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Supplementary Information:

Experimental

All reactions were performed under an atmosphere of dry, oxygen-free nitrogen using Schlenk techniques or in a nitrogen-filled MBraun 150 G1 glovebox. Pentane was dried over Na sand and distilled under nitrogen. Toluene-d8 was purchased from Cambridge Isotopes, dried over Na/benzophenone, distilled prior to use and stored in the glovebox. 1D-NMR spectra [1H (300.1 MHz), 13C (75.5 MHz) and 7Li (116.6 MHz)] were recorded on a Varian INova 300 spectrometer and 2D-NMR spectra (1H-1H COSY, 1H-13C HETCOR) were recorded on a Varian INova 500 spectrometer. All NMR spectra were obtained in toluene-d8. Chemical shift values are reported in ppm (δ) and referenced internally to residual solvent signals (1H, 13C) or externally (7Li, 1.0 M LiCl in D2O, δ = 0.00). All reagents were purchased from Acros Chemicals and used as received. 1,3-bis(dimethylaminomethyl)benzene and 1,3-bis(diethylaminomethyl) benzene were synthesized via a modified literature procedure (D. Y. Curtin and E. W. Flynn, *J. Am. Chem. Soc.,* 1959, **81**, 4714) employing benzene as a solvent. The temperature of the NMR spectrometer was calibrated using 100% proteo-ethanol. Elemental analyses were performed by Dornis & Kolbe Microanalysis Laboratories, Mülheim a/d Ruhr, Germany.

Alternate Synthesis of [^{Me}NCNLi]$_2$ ($\mathbf{3_2}$): To a solution of 1,3-bis(dimethylaminomethyl)benzene [^{Me}NCN(H)] (1.62 g, 8.4 mmol) in dry pentane (100 ml) at -78ºC was added *n*BuLi (5.3 ml, 8.4 mmol, 1.6 M in hexanes) dropwise via syringe over 5 minutes. The reaction was allowed to stir at low temperature for 20 minutes and was subsequently slowly warmed to room temperature over three hours to give a yellow solution. The solvent was removed *in vacuo*, fresh dry pentane (120 ml) was added to the orange solid and then the solution was re-cooled to -78ºC for one hour without stirring. The resulting suspension was cold filtered and the collected solid was washed once with cold, dry pentane (10 ml). The solvent was removed *in vacuo* and the white solid dried *in vacuo* to give $\mathbf{3_2}$ as a white, air sensitive powder. Yield: 1.31 g, 78%. NMR data are

consistent with those previously reported.[9] **^{1}H NMR** (25°C): δ 7.13 (t, 2H, $^3J_{HH}$ = 7.2 Hz, Ar*H*), 6.99 (d, 4H, $^3J_{HH}$ = 7.1 Hz, Ar*H*), 4.6-2.8 (br, 8H, benzylic CH_2), 1.92 (s, 24H, N(CH_3)$_2$). **^{13}C{^{1}H} NMR** (25°C): δ 188.5 (septet, $^1J_{CLi}$ = 21 Hz, Ar*C*Li), 151.7 (Ar*C*CH$_2$), 124.3 (*p*-Ar*C*), 123.6 (*m*-Ar*C*), 72.8 (benzylic *C*H$_2$), 44.9 (br, N(*C*H$_3$)$_2$). **^{7}Li{^{1}H} NMR** (25°C): δ 0.96 (s). **^{1}H NMR** (-50°C): δ 7.27 (t, 2H, $^3J_{HH}$ = 7.2 Hz, Ar*H*), 7.11 (d, 4H, $^3J_{HH}$ = 7.2 Hz, Ar*H*), 4.06 (d, 4H, J_{gem} = 10.8 Hz, benzylic C*H*H), 2.89 (d, 4H, J_{gem} = 11.4 Hz, benzylic C*H*H), 1.94 (s, 12H, NCH_3), 1.79 (s, 12H, NCH_3). **^{13}C{^{1}H} NMR** (-50°C): δ 188.9 (septet, $^1J_{CLi}$ = 21Hz, Ar*C*Li), 152.2 (Ar*C*CH$_2$), 124.7 (*p*-Ar*C*), 123.9 (*m*-Ar*C*), 73.0 (benzylic *C*H$_2$), 47.5 (N(*C*H$_3$)$_2$), 43.5 (N(*C*H$_3$)$_2$). **^{7}Li{^{1}H} NMR** (-50°C): δ 0.99 (s).

Alternate Synthesis of [^{Et}NCNLi]$_2$ (4$_2$): To a solution of 1,3-bis(diethylaminomethyl)benzene [^{Et}NCN(H)] (3.92 g, 15.8 mmol) in dry pentane (100 ml) at -78ºC was added *n*BuLi (9.9 ml, 15.8 mmol, 1.6 M in hexanes) dropwise via syringe over 5 minutes. The reaction was allowed to stir at low temperature for 20 minutes and was subsequently slowly warmed to room temperature over three hours to give a yellow solution. The solvent was removed *in vacuo*, fresh dry pentane (120 ml) was added to the orange solid and then the solution was re-cooled to -78ºC for one hour without stirring. The resulting suspension was cold filtered and the collected solid was washed once with cold, dry pentane (10 ml). The solvent was removed *in vacuo* and the white solid dried *in vacuo* to give **4$_2$** as a white, air sensitive powder. Yield: 2.57 g, 64%. NMR data are consistent with those previously reported.[10a] The coalescence temperatures for the benzylic CH_2 and the terminal methyl groups of the NEt_2 were 11ºC and -26ºC, respectively. **^{1}H NMR** (25°C): δ 7.15 (t, 2H, $^3J_{HH}$ = 6.9 Hz, Ar*H*), 7.02 (d, 4H, $^3J_{HH}$ = 7.0 Hz, Ar*H*), 3.71 (br, 8H, benzylic CH_2), 2.46 (br m, 16H, NCH_2), 0.80 (t, 24H, $^3J_{HH}$ = 7.2 Hz, NCH$_2$CH_3). **^{13}C{^{1}H} NMR** (25°C): δ 189.9 (Ar*C*Li, *J* not resolved), 151.5 (Ar*C*CH$_2$), 124.5 (*p*-Ar*C*), 124.1 (*m*-Ar*C*), 62.0 (benzylic *C*H$_2$), 46.5 (br, N*C*H$_2$), 9.0 (br, NCH$_2$*C*H$_3$). **^{7}Li{^{1}H} NMR** (25°C): δ 0.58 (s). **^{1}H NMR** (-50°C): δ 7.28 (t, 2H, $^3J_{HH}$ = 7.3 Hz, Ar*H*), 7.14 (d, 4H, $^3J_{HH}$ = 7.2 Hz Ar*H*), 4.12 (d, 4H, J_{gem} = 11.4 Hz, benzylic C*H*H), 3.22 (d, 4H, J_{gem} = 11.7 Hz, benzylic C*H*H), 2.53 (d of q, 4H, $^3J_{HH}$ = 6.8, J_{gem} 14 Hz, NC*H*H), 2.31 (m, 4H, NC*H*H), 2.17 (m, 8H, 2 x NC*H*H), 0.89 (t, 12H, $^3J_{HH}$ = 6.8 Hz,

NCH_2CH_3), 0.79 (t, 12H, $^3J_{HH}$ = 6.9 Hz, NCH_2CH_3). **$^{13}C\{^1H\}$ NMR** (-50°C): δ 190.0 (Ar*C*Li, *J* not resolved), 151.4 (Ar*C*CH_2), 124.4 (*p*-Ar*C*), 123.9 (*m*-Ar*C*), 60.1 (benzylic *C*H_2), 48.2 (N*C*H_2), 44.6 (N*C*H_2), 13.0 (NCH_2CH_3), 4.6 (NCH_2CH_3). **$^7Li\{^1H\}$ NMR** (-50°C): δ 0.59 (s).

Synthesis of $[^{Me}NCNLi]_2[n BuLi]_2$ (3_2•$[n BuLi]_2$): To a solution of **3** (0.251 g, 1.27 mmol) in dry pentane (20 ml) at 0ºC was added *n*BuLi (0.79 ml, 1.27 mmol, 1.6 M in hexanes) dropwise via syringe. The reaction was allowed to warm to room temperature for 2 hours. The solvent was removed *in vacuo* and the white solid obtained was dried *in vacuo* to yield a solid with composition [Me_4NCNLi][*n*BuLi] by elemental analysis. Yield 0.333g, 100%. Crystals for X-ray diffraction were obtained by cooling of a pentane solution to -35ºC for several weeks. *Anal.* Calcd: C 73.27, H 10.76, N 10.68. Found: C 73.10, H 10.71, N 10.73. Room temperature spectra of equilibrium mixture: **^1H NMR** (25°C): δ 7.13 (t, $^3J_{HH}$ = 6.9 Hz, **3_2**), 7.05 (t, 2H, $^3J_{HH}$ = 7.6 Hz, Ar*H*), 6.97 (d, $^3J_{HH}$ = 7.1 Hz, **3_2**), 6.88 (d, 4H, $^3J_{HH}$ = 7.4 Hz, Ar*H*), 3.45 (br, 8H, benzylic CH_2) 1.92 (s, 24H, N(CH_3)$_2$) 1.58 (quintet, 4H, $^3J_{HH}$ = 6.8 Hz, *n*BuCH_2), 1.46 (br, 4H, *n*BuCH_2), 1.07 (t, 6H, $^3J_{HH}$ = 7.0 Hz, *n*BuCH_3), -0.82 (br, 4H, LiCH_2). **$^{13}C\{^1H\}$ NMR** (25°C): δ 188.7 (*J* not resolved, **3_2**), 179.5 (br, Ar*C*Li), 151.7 (Ar*C*CH_2, **3_2**), 151.5 (Ar*C*CH_2), 127.1 (*m*- and *p*-Ar*C*), 124.3 (*p*-Ar*C*, **3_2**), 123.6 (*m*-Ar*C,* **3_2**), 72.8 benzylic *C*H_2, **3_2**), 70.0 (benzylic *C*H_2), 45.1 (br, N*C*H_3), 44.6 (v. br, N*C*H_3, **3_2**), 32.8, (br, *n*Bu*C*H_2), 32.5 (v. br, *n*Bu*C*H_2), 14.0 (*n*Bu*C*H_3), 9.9 (v. br, Li*C*H_2). **$^7Li\{^1H\}$ NMR** (25°C): δ 1.07 (s, **3_2**), 0.38 (v. br). LT NMR data given for signals corresponding to **3•$[n BuLi]_2$** only. **^1H NMR** (-50°C): δ 7.14 (m, 2H, Ar*H*), 6.95 (d, 2H, $^3J_{HH}$ = 7.1 Hz, Ar*H*), 6.93 (d, 2H, $^3J_{HH}$ = 7.1 Hz, Ar*H*), 4.44 (d, 2H, J_{gem} = 11.7 Hz, benzylic C*H*H), 3.89 (d, 2H, J_{gem} = 12.6 Hz, benzylic C*H*H), 2.87 (d, 2H, J_{gem} = 11.1 Hz, benzylic C*H*H), 2.56 (d, 2H, J_{gem} = 12.9 Hz, benzylic C*H*H), 2.30 (s, 6H, N*C*H_3), 1.82 (s, 12H, 2 x N*C*H_3), 1.74 (s, 6H, N*C*H_3), 1.49 (br, 8H, 2 x *n*BuCH_2), 1.18 (t, 6H, $^3J_{HH}$ = 7.0 Hz, *n*BuCH_3), -0.30 (br m, 2H, LiC*H*H), -0.54 (br m, 2H, LiC*H*H). **$^{13}C\{^1H\}$ NMR** (-50°C): δ 178.8 (Ar*C*Li, *J* not resolved), 152.1 (Ar*C*CH_2), 150.5 (Ar*C*CH_2), 127.0-126.8 (*m*- and *p*-Ar*C*), 70.3 (benzylic *C*H_2), 68.7 (benzylic *C*H_2), 46.6 (N*C*H_3), 45.0 (N*C*H_3), 43.1 (N*C*H_3), 42.5 (N*C*H_3), 33.8 (*n*Bu*C*H_2), 33.2 (*n*Bu*C*H_2), 14.4 (*n*Bu*C*H_3), 10.9 (v. br, Li*C*H_2). **$^7Li\{^1H\}$ NMR** (-50°C): δ 0.87 (s, 2Li), 0.44 (s, 2Li).

Synthesis of [^{Et}NCNLi]$_2$[*n*BuLi]$_2$ (4$_2$•[*n*BuLi]$_2$): To a solution of **4** (0.380 g, 0.75 mmol) in dry pentane (15 ml) at 0ºC was added *n*BuLi (0.47 ml, 0.75 mmol, 1.6 M in hexanes) dropwise via syringe. The reaction was allowed to warm to room temperature for 2 hours. The solvent was removed *in vacuo* and the white solid obtained was dried *in vacuo* to yield a solid with composition [Et$_4$NCNLi]$_2$[*n*BuLi]$_2$ by elemental analysis. Yield 0.468g, 98.5%. Crystals for X-ray diffraction were obtained by cooling of a pentane solution to -35ºC for several days. *Anal.* Calcd: C 75.68, H 11.12, N 8.83. Found: C 75.53, H 11.02, N 8.65. Room temperature spectra of equilibrium mixture: **^{1}H NMR** (25°C): δ 7.13 (t, $^3J_{HH}$ = 6.6 Hz, Ar*H*, **4$_2$**), 7.10 (t, 2H, $^3J_{HH}$ = 6.7 Hz, Ar*H*), 7.02 (d, $^3J_{HH}$ = 7.2 Hz, Ar*H*, **4$_2$**), 6.95 (d, 4H, $^3J_{HH}$ = 7.1 Hz, Ar*H*), 3.68 (br, 8H, benzylic C*H*$_2$), 2.49-2.43 (br m, 16H, NC*H*$_2$CH$_3$), 1.61 (br, 8H, 2 x *n*BuC*H*$_2$), 1.11 (t, 6H, $^3J_{HH}$ = 7.1 Hz, *n*BuC*H*$_3$), 0.80 (t, 24H, $^3J_{HH}$ = 7.2 Hz, NCH$_2$C*H*$_3$), -0.67 (br, 4H, LiC*H*$_2$). **^{13}C{^{1}H} NMR** (25°C): δ 189.8 (septet, $^1J_{CLi}$ = 19.8 Hz, **4$_2$**), 179.7 (br, Ar*C*Li), 151.5 (Ar*C*CH$_2$, **4$_2$**), 151.1 (Ar*C*CH$_2$), 126.8 (*m*- and *p*-Ar*C*), 124.5 (*p*-Ar*C*, **4$_2$**), 124.0 (*m*-Ar*C,* **4$_2$**), 64.3 (benzylic *C*H$_2$), 62.0 (benzylic *C*H$_2$, **4$_2$**), 46.5 (br, N*C*H$_2$CH$_3$, **4$_2$**), 43.6 (br, N*C*H$_2$CH$_3$), 33.1 (*n*Bu*C*H$_2$), 32.8 (*n*Bu*C*H$_2$), 14.0 (*n*Bu*C*H$_3$), 9.8 (br, Li*C*H$_2$), 8.9 (br, NCH$_2$*C*H$_3$)**.** **^{7}Li{^{1}H} NMR** (25°C): δ 0.59 (s, **4$_2$**), 0.37 (br). LT NMR data given for signals corresponding to **4$_2$•[*n*BuLi]$_2$** only. **^{1}H NMR** (-50°C): δ 7.21 (t, 2H $^3J_{HH}$ = 7.2 Hz, Ar*H*), 7.07 (d, 2H, $^3J_{HH}$ = 7.4 Hz, Ar*H*), 6.96 (d, 2H, $^3J_{HH}$ = 7.4 Hz, Ar*H*), 4.47 (d, 2H, J_{gem} = 12.0 Hz, benzylic C*H*H), 3.93 (d, 2H, J_{gem} = 12.0 Hz, benzylic C*H*H), 3.77 (d, 2H, J_{gem} = 12.0 Hz, benzylic C*H*H), 3.15 (d, 2H, J_{gem} = 12.0 Hz, benzylic C*H*H), 3.03 (m, 2H, NC*H*(H)CH$_3$), 2.68-2.52 (m, 10H, 5 x NC*H*(H)CH$_3$), 2.18 (m, 4H, 2 x NC*H*(H)CH$_3$), 1.76 (br, 8H, 2 x *n*BuC*H*$_2$), 1.28 (t, 6H, $^3J_{HH}$ = 6.3 Hz, *n*BuC*H*$_3$), 1.12 (t, 6H, $^3J_{HH}$ = 6.0 Hz, NCH$_2$C*H*$_3$), 0.91 (t, 6H, $^3J_{HH}$ = 6.0 Hz, NCH$_2$C*H*$_3$), 0.61 (t, 6H, $^3J_{HH}$ = 6.0 Hz, NCH$_2$C*H*$_3$), 0.48 (t, 6H, $^3J_{HH}$ = 6.0 Hz, NCH$_2$C*H*$_3$), -0.21 (br, 2H, LiC*H*H), -0.34 (br, 2H, LiC*H*H). **^{13}C{^{1}H} NMR** (-50°C): δ 180.1 (Ar*C*Li, *J* not resolved), 151.7 (Ar*C*CH$_2$), 150.0 (Ar*C*CH$_2$), 126.8 (*m*-Ar*C*), 126.7 (*m*-Ar*C*), 125.2 (*p*-Ar*C*), 64.3 (benzylic *C*H$_2$), 62.5 (benzylic *C*H$_2$), 45.7 (N*C*H$_2$), 44.8 (N*C*H$_2$), 44.6 (N*C*H$_2$), 39.0 (N*C*H$_2$), 34.3 (*n*Bu*C*H$_2$), 33.4 (*n*Bu*C*H$_2$), 14.4 (*n*Bu*C*H$_3$), 11.9 (2x NCH$_2$*C*H$_3$), 9.5 (br, Li*C*H$_2$) 4.4 (NCH$_2$*C*H$_3$), 3.8 (NCH$_2$*C*H$_3$). **^{7}Li{^{1}H} NMR** (-50°C): δ 0.76 (s, 2Li), 0.10 (s, 2Li).

