Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for:

Structural and Electronic Studies of Substituted *m*-Terphenyl Lithium Complexes

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S1. General Experimental

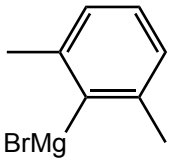
All air-sensitive manipulations were performed using standard Schlenk line and glovebox techniques under an atmosphere of argon or nitrogen respectively. All solvents were pre-dried, either via passage through a drying column of 4 Å molecular sieves (*iso*hexane), or via distilling over molten potassium (toluene) or sodium/benzophenone (THF). The solvents were stored over a potassium mirror (*iso*hexane, toluene) or 4 Å molecular sieves (THF) and degassed *in vacuo* prior to use. d_6-Benzene was dried over potassium and degassed via three freeze-pump-thaw cycles. All reagents and solvents were acquired commercially and used as received unless otherwise stated. ^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, ^{29}Si{^{1}H} and ^{7}Li{^{1}H} NMR spectra were recorded using Bruker DPX300, AV400, AV(III)400, and AV(III)500 spectrometers. Chemical shifts are quoted in ppm relative to TMS (for ^{1}H, ^{13}C{1H} and ^{29}Si{^{1}H} NMR), to $CFCl_3$ (for ^{19}F{^{1}H} NMR) and to a 1.0 M LiCl/D_2O solution (for ^{7}Li{^{1}H} NMR). An optimised ^{13}C{^{1}H} NMR spectrum was acquired for a saturated solution of **3** in C_6D_6 on a Bruker AV(III)500 spectrometer (25 °C, 126 MHz) to resolve coupling to the *ipso*-C (Fig 2, main manuscript). The spectrum was acquired with 16384 scans, 32 dummy scans, and delay of 10 s by Kevin Butler at the University of Nottingham. The spectrum was simulated using the Spin Simulation module of MestreNova. The resonance was centred at 172.73 ppm and modelled as coupling to two equivalent nuclei with I = 3/2, J = 23.3 Hz, and a linewidth of 10 Hz. DOSY experiments were performed on a Bruker AV(III)400HD spectrometer using the PFGSE (Pulsed-Field Gradient Spin-Echo) NMR Diffusion method. The variation in intensity (integral) of a selected ^{1}H NMR signal (I) is related to the gradient strength (g) by the equation: $\ln(I/I_0) = -(\gamma g\delta)^2 D[\Delta-(\delta/3)]$, where D is the diffusion coefficient, γ is the gyromagnetic ratio of the proton (4257.7 Hz G^{-1}), δ (small delta) is the length of the gradient pulse, and Δ (big delta) is the delay between the midpoints of the gradients. For all data recorded, experimental values of δ = 2 ms and Δ = 200 ms were used, and the gradient was varied across 32 spectra (following a dstebpgp3s sequence). Data analysis was carried out with TopSpin software by plotting straight-line graphs of ln(I) versus g^2 to deduce the diffusion coefficients, D. Hydrodynamic radii, r_s, were then calculated, assuming a spherical system, using the

Stokes-Einstein equation: $r_s = (kT/6\pi\eta D)$, where k is the Boltzmann constant, T is the absolute temperature, η is the solvent viscosity, and *D* is the diffusion coefficient. Two-dimensional ^{7}Li-^{1}H HOESY experiments were performed by Dr Huw Williams on a Bruker AV(III)600 spectrometer using echo and anti-echo quadrature detection running a 64 point T1 acquisition and 64 scans with a recycling delay of 3 s.[1,2] Elemental analyses (CHN) were performed by Dr Tong Liu at the University of Nottingham. Mass spectrometry was carried out by Dr Mick Cooper at the University of Nottingham.

S2. Synthetic Procedures

S2.1. Grignard Synthesis

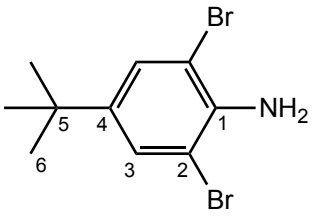
S2.1.1. (2,6-Dimethylphenyl)magnesium bromide



Magnesium turnings (9.85 g, 405 mmol) were activated by stirring in a solution of iodine (*ca.* 50 mg) in acetone (30 mL) for 20 min, after which time the magnesium was washed with acetone (4 × 20 mL), oven-dried for 10 min, then gently stirred under vacuum for 16 h. To the magnesium, dry THF (*ca.* 150 mL) was added. This mixture was heated to reflux, then a solution of 2-bromo-1,3-dimethylbenzene (50.0 g, 270 mmol) in THF (*ca.* 100 mL) was added dropwise over 1 h. The resultant black mixture was refluxed at 90 °C under argon for 4 h, then was cooled to room temperature and left to settle over 12 h. After this time, the mixture was filtered to give a brown solution of the product (*ca.* 56.6 g, 270 mmol) which was stored under argon until its direct use in later reaction steps. This was not characterised, as it was used as synthesised for the next step.

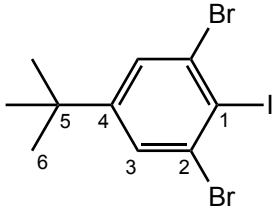
S2.2 Ligand Synthesis: *t*-Bu

S2.2.1. 2,6-Dibromo-4-*tert*-butylaniline



Synthesised according to modification of a literature procedure.[3] 4-*tert*-Butylaniline (16.0 g, 107 mmol) was dissolved in dichloromethane (250 mL) under argon, then a solution of bromine (13.8 mL, 268 mmol) in dichloromethane (100 mL) was added dropwise. The resultant dark red solution was stirred for 16 h at room temperature. After this, an orange solid had precipitated. The mixture was poured onto deionised water (200 mL) at 0 °C, then aqueous sodium bicarbonate (200 mL, 1 M) was added. The organic layer was separated, and the aqueous phase was washed with diethyl ether (3 × 50 mL), then the organics were combined, dried over $MgSO_4$, and filtered. The filtrate was reduced under vacuum to yield a dark red-purple oil that was purified by plug column chromatography on silica gel eluted with petroleum ether (40-60)/dichloromethane 5:1 (v/v) to afford the crude product (30.4 g, 92%) as a red oil. The compound was used directly in the next reaction without further purification. IR ν_{max}(neat)/cm^{-1} 3477(w), 3379(w), 2960(m), 2905(w), 2866(w), 1611(m), 1577(m), 1540(m), 1479(s), 1392(m), 1362(m), 1291(m), 1256(m), 1059(w), 869(m), 731(s), 709(m); ^{1}H NMR δ_H (400 MHz; $CDCl_3$): 7.34 (2H, s, H-3), 4.36 (2H, br s, NH_2), 1.21 (9H, s, H-6); ^{13}C NMR δ_C (101 MHz; $CDCl_3$): 143.0 (C-4), 139.5 (C-1), 128.9 (C-3), 108.8 (C-2), 34.1 (C-5), 31.4 (C-6); HRMS (ESI), m/z: (Found: 305.9490. Calc. for $C_{10}H_{13}Br_2N$: 305.9488.)

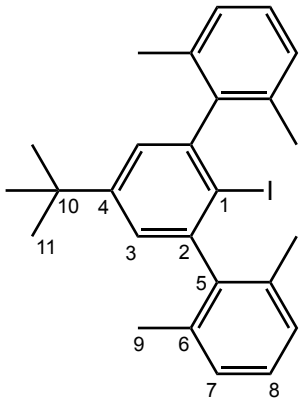
S2.2.2. 1-Iodo-2,6-dibromo-4-*tert*-butylbenzene



Synthesised according to modification of a literature procedure.[4] To a mixture of sodium nitrite (3.75 g, 54.3 mmol) in concentrated sulfuric acid (32 mL) kept at 0 °C, a solution of 2,6-dibromo-4-*tert*-butylaniline (15.0 g, 48.9 mmol) in glacial acetic acid (160 mL) was added slowly. The resultant black slurry was stirred at room temperature for 4 h. After this time, a solution of potassium iodide (58.7 g, 354 mmol) and iodine (13.8 g, 54.3 mmol) in deionised water (120 mL) was added slowly to the reaction mixture. The resultant dark purple mixture was stirred at room temperature for 16 h. The mixture was then carefully poured into an aqueous solution of sodium hydroxide (1.5 L, 30%) to give a cloudy orange

mixture that was extracted with ethyl acetate (3 × 400 mL). The combined organics were washed with aqueous sodium thiosulfate (300 mL, 10%), brine (300 mL), and deionised water (300 mL), then were dried over $MgSO_4$, and filtered. The filtrate was reduced under vacuum to yield a brown-black oil that was purified by plug column chromatography on silica gel eluted with petroleum ether (40-60) to afford the crude product (16.8 g, 82%) as an orange liquid. The compound was used directly in the next reaction without further purification. IR ν_{max}(neat)/cm^{-1} 2962(m), 2905(w), 2866(w), 2109(w), 1571(w), 1522(m), 1499(m), 1373(m), 1259(m), 1212(w), 1183(w), 1000(w), 869(m), 768(w), 735(s), 690(w); ^{1}H NMR δ_H (400 MHz; $CDCl_3$): 7.55 (2H, s, H-3), 1.28 (9H, s, H-6); ^{13}C NMR δ_C (101 MHz; $CDCl_3$): 154.6 (C-4), 131.0 (C-2), 128.8 (C-3), 105.1 (C-1), 35.0 (C-5), 31.0 (C-6); HRMS (EI), m/z: (Found: 415.8286. Calc. for $C_{10}H_{11}Br_2I$: 415.8267.)

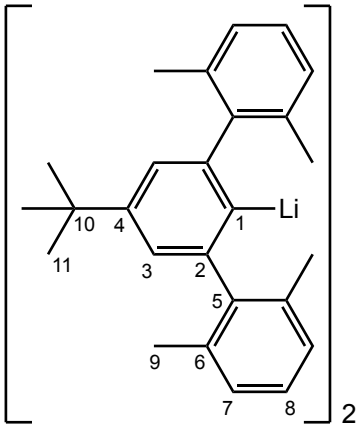
S2.2.3. *t*-Bu-Ar$^{\#}$-I



1-Iodo-2,6-dibromo-4-*tert*-butylbenzene (33.0 g, 79.0 mmol) was dissolved in dry THF (*ca.* 400 mL) at 0 °C under argon. To this, the pre-prepared Grignard of (2,6-dimethylphenyl)magnesium bromide (*ca.* 53.6 g, 256 mmol) in THF (*ca.* 200 mL) was added dropwise at 0 °C over 1 h. The red solution was then refluxed at 85 °C for 16 h. After this time, the solution was cooled to 0 °C, then iodine (105 g, 413 mmol) was added over 1 h. The mixture was heated at reflux at 85 °C for 16 h. After this, the solution was cooled to room temperature, and aqueous sodium sulfite (1.7 L, 1 M) was added. The organic layer was separated and the aqueous phase was washed with diethyl ether (3 × 200 mL). The combined organics were washed with aqueous sodium thiosulfate (300 mL, 10%) and deionised water (2 × 100 mL), then were dried over $MgSO_4$, and filtered. The filtrate was reduced under vacuum to give a brown oily-solid which was heated at 150 °C under vacuum for 1 h to remove any residual 2,6-Xyl-I impurity from the mixture. The resultant brown solid was purified by plug column chromatography on silica gel eluted with petroleum ether (40-60) to afford a pale orange-white solid. This solid was recrystallised

from boiling ethanol (450 mL) to form crystals on cooling to room temperature. The solid was collected by suction filtration, washing with cold methanol (2 × 100 mL), to yield product (33.1 g, 89%) as white crystalline needles. Elemental analysis: (Found: C, 66.5; H, 6.3. Calc. for $C_{26}H_{29}I$: C, 66.7; H, 6.2%); IR ν_{max}(neat)/cm^{-1} 2960(m), 2902(m), 2867(w), 1474(m), 1393(m), 1240(w), 1056(m), 881(m), 768(s); ^{1}H NMR δ_H (400 MHz; $CDCl_3$): 7.23 (2H, dd, *J* = 8.3, 6.7 Hz, H-8), 7.14 (4H, d, *J* = 7.4 Hz, H-7), 7.12 (2H, s, H-3), 2.02 (12H, s, H-9), 1.31 (9H, s, H-11); ^{13}C NMR δ_C (101 MHz; $CDCl_3$): 152.6 (C-4), 146.6 (C-2), 145.3 (C-5), 135.8 (C-6), 127.7 (C-8), 127.4 (C-7), 125.0 (C-3), 102.4 (C-1), 34.9 (C-10), 31.5 (C-11), 20.5 (C-9); HRMS (FD), m/z: (Found: 468.1304. Calc. for $C_{26}H_{29}I$: 468.1309.)

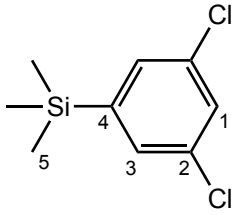
S2.2.4. [*t*-Bu-Ar$^{\#}$-Li]$_2$ (1)



t-Bu-Ar$^{\#}$-I (5.00 g, 10.7 mmol) was dried under vacuum for 16 h. Hexane (*ca.* 70 mL) was added and the white mixture was cooled to 0 °C. Once cooled, *n*-butyllithium (7.7 mL, 2.5 M in hexanes, 19.2 mmol) was added slowly, then the pale yellow solution was stirred for 16 h, allowing to warm to room temperature. After this time, a white solid impurity had precipitated, which was left to settle for 1 h. The mixture was filtered, and the residue was washed with hexane (2 × 10 mL), to afford a yellow solution that was concentrated to 30 mL under vacuum, causing a white solid to precipitate. This mixture was stirred for 2 h, after which the solid was left to settle for 1 h. The solid was filtered, washed with hexane (5 × 10 mL), and dried under vacuum for 6 h to yield product **1** (1.40 g, 38%) as a white powder. ^{1}H NMR δ_H (400 MHz; C_6D_6): 7.01 (12H, s, H-7 and H-8), 6.85 (4H, s, H-3), 1.83 (24H, s, H-9), 1.23 (18H, s, H-11); ^{13}C NMR δ_C (101 MHz; C_6D_6): 168.1 (m, C-1), 152.0 (C-2), 148.7 (C-4), 147.1 (C-5), 136.4 (C-6), 128.9 (C-7), 127.3 (C-8), 120.4 (C-3), 34.4 (C-10), 31.7 (C-11), 21.8 (C-9); ^{7}Li NMR δ_{Li} (155 MHz; C_6D_6): 1.60 (s).

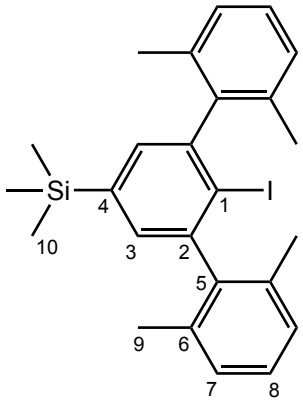
S2.3. Ligand Synthesis: $SiMe_3$

S2.3.1. 3,5-Dichloro-1-trimethylsilylbenzene



Synthesised according to modification of a literature procedure.[5] Magnesium turnings (6.70 g, 276 mmol) were activated by stirring in a solution of iodine (*ca.* 50 mg) in acetone (30 mL) for 20 min, after which the magnesium was washed with acetone (4 × 20 mL), oven-dried for 10 min, then stirred under vacuum over 16 h. To the magnesium, dry THF (*ca.* 100 mL) and trimethylchlorosilane (69.9 mL, 551 mmol) were added. This mixture was then heated as a stirred solution of 1,3,5-trichlorobenzene (50.0 g, 276 mmol) in dry THF (*ca.* 100 mL) was added dropwise over 1 h. The resultant grey mixture was refluxed at 90 °C under argon for 16 h. After this time, the beige mixture was reduced under vacuum, then petroleum ether (40-60) (250 mL) was added and the mixture was filtered. The yellow filtrate was reduced under vacuum to give the crude product as a yellow liquid. This liquid was purified via distillation by heating to 45 °C under vacuum (*ca.* 10^{-4} mbar) to collect the product (51.2 g, 85%) as a colourless liquid. IR ν_{max}(neat)/cm^{-1} 3067(w), 2958(s), 2898(w), 1570(m), 1551(s), 1392(m), 1371(s), 1252(s), 1137(s), 1100(m), 839(s), 797(s), 755(s); ^{1}H NMR δ_H (400 MHz; $CDCl_3$): 7.33 (3H, m, H-1/3), 0.28 (9H, s, H-5); ^{13}C NMR δ_C (101 MHz; $CDCl_3$): 145.2 (C-4), 134.9 (C-2), 131.4 (C-3), 128.9 (C-1), –1.2 (C-5); ^{29}Si NMR δ_{Si} (79 MHz; $CDCl_3$): –2.1 (s); HRMS (EI), m/z: (Found: 218.0076. Calc. for $C_9H_{12}Cl_2Si$: 218.0080.)

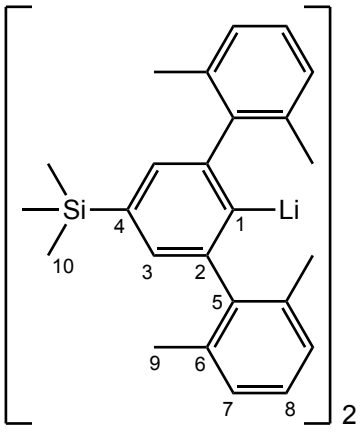
S2.3.2. Me_3Si-$Ar^{\#}$-I



To a solution of 3,5-dichloro-1-trimethylsilylbenzene (26.9 g, 123 mmol) in dry THF (*ca.* 250 mL) at –78 °C, *n*-butyllithium (54.0 mL, 2.5 M in hexanes, 135 mmol) was added dropwise over 1 h. The pale yellow mixture was stirred at –78 °C for 2 h, then the pre-prepared Grignard of (2,6-dimethylphenyl)magnesium bromide (*ca.* 56.6 g, 270 mmol) in THF (*ca.* 300 mL) was added dropwise at –78 °C over 1 h. The dark brown

solution was warmed to room temperature over 16 h, then was refluxed at 90 °C for 2 h. The solution was cooled to 0 °C, and iodine (46.7 g, 184 mmol) was added over 1 h. The dark purple solution was refluxed at 90 °C for 2 h, then was cooled to room temperature and stirred for 16 h. Aqueous sodium sulfite (500 mL, 1 M) was added, then the organic and aqueous phases were separated, washing the aqueous with diethyl ether (3 × 100 mL). The organics were combined, dried over $MgSO_4$, filtered, then the filtrate was reduced to dryness to give a beige powder that was recrystallised from hot diethyl ether (300 mL). The crystals were collected by suction filtration, washing with cold methanol (3 × 50 mL), to yield product (25.7 g, 43%) as a white crystalline solid. Elemental analysis: (Found: C, 62.0; H, 6.1. Calc. for $C_{25}H_{29}SiI$: C, 62.0; H, 6.0%); IR ν_{max}(neat)/cm^{-1} 3019(w), 2949(w), 2910(w), 1462(w), 1442(w), 1356(w), 1248(m), 1037(w), 860(s), 834(s), 770(s), 694(m); ^{1}H NMR δ_H (400 MHz; $CDCl_3$): 7.23 (2H, dd, *J* = 8.3, 6.7 Hz, H-8), 7.20 (2H, s, H-3), 7.14 (4H, d, *J* = 7.5 Hz, H-7), 2.02 (12H, s, H-9), 0.25 (9H, s, H-10); ^{13}C NMR δ_C (101 MHz; $CDCl_3$): 146.3 (C-2), 145.1 (C-5), 141.7 (C-4), 135.8 (C-6), 132.3 (C-3), 127.7 (C-8), 127.4 (C-7), 107.7 (C-1), 20.6 (C-9), –1.0 (C-10); ^{29}Si{^{1}H} NMR δ_{Si} (79 MHz; $CDCl_3$): –3.3 (s); HRMS (FD), m/z: (Found: 484.1086. Calc. for $C_{25}H_{29}SiI$: 484.1078.)

S2.3.3. [Me$_3$Si-Ar$^{\#}$-Li]$_2$ (2)

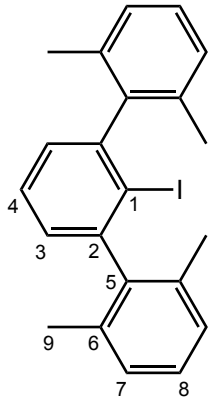


Me_3Si-$Ar^{\#}$-I (5.00 g, 10.3 mmol) was dried under vacuum for 16 h. Hexane (*ca.* 70 mL) was added and the white mixture was cooled to 0 °C. Once cooled, *n*-butyllithium (7.4 mL, 2.5 M in hexanes, 18.6 mmol) was added slowly, then the white mixture was stirred for 16 h, allowing to warm to room temperature. After this time, the solid was left to settle for 1 h. The solid was filtered, washed with hexane (2 × 10 mL), and dried under vacuum for 16 h to yield the product **2** (2.27 g, 60%) as a white powder. ^{1}H NMR δ_H (400 MHz; C_6D_6): 7.04 (4H, s, H-3), 6.99 (12H, s, H-7 and H-8), 1.81 (24H, s, H-9), 0.21 (18H, s, H-10); ^{13}C NMR δ_C (101 MHz; C_6D_6): 174.2 (C-1), 151.6 (C-2), 146.7 (C-5), 136.5 (C-4),

136.4 (C-6), 129.0 (C-7), 128.1 (C-3), 127.4 (C-8), 21.9 (C-9), –0.8 (C-10); $^{29}Si\{^{1}H\}$ NMR δ_{Si} (79 MHz; C_6D_6): –5.59 (s); ^{7}Li NMR δ_{Li} (155 MHz; C_6D_6): 1.5 (s).

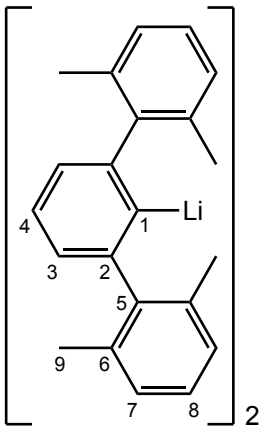
S2.4. Ligand Synthesis: H

S2.4.1. H-Ar#-I



Synthesised according to modification of a literature procedure.[6] To a solution of 1,3-dichlorobenzene (18.1 g, 123 mmol) in dry THF (*ca.* 200 mL) at –78 °C, *n*-butyllithium (59.0 mL, 2.5 M in hexanes, 148 mmol) was added dropwise over 1 h. The white mixture was stirred at –78 °C for 1 h, then the pre-prepared Grignard of (2,6-dimethylphenyl)magnesium bromide (*ca.* 56.6 g, 270 mmol) in THF (*ca.* 200 mL) was added dropwise at –78 °C over 1 h. The brown solution was warmed to room temperature over 16 h, refluxed at 90 °C for 2 h, cooled to 0 °C, then iodine (46.7 g, 184 mmol) was added over 1 h. The purple mixture was refluxed at 90 °C for 2 h, cooled to room temperature, then aqueous sodium sulfite (500 mL, 1 M) was added. The organic and aqueous phases were separated, and the aqueous was washed with diethyl ether (3 × 100 mL). The organics were combined, dried over $MgSO_4$, filtered, then the filtrate was dried to give a yellow solid that was recrystallised in boiling ethanol (500 mL). The solid was collected, washing with cold methanol (3 × 50 mL), to give product (20.7 g, 41%) as a beige crystalline powder. IR ν_{max}(neat)/cm^{-1} 3037(w), 2968(w), 2933(w), 2911(w), 2852(w), 1579(w), 1457(m), 1385(w), 1163(w), 1079(w), 1012(w), 1001(w), 803(m), 768(s), 734(s), 694(w), 549(w); ^{1}H NMR δ_H (400 MHz; $CDCl_3$): 7.52 (1H, t, *J* = 7.5 Hz, H-4), 7.26 (2H, t, *J* = 7.5 Hz, H-8), 7.17 (4H, d, *J* = 7.7 Hz, H-7), 7.14 (2H, d, *J* = 7.5 Hz, H-3), 2.06 (12H, s, H-9); ^{13}C NMR δ_C (101 MHz; $CDCl_3$): 147.3 (C-2), 144.8 (C-5), 135.7 (C-6), 129.1 (C-4), 127.8 (C-3), 127.7 (C-8), 127.4 (C-7), 106.9 (C-1), 20.5 (C-9).

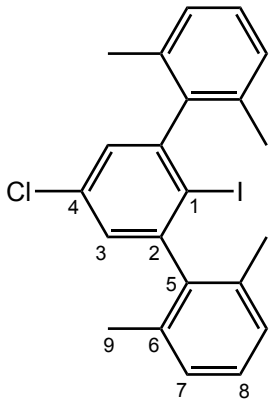
S2.4.1. [H-Ar$^{\#}$-Li]$_2$ (3)



Synthesised according to modification of a literature procedure.[7] H-Ar$^{\#}$-I (5.00 g, 12.1 mmol) was dried under vacuum for 16 h. Hexane (*ca.* 70 mL) was added and the yellow mixture was cooled to 0 °C, then *n*-butyllithium (7.2 mL, 2.5 M in hexanes, 18.2 mmol) was added slowly. The mixture was stirred for 16 h, warmed to room temperature, then left to settle for 1 h. The solid was filtered, washed with hexane (2 × 10 mL), and dried under vacuum for 16 h to yield product **3** (3.49 g, 99%) as a white powder. ^{1}H NMR δ_H (400 MHz; C_6D_6): 7.19 (2H, t, J = 7.5 Hz, H-4), 6.98 (12H, s, H-7 and H-8), 6.77 (4H, d, J = 7.5 Hz, H-3), 1.80 (24H, s, H-9); ^{13}C NMR δ_C (126 MHz; C_6D_6): 172.7 (sept, J = 23.3 Hz, C-1), 152.0 (C-2), 146.4 (C-5), 136.3 (C-6), 129.0 (C-7), 127.4 (C-8), 126.3 (C-4), 123.6 (C-3), 21.8 (C-9); ^{7}Li NMR δ_{Li} (155 MHz; C_6D_6): 1.5 (s).

