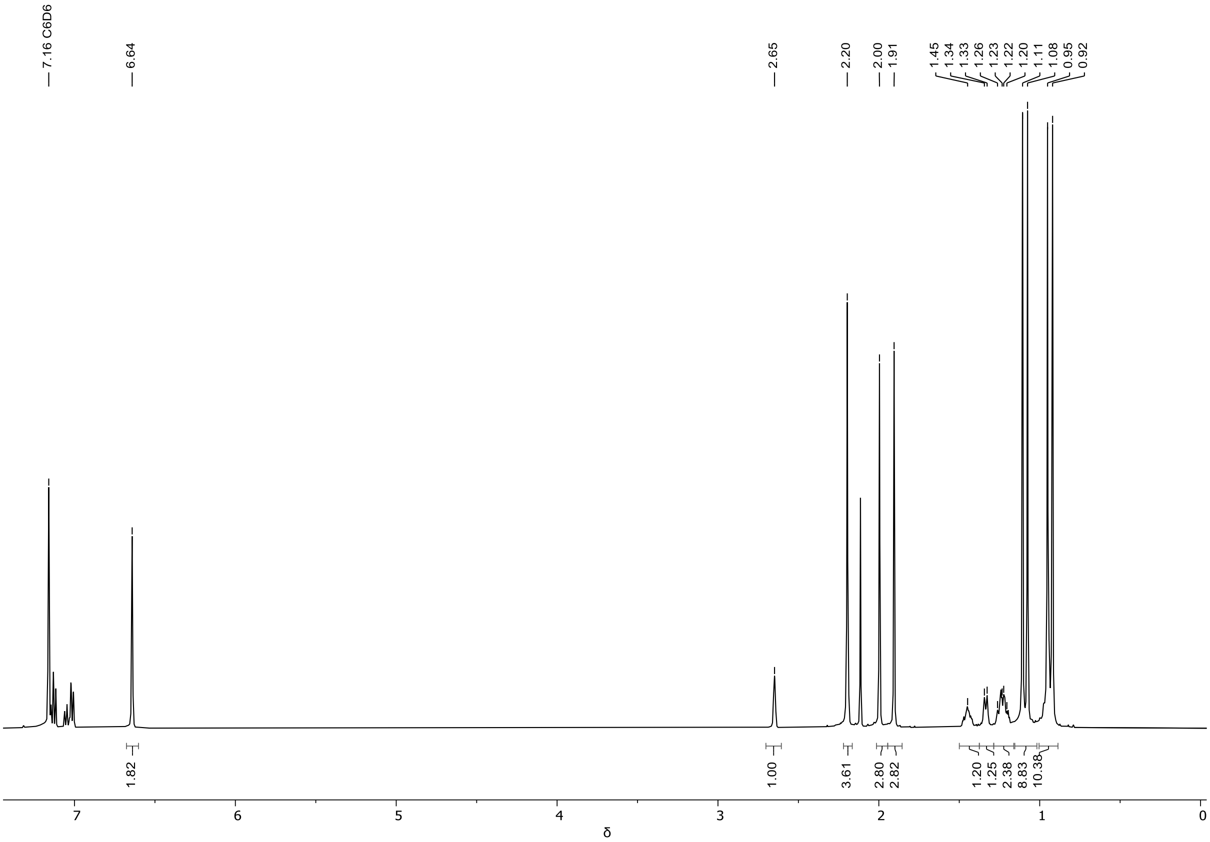


Figure S24. 1H NMR spectrum of **3**.

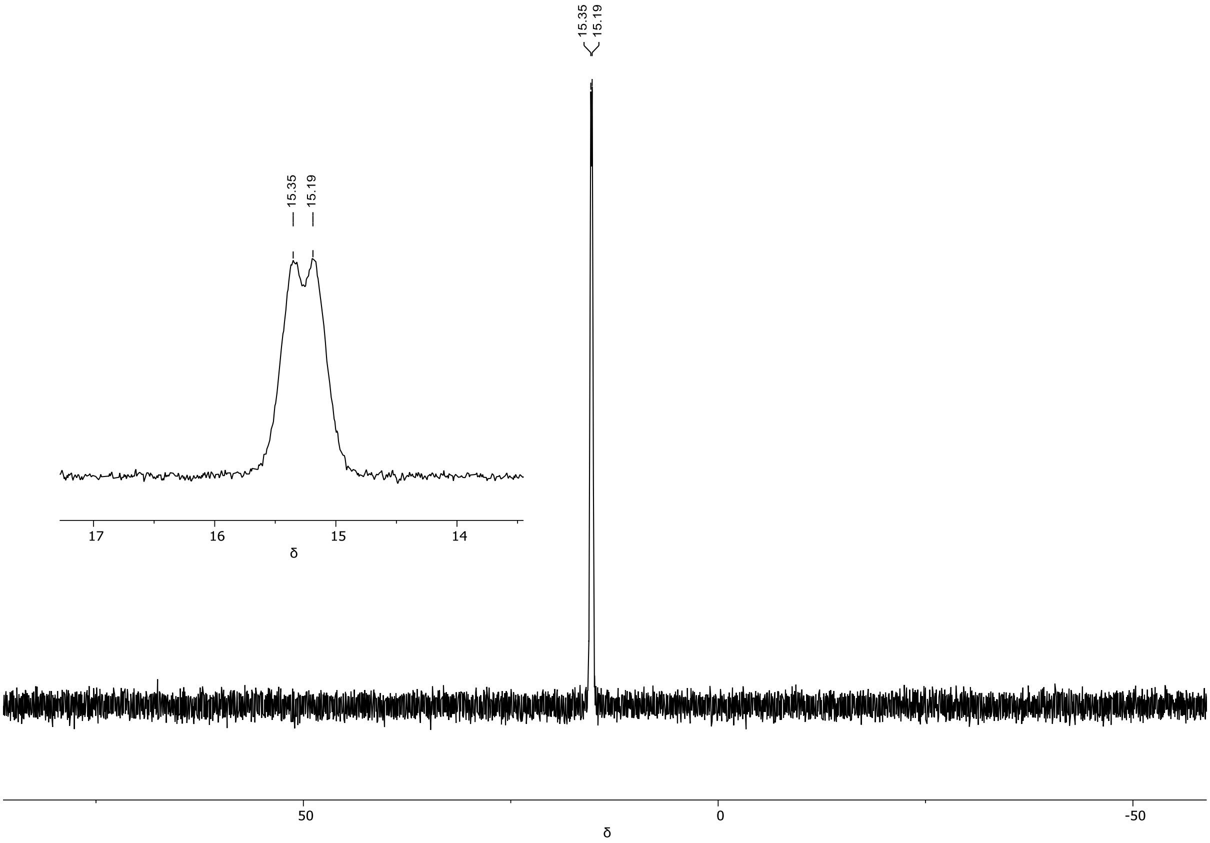


Figure S25. ^{31}P{^{1}H} NMR spectrum of **3**.

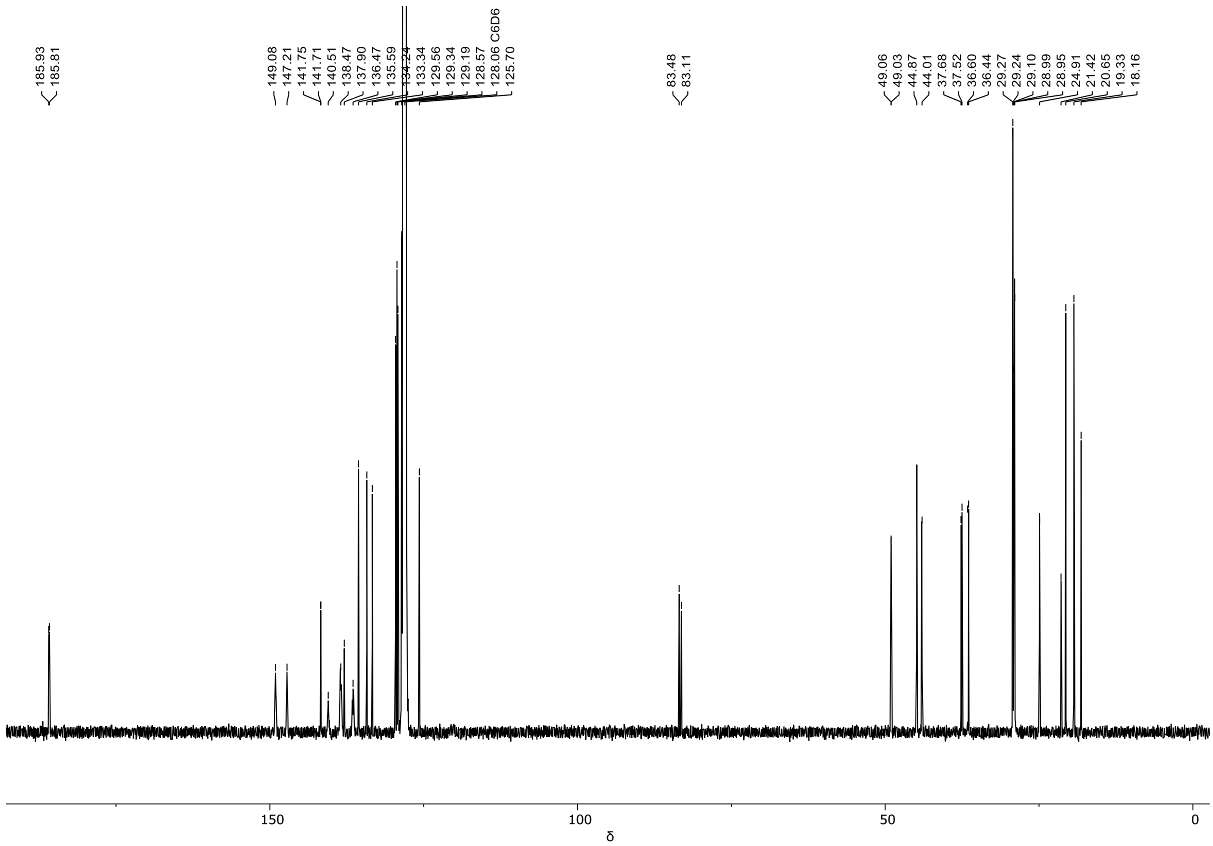


Figure S26. $^{13}C\{^1H\}$ NMR spectrum of **3**.

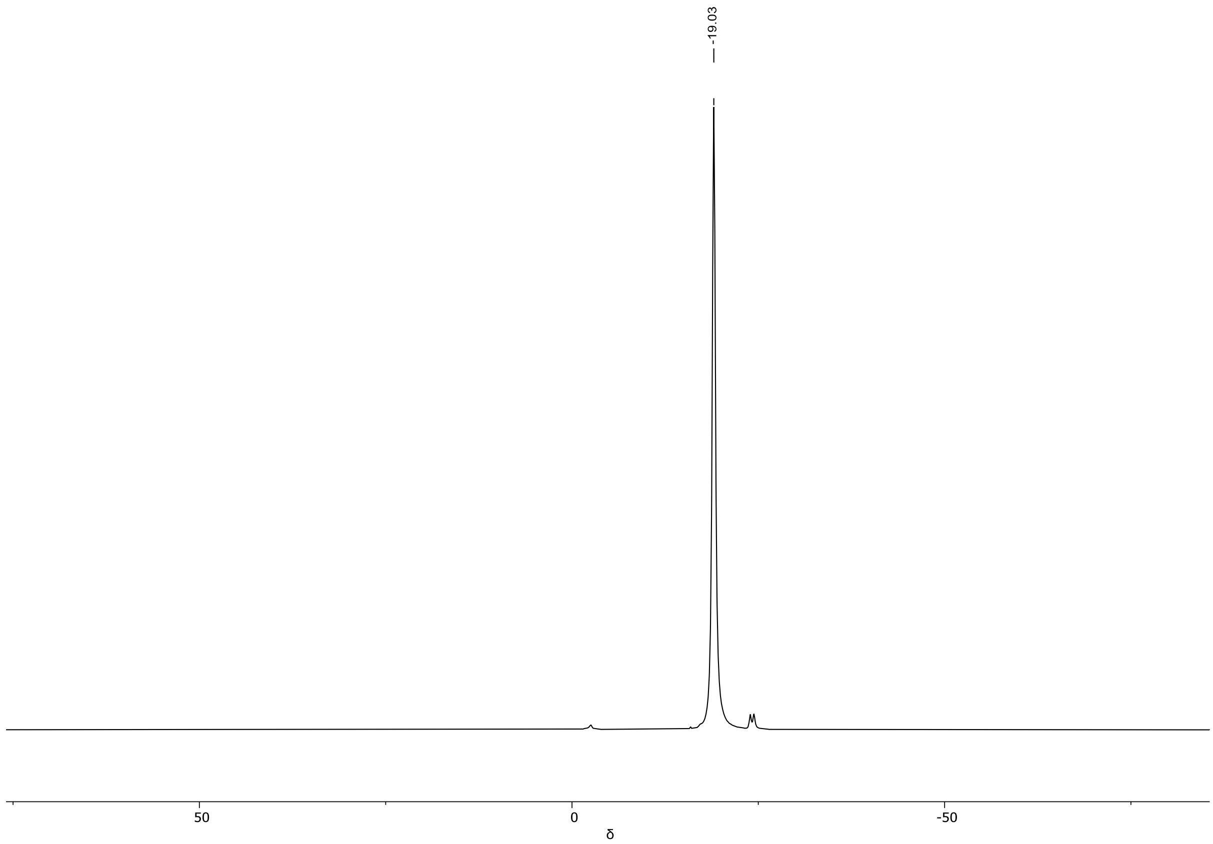


Figure S27. ^{11}B NMR spectrum of **3**.

