Electronic Supporting Information for:

# Ring expansion of an antiaromatic beryllole: Synthesis of novel five-, seven- and nine-membered beryllacycles

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**Synthetic Details**

**General synthetic considerations. WARNING: beryllium-containing compounds are generally considered to be highly toxic to humans; all appropriate laboratory safety measures must be followed, and all wastes must be disposed of according to local regulations**.[1-3] All reactions were performed under an atmosphere of dry argon using standard Schlenk or glovebox techniques. To minimize contact with the reaction media, reactions were performed in J. Young flasks or sealable NMR tubes. $BeCl_2$ was purchased from ONYXMET, and sulphur powder and $CS_2$ were purchased from Thermo Scientific Chemicals and used as received. All solvents were purified by distillation using the appropriate drying agents, deoxygenated using three freeze–pump–thaw cycles, and stored over molecular sieves under dry argon before use. The deuterated solvents used for NMR spectroscopy were purchased from Cambridge Isotope Laboratories, deoxygenated by freeze–pump–thaw cycles, and dried under an argon atmosphere over molecular sieves. The following compounds were synthesized according to literature methods: CAAC,[4,5] 1,4-dilithiotetraphenylbutadiene[6], CAAC-tetraphenylberyllole[7] (**1**), 2,6-dibromo-4-methylphenyl azide[8] and (tert-butylimino)mesitylborane[9]. NMR chemical shifts are reported in ppm and coupling constants in Hz. $^{1}H$, $^{9}Be$, and $^{13}C$ NMR spectroscopy data were obtained at ambient temperature using either a Bruker DRX-400 (operating at 400 MHz for $^{1}H$, 56 MHz for $^{9}Be$ and 100 MHz for $^{13}C$) or a Bruker Avance 500 NMR spectrometer (operating at 500 MHz for $^{1}H$ and 125 MHz for $^{13}C$). $^{1}H$ NMR spectra were referenced via residual proton resonances of $C_6D_6$ ($^{1}H$, 7.16 ppm) and THF-$d_8$ ($^{1}H$, 3.58, 1.72 ppm). $^{13}C$ NMR spectra were referenced to $C_6D_6$ ($^{13}C$, 128.06 ppm), THF-$d_8$ ($^{13}C$, 67.21, 25.31 ppm).

**Synthesis of [(CAAC)$BeS_2C_4Ph_4$] (2).** Sulphur (14.8 mg, 57.6 µmol, 0.25 equiv.) was added to a solution of **1** (150 mg, 230 µmol, 1.0 equiv.) in hexane. The solution was stirred overnight, and a color change to pale yellow was observed. The solvent was removed *in vacuo*, at which point the pale-yellow residue was washed with pentane (3 x 1.0 mL) and recrystallized from toluene at –30 °C to yield **2** as yellow crystals (44%, 102 mg, 102 µmol). **$^{1}H$ NMR** (500.1 MHz, $C_6D_6$): *δ* 7.40 – 7.37 (m, 4H, C$H_{aromatic}$), 7.11 – 7.10 (m, 2H, C$H_{aromatic}$), 7.07 – 7.04 (m, 4H, C$H_{aromatic}$), 7.00 – 6.98 (m, 5H, C$H_{aromatic}$), 6.96 – 6.95 (m, 1H, C$H_{aromatic}$), 6.95 – 6.92 (m, 2H, C$H_{aromatic}$), 6.92 – 6.91 (m, 2H, C$H_{aromatic}$), 6.90 – 6.89 (m, 3H, C$H_{aromatic}$), 2.87 (sept., 2H, $^{3}J$ = 6.82 Hz, C$H_{i\mathrm{Pr}}$), 1.78 (s, 2H, C$H_{2\text{-CAAC}}$), 1.46 (s, 6H, C$H_{3\text{-CAAC}}$), 1.39 (d, 6H, $J^{3}$ = 6.82 Hz, C$H_{3\text{-}i\mathrm{Pr}}$), 1.19 (d, 6H, $J^{3}$ = 6.82 Hz, C$H_{3\text{-}i\mathrm{Pr}}$), 0.98 (s, 6H, C$H_{3\text{-CAAC}}$). **$^{9}Be$ NMR** ($C_6D_6$, 56 MHz): δ 18.7 (s). **$^{13}C\{^{1}H\}$ NMR** (125.8 MHz, $C_6D_6$): *δ* 213.53 ($Cq_{Carbene}$), 147.86 (Cq), 140.11 (Cq), 139.31 (Cq), 137.13 (Cq), 134.88 (Cq), 133.77 (Cq), 131.30 ($CH_{aromatic}$), 130.84 ($CH_{aromatic}$), 129.65 ($CH_{aromatic}$), 128.78 ($CH_{aromatic}$), 127.60 ($CH_{aromatic}$), 127.05 ($CH_{aromatic}$), 126.98 ($CH_{aromatic}$),

124.82 ($CH_{aromatic}$), 68.21 ($Cq_{CAAC}$), 51.25 ($CH_{2\text{-}CAAC}$), 49.98 ($Cq_{CAAC}$), 31.65 ($CH_{3\text{-}CAAC}$), 29.64 ($CH_{i\text{Pr}}$), 28.96 ($CH_{3\text{-}i\text{Pr}}$), 27.01 ($CH_{3\text{-}iPr}$), 23.49 ($CH_{3\text{-}CAAC}$) ppm. **Elemental analysis:** Calculated for $C_{48}H_{51}BeNS_2$: C 80.62, H 7.19, N 1.96, S 8.97; found C 79.07, H 7.47, N 2.06, S 10.24.

**Synthesis of [(THF)$_2$BeS$_2$C$_4$Ph$_4$] (3).** Sulphur (7.88 mg, 30.7 µmol, 0.5 equiv.) was added to a solution of **1** (40.0 mg, 61.5 µmol, 1.0 equiv.) in THF (2.0 mL). The solution was stirred overnight, and a color change to pale yellow was observed. The solvent was removed in vacuo at which point the pale-yellow residue was washed with pentane (3 x 1.0 mL) and recrystallized from dichloromethane at –30 °C to yield **3** as colorless crystals (79%, 28.0 mg, 49.0 µmol). **$^1$H NMR** (500.1 MHz, $CD_2Cl_2$): *δ* 7.30 – 7.27 (m, 4H, C*H*$_{aromatic}$), 7.25 – 7.21 (m, 1H, C*H*$_{aromatic}$), 7.08 – 7.03 (m, 7H, C*H*$_{aromatic}$), 7.01 – 6.97 (m, 2H, C*H*$_{aromatic}$), 6.93 – 6.88 (m, 4H, C*H*$_{aromatic}$), 6.88 – 6.84 (m, 2H, C*H*$_{aromatic}$), 3.87 (bs, 8H, C*H*$_{2\text{-THF}}$), 1.73 (bs, 8H, C*H*$_{2\text{-THF}}$) ppm. **$^9$Be NMR** ($CD_2Cl_2$, 56 MHz): δ 10.0 (s). **$^{13}$C{$^1$H}** NMR ($CD_2Cl_2$, 125 MHz): *δ* 148.4 (*C*q$_{aromatic}$), 144.2 (*C*q$_{aromatic}$), 142.3 (*C*q$_{aromatic}$), 139.8 (*C*q$_{aromatic}$), 130.8 (*C*H$_{aromatic}$), 130.2 (*C*H$_{aromatic}$), 127.3 (*C*H$_{aromatic}$), 127.3 (*C*H$_{aromatic}$), 125.4 (*C*H$_{aromatic}$), 125.4 (*C*H$_{aromatic}$), 25.5 (*C*H$_{2\text{-THF}}$) ppm. **Elemental analysis:** Calculated for $C_{36}H_{36}BeO_2S_2$: C 75.35, H 6.32, S 11.17; found C 74.77, H 7.61, S 13.19.

**Synthesis of [(CAAC)Be(*p*-Me-2,6-Br$_2$-(C$_6$H$_2$)$_2$C$_4$Ph$_4$] (4).** 2,6-dibromo-4-methylphenylazide (134 mg, 461 µmol, 2.0 equiv.) was added to a solution of **1** (150 mg, 230 µmol, 1.0 equiv.) in benzene (3.0 mL). The solution was stirred for 1 h, and the solvent was removed in vacuo. The residue was then washed with pentane (3 x 1.0 mL) and recrystallized from a saturated benzene solution. Compound **4** was obtained as yellow crystals (56%, 158 mg, 128 µmol). **$^1$H NMR** ($C_6D_6$, 500 MHz): *δ* 7.44 (bs, 5H, $CH_{aromatic}$), 7.19 – 7.18 (m, 5H, $CH_{aromatic}$), 7.03 (dd, 2H, $^3J$ = 7.93 Hz, $^4J$ = 1.73 Hz, $CH_{meta\text{-}Dipp}$), 6.95 – 6.80 (m, 15H, $CH_{aromatic}$), 3.51 (sept, 1H, $^3J$ = 6.56 Hz, $CH_{iPr\text{-}Dipp}$), 2.46 (sept, 1H, $^3J$ = 6.66 Hz, $CH_{iPr\text{-}Dipp}$), 1.73 (s, 6H, $CH_{3\text{-}para}$), 1.70 (s, 3H, $CH_{3\text{-}CAAC}$), 1.58 (s, 3H, $CH_{3\text{-}CAAC}$), 1.44 (d, 3H, $^3J$ = 6.56 Hz, $CH_{3\text{-}iPr\text{-}Dipp}$), 1.39 (s, 1H, $CH_{2\text{-}CAAC}$), 1.36 (s, 1H, $CH_{2\text{-}CAAC}$), 1.06 (s, 3H, $CH_{3\text{-}CAAC}$), 1.05 (d, 3H, $^3J$ = 6.66 Hz, $CH_{3\text{-}iPr\text{-}Dipp}$), 0.99 – 0.96 (m, 6H, $CH_{3\text{-}Dipp}$ + $CH_{3\text{-}CAAC}$), 0.67 (s, 3H, $CH_{3\text{-}CAAC}$). **$^9$Be NMR** ($C_6D_6$, 56 MHz): δ 14.3 (br). **$^{13}$C{$^1$H} NMR** ($C_6D_6$, 125 MHz): *δ* 241.5 (*C*$_q$ CAAC HMBC), 146.9 (*C*$_q$), 145.7 (*C*$_q$), 140.6 (*C*$_q$), 136.1 (*C*$_q$), 133.4 (*C*$_q$), 133.2 (*C*H$_{aromatic}$), 132.0 (*C*H$_{aromatic}$), 130.3 (*C*H$_{aromatic}$), 128.40 (*C*q), 128.2 (*C*H$_{aromatic}$), 128.1 (*C*q), 128.1 (*C*q), 127.9 (*C*q), 127.4 (*C*H$_{aromatic}$), 127.2 (*C*H$_{aromatic}$), 126.5 (*C*H$_{aromatic}$), 126.4 (*C*H$_{aromatic}$), 126.3 (*C*H$_{aromatic}$), 125.4 (*C*H$_{aromatic}$), 83.5 (Cq), 56.2 (*C*q), 49.8 (*C*H$_2$), 30.9 (*C*H$_3$), 30.8 (*C*H$_3$), 30.2 (*C*H$_3$), 29.8 (CH), 28.6 (*C*H$_3$), 28.1 (CH), 27.4 (*C*H$_3$), 26.7 (*C*H$_3$), 24.1 (*C*H$_3$), 23.4 (*C*H$_3$), 19.7 (*C*H$_3$). **HRMS (LIFDI):** calculated for $C_{62}H_{61}BeBr_4N_7$ ($M^+$+H): 1228.1838; found 1228.1776.

