Supporting Information for

Dibenzoberylloles: antiaromatic s-block fluorene analogues

Tobias Tröster,[a,b] Franziska Endres,[a,b] Merle Arrowsmith,[a,b] Lukas Endres,[a,b] Felipe Fantuzzi,[c] Holger Braunschweig*,[a,b]

[a] Institute for Inorganic Chemistry, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg (Germany)

[b] Institute for Sustainable Chemistry & Catalysis with Boron, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg (Germany)

[c] School of Chemistry and Forensic Science, University of Kent, Park Wood Rd, Canterbury, CT2 7NH (United Kingdom)

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. NMR spectra were acquired either on a Bruker Avance 500 (operating at 500 MHz for ^1H, 125 MHz for ^{13}C and 160 MHz for ^{31}P) or a Bruker Avance 400 NMR (operating at 400 MHz for ^1H, 56 MHz for ^9Be and 100 MHz for ^{13}C) spectrometer. Chemical shifts (δ) are reported in ppm and internally referenced to the carbon nuclei ($^{13}C\{^1H\}$) or residual protons (^1H) of the solvent. Microanalyses (C, H, N, S) were performed on an Elementar vario MICRO cube elemental analyzer. *Note: both elemental analyses and HRMS were carried out for all new compounds but in some cases these decomposed too rapidly and only one type of analysis was possible.*

1,2-Dibromobenzene was purchased from abcr and used as received. $[(Et_2O)BeBr_2]$,[1] CAAC^{Me} (1-(2,6-di*iso*propylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene),[2-3] PMe_3,[4] SIMes (1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene),[5] IDipp ((1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene),[6] $[(Me_3P)_2BeBr_2]$,[7] $[(IDipp)BeBr_2]$,[8] 2,2'-dibromobiphenyl,[9] and 2,2'-dilithiobiphenyl[10] were synthesized following literature procedures.

CAUTION: Beryllium and its compounds are extremely toxic. Suitable precautions (e.g., use of protective clothing, breathing apparatus, well-ventilated fume cupboard, special hazards labelling, special waste disposal measures) were taken for all manipulations involving these species.[11]

Synthetic procedures

Synthesis of 1

2,2'-Dilithiobiphenyl (62.8 mg, 378 *m*mol, 1.20 equiv.) and [$(Et_2O)_2BeBr_2$] (100 mg, 315 *m*mol, 1.00 equiv.) were dissolved in toluene (50 mL). After stirring for three days at room temperature the colourless suspension was filtered and all volatiles were removed from the filtrate *in vacuo*. The beige residue was then washed with diethyl ether (3 x 10 mL) to yield **1** as a colourless solid (43.0 mg, 183 *m*mol, 58%). ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ = 8.07 (d, 2H, ^{3}J = 7.0 Hz, CH_{α}), 7.10 (d, 2H, ^{3}J = 7.6 Hz, CH_{α}), 7.30 (t, 2H, ^{3}J = 7.6 Hz, CH_{β}), 7.16 (t, 2H, ^{3}J = 7.0 Hz, CH_{β}), 6.38 (q, 4H, ^{3}J = 7.0 Hz, $CH_{2\text{-Et2O}}$), 0.61 (t, 6H, ^{3}J = 7.0 Hz, $CH_{3\text{-Et2O}}$) ppm. $^{13}C\{^{1}H\}$ NMR (125.8 MHz, CD_2Cl_2): δ = 158.4 ($C_{\text{q-BiPh}}$) 156.4 ($C_{\text{q-BiPh}}$), 142.5 (CH_{α}), 128.5 (CH_{β}), 125.3 (CH_{β}), 121.4 (CH_{α}), 67.4 ($CH_{2\text{-Et2O}}$), 13.0 ($CH_{3\text{-Et2O}}$) ppm. ^{9}Be NMR (56.2 MHz, C_6D_6): δ = 10.8 (fwmh ≈ 120 Hz) ppm. Elemental analysis [%] calculated for $C_{16}H_{18}BeO$: C 81.66, H 7.71; found C 80.54, H 7.61.

Synthesis of 2

2,2'-Dilithiobiphenyl (2.00 g, 12.0 mmol, 1.20 equiv.) and [$(Me_3P)_2BeBr_2$] (3.22 g, 10.0 mmol, 1.00 equiv.) were dissolved in toluene (150 mL). After stirring for 16 h at room temperature the colourless suspension was filtered, the remaining colourless residue extracted with dichloromethane (3 x 60 mL). All volatiles were removed *in vacuo* from the combined filtrates, yielding **2** as a colourless solid (743 mg, 3.13 mmol, 31%). ^{1}H NMR (400.3 MHz, CD_2Cl_2, –60 °C): δ = 8.26 (dd, 1H, ^{3}J = 7.2 Hz, ^{4}J = 1.1 Hz, CH_{α}), 7.78 (dd, 1H, ^{3}J = 6.6 Hz, ^{4}J = 1.1 Hz, CH_{α}), 7.71 (d, 2H, ^{3}J = 6.6 Hz, CH_{β}), 7.35 (d, 1H, ^{3}J = 7.2 Hz, CH_{β}), 7.20-7.09 (m, 3H, CH_{β} + 2CH_{α}), 0.32 (d, 9H, $^{3}J_{\text{H-P}}$ = 7.5 Hz, P*Me*$_3$) ppm. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100.7 MHz, –60 °C): δ = 167.8 (2 x C_q, detected by HMBC), 161.4 ($C_{\text{q-BiPh}}$), 153.2 ($C_{\text{q-BiPh}}$), 146.4 (CH_{α}), 138.2 (CH_{α}), 129.5 (CH_{β}), 125.3 (CH_{β}), 125.1 (CH_{β}), 123.7 (CH_{β}), 121.9 (CH_{α}), 119.5 (CH_{α}), 9.23 (d, ^{1}J = 21.2 Hz, PCH_3) ppm. ^{9}Be NMR (56.2 MHz, CD_2Cl_2): δ = 8.3 (d, $^{1}J_{\text{Be-P}}$ = 27.8 Hz, fwmh ≈ 90 Hz) ppm. ^{31}P NMR (160.5 MHz, CD_2Cl_2): δ = –38.4 (br m) ppm. HRMS-LIFDI pos. [*m*/*z*] calculated for $[C_{30}H_{34}BeP]^{+}$ = $[M]^{+}$: 474.2374; found 474.2367.

Synthesis of 3

2,2'-Dilithiobiphenyl (1.48 g, 8.88 mmol, 1.10 equiv.) and [(IDipp)$BeBr_2$] (4.52 g, 8.07 mmol, 1.00 equiv.) were dissolved in toluene (60 mL). Stirring for 16 h at room temperature provided an orange suspension. All volatiles were removed *in vacuo* and the orange residue was washed with hot hexane (3 x 20 mL) to yield **3** as an off-white solid (1.92 g, 3.49 mmol, 43%). ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ = 7.59 (t, 2H, ^3J = 7.8 Hz, p-CH_{Dipp}), 7.38 (d, 4H, ^3J = 7.8 Hz, m-CH_{Dipp}), 7.33 (bs, 2H, NCH_{NHC}), 7.30 (d, 2H, ^3J = 7.6 Hz, CH_{α}), 6.85 (dt, 2H, ^3J = 7.6 Hz, ^4J = 1.2 Hz, CH_{β}), 6.52 (dt, 2H, ^3J = 7.1 Hz, ^4J = 1.2 Hz, CH_{β}), 5.68 (br d, 2H, ^3J = 7.1 Hz, CH_{α}), 2.76 (sept, 4H, ^3J = 6.9 Hz, CH_{iPr}), 1.23 (d, 12H, ^3J = 6.9 Hz, C$H_{3\text{-iPr}}$), 1.09 (d, 12H, ^3J = 6.9 Hz, C$H_{3\text{-iPr}}$) ppm. ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ = 205.2 ($C_{\text{q-carbene}}$ (HMBC)), 176.2 ($C_{\text{q-Dipp}}$), 158.4 ($C_{\text{q-BiPh}}$), 158.0 ($C_{\text{q-BiPh}}$), 145.9 ($C_{\text{q-Dipp}}$), 137.2 (CH$_{\beta}$), 135.6 (CH$_{\alpha}$), 130.9 (p-CH$_{\mathrm{Dipp}}$), 126.8 (CH$_{\beta}$), 125.5 (NCH$_{\mathrm{NHC}}$), 125.0 (m-CH$_{\mathrm{Dipp}}$), 118.1 (CH$_{\alpha}$), 29.2 (CH$_{\mathrm{iPr}}$), 24.6 (CH$_{3\text{-iPr}}$), 23.9 (CH$_{3\text{-iPr}}$) ppm. ^{9}Be NMR (56.2 MHz, C_6D_6): δ = 23.0 (fwmh ≈ 380 Hz) ppm. HRMS-LIFDI pos. [m/z] calculated for $[C_{39}H_{44}BeN_2]^+ = [M]^+$: 549.3621; found 549.3612.

Synthesis of 4

1 (50.0 mg, 213 *m*mol, 1.00 equiv.) was dissolved in THF (1 mL) and the solution heated to 80 °C for 16 h. The solvent was removed *in vacuo* to yield **4** as a colourless solid (63.0 mg, 206 *m*mol, 97%). ^{1}H NMR (500 MHz, C_6D_6): δ = 8.10 (bs, 2H, CH_{α}), 7.50-7.43 (m, 4H, 2CH_{α} + 2 CH_{β}), 7.23-7.19 (m, 1H, CH_{β}), 7.14-7.11 (s, 1H, CH_{β}), 3.56 (s, 8H, CH_2), 1.21 (s, 8H, CH_2) ppm. ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ = 164.3 ($C_{\text{q-BiPh}}$), 157.4 ($C_{\text{q-BiPh}}$), 141.8 ($C_{\text{q-BiPh}}$), 136.3 ($C_{\text{q-BiPh}}$), 129.1 (CH$_{\alpha}$ + CH$_{\mathrm{Ar}}$, detected by HMBC), 128.1 (CH$_{\mathrm{Ar}}$ detected by HMBC), 127.5 (CH$_{\mathrm{Ar}}$), 127.5 (CH$_{\beta}$), 125.4 (CH$_{\mathrm{Ar}}$), 119.9 (CH$_{\alpha}$), 69.5 (CH$_2$), 25.3 (CH$_2$) ppm. ^{9}Be NMR (56.2 MHz, C_6D_6): δ = 13.2 (fwmh ≈ 80 Hz) ppm. Elemental analysis [%] calculated for$C_{20}H_{24}BeO_2$: C 81.66, H 7.71; found C 80.54, H 7.74.

Synthesis of 5

1 (60.0 mg, 255 *m*mol, 1.00 equiv.) was dissolved in benzene (4 mL) and SIMes (78.1 mg, 255 *m*mol, 1.00 equiv.) was added. Upon stirring for 16 h a colourless solid precipitated. This solid was isolated by filtration and recrystallized from a saturated dichloromethane solution at room temperature to yield **5** as colourless crystals (40.0 mg, 83.5 *m*mol, 34%). ^{1}H NMR (500.1 MHz, CD_2Cl_2): δ = 7.33 (d, 2H, ^3J = 6.7 Hz, CH_{α}), 7.28 (d, 2H, ^3J = 7.6 Hz, CH_{α}), 6.93 (dd, 2H, ^3J = 7.6 Hz, ^4J = 1.3 Hz, CH_{β}), 6.88 (s, 4H, CH_{Mes}), 6.83 (dd, 2H, ^3J = 6.7 Hz, ^4J = 1.3 Hz, CH_{β}), 4.16 (s, 4H, C$H_{2\text{-SIMes}}$), 2.49 (s, 12H, o-C$H_{3\text{-Mes}}$), 2.18 (s, 6H, p-C$H_{3\text{-Mes}}$) ppm. ^{13}C{^{1}H} NMR

(125.8 MHz, CD_2Cl_2): *δ* = 202.3 ($C_{\text{q-carbene}}$), 158.6 ($C_{\text{q-BiPh}}$), 158.3 ($C_{\text{q-BiPh}}$), 139.4 ($C_{\text{q-Mes}}$), 136.3 ($C\mathrm{H}_\alpha$), 136.1 ($C_{\text{q-Mes}}$), 134.1 ($C_{\text{q-Mes}}$), 129.9 ($C\mathrm{H}_{\text{Mes}}$), 127.3 ($C\mathrm{H}_\beta$), 125.8 ($C\mathrm{H}_\beta$), 118.7 ($C\mathrm{H}_\alpha$), 52.1 ($C\mathrm{H}_{\text{2-SIMes}}$), 21.1 ($C\mathrm{H}_{\text{3-Mes-para}}$), 18.1 ($C\mathrm{H}_{\text{3-Mes-ortho}}$) ppm. ^{9}Be NMR (56.2 MHz, C_6D_6): *δ* = 24.3 (fwmh ≈ 380 Hz) ppm. *Note: Mass spectra or elemental analysis could not be obtained for **5** due to rapid decomposition.*

Synthesis of 6

1 (100 mg, 425 *m*mol, 1.00 equiv.) was dissolved in benzene (10 mL) and CAAC (121 mg, 425 *m*mol, 1.00 equiv.) was added. After stirring for 16 h the colourless suspension was filtered and the residual solid recrystallized from a saturated dichloromethane solution at room temperature to yield **6** as colourless crystals (69.0 mg, 155 *m*mol, 36%). *Note: compound **6** showed low solubility in hydrocarbon solvent and therefore had to be recrystallised from dichloromethane, in which it slowly decomposes, hence the low isolated yield. As a result, the NMR spectra of **6** in CD_2Cl_2 are contaminated with ca. 10% and 3% of two unidentified decomposition products, presenting asymmetric CAAC ligands.* ^{1}H NMR (500.1 MHz, CD_2Cl_2): *δ* = 7.49 (d, 2H, ^3J = 7.8 Hz, *m*-CH_{Dipp}), 7.43 (t, 1H, ^3J = 7.8 Hz, *p*-CH_{Dipp}), 7.40 (d, 2H, ^3J = 6.5 Hz, CH_α), 7.37 (d, 2H, ^3J = 7.6 Hz, CH_α), 7.06 (td, 2H, ^3J = 7.6 Hz, ^4J = 1.3 Hz, CH_β), 7.06 (td, 2H, ^3J = 6.8 Hz, ^4J = 1.3 Hz, CH_β), 3.14 (sept, 2H, ^3J = 6.7 Hz, CH_{iPr}), 2.18 (s, 2H, CH_2), 1.65 (s, 6H, C$H_{\text{3-CAAC}}$), 1.49 (s, 6H, C$H_{\text{3-CAAC}}$), 1.44 (d, 6H, ^3J = 6.7 Hz, C$H_{\text{3-iPr}}$), 1.19 (d, 6H, ^3J = 6.7 Hz, C$H_{\text{3-iPr}}$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz): δ = 251.2 ($C_{\text{q-carbene}}$), 160.6 ($C_{\text{q-BiPh}}$), 158.2 ($C_{\text{q-BiPh}}$), 146.0 ($C_{\text{q-Dipp}}$), 138.0 ($C\mathrm{H}_\beta$), 133.5 ($C_{\text{q-Dipp}}$), 130.0 (*p*-$C\mathrm{H}_{\text{Dipp}}$), 127.3 ($C\mathrm{H}_\beta$), 125.6 ($C\mathrm{H}_\beta$), 125.4 ($C\mathrm{H}_\alpha$), 118.7 (*m*-$C\mathrm{H}_{\text{Dipp}}$), 83.3 ($C_{\text{q-CAAC}}$), 55.5 ($C_{\text{q-CAAC}}$), 50.8 ($C\mathrm{H}_{\text{2-CAAC}}$), 29.6 ($C\mathrm{H}_{\text{3-CAAC}}$), 29.5 ($C\mathrm{H}_{\text{3-CAAC}}$), 29.1 ($C\mathrm{H}_{\text{3-iPr}}$), 28.8 ($C\mathrm{H}_{iPr}$), 23.8 ($C\mathrm{H}_{\text{3-iPr}}$) ppm. ^{9}Be NMR ($CD_2Cl_2$, 56 MHz): *δ* = 23.6 (fwmh ≈ 320 Hz) ppm. Elemental analysis [%] calculated for$C_{32}H_{39}BeN$: C 86.05, H 8.80, N 3.14; found: C 85.14, H 9.02, N 3.06.

Synthesis of 7

6 (20.0 mg, 44.8 *m*mol, 1.00 equiv.) was dissolved in toluene (1 mL) and heated to 100 °C for four weeks. All volatiles were removed *in vacuo* and the colourless residue was then extracted with hexane (3 x 1 mL). After the removal of the solvent, **7** (20.3 mg, 44.0 *m*mol, 98 %) was obtained as a colourless solid. ^{1}H NMR (500.1 MHz, C_6D_6): *δ* = 7.78 (d, 1H, ^3J = 8.0 Hz, CH_α), 7.70 (d, 1H, ^3J = 8.0 Hz, CH_α), 7.34 (t, 1H, ^3J = 4.8 Hz, *p*-CH_{Dipp}), 7.31 (d, 2H, ^3J = 4.8 Hz, *m*-CH_{Dipp}), 7.19-7.18 (m, 1H, CH_α), 7.15 (d, 1H, ^4J = 1.8 Hz, CH_α), 7.07 (dt, 1H, ^3J = 7.5 Hz, ^4J = 1.2 Hz, CH_β), 6.92 (dt, 1H, ^3J = 7.2 Hz, ^4J = 1.2 Hz, CH_β), 6.87 (dd, 1H, ^3J = 7.2 Hz, ^4J

= 1.7 Hz, CH_{β}), 6.64 (dd, 1H, ^3J = 7.5 Hz, ^4J = 1.7 Hz, CH_{β}), 3.87-3.76 (m, 2H, CH_{iPr}), 3.02 (d, 1H, ^3J = 12.8 Hz, CH_2), 2.12 (d, 1H, ^3J = 12.8 Hz, CH_2), 2.06 (d, 3H, ^4J = 1.2 Hz, CH_3), 1.39 (d, 3H, ^3J = 6.9 Hz, C$H_{3\text{-}iPr}$), 1.37 (s, 3H, CH_3), 1.34 (d, 3H, ^3J = 6.9 Hz, C$H_{3\text{-}iPr}$), 1.15-1.13 (m, 6H, CH_3 + C$H_{3\text{-iPr}}$), 1.11 (d, 3H, ^3J = 6.9 Hz, C$H_{3\text{-}iPr}$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 149.5 ($C_{\text{q-Dipp}}$), 149.1 ($C_{\text{q-Dipp}}$), 148.8 ($C_{\text{q-BiPh}}$), 144.9 ($C_{\text{q-BiPh}}$), 144.4 ($C_{\text{q-alkene}}$), 143.9 ($C_{\text{q-BiPh}}$), 143.3 ($C_{\text{q-alkene}}$), 141.1 (CH$_{\beta}$), 138.1 ($C_{\text{q-BiPh}}$), 129.4 (CH$_{\alpha}$), 129.1 (CH$_{\beta}$), 128.9 (CH$_{\alpha}$), 128.7 (CH$_{\alpha}$), 126.6 (CH$_{\beta}$),126.4 (CH$_{\alpha}$), 126.1 (CH$_{\beta}$), 125.7 (*m*-CH$_{\text{Dipp}}$), 124.6 (*m*-CH$_{\text{Dipp}}$), 124.2 (*p*-CH$_{\text{Dipp}}$), 67.6 (C_q), 49.1 (2 x CH$_2$), 32.3 (CH$_3$), 31.2 (CH$_3$), 28.9 (CH$_{iPr}$), 28.2 (CH$_{iPr}$), 26.3 (CH$_{3\text{-iPr}}$), 25.9 (CH$_{3\text{-iPr}}$), 24.3 (CH$_{3\text{-iPr}}$), 23.9 (CH$_{3\text{-iPr}}$), 22.9 (CH$_3$), 22.1 (CH$_3$) ppm. ^{9}Be NMR (56.2 MHz, C_6D_6): δ = 14.3 (fwmh ≈ 360 Hz) ppm. HRMS-LIFDI pos. [*m*/*z*] calculated for $[C_{32}H_{40}BeN]^+$ = $[M - CH_3]^+$: 447.3232; found 447.3223.