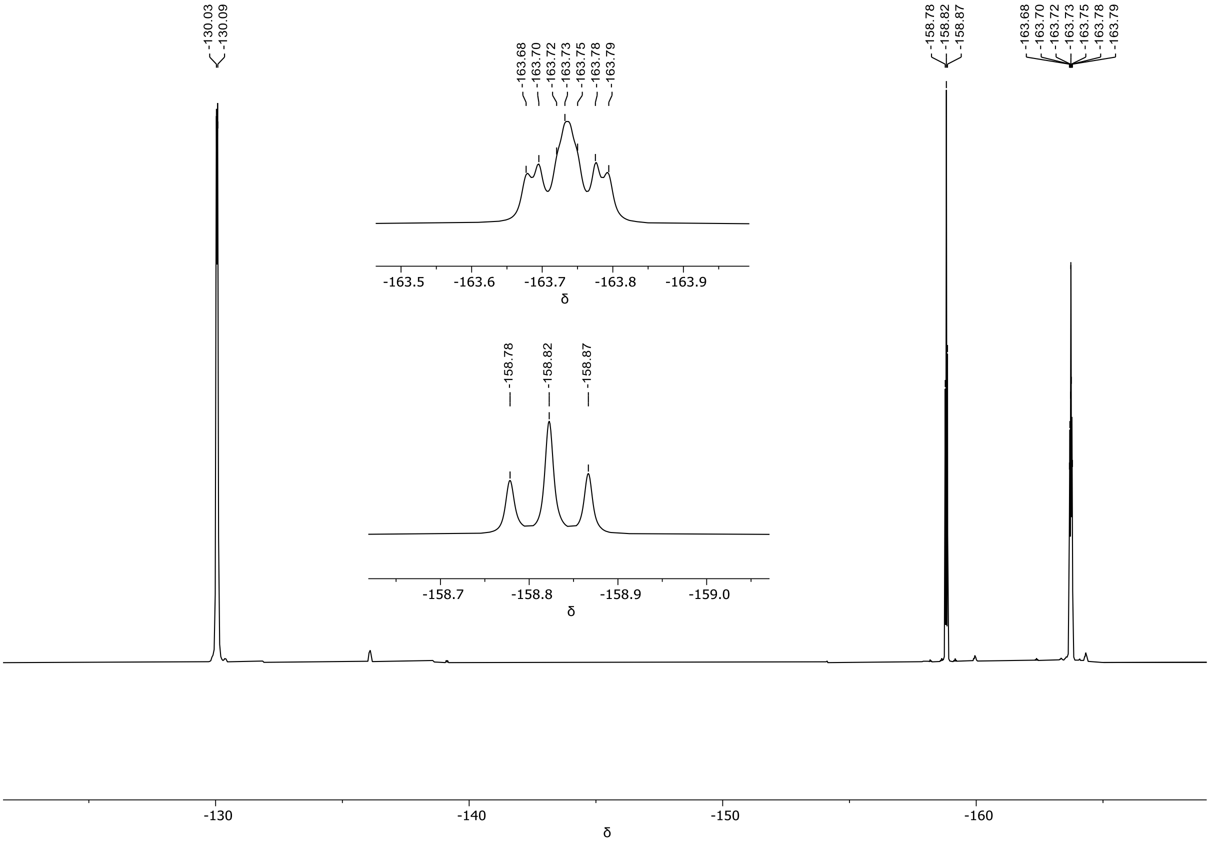


Figure S28. ^{19}F NMR spectrum of **3**.

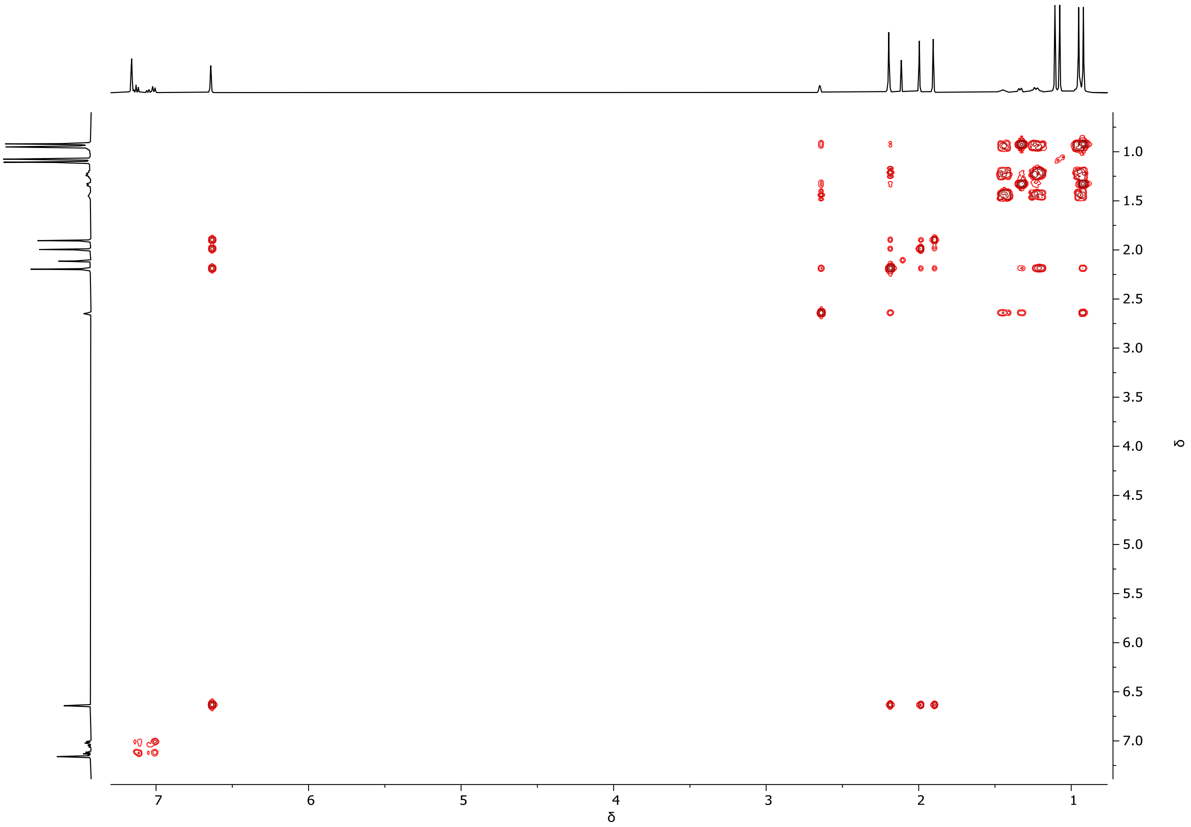


Figure S29. COSY NMR spectrum of **3**.

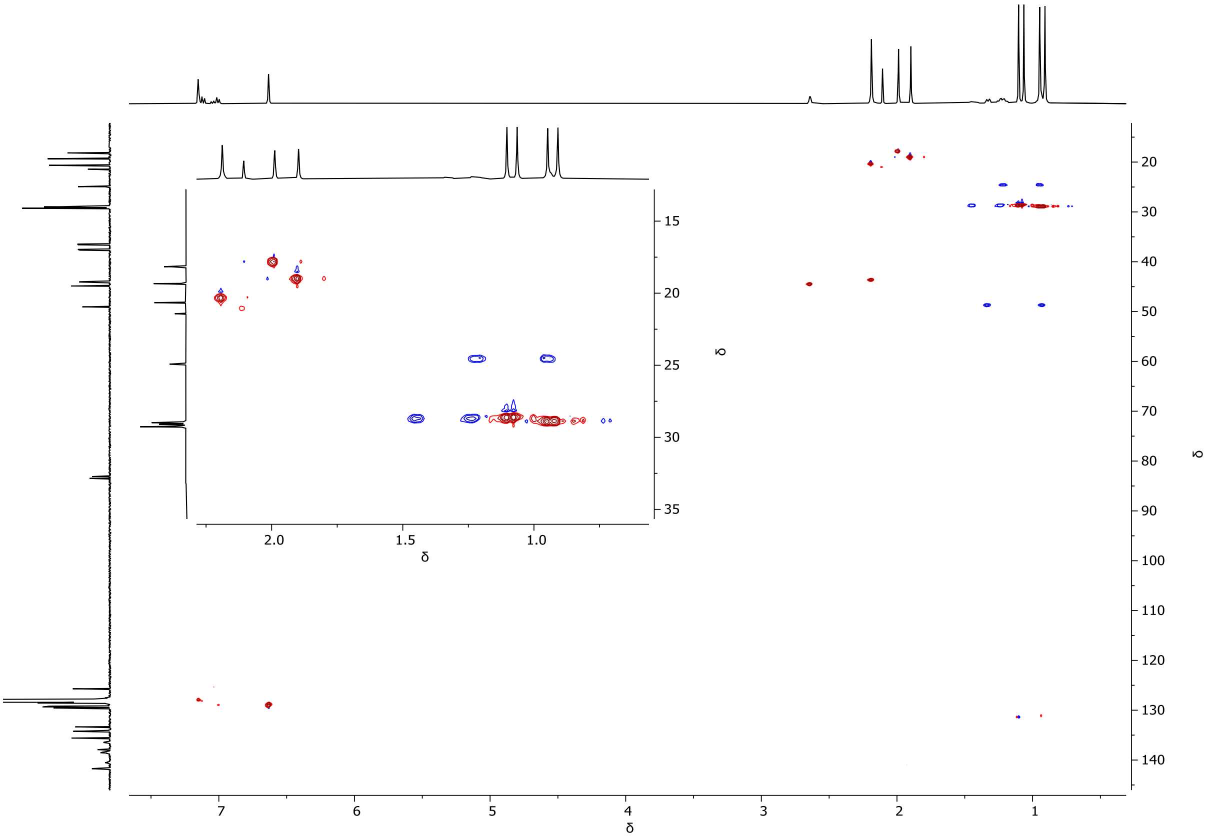


Figure S30. HSQC spectrum of **3**.

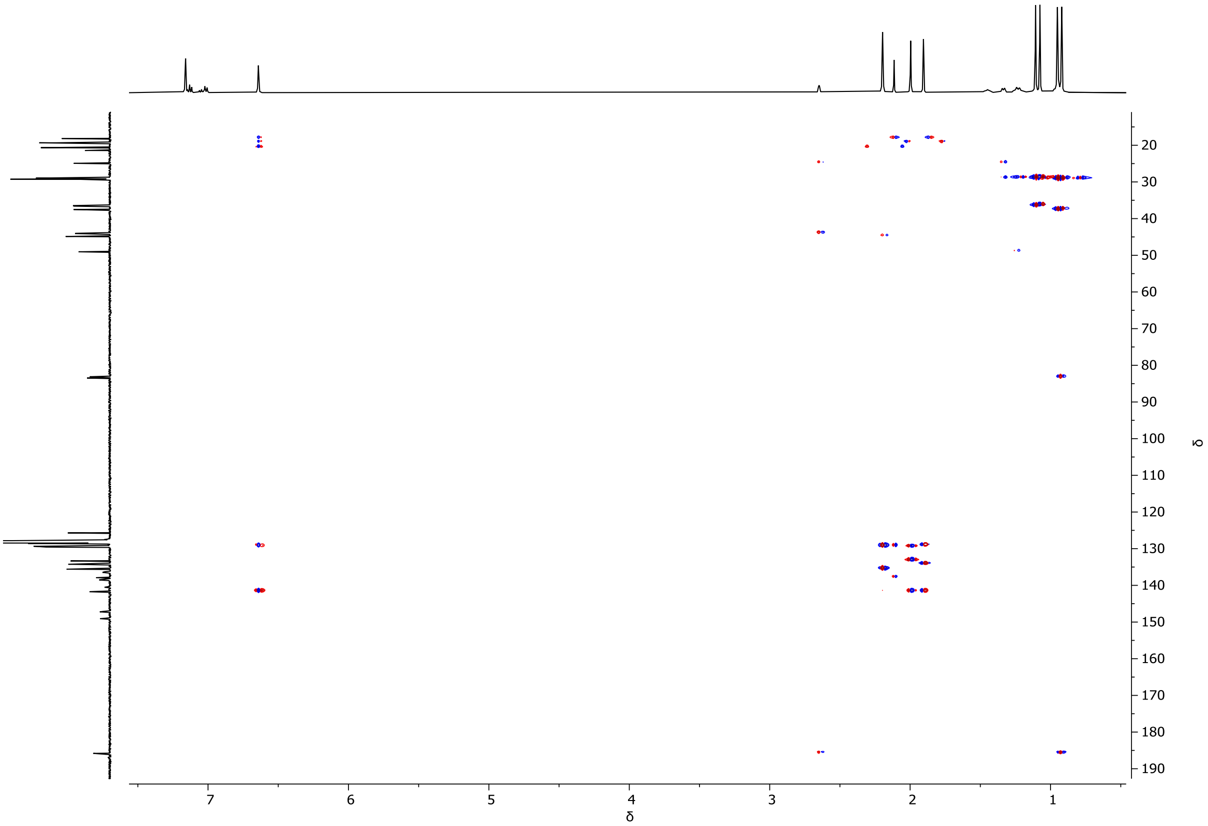


Figure S31. HMBC NMR spectrum of **3**.

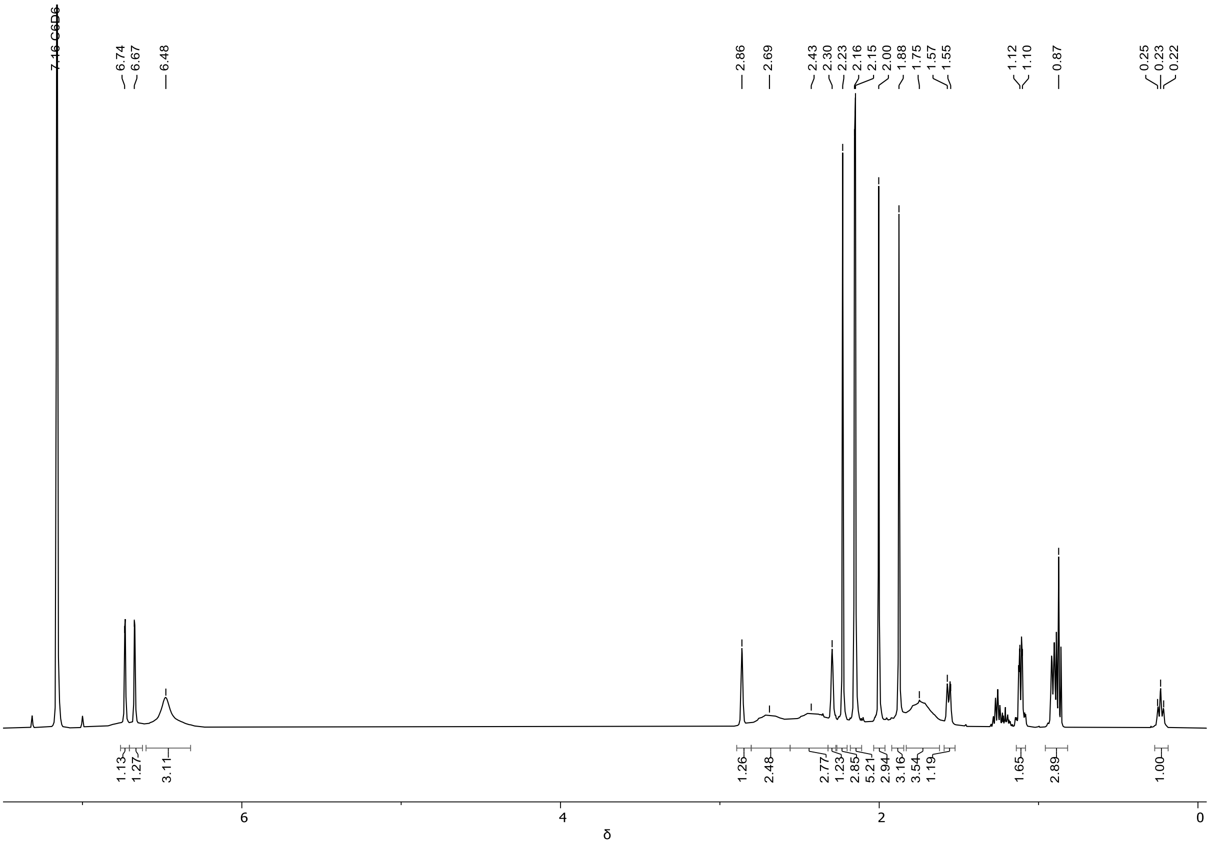


Figure S32. ^{1}H NMR spectrum of **4**.

