

Electronic Supplementary Information

Vanadium Complexes with N-Heterocyclic Vinylidene Ligands

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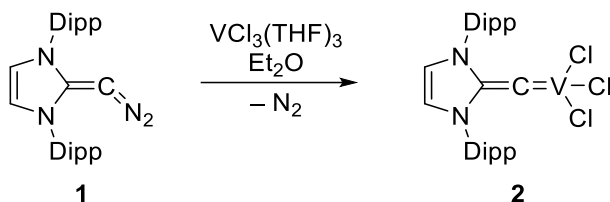
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1. General

Unless stated otherwise, reactions were performed under an atmosphere of dry dinitrogen using a glove box. Solvents were purified and dried using an innovation technology SPS solvent system, after which they were stored under molecular sieves for a minimum of two days. The diazoolefins **1** and **3** were synthesized as described in literature.^{1,2} All products were dried overnight under high vacuum using a diffusion pump. If not stated otherwise, all reagents were obtained from commercial sources and used without further purification. NMR spectra were measured on a Bruker Avance III-400 (¹H: 400 MHz) equipped with a 5 mm BBO probe, Bruker Avance IIIHD-600 (¹H: 600 MHz) equipped with a 5 mm BBO Prodigy N2 cooled cryoprobe and Bruker Avance IV-800 (¹H: 800 MHz) equipped with a 5 mm TBI He cooled cryoprobe at 298 K if not stated otherwise. Chemical shifts are given in parts per million (ppm) relative to their solvent signals [CD₂Cl₂, 5.32 (¹H-NMR) 53.84 (¹³C-NMR), d₈-thf, 3.58 (¹H-NMR) 67.21 (¹³C-NMR)]. ⁵¹V Solid-state NMR spectra were recorded on a 500 MHz Bruker spectrometer (11.7 T) equipped with an Avance III console and a 3.2 mm three-channel low temperature magic-angle spinning (MAS) probe. The sample was packed into a 3.2 mm zirconia rotor in a glove box and spun between 17 and 24 kHz spinning speed using dry nitrogen gas. Spectra were acquired at room temperatures using a one-pulse sequence with $\pi/32$ pulse of 0.23 μ s (72 kHz). Recycle delays were set to 0.8 s. ⁵¹V Chemical shifts were referenced to the signal of pure VOCl₃. The isotropic shift of the signal was identified by comparing ⁵¹V solid-state NMR spectra recorded at various sample spinning speeds (17 kHz, 20.5 kHz and 24 kHz). While the center band appears at the isotropic shift and remains unchanged upon varying the sample spinning speed (ν_r), the spinning sidebands, which are shifted by multiples of ν_r relative to the centerband, change in position, intensity and number with variable ν_r . UV-vis data were recorded on a Cary 60 Spectrometer (Agilent Technologies). Mass spectrometry analyses were performed on a LTQ Orbitrap FTMS instrument (LTQ Orbitrap Elite FTMS, Thermo Scientific) operated in the positive mode coupled with a robotic chip-based nano-ESI source (TriVersa Nanomate, Advion Biosciences). A standard data acquisition and instrument control system was utilized (Thermo Scientific) whereas the ion source was controlled by Chipsoft 8.3.1 software (Advion BioScience). Samples were loaded onto a 96-well plate within an injection volume of 5 μ l. The experimental conditions for the ionization voltage were +1.4 kV and the gas pressure was set at 0.30 psi. The temperature of ion transfer capillary was 200 °C. FTMS spectra were obtained in the 100-1000 m/z range in the reduce profile mode with a resolution set to 120,000. In all spectra 1 microscan was acquired with a maximum injection time value of 1000 ms. Due to the high sensitivity of the compounds when removed from the glove box, elemental analyses were not attempted.

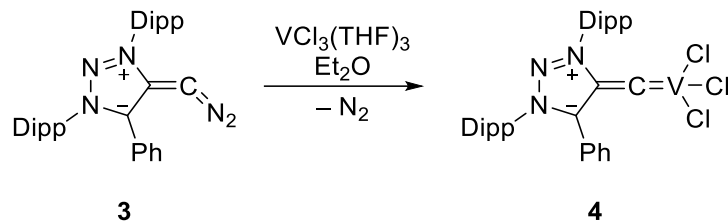
2. Synthesis



Complex 2: Diazoolefin **1** (50.0 mg, 117 μmol , 1.00 eq.) and $\text{VCl}_3(\text{THF})_3$ (45.0 mg, 117 μmol , 1.00 eq.) were combined in a vial and diethyl ether (2 mL) was added at $-40\text{ }^\circ\text{C}$ while stirring. The suspension was allowed to warm up to room temperature and was stirred for 2 d. The suspension was filtered and the green residue was washed with diethyl ether (2 x 1 mL) and pentane (3 x 1 mL). The residue was extracted with a minimal amount of DCM ($\sim 5\text{ mL}$) until the extract became almost colourless. The filtrate was then placed in a freezer at $-40\text{ }^\circ\text{C}$ for 3 d, after which green crystals had formed. The mother liquor was carefully removed by decantation. The remaining crystals were washed with pentane and were dried under reduced pressure to afford complex **2** as a green, crystalline solid (26.0 mg). Pentane was added to the decanted mother liquor until it started to become cloudy, and the solution was placed in a freezer at $-40\text{ }^\circ\text{C}$. After 29 h, a second batch of green crystals was obtained after carefully decanting the liquid. The crystals were washed with pentane and dried under reduced pressure (10.4 mg, 36.4 mg total, 56%).

Single crystals that were suitable for X-ray analysis were obtained by layering a benzene solution of **2** with pentane. These crystals appeared green in color.

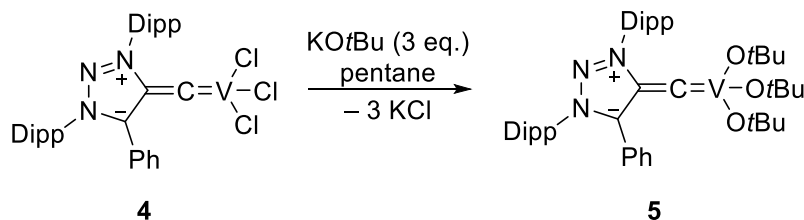
$^1\text{H NMR}$ (800 MHz, CD_2Cl_2) δ 7.63 (t, $J = 7.8\text{ Hz}$, 2H, CH_{arom} , Dipp, *para*), 7.45 (d, $J = 7.7\text{ Hz}$, 4H, CH_{arom} , Dipp, *meta*), 6.75 (s, 2H, CH, imidazole), 2.61 (hept, $J = 6.7\text{ Hz}$, 4H, $\text{CH}(\text{CH}_3)_2$), 1.56 (d, $J = 6.8\text{ Hz}$, 12H, CH_3), 1.22 (d, $J = 6.8\text{ Hz}$, 12H, CH_3). **$\{^1\text{H}\}^{13}\text{C NMR}$** (201 MHz, CD_2Cl_2) δ 146.44 (Dipp, *ortho*), 131.93 (Dipp, *para*), 130.54 (Dipp, *ipso*), 124.92 (Dipp, *meta*), 119.37 ($\text{CH}_{\text{imidazole}}$), 29.75 ($\text{CH}(\text{CH}_3)_2$), 24.66 ($\text{CH}(\text{CH}_3)_2$), 23.73 ($\text{CH}(\text{CH}_3)_2$). *Note:* the $\text{C}=\text{C}=\text{V}$ and $\text{C}=\text{C}=\text{V}$ signals were not observed. **UV/Vis** (DCM, λ_{max} , nm): 396 ($\epsilon = 0.22 \times 10^4\text{ M}^{-1}\text{cm}^{-1}$), 271 ($\epsilon = 0.80 \times 10^4\text{ M}^{-1}\text{cm}^{-1}$), 265 ($\epsilon = 0.84 \times 10^4\text{ M}^{-1}\text{cm}^{-1}$). **HRMS** (nanochip-ESI/LTQ-Orbitrap) m/z : $[\text{M} + \text{H}]^+$ Calcd. for $\text{C}_{28}\text{H}_{37}\text{Cl}_3\text{N}_2\text{V}^+$ 557.1456; Found 557.1430.



Complex 4: Diazoolefin **3** (40.0 mg, 79.0 μmol , 1.00 eq.) and $\text{VCl}_3(\text{THF})_3$ (30.0 mg, 79.0 μmol , 1.00 eq.) were combined in a vial, and diethyl ether (2.5 mL) was added at -40°C . The resulting suspension was stirred at room temperature for 2 h. The bright green suspension was filtered, and the residue was washed with diethyl ether (1 mL) and pentane (3 x 1 mL). The powder was then extracted with DCM (~ 2 mL) until the extract became colourless. The solvent was removed under reduced pressure to give complex **4** as a green powder (41.0 mg, 82%).

Single crystals that were suitable for X-ray analysis were obtained by layering a benzene solution of **4** with pentane. These crystals appeared green in colour.

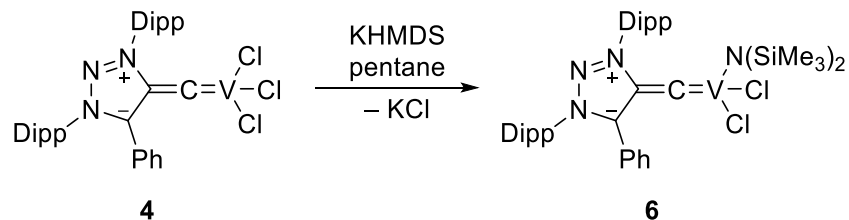
$^1\text{H NMR}$ (800 MHz, CD_2Cl_2) δ 7.90 (d, $J = 7.7$ Hz, 2H, CH_{arom} , Ph, *ortho*), 7.74 (t, $J = 7.9$ Hz, 1H, CH_{arom} , Dipp, *para*), 7.65 (t, $J = 7.8$ Hz, 1H, CH_{arom} , Dipp, *para*), 7.57 – 7.46 (m, 5H, CH_{arom} , Dipp, *meta*, and CH_{arom} , Ph, *meta+para*), 7.36 (d, $J = 7.8$ Hz, 2H, CH_{arom} , Dipp, *meta*), 2.52 (hept, $J = 6.8$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 2.23 (hept, $J = 7.0$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 1.61 (d, $J = 6.8$ Hz, 6H, CH_3), 1.17 (d, $J = 6.9$ Hz, 6H, CH_3), 1.12 (d, $J = 6.9$ Hz, 6H, CH_3), 0.95 (d, $J = 6.7$ Hz, 6H, CH_3). **$\{^1\text{H}\}^{13}\text{C NMR}$** (126 MHz, CD_2Cl_2) δ 315.00 ($\text{C}=\underline{\text{C}}=\text{V}$ or $\underline{\text{C}}=\text{C}=\text{V}$), 146.34 (C_q , Dipp, *ortho*), 145.49 (C_q , Dipp, *ortho*), 139.38 (triaz- C_q), 133.40 (CH_{arom} , Dipp, *para*), 133.05 (CH_{arom} , Dipp, *para*), 132.54 (CH_{arom} , Ph, *para*), 130.57 (C_q , Dipp, *ipso*), 130.23 (C_q , Dipp, *ipso*), 129.58 (CH_{arom} , Ph, *ortho or meta*), 129.56 (CH_{arom} , Ph, *ortho or meta*), 125.73 (CH_{arom} , Dipp, *meta*), 125.11 (CH_{arom} , Dipp, *meta*), 122.10 (C_q , Ph), 29.95 ($\underline{\text{C}}\text{H}(\text{CH}_3)_2$), 29.64 ($\underline{\text{C}}\text{H}(\text{CH}_3)_2$), 25.37 (CH_3), 25.19 (CH_3), 23.14 (CH_3), 22.64 (CH_3). *Note:* the $\underline{\text{C}}=\text{C}=\text{V}$ and $\text{C}=\underline{\text{C}}=\text{V}$ signals were not observed. **$^{51}\text{V NMR}$** (132 MHz, solid-state NMR, isotropic shift) $\delta - 1290$. **UV/Vis** (THF, λ_{max} , nm): 384 ($\epsilon = 1.21 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), 268 ($\epsilon = 3.48 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). **HRMS** (nanochip-ESI/LTQ-Orbitrap) m/z : $[\text{M} + \text{H}]^+$ Calcd. for $\text{C}_{33}\text{H}_{40}\text{Cl}_3\text{N}_3\text{V}^+$ 634.1722; Found 634.1699.



Complex 5: Complex **4** (10.0 mg, 15.8 μmol , 1.00 eq.) and potassium *tert*-butoxide (5.6 mg, 49 μmol , 3.1 eq.) were combined in a vial and cold pentane (1.5 mL) was added at $-40\text{ }^\circ\text{C}$ while stirring. The suspension started to turn red after several minutes and was allowed to stir vigorously for 30 min at room temperature. The dark red suspension was then filtered, and the filtrate was evaporated under reduced pressure to afford complex **5** as a red solid (9.4 mg, 82%).

Single crystals that were suitable for X-ray analysis were obtained by slow evaporation of a pentane solution of **5**. These crystals appeared dark orange in colour.

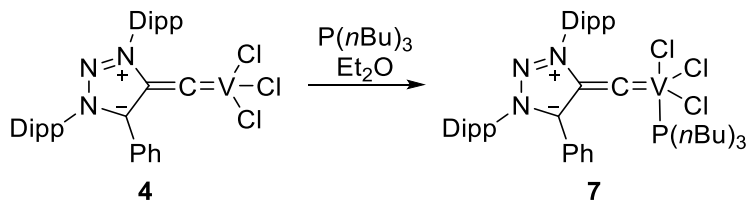
^1H NMR (400 MHz, CD_2Cl_2) δ 8.09 – 8.01 (m, 2H, CH_{arom} , Ph, *ortho*), 7.57 (t, $J = 7.8$ Hz, 1H, CH_{arom} , Dipp, *para*), 7.54 (t, $J = 7.8$ Hz, 1H, CH_{arom} , Dipp, *para*), 7.37 (d, $J = 7.8$ Hz, 2H, CH_{arom} , Dipp, *meta*), 7.36 – 7.18 (m, 5H, CH_{arom} , Ph, *meta+para* and CH_{arom} , Dipp, *meta*), 2.78 (hept, $J = 6.9$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 2.49 (hept, $J = 6.8$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 1.46 (d, $J = 6.8$ Hz, 6H, Dipp, CH_3), 1.12 (d, $J = 6.8$ Hz, 6H, Dipp, CH_3), 1.12 (s, 27H, OtBu_3 , CH_3), 1.09 (d, $J = 6.9$ Hz, 6H, Dipp, CH_3), 0.92 (d, $J = 6.8$ Hz, 6H, Dipp, CH_3). **$\{^1\text{H}\}^{13}\text{C}$ NMR** (101 MHz, CD_2Cl_2) δ 146.84 (C_q , Dipp, *ortho*), 145.56 (C_q , Dipp, *ortho*), 140.32 (triazolene- C_q), 132.83 (C_q , Dipp, *ipso*), 132.35 (CH_{arom} , Dipp, *para*), 132.07 (C_q , Dipp, *ipso*), 131.78 (CH_{arom} , Dipp, *para*), 129.92 (CH_{arom} , Ph, *para*), 129.25 (CH_{arom} , Ph, *ortho*), 128.48 (CH_{arom} , Ph, *meta*), 125.42 (C_q , Ph, *ipso*), 125.34 (CH_{arom} , Dipp, *meta*), 124.82 (CH_{arom} , Dipp, *meta*), 76.37 ($\text{OC}(\text{CH}_3)_3$), 33.20 ($\text{OC}(\text{CH}_3)_3$), 29.43 ($\text{CH}(\text{CH}_3)_2$), 29.25 ($\text{CH}(\text{CH}_3)_2$), 25.74 ($\text{CH}(\text{CH}_3)_2$), 25.34 ($\text{CH}(\text{CH}_3)_2$), 23.14 ($\text{CH}(\text{CH}_3)_2$), 22.78 ($\text{CH}(\text{CH}_3)_2$). *Note:* the $\text{C}=\text{C}=\text{V}$ and $\text{C}=\text{C}=\text{V}$ signals were not observed. **UV/Vis** (*n*-pentane, λ_{max} , nm): 323_{sh} ($\epsilon = 0.50 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), 266 ($\epsilon = 1.15 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). **HRMS** (nanochip-ESI/LTQ-Orbitrap) *m/z*: $[\text{M} + \text{H}]^+$ Calcd. for $\text{C}_{45}\text{H}_{67}\text{N}_3\text{O}_3\text{V}^+$ 748.4617; Found 748.4611.



Complex 6: Complex **4** (10.2 mg, 16.0 μmol , 1.00 eq.) and KHMDS (3.5 mg, 17 μmol , 1.1 eq.) were combined in a vial, after which cold pentane (1.5 mL) was added at $-40\text{ }^\circ\text{C}$ while stirring. The solution was allowed to warm up to room temperature and was stirred vigorously for 3 h. The precipitate was isolated by filtration and then suspended in pentane (1.5 mL) using sonification. Filtration and drying under reduced pressure gave complex **6** as a dark green solid (8.3 mg, 69%).

Single crystals that were suitable for X-ray analysis were obtained by slow evaporation of a pentane solution of **6**. These crystals appeared dark yellow in colour.

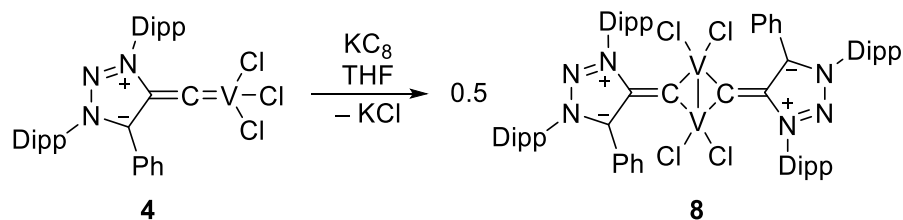
$^1\text{H NMR}$ (800 MHz, CD_2Cl_2) δ 7.71 (d, $J = 7.7$ Hz, 2H, CH_{arom} , Ph, *ortho*), 7.66 (t, $J = 7.7$ Hz, 1H, CH_{arom} , Dipp, *para*), 7.61 (t, $J = 7.7$ Hz, 1H, CH_{arom} , Dipp, *para*), 7.47 (d, $J = 7.8$ Hz, 2H, CH_{arom} , Dipp, *meta*), 7.41 (t, $J = 7.3$ Hz, 2H, CH_{arom} , Ph, *para*), 7.37-7.33 (m, 4H, CH_{arom} , Ph, *meta* and CH_{arom} , Dipp, *meta*) 2.65 (hept, $J = 7.0$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 2.31 (hept, $J = 8.0$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 1.54 (d, $J = 6.7$ Hz, 6H, Dipp, CH_3), 1.17 (d, $J = 6.8$ Hz, 6H, Dipp, CH_3), 1.14 (d, $J = 6.8$ Hz, 6H, Dipp, CH_3), 0.92 (d, $J = 6.7$ Hz, 6H, Dipp, CH_3), 0.06 (s, 18H, HMDS, CH_3). **$\{^1\text{H}\}^{13}\text{C NMR}$** (201 MHz, CD_2Cl_2) δ 146.39 (C_q , Dipp, *ortho*), 145.59 (C_q , Dipp, *ortho*), 137.76 (triaz- C_q), 133.04 (CH_{arom} , Dipp, *para*), 132.38 (CH_{arom} , Dipp, *para*), 131.49 (C_q , Dipp, *ipso*), 131.47 (CH_{arom} , Ph, *para*), 130.32 (C_q , Dipp, *ipso*), 130.09 (CH_{arom} , Ph, *ortho*), 129.27 (CH_{arom} , Ph, *meta*), 125.43 (CH_{arom} , Dipp, *meta*), 125.18 (CH_{arom} , Dipp, *meta*), 123.71 (C_q , Ph, *ipso*), 29.88 ($\text{CH}(\text{CH}_3)_2$), 29.51 ($\text{CH}(\text{CH}_3)_2$), 25.39 (Dipp, CH_3), 25.29 (Dipp, CH_3), 23.71 (Dipp, CH_3), 22.62 (Dipp, CH_3), 4.61 (b, HMDS, CH_3). *Note:* the $\text{C}=\text{C}=\text{V}$ and $\text{C}=\text{C}=\text{V}$ signals were not observed. **UV/Vis** (THF, λ_{max} , nm): 391 ($\epsilon = 0.58 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), 257_{sh} ($\epsilon = 2.19 \times 10^4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). **HRMS** (nanochip-ESI/LTQ-Orbitrap): complex **6** could not be detected by mass spectrometry.



Complex 7: Complex **4** (12.8 mg, 20.2 μmol , 1.00 eq.) was suspended in diethyl ether (2 mL) and was cooled to $-40\text{ }^\circ\text{C}$. $\text{P}(n\text{Bu})_3$ (5.10 μL , 20.4 μmol , 1.01 eq) was then added to the suspension while stirring using a microsyringe. The suspension was allowed to warm up to room temperature and was stirred vigorously for 3 h, after which it was filtered. The yellow residue was washed with diethyl ether (1 mL) and pentane (3 x 1 mL), after which it was dried under reduced pressure to afford complex **7** as a light green solid (13.4 mg, 89%).

Single crystals that were suitable for X-ray analysis were obtained by layering a THF solution of **7** with pentane. These crystals appeared yellow in colour.