***In situ* generation of [^{Me}NCNLi][*n*BuLi]$_3$ (6):** In the glovebox, **3** (25.9 mg, 0.13 mmol) was weighed into an NMR tube and toluene-d_8 (~ 0.5 ml) was added. To this was added a prepared solution of *n*BuLi (0.073 ml, 0.39 mmol, 5.3 M in toluene-d_8) via syringe and the tube was capped with a septa and shaken. Unlike **7**, signals for dimer **3** and **3•[*n*BuLi]$_2$** were readily apparent in the room temperature NMR spectra (see above for discussion). NMR data for signals corresponding to **6** only: **^{1}H NMR** (25°C): δ 7.05 (t, 1H, $^3J_{HH}$= 7.5 Hz, Ar*H*), 6.88 (d, 2H, $^3J_{HH}$= 7.5 Hz, Ar*H*), 3.47 (v. br, 4H, benzylic CH_2), 1.92 (br, 12H, N(CH_3)$_2$), 1.54-1.42 (m, 12H, 2 x *n*BuCH_2), 1.04 (t, 9H, $^3J_{HH}$= 7.1 Hz, *n*BuCH_3), -0.86 (br, 6H, LiCH_2). **^{13}C{^{1}H} NMR** (25°C): δ 177.9 (Ar*C*Li, *J* not resolved), 151.7 (Ar*C*CH$_2$), 127.1 (*m*- and *p*-Ar*C*), 70.0 (benzylic *C*H$_2$), 44.5 (br, N(*C*H$_3$)$_2$), 32.5 (br, *n*Bu*C*H$_2$), 32.0 (br, *n*Bu*C*H$_2$), 14.0 (br, *n*Bu*C*H$_3$), 10.4 (v. br, Li*C*H$_2$). **^{7}Li{^{1}H} NMR** (25°C): δ 1.06 (**3**), 0.05 (v. br). LT NMR data for signals corresponding to **6** only: **^{1}H NMR** (-50°C): δ 7.15 (m, 1H, Ar*H*), 6.90 (d, 2H, $^3J_{HH}$= 7.5 Hz, Ar*H*), 4.11 (d, 2H, J_{gem} = 11.7 Hz, benzylic C*H*H), 2.74 (d, 2H, J_{gem} = 12.0 Hz, benzylic C*H*H), 2.17 (s, 6H, NCH_3), 1.73 (s, 6H, NCH_3), 1.66 (m, 6H, *n*BuCH_2), 1.39 (m, 6H, *n*BuCH_2), 1.17 (t, 9H, $^3J_{HH}$= 6.8 Hz, *n*BuCH_3), -0.63 (br, 2H, LiCH_2), -0.76 (br, 2H, LiCH_2), -1.03 (br, 2H, LiCH_2). **^{13}C{^{1}H} NMR** (-50°C): δ 178.2 (Ar*C*Li, *J* not resolved), 151.7 (Ar*C*CH$_2$), 126.9 (*m* and *p*-Ar*C*), 69.5 (benzylic *C*H$_2$), 46.1 (N*C*H$_3$), 42.5 (N*C*H$_3$), 32.9 (2 x *n*Bu*C*H$_2$), 14.2 (*n*Bu*C*H$_3$), 9.6 (v. br, 2 x Li*C*H$_2$), 8.3 (v. br, Li*C*H$_2$). **^{7}Li{^{1}H} NMR** (-50°C): δ 0.44 (s, 2Li), 0.07 (s, 1Li), -1.36 (s, 1Li).

Synthesis of [^{Et}NCNLi][*n*BuLi]$_3$ (7): To a solution of **4** (0.207 g, 0.40 mmol) in dry pentane (30 ml) at 0ºC was added *n*BuLi (2.03 ml, 3.26 mmol, 1.6 M in hexanes, 4 equiv./ Et$_4$NCNLi) dropwise via syringe over 5 minutes. The reaction was warmed to room temperature over 2 hours and the solvent was removed *in vacuo* to yield a light yellow that solidifies on standing. Yield: 0.401 g, 96.9% based on composition [^{Et}NCN]*n*Bu$_3$Li$_4$ + one additional *n*BuLi, which was confirmed by integration of the ^{1}H NMR spectrum. Attempts to obtain crystals from concentrated pentane solutions were unsuccessful. **^{1}H NMR** (25°C): δ 7.09 (t, 1H, $^3J_{HH}$= 7.5 Hz, Ar*H*), 6.94 (d, 2H, $^3J_{HH}$ = 7.2 Hz), 3.66 (br, 4H benzylic CH_2), 2.61 (br, 4H, NCH_2CH$_3$), 2.40 (virtual quintet, 4H, $^3J_{HH}$

= 6.8 Hz, NCH_2CH$_3$), 1.57 (m, 12H, *n*BuCH_2), 1.08 (t, 9H, $^3J_{HH}$ = 6.9 Hz, *n*BuCH_3), 0.82 (br, 12H, NCH$_2$CH_3), -0.79 (br s, 6H, LiCH_2). **^{7}Li{^{1}H} NMR** (25°C): δ 0.02 (br s). **^{1}H NMR** (-50°C): δ 7.17 (t, 1H, $^3J_{HH}$ = 7.4 Hz) Ar*H*), 6.97 (d, 2H, $^3J_{HH}$ = 7.8Hz), 3.94 (d, 2H, J_{gem} = 12 Hz, benzylic C*H*H), 3.36 (d, 2H, J_{gem} = 13 Hz, benzylic C*H*H), 2.80 (virtual quintet, 2H, $^3J_{HH}$ = 7.2, NC*H*H), 2.50 (m, 2H, NC*H*H), 2.38 (m, 4H, 2 x NC*H*H), 1.70 (br, 8H, *n*BuCH_2), 1.51 (br, 4H, *n*BuCH$_2$), 1.19 (t, 9H, $^3J_{HH}$ = 6.8 Hz, *n*BuCH_3), 1.01 (t, 6H, $^3J_{HH}$ = 6.9 Hz, NCH$_2$CH_3), 0.57 (t, 6H, $^3J_{HH}$ = 6.9 Hz, NCH$_2$CH_3), -0.56 (br, 2H, LiCH_2), -0.68 (br, 2H, LiCH_2), -1.02 (br, 2H, LiCH_2). **^{13}C{^{1}H} NMR** (-50°C): δ 179.4 (Ar*C*Li), *J* not resolved), 151.1 (Ar*C*CH$_2$), 126.8 (*m*-Ar*C*H), 125.6 (*p*-Ar*C*H), 63.8 (benzylic *C*H$_2$), 45.8 (NCH$_2$), 39.1 (NCH$_2$), 33.1 (*n*BuCH$_2$), 32.9 (*n*BuCH$_2$), 14.1 (*n*BuCH$_3$), 11.8 (NCH$_2$CH$_3$), 9.5 (br, LiCH$_2$), 5.2 (NCH$_2$CH$_3$). **^{7}Li{^{1}H} NMR** (-50°C): δ 0.54 (s, 2Li), 0.08 (s, 1Li), -1.29 (s, 1Li).

Dynamic processes involving 3_2 and 4_2:

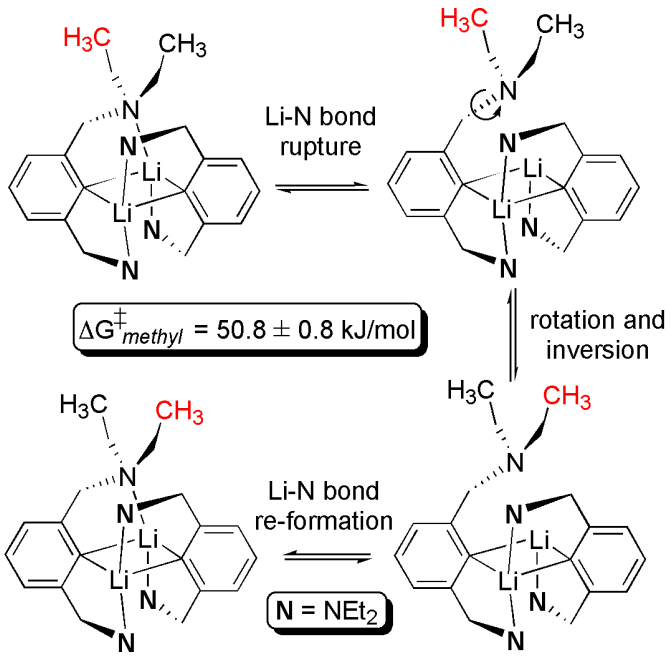

Figure S1: Depiction of process for exchange of NEt$_2$ groups ($\Delta G^{\ddagger}_{methyl}$)

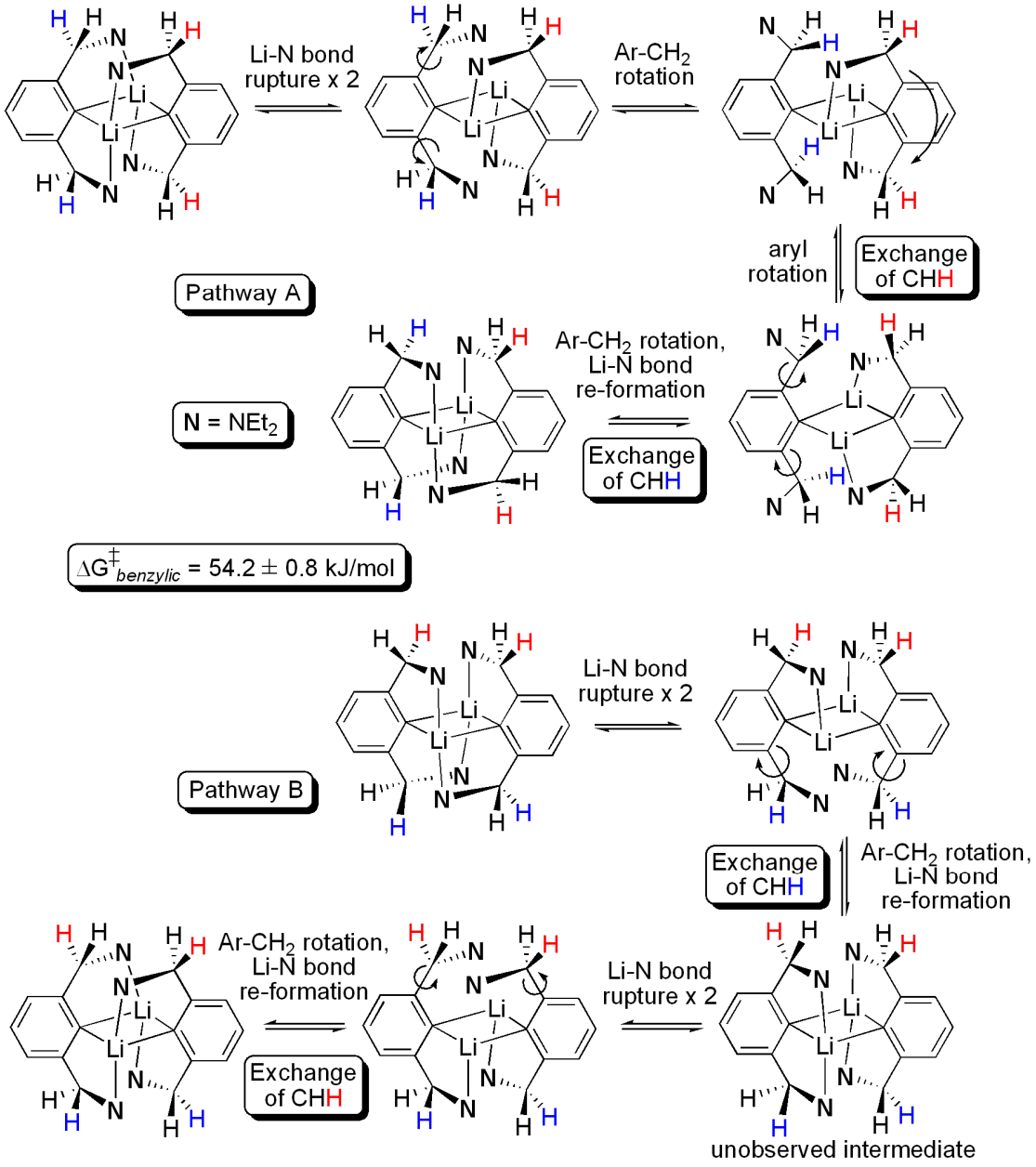

Figure S2: Depiction of processes for exchange of benzylic $ArCH_2N$ protons ($\Delta G^{\ddagger}_{benzylic}$)

<u>Representative NMR spectra of aggregates containing [^{Me}NCN] pincers (3-series):</u>

