

Supporting Information

**Diphenylacetylene Stabilised Alkali-Metal Nickelates: Synthesis, Structure
and Catalytic Applications**

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Table of Contents

Experimental	3
General Considerations	3
Synthesis of Organolithiums	3
Synthesis of 4- ^t Bu-C ₆ H ₄ -Li	3
Synthesis of 1-Naph-Li	4
Synthesis of <i>o</i> -Tol-Li	4
Synthesis of 2,6-Me ₂ -C ₆ H ₃ -Li	5
Synthesis of 2,2'-Dilithiobiphenyl	5
Synthesis of Known Nickel Complexes	6
Synthesis of [(COD)Ni] ₂ {μ ₂ :η ² ,η ² -Ph-C≡C-Ph}	6
Synthesis of Ni ₂ (COT) ₂	6
Synthesis of Alkali-Metals Nickelates	6
Synthesis of Li ₂ (Et ₂ O) ₄ Ph ₄ Ni ₂ {μ ₂ :η ² ,η ² -Ph-C≡C-Ph}, 1a	7
Synthesis of Na ₂ (THF) ₆ Ph ₄ Ni ₂ {μ ₂ :η ² ,η ² -Ph-C≡C-Ph}, 1b	7
Synthesis of K ₄ (THF) ₄ Ph ₄ Ni ₂ {μ ₂ :η ² ,η ² -Ph-C≡C-Ph}, 1c	8
Synthesis of Li ₂ (Et ₂ O) ₄ (4- ^t Bu-C ₆ H ₄) ₄ Ni ₂ {μ ₂ :η ² ,η ² -Ph-C≡C-Ph}, 1d	9
Crystallisation of Li ₂ (Et ₂ O) ₄ (<i>o</i> -Tol) ₄ Ni ₂ {μ ₂ :η ² ,η ² -Ph-C≡C-Ph}, 1e	10
Crystallisation of Li ₂ (THF) ₆ (1-Naph) ₄ Ni ₂ {μ ₂ :η ² ,η ² -Ph-C≡C-Ph}, 1f	10
Synthesis of Li ₂ (THF) ₂ (<i>o</i> -Tol) ₂ Ni{η ² -Ph-C≡C-Ph}, 2a	11
Synthesis of Li ₂ (Et ₂ O) ₂ (1-Naph) ₂ Ni{η ² -Ph-C≡C-Ph}, 2b	11
Synthesis of Li ₂ (Et ₂ O) ₂ (2,6-Me ₂ -C ₆ H ₃) ₂ Ni{η ² -Ph-C≡C-Ph}, 2c	12
Synthesis of Li ₂ (THF) ₄ (2,2'-biphenyl)Ni{η ² -Ph-C≡C-Ph}, 2d	13
NMR Spectroscopy Studies	14
[(COD)Ni] ₂ {μ ₂ :η ² ,η ² -Ph-C≡C-Ph} + PhLi	14
Variable Temperature NMR Spectroscopy of 1d	14
Catalytic Reactions	16
Cyclotrimerisation of Diphenylacetylene	16
Cyclotrimerisation of Phenylacetylene	18
Insertion of Diphenylacetylene into Biphenylene	19
X-ray Crystallography	20
Molecular Structure of Li ₂ (Et ₂ O) ₄ Ph ₄ Ni ₂ {μ ₂ :η ² ,η ² -Ph-C≡C-Ph}, 1a	25
Molecular Structure of Na ₂ (THF) ₆ Ph ₄ Ni ₂ {μ ₂ :η ² ,η ² -Ph-C≡C-Ph}, 1b	25
Molecular Structure of Li ₂ (Et ₂ O) ₄ (4- ^t Bu-C ₆ H ₄) ₄ Ni ₂ {μ ₂ :η ² ,η ² -Ph-C≡C-Ph}, 1d	26
Molecular Structure of Li ₂ (Et ₂ O) ₄ (<i>o</i> -Tol) ₄ Ni ₂ {μ ₂ :η ² ,η ² -Ph-C≡C-Ph}, 1e	26
Molecular Structure of Li ₂ (THF) ₆ (1-Naph) ₄ Ni ₂ {μ ₂ :η ² ,η ² -Ph-C≡C-Ph}, 1f	27
Molecular Structure of Li ₂ (Et ₂ O) ₂ (2,6-Me ₂ -C ₆ H ₃) ₂ Ni{η ² -Ph-C≡C-Ph}, 2c	27
Molecular Structure of Li ₂ (THF) ₄ (2,2'-biphenyl)Ni{η ² -Ph-C≡C-Ph}, 2d	28
NMR Spectra of Reported Compounds	29
References	49

Experimental

General Considerations

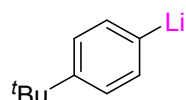
All manipulations were carried out under an inert atmosphere of argon using standard Schlenk line¹ or glovebox techniques (MBraun UNILab Pro ECO, <0.1 ppm H₂O and O₂). Due to the extreme air, moisture, and often temperature sensitivity of described compounds, rigorously inert conditions must be maintained to allow for the isolation of crystalline and pure samples. All manipulations, except for the preparation of starting materials, must avoid the use of Teflon-coated stir bars and Teflon cannulae, and glass-coated stir bars should be used. Specific experimental details can be found below. THF was dried and distilled from Na/benzophenone and stored over 4 Å molecular sieves, then further dried and vacuum distilled over NaK_{2.8} or a sodium mirror. Hexane, pentane, Et₂O, toluene and benzene were pre-dried using a MBraun MBSPS 5, then further dried and vacuum distilled over NaK_{2.8} or a sodium mirror, and stored over 4 Å molecular sieves. (Me₃Si)₂O was dried and distilled over CaH₂ and stored over 4 Å molecular sieves. THF-d₈ and C₆D₆ were dried and distilled over NaK_{2.8} and stored over 4 Å molecular sieves in a glovebox prior to use. Li₄(Et₂O)₄(C≡C-Ph)₄Ni₂{μ₂:η²,η²-Ph-C≡C-Ph} was prepared as previously described.² Ni(COD)₂ was purchased from Sigma-Aldrich. Diphenylacetylene was dried *in vacuo* prior to use. All other reagents were used as supplied.

NMR spectra were recorded on Bruker Avance III HD 300 MHz or 400 MHz spectrometers at 300 K unless otherwise specified. ¹H NMR spectra were referenced internally to the corresponding residual *protio* solvent peaks. CHN elemental microanalyses were performed on a Flash 2000 Organic Elemental Analyser (Thermo Scientific). Samples were prepared and crimped in tin capsules in an argon filled glovebox. Analyses were performed in triplicate, and reference standards (e.g. nicotinamide) were measured prior to use as controls.

Synthesis of Organolithiums

PhLi and PhNa were prepared as previously reported.^{3,4} All other organolithiums were prepared *via* lithium-halogen exchange of the corresponding commercially available iodo- or bromo-arenes and isolated as solids which were stored in a glovebox freezer (-30 °C). When performing the reactions with bromoarenes, it was found that the addition of Et₂O was necessary to precipitate the product from hexane solution.

Synthesis of 4-^tBu-C₆H₄-Li



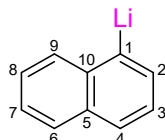
4-*tert*-Butyl-iodobenzene (1.8 mL, 10 mmol) was dissolved in hexane (30 mL) and cooled to -78 °C. ⁿBuLi (1.6 M, 6.25 mL, 10 mmol) was added dropwise and the reaction mixture was then slowly warmed to room temperature and stirred for 1 hour to give a colourless suspension. The solids were collected on a glass frit, washed with pentane (2 × 7.5 mL) and dried *in vacuo*. Yield – 1.37 g (98%).

$^1\text{H NMR}$ (300.1 MHz, 5:1 $\text{C}_6\text{D}_6/\text{THF-d}_8$): δ 8.29 (d, $J = 7.7$ Hz, 2H, $o\text{-CH}$), 7.37 (d, $J = 7.7$ Hz, 2H, $m\text{-CH}$), 1.40 (s, 9H, $^t\text{Bu-C}(\text{CH}_3)_3$).

$^7\text{Li NMR}$ (116.6 MHz, 5:1 $\text{C}_6\text{D}_6/\text{THF-d}_8$): δ 2.21 (s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, 5:1 $\text{C}_6\text{D}_6/\text{THF-d}_8$): δ 177.4 (s, $ipso\text{-C}$), 146.4 (s, $\text{C-}^t\text{Bu}$), 143.5 (s, $o\text{-CH}$), 122.8 (s, $m\text{-CH}$), 34.7 (s, $^t\text{Bu-C}(\text{CH}_3)_3$), 32.3 (s, $^t\text{Bu-C}(\text{CH}_3)_3$).

Synthesis of 1-Naph-Li



1-Bromonaphthalene (1.4 mL, 10 mmol) was dissolved in hexane (30 mL) and cooled to -78 °C. $^n\text{BuLi}$ (1.6 M, 6.25 mL, 10 mmol) was added dropwise and the reaction mixture was then slowly warmed to room temperature and stirred for 1 hour to give a colourless solution. Et_2O (2.5 mL) was slowly added leading to the precipitation of a colourless solid. After stirring for an additional 30 minutes at room temperature, the solids were collected on a glass frit, washed with hexane (2×7.5 mL) and dried *in vacuo*. Yield – 1.125 g (72%).

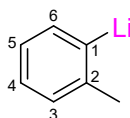
$^1\text{H NMR}$ spectroscopy indicates 0.3 equivalents of coordinated Et_2O .

$^1\text{H NMR}$ (300.1 MHz, 5:1 $\text{C}_6\text{D}_6/\text{THF-d}_8$): δ 8.57 (d, $J = 6.0$ Hz, 1H, H_9), 8.47 (d, $J = 8.1$ Hz, 1H, H_2), 7.87 (d, $J = 7.9$ Hz, 1H, H_7), 7.74 (d, $J = 7.9$ Hz, 1H, H_8), 7.57–7.46 (m, 2H, $H_{3,4}$), 7.40 (dt, $J = 1.1, 7.8$ Hz, 1H, H_6), 3.26 (q, Et_2O), 1.08 (t, Et_2O).

$^7\text{Li NMR}$ (116.6 MHz, 5:1 $\text{C}_6\text{D}_6/\text{THF-d}_8$): δ 2.40 (s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, 5:1 $\text{C}_6\text{D}_6/\text{THF-d}_8$): δ 192.8 (s, C1), 148.8 (s, C10), 141.3 (s, C9), 138.3 (s, C2), 134.1 (s, C5), 129.3 (s, C7), 124.8 (s, C4), 124.4 (s, C8), 123.9 (s, C6), 122.9 (s, C3), 66.2 (s, Et_2O), 15.9 (s, Et_2O).

Synthesis of *o*-Tol-Li



2-Bromotoluene (1.2 mL, 10 mmol) was dissolved in hexane (30 mL) and cooled to -78 °C. $^n\text{BuLi}$ (1.6 M, 6.25 mL, 10 mmol) was added dropwise and the reaction mixture was then slowly warmed to room temperature and stirred for 2 hours to give a colourless solution. Et_2O (2.5 mL) was slowly added leading to the precipitation of a colourless solid. After stirring for an additional hour at room temperature, the solids were collected on a glass frit, washed with hexane (2×7.5 mL) and dried *in vacuo*. Yield – 0.76 g (78%).

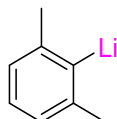
$^1\text{H NMR}$ spectroscopy indicates 1% residual coordinated Et_2O .

^1H NMR (300.1 MHz, 5:1 $\text{C}_6\text{D}_6/\text{THF-d}_8$): δ 8.26–8.19 (m, 1H, H6), 7.37–7.22 (m, 3H, H3,4,5), 2.78 (s, 3H, CH₃).

^7Li NMR (116.6 MHz, 5:1 $\text{C}_6\text{D}_6/\text{THF-d}_8$): δ 2.03 (s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, 5:1 $\text{C}_6\text{D}_6/\text{THF-d}_8$): δ 183.9 (s, C1), 151.0 (s, C2), 143.5 (s, C6), 125.5, 125.3, 123.1 (s, C4), 29.5 (s, CH₃).

Synthesis of 2,6-Me₂-C₆H₃-Li



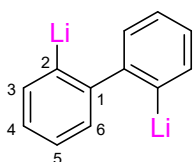
2-Iodo-1,3-dimethylbenzene (1 mL, 6.9 mmol) was dissolved in hexane (20 mL) and cooled to $-78\text{ }^\circ\text{C}$. $n\text{BuLi}$ (1.6 M, 4.3 mL, 6.9 mmol) was added dropwise and the reaction mixture was then slowly warmed to room temperature and stirred for 1 hour to give a colourless suspension. The solids were collected on a glass frit, washed with hexane ($2 \times 5\text{ mL}$) and dried *in vacuo*. Yield – 723 mg (93%).

^1H NMR (300.1 MHz, 5:1 $\text{C}_6\text{D}_6/\text{THF-d}_8$): δ 7.38–7.32 (m, 1H, p-CH), 7.30–7.25 (m, 2H, m-CH), 2.95 (s, 6H, o-CH₃). AA'B spin system.

^7Li NMR (116.6 MHz, 5:1 $\text{C}_6\text{D}_6/\text{THF-d}_8$): δ 2.72 (s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, 5:1 $\text{C}_6\text{D}_6/\text{THF-d}_8$): δ 181.2 (s, ipso-C), 150.3 (s, C-CH₃), 126.1 (s, p-CH), 123.2 (s, m-CH), 29.1 (s, C-CH₃).

Synthesis of 2,2'-Dilithiobiphenyl



Adapted from literature procedures.⁵ 2,2'-Dibromobiphenyl (1.248 g, 4 mmol) was dissolved in hexane (40 mL) and cooled to $-78\text{ }^\circ\text{C}$. $n\text{BuLi}$ (1.6 M, 5.25 mL, 8.4 mmol) was added dropwise and the reaction was maintained at $-78\text{ }^\circ\text{C}$ for 1 hour then warmed to room temperature and stirred for 48 hours to give a colourless suspension. The solids were collected on a glass frit, washed with hexane ($2 \times 10\text{ mL}$) and dried *in vacuo*. Yield – 610 mg (92%).

Samples may contain small amounts of the mono-lithiated species which can be removed by recrystallisation from THF (5 mL per 100 mg; 54% recovery as $\text{THF}_{1.75}$ solvate).

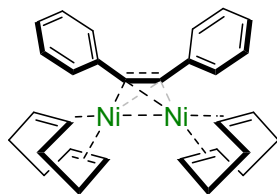
^1H NMR (300.1 MHz, THF-d_8): δ 8.00–7.91 (m, 4H, H3 + H6), 7.11 (t, $J = 7.0\text{ Hz}$, 2H, H5), 6.87 (t, $J = 7.0\text{ Hz}$, 2H, H4), 3.62 (m, THF), 1.78 (m, THF).

^7Li NMR (116.6 MHz, THF-d_8): δ 2.18 (s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, THF- d_8): δ 176.0 (br, $\underline{\text{C2}}$), 156.5 ($\underline{\text{C1}}$), 143.9 ($\underline{\text{C3}}$), 127.0 ($\underline{\text{C5}}$), 124.1 ($\underline{\text{C4}}$ + $\underline{\text{C6}}$), 68.4 (THF), 26.6 (THF).

Synthesis of Known Nickel Complexes

Synthesis of $[(\text{COD})\text{Ni}]_2\{\mu_2:\eta^2,\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$

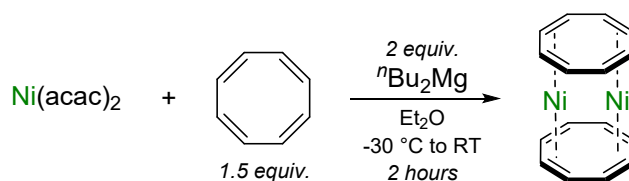


$[(\text{COD})\text{Ni}]_2\{\mu_2:\eta^2,\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$ was prepared according to literature procedures.⁶ The previously missing $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopic data is provided for completeness.

^1H NMR (300.1 MHz, C_6D_6): δ 7.46 (d, $J = 7.7$ Hz, 4H, $o\text{-CH}$), 7.21 (t, $J = 7.3, 7.7$ Hz, 4H, $m\text{-CH}$), 7.06 (t, $J = 7.3$ Hz, 2H, $p\text{-CH}$), 5.17 (m, 4H, COD- $\underline{\text{CH}}$), 4.79 (m, 4H, COD- $\underline{\text{CH}}$), 2.35–2.19 (m, 4H, COD- $\underline{\text{CH}_2}$), 2.06–1.93 (m, 4H, COD- $\underline{\text{CH}_2}$), 1.90–1.80 (m, 4H, COD- $\underline{\text{CH}_2}$), 1.80–1.68 (m, 4H, COD- $\underline{\text{CH}_2}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): δ 142.3 ($ipso\text{-}\underline{\text{C}}$), 129.1 ($o\text{-}\underline{\text{CH}}$), 127.1 ($m\text{-}\underline{\text{CH}}$), 124.2 ($p\text{-}\underline{\text{CH}}$), 106.9 ($\text{Ph-}\underline{\text{C}}\equiv\text{C-Ph}$), 100.5 (COD- $\underline{\text{CH}}$), 97.2 (COD- $\underline{\text{CH}}$), 31.3 (COD- $\underline{\text{CH}_2}$), 30.5 (COD- $\underline{\text{CH}_2}$).

Synthesis of $\text{Ni}_2(\text{COT})_2$



Freshly sublimed and finely ground anhydrous $\text{Ni}(\text{acac})_2$ (1.028 g, 4 mmol) and cyclooctatetraene (0.7 mL, 6 mmol, 1.5 equiv) were combined in Et_2O (20 mL) and cooled to -30 °C. $n\text{Bu}_2\text{Mg}$ (16 mL, 0.5M, 8 mmol, 2 equiv) was added dropwise and the reaction mixture was allowed to warm to room temperature and stir for 2 hours. Over the course of the reaction, the green $\text{Ni}(\text{acac})_2$ is consumed and a tan solid precipitates from solution. The supernatant was removed *via* filter cannula and the solids were washed with Et_2O (2×10 mL) and dried *in vacuo*. Yield – 642 mg (98%).

$\text{Ni}_2(\text{COT})_2$ is poorly soluble in most organic solvents. Ni_2COT_2 is pyrophoric!

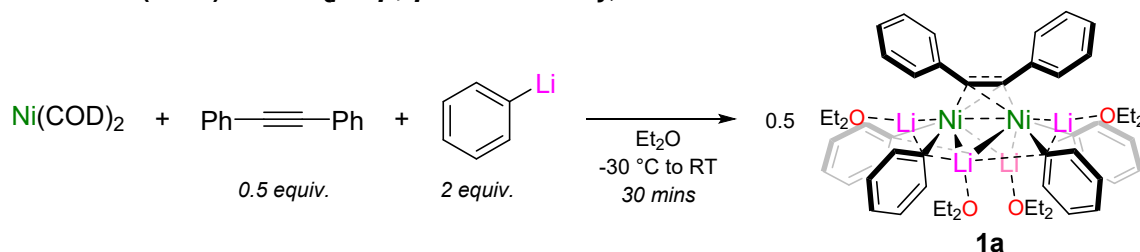
^1H NMR (300.1 MHz, C_6D_6): δ 4.64 (s, $\underline{\text{CH}}$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): δ 79.2 (s, $\underline{\text{CH}}$).

Synthesis of Alkali-Metals Nickelates

All alkali-metal nickelates were prepared in an argon filled glovebox using glass-coated stir bars unless otherwise specified. This is due to their propensity to decompose when placed under prolonged vacuum (due to facile desolvation), as well as their reaction towards PTFE (stir bars and cannulae) which limits manipulation using standard Schlenk line techniques.

Synthesis of $\text{Li}_2(\text{Et}_2\text{O})_4\text{Ph}_4\text{Ni}_2\{\mu_2:\eta^2,\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$, **1a**



$\text{Ni}(\text{COD})_2$ (138 mg, 0.5 mmol) and diphenylacetylene (45 mg, 0.25 mmol, 0.5 equiv) were combined in Et_2O (5 mL) and stirred at room temperature for 15 minutes. The resulting ruby/purple solution was cooled to $-30\text{ }^\circ\text{C}$ in a glovebox freezer then PhLi (84 mg, 1 mmol, 2 equiv) was added. The deep red reaction mixture was warmed to room temperature, stirred for 30 minutes, then evaporated to dryness. The residues were washed with hexane (1 mL) then extracted into hexane (1 mL) and Et_2O (2.5 mL), filtered through a glass wool plug and stored at $-30\text{ }^\circ\text{C}$ for 1 week affording a crop of dark red crystals. The supernatant was decanted, and the solids were washed with cold pentane ($2 \times 0.5\text{ mL}$) and dried under argon. Yield – 96 mg (41%). The crystals obtained *via* this method were suitable for single-crystal X-ray diffraction studies.

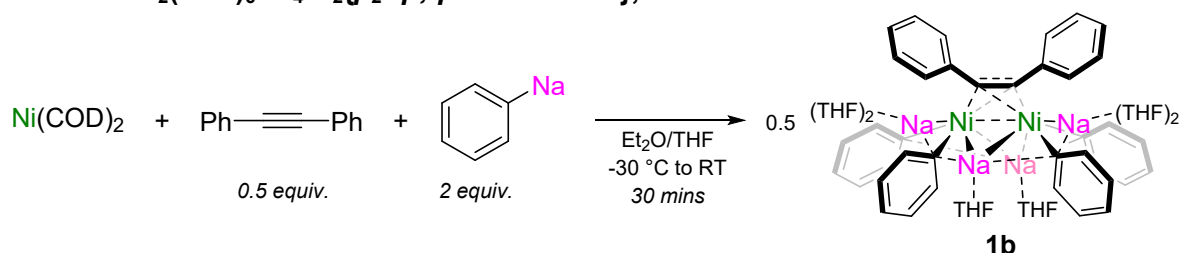
^1H NMR (300.1 MHz, C_6D_6): δ 8.35 (d, $J = 6.6\text{ Hz}$, 8H, $\text{Ph-Ni-}o\text{-CH}$), 7.60 (m, 4H, $\text{Ph-C}\equiv\text{C-Ph-}o\text{-CH}$), 7.20 (t, $J = 7.4, 7.7\text{ Hz}$, 4H, $\text{Ph-C}\equiv\text{C-Ph-}m\text{-CH}$), 7.06–6.97 (m, 8H + 2H, $\text{Ph-Ni-}m\text{-CH}$ and $\text{Ph-C}\equiv\text{C-Ph-}p\text{-CH}$), 6.81 (m, 4H, $\text{Ph-Ni-}p\text{-CH}$), 2.76 (q, Et_2O), 0.71 (t, Et_2O).

^7Li NMR (116.6 MHz, C_6D_6): δ 0.66 (br).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): δ 182.0 ($\text{Ph-Ni-}ipso\text{-C}$), 151.3 ($\text{Ph-C}\equiv\text{C-Ph-}ipso\text{-C}$), 143.4 ($\text{Ph-Ni-}o\text{-CH}$), 128.9 ($\text{Ph-C}\equiv\text{C-Ph-}m\text{-CH}$), 128.5 ($\text{Ph-Ni-}m\text{-CH}$), 127.9 ($\text{Ph-C}\equiv\text{C-Ph-}o\text{-CH}$), 123.0 ($\text{Ph-Ni-}p\text{-CH}$), 120.3 ($\text{Ph-C}\equiv\text{C-Ph-}p\text{-CH}$), 71.2 ($\text{Ph-C}\equiv\text{C-Ph}$), 65.7 (Et_2O), 14.9 (Et_2O).

Elemental Analysis: Calculated for $\text{C}_{54}\text{H}_{70}\text{Li}_4\text{Ni}_2\text{O}_4$: C, 69.87; H, 7.60. Found: C, 69.97; H, 7.36.

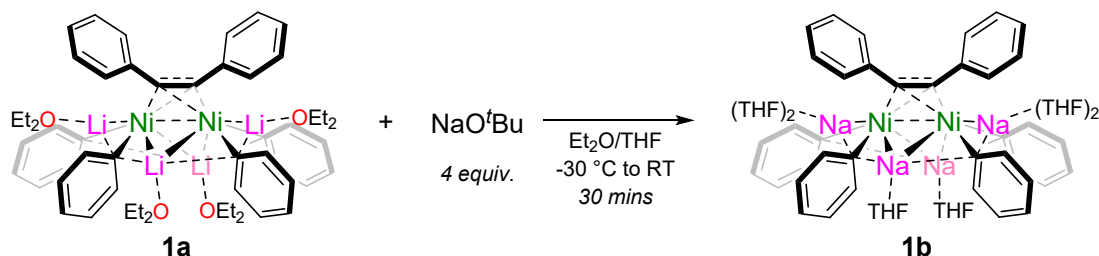
Synthesis of $\text{Na}_2(\text{THF})_6\text{Ph}_4\text{Ni}_2\{\mu_2:\eta^2,\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$, **1b**



$\text{Ni}(\text{COD})_2$ (55 mg, 0.2 mmol) and diphenylacetylene (18 mg, 0.1 mmol, 0.5 equiv) were combined in Et_2O (2 mL) and stirred at room temperature for 15 minutes. The resulting ruby/purple solution was cooled to $-30\text{ }^\circ\text{C}$ in a glovebox freezer then PhNa (40 mg, 0.4 mmol, 2 equiv) was added. The deep red reaction mixture was warmed to room temperature, stirred for 30 minutes, then filtered through a glass wool plug. THF (0.2 mL) was added to the filtrate which was then stored at $-30\text{ }^\circ\text{C}$ for 1 week affording a crop of large dark red/black crystals. The supernatant was decanted, and the solids were

washed with cold pentane (2 × 0.5 mL) and dried under argon. Yield – 51 mg (45%). The crystals obtained *via* this method were suitable for single-crystal X-ray diffraction studies.

Crystalline samples were plagued with Ni(COD)₂ and another unidentified impurity and could therefore not be obtained in analytically pure form using this method.



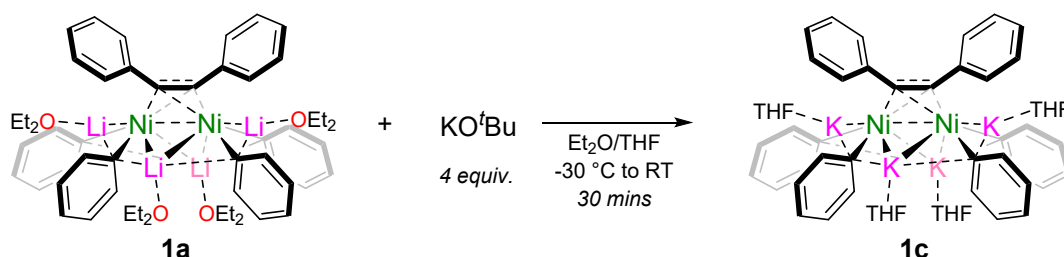
1a (46.4 mg, 0.05 mmol) was dissolved in Et₂O (2 mL) and cooled to -30 °C. NaO^tBu (19.2 mg, 0.20 mmol, 4 equiv.) was then added and the deep red reaction mixture was warmed to room temperature and stirred for 30 minutes. THF (0.2 mL) was added and the reaction mixture was filtered through glass wool, layered with pentane (2.5 mL), then stored at -30 °C for 48 hours affording dark red/black crystals. The supernatant was decanted, and the solids were washed with cold pentane (2 × 0.5 mL), and dried under argon. Yield – 27 mg (55%).

¹H NMR (300.1 MHz, THF-*d*₈): δ 7.96 (d, *J* = 6.7 Hz, 8H, Ph-Ni-*o*-CH), 7.10 (d, *J* = 7.3 Hz, 4H, Ph-C≡C-Ph-*o*-CH), 6.68 (t, *J* = 7.3 Hz, 4H, Ph-C≡C-Ph-*m*-CH), 6.55 (t, *J* = 7.2 Hz, 8H, Ph-Ni-*m*-CH), 6.41-6.32 (m, 4H + 2H, Ph-Ni-*p*-CH + Ph-C≡C-Ph-*p*-CH), 3.62 (m, THF), 1.78 (m, THF).

¹³C{¹H} NMR (75.5 MHz, THF-*d*₈): δ 195.8 (Ph-Ni-*ipso*-C), 156.9 (Ph-C≡C-Ph-*ipso*-C), 142.6 (Ph-Ni-*o*-CH), 128.4 (Ph-C≡C-Ph-*o*-CH), 127.5 (Ph-C≡C-Ph-*m*-CH), 125.7 (Ph-Ni-*m*-CH), 118.3 (Ph-Ni-*p*-CH), 114.3 (Ph-C≡C-Ph-*p*-CH), 68.6 (Ph-C≡C-Ph), 68.4 (THF), 26.6 (THF).

Elemental Analysis: Calculated for C₅₄H₆₂Na₄Ni₂O₄: C, 65.89; H, 6.35. Found: C, 65.80; H, 6.99.

Synthesis of K₄(THF)₄Ph₄Ni₂{μ₂:η²,η²-Ph-C≡C-Ph}, **1c**



1a (46.4 mg, 0.05 mmol) was dissolved in Et₂O (2 mL) and cooled to -30 °C. KO^tBu (22.4 mg, 0.20 mmol, 4 equiv.) was then added and the deep red reaction mixture was warmed to room temperature and stirred for 30 minutes. THF (0.5 mL) was added and reaction mixture was filtered through glass wool, layered with pentane (2.5 mL), then stored at -30 °C for 48 hours affording a dark red/purple

microcrystalline solid. The supernatant was decanted, and the solids were washed with cold pentane (2 × 0.5 mL), and dried under argon. Yield – 37 mg (79%).

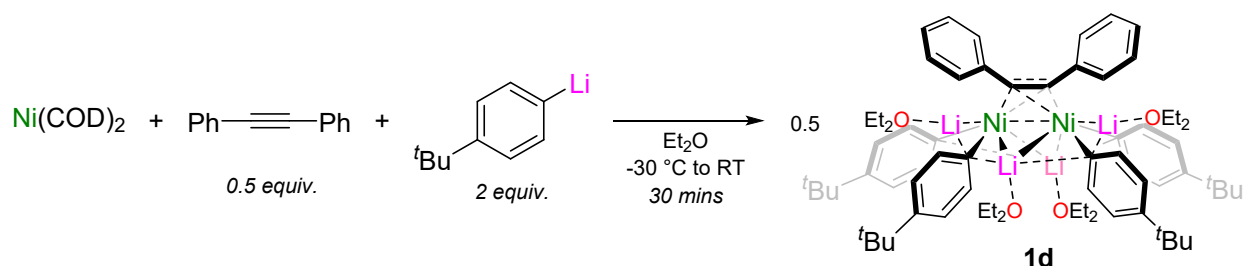
Single crystals of **1c** were observed to immediately desolvate and lose crystallinity when removed from the mother liquor. Attempts to grow single crystals with the aid of other donors such as TMEDA, DME, 1,4-dioxane or PMDETA failed.

¹H NMR (300.1 MHz, THF-*d*₈): δ 7.88 (d, *J* = 6.3 Hz, 8H, Ph-Ni-*o*-CH), 6.96 (d, *J* = 7.1 Hz, 4H, Ph-C≡C-Ph-*o*-CH), 6.62 (t, *J* = 7.1 Hz, 4H, Ph-C≡C-Ph-*m*-CH), 6.45 (t, *J* = 7.3 Hz, 8H, Ph-Ni-*m*-CH), 6.29–6.19 (m, 6H, Ph-Ni-*p*-CH + Ph-C≡C-Ph-*p*-CH), 3.62 (m, THF), 1.78 (m, THF).

¹³C{¹H} NMR (75.5 MHz, THF-*d*₈): δ 203.8 (Ph-Ni-*ipso*-C), 158.1 (Ph-C≡C-Ph-*ipso*-C), 142.6 (Ph-Ni-*o*-CH), 127.7 (Ph-C≡C-Ph-*m*-CH), 127.4 (Ph-C≡C-Ph-*o*-CH), 124.9 (Ph-Ni-*m*-CH), 116.4 (Ph-Ni-*p*-CH), 111.7 (Ph-C≡C-Ph-*p*-CH), 74.1 (Ph-C≡C-Ph), 68.4 (THF), 26.6 (THF).

Elemental Analysis: Calculated for C₅₄H₆₂K₄Ni₂O₄: C, 61.84; H, 5.96. Found: C, 62.17; H, 5.62.