**Synthesis of [(CAAC)Be($CS_2$)$C_4Ph_4$] (5).** **1** (20.0 mg, 30.7 µmol, 1.0 equiv.) was dissolved in toluene (1 mL) and cooled to –77 °C. $CS_2$ (153.5 µmol, 0.01 mL, 5.0 equiv.) was added dropwise, and the reaction was allowed to warm up to room temperature. During this process, a color change to dark red was observed. After 1 h at room temperature, the solvent was removed in vacuo and the residue was washed with hexane (2 x 0.5 mL). The residue was then recrystallized from a saturated benzene/hexane solution to give **5** (95%, 21.2 mg, 29.2 µmol) as red crystals. **$^1$H NMR** ($C_6D_6$, 500 MHz): *δ* 8-09 – 8.06 (m, 2H, $H_{aromatic}$), 7.65 – 7.62 (m, 2H, $H_{aromatic\text{-}Dipp\text{-}meta}$), 7.62 – 7.56 (m, 2H, $H_{aromatic}$), 7.12 – 7.14 (m, 5H, $H_{aromatic}$), 7.07 – 7.02 (m, 3H, $H_{aromatic}$), 7.01 – 6.96 (m, 2H, $H_{aromatic}$), 6.93 (s, 1H, $H_{aromatic}$), 6.92 – 6.90 (m, 1H, $H_{aromatic}$), 6.90 – 6.89 (m, 1H, $H_{aromatic}$), 6.88 – 6.87 (m, 1H, $H_{aromatic}$), 6.85 – 6.82 (m, 3H, $H_{aromatic}$), 6.79 (tt, 1H, $^3$J = 7.38 Hz, $^4$J = 1.40 Hz $H_{aromatic\text{-}Dipp\text{-}para}$), 2.45 (sept., 2H, $^3$J = 6.73 Hz, CH), 1.39 (d, 3H, $^3$J = 6.73 Hz, $CH_{3\text{-}iPr}$), 1.31 (s, 3H, $CH_3$), 1.26 (s, 3H, $CH_3$), 1.21 (s, 2H, $CH_2$), 1.20 (d, 3H, $^3$J = 6.73 Hz, $CH_{3\text{-}iPr}$), 1.00 (d, 3H, $^3$J = 6.73 Hz, $CH_{3\text{-}iPr}$), 0.95 (d, 3H, $^3$J = 6.73 Hz, $CH_{3\text{-}iPr}$), 0.74 (s, 3H, $CH_3$), 0.72 (s, 3H, $CH_3$). **$^9$Be NMR** ($C_6D_6$, 56 MHz): δ 23.1 (br). **$^{13}$C{$^1$H}** NMR ($C_6D_6$,125 MHz): *δ* 239.3 (carbene *C*q), 161.8 (*C*$q_{aromatic}$), 149.5 (*C*$q_{aromatic\text{-}Dipp}$), 145.0 (*C*$q_{aromatic\text{-}Dipp}$), 145.0 (*C*$q_{aromatic}$), 144.6 (*C*$q_{aromatic}$), 138.0 (*C*$q_{aromatic}$), 137.9 (*C*$q_{aromatic}$), 137.6 (*C*$q_{aromatic}$), 137.2 (*C*$q_{aromatic}$), 133.2 (*C*$q_{aromatic}$), 131.0 (*C*$H_{aromatic}$), 130.7 (*C*$H_{aromatic}$), 130.6 (*C*$H_{aromatic\text{-}Dipp\text{-}meta}$), 130.5 (*C*$H_{aromatic}$), 127.5 (*C*$H_{aromatic}$), 126.4 (*C*$H_{aromatic}$), 126.1 (*C*$H_{aromatic\text{-}Dipp\text{-}para}$), 125.9 (*C*$H_{aromatic}$), 125.8 (*C*$H_{aromatic}$), 125.8 (*C*$H_{aromatic}$), 125.5 (*C*$H_{aromatic}$), 82.1 ($Cq_{CAAC\text{-}CH3}$), 77.9 ($Cq_{CAAC\text{-}CH3}$), 54.3 ($Cq_{CAAC\text{-}CH2}$), 50.0 (*C*$H_2$), 29.3 ($CH_{iPr}$), 29.0 ($CH_{iPr}$), 28.7 ($Cq_{CAAC\text{-}CH3}$), 28.2 ($Cq_{CAAC\text{-}CH3}$), 28.2 ($Cq_{CAAC\text{-}CH3}$), 27.7 ($Cq_{CAAC\text{-}CH3}$), 26.8 ($Cq_{Dipp\text{-}CH3}$), 26.7 ($Cq_{Dipp\text{-}CH3}$), 24.4 ($Cq_{Dipp\text{-}CH3}$), 24.4 ($Cq_{Dipp\text{-}CH3}$). **HRMS (LIFDI):** calculated for $C_{49}H_{51}BeNS_2$ ($M^+$): 726.3579; found 726.3569.

**Synthesis of [(MesBN*t*Bu)$_2$Be$C_4Ph_4$] (6).** [MesBN*t*Bu] (185 mg, 922 µmol, 0.84 M in heptane, 3.0 equiv) was added dropwise to a solution of **1** (200 mg, 307 µmol, 1.0 equiv) in toluene at –77 °C. Upon addition, a color change to green was observed. After stirring the reaction mixture for 1 h at –77 °C, the solution was allowed to warm up to room temperature. The solvent was removed in vacuo, and the green residue was washed with hexamethyldisiloxane (3 x 8 mL) and recrystallized from hexane at –30 °C. Compound **6** was obtained as colorless crystals (48.0 mg, 62.5 µmol, 20%). **$^1$H NMR** ($C_6D_6$, 500 MHz): *δ* 7.84 (dd, 4H, $^3$J = 8.50 Hz, $^4$J = 1.14 Hz, C*H*$_{Ph}$), 7.69 (bs, 2H, C*H*$_{Ph}$), 7.16 (bs, 2H, C*H*$_{Ph}$), 7.06 (bs, 2H, C*H*$_{Ph}$), 6.99 (dd, 4H, $^3$J = 8.14 Hz, $^3$J = 7.55 Hz, C*H*$_{Ph}$), 6.86 – 6.83 (m, 2H, C*H*$_{Ph}$), 6.79 (bs, 2H, C*H*$_{Ph}$), 6.70 – 6.68 (m, 2H, C*H*$_{Ph}$), 6.60 (bs, 2H, $CH_{Mes}$), 6.43 (bs, 2H, $CH_{Mes}$), 2.56 (s, 6H, $CH_{3\text{-}Mes}$), 1.93 (s, 6H, $CH_{3\text{-}Mes}$), 1.57 (s, 18H, $CH_{3\text{-}tBu}$), 1.31 (s, 6H, $CH_{3\text{-}Mes}$). **$^9$Be NMR** ($C_6D_6$, 56 MHz): δ 10.9 (br). **$^{11}$B NMR** (160.47 MHz, $C_6D_6$): *δ* 41.3. **$^{13}$C{$^1$H} NMR** ($C_6D_6$, 125 MHz): *δ* 149.6 (*C*$_q$), 145.7 (*C*$_q$), 143.8 (*C*$_{q\text{-}Ph}$), 138.9 (*C*$_q$-Mes), 138.1 (*C*$_q$-Mes), 136.0 (*C*$_{q\text{-}Ph}$), 133.2 (*C*H$_{Ph}$), 128.5 (*C*H$_{Ph}$), 129.3

($CH_{Ph}$), 127.5 ($CH_{Ph}$), 127.2 ($CH_{Mes}$), 126.6 ($CH_{Mes}$), 126.0 ($CH_{Ph}$), 53.2 ($C_{q\text{-}t\text{Bu}}$), 33.4 ($CH_{3\text{-}t\text{Bu}}$), 25.8 ($CH_{3\text{-Mes}}$), 22.1 ($CH_{3\text{-Mes}}$), 21.0 ($CH_{3\text{-Mes}}$). calculated for $C_{54}H_{60}BeB_2N_2$ ($M^+$): 767.5059; found 767.5041.