^1H NMR (400 MHz, CD_2Cl_2) δ 7.81 – 7.78 (m, 2H, CH_{arom} , Ph, *ortho*), 7.69 (t, $J = 7.8$ Hz, 1H, CH_{arom} , Dipp, *para*), 7.60 (t, $J = 7.8$ Hz, 1H, CH_{arom} , Dipp, *para*), 7.56 – 7.40 (m, 5H, CH_{arom} , Ph, *para/meta*, CH_{arom} , Dipp, *meta*), 7.31 (d, $J = 7.8$ Hz, 2H, CH_{arom} , Dipp, *meta*), 2.62 (hept, $J = 7.0$ Hz, 2H, $\underline{\text{C}}\text{H}(\text{CH}_3)_2$), 2.22 (hept, $J = 6.8$ Hz, 2H, $\underline{\text{C}}\text{H}(\text{CH}_3)_2$), 1.69 (d, $J = 6.7$ Hz, 6H, Dipp, CH_3), 1.63 – 1.40 (m, 6H, *n*Bu, CH_2), 1.27 – 0.95 (m, 24H, Dipp, CH_3 , *n*Bu, CH_2), 0.87 (d, $J = 6.7$ Hz, 6H, Dipp, CH_3), 0.79 (t, $J = 6.8$ Hz, 9H, *n*Bu, CH_3). **$\{^1\text{H}\}^{31}\text{P}$ NMR** (162 MHz, CD_2Cl_2) δ 30.82. **$\{^1\text{H}\}^{13}\text{C}$ NMR** (101 MHz, CD_2Cl_2) δ 146.60 (C_q , Dipp, *ortho*), 145.58 (C_q , Dipp, *ortho*), 138.50 (triaz- C_q), 133.16 (CH_{arom} , Dipp, *para*), 132.64 (CH_{arom} , Dipp, *para*), 132.02 (CH_{arom} , Ph, *ortho*), 131.17 (C_q , Dipp, *ipso*), 130.72 (CH_{arom} , Ph, *ortho*), 130.02 (C_q , Dipp, *ipso*), 129.74 (CH_{arom} , Dipp, *meta*), 125.60 (CH_{arom} , Dipp, *meta*), 124.50 (CH_{arom} , Ph, *meta*), 122.77 (C_q , Ph, *ipso*), 30.13 ($\underline{\text{C}}\text{H}(\text{CH}_3)_2$), 29.5ff3 ($\underline{\text{C}}\text{H}(\text{CH}_3)_2$), 26.52 (*n*Bu, $\underline{\text{C}}\text{H}_2$), 26.17 (Dipp, $\underline{\text{C}}\text{H}_3$), 25.65 (Dipp, $\underline{\text{C}}\text{H}_3$), 25.64 (d, $J = 16.2$ Hz, *n*Bu, $\underline{\text{C}}\text{H}_2$), 24.82 (d, $J = 11.2$ Hz, *n*Bu, $\underline{\text{C}}\text{H}_2$), 22.76 (Dipp, $\underline{\text{C}}\text{H}_3$), 22.64 (Dipp, $\underline{\text{C}}\text{H}_3$), 13.99 (*n*Bu, $\underline{\text{C}}\text{H}_3$). *Note:* the $\underline{\text{C}}=\text{C}=\text{V}$ and $\text{C}=\underline{\text{C}}=\text{V}$ signals were not observed. **UV/Vis** (THF, λ_{max} , nm): 384 ($\epsilon = 0.71 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), 268 ($\epsilon = 1.77 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). **HRMS** (nanochip-ESI/LTQ-Orbitrap): complex **7** could not be detected by mass spectrometry.



Complex 8: Complex **4** (7.0 mg, 11 μmol , 1.0 eq.) and KC_8 (1.6 mg, 12 μmol , 1.1 eq.) were combined in a vial and cold THF (1.5 mL) was added at -40°C while stirring. The suspension was allowed to warm up to room temperature and was stirred for 2 h, after which it was filtered. The solvent was removed under reduced pressure, and the residue was suspended in diethyl ether (1 mL) using sonification. The product was isolated by filtration, washed with diethyl ether (~ 0.5 mL) and pentane (3 x 1 mL), and dried under vacuum to give complex **8** as a dark solid (4.3 mg, 65%).

Single crystals that were suitable for X-ray analysis were obtained by layering a benzene solution of **8** with pentane. These crystals appeared dark yellow in colour.

^1H NMR (600 MHz, CD_2Cl_2) δ 7.57 – 7.45 (m, 4H, CH_{arom} , Dipp, *para* and CH_{arom} , Ph, *ortho*), 7.35 – 7.26 (m, 7H, CH_{arom} , Ph, *para*, CH_{arom} , Ph, *meta*, and CH_{arom} , Dipp, *meta*), 2.57 (hept, $J = 6.9$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.25 (d, $J = 6.7$ Hz, 6H, CH_3), 1.13 (d, $J = 6.8$ Hz, 6H, CH_3), 1.04 (d, $J = 6.8$ Hz, 6H, CH_3), 0.98 (d, $J = 6.7$ Hz, 6H, CH_3). **$\{^1\text{H}\}^{13}\text{C}$ NMR** (151 MHz, CD_2Cl_2) δ 146.18 (C_q , Dipp, *ortho*), 146.11 (C_q , Dipp, *ortho*), 132.44 (CH_{arom} , Dipp, *para*), 132.05 (C_q , Dipp, *ipso*), 132.00 (CH_{arom} , Dipp, *para*), 131.46 (CH_{arom} , Ph, *ortho*), 130.49 (C_q , Dipp, *ipso*), 129.74 (CH_{arom} , Ph, *para*), 128.49 (CH_{arom} , Ph, *meta*), 125.67 (C_q triaz), 125.25 (C_q , Ph), 125.17 (CH_{arom} , Dipp, *meta*), 124.56 (CH_{arom} , Ph, *meta*), 29.38 ($\underline{\text{C}}\text{H}(\text{CH}_3)_2$), 29.35 ($\underline{\text{C}}\text{H}(\text{CH}_3)_2$), 26.54 (CH_3), 25.99 (CH_3), 22.93 (CH_3). *Note:* the $\underline{\text{C}}=\text{C}=\text{V}$ and $\text{C}=\underline{\text{C}}=\text{V}$ signals were not observed. **UV/Vis** (THF, λ_{max} , nm): 326 ($\epsilon = 0.43 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$), 276 ($\epsilon = 0.89 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$). **HRMS** (nanochip-ESI/LTQ-Orbitrap): complex **8** could not be detected by mass spectrometry.

3. NMR data

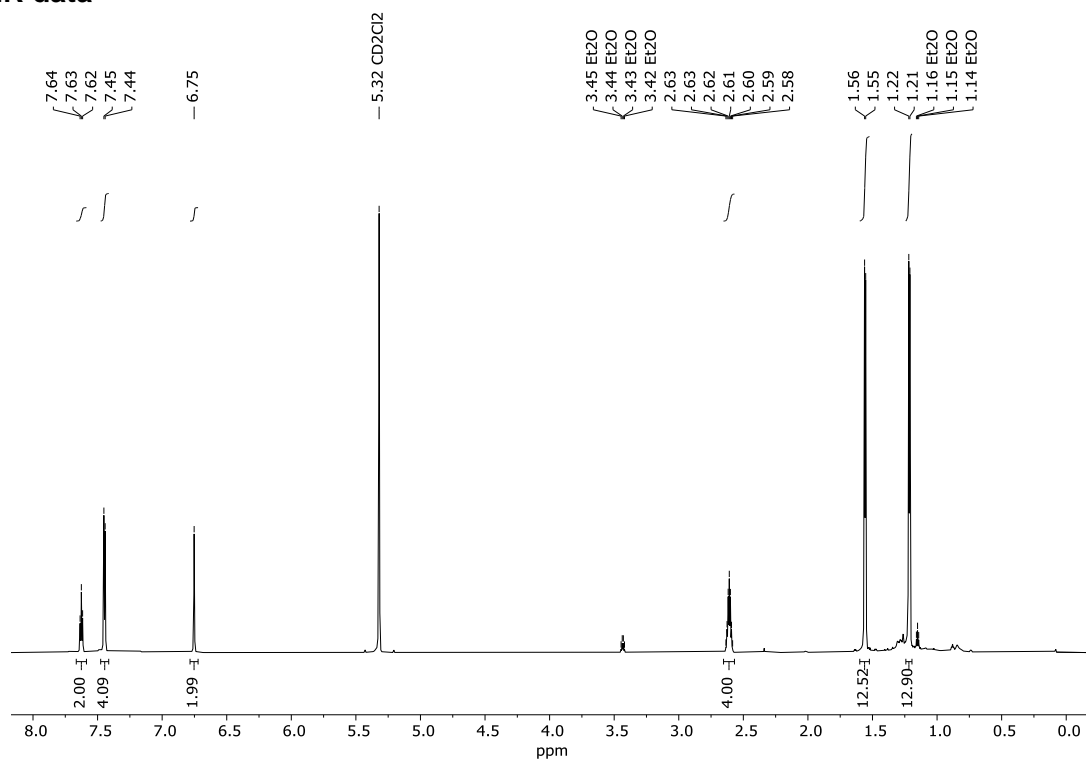


Figure S1. ¹H NMR (800 MHz, CD₂Cl₂) spectrum of 2.

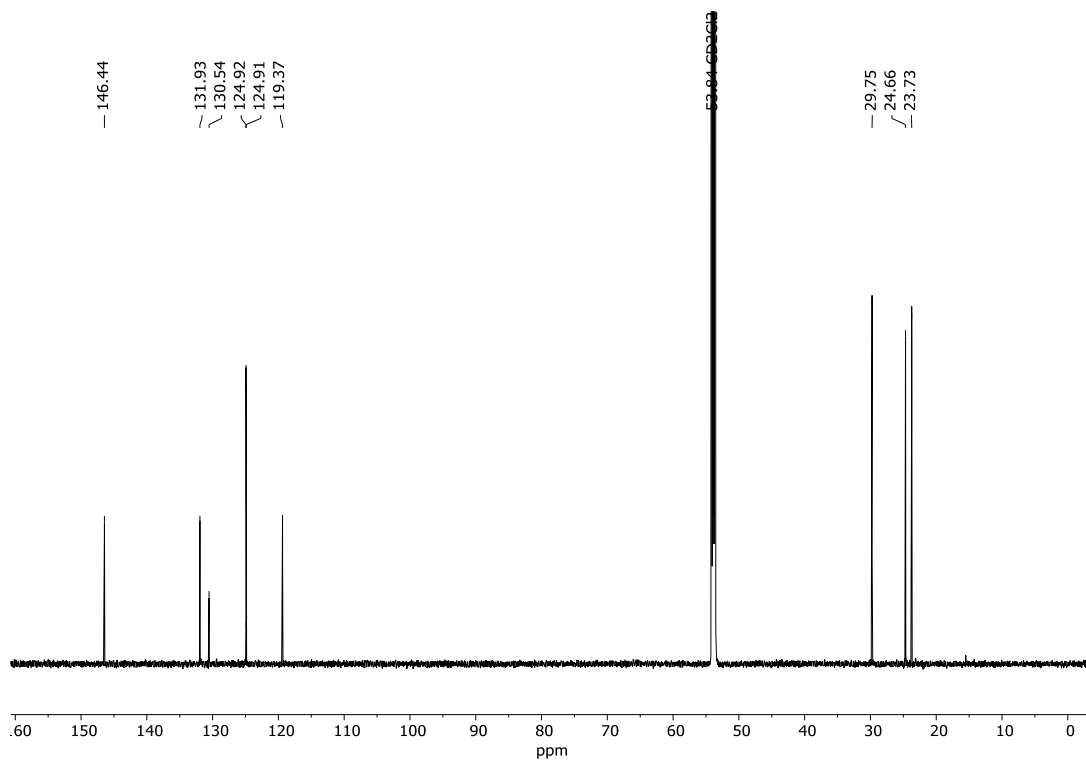


Figure S2. ¹H¹³C NMR (200 MHz, CD₂Cl₂) spectrum of 2.

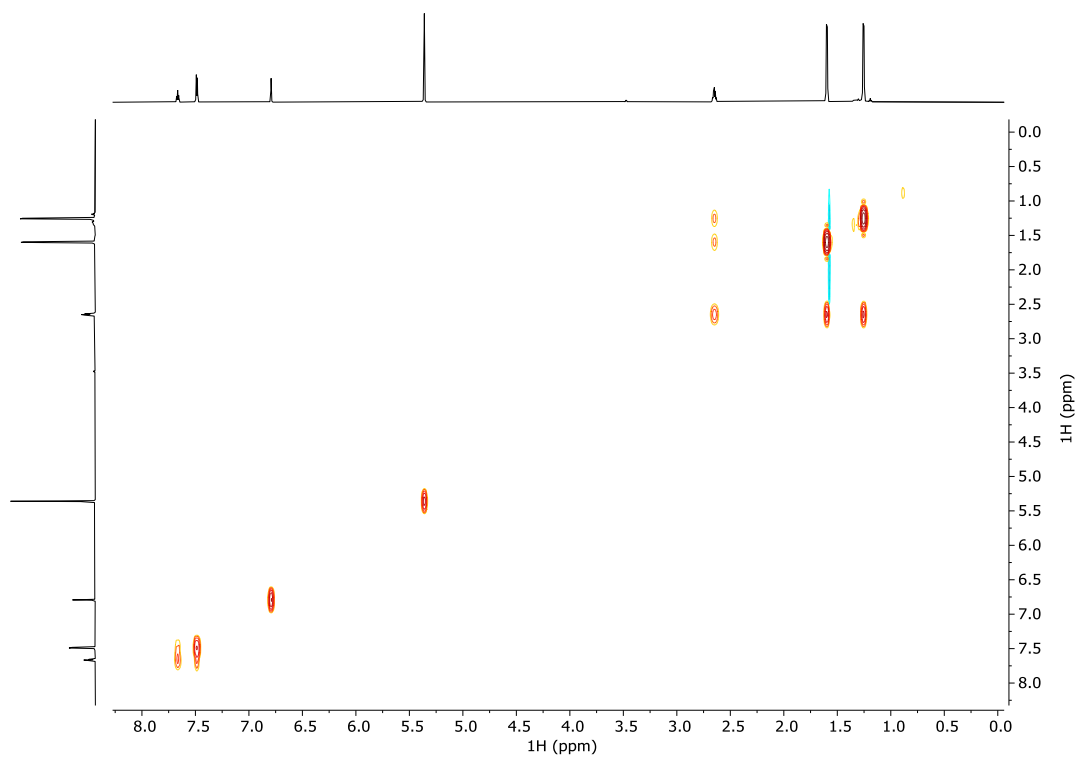


Figure S3. ^1H COSY NMR (CD_2Cl_2) spectrum of **2**.

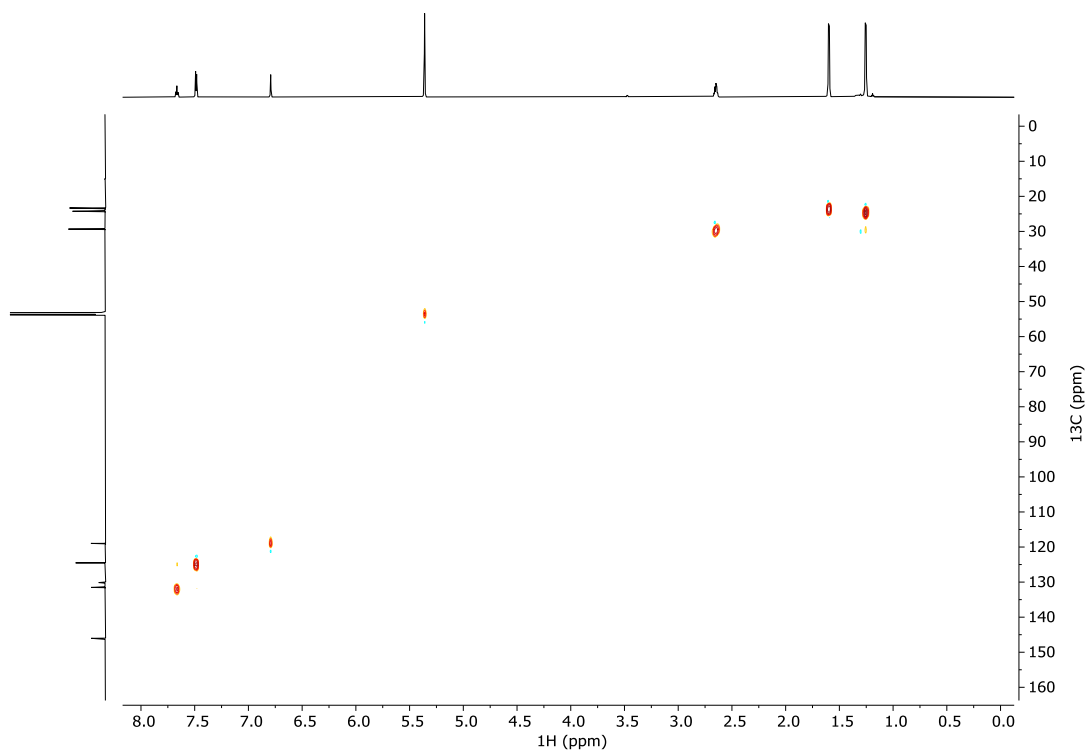


Figure S4. $^1\text{H}/^{13}\text{C}$ HSQC NMR (CD_2Cl_2) spectrum of **2**.

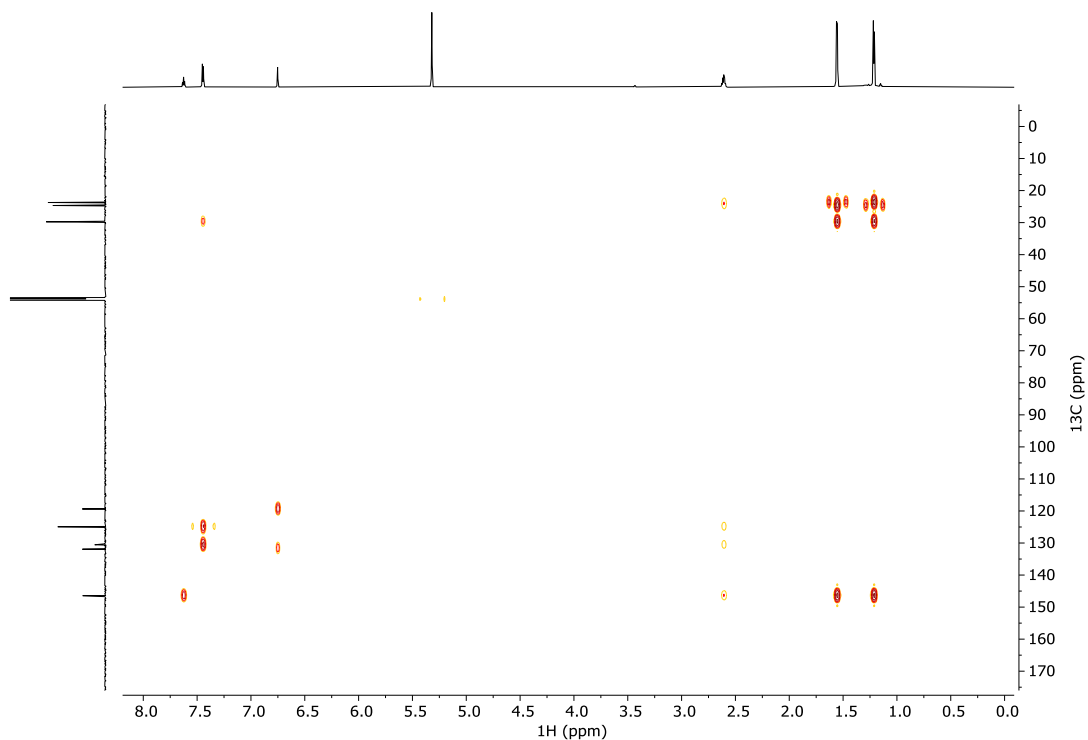


Figure S5. $^1\text{H}/^{13}\text{C}$ HMBC NMR (CD_2Cl_2) spectrum of **2**.

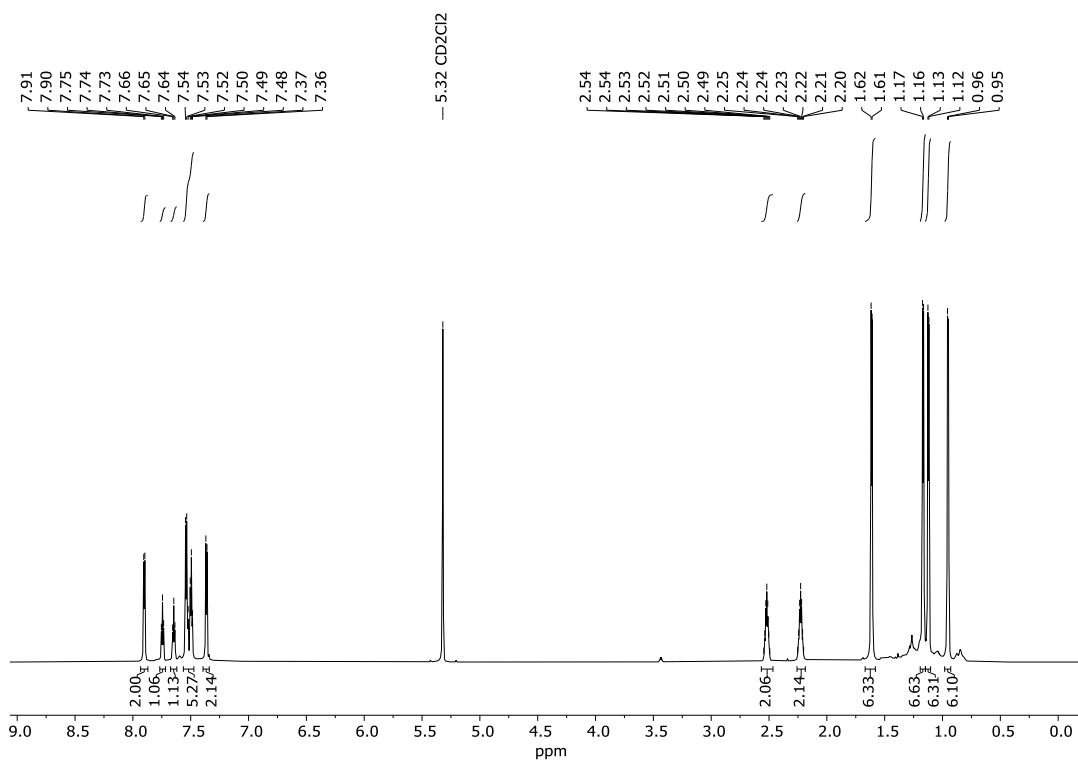


Figure S6. ^1H NMR (800 MHz, CD_2Cl_2) spectrum of **4**.