Synthesis of Li₂(Et₂O)₄(4-*t*Bu-C₆H₄)₄Ni₂{μ₂:η²,η²-Ph-C≡C-Ph}, **1d**



Ni(COD)₂ (55 mg, 0.2 mmol) and diphenylacetylene (18 mg, 0.1 mmol, 0.5 equiv) were combined in Et₂O (2 mL) and stirred at room temperature for 15 minutes. The resulting ruby/purple solution was cooled to -30 °C in a glovebox freezer then 4-*t*Bu-C₆H₄-Li (56.1 mg, 0.4 mmol, 2 equiv) was added. The deep red reaction mixture was warmed to room temperature and stirred for 30 minutes then filtered through Celite/glass wool. Storage of the filtrate at -30 °C for 48 hours afforded a crop of dark red needles. The supernatant was decanted, and the solids were washed with cold pentane (2 × 0.5 mL) and dried under argon. Yield – 38 mg (33%). The crystals obtained *via* this method were suitable for single-crystal X-ray diffraction studies.

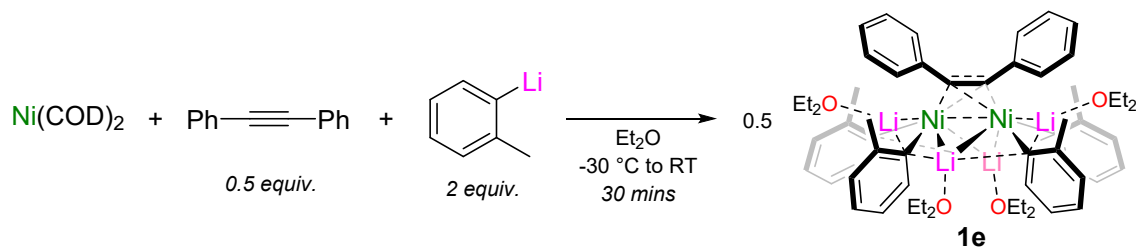
¹H NMR (400.1 MHz, THF-*d*₈, -40 °C): δ 8.69 (d, *J* = 7.8 Hz, 4H, 4-*t*Bu-C₆H₄-Ni-*o*-CH), 7.79 (d, *J* = 7.6 Hz, 4H, 4-*t*Bu-C₆H₄-Ni-*o*-CH), 7.27 (d, *J* = 7.3 Hz, 4H, Ph-C≡C-Ph-*o*-CH), 6.94 (dd, *J* = 2.0, 7.8 Hz, 4H, 4-*t*Bu-C₆H₄-Ni-*m*-CH), 6.73 (t, *J* = 7.2 Hz, 4H, Ph-C≡C-Ph-*m*-CH), 6.65 (dd, *J* = 2.0, 7.6 Hz, 4H, 4-*t*Bu-C₆H₄-Ni-*m*-CH), 6.52 (t, *J* = 7.2 Hz, 2H, Ph-C≡C-Ph-*p*-CH), 3.39 (q, Et₂O), 1.13 (t, Et₂O), 1.12 (s, 36H, 4-*t*Bu-C₆H₄-Ni).

⁷Li NMR (155.5 MHz, THF-*d*₈, -40 °C): δ 0.26 (br), -0.59 (s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, THF- d_8 , $-40\text{ }^\circ\text{C}$): δ 181.9 (br, 4- t Bu-C $_6$ H $_4$ -Ni-*ipso*-C), 157.1 (s, Ph-C \equiv C-Ph-*ipso*-C), 144.0 (s, 4- t Bu-C $_6$ H $_4$ -Ni-*o*-CH), 143.1 (s, 4- t Bu-C $_6$ H $_4$ -Ni-*o*-CH), 141.4 (s, C- t Bu), 130.6 (s, Ph-C \equiv C-Ph-*m*-CH), 129.3 (s, 4- t Bu-C $_6$ H $_4$ -Ni-*p*-CH), 126.6 (s, Ph-C \equiv C-Ph-*o*-CH), 123.7 (s, 4- t Bu-C $_6$ H $_4$ -Ni-*m*-CH), 123.1 (s, 4- t Bu-C $_6$ H $_4$ -Ni-*m*-CH), 118.3 (s, Ph-C \equiv C-Ph-*p*-CH), 76.6 (br, (s, Ph-C \equiv C-Ph), 66.7 (Et $_2$ O), 34.5 (s, C(CH $_3$) $_3$), 32.0 (s, C(CH $_3$) $_3$), 16.0 (s, Et $_2$ O).

Elemental Analysis: Calculated for C $_{70}$ H $_{102}$ Li $_4$ Ni $_2$ O $_4$: C, 72.94; H, 8.92. Found: C, 73.17; H, 8.40.

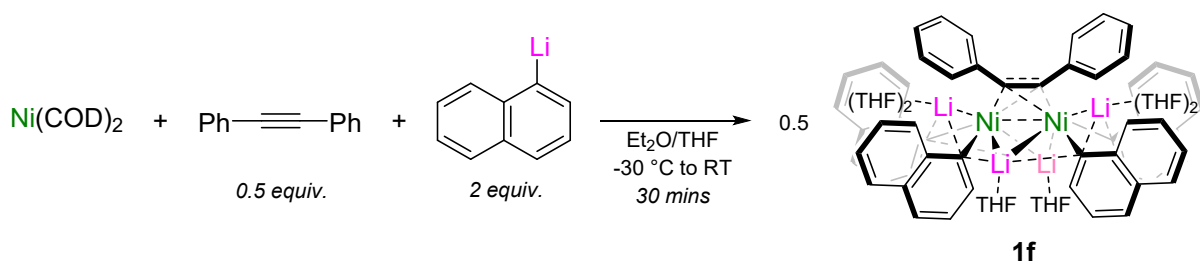
Crystallisation of Li $_2$ (Et $_2$ O) $_4$ (*o*-Tol) $_4$ Ni $_2$ { μ_2 : η^2 , η^2 -Ph-C \equiv C-Ph}, **1e**



Ni(COD) $_2$ (27.5 mg, 0.1 mmol) and diphenylacetylene (9 mg, 0.05 mmol, 0.5 equiv) were combined in Et $_2$ O (1 mL) and stirred at room temperature for 15 minutes. The resulting ruby/purple solution was cooled to $-30\text{ }^\circ\text{C}$ in a glovebox freezer then *o*-Tol-Li (19.6 mg, 0.2 mmol, 2 equiv) was added. The deep red reaction mixture was warmed to room temperature and stirred for 30 minutes. Hexane (1 mL) was added to the reaction mixture, which was then filtered through Celite/glass wool. Storage of the filtrate at $-30\text{ }^\circ\text{C}$ for 48 hours afforded dark red single crystals of **1e** alongside Ni(COD) $_2$.

Compound **1e** could not be isolated in pure form.

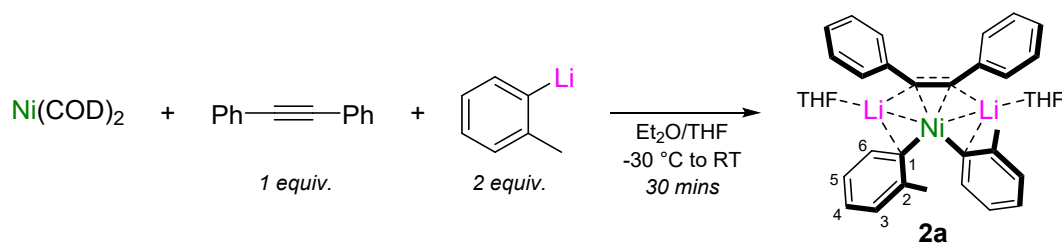
Crystallisation of Li $_2$ (THF) $_6$ (1-Naph) $_4$ Ni $_2$ { μ_2 : η^2 , η^2 -Ph-C \equiv C-Ph}, **1f**



Ni(COD) $_2$ (27.5 mg, 0.1 mmol) and diphenylacetylene (17.8 mg, 0.1 mmol, 1 equiv) were combined in Et $_2$ O (1 mL) and stirred at room temperature for 15 minutes. The resulting ruby/purple solution was cooled to $-30\text{ }^\circ\text{C}$ in a glovebox freezer then 1-Naph-Li (31.3 mg, 0.2 mmol, 2 equiv) was added. The deep red reaction mixture was warmed to room temperature and stirred for 30 minutes. Hexane (1 mL) was added to the reaction mixture, which was then filtered through Celite/glass wool. THF (0.1 mL) was added to the filtrate and storage at $-30\text{ }^\circ\text{C}$ for 48 hours afforded dark red/purple single crystals of **1f**.

Compound **1f** could not be isolated in pure form.

Synthesis of $\text{Li}_2(\text{THF})_2(\text{o-Tol})_2\text{Ni}\{\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$, **2a**



$\text{Ni}(\text{COD})_2$ (55 mg, 0.2 mmol) and diphenylacetylene (36 mg, 0.2 mmol, 1 equiv) were combined in Et_2O (2 mL) and stirred at room temperature for 15 minutes. The resulting ruby/purple solution was cooled to $-30\text{ }^\circ\text{C}$ in a glovebox freezer then *o*-Tol-Li (39.2 mg, 0.4 mmol, 2 equiv) was added. The deep red reaction mixture was warmed to room temperature and stirred for 30 minutes then filtered through a glass wool plug. THF (0.2 mL) was added to the filtrate and storage at $-30\text{ }^\circ\text{C}$ for 48 hours afforded red polycrystalline crystals. The supernatant was decanted and the solids were washed with cold pentane (0.5 mL) and dried under argon. Yield – 34 mg (29%).

Despite repeated efforts and changing the donor/solvent, it was not possible to grow single crystals of **2a** suitable for X-ray diffraction studies.

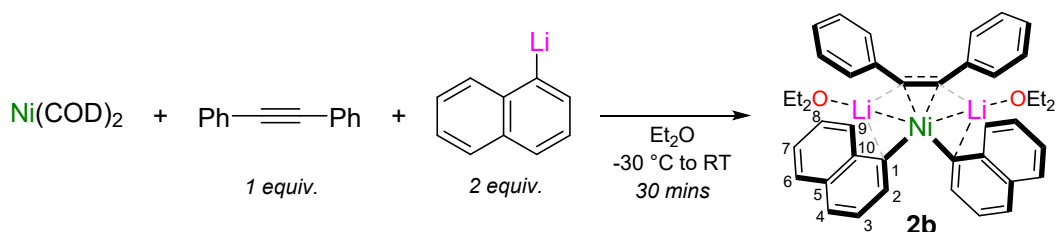
^1H NMR (300.1 MHz, THF-d_8): δ 7.80 (dd, $J = 2.0, 6.3$ Hz, 2H, H6), 7.01–6.91 (m, 8H, Ph-C \equiv C-Ph-*o,m*-CH), 6.76 (tt, $J = 2.3, 6.3$ Hz, 2H, H4), 6.66 (dd, $J = 1.9, 6.3$ Hz, 2H, H3), 6.53–6.42 (m, 4H, H5 + Ph-C \equiv C-Ph-*p*-CH), 3.63 (m, THF), 2.70 (s, 6H, CH₃), 1.78 (m, THF).

^7Li NMR (116.6 MHz, THF-d_8): δ 0.24 (s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, THF-d_8): δ 182.9 (s, C1), 150.8 (s, Ph-C \equiv C-Ph), 150.2 (s, C2), 144.7 (s, Ph-C \equiv C-Ph-*ipso*-C), 142.8 (s, C6), 128.4 (s, Ph-C \equiv C-Ph-*m*-CH), 126.6 (s, Ph-C \equiv C-Ph-*o*-CH), 125.5 (s, C3), 123.0 (s, C4), 122.6 (s, Ph-C \equiv C-Ph-*p*-CH), 120.8 (s, C5), 68.4 (s, THF), 30.0 (s, CH₃), 26.5 (s, THF).

Elemental Analysis: Despite appearing pure by multinuclear NMR spectroscopy (see Spectra S30–32), combustion values were considerably lower than expected and inconsistent between repeat samples suggesting incomplete combustion.

Synthesis of $\text{Li}_2(\text{Et}_2\text{O})_2(1\text{-Naph})_2\text{Ni}\{\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$, **2b**



$\text{Ni}(\text{COD})_2$ (55 mg, 0.2 mmol) and diphenylacetylene (36 mg, 0.2 mmol, 1 equiv) were combined in Et_2O (2 mL) and stirred at room temperature for 15 minutes. The resulting ruby/purple solution was cooled

to -30 °C in a glovebox freezer then 1-Naph-Li (63 mg, 0.4 mmol, 2 equiv) was added. The deep red reaction mixture was warmed to room temperature and stirred for 30 minutes then filtered through glass wool. Pentane (2 mL) was added to the filtrate and storage at -30 °C for 48 hours afforded a deep red polycrystalline solid. The supernatant was decanted, and the solids were washed with cold pentane (2 × 0.5 mL) and dried under argon. Yield – 38 mg (29%).

Despite repeated efforts and changing the donor/solvent, it was not possible to grow single crystals of **2b** suitable for X-ray diffraction studies.

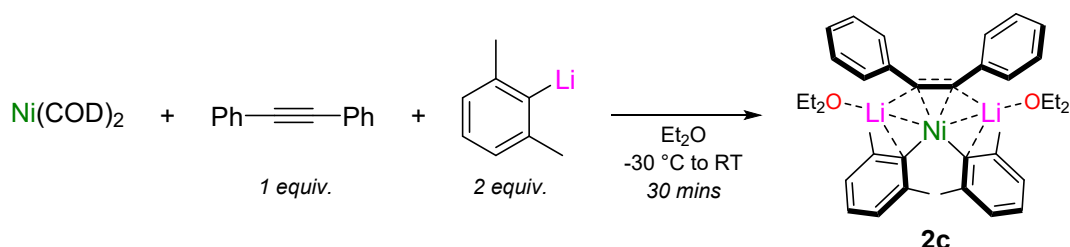
¹H NMR (300.1 MHz, THF-*d*₈): δ 9.56 (d, *J* = 8.1 Hz, 2H, H9), 7.84 (d, *J* = 6.0 Hz, 2H, H2), 7.47 (d, *J* = 7.5 Hz, 2H, H4), 7.27 (td, *J* = 8.1, 6.7, 1.3 Hz, 2H, H8), 7.18 (td, *J* = 8.1, 6.7, 1.3 Hz, 2H, H7), 7.08–6.98 (m, 6H, Ph-C≡C-Ph-*m*-CH + H3), 6.92 (t, *J* = 7.7 Hz, 4H, Ph-C≡C-Ph-*o*-CH), 6.79–6.69 (m, 4H, Ph-C≡C-Ph-*p*-CH + H6), 3.41 (q, Et₂O), 1.14 (t, Et₂O).

⁷Li NMR (116.6 MHz, THF-*d*₈): δ 0.14 (s).

¹³C{¹H} NMR (75.5 MHz, THF-*d*₈): δ 191.1 (s, C1), 150.5 (s, Ph-C≡C-Ph-*ipso*-C), 147.3 (s, C10), 143.6 (s, Ph-C≡C-Ph), 139.6 (s, C9), 139.1 (s, C2), 134.5 (s, C5), 128.4 (s, Ph-C≡C-Ph-*m*-CH), 128.3 (s, C4), 127.0 (s, Ph-C≡C-Ph-*o*-CH), 124.9 (s, C6), 124.3 (s, C7), 122.9 (s, Ph-C≡C-Ph-*p*-CH), 121.7 (s, C8), 120.3 (s, C3), 66.5 (s, Et₂O), 15.9 (s, Et₂O).

Elemental Analysis: Calculated for C₄₂H₄₄Li₂NiO₂: C, 77.21; H, 6.79. Found: C, 76.87; H, 6.51.

Synthesis of Li₂(Et₂O)₂(2,6-Me₂-C₆H₃)₂Ni{*η*²-Ph-C≡C-Ph}, **2c**



Ni(COD)₂ (55 mg, 0.2 mmol) and diphenylacetylene (36 mg, 0.2 mmol, 1 equiv) were combined in Et₂O (2 mL) and stirred at room temperature for 15 minutes. The resulting ruby/purple solution was cooled to -30 °C in a glovebox freezer then 2,6-Me₂-C₆H₃-Li (45 mg, 0.4 mmol, 2 equiv) was added. The deep red reaction mixture was warmed to room temperature and stirred for 30 minutes then filtered through Celite/glass wool. Pentane (2 mL) was added to the filtrate and storage at -30 °C for 48 hours afforded deep red crystals of **2c**. The supernatant was decanted, and the solids were washed with cold pentane (2 × 0.5 mL) and dried under argon. Yield – 52 mg (41%). The crystals obtained *via* this method were suitable for single-crystal X-ray diffraction studies.

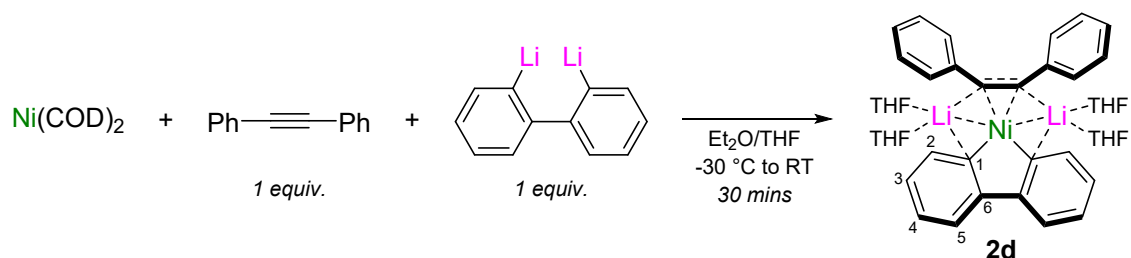
¹H NMR (300.1 MHz, THF-*d*₈): δ 7.06-6.94 (m, 8H, Ph-C≡C-Ph-*o,m*-CH), 6.78 (t, *J* = 6.9 Hz, 2H, Ph-C≡C-Ph-*p*-CH), 6.53-6.42 (m, 6H, *Xy-m,p*-CH), 3.40 (q, Et₂O), 2.63 (s, 12H, *Xy-CH*₃), 1.13 (t, Et₂O).

^7Li NMR (116.6 MHz, THF- d_8): δ 0.17 (s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, THF- d_8): δ 177.2 (Xy-Ni-*ipso*-C), 150.7 (Ph-C \equiv C-Ph-*ipso*-C), 150.4 (Xy-C-CH₃), 144.6 (Ph-C \equiv C-Ph), 128.5 (Ph-C \equiv C-Ph-*m*-CH), 126.4 (Ph-C \equiv C-Ph-*o*-CH), 123.2 (Xy-*m*-CH), 122.7 (Ph-C \equiv C-Ph-*p*-CH), 121.7 (Xy-*p*-CH), 66.5 (Et₂O), 30.0 (Xy-CH₃), 15.9 (Et₂O).

Elemental Analysis: Calculated for C₃₈H₄₈Li₂NiO₂: C, 74.90; H, 7.94. Found: C, 74.47; H, 7.94.

Synthesis of Li₂(THF)₄(2,2'-biphenyl)Ni{ η^2 -Ph-C \equiv C-Ph}, **2d**



2,2'-Dilithiobiphenyl (55 mg, 0.2 mmol) was dissolved in Et₂O (2 mL) and cooled to -30 °C. Ni(COD)₂ (55 mg, 0.2 mmol) was added and the reaction was then warmed to room temperature. THF (2 mL) was added, and the dark red solution was stirred for 1 hour. Diphenylacetylene (36 mg, 0.2 mmol) was added resulting in a colour change to blood red, and the solution was stirred for a further 30 minutes at room temperature. Layering with pentane (2 mL) and storage at -30 °C for 1 week afforded **2d** as dark red blocky crystals. The supernatant was decanted, and the solids were washed with cold pentane (2 × 0.5 mL) and dried under argon. Yield – 66 mg (48%). The crystals obtained *via* this method were suitable for single-crystal X-ray diffraction studies.

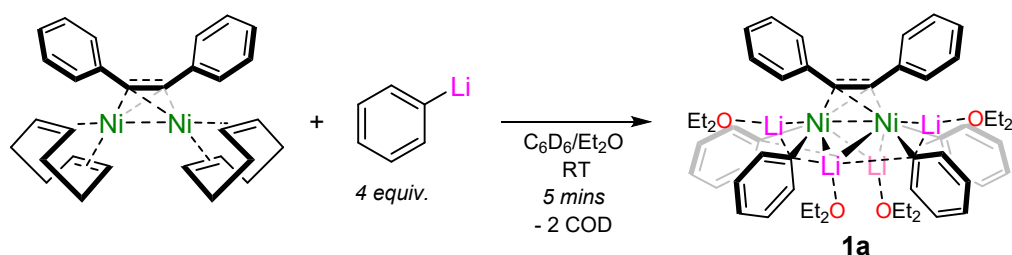
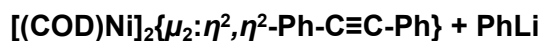
^1H NMR (300.1 MHz, THF- d_8): δ 8.19 (m, 2H, H2), 7.32-7.26 (m, 6H, Ph-C \equiv C-Ph-*o,p*-CH), 7.09 (m, 4H, Ph-C \equiv C-Ph-*m*-CH), 6.83 (m, 2H, H3), 6.75 (m, 2H, H4), 6.70 (m, 2H, H5), 3.62 (m, THF), 1.77 (m, THF).

^7Li NMR (116.6 MHz, THF- d_8): δ 0.06 (s).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, THF- d_8): δ 180.2 (C1), 161.0 (C6), 156.7 (Ph-C \equiv C-Ph-*ipso*-C), 144.9 (Ph-C \equiv C-Ph), 144.5 (C2), 128.4 (Ph-C \equiv C-Ph-*m*-CH), 127.0 (Ph-C \equiv C-Ph-*o*-CH), 124.6 (C5), 122.5 (C3), 121.7 (C4), 118.8 (Ph-C \equiv C-Ph-*p*-CH), 68.4 (THF), 26.6 (THF).

Elemental Analysis: Calculated for C₄₃H₅₃Li₂NiO₄: C, 73.11; H, 7.56. Found: C, 72.69; H, 7.26.

NMR Spectroscopy Studies



$[(\text{COD})\text{Ni}]_2\{\mu_2:\eta^2,\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$ (14.3 mg, 0.025 mmol) was dissolved in C_6D_6 (0.5 mL) and a ^1H NMR spectrum was recorded (Figure S1, blue trace). PhLi (8.4 mg, 0.10 mmol, 4 equiv) was dissolved in Et_2O (0.1 mL) and added to the NMR tube to give a deep red solution. The ^1H NMR spectrum (Figure S1, red trace) shows clean conversion to $\text{Li}_2(\text{Et}_2\text{O})_4\text{Ph}_4\text{Ni}_2\{\mu_2:\eta^2,\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$ (**1a**) alongside COD as the sole by-product.

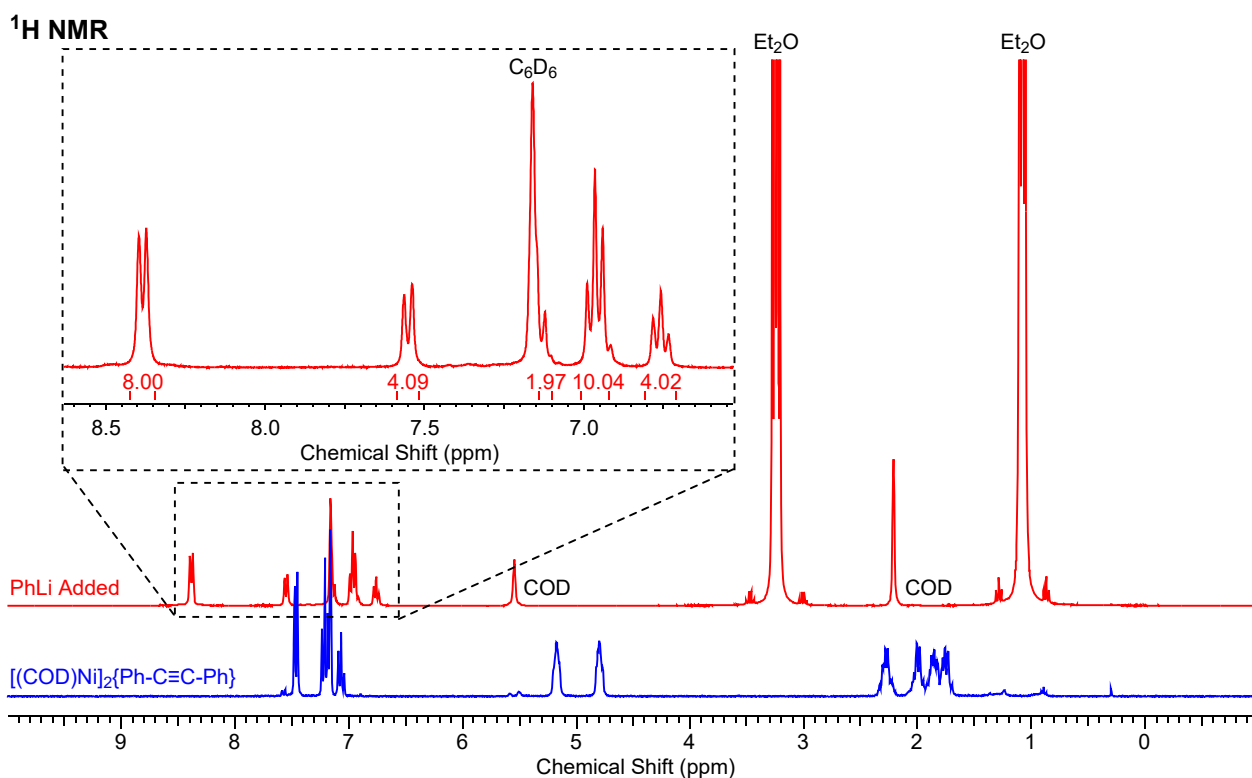
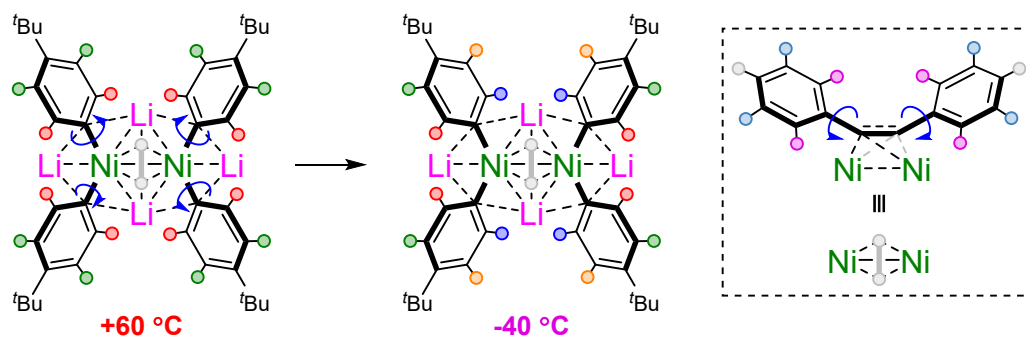


Figure S1: Stacked ^1H NMR spectra showing the reaction of $[(\text{COD})\text{Ni}]_2\{\mu_2:\eta^2,\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$ with four equivalents of PhLi in C_6D_6 and Et_2O to form $\text{Li}_2(\text{Et}_2\text{O})_4\text{Ph}_4\text{Ni}_2\{\mu_2:\eta^2,\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$ (**1a**).

Variable Temperature NMR Spectroscopy of **1d**

1d (30 mg) was added to a J. Young's NMR tube, dissolved in THF-d_8 (0.5 mL) and analysed by ^1H and ^7Li NMR spectroscopy at $+60\text{ }^\circ\text{C}$, $+40\text{ }^\circ\text{C}$, $+20\text{ }^\circ\text{C}$, $0\text{ }^\circ\text{C}$, $-20\text{ }^\circ\text{C}$ and $-40\text{ }^\circ\text{C}$ (Figures S2–3). A $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum was also recorded at $-40\text{ }^\circ\text{C}$ (see Spectra S29). The fluxional behaviour is attributed to restricted rotation around the Ni-C_{Ar} bonds where rotation is frozen at low temperatures ($-40\text{ }^\circ\text{C}$, purple trace, Figure S1), giving rise to two unique signals for both the *ortho* and *meta* aromatic

protons. These signals coalesce at higher temperature (+60 °C, red trace, Figure S1) to give a single signal for both *ortho* and *meta* proton signals. Similarly, the ^7Li NMR spectrum displays a single broad peak at +60 °C (red trace, Figure S2) which splits into two broad signals at -40 °C (purple trace, Figure S2).



^1H NMR

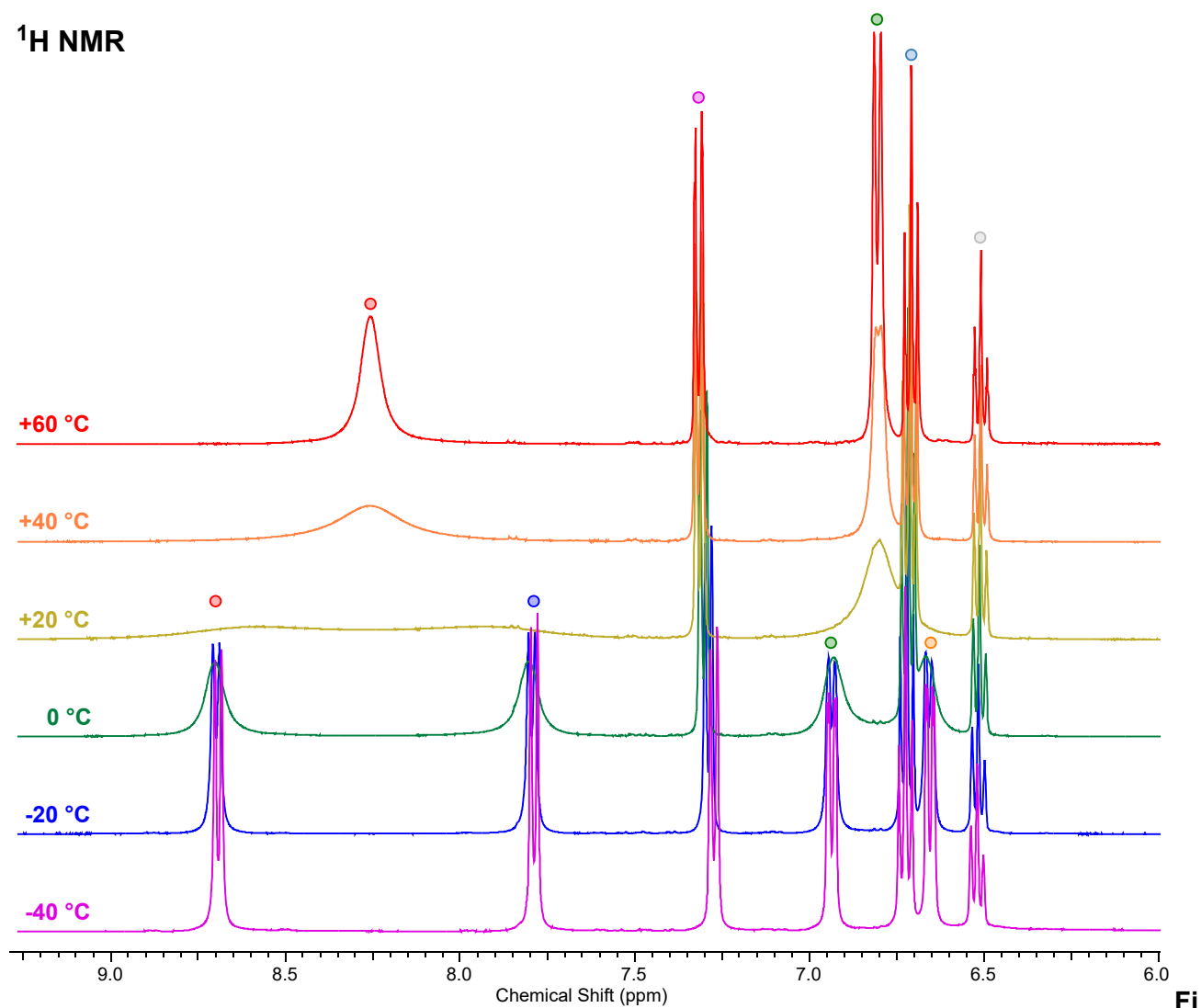


Figure S2: Stacked ^1H NMR spectra (aromatic region) of **1d** at variable temperatures in THF-d_8 .

