Supporting Information for

N–H / P–H bond activation of ammonia, amines and phosphines at a transient borylene

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Contents

Methods and materials

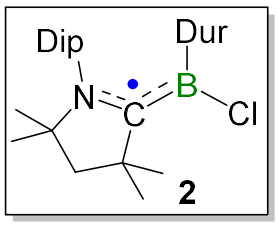
All manipulations were performed either under an atmosphere of dry argon or *in vacuo* using standard Schlenk line or glovebox techniques. Deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles prior to use. All other solvents were distilled and degassed from appropriate drying agents. Both deuterated and non-deuterated solvents were stored under argon over activated 4 Å molecular sieves. Liquid-phase NMR spectra were acquired on a Bruker Avance 400 (^{1}H: 400 MHz, ^{11}B: 129 MHz), 500 (^{1}H: 500 MHz, ^{11}B: 160 MHz, ^{13}C: 125 MHz, ^{15}N: 50.7 MHz, ^{31}P: 202.5 MHz) or 600 (^{1}H: 600 MHz, ^{11}B: 193 MHz, ^{13}C: 151 MHz, ^{15}N: 60.8 MHz) spectrometer. Chemical shifts (δ) are reported in ppm and internally referenced to the carbon nuclei (^{13}C{^{1}H}) or residual protons (^{1}H) of the solvent. Heteronuclei NMR spectra are referenced to external standards (^{11}B: $BF_3{\cdot}OEt_2$, ^{15}N: 90% nitromethane + 10% $CDCl_3$, ^{31}P: 85% H_3PO_4). Resonances are identified as singlet (s), doublet (d), triplet (t), septet (sept), multiplet (m) or broad (br). Coupling constants are ^{1}H-^{1}H coupling constants unless specified otherwise. Unless otherwise stated, NMR spectra were recorded at 25 ºC. High-resolution mass spectrometry (HRMS) data were obtained from a Thermo Scientific Exactive Plus spectrometer. Solid-state IR spectra were recorded on a Bruker FT-IR spectrometer ALPHA II inside a glovebox. UV-vis spectra were acquired on a METTLER TOLEDO UV-vis-Excellence UV5 spectrophotometer inside a glovebox.

Solvents and reagents were purchased from Sigma-Aldrich, abcr or Alfa Aesar. CAAC (= 1-(2,6-di*iso*propylphenyl)-3,3,5,5-tetramethyl-pyrrolidin-2-ylidene) and [(CAAC)BCl_2(Dur)] (**1**) were prepared by literature methods.[1,2]

Synthetic procedures

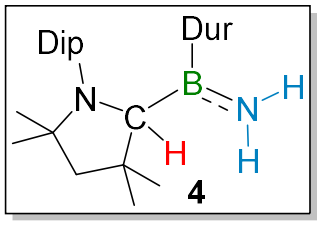
Preparation of [(CAAC)B(Dur)Cl]•, 2

Toluene (20 mL) was added to a mixture of the durylborane adduct **1** (500 mg, 1.00 mmol, 1 eq.) and KC_8 (270 mg, 2.00 mmol, 2 eq.) at 0 °C. The reaction mixture was allowed to warm up to room temperature and was stirred for 4 h. The solution was filtered, and the solvent was removed *in vacuo*. The product **2** was isolated as an orange solid (385 mg, 828 μmol, 83%). Single crystals were obtained by slow evaporation of a saturated solution of **2** in hexane at –30 °C. Compound **2** was previously isolated and characterized.[2]



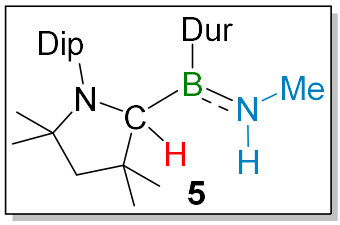
Preparation of [(CAACH)B(Dur)NH$_2$], 4

The durylborane adduct **1** (200 mg, 400 μmol, 1 eq.) and KC_8 (540 mg, 4.00 mmol, 10 eq.) were placed in a high-pressure flask and cooled to –90 °C. Then cold toluene (15 mL, –90 °C) was added and the mixture was frozen. The argon atmosphere was replaced by ammonia and a pressure of 3 bar was applied. The mixture was thawed and was stirred at –90 °C for 1 h. Afterwards the reaction was allowed to warm to room temperature and stirred at 25 °C for 1 h. The solution was filtered and the solvent was removed *in vacuo*. The residue was washed twice with pentane (2 x 1 mL) which led to the isolation of **4** as a colorless solid (161 mg, 361 μmol, 90%). Single crystals were obtained by slow evaporation of a saturated solution of **4** in benzene at 25 °C. This product was previously isolated and characterized.[3]



Preparation of [(CAACH)B(Dur)NHMe], 5

The durylborane adduct **1** (250 mg, 500 μmol, 1 eq.) and KC_8 (675 mg, 5.00 mmol, 10 eq.) were placed in a high-pressure flask and cooled to –90 °C. Then cold toluene (20 mL, –90 °C) was added and the mixture was frozen. The argon atmosphere was replaced by methylamine and a pressure of 3 bar was applied. The mixture was thawed and was stirred at –90 °C for 10 min. Afterwards the reaction was allowed to warm to room temperature and stirred at 25 °C for 3 h. The solution was filtered and the solvent was removed *in vacuo*. The residue was recrystallized from pentane yielding **5** as a colorless solid (154 mg, 334 μmol, 67%). Single crystals were obtained by slow evaporation of a saturated solution of **5** in pentane at 25 °C.



^{1}H NMR (500 MHz, C_6D_6): δ = 7.23 – 7.20 (m, 2H, *para*-Dip-C*H* + *meta*-Dip-C*H*), 7.16 – 7.14 (m, 1H, *meta*-Dip-C*H*), 6.89 (s, 1H, *para*-Dur-C*H*), 4.32 (sept., ^3J = 6.8 Hz, 1H, Dip-*i*Pr-C*H*), 4.03 (s, 1H, NC*H*), 4.03 (s, 1H, N*H*), 3.60 (sept., ^3J = 6.7 Hz, 1H, Dip-*i*Pr-C*H*), 2.22 (s, 3H, *ortho*-Dur-CH_3), 2.19 (s, 3H, *ortho*-Dur-CH_3), 2.15 (s, 3H, *meta*-Dur-CH_3), 2.14 (s, 3H, *meta*-Dur-CH_3), 2.02 (d, ^3J = 6.0 Hz

3H, NCH_3), 1.85 (d, ^2J = 12.5 Hz, 1H, CH_2^{CAAC}), 1.71 (d, ^2J = 12.4 Hz, 1H, CH_2^{CAAC}), 1.40 (d, ^3J = 6.7 Hz, 3H, Dip-*i*Pr-CH_3), 1.38 (s, 3H, C_qCH_3^{CAAC}), 1.37 (d, ^3J = 6.8 Hz, 3H, Dip-*i*Pr-CH_3), 1.32 (d, ^3J = 6.8 Hz, 6H, Dip-*i*Pr-CH_3), 1.26 (s, 3H, C_qCH_3^{CAAC}), 1.08 (s, 3H, C_qCH_3^{CAAC}), 0.87 (s, 3H, C_qCH_3^{CAAC}) ppm.

^{11}B NMR (193 MHz, C_6D_6): δ = 44.4 ppm.

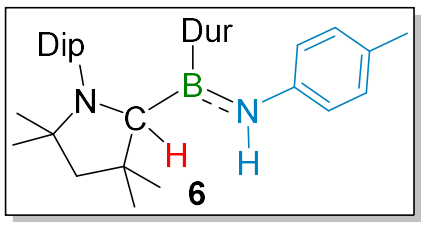
^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ = 153.1 (Dip-C_o), 152.2 (Dip-C_o), 142.2 (*ipso*-Dur-C_q), 141.9 (*ipso*-Dip-C_q), 134.8 (Dur-C_o), 134.3 (Dur-C_o), 133.5 (Dur-C_m), 133.0 (Dur-C_m), 130.9 (Dur-C_p), 127.2 (Dip-C_p), 125.2 (Dip-C_m), 124.9 (Dip-C_m), 68.6 (CCHN^{CAAC}), 61.8 (C_q(CH$_3$)$_2^{CAAC}$), 60.3 (CH$_2^{CAAC}$), 41.0 (C_q(CH$_3$)$_2^{CAAC}$), 34.4 (NCH$_3$), 30.9 (C_q(CH$_3$)$_2^{CAAC}$), 29.6 (*i*Pr-CH), 28.9 (C_q(CH$_3$)$_2^{CAAC}$), 28.4 (C_q(CH$_3$)$_2^{CAAC}$), 28.2 (C_q(CH$_3$)$_2^{CAAC}$), 27.8 (*i*Pr-CH), 25.9 (*i*Pr-CH$_3$), 25.8 (*i*Pr-CH$_3$), 24.8 (*i*Pr-CH$_3$), 24.6 (*i*Pr-CH$_3$), 22.7 (*ortho*-Dur-CH$_3$), 20.4 (*ortho*-Dur-CH$_3$), 20.3 (*meta*-Dur-CH$_3$), 20.1 (*meta*-Dur-CH$_3$) ppm.

^{15}N NMR (50.7 MHz, C_6D_6): δ = –281.7 (BNHMe), –320.7 (N^{CAACH}) ppm.

HRMS LIFDI for $[C_{31}H_{48}BN_2]^+ = [M]^+$: *m*/*z*: calcd. 459.3905; found: 459.3904.

Preparation of [(CAACH)B(Dur)NH(*p*-Me-C$_6$H$_4$)], 6

The durylborane adduct **1** (200 mg, 400 μmol, 1 eq.), KC_8 (540 mg, 4.00 mmol, 10 eq.) and *p*-toluidine (85.7 mg, 800 μmol, 2 eq.), were cooled to –100 °C. Then cold Et_2O (12 mL, –100 °C) was added and the mixture was stirred at –100 °C for 10 min. Afterwards the reaction was allowed to warm to room temperature and stirred at 25 °C for 3 h. The solution was filtered and the solvent was removed *in vacuo*. The residue was recrystallized from pentane yielding **6** as a light red solid (181 mg, 337 μmol, 84%). Single crystals were obtained by slow evaporation of a saturated solution of **6** in pentane at 25 °C.



^{1}H NMR (500 MHz, C_6D_6): δ = 7.30 – 7.28 (m, 2H, *para*-Dip-CH + *meta*-Dip-CH), 7.18 (dd, ^3J = 5.3 Hz, ^3J = 4.3 Hz, 1H, *meta*-Dip-CH), 6.91 (s, 1H, *para*-Dur-CH), 6.61 – 6.58 (m, 3H, *p*Tol-CH + NH), 6.31 – 6.28 (m, 2H, *p*Tol-CH), 4.40 (sept., ^3J = 6.8 Hz, 1H, Dip-*i*Pr-CH), 4.18 (s, 1H, NCH), 3.59 (sept., ^3J = 6.7 Hz, 1H, Dip-*i*Pr-CH), 2.24 (s, 3H, *ortho*-Dur-CH_3), 2.18 (s, 3H, *ortho*-Dur-CH_3), 2.14 (s, 3H, *meta*-Dur-CH_3), 2.05 (s, 3H, *meta*-Dur-CH_3), 1.88 (d, ^2J = 12.7 Hz, 1H, CH_2^{CAAC}), 1.86 (s, 3H, *para*-*p*Tol-CH_3), 1.73 (d, ^2J = 12.4 Hz, 1H, CH_2^{CAAC}), 1.44 (s, 3H, C_qCH_3^{CAAC}), 1.37 (d, ^3J = 6.6 Hz, 3H, Dip-*i*Pr-CH_3), 1.37 (d, ^3J = 6.8 Hz, 3H, Dip-*i*Pr-CH_3), 1.36 (d, ^3J = 6.4 Hz, 3H, Dip-*i*Pr-CH_3), 1.31 (s, 3H, C_qCH_3^{CAAC}), 1.28 (d, ^3J = 6.6 Hz, 3H, Dip-*i*Pr-CH_3), 1.11 (s, 3H, C_qCH_3^{CAAC}), 0.88 (s, 3H, C_qCH_3^{CAAC}) ppm.

^{11}B NMR (193 MHz, C_6D_6): δ = 44.8 ppm.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ = 153.4 (Dip-C_o), 152.3 (Dip-C_o), 142.8 (*ipso*-Dur-C_q), 142.0 (*ipso*-Dip-C_q), 141.0 (*ipso*-*p*Tol-C_q), 134.8 (Dur-C_o), 134.0 (Dur-C_o), 134.0 (Dur-C_m), 133.5 (Dur-C_m), 131.5

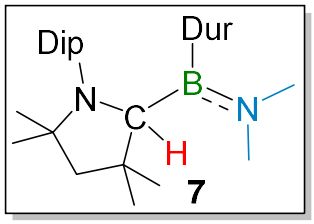
(*p*Tol-*C*H), 131.5 (*p*Tol-*C*H), 129.6 (Dur-C_p), 127.5 (Dip-C_p), 125.8 (Dip-C_m), 125.2 (Dip-C_m), 119.9 (2 x *p*Tol-*C*H), 69.3 (C*C*HN^{CAAC}), 62.0 ($C_q(CH_3)_2^{CAAC}$), 60.4 (CH_2^{CAAC}), 41.5 ($C_q(CH_3)_2^{CAAC}$), 30.7 ($C_q(CH_3)_2^{CAAC}$), 29.6 (*i*Pr-*C*H), 29.2 ($C_q(CH_3)_2^{CAAC}$), 28.6 ($C_q(CH_3)_2^{CAAC}$), 28.1 ($C_q(CH_3)_2^{CAAC}$), 28.1 (*i*Pr-*C*H), 26.0 (*i*Pr-*C*H_3), 25.6 (*i*Pr-*C*H_3), 25.1 (*i*Pr-*C*H_3), 24.6 (*i*Pr-*C*H_3), 20.4 (*p*Tol-*C*H_3), 20.4 (*ortho*-Dur-*C*H_3), 20.3 (*ortho*-Dur-*C*H_3), 19.9 (*meta*-Dur-*C*H_3), 19.9 (*meta*-Dur-*C*H_3) ppm.

^{15}N NMR (50.7 MHz, C_6D_6): δ = –246.9 (B*N*H*p*Tol), –320.0 (N^{CAACH}) ppm.

HRMS LIFDI for $[C_{37}H_{53}BN_2]^+ = [M]^+$: *m*/*z*: calcd. 536.4296; found: 536.4285.

Preparation of [(CAACH)B(Dur)NMe$_2$], 7

The durylborane adduct **1** (300 mg, 600 μmol, 1 eq.) and KC_8 (810 mg, 6.00 mmol, 10 eq.) were placed in a high-pressure flask and cooled to –90 °C. Then cold toluene (30 mL, –90 °C) was added and the mixture was frozen. The argon atmosphere was replaced by dimethylamine and a pressure of 1 bar was quickly applied and the flask rapidly and tightly closed again. The mixture was thawed and was stirred at –90 °C for 20 min. Afterwards the reaction was slowly allowed to warm to room temperature and stirred at 25 °C for 2 h. During this time the pressure was adjusted multiple times until it remained constant. The red solution was filtered and the solvent was removed *in vacuo*. The product was extracted from the residue with pentane (10 mL) and recrystallized from benzene yielding **7** as a light red solid (176 mg, 371 μmol, 62%). Single crystals were obtained by slow evaporation of a saturated solution of **7** in benzene at 25 °C.



^{1}H NMR (500 MHz, C_6D_6): δ = 7.17 – 7.15 (m, 2H, *para*-Dip-C*H* + *meta*-Dip-C*H*), 7.08 (dd, ^3J = 5.3 Hz, ^3J = 4.3 Hz, 1H, *meta*-Dip-C*H*), 6.80 (s, 1H, *para*-Dur-C*H*), 4.40 (sept., ^3J = 6.9 Hz, 1H, Dip-*i*Pr-C*H*), 3.75 (s, 1H, NC*H*), 3.36 (s, 3H, N-CH_3), 3.10 (sept., ^3J = 6.7 Hz, 1H, Dip-*i*Pr-C*H*), 2.44 (s, 3H, N-CH_3), 2.24 (s, 3H, *ortho*-Dur-CH_3), 2.19 (d, ^2J = 12.9 Hz, 1H, CH_2^{CAAC}), 2.13 (s, 3H, *ortho*-Dur-CH_3), 2.02 (s, 3H, *meta*-Dur-CH_3), 1.85 (d, ^2J = 12.7 Hz, 1H, CH_2^{CAAC}), 1.64 (s, 3H, *meta*-Dur-CH_3), 1.64 (s, 3H, $C_qCH_3^{CAAC}$), 1.30 (d, ^3J = 6.9 Hz, 3H, Dip-*i*Pr-CH_3), 1.29 (d, ^3J = 7.0 Hz, 3H, Dip-*i*Pr-CH_3), 1.22 (s, 3H, $C_qCH_3^{CAAC}$), 1.19 (d, ^3J = 6.7 Hz, 3H, Dip-*i*Pr-CH_3), 1.14 (s, 3H, $C_qCH_3^{CAAC}$), 1.03 (d, ^3J = 6.6 Hz, 3H, Dip-*i*Pr-CH_3), 0.96 (s, 3H, $C_qCH_3^{CAAC}$) ppm.

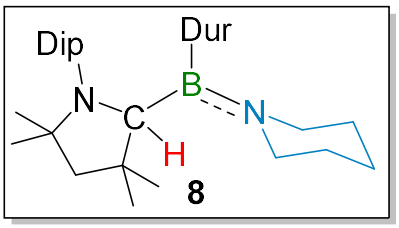
^{11}B NMR (193 MHz, C_6D_6): δ = 45.7 ppm.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ = 151.0 (Dip-C_o), 149.6 (Dip-C_o), 147.5 (*ipso*-Dur-C_q), 147.0 (*ipso*-Dip-C_q), 134.7 (Dur-C_o), 133.3 (Dur-C_o), 132.9 (Dur-C_m), 132.2 (Dur-C_m), 130.3 (Dur-C_p), 126.4 (Dip-C_p), 126.2 (Dip-C_m), 124.3 (Dip-C_m), 73.3 (C*C*HN^{CAAC}), 65.0 ($C_q(CH_3)_2^{CAAC}$), 60.3 (CH_2^{CAAC}), 43.2 ($C_q(CH_3)_2^{CAAC}$), 42.2 (NCH_3), 40.8 (NCH_3), 32.6 ($C_q(CH_3)_2^{CAAC}$), 32.5 ($C_q(CH_3)_2^{CAAC}$), 29.7 ($C_q(CH_3)_2^{CAAC}$), 29.6 ($C_q(CH_3)_2^{CAAC}$), 29.3 (*i*Pr-*C*H), 27.1 (*i*Pr-*C*H), 25.8 (*i*Pr-*C*H_3), 25.3 (*i*Pr-*C*H_3), 24.7 (*i*Pr-*C*H_3), 24.1 (*i*Pr-*C*H_3), 20.5 (*ortho*-Dur-*C*H_3), 20.1 (*ortho*-Dur-*C*H_3), 19.7 (*meta*-Dur-*C*H_3), 17.4 (*meta*-Dur-*C*H_3) ppm.

^{15}N NMR (50.7 MHz, C_6D_6): δ = –281.5 (B*N*Me$_2$), –315.6 (*N*^{CAACH}) ppm.

HRMS LIFDI for $[C_{32}H_{51}BN_2]^+ = [M]^+$: *m*/*z*: calcd. 474.4140; found: 474.4119.

Preparation of [(CAACH)B(Dur)NC$_5$H$_{10}$], 8



8

The [(CAAC)B(Dur)(Pip)] (**9**) (30 mg, 58.3 μmol) was heated to 80 °C without solvent for 16 h. The residue was extracted with pentane (2 mL) and the product was recrystallized from pentane. The colorless solid was washed with cold pentane (0.5 mL) and was dried *in vacuo*, providing compound **8** as a colorless solid (25.8 mg, 50.1 μmol, 86%). Single crystals were obtained by slow evaporation of a saturated solution of **8** in pentane at 25 °C.

^{1}H NMR (600.2 MHz, C_6D_6): δ = 7.17 – 7.15 (m, 2H, *meta*-Dip-C*H*), 7.07 (dd, ^3J = 5.3 Hz, ^3J = 4.8 Hz, 1H, *para*-Dip-C*H*), 6.79 (s, 1H, *para*-Dur-C*H*), 5.09 (br d, ^3J = 8.2 Hz, 1H, NCH_2^{Pip}), 4.45 (sept., ^3J = 6.9 Hz, 1H, Dip-*i*Pr-C*H*), 3.81 (s, 1H, NCH^{CAAC}), 3.33 (d, ^2J = 12.7 Hz, 1H, NCH_2^{Pip}), 3.19 – 3.13 (m, 1H, NCH_2^{Pip}), 3.11 (sept., ^3J = 6.9 Hz, 1H, Dip-*i*Pr-C*H*), 2.49 (td, ^2J = 12.6 Hz, ^3J = 2.1 Hz, 1H, NCH_2^{Pip}), 2.38 (s, 3H, *ortho*-Dur-CH_3), 2.22 (d, ^2J = 12.8 Hz, 1H, CH_2^{CAAC}), 2.12 (s, 3H, *ortho*-Dur-CH_3), 2.03 (s, 3H, *meta*-Dur-CH_3), 1.87 (d, ^2J = 12.8 Hz, 1H, CH_2^{CAAC}), 1.71 (s, 3H, *meta*-Dur-CH_3), 1.66 (s, 3H, C$_q$CH_3^{CAAC}), 1.63 – 1.57 (m, 2H, NCH$_2$CH_2^{Pip}), 1.44 – 1.39 (m, 1H, NCH$_2$CH_2^{Pip}), 1.37 (d, ^3J = 6.9 Hz, 3H, Dip-*i*Pr-CH_3), 1.30 (d, ^3J = 6.9 Hz, 3H, Dip-*i*Pr-CH_3), 1.28 (s, 3H, C$_q$CH_3^{CAAC}), 1.27 – 1.24 (m, 1H, NCH$_2$CH_2^{Pip}), 1.21 – 1.17 (m, 1H, NCH$_2$CH$_2$CH_2^{Pip}), 1.19 (d, ^3J = 6.7 Hz, 3H, Dip-*i*Pr-CH_3), 1.17 – 1.15 (m, 1H, NCH$_2$CH$_2$CH_2^{Pip}), 1.14 (s br, 3H, C$_q$CH_3^{CAAC}), 0.98 (d, ^3J = 6.6 Hz, 3H, Dip-*i*Pr-CH_3), 0.95 (s, 3H, C$_q$CH_3^{CAAC}) ppm.

^{11}B NMR (192.6 MHz, C_6D_6): δ = 44.4 ppm.

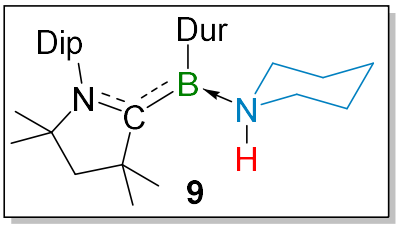
^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6): δ = 151.0 (Dip-*C*$_o$), 149.5 (Dip-*C*$_o$), 147.6 (*ipso*-Dur-*C*$_q$), 147.2 (*ipso*-Dip-*C*$_q$), 134.6 (Dur-*C*$_o$), 133.3 (Dur-*C*$_o$), 133.0 (Dur-*C*$_m$), 132.0 (Dur-*C*$_m$), 130.1 (Dur-*C*$_p$), 126.3 (Dip-*C*$_p$), 126.2 (Dip-*C*$_m$), 124.3 (Dip-*C*$_m$), 73.5 (C*C*HN^{CAAC}), 64.8 (*C*$_q$(CH$_3$)$_2^{CAAC}$), 60.5 (*C*H$_2^{CAAC}$), 51.4 (N*C*H$_2^{Pip}$), 49.1 (N*C*H$_2^{Pip}$), 42.4 (*C*$_q$(CH$_3$)$_2^{CAAC}$), 32.6 (C$_q$(*C*H$_3$)$_2^{CAAC}$), 32.4 (C$_q$(*C*H$_3$)$_2^{CAAC}$), 30.8 (C$_q$(*C*H$_3$)$_2^{CAAC}$), 29.6 (C$_q$(*C*H$_3$)$_2^{CAAC}$), 29.2 (*i*Pr-*C*H), 27.6 (NCH$_2$*C*H$_2^{Pip}$), 27.4 (NCH$_2$*C*H$_2^{Pip}$), 26.8 (*i*Pr-*C*H), 26.0 (*i*Pr-*C*H$_3$), 25.5 (NCH$_2$CH$_2$*C*H$_2^{Pip}$), 25.3 (*i*Pr-*C*H$_3$), 25.0 (*i*Pr-*C*H$_3$), 24.1 (*i*Pr-*C*H$_3$), 21.8 (*ortho*-Dur-*C*H$_3$), 20.1 (*ortho*-Dur-*C*H$_3$), 19.8 (*meta*-Dur-*C*H$_3$), 17.2 (*meta*-Dur-*C*H$_3$) ppm.

^{15}N NMR (60.8 MHz, C_6D_6): δ = –257.0 (B*N*^{Pip}), –314.8 (*N*^{CAACH}) ppm.

HRMS LIFDI for $[C_{35}H_{54}BN_2]^+ = [M]^+$: *m*/*z*: calcd. 513.4375; found: 513.4374.

Preparation of [(CAAC)B(Dur)(Pip)], 9

The durylborane adduct **1** (200 mg, 400 μmol, 1 eq.) and KC_8 (540 mg, 4.00 mmol, 10 eq.) were cooled to –90 °C. Then cold toluene (15 mL, –90 °C) and piperidine (68.1 mg, 800 μmol, 2 eq.) were added



and the mixture was stirred at –90 °C for 10 min. Afterwards the reaction was allowed to warm to room temperature and stirred at 25 °C for 2 h. The orange solution was filtered and the solvent was removed *in vacuo*. The residue was washed with pentane (2 mL) and the product was extracted with benzene (5 mL). Recrystallization from benzene provided compound **9** as an orange solid (109 mg, 212 μmol, 53%). Single crystals were obtained by slow evaporation of a saturated solution of **9** in pentane at 25 °C.

^{1}H NMR (500 MHz, C_6D_6): δ = 7.20 (dd, ^{3}J = 7.6 Hz, ^{3}J = 1.6 Hz, 1H, *meta*-Dip-C*H*), 7.15 – 7.12 (m, 1H, *para*-Dip-C*H*), 6.90 (dd, ^{3}J = 7.5 Hz, ^{3}J = 1.7 Hz, 1H, *meta*-Dip-C*H*), 6.85 (s, 1H, *para*-Dur-C*H*), 4.30 (t, ^{3}J = 11.4 Hz, 1H, N*H*), 3.78 (sept., ^{3}J = 6.8 Hz, 1H, Dip-*i*Pr-C*H*), 3.34 (sept., ^{3}J = 6.7 Hz, 1H, Dip-*i*Pr-C*H*), 3.09 (d, ^{2}J = 13.0 Hz, 1H, CH_2^{Pip}), 2.95 (d, ^{2}J = 13.6 Hz, 1H, CH_2^{Pip}), 2.73 (s, 3H, *ortho*-Dur-CH_3), 2.32 (s, 3H, *ortho*-Dur-CH_3), 2.24 (d, ^{2}J = 12.1 Hz, 1H, CH_2^{CAAC}), 2.22 – 2.16 (m, 1H, CH_2^{Pip}), 2.16 – 2.09 (m, 1H, CH_2^{Pip}), 2.13 (s, 3H, *meta*-Dur-CH_3), 1.95 (d, ^{2}J = 12.1 Hz, 1H, CH_2^{CAAC}), 1.88 – 1.80 (m, 1H, CH_2^{Pip}), 1.74 (s, 3H, *meta*-Dur-CH_3), 1.72 (s, 3H, $C_qCH_3^{CAAC}$), 1.72 (s, 3H, $C_qCH_3^{CAAC}$), 1.67 – 1.63 (m, 1H, CH_2^{Pip}), 1.65 (s, 3H, $C_qCH_3^{CAAC}$), 1.61 (d, ^{3}J = 6.8 Hz, 3H, Dip-*i*Pr-CH_3), 1.40 (d, ^{3}J = 6.9 Hz, 3H, Dip-*i*Pr-CH_3), 1.39 – 1.36 (m, 2H, CH_2^{Pip}), 1.30 – 1.27 (m, 1H, CH_2^{Pip}), 1.24 (d, ^{3}J = 6.7 Hz, 3H, Dip-*i*Pr-CH_3), 1.25 – 1.21 (m, 1H, CH_2^{Pip}), 1.10 (s, 3H, $C_qCH_3^{CAAC}$), 0.20 (d, ^{3}J = 6.7 Hz, 3H, Dip-*i*Pr-CH_3), ppm.

^{11}B NMR (193 MHz, C_6D_6): δ = 24.7 ppm.

