

## Supplementary Information

### Low-coordinate bis-phosphine and monophosphine Ni(0) complexes: synthesis and reactivity in C-S cross-coupling

M. Trinidad Martín,<sup>a</sup> Carlos J. Carrasco,<sup>a</sup> Nazaret Santamaría,<sup>a</sup> Celia Maya,<sup>b</sup> Auxiliadora Prieto,<sup>\*a</sup> Agustín Galindo,<sup>\*a</sup> M. Carmen Nicasio<sup>\*a</sup>

<sup>a</sup> Departamento de Química Inorgánica, Universidad de Sevilla, 41012 Sevilla, Spain.

<sup>b</sup> Instituto de Investigaciones Químicas (IIQ), Departamento de Química Inorgánica and Centro de Innovación en Química Avanzada (ORFEO-CINQA), Consejo Superior de Investigaciones Científicas (CSIC) and Universidad de Sevilla, Avenida Américo Vespucio 49, 41092 Sevilla, Spain

[mprieto2@us.es](mailto:mprieto2@us.es); [galindo@us.es](mailto:galindo@us.es); [mnicasio@us.es](mailto:mnicasio@us.es)

#### Table of contents

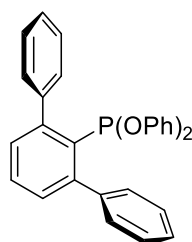
1. General considerations	S2
2. Synthesis and characterization of the ligand P(OPh) <sub>2</sub> Ar <sup>Ph2'</sup>	S2
3. Synthesis and characterization of bis-phosphine and monophosphine Ni(0) compounds	S3
3.1. General procedure for the synthesis of [Ni(PR <sub>2</sub> Ar') <sub>2</sub> ] complexes	S3
3.2. Improved synthesis of [Ni(PMe <sub>2</sub> Ar <sup>Dtbp2</sup> ) <sub>2</sub> ], <b>2</b>	S4
3.3. General procedure for the synthesis of [Ni(PR <sub>2</sub> Ar')(DVDS)] complexes	S4
4. Computational details	S7
5. C-S coupling reactions catalyzed by Ni(0) complexes	S15
5.1. Screening of precatalysts	S15
5.2. Catalytic procedures for the C-S coupling of aryl iodides and bromides with aromatic and aliphatic thiols	S16
5.3. General catalytic procedures for the C-S coupling of aryl tosylates with aromatic and aliphatic thiols	S17
5.4. General catalytic procedures for the C-S coupling of aryl chlorides with aliphatic thiols	S17
5.5. Characterization data for C-S coupling products	S17
6. NMR spectra of compounds	S22
7. X-ray structural data of Ni(0) complexes	S44

## 1. General considerations

All preparations and manipulations were carried out under an oxygen-free nitrogen atmosphere using standard Schlenk techniques. Solvents were rigorously dried and degassed before use. Reagents were purchased from commercial suppliers and used without further purification. Dimethylterphenyl phosphines  $\text{PMe}_2\text{Ar}^{\text{Ph}_2}$ ,<sup>1</sup>  $\text{PMe}_2\text{Ar}^{\text{m-Xyl}_2}$ ,<sup>2</sup>  $\text{PMe}_2\text{Ar}^{\text{o-Xyl}_2}$ ,<sup>1</sup>  $\text{PMe}_2\text{Ar}^{\text{Dtbp}_2}$ ,<sup>3</sup>  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{Ph}_2})_2]$ <sup>4</sup> and  $\text{Ni}(\text{COD})_2$ <sup>5</sup> were synthesized following described procedures.  $[\text{Ni}(\text{COD})_2]$  was purified by recrystallization from THF prior to use. Solution NMR spectra were recorded on Bruker Avance III 300 MHz and Avance III 500 MHz spectrometers. The  $^1\text{H}$  and  $^{13}\text{C}$  resonances of the solvent were used as the internal standard and the chemical shifts are reported relative to TMS while  $^{31}\text{P}$  was referenced to external  $\text{H}_3\text{PO}_4$ . Elemental analyses were performed by the Servicio de Microanálisis of the Instituto de Investigaciones Químicas (IIQ). X-ray diffraction studies were accomplished at Centro de Investigación, Tecnología e Innovación de la Universidad de Sevilla (CITIUS) and at the Instituto de Investigaciones Químicas (IIQ).