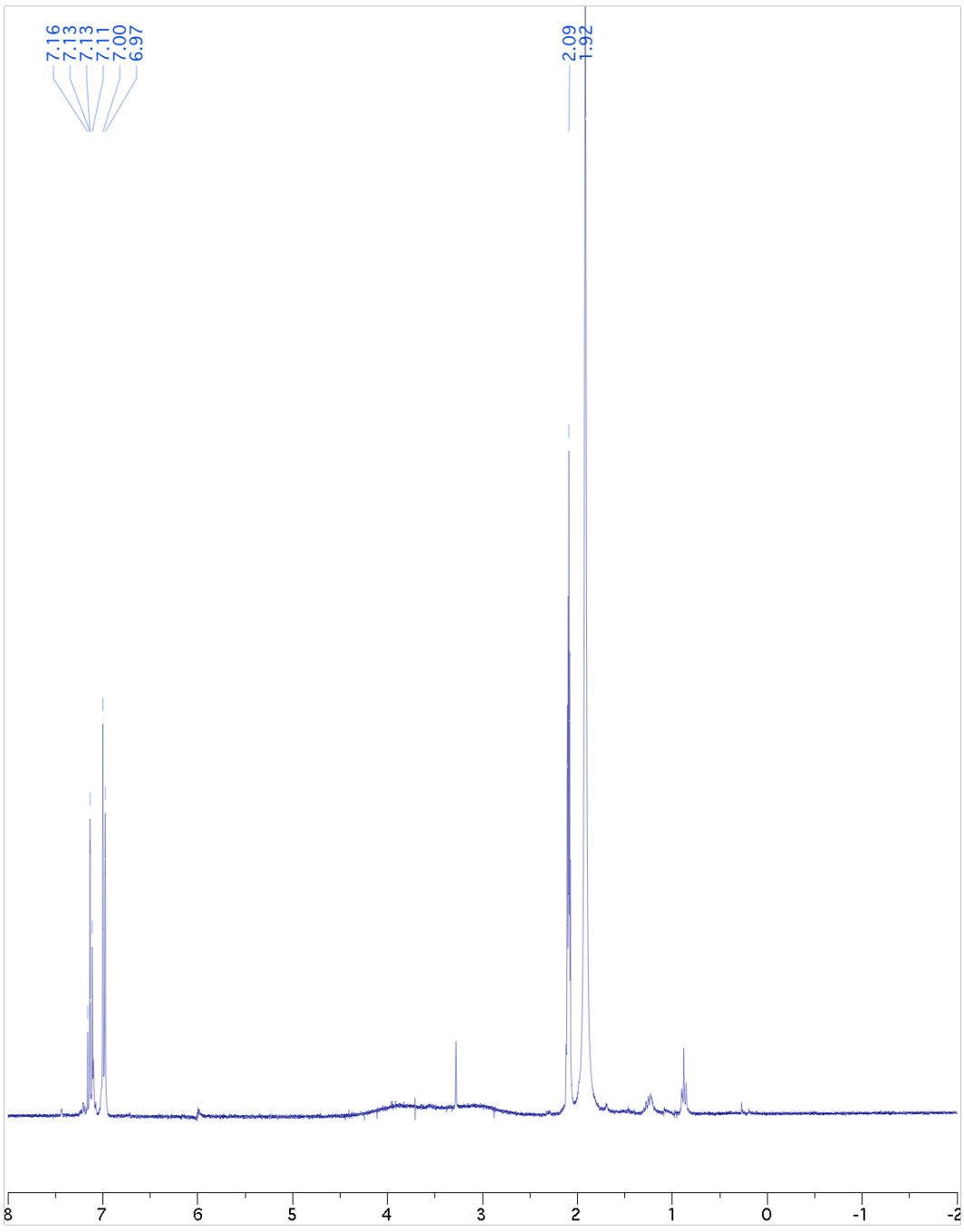

Figure S3: ^{1}H NMR spectrum of $\mathbf{3_2}$ at RT.

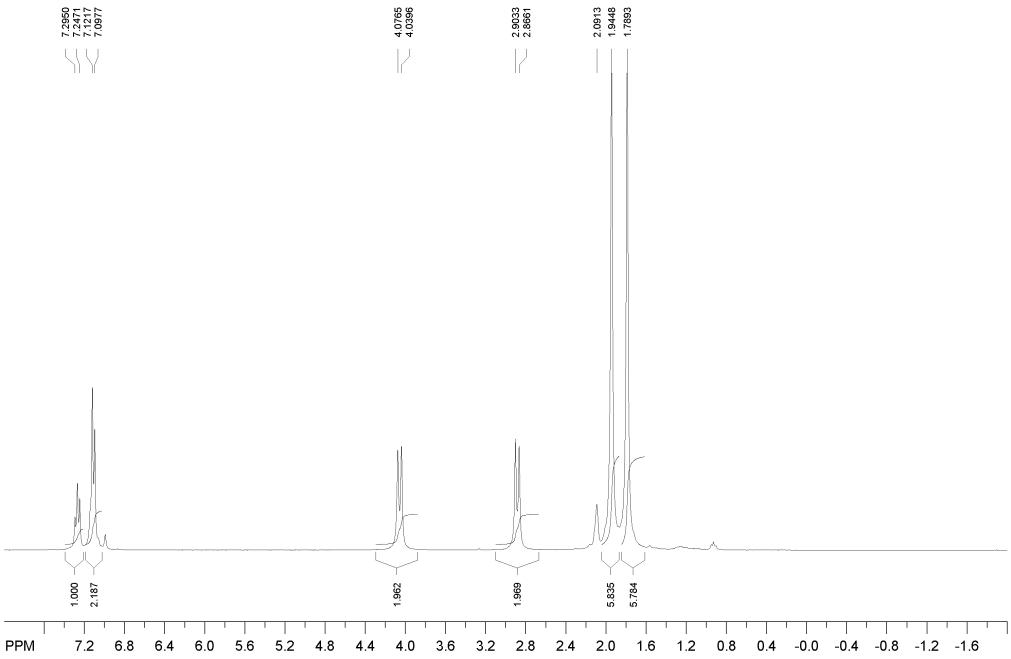

Figure S4: ^{1}H NMR spectrum of $\mathbf{3_2}$ at -50ºC.

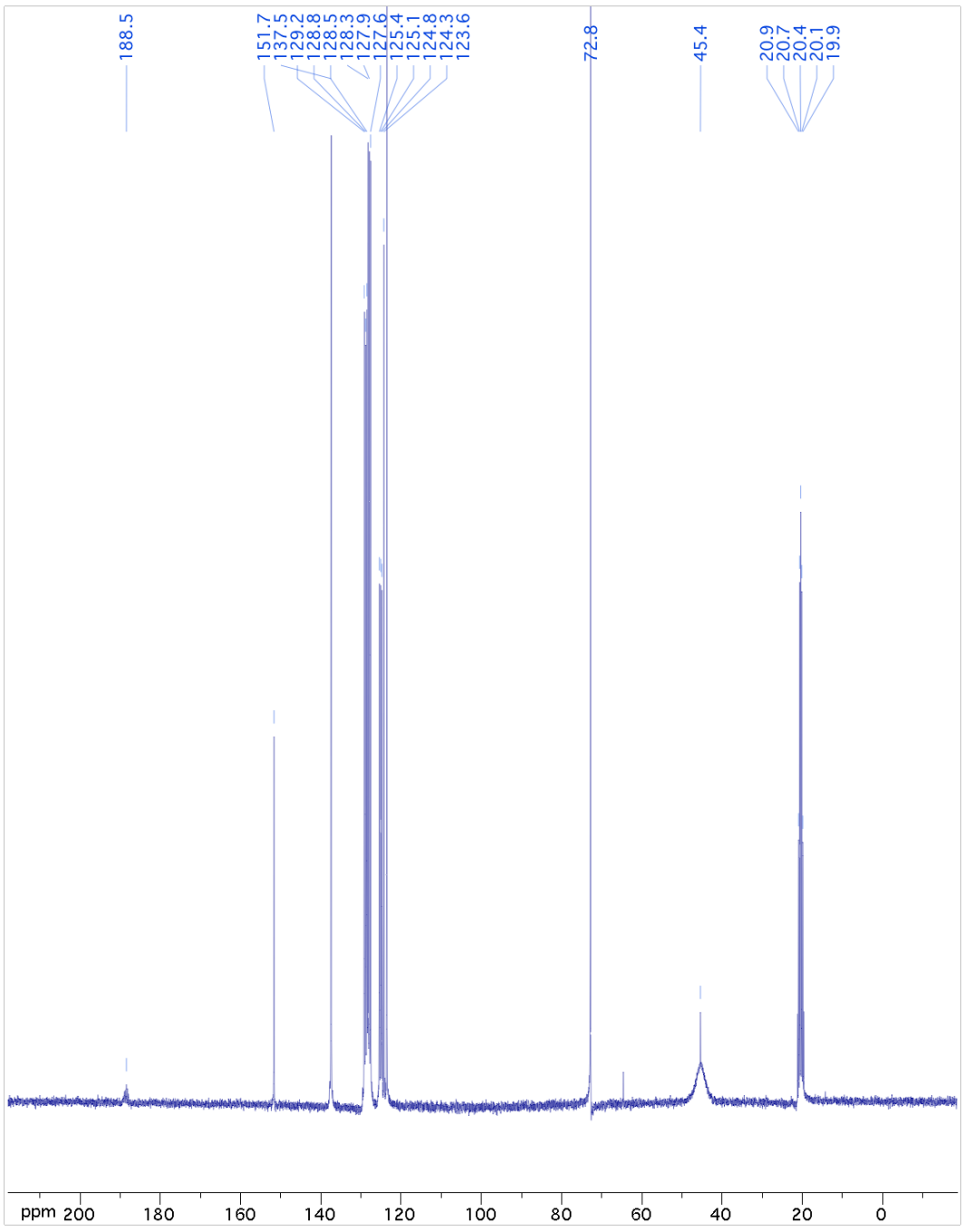

Figure S5: $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{3_2}$ at RT.

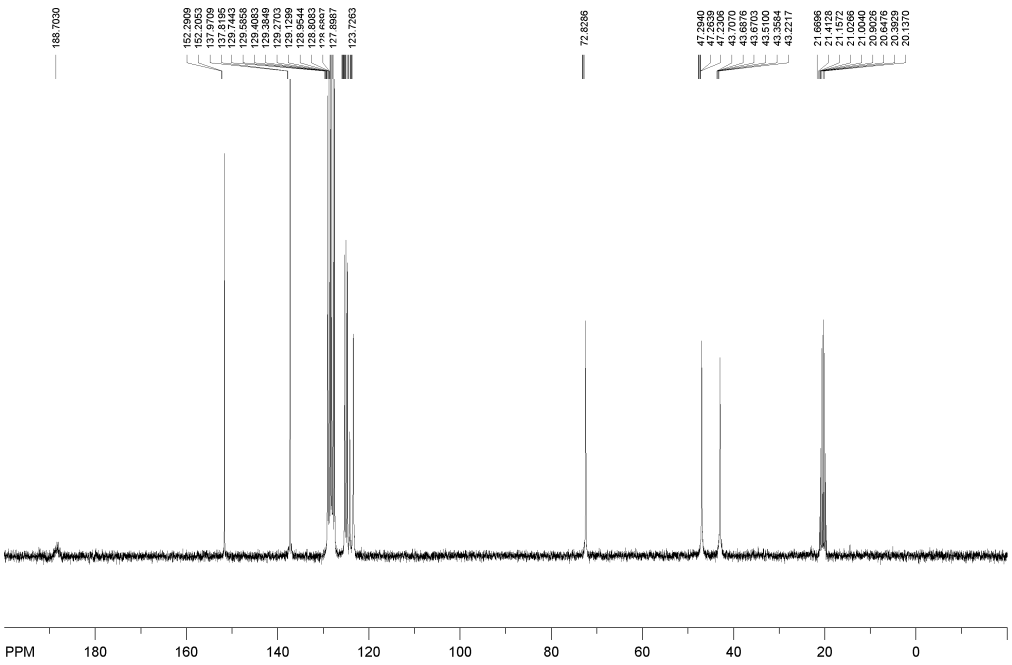

Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{3_2}$ at -50ºC.

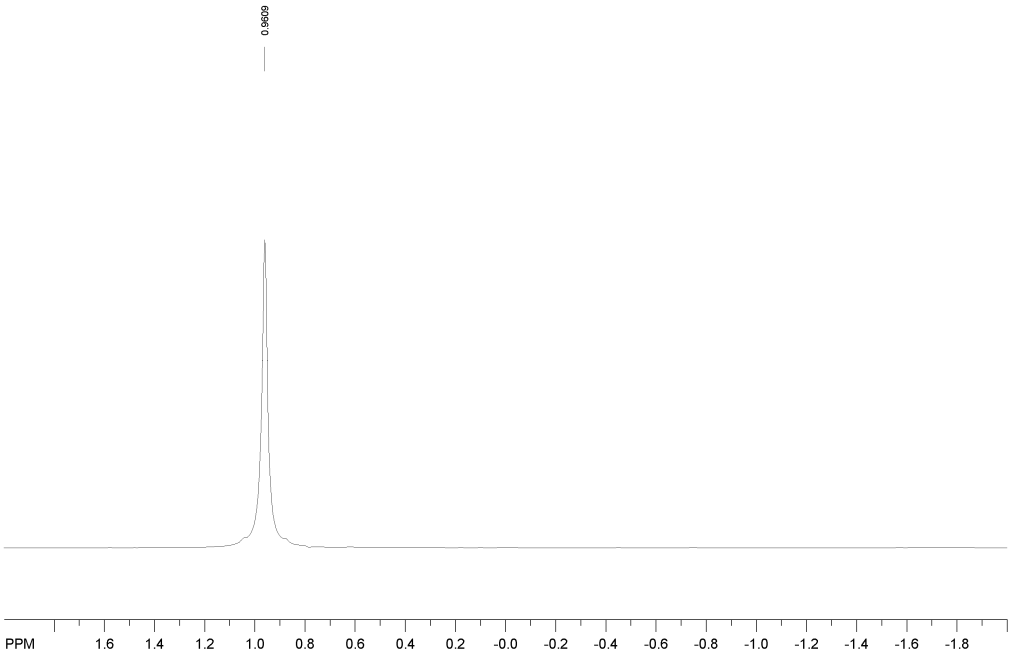

Figure S7: $^{7}Li\{^{1}H\}$ NMR spectrum of $\mathbf{3_2}$ at RT.