S2.5. Ligand Synthesis: Cl

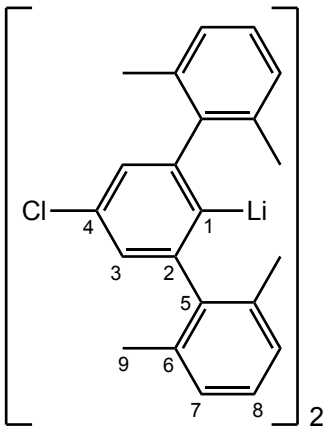
S2.5.1. Cl-Ar$^{\#}$-I



To a solution of 1,3,5-trichlorobenzene (22.3 g, 123 mmol) in dry THF (*ca.* 200 mL) at –78 °C, *n*-butyllithium (54.0 mL, 2.5 M in hexanes, 135 mmol) was added dropwise over 1 h. The pale yellow solution was stirred at –78 °C for 1 h, then the Grignard of (2,6-dimethylphenyl)magnesium bromide (*ca.* 56.6 g, 270 mmol) in THF (*ca.* 200 mL) was added dropwise at –78 °C over 1 h. The brown solution was warmed to room temperature over 16 h, then was refluxed at 90 °C for 2 h. The solution was cooled to 0 °C, and iodine (46.7 g, 184 mmol) was added over 1 h. The dark purple mixture was refluxed at 90 °C for 2 h, cooled to room temperature, then aqueous sodium sulfite (500 mL, 1 M) was added. The organic and aqueous phases were separated, washing the aqueous with diethyl ether (3 × 100 mL), then the organics were combined, dried over $MgSO_4$, and filtered. The filtrate was dried to give an orange oil which was heated under vacuum for 1 h at 80 °C to remove any 2,6-Xyl-I impurity. The crude product was recrystallised in diethyl ether

(300 mL) via solvent evaporation over 5 days. The solid was isolated by suction filtration, washing with cold diethyl ether (3 × 50 mL), to give product (12.7 g, 23%) as white needles. IR ν_{max}(neat)/cm^{-1} 3055(w), 3021(w), 2942(w), 2912(w), 2852(w), 1583(w), 1561(w), 1461(m), 1440(w), 1379(m), 1296(w), 1110(m), 1001(s), 870(m), 828(w), 777(s), 765(s), 551(w), 474(m); ^{1}H NMR δ_H (400 MHz; $CDCl_3$): 7.23 (2H, dd, *J* = 8.2, 6.8 Hz, H-8), 7.14 (2H, s, H-3), 7.13 (4H, br d, *J* = 7.3 Hz, H-7), 2.03 (12H, s, H-9); ^{13}C NMR δ_C (101 MHz; $CDCl_3$): 148.9 (C-2), 143.6 (C-5), 135.5 (C-6), 135.2 (C-4), 128.2 (C-8), 127. 7 (C-3), 127.6 (C-7), 104.7 (C-1), 20.4 (C-9); HRMS (EI), m/z: (Found: 446.0289. Calc. for $C_{22}H_{20}ClI$: 446.0293.)

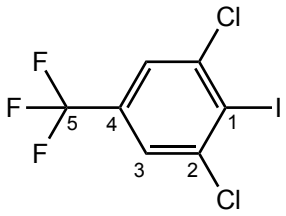
S2.5.2. [Cl-Ar$^{\#}$-Li]$_2$ (4)



Cl-Ar$^{\#}$-I (5.00 g, 11.2 mmol) was dried under vacuum for 16 h. Hexane (*ca.* 70 mL) was added and the white mixture was cooled to 0 °C. Once cooled, *n*-butyllithium (8.1 mL, 2.5 M in hexanes, 20.2 mmol) was added slowly, then the white mixture was stirred for 16 h, allowing to warm to room temperature. After this time, the solid was left to settle for 1 h. The solid was filtered, washed with hexane (2 × 10 mL), and dried under vacuum for 16 h to yield the product **4** (3.59 g, 98%) as a white powder. ^{1}H NMR δ_H (400 MHz; C_6D_6): 6.95 (4H, dd, *J* = 8.5, 6.4 Hz, H-8), 6.87 (8H, br d, *J* = 7.5 Hz, H-7), 6.78 (4H, s, H-3), 1.61 (24H, s, H-9); ^{13}C NMR δ_C (101 MHz; C_6D_6): 170.7 (C-1), 153.6 (C-2), 144.8 (C-5), 136.1 (C-6), 132.9 (C-4), 129.0 (C-7), 127.8 (C-8), 123.6 (C-3), 21.5 (C-9); ^{7}Li NMR δ_{Li} (155 MHz; C_6D_6): 1.1 (s).

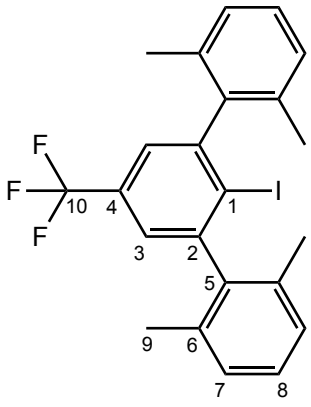
S2.6. Ligand Synthesis: CF_3

S2.6.1. 1-Iodo-2,6-dichloro-4-trifluoromethylbenzene



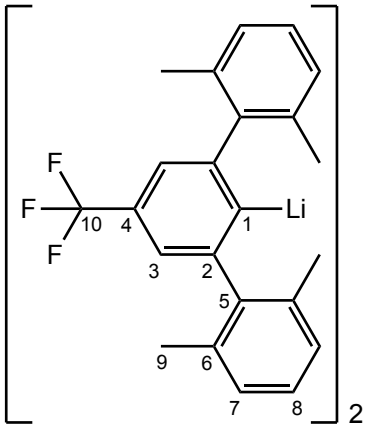
Synthesised according to modification of a literature procedure.[8] To a mixture of sodium nitrite (5.00 g, 72.5 mmol) in conc. sulfuric acid (40 mL) cooled to 0 °C, a stirred solution of 2,6-dichloro-4-trifluoromethylaniline (15.0 g, 65.2 mmol) in glacial acetic acid (180 mL) was added slowly. The resultant pale yellow mixture was stirred at room temperature for 4 h. After this time, a solution of potassium iodide (78.6 g, 474 mmol) and iodine (18.4 g, 72.5 mmol) in deionised water (135 mL) was added slowly to the reaction mixture. The resultant black solution was stirred at room temperature for 16 h. The solution was then carefully poured into an aqueous solution of sodium hydroxide (1.5 L, 30%) to give a yellow mixture that was divided into two fractions. Each fraction was extracted with ethyl acetate (3 × 200 mL), then the organics were combined, dried over $MgSO_4$, and filtered. The filtrate was reduced under vacuum to yield the crude product (20.2 g, 91%) as a dark red liquid. The compound was used directly in the next reaction without further purification. IR ν_{max}(neat)/cm^{-1} 3080(w), 1595(w), 1555(w), 1379(m), 1303(s), 1259(w), 1197(m), 1171(m), 1133(s), 1102(s), 1014(m), 879(m), 808(m), 706(w), 697(w); ^{1}H NMR δ_H (400 MHz; $CDCl_3$): 7.57 (2H, s, H-3); ^{13}C NMR δ_C (101 MHz; $CDCl_3$): 141.9 (C-2), 132.5 (q, J = 34.2 Hz, C-4), 123.9 (q, J = 3.7 Hz, C-3), 122.7 (q, J = 273.0 Hz, C-5), 108.9 (C-1); ^{19}F NMR δ_F (376 MHz; $CDCl_3$): –63.2 (s); HRMS (EI), m/z: (Found: 339.8521. Calc. for $C_7H_2F_3Cl_2I$: 339.8525.)

S2.6.2. F_3C-Ar$^{\#}$-I



1-Iodo-2,6-dichloro-4-trifluoromethylbenzene (30.0 g, 88.0 mmol) was dissolved in dry THF (*ca.* 200 mL) at –20 °C under argon. To this, the pre-prepared (2,6-dimethylphenyl)magnesium bromide (*ca.* 60.8 g, 290 mmol) in THF (*ca.* 200 mL) was slowly added dropwise at –20 °C. The dark brown mixture was refluxed at 85 °C for 16 h, then was cooled to 0 °C, and iodine (39.6 g, 156 mmol) was added over 1 h. The mixture was stirred at room temperature for 4 h, then aqueous sodium sulfite (300 mL, 1 M) was added. The organic layer was separated and the aqueous phase was washed with diethyl ether (3 × 200 mL), then the organics were combined, dried over $MgSO_4$, and filtered. The filtrate was reduced under vacuum to give a black oil which was heated at 150 °C under vacuum for 1 h to remove any residual 2,6-Xyl-I impurity from the mixture. The resultant black solid was recrystallised from boiling ethanol (180 mL) to yield white crystals. These crystals were collected by filtration, washed with cold methanol (3 × 50 mL), and dried under vacuum to yield product (14.9 g, 35%). IR ν_{max}(neat)/cm^{-1} 3055(w), 3020(w), 2945(w), 2915(w), 2857(w), 1595(w), 1437(w), 1346(s), 1261(s), 1243(m), 1173(s), 1136(m), 1107(s), 1035(w), 1004(m), 890(m), 777(s), 766(s), 746(m), 699(m), 551(w); ^{1}H NMR δ_H (400 MHz; $CDCl_3$): 7.37 (2H, s, H-3), 7.25 (2H, dd, J = 8.2, 6.8 Hz, H-8), 7.15 (4H, d, J = 7.7 Hz, H-7), 2.01 (12H, s, H-9); ^{13}C NMR δ_C (101 MHz; $CDCl_3$): 148.5 (C-2), 143.6 (C-5), 135.5 (C-6), 131.7 (q, J = 32.6 Hz, C-4), 128.4 (C-8), 127.7 (C-7), 124.3 (q, J = 3.6 Hz, C-3), 124.1 (q, J = 272.7 Hz, C-10), 111.8 (C-1), 20.5 (C-9); ^{19}F NMR δ_F (376 MHz; $CDCl_3$): –62.5 (s); HRMS (EI), m/z: (Found: 480.0562. Calc. for $C_{23}H_{20}F_3I$: 480.0556.)

S2.6.3. $[F_3C\text{-}Ar^{\#}\text{-}Li]_2$ (5)



$F_3C\text{-}Ar^{\#}$-I (4.88 g, 10.2 mmol) was dried at 60 °C under vacuum for 3 h. Hexane (*ca.* 80 mL) was added and the mixture was cooled to 0 °C, then *n*-butyllithium (7.3 mL, 2.5 M in hexanes, 18.3 mmol) was added slowly. The white mixture was stirred for 16 h, warmed to room temperature, then left to settle for 1 h. The solid was filtered, washed with hexane (2 × 10 mL), and dried under vacuum for 16 h to yield product **5** (3.58 g, 95%) as a white powder. ^{1}H NMR δ_H (400 MHz; C_6D_6): 6.99 (4H, s, 4 × H-3), 6.94 (4H, dd, J = 8.4, 6.6 Hz, H-8), 6.86 (8H, br d, J = 7.5 Hz, H-7), 1.55 (24H, s, H-9); ^{13}C NMR δ_C (126 MHz; C_6D_6): 180.2 (m, C-1), 152.4 (C-2), 144.7 (C-5), 136.1 (C-6), 129.1 (C-7), 128.0 (C-8), 126.0 (q, J = 271.7 Hz, C-10), 119.5 (q, J = 2.8 Hz, C-3), 21.5 (C-9);* ^{19}F NMR δ_F (376 MHz; C_6D_6): –61.6 (s); ^{7}Li NMR δ_{Li} (155 MHz; C_6D_6): 0.9 (s). *C-4 not observed.

*Note: Elemental analysis and mass spectrometry data has not been reported for the m-terphenyl lithium complexes, **1**–**5**, due to their highly air- and moisture-sensitive nature. This is also the case for other m-terphenyl lithium species previously reported in the literature.*[9,10,11,12,7,13]

S3. Reproductions of NMR Spectra

S3.1. *t*Bu-Ar$^{\#}$-I

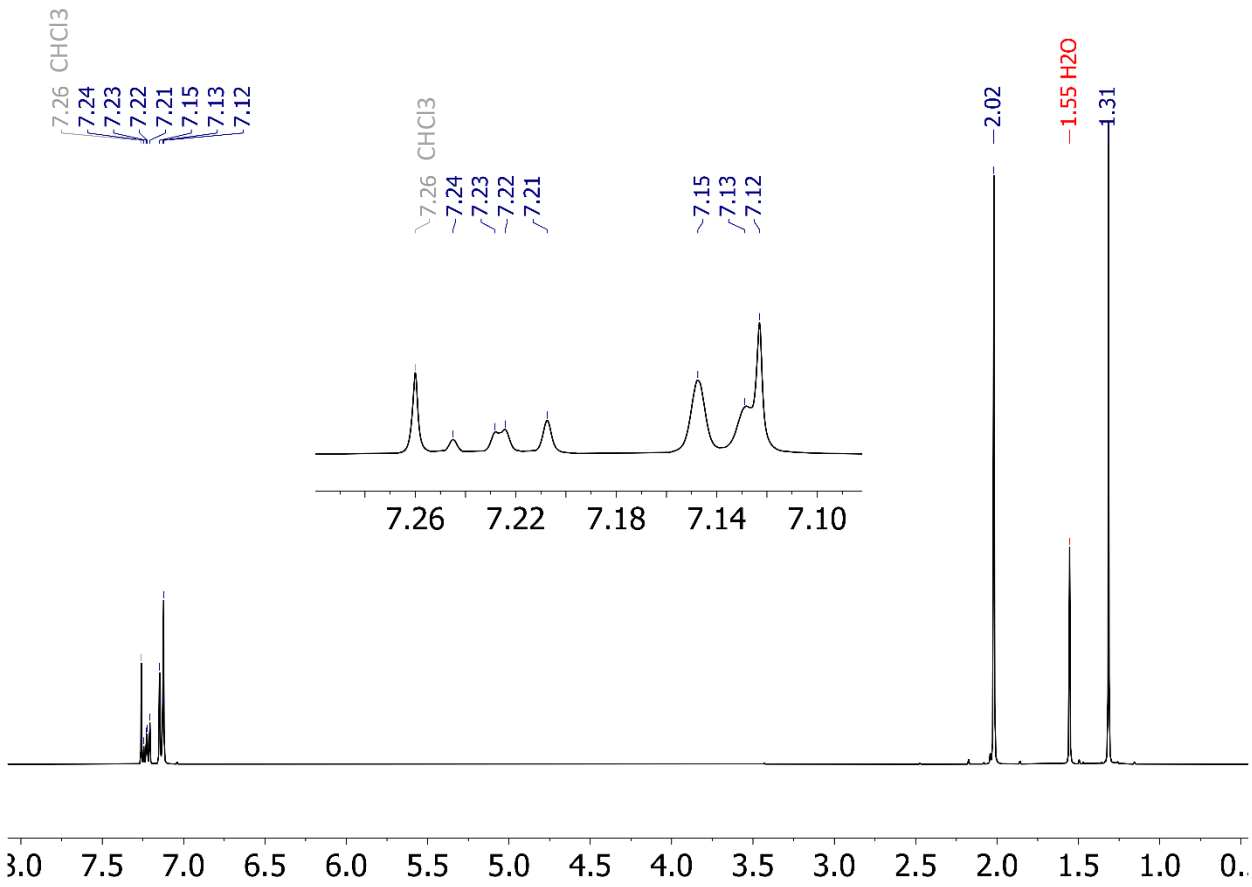


Figure S1: ^{1}H NMR (400 MHz, 25 °C) spectrum for *t*Bu-Ar$^{\#}$-I in $CDCl_3$

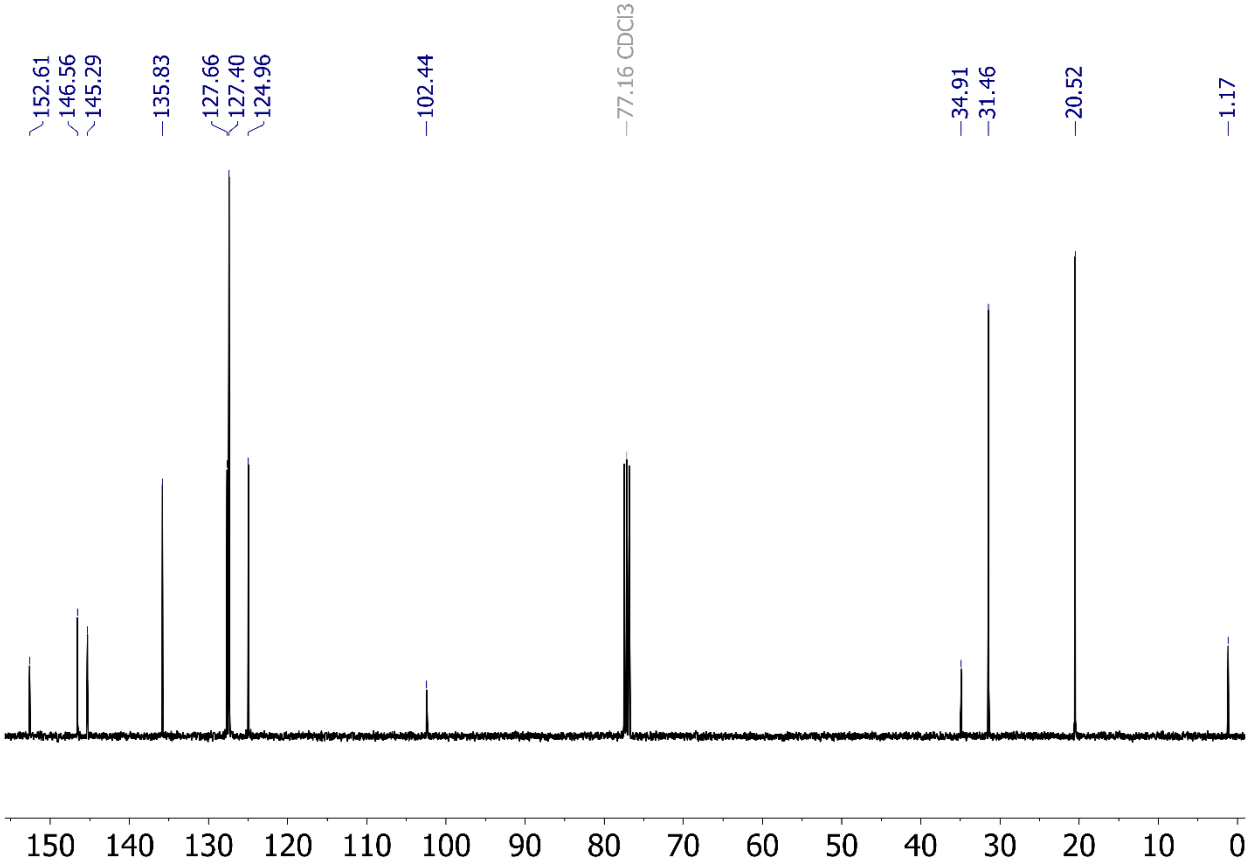


Figure S2: $^{13}C\{^{1}H\}$ NMR (126 MHz, 25 °C) spectrum for *t*Bu-Ar$^{\#}$-I in $CDCl_3$

S3.2. [*t*Bu-Ar$^{\#}$-Li]$_2$ (1)

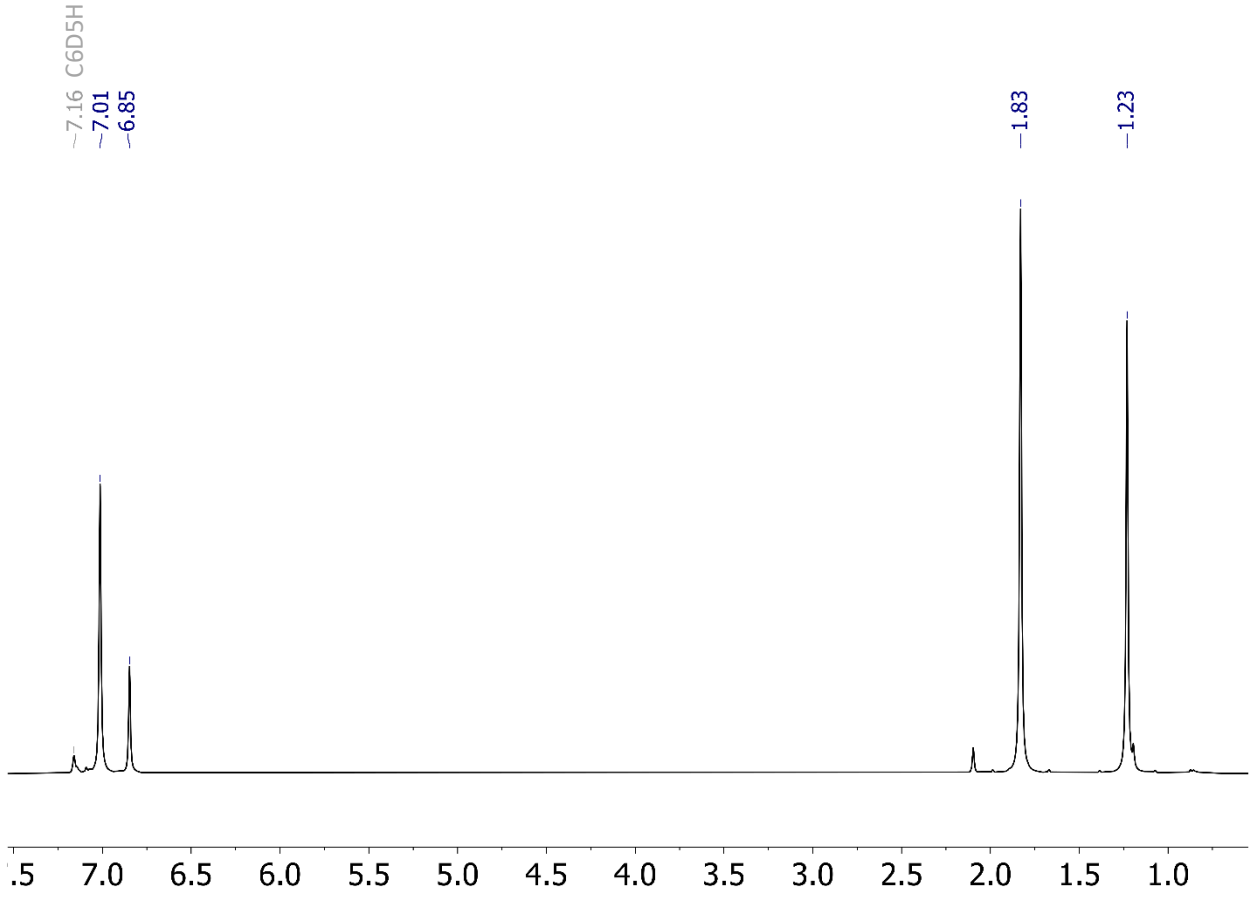


Figure S3: ^{1}H NMR (400 MHz, 25 °C) spectrum for [*t*Bu-Ar$^{\#}$-Li]$_2$ (**1**) in C_6D_6

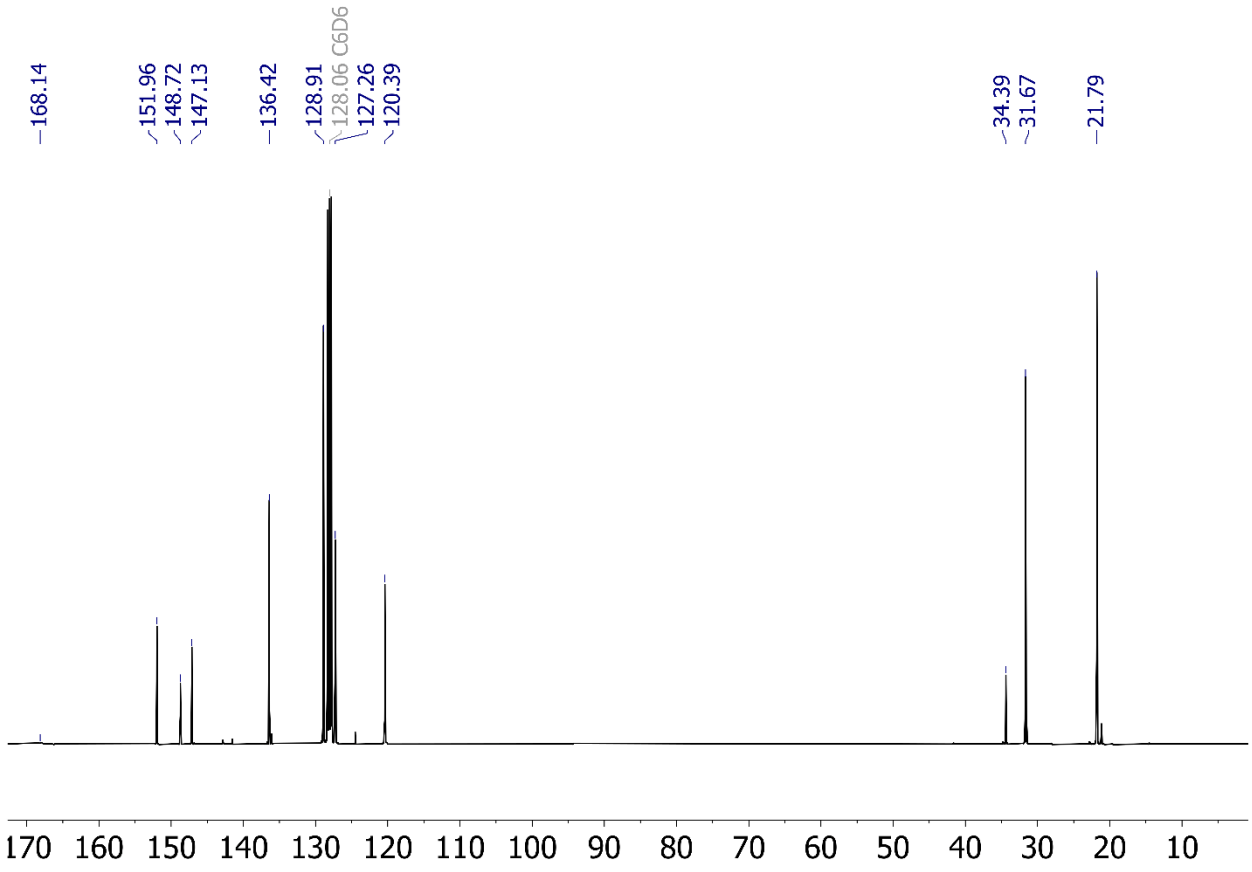


Figure S4: $^{13}C\{^{1}H\}$ NMR (126 MHz, 25 °C) spectrum for [*t*Bu-Ar$^{\#}$-Li]$_2$ (**1**) in C_6D_6.