## 2. Synthesis and characterization of $\text{P}(\text{OPh})_2\text{Ar}^{\text{Ph}_2}$

A freshly prepared solution of  $\text{PX}_2\text{Ar}^{\text{Ph}_2}$  (500 mg, 1.12 mmol) in THF (ca. 5 mL) was added to a solution of phenol (210.8 mg, 2.24 mmol) in THF (ca. 5 mL) at room temperature. To the resulting mixture, triethylamine (624.4  $\mu\text{L}$ , 4.48 mmol) was added at 0°C. The reaction mixture was stirred at room temperature for 24 hours, filtered, and all volatiles were removed by evaporation under reduced pressure. The solid residue was washed with pentane (2 x 3 mL) and dried under vacuum. The title compound was obtained as a white crystalline solid. Yield: 390 mg (78%).



$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  7.62-7.57 (m, 4H,  $p\text{-C}_6\text{H}_5$ ,  $m\text{-C}_6\text{H}_3$ ), 7.55-7.50 (m, 1H,  $p\text{-C}_6\text{H}_3$ ), 7.42-7.34 (m, 8H,  $o\text{-C}_6\text{H}_5$ ,  $m\text{-C}_6\text{H}_5$ ), 7.05 (t, 4H,  $^3J_{\text{HH}} = 7.8\text{ Hz}$ ,  $m\text{-C}_6\text{H}_5\text{O}$ ), 6.88 (t, 2H,  $^3J_{\text{HH}} = 7.2\text{ Hz}$ ,  $p\text{-C}_6\text{H}_5\text{O}$ ), 6.55 (d, 4H,  $^3J_{\text{HH}} = 7.8\text{ Hz}$ ,  $o\text{-C}_6\text{H}_5\text{O}$ ).

<sup>1</sup> L. Ortega-Moreno, M. Fernández-Espada, J. J. Moreno, C. Navarro-Gilabert, J. Campos, S. Conejero, J. López-Serrano, C. Maya, R. Peloso, and E. Carmona, *Polyhedron* 2016, **116**, 170–181.

<sup>2</sup> M. T. Martín, M. Marín, C. Maya, A. Prieto and M. C. Nicasio, *Chem. Eur. J.*, 2021, **27**, 12320-12326.

<sup>3</sup> M. Marín, J. J. Moreno, C. Navarro-Gilabert, E. Álvarez, C. Maya, R. Peloso, M. C. Nicasio and E. Carmona, *Chem. Eur. J.*, 2019, **25**, 260-272.

<sup>4</sup> M. T. Martín, M. Marín, R. J. Rama, E. Álvarez, C. Maya, F. Molina and M. C. Nicasio, *Chem. Commun.*, 2021, **57**, 3083-3086.

<sup>5</sup> M. M. Colquhoun, J. Holton, D. J. Thompson and M. V. Twigg in *New Pathways for Organic Synthesis. Practical Applications of Transition Metals*, Plenum Press, New York, 1984.