Synthesis of 8

6 (40.0 mg, 89.6 *m*mol, 1.00 equiv.) was dissolved in diethyl ether (3 mL) and lithium sand (1.43 mg, 206 *m*mol, 2.30 equiv.) was added. Upon stirring this suspension for 16 h a colour change to deep violet occurred. After the suspension was filtered and the solvent removed *in vacuo* **8** was obtained as a purple powder (50.3 mg, 82.6 *m*mol, 92%). ^{1}H NMR (500.1 MHz, C_6D_6): δ = 8.13 (bs, 3H, CH_{BiPh}), 7.50 (t, 1H, ^3J = 7.7 Hz, *p*-CH_{Dipp}), 7.40 (d, 2H, ^3J = 7.7 Hz, *m*-CH_{Dipp}), 6.93-6.33 (br m, 5H, CH_{BiPh}), 3.50 (bs, 2H, CH_{iPr}), 2.69 (q, 8H, ^3J = 6.9 Hz, C$H_{2\text{-Et2O}}$), 2.29 (bs, 6H, C$H_{3\text{-CAAC}}$), 2.14 (bs, 2H, C$H_{2\text{-CAAC}}$), 1.41-1.30 (m, 18H, C$H_{3\text{-CAAC}}$ + C$H_{3\text{-iPr}}$), 0.61 (t, 12H, ^3J = 6.9 Hz, CH$_{3\text{-Et2O}}$) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 172.9 ($C_{\text{q-carbene}}$ (HMBC)), 150.8 ($C_{\text{q-carbene}}$), 150.8 ($C_{\text{q-Dipp}}$), 145.6 ($C_{\text{q-BiPh}}$), 140.2 ($C_{\text{q-Dipp}}$), 127.7 (*p*-CH$_{\text{Dipp}}$), 125.5 (*m*-CH$_{\text{Dipp}}$), 122.3 (CH$_{\text{BiPh}}$), 66.0 (CH$_{2\text{-Et2O}}$), 57.1 (CH$_{2\text{-CAAC}}$), 52.2 ($C_{\text{q-CAAC}}$), 35.3 (CH$_{3\text{-CAAC}}$), 30.2 (CH$_{3\text{-CAAC}}$), 29.1 (CH$_{iPr}$), 28.5 (CH$_{3\text{-iPr}}$), 24.6 (CH$_{3\text{-iPr}}$), 14.4 (CH$_{3\text{-Et2O}}$) ppm. ^{9}Be NMR (56.2 MHz, C_6D_6): δ = 7.6 (fwmh ≈ 155 Hz) ppm. *Note: Mass spectra or elemental analysis could not be obtained for* ***8*** *due to rapid decomposition.*

NMR spectra of isolated compounds

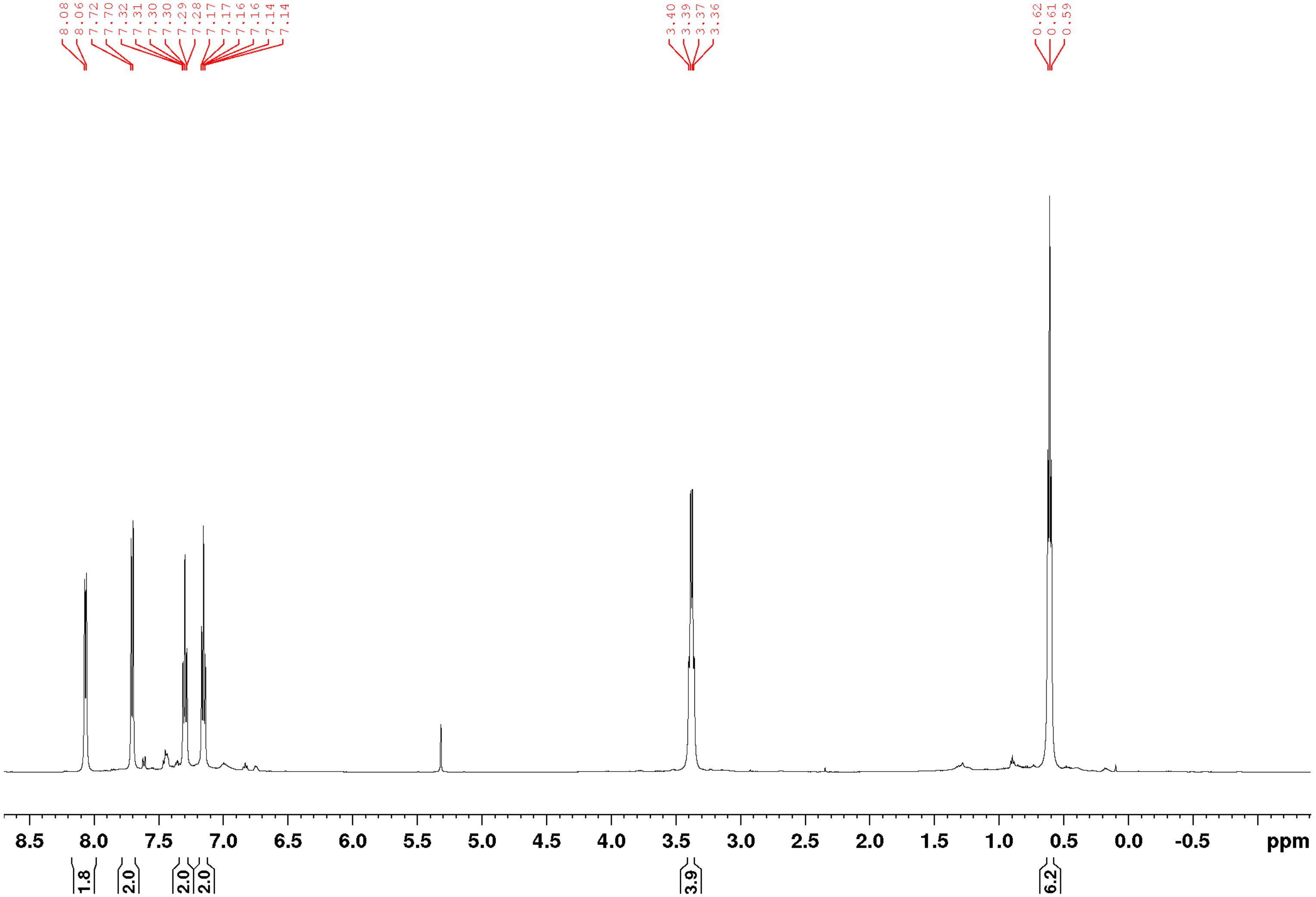


Figure S1. ^{1}H NMR spectrum of **1** in CD_2Cl_2.

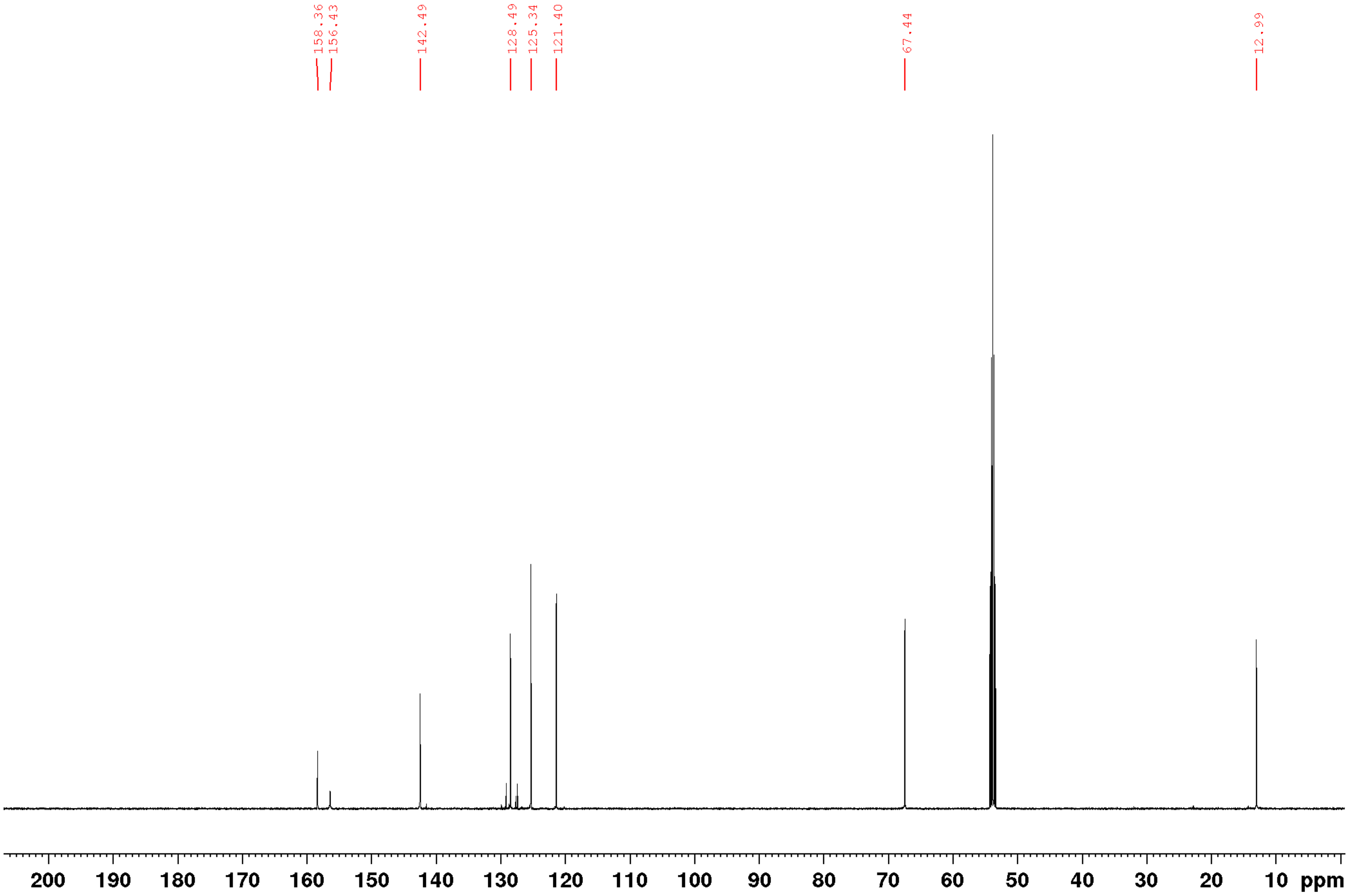


Figure S2. $^{13}C\{^1H\}$ NMR spectrum of **1** in CD_2Cl_2.

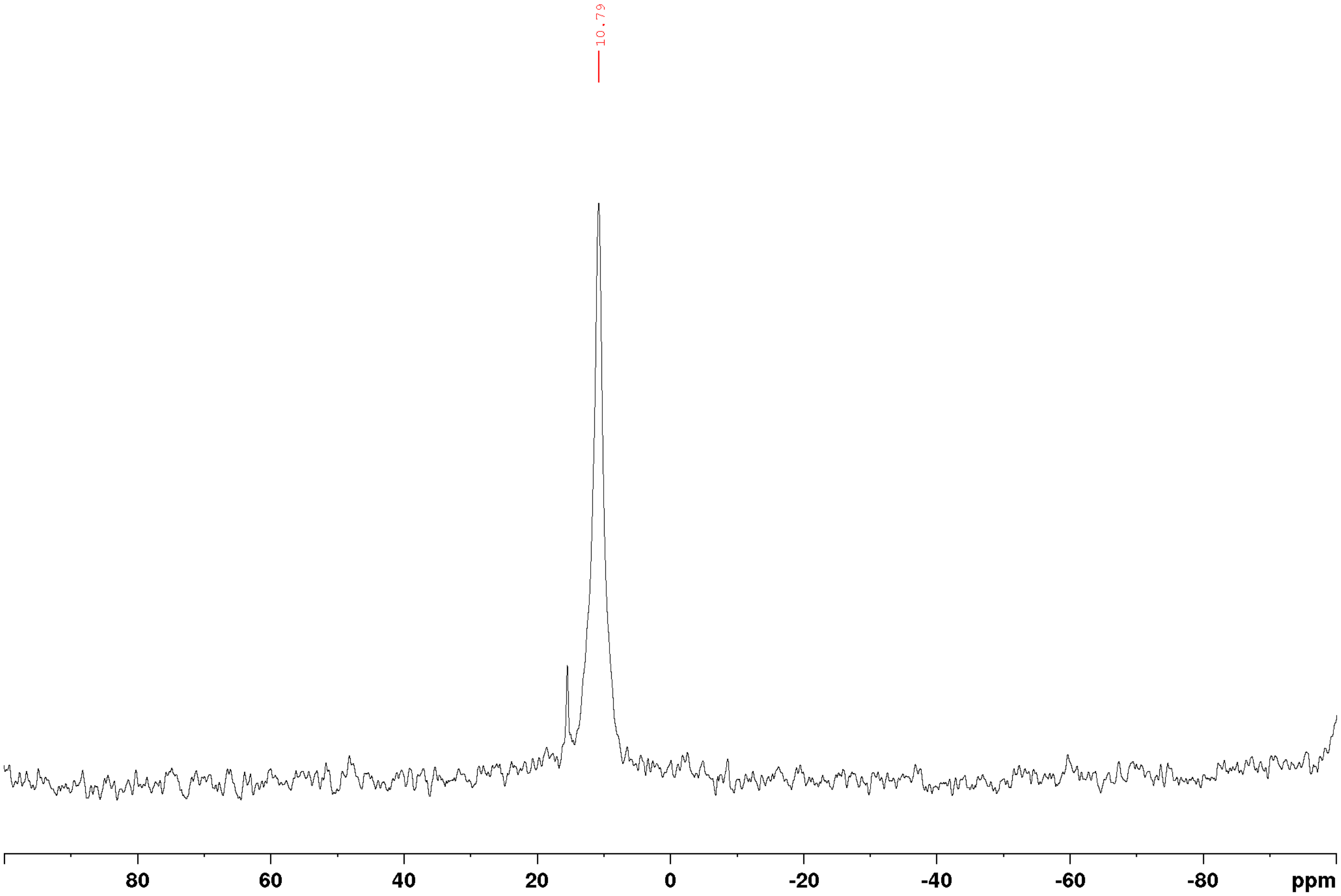


Figure S3. ^{9}Be NMR spectrum of **1** in C_6D_6.

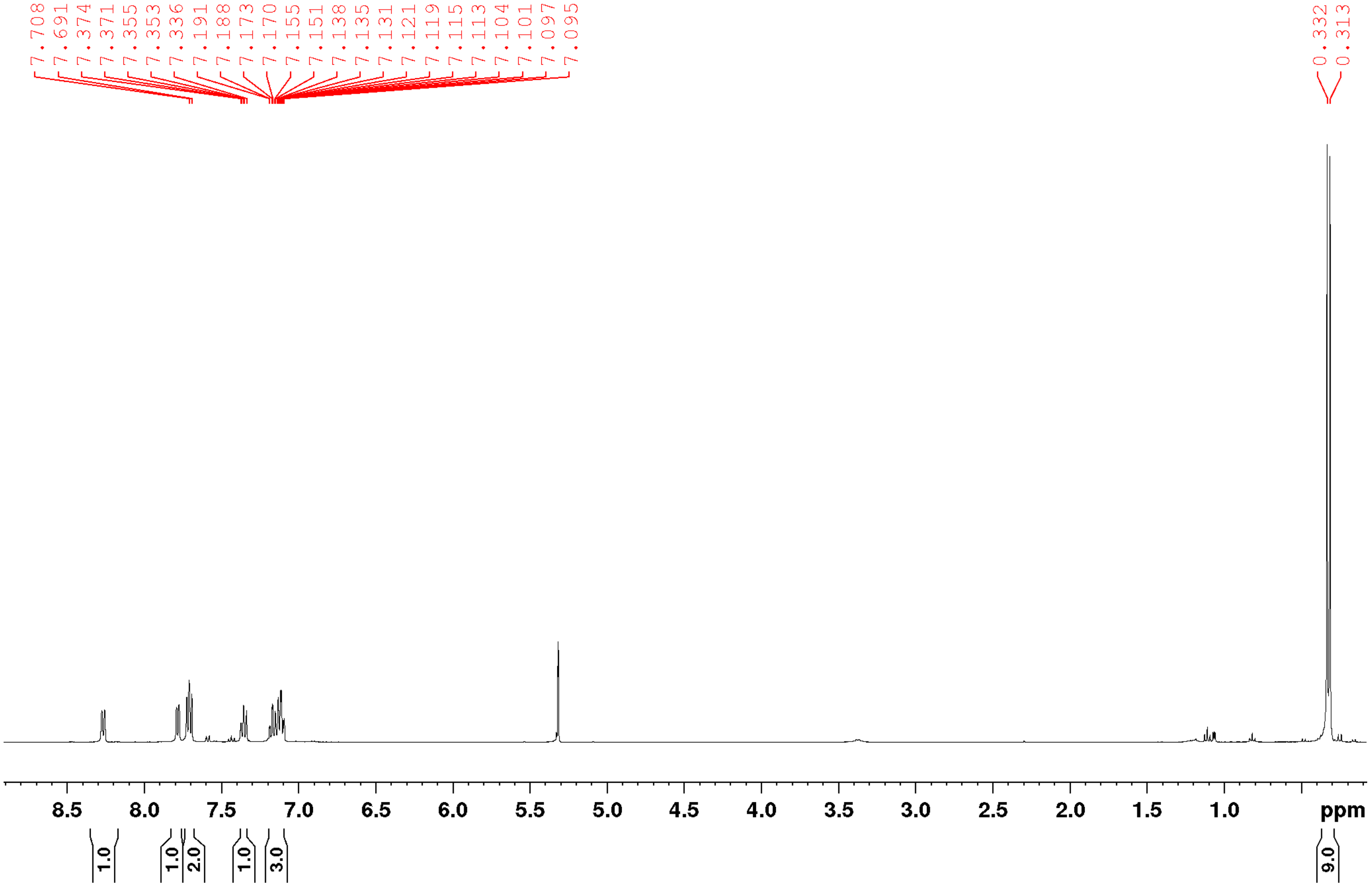


Figure S4. ^{1}H NMR spectrum **2** in CD_2Cl_2 at –60 °C.