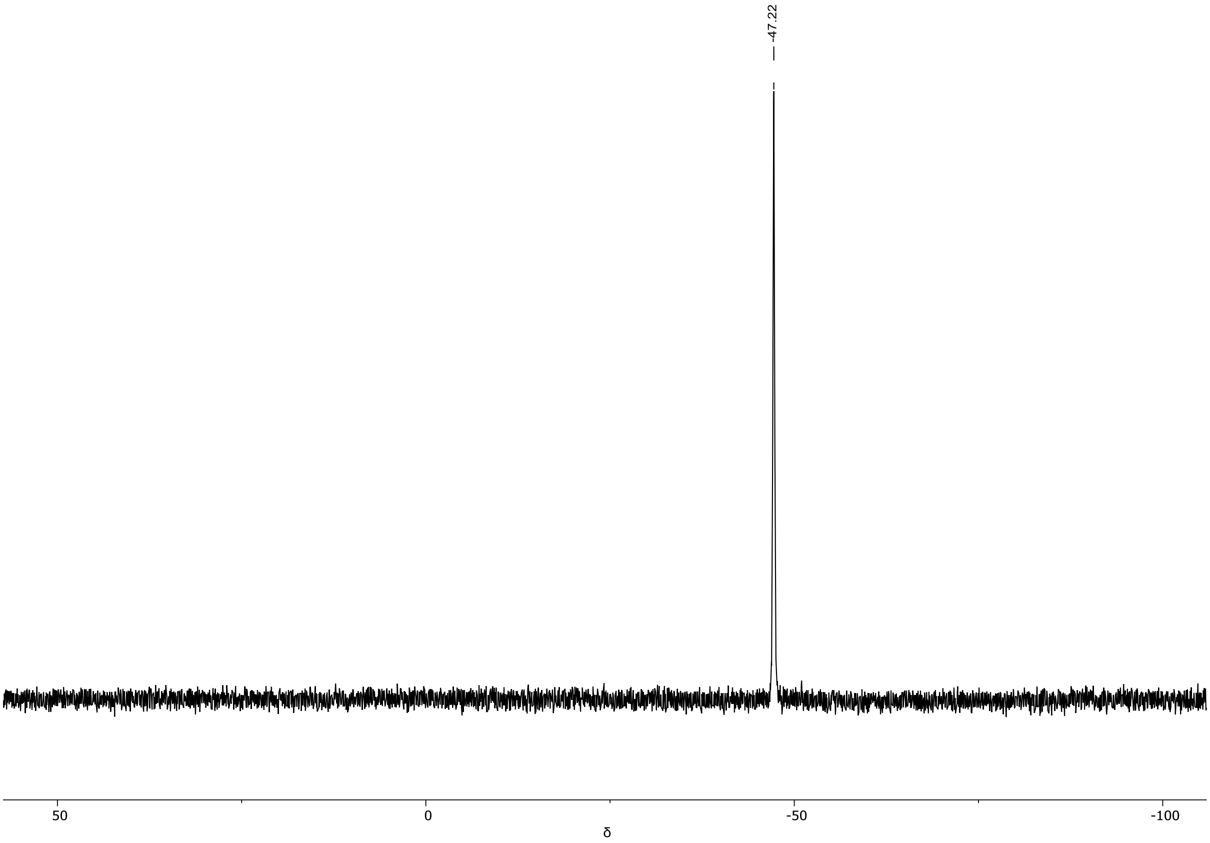


Figure S33. ^{31}P{^{1}H} NMR spectrum of 4.

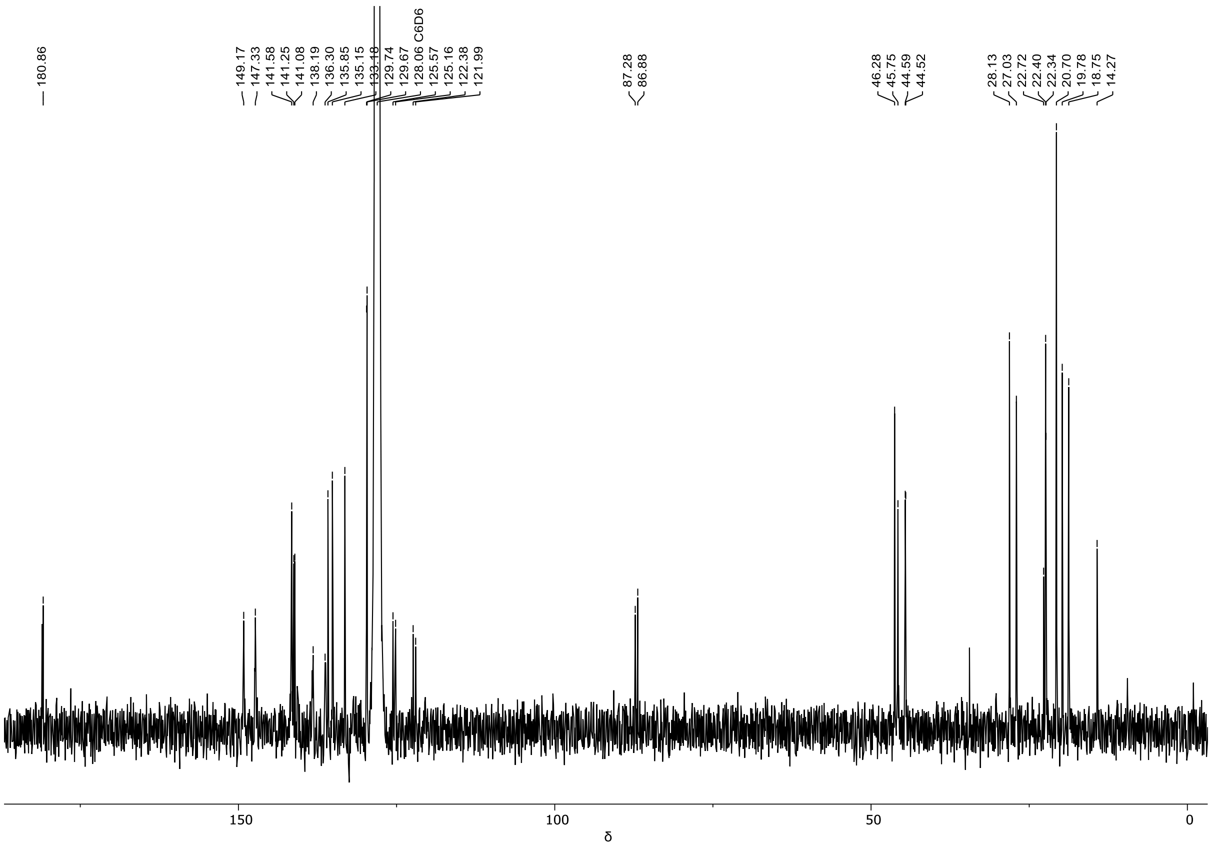


Figure S34. $^{13}C\{^1H\}$ NMR spectrum of **4**.

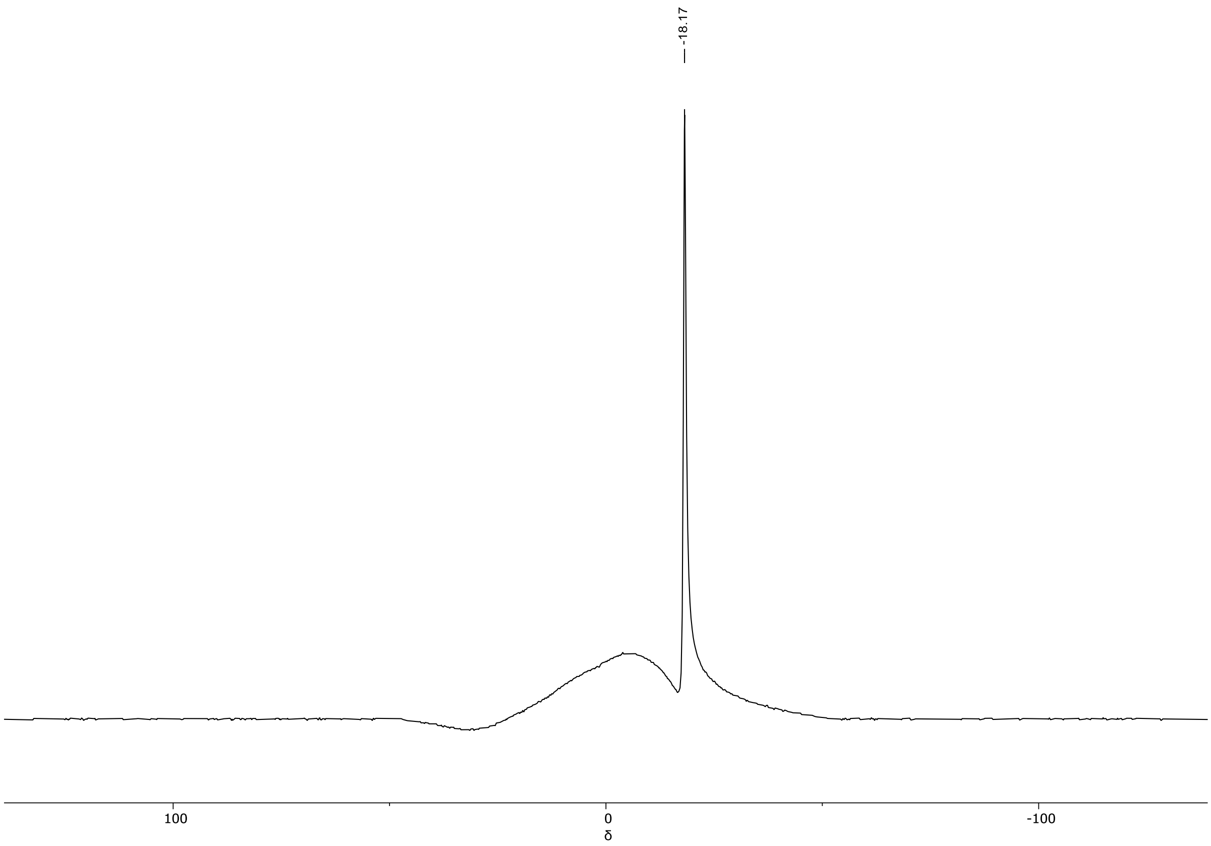


Figure S35. ^{11}B NMR spectrum of **4**.

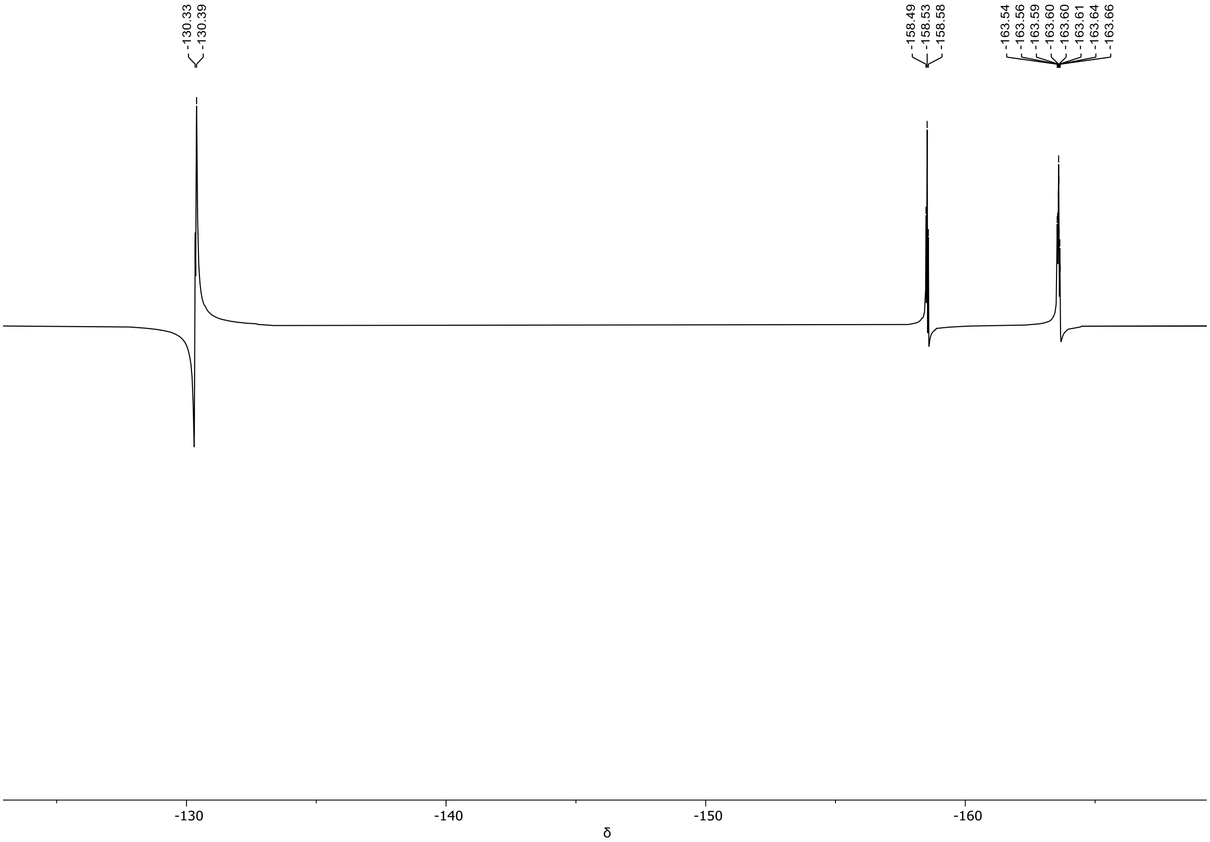


Figure S36. ^{19}F NMR spectrum of **4**.