$^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  155.1 (d,  $^2J_{\text{CP}} = 12$  Hz, C-O), 147.5 (d,  $^2J_{\text{CP}} = 19$  Hz, *o*- $\text{C}_6\text{H}_3$ ), 142.5 (d,  $^3J_{\text{CP}} = 6$  Hz, *ipso*- $\text{C}_6\text{H}_5$ ), 136.6 (d,  $^1J_{\text{CP}} = 25$  Hz, C-P), 130.3 (d,  $^3J_{\text{CP}} = 3$  Hz, *m*- $\text{C}_6\text{H}_3$ ), 130.2 (*p*- $\text{C}_6\text{H}_3$ ), 130.0 (*o*- $\text{C}_6\text{H}_5$ ), 129.2 (*p*- $\text{C}_6\text{H}_5$ ), 127.5 (*m*- $\text{C}_6\text{H}_5$ ), 127.2 (*p*- $\text{C}_6\text{H}_5\text{O}$ ), 122.9 (d,  $^4J_{\text{CP}} = 2$  Hz, *m*- $\text{C}_6\text{H}_5\text{O}$ ), 119.2 (d,  $^3J_{\text{CP}} = 7$  Hz, *o*- $\text{C}_6\text{H}_5\text{O}$ ).

$^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  163.7

Elemental analysis calculated (found) for  $\text{C}_{30}\text{H}_{23}\text{O}_2\text{P}$ : C, 80.70 (80.59); H, 5.19 (5.51).

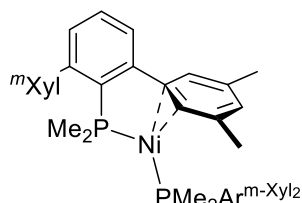
### 3. Synthesis and characterization of bis-phosphine and monophosphine Ni(0) compounds

#### 3.1. General procedure for the synthesis of $[\text{Ni}(\text{PR}_2\text{Ar}')_2]$ complexes

A solution of the phosphine (0.2 mmol) in THF (1 mL) was added to a solution of  $\text{Ni}(\text{COD})_2$  (27.6 mg, 0.1 mmol) in THF (1 mL) under nitrogen. The resulting dark red solution was stirred for 5 minutes and petroleum ether was added to precipitate the corresponding complex. The title compound was obtained as dark red crystals after recrystallization.

#### $[\text{Ni}(\text{PMe}_2\text{Ar}^{m\text{-Xyl}2})_2]$ , **3**

Following the general procedure,  $\text{PMe}_2\text{Ar}^{m\text{-Xyl}2}$  (69.2 mg, 0.2 mmol) and  $\text{Ni}(\text{COD})_2$  (27.6 mg, 0.1 mmol) were reacted in THF (2 mL). Recrystallization from diethyl ether:petroleum ether (1:2) mixtures at  $-20$  °C, rendered **3** as reddish orange crystals. Yield: 54 mg (72%).



$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  7.06 (d, 4H,  $^3J_{\text{HH}} = 8$  Hz, *m*- $\text{C}_6\text{H}_3$ ), 6.98 (t, 2H,  $^4J_{\text{HH}} = 7.2$  Hz, *p*- $\text{C}_6\text{H}_3$ ), 6.72 (br s, 8H, *o*- $^m\text{Xyl}$ ), 6.58 (br s, 4H, *p*- $^m\text{Xyl}$ ), 2.12 (s, 24H,  $\text{CH}_3$ ), 1.03 (t, 12H,  $J_{\text{app}} = 2.4$  Hz,  $\text{PCH}_3$ ).

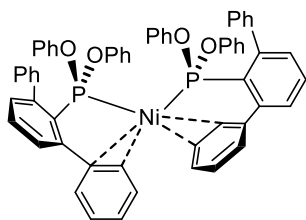
$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  148.7 (t,  $J_{\text{app}} = 8$  Hz, *o*- $\text{C}_6\text{H}_3$ ), 140.8 (t,  $J_{\text{app}} = 12$  Hz, *ipso*- $\text{C}_6\text{H}_3$ ), 136.0 (s, *ipso*- $^m\text{Xyl}$ ), 128.8 (t,  $J_{\text{app}} = 3$  Hz, *m*- $\text{C}_6\text{H}_3$ ), 128.0 (s, *p*- $\text{C}_6\text{H}_3$ ), 125.7 (s, *o*- $^m\text{Xyl}$ ), 119.0 (s, *p*- $^m\text{Xyl}$ ), 21.1 (s,  $\text{CH}_3$ ), 17.0 (t,  $J_{\text{app}} = 9$  Hz,  $\text{PCH}_3$ ).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  -0.48.