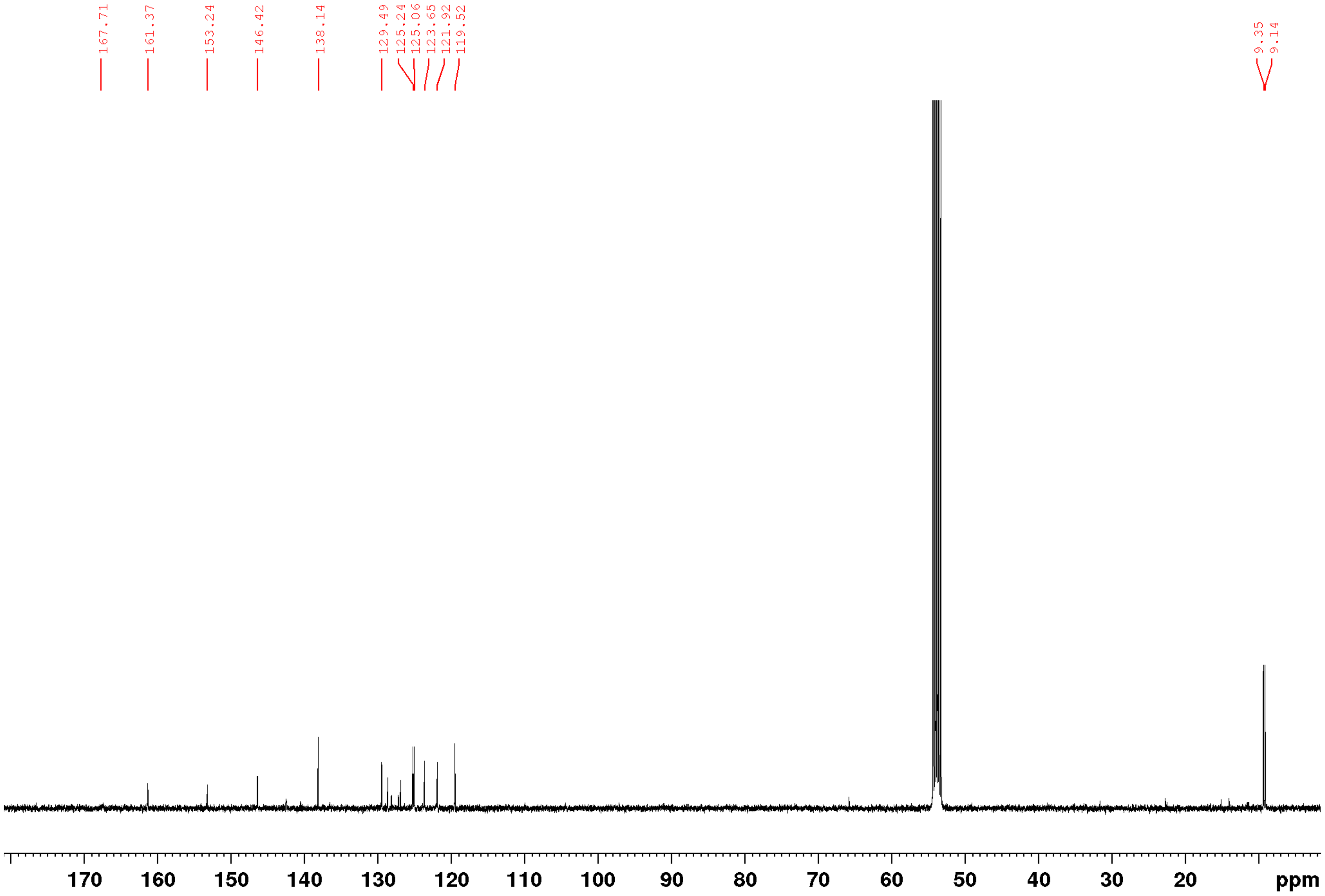


Figure S5. $^{13}C\{^1H\}$ NMR spectrum of **2** in CD_2Cl_2 at –60 °C.

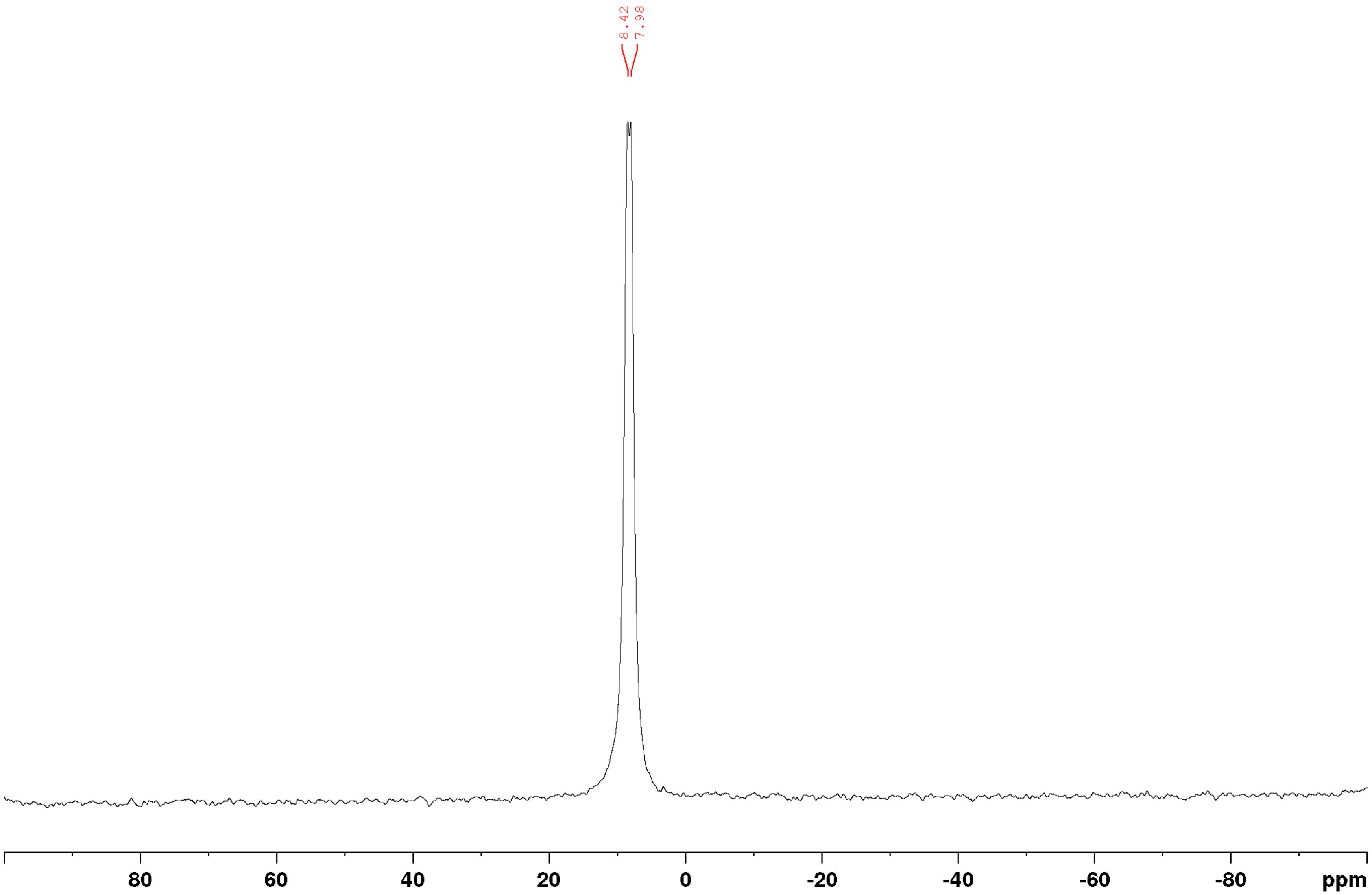


Figure S6. ^{9}Be NMR spectrum of **2** in C_6D_6.

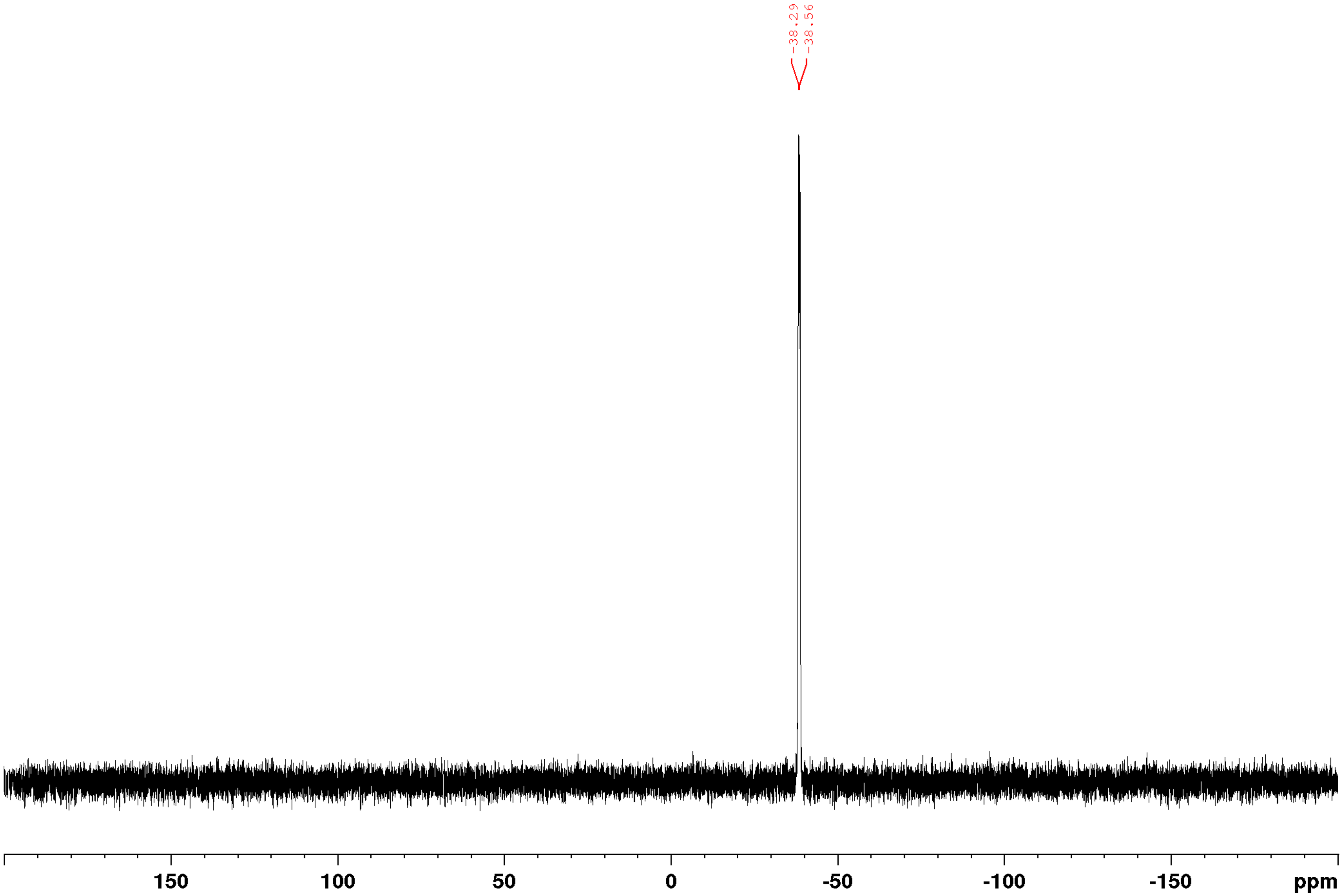


Figure S7. ^{31}P NMR spectrum of **2** in C_6D_6.

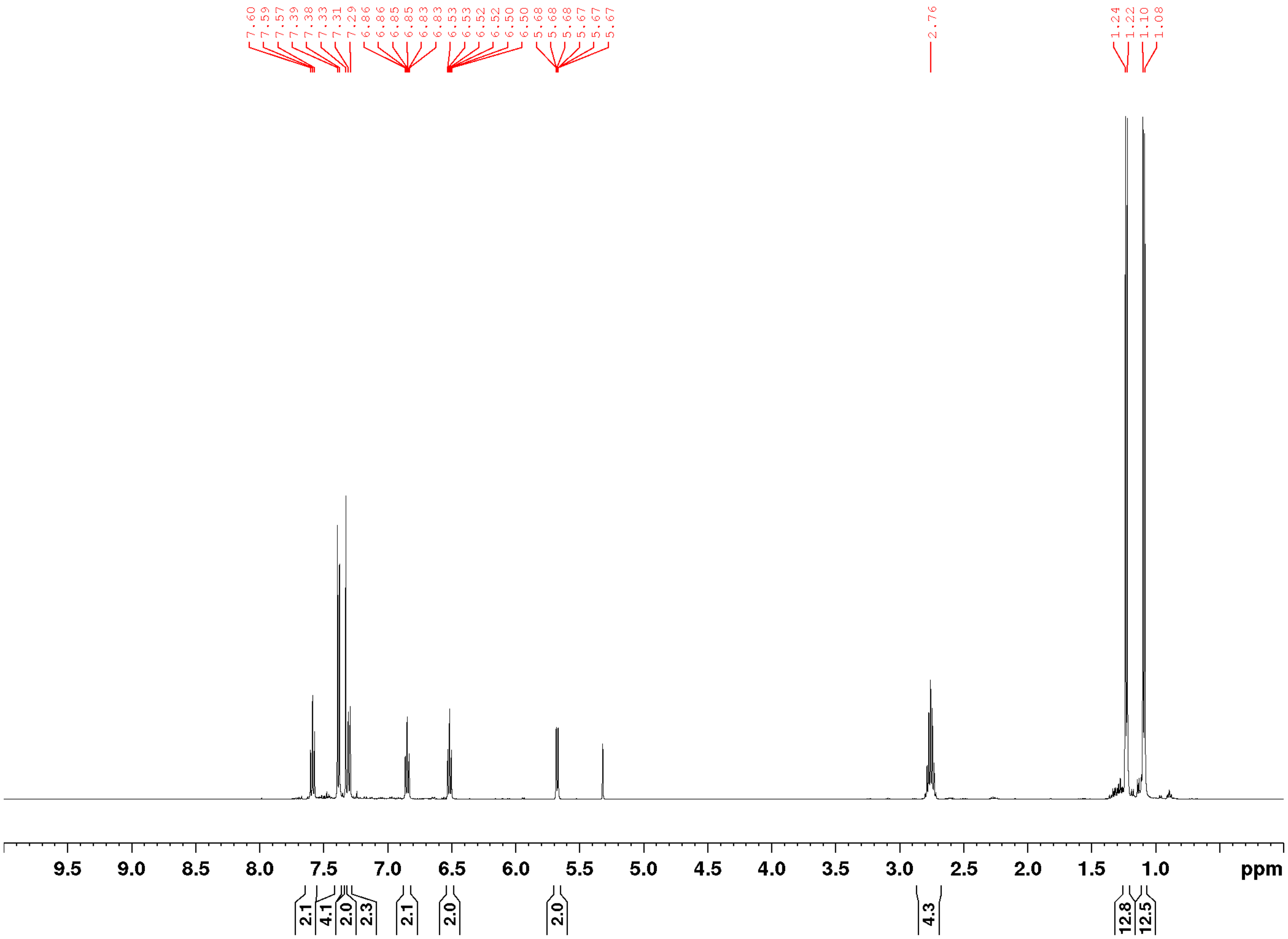


Figure S8. ^{1}H NMR spectrum of **3** in CD_2Cl_2.

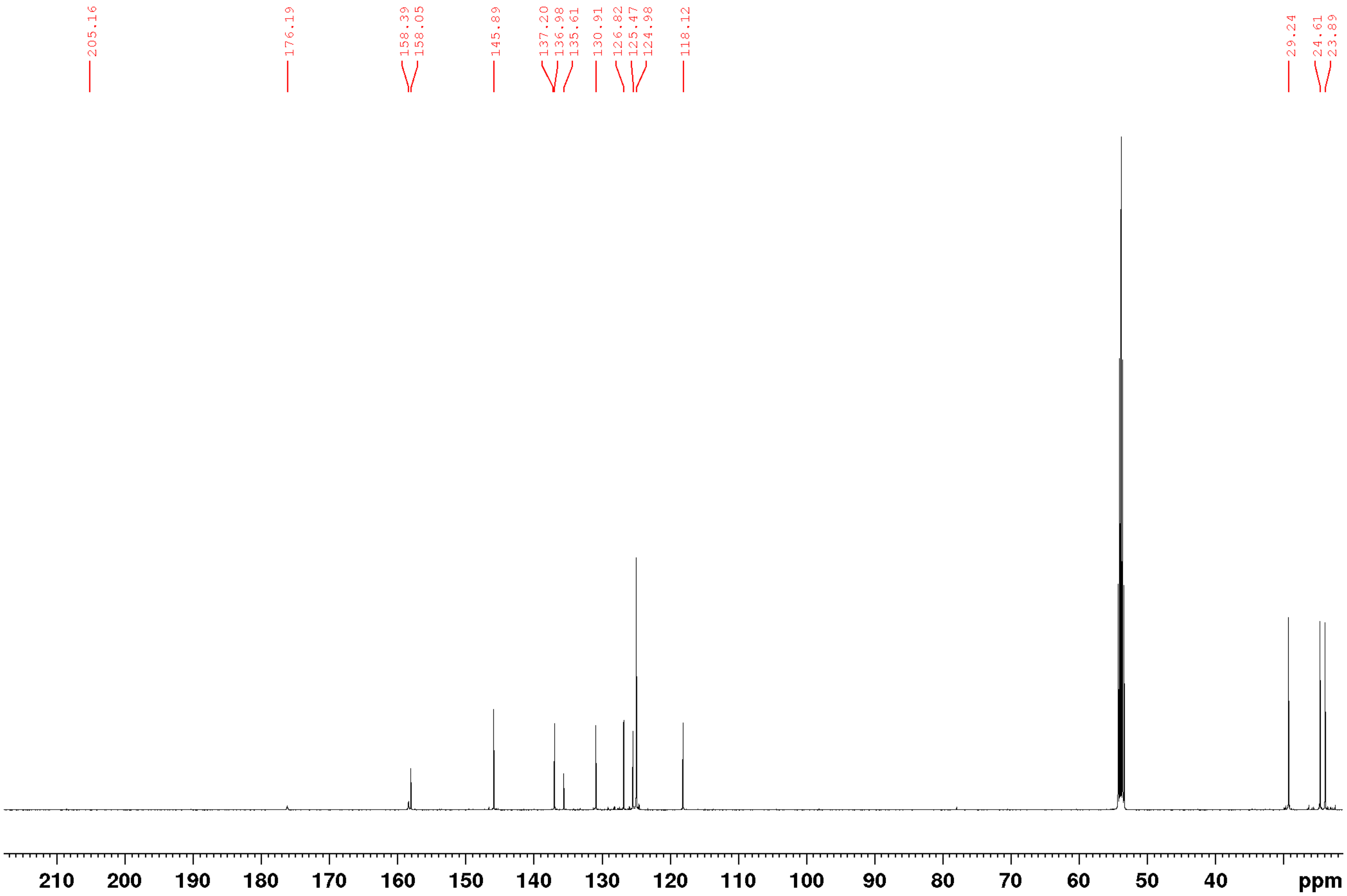


Figure S9. $^{13}C\{^1H\}$ NMR spectrum of **3** in CD_2Cl_2.

