Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

2,3-Diamino-4,5-diaryl cyclopentadienone iron carbonyl complexes as catalysts for reductive amination reactions

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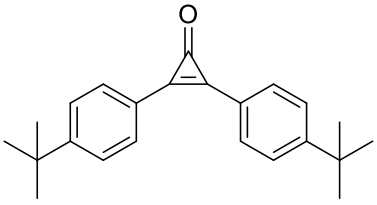
Content

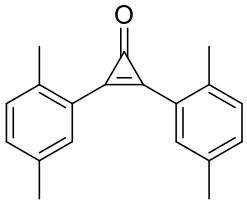
S1 Experimental Procedures

S1.1 Materials and Methods

Unless otherwise noted, all reactions have been performed in dry argon atmosphere in a Glove Box (MBraun 200B) or using a high vacuum line with common Schlenk techniques. Elevated temperatures were achieved by a silicone oil bath, whereas low temperatures were provided by an isopropanol cooling bath. Starting materials, including diphenylcyclopropenone (**2a**), were purchased from commercial sources (TCI, abcr, Merck, Roth, Alfa-Aesar) and if necessary purified by conventional techniques or dried over CaH_2. Compounds **1**, [1] **IVa** [2] and **7** [3] were prepared according to literature procedures. Solvents were dried either over Na/benzophenone, CaH_2 (chlorinated solvents) and distilled or dried by a SPS (solvent purification system) with subsequent degassing ("freeze-pump" or ultrasonic bath). They were stored in dry argon atmosphere over molecular sieves (4 Å). NMR spectra were recorded on Bruker AVII300, AVIIHD300 (300 MHz), AVIII400 (400 MHz), AVII500 (500 MHz) or AVII600 (600 MHz) if not indicated otherwise at ambient temperature. ^{1}H NMR spectra were calibrated to the residual undeuterated solvent signal (^{1}H NMR) and ^{13}C{^{1}H} NMR spectra to the solvent signal itself. ^{19}F NMR spectra were calibrated externally to $CFCl_3$. Coupling constants (*J*) are indicated in Hertz (Hz) and splitting patterns are specified as multiplett (m), singlet (s), doublet (d), triplet (t), quartet (q) or septett (sept). Elemental analyses were performed on a Vario Micro Cube System. The FTIR spectra were measured on a Vertex 70 device from Bruker either as an ATR spectrum (diamond ATR method with a Pike-MIRacle device) or as a transmission spectrum of a solution (liquid cuvette with potassium chloride window). High-resolution-mass-spectrometric-measurements (HRMS) were performed using a linear ion trap coupled with orbitrap mass analyser from ThermoFisher Scientific Inc. (LTQ-Orbitrap Velos) with a resolution of 100000 FWHM (at m/z = 400 amu) in MeOH spiked with 0.1 mg/mL tetradecyltrimethylammonium bromide as internal mass reference. Electrospray-measurements were performed in direct infusion mode using a custom made microspray-device mounted on a Proxeon nanospray ion source. Gas chromatographic measurements with mass spectrometric coupling (GC/MS) were performed on a Shimadzu GC-2010 Plus with GCMS-QP2010 SE MS detector (positive EI mode, 70 eV, 60-700 m/z). The injection was carried out at a temperature of 250 °C followed by a holding time of the temperature program at 50 °C for three minutes. Heating was carried out at a rate of 12 °C/mL for 8 minutes until the final temperature of 300 °C was reached and the final temperature was maintained for a further 8 minutes. The column used (30 m x 0.25 mm, 0.25 µm film thickness) consisted of 5% phenyl arylene and 95% dimethylpolysiloxane. Helium (volume flow 1.5 mL/min) was used as carrier gas.

S1.2 Synthesis of Diarylcyclopropenones 2

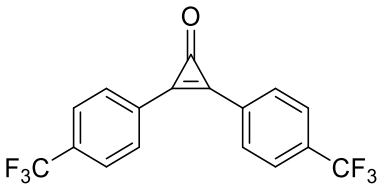




Diarylcyclopropenones 2b (R = 4-tert-butyl) and **2c** (R = 2,4-dimethyl) were prepared according to slightly adapted literature procedures:[4,5]

To a suspension of tetrachlorocyclopropene (0.28 mL, 1 eq.) and $AlCl_3$ (375.0 mg, 1 eq.) in DCM (5 mL) at -78 °C a solution of ^{t}Bu-benzene (for **2b**, 2 eq., 0.87 mL) and *p*-xylene (for 2**c**, 2 eq., 0.69 mL), respectively, in DCM (1 mL) was added. The reaction mixture was warmed up to ambient temperature

overnight and treated with H_2O (10 mL). The aqueous layer was extracted with DCM (2 x 10 mL) and the combined organic layers were washed with brine. Drying over anhydrous $MgSO_4$ and removing the solvent in vacuum lead to the desired products as colourless to beige solids. **2b** was further purified by crystallization from *n*-hexane solution.

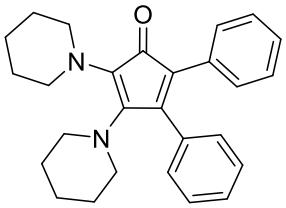


Bis(4-trifluormethylphenyl)cyclopropenone (2d) was synthesized in three steps according to slightly adapted literature procedures as follows:[6–8]

A solution of 4-(bromomethyl)(trifluoromethyl)benzene (2.19 g, 1 eq.) and $Fe_2(CO)_9$ (5.0 g, 1.5 eq.) in n-octane (50 mL) was heated to reflux for 18 h. After cooling to rt the precipitate was filtered off and extracted with hot toluene (3 x 20 mL). The solvents were removed in vacuum and the crude product was purified by column chromatography on neutral alumina (diethylether/n-hexane 2:5) affording 1,3-bis(4-(trifluoromethyl)phenyl)propan-2-one. The dibenzylketone was dissolved in glacial acid and a solution of bromine (2.2 eq.) in glacial acid was added drop by drop. The reaction mixture was stirred overnight and H_2O (15 mL) was added and it was stirred for another 30 minutes, resulting in a sticky yellow precipitate which was isolated by decantation of the supernatant solution and dried in high vacuum. Crystallization from hot n-hexane solution gave the dibromoketone. The dibromoketone was dissolved in DCM (5 mL), added to a solution of NEt_3 (2.5 eq.) in DCM (20 mL) and stirred for 45 min. It was washed with 1 M HCl (2 x 25 mL) and brine (2 x 20 mL) and dried over anhydrous $MgSO_4$. The solvent was removed in vacuum and the crude product was purified by column chromatography on silica gel (ethylacetate/n-hexane 1:4) affording pure **2d** as a colorless solid.

S1.3 Synthesis of 2,3-Diamino-4,5-diarylcyclopentadienones 3

General procedure: To a solution of the corresponding diarylcyclopropenone **2** (1 eq.) in toluene (V_A) a solution of dipiperidinoacetylene in toluene (V_B) was added at temperature T. The reaction mixture was stirred for a time t during which the colour changed to deep purple. The solvent was removed in vacuum and the crude product was purified by flash chromatography on neutral alumina with *n*-hexane/diethylether as eluent to obtain the pure product as a purple solid.



2,3-Dipiperidino-4,5-diphenylcyclopentadienone (3a). 321.7 mg diphenylcyclopropenone (**2a**), 300.0 mg dipiperidinoacetylene, V_A = 25 mL, V_B = 5 mL, 300 mg dipiperidinoacetylene, V_B = 5 mL, T = rt, t = 30 min, eluent = diethylether, yield: 363.5 mg (58%).

^{1}H-NMR (500 MHz; $CDCl_3$): δ (ppm) = 7.24–7.18 (m, 3H, Ph), 7.16–7.14 (m, 2H, Ph), 7.09–7.02 (m, 5H, Ph), 3.20–3.15 and 3.01–2.97 (m, 2 x 4H, pip-α-CH_2), 1.52–1.37 (m, 12H, pip-β/γ-CH_2).

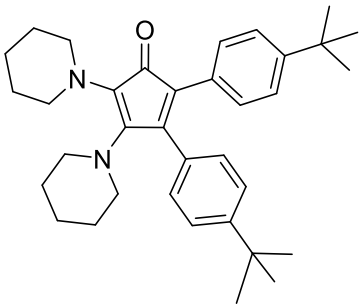
^{13}C{^{1}H}-NMR (126 MHz; $CDCl_3$): δ (ppm) = 197.7 (C=O), 161.8 (C_q–pip), 142.0 (C_q), 134.8 (C_q), 131.2 (C_q), 130.5 (CH), 128.9 (CH), 128.5 (CH), 127.8 (CH), 127.7 (CH), 127.4 (C_q), 127.2 (CH), 116.8 (C_q–pip), 53.2 and 51.5 (pip-α-CH_2), 27.0 and 26.6 (pip-β-CH_2), 2 x 24.3 (pip-γ-CH_2).

IR (neat, ATR): $\tilde{\nu}$ (cm^{-1}) = 2931 (m, CH), 2913 (m, CH), 2847 (m, CH), 1669 (m, C=C), 1623 (m, C=C), 1575 (s, C=O).

UV/Vis maximum (Et_2O): λ = 511 nm.

EA. Anal. calc. for $C_{27}H_{30}N_2O$: C 81.37, H 7.59, N 7.03; found: C 81.00, H 7.55, N 6.86.

HRMS (ESI, MeOH): exact mass calc. for $C_{27}H_{30}N_2O$: 398.23581; found: 398.23546 m/z.



2,3-Dipiperidino-4,5-bis(4-*tert*-butylphenyl)cyclopentadienone (3b). 414.0 mg bis(4-*tert*-butyl)phenylcyclopropenone (**2b**), 250 mg dipiperidinoacetylene, V_A = 25 mL, VB = 5 mL, T = rt, t = 16h, eluent = diethylether, yield: 464 mg (70%).

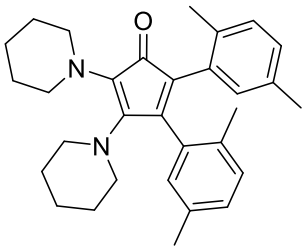
^{1}H-NMR (300 MHz; $CDCl_3$): δ (ppm) = 7.34–7.28 (m, 2H, Ar), 7.19–7.13 (m, 4H, Ar), 7.12–7.06 (m, 2H, Ar), 3.28–3.18 and 3.11–3.01 (m, 2 x 4H, pip-α-CH_2), 1.56–1.41 (m, 12H, pip-β/γ-CH_2), 1.32 and 1.24 (s, 2 x 9H, *t*Bu)

^{13}C{^{1}H}-NMR (76 MHz; $CDCl_3$): δ (ppm) = 198.2 (C=O), 162.1 (C_q–pip), 150.8 (C_q), 149.8 (C_q), 141.4 (C_q), 131.8 (C_q), 130.1 (CH), 128.6 (CH), 128.3 (C_q), 126.6 (C_q), 125.3 (CH), 124.6 (CH), 116.7 (Cq–pip), 53.2 and 51.4 (pip-α-CH_2), 34.8 and 34.6 (C_q, ^{t}Bu), 31.5 and 31.4 (CH_3, ^{t}Bu), 27.0 and 26.6 (pip-β-CH_2), 2 x 24.3 (pip-γ-CH_2).

IR (neat, ATR): $\tilde{\nu}$ (cm^{-1}) = 2961 (m, ν(CH_3)), 2929 (s, ν(CH)), 2985 (m, ν(CH)), 2791 (w, ν(CH_2)), 1682 (s, ν(C=O)).

UV/Vis maximum (Et_2O): 508 nm.

HRMS (ESI, MeOH): exact mass calc. for $C_{35}H_{46}N_2O{\cdot}H^+$: 511.36884; found: 511.36780 m/z.



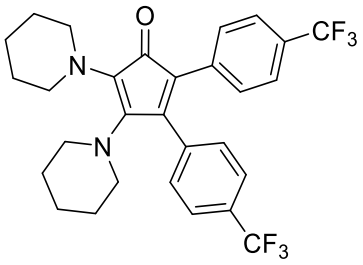
2,3-Dipiperidino-4,5-bis(2,5-dimethylphenyl)cyclopentadienone (3c). 341.1 mg bis(2,5-dimethylphenyl)cyclopropenone (**2c**), 250 mg dipiperidinoacetylene, V_A = 25 mL, V_B = 5 mL, T = rt, t = 16h., eluent = diethylether/n-hexane (1:1), yield: 223 mg (38 %).

IR (neat, ATR): $\tilde{\nu}$ (cm^{-1}) = 2922 (m, $\nu(CH_2)$), 2851 (m, $\nu(CH_2)$), 1682 (s, ν(C=O)).

UV/Vis maximum (Et_2O): λ = 506 nm.

EA. Anal. calc. for $C_{31}H_{38}N_2O$: C 81.89, H 8.42, N 6.16; found: C 81.41, H 8.44, N 5.74.

HRMS (ESI, MeOH): exact mass calc. for $C_{31}H_{38}N_2O{\cdot}H^+$: 455.30624; found: 455.30443 m/z.



2,3-Dipiperidino-4,5-bis(4-trifluormethylphenyl)cyclopentadienone (3d). 200 mg bis((*p*-trifluoromethyl)-phenyl)cyclopropenone (**2d**), 112.2 mg dipiperidinoacetylene, V_A = 20 mL, V_B = 5 mL, T = – 50 °C to rt, t = 16h, eluent = diethylether, yield = 203 mg (65 %).

^{1}H-NMR (500 MHz; $CDCl_3$): δ (ppm) = 7.63–7.58 (dm, $^3J_{H,H}$ = 8.2 Hz, 2H, Ar), 7.44–7.41 (dm, $^3J_{H,H}$ = 8.2 Hz, 2H, Ar), 7.37–7.34 (dm, $^3J_{H,H}$ = 8.2 Hz, 2H, Ar), 7.19–7.16 (dm, $^3J_{H,H}$ = 8.2 Hz, 2H, Ar), 3.24–3.19 and 3.07–3.02 (m, 2 x 4H, pip-α-CH_2), 1.61–1.53 and 1.53–1.46 (m, 2 x 6H, pip-β/γ-CH_2).

^{13}C{^{1}H}-NMR (126 MHz; $CDCl_3$): δ (ppm) = 196.3 (C=O), 142.3 (C_q-pip), 138.0–137.9 (m, C_{ipso}), 134.2–134.1 (m, C_{ipso}), 130.7 (*o*-CH), 130.3 (q, $^2J_{C,F}$ = 30.5 Hz, *C*–CF_3), 129.4 (q, $^2J_{C,F}$ = 30.5 Hz, *C*–CF_3), 129.1 (*o*-CH), 127.0 (C_q–Ar), 125.6 (q, $^3J_{C,F}$ = 3.8 Hz, *m*-CH), 124.9 (q, $^3J_{C,F}$ = 3.8 Hz, *m*-CH), 124.3 (q, $^1J_{C,F}$ = 272.2 Hz, CF_3), 124.1 (q, $^1J_{C,F}$ = 272.2 Hz, CF_3), 117.6 (C_q-pip), 53.2 and 51.6 (pip-α-CH_2), 26.9 and 26.6 (pip-β-CH_2), 24.2 and 24.1 (pip-γ-CH_2), .

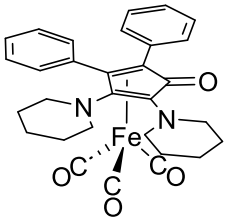
^{19}F{^{1}H}-NMR (377 MHz; $CDCl_3$): δ (ppm) = – 63.0 (s), – 63.1 (s).

IR (neat, ATR): $\tilde{\nu}$ (cm^{-1}) = 2935 (m, $\nu(CH_2)$), 2852 (w, $\nu(CH_2)$), 1681 (m, ν(C=O)).

HRMS (ESI, MeOH): exact mass calc. for $C_{29}H_{28}F_6N_2O$: 534.21058; found: 534.21025 m/z.

S1.4 Synthesis of CPD Iron Tricarbonyl Complexes 4

General procedure: A solution of the corresponding cyclopentadienone **3** (1 eq.) and $Fe_2(CO)_9$ (2 eq.) in toluene (V) was heated to 110 °C for 16h. The solvent was removed in vacuum and the crude product was purified by flash chromatography on neutral alumina with DCM as eluent to afford the pure product as a yellow solid.



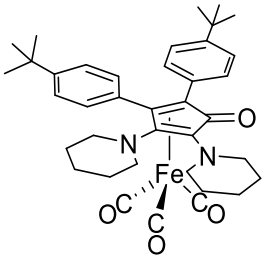
[(2a)Fe(CO)$_3$] (4a). 363.5 mg cyclopentadienone **3a**, 663.6 mg $Fe_2(CO)_9$, V = 40 mL, yield: 414 mg (84%).

^{1}H-NMR (500 MHz; $CDCl_3$): δ (ppm) = 7.43–7.38 (m, 2H, Ph), 7.36–7.30 (m, 3H, Ph), 7.20–7.15 (m, 2H, Ph), 7.08–7.03 (m, 3H, Ph), 3.66–3.49 and 3.40–3.30 (m, 2 x 2H, pip-α-CH_2), 2.95–2.76 (m, 4H, pip-α-CH_2), 1.77–1.57 and 1.47–1.32 (m, 2 x 6H, pip-β/γ-CH_2).

^{13}C{^{1}H}-NMR (75 MHz; $CDCl_3$): δ (ppm) = 211.0 (C≡O), 165.9 (C=O), 133.2 (*ipso*-C_q), 132.9 (CH), 131.8 (*ipso*-C_q), 131.0 (CH), 2 x 128.5 (2 x CH), 127.6 (CH), 127.0 (CH), 118.5 and 108.0 (C_q–pip), 82.6 and 74.1 (C_q–Ph), 50.7 and 49.6 (pip-α-CH_2), 2 x 25.8 (pip-β-CH_2), 24.3 and 23.8 (pip-γ-CH_2).

IR (neat, ATR): $\tilde{\nu}$ (cm^{-1}) = 2938 (w, CH_2), 2853 (w, CH_2), 2031 (m, C≡O), 1973 (s, C≡O), 1643 (m, C=O).

EA. Anal. calc. for $C_{30}H_{30}N_2O_4Fe$: C 66.92, H 5.62, N 5.20; found: C 66.71, H 5.64, N 5.10.



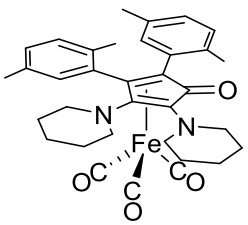
[(3b)Fe(CO)$_3$] (4b). 169.0 mg cyclopentadienone **3b**, 240.7 mg $Fe_2(CO)_{12}$, V = 10 mL, yield: 143.0 mg (66%).

^{1}H-NMR (300 MHz; $CDCl_3$): δ (ppm) = 7.37–7.30 (m, 4H, Ar), 7.12–7.02 (m, 4H, Ar), 3.64–3.49 and 3.40–3.28 (m, 2 x 2H, pip-α-CH_2), 2.95–2.74 (m, 4H, pip-α-CH_2), 1.77–1.57 (m, 6H, pip-β/γ-CH_2), 1.44–1.32 (m, 15H, pip-β/γ-CH_2 and *t*Bu), 1.20 (s, 9H, *t*Bu).

^{13}C{^{1}H}-NMR (75 MHz; $CDCl_3$): δ (ppm) = 211.1 (C≡O), 165.8 (C=O), 151.6 and 149.6 (C–*t*Bu), 132.5 (CH), 130.4 (CH), 130.0 and 128.6 (*ipso*–C_q), 125.4 (CH), 124.5 (CH), 118.6 and 107.9 (C_q–pip), 82.5 and 74.0 (C_q–Ar), 50.7 and 49.5 (pip-α-CH_2), 34.8 and 34.5 (C_q, tBu), 31.5 and 31.3 (CH_3, *t*Bu), 25.8 (pip-β-CH_2), 24.3 and 23.9 (pip-γ-CH_2).

IR (neat, ATR): $\tilde{\nu}$ (cm^{-1}) = 2922 (w, CH_2), 2856 (w, CH_2), 2031 (m, C≡O), 1960 (s, C≡O), 1636 (m, C=O).

EA. Anal. calc. for $C_{38}H_{46}N_2O_4Fe{\cdot}CHCl_3$: C 60.83, H 6.15, N 3.64; found: C 60.38, H 6.09, N 3.57.



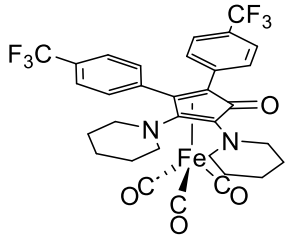
[(3c)Fe(CO)$_3$] (4c). 172.0 mg cyclopentadienone **3c**, 275.2 mg $Fe_2(CO)_9$, V = 10 mL, yield: 183.0 mg (81%).

^{1}H-NMR (400 MHz; $CDCl_3$): δ (ppm) = 7.16 (s, 1H, *o*-CH), 7.13−7.09 and 7.06−7.01 (m, 2 x 1H, *m/p*-CH), 6.98−6.93 and 6.84−6.79 (m, 2 x 1H, *m/p*-CH), 6.53 (s, 1H, *o*-CH), 3.67−3.45 and 3.31−3.19 (m, 2 x 2H, pip-α-CH_2), 3.08−2.92 and 2.87−2.76 (m, 2 x 2H, pip-α-CH_2), 2.41 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 1.92 (s, 3H, CH_3), 1.77−1.58 and 1.49−1.32 (m, 6H, pip-β/γ-CH_2).

^{13}C{^{1}H}-NMR (101 MHz; $CDCl_3$): δ (ppm) = 211.3 (C≡O), 164.4 (C=O), 136.3 (*o*-C_q), 135.9 (*ipso*-C_q), 135.6 (*o*-C_q), 134.9 (*o*-CH), 133.5 (*ipso*-C_q), 132.6 (*m*-C_q), 132.1 (*o*-CH), 131.0 (*m*-CH), 129.5 (*m*-CH), 129.4 (*m*-C_q), 129.2 (p-CH), 128.2 (p-CH), 119.4 and 108.7 (C_q−pip), 80.3 (C_q−Ar, only one peak with $^3J_{C,H}$ correlation to the *ortho*-proton in ^{1}H,^{13}C-HMBC could be observed), 51.1 and 48.1 (pip-α-CH_2), 2x 25.8 (pip-β-CH_2), 24.2 and 23.8 (pip-γ-CH_2), 22.3 (*o*-CH_3), 21.1 (*m*-CH_3), 20.8 (*o*-CH_3), 20.7 (*m*-CH_3).

IR (neat, ATR): ν (cm^{-1}) = 2981 (w, CH_2), 2935 (w, CH_2), 2853 (w, CH_2), 2032 (m, C≡O), 1975 (s, C≡O), 1959 (s, C≡O), 1635 (m, C=O).

EA. Anal. calc. for $C_{34}H_{38}FeN_2O_4$: C 68.69, H 6.44, N 4.71; found: C 68.11, H 6.51, N 4.60.



[(3d)Fe(CO)$_3$] (4d). 187.0 mg cyclopentadienone **3d**, 254.5 mg $Fe_2(CO)_9$, V = 20 mL, yield: 171 mg (72 %).

^{1}H-NMR (600 MHz; $CDCl_3$): δ (ppm) = 7.67−7.61 (m, 2H, *m*-CH), 7.59−7.53 (m, 2H, *o*-CH), 7.37−7.31 (m, 2H, *m*-CH), 7.30−7.24 (m, 2H, *o*-CH), 3.67−3.48 and 3.39−3.28 (m, 2 x 2H, pip-α-CH_2), 2.95−2.75 (m, 4H, pip-α-CH_2), 1.78−1.58 and 1.49−1.32 (m, 2 x 6H, pip-β/γ-CH_2).

^{13}C{^{1}H}-NMR (125 MHz; $CDCl_3$): δ (ppm) = 209.9 (C≡O), 165.5 (C=O), 137.0 and 135.6 (C_q, *ipso*-Ar), 132.8 (*o*-CH), 130.7 (q, $^2J_{C-F}$ = 32.7 Hz, *C*-CF_3), 130.5 (*o*-CH), 128.6 (q, $^2J_{C-F}$ = 32.5 Hz, *C*-CF_3), 125.4 and 124.4 (m, *m*-CH), 123.8 (q, $^1J_{C-F}$ = 272.3 Hz, CF_3), 123.7 (q, $^1J_{C-F}$ = 272.6 Hz, CF_3), 118.2 and 108.5 (C_q−pip), 79.5 and 71.3 (C_q−Ar), 50.3 and 49.3 (pip-α-CH_2), 25.4 and 25.3 (pip-β-CH_2), 23.8 and 23.3 (pip-γ-CH_2).

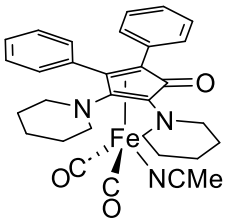
^{19}F{^{1}H}-NMR (471 MHz; $CDCl_3$): δ (ppm) = − 63.1 (s), − 63.3 (s).

IR (neat, ATR): $\tilde{\nu}$ (cm^{-1}) = 2037 (s, C≡O), 1967 (s, C≡O), 1631 (m, C=O).

EA. Anal. calc. for $C_{32}H_{28}F_6FeN_2O_4$: C 56.99, H 4.18, N 4.15; found: C 56.87, H 4.28, N 4.05.

S1.5 Synthesis of CPD Iron Dicarbonyl Acetonitrile Complexes 5 and 6

General procedure: The corresponding iron tricarbonyl complex **4** (1 eq.) was dissolved in toluene (V_A) and a solution of trimethyl-*N*-oxide (1 eq.) in acetonitrile (V_B) was carefully added at ambient temperature by which a gas evolution could be observed. After stirring for 3h, the solvent was removed *in vacuo* remaining a sticky residue. It was crystallized from toluene/*n*-hexane or acetonitrile (V_C) at −40 °C to afford the desired complex as an orange solid.



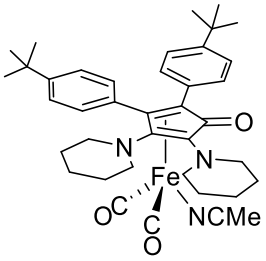
[(3a)Fe(CO)$_2$(NCMe)] (5a). 200.0 mg **4a**, 27.9 mg trimethyl-*N*-oxide, V_A = 10 mL, V_B = 1 mL, V_C (toluene/*n*-hexane) = 1 : 1.5 mL, yield = 120 mg (59 %).

^{1}H-NMR (500 MHz; dcm-d$_2$): δ (ppm) = 7.41–7.34 and 7.34–7.28 (m, 2H, *o*-CH), 7.27–7.19 and 7.09–7.02 (m, 3H, *m*/*p*-CH), 3.55–3.43 and 3.42–3.30 (m, 2 x 2H, pip-α-CH$_2$), 2.80 (br s, 4H, pip-α-CH$_2$), 2.20 (s, 3H, NCCH$_3$), 1.71–1.52 and 1.42–1.29 (m, 6H, pip-β/γ-CH$_2$).

^{13}C{^{1}H}-NMR (126 MHz; dcm-d$_2$): δ (ppm) = 216.0 and 214.1 (C≡O), 164.5 (C=O), 135.2 and 135.1 (*ipso*-C$_q$), 132.8 and 130.9 (*o*-CH), 128.0 (*m*-CH), 127.7 (*p*-CH), 127.4 (*m*-CH and NC$\underline{C}$H$_3$), 126.0 (*p*-CH), 120.2 and 101.2 (C$_q$–pip), 82.6 and 73.0 (C$_q$–Ar), 51.2 and 50.5 (pip-α-CH$_2$), 26.9 and 26.5 (pip-β-CH$_2$), 24.8 and 24.4 (pip-γ-CH$_2$), 4.8 (NC$\underline{C}$H$_3$).

IR (TM, THF): $\tilde{\nu}$ (cm^{-1}) = 1981 (s, C≡O), 1926 (s, C≡O), 1617 (m, C=O).

EA. Anal. calc. for $C_{31}H_{33}N_3O_3Fe$: C 67.52, H 6.03, N 7.62; found: C 67.87, H 6.20, N 7.30.



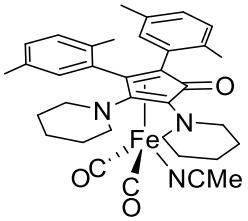
[(3b)Fe(CO)$_2$(NCMe)] (5b). 200.0 mg **4b**, 23.1 mg trimethyl *N*-oxide, V_A = 10 mL, V_B = 1 mL, V_C (toluene/*n*-hexane) = 2 : 4 mL, yield = 116 mg (57 %).

^{1}H-NMR (400 MHz; dcm-d$_2$): δ (ppm) = 7.31 (d, $^3J_{H,H}$ = 8.3 Hz, 2H, *m*-CH), 7.28–7.21 (m, 4H, *o*/*m*-CH), 7.10 (d, $^3J_{H,H}$ = 8.3 Hz, 2H, *o*-CH), 3.55–3.42 and 3.40–3.30 (m, 2 x 2H, pip-α-CH$_2$), 2.78 (br s, 4H, pip-α-CH$_2$), 2.20 (s, 3H, NCCH$_3$), 1.68–1.51 (m, 6H, pip-β/γ-CH$_2$), 1.38–1.27 (m, 15H, pip-β/γ-CH$_2$ and *t*Bu), 1.24 (s, 9H, *t*Bu).

^{13}C{^{1}H}-NMR (101 MHz; dcm-d$_2$): δ (ppm) = 216.1 and 214.3 (C≡O), 164.6 (C=O), 151.1 and 148.8 ($\underline{C}$–*t*Bu), 132.5 (*m*-CH), 132.1 and 131.8 (*ipso*-C$_q$), 130.5 (*m*-CH), 127.4 (N$\underline{C}$CH$_3$), 125.0 (*o*-CH), 124.4 (*o*-CH), 120.2 and 101.3 (C$_q$–pip), 82.6 and 73.2 (C$_q$–Ar), 51.3 and 50.5 (pip-α-CH$_2$), 34.8 and 34.6 (C$_q$, *t*Bu), 2 x 31.4 (CH$_3$, *t*Bu), 26.9 and 26.5 (pip-β-CH$_2$), 24.9 and 24.5 (pip-γ-CH$_2$), 4.8 (NC$\underline{C}$H$_3$).

IR (TM, THF): $\tilde{\nu}$ (cm^{-1}) = 1980 (s, C≡O), 1923 (s, C≡O), 1616 (m, C=O).

EA. Anal. calc. for $C_{39}H_{49}FeN_3O_3$: C 70.58, H 7.44, N 6.33; found: C 70.65, H 7.44, N 6.10.



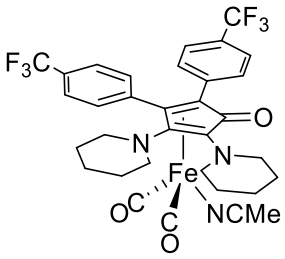
[(3c)Fe(CO)$_2$(NCMe)] (5c). 135.0 mg **4c**, 17.1 mg trimethyl-*N*-oxide, V_A = 10 mL, V_B = 1 mL, V_C (toluene/*n*-hexane) = 1 : 4 mL, yield = 71 mg (51 %).

^{1}H-NMR (500 MHz; dcm-d$_2$): δ (ppm) = 7.26 (s, 1H, *o*-CH), 7.06 (s, 1H, *o*-CH), 6.96–6.91 (m, 1H, m-CH), 6.91–6.85 (m, 2H, p-CH), 6.84–6.77 (m, 1H, m-CH), 3.56–3.36 and 2.87–2.69 (m, 2 x 4H, pip-α-CH$_2$), 2.29 (s, 3H, o-CH$_3$), 2.21 (s, 6H, m-CH$_3$ and CH$_3$CN), 2.18 (s, 3H, m-CH$_3$), 2.10 (s, 3H, o-CH$_3$), 1.73–1.51 and 1.43–1.29 (m, 2x 6H pip-β/γ-CH$_2$).

^{13}C{^{1}H}-NMR (126 MHz; dcm-d$_2$): δ (ppm) = 217.4 and 214.1 (C≡O), 163.6 (C=O), 136.8 (*ipso*-C$_q$), 135.2 (*o*-C$_q$), 135.1 (*ipso*-C$_q$), 134.7 (*m*-C$_q$), 134.3 (*o*-CH), 134.1 (*o*-C$_q$), 133.8 (*m*-C$_q$), 132.6 (*o*-CH), 130.2 (*p*-CH), 129.5 (*m*-CH), 128.4 (*p*-CH), 127.5 (*m*-CH), 127.4 (CH$_3$<u>C</u>N), 118.0 and 104.8 (C$_q$–pip), 80.3 (C$_q$–Ar, only one peak with $^3J_{C,H}$ correlation to the *ortho*-proton in ^{1}H,^{13}C-HMBC could be observed), 51.8 and 49.0 (pip-α-CH$_2$), 26.9 and 26.3 (pip-β-CH$_2$), 24.8 and 24.4 (pip-γ-CH$_2$), 21.3 (*m*-CH$_3$), 20.9 (*m*-CH$_3$), 20.7 (*o*-CH$_3$), 20.6 (*o*-CH$_3$), 4.7 (<u>C</u>H$_3$CN).

IR (TM, THF): $\tilde{\nu}$ (cm^{-1}) = 1976 (s, C≡O), 1922 (s, C≡O), 1615 (s, C=O).

EA. Anal. calc. for $C_{35}H_{41}FeN_3O_3$: C 69.19, H 6.80, N 6.92; found: C 68.75, 6.96, 6.48.



[(3d)Fe(CO)$_2$(NCMe)] (5d). 100.0 mg **4d**, 11.1 mg trimethyl-*N*-oxide, V_A = 5 mL, V_B = 0.5 mL, V_C (acetonitrile) = 1 mL, product was additionally washed with 5 portions of 0.5 mL cold *n*-hexane. Yield = 65 mg (64 %).

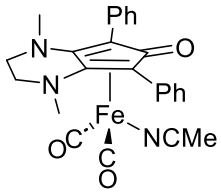
^{1}H-NMR (500 MHz; dcm-d$_2$): δ (ppm) = 7.58–7.50 (m, 4H,), 7.49–7.43 (m, 2H,), 7.35–7.29 (m, 2H,), 3.54–3.42 and 3.40–3.29 (m, 2 x 2H,), 2.90–2.74 (m, 4H,), 2.21 (s, 3H, CH$_3$CN), 1.72–1.52 and 1.43–1.29 (2 x 6H,).

