Supplementary Information (SI) for Dalton Transactions.

Supporting Information for

Synthesis and Structures of Molecular Beryllium Grignard Analogues Featuring Terminal and Bridging Pseudohalides

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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. NMR spectra were acquired either on a Bruker Avance 500 (operating at 500 MHz for ^{1}H, 125 MHz for ^{13}C and 202 Hz for ^{31}P), a Bruker Avance 400 NMR (operating at 400 MHz for ^{1}H, 56 MHz for ^{9}Be, 100 MHz for ^{13}C and 162 Hz for ^{31}P) or a Bruker Avance Neo I 600 (operating at 600 MHz for ^{1}H, 84.3 MHz for ^{9}Be and 150 MHz for ^{13}C and 243 Hz for ^{31}P) spectrometer. Chemical shifts (δ) are provided in ppm and internally referenced to the carbon nuclei (^{13}C{^{1}H}) or residual protons (^{1}H) of the solvent. The multiplicity of the NMR resonances is given as s (singlet), d (doublet), t (triplet), q (quartet), sept (septet) or br (broad). For broad ^{9}Be NMR resonances an estimate of the full width at half-maximum ($\omega_{1/2}$) to the nearest 10 Hz is provided. High-resolution mass spectrometry (HRMS) was carried out on an Exactive Plus spectrometer with Orbitrap detector from ThermoFisher Scientific. The ion source was a Liquid Injection Field Desorption Ionisation (LIFDI) unit from Linden CMS.

Solid-state IR spectra were recorded on a Bruker FT-IR spectrometer ALPHA II inside a glovebox. Microanalyses (C, H, N, S) were performed on an Elementar vario MICRO cube elemental analyzer. UV-vis spectra were acquired on a METTLER TOLEDO UV-vis-Excellence UV5 spectrophotometer. *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.*

NaNCS and KOCN were purchased from various chemicals companies, transferred into a glovebox and used as received. [(CAAC)(CAACH)BeBr] (**1a**, CAAC = 1-(2,6-di*iso*propylphenyl)-2,2,4,4-tetramethylpyrrolidin-2-ylidene; CAACH = 1-(2,6-di*iso*propyl-phenyl)-2,2,4,4-tetramethylpyrrolidin-2-yl),[1] [(CAAC)(Dur)BeBr] (**1b**, Dur = 2,3,5,6-tetramethylphenyl),[2] [Na(OCP)(dioxane)$_{2.3}$],[3] and [K(SeCN)][4] were synthesised following literature procedures.

Caution!

Beryllium and its compounds are regarded as toxic and carcinogenic. Because the biochemical mechanisms that cause beryllium-associated diseases are still unknown, special (safety) precautions are strongly advised.[5]

Synthetic procedures

Synthesis of [(CAAC)(CAACH)Be(NCS)], 2a

1a (60.0 mg, 0.908 mmol, 1.10 equiv.) and [Na(NCS)] (8.10 mg, 0.998 mmol, 1.10 equiv.) were dissolved in 2 mL THF and the orange solution was stirred for 3 h, turning into a yellow suspension. After removal of all volatiles *in vacuo* the residual yellow solid was washed with pentane (3 × 0.5 mL) and extracted with benzene. (3 × 1 mL) Removal of the solvent *in vacuo* yielded **2a** as a yellow solid (43.4 mg, 0.680 mmol, 75%). ^{1}H NMR (500.1 MHz, C$_6$D$_6$): δ = 7.35 (dd, ^3J = 7.6 Hz, ^4J = 1.8 Hz, 1H, m-CH_{Dip}), 7.20 (t, ^3J = 7.6 Hz, 1H, p-CH_{Dip}), 7.11 (dd, ^3J = 7.6 Hz, ^4J = 1.8 Hz, 1H, m-CH_{Dip}), 7.04 (m, 2H, CH_{Dip}), 6.91 (dd, ^3J = 7.1 Hz, ^4J = 2.3 Hz, 1H, m-CH_{Dip}), 4.66 (sept, ^3J = 6.7 Hz, 1H, CH(CH$_3$)$_2$), 3.56 (sept, ^3J = 6.5 Hz, 1H, CH(CH$_3$)$_2$), 2.90 (sept, ^3J = 6.5 Hz, 1H, CH(CH$_3$)$_2$), 2.89 (s, 1H, BeCH), 2.48 (sept, ^3J = 6.6 Hz, 1H, CH(CH$_3$)$_2$), 1.93 (d, ^3J = 6.5 Hz, 3H, CH_2), 1.91 (d, ^2J = 11.8 Hz, 1H, CH_2), 1.81 (d, ^2J = 11.8 Hz, 1H, CH_2), 1.75 (d, ^3J = 6.5 Hz, 3H, CH(CH_3)$_2$), 1.67 (s, 3H, C(CH_3)$_2$), 1.46 (s, 3H, C(CH_3)$_2$), 1.44 (d, ^3J = 6.7 Hz, 3H, CH(CH_3)$_2$), 1.36 (s, 3H, C(CH_3)$_2$), 1.33-1.30 (m, 9H, 3 x 3H from C(CH_3)$_2$, identified by HSQC), 1.16 (s, 3H, C(CH_3)$_2$), 1.10 (d, ^2J = 12.7 Hz, 2H, CH_2), 1.06 (d, ^3J = 6.6 Hz, 3H, CH(CH_3)$_2$), 1.00 (d, ^3J = 5.5 Hz, 3H, CH(CH_3)$_2$), 0.90 (s, 3H, C(CH_3)$_2$), 0.67 (s, 3H, C(CH_3)$_2$), 0.51 (s, 3H, C(CH_3)$_2$), 0.48 (s, 3H, C(CH_3)$_2$) ppm. ^{9}Be NMR (56.3 MHz, C$_6$D$_6$): δ = 15.5 ($\omega_{1/2} \approx 420$ Hz) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C$_6$D$_6$): δ = 249.6 (C_{carbene}), 153.2 (o-C_{Dip}), 151.4 (o-C_{Dip}), 146.1 (NC_{Dip}), 145.9 (o-C_{Dip}), 145.3 (o-C_{Dip}), 134.3 (NC_{Dip}), 130.1 (CH$_{\mathrm{Dip}}$), 126.4 (CH$_{\mathrm{Dip}}$), 125.7 (CH$_{\mathrm{Dip}}$), 125.6 (CH$_{\mathrm{Dip}}$), 124.8 (CH$_{\mathrm{Dip}}$), 124.8 (CH$_{\mathrm{Dip}}$), 82.1 (NC(CH$_3$)$_2$), 69.7 (CH, BeCH), 64.3 (NC(CH$_3$)$_2$), 62.6 (CH$_2$), 55.3 (C(CH$_3$)$_2$), 51.0 (CH$_2$), 41.7 (C(CH$_3$)$_2$), 33.1 (C(CH$_3$)$_2$), 31.8 (C(CH$_3$)$_2$), 31.3 (C(CH$_3$)$_2$) , 29.8 (C(CH$_3$)$_2$), 29.7 (C(CH$_3$)$_2$), 29.4 (CH(CH$_3$)$_2$), 29.2 (CH(CH$_3$)$_2$), 28.7 (CH(CH$_3$)$_2$), 28.5 (C(CH$_3$)$_2$), 28.1 (C(CH$_3$)$_2$), 28.0 (CH(CH$_3$)$_2$), 27.9 (CH(CH$_3$)$_2$), 27.7 (C(CH$_3$)$_2$), 27.4 (CH(CH$_3$)$_2$), 27.2 (C(CH$_3$)$_2$), 26.4 (CH(CH$_3$)$_2$), 26.3 (CH(CH$_3$)$_2$), 25.9 (CH(CH$_3$)$_2$), 25.8 (CH(CH$_3$)$_2$), 24.5 (CH(CH$_3$)$_2$) ppm. *Note: The $^{13}C\{^1H\}$ NMR resonance of C_{NCS} could not be detected due to broadening caused by the adjacent ^9Be quadrupole.* Elemental analysis (%) calcd. for C$_{41}$H$_{63}$BeN$_3$S [639.05g mol^{-1}]: C 77.05, H 9.94, N 6.58, S 5.02; found: C 76.09, H 10.15, N 6.46, S 5.03. FT-IR (solid-state): $\tilde{\nu}$(NCS) = 2100 cm^{-1}.

Synthesis of [(CAAC)(Dur)Be(NCS)], 2b

A suspension of **1b** (62.0 mg, 0.122 mmol, 1.00 equiv.) in 4 mL THF was cooled to −78 °C. A solution of [Na(NCS)] (9.90 mg, 0.122 mmol, 1.00 equiv.) in 2 mL THF was added dropwise. The colourless suspension was allowed to reach room temperature and stirred for 3 h. After removal of all volatiles *in vacuo* the remaining colourless solid was washed with pentane (3 × 1 mL) and cold benzene (1 × 0.5 mL) and afterwards extracted with benzene (5 × 1 mL). By evaporation of benzene at room temperature, **2b** was obtained as a colourless crystalline solid (34.7 mg, 76.9 µmol, 58%). ^{1}H NMR (500 MHz, C_6D_6): δ = 7.31 (m, 1H, *p*-CH_{Dip}), 7.19 (d, ^{3}J = 7.7 Hz, 2H, *m*-CH_{Dip}), 6.94 (s, 1H, CH_{Dur}), 2.58 (br sept, ^{3}J ≈ 6.2 Hz, 2H, CH(CH$_3$)$_2$), 2.25 (s, 6H, (CH_3)$_{\mathrm{Dur}}$), 2.13 (br s, 6H, (CH_3)$_{\mathrm{Dur}}$), 1.41 (br d, 6H, CH(CH_3)$_2$), 1.24 (s, 2H, CH_2), 1.19 (s, 6H, C(CH_3)$_2$), 1.10 (d, ^{3}J = 6.6 Hz, 6H, CH(CH_3)$_2$), 0.70 (s, 6H, C(CH_3)$_2$) ppm. ^{9}Be NMR (56.3 MHz, C_6D_6): δ = 14.8 ($\omega_{1/2}$ ≈ 210 Hz) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6 MHz, C_6D_6): δ = 240.1 (C_{carbene}, detected by HMBC), 158.3 (BeC_{Dur}, detected by HMBC), 144.4 (*o*-C_{Dip}), 139.5 (*o*-C_{Dur}), 133.1 (NC_{Dip}), 131.9 (*m*-C_{Dur}), 131.4 (*p*-CH$_{\mathrm{Dip}}$), 130.3 (*p*-CH$_{\mathrm{Dur}}$), 126.0 (*m*-CH$_{\mathrm{Dip}}$), 81.6 (NC(CH$_3$)$_2$), 55.7 (C(CH$_3$)$_2$), 50.6 (CH$_2$), 29.4 (CH(CH$_3$)$_2$), 28.5 (C(CH$_3$)$_2$), 27.4 (C(CH$_3$)$_2$), 25.4 (CH(CH$_3$)$_2$), 24.3 (CH(CH$_3$)$_2$), 23.7 (C(CH$_3$)$_{\mathrm{Dur}}$), 20.1 (C(CH$_3$)$_{\mathrm{Dur}}$) ppm. *Note The $^{13}C\{^{1}H\}$ NMR resonance of C_{NCS} could not be detected due to broadening caused by the adjacent ^{9}Be quadrupole.* Elemental analysis (%) calcd. for $C_{31}H_{44}BeN_2S$ [485.78 g mol^{-1}]: C 76.65, H 9.13, N 5.77, S 6.60; found: C 77.56, H 8.85, N 5.30, S 5.82. FT-IR (solid-state): $\tilde{\nu}$(NCS) = 2089 cm^{-1}. *Note: **2b** decomposes slowly in benzene, relatively rapidly in chlorinated solvents and after prolonged time under vacuum. Therefore, the IR data and elemental analysis were acquired immediately after preparation and the compound was not redissolved.*

Synthesis of [(THF)$_2$(CAACH)Be(OCP)], 3

1a (200 mg, 0.302 mmol, 1.00 equiv.) and [Na(OCP)(dioxane)$_{2.3}$] (86.1 mg, 0.302 mmol, 1.00 equiv.) were dissolved in 10 mL THF, resulting in an immediately colour change to dark purple, turning dark brown after 2 min stirring. The reaction mixture was stirred for an additional 2 h before removing the solvent *in vacuo*. NMR-spectroscopic analysis showed the formation of two tetracoordinate beryllium complexes at $\delta_{9\mathrm{Be}}$ = 7.1 (s, $\omega_{1/2}$ ≈ 150 Hz, minor rotamer **3'**) and 4.3 (s, $\omega_{1/2}$ ≈ 150 Hz, major rotamer **3**) ppm, corresponding to a slightly unsymmetrical ^{31}P NMR singlet at −344.4 ppm (**3** + **3'**, ca. 96%), as well as very minor tricoordinate beryllium complex (broad shoulder, $\delta_{9\mathrm{Be}}$ ≈ 10-15 ppm), corresponding to a ^{31}P NMR singlet at −339.4 ppm (**4a**, ca. 4%). The residual solid was extracted with pentane (4 ×

1 mL) and the extract filtered over Celite. The pentane solution was left to crystallise at −30 °C, yielding a crop of crystals, which were further washed with cold pentane (2 × 0.2 mL) to yield pure **3** (50.0 mg, 0.101 mmol, 33%). Further recrystallisation also yielded a few single crystals of **4a** suitable for X-ray diffraction analysis. Although this observation was reproducible **4a** could not be isolated in sufficient amounts for full characterisation. *Note: The dropwise addition of [Na(OCP)(dioxane)$_{2.3}$] to* ***1a*** *did not result in improved selectivity. The reaction was also monitored at low temperatures by variable-temperature NMR spectroscopy and a reaction was observed only above −20 °C, albeit with the same selectivity as the reference reaction at room temperature.* ^{1}H NMR (500.1 MHz, C_6D_6) for major rotamer **3** (88%): δ = 7.12-7.04 (m, 3H, CH_{Dip}), 4.38 (sept, ^3J = 6.8 Hz, 1H, CH(CH$_3$)$_2$), 3.58 (sept, ^3J = 6.8 Hz, 1H, CH(CH$_3$)$_2$), 3.41 (m, 8H, OCH_2), 2.68 (s, 1H, BeCH), 2.16 (d, ^2J = 12.0 Hz, 1H, CH_2), 1.95 (d, ^2J = 12.0 Hz, 1H, CH_2), 1.57 (s, 3H, C(CH_3)$_2$), 1.54 (s, 3H, C(CH_3)$_2$), 1.43 (s, 3H, C(CH_3)$_2$), 1.34 (d, ^3J = 6.8 Hz, 3H, CH(CH_3)$_2$), 1.32 (d, ^3J = 6.8 Hz, 3H, CH(CH_3)$_2$, overlapping with resonance at 1.30 ppm), 1.30 (d, ^3J = 6.8 Hz, 3H, CH(CH_3)$_2$), 1.90 (m, 8H, OCH$_2$CH_2), 1.16 (s, 3H, C(CH_3)$_2$) ppm; for minor rotamer **3'** (12%): δ = 7.12-7.04 (m, 2H, CH_{Dip}, overlapping with **3**), 7.01 (dm, ^3J = 7.0 Hz, 1H, *m*-CH_{Dip},) 4.35 (sept, ^3J = 6.8 Hz, 1H, CH(CH$_3$)$_2$), 3.68 (sept, ^3J = 6.8 Hz, 1H, CH(CH$_3$)$_2$), 3.41 (m, 8H, OCH_2), 2.11 (s, 1H, BeCH), 2.10 (d, ^2J = 12.3 Hz, 1H, CH_2), 1.93 (d, ^2J = 12.3Hz, 1H, CH_2), 1.68 (s, 3H, C(CH_3)$_2$), 1.59 (s, 3H, C(CH_3)$_2$), 1.48 (s, 3H, C(CH_3)$_2$), 1.42 (d, ^3J = 6.8 Hz, 3H, CH(CH_3)$_2$) ppm. *Note: the remaining CAAC-CH$_3$ ^{1}H NMR resonances of* ***3'*** *are hidden under those of* ***3****.* ^{9}Be NMR (56.3 MHz, C_6D_6): δ = 7.1 ($\omega_{1/2} \approx$ 150 Hz, **3'**), 4.7 ($\omega_{1/2} \approx$ 150 Hz, **3**) ppm. ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6): δ = 156.6 (br d, $^1J_{C\text{-}P}$ = 13.3 Hz, OCP), 152.5 (*o*-C_{Dip}), 151.5 (*o*-C_{Dip}), 147.8 (NC_{Dip}), 125.3 (CH$_{Dip}$), 125.3 (CH$_{Dip}$), 123.9 (CH$_{Dip}$), 69.9 (OCH$_2$), 69.1 (BeCH), 64.1 (NC(CH$_3$)$_2$), 61.7 (CH$_2$), 42.3 (C(CH$_3$)$_2$), 32.9 (C(CH$_3$)$_2$), 32.8 (C(CH$_3$)$_2$), 31.9 (C(CH$_3$)$_2$), 28.8 (CH(CH$_3$)$_2$), 28.6 (C(CH$_3$)$_2$), 27.3 (CH(CH$_3$)$_2$), 26.1 (CH(CH$_3$)$_2$), 25.6 (CH(CH$_3$)$_2$), 25.5 (CH(CH$_3$)$_2$), 25.1 (OCH$_2$$CH_2$) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ = −342.6 (unsymmetrical s, both rotamers) ppm. Elemental analysis (%) calcd. for $C_{29}H_{46}BeNO_3P$ [496.68 g mol^{-1}]: C 70.13, H 9.34, N 2.82; found: C 68.73, H 10.11, N 2.73. FT-IR (solid-state): $\tilde{\nu}$(OCP) = 1727 cm^{-1}.