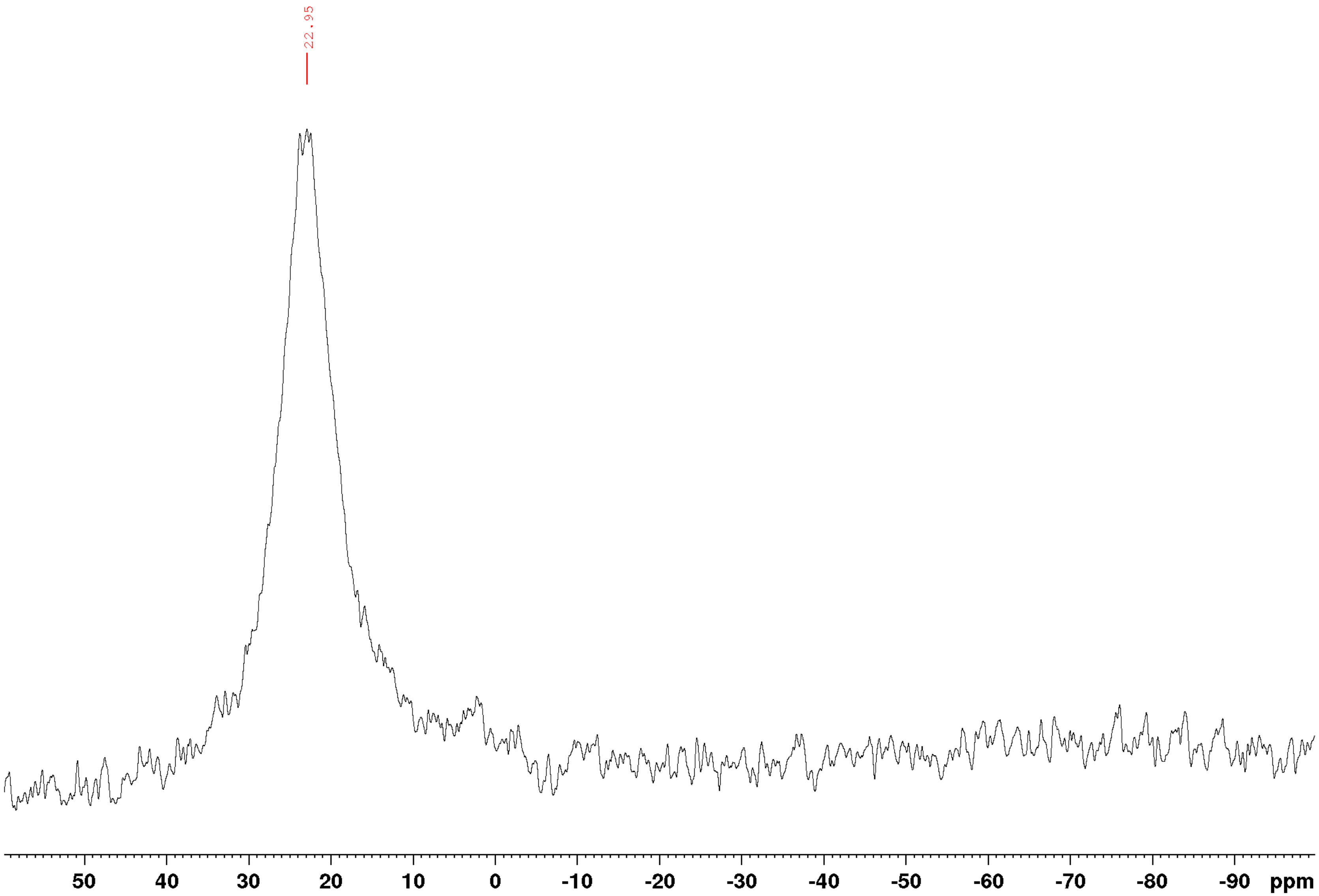


Figure S10. ^{9}Be NMR spectrum of **3** in C_6D_6.

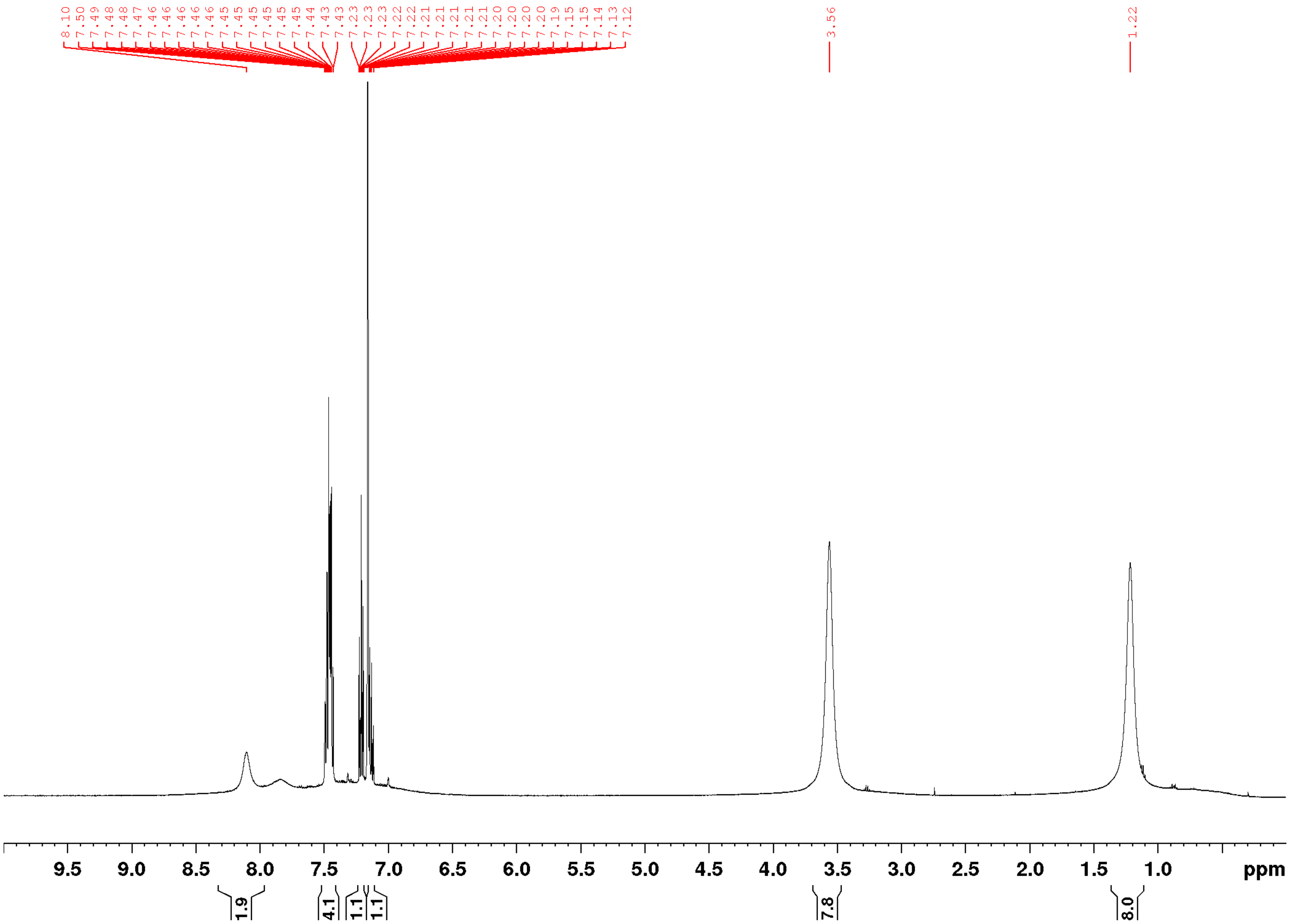


Figure S11. ^{1}H NMR spectrum of **4** in C_6D_6.

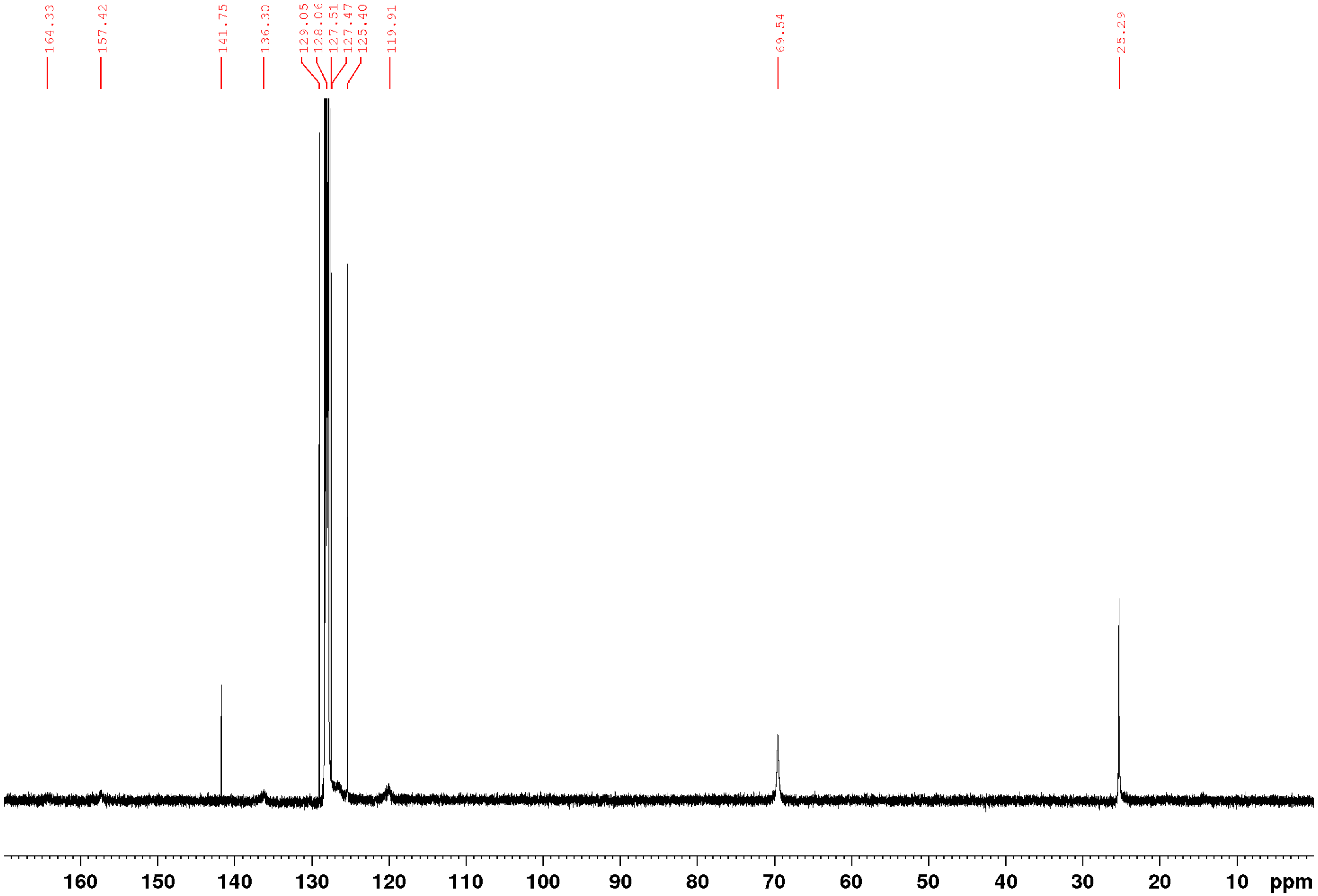


Figure S12. $^{13}C\{^1H\}$ NMR spectrum of **4** in C_6D_6.

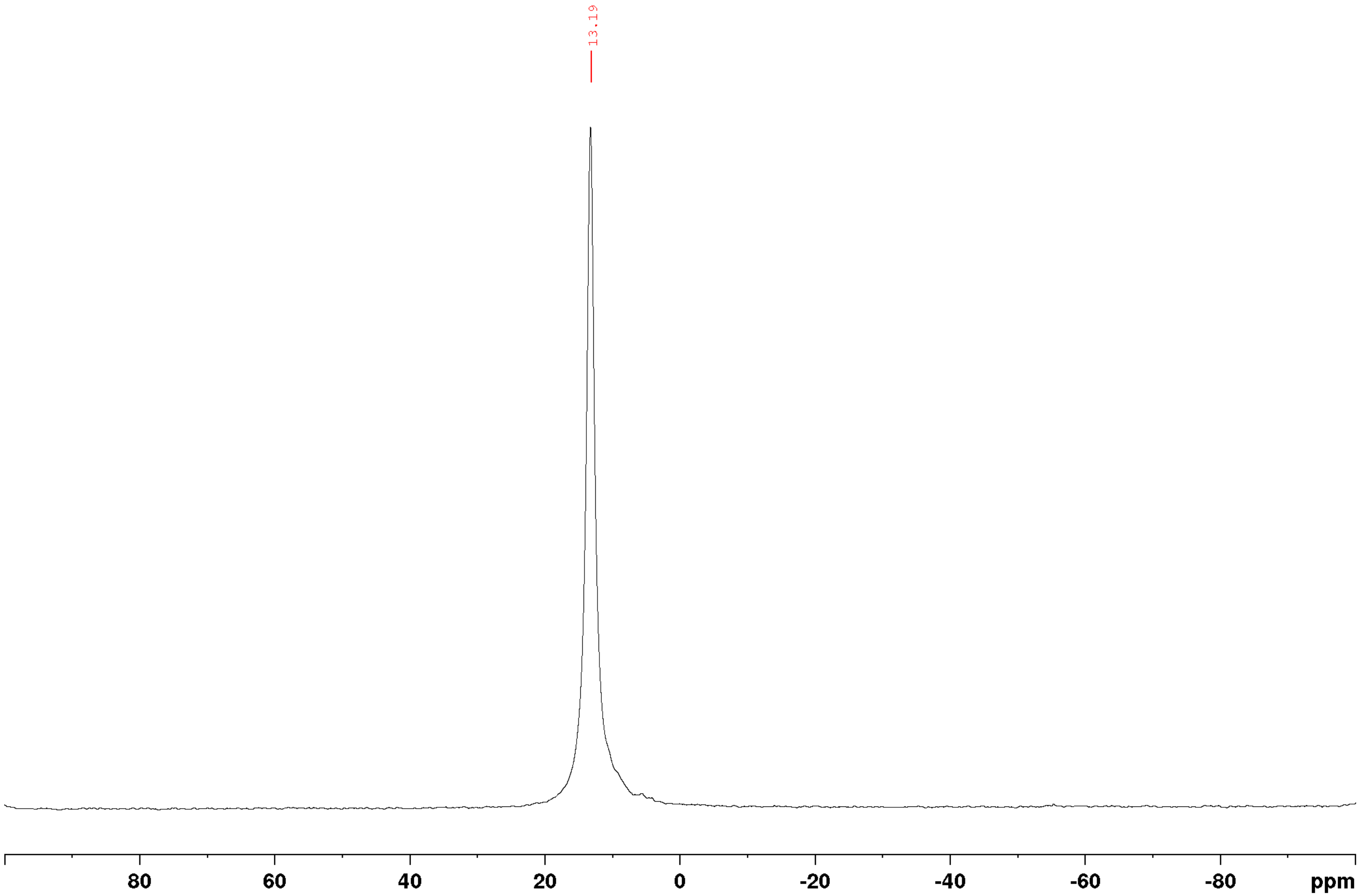


Figure S13. ^{9}Be NMR spectrum of **4** in C_6D_6.

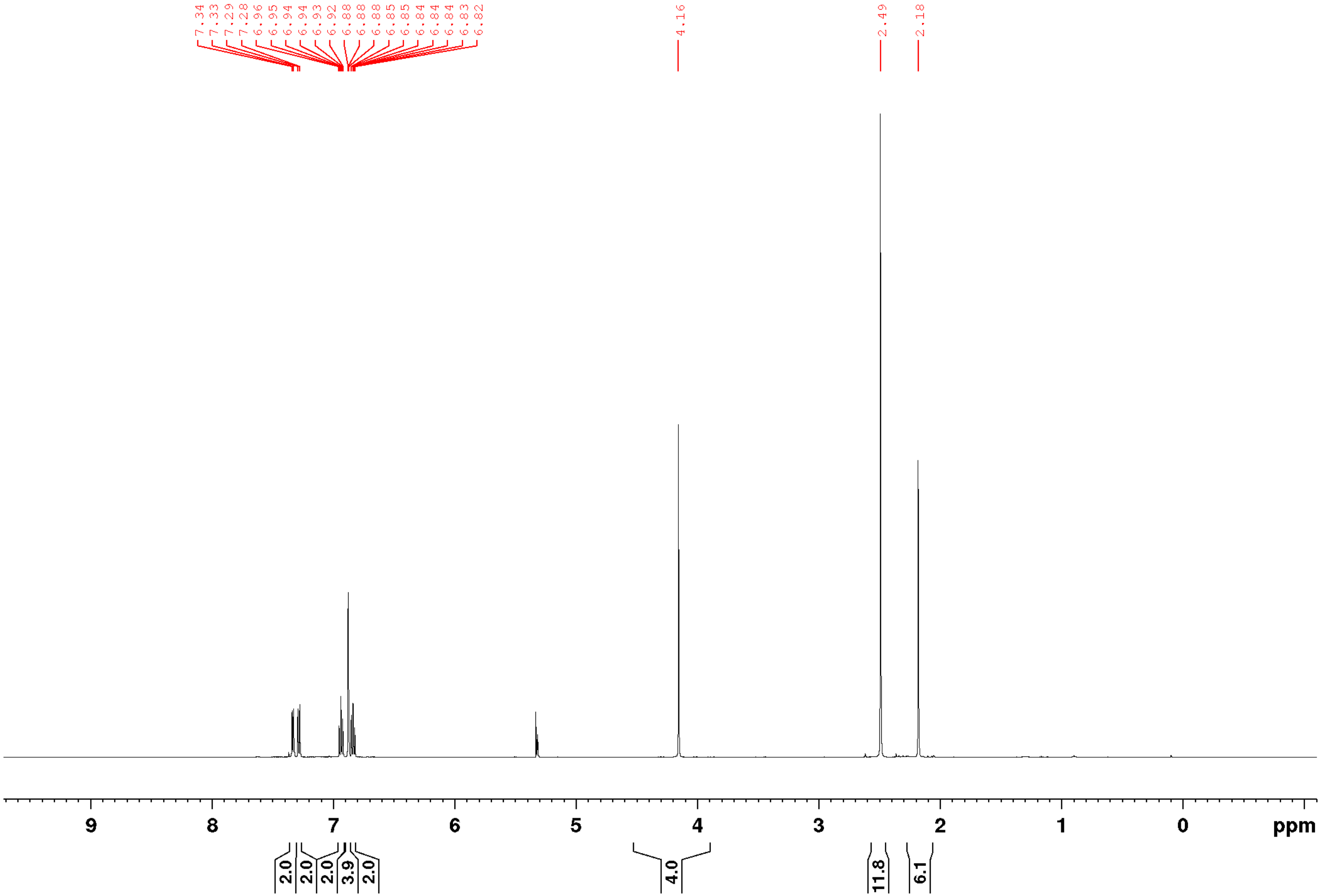


Figure S14. ^{1}H NMR spectrum of **5** in C_6D_6.

