Supporting Information

for

Bis-cyclic(alkyl)(amino)carbene Isomers: Stable *trans*-bis(CAAC) versus Facile Olefin Formation for *cis*-bis(CAAC)

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General Considerations

Unless otherwise stated, the synthesis and handling of the compounds was performed under strict exclusion of air and moisture in an argon atmosphere, using a double-manifold vacuum line and an MBRAUN glove box operating with argon.

Pentane was dried using an MBRAUN solvent purification system and stored in a 500 mL glass vessel containing sodium. Benzene, toluene, and tetrahydrofuran were dried over potassium, distilled for storage into 500 mL air-tight vessels containing sodium/benzophenone ketyl, and vacuum-transferred into the reaction vessel. Acetonitrile and dichloromethane were dried over CaH_2 and stored in 500 mL air-tight vessels over 4 Å molecular sieves. 2,6-Diisopropylaniline (90%, Millipore-Sigma) was distilled prior to use. Cyclohexane-1,4-dimethanol (*cis*-*trans* mixture, Millipore-Sigma), chloro(1,5-cyclooctadiene)rhodium(I) dimer (STREM), iridium trichloride (Pressure Chemicals), 3-bromo-2-methylprop-1-ene (Oakwood Chemicals), and all other reagents (Millipore-Sigma, Oakwood Chemicals) were used as received.

Nuclear magnetic resonance (NMR) spectra were acquired on Bruker Avance and Avance III 400 MHz spectrometers at 298 K, unless otherwise noted. ^{1}H and ^{13}C NMR chemical shifts were referenced to residual solvent peaks and naturally abundant ^{13}C resonances for all deuterated solvents: $CHCl_3$ (7.26 ppm, ^{1}H) and $CHCl_3$-d_1 (77.16 ppm, ^{13}C); CH_2Cl_2-d_1 (5.32 ppm, ^{1}H) and CH_2Cl_2-d_2 (54.00 ppm, ^{13}C); tetrahydrofuran-d_7 (3.58 ppm, ^{1}H) and tetrahydrofuran-d_8 (67.21 ppm, ^{13}C); toluene-d_7 (2.08 ppm, ^{1}H) and tolune-d_8 (137.48 ppm, ^{13}C).[1]

X-ray crystallographic analyses were performed on a Bruker SMART APEX II CCD diffractometer using suitable single crystals coated in Paratone 8277 oil (Exxon) and mounted on glass-fiber loops. Measurements were processed with the Apex III software suite. Structures were solved using the SHELXT[2] structure solution program with intrinsic phasing and refined using the SHELXL[3] refinement package with least squares minimization, all under the Olex2 platform.[4] Full crystallographic details can be found in each independently uploaded crystallographic information file (.cif).

The X-band EPR spectrum (9.34 GHz) was recorded on a Bruker EMX 10/12 spectrometer equipped with variable temperature capabilities with a 10-inch magnet and a 12 kV power supply. 2-MeTHF (dried over Na/benzophenone and freshly distilled prior to use) was used as the solvent. The simulated spectrum was generated using EasySpin.[5]

All elemental analyses were obtained on a Perkin-Elmer Model 2400 series II analyzer. High-resolution electrospray mass spectra (HRESI-MS) were obtained with a Kratos MS-80 spectrometer using samples prepared in the glovebox and transferred in a gas-tight syringe.

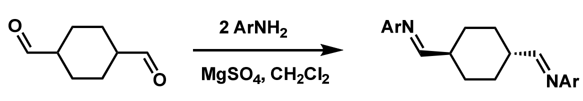
Experimental Procedures

Synthesis of cyclohexane-1,4-dicarbaldehyde[6]

In air, a 1 L round-bottom flask was charged with cyclohexane-1,4-dimethanol (12.0 g, 83.2 mmol, mixture of isomers) and dichloromethane (160 mL); the diol was poorly soluble. TEMPO (0.52 g, 3.33 mmol), potassium bromide (0.380 g, 3.19 mmol), water (32 mL), and dichloromethane (8 mL) were then added to the cyclohexane-1,4-dimethanol mixture. A solution of potassium bicarbonate (7.42 g, 74.1 mmol), sodium hypochlorite (165 mL, 13% in water), and water (200 mL) were slowly added to the reaction mixture so that a gentle reflux was maintained. After complete addition, the reaction was stirred at room temperature for 1 h. The biphasic mixture was separated and the aqueous phase was extracted twice with dichloromethane (40 mL × 2). The combined organic phases were treated with a solution of potassium iodide (1.10 g, 6.63 mmol) in water (45 mL) and concentrated hydrochloric acid (37%, 17 mL). The organic phase was then treated with a saturated solution of sodium thiosulfate in water (50 mL), washed twice with water (50 mL × 2), and dried with sodium sulfate. The solvent was removed *in vacuo*, and the cyclohexane-1,4-dicarbaldehyde was isolated as a pale-yellow oil (5.72 g, 40.8 mmol, 49.0% yield, mixture of isomers) that was used immediately and without further purification for the synthesis of the aldimine. The crude product, which was used without further purification in the subsequent synthetic step, matched the reported NMR data and was found to be a 92% mixture of *cis* and *trans* isomers by GC-MS.

Dialdehydes have been shown to be unstable in pure form, resulting in the formation of polymers/oligomers.[7] The cyclohexane-1,4-dicarbaldehyde was isolated as a thin, pale-yellow oil that was immediately used for the subsequent reaction step. When left overnight either in air or under an inert atmosphere, the oil solidified into a glassy solid and yields were drastically reduced when this material was used for dialdimine syntheses. No attempts were made to reconvert the oligomerized material back to dialdehyde by vacuum distillation.

Synthesis of dialdimine *trans*-1a



***trans*-1a,b**

Ar = 2,6-diisopropylphenyl (Dipp), 1a
2,4,6-diisopropylphenyl (Tripp), 1b

In air, a 1000 mL round-bottom flask was charged with cyclohexane-1,4-dicarbaldehyde (22.0 g, 157 mmol), 2,6-diisopropylaniline (55.7 g, 314 mmol), magnesium sulphate (94.5 g, 785 mmol), and dichloromethane (500 mL), prior to sparging the mixture with argon for five minutes. The reaction was stirred for 16 h at room temperature under an argon atmosphere. The magnesium sulphate was removed by filtration and the solvent was removed *in vacuo* to isolate a yellow oil. Treatment of the oil with pentane (250 mL) led to the crystallization of *trans*-**1a** as a yellow solid that was isolated by vacuum filtration (42.3 g, 92.2 mmol, 59% yield). Anal. calcd. for $C_{32}H_{46}N_2$:

C 83.79; H 10.11; N 6.11. Found: C 83.16; H 10.15; N 6.14. The identity of the compound was confirmed by single-crystal X-ray crystallography (*vide infra*).

Dialdimine *trans*-**1a** was stored under an inert argon atmosphere in the glovebox because when exposed to in air it was found to slowly degrade, over several weeks, turning from bright yellow to brown/orange.

^{1}H NMR ($CDCl_3$, 25 °C, 400 MHz): δ = 7.58 (d, $^3J_{HH}$ = 4.59 Hz, 2H, C***H***=N), 7.05–7.14 (m, 6H, *m,p*-C_6***H***$_3$), 2.93 (sept, $^3J_{HH}$ = 6.93 Hz, 4H, C***H***$(CH_3)_2$), 2.53 (broad m, 2H, Cy-C***H***), 2.22 (m, 4H, Cy-C***H***$_2$), 1.58 (m, 4H, Cy-C***H***$_2$), 1.18 (d, $^3J_{HH}$ = 6.93 Hz, 24H, CH(C***H***$_3$)$_2$) ppm. **^{13}C NMR** ($CDCl_3$, 25°C, 101 MHz): δ = 170.2 (***C***H=N), 149.0 (N-***C***$_6$H$_3$), 137.5 (*o*-***C***$_6$H$_3$), 124.0 (*p*-***C***$_6$H$_3$), 123.0 (*m*-***C***$_6$H$_3$), 43.9 (Cy-***C***H), 28.6 (Cy-***C***H$_2$), 27.8 (***C***H$(CH_3)_2$), 23.5 (CH(***C***H$_3$)$_2$) ppm.

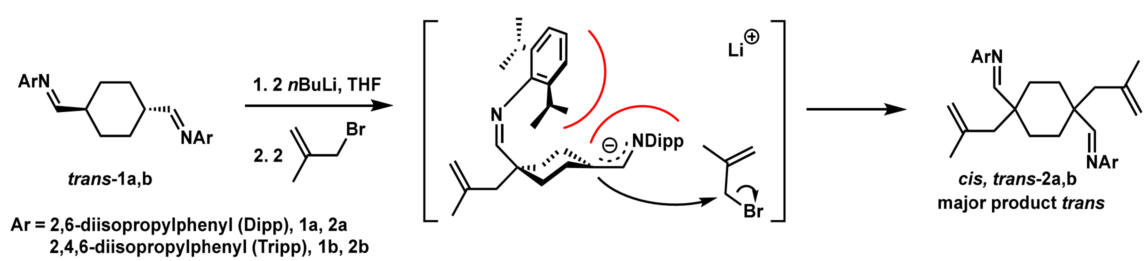
Synthesis of dialdimine *trans*-1b

Derivative *trans*-**1b** was synthesized using the same procedure *trans*-**1a**, using cyclohexane-1,4-dicarbaldehyde (1.89 g, 13.5 mmol), 2,4,6-triisopropylaniline (5.91 g, 26.9 mmol), and magnesium sulphate (8.12 g, 67.5 mmol) in dichloromethane (60 mL). Product *trans*-**1b** was isolated as a pale yellow solid (3.61 g, 6.65 mmol, 49.3% yield). Anal. calcd. for $C_{38}H_{58}N_2$: C 84.07; H 10.77; N 5.16. Found: C 83.70; H 11.15; N 5.21.

Dialdimine *trans*-**1b** was stored under an inert argon atmosphere in the glovebox because when exposed to in air it was found to slowly degrade, over several weeks, turning from bright yellow to brown/orange.

^{1}H NMR ($CDCl_3$, 25°C, 400 MHz): δ = 7.58 (d, $^3J_{HH}$ = 4.75 Hz, 2H, C***H***=N), 6.97 (s, 4H, *m*-C_6***H***$_2$), 2.92 (sept, $^3J_{HH}$ = 6.90 Hz, 4H, *o*-C***H***$(CH_3)_2$), 2.88 (sept, $^3J_{HH}$ = 6.90 Hz, 2H, *p*-C***H***$(CH_3)_2$), 2.51 (broad m, 2H, Cy-C***H***), 2.19 (m, 4H, Cy-C***H***$_2$), 1.55 (m, 4H, Cy-C***H***$_2$), 1.27 (d, $^3J_{HH}$ = 6.90 Hz, 12H, *p*-CH(C***H***$_3$)$_2$), 1.17 (d, $^3J_{HH}$ = 6.90 Hz, 24H, *o*-CH(C***H***$_3$)$_2$) ppm. **^{13}C NMR** ($CDCl_3$, 25°C, 101 MHz): δ = 170.3 (***C***H=N), 146.9 (N-***C***$_6$H$_2$), 144.0 (*o*-***C***$_6$H$_2$), 137.2 (*p*-***C***$_6$H$_2$), 120.9 (*m*-***C***$_6$H$_2$), 43.9 (Cy-***C***H), 34.1 (*p*-***C***H$(CH_3)_2$), 28.6 (Cy-***C***H$_2$), 27.9 (*o*-***C***H$(CH_3)_2$), 24.3 (*p*-CH(***C***H$_3$)$_2$), 23.6 (*o*-CH(***C***H$_3$)$_2$) ppm.

Synthesis of alkylated dialdimine as a mixture of isomers *cis*- and *trans*-2a



A 1000 mL 2-neck round-bottom flask was charged with *trans*-**1a** (36.0 g, 78.5 mmol) and THF (300 mL) and 2.5 M *n*-butyl lithium in hexanes (69.1 mL, 173 mmol) was added dropwise at

−78°C. After stirring for 15 min, the reaction was allowed to warm up to room temperature and stirred for an additional hour. The mixture was cooled back to −78°C and 3-bromo-2-methylpropene (18.0 mL, 179 mmol) was added dropwise. The reaction was allowed to warm up to room temperature and stirring was continued for 16 h. Solvent was removed *in vacuo*, yielding a thick yellow oil that was subjected to two cycles of pentane addition, sonication, and solvent removal for complete elimination of traces of THF. Pentane (100 mL) was added a third time and the solids were filtered off. The solvent was removed from the filtrate *in vacuo* to generate a waxy white solid that was washed with acetonitrile (200 mL), yielding *cis*- and *trans*-**2a** (33.9 g, 59.8 mmol, 76% yield), which was collected as a white powder *via* vacuum filtration. Anal. calcd. for $C_{40}H_{58}N_2$: C 84.75; H 10.31; N 4.99. Found: C 84.51; H 10.83; N 4.91.

Upon recrystallization of the alkylated dialdimines *cis*- and *trans*-**2a** from benzene and acetonitrile, the two stereoisomers generated distinct crystals. *trans*-**2a** yielded clear, colourless bars, while the *cis*-**2a** formed clear, colourless blocks. We found that crystallizations from isomeric mixtures with *trans*-**2a**:*cis*-**2a** ratios of 0.6:1 or greater in favor of the *trans*-isomer selectively yielded *trans*-**2a**. This crystallization procedure was used to selectively isolate this isomer from the mixture.

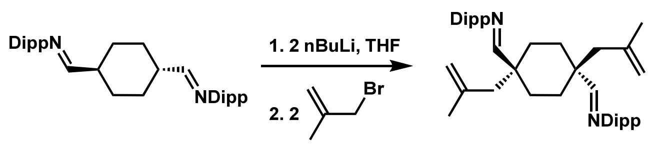
^{1}H NMR ($CDCl_3$, 25°C, 400 MHz): *cis*-**2a** *(major product)* δ = 7.64 (s, 2H, C***H***=N), 7.10 (m, 6H, *m,p*-C_6***H_3***), 4.97 (m, 2H, C***H_2***=C), 4.82 (m, 2H, C***H_2***=C), 3.00 (sept, $^3J_{HH}$ = 6.90 Hz, 4H, C***H***$(CH_3)_2$), 2.43 (s, 4H, CC***H_2***C), 2.07 (m, 4H, Cy-C***H_2***), 1.85 (s, 6H, C***H_3***C), 1.85 (m, 4H, Cy-C***H_2***), 1.14 (d, $^3J_{HH}$ = 6.90 Hz, 24H, CH(C***H_3***$)_2$) ppm. *trans*-**2a** *(minor product)* δ = 7.60 (s, 2H, C***H***=N), 7.10 (m, 6H, *m,p*-C_6***H_3***), 4.91 (m, 2H, C***H_2***=C), 4.75 (m, 2H, C***H_2***=C), 3.06 (sept, $^3J_{HH}$ = 6.90 Hz, 4H, C***H***$(CH_3)_2$), 2.31 (s, 4H, CC***H_2***C), 2.13 (m, 4H, Cy-C***H_2***), 1.85 (m, 4H, Cy-C***H_2***), 1.81 (s, 6H, C***H_3***C), 1.22 (d, $^3J_{HH}$ = 6.90 Hz, 24H, CH(C***H_3***$)_2$) ppm. **^{13}C NMR** ($CDCl_3$, 25°C, 101 MHz): *cis*-**2a** *(major product)* δ = 173.3 (***C***H=N), 148.9 (N-***C_6***H_3), 142.3 (***C***=CH_2), 137.8 (*o*-***C_6***H_3), 123.9 (*p*-***C_6***H_3), 123.0 (*m*-***C_6***H_3), 115.5 (***C***=CH_2), 43.49 (Cy-***C***H), 29.1 (Cy-***C***H_2), 27.6 (***C***H$(CH_3)_2$), 25.4 (***C***H_3C), 23.9 (CH(***C***H_3)$_2$) ppm. *trans*-**2a** *(minor product)* δ = 172.5 (***C***H=N), 149.0 (N-***C_6***H_3), 141.8 (***C***=CH_2), 137.6 (*o*-***C_6***H_3), 124.0 (*p*-***C_6***H_3), 123.1 (*m*-***C_6***H_3), 115.8 (C=***C***H_2), 44.0 (Cy-***C***H), 30.3 (Cy-***C***H_2), 27.8 (***C***H$(CH_3)_2$), 25.6 (***C***H_3C), 23.9 (CH(***C***H_3)$_2$) ppm. *Cis*:*trans* ratio *ca.* 3.3:1.

Synthesis of alkylated dialdimine as a mixture of isomers *cis*- and *trans*-2b

Derivatives *cis*- and *trans*-**2b** were synthesized following the same procedure as described above for *cis*- and *trans*-**2a**, but using *trans*-**1b** (3.15 g, 5.80 mmol), 2.5 M n-butyl lithium in hexanes (5.10 mL, 12.8 mmol), and 3-bromo-2-methylpropene (1.34 mL, 13.3 mmol) in THF (50 mL). *Cis*- and *trans*-**2b** (2.60 g, 3.99 mmol, 69% yield) were collected as a white powder after vacuum filtration. Anal. calcd. for $C_{46}H_{70}N_2$: C 84.86; H 10.84; N 4.30. Found: C 84.04; H 10.71; N 4.26.

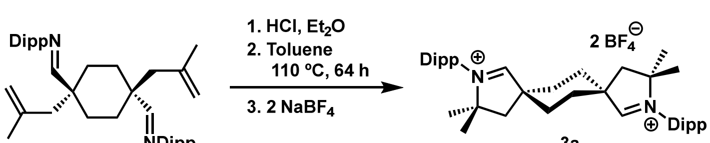
^{1}H NMR ($CDCl_3$, 25°C, 400 MHz): *cis*-**2b** *(major product)* δ = 7.63 (s, 2H, C***H***=N), 6.94 (s, 4H *m*-C_6***H_2***), 4.95 (m, 2H, C=C***H_2***), 4.81 (m, 2H, C=C***H_2***), 2.97 (sept, $^3J_{HH}$ = 6.90 Hz, 4H, *o*-C***H***$(CH_3)_2$), 2.87 (sept, $^3J_{HH}$ = 6.90 Hz, 2H, *p*-C***H***$(CH_3)_2$), 2.41 (s, 4H, CC***H_2***C), 2.03 (m, 4H, Cy-C***H_2***), 1.84 (s, 6H, C***H_3***C), 1.84 (m, 4H, Cy-C***H_2***), 1.25 (d, $^3J_{HH}$ = 6.90 Hz, 12H, *p*-CH(C***H_3***$)_2$), 1.13 (d, $^3J_{HH}$ = 6.90 Hz, 24H, *o*-CH(C***H***$_3$)$_2$) ppm. *trans*-**2b** *(minor product)* δ = 7.60 (s, 2H, C***H***=N), 7.00 (s, 4H *m*-C$_6$***H***$_2$), 4.88 (m, 2H, C=C***H***$_2$), 4.73 (m, 2H, C=C***H***$_2$), 3.05 (sept, $^3J_{HH}$ = 8.00 Hz, 4H, *o*-C***H***(CH$_3$)$_2$), 2.88 (sept, $^3J_{HH}$ = 8.00 Hz, 2H, *p*-C***H***(CH$_3$)$_2$), 2.28 (s, 4H, CC***H***$_2$C), 2.10 (m, 4H, Cy-C***H***$_2$), 1.84 (m, 4H, Cy-C***H***$_2$), 1.79 (s, 6H, C***H***$_3$C), 1.28 (d, $^3J_{HH}$ = 8.00 Hz, 12H, *p*-CH(C***H***$_3$)$_2$), 1.21 (d, $^3J_{HH}$ = 8.00 Hz, 24H, *o*-CH(C***H***$_3$)$_2$) ppm. **^{13}C NMR** (CDCl$_3$, 25°C, 101 MHz): *cis*-**2b** *(major product)* δ = 173.1 (***C***H=N), 146.7 (N-***C***$_6$H$_2$), 143.7 (*p*-***C***$_6$H$_2$), 142.5 (***C***=CH$_2$), 137.4 (*o*-***C***$_6$H$_2$), 120.9 (*m*-***C***$_6$H$_2$), 115.4 (C=***C***H$_2$), 43.4 (Cy-***C***H), 34.1 (*p*-***C***H(CH$_3$)$_2$), 29.1 (Cy-***C***H$_2$), 27.7 (*o*-***C***H(CH$_3$)$_2$), 25.4 (***C***H$_3$C), 24.3 (*p*-CH(***C***H$_3$)$_2$), 24.0 (*o*-CH(***C***H$_3$)$_2$) ppm. *trans*-**2b** *(minor product)* δ = 172.3 (***C***H=N), 146.8 (N-***C***$_6$H$_2$), 143.9 (*p*-***C***$_6$H$_2$), 141.9 (***C***=CH$_2$), 137.2 (*o*-***C***$_6$H$_2$), 121.0 (*m*-***C***$_6$H$_2$), 115.6 (C=***C***H$_2$), 44.0 (Cy-***C***H), 34.1 (*p*-***C***H(CH$_3$)$_2$), 30.4 (Cy-***C***H$_2$), 27.8 (*o*-***C***H(CH$_3$)$_2$), 25.6 (***C***H$_3$C), 24.4 (*p*-CH(***C***H$_3$)$_2$), 23.9 (*o*-CH(***C***H$_3$)$_2$) ppm. *Cis*:*trans* ratio *ca.* 3.4:1.0.

Synthesis of *trans*-alkylated dialdimine *trans*-2a



A 150 mL 2-neck round-bottom flask was charged with *trans*-**1a** (6.10 g, 13.3 mmol) and THF (50 mL) and 2.5 M *n*-butyl lithium in hexanes (11.7 mL, 29.3 mmol) was added dropwise at −78°C. After stirring for 15 min, the reaction was allowed to warm up to room temperature and stirred for an additional hour. The mixture was cooled back to −78°C and 3-bromo-2-methylpropene (3.09 mL, 30.7 mmol) was added dropwise. The reaction was allowed to warm up to room temperature and stirring was continued for 16 h. Solvent was removed *in vacuo*, yielding a thick yellow oil that was subjected to two cycles of pentane addition, sonication, and solvent removal for complete elimination of traces of THF. The resulting solid was extracted with pentane (20 mL) followed by hot hexanes (100 mL) and the two filtrates were kept separate. The product obtained from the pentane extraction was carried forward as a mixture of stereoisomers for the synthesis of **4a** (*vide infra*). The solvent was removed *in vacuo* from the hot hexanes filtrate, generating a waxy yellow solid. This solid was washed with acetonitrile (30 mL) to yield a white solid (3.05 g) that was recrystalized overnight by layering a concentrated benzene solution with acetonitrile. The clear and colourless crystals of *trans*-**2a** were collected and dried in vacuo (0.762 g, 1.34 mmol, 10% yield).

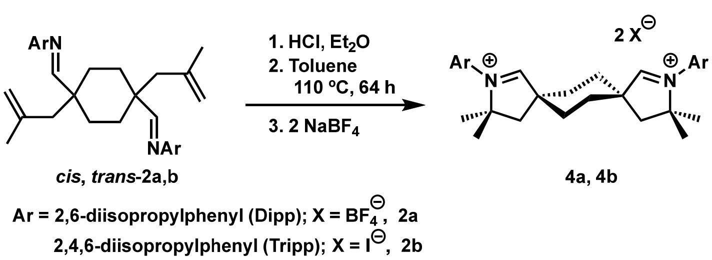
Synthesis of *trans*-iminium salt 3a



A 250 mL pressure flask was charged with *trans*-**2a** (3.10 g, 5.47 mmol), a magnetic stir bar, and diethyl ether (25 mL) and hydrochloric acid (12.3 mL, 2.0 M in diethyl ether, 24.6 mmol) was added at −78°C. After 15 min the reaction was allowed to warm up to room temperature and stirred for another three hours. Volatiles were removed *in vacuo*, 30 mL of dry toluene was added to the residue and the flask was stirred at 110 °C for 64 hours. The white precipitate was filtered in air and washed twice with diethyl ether (2 × 50 mL) to obtain the HCl_2 salt of the aldiminium (3.89 g). This was then placed in an Erlenmeyer flask with dichloromethane (150 mL) and $NaBF_4$ (1.26 g, 11.5 mmol). The mixture was stirred for 2 hours and then filtered; the solvent was removed *in vacuo* from the filtrate and the resulting solid was triturated with THF to yield **3a** as a white powder (3.67 g, 4.94 mmol, 90.4% yield). Crystalline plates were obtained following CH_2Cl_2-hexanes layering experiments. Anal. calcd. for $C_{40}H_{60}B_2F_8N_2$: C 64.13; H 8.08; N 3.73. Found: C 64.40; H 8.37; N 3.65.

^{1}H NMR (CD_3CN, 25°C, 400 MHz): δ = 8.90 (s, 2H, C***H***=N), 7.63 (t, $^3J_{HH}$ = 7.89 Hz, 2H, *p*-C_6***H***$_3$), 7.50 (d, $^3J_{HH}$ = 7.77 Hz, 4H, *m*-C_6***H***$_3$), 2.74 (sept, $^3J_{HH}$ = 6.72 Hz, 4H, C***H***$(CH_3)_2$), 2.62 (s, 4H, CC***H***$_2$C), 2.27 (m, 4H, Cy-C***H***$_2$), 2.12 (m, 4H, Cy-C***H***$_2$), 1.58 (s, 12H, C(C***H***$_3$)$_2$), 1.36 (d, 12H, CH(C***H***$_3$)$_2$), 1.12 (d, $^3J_{HH}$ = 6.72 Hz, 12H, CH(C***H***$_3$)$_2$) ppm. **^{13}C NMR** (CD_3CN, 25°C, 101 MHz): δ = 190.2 (***C***H=N), 145.4 (*o*-***C***$_6$H$_3$), 133.1 (*p*-***C***$_6$H$_3$), 130.0 (N-***C***$_6$H$_3$), 126.6 (*m*-***C***$_6$H$_3$), 85.7 (***C***$(CH_3)_2$), 52.2 (***C***1-Cy), 44.1 (C***C***H$_2$C), 30.4 (***C***H$(CH_3)_2$), 28.8 (C(***C***H$_3$)$_2$) 28.6 (Cy-***C***H$_2$), 26.2 (CH(***C***H$_3$)$_2$), 22.2 (CH(***C***H$_3$)$_2$) ppm.

Synthesis of *cis*-iminium salt 4a



A 250 mL pressure flask was charged with *cis*- and *trans*-**2a** (6.24 g, 11.0 mmol), a magnetic stir bar, and diethyl ether (60 mL) and hydrochloric acid (22.0 mL, 2.0 M in diethyl ether, 44.0 mmol) was added at -78°C. After 15 min the reaction was allowed to warm to room temperature and stirred for another three hours. Volatiles were removed *in vacuo*, 60 mL of dry toluene was added to the residue and the flask was stirred at 110 °C for 64 hours. The white precipitate was filtered in air and washed twice with diethyl ether (2 × 50 mL) to obtain the HCl_2 salt of the aldiminium (6.89 g) as a mixture of isomers. This was then placed in an Erlenmeyer flask with dichloromethane (175 mL) and $NaBF_4$ (2.23 g, 20.3 mmol). The mixture was stirred for 1.5 hours and then filtered; the solvent was removed *in vacuo* from the filtrate and the resulting solid was sonicated with diethyl ether. The ether slurry was then filtered, and the BF_4 diiminium salt was isolated as a crude mixture of isomers (7.17 g, 9.66 mmol). This was placed in an Erlenmeyer flask with chloroform (50 mL) and swirled vigorously. The slurry was filtered, and the filtrate was collected. The solid was extracted again with chloroform (30 mL) and filtered. The filtrates were combined and the solid was discarded. After solvent removal *in vacuo*, the solid was recrystalized overnight by layering a concentrated dichloromethane solution with pentane. The crystals were collected and triturated with THF to remove the co-crystalized dichloromethane, and [**4a**$(BF_4)_2$] was obtained as a white powder (5.43 g, 7.31 mmol, 67% yield based on the quantity of *cis*- and *trans*-**2a** mixture). Anal. calcd. for $C_{40}H_{60}B_2F_8N_2$: C 64.13; H 8.08; N 3.73. Found: C 63.60; H 8.58; N 3.52. Needle-shaped crystals were obtained following CH_2Cl_2-hexanes layering experiments.

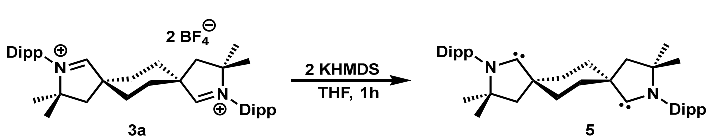
^{1}H NMR (CD_2Cl_2, 25°C, 400 MHz): δ = 9.36 (s, 2H, C***H***=N), 7.58 (t, $^3J_{HH}$ = 7.83 Hz, 2H, *p*-C_6***H_3***), 7.40 (d, $^3J_{HH}$ = 7.83 Hz, 4H, *m*-C_6***H_3***), 2.66 (s, 4H, CC***H_2***C), 2.64 (sept, $^3J_{HH}$ = 6.72 Hz, 4H, C***H***$(CH_3)_2$), 2.54 (m, 4H, Cy-C***H_2***), 2.18 (m, 4H, Cy-C***H_2***), 1.59 (s, 12H, C(C***H_3***$)_2$), 1.37 (d, $^3J_{HH}$ = 6.72 Hz, 12H, CH(C***H_3***$)_2$), 1.14 (d, $^3J_{HH}$ = 6.72 Hz, 12H, CH(C***H_3***$)_2$) ppm. **^{13}C NMR** (CD_2Cl_2, 25°C, 101 MHz): δ = 190.0 (***C***H=N), 144.5 (*o*-C_6H_3), 132.5 (*p*-***C***$_6H_3$), 129.2 (N-***C***$_6H_3$), 125.8 (*m*-***C***$_6H_3$), 84.2 (***C***$(CH_3)_2$), 51.8 (Cy-***C***H), 46.8 (C***C***H_2C), 30.8 (Cy-***C***H_2), 30.3 (***C***H$(CH_3)_2$), 28.8 (C(***C***$H_3)_2$), 26.1 (CH(***C***$H_3)_2$), 22.1 (CH(***C***$H_3)_2$) ppm.

Synthesis of *cis*-iminium salt 4b

Cis-derivative **4b** was synthesized using a similar procedure from *cis*- and *trans*-**2b** (2.10 g, 3.23 mmol), diethyl ether (20 mL) and hydrochloric acid (8.07 mL, 2.0 M in diethyl ether, 16.1 mmol) in a 50 mL pressure flask. The solid HCl_2 iminium salt (1.89 g) was obtained as a mixture of isomers, to which acetone (20 mL) was added. The mixture was filtered and the solid was discarded as **4b** dissolved while most of the unwanted **3b** isomer did not. Sodium iodide (1.78 g, 11.9 mmol) was added to the filtrate containing dissolved **4b** and the reaction was stirred for 4 hours. The mixture was filtered and removal of the volatiles from the filtrate *in vacuo* yielded (**4a**)I_2 (1.49 g, 1.96 mmol, 50.9% yield) as a yellow solid.

^{1}H NMR ($CDCl_3$, 25°C, 400 MHz): **4b** *(major product)* δ = 10.36 (s, 2H, C***H***=N), 7.11 (s, 2H, *m*-C_6***H_2***), 2.90 (m, 4H, Cy-C***H_2***), 2.90 (sept, $^3J_{HH}$ = 6.90 Hz, 2H, *p*-C***H***$(CH_3)_2$), 2.85 (s, 4H, CC***H_2***C), 2.59 (sept, $^3J_{HH}$ = 6.90 Hz, 4H, *o*-C***H***$(CH_3)_2$), 1.60 (s, 12H, C(C***H_3***$)_2$), 1.33 (d, $^3J_{HH}$ = 6.90 Hz, 12H, *o*-CH(C***H_3***$)_2$), 1.24 (d, $^3J_{HH}$ = 6.90 Hz, 12H, *p*-CH(C***H_3***$)_2$), 1.21 (d, $^3J_{HH}$ = 6.90 Hz, 12H, *o*-CH(C***H_3***$)_2$) ppm. **3b** *(minor product)* δ = 10.51 (s, 2H, C***H***=N), 7.13 (s, 2H, *m*-C_6***H_2***), 3.13 (d, $^2J_{HH}$ = 9.50 Hz, 4H, Cy-C***H_2***), 2.82 (s, 4H, CC***H_2***C), 1.95 (d, $^2J_{HH}$ = 9.50 Hz, 4H, Cy-C***H_2***), 1.55 (s, 12H, C(C***H_3***$)_2$), 1.33 (d, $^3J_{HH}$ = 6.90 Hz, 12H, *o*-CH(C***H_3***$)_2$), 1.26 (d, 12H, *p*-CH(C***H_3***$)_2$), 1.21 (d, 12H, *o*-CH(C***H_3***$)_2$) ppm. **^{13}C NMR** ($CDCl_3$, 25°C, 101 MHz): **4b** *(major product)* δ = 189.5 (***C***=N), 152.9 (*p*-C_6H_2), 143.9 (*o*-C_6H_2), 126.6 (N-***C***$_6H_2$), 123.3 (*m*-***C***$_6H_2$), 83.7 (***C***$(CH_3)_2$), 52.1 (Cy-***C***H), 47.6 (C***C***H_2C), 34.2 (*p*-***C***H$(CH_3)_2$), 31.3 (Cy-***C***H_2), 30.0 (*o*-***C***H$(CH_3)_2$), 29.0 (C(***C***$H_3)_2$), 27.1 (*o*-CH(***C***$H_3)_2$), 23.7 (*p*-CH(***C***$H_3)_2$), 22.2 (*o*-CH(***C***$H_3)_2$) ppm. *Trans-isomer (minor product) not sufficiently visible in DEPTQ NMR.* **4b**:**3b** ratio *ca.* 13.7:1.0.

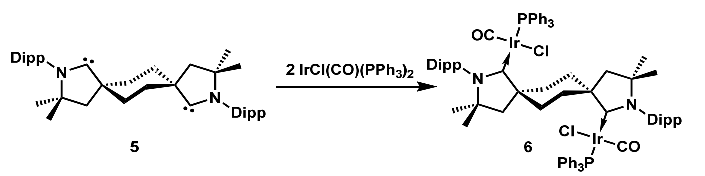
Synthesis of free *trans*-bis(CAAC) 5



THF (30 mL) was condensed onto **3a** (0.640 g, 0.862 mmol) and KHMDS (0.361 g, 1.81 mmol) in a 50 mL one-neck round-bottomed flask fitted with a swivel-frit. The flask was allowed to slowly warm up to room temperature and stirring was continued for one hour. Volatiles were removed *in vacuo*, the residue was extracted with anhydrous benzene (30 mL), and the mixture was filtered to remove KBF_4. The filtrate was dried *in vacuo* and the residue was washed with pentane (30 mL), yielding dicarbene **5** as a white powder (0.331 g, 0.584 mmol, 67.7% yield). The product was stable for months at −40°C under an argon atmosphere. Anal. calcd. for $C_{40}H_{58}N_2$: C 84.79; H 10.31; N 4.91. Found: C 84.73; H 10.78; N 4.79.

^{1}H NMR (C_6D_6, 25°C, 400 MHz): δ = 7.22 (m, 2H, *p*-C_6***H***$_3$), 7.13 (m, 4H, *m*-C_6***H***$_3$), 3.20 (sept, $^3J_{HH}$ = 6.81 Hz, 4H, C***H***$(CH_3)_2$), 2.50 (d, $^2J_{HH}$ = 9.35 Hz, 4H, Cy-C***H***$_2$), 1.72 (d, $^2J_{HH}$ = 9.35 Hz, 4H, Cy-C***H***$_2$), 1.70 (s, 4H, CC***H***$_2$C), 1.25 (d, $^3J_{HH}$ = 6.81 Hz, 12H, CH(C***H***$_3)_2$), 1.25 (d, $^3J_{HH}$ = 6.81 Hz, 12H, CH(C***H***$_3)_2$), 1.08 (s, 12H, C(C***H***$_3)_2$) ppm. **^{13}C NMR** (C_6D_6, 25°C, 101 MHz): δ = 315.2 (***C***$_{carbene}$), 146.1 (*o*-***C***$_6H_3$), 138.3 (*i*-***C***$_6H_3$), 128.1 (*p*-***C***$_6H_3$), 123.9 (*m*-***C***$_6H_3$), 81.5 (***C***$(CH_3)_2$), 63.5 (Cy-***C***$_1$), 47.3 (C***C***H_2C), 32.3 (Cy-***C***H_2), 29.6 (***C***$H(CH_3)_2$), 29.5 (C(***C***$H_3)_2$), 26.2 (CH(***C***$H_3)_2$), 22.0 (CH(***C***$H_3)_2$) ppm.

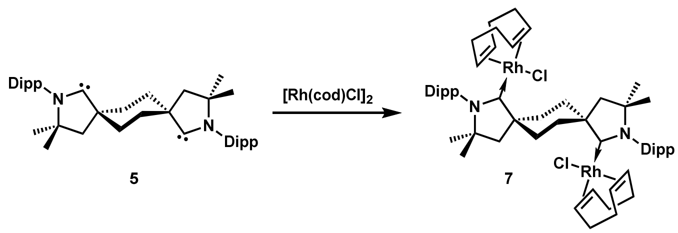
Synthesis of iridium complex 6



Anhydrous benzene (20 mL) was condensed over free dicarbene **5** (0.225 g, 0.397 mmol) and *trans*-carbonylchlorobis(triphenylphosphine)iridium (0.620 g, 0.791 mmol) in a 50 mL one-neck round-bottomed flask connected to a swivel-frit. The mixture was stirred at room temperature for 63 hours and filtered. The precipitate was dried to yield complex **6** as a bright yellow solid (0.510 g, 0.318 mmol, 80.2% yield).

^{1}H NMR (CD_2Cl_2, 25°C, 400 MHz): δ = 7.54 (m, 12H, *o*-P(C_6***H***$_5)_3$), 7.49 (t, $^3J_{HH}$ = 7.66 Hz, 2H, *p*-C_6***H***$_3$), 7.35 (d, 4H, *m*-C_6***H***$_3$), 7.35 (m, 6H, *p*-P(C_6***H***$_5)_3$), 7.28 (m, 12H, *m*-P(C_6***H***$_5)_3$), 3.11 (d, $^2J_{HH}$ = 9.36 Hz, 4H, Cy-C***H***$_2$), 3.10 (sept, $^3J_{HH}$ = 6.42 Hz, 4H, C***H***$(CH_3)_2$), 2.43 (s, 4H, CC***H***$_2$C), 1.92 (d, $^2J_{HH}$ = 9.46 Hz, 4H, Cy-C***H***$_2$), 1.45 (s, 12H, C(C***H***$_3)_2$), 1.31 (d, $^3J_{HH}$ = 6.54 Hz, 12H, CH(C***H***$_3)_2$), 1.23 (d, $^3J_{HH}$ = 6.42 Hz, 12H, CH(C***H***$_3)_2$) ppm. **^{13}C NMR** (CD_2Cl_2, 25°C, 101 MHz): δ = 254.9 (***C***$_{carbene}$), 174.2 (***C***O), 147.1 (*o*-***C***$_6H_3$), 135.1 (d, $^2J_{CP}$ = 10.8 Hz, *o*-P(***C***$_6H_5)_3$), 133.8 (*i*-***C***$_6H_3$), 130.0 (*p*-P(***C***$_6H_5)_3$), 129.2 (*p*-***C***$_6H_3$), 128.0 (d, $^3J_{CP}$ = 10.0 Hz, *m*-P(***C***$_6H_5)_3$), 125.6 (*m*-***C***$_6H_3$), 80.9 (***C***$(CH_3)_2$), 46.0 (C***C***H_2C), 34.6 (Cy-***C***H_2), 31.1 (C(***C***$H_3)_2$), 29.2 (***C***$H(CH_3)_2$), 28.5 (CH(***C***$H_3)_2$), 25.4 (CH(***C***$H_3)_2$) ppm. **^{31}P{^{1}H} NMR** (CD_2Cl_2, 25°C, 162 MHz): δ = 22.46 (Ir-***P***$(Ph)_3$) ppm. Anal. calcd. for $C_{78}H_{88}N_2Cl_2Ir_2O_2P_2$: C 58.45; H 5.53; N 1.75. Found: C 59.01; H 4.84; N 0.81. **FT-IR** (KBr pellet, cm^{-1}): 1950 (vs, ν_{CO}), 1430 (m), 1100 (s), 746 (m), 706 (m), 694 (s), 523 (s).

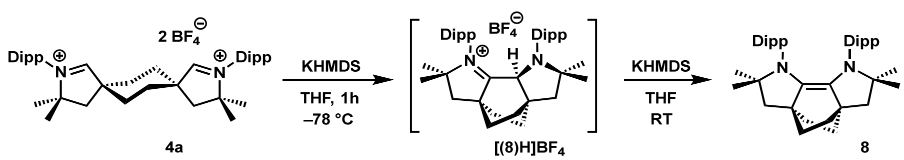
Synthesis of rhodium complex 7



In a 50 mL one-neck round-bottomed flask connected to a swivel frit, THF (25 mL) was condensed at -78°C over carbene precursor **3a** (0.214 g, 0.288 mmol) and KHMDS (0.115 g, 0.577 mol). The mixture was allowed to warm up to room temperature and, after stirring for one hour, the solvent was removed in vacuo and the residue was extracted with benzene (25 mL), filtering off insoluble materials. Chloro(1,5-cyclooctadiene)rhodium(I) dimer (0.142 g, 0.288 mmol) was added to the benzene solution in one portion, and stirring was continued overnight. The mixture was subsequently filtered, and the precipitate was dried *in vacuo* to yield complex **7** as a bright yellow solid (0.177 g, 0.158 mmol, 54.7% yield).

^{1}H NMR (CD_2Cl_2, 25°C, 400 MHz): δ = 7.49 (dd, $^3J_{HH}$ = 7.80 Hz, $^4J_{HH}$ = 1.77 Hz 2H, *m*-$C_6\boldsymbol{H}_3$), 7.44 (vt, $^3J_{HH}$ = 7.80 Hz, 2H, *p*-$C_6\boldsymbol{H}_3$), 7.22 (dd, $^3J_{HH}$ = 7.80 Hz, $^4J_{HH}$ = 1.77 Hz, 2H, *m*-$C_6\boldsymbol{H}_3$), 5.22 (m, 2H), 4.52 (q, J = 8.02 Hz, 2H), 3.95 (sept, $^3J_{HH}$ = 6.58 Hz, 2H, C***H***$(CH_3)_2$), 3.54 (m, 2H), 3.20 (dt, J = Hz, J = Hz, 2H), 2.96 (m, 2H), 2.81 (dt, J = Hz, J = Hz, 2H), 2.68 (sept, $^3J_{HH}$ = 6.67 Hz, 2H, C***H***$(CH_3)_2$), 2.50 (m, 2H), 2.35 (m, 2H), 2.32 (m, 2H), 2.26 (m, 2H), 2.10 (m, 4H), 1.76 (m, 4H), 1.74 (d, $^3J_{HH}$ = 6.58 Hz, 6H, $CH(C\boldsymbol{H}_3)_2$), 1.61 (m, 4H), 1.58 (s, 6H, $C(C\boldsymbol{H}_3)_2$), 1.53 (m, 2H), 1.41 (m, 2H), 1.32 (s, 6H, $C(C\boldsymbol{H}_3)_2$), 1.29 (d, $^3J_{HH}$ = 6.67 Hz, 6H, $CH(C\boldsymbol{H}_3)_2$), 1.28 (d, $^3J_{HH}$ = 6.58 Hz, 6H, $CH(C\boldsymbol{H}_3)_2$), 0.99 (d, $^3J_{HH}$ = 6.67 Hz, 6H, $CH(C\boldsymbol{H}_3)_2$). **^{13}C NMR** (CD_2Cl_2, 25°C, 101 MHz): δ = 272.5 (d, $^1J_{RhC}$ = 44.5 Hz, $\boldsymbol{C}_{carbene}$), 148.3, 147.1, 137.2, 129.3, 126.7, 124.7, 101.2 (d, J = 6 Hz), 97.7 (d, J = 5 Hz), 78.8, 72.7 (d, J = 15 Hz), 65.4 (d, J = 14 Hz), 64.1, 45.1, 39.1, 35.5, 34.5, 34.0, 31.1, 31.0, 29.1, 28.7, 28.3, 26.6, 26.3, 26.2, 25.4, 24.6 ppm. Anal. calcd. for $C_{60}H_{96}N_2Cl_2Rh_2$: C 64.22; H 8.62; N 2.50. Found: C 64.33; H 7.49; N 1.58.

Synthesis of olefin 8

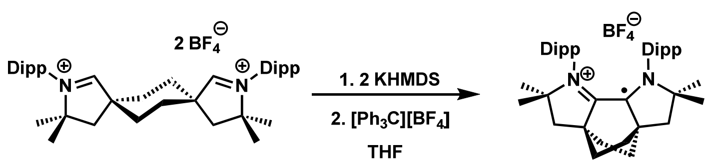


METHOD A: In a 50 mL one-neck round-bottomed flask connected to a swivel-frit, THF (30 mL) was condensed at −78°C over a mixture of **4a** (0.500 g, 0.673 mmol) and KHMDS (0.275 g, 1.38 mmol). The flask was allowed to warm up to room temperature and stirring was continued for one hour. Volatiles were removed *in vacuo*, the residue extracted with anhydrous benzene (30 mL), and the mixture filtered to remove KBF_4. The filtrate was dried *in vacuo* and the residue was washed with acetonitrile (2 × 30 mL), yielding **8** as a white powder (0.155 g, 0.273 mmol, 40.6% yield). Compound **8** was found to be stable in air for weeks in the solid state. Anal. calcd. for $C_{40}H_{58}N_2$: C 84.75; H 10.31; N 4.94. Found: C 84.84; H 10.00; N 5.05.

METHOD B: A 50 mL one-neck round-bottomed flask was charged with radical cation **9** (*vide infra*) (0.538 g, 0.823 mmol), KC_8 (0.167 g, 1.23 mmol), and anhydrous THF (30 mL). The mixture was stirred in a glovebox for seven days. The mixture was then filtered through celite and the filtrate was transferred to a swivel frit. Volatiles were removed *in vacuo* and the residue was extracted with pentane (40 mL). Renewed solvent removal gave **8** as an off-white powder (0.245 g, 0.432 mmol, 52.5% yield). Anal. calcd. for $C_{40}H_{58}N_2$: C 84.75; H 10.31; N 4.94. Found: C 85.17; H 10.22; N 4.20.

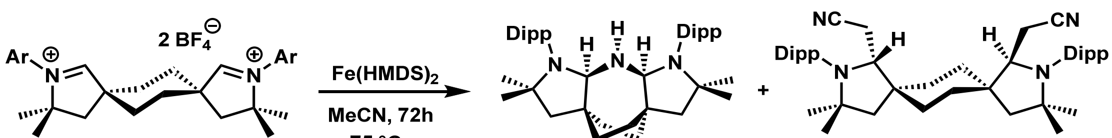
^{1}H NMR (C_6D_6, 25°C, 400 MHz): δ = 6.99 (m, 4H, *m*-$C_6\boldsymbol{H}_3$), 6.88 (dd, $^3J_{HH}$ = 6.49 Hz, $^3J_{HH}$ = 2.99 Hz, 2H, *p*-$C_6\boldsymbol{H}_3$), 3.58 (sept, $^3J_{HH}$ = 6.84 Hz, 2H, C***H***$(CH_3)_2$), 3.29 (sept, $^3J_{HH}$ = 6.80 Hz, 2H, C***H***$(CH_3)_2$), 2.19 (m, 2H, Cy-C$\boldsymbol{H}_2$), 1.74 (m, 4H, Cy-C$\boldsymbol{H}_2$), 1.74 (m, 2H, CC$\boldsymbol{H}_2$C), 1.74 (m, 2H, CC$\boldsymbol{H}_2$C), 1.60 (m, 2H, Cy-C$\boldsymbol{H}_2$), 1.51 (s, 6H, C(C$\boldsymbol{H}_3$)$_2$), 1.44 (d, $^3J_{HH}$ = 6.80 Hz, 6H, CH(C$\boldsymbol{H}_3$)$_2$), 1.21 (d, $^3J_{HH}$ = 6.84 Hz, 6H, CH(C$\boldsymbol{H}_3$)$_2$), 1.18 (d, $^3J_{HH}$ = 6.80 Hz, 6H, CH(C$\boldsymbol{H}_3$)$_2$), 0.57 (s, 6H, C(C$\boldsymbol{H}_3$)$_2$), 0.07 (d, $^3J_{HH}$ = 6.84 Hz, 6H, CH(C$\boldsymbol{H}_3$)$_2$) ppm. **^{13}C NMR** (C_6D_6, 25°C, 101 MHz): δ = 149.1 (*o*-$\boldsymbol{C}_6$H$_3$), 148.7 (*o*-$\boldsymbol{C}_6$H$_3$), 141.6 (*i*-$\boldsymbol{C}_6$H$_3$), 126.7 (***C***=***C***), 126.2 (*m*-$\boldsymbol{C}_6$H$_3$), 124.7 (*p*-$\boldsymbol{C}_6$H$_3$), 124.4 (*m*-$\boldsymbol{C}_6$H$_3$), 67.0 (***C***$(CH_3)_2$), 52.9 (C***C***H_2C), 46.5 (***C***1_{Cy}), 38.6 (Cy-***C***H_2), 36.3 (Cy-***C***H_2), 31.3 (C(***C***H_3)$_2$), 28.4 (***C***H$(CH_3)_2$), 27.5 (C(***C***H_3)$_2$), 26.8 (***C***H$(CH_3)_2$), 25.9 (CH(***C***H_3)$_2$), 25.8 (CH(***C***H_3)$_2$), 25.1 (CH(***C***H_3)$_2$), 24.9 (CH(***C***H_3)$_2$) ppm.