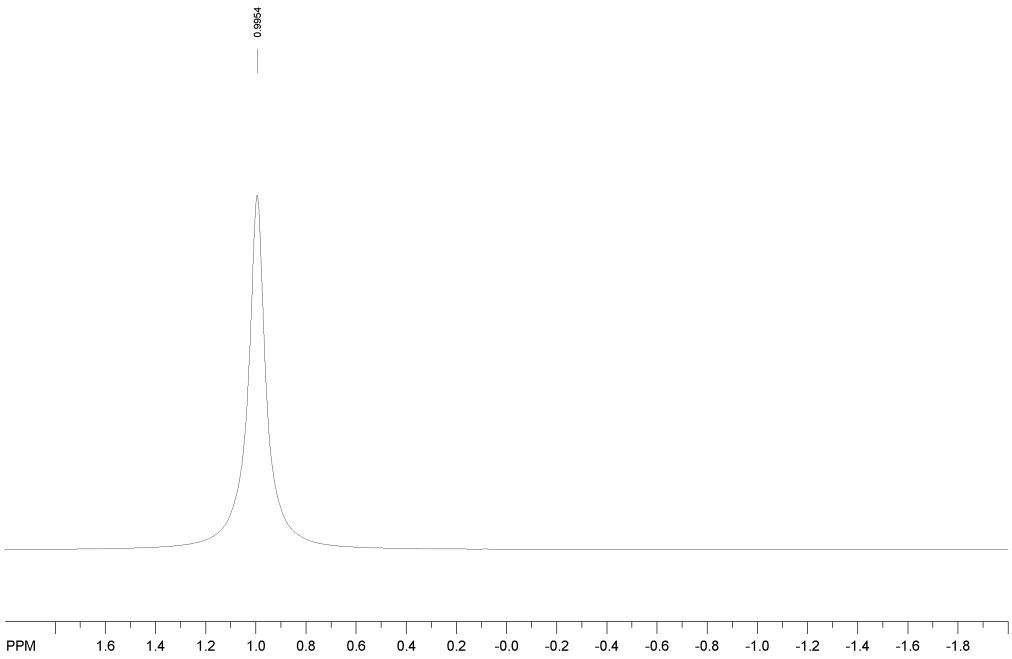

Figure S8: $^{7}Li\{^{1}H\}$ NMR spectrum of $\mathbf{3_2}$ at -50ºC.

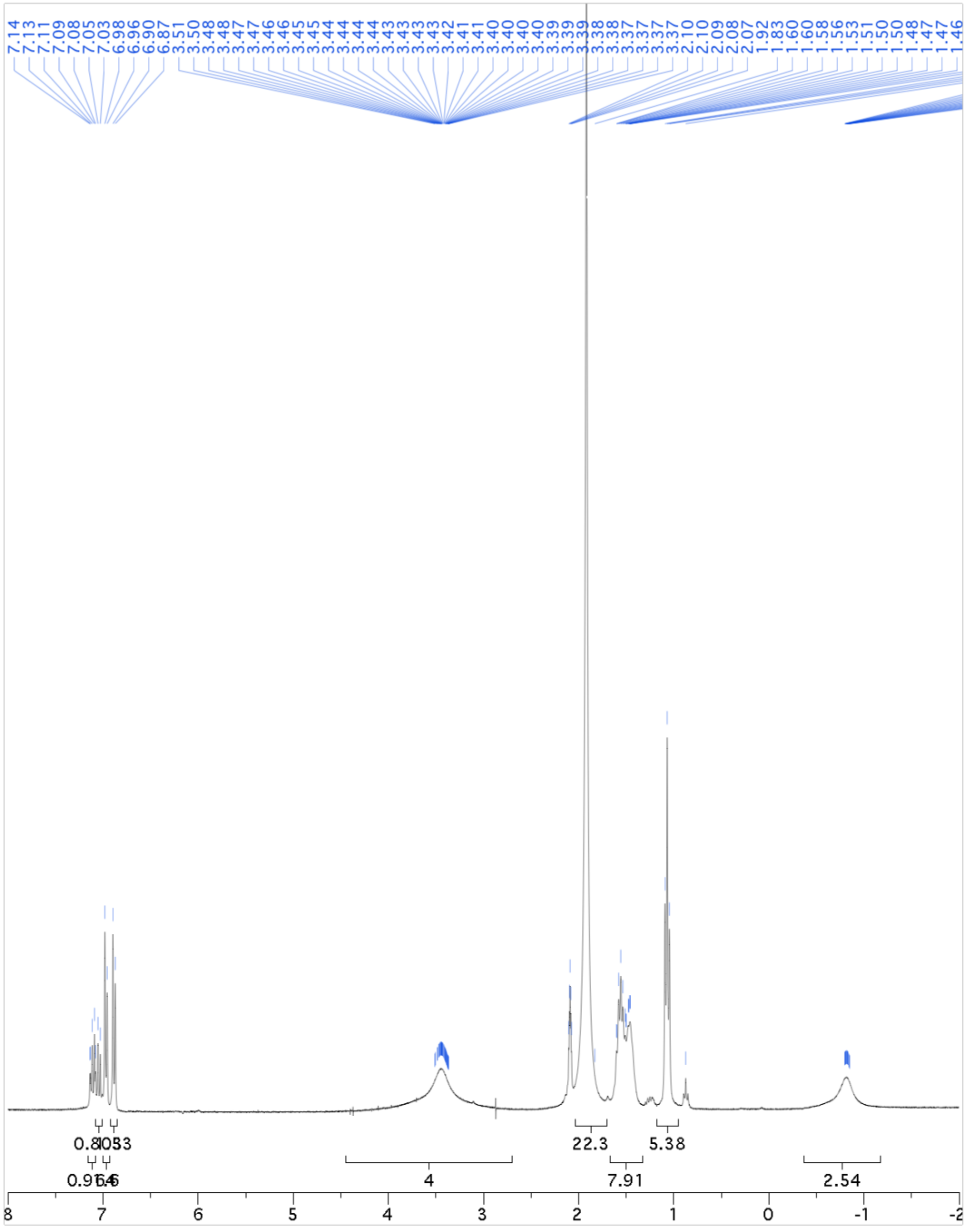

Figure S9: ^{1}H NMR spectrum of 1:2 mixture of $\mathbf{3_2}$ and *n*BuLi at RT.

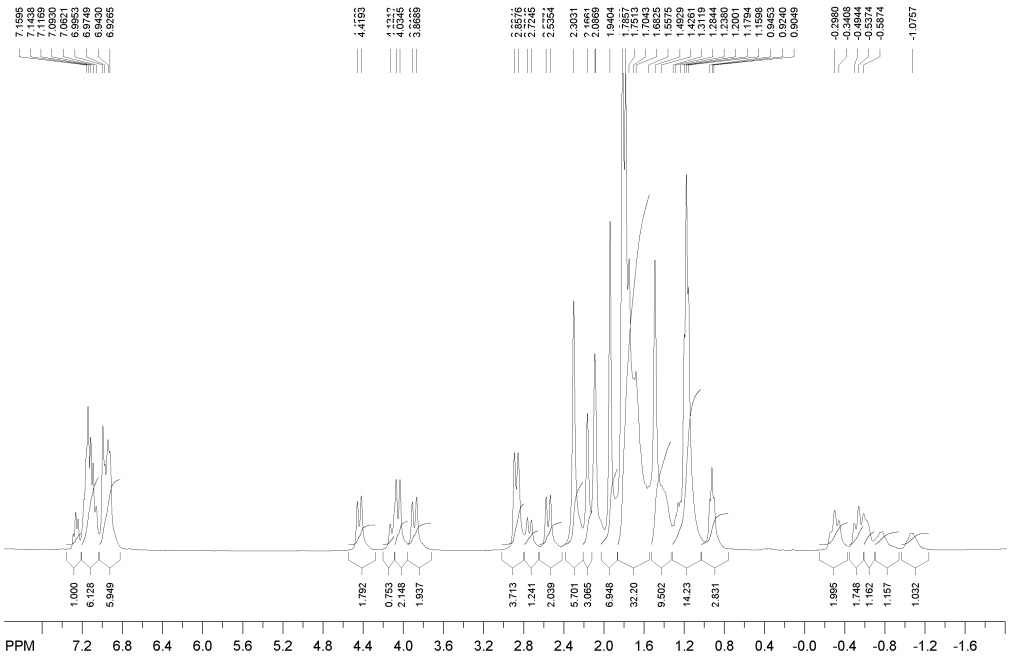

Figure S10: ^{1}H NMR spectrum of 1:2 mixture of $\mathbf{3_2}$ and *n*BuLi at -50ºC.

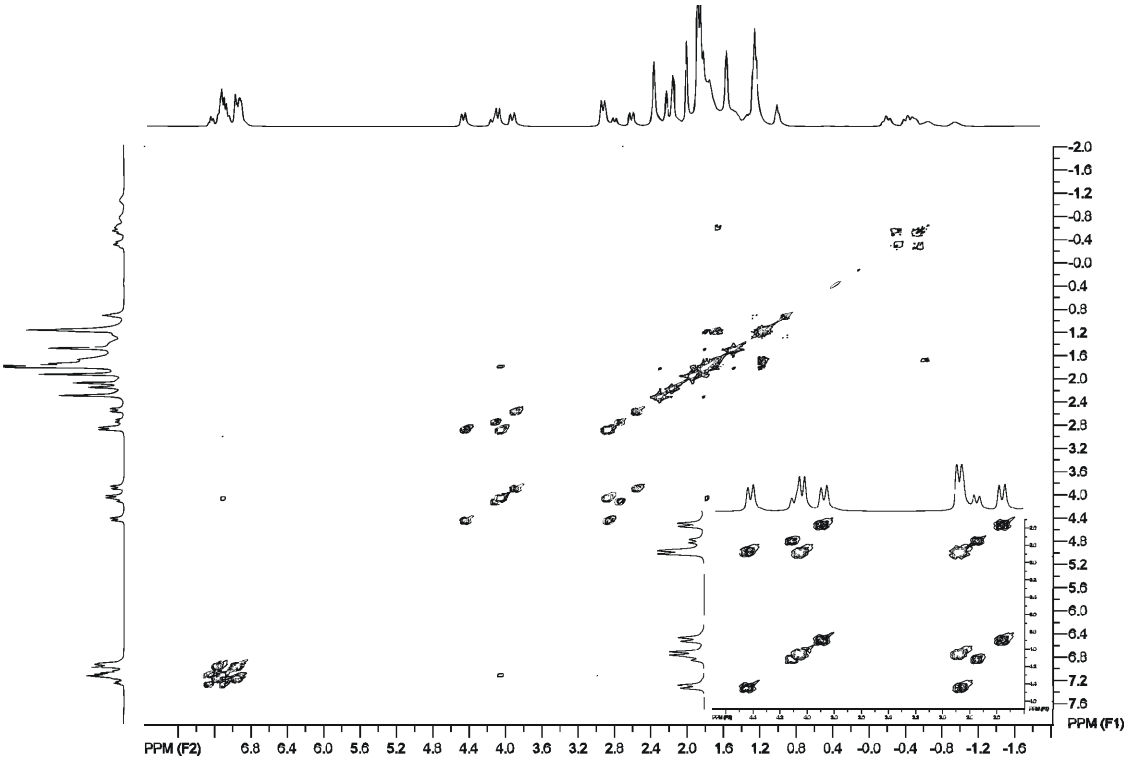

Figure S11: ^{1}H-^{1}H COSY NMR spectrum of 1:2 mixture of $\mathbf{3_2}$ and *n*BuLi at -50ºC. Inset: expansion of benzylic CH_2 region.

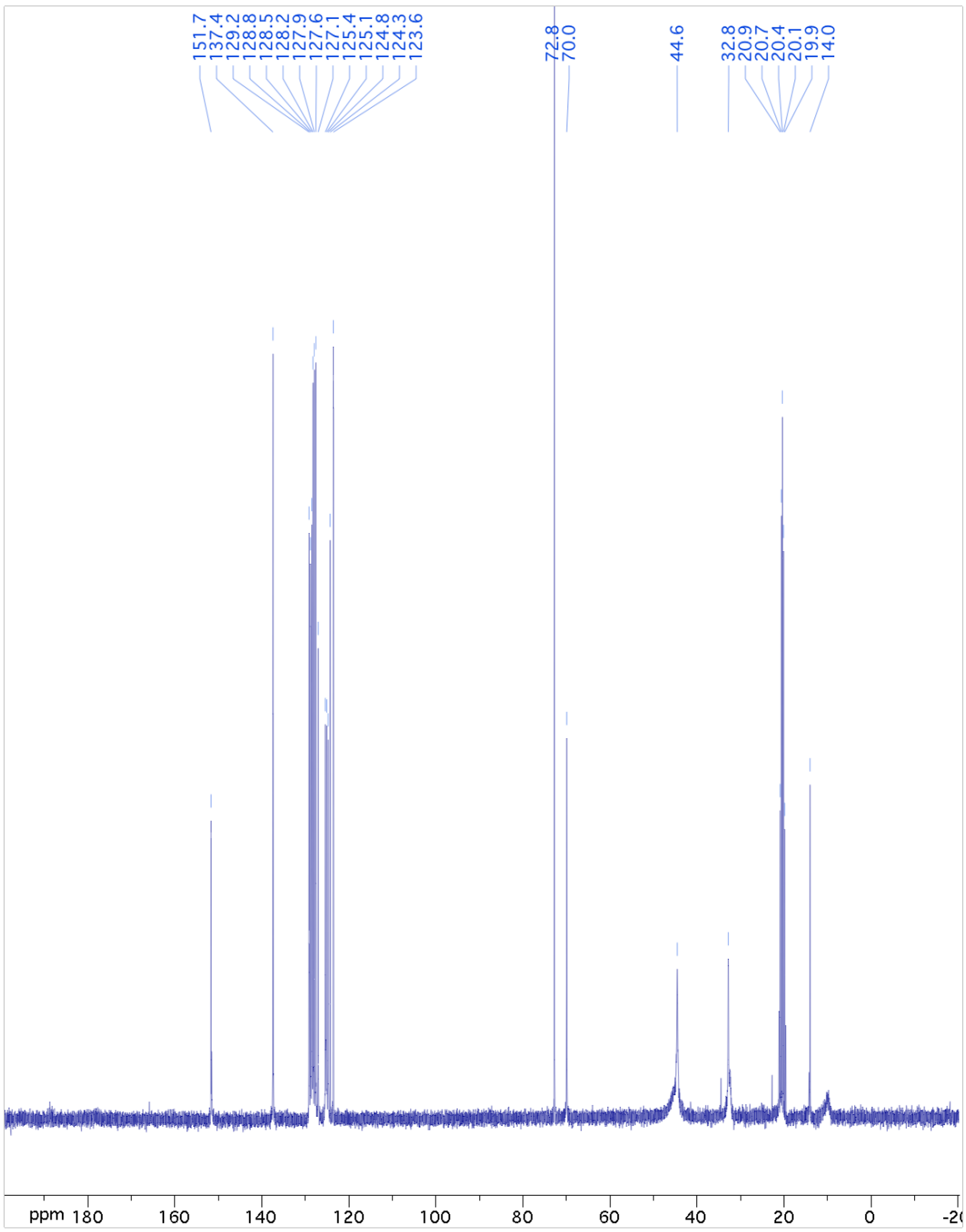

Figure S12: $^{13}C\{^{1}H\}$ NMR spectrum of 1:2 mixture of $\mathbf{3_2}$ and *n*BuLi at RT.