Elemental analysis calculated (found) for  $\text{C}_{48}\text{H}_{54}\text{NiP}_2$ : C, 76.71 (76.61); H, 7.24 (7.46).

#### $[\text{Ni}(\text{P}(\text{OPh})_2\text{Ar}^{\text{Ph}2})_2]$ , **4**

Following the general procedure,  $\text{P}(\text{OPh})_2\text{Ar}^{\text{Ph}2}$  (89.2 mg, 0.2 mmol) and  $\text{Ni}(\text{COD})_2$  (27.6 mg, 0.1 mmol) were reacted in THF (2 mL). Recrystallization from benzene: petroleum ether (1:4) mixtures at  $-20$  °C, rendered **3** as reddish orange crystals. Yield: 63 mg (66%).



$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  7.15 (br s, 4H), 6.99-6.79 (m, 32H,  $\text{CH}_{\text{Ar}}$ ), 6.68 (t, 4H,  $^3J_{\text{HH}} = 7.5$  Hz,  $\text{CH}_{\text{Ar}}$ ), 6.58 (d, 6H,  $^3J_{\text{HH}} = 7.2$  Hz,  $\text{CH}_{\text{Ar}}$ ).

$^{13}\text{C}\{^1\text{H}\}$  RMN (125 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  153.7 (C-O), 146.8 (t,  $J_{\text{app}} = 8$  Hz,  $o\text{-C}_6\text{H}_3$ ), 136.8 (t,  $J_{\text{app}} = 20$  Hz,  $ipso\text{-C}_6\text{H}_3$ ), 133.6, 130.2, 129.2, 128.8, 125.6, 125.0, 122.8, 121.2, 120.4 ( $\text{C}_{\text{Ar}}$ ).

$^{31}\text{P}\{^1\text{H}\}$  RMN (202 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  160.4.

Elemental analysis calculated (found) for  $\text{C}_{60}\text{H}_{46}\text{NiO}_4\text{P}_2$ : C, 75.73 (75.68); H, 4.87 (4.78).

### 3.2. Improved synthesis of $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{Dtbp}2})_2]$ , **2**

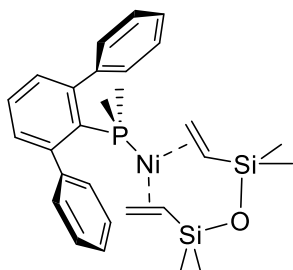
$\text{PMe}_2\text{Ar}^{\text{Dtbp}2}$  (103 mg, 0.2 mmol) and  $\text{Ni}(\text{acac})_2$  (26 mg, 0.1 mmol) were dissolved in  $\text{Et}_2\text{O}$  (1 mL) and cooled to  $-40$  °C. A solution of  $\text{AlMe}_3$  (120  $\mu\text{L}$ , 0.22 mmol) in hexane (1 mL) also cooled to  $-40$  °C was added dropwise to the dark green Ni/P solution. The resulting dark red solution was stirred for 1 h at room temperature and the volatiles were evaporated to dryness. The reaction crude was extracted with the minimum amount of petroleum ether, filtered and stored at  $-18$  °C overnight. Compound **2** crystallizes as reddish crystals from the organic solution. Yield: 91 mg (85%).

### 3.3. General procedure for the synthesis of $[\text{Ni}(\text{PR}_2\text{Ar}')(\text{DVDS})]$ complexes

To a solution of  $\text{Ni}(\text{COD})_2$  (44.3 mg, 0.16 mmol) in THF (2 mL), 1,3-divinyltetramethyldisiloxane (72  $\mu\text{L}$ , 0.36 mmol) was added. The reaction was stirred for 5 minutes at room temperature, after which a solution of the ligand  $\text{PR}_2\text{Ar}$  (0.16 mmol) in THF (2 mL) was added. The mixture was stirred for 1 h and the product was precipitated by adding pentane. The solid was purified by recrystallization in a mixture of THF: petroleum ether (1: 2).