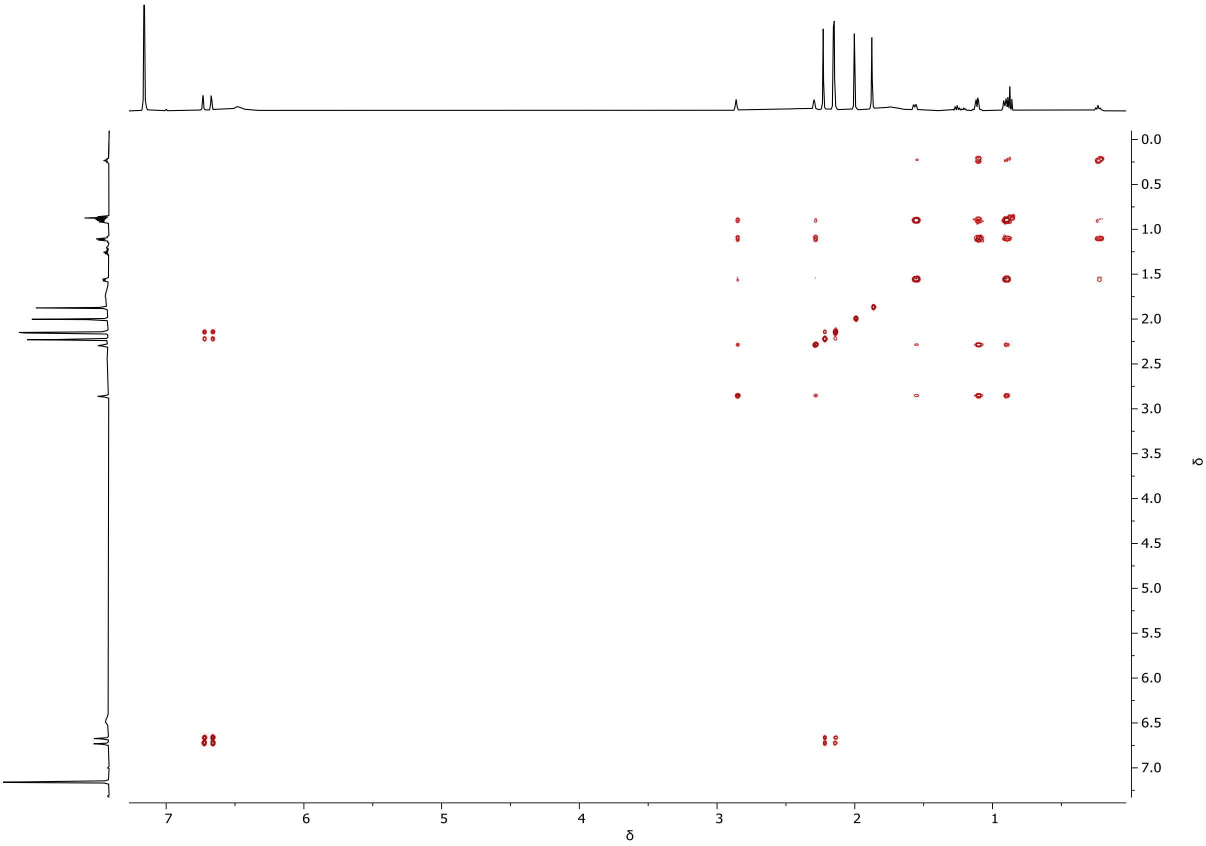


Figure S37. COSY NMR spectrum of **4**.

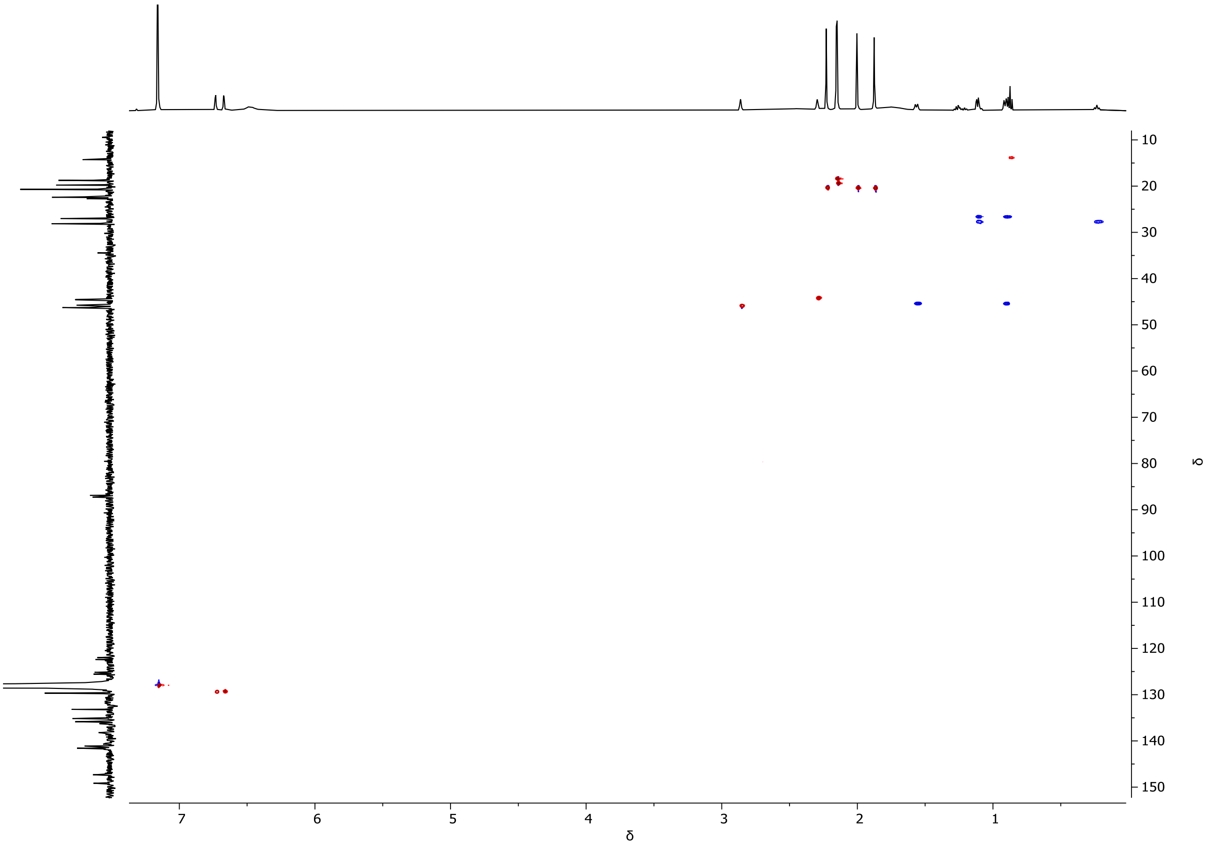


Figure S38. HSQC spectrum of **4**.

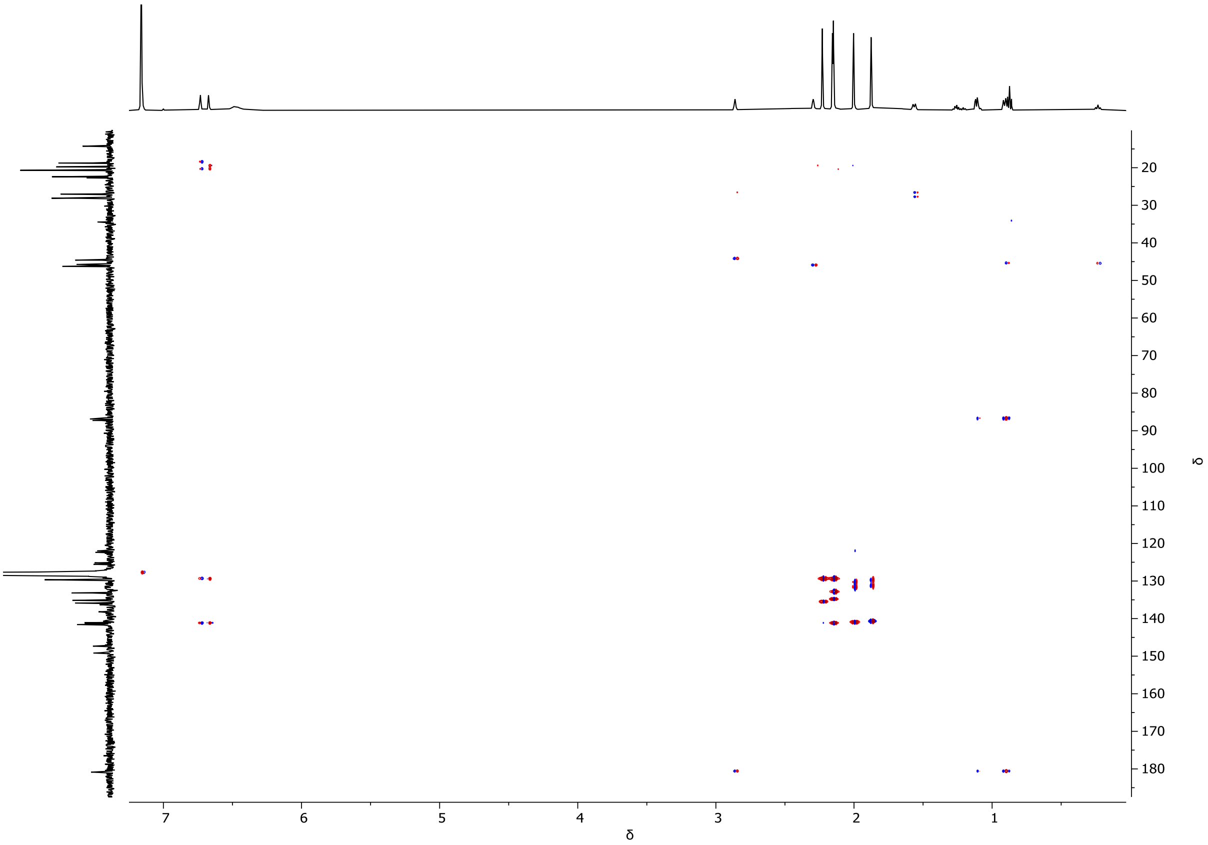


Figure S39. HMBC NMR spectrum of **4**.

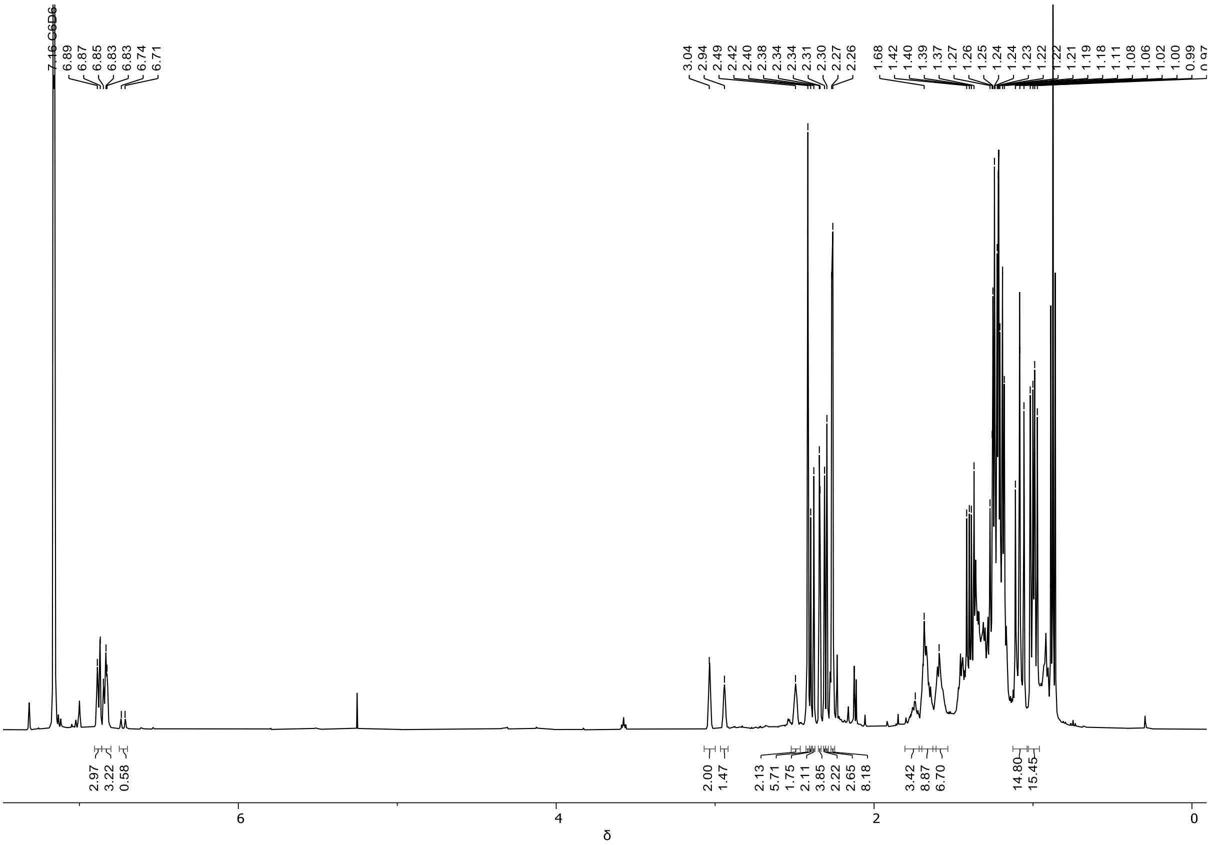


Figure S40. ^{1}H NMR spectrum of **6**.