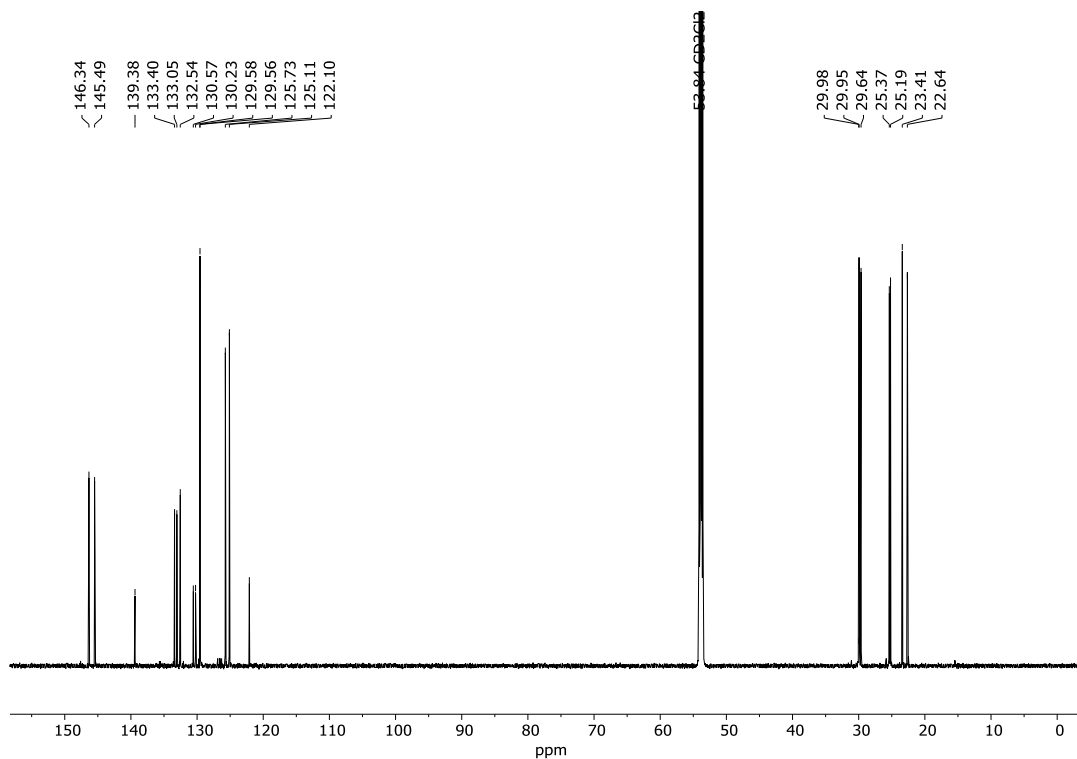


Figure S7. $\{^1\text{H}\}^{13}\text{C}$ NMR (200 MHz, CD_2Cl_2) spectrum of **4**.

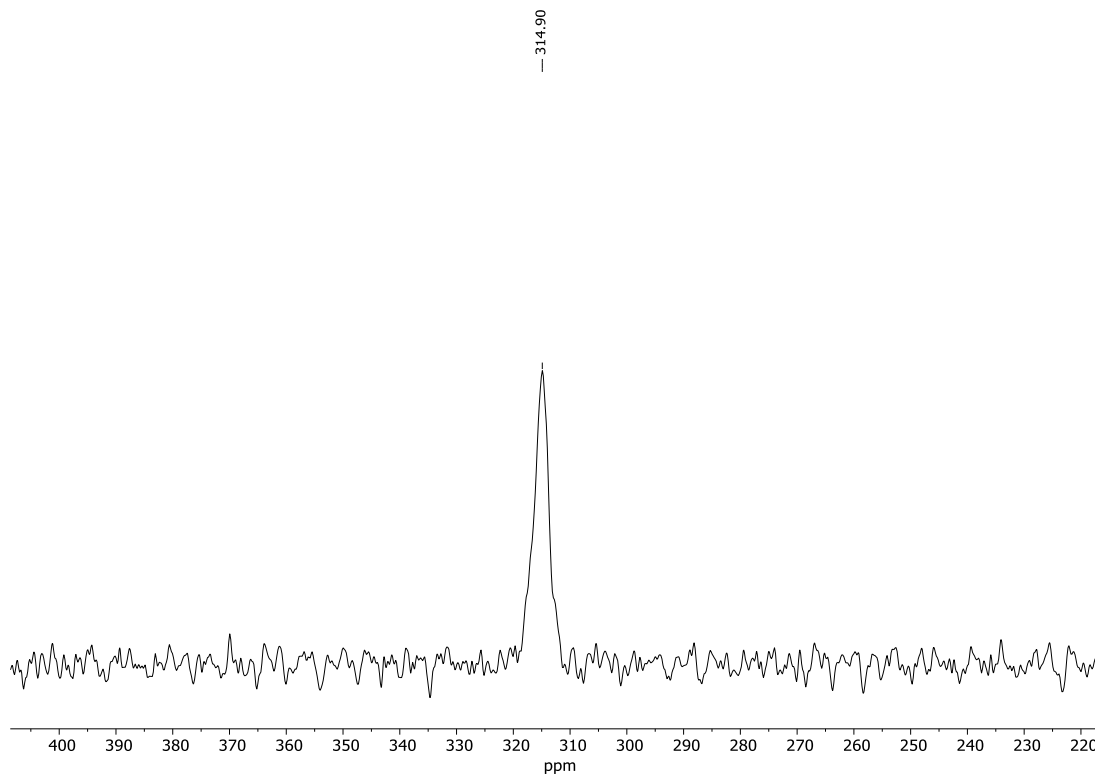


Figure S8. $\{^1\text{H}\}^{13}\text{C}$ NMR (400 MHz, CD_2Cl_2) spectrum of **4** in the 400-220 ppm region.

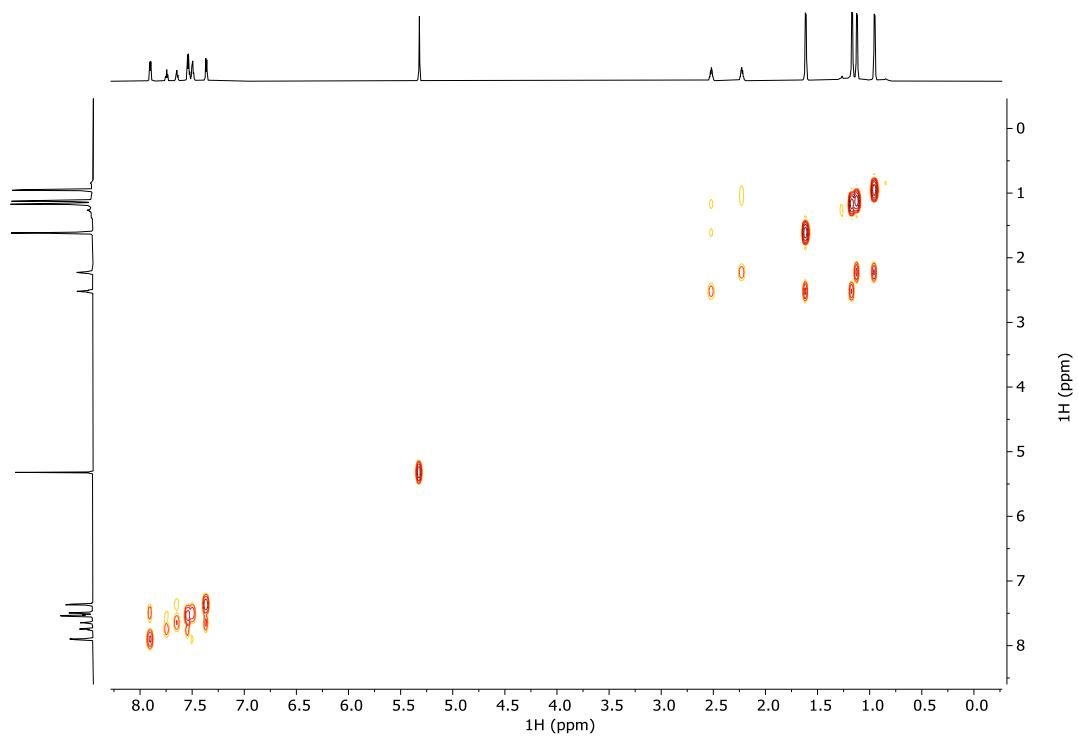


Figure S9. ^1H COSY NMR (CD_2Cl_2) spectrum of **4**.

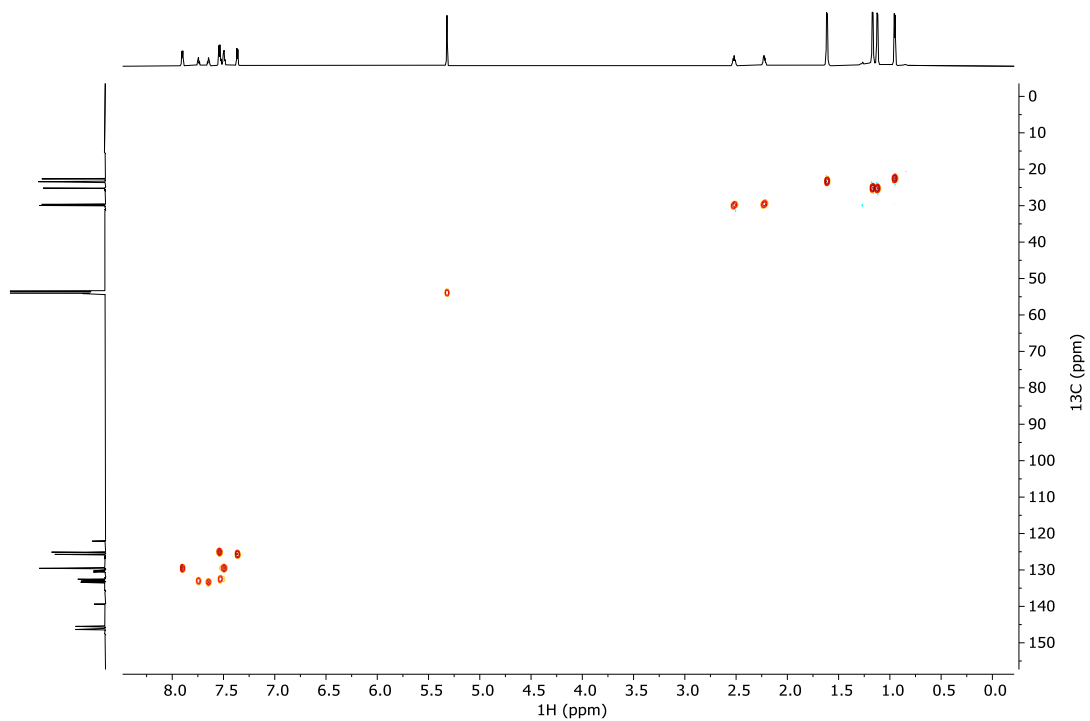


Figure S10. $^1\text{H}/^{13}\text{C}$ HSQC NMR (CD_2Cl_2) spectrum of **4**.

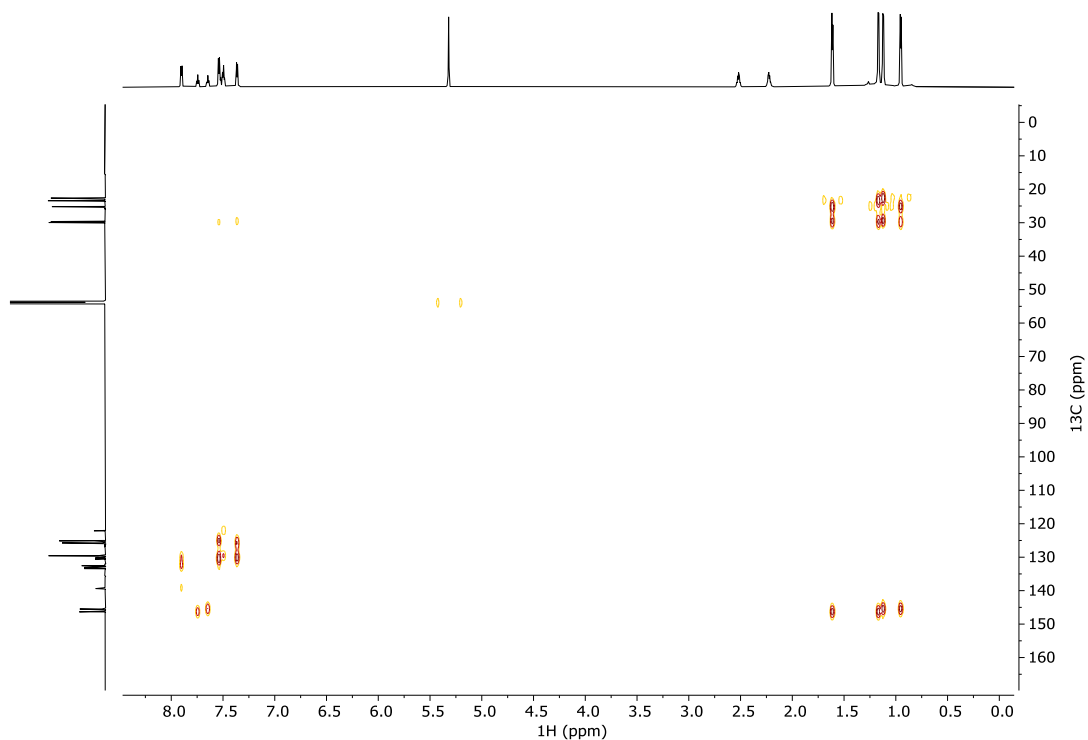


Figure S11. $^1\text{H}/^{13}\text{C}$ HMBC NMR (CD_2Cl_2) spectrum of **4**.

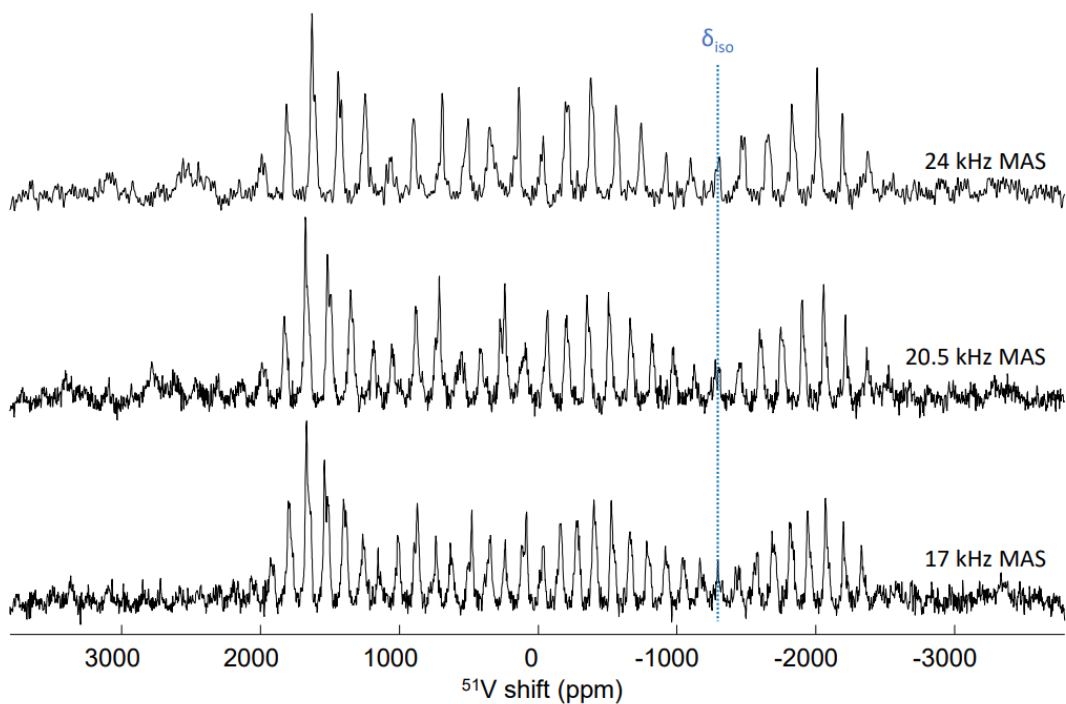


Figure S12: ^{51}V MAS NMR spectra of **4** in solid-state recorded at variable spinning speeds. The isotropic shift is indicated by the blue, dotted line. All other peaks are spinning sidebands, which are observed at multiples of the spinning speed.

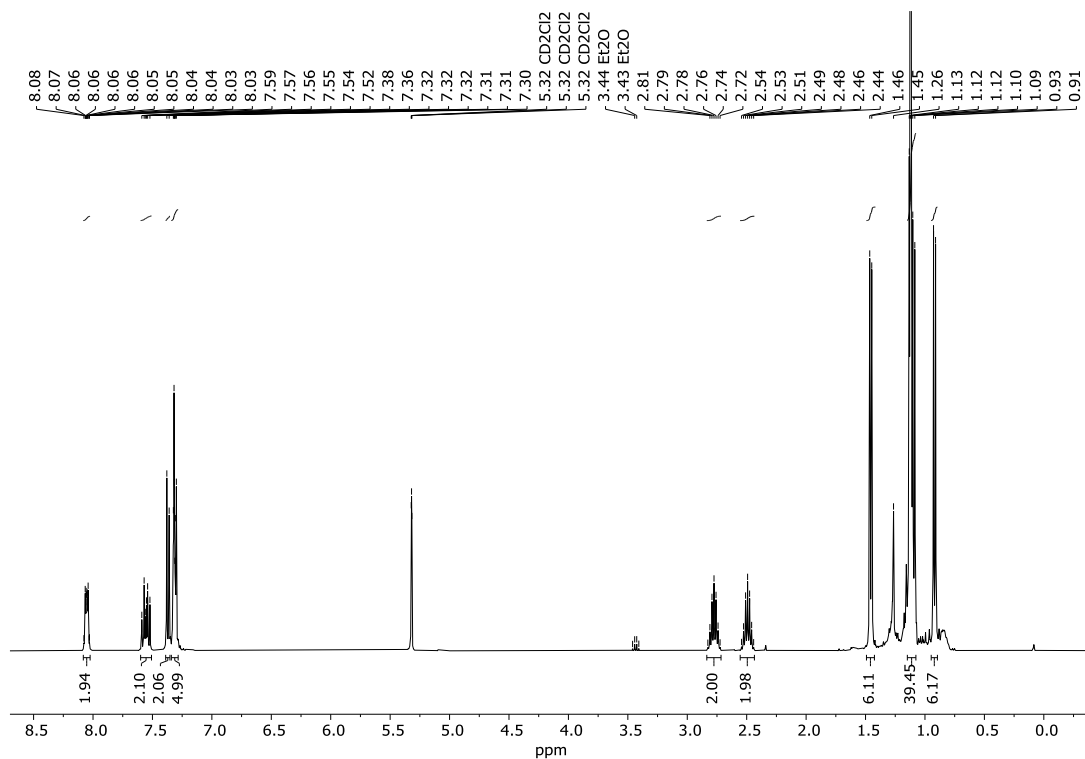


Figure S13. ^1H NMR (800 MHz, CD_2Cl_2) spectrum of **5**. The peak at 1.26 ppm is confirmed by ^1H NMR to be an impurity that was present in the KO^tBu reagent.

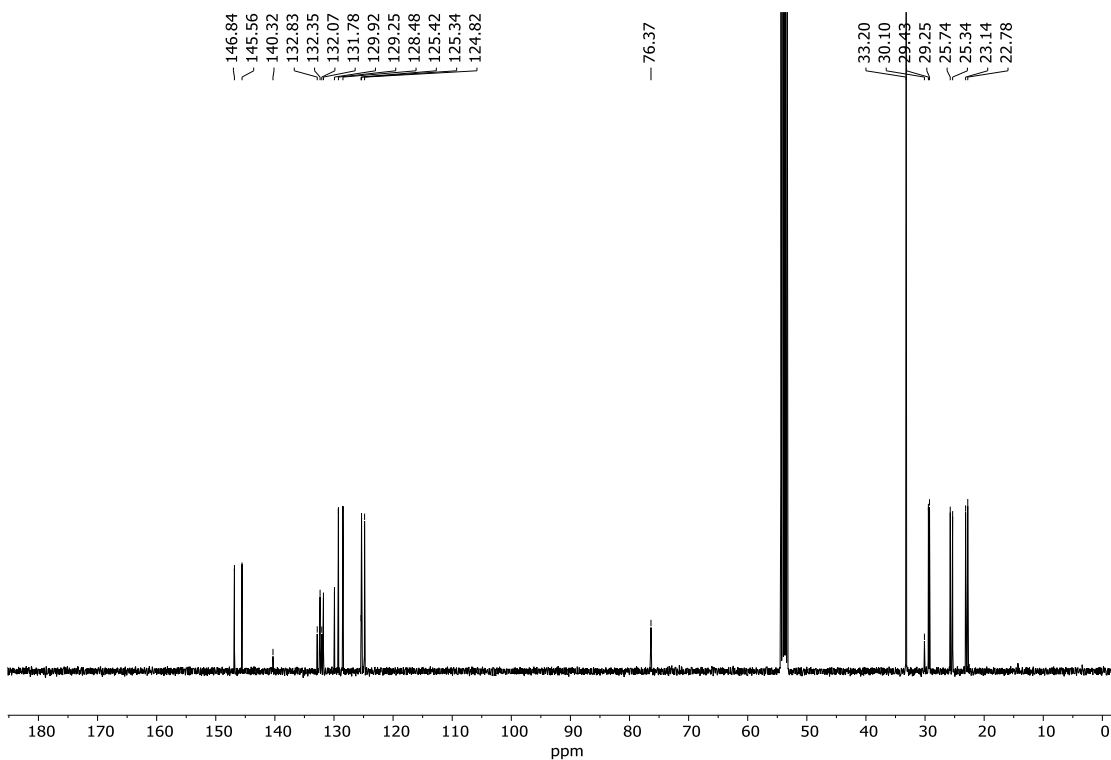


Figure S14. $\{^1\text{H}\}^{13}\text{C}$ NMR (200 MHz, CD_2Cl_2) spectrum of **5**. The peak at 30.10 ppm is confirmed by NMR to be an impurity that was present in the KO^tBu reagent.