#### $[(\text{PMe}_2\text{Ar}^{\text{Ph}2})\text{Ni}(\text{DVDS})]$ , **5**

Following the general procedure, the title compound was obtained as a yellow crystalline solid. Yield: 68 mg (79%). From 0.86 mmol of  $\text{Ni}(\text{COD})_2$ , 378 mg (74%) of complex **5** was obtained.



Crystals suitable for the X-ray diffraction study were obtained from a mixture of petroleum ether: THF (4:1) at  $-20$  °C.

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  7.12-7.07 (m, 4H,  $o\text{-C}_6\text{H}_5$ ), 7.05-7.00 (m, 6H,  $m\text{-C}_6\text{H}_5$ ,  $p\text{-C}_6\text{H}_5$ ), 6.99-6.96 (m, 3H,  $m\text{-C}_6\text{H}_3$ ,  $p\text{-C}_6\text{H}_3$ ), 2.48-2.33 (m, 4H,  $\text{CH}_2$ ), 2.28-2.19 (m, 2H, CH), 0.99 (d, 6H,  $^2J_{\text{HP}} = 5.8$  Hz,  $\text{PCH}_3$ ), 0.55 (s, 6H,  $\text{SiCH}_3$ ),  $-0.18$  (s, 6H,  $\text{SiCH}_3$ ).

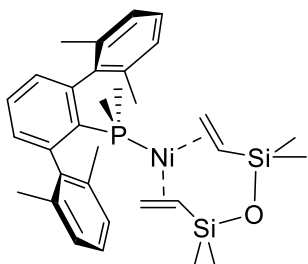
$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  146.6 (d,  $^2J_{\text{CP}} = 9$  Hz, *o*- $\text{C}_6\text{H}_3$ ), 142.9 (d,  $^3J_{\text{CP}} = 5$  Hz, *ipso*- $\text{C}_6\text{H}_5$ ), 135.5 (d,  $^1J_{\text{CP}} = 25$  Hz, C-P), 130.6 (d,  $^3J_{\text{CP}} = 7$  Hz, *m*- $\text{C}_6\text{H}_3$ ), 129.7 (*p*- $\text{C}_6\text{H}_5$ ), 127.2 (*p*- $\text{C}_6\text{H}_3$ ), 59.5 (d,  $^2J_{\text{CP}} = 3$  Hz,  $\text{CH}_2$ ), 56.5 (d,  $^2J_{\text{CP}} = 9$  Hz, CH), 17.4 (d,  $^1J_{\text{CP}} = 24$  Hz,  $\text{PCH}_3$ ), 1.7 (SiCH<sub>3</sub>), -0.9 (SiCH<sub>3</sub>).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  11.3.

Elemental analysis calculated (found) for  $\text{C}_{28}\text{H}_{37}\text{NiOPSi}_2$ : C, 62.81 (62.84); H, 6.97 (7.11).

### **$[(\text{PMe}_2\text{Ar}^{o\text{-Xyl}2})\text{Ni}(\text{DVDS})]$ , 6**

Following the general procedure, the title compound was obtained as a yellow crystalline solid. Yield: 60.3 mg (75 %). Crystals suitable for the X-ray diffraction study were obtained from a mixture of petroleum ether: THF (4:1) at -20 °C



$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  7.07-6.96 (m, 3H, *p*- $\text{C}_6\text{H}_3$ , *p*-Xyl), 6.89 (d, 4H,  $^3J_{\text{HH}} = 7.6$  Hz, *m*-Xyl), 6.62 (dd, 2H,  $^3J_{\text{HH}} = 7.4$  Hz,  $^4J_{\text{HP}} = 1.9$  Hz, *m*- $\text{C}_6\text{H}_3$ ), 2.44-2.27 (m, 6H,  $\text{CH}_{\text{vinyl}}$ ), 1.97 (s, 12 H,  $\text{CH}_3$ ), 1.03 (d, 6H,  $^2J_{\text{HP}} = 6.2$  Hz,  $\text{PCH}_3$ ), 0.54 (s, 6H, SiCH<sub>3</sub>), -0.16 (s, 6H, SiCH<sub>3</sub>).