Synthesis of radical cation 9



In a 50 mL one-neck round-bottomed flask connected to a swivel-frit, THF (30 mL) was condensed at −78°C over a mixture of **4a** (0.500 g, 0.673 mmol) and KHMDS (0.275 g, 1.38 mmol). The flask was allowed to warm up to room temperature and stirring was continued for one hour. Volatiles were removed *in vacuo*, the residue was extracted with anhydrous benzene (30 mL), and the mixture was filtered to remove KBF_4. Triphenylcarbenium tetrafluoroborate (0.222 g, 0.673 mmol) was subsequently added in one portion and the mixture was stirred overnight. The precipitate was isolated by filtration and dried *in vacuo* to yield **9** as a purple powder (0.296 g, 0.453 mmol, 67.2% yield). X-ray quality crystals of **9** were grown overnight by layering a concentrated solution in dichloromethane with pentane. Anal. calcd. for $C_{40}H_{58}N_2BF_4$: C 73.49; H 8.94; N 4.29. Found: C 74.15; H 9.10; N 3.40. HRMS (ESI) m/z: $[M]^+$ Calcd. for $C_{40}H_{58}N_2$ 566.4600; Found: 566.4602.

Synthesis of ammonia activation product 10

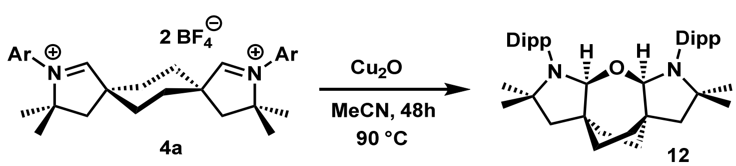


In a 50 mL one-neck round-bottomed flask connected to a swivel-frit, acetonitrile (30 mL) was condensed at −78°C over a mixture of **4a** (0.318 g, 0.428 mmol) and $Fe(HMDS)_2$ (0.161 g, 0.428 mmol). The flask was allowed to slowly warm up to room temperature and subsequently heated to 75°C for 72 hours. The mixture was then cooled to room temperature, volatiles were removed *in vacuo*, and the residue was extracted with anhydrous pentane (2 × 30 mL). After the solids were filtered off, removal of pentane from the filtrate gave compound **10** as a white powder (0.077 g, 0.119 mmol, 28% yield). Anal. calcd. for $C_{40}H_{61}N_3$: C 82.27; H 10.53; N 7.20. Found: C 82.43; H 10.16; N 6.94. HRMS (ESI) m/z: $[M+H]^+$ Calcd. for $C_{40}H_{62}N_3$ 584.4944; Found: 584.4952.

^{1}H NMR (CD_2Cl_2, 25°C, 400 MHz): δ = 7.02 (dd, $^3J_{HH}$ = 7.52 Hz, $^3J_{HH}$ = 7.52 Hz, 2H, *p*-$C_6\boldsymbol{H}_3$), 6.96 (dd, $^3J_{HH}$ = 7.70 Hz, $^4J_{HH}$ = 1.95 Hz, 2H, *m*-$C_6\boldsymbol{H}_3$), 6.91 (dd, $^3J_{HH}$ = 7.43 Hz, $^4J_{HH}$ = 1.95 Hz, 2H, *m*-$C_6\boldsymbol{H}_3$), 4.18 (d, $^3J_{HH}$ = 7.23 Hz, 2H, C***H***NH), 3.74 (sept, $^3J_{HH}$ = 6.86 Hz, 2H, C***H***$(CH_3)_2$), 3.07 (sept, $^3J_{HH}$ = 6.70 Hz, 2H, C***H***$(CH_3)_2$), 2.59 (m, 2H, Cy-C$\boldsymbol{H}_2$), 1.83 (d, $^2J_{HH}$ = 12.9 Hz 2H, CC$\boldsymbol{H}_2$C), 1.77 (m, 2H, Cy-C$\boldsymbol{H}_2$), 1.69 (m, 2H, Cy-C$\boldsymbol{H}_2$), 1.68 (d, $^2J_{HH}$ = 12.9 Hz 2H, CC$\boldsymbol{H}_2$C), 1.37 (m, 2H, Cy-C$\boldsymbol{H}_2$), 1.18 (s, 6H, C(C$\boldsymbol{H}_3)_2$), 1.13 (d, $^3J_{HH}$ = 6.86 Hz, 6H, CH(C$\boldsymbol{H}_3)_2$), 1.09 (d, $^3J_{HH}$ = 6.86 Hz, 6H, CH(C$\boldsymbol{H}_3)_2$), 0.85 (s, 6H, C(C$\boldsymbol{H}_3)_2$), 0.73 (d, $^3J_{HH}$ = 6.70 Hz, 6H, CH(C$\boldsymbol{H}_3)_2$), 0.66 (d, $^3J_{HH}$ = 6.70 Hz, 6H, CH(C$\boldsymbol{H}_3)_2$). **^{13}C NMR** (CD_2Cl_2, 25°C, 101 MHz): δ = 152.9 (*o*-$\boldsymbol{C}_6H_3$), 150.8 (*o*-$\boldsymbol{C}_6H_3$), 138.6 (*i*-$\boldsymbol{C}_6H_3$), 126.5 (*p*-$\boldsymbol{C}_6H_3$), 124.4 (*m*-$\boldsymbol{C}_6H_3$), 124.1 (*m*-$\boldsymbol{C}_6H_3$), 86.0 (***C***HNH), 60.8 (***C***$(CH_3)_2$), 55.9 (C***C***H_2C), 44.5 (Cy-$\boldsymbol{C}_1$), 35.2 (Cy-***C***H_2), 32.0 (C(***C***$H_3)_2$), 31.5 (Cy-***C***H_2), 29.1 (***C***H$(CH_3)_2$), 28.7 (C(***C***$H_3)_2$), 27.8 (***C***H$(CH_3)_2$), 25.5 (CH(***C***$H_3)_2$), 24.9 (CH(***C***$H_3)_2$), 24.5 (CH(***C***$H_3)_2$), 24.0 (CH(***C***$H_3)_2$) ppm.

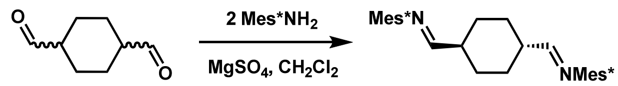
When performing the synthesis of **10** on NMR scale, incipient crystallization of a colorless compound was noticed upon cooling the reaction mixture after the 72 hour reflux. X-ray diffraction analysis revealed this to be **11**, presumably formed as a minor byproduct upon C–H activation of the reaction solvent (Figure S63). Efforts to deliberately synthesize this compound on a larger scale were unsuccessful.

Synthesis of water activation product 12



A J. Young tube was loaded with **4a** (0.015 g, 0.020 mmol), Cu_2O (0.015 g, 0.105 mmol), and acetonitrile (1.5 mL). The mixture was heated to 90°C for 48 hours. Upon cooling to room temperature, colorless blocks crystallized along the walls of the tube. They were identified as compound **12** by single-crystal X-ray diffraction. Attempts to upscale reaction conditions for product isolation were so far unsuccessful.

Attempted synthesis of *trans*-cyclohexane-1,4-bis(2,4,6-tri-*tert*-butylphenylaldimine), *trans*-1c



trans-1c

In air, a 100 mL round-bottom flask fitted with a reflux condenser was charged with cyclohexane-1,4-dicarbaldehyde (0.76 g, 5.42 mmol), 2,4,6-tri-tert-butylaniline (2.82 g, 10.8 mmol), toluene (60 mL), magnesium sulphate (20 g), and *p*-toluenesulfonic acid (20.5 mg, 0.12 mmol). The reaction was refluxed under argon for 48 h at 110°C. Magnesium sulphate was then removed by filtration and the solvent was removed *in vacuo*, leaving behind an oil. Treatment of the oil with absolute ethanol (30 mL) afforded *trans*-**1c** as a white solid, which was isolated by vacuum filtration (43.0 mg, 0.069 mmol, 1.3% yield). Because of the low yield, the synthesis of a bis(CAAC) ligand incorporating Mes* was not further pursued.

^{1}H NMR ($CDCl_3$, 25°C, 400 MHz): δ = 7.52 (d, 2H, 3.26 Hz, C***H***=N), 7.31 (s, 4H, *m*-C_6***H***$_2$), 2.45 (broad m, 2H, Cy-C***H***), 2.32 (m, 4H, Cy-C***H***$_2$), 1.58 (m, 4H, Cy-C***H***$_2$), 1.34 (s, 36H, *o*-C(C***H***$_3$)$_3$), 1.32 (s, 18H, *p*-C(C***H***$_3$)$_3$) ppm.

Spectral data

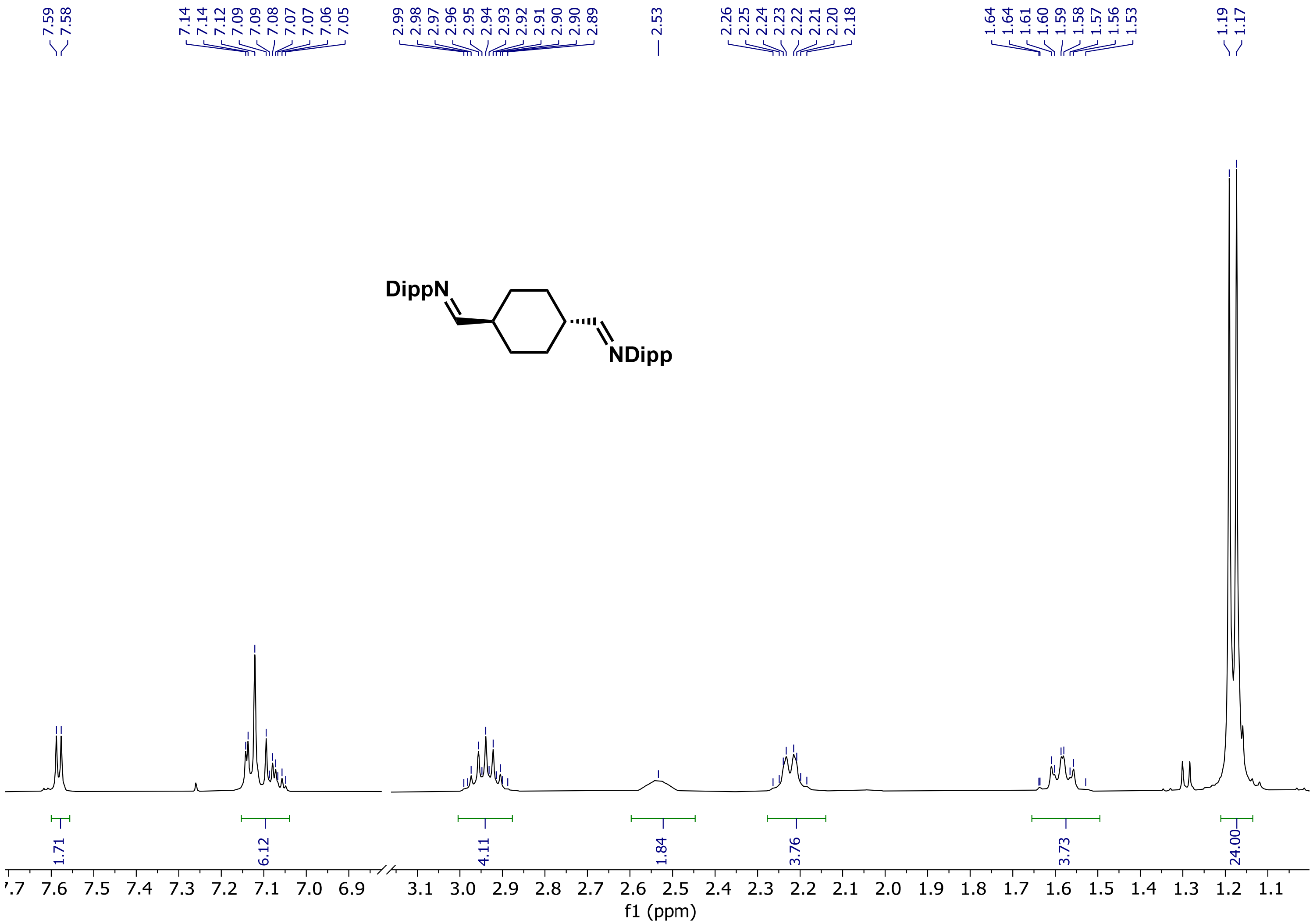


Figure S1. ^{1}H NMR spectrum of *trans*-**1a** ($CDCl_3$, 25°C, 400 MHz).

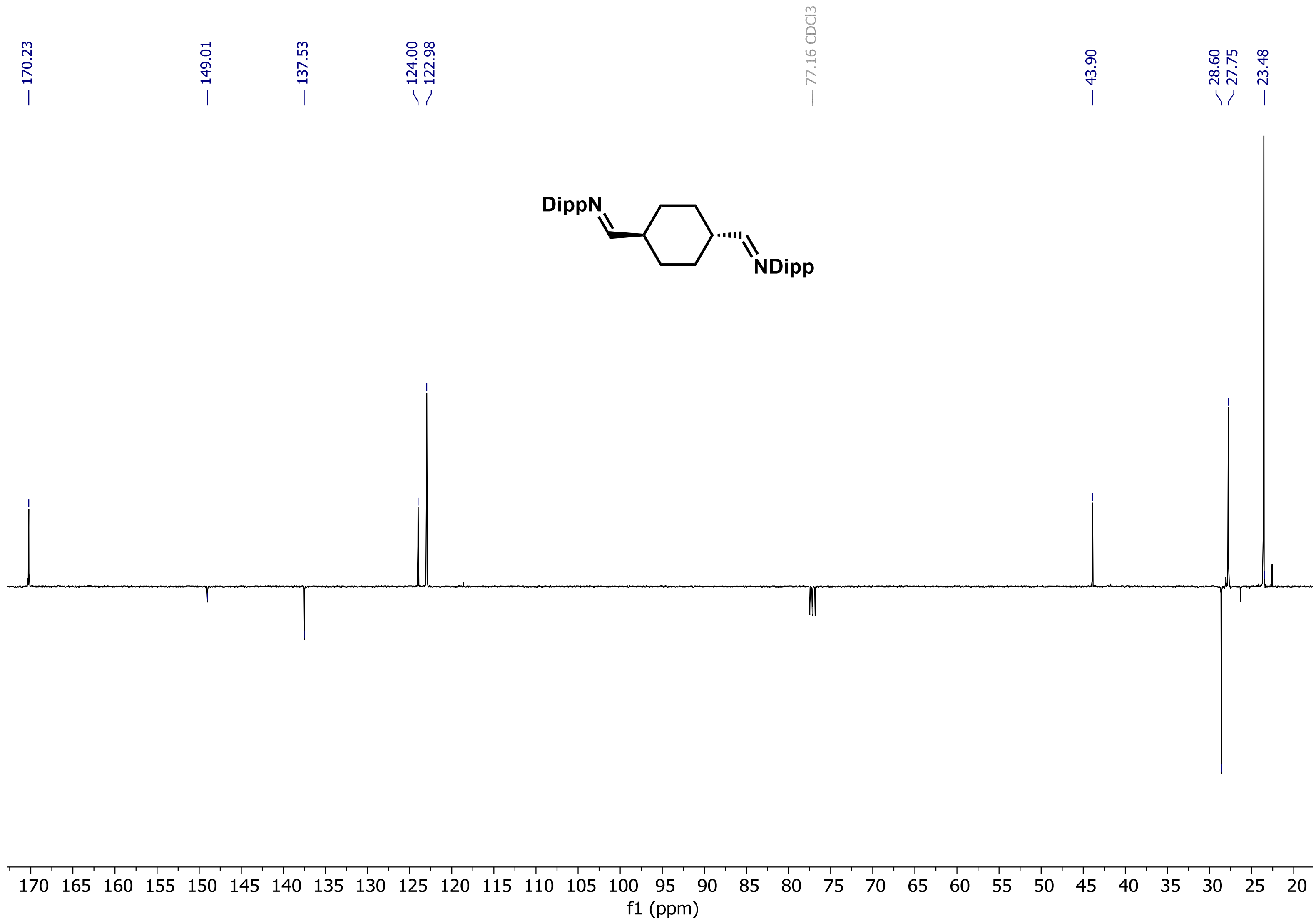


Figure S2. ^{13}C DEPTQ NMR spectrum of *trans*-**1a** ($CDCl_3$, 25°C, 101 MHz).

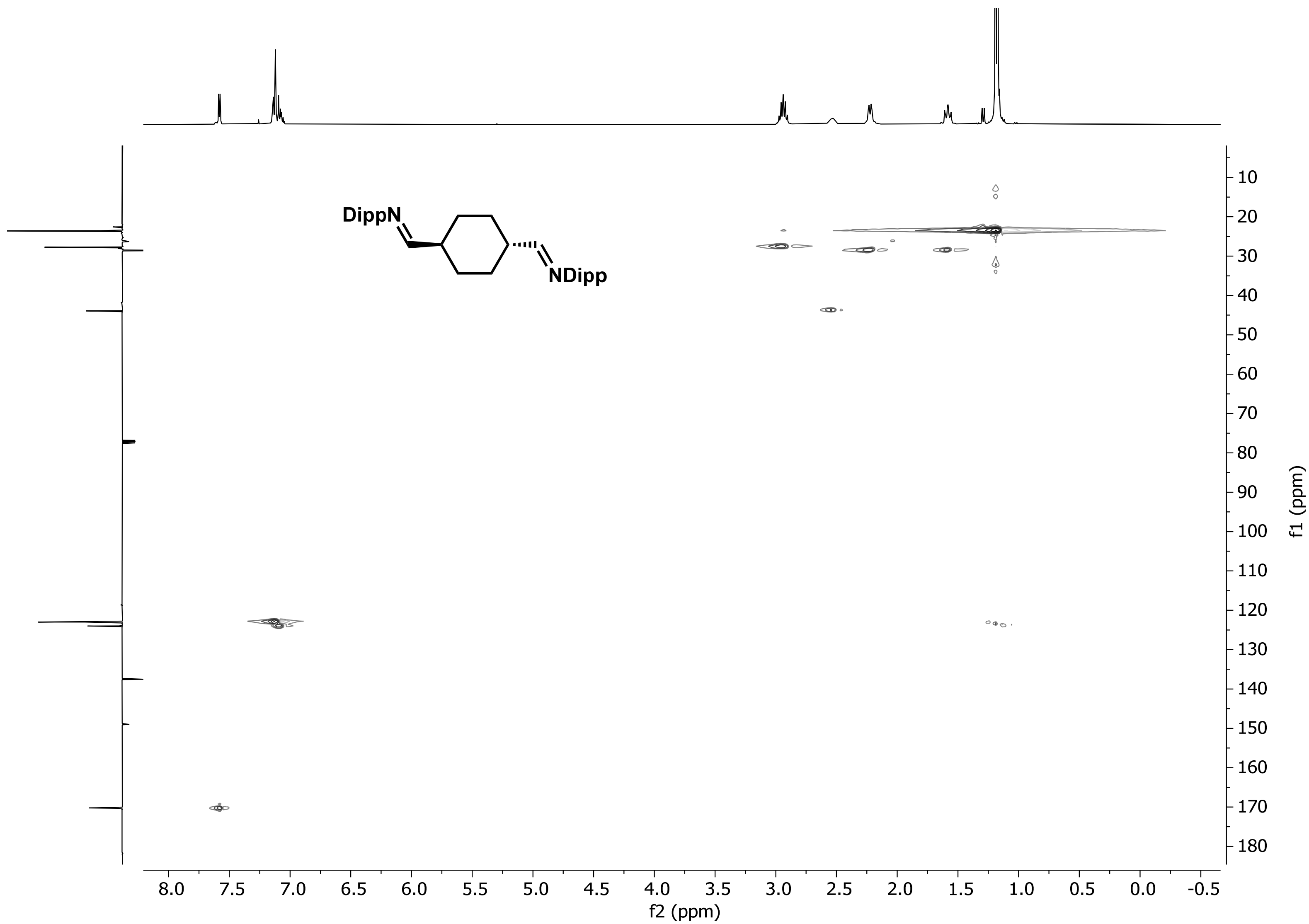


Figure S3. ^{1}H-^{13}C HSQC NMR spectrum of *trans*-**1a** ($CDCl_3$, 25°C, 400 MHz).

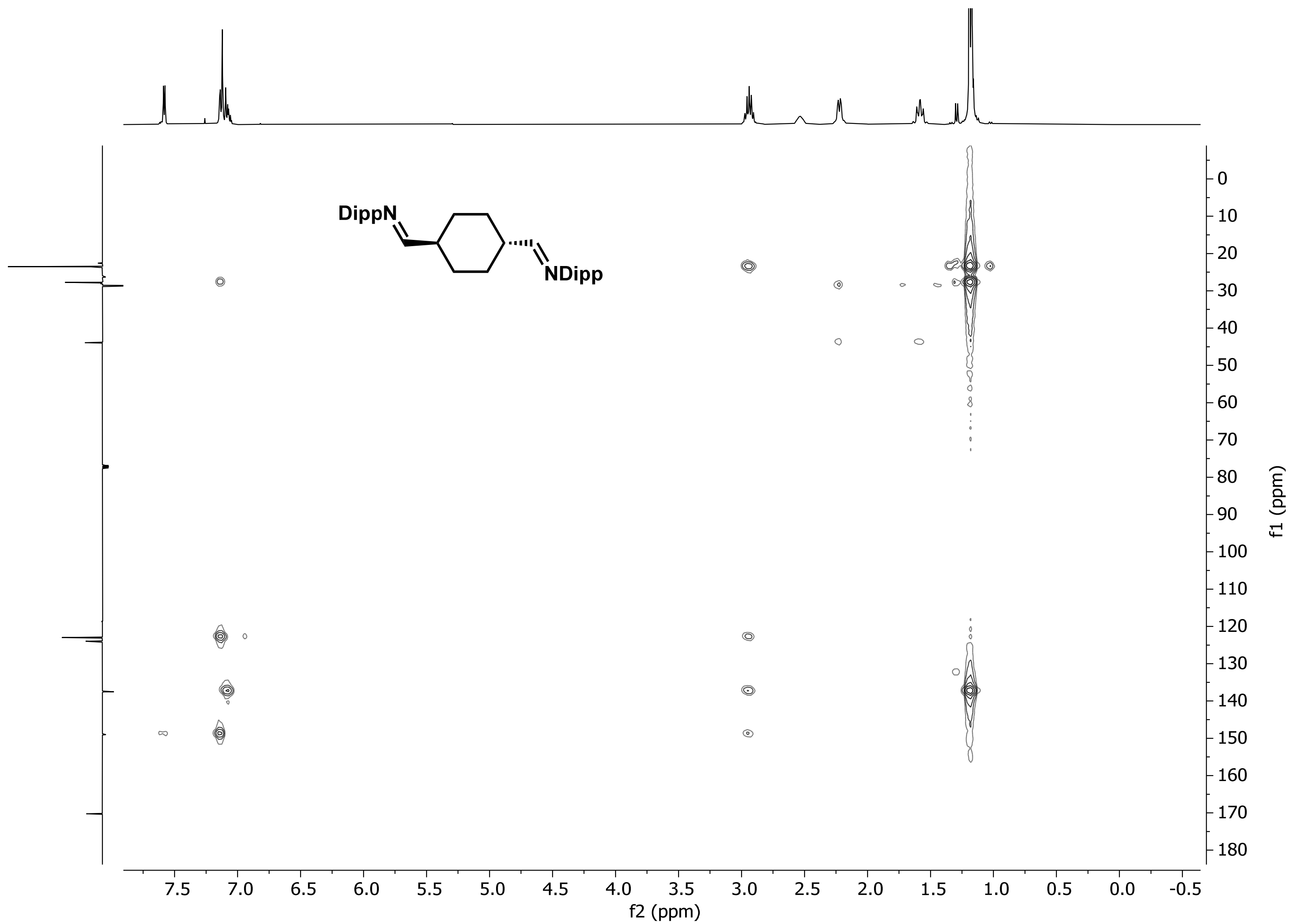


Figure S4. ^{1}H-^{13}C HMBC NMR spectrum of *trans*-**1a** ($CDCl_3$, 25°C, 400 MHz).

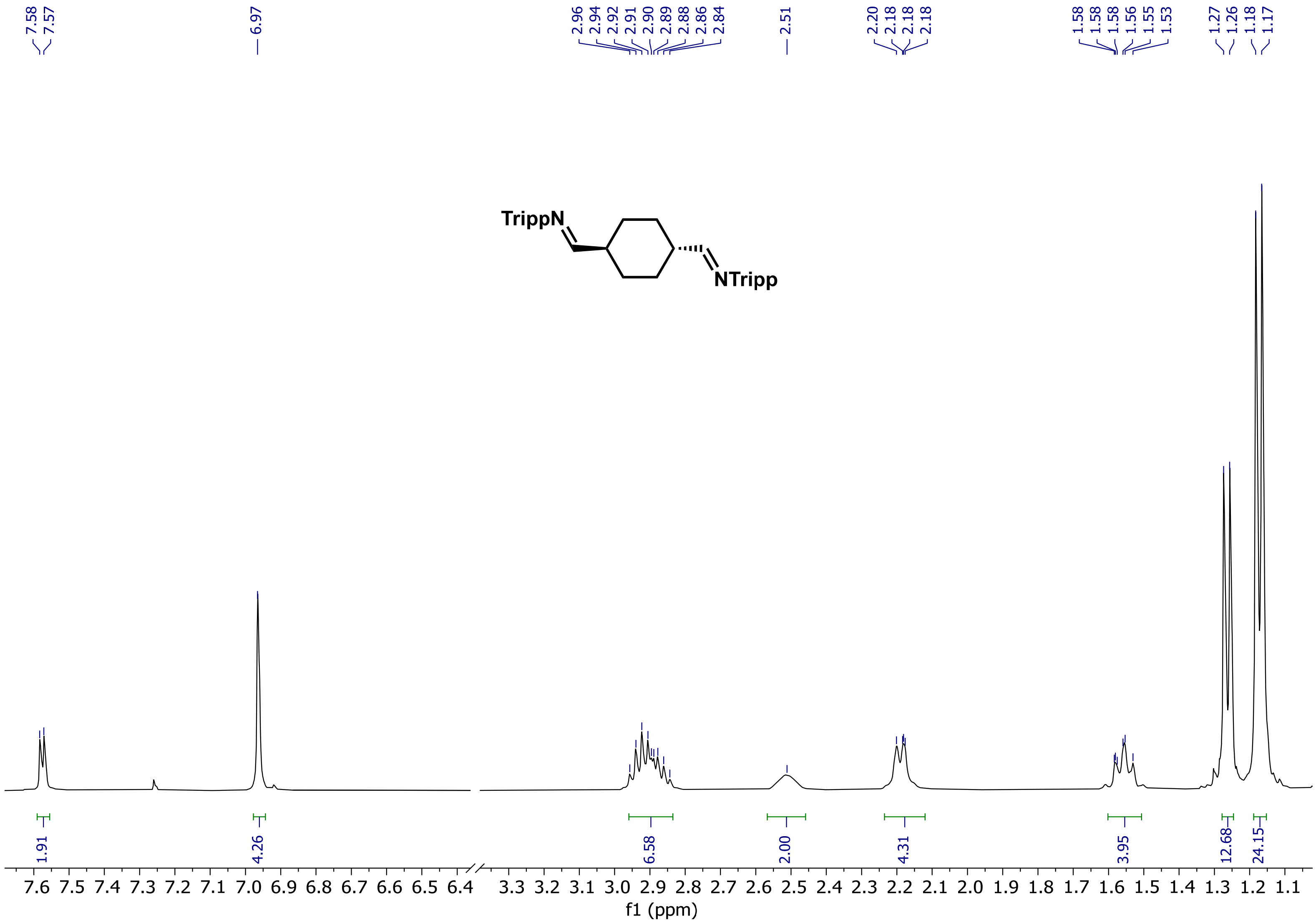


Figure S5. ^{1}H NMR spectrum of aldimine *trans*-**1b** ($CDCl_3$, 25°C, 400 MHz).

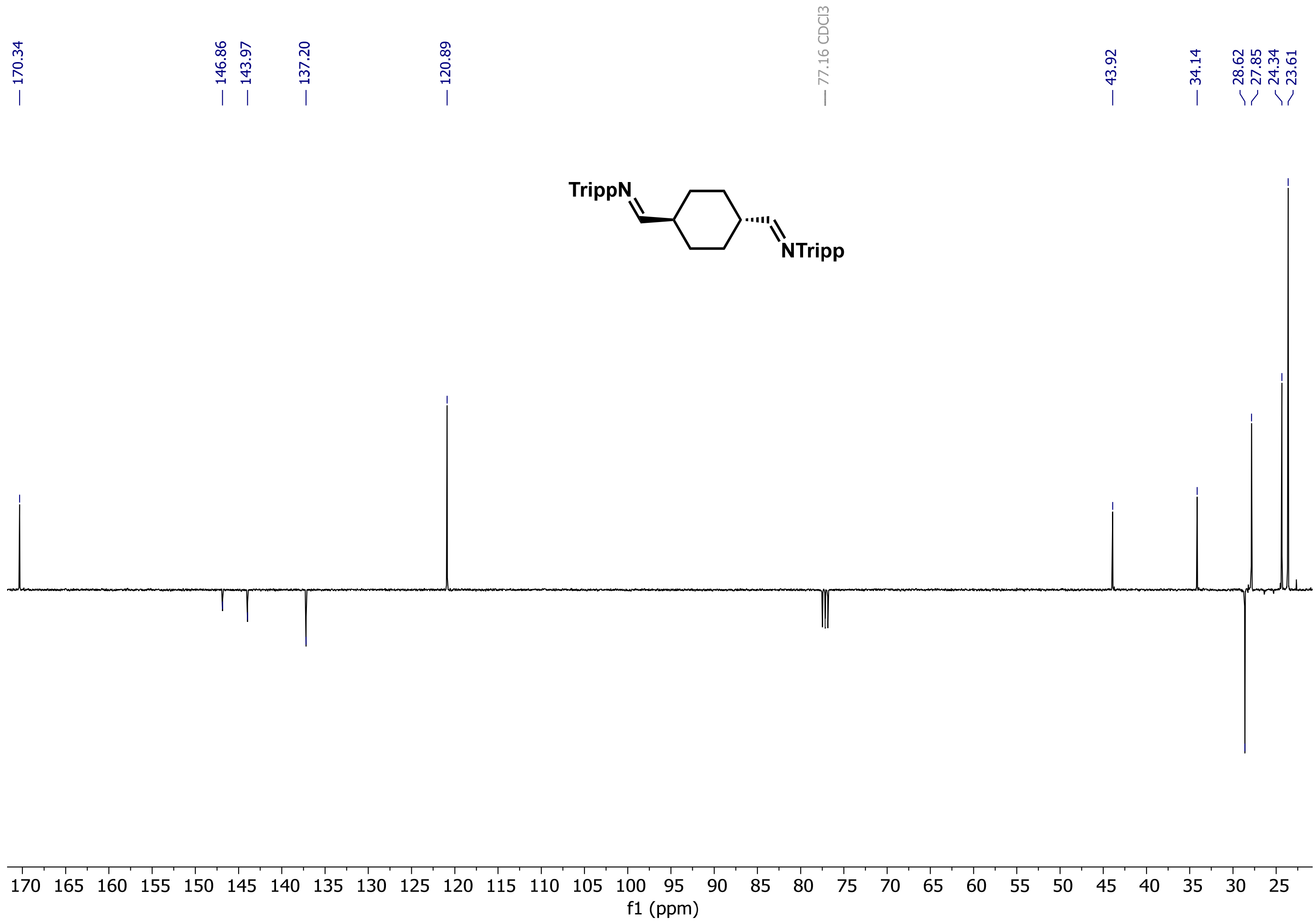


Figure S6. ^{13}C DEPTQ NMR spectrum of aldimine *trans*-**1b** ($CDCl_3$, 25°C, 101 MHz).

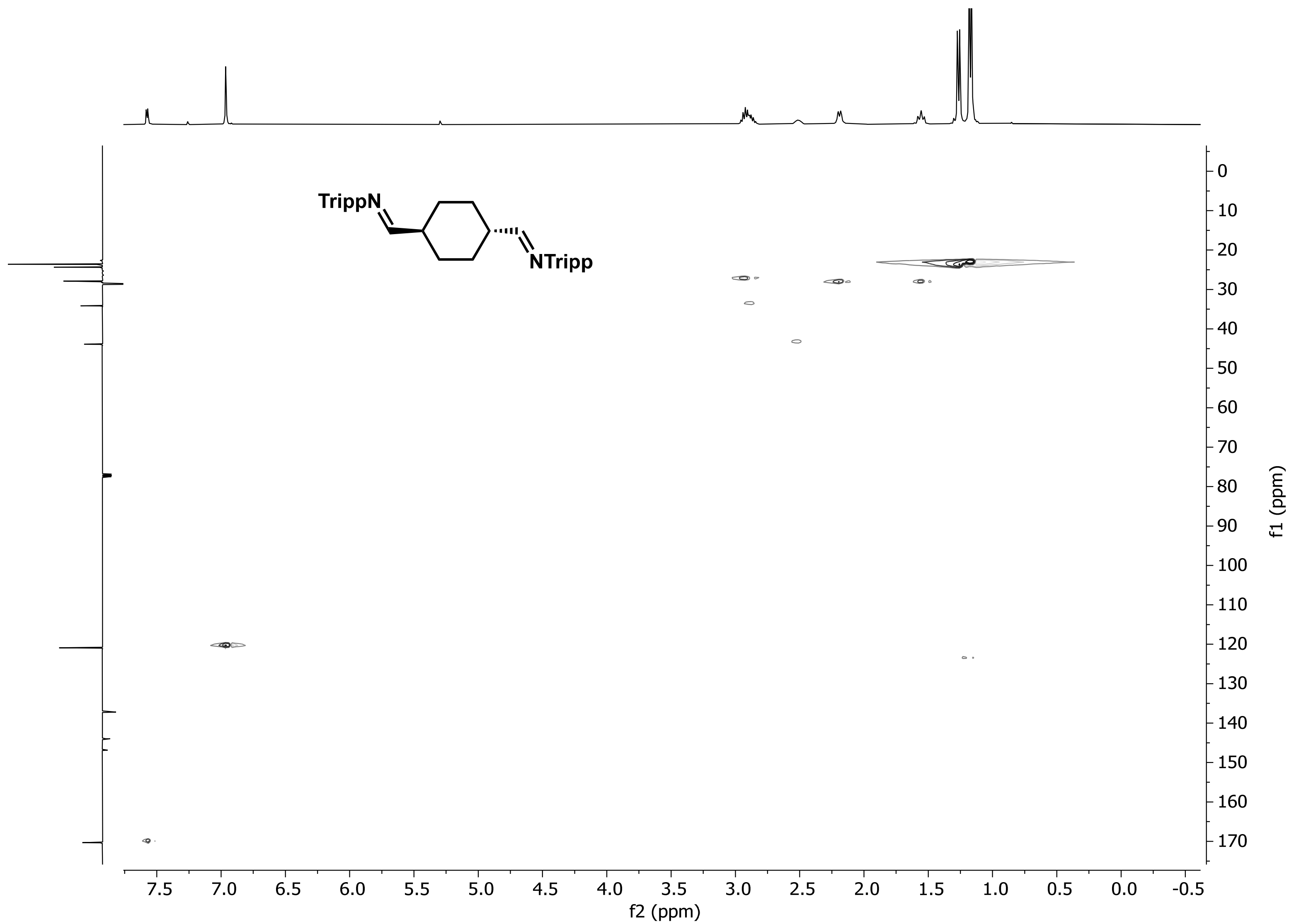


Figure S7. ^{1}H-^{13}C HSQC NMR spectrum of aldimine *trans*-**1b** ($CDCl_3$, 25°C, 400 MHz).

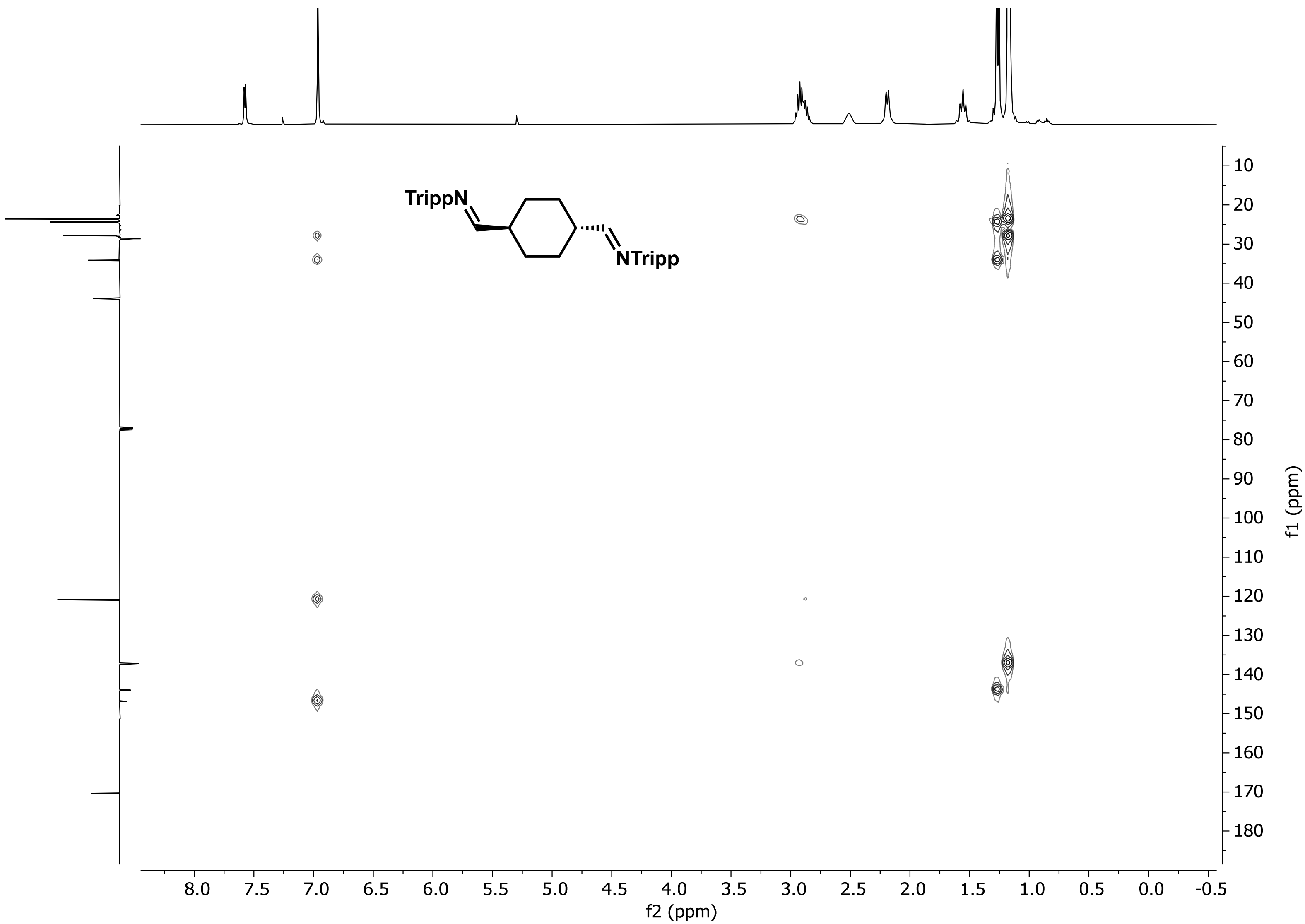


Figure S8. ^{1}H-^{13}C HMBC NMR spectrum of aldimine *trans*-**1b** ($CDCl_3$, 25°C, 400 MHz).

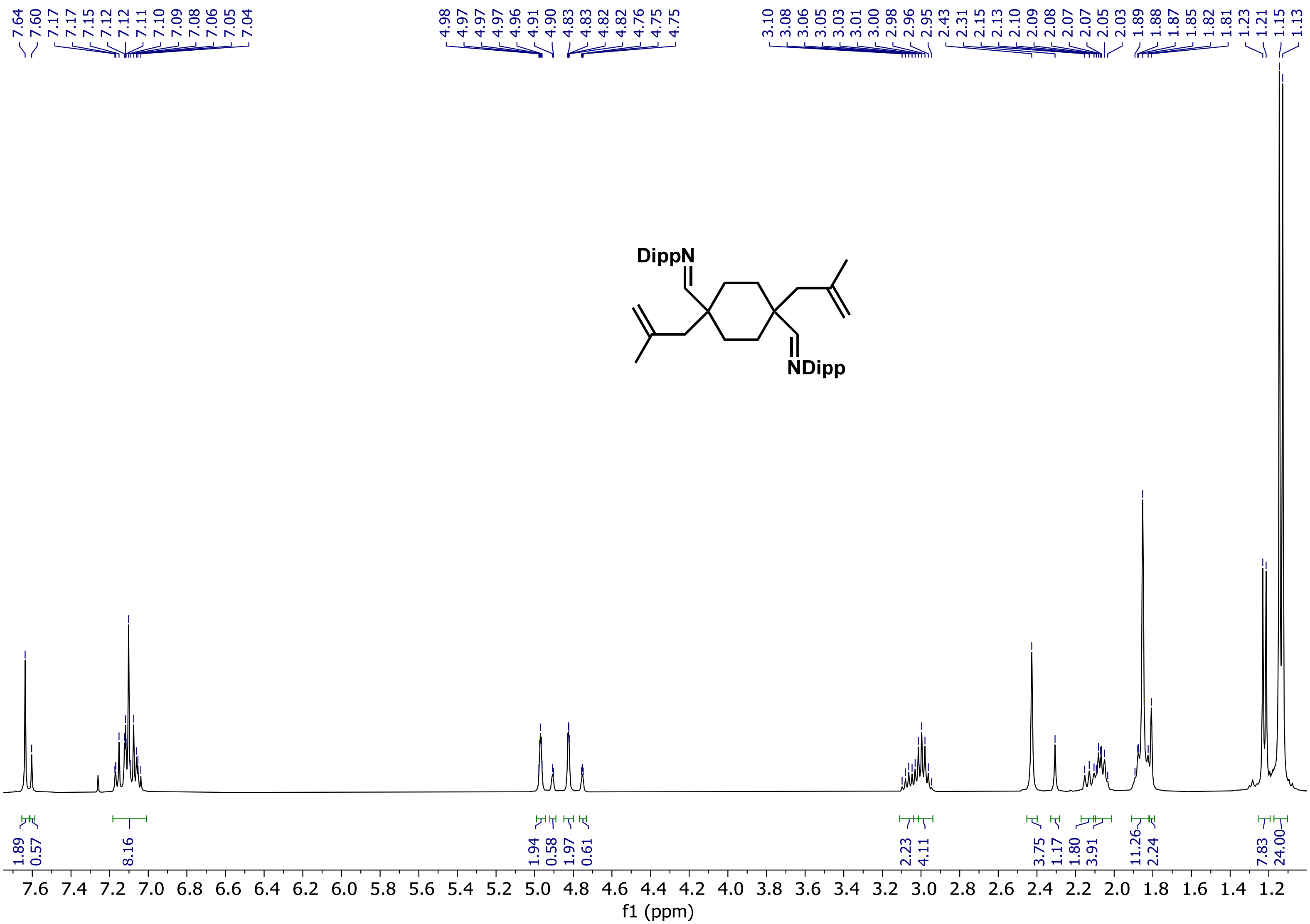


Figure S9. ^{1}H NMR spectrum of *cis- and trans*-**2a** ($CDCl_3$, 25°C, 400 MHz).

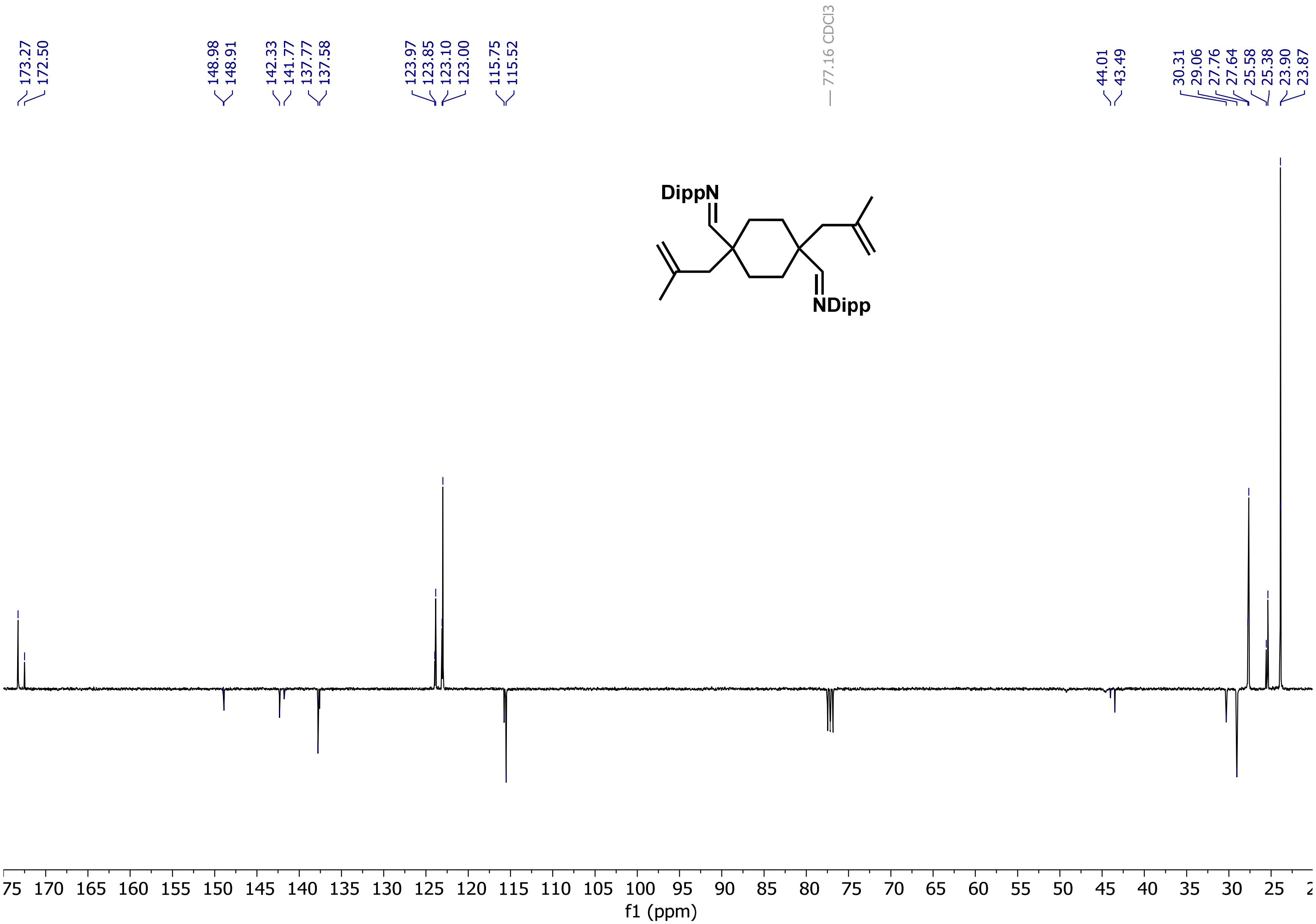


Figure S10. ^{13}C DEPTQ NMR spectrum of alkylated *cis- and trans*-**2a** ($CDCl_3$, 25°C, 101 MHz).