^{13}C{^{1}H}-NMR (126 MHz; dcm-d$_2$): δ (ppm) = 215.2 and 213.4 (C≡O), 164.5 (C=O), 139.7 and 139.5 (*ipso*-C$_q$), 133.3 and 130.5 (*o*-CH), 129.9 (q, $^2J_{C-F}$ = 32.4 Hz, <u>*C*</u>–CF$_3$), 127.8 (CH$_3$<u>*C*</u>N), 127.4 (q, $^2J_{C-F}$ = 32.2 Hz, <u>*C*</u>–CF$_3$), 125.2 (q, $^3J_{C-F}$ = 3.8 Hz, *m*-CH), 124.9 (q, $^1J_{C-F}$ = 271.4 Hz, CF$_3$), 124.6 (q, $^1J_{C-F}$ = 272.0 Hz, CF$_3$), 124.4 (q,f $^3J_{C-F}$ = 3.8 Hz, *m*-CH), 121.2 and 101.0 (C$_q$–pip), 80.9 and 70.0 (C$_q$–Ar), 51.3 and 50.7 (pip-α-CH$_2$), 26.9 and 26.4 (pip-β-CH$_2$), 24.7 and 24.3 (pip-γ-CH$_2$), 4.8 (<u>*C*</u>H$_3$CN).

^{19}F{^{1}H}-NMR (471 MHz; CDCl$_3$): δ (ppm) = −62.7, −62.8.

IR (TM, THF): $\tilde{\nu}$ (cm^{-1}) = 1987 (s, C≡O), 1932 (s, C≡O), 1623 (s, C=O).

EA. Anal. calc. for $C_{33}H_{31}F_6FeN_3O_3$: C 57.66, H 4.55, N 6.11; found: C 57.25, H 4.43, N 5.83.



[(II)Fe(CO)$_2$NCMe] (6). The 3,4-diamino-2,5-diphenylcyclo-pentadienone **II** and [(**II**)Fe(CO)$_3$] were prepared according to literature procedures.[9,10] Then, **6** was prepared according to the general procedure for the CPD iron dicarbonyl acetonitrile complexes: 100 mg [(**II**)Fe(CO)$_3$], 17.6 mg trimethyl-*N*-oxide, V_A = 5 mL, VB = 0.5 mL, V_C (toluene/*n*-hexane) = 5 : 8 mL, yield = 83 mg (75%).

^{1}H-NMR (300 MHz; dcm-d$_2$): δ (ppm) = 7.61−7.52 (m, 4H, Ph), 7.44−7.29 (m, 6H, Ph), 3.26−3.14 and 2.69−2.58 (m, 2 x 2H, NCH_2), 2.25 (s, 6H, NCH_3), 2.14 (s, 3H, CH_3CN).

^{13}C{^{1}H}-NMR (76 MHz; dcm-d$_2$): δ (ppm) = 214.8 (C≡O), 164.1 (C=O), 135.0 (*i*-Ph), 132.7 and 128.4 (*o*/*m*-Ph), 127.4 (*p*-Ph), 125.8 ($CH_3\underline{C}N$), 111.6 (C_q−N), 70.1 (C_q−Ph), 50.1 (CH_3−N), 41.5 (CH_2−N), 4.6 (CH_3CN).

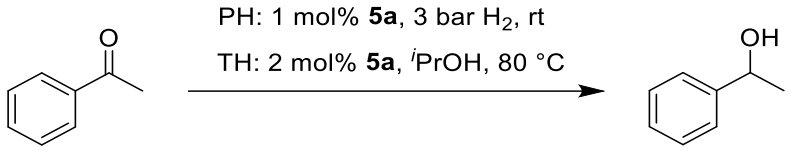
IR (TM, THF): $\tilde{\nu}$ (cm^{-1}) = 1970 (s, C≡O), 1909 (s, C≡O), 1627 (s, C=O).

EA. Anal. calc. for $C_{25}H_{23}FeN_3O_3$: C 63.98, H 4.94, N 8.95; found: C 64.43, H 4.93, N 8.45.

S1.6 Catalytic (Transfer-)Hydrogenation of Acetophenone

Pressure-Hydrogenation (PH): Acetophenone (60.0 mg, 0.5 mmol, 1 Äq.), **5a** (2.8 mg, 1 mol%) and *n*-decane (10 mg) as internal standard were dissolved in toluene (2 mL), transferred in a Büchi® 20 mL "tiny clave" pressure reactor and a T_0 sample was taken. It was purged with hydrogen, charged with 3 bar and stirred at ambient temperature for 16h and a second sample was taken. The conversion was determined by GC/MS: >99%.

Transfer-Hydrogenation (TH): Acetophenone (120.0 mg, 1.0 mmol, 1 Äq.), **5a** (11.0 mg, 2 mol%) and *n*-decane as internal standard were dissolved in isopropanol (2 mL) and a T_0 sample was taken. The reaction mixture was heated to 80 °C and samples were taken after certain times. The conversions were determined by GC/MS. Conversion after 16h: 93%.



Scheme S1: (Transfer-)Hydrogenation of acetophenone using **4a** as precatalyst.

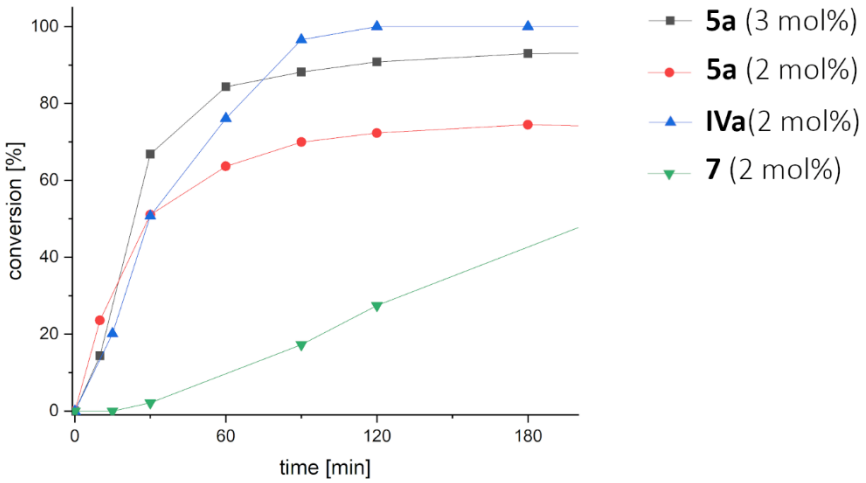
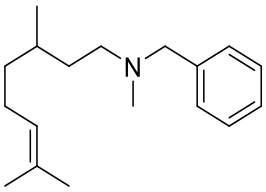


Figure S1: Time conversion diagram of the transfer-hydrogenation of acetophenone using 5a, IVa and 7 as precatalysts.[2]

S1.7 Catalytic Reductive Amination Reactions

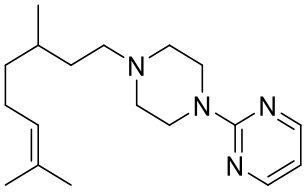
Citronellal (**8**, 77.1 mg, 0.5 mmol, 1 eq.), the secondary amine (0.6 mmol, 1.2 eq.) and the precatalyst [Fe] in 1 mL EtOH were submitted to a Büchi® 20 mL "tiny clave" pressure reactor and charged with 5 bar hydrogen pressure (after flushing 4 times). The mixture was stirred at a certain temperature for 16h. DCM (10 mL) was added, and it was washed with a saturated $NaHCO_3$ solution (10 mL). It was dried over anhydrous $MgSO_4$ and the solvent was evaporated in vacuum. In case of incomplete conversion, the product was separated by column chromatography on silica gel (*n*-hexane/ethylacetate), yielding the products as yellow to colourless oils.



***N*-benzyl-*N*-3,7-trimethyloct-6-en-1-amine (10).** Yield: 115 mg (89%). The NMR data fits to those reported in the literature.[11]

^{1}H-NMR (300 MHz; $CDCl_3$): δ (ppm) = 7.39-7.24 (m, 5H, CH_{Ar}), 5.20-5.09 (m, 1H, $\underline{H}C{=}CMe_2$), 3.59-3.45 (m, 2H, N−CH_2−Ph), 2.43 (t, $^3J_{H,H}$ = 8.0 Hz, N−CH_2), 2.22 (s, 3H, N−CH_3), 2.11-1.93 (m, 2H, CH_2), 1.73 (s, 3H, =$C(CH_3)_2$), 1.64 (s, 3H, =$C(CH_3)_2$), 1.61-1.46 (m, 2H, CH_2), 1.44-1.29 (m, 2H, CH_2), 1.27-1.20 (m, 1H, $C\underline{H}$−CH_3), 0.91 (d, $^3J_{H,H}$ = 6.7 Hz, 3H, CH−$C\underline{H}_3$).

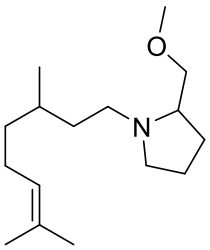
^{13}C{^{1}H}-NMR (76 MHz; $CDCl_3$): δ (ppm) = 139.4 (*i*-C_q), 131.2 (CH=$\underline{C}Me_2$), 129.2 (CH_{Ar}), 128.3 (CH_{Ar}), 127.0 (CH_{Ar}), 125.1 ($H\underline{C}{=}CMe_2$), 62.5 (N−CH_2−Ph), 55.7 (N−CH_2), 42.4 (N−CH_3), 37.4 (CH_2), 34.6 (CH_2), 31.0 ($\underline{C}$H−Me), 25.9 (C=C($\underline{C}H_3)_2$), 25.6 ((=CH−$\underline{C}H_2$), 19.8 (CH−$\underline{C}H_3$), 17.8 (C=C($\underline{C}H_3)_2$).



2-(4-(3,7-dimethyloct-6-en-1-yl)piperazin-1-yl)pyrimidine (11). Yield 144 mg (95%). The NMR data fits to those reported in the literature.[12]

^{1}H-NMR (300 MHz; $CDCl_3$): δ (ppm) = 8.30 (d, $^3J_{H,H}$ = 4.7 Hz, 2H, *m*-CH), 6.47 (t, $^3J_{H,H}$ = 4.7 Hz, 1H, *p*-CH), 5.13-5.05 (m, 1H, $\underline{H}C{=}CMe_2$), 3.89-3.75 (m, 4H, N−CH_2), 2.54−2.45 (m, 4H, N−CH_2), 2.43-2.33 (m, 2H, CH_2), 2.05-1.89 (m, 2H, CH_2), 1.70-1.66 (m, 3H, =$C(CH_3)_2$), 1.61-1.58 (m, 3H, =$C(CH_3)_2$), 1.55-1.40 (m, 2H, CH_2), 1.40-1.26 (m, 2H, CH_2), 1.25-1.09 (m, 1H, $C\underline{H}$−CH_3), 0.90 (d, $^3J_{H,H}$ = 6.4 Hz, 3H, CH−$C\underline{H}_3$).

^{13}C{^{1}H}-NMR (76 MHz; $CDCl_3$): δ (ppm) = 161.8 (*i*-C_q), 157.8 (*m*-CH), 131.3 (CH=$\underline{C}Me_2$), 124.9 ($H\underline{C}{=}CMe_2$), 109.9 (*p*-CH), 57.1 (N−CH_2), 53.4 (N−CH_2), 43.9 (N−CH_2), 37.4 (CH_2), 34.0 (CH_2), 31.3 ($\underline{C}$H−Me), 25.9 (C=C($\underline{C}H_3)_2$), 25.5 (C=CH−$\underline{C}H_2$), 19.9 (CH−$\underline{C}H_3$), 17.8 (C=C($\underline{C}H_3)_2$).

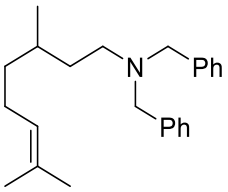


1-(3,7-dimethyloct-6-en-1-yl)-2-(methoxymethyl)pyrrolidine (12). Yield 119 mg (94%).

^{1}H-NMR (300 MHz; $CDCl_3$): δ (ppm) = 5.12–5.06 (m, 1H, $\underline{H}C{=}CMe_2$), 3.44–3.39 (m, 1H, O–CH_2), 3.34 (s, 3H, OCH_3), 3.29–3.23 (m, 1H, O–CH_2), 3.17–3.10 (m, 1H, N–CH_2), 2.91–2.78 (m, 1H, N–CH_2), 2.58–2.48 (m, 1H, N–CH_2), 2.28–2.18 (m, 1H, N–CH_2), 2.18–2.08 (m, 1H, N–CH_2), 2.04–1.92 (m, 2H, =CH–C$\underline{H}_2$) 1.92–1.82 (m, 1H, CH_2), 1.79–1.68 (m, 2H, CH_2), 1.67 (s, 3H, =C(C$\underline{H}_3$)$_2$), 1.66–1.60 (m, 1H, CH_2), 1.59 (s, 3H, =C(C$\underline{H}_3$)$_2$), 1.57–1.40 (m, 1H, C$\underline{H}$–Me), 1.38–1.24 (m, 3H, CH_2), 1.22–1.10 (m, 1H, CH_2), 0.89/0.87 (2 x d, 3H, CH–C$\underline{H}_3$).

^{13}C{^{1}H}-NMR (76 MHz; $CDCl_3$): δ (ppm) = 131.2 (CH=$\underline{C}Me_2$), 125.1 (H$\underline{C}$=CMe_2), 76.5 (O–CH_2), 63.9/63.8 (N–CH), 59.2 (O–CH_3), 54.8/54.6 (N–CH_2), 54.0/53.8 (N–CH_2), 37.6/37.2 (CH_2), 36.0/35.9 (CH_2), 31.3/31.2 ($\underline{C}$H–Me), 28.6 (CH_2), 25.9 (C=C($\underline{C}H_3$)$_2$), 25.7/25.6 (=CH–$\underline{C}H_2$), 23.1/23.0 (CH_2), 20.0/19.8 (CH–$\underline{C}H_3$), 17.8 (C=C($\underline{C}H_3$)$_2$).

HRMS (ESI, MeOH): exact mass calc. for $C_{16}H_{31}NO{\cdot}H^+$: 254.24839; found: 254.24800 m/z.

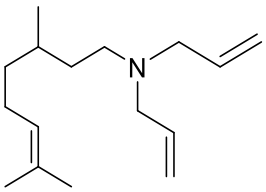


N,N-dibenzyl-3,7-dimethyloct-6-en-1-amine (16). Yield: 103 mg (61%).

^{1}H-NMR (400 MHz; $CDCl_3$): δ (ppm) = 7.39-7.35 (m, 4H, *o*-CH_{Ar}), 7.33-7.28 (m, 4H, *m*-CH_{Ar}), 7.25-7.20 (m, 2H, *p*-CH_{Ar}), 5.09-5.03 (m, 1H, $\underline{H}C{=}CMe_2$), 3.59 (d, $^2J_{H,H}$ = 13.6 Hz, 2H, N–CH_2–Ph), 3.51 (d, $^2J_{H,H}$ = 13.6 Hz, 2H, N–CH_2–Ph), 2.46-2.40 (m, 2H, N–CH_2), 2.02-1.82 (m, 2H, CH_2), 1.69-1.67 (m, 3H, =C(CH_3)$_2$), 1.59-1.57 (m, 3H, =C(CH_3)$_2$), 1.56-1.42 (m, 2H, CH_2), 1.35-1.20 (m, 2H, CH_2), 1.13-1.03 (m, 1H, C$\underline{H}$–CH_3), 0.76 (d, $^3J_{H,H}$ = 6.6 Hz, 3H, CH–C$\underline{H}_3$).

^{13}C{^{1}H}-NMR (101 MHz; $CDCl_3$): δ (ppm) = 140.2 (*i*-C_q), 131.1 (CH=$\underline{C}Me_2$), 128.9 (CH_{Ar}), 128.2 (CH_{Ar}), 126.8 (CH_{Ar}), 125.1 (H$\underline{C}$=CMe_2), 58.5 (N–CH_2–Ph), 51.5 (N–CH_2), 37.3(CH_2), 34.2 (CH_2), 30.5 ($\underline{C}$H–Me), 25.9 (C=C($\underline{C}H_3$)$_2$), 25.6 (C=CH–$\underline{C}H_2$), 19.8 (CH–$\underline{C}H_3$), 17.8 (C=C($\underline{C}H_3$)$_2$).

HRMS (ESI, MeOH): exact mass calc. for $C_{24}H_{33}N{\cdot}H^+$: 336.26912; found: 336.26876.

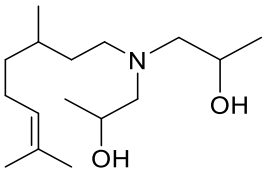


N,N-diallyl-3,7-dimethyloct-6-en-1-amine (18). Yield: 104 mg (89%).

^{1}H-NMR (300 MHz; $CDCl_3$): δ (ppm) = 5.94–5.77 (m, 2H, H<u>C</u>=), 5.21-5.04 (m, 4H, HC=C<u>H</u>$_2$), 3.14–3.00 (m, 4H, allyl NCH_2), 2.04–1.88 (m, 2H, NCH_2), 1.68 (s, CH_3, =CMe_3), 1.60 (s, CH_3, =CMe_3), 1.56–1.07 (m, 5H, CH and 2 x CH_2), 0.87 (d, $^{3}J_{H,H}$ = 0.87 Hz).

^{13}C{^{1}H}-NMR (76 MHz; $CDCl_3$): δ (ppm) = 136.0 (H<u>C</u>=CH_2), 131.2 (CH=<u>C</u>Me_2), 125.0 (H<u>C</u>=CMe_2), 117.4 (HC=<u>C</u>H_2), 57.0 (allyl CH_2), 51.4 (N–CH_2), 37.4 (CH_2), 33.9 (CH_2), 31.1 (CH/CH_3), 25.9 (CH/CH_3), 25.6 (CH_2), 19.9 (CH/CH_3), 17.8 (CH/CH_3).

HRMS (ESI, MeOH): exact mass calc. for $C_{16}H_{29}N{\cdot}H^+$: 236.23783; found: 236.23740.

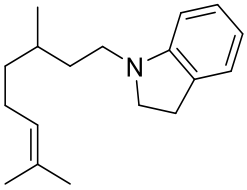


1,1'-((3,7-dimethyloct-6-en-1-yl)azanediyl)bis(propan-2-ol) (19). Yield: 131 mg (97%).

^{1}H-NMR (400 MHz; $CDCl_3$): δ (ppm) = 5.12–5.03 (m, 1H, C=CH), 3.87–3.73 (m, 2H, HOC<u>H</u>), 3.17–2.81 (br m, 2H, OH), 2.68–2.47 (m, 2H, N–CH_2), 2.46–2.29 (m, 4H, N–CH_2), 2.06–1.86 (m, 2H, =CH–C<u>H</u>$_2$), 1.68 and 1.59 (s, 2 x 3H, C=C(CH_3)$_2$), 1.54–1.20 (m, 5H, 2 x CH_2 and C<u>H</u>–Me), 1.16–1.09 (m, 6H, HOCH–C<u>H</u>$_3$), 0.90–0.85 (m, 3H, CH–C<u>H</u>$_3$).

^{13}C{^{1}H}-NMR (101 MHz; $CDCl_3$): δ (ppm) = 131.8 (CH=<u>C</u>Me_2), 125.1 (H<u>C</u>=CMe_2), 77.7 (HOC<u>H</u>), 65.9/65.7 (HOC<u>H</u>), 64.4/64.3 (HOC<u>H</u>), 64.3 (N–CH_2), 63.1/63.0 (N–CH_2), 54.2 (N–CH_2), 53.7/53.5 (N–CH_2), 37.8/37.6/37.3 (CH_2), 34.4 (CH_2), 31.2 (CH), 26.2 (C=C(<u>C</u>H_3)$_2$), 25.9 (CH_2), 21.0/20.9 (HOCH–<u>C</u>H_3), 20.6 (HOCH–<u>C</u>H_3), 20.3/20.1/20.0 (<u>C</u>H–Me), 18.1 (C=C(<u>C</u>H_3)$_2$).

HRMS (ESI, MeOH): exact mass calc. for $C_{16}H_{33}NO_2{\cdot}H^+$: 272.25895; found: 272.25852 m/z.



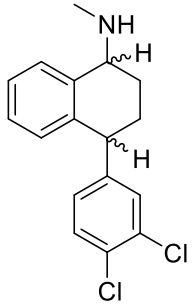
.1-(3,7-dimethyloct-6-en-1-yl)indoline (20). Yield: 101 mg (79%).

^{1}H-NMR (300 MHz; $CDCl_3$): δ (ppm) = 7.10-7.03 (m, 2H, CH_{Ar}), 6.63 (td, $^{3}J_{H,H}$ = 7.4 Hz, $^{4}J_{H,H}$ = 1.0 Hz, 1H, CH_{Ar}), 6.50-6.45 (m, 1H, CH_{Ar}), 5.17-5.07 (m, 1H, C=CH), 3.40-3.26 (m, 2H, N–CH_2),

^{13}C{^{1}H}-NMR (76 MHz; $CDCl_3$): δ (ppm) = 152.8 (C_q), 131.4 (CH=<u>C</u>Me_2), 130.2 (C_q), 127.4 (CH), 124.9 (H<u>C</u>=CMe_2), 124.5 (CH), 117.4 (CH), 107.0 (CH), 53.1 (N–CH_2), 47.3 (N–CH_2), 37.3 (CH_2), 34.1 (CH_2), 30.7 (<u>C</u>H–Me), 28.7 (CH_2), 25.9 (C=C(<u>C</u>H_3)$_2$), 25.6 (CH_2), 19.8 (CH–<u>C</u>H_3), 17.8 (C=C(<u>C</u>H_3)$_2$).

HRMS (ESI, MeOH): exact mass calc. for $C_{18}H_{27}N{\cdot}H^+$: 258.22218; found: 258.22156 m/z.

S1.7 Reductive Amination affording Sertraline



4-(3,4-dichlorophenyl)-N-methyl-1,2,3,4-tetrahydronaphthalen-1-amine (**22**):

Tetralone derivative **21** (200 mg, 0.69 mmol, 1 eq.) and molecular sieves (4 Å, 680 mg) were treated with a methylamine solution (2M in ethanol, 2.08 mL, 4.16 mmol, 6 eq.) and stirred at ambient temperature for 48h. DCM (6 mL) was added, it was filtrated over Celite and the solvent was removed in vacuum, yielding a colourless solid. GC/MS analysis confirmed full conversion towards the intermediate imine of which 152.1 mg (0.5 mmol) were dissolved in ethanol (0.5 mL) and submitted to a Büchi® 20 mL "tiny clave" pressure reactor. Precatalyst **5a** (5.5 mg, 2 mol%, in 0.5 mL ethanol) was added and the reactor was flushed 4 times with H_2, then pressured with 5 bar H_2 and heated to 85 °C. After stirring for 16h at that temperature, the pressure was released, DCM (2 mL) was added, it was filtrated over Celite, and the solvent was removed in vacuum. GC/MS analysis revealed full conversion of the imine and two products which could be identified as the two diastereomers of **22** were detected. The ratio was determined according to the signal integrals, analogous to literature procedures.[13] Comparison with the retention time of a (S,S)-**22** (*cis*-diastereomer) sample, which was obtained by deprotonation of Sertralin·HCl (1A Pharma GmbH) with NaOH solution, allowed the assignment of the diastereomers.

Recorded NMR spectra fit to those of the cis and trans diastereomers reported in the literature (Figure 47 and 48).[14]

S2 NMR spectra

S2.1 2,3-Dipiperidino-4,5-diphenylcylopentadienone (3a)

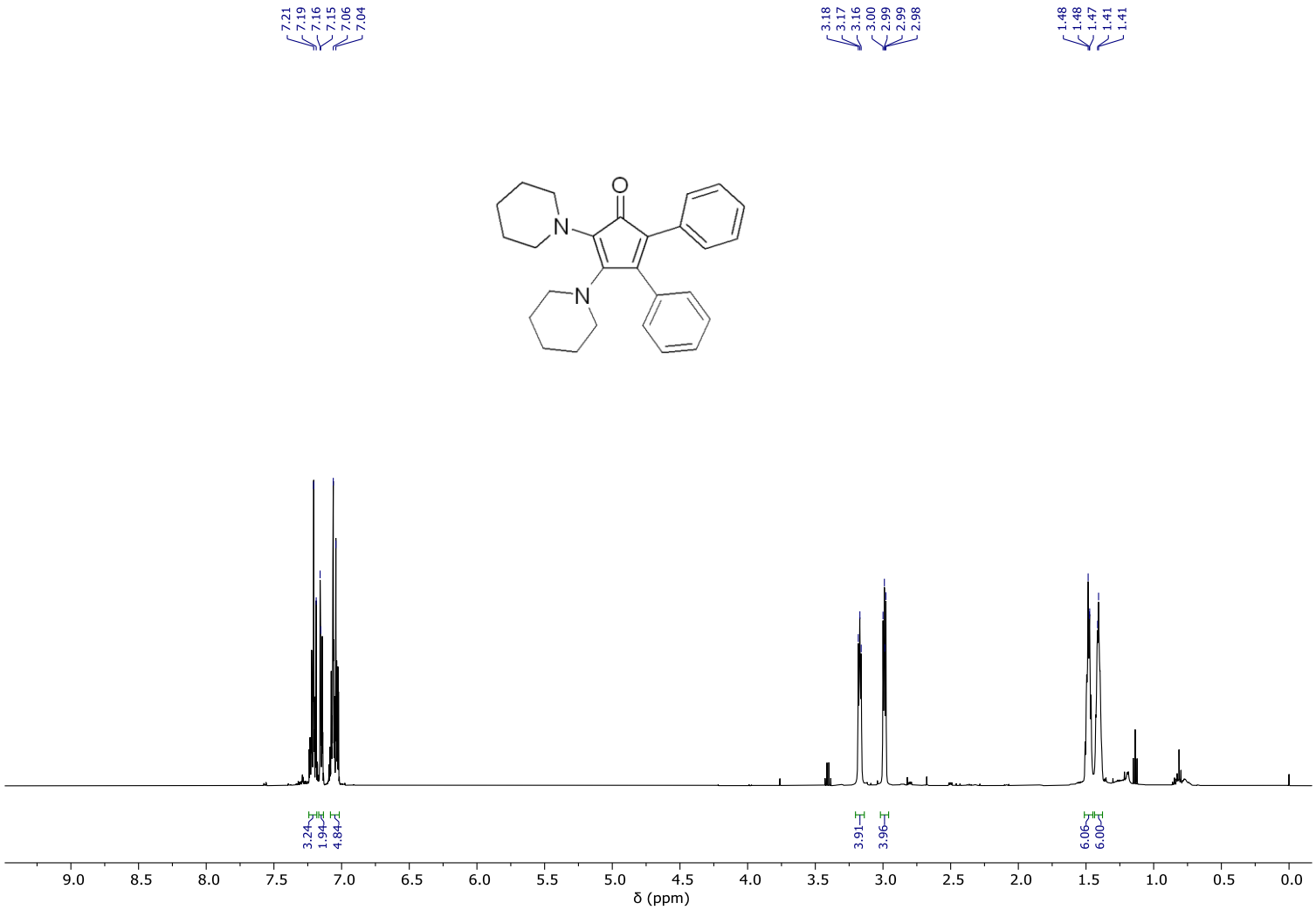


Figure S2: ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **3a**.

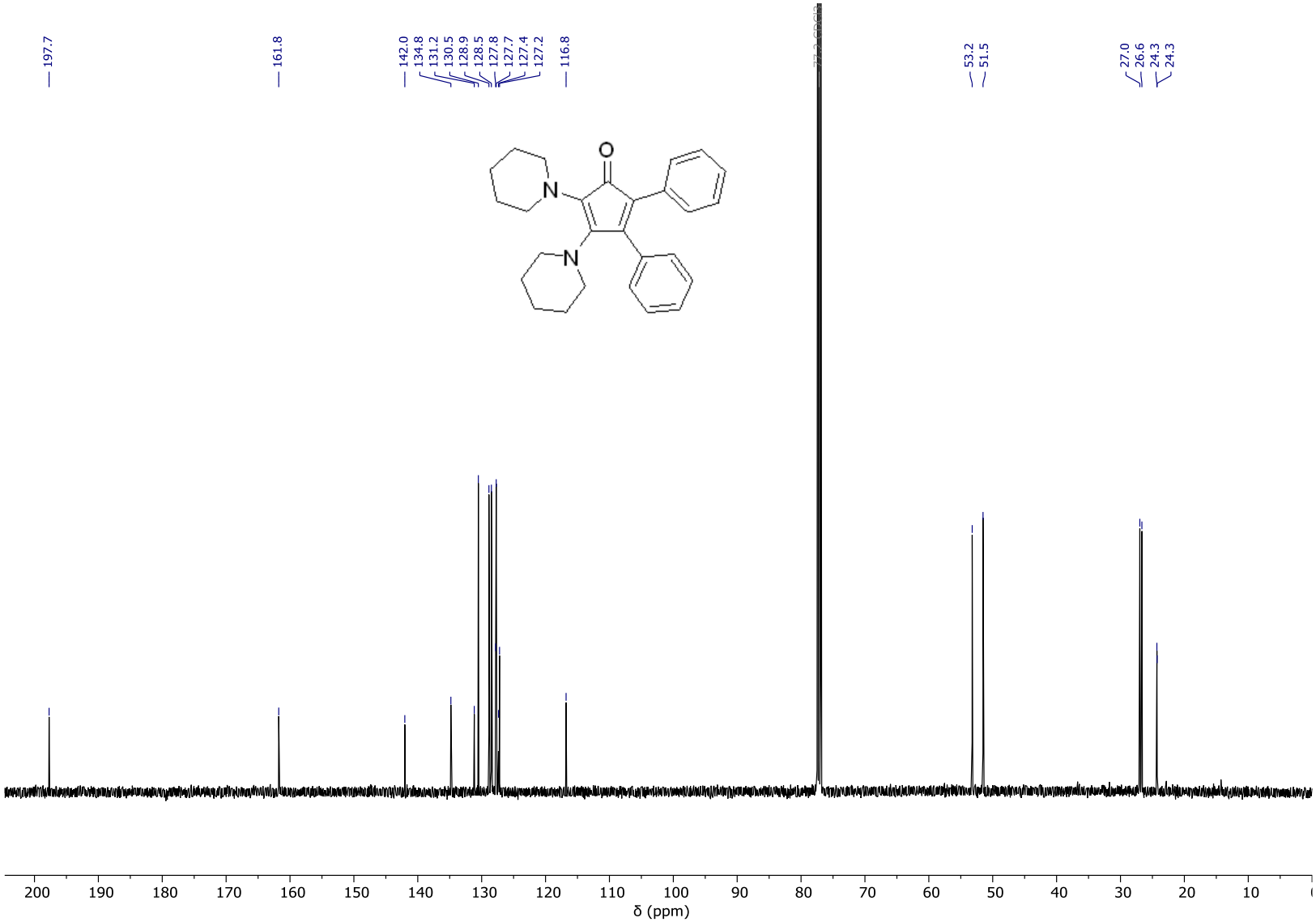


Figure S3: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 126 MHz) of **3a**.

S2.2 2,3-Dipiperidino-4,5-bis(tertbutylphenyl)cylopentadienone (3b)

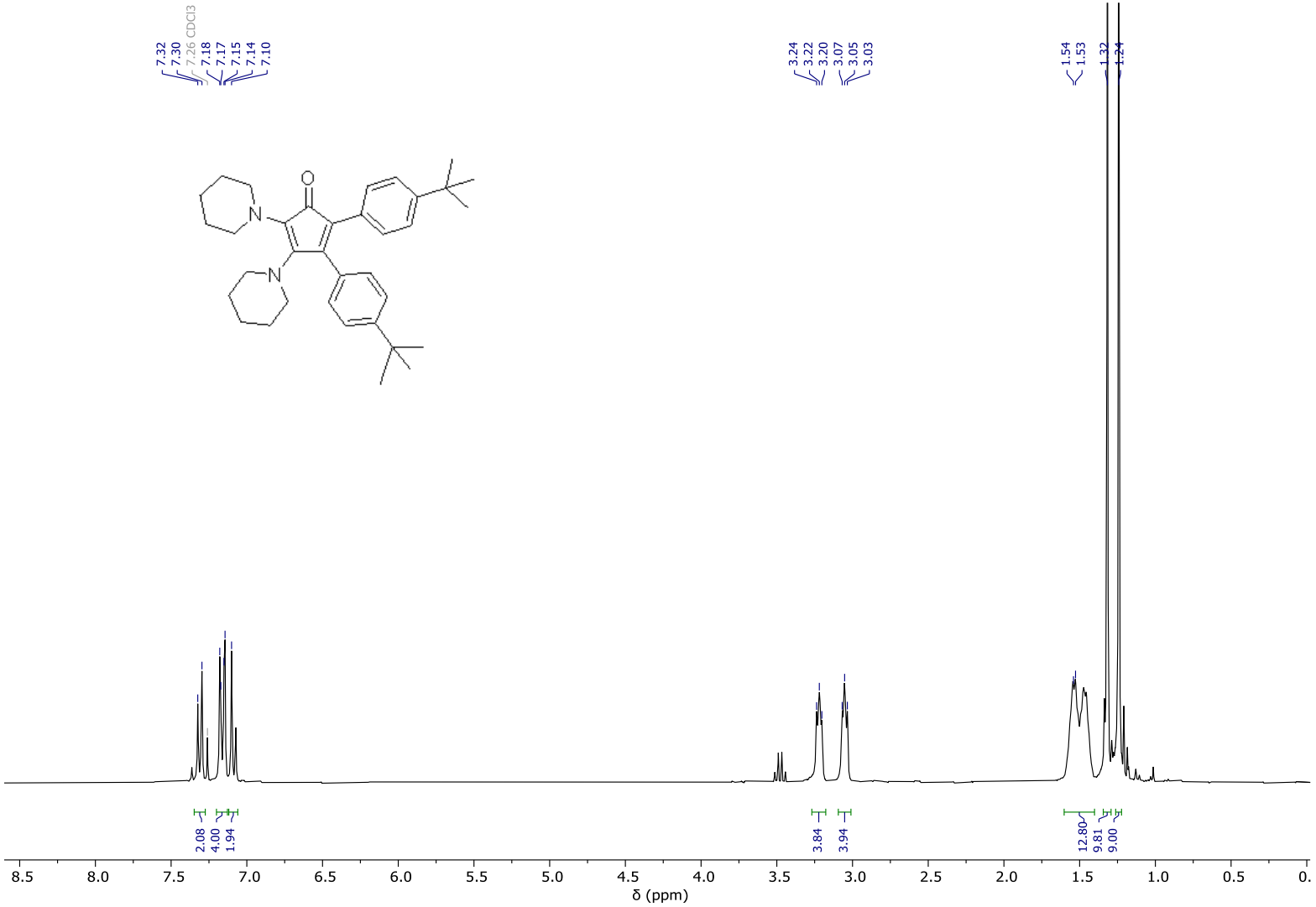


Figure S4: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **3b**.