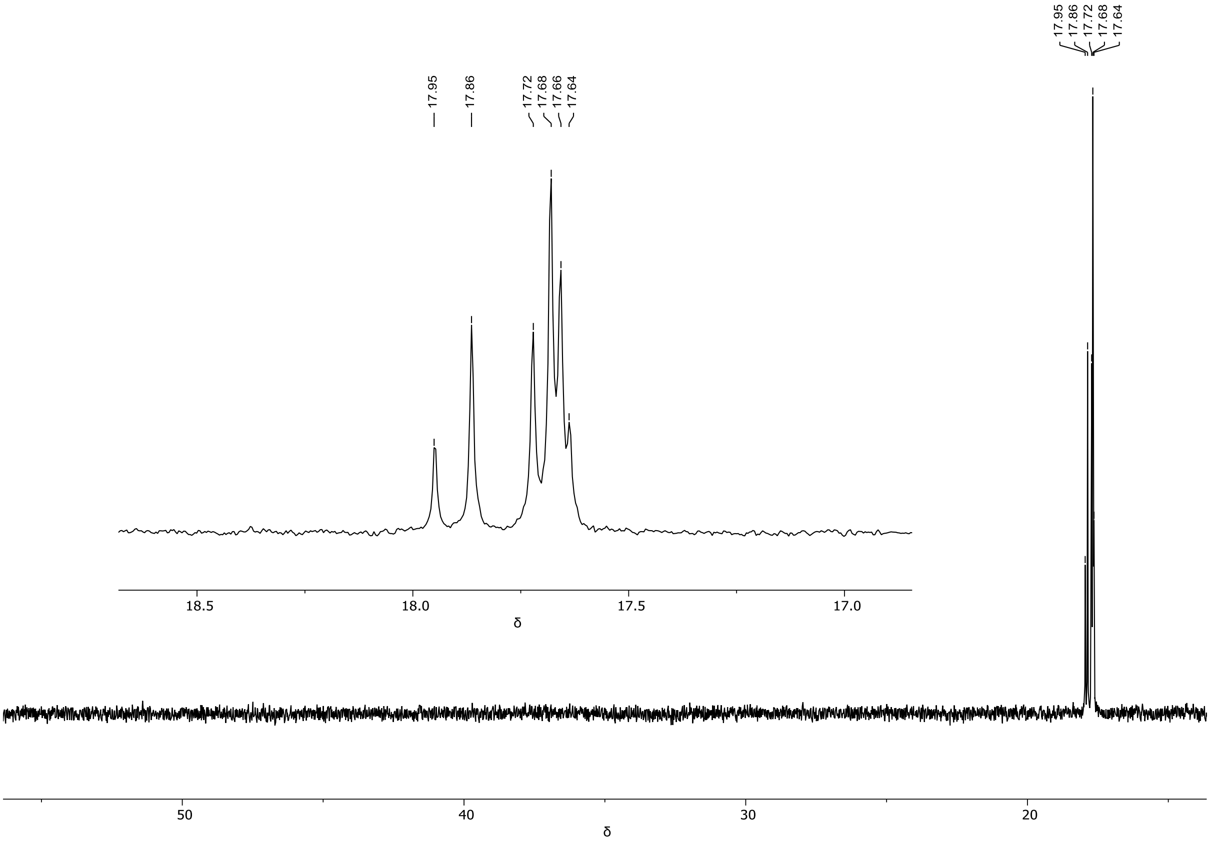


Figure S41. ^{31}P{^{1}H} NMR spectrum of **6**.

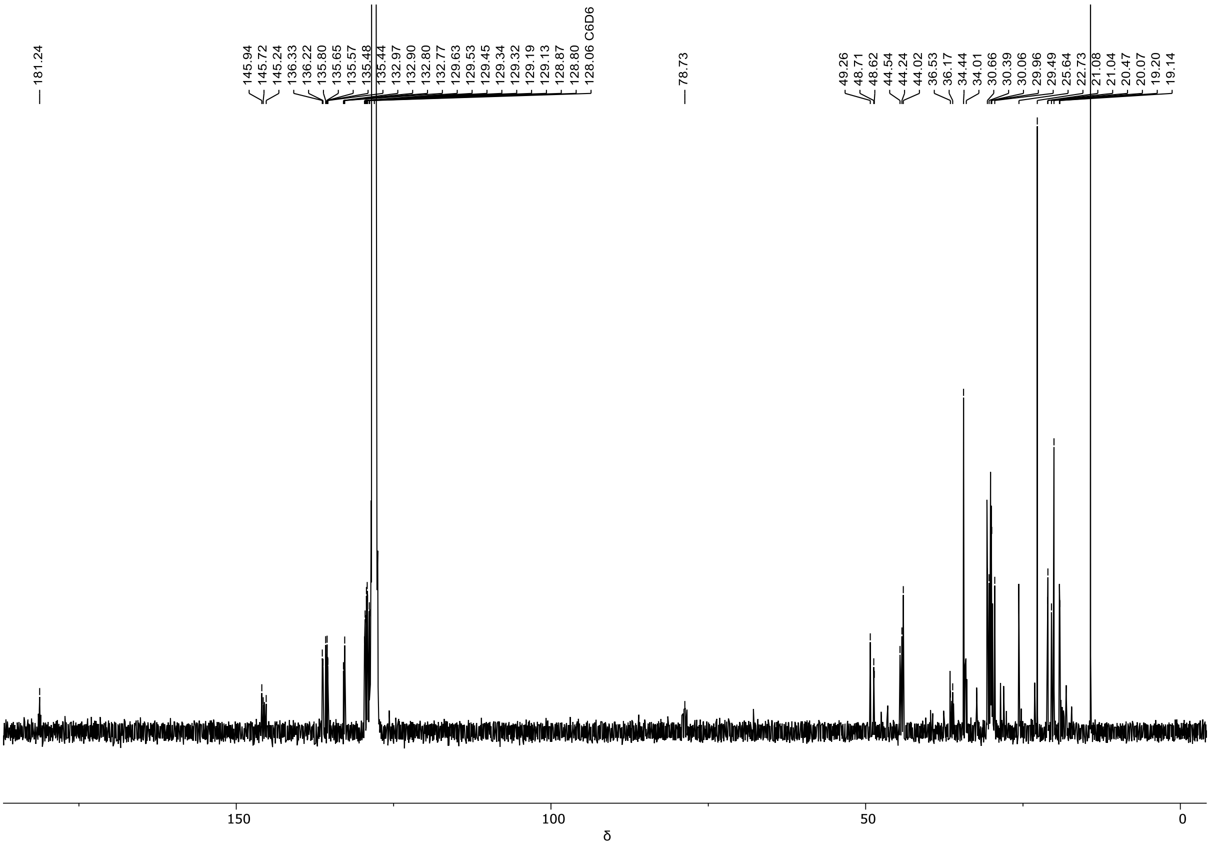


Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum of **6**.

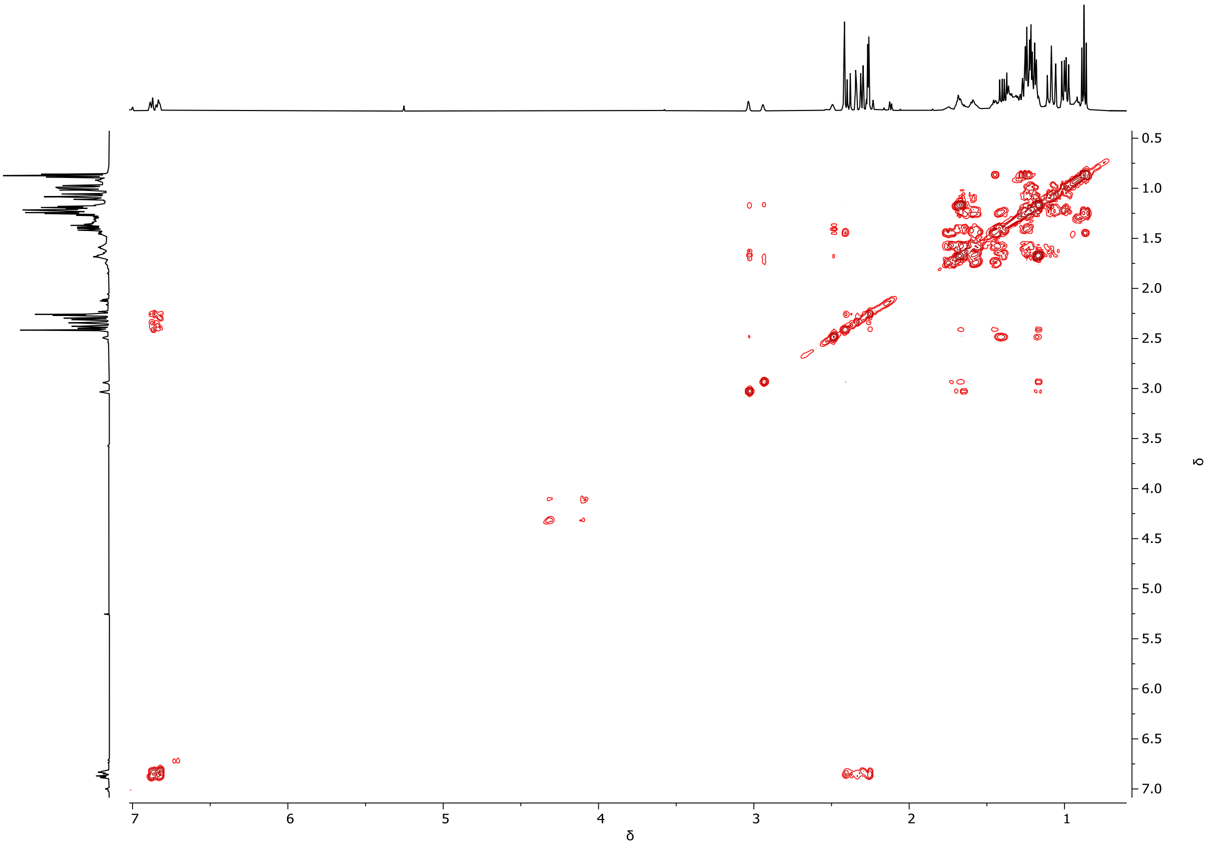


Figure S43. COSY NMR spectrum of **6**.

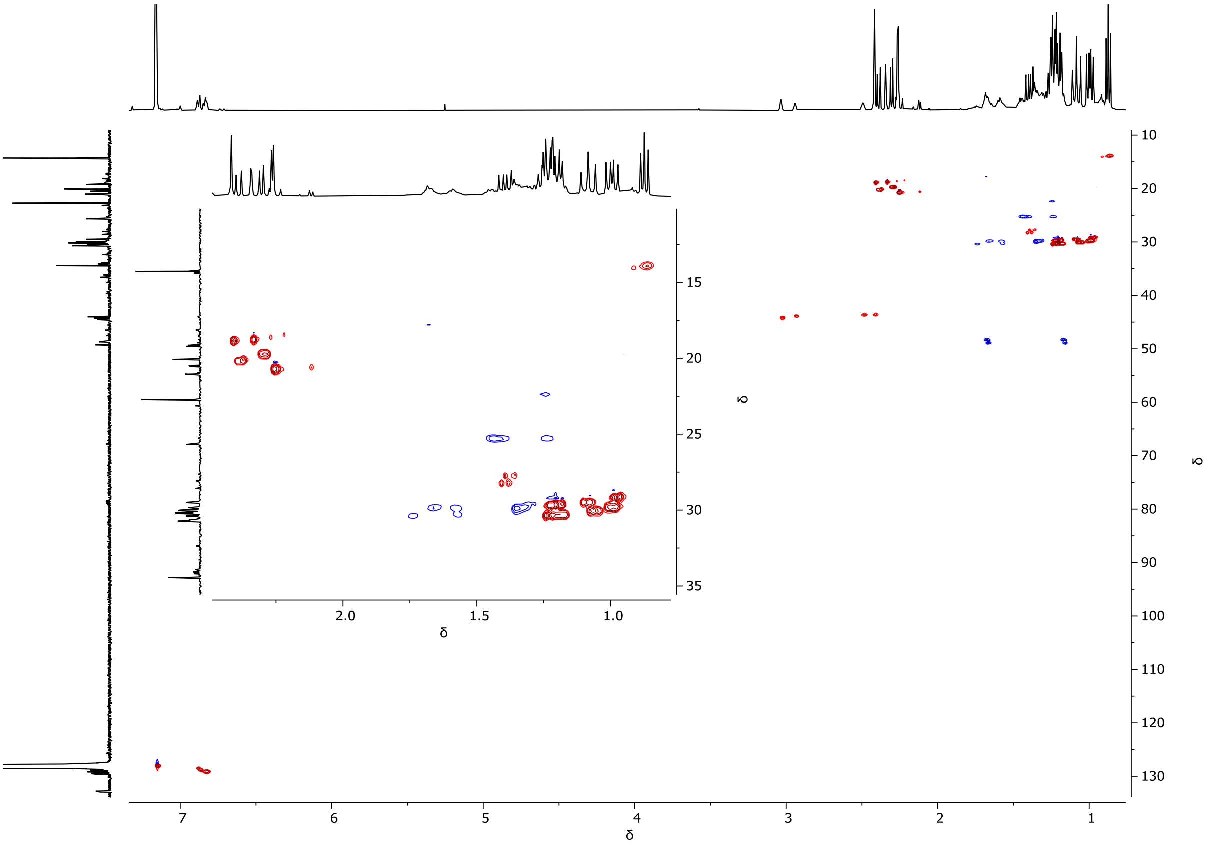


Figure S44. HSQC NMR spectrum of **6**.

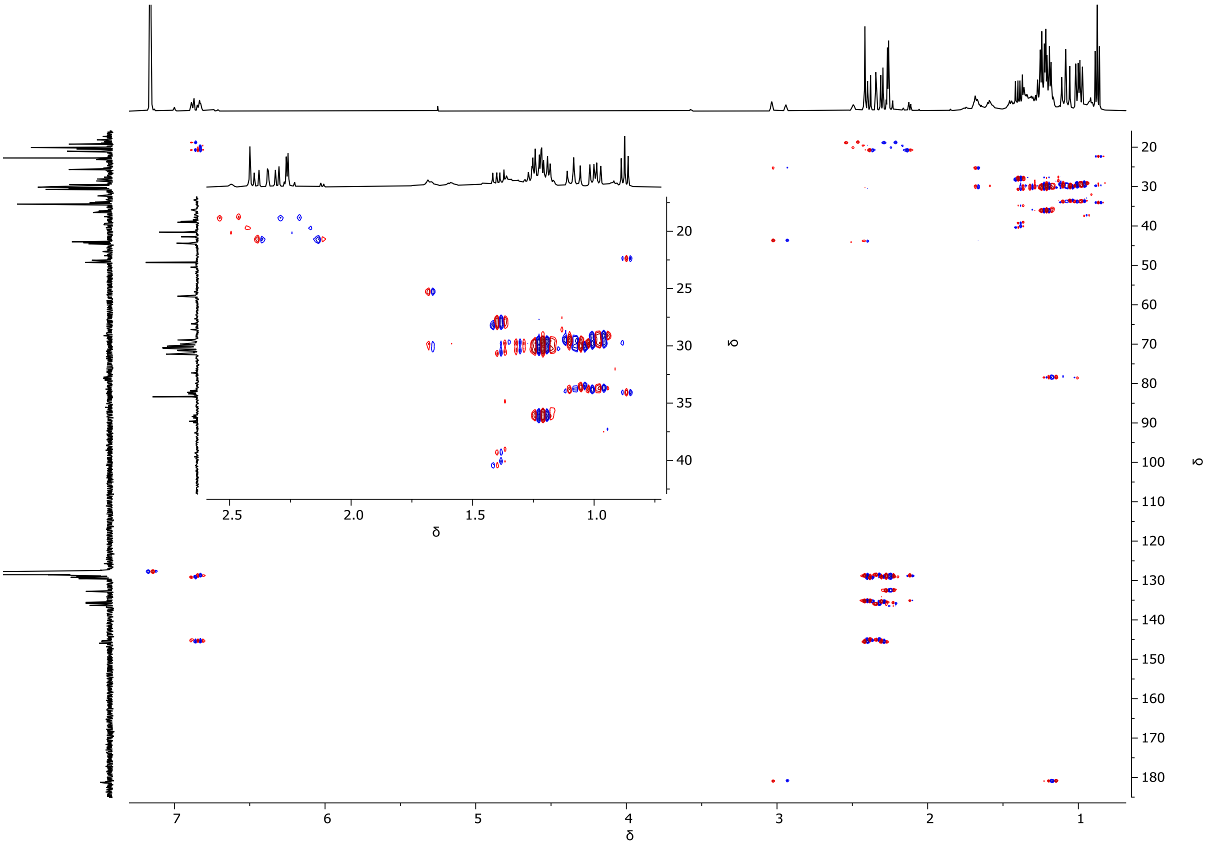


Figure S45. HMBC NMR spectrum of **6**.