^7Li NMR

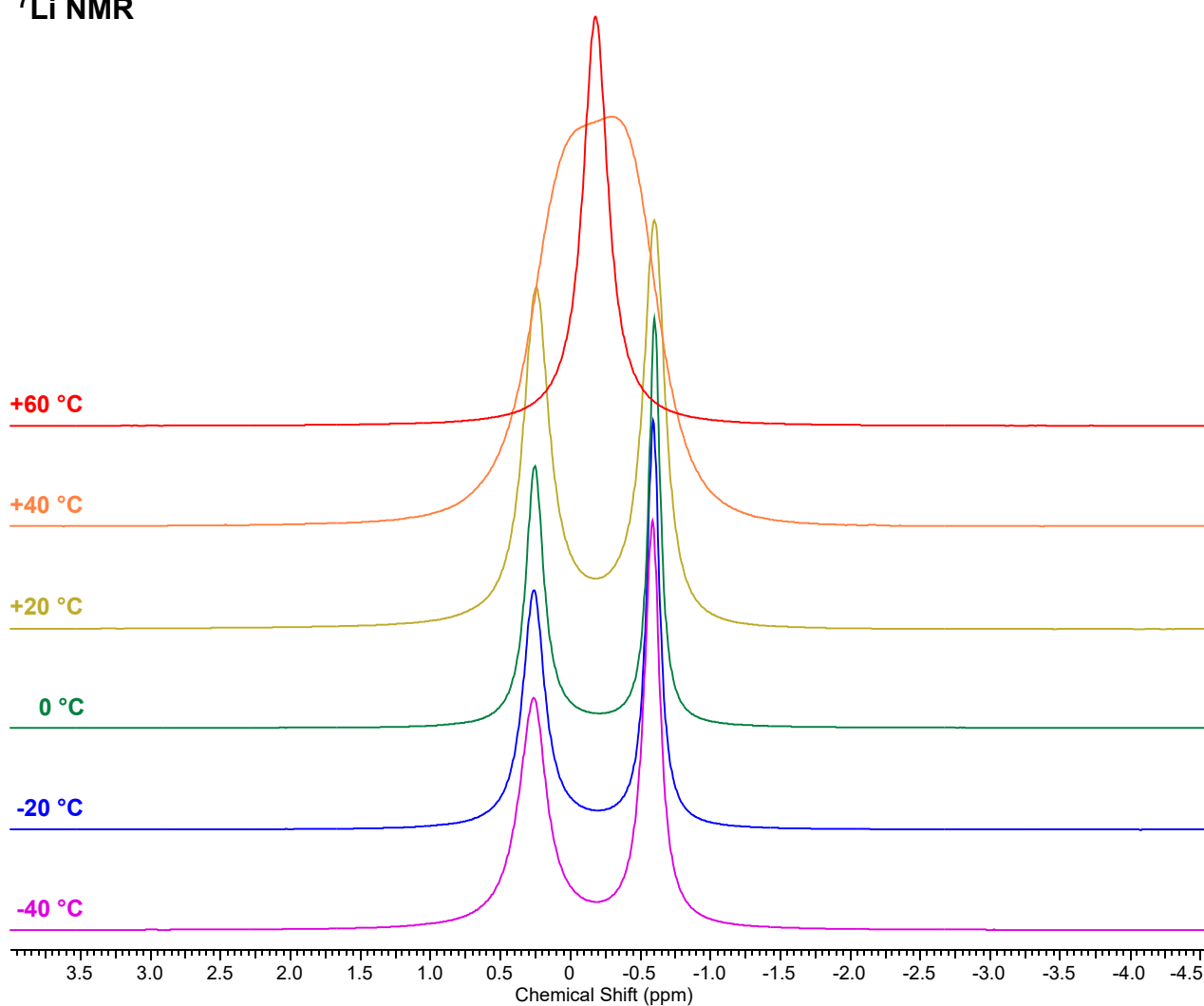
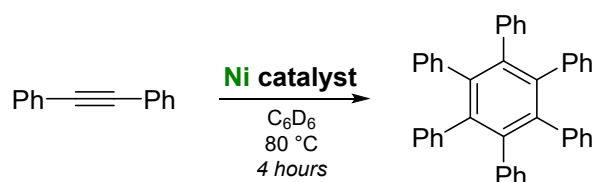


Figure S3: Stacked ^7Li NMR spectrum of **1d** at variable temperatures in THF-d_8 .

Catalytic Reactions

Cyclotrimerisation of Diphenylacetylene



Diphenylacetylene (17.8 mg, 0.1 mmol) and hexamethylbenzene (1.6 mg, 0.01 mmol, internal standard) were dissolved in C_6D_6 (0.6 mL) in a J. Young's NMR tube, then the corresponding nickel catalyst was added (5 mol% for dinickel compounds, 10 mol% for mononickel compounds). A ^1H NMR spectrum was recorded to establish the ratio of $\text{Ph-C}\equiv\text{C-Ph}$ to the internal standard. The NMR tube was then heated for 4 hours at $80\text{ }^\circ\text{C}$. A ^1H NMR spectrum was recorded to measure the conversion of $\text{Ph-C}\equiv\text{C-Ph}$ against the internal standard. Since hexaphenylbenzene is poorly soluble in C_6D_6 , it was not possible to directly measure the spectroscopic yield of the cyclotrimerization product. A representative example of the NMR spectra when using **2a** as the catalyst is shown in Figure S4.

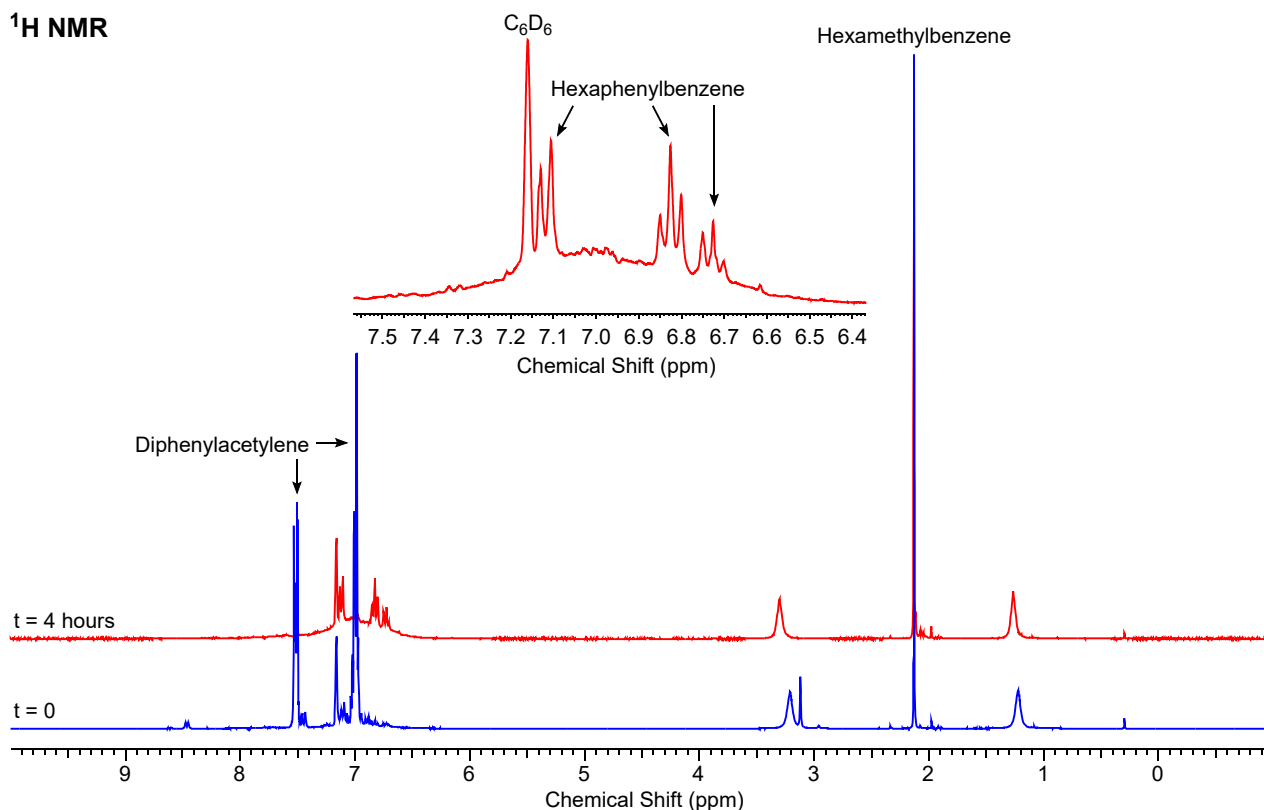


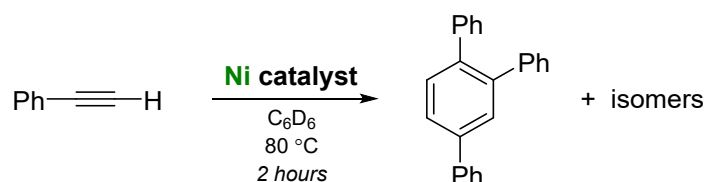
Figure S4: Stacked ¹H NMR spectra showing the cyclotrimerisation of diphenylacetylene catalysed by **2a**.

Comparison of different nickel catalysts illustrates that mononickelate derivatives bearing electron-rich substituents (**2a** and **2c**) show the best catalytic activity (Table S1) for the cyclotrimerisation of diphenylacetylene. No cyclotrimerisation is observed in the absence of a nickel catalyst.

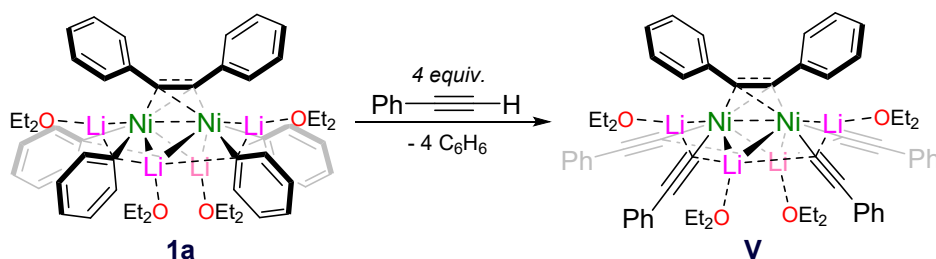
Entry	Nickel Catalyst	Conversion (%)
1	[(COD)Ni] ₂ {PhCCPh} (5 mol%)	38
2	Ni ₂ COT ₂ (5 mol%)	41
3	Li ₄ (Et ₂ O) ₄ Ph ₄ Ni ₂ {PhCCPh}, 1a (5 mol%)	74
4	Na ₄ (THF) ₆ Ph ₄ Ni ₂ {PhCCPh}, 1b (5 mol%)	73
5	K ₄ (THF) ₄ Ph ₄ Ni ₂ {PhCCPh}, 1c (5 mol%)	78 ^a
6	Li ₄ (Et ₂ O) ₄ (4- <i>t</i> -Bu-C ₆ H ₄) ₄ Ni ₂ {PhCCPh}, 1d (5 mol%)	85
7	Li ₄ (Et ₂ O) ₄ (CCPh) ₄ Ni ₂ {PhCCPh}, V (5 mol%)	<5
8	Li ₂ (THF) ₂ (<i>o</i> -Tol) ₂ Ni{PhCCPh}, 2a (10 mol%)	>95
9	Li ₂ (Et ₂ O) ₂ (1-Naph) ₂ Ni{PhCCPh}, 2b (10 mol%)	71
10	Li ₂ (Et ₂ O) ₂ (2,6-Me ₂ -C ₆ H ₃) ₂ Ni{PhCCPh}, 2c (10 mol%)	>95
11	Li ₂ (THF) ₄ (2,2'-biphenyl)Ni{PhCCPh}, 2d (10 mol%)	26 ^a
12	No catalyst	0
13	PhLi(THF) (20 mol%)	0

Table S1: Cyclotrimerisation of diphenylacetylene catalysed by different nickel complexes. ^a Reaction performed in THF-d₈.

Cyclotrimerisation of Phenylacetylene



Whilst $\text{Li}_4(\text{Et}_2\text{O})_4(\text{C}\equiv\text{C}-\text{Ph})_4\text{Ni}_2\{\mu_2:\eta^2,\eta^2-\text{Ph}-\text{C}\equiv\text{C}-\text{Ph}\}$ (**V**) is unable to catalyse the cyclotrimerisation of diphenylacetylene, it is able to catalyse the cyclotrimerisation of phenylacetylene. Using 2.5 mol% of **V**, full conversion (>95%) of phenylacetylene is observed after 2 hours of heating at 80 °C to primarily give 1,2,4-triphenylbenzene with trace amounts of other species (1,3,5-triphenylbenzene or cyclooctatetraenes). Using Ni_2COT_2 (2.5 mol%) as the catalyst, the conversion of phenylacetylene after 2 hours of heating at 80 °C is 74%. Compound **V** can also be prepared *in situ* by treating $\text{Li}_4(\text{Et}_2\text{O})_4\text{Ph}_4\text{Ni}_2\{\mu_2:\eta^2,\eta^2-\text{Ph}-\text{C}\equiv\text{C}-\text{Ph}\}$ (**1a**) with 4 equivalents of phenylacetylene (Figure S5).



¹H NMR

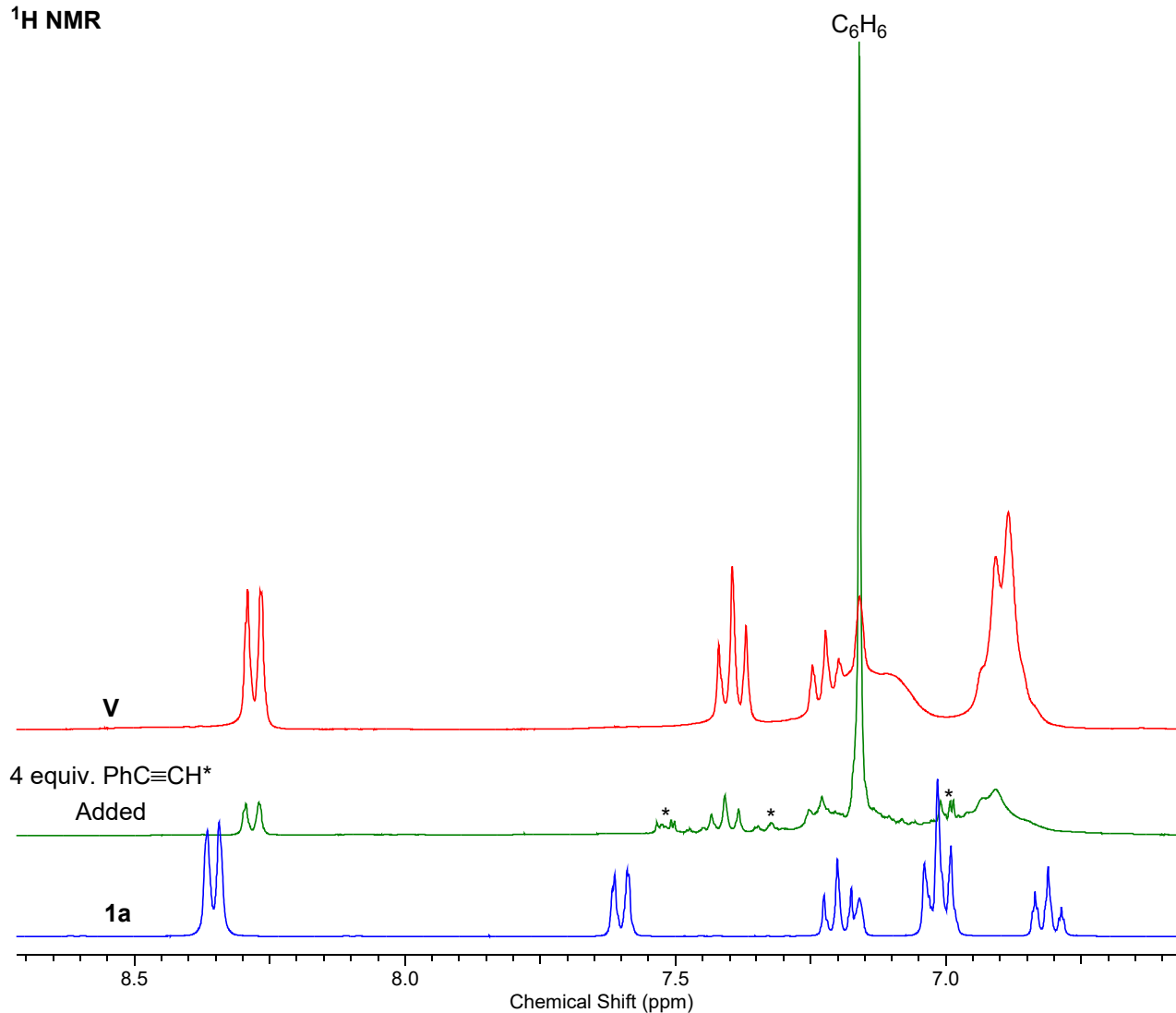
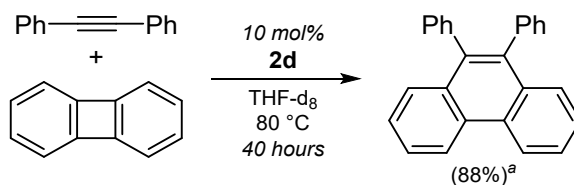


Figure S5: Stacked ¹H NMR spectra (aromatic region) showing the conversion of $\text{Li}_4(\text{Et}_2\text{O})_4\text{Ph}_4\text{Ni}_2\{\mu_2\text{:}\eta^2,\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$ (**1a**) into $\text{Li}_4(\text{Et}_2\text{O})_4(\text{C}\equiv\text{C-Ph})_4\text{Ni}_2\{\mu_2\text{:}\eta^2,\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$ (**V**) upon treatment with four equivalents of phenylacetylene.

Insertion of Diphenylacetylene into Biphenylene



Biphenylene (15.2 mg, 0.1 mmol) and hexamethylbenzene (1.6 mg, 0.01 mmol) were dissolved in THF-d_8 (0.6 mL) in a J. Young's NMR tube (Figure S6, blue trace). Diphenylacetylene (17.8 mg, 0.1 mmol) was added (Figure S6 green trace), followed by $\text{Li}_2(\text{THF})_4(2,2'\text{-biphenyl})\text{Ni}\{\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$ (**2d**) (6.9 mg, 0.01 mmol) (Figure S6, red trace). The NMR tube was heated to 80 °C and periodically monitored by ¹H NMR spectroscopy. After 40 hours, a spectroscopic yield of 9,10-diphenylphenanthrene (88%) was observed by comparison with the internal standard (Figure S6, yellow trace).

¹H NMR

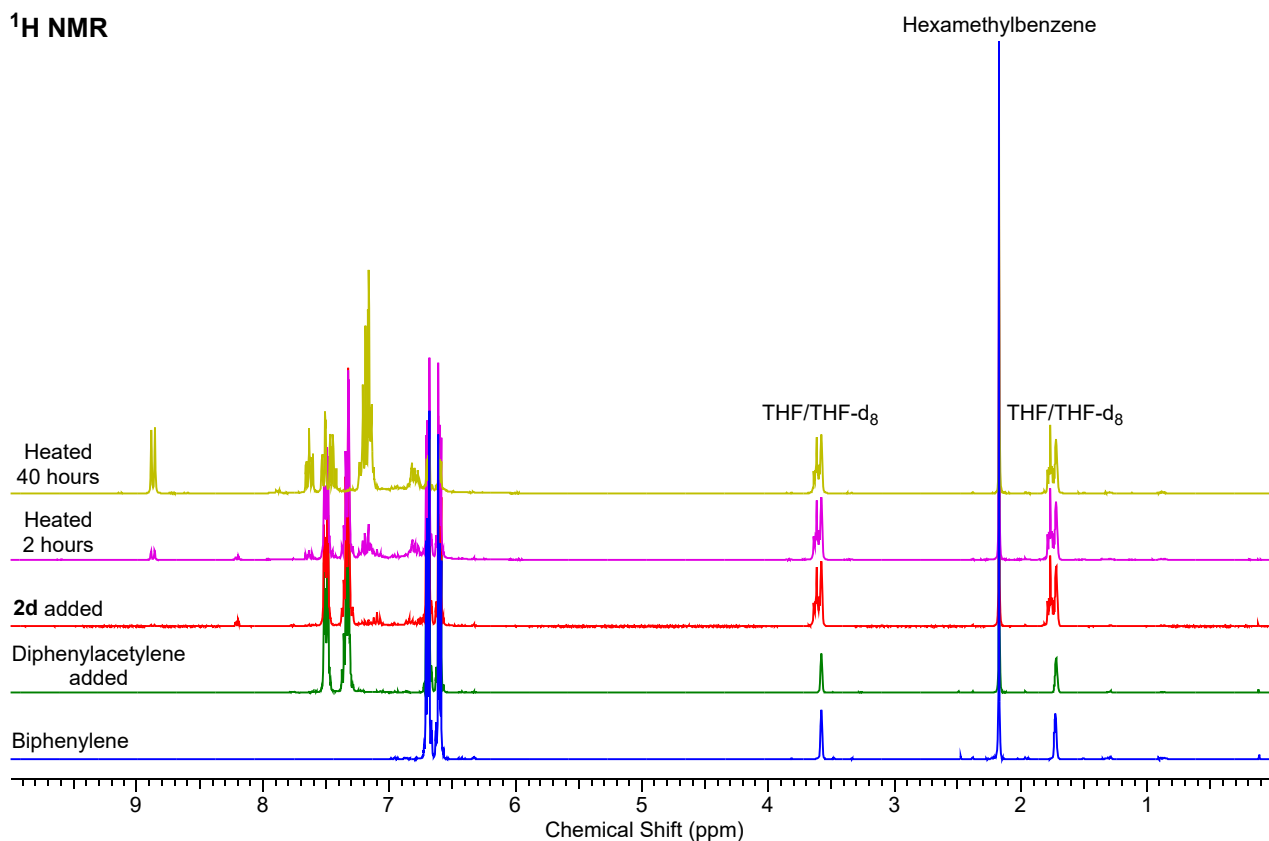


Figure S6: Stacked ¹H NMR spectra showing the insertion of diphenylacetylene into biphenylene catalysed by $\text{Li}_2(\text{THF})_4(2,2'\text{-biphenyl})\text{Ni}\{\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$ (**2d**).

X-ray Crystallography

The crystal structures of all novel compounds have been deposited into the Cambridge Crystallographic Data Centre (CCDC) and have been assigned the following numbers: **1a** – 2221333; **1b** – 2221334; **1d** – 2221335; **1e** – 2221336; **1f** – 2221337; **2c** – 2221338; **2d** – 2221339. Selected crystallographic and refinement parameters are presented below (**Tables S2–4**). In all cases, crystals immersed in an inert parabar oil were mounted at ambient conditions and transferred into the nitrogen stream (100 or 173 K). Perfluorinated oil should be avoided for the alkali-metal nickelates.

All measurements were made on a *RIGAKU Synergy S* area-detector diffractometer using mirror optics monochromated Cu *K* α radiation ($\lambda = 1.54184 \text{ \AA}$). Data reduction was performed using the *CrysAlisPro* program.⁷ The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the Gaussian method using SCALE3 ABSPACK in *CrysAlisPro* was applied. The structure was solved by direct methods or intrinsic phasing using *SHELXT*,⁸ which revealed the positions of all non-hydrogen atoms of the compounds. All non-hydrogen atoms were refined anisotropically. H-atoms were assigned in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2U_{eq} of its parent atom (1.5U_{eq} for methyl groups). Refinement of the structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\sum w(F_o^2 - F_c^2)^2$. The

weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. All calculations were performed using the *SHELXL-2014/7*⁹ program in OLEX2.¹⁰

For **1a**, a disorder model was included for parts of the structure where the occupancies of each disorder component were refined through the use of a free variable. The sum of equivalent components was constrained to 1 i.e. 100%.

For **1b**, a disorder model was used for parts of the structure where the occupancies of each disorder component was refined through the use of a free variable. The sum of equivalent components was constrained to 1, i.e. 100%. Four component twins could be found on the frames, therefore the structure was refined against the hkl for the isolated 1st/major component.

For **1d**, areas containing one disordered Et₂O solvent molecule was found where a satisfactory solvent model could not be achieved, therefore, a solvent mask was used to include the contribution of electron density found in void areas into the calculated structure factor.

For **1e**, a disorder model was used for parts of the structure where the occupancies of each disorder component was refined through the use of a free variable. The sum of equivalent components was constrained to 1, i.e. 100%.

For **1f**, a disorder model was used for parts of the structure where the occupancies of each disorder component was refined through the use of a free variable. The sum of equivalent components was constrained to 1, i.e. 100%. Areas containing disorder solvents were found where a satisfactory solvent model could not be achieved, therefore, a solvent mask was used to include the contribution of electron density found in void areas into the calculated structure factor.

Compound	1a	1b	1d
CCDC number	2221333	2221334	2221335
Empirical formula	C ₅₄ H ₇₀ Li ₄ Ni ₂ O ₄	C ₆₂ H ₇₈ Na ₄ Ni ₂ O ₆	C ₇₀ H ₁₀₂ Li ₄ Ni ₂ O ₄
Formula weight	928.28	1128.62	1152.69
Temperature/K	173.01(10)	173.01(10)	173.00(10)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	C2/c	C2/c	Pbca
a/Å	15.10128(7)	20.9102(2)	12.16221(10)
b/Å	32.53880(15)	17.56450(10)	28.5694(3)
c/Å	20.86994(9)	16.23570(10)	42.1061(3)
α/°	90	90	90
β/°	94.9245(4)	90.2810(10)	90
γ/°	90	90	90
Volume/Å ³	10217.16(8)	5962.93(8)	14630.5(2)
Z	8	4	8
ρ _{calc} /cm ³	1.207	1.257	1.047
μ/mm ⁻¹	1.226	1.444	0.936
F(000)	3952	2392	4976
Crystal size/mm ³	0.224 × 0.169 × 0.094	0.408 × 0.31 × 0.081	0.385 × 0.305 × 0.141
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	5.432 to 149.53	6.572 to 146.532	6.188 to 133.83
Index ranges	-18 ≤ h ≤ 18, -38 ≤ k ≤ 40, -26 ≤ l ≤ 25	-25 ≤ h ≤ 23, -21 ≤ k ≤ 21, -20 ≤ l ≤ 20	-11 ≤ h ≤ 14, -34 ≤ k ≤ 34, -50 ≤ l ≤ 50
Reflections collected	102249	57329	133411
Independent reflections	10477 [R _{int} = 0.0327, R _{sigma} = 0.0157]	5979 [R _{int} = 0.0402, R _{sigma} = 0.0176]	13013 [R _{int} = 0.0576, R _{sigma} = 0.0228]
Data/restraints/parameters	10477/54/729	5979/264/549	13013/6/741
Goodness-of-fit on F ²	1.016	1.059	1.069
Final R indexes [I ≥ 2σ(I)]	R ₁ = 0.0343, wR ₂ = 0.0941	R ₁ = 0.0665, wR ₂ = 0.2015	R ₁ = 0.0524, wR ₂ = 0.1352
Final R indexes [all data]	R ₁ = 0.0360, wR ₂ = 0.0954	R ₁ = 0.0725, wR ₂ = 0.2093	R ₁ = 0.0566, wR ₂ = 0.1377
Largest diff. peak/hole / e Å ⁻³	0.54/-0.25	0.41/-0.47	0.68/-0.40

Table S2: Crystal data and structure refinement details for compounds **1a**, **1b** and **1d**.

Compound	1e	1f
CCDC number	2221336	2221337
Empirical formula	C ₅₈ H ₇₇ Li ₄ Ni ₂ O ₄	C ₇₈ H ₈₆ Li ₄ Ni ₂ O ₆
Formula weight	983.37	1264.64
Temperature/K	173.00(10)	173.00(10)
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /n	P2/n
a/Å	12.37091(7)	24.15833(13)
b/Å	19.44400(10)	11.80124(6)
c/Å	23.57916(13)	25.58438(14)
α/°	90	90
β/°	101.8680(5)	106.3646(6)
γ/°	90	90
Volume/Å ³	5550.49(5)	6998.56(7)
Z	4	4
ρ _{calc} /cm ³	1.177	1.2
μ/mm ⁻¹	1.155	1.054
F(000)	2100	2680
Crystal size/mm ³	0.233 × 0.171 × 0.103	0.26 × 0.13 × 0.11
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	5.944 to 136.48	4.444 to 140.148
Index ranges	-14 ≤ h ≤ 14, -23 ≤ k ≤ 23, -28 ≤ l ≤ 28	-28 ≤ h ≤ 29, -14 ≤ k ≤ 14, -31 ≤ l ≤ 31
Reflections collected	107510	133747
Independent reflections	10163 [R _{int} = 0.0380, R _{sigma} = 0.0187]	13317 [R _{int} = 0.0498, R _{sigma} = 0.0217]
Data/restraints/parameters	10163/216/741	13317/55/923
Goodness-of-fit on F ²	1.032	1.063
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0411, wR ₂ = 0.1172	R ₁ = 0.0692, wR ₂ = 0.1850
Final R indexes [all data]	R ₁ = 0.0441, wR ₂ = 0.1201	R ₁ = 0.0708, wR ₂ = 0.1863
Largest diff. peak/hole / e Å ⁻³	0.61/-0.38	1.50/-0.60

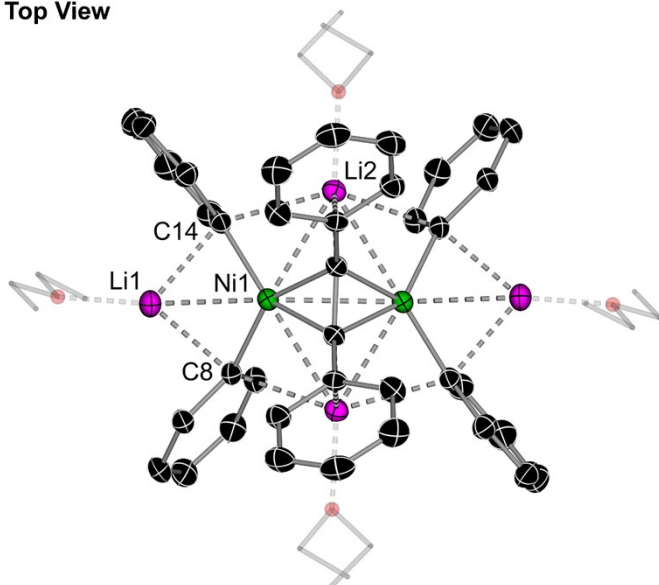
Table S3: Crystal data and structure refinement details for compounds **1e** and **1f**.

Compound	2c	2d
CCDC number	2221338	2221339
Empirical formula	C ₃₈ H ₄₈ Li ₂ NiO ₂	C ₄₂ H ₅₀ Li ₂ NiO ₄
Formula weight	609.35	691.41
Temperature/K	173.00(10)	173.00(10)
Crystal system	monoclinic	orthorhombic
Space group	P2 ₁ /c	Pbca
a/Å	17.30135(14)	15.49117(5)
b/Å	14.29224(10)	19.31164(7)
c/Å	15.04570(13)	24.55861(9)
α/°	90	90
β/°	115.1129(10)	90
γ/°	90	90
Volume/Å ³	3368.74(5)	7346.96(5)
Z	4	8
ρ _{calc} /cm ³	1.201	1.25
μ/mm ⁻¹	1.048	1.067
F(000)	1304	2944
Crystal size/mm ³	0.336 × 0.242 × 0.176	0.508 × 0.423 × 0.186
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	5.642 to 149.512	7.2 to 149.004
Index ranges	-21 ≤ h ≤ 20, -17 ≤ k ≤ 17, -18 ≤ l ≤ 18	-19 ≤ h ≤ 18, -24 ≤ k ≤ 23, -27 ≤ l ≤ 30
Reflections collected	67317	72965
Independent reflections	6899 [R _{int} = 0.0323, R _{sigma} = 0.0138]	7508 [R _{int} = 0.0302, R _{sigma} = 0.0125]
Data/restraints/parameters	6899/0/581	7508/0/619
Goodness-of-fit on F ²	1.041	1.041
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0300, wR ₂ = 0.0794	R ₁ = 0.0395, wR ₂ = 0.1031
Final R indexes [all data]	R ₁ = 0.0305, wR ₂ = 0.0798	R ₁ = 0.0405, wR ₂ = 0.1038
Largest diff. peak/hole / e Å ⁻³	0.26/-0.28	0.70/-0.48

Table S4: Crystal data and structure refinement details for compounds **2c** and **2d**.

Molecular Structure of $\text{Li}_2(\text{Et}_2\text{O})_4\text{Ph}_4\text{Ni}_2\{\mu_2:\eta^2,\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$, **1a**

Top View



Side View

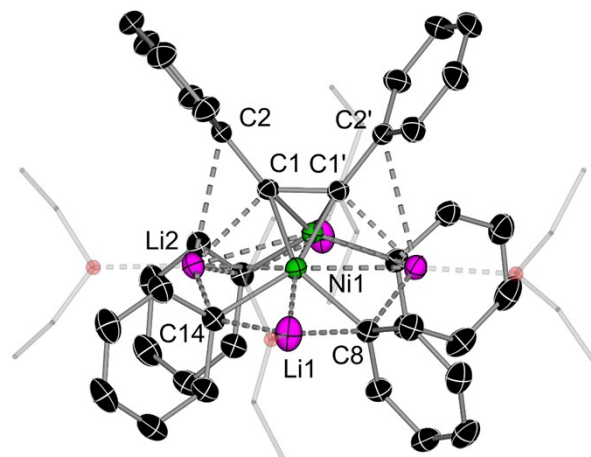


Figure S7: Molecular structure of **1a**. Thermal ellipsoids shown at 30% probability. Hydrogen atoms omitted and coordinated Et_2O shown as wireframes for clarity.