Synthesis of [(CAAC)(Dur)Be(OCP)], 4b

1b (30.0 mg, 59.1 µmol, 1.00 equiv.) and [Na(OCP)(dioxane)$_{2.3}$] (16.8 mg, 59.1 µmol, 1.00 equiv.) were dissolved in 2 mL THF, resulting in an immediately colour change to dark purple, and turning dark brown after 0.5 min stirring. The reaction mixture was stirred for an additional 30 minutes, at which point NMR-spectroscopic analysis showed the formation of several products at $\delta_{9\text{Be}} \approx 17.4$, 14.1 (two overlapping br, $\omega_{1/2} \approx 650$ and 400 Hz, respectively), 4.7 and 1.8 (overlapping s and br, $\omega_{1/2} \approx 100$ and 400 Hz, respectively) ppm, and $\delta_{31\text{P}} = -328.6$ (s, ca. 48%), −339.6 (s, ca. 3%) −342.1 + −343.1 (overlapping s + br, $\omega_{1/2} \approx 320$ Hz, ca. 36%) and −380.2 (v. br, $\omega_{1/2} \approx 400$ Hz, ca. 13%) ppm. While the two ^{31}P NMR singlets at 329 and 340 ppm are indicative of BeOC*P* moieties, the two broad resonances at −342 and −380 ppm suggest Be−*P* bonding, as the adjacent quadrupolar ^{9}Be nucleus would cause broadening of the ^{31}P NMR resonances. Furthermore, EPR spectroscopy showed the presence of three distinct radical species, presumably accounting for the intense coloration of the reaction mixture, which could not be further identified. All volatiles were removed *in vacuo* and the residual brown solid was washed with pentane (2 × 0.4 mL) and extracted with benzene (2 × 2 mL). By diffusion of hexane into a saturated benzene solution of the crude product mixture at room temperature single crystals of the main reaction product, [(CAAC)(Dur)Be(OCP)] (**4b**, ca. 48% of the phosphorus-containing diamagnetic products) suitable for X-ray crystallographic analysis were obtained. Clean NMR data of **4b** could not be obtained as it systematically crystallised together with a compound of formula "(Dur)Be(OCP)" (**6**, 27%). The amount of isolated **4b** was insufficient for ^{13}C{^{1}H} NMR spectroscopy. *Note: The dropwise addition of [Na(OCP)(dioxane)$_{2.3}$] to **1b** at low temperature did not result in improved selectivity.* NMR data for **4b**: ^{1}H NMR (500 MHz, C_6D_6): $\delta = 7.21$ (d, $^{3}J = 7.3$, 8.0 Hz, 1H, *p*-CH_{Dip}), 7.09 (two overlapping d, $^{3}J = 7.3$, 8.0 Hz, 2H, *m*-CH_{Dip}), 6.93 (s, 1H, *p*-CH_{Dur}), 2.58 (sept, $^{3}J = 6.7$ Hz, 2H, C*H*(CH$_3$)$_2$), 2.24 (s, 6H, (CH_3)$_{\text{Dur}}$), 2.08 (s, 6H, (CH_3)$_{\text{Dur}}$), 1.37 (d, $^{3}J = 6.7$ Hz, 6H, CH(CH_3)$_2$), 1.25 (s, 2H, CH_2), 1.20 (s, 6H, C(CH_3)$_2$), 1.09 (d, $^{3}J = 6.7$ Hz, 6H, CH(CH_3)$_2$), 0.78 (s, 3H, C(CH_3)$_2$) ppm. ^{9}Be NMR (56.2 MHz, C_6D_6): $\delta = 14.1$ (br, $\omega_{1/2} \approx 470$ Hz) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): $\delta = -328.4$ (s) ppm. NMR data for **6**: ^{1}H NMR (400 MHz, C_6D_6): 6.86 (s, 1H, *p*-CH_{Dur}), 2.33 (s, 6H, (CH_3)$_{\text{Dur}}$), 2.27 (s, 6H, (CH_3)$_{\text{Dur}}$) ppm. ^{9}Be NMR (56.2 MHz, C_6D_6): $\delta = 1.4$ (br, $\omega_{1/2} \approx 280$ Hz) ppm. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): $\delta = -339.6$ (s) ppm. FT-IR (solid-state): $\tilde{\nu}$(OCP) = 1691 cm^{-1}.

Synthesis of [(CAAC)Be(OCN)Br]$_6$, 7

1a (30.0 mg, 454 µmol, 1.00 equiv.) and [K(OCN)] (4.42 mg, 545 µmol, 1.20 equiv.) were suspended in 0.5 mL of a benzene/THF mixture. Since ^{9}Be NMR spectra after several hours at rt showed incomplete conversion, the mixture was heated to 60 °C for 12 h. All volatile components were removed from the resulting pale yellow suspension *in vacuo*. The yellow residue was washed with pentane (1 × 0.3 mL) and extracted with benzene (2 × 1 mL). The ^{9}Be NMR spectrum of the crude product systematically showed a mixture of several tetracoordinate beryllium complexes in varying ratios (δ_{9Be} = 8.8, 7.0, 4.0, 2.0 ppm). By evaporation of a saturated benzene solution, a few colourless single crystals suitable for X-ray crystallographic analysis of the hexameric complex **7** were obtained. Attempts to isolate this complex or any of the other products in sufficient quantities for full characterisation failed. *Note: attempts to synthesise **7** from the 1:1 reaction of [(CAAC)BBr$_2$] with [K(OCN)] also yielded intractable mixtures of products.*

Synthesis of [(CAACH)(THF)Be(CN)]$_4$, 8

1a (30.0 mg, 454 µmol, 1.00 equiv.) and [K(SeCN)] (7.20 mg, 499 µmol, 1.10 equiv.) were combined in 1 mL THF and the mixture stirred at rt for 45 min, yielding a colourless suspension. All volatiles were removed *in vacuo*. Extraction with pentane (1 × 0.3 mL) and crystallisation at −30 °C yielded a 1:1 mixture of CAAC=Se[6] and the tetrameric complex **8**, which could not be separated from each other. The latter was identified by X-ray structural analysis. A single resonance in the ^{9}Be NMR spectrum of the crude product suggests the formation of **8** as the sole product of the reaction. *Note: Similar results were obtained when using [Na(SeCN)].* Unfortunately, rapid and systematic decomposition upon workup prevented the full characterisation of **8**. The ^{1}H NMR spectrum of the crude mixture of **8** and CAAC=Se (Figure S20) shows the presence of multiple diastereomers of **8**, which could not be deconvoluted. NMR data for **8**: ^{1}H NMR (400 MHz, C_6D_6): δ = 7.15-7.01 (m, 3H, CH_{Dip}), 4.45 (unresolved sept, 1H, $CH(CH_3)_2$), 3.73-3.38 (v. br, 9H, $(OCH_2)_{THF}$ + $CH(CH_3)_2$), 2.58, 2.55, 2.51, 2.48, 2.45 (multiple overlapping s, 1H, BeCH), 2.28 (multiple overlapping d, 1H, CH_2), 1.97 (multiple overlapping d, 1H, CH_2), 1.75-1.69 (multiple overlapping s, 3H, CH_3), 1.59-1.48 (multiple overlapping s/d, 9H, CH_3), 1.41-1.30 (multiple overlapping br/d/s, 15H, $(CH_2)_{THF}$ + CH_3), 1.28-1.25 (multiple overlapping s/d, 6H, CH_3) ppm. ^{9}Be NMR (56.2 MHz, C_6D_6): δ = 3.4 ($\omega_{1/2} \approx$ 440 Hz) ppm.

NMR spectra of isolated compounds

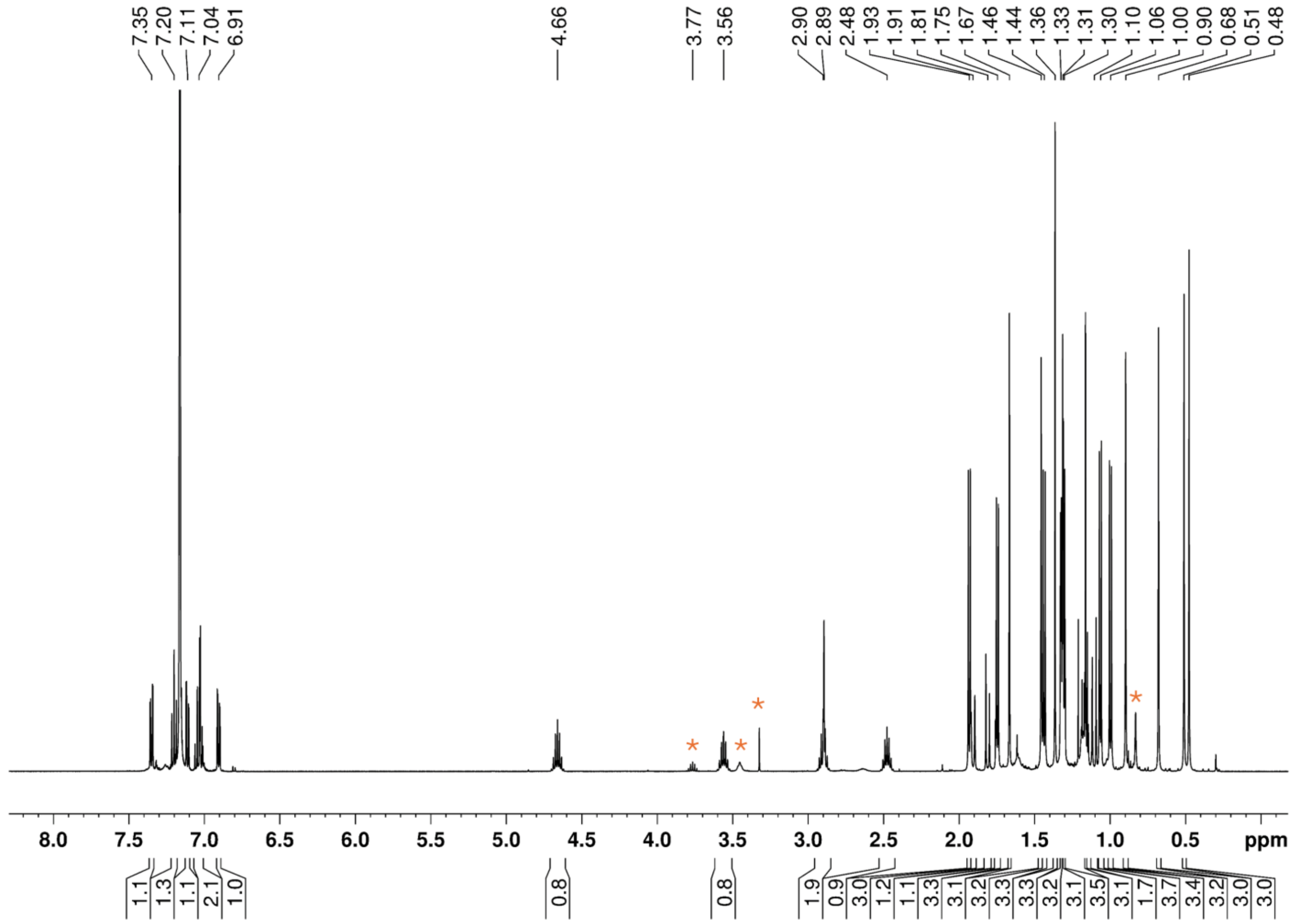

Figure S1. ^{1}H NMR spectrum of **2a** in C_6D_6. The resonances marked with a * correspond to an unknown side product.

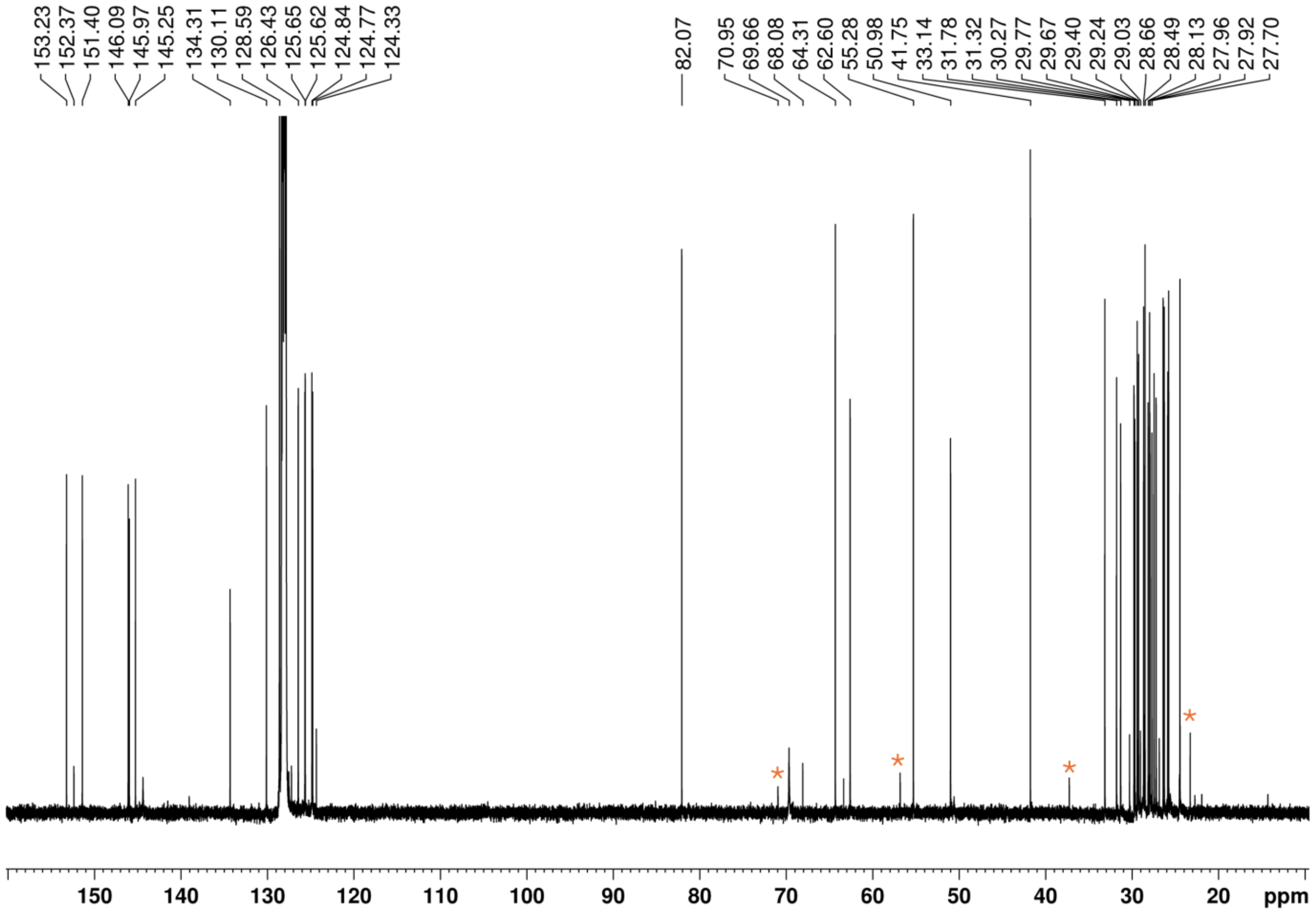

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in C_6D_6. The resonances marked with a * correspond to an unknown side product.

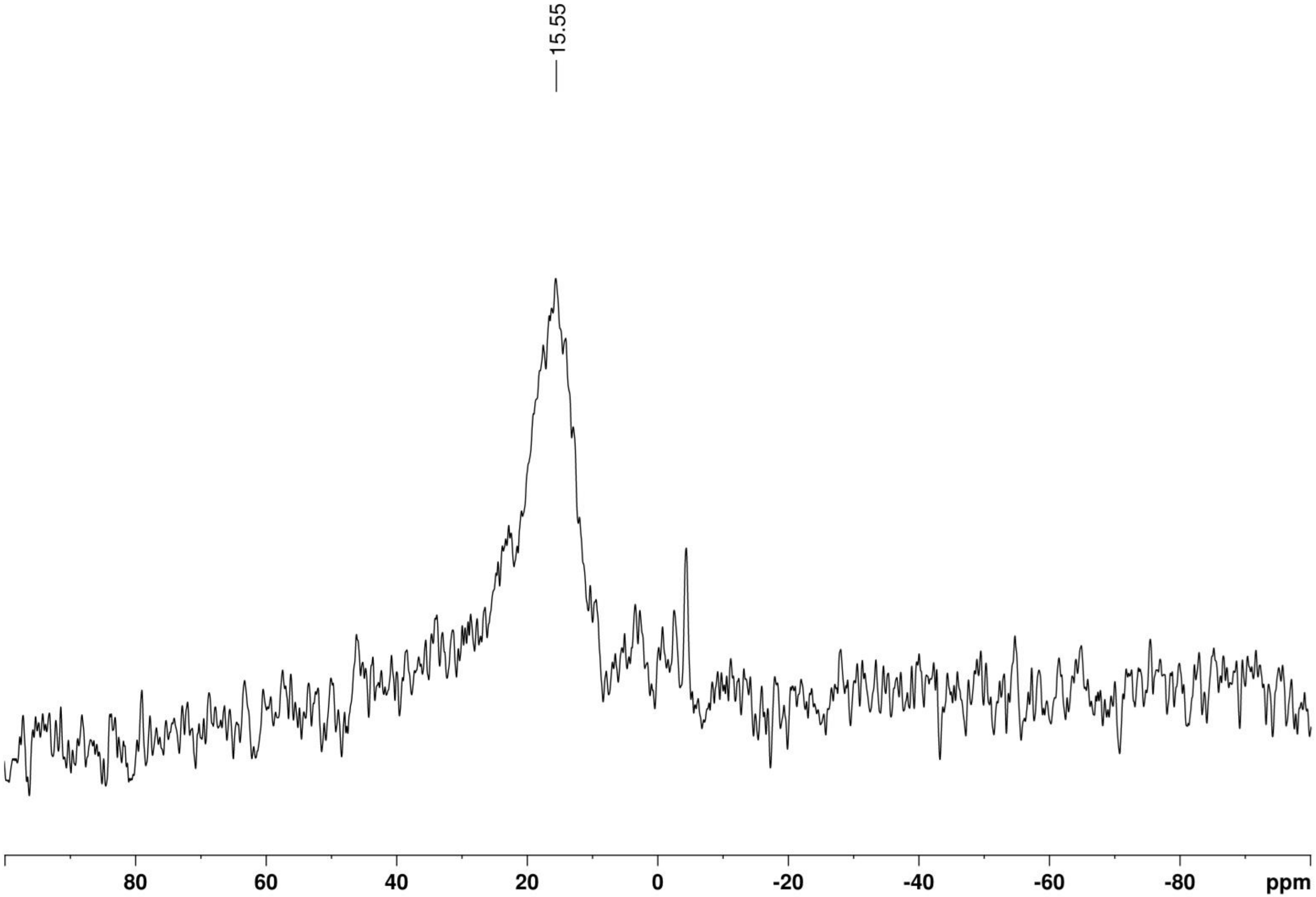
15.55
80
60
40
20
0
-20
-40
-60
-80
ppm

Figure S3. ^{9}Be NMR spectrum of **2a** in C_6D_6.