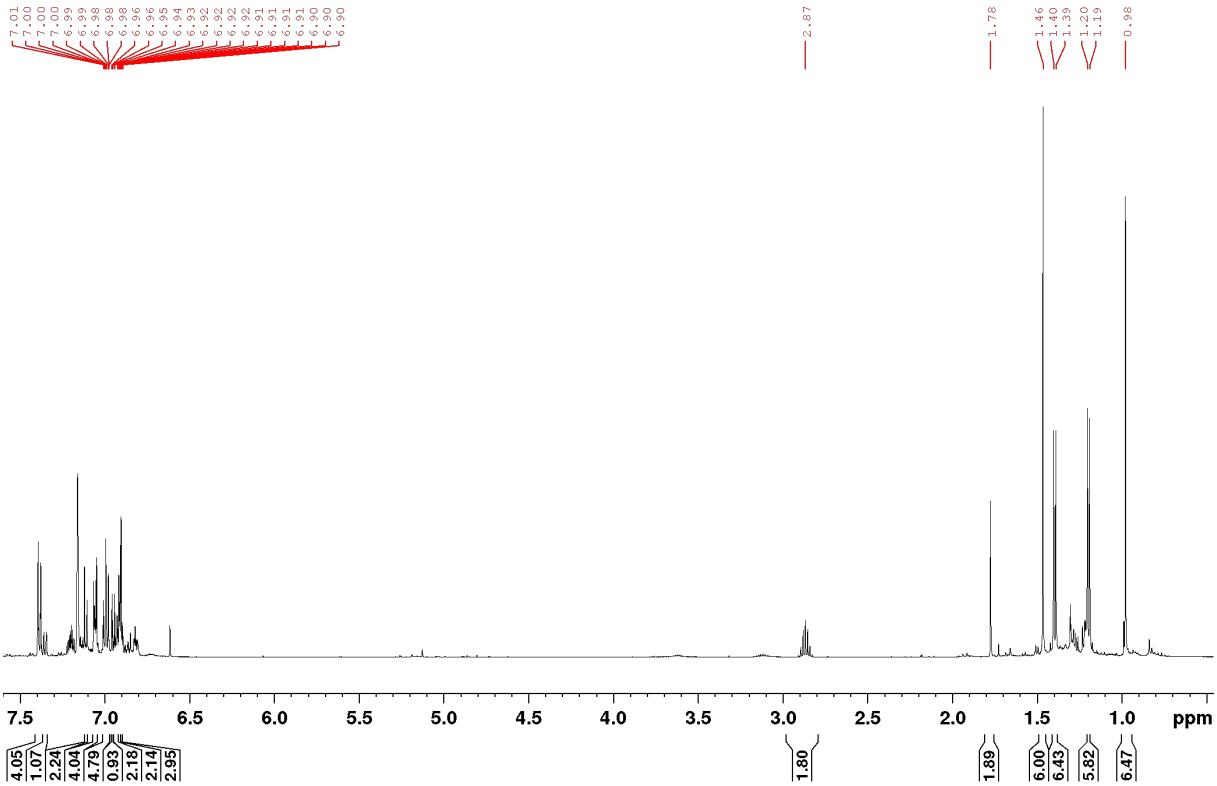


**Fig. S1.** $^1$H NMR spectrum of **2**.

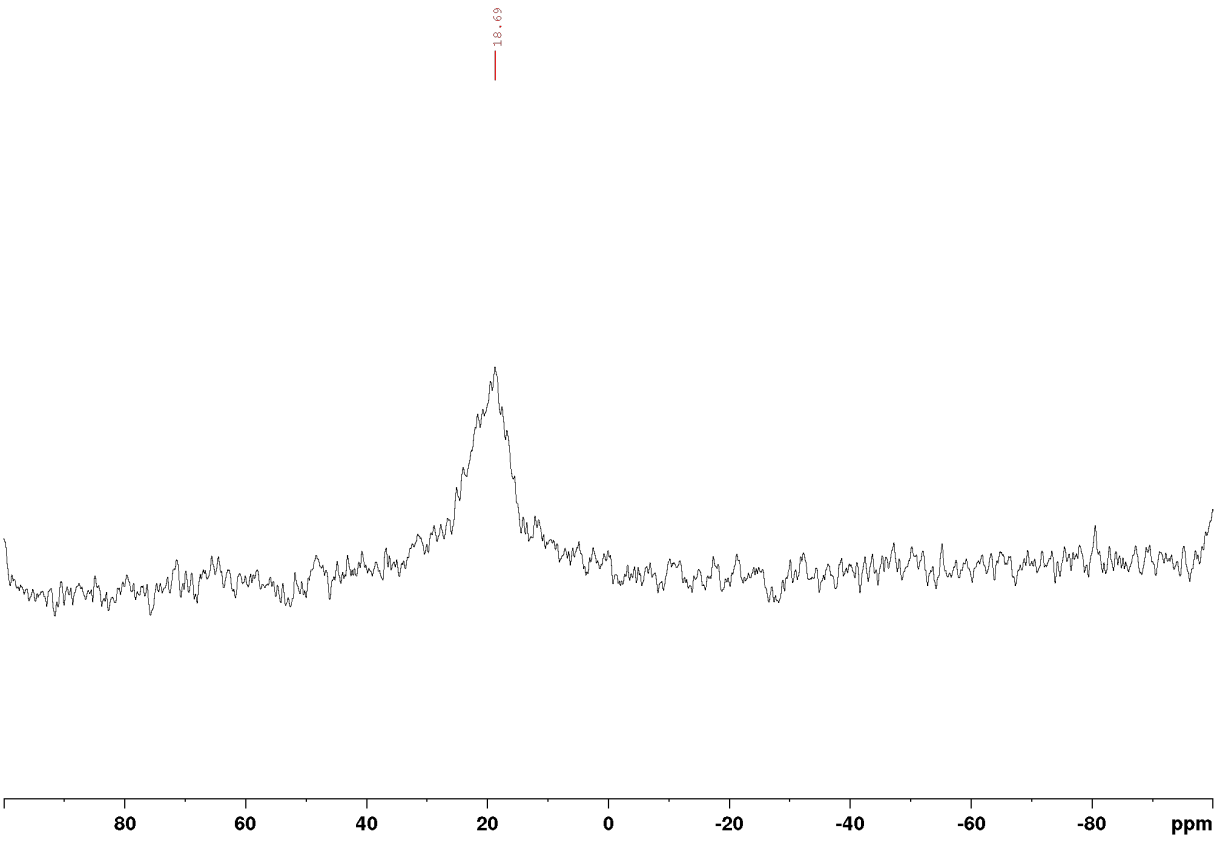


**Fig. S2.** $^{9}$Be NMR spectrum of **2**.

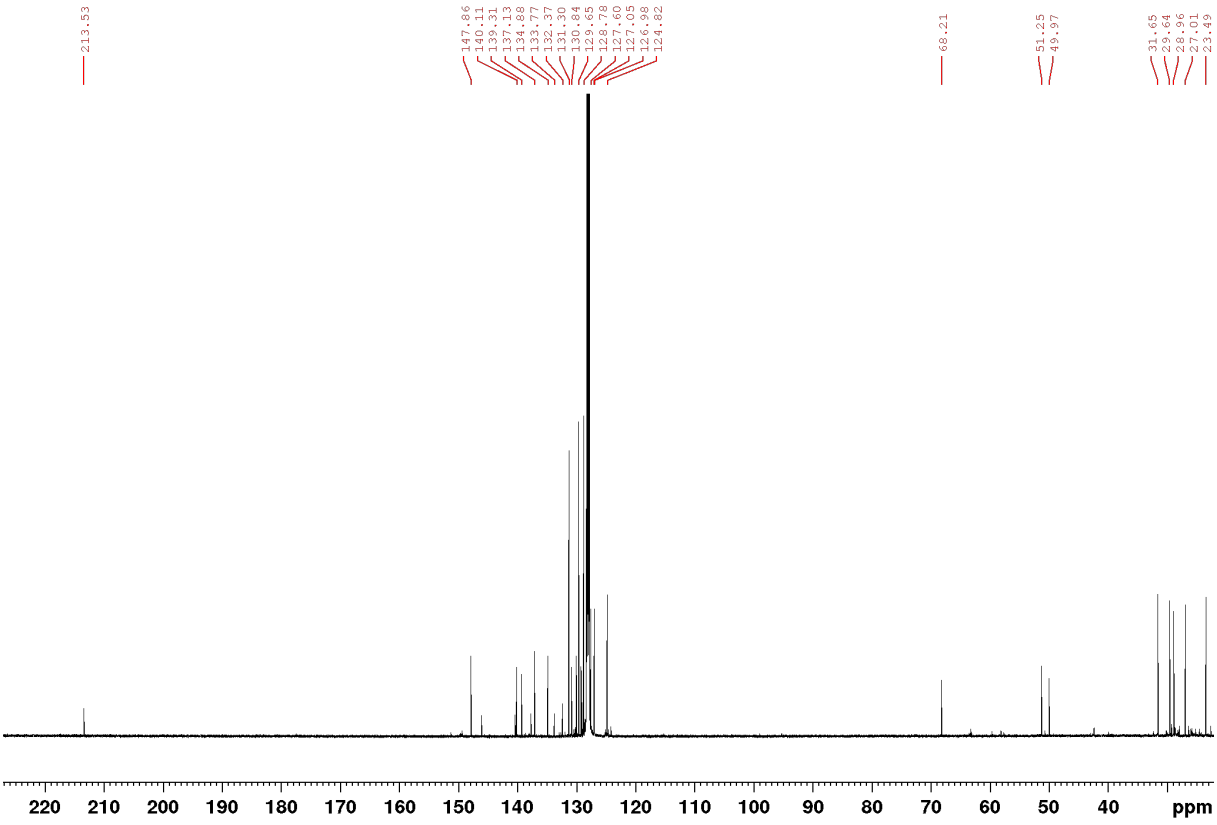


**Fig. S3.** $^{13}$C{$^{1}$H} NMR spectrum of **2**.

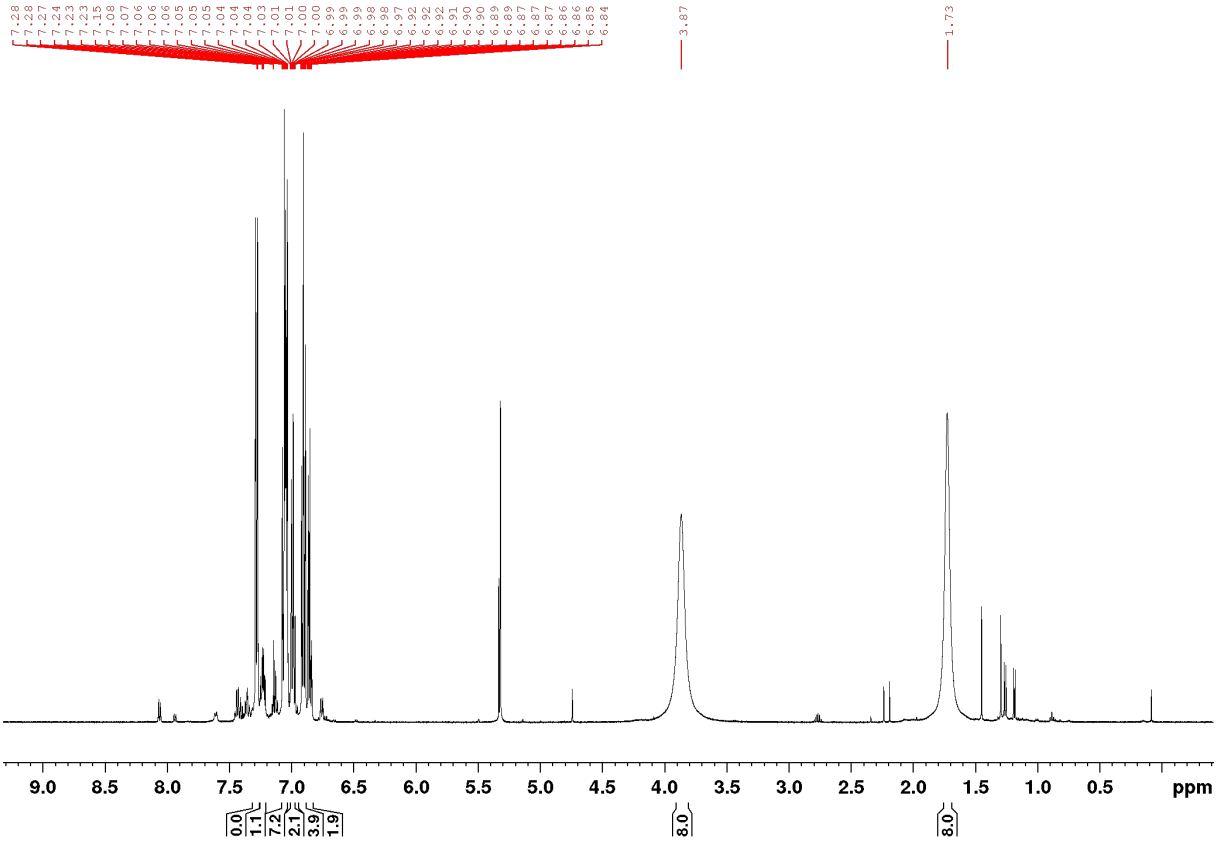