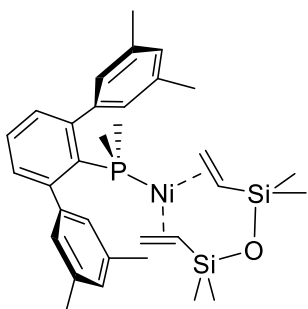
$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  144.9 (d,  $^2J_{\text{CP}} = 10$  Hz, *o*- $\text{C}_6\text{H}_3$ ), 142.2 (d,  $^3J_{\text{CP}} = 4$  Hz, *ipso*-Xyl), 136.2 (*o*-Xyl), 134.3 (d,  $^1J_{\text{CP}} = 18$  Hz, *ipso*- $\text{C}_6\text{H}_3$ ), 130.3 (d,  $^3J_{\text{CP}} = 6$  Hz, *m*- $\text{C}_6\text{H}_3$ ), 129.1 (*p*-Xyl), 127.3 (*p*- $\text{C}_6\text{H}_3$ ), 58.7 (d,  $^2J_{\text{CP}} = 2$  Hz,  $\text{CH}_2$ ), 57.4 (d,  $^2J_{\text{CP}} = 8$  Hz, CH), 21.1 ( $\text{CH}_3$  Xyl), 16.7 (d,  $^1J_{\text{CP}} = 25$  Hz,  $\text{PCH}_3$ ), 1.7 (SiCH<sub>3</sub>), -0.7 (SiCH<sub>3</sub>).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  6.8 (s).

Elemental analysis calculated (found) for  $\text{C}_{32}\text{H}_{45}\text{NiOPSi}_2$ : C, 64.97 (64.71); H, 7.67 (7.91).

### **$[(\text{PMe}_2\text{Ar}^{m\text{-Xyl}2})\text{Ni}(\text{DVDS})]$ , 7**

Following the general procedure, the title compound was obtained as a yellow crystalline solid. Yield: 67.9 mg (72%).



$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  7.10-7.08 (m, 2H, *m*- $\text{C}_6\text{H}_3$ ), 7.05-7.02 (m, 1H, *p*- $\text{C}_6\text{H}_3$ ), 6.85 (br s, 4H, *o*-Xyl<sup>m</sup>), 6.74 (br s, 2H, *p*-Xyl<sup>m</sup>), 2.52-2.41 (m, 4H,  $\text{CH}_2$ ), 2.32-2.28 (m, 2H, CH), 2.14 (s, 3H,  $\text{CH}_3$ ), 1.07 (d, 6H,  $^2J_{\text{HP}} = 5.7$  Hz,  $\text{PCH}_3$ ), 0.55 (s, 6H, SiCH<sub>3</sub>), -0.17 (s, 6H, SiCH<sub>3</sub>).

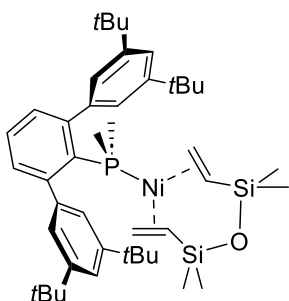
$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  146.8 (d,  $^2J_{\text{CP}} = 9$  Hz, *o*- $\text{C}_6\text{H}_3$ ), 142.9 (d,  $^3J_{\text{CP}} = 4$  Hz, *ipso*-Xyl), 136.8 (*p*-Xyl), 135.6 (d,  $^1J_{\text{CP}} = 24$  Hz, C-P), 130.3 (d,  $^3J_{\text{CP}} = 6$  Hz, *m*- $\text{C}_6\text{H}_3$ ), 128.7 (*p*- $\text{C}_6\text{H}_3$ ), 127.3 (*o*-Xyl), 59.5 (d,  $^2J_{\text{CP}} = 3$  Hz,  $\text{CH}_2$ ), 56.4 (d,  $^2J_{\text{CP}} = 8$  Hz, CH), 20.9 ( $\text{CH}_3$ ), 17.5 (d,  $^1J_{\text{CP}} = 24$  Hz,  $\text{PCH}_3$ ), 1.7 ( $\text{SiCH}_3$ ), -0.8 ( $\text{SiCH}_3$ ).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  9.1.