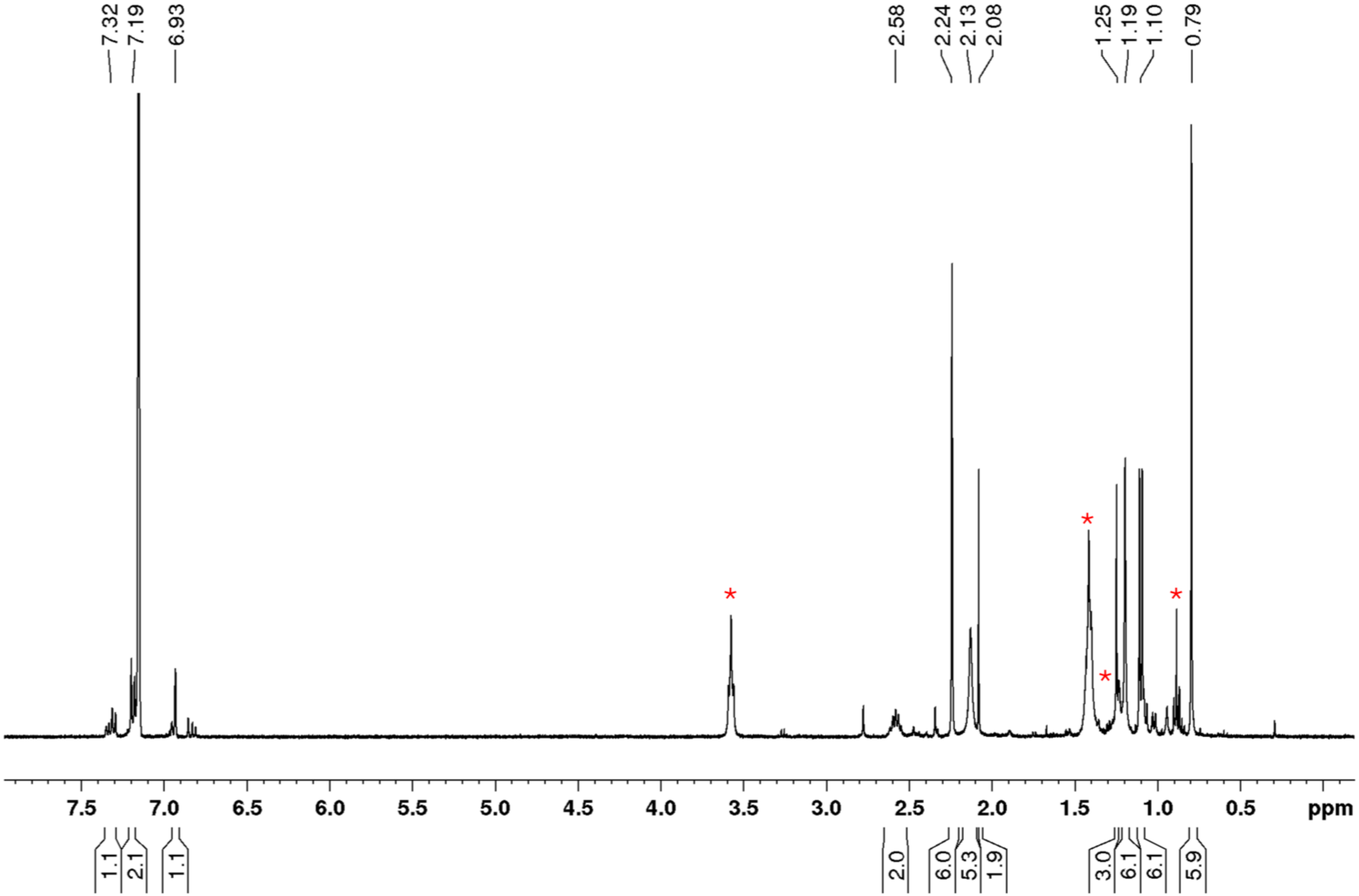

Figure S4. ^{1}H NMR spectrum of **2b** in C_6D_6. The resonances marked with a * correspond to THF and hexane, which were used to grow crystals.

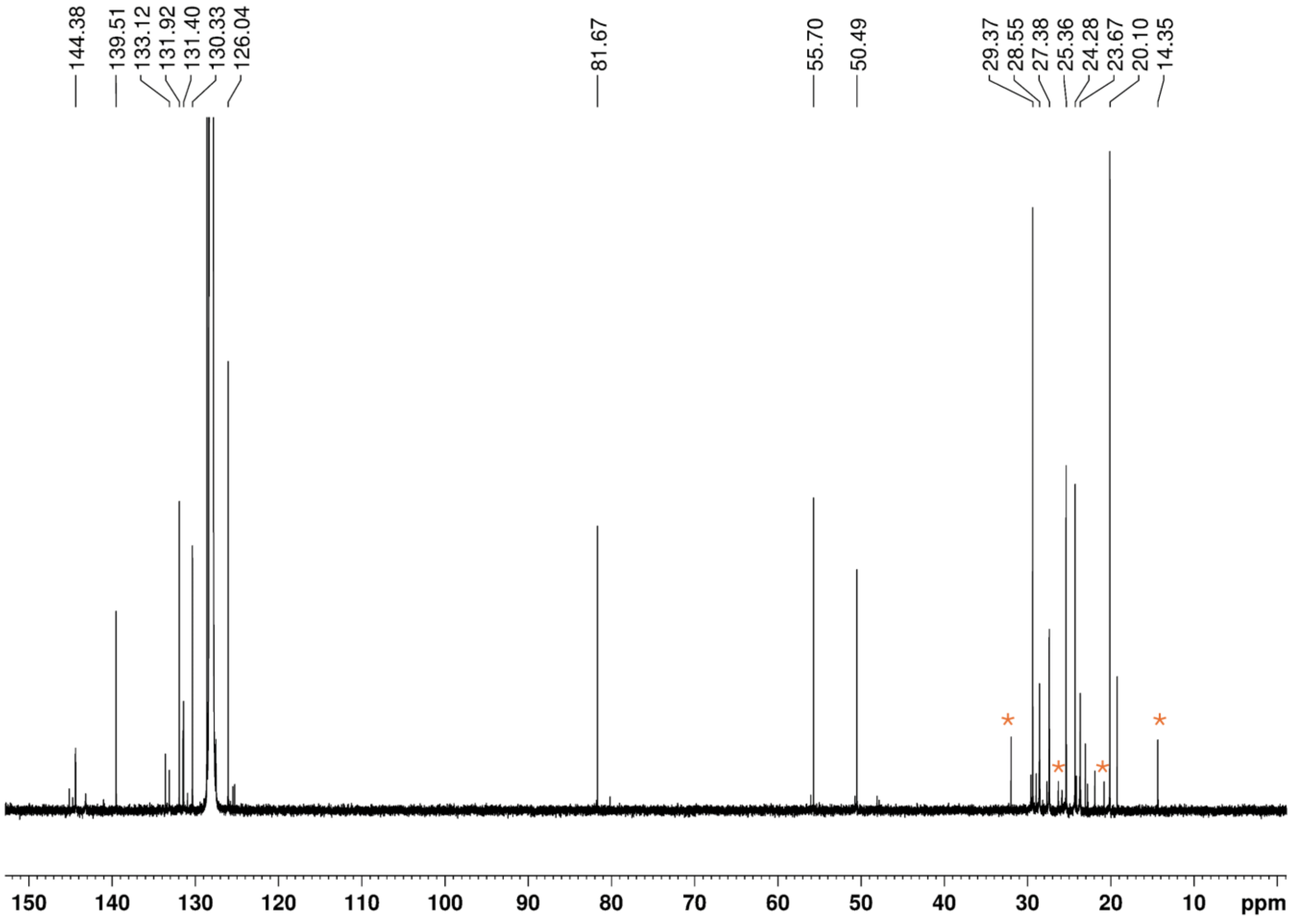

Figure S5. $^{13}C\{^1H\}$ NMR spectrum of **2b** in C_6D_6. The resonances marked with a * correspond to THF and hexane, which were used to grow crystals.

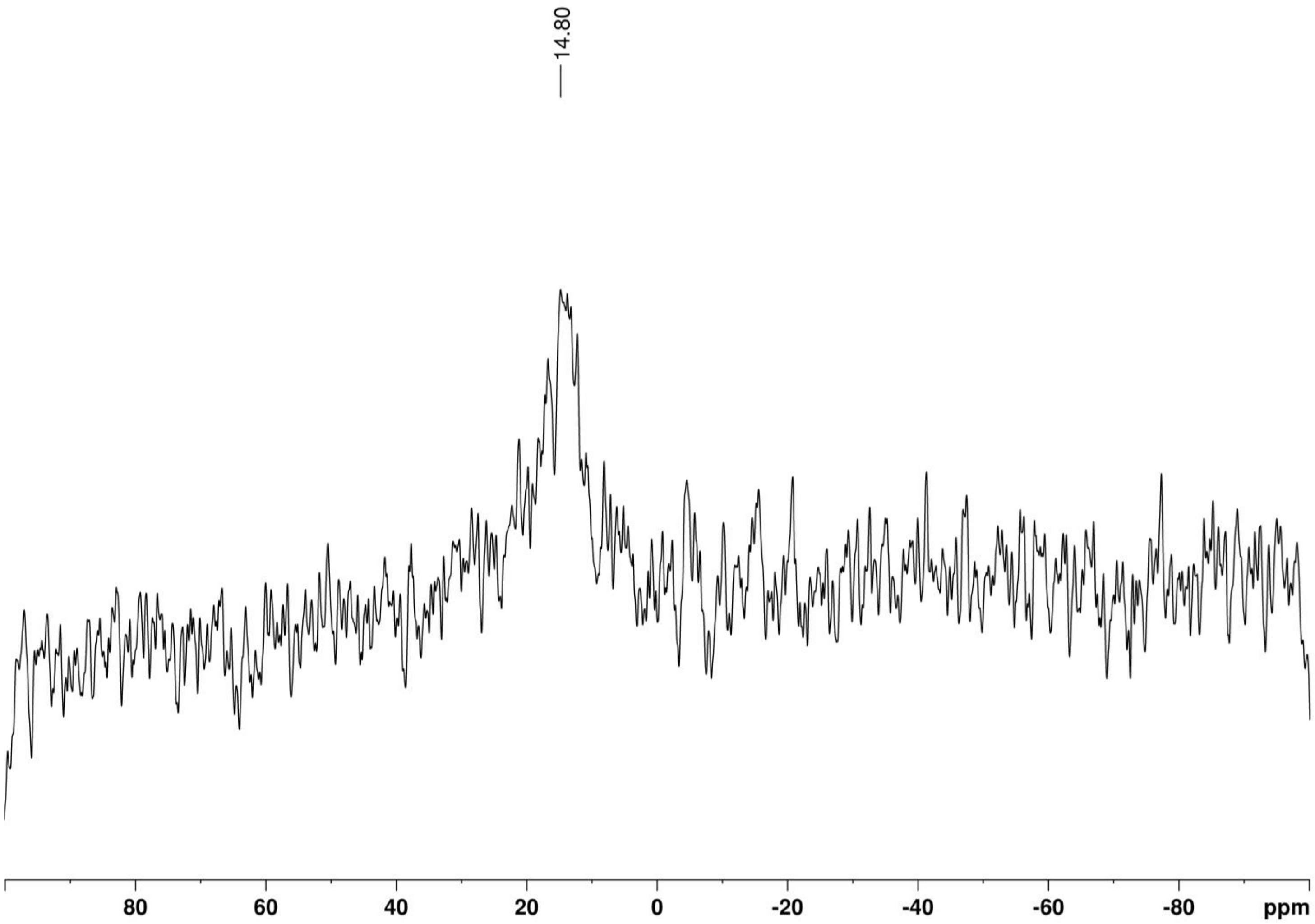

Figure S6. ^{9}Be NMR spectrum of **2b** in C_6D_6.

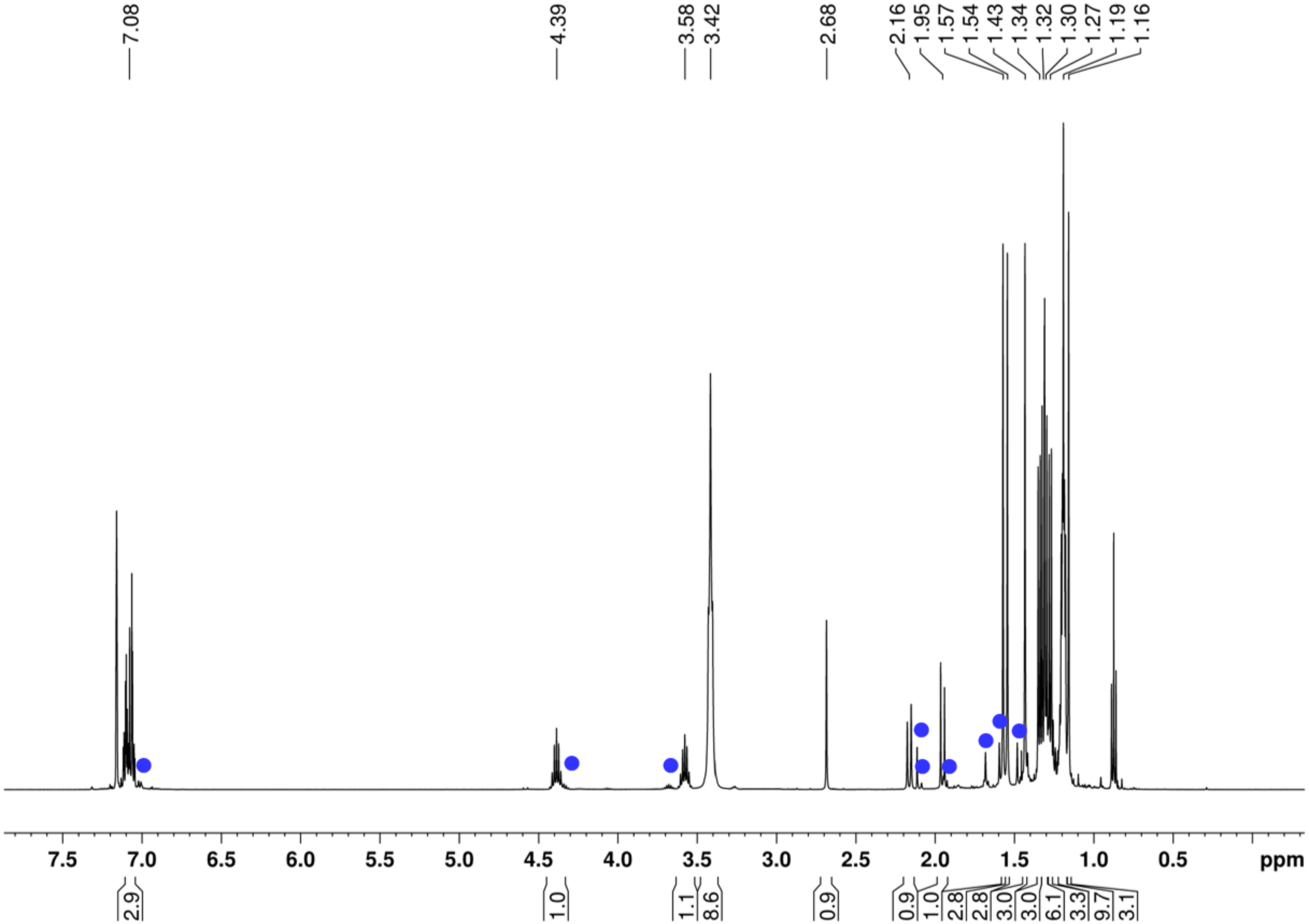

Figure S7. ^{1}H NMR spectrum of **3** in C_6D_6 with some pentane out of the crystals. The minor resonances marked with ● correspond to **3'**.