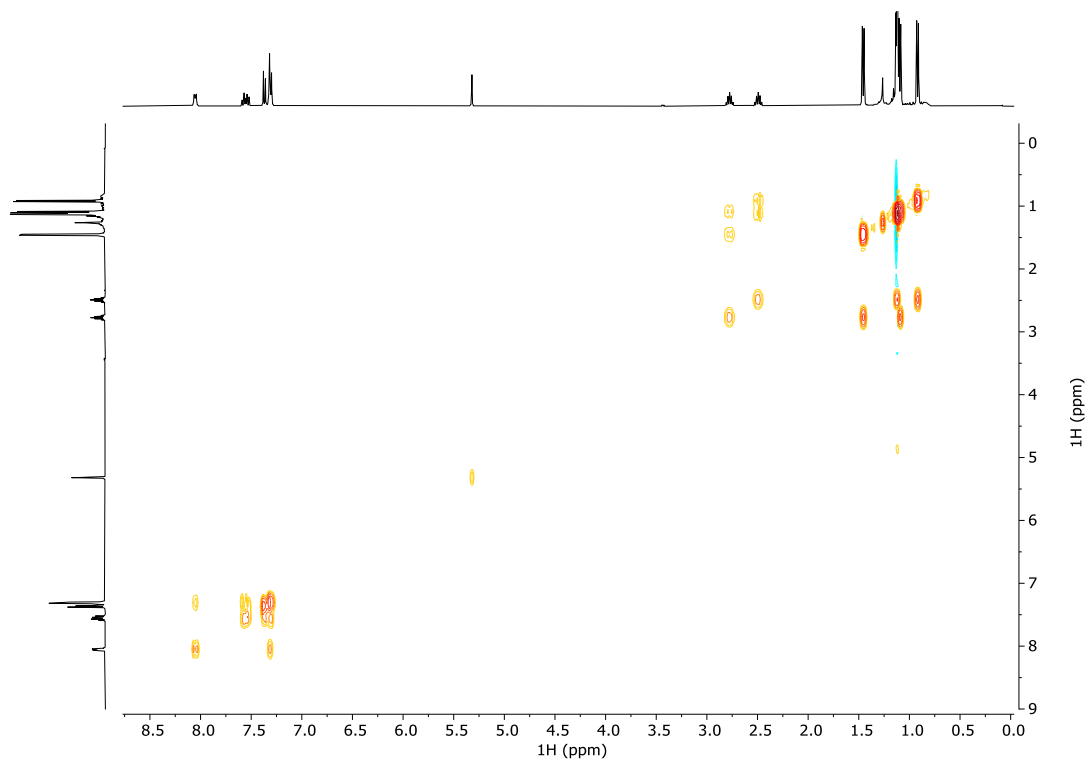


Figure S15. ^1H COSY NMR (CD_2Cl_2) spectrum of **5**.

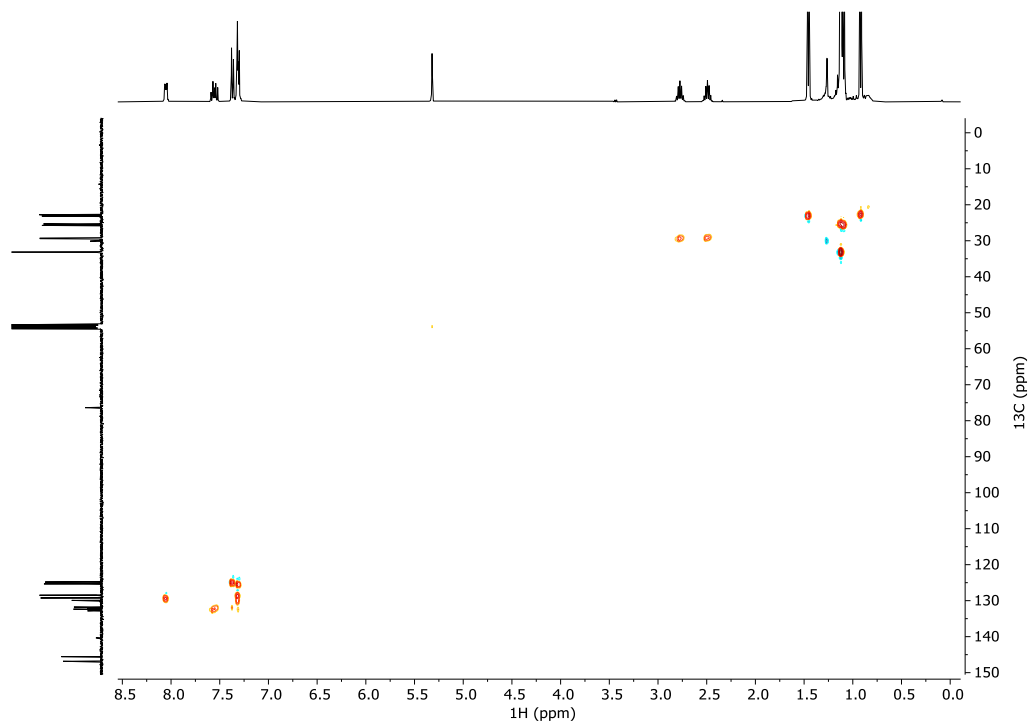


Figure S16. $^1\text{H}/^{13}\text{C}$ HSQC NMR (CD_2Cl_2) spectrum of **5**.

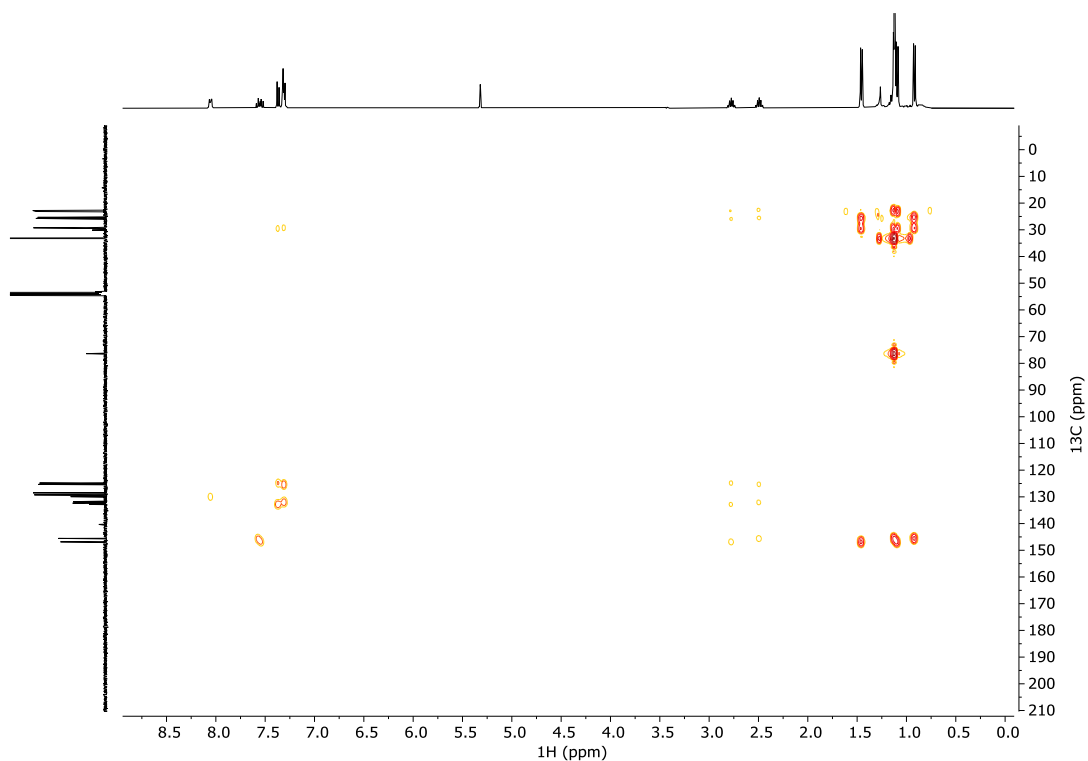


Figure S17. $^1\text{H}/^{13}\text{C}$ HMBC NMR (CD_2Cl_2) spectrum of **5**.

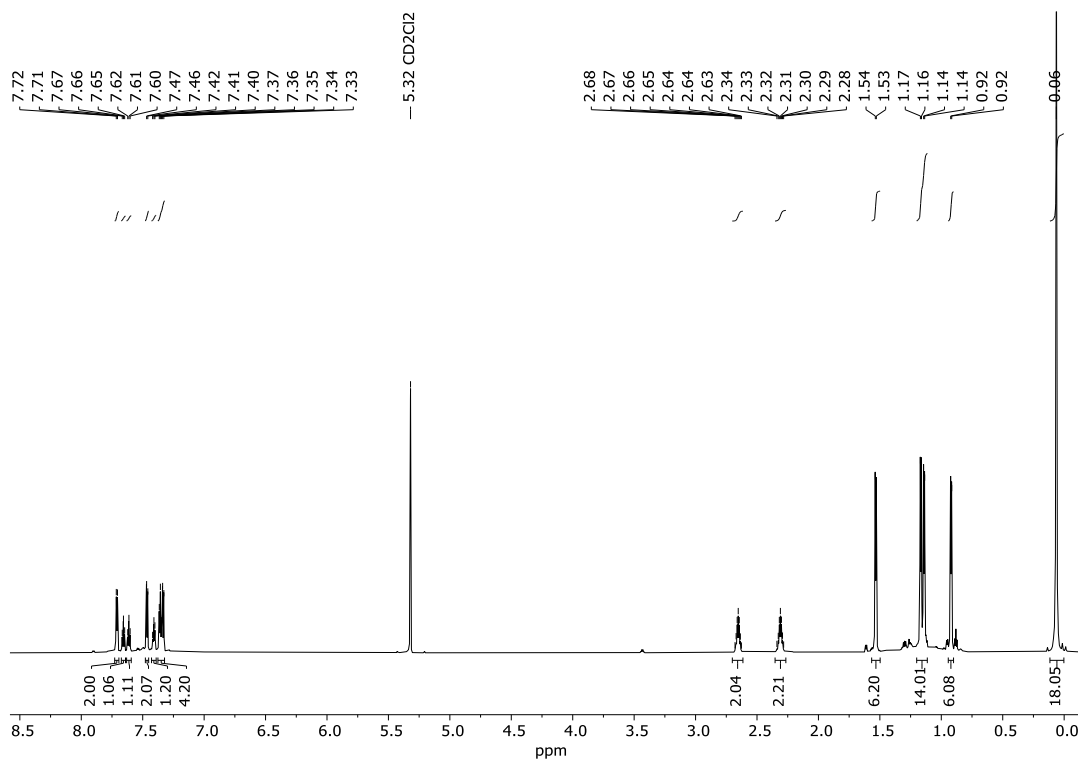


Figure S18. ^1H NMR (800 MHz, CD_2Cl_2) spectrum of **6**.

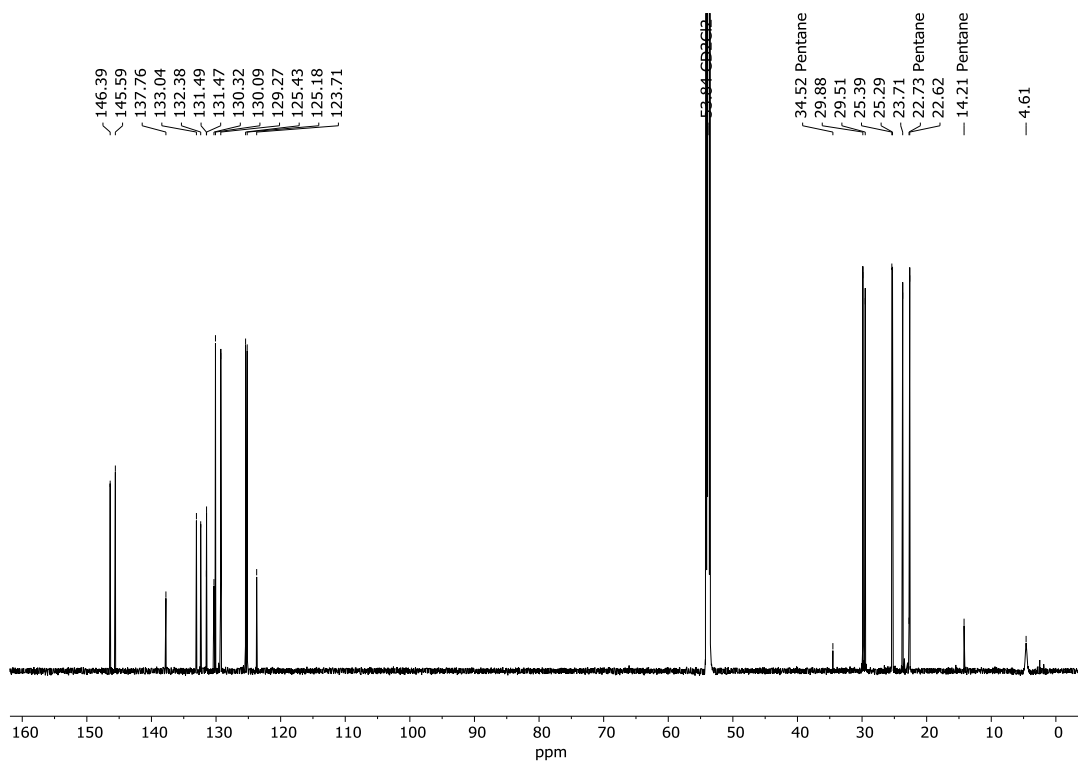


Figure S19. $\{^1\text{H}\}^{13}\text{C}$ NMR (200 MHz, CD_2Cl_2) spectrum of **6**.

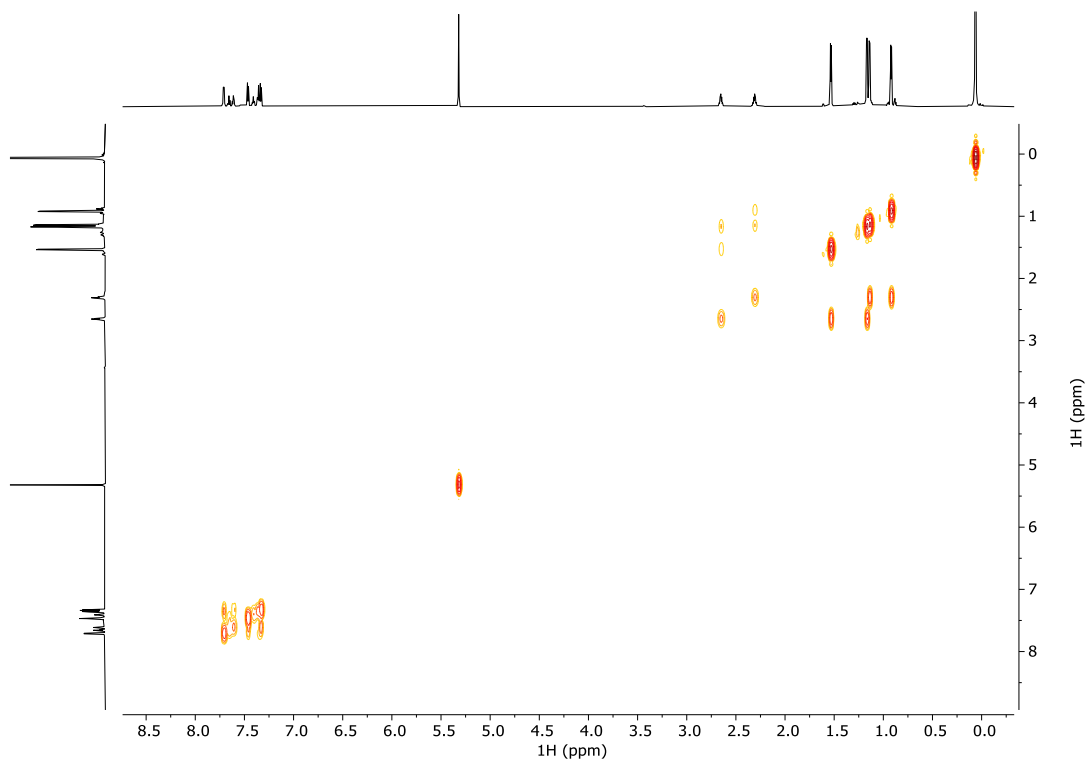


Figure S20. ^1H COSY NMR (CD_2Cl_2) spectrum of **6**.

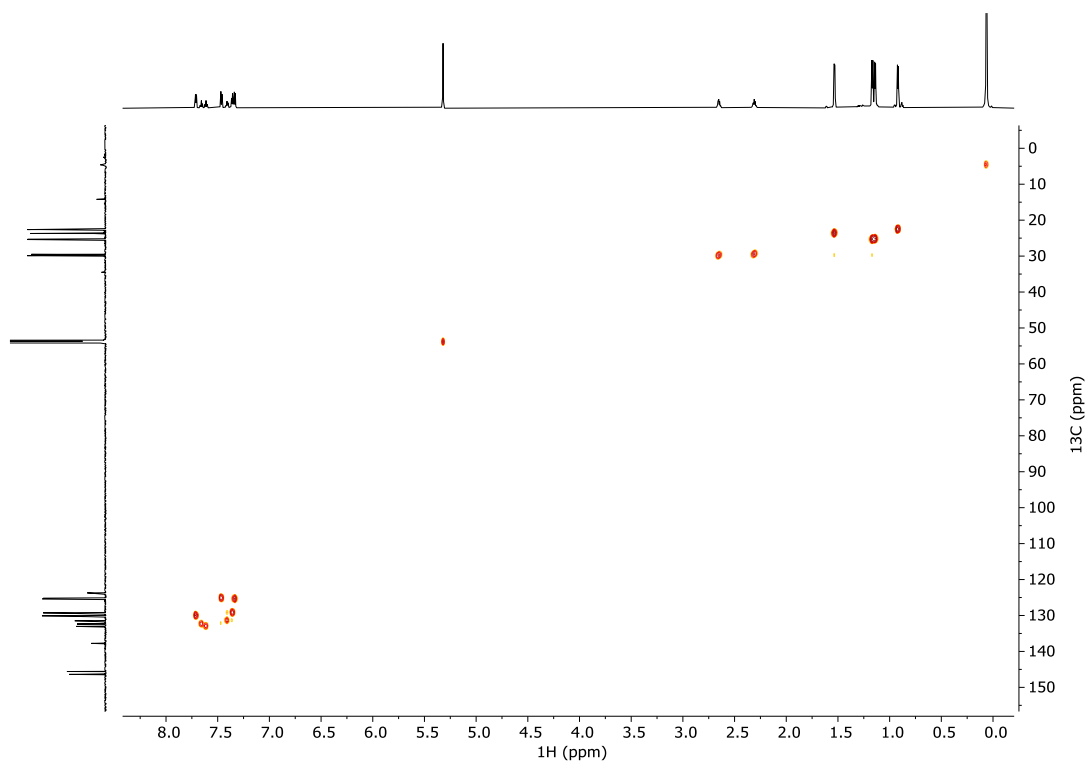


Figure S21. $^1\text{H}/^{13}\text{C}$ HSQC NMR (CD_2Cl_2) spectrum of **6**.

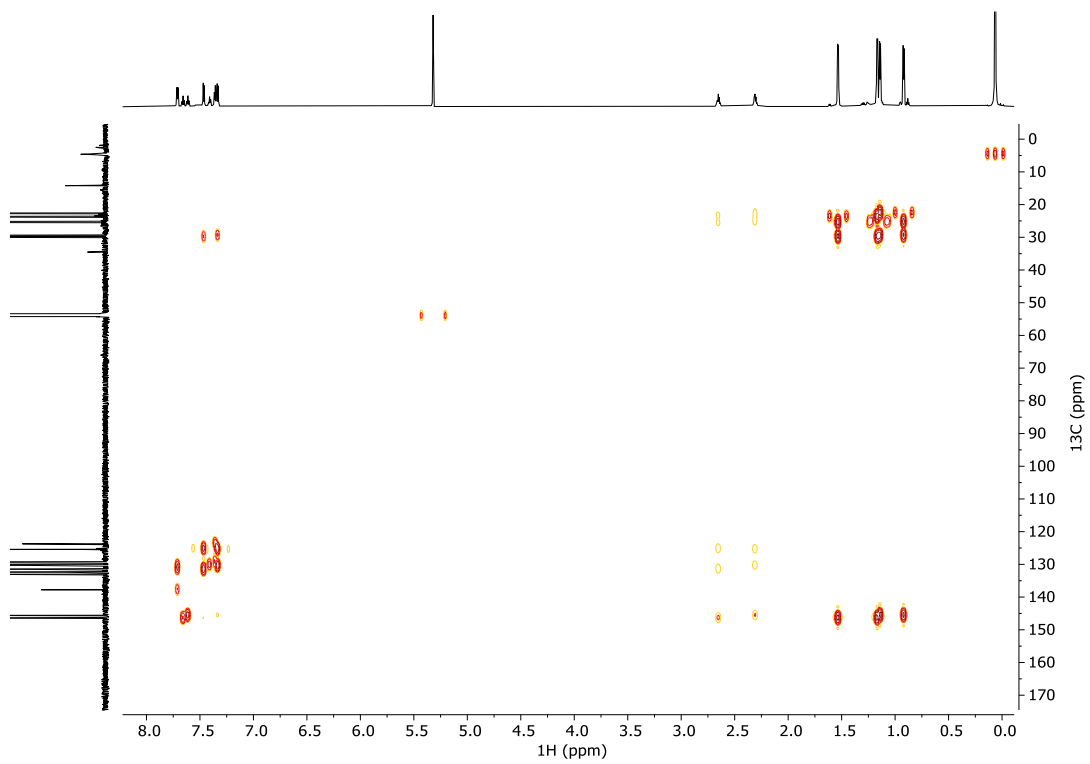


Figure S22. $^1\text{H}/^{13}\text{C}$ HMBC NMR (CD_2Cl_2) spectrum of **6**.