^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ = 151.4 (Dip-C_o), 148.9 (Dip-C_o), 147.3 (*ipso*-Dur-C_q), 145.4 (*ipso*-Dip-C_q), 139.4 (Dur-C_o), 139.3 (Dur-C_o), 132.6 (Dur-C_m), 132.1 (Dur-C_m), 129.9 (Dur-C_p), 124.6 (2 x Dip-C_m), 123.2 (Dip-C_p), 62.0 (CH_2^{CAAC}), 61.4 ($C_q(CH_3)_2^{CAAC}$), 52.9 (CH_2^{Pip}), 49.3 (CH_2^{Pip}), 42.9 ($C_q(CH_3)_2^{CAAC}$), 35.1 ($C_q(CH_3)_2^{CAAC}$), 35.0 ($C_q(CH_3)_2^{CAAC}$), 30.6 ($C_q(CH_3)_2^{CAAC}$), 27.9 (*i*Pr-CH), 27.6 ($C_q(CH_3)_2^{CAAC}$), 27.3 (*i*Pr-CH), 27.0 (*i*Pr-CH_3), 26.0 (*i*Pr-CH_3), 25.6 (CH_2^{Pip}), 25.0 (CH_2^{Pip}), 24.9 (*i*Pr-CH_3), 23.1 (*i*Pr-CH_3), 23.1 (*ortho*-Dur-CH_3), 22.3 (*ortho*-Dur-CH_3), 21.4 (CH_2^{Pip}), 21.0 (*meta*-Dur-CH_3), 20.8 (*meta*-Dur-CH_3) ppm.

Note: The signal of the ipso-Dur carbon atom was assigned with the help of a 2D-$^{13}C\{^{1}H\}$-HMBC NMR experiment. The signal of the carbene carbon atom could not be determined.

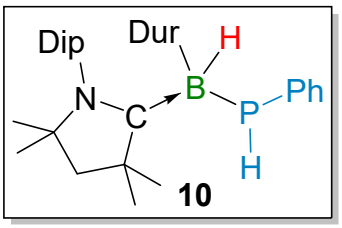
^{15}N NMR (50.7 MHz, C_6D_6): δ = –326.3 (N^{CAAC}) ppm.

Note: The signal of the piperidine-nitrogen atom could not be determined due to its direct proximity to the quadrupole core boron.

HRMS LIFDI for $[C_{35}H_{54}BN_2]^+ = [M]^+$: *m*/*z*: calcd. 513.4375; found: 513.4374.

Preparation of [(CAAC)BH(Dur)(PHPh)], 10

The durylboryl radical **2** (200 mg, 430 μmol, 1 eq.) and KC_8 (582 mg, 4.30 mmol, 10 eq.) were cooled to –90 °C. Then a cold solution of phenylphosphane (–90 °C, 47.3 mg, 860 μmol, 2 eq.) in toluene



(12 mL) was added and the mixture was stirred at –90 °C for 10 min. Afterwards the reaction was allowed to warm up to room temperature and stirred at 25 °C for 90 min. The orange solution was filtered and the solvent was removed *in vacuo*. The residue was recrystallized from benzene yielding **10** as an orange solid (186 mg, 345 μmol, 80%). Single crystals were obtained by slow evaporation of a saturated solution of **10** in benzene at 25 °C.

^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.51 (dd, ^{3}J = 7.8 Hz, ^{3}J = 7.8 Hz, 1H, *para*-Dip-C*H*), 7.41 (dd, ^{3}J = 7.7 Hz, ^{3}J = 7.7 Hz, 1H, *para*-Ph-C*H*), 7.37 – 7.34 (m, 1H, *meta*-Dip-C*H*), 7.33 – 7.31 (m, 1H, *meta*-Dip-C*H*), 6.85 (s, 1H, *para*-Dur-C*H*), 6.78 (tt, ^{3}J = 7.5 Hz, ^{4}J = 1.2 Hz, 2H, *meta*-Ph-C*H*), 6.62 (td, ^{3}J = 7.4 Hz, ^{4}J = 1.4 Hz, 2H, *ortho*-Ph-C*H*), 6.16 – 6.12 (m, 1H, P*H*), 3.50 (q br, $^{2}J_{B–H}$ = 84 Hz, 1H, B*H*), 3.12 (sept., ^{3}J = 6.6 Hz, 1H, Dip-*i*Pr-C*H*), 2.67 (sept., ^{3}J = 6.6 Hz, 1H, Dip-*i*Pr-C*H*), 2.37 (s, 3H, *ortho*-Dur-CH_3), 2.18 (s, 3H, *ortho*-Dur-CH_3), 2.13 (s, 3H, *meta*-Dur-CH_3), 2.10 (d, ^{2}J = 12.8 Hz, 1H, CH_2^{CAAC}), 2.10 (s, 3H, *meta*-Dur-CH_3), 1.98 (d, ^{2}J = 12.8 Hz, 1H, CH_2^{CAAC}), 1.93 (s, 3H, C_qCH_3^{CAAC}), 1.74 (d, ^{3}J = 6.7 Hz, 3H, Dip-*i*Pr-CH_3), 1.69 (d, ^{3}J = 6.6 Hz, 3H, Dip-*i*Pr-CH_3), 1.67 (s, 3H, C_qCH_3^{CAAC}), 1.36 (s, 6H, C_qCH_3^{CAAC}), 1.35 (d, ^{3}J = 6.6 Hz, 3H, Dip-*i*Pr-CH_3), 1.29 (d, ^{3}J = 6.8 Hz, 3H, Dip-*i*Pr-CH_3) ppm.

*Note: The P–H activation product **10** is poorly soluble in benzene and was therefore measured in deuterated dichloromethane. In this solution, the product slowly decomposes to multiple phosphorus-containing products, which could not be further isolated and characterized.*

^{11}B{^{1}H} NMR (193 MHz, CD_2Cl_2): δ = –16.3 (d, $^{2}J_{B–P}$ = 24 Hz) ppm.

^{11}B NMR (193 MHz, CD_2Cl_2): δ = –16.3 (dd, $^{2}J_{B–H}$ = 84 Hz, $^{2}J_{B–P}$ = 24 Hz) ppm.

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ = 148.6 (Dip-C_o), 148.5 (*ipso*-Dur-C_q), 146.3 (Dip-C_o), 143.0 (*ipso*-Ph-C_q), 139.9 (*ipso*-Dip-C_q), 138.2 (Dur-C_o), 134.5 (Dur-C_o), 134.9 (*meta*-Dip-*C*H), 134.2 (Ph-*C*H), 133.7 (Dur-C_m), 131.9 (Dur-C_m), 131.4 (*para*-Dur-*C*H), 126.1 (Ph-*C*H), 126.0 (*meta*-Dip-*C*H), 125.1 (*meta*-Dip-*C*H), 124.2 (Ph-*C*H), 76.8 (C_q(CH$_3$)$_2^{CAAC}$), 70.7 (C_q(CH$_3$)$_2^{CAAC}$), 59.8 (*C*H$_2^{CAAC}$), 32.1 (C_q(*C*H$_3$)$_2^{CAAC}$), 31.1 (C_q(*C*H$_3$)$_2^{CAAC}$), 30.8 (C_q(*C*H$_3$)$_2^{CAAC}$), 29.8 (*i*Pr-*C*H), 29.6 (*i*Pr-*C*H), 29.2 (C_q(*C*H$_3$)$_2^{CAAC}$), 27.5 (*i*Pr-*C*H$_3$), 26.4 (*i*Pr-*C*H$_3$), 25.8 (*i*Pr-*C*H$_3$), 24.8 (*i*Pr-*C*H$_3$), 21.5 (*ortho*-Dur-*C*H$_3$), 20.8 (*ortho*-Dur-*C*H$_3$), 20.7 (*meta*-Dur-*C*H$_3$), 19.8 (*meta*-Dur-*C*H$_3$) ppm.

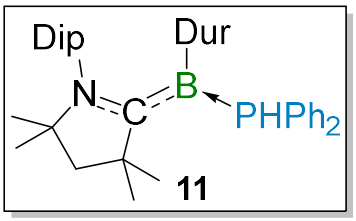
Note: The signal of the ipso-Dur carbon atom was assigned with the help of 2D-^{13}C{^{1}H}-HMBC NMR experiment. The signal of the carbene carbon atom could not be determined.

^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ = –91.9 ppm.

HRMS LIFDI for $[C_{36}H_{50}BNP]^+ = [M]^+$: *m/z*: calcd. 538.3768; found: 538.3768.

Preparation of [(^{Me}CAAC)B(Dur)(PHPh$_2$)], 11

The durylboryl radical **2** (120 mg, 258 μmol, 1 eq.) and KC_8 (279 mg, 2.06 mmol, 8 eq.) were cooled to –80 °C. Then a cold solution of diphenylphosphane (–90 °C, 48.1 mg, 258 μmol, 1 eq.) in toluene



(36 mL) was added and the mixture was stirred at –90 °C for 30 min. Afterwards the reaction was allowed to warm to room temperature and stirred at 25 °C for 60 min. The red suspension was filtered and the solvent was removed *in vacuo*. The residue was recrystallized from pentane at –30 °C yielding **11** as an orange-red solid (92.4 mg, 150 μmol, 58%). Single crystals were obtained by slow evaporation of a saturated solution of **11** in pentane at –30 °C.

^{1}H NMR (600.2 MHz, C_6D_6): δ = 7.24 – 7.21 (m, 2H, *meta*-Dip-C*H*), 7.16 – 7.12 (m, 1H, *para*-Dip-C*H*), 7.01 – 7.00 (m, 1H, *para*-Dip-C*H*), 6.96 – 6.91 (m, 4H, *ortho*-Ph-C*H*), 6.87 – 6.84 (m, 2H, *para*-Ph-C*H*), 6.83 – 6.80 (m, 4H, *meta*-Ph-C*H*), 5.88 (d, $^{1}J_{P\text{-}H}$= 398 Hz, 1H, P*H*), 3.80 (sept., ^{3}J = 6.8 Hz, 2H, Dip-*i*Pr-C*H*), 2.33 (s, 6H, *ortho*-Dur-CH_3), 2.21 (s, 6H, *meta*-Dur-CH_3), 1.99 (d, ^{2}J = 12.1 Hz, 1H, CH_2^{CAAC}), 1.81 (d, ^{2}J = 12.0 Hz, 1H, CH_2^{CAAC}), 1.53 (s, 6H, C$_q$CH_3^{CAAC}), 1.39 (s, 6H, C$_q$CH_3^{CAAC}), 1.31 (d, ^{3}J = 6.7 Hz, 6H, Dip-*i*Pr-CH_3), 1.13 (d, ^{3}J = 6.8 Hz, 6H, Dip-*i*Pr-CH_3) ppm.

*Note: Due to the slow decomposition in vacuum and the heat sensitivity of compound **11**, the reactant Ph_2PH partly remains in the product. A complete elimination of the remaining Ph_2PH was not possible without formation of several decomposition products.*

^{11}B NMR (192.6 MHz, C_6D_6): δ = 0.7 ppm.

^{13}C{^{1}H} NMR (150.9 MHz, C_6D_6): δ = 168.3 (carbene-C$_q^{CAAC}$), 151.7 (*ipso*-Dur-*C$_q$*), 150.5 (*ipso*-Dip-*C$_q$*), 145.3 (2 x Dur-*C$_o$*), 145.0 (Dip-*C$_o$*), 140.4 (Dip-*C$_o$*), 132.9 (2 x Dur-*C$_m$*), 132.9 (2 x Ph-*C$_o$*), 132.8 (2 x Ph-*C$_o$*), 131.2 (2 x *ipso*-Ph-*C$_q$*), 130.1 (Dur-*C$_p$*), 129.9 (2 x Ph- *C$_p$*), 128.1 (2 x Ph-*C$_m$*), 128.0 (2 x Ph-*C$_o$*), 125.9 (Dip-*C$_p$*), 121.6 (Dip-*C$_m$*), 121.0 (Dip-*C$_m$*), 63.6 (*C$_q$*(CH$_3$)$_2^{CAAC}$), 60.5 (*C*H$_2^{CAAC}$), 47.1 (*C$_q$*(CH$_3$)$_2^{CAAC}$), 32.2 (C$_q$(*C*H$_3$)$_2^{CAAC}$), 32.2 (C$_q$(*C*H$_3$)$_2^{CAAC}$), 29.0 (2 x C$_q$(*C*H$_3$)$_2^{CAAC}$), 27.8 (*i*Pr-*C*H), 26.8 (*i*Pr-*C*H$_3$), 26.0 (*i*Pr-*C*H$_3$), 24.4 (2 x *ortho*-Dur-*C*H$_3$), 21.2 (*meta*-Dur-*C*H$_3$) ppm.

Note: The signals of the carbon atoms of the phenyl substituents, the carbene carbon atom and the ipso-Dur carbon atom were assigned with the help of a 2D-^{13}C{^{1}H}-HMBC NMR experiment.

^{15}N NMR (60.8 MHz, C_6D_6): δ = –279.1 ppm.

^{31}P{^{1}H} NMR (202 MHz, C_6D_6): δ = –23.9 ppm.

^{31}P NMR (202 MHz, C_6D_6): δ = –23.9 (d, $^{2}J_{P–H}$ = 398 Hz) ppm.

HRMS LIFDI for $[C_{42}H_{55}BNP]^+ = [M]^+$: *m*/*z*: calcd. 615.4160; found: 615.4145.

NMR of isolated compounds

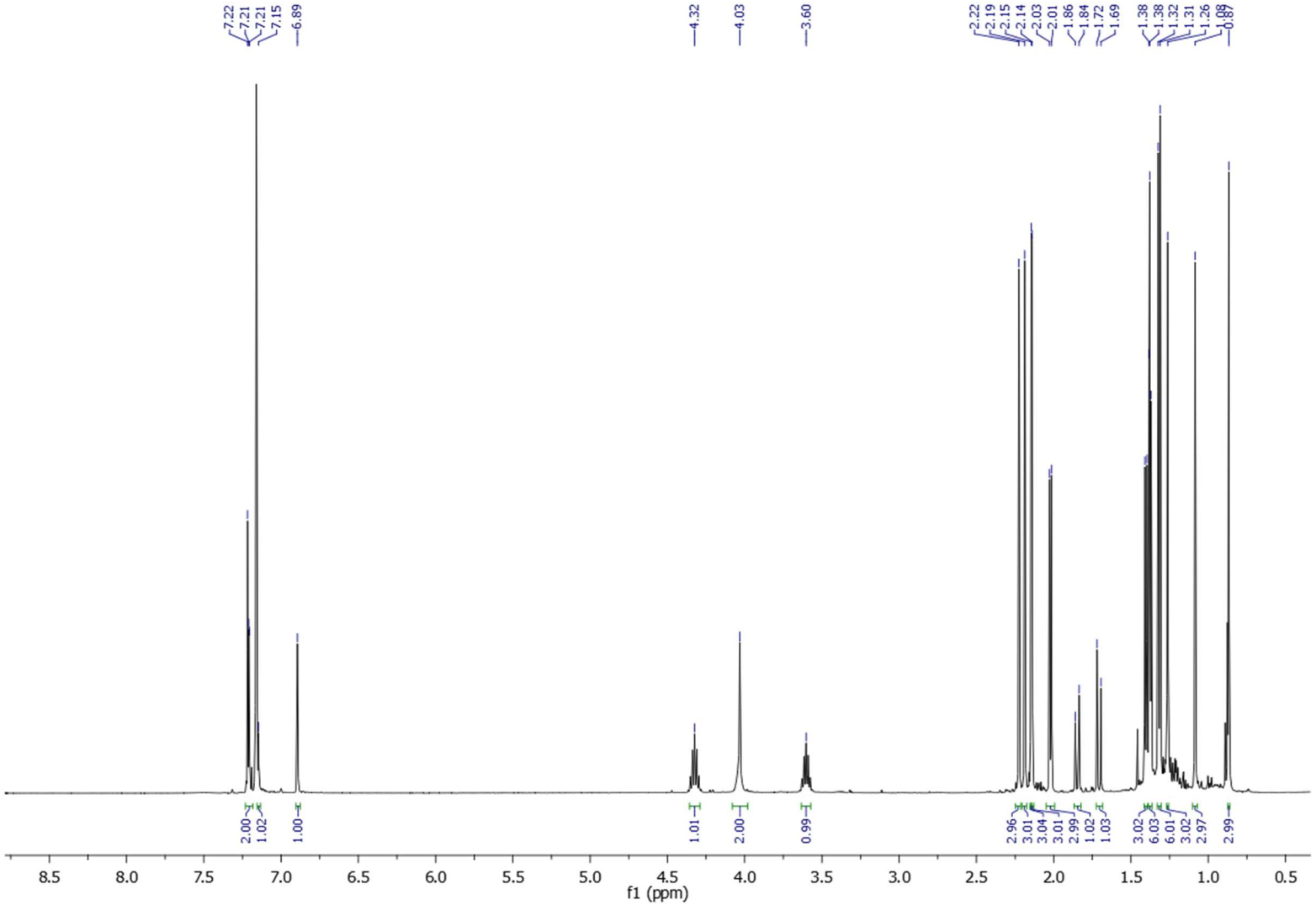


Fig. S1 ^{1}H NMR spectrum of **5** in C_6D_6.

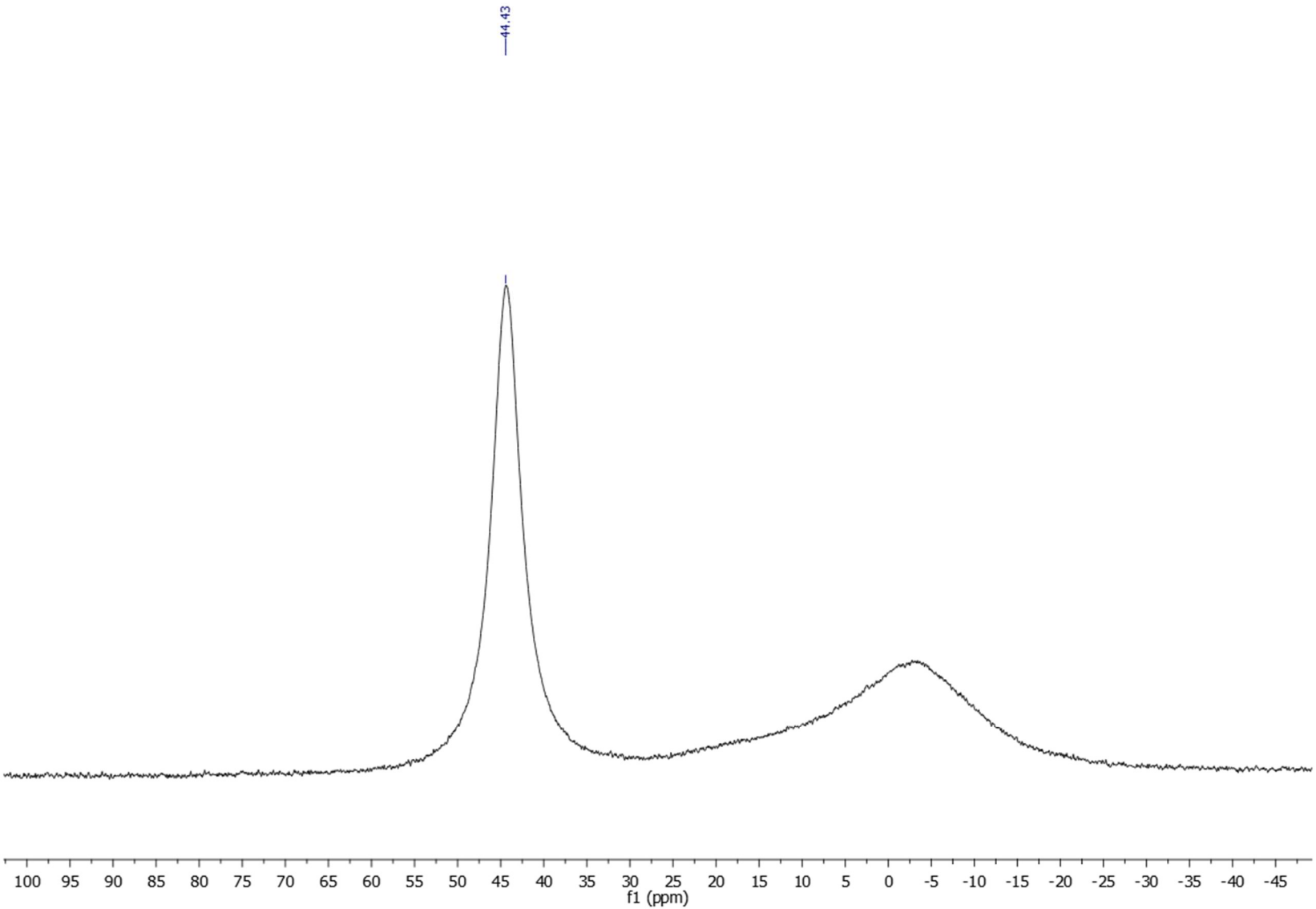


Fig. S2 ^{11}B NMR spectrum of **5** in C_6D_6.

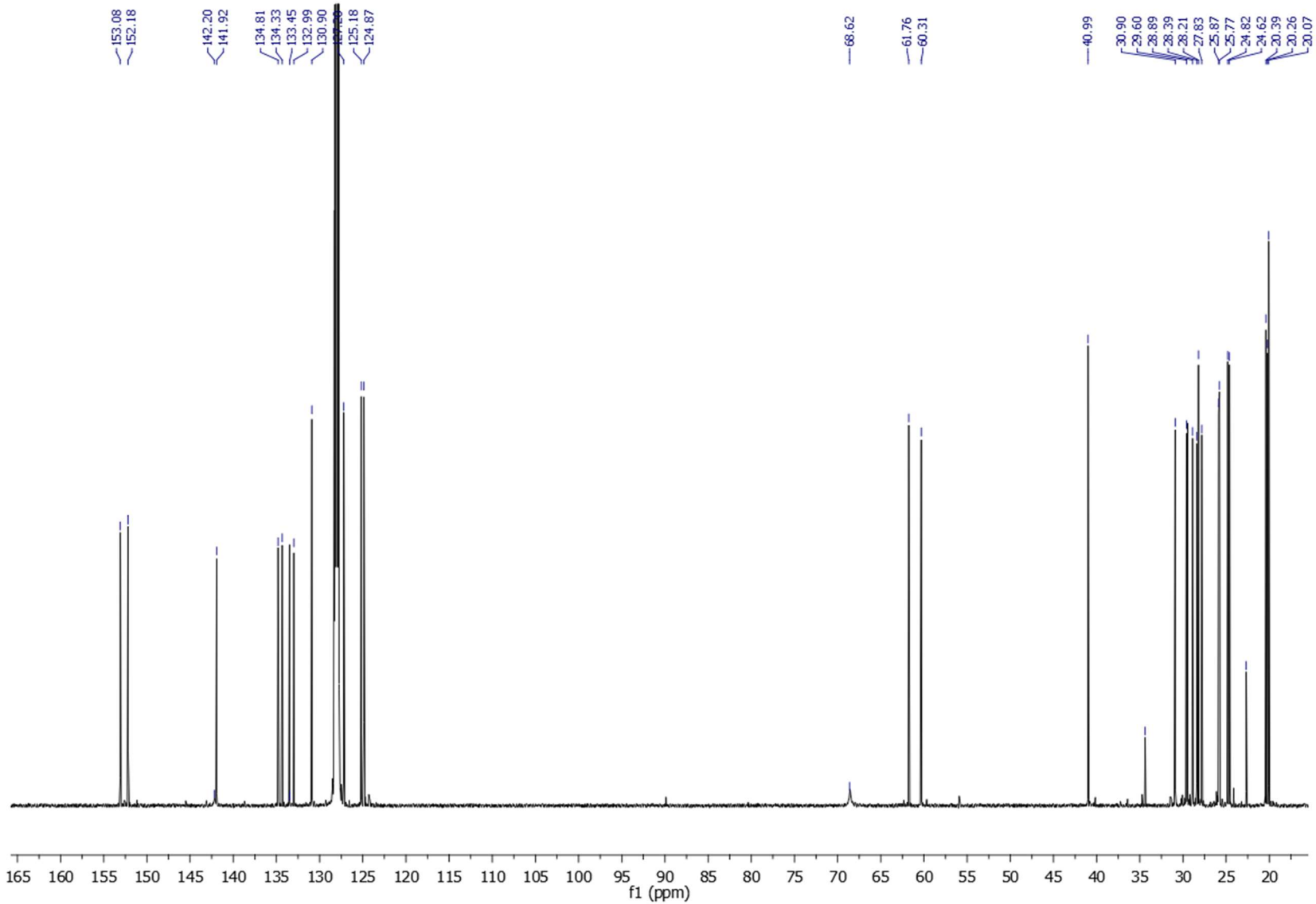


Fig. S3 $^{13}C\{^{1}H,^{11}B\}$ NMR spectrum of **5** in C_6D_6.

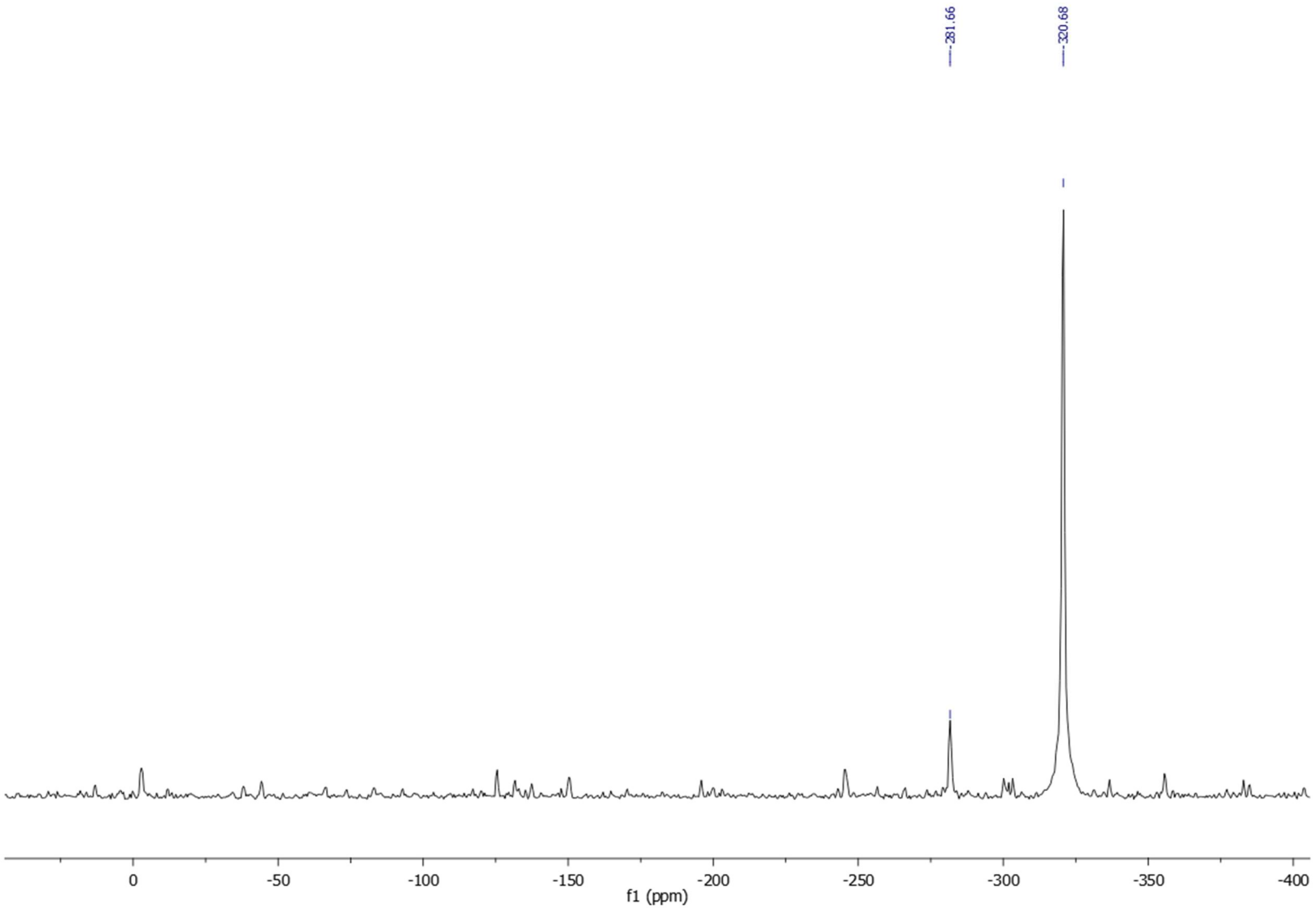


Fig. S4 ^{15}N NMR spectrum of **5** in C_6D_6.