Molecular Structure of $\text{Na}_2(\text{THF})_6\text{Ph}_4\text{Ni}_2\{\mu_2:\eta^2,\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$, **1b**

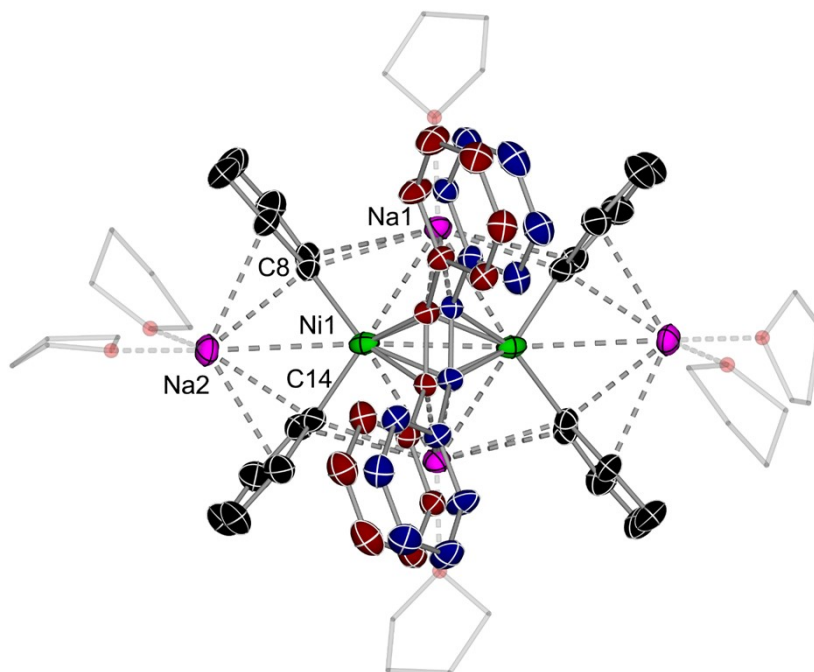
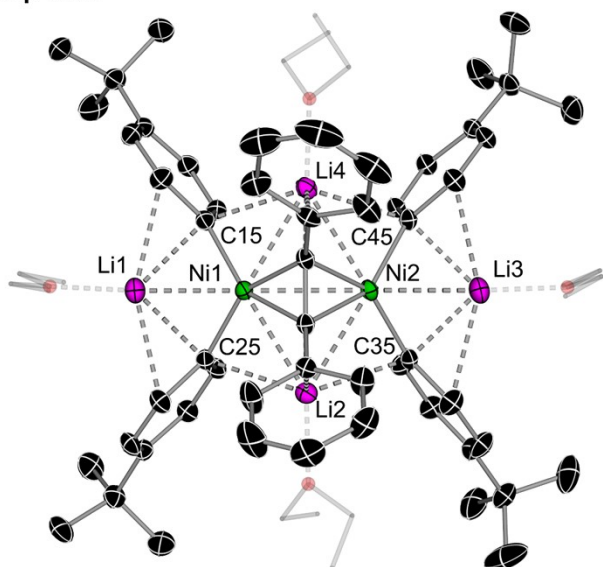


Figure S8: Molecular structure of **1b**. Thermal ellipsoids shown at 30% probability. Hydrogen atoms omitted and coordinated THF shown as wireframes for clarity. The coordinated $\text{Ph-C}\equiv\text{C-Ph}$ is disordered over two positions (shown in maroon and blue).

Molecular Structure of $\text{Li}_2(\text{Et}_2\text{O})_4(4\text{-}^t\text{Bu-C}_6\text{H}_4)_4\text{Ni}_2\{\mu_2:\eta^2,\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$, 1d

Top View



Side View

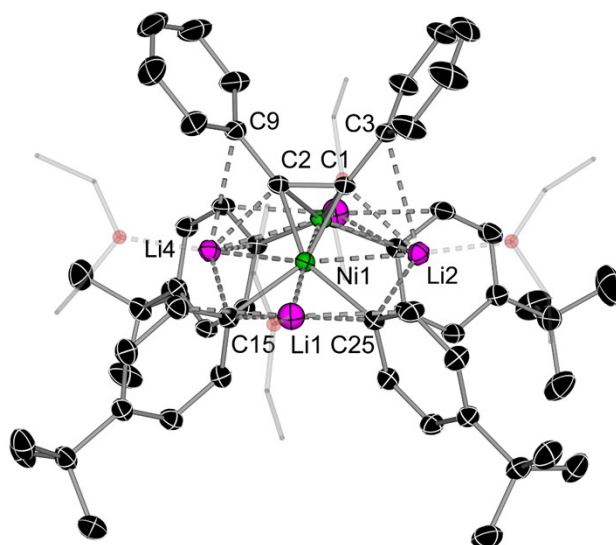
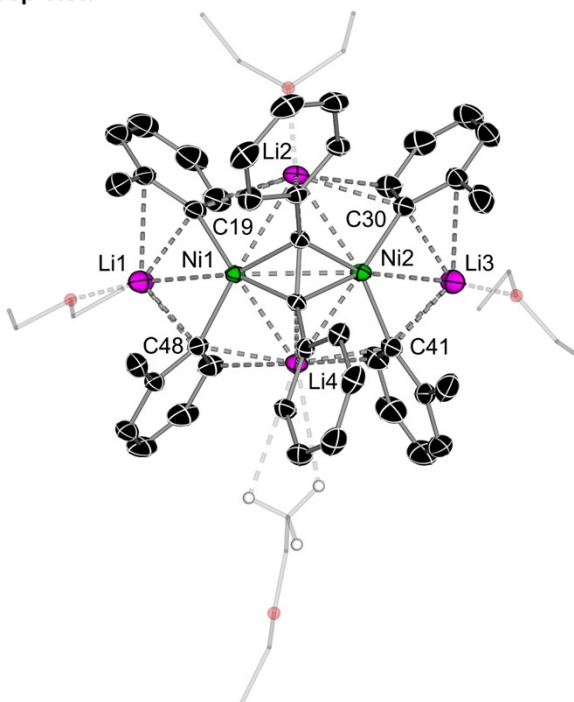


Figure S9: Molecular structure of **1d**. Thermal ellipsoids shown at 30% probability. Hydrogen atoms omitted and coordinated Et_2O shown as wireframes for clarity.

Molecular Structure of $\text{Li}_2(\text{Et}_2\text{O})_4(o\text{-Tol})_4\text{Ni}_2\{\mu_2:\eta^2,\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$, 1e

Top View



Side View

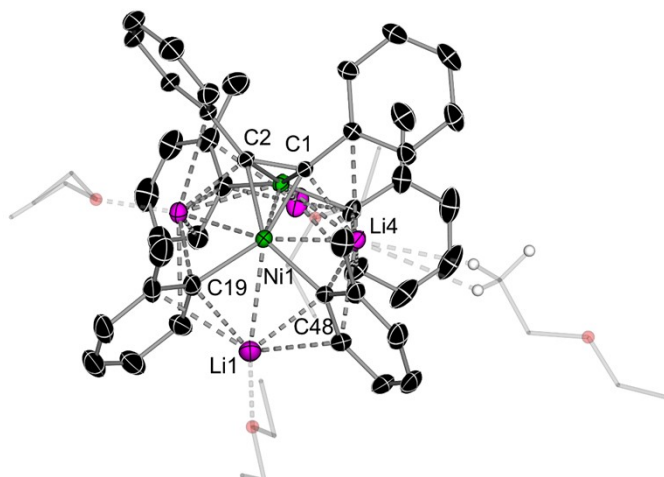
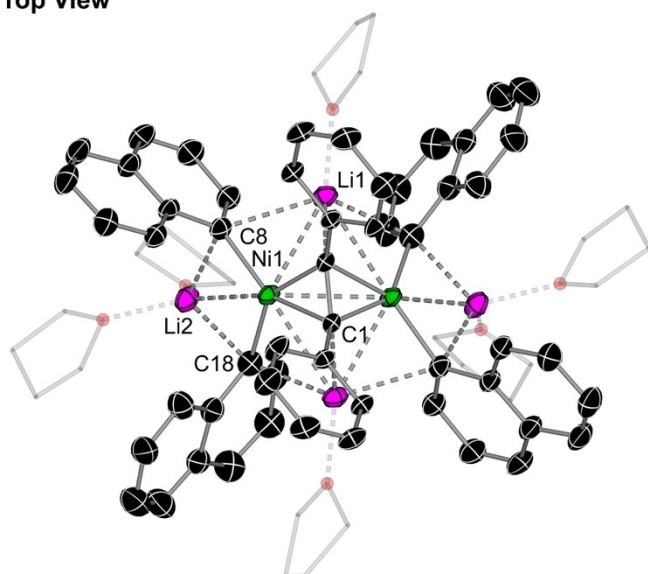


Figure S10: Molecular structure of **1e**. Thermal ellipsoids shown at 30% probability. Hydrogen atoms omitted and coordinated Et_2O shown as wireframes for clarity.

Molecular Structure of $\text{Li}_2(\text{THF})_6(1\text{-Naph})_4\text{Ni}_2\{\mu_2:\eta^2,\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$, **1f**

Top View



Side View

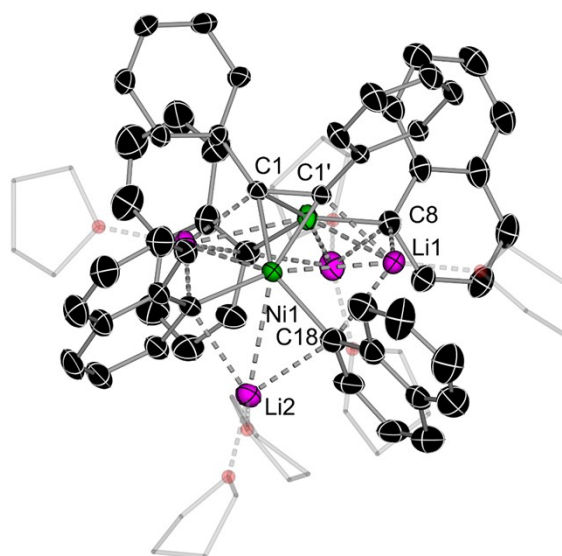


Figure S11: Molecular structure of **1f**. Thermal ellipsoids shown at 30% probability. Hydrogen atoms omitted and coordinated THF shown as wireframes for clarity.

Molecular Structure of $\text{Li}_2(\text{Et}_2\text{O})_2(2,6\text{-Me}_2\text{-C}_6\text{H}_3)_2\text{Ni}\{\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$, **2c**

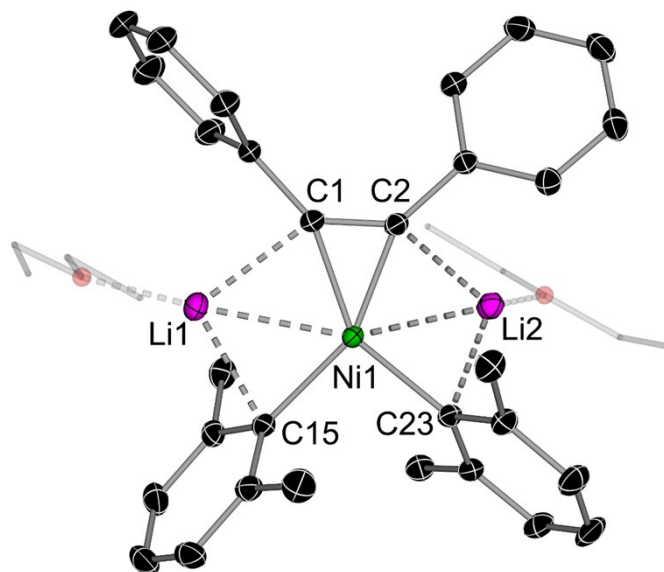
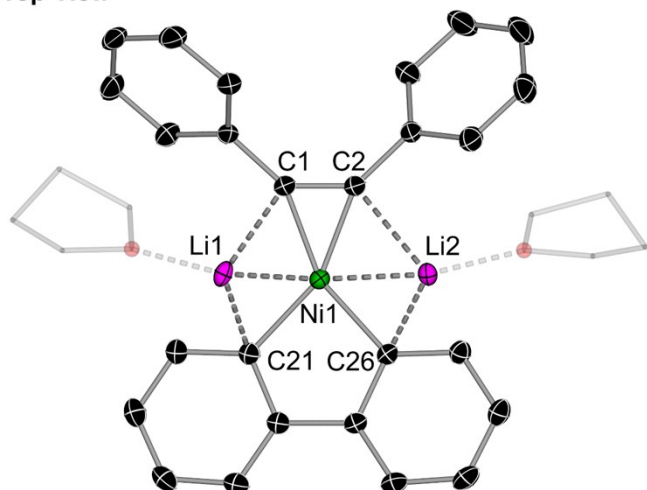


Figure S12: Molecular structure of **2c**. Thermal ellipsoids shown at 30% probability. Hydrogen atoms omitted and coordinated Et_2O shown as wireframes for clarity.

Molecular Structure of $\text{Li}_2(\text{THF})_4(2,2'\text{-biphenyl})\text{Ni}\{\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$, **2d**

Top View



Side View

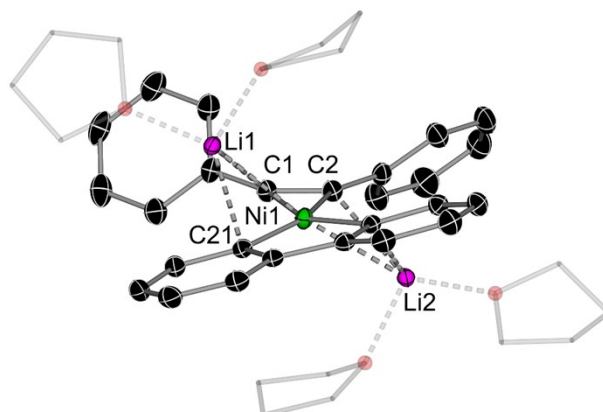
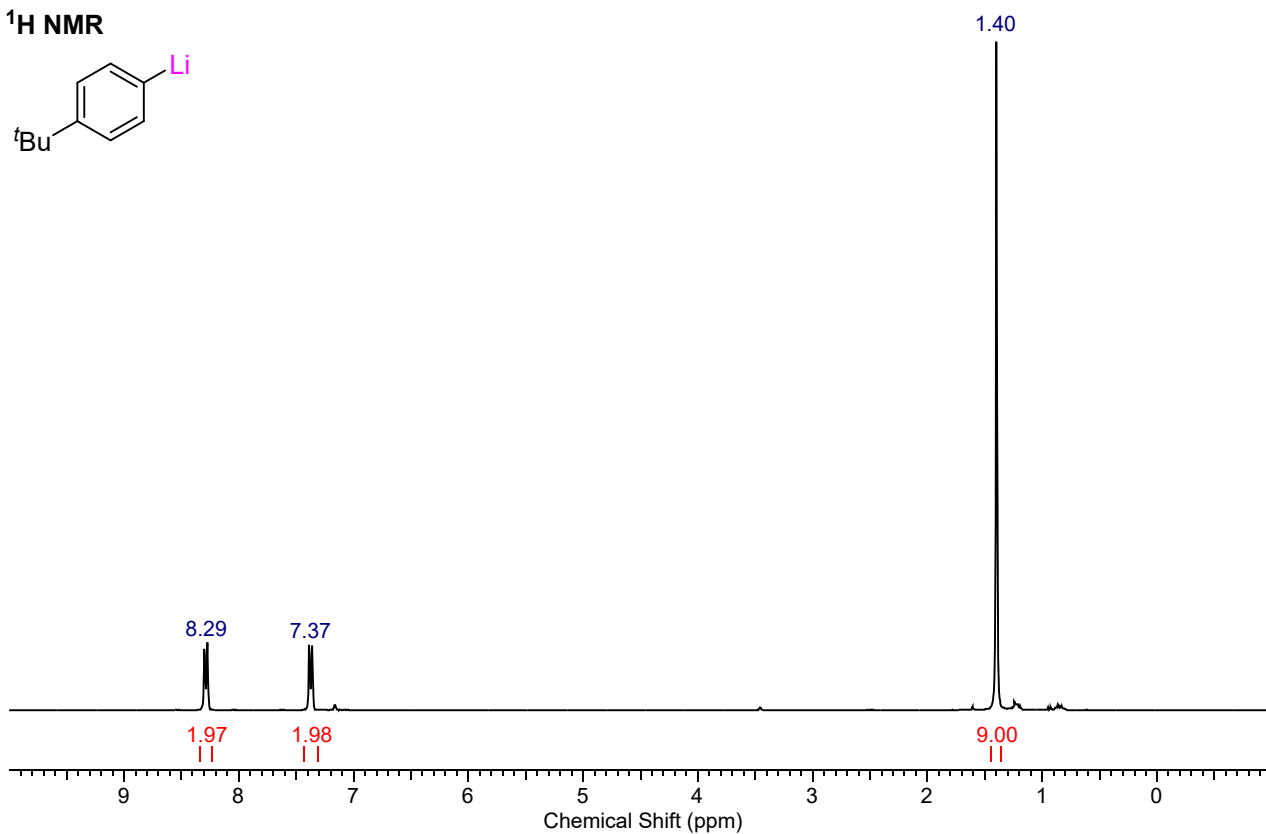
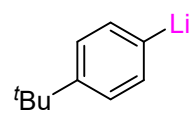


Figure S13: Molecular structure of **2d**. Thermal ellipsoids shown at 30% probability. Hydrogen atoms omitted and coordinated THF shown as wireframes for clarity. Two of the coordinated THF molecules have been removed from the top view for clarity.

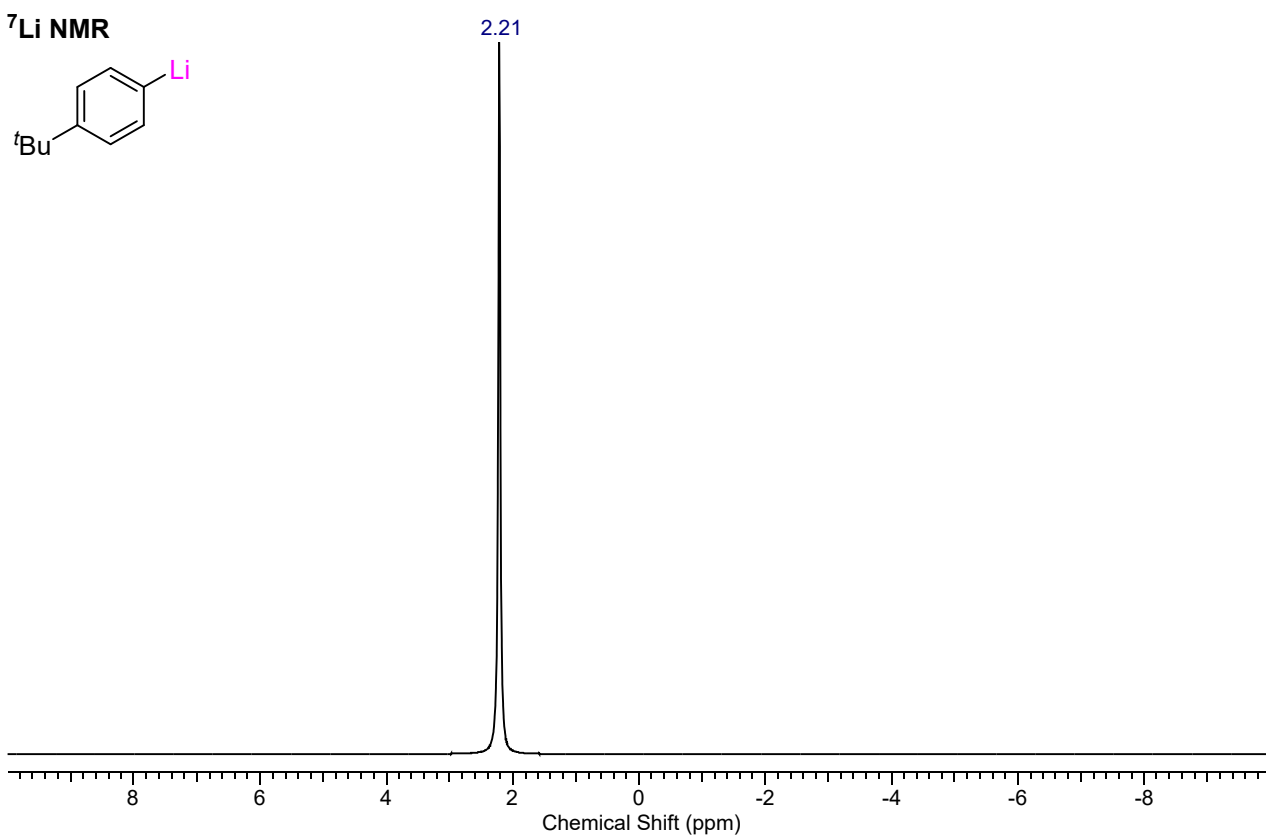
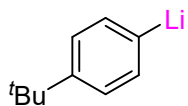
NMR Spectra of Reported Compounds

^1H NMR



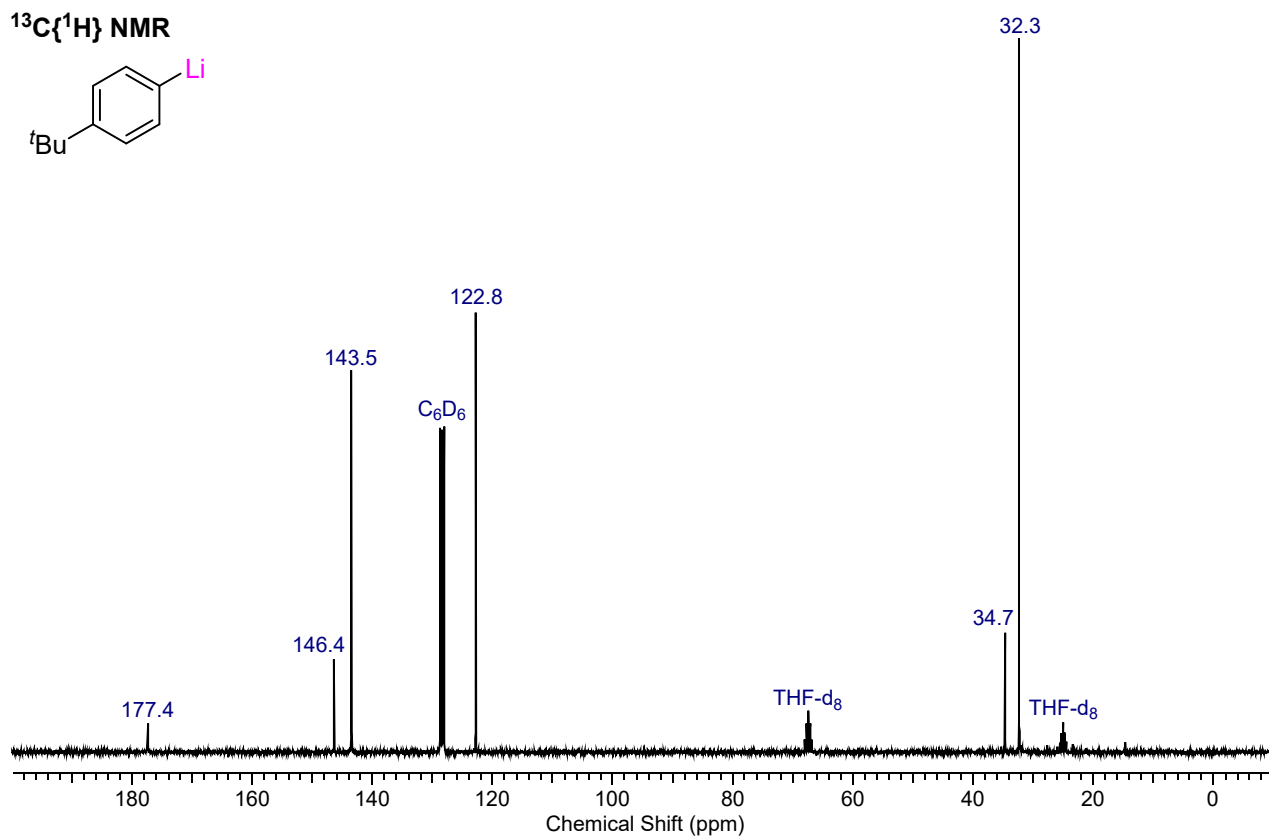
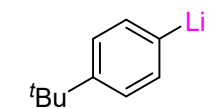
Spectra S1: ^1H NMR spectrum of 4-*t*Bu-C₆H₄-Li in C₆D₆/THF-d₈.

^7Li NMR



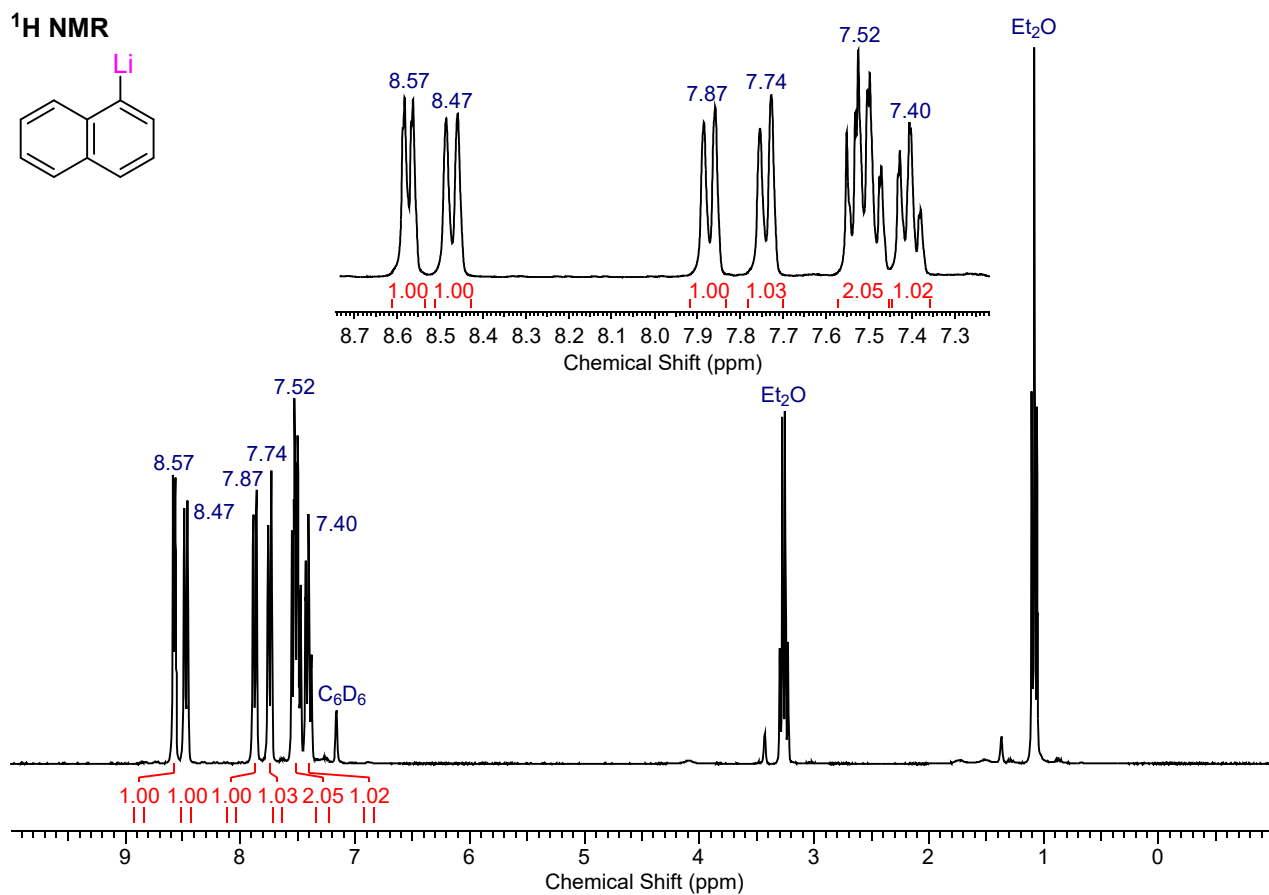
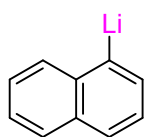
Spectra S2: ^7Li NMR spectrum of 4-*t*Bu-C₆H₄-Li in C₆D₆/THF-d₈.

$^{13}\text{C}\{^1\text{H}\}$ NMR

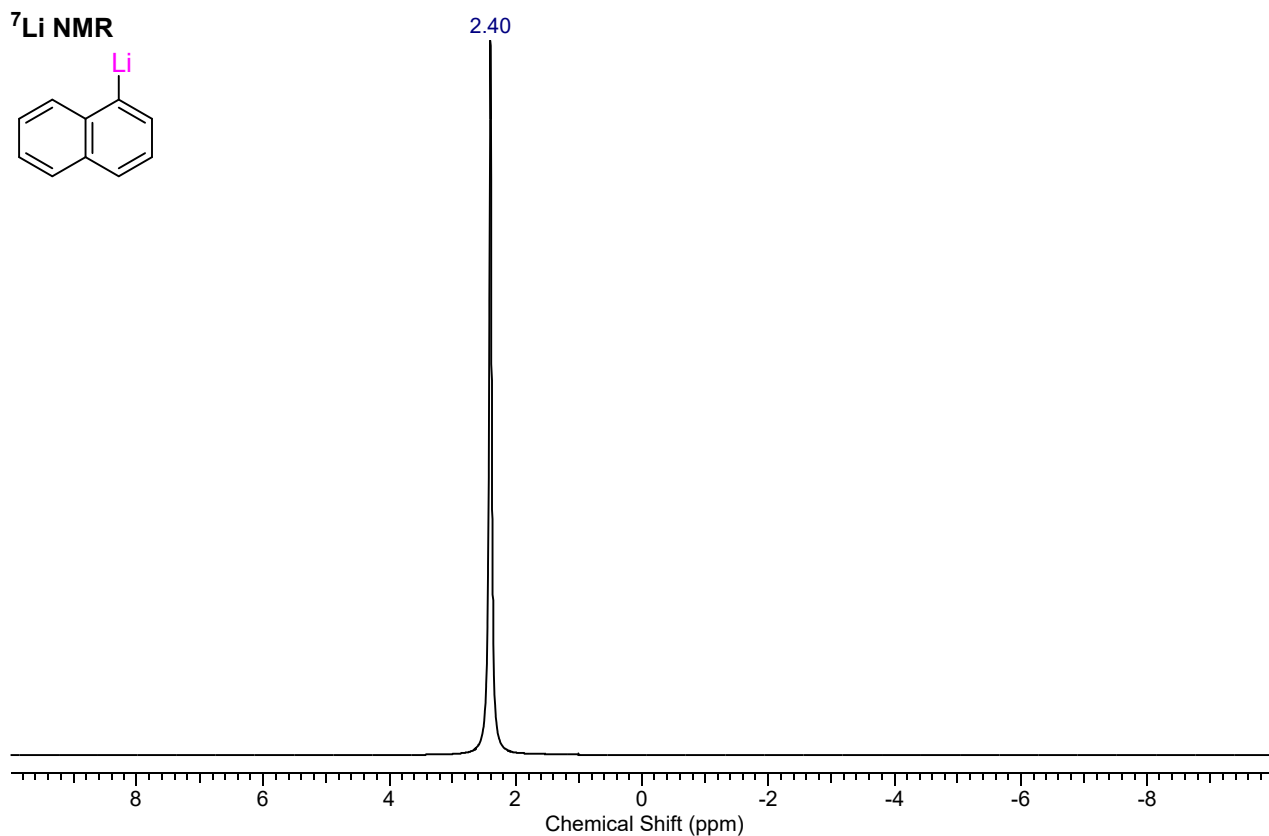


Spectra S3: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 4-*t*-Bu-C₆H₄-Li in C₆D₆/THF-d₈.