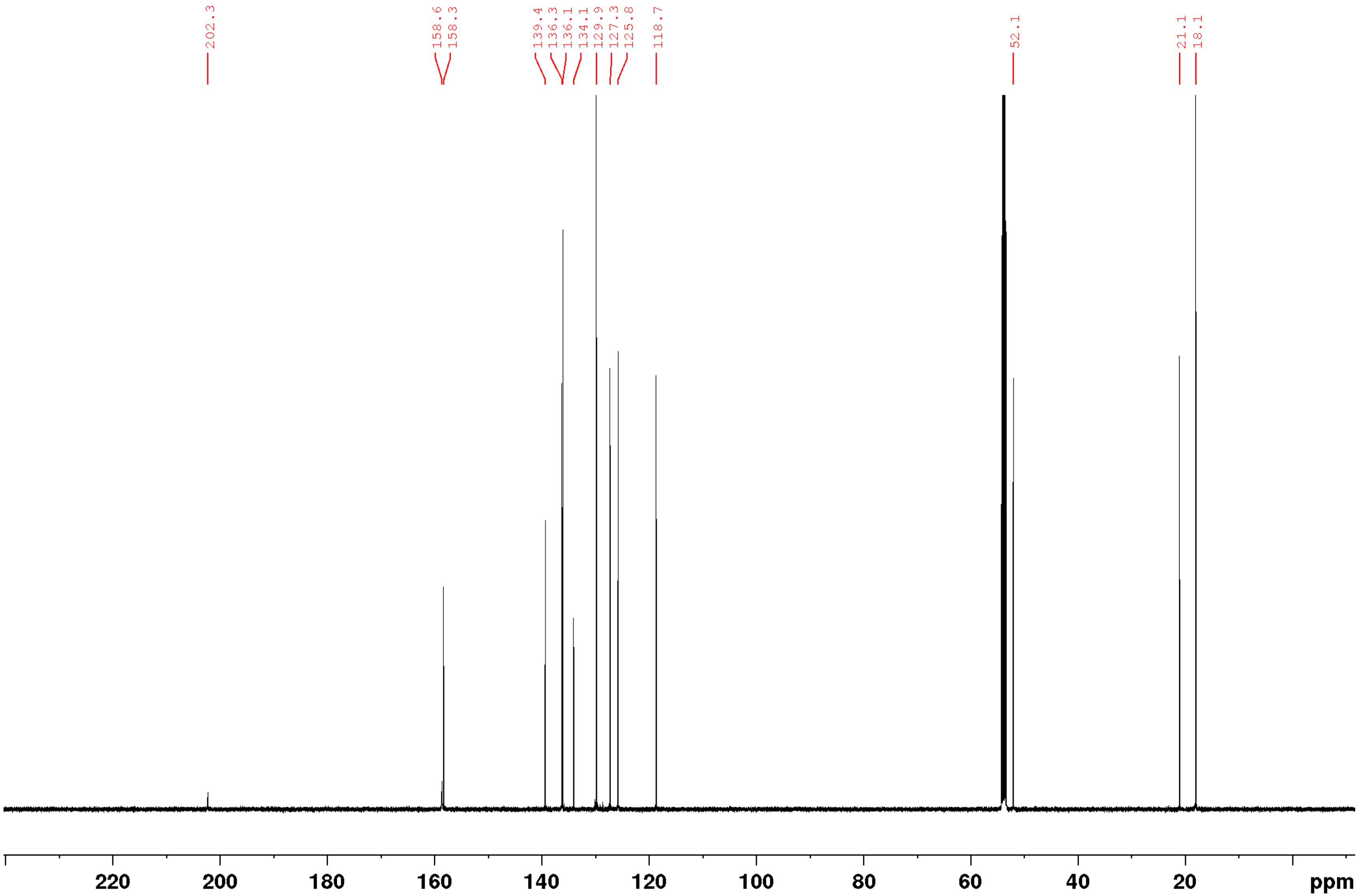


Figure S15. $^{13}C\{^1H\}$ NMR spectrum of **5** in C_6D_6.

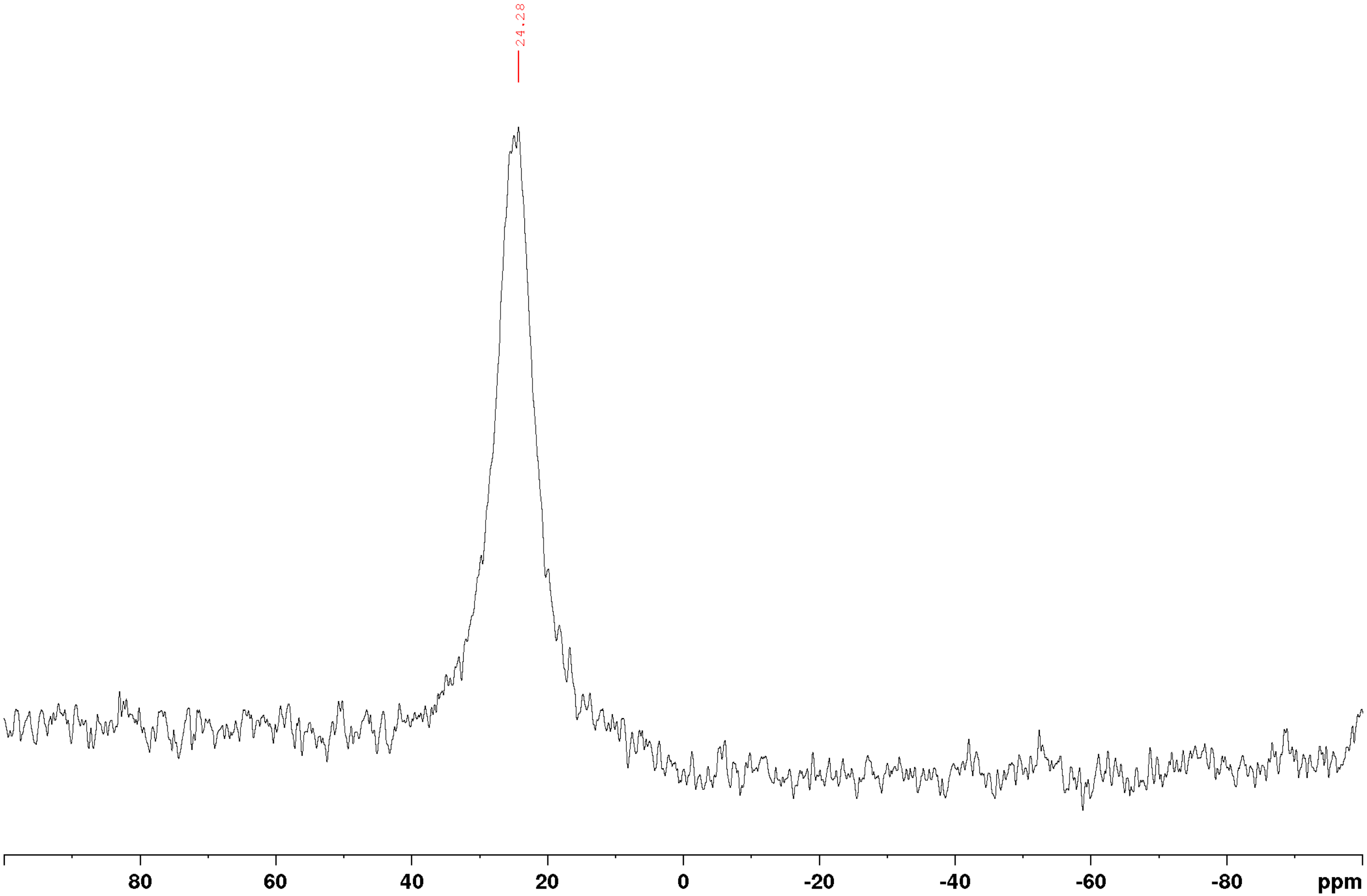


Figure S16. ^{9}Be NMR spectrum of **5** in C_6D_6.

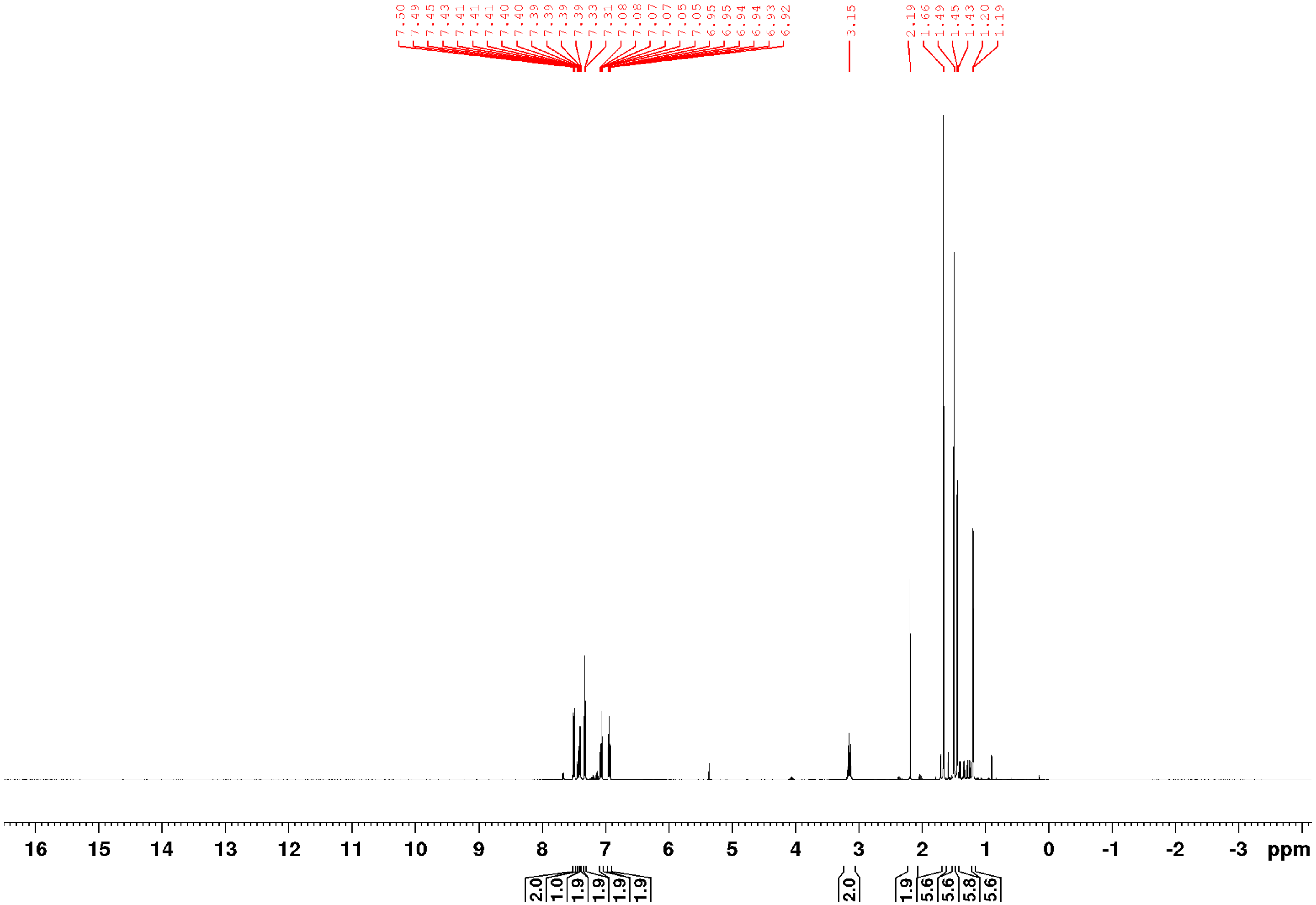


Figure S17. ^{1}H NMR spectrum of **6** in CD_2Cl_2. Due to slow decomposition of **6** in dichloromethane, the spectra are contaminated with two unidentified decomposition products (ca. 13%).

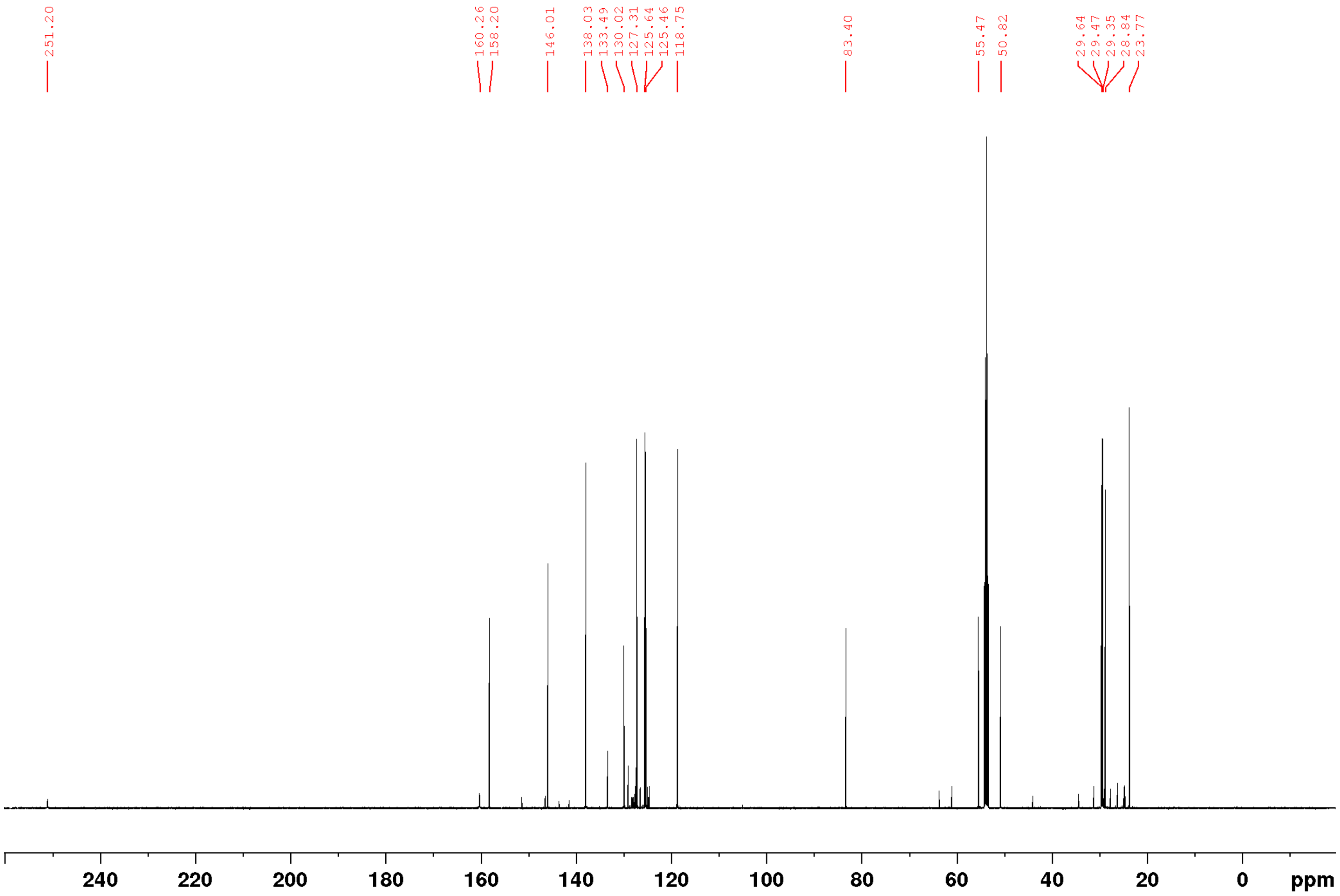


Figure S18. $^{13}C\{^1H\}$ NMR spectrum of **6** in CD_2Cl_2. Due to slow decomposition of **6** in dichloromethane, the spectra are contaminated with two unidentified decomposition products (ca. 13%).