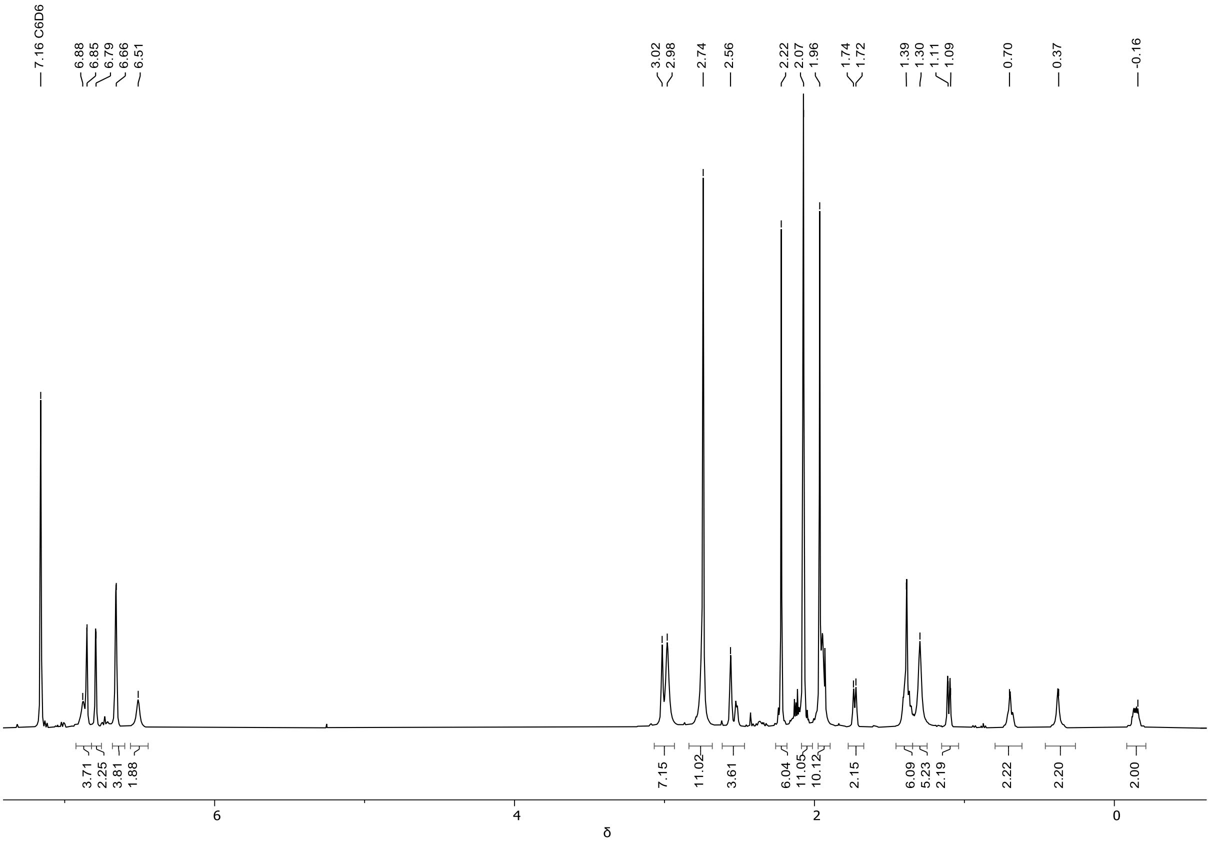


Figure S46. ^{1}H NMR spectrum of **7**.

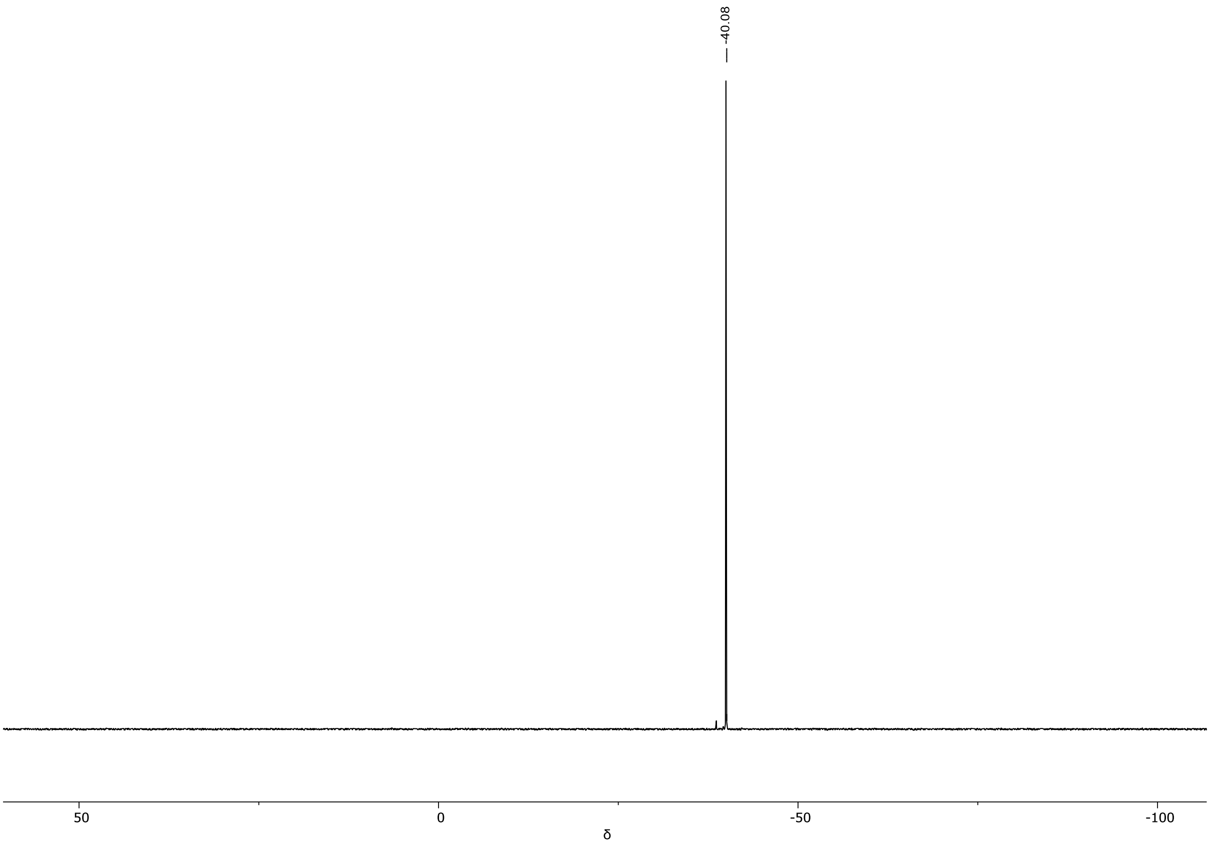


Figure S47. ^{31}P{^{1}H} NMR spectrum of **6**.

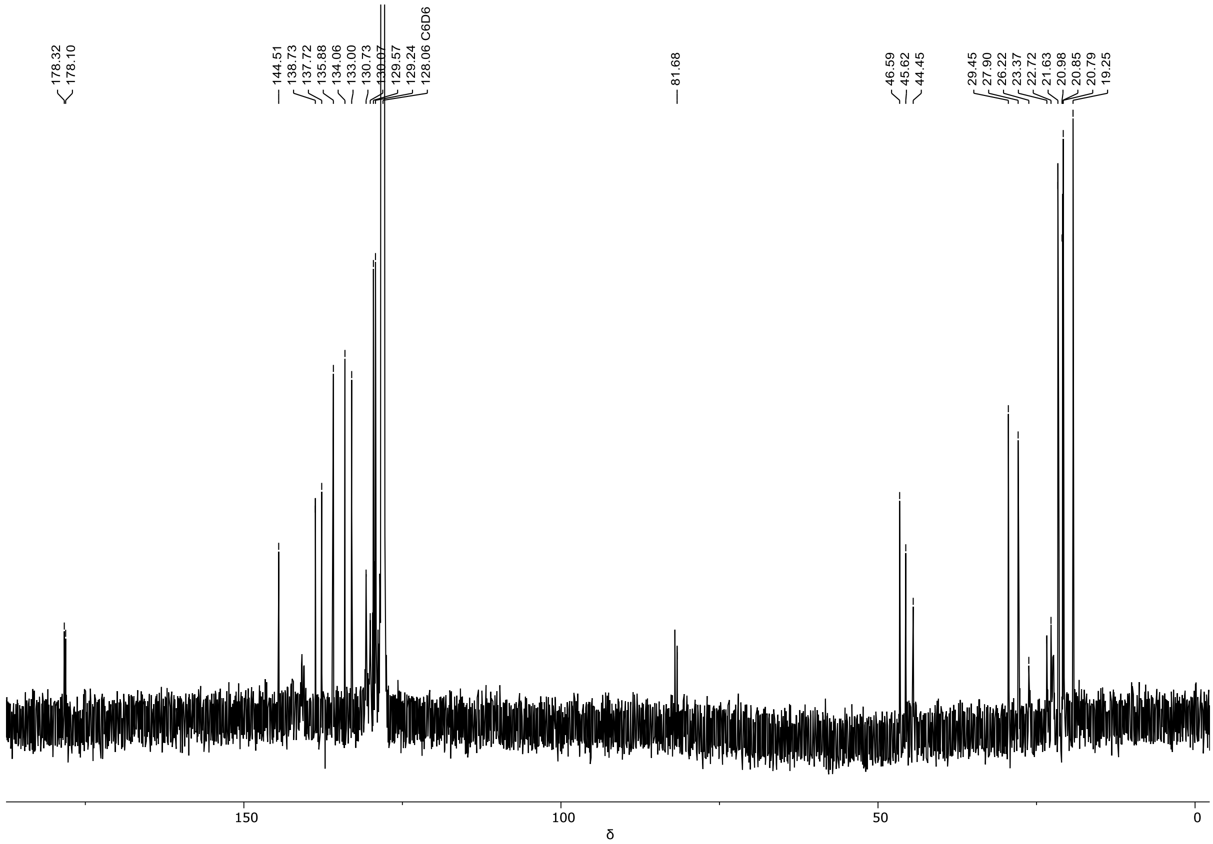


Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum of **7**.

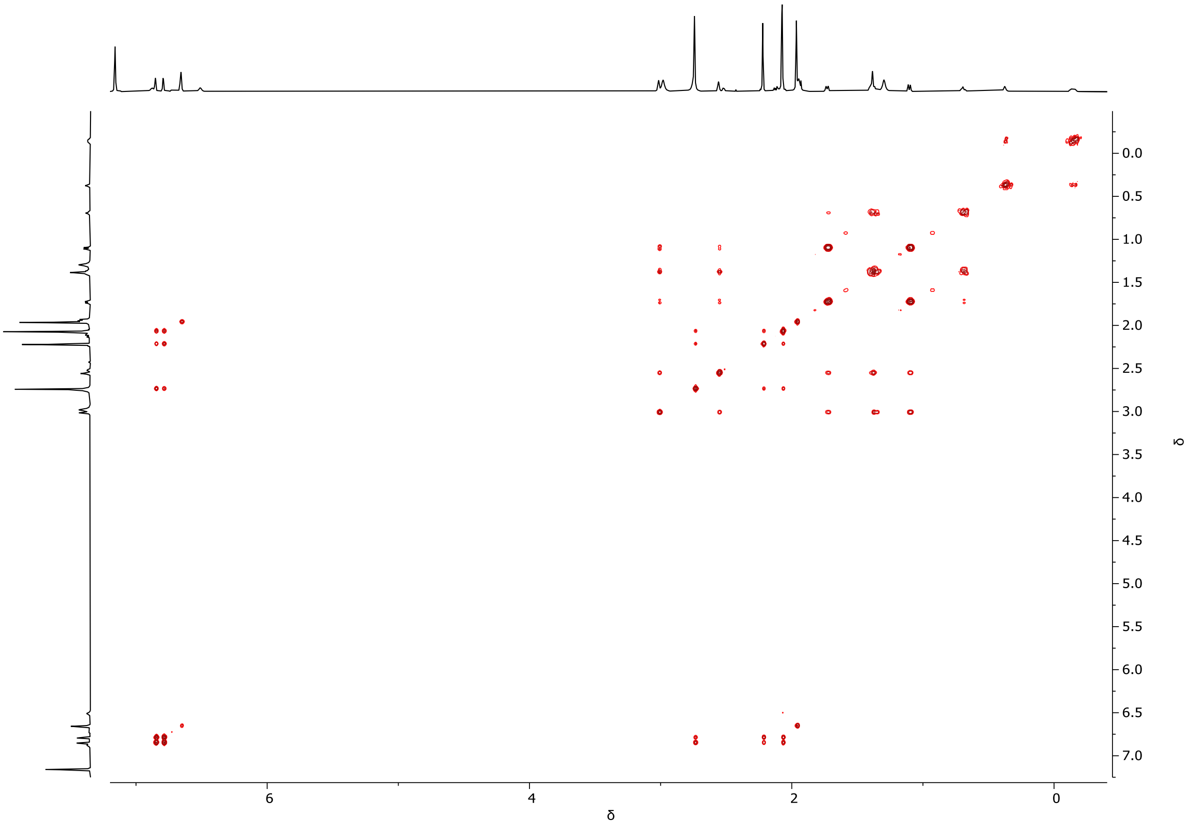


Figure S49. COSY NMR spectrum of **7**.