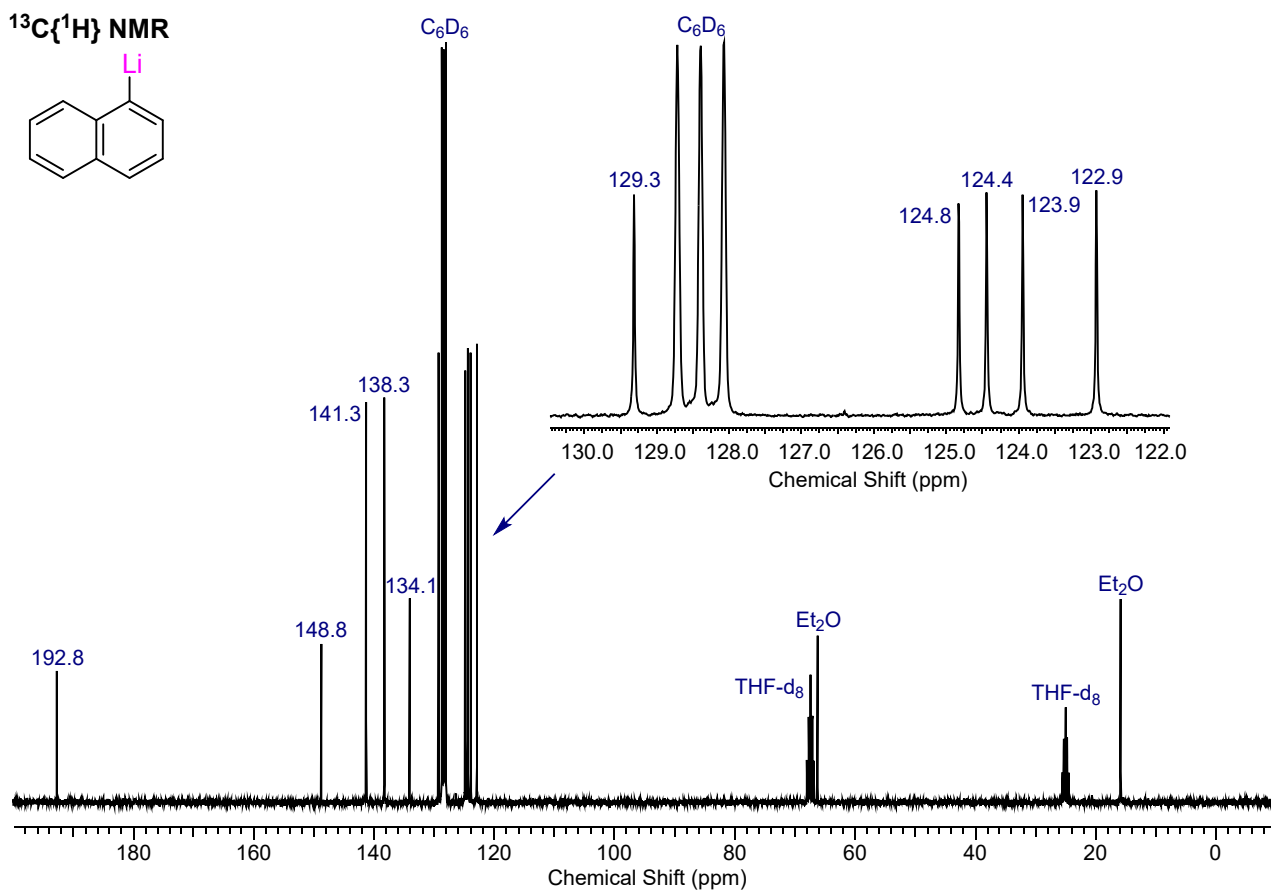
^1H NMR



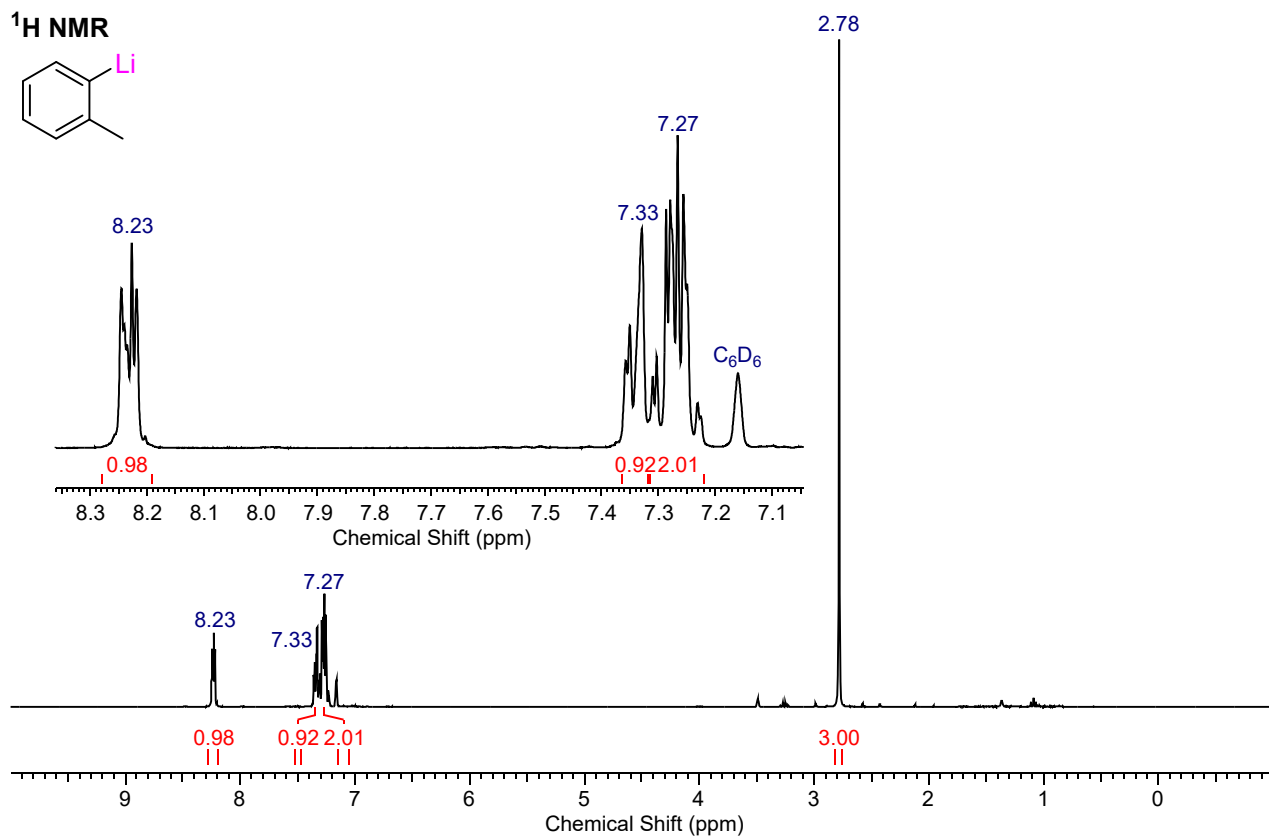
Spectra S4: ^1H NMR spectrum of 1-Naph-Li in C₆D₆/THF-d₈.



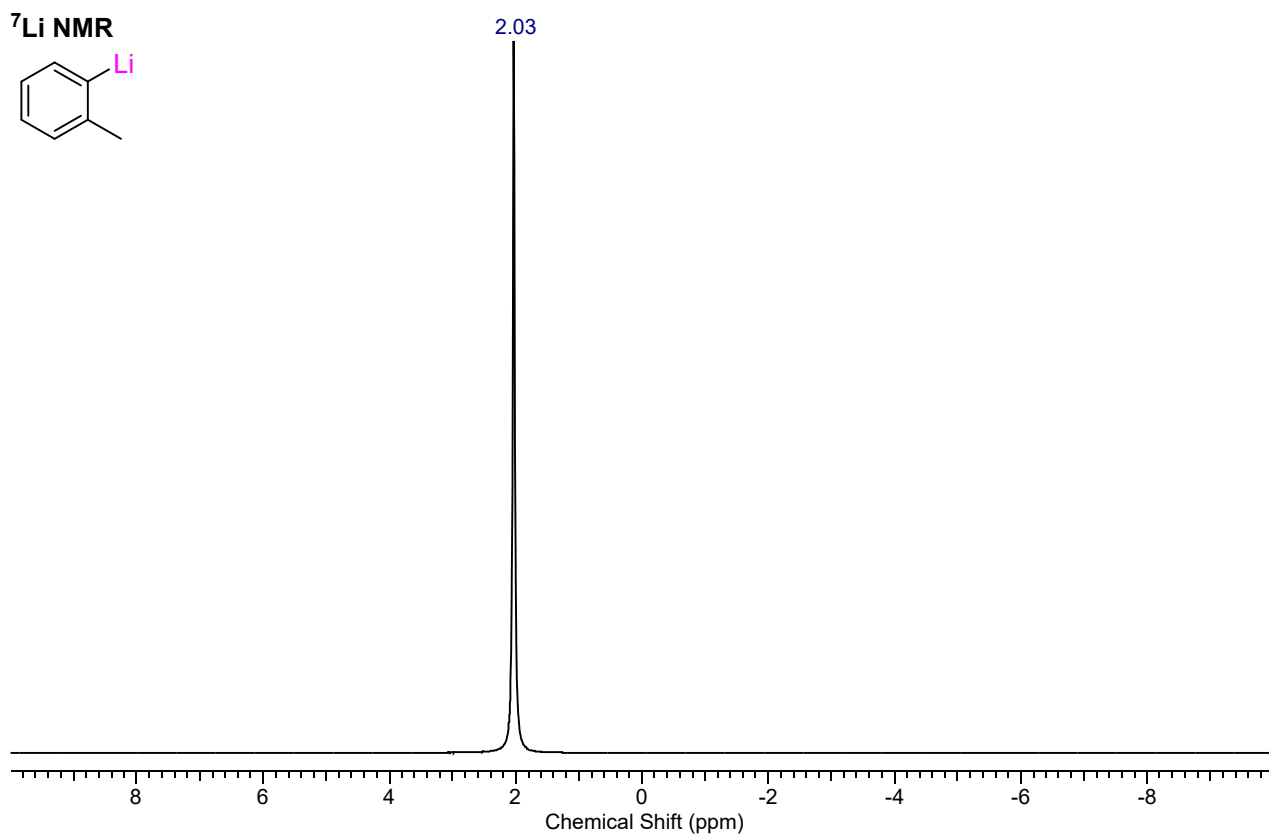
Spectra S5: ^7Li NMR spectrum of 1-Naph-Li in $\text{C}_6\text{D}_6/\text{THF-d}_8$.



Spectra S6: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 1-Naph-Li in $\text{C}_6\text{D}_6/\text{THF-d}_8$.

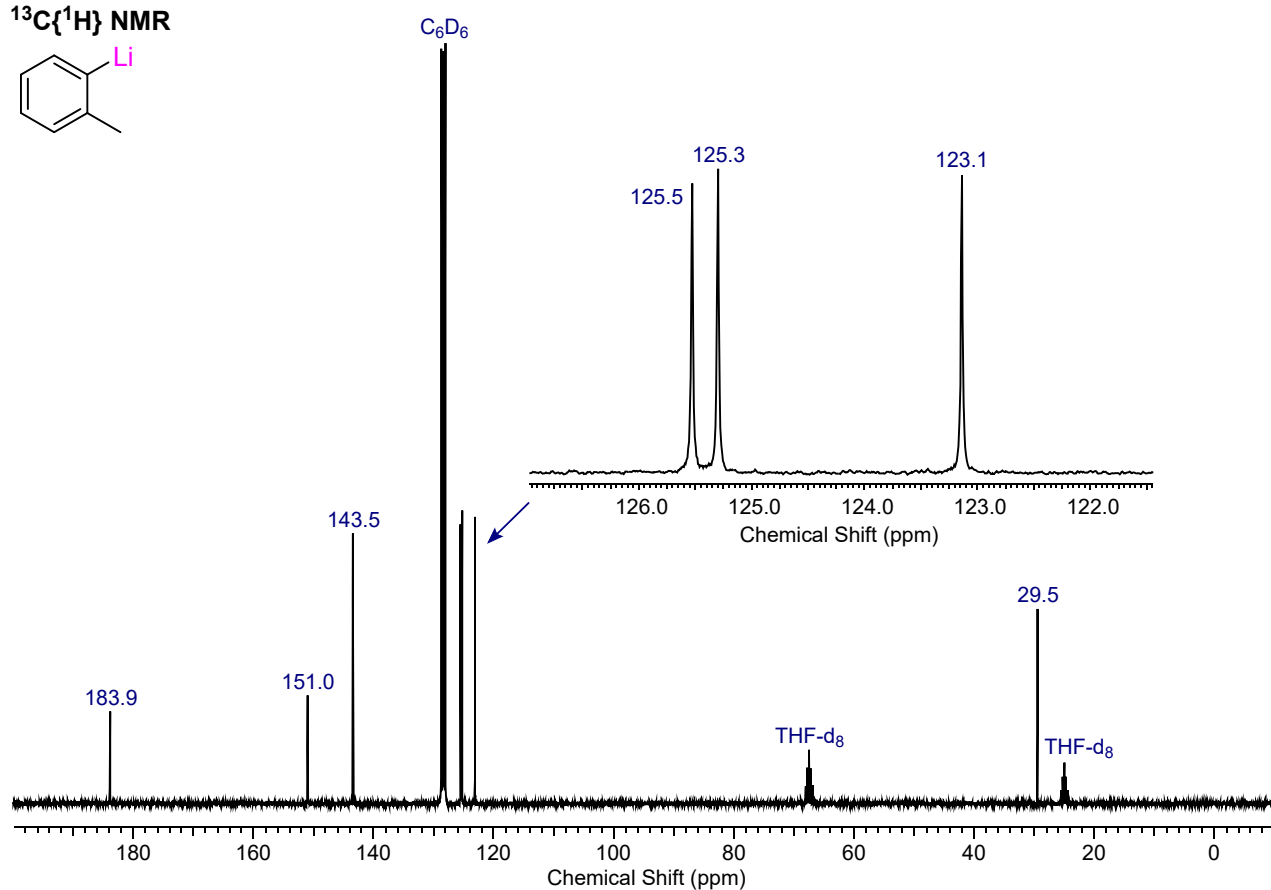
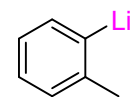


Spectra S7: ¹H NMR spectrum of *o*-Tol-Li in C₆D₆/THF-d₈.



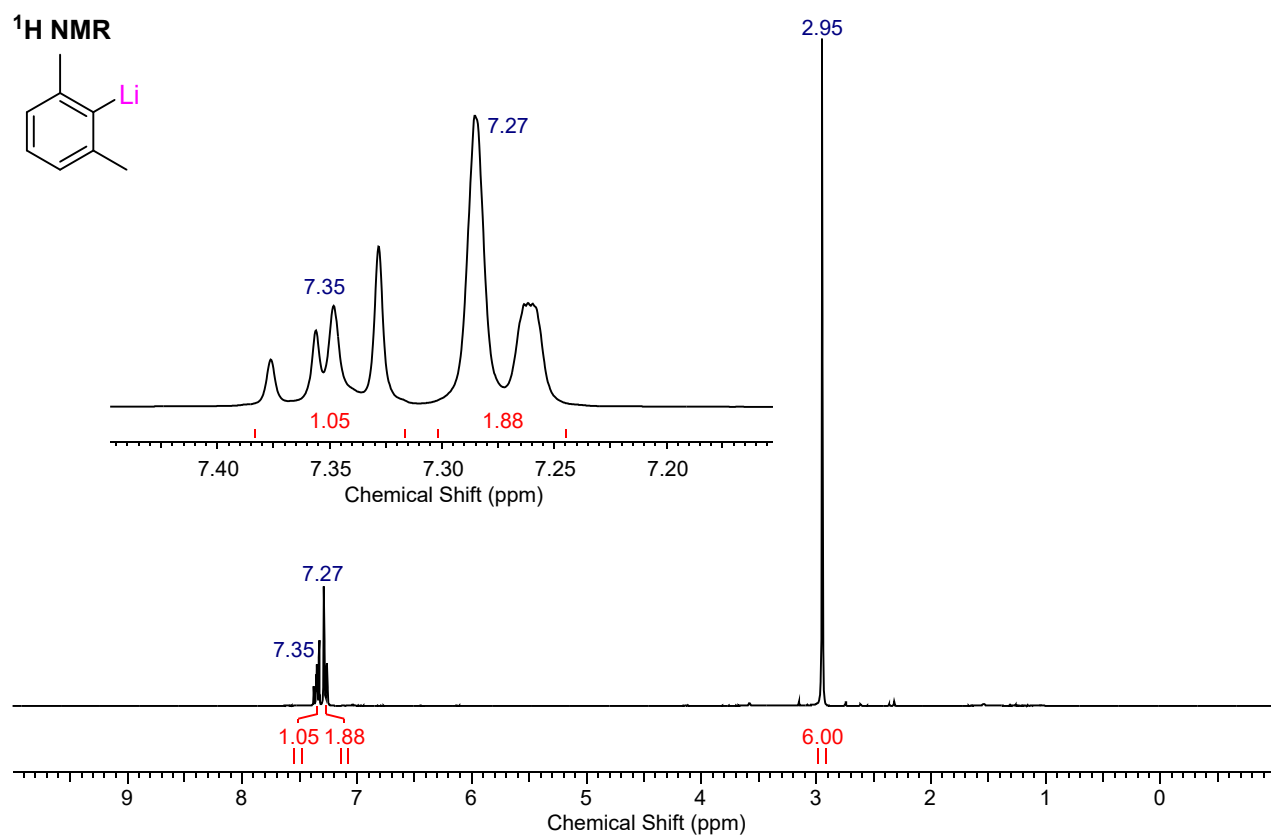
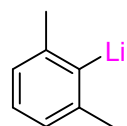
Spectra S8: ⁷Li NMR spectrum of *o*-Tol-Li in C₆D₆/THF-d₈.

$^{13}\text{C}\{^1\text{H}\}$ NMR



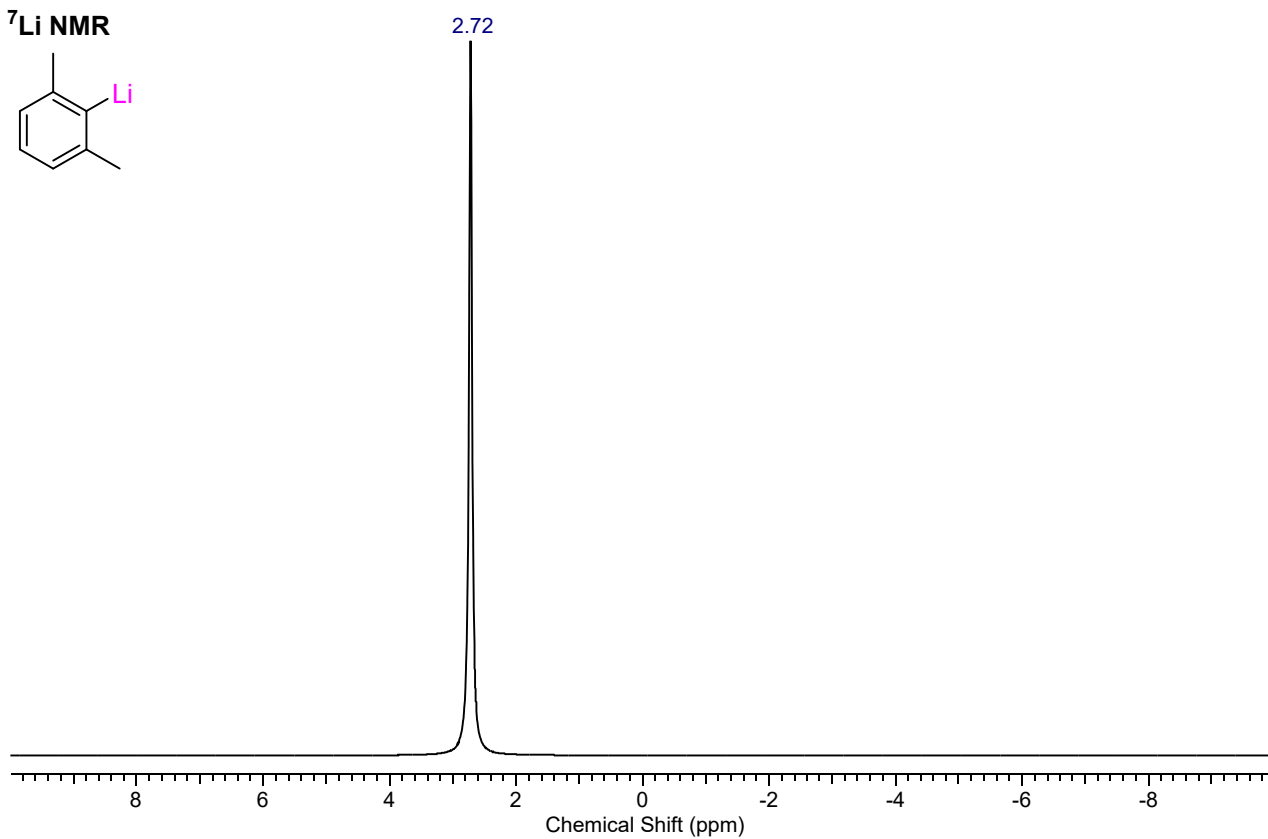
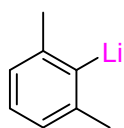
Spectra S9: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of *o*-Tol-Li in $\text{C}_6\text{D}_6/\text{THF-d}_8$.

^1H NMR



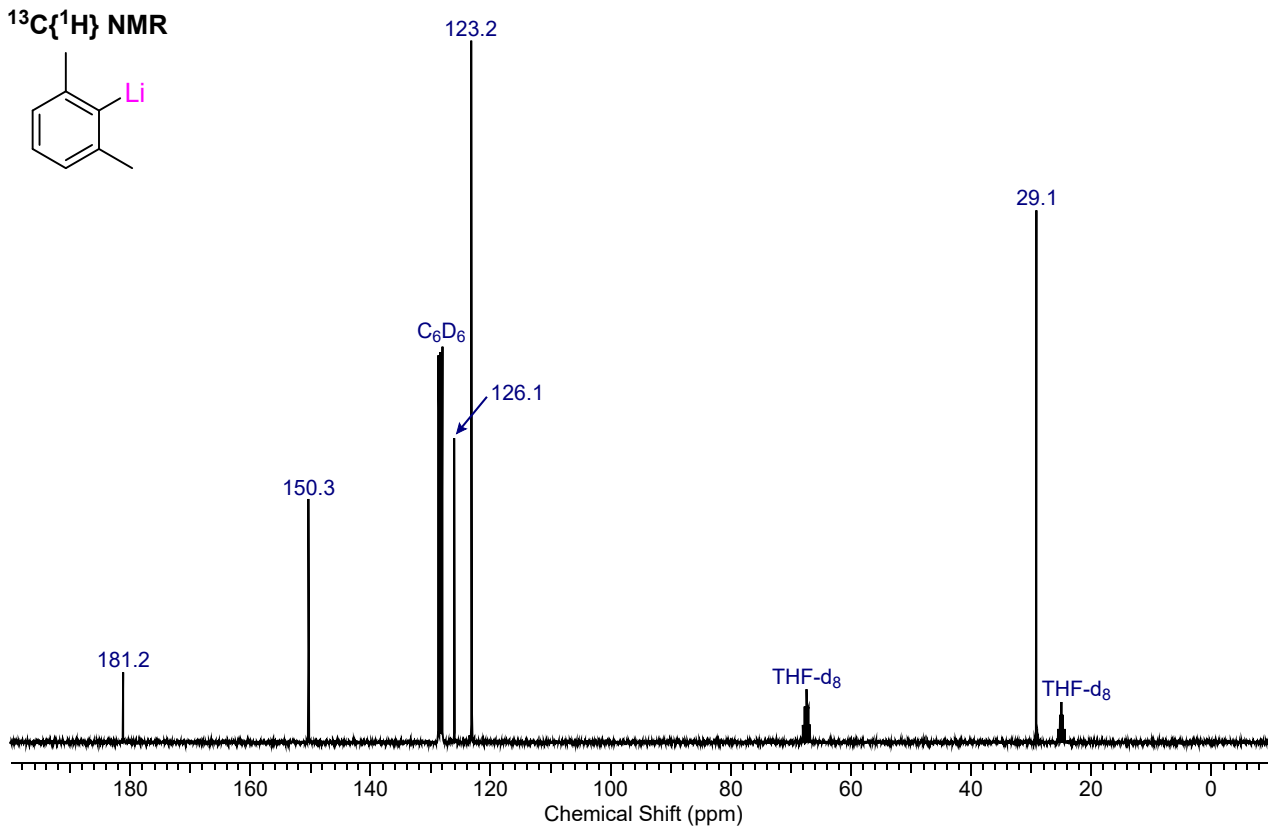
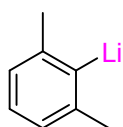
Spectra S10: ^1H NMR spectrum of 2,6-Me₂-C₆H₃-Li in $\text{C}_6\text{D}_6/\text{THF-d}_8$.

⁷Li NMR



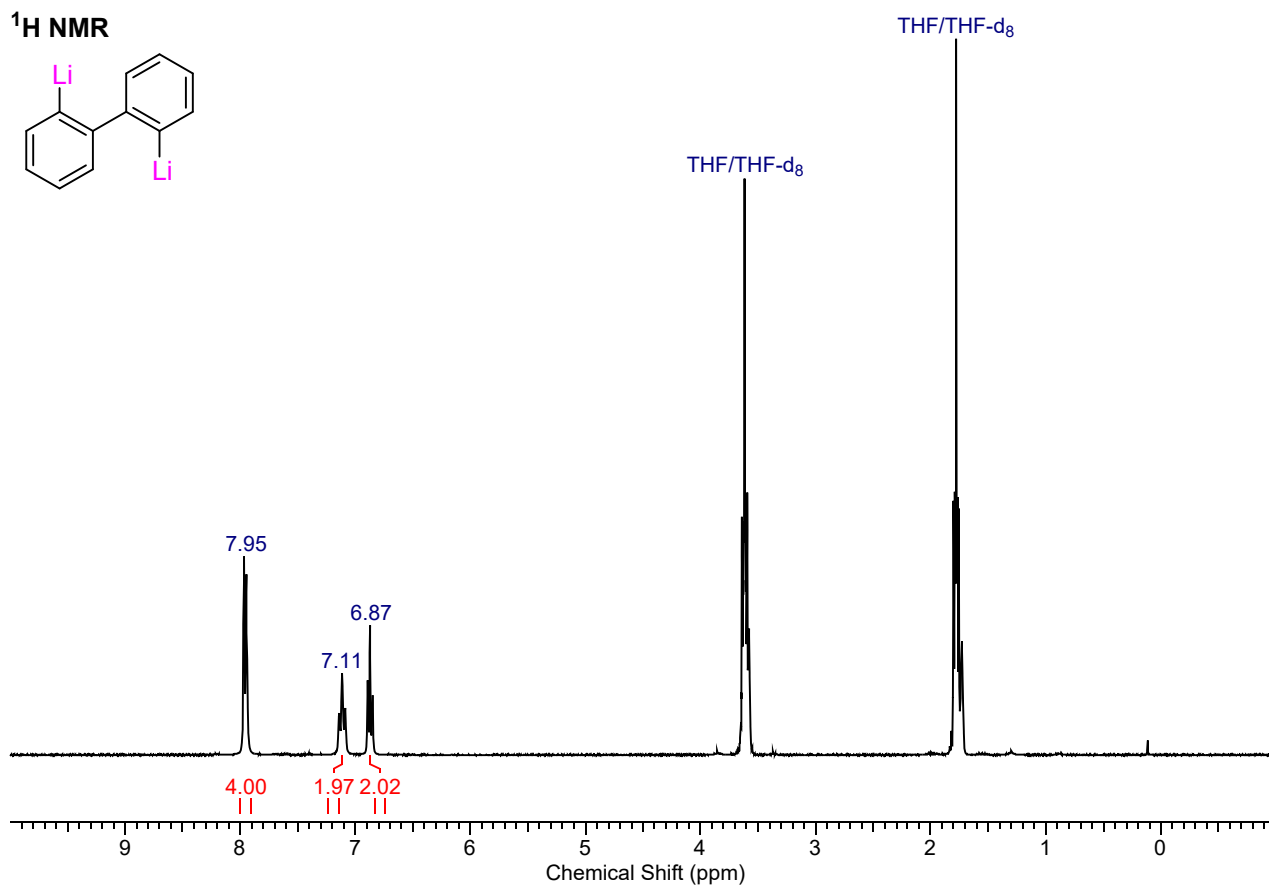
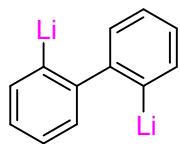
Spectra S11: ⁷Li NMR spectrum of 2,6-Me₂-C₆H₃-Li in C₆D₆/THF-d₈.

¹³C{¹H} NMR



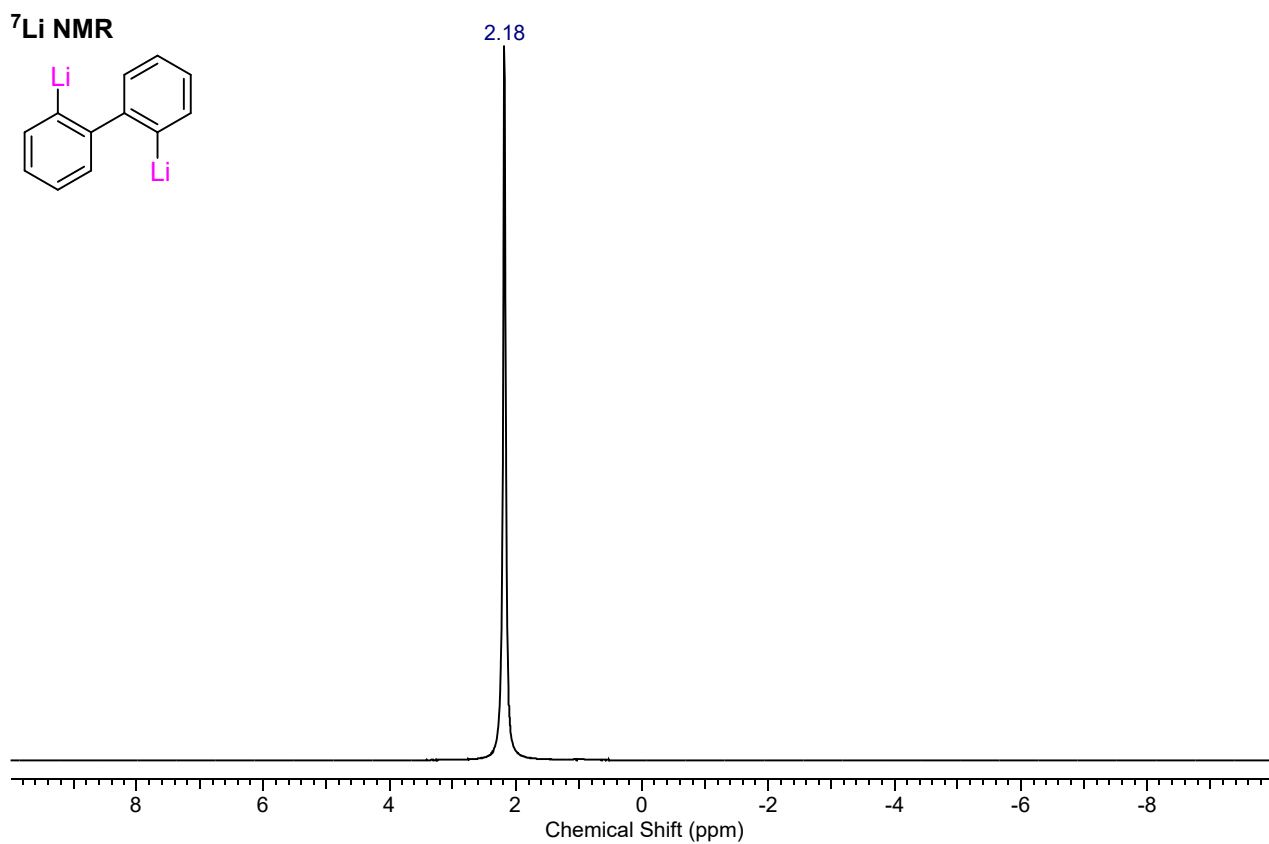
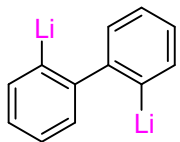
Spectra S12: ¹³C{¹H} NMR spectrum of 2,6-Me₂-C₆H₃-Li in C₆D₆/THF-d₈.