**Fig. S4.** $^{1}$H NMR spectrum of **3**.

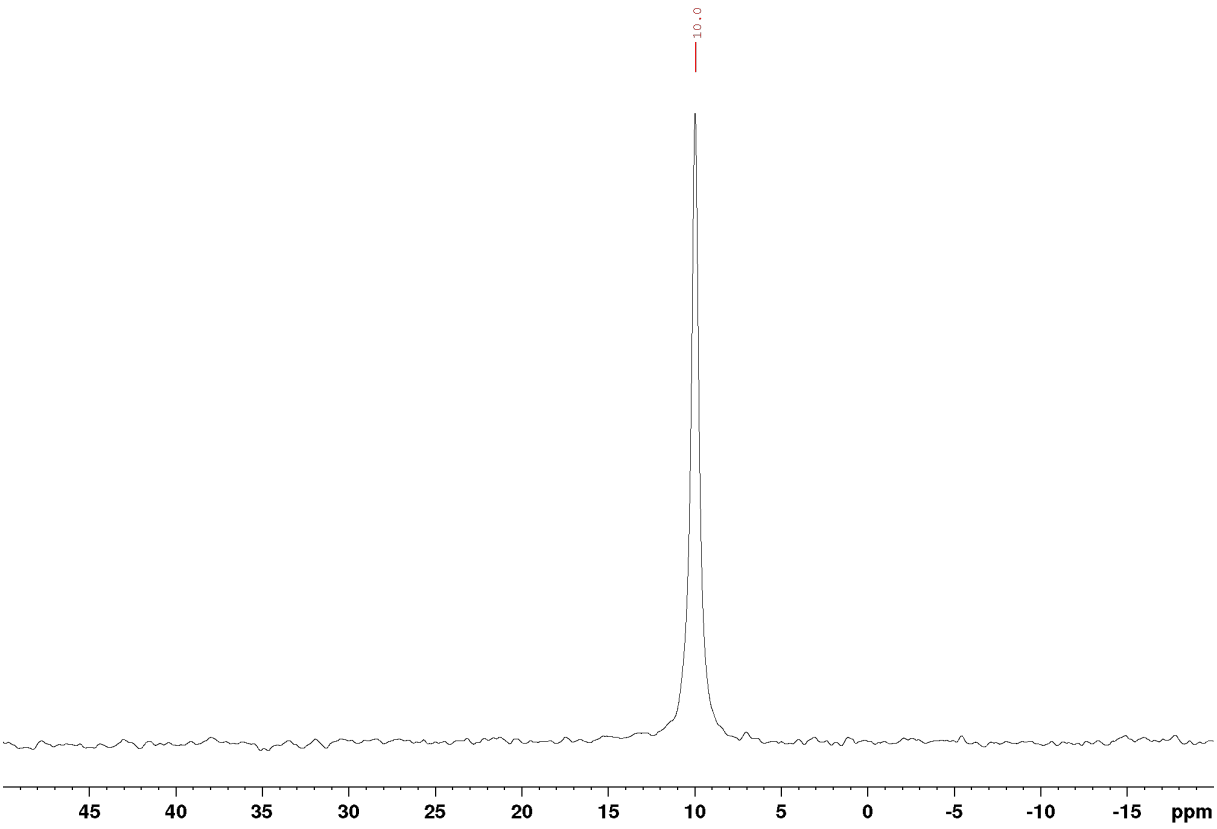


**Fig. S5.** $^{9}$Be NMR spectrum of **3**.

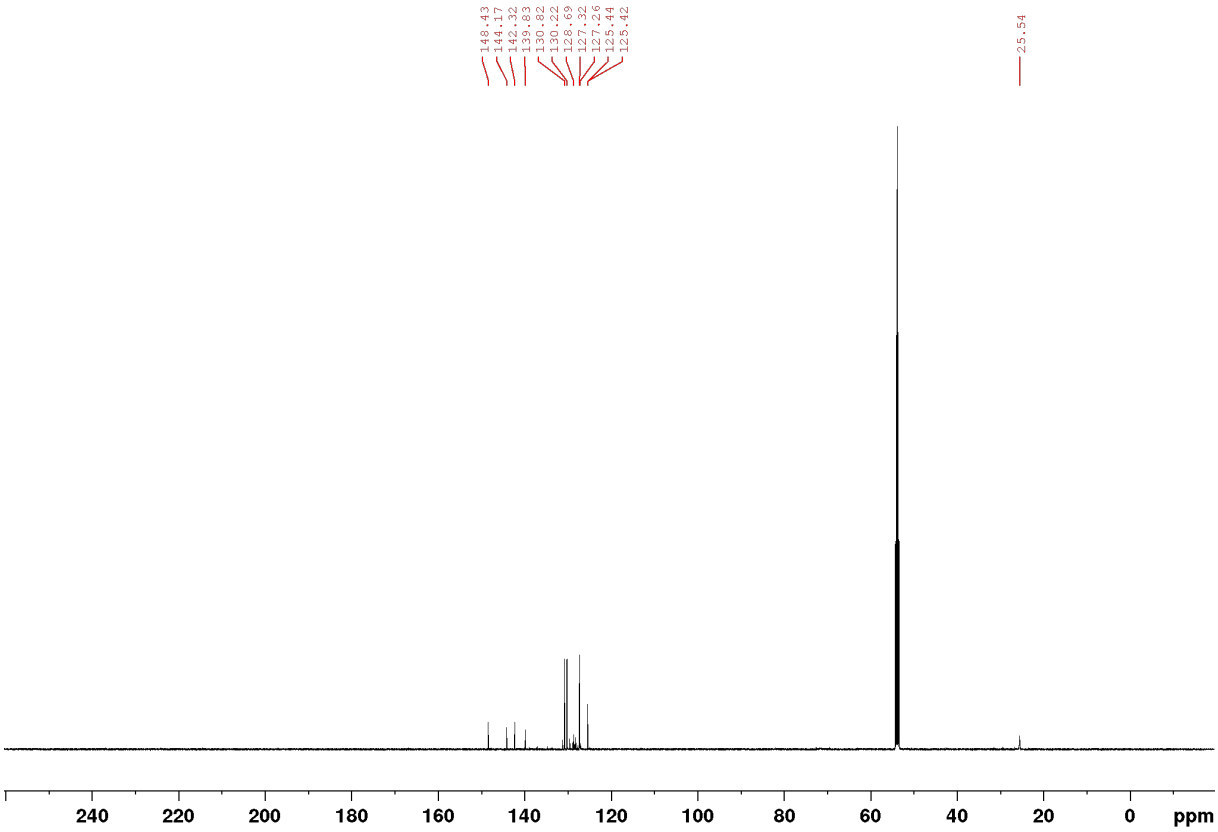


**Fig. S6.** $^{13}C\{^{1}H\}$ NMR spectrum of **3**.

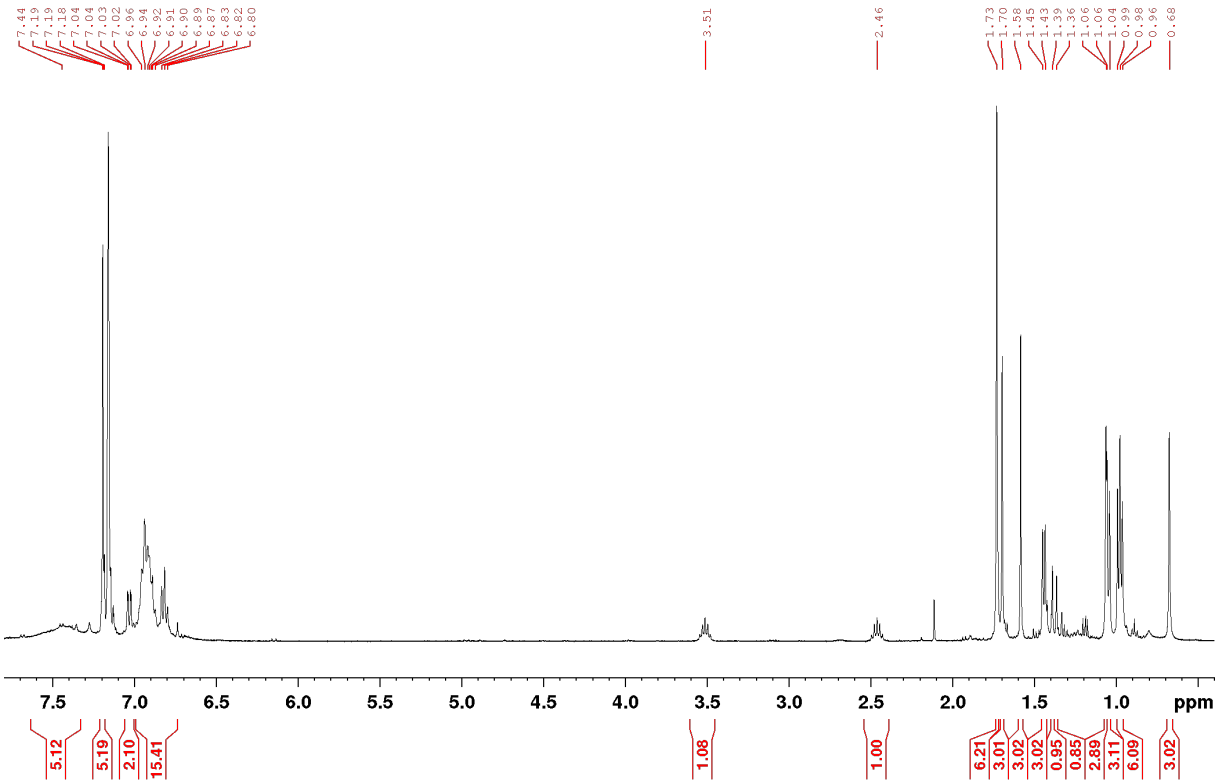


**Fig. S7.** $^{1}H$ NMR spectrum of **4**.

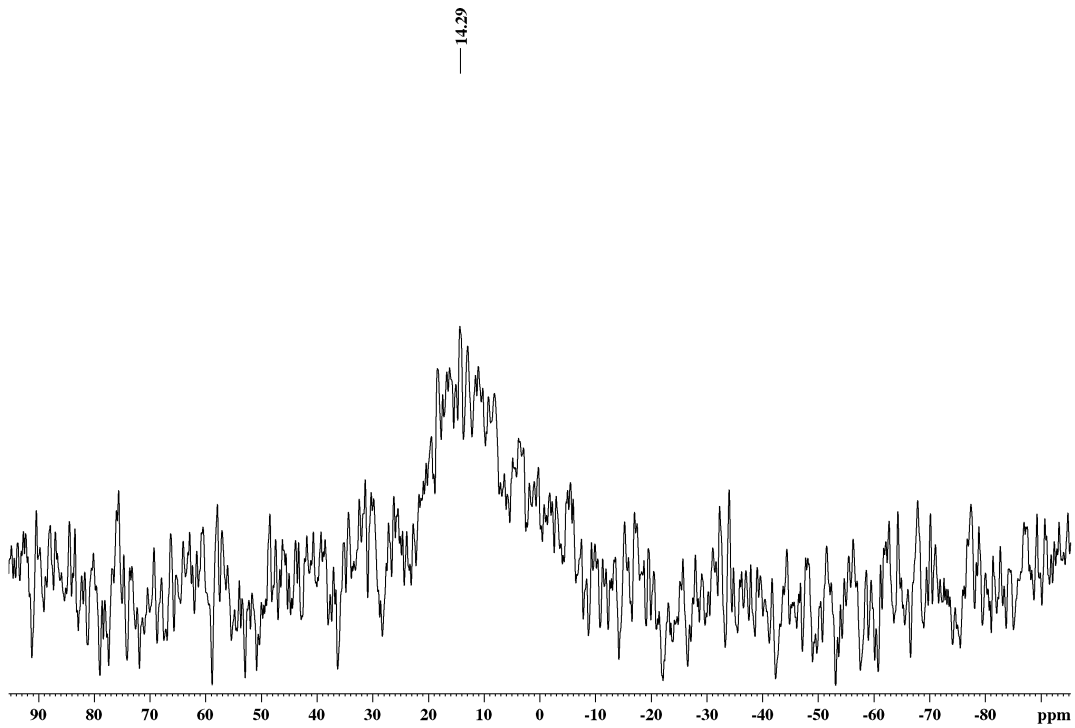