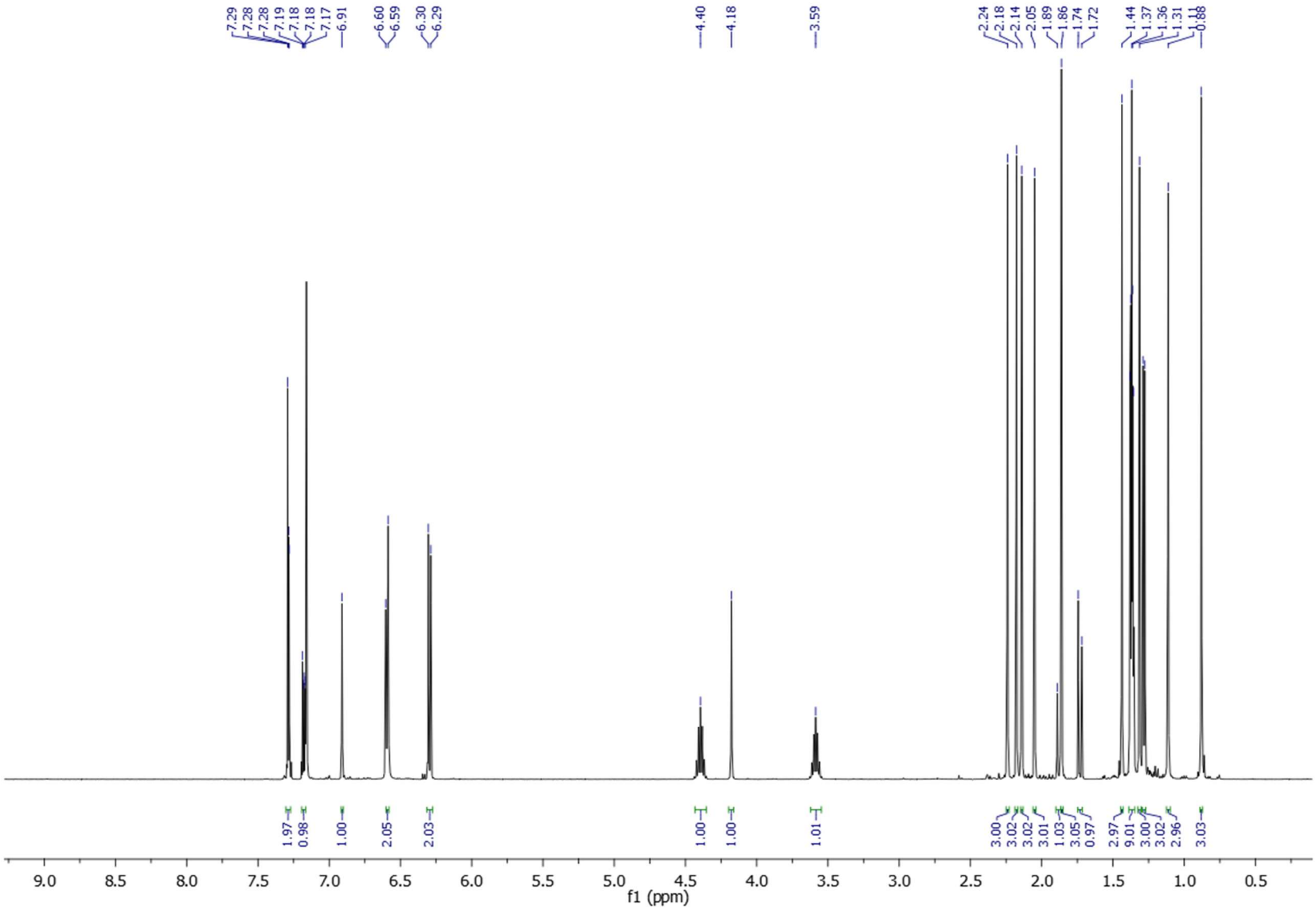


Fig. S5 ^{1}H NMR spectrum of **6** in C_6D_6.

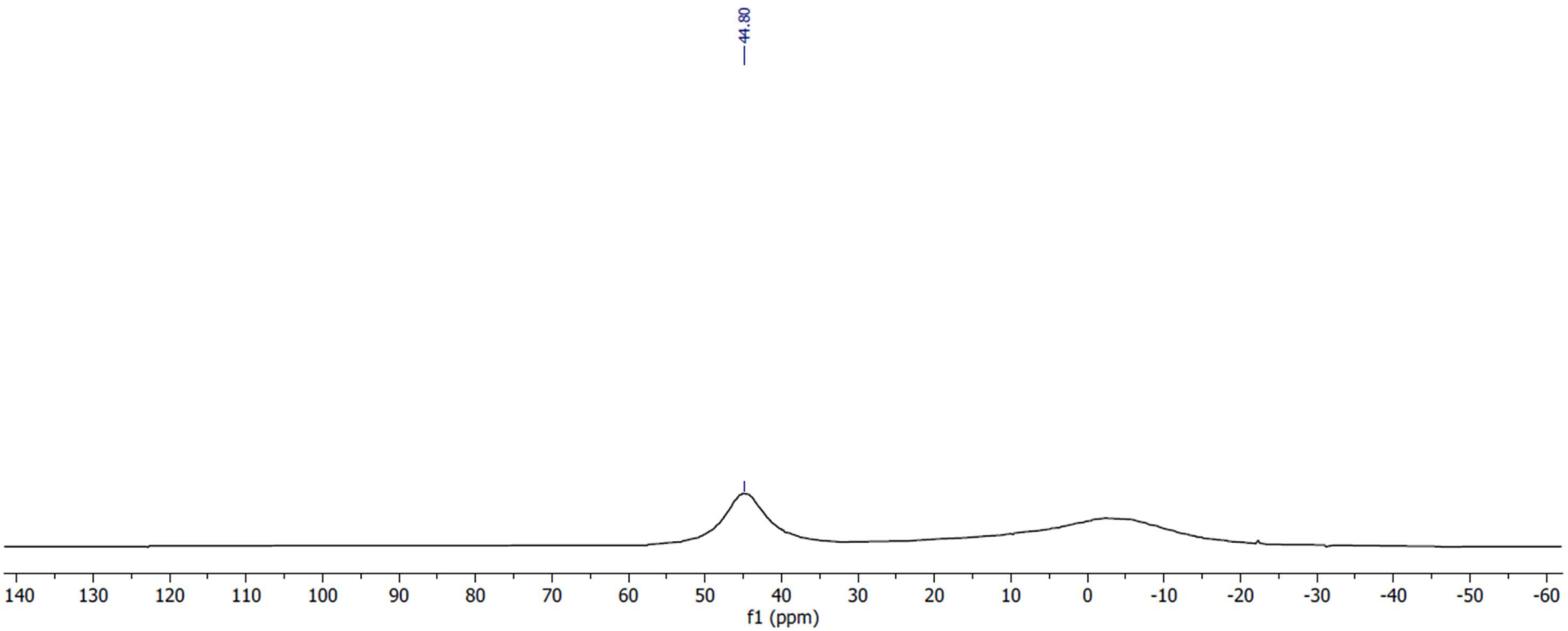


Fig. S6 ^{11}B NMR spectrum of **6** in C_6D_6.

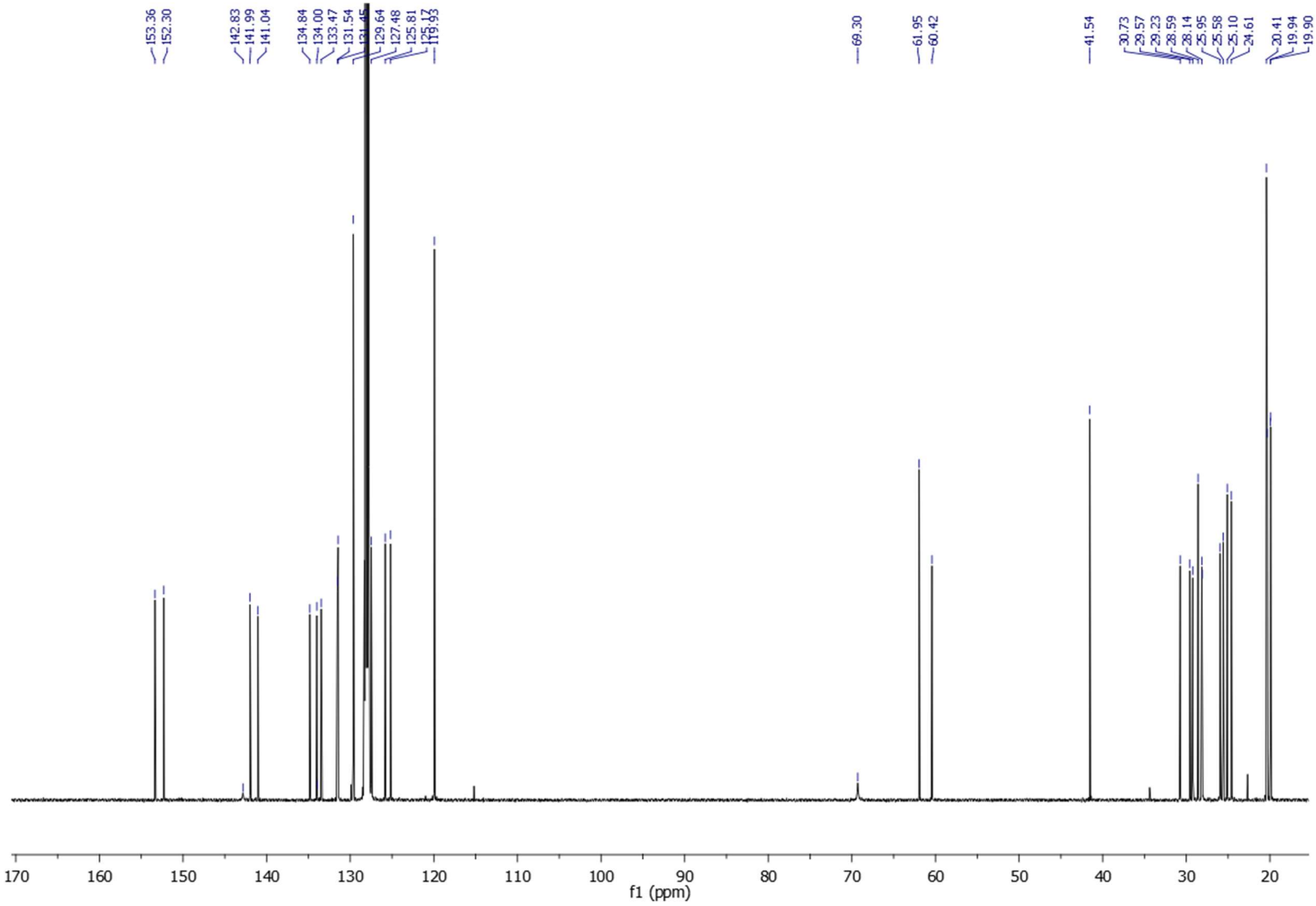


Fig. S7 $^{13}C\{^{1}H,^{11}B\}$ NMR spectrum of **6** in C_6D_6.

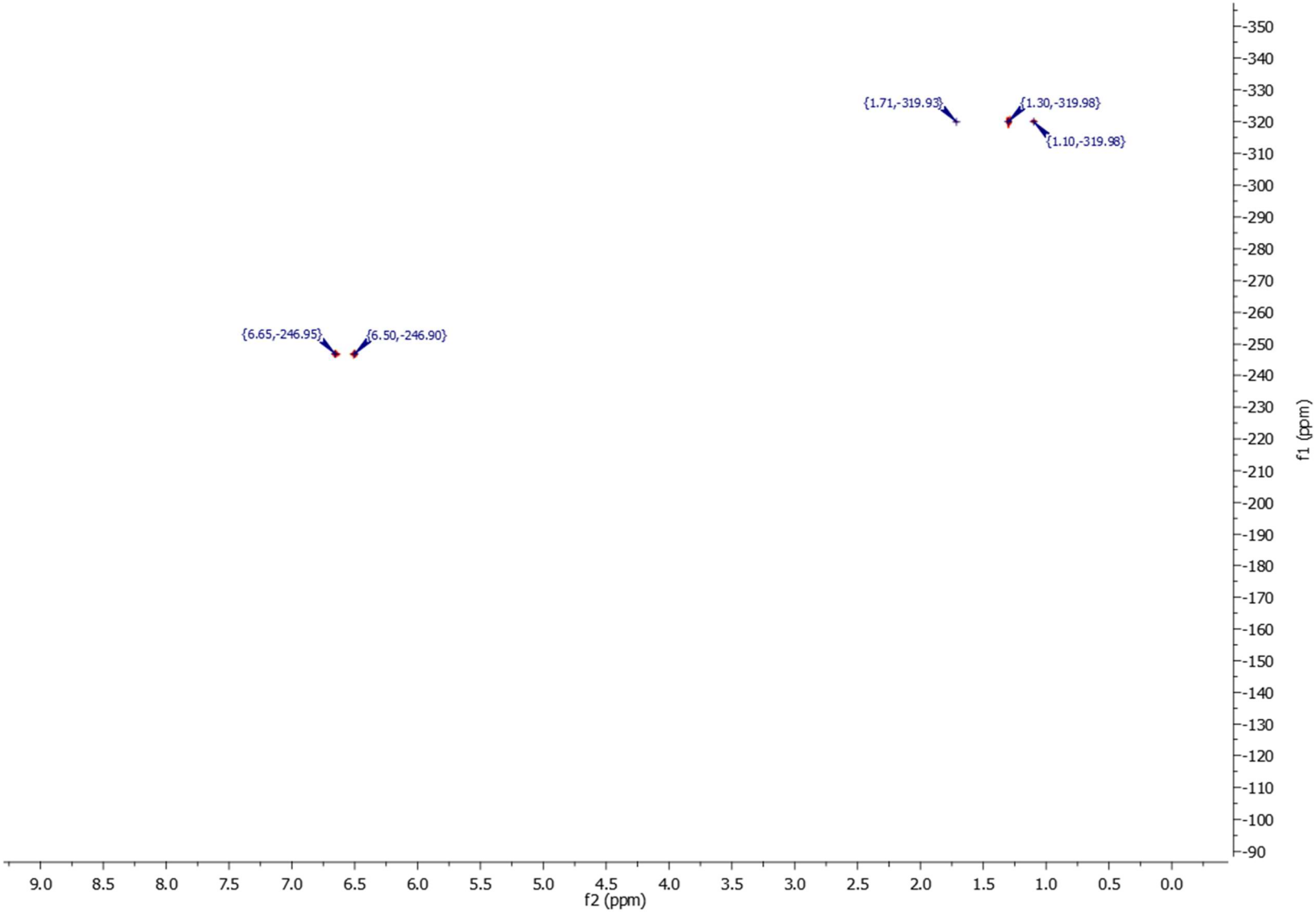


Fig. S8 2D $^{1}H,^{15}N$-HMBC NMR spectrum of **6** in C_6D_6.

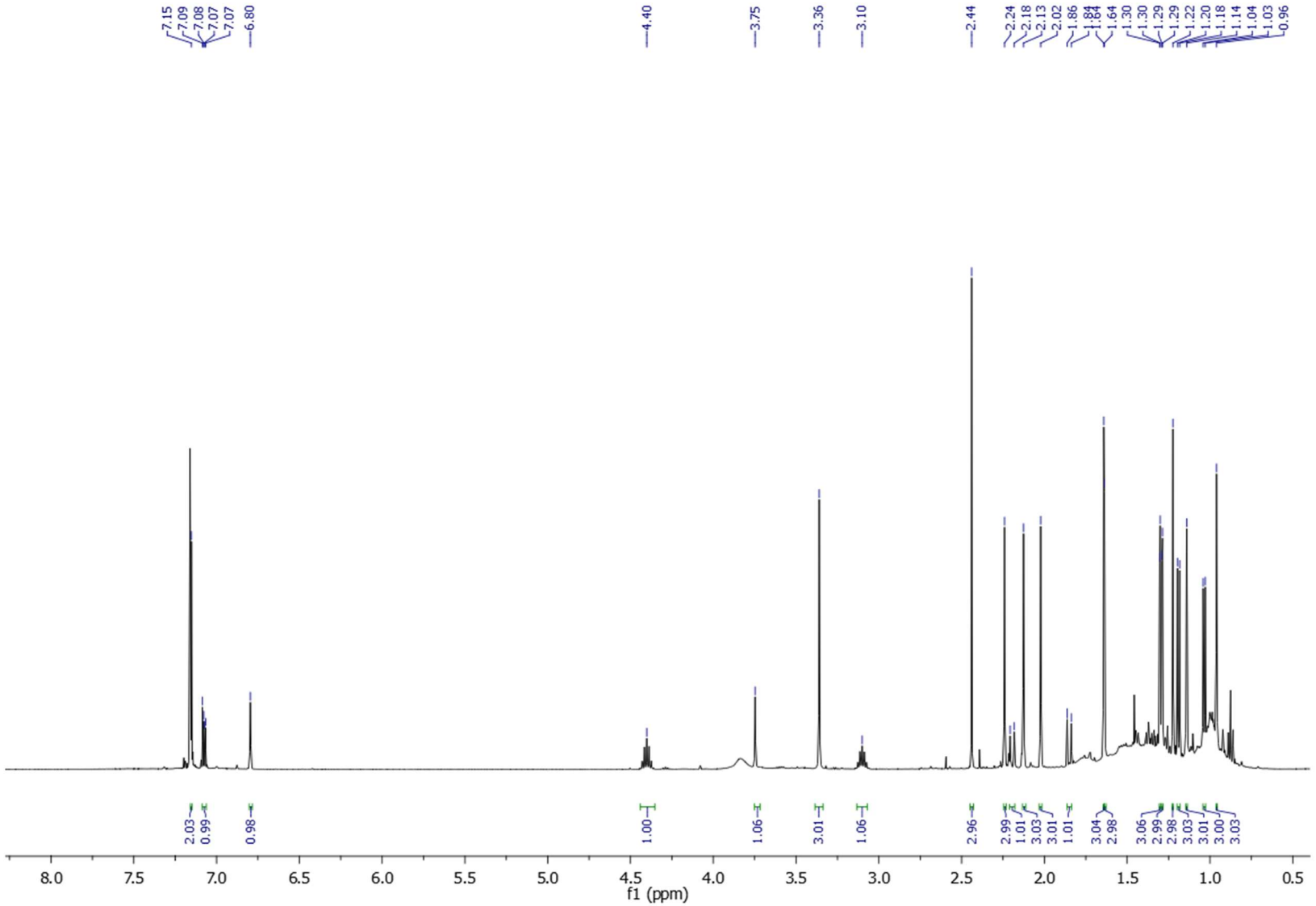


Fig. S9 ^{1}H NMR spectrum of **7** in C_6D_6.

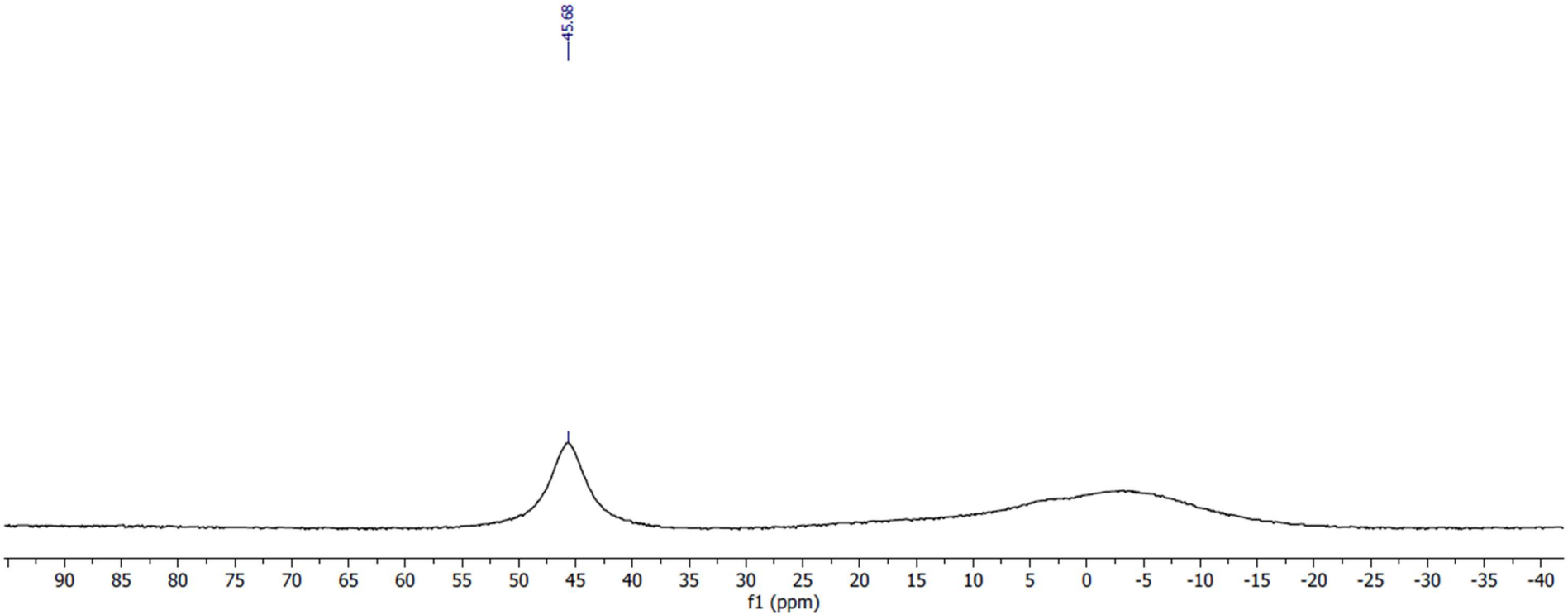


Fig. S10 ^{11}B NMR spectrum of **7** in C_6D_6.

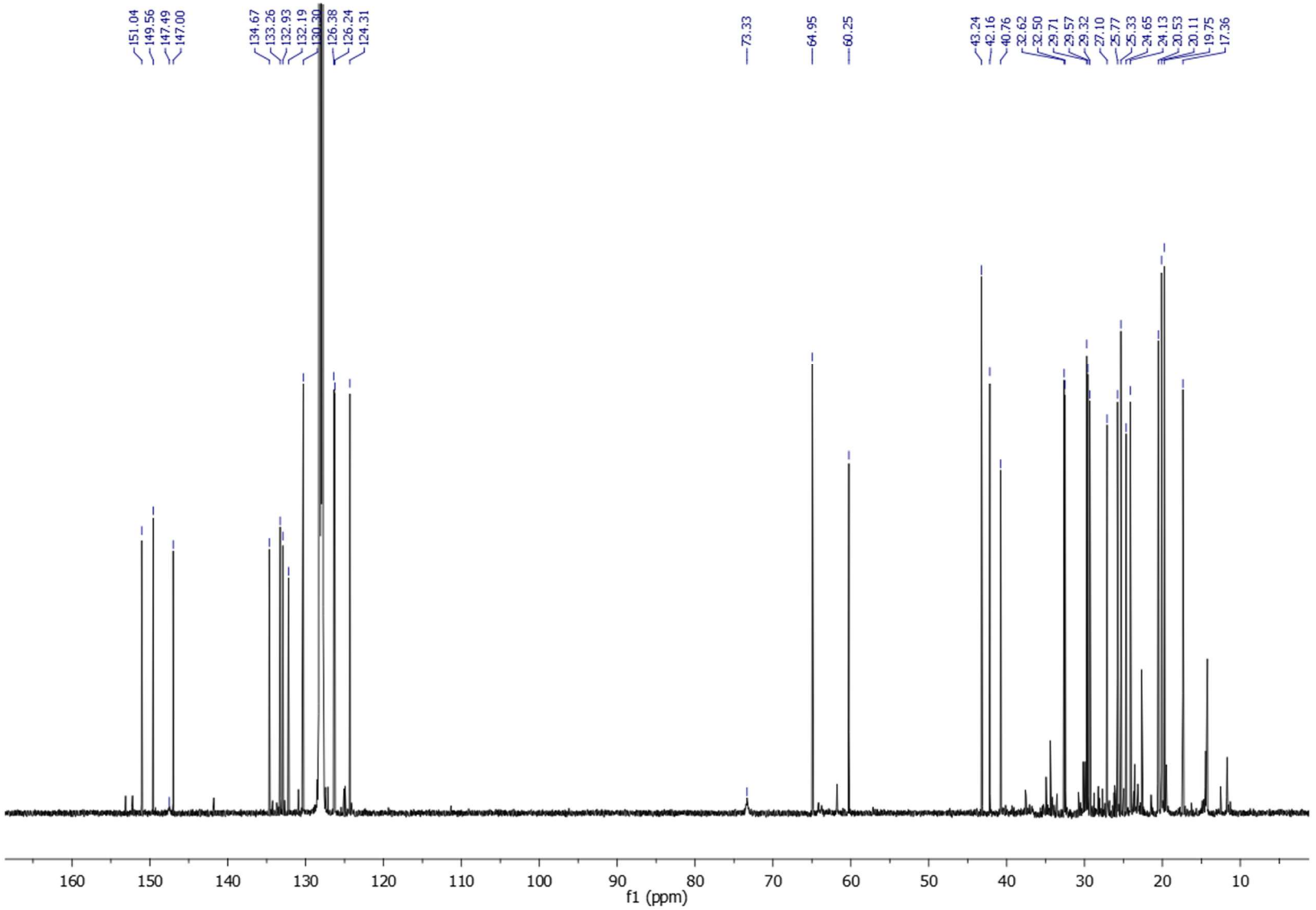


Fig. S11 $^{13}C\{^{1}H,^{11}B\}$ NMR spectrum of **7** in C_6D_6.

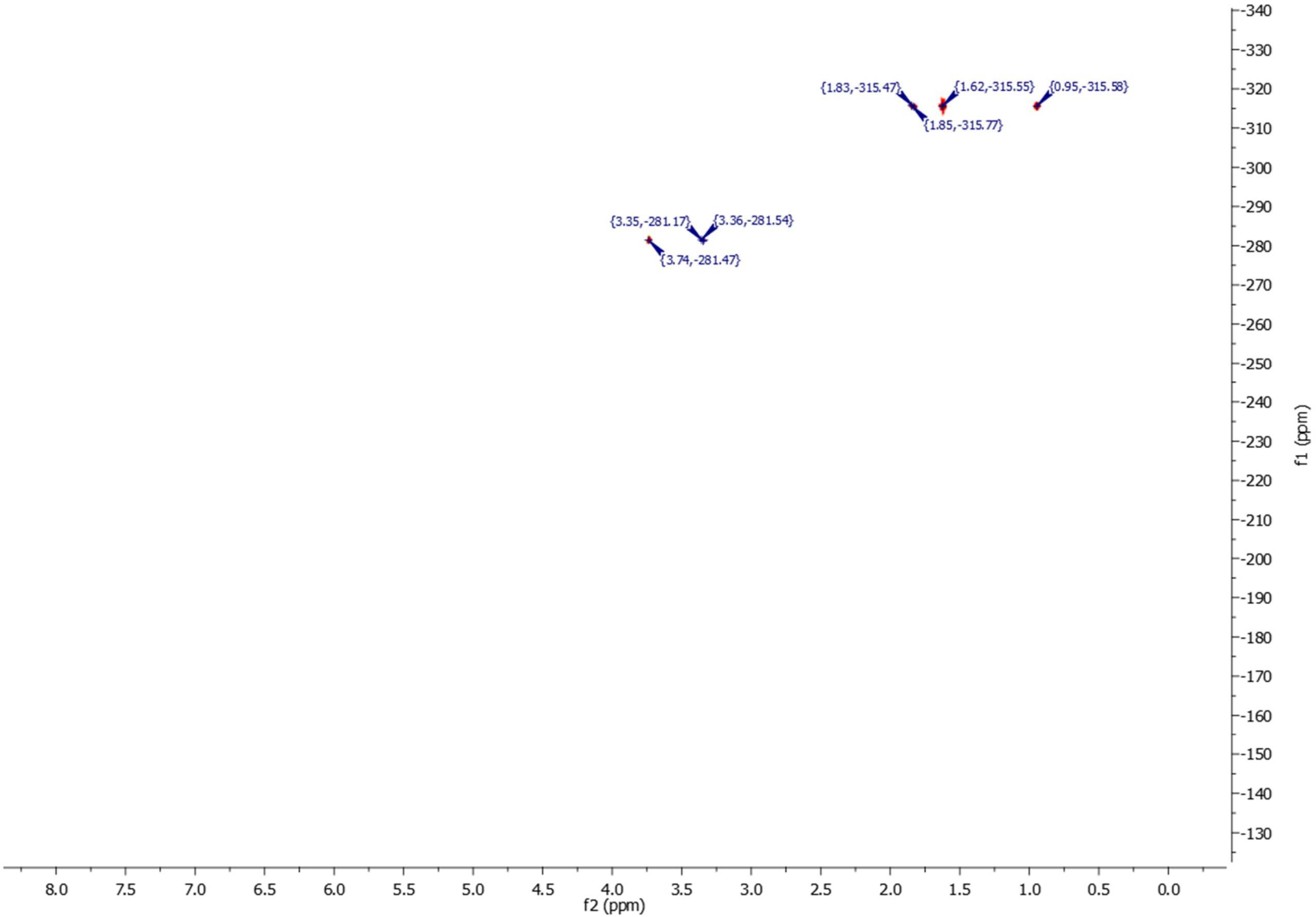


Fig. S12 2D $^{1}H,^{15}N$-HMBC NMR spectrum of **7** in C_6D_6.