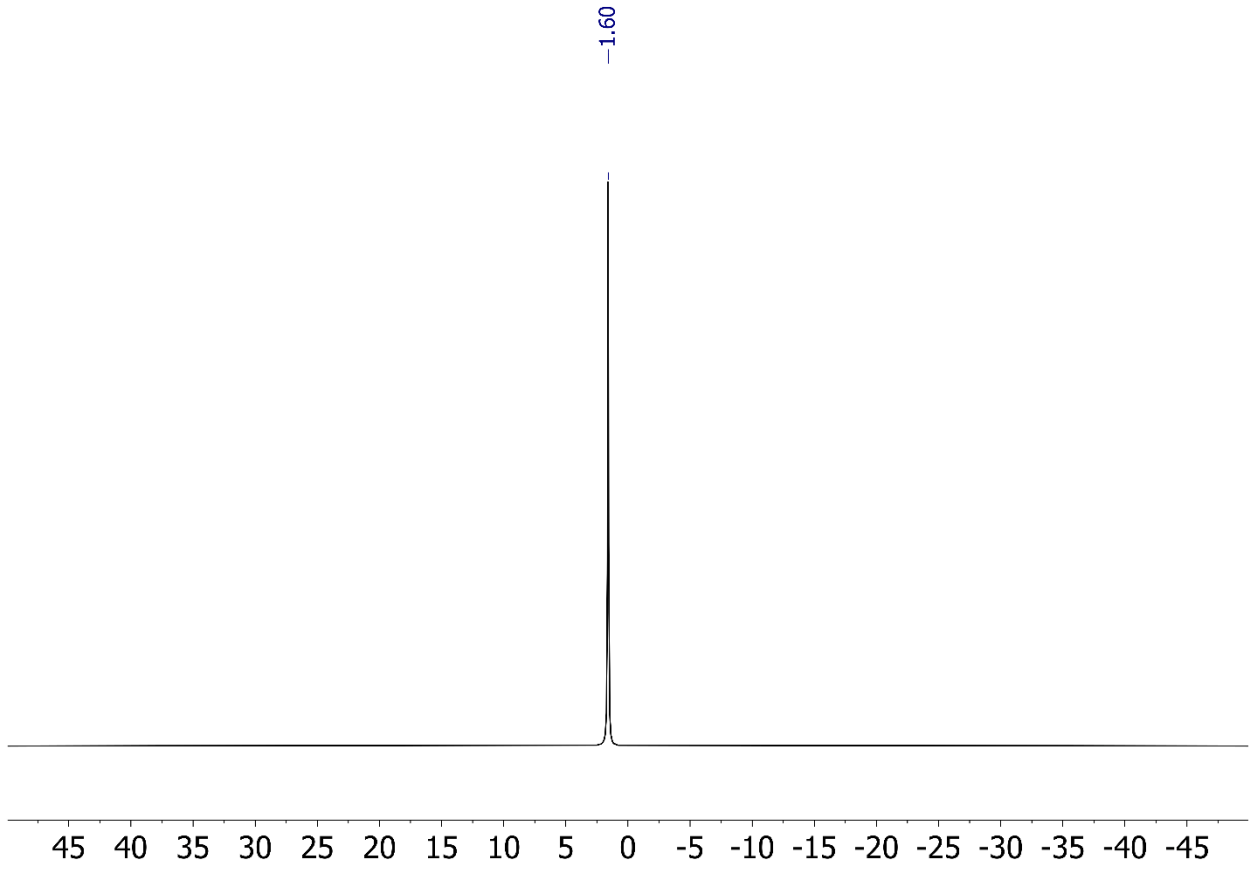


Figure S5: $^{7}Li\{^{1}H\}$ NMR (155 MHz, 25 °C) spectrum for [*t*Bu-Ar$^{\#}$-Li]$_2$ (**1**) in C_6D_6

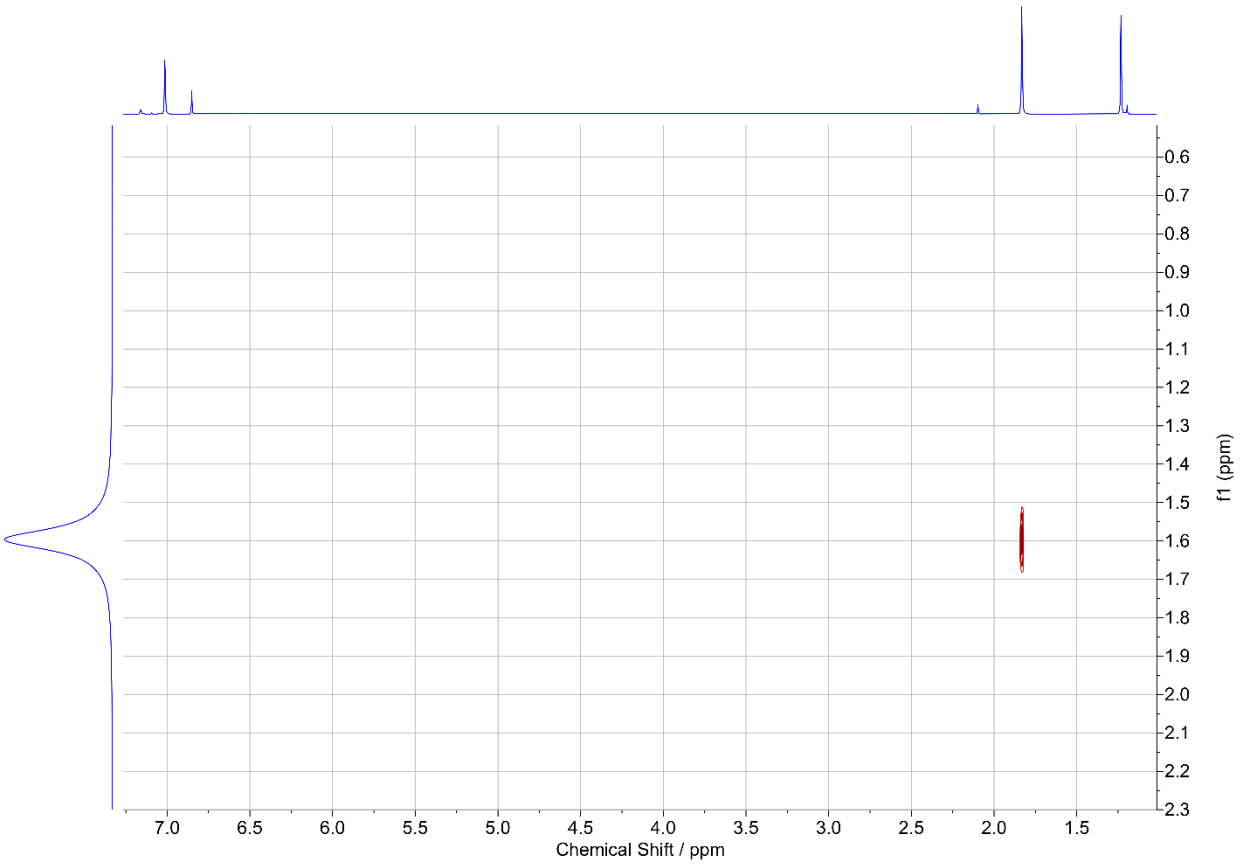


Figure S6: ^{7}Li-^{1}H HOESY spectrum for [*t*Bu-Ar$^{\#}$-Li]$_2$ (**1**) in C_6D_6.

S3.3. $Me_3Si\text{-}Ar^{\#}\text{-}I$

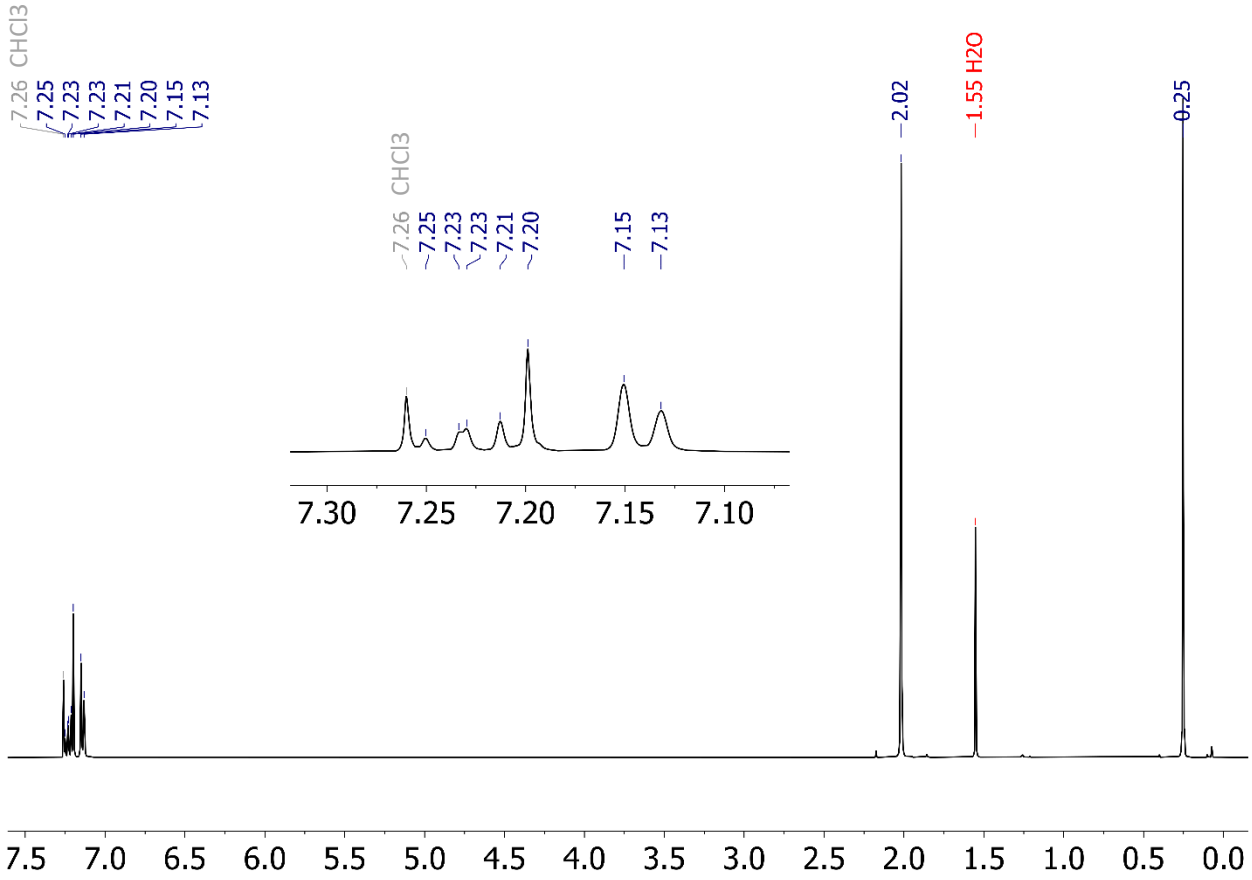


Figure S7: ^{1}H NMR (400 MHz, 25 °C) spectrum for $Me_3Si\text{-}Ar^{\#}\text{-}I$ in $CDCl_3$

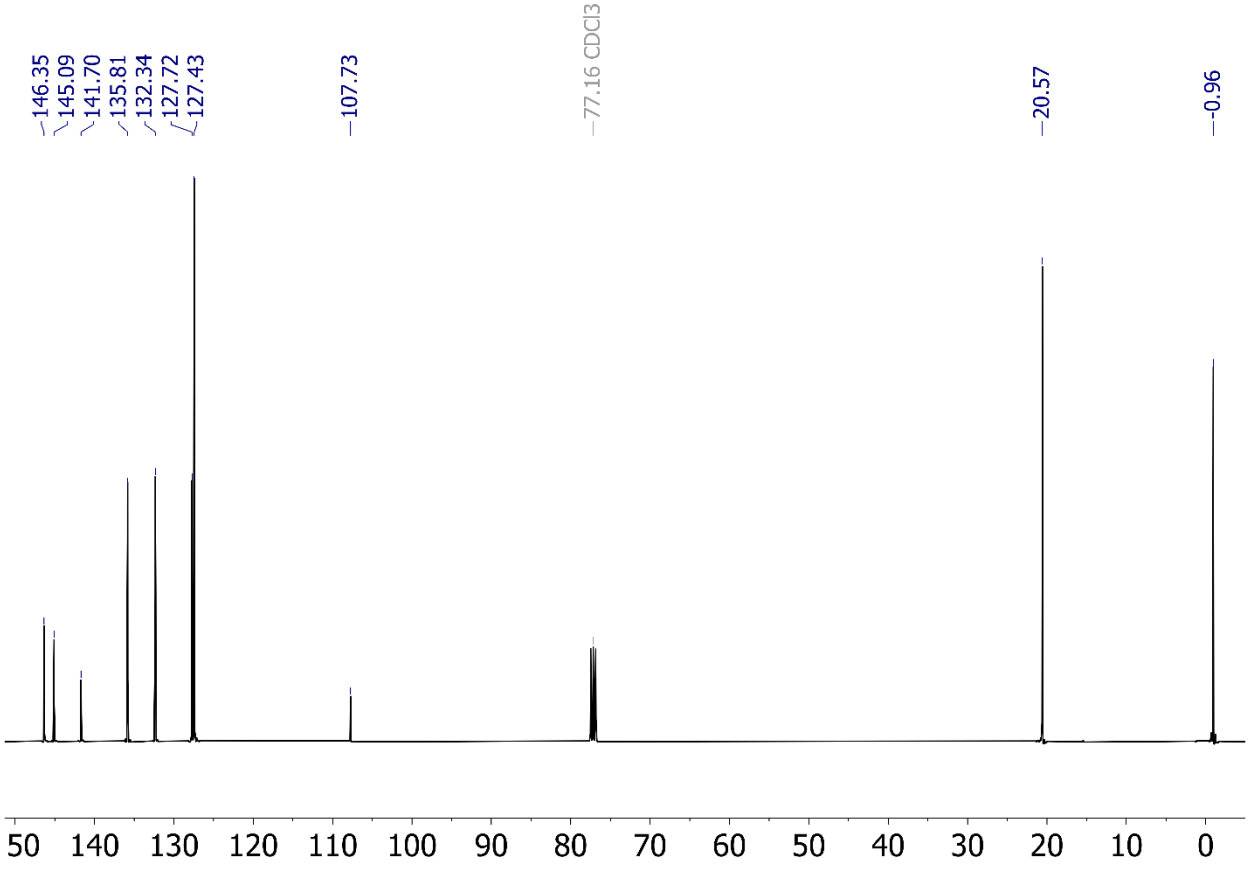


Figure S8: $^{13}C\{^{1}H\}$ NMR (126 MHz, 25 °C) spectrum for $Me_3Si\text{-}Ar^{\#}\text{-}I$ in $CDCl_3$

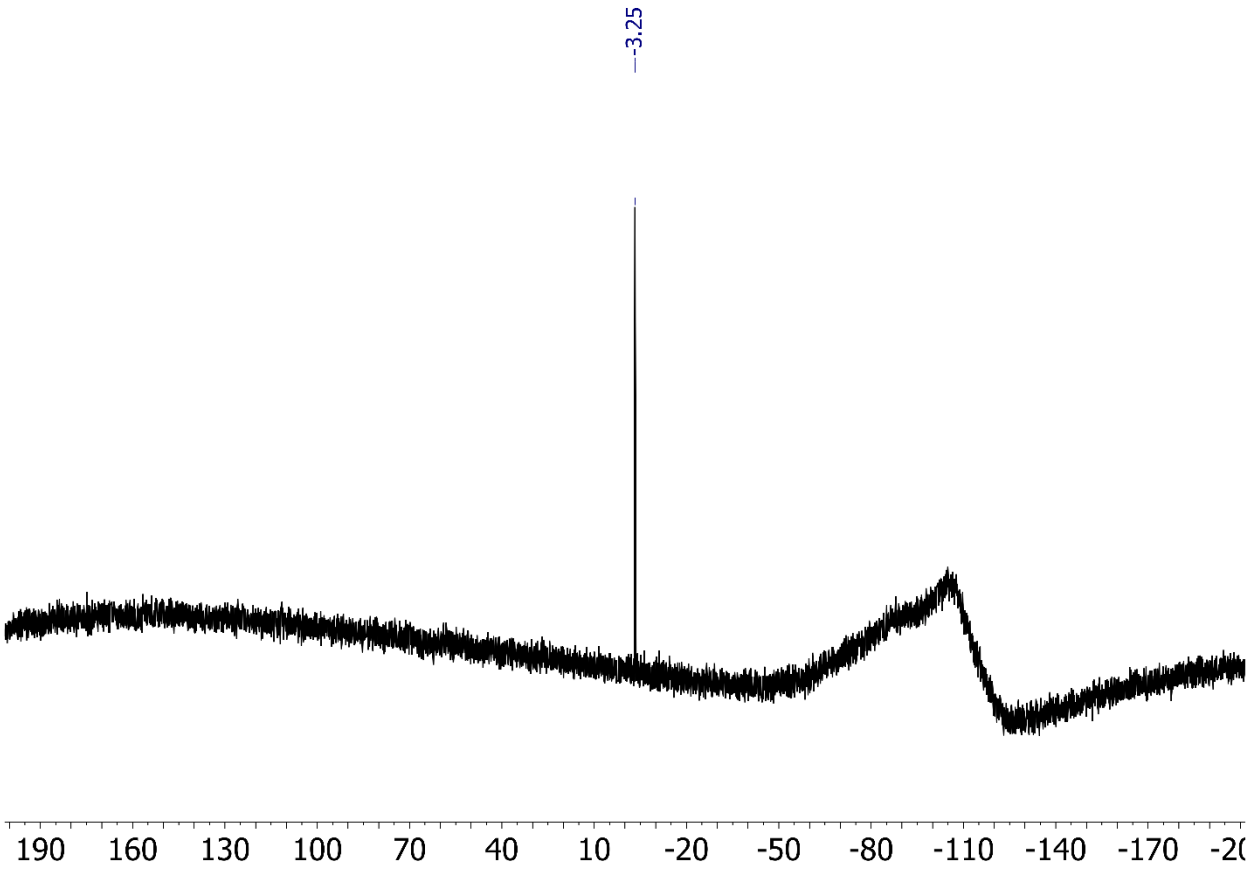


Figure S9: $^{29}Si\{^{1}H\}$ NMR (79 MHz, 25 °C) spectrum for $Me_3Si\text{-}Ar^{\#}\text{-}I$ in $CDCl_3$

S3.4. $[Me_3Si\text{-}Ar^{\#}\text{-}Li]_2$ (2)

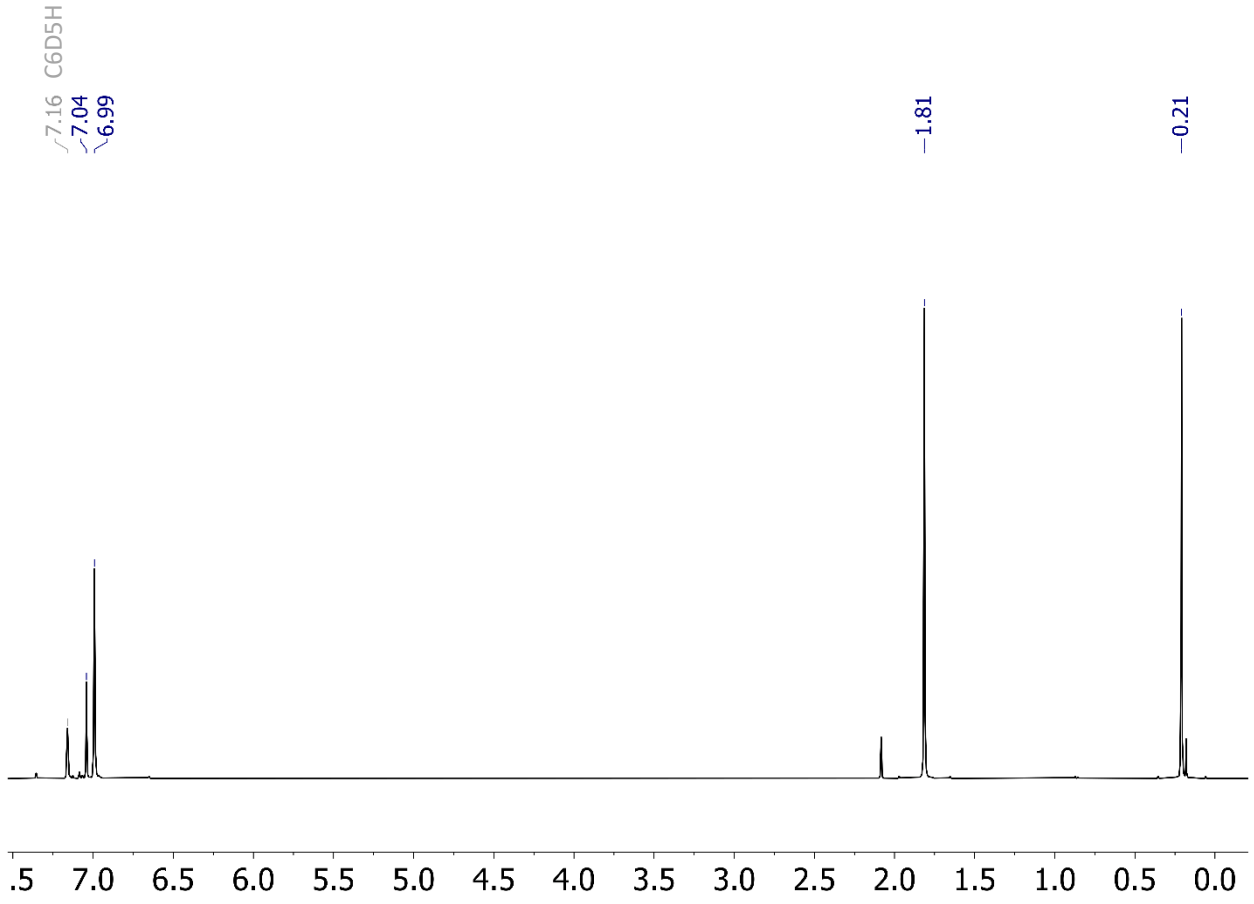


Figure S10: ^{1}H NMR (400 MHz, 25 °C) spectrum for $[Me_3Si\text{-}Ar^{\#}\text{-}Li]_2$ (**2**) in C_6D_6

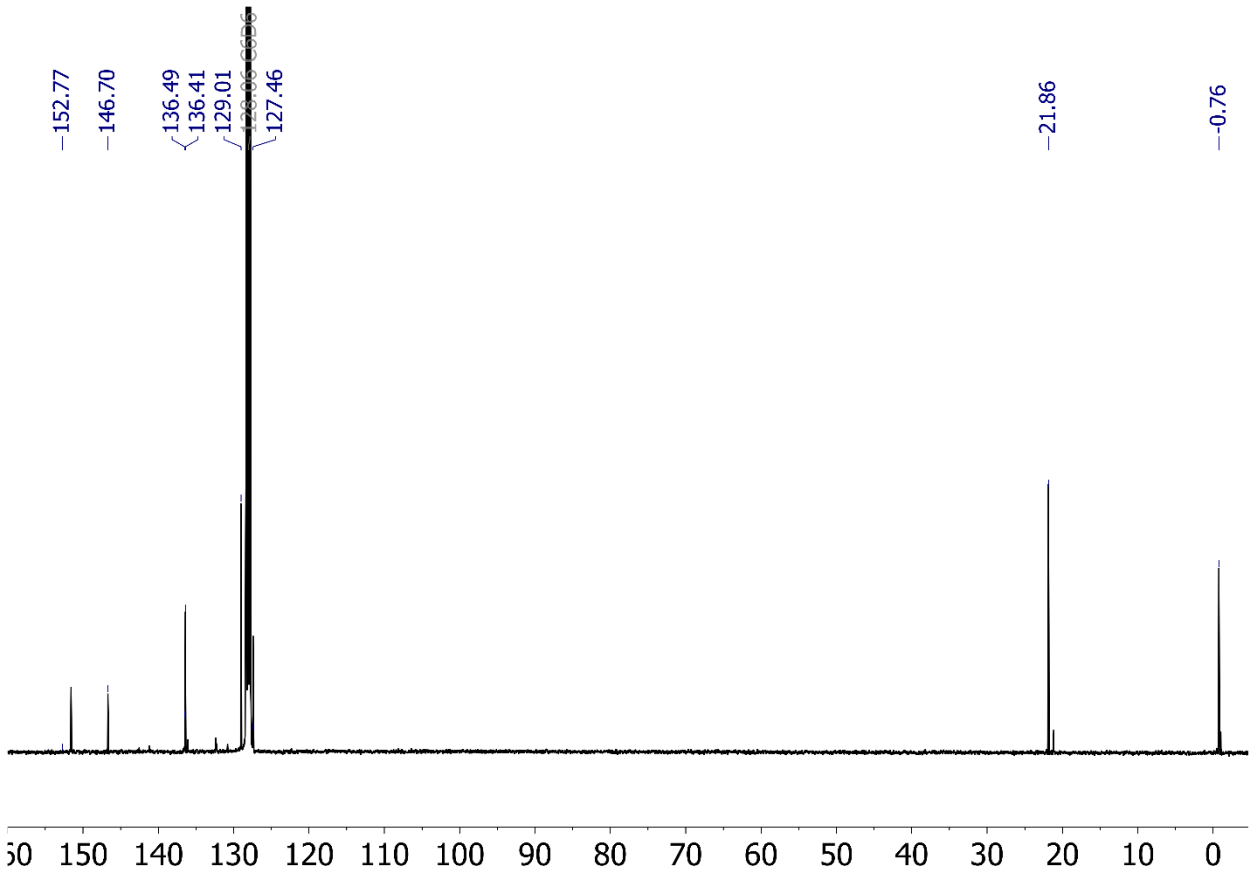


Figure S11: $^{13}C\{^{1}H\}$ NMR (126 MHz, 25 °C) spectrum for $[Me_3Si\text{-}Ar^{\#}\text{-}Li]_2$ (**2**) in C_6D_6