**Fig. S8.** $^{9}$Be NMR spectrum of **4**.

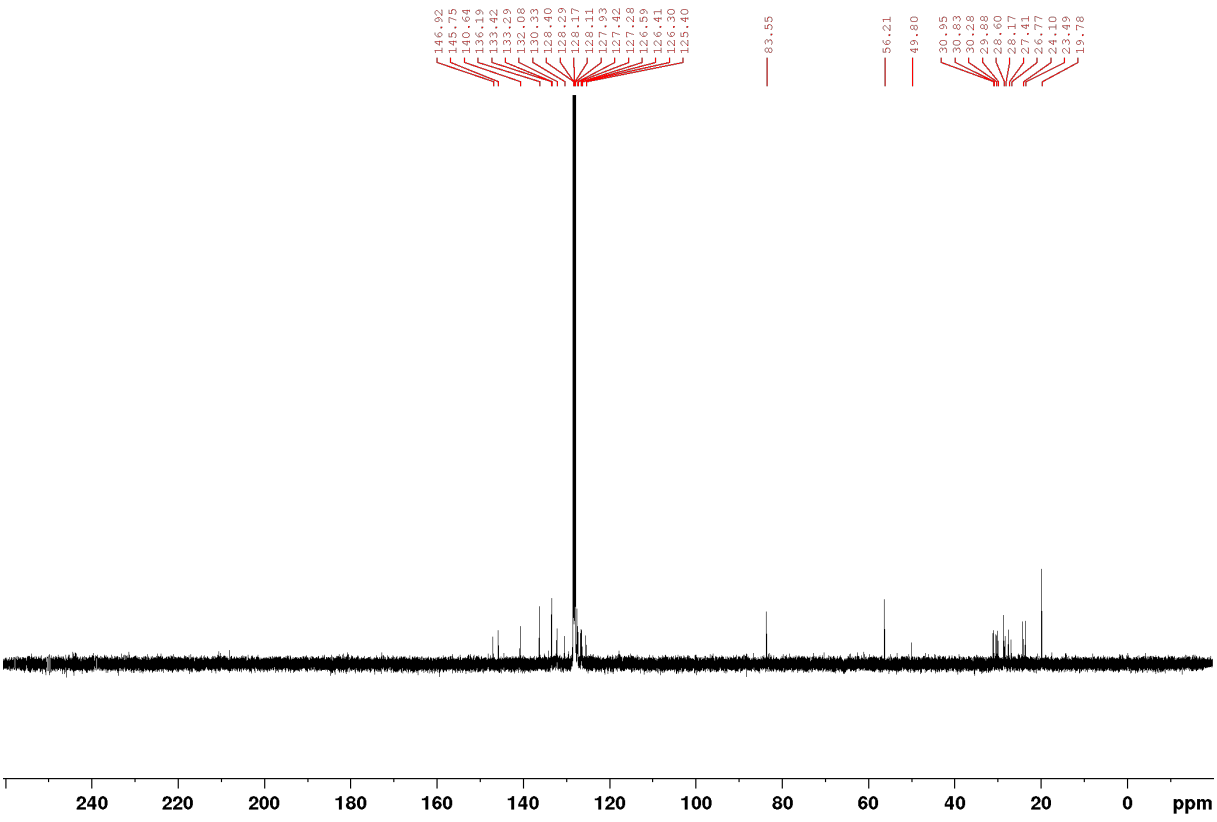


**Fig. S9.** $^{13}$C{$^{1}$H} NMR spectrum of **4**.

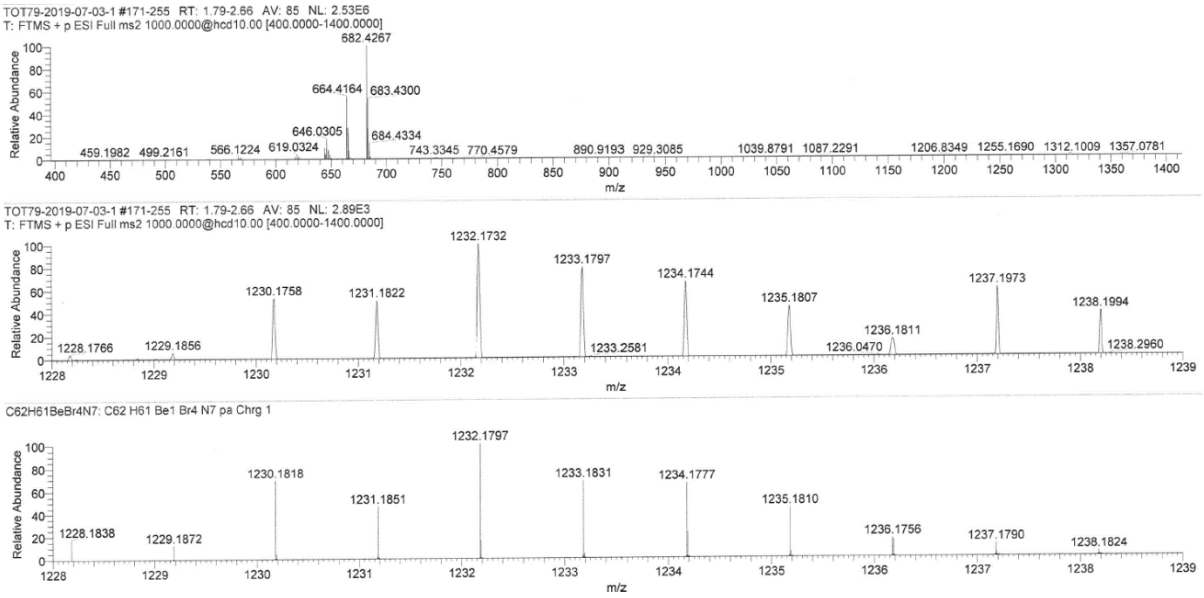


**Fig. S10.** High-resolution LIFDI mass spectrum of **4** (top and middle). Calculated isotope pattern for $[M]^+$ (bottom).