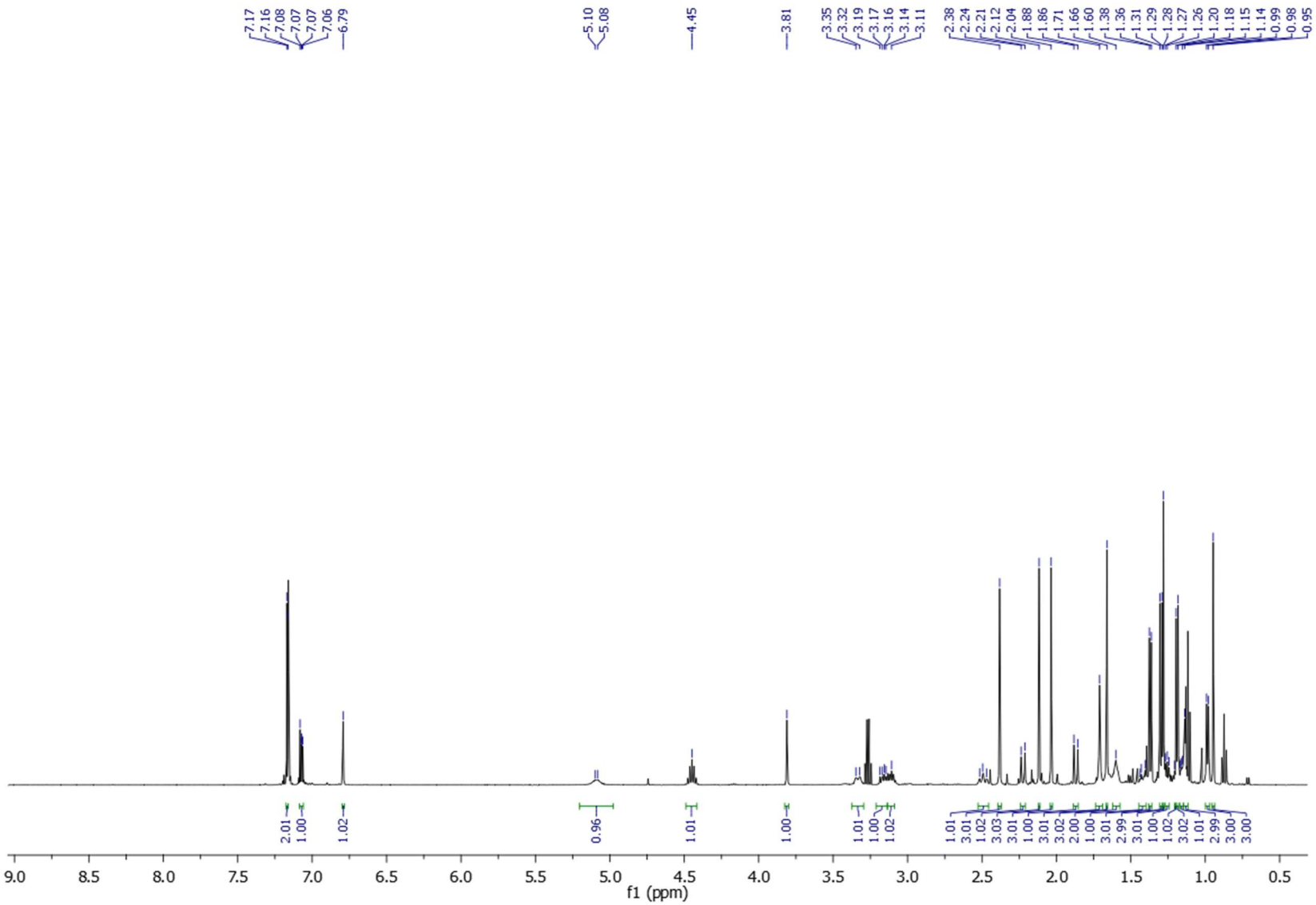


Fig. S13 ^{1}H NMR spectrum of **8** in C_6D_6.

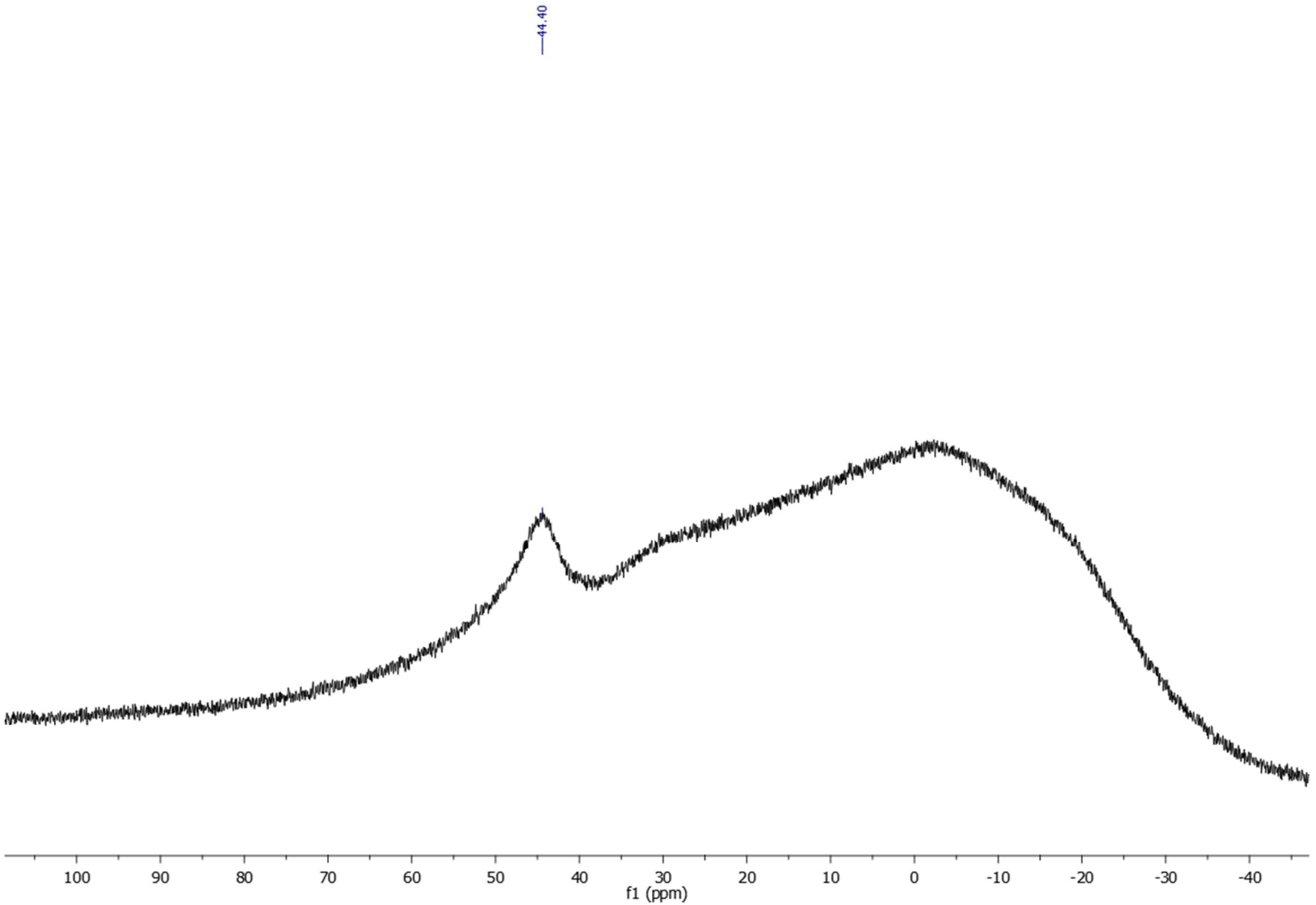


Fig. S14 ^{11}B NMR spectrum of **8** in C_6D_6.

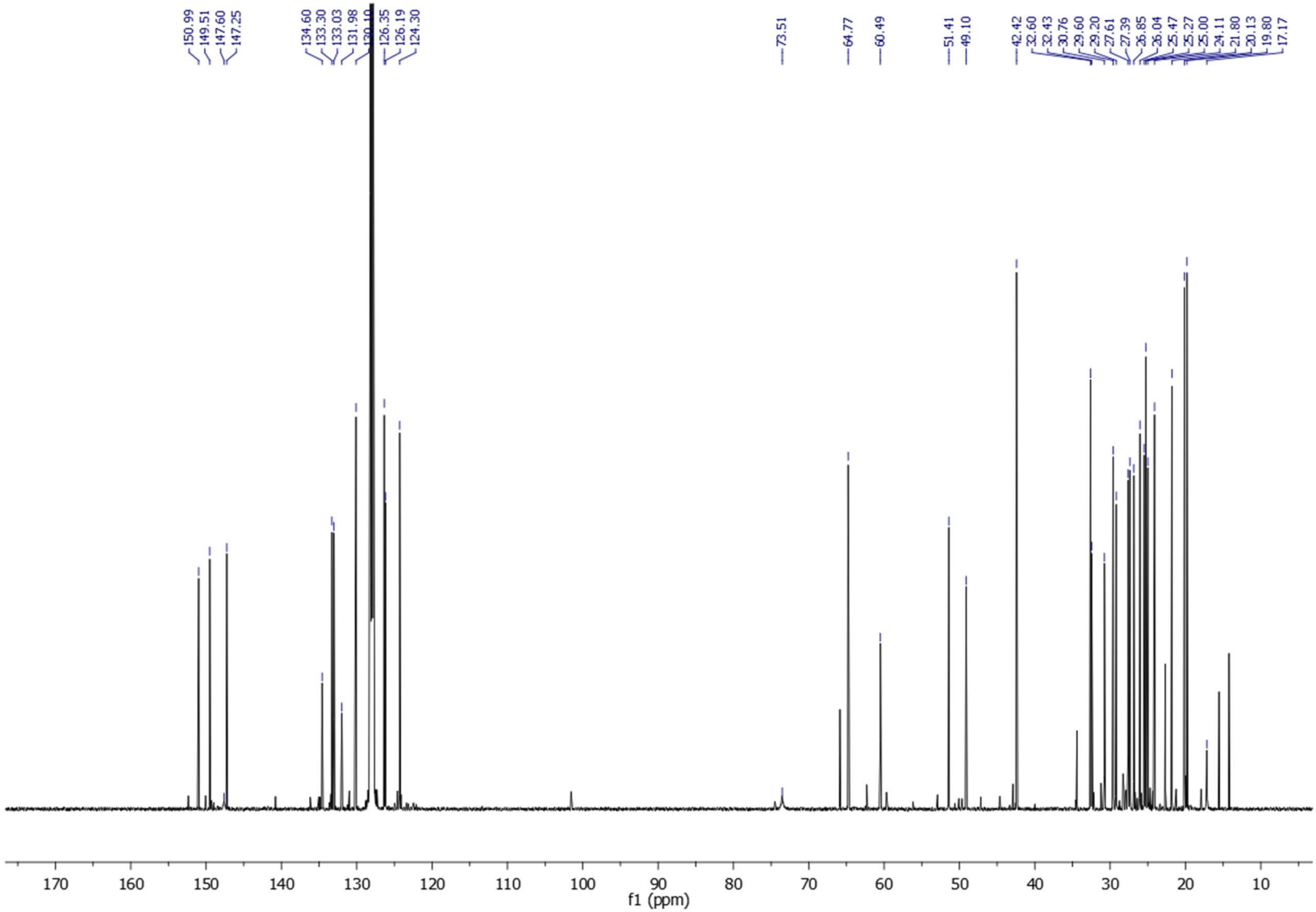


Fig. S15 $^{13}C\{^{1}H,^{11}B\}$ NMR spectrum of **8** in C_6D_6.

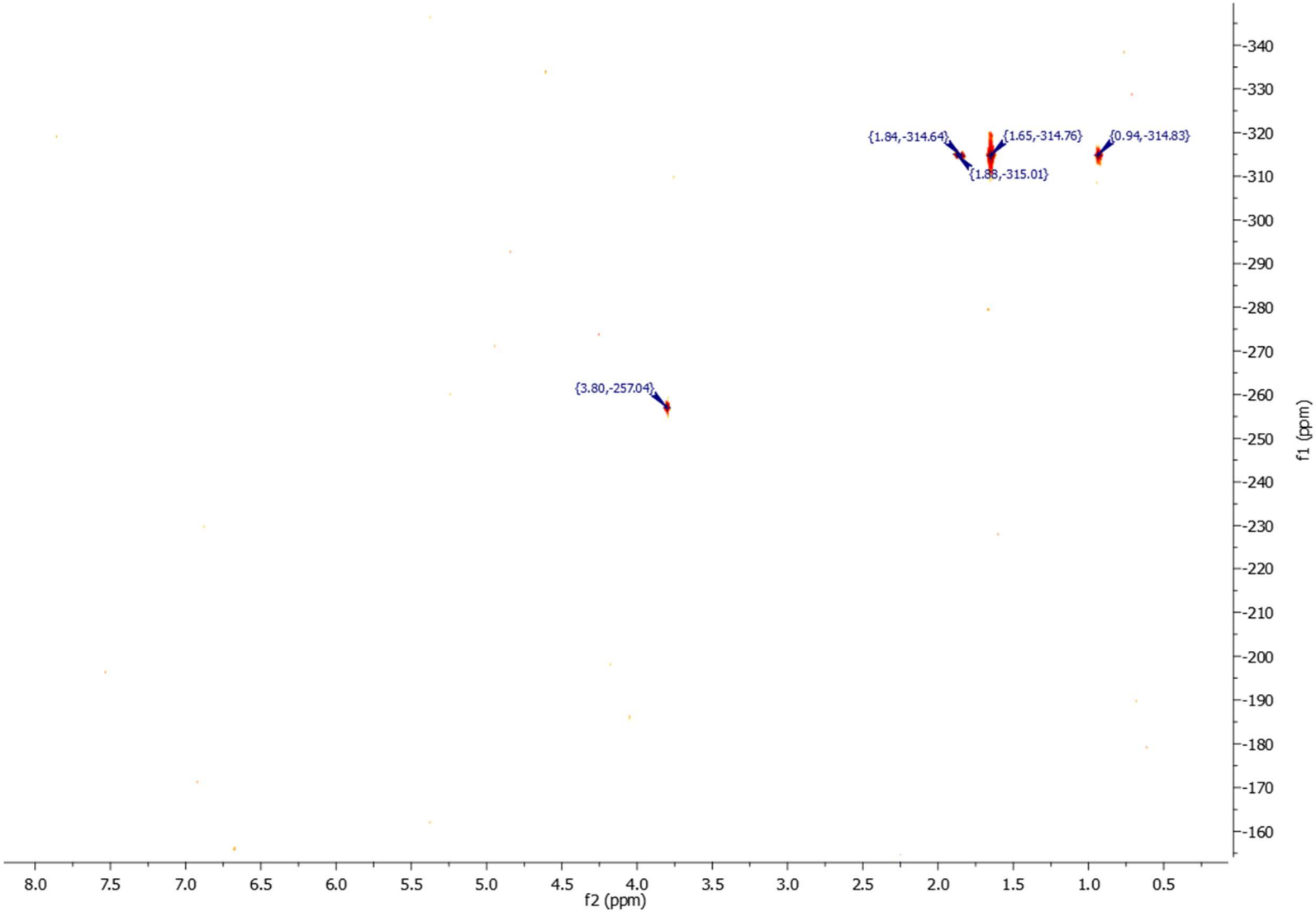


Fig. S16 2D $^{1}H,^{15}N$-HMBC NMR spectrum of **8** in C_6D_6.

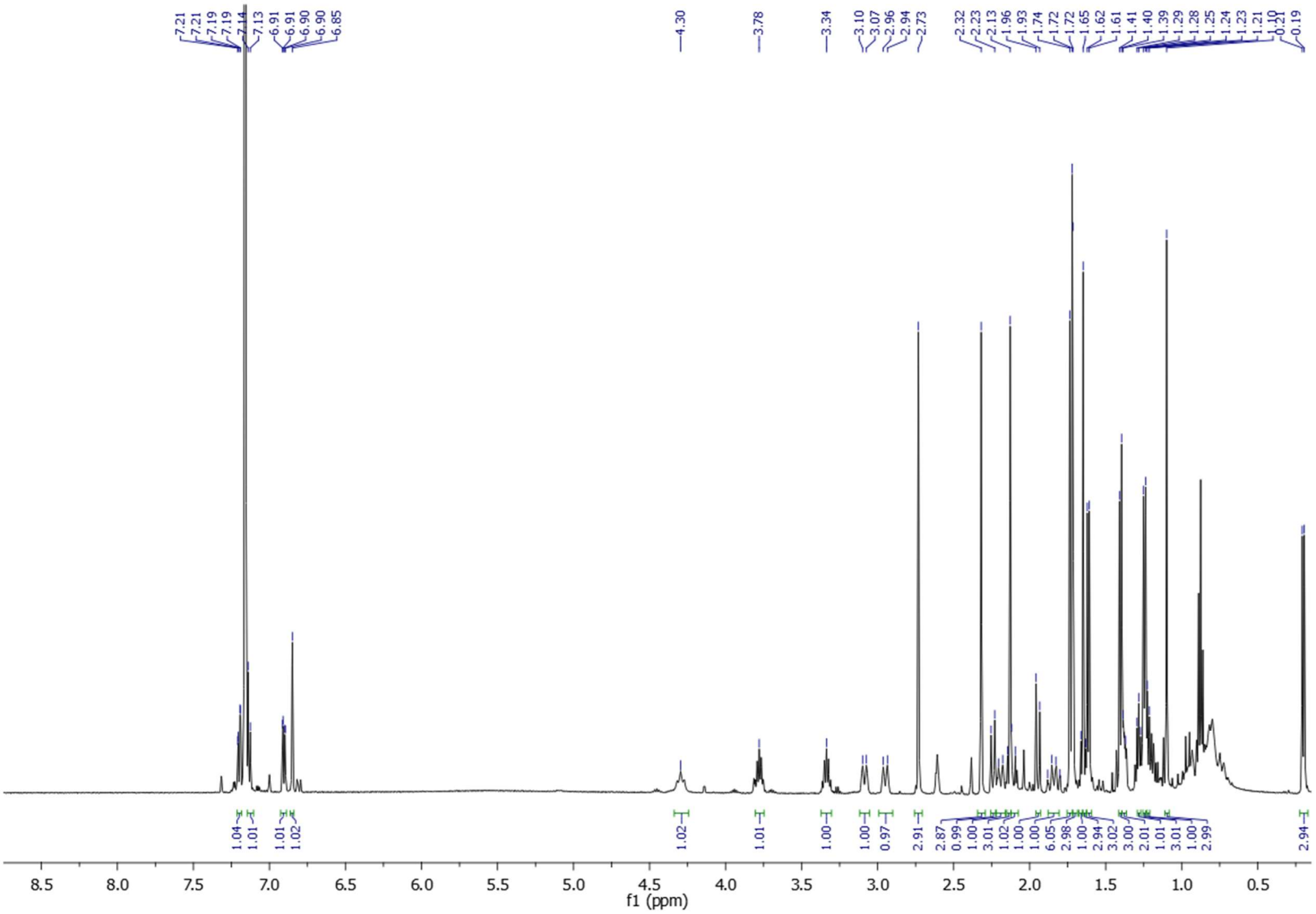


Fig. S17 ^{1}H NMR spectrum of **9** in C_6D_6.

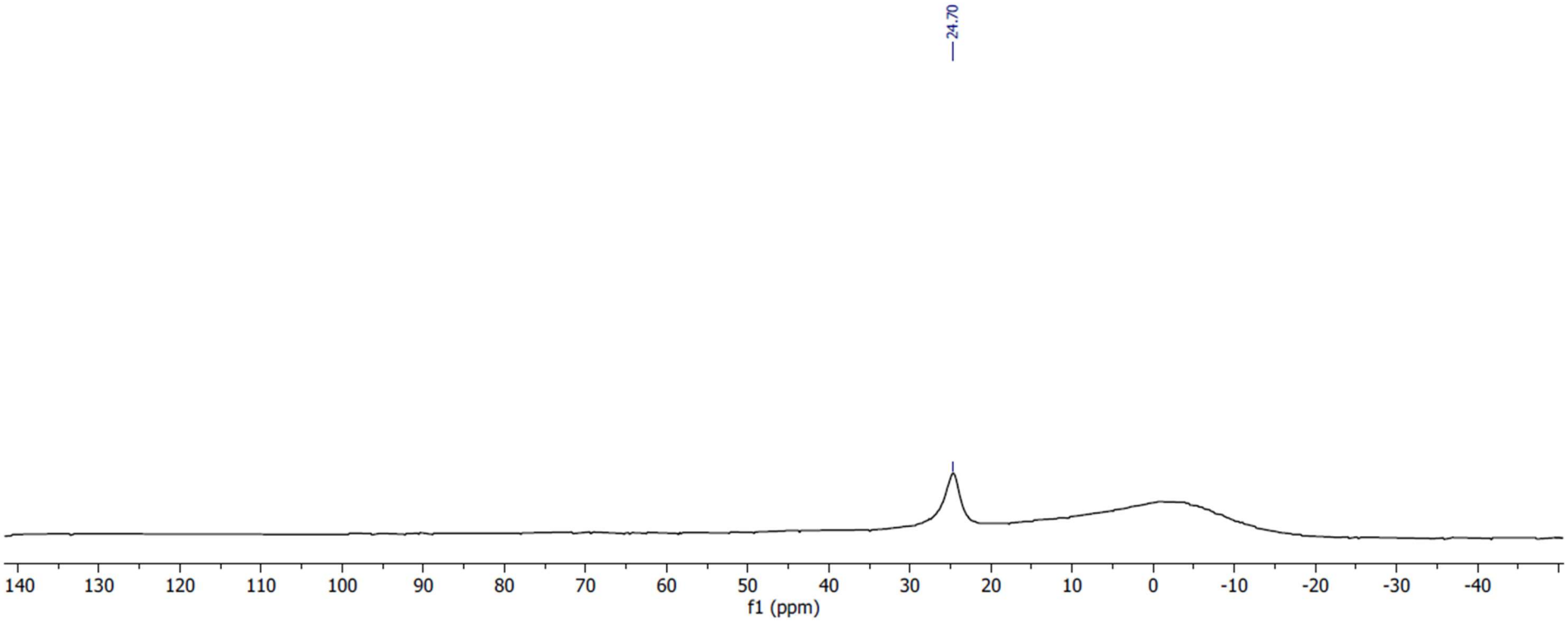


Fig. S18 ^{11}B NMR spectrum of **9** in C_6D_6.

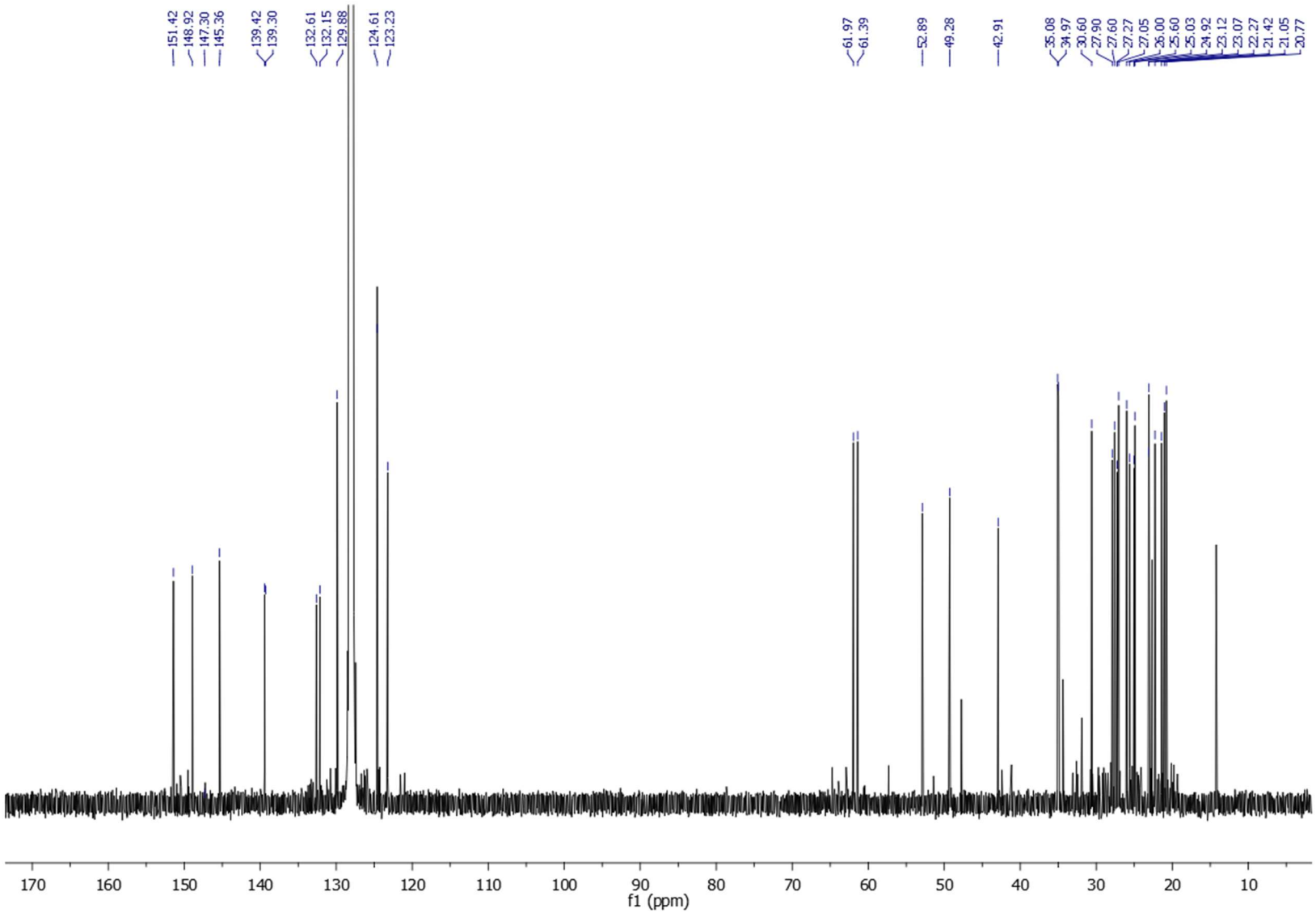


Fig. S19 $^{13}C\{^{1}H,^{11}B\}$ NMR spectrum of **9** in C_6D_6.

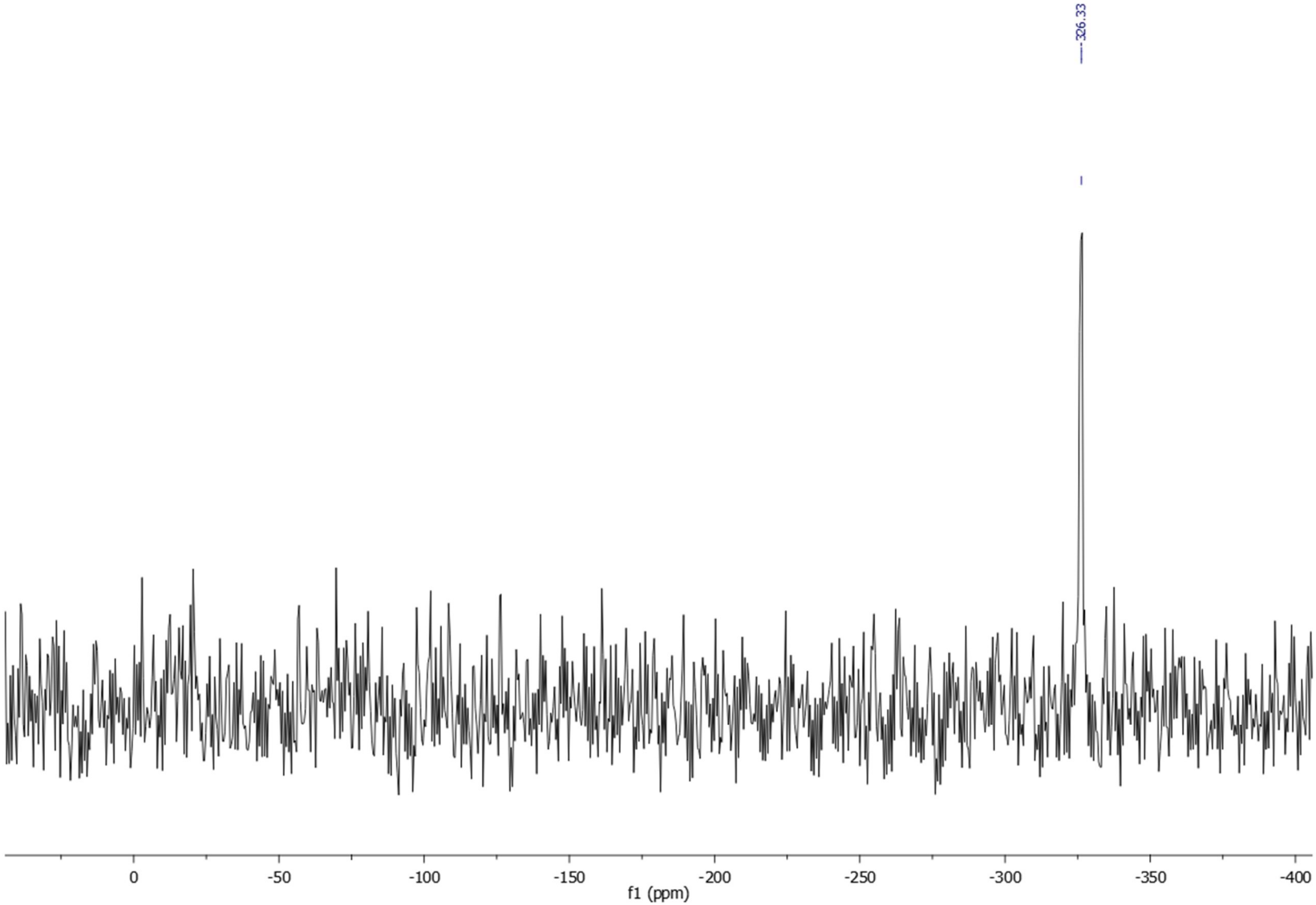


Fig. S20 ^{15}N NMR spectrum of **9** in C_6D_6.