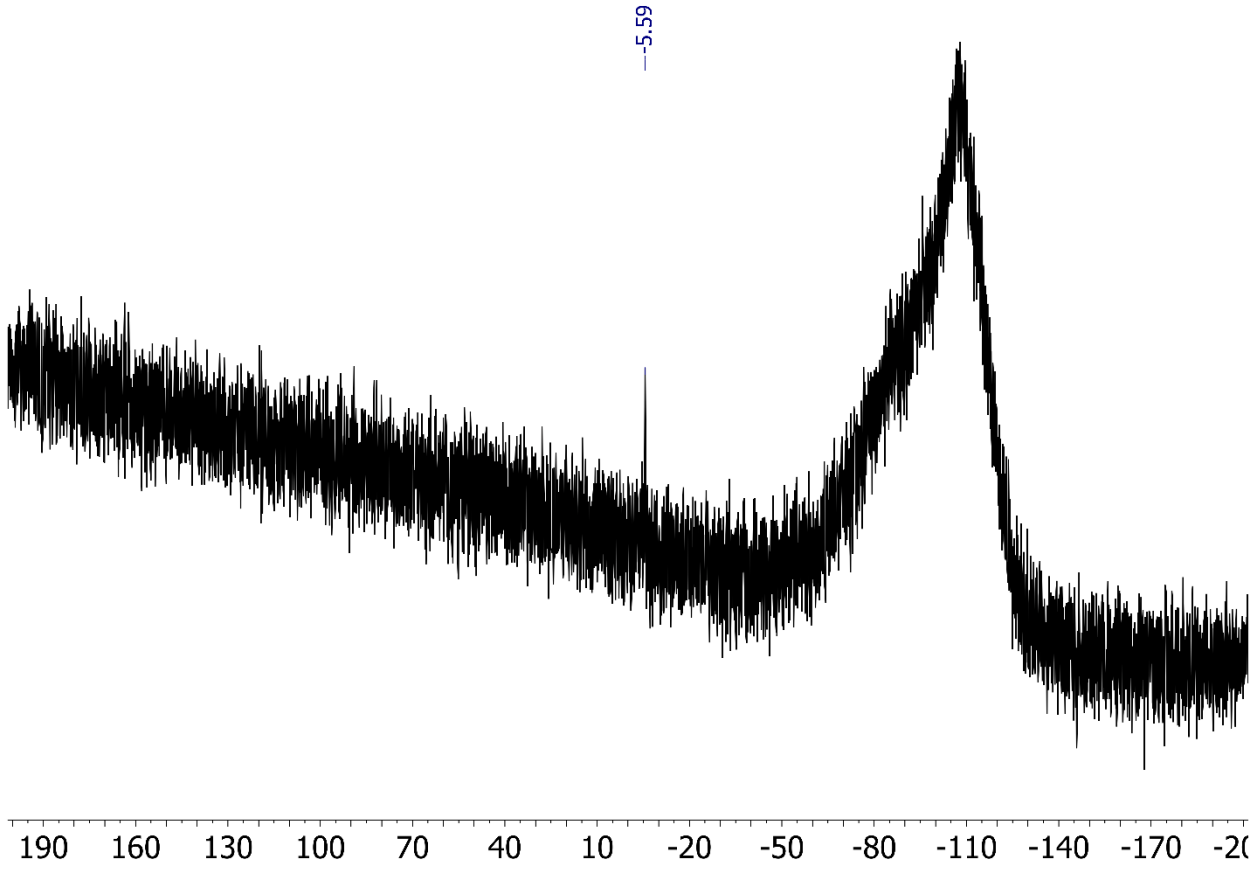


Figure S12: $^{29}Si\{^{1}H\}$ NMR (79 MHz, 25 °C) spectrum for $[Me_3Si\text{-}Ar^{\#}\text{-}Li]_2$ (**2**) in C_6D_6

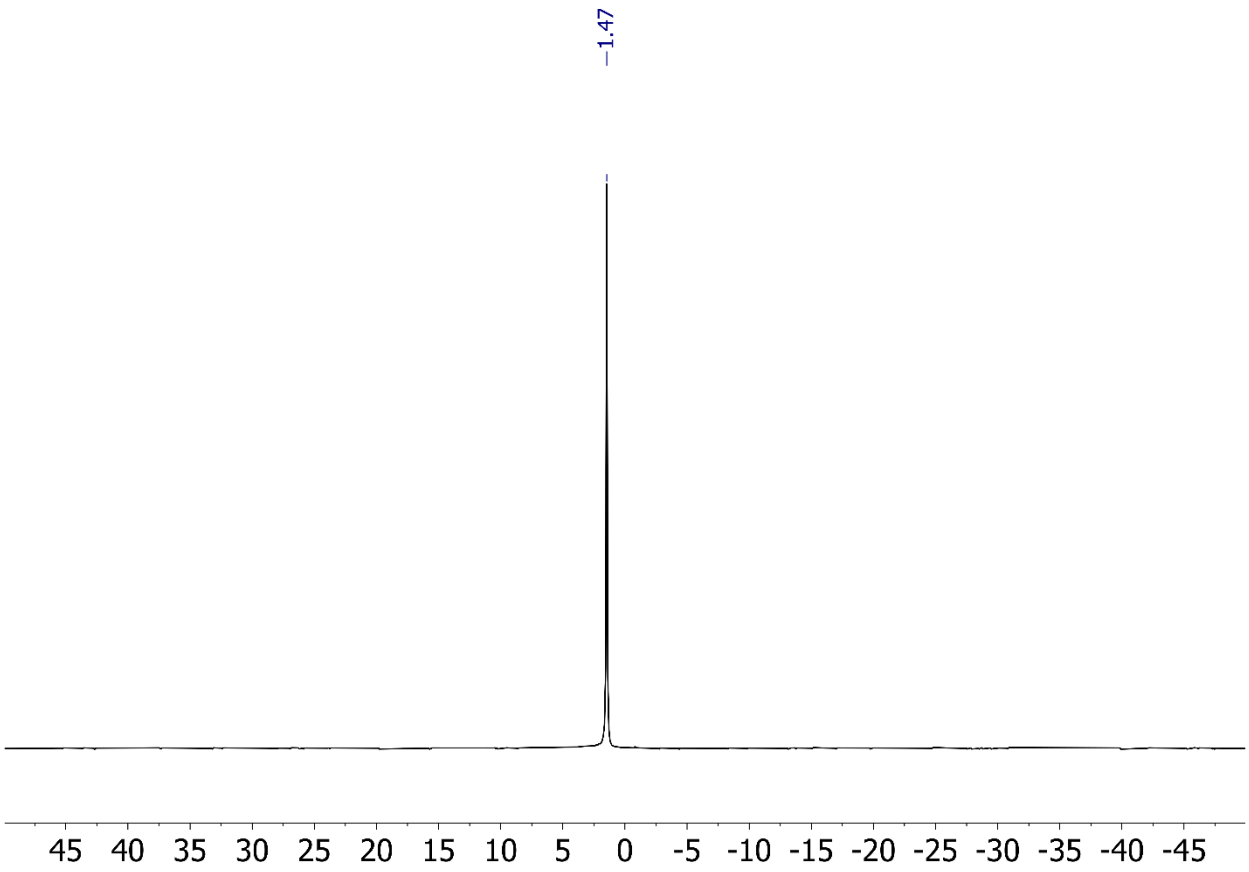


Figure S13: $^{7}Li\{^{1}H\}$ NMR (155 MHz, 25 °C) spectrum for $[Me_3Si\text{-}Ar^{\#}\text{-}Li]_2$ (**2**) in C_6D_6

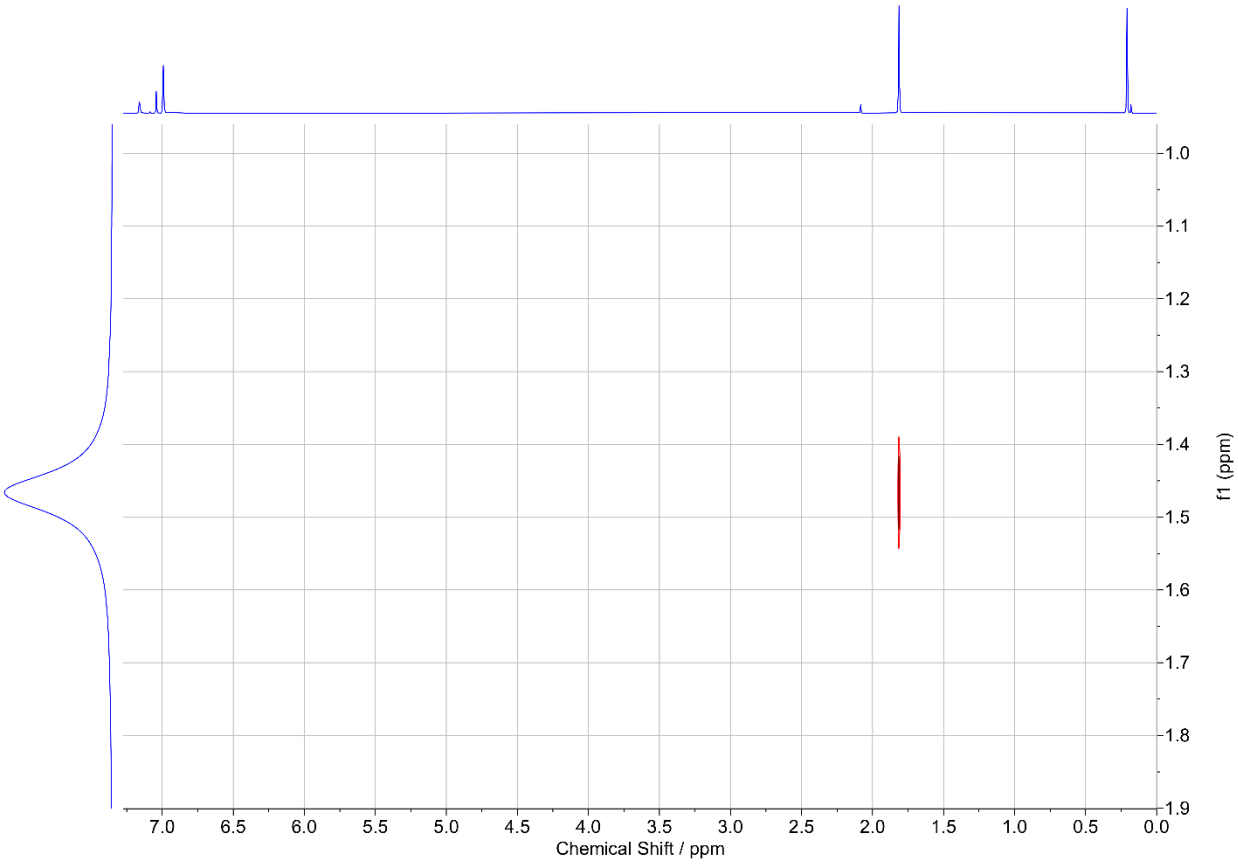


Figure S14: $^{7}Li\text{-}^{1}H$ HOESY spectrum for $[Me_3Si\text{-}Ar^{\#}\text{-}Li]_2$ (**2**) in C_6D_6.

S3.5. [H-Ar$^{\#}$-Li]$_2$ (3)

Note: Compounds H-Ar$^{\#}$-I and [H-Ar$^{\#}$-Li]$_2$ have been published previously,[6,7] and thus their ^{1}H, ^{13}C{^{1}H} and ^{7}Li NMR spectra are not reproduced here. The ^{7}Li-^{1}H HOESY for [H-Ar$^{\#}$-Li]$_2$, as the only spectra not previously published, is provided below.

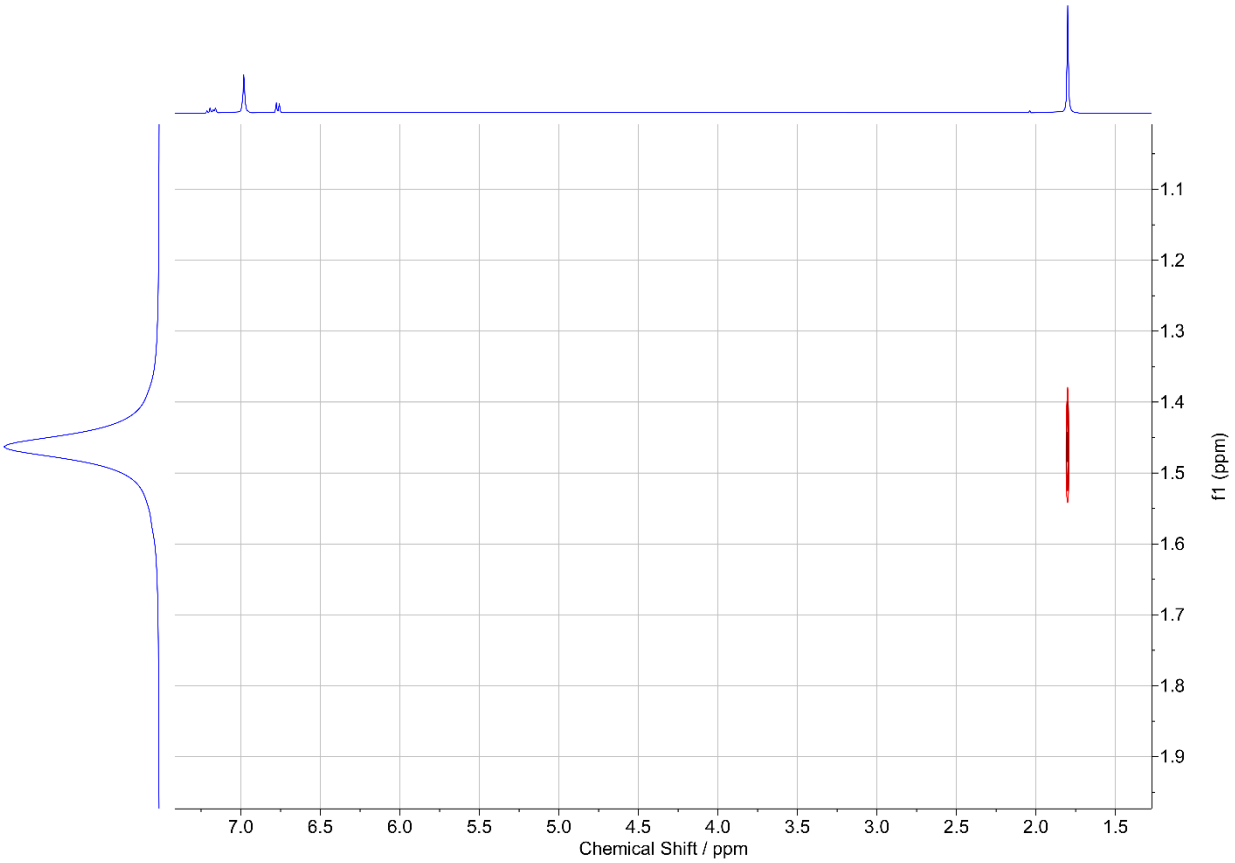


Figure S15: ^{7}Li-^{1}H HOESY spectrum for [H-Ar$^{\#}$-Li]$_2$ (**3**) in C_6D_6.

S3.6. Cl-Ar$^{\#}$-I

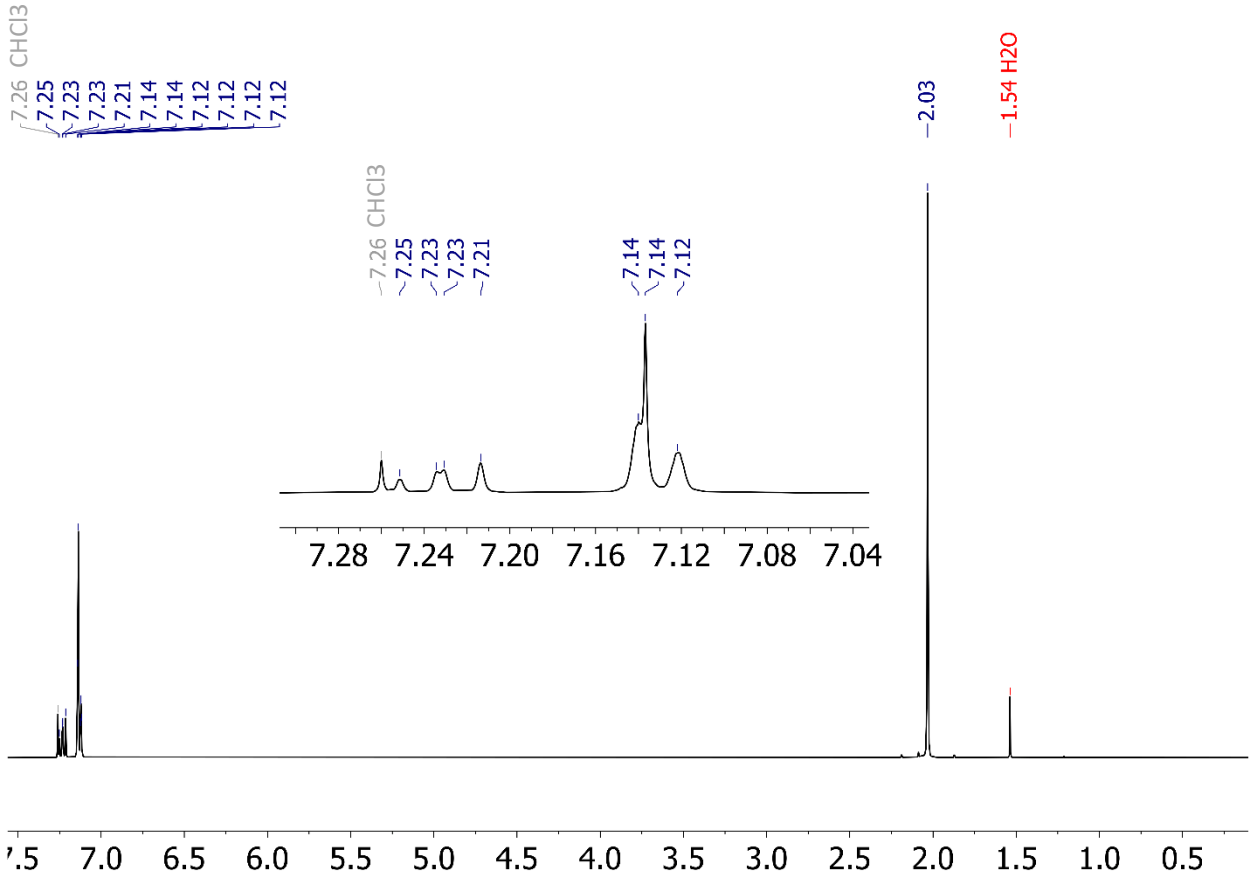


Figure S16: ^{1}H NMR (400 MHz, 25 °C) spectrum for Cl-Ar$^{\#}$-I in $CDCl_3$

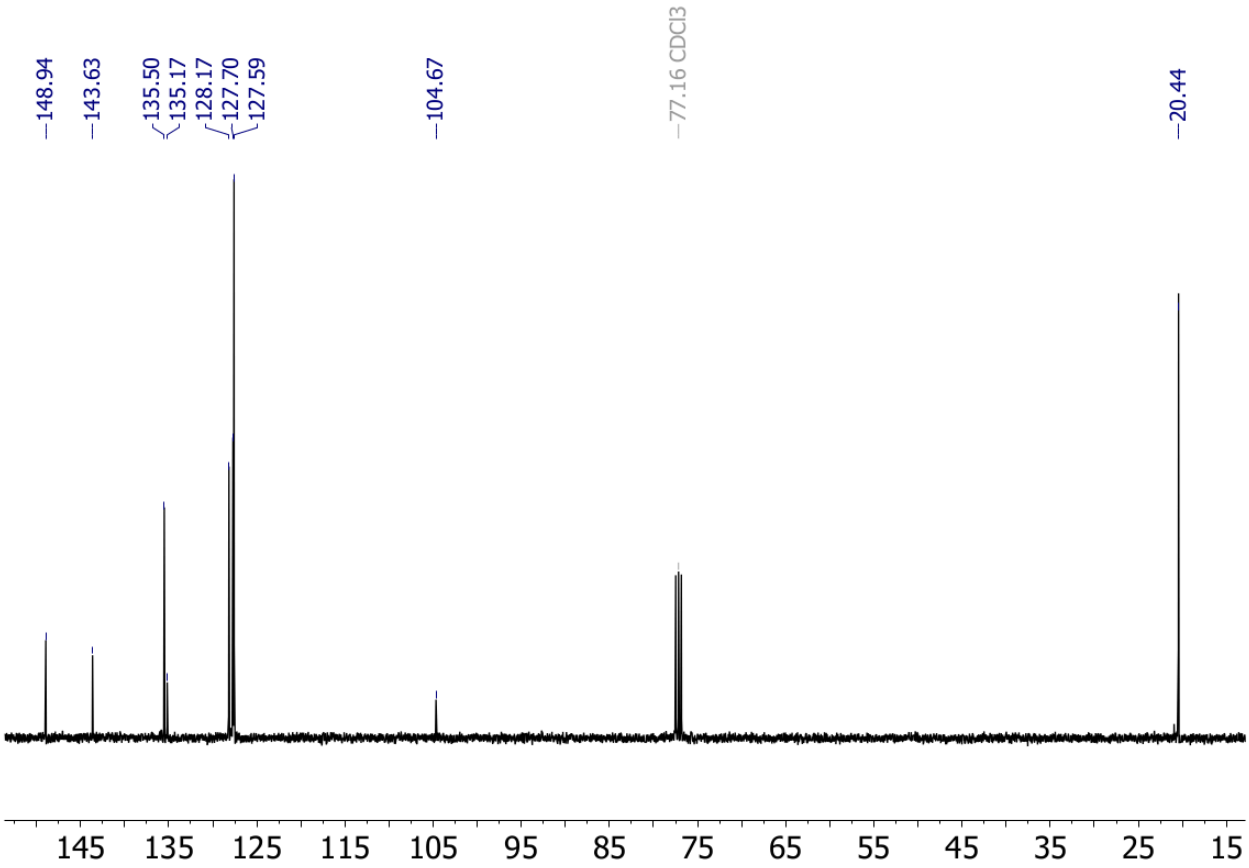


Figure S17: $^{13}C\{^{1}H\}$ NMR (126 MHz, 25 °C) spectrum for Cl-Ar$^{\#}$-I in $CDCl_3$

S3.7. [Cl-Ar$^{\#}$-Li]$_2$ (4)

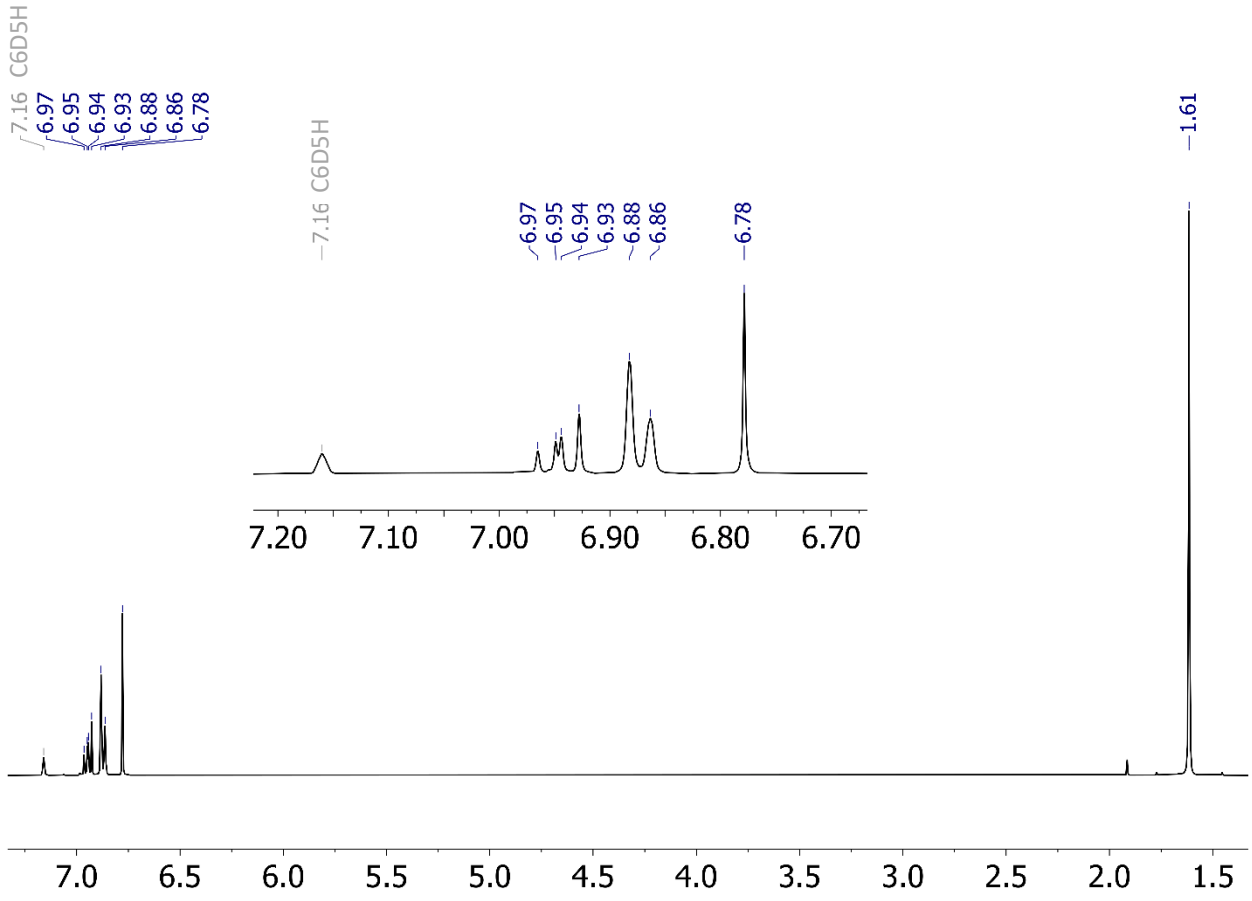


Figure S18: ^{1}H NMR (400 MHz, 25 °C) spectrum for [Cl-Ar$^{\#}$-Li]$_2$ (**4**) in C_6D_6