¹H NMR



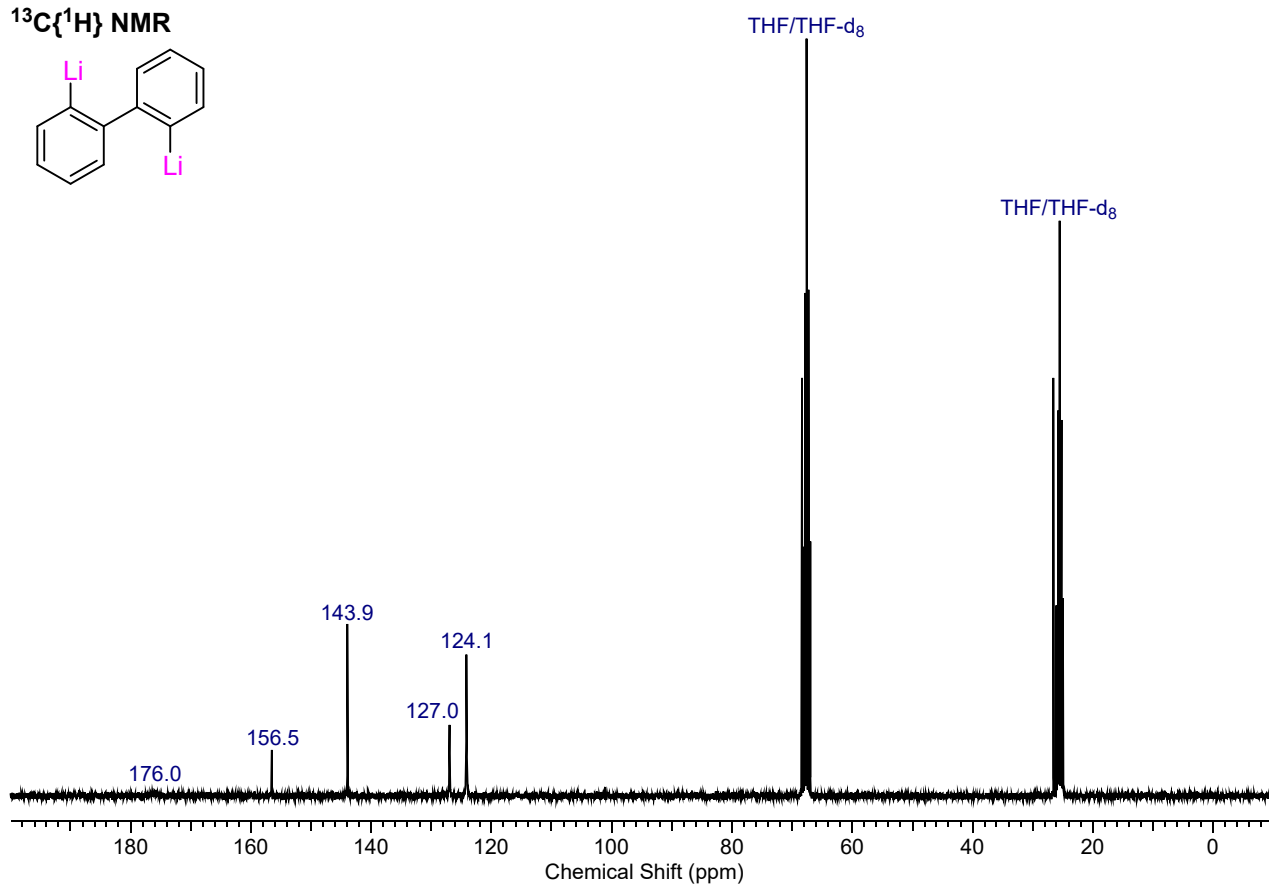
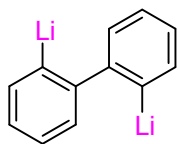
Spectra S13: ¹H NMR spectrum of 2,2'-dilithiobiphenyl in THF-d₈.

⁷Li NMR



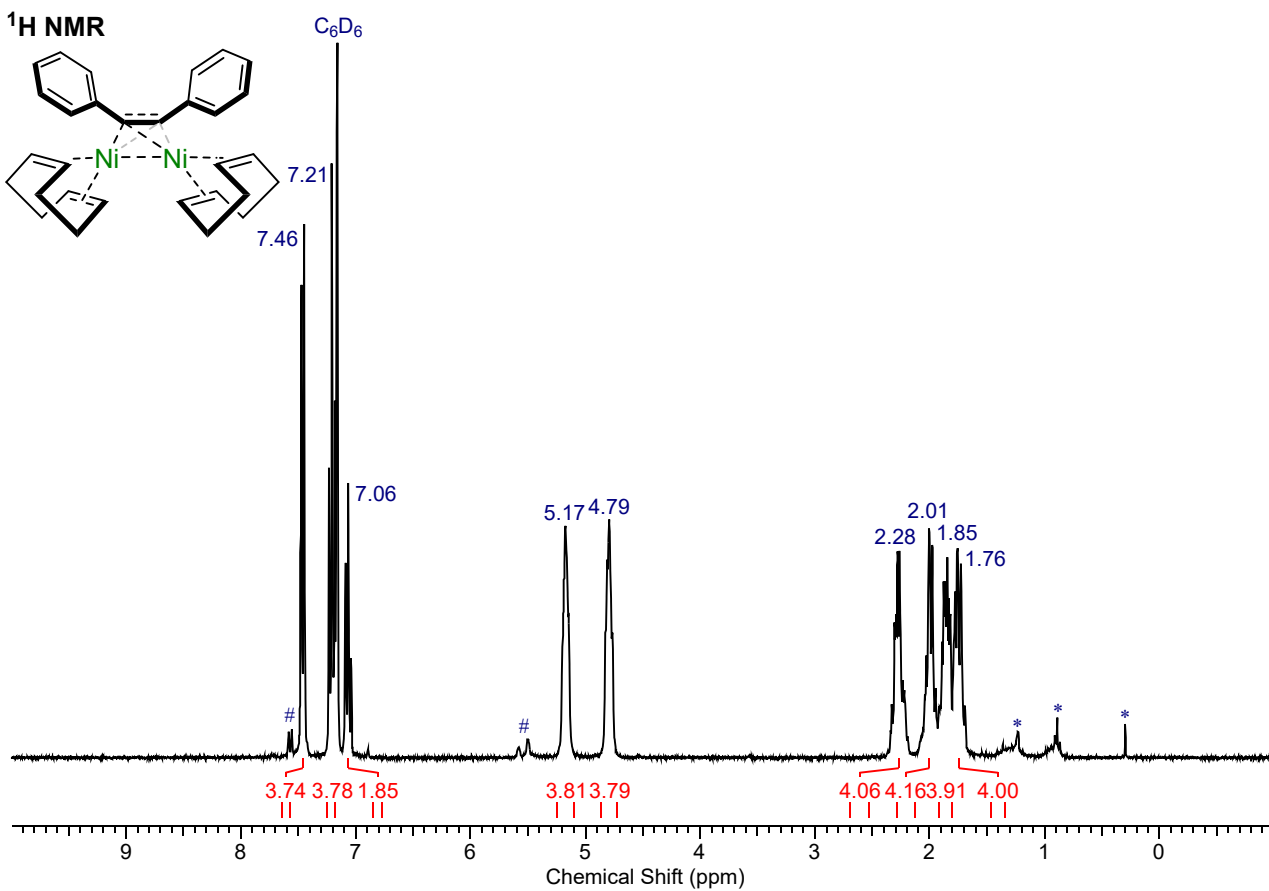
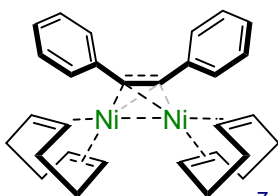
Spectra S14: ⁷Li NMR spectrum of 2,2'-dilithiobiphenyl in THF-d₈.

$^{13}\text{C}\{^1\text{H}\}$ NMR

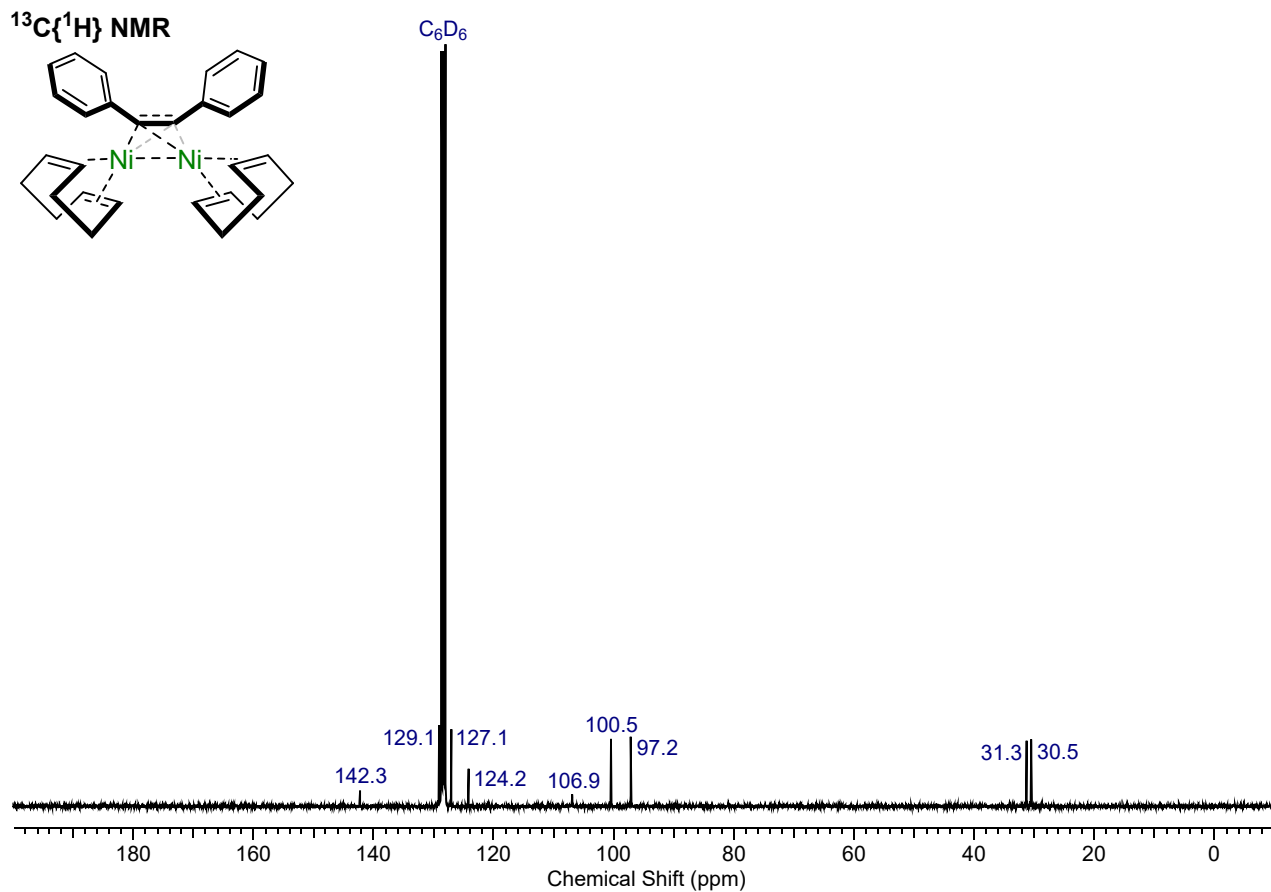


Spectra S15: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2,2'-dilithiobiphenyl in THF-d₈.

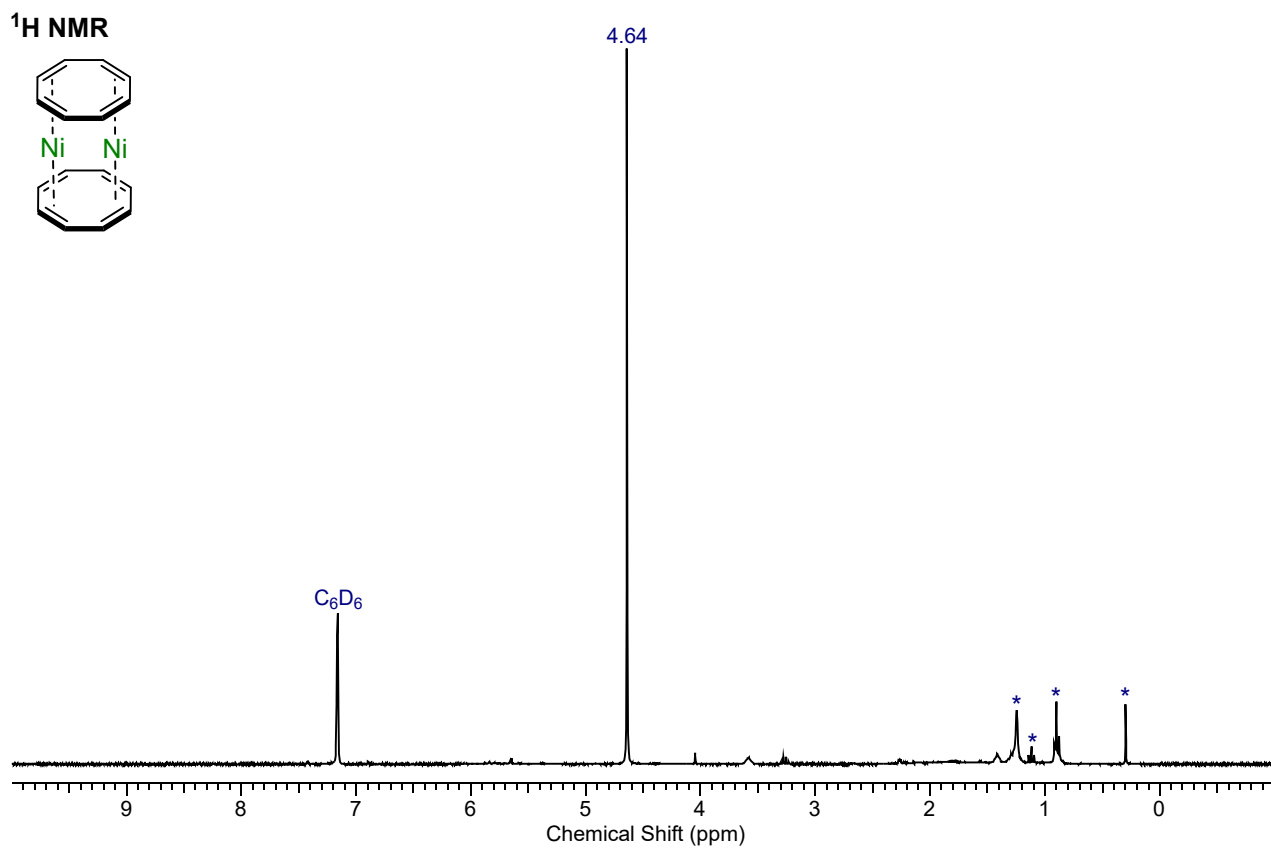
^1H NMR



Spectra S16: ^1H NMR spectrum of $[(\text{COD})\text{Ni}]_2[\mu_2:\eta^2,\eta^2\text{-Ph-C}\equiv\text{C-Ph}]$ in C₆D₆. # = Trace (COD)Ni $\{\eta^2\text{-Ph-C}\equiv\text{C-Ph}\}$; * = Residual solvent/grease.

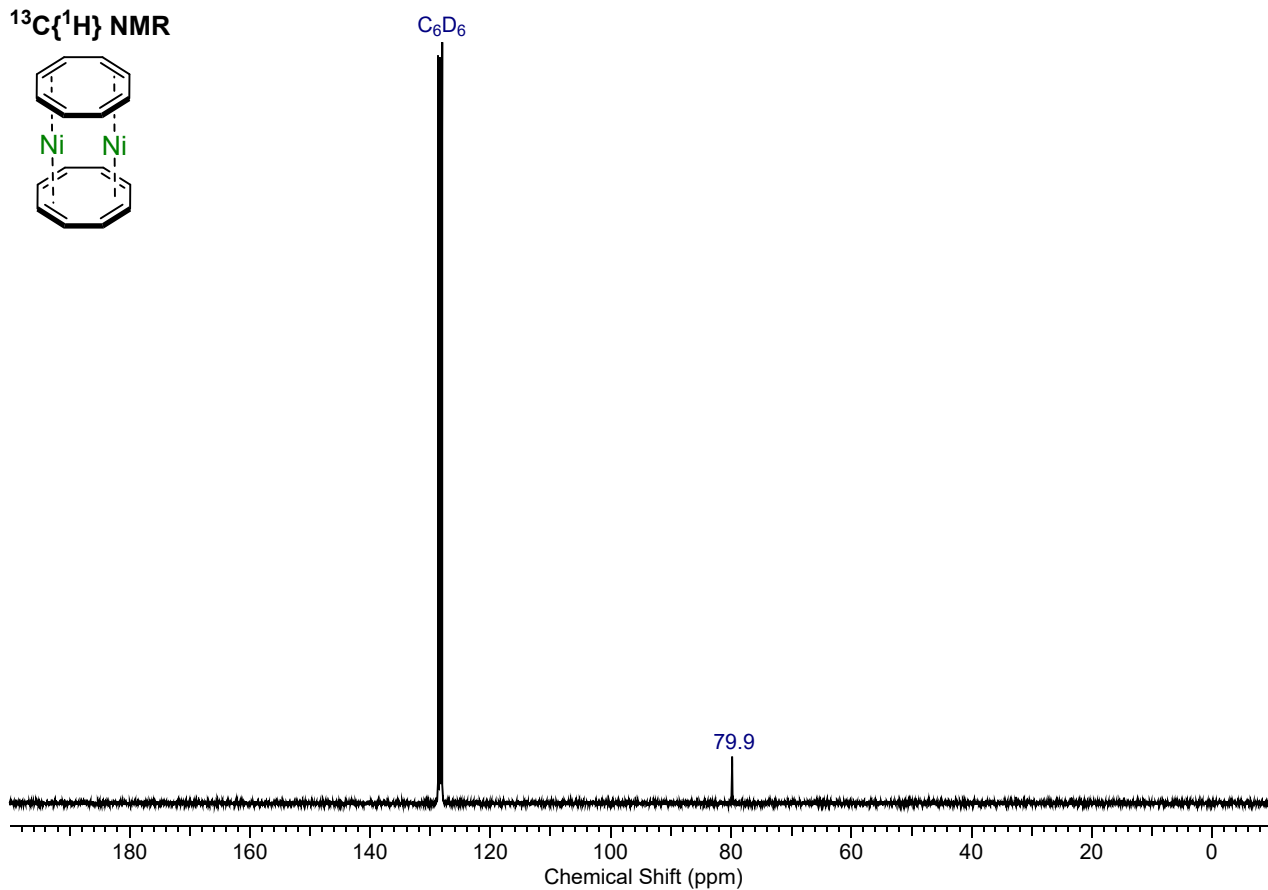
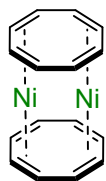


Spectra S17: ¹³C{¹H} NMR spectrum of [(COD)Ni]₂{μ₂:η²,η²-Ph-C≡C-Ph} in C₆D₆.



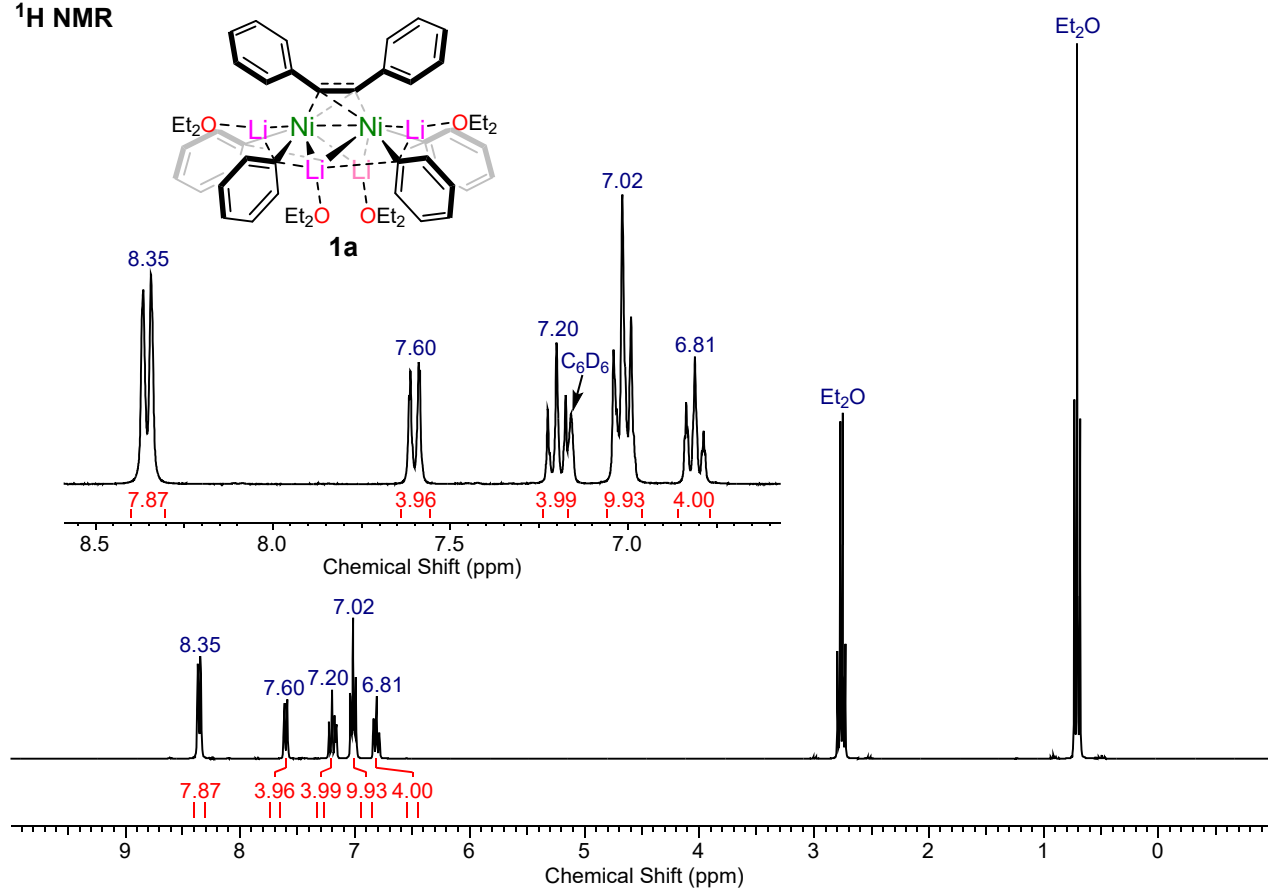
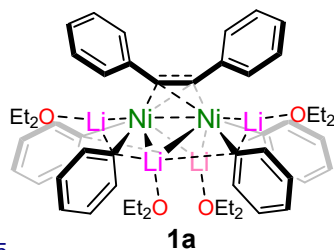
Spectra S18: ¹H NMR spectrum of Ni₂COT₂ in C₆D₆. * = Residual solvent/grease.

$^{13}\text{C}\{^1\text{H}\}$ NMR



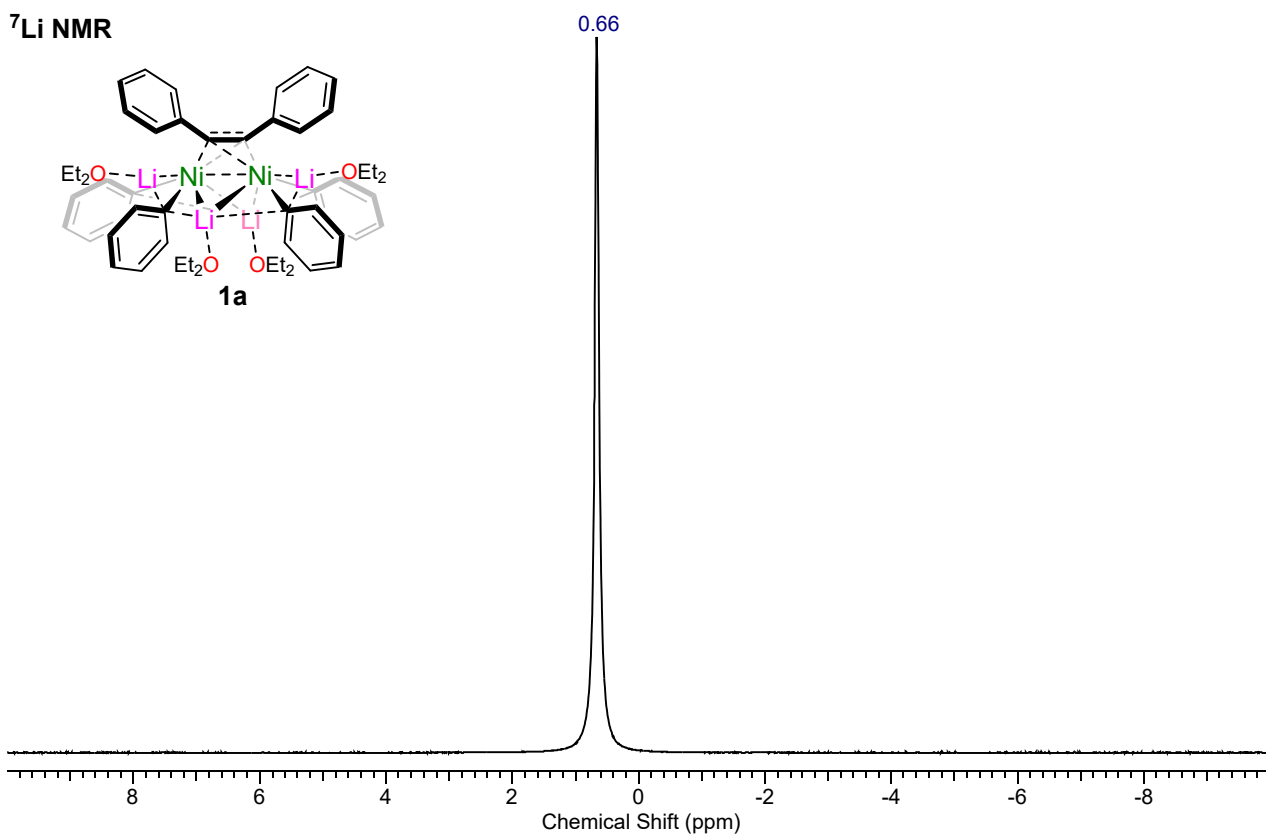
Spectra S19: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of Ni_2COT_2 in C_6D_6 .

^1H NMR



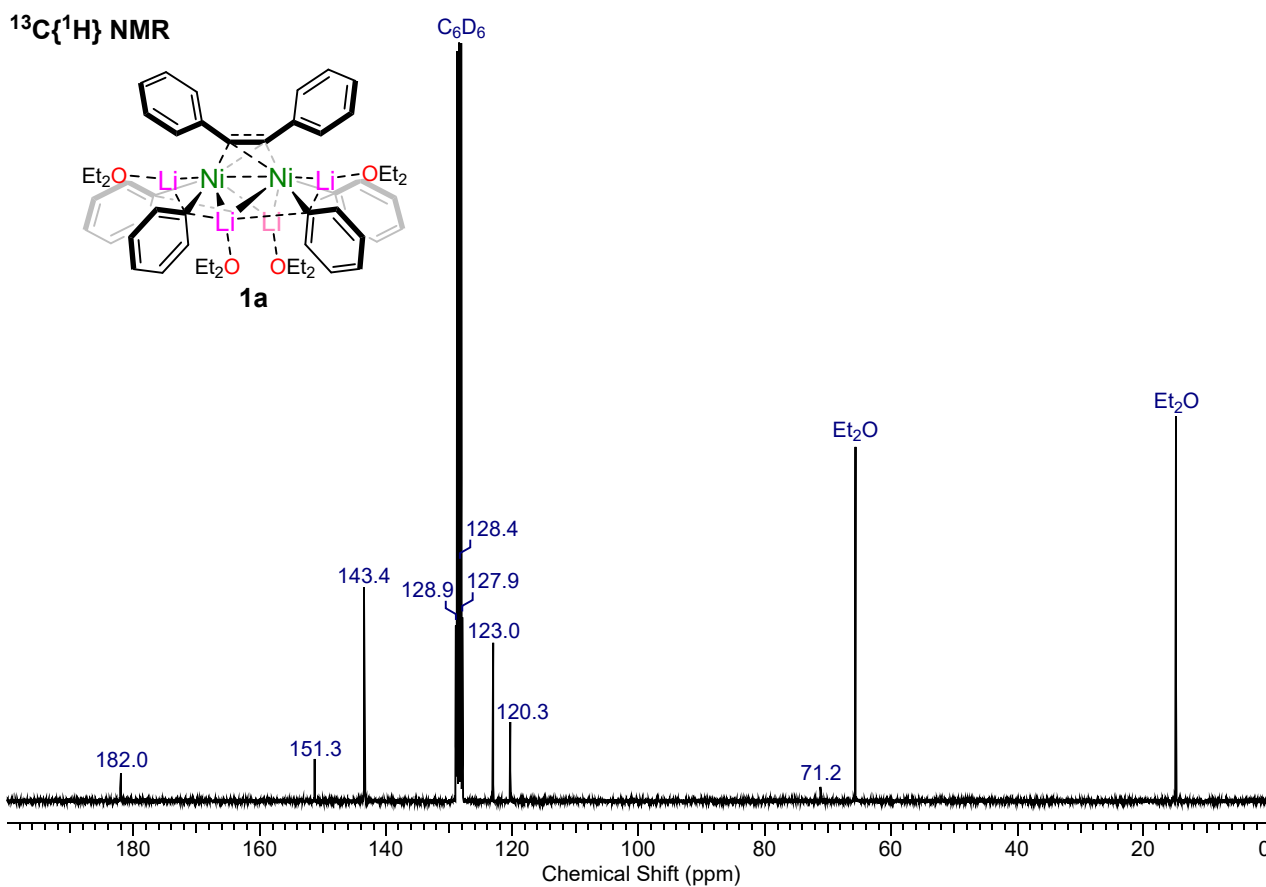
Spectra S20: ^1H NMR spectrum of **1a** in C_6D_6 .

^7Li NMR

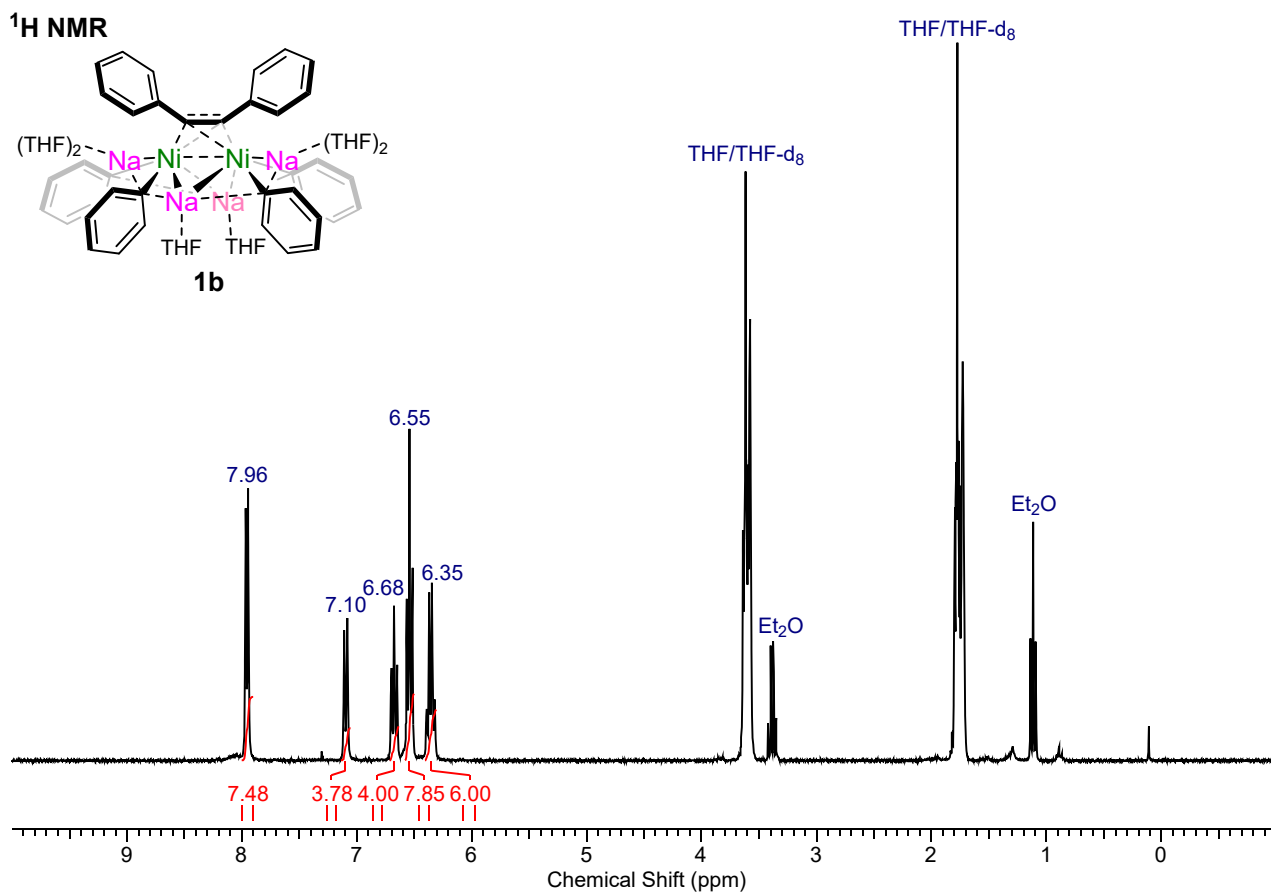


Spectra S21: ^7Li NMR spectrum of **1a** in C_6D_6 .