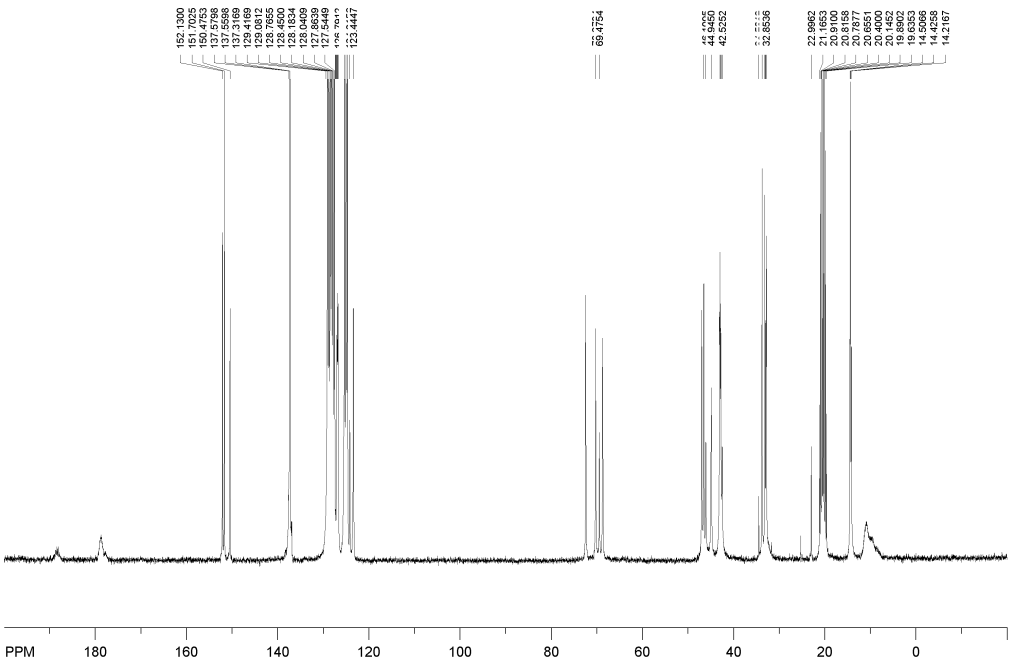

Figure S13: $^{13}C\{^{1}H\}$ NMR spectrum of 1:2 mixture of $\mathbf{3_2}$ and *n*BuLi at -50ºC.

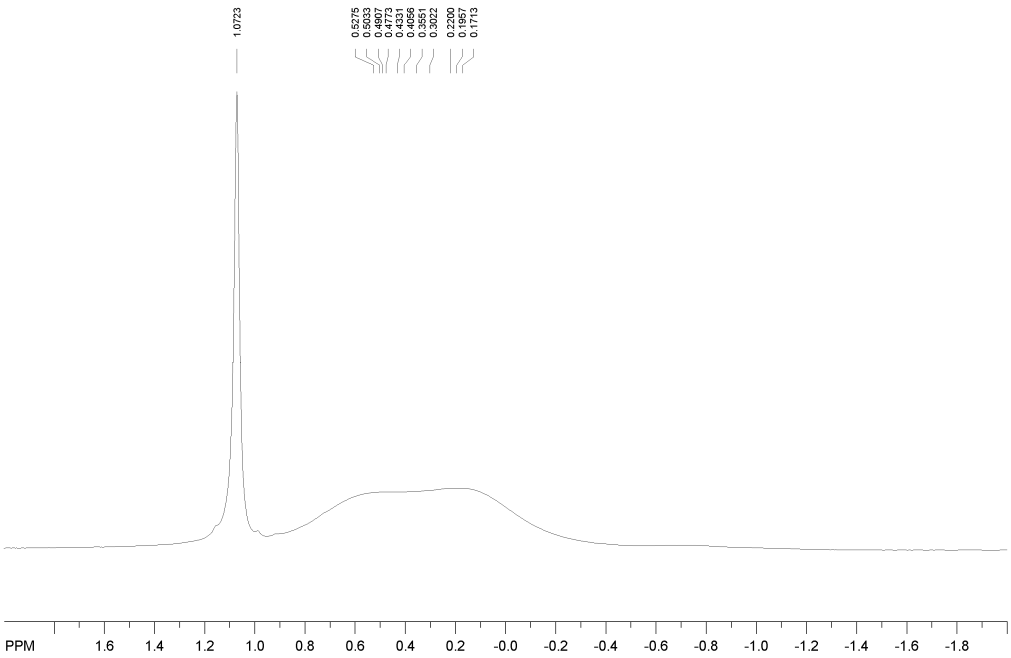

Figure S14: $^{7}Li\{^{1}H\}$ NMR spectrum of 1:2 mixture of $\mathbf{3_2}$ and *n*BuLi at RT.

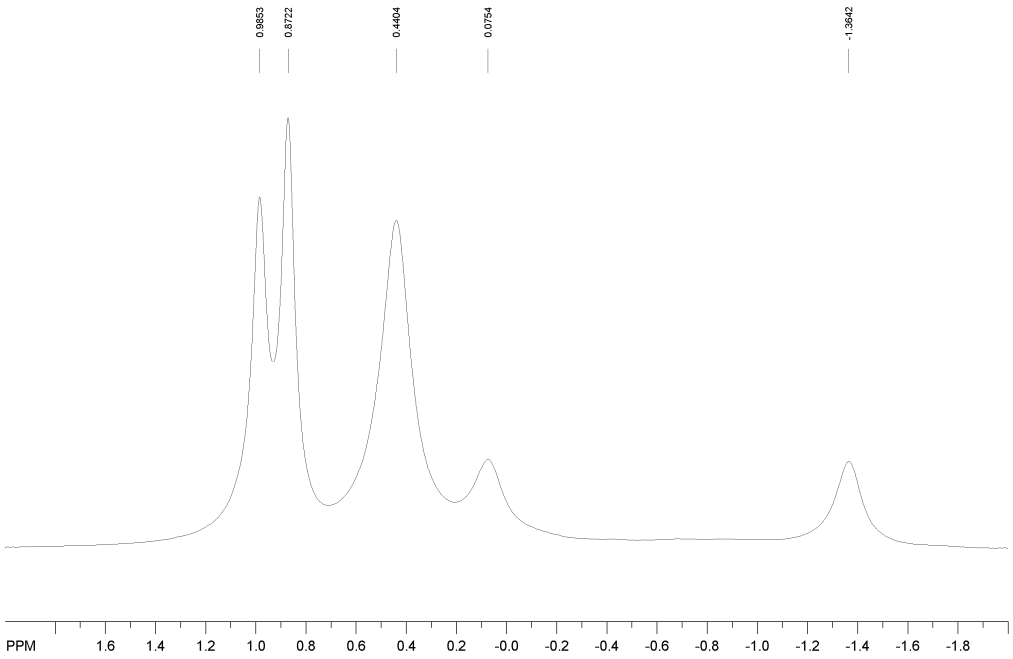

Figure S15: ^{7}Li{^{1}H} NMR spectrum of 1:2 mixture of $\mathbf{3_2}$ and *n*BuLi at -50ºC.

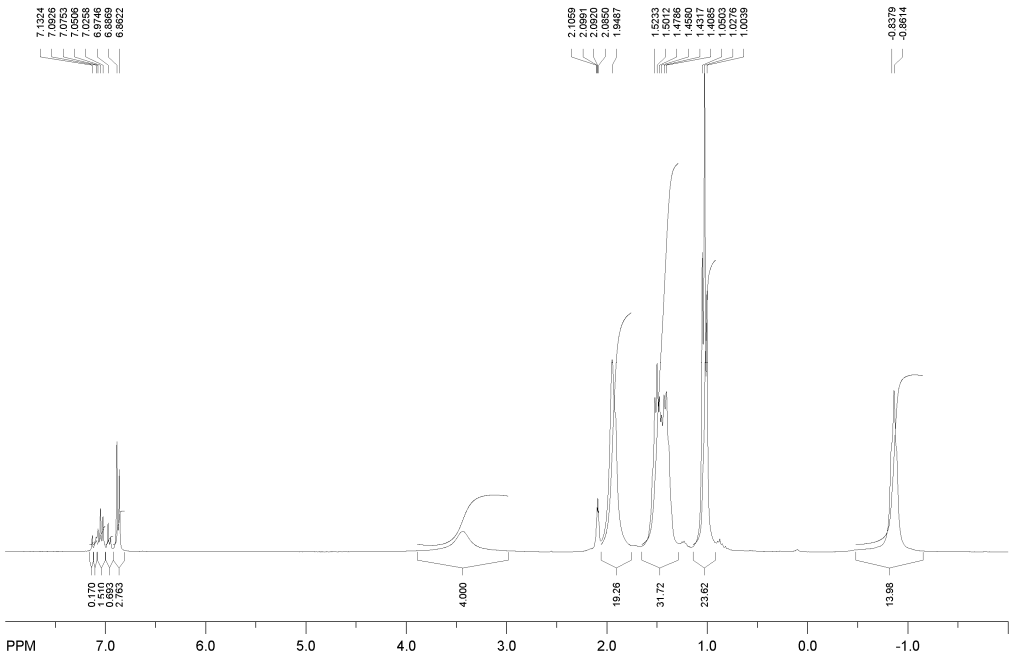

Figure S16: ^{1}H NMR spectrum of 1:9 mixture of $\mathbf{3_2}$ and *n*BuLi at RT.

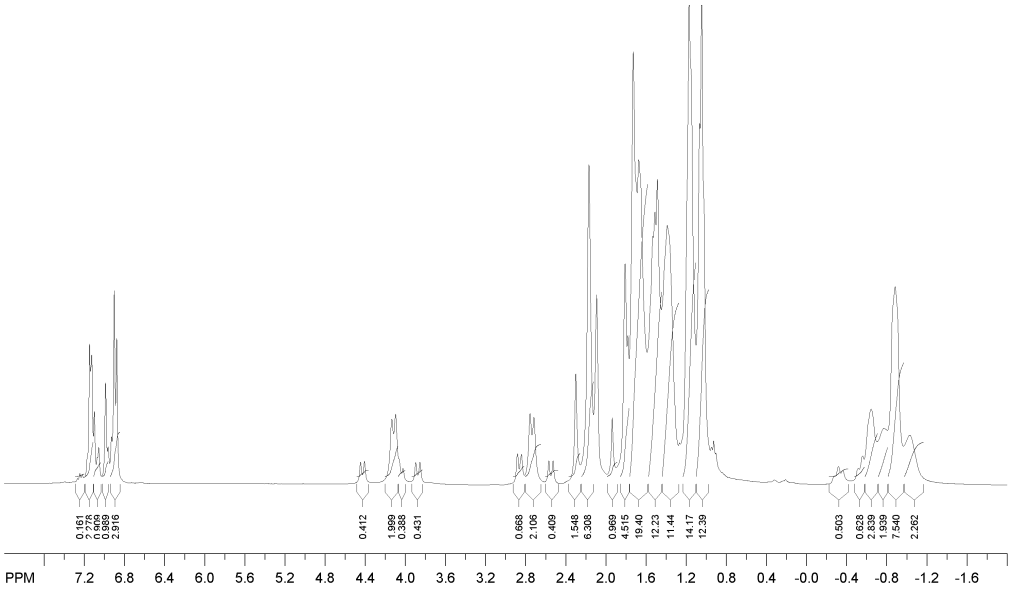

Figure S17: ^{1}H NMR spectrum of 1:9 mixture of $\mathbf{3_2}$ and *n*BuLi at -50ºC.

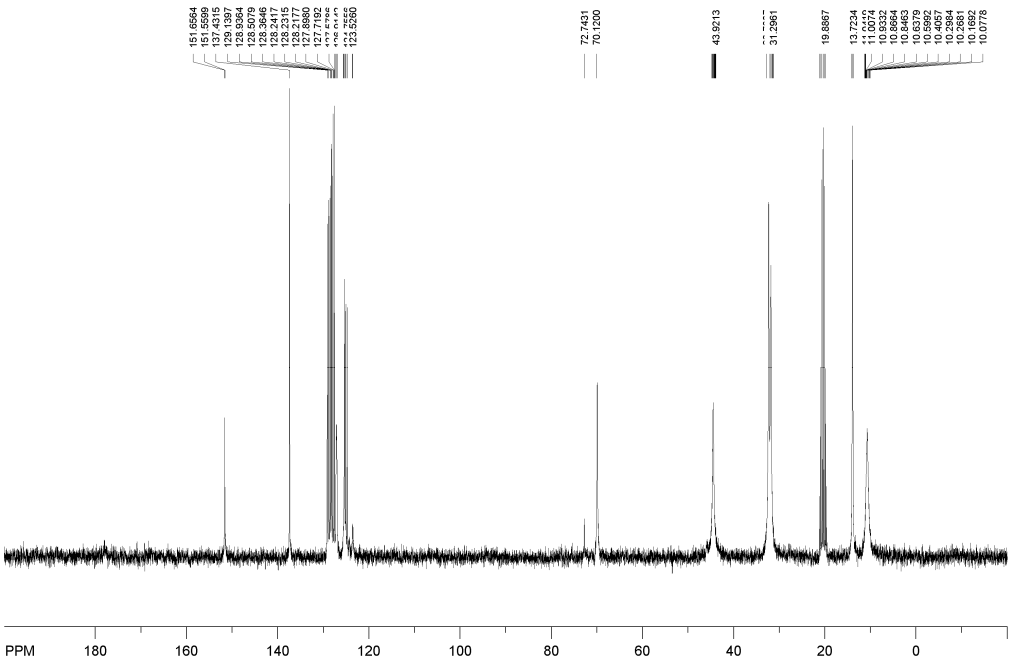

Figure S18: ^{13}C{^{1}H} NMR spectrum of 1:9 mixture of $\mathbf{3_2}$ and *n*BuLi at RT.

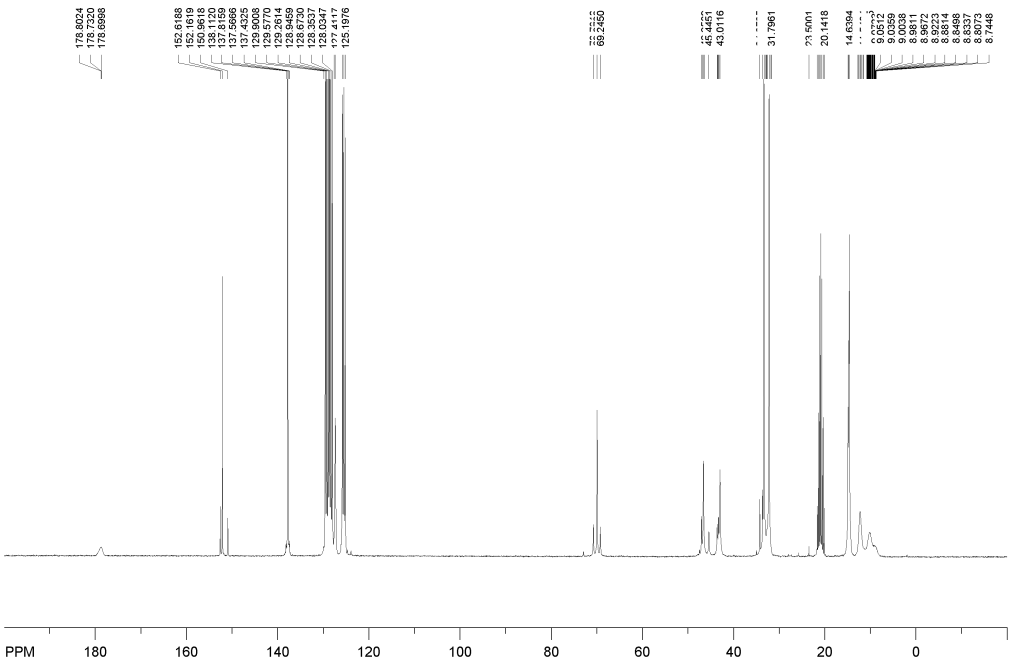

Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum of 1:9 mixture of $\mathbf{3_2}$ and *n*BuLi at -50ºC.