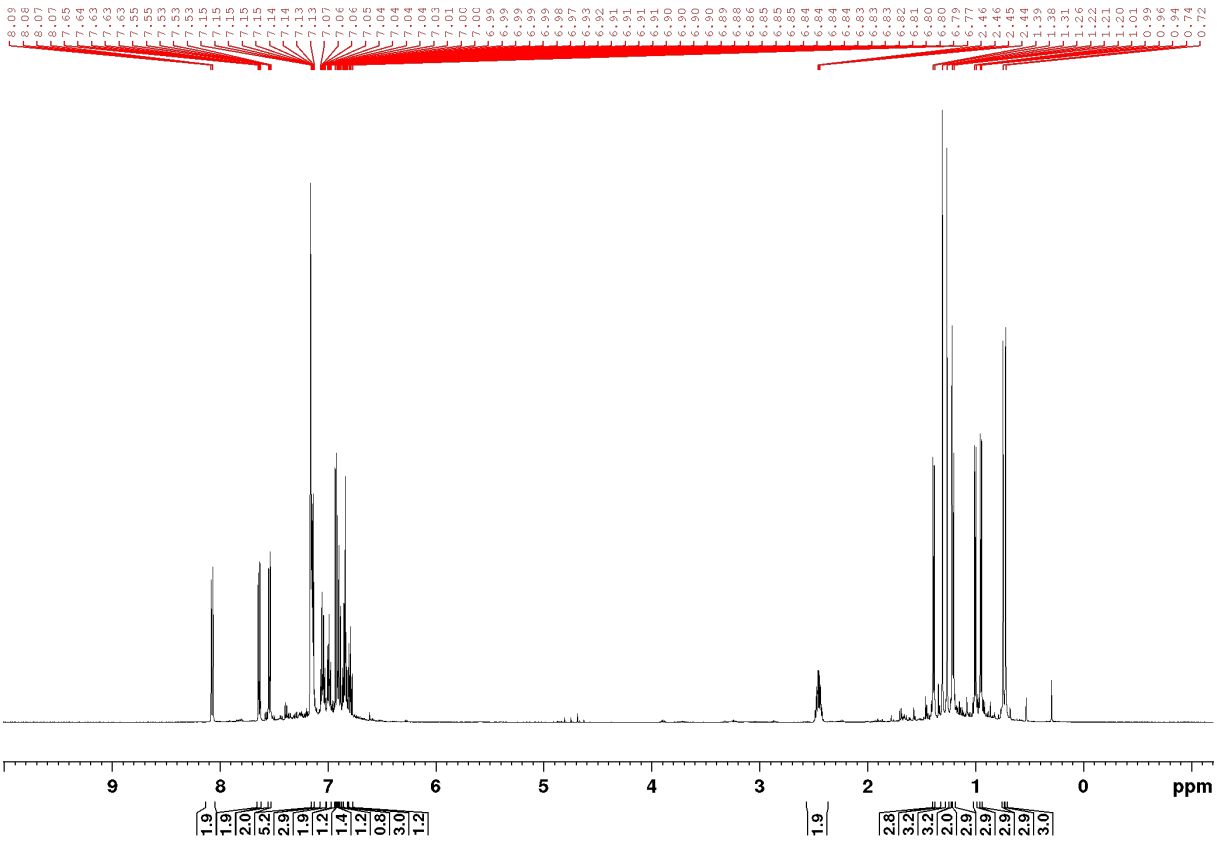


**Fig. S11.** $^1$H NMR spectrum of **5**.

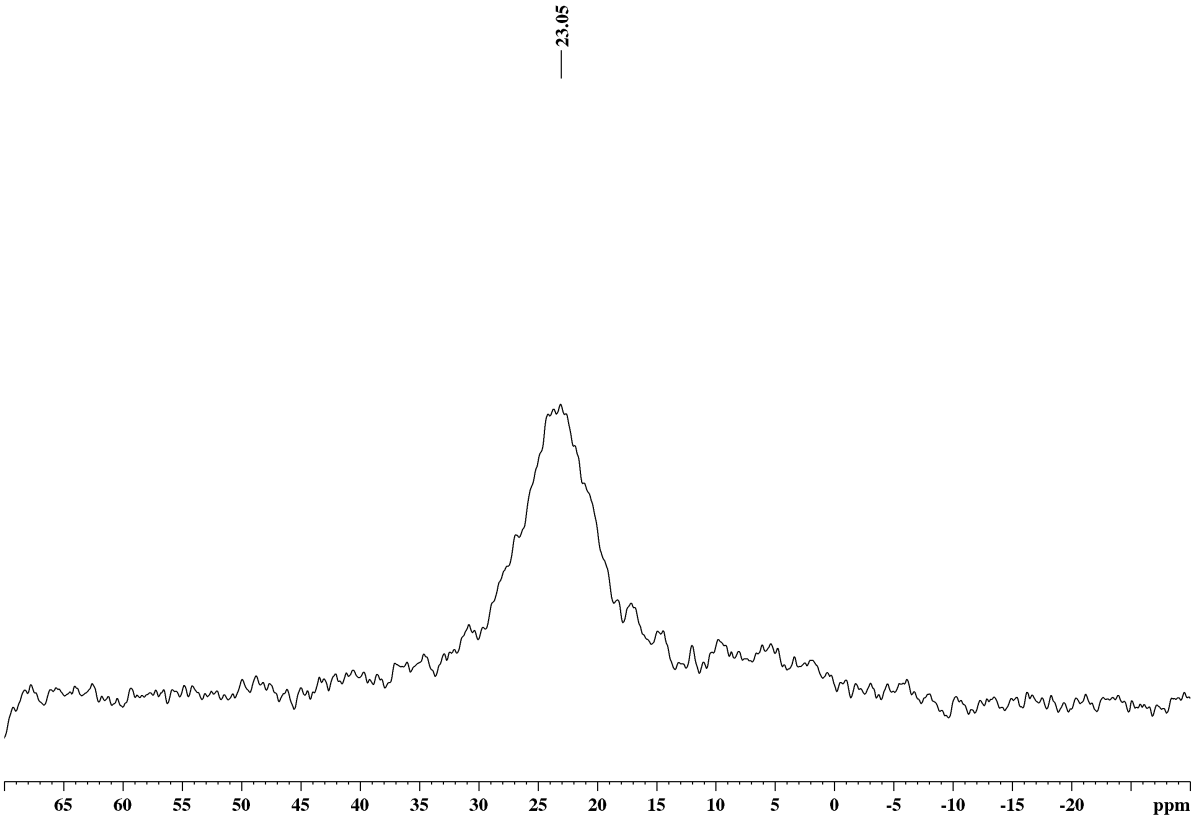


**Fig. S12.** $^{9}$Be NMR spectrum of **5**.

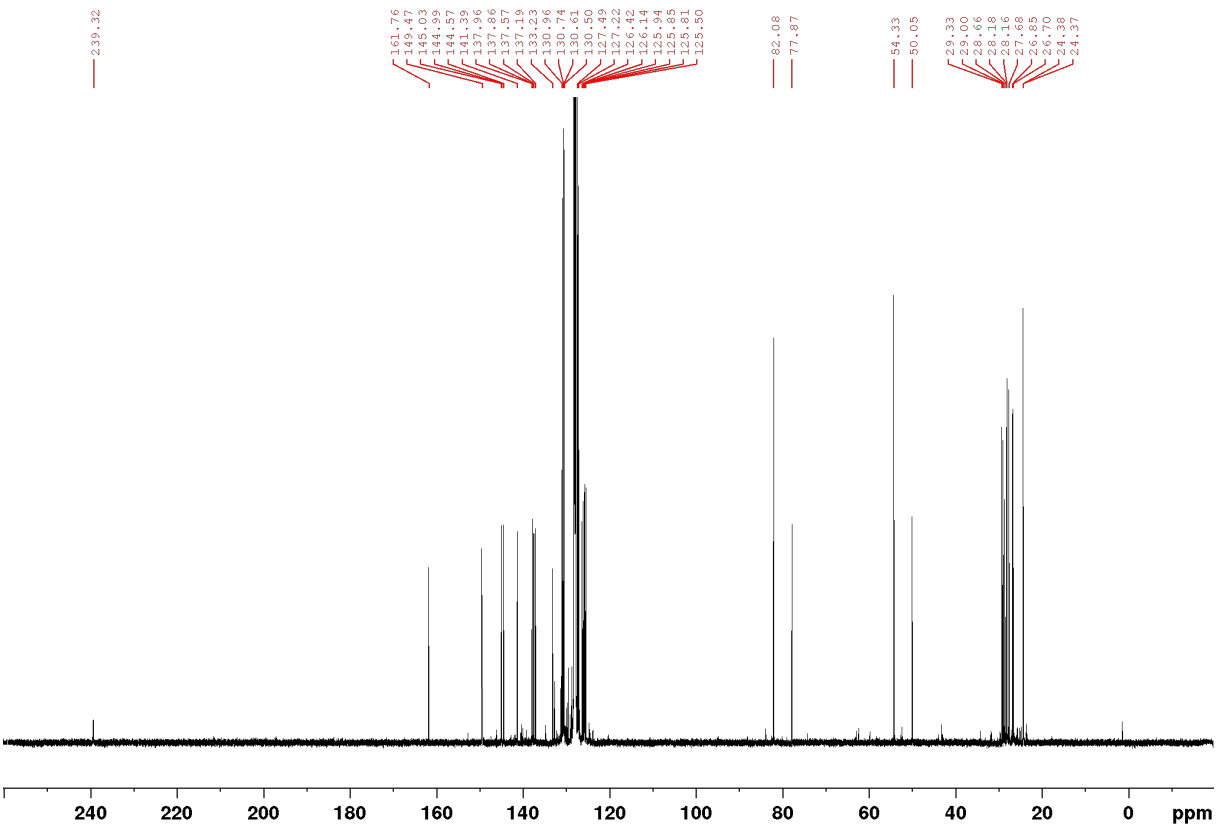


**Fig. S13.** $^{13}C\{^{1}H\}$ NMR spectrum of **5**.

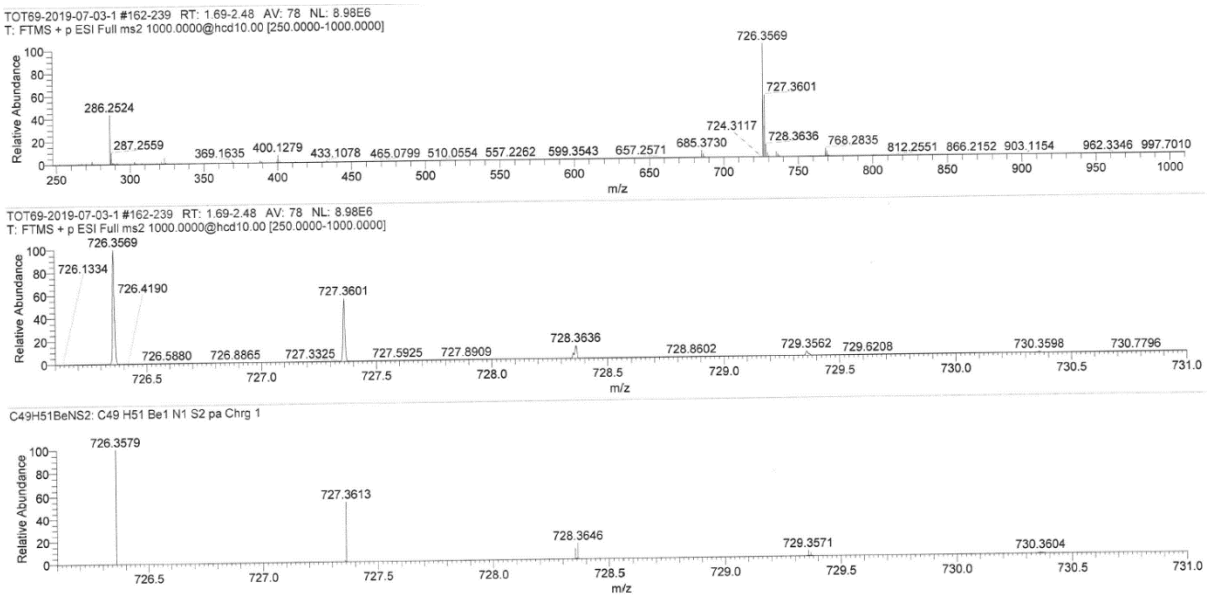


**Fig. S14.** High-resolution LIFDI mass spectrum of **5** (top and middle). Calculated isotope pattern for $[M]^+$ (bottom).