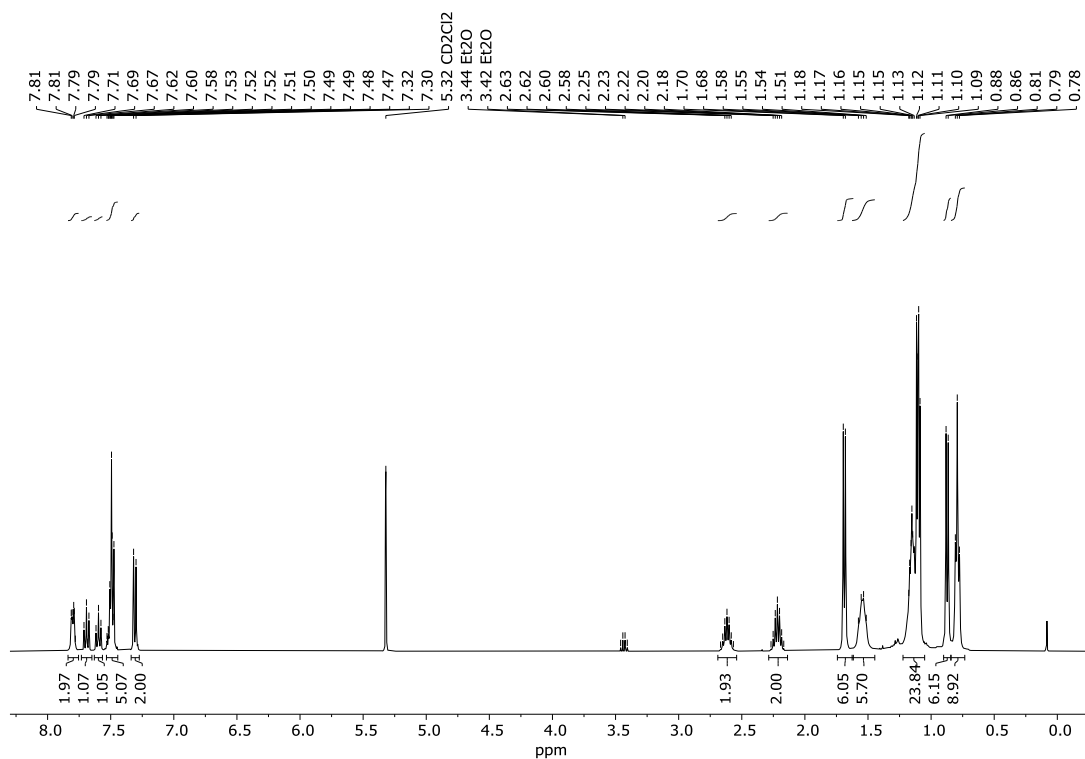


Figure S23. ¹H NMR (600 MHz, CD₂Cl₂) spectrum of 7.

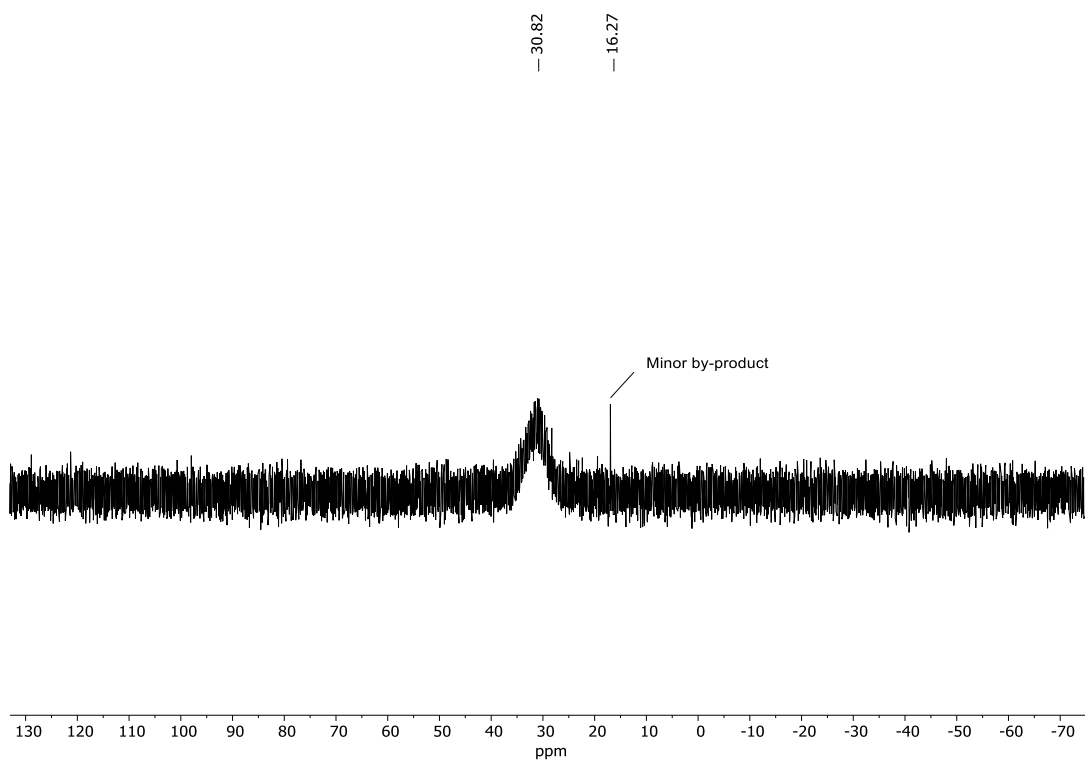


Figure S24. ¹H³¹P NMR (162 MHz, CD₂Cl₂) spectrum of 7.

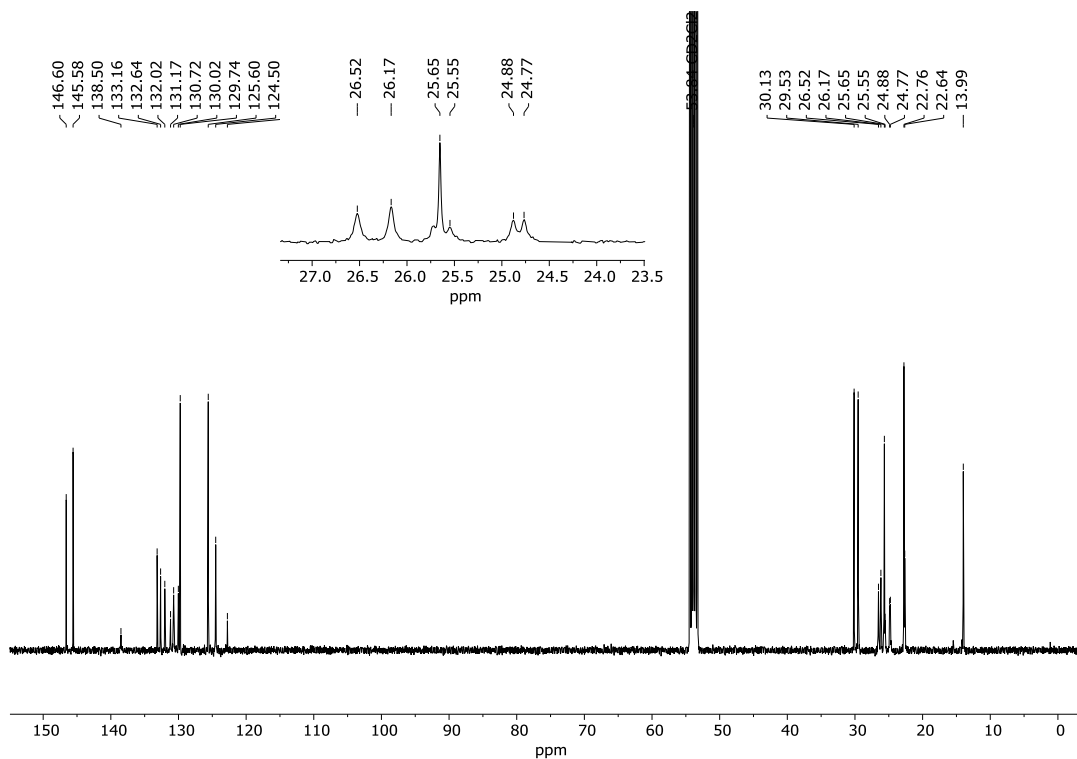


Figure S25. $\{^1\text{H}\}^{13}\text{C}$ NMR (100 MHz, CD_2Cl_2) spectrum of **7**.

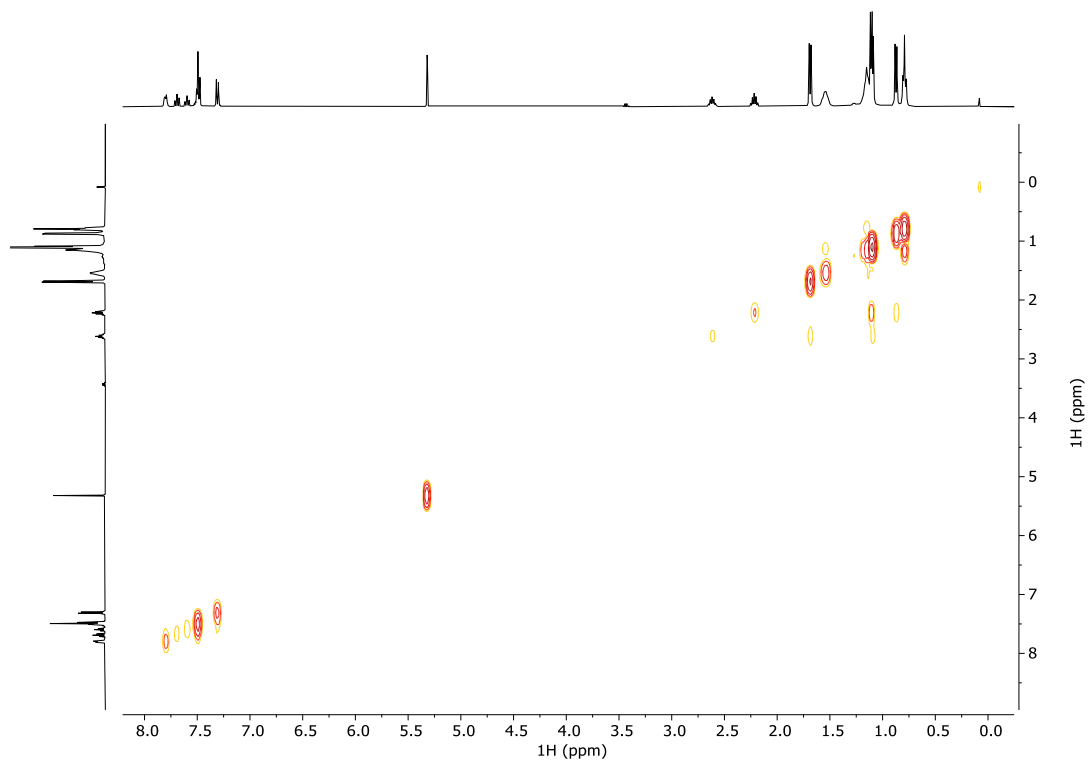


Figure S26. ^1H COSY NMR (CD_2Cl_2) spectrum of **7**.

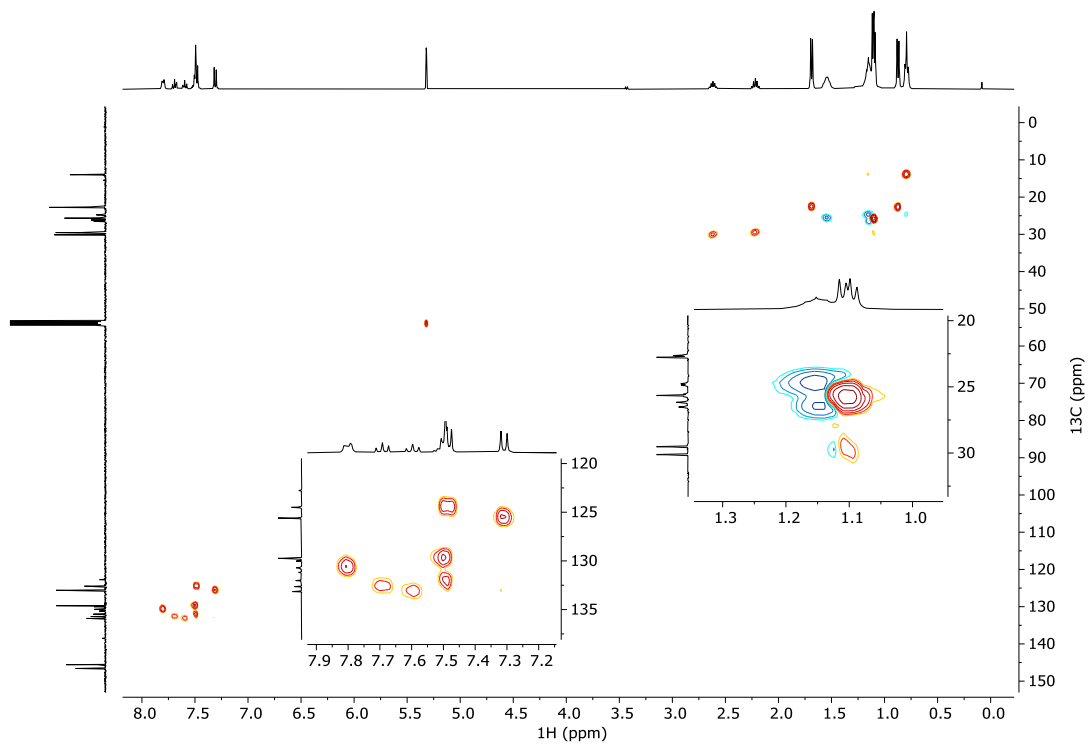


Figure S27. $^1\text{H}/^{13}\text{C}$ HSQC NMR (CD_2Cl_2) spectrum of **7**.

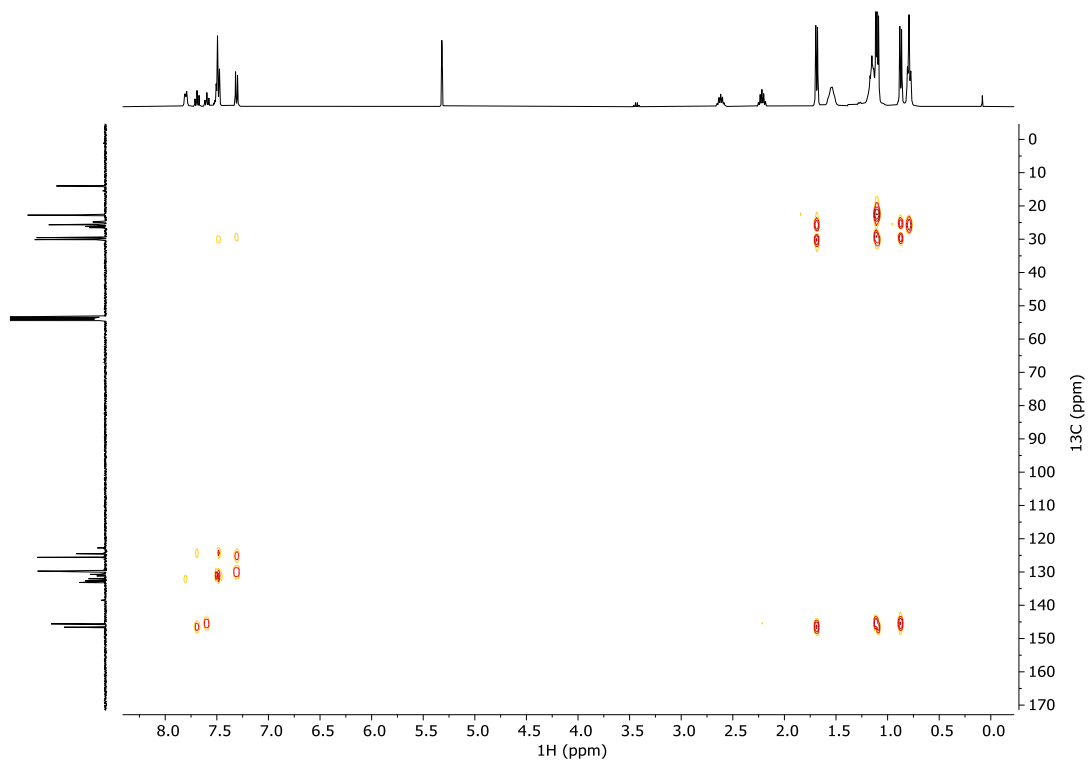


Figure S28. $^1\text{H}/^{13}\text{C}$ HMBC NMR (CD_2Cl_2) spectrum of **7**.

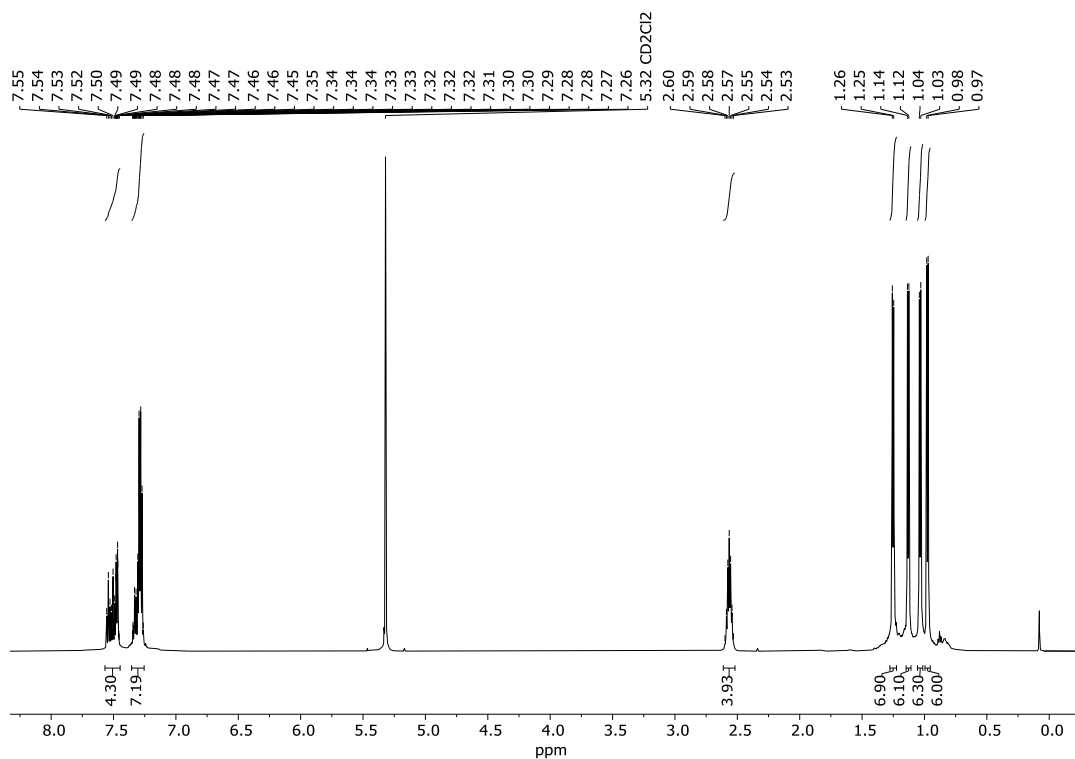


Figure S29. ¹H NMR (800 MHz, CD₂Cl₂) spectrum of **8**.

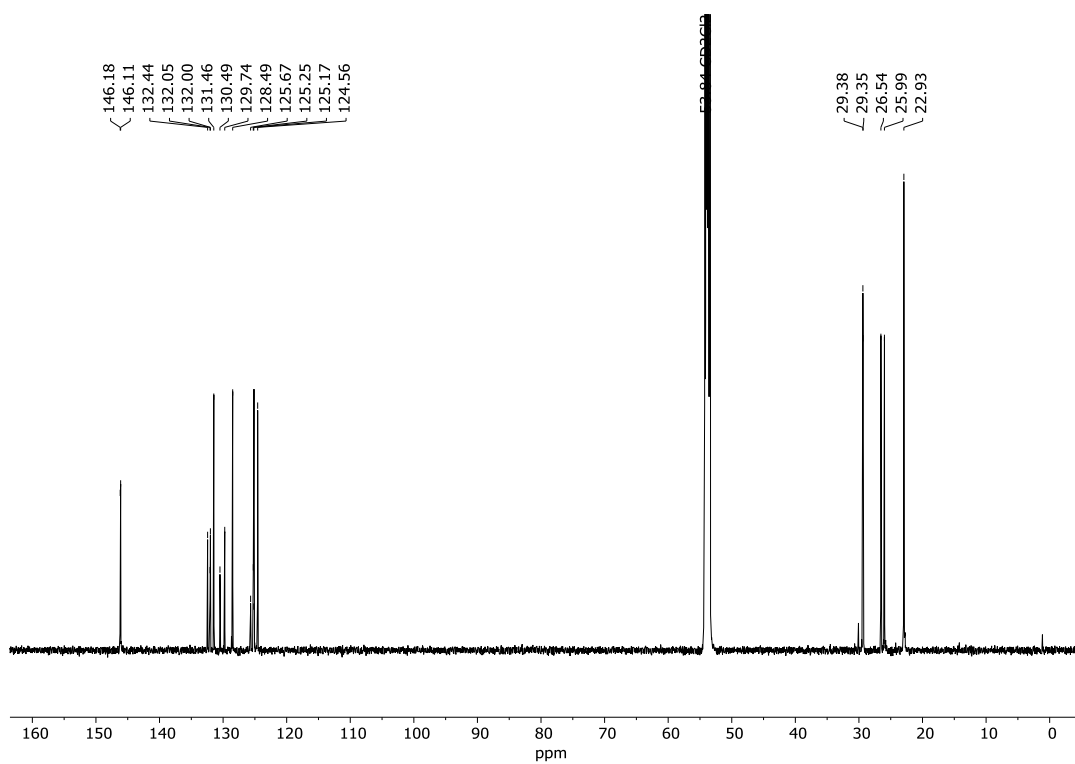


Figure S30. ¹H¹³C NMR (200 MHz, CD₂Cl₂) spectrum of **8**.