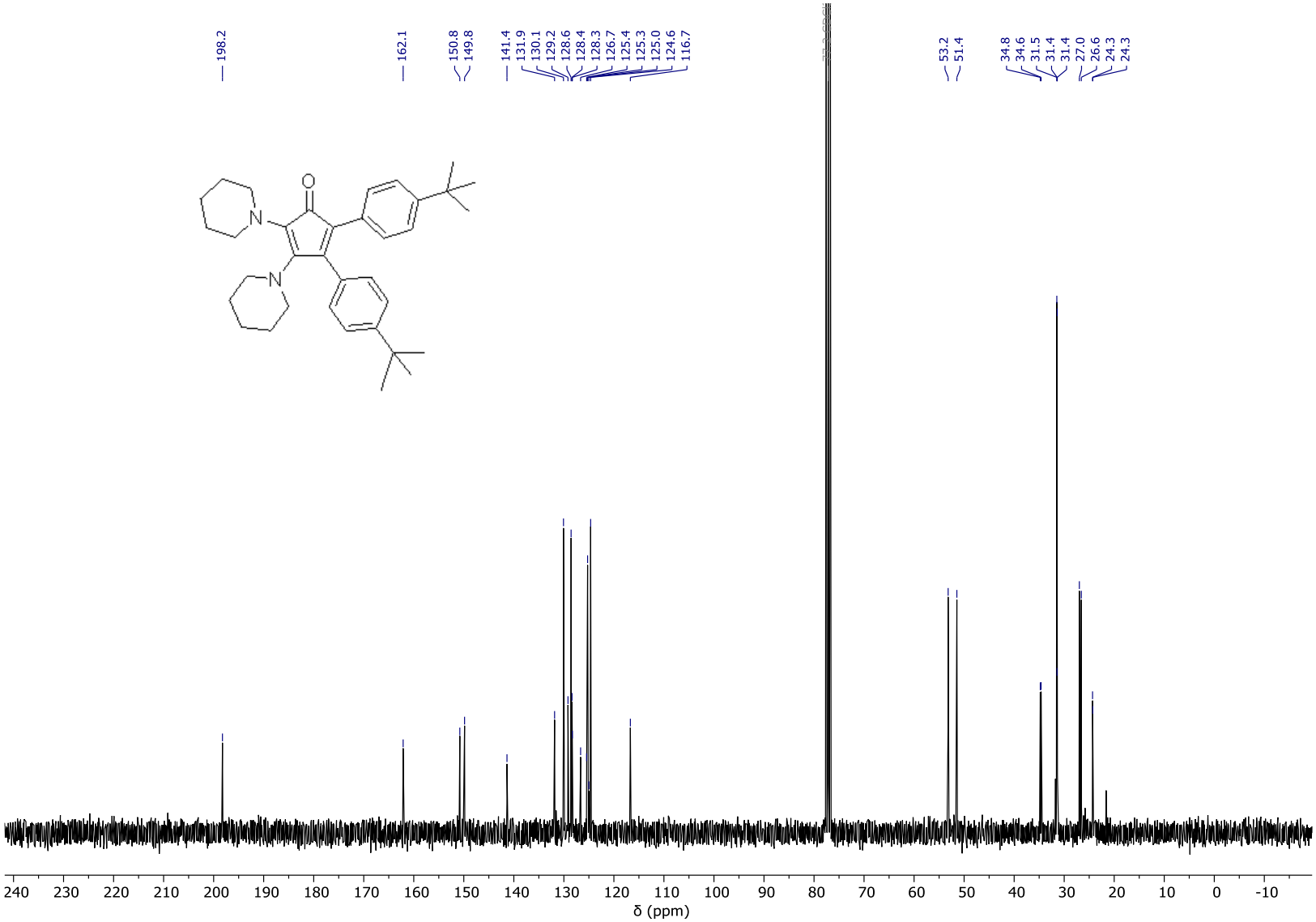


Figure S5: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 76 MHz) of **3b**.

S2.3 2,3-Dipiperidino-4,5-bis(2,5-dimethylphenyl)cylopentadienone (3c)

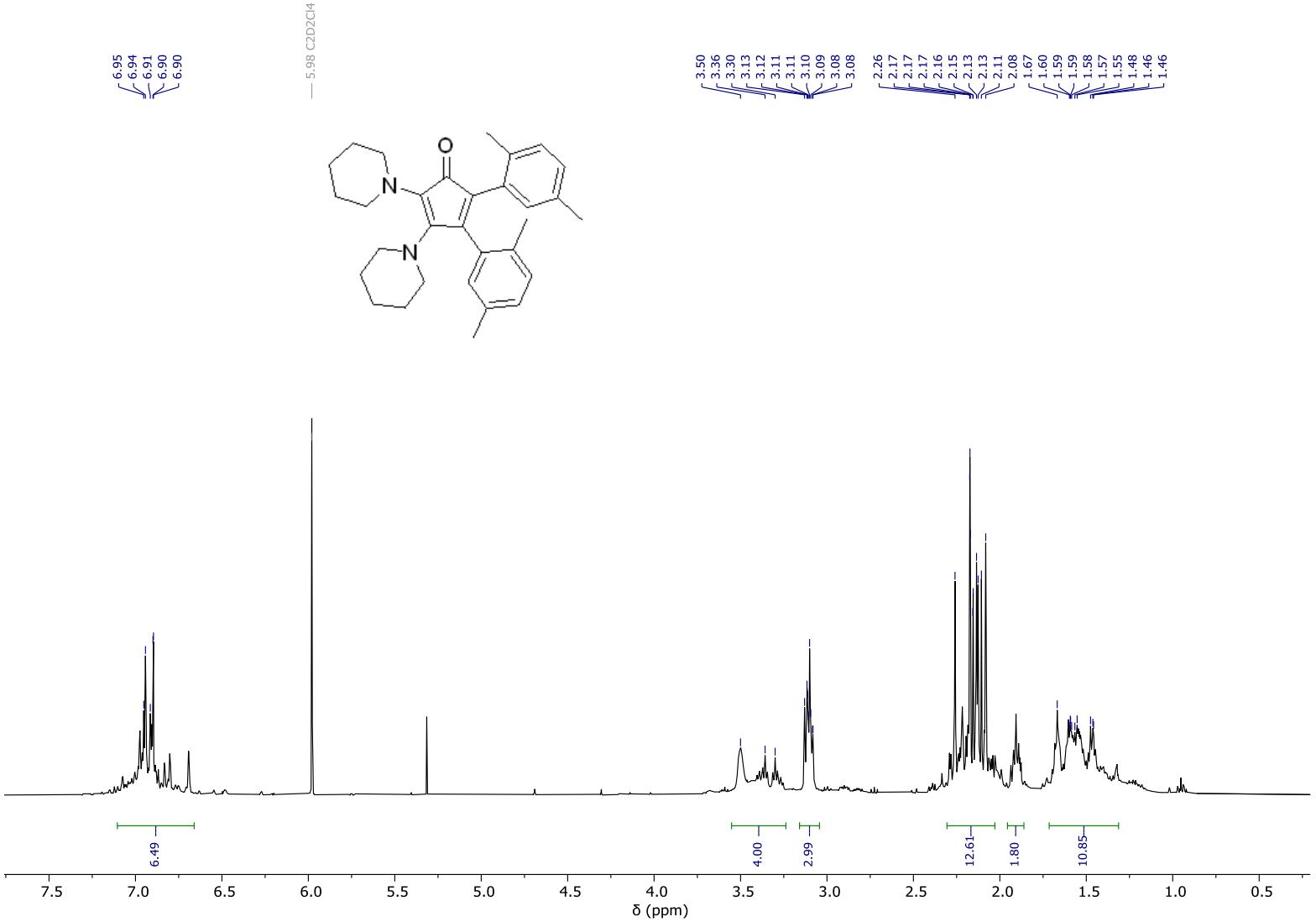


Figure S6: ^{1}H NMR spectrum at 100 °C ($C_2D_2Cl_4$, 500 MHz) of **3c**.

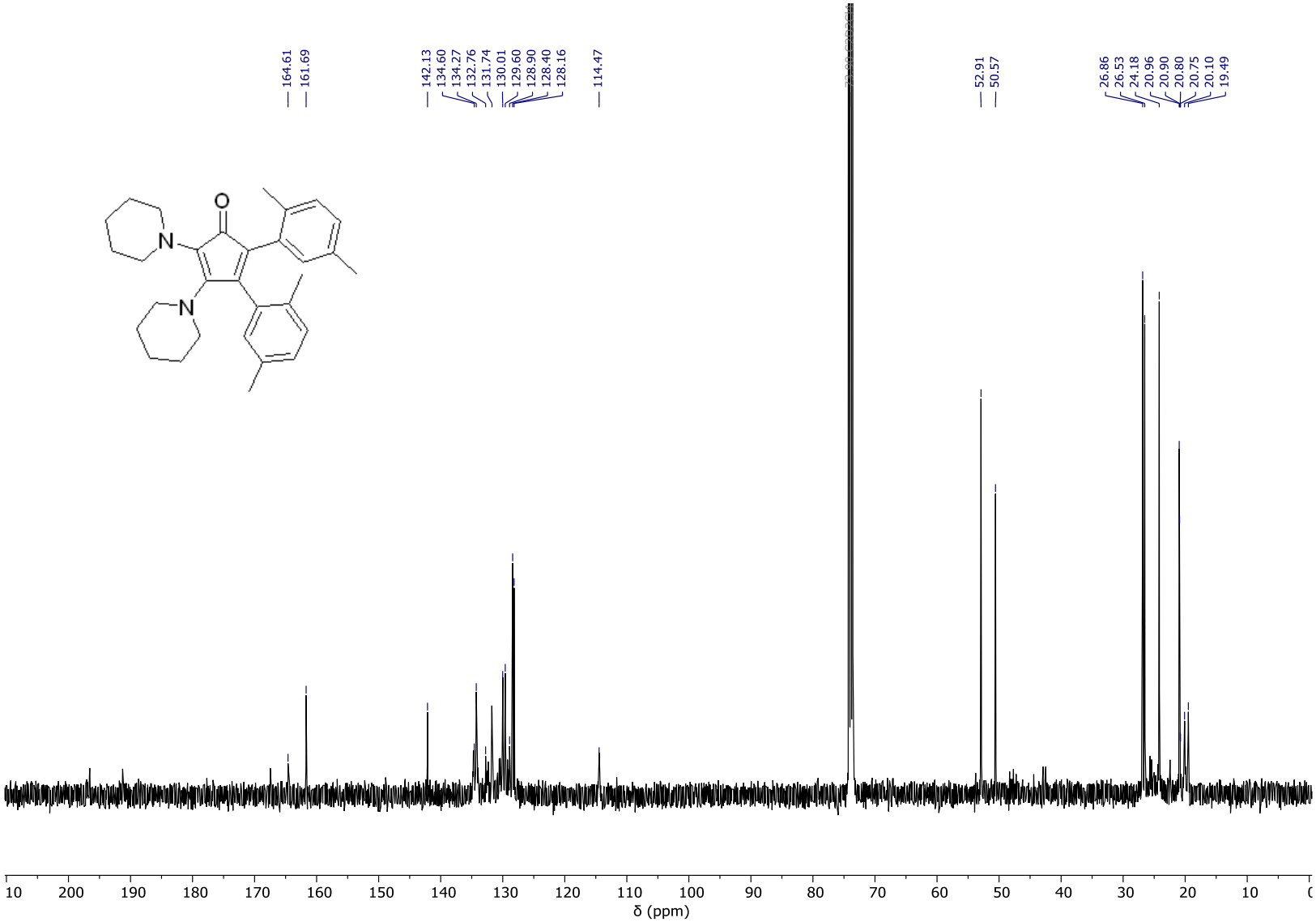


Figure S7: $^{13}C\{^{1}H\}$ NMR spectrum ($C_2D_2Cl_4$, 126 MHz) of **3c**.

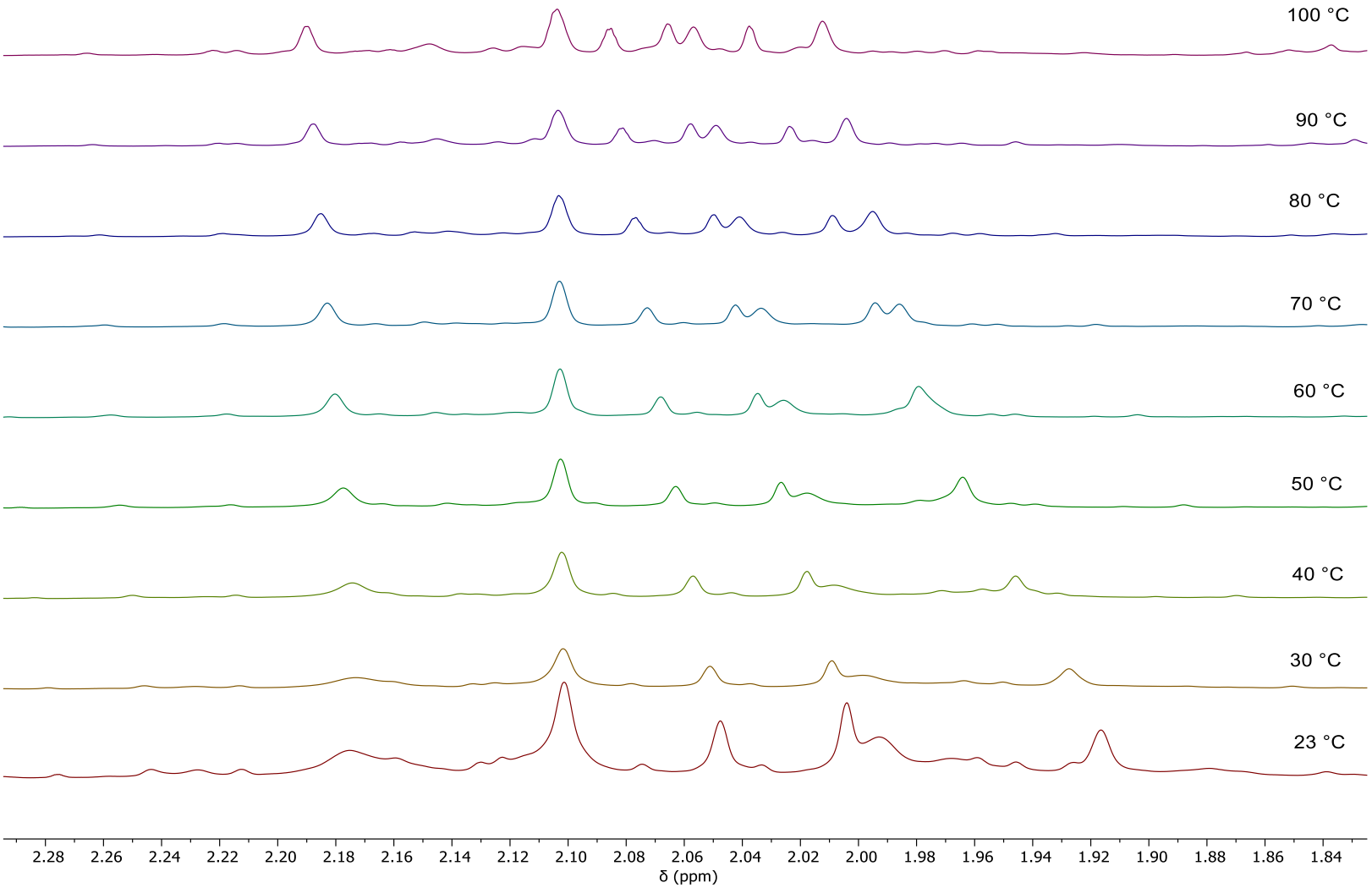


Figure S8: Variable temperature ^{1}H NMR spectrum ($C_2D_2Cl_4$, 500 MHz) of **3c**.

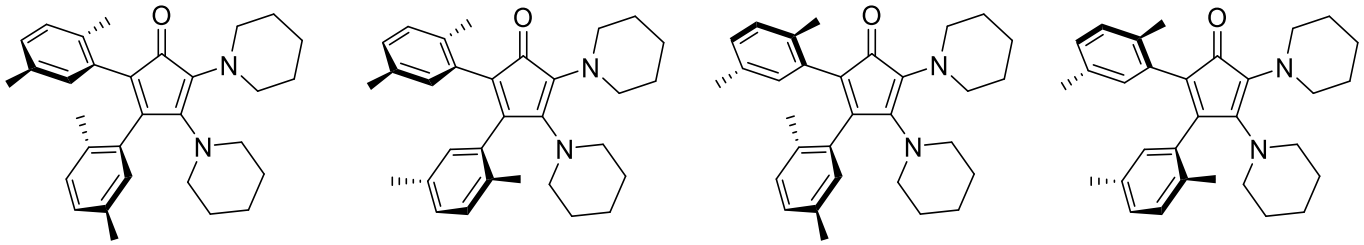


Figure S9: Atropisomers of 3c.

S2.4 2,3-Dipiperidino-4,5-bis(4-(trifluoromethyl)phenyl)cylopentadienone (3d)

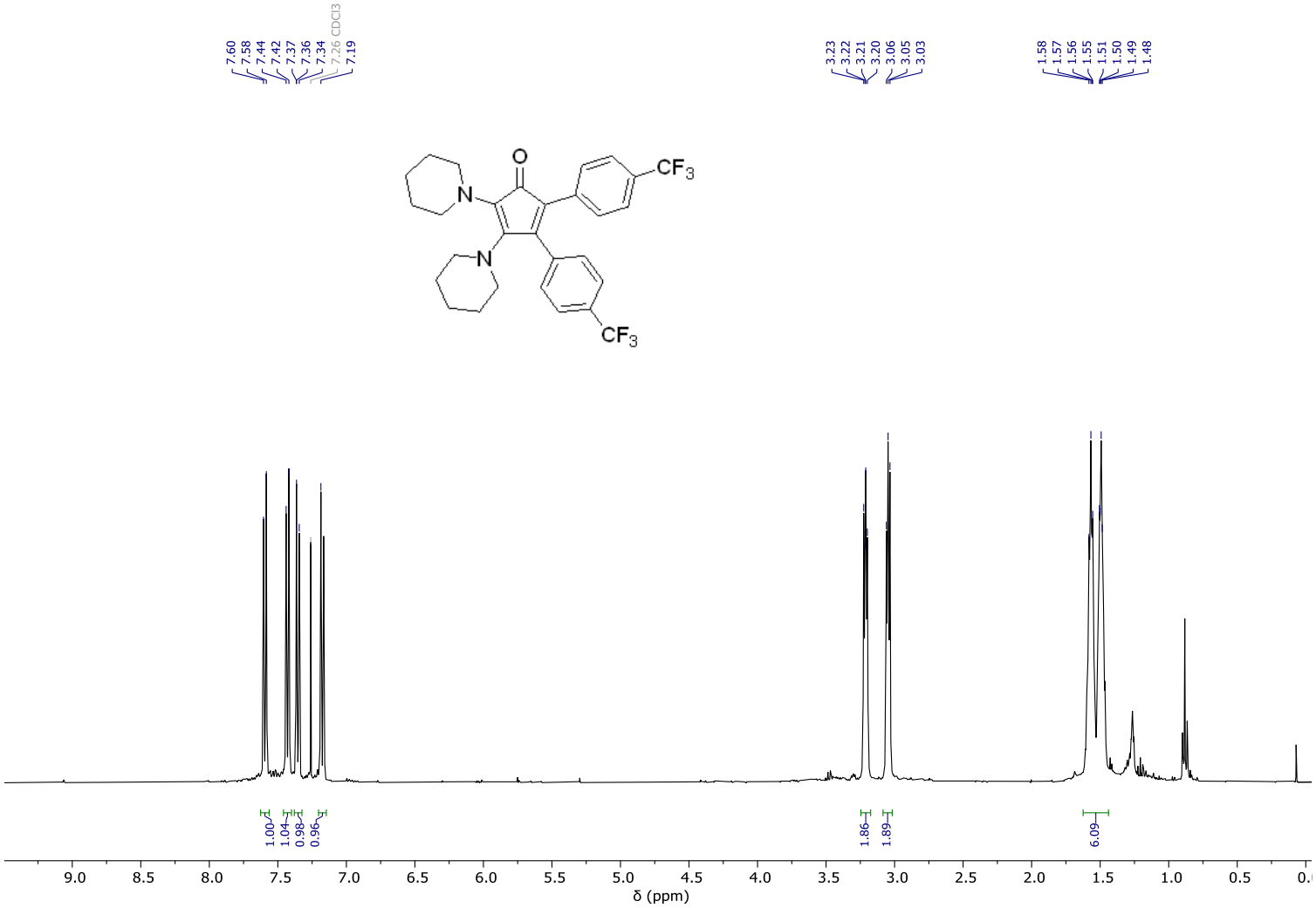


Figure S10: ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **3d**.

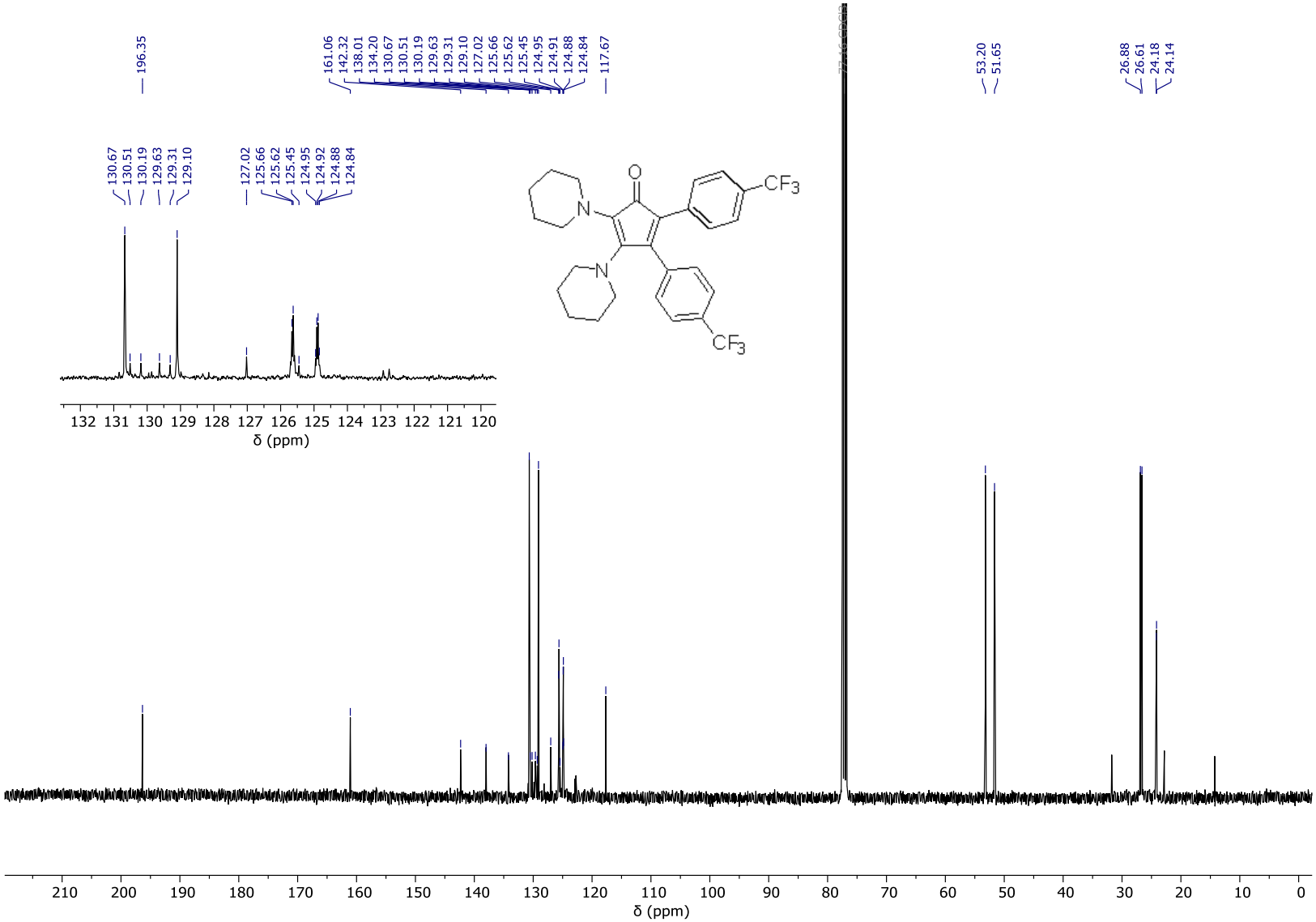


Figure S11: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 126 MHz) of **3d**.

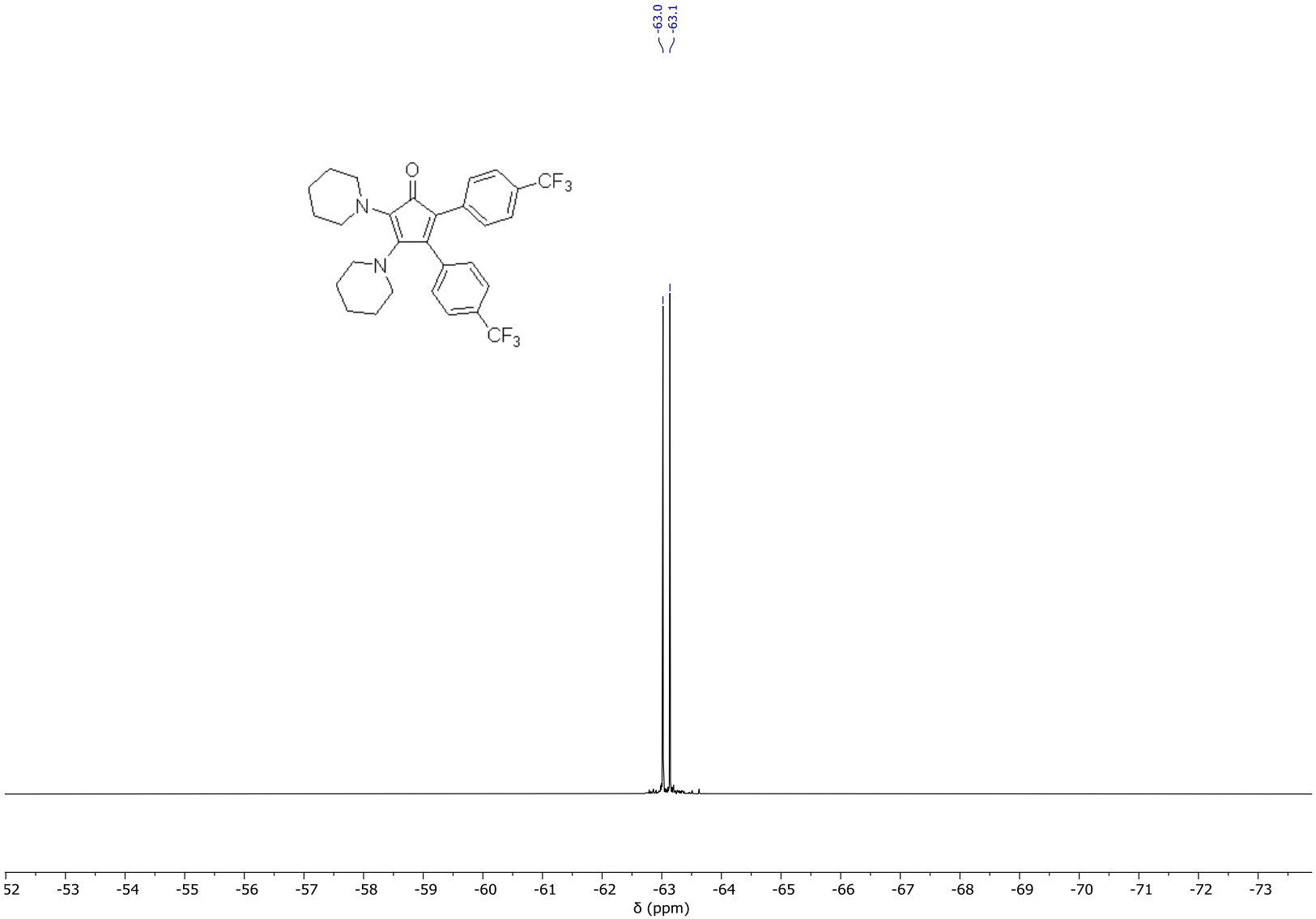


Figure S12: $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$, 377 MHz) of **3d**.

S2.5 (2,3-Dipiperidino-4,5-diphenylcylopentadienone)iron tricarbonyl (4a)

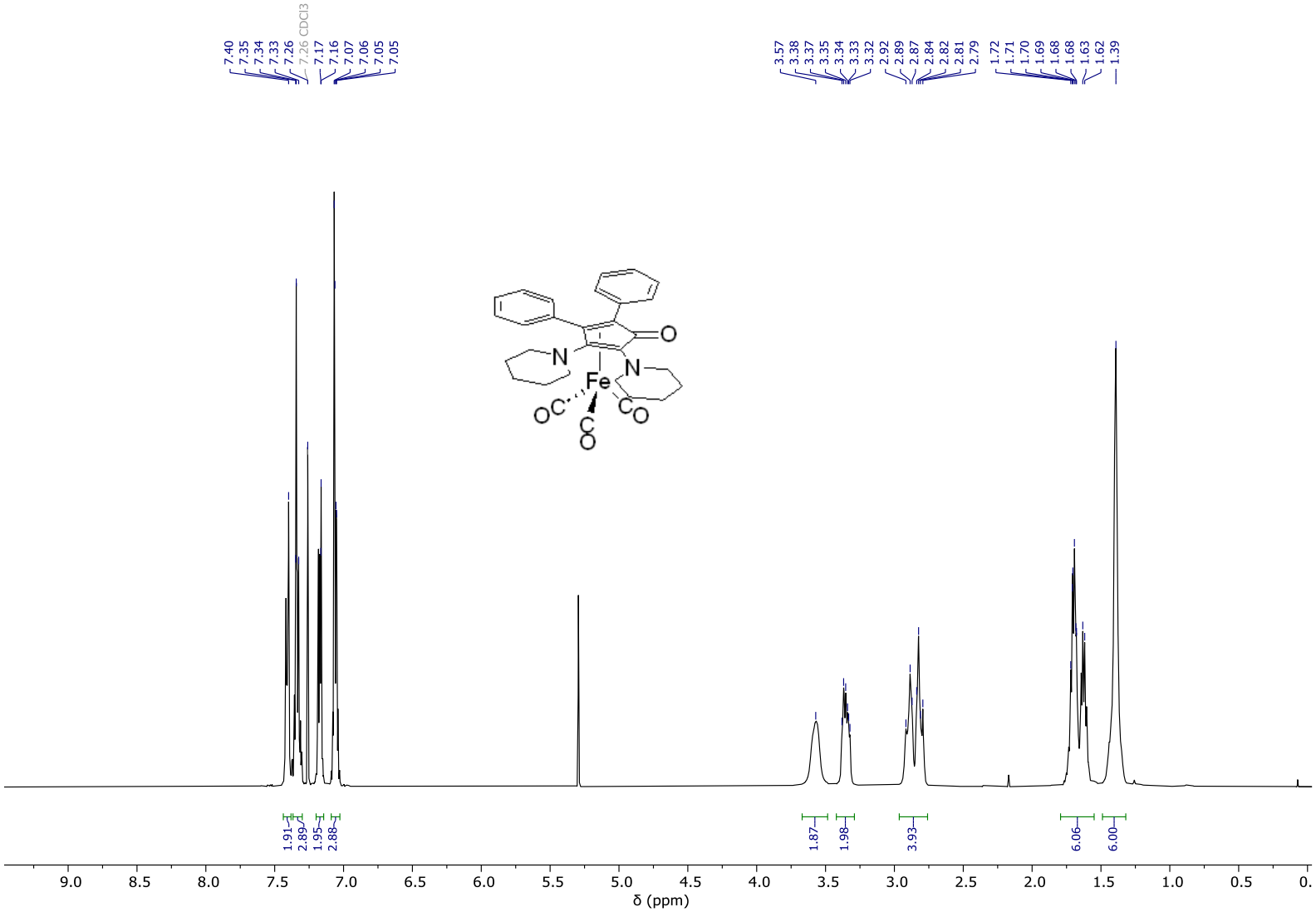


Figure S13: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **4a**.

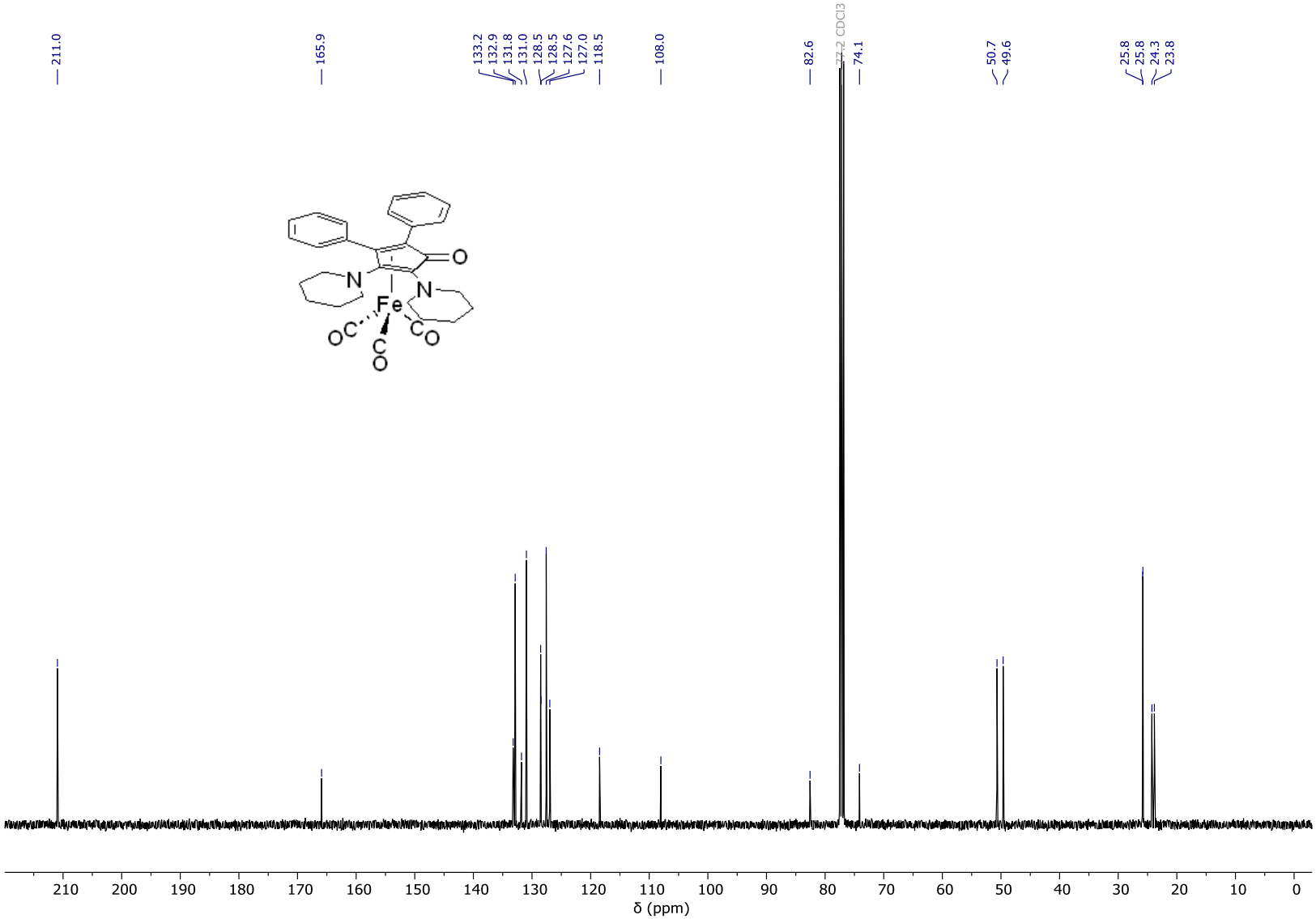


Figure S14: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of **4a**.