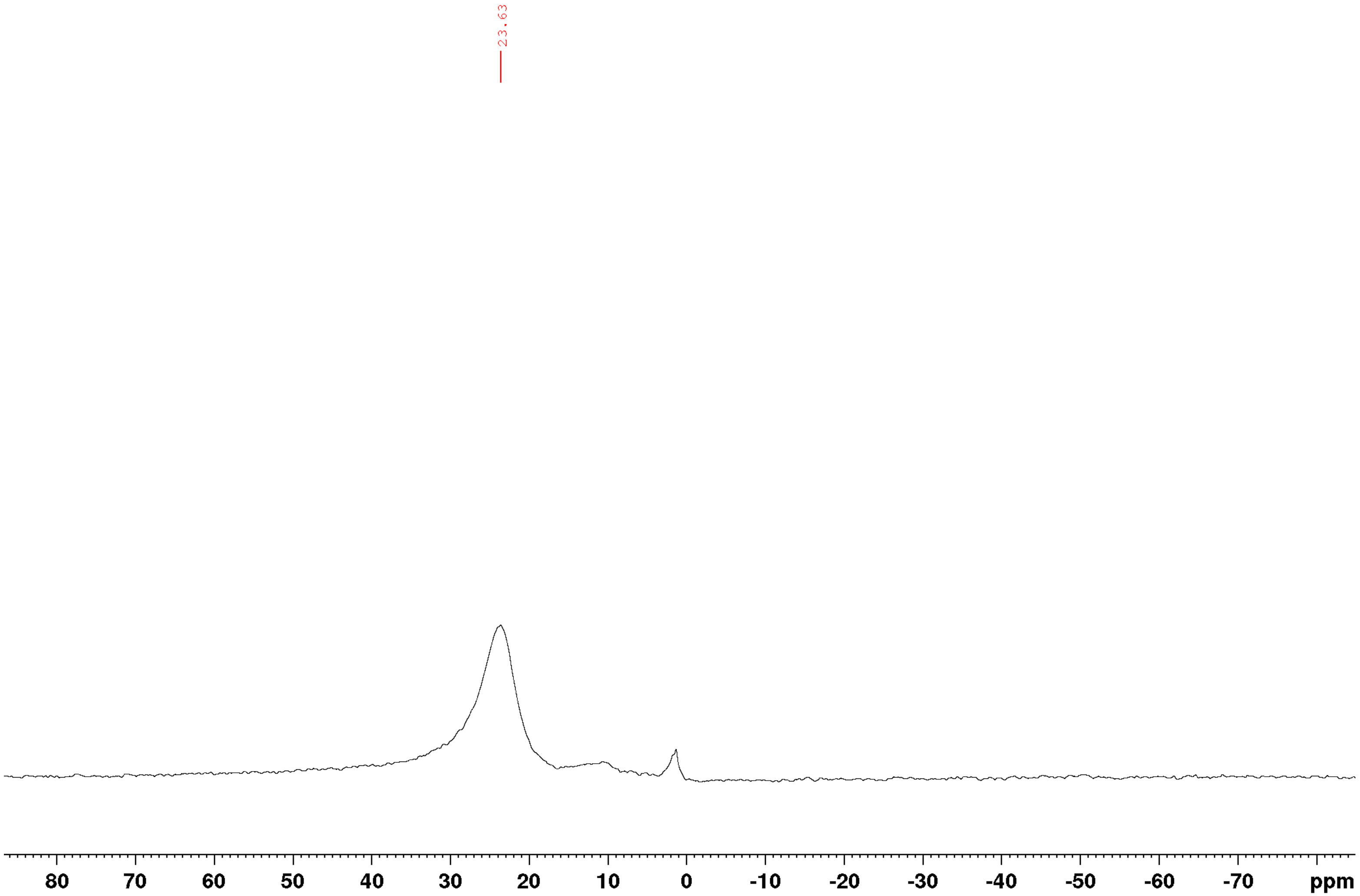


Figure S19. ^{9}Be NMR spectrum of **6** in CD_2Cl_2. Due to slow decomposition of **6** in dichloromethane, the spectra are contaminated with two unidentified decomposition products (ca. 13%).

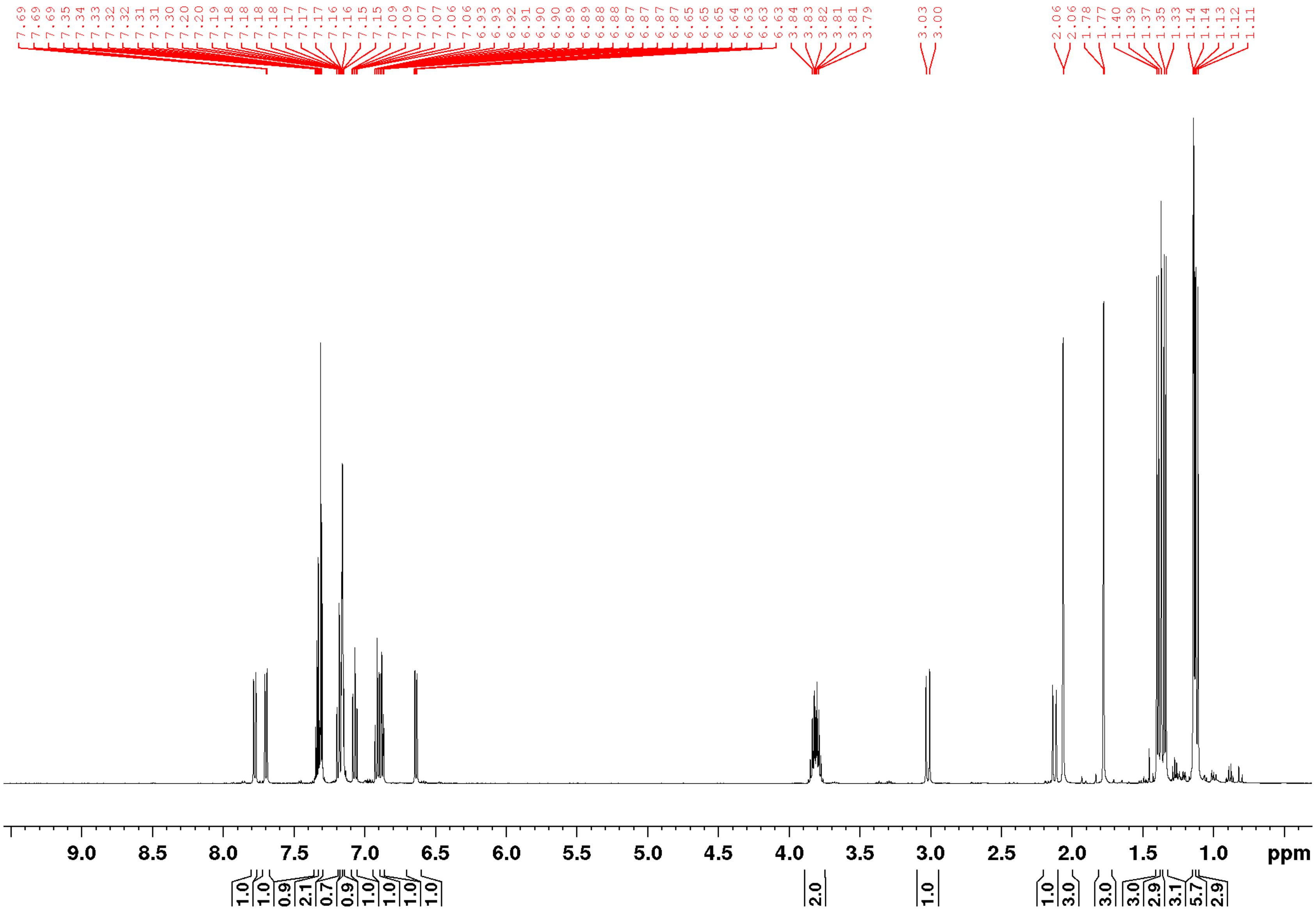


Figure S20. ^{1}H NMR spectrum of **7** in C_6D_6.

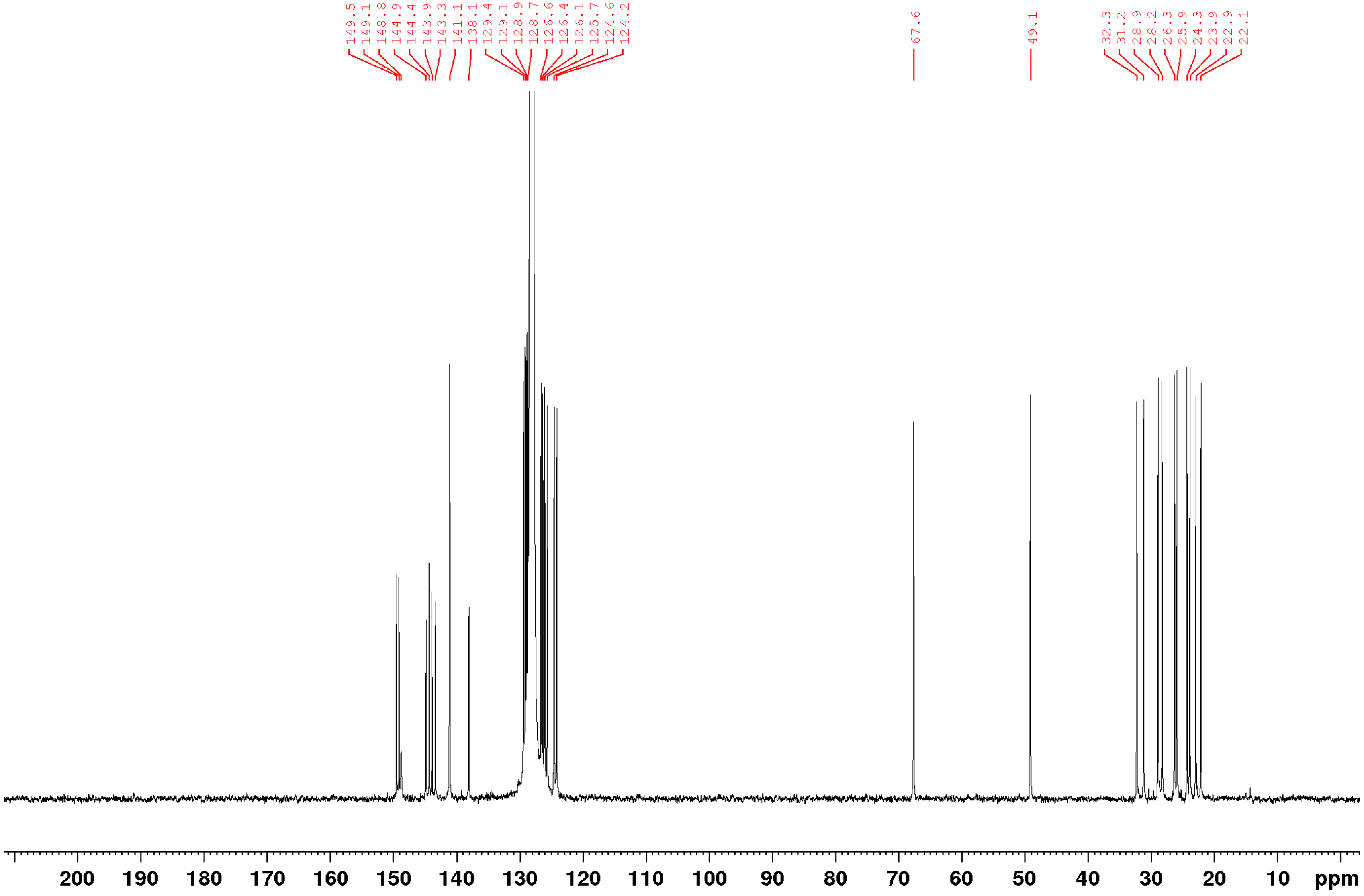


Figure S21. $^{13}C\{^1H\}$ NMR spectrum of **7** in C_6D_6.

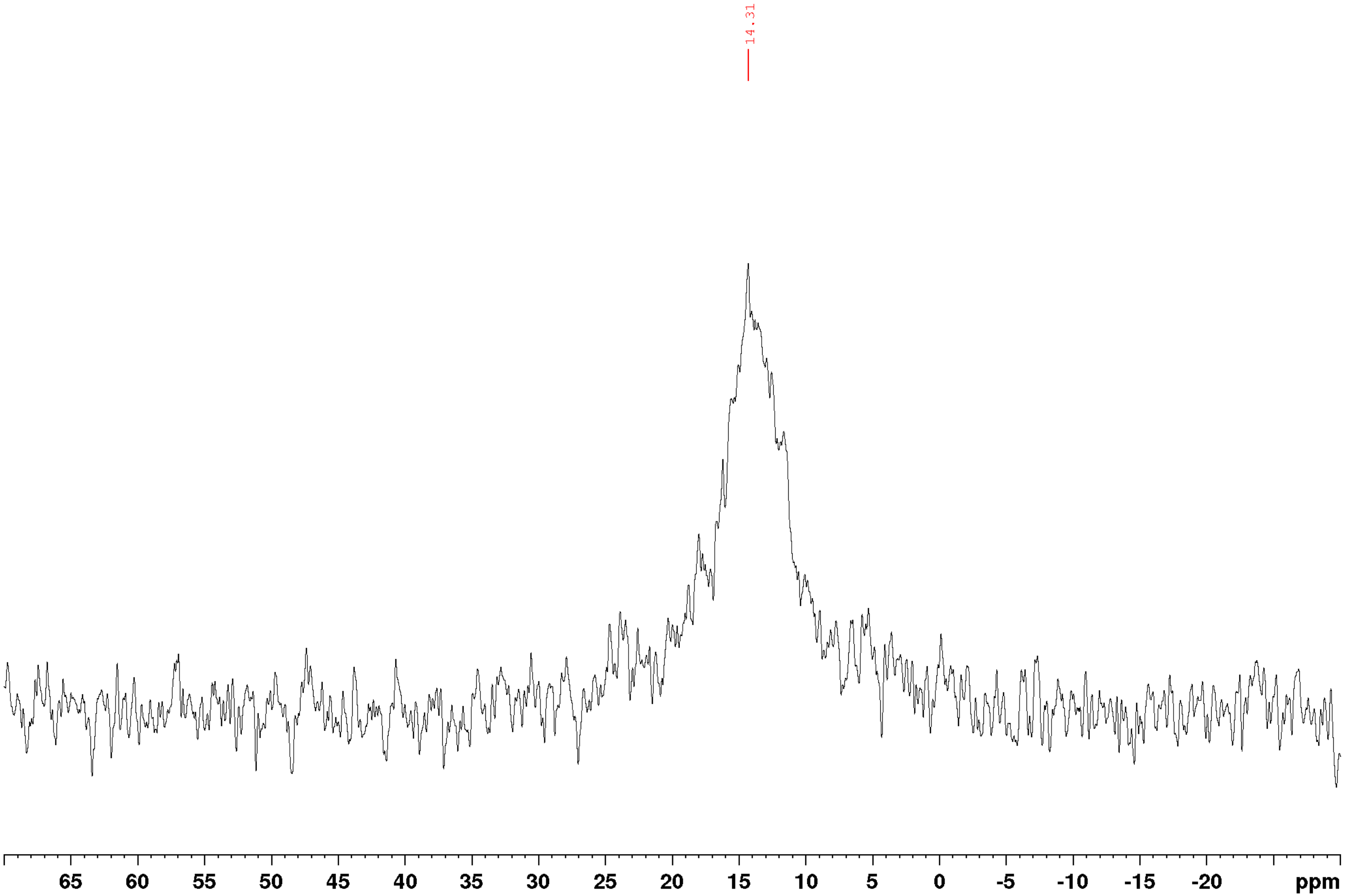


Figure S22. ^{9}Be NMR spectrum of **7** in C_6D_6.

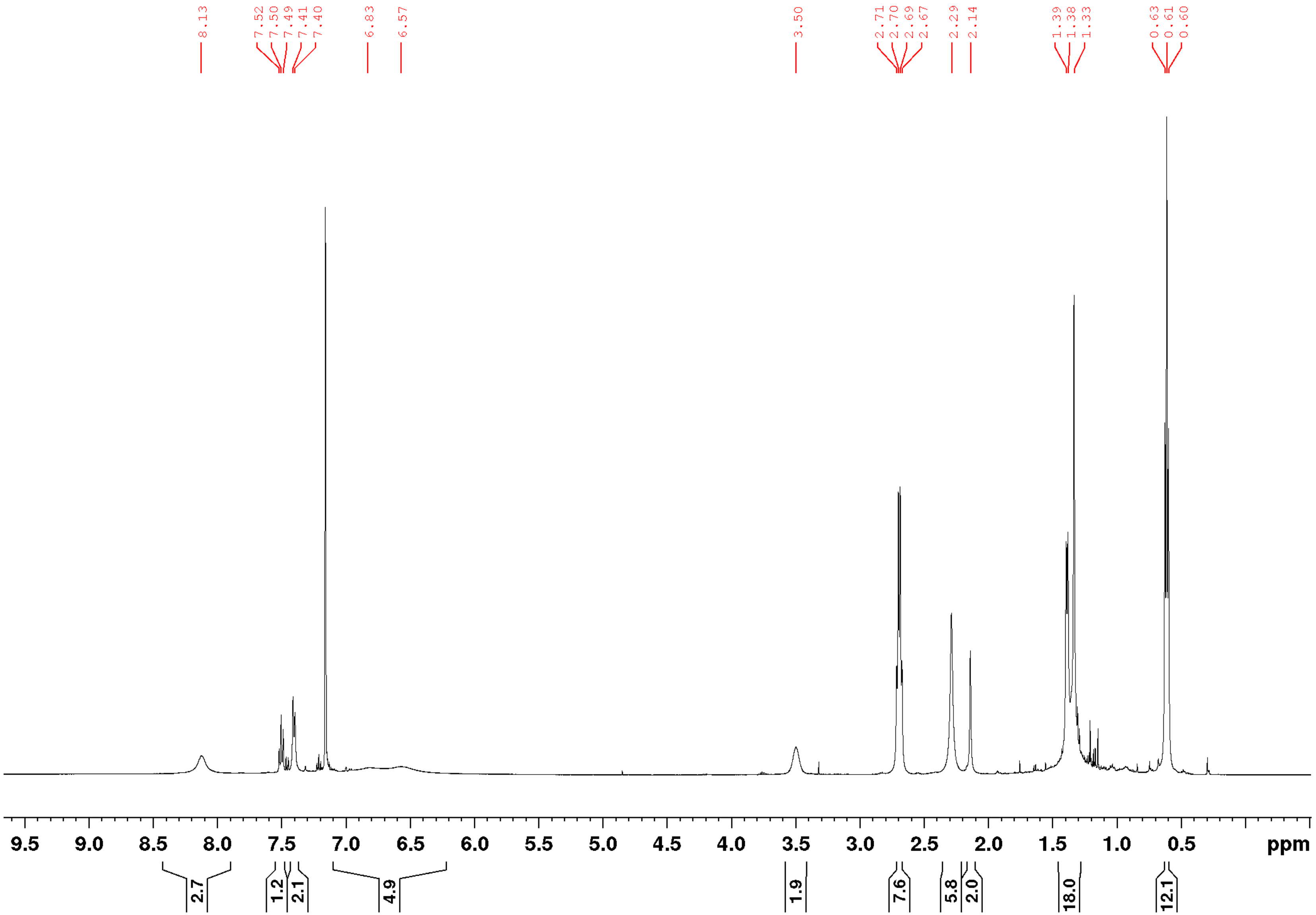


Figure S23. ^{1}H NMR spectrum of **8** in C_6D_6.