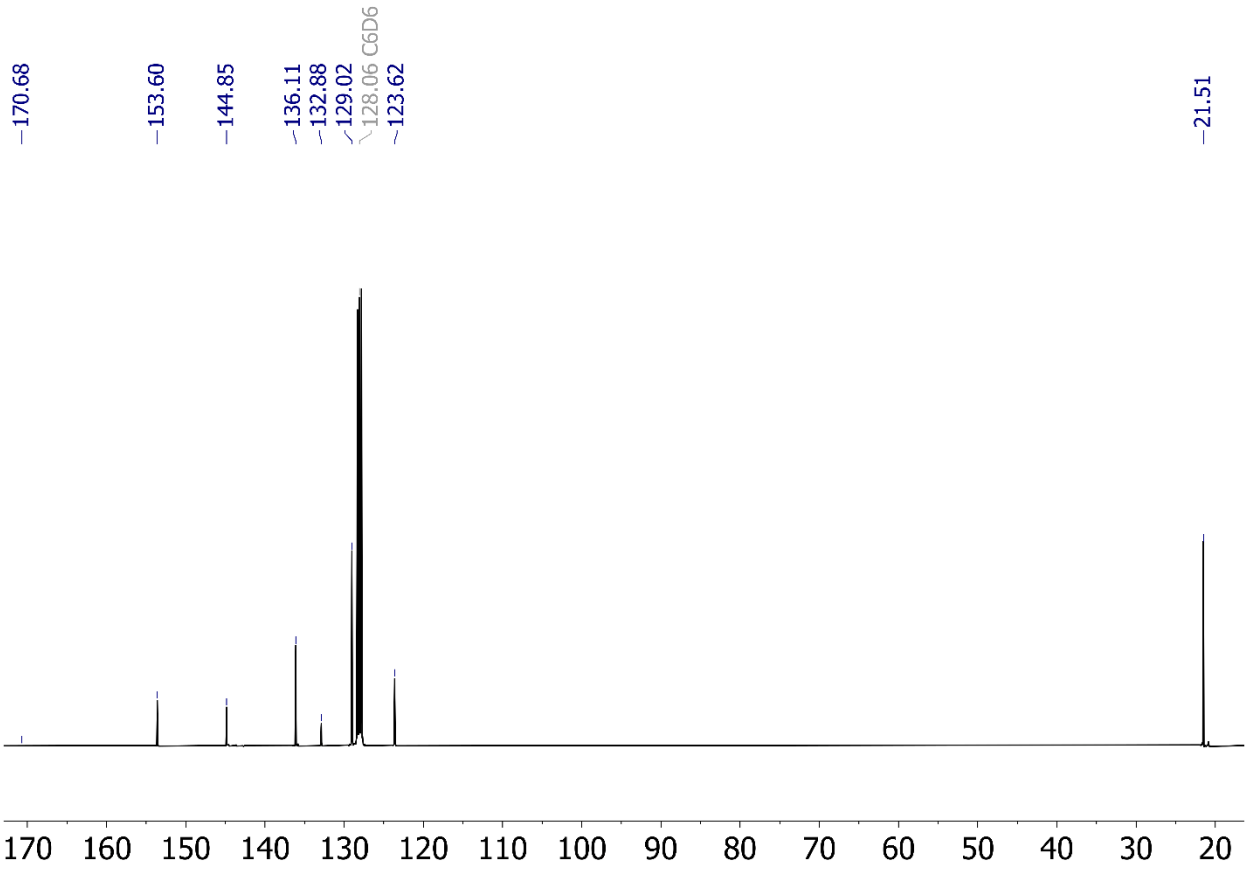


Figure S19: $^{13}C\{^{1}H\}$ NMR (126 MHz, 25 °C) spectrum for [Cl-Ar$^{\#}$-Li]$_2$ (**4**) in C_6D_6

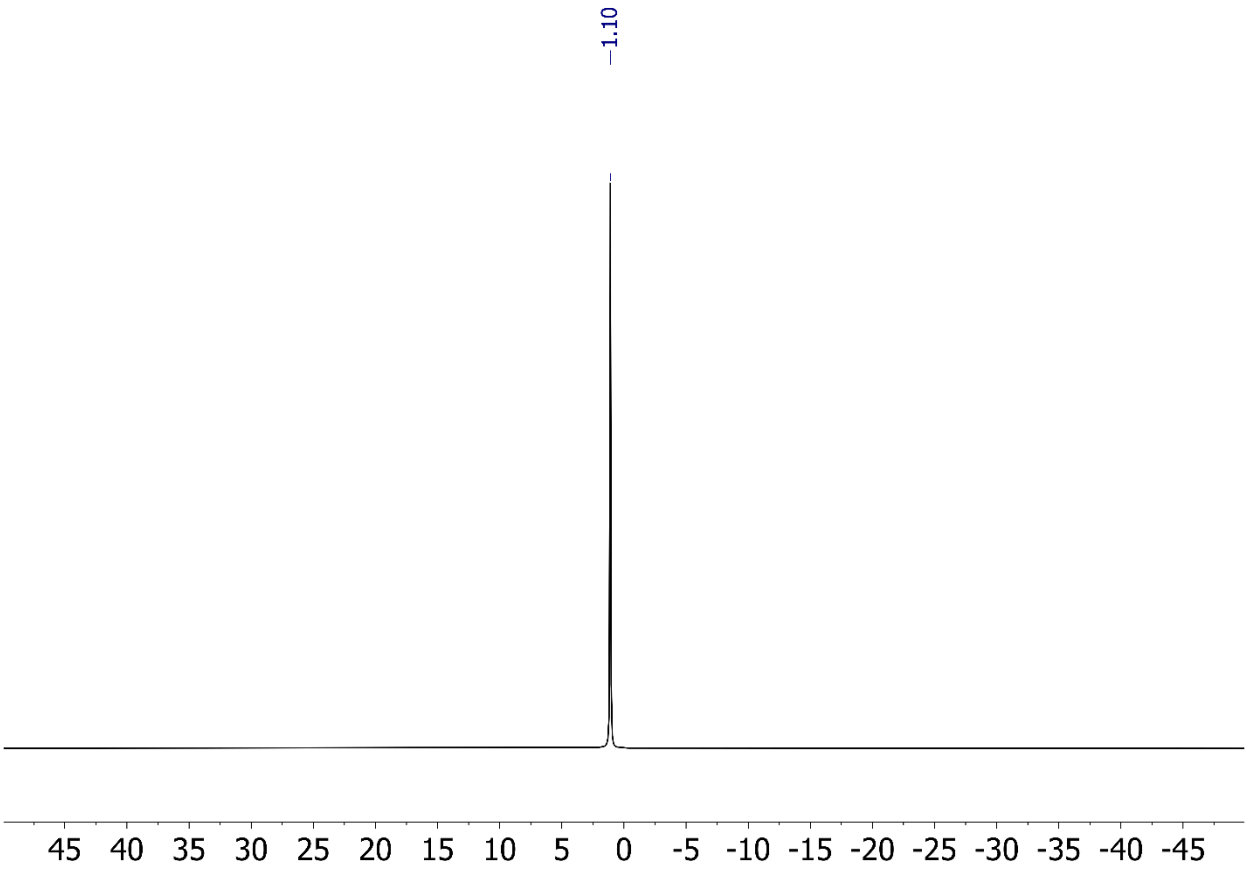


Figure S20: $^{7}Li\{^{1}H\}$ NMR (155 MHz, 25 °C) spectrum for [Cl-Ar$^{\#}$-Li]$_2$ (**4**) in C_6D_6

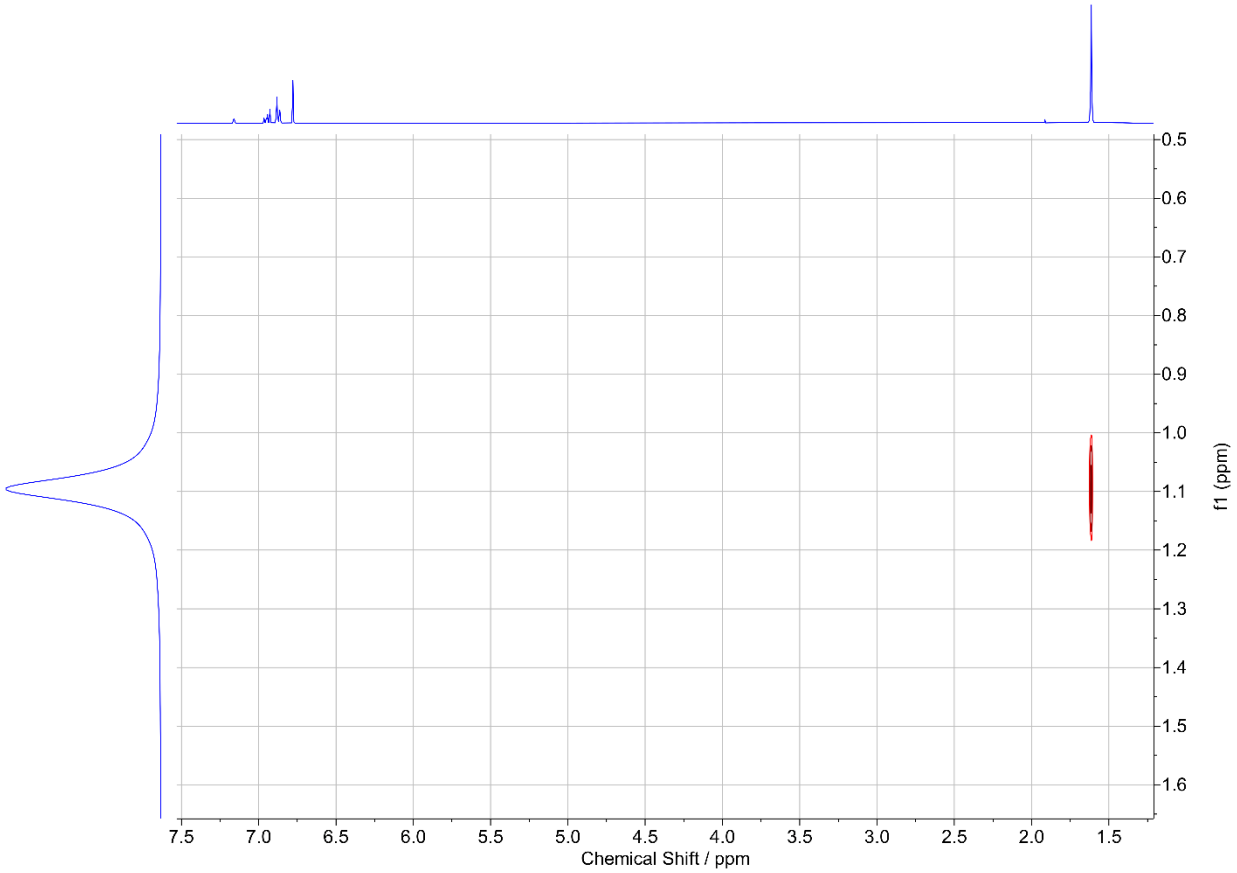


Figure S21: ^{7}Li-^{1}H HOESY spectrum for [Cl-Ar$^{\#}$-Li]$_2$ (**4**) in C_6D_6.

S3.8. F_3C-$Ar^{\#}$-I

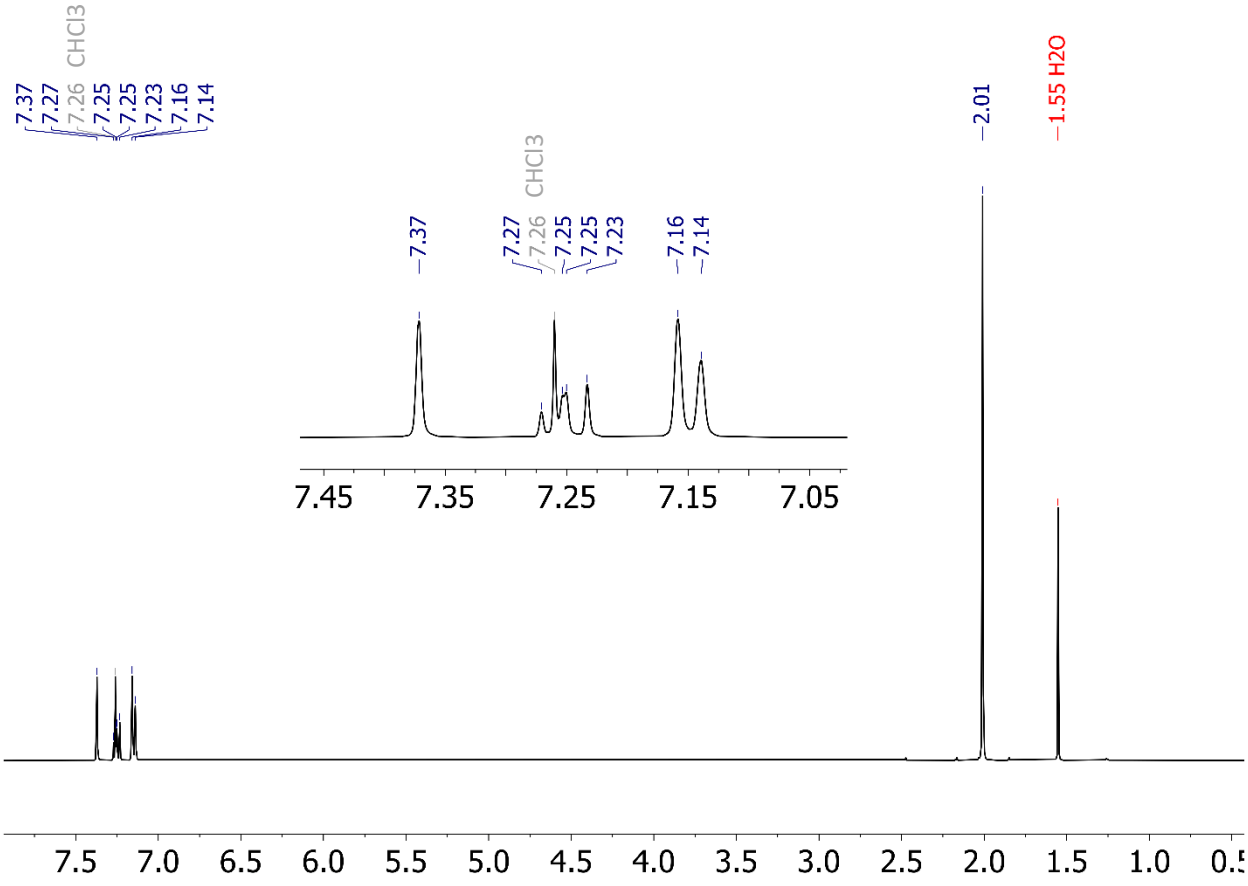


Figure S22: ^{1}H NMR (400 MHz, 25 °C) spectrum for F_3C-$Ar^{\#}$-I in $CDCl_3$

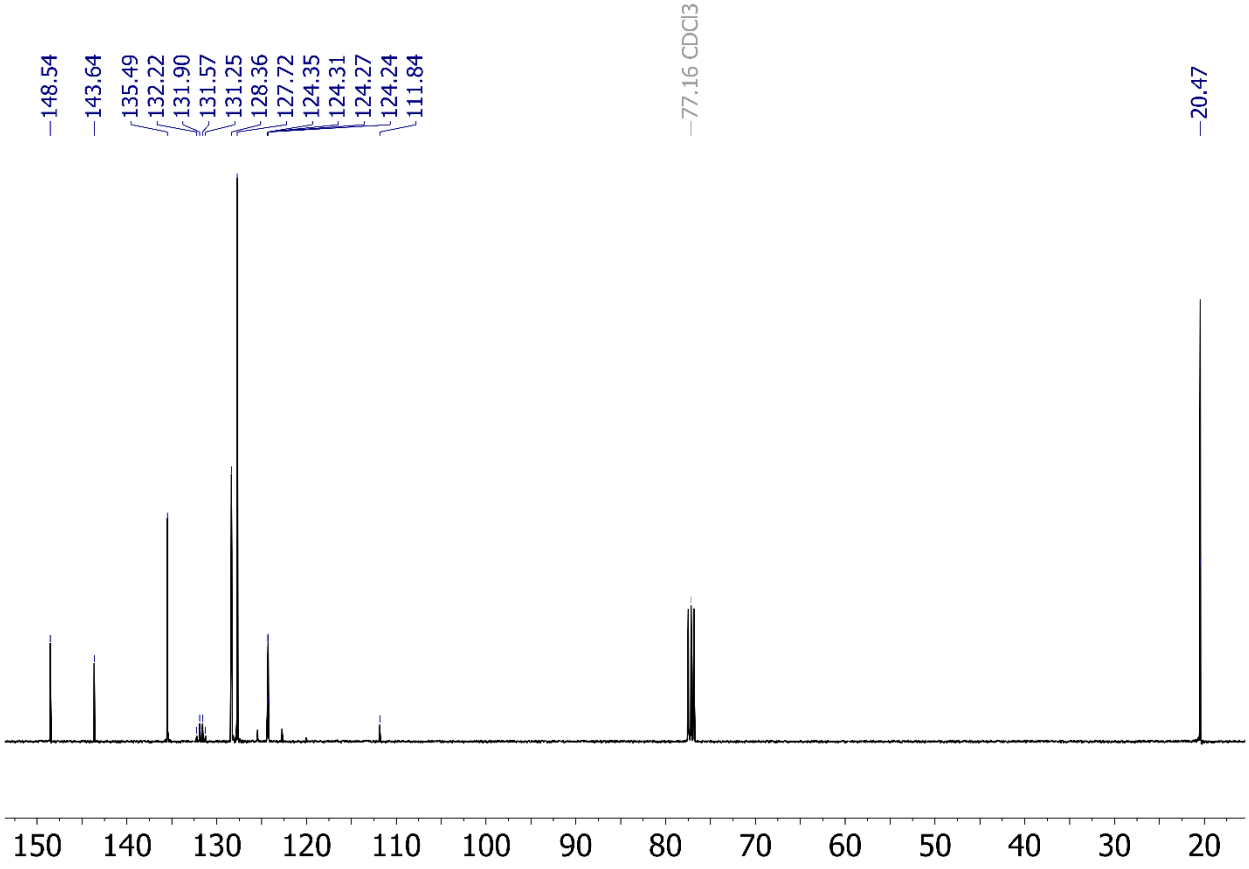


Figure S23: $^{13}C\{^{1}H\}$ NMR (126 MHz, 25 °C) spectrum for F_3C-Ar$^{\#}$-I in $CDCl_3$

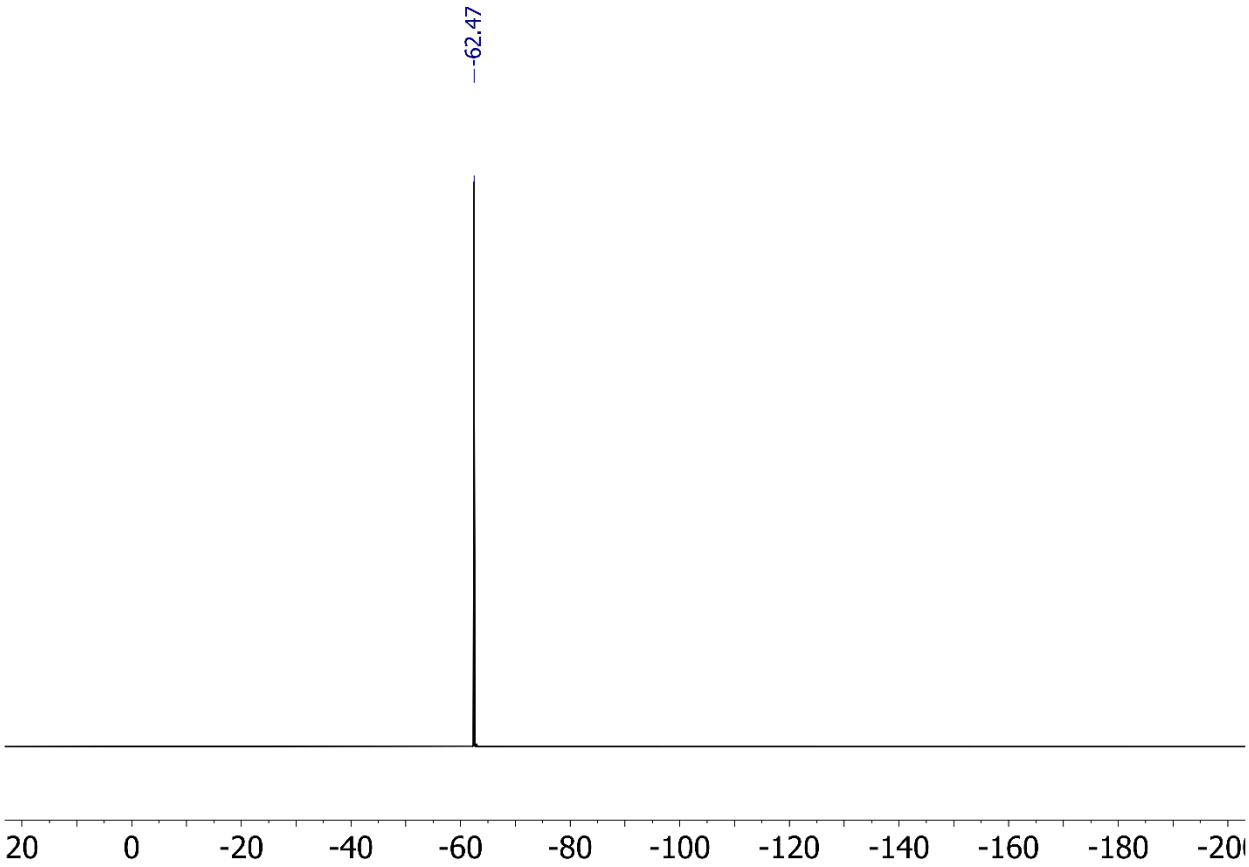


Figure S24: $^{19}F\{^{1}H\}$ NMR (376 MHz, 25 °C) spectrum for F_3C-Ar$^{\#}$-I in $CDCl_3$

S3.9. [F_3C-$Ar^{\#}$-Li]$_2$ (5)

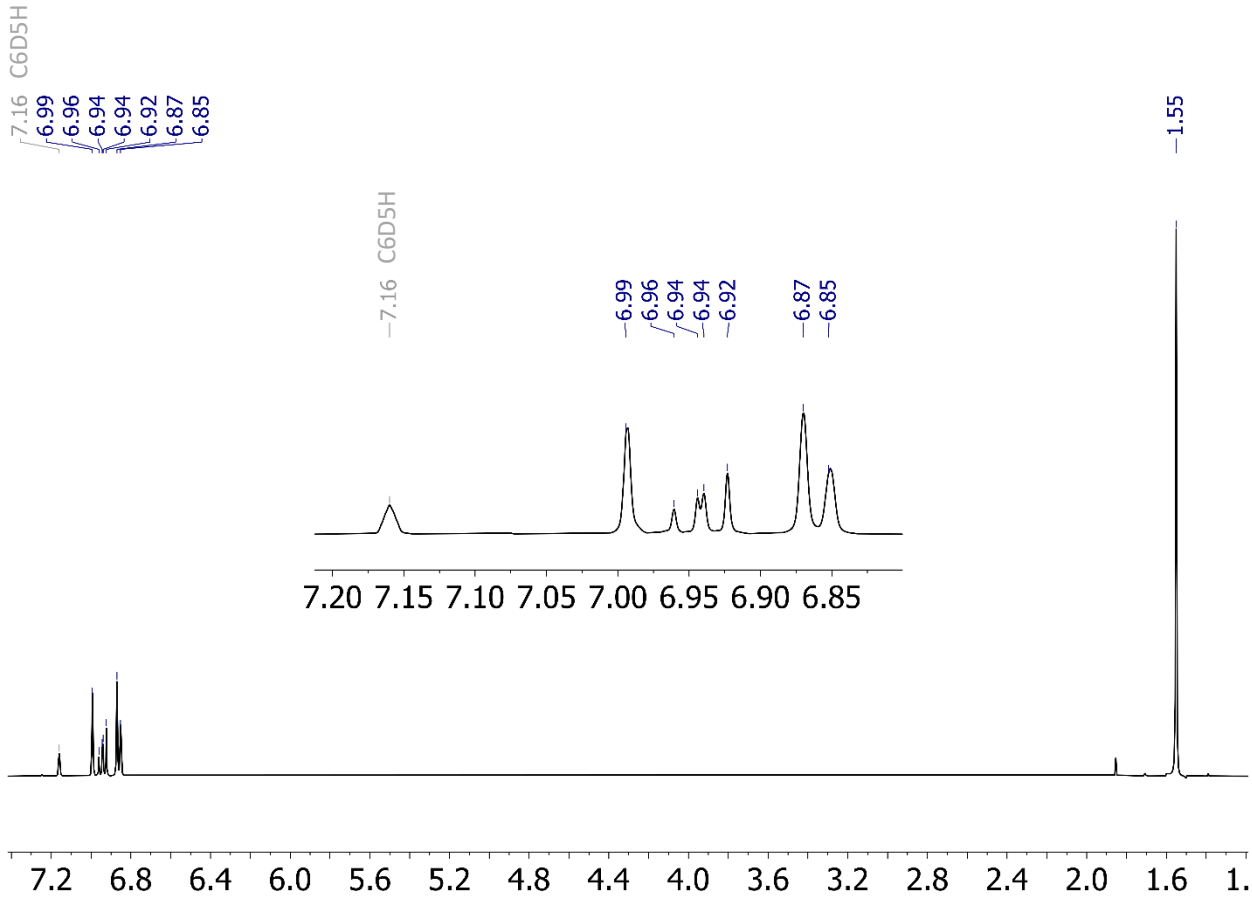


Figure S25: ^{1}H NMR (400 MHz, 25 °C) spectrum for [F_3C-$Ar^{\#}$-Li]$_2$ (**5**) in C_6D_6