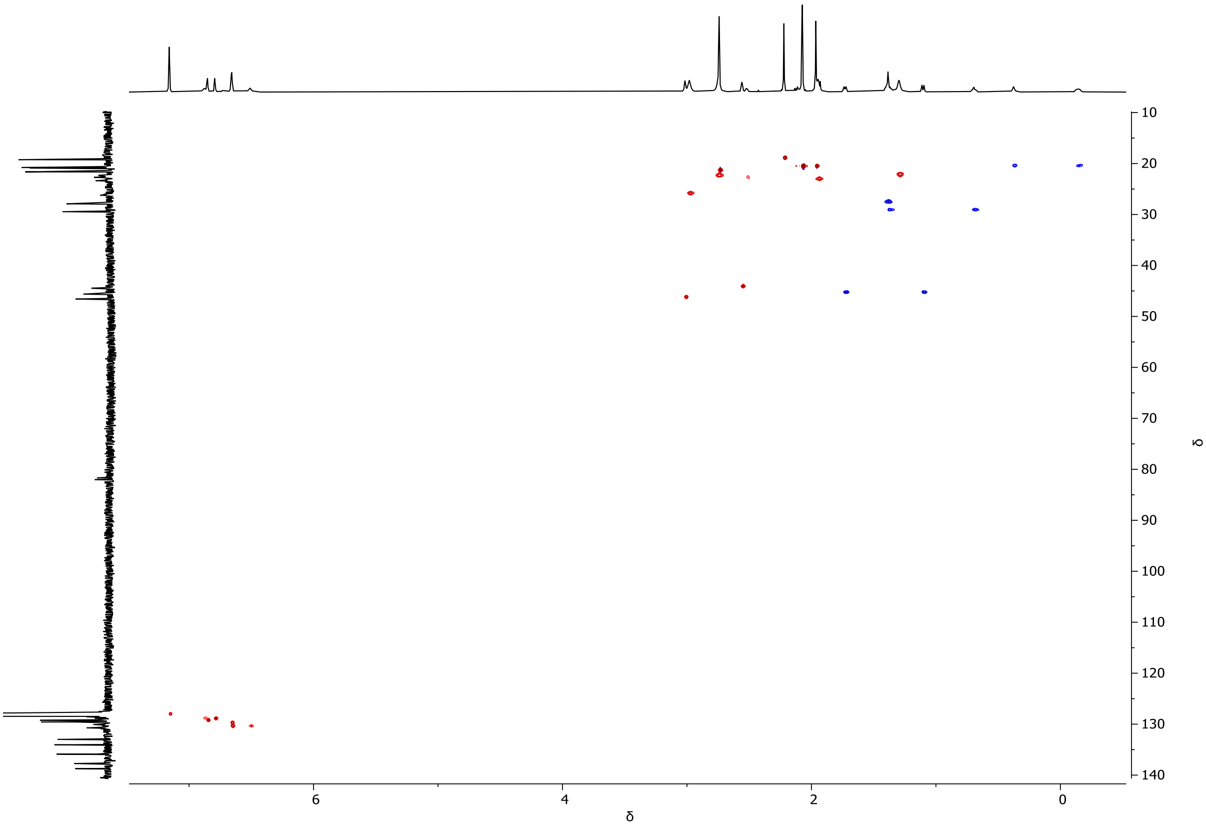


Figure S50. HSQC NMR spectrum of **7**.

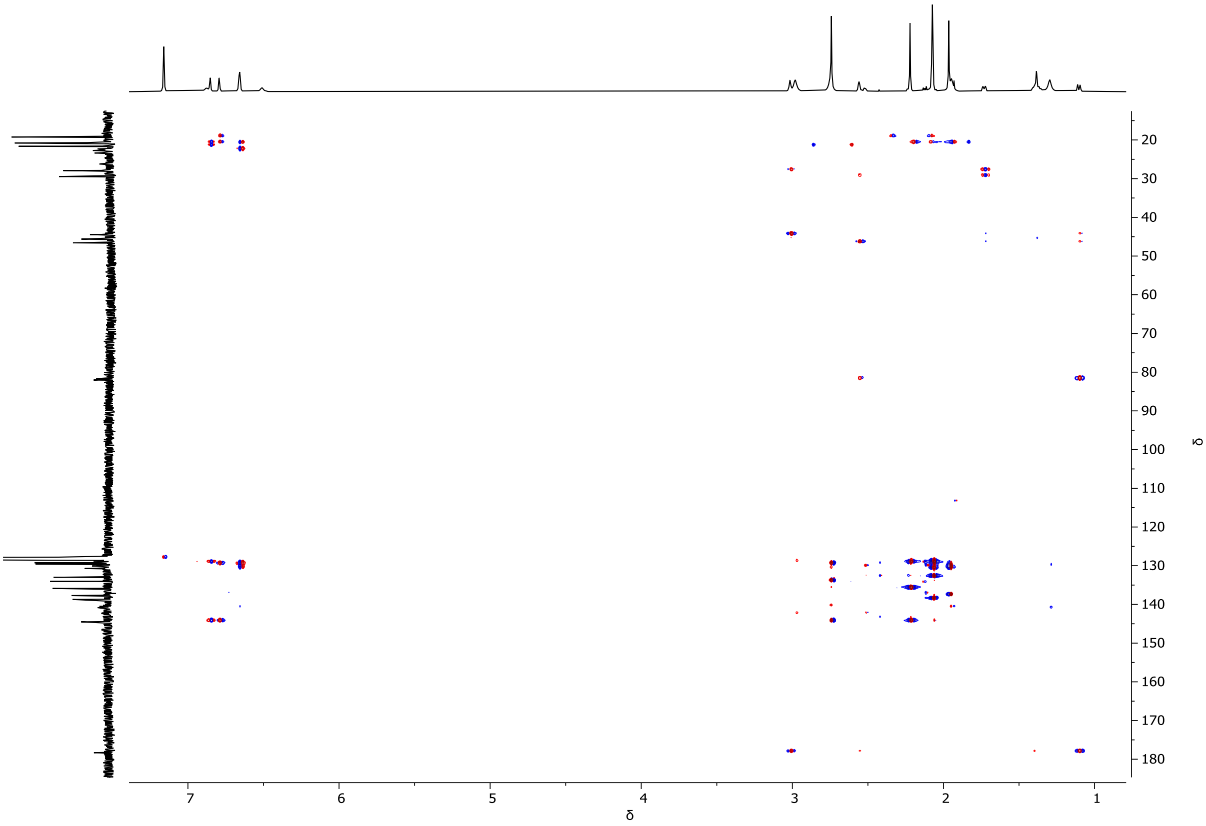


Figure S51. HMBC NMR spectrum of **7**.

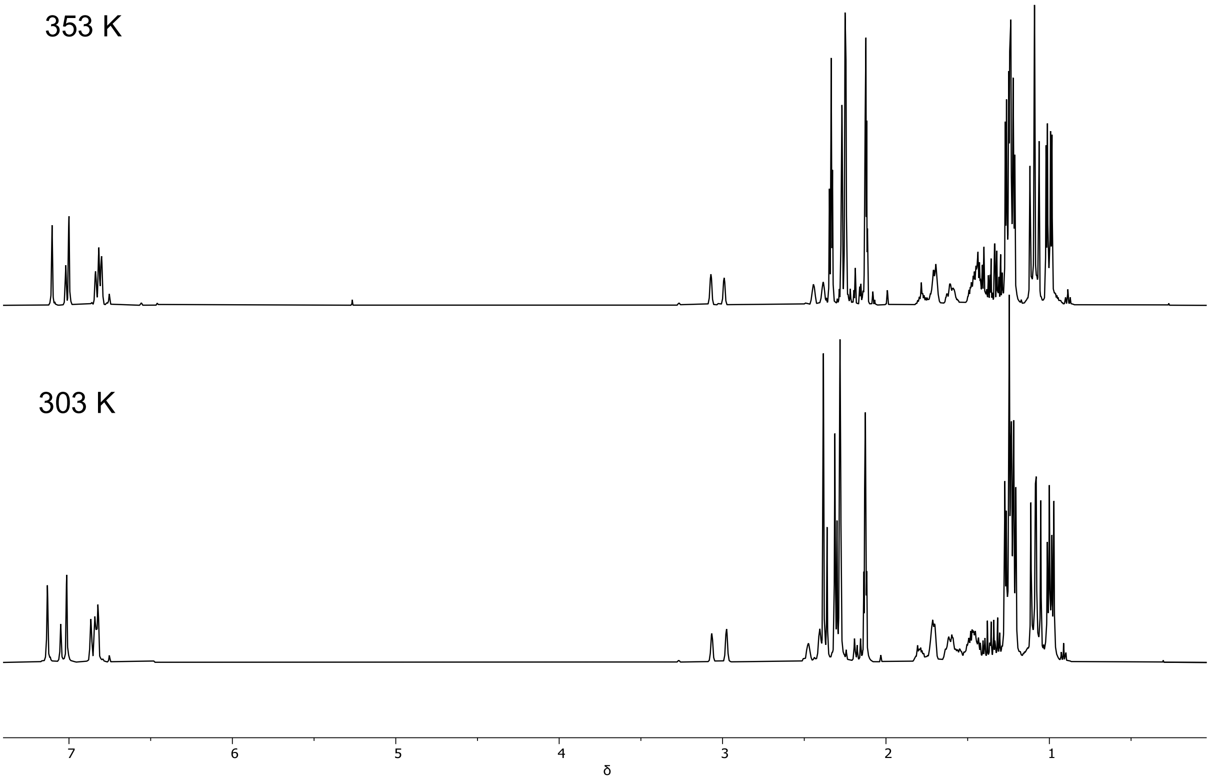


Figure S52. ^{1}H VT NMR spectra of **6** showing the loss of ethene (5.25 ppm) at elevated temperatures.

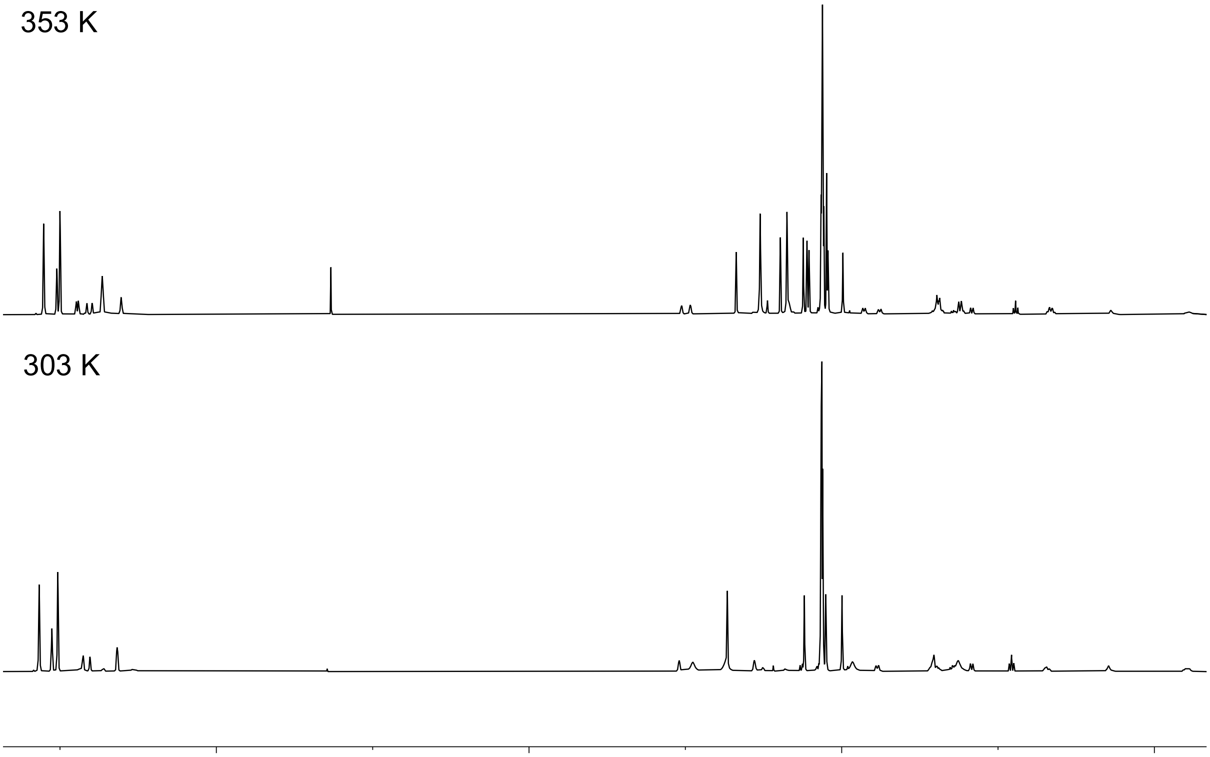


Figure S53. ^{1}H VT NMR spectra of **7** showing the loss of ethene (5.25 ppm) at elevated temperatures.

1.6.2 UV-visible spectra

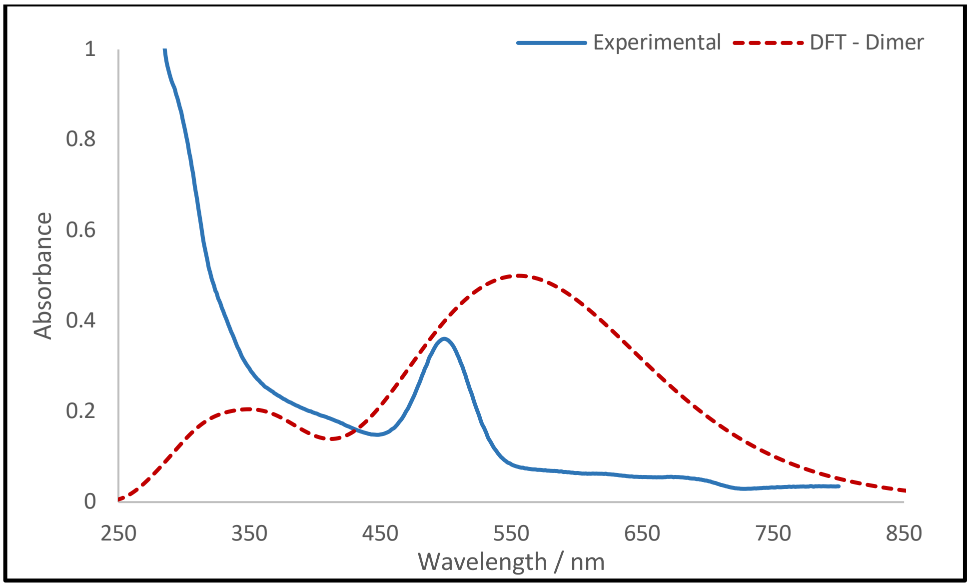


Figure S54. UV-visible spectrum of **1** in Et$_2$O at 298 K. TD-DFT determined spectrum for **1B** shown in dashed red.