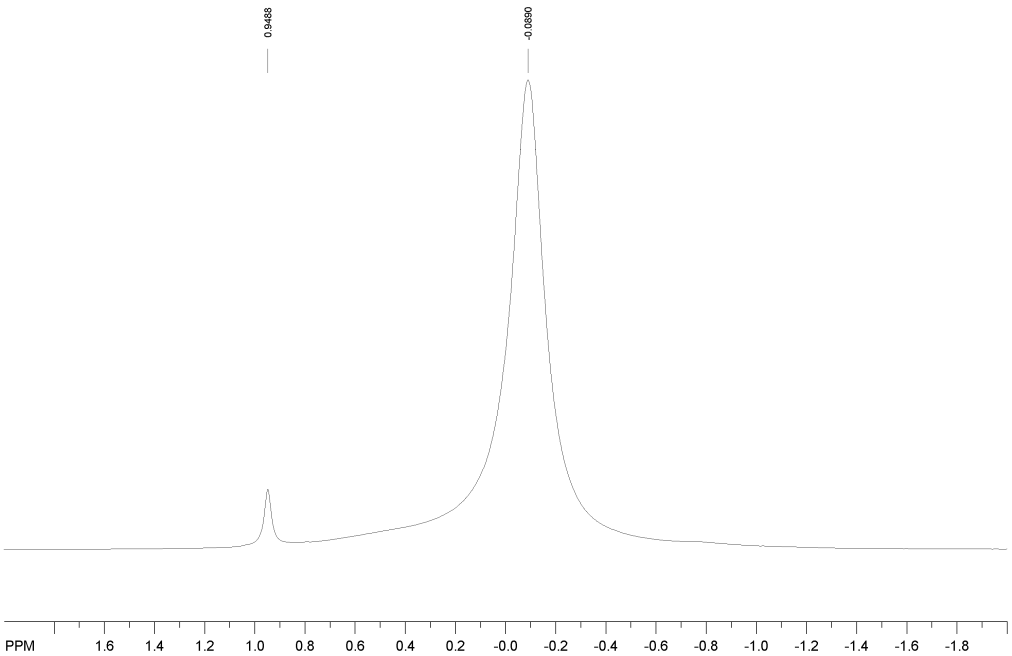

Figure S20: $^{7}Li\{^{1}H\}$ NMR spectrum of 1:9 mixture of $\mathbf{3_2}$ and *n*BuLi at RT.

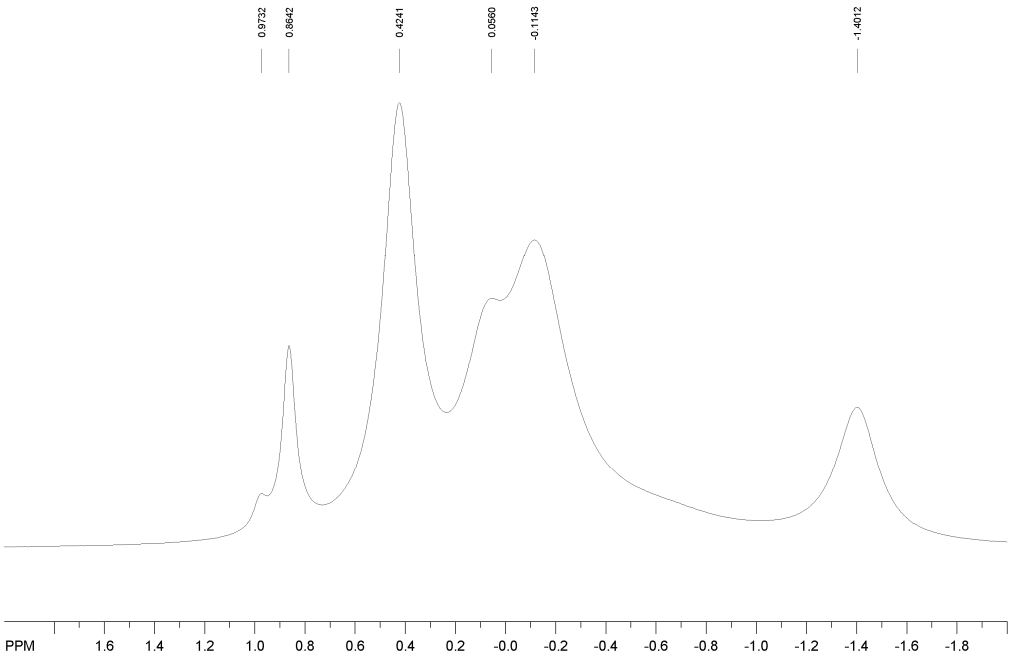

Figure S21: ^{7}Li{^{1}H} NMR spectrum of 1:9 mixture of $\mathbf{3_2}$ and *n*BuLi at -50ºC.

Representative NMR spectra of aggregates containing [^{Et}NCN] pincers (4):

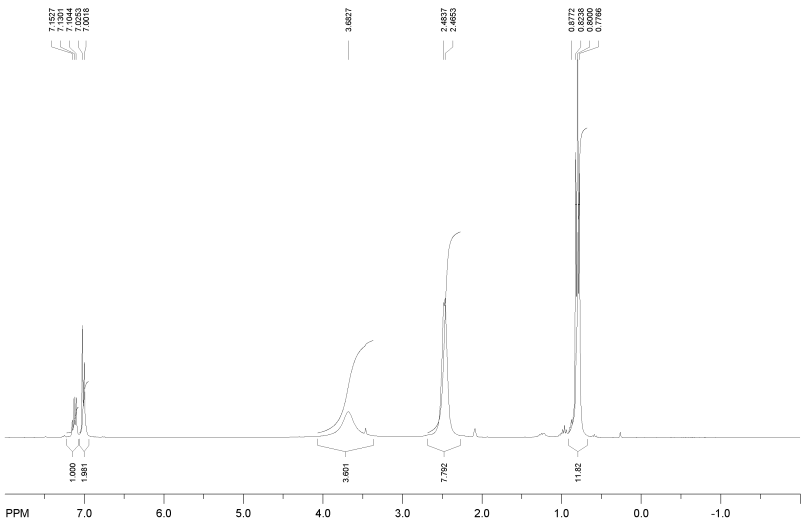

Figure S22: ^{1}H NMR spectrum of $\mathbf{4_2}$ at RT.

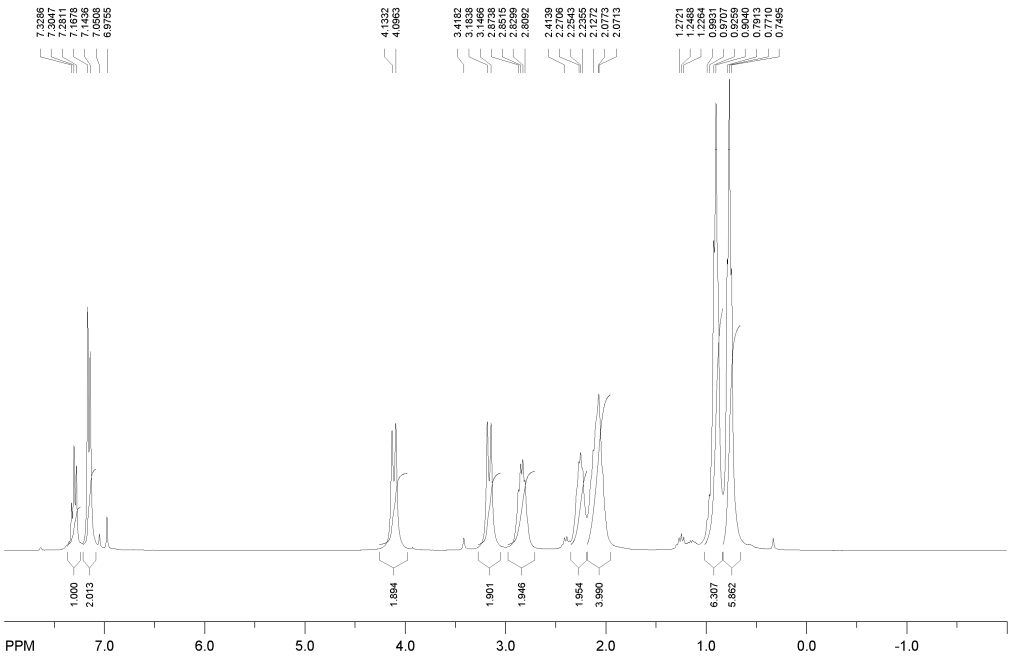

Figure S23: ^{1}H NMR spectrum of $\mathbf{4_2}$ at -60ºC.

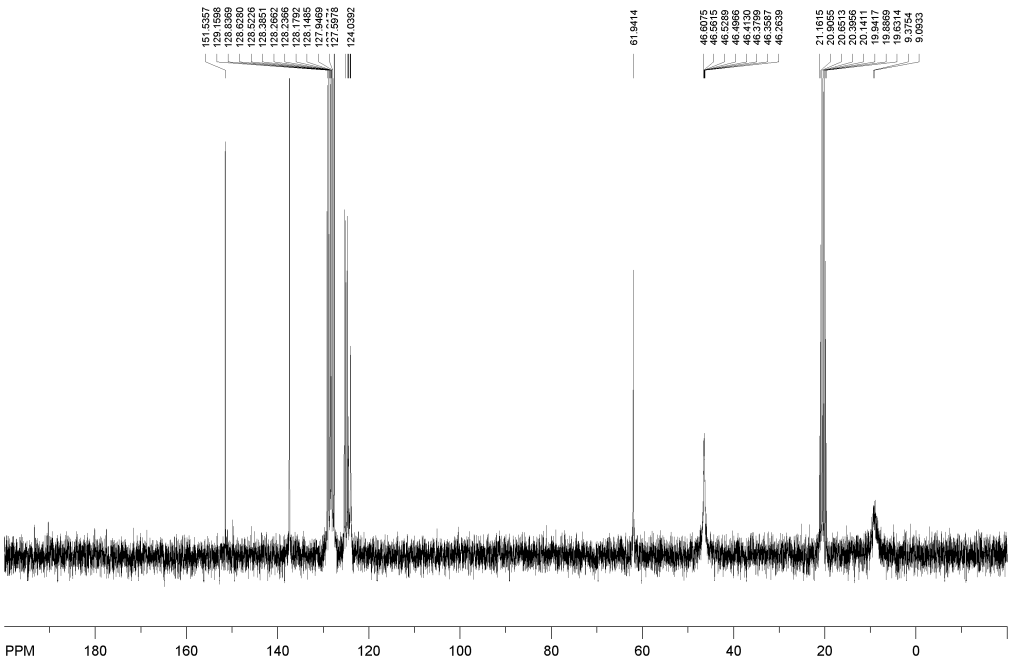

Figure S24: ^{13}C{^{1}H} NMR spectrum of $\mathbf{4_2}$ at RT.

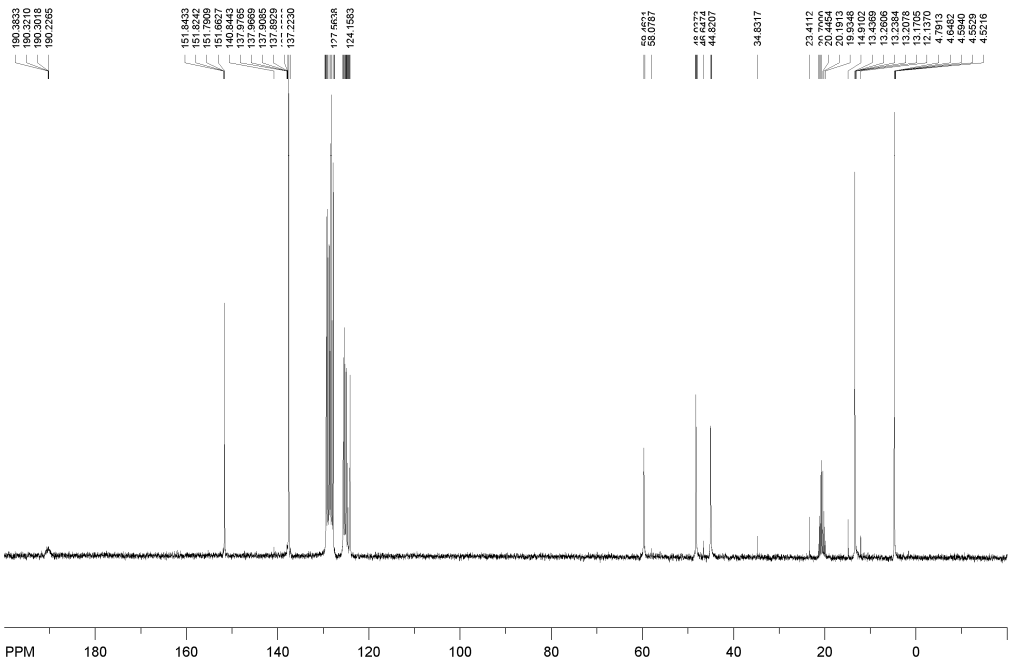

Figure S25: $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{4_2}$ at -60ºC.

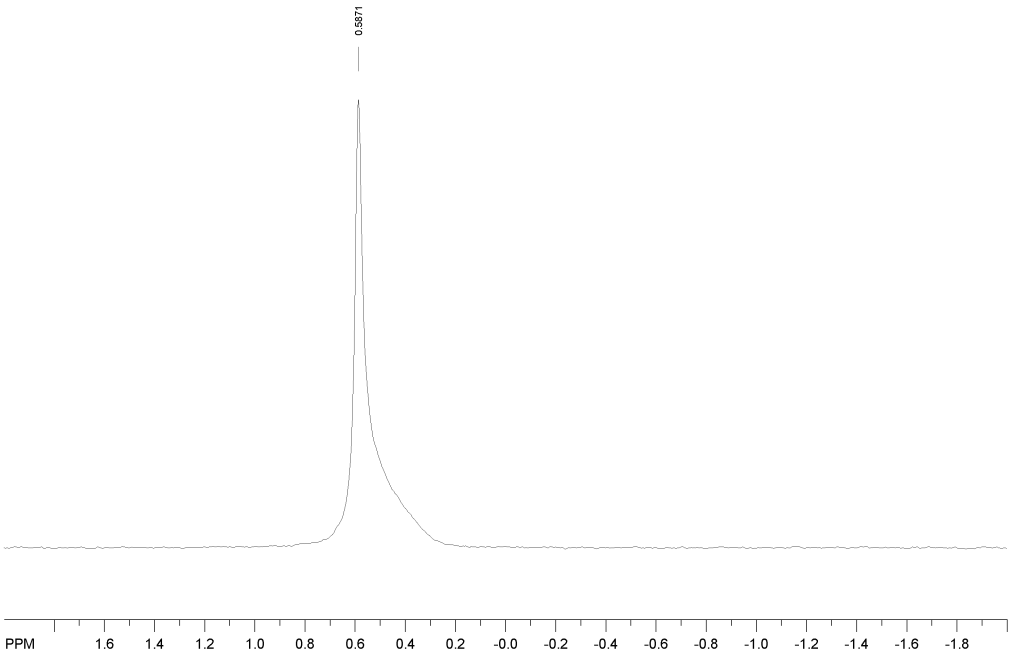

Figure S26: $^{7}Li\{^{1}H\}$ NMR spectrum of $\mathbf{4_2}$ at RT.