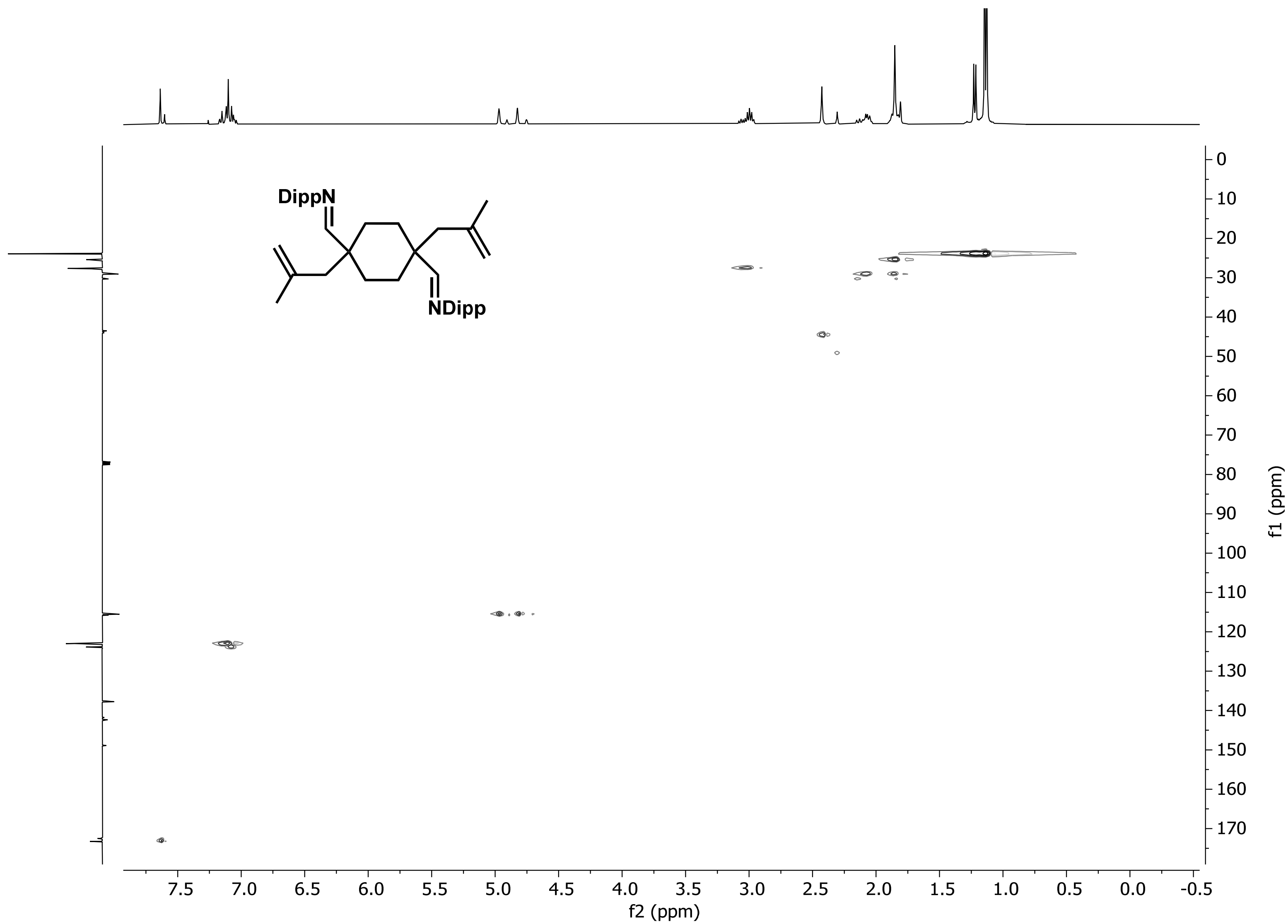


Figure S11. ^{1}H-^{13}C HSQC NMR spectrum of alkylated *cis- and trans*-**2a** ($CDCl_3$, 25°C, 400 MHz).

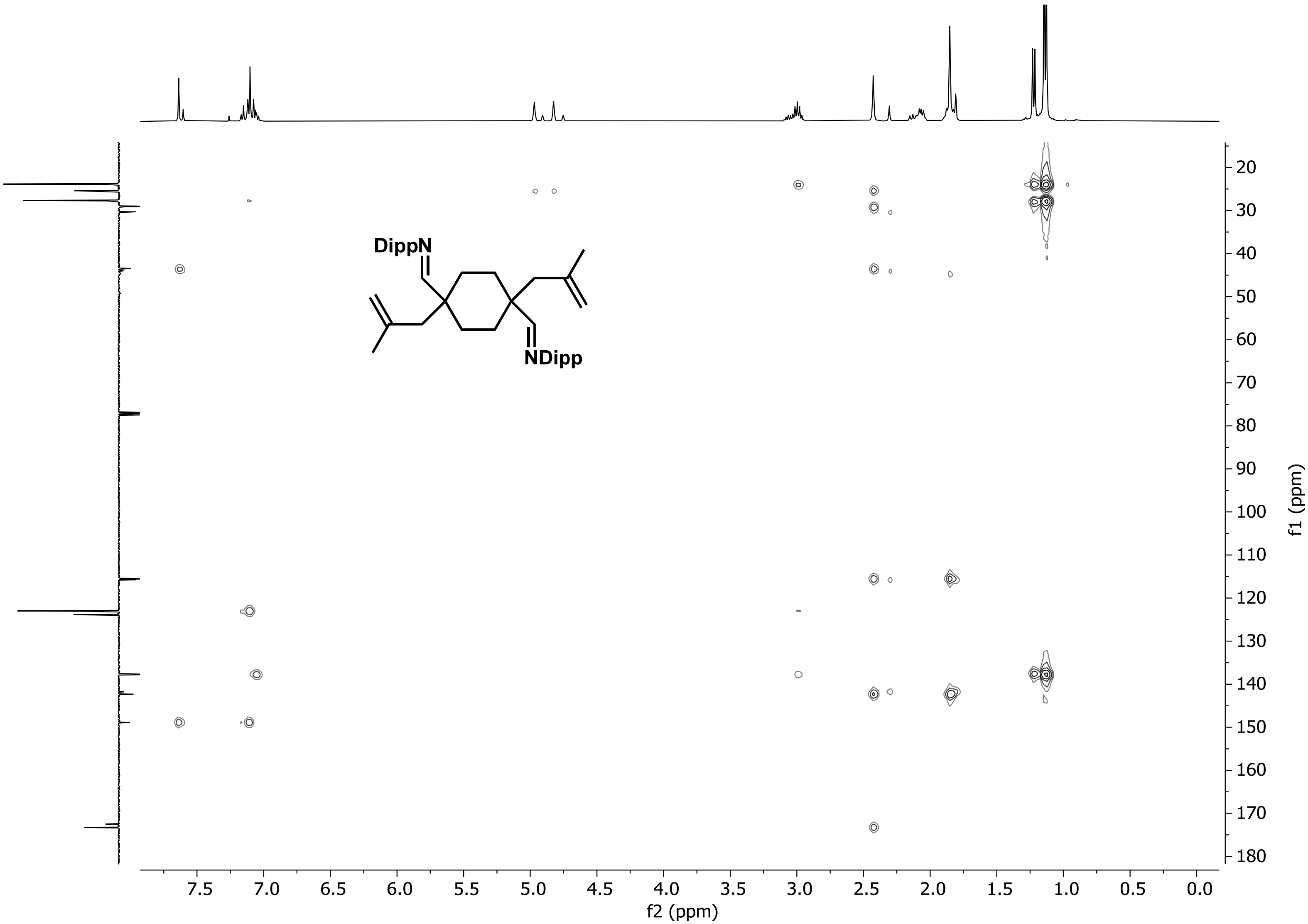


Figure S12. ^{1}H-^{13}C HMBC NMR spectrum of alkylated *cis- and trans*-**2a** ($CDCl_3$, 25°C, 400 MHz).

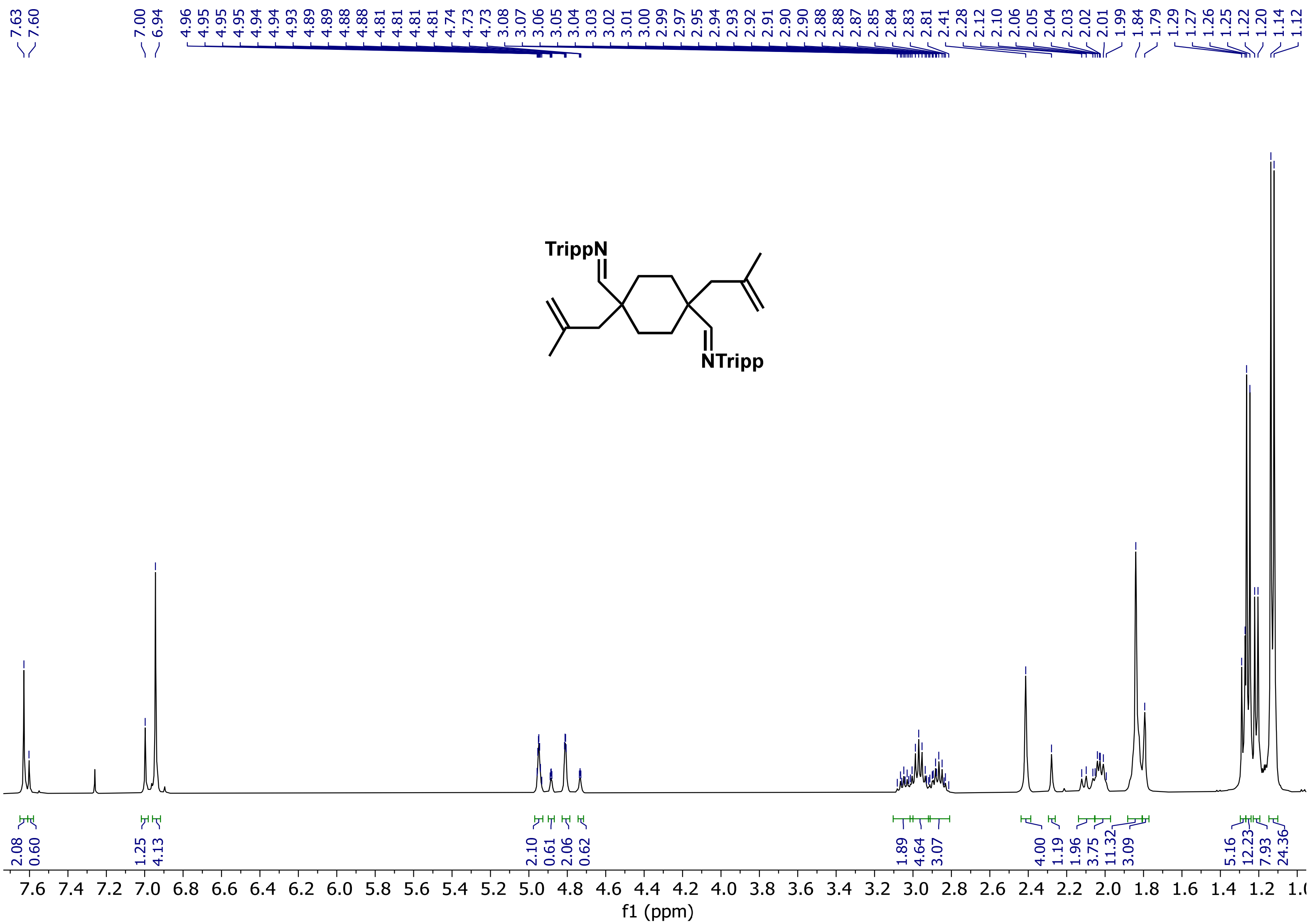


Figure S13. ^{1}H NMR spectrum of alkylated aldimine *cis- and trans*-**2b** ($CDCl_3$, 25°C, 400 MHz).

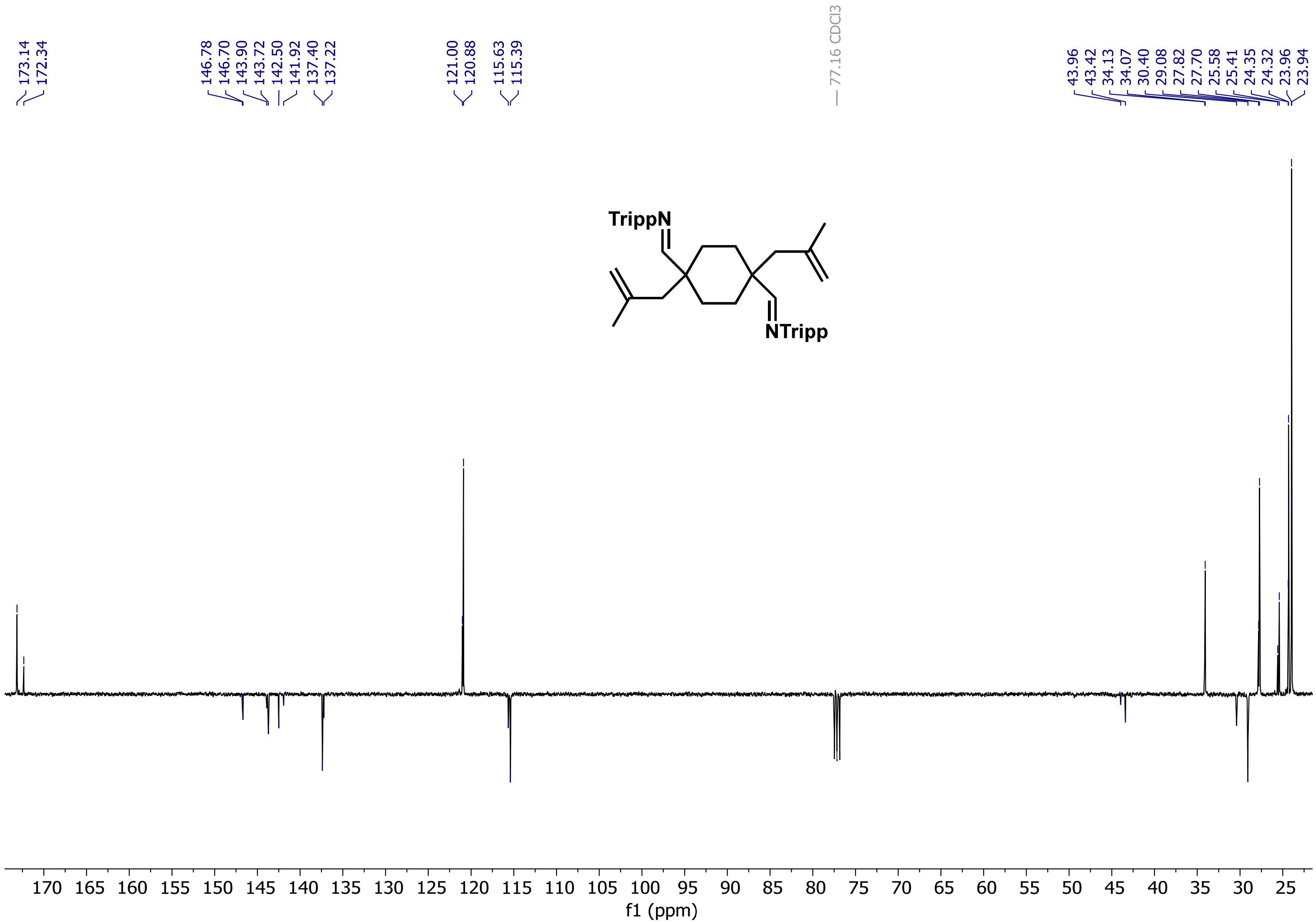


Figure S14. ^{13}C DEPTQ NMR spectrum of alkylated aldimine *cis- and trans*-**2b** ($CDCl_3$, 25°C, 101 MHz).

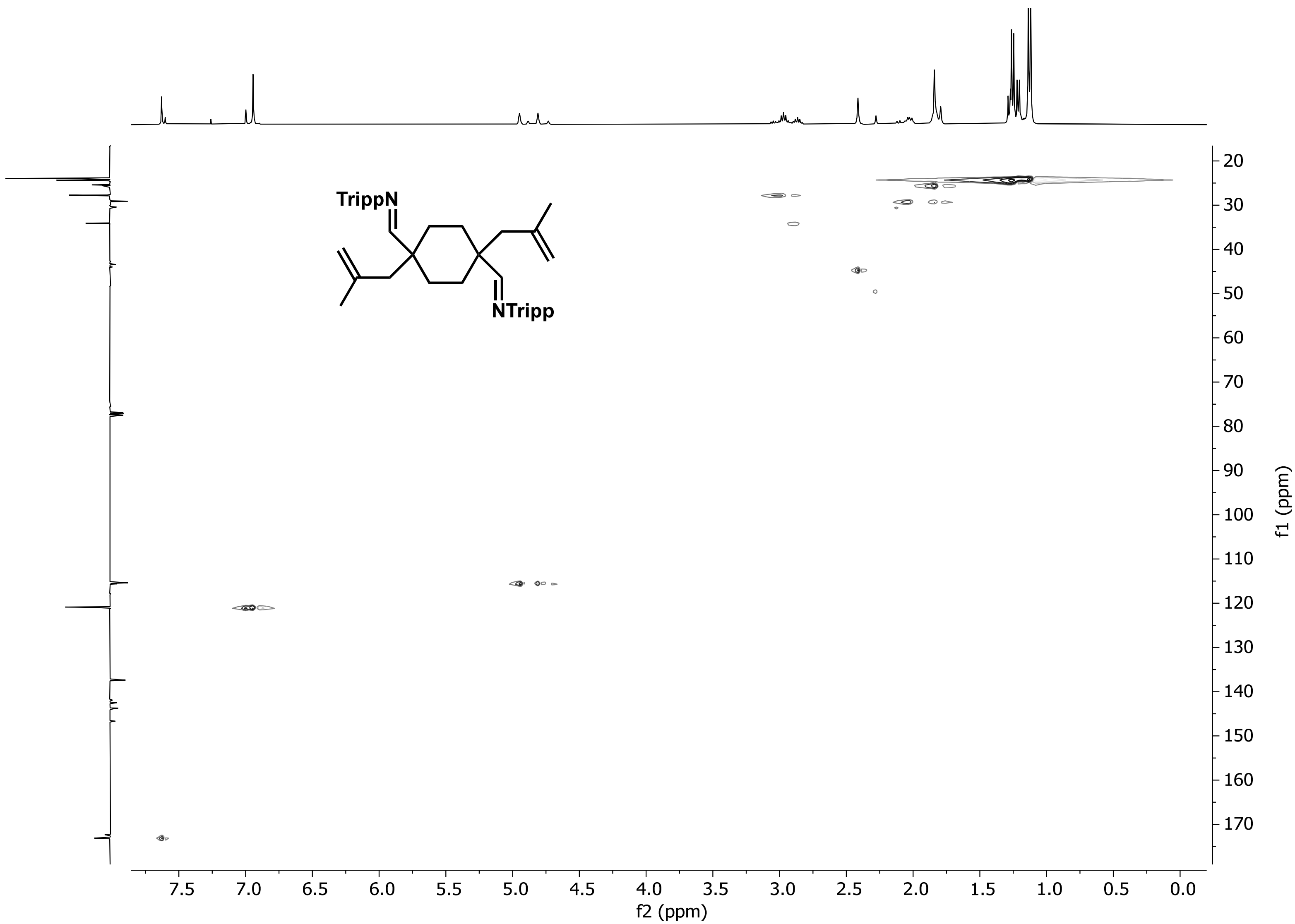


Figure S15. ^{1}H-^{13}C HSQC NMR spectrum of alkylated aldimine *cis- and trans*-**2b** ($CDCl_3$, 25°C, 400 MHz).

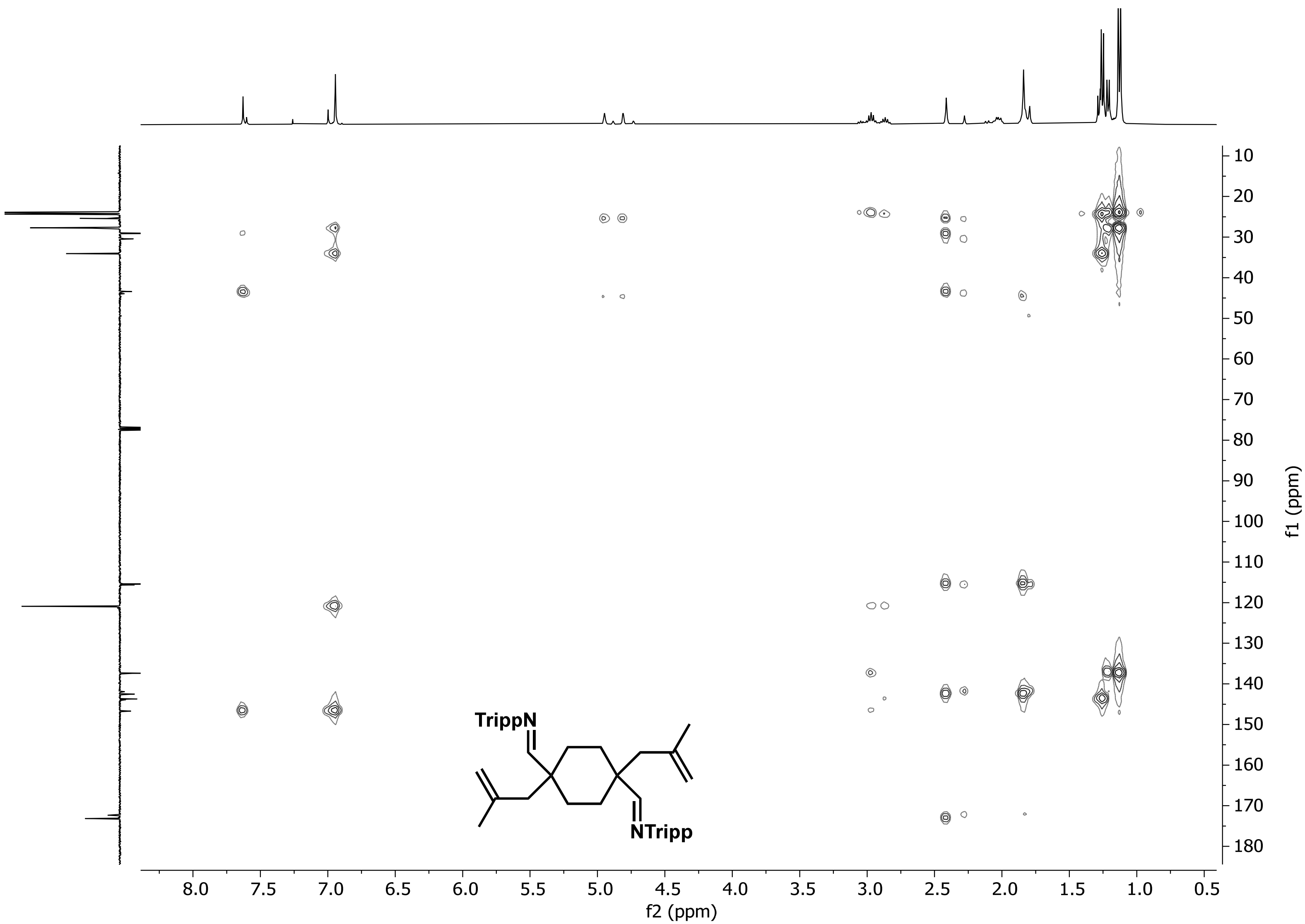


Figure S16. ^{1}H-^{13}C HMBC NMR spectrum of alkylated aldimine *cis- and trans*-**2b** ($CDCl_3$, 25°C, 400 MHz).

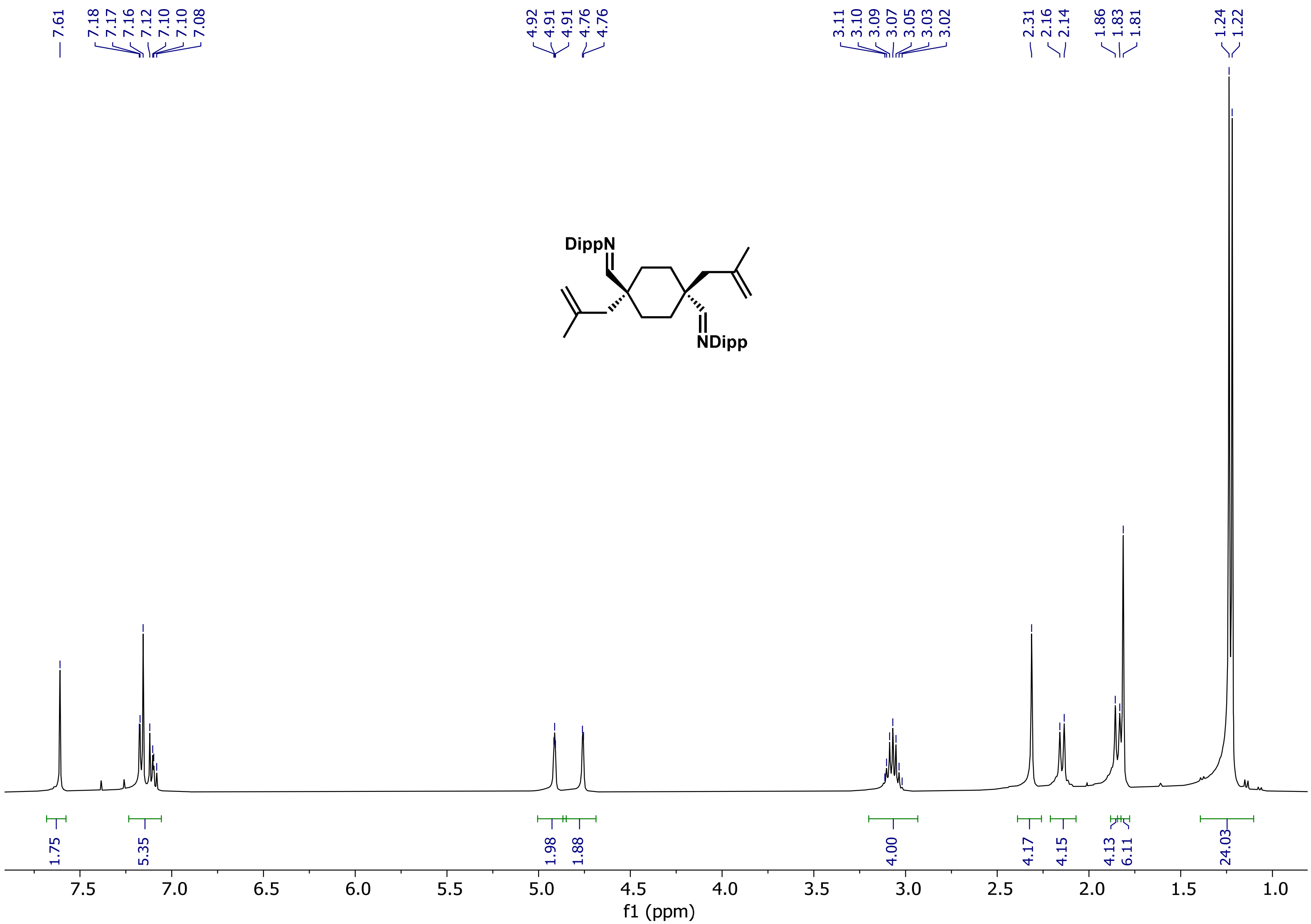


Figure S17. ^{1}H NMR spectrum of *trans*-**2a** ($CDCl_3$, 25°C, 400 MHz).

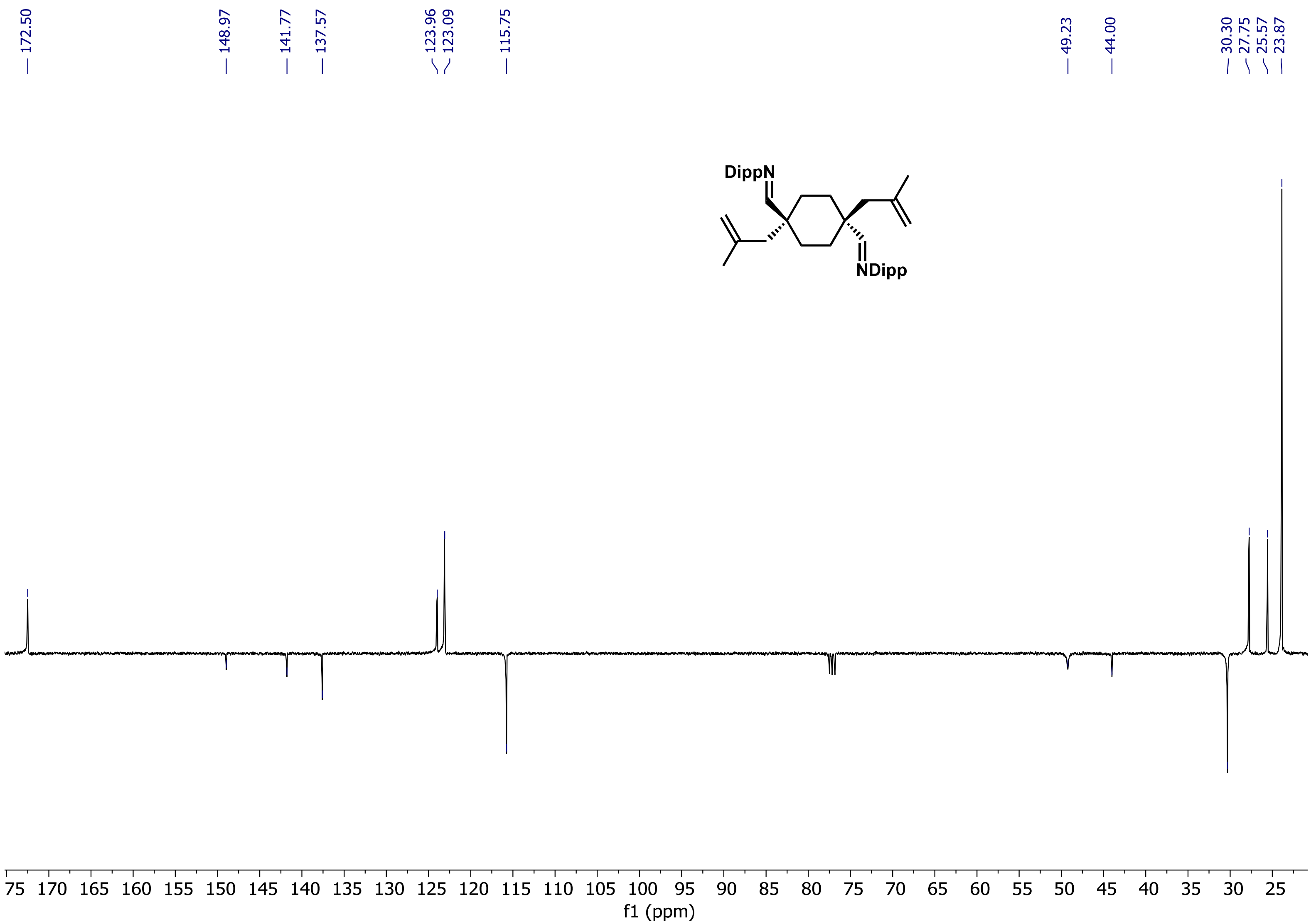


Figure S18. ^{13}C DEPTQ NMR spectrum of *trans*-**2a** ($CDCl_3$, 25°C, 101 MHz).

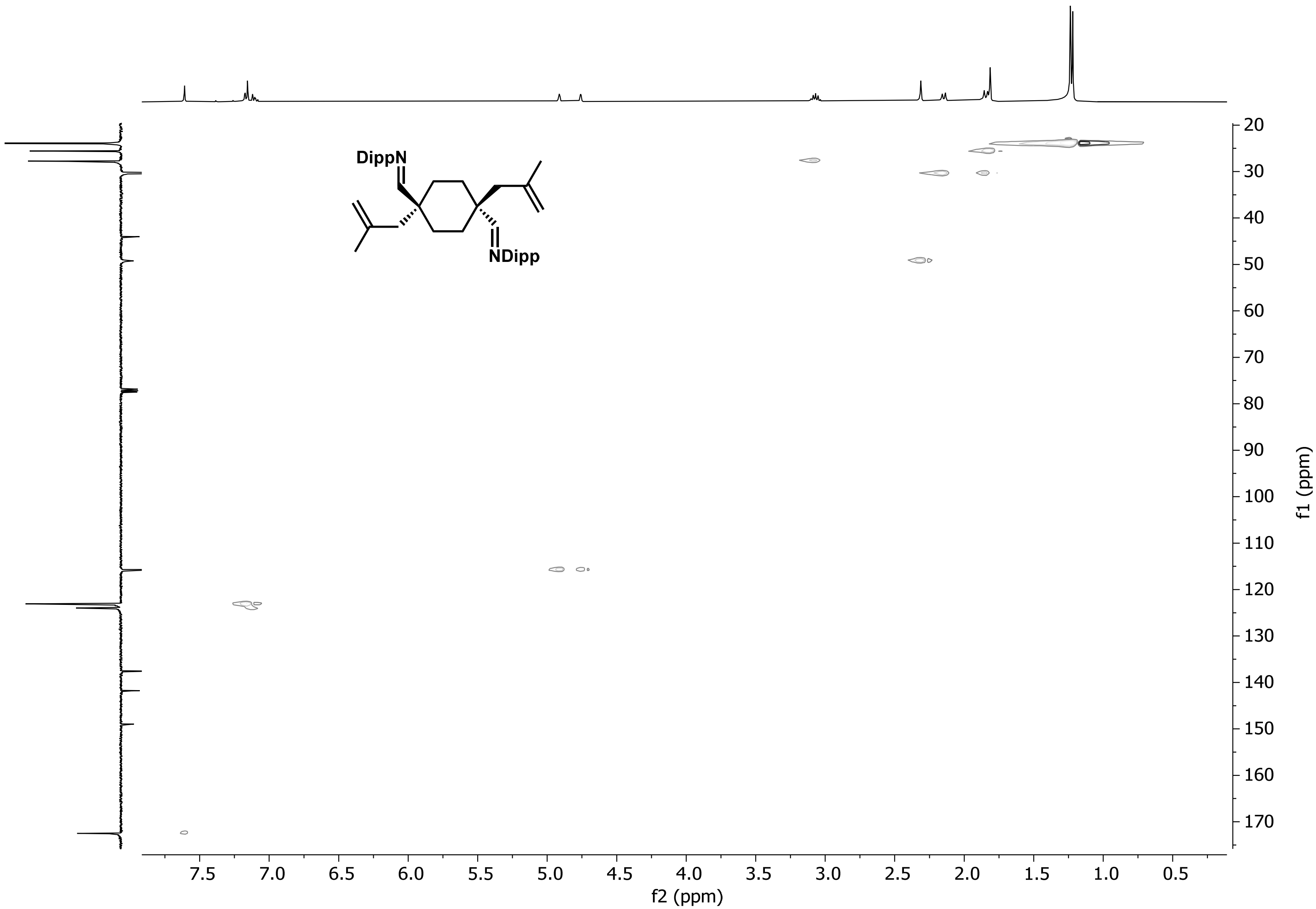


Figure S19. ^{1}H-^{13}C HSQC NMR spectrum of *trans*-**2a** ($CDCl_3$, 25°C, 400 MHz).

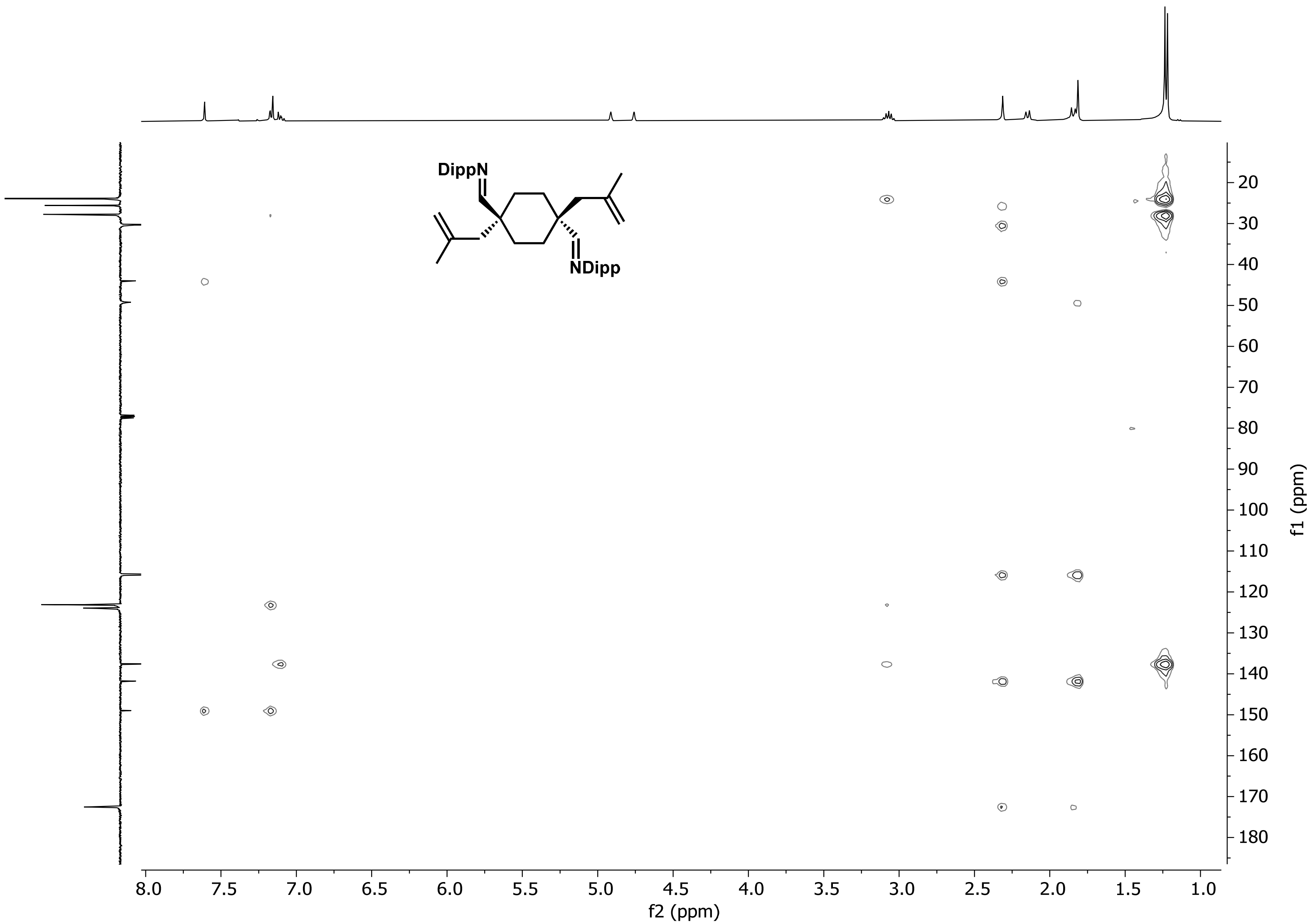


Figure S20. ^{1}H-^{13}C HMBC NMR spectrum of *trans*-**2a** ($CDCl_3$, 25°C, 400 MHz).

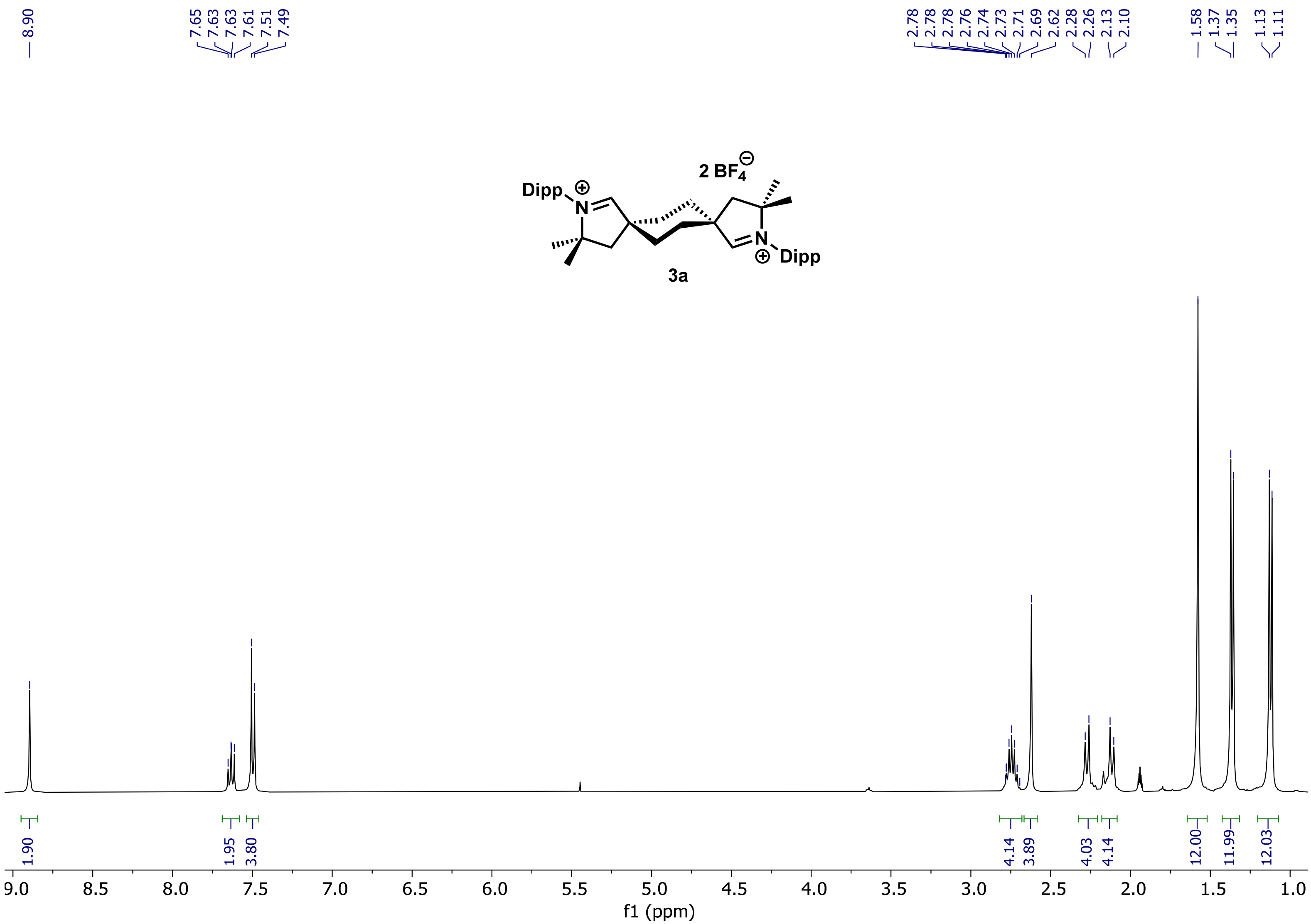


Figure S21. ^{1}H NMR spectrum of **3a** (CD_3CN, 25°C, 400 MHz).

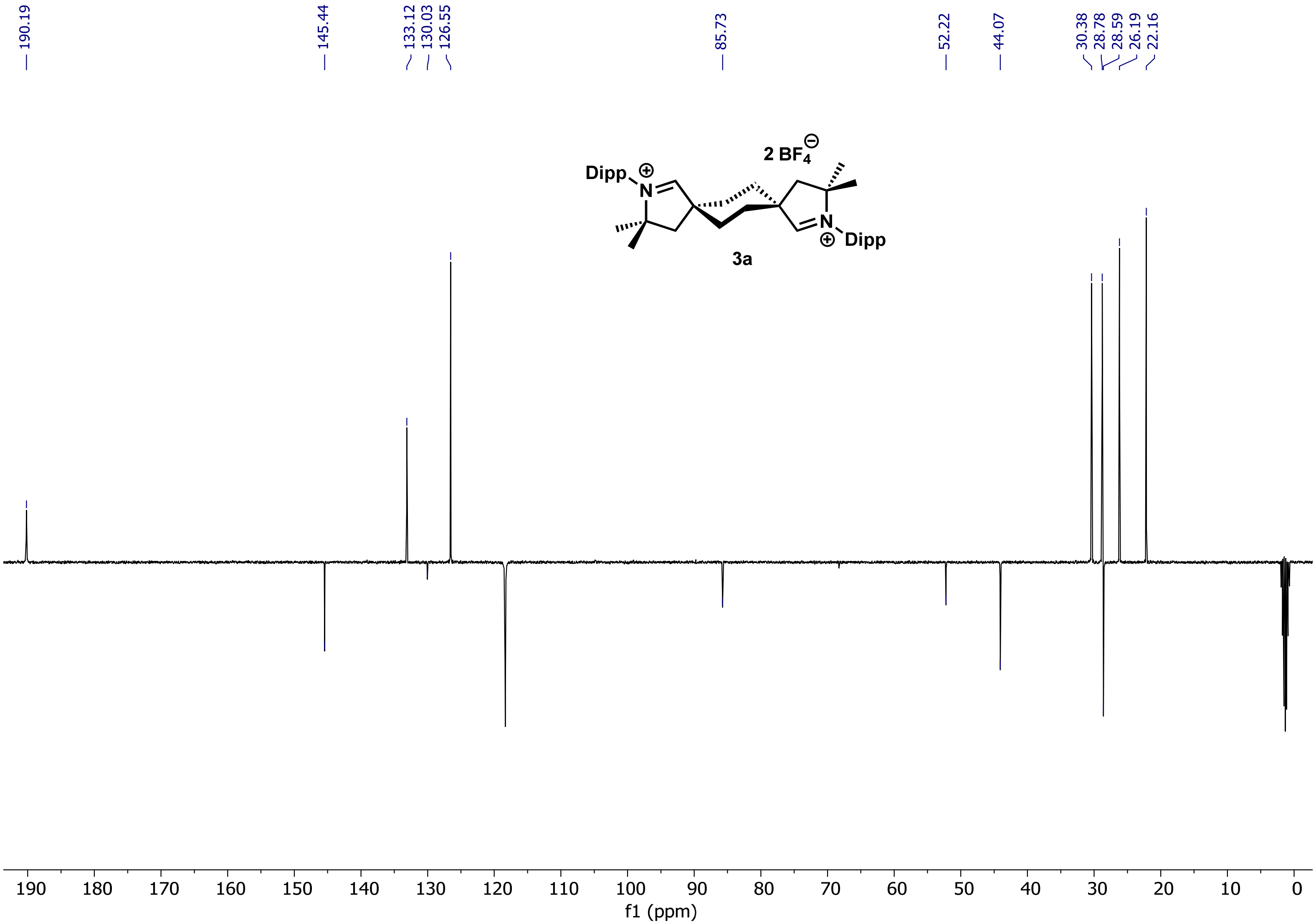


Figure S22. ^{13}C DEPTQ NMR spectrum of **3a** (CD_3CN, 25°C, 101 MHz).

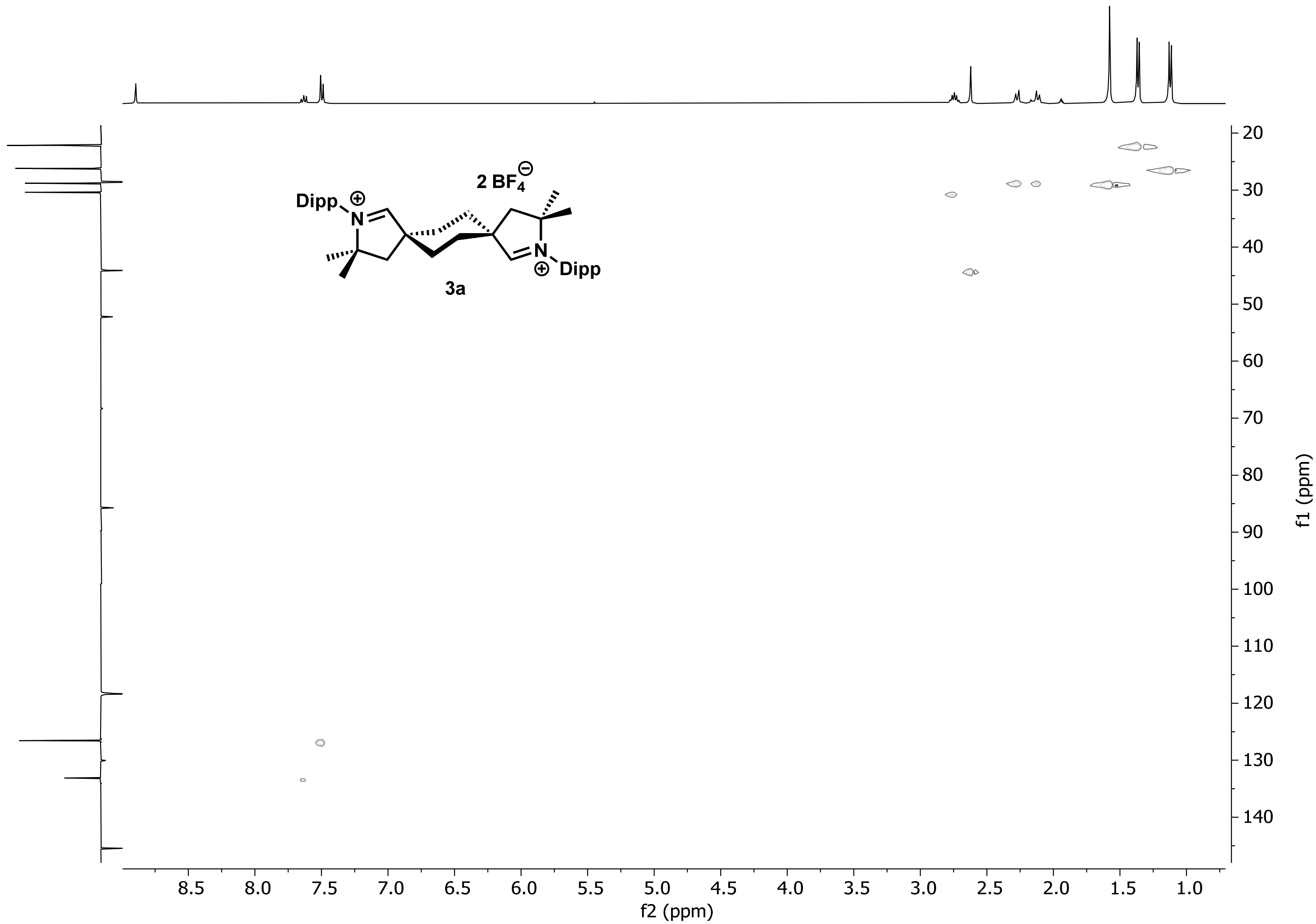


Figure S23. ^{1}H-^{13}C HSQC NMR spectrum of **3a** (CD_3CN, 25°C, 400 MHz).