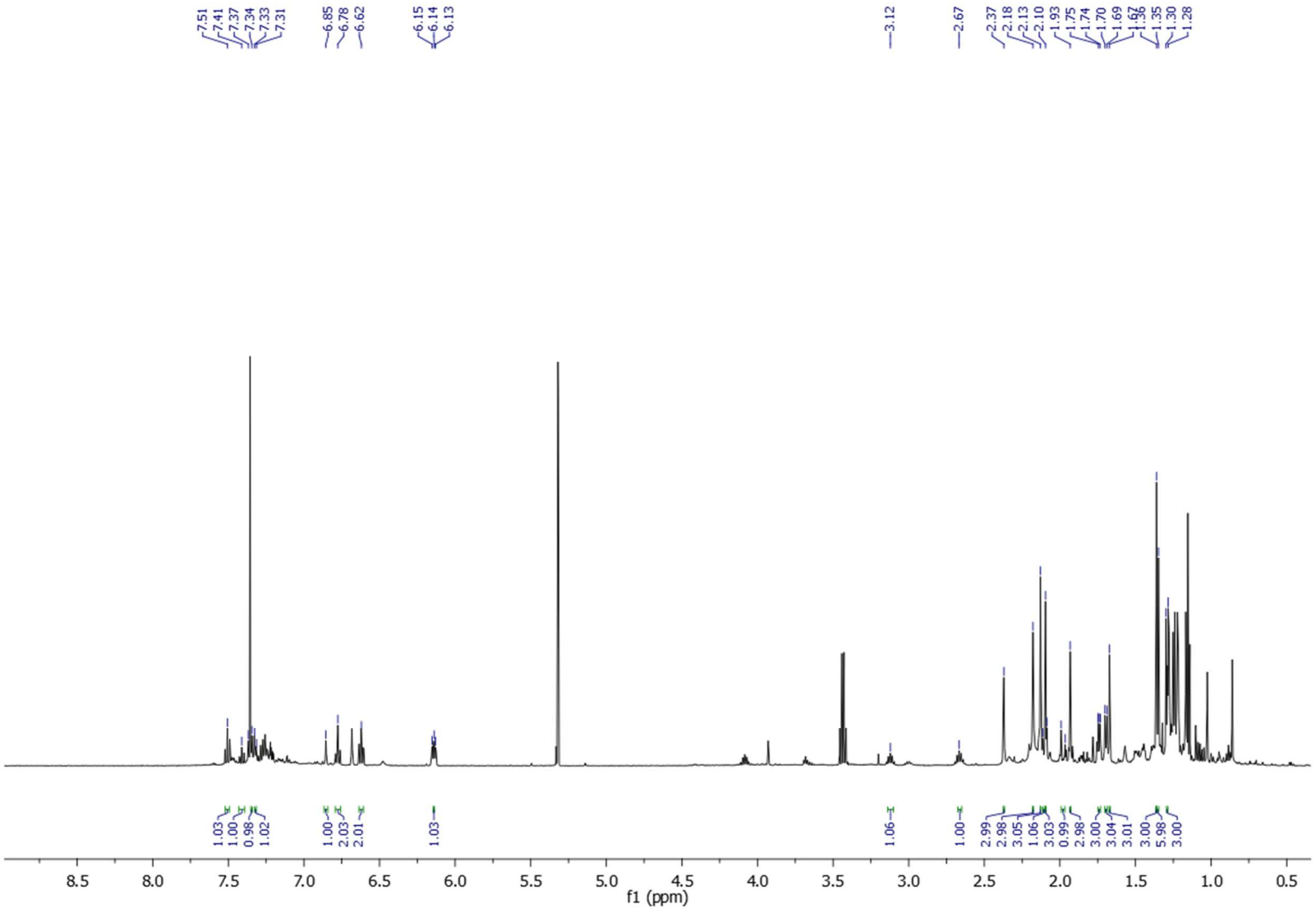


Fig. S21 ^{1}H NMR spectrum of **10** in CD_2Cl_2.

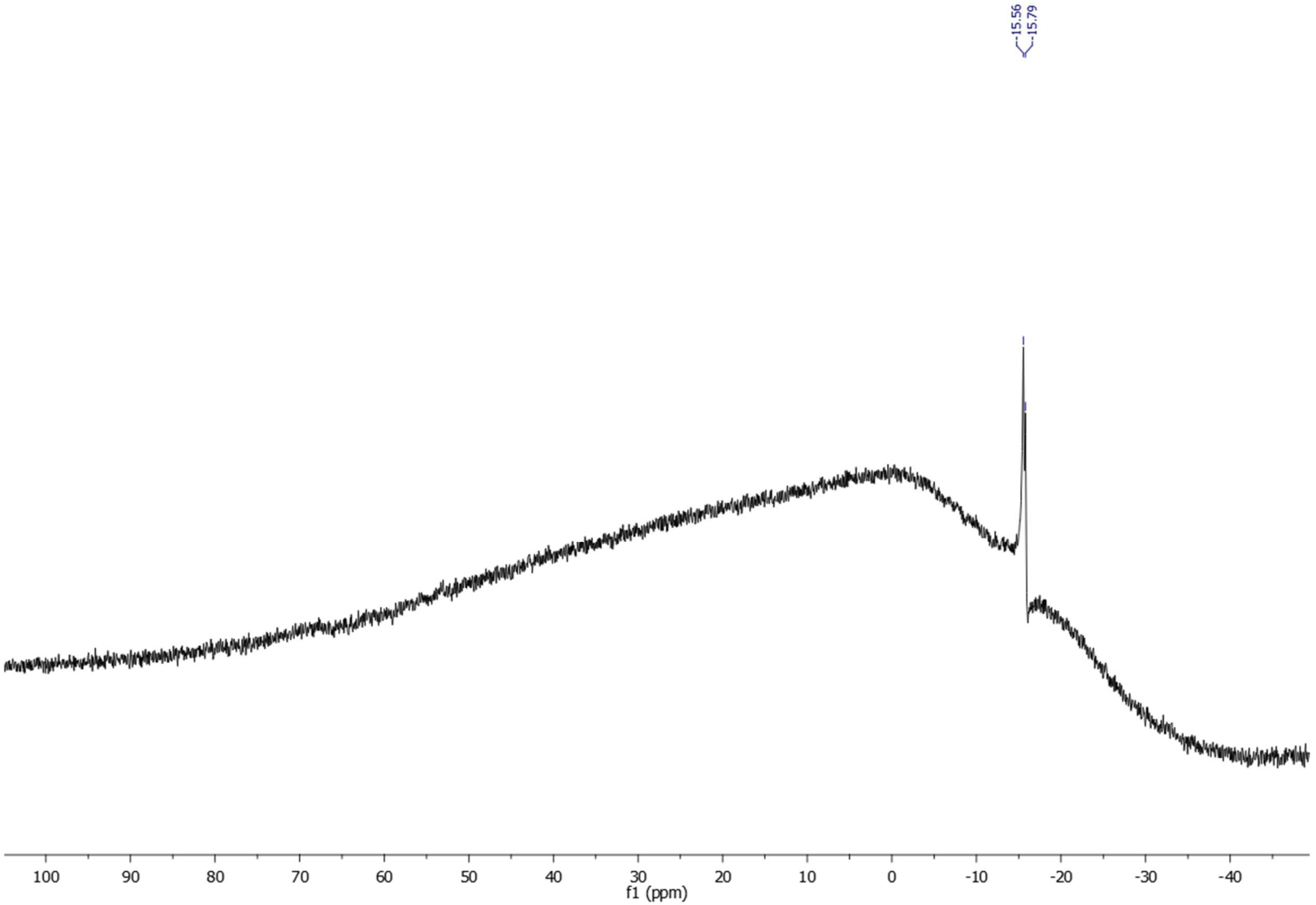


Fig. S22 ^{11}B NMR spectrum of **10** in C_6D_6.

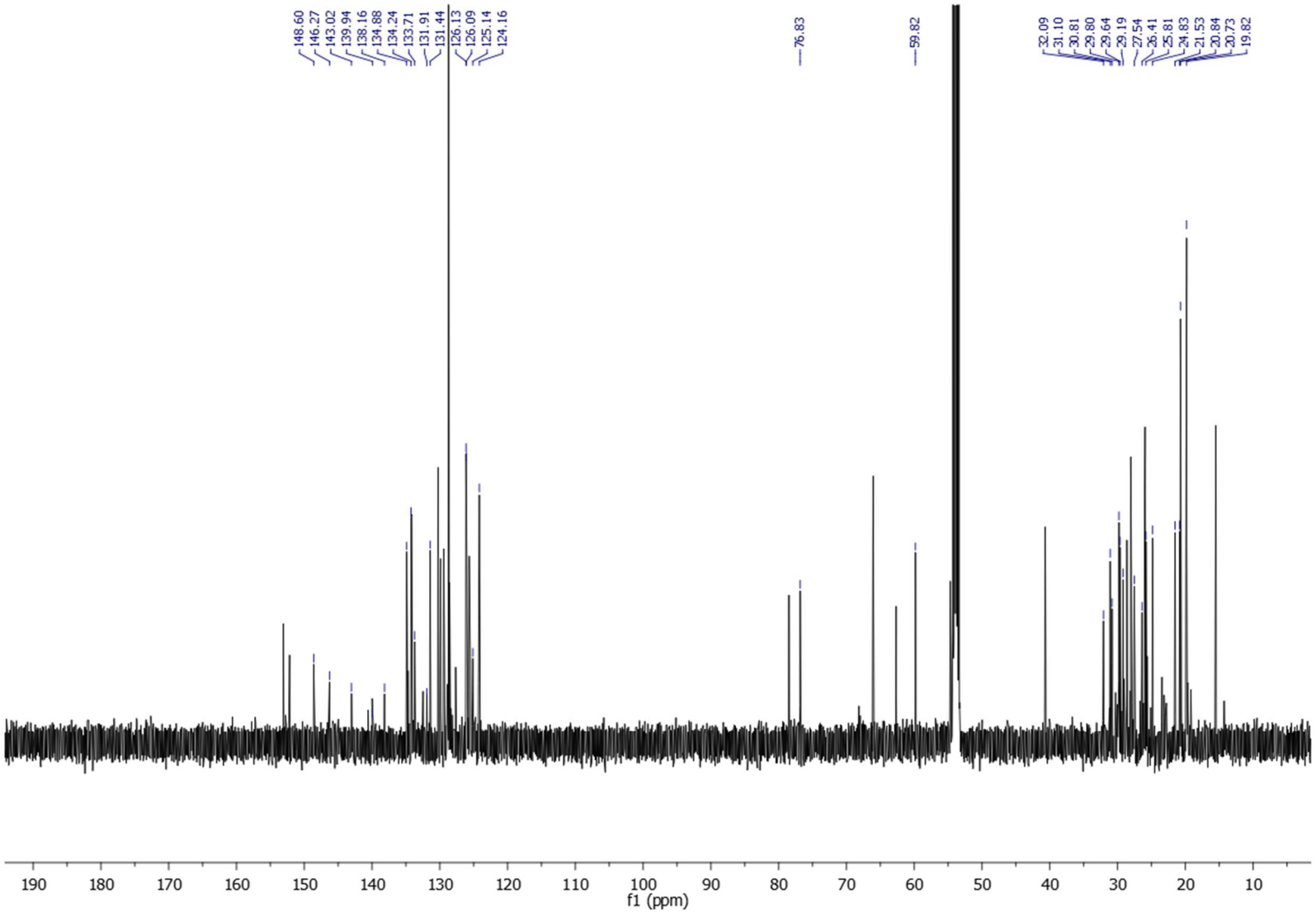


Fig. S23 $^{13}C\{^{1}H,^{11}B\}$ NMR spectrum of **10** in CD_2Cl_2.

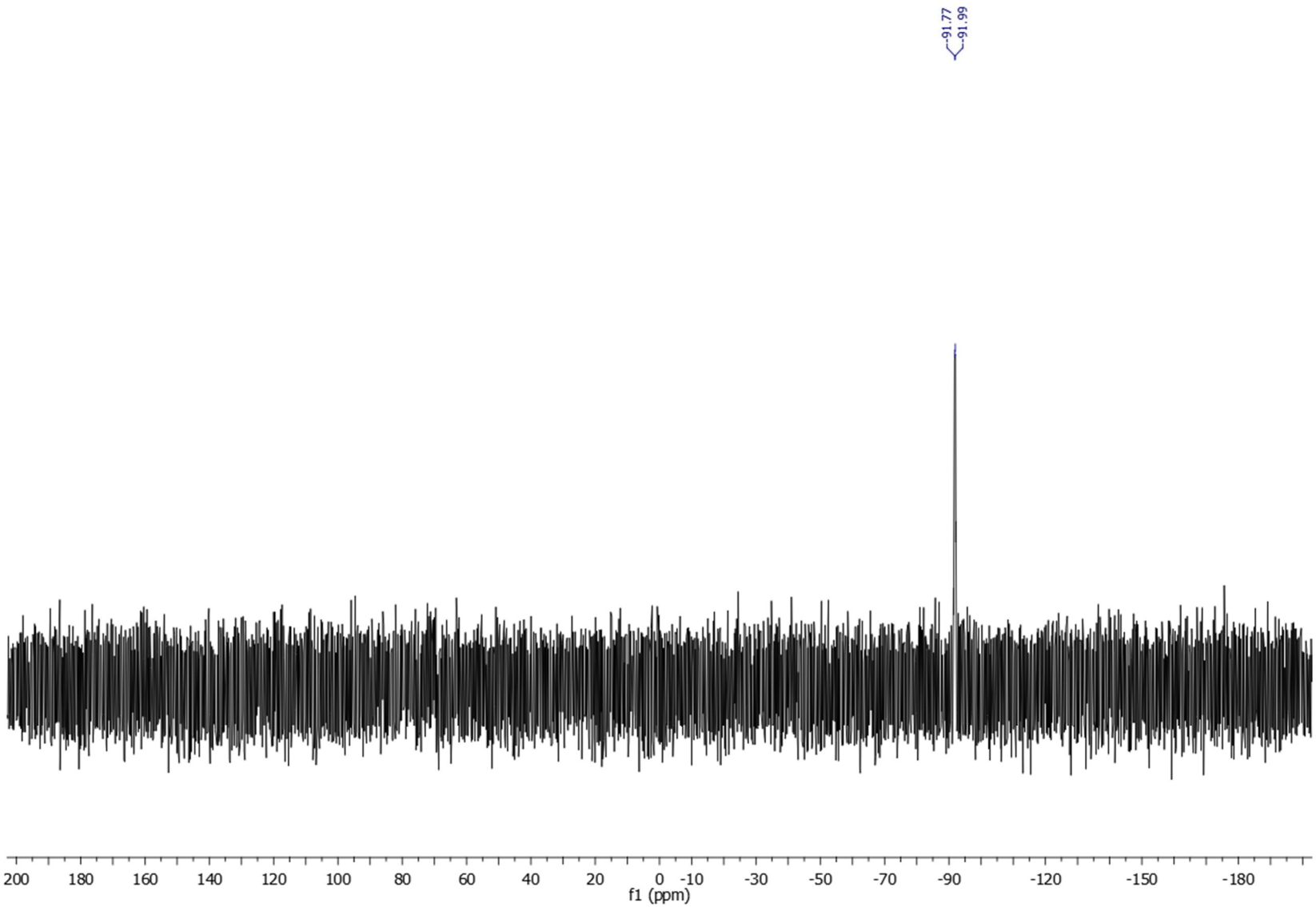


Fig. S24 ^{31}P NMR spectrum of **10** in C_6D_6.

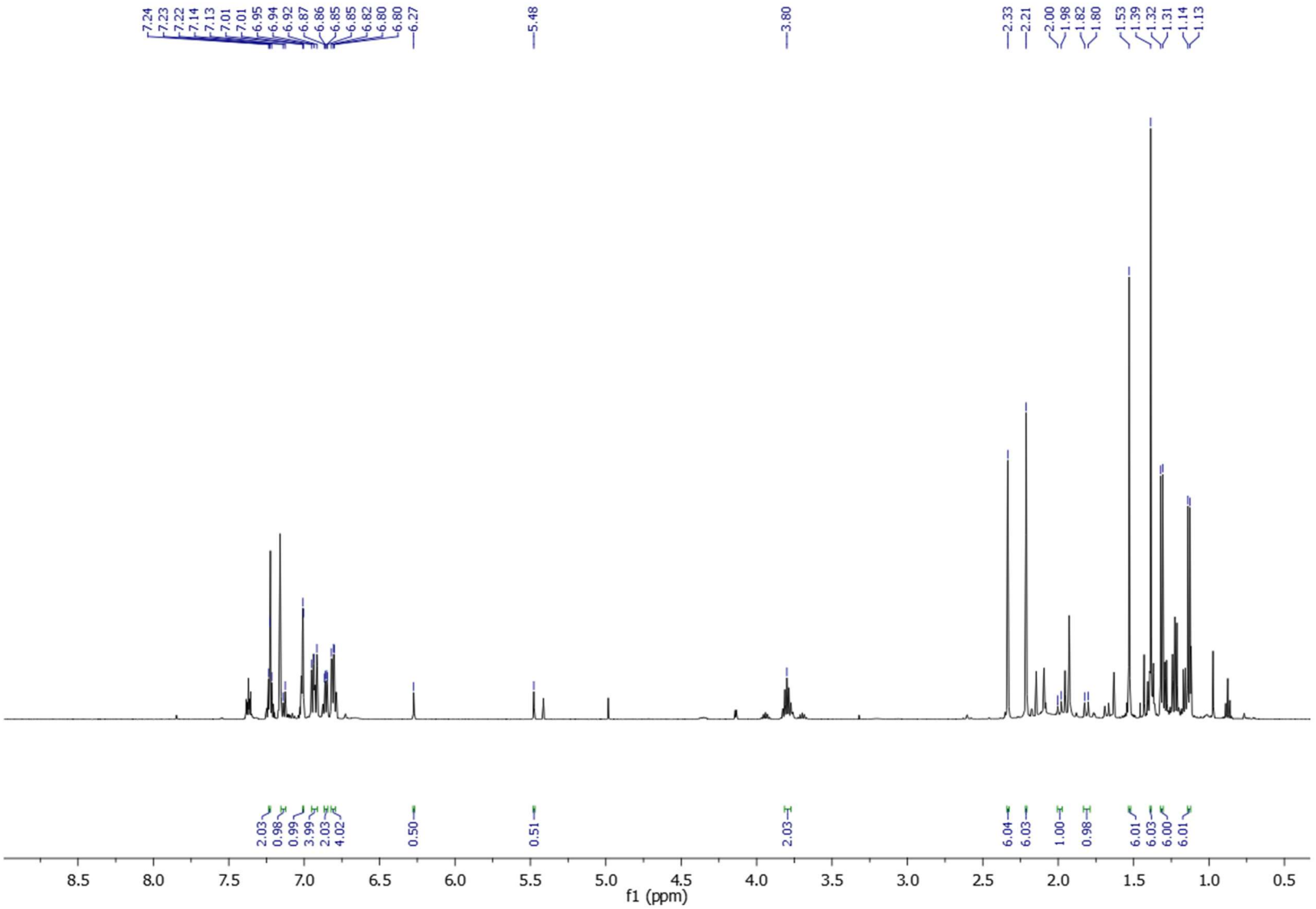


Fig. S25 ^{1}H NMR spectrum of **11** in C_6D_6.

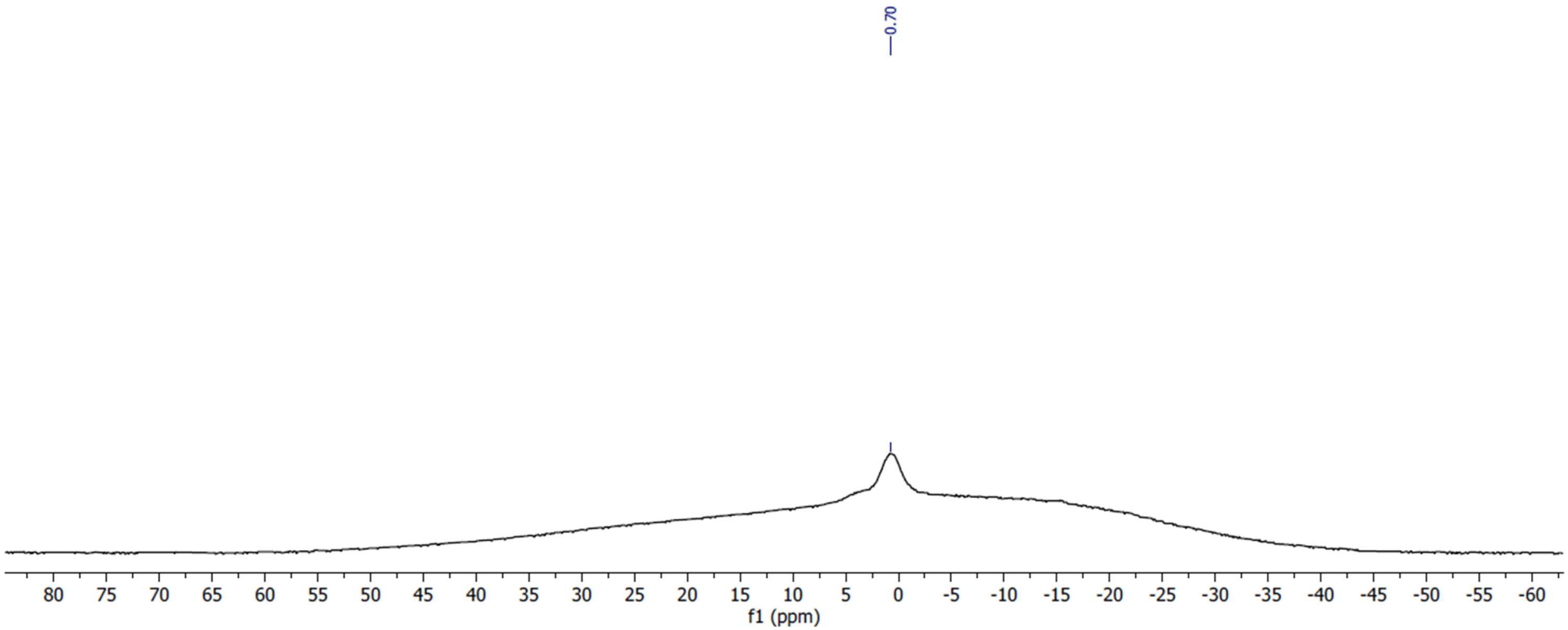


Fig. S26 ^{11}B NMR spectrum of **11** in C_6D_6.

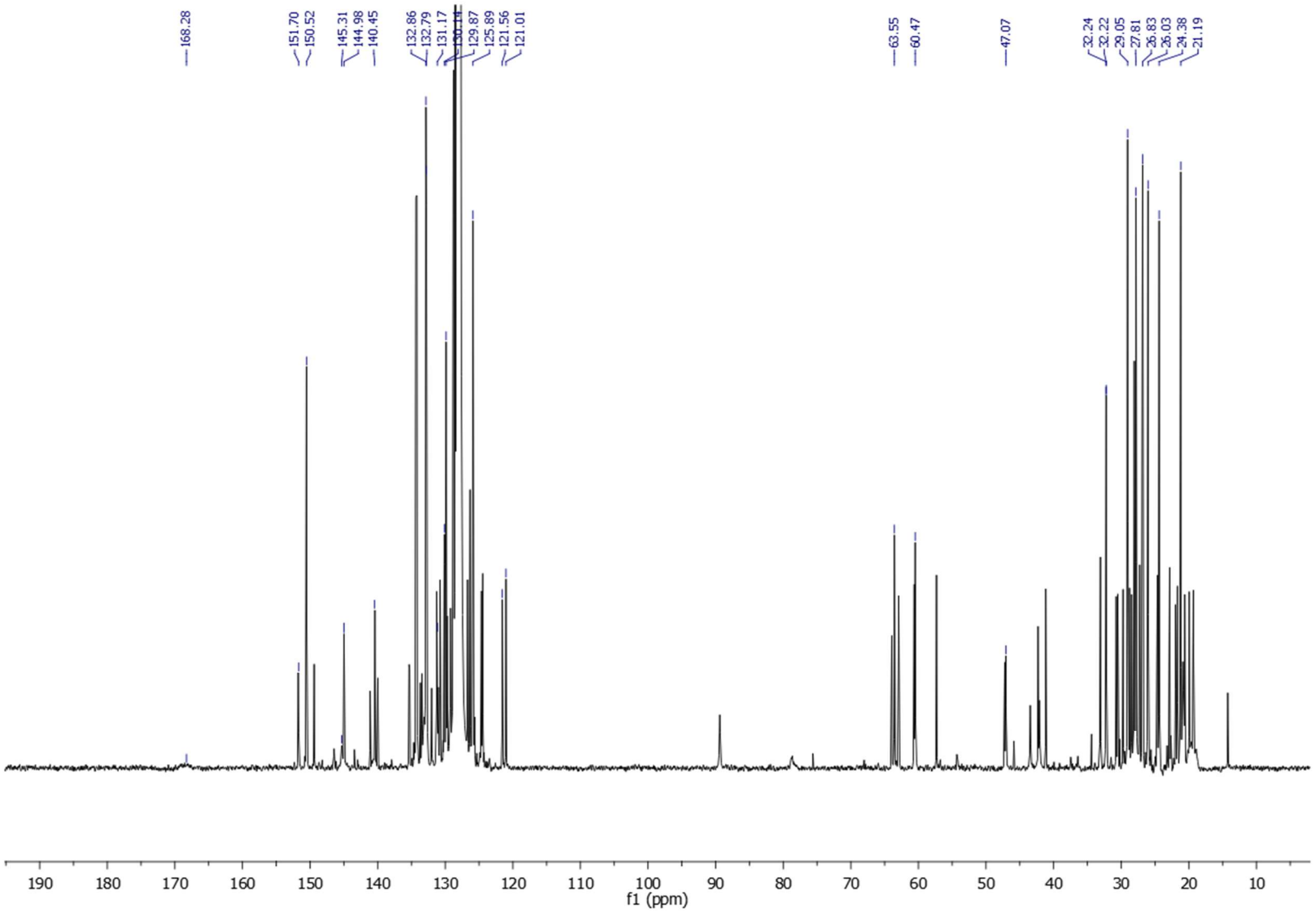


Fig. S27 $^{13}C\{^{1}H,^{11}B\}$ NMR spectrum of **11** in C_6D_6.

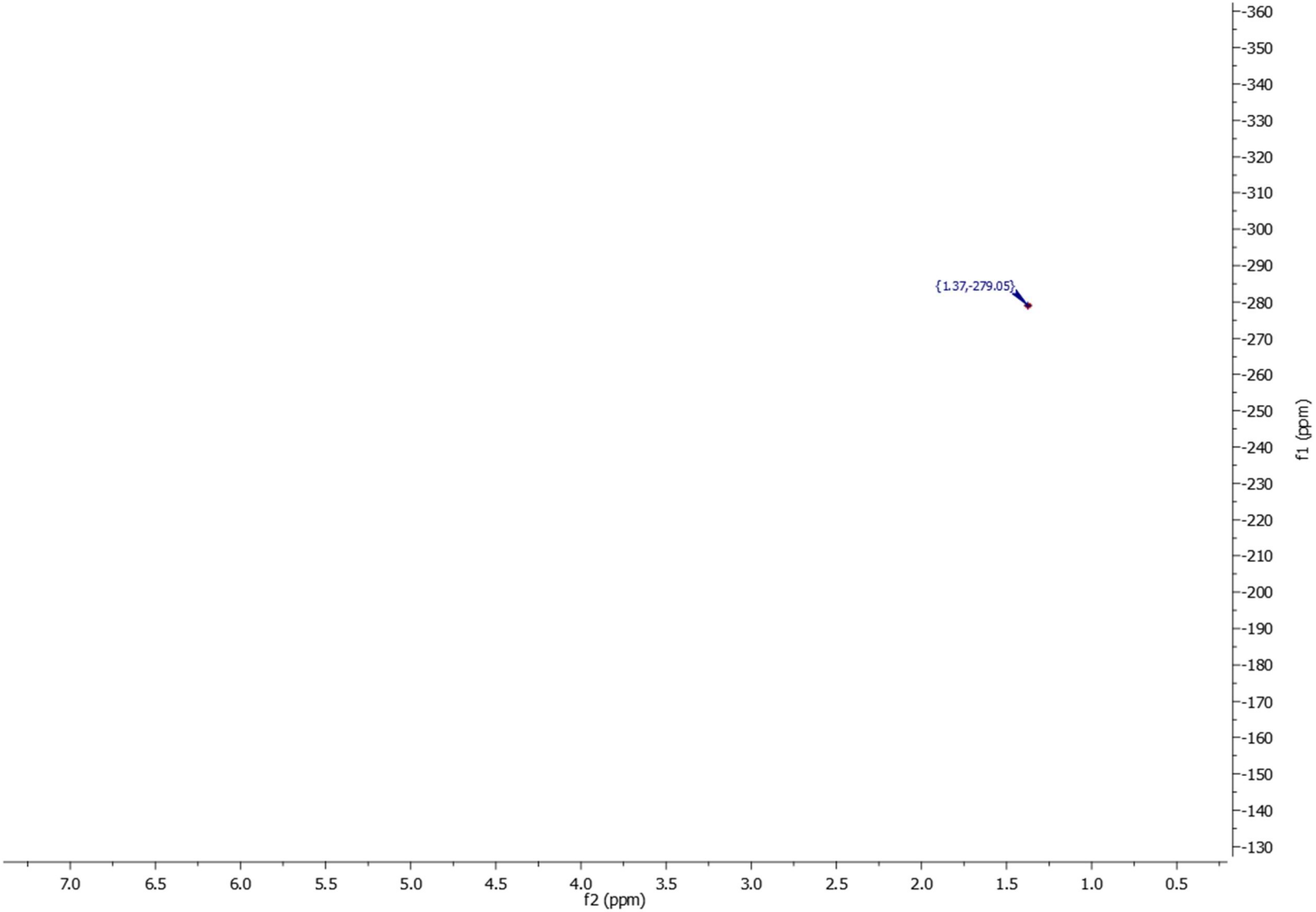


Fig. S28 2D $^{1}H,^{15}N$-HMBC NMR spectrum of **11** in C_6D_6.