Elemental analysis calculated (found) for  $\text{C}_{32}\text{H}_{45}\text{NiOPSi}_2$ : C, 64.97 (64.61); H, 7.67 (7.76).

### **$[(\text{PMe}_2\text{Ar}^{\text{Dtbp}2})\text{Ni}(\text{DVDS})]$ , 8**

Any attempts to obtain solid samples of compound **8** resulted fruitless. The compound was characterized in situ by  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy.

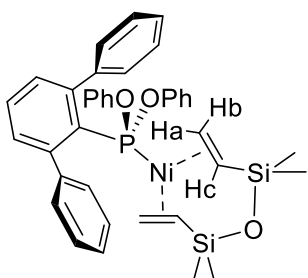


$^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  7.49 (bs, 2H, Ar), 7.22-7.13 (m, 7H, Ar), 2.4-2.37 (m, 3H,  $\text{CH}_{\text{vinyl}}$ ), 2.10-2.13 (m, 3H,  $\text{CH}_{\text{vinyl}}$ ), 1.35 (s, 36H,  $\text{C}(\text{CH}_3)_3$ ), 1.28 (sa, 6H,  $\text{PCH}_3$ ), 0.46 (s, 6H,  $\text{SiCH}_3$ ), -0.19 (s, 6H,  $\text{SiCH}_3$ ).

$^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  10.9 (s).

### **$[(\text{P}(\text{OPh})_2\text{Ar}^{\text{Ph}2})\text{Ni}(\text{DVDS})]$ , 9**

Following the general procedure, the title compound was obtained as a pale yellow crystalline solid. Yield: 68.5 mg (62%).



$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  7.08-7.05 (m, 10H,  $\text{CH}_{\text{Ar}}$ ), 6.93-6.85 (m, 7H,  $\text{CH}_{\text{Ar}}$ ), 6.71-6.68 (m, 6H,  $\text{CH}_{\text{Ar}}$ ), 2.99 (dd, 2H,  $^3J_{\text{HH}} = 7.8$ ,  $^4J_{\text{PH}} = 6.2$  Hz, Ha), 2.83 (t, 2H,  $^3J_{\text{HH}} = 11.2$  Hz, Hb), 2.42 (ddd, 2H,  $^3J_{\text{HH}} = 8.4$ ,  $^4J_{\text{PH}} = 6.5$ ,  $^4J_{\text{HH}} = 2.1$  Hz, Hc), 2.42 0.48 (s, 6H,  $\text{SiCH}_3$ ), -0.48 (s, 6H,  $\text{SiCH}_3$ ).

$^{31}\text{P}\{^1\text{H}\}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  172.1.

Elemental analysis calculated (found) for  $\text{C}_{38}\text{H}_{41}\text{NiO}_3\text{PSi}_2$ : C, 66.00 (66.24); H, 5.98 (6.12).

#### 4. Computational details.

The electronic structure and geometries of the compounds were investigated by using density functional theory (DFT) at the B3LYP level,<sup>6,7</sup> using the 6-311G(d) basis set. Molecular geometries were optimized without symmetrical restrictions. Frequency calculations were carried out at the same level of theory to identify all stationary points as minima (zero imaginary frequencies) and to provide the thermal correction to free energy at 298.15 K and 1 atm. The energies of the reaction between [M(PMe<sub>2</sub>Ph)<sub>2</sub>] complexes and ethylene were calculated from the optimized reactants and products using the 6-311++G(d,p) basis set and LANL2DZ<sup>8</sup> for Pd and Pt atoms. The energies of the fluxional behaviour of complex **1** were calculated out using single point calculations with the 6-311++G(d,p) basis set. In this case, solution-phase SCF energies were calculated using the CPCM solvation model in toluene.<sup>9</sup> The DFT calculations were carried out using the Gaussian 09 program package.<sup>10</sup>

---

<sup>6</sup> D. J. Becke, *Chem. Phys.*, 1993, **98**, 5648–5652.