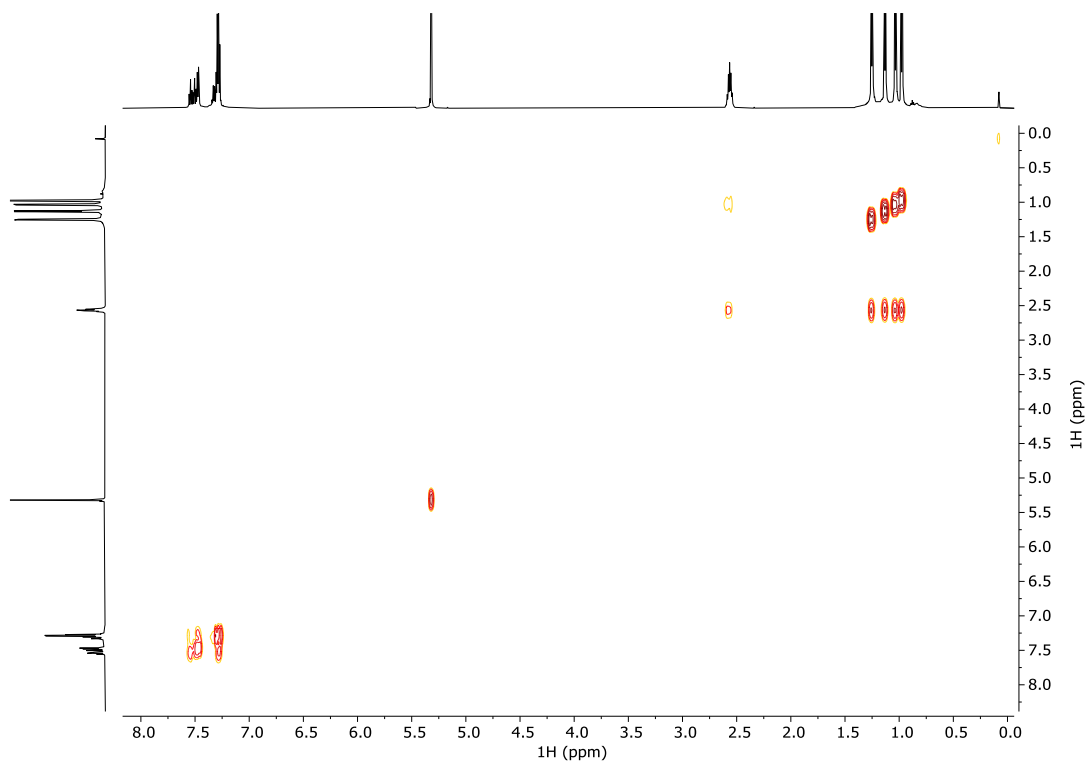


Figure S31. ^1H COSY NMR (CD_2Cl_2) spectrum of **8**.

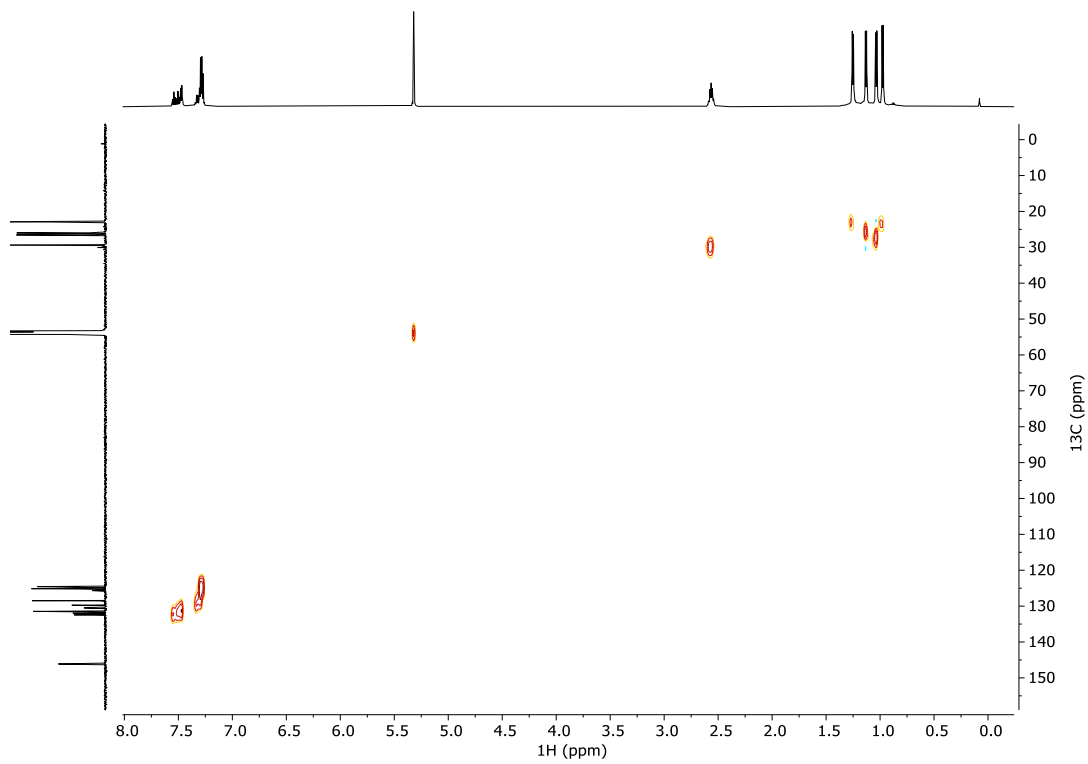


Figure S32. $^1\text{H}/^{13}\text{C}$ HSQC NMR (CD_2Cl_2) spectrum of **8**.

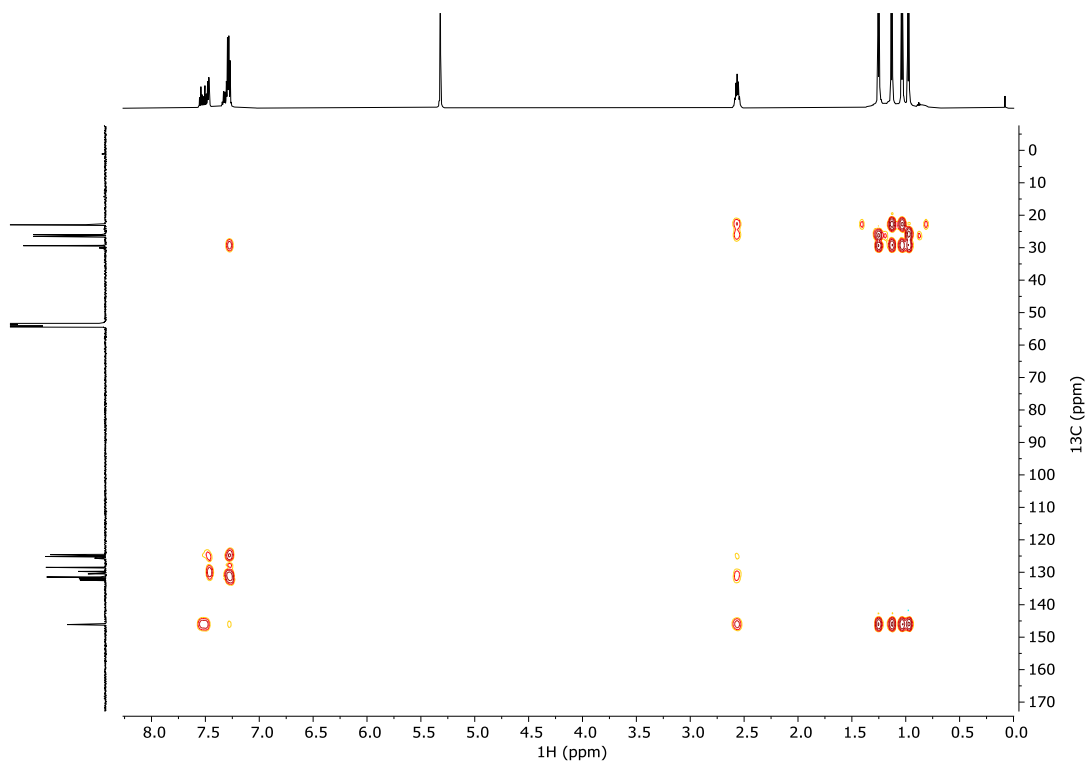


Figure S33. $^1\text{H}/^{13}\text{C}$ HMBC NMR (CD_2Cl_2) spectrum of **8**.

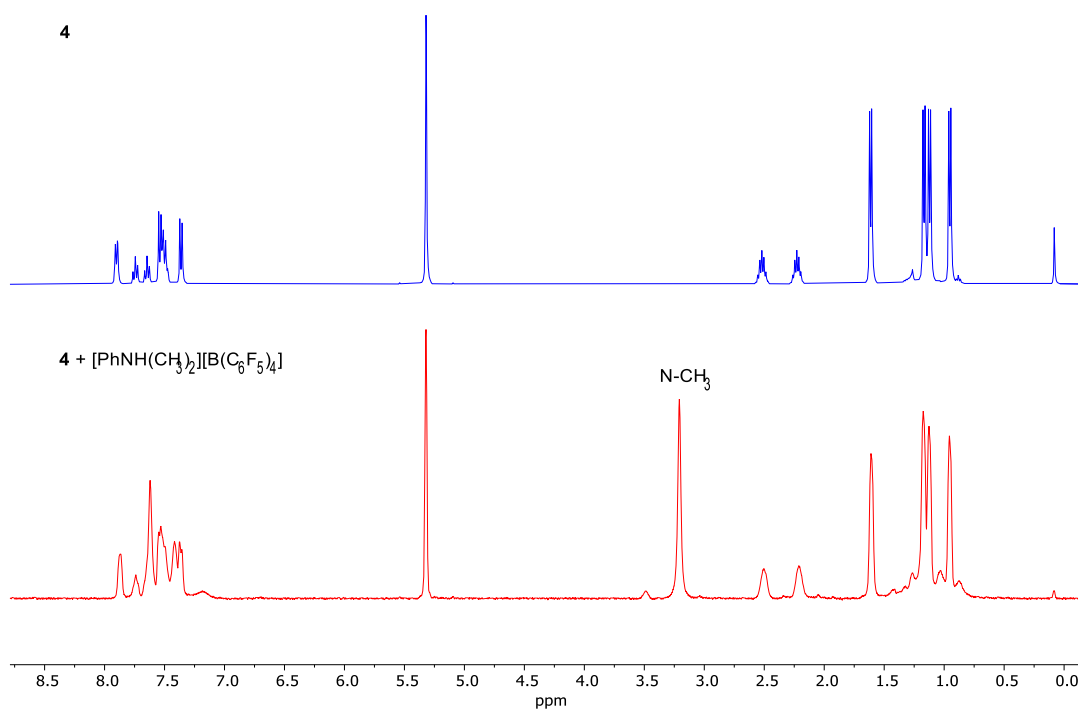


Figure S34. ^1H NMR (400 MHz, CD_2Cl_2) stacked spectra of complex **4** (top) and of a mixture of complex **4** and $[\text{PhNH}(\text{CH}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ in CD_2Cl_2 after stirring for 1 h at room temperature (bottom).

4. Single crystal X-ray analyses

Structure Quality Indicators of 2

Reflections:	d min (Cu α) 2 θ =145.1°	0.81	I/ σ (I) CIF	29.8	Rint CIF	3.11%	Full 135.4° 98% to 145.1°	100
Refinement:	Shift CIF	0.002	Max Peak CIF	0.3	Min Peak CIF	-0.5	Goof CIF	1.045

A clear light green plate-shaped crystal with dimensions of 0.11 × 0.07 × 0.02 mm³ was mounted. Data were collected using a SuperNova, Dual, Cu at home/near, Atlas diffractometer operating at $T = 140.00(10)$ K. Data were measured using ω scans using CuK α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlis^{Pro} 1.171.41.113a (Rigaku OD, 2021).³ The maximum resolution achieved was $\Theta = 72.529^\circ$ (0.81 Å). The unit cell was refined using CrysAlis^{Pro} 1.171.41.113a (Rigaku OD, 2021) on 7502 reflections, 44% of the observed reflections. Data reduction, scaling and absorption corrections were performed using CrysAlis^{Pro} 1.171.41.113a (Rigaku OD, 2021). The structure was solved in the space group $P2_1/n$ (# 14) by the ShelXT 2018/2 (Sheldrick, 2015) structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL** 2018/3 (Sheldrick, 2015).^{4,5} All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

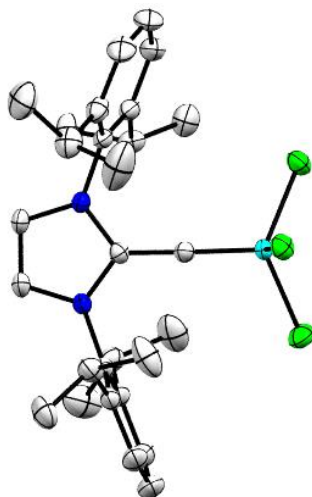


Figure S35. Molecular structure of complex **2** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S1. Crystal data and structure refinement for **2**.

Compound	BK122
Formula	C ₃₄ H ₄₂ Cl ₃ N ₂ V
$D_{calc.}/g\text{ cm}^{-3}$	1.243
μ/mm^{-1}	4.784
Formula Weight	635.98
Colour	clear light green
Shape	plate-shaped
Size/mm ³	0.11×0.07×0.02
T/K	140.00(10)
Crystal System	monoclinic
Space Group	$P2_1/n$
$a/\text{Å}$	16.7785(3)
$b/\text{Å}$	9.29150(18)
$c/\text{Å}$	22.4036(4)
α°	90
β°	103.312(2)
γ°	90
$V/\text{Å}^3$	3398.82(12)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	CuK α
Θ_{min}°	3.737
Θ_{max}°	72.529
Measured Refl's.	17167
Indep't Refl's	6581
Refl's $I \geq 2\sigma(I)$	5506
R_{int}	0.0311
Parameters	400
Restraints	174
Largest Peak/e Å^{-3}	0.336
Deepest Hole/e Å^{-3}	− 0.470
Goof	1.045
wR_2 (all data)	0.1017
wR_2	0.0954
R_1 (all data)	0.0499
R_1	0.0387
<i>CCDC number</i>	2105986

Structure Quality Indicators of 4

Reflections:	d min (Cu α) 2 θ =151.3°	0.80	I/ σ (I) CIF	80.0	Rint CIF	2.08%	Full 135.4° 98% to 151.3°	100
Refinement:	Shift CIF	0.001	Max Peak CIF	0.7	Min Peak CIF	-0.4	Goof CIF	1.066

A clear intense green prism-shaped crystal with dimensions of 0.10 × 0.07 × 0.03 mm³ was mounted. Data were collected using a XtaLAB Synergy R, DW system, HyPix-Arc 150 diffractometer operating at $T = 139.99(10)$ K. Data were measured using ω scans using CuK α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlis^{Pro} 1.171.41.113a (Rigaku OD, 2021).³ The maximum resolution that was achieved was $\Theta = 75.658^\circ$ (0.80 Å). The unit cell was refined using CrysAlis^{Pro} 1.171.41.113a (Rigaku OD, 2021) on 31694 reflections, 58% of the observed reflections. Data reduction, scaling and absorption corrections were performed using CrysAlis^{Pro} 1.171.41.113a (Rigaku OD, 2021). The structure was solved in the space group $P2_1/n$ (# 14) by the ShelXT 2018/2 (Sheldrick, 2015) structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL** 2018/3 (Sheldrick, 2015).^{4,5} All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

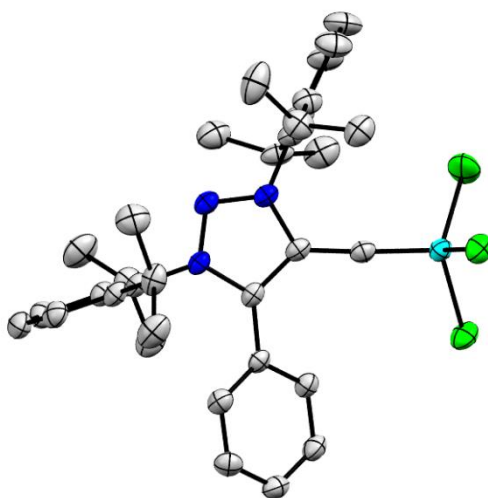


Figure S36. Molecular structure of complex **4** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S2. Crystal data and structure refinement for **4**.

Compound	BK100.2
Formula	C ₃₃ H ₃₉ Cl ₃ N ₃ V
$D_{calc.}/g\text{ cm}^{-3}$	1.277
μ/mm^{-1}	4.933
Formula Weight	634.96
Colour	clear intense green
Shape	prism-shaped
Size/ mm^3	0.10×0.07×0.03
T/K	139.99(10)
Crystal System	monoclinic
Space Group	$P2_1/n$
$a/\text{\AA}$	12.08899(15)
$b/\text{\AA}$	19.34274(17)
$c/\text{\AA}$	14.78739(17)
α°	90
β°	107.2322(12)
γ°	90
$V/\text{\AA}^3$	3302.59(7)
Z	4
Z'	1
Wavelength/ \AA	1.54184
Radiation type	CuK α
Θ_{min}°	3.875
Θ_{max}°	75.658
Measured Refl's.	54724
Indep't Refl's	6754
Refl's $I \geq 2\sigma(I)$	6266
R_{int}	0.0208
Parameters	369
Restraints	0
Largest Peak/ $e\text{ \AA}^{-3}$	0.674
Deepest Hole/ $e\text{ \AA}^{-3}$	– 0.358
GooF	1.066
wR_2 (all data)	0.1027
wR_2	0.1012
R_1 (all data)	0.0368
R_1	0.0345
<i>CCDC number</i>	2101114

Structure Quality Indicators of 5

Reflections:	d min (Cu\Å) 2 Θ =145.3°	0.81	I/ σ (I)	20.8	R _{int}	4.03%	CAP 133.9° 98% to 145.3°	99.8
Refinement:	Shift	0.001	Max Peak	0.3	Min Peak	-0.3	Goof	1.033

A clear dark orange plate-shaped crystal with dimensions of 0.27 × 0.20 × 0.08 mm³ was mounted. Data were collected using a SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer operating at $T = 220.00(10)$ K. Data were measured using ω scans with CuK α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlis^{Pro} 1.171.41.117a (Rigaku OD, 2021).³ The maximum resolution that was achieved was $\Theta = 72.644^\circ$ (0.81 Å). The unit cell was refined using CrysAlis^{Pro} 1.171.41.117a (Rigaku OD, 2021) on 4612 reflections, 18% of the observed reflections. Data reduction, scaling and absorption corrections were performed using CrysAlis^{Pro} 1.171.41.117a (Rigaku OD, 2021). The structure was solved in the space group $P2_1/n$ (# 14) by the ShelXT (Sheldrick, 2015) structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL** (Sheldrick, 2015).^{4,5} All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. A solvent mask was calculated and 144 electrons were found in a volume of 1154 Å³ in 1 void per unit cell. This is consistent with the presence of 0.85 [C₅H₁₂] per Asymmetric Unit which account for 143 electrons per unit cell.

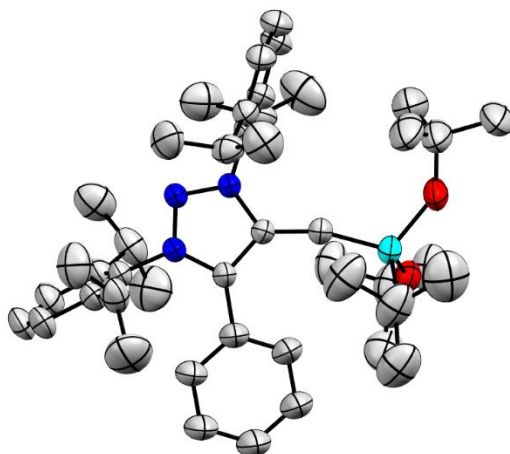


Figure S37. Molecular structure of complex **5** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S3. Crystal data and structure refinement for **5**.