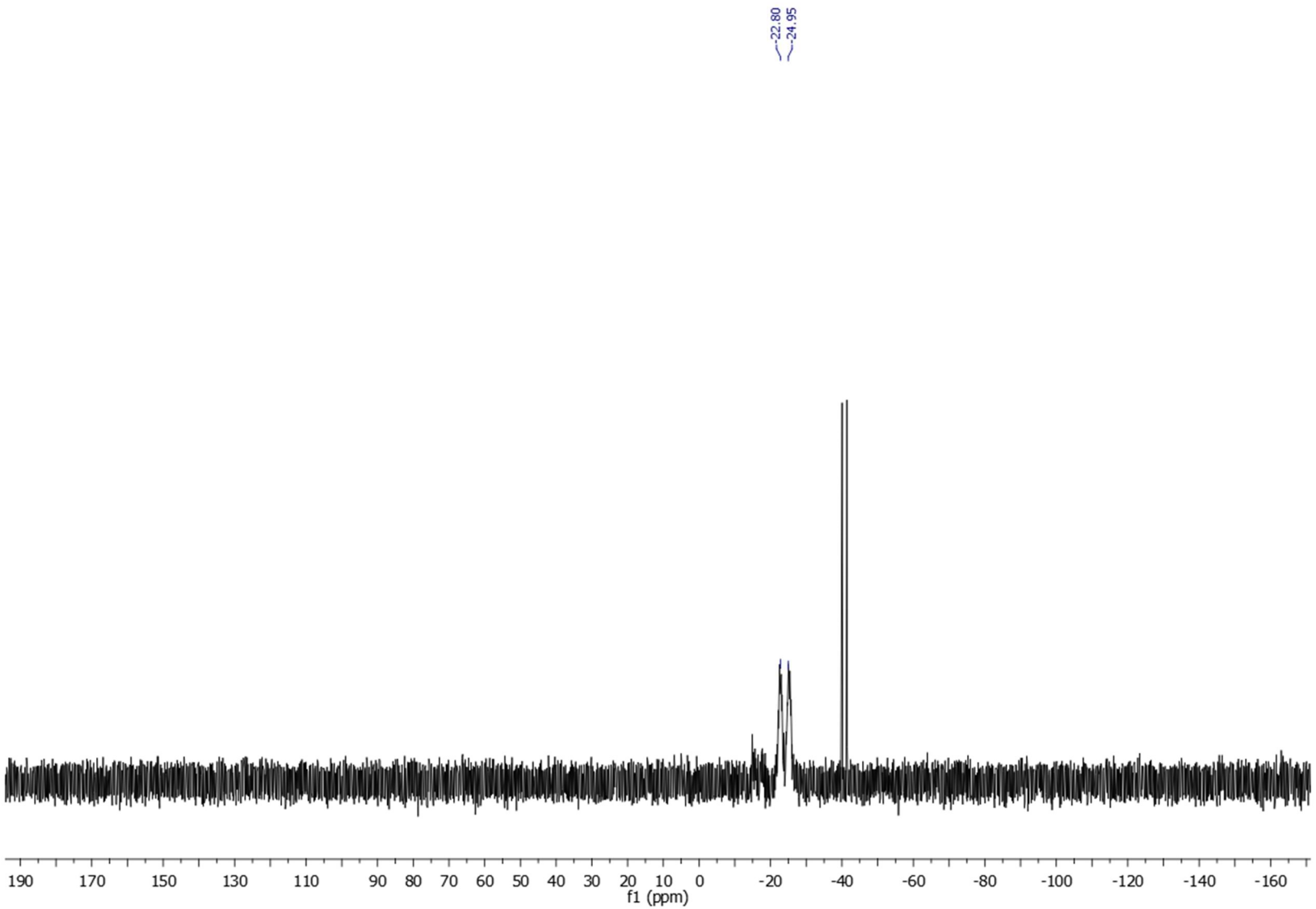


Fig. S29 ^{31}P NMR spectrum of **11** in C_6D_6

X-ray crystallographic data:

The crystal data were collected on a *XtaLAB Synergy Dualflex HyPix* diffractometer with a Hybrid Pixel array detector and multi-layer mirror monochromated $Cu_{K\alpha}$ radiation. The structures were solved using the intrinsic phasing method,[4] refined with the ShelXL program[5] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC- 2521121 (**5**), 2521122 (**6**) 2521123 (**7**), 2521124 (**8**), 2521125 (**9**), and 2521126 (**10**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for 5: $C_{62}H_{98}B_2N_4$, M_r = 921.06, colorless block, 0.630×0.250×0.180 mm^3, monoclinic space group $P2_1/n$, a = 9.18720(10) Å, b = 38.0186(3) Å, c = 16.41330(10) Å, β = 96.3730(10)°, V = 5697.48(8) Å^3, Z = 4, ρ_{calcd} = 1.074 g·cm^{-3}, μ = 0.450 mm^{-1}, $F(000)$ = 2032, T = 100(2) K, R_1 = 0.0493, wR_2 = 0.1268, 11282 independent reflections [$2\theta \leq 150.196°$] and 1272 parameters.

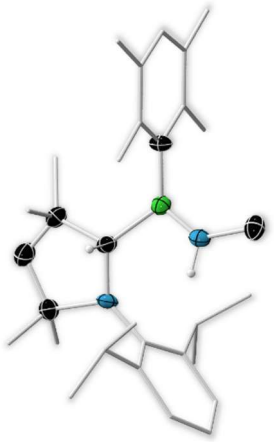


Fig. S30 Solid-state structure of **5**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of hydrogen atoms (except the nitrogen and previous carbene carbon atom bonded hydrogen atoms) and carbon atoms of Dip, CAAC methyl and Dur (except the *ipso* carbon atom) groups are omitted for clarity.

Crystal data for 6: $C_{37}H_{53}BN_2$, M_r = 536.62, light red block, 0.481×0.096×0.062 mm^3, triclinic space group $P\bar{1}$, a = 9.58380(10) Å, b = 19.0377(2) Å, c = 26.7818(4) Å, α = 88.8280(10)°, β = 84.8350(10)°, γ = 87.8740(10)°, V = 4862.52(10) Å^3, Z = 6, ρ_{calcd} = 1.100 g·cm^{-3}, μ = 0.463 mm^{-1}, $F(000)$ = 1764, T = 100(2) K, R_1 = 0.0494, wR_2 = 0.1261, 28864 independent reflections [$2\theta \leq 146.364°$] and 1293 parameters.

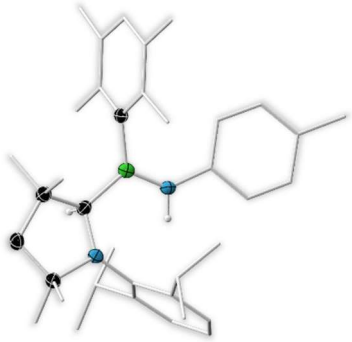


Fig. S31 Solid-state structure of **6**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of hydrogen atoms (except the nitrogen and previous carbene carbon atom bonded hydrogen atoms) and carbon atoms of Dip, CAAC methyl, Dur (except the *ipso* carbon atom) and *p*Tol groups are omitted for clarity.

Crystal data for 7: $C_{32}H_{51}BN_2$, M_r = 474.55, light red plate, 0.170×0.110×0.060 mm^3, monoclinic space group $P2_1/n$, a = 9.5748(2) Å, b = 25.2253(4) Å, c = 12.8086(2) Å, β = 106.499(2)°, V = 2966.24(10) Å^3, Z = 4, ρ_{calcd} = 1.063 g·cm^{-3}, μ = 0.445 mm^{-1}, $F(000)$ = 1048, T = 100(2) K, R_1 = 0.0472, wR_2 = 0.1100, 5842 independent reflections [$2\theta \leq 146.584°$] and 330 parameters.

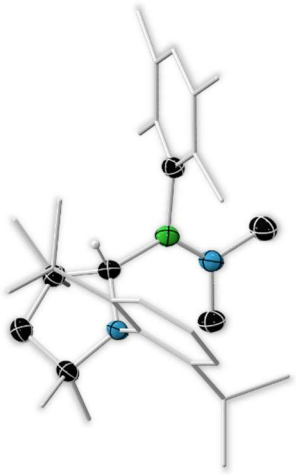


Fig. S32 Solid-state structure of **7**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of hydrogen atoms (except the CAAC-H hydrogen atom) and carbon atoms of Dip, CAAC methyl groups and Dur (except the *ipso* carbon atom) group are omitted for clarity.

Crystal data for 8: $C_{35}H_{55}BN_2$, M_r = 514.62, yellow block, 0.160×0.140×0.080 mm^3, monoclinic space group $P2_1/c$, a = 16.9366(3) Å, b = 9.8374(2) Å, c = 19.1534(3) Å, β = 100.259(2)°, V = 3140.17(10) Å^3, Z = 4, ρ_{calcd} = 1.089 g·cm^{-3}, μ = 0.455 mm^{-1}, $F(000)$ = 1136, T = 100(2) K, R_1 = 0.0460, wR_2 = 0.1094, 5972 independent reflections [$2\theta \leq 142.768°$] and 355 parameters.

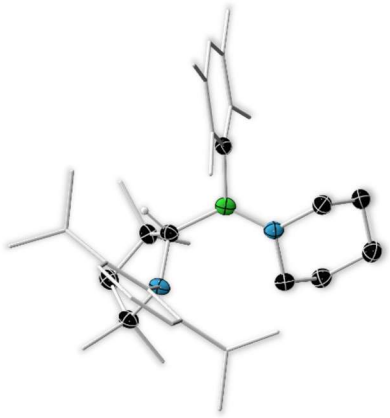


Fig. S33 Solid-state structure of **8**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of hydrogen atoms (except the CAAC-H hydrogen atom) and carbon atoms of Dip, CAAC methyl and Dur (except the *ipso* carbon atom) groups are omitted for clarity.

Crystal data for 9: $C_{65}H_{99}B_2ClN_3$, M_r = 979.54, orange block, 0.230×0.210×0.100 mm^3, orthorhombic space group $Pbca$, a = 17.7397(2) Å, b = 19.4055(2) Å, c = 34.7313(4) Å, V = 11956.2(2) Å^3, Z = 8,

ρ_{calcd} = 1.088 g·cm^{-3}, μ = 0.853 mm^{-1}, F(000) = 4296, T = 100(2) K, R_1 = 0.0545, wR_2 = 0.1373, 11358 independent reflections [2θ≤142.658°] and 667 parameters.

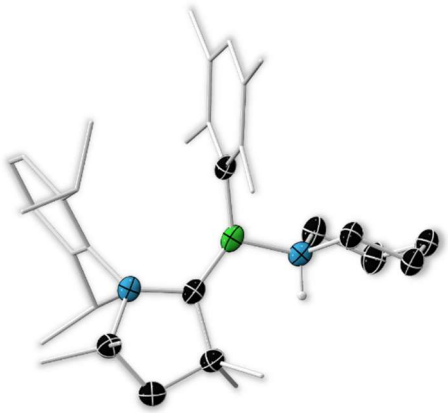


Fig. S34 Solid-state structure of **9**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of hydrogen atoms (except the nitrogen-bound hydrogen atom) and carbon atoms of Dip, CAAC methyl and Dur (except the *ipso* carbon atom) groups are omitted for clarity.

Crystal data for 10: $C_{36}H_{51}BNP$, M_r = 539.55, orange block, 0.349×0.146×0.091 mm^3, monoclinic space group $C2/c$, a = 30.8495(2) Å, b = 11.48758(7) Å, c = 18.28097(13) Å, β = 103.1624(8)°, V = 6308.31(8) Å^3, Z = 8, ρ_{calcd} = 1.136 g·cm^{-3}, μ = 0.934 mm^{-1}, F(000) = 2352, T = 100(2) K, R_1 = 0.0354, wR_2 = 0.0916, 6294 independent reflections [2θ≤150.378°] and 373 parameters.

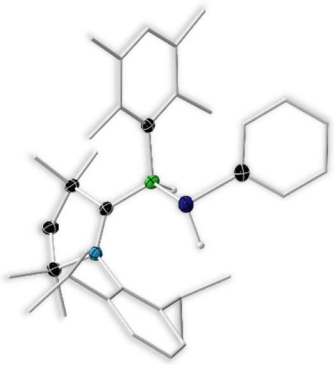


Fig. S35 Solid-state structure of **10**. Atomic displacement ellipsoids represented at 50%. Ellipsoids of hydrogen atoms (except the boron and phosphorus-bound hydrogen atoms) and carbon atoms of Dip, CAAC methyl, Dur (except the *ipso* carbon atom) and Ph (except the *ipso* carbon atom) groups are omitted for clarity.

Computational details

All molecules were fully optimized using the Gaussian 16, Rev. C.01[6] quantum chemistry program package at the ωB97X-D[7]/Def2-SVP[8] level of theory. The model compounds were fully optimized in the gaseous state (no solvent effects) starting from the X-ray crystallographic structural coordinates. Frequency calculations were performed at the same level of theory to verify the nature of the stationary states and the absence of any imaginary frequencies to confirm that all structures represent minima on the potential energy hypersurface. Transition state geometries were located using the algorithm opt = (ts, noeigentest, calcfc).[9] The optimized transition state structures were confirmed as first-order saddle points with only one imaginary frequency. Additionally, the transition state found was made sure to be on the desired reaction coordinate by performing the "plus-and-minus-displacement" minimization computations, which involve the displacement of the transition state structure by ~0.05 Å or 5° to 10° by the imaginary frequency normal mode in both directions,[10] and the displaced geometries were then optimized to the closest minimum structures. The zero-point vibrational energies (ZPVE) and thermal corrections were computed from frequency calculations with a standard state of 298 K and 1 atm. Single-point energies were computed with the ORCA 5.0.4 program[11] based on ωB97X-D/Def2-SVP optimized structures using the domain-based local pair natural orbital approximation of CCSD(T)[12] as well as the solvation model based on density (SMD) continuum[13] (solvent: toluene). The Def2-SVP basis set in combination with the resolution of identity approximation for Coulomb integrals (RI-J) and the numerical chain-of-spheres integration for the Hartree–Fock exchange integrals (COSX)[14] was chosen for these calculations. For this purpose, Def2/J and Def2-SVP/C were used as auxiliary basis sets. Natural bonding analyses were performed with the natural bond orbital (NBO 7.0)[15] partitioning scheme as implemented in the Gaussian 16 suite of programs. To analyse the bonding situation, the Mayer bond orders (MBOs)[16] and Wiberg bond indices (WBIs)[17] were obtained from NBO analysis and using the Multiwfn V.3.8 package.[18] Pictures of MOs orbitals were generated by means of the ChemCraft1.8 program.[19]

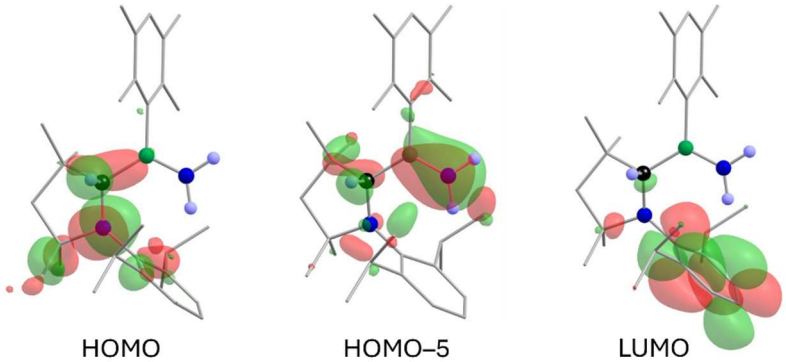


Fig. S36 Selected frontier molecular orbitals of **4** (isovalue 0.043 au).

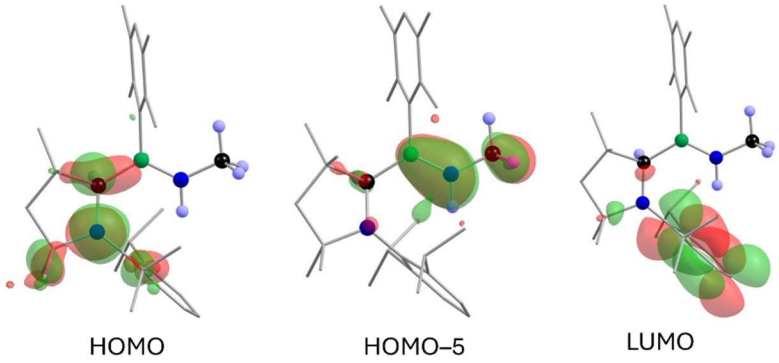


Fig. S37 Selected frontier molecular orbitals of **5** (isovalue 0.043 au).

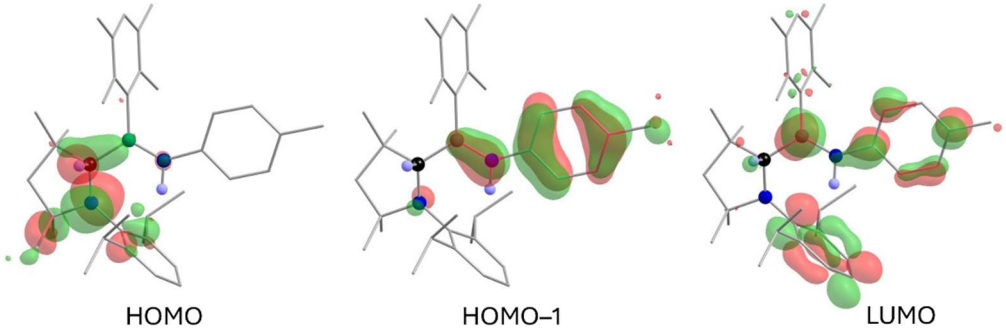


Fig. S38 Selected frontier molecular orbitals of **6** (isovalue 0.043 au).

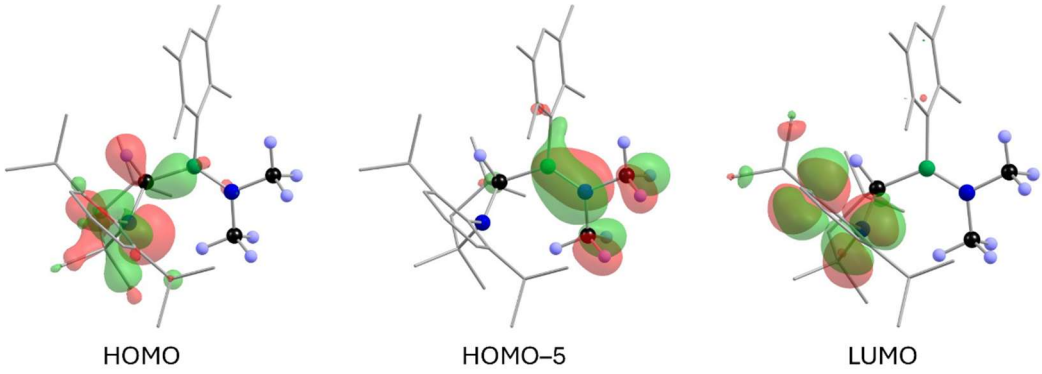


Fig. S39 Selected frontier molecular orbitals of **7** (isovalue 0.043 au).

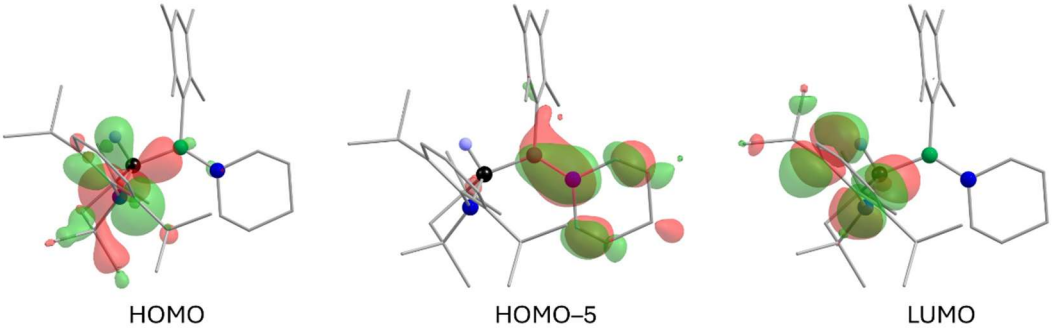


Fig. S40 Selected frontier molecular orbitals of **8** (isovalue 0.043 au).

Table S1. Calculated natural charges (q), and natural valence population (Pop).

Compounds	Natural charges					Natural valence population				
	q_B	q_C	q_N	q_P	q_H	Pop_B	Pop_C	Pop_N	Pop_P	Pop_H
3	0.87	–0.42	-	-	-	2.11	4.40	-	-	-
4^{Int}	0.53	–0.31	–0.96	-	0.42	2.45	4.29	5.95	-	0.57
4^{TS}	0.46	–0.19	–1.09	-	0.44	2.51	4.17	6.08	-	0.55
4	1.03	–0.39	–1.11	-	0.22	1.95	4.37	6.10	-	0.78
10^{TS1}	0.43	–0.25	-	0.45	0.01	2.54	4.22	-	4.51	0.99
10^{Int}	–0.05	0.24	-	0.25	0.05	3.03	3.73	-	4.72	0.94
10^{TS2}	–0.07	0.26	-	0.19	0.05	3.05	3.71	-	4.78	0.94
10	–0.07	0.26	-	0.24	0.04	3.05	3.71	-	4.72	0.95

N = nitrogen of ammonia, P = phosphorus of $PPhH_2$, H = migrating hydrogen

Table S2. Calculated Mayer bond orders and Wiberg bond indices for B–N bonding interactions in compounds **4**–**8**.

Compounds	B–N	
	MBO	WBI
4	1.59	1.52
5	1.54	1.50
6	1.47	1.42
7	1.46	1.48
8	1.48	1.50

Coordinates of optimized geometries

Compound **3**, ωB97X-D/Def2-SVP

Energy = –1248.048828 Eh

Imaginary frequency = 0

C	-2.200799000000	0.320391000000	-0.558141000000
B	-0.773444000000	0.843649000000	-0.518690000000
C	-3.273155000000	1.148635000000	-0.132124000000
C	-4.583147000000	0.647427000000	-0.139281000000
C	-4.790258000000	-0.680825000000	-0.516471000000
H	-5.811353000000	-1.075351000000	-0.501010000000
C	-3.753151000000	-1.530560000000	-0.902502000000
C	-2.445189000000	-1.023243000000	-0.946728000000
C	-3.021533000000	2.561802000000	0.320334000000
H	-3.602414000000	2.806733000000	1.221881000000
H	-3.310644000000	3.291198000000	-0.455092000000
H	-1.955989000000	2.714723000000	0.542939000000
C	-5.750217000000	1.508198000000	0.270901000000
H	-5.679226000000	1.808898000000	1.328918000000
H	-6.702330000000	0.975648000000	0.139898000000
H	-5.797666000000	2.435307000000	-0.321582000000
C	-4.041318000000	-2.963736000000	-1.266758000000
H	-3.452351000000	-3.660932000000	-0.650331000000
H	-3.784369000000	-3.173644000000	-2.317587000000
H	-5.104385000000	-3.204338000000	-1.127770000000
C	-1.313560000000	-1.929693000000	-1.342859000000
H	-0.396324000000	-1.358083000000	-1.528641000000
H	-1.551763000000	-2.513016000000	-2.244761000000
H	-1.080827000000	-2.648139000000	-0.538854000000
N	1.597346000000	0.652129000000	0.257730000000
C	0.563766000000	1.294683000000	-0.459628000000
C	1.163796000000	2.555365000000	-1.111893000000
C	2.583392000000	2.608768000000	-0.477989000000
H	3.329903000000	2.263808000000	-1.210423000000
H	2.864721000000	3.632049000000	-0.186834000000
C	2.579740000000	1.639008000000	0.724271000000
C	1.264452000000	2.393063000000	-2.636445000000
H	1.802128000000	3.244197000000	-3.087283000000

H	0.264023000000	2.340446000000	-3.093506000000
H	1.801527000000	1.470780000000	-2.898867000000
C	0.355183000000	3.821257000000	-0.803083000000
H	0.262519000000	3.990011000000	0.279269000000
H	-0.661980000000	3.750301000000	-1.219488000000
H	0.835605000000	4.707219000000	-1.248953000000
C	2.114007000000	2.372961000000	1.995575000000
H	2.759767000000	3.241003000000	2.200035000000
H	2.152108000000	1.712423000000	2.871967000000
H	1.080408000000	2.732189000000	1.884645000000
C	3.944215000000	1.009385000000	0.986482000000
H	4.652663000000	1.780110000000	1.324291000000
H	4.358017000000	0.537923000000	0.085321000000
H	3.876514000000	0.242753000000	1.773703000000
C	1.579670000000	-0.746822000000	0.500730000000
C	0.876332000000	-1.290946000000	1.599251000000
C	0.838484000000	-2.680549000000	1.761145000000
H	0.304241000000	-3.107073000000	2.613776000000
C	1.462102000000	-3.527460000000	0.854709000000
H	1.418978000000	-4.610082000000	0.994354000000
C	2.135638000000	-2.989566000000	-0.236322000000
H	2.611861000000	-3.660658000000	-0.955551000000
C	2.206791000000	-1.608723000000	-0.432738000000
C	0.170509000000	-0.412066000000	2.618583000000
H	0.198768000000	0.615439000000	2.232362000000
C	0.910339000000	-0.442483000000	3.961670000000
H	0.843129000000	-1.439738000000	4.425696000000
H	0.476808000000	0.285464000000	4.665328000000
H	1.978850000000	-0.209416000000	3.840981000000
C	-1.303588000000	-0.788912000000	2.804931000000
H	-1.416450000000	-1.787034000000	3.257494000000
H	-1.847288000000	-0.785320000000	1.849867000000
H	-1.796937000000	-0.068193000000	3.475552000000
C	2.920427000000	-1.074477000000	-1.664436000000
H	2.984816000000	0.014244000000	-1.545134000000
C	4.346021000000	-1.619730000000	-1.793963000000
H	4.921978000000	-1.467821000000	-0.868667000000

H	4.877267000000	-1.114268000000	-2.615394000000
H	4.352988000000	-2.698727000000	-2.015393000000
C	2.112187000000	-1.336365000000	-2.939926000000
H	2.643446000000	-0.943392000000	-3.821360000000
H	1.130095000000	-0.844866000000	-2.892709000000
H	1.948153000000	-2.414653000000	-3.097516000000

NH_3, ωB97X-D/Def2-SVP

Energy = –56.491886 Eh

Imaginary frequency = 0

N	0.000000000000	0.000000000000	0.119782000000
H	0.000000000000	0.938245000000	-0.279491000000
H	-0.812544000000	-0.469123000000	-0.279491000000
H	0.812544000000	-0.469123000000	-0.279491000000

Compound **4^{Int}**, ωB97X-D/Def2-SVP

Energy = –1304.599928 Eh

Imaginary frequency = 0

C	0.095616000000	0.046153000000	0.808883000000
C	0.968773000000	0.382344000000	3.029448000000
H	1.019057000000	-0.055019000000	4.038737000000
H	1.004466000000	1.477261000000	3.148188000000
C	-0.331378000000	0.010308000000	2.286542000000
C	-1.417578000000	1.028290000000	2.655934000000
H	-1.125792000000	2.042978000000	2.346009000000
H	-1.576312000000	1.034434000000	3.747685000000
H	-2.377259000000	0.789210000000	2.178062000000
C	-0.836894000000	-1.388723000000	2.682435000000
H	-0.149641000000	-2.183406000000	2.359230000000
H	-1.809008000000	-1.582693000000	2.206562000000
H	-0.970474000000	-1.470220000000	3.774664000000
C	2.148577000000	-0.049989000000	2.148611000000
C	3.328494000000	0.918617000000	2.290738000000
H	4.118304000000	0.698619000000	1.554913000000
H	3.771113000000	0.824580000000	3.293773000000
H	3.013148000000	1.961707000000	2.162922000000
C	2.667085000000	-1.447106000000	2.536911000000