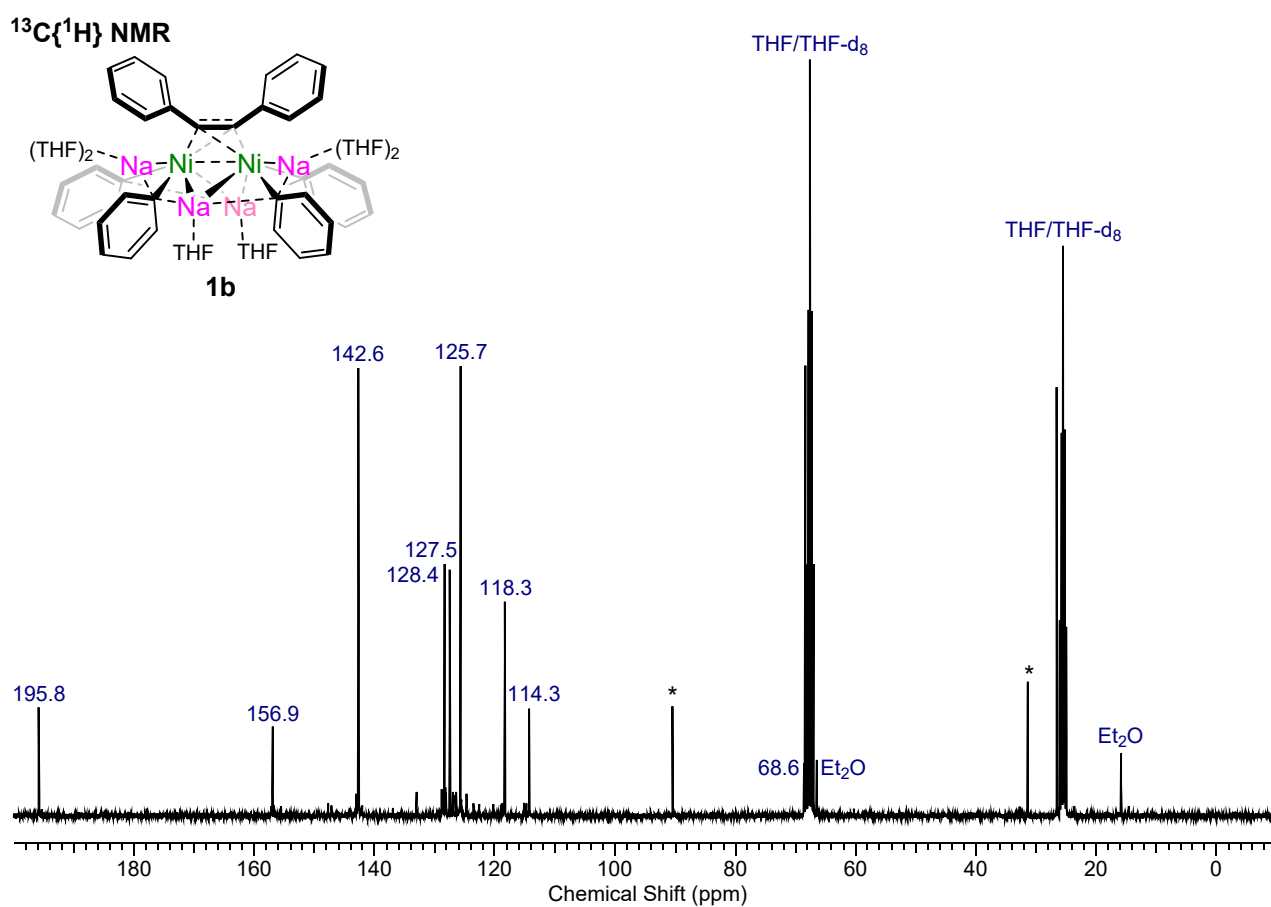
$^{13}\text{C}\{^1\text{H}\}$ NMR



Spectra S22: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1a** in C_6D_6 .

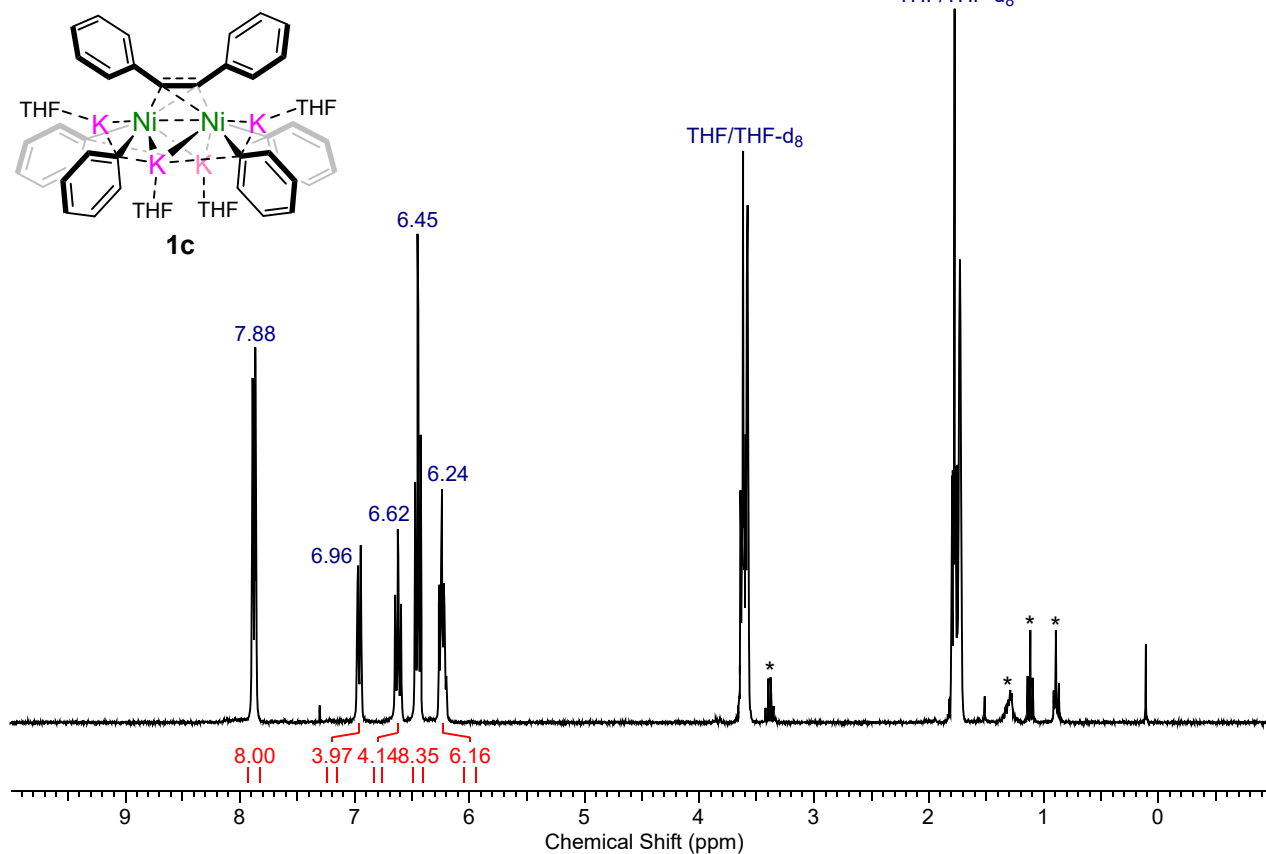


Spectra S23: ¹H NMR spectrum of **1b** in THF-d₈.



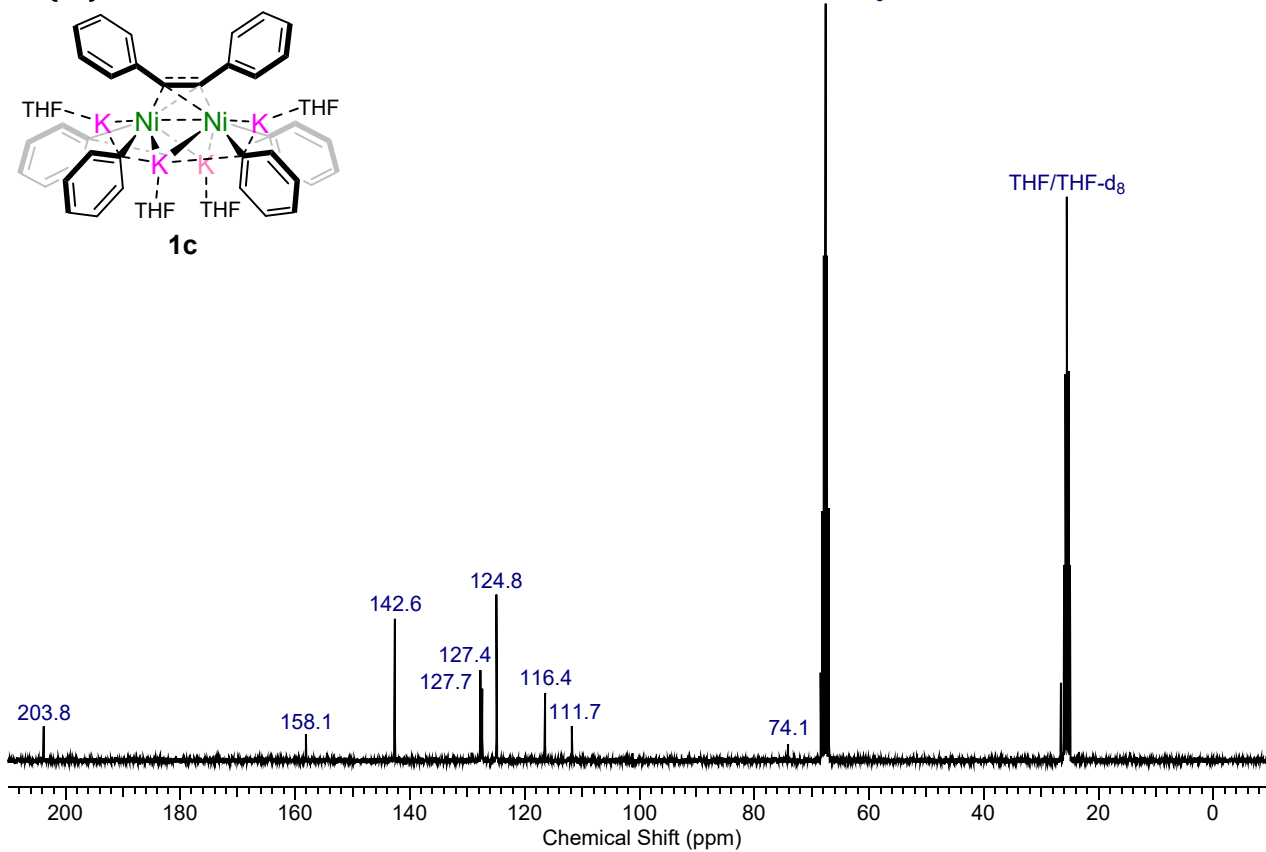
Spectra S24: ¹³C{¹H} NMR spectrum of **1b** in THF-d₈. * Trace Ni(COD)₂.

¹H NMR



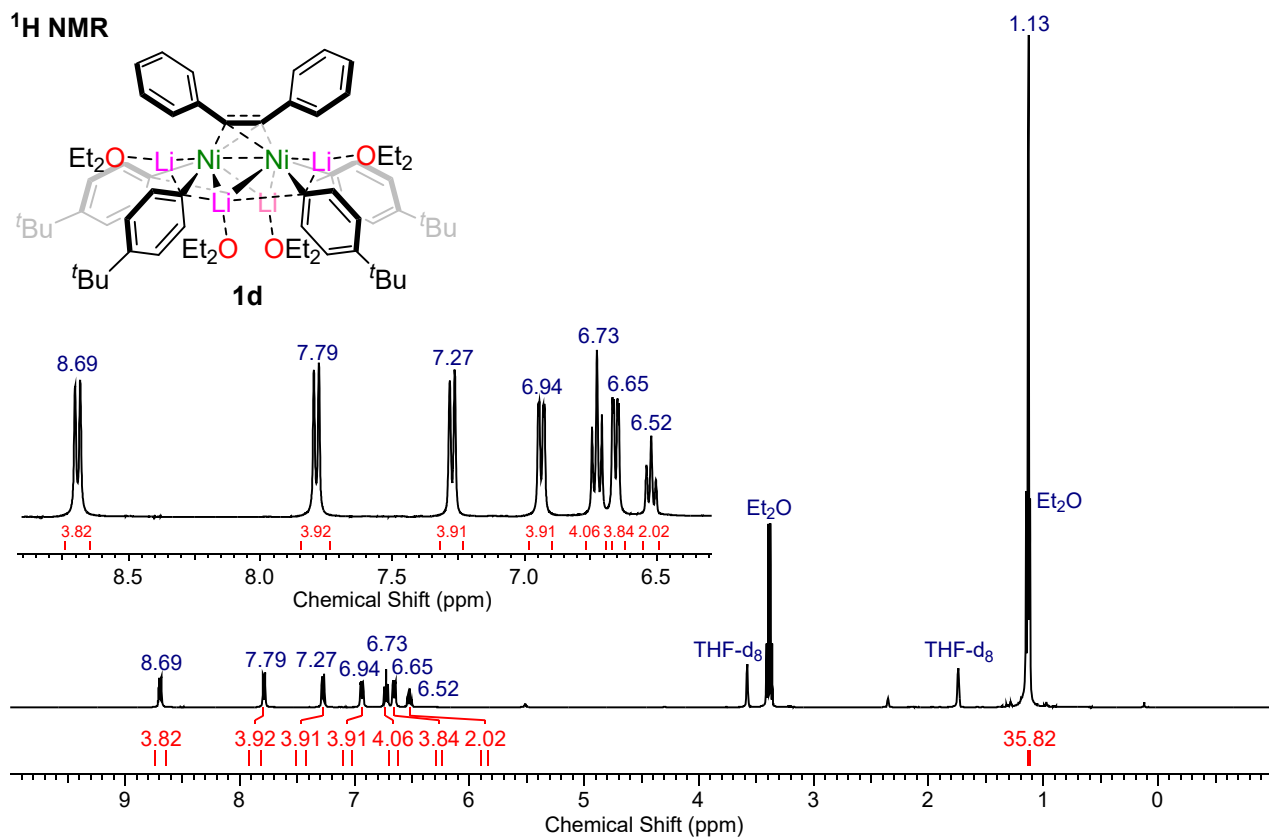
Spectra S25: ¹H NMR spectrum of **1c** in THF-d₈. * = Residual Et₂O/pentane.

¹³C{¹H} NMR



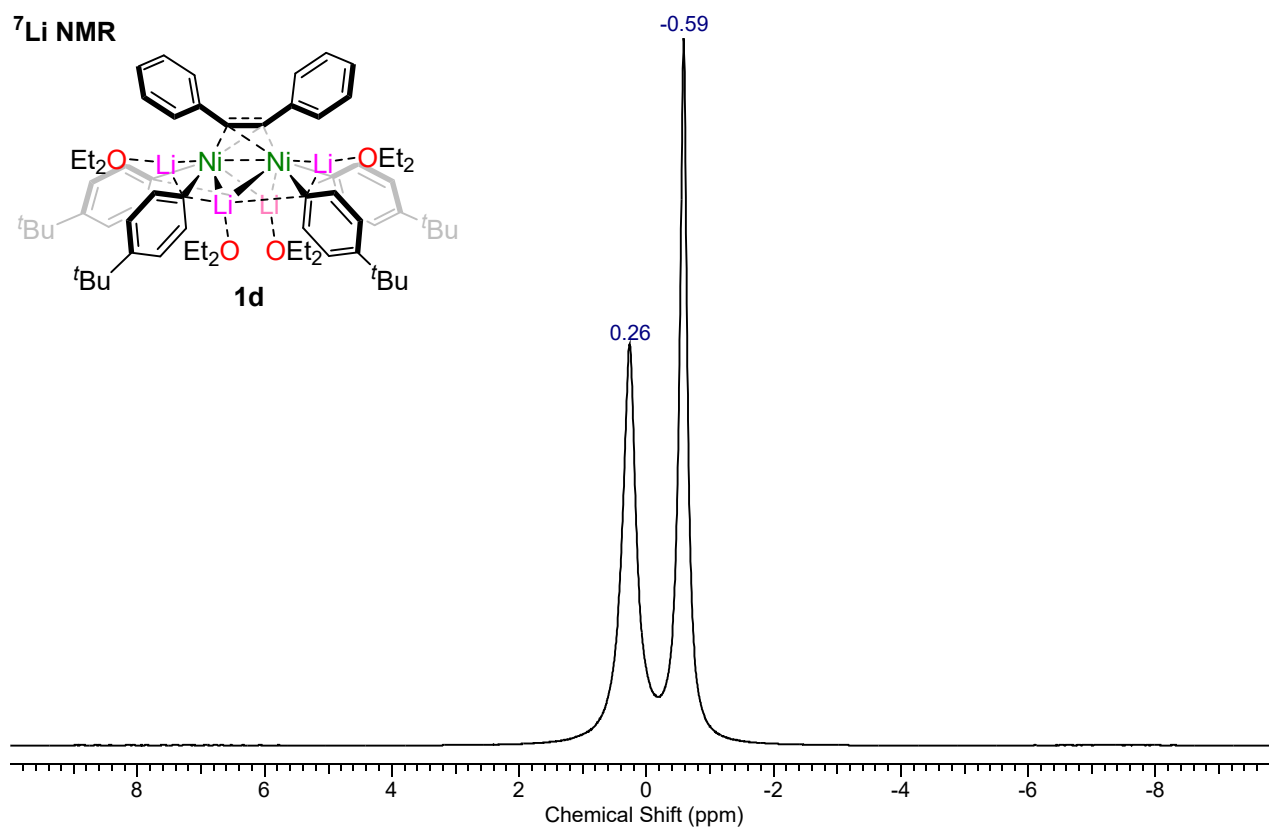
Spectra S26: ¹³C{¹H} NMR spectrum of **1c** in THF-d₈.

¹H NMR



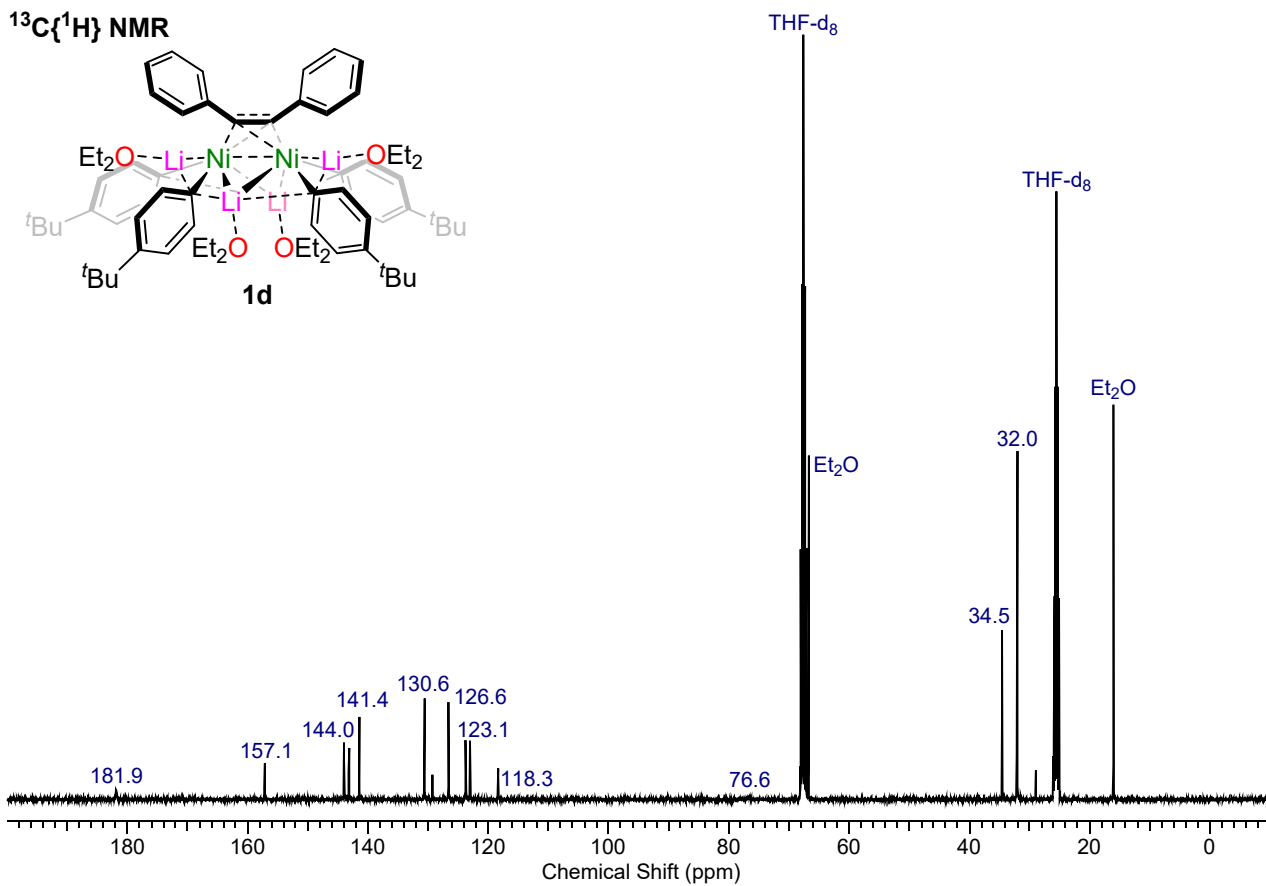
Spectra S27: ¹H NMR spectrum of **1d** in THF-d₈ at -40 °C.

⁷Li NMR



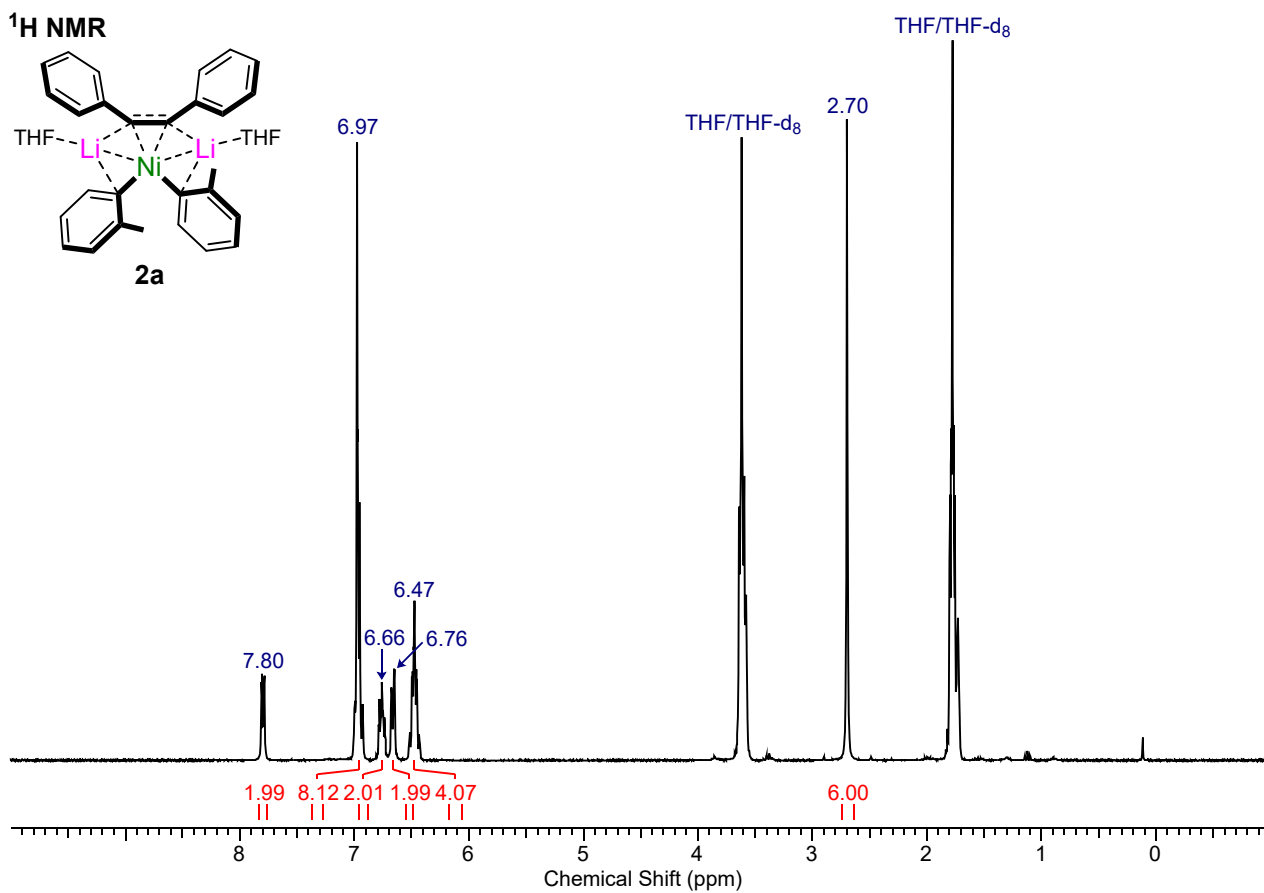
Spectra S28: ⁷Li NMR spectrum of **1d** in THF-d₈ at -40 °C.

$^{13}\text{C}\{^1\text{H}\}$ NMR

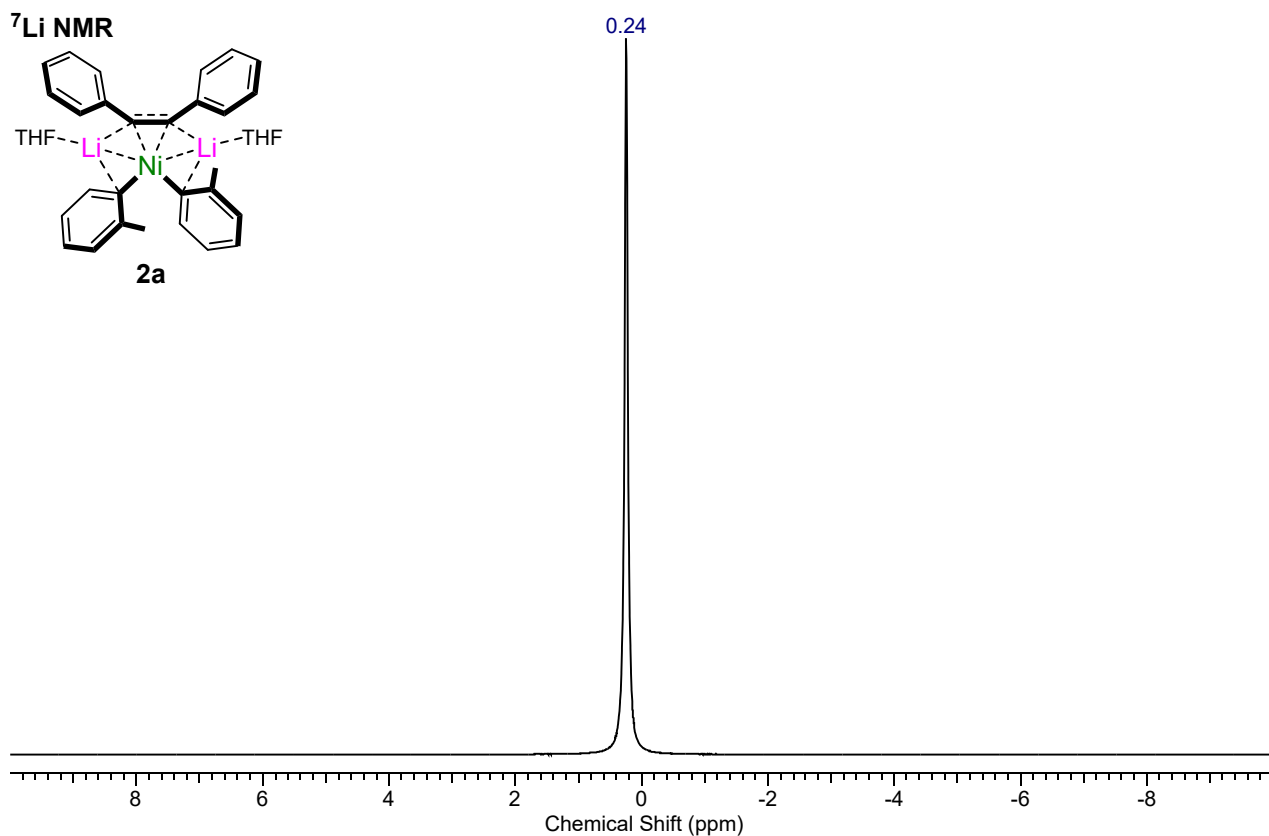


Spectra S29: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1d** in THF- d_8 at $-40\text{ }^\circ\text{C}$.