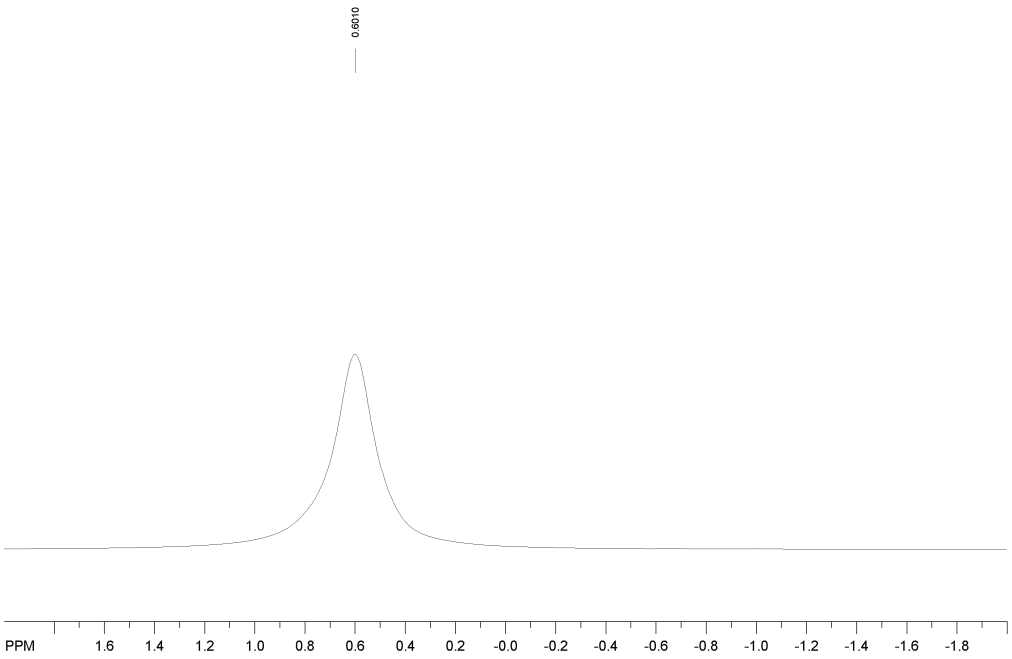

Figure S27: ^{7}Li{^{1}H} NMR spectrum of $\mathbf{4_2}$ at -60ºC.

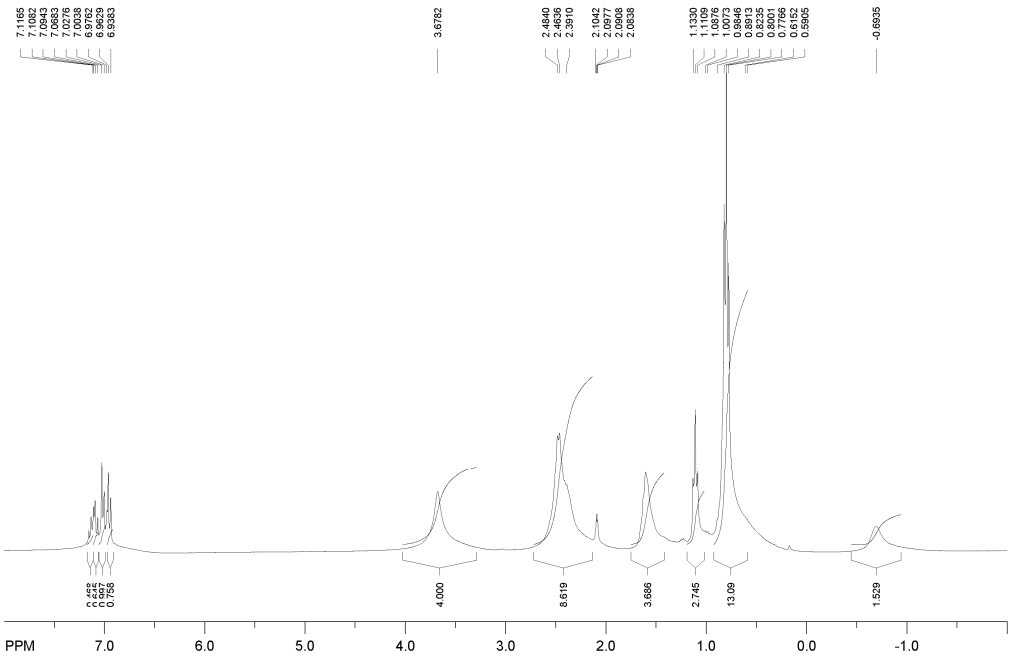

Figure S28: ^{1}H NMR spectrum of 1:2 mixture of $\mathbf{4_2}$ and *n*BuLi at RT.

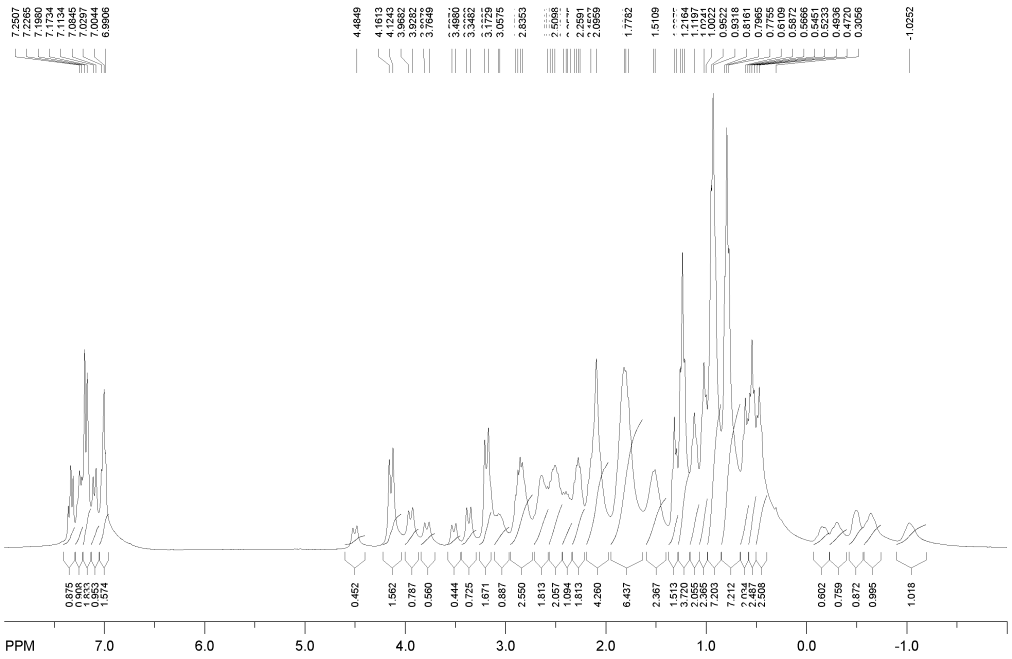

Figure S29: ^{1}H NMR spectrum of 1:2 mixture of $\mathbf{4_2}$ and *n*BuLi at -60ºC.

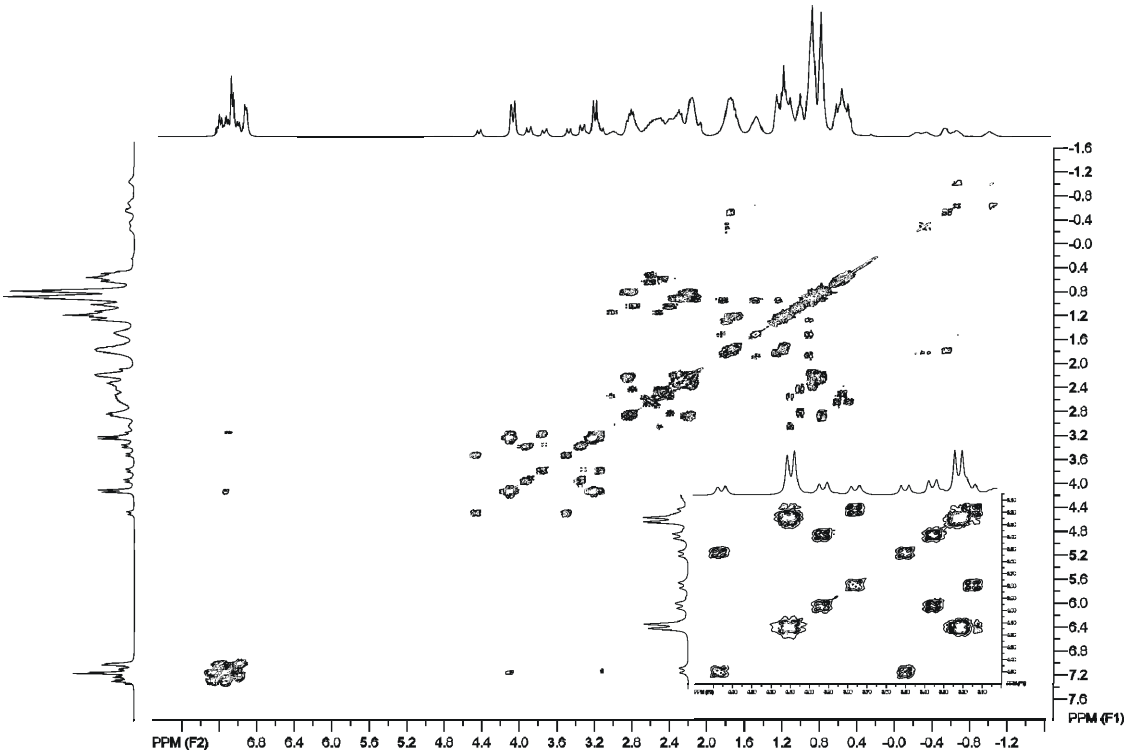

Figure S30: ^{1}H-^{1}H COSY NMR spectrum of 1:2 mixture of $\mathbf{4_2}$ and *n*BuLi at -60ºC. Inset: expansion of benzylic CH_2 region.

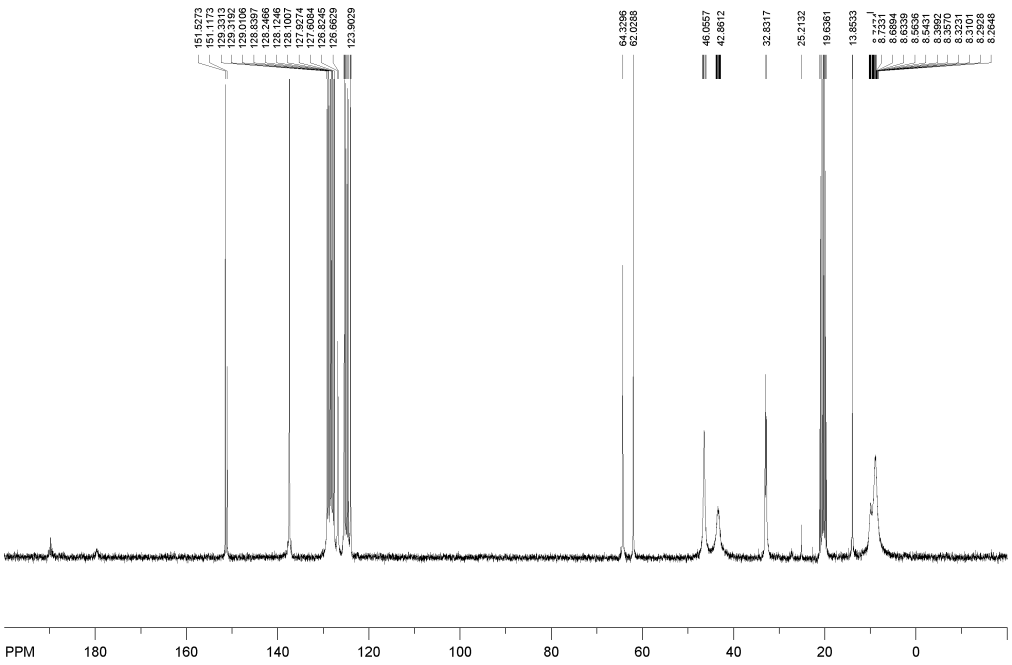

Figure S31: $^{13}C\{^{1}H\}$ NMR spectrum of 1:2 mixture of $\mathbf{4_2}$ and *n*BuLi at RT.

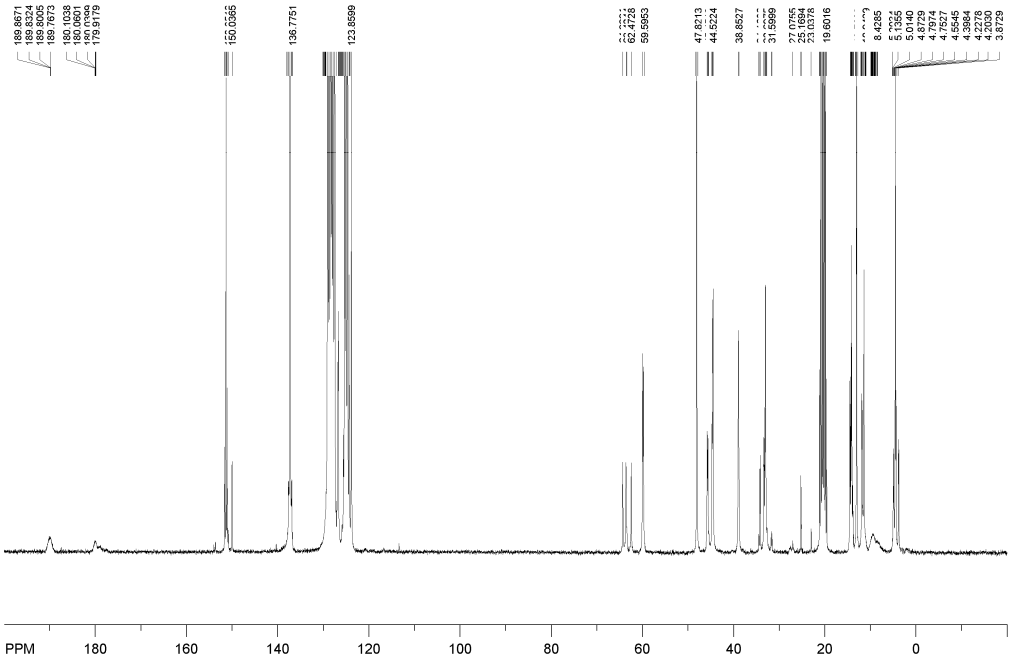

Figure S32: $^{13}C\{^{1}H\}$ NMR spectrum of 1:2 mixture of $\mathbf{4_2}$ and *n*BuLi at -60ºC.