S2.6 (2,3-Dipiperidino-4,5-bis(4-tertbutylphenyl)cylopentadienone)iron tricarbonyl (4b)

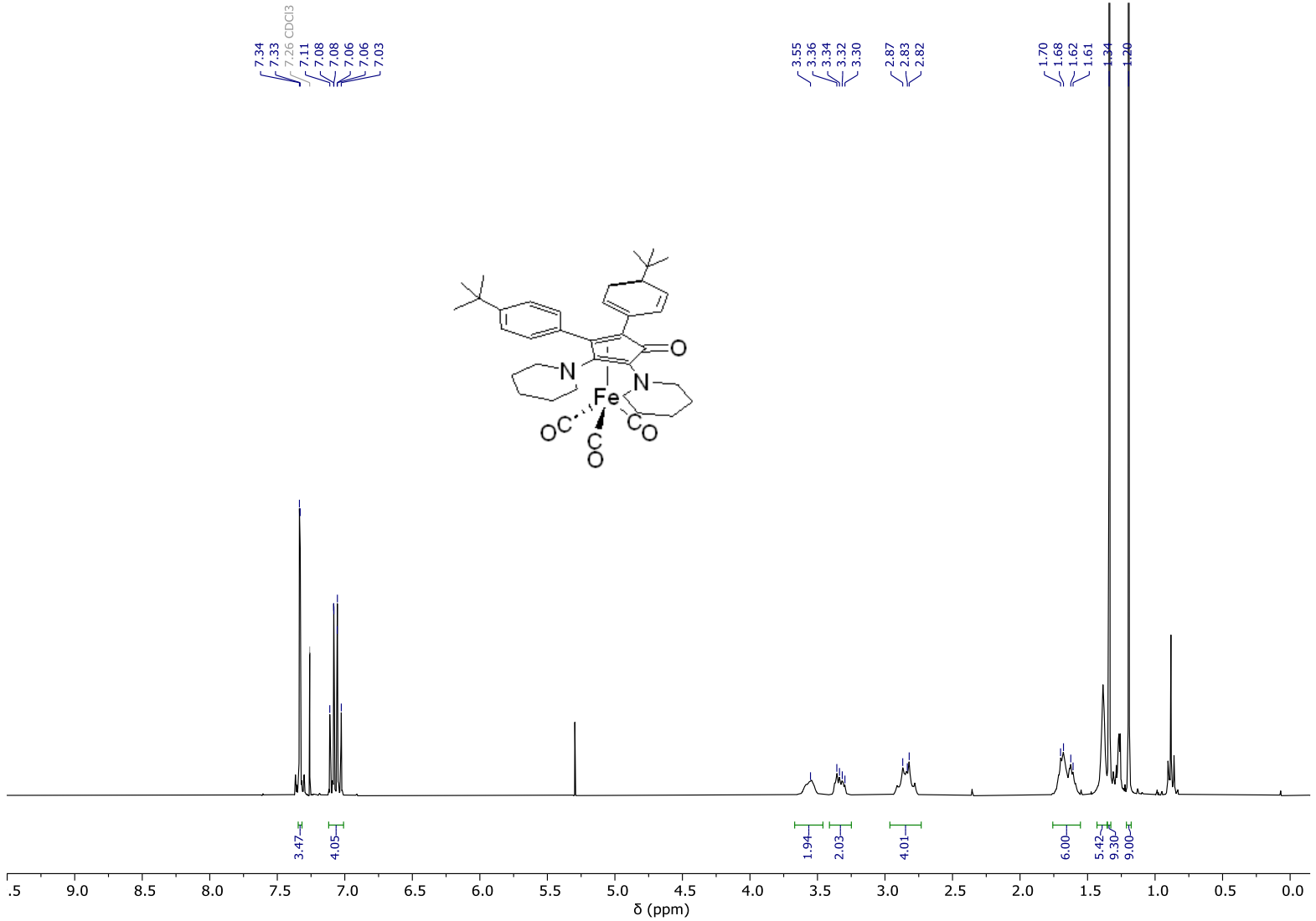


Figure S15: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **4b**.

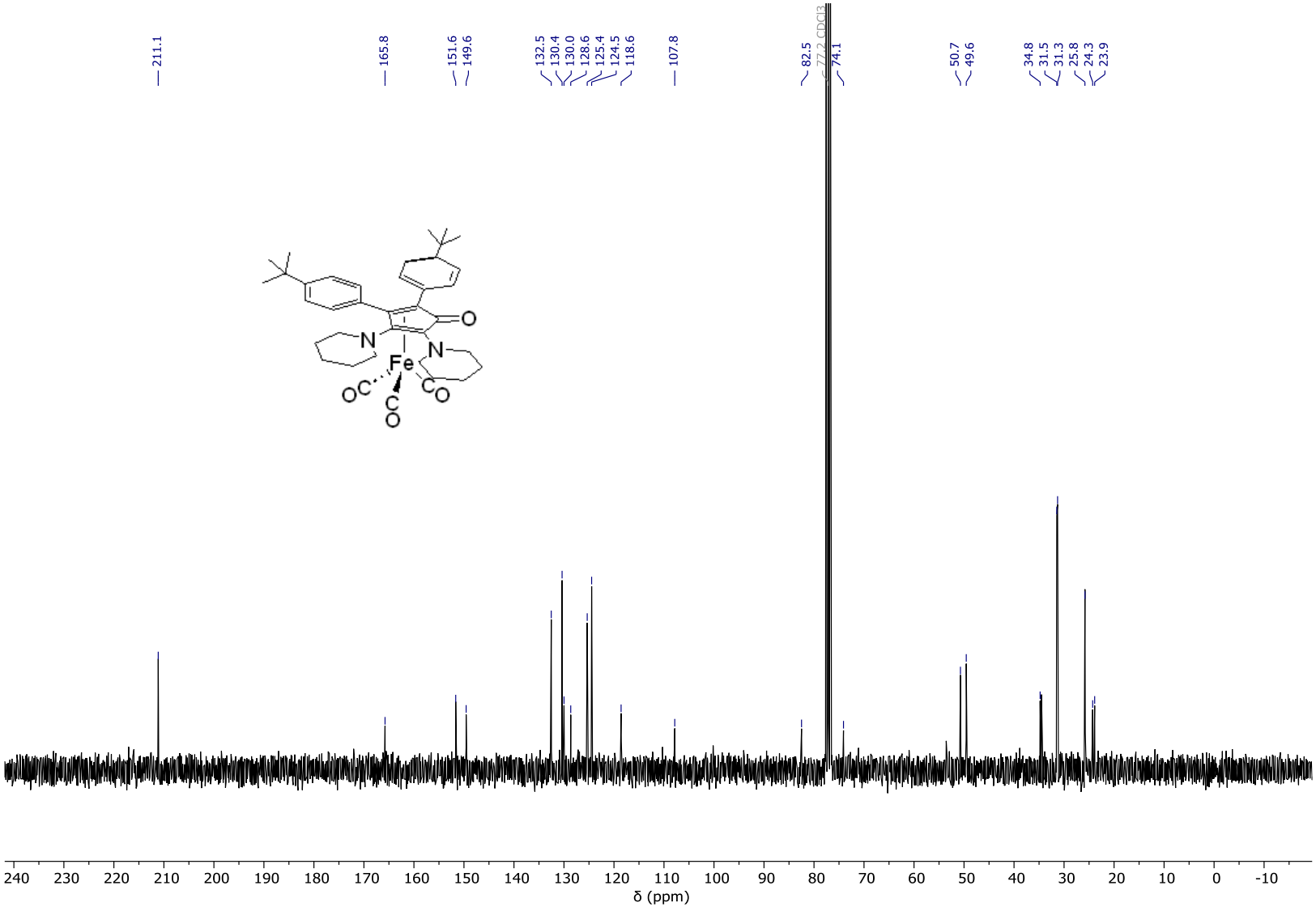


Figure S16: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 76 MHz) of **4b**.

S2.7 (2,3-Dipiperidino-4,5-bis(2,5-dimethylphenyl)cylopentadienone)iron tricarbonyl (4c)

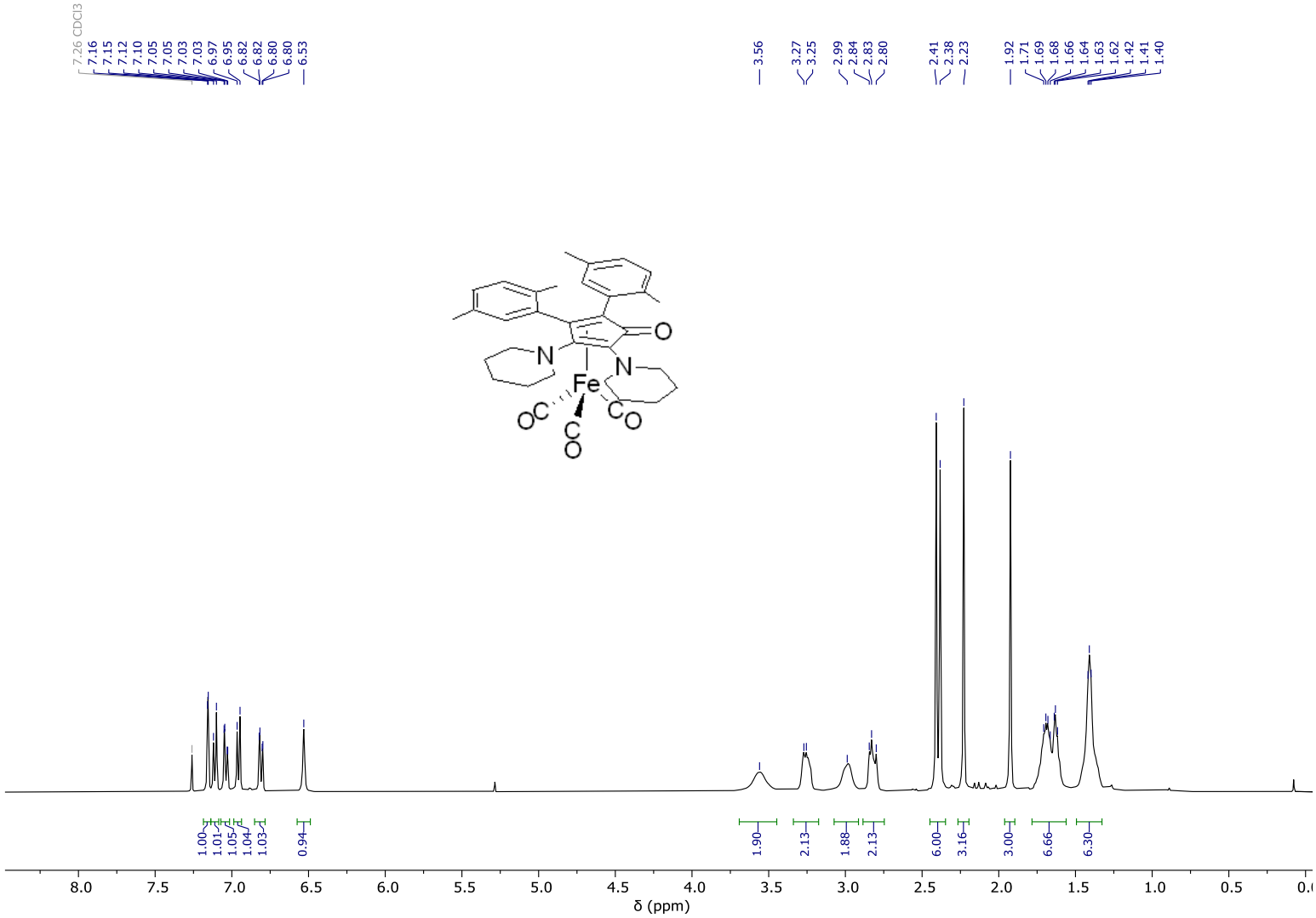


Figure S17: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **4c**.

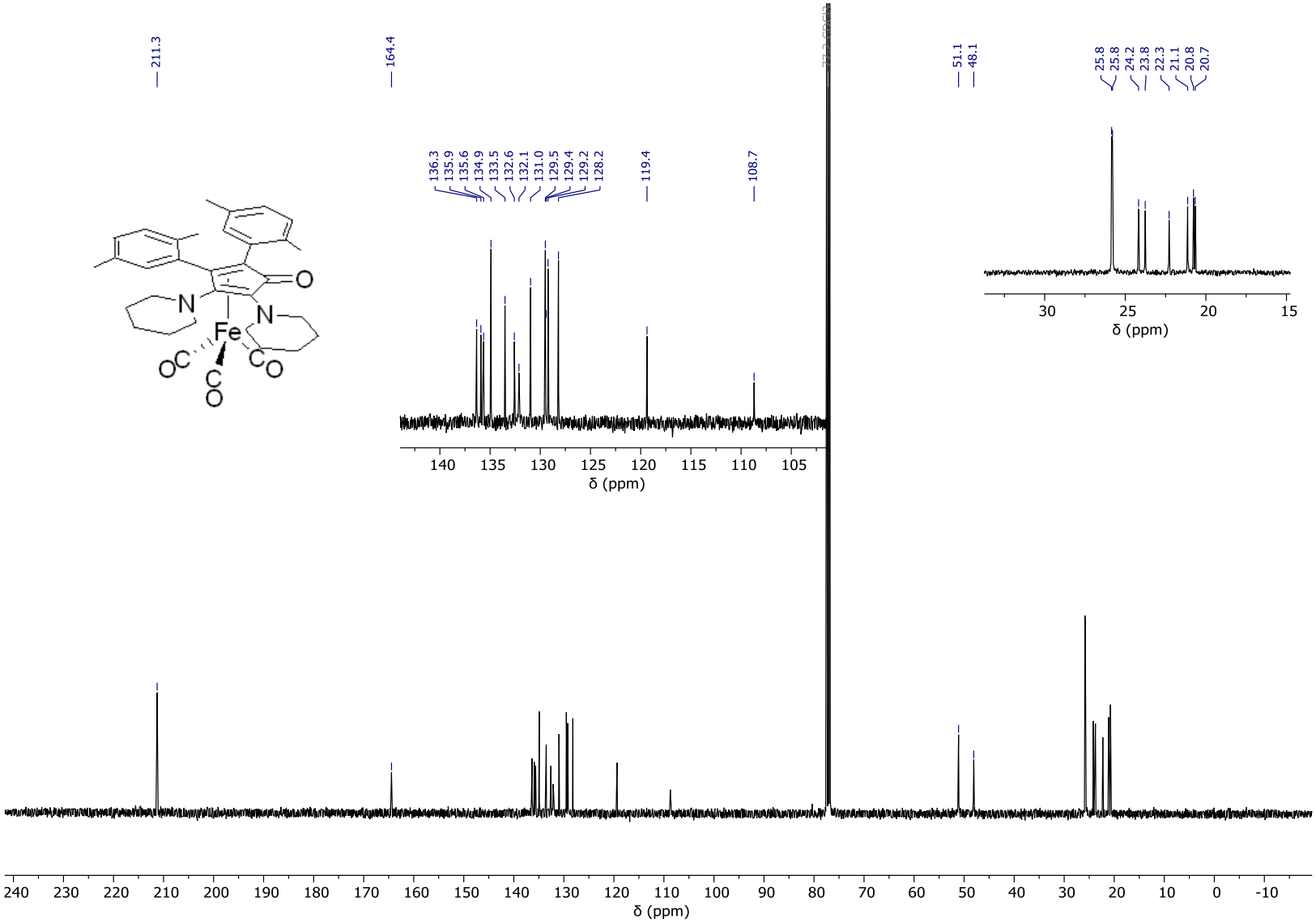


Figure S18: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of **4c**.

S2.8 (2,3-Dipiperidino-4,5-bis(4-trifluoromethylphenyl)cylopentadienone)iron tricarbonyl (4d)

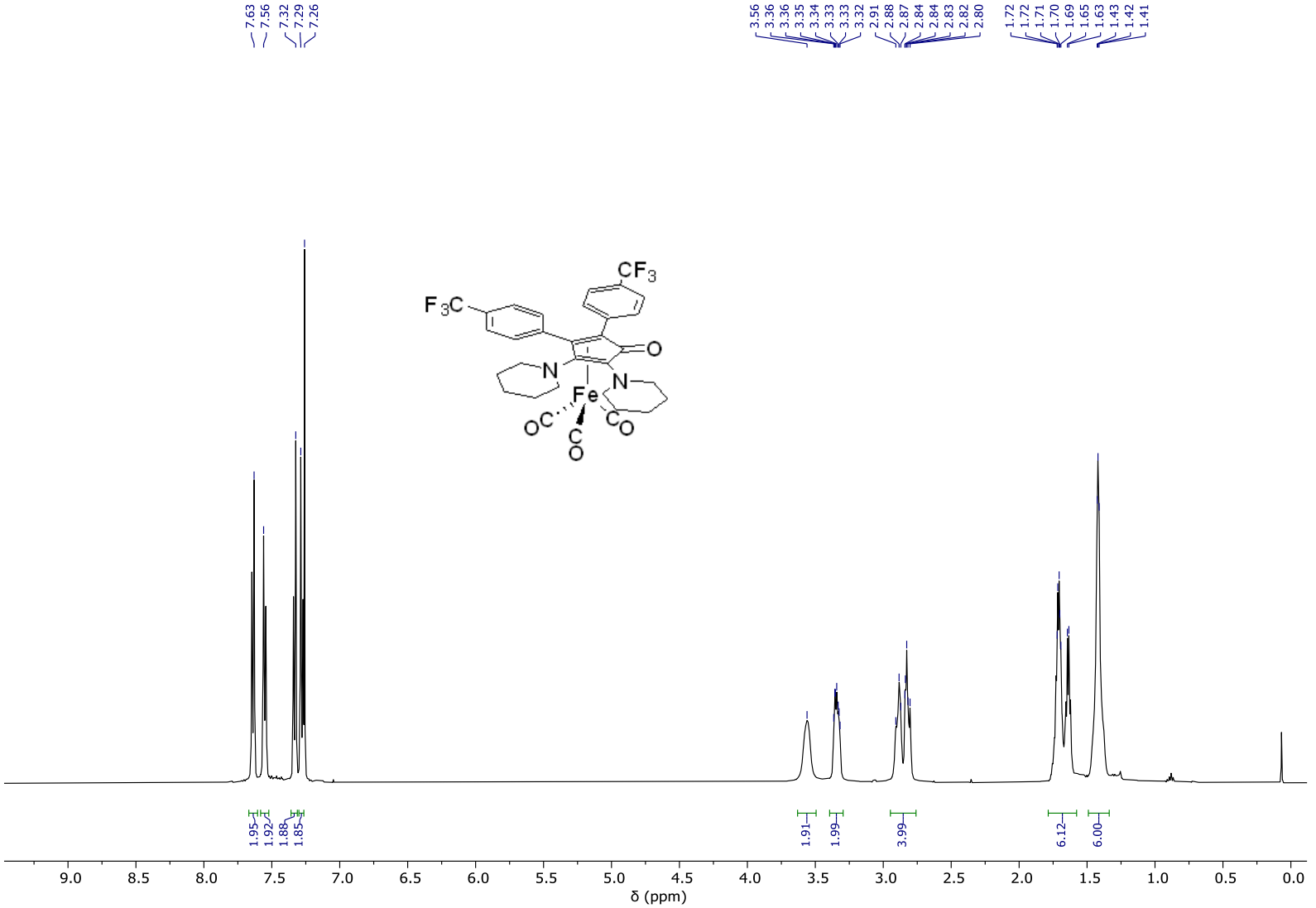


Figure S19: ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of **4d**.

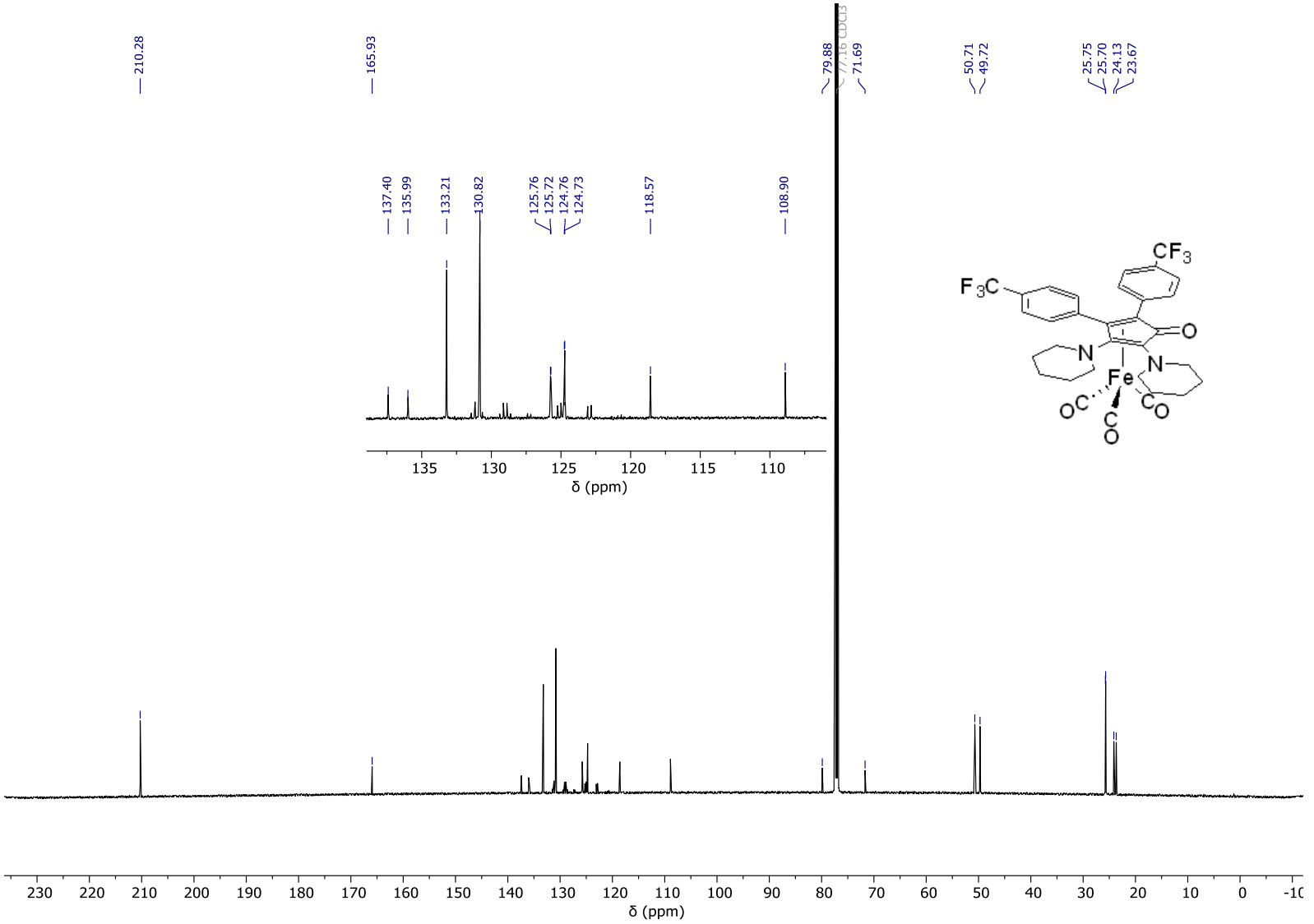


Figure S20: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 126 MHz) of **4d**.

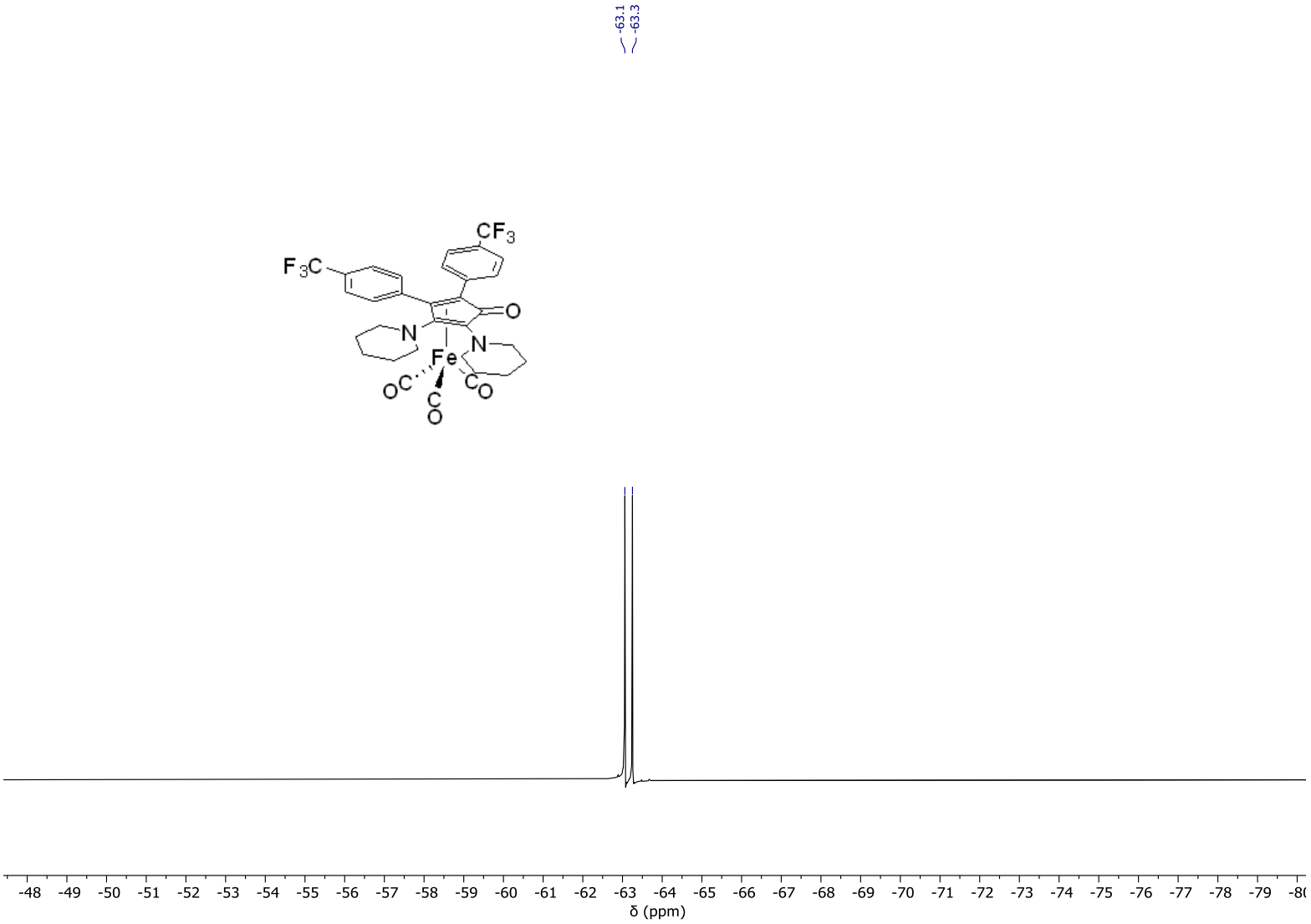


Figure S21: $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$, 471 MHz) of **4d**.

S2.9 (2,3-Dipiperidino-4,5-diphenylcylopentadienone)iron acetonitrile dicarbonyl (5a)

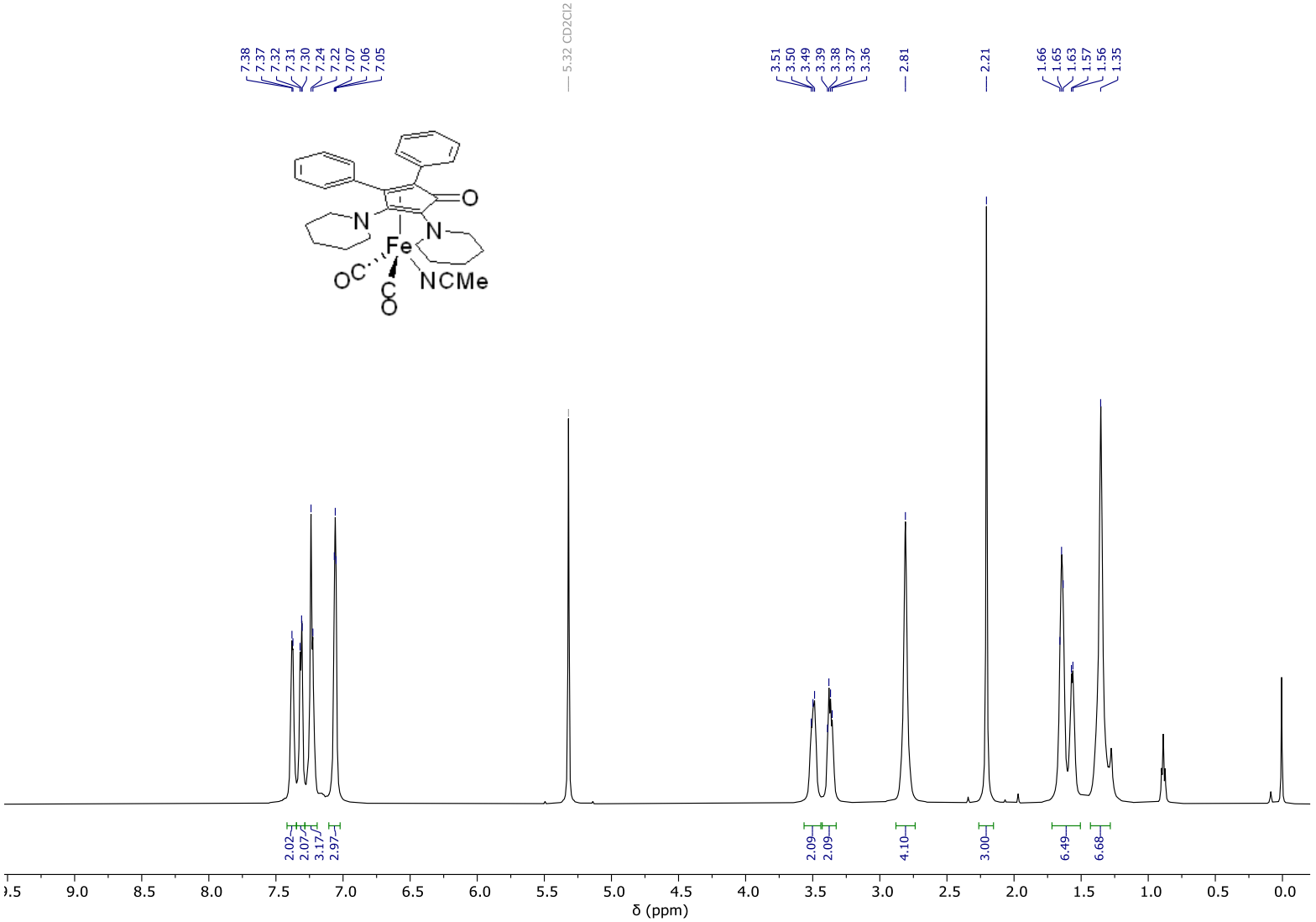


Figure S22: ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz) of **5a**.

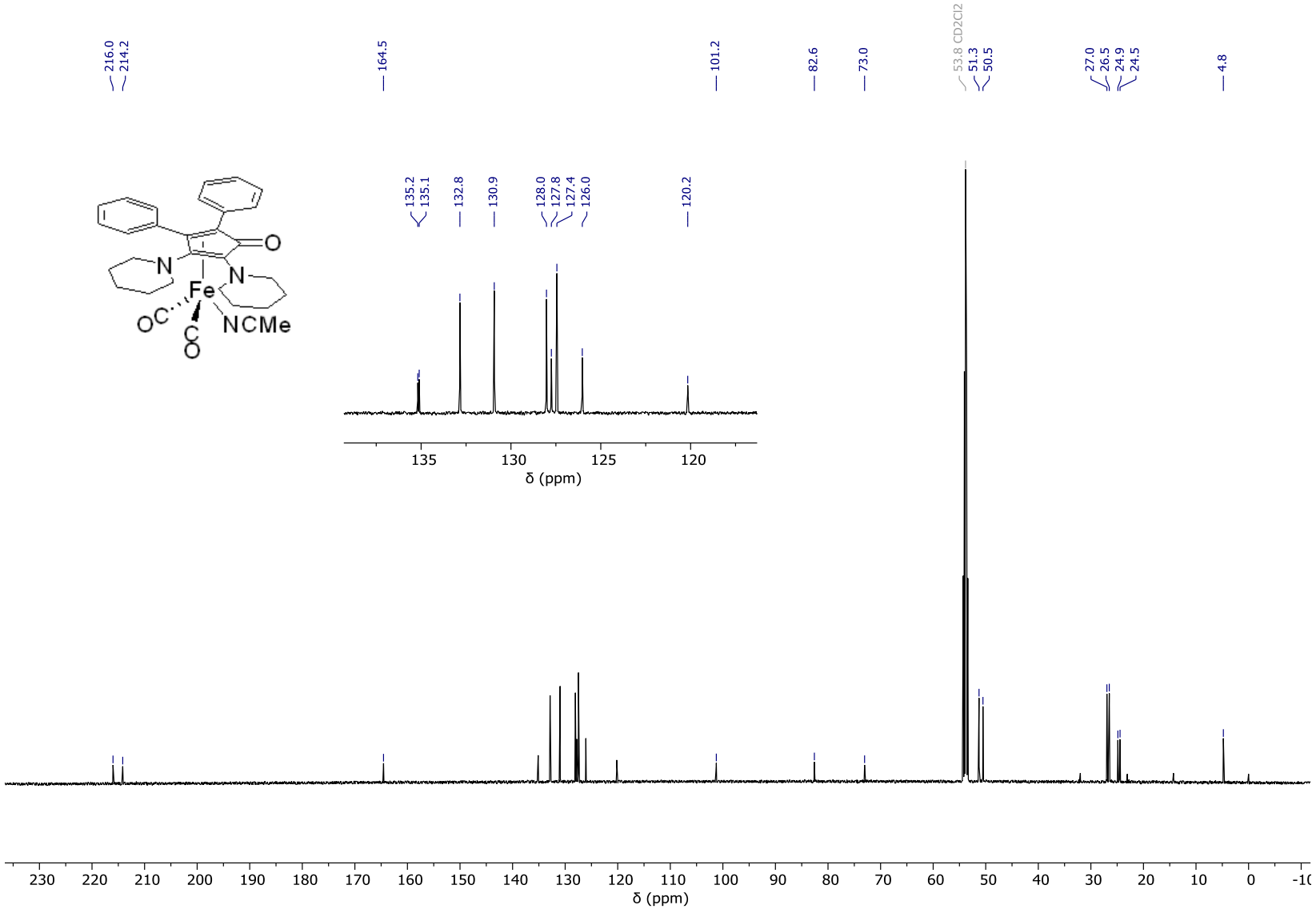


Figure S23: $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 126 MHz) of **5a**.