Compound	bk135
Formula	C ₄₅ H ₆₆ N ₃ O ₃ V
Dcalc	0.942
μ/mm^{-1}	1.822
Formula Weight	747.94
Colour	clear dark orange
Shape	plate-shaped
Size/mm ³	0.27×0.20×0.08
<i>T</i> /K	220.00(10)
Crystal System	monoclinic
Space Group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	10.9179(4)
<i>b</i> /Å	19.6672(5)
<i>c</i> /Å	24.8242(7)
α /°	90
β /°	98.425(3)
γ /°	90
<i>V</i> /Å ³	5272.8(3)
<i>Z</i>	4
<i>Z</i> '	1
Wavelength/Å	1.54184
Radiation type	CuK α
Θ_{min} /°	3.600
Θ_{max} /°	72.644
Measured Refl's.	25540
Indep't Refl's	10235
Refl's $I \geq 2\sigma(I)$	6724
<i>R</i> _{int}	0.0403
Parameters	640
Restraints	1102
Largest Peak	0.312
Deepest Hole	− 0.306
GooF	1.033
<i>wR</i> ₂ (all data)	0.1880
<i>wR</i> ₂	0.1683
<i>R</i> ₁ (all data)	0.0909
<i>R</i> ₁	0.0611
<i>CCDC number</i>	2148180

Structure Quality Indicators of 6

Reflections:	d min (Cu\Å) 2 θ =151.0° 0.80	I/σ(I) CIF 39.7	Rint CIF 3.52%	Full 135.4° 97% to 151.0° 100
Refinement:	Shift CIF 0.001	Max Peak CIF 0.5	Min Peak CIF -0.3	Goof CIF 1.037

A clear dark yellow plate-shaped crystal with dimensions of 0.22 × 0.12 × 0.02 mm³ was mounted. Data were collected using a XtaLAB Synergy R, DW system, HyPix-Arc 150 diffractometer operating at $T = 140.00(10)$ K. Data were measured using ω scans with CuK α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlis^{Pro} 1.171.41.121a (Rigaku OD, 2021).³ The maximum resolution achieved was $\Theta = 75.496^\circ$ (0.80 Å). The unit cell was refined using CrysAlis^{Pro} 1.171.41.121a (Rigaku OD, 2021) on 18924 reflections, 33% of the observed reflections. Data reduction, scaling and absorption corrections were performed using CrysAlis^{Pro} 1.171.41.121a (Rigaku OD, 2021). The structure was solved in the space group $P2/n$ (# 13) by the ShelXT 2018/2 (Sheldrick, 2015) structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL** 2018/3 (Sheldrick, 2015).^{4,5} All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

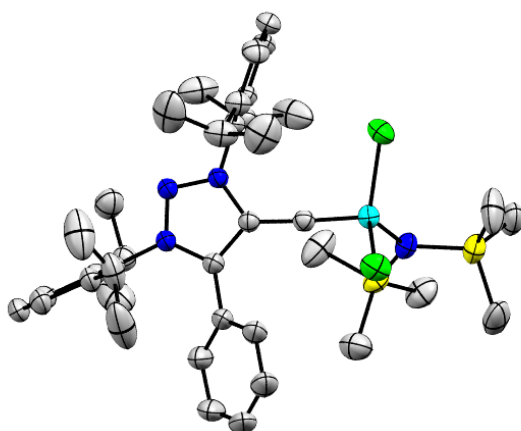


Figure S38. Molecular structure of complex **6** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S4. Crystal data and structure refinement for **6**.

Compound	BK183
Formula	C ₃₉ H ₅₇ Cl ₂ N ₄ Si ₂ V
<i>D</i> _{calc.} / g cm ⁻³	1.178
μ /mm ⁻¹	3.842
Formula Weight	759.90
Colour	clear dark yellow
Shape	plate-shaped
Size/mm ³	0.22x0.12x0.02
<i>T</i> /K	140.00(10)
Crystal System	monoclinic
Space Group	<i>P2</i> / <i>n</i>
<i>a</i> /Å	15.1641(2)
<i>b</i> /Å	12.35741(14)
<i>c</i> /Å	24.0239(3)
α /°	90
β /°	107.8825(14)
γ /°	90
<i>V</i> /Å ³	4284.32(10)
<i>Z</i>	4
<i>Z</i> '	1
Wavelength/Å	1.54184
Radiation type	CuK α
Θ _{min} /°	3.079
Θ _{max} /°	75.496
Measured Refl's.	56762
Indep't Refl's	8625
Refl's $I \geq 2\sigma(I)$	7129
<i>R</i> _{int}	0.0352
Parameters	447
Restraints	0
Largest Peak/e Å ⁻³	0.523
Deepest Hole/e Å ⁻³	- 0.324
Goof	1.037
<i>wR</i> ₂ (all data)	0.1372
<i>wR</i> ₂	0.1311
<i>R</i> ₁ (all data)	0.0587
<i>R</i> ₁	0.0482
<i>CCDC number</i>	2130296

Structure Quality Indicators of 7

Reflections:	$d \text{ min (Cu}\backslash\text{a)}$ $2\Theta=134.2^\circ$	0.84	$I/\sigma(I)$ CIF	13.2	R_{int} CIF	7.27%	Full 134.2°	99.5
Refinement:	Shift CIF	0.000	Max Peak CIF	1.1	Min Peak CIF	-0.7	Goof CIF	1.058

A clear intense yellow plate-shaped crystal with dimensions of $0.23 \times 0.09 \times 0.02 \text{ mm}^3$ was mounted. Data were collected using a XtaLAB Synergy R, DW system, HyPix-Arc 150 diffractometer operating at $T = 140.00(10) \text{ K}$. Data were measured using ω scans with $\text{CuK}\alpha$ radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlis^{Pro} 1.171.41.122a (Rigaku OD, 2021).³ The maximum resolution achieved was $\Theta = 67.076^\circ$ (0.84 \AA). The unit cell was refined using CrysAlis^{Pro} 1.171.41.122a (Rigaku OD, 2021) on 9104 reflections, 30% of the observed reflections. Data reduction, scaling and absorption corrections were performed using CrysAlis^{Pro} 1.171.41.122a (Rigaku OD, 2021). The structure was solved in the space group $P\bar{1}$ (# 2) by the ShelXT 2018/2 (Sheldrick, 2015) structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL** 2018/3 (Sheldrick, 2015).^{4,5} All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. A solvent mask was calculated with the help of the solvent-masking program in OLEX2^[6] and 74.0 electrons were found in a volume of 241.4 \AA^3 in one void. This is consistent with the presence of one solvent molecule of THF per asymmetric unit which accounts for 80 electrons per unit cell.

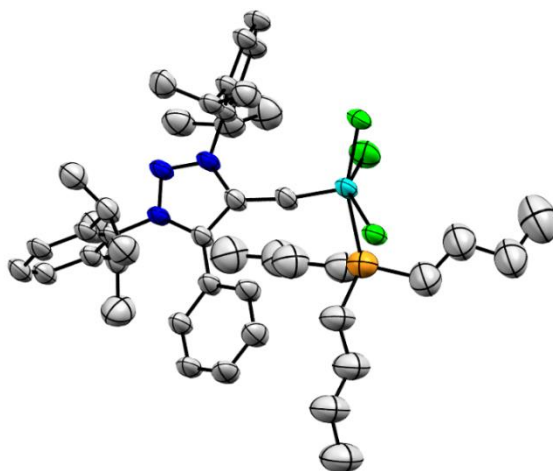


Figure S39. Molecular structure of complex **7** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S5. Crystal data and structure refinement for **7**.

Compound	BK212
Formula	C ₄₅ H ₆₆ Cl ₃ N ₃ PV
<i>D</i> _{calc.} / g cm ⁻³	1.113
<i>μ</i> /mm ⁻¹	3.658
Formula Weight	837.26
Colour	clear intense yellow
Shape	plate-shaped
Size/mm ³	0.23×0.09×0.02
<i>T</i> /K	140.00(10)
Crystal System	triclinic
Space Group	<i>P</i> $\bar{1}$
<i>a</i> /Å	11.3015(6)
<i>b</i> /Å	11.6166(3)
<i>c</i> /Å	20.8002(9)
<i>α</i> /°	84.755(3)
<i>β</i> /°	81.999(5)
<i>γ</i> /°	67.677(4)
<i>V</i> /Å ³	2499.3(2)
<i>Z</i>	2
<i>Z</i> '	1
Wavelength/Å	1.54184
Radiation type	CuKα
<i>θ</i> _{min} /°	4.118
<i>θ</i> _{max} /°	67.076
Measured Refl's.	30255
Indep't Refl's	8894
Refl's <i>I</i> ≥2σ(<i>I</i>)	5416
<i>R</i> _{int}	0.0727
Parameters	631
Restraints	1141
Largest Peak/e Å ⁻³	1.058
Deepest Hole/e Å ⁻³	− 0.708
GooF	1.058
<i>wR</i> ₂ (all data)	0.2894
<i>wR</i> ₂	0.2637
<i>R</i> ₁ (all data)	0.1319
<i>R</i> ₁	0.0931
<i>CCDC number</i>	2142648

Structure Quality Indicators of 8

Reflections:	d min (Cu\α) 2 θ =152.1°	0.79	I/ σ (I) CIF	46.5	Rint CIF	3.11%	Full 135.4° 99% to 152.1°	100
Refinement:	Shift CIF	0.001	Max Peak CIF	0.3	Min Peak CIF	-0.5	Goof CIF	1.074

A clear dark yellow plate-shaped crystal with dimensions of 0.21 × 0.14 × 0.04 mm³ was mounted. Data were collected using a SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer operating at $T = 229.99(10)$ K. Data were measured using ω scans with CuK α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlis^{Pro} 1.171.41.118a (Rigaku OD, 2021).³ The maximum resolution achieved was $\Theta = 76.061^\circ$ (0.79 Å). The unit cell was refined using CrysAlis^{Pro} 1.171.41.118a (Rigaku OD, 2021) on 17787 reflections, 39% of the observed reflections. Data reduction, scaling and absorption corrections were performed using CrysAlis^{Pro} 1.171.41.118a (Rigaku OD, 2021). The structure was solved in the space group C2/c (# 15) by the ShelXT 2018/2 (Sheldrick, 2015) structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL** 2018/3 (Sheldrick, 2015).^{4,5} All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

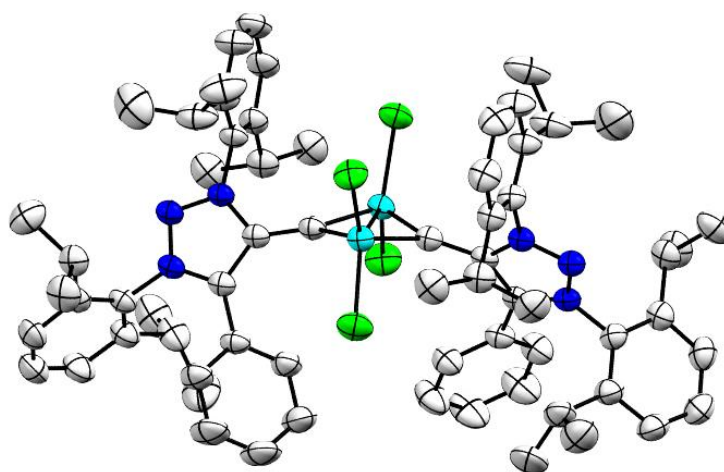


Figure S40. Molecular structure of complex **8** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S6. Crystal data and structure refinement for **8**.

Compound	BK142
Formula	C ₇₈ H ₉₀ Cl ₄ N ₆ V ₂
<i>D</i> _{calc.} / g cm ⁻³	1.203
<i>μ</i> /mm ⁻¹	3.746
Formula Weight	1355.23
Colour	clear dark yellow
Shape	plate-shaped
Size/mm ³	0.21×0.14×0.04
<i>T</i> /K	229.99(10)
Crystal System	monoclinic
Space Group	<i>C2/c</i>
<i>a</i> /Å	23.2710(5)
<i>b</i> /Å	23.7721(4)
<i>c</i> /Å	13.68963(17)
<i>α</i> /°	90
<i>β</i> /°	98.8968(15)
<i>γ</i> /°	90
<i>V</i> /Å ³	7482.0(2)
<i>Z</i>	4
<i>Z</i> '	0.5
Wavelength/Å	1.54184
Radiation type	CuKα
<i>θ</i> _{min} /°	3.719
<i>θ</i> _{max} /°	76.061
Measured Refl's.	45562
Indep't Refl's	7784
Refl's <i>I</i> ≥2σ(<i>I</i>)	6691
<i>R</i> _{int}	0.0311
Parameters	430
Restraints	42
Largest Peak/e Å ⁻³	0.310
Deepest Hole/e Å ⁻³	– 0.520
GooF	1.074
<i>wR</i> ₂ (all data)	0.1153
<i>wR</i> ₂	0.1104
<i>R</i> ₁ (all data)	0.0446
<i>R</i> ₁	0.0383
<i>CCDC number</i>	2114605

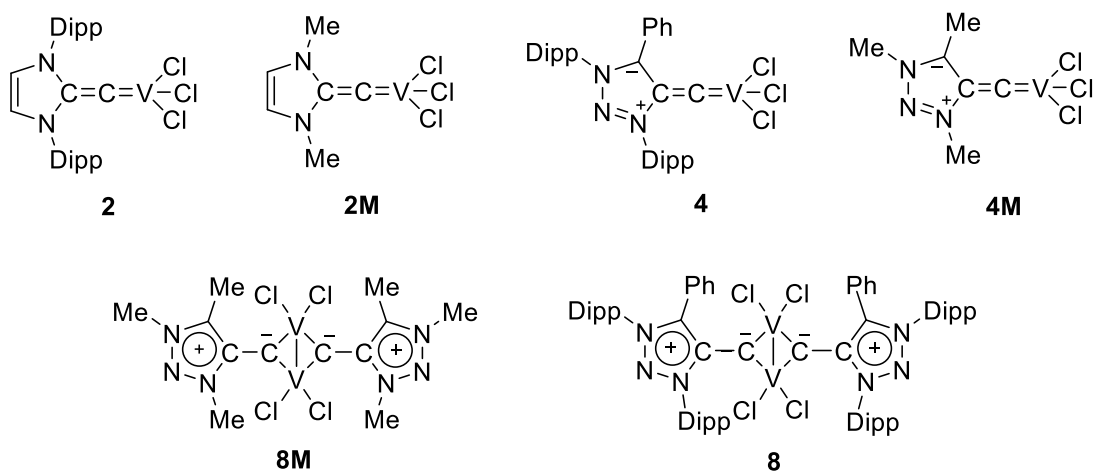
5. Quantum chemical calculations

All DFT computations were carried out using the Gaussian16 package (revision C.01).⁷ Gas phase geometry optimizations were performed using the BP86 functional⁸ along with the def2-TZVP basis set for all atoms.⁹ Frequency computations confirmed that all optimized molecular geometries were minima (Number of imaginary frequencies (NIMAG): 0). The NBO analyses¹⁰ were performed with the Version 3.1 of the NBO program which was implemented in the G16 C.01 version of the Gaussian program.¹¹ For visualization of the natural bond orbitals the program Jmol was used.¹²

Table S7. Calculated absolute energies, $E(\text{SCF})$, and free energies at 298 K, G^{298} , for compounds of interest.

Compound	Method/basis set	$E(\text{SCF})$ [a.u.]	NIMAG ZPVE [kJ mol ⁻¹]	G^{298} [a.u.]
2M	BP86/def2-TZVP	-2668.16595	0,352	-2668.07915
2	BP86/def2-TZVP	-3523.66041	0,1476	-3523.17471
4M	BP86/def2-TZVP	-3456.21679	0,1073	-3455.87696
4	BP86/def2-TZVP	-3770.80242	0,1650	-3770.25625
8M	BP86/def2-TZVP	-4526.47849	0,780	-4526.24992

Table S8. Comparison of the structural parameters of compounds **2**, **2M**, **4**, **4M**, **8** and **8M**; experimental data from XRD and computed data calculated at the BP86/def2-TZVP level.



	2 (exp.)	2 (calc.)	2M (calc.)	4 (exp.)	4 (calc.)	4M	8 (exp.)	8M
C–N [Å]	1.358(3)	1.387	1.381	1.376(2)	1.400	1.397	1.385(2)	1.388
WBI	–	1.15	1.16	–	1.11	1.12	–	1.15
C–C [Å]	1.412(3)	1.389	1.387	1.423(2)	1.394	1.392	1.419(2)	1.412
WBI	–	1.32	1.32	–	1.30	1.30	–	1.25
C–V [Å]	1.706(2)	1.706	1.702	1.704(17)	1.704	1.699	1.899(16)	1.889
WBI	–	2.09	2.10	–	2.10	2.13	–	1.10
V–Cl [Å]	2.204(6)	2.195	2.205	2.210(5)	2.206	2.210	2.234(5)	2.224
WBI	–	0.97	0.95	–	0.96	0.97	–	0.88
V–V [Å]	–	–	–	–	–	–	2.471(5)	2.458
WBI	–	–	–	–	–	–	–	0.88
∠C–C–V [°]	178.6	179.0	178.3	177.0	179.5	178.1	137.8	139.4

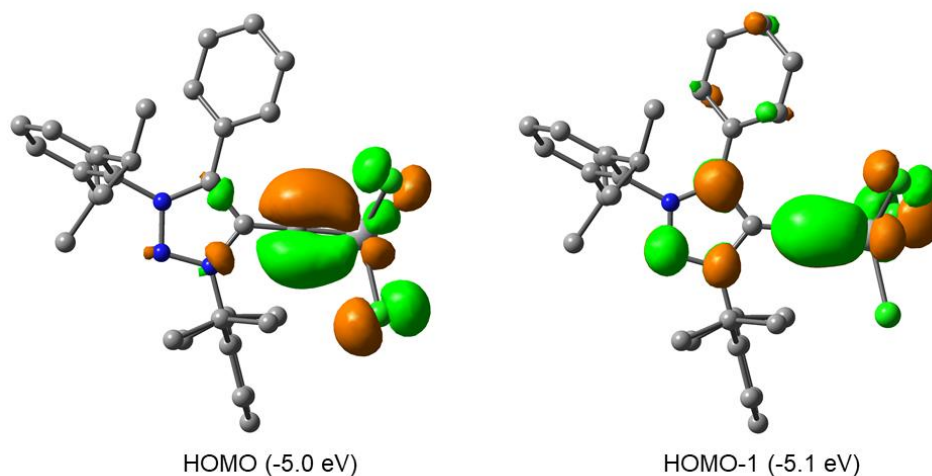


Figure S41. Selected surface diagrams of the frontier orbitals of vinylidene complex **4** (isovalue = 0.04; calculated at BP86/def2-TZVP level of theory).

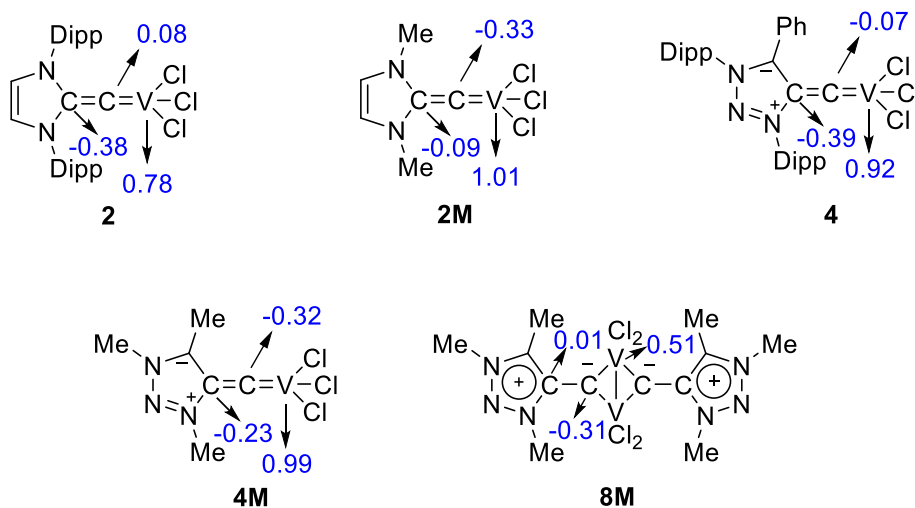
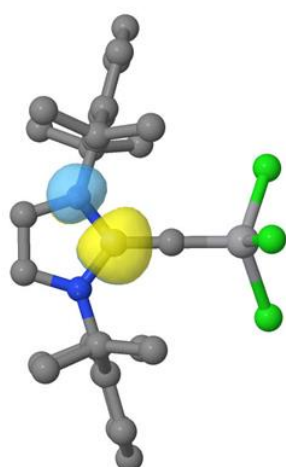
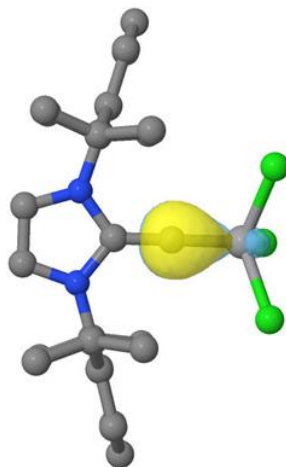


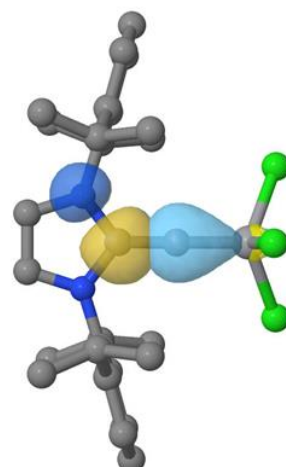
Figure S42. Calculated NPA charges of compounds **2M**, **2**, **4M**, **4**, and **8M** (calculated at BP86/def2-TZVP//BP86/def2-TZVP level, calculated NPA charges in [a.u.]).



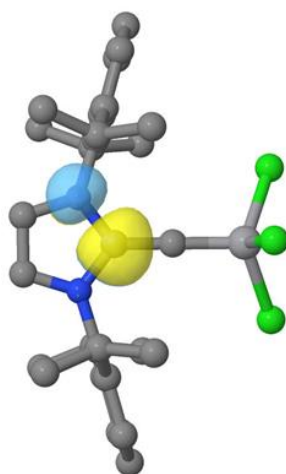
NBO 155
 π^* -orbital (C-N)
0.7e



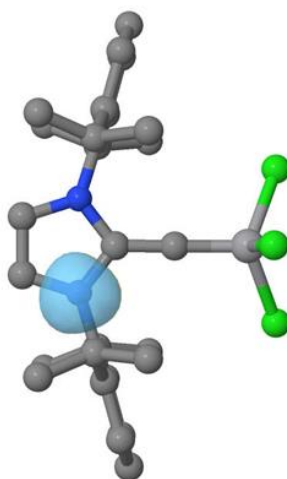
NBO 70
 π -orbital (C-V)
1.7e



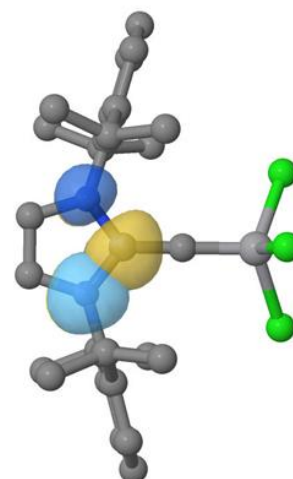
NBO 70/155
 π - π^* conjugation
 $E_{ij} = 56.8$ kcal/mol



NBO 155
 π^* -orbital (C-N)
0.7e



NBO 64
 π -orbital (C-V)
1.5e



NBO 64/155
 n - π^* interaction
 $E_{ij} = 57.4$ kcal/mol

Figure S43. The calculated natural bond orbitals (NBOs) of **2** (BP86/def2-TZVP//BP86/def2-TZVP, at an isodensity value of 0.04; the orbital occupancy and the second-order perturbation energy (E_{ij}) are given in italic).