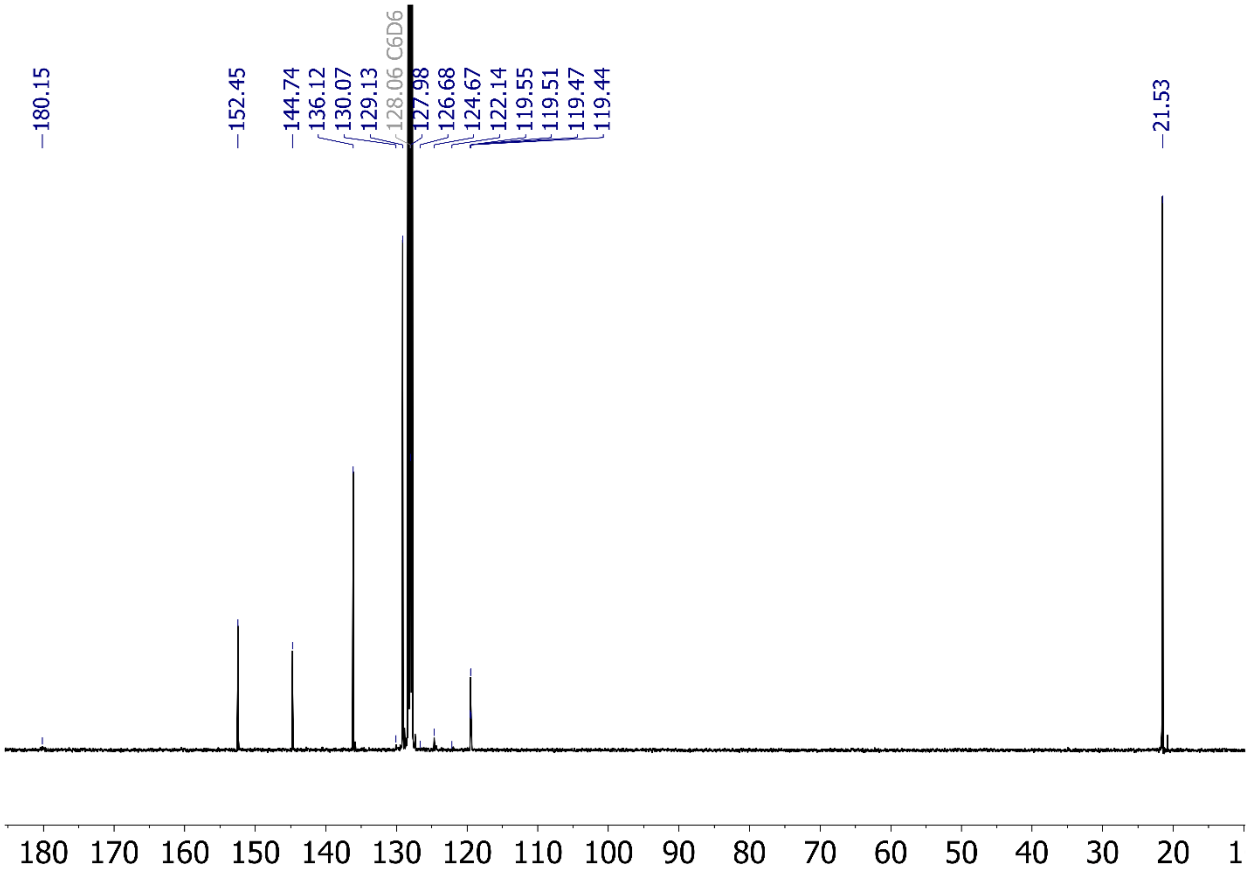


Figure S26: $^{13}C\{^{1}H\}$ NMR (126 MHz, 25 °C) spectrum for $[F_3C\text{-}Ar^{\#}\text{-}Li]_2$ (**5**) in C_6D_6

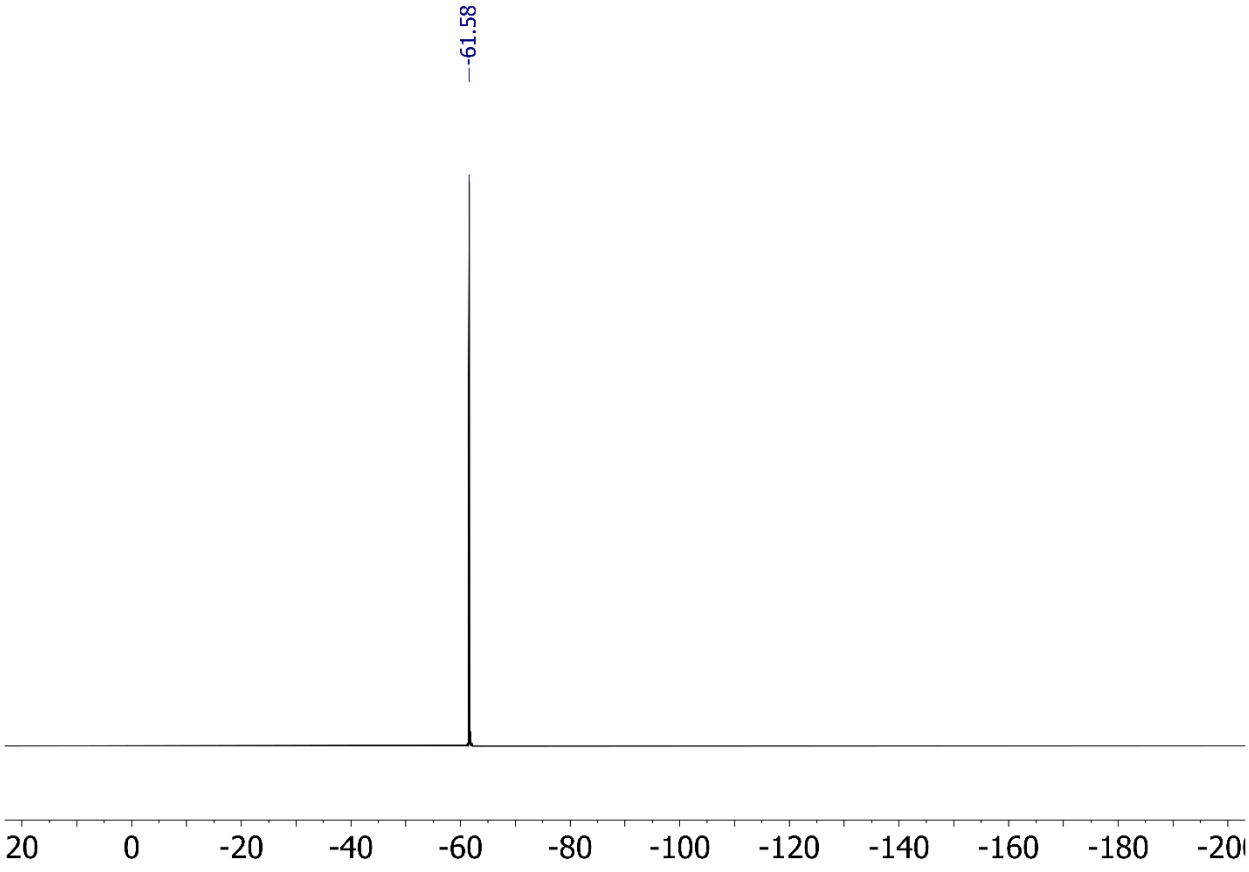


Figure S27: $^{19}F\{^{1}H\}$ NMR (376 MHz, 25 °C) spectrum for $[F_3C\text{-}Ar^{\#}\text{-}Li]_2$ (**5**) in C_6D_6

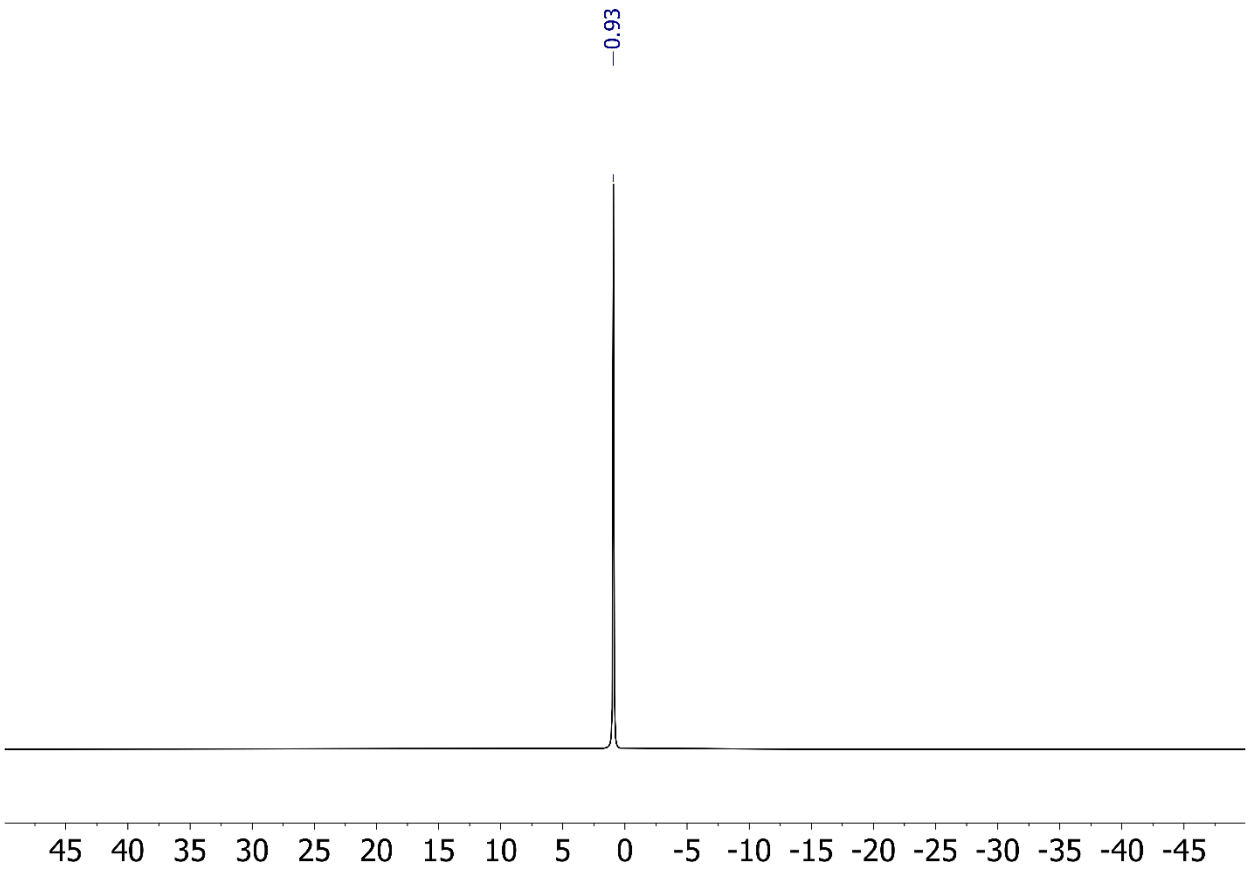


Figure S28: $^{7}Li\{^{1}H\}$ NMR (155 MHz, 25 °C) spectrum for $[F_3C\text{-}Ar^{\#}\text{-}Li]_2$ (**5**) in C_6D_6

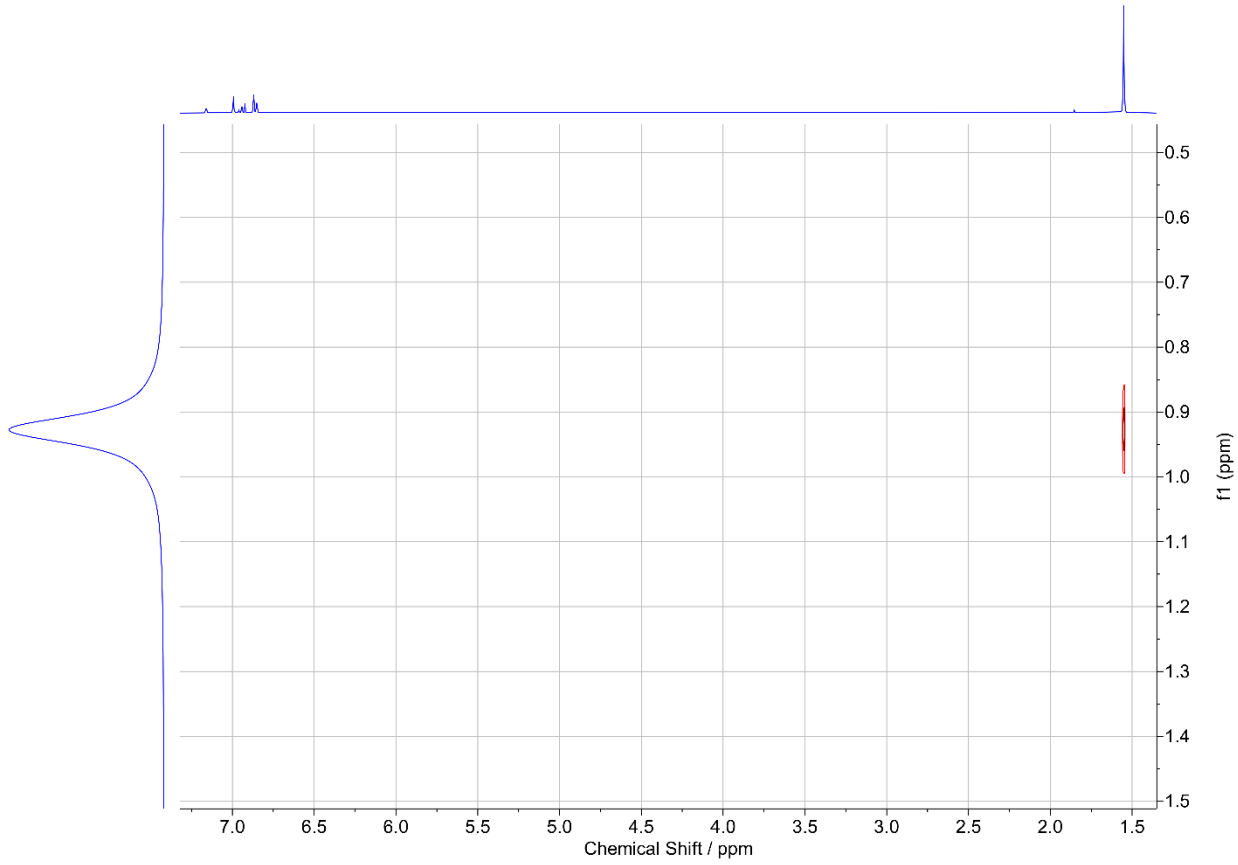


Figure S29: $^{7}Li\text{-}^{1}H$ HOESY spectrum for $[F_3C\text{-}Ar^{\#}\text{-}Li]_2$ (**5**) in C_6D_6.

S4. Crystallography

S4.1. Crystallographic Methodology

Crystals of R-Ar$^{\#}$-I (R = *t*-Bu, $SiMe_3$, Cl, CF_3) and complexes **1**, **2**, **4** and **5** were transferred into YR-1800 perfluoropolyether oil then mounted onto a MiTeGen MicroMount™ and cooled rapidly in a cold nitrogen stream using an Oxford Cryosystems open flow cryostat.[14] Diffraction data was collected using an Agilent SuperNova diffractometer (either using mirror-monochromated Mo-Kα radiation, λ = 0.71073 Å, ω scans or using mirror-monochromated Cu-Kα radiation, λ = 1.54184 Å, ω scans) operating with either an Atlas, AtlasS2 or TitanS2 CCD area detector. Cell parameters were refined in each data set from the observed positions of all strong reflections, and Gaussian based absorption corrections with a beam profile correction (CrysAlisPro) were applied.[15] Structures were located using direct or iterative solution methods and non-hydrogen atoms were refined using anisotropic displacement parameters, with the exception of some disordered atoms (see enclosed CIF files) which were instead refined with isotropic displacement parameters. Hydrogen atoms were geometrically constrained in calculated positions and refined using a riding model. For complex **1**, Platon SQUEEZE[16] was applied to disordered solvent (*iso*hexane) molecules that could not be modelled sensibly. Programs used include CrysAlisPro[15] (data collection and processing), OLEX2[17] (molecular graphics), SHELXT[18] (structure solution) and SHELX[19] (structure refinement). CIF files were checked by Dr William Lewis and Dr Stephen Argent at the University of Nottingham Crystal Structure Service. CCDC 2045214-2045221 contain the supplementary data for these complexes. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

S4.2. Crystallographic Data

S4.2.1. Crystal Structure Figures

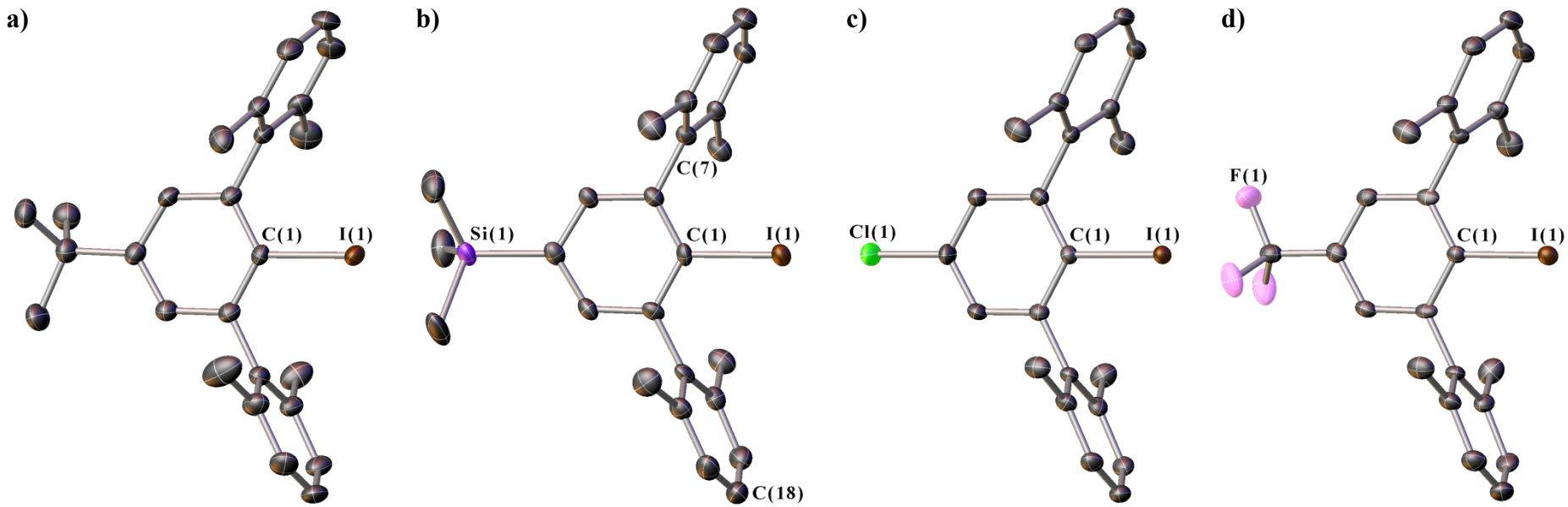


Fig. S30 Crystal structures of the *m*-terphenyl iodides, R-Ar$^{\#}$-I, where a) R = *t*-Bu, b) R = $SiMe_3$, c) R = Cl and d) R = CF_3. Ellipsoids set at 50% probability. Hydrogen atoms are omitted for clarity. For R = Cl and CF_3 second molecule in the asymmetric unit is omitted for clarity.

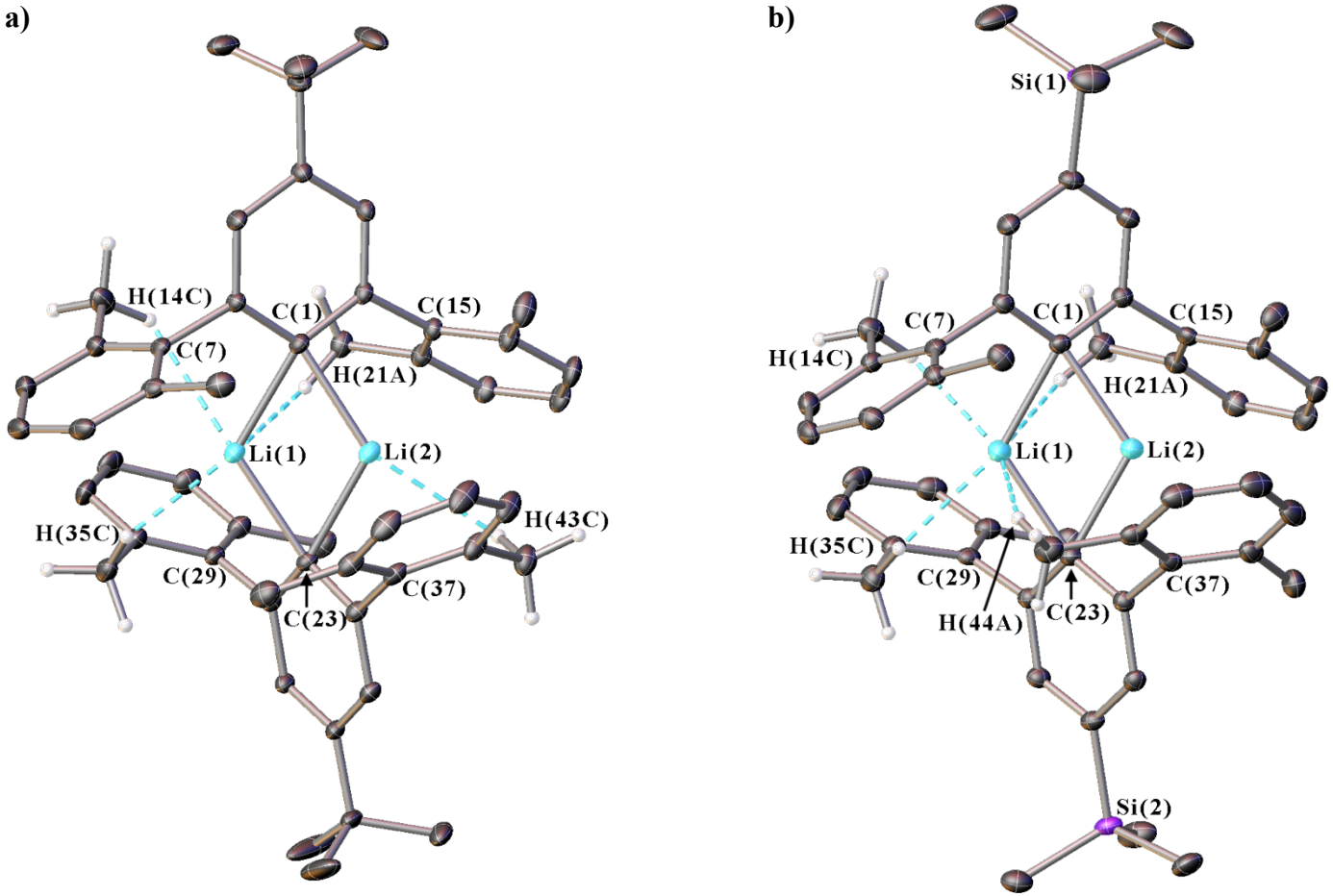


Fig. S31 Crystal structures of the *m*-terphenyl lithium complexes, [R-Ar$^{\#}$-Li]$_2$, where a) R = *t*-Bu (**1**) and b) R = SiMe$_3$ (**2**). Dashed lines indicate the short Li···H–C anagostic contacts. Ellipsoids set at 20% and 40% probability, respectively. The hydrogen atoms are placed in idealised positions for structure refinement. All non-anagostic hydrogen atoms and residual solvent molecules are omitted for clarity.

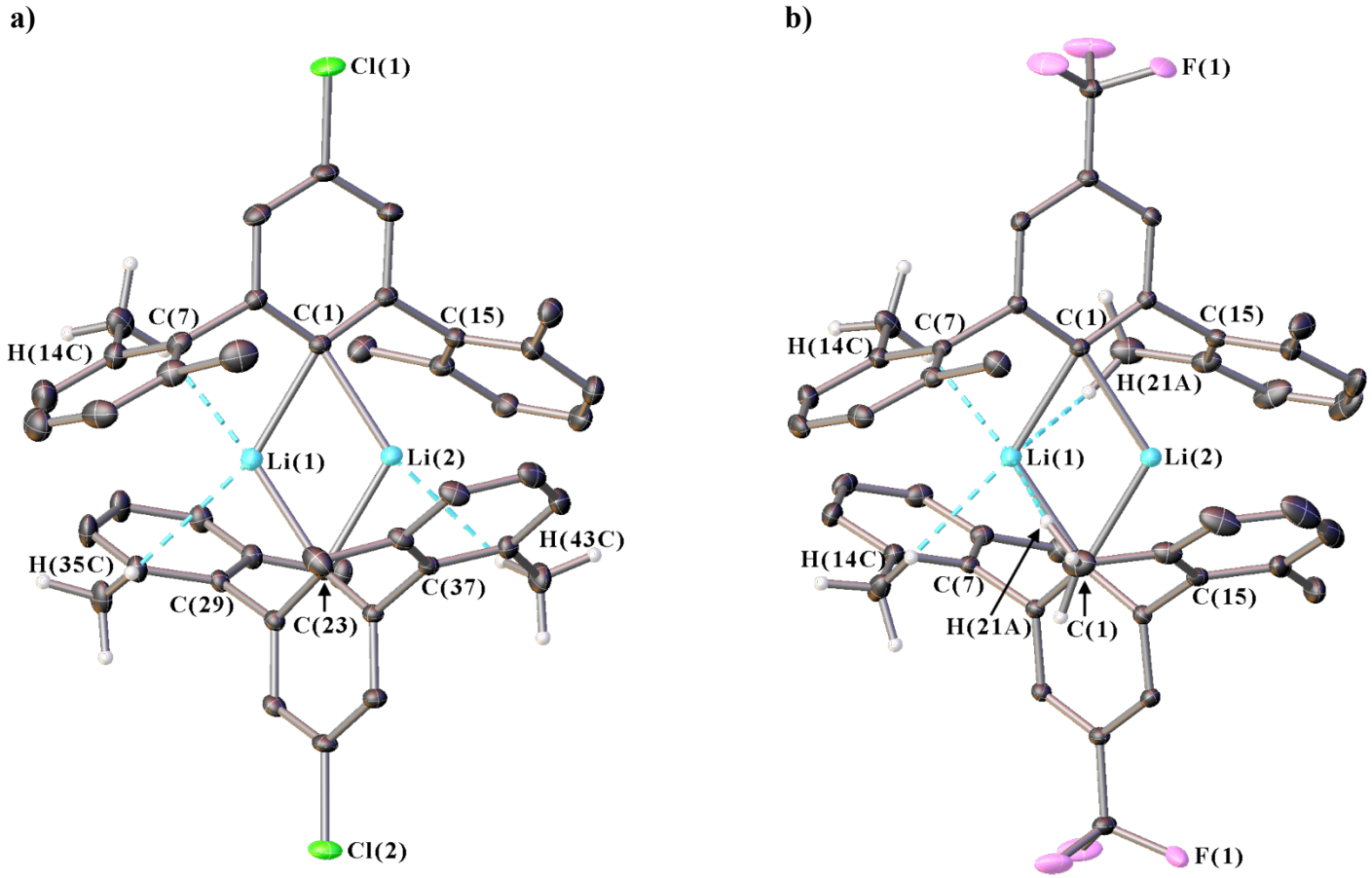


Fig. S32 Crystal structures of the *m*-terphenyl lithium complexes, [R-Ar$^{\#}$-Li]$_2$, where a) R = Cl (**4**) and b) R = CF_3 (**5**). Dashed lines indicate the short Li···H–C anagostic contacts. Ellipsoids set at 15% and 25% probability, respectively. The hydrogen atoms are placed in idealised positions for structure refinement All non-anagostic hydrogen atoms and residual solvent molecules are omitted for clarity.