S2.10 (2,3-Dipiperidino-4,5-bis(4-tertbutylphenyl)cylopentadienone iron acetonitrile dicarbonyl (5b)

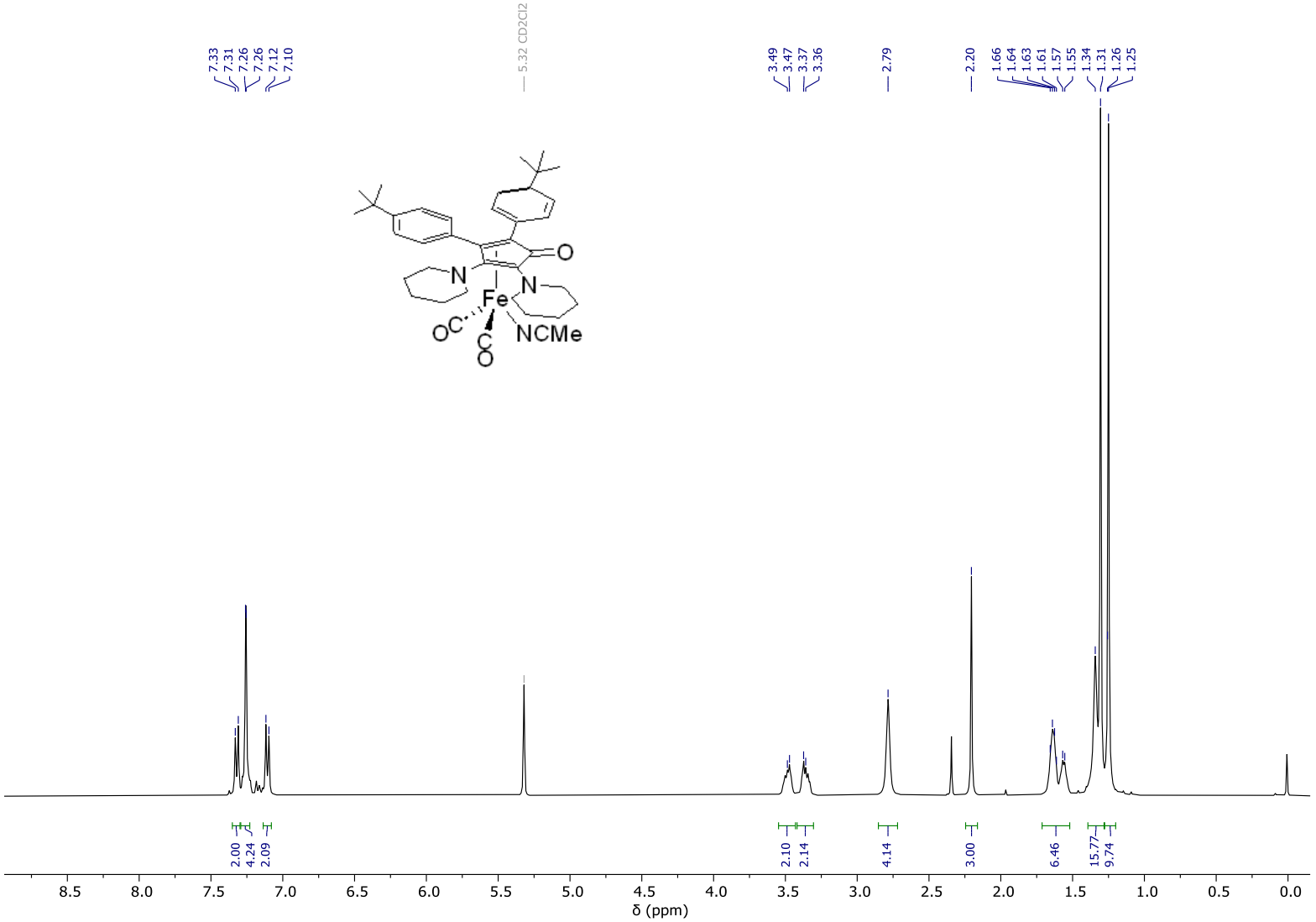


Figure S24: ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of **5b**.

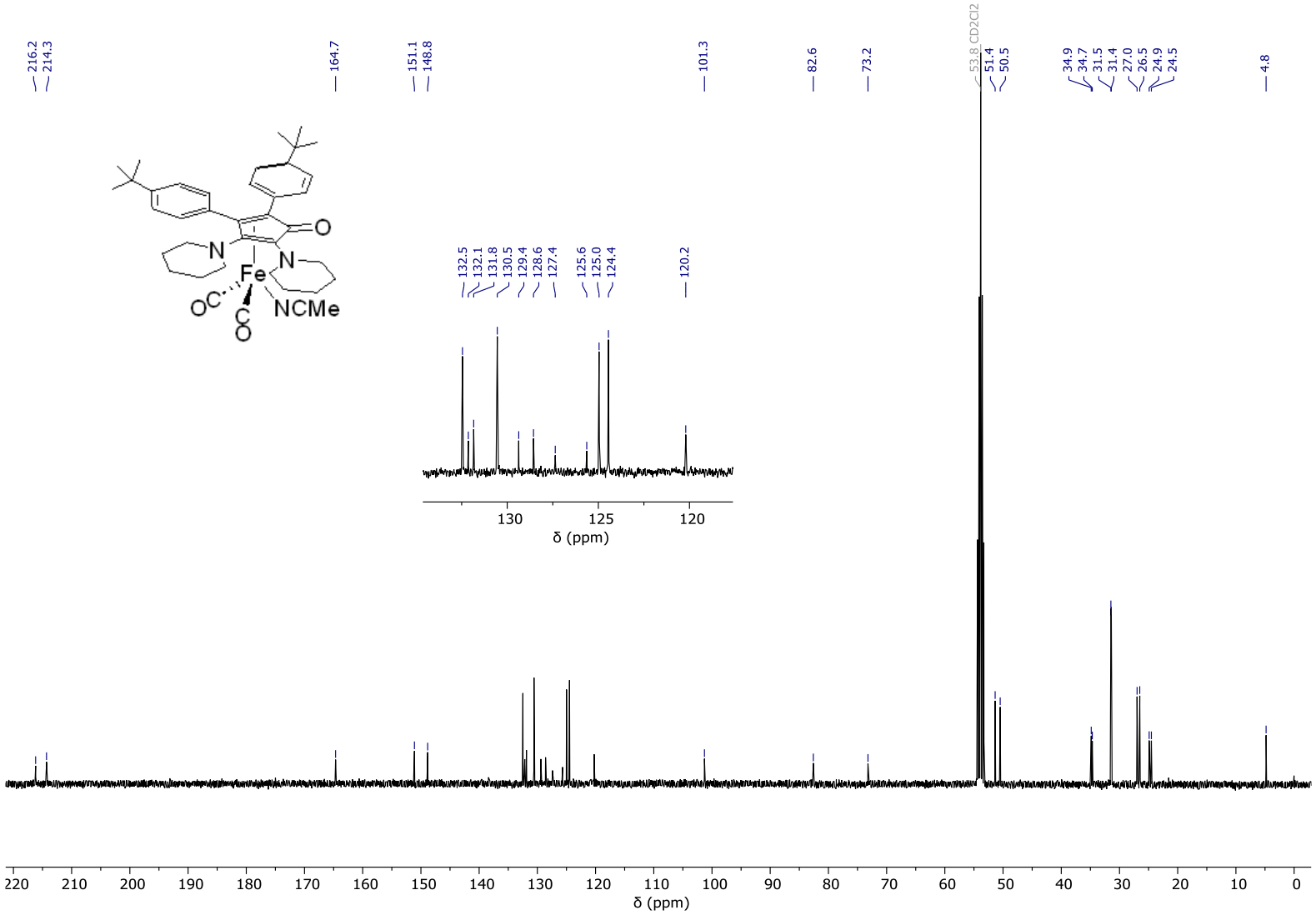


Figure S25: $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 101 MHz) of **5b**.

S2.11 (2,3-Dipiperidino-4,5-bis(2,5-dimethylphenyl)cylopentadienone)iron acetonitrile dicarbonyl (5c)

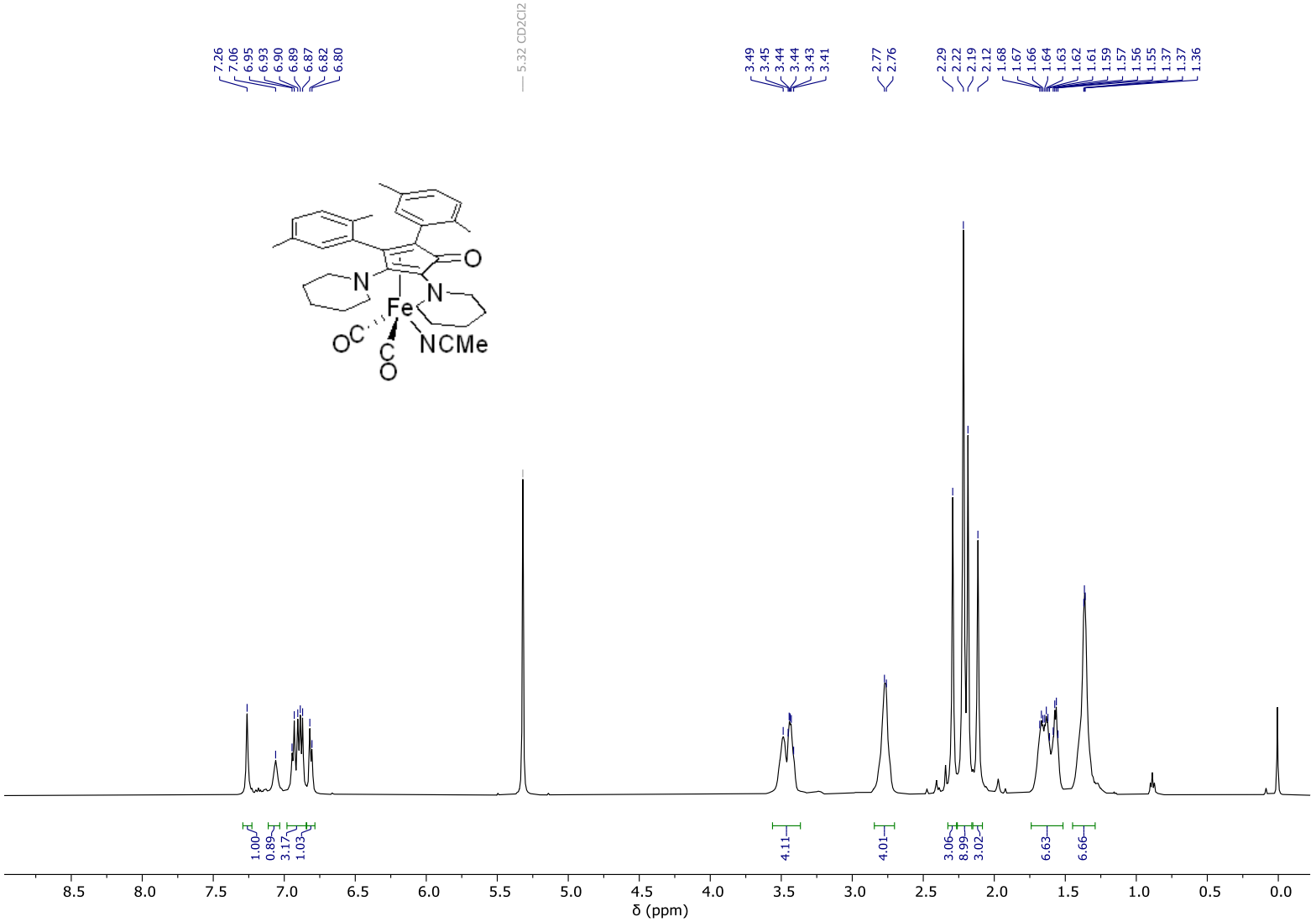


Figure S26: ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz) of **5c**.

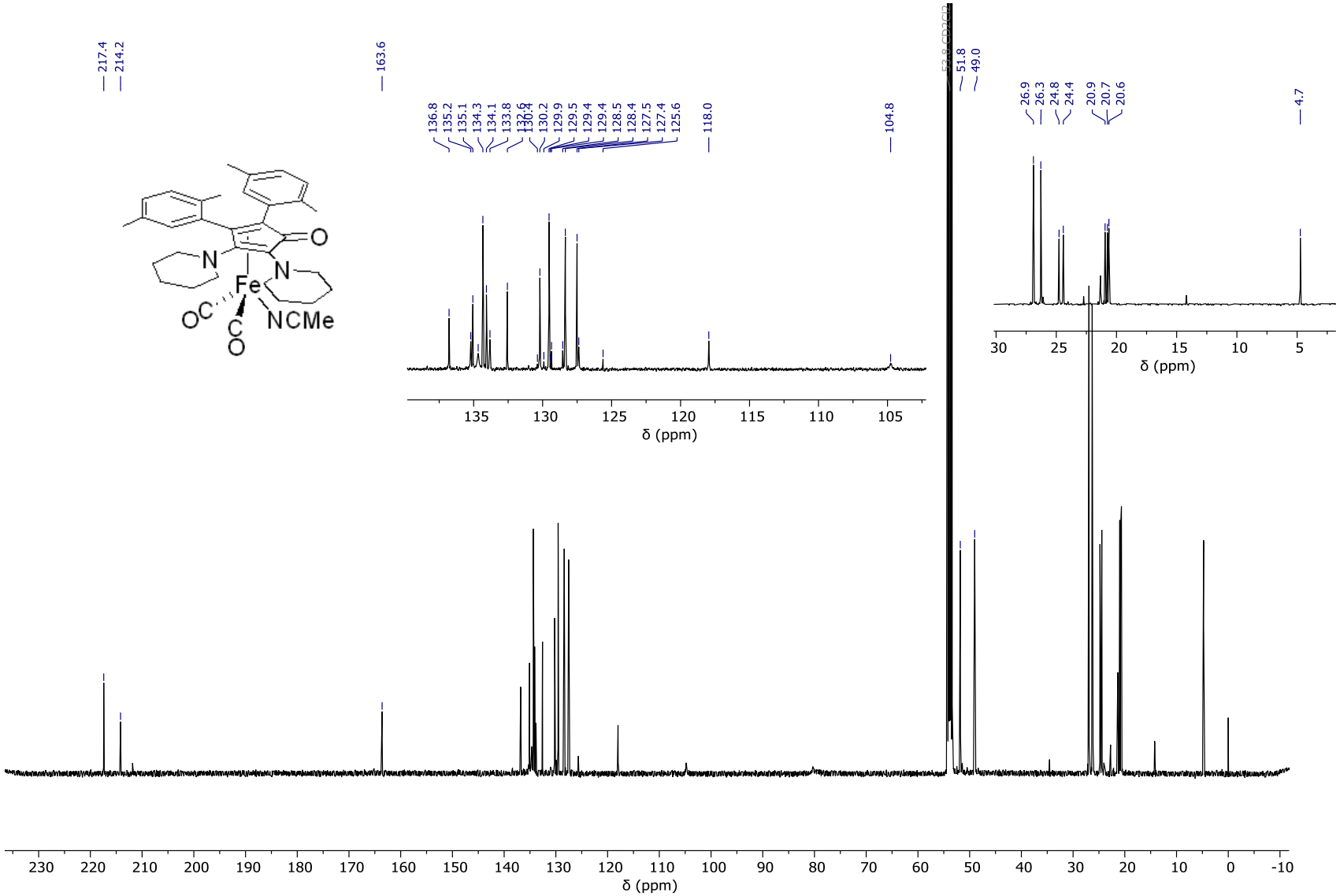


Figure S27: $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 126 MHz) of **5c**.

S2.12 (2,3-Dipiperidino-4,5-bis(4-trifluoromethylphenyl)cylopentadienone)iron acetonitrile dicarbonyl (5d)

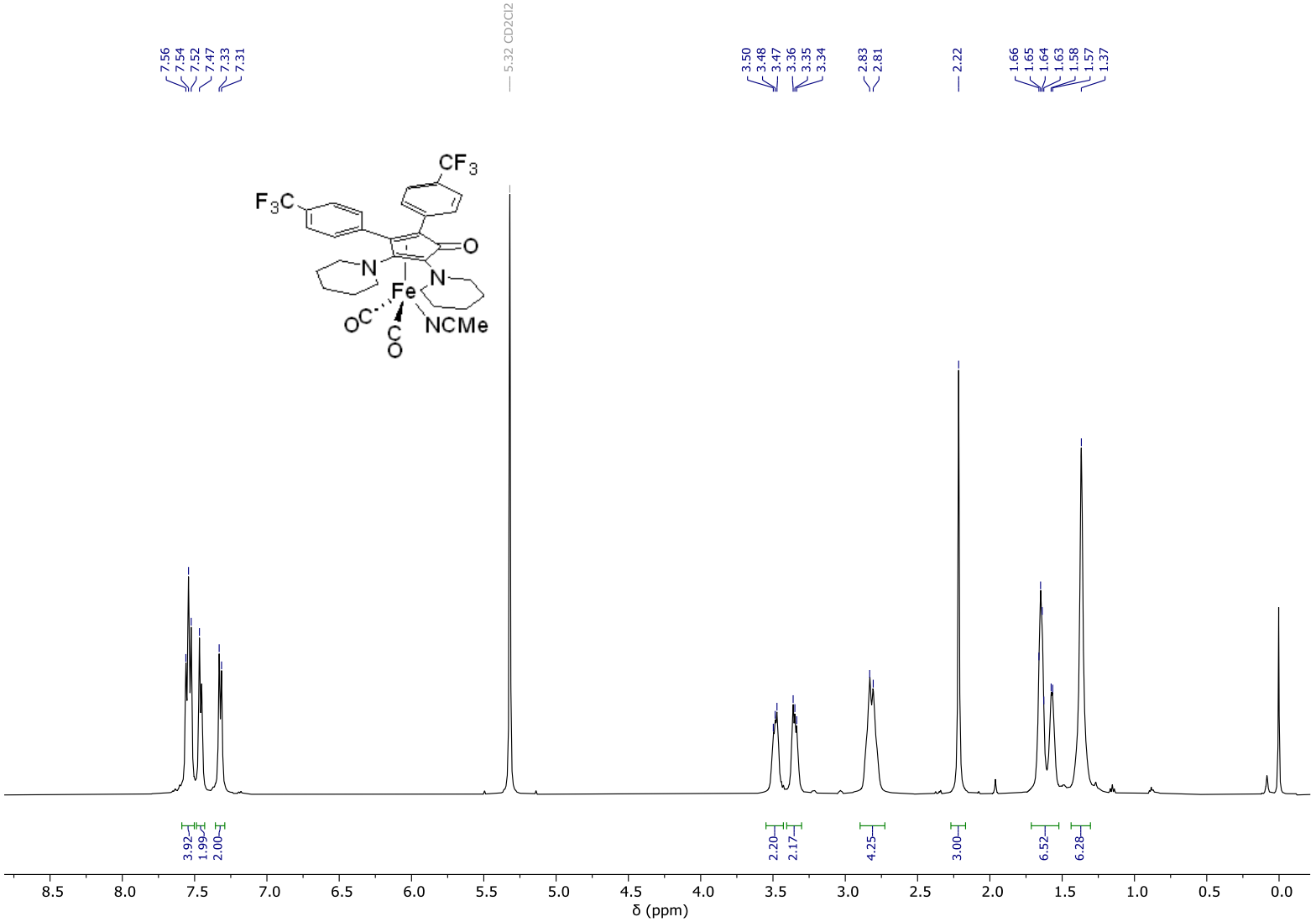


Figure S28: ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz) of **5d**.

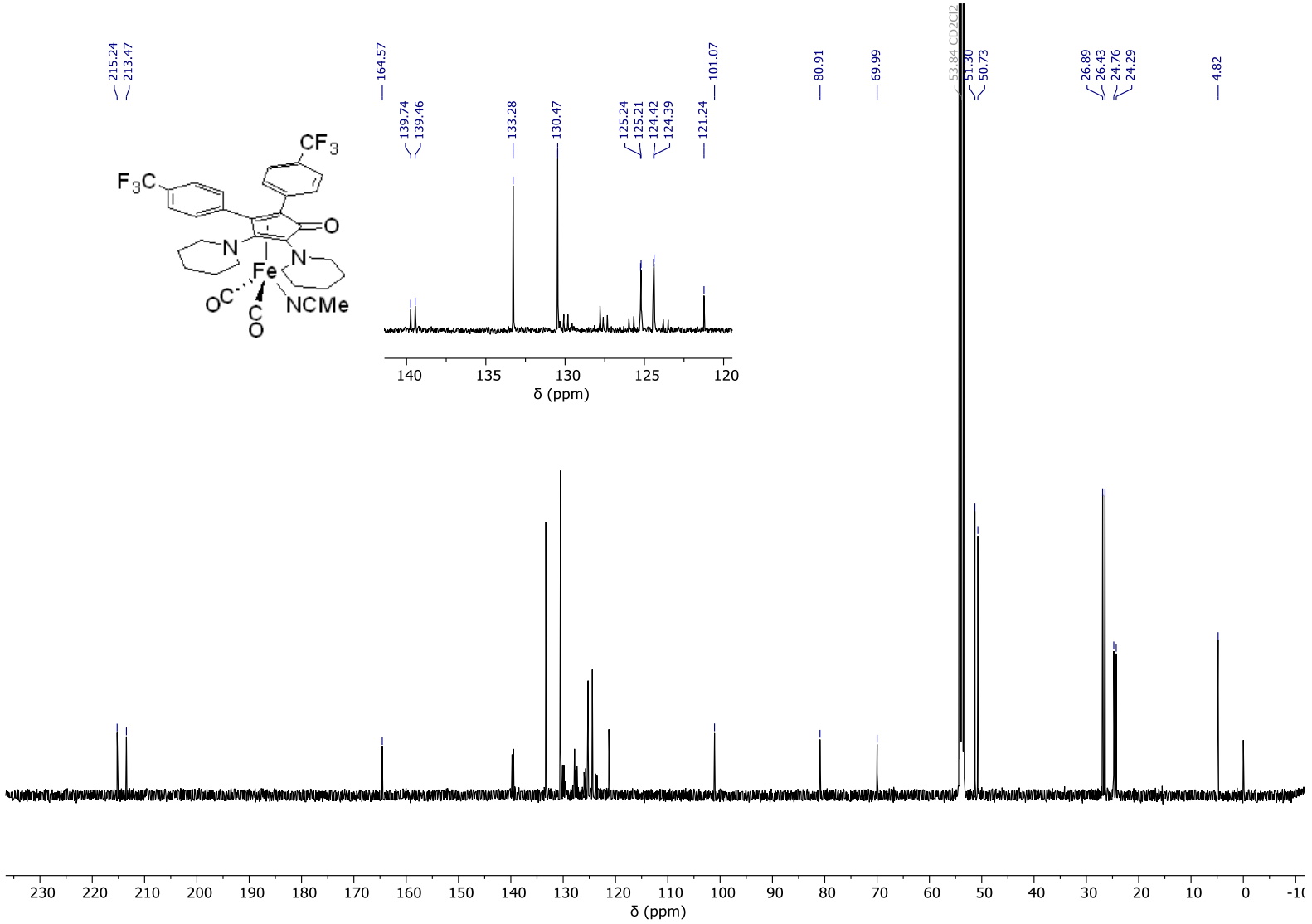


Figure S29: $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 126 MHz) of **5d**.

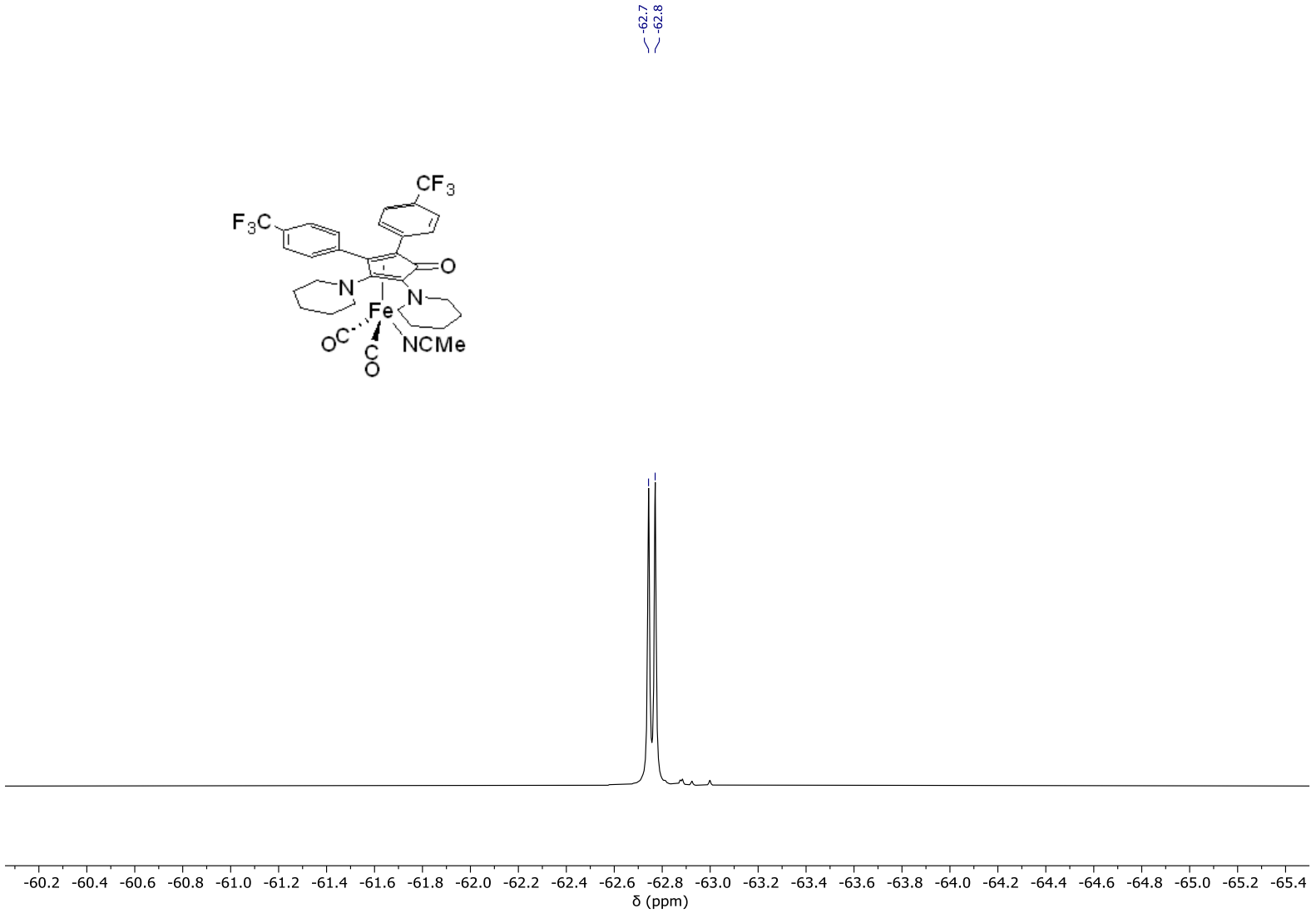


Figure S30: $^{19}F\{^{1}H\}$ NMR spectrum ($CDCl_3$, 471 MHz) of **5d**.

S2.13 (1,4-dimethyl-5,7-diphenyl-1,2,3,4-tetrahydro-6H-cyclopenta[b]pyrazin-6-one)iron acetonitrile dicarbonyl (6)

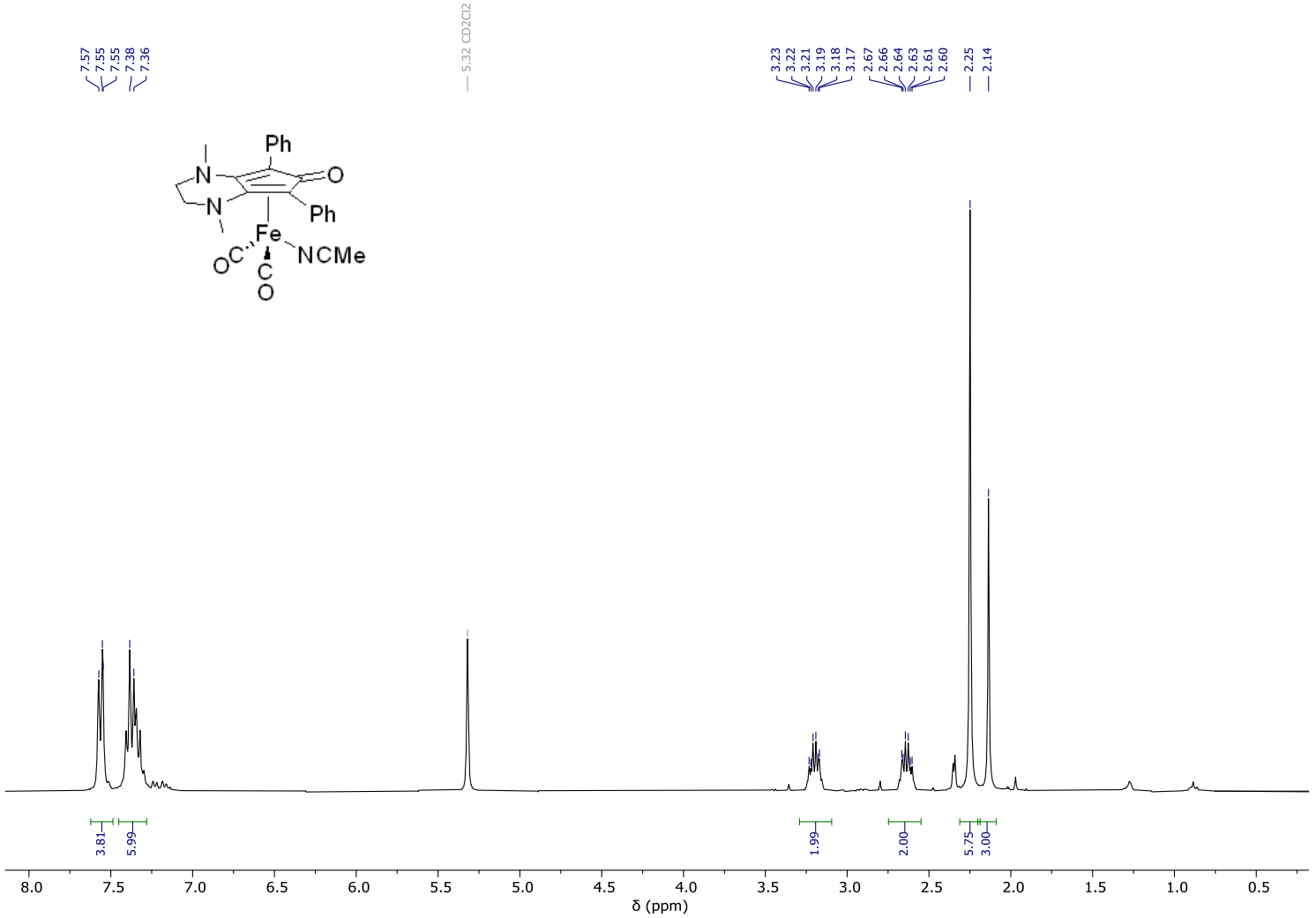


Figure S31: ^{1}H NMR spectrum (CD_2Cl_2, 300 MHz) of **6**.

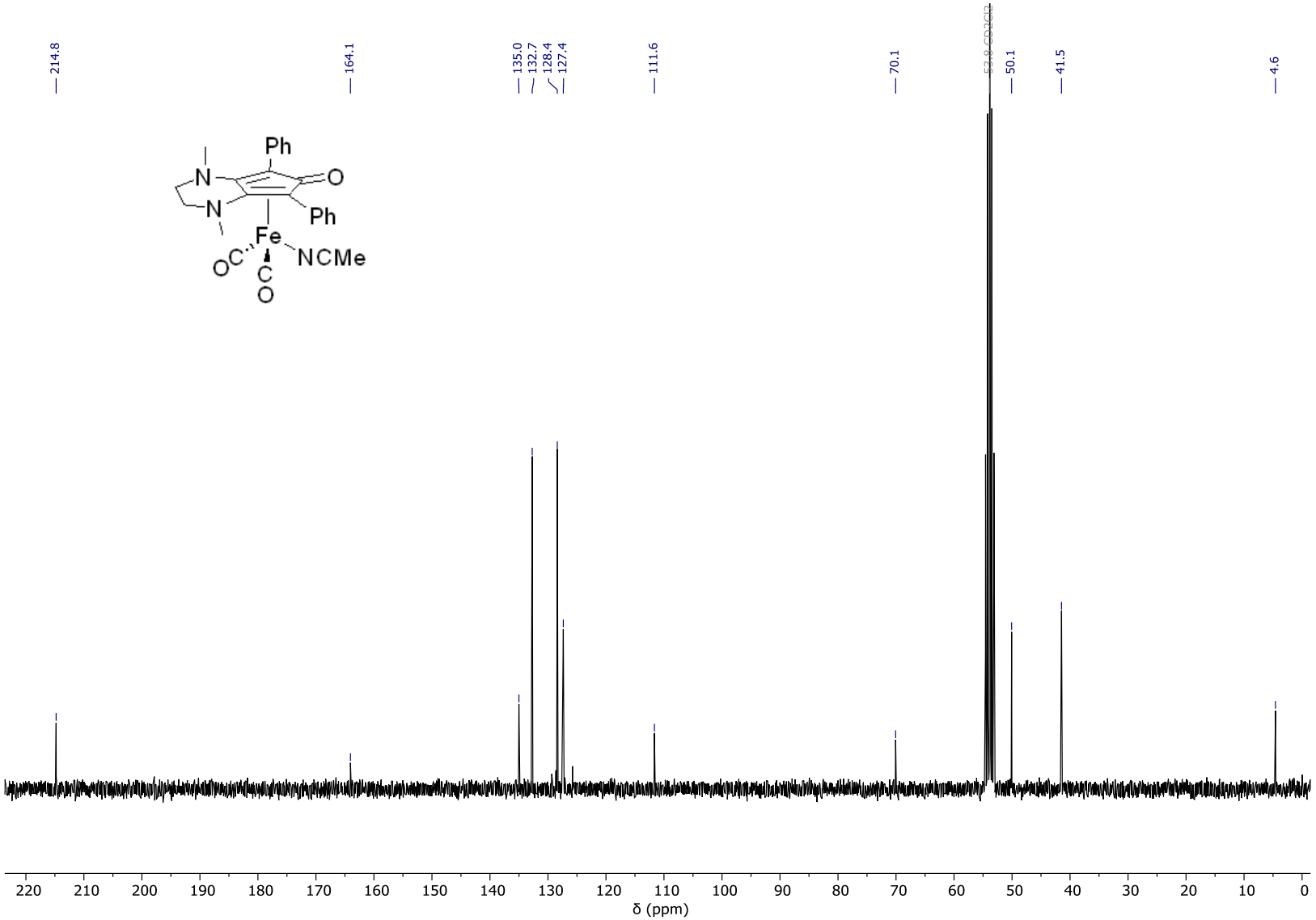


Figure S32: $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 76 MHz) of **6**.