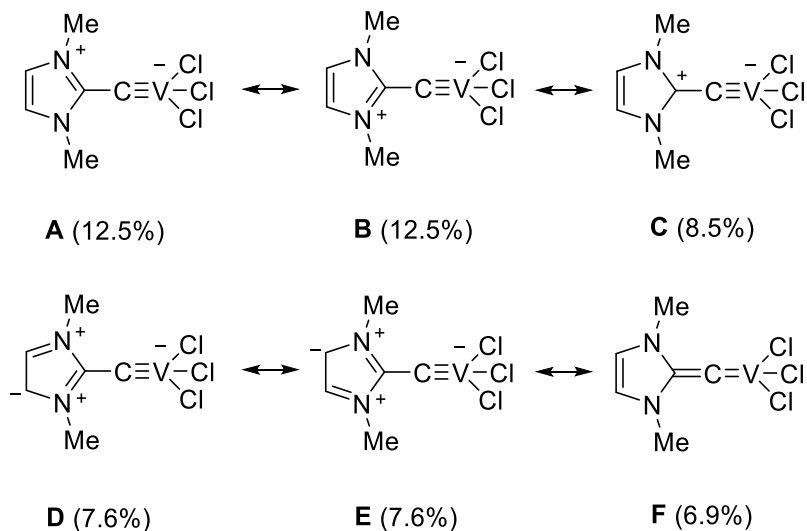


Figure S44. Leading resonance structures for model **2M** according to natural resonance theory (calculated at BP86/def2-TZVP//BP86/def2-TZVP level). The remaining 44.4% consists of multiple resonance structures of which each had a small contribution.

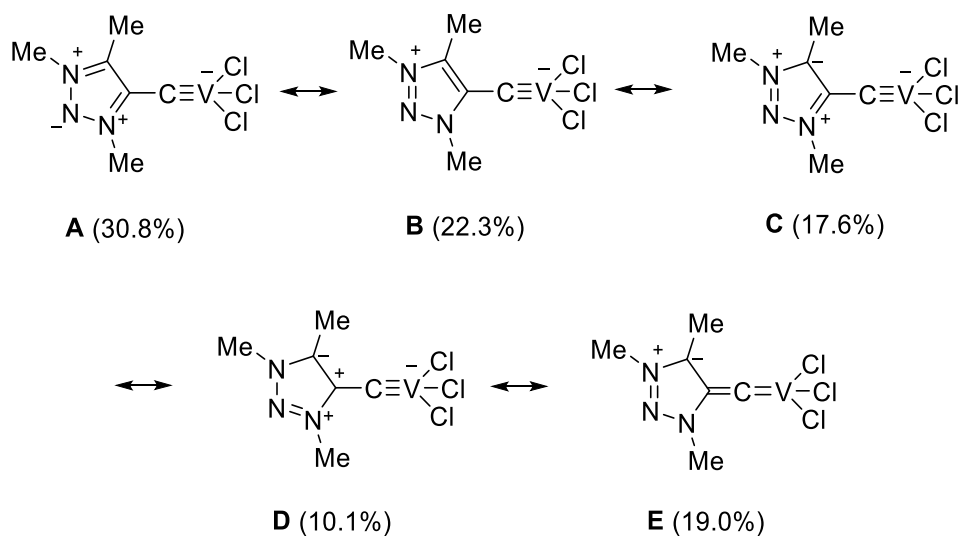


Figure S45. Leading resonance structures for model **4M** according to natural resonance theory (calculated at BP86/def2-TZVP//BP86/def2-TZVP level).

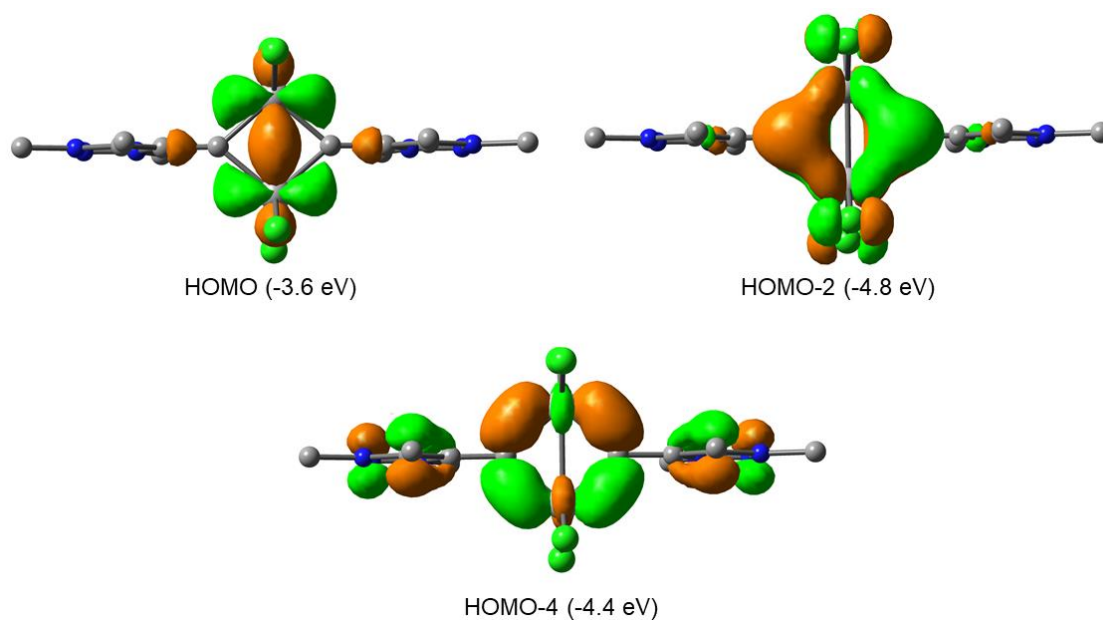


Figure S46. Selected surface diagrams of the frontier orbitals of vinylidene complex **8** (isovalue = 0.04; calculated at BP86/def2-TZVP level of theory).

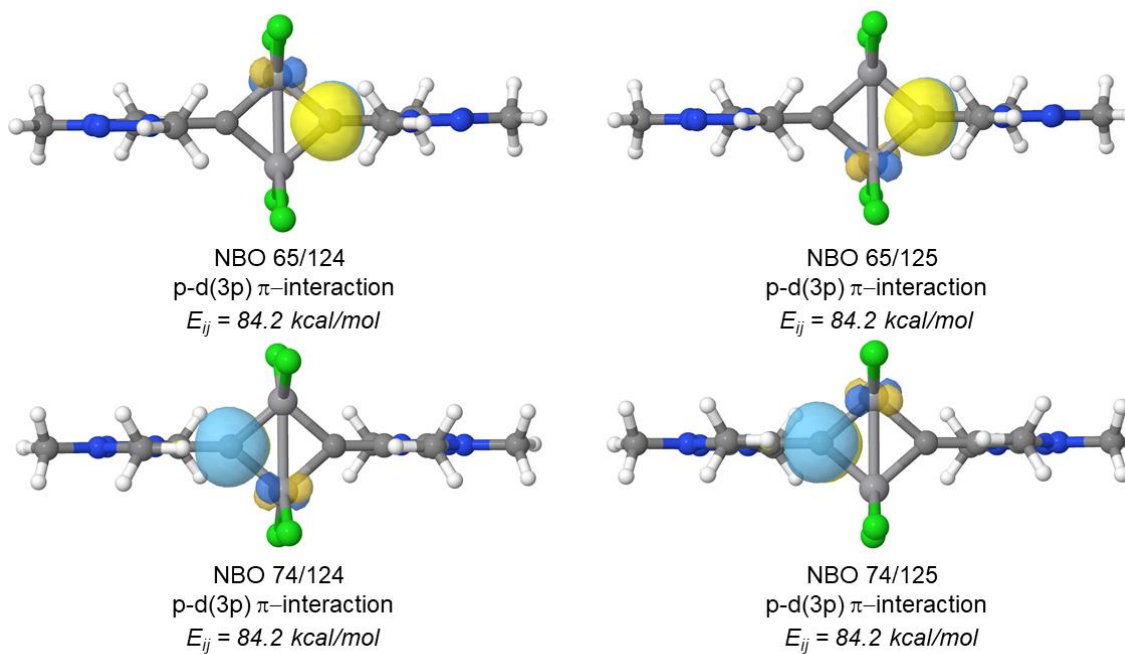


Figure S47. The calculated natural bond orbitals (NBOs) of **8M** (BP86/def2-TZVP//BP86/def2-TZVP, at an isodensity value of 0.04; the second-order perturbation energy (E_{ij}) are given in italic).

Cartesian Coordinates of Computed Structures

2M, BP86/def2-TZVP

V	-1.43329750	-0.01214486	-0.00000002	C	-0.68188996	-0.29406577	-2.75674943
Cl	-2.01034032	2.11590900	-0.00002637	C	-2.48357674	-0.12477071	-1.01794748
Cl	-2.05414086	-1.05221368	1.82552371	H	1.39071969	-0.38045116	-3.57139622
Cl	-2.05414333	-1.05226117	-1.82549607	C	3.11959490	-1.34655088	-0.71159430
C	0.26897420	-0.03463587	-0.00000048	C	3.14489173	1.12031160	-0.96141337
C	1.65593165	-0.01289482	-0.00000020	H	-1.39069445	-0.38046218	-3.57140471
N	2.51481853	-1.09497624	-0.00000001	C	-3.11958008	-1.34656166	-0.71159328
N	2.47080517	1.10173787	0.00000063	C	-3.14489208	1.12029674	-0.96145166
C	3.82480245	-0.65278745	0.00000048	C	4.47102664	-1.29149390	-0.34327631
C	3.79702587	0.71319448	0.00000068	C	2.40698442	-2.69135998	-0.79087785
H	4.66465413	-1.33780933	0.00000106	C	4.49581493	1.11209438	-0.58640792
H	4.60849522	1.43164612	0.00000133	C	2.46113333	2.43685642	-1.31024139
C	1.96394496	2.46956607	-0.00000232	C	-4.47101411	-1.29150791	-0.34328425
H	2.30840993	3.00067146	-0.89815223	C	-2.40695814	-2.69136629	-0.79085048
H	0.86728641	2.42249385	0.00002159	C	-4.49581714	1.11207656	-0.58645303
H	2.30845033	3.00068877	0.89812168	C	-2.46113890	2.43684324	-1.31028319
C	2.06984010	-2.48285867	-0.00000086	H	4.99422865	-2.21652965	-0.09405739
H	0.97292443	-2.47912367	0.00000912	C	5.15325915	-0.07802736	-0.28110991
H	2.43487039	-2.99922195	-0.89853998	H	1.33566157	-2.49811228	-0.95473693
H	2.43488711	-2.99922782	0.89852801	C	2.91863343	-3.51509023	-1.99015944

2, BP86/def2-TZVP

V	-0.00001068	0.31457392	2.46569336	C	2.52849868	-3.48893182	0.52011400
Cl	-1.81216169	-0.65382974	3.24403197	H	5.03886980	2.05723397	-0.52767038
Cl	0.00008005	2.48227592	2.81055093	H	1.38762763	2.23592269	-1.44814734
Cl	1.81203247	-0.65400020	3.24407108	C	3.00239484	3.00203646	-2.63924008
C	-0.00000345	0.09195877	0.77469817	C	2.58671841	3.47131927	-0.17726988
C	0.00000221	-0.06536091	-0.60497673	H	-4.99421153	-2.21654285	-0.09405261
N	1.10102924	-0.15522200	-1.44291850	C	-5.15325522	-0.07804474	-0.28114085
N	-1.10101856	-0.15523064	-1.44292554	H	-1.33563297	-2.49811135	-0.95468635
C	0.68190973	-0.29406032	-2.75674515	C	-2.52849574	-3.48892975	0.52014417
C	2.48358469	-0.12475937	-1.01793149	C	-2.91857422	-3.51510862	-1.99013784
				H	-5.03887804	2.05721383	-0.52773138

H	-1.38764049	2.23590508	-1.44823889	Cl	2.48039214	1.98078145	0.10614205
C	-3.00244949	3.00205882	-2.63924645	C	0.06603241	-0.00412165	-0.01688478
C	-2.58667140	3.47127957	-0.17728086	C	-1.32019829	0.12143486	-0.01196505
H	6.20438374	-0.05902695	0.01389105	N	-2.01634216	1.33271417	0.00220537
H	3.98884559	-3.74859509	-1.87969775	C	-2.35507420	-0.84245591	-0.01127782
H	2.79148000	-2.97467227	-2.94032517	N	-3.34261946	1.19052816	0.00537429
H	2.37212265	-4.46780817	-2.06312098	N	-3.51687257	-0.13209762	-0.00115532
H	1.93551176	-4.41383847	0.45488602	C	-2.25349640	-2.32366697	-0.01635151
H	2.16809600	-2.90347931	1.37721744	H	-2.72409764	-2.77355319	0.87224038
H	3.57103797	-3.77998399	0.72024361	H	-2.72090478	-2.76720353	-0.90991511
H	4.07535648	3.23591073	-2.56085412	H	-1.18958215	-2.59416999	-0.01544034
H	2.47434998	3.93055466	-2.90499705	C	-1.41323146	2.65847889	-0.02198495
H	2.87634927	2.28823249	-3.46727018	H	-0.38305687	2.55706918	0.34336038
H	2.17512521	3.08448605	0.76502313	H	-1.39244801	3.04405922	-1.05090697
H	2.03524539	4.38678441	-0.43990366	H	-1.99753051	3.32899679	0.61824888
H	3.63577059	3.75623033	-0.00454850	C	-4.87918306	-0.65230918	0.01292597
H	-6.20438157	-0.05904697	0.01385394	H	-5.04938056	-1.27485014	-0.87522047
H	-1.93549565	-4.41382943	0.45493795	H	-5.04096991	-1.25213014	0.91829257
H	-3.57103626	-3.77999388	0.72024999	H	-5.56027316	0.20446133	0.00536195
H	-2.16812149	-2.90346654	1.37725217	4, BP86/def2-TZVP			
H	-3.98878718	-3.74862030	-1.87969812	V	3.13486045	1.77866346	-0.34137976
H	-2.37205475	-4.46782303	-2.06308100	Cl	2.92524720	3.62914147	0.84176748
H	-2.79140359	-2.97469597	-2.94030431	Cl	3.45132083	2.15141782	-2.47966651
H	-2.87644555	2.28827228	-3.46729782	Cl	4.66702752	0.45307908	0.51870351
H	-2.47440524	3.93057722	-2.90500372	C	1.64255616	0.96619710	-0.21266061
H	-4.07540510	3.23594416	-2.56081243	C	0.42596575	0.29493082	-0.09987862
H	-3.63571695	3.75617955	-0.00450116	N	0.29849192	-1.07466874	0.16168437
H	-2.03521561	4.38675372	-0.43991976	C	-0.92624008	0.73547610	-0.20906826
H	-2.17503129	3.08442581	0.76498327	N	-0.96938224	-1.48891977	0.23988020
4M, BP86/def2-TZVP				C	1.37361055	-2.02269513	0.36489696
V	1.76170741	-0.10672674	-0.00072045	N	-1.69068274	-0.38715621	0.01305585
Cl	2.33042593	-1.10205790	-1.87080133	C	-1.42357747	2.08240677	-0.47926175
Cl	2.28334184	-1.26108460	1.79164796	C	1.82441202	-2.24460899	1.68182656

C	1.92236704	-2.66776077	-0.76168627	H	1.15756020	-3.30119483	4.19674808
C	-3.13481384	-0.50863110	0.10233070	H	2.84401858	-0.06334497	3.04547991
C	-2.62168745	2.32613168	-1.18327721	H	3.03953620	-1.45549216	4.13505298
C	-0.65669378	3.18367537	-0.04344063	H	1.83331496	-0.20757904	4.50949910
C	2.86334246	-3.16960812	1.85111428	H	2.95670477	-0.90649134	-2.65489356
C	1.23049662	-1.53976220	2.89423345	H	2.17491695	-1.63311291	-4.07938594
C	2.96111724	-3.57940612	-0.52796319	H	3.39419148	-2.55389071	-3.17111758
C	1.43959765	-2.42100568	-2.18510246	H	1.62200790	-4.48614849	-2.90130060
C	-3.82518461	-1.09821910	-0.97795003	H	0.45843882	-3.49895041	-3.80894920
C	-3.77260895	-0.04998248	1.27353345	H	0.03717133	-4.11388161	-2.18724773
H	-3.22142462	1.49455365	-1.55150233	H	-5.78842852	-1.65874291	-1.67217821
C	-3.04251919	3.63221095	-1.43065572	C	-5.88450991	-0.74740861	0.27591395
C	-1.08576268	4.48627031	-0.29686001	H	-2.07292669	-1.31471875	-2.18950486
H	0.28086189	3.01643659	0.48885838	C	-3.14447468	-3.17426995	-2.22603282
H	3.24243678	-3.36719589	2.85544830	C	-3.73079277	-1.07121800	-3.52320354
C	3.42627431	-3.83016224	0.76114061	H	-5.69925522	0.16508785	2.21650124
H	0.49979635	-0.79853851	2.53553606	H	-1.95445639	0.57591818	2.21962828
C	0.47452523	-2.53771877	3.79361491	C	-3.18033017	-0.36448015	3.70616298
C	2.30260289	-0.77074480	3.68847619	C	-3.47804866	1.97878731	2.76840187
H	3.41569791	-4.09676035	-1.37488694	H	-2.61017616	5.73849196	-1.18686805
H	0.63341172	-1.67179283	-2.14952572	H	-6.97041591	-0.83885187	0.34365569
C	2.55997399	-1.84286608	-3.06986713	H	-2.66659955	-3.57907825	-1.32295059
C	0.85234088	-3.70551240	-2.80201769	H	-2.60897109	-3.56184516	-3.10541716
C	-5.21795608	-1.20624166	-0.85914574	H	-4.17714630	-3.55419696	-2.26469586
C	-3.12619804	-1.63237824	-2.22272926	H	-4.77309505	-1.39556785	-3.66169705
C	-5.16814268	-0.17955600	1.32733448	H	-3.15629711	-1.43120433	-4.38954134
C	-3.02628920	0.53742292	2.46526569	H	-3.71295699	0.02823473	-3.54058665
H	-3.96853573	3.80211763	-1.98322441	H	-4.23060875	-0.42030827	4.03077721
C	-2.27899947	4.71756558	-0.98746011	H	-2.59301811	0.04059381	4.54377517
H	-0.47568586	5.32307523	0.04708405	H	-2.83356346	-1.38821145	3.50563070
H	4.24028239	-4.54095789	0.91700864	H	-3.35090077	2.63249210	1.89427491
H	-0.32032671	-3.05715984	3.23851222	H	-2.88401223	2.39451620	3.59579357
H	0.01700862	-2.01458380	4.64714107	H	-4.53657738	2.01135465	3.06887329

8M, BP86/def2-TZVP

V	0.00002716	-0.21426842	1.22909390	H	2.80397019	-2.56147533	0.00094874
Cl	0.00006612	1.62561005	2.52043938	C	6.40774804	-0.45921944	0.00009888
Cl	0.00006732	-2.18553380	2.25870062	H	6.60080227	-1.06303843	0.89678930
N	-3.45811638	1.39062335	0.00038238	H	6.60075999	-1.06346360	-0.89631296
N	-4.79280543	1.31380936	0.00036354	H	7.05206696	0.42565011	-0.00012164
N	-5.02566091	0.00183766	0.00003247	C	2.79035899	2.68498223	-0.00031666
C	-2.82129090	0.15764006	0.00006272	H	2.15288931	2.75802676	-0.89305585
C	-3.89315609	-0.75946566	-0.00017237	H	2.15322376	2.75839101	0.89262994
C	-1.42190361	-0.02663195	0.00001879	H	3.56106460	3.46261342	-0.00061038
V	-0.00002794	-0.21403696	-1.22915351	C	-2.79037428	2.68499656	0.00067767
Cl	-0.00003621	1.62608410	-2.52015555	H	-2.15291516	2.75793782	0.89343271
Cl	-0.00010098	-2.18510345	-2.25913400	H	-2.15322996	2.75851823	-0.89225309
N	3.45810997	1.39061344	-0.00018563	H	-3.56108503	3.46262261	0.00105837
N	4.79279936	1.31380807	-0.00014722	C	-3.85491781	-2.24435732	-0.00052529
N	5.02566321	0.00183809	0.00001744	H	-4.34091362	-2.67101138	0.89145388
C	2.82129207	0.15762581	-0.00003629	H	-4.34162281	-2.67060593	-0.89230701
C	3.89316326	-0.75947265	0.00010668	H	-2.80394602	-2.56146136	-0.00099962
C	1.42190508	-0.02664963	-0.00004282	C	-6.40774397	-0.45922612	-0.00007810
C	3.85493899	-2.24436473	0.00026644	H	-6.60080079	-1.06297277	-0.89681635
H	4.34071735	-2.67089231	-0.89189323	H	-6.60075015	-1.06354280	0.89628636
H	4.34186860	-2.67073408	0.89186714	H	-7.05206537	0.42564158	0.00021822

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