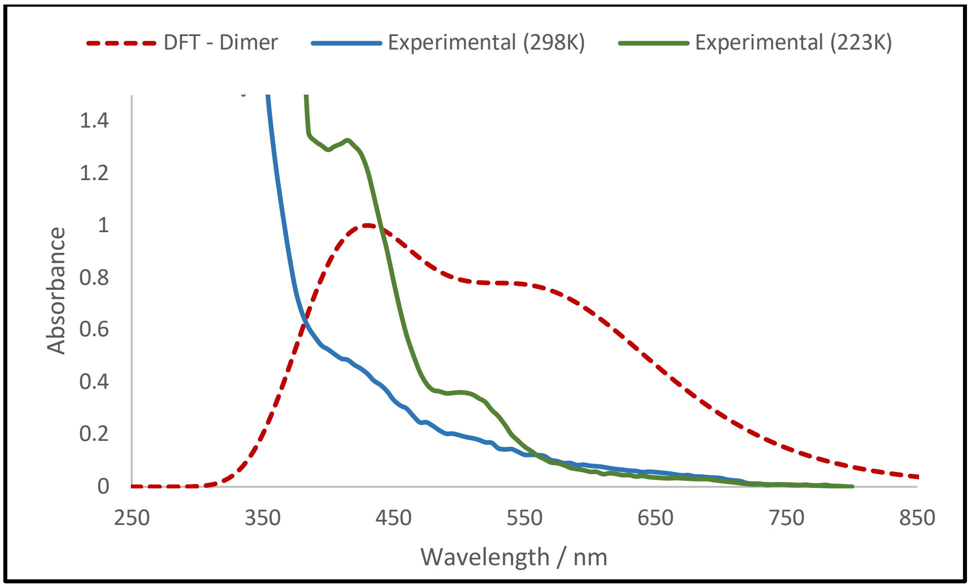


Figure S55. UV-visible spectrum of **2**/ [**2**]$_2$ in Et$_2$O at 298 K (blue) and 223 K (green). TD-DFT determined spectrum for [**2**]$_2$ shown in dashed red.

Table S7. Table of UV-visible absorptions and maximum extinction coefficient limits

Compound	**λ_{max} / nm**	**ε / L mol^{-1} cm^{-1}**
1 (298 K)	501	9847
	398 (shoulder)	1752
2 (298 K)	440	2081
2 (223 K)	510	3256 (minimum limit)
	414	6014 (minimum limit)

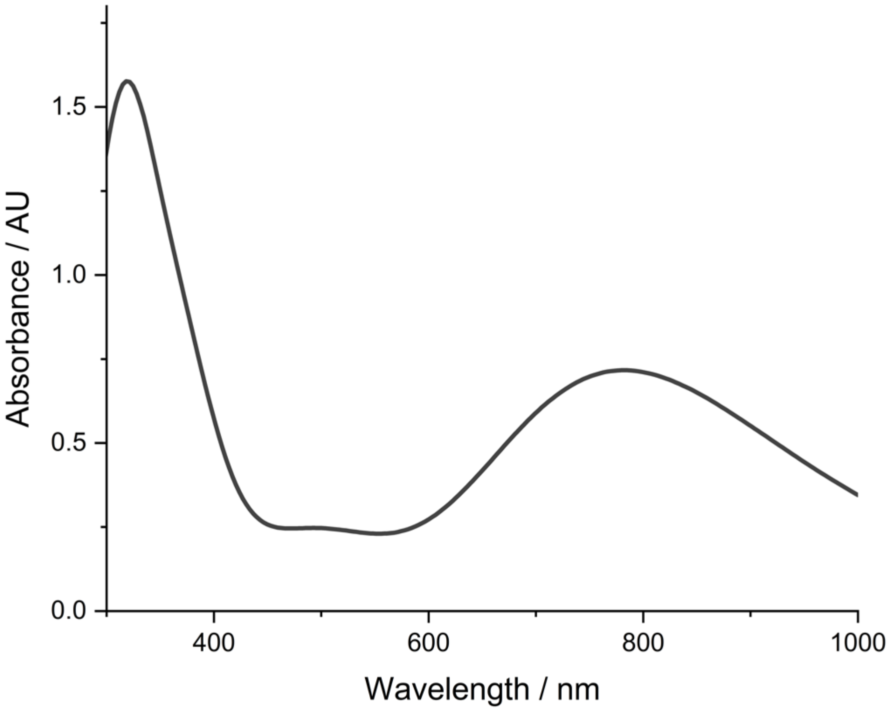


Figure S56. TD-DFT determined UV-visible spectrum for **5**.

S1.7 Solvates and orbitals of 5

Table S8. Table of bond lengths (Å), angles (°) and torsions (°) of the two different solvates of **5**.

	·2 PhF	**·4 PhF**
Ga – Ga	2.390(2)	2.4076(19)
Ga – N	1.834(7)	1.859(6)
Ga – P	2.338(3)	2.3489(19)
N – Ga – P	92.0(3)	91.07(19)
N – Ga – Ga – P	8.36	10.12

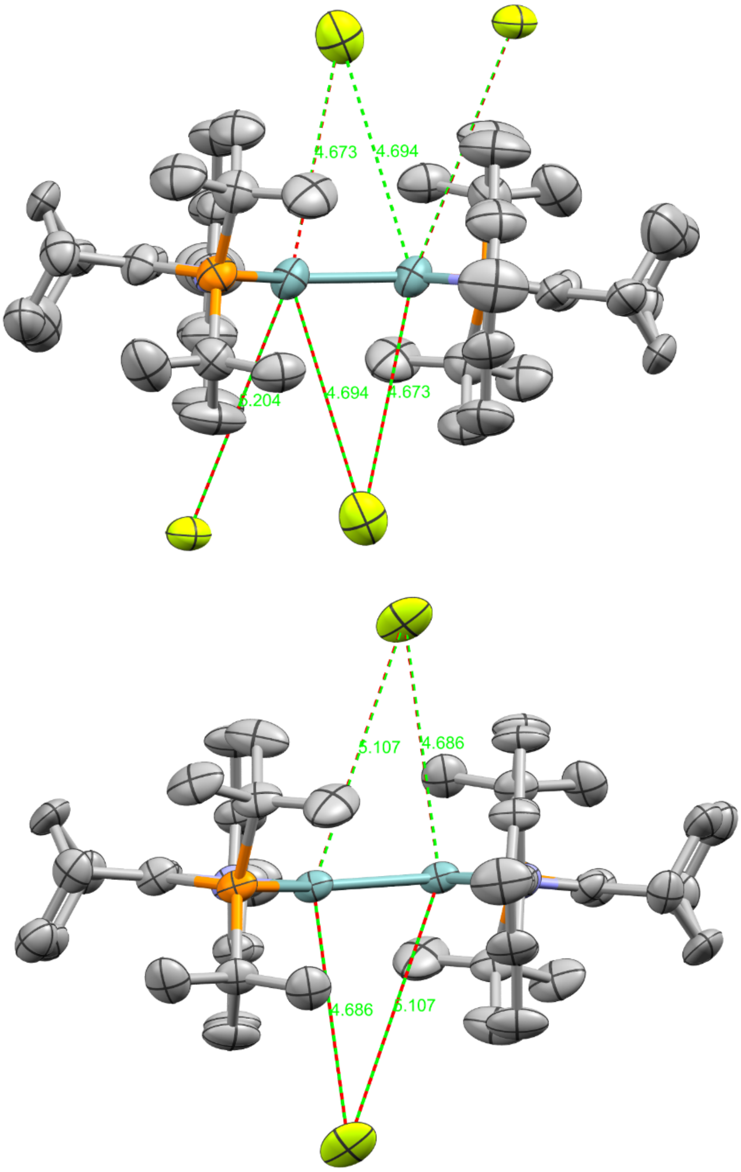
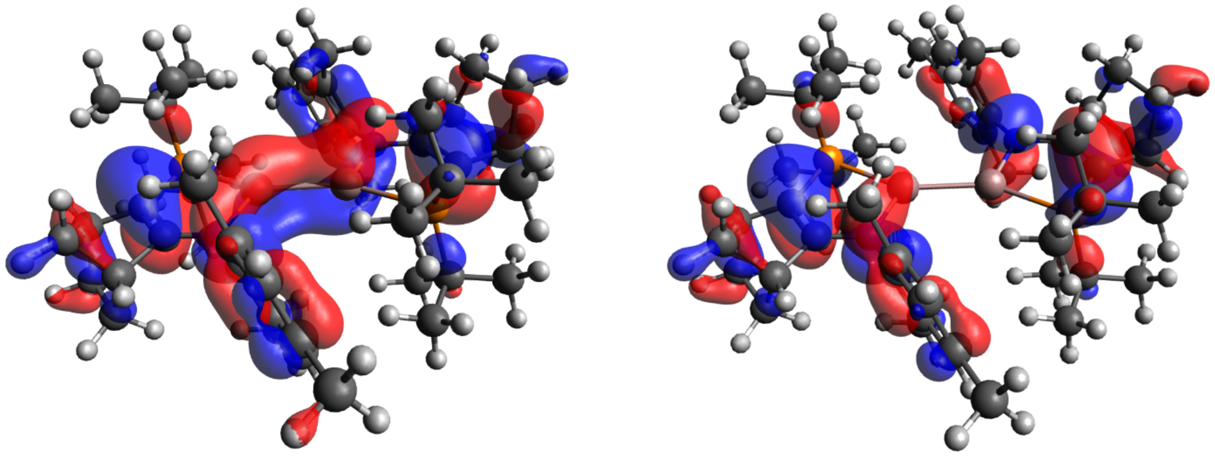
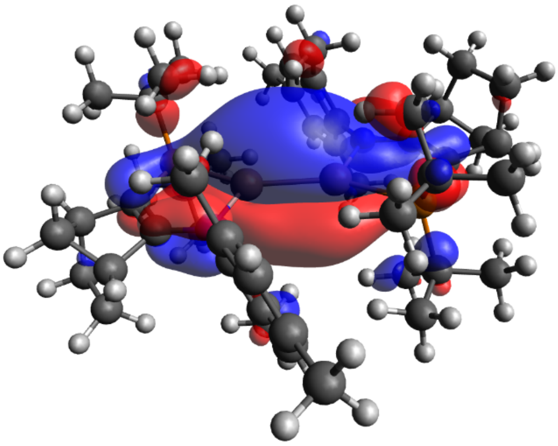


Figure S57. Ga-F contacts in the disolvate (top) and tetrasolvate (bottom) of **5**.



HOMO-1

HOMO



LUMO

Figure S58. HOMO-1, HOMO and LUMO of **5**.

S1.8 Stereoisomers of digallene 1

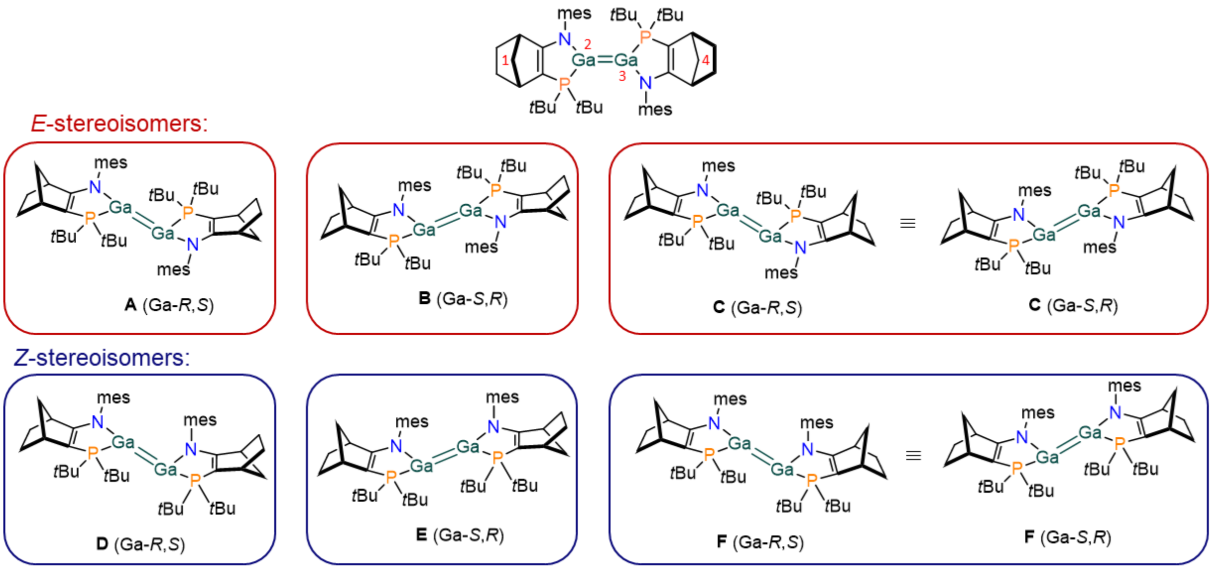


Figure S59. Stereoisomers **1A–1F** of digallene **1**.

S1.9 Transition states for ethene addition

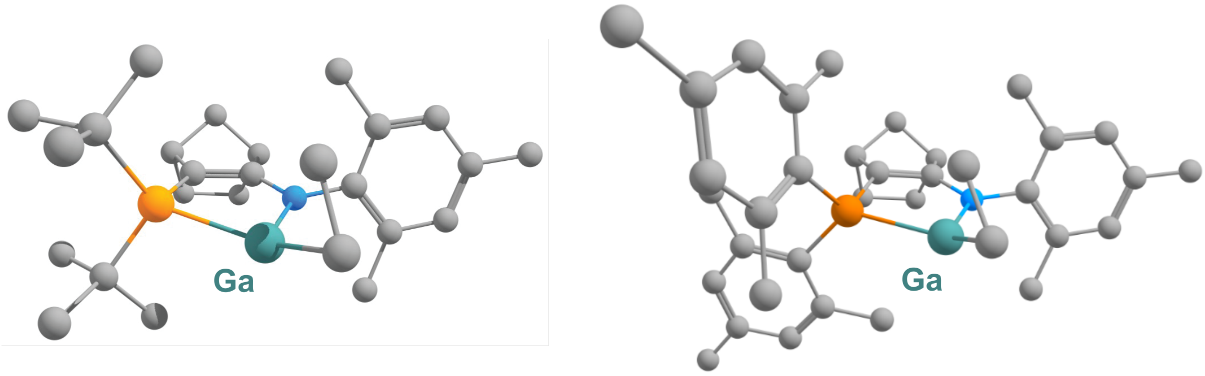


Figure S60. Transition states TS2 (left) and TS4 (right). (Addition of ethene from opposite face of Ga(I) monomer.)

References

1. M. Wang, F. Nudelman, R. R. Matthes and M. P. Shaver, *J. Am. Chem. Soc.*, 2017, **139**, 14232–14236.

2. R. L. Falconer, G. S. Nichol, I. V. Smolyar, S. L. Cockroft and M. J. Cowley, *Angew. Chem.*, 2021, **133**, 2075–2080.

3. P. Jutzi and L. O. Schebaum, *J. Organomet. Chem.*, 2002, **654**, 176–179.

4. Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

5. a) Boys, S. F.; Bernardi, F. Mol. Phys., 1970, 19, 553. b) Simon, S.; Duran, M.; Dannenberg, J. J. J. Chem. Phys., 1996, 105, 11024-11031.