S2.14 Products of the Catalytic Reductive Aminations

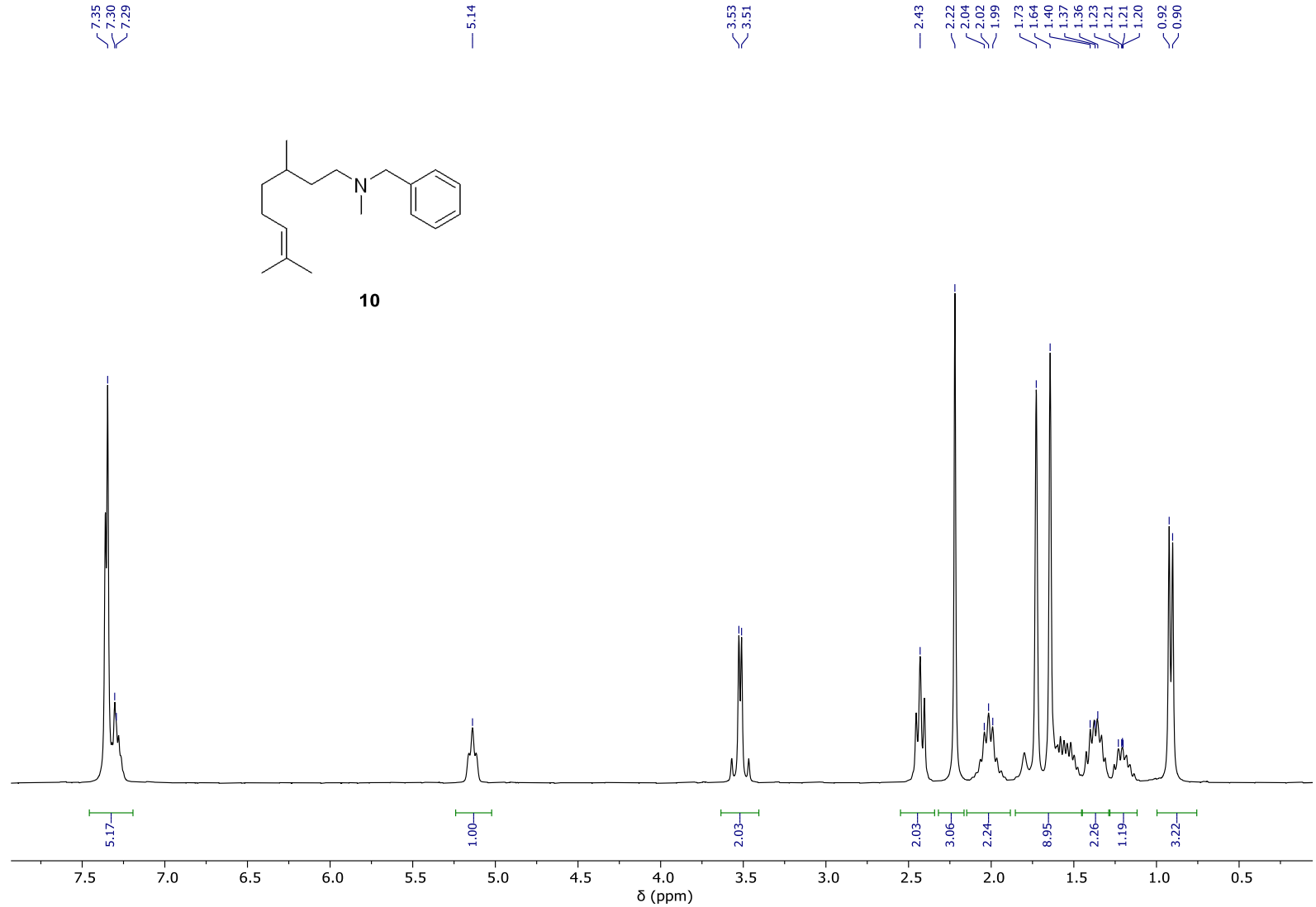


Figure S33: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **10**.

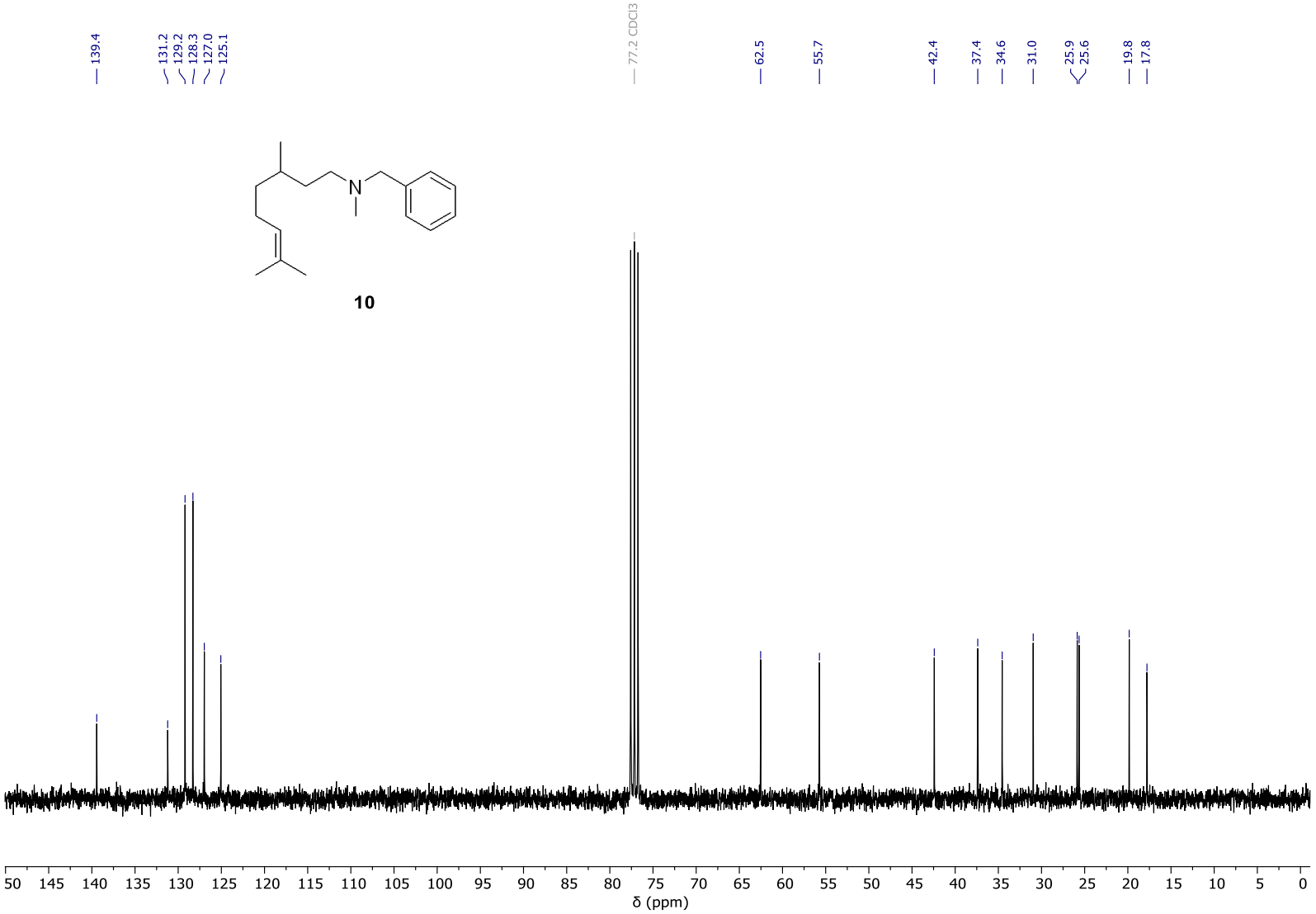


Figure S34: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 76 MHz) of **10**.

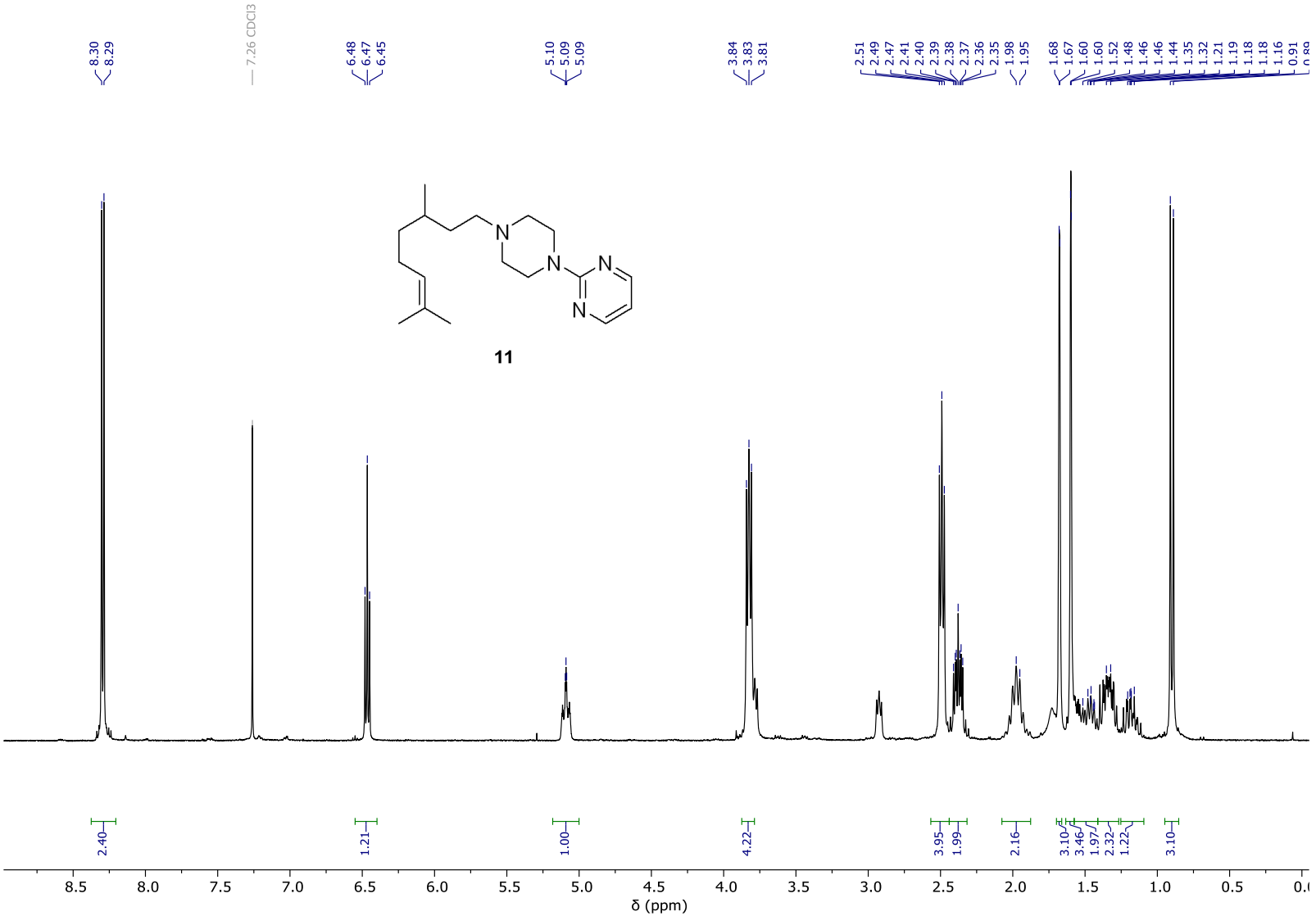


Figure S35: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **11**.

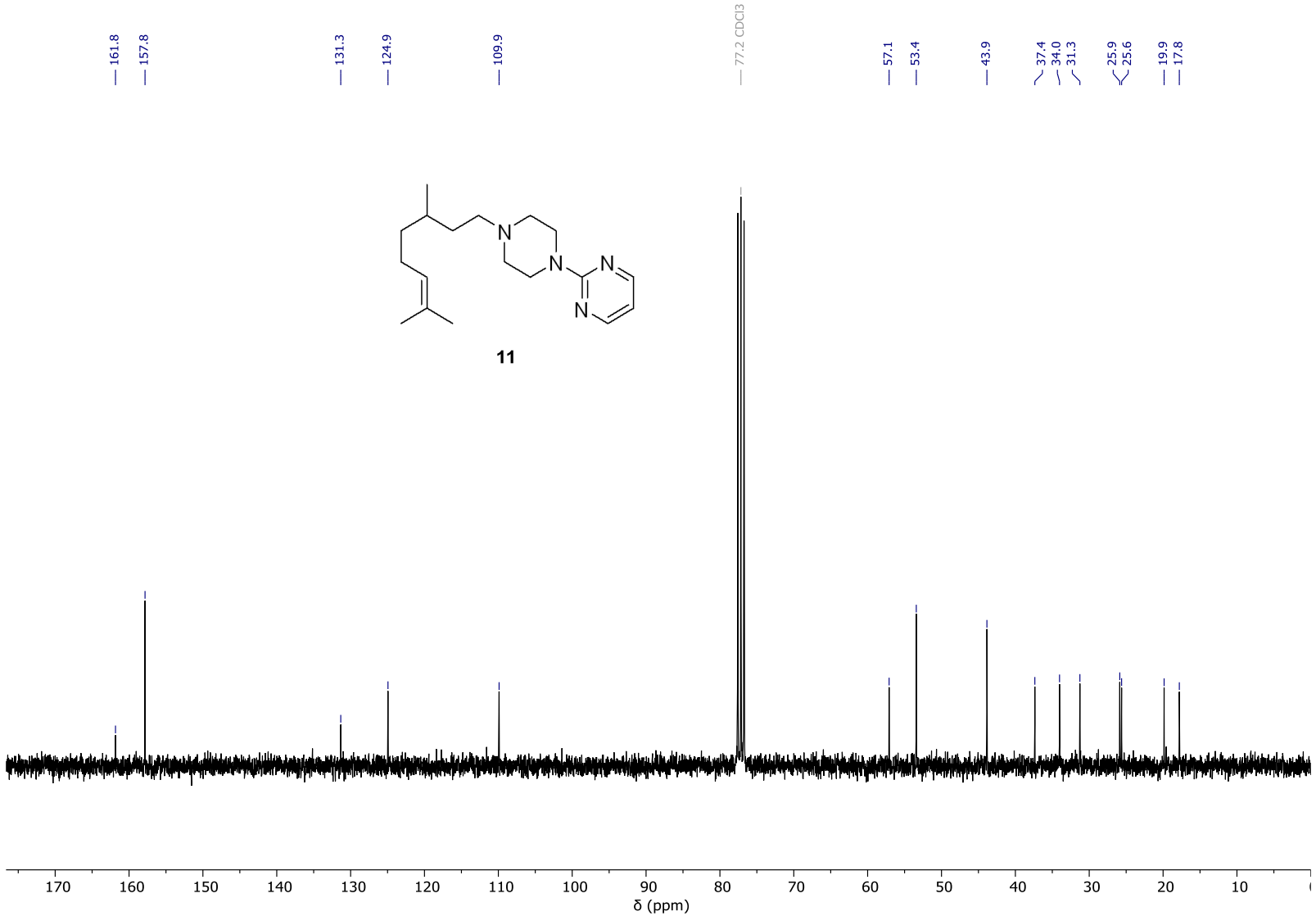


Figure S36: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 300 MHz) of **11**.

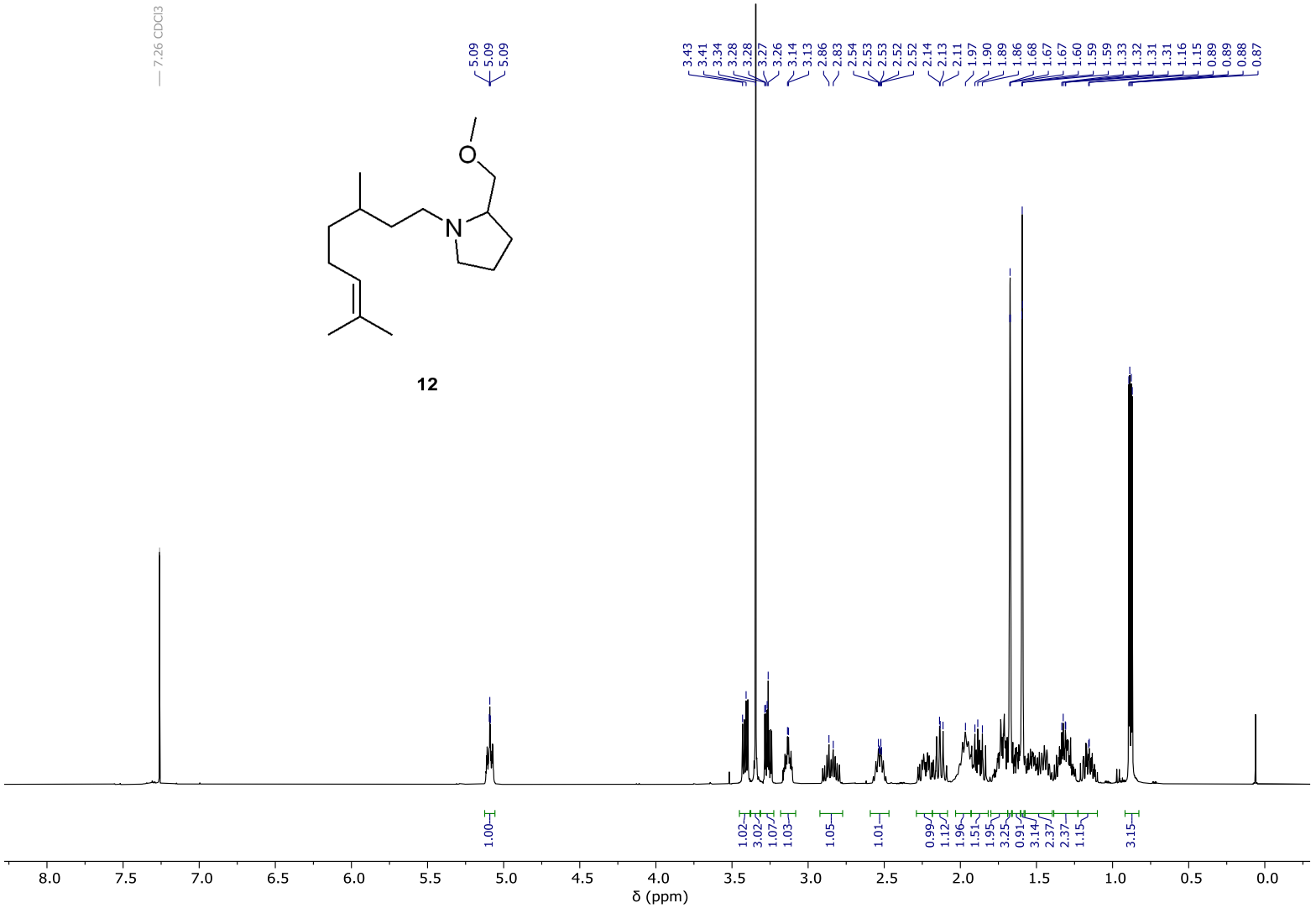


Figure S37: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **12**.

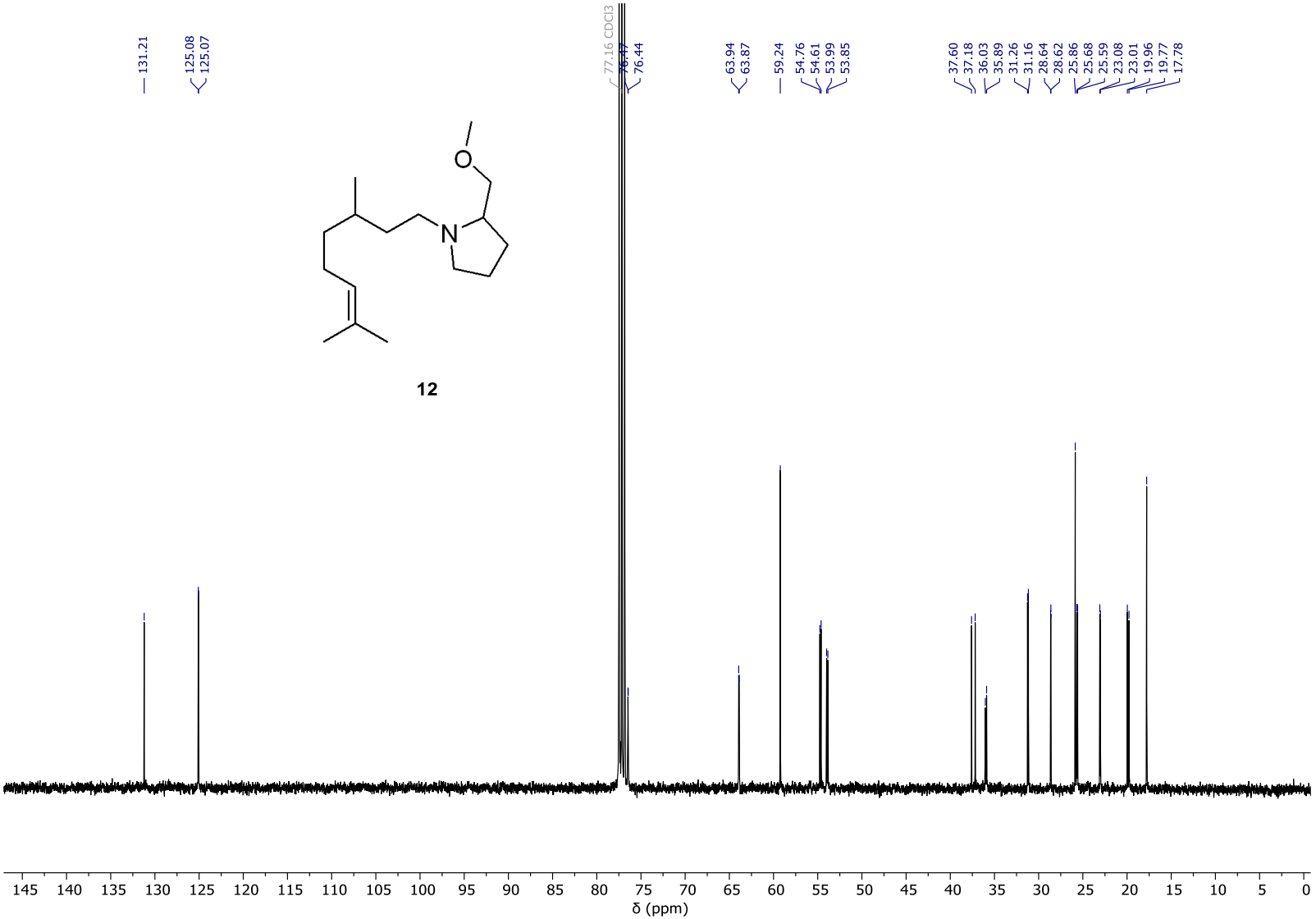


Figure S38: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of **12**.

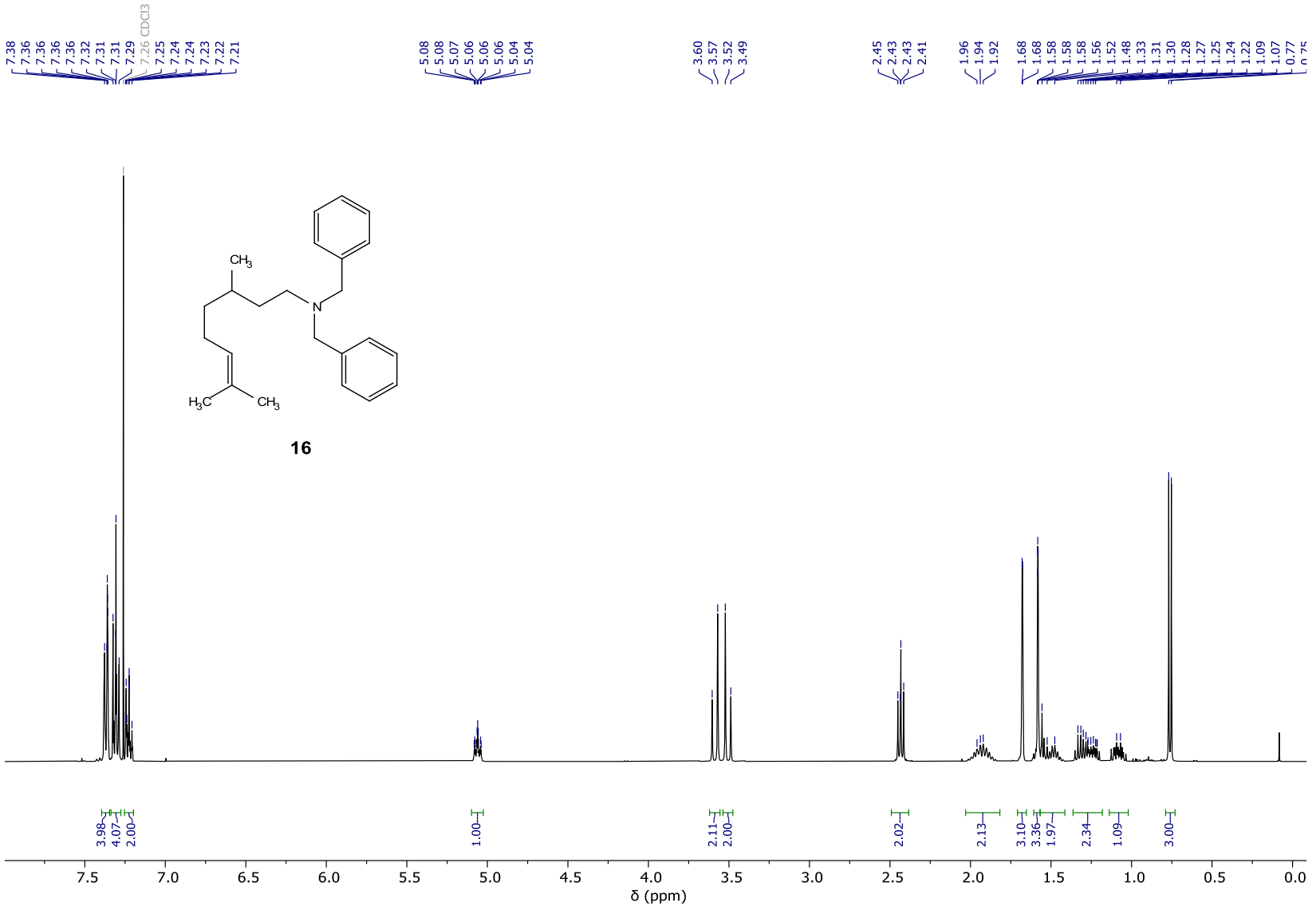


Figure S39: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **16**.

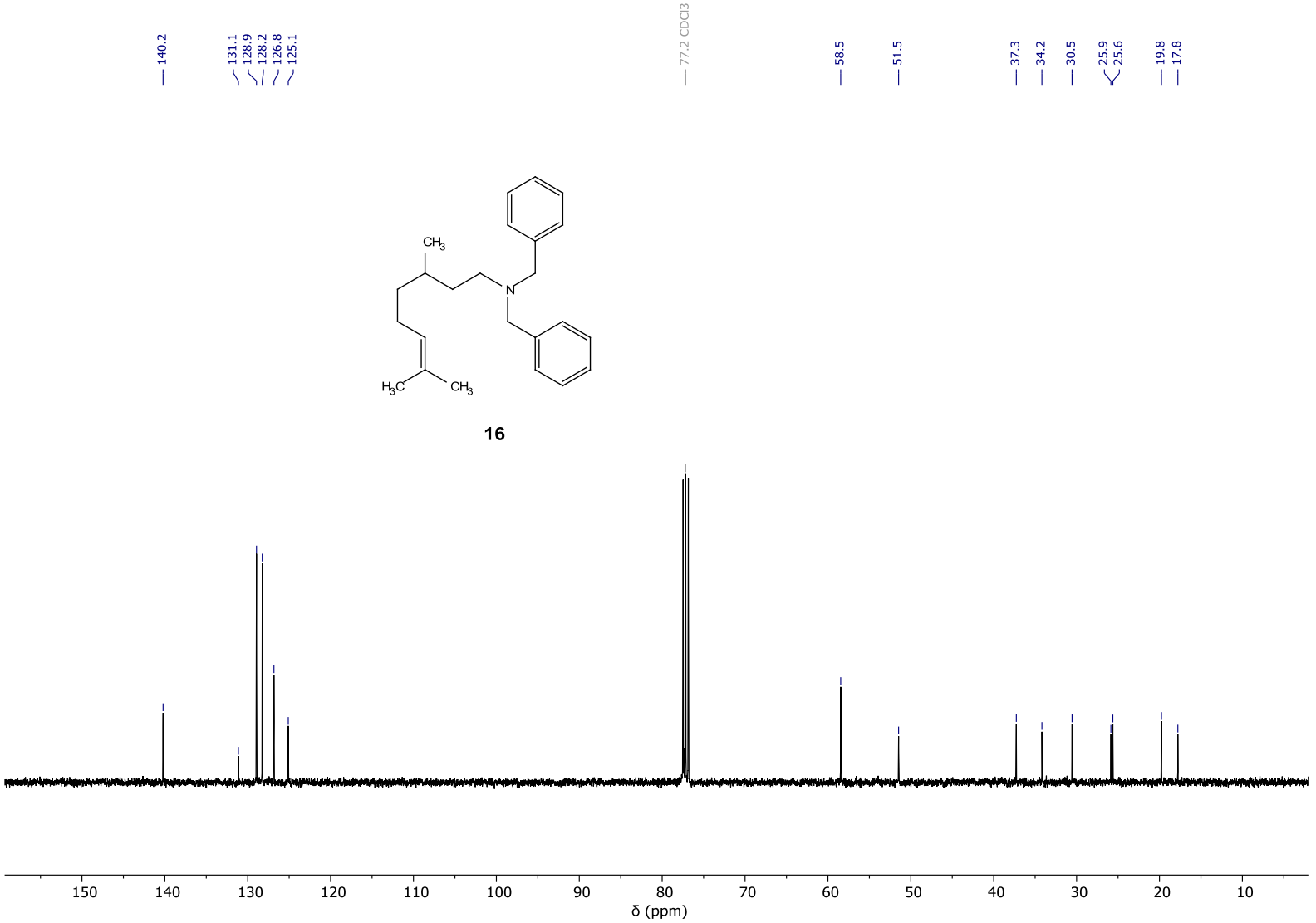


Figure S40: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of **16**.

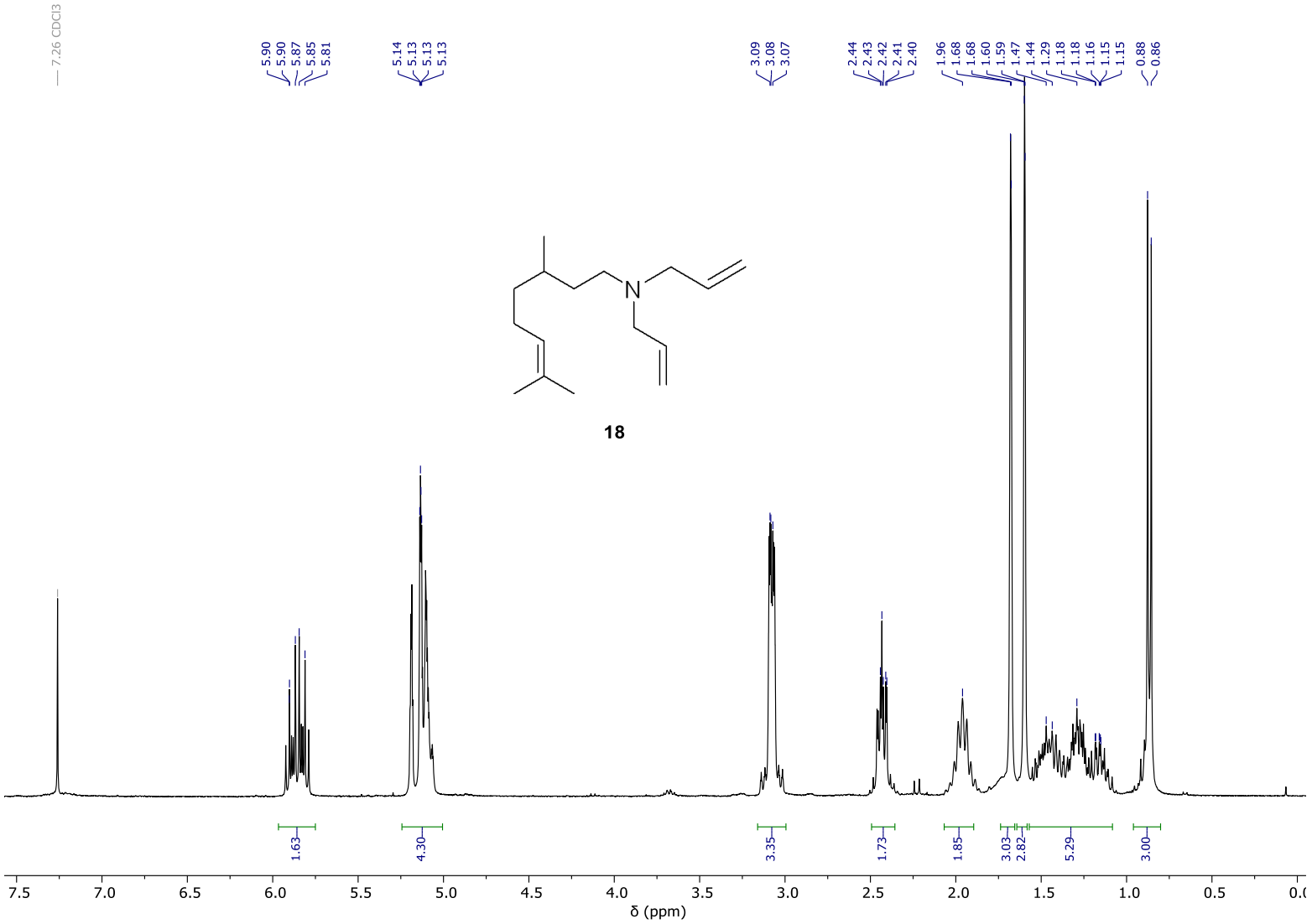


Figure S41: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **18**.