H	3.500926000000	-1.744362000000	1.885701000000
H	1.885786000000	-2.214456000000	2.471538000000
H	3.042445000000	-1.437169000000	3.571803000000
N	1.529939000000	-0.001012000000	0.813340000000
H	-0.703906000000	-0.743538000000	-2.323814000000
N	-0.343177000000	0.072341000000	-1.822325000000
H	0.678121000000	0.075791000000	-1.906642000000
B	-0.838495000000	0.065847000000	-0.295091000000
C	-2.440831000000	0.039470000000	-0.317329000000
C	-5.235929000000	-0.022171000000	-0.544078000000
H	-6.327243000000	-0.045975000000	-0.629435000000
C	-4.590095000000	1.211875000000	-0.479775000000
C	-3.188492000000	1.240781000000	-0.369519000000
C	-2.384290000000	-2.505384000000	-0.366516000000
H	-2.465740000000	-3.042501000000	-1.328275000000
H	-2.783621000000	-3.186618000000	0.401830000000
H	-1.322526000000	-2.337414000000	-0.140698000000
C	-5.278424000000	-2.535241000000	-0.577746000000
H	-4.933988000000	-3.152425000000	-1.423293000000
H	-6.359080000000	-2.374416000000	-0.697536000000
H	-5.128501000000	-3.137883000000	0.332984000000
C	-5.391430000000	2.487558000000	-0.522947000000
H	-5.078203000000	3.137666000000	-1.355863000000
H	-5.263656000000	3.076366000000	0.400109000000
H	-6.464436000000	2.281639000000	-0.642495000000
C	-2.501970000000	2.582317000000	-0.288390000000
H	-1.426264000000	2.453221000000	-0.108488000000
H	-2.903590000000	3.189506000000	0.539019000000
H	-2.645545000000	3.175259000000	-1.208588000000
C	-3.132369000000	-1.193689000000	-0.393397000000
C	-4.535239000000	-1.226040000000	-0.503572000000
C	2.272604000000	0.016880000000	-0.387941000000
C	2.619824000000	1.258376000000	-0.986448000000
C	3.337509000000	1.263625000000	-2.187292000000
H	3.614914000000	2.217948000000	-2.642595000000
C	3.698277000000	0.078399000000	-2.817838000000
H	4.264426000000	0.101690000000	-3.751714000000

C	3.317054000000	-1.135604000000	-2.259819000000
H	3.577535000000	-2.065391000000	-2.772322000000
C	2.595222000000	-1.190946000000	-1.061560000000
C	2.122031000000	-2.546845000000	-0.561976000000
H	1.572550000000	-2.367495000000	0.369859000000
C	3.287911000000	-3.501053000000	-0.279962000000
H	2.925281000000	-4.419818000000	0.206220000000
H	4.042373000000	-3.045352000000	0.375863000000
H	3.795877000000	-3.798741000000	-1.211390000000
C	1.144009000000	-3.197623000000	-1.547322000000
H	1.619236000000	-3.404310000000	-2.519740000000
H	0.265020000000	-2.562577000000	-1.719800000000
H	0.772834000000	-4.153198000000	-1.146396000000
C	2.184472000000	2.589401000000	-0.393050000000
H	1.663612000000	2.363371000000	0.546874000000
C	3.375479000000	3.508633000000	-0.098726000000
H	4.141833000000	3.002832000000	0.504503000000
H	3.043835000000	4.403828000000	0.449777000000
H	3.856982000000	3.853042000000	-1.028004000000
C	1.180220000000	3.303935000000	-1.304691000000
H	1.621738000000	3.551103000000	-2.283827000000
H	0.841385000000	4.244081000000	-0.843131000000
H	0.285951000000	2.688267000000	-1.469514000000
H	-0.708241000000	0.892754000000	-2.312555000000

Compound **4**^{TS}, ωB97X-D/Def2-SVP

Energy = – 1304.549772 Eh

Imaginary frequency = 1

C	-0.077373000000	-0.120591000000	0.773527000000
C	-0.918323000000	-0.447203000000	3.010309000000
H	-0.901223000000	-0.005207000000	4.017961000000
H	-1.062878000000	-1.532184000000	3.133806000000
C	0.393467000000	-0.202366000000	2.237593000000
C	1.354776000000	-1.367817000000	2.504900000000
H	0.929216000000	-2.317336000000	2.146280000000
H	1.538148000000	-1.460988000000	3.588143000000
H	2.323317000000	-1.217480000000	2.009957000000

C	1.081290000000	1.099826000000	2.681582000000
H	0.488024000000	1.991253000000	2.433994000000
H	2.058199000000	1.201661000000	2.189589000000
H	1.250350000000	1.093166000000	3.770762000000
C	-2.064134000000	0.101461000000	2.156070000000
C	-3.338471000000	-0.722869000000	2.354078000000
H	-4.126453000000	-0.422607000000	1.646628000000
H	-3.723305000000	-0.561000000000	3.372017000000
H	-3.150915000000	-1.797256000000	2.236788000000
C	-2.408856000000	1.558425000000	2.507196000000
H	-3.220205000000	1.921955000000	1.860696000000
H	-1.549385000000	2.230211000000	2.391037000000
H	-2.755794000000	1.627209000000	3.549356000000
N	-1.488477000000	-0.023189000000	0.799113000000
H	0.885886000000	-0.796945000000	-2.461764000000
N	0.230537000000	-0.466957000000	-1.763850000000
H	-0.586750000000	0.001082000000	-2.145260000000
B	0.861639000000	-0.118088000000	-0.364338000000
C	2.456639000000	-0.139604000000	-0.369603000000
C	5.250292000000	-0.104213000000	-0.547375000000
H	6.342758000000	-0.091012000000	-0.616190000000
C	4.585319000000	-1.327918000000	-0.608350000000
C	3.181311000000	-1.347202000000	-0.519534000000
C	2.440107000000	2.402214000000	-0.206352000000
H	2.557586000000	3.004250000000	-1.123078000000
H	2.832599000000	3.010080000000	0.624433000000
H	1.368296000000	2.252115000000	-0.033178000000
C	5.331552000000	2.400288000000	-0.356135000000
H	5.014677000000	3.089305000000	-1.155482000000
H	6.412008000000	2.231985000000	-0.465884000000
H	5.169523000000	2.928343000000	0.597678000000
C	5.374095000000	-2.602895000000	-0.765715000000
H	5.053554000000	-3.174718000000	-1.651289000000
H	5.247017000000	-3.269303000000	0.103212000000
H	6.448022000000	-2.395077000000	-0.871301000000
C	2.494192000000	-2.691657000000	-0.581627000000
H	1.427513000000	-2.622358000000	-0.334153000000

H	2.941100000000	-3.401809000000	0.131521000000
H	2.588071000000	-3.150471000000	-1.580807000000
C	3.163832000000	1.083407000000	-0.323364000000
C	4.568315000000	1.101968000000	-0.407260000000
C	-2.294122000000	0.125241000000	-0.364909000000
C	-2.933256000000	-1.017776000000	-0.911844000000
C	-3.769617000000	-0.865580000000	-2.020324000000
H	-4.269765000000	-1.741944000000	-2.440092000000
C	-3.957164000000	0.376114000000	-2.615388000000
H	-4.616482000000	0.479039000000	-3.480100000000
C	-3.274551000000	1.479476000000	-2.120948000000
H	-3.392278000000	2.446191000000	-2.616793000000
C	-2.432156000000	1.379560000000	-1.006954000000
C	-1.638856000000	2.611601000000	-0.595436000000
H	-1.038306000000	2.337843000000	0.281797000000
C	-2.535904000000	3.797217000000	-0.222841000000
H	-1.927469000000	4.631923000000	0.158209000000
H	-3.270592000000	3.533649000000	0.549732000000
H	-3.092233000000	4.168912000000	-1.097966000000
C	-0.666891000000	3.024105000000	-1.709647000000
H	-1.209276000000	3.337894000000	-2.615777000000
H	0.008392000000	2.201686000000	-1.984157000000
H	-0.045104000000	3.871877000000	-1.384029000000
C	-2.664162000000	-2.425112000000	-0.395114000000
H	-2.036022000000	-2.323322000000	0.501184000000
C	-3.946798000000	-3.173973000000	-0.015796000000
H	-4.576074000000	-2.594378000000	0.673001000000
H	-3.702826000000	-4.132861000000	0.467322000000
H	-4.552906000000	-3.403066000000	-0.906612000000
C	-1.868253000000	-3.245306000000	-1.421224000000
H	-2.461340000000	-3.424167000000	-2.332650000000
H	-1.596837000000	-4.226402000000	-1.001477000000
H	-0.946047000000	-2.731041000000	-1.723904000000
H	0.105801000000	-1.210179000000	-0.675400000000

Compound **4**, ωB97X-D/Def2-SVP

Energy = –1304.666425 Eh

Imaginary frequency = 0

C	-0.014268000000	-0.466085000000	0.730134000000
C	-0.701012000000	-0.459995000000	3.002704000000
H	-0.692685000000	0.052528000000	3.976978000000
H	-0.681965000000	-1.542265000000	3.209141000000
C	0.525840000000	-0.108161000000	2.143933000000
C	1.722148000000	-0.956212000000	2.582028000000
H	1.516541000000	-2.031718000000	2.458348000000
H	1.936576000000	-0.778268000000	3.648158000000
H	2.628981000000	-0.712273000000	2.011924000000
C	0.892073000000	1.375132000000	2.275380000000
H	0.147063000000	2.025015000000	1.795746000000
H	1.867517000000	1.575627000000	1.812562000000
H	0.962916000000	1.664980000000	3.335546000000
C	-1.959125000000	-0.123060000000	2.180564000000
C	-3.020972000000	-1.219043000000	2.362925000000
H	-3.887102000000	-1.050107000000	1.704644000000
H	-3.383076000000	-1.216041000000	3.402446000000
H	-2.618215000000	-2.219821000000	2.159329000000
C	-2.598017000000	1.196859000000	2.633529000000
H	-3.463832000000	1.438941000000	2.001285000000
H	-1.890586000000	2.035071000000	2.591535000000
H	-2.958788000000	1.107433000000	3.669455000000
N	-1.413522000000	-0.028375000000	0.803509000000
H	0.846827000000	0.253816000000	-2.646009000000
N	0.276265000000	0.096975000000	-1.825398000000
H	-0.719597000000	0.095836000000	-2.004768000000
B	0.859117000000	-0.083246000000	-0.565436000000
C	2.452403000000	-0.041092000000	-0.532637000000
C	5.235741000000	0.055381000000	-0.466950000000
H	6.329073000000	0.092881000000	-0.430217000000
C	4.604337000000	-1.188256000000	-0.480658000000
C	3.200129000000	-1.235720000000	-0.526349000000
C	2.346123000000	2.499950000000	-0.620202000000
H	2.500552000000	2.999051000000	-1.591812000000
H	2.668163000000	3.211890000000	0.155667000000
H	1.266451000000	2.351109000000	-0.500757000000

C	5.251497000000	2.570326000000	-0.522255000000
H	4.988532000000	3.171981000000	-1.407029000000
H	6.340378000000	2.422945000000	-0.527878000000
H	5.000553000000	3.180220000000	0.360890000000
C	5.422394000000	-2.453119000000	-0.444571000000
H	5.273202000000	-3.059207000000	-1.353093000000
H	5.145255000000	-3.090768000000	0.410121000000
H	6.495547000000	-2.231140000000	-0.364129000000
C	2.523080000000	-2.585051000000	-0.551099000000
H	1.445126000000	-2.510878000000	-0.739110000000
H	2.656772000000	-3.118364000000	0.404835000000
H	2.943995000000	-3.231274000000	-1.337005000000
C	3.116614000000	1.202216000000	-0.547008000000
C	4.521902000000	1.252001000000	-0.511052000000
C	-2.297224000000	0.011464000000	-0.312862000000
C	-2.760916000000	-1.176134000000	-0.939678000000
C	-3.654906000000	-1.084309000000	-2.011256000000
H	-4.006320000000	-1.998672000000	-2.495346000000
C	-4.104830000000	0.144587000000	-2.475761000000
H	-4.812854000000	0.194948000000	-3.305991000000
C	-3.625575000000	1.308262000000	-1.889896000000
H	-3.949160000000	2.276355000000	-2.280594000000
C	-2.714054000000	1.268261000000	-0.829790000000
C	-2.123232000000	2.585813000000	-0.349678000000
H	-1.453815000000	2.340014000000	0.483484000000
C	-3.180356000000	3.580068000000	0.141695000000
H	-2.696621000000	4.471856000000	0.569797000000
H	-3.833330000000	3.147866000000	0.911577000000
H	-3.822992000000	3.922646000000	-0.685091000000
C	-1.274857000000	3.234577000000	-1.452355000000
H	-1.899793000000	3.551750000000	-2.302842000000
H	-0.514878000000	2.539055000000	-1.831799000000
H	-0.759855000000	4.128390000000	-1.066457000000
C	-2.266005000000	-2.562145000000	-0.547391000000
H	-1.683007000000	-2.457504000000	0.373933000000
C	-3.406406000000	-3.544032000000	-0.260215000000
H	-4.110563000000	-3.141977000000	0.481844000000

H	-3.003982000000	-4.492179000000	0.129069000000
H	-3.978263000000	-3.782744000000	-1.170380000000
C	-1.324110000000	-3.124665000000	-1.620308000000
H	-1.863815000000	-3.310259000000	-2.562994000000
H	-0.885068000000	-4.079730000000	-1.291713000000
H	-0.506158000000	-2.423796000000	-1.838403000000
H	0.051014000000	-1.584103000000	0.689980000000

Compound **5**, ωB97X-D/Def2-SVP

Energy = –1343.934300 Eh

Imaginary frequency = 0

N	-0.228546000000	0.143738000000	-1.741524000000
H	0.783316000000	0.139410000000	-1.797063000000
N	1.440634000000	-0.049615000000	0.886059000000
B	-0.837507000000	-0.055338000000	-0.496937000000
C	-0.866861000000	0.385150000000	-3.015736000000
H	-0.537571000000	-0.347157000000	-3.770822000000
H	-0.631910000000	1.392501000000	-3.401163000000
H	-1.956863000000	0.304571000000	-2.914050000000
C	-2.430670000000	-0.038392000000	-0.440169000000
C	-3.158143000000	-1.244433000000	-0.399952000000
C	-4.559013000000	-1.220148000000	-0.286227000000
C	-5.209449000000	0.012956000000	-0.243105000000
H	-6.300017000000	0.032844000000	-0.151652000000
C	-4.518682000000	1.220747000000	-0.331856000000
C	-3.116514000000	1.193202000000	-0.436503000000
C	-2.459676000000	-2.581370000000	-0.463614000000
H	-2.513202000000	-3.110885000000	0.502374000000
H	-1.400281000000	-2.486129000000	-0.730260000000
H	-2.923133000000	-3.240869000000	-1.213500000000
C	-5.353537000000	-2.498039000000	-0.207883000000
H	-5.247113000000	-3.099331000000	-1.125609000000
H	-6.423744000000	-2.293357000000	-0.065824000000
H	-5.018131000000	-3.133224000000	0.627492000000
C	-5.269767000000	2.526902000000	-0.321828000000
H	-6.354674000000	2.362356000000	-0.264195000000
H	-5.066638000000	3.118115000000	-1.229176000000

H	-4.979723000000	3.154771000000	0.536338000000
C	-2.372776000000	2.499856000000	-0.583503000000
H	-1.285991000000	2.369515000000	-0.513379000000
H	-2.667537000000	3.232914000000	0.183310000000
H	-2.584328000000	2.962792000000	-1.562371000000
C	-0.505115000000	-0.035292000000	2.214565000000
C	0.699829000000	-0.428685000000	3.086452000000
H	0.625470000000	-1.503365000000	3.317988000000
H	0.712687000000	0.106037000000	4.048698000000
C	1.977038000000	-0.172536000000	2.264130000000
C	-1.739988000000	-0.817161000000	2.669610000000
H	-1.594297000000	-1.902414000000	2.546202000000
H	-2.641463000000	-0.527376000000	2.113460000000
H	-1.927681000000	-0.626274000000	3.738648000000
C	-0.801454000000	1.465477000000	2.317250000000
H	-0.877656000000	1.774871000000	3.371546000000
H	-1.757457000000	1.705323000000	1.833543000000
H	-0.017563000000	2.071302000000	1.842359000000
C	2.694690000000	1.105974000000	2.717189000000
H	3.063892000000	0.986518000000	3.747063000000
H	2.032529000000	1.981366000000	2.694941000000
H	3.563887000000	1.307978000000	2.075102000000
C	2.966916000000	-1.333649000000	2.447667000000
H	3.315507000000	-1.365066000000	3.491397000000
H	3.849893000000	-1.211504000000	1.801510000000
H	2.504312000000	-2.304707000000	2.226483000000
C	2.336365000000	-0.021839000000	-0.221201000000
C	2.769150000000	-1.212105000000	-0.865017000000
C	3.677730000000	-1.129712000000	-1.925132000000
H	4.005239000000	-2.046284000000	-2.421693000000
C	4.170017000000	0.091912000000	-2.364448000000
H	4.887368000000	0.134150000000	-3.187062000000
C	3.720315000000	1.259939000000	-1.763950000000
H	4.076462000000	2.224095000000	-2.135443000000
C	2.798651000000	1.230051000000	-0.712724000000
C	2.220694000000	-2.587754000000	-0.510262000000
H	1.616702000000	-2.480633000000	0.397100000000

C	1.290514000000	-3.098750000000	-1.618765000000
H	1.848938000000	-3.286331000000	-2.549959000000
H	0.503229000000	-2.365671000000	-1.843715000000
H	0.809608000000	-4.043304000000	-1.319991000000
C	3.320858000000	-3.611769000000	-0.213706000000
H	2.877820000000	-4.554699000000	0.142720000000
H	4.015971000000	-3.249188000000	0.556496000000
H	3.910408000000	-3.848598000000	-1.113048000000
C	2.243155000000	2.556247000000	-0.215257000000
H	1.582761000000	2.319481000000	0.626223000000
C	1.386276000000	3.225705000000	-1.298136000000
H	1.996844000000	3.521912000000	-2.166408000000
H	0.904792000000	4.133793000000	-0.902573000000
H	0.597444000000	2.550337000000	-1.654253000000
C	3.327019000000	3.525217000000	0.266889000000
H	3.981166000000	3.072214000000	1.024169000000
H	2.867393000000	4.422535000000	0.709666000000
H	3.964961000000	3.862744000000	-0.565558000000
C	0.026756000000	-0.441583000000	0.808695000000
H	-0.074689000000	-1.556938000000	0.796047000000

Compound **6**, ωB97X-D/Def2-SVP

Energy = –1574.758456 Eh

Imaginary frequency = 0

C	2.960721000000	-2.163666000000	-0.272700000000
N	2.013619000000	-1.029370000000	-0.133345000000
C	0.669847000000	-1.477792000000	0.261845000000
H	0.631454000000	-1.689361000000	1.362008000000
C	0.585452000000	-2.887979000000	-0.393186000000
C	2.024488000000	-3.381412000000	-0.165149000000
H	2.090839000000	-3.802352000000	0.850975000000
H	2.306935000000	-4.184175000000	-0.863450000000
C	3.698762000000	-2.132030000000	-1.617591000000
H	4.374305000000	-2.997108000000	-1.697546000000
H	4.313052000000	-1.223907000000	-1.697765000000
H	3.007367000000	-2.162429000000	-2.469668000000
C	4.031760000000	-2.220654000000	0.827617000000

H	4.690754000000	-3.086522000000	0.661075000000
H	3.587774000000	-2.332703000000	1.825652000000
H	4.658384000000	-1.315446000000	0.822927000000
C	-0.393296000000	-3.843546000000	0.294426000000
H	-0.240765000000	-4.866737000000	-0.085255000000
H	-1.440079000000	-3.569126000000	0.108314000000
H	-0.231862000000	-3.865895000000	1.384220000000
C	0.249476000000	-2.823329000000	-1.887968000000
H	0.494400000000	-3.777236000000	-2.380910000000
H	0.805690000000	-2.025936000000	-2.399474000000
H	-0.822870000000	-2.640870000000	-2.037687000000
N	-0.350865000000	0.916858000000	0.202232000000
H	0.626063000000	1.186554000000	0.211397000000
B	-0.584907000000	-0.471005000000	0.131345000000
C	2.519573000000	0.291369000000	0.043982000000
C	2.797046000000	0.819385000000	1.334303000000
C	3.315168000000	2.113057000000	1.450861000000
H	3.519759000000	2.519816000000	2.443962000000
C	3.570956000000	2.894843000000	0.332140000000
H	3.986928000000	3.898505000000	0.444335000000
C	3.264850000000	2.398058000000	-0.927584000000
H	3.424549000000	3.029165000000	-1.805316000000
C	2.723129000000	1.119525000000	-1.094474000000
C	-1.165338000000	2.064894000000	0.214823000000
C	-0.529112000000	3.306021000000	0.064397000000
H	0.558423000000	3.335910000000	-0.055874000000
C	-1.258928000000	4.489095000000	0.060764000000
H	-0.730624000000	5.438440000000	-0.063463000000
C	-2.649725000000	4.485150000000	0.208648000000
C	-3.273494000000	3.243597000000	0.365817000000
H	-4.359386000000	3.200934000000	0.488944000000
C	-2.556314000000	2.049803000000	0.375488000000
H	-3.084775000000	1.108422000000	0.510885000000
C	-3.439238000000	5.768222000000	0.234509000000
H	-4.457016000000	5.622001000000	-0.155599000000
H	-2.954317000000	6.551130000000	-0.366648000000
H	-3.534158000000	6.154983000000	1.262600000000

C	-2.066420000000	-1.035833000000	0.066771000000
C	-2.697461000000	-1.525484000000	1.225821000000
C	-3.994669000000	-2.060620000000	1.145107000000
C	-4.642726000000	-2.068781000000	-0.090296000000
H	-5.653116000000	-2.484803000000	-0.153731000000
C	-4.055889000000	-1.547271000000	-1.243427000000
C	-2.754393000000	-1.023447000000	-1.162043000000
C	-2.007167000000	-1.483036000000	2.567429000000
H	-1.732682000000	-2.493718000000	2.912893000000
H	-2.659558000000	-1.047684000000	3.339788000000
H	-1.090813000000	-0.879848000000	2.546381000000
C	-4.680918000000	-2.616890000000	2.365547000000
H	-5.661023000000	-3.043777000000	2.111661000000
H	-4.842434000000	-1.839155000000	3.129735000000
H	-4.081030000000	-3.408915000000	2.841488000000
C	-4.816517000000	-1.535883000000	-2.543880000000
H	-4.918883000000	-0.513953000000	-2.942494000000
H	-5.826189000000	-1.950909000000	-2.418592000000
H	-4.303962000000	-2.129087000000	-3.318509000000
C	-2.138674000000	-0.385331000000	-2.383541000000
H	-2.255681000000	-1.007500000000	-3.283742000000
H	-1.066290000000	-0.192871000000	-2.254847000000
H	-2.617002000000	0.586242000000	-2.593904000000
C	2.471152000000	0.070379000000	2.619614000000
H	2.177057000000	-0.948419000000	2.344795000000
C	1.275348000000	0.714140000000	3.334927000000
H	0.981590000000	0.117602000000	4.212692000000
H	0.405899000000	0.798474000000	2.668449000000
H	1.521782000000	1.728813000000	3.686044000000
C	3.671411000000	-0.035240000000	3.566039000000
H	3.422937000000	-0.676179000000	4.426113000000
H	3.961324000000	0.948708000000	3.966337000000
H	4.549475000000	-0.464266000000	3.063253000000
C	2.259431000000	0.720931000000	-2.487490000000
H	1.896482000000	-0.310308000000	-2.409906000000
C	1.080490000000	1.595310000000	-2.936892000000
H	0.680132000000	1.235514000000	-3.897618000000

H	1.389177000000	2.643840000000	-3.076236000000
H	0.263063000000	1.585322000000	-2.204301000000
C	3.375456000000	0.773217000000	-3.535446000000
H	3.012148000000	0.382966000000	-4.498790000000
H	4.251941000000	0.180985000000	-3.239968000000
H	3.714662000000	1.806841000000	-3.709828000000

Compound **7**, ωB97X-D/Def2-SVP

Energy = –1383.192703 Eh

Imaginary frequency = 0

N	-0.657141000000	-1.929051000000	-1.687121000000
C	0.428385000000	-2.880440000000	-1.753912000000
H	1.154599000000	-2.674889000000	-0.966011000000
H	0.945796000000	-2.817266000000	-2.725289000000
H	0.056058000000	-3.914801000000	-1.642199000000
B	-0.901041000000	-1.058862000000	-0.611312000000
C	-1.543835000000	-2.035138000000	-2.830051000000
H	-2.351212000000	-1.296776000000	-2.765174000000
H	-1.993876000000	-3.042705000000	-2.889755000000
H	-0.986506000000	-1.865538000000	-3.768215000000
C	-2.237279000000	-0.175000000000	-0.610014000000
C	-2.150358000000	1.184893000000	-0.973034000000
C	-3.249319000000	2.041206000000	-0.788135000000
C	-4.430632000000	1.516179000000	-0.265391000000
H	-5.283292000000	2.183904000000	-0.106347000000
C	-4.570218000000	0.160600000000	0.029278000000
C	-3.469856000000	-0.694966000000	-0.164116000000
C	-0.900405000000	1.733695000000	-1.612673000000
H	-0.472608000000	2.577445000000	-1.050136000000
H	-1.115600000000	2.103678000000	-2.628630000000
H	-0.111552000000	0.977307000000	-1.706127000000
C	-3.153074000000	3.501349000000	-1.143568000000
H	-4.088820000000	4.031360000000	-0.917710000000
H	-2.933778000000	3.643980000000	-2.214077000000
H	-2.340089000000	3.995975000000	-0.587588000000
C	-5.884392000000	-0.372762000000	0.538467000000
H	-5.764702000000	-0.902676000000	1.496997000000

H	-6.330856000000	-1.092717000000	-0.167132000000
H	-6.610706000000	0.437633000000	0.690828000000
C	-3.655759000000	-2.174358000000	0.075461000000
H	-3.827886000000	-2.412193000000	1.138593000000
H	-2.785986000000	-2.750920000000	-0.262415000000
H	-4.530998000000	-2.553863000000	-0.475168000000
N	1.507243000000	-0.621241000000	0.495942000000
C	0.052661000000	-0.824452000000	0.692285000000
H	-0.358767000000	0.114996000000	1.087744000000
C	-0.088554000000	-1.836645000000	1.881679000000
C	1.286082000000	-1.729779000000	2.578220000000
H	1.249787000000	-0.938009000000	3.343070000000
H	1.555538000000	-2.660250000000	3.102286000000
C	2.323855000000	-1.343841000000	1.507618000000
C	-1.213248000000	-1.380757000000	2.821144000000
H	-1.023963000000	-0.367740000000	3.208187000000
H	-1.307847000000	-2.061584000000	3.682158000000
H	-2.180892000000	-1.355720000000	2.299096000000
C	-0.371148000000	-3.290943000000	1.477097000000
H	-0.409755000000	-3.926192000000	2.376097000000
H	0.396181000000	-3.707754000000	0.816176000000
H	-1.337849000000	-3.386635000000	0.966211000000
C	3.007726000000	-2.588362000000	0.907845000000
H	3.705573000000	-2.297909000000	0.109527000000
H	2.292101000000	-3.304414000000	0.487932000000
H	3.583793000000	-3.118917000000	1.681755000000
C	3.443253000000	-0.485774000000	2.104573000000
H	3.059102000000	0.406989000000	2.608665000000
H	4.151312000000	-0.158294000000	1.328725000000
H	4.000670000000	-1.077379000000	2.845944000000
C	1.910556000000	0.673035000000	0.032026000000
C	1.631264000000	1.870999000000	0.749316000000
C	2.002634000000	3.098751000000	0.193934000000
H	1.777369000000	4.018790000000	0.738713000000
C	2.654039000000	3.184153000000	-1.029220000000
H	2.934425000000	4.156767000000	-1.439533000000
C	2.948899000000	2.017114000000	-1.716451000000

H	3.467053000000	2.075278000000	-2.677171000000
C	2.585463000000	0.765986000000	-1.208465000000
C	0.941828000000	1.923665000000	2.111019000000
H	0.844825000000	0.897146000000	2.481421000000
C	-0.468737000000	2.523252000000	2.020169000000
H	-0.955270000000	2.514143000000	3.008192000000
H	-1.115831000000	1.972388000000	1.322829000000
H	-0.427060000000	3.570468000000	1.679933000000
C	1.765387000000	2.695891000000	3.151556000000
H	1.793187000000	3.773845000000	2.930508000000
H	2.806097000000	2.344137000000	3.200595000000
H	1.317694000000	2.579942000000	4.150842000000
C	2.918945000000	-0.462404000000	-2.034339000000
H	2.526148000000	-1.318724000000	-1.479154000000
C	4.431571000000	-0.652522000000	-2.180879000000
H	4.891320000000	0.164516000000	-2.759976000000
H	4.657132000000	-1.597074000000	-2.700932000000
H	4.926303000000	-0.678694000000	-1.197703000000
C	2.219499000000	-0.433529000000	-3.396650000000
H	1.128276000000	-0.356163000000	-3.274720000000
H	2.437082000000	-1.351961000000	-3.965202000000
H	2.551349000000	0.418855000000	-4.010586000000