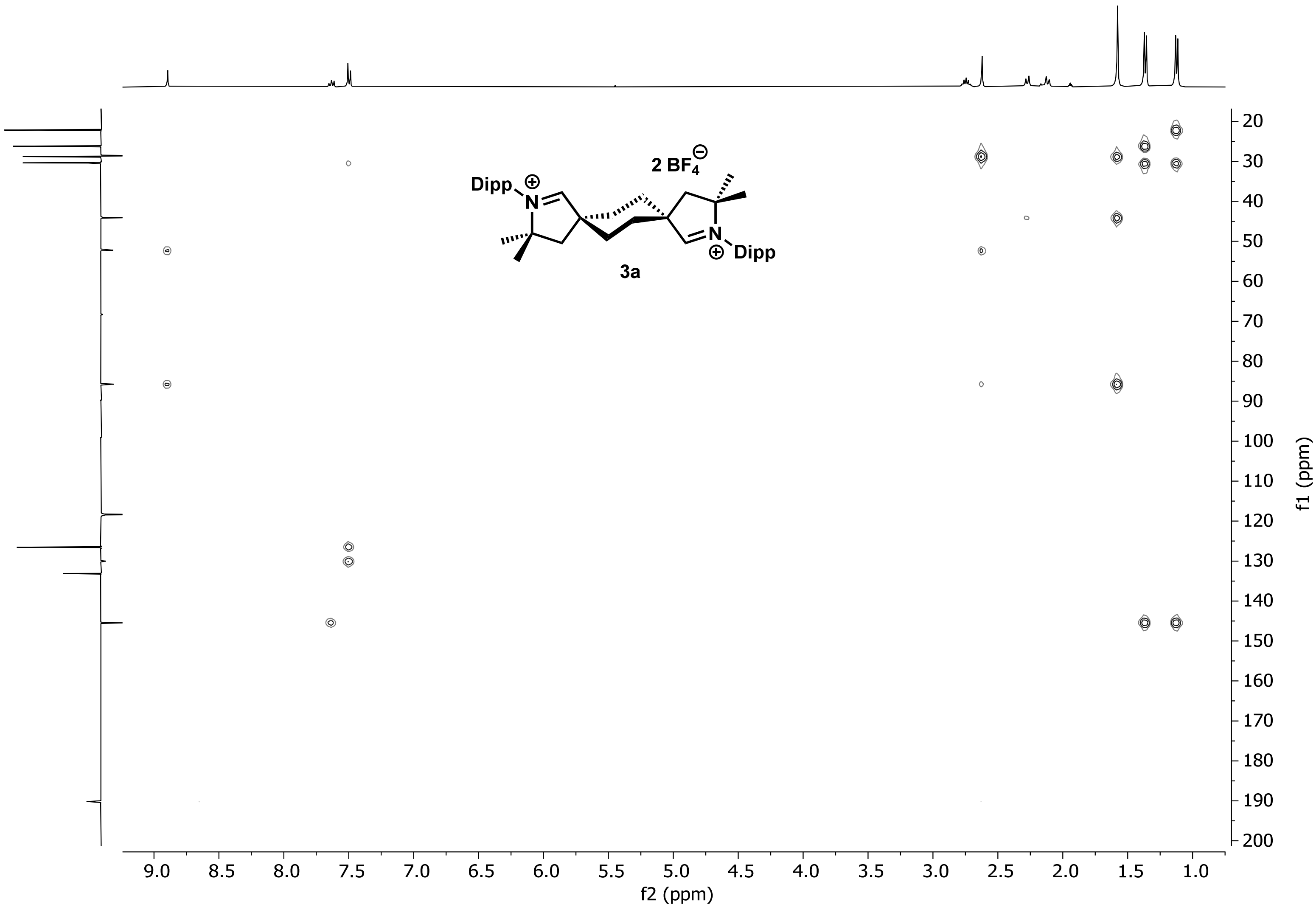


Figure S24. ^{1}H-^{13}C HMBC NMR spectrum of **3a** (CD_3CN, 25°C, 400 MHz).

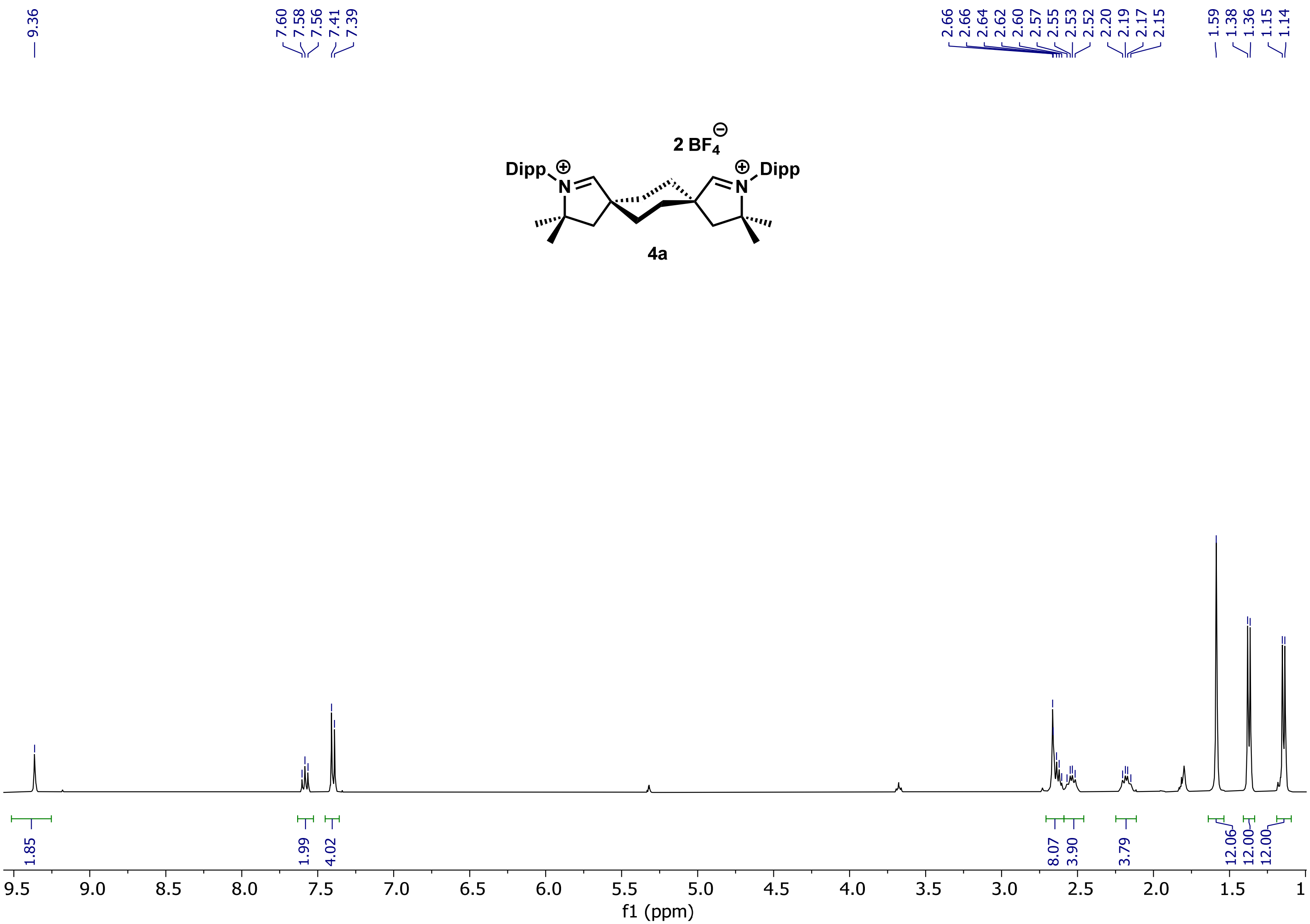


Figure S25. ^{1}H NMR spectrum of **4a** (CD_2Cl_2, 25°C, 400 MHz).

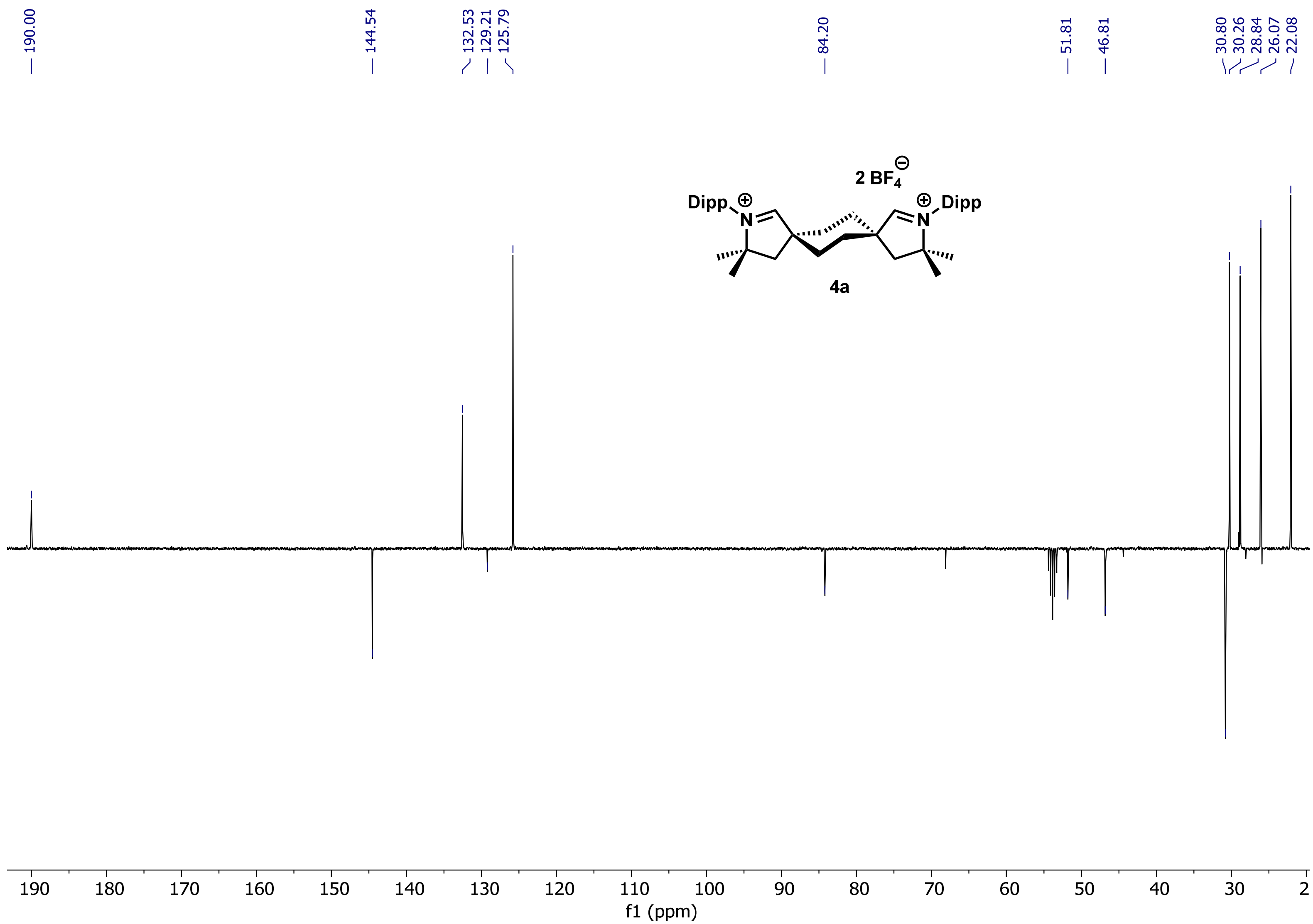


Figure S26. ^{13}C DEPTQ NMR spectrum of **4a** (CD_2Cl_2, 25°C, 101 MHz).

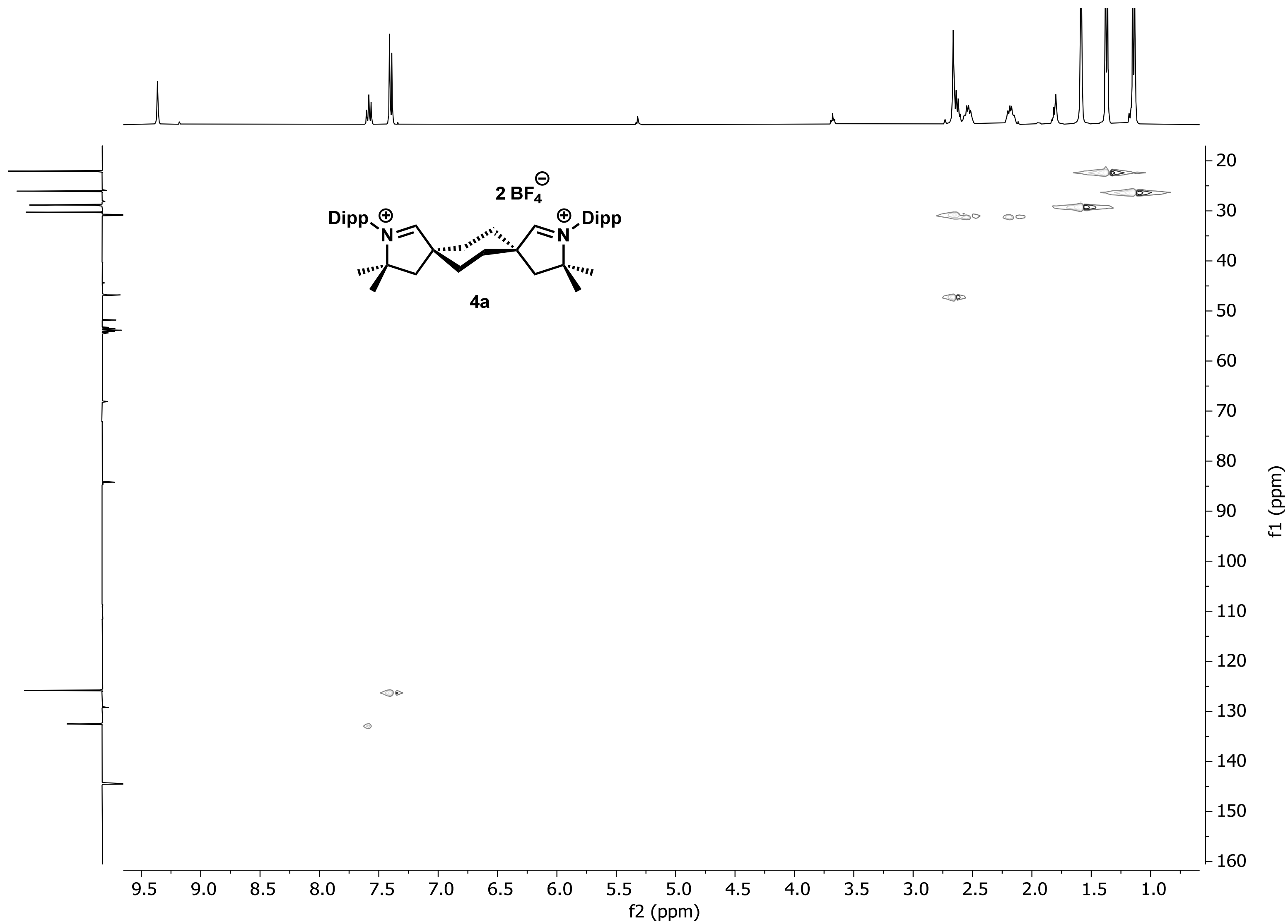


Figure S27. ^{1}H-^{13}C HSQC NMR spectrum of **4a** (CD_2Cl_2, 25°C, 400 MHz).

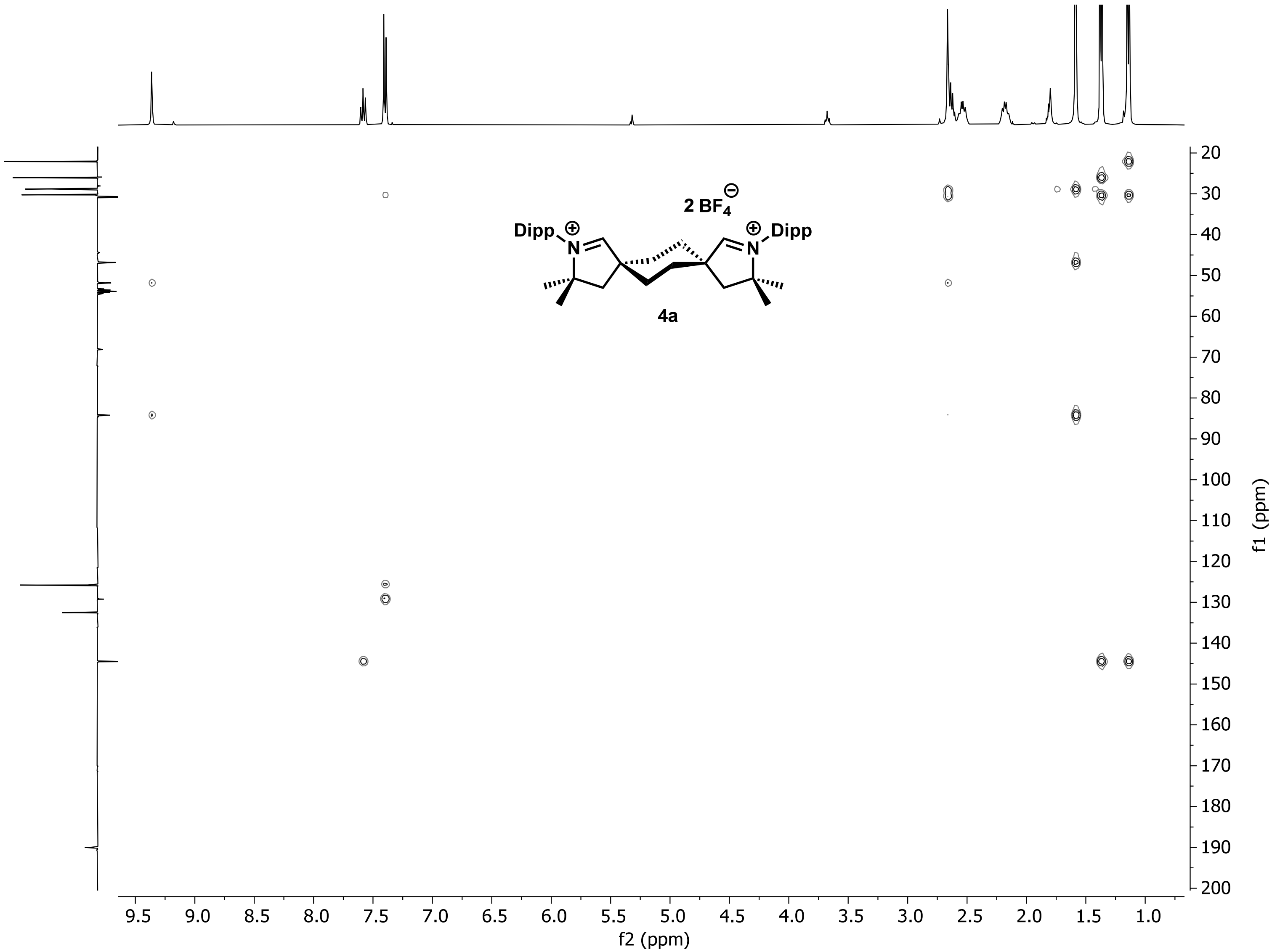


Figure S28. ^{1}H-^{13}C HMBC NMR spectrum of **4a** (CD_2Cl_2, 25°C, 400 MHz).

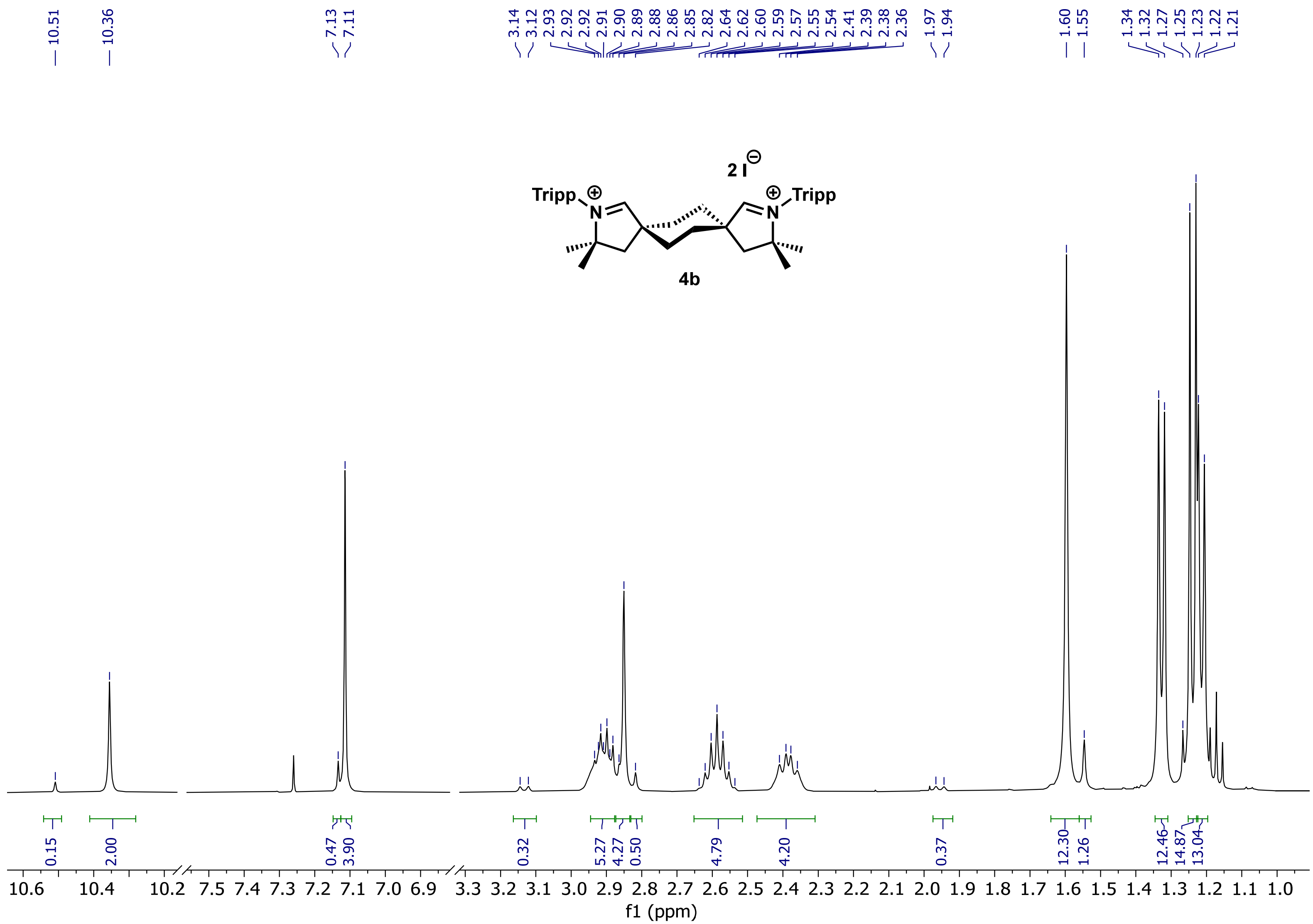


Figure S29. ^{1}H NMR spectrum of iminium salt **4b** ($CDCl_3$, 25°C, 400 MHz).

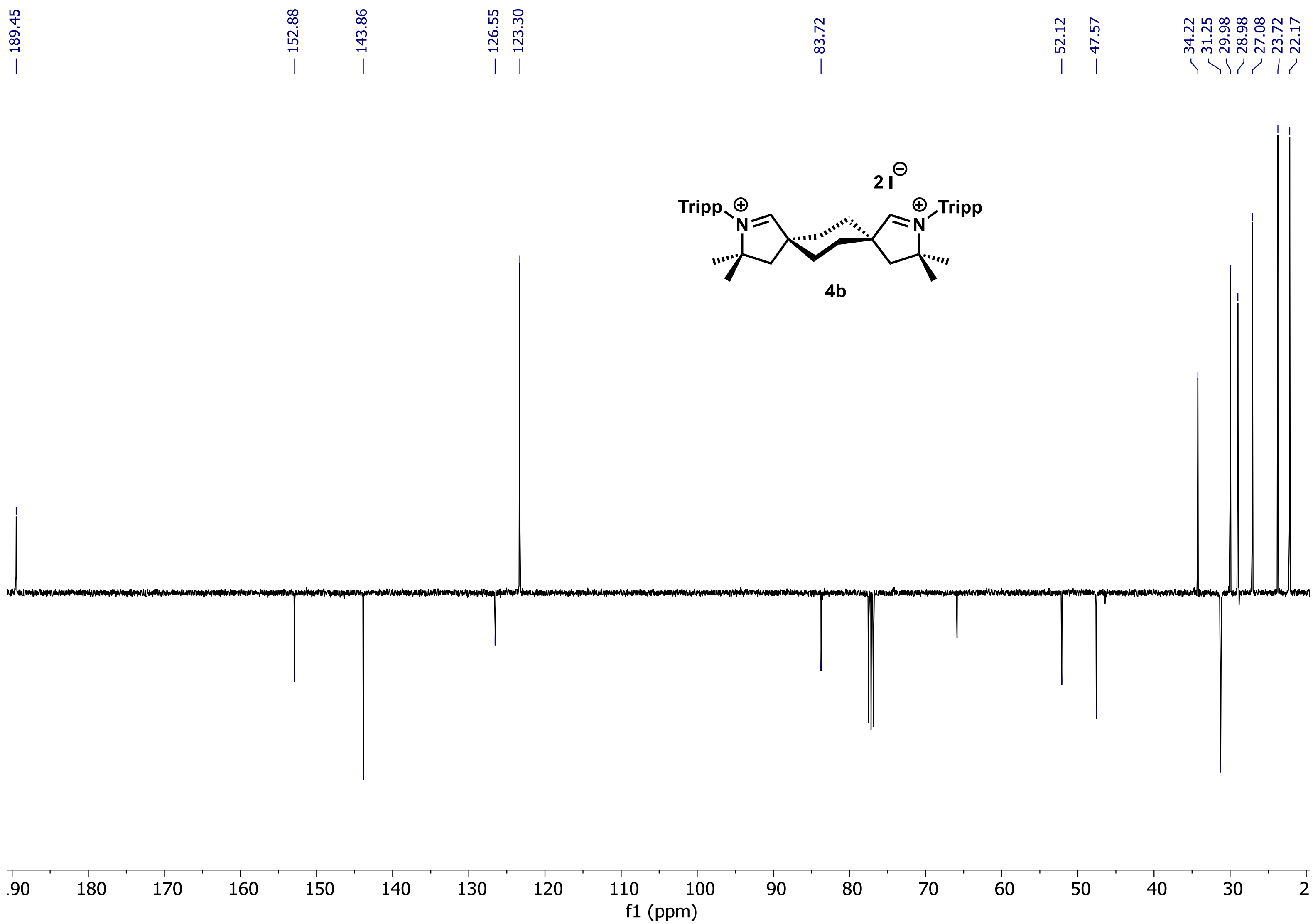


Figure S30. ^{13}C DEPTQ NMR spectrum of iminium salt **4b** ($CDCl_3$, 25°C, 101 MHz).

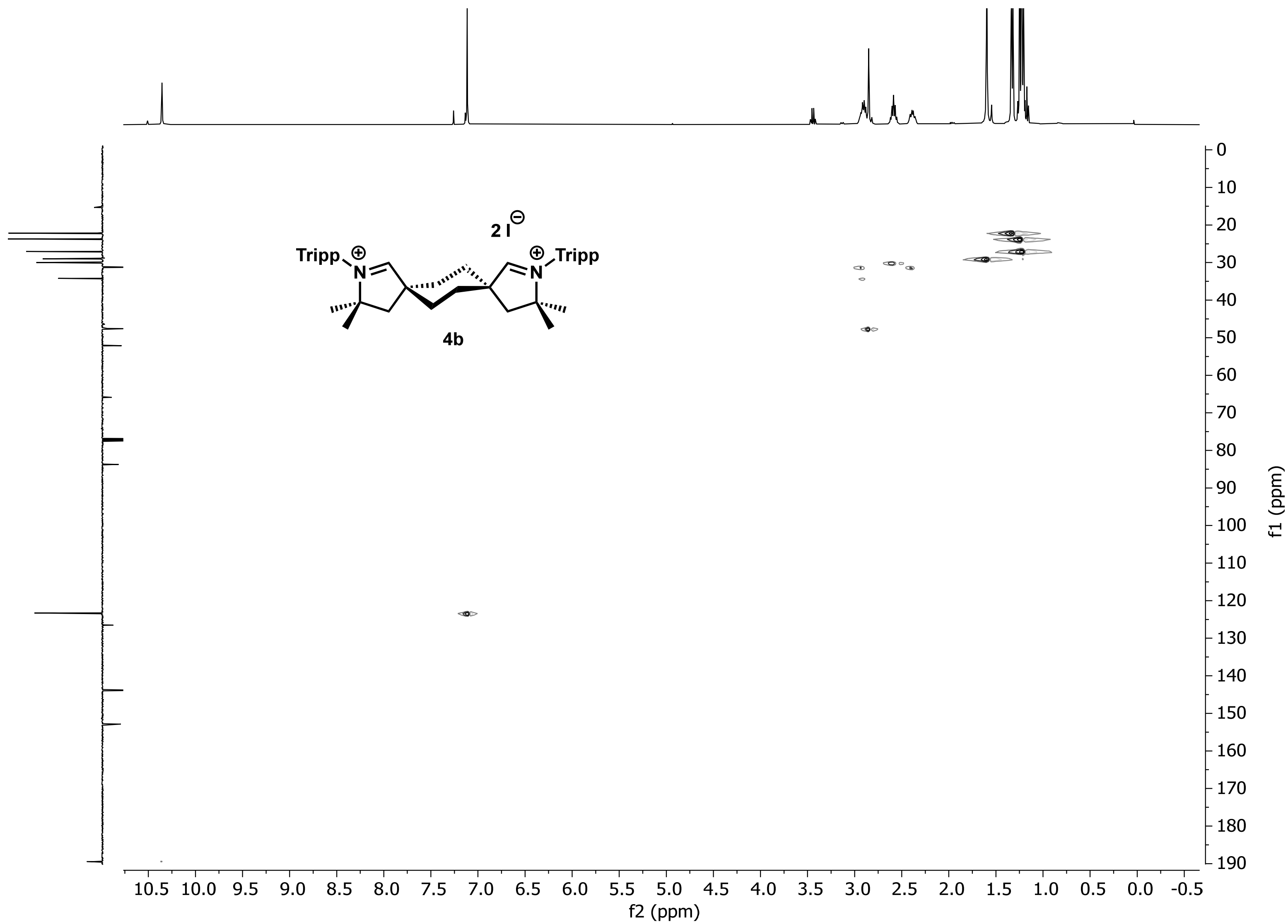


Figure S31. ^{1}H-^{13}C HSQC NMR spectrum of iminium salt **4b** ($CDCl_3$, 25°C, 400 MHz).

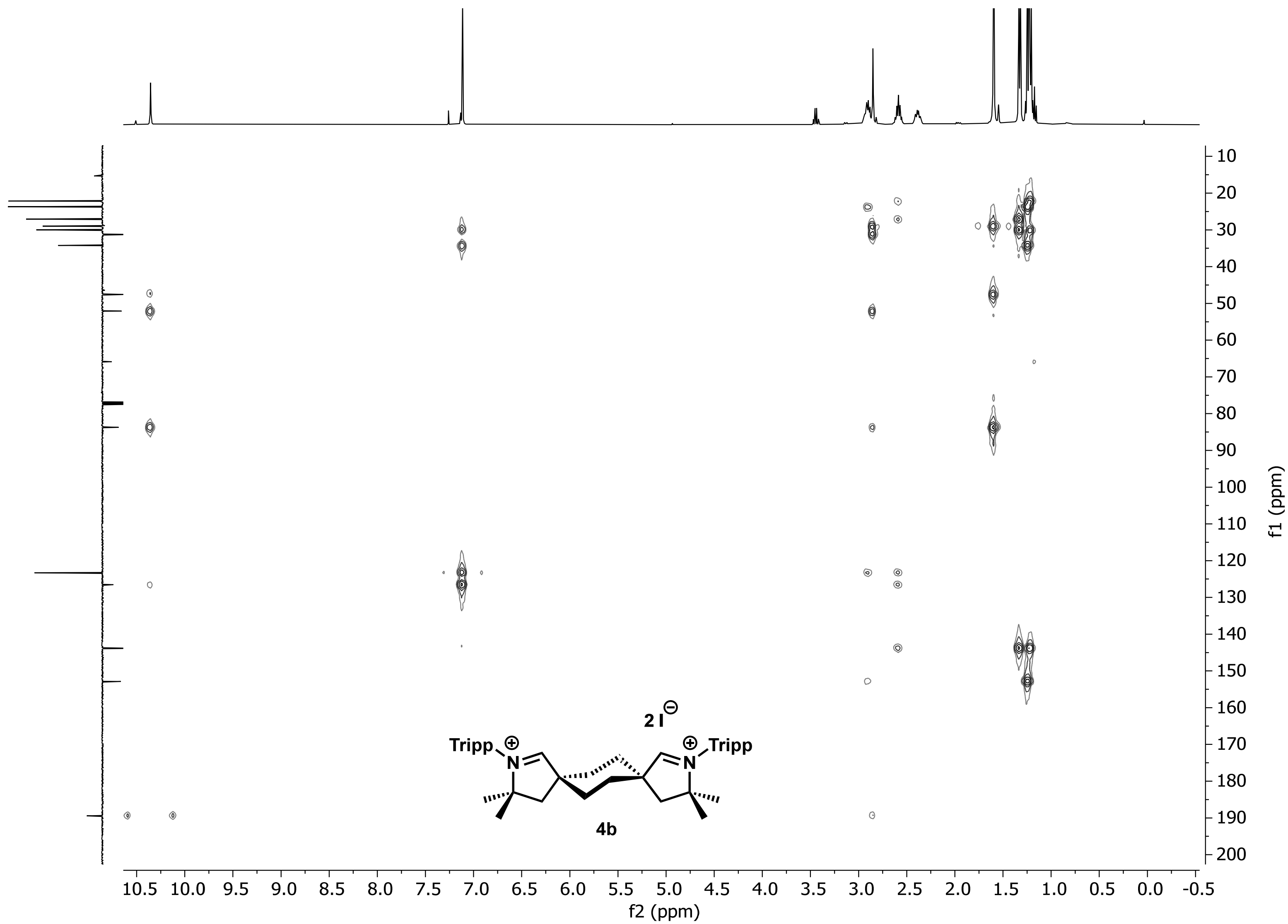


Figure S32. ^{1}H-^{13}C HMBC NMR spectrum of iminium salt **4b** ($CDCl_3$, 25°C, 400 MHz).

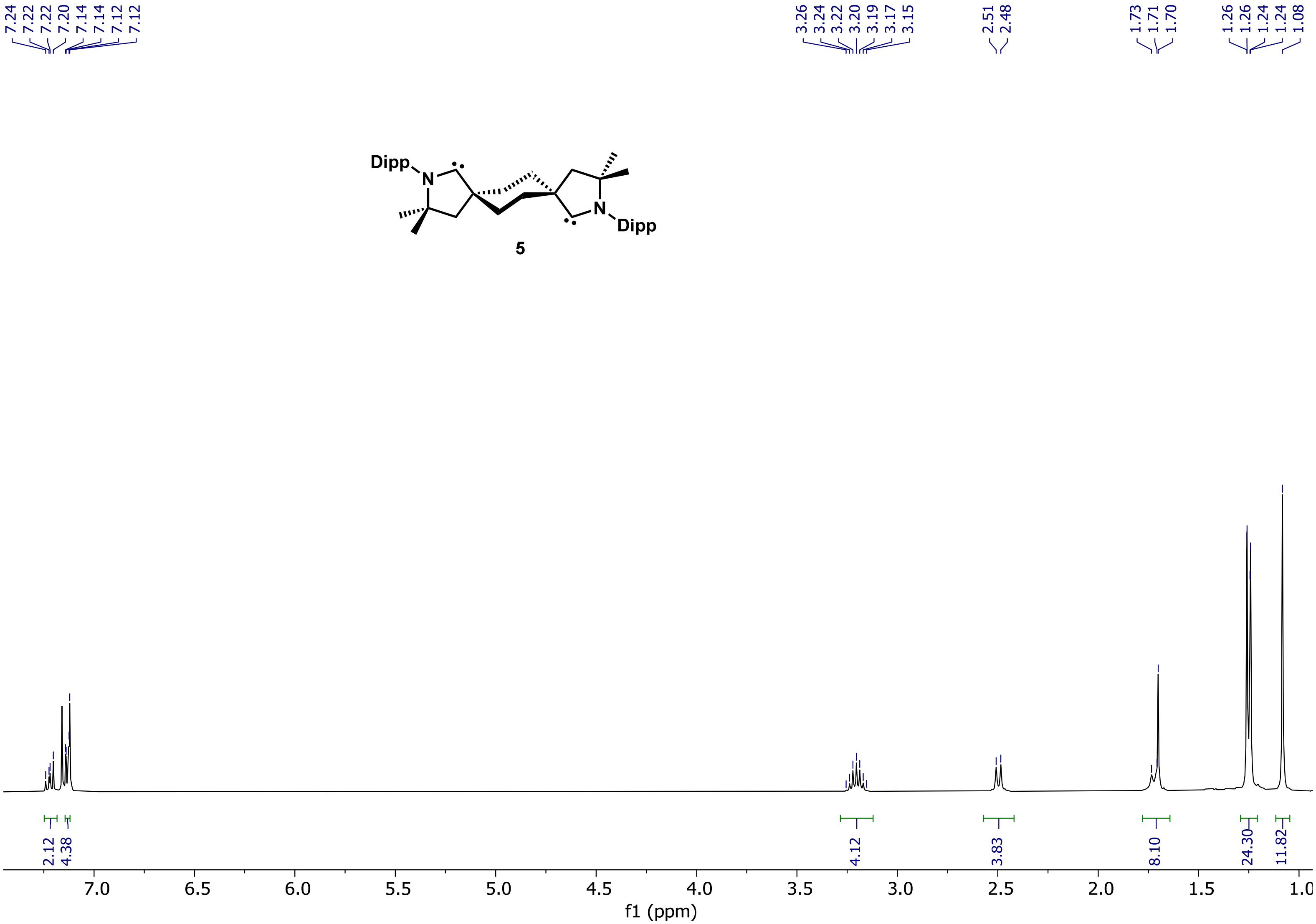


Figure S33. ^{1}H NMR spectrum of free carbene **5** (C_6D_6, 25°C, 400 MHz).

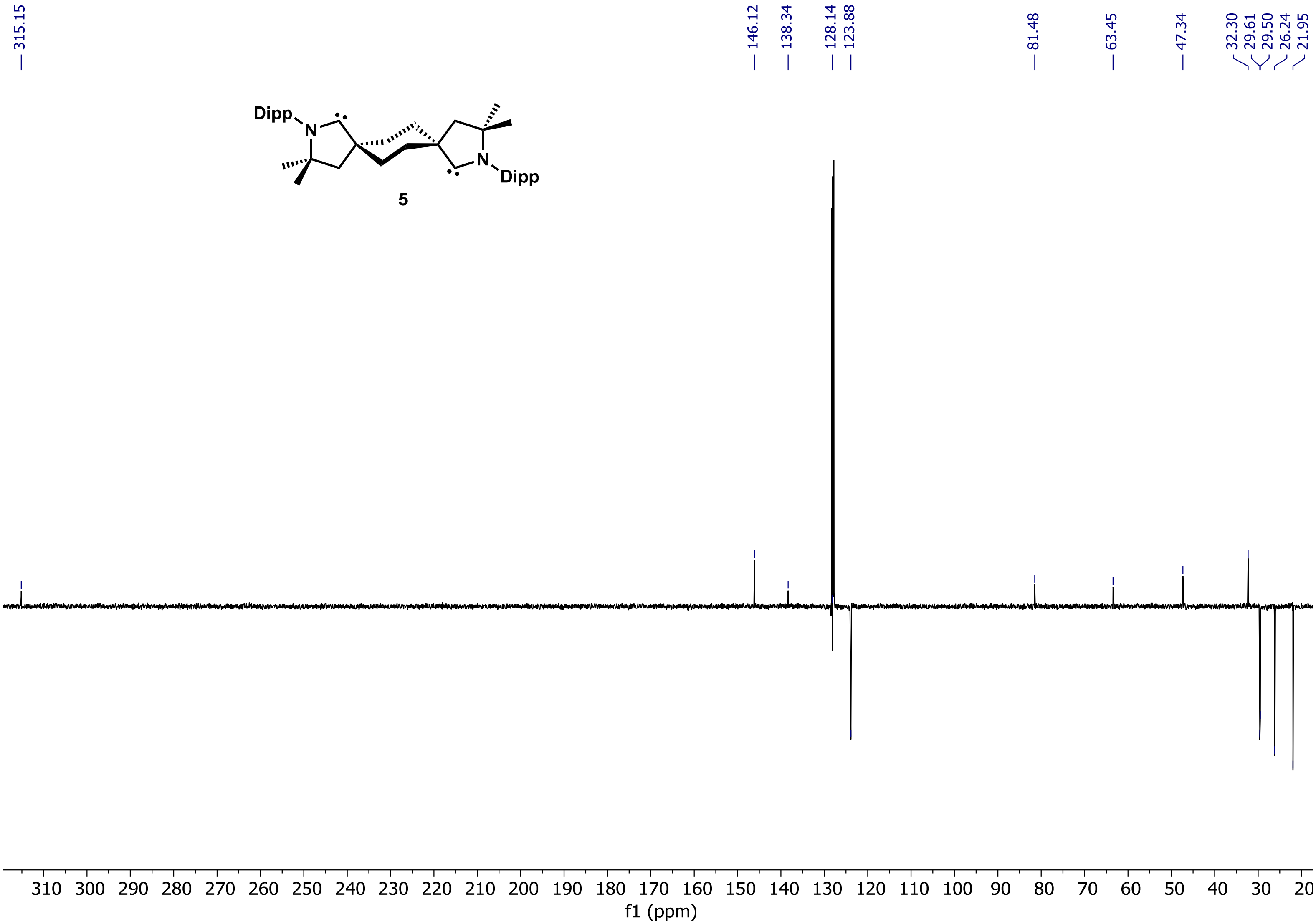


Figure S34. ^{13}C DEPTQ NMR spectrum of free carbene **5** (C_6D_6, 25°C, 101 MHz).

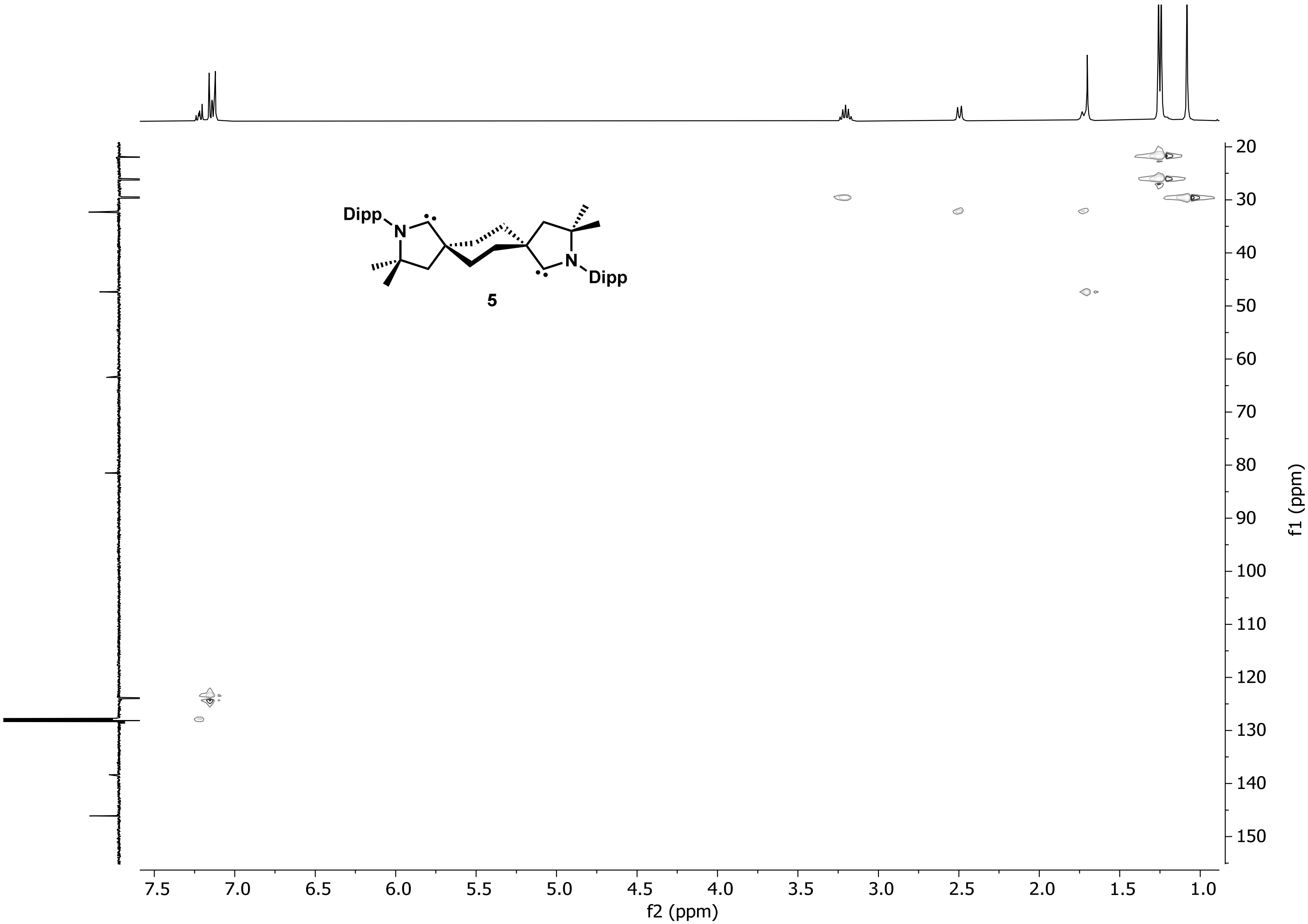


Figure S35. ^{1}H-^{13}C HSQC NMR spectrum of free carbene **5** (C_6D_6, 25°C, 400 MHz).