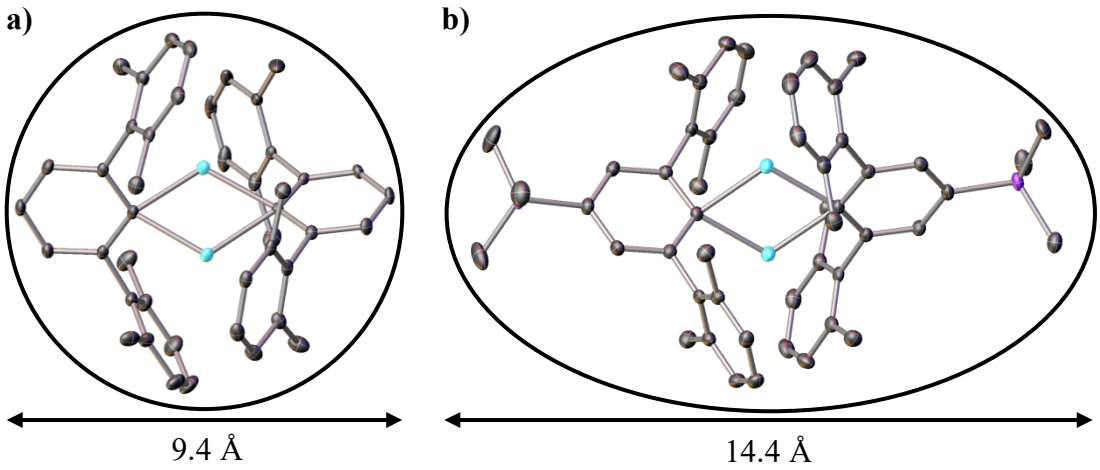


Fig. S33 Crystal structures of the *m*-terphenyl lithium complexes [R-Ar$^{\#}$-Li]$_2$ comparing the length of a) the approximately spherical complex **3** (9.4 Å) against that of b) the ellipsoidal complex **2** (14.4 Å). The widths (measured between C···C for the outermost carbon atoms of the flanking aryl rings on each *m*-terphenyl ligand) of both are 9.9 Å. Ellipsoids set at 20% and 40% probability for **3** and **4** respectively. Hydrogen atoms and residual solvent molecules are omitted for clarity.

S4.2.2. Data Tables

Table S1 Selected bond lengths (Å) and angles (°) for the planar Li_2C_2 core of the *m*-terphenyl lithium complexes [R-Ar$^{\#}$-Li]$_2$ (**1**, **2**, **4**, **5**).

Li_2C_2 Core	Bond Lengths (Å) and Angles (°)			
	1 (R = *t*-Bu)	**2** (R = $SiMe_3$)	**4** (R= Cl)	**5** (R = CF_3)
Li(1)–C(1)	2.186(2)	2.173(4)	2.188(8)	2.1985(18)
Li(1)–C(23) [a]	2.178(3)	2.186(5)	2.186(7)	-
Li(2)–C(1)	2.158(3)	2.192(5)	2.174(7)	2.1755(18)
Li(2)–C(23) [a]	2.178(2)	2.186(4)	2.176(8)	-
Li(1)···Li(2)	2.304(3)	2.318(6)	2.316(9)	2.332(4)
C(1)···C(23)	3.6893(18)	3.702(3)	3.695(4)	3.700(2)
C(1)–Li(1)–C(23) [a]	115.43(10)	116.30(19)	115.3(3)	114.59(13)
C(1)–Li(2)–C(23) [a]	116.60(10)	115.48(19)	116.3(3)	116.51(13)

[a] For **5**, C(23) = C(1) due to only half the molecule in the asymmetric unit.

Table S2 Intramolecular distances (Å) between the lithium ions and 2,6-Xyl flanking groups of the *m*-terphenyl lithium complexes [R-Ar$^{\#}$-Li]$_2$ (**1**, **2**, **4**, **5**).

Li···(2,6-Xyl)	Intramolecular Distances (Å)			
	1 (R = *t*-Bu)	**2** (R = $SiMe_3$)	**4** (R= Cl)	**5** (R = CF_3)
Li(1)···C(7)	2.655(3)	2.729(4)	2.541(6)	2.6635(16)
Li(1)···C(29) [a]	2.693(3)	2.649(3)	2.558(7)	2.6635(16)
Li(2)···C(15)	2.538(3)	2.437(4)	2.613(8)	2.4244(15)
Li(2)···C(37) [a]	2.505(3)	2.468(5)	2.587(7)	2.4244(15)
Li(1)···H(14C)	2.870(3)	2.476(5)	2.770(7)	2.4855(16)
Li(1)···H(21A)	2.794(3)	2.920(3)	-	2.8898(9)
Li(1)···H(35C) [a]	2.338(2)	2.527(3)	2.832(7)	2.4855(16)
Li(1)···H(44A) [a]	-	2.803(3)	-	2.8898(9)
Li(2)···H(43C) [a]	2.644(3)	-	2.596(5)	-

[a] For **5**, C(29) = C(7), C(37) = C(15), H(35C) = H(14C), H(44A) = H(21A), and H(43C) = H(22C) due to only half the molecule in the asymmetric unit.

Table S3 Crystallographic data for the *m*-terphenyl iodides R-Ar$^{\#}$-I.

	***t*-Bu-Ar$^{\#}$-I**	**Me$_3$Si-Ar$^{\#}$-I**	**Cl-Ar$^{\#}$-I**	**F$_3$C-Ar$^{\#}$-I**
CCDC deposition number	2045214	2045215	2045216	2045217
Formula	$C_{26}H_{29}I$	$C_{25}H_{29}ISi$	$C_{22}H_{20}ClI$	$C_{23}H_{20}F_3I$
M_W	468.39	484.47	446.73	480.29
T (K)	120(2)	120(2)	120(2)	120(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space Group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	13.1749(2)	6.3663(4)	8.3499(2)	8.51060(10)
b (Å)	13.2712(2)	17.8142(9)	34.7269(7)	35.0225(4)
c (Å)	13.8896(2)	20.5558(14)	13.4766(3)	13.61300(10)
α (°)	90	90	90	90
β (°)	109.910(2)	96.860(6)	100.064(2)	99.1350(10)
γ (°)	90	90	90	90
V (Å^3)	2283.39(6)	2314.6(2)	3847.63(15)	4006.06(7)
Z	4	4	8	8
D_{calc} (g cm^{-3})	1.362	1.39	1.542	1.593
μ (mm^{-1})	11.046	11.395	14.332	12.836
F_{000}	1060	984	1776	1904
Crystal size (mm^3)	0.14 × 0.08 × 0.05	0.48 × 0.26 × 0.07	0.65 × 0.11 × 0.08	0.46 × 0.22 × 0.10
λ (Å)	1.54184	1.54184	1.54184	1.54184
2θ range for data collection (°)	7.992 to 147.16	6.586 to 149.004	7.132 to 147.398	7.044 to 147.47
Reflections collected	8951	9764	16211	61587
Independent reflections	4470	4520	7564	8027
R_{int}	0.024	0.0505	0.0427	0.0535
GooF on F^2	1.023	1.054	1.034	1.112
R_1, wR_2 [$I > 2\sigma(I)$]	0.0256, 0.0621	0.0580, 0.1477	0.0399, 0.1019	0.0450, 0.0899
R_1, wR_2 (all data)	0.0298, 0.0645	0.0648, 0.1524	0.0436, 0.1055	0.0465, 0.0905
Largest diff. peak/hole (e Å^{-3})	1.39/–0.84	3.02/–1.49	1.17/–1.32	2.04/–1.00

Table S4 Crystallographic data for the *m*-terphenyl lithium complexes [R-Ar$^{\#}$-Li]$_2$ (**1**, **2**, **4**, **5**).

	1	**2**	**4**	**5**
CCDC deposition number	2045218	2045219	2045220	2045221
Formula	$C_{52}H_{58}Li_2$	$C_{50}H_{58}Li_2Si_2$	$C_{47}H_{47}Cl_2Li_2$	$C_{46}H_{40}F_6Li_2$
M_W	696.86	729.02	696.62	720.66
T (K)	120(2)	120(2)	120(2)	120.01(10)
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space Group	*P*-1	*P*-1	$P2_1/c$	$C2/c$
a (Å)	11.9982(4)	11.7845(5)	12.1125(11)	16.2343(6)
b (Å)	15.2538(10)	13.7778(6)	16.8343(14)	16.3983(5)
c (Å)	15.4697(9)	16.2675(8)	19.6420(14)	15.5748(5)
α (°)	113.742(6)	69.756(4)	90	90
β (°)	101.077(4)	85.404(4)	103.471(9)	115.087(4)
γ (°)	104.484(4)	64.756(4)	90	90
V (Å^3)	2368.3(2)	2234.36(19)	3894.9(6)	3755.1(2)
Z	2	2	4	4
D_{calc} (g cm^{-3})	0.977	1.084	1.188	1.275
μ (mm^{-1})	0.399	0.938	1.72	0.763
F_{000}	752	784	1476	1504
Crystal size (mm^3)	0.62 × 0.35 × 0.22	0.20 × 0.14 × 0.07	0.25 × 0.13 × 0.10	0.49 × 0.11 × 0.09
λ (Å)	1.54184	1.54184	1.54184	1.54184
2θ range for data collection (°)	6.614 to 148.726	5.808 to 147.602	7 to 151.612	8.076 to 149.072
Reflections collected	18068	16819	20656	21864
Independent reflections	9359	8737	7768	3818
R_{int}	0.0213	0.0335	0.056	0.0275
GooF on F^2	1.029	1.066	1.032	1.039
R_1, wR_2 [$I > 2\sigma(I)$]	0.0484, 0.1327	0.0482, 0.1148	0.0705, 0.1573	0.0390, 0.1038
R_1, wR_2 (all data)	0.0548, 0.1392	0.0598, 0.1212	0.1286, 0.1945	0.0430, 0.1075
Largest diff. peak/hole (e Å^{-3})	0.22/–0.20	0.33/–0.30	0.26/–0.38	0.28/–0.24

S5. Simulation of NMR Parameters

S5.1. Computational Details

All calculations were carried out at the structures provided directly from X-ray crystallography and on structures obtained by re-optimizing the positions of the H atoms, whilst keeping the positions of the heavier atoms fixed.

S5.1.1. Geometry Optimisations

All geometry optimizations were carried out using the ORCA program.[20,21] These optimizations were performed at the (non-relativistic) density-functional level using the PBE0[22,23] functional with RI-J acceleration of the Coulomb contribution[24,25] and COSX acceleration of the exchange contribution.[26] The auxiliary basis sets of Weigend[27] were used for all density-fitting (RI) contributions and Grimme's D3 dispersion correction was included with the Becke-Johnson damping function (D3-BJ).[28,29] The def2-TZVP basis set[30] was used for all geometry optimizations and the calculations were performed on 32 cores using MPI starting from the crystallographic structures.

Calculations were performed to generate fully optimised structures, where the positions of all atoms were relaxed, and also to generate partially optimised structures where only the H atom positions were relaxed. Preliminary analysis showed that the fully optimised structures led to significant deviations from the atomic positions in the crystallographic structures and furthermore that using these structures to calculate NMR parameters gave slightly poorer agreement with the experimental values than using the partially optimised structures. The structures obtained by optimizing only the H atom positions were therefore adopted in the rest of this study.

S5.1.2. NMR Calculations

The NMR calculations were carried out using the ReSpect program.[31–36] This program allows for a relativistic 4 component SCF treatment at the density functional level, from which NMR parameters may then be calculated via response theory. This relativistic program was utilised to allow calculations on analogous compounds containing heavy elements in place of Li to be performed in a consistent manner, these results will be reported elsewhere. All calculations in this work use the KT2 density-functional approximation,[37] which was specially designed for the calculation of NMR shielding constants. We have also performed similar calculations using the GGA functionals BLYP,[38] BP86,[38,39] PP86,[39,40] and PBE,[22] along with the PBE0 hybrid functional,[22,23] to facilitate comparison of the performance of KT2 with other functionals. For details of how these functionals are implemented for use in non-collinear spin-DFT (SDFT) see Komorovsky et al. and Ekström et al.[34,41] Jensen's pcS-*n* basis sets[42] have been employed (n = 1, 2), these basis sets were optimised for the calculation of NMR shielding constants and are utilized in the ReSpect program in an uncontracted form. The RI-J approximation is used for the computation of electron-repulsion integrals, using the default matching auxiliary basis set in the ReSpect basis library. London orbitals[43–45] (also known as gauge-including atomic orbitals (GIAOs)) were used to determine the magnetic response parameters and the restricted magnetic balance condition[32,33,36,46–49] was employed in the 4 component relativistic calculations. All calculations were performed using 32 threads on a single node with shared memory.

The calculations yield absolute shielding constants. To facilitate comparison with experiment the shielding constants for nuclei in magnetically equivalent environments were first averaged, then to

obtain chemical shifts a reference shielding value was determined by constructing correlation plots between the calculated absolute shieldings and the experimentally obtained shifts for each type of nucleus in each compound. Linear regression was then applied, with the intercept providing the required reference shielding value. For the ^{7}Li NMR linear regression could not be used since there are only two nuclei present, so in this case calculations were performed on the reference compound LiCl with each functional and basis set to provide a reference absolute shielding.

S5.2. Results

Table S5 Summary of computed paramagnetic (para.) and diamagnetic (dia.) contributions to the absolute NMR shielding constant for H-9 and Li NMR resonances. Values computed with KT2, functional at the 4-component density-functional level. Results using the pcS-1 and pcS-2 basis sets are presented.

[R-Ar$^{\#}$-Li]$_2$	R Group	Nuc.	KT2[a]		KT2[b]	
			Para.	Dia.	Para.	Dia.
1	*t*-Bu	H-9	36.59	-6.77	42.24	-12.61
		Li	113.50	-21.59	132.34	-41.22
2	$SiMe_3$	H-9	38.47	-8.78	43.43	-13.89
		Li	116.51	-24.99	135.06	-44.28
3	H	H-9	34.67	-4.87	38.65	-9.03
		Li	109.43	-17.31	127.65	-36.15
4	Cl	H-9	34.27	-4.46	38.42	-8.74
		Li	108.86	-16.93	126.30	-34.93
5	CF_3	H-9	35.53	-5.65	38.65	-9.03
		Li	110.43	-18.04	127.65	-36.15

[a] pcS-1 basis set
[b] pcS-2 basis set

Table S6 Comparison of experimental (Exp.) ^{7}Li chemical shifts with computed values using KT2, BLYP, BP86, PBE, PBE0, and PP86 functionals. KT2 results are given for the pcS-1 and pcS-2 basis sets, all other results use the pcS-1 basis. Chemical shifts have been corrected by comparison with the computed shifts for the reference compound (lithium chloride) and averaged over the two magnetically equivalent Li atoms.

[R-Ar$^{\#}$-Li]$_2$	R Group	^{7}Li NMR Chemical Shifts, δ (ppm)							
		Exp.	Calculated (Corrected) Chemical Shift						
			KT2[a]	KT2[b]	BLYP	BP86	PBE	PBE0	PP86
1	*t*-Bu	1.60	-1.43	-0.92	-2.61	-1.90	-2.72	-1.98	-1.95
2	$SiMe_3$	1.47	-1.05	-0.59	-2.28	-1.56	-2.38	-2.30	-1.60
3	H	1.46	-1.64	-1.30	-2.79	-2.11	-2.93	-2.07	-2.12
4	Cl	1.10	-1.45	-1.17	-2.63	-1.94	-2.75	-2.24	-1.95
5	CF_3	0.93	-1.91	-1.62	-3.09	-2.37	-3.21	-2.13	-2.42

[a] pcS-1 basis set
[b] pcS-2 basis set

Table S7 Comparison of experimental (Exp.) ^{1}H chemical shifts for the H-9 protons with computed values using KT2, BLYP, BP86, PBE, PBE0, and PP86 functionals. Chemical shifts have been corrected by comparison with the computed shifts for the reference compound (TMS) and averaged over the 24 magnetically equivalent H-9 atoms.

[R-Ar$^{\#}$-Li]$_2$	R Group	^{1}H NMR Chemical Shifts, δ (ppm)							
		Exp.	Calculated (Corrected) Chemical Shift						
			KT2[a]	KT2[b]	BLYP	BP86	PBE	PBE0	PP86
1	*t*-Bu	1.83	1.87	1.95	1.86	1.88	1.89	1.89	1.88
2	$SiMe_3$	1.81	1.93	1.92	1.91	1.93	1.92	1.85	1.93
3	H	1.80	1.84	1.81	1.88	1.90	1.92	1.97	1.73
4	Cl	1.61	1.59	1.60	1.62	1.64	1.65	1.72	1.62
5	CF_3	1.55	1.55	1.53	1.58	1.59	1.60	1.66	1.58

[a] pcS-1 basis set
[b] pcS-2 basis set

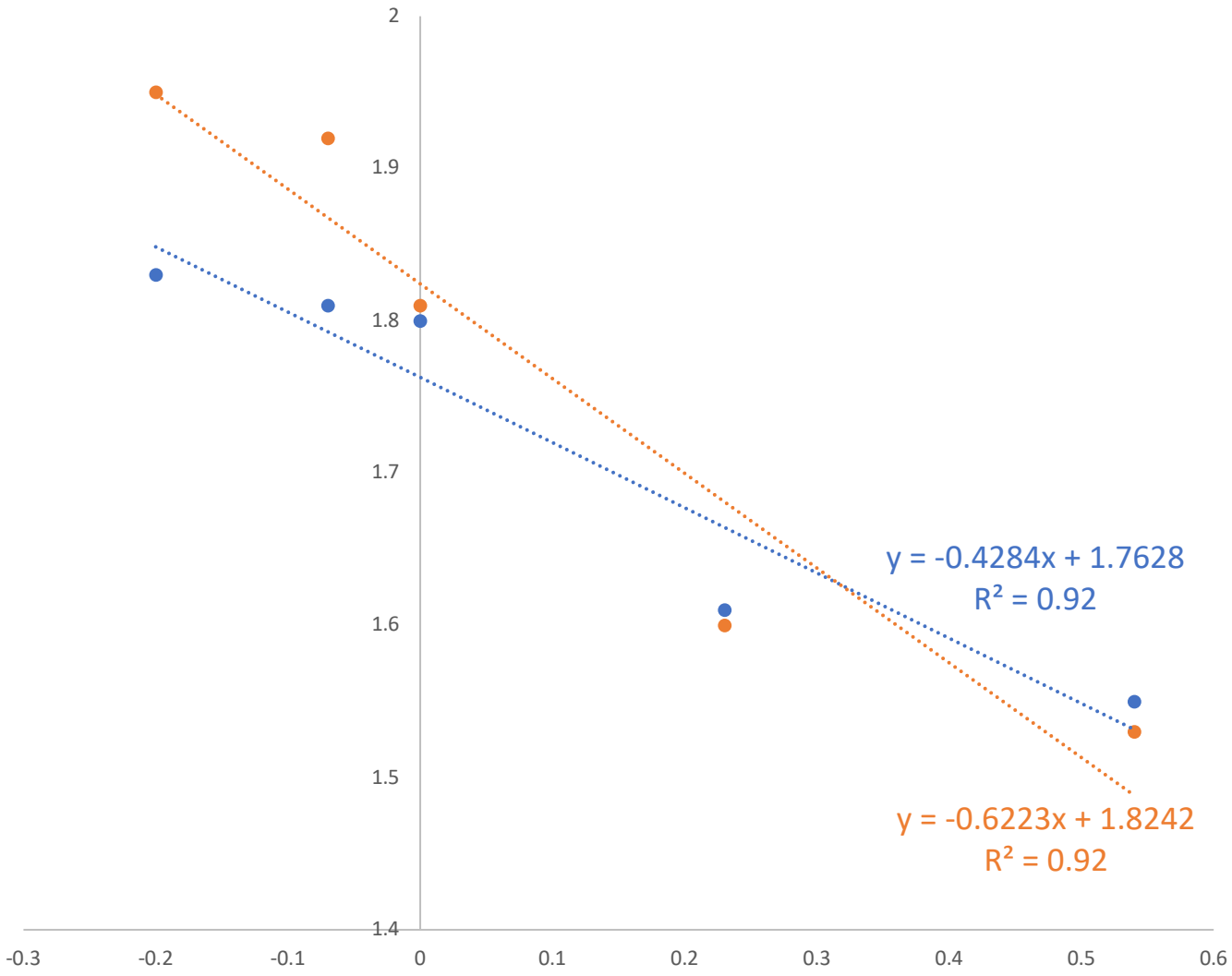


Fig. S34 Plot of the computed (KT2/pcS-2) and experimental ^{1}H (for flanking methyl protons, H-9) chemical shifts (δ) for the *para*-substituted lithium complexes [R-Ar$^{\#}$-Li]$_2$ (**1**–**5**) versus their corresponding literature Hammett constants (σ_{para}). The experimental data points are shown in blue and the calculated in orange.

S5.3. H-Optimised Coordinates

S5.3.1. [*t*-Bu-Ar$^{\#}$-Li]$_2$ (1)

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C	-1.04210981134776	2.56630030603508	10.65086889419712
C	2.17092800403163	-0.86638917123743	7.67154248055483
C	-0.31498237327952	1.05425704663125	5.60985551480236
C	1.03963240108981	-0.05908533288702	7.40297615816993
C	-1.24092342135369	1.37142734952326	9.92086544358380
C	0.30460116247106	3.22668442955504	10.56217939643608
C	-2.52185096015243	0.80421985385675	10.12850249591841
C	-2.01966848515234	3.14463959282455	11.47382866026021
C	2.59560470104324	-1.07567062404481	9.09638105088053
C	0.81708109991438	0.14668694536801	6.02450314743565
C	-3.27725480909071	2.55962263928758	11.62760216616293
C	1.62217478046802	-0.40201472586379	5.01564316437071
C	-2.81601716591771	-0.48565420570753	9.41975429106939
C	2.72455171068426	-1.20018067801646	5.32484132494479
C	-3.50440663536320	1.36722429406244	10.94237447073085
C	2.98030753633527	-1.41539074618253	6.67858723254175
C	-0.22510064356028	2.43837081179214	5.86232787203260
C	0.49604278783198	4.36265427941029	9.75812292216825
C	1.39453797738650	2.66879223214435	11.26177786003200
C	-1.46347889686243	0.54836932397907	4.97520882337060
C	-1.27839127469225	3.27318659145027	5.48643394334228
C	3.55996734022636	-0.22135701827448	9.64670728294679
C	2.05249313560473	-2.12285256315191	9.86477370045212
C	1.00939806146811	3.03681748889141	6.48574288298646
C	-3.52448049440846	-0.48687793838841	8.20302880511561
C	3.65978500195112	-1.81178269088048	4.26732394460200
C	-2.33676882159685	-1.69989800378010	9.95980606043791
C	-4.37665781960447	3.16564966810632	12.51632760757825
C	-2.40129762442042	2.77279602142521	4.86568571237752
C	-2.49330390851921	1.42133918066097	4.60907068300927
C	1.76415970376762	4.92374154078698	9.64738461688261
C	2.65007080700902	3.25965793588018	11.12511151387102
C	-1.58652939848364	-1.71473841773330	11.27155587979984
C	2.47355023820165	-2.28240882140559	11.18416180626705
C	1.22715537575923	1.49222952884579	12.18090658434376
C	3.96589857260077	-0.43134996287281	10.97090599391557
C	1.07329220207697	-3.08431250076852	9.24441468820505
C	2.83710904363640	4.36934056598950	10.33174814463529
C	-0.65853672260061	4.95778208097821	8.98809367509358
C	-4.09914901767414	0.79870705735542	7.64440634953411
C	3.42250229906950	-1.43894874812573	11.73408691272195
C	-2.56436977697814	-2.87820604679264	9.25746948460529

C	-3.70934845939958	-1.69148403484698	7.51739642531315
C	-1.58546977103225	-0.92312560301919	4.66646986588778
C	4.16994029596534	0.87917214478339	8.82885885559520
C	-3.23038400747417	-2.87550764925599	8.04795841533896
C	3.55440180291345	-3.33674380039854	4.30260463307005
C	-5.63776281642882	3.38609839155084	11.71155250823023
C	5.09662709714902	-1.41180588270226	4.56047124168696
C	3.30410077713794	-1.34016231736989	2.86373381995029
C	-4.70772159168678	2.19831037724473	13.64677174279184
C	-3.95673709412383	4.45779459026747	13.12015010387637
H	-1.77773446238423	4.06369715723270	11.99491223096581
H	1.38575161245971	-0.17287216607440	3.98267870795691
H	-4.45531595435992	0.85240841376130	11.04143855849955
H	3.83282132120701	-2.01732194467771	6.97976555262220
H	-1.19137407676844	4.33850869829610	5.67035158366631
H	1.05606681484511	2.84221876165790	7.55921979118579
H	1.02263855759455	4.11828430176608	6.34054985554038
H	1.91112090303119	2.60676008070086	6.04694101442751
H	-3.20562434460451	3.43801386896016	4.57332920365159
H	-3.37243204852334	1.01502596058861	4.12114427559190
H	1.90786630342771	5.79385531430835	9.01716829054927
H	3.48813390910795	2.83497893460775	11.66794448737415
H	-0.57476807718857	-1.31901665072614	11.15127913353732
H	-1.51417621351455	-2.73391786635284	11.65359521866479
H	-2.08668725534185	-1.09060113731673	12.01347184195000
H	2.04509742543995	-3.08313706533223	11.77840470887665
H	0.26211598540516	1.52606357448577	12.68676320175272
H	2.02318933277431	1.48371904607919	12.92675786136537
H	1.28016296055380	0.52440845457926	11.66802337814820
H	4.71223730465605	0.23029468105586	11.39885930204236
H	0.28760532249811	-2.55973152062999	8.70011098586688
H	0.61517891852319	-3.72159155463211	10.00109902960349
H	1.58825757503570	-3.72293496234220	8.52019795316454
H	3.82379466380743	4.80804137658022	10.23517331685495
H	-1.18566721475707	4.18520455682811	8.42271540965988
H	-0.30690647410892	5.72478366138976	8.29732602227696
H	-1.39127552465113	5.41188599732058	9.65964553568721
H	-4.88414465615599	1.18530528243345	8.29896350239962
H	-4.51658225146145	0.63671203668074	6.65219553252838
H	-3.34846457705884	1.59074333437627	7.57443687260707
H	3.74606939718573	-1.58484058112087	12.75829882100593
H	-2.20704347711885	-3.81468885541121	9.67169792547221
H	-4.24167773538731	-1.69068318453296	6.57338772942535
H	-0.85890449560487	-1.23003273882833	3.91123233399742
H	-2.58370161947645	-1.15880411327844	4.29464783705408
H	-1.39221970660800	-1.53485999022365	5.55023141516654
H	4.77324569769007	0.46427066047432	8.01672256584408
H	4.80445799308438	1.51704541367788	9.44484636081192
H	3.41105489346286	1.50379556643394	8.35184668217893