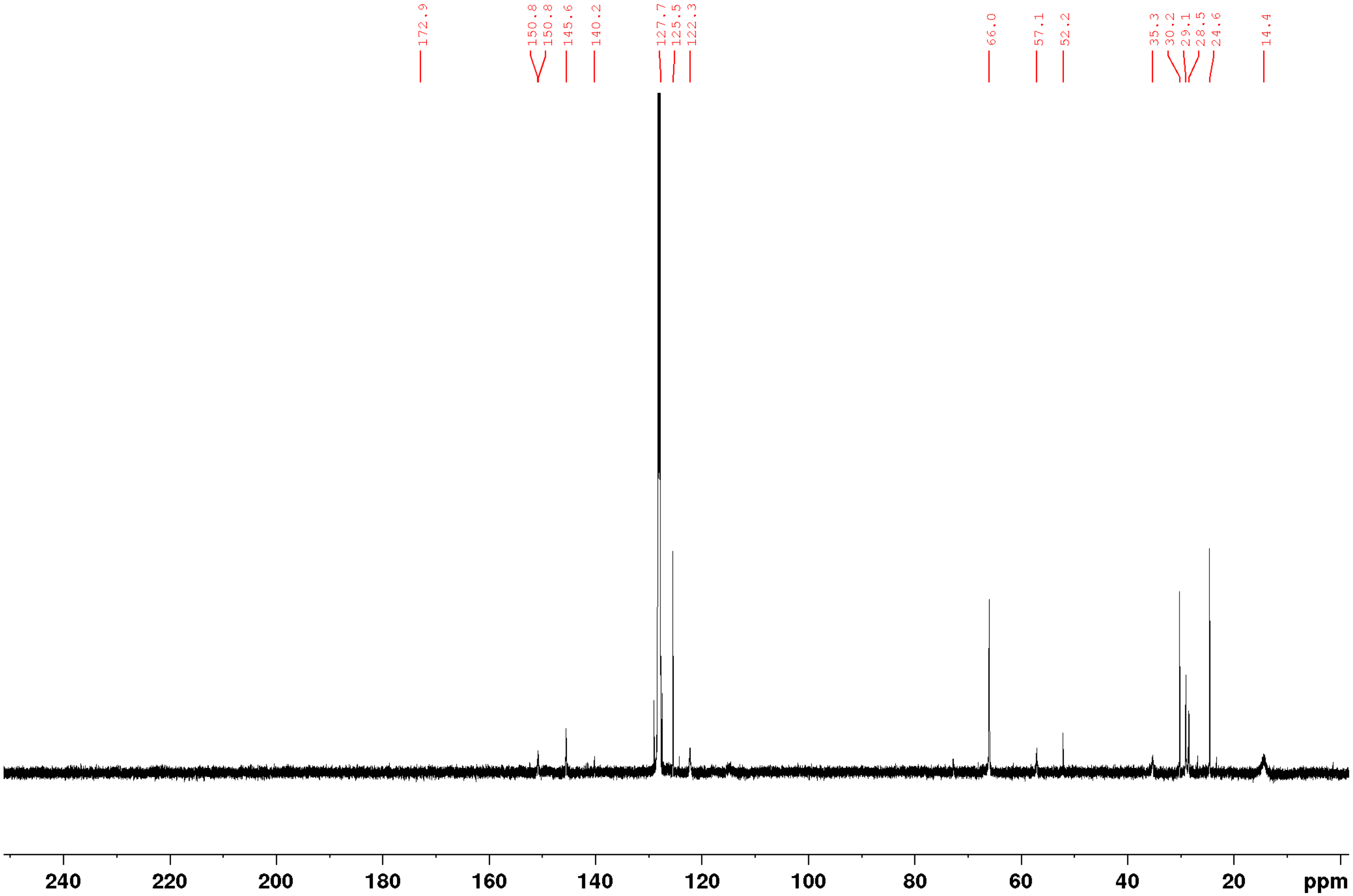


Figure S24. $^{13}C\{^1H\}$ NMR spectrum of **8** in C_6D_6.

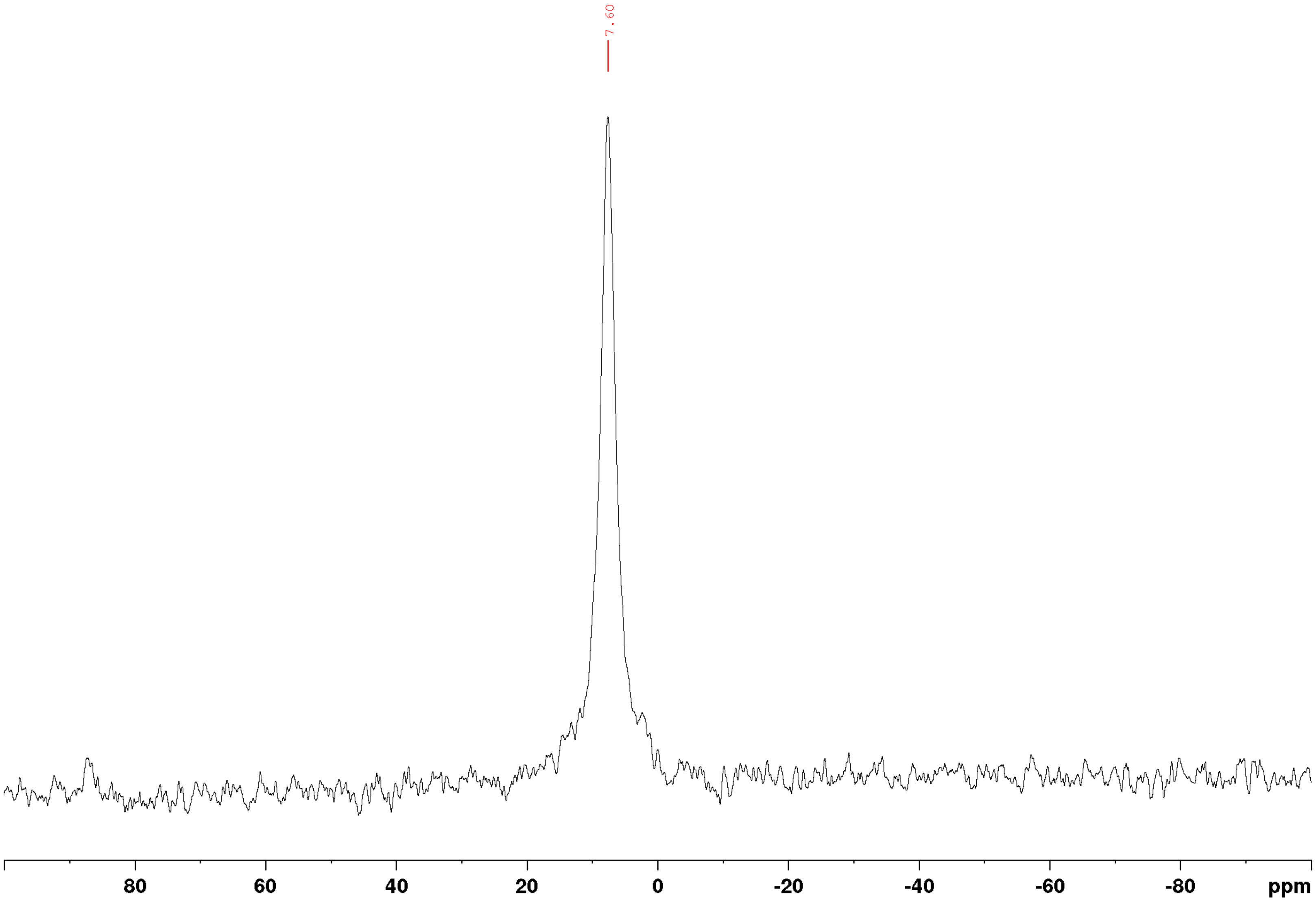


Figure S25. ^{9}Be NMR spectrum of **8** in C_6D_6.

X-ray crystallographic details

The crystal data of **7** were collected on a BRUKER X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The crystal data of **1**, **2**, **3**, **4** and **6** were collected on a BRUKER D8-QUEST diffractometer with a CPA area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The crystal data of **5** and **8** were collected on a RIGAKU XTALAB SYNERGY-R diffractometer with a HPA area detector and multi-layer mirror monochromated $Cu_{K\alpha}$ radiation. The structures were solved using the intrinsic phasing method,[12] refined with the ShelXL program[13] 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 idealised geometric positions.

X-ray data are available free of charge from the Cambridge Crystallographic Data Centre under reference numbers CCDC 2253157 (**1**), 2253158 (**6**), 2253159 (**3**), 2253160 (**7**), 2253161 (**8**), 2253162 (**4**), 2253163 (**5**), 2253164 (**2**).

Refinement details for 1: The asymmetric unit contained a partially occupied and highly disordered diethyl ether molecule located on the intersection of all the rotational axes, which could not be modelled satisfactorily and was therefore suppressed with the Platon program SQUEEZE.[14] 92 electrons were thus removed, corresponding to only ca. two Et_2O molecules per unit cell, i.e. 0.25 per asymmetric unit. The atoms C2, C3 and C4 of the adducted Et_2O residue were modelled as twofold disordered (RESI 11 and 12 Et2O) in a 49:51 ratio. ADPs within the residues were restrained to similarity with SIMU 0.005.

Refinement details for 2: The data showed some twinning but could not be solved satisfactorily as a two- or three-component twin and was integrated as a single domain. Two low-resolution outlying reflections were removed from refinement (0 1 1 and 0 -1 1). Due to a disorder (< 5%) in one PMe_3 group (RESI 4 PHOS), which could not be satisfactorily resolved, the ADPs of P1 and C1 had to be restrained with DELU to avoid Hirschfeld test issues.

Refinement details for 3: The asymmetric unit contains a diethyl ether molecule presenting a 48:52 disorder. The ADP restraints ISOR, SIMU and RIGU were applied to all atoms of this disorder. Nine outlying reflections were omitted.

Refinement details for 4: Both THF ligands were modelled as disordered, one twofold in a 47:53 ratio, the other threefold in a 27:25:48 ratio using the keyword SUMP to add the three free variables up to 1. The ADP restraints SIMU and RIGU were applied to all atoms of these disorders. The outlying reflections 1 2 8 and 2 0 4 were omitted.

Refinement details for 5: The asymmetric unit contains two molecules of 5 and a partially occupied molecule (ca. 39%) of DCM positioned on an inversion centre and modelled as twofold disordered (RESI 5 and 51 DCM) in a 30:9 ratio. ADPs within this disorder were restrained with SIMU 0.005. 1,2- and 1,3-distances within this disorder were restrained to similarity with SAME. One CH_3 group (C12 in RESI 4 NHC) was modelled as twofold rotationally disordered in the three hydrogen atoms and modelled with PART 1 21 and PART 2 -21 in 51:49 ratio.

Refinement details for 6: The CAAC backbone was modelled as twofold disordered in a 16:84 ratio. The ADP restraints SIMU and RIGU were applied to all atoms of these disorders. The ADPs of the atoms C3_2 and C3_12 were additionally equalised using EADP. The outlying reflections 1 1 0, -1 0 1 and -7 1 8 were omitted.

Refinement details for 7: A low-resolution reflection affected by beamstop [0 0 2] was removed from refinement.

Refinement details for 8: Refined as a 2-component twin. Component 2 rotated by -179.6974\% around [0.01 1.00 -0.00] (reciprocal) or [0.01 1.00 -0.00] (direct). The BASF parameter was refined to 28.1%. One Et_2O residue was modelled as twofold disordered (RESI 6 and 16 ETHE) in a 48:52 ratio. ADPs within this disorder were restrained wit SIMU 0.003.

Table S1. Crystal data for **1**.

Empirical formula	$\mathbf{C_{32}H_{36}Be_2O_2\cdot[squeezed\ (C_4H_{10}O)_{0.25}]}$
Formula weight [g/mol]	489.19
Temperature [K]	100(2)
Radiation, λ [Å]	$Mo_{K\alpha}$, 0.71073
Crystal system	tetragonal
Space group	*P*4/*nnc*
Unit cell dimensions	
a [Å]	17.323(3)
b [Å]	17.323(3)
c [Å]	18.354(4)
α [°]	90
β [°]	90
γ [°]	90
Volume [$Å^3$]	5508(2)
Z	8
Calculated density [$Mg\cdot m^{-3}$]	1.180
Absorbtion coefficient [mm^{-1}]	0.070
F(000)	2016
Theta range of collection	1.616 to 25.636°
Reflections collected	16085
Independent reflections	2612
Minimum / maximum transmission	0.6351/0.7453
Refinement method	Full-matrix least-squares on F^2
Data/ parameters/ restraints	2612 / 195 / 144
Goodness-of-fit on F^2	0.995
Final R-indices [$I>2\sigma(I)$]	$R_1 = 0.0484$, $wR_2 = 0.1006$
R indices (all data)	$R_1 = 0.0689$, $wR_2 = 0.1092$
maximum / minimum residual electron density [$e\cdot Å^{-3}$]	0.039 / –0.165

Table S2. Crystal data for **2**.

Empirical formula	$\mathbf{C_{30}H_{34}Be_2P_2}$
Formula weight [g/mol]	474.53
Temperature [K]	100(2)
Radiation, λ [Å]	$Mo_{K\alpha}$, 0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a [Å]	9.580(3)
b [Å]	10.081(3)
c [Å]	14.317(5)
α [°]	82.393(6)
β [°]	76.096(12)
γ [°]	86.912(6)
Volume [$Å^3$]	1330.0(7)
Z	2
Calculated density [$Mg{\cdot}m^{-3}$]	1.185
Absorbtion coefficient [mm^{-1}]	0.180
$F(000)$	504
Theta range of collection	2.917 to 25.680°
Reflections collected	21187
Independent reflections	5024
Minimum / maximum transmission	0.191697/0.745319
Refinement method	Full-matrix least-squares on F^2
Data/ parameters/ restraints	5024 / 313/ 2
Goodness-of-fit on F^2	1.070
Final R-indices [$I>2\sigma(I)$]	$R_1 = 0.0466$, $wR_2 = 0.1148$
R indices (all data)	$R_1 = 0.0538$, $wR_2 = 0.1203$
maximum / minimum residual electron density [$e{\cdot}Å^{-3}$]	0.534 / –0.445

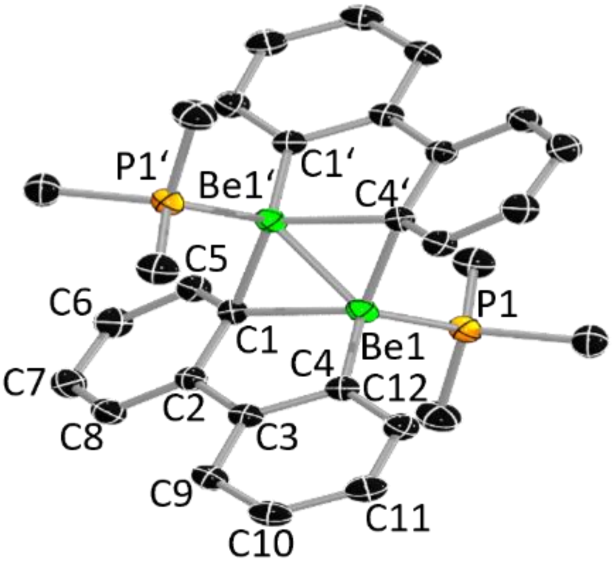


Figure S26 Molecular structure of **2** with atomic displacement ellipsoids shown at the 50% probability level. All H atoms are omitted for clarity. Selected bond lengths [Å] for one of the two dimers present in the asymmetric unit: Be1–P1 2.119(3), Be1–C1 1.929(3), Be1–C1' 1.930(3), Be1–C4 1.759(3), Be1···Be1' 2.048(5), C1–C2 1.431(3), C2–C3 1.485(3), C3–C4 1.418(3).

Table S3. Crystal data for **3**.

Empirical formula	$\mathbf{C_{82}H_{98}Be_2N_4O}$
Formula weight [g/mol]	1173.66
Temperature [K]	100(2)
Radiation, λ [Å]	$Mo_{K\alpha}$, 0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a [Å]	21.498(6)
b [Å]	16.760(4)
c [Å]	20.238(4)
α [°]	90
β [°]	102.810(10)
γ [°]	90
Volume [Å^3]	7110(3)
Z	4
Calculated density [Mg·m^{-3}]	1.096
Absorbtion coefficient [mm^{-1}]	0.063
F(000)	2536
Theta range of collection	2.292 bis 27.505°
Reflections collected	95819
Independent reflections	16312
Minimum / maximum transmission	0.6818/0.7456
Refinement method	Full-matrix least-squares on F^2
Data/ parameters/ restraints	16312 / 868 / 228
Goodness-of-fit on F^2	1.059
Final R-indices [I>2σ(I)]	$R_1 = 0.0475$, $wR_2 = 0.1115$
R indices (all data)	$R_1 = 0.0630$, $wR_2 = 0.1208$
maximum / minimum residual electron density [e· Å^{-3}]	0.547 / –0.445

Table S4. Crystal data for **4**.

Empirical formula	**$C_{20}H_{24}BeO_2$**
Formula weight [g/mol]	305.40
Temperature [K]	100(2)
Radiation, λ [Å]	$Mo_{K\alpha}$,0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a [Å]	8.0692(2)
b [Å]	11.8599(3)
c [Å]	17.4163(4)
α [°]	90
β [°]	99.3000(10)
γ [°]	90
Volume [$Å^3$]	1644.83(7)
Z	4
Calculated density [$Mg\cdot m^{-3}$]	1.233
Absorbtion coefficient [mm^{-1}]	0.076
F(000)	656
Theta range of collection	2.086 to 25.737°
Reflections collected	24102
Independent reflections	3141
Minimum / maximum transmission	0.5189/0.7453
Refinement method	Full-matrix least-squares on F^2
Data/ parameters/ restraints	3141 / 347 / 667
Goodness-of-fit on F^2	1.060
Final R-indices [I>2σ(I)]	R_1 = 0.0494, wR^2 = 0.1356
R indices (all data)	R_1 = 0.0563, wR^2 = 0.1435
maximum / minimum residual electron density [$e\cdot Å^{-3}$]	0.353 / –0.258

Table S5. Crystal data for **5**.

Empirical formula	$\mathbf{C_{33}H_{34}BeN_2\cdot(CH_2Cl_2)_{0.2}}$
Formula weight [g/mol]	484.45
Temperature [K]	100.00(10)
Radiation, λ [Å]	$\mathrm{Cu}_{K\alpha}$, 1.54184
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a [Å]	18.4121(2)
b [Å]	16.0444(2)
c [Å]	19.7334(3)
α [°]	90
β [°]	108.7170(10)
γ [°]	90
Volume [$Å^3$]	5521.17(13)
Z	8
Calculated density [$Mg\cdot m^{-3}$]	1.166
Absorbtion coefficient [mm^{-1}]	0.846
F(000)	2067
Theta range of collection	3.631 to 70.074°
Reflections collected	55988
Independent reflections	10464
Minimum / maximum transmission	0.648/1.000
Refinement method	Full-matrix least-squares on F^2
Data/ parameters/ restraints	10464 / 718 / 69
Goodness-of-fit on F^2	1.031
Final R-indices [$I>2\sigma(I)$]	$R_1 = 0.0416$, $wR_2 = 0.1057$
R indices (all data)	$R_1 = 0.0531$, $wR_2 = 0.1118$
maximum / minimum residual electron density [$e\cdot Å^{-3}$]	0.188 / –0.230

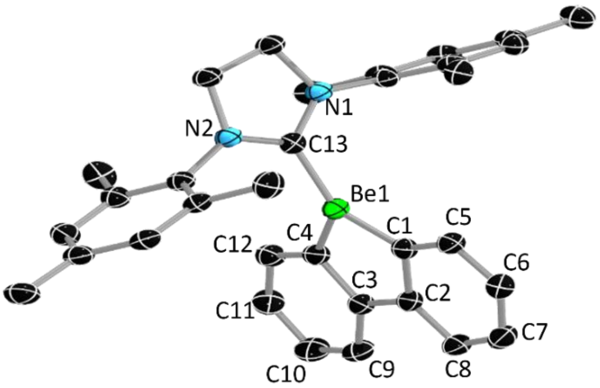


Figure S26 Molecular structure of **5** with atomic displacement ellipsoids shown at the 50% probability level. All H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for one of the two molecules of **5** present in the asymmetric unit: Be1–C13 1.784(2), Be1–C1 1.751(2), Be1–C4 1.745(2), C1–C2 1.4259(18), C2–C3 1.4922(19), C3–C4 1.4212(18).