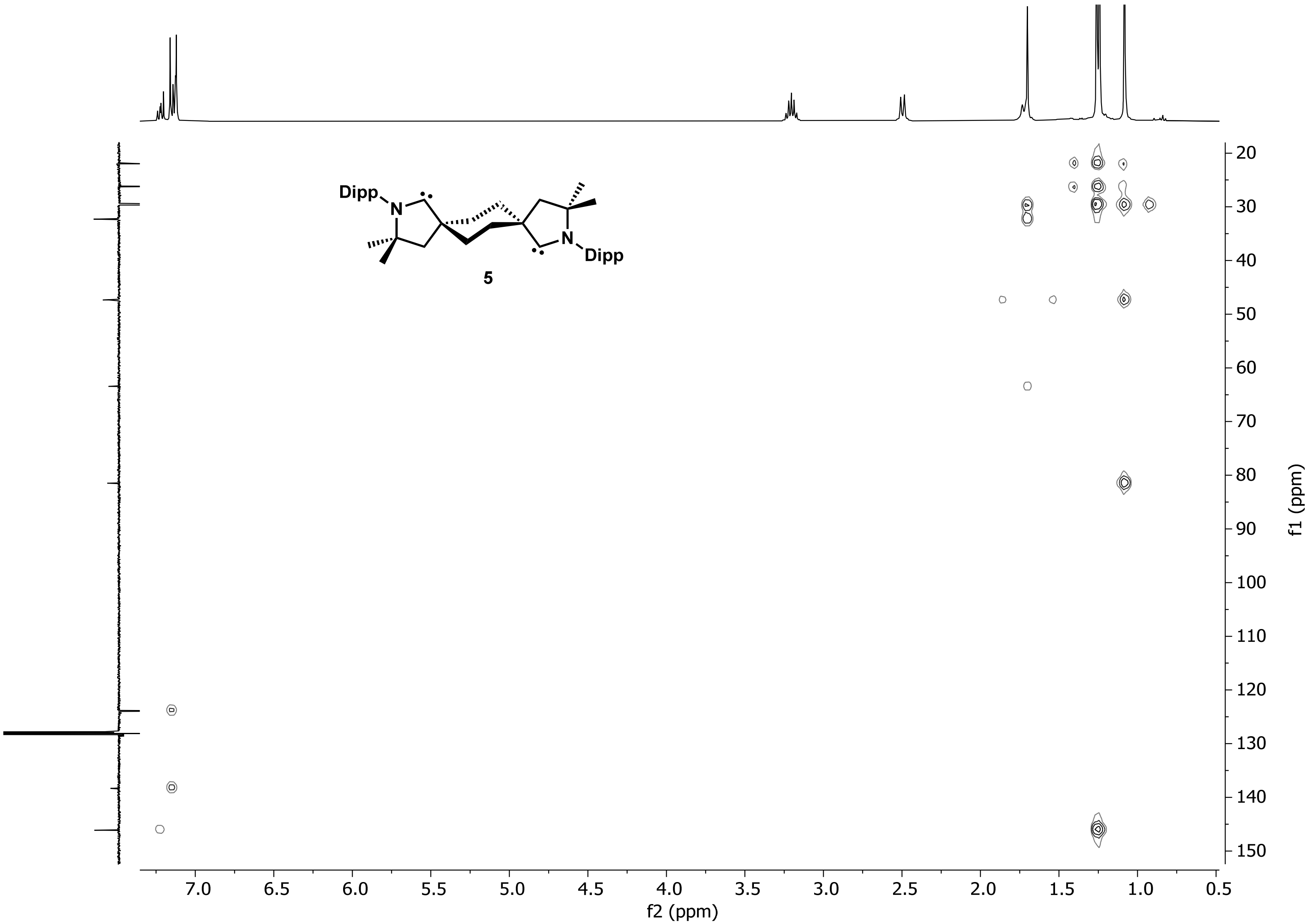


Figure S36. ^{1}H-^{13}C HMBC NMR spectrum of free carbene **5** (C_6D_6, 25°C, 400 MHz).

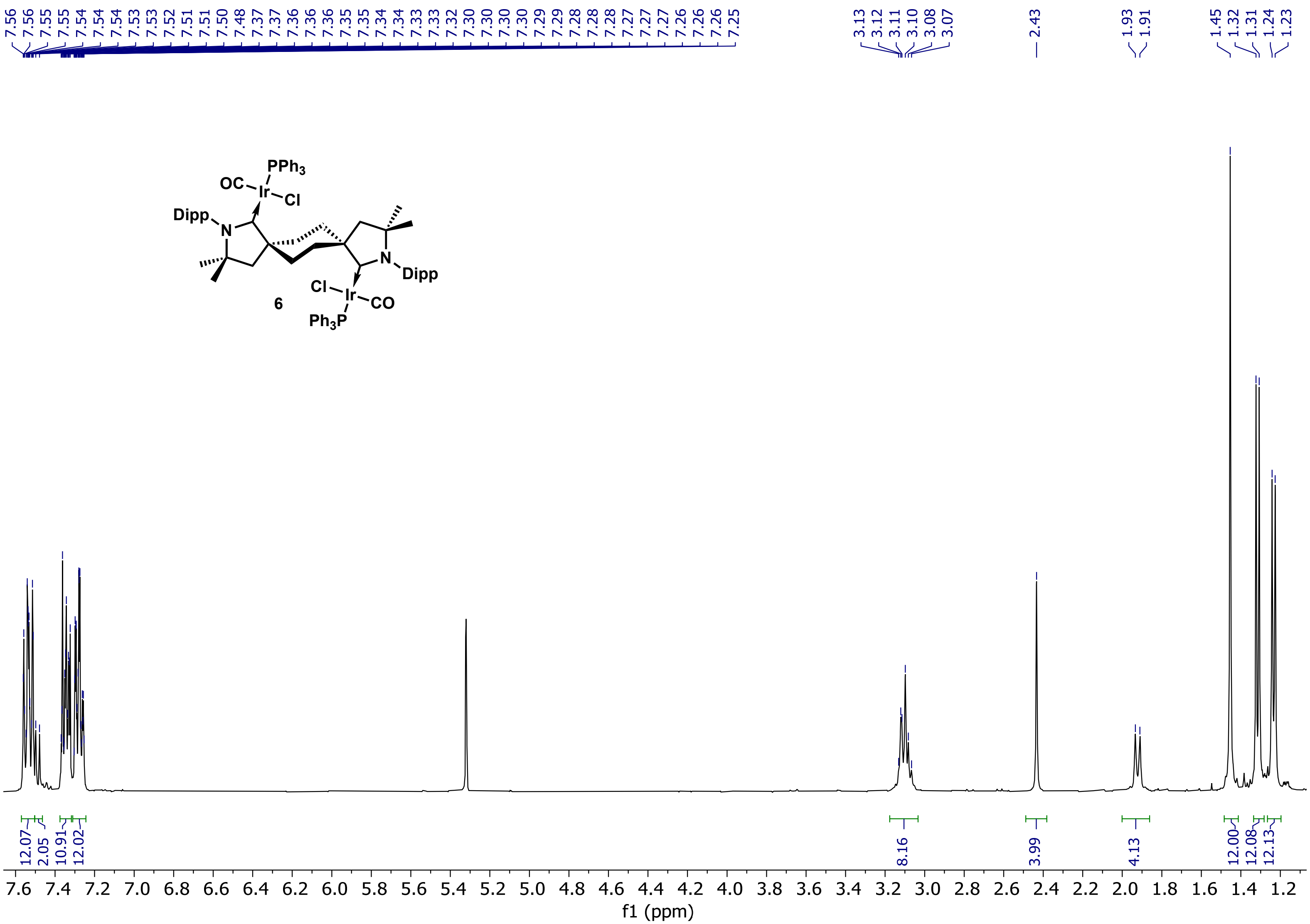


Figure S37. ^{1}H NMR spectrum of complex **6** (C_6D_6, 25°C, 400 MHz).

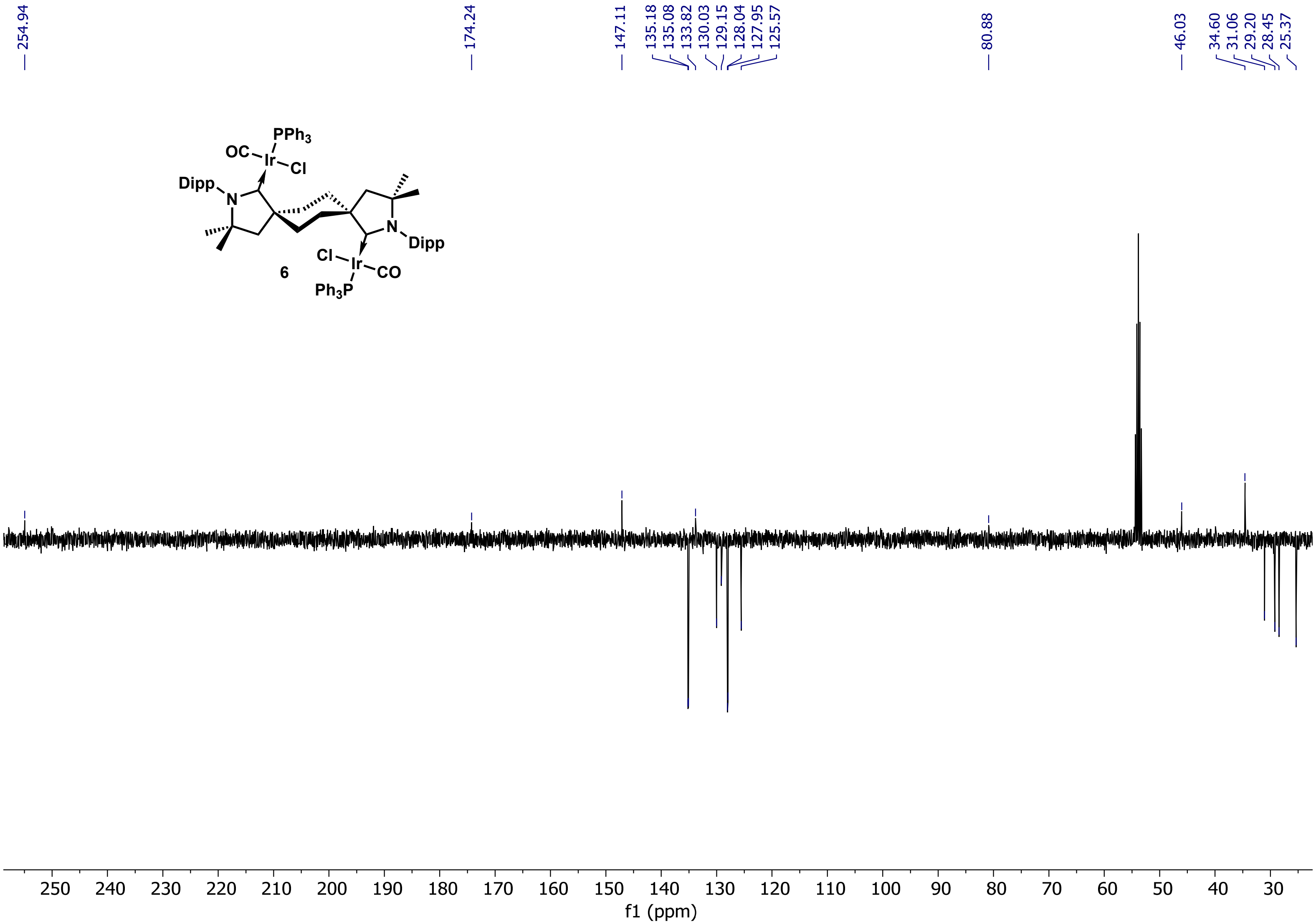


Figure S38. ^{13}C DEPTQ NMR spectrum of complex **6** (C_6D_6, 25°C, 101 MHz).

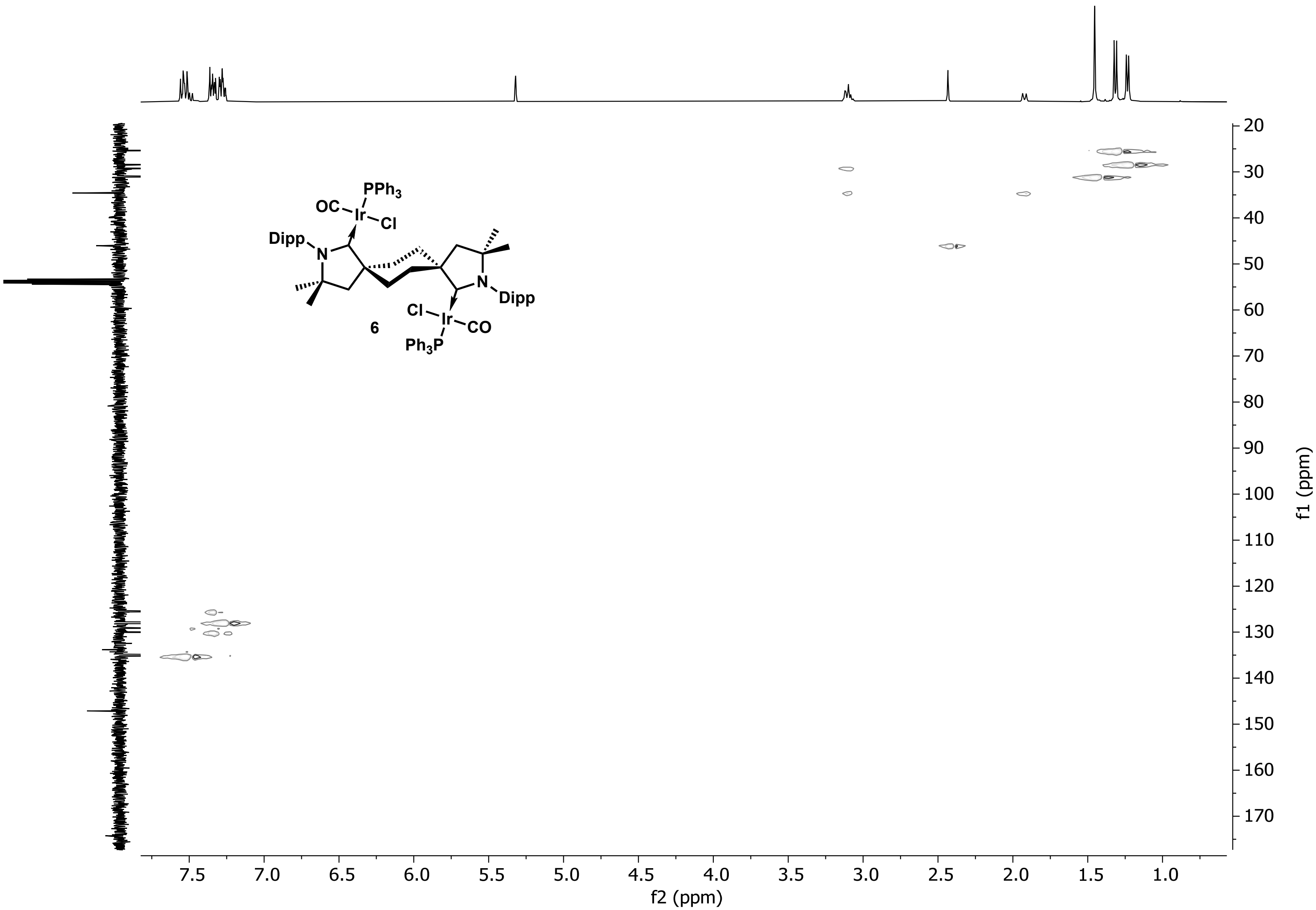


Figure S39. ^{1}H-^{13}C HSQC NMR spectrum of complex **6** (C_6D_6, 25°C, 400 MHz).

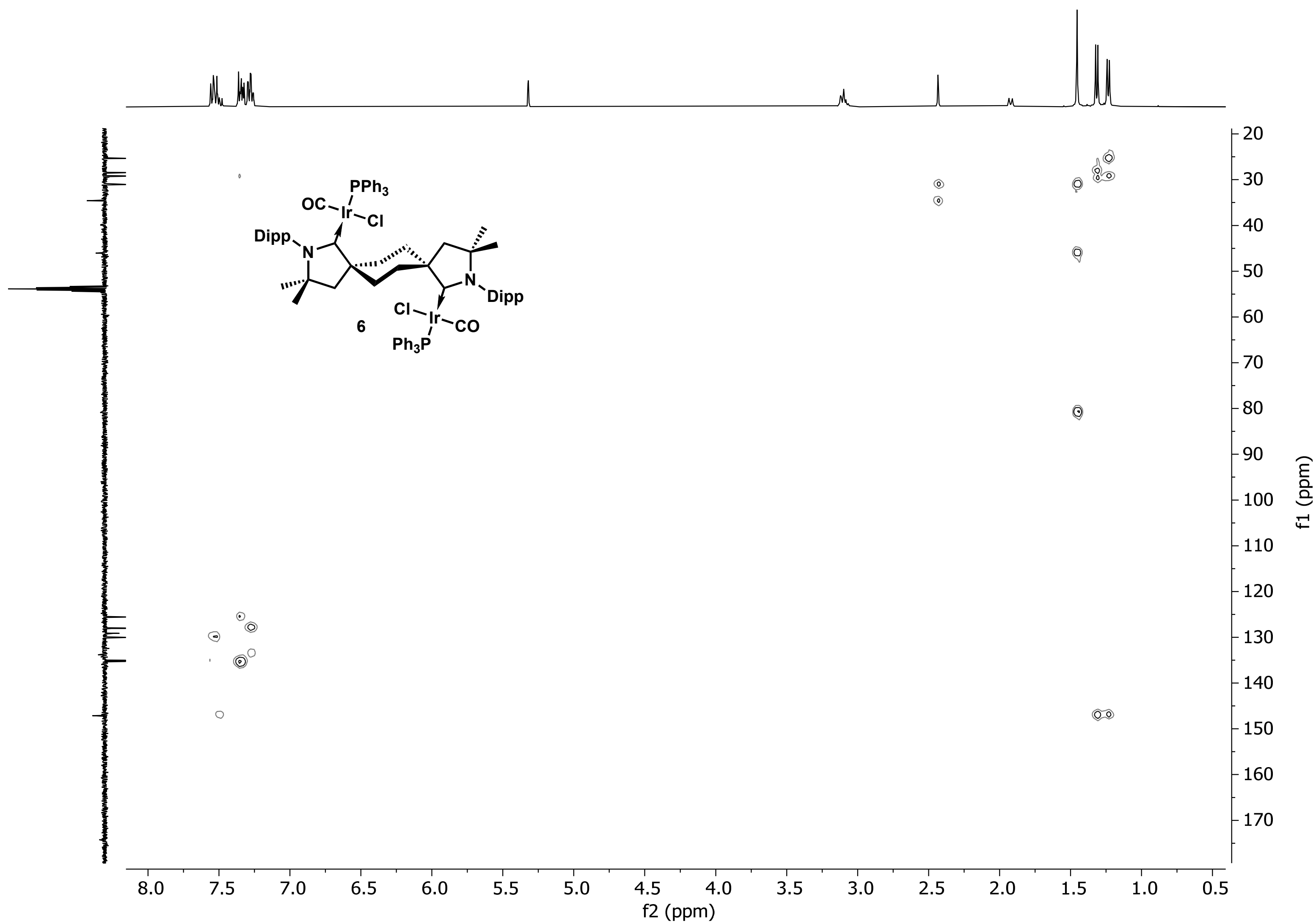


Figure S40. ^{1}H-^{13}C HMBC NMR spectrum of complex **6** (C_6D_6, 25°C, 400 MHz).

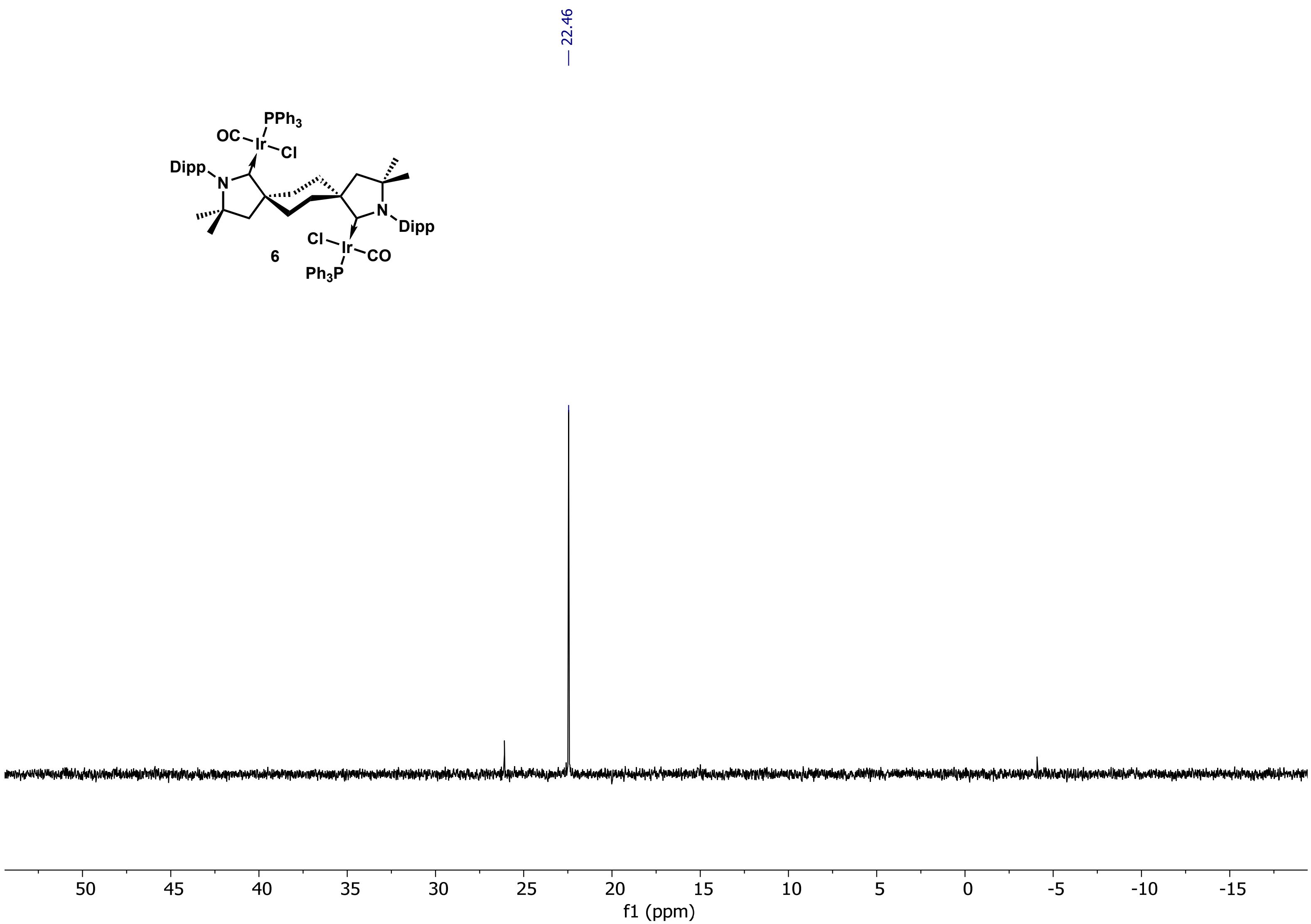


Figure S41. $^{31}P\{^1H\}$ NMR spectrum of complex **6** (C_6D_6, 25°C, 162 MHz).

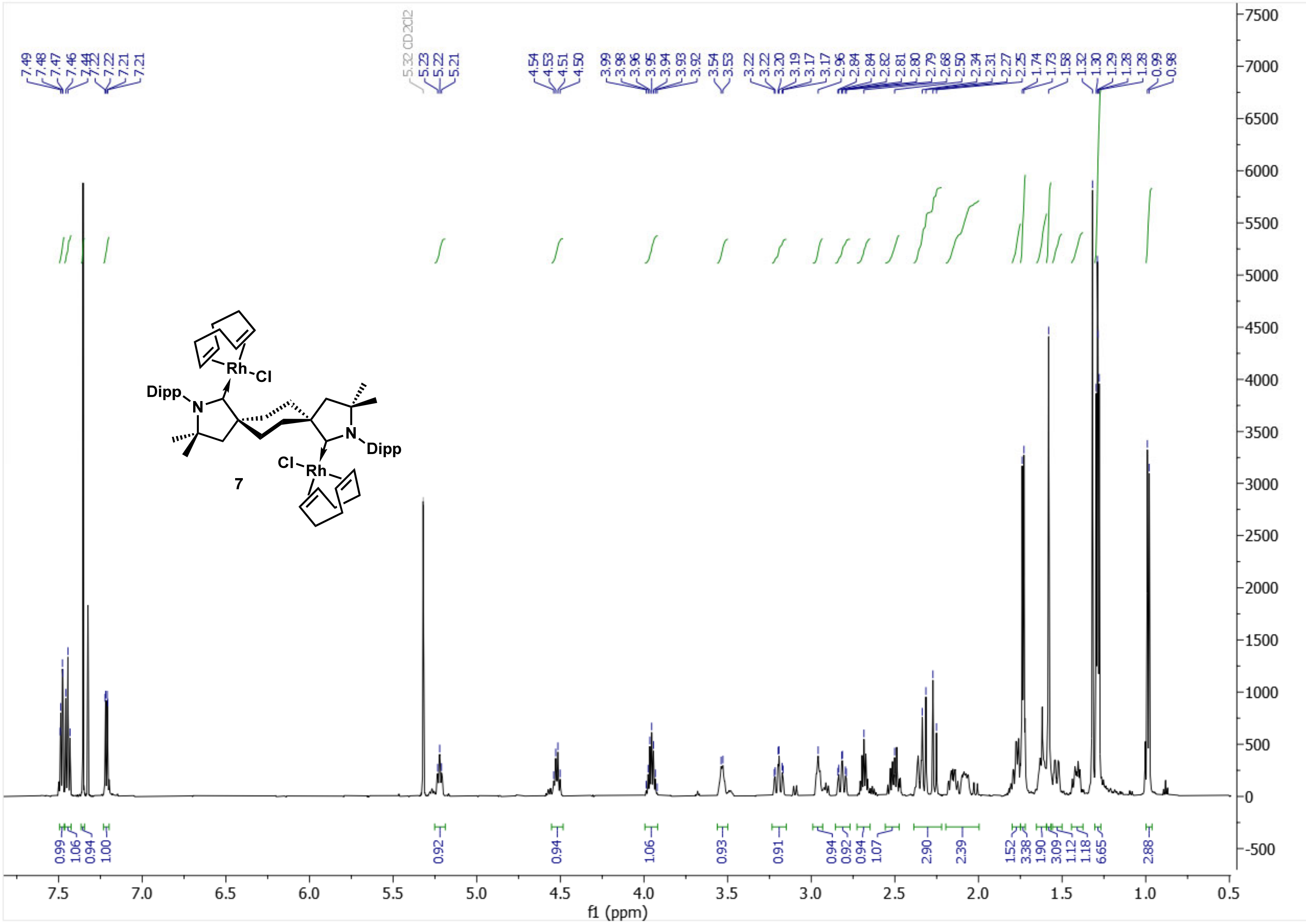


Figure S42. ^{1}H NMR spectrum of complex **7** (CD_2Cl_2, 25°C, 400 MHz).

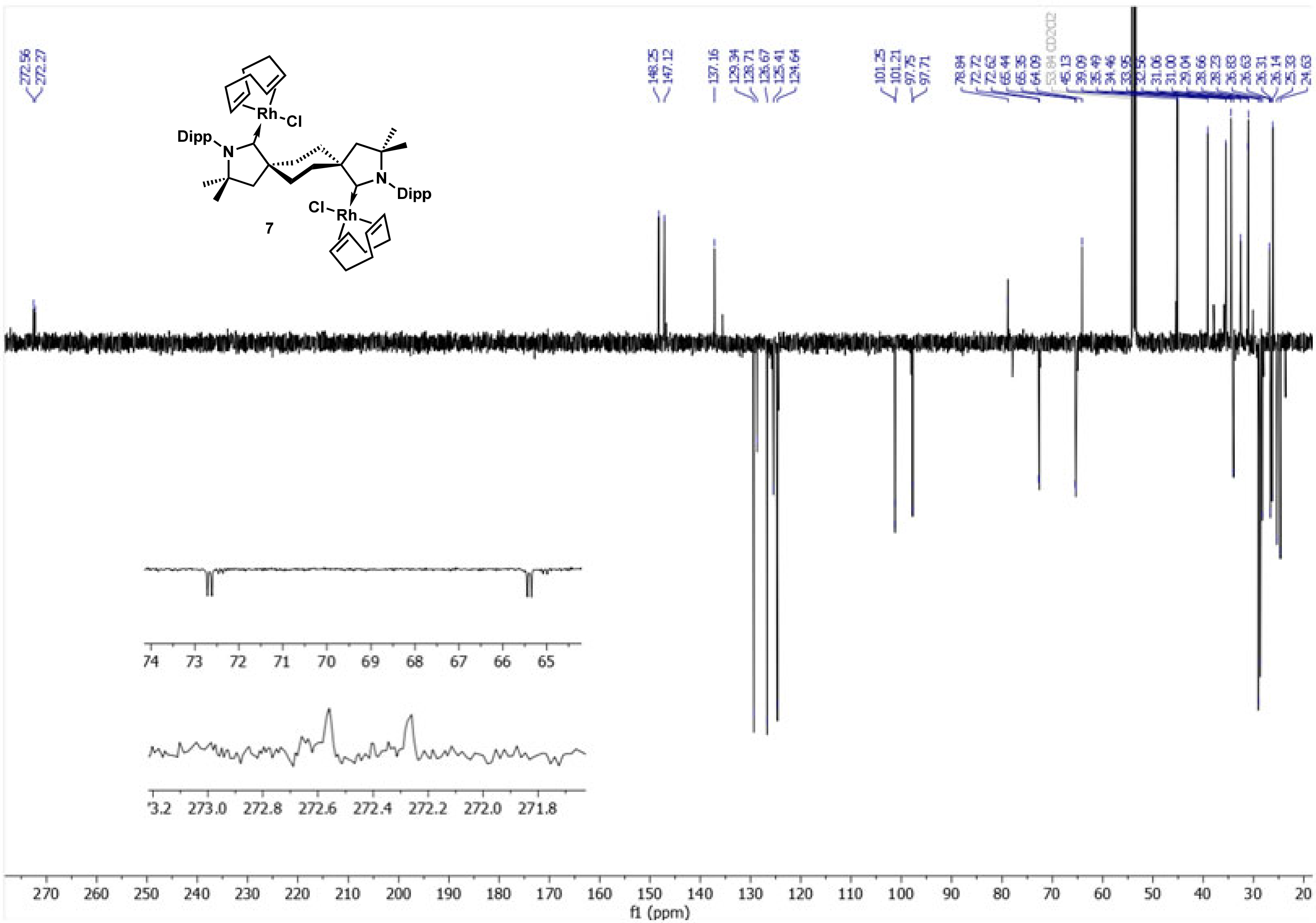


Figure S43. ^{13}C DEPTQ NMR spectrum of complex **7** (CD_2Cl_2, 25°C, 101 MHz).

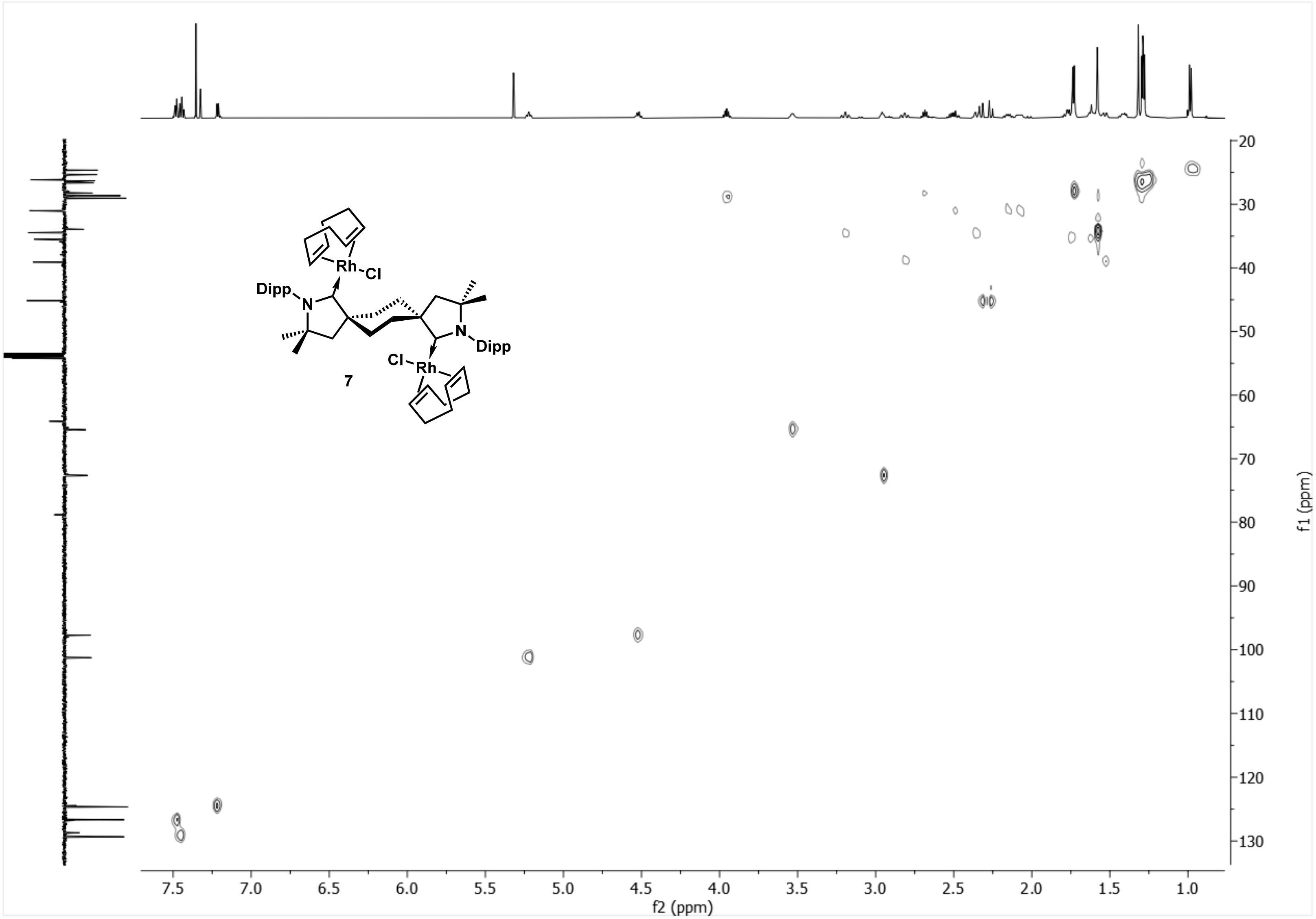


Figure S44. ^{1}H-^{13}C HSQC NMR spectrum of complex **7** (CD_2Cl_2, 25°C, 400 MHz).

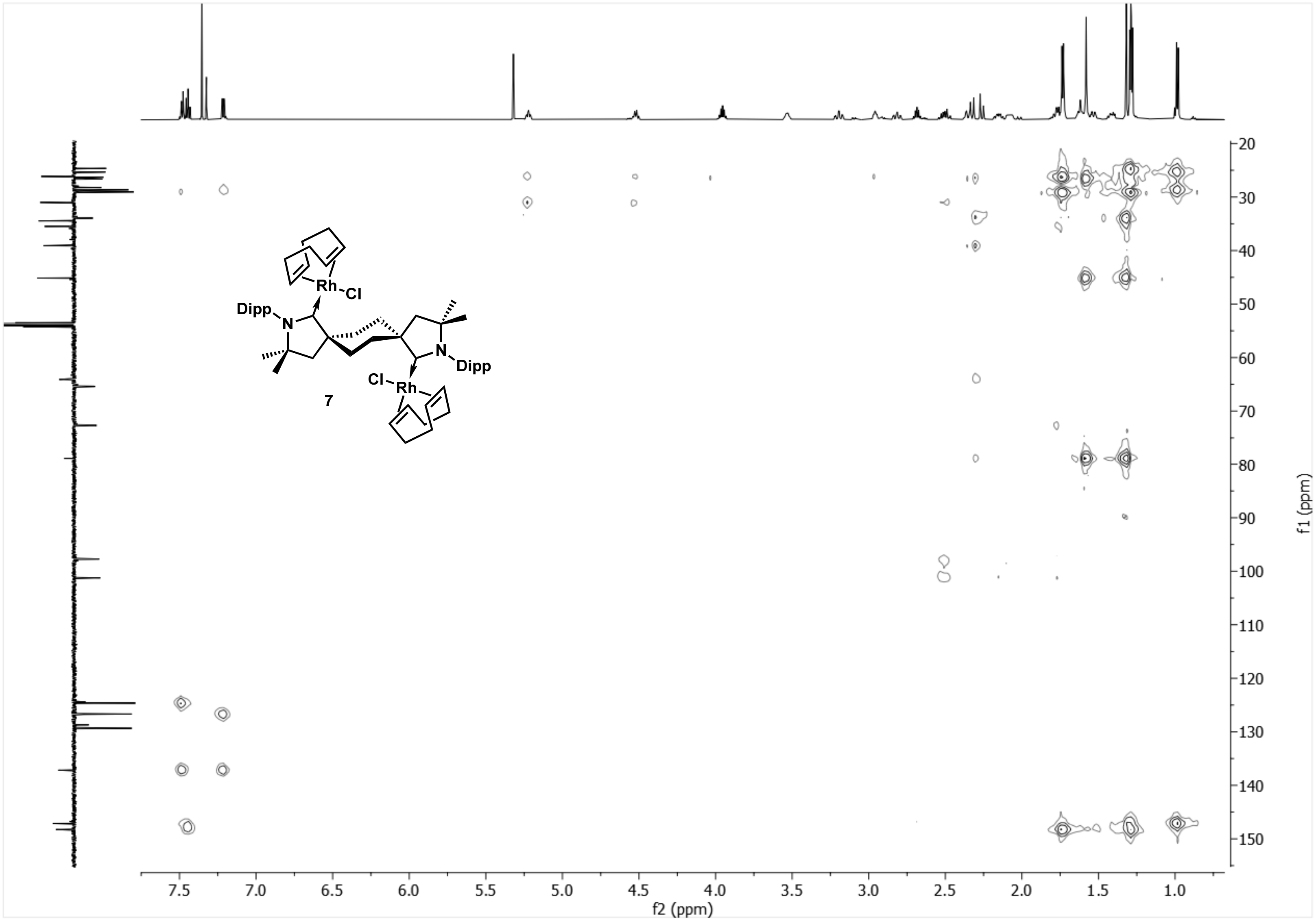


Figure S45. ^{1}H-^{13}C HMBC NMR spectrum of complex **7** (CD_2Cl_2, 25°C, 400 MHz).

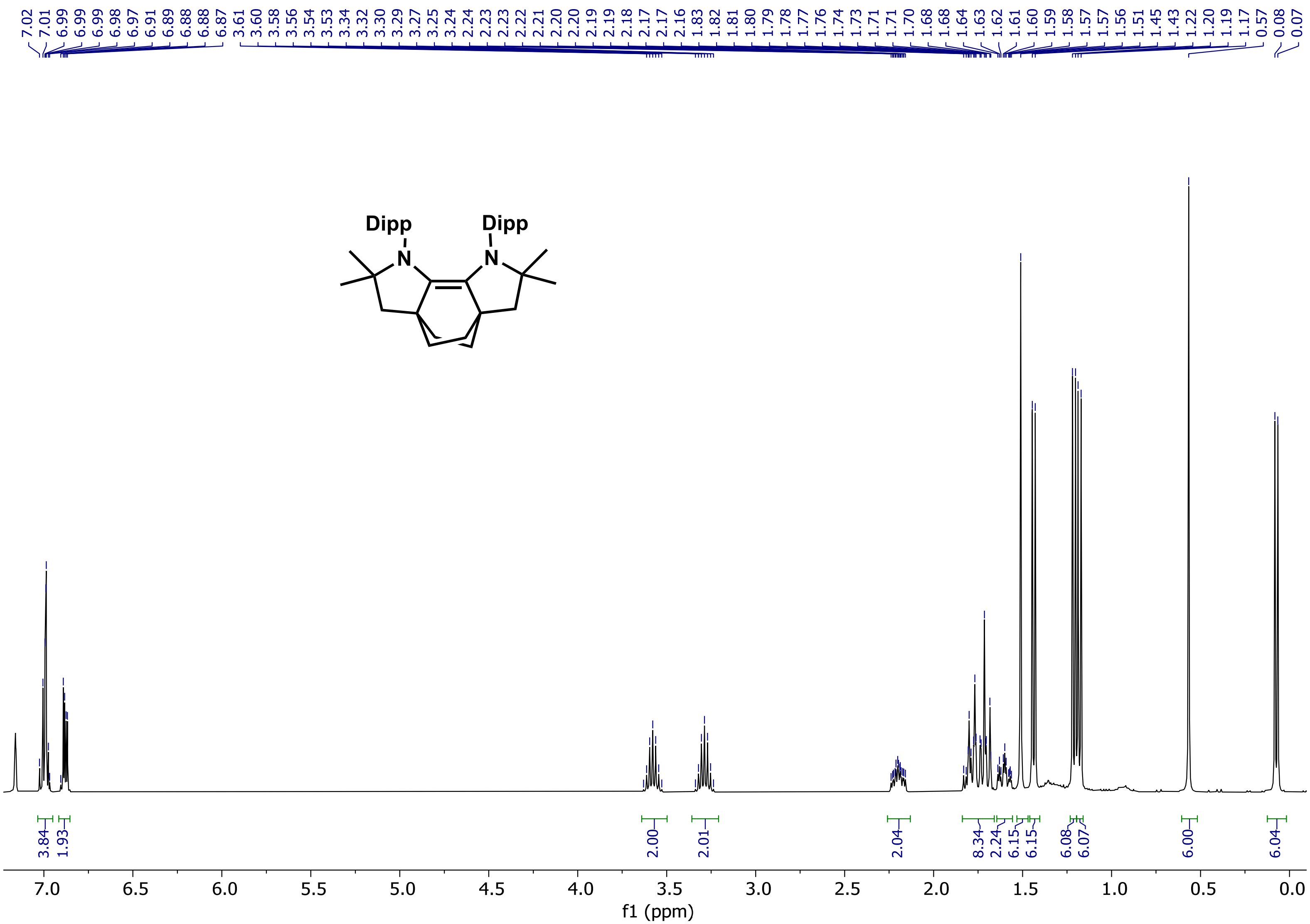


Figure S46. ^{1}H NMR spectrum of **8** (C_6D_6, 25°C, 400 MHz).

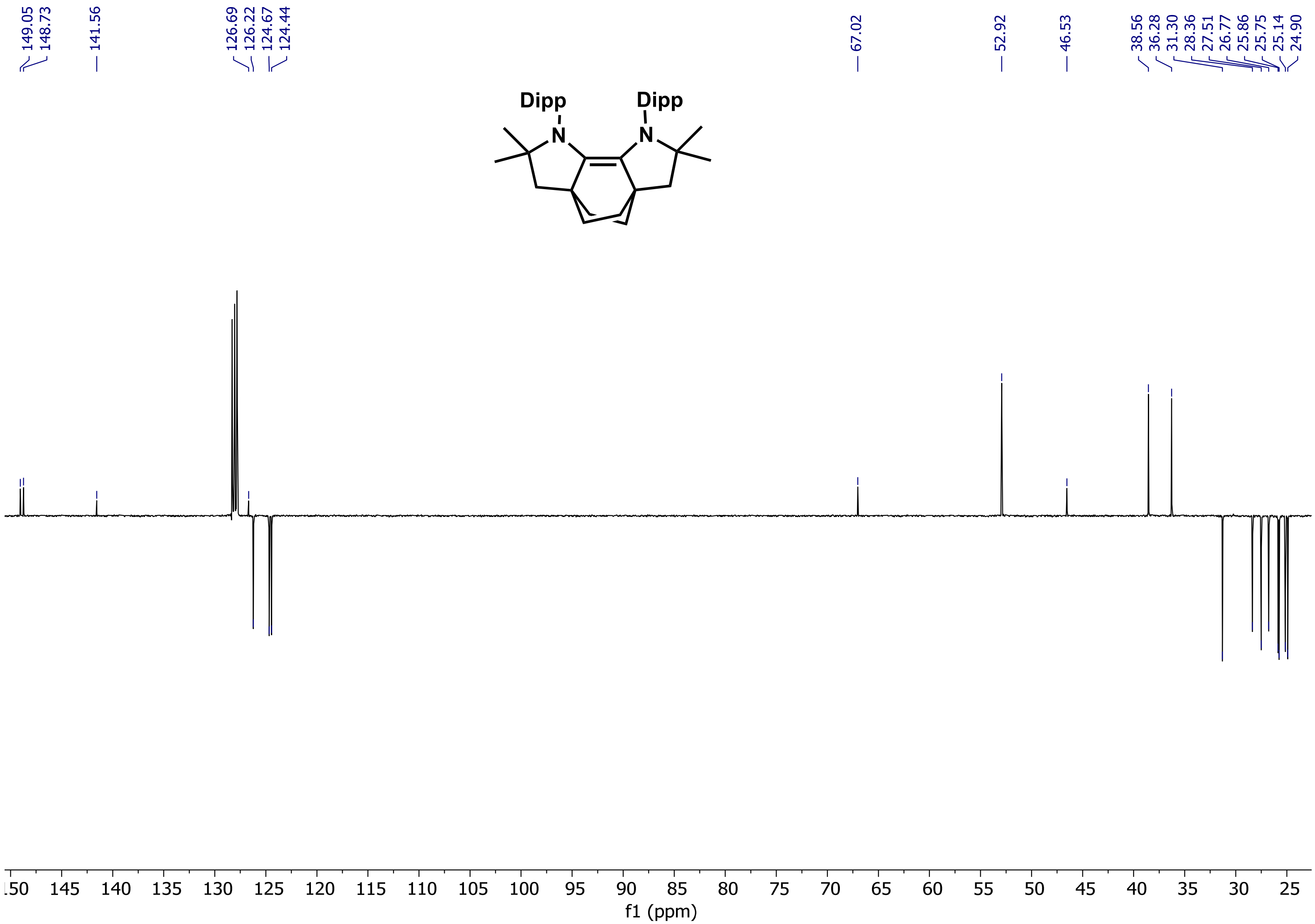


Figure S47. ^{13}C DEPTQ NMR spectrum of **8** (C_6D_6, 25°C, 101 MHz).

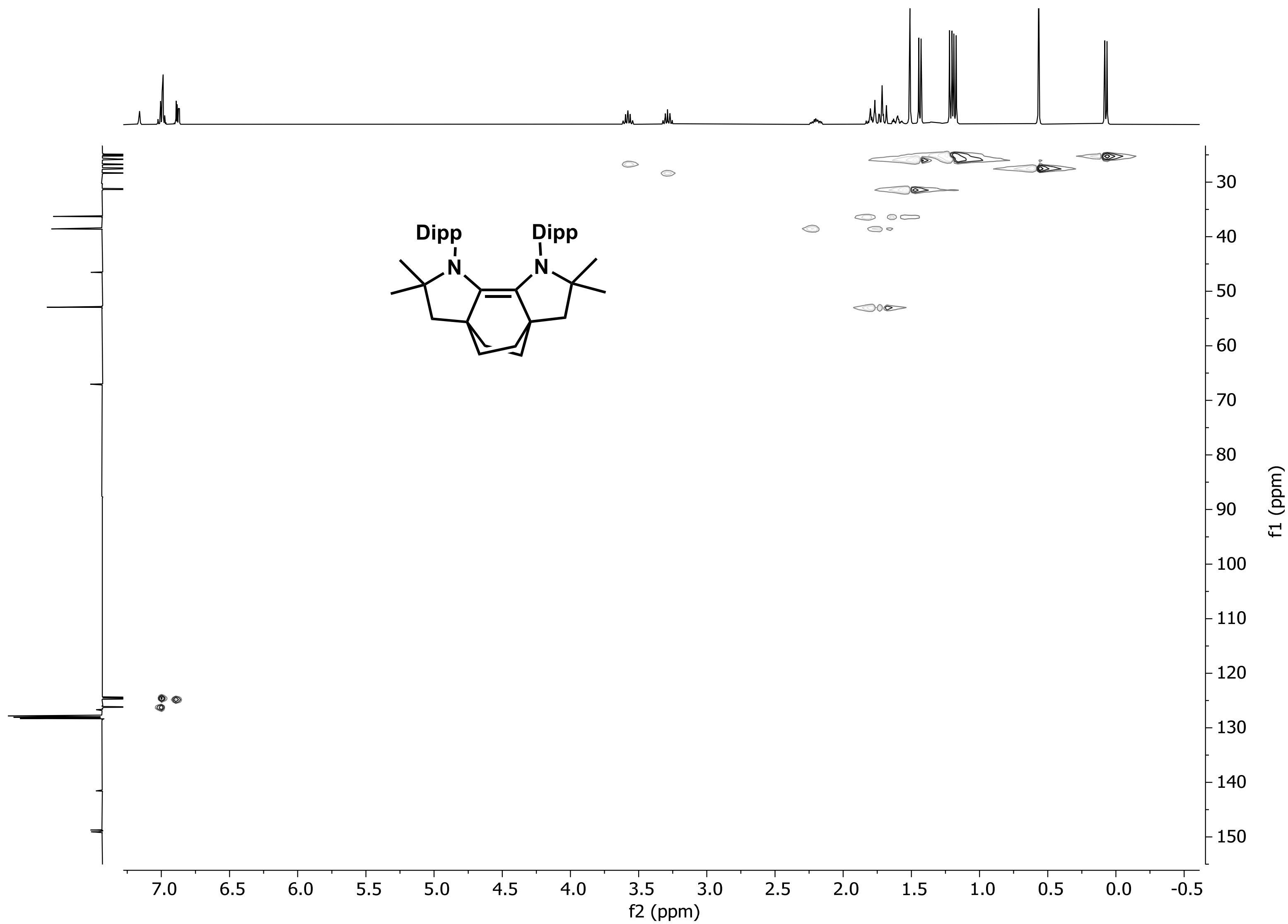


Figure S48. ^{1}H-^{13}C HSQC NMR spectrum of **8** (C_6D_6, 25°C, 400 MHz).