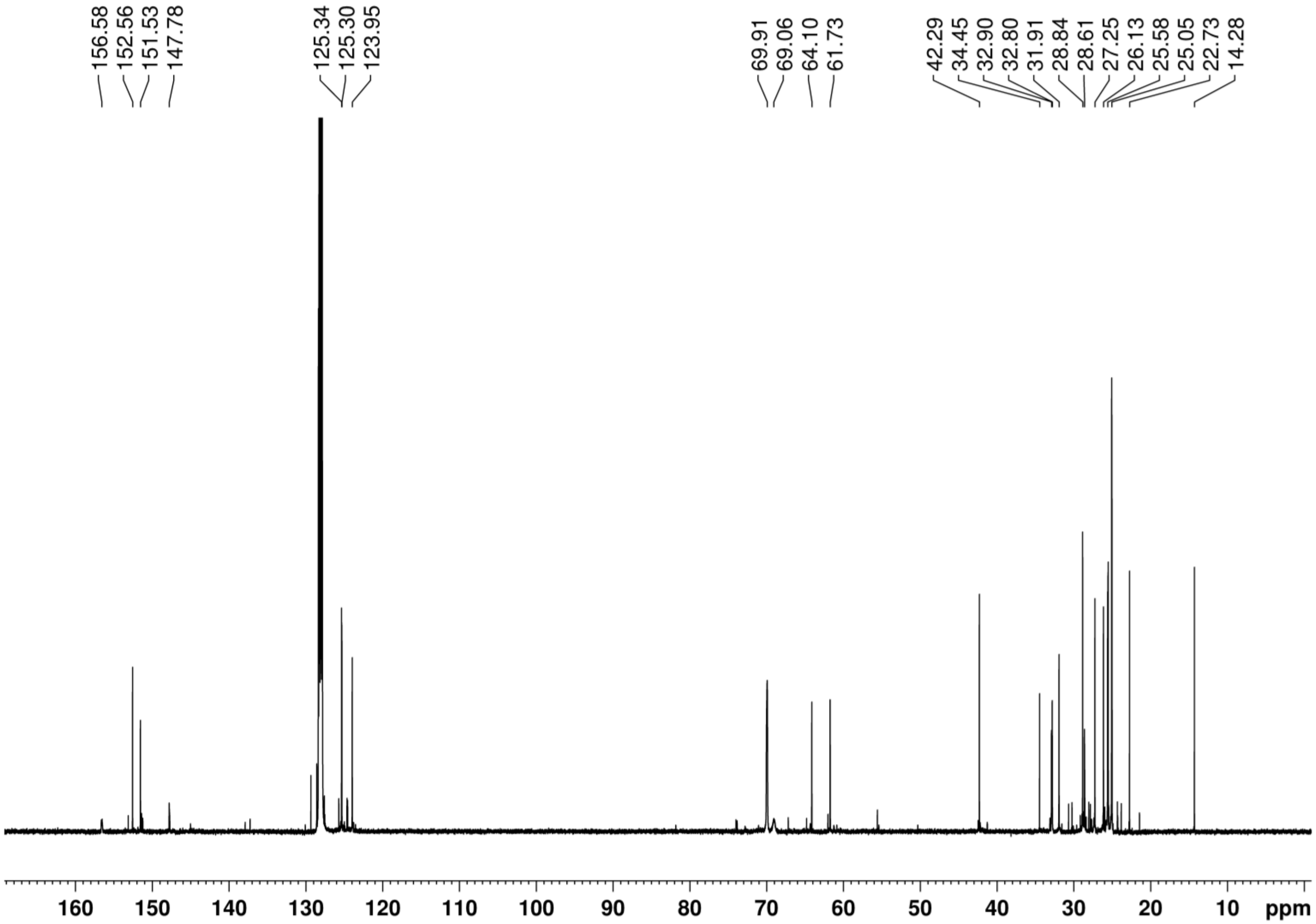

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6. The minor resonances correspond to the rotamer **3'** and the byproduct **4a**.

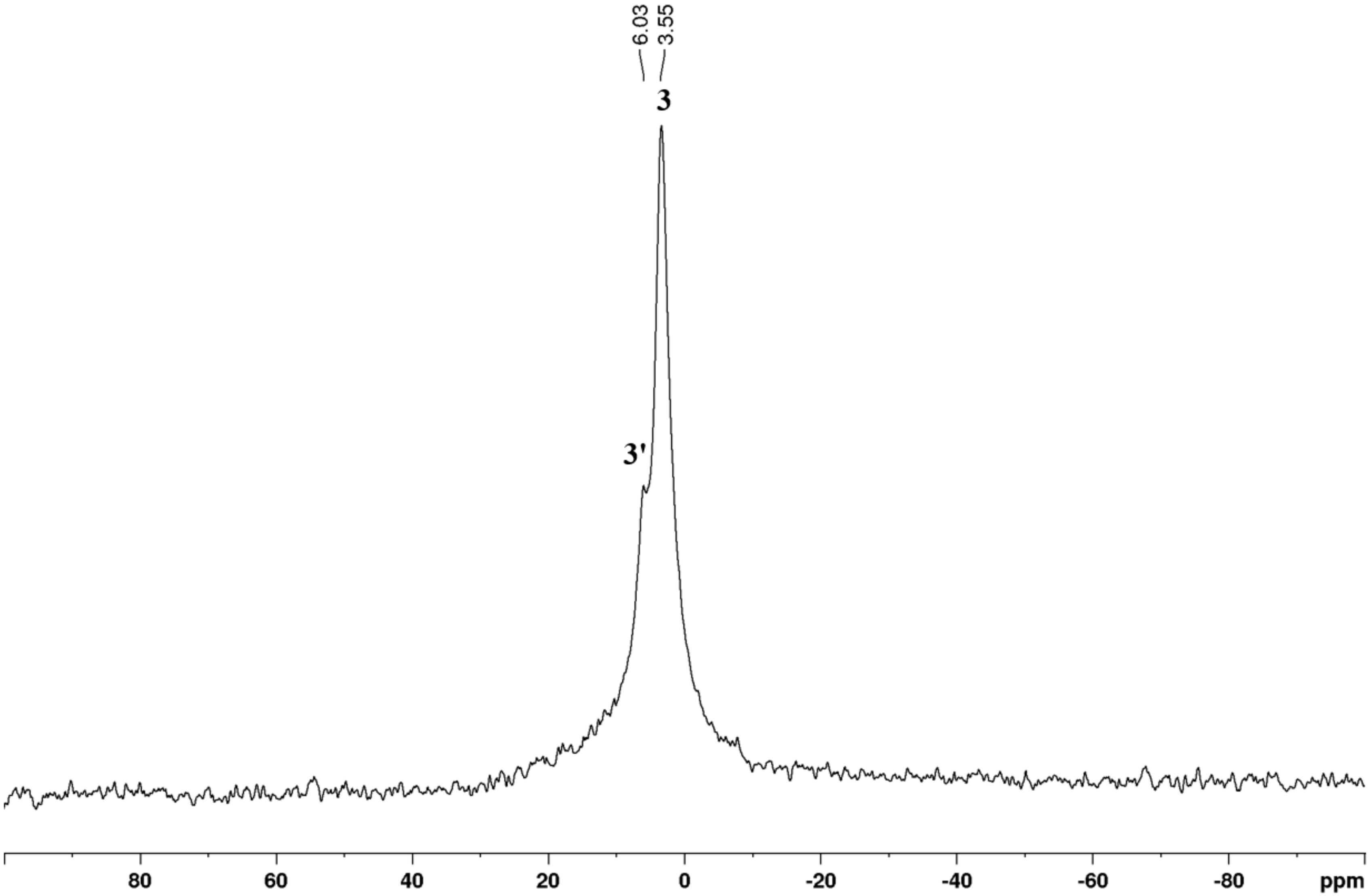

Figure S9. ^{9}Be NMR spectrum of **3/3'** in C_6D_6.

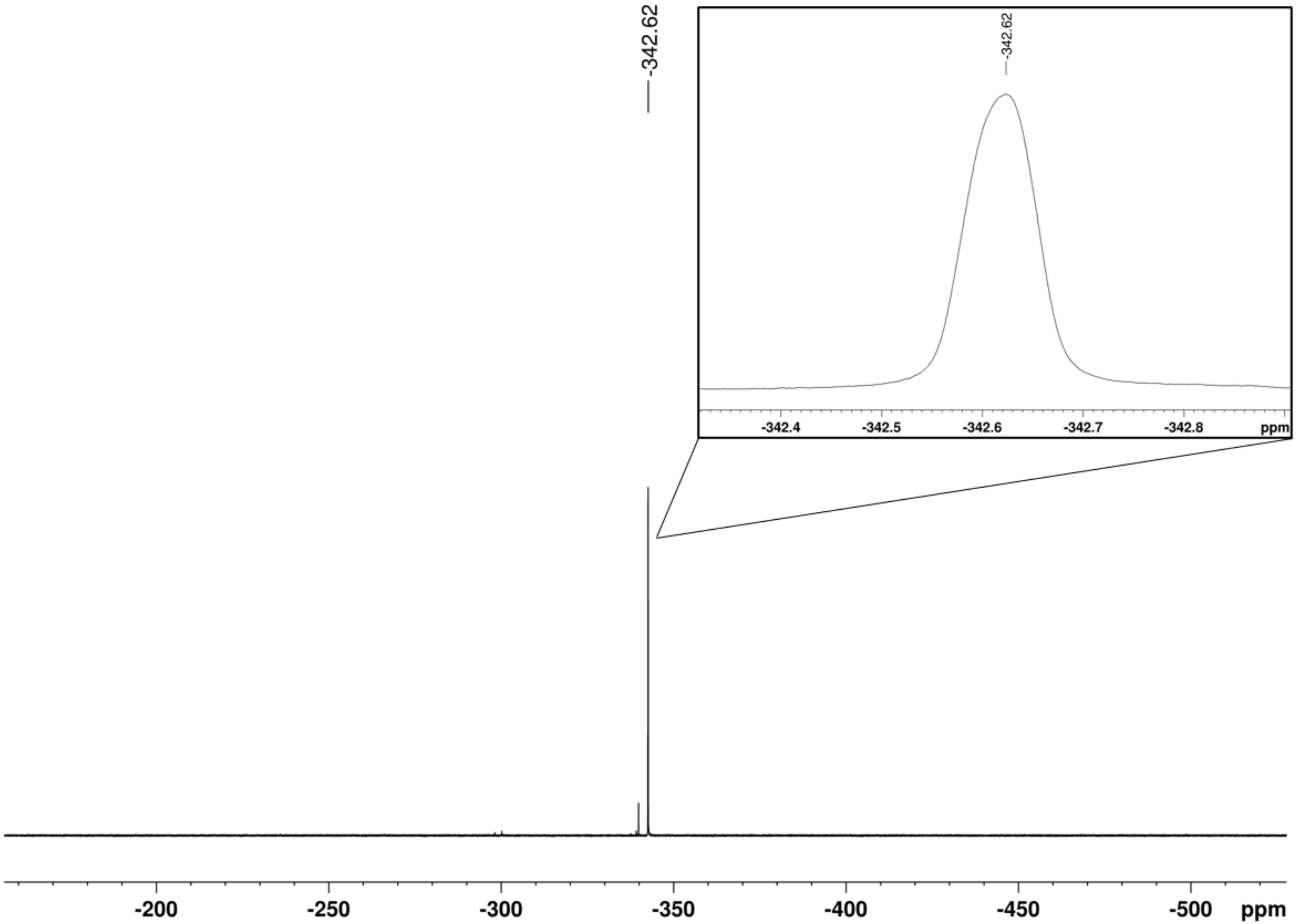

Figure S10. ^{31}P NMR spectrum of **3/3'** in C_6D_6 (insert zooming in on the asymmetry of the resonance). The impurity at 339.8 ppm corresponds to the byproduct **4a** (< 2%).

NMR spectra of product mixtures or non-isolated products

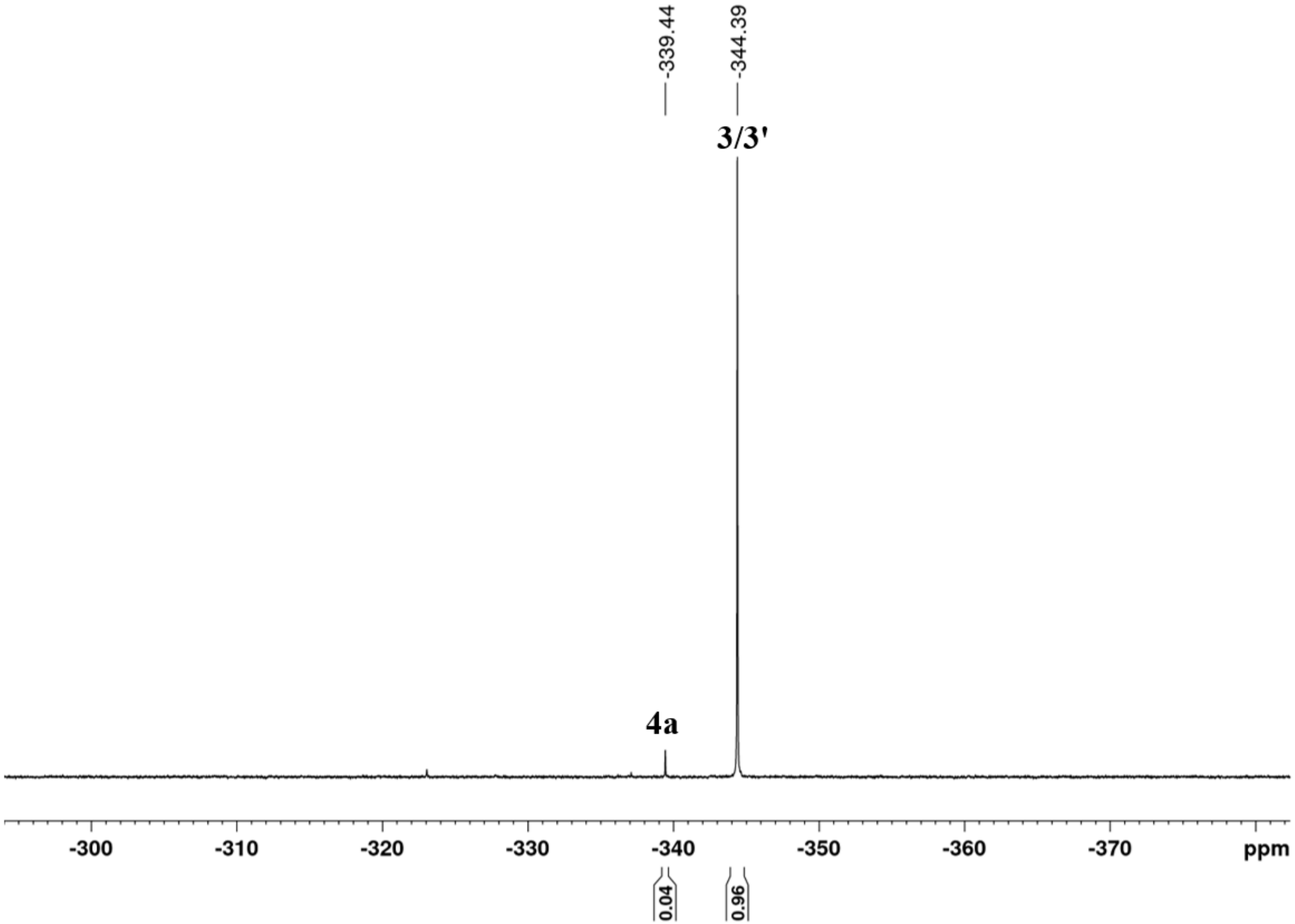

Figure S11. Annotated crude ^{31}P NMR spectrum of the reaction of **1a** with [Na(OCP)(dioxane)$_{2.3}$]).

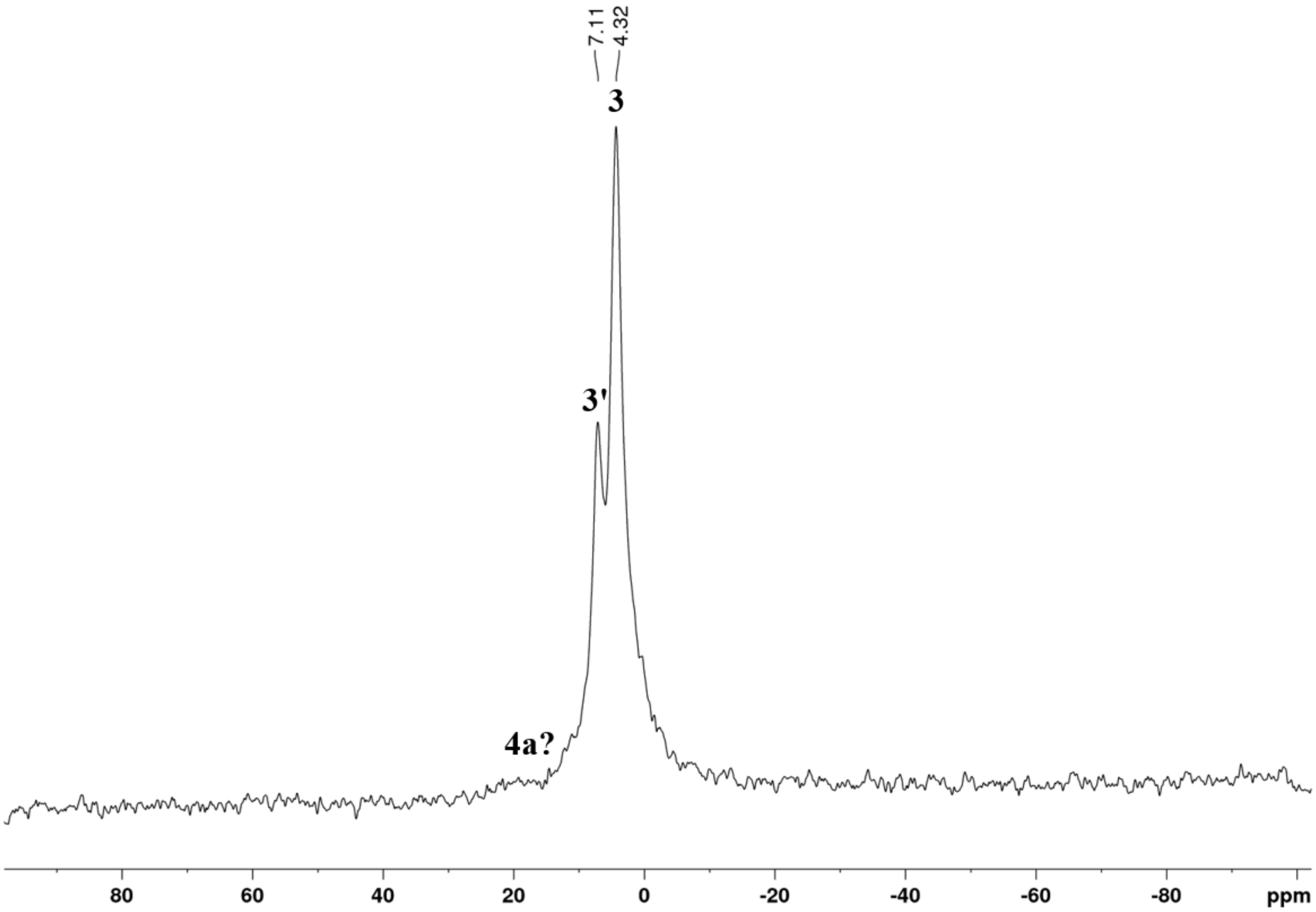

Figure S12. Annotated crude ^{9}Be NMR spectrum of the reaction of **1a** with [Na(OCP)(dioxane)$_{2.3}$]).