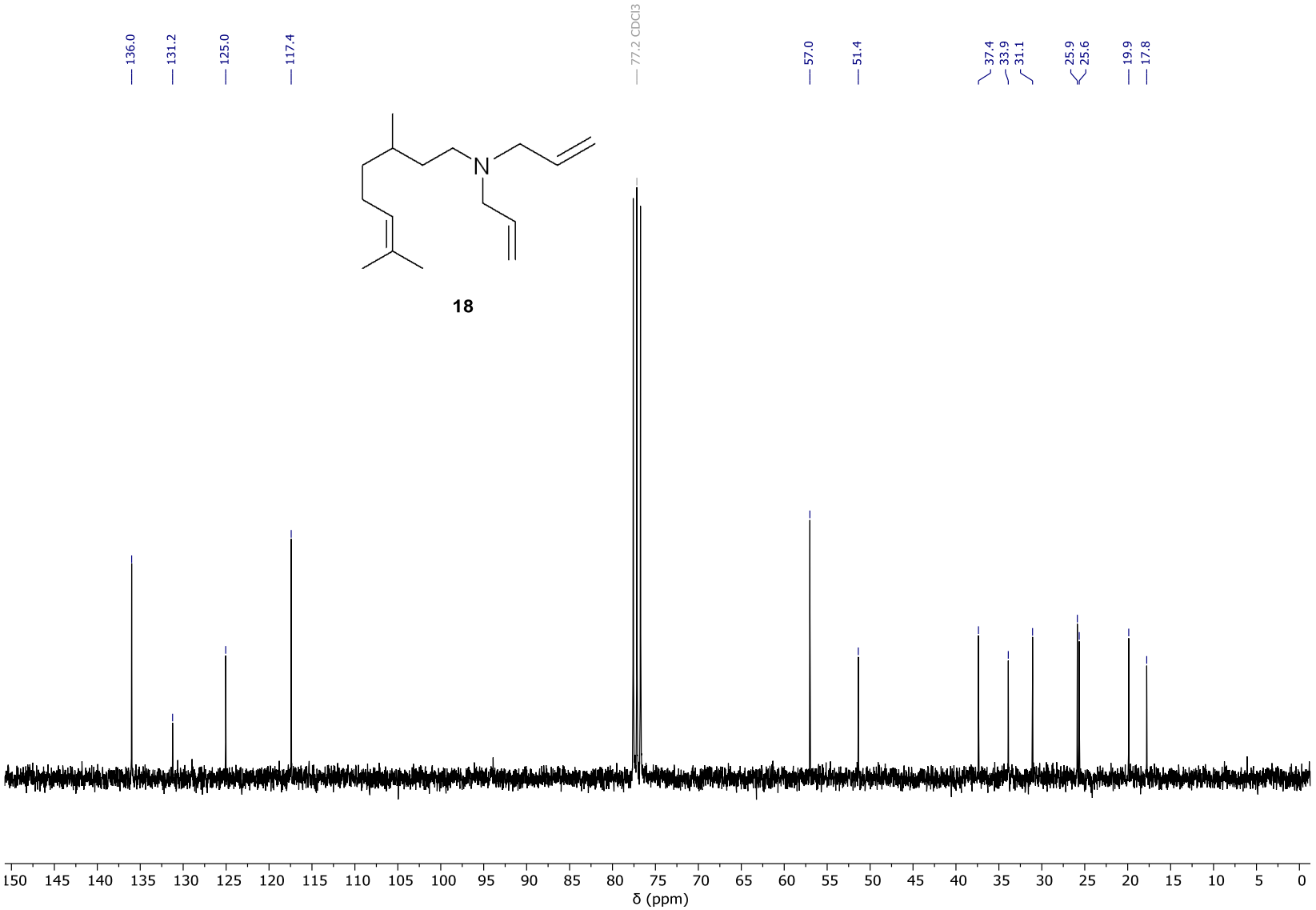


Figure S42: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 76 MHz) of **18**.

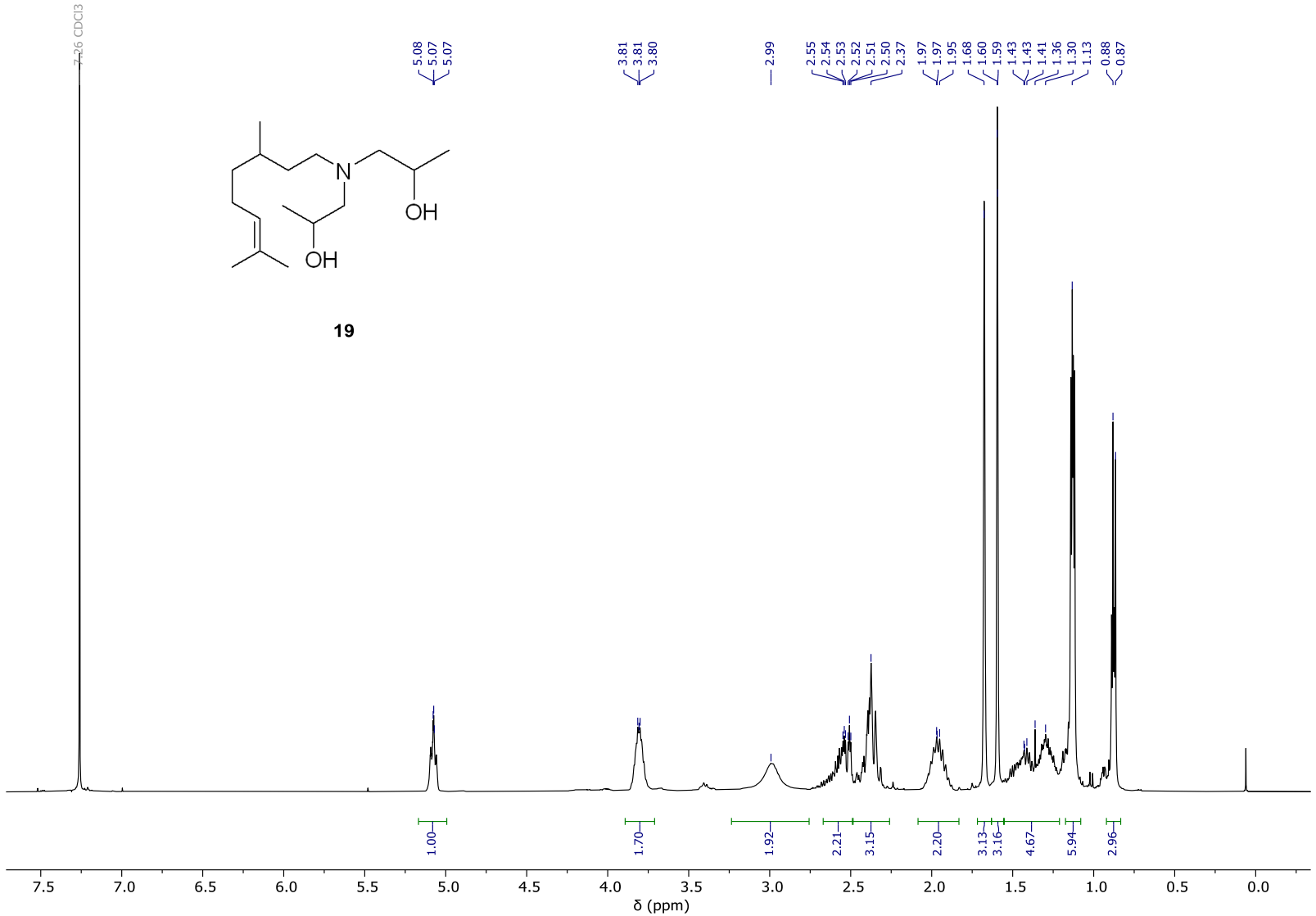


Figure S43: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **19**.

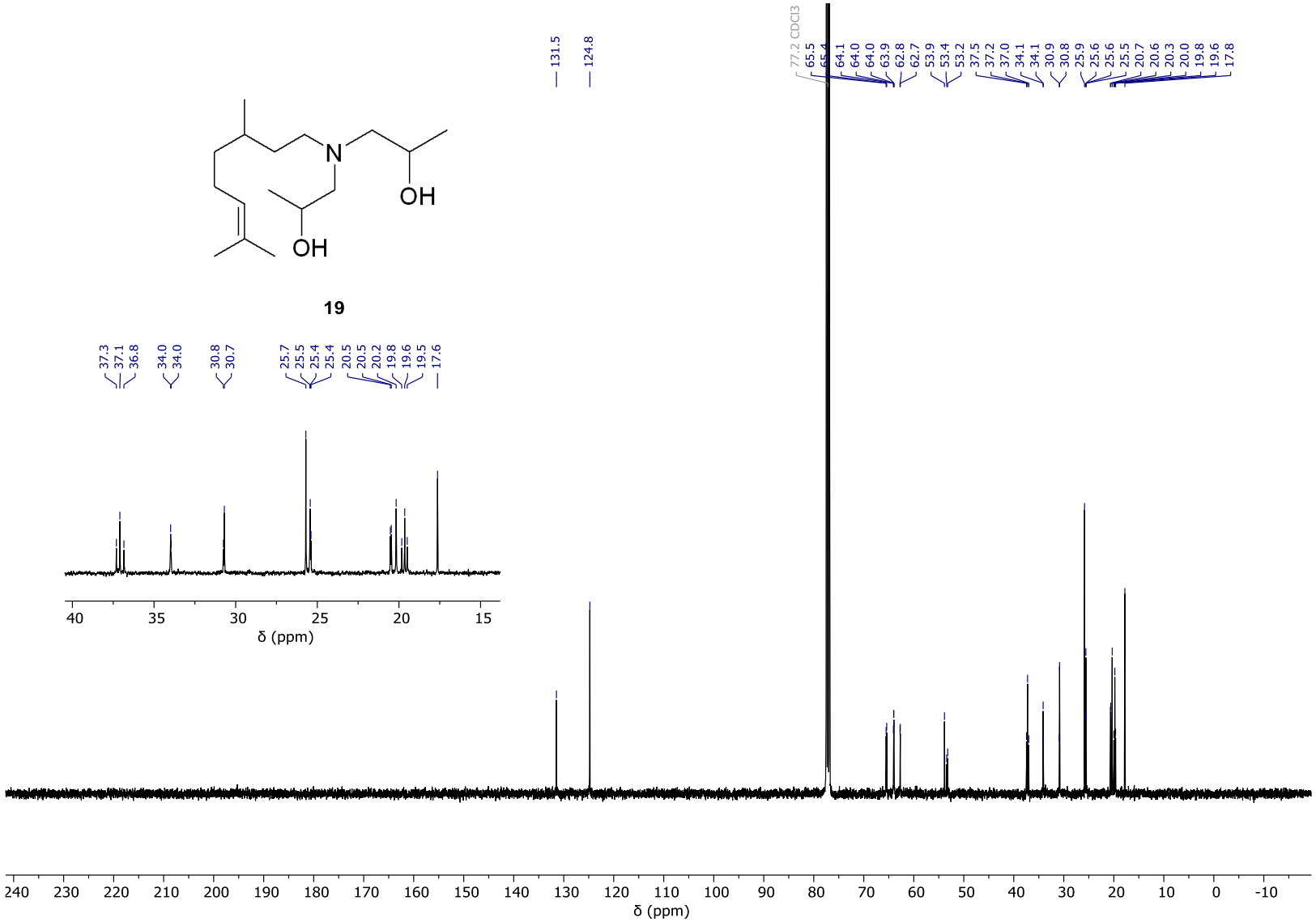


Figure S44: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 101 MHz) of **19**.

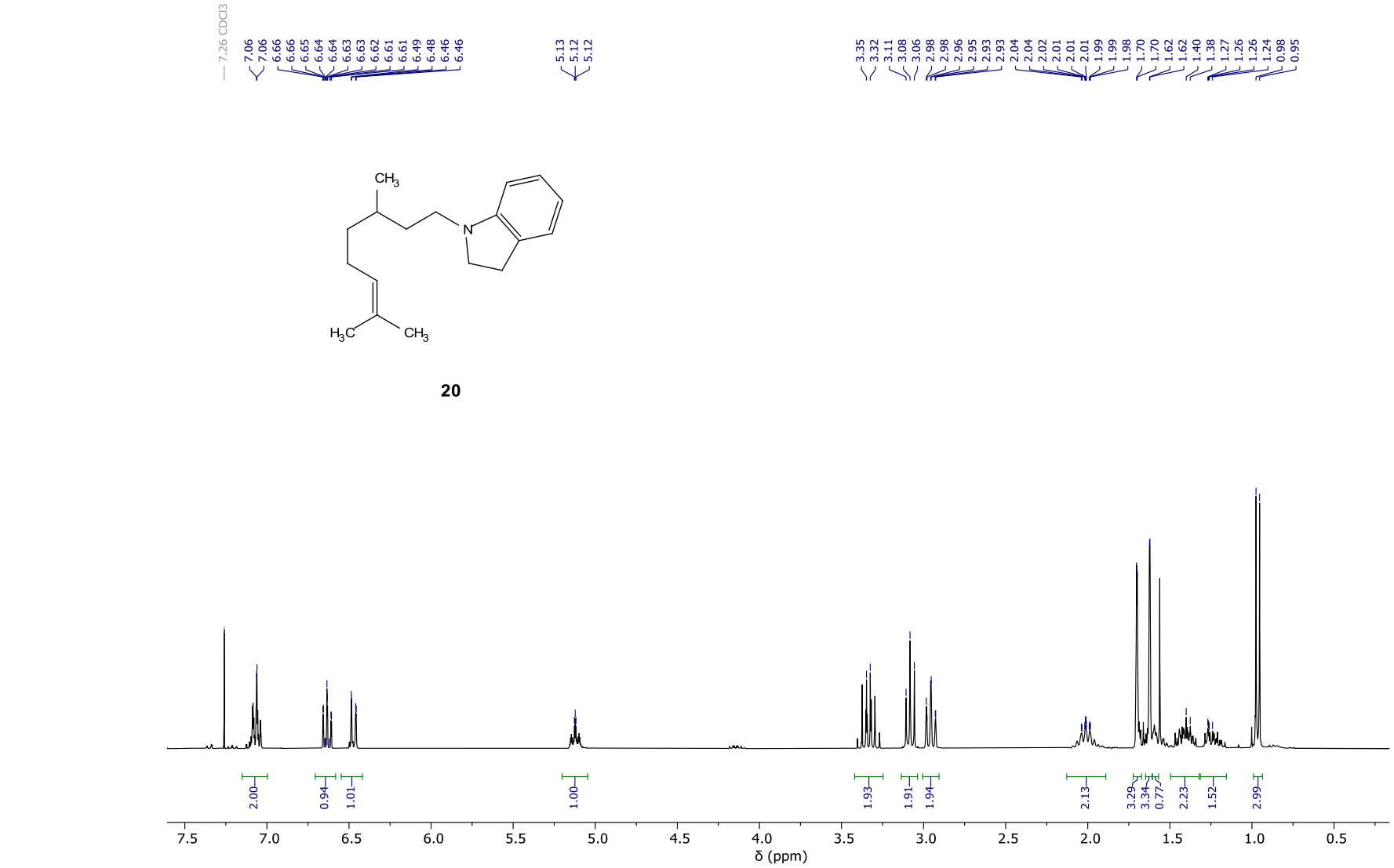


Figure S45: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **20**.

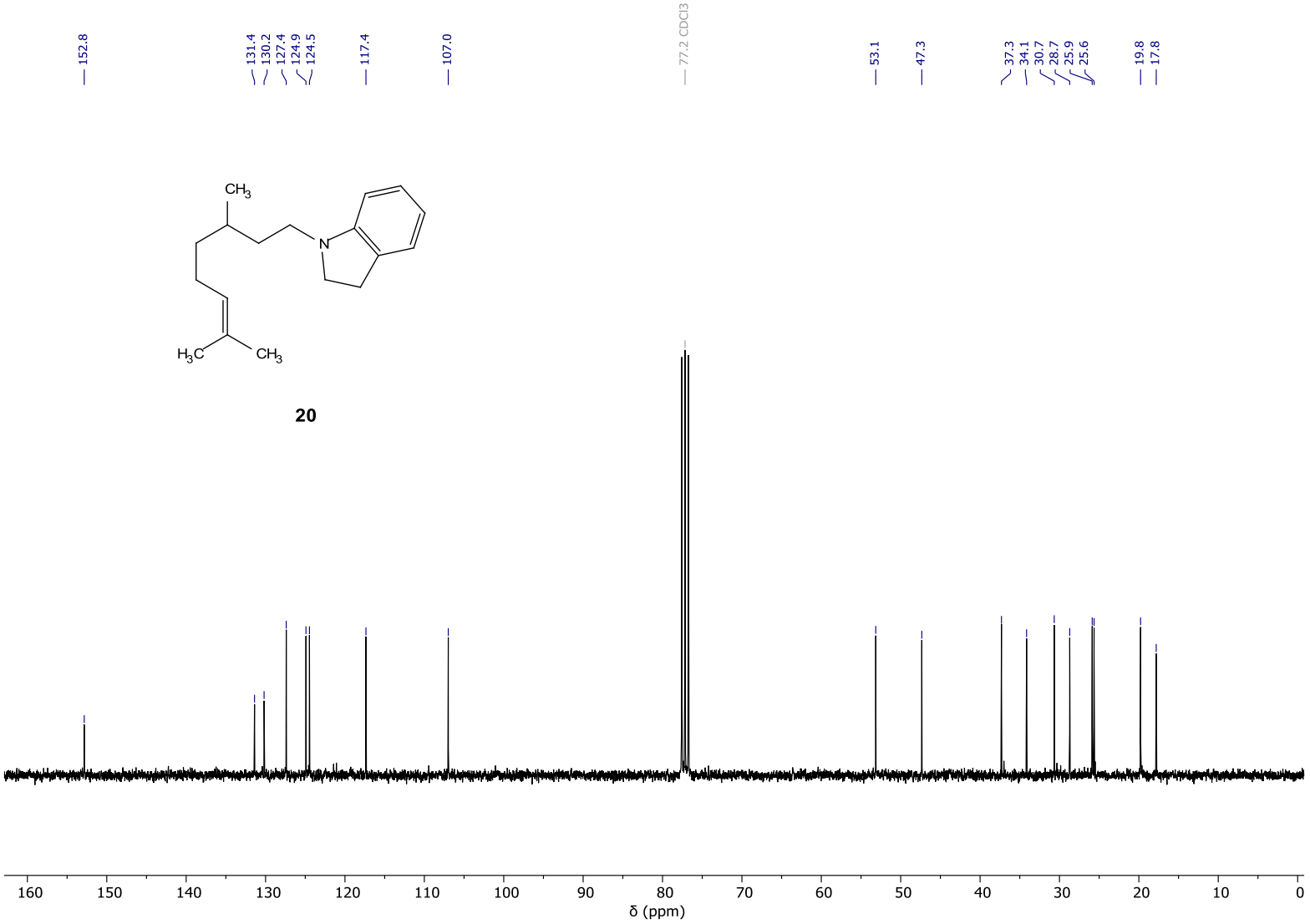


Figure S46: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 76 MHz) of **20**.

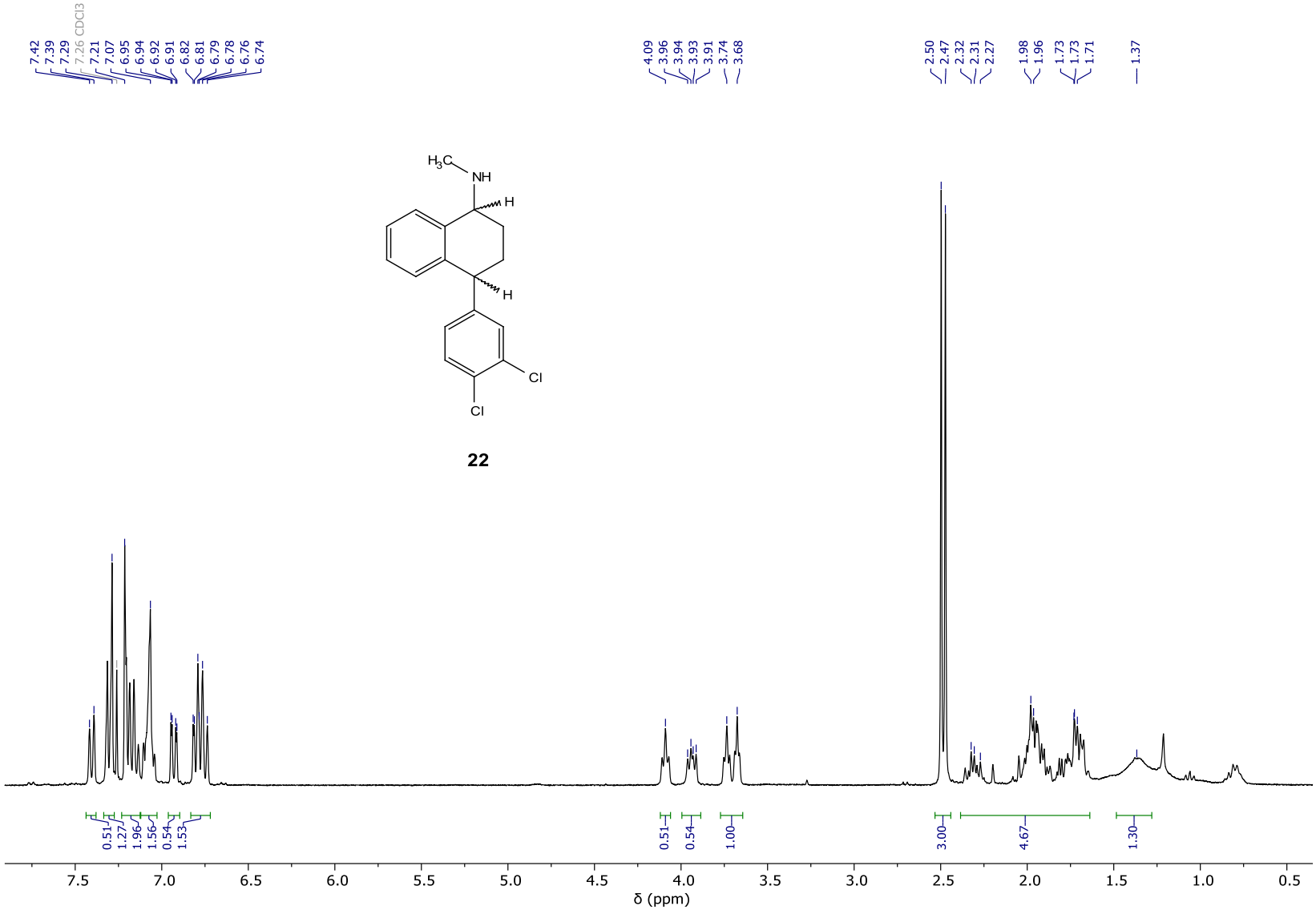


Figure S47: ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of **22**.

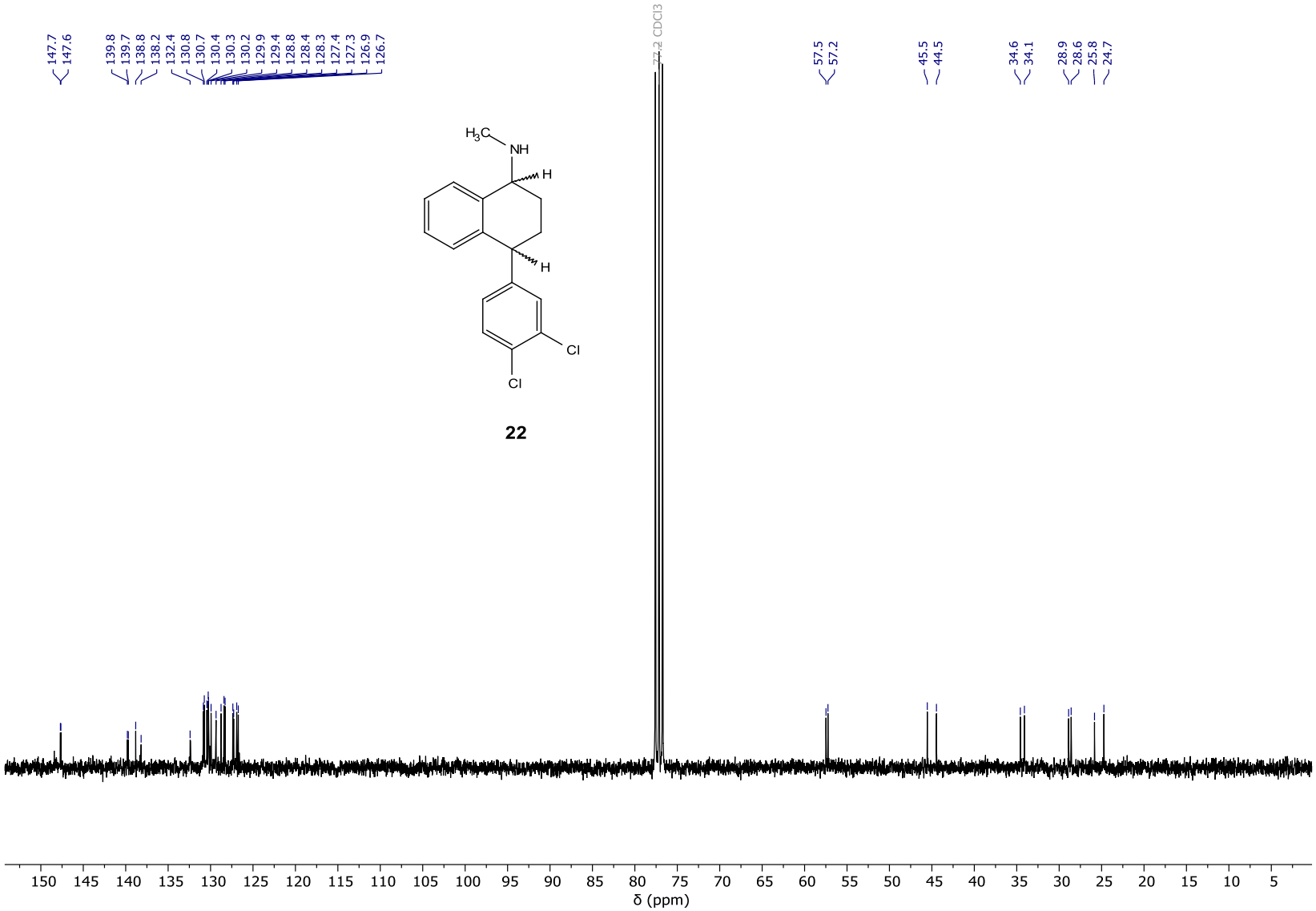


Figure S48: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 76 MHz) of **22**.

S3 Crystallographic Details

Crystals were mounted on top of a human hair (**3a**, **4a**, **4b**·$CHCl_3$, **4c**, **4d**·C_6H_{12}, **5a**·0.5C_7H_8, **5b**·0.5C_6H_{14}, **5d**·MeCN and **6**) or on a Hampton Research CryoLoop™ (**3d** and **5c**·0.7C_5H_8·0.3C_6H_{14}) with per-fluorinated inert oil. Data from compound **4a** were recorded with monochromated Mo-Kα radiation on an Oxford Diffraction Xcalibur EOS diffractometer equipped with a CCD detector. All other data were recorded on Rigaku XtaLAB Synergy S Single Source diffractometers equipped with either a PhotonJet Cu-microfocus source (**3a**, **3d**, **4b**·$CHCl_3$ and **5d**·MeCN) or a PhotonJet Mo-microfocus source (**4c**, **4d**·C_6H_{12}, **5a**·0.5C_7H_8, **5b**·0.5C_6H_{14}, **5c**·0.7C_5H_8·0.3C_6H_{14} and **6**) and a HyPix-6000HE detector. Data reduction was performed with CrysalisPro.[15] Absorption correction was based on multi-scans and additionally face indexation and integration on a Gaussian grid was applied for **3d**, **4a**, **4b**·$CHCl_3$, **4c**, **4d**·C_6H_{12}, **5b**·0.5C_6H_{14}, **5c**·0.7C_5H_8·0.3C_6H_{14}, **5d**·MeCN and **6**. The structures were solved by intrinsic phasing with SHELXT-2018 [16] and refined on F^2 using the program SHELXL-2018 [17] in OLEX2.[18] H atoms were placed in idealized positions and refined using a riding model.

Compound **3d** crystallized with two independent molecules in the asymmetric unit and was refined as non-merohedral twin. The second component (48.5 %) is rotated by -179.3° around the *c* axis. Two CF_3 groups exhibit rotational disorder and were described with a disorder model.

Compound **4d** crystallized as **4d**·C_6H_{12} with two independent molecules in the asymmetric unit and was refined as non-merohedral twin. The minor component (14.9 %) is rotated by -180° around [0.00 0.71 -0.71] in reciprocal space or [0.21 0.93 -0.30] in direct space. Additionally, two CF_3 groups exhibiting rotational disorder were refined with a disorder model.

In **5a**·0.5C_7H_8 one phenyl ligand was found disordered and refined accordingly. Furthermore, the toluene molecule is refined to a s.o.f. of 0.5 and is disordered via the *c* glide plane.

5b crystallized as **5b**·0.5C_6H_{14} with one half molecule of hexane in the asymmetric unit. One *tert*-butyl group of **5b** was refined with a disorder model. Additionally, the structure was refined as a non-merohedral twin with the minor component (42.9 %) rotated by 0.8° around [0.13 0.08 -0.99] (reciprocal) or [0.52 -0.01 -0.85] (direct).

In the crystals obtained from compound **5c** the solvent molecules were found disordered and refined with a disorder model comprising of 0.705 molecules of toluene and 0.295 molecules of n-hexane per asymmetric unit whereas two different orientations were identified for the toluene molecule. Chemically equivalent C-C distances have been restrained in these solvent molecules.

Compound **5d** crystallized as **5d**·MeCN and was refined as a non-merohedral twin. The second component (45.5 %) is rotated by 0.9° around [0.28 -0.94 0.21] (reciprocal) or [0.25 -0.97 -0.01] (direct). One CF_3 group was refined with a 3-component disorder model. Chemically equivalent C-F and F-F distances were restrained to be equal. Furthermore, 0.5 molecules of acetonitrile per Asymmetric unit have been identified but could not be refined satisfactorily. Therefore, a solvent mask, the Olex2 implementation of the program SQUEEZE [Spek, A. L. (**2015**). *Acta Cryst.* C71, 9-18.] has been used to mathematically remove the electron density of these molecules. 21 electrons were found in a volume of 129 $Å^3$ in one void per unit cell which is consistent with the presence of 0.5 molecules of acetonitrile per Asymmetric Unit which account for 22 electrons per unit cell. The sum formula and derived parameters are based

on 0.5 molecules of acetonitrile per Asymmetric unit.

Complete data have been deposited with the Cambridge Crystallographic Data Centre under the CCDC numbers 2338289 – 2338299. These data can be obtained free of charge from http://www.ccdc.cam.ac.uk/.

Table S1. Crystal data and structure refinement of **3a**.

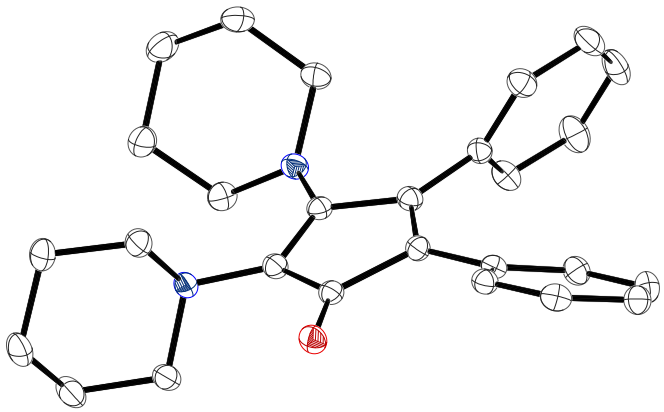
	CCDC	2338289
	Empirical formula	$C_{27}H_{30}N_2O$
	Formula weight	398.53
	Temperature	100(2) K
	Wavelength	1.54184 Å
	Crystal system	Monoclinic
	Space group	$P2_1/c$
	Unit cell dimensions	
	a = 19.5712(6) Å	α = 90°
	b = 5.91540(10) Å	β = 115.442(4)°
	c = 20.8266(6) Å	γ = 90°
Volume	2177.30(12) Å^3	
Z	4	
Density (calculated)	1.216 Mg/m^3	
Absorption coefficient	0.569 mm^{-1}	
F(000)	856	
Crystal habitus	needle (brown)	
Crystal size	0.540 x 0.050 x 0.030 mm^3	
ϑ range for data collection	2.500 to 77.378°	
Index ranges	$-24 \le h \le 24$, $-7 \le k \le 5$, $-26 \le l \le 26$	
Reflections collected	34754	
Independent reflections	4537[R_{int} = 0.0433]	
Completeness to ϑ = 67.684°	99.9 %	
Max. and min. transmission	1.00000 and 0.65030	
Data / restraints / parameters	4537 / 0 / 272	
Goodness-of-fit on F^2	1.025	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0367, wR_2 = 0.0886	
R indices (all data)	R_1 = 0.0440, wR_2 = 0.0926	
Largest diff. peak and hole	0.266 and -0.184 e·Å^3	
Crystallisation Details:	from Et_2O / n-hexan, -40 °C	

Table S2. Crystal data and structure refinement of **3d**.