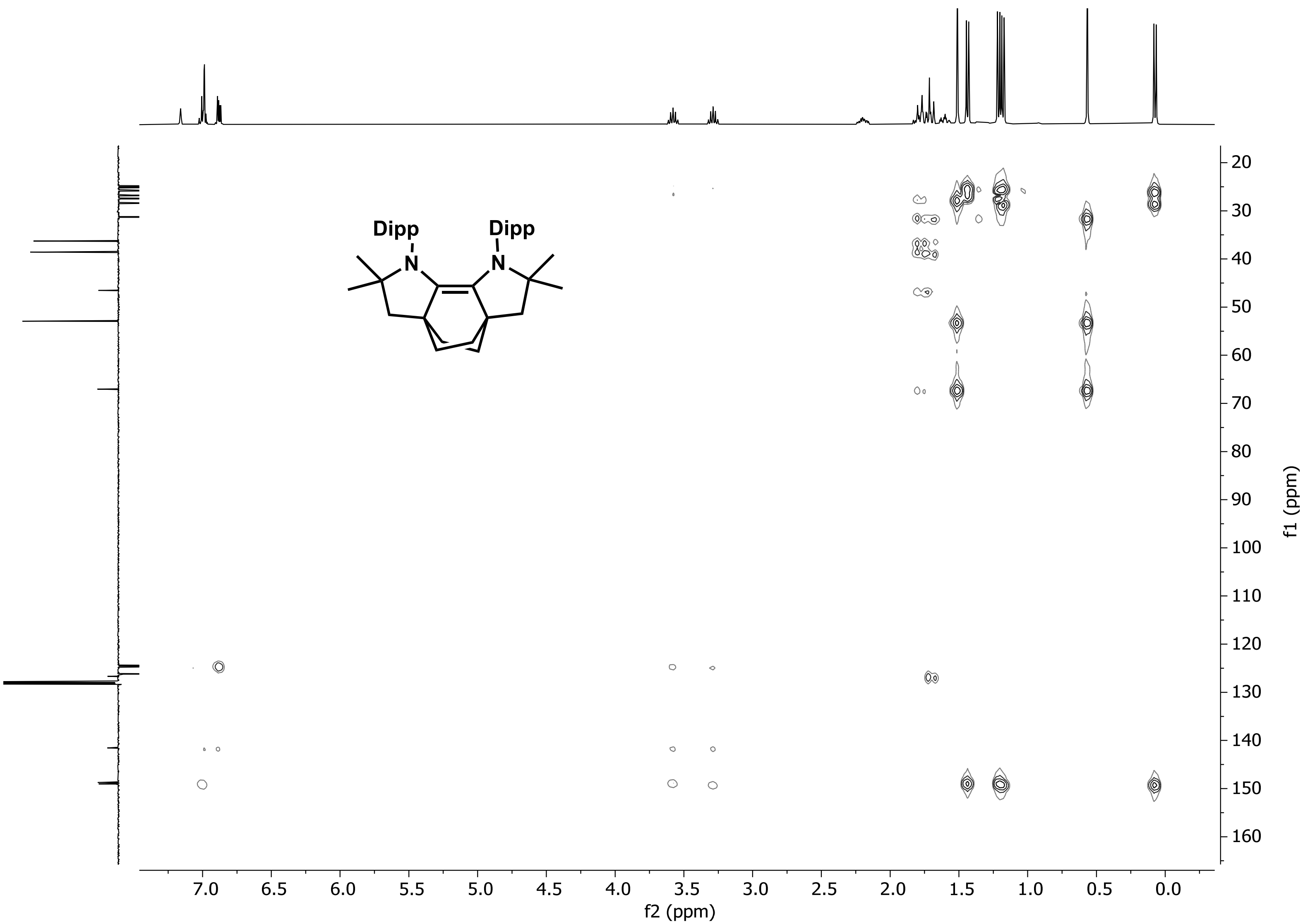


Figure S49. ^{1}H-^{13}C HMBC NMR spectrum of **8** (C_6D_6, 25°C, 400 MHz).

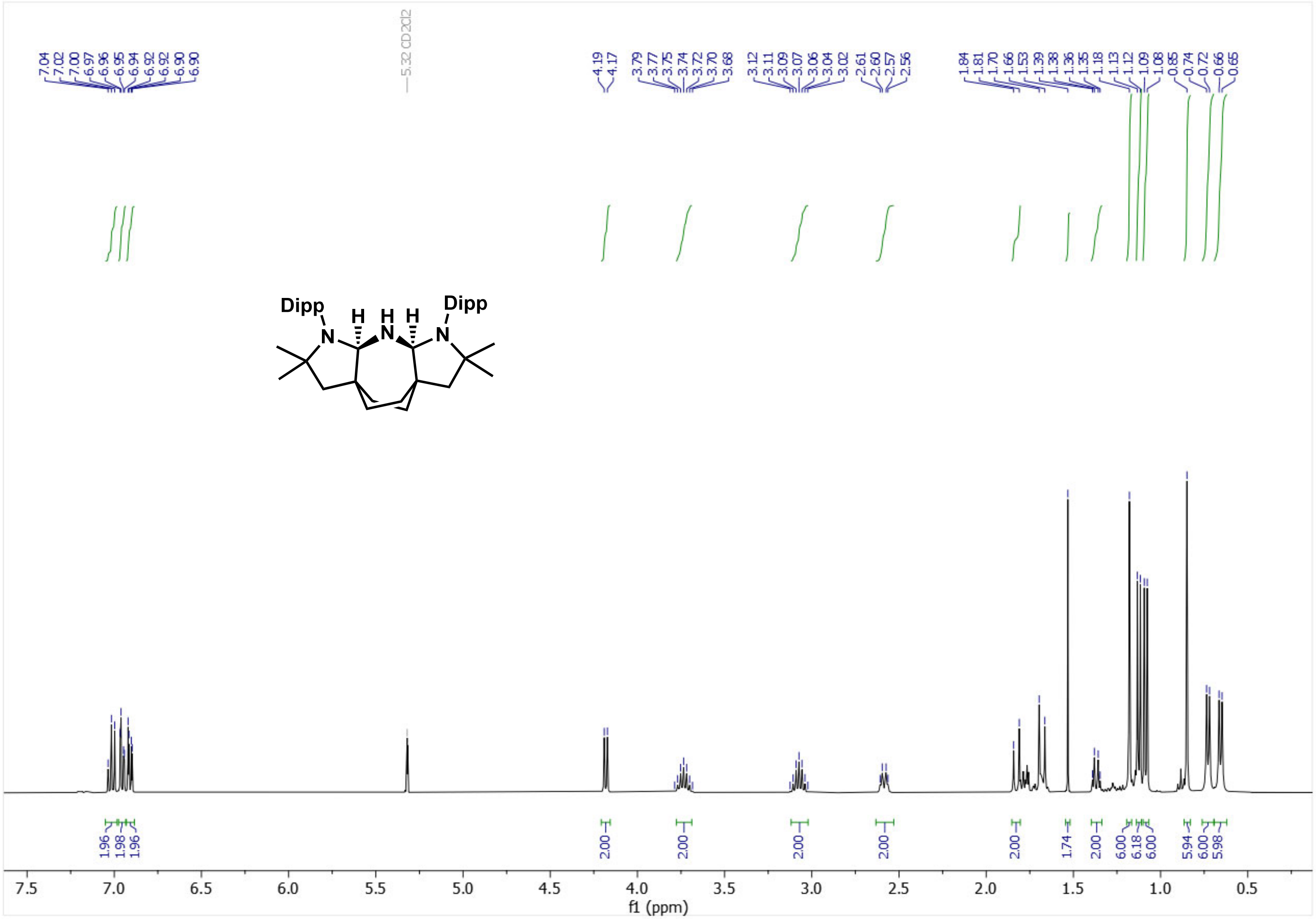


Figure S50. ^{1}H NMR spectrum of **10** (CD_2Cl_2, 25°C, 400 MHz).

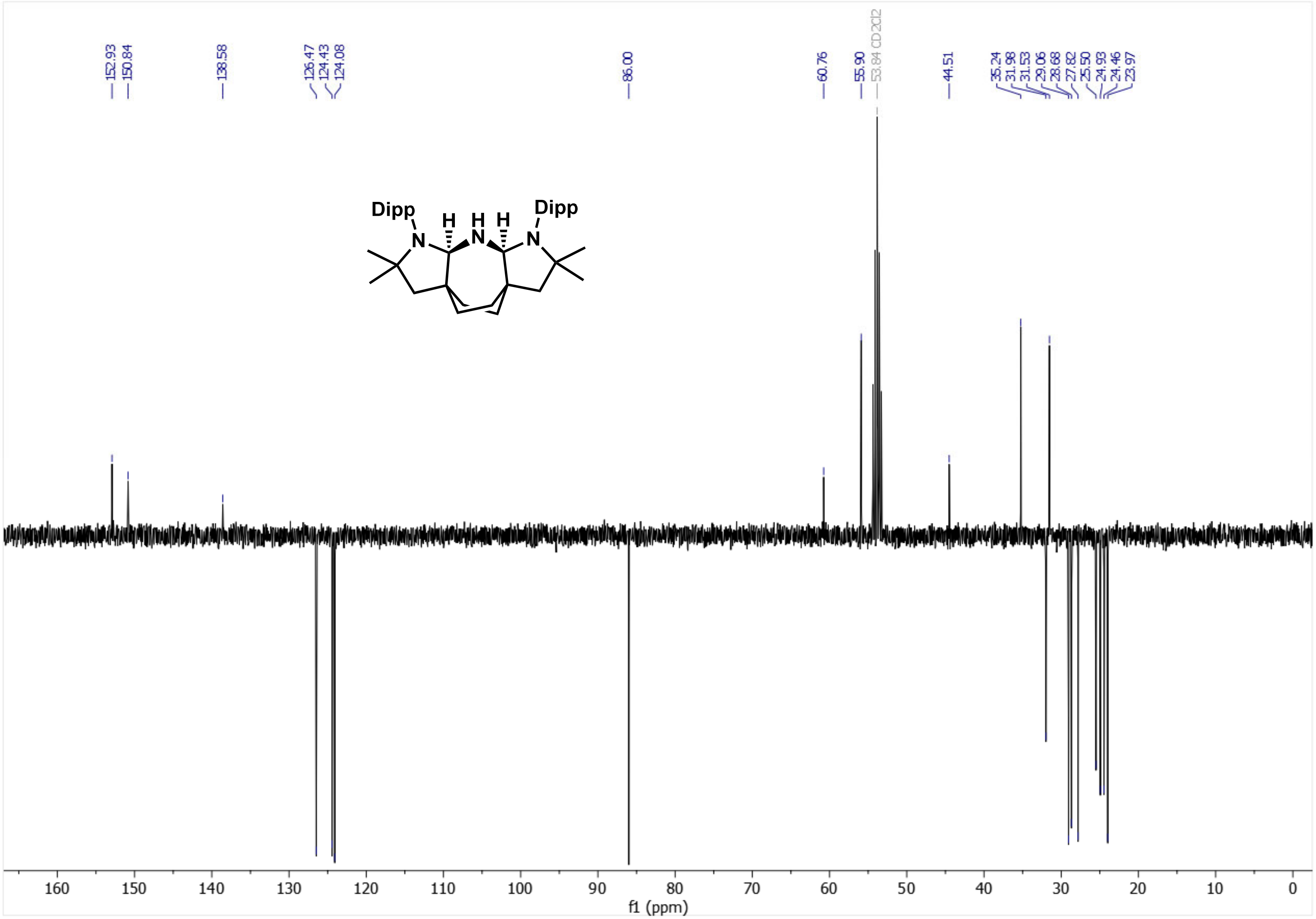


Figure S51. ^{13}C DEPTQ NMR spectrum of **10** (CD_2Cl_2, 25°C, 101 MHz).

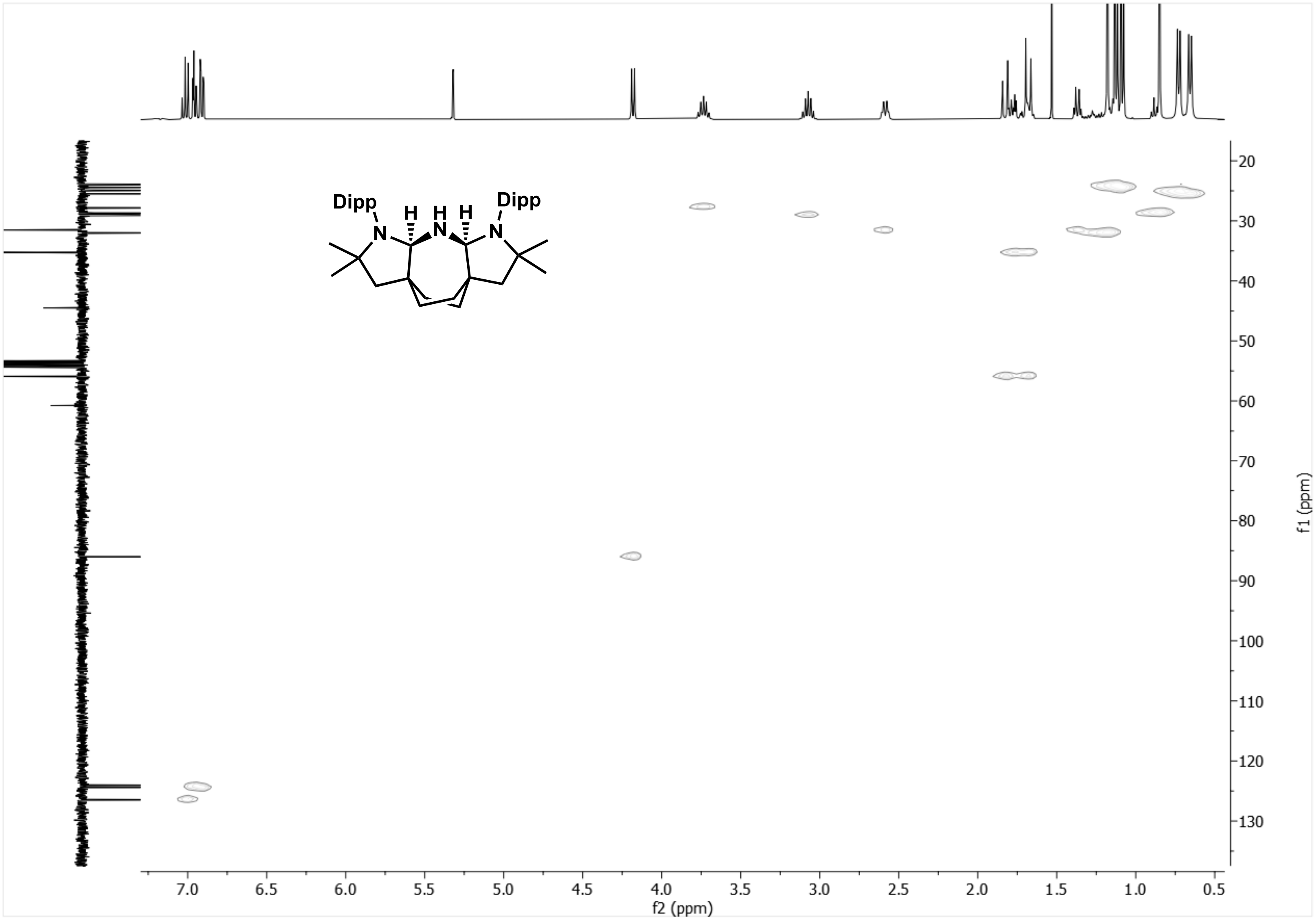


Figure S52. ^{1}H-^{13}C HSQC NMR spectrum of **10** (CD_2Cl_2, 25°C, 400 MHz).

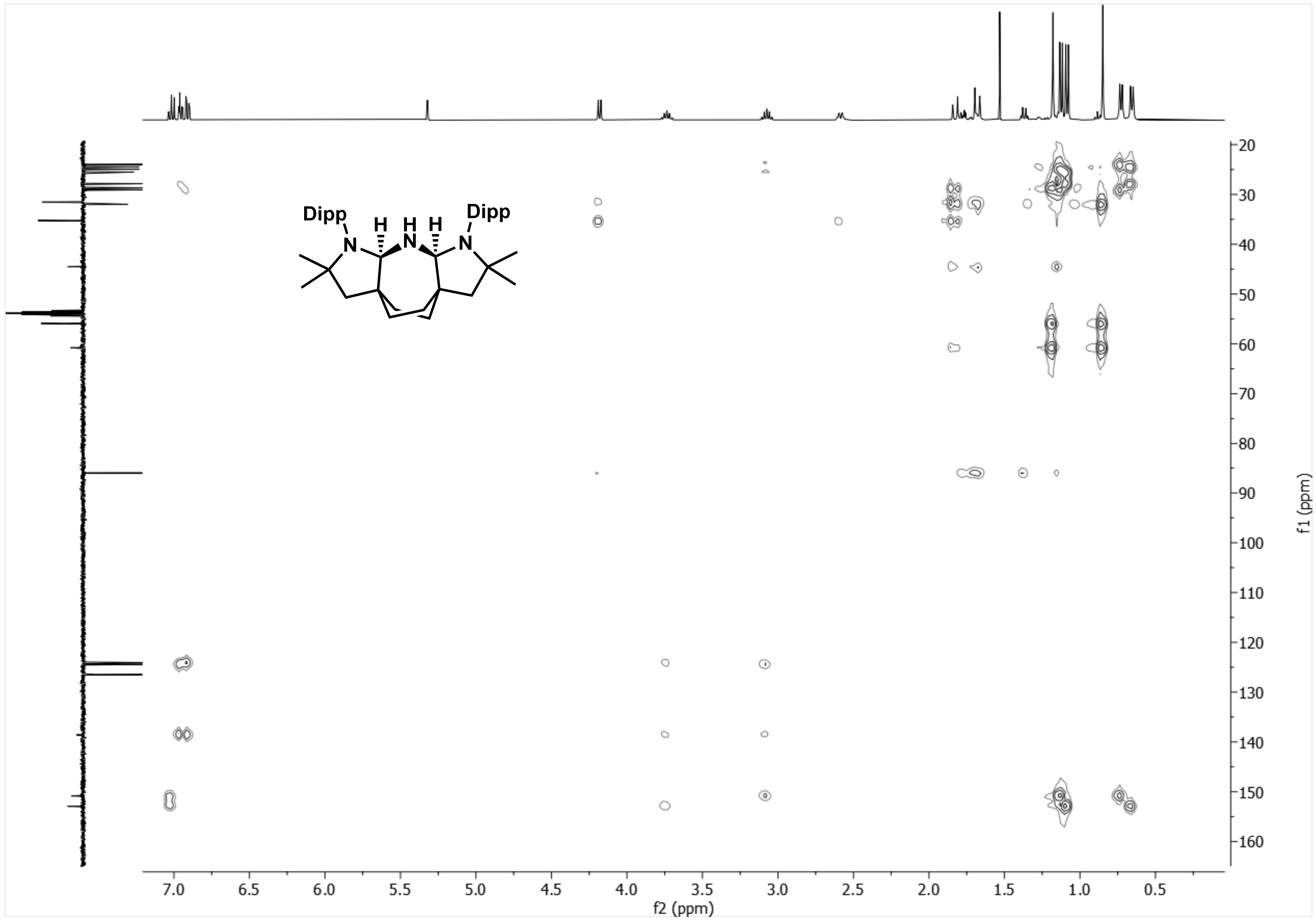


Figure S53. ^{1}H-^{13}C HMBC NMR spectrum of **10** (CD_2Cl_2, 25°C, 400 MHz).

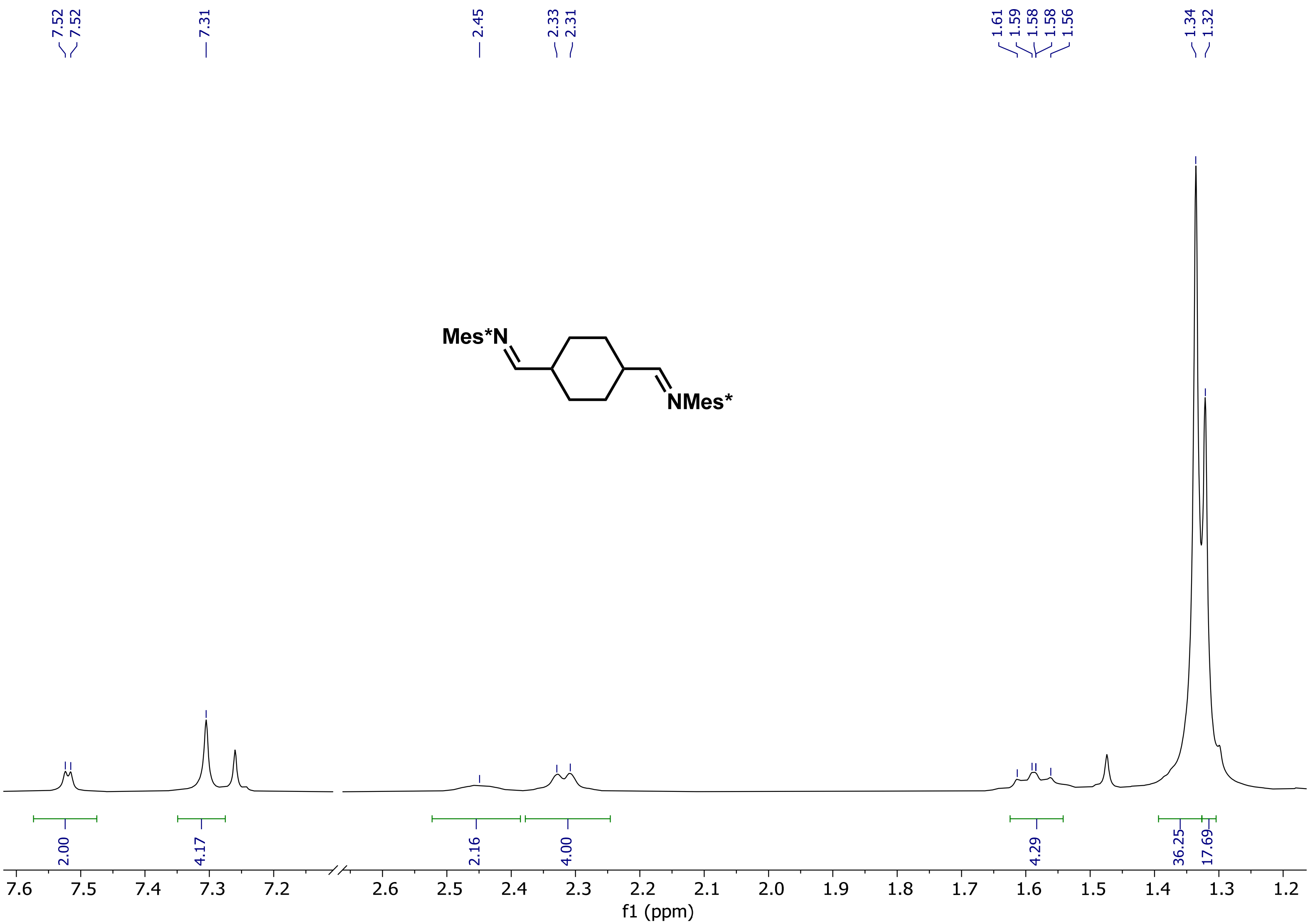


Figure S54. ^{1}H NMR spectrum of aldimine *trans*-**1c** ($CDCl_3$, 25°C, 400 MHz).

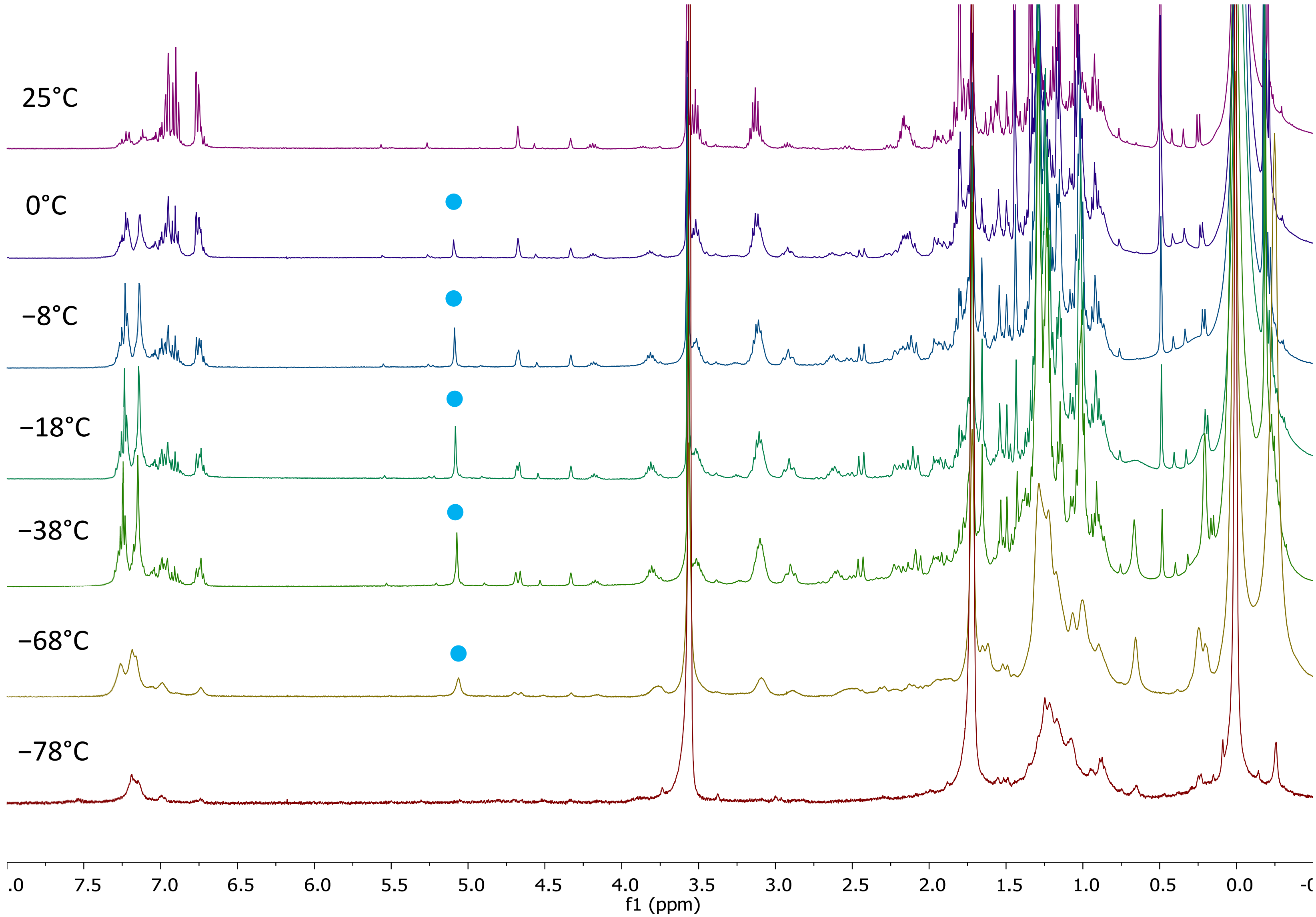


Figure S55. Variable temperature ^{1}H NMR spectra of the reaction between **4a** and 2 equivalents of KHMDS (THF-d_8, 400 MHz). The resonance corresponding to the trademark proton of the transient intermediate [(**8**)H]$^+$ is marked in blue.

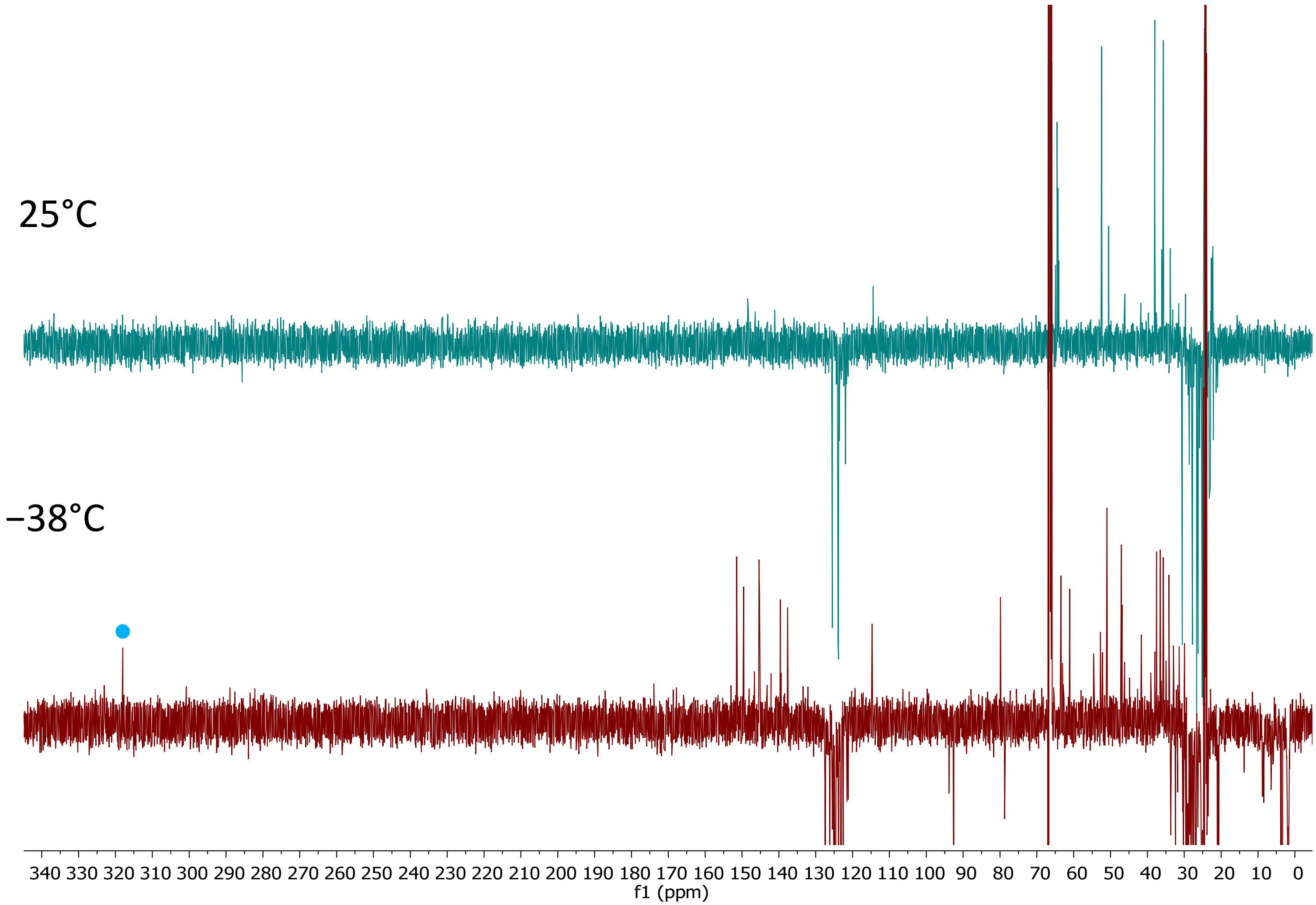


Figure S56. Variable temperature ^{13}C DEPTQ NMR spectrum of the reaction between **4a** and 2 equivalents of KHMDS (THF-d_8, 101 MHz).

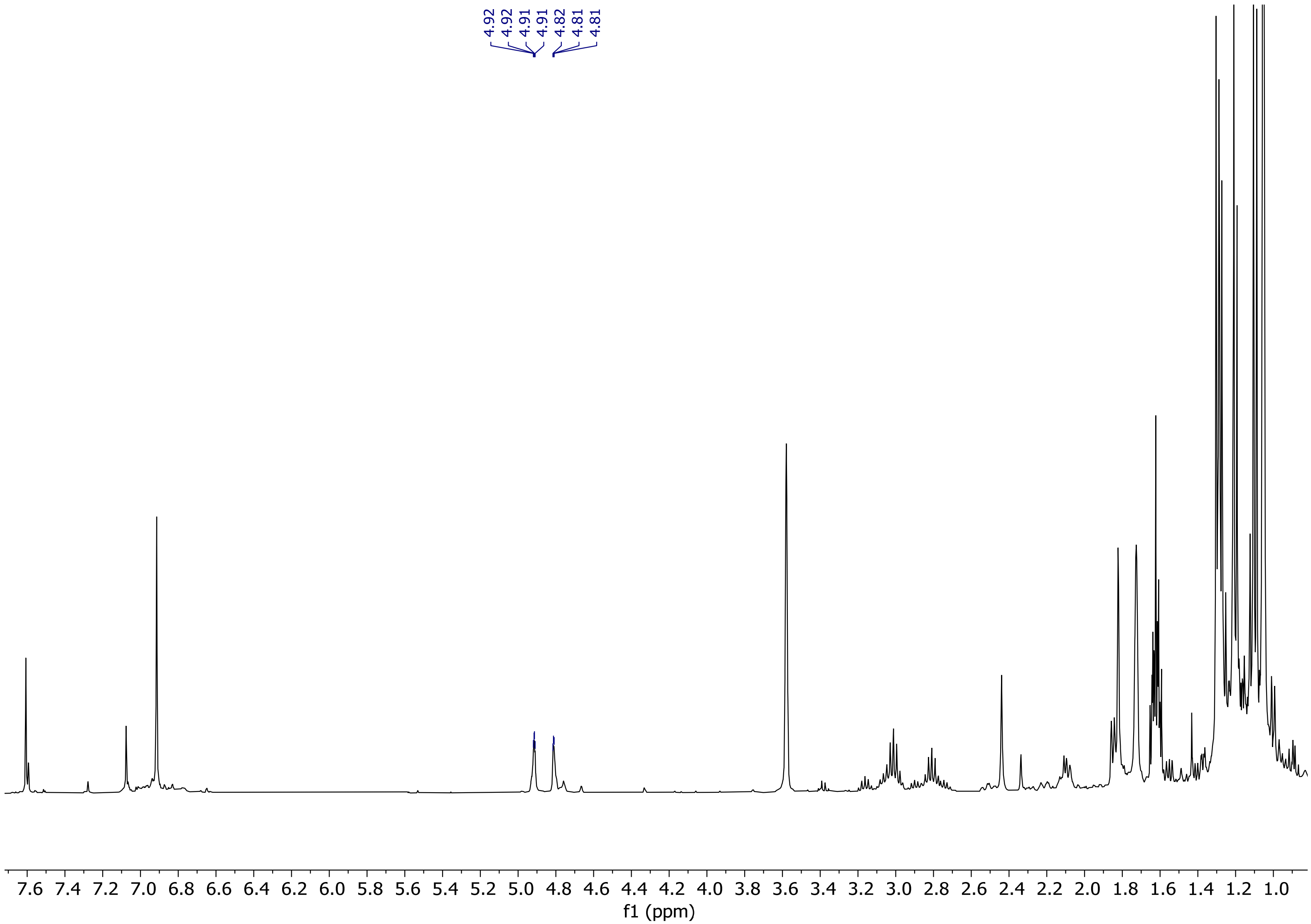


Figure S57. ^{1}H NMR of the reaction of **4a** with 2 equivalents of LiTMP (THF-d_8, 25°C, 400 MHz). Note the similarity of this spectrum to Figure S13, as deprotonation with LiTMP leads to reformation of *cis*-**2a**.

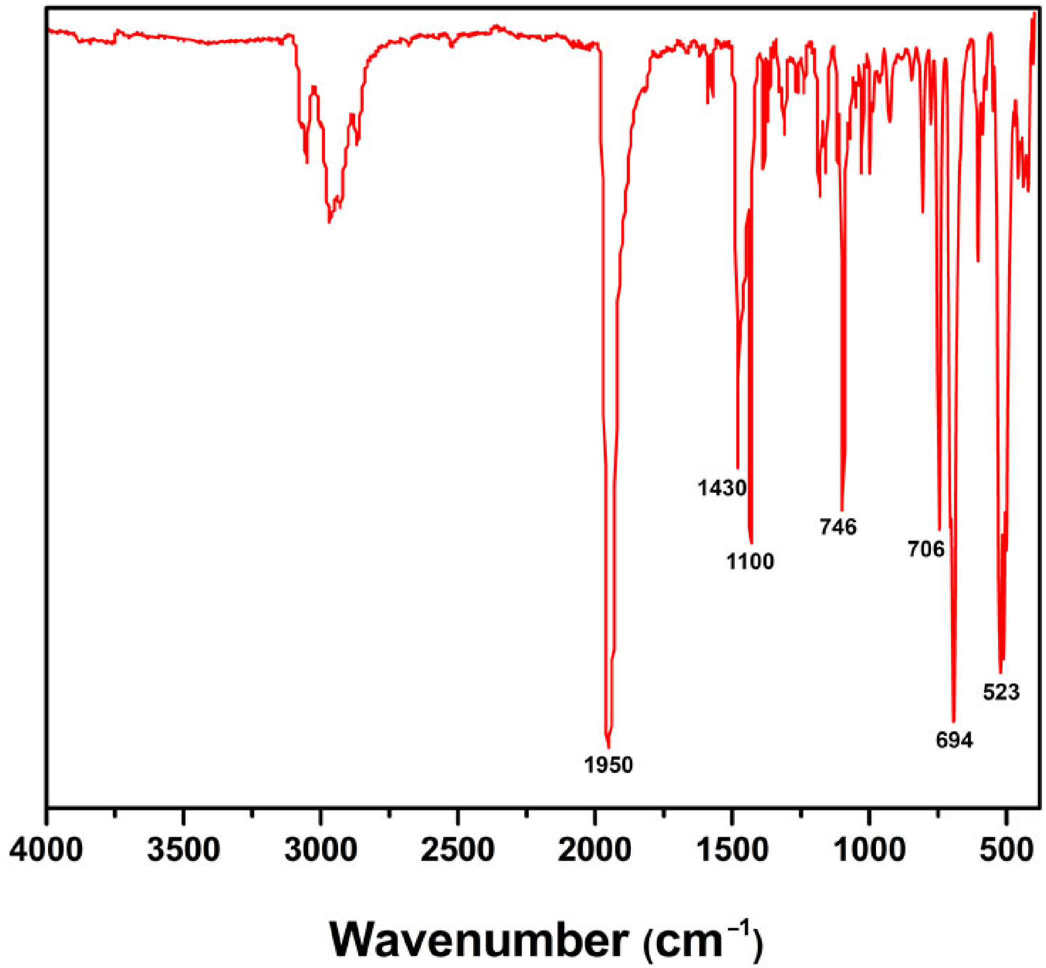


Figure S58. Infrared spectrum of **6** (KBr pellet).

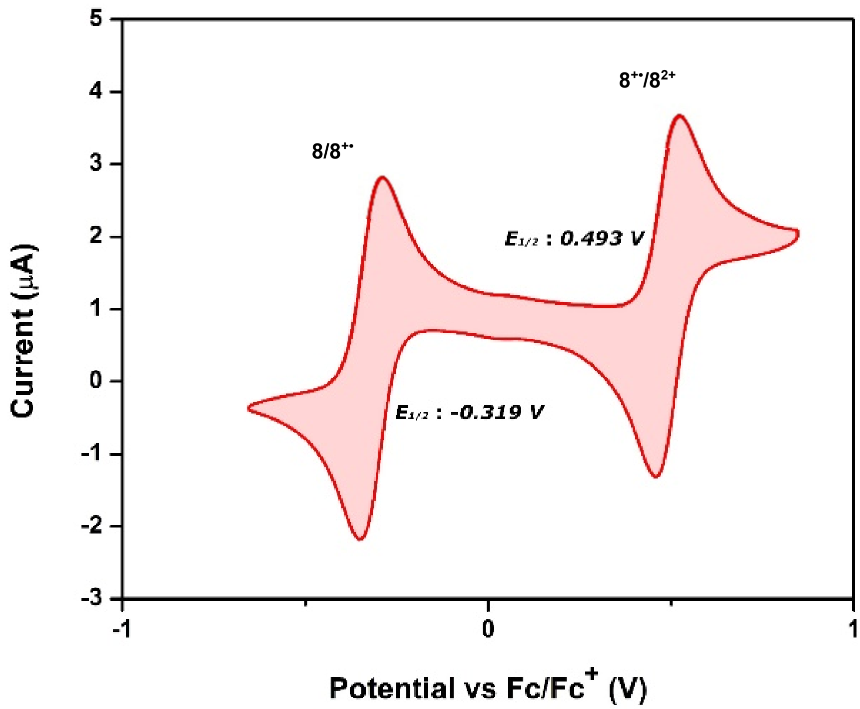


Figure S59. Cyclic voltammogram displaying two reversible redox events for compound **8** vs. Fc/Fc^+. Electrolyte 0.1 M $[nBu_4N][PF_6]$ in THF, GC working electrode, and 100 mV/s scan rate.

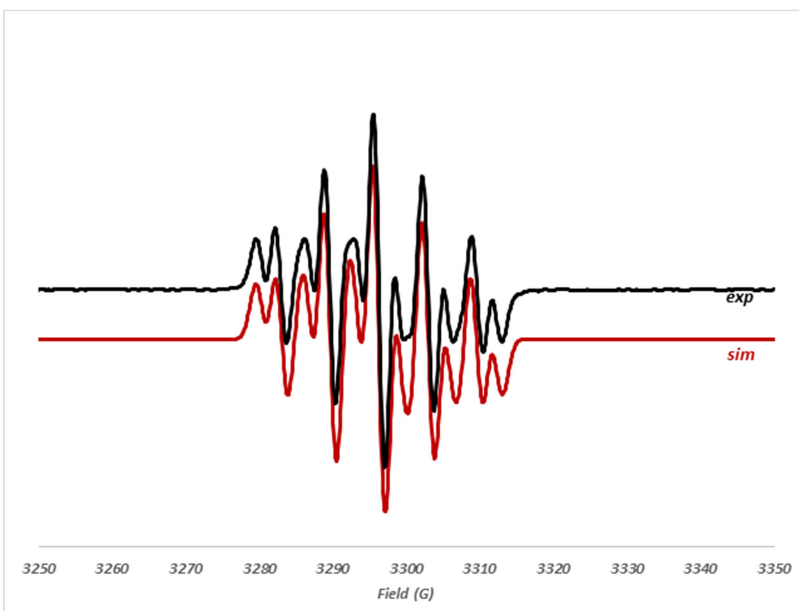


Figure S60. Experimental (black) and simulated (red) EPR spectra of **9**. The experimental spectrum was recorded in 2-MeTHF at 298K, using an X-band spectrometer operating at 9.34 GHz (g-value of 2.00459). Simulation parameters: $2 \times A_N = 6.63$ G, $2 \times A_H = 2.49$ G, and $2 \times A_H = 0.82$ G, line-width = 1.99 G, and line shape = 100% Gaussian. Calculated coupling constants: $2 \times A_N = 5.19$ G, $2 \times A_H = 2.23$ G (with two cyclohexane protons), and $2 \times A_H = 0.89$ G.

Crystallographic data

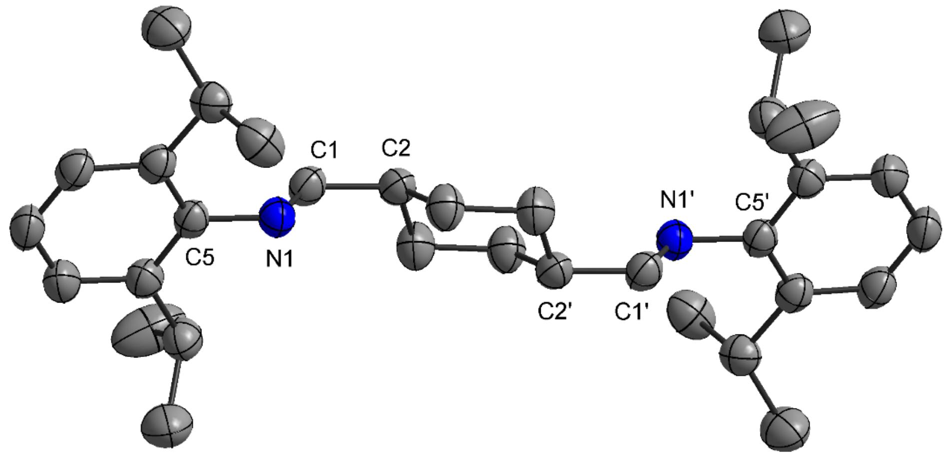


Figure S61. Solid state structure of *trans*-**1a** with thermal ellipsoids drawn at 50% probability and hydrogen atoms omitted for clarity. Select bond distances (Å) and angles (°): N1–C1 1.242(2), N1–C5 1.4261(19); C1–N1–C5 120.71(14).

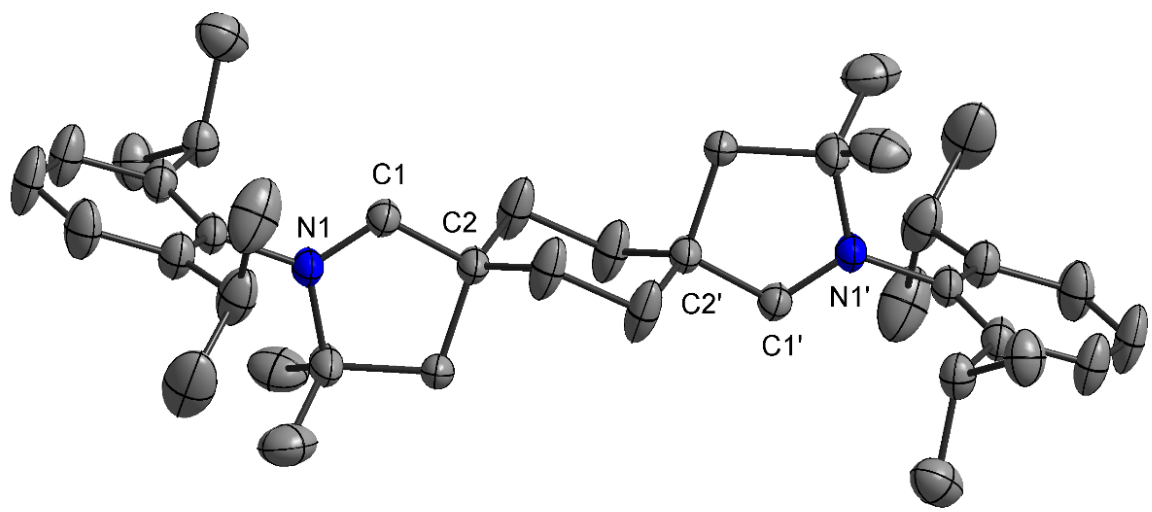


Figure S62. Solid state structure of the dication in **3a** with 50% probability ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–N1 1.272(4), C1–C2 1.491(4); N1–C1–C2 114.7(2).