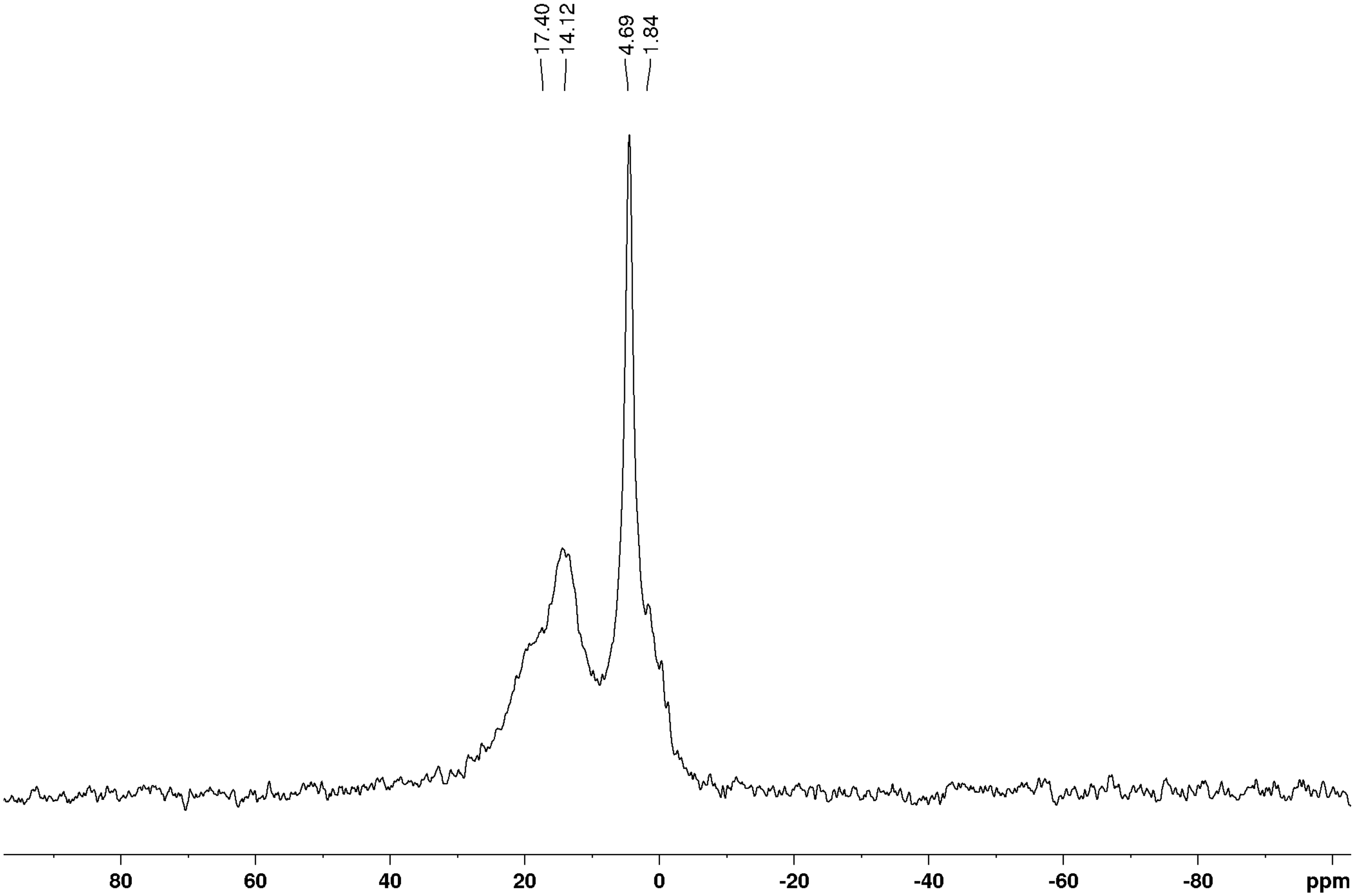

Figure S13. Crude ^{9}Be NMR spectrum of the reaction of **1b** with [Na(OCP)(dioxane)$_{2.3}$]).

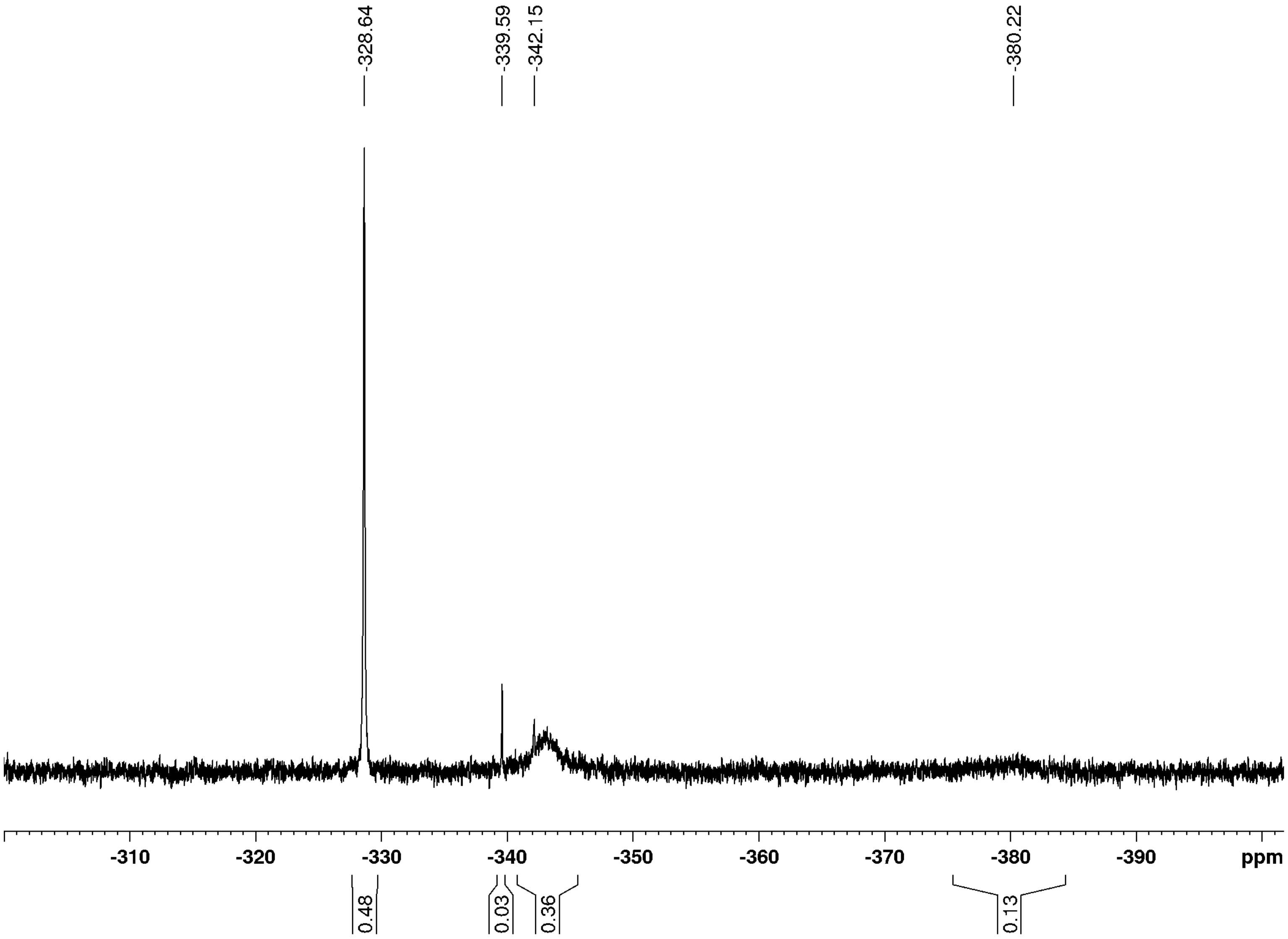

Figure S14. Crude $^{31}P\{^1H\}$ NMR spectrum of the reaction of **1b** with [Na(OCP)(dioxane)$_{2.3}$]).

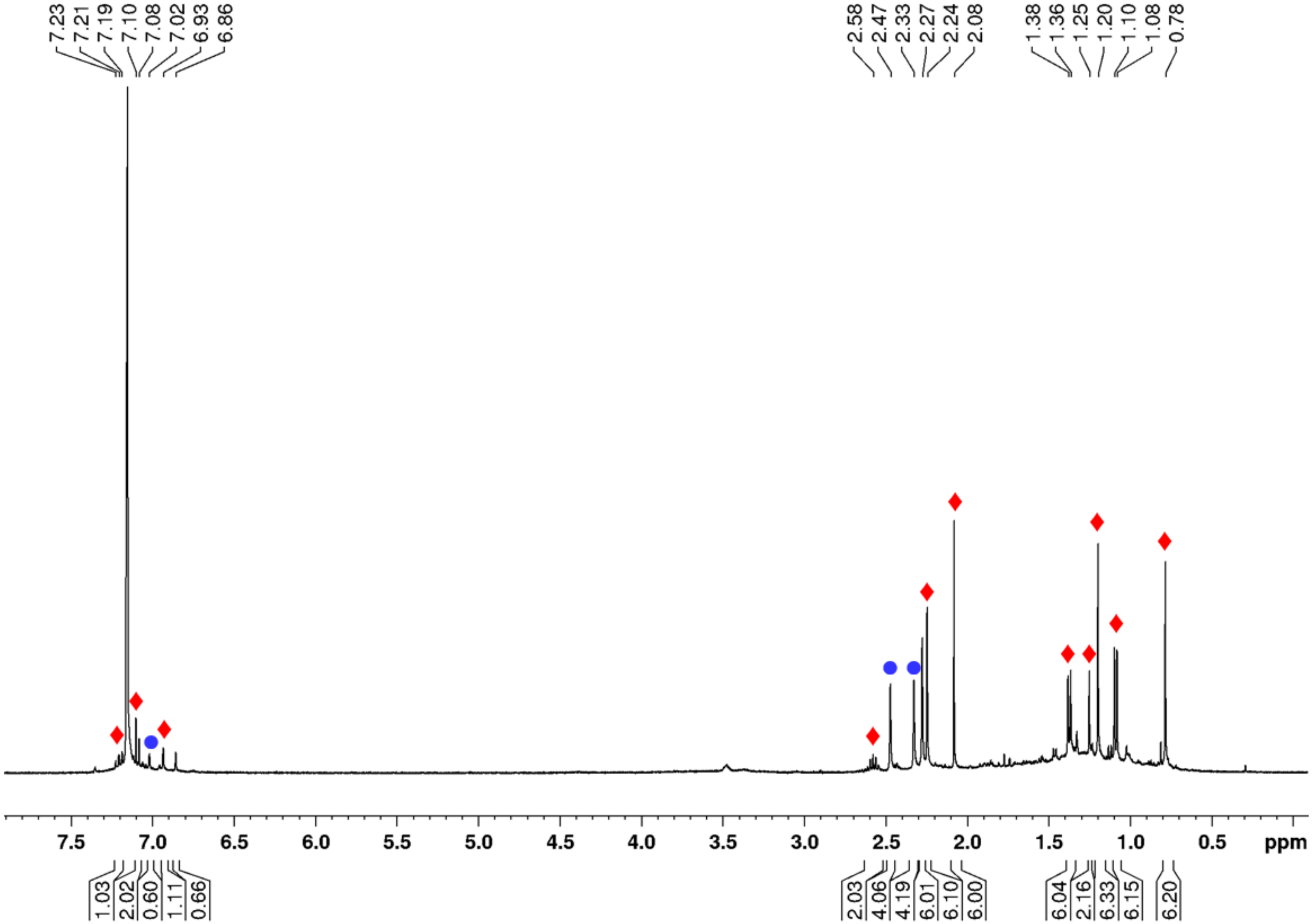

Figure S15. Annotated ^{1}H NMR spectrum of a 3:1 mixture of **4b** (♦) and **6** (●) (C_6D_6 extract of the crude product mixture from the reaction of **1b** with [Na(OCP)(dioxane)$_{2.3}$]).

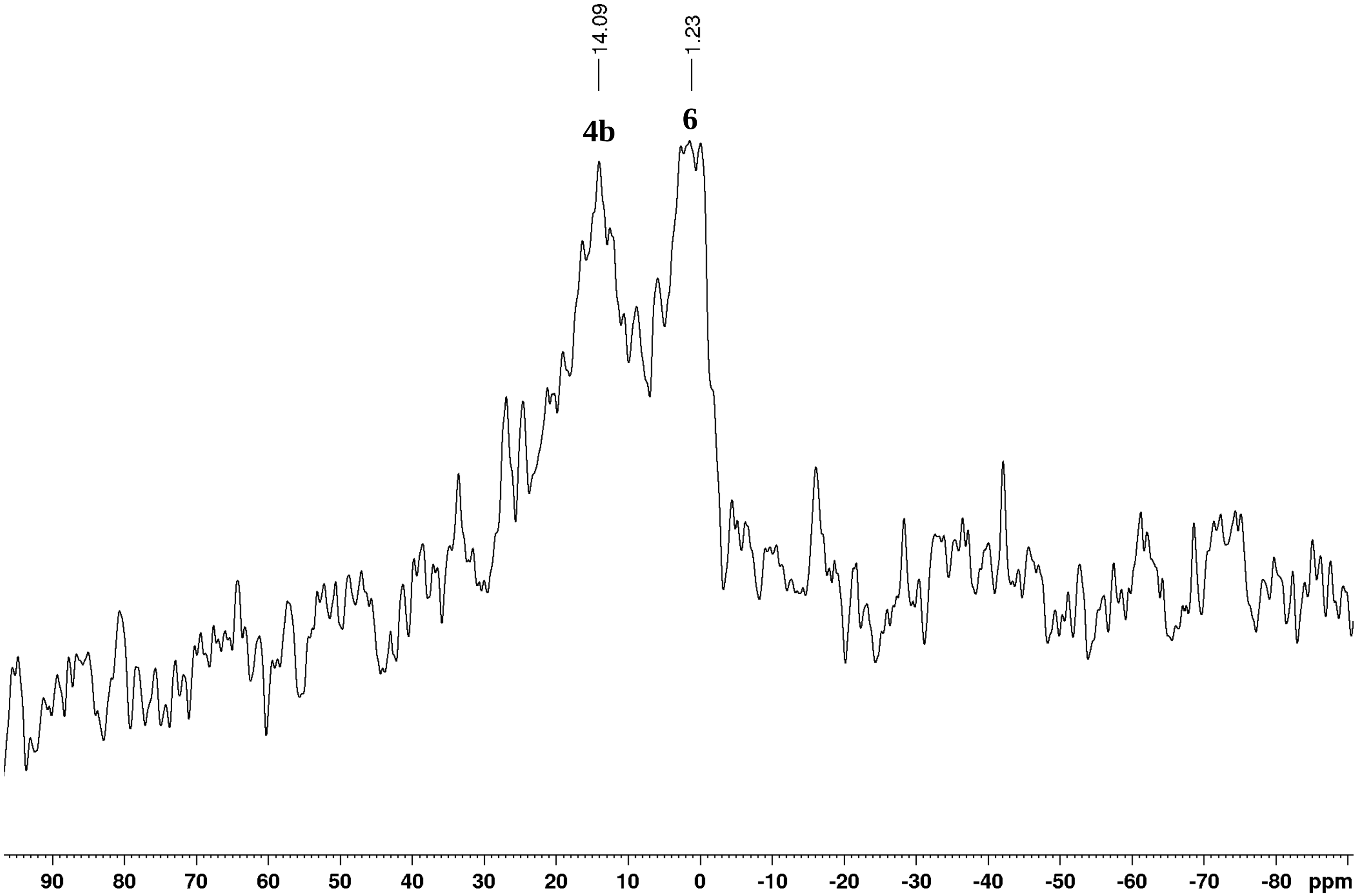

Figure S16. Annotated ^{9}Be NMR spectrum of a 3:1 mixture of **4b** and **6** (C_6D_6 extract of the crude product mixture from the reaction of **1b** with [Na(OCP)(dioxane)$_{2.3}$]).

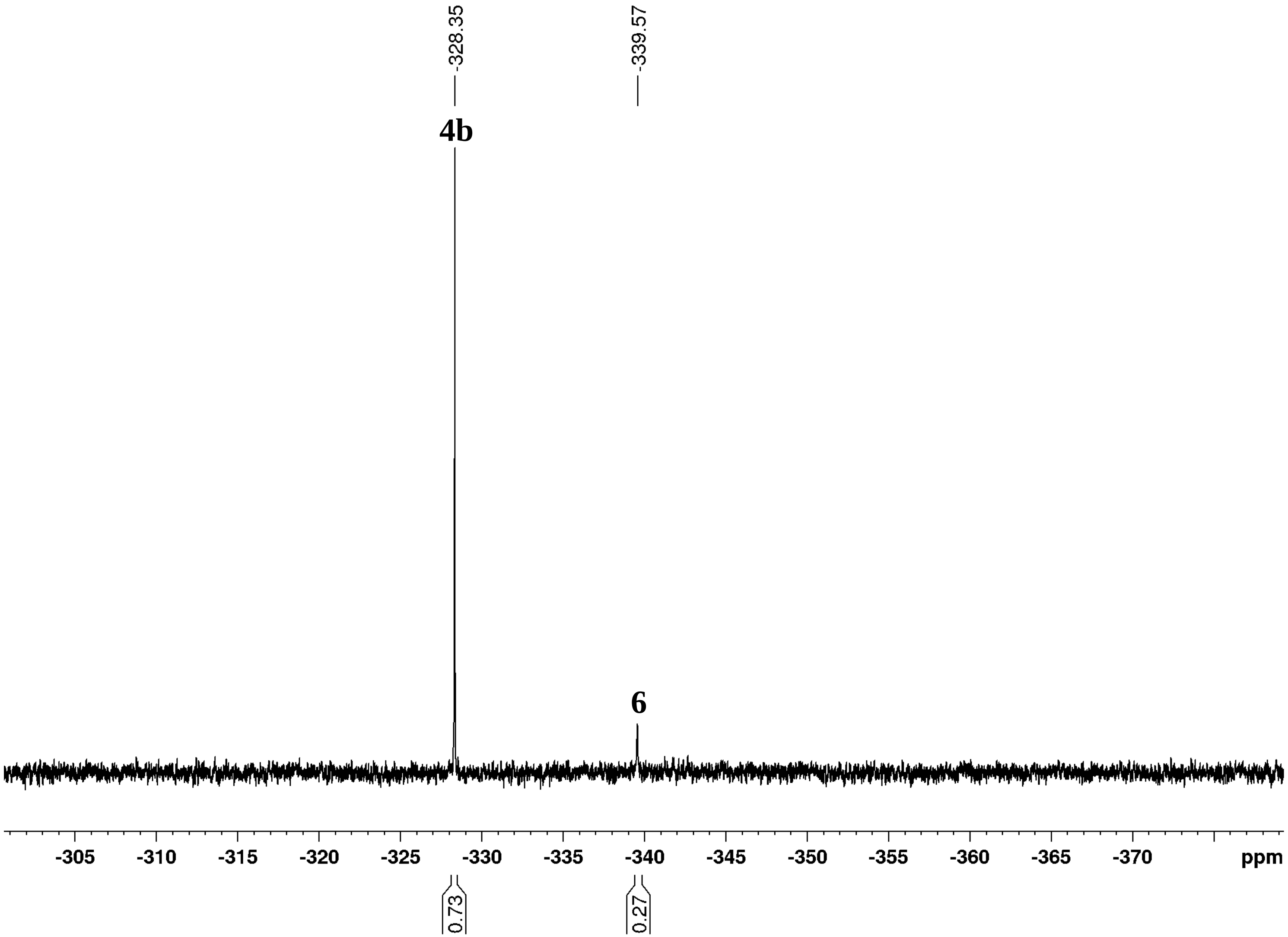

Figure S17. Annotated $^{31}P\{^1H\}$ NMR spectrum of a 3:1 mixture of **4b** and **6** (C_6D_6 extract of the crude product mixture from the reaction of **1b** with [Na(OCP)(dioxane)$_{2.3}$]).