H	-3.38875247778629	-3.80751204341775	7.51723652097846
H	3.83356366316065	-3.73245959566636	5.28146131844415
H	4.22777524452393	-3.77639198118041	3.56157113526583
H	2.53782124291951	-3.66639076340039	4.07574077961430
H	-5.46211614432015	4.07871966473649	10.88456790382326
H	-6.42146529970868	3.81186206918160	12.34517936316825
H	-6.02133489022673	2.45617395656771	11.28757979646962
H	5.22084629884102	-0.32714116097537	4.49846771387421
H	5.77149421113343	-1.86484598599751	3.82899465589845
H	5.42281691970994	-1.73553094940690	5.54988624557959
H	2.29161050368460	-1.63527142931598	2.57920211630891
H	3.99105515017152	-1.78753131815485	2.14149081765335
H	3.38823709741197	-0.25396569504458	2.77127509613237
H	-5.04602562546187	1.23274378136780	13.26563873431958
H	-5.50330571571549	2.60897364374714	14.27551597284246
H	-3.83502634899110	2.01941695028391	14.28004634375798
H	-3.07329820354267	4.35024644021402	13.75358934274615
H	-4.75709732042781	4.85464910124692	13.75007265267830
H	-3.73918764859507	5.21220213935543	12.35941209834240
Li	-0.98223951343514	0.42852203373290	7.98101549883754
Li	0.80297101534898	0.86189555435070	9.37089160916366

S5.3.2. [Me_3Si-$Ar^{\#}$-Li]$_2$ (2)

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Si	6.31892126296107	14.04402828158331	4.85486385245514
Si	6.31984119486382	1.04752928421426	2.67431099138637
C	6.88660497470321	9.34228996447795	4.28353093071252
C	7.78497644268818	10.30771569444591	3.76480700075296
C	7.64757766543195	11.67611021617964	3.98899436096805
C	6.59383514814869	12.19223139841876	4.74765829811106
C	5.69829148034223	11.26698825816272	5.28507016116250
C	5.84460510376081	9.89230226870430	5.06377790620761
C	8.92492159714644	9.83049331661753	2.91756351046897
C	8.83080414783453	9.85199446183538	1.51494714252165
C	9.89255424345977	9.36556804428098	0.75367712795060
C	11.04798702613011	8.89440367693200	1.36563689415317
C	11.14015631755508	8.89366428068690	2.74785358902636
C	10.09246028692669	9.35073492619967	3.54002548311540
C	7.60552207198695	10.41166001881284	0.84177784260460
C	10.21884139001243	9.36843658780262	5.04850683596873
C	4.80278056543475	8.94763813178634	5.59862850448773
C	5.12275970708655	8.06109789363763	6.64802571445238
C	4.16548911261628	7.13360032436958	7.06616431605096
C	2.91655934426857	7.07884208382702	6.47690278061166
C	2.60016471986949	7.97138041154778	5.46568955737147
C	3.52417207767644	8.91889813745538	5.02137247374823

C	6.45290799229944	8.13186526489186	7.34422730686657
C	3.12472728633345	9.90090769367336	3.94210317733229
C	7.82229529061406	14.91071030534822	5.53290949481535
C	4.81733129407427	14.38009374190232	5.91325009650436
C	6.02542896599561	14.66299644879490	3.11885454716472
C	6.82012544852911	5.72759244979713	3.48656038616497
C	5.85597567819622	5.21325473326625	2.58901100706347
C	5.70783588644211	3.84577211567160	2.32863893633684
C	6.53005545033620	2.89163541820277	2.93605710555229
C	7.50518141539096	3.37296558407383	3.81445592297670
C	7.63935969203925	4.73887422853439	4.08167718446824
C	4.93969611560462	6.18385571278518	1.89471683503186
C	5.47305585567275	7.06665048612798	0.92953565969427
C	4.62246161580211	7.99968401737964	0.32365399597547
C	3.28561437645467	8.05798185889991	0.64916942734888
C	2.76298278857686	7.17602611443179	1.57479214309186
C	3.57090247582817	6.23207156233832	2.20502727259687
C	6.91322780769540	6.97951842592149	0.51061303377097
C	2.95453666992177	5.26236448528439	3.18076738274328
C	8.72100115963777	5.17125414741154	5.02719198734871
C	8.50222114070676	5.15359076812755	6.41735722452310
C	9.51716670296475	5.58349367569416	7.26931139725153
C	10.74476171495377	5.98101431557967	6.77175367772473
C	10.96812579106252	5.97137390812566	5.40655593837175
C	9.96693315531860	5.57725888905527	4.51821649745859
C	7.19117822694004	4.64560789321984	6.96869637027622
C	10.22420503326064	5.55105267041488	3.03161599960503
C	7.89024491966957	0.31081713176036	1.98283339797104
C	4.88565017885400	0.73961401264910	1.52381292642008
C	5.98703178223463	0.24767663883207	4.33319859143397
H	8.37735178844410	12.35180466609264	3.54611058337123
H	4.85518603019304	11.61344417423418	5.87640361323598
H	9.81868642093049	9.38333771395296	-0.32857311800677
H	11.87440021095782	8.53283807154559	0.76505350239988
H	12.04801822531653	8.54508356500924	3.22765006035794
H	6.70571333083746	9.89960248167219	1.18909608334508
H	7.67760360351038	10.30180498215947	-0.24124345826343
H	7.47134210239838	11.46927587554270	1.08053939550224
H	9.86882206177370	10.31821230603519	5.45574794470332
H	11.25352233649121	9.20491747538634	5.35050203017997
H	9.62238628121803	8.58812865269334	5.53336919809965
H	4.41671368303683	6.44907378649657	7.86967896528964
H	2.18744694947781	6.34753223085637	6.80586538186561
H	1.61920377559590	7.93979638687779	5.00338969940738
H	7.27113128287277	7.91313101344888	6.65525360364666
H	6.49939860122137	7.42511713122393	8.17310360731724
H	6.63917207737280	9.13845543613585	7.72576765199710
H	2.81202144739566	10.84766500527489	4.39234686966693
H	2.28997091721634	9.50414266570568	3.36345133681675

H	3.95001053293792	10.12575338221534	3.26626312989721
H	8.01335189538377	14.64170715508361	6.57494433303238
H	7.70251932408036	15.99669390062433	5.47698122009409
H	8.71162053773784	14.64652066730307	4.95483045212892
H	3.93317998244683	13.88765791535465	5.49976372967789
H	4.60613319919486	15.45139468477709	5.96400033569683
H	4.95774760069048	14.01633727483851	6.93473087087444
H	5.72664804117744	15.71490333611943	3.10103782240150
H	5.23964751374420	14.08124538833752	2.63069322729709
H	6.93249279714524	14.55908136925745	2.51746744195429
H	4.93424962738250	3.52840421831254	1.63474038825010
H	8.18009359827708	2.67739317158274	4.31044881925610
H	5.03257074977950	8.68030438553045	-0.41486408568580
H	2.64258589834581	8.79175407070811	0.17677716165622
H	1.70877081030818	7.21960823575630	1.82899070405811
H	7.58319719541096	7.34808861144133	1.28978949584478
H	7.08724985870938	7.57639681571934	-0.38519739662211
H	7.20251097155866	5.94543059662599	0.31410636346590
H	2.62426611653428	4.35783036802290	2.66079354421897
H	2.08345453010048	5.70929619621834	3.66156249563841
H	3.66308095043335	4.95376620324883	3.94863374125054
H	9.34123559987311	5.57797923092303	8.34019195549011
H	11.52973714369585	6.29804148217714	7.44852682557257
H	11.93206553091056	6.27135653411780	5.01112908779519
H	6.35395943373691	5.19168058790041	6.52789785311232
H	7.15598035313111	4.75891984019016	8.05338410239343
H	7.04250816396083	3.59273511985067	6.71880502927922
H	10.15346045665583	4.52944420891609	2.64913237695366
H	11.21058150094230	5.94956375005116	2.79820232820947
H	9.48770489366047	6.12838191487795	2.46645755261726
H	8.17361771646282	0.79288833309929	1.04390267671890
H	7.78292264469062	-0.76061112252949	1.79298987087173
H	8.71827587505872	0.44572012166317	2.68402681792277
H	3.95453449213616	1.12516276502320	1.94769470587918
H	4.75266199657511	-0.32953358938416	1.34073952961559
H	5.04204264740793	1.22519280687897	0.55684693558864
H	6.87098181649962	0.30160947402867	4.97452877851706
H	5.70913516961864	-0.80489233690659	4.22961883604479
H	5.17271007963375	0.76022653391434	4.85183199793186
Li	7.99798867652201	7.49872516480592	3.98987140445424
Li	5.68939015887374	7.57311625280661	3.79223939154160

S5.3.3. [H-Ar$^{\#}$-Li]$_2$ (3)

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Li	5.82312255831890	5.98134047528585	-0.36756021208942
Li	4.97923645892396	4.64513227368087	1.30186615999263
C	3.91522224478239	6.40356055437784	0.55579684975824

C	3.99017048308419	7.80569615790542	0.38557013011732
C	2.88554987663874	8.65223168979582	0.32194872537093
C	1.61127973324588	8.10251398357534	0.44658598961361
C	1.46362610520521	6.73448212876830	0.63644108523460
C	2.59437199412900	5.91246258918249	0.68864197949153
C	2.41322248735403	4.42997534826949	0.95123595491270
C	2.28622947582882	3.53710957521152	-0.10662181848035
C	2.19924704244206	2.17244264780541	0.14235627434568
C	2.23946380619581	1.70043771639510	1.44919136219712
C	2.36645700943425	2.59309847022277	2.50704920725139
C	2.45343924315291	3.95797039786584	2.25807204021884
C	2.52347962991787	4.91873262865411	3.42036550402406
C	2.16413072381387	4.05634942822931	-1.52342784304198
C	5.35718724174115	8.43659999530250	0.26765226135446
C	6.08262260506299	8.71957157503882	1.42267466665451
C	7.35003191556765	9.30119840684648	1.34757310752970
C	7.88580856627559	9.61425833105907	0.13141678148454
C	7.17681386577277	9.35188670459863	-1.01470445282973
C	5.91355179346828	8.76613824526876	-0.97707771288868
C	5.10991883692434	8.55304507514691	-2.24207204419826
C	5.47672961624165	8.44146999439338	2.77248613872760
C	6.92802709831715	4.30157541783670	0.37153194898811
C	7.55703682742792	3.98200350714894	-0.85392172146982
C	8.81384994690990	3.37145782500830	-0.92840951855589
C	9.48082174556344	3.01157148398640	0.23086055540256
C	8.89633215277346	3.26676187107866	1.45668127707063
C	7.65781351722586	3.91210708003002	1.51973999915820
C	7.04748526261431	4.18973805862583	2.86368950483352
C	7.40378702661115	5.32417730467532	3.59609987970780
C	6.76415371948936	5.57025522746039	4.81044623258622
C	5.79885047301697	4.72082445940685	5.28985642015827
C	5.45507194674254	3.59628469801473	4.58699200856462
C	6.07601680903067	3.30511243418699	3.37454803044212
C	5.73878874027058	2.02640524961879	2.64187180114249
C	8.47936262991869	6.25047989552882	3.08816839922795
C	6.82267659945920	4.30330624203402	-2.12821088991388
C	5.75758220838263	3.47825165077487	-2.54393357445208
C	5.03566477535854	3.81688895836742	-3.69021771502175
C	5.34182035993032	4.94884878061880	-4.41603406013992
C	6.39480599528236	5.75453914368559	-4.02254859821748
C	7.15232069851829	5.44001363065005	-2.89244270874773
C	8.34008912004242	6.30181131067958	-2.52300970298509
C	5.40356266413113	2.22069816611818	-1.78286538222738
H	3.01469957757946	9.72113230860805	0.18630234056911
H	0.73569374364168	8.74092510651562	0.40150070553299
H	0.47303306246333	6.30531476031831	0.75137127488928
H	2.08913129811456	1.48085691453293	-0.68547438568579
H	2.17146941503305	0.63571858025539	1.64377445558604
H	2.38097873767379	2.23098260413029	3.52900849423030

H	3.48150254947961	5.44346661929281	3.47086981295395
H	2.38770985583812	4.38640375433343	4.36180313429967
H	1.75806930157217	5.69182786137766	3.33337396416509
H	1.33119865038726	4.75709019243985	-1.60925330058639
H	2.00361445849661	3.23457562716340	-2.22219413777143
H	3.06242836316324	4.59732581249556	-1.82720846936903
H	7.88943432304980	9.51336772900338	2.26388427803990
H	8.86805996552556	10.06821383845868	0.06344513128948
H	7.60037052464001	9.61381120281325	-1.97950793894929
H	4.70992217783319	7.53988587699198	-2.32268985837358
H	5.72461938929346	8.74876374189598	-3.12175300165444
H	4.24824613774004	9.22417845220536	-2.26816426996484
H	4.55952122827206	9.01963156251732	2.90853710690589
H	6.17179849616453	8.70624769294484	3.56998949559937
H	5.19824235246123	7.39203903887361	2.88505606916382
H	9.25368918831273	3.15452978301322	-1.89769912217479
H	10.44773491975471	2.52433368855636	0.17493138184075
H	9.39930675100485	2.97015807131064	2.37286199210324
H	7.04071738881195	6.45321435613229	5.37733746479223
H	5.31027844744769	4.94355890324234	6.23194055938285
H	4.70687321648459	2.91263177721873	4.97428509290155
H	5.11090120605703	2.18905355295474	1.75960708007540
H	5.19348891606088	1.34602948664773	3.29615214868598
H	6.64402284033278	1.53579512218092	2.28048024082456
H	8.48105973300199	7.18428485479808	3.65034803606547
H	8.33721306121715	6.47654494261255	2.03063074300121
H	9.46365177713389	5.78608596139560	3.19490753837162
H	4.22071719418899	3.17345840387129	-4.00401542080523
H	4.76185389251987	5.20931978463376	-5.29402668539876
H	6.64592756296305	6.63875709165406	-4.59788929968861
H	9.27255935615472	5.79101594181724	-2.77786142810627
H	8.38817826388138	6.51892593230455	-1.45382946241486
H	8.31332950851358	7.24668736728034	-3.06523208353685
H	6.13602041855221	1.43520791671285	-1.99341806580963
H	4.41919275237073	1.85487532594867	-2.07195638687377
H	5.41938036627326	2.38986567013103	-0.70626254440871

S5.3.4. [Cl-Ar$^{\#}$-Li]$_2$ (4)

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Cl	2.99609094007978	13.77396468882212	0.54196545884590
Cl	1.51815820555382	3.78026370516437	8.42856023951192
C	2.59170552292269	10.02366770270422	3.15026536190377
C	3.67796538914598	10.22691339427076	2.26056750541063
C	3.81372528785359	11.37071859987854	1.46999404603925
C	2.84121042588843	12.33992661039082	1.52444730512797
C	1.74692762906150	12.21078969351586	2.36664865593304
C	1.64652040165813	11.07238688372907	3.15626884758906

C	4.73937423459192	9.17697097339914	2.16878459492157
C	4.54036980113421	8.05644330953541	1.35676026301515
C	5.52504794454562	7.07883244161068	1.29198317321227
C	6.68193377614273	7.20661898134119	2.00445407480337
C	6.88700135469400	8.31875006684875	2.79622126996190
C	5.92797418655301	9.32159644970331	2.89043477186536
C	3.27915015256652	7.92872067741804	0.52357931481856
C	6.17080362959338	10.55994828947877	3.74190738303970
C	0.43926894117428	10.93458143842909	4.04030748325995
C	0.47512916425331	11.41134778761191	5.36733289841093
C	-0.66475129661738	11.25024448219670	6.16729616024572
C	-1.78957059323413	10.64585670226701	5.68552883669558
C	-1.83206811821070	10.18236209712365	4.38621393874153
C	-0.71392999729178	10.32329147639747	3.54554829230803
C	1.67865231580287	12.12346769654393	5.89464758741532
C	-0.78017334827676	9.85148828551015	2.11270870597799
C	2.28361594040890	7.04464556903182	5.31474272512719
C	1.29493993928041	6.04510451213035	5.14492117042105
C	1.03931932972063	5.05430801020272	6.08692985212901
C	1.81544456417934	5.01657939979575	7.23137603897193
C	2.82204256066647	5.93090003192312	7.45288512253513
C	3.03924465982926	6.92842046780663	6.50439279093545
C	0.49650651448488	6.02065242536280	3.87110446063417
C	1.12017097443911	5.58090146766733	2.68309633355426
C	0.38705295696756	5.58670083047792	1.49563795340667
C	-0.92151984491104	6.01378442928821	1.46178279119120
C	-1.52709163253348	6.42663337832592	2.61977603882263
C	-0.85533910819783	6.41572445299683	3.84601294643716
C	2.53190421351905	5.05118638830209	2.70099480588216
C	-1.57704568880675	6.77119152830699	5.11475772886212
C	4.18491000056792	7.88317818447440	6.75209076301527
C	3.98505251245711	9.08612245020460	7.45936467768698
C	5.07950124129020	9.94999299494396	7.66305405108123
C	6.31984582926454	9.61256316888790	7.17743215096024
C	6.51584191267193	8.45673013304324	6.49636938985423
C	5.45280636581835	7.57438207401785	6.26267005167980
C	2.63965069821885	9.38133460665805	8.04486228753898
C	5.70979105943648	6.28393638383274	5.53945814674493
H	4.66594280018511	11.49254504567532	0.81050286209225
H	0.98971480431316	12.98663302553419	2.39989411440987
H	5.36545960513935	6.21478167143448	0.65528948393636
H	7.44748304778684	6.44022849225608	1.94697368242198
H	7.81295855012458	8.42254010915772	3.35114717090054
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H	3.32600567376318	7.04194944732935	-0.10916151276532
H	3.14015858696620	8.80767948935455	-0.10949649058366
H	6.22184884607886	11.45136207968336	3.11268350336166
H	7.10346192697001	10.46524405741536	4.29680662311171
H	5.36094418271830	10.72900646400673	4.45631422778530

H	-0.64310386224658	11.62773584689914	7.18433306975985
H	-2.65840808600586	10.53105771211788	6.32497094404533
H	-2.72745659333719	9.71136915891388	3.99751533958080
H	2.53473728602274	11.44675726817634	5.97881680012350
H	1.47934822161048	12.54749471049107	6.87936641408634
H	1.99023488668036	12.92707201212066	5.22440498066259
H	-0.68914646759681	10.69451812094225	1.42365508723240
H	-1.72162059575279	9.33925554843481	1.91757963166431
H	0.03490805516938	9.16768382521935	1.85806296007059
H	0.27192756534892	4.30533205976795	5.92943969177410
H	3.43344152992634	5.86218806627353	8.34555112017788
H	0.86418566670863	5.23153448064787	0.58789724258137
H	-1.47098603302070	6.01896939739594	0.52709821458138
H	-2.56557187934050	6.74139013297929	2.60352698093065
H	3.26260268228944	5.86553348401118	2.70066147613786
H	2.71867826568664	4.43825563331968	1.81720464583482
H	2.72100113768433	4.45473981136710	3.59383804681604
H	-1.77366184782051	5.87676795123539	5.71077852631784
H	-2.53027752782999	7.25369637774985	4.89950301935163
H	-0.98782198974277	7.44108417554358	5.74533597346789
H	4.93136498880058	10.86872498968478	8.21943636618959
H	7.15699588803631	10.28279293094873	7.34631824887258
H	7.50024405458680	8.19702924628255	6.12473823816603
H	1.86029499544195	9.36941137414340	7.27878558029212
H	2.62616076739006	10.35442486603544	8.53639209160896
H	2.36180670207861	8.61930931518417	8.77723278160539
H	5.44796876967320	5.43188059103489	6.17203946251436
H	6.75723127036784	6.19706152399524	5.25317772381425
H	5.10351259349300	6.18483247367481	4.63412777815628
Li	3.60096760853413	8.50792518174555	4.35927765378778
Li	1.30937900131754	8.49886070790735	4.02525393066188

S5.3.5. $[F_3C\text{-}Ar^{\#}\text{-}Li]_2$ (5)

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C	4.87597323409663	1.94100214167327	4.53639758285435
C	4.66875846088824	5.20524707418885	3.96393913138642
C	3.85224758384208	6.24473557050926	3.45407320542683
C	2.48840336127518	6.35230760541720	3.73711738972473
C	1.87753739247540	5.39710604861478	4.53856026635856
C	2.62369432633197	4.35253449756663	5.06218642916274
C	3.98755514627454	4.27316748829272	4.78154021786797
C	4.45297244561383	7.28652011190135	2.55235141657582
C	4.80056388525484	6.94756753416856	1.23042004548398
C	5.30112685289609	7.94409300415844	0.39623124863903
C	5.47605348226114	9.22873506961536	0.83937766368260
C	5.16916894681027	9.55571666726352	2.13841334424339
C	4.65090741360222	8.59756419065265	3.01677160799478

C	4.60326652591243	5.55797546780515	0.69998509756200
C	4.31152077893739	8.97964375186820	4.43235504903897
C	4.73844857945410	3.09330993644758	5.33012717326634
C	5.26689078045554	3.11692412390276	6.63191391704003
C	5.93616945129692	1.99331251858950	7.10611342099654
C	6.07854260012031	0.86248672002151	6.33015052814034
C	5.54537582294004	0.83264153369825	5.05516998455291
C	5.07550569550676	4.31842685697131	7.52190269904883
C	4.26814466311669	1.88705089831991	3.15232192760001
C	0.40558103271788	5.46761697405901	4.77686712134205
C	8.05652187347753	1.94100464905825	2.51637526189107
C	8.26373206787972	5.20524971248063	3.08883359194130
C	9.08024148588478	6.24473921657889	3.59869979970593
C	10.44408555920152	6.35231324266750	3.31565664341865
C	11.05495286337197	5.39711275732270	2.51421350685555
C	10.30879639594585	4.35254030404151	1.99058706416736
C	8.94493568850718	4.27317130559260	2.27123325748195
C	8.47951416250140	7.28652267333246	4.50042286990851
C	8.13192420263793	6.94756924801393	5.82235414788207
C	7.63135983436710	7.94409378672164	6.65654221825908
C	7.45643040258744	9.22873572653831	6.21339715122481
C	7.76331547416966	9.55571811015011	4.91436155452017
C	8.28157835240020	8.59756659751607	4.03600303262127
C	8.32922352100971	5.55797731650182	6.35278872040453
C	8.62096444927555	8.97964701824872	2.62041969463417
C	8.19404491013313	3.09331285219619	1.72264598391137
C	7.66560167349743	3.11692665483959	0.42085924840857
C	6.99632557260187	1.99331423672030	-0.05334055839850
C	6.85395300806161	0.86248803197302	0.72262202830554
C	7.38712083062850	0.83264324580179	1.99760256331471
C	7.85698507055928	4.31842989819058	-0.46912920767378
C	8.66435051987382	1.88705388328900	3.90045090264162
C	12.52690912356988	5.46762580991867	2.27590567186634
H	1.90302311211355	7.16175470181939	3.31390854795562
H	2.14454654656281	3.59797213627069	5.67690610238520
H	5.55849367865781	7.68544153978550	-0.62575885319301
H	5.86713403859935	9.98568039226796	0.16901550028732
H	5.31483649351670	10.56748309765120	2.49957878858099
H	5.35463723773783	4.86879852040720	1.09656072800290
H	4.68214036149498	5.54695143464535	-0.38754874733538
H	3.63126719810166	5.15571429103246	0.99134696935424
H	3.23303885117544	8.96850266573552	4.60628237275970
H	4.68792822739948	9.97629712973368	4.66056399589170
H	4.74883197197150	8.27971833680480	5.14843292945802
H	6.34910196556726	2.01451893700986	8.10898920988497
H	6.59949020023784	-0.00266711150267	6.72445301821775
H	5.63508872072296	-0.05960491919974	4.44577875082453
H	5.35492078796779	5.24015409341704	7.00745726609200
H	5.67177498136282	4.22132616930833	8.42867500317942

H	4.02714465893193	4.42836599936901	7.81134576196918
H	3.27616037054575	2.33894874312637	3.13852335756345
H	4.19836337178037	0.85595316193902	2.80597035050120
H	4.86793831552703	2.42569053192399	2.41087370727086
H	11.02946711021120	7.16175550557067	3.73887231407168
H	10.78794191037426	3.59797780040939	1.37586712175820
H	7.37400750003090	7.68545348652604	7.67853667471427
H	7.06536863799207	9.98567416572403	6.88377531382164
H	7.61763842613763	10.56747974673549	4.55319194140585
H	7.57782093691521	4.86879621600535	5.95627483515265
H	8.25040606376316	5.54697715022100	7.44032798526484
H	9.30120373465493	5.15570212662869	6.06138542328240
H	9.69944202065565	8.96843071623957	2.44647650967800
H	8.24461497310143	9.97632503111249	2.39222691609414
H	8.18358693910288	8.27974474513336	1.90435786425159
H	6.58340426453430	2.01453151289026	-1.05622107760343
H	6.33297241232350	-0.00265221191229	0.32833607399530
H	7.29737259699138	-0.05958196001416	2.60701573706003
H	7.57762670686842	5.24015941991635	0.04534531359827
H	7.26067598009338	4.22136113437144	-1.37587903361643
H	8.90533796356850	4.42833052382561	-0.75862118463856
H	9.65638291275210	2.33885060607031	3.91421777986526
H	8.73402142384398	0.85597236883901	4.24686799611694
H	8.06462735938732	2.42581688357606	4.64186893129382
Li	6.46624446121090	6.35067039263854	3.52638701669329
Li	6.46624609682617	4.01735639529367	3.52638670153903
F	-0.29861062003720	5.33052662399958	3.68333140084852
F	0.07667477067021	6.70962468881286	5.14566553868343
F	-0.03972862263262	4.71723053493785	5.70437337333291
F	13.23109997164856	5.33053615544375	3.36944235215823
F	12.85581364631986	6.70963408518434	1.90710759101187
F	12.97221982849347	4.71724024087575	1.34840021523413

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