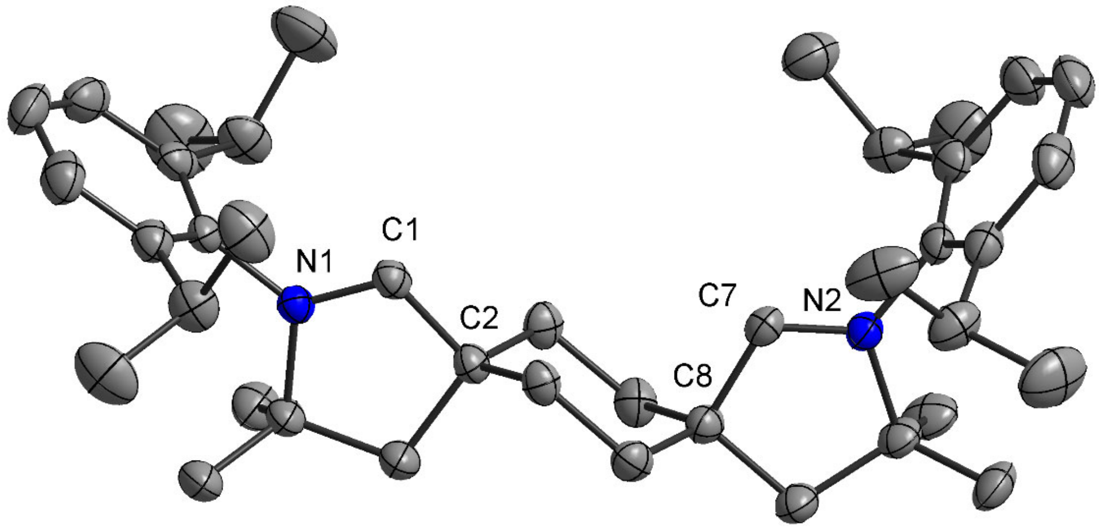


Figure S63. Solid state structure of the dication in **4a** with 50% probability ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–N1 1.275(2), C1–C2 1.482(3); N1–C1–C2 114.76(17).

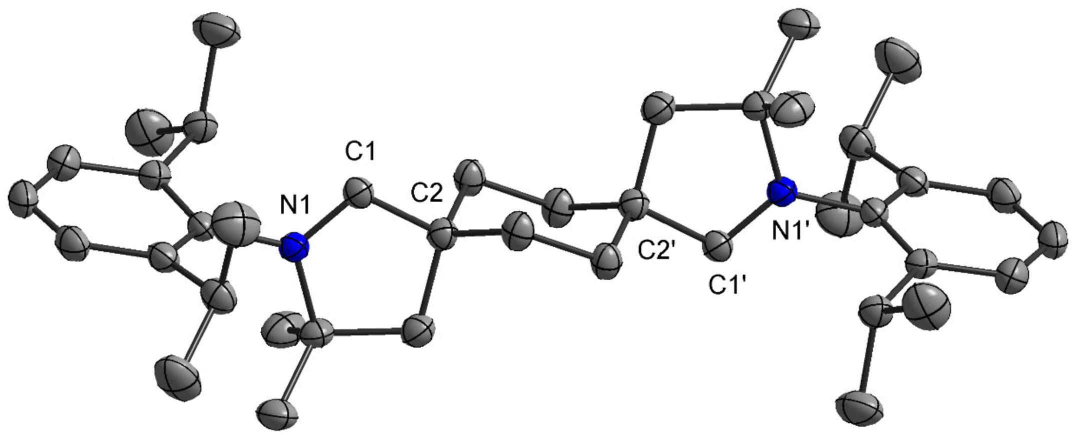


Figure S64. Solid state structure of **5** with 50% probability ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–C1 1.3065(16), C1–C2 1.5232(17); N1–C1–C2 105.92(10); sum of angles at N1 359.9(1).

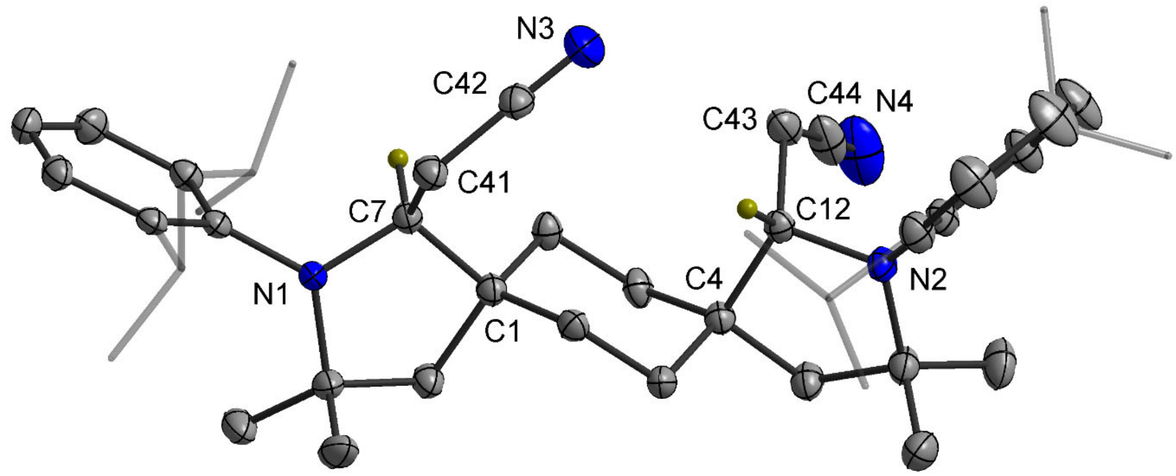


Figure S65. Solid state structure of **11** with 50% probability ellipsoids and the co-crystallized acetonitrile molecule and hydrogen atoms, except those on C7 and C12, omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–C7 1.4507(16), N2–C12 1.4587(16), C1–C7 1.5694(18), C4–C12 1.5598(18), C7–C41 1.5463(18), C12–C43 1.5523(18), C41–C42 1.466(2), C43–C44 1.466(2), C42–N3 1.1390(19), C44–N4 1.145(2); N1–C7–C41 110.50(11), N2–C12–C43 110.13(10), C41–C42–N3 179.32(16), C43–C44–N4 179.03(17), C7–C41–C42 112.59(12), C12–C43–C44 115.13(13), N1–C7–C41 110.50(11), C1–C7–C41 116.14(10), N2–C12–C43 110.13(10), C4–C12–C43 116.30(11); sum of angles about N1 356.39(10), sum of angles about N2 358.10(11).

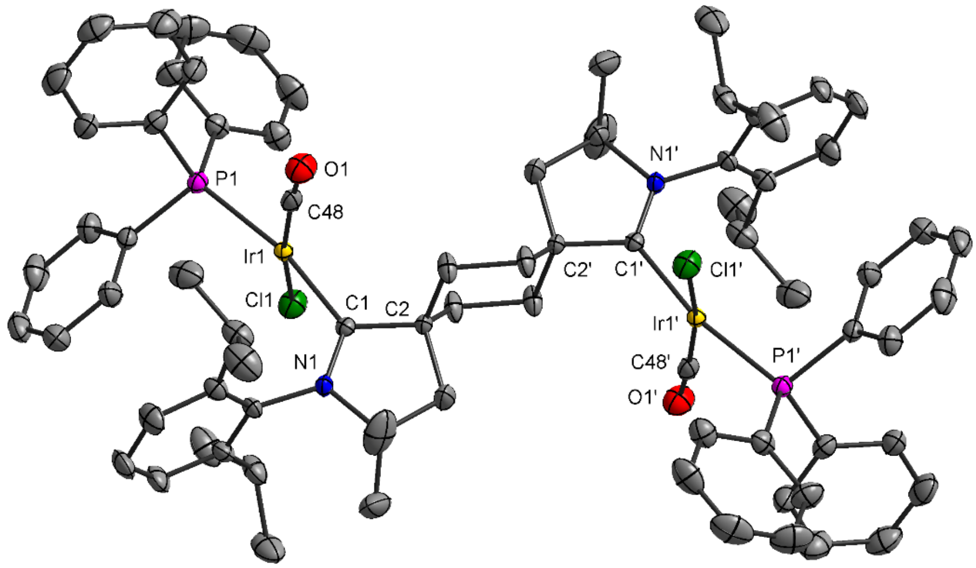


Figure S66. Solid state structure of **6** with 50% probability ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ir1–C1 2.035(3), Ir1–P1 2.3111(8), Ir1–Cl1 2.3681(8), Ir1–C48 1.835(3), O1–C48 1.100(3), N1–C1 1.313(3); C1–Ir1–P1 168.68(7), C48–Ir1–Cl1 168.69(9), C1–Ir1–Cl1 87.63(7), C1–Ir1–C48 92.19(11), P1–Ir1–Cl1 87.98(3), P1–Ir1–C48 94.15(9), N1–C1–C2 109.3(2), N1–C1–Ir1 125.35(18), C2–C1–Ir1 125.33(17), $Ir1_{plane}/C1_{plane}$ 89.54(6); τ_4' = 0.158.[8]

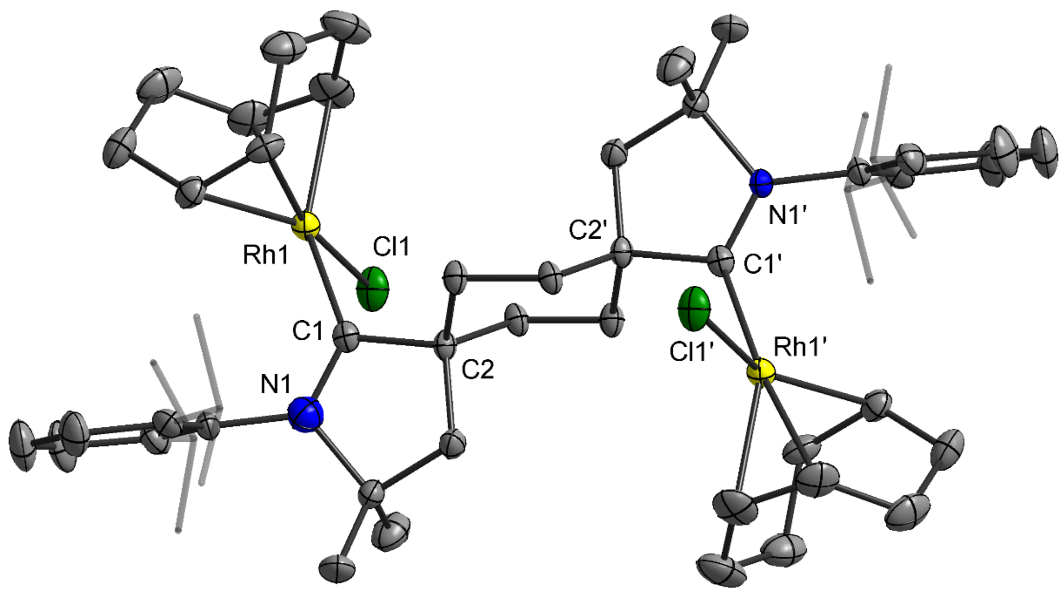


Figure S67. Solid state structure of **7** with 50% probability ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh1–C1 2.008(3), Rh1–Cl1 2.3983(8), Rh1–C_{COD} 2.100(3)–2.225(3), N1–C1 1.317(3), C1–C2 1.541(4); N1–C1–C2 108.0(2), C1–Rh1–Cl1 87.65(8), N1–C1–Rh1 131.5(2), C2–C1–Rh1 120.06(18), $Rh1_{plane}/C1_{plane}$ 74.21(5).

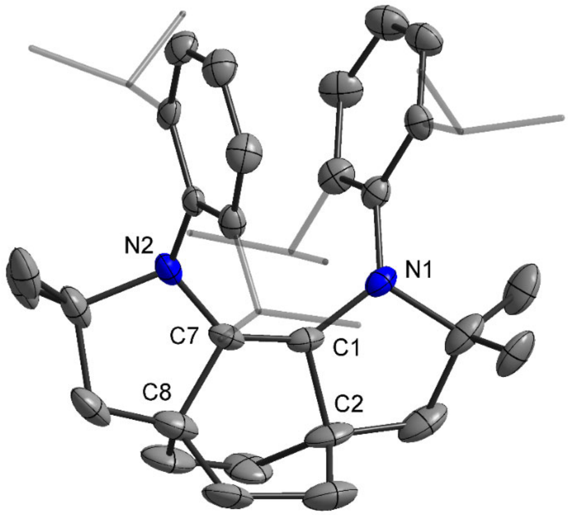


Figure S68. Solid state structure of **8** with 25% probability ellipsoids and hydrogen atoms omitted for clarity. It featured whole-molecule disorder across special positions (mirror planes). Selected bond lengths [Å] and angles [°]: C1–C7 1.332(7), C1–N1 1.443(7), C7–N2 1.435(7), C1–C2 1.541(8), C7–C8 1.542(8); N1–C1–C2 110.3(5), N2–C7–C8 107.7(5), N1–C1–C7 137.7(5), C1–C7–N2 136.6(5), C2–C1–C7 111.3(6), C1–C7–C8 115.3(6); $C1_{plane}/C7_{plane}$ 5.9(3), sum of angles at N1 351.5(4), sum of angles at N2 351.9(4), sum of angles at C1 359.3(4), sum of angles at C7 359.8(5).

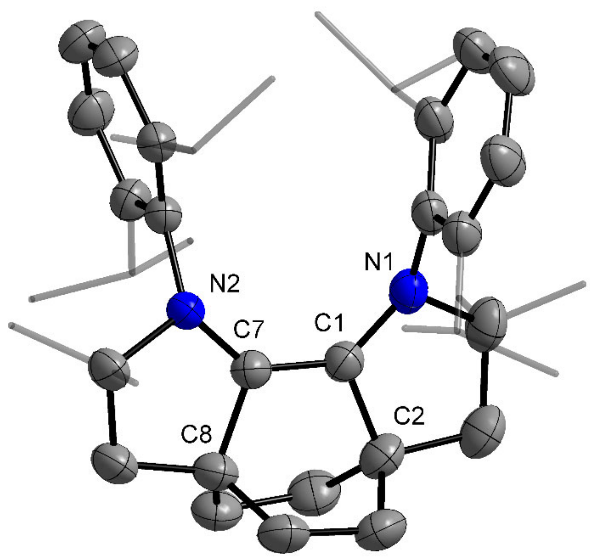


Figure S69. Solid state structure of the cation in **9** with 50% probability ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–C7 1.409(3), C1–N1 1.357(3), C7–N2 1.360(3), C1–C2 1.534(3), C7–C8 1.528(3); N1–C1–C2 111.19(18), N2–C7–C8 111.03(18), N1–C1–C7 136.7(2), C1–C7–N2 136.61(19), C2–C1–C7 112.10(18), C1–C7–C8 112.32(18); $C1_{plane}/C7_{plane}$ 2.6(1), sum of angles at N1 356.1(2), sum of angles at N2 355.9(2), sum of angles at C1 360.0(2), sum of angles at C7 360.0(2).

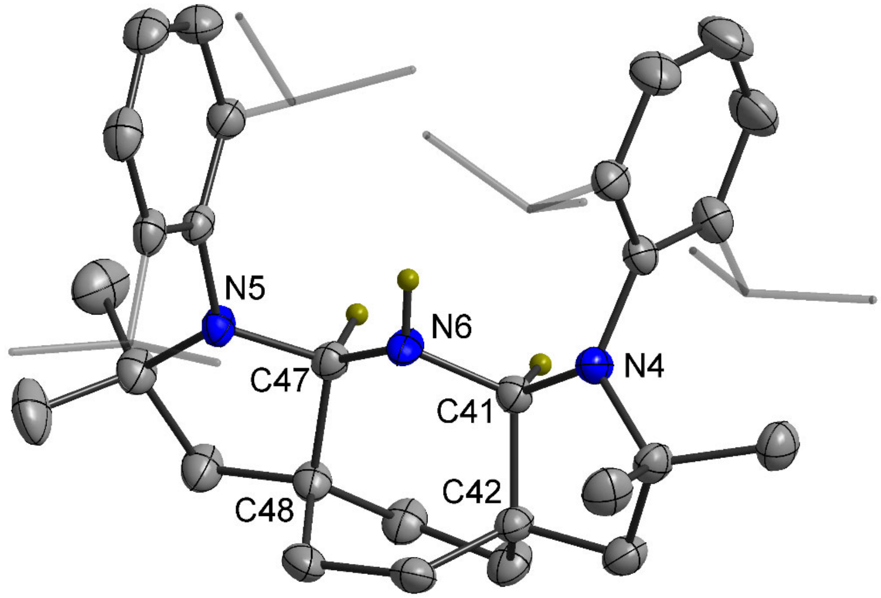


Figure S70. Structure of one of the two independent molecules of **10** in the solid state, with thermal ellipsoids at 50% probability and hydrogen atoms except those on C41, C47 and N6 omitted for clarity. Selected bond lengths [Å] and angles [°]: N6–C41 1.461(3), N6–C47 1.448(3), N4–C41 1.446(3), N5–C47 1.453(3); C41–N6–C47 111.01(18), sum of angles about N4 355.19(19), sum of angles about N5 353.52(18).

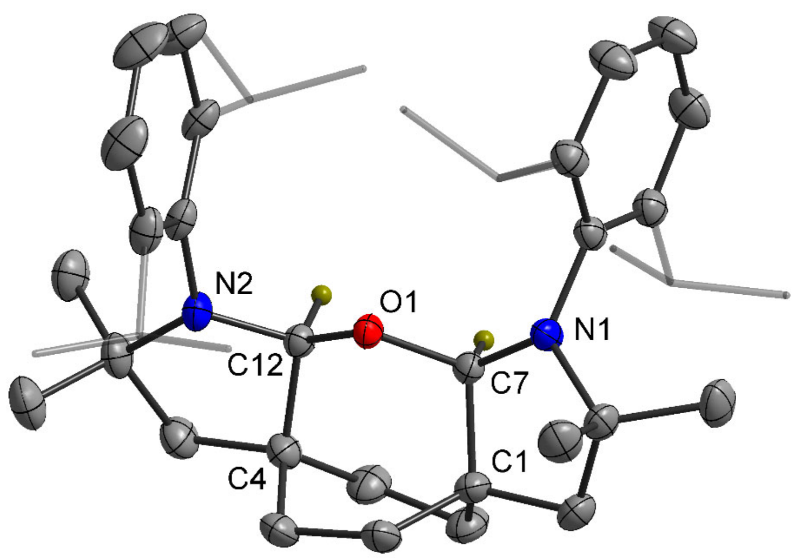


Figure S71. Solid state structure of **12** with thermal ellipsoids at 50% probability and hydrogen atoms except those on C7 and C12 omitted for clarity Selected bond lengths [Å] and angles [°]: O1–C7 1.4453(17), O1–C12 1.4194(16), N1–C7 1.4221(18), N2–C12 1.4402(18), C4–C12 1.540(2), C1–C7 1.552(2); C7–O1–C12 108.22(10), N2–C12–C4 103.64(12), N1–C7–C1 107.14(11), sum of angles at N1 355.88(12), sum of angles at N2 354.51(12).

Table S1. Summary of crystallographic data for compounds *trans*-**1a**, **3a**, **4a**, **5** and **6**.

	trans-**1a**	**3a**	**4a**	**5**	**6**
CCDC Deposition #	2131007	2131008	2131009	2131010	2131011
Formula	$C_{32}H_{46}N_2$	$C_{40}H_{60}B_2F_8N_2$	$C_{41}H_{62}B_2Cl_2F_8N_2$	$C_{40}H_{58}N_2$	$C_{96}H_{106}Cl_2Ir_2N_2O_2P_2$
Formula weight	458.71	742.52	827.44	566.88	1837.06
Crystal system	Orthorhombic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P b c a	P-1	P-1	P 2_1/n	P 2_1/c
a (Å)	7.8016(2)	11.0116(3)	9.5425(8)	9.2714(14)	19.478(2)
b (Å)	17.7157(4)	14.7548(4)	10.9809(9)	12.6303(19)	12.9125(16)
c (Å)	20.7203(4)	15.4039(4)	22.1072(19)	15.352(2)	18.832(2)
α (°)	90	101.896(2)	102.6880(10)	90	90
β (°)	90	110.7630(10)	91.3310(10)	99.001(2)	117.1090(10)
γ (°)	90	111.6370(10)	94.5830(10)	90	90
Volume (Å^3)	2863.77(11)	2005.29(10)	2250.7(3)	1775.6(5)	4216.1(9)
Z	4	2	2	2	2
Temperature (K)	173.15	173.15	173.15	173.15	173.15
λ (Å)	1.54178	1.54178	0.71073	0.71073	0.71073
$\rho_{calc.}$ (gcm^{-3})	1.064	1.230	1.221	1.060	1.447
F(000)	1008.0	792.0	876.0	624.0	1860.0
R(int)	0.0313	0.0324	0.0388	0.0402	0.0617
μ (mm^{-1})	0.454	0.803	0.207	0.060	3.304
θ range (°)	8.534−136.766	6.656−140.118	3.78−54.908	4.198−55.028	3.932−56.562
Total data	18261	30428	41966	25587	98144
Unique	2631	7319	10286	4076	10460
Completeness (%)	100	96.3	99.8	100	100
Parameters	169	621	657	196	484
R (>2σ)	0.0544	0.0839	0.0546	0.0451	0.0244
R_w (all data)	0.1683	0.2092	0.1497	0.1184	0.0538
GOF	1.065	1.086	1.032	1.018	1.022

Table S2. Summary of crystallographic data for compounds **7**, **8**, **9**, **10**, **11** and **12**.

	7	**8**	**9**	**10**	**11**	**12**
CCDC Deposition #	2131012	2131013	2131014	2131015	2131016	2131017
Formula	$C_{56}H_{82}Cl_2N_2Rh_2$	$C_{40}H_{58}N_2$	$C_{40}H_{58}BF_4N_2$	$C_{40}H_{61}N_3$	$C_{90}H_{131}N_9$	$C_{40}H_{60}N_2O$
Formula weight	1059.95	566.88	653.69	583.91	1339.03	584.90
Crystal system	Triclinic	Orthorhombic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	P-1	P n m a	P 2_1/n	P-1	P-1	P 2_1/c
a (Å)	10.0958(7)	21.3426(7)	10.1982(2)	9.9563(10)	10.1013(11)	11.5644(14)
b (Å)	10.4702(8)	13.8099(5)	22.5087(5)	16.8762(17)	14.1448(16)	18.697(2)
c (Å)	13.2620(10)	11.6460(3)	17.5373(4)	22.908(2)	14.8032(17)	16.3994(19)
α (°)	70.5240(10)	90	90	108.7680(10)	96.8960(10)	90
β (°)	86.6190(10)	90	100.0210(10)	96.6350(10)	101.8520(10)	95.825(2)
γ (°)	83.2740(10)	90	90	99.3050(10)	100.5620(10)	90
Volume (Å^3)	1312.25(17)	3432.53(19)	3964.24(15)	3538.2(6)	2007.4(4)	3527.5(7)
Z	1	4	4	4	1	4
Temperature (K)	173.15	173.15	173.15	173.15	173.15	173.15
λ (Å)	0.71073	1.54178	1.54178	0.71073	0.71073	0.71073
$\rho_{calc.}$ (gcm^{-3})	1.341	1.097	1.095	1.096	1.108	1.101
F(000)	556.0	1248.0	1412.0	1288.0	734.0	1288.0
R(int)	0.0391	0.0277	0.0479	0.0653	0.0411	0.0683
μ (mm^{-1})	0.767	0.464	0.607	0.063	0.064	0.065
θ range (°)	3.258−54.992	8.286−133.176	6.45−136.844	1.908−55.074	2.85−56.678	3.314−55.042
Total data	16096	11119	52065	65921	31614	45584
Unique	5994	3161	7268	16272	9983	8120
Completeness (%)	99.6	99.8	99.7	99.9	99.7	99.9
Parameters	286	391	436	889	473	400
R (>2σ)	0.0391	0.0867	0.0661	0.0755	0.0493	0.0490
R_w (all data)	0.0929	0.2676	0.1887	0.2041	0.1237	0.1233
GOF	1.030	1.047	1.029	1.024	1.028	1.022

Computational Details

Geometries of all studied systems were optimized in the gas phase with dispersion corrected density functional theory, namely the PBE1PBE functional,[9] def2-TZVP basis set,[10] and Grimme's D3 correction with Becke-Johnson damping,[11] using the Gaussian 16-C.01 program suite.[12] The structures were confirmed to be minima or transition states on the singlet potential energy hypersurface *via* calculation of the associated vibrational frequencies (all positive or one imaginary frequency, respectively). NMR chemical shifts of [**8**(H)]$^+$ and EPR hyperfine coupling constants of **9**$^+$ were calculated using the same functional-basis set combination employed in geometry optimization. GIAO formalism[13] was used for the NMR calculations.

A single deprotonation of **4a** can involve either an "axial" or an "equatorial" C–H proton. Calculations show the deprotonation from the equatorial position to be slightly more favoured (Figure S72). Small energy barriers separate the two possible chair conformers from the twist boat form that easily undergoes a second conformational change to give [**8**(H)]$^+$ with the cyclohexane ring in a boat conformation. The boat conformer is the global minimum on the potential energy surface with a relative $\Delta G = -72$ kJ mol^{-1} (298 K, 1 atm) due to the formation of a C–C bond.

A double deprotonation of **4a** gave a potential energy similar to the single deprotonation (Figure S73). However, the barriers associated with conformational changes are slightly higher and the boat conformation of **8** has a very negative relative $\Delta G = -262$ kJ mol^{-1} (298 K, 1 atm) due to the formation of a C=C double bond. The potential energy surface calculated for **8** compares well with that of free cyclohexane (Figure S74) with the exception that the boat conformer of cyclohexane is a transition state connecting two equivalent twist boat conformers.

For comparison purposes, the dimerization of two molecules of Me_2CAAC was also examined computationally. The results show that dimerization is exergonic for both *cis* and *trans* geometries, $\Delta G_{dimer} = -75$ and -99 kJ mol^{-1} (298 K, 1 atm), respectively, but kinetically blocked by very high activation barriers ($\Delta G^{\ddagger} = 189$ and 188 kJ mol^{-1}, respectively). The barriers arise in large part from the entropic penalty of dimerization ($-T\Delta S = 81$ kJ mol^{-1} at 298 K) that is mostly absent when the CAAC moieties are bound to the same linker as in [**8**(H)]$^+$ and **8**.

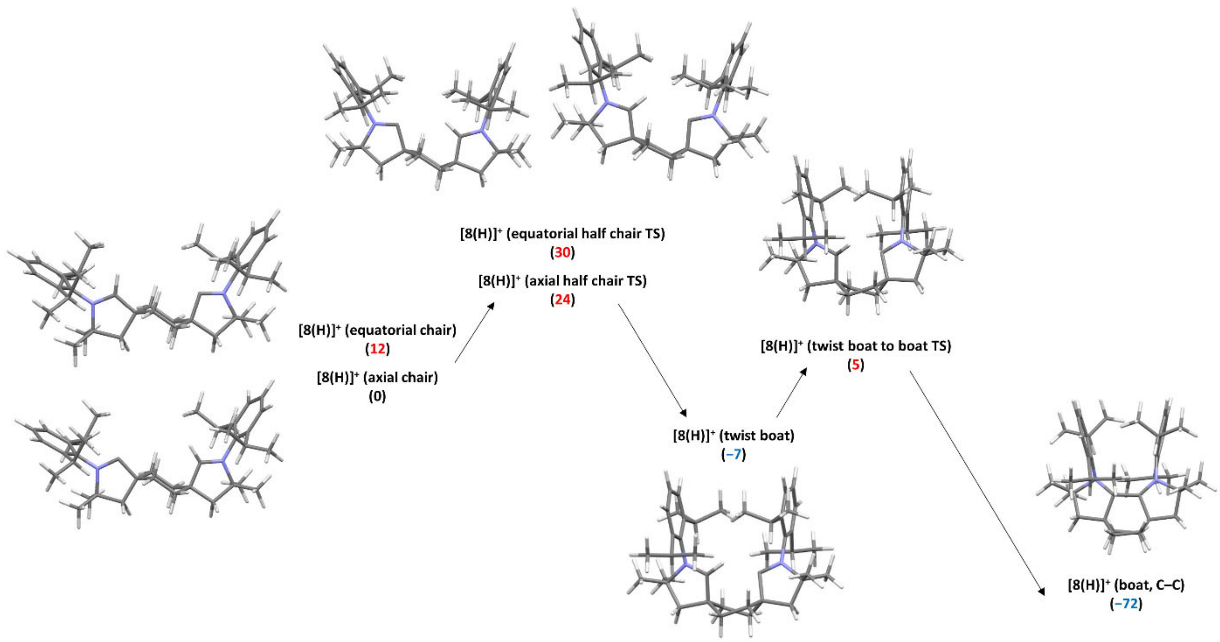


Figure S72. Calculated pathway for the conversion of singly deprotonated **4a** to [**8**(H)]$^+$. Relative Gibbs energies (298 K, 1 atm) are reported in kJ mol^{-1}.

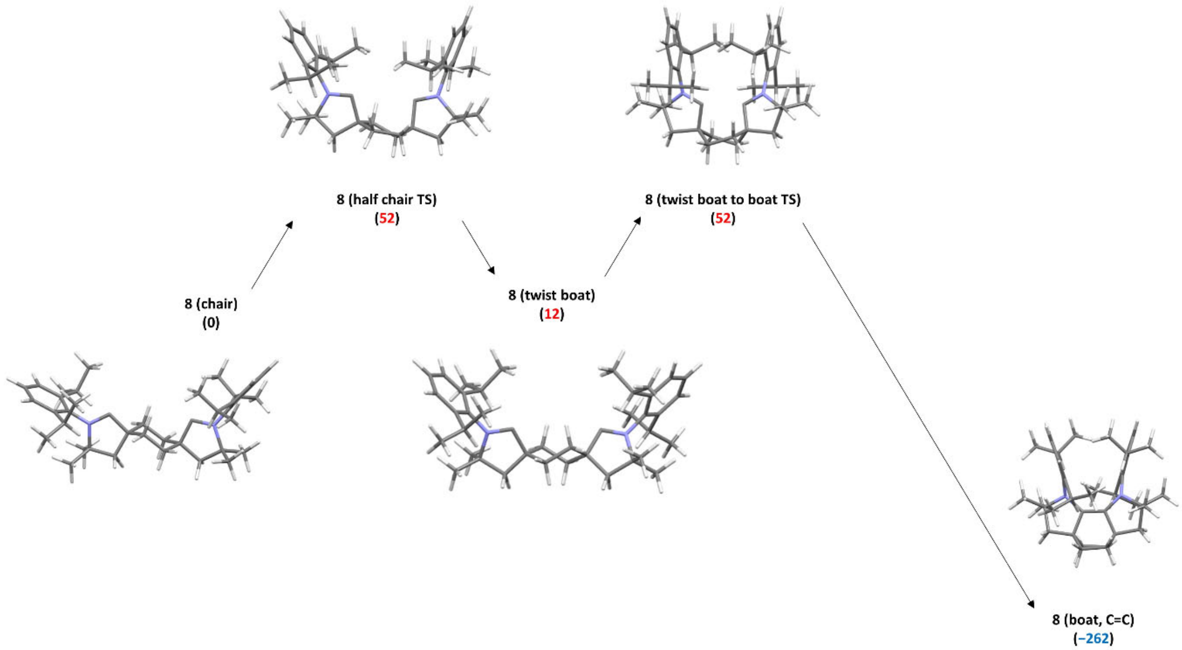


Figure S73. Calculated pathway for the conversion of doubly deprotonated **4a** (free bis(CAAC) intermediate) to **8**. Relative Gibbs energies (298 K, 1 atm) are reported in kJ mol^{-1}.

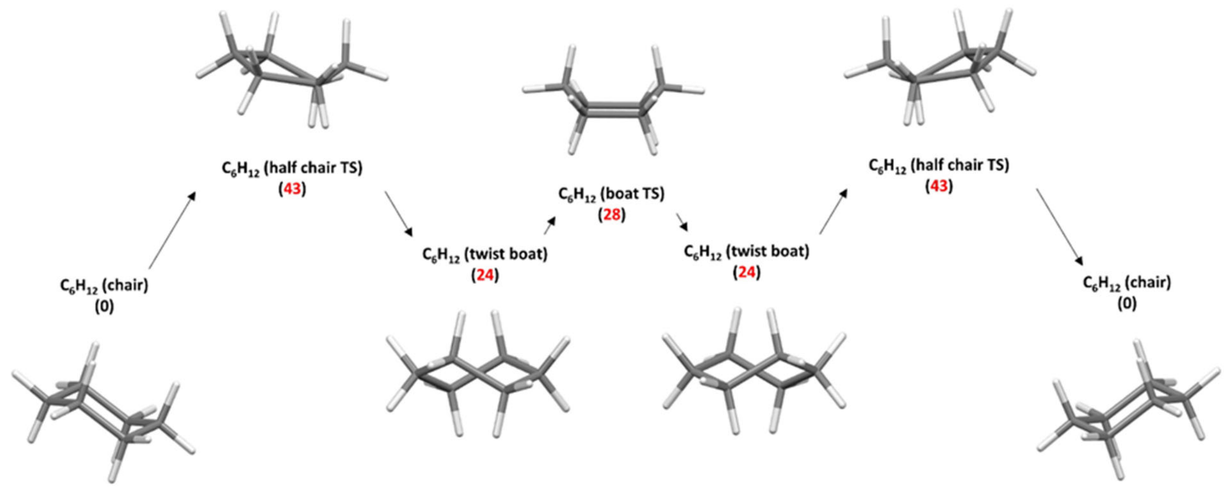


Figure S74. Calculated potential energy surface for cyclohexane ring flip. Relative Gibbs energies (298 K, 1 atm) are reported in kJ mol^{-1}.

Optimized coordinates

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[**8**(H)]+ equatorial chair

C	-4.654214913559	-1.286644077140	-1.279065010244
C	-4.442357053456	-0.073961138260	-0.613697128152
C	-5.034164366342	1.118743988422	-1.044457976172
C	-5.940885089409	1.051650881772	-2.096303806112
C	-6.229742537957	-0.150661277269	-2.715226690500
C	-5.571187840469	-1.301752626227	-2.324816003443
N	-3.558327165916	-0.037264745435	0.520599902013
C	-4.107149436111	-0.237195798387	1.922401785870
C	-2.869531153473	0.126012611745	2.745959466829
C	-1.683409387642	0.083599601358	1.769593092344
C	-2.280969134460	0.129985102516	0.376683573547
C	-0.865623697126	-1.209757486792	1.892559952105
C	0.288561725975	-1.258820533687	0.905236253246
C	1.233039509083	-0.061019713840	1.088301241780
C	0.424932137383	1.251353630573	0.983334552105
C	-0.739164976478	1.271264137852	1.959890707389
C	2.241532552058	-0.055277102534	0.017185034782
N	3.451306694930	0.041215315755	0.411061946626
C	3.561014225142	0.161108939095	1.921979418080
C	2.116107785008	-0.153996160456	2.349164021435
C	4.584595102352	0.078845419368	-0.482719424914
C	5.215291868679	-1.131631364138	-0.794446559770
C	6.348378548332	-1.065218099059	-1.596197233632
C	6.813028301879	0.143814456427	-2.080465712224
C	6.122266572040	1.310907908687	-1.813956053422
C	4.981214206409	1.309485325058	-1.018927218579
C	4.651363970268	-2.481477395446	-0.410447495925
C	3.973568244378	-3.115054771982	-1.626037031421
C	4.173866255481	2.580407252856	-0.878655403306
C	3.433691384545	2.863368524815	-2.186577143032
C	3.989092756250	1.575006983357	2.280897701005
C	4.573998994354	-0.823080012432	2.472091138381
C	-5.291970663958	0.669489679212	2.206799311407
C	-4.547686676992	-1.680964419246	2.122917447593
C	-4.615163209590	2.466613030213	-0.502865127546
C	-3.609129641956	3.099560941330	-1.464157308022
C	-3.824797412922	-2.518460669971	-0.996436491801
C	-2.700249314160	-2.609983148764	-2.028013082563
C	-5.784998054448	3.402088602246	-0.229651417577
C	-4.637783493664	-3.804854916389	-0.949284361186
C	5.016962150358	3.780309718439	-0.463776603762
C	5.697168958264	-3.418996961647	0.180404715822
H	-5.429290344376	4.323600831590	0.237150308472
H	-6.520221501751	2.944646721705	0.435555989805
H	-6.299708336908	3.686546553343	-1.149780255027
H	4.376456766517	4.649178997164	-0.300213249255
H	-5.650809182634	0.474106554001	3.219303862406
H	5.573741923825	3.590204319135	0.455543988287
H	5.736974884525	4.051292806937	-1.238192931163
H	-5.026769450126	1.724221771192	2.145888983596
H	-6.115487736616	0.474410739712	1.517438377684
H	-3.259871000256	4.060220283867	-1.075869555616

H	2.809104641151	3.753428300472	-2.085441561361
H	-4.088343213172	2.305982219315	0.437932887839
H	4.096097287154	1.632369759008	3.364973901260
H	3.255399230986	2.321108537885	1.977030470420
H	-1.292249568533	2.204217218366	1.817616102998
H	-4.064257945208	3.275707577578	-2.442024673416
H	-6.417727231078	1.959217323655	-2.446307523033
H	4.954256608296	1.821513454141	1.836806132207
H	1.084510573959	2.106429255978	1.157746281728
H	-0.377846126537	1.278581527973	2.995406955714
H	3.416249969665	2.430759501325	-0.108695433681
H	-2.980500320862	1.136506812664	3.148258674724
H	4.138102043836	3.036447402801	-3.003017912134
H	-4.964575174448	-1.789917909662	3.125919378936
H	-2.747851685522	2.442370006646	-1.603359796819
H	6.464273345948	2.243769365851	-2.244720030938
H	1.788589803166	0.532644766932	3.128750430092
H	-5.324907577671	-1.956042051933	1.407965561402
H	2.792219754491	2.028491328905	-2.479105543588
H	0.019928727729	1.334909860598	-0.028792053818
H	-6.947492270269	-0.184738899118	-3.526476470533
H	4.637727617476	-0.675215802675	3.551181235192
H	-2.742863238208	-0.548268221426	3.595436022584
H	-3.721138236178	-2.385317527097	2.026579422876
H	5.566425754035	-0.650931239158	2.052239490112
H	2.065683435660	-1.163867078749	2.760790203867
H	-0.493796406667	-1.291802931945	2.921092689515
H	7.703275843887	0.172190303232	-2.697298490858
H	-5.457663894795	-3.738793869315	-0.231047150396
H	4.285091529951	-1.857709943660	2.295022719156
H	-5.759669100332	-2.228492780590	-2.853182028830
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H	-1.505480836875	-2.079458437305	1.724517064676
H	-0.121275843305	-1.236182870510	-0.108036065420
H	0.853689870777	-2.188768955793	1.022973002834
H	-5.067499823698	-4.049623927375	-1.922933610101
H	6.865722964299	-1.979802101352	-1.858040337055
H	3.876664230145	-2.335039742403	0.344296362502
H	-3.999824483185	-4.643268129185	-0.659799124569
H	6.209310323689	-2.970363248126	1.033401201620
H	-2.096106803588	-1.700071058502	-2.011926359697
H	-3.105560501286	-2.731622864443	-3.035637651931
H	3.188197045217	-2.472871621735	-2.032507758466
H	-2.055546958749	-3.468301234527	-1.817803748727
H	6.454291234671	-3.691078623648	-0.557289931596
H	5.224692699299	-4.345217292717	0.513583059613
H	4.696468981754	-3.293979712505	-2.424885562979
H	3.524955459895	-4.073391203247	-1.355795387428
H	2.017696985874	-0.111140649455	-1.043984814698

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[**8**(H)]+ equatorial half chair (chair to twist boat) TS

C	3.592663721247	1.770909425291	-0.275300010445
C	3.225208433927	0.688920643159	0.534483762460
C	3.112749880917	0.809242648123	1.923107796860
C	3.469177082541	2.023960334156	2.500756991489
C	3.897441177034	3.085815536337	1.727040429664

C	3.935876226206	2.963821707681	0.349579183916
N	2.923092000295	-0.564263892368	-0.102963955900
C	1.713345709407	-0.880100036780	-0.447138199133
C	1.794455487001	-2.229244230748	-1.127301151496
C	3.289998589527	-2.531022044127	-1.308410704141
C	4.023547945687	-1.582313237905	-0.359696821459
C	1.075543550714	-3.279627496275	-0.281363077725
C	-0.366902578570	-2.913268645159	0.042027425443
C	-1.155288339237	-2.083405182733	-1.012958280092
C	-0.384783139023	-1.677370024943	-2.313020987667
C	1.042325807306	-2.186723177532	-2.453961497410
C	-2.550623201361	-2.676264218007	-1.305144480684
C	-3.545336279636	-1.508196209312	-1.290695318163
N	-2.772765198256	-0.508947130068	-0.446072772765
C	-1.533084552115	-0.808395225338	-0.360320739895
C	-3.377240159765	0.655473995125	0.155726183865
C	-3.372105039927	1.870094291187	-0.537728731404
C	-4.041601261604	2.937881712778	0.051393279699
C	-4.663400389311	2.807655172557	1.277934559263
C	-4.593138423869	1.610834660690	1.967119587721
C	-3.942702751757	0.507507980202	1.429176439259
C	-2.592516601407	2.106454718664	-1.810548610905
C	-1.366491908724	2.965202994486	-1.502122790966
C	-3.780060116173	-0.739003425383	2.270741048833
C	-2.725233404066	-0.492918998490	3.348829370114
C	-3.784991638032	-0.904991101198	-2.666578339609
C	-4.877014218093	-1.865366181960	-0.664816199839
C	5.267454318005	-0.965464983209	-0.974599277113
C	4.421551675235	-2.253335443931	0.948462638880
C	2.501504320505	-0.271270404926	2.784467578504
C	1.054365736552	0.098934996907	3.102518525176
C	3.504707700701	1.709389373898	-1.783931166481
C	2.160961173584	2.278577767497	-2.233483382182
C	3.287450730846	-0.551609373743	4.058391571420
C	4.665105979471	2.395988654019	-2.490228795661
C	-5.088866464375	-1.212490665513	2.892127147306
C	-3.432844322960	2.742878799484	-2.911865883027
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H	5.628191772666	2.014997186656	-2.144544911444
H	4.656683793078	3.476358440198	-2.331438064744
H	-2.848980516977	2.820676096970	-3.831186655148
H	6.025335104929	-1.743569322443	-1.083664571058
H	-4.333049679504	2.164879120318	-3.128470227596
H	-3.746337896793	3.752828056419	-2.640611995642
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H	5.682709244075	-0.184970749770	-0.334389956824
H	2.065454537646	2.226624905106	-3.321641441517
H	-0.766762316457	3.109765550478	-2.402811352991
H	3.508652217715	0.661133285416	-2.081446948001
H	-4.323025566537	-1.635430656053	-3.272470960408
H	-2.857349603670	-0.655417284187	-3.180421758136
H	1.563956274605	-1.541424982414	-3.165733221936
H	2.058769732573	3.324409350159	-1.932536194378
H	4.229690370677	3.815003996194	-0.252295394449
H	-4.403050729098	-0.009446584741	-2.598468074576
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H	1.051717812985	-3.195951485602	-2.880077302488

H	-2.230372628139	1.147207044701	-2.183374184543
H	3.589350618801	-2.323541773217	-2.338930998457
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H	5.207886066420	-2.983254009751	0.748159992475
H	1.342979833585	1.713777771224	-1.781817807798
H	-4.060149464295	3.893554381197	-0.457816379731
H	-2.583057905916	-3.218503399982	-2.249673146703
H	4.817310990175	-1.525463174136	1.658530370151
H	-0.731745263946	2.506065942288	-0.741306803566
H	-0.349893706036	-0.585086312203	-2.365347865499
H	4.179615810686	4.020707338405	2.196841856523
H	-5.390611879293	-2.559111152988	-1.332293790641
H	3.538947400608	-3.573593503544	-1.102520970657
H	3.588140896630	-2.778755049310	1.415347652155
H	-5.510789619859	-0.984963887620	-0.546998887364
H	-2.823569125864	-3.375277417450	-0.511907716700
H	1.111184755469	-4.221484522468	-0.838650765571
H	-5.183577203865	3.652554002560	1.713186367113
H	4.329203361375	-0.797730621308	3.844121875754
H	-4.764204587547	-2.354717218183	0.300545169486
H	3.397025284411	2.142490136716	3.575281169558
H	2.468829311407	-1.190759573631	2.202121059880
H	1.604271268784	-3.456009236032	0.657843661815
H	-0.373753217024	-2.351080774093	0.982154101762
H	-0.930821716476	-3.825830965221	0.244899906701
H	3.281896652106	0.305589807338	4.734930554818
H	-5.042069649610	1.533219119496	2.949529000464
H	-3.404396672129	-1.543935409047	1.635559129160
H	2.844905678774	-1.392092652127	4.598008105529
H	-5.869792960329	-1.352937171866	2.142830365063
H	0.495842666981	0.260991672852	2.177457340817
H	1.002462784128	1.018251770467	3.691043007592
H	-1.771392928037	-0.185364344862	2.916790774416
H	0.569774146594	-0.696766459130	3.674682022526
H	-5.461618617650	-0.499649131138	3.629983705367
H	-4.935969661871	-2.161446446219	3.410296378045
H	-3.046457365437	0.296502140957	4.032041766691
H	-2.560585767232	-1.399719657830	3.935356833943
H	-0.798345484845	-0.173284122203	0.129717073028

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[**8**(H)]+ axial chair

C	5.017374713506	1.303678801241	-0.997900527622
C	4.591562962190	0.082046718318	-0.465001857857
C	5.241642808585	-1.121423946396	-0.762199752789
C	6.406755267789	-1.061146470957	-1.518164713820
C	6.894013436744	0.145784115398	-1.985081010810
C	6.189141771874	1.310792877893	-1.747675361340
N	3.429279905148	0.046565553722	0.382821285094
C	2.234814291992	-0.077649941947	-0.108417848083
C	1.282979327226	-0.065440076260	1.070251803606
C	2.155975461485	-0.142325632419	2.337308340841
C	3.582981544832	0.186572772214	1.884375268991
C	0.476991603427	1.237024614254	0.974798866925
C	-0.700166800235	1.288399933495	1.934523982194
C	-1.647116287405	0.088374137945	1.793291670242
C	-0.821545002689	-1.209718022296	1.914080613349

C	0.334312123693	-1.256445045779	0.930795170412
C	-2.328955977883	0.106260986742	0.481773633885
N	-3.595376818489	-0.034696210610	0.536050652131
C	-4.103923639051	-0.219166429648	1.955865487699
C	-2.844699854664	0.146324768055	2.759184515222
C	-4.439788271512	-0.079004827012	-0.634457764526
C	-4.603925266862	-1.300350455163	-1.298237015955
C	-5.480934583160	-1.315410084147	-2.377384169835
C	-6.134652613958	-0.168475767954	-2.786997006830
C	-5.887710627766	1.036799235322	-2.155458772153
C	-5.023922531623	1.116013117132	-1.069847194863
C	-3.796287716180	-2.538536437584	-0.979437033242
C	-4.651404362006	-3.794433540226	-0.861205281156
C	-4.653880628202	2.469243961122	-0.505062871414
C	-5.865425264495	3.342160005261	-0.202534915018
C	-5.279408732448	0.695319608866	2.236969586043
C	-4.536935655387	-1.664267206562	2.147255242966
C	4.001184795614	1.604552627279	2.248861407641
C	4.613713813089	-0.776984475609	2.447062685350
C	4.647463421975	-2.467025592913	-0.412538581282
C	5.666355784113	-3.456602220189	0.136323057405
C	4.182959597084	2.561019373212	-0.910745657685
C	4.991237176707	3.806228480992	-0.571577622746
C	3.929802459507	-3.029308724520	-1.639517720809
C	3.411853867809	2.739222914191	-2.218533747760
C	-3.695184242845	3.175657027446	-1.464548789763
C	-2.702112216301	-2.722228044516	-2.032097111712
H	-5.548315007014	4.271039086818	0.275676311160
H	-6.572314874293	2.840176432422	0.460458896625
H	-6.400049960208	3.615682726828	-1.113976306890
H	4.325790410441	4.663133770862	-0.442530962995
H	-5.623376837840	0.500631630470	3.253897942114
H	5.564892530974	3.680049504365	0.349153731404
H	5.693493340120	4.062742670773	-1.367566372205
H	-5.011070453104	1.748385811972	2.173095244237
H	-6.110956884760	0.495327913387	1.559262331420
H	-3.385419416041	4.138860277410	-1.053460276770
H	2.770970463225	3.623882386709	-2.167414580395
H	-4.112864128535	2.321012028612	0.431341228346
H	4.132055732666	1.671816474067	3.330679446561
H	3.258003215268	2.345534690071	1.952827285594
H	-1.260892596684	2.219078864958	1.800189171469
H	-4.174519569776	3.358587065905	-2.428633324948
H	-6.361193058376	1.938916021761	-2.522404208518
H	4.952627683905	1.863241002617	1.781628481163
H	1.130085800028	2.091826022862	1.165511138732
H	-0.348600184865	1.288270037515	2.971766743048
H	3.440028513150	2.421339809272	-0.126676329731
H	-2.943655412061	1.159839294179	3.153914508470
H	4.097778936256	2.868017129770	-3.059545246020
H	-4.930657642624	-1.769585140498	3.159054209391
H	-2.798359747808	2.579923266651	-1.653121518030
H	6.544759779650	2.243650329266	-2.168233137293
H	1.834932948714	0.538513973385	3.128675697252
H	-5.331318595899	-1.934051495061	1.450281999757
H	2.788432682700	1.864902107414	-2.416047589854
H	0.140551562438	1.353051731455	-0.061329415594