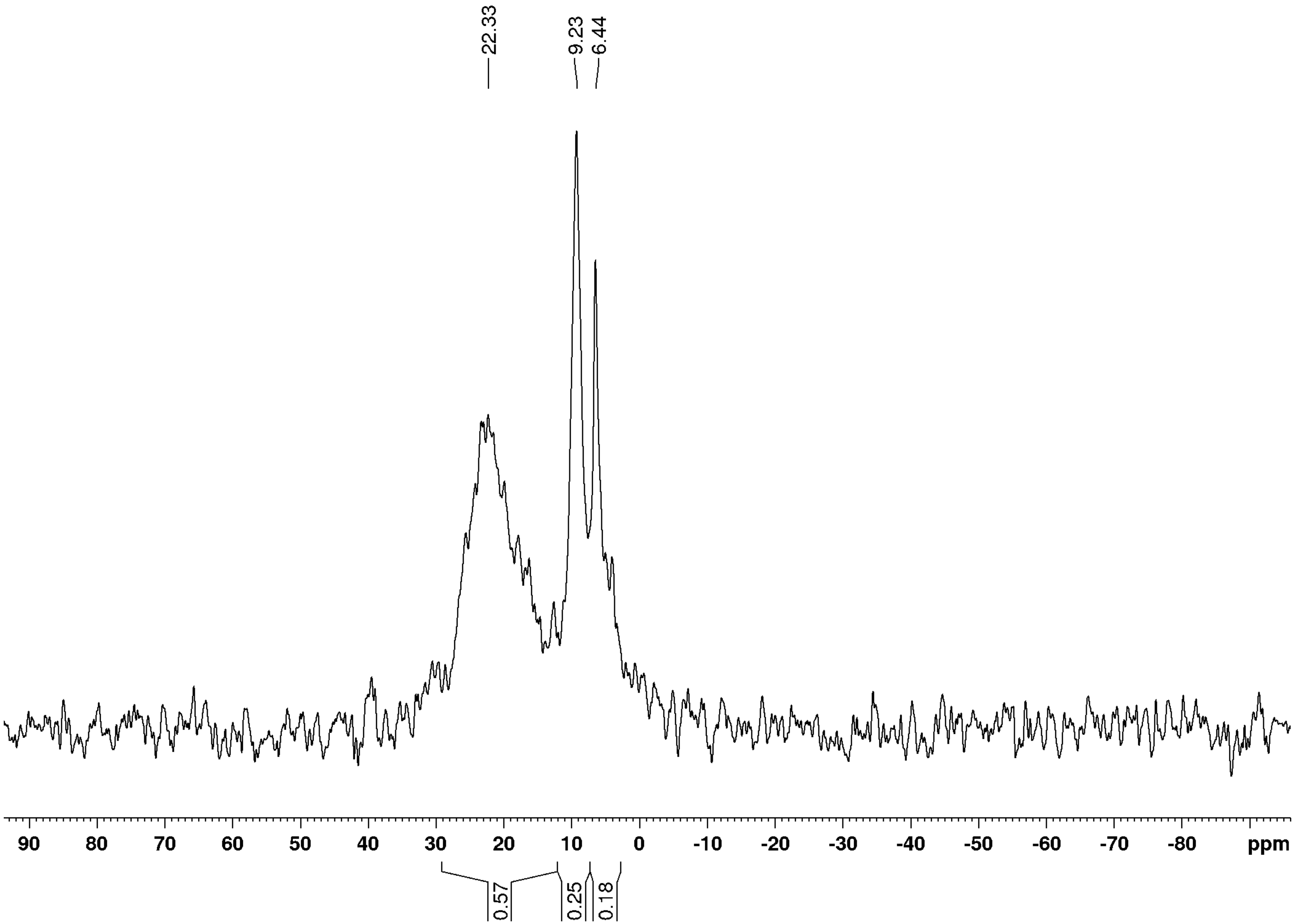

Figure S18. ^{9}Be NMR spectrum of the reaction mixture of **1a** with [K(OCN)] after 18 h at rt.

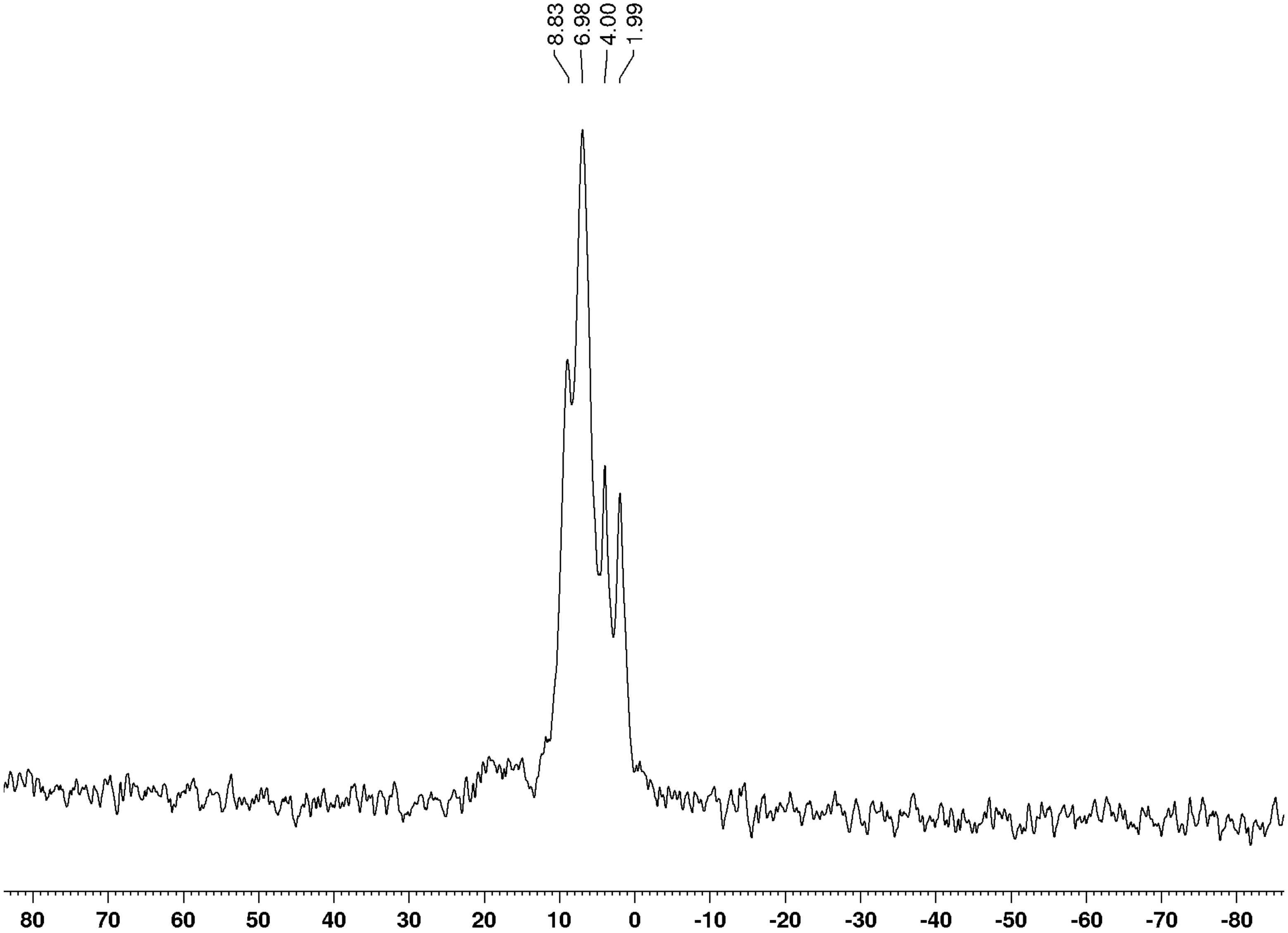

Figure S19. ^{9}Be NMR spectrum of the reaction mixture of **1a** with [K(OCN)] after 12 h at 60 °C.

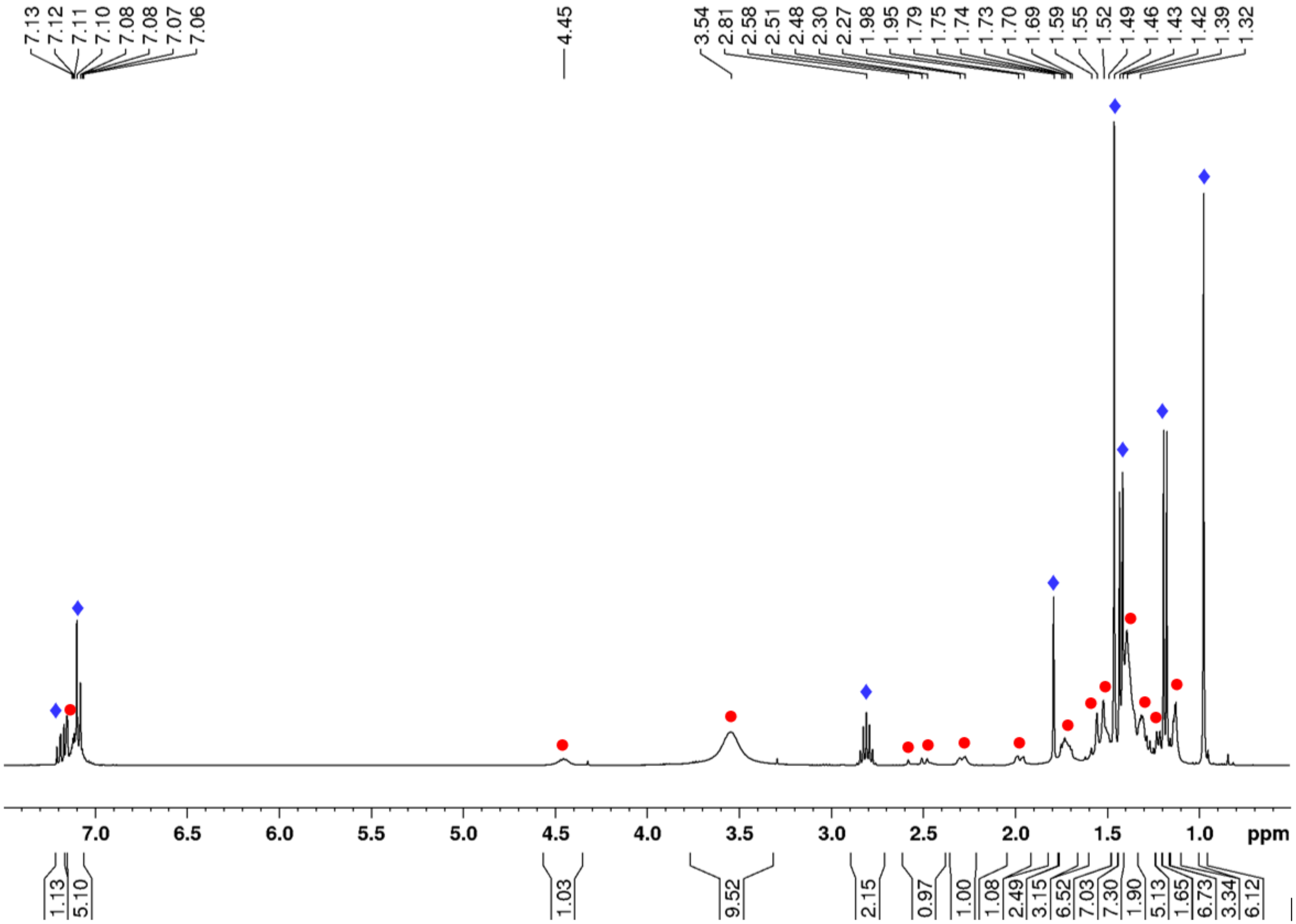

Figure S20. Annotated in-situ ^{1}H NMR spectrum of the 1:1 mixture of **8** (●) and CAAC=Se (♦) obtained from the reaction of **1a** with [K(SeCN)].

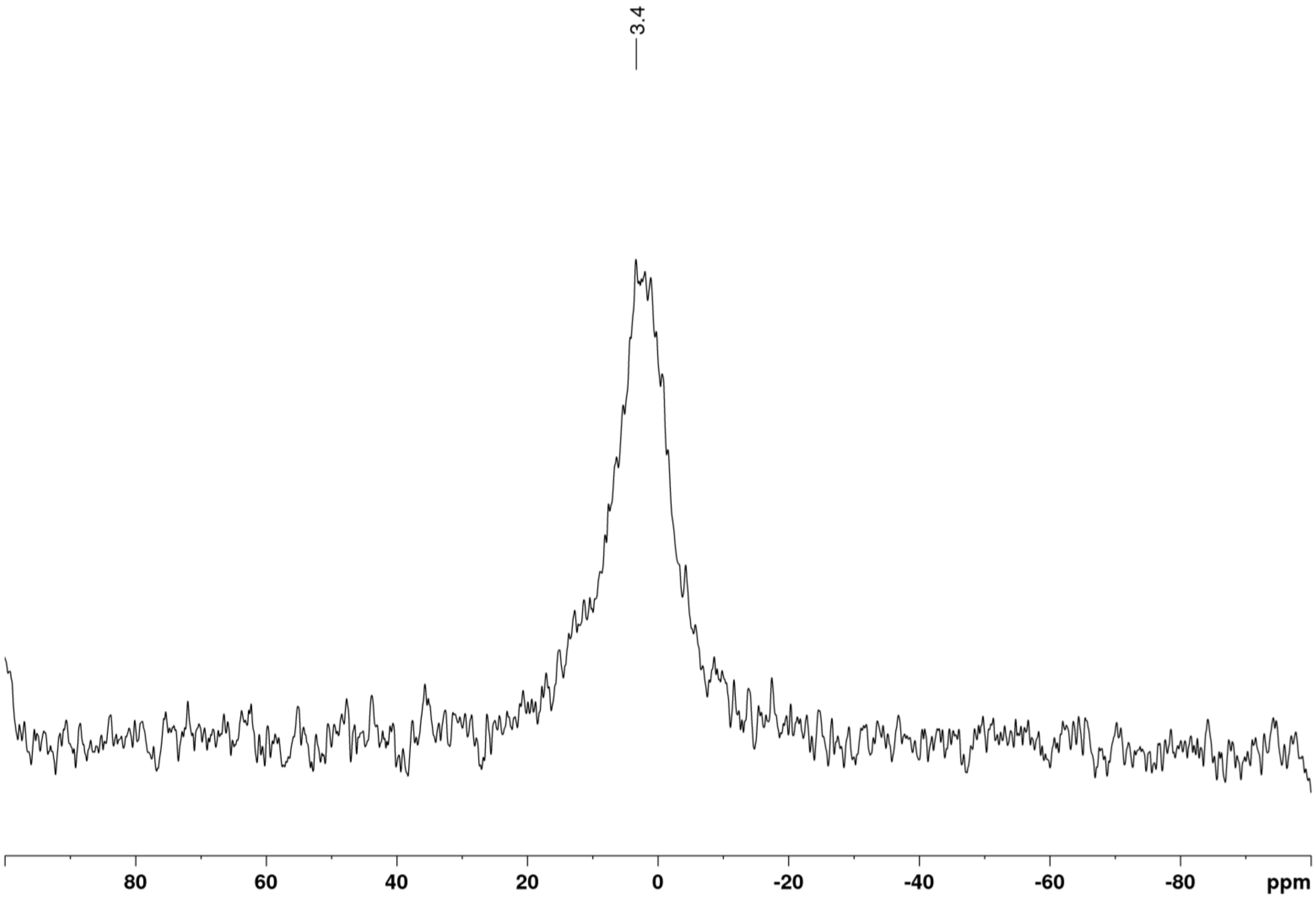

Figure S21. In-situ ^{9}Be NMR spectrum of **8**.