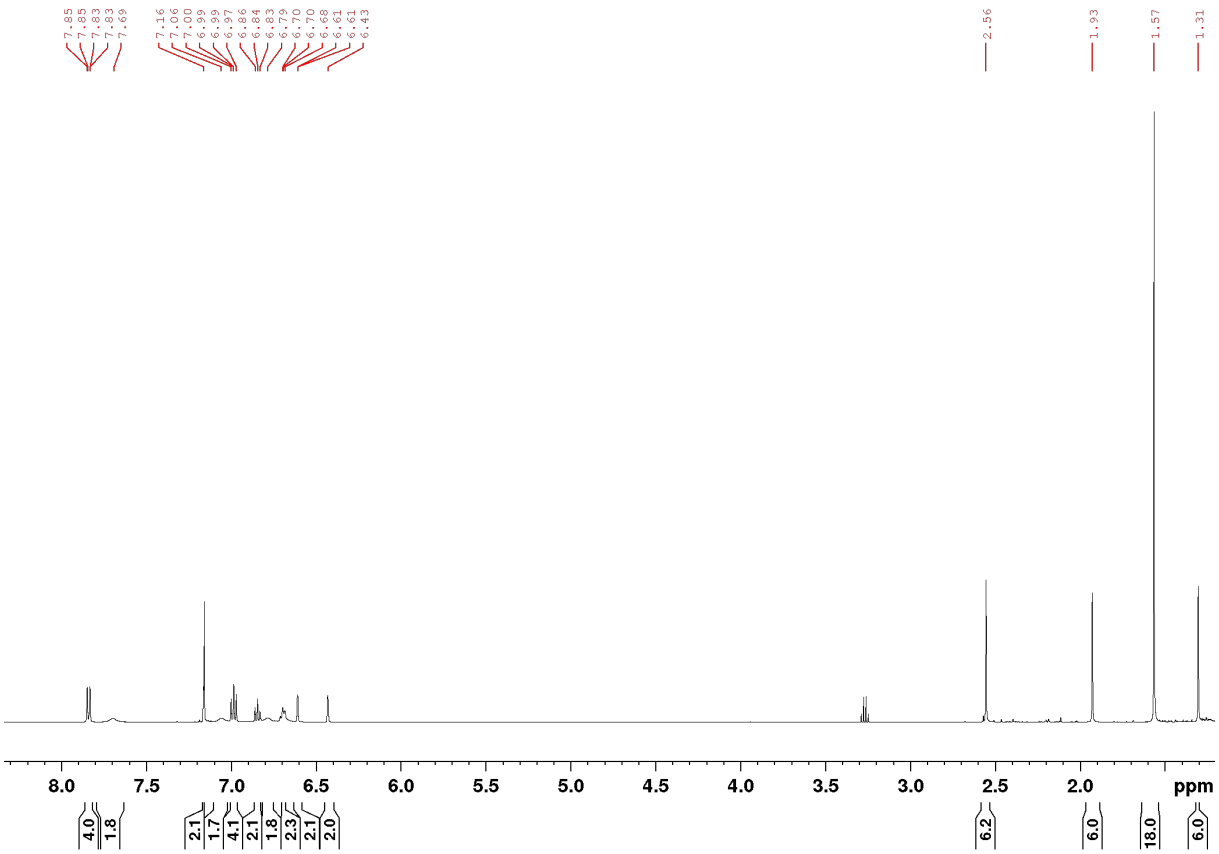


**Fig. S15.** $^{1}$H NMR spectrum of **6**.

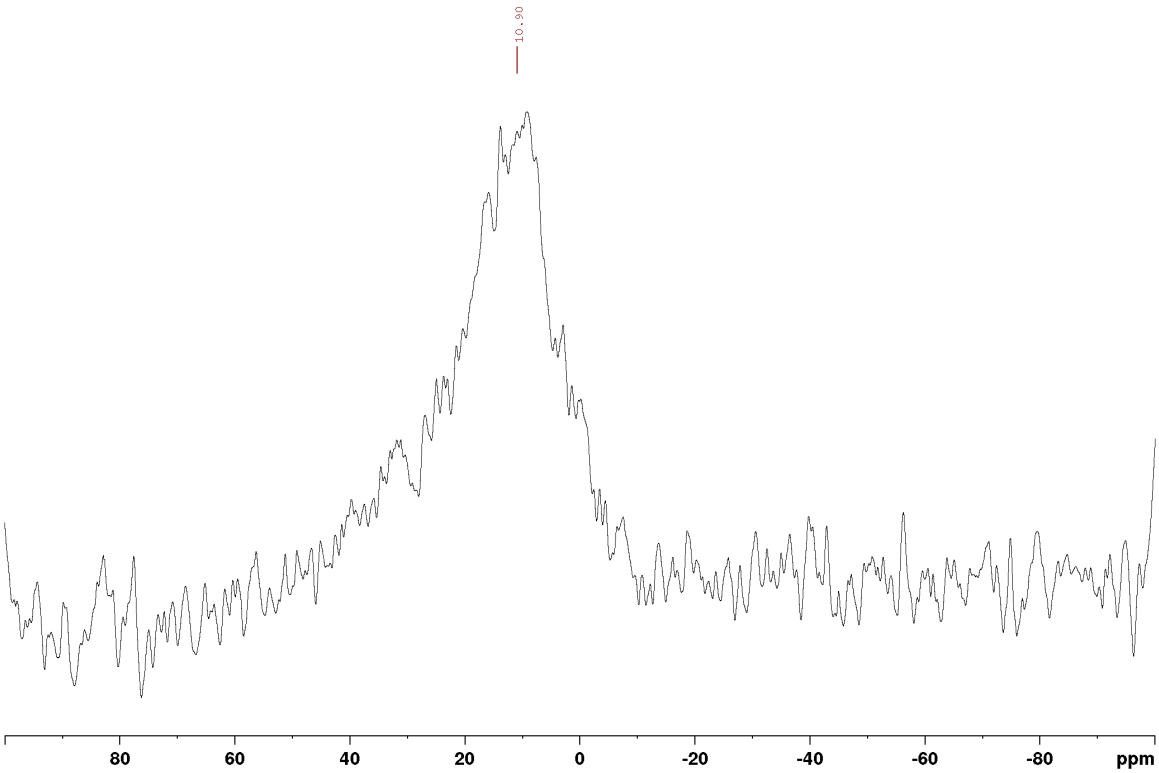


**Fig. S16.** $^{9}$Be NMR spectrum of **6**.

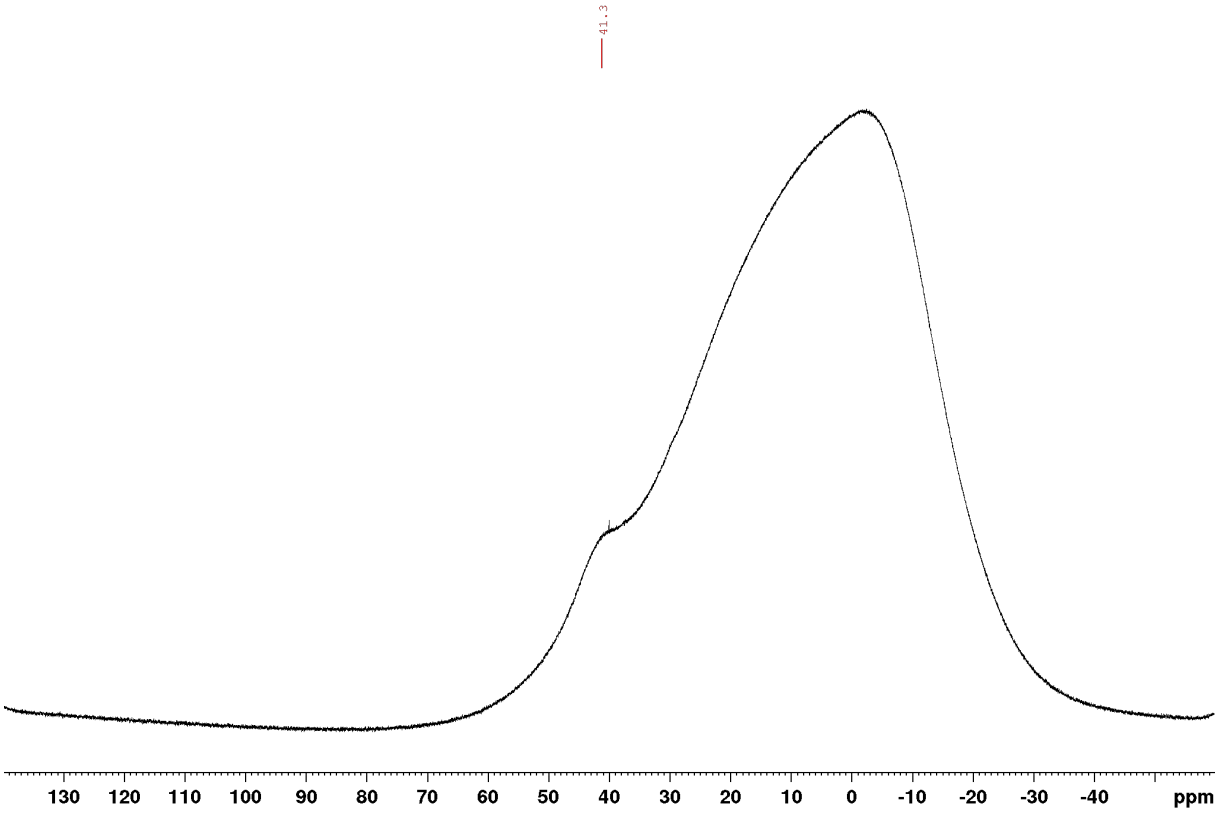


**Fig. S17.** $^{11}$B NMR spectrum of **6**.

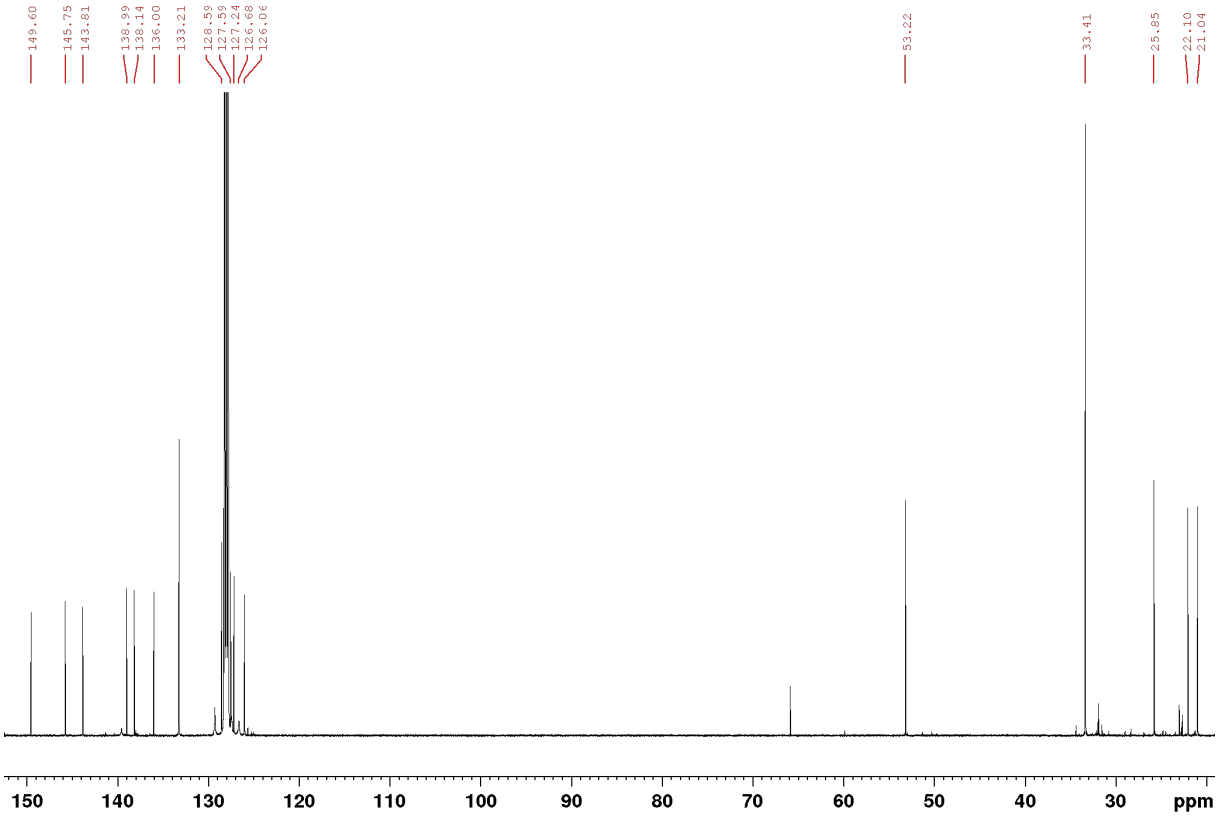


**Fig. S18.** $^{13}$C{$^{1}$H} NMR spectrum of **6**.

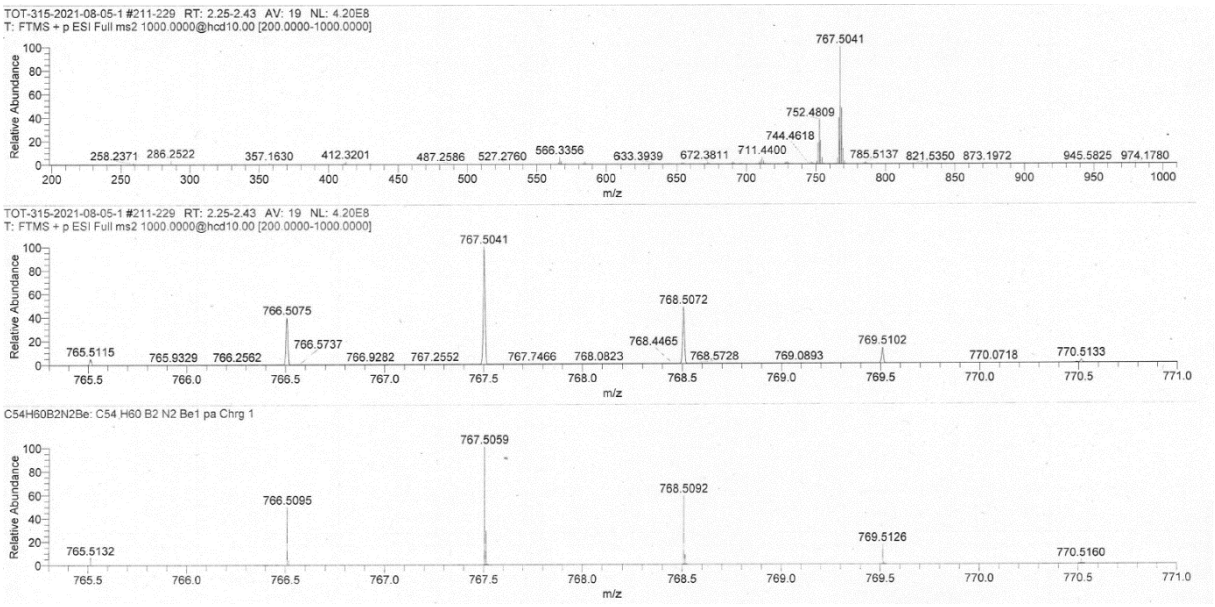


**Fig. S19.** High-resolution LIFDI mass spectrum of **6** (top and middle). Calculated isotope pattern for $[M]^+$ (bottom).

**Crystallographic Details**

The crystal data of **2** were collected on a Bruker X8-APEX II diffractometer with a CCD area detector using Mo-$K_\alpha$ radiation. The crystal data of **4** and **5** were collected on a Bruker D8 Quest with a CCD area detector using Mo-$K_\alpha$ radiation, those of **3** on a Rigaku Oxford Diffraction Synergy-R equipped with a HPA area detector using Cu-$K_a$ radiation, and **6** on a Rigaku Oxford Diffraction Synergy-S equipped with a HPA area detector using Cu-$K_a$ radiation. Both diffractometers are equipped with multi-layer mirror monochromators and a FR-591 rotating anode source or a microfocus seal-tube, respectively. The structures were solved using intrinsic phasing methods;[10] were refined with the SHELXL program[11] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. The solvent molecule (toluene) in the crystal data of **2** is disordered. Geometry of the atoms C70, C72, C73, C71, C75, C76, and C74 was constrained during refinement. The displacement parameters of the oxygen atoms of the thf molecules in the crystal data of **3** were constrained to the same value with the EADP keyword. The coordinates of the oxygen atoms of the thf molecules were constrained to the same value. The atomic displacement parameters of atoms of the thf residues were restrained with the RIGU keyword in ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list). The displacement parameters of atoms of the thf residue were restrained to the same value with a similarity restraint SIMU. The solvent molecule (hexane) in the crystal data of **5** is disordered. The geometry of the atoms of the hexane molecule was constrained during refinement. Hydrogen atoms were assigned to idealized geometric positions and included in structure-factor calculations. X-ray data are available free of charge from the Cambridge Crystallographic Data Centre under reference numbers CCDC- 2494262 (**2**), 2494263 (**3**), 2494264 (**4**), 2494265 (**5**), and 2494266 (**6**).

**Table S1. Crystal data for 2.**

| Data | **2** |
|---|---|
| Empirical formula | $C_{103}H_{110}Be_2N_2S_4$ |
| Formula weight ($g \cdot mol^{-1}$) | 1522.18 |
| 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) | 12.060(3) |
| *b* (Å) | 13.360(3) |
| *c* (Å) | 15.212(3) |
| α (°) | 95.952(5) |
| β (°) | 111.349(5) |
| γ (°) | 101.372(5) |
| Volume ($Å^3$) | 2196.3(8) |
| *Z* | 1 |
| Calculated density ($Mg \cdot m^{-3}$) | 1.151 |
| Absorption coefficient ($mm^{-1}$) | 0.156 |
| *F*(000) | 814 |
| Theta range for collection | 1.464 to 27.802° |
| Reflections collected | 28426 |
| Independent reflections | 10137 |
| Minimum/maximum transmission | 0.6384/0.7456 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / parameters / restraints | 10137 / 491 / 0 |
| Goodness-of-fit on $F^2$ | 1.023 |
| Final R indices [I>2σ(I)] | $R_1$ = 0.0614, $wR_2$ = 0.1338 |
| R indices (all data) | $R_1$ = 0.1119, $wR_2$ = 0.1560 |
| Maximum/minimum residual electron density ($e \cdot Å^{-3}$) | 0.979 / –0.642 |

**Table S2. Crystal data for 3.**

| Data | **3** |
|---|---|
| Empirical formula | $C_{36}H_{36}BeO_2S_2$ |
| Formula weight ($g \cdot mol^{-1}$) | 573.78 |
| Temperature (K) | 100.00(11) |
| Radiation, λ (Å) | $Cu_{K\alpha}$, 1.54184 |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| *Unit cell dimensions* | |
| *a* (Å) | 16.2072(8) |
| *b* (Å) | 10.3142(3) |