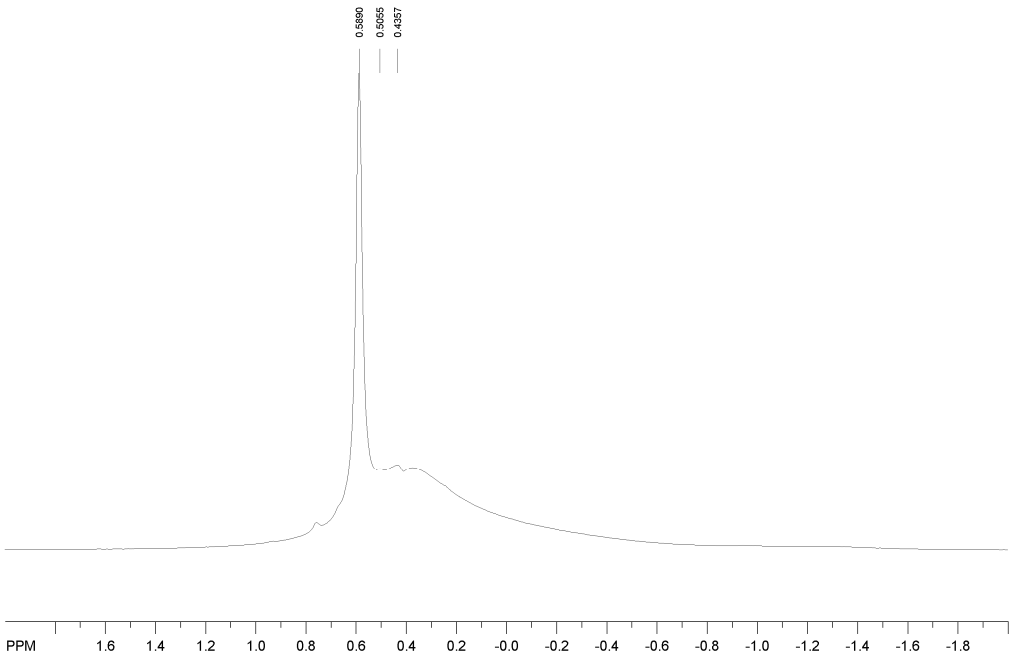

Figure S33: ^{7}Li NMR spectrum of 1:2 mixture of $\mathbf{4_2}$ and *n*BuLi at RT.

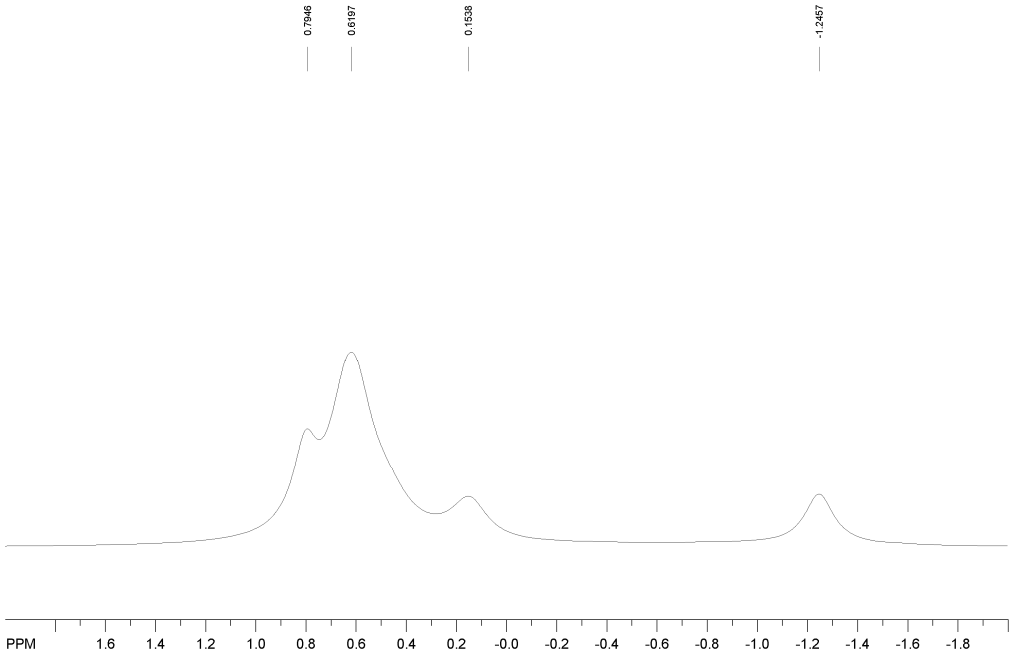

Figure S34: ^{7}Li NMR spectrum of 1:2 mixture of $\mathbf{4_2}$ and *n*BuLi at -60ºC.

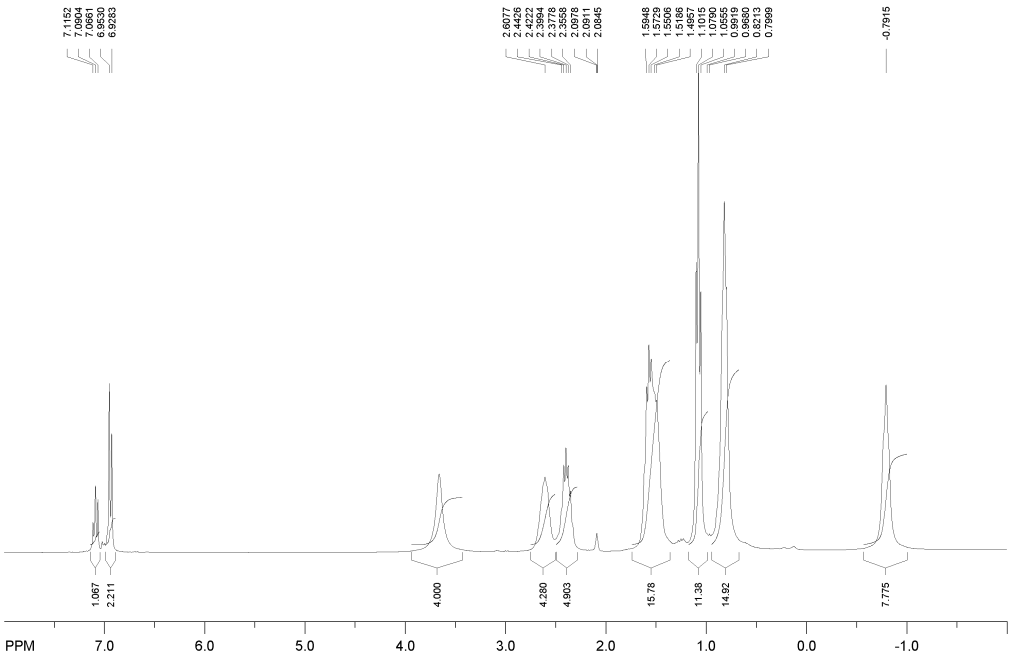

Figure S35: ^{1}H NMR spectrum of 1:8 mixture of $\mathbf{4_2}$ and *n*BuLi at RT.

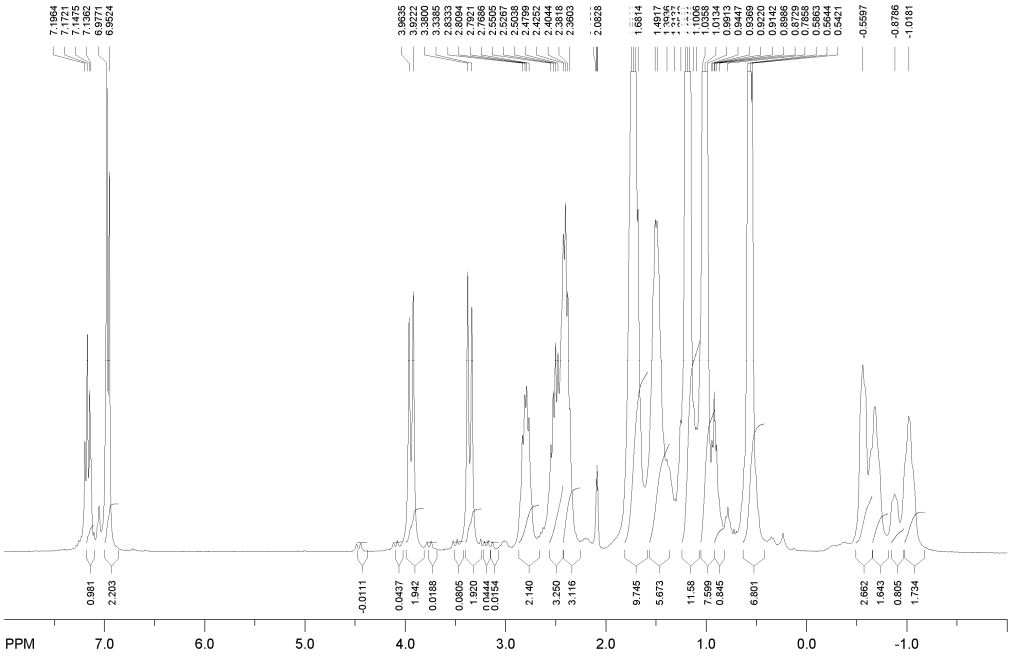

Figure S36: ^{1}H NMR spectrum of 1:8 mixture of $\mathbf{4_2}$ and *n*BuLi at -50ºC.

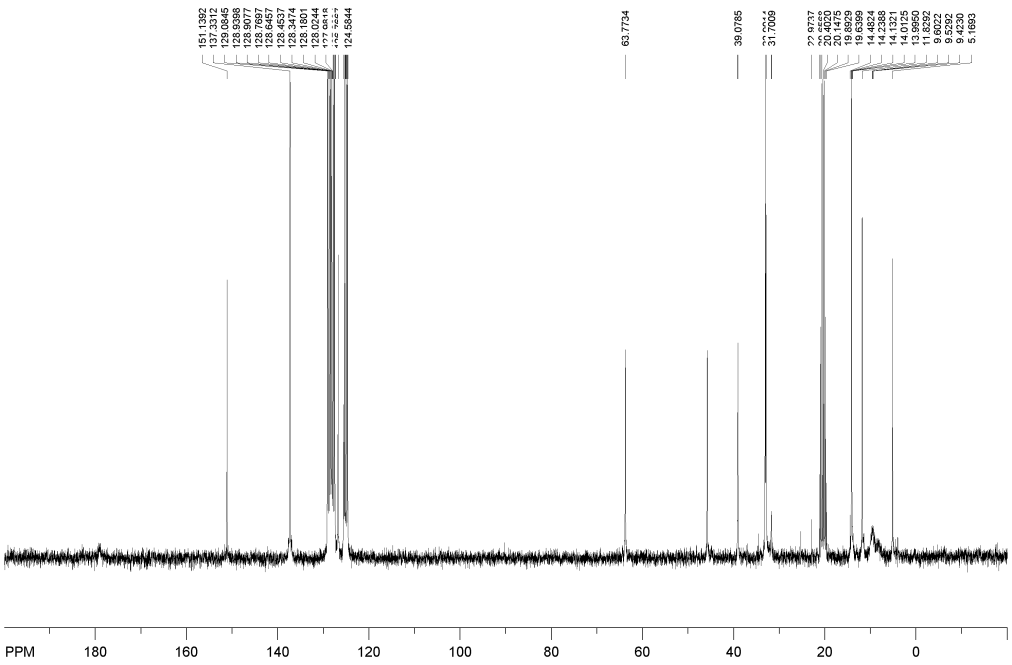

Figure S37: $^{13}C\{^{1}H\}$ NMR spectrum of 1:8 mixture of $\mathbf{4_2}$ and *n*BuLi at -50ºC.

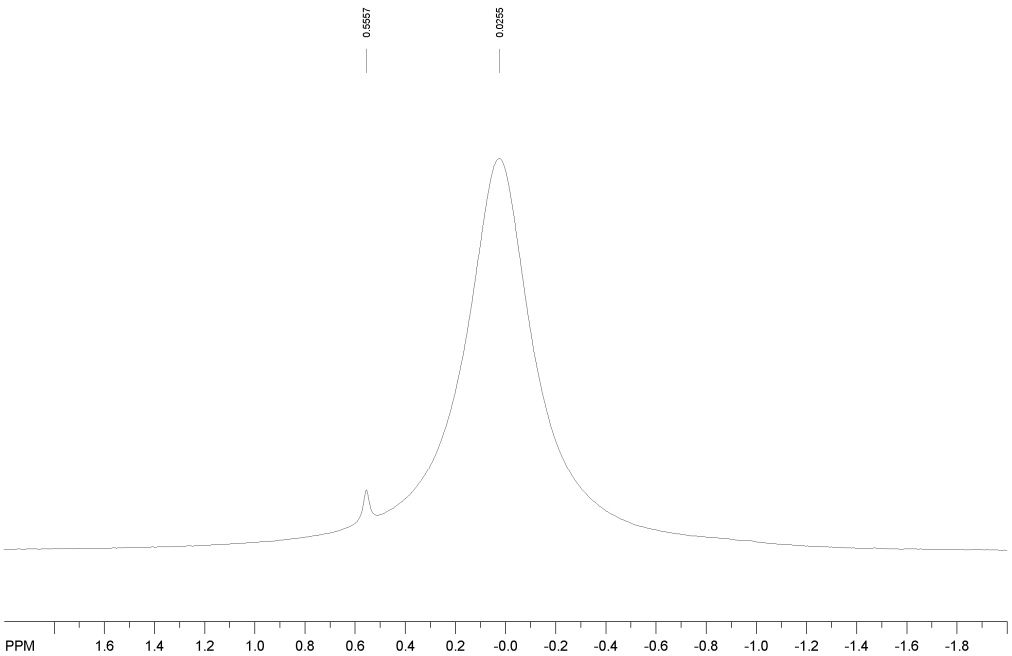

Figure S38: $^{7}Li\{^{1}H\}$ NMR spectrum of 1:8 mixture of $\mathbf{4_2}$ and *n*BuLi at RT.

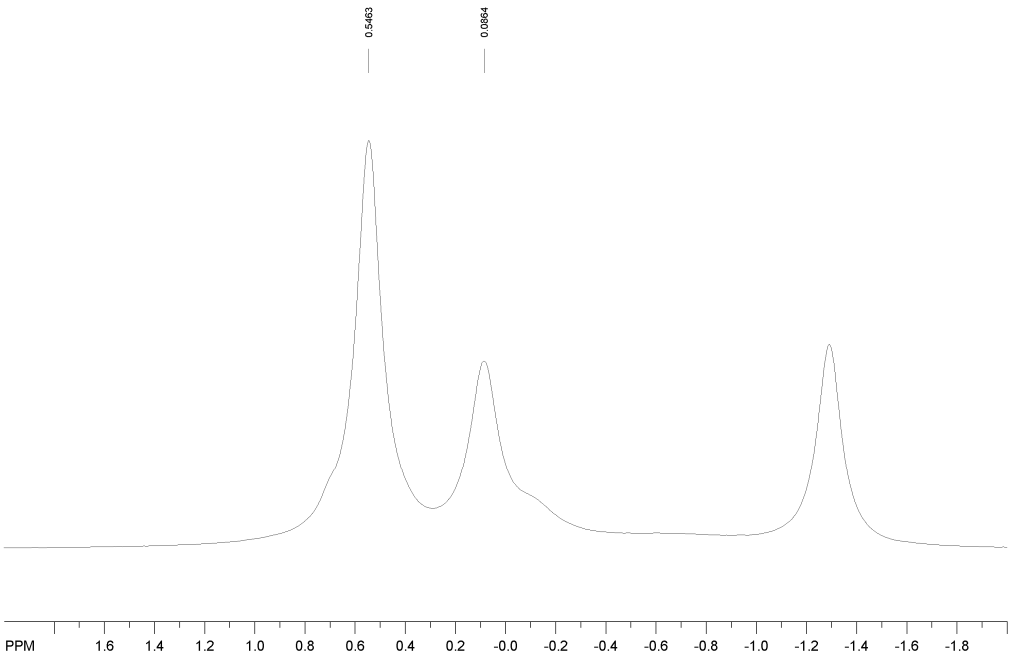

Figure S39: $^{7}Li\{^{1}H\}$ NMR spectrum of 1:8 mixture of $\mathbf{4_2}$ and *n*BuLi at -50ºC.