H	-6.817921546308	-0.207650647116	-3.626884041766
H	4.691314537819	-0.623011818234	3.525287470971
H	-2.711874276983	-0.526502457991	3.606158871230
H	-3.711127022766	-2.365888051819	2.035137301293
H	5.599113137068	-0.599682584472	2.012633591143
H	2.127893856852	-1.152546220892	2.754554547063
H	-0.449614630206	-1.243112328532	2.943734998432
H	7.809129440978	0.173736288275	-2.564955236590
H	-5.453610706048	-3.674607537741	-0.130760331791
H	4.339516473661	-1.817461655841	2.276922182262
H	-5.639720990996	-2.241431368337	-2.915844299667
H	-3.296915206281	-2.393474414048	-0.020780842904
H	-1.468535817489	-2.082510885572	1.788155552316
H	-0.029334369225	-1.285296309672	-0.101943714975
H	0.893956250629	-2.184915057780	1.070650652044
H	-5.108354059398	-4.059969059561	-1.816285337050
H	6.932461511013	-1.977177759470	-1.758995429665
H	3.884611870676	-2.313958330064	0.351213902711
H	-4.033685921550	-4.640185307026	-0.552933842577
H	6.201498988987	-3.050095185316	0.997096724076
H	-2.052288750688	-1.846449281907	-2.103070357721
H	-3.136762750333	-2.886774820064	-3.020351548957
H	3.158643988839	-2.336703416485	-1.983200549783
H	-2.080992597913	-3.586842536993	-1.788734446324
H	6.407838857612	-3.733462178017	-0.616010510006
H	5.167108338096	-4.377104223004	0.448117398437
H	4.633399356196	-3.190973556939	-2.460001414637
H	3.460648401027	-3.988283753190	-1.402917616386
H	-1.845372926956	0.212254824111	-0.483166351465

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[**8**(H)]+ axial half chair (chair to twist boat) TS

C	-4.473721687374	-0.891631422265	1.171349759741
C	-3.894684279359	0.208814882113	0.529453594643
C	-4.099254951709	1.518992805223	0.976166653108
C	-5.001981181478	1.715475528666	2.015899381600
C	-5.651880446527	0.649508006209	2.609724496605
C	-5.366877143528	-0.642391373722	2.207292017927
N	-3.025236523162	-0.024940718221	-0.592800612871
C	-3.583017412348	-0.068261390336	-2.002469935319
C	-2.344945129184	-0.548186958055	-2.773883844652
C	-1.149748705587	-0.354968310743	-1.820881415783
C	-1.747268639486	-0.172930179743	-0.434603112786
C	-0.409859503081	0.983404775469	-2.075804822689
C	0.883948016394	0.902142440036	-2.869637743287
C	1.795028868195	-0.210294968816	-2.341714700833
C	1.043496934963	-1.533509837526	-2.572883213378
C	-0.227585062818	-1.588732699153	-1.745655318702
C	3.228454893991	-0.187037638725	-2.896375800054
C	4.178181442417	-0.422862276819	-1.707403611144
N	3.253397584483	-0.121011113850	-0.540366324619
C	2.030481862501	-0.040140107734	-0.889907016565
C	3.688134657355	-0.026093362066	0.832534515485
C	4.113418243495	1.221518474955	1.302098215459
C	4.597860406733	1.274367779504	2.603120147494
C	4.626910670354	0.144860484593	3.401097623802
C	4.117923294317	-1.051713418518	2.932513546955

C	3.618607378969	-1.167284820684	1.639473823218
C	3.926061543158	2.499518951970	0.515785047127
C	5.153481284726	3.401104947223	0.532663669310
C	2.924059224468	-2.444238314107	1.221969291146
C	3.751698569430	-3.692587914764	1.502685489900
C	5.380519952828	0.499465084476	-1.709383375781
C	4.651253279383	-1.864047828851	-1.595622569376
C	-4.058160517691	1.312493551770	-2.433974999111
C	-4.751526762975	-1.032159155814	-2.119034035268
C	-3.275760341059	2.682683701848	0.472735079240
C	-4.094405268840	3.938201299517	0.204619276312
C	-4.052738363909	-2.312388702093	0.871222261080
C	-5.219908170483	-3.286089911255	0.782919169847
C	-2.143657104388	2.959366112417	1.462482346528
C	-3.030350020739	-2.761117866933	1.915774061880
C	1.557685555879	-2.528567249263	1.905763186522
C	2.692795980049	3.237465281283	1.040197251971
H	4.991641170354	4.267253387646	-0.112073861031
H	6.045627175932	2.877508315635	0.184159414393
H	5.359553101910	3.780593024793	1.535164552186
H	-3.461601036507	4.714279622518	-0.232354024049
H	6.027095784525	0.211691747979	-2.539755997669
H	-4.918482800027	3.744246879200	-0.485094424948
H	-4.519208206155	4.349522510715	1.122707776354
H	5.103734520591	1.542935491439	-1.850096654490
H	5.957526250536	0.402991235285	-0.788149954644
H	2.514178311445	4.143197565231	0.456447638075
H	-1.505570614391	3.769568062977	1.097675423752
H	3.721668967415	2.241784187893	-0.524882048648
H	-4.479563769554	1.245628447411	-3.438702517996
H	-3.251471706460	2.045158399795	-2.456026709983
H	1.398364391685	1.866905951093	-2.829338580042
H	2.830081321974	3.529603426497	2.083572193602
H	4.939545105174	2.220564669326	3.003774428538
H	-4.840958065666	1.680801072047	-1.768719521725
H	-1.093260455783	1.669869060836	-2.577552217255
H	0.693972884445	0.688080470192	-3.926185451249
H	-2.806339066040	2.385628664266	-0.463887079706
H	3.434067081494	0.789074045594	-3.340818326317
H	-2.541557006061	3.256483932900	2.435982503337
H	5.336387153213	-2.064583417730	-2.420312598064
H	1.795261277517	2.615264390612	0.990960823784
H	-5.185337200640	2.719915373167	2.377853784766
H	-2.234962914113	-0.007847955754	-3.716367950895
H	5.192626822770	-2.029010507451	-0.663027206783
H	-1.532995097888	2.064718029595	1.602901858907
H	-0.201450300459	1.446949186934	-1.104575940289
H	5.016319902867	0.207086932147	4.410221751665
H	-5.122008402385	-1.016361178557	-3.145899827237
H	3.377012263632	-0.940184721293	-3.670103170294
H	3.830520964554	-2.577647933808	-1.659452461458
H	-5.573220771911	-0.738730227080	-1.463108623681
H	-2.463720558092	-1.604902034515	-3.022181727642
H	0.835547637930	-1.591404061816	-3.645964590187
H	-6.358747505646	0.824128913040	3.412391943495
H	4.737966115471	-3.641040156179	1.037635606237
H	-4.464368325908	-2.056349989094	-1.883916056769

H	4.088557856388	-1.912715289273	3.588644962752
H	2.743282866291	-2.409932649339	0.146501868589
H	1.679576496542	-2.387818968547	-2.326602598579
H	0.040340121662	-1.734949919250	-0.693762975207
H	-0.801067827589	-2.476143986709	-2.020781475250
H	3.896281171588	-3.845439293243	2.573793343968
H	-5.834837437794	-1.475250644051	2.717998197486
H	-3.538332981279	-2.318978317048	-0.089823909602
H	3.239048238282	-4.576014357699	1.117016841635
H	-5.964724572343	-2.957545449431	0.055115782627
H	0.930158647088	-1.661992366354	1.682340172798
H	1.670339255202	-2.580977450284	2.990870428444
H	-2.170393795776	-2.087684653691	1.923944948850
H	1.024948161372	-3.424735840229	1.579762178751
H	-5.723371931599	-3.403812226950	1.744783870465
H	-4.863852230420	-4.274723094723	0.483933899855
H	-3.471498182546	-2.762517172330	2.915646477834
H	-2.681098872250	-3.774365681883	1.698846669023
H	1.259614983932	0.120998976328	-0.140788651085

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[**8**(H)]+ twist boat

C	3.493103763271	1.067966920811	-0.906899002965
C	2.814110446112	0.771032105025	0.283505285804
C	2.396070145960	1.770515512372	1.166401750127
C	2.747592757341	3.084650990581	0.869688569603
C	3.463741464627	3.396491368139	-0.269174278824
C	3.815684172492	2.395500726627	-1.157268630380
N	2.493096703984	-0.609554806430	0.533192139581
C	1.390419564095	-1.122177370968	0.092494118368
C	1.424246773609	-2.605329387118	0.387558657835
C	2.866282681128	-2.885153112275	0.850248159082
C	3.435308507830	-1.534623228348	1.284049593217
C	0.347351397132	-2.945643556709	1.449835902085
C	-0.995239864696	-3.378181289264	0.854564863781
C	-1.350934754342	-2.593047892623	-0.411132462955
C	-0.257561280925	-2.866457962937	-1.486081989027
C	1.067039442152	-3.344665091950	-0.902098493180
C	-2.777293775580	-2.850283238447	-0.936773333907
C	-3.302415171425	-1.500479590097	-1.448513364086
N	-2.475695519506	-0.567527556720	-0.588168013886
C	-1.455278934213	-1.147953344295	-0.076211355314
C	-2.829942896745	0.789393558764	-0.249781884889
C	-2.381449716484	1.845213702492	-1.046350153181
C	-2.761571632128	3.129245048785	-0.666711728038
C	-3.527199711007	3.348382547429	0.461268053065
C	-3.910361403425	2.284155056880	1.258022384177
C	-3.566600639095	0.979904788325	0.928099394888
C	-1.451737062399	1.675466922789	-2.225294675240
C	-0.086298848430	2.287331432320	-1.916045699749
C	-3.914367536777	-0.144759157948	1.880163526837
C	-2.965661207446	-0.136827820042	3.078198694108
C	-2.992649095306	-1.266369105250	-2.919455321080
C	-4.784365870162	-1.295500774080	-1.209889250597
C	4.889104766400	-1.331287933769	0.901939834674
C	3.285411168922	-1.305352501958	2.781697318046
C	1.501350969848	1.507646503024	2.356369527809

C	0.108012779265	2.080566325646	2.101547660331
C	3.779718964540	0.017207001953	-1.957948805469
C	2.705134656387	0.060732317417	-3.042917825788
C	2.074768621947	2.062872007756	3.655627901254
C	5.174381275858	0.133282092363	-2.558544700392
C	-5.367371397245	-0.100009481979	2.338817630496
C	-2.037124680253	2.272251214873	-3.501469615622
H	5.365297026444	-0.706854819805	-3.229963078116
H	5.945944126413	0.135470378792	-1.785954365710
H	5.289096892235	1.046229511475	-3.146514095065
H	-1.390425710518	2.049880108624	-4.352674696217
H	5.507721892853	-1.997651645301	1.506049541231
H	-3.034439709974	1.883661761452	-3.718465126232
H	-2.118973225679	3.358774574661	-3.428024051076
H	5.081491905439	-1.560689259982	-0.144858536715
H	5.211028537645	-0.307432636014	1.101095975703
H	2.883083330731	-0.718187963828	-3.788907391334
H	0.568010454123	2.201464062137	-2.784958459812
H	3.704284904605	-0.963475475560	-1.488167408150
H	-3.562589124985	-1.985247483664	-3.510173611300
H	-1.936192857264	-1.402417050649	-3.148470374577
H	1.853243126143	-3.193457079685	-1.645905019676
H	2.709636868303	1.025863695325	-3.555781773430
H	4.342407475844	2.652771101572	-2.068064038545
H	-3.294739709407	-0.266903401567	-3.231390502598
H	-0.648182796471	-3.626376501613	-2.167051253143
H	1.038220750554	-4.420206912333	-0.699476186475
H	-1.293838870329	0.608948799086	-2.392616170631
H	3.450161777684	-3.272474828885	0.010955929891
H	-0.175308444452	3.347396421187	-1.669216954442
H	3.934397468820	-2.002115043261	3.315242085417
H	1.714609817981	-0.089161306649	-2.607168790627
H	-2.432829364329	3.972552094156	-1.261737420772
H	-2.804975856593	-3.612613417445	-1.714060139300
H	3.586221873175	-0.294661426137	3.058425985235
H	0.401616990106	1.783339106049	-1.080347675217
H	-0.084402298628	-1.963772634511	-2.072274250189
H	3.731862636773	4.425575926849	-0.477512475077
H	-5.333373588099	-1.987235933003	-1.850710697951
H	2.924676308266	-3.620882099521	1.653292510152
H	2.261875809917	-1.471367356586	3.121080332242
H	-5.090738727871	-0.281498977616	-1.472175150998
H	-3.411012752284	-3.190133212497	-0.112815529559
H	0.721352905483	-3.753598972455	2.082379022361
H	-3.811234573347	4.357565420165	0.734905916994
H	3.084666454371	1.695480924040	3.846027685344
H	-5.073041902249	-1.495276532549	-0.179597166654
H	2.440136854284	3.878684418448	1.540070898965
H	1.393373288745	0.428453121692	2.468159451989
H	0.198786292723	-2.089601197183	2.116069357096
H	-1.785961486859	-3.270941570760	1.602327471952
H	-0.969943695986	-4.437810118798	0.585759675119
H	2.121867584546	3.153828462439	3.634412906002
H	-4.479107806848	2.471103861567	2.160386988814
H	-3.767227371053	-1.096107931638	1.365312160707
H	1.444438219442	1.779456553071	4.501644983010
H	-6.056858311472	-0.066090789056	1.493093624777

H	-0.341350343451	1.660009134268	1.199761333402
H	0.147227386357	3.163965634056	1.967470128297
H	-1.922363468025	-0.235306398860	2.768992619283
H	-0.552817603755	1.874337740067	2.946512345012
H	-5.565699086595	0.772523999150	2.963966213339
H	-5.599858990487	-0.984044871577	2.936124487492
H	-3.054019111830	0.797831421150	3.636691499726
H	-3.201566783617	-0.959301642249	3.757331556562
H	-0.765926723889	-0.596933024101	0.547103294186

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[**8**(H)]+ twist boat to boat TS

C	-2.219751653588	-1.775897040392	1.186969578601
C	-2.594336165902	-0.783932379329	0.276595025069
C	-3.225403882841	-1.089013311680	-0.939152255261
C	-3.542604326509	-2.417564192017	-1.189585190828
C	-3.232440219846	-3.411298280438	-0.278142665913
C	-2.562814368894	-3.091692105191	0.886161061452
N	-2.329240923047	0.605671663009	0.545421406149
C	-3.340802634695	1.465428877206	1.292365134723
C	-2.869969233032	2.856877997979	0.870857407846
C	-1.425688702976	2.685531046636	0.371324235677
C	-1.283793664210	1.209745013607	0.084825815062
C	-0.351292727880	3.147927931851	1.385777153617
C	0.987818545135	3.508673597039	0.730347509619
C	1.248811975676	2.637015706456	-0.497779395406
C	0.154694004452	2.949731331462	-1.553347343377
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[**8**(H)]+ boat, C-C

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H	2.322547576239	-1.668988941298	2.072121799323
H	3.392110136571	-2.689924870767	3.051076754556
H	-3.343038820767	-2.300084262299	2.018534890646
H	2.262624789210	-3.434319399035	1.907788926869
H	-6.524139000532	-3.744930613092	0.534312355634
H	-5.228471479950	-4.395477484396	-0.459830791815
H	-4.836076308890	-3.151309931078	2.454273337930
H	-3.612838958535	-3.963959391568	1.464047085064

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8 half chair (chair to twist boat) TS

C	4.006023808924	1.693863072114	0.116521451287
C	3.522323161538	0.493232923508	0.648084455959
C	3.384149656901	0.303171505595	2.028056242595
C	3.868555471462	1.296374709092	2.873147803849
C	4.436514044754	2.451564890455	2.367615804279
C	4.476766228551	2.658226392365	1.000690578383
N	3.092305577421	-0.540854945449	-0.248942363854
C	1.848090769772	-0.620220991867	-0.617480158420
C	1.736621625314	-1.855130374280	-1.478543431936
C	3.187376984046	-2.257413553403	-1.810866545708
C	4.062969074027	-1.594060658363	-0.747157556963
C	1.020685991899	-2.949098569642	-0.669600807283
C	-0.501829591785	-2.813915261508	-0.504642001381
C	-1.267657049721	-1.708439650359	-1.269829219572
C	-0.444315836612	-0.959489085349	-2.349047529741
C	0.886761740455	-1.591301393315	-2.714916049262
C	-2.597168406260	-2.253575679535	-1.838599374093
C	-3.638211636291	-1.156033009454	-1.620445235549
N	-2.946067995795	-0.384252292709	-0.517468263723

C	-1.691442248773	-0.639503096473	-0.274756983370
C	-3.651059701101	0.616297787028	0.230075171194
C	-3.609655084161	1.948922539506	-0.195014587376
C	-4.361947049687	2.882426613419	0.510899729798
C	-5.101253744357	2.513722815014	1.619664522422
C	-5.055178454320	1.208285446452	2.074685799416
C	-4.319506610340	0.239847895627	1.400955110833
C	-2.664854328295	2.408639285783	-1.280857053509
C	-1.375670970478	2.918298628760	-0.635953926883
C	-4.134424810715	-1.128623725760	2.015031485680
C	-3.048575286515	-1.046097129592	3.087998661340
C	-3.866925024813	-0.275095167704	-2.842702553942
C	-4.985176681379	-1.703508676681	-1.176369814194
C	5.329811460595	-0.978799957841	-1.318674014207
C	4.459900579550	-2.542528482174	0.377830190285
C	2.602075615608	-0.858552002384	2.595819040127
C	1.145637134951	-0.435648394118	2.796263203426
C	3.872845905558	2.018456674785	-1.353320642028
C	2.595080040204	2.831462888865	-1.561215299155
C	3.200065480996	-1.430410820342	3.873422784325
C	5.088627505660	2.721564520359	-1.939119261022
C	-5.420097737757	-1.730056300907	2.564831278848
C	-3.268505215438	3.445106973169	-2.218015980379
H	4.962583005408	2.855163793860	-3.016435688485
H	6.003494432769	2.148585649824	-1.771069430317
H	5.231634517096	3.714731702998	-1.506791298710
H	-2.571435124973	3.664074804289	-3.030506568328
H	5.996805307758	-1.778928378280	-1.647455120738
H	-4.205152739960	3.094826212824	-2.658608812422
H	-3.471736860288	4.388995256412	-1.706325312249
H	5.124678005927	-0.343182062270	-2.179446065724
H	5.859147580744	-0.389295373472	-0.566802281052
H	2.443867355280	3.044755145772	-2.623351536273
H	-0.668605230474	3.243554957535	-1.404034352888
H	3.733002762061	1.083136353830	-1.894071952948
H	-4.372138158739	-0.858106707908	-3.616019690558
H	-2.935591148834	0.104347957136	-3.260630946074
H	1.418810447770	-0.919803826398	-3.397197987585
H	2.648656917854	3.783486105409	-1.026061035997
H	4.861093056850	3.594306246448	0.613190777080
H	-4.506917056048	0.574492939775	-2.594333502401
H	-1.049996990480	-0.854455841175	-3.252101659867
H	0.742611887082	-2.537473809771	-3.253306057827
H	-2.389508379550	1.541862965066	-1.878357144927
H	3.455080190160	-1.867487148377	-2.797308938824
H	-1.579659467438	3.768563711370	0.020868710753
H	5.192756763460	-3.259617548049	0.001362654444
H	1.731447643638	2.276876447247	-1.188614627158
H	-4.351097436751	3.919639081409	0.197905360445
H	-2.523080394726	-2.547269530657	-2.888286776953
H	4.920076673166	-1.997321371703	1.204878189187
H	-0.906341223307	2.126511472092	-0.047766913028
H	-0.233907058932	0.045828715155	-1.973912002082
H	4.815186607347	3.210591819009	3.042837373231
H	-5.437069296862	-2.252020515709	-2.005935143571
H	3.335464398256	-3.339117502052	-1.835928895832
H	3.609426568842	-3.105350912019	0.761403228232

H	-5.668044485762	-0.898854615042	-0.895133918239
H	-2.901949541863	-3.138149184118	-1.272188586430
H	1.235856396566	-3.886945507681	-1.192380019298
H	-5.687201474248	3.254158329860	2.152471416947
H	4.250593799635	-1.702059398883	3.742829510690
H	-4.890912536652	-2.390254299573	-0.335879193843
H	3.780771544614	1.170982687896	3.945549776707
H	2.594976116305	-1.653359683023	1.852266129135
H	1.479711143727	-3.041984385452	0.317417490902
H	-0.728091385562	-2.664702096787	0.554538992073
H	-0.945499855159	-3.776215125888	-0.772417235666
H	3.136719318823	-0.724601027735	4.705164097762
H	-5.585361215346	0.939882152118	2.980792647584
H	-3.754642728862	-1.796728163919	1.242328255531
H	2.651206917122	-2.326680903308	4.172394167544
H	-6.204215472681	-1.765892891551	1.804943501859
H	0.692888388908	-0.135894068456	1.847725081792
H	1.079429688362	0.400512823962	3.498247976452
H	-2.117085194867	-0.674769682495	2.655735336014
H	0.564120650575	-1.267203930048	3.205318003105
H	-5.804026249313	-1.160892322835	3.414786460840
H	-5.237883709758	-2.748751676546	2.916069532985
H	-3.349697429233	-0.369997332404	3.892940823563
H	-2.863474182632	-2.032531325657	3.522775866047

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8 twist boat

C	-5.363491725524	-0.999390818280	0.555875351540
C	-4.537252625974	0.130617895814	0.536658387972
C	-4.646813159607	1.136455093325	1.503650090770
C	-5.686674430660	1.046006766497	2.423657322632
C	-6.566419853331	-0.020312855207	2.406429277385
C	-6.386148072003	-1.046372401515	1.496510174596
N	-3.524560318736	0.232001219823	-0.474431218431
C	-3.831969147750	0.898876087431	-1.801513761591
C	-2.580188303535	0.497296649694	-2.581947206164
C	-1.533626535953	0.099124707394	-1.526579514390
C	-2.318689893211	-0.218066200225	-0.275106350694
C	-0.560229543265	1.246634868253	-1.169218141082
C	0.731907907020	1.138572551510	-1.954273326951
C	1.533696232775	-0.098460987613	-1.526629828040
C	0.560295135982	-1.245965882463	-1.169288391167
C	-0.731820078844	-1.137858585716	-1.954358692036
C	2.580149634124	-0.496631047103	-2.582094180060
C	3.831950476582	-0.898380848302	-1.801750517729
N	3.524639647845	-0.231716318889	-0.474548849286
C	2.318846507020	0.218539348835	-0.275164463414
C	4.537271203915	-0.130846291670	0.536671069364
C	5.363814833742	0.998912226841	0.556280959282
C	6.386417941180	1.045340595717	1.497019686358
C	6.566333134379	0.018979610006	2.406655193848
C	5.686241377090	-1.047072172565	2.423553510233
C	4.646410964223	-1.136942880600	1.503470359406
C	5.081085669488	2.206956772740	-0.306871888495
C	6.330114220410	2.819595182065	-0.925067769909
C	3.595600165617	-2.211031072590	1.663126889413
C	4.172675118213	-3.594909665863	1.927014437547

C	5.112000248311	-0.367600715539	-2.426192950820
C	3.977842458259	-2.404861116859	-1.628604448352
C	-3.977874603288	2.405318209159	-1.628051573895
C	-5.112052511532	0.368146766390	-2.425932701027
C	-3.596432549559	2.210938885493	1.663564262055
C	-4.174088564135	3.594604708551	1.927276968345
C	-5.080321200059	-2.207061621092	-0.307643430713
C	-6.329151232743	-2.820188987637	-0.925747941532
C	-2.621731509507	1.793461354993	2.764538174785
C	-4.299698056128	-3.233206557294	0.513213994986
C	2.620790549805	-1.793166801545	2.763868450582
C	4.301188512726	3.233300495790	0.514412429337
H	6.054330119607	3.631731057157	-1.602314441402
H	6.901751019378	2.081388015272	-1.492133719484
H	6.992060566038	3.244164078028	-0.166651201723
H	-3.372237775107	4.336558553975	1.948162836126
H	5.286163003657	-0.886143221891	-3.371642436884
H	-4.888939417681	3.888492042913	1.155076249409
H	-4.684821811611	3.645430265356	2.891883986579
H	5.051963918462	0.699187923913	-2.638821075840
H	5.974722215885	-0.548014376668	-1.781245164110
H	4.050474782840	4.103815552135	-0.098265584329
H	-1.826775302824	2.536190679255	2.872865931981
H	4.422905181288	1.895688853149	-1.117691054111
H	-4.210742661885	2.856530599638	-2.595055123469
H	-3.066594103538	2.868260676284	-1.251349895808
H	1.346600094885	2.031679918056	-1.805487297083
H	4.891543851067	3.576525056360	1.368369125382
H	7.041613827399	1.907821442486	1.529281745469
H	-4.795702527745	2.641550331158	-0.944005497734
H	-1.042129587984	2.209982023608	-1.349252174760
H	0.517580242762	1.080803701896	-3.028313704000
H	-3.019483251554	2.260042335910	0.742013797410
H	2.811357854146	0.367858161540	-3.211672752149
H	-3.136458136724	1.701079786039	3.724945199177
H	4.210784643850	-2.855860914981	-2.595692102142
H	3.375279985608	2.792997812337	0.890116539936
H	-5.795253796934	1.814984498071	3.179316619218
H	-2.236398740127	1.298069012768	-3.240726016180
H	4.795612050009	-2.641248422597	-0.944546204262
H	-2.165248731242	0.832152044050	2.521107186589
H	-0.319993377086	1.204015187268	-0.102424361873
H	7.374486347079	0.067713809423	3.127684646321
H	-5.286402297365	0.886950831305	-3.371203707324
H	2.236251514932	-1.297339913818	-3.240893717012
H	3.066520679248	-2.867878711331	-1.252095838277
H	-5.974695622284	0.548300137108	-1.780806040016
H	-2.811364272120	-0.367180465227	-3.211552542636
H	1.042179242157	-2.209334725373	-1.349285359943
H	-7.374603051751	-0.069500186687	3.127394056137
H	4.887793960964	-3.888978751474	1.155132903805
H	-5.051963887523	-0.698577753744	-2.638884276532
H	5.794528753168	-1.816276575373	3.179026228081
H	3.018847897923	-2.259958033772	0.741447471944
H	0.320029617634	-1.203332289627	-0.102500028864
H	-1.346501273729	-2.031002156053	-1.805697598846
H	-0.517457869899	-1.079973347120	-3.028390300388

H	4.682908660514	-3.645984069921	2.891874899922
H	-7.041109681505	-1.909042236940	1.528491212332
H	-4.422494240705	-1.895253202863	-1.118539435436
H	3.370561078556	-4.336595587891	1.947461782203
H	-6.901338607574	-2.082104511996	-1.492421406173
H	2.164755789976	-0.831676011237	2.520320787552
H	3.135337953555	-1.701006744716	3.724391331294
H	-3.373938019655	-2.792497745965	0.888819386540
H	1.825511368521	-2.535581774763	2.871998090484
H	-6.990680963211	-3.245422103077	-0.167338341576
H	-6.053064173079	-3.631926474113	-1.603350536302
H	-4.889698401795	-3.576941155378	1.367209495204
H	-4.048672106159	-4.103434829337	-0.099741572683

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8 twist boat to boat TS

C	-0.116600332140	2.448525453056	-1.843666759257
C	0.772495449235	2.484741990806	-0.765831400013
C	2.149385990486	2.685716724388	-0.961496396189
C	2.604761659378	2.897010240706	-2.256124059187
C	1.732962453211	2.905200905354	-3.331050761409
C	0.388760209047	2.672615824391	-3.122035160421
N	0.305229339285	2.286234241080	0.574657945564
C	-0.179461813711	3.451810604883	1.410392017686
C	0.179463775226	2.911812057869	2.794385240936
C	0.144922387793	1.383862272026	2.653186127711
C	0.525365906176	1.150093003966	1.192582552685
C	-1.242442591441	0.812152146033	3.044949647151
C	-1.188487921103	-0.647941391218	3.486866076041
C	-0.144922387793	-1.383862272026	2.653186127711
C	1.242442591441	-0.812152146033	3.044949647151
C	1.188487921103	0.647941391218	3.486866076041
C	-0.525365906176	-1.150093003966	1.192582552685
N	-0.305229339285	-2.286234241080	0.574657945564
C	0.179461813711	-3.451810604883	1.410392017686
C	-0.179463775226	-2.911812057869	2.794385240936
C	-0.772495449235	-2.484741990806	-0.765831400013
C	-2.149385990486	-2.685716724388	-0.961496396189
C	-2.604761659378	-2.897010240706	-2.256124059187
C	-1.732962453211	-2.905200905354	-3.331050761409
C	-0.388760209047	-2.672615824391	-3.122035160421
C	0.116600332140	-2.448525453056	-1.843666759257
C	-3.149358720760	-2.601197813492	0.170706310840
C	-3.797643276955	-1.218665313709	0.197444986747
C	1.576662803556	-2.091767275035	-1.693468310153
C	1.864751880848	-0.745653942578	-2.350599036494
C	1.674603713295	-3.698507701766	1.254261371962
C	-0.561571430628	-4.732185223161	1.066802956131
C	0.561571430628	4.732185223161	1.066802956131
C	-1.674603713295	3.698507701766	1.254261371962
C	3.149358720760	2.601197813492	0.170706310840
C	3.797643276955	1.218665313709	0.197444986747
C	-1.576662803556	2.091767275035	-1.693468310153
C	-1.864751880848	0.745653942578	-2.350599036494
C	4.202430367899	3.701522124175	0.121158529268
C	-2.492658608603	3.171627178437	-2.260971485219
C	2.492658608603	-3.171627178437	-2.260971485219

C	-4.202430367899	-3.701522124175	0.121158529268
H	4.825370984808	3.663357731636	1.018292384865
H	3.748110105651	4.693414014968	0.061990539987
H	4.868240722943	3.589455069039	-0.737810370408
H	3.537391898660	-2.937399369012	-2.041498878947
H	0.231379573418	5.525477772334	1.741554575360
H	2.269571957608	-4.158759573157	-1.849989291880
H	2.393117843781	-3.241076014708	-3.347304885847
H	1.639772028134	4.622372883240	1.180276279458
H	0.353496864603	5.051449594043	0.043591203811
H	4.492892213540	1.138374439446	1.038108963414
H	2.922713424016	-0.493094255543	-2.251380913033
H	2.603484620711	2.707484263814	1.109084302870
H	1.986760882707	-4.466020371223	1.966692007680
H	2.260322535483	-2.800634557365	1.446999678159
H	2.172312823281	1.108279236070	3.356772273902
H	4.356907445442	1.034456030619	-0.724139927063
H	3.663570607654	3.049465698978	-2.428970090559
H	1.913004433805	-4.060846499137	0.254723709795
H	1.645058517319	-1.424692498902	3.858638949606
H	0.939842949925	0.731938354200	4.550990796062
H	1.786090363655	-1.977214090575	-0.630201685405
H	1.195270221541	3.233264246596	3.047612898913
H	1.622580842209	-0.764600377261	-3.416274358902
H	-1.986760882707	4.466020371223	1.966692007680
H	3.027527212407	0.452349929279	0.302620360052
H	0.286935149775	-2.642250190954	-3.969218056283
H	0.489383674088	-3.290099570333	3.570080730323
H	-1.913004433805	4.060846499137	0.254723709795
H	1.284751050187	0.049021668617	-1.882842628304
H	1.921800384437	-0.894398246091	2.197927626836
H	2.107713161228	3.074964222197	-4.334091793622
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(Me2CAAC)2 cis TS

C	2.603433024682	-0.673845682316	-1.515889780763
C	2.162507279492	-0.733672712477	-0.178031261385
C	2.139755607323	-1.967182716314	0.496572466246
C	2.607736892083	-3.102633135126	-0.158420330470
C	3.063054040767	-3.050410465314	-1.459117522705
C	3.033683053891	-1.843980322952	-2.131181100130
N	1.924983770073	0.491498553953	0.529254332838
C	1.135163787642	1.472850764625	0.058321408373
C	1.610322244735	2.760379797536	0.790641237454
C	3.027221193685	2.395788694872	1.235153095170
C	3.011957232559	0.908646812535	1.520794887434
C	4.359358918364	0.295320537128	1.173729338782
C	2.699183769264	0.620872311573	2.992571708915
C	1.762740734159	3.967399229417	-0.138770662999
C	0.768906145067	3.143324043690	2.015180720992
C	1.611039938603	-2.149397817745	1.900545474102
C	0.337036025692	-2.981440392741	1.897515711453
C	2.649269231882	0.598873718712	-2.328468387139
C	1.517115632308	0.595261988278	-3.349271371916

C	2.637893770310	-2.792187446091	2.830600323176
C	4.000716040887	0.834915779605	-2.992722402819
C	-1.135228456044	1.472828264383	-0.058298616040
N	-1.925014765353	0.491455328819	-0.529240733959
C	-3.012015922940	0.908577026832	-1.520761993785
C	-3.027319389989	2.395716822994	-1.235113509619
C	-1.610428217337	2.760347470375	-0.790608133429
C	-2.162470519238	-0.733741007849	0.178022279988
C	-2.139654354117	-1.967235257692	-0.496607509579
C	-2.607577934969	-3.102723109086	0.158360766385
C	-3.062900500443	-3.050550552124	1.459057850762
C	-3.033593002735	-1.844132696680	2.131147370432
C	-2.603402552857	-0.673962850269	1.515880808557
C	-1.610931035938	-2.149395995552	-1.900584433750
C	-2.637751269046	-2.792229066360	-2.830646754014
C	-2.649314952387	0.598741541009	2.328478638863
C	-4.000787036760	0.834709944308	2.992707825968
C	-0.769021025782	3.143317379577	-2.015149370489
C	-1.762880472303	3.967361111430	0.138805880383
C	-2.699261242577	0.620820957085	-2.992544716454
C	-4.359390498352	0.295204484048	-1.173673970520
C	-1.517186371180	0.595172763559	3.349309839627
C	-0.336881531081	-2.981369268920	-1.897571180148
H	4.221684455902	0.088222128351	-3.759502961520
H	4.009521332113	1.813130255416	-3.480534379644
H	1.621261789133	-0.238087774789	-4.050017853059
H	3.373840471065	-1.799794707488	-3.159326630723
H	4.814853065449	0.812934031597	-2.264405885356
H	1.506211439932	1.525609976009	-3.923424181058
H	3.422094235912	-3.945971519412	-1.953024730478
H	0.043504025423	-3.097544503803	-2.915546326325
H	-2.284084323097	-2.760791198296	-3.864550847458
H	0.561693350774	0.498064810722	-2.832484296473
H	2.449887930375	1.432411825149	-1.653455231248
H	-0.513531380397	-3.979323943671	-1.487258610247
H	0.435457359685	-2.504336345347	-1.301840141243
H	-2.790517596818	-3.842963039110	-2.571868267015
H	-1.640889034313	0.725929680700	-3.223846933031
H	4.630431262303	0.493880338313	0.135845550830
H	-1.340023458958	-1.169485322144	-2.285614488207
H	-3.012785532865	-0.376182027887	-3.289823808258
H	-3.612797150311	-2.303786562591	-2.788204637731
H	-3.249097396904	1.329811149541	-3.615525638038
H	2.596090006540	-4.051348211656	0.365481372510
H	3.721963580205	2.585781890787	0.410579700170
H	5.118263884665	0.749220518104	1.816392658489
H	4.384208622747	-0.782874944103	1.329951609116
H	-2.595882548931	-4.051426071813	-0.365561575833
H	-3.358520412250	2.989619756203	-2.090039302054
H	-4.384199485392	-0.782994684839	-1.329878452709
H	3.358399036352	2.989697544211	2.090083939421
H	2.790738277346	-3.842902772290	2.571792252364
H	-5.118321392006	0.749065337787	-1.816334154696
H	3.612904814794	-2.303672967383	2.788185687724
H	-0.435326329288	-2.504445579247	1.301784316224
H	0.513743845780	-3.979381441203	1.487194489285
H	1.340080861260	-1.169507867601	2.285590486049

H	-3.722061380049	2.585687044949	-0.410534355865
H	-4.630458385699	0.493768846008	-0.135789741459
H	3.012775791882	-0.376107014790	3.289861179380
H	3.248947562537	1.329904432533	3.615568470978
H	2.284211528627	-2.760805287726	3.864500907356
H	-3.421895703300	-3.946140120935	1.952945966660
H	1.640797635474	0.725901011440	3.223842637264
H	-0.043349511943	-3.097647731135	2.915487180231
H	-2.449957158603	1.432298745617	1.653481856164
H	-0.561745472339	0.498030165781	2.832547984275
H	-3.373757831669	-1.799985440757	3.159292106371
H	-4.814908968108	0.812700193516	2.264375408523
H	-1.506343604753	1.525514479097	3.923474082970
H	-1.621308046661	-0.238190194626	4.050043827361
H	-4.009648445668	1.812916859934	3.480534110388
H	-4.221734832912	0.087993923824	3.759472739140
H	0.966693177652	4.184964596144	2.289652876911
H	-0.289155405306	3.014943488666	1.825196286964
H	1.016132766467	2.529728792954	2.878099985778
H	-2.372307642436	4.720574389754	-0.370888209545
H	-2.284804729266	3.689684433969	1.058265564724
H	-0.826952710474	4.439485572400	0.417211405626
H	-0.966769793038	4.184978511696	-2.289569786387
H	0.289039338161	3.014882991838	-1.825190156064
H	-1.016286978971	2.529774081676	-2.878095276180
H	2.372120999431	4.720642220046	0.370935606257
H	2.284700438142	3.689743753057	-1.058216544546
H	0.826797059642	4.439476629673	-0.417201784666

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(Me2CAAC)2 cis

C	-1.955318854645	-1.988010465988	-0.385355485383
C	-1.743420977624	-0.753420543280	0.278592257588
C	-2.044861349447	-0.664832110139	1.654742753263
C	-2.604491865501	-1.762686887931	2.301596368313
C	-2.910633627045	-2.928446992890	1.629932540435
C	-2.566801745750	-3.033369710325	0.297801789933
N	-1.487708031950	0.399159832049	-0.524867747925
C	-0.646839587117	1.524640827300	-0.220720413849
C	-1.429951677605	2.812379809906	-0.638982858019
C	-2.834937161211	2.268314281315	-0.837805766918
C	-2.690449066057	0.844809542810	-1.313835370644
C	0.647779805952	1.524129326656	0.221104330325
N	1.487710443700	0.397839113550	0.525145553416
C	2.690692269962	0.842538048543	1.314306857571
C	2.836417919762	2.265924855271	0.838288534360
C	1.431911600583	2.811210248445	0.639530640913
C	1.742929747555	-0.754502249737	-0.278805179012
C	2.044792126130	-0.665507663575	-1.654825247462
C	2.603701250482	-1.763501186747	-2.302083939194
C	2.908853390405	-2.929774878851	-1.630875234141
C	2.564768288528	-3.035000157090	-0.298825945563
C	1.953882268823	-1.989525590080	0.384671458612
C	1.903800826838	0.600182466223	-2.473023602907
C	3.265199316900	1.192002036093	-2.831161911361
C	1.535002245418	-2.267635554102	1.815878736908
C	2.676478280601	-2.698073116302	2.737252060290

C	2.446826745380	0.783848808469	2.821595492779
C	3.988256448402	0.117193988646	0.983103546901
C	-1.607281581562	3.917988320701	0.406437844669
C	-0.941019589832	3.435593931423	-1.975256741835
C	-3.988466586764	0.120393818382	-0.982377593171
C	-2.447121397254	0.786176295804	-2.821233738584
C	-1.902758244746	0.600404827709	2.473471377668
C	-1.101473842190	0.360874300480	3.749701955406
C	-1.536834958959	-2.265851219021	-1.816715768952
C	-0.483478616853	-3.367287060915	-1.850310777663
C	-3.263646288811	1.193520101611	2.831391691459
C	-2.678769370769	-2.695417599951	-2.737930032764
C	0.481108297227	-3.368584090635	1.848893843958
C	1.101714947300	0.361909629142	-3.748964977908
H	-3.830500737569	0.510498187756	3.469580753398
H	-3.140277891985	2.133799783295	3.376509260129
H	-1.657464344879	-0.254208988393	4.461820234929
H	-2.851900252011	-1.676739319134	3.353656967924
H	-3.869991742449	1.394138017236	1.947210950235
H	-0.879847924902	1.310052892005	4.245436039220
H	-3.387204525986	-3.754204425436	2.145312925671
H	0.101445942784	-3.499062055723	2.865242943187
H	2.289375535376	-2.864846361326	3.746182152388
H	-0.159423898853	-0.143921201576	3.539634141258
H	-1.358354817516	1.326729176074	1.872559968719
H	0.904132584739	-4.323537984651	1.524426221323
H	-0.357513638909	-3.134260140615	1.202676451659
H	3.108773472356	-3.642883747936	2.397861773289
H	1.479564493210	1.202291346610	3.085095734703
H	-4.202469450229	0.146818972511	0.085982968789
H	1.074282674533	-1.358206235247	2.200975588510
H	2.484523188828	-0.234304773292	3.198675549069
H	3.488213583722	-1.976004274523	2.810491968039
H	3.219849297302	1.355099311655	3.342892833740
H	-2.757078127756	-3.961555406393	-0.229101315141
H	-3.355431582741	2.255250674503	0.122415980651
H	-4.794707772146	0.643316505292	-1.503653792052
H	-4.006478119833	-0.918974250101	-1.294248235340
H	2.754367159560	-3.963528491959	0.227718611119
H	3.419950998690	2.888193277727	1.519870155370
H	4.005381168136	-0.922279866280	1.294631612700
H	-3.417860309523	2.891073003171	-1.519461995423
H	-3.111122397444	-3.640368406565	-2.399013430548
H	4.794701211516	0.639340509538	1.504845735746
H	-3.490377110167	-1.973110178071	-2.810283065136
H	0.355432265296	-3.133523430036	-1.204264798549
H	-0.906855929613	-4.322131805584	-1.525973677564
H	-1.075738141260	-1.356543989178	-2.201642165650
H	3.356816802209	2.252343047213	-0.121990039307
H	4.202685823471	0.143804033752	-0.085168196741
H	-2.485579012158	-0.231849688466	-3.198544359272
H	-3.220015526296	1.358007158384	-3.342083796655
H	-2.292133152745	-2.861577518288	-3.747140131255
H	3.384879360648	-3.755677409289	-2.146527202228
H	-1.479745022630	1.204144822146	-3.085056775107
H	-0.104155726492	-3.497661933158	-2.866800645303
H	1.360393843793	1.326875728426	-1.871671775170

H	0.158989477734	-0.141444186084	-3.538484358531
H	2.851331914325	-1.677270064940	-3.354071694378
H	3.872106490145	1.391408166186	-1.947078526035
H	0.881348478574	1.311393513371	-4.244680228902
H	1.656506900919	-0.254098879133	-4.461219992232
H	3.142633405532	2.132755553905	-3.375640510159
H	3.831082127078	0.508790247491	-3.470003192825
C	0.943532455721	3.434759065412	1.975906433291
C	1.610226288701	3.916786905987	-0.405776242300
H	-0.776892747210	4.509420533759	-1.874252969439
H	-0.013131537692	2.992196209372	-2.329521186043
H	-1.684176160292	3.308549314222	-2.761116391495
H	2.408209948298	4.576908448384	-0.051499495715
H	1.928260366783	3.508593029879	-1.365881815646
H	0.736907093178	4.535480455083	-0.569068882866
H	0.780641183724	4.508800660433	1.875074427495
H	0.015088484332	2.992385143186	2.330001530592
H	1.686437674660	3.306740415427	2.761841003347
H	-2.404687770514	4.578854946467	0.052245929900
H	-1.925691314227	3.509911526282	1.366470172165
H	-0.733431933254	4.535891628824	0.569857294924

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(Me2CAAC)2 trans TS

C	-2.838775298264	1.646392886128	-0.593969060512
C	-3.003489270331	0.317123684471	-0.141083362977
C	-4.064476276040	-0.018386099885	0.719301000283
C	-4.994739582493	0.965394686451	1.044242415754
C	-4.897289441980	2.243512307913	0.541763433271
C	-3.815564889285	2.575424047006	-0.250717743128
N	-2.115849353861	-0.681419329112	-0.688102724845
C	-0.835687699550	-0.877852964007	-0.388865494442
C	-0.276406999573	-1.755618684046	-1.504258557043
C	-1.394160044554	-1.877060534530	-2.554154790070
C	-2.675958325895	-1.549247269812	-1.822053053228
C	0.697771429818	0.480215009162	0.573678995805
N	1.939435673618	-0.018452923085	0.834724598847
C	2.250194959302	-0.241420907351	2.301970188385
C	1.300781217792	0.779720989815	2.900288496257
C	0.091945898541	0.822666143029	1.964301503629
C	3.064640504757	0.128422362691	-0.048567996509
C	3.408383346026	1.411192663075	-0.524258073961
C	4.584700385705	1.574695481917	-1.247511346505
C	5.428679362289	0.517602829074	-1.518622517788
C	5.074863404688	-0.739933962843	-1.079007384484
C	3.907550357585	-0.962915771528	-0.355778134796
C	2.592044736376	2.656492027284	-0.263353662162
C	3.293344017986	3.600117901273	0.707955875842
C	3.613469629632	-2.405011643785	0.005427183442
C	4.649956694832	-3.010235453907	0.951454121824
C	-0.487132068009	2.237714876285	1.962539196386
C	-0.998836178026	-0.096929217729	2.492153691515
C	3.680862544764	0.102419527645	2.679114978519
C	1.912209320397	-1.663872799964	2.751382787160
C	-3.297211005326	-2.841992029092	-1.291453565320
C	-3.728208337852	-0.848067446619	-2.662120276356
C	0.129968405747	-3.108274364866	-0.921746603963

C	0.915290298798	-1.089553214648	-2.179202235238
C	-4.270219487765	-1.373565769773	1.366323458704
C	-4.183389156196	-1.308924809632	2.891908113850
C	-1.609530174586	2.134944806072	-1.346300335634
C	-1.386539241548	3.634057753542	-1.165928255900
C	-5.632694642522	-1.965086729971	0.994029827711
C	-1.610403568026	1.853739023552	-2.846101273980
C	3.545682024215	-3.289043619306	-1.241573665549
C	2.258275110814	3.376871501905	-1.564321682476
H	4.244091829505	3.957466147540	0.301786054985
H	2.666650564238	4.473445597364	0.909072722887
H	3.155551670766	3.698564725202	-2.098493770861
H	4.852404299894	2.567477214917	-1.590377544289
H	3.504184004466	3.113674561508	1.662146867968
H	1.667222338124	4.271979464408	-1.358060447605
H	6.347203135499	0.671441314286	-2.073264681752
H	-4.353431812385	-2.304340534616	3.310913956737
H	-5.681823862783	-3.021389931563	1.270149590763
H	1.685534598040	2.727525903714	-2.230061078288
H	1.642041957318	2.334700733381	0.164903317855
H	-4.948559493396	-0.644565411162	3.300606788269
H	-3.213659966191	-0.957217717470	3.235449882300
H	-6.431021334920	-1.449331752821	1.533280804187
H	-2.666370452891	-3.333473665418	-0.552923411632
H	3.932626209648	1.122689640089	2.389177208562
H	-3.478399314582	-2.038824138035	1.025497578342
H	-4.279247087225	-2.683389646951	-0.860095447181
H	-5.858580483351	-1.874816719292	-0.069527195465
H	-3.421382167528	-3.524817153912	-2.134759290911
H	5.718222402101	-1.582447297967	-1.305593019133
H	1.798234951192	1.754760900557	2.898597641125
H	3.780117708324	0.023951578073	3.765016868403
H	4.414628689278	-0.559500898190	2.224617052374
H	-5.812936507399	0.713533762097	1.708648521846
H	-1.428961149039	-2.868510321615	-3.008928978679
H	-4.609049141518	-0.601688020744	-2.066374110364
H	1.027071628135	0.549242271577	3.932826161527
H	5.634721396700	-3.031896870054	0.477988398456
H	-4.043205292124	-1.528113944538	-3.457365968604
H	4.749725208921	-2.461246418045	1.886837131194
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(Me2CAAC)2 trans

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H	-1.964867988123	0.892574621207	2.007425205072

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