IR spectra

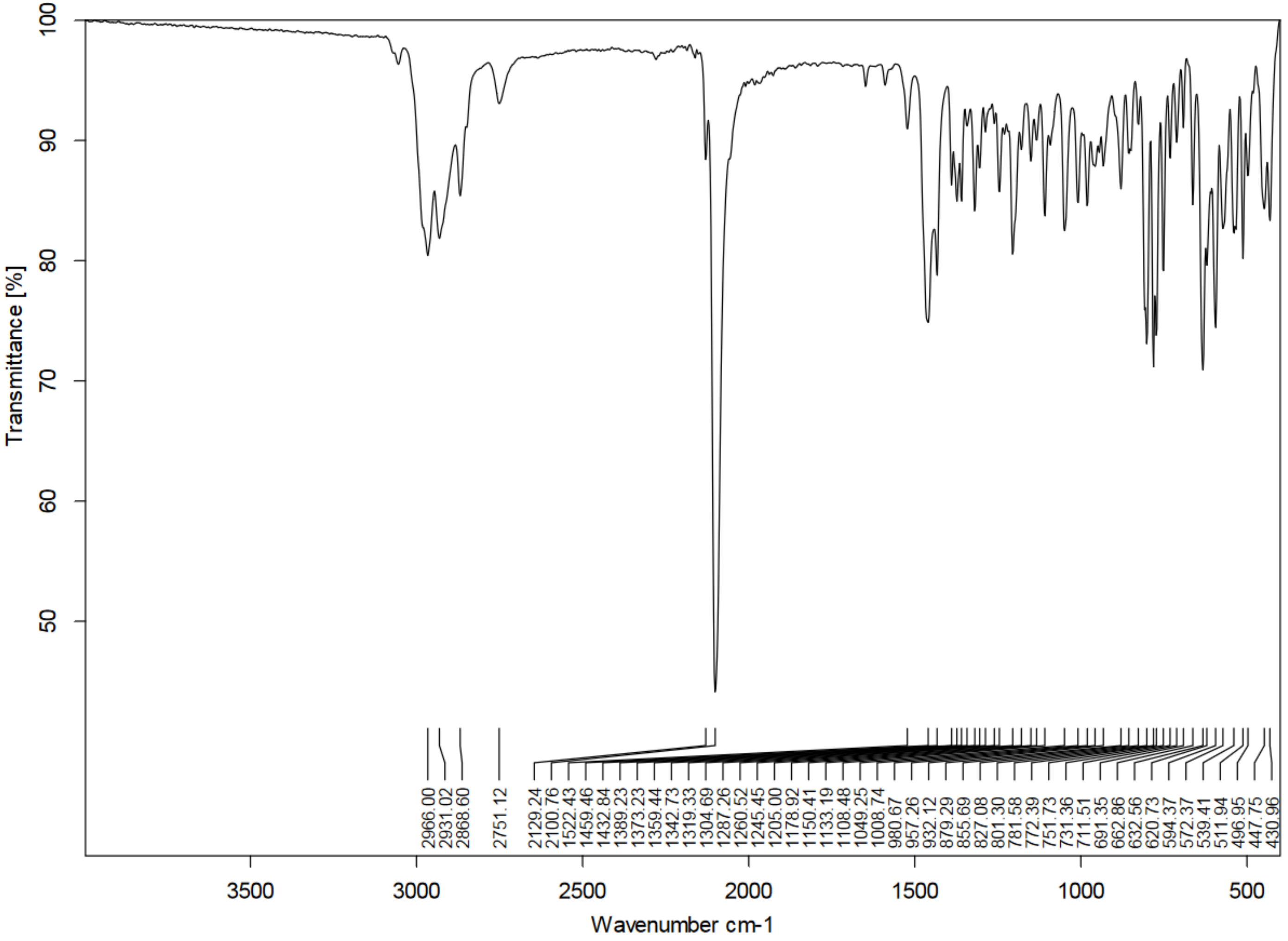

Figure S22. Solid-state IR spectrum of **2a**.

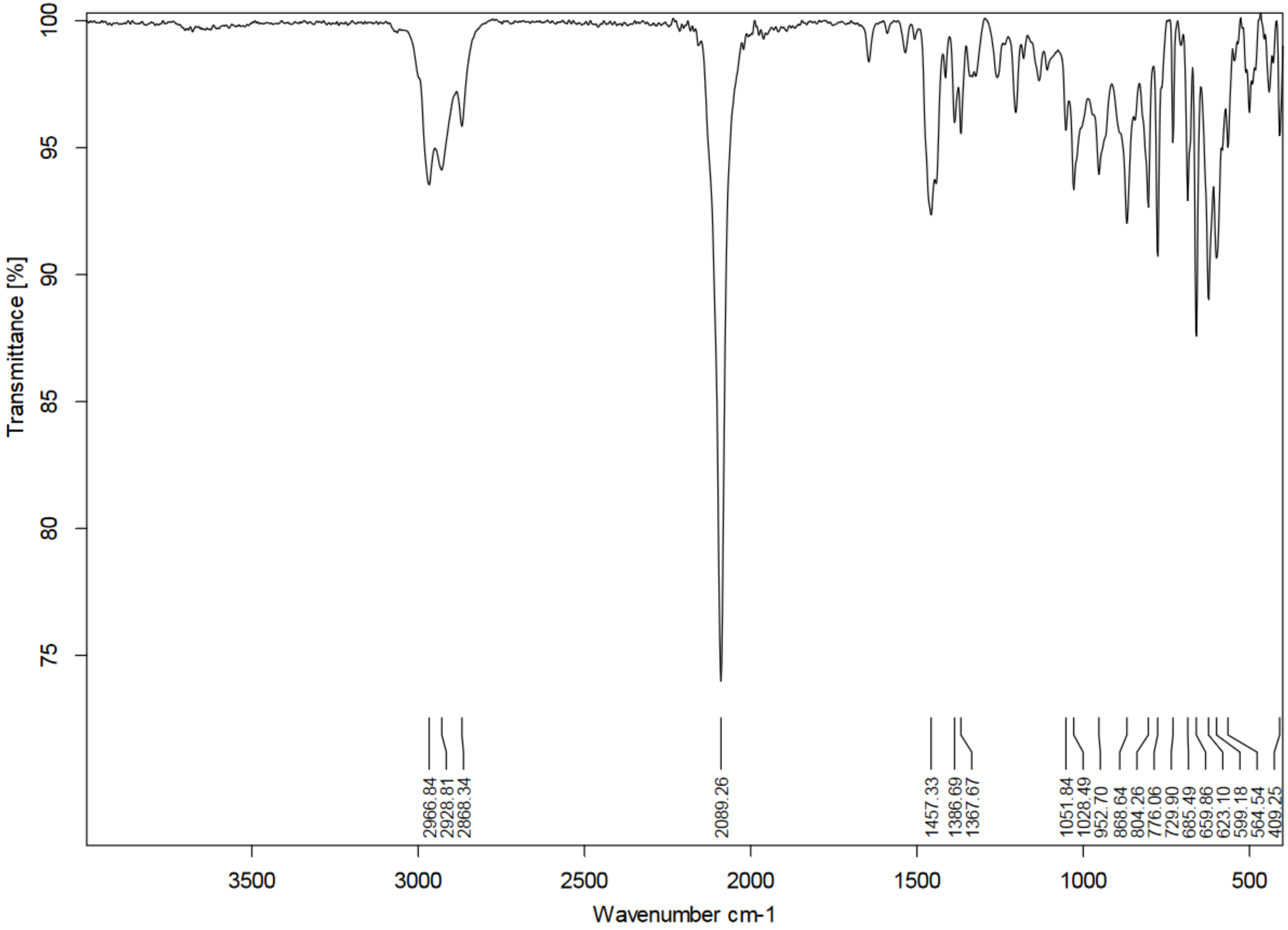

Figure S23. Solid-state IR spectrum of **2b**.

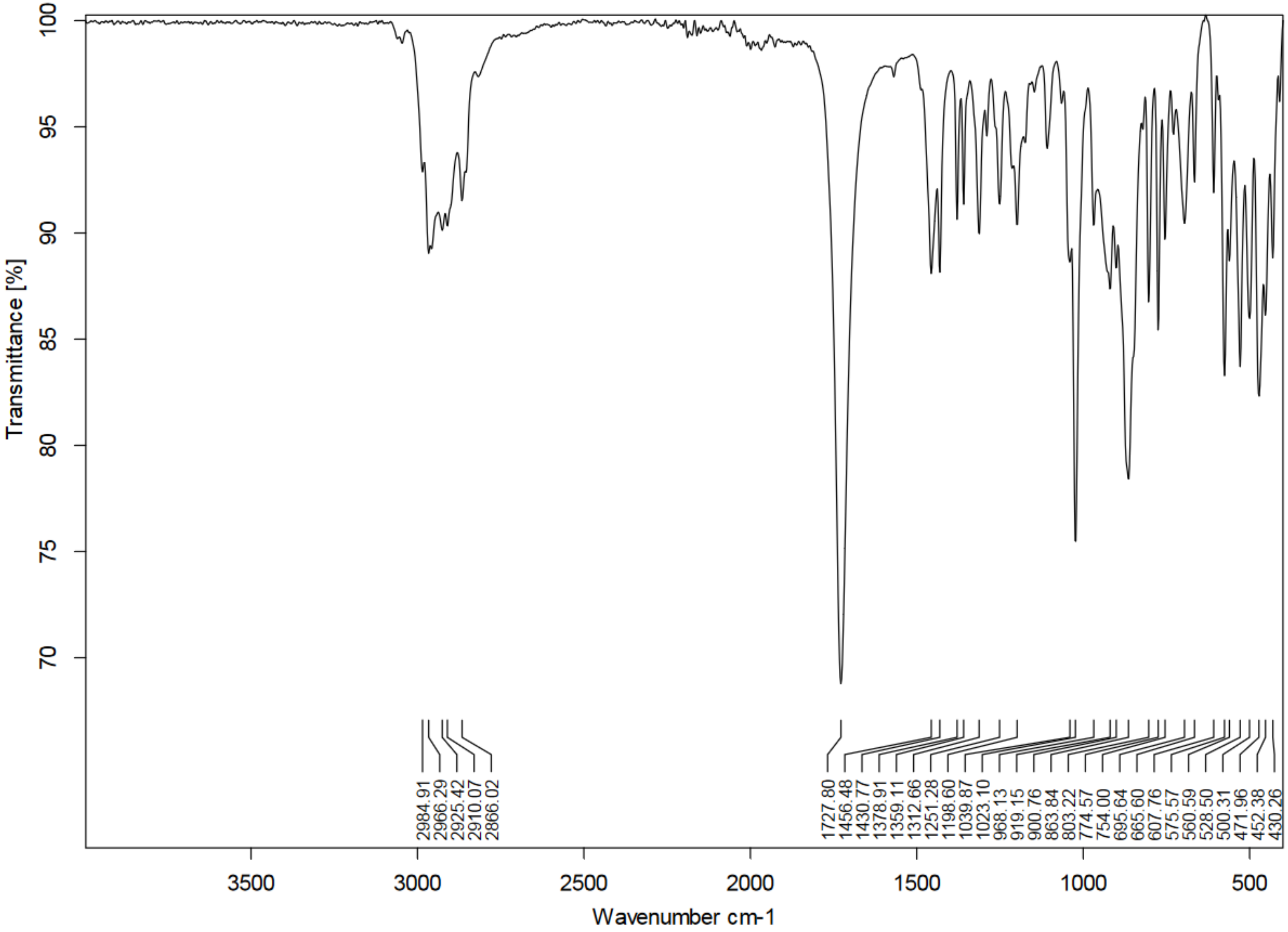

Figure S24. Solid-state IR spectrum of **3**.

X-ray crystallographic details

The crystal data of all compounds 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 intrinsic phasing method,[7] refined with the ShelXL program[8] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factors calculations. All hydrogen atoms were assigned to idealised geometric positions.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. 2379134 (**5**), 2379135 (**2a**), 2379136 (**3**), 2379137 (**7**), 2379138 (**2b**), 2379139 (**8**), 2379140 (**4b**), 2379141 (**4a**). 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 2a: $C_{41}H_{63}BeN_3S$, M_r = 639.01, yellow block, 0.786×0.674×0.442 mm^3, triclinic space group $P\bar{1}$, a = 9.8120(16) Å, b = 11.110(3) Å, c = 18.791(3) Å, α = 73.825(10)°, β = 83.585(9)°, γ = 78.758(16)°, V = 1926.0(7) Å^3, Z = 2, ρ_{calcd} = 1.102 g·cm^{-3}, μ = 0.115 mm^{-1}, $F(000)$ = 700, T = 100(2) K, R_1 = 0.0489, wR^2 = 0.1068, 8278 independent reflections [$2\theta \leq 53.82°$] and 431 parameters.

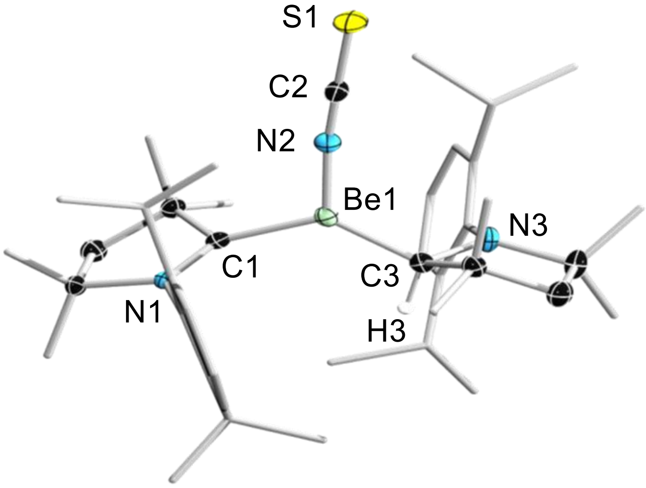

Figure S25. Crystallographically-derived molecular structure of **2a**. Atomic displacement ellipsoids set at 50% probability. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity except for protonated C3.

Refinement details for 2b: Refined as a 2-component twin. Component 2 rotated by 179.9521° around [–0.00 1.00 0.01] (reciprocal) or [–0.01 1.00 0.02] (direct) The BASF parameter was refined to 23.2%. One reflection was removed from refinement as an outlier (-4 0 -4).

Crystal data for 2b: $C_{31}H_{44}BeN_2S$, $M_r = 485.75$, colourless block, $0.472\times0.241\times0.159$ mm^3, monoclinic space group $P2_1/n$, $a = 10.4324(5)$ Å, $b = 18.541(5)$ Å, $c = 15.2352(7)$ Å, $\beta = 93.294(6)°$, $V = 2942.1(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.097$ g·cm^{-3}, $\mu = 1.108$ mm^{-1}, $F(000) = 1056$, $T = 100(2)$ K, $R_1 = 0.0443$, $wR_2 = 0.1196$, 11874 independent reflections [$2\theta\leq140.146°$] and 329 parameters.

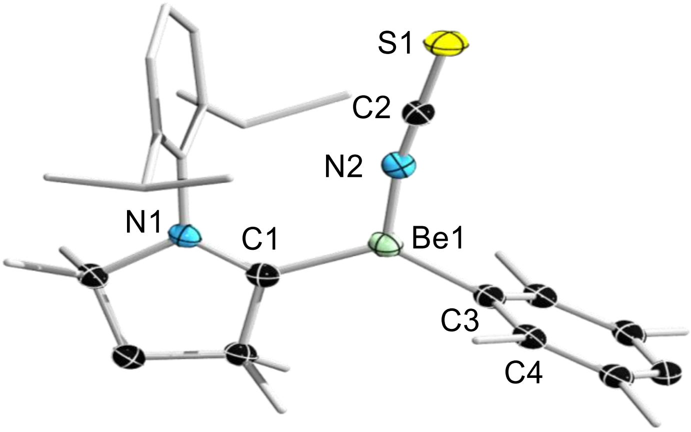

Figure S26. Crystallographically-derived molecular structure of **2b**. Atomic displacement ellipsoids set at 50% probability. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Refinement details for 3: The asymmetric unit contains three distinct molecules of the compound presenting various degrees of disorder in the THF and OCP ligands. Complex centered around Be1: the OCP ligand was modelled as threefold disordered (RESI 11, 12 and 13 OCP) with three FVAR summed up to 1 with SUMP in a 5:83:12 ratio, and one THF ligand as twofold disordered (RESI 51 and 52 THF) in a 51:49 ratio. Complex centered around Be1_6: one THF ligand was modelled as twofold disordered (RESI 101 and 102 THF) in an 83:17 ratio. Complex centered around Be1_110: the OCP ligand was modelled as twofold disordered (RESI 111 and 112 OCP) in an 83:17 ratio, and both THF ligands as twofold disordered (RESI 141 and 142 THF, and RESI 151 and 152 THF) in an 83:17 and 38:62 ratio, respectively. All ADPs within the disorders were restrained to similarity with SIMU 0.005. The 1,2 and 1,3 distances in all disordered OCP ligands were restrained to similarity with SAME 0.001. As a result, only the bonding parameters of the unrestrained BeOCP residue at Be1_6 may be used for discussion.

Crystal data for 3: $C_{29}H_{48}BeNO_3P$, $M_r = 498.66$, clear colourless block, 0.440×0.200×0.080 mm^3, orthorhombic space group *Pbcn*, $a = 61.1639(3)$ Å, $b = 15.54960(10)$ Å, $c = 18.65630(10)$ Å, $V = 17743.53(17)$ Å^3, $Z = 24$, $\rho_{calcd} = 1.120$ g·cm^{-3}, $\mu = 1.031$ mm^{-1}, $F(000) = 6528$, $T = 100(2)$ K, $R_1 = 0.0498$, $wR_2 = 0.11252$, 16840 independent reflections [$2\theta \leq 140.152°$] and 1057 parameters.

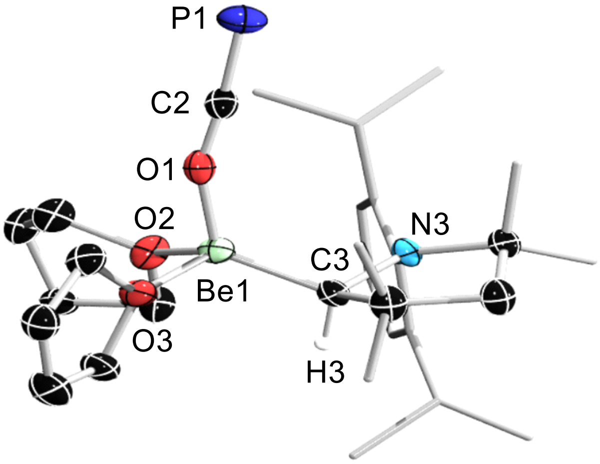

Figure S27. Crystallographically-derived molecular structure of **3**. Atomic displacement ellipsoids set at 50% probability. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity except for protonated C3.