Table S6. Crystal data for **6**.

Empirical formula	$\mathbf{C_{32}H_{39}BeN}$
Formula weight [g/mol]	446.65
Temperature [K]	100(2)
Radiation, λ [Å]	$\mathrm{Mo}_{\mathrm{K}\alpha}$, 0.71073
Crystal system	monoclinic
Space group	$P1_21/n1$
Unit cell dimensions	
a [Å]	9.619(4)
b [Å]	22.075(5)
c [Å]	13.102(5)
α [°]	90
β [°]	109.446(7)
γ [°]	90
Volume [$Å^3$]	2623.4(15)
Z	4
Calculated density [$\mathrm{Mg{\cdot}m^{-3}}$]	1.131
Absorbtion coefficient [$\mathrm{mm^{-1}}$]	0.063
F(000)	968
Theta range of collection	2.47 to 26.43°
Reflections collected	26469
Independent reflections	5395
Minimum / maximum transmission	0.6560/0.7454
Refinement method	Full-matrix least-squares on F^2
Data/ parameters/ restraints	5395 / 377 / 270
Goodness-of-fit on F^2	1.164
Final R-indices [$I>2\sigma(I)$]	$R_1 = 0.0516$, $wR_2 = 0.1165$
R indices (all data)	$R_1 = 0.0599$, $wR_2 = 0.1207$
maximum / minimum residual electron density [$e{\cdot}Å^{-3}$]	0.274 / –0.207

Table S7. Crystal data for **7**.

Empirical formula	$\mathbf{C_{32}H_{39}BeN}$
Formula weight [g/mol]	446.65
Temperature [K]	100(2)
Radiation, λ [Å]	$Mo_{K\alpha}$, 0.71073
Crystal system	orthorhombic
Space group	*Pbca*
Unit cell dimensions	
a [Å]	17.0285(17)
b [Å]	10.2006(11)
c [Å]	30.307(3)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å^3]	5264.3(9)
Z	8
Calculated density [Mg·m^{-3}]	1.127
Absorbtion coefficient [mm^{-1}]	0.063
F(000)	1936
Theta range of collection	2.423 to 25.679°
Reflections collected	48426
Independent reflections	4996
Minimum / maximum transmission	0.5592/0.7453
Refinement method	Full-matrix least-squares on F^2
Data/ parameters/ restraints	4996 / 316 / 0
Goodness-of-fit on F^2	1.066
Final R-indices [I>2σ(I)]	$R_1 = 0.0620$, $wR_2 = 0.1265$
R indices (all data)	$R_1 = 0.1075$, $wR_2 = 0.1466$
maximum / minimum residual electron density [e· Å^{-3}]	0.243 / –0256

Table S8. Crystal data for **8**.

Empirical formula	$\mathbf{C_{40}H_{59}BeLi_2NO_2}$
Formula weight [g/mol]	608.77
Temperature [K]	100.01(10)
Radiation, λ [Å]	$Cu_{K\alpha}$, 1.54184
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a [Å]	15.8169(2)
b [Å]	15.1518(2)
c [Å]	15.87870(10)
α [°]	90
β [°]	98.2660(10)
γ [°]	90
Volume [$Å^3$]	3765.87(7)
Z	4
Calculated density [$Mg{\cdot}m^{-3}$]	1.074
Absorbtion coefficient [mm^{-1}]	0.472
F(000)	1328
Theta range of collection	2.823 bis 74.946°
Reflections collected	36169
Independent reflections	11142
Minimum / maximum transmission	0.59373/1.00000
Refinement method	Full-matrix least-squares on F^2
Data/ parameters/ restraints	11142 / 476 / 126
Goodness-of-fit on F^2	1.035
Final R-indices [$I>2\sigma(I)$]	$R_1 = 0.0465$, $wR_2 = 0.1125$
R indices (all data)	$R_1 = 0.0569$, $wR_2 = 0.1176$
maximum / minimum residual electron density [$e{\cdot}Å^{-3}$]	0.201 / –0.197

Computational details

All calculations were performed using the Gaussian 16, Revision C.01[15] and the ORCA 5.0.3[16] quantum chemistry program packages. Geometry optimisations were performed at the ωB97X-D[17]/6-31+G(d,p)[18-25] level of theory for i) **7**, ii) a model system of Li_2[**8**] where the Et_2O moieties at the alkali metals were removed, and iii) for the bare dianionic $[\mathbf{8}]^{2-}$ system. Vertical and adiabatic singlet-triplet energy gaps were obtained for Li_2[**8**] and $[\mathbf{8}]^{2-}$ from single-point calculations at the (U)ωB97X-D/6-311++G(d,p)[26,27] level of theory using the appropriate geometries. All optimised geometries were characterised as minima on the corresponding potential energy surfaces by vibrational frequency calculations, which revealed that all eigenvalues in the Hessian matrices are positive.

To assess the biradical/biradicaloid character and the ground-state multiplicity of Li_2[**8**] and $[\mathbf{8}]^{2-}$,[28] single-point calculations using the complete active space self-consistent field (CASSCF)[29] method and broken-symmetry DFT (BS-DFT) were performed. The ma-def2-TZVP[30,31] basis set was chosen for the CASSCF calculations, which were done in combination with the resolution of identity approximation for coulomb integrals (RI-J)[32,33] and the numerical chain-of-spheres integration for the Hartree-Fock exchange integrals (COSX).[34-36] Despite our best efforts, all attempts to optimise the CASSCF wave function of the bare $[\mathbf{8}]^{2-}$ system have failed, which prompted us to use BS-DFT for this system instead. The biradical character y_0[36-38] was obtained using the natural orbital occupation numbers (NOON)[39] from either CASSCF(2,2) or BS-DFT calculations:

$$y_0 = 1 - \frac{ON_{HONO} - ON_{LUNO}}{1 + \left(\frac{ON_{HONO} - ON_{LUNO}}{2}\right)^2} \tag{S1}$$

where ON_{HONO} and ON_{LUNO} are the occupation numbers of the highest occupied natural orbital (HONO) and the lowest unoccupied natural orbital (LUNO). Plots of the CASSCF active space natural orbitals of Li_2[**8**] and the singly-occupied molecular orbitals of $[\mathbf{8}]^{2-}$ are shown in Figures S27-28.

To investigate the aromaticity character of **3**, **6** and Li_2[**8**], calculations of the nucleus-independent chemical shift (NICS)[40-42] at the ωB97X-D/6-311++G(d,p) level of theory were performed. These were accomplished by using the gauge independent atomic orbital (GIAO)[43-45] method. The corresponding values were obtained by placing dummy atoms in the centres of the different rings and at distances of 0.1 Å along the axis perpendicular to the ring centres. For the NICS$_{zz}$-scan, the zz-component of the magnetic shielding tensor was used.[46] For the systems containing alkali metals the NICS$_{zz}$-scan was obtained by calculating the difference of the magnetic shieldings between the full system and the sole metal atoms in the same geometry. Furthermore, the anisotropy of the induced current density (ACID)[47-48] method at the ωB97X-D/6-311++G(d,p) level of theory was used to further confirm and support the results.

Finally, the bonding situation of **7** was evaluated by calculations based on the intrinsic bond orbital (IBO) method.[49] The beryllium-alkene interaction in **7** was also evaluated by distinct bond order analyses, namely Mayer bond order,[50] fuzzy bond order,[51] Wiberg bond index,[52] and natural binding index.[53] The IBO calculations were performed using the IBOView software, version v20211019-RevA,[49,54] while the bond order and BS-DFT analyses were done in Multiwfn 3.8.[55]

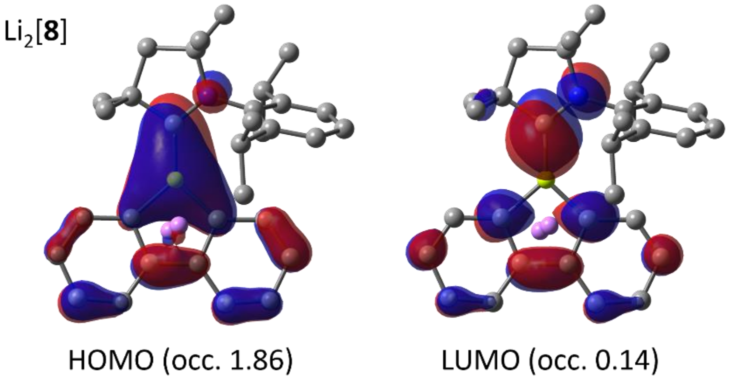
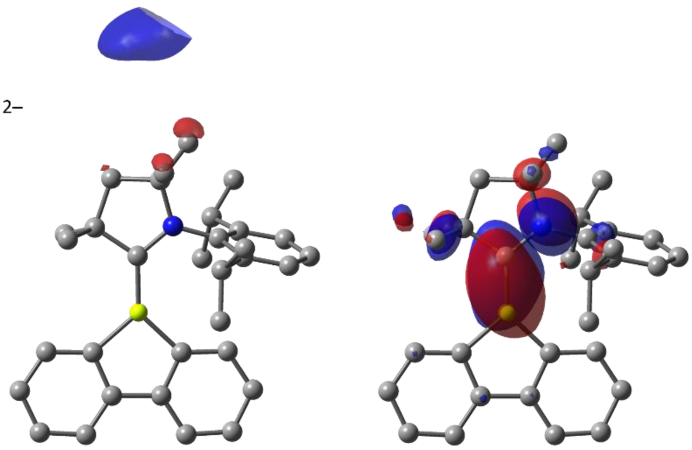


Figure S27. Active space natural orbitals of the lowest singlet state of Li$_2$[**8**] calculated at the CASSCF(2,2)/ma-def2-TZVP level of theory. Orbital occupancies (occ.) are shown in parenthesis. Isosurface values = 0.03.

[**8**]$^{2-}$



SOMO$_1$ (occ. 1.01) SOMO$_2$ (occ. 0.99)

Figure S28. Frontier singly-occupied molecular orbitals of the open-shell singlet state of [**8**]$^{2-}$ calculated at the UωB97X-D/6-311++G(d,p) level of theory. Natural orbital occupancies (occ.) are shown in parenthesis. Isosurface values = 0.03.

Cartesian coordinates

Model system of Compound 8, ωB97X-D/6-31+G(d,p)

Geometry of the lowest singlet state

Energy = –1327.19672937 E_h

C	-2.805409000	0.999375000	-0.365230000
Be	-1.119310000	0.459023000	-0.508848000
C	-3.525317000	2.238425000	-0.309246000
H	-2.977042000	3.172815000	-0.408065000
C	-4.887762000	2.332679000	-0.145047000
H	-5.366076000	3.308260000	-0.116199000
C	-5.679165000	1.159885000	-0.018474000
H	-6.754758000	1.239035000	0.110303000
C	-5.076003000	-0.071121000	-0.061064000
H	-5.683669000	-0.967884000	0.036795000
C	-3.663916000	-0.180894000	-0.229293000
C	-2.925471000	-1.441310000	-0.289228000
C	-3.509574000	-2.739543000	-0.194870000
H	-4.585322000	-2.847871000	-0.076102000
C	-2.720857000	-3.860880000	-0.248092000
H	-3.168456000	-4.847695000	-0.170656000
C	-1.315550000	-3.726137000	-0.410109000
H	-0.691107000	-4.614944000	-0.452474000
C	-0.744545000	-2.479901000	-0.519496000
H	0.330974000	-2.431064000	-0.649163000
C	-1.485660000	-1.257130000	-0.459419000
C	0.307405000	1.376573000	-0.273642000
N	1.552702000	0.968831000	0.038434000
C	0.340329000	2.907717000	-0.290098000
C	1.840143000	3.269545000	-0.265230000
H	2.185502000	3.476051000	-1.284229000
H	2.043863000	4.162055000	0.334365000
C	2.577682000	2.040818000	0.278417000
C	-0.373168000	3.454254000	0.962157000

H	-1.410109000	3.118814000	0.999748000
H	-0.354787000	4.550855000	0.956698000
H	0.118693000	3.115243000	1.879055000
C	-0.317801000	3.465340000	-1.558749000
H	-1.362206000	3.160769000	-1.631649000
H	0.195455000	3.090787000	-2.450504000
H	-0.264334000	4.561145000	-1.564789000
C	2.912543000	2.157151000	1.769604000
H	2.022031000	2.303231000	2.383778000
H	3.579392000	3.010192000	1.927831000
H	3.432459000	1.258711000	2.111947000
C	3.888933000	1.796222000	-0.472087000
H	4.581087000	2.611901000	-0.240698000
H	3.741907000	1.782713000	-1.553091000
H	4.360701000	0.857268000	-0.167447000
C	1.918024000	-0.409713000	0.203938000
C	1.736349000	-1.052715000	1.445952000
C	2.231364000	-2.350045000	1.596419000
H	2.100817000	-2.862741000	2.545112000
C	2.867088000	-3.007023000	0.552068000
H	3.251127000	-4.012480000	0.693266000
C	2.965371000	-2.389377000	-0.686863000
H	3.406269000	-2.930823000	-1.518337000
C	2.477580000	-1.096564000	-0.891918000
C	1.742680000	-0.303941000	3.896119000
H	1.118924000	0.149431000	4.674244000
H	2.631202000	0.316399000	3.772797000
H	2.068714000	-1.282351000	4.264492000
C	0.939168000	-0.447923000	2.595578000
H	0.598586000	0.541056000	2.277205000
C	-0.311667000	-1.304879000	2.883005000
H	-1.045481000	-0.727529000	3.464601000
H	-0.062751000	-2.182470000	3.488401000
H	-0.752179000	-1.690542000	1.957874000

C	1.382631000	-1.216443000	-3.143666000
H	0.400163000	-1.075418000	-2.684673000
H	1.572641000	-2.292265000	-3.231071000
H	1.362930000	-0.790335000	-4.152986000
C	2.470514000	-0.527921000	-2.304046000
H	2.193670000	0.526765000	-2.242570000
C	3.832738000	-0.635030000	-3.001974000
H	4.640640000	-0.223158000	-2.390860000
H	3.810147000	-0.091904000	-3.952436000
H	4.084689000	-1.676020000	-3.230446000
Li	-2.179146000	-0.224675000	1.361160000
Li	-2.580201000	-0.302285000	-2.099899000

Model system of Compound 8, ωB97X-D/6-31+G(d,p)

Geometry of the lowest triplet state

Energy = –1327.17694259 E_h

C	-2.805409000	0.999375000	-0.365230000
Be	-1.119310000	0.459023000	-0.508848000
C	-3.525317000	2.238425000	-0.309246000
H	-2.977042000	3.172815000	-0.408065000
C	-4.887762000	2.332679000	-0.145047000
H	-5.366076000	3.308260000	-0.116199000
C	-5.679165000	1.159885000	-0.018474000
H	-6.754758000	1.239035000	0.110303000
C	-5.076003000	-0.071121000	-0.061064000
H	-5.683669000	-0.967884000	0.036795000
C	-3.663916000	-0.180894000	-0.229293000
C	-2.925471000	-1.441310000	-0.289228000
C	-3.509574000	-2.739543000	-0.194870000
H	-4.585322000	-2.847871000	-0.076102000
C	-2.720857000	-3.860880000	-0.248092000
H	-3.168456000	-4.847695000	-0.170656000
C	-1.315550000	-3.726137000	-0.410109000
H	-0.691107000	-4.614944000	-0.452474000

C	-0.744545000	-2.479901000	-0.519496000
H	0.330974000	-2.431064000	-0.649163000
C	-1.485660000	-1.257130000	-0.459419000
C	0.307405000	1.376573000	-0.273642000
N	1.552702000	0.968831000	0.038434000
C	0.340329000	2.907717000	-0.290098000
C	1.840143000	3.269545000	-0.265230000
H	2.185502000	3.476051000	-1.284229000
H	2.043863000	4.162055000	0.334365000
C	2.577682000	2.040818000	0.278417000
C	-0.373168000	3.454254000	0.962157000
H	-1.410109000	3.118814000	0.999748000
H	-0.354787000	4.550855000	0.956698000
H	0.118693000	3.115243000	1.879055000
C	-0.317801000	3.465340000	-1.558749000
H	-1.362206000	3.160769000	-1.631649000
H	0.195455000	3.090787000	-2.450504000
H	-0.264334000	4.561145000	-1.564789000
C	2.912543000	2.157151000	1.769604000
H	2.022031000	2.303231000	2.383778000
H	3.579392000	3.010192000	1.927831000
H	3.432459000	1.258711000	2.111947000
C	3.888933000	1.796222000	-0.472087000
H	4.581087000	2.611901000	-0.240698000
H	3.741907000	1.782713000	-1.553091000
H	4.360701000	0.857268000	-0.167447000
C	1.918024000	-0.409713000	0.203938000
C	1.736349000	-1.052715000	1.445952000
C	2.231364000	-2.350045000	1.596419000
H	2.100817000	-2.862741000	2.545112000
C	2.867088000	-3.007023000	0.552068000
H	3.251127000	-4.012480000	0.693266000
C	2.965371000	-2.389377000	-0.686863000
H	3.406269000	-2.930823000	-1.518337000

C	2.477580000	-1.096564000	-0.891918000
C	1.742680000	-0.303941000	3.896119000
H	1.118924000	0.149431000	4.674244000
H	2.631202000	0.316399000	3.772797000
H	2.068714000	-1.282351000	4.264492000
C	0.939168000	-0.447923000	2.595578000
H	0.598586000	0.541056000	2.277205000
C	-0.311667000	-1.304879000	2.883005000
H	-1.045481000	-0.727529000	3.464601000
H	-0.062751000	-2.182470000	3.488401000
H	-0.752179000	-1.690542000	1.957874000
C	1.382631000	-1.216443000	-3.143666000
H	0.400163000	-1.075418000	-2.684673000
H	1.572641000	-2.292265000	-3.231071000
H	1.362930000	-0.790335000	-4.152986000
C	2.470514000	-0.527921000	-2.304046000
H	2.193670000	0.526765000	-2.242570000
C	3.832738000	-0.635030000	-3.001974000
H	4.640640000	-0.223158000	-2.390860000
H	3.810147000	-0.091904000	-3.952436000
H	4.084689000	-1.676020000	-3.230446000
Li	-2.179146000	-0.224675000	1.361160000
Li	-2.580201000	-0.302285000	-2.09989900

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