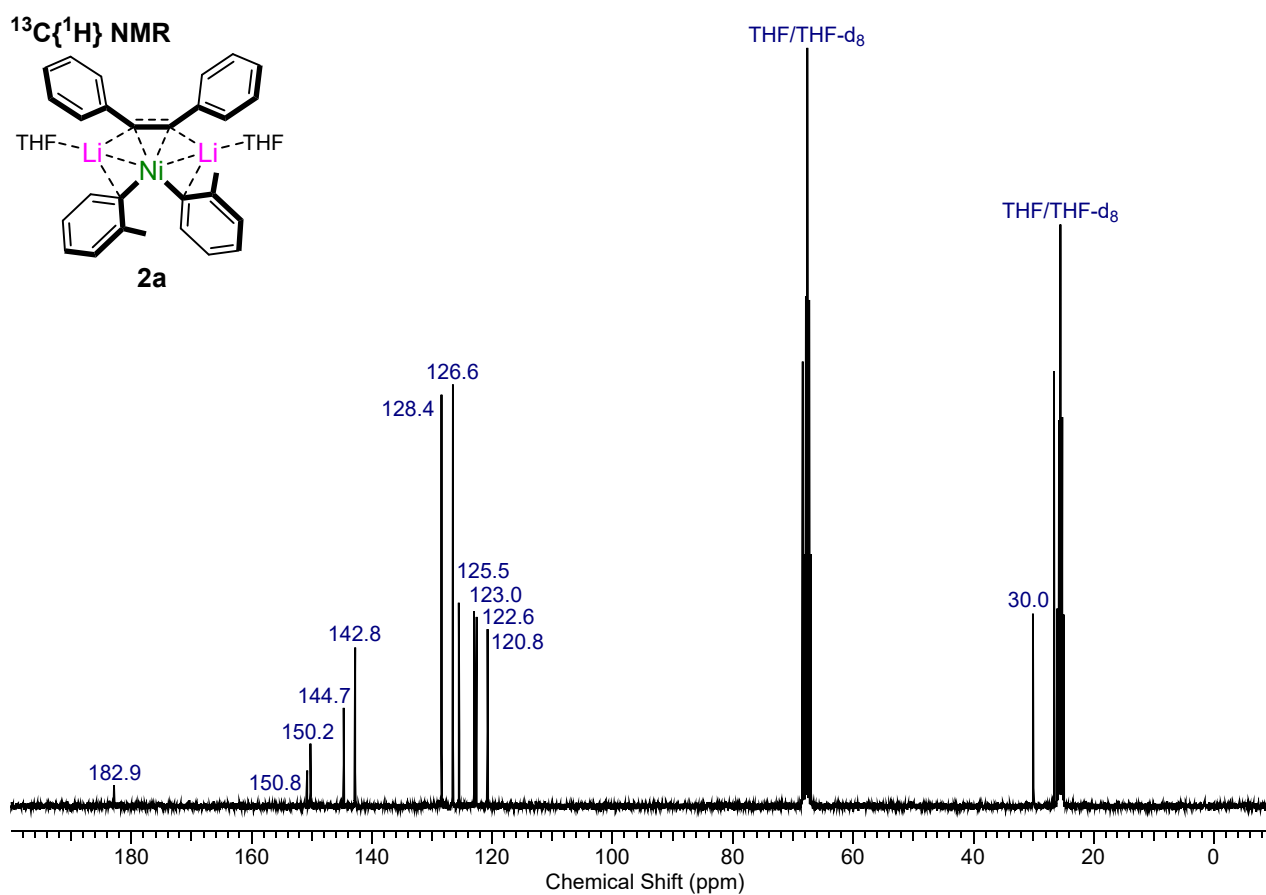
^1H NMR



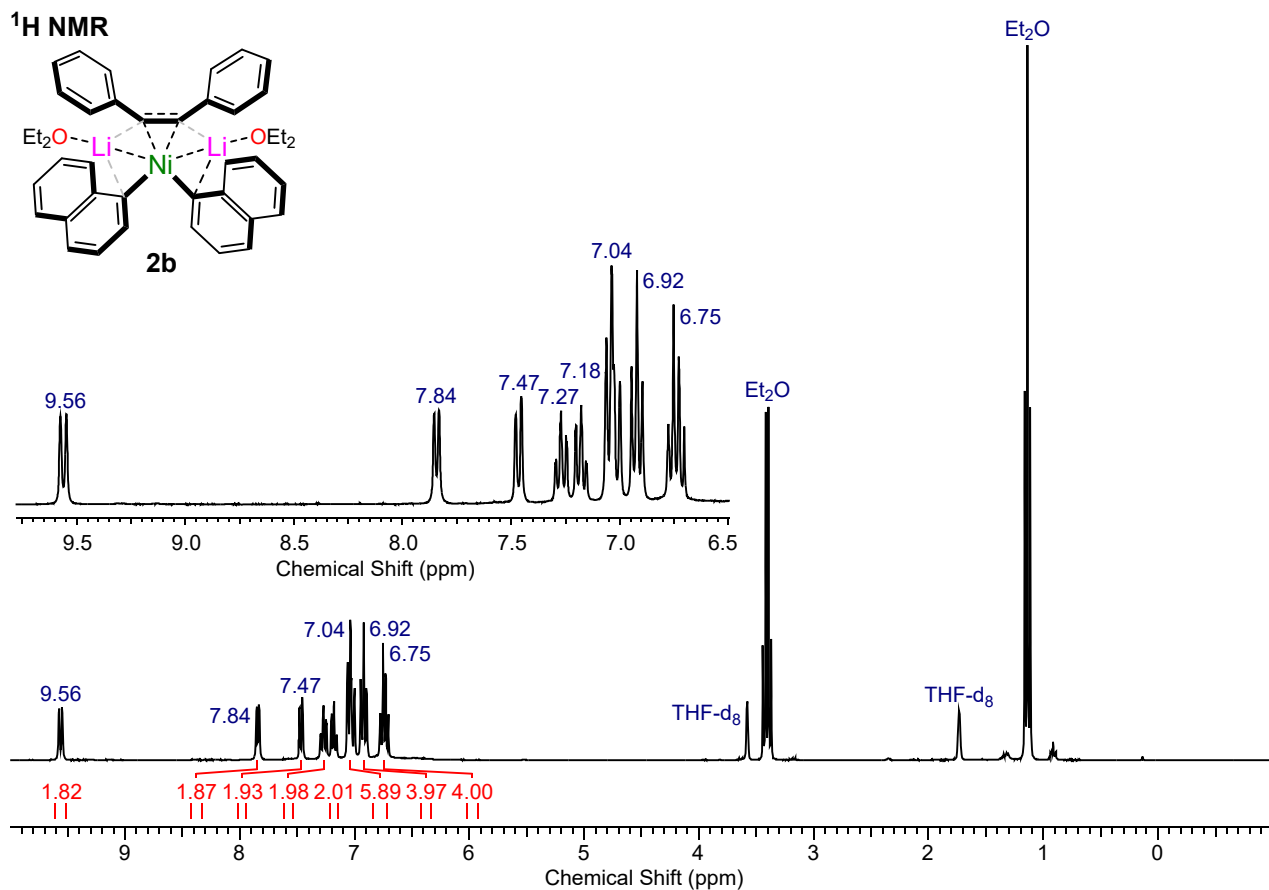
Spectra S30: ^1H NMR spectrum of **2a** in THF- d_8 .



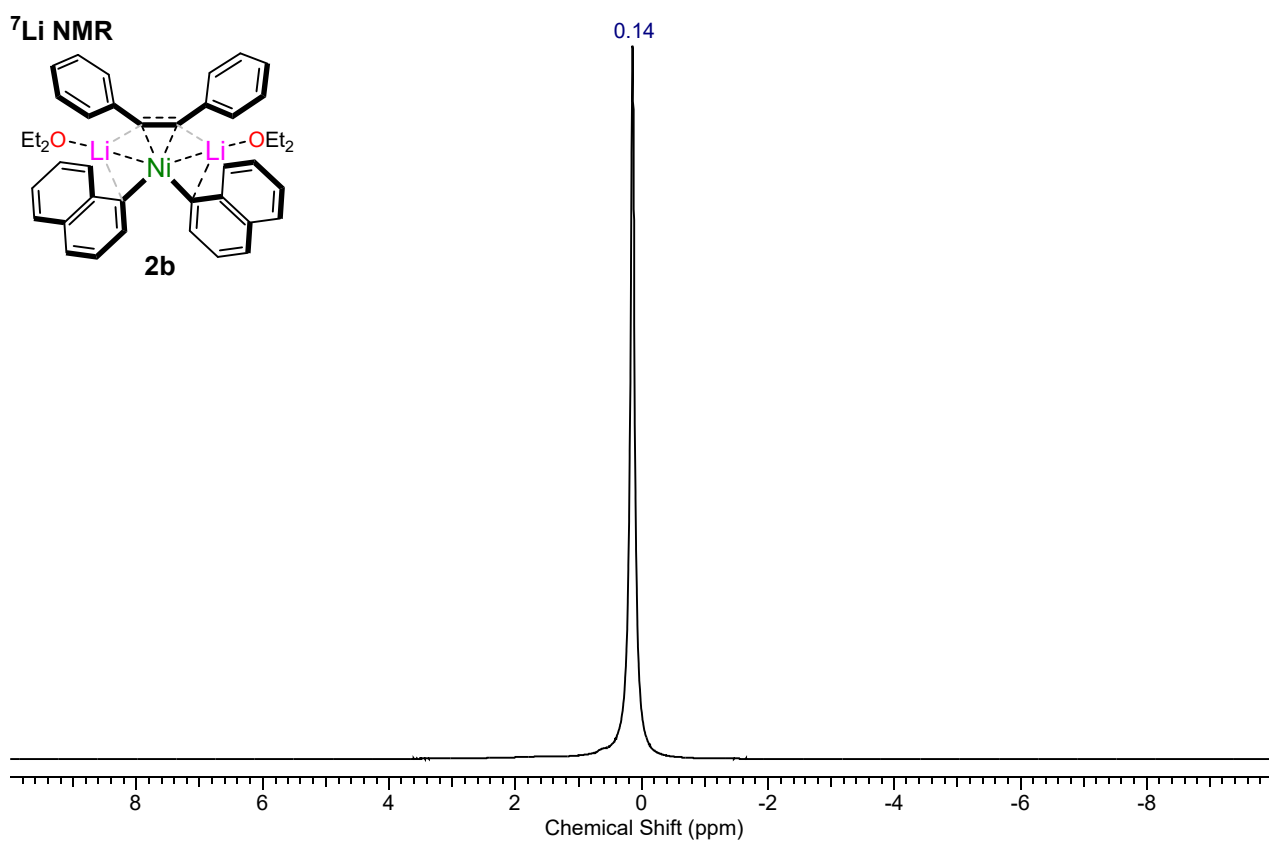
Spectra S31: ⁷Li NMR spectrum of **2a** in THF-d₈.



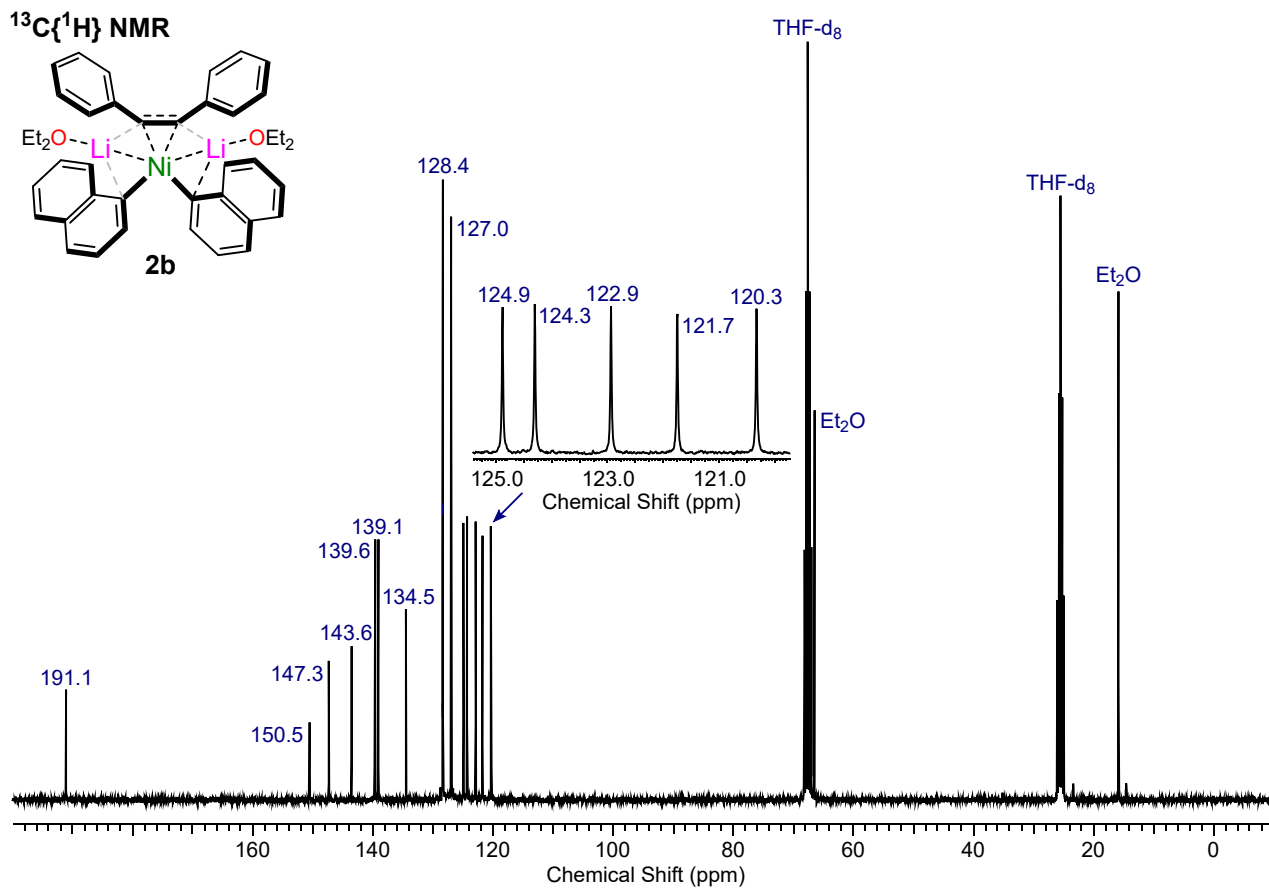
Spectra S32: ¹³C{¹H} NMR spectrum of **2a** in THF-d₈.



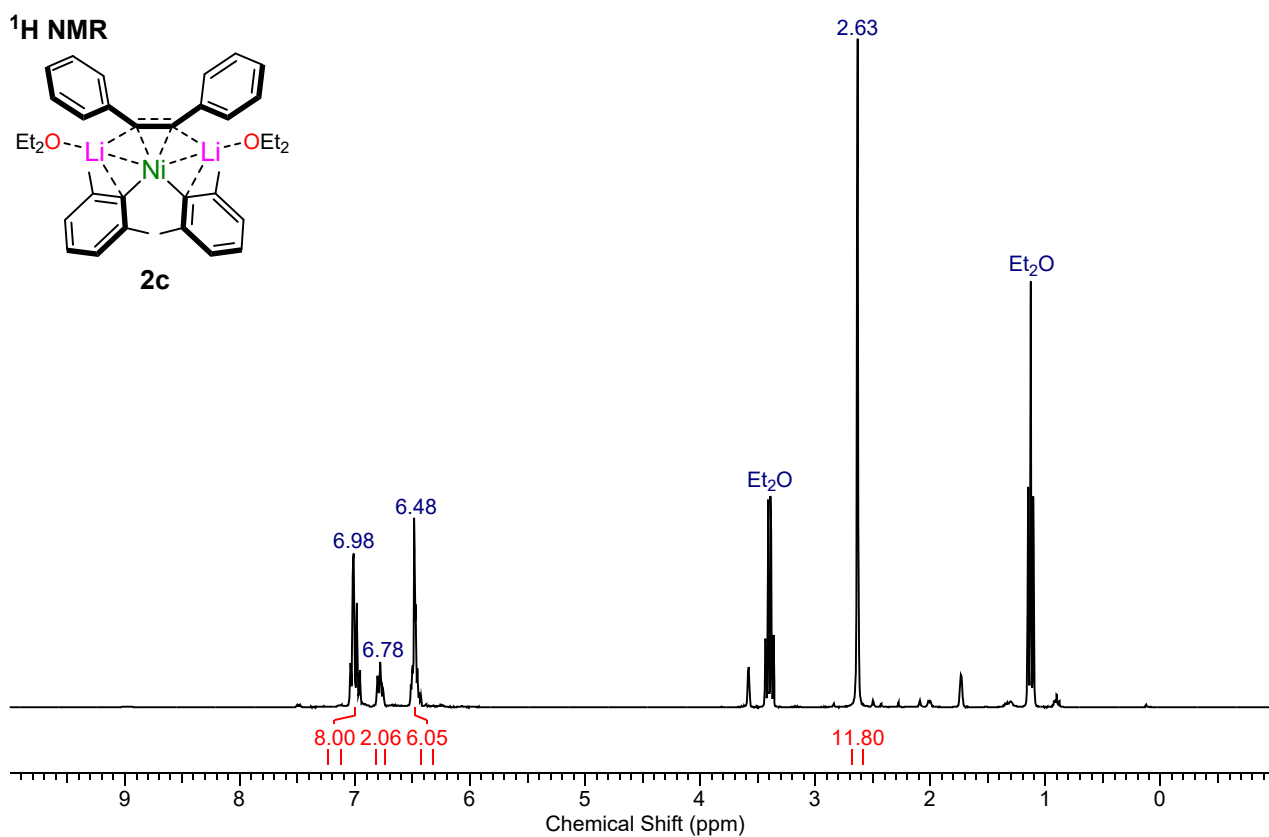
Spectra S33: ¹H NMR spectrum of **2b** in THF-d₈.



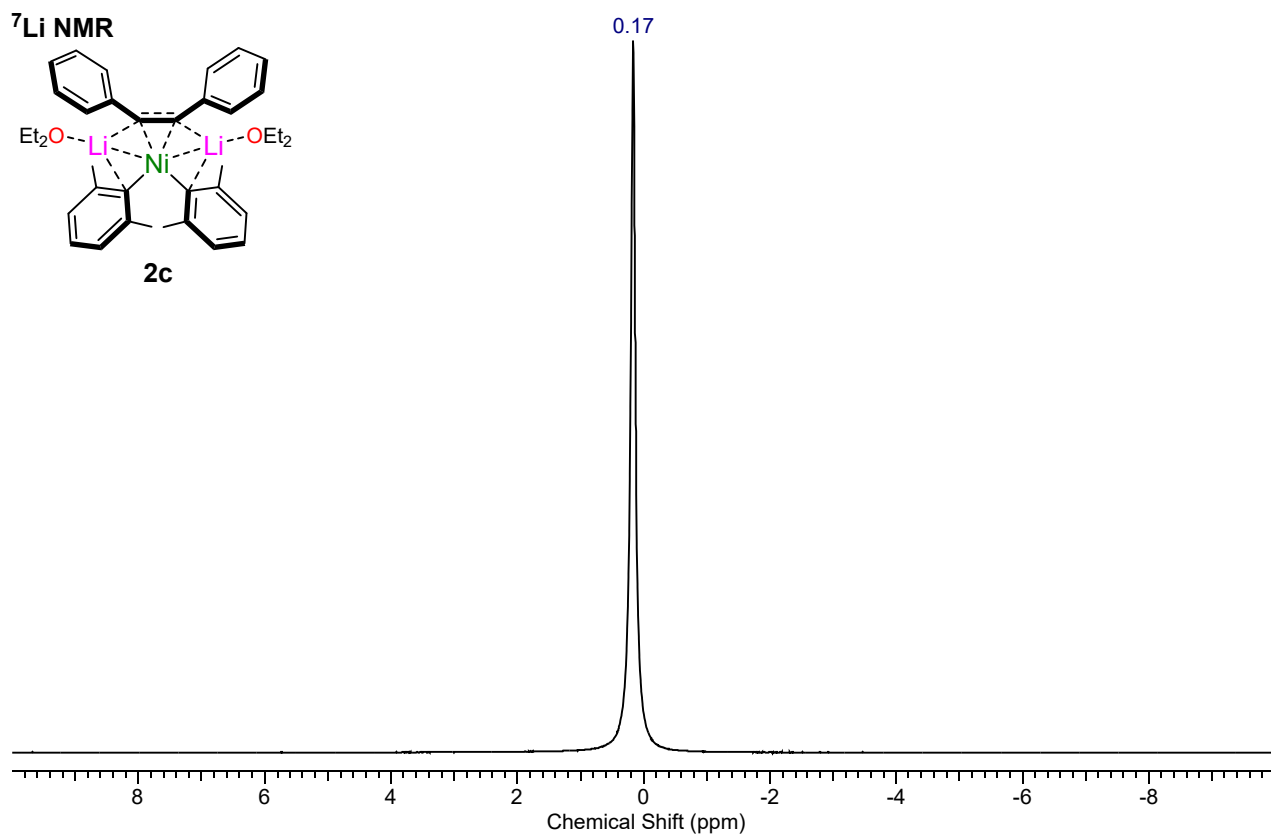
Spectra S34: ⁷Li NMR spectrum of **2b** in THF-d₈.



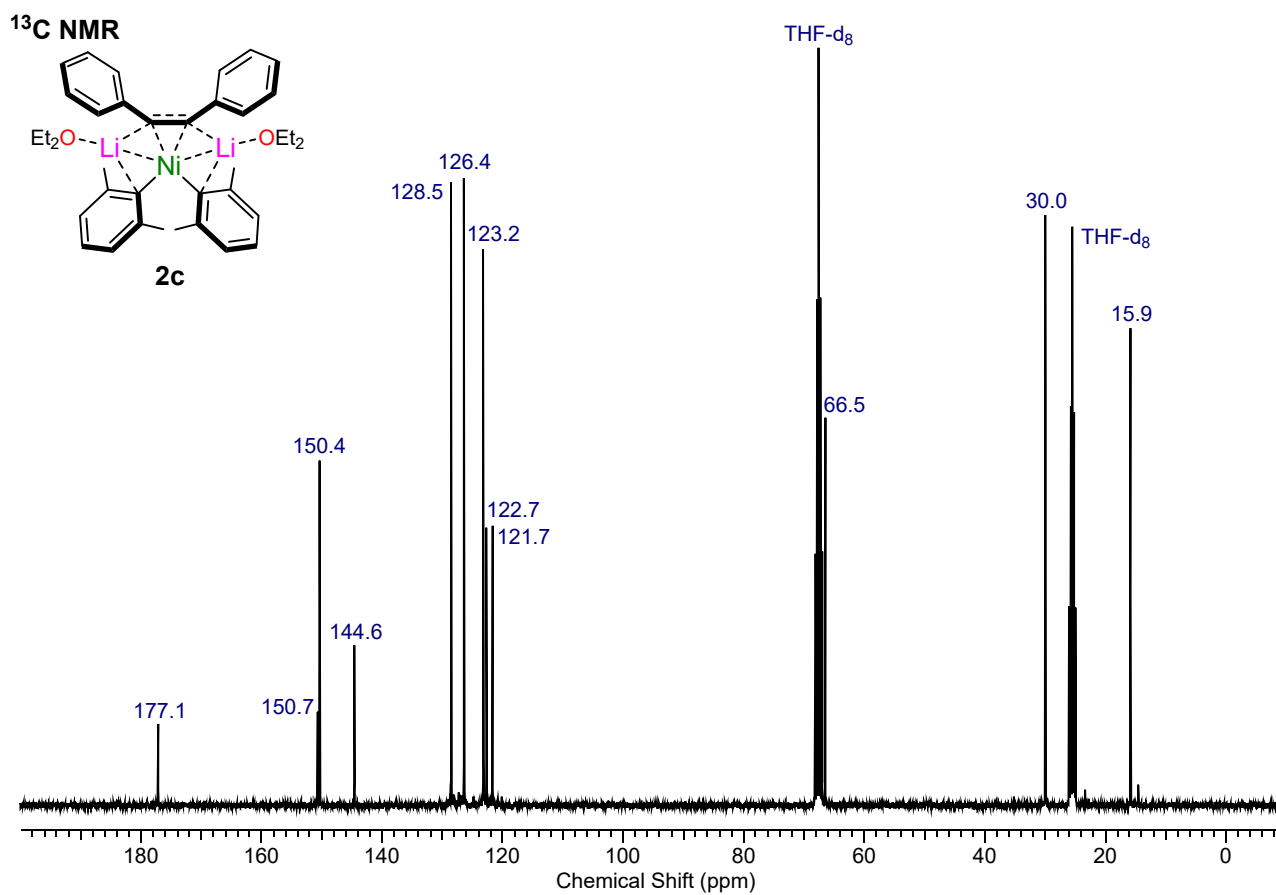
Spectra S35: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2b** in THF-d₈.



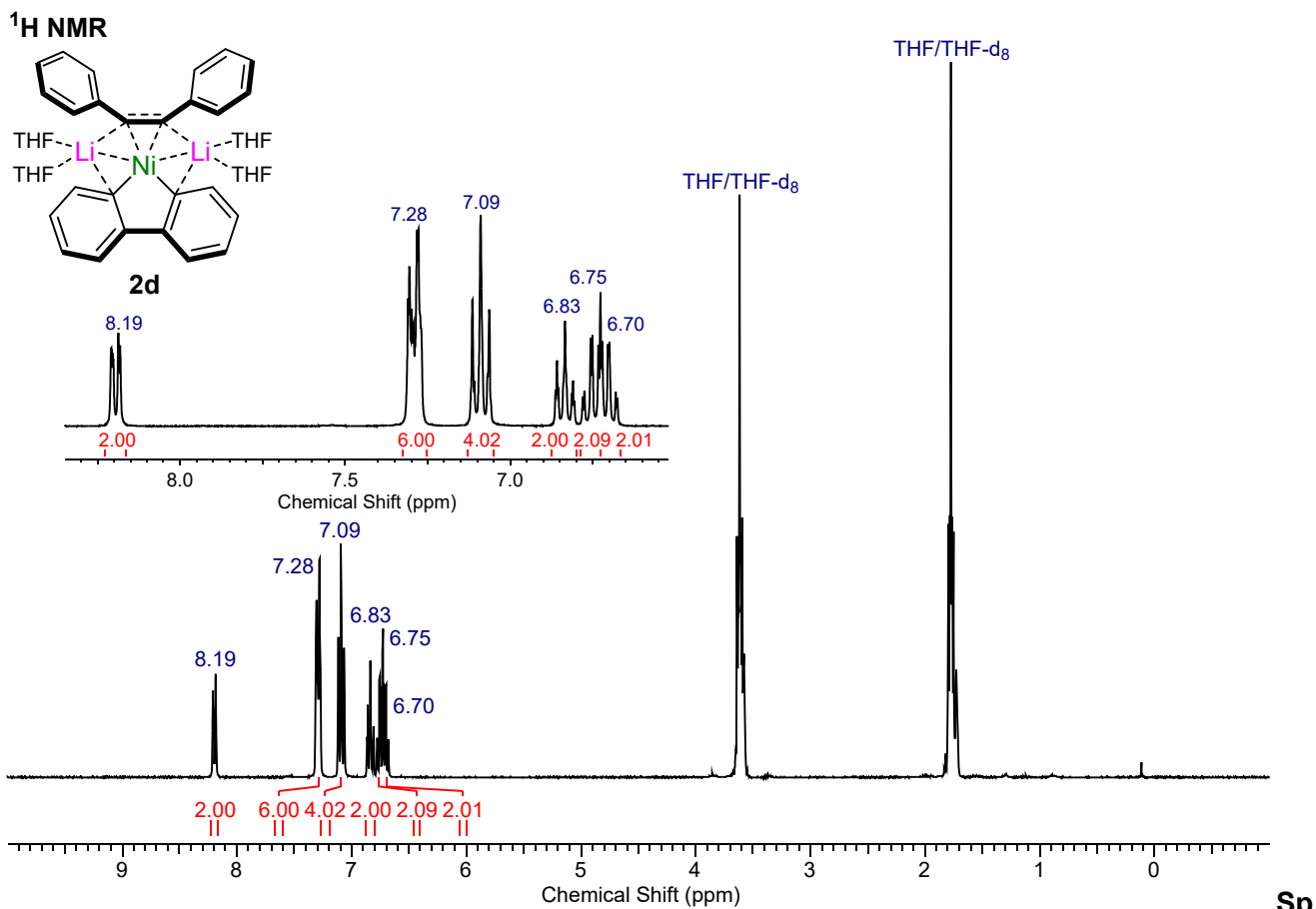
Spectra S36: ^1H NMR spectrum of **2c** in THF-d₈.



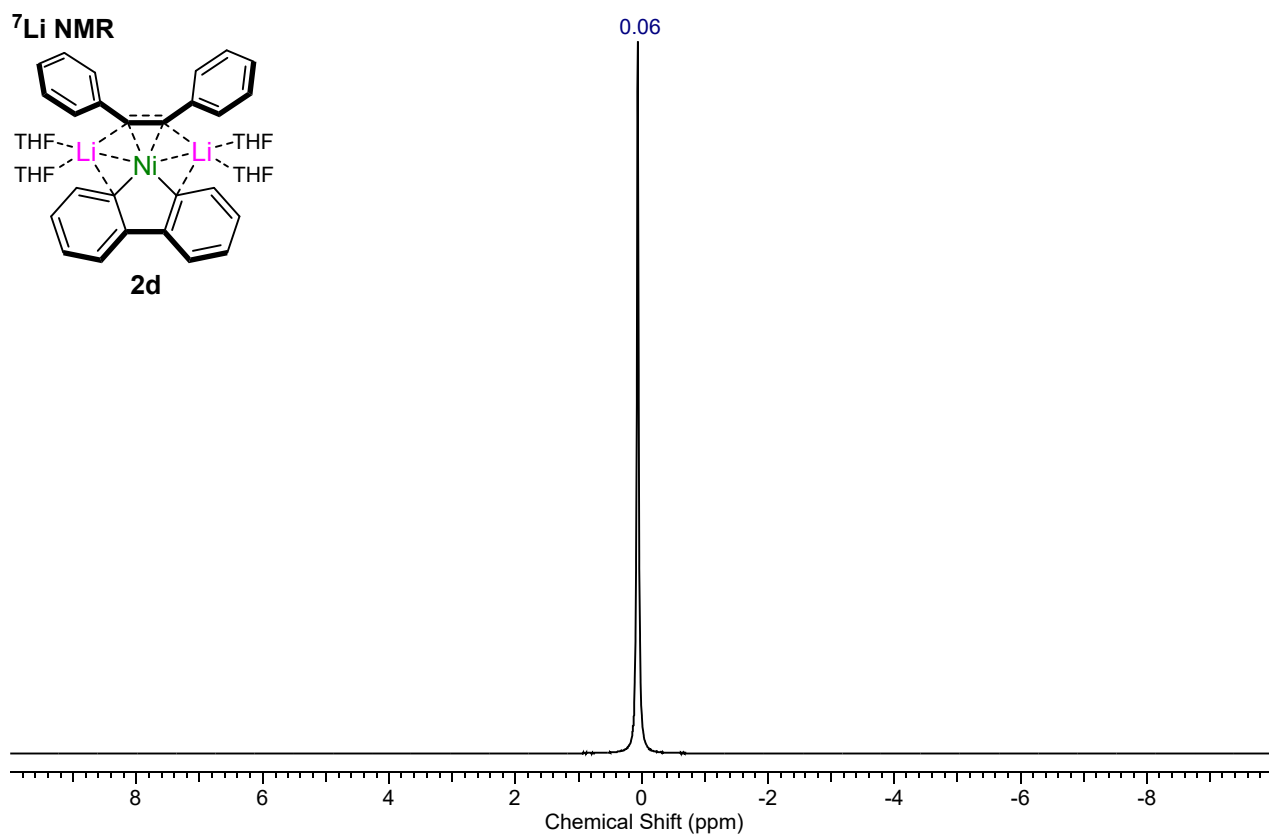
Spectra S37: ⁷Li NMR spectrum of **2c** in THF-d₈.



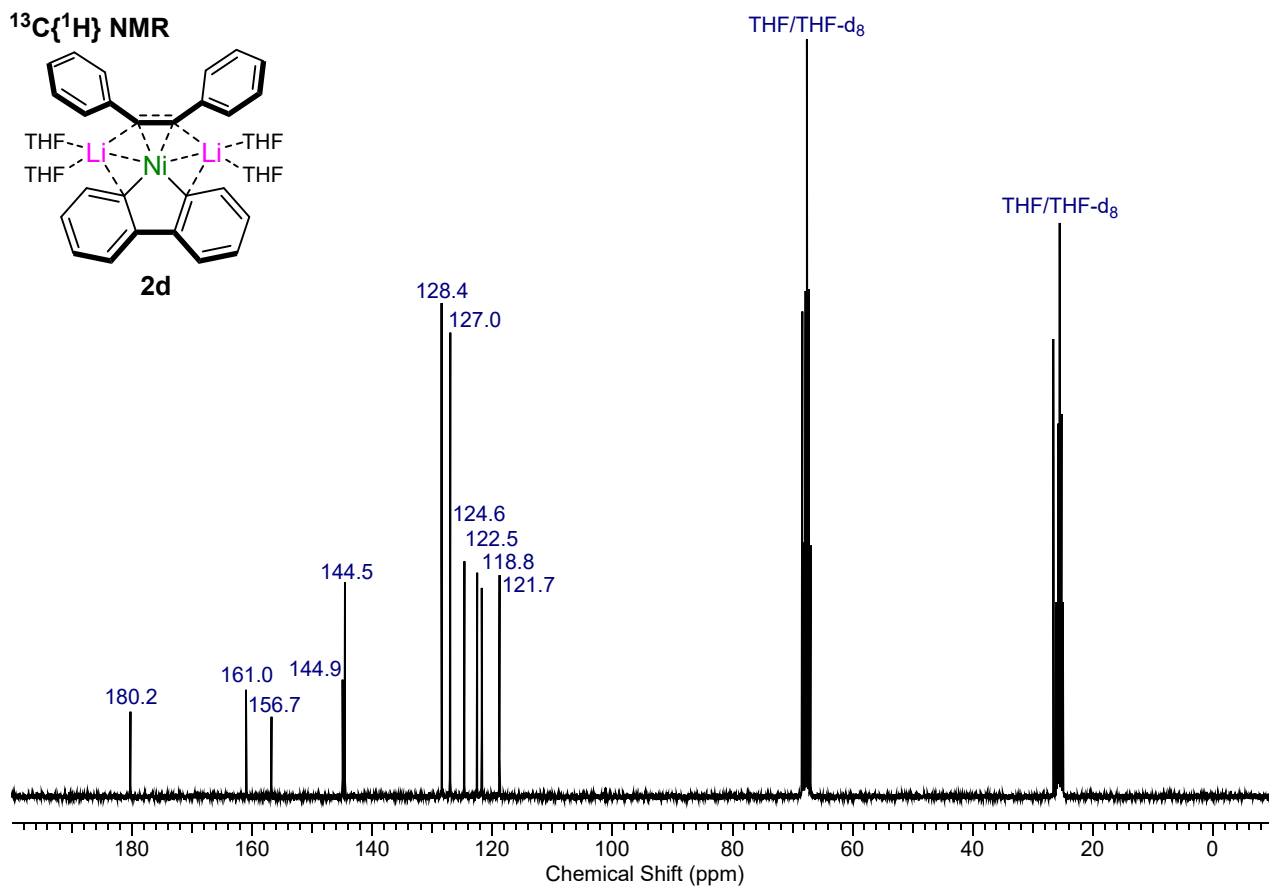
Spectra S38: ¹³C{¹H} NMR spectrum of **2c** in THF-d₈.



Spectra S39: ¹H NMR spectrum of **2d** in THF-d₈.



Spectra S40: ⁷Li NMR spectrum of **2d** in THF-d₈.



Spectra S41: ¹³C{¹H} NMR spectrum of **2d** in THF-d₈.

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