| *c* (Å) | 19.7310(9) |
| α (°) | 90 |
| β (°) | 111.967(5) |
| γ (°) | 90 |
| Volume ($Å^3$) | 3058.9(2) |
| *Z* | 4 |
| Calculated density ($Mg \cdot m^{-3}$) | 1.246 |
| Absorption coefficient ($mm^{-1}$) | 1.808 |
| *F*(000) | 1216 |
| Theta range for collection | 3.027 to 74.729° |
| Reflections collected | 29971 |
| Independent reflections | 6108 |
| Minimum/maximum transmission | 0.446/1.000 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / parameters / restraints | 6108 / 444 / 432 |
| Goodness-of-fit on $F^2$ | 1.083 |
| Final R indices [I>2σ(I)] | $R_1$ = 0.0567, $wR_2$ = 0.1576 |
| R indices (all data) | $R_1$ = 0.0683, $wR_2$ = 0.1653 |
| Maximum/minimum residual electron density ($e \cdot Å^{-3}$) | 0.409 / –0.521 |

**Table S3. Crystal data for 4.**

| Data | **4** |
|---|---|
| Empirical formula | $C_{77}H_{76}BeBr_4N_7$ |
| Formula weight ($g \cdot mol^{-1}$) | 1428.09 |
| 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) | 14.361(5) |
| *b* (Å) | 15.539(7) |
| *c* (Å) | 18.590(5) |
| α (°) | 82.622(8) |
| β (°) | 67.945(15) |
| γ (°) | 64.377(8) |
| Volume ($Å^3$) | 3464(2) |
| *Z* | 2 |
| Calculated density ($Mg \cdot m^{-3}$) | 1.369 |
| Absorbtion coefficient ($mm^{-1}$) | 2.372 |
| *F*(000) | 1462 |
| Theta range for collection | 1.183 to 26.021° |
| Reflections collected | 97349 |
| Independent reflections | 13638 |
| Minimum/maximum transmission | 0.5289/0.7455 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / parameters / restraints | 13638 / 812 / 0 |
| Goodness-of-fit on $F^2$ | 1.035 |
| Final R indices [I>2σ(I)] | $R_1$ = 0.0244, $wR^2$ = 0.0594 |
| R indices (all data) | $R_1$ = 0.0302, $wR^2$ = 0.0617 |
| Maximum/minimum residual electron density ($e \cdot Å^{-3}$) | 0.420 / –0.345 |

**Table S4. Crystal data for 5.**

| Data | **5** |
|---|---|
| Empirical formula | $C_{55}H_{65}BeNS_2$ |
| Formula weight ($g \cdot mol^{-1}$) | 813.21 |
| 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) | 10.9982(9) |
| *b* (Å) | 14.4252(12) |
| *c* (Å) | 15.7174(13) |
| α (°) | 91.496(2) |
| β (°) | 98.370(2) |
| γ (°) | 108.461(2) |
| Volume ($Å^3$) | 2333.1(3) |
| *Z* | 2 |
| Calculated density ($Mg \cdot m^{-3}$) | 1.158 |
| Absorption coefficient ($mm^{-1}$) | 0.151 |
| *F*(000) | 876 |
| Theta range for collection | 1.911 to 29.722° |
| Reflections collected | 54552 |
| Independent reflections | 13193 |
| Minimum/maximum transmission | 0.7136/0.7459 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / parameters / restraints | 13193 / 540 / 0 |
| Goodness-of-fit on $F^2$ | 1.146 |
| Final R indices [I>2σ(I)] | $R_1$ = 0.0500, $wR_2$ = 0.1172 |
| R indices (all data) | $R_1$ = 0.0805, $wR_2$ = 0.1345 |
| Maximum/minimum residual electron density ($e \cdot Å^{-3}$) | 1.311 / –0.602 |

**Table S5. Crystal data for 6.**

| Data | **6** |
|---|---|
| Empirical formula | $C_{54}H_{60}B_2BeN_2$ |
| Formula weight ($g \cdot mol^{-1}$) | 767.67 |
| Temperature (K) | 100.00(10) |
| Radiation, λ (Å) | $Cu_{K\alpha}$, 1.54184 |
| Crystal system | Monoclinic |
| Space group | *C*2/*c* |
| *Unit cell dimensions* | |
| *a* (Å) | 20.23120(10) |
| *b* (Å) | 12.89530(10) |
| *c* (Å) | 16.69960(10) |
| α (°) | 90 |
| β (°) | 94.5530(10) |
| γ (°) | 90 |
| Volume ($Å^3$) | 4342.97(5) |
| *Z* | 4 |
| Calculated density ($Mg \cdot m^{-3}$) | 1.174 |
| Absorption coefficient ($mm^{-1}$) | 0.492 |
| *F*(000) | 1648 |
| Theta range for collection | 4.069 to 72.127° |
| Reflections collected | 85778 |
| Independent reflections | 4274 |
| Minimum/maximum transmission | 0.545/1.000 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / parameters / restraints | 4274 / 287 / 18 |
| Goodness-of-fit on $F^2$ | 1.041 |
| Final R indices [I>2σ(I)] | $R_1$ = 0.0404, $wR_2$ = 0.1044 |
| R indices (all data) | $R_1$ = 0.0415, $wR_2$ = 0.1052 |
| Maximum/minimum residual electron density ($e \cdot Å^{-3}$) | 0.329 / –0.211 |

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