Compound **8**, ωB97X-D/Def2-SVP

Energy = –1499.827347 Eh

Imaginary frequency = 0

C	2.118709000000	-0.422685000000	-0.344864000000
B	0.984419000000	0.659241000000	-0.007551000000
C	3.352899000000	-0.444994000000	0.335620000000
C	4.239552000000	-1.523637000000	0.160093000000
C	3.890490000000	-2.547812000000	-0.718782000000
H	4.574507000000	-3.392655000000	-0.847406000000
C	2.711272000000	-2.513168000000	-1.462261000000
C	1.828093000000	-1.434820000000	-1.283301000000
C	3.776858000000	0.695641000000	1.229103000000
H	4.748119000000	1.105251000000	0.907309000000
H	3.901412000000	0.387125000000	2.280359000000

H	3.054360000000	1.519860000000	1.201213000000
C	5.550704000000	-1.573978000000	0.900865000000
H	6.094138000000	-2.504587000000	0.686144000000
H	5.404629000000	-1.513106000000	1.991324000000
H	6.206233000000	-0.732389000000	0.622671000000
C	2.388860000000	-3.615780000000	-2.435862000000
H	1.426153000000	-4.094536000000	-2.193826000000
H	3.164798000000	-4.393896000000	-2.431366000000
H	2.299633000000	-3.233808000000	-3.465755000000
C	0.591133000000	-1.358598000000	-2.141553000000
H	-0.074667000000	-2.223868000000	-1.999992000000
H	0.859730000000	-1.333079000000	-3.210304000000
H	-0.002804000000	-0.459927000000	-1.935876000000
N	1.018021000000	1.903968000000	-0.657015000000
C	0.146248000000	3.031050000000	-0.370561000000
H	-0.595700000000	2.722468000000	0.368388000000
H	-0.406710000000	3.302945000000	-1.287377000000
C	0.938943000000	4.252935000000	0.090984000000
H	1.440540000000	4.020446000000	1.044824000000
H	0.246609000000	5.087745000000	0.284492000000
C	1.981757000000	4.642141000000	-0.955954000000
H	1.465094000000	4.998518000000	-1.865174000000
H	2.602150000000	5.478858000000	-0.598873000000
C	2.850826000000	3.436950000000	-1.313210000000
H	3.481762000000	3.164568000000	-0.450914000000
H	3.532308000000	3.678314000000	-2.144007000000
C	1.990994000000	2.232448000000	-1.695227000000
H	1.441365000000	2.463933000000	-2.628720000000
H	2.617429000000	1.354822000000	-1.894931000000
N	-1.571929000000	0.324190000000	0.728027000000
C	-0.139171000000	0.130656000000	1.054787000000
H	0.056005000000	-0.950607000000	1.032587000000
C	0.018518000000	0.513257000000	2.567689000000
C	-1.432142000000	0.425095000000	3.090547000000
H	-1.633127000000	-0.596915000000	3.448585000000
H	-1.602564000000	1.096703000000	3.946669000000
C	-2.372812000000	0.735401000000	1.911433000000

C	0.595828000000	1.908982000000	2.839432000000
H	0.633524000000	2.091900000000	3.924875000000
H	-0.002192000000	2.712281000000	2.395519000000
H	1.619651000000	2.003888000000	2.455385000000
C	0.915481000000	-0.513388000000	3.272680000000
H	1.010756000000	-0.282485000000	4.345737000000
H	1.924693000000	-0.524179000000	2.836653000000
H	0.507397000000	-1.531398000000	3.179326000000
C	-2.743659000000	2.230730000000	1.861021000000
H	-3.305977000000	2.516597000000	2.763482000000
H	-3.377428000000	2.442179000000	0.988488000000
H	-1.865327000000	2.883824000000	1.804504000000
C	-3.691936000000	-0.031652000000	2.042093000000
H	-4.225760000000	0.310828000000	2.941059000000
H	-3.536127000000	-1.111665000000	2.134821000000
H	-4.343078000000	0.142473000000	1.172579000000
C	-2.132669000000	-0.564487000000	-0.246030000000
C	-2.148199000000	-1.978981000000	-0.083369000000
C	-2.663906000000	-2.776736000000	-1.108907000000
H	-2.663825000000	-3.862804000000	-0.989054000000
C	-3.183567000000	-2.229213000000	-2.274136000000
H	-3.583804000000	-2.875674000000	-3.058248000000
C	-3.193236000000	-0.851129000000	-2.422428000000
H	-3.607247000000	-0.411541000000	-3.333527000000
C	-2.672822000000	-0.012412000000	-1.432049000000
C	-1.635635000000	-2.712717000000	1.153505000000
H	-1.408515000000	-1.964347000000	1.920479000000
C	-0.346327000000	-3.494080000000	0.862752000000
H	0.030208000000	-3.972948000000	1.780329000000
H	0.453323000000	-2.852348000000	0.466005000000
H	-0.530831000000	-4.290413000000	0.123894000000
C	-2.689178000000	-3.654207000000	1.753678000000
H	-2.338692000000	-4.046613000000	2.720977000000
H	-2.881861000000	-4.519978000000	1.101826000000
H	-3.650935000000	-3.147350000000	1.919381000000
C	-2.696161000000	1.484010000000	-1.679961000000
H	-2.190969000000	1.941296000000	-0.823613000000

C	-4.128742000000	2.024094000000	-1.727958000000
H	-4.129772000000	3.122559000000	-1.811710000000
H	-4.688336000000	1.751422000000	-0.820053000000
H	-4.684817000000	1.622677000000	-2.590558000000
C	-1.913536000000	1.862787000000	-2.940848000000
H	-1.898666000000	2.956322000000	-3.075602000000
H	-2.360165000000	1.427821000000	-3.848947000000
H	-0.872175000000	1.511984000000	-2.877528000000

$PPhH_2$, ωB97X-D/Def2-SVP

Energy = –573.837385 Eh

Imaginary frequency = 0

P	-2.334404000000	-0.104005000000	-0.048102000000
C	0.217453000000	1.204383000000	-0.006677000000
H	-0.325582000000	2.152930000000	-0.006555000000
C	1.610677000000	1.212013000000	0.006724000000
H	2.147512000000	2.163357000000	0.012531000000
C	2.317974000000	0.009625000000	0.016071000000
H	3.410142000000	0.016372000000	0.028535000000
C	1.625542000000	-1.199355000000	0.003728000000
H	2.172387000000	-2.144898000000	0.005002000000
C	0.231007000000	-1.205262000000	-0.021652000000
H	-0.303633000000	-2.158896000000	-0.049669000000
C	-0.490905000000	-0.004999000000	-0.018098000000
H	-2.587486000000	1.230796000000	-0.475101000000
H	-2.567775000000	0.201982000000	1.326210000000

Compound **10^{TS1}**, ωB97X-D/Def2-SVP

Energy = –1821.896515 Eh

Imaginary frequency = 1

B	0.321579000000	-0.645321000000	-0.023882000000
C	1.857665000000	-0.924905000000	-0.178750000000
C	2.588309000000	-0.416120000000	-1.279834000000
C	3.976805000000	-0.623783000000	-1.365018000000
C	4.614218000000	-1.350364000000	-0.362097000000
H	5.695899000000	-1.506069000000	-0.429004000000
C	3.924917000000	-1.874845000000	0.729915000000

C	2.540619000000	-1.658010000000	0.824531000000
C	1.921852000000	0.370945000000	-2.377558000000
H	0.840236000000	0.435856000000	-2.212388000000
H	2.088593000000	-0.094400000000	-3.362850000000
H	2.329578000000	1.392580000000	-2.436835000000
C	4.774282000000	-0.048254000000	-2.504846000000
H	4.687006000000	1.050473000000	-2.531436000000
H	4.421751000000	-0.419120000000	-3.480634000000
H	5.840362000000	-0.299542000000	-2.413925000000
C	4.667892000000	-2.634529000000	1.798076000000
H	4.542310000000	-2.167453000000	2.788710000000
H	5.744450000000	-2.677706000000	1.581086000000
H	4.303357000000	-3.670398000000	1.891012000000
C	1.808115000000	-2.213329000000	2.019490000000
H	0.722759000000	-2.103468000000	1.901983000000
H	2.108004000000	-1.702355000000	2.951379000000
H	2.026822000000	-3.282830000000	2.164945000000
P	0.373077000000	1.545972000000	1.605194000000
H	0.132892000000	0.054435000000	1.207788000000
C	3.143253000000	1.373038000000	1.741444000000
H	2.958383000000	0.694745000000	2.578169000000
C	4.452061000000	1.650884000000	1.360320000000
H	5.282055000000	1.180483000000	1.891158000000
C	4.701282000000	2.524640000000	0.303054000000
H	5.728704000000	2.744291000000	0.004769000000
C	3.635175000000	3.121126000000	-0.369007000000
H	3.823992000000	3.814770000000	-1.191574000000
C	2.324423000000	2.823276000000	-0.004156000000
H	1.496643000000	3.280151000000	-0.550996000000
C	2.062323000000	1.934860000000	1.047509000000
N	-2.264046000000	-0.679779000000	-0.469248000000
C	-0.936580000000	-1.116450000000	-0.556928000000
C	-0.943887000000	-2.426005000000	-1.380234000000
C	-2.428458000000	-2.836478000000	-1.315358000000
H	-2.741029000000	-3.415268000000	-2.197720000000
H	-2.577299000000	-3.479259000000	-0.433373000000
C	-3.253871000000	-1.558028000000	-1.135306000000

C	-0.471314000000	-2.167097000000	-2.820768000000
H	0.612904000000	-1.988908000000	-2.834320000000
H	-0.955110000000	-1.287483000000	-3.267608000000
H	-0.679843000000	-3.039689000000	-3.461422000000
C	-0.088499000000	-3.552433000000	-0.787530000000
H	-0.347966000000	-3.730481000000	0.266681000000
H	0.984225000000	-3.321690000000	-0.839653000000
H	-0.261583000000	-4.486067000000	-1.347924000000
C	-3.753553000000	-1.009247000000	-2.482989000000
H	-4.428315000000	-1.741151000000	-2.952045000000
H	-2.936204000000	-0.810656000000	-3.186815000000
H	-4.321930000000	-0.080726000000	-2.338427000000
C	-4.492207000000	-1.812878000000	-0.272134000000
H	-4.239574000000	-2.333761000000	0.659010000000
H	-5.203871000000	-2.443592000000	-0.825239000000
H	-5.003293000000	-0.870692000000	-0.020886000000
C	-2.614043000000	0.507871000000	0.228567000000
C	-2.673765000000	1.746965000000	-0.454926000000
C	-3.020670000000	2.897799000000	0.259613000000
H	-3.074223000000	3.856947000000	-0.261646000000
C	-3.272268000000	2.850834000000	1.625055000000
H	-3.532470000000	3.761866000000	2.168298000000
C	-3.175214000000	1.640138000000	2.297786000000
H	-3.355558000000	1.610972000000	3.375096000000
C	-2.849533000000	0.457041000000	1.625548000000
C	-2.306220000000	1.893326000000	-1.924256000000
H	-2.097279000000	0.888254000000	-2.307039000000
C	-1.021098000000	2.708630000000	-2.105648000000
H	-1.130614000000	3.733434000000	-1.714568000000
H	-0.760199000000	2.782670000000	-3.172907000000
H	-0.177469000000	2.229390000000	-1.592644000000
C	-3.442726000000	2.507889000000	-2.748767000000
H	-4.397909000000	1.988356000000	-2.587056000000
H	-3.207547000000	2.463325000000	-3.823459000000
H	-3.597346000000	3.567460000000	-2.489919000000
C	-2.785709000000	-0.836923000000	2.428500000000
H	-2.545441000000	-1.643469000000	1.722458000000

C	-4.136067000000	-1.143033000000	3.092818000000
H	-4.131916000000	-2.156305000000	3.524041000000
H	-4.972722000000	-1.075241000000	2.384529000000
H	-4.340413000000	-0.438215000000	3.914373000000
C	-1.685778000000	-0.829815000000	3.496127000000
H	-1.828377000000	-0.012755000000	4.221049000000
H	-0.687078000000	-0.717724000000	3.058249000000
H	-1.700445000000	-1.778485000000	4.055005000000
H	-0.344021000000	2.179563000000	0.567309000000

Compound **10**$^{\mathbf{Int}}$, ωB97X-D/Def2-SVP

Energy = –1821.960057 Eh

Imaginary frequency = 0

B	0.351863000000	-0.607992000000	0.446914000000
C	1.858555000000	-0.903401000000	-0.077388000000
C	2.345513000000	-0.210437000000	-1.212114000000
C	3.691262000000	-0.310255000000	-1.601474000000
C	4.543653000000	-1.137667000000	-0.874926000000
H	5.591105000000	-1.223649000000	-1.180795000000
C	4.103422000000	-1.840087000000	0.242523000000
C	2.764137000000	-1.705383000000	0.658782000000
C	1.460009000000	0.701003000000	-2.024591000000
H	0.423811000000	0.693401000000	-1.670414000000
H	1.453034000000	0.421692000000	-3.090729000000
H	1.817558000000	1.741145000000	-1.971644000000
C	4.223984000000	0.487941000000	-2.762221000000
H	4.116970000000	1.569288000000	-2.575333000000
H	3.685649000000	0.269838000000	-3.698911000000
H	5.290038000000	0.281163000000	-2.931270000000
C	5.075349000000	-2.700607000000	1.009245000000
H	5.253904000000	-2.304938000000	2.023145000000
H	6.046857000000	-2.752754000000	0.497961000000
H	4.704159000000	-3.730246000000	1.134404000000
C	2.369223000000	-2.428381000000	1.926315000000
H	1.382463000000	-2.123890000000	2.289412000000
H	3.094562000000	-2.239503000000	2.733234000000
H	2.346033000000	-3.522281000000	1.778893000000

P	0.343088000000	1.121099000000	1.523605000000
H	-0.013437000000	-1.466476000000	1.267997000000
C	3.125838000000	1.229988000000	1.866377000000
H	2.970894000000	0.384513000000	2.540712000000
C	4.419861000000	1.684692000000	1.630790000000
H	5.264156000000	1.185199000000	2.111801000000
C	4.639414000000	2.772117000000	0.785437000000
H	5.654527000000	3.129339000000	0.597902000000
C	3.548753000000	3.407835000000	0.195077000000
H	3.703691000000	4.274435000000	-0.452865000000
C	2.255582000000	2.935503000000	0.419373000000
H	1.413829000000	3.439901000000	-0.062342000000
C	2.020640000000	1.820741000000	1.235655000000
N	-2.102355000000	-0.665053000000	-0.526464000000
C	-0.850629000000	-1.093760000000	-0.477246000000
C	-0.752039000000	-2.402394000000	-1.280887000000
C	-2.227526000000	-2.809805000000	-1.439694000000
H	-2.416643000000	-3.348026000000	-2.379058000000
H	-2.504558000000	-3.483262000000	-0.613663000000
C	-3.047932000000	-1.526878000000	-1.334796000000
C	-0.066014000000	-2.150459000000	-2.636908000000
H	1.005001000000	-1.960541000000	-2.494428000000
H	-0.491561000000	-1.296190000000	-3.179955000000
H	-0.178407000000	-3.045840000000	-3.266753000000
C	0.008279000000	-3.518681000000	-0.554863000000
H	-0.384953000000	-3.678988000000	0.459359000000
H	1.078735000000	-3.297494000000	-0.478623000000
H	-0.113548000000	-4.453474000000	-1.124551000000
C	-3.338577000000	-0.919699000000	-2.710569000000
H	-3.920005000000	-1.645430000000	-3.297016000000
H	-2.426403000000	-0.687792000000	-3.273142000000
H	-3.939576000000	-0.008125000000	-2.624418000000
C	-4.378330000000	-1.752989000000	-0.625654000000
H	-4.249127000000	-2.294317000000	0.317564000000
H	-5.021273000000	-2.364594000000	-1.275035000000
H	-4.900712000000	-0.806367000000	-0.424374000000
C	-2.600688000000	0.466242000000	0.227811000000

C	-2.724179000000	1.734746000000	-0.378416000000
C	-3.231555000000	2.784368000000	0.392309000000
H	-3.328604000000	3.775320000000	-0.056104000000
C	-3.585627000000	2.603921000000	1.721524000000
H	-3.964540000000	3.443351000000	2.307830000000
C	-3.440844000000	1.354392000000	2.304998000000
H	-3.703773000000	1.220906000000	3.356161000000
C	-2.956657000000	0.261041000000	1.581606000000
C	-2.291106000000	2.054556000000	-1.803359000000
H	-1.899640000000	1.133710000000	-2.253731000000
C	-1.157546000000	3.086858000000	-1.843258000000
H	-1.484754000000	4.058683000000	-1.442581000000
H	-0.827666000000	3.246099000000	-2.881393000000
H	-0.290814000000	2.755017000000	-1.260874000000
C	-3.467183000000	2.557062000000	-2.653149000000
H	-4.357356000000	1.918165000000	-2.565322000000
H	-3.182601000000	2.608037000000	-3.715286000000
H	-3.767370000000	3.570335000000	-2.344267000000
C	-2.858470000000	-1.076840000000	2.309802000000
H	-2.496547000000	-1.831059000000	1.595689000000
C	-4.230692000000	-1.527585000000	2.836512000000
H	-4.176147000000	-2.564236000000	3.203073000000
H	-5.019387000000	-1.471841000000	2.074126000000
H	-4.550230000000	-0.900183000000	3.682730000000
C	-1.861380000000	-1.040525000000	3.475494000000
H	-2.210068000000	-0.362238000000	4.270125000000
H	-0.871405000000	-0.692308000000	3.157715000000
H	-1.764035000000	-2.045448000000	3.914713000000
H	-0.349973000000	2.037749000000	0.698225000000

Compound **10**^{TS2}, ωB97X-D/Def2-SVP

Energy = –1821.935228 Eh

Imaginary frequency = 1

B	-0.376356000000	-0.681425000000	-0.598968000000
C	-1.874803000000	-1.123001000000	-0.168047000000
C	-2.382710000000	-0.819863000000	1.114102000000
C	-3.707297000000	-1.152399000000	1.454200000000

C	-4.504128000000	-1.788929000000	0.507754000000
H	-5.531953000000	-2.054355000000	0.774699000000
C	-4.047106000000	-2.074352000000	-0.780312000000
C	-2.731322000000	-1.718620000000	-1.127961000000
C	-1.574383000000	-0.053630000000	2.131173000000
H	-0.523985000000	0.046877000000	1.839443000000
H	-1.611850000000	-0.519749000000	3.128087000000
H	-1.971300000000	0.970031000000	2.236266000000
C	-4.276733000000	-0.797336000000	2.803144000000
H	-4.239272000000	0.290031000000	2.977724000000
H	-3.715169000000	-1.271123000000	3.624834000000
H	-5.325263000000	-1.115234000000	2.887872000000
C	-4.988868000000	-2.735640000000	-1.758458000000
H	-5.226523000000	-2.075189000000	-2.607823000000
H	-5.938050000000	-2.996378000000	-1.269566000000
H	-4.564756000000	-3.661758000000	-2.176826000000
C	-2.251559000000	-1.930657000000	-2.545334000000
H	-1.492393000000	-2.727016000000	-2.605244000000
H	-1.785303000000	-1.012337000000	-2.932493000000
H	-3.067870000000	-2.203187000000	-3.224604000000
P	-0.476641000000	1.243575000000	-0.964079000000
H	-0.002340000000	-1.287564000000	-1.608700000000
C	-3.243700000000	1.838515000000	-0.681689000000
H	-3.463458000000	0.779632000000	-0.812362000000
C	-4.296675000000	2.724239000000	-0.462967000000
H	-5.314819000000	2.330357000000	-0.408420000000
C	-4.069764000000	4.094215000000	-0.338362000000
H	-4.901310000000	4.783678000000	-0.177265000000
C	-2.761063000000	4.569641000000	-0.428311000000
H	-2.558719000000	5.639858000000	-0.335414000000
C	-1.700674000000	3.688194000000	-0.613864000000
H	-0.679040000000	4.077563000000	-0.645681000000
C	-1.914700000000	2.300314000000	-0.747800000000
N	2.055772000000	-0.801137000000	0.407270000000
C	0.843178000000	-1.292582000000	0.248541000000
C	0.827051000000	-2.747595000000	0.735091000000
C	2.326076000000	-3.078611000000	0.855776000000

H	2.537372000000	-3.783867000000	1.671628000000
H	2.669742000000	-3.546052000000	-0.080128000000
C	3.050943000000	-1.746865000000	1.044889000000
C	0.099983000000	-2.864995000000	2.088533000000
H	-0.978928000000	-2.714337000000	1.961422000000
H	0.458667000000	-2.139538000000	2.830500000000
H	0.263201000000	-3.875399000000	2.492724000000
C	0.155822000000	-3.703794000000	-0.258674000000
H	0.600228000000	-3.617034000000	-1.260627000000
H	-0.921115000000	-3.511246000000	-0.339228000000
H	0.297601000000	-4.737393000000	0.093970000000
C	3.267885000000	-1.404876000000	2.520903000000
H	3.899305000000	-2.181902000000	2.974988000000
H	2.329369000000	-1.357816000000	3.086295000000
H	3.789364000000	-0.447351000000	2.629706000000
C	4.404159000000	-1.727680000000	0.343462000000
H	4.324753000000	-2.052501000000	-0.699611000000
H	5.074195000000	-2.429442000000	0.860985000000
H	4.866870000000	-0.730703000000	0.371382000000
C	2.499295000000	0.491471000000	-0.076608000000
C	2.522658000000	1.611510000000	0.780302000000
C	3.026741000000	2.812191000000	0.273735000000
H	3.045511000000	3.693782000000	0.917617000000
C	3.469955000000	2.918891000000	-1.036943000000
H	3.850695000000	3.870935000000	-1.412348000000
C	3.407093000000	1.813987000000	-1.873834000000
H	3.730477000000	1.909911000000	-2.912300000000
C	2.925796000000	0.582145000000	-1.421597000000
C	1.955133000000	1.626431000000	2.192932000000
H	1.599282000000	0.613900000000	2.425521000000
C	0.744902000000	2.565969000000	2.289523000000
H	1.050344000000	3.617386000000	2.170556000000
H	0.265296000000	2.467285000000	3.275545000000
H	0.006572000000	2.335331000000	1.509543000000
C	3.005961000000	2.025232000000	3.237597000000
H	3.935689000000	1.444545000000	3.153718000000
H	2.606142000000	1.887753000000	4.253881000000

H	3.277976000000	3.087118000000	3.135008000000
C	2.847319000000	-0.557680000000	-2.432460000000
H	2.503696000000	-1.461761000000	-1.908597000000
C	4.212177000000	-0.860140000000	-3.069106000000
H	4.154212000000	-1.778021000000	-3.673885000000
H	5.009685000000	-0.987728000000	-2.324381000000
H	4.522306000000	-0.047157000000	-3.743345000000
C	1.826321000000	-0.256522000000	-3.539915000000
H	2.161886000000	0.590102000000	-4.159707000000
H	0.838390000000	-0.004497000000	-3.132907000000
H	1.717952000000	-1.130464000000	-4.200613000000
H	0.509852000000	2.020411000000	-1.583192000000

Compound **10**, ωB97X-D/Def2-SVP

Energy = –1821.967790 Eh

Imaginary frequency = 0

B	-0.474515000000	-0.060643000000	-0.377974000000
C	-1.880529000000	-0.873762000000	-0.291217000000
C	-2.066956000000	-1.870229000000	0.695693000000
C	-3.324277000000	-2.475111000000	0.880924000000
C	-4.389264000000	-2.066209000000	0.084280000000
H	-5.370455000000	-2.527584000000	0.234970000000
C	-4.251313000000	-1.074226000000	-0.886659000000
C	-2.992057000000	-0.475550000000	-1.078371000000
C	-0.952388000000	-2.304345000000	1.618976000000
H	0.010738000000	-1.854745000000	1.356048000000
H	-0.824744000000	-3.398758000000	1.615767000000
H	-1.164682000000	-2.010641000000	2.659610000000
C	-3.533538000000	-3.534670000000	1.932604000000
H	-3.273302000000	-3.167277000000	2.938321000000
H	-2.905508000000	-4.422202000000	1.749508000000
H	-4.580733000000	-3.867167000000	1.957816000000
C	-5.473725000000	-0.645782000000	-1.662588000000
H	-5.707448000000	0.416640000000	-1.486091000000
H	-6.352212000000	-1.233929000000	-1.361526000000
H	-5.345191000000	-0.775215000000	-2.748841000000
C	-2.861194000000	0.645132000000	-2.084817000000

H	-2.041304000000	0.467303000000	-2.794214000000
H	-2.640236000000	1.596090000000	-1.576018000000
H	-3.776620000000	0.791070000000	-2.669181000000
P	-0.465460000000	1.114125000000	1.264597000000
H	-0.423385000000	0.647745000000	-1.383105000000
C	-3.252652000000	1.488927000000	1.355692000000
H	-3.278205000000	0.483858000000	1.784295000000
C	-4.449644000000	2.167110000000	1.136130000000
H	-5.395409000000	1.686849000000	1.398848000000
C	-4.443011000000	3.449778000000	0.588189000000
H	-5.381691000000	3.982658000000	0.419325000000
C	-3.225830000000	4.049679000000	0.267520000000
H	-3.205449000000	5.057904000000	-0.153709000000
C	-2.030396000000	3.361282000000	0.470981000000
H	-1.084934000000	3.837947000000	0.198761000000
C	-2.021235000000	2.063403000000	1.004823000000
N	2.087395000000	-0.645361000000	-0.548300000000
C	0.817896000000	-0.901773000000	-0.805072000000
C	0.745263000000	-2.028623000000	-1.847028000000
C	2.192128000000	-2.099040000000	-2.369900000000
H	2.485756000000	-3.116913000000	-2.662039000000
H	2.285819000000	-1.460734000000	-3.262463000000
C	3.079292000000	-1.539469000000	-1.260188000000
C	0.292111000000	-3.356412000000	-1.212150000000
H	-0.764060000000	-3.303791000000	-0.921301000000
H	0.876388000000	-3.628268000000	-0.323598000000
H	0.406844000000	-4.161013000000	-1.954132000000
C	-0.207685000000	-1.698599000000	-3.001957000000
H	0.022693000000	-0.718277000000	-3.443856000000
H	-1.253155000000	-1.694265000000	-2.671468000000
H	-0.093626000000	-2.465075000000	-3.784531000000
C	3.601565000000	-2.640682000000	-0.332622000000
H	4.199632000000	-3.346701000000	-0.926383000000
H	2.793842000000	-3.204188000000	0.149655000000
H	4.251869000000	-2.228684000000	0.446179000000
C	4.273691000000	-0.767170000000	-1.807984000000
H	3.971770000000	-0.028873000000	-2.558613000000

H	4.954847000000	-1.479098000000	-2.296224000000
H	4.830927000000	-0.255135000000	-1.010220000000
C	2.548211000000	0.474910000000	0.245615000000
C	2.848384000000	0.314901000000	1.613951000000
C	3.316400000000	1.430580000000	2.316684000000
H	3.542258000000	1.330766000000	3.380133000000
C	3.484027000000	2.659807000000	1.698916000000
H	3.847271000000	3.516501000000	2.270087000000
C	3.170501000000	2.799843000000	0.353560000000
H	3.280929000000	3.776402000000	-0.122305000000
C	2.691983000000	1.726062000000	-0.399324000000
C	2.679998000000	-0.985335000000	2.388044000000
H	2.276380000000	-1.738112000000	1.698310000000
C	1.679399000000	-0.846160000000	3.542732000000
H	2.072478000000	-0.183962000000	4.330160000000
H	1.494343000000	-1.830860000000	3.999409000000
H	0.725569000000	-0.425630000000	3.196883000000
C	4.025169000000	-1.490188000000	2.931078000000
H	4.818066000000	-1.497142000000	2.169403000000
H	3.921210000000	-2.510723000000	3.330411000000
H	4.377126000000	-0.849370000000	3.754307000000
C	2.311028000000	1.998306000000	-1.851314000000
H	2.012489000000	1.047152000000	-2.316013000000
C	3.485186000000	2.577994000000	-2.654239000000
H	3.233645000000	2.612492000000	-3.725290000000
H	4.408584000000	1.994527000000	-2.535160000000
H	3.708042000000	3.609273000000	-2.340301000000
C	1.108059000000	2.946801000000	-1.950304000000
H	1.353944000000	3.938292000000	-1.537864000000
H	0.238491000000	2.554576000000	-1.409767000000
H	0.822226000000	3.085328000000	-3.004374000000
H	0.413313000000	2.172759000000	0.915447000000

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