Refinement details for 4a: One reflection was removed from refinement as an outlier (4 0 0). The compound was modelled as a 93:7 mixture of (CAAC)(CAACH)BeOCP and the starting material (CAAC)(CAACH)BeBr. The ADPs of the disordered parts (RESI 1 MAIN and RESI 21/22 FLIP) were restrained with SIMU 0.005 and SIMU 0.007, respectively. Due to the presence of 7% of the heavy bromine atom, the bonding parameters within RESI 1 MAIN are not suitable for discussion.

Crystal data for 4a: $[C_{41}H_{63}BeN_2OP]_{0.93}\cdot[C_{40}H_{63}BeBrN_2]_{0.07}$, $M_r = 641.30$, brown plate, $0.120\times0.070\times0.020$ mm^3, triclinic space group $P\bar{1}$, $a = 9.8175(2)$ Å, $b = 11.1664(3)$ Å, $c = 18.8250(4)$ Å, $\alpha = 73.555(2)°$, $\beta = 83.483(2)°$, $\gamma = 78.427(2)°$, $V = 1935.52(8)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.100$ g·cm^{-3}, $\mu = 0.907$ mm^{-1}, $F(000) = 701$, $T = 100(2)$ K, $R_1 = 0.0644$, $wR_2 = 0.1377$, 7274 independent reflections [$2\theta\leq140.138°$] and 470 parameters.

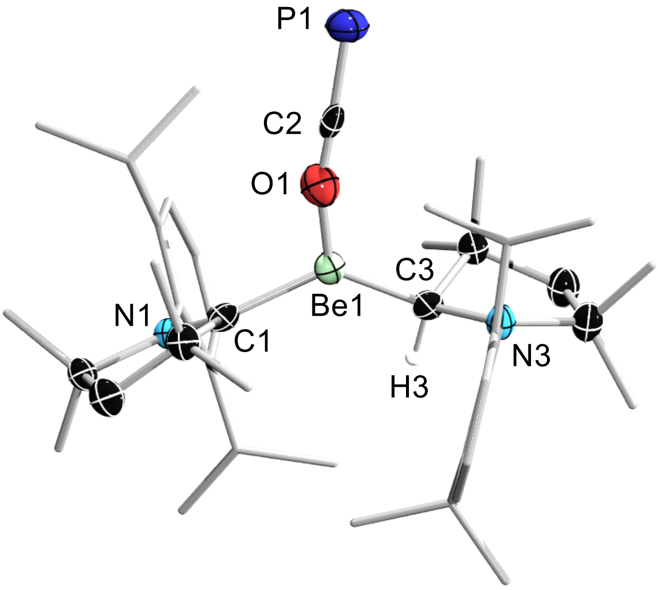

Figure S28. Crystallographically-derived molecular structure of **4a**. Atomic displacement ellipsoids set at 50% probability. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity except for protonated C3.

Crystal data for 4b: $C_{31}H_{44}BeNOP$, M_r = 486.65, light brown plate, 0.440×0.180×0.160 mm^3, orthorhombic space group *Pbca*, a = 18.2979(2) Å, b = 16.8696(2) Å, c = 18.7109(2) Å, V = 5775.65(11) Å^3, Z = 8, ρ_{calcd} = 1.119 g·cm^{-3}, μ = 0.996 mm^{-1}, $F(000)$ = 2112, T = 100(2) K, R_1 = 0.0509, wR_2 = 0.1280, 5478 independent reflections [$2\theta \leq 140.142°$] and 328 parameters.

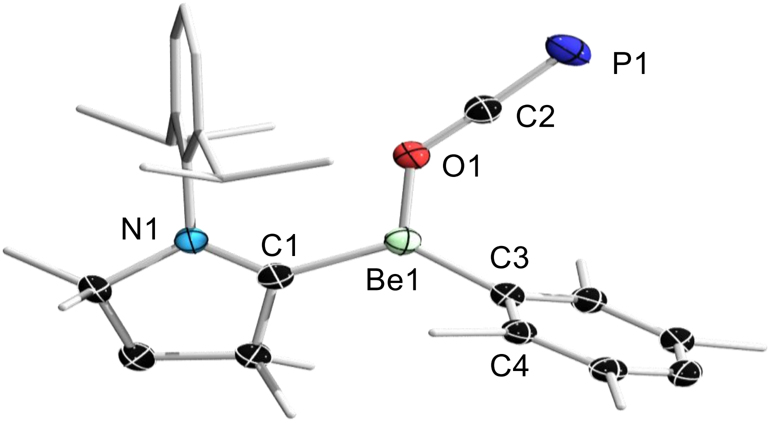

Figure S29. Crystallographically-derived molecular structure of **4b**. Atomic displacement ellipsoids set at 50% probability. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Refinement details for 5: Independent of crystallisation conditions, crystals of compound **5** were heavily twinned and decomposed during selection. The structure was solved as a three-component merohedral twin and refined with BASF and HKLF5 in ShelxLe. Component 2 rotated by 179.6553° around [–0.00 1.00 0.02] (reciprocal) or [0.00 1.00 0.10] (direct). Component 3 rotated by 1.7901° around [0.99 0.10 0.04] (reciprocal) or [0.85 0.18 0.50] (direct). As checkcif highlighted the existence of possible inversion twin components, these were added to the existing twin components 1 and 2 using the software HKLF5Tools,[9] and two more BASF parameters were added before further refinement with ShelxLe. The final twin composition was refined to 2:24:23:50:1, where the first 3 parameters refer to the merohedral twin components, and the last 2 to the inversion twin components. The asymmetric unit contains two half pentane molecules positioned on the glide planes, and modelled as twofold disordered (RESI 81/82 and 91/91 SOLV) in a 66:34 and 76:24 ratio using PARTs -1 and -2, respectively. 1,2- and 1,3-distances within the pentane residues were restrained to similarity using SAME C1 > C5 and SAME C5 > C1, and ADPs with SIMU 0.005 and ISOR 0.01. One of the Be-bound THF molecules (RESI 6 THF) was modelled with a twofold disorder in the atom C3. ADPs within this THF residue were restrained with SIMU 0.01.

Crystal data for 5: $C_{60}H_{92}BeN_2O_4P_2\cdot(C_5H_{12})$, $M_r = 1048.45$, brown plate, 0.118×0.070×0.052 mm^3, monoclinic space group *Cc*, $a = 30.9641(3)$ Å, $b = 21.1528(4)$ Å, $c = 9.8832(4)$ Å, $\beta = 93.364(2)°$, $V = 6462.1(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.078$ g·cm^{-3}, $\mu = 0.944$ mm^{-1}, $F(000) = 2296$, $T = 100(2)$ K, $R_1 = 0.0706$, $wR_2 = 0.2047$, Flack parameter = –0.004(12), 32506 independent reflections [$2\theta \leq 140.146°$] and 838 parameters.

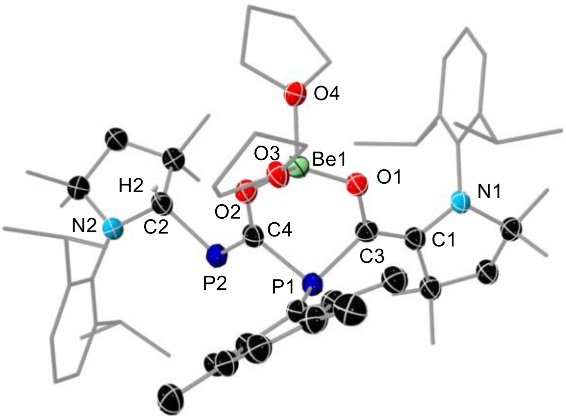

Figure S30. Crystallographically-derived molecular structure of **5**. Atomic displacement ellipsoids set at 50% probability. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity, except for the protonated C3 centre.

Refinement details for 7: The asymmetric unit contains two benzene molecules, one positioned on an inversion centre and modelled as half-occupied, the other modelled as fully occupied and twofold disordered in a 52:48 ratio. The benzene rings were idealised with AFIX 6 and all their ADPs restrained with SIMU 0.006.

Crystal data for 7: $[C_{21}H_{31}BeBrN_2O]_6\cdot(C_6H_6)_3$, $M_r = 2732.70$, colourless block, 0.253×0.123×0.067 mm^3, monoclinic space group $I2/a$, $a = 18.35350(10)$ Å, $b = 30.9252(2)$ Å, $c = 25.8198(2)$ Å, $\beta = 95.1780(10)°$, $V = 14595.14(17)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.244$ g·cm^{-3}, $\mu = 2.408$ mm^{-1}, $F(000) = 5736$, $T = 100.00(10)$ K, $R_1 = 0.0624$, $wR_2 = 0.1497$, 14343 independent reflections [$2\theta \leq 144.252°$] and 855 parameters.

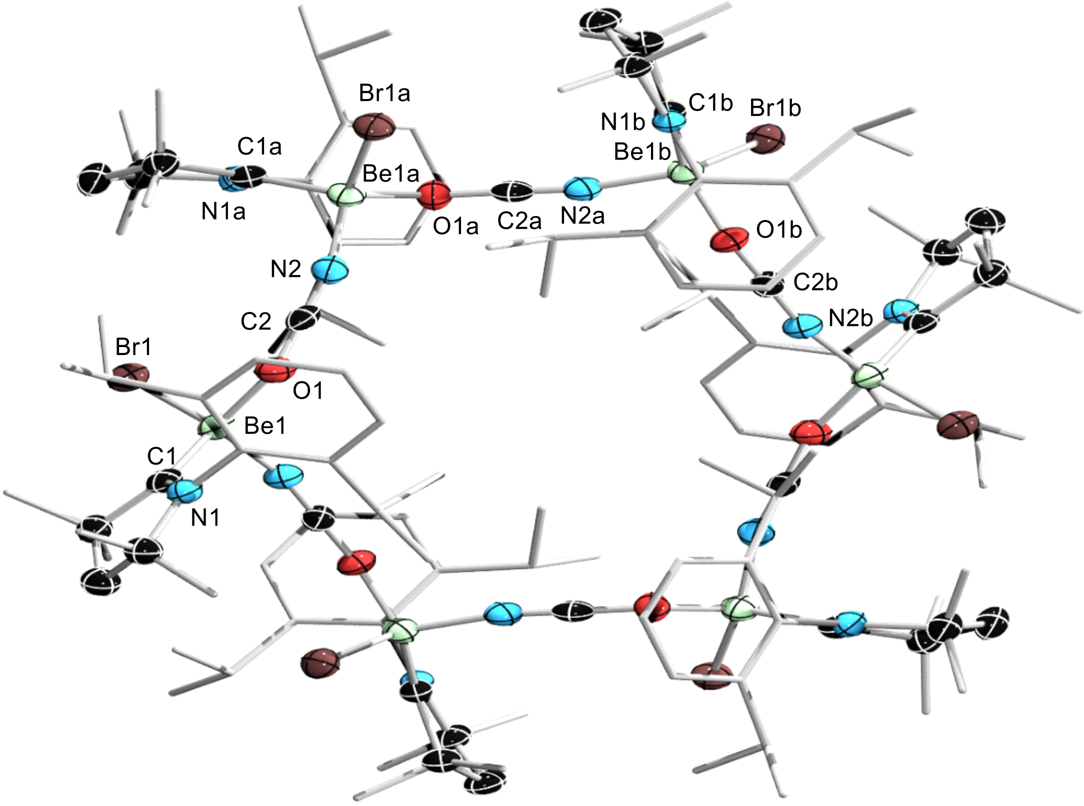

Figure S31. Crystallographically-derived molecular structure of **7** (centrosymmetric structure). Atomic displacement ellipsoids set at 50% probability. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

Refinement details for 8: This data set was the best of the X-ray crystallographic experiments carried out on multiple crystals of **8** from various recrystallisation attempts, all providing extremely sensitive and highly twinned crystals, which decomposed during crystal selection and further during data acquisition. Refined as a two-component twin. Component 2 rotated by 1.6854° around [0.07 0.58 0.81] (reciprocal) or [0.07 0.82 0.57] (direct). The BASF parameter was refined to 20%. Due to very weak diffraction at high angles and rapid crystal decomposition the data was cut at 0.85 Å. Two outlying reflections were omitted (-2 -1 -1 and -6 -1 7). Data completeness could not be reached (95%) but the data provides unambiguous proof of connectivity of the tetrameric nature of the complex and its CN/NC isomerism. The unit cell contains 1.5 formula units of the tetramer **8**, the second half being generated by C_2 rotation. The unit cell contains several highly disordered and partially occupied pentane molecules, which have been treated as a diffuse contribution to the overall scattering without specific atom positions by the Platon program Squeeze.[10] 970 electrons were thus masked, which corresponds to ca. 23 pentane molecules, i.e. ca. 3 per asymmetric unit (two full molecules and two half molecules positioned on the C_2 axes), or two pentane molecules per tetramer molecule. The 1.5 $(BeCN)_4$ cores present CN/NC isomerism in all six positions (RESI CN), modelled with 6 FVAR refined to a 58:42, 56:44, 51:49, 62:38, 49:51 and 58:42 ratio, respectively, the C−N distance being restrained with SAME and the ADPs of the $(BeCN)_4$ cores with SIMU 0.005. Furthermore, one CAAC ligand in each tetramer was modelled as twofold rotationally disordered (RESI DIS), with 2 FVAR refined to an 86:14 and 67:33 ratio, respectively. The benzene rings of the Dip substituents in these disorders were idealised with AFIX 66, 1,2- and 1,3-distances in the residues restrained to similarity with SAME and ADPs with SIMU 0.005 and 0.01, respectively. Finally, five of the six adducted THF molecules were modelled as twofold disordered and one as threefold disordered. The corresponding ratios were first refined with 13 FVAR, later replaced by corresponding fixed ratios to limit the number of variables and speed up refinement.

Crystal data for 8: $C_{100}H_{160}Be_4N_8O_4\cdot[(C_5H_{12})_2]_{\text{squeezed}}$, M_r = 1718.78, colourless plate, 0.146×0.071×0.034 mm^3, monoclinic space group $I2/a$, a = 35.978(6) Å, b = 25.4382(16) Å, c = 36.315(3) Å, β = 92.089(10)°, V = 33214(6) Å^3, Z = 12, ρ_{calcd} = 1.031 g·cm^{-3}, μ = 0.458 mm^{-1}, F(000) = 11376 T = 100(2) K, R_1 = 0.1550, wR_2 = 0.4805, 65532 independent reflections [$2\theta \leq 130.172°$] and 2322 parameters.

Note: other crystals of ***8*** *with a different unit cell (monoclinic space group C2/c, a = 16.5258(7) Å, b = 25.0720(9) Å, c = 27.6146(10) Å, β = 104.868(4)°) and without lattice solvent were also obtained but decomposed too fast on the diffractometer to obtain more than a proof of connectivity.*

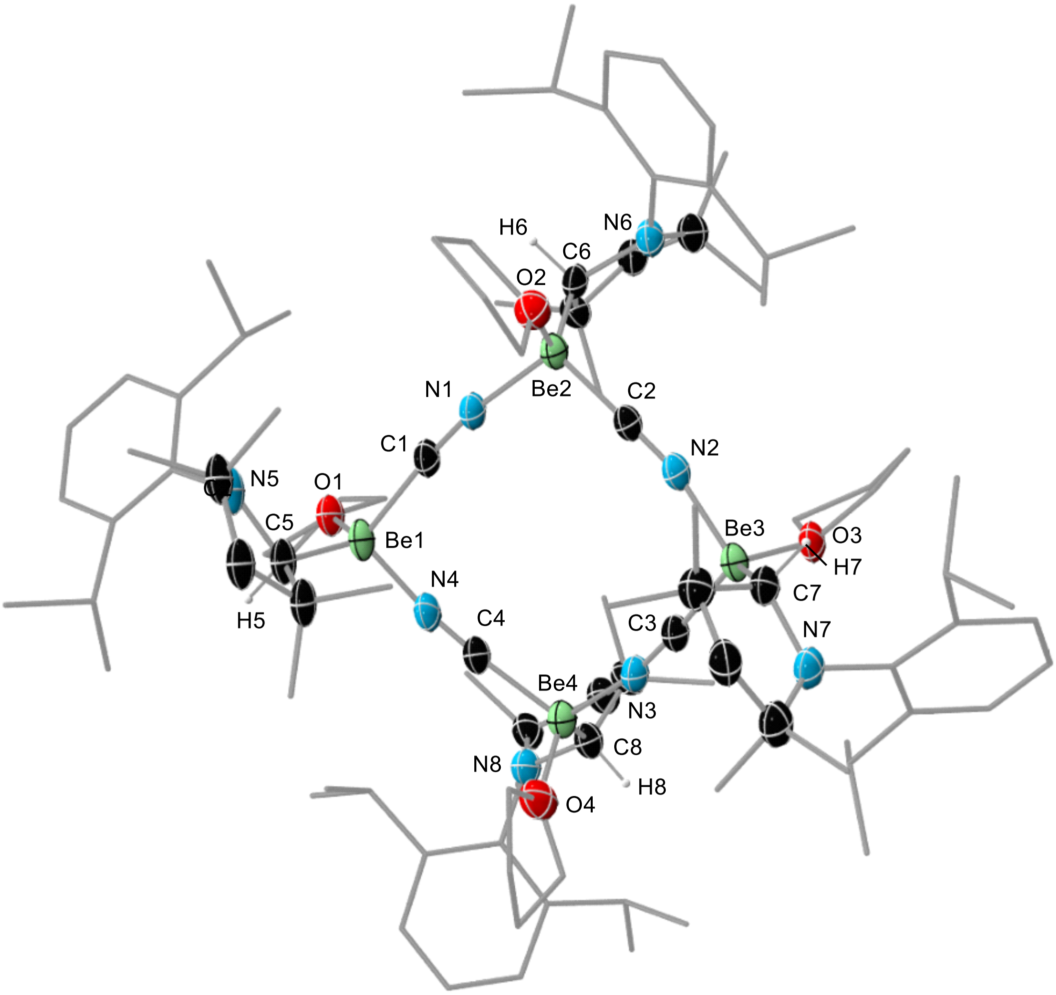

Figure S32. Crystallographically-derived molecular structure of **8** (one of the 1.5 tetramers present in the asymmetric unit, showing only the major part of the four CN/NC isomerisms). Atomic displacement ellipsoids set at 30% probability. Ellipsoids of ligand periphery and hydrogen atoms omitted for clarity.

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