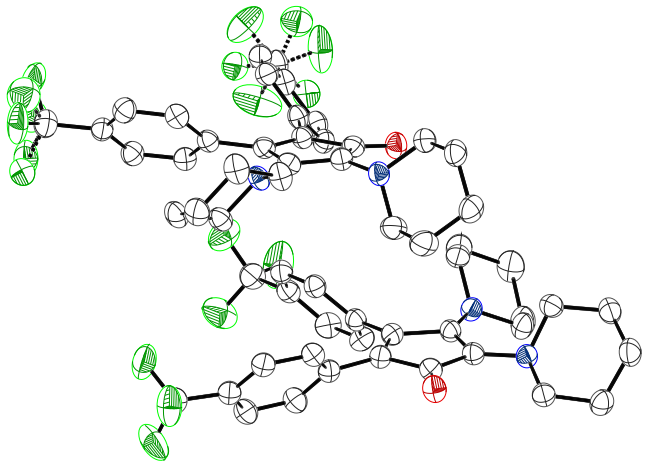
	CCDC	2338290
	Empirical formula	$C_{29}H_{28}F_6N_2O$
	Formula weight	534.53
	Temperature	100(2) K
	Wavelength	1.54184 Å
	Crystal system	Orthorhombic
	Space group	*Pbca*
	Unit cell dimensions	
	a = 18.6211(6) Å	α = 90°
	b = 16.9942(4) Å	β = 90°
	c = 32.0027(8) Å	γ = 90°
Volume	10127.3(5) Å^3	
Z	16	
Density (calculated)	1.402 Mg/m^3	
Absorption coefficient	0.990 mm^{-1}	
F(000)	4448	
Crystal habitus	plate (brown)	
Crystal size	0.100 x 0.050 x 0.030 mm^3	
ϑ range for data collection	2.761 to 76.274°	
Index ranges	$-23 \le h \le 23$, $-21 \le k \le 21$, $-39 \le l \le 39$	
Reflections collected	26477	
Independent reflections	26477	
Completeness to ϑ = 67.684°	99.6 %	
Max. and min. transmission	1.000 and 0.845	
Data / restraints / parameters	26477 / 42 / 742	
Goodness-of-fit on F^2	1.015	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0622, wR_2 = 0.1503	
R indices (all data)	R_1 = 0.1081, wR_2 = 0.1727	
Largest diff. peak and hole	0.385 and -0.255 e·Å^3	
Crystallisation Details:	from *n*-hexane, -40 °C	

Table S3. Crystal data and structure refinement of **4a**.

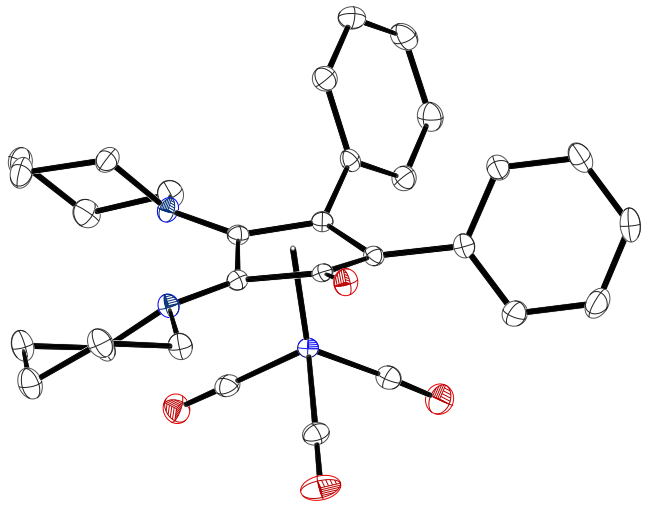
	CCDC	2338291
	Empirical formula	$C_{30}H_{30}FeN_2O_4$
	Formula weight	538.41
	Temperature	110(2) K
	Wavelength	0.71073 Å
	Crystal system	Monoclinic
	Space group	$P2_1/n$
	Unit cell dimensions	
	a = 9.5244(5) Å	α = 90°
	b = 27.7280(10) Å	β = 114.029(7)°
	c = 10.4699(5) Å	γ = 90°
Volume	2525.4(2) Å^3	
Z	4	
Density (calculated)	1.416 Mg/m^3	
Absorption coefficient	0.637 mm^{-1}	
F(000)	1128	
Crystal habitus	irregular (yellow)	
Crystal size	0.330 x 0.280 x 0.200 mm^3	
ϑ range for data collection	2.253 to 30.996°	
Index ranges	$-13 \le h \le 13$, $-40 \le k \le 40$, $-14 \le l \le 15$	
Reflections collected	58781	
Independent reflections	8034[R_{int} = 0.0748]	
Completeness to ϑ = 25.242°	100.0 %	
Max. and min. transmission	0.950 and 0.859	
Data / restraints / parameters	8034 / 0 / 334	
Goodness-of-fit on F^2	1.046	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0417, wR_2 = 0.0900	
R indices (all data)	R_1 = 0.0638, wR_2 = 0.1007	
Largest diff. peak and hole	0.494 and -0.425 e·Å^3	
Crystallisation Details:	THF / n-hexane, rt	

Table S4. Crystal data and structure refinement of **4b**·$CHCl_3$.

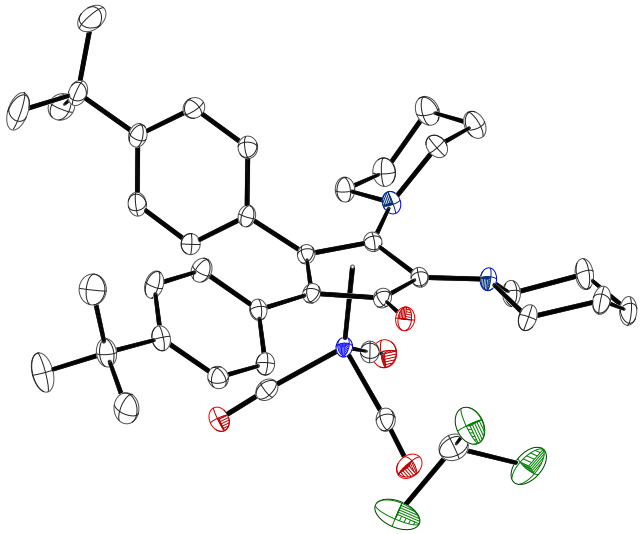
	CCDC	2338292
	Empirical formula	$C_{39}H_{47}Cl_3FeN_2O_4$
	Formula weight	769.98
	Temperature	100(2) K
	Wavelength	1.54184 Å
	Crystal system	Triclinic
	Space group	$P\bar{1}$
	Unit cell dimensions	
	a = 12.3708(3) Å	α = 99.388(2)°
	b = 12.4378(2) Å	β = 97.450(2)°
	c = 13.3652(3) Å	γ = 109.190(2)°
Volume	1878.73(7) $Å^3$	
Z	2	
Density (calculated)	1.361 Mg/m^3	
Absorption coefficient	5.516 mm^{-1}	
F(000)	808	
Crystal habitus	fragment of block (yellow)	
Crystal size	0.290 x 0.100 x 0.090 mm^3	
ϑ range for data collection	3.419 to 77.751°	
Index ranges	$-13 \le h \le 15$, $-15 \le k \le 15$, $-16 \le l \le 16$	
Reflections collected	81045	
Independent reflections	7933[R_{int} = 0.0364]	
Completeness to ϑ = 67.684°	100.0 %	
Max. and min. transmission	1.000 and 0.331	
Data / restraints / parameters	7933 / 0 / 448	
Goodness-of-fit on F^2	1.083	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0322, wR_2 = 0.0859	
R indices (all data)	R_1 = 0.0326, wR_2 = 0.0862	
Largest diff. peak and hole	0.801 and -0.701 e·$Å^3$	
Crystallisation Details:	from chloroform / n-hexane, +3 °C	

Table S5. Crystal data and structure refinement of **4c**.

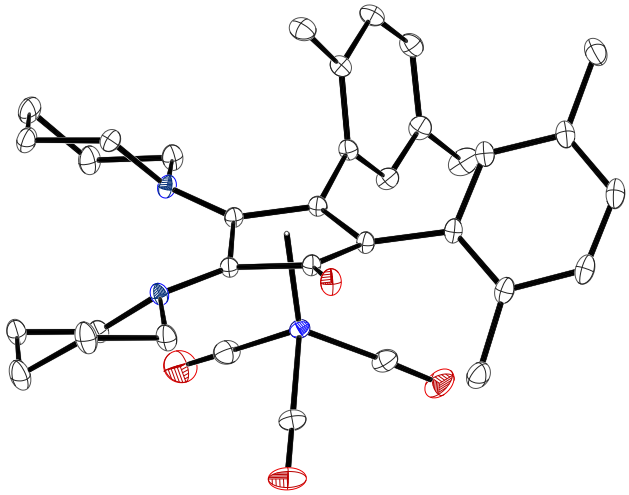
	CCDC	2338293
	Empirical formula	$C_{34}H_{38}FeN_2O_4$
	Formula weight	594.51
	Temperature	100(2) K
	Wavelength	0.71073 Å
	Crystal system	Triclinic
	Space group	$P\bar{1}$
	Unit cell dimensions	
	a = 9.9427(2) Å	α = 105.1650(10)°
	b = 10.8687(2) Å	β = 92.6020(10)°
	c = 16.2473(3) Å	γ = 114.222(2)°
Volume	1521.98(6) Å^3	
Z	2	
Density (calculated)	1.297 Mg/m^3	
Absorption coefficient	0.535 mm^{-1}	
F(000)	628	
Crystal habitus	block (yellow)	
Crystal size	0.324 x 0.194 x 0.178 mm^3	
ϑ range for data collection	2.156 to 44.910°	
Index ranges	$-19 \le h \le 19$, $-21 \le k \le 21$, $-32 \le l \le 32$	
Reflections collected	250909	
Independent reflections	24953[R_{int} = 0.0408]	
Completeness to ϑ = 25.242°	99.8 %	
Max. and min. transmission	1.000 and 0.525	
Data / restraints / parameters	24953 / 0 / 374	
Goodness-of-fit on F^2	1.057	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0302, wR_2 = 0.0860	
R indices (all data)	R_1 = 0.0371, wR_2 = 0.0885	
Largest diff. peak and hole	0.622 and -0.354 e·Å^3	
Crystallisation Details:	from hot *n*-hexane	

Table S6. Crystal data and structure refinement of **4d**·C_6H_{12}.

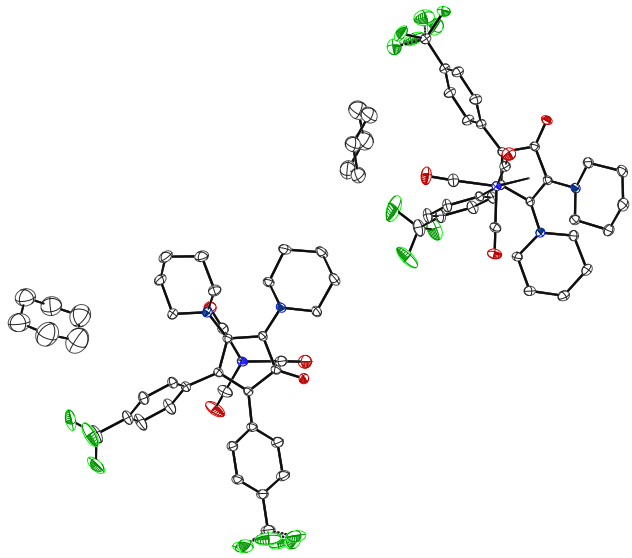
	CCDC	2338294
	Empirical formula	$C_{38}H_{40}F_6FeN_2O_4$
	Formula weight	758.57
	Temperature	100(2) K
	Wavelength	0.71073 Å
	Crystal system	Triclinic
	Space group	$P\bar{1}$
	Unit cell dimensions	
	a = 10.59054(12) Å	α = 101.0985(12)°
	b = 15.4277(2) Å	β = 99.2340(10)°
	c = 23.2167(3) Å	γ = 103.2907(8)°
Volume	3538.46(8) Å^3	
Z	4	
Density (calculated)	1.424 Mg/m^3	
Absorption coefficient	0.501 mm^{-1}	
F(000)	1576	
Crystal habitus	irregular (yellow)	
Crystal size	0.400 x 0.230 x 0.017 mm^3	
ϑ range for data collection	2.020 to 40.327°	
Index ranges	$-19 \le h \le 19$, $-28 \le k \le 28$, $-42 \le l \le 42$	
Reflections collected	78215	
Independent reflections	78215	
Completeness to ϑ = 25.242°	99.9 %	
Max. and min. transmission	1.000 and 0.407	
Data / restraints / parameters	78215 / 144 / 976	
Goodness-of-fit on F^2	1.049	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0855, wR_2 = 0.2310	
R indices (all data)	R_1 = 0.1161, wR_2 = 0.2484	
Largest diff. peak and hole	2.068 and -0.969 e·Å^3	
Crystallisation Details:	from cyclohexane, rt	

Table S7. Crystal data and structure refinement of **5a**·0.5C_7H_8.

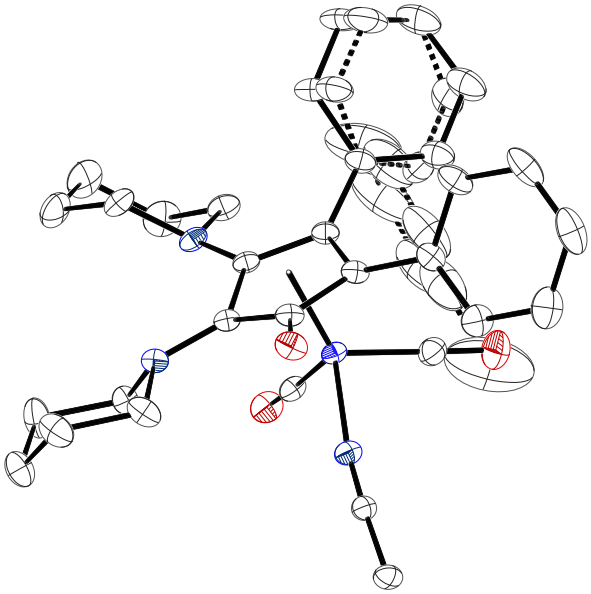
	CCDC	2338295
	Empirical formula	$C_{34.50}H_{37}FeN_3O_3$
	Formula weight	597.52
	Temperature	100(2) K
	Wavelength	0.71073 Å
	Crystal system	Monoclinic
	Space group	$P2_1/c$
	Unit cell dimensions	
	a = 11.3890(5) Å	α = 90°
	b = 28.6159(7) Å	β = 117.667(5)°
	c = 10.6867(5) Å	γ = 90°
Volume	3084.6(2) Å^3	
Z	4	
Density (calculated)	1.287 Mg/m^3	
Absorption coefficient	0.527 mm^{-1}	
F(000)	1260	
Crystal habitus	irregular (yellow)	
Crystal size	0.200 x 0.130 x 0.100 mm^3	
ϑ range for data collection	2.141 to 38.567°	
Index ranges	$-19 \le h \le 19$, $-50 \le k \le 50$, $-18 \le l \le 18$	
Reflections collected	202323	
Independent reflections	17413[R_{int} = 0.0723]	
Completeness to ϑ = 25.242°	99.9 %	
Max. and min. transmission	1.00000 and 0.84183	
Data / restraints / parameters	17413 / 42 / 445	
Goodness-of-fit on F^2	1.056	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0522, wR_2 = 0.1229	
R indices (all data)	R_1 = 0.0724, wR_2 = 0.1312	
Largest diff. peak and hole	0.832 and -0.435 e·Å^3	
Crystallisation Details:	toluene / n-hexane, -40 °C	

Table S8. Crystal data and structure refinement of **5b**·0.5C_6H_{14}.

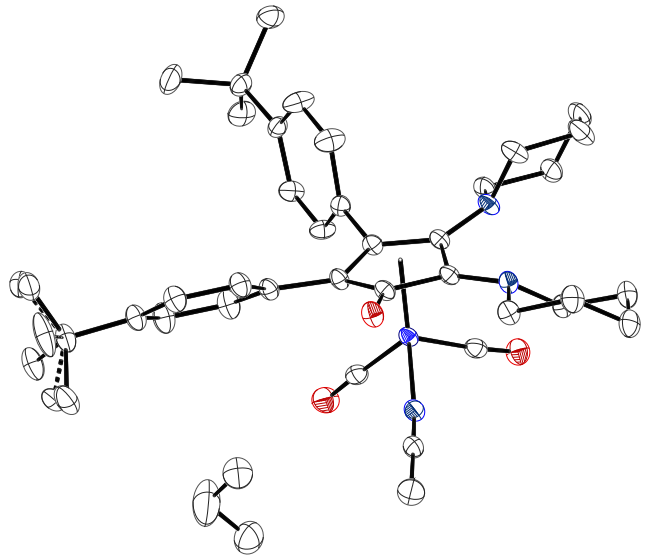
	CCDC	2338296
	Empirical formula	$C_{42}H_{56}FeN_3O_3$
	Formula weight	706.74
	Temperature	101(2) K
	Wavelength	0.71073 Å
	Crystal system	Triclinic
	Space group	$P\bar{1}$
	Unit cell dimensions	
	a = 11.1854(5) Å	α = 86.447(4)°
	b = 12.6987(5) Å	β = 71.724(4)°
	c = 14.8312(7) Å	γ = 71.449(4)°
Volume	1894.75(16) Å^3	
Z	2	
Density (calculated)	1.239 Mg/m^3	
Absorption coefficient	0.440 mm^{-1}	
F(000)	758	
Crystal habitus	plate (yellow)	
Crystal size	0.220 x 0.140 x 0.030 mm^3	
ϑ range for data collection	2.020 to 32.037°	
Index ranges	$-16 \le h \le 16$, $-18 \le k \le 18$, $-22 \le l \le 22$	
Reflections collected	25609	
Independent reflections	25609	
Completeness to ϑ = 25.242°	100.0 %	
Max. and min. transmission	1.000 and 0.589	
Data / restraints / parameters	25609 / 0 / 482	
Goodness-of-fit on F^2	1.089	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0847, wR_2 = 0.1506	
R indices (all data)	R_1 = 0.1178, wR_2 = 0.1632	
Largest diff. peak and hole	0.749 and -0.620 e·Å^3	
Crystallisation Details:	from n-hexane, -40 °C	

Table S9. Crystal data and structure refinement of **5c**·0.7C_5H_8·0.3C_6H_{14}.

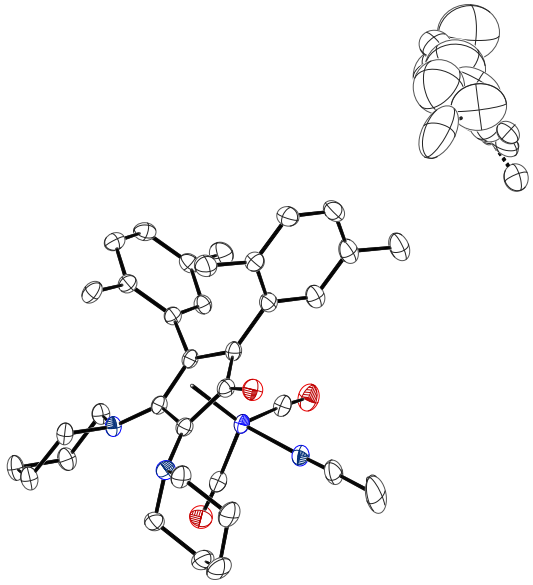
	CCDC	2338297
	Empirical formula	$C_{41.71}H_{50.77}FeN_3O_3$
	Formula weight	697.93
	Temperature	100(2) K
	Wavelength	0.71073 Å
	Crystal system	Monoclinic
	Space group	$P2_1/n$
	Unit cell dimensions	
	a = 11.1925(5) Å	α = 90°
	b = 28.2554(8) Å	β = 113.551(6)°
	c = 12.9763(6) Å	γ = 90°
Volume	3761.9(3) Å^3	
Z	4	
Density (calculated)	1.232 Mg/m^3	
Absorption coefficient	0.442 mm^{-1}	
F(000)	1488	
Crystal habitus	irregular (orange)	
Crystal size	0.230 x 0.190 x 0.050 mm^3	
ϑ range for data collection	2.112 to 32.577°	
Index ranges	$-16 \le h \le 16$, $-42 \le k \le 42$, $-19 \le l \le 19$	
Reflections collected	133590	
Independent reflections	13691[R_{int} = 0.0712]	
Completeness to ϑ = 25.242°	100.0 %	
Max. and min. transmission	1.000 and 0.516	
Data / restraints / parameters	13691 / 247 / 547	
Goodness-of-fit on F^2	1.125	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0675, wR_2 = 0.1425	
R indices (all data)	R_1 = 0.0916, wR_2 = 0.1516	
Largest diff. peak and hole	0.833 and -0.784 e·Å^3	
Crystallisation Details:	toluene / n-hexane, rt	

Table S10. Crystal data and structure refinement of **5d**·MeCN.

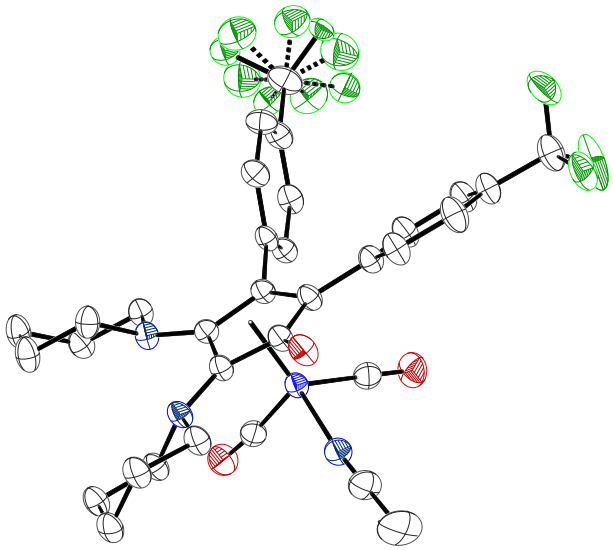
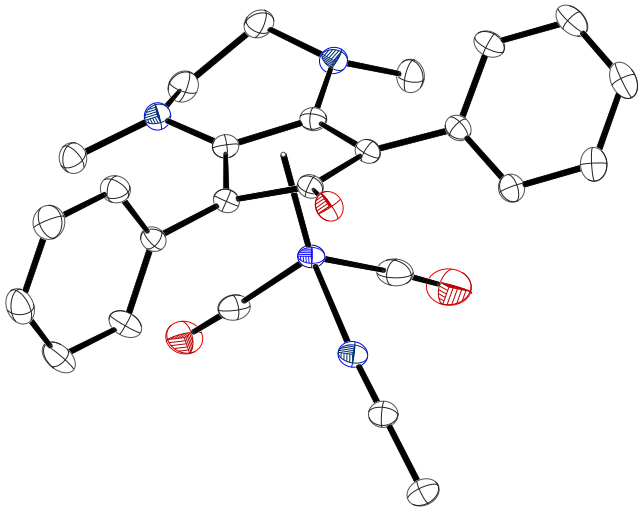
	CCDC	2338298
	Empirical formula	$C_{34}H_{32.50}F_6FeN_{3.50}O_3$
	Formula weight	707.98
	Temperature	100(2) K
	Wavelength	1.54184 Å
	Crystal system	Triclinic
	Space group	$P\bar{1}$
	Unit cell dimensions	
	a = 10.7552(4) Å	α = 106.515(3)°
	b = 11.5325(3) Å	β = 110.781(4)°
	c = 14.6781(6) Å	γ = 94.220(3)°
Volume	1600.72(11) Å^3	
Z	2	
Density (calculated)	1.469 Mg/m^3	
Absorption coefficient	4.446 mm^{-1}	
F(000)	730	
Crystal habitus	irregular (orange)	
Crystal size	0.200 x 0.160 x 0.060 mm^3	
ϑ range for data collection	3.415 to 80.574°	
Index ranges	$-13 \le h \le 12$, $-14 \le k \le 14$, $-18 \le l \le 18$	
Reflections collected	6848	
Independent reflections	6848	
Completeness to ϑ = 67.684°	99.9 %	
Max. and min. transmission	1.000 and 0.358	
Data / restraints / parameters	6848 / 127 / 474	
Goodness-of-fit on F^2	1.054	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0606, wR_2 = 0.1657	
R indices (all data)	R_1 = 0.0619, wR_2 = 0.1675	
Largest diff. peak and hole	1.052 and -0.814 e·Å^3	
Crystallisation Details:	from MeCN, -40 °C	

Table S11. Crystal data and structure refinement of **6**.

	CCDC	2338299
	Empirical formula	$C_{25}H_{23}FeN_3O_3$
	Formula weight	469.31
	Temperature	100(2) K
	Wavelength	0.71073 Å
	Crystal system	Monoclinic
	Space group	$P2_1/n$
	Unit cell dimensions	
	a = 7.1127(2) Å	α = 90°
	b = 14.3100(4) Å	β = 98.189(3)°
	c = 21.7165(6) Å	γ = 90°
Volume	2187.83(11) Å^3	
Z	4	
Density (calculated)	1.425 Mg/m^3	
Absorption coefficient	0.722 mm^{-1}	
F(000)	976	
Crystal habitus	block (yellow)	
Crystal size	0.120 x 0.090 x 0.070 mm^3	
ϑ range for data collection	2.370 to 37.924°	
Index ranges	$-11 \le h \le 12$, $-23 \le k \le 24$, $-37 \le l \le 37$	
Reflections collected	110079	
Independent reflections	11282[R_{int} = 0.0561]	
Completeness to ϑ = 25.242°	99.9 %	
Max. and min. transmission	1.000 and 0.712	
Data / restraints / parameters	11282 / 0 / 292	
Goodness-of-fit on F^2	1.056	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0356, wR_2 = 0.0942	
R indices (all data)	R_1 = 0.0484, wR_2 = 0.0987	
Largest diff. peak and hole	0.604 and -0.292 e·Å^3	
Crystallisation Details:	from toluene / n-hexane, -40 °C	

S4 Computational details

All calculations were performed using the density functional method ωB97XD,[17] which includes a version of Grimme's D2 dispersion model as implemented in the program Gaussian16.[18] For all main group elements (C, H, N and O) the People type all-electron triple-ζ basis set was used, extended by a set of polarisation functions 6-311G(d,p). Solvent effects were included by a continuum using a universal solvent model (SMD) for toluene.[19] Harmonic vibrational frequencies are calculated to characterise the respective minima (without imaginary frequency) and transition state structures (with an imaginary frequency).

Table S12: Energies for all optimized structures.

Compound		$E_{0K}{}^{a}$ / [Ha]	$E_{298K}{}^{b}$ / [Ha]	$H_{298K}{}^{b}$ / [Ha]	$G_{298K}{}^{b}$ / [Ha]
dipiperidinoacetylene	(**1**)	-578.425735	-578.412254	-578.411310	-578.467284
diphenylcyclopropenone	(**2a**)	-652.515699	-652.503364	-652.502420	-652.556381
addition at C1	vdW	-1230.955753	-1230.928337	-1230.927393	-1231.016473
	TS1a	-1230.914031	-1230.887535	-1230.886591	-1230.973973
	IN1a	-1230.926302	-1230.900021	-1230.899077	-1230.985531
	TS2a	-1230.920877	-1230.894648	-1230.893704	-1230.981755
	(**3a**)	-1231.063883	-1231.038439	-1231.037494	-1231.120243
addition at C2	vdW	-1230.954483	-1230.927032	-1230.926088	-1231.015301
	TS1b	-1230.934096	-1230.907799	-1230.906855	-1230.993007
	IN1b	-1230.986645	-1230.960274	-1230.959330	-1231.045282
	TS2b	-1230.983863	-1230.958385	-1230.957441	-1231.039925

[a] DFT energy incl. ZPE.
[b] standard conditions T = 298.15 K and p = 1 atm.

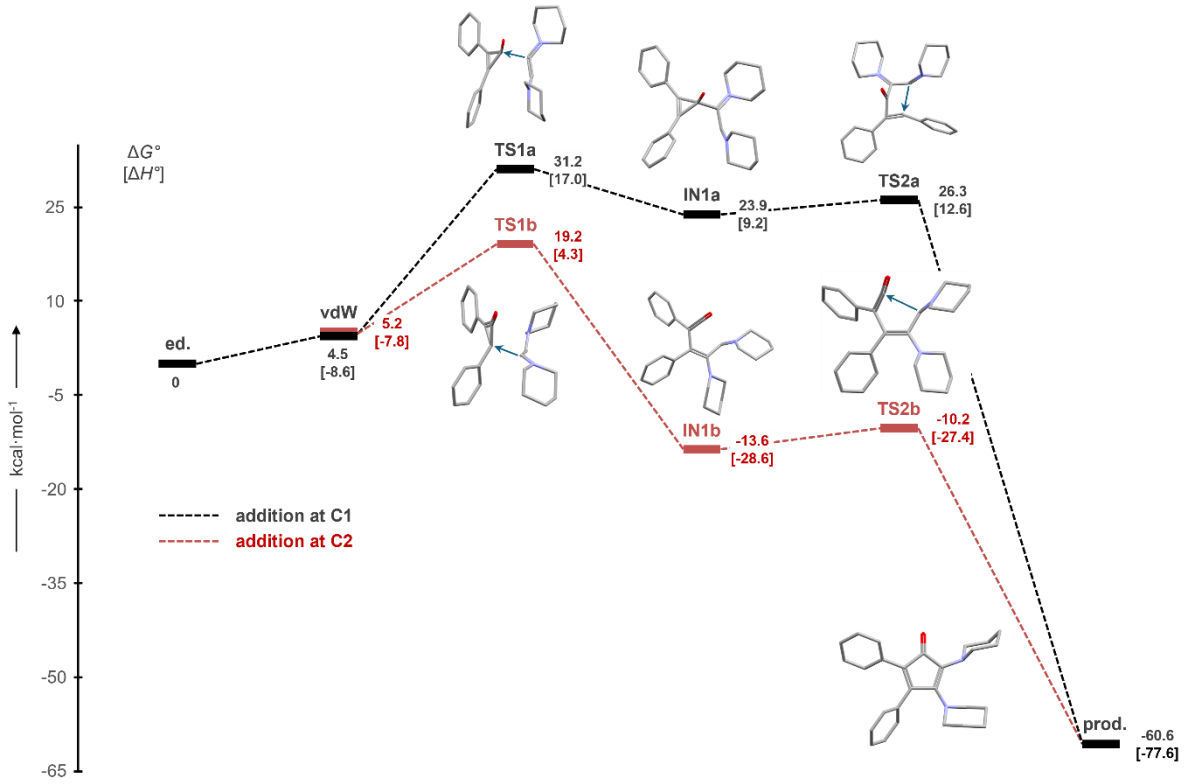


Figure S41: Calculated energy profile for the formation of 2,3-dipiperidinyl-4,5-diphenylcyclopentadienone (**3a**) from dipiperidinoacetylene (**1**) and diphenylcyclopropenone (**2a**), scaled to standard Gibbs free energies (ΔG°); standard enthalpies are given in square brackets.

S5 References

1 A. R. Petrov, C. G. Daniliuc, P. G. Jones and M. Tamm, A novel synthetic approach to diaminoacetylenes: structural characterization and reactivity of aromatic and aliphatic ynediamines, *Chem. Eur. J.*, 2010, **16**, 11804–11808.

2 L. Hackl, L. P. Ho, D. Bockhardt, T. Bannenberg and M. Tamm, Tetraaminocyclopentadienone Iron Complexes as Hydrogenation Catalysts, *Organometallics*, 2022, **41**, 836–851.

3 T. N. Plank, J. L. Drake, D. K. Kim and T. W. Funk, Air‐Stable, Nitrile‐Ligated (Cyclopentadienone)iron Dicarbonyl Compounds as Transfer Reduction and Oxidation Catalysts, *Adv. Synth. Catal.*, 2012, **354**, 597–601.

4 S. Staicu, I. G. Dinulescu, F. Chiraleu and M. Avram, Reactions of acetylenes with transition metals, *J. Organomet. Chem.*, 1976, **117**, 385–394.

5 C. M. Vanos and T. H. Lambert, Development of a catalytic platform for nucleophilic substitution: cyclopropenone-catalyzed chlorodehydration of alcohols, *Angew. Chem. Int. Ed.*, 2011, **50**, 12222–12226.

6 C. Reichardt, M. Eschner and G. Schäfer, Syntheses and UV-visible spectroscopic properties of new 'fluorophilic' fluorine- and perfluoroalkyl-substituted solvatochromic pyridinium N - phenolate betaine dyes, *J. Phys. Org. Chem.*, 2001, **14**, 737–751.

7 J. Chen, B. Tang, X. Liu, G. Lv, Y. Shi, T. Huang, H. Xing, X. Guo, L. Hai and Y. Wu, Ruthenium(ii)-catalyzed [5 + 1] annulation reaction: a facile and efficient approach to construct 6-ethenyl phenanthridines utilizing a primary amine as a directing group, *Org. Chem. Front.*, 2020, **7**, 2944–2949.

8 R. Li, B. Li, H. Zhang, C.-W. Ju, Y. Qin, X.-S. Xue and D. Zhao, A ring expansion strategy towards diverse azaheterocycles, *Nat. Chem.*, 2021, **13**, 1006–1016.

9 E. Haak, Ruthenium Complexes of Electronically Coupled Cyclopentadienone Ligands – Catalysts for Transformations of Propargyl Alcohols, *Eur. J. Org. Chem.*, 2007, **2007**, 2815–2824.

10 T.-T. Thai, D. S. Mérel, A. Poater, S. Gaillard and J.-L. Renaud, Highly active phosphine-free bifunctional iron complex for hydrogenation of bicarbonate and reductive amination, *Chem. Eur. J.*, 2015, **21**, 7066–7070.

11 S. Hanada, E. Tsutsumi, Y. Motoyama and H. Nagashima, Practical access to amines by platinum-catalyzed reduction of carboxamides with hydrosilanes: synergy of dual Si-H groups leads to high efficiency and selectivity, *J. Am. Chem. Soc.*, 2009, **131**, 15032–15040.

12 Z. Wu, S. D. Laffoon and K. L. Hull, Asymmetric synthesis of γ-branched amines via rhodium-catalyzed reductive amination, *Nat. Commun.*, 2018, **9**, 1185.

13 A. J. Blacker, S. Brown, B. Clique, B. Gourlay, C. E. Headley, S. Ingham, D. Ritson, T. Screen, M. J. Stirling, D. Taylor and G. Thompson, A Low-Waste Process To Sertraline By Diastereomeric Crystal Resolution and Waste Isomer Racemisation, *Org. Process Res. Dev.*, 2009, **13**, 1370–1378.

14 R. Kalshetti, V. Venkataramasubramanian, S. Kamble and A. Sudalai, Concise enantioselective synthesis of (+)-sertraline and (−)-CP-52002 using proline catalysis, *Tetrahedron Lett.*, 2016, **57**, 1053–1055.

15 Rigaku Oxford Diffraction, CrysAlisPRO Software System, versions 1.171.41.112a (2021), 1.171.41.122a (2021), 1.171.42.56a (2022) and 1.171.42.64a (2022), Rigaku Corporation, Oxford, UK.

16 G. M. Sheldrick, SHELXT - integrated space-group and crystal-structure determination, *Acta Cryst. Section A*, 2015, **71**, 3–8.

17 G. M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Cryst. Section C*, 2015, **71**, 3–8.

18 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J.A.K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, 2009, **42**, 339–341.
17 J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys. 2008*, **10**, 6615-6620.
18 Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, *2016*.
19 A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B*, *2009*, **113**, 6378–6396.