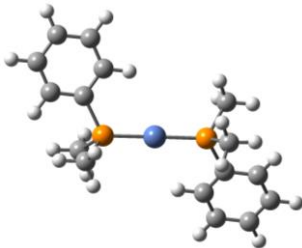
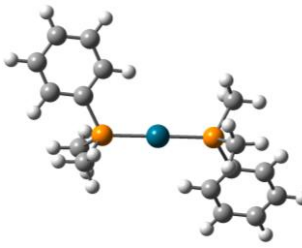
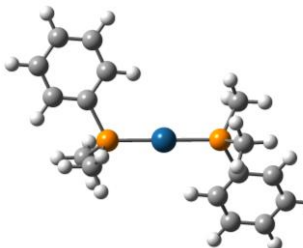
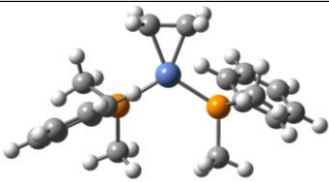
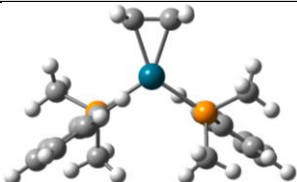
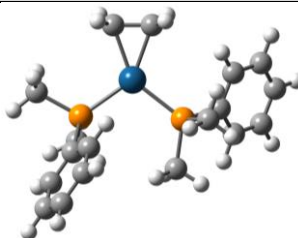
<sup>7</sup> L. W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.

<sup>8</sup> P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299–310.

<sup>9</sup> M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.*, 2003, **24**, 669–681

<sup>10</sup> M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford, CT, 2016

**Figure S1.** Optimized structures of  $[M(\text{PMe}_2\text{Ph})_2]$  and  $[M(\text{C}_2\text{H}_4)(\text{PMe}_2\text{Ph})_2]$  complexes ( $M = \text{Ni}, \text{Pd}, \text{Pt}$ ) and selected structural parameters (bond distances, Å, and angles, °).

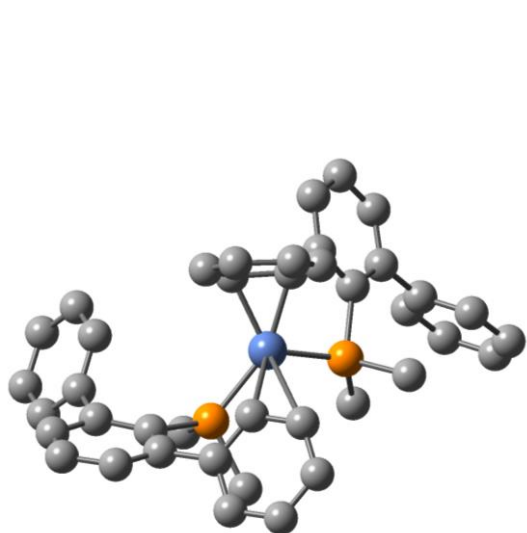
	$[\text{Ni}(\text{PMe}_2\text{Ph})_2]$	$[\text{Pd}(\text{PMe}_2\text{Ph})_2]$	$[\text{Pt}(\text{PMe}_2\text{Ph})_2]$
			
M-P	2.153	2.328	2.287
P-M-P	178.6	179.2	179.1
	$[\text{Ni}(\text{C}_2\text{H}_4)(\text{PMe}_2\text{Ph})_2]$	$[\text{Pd}(\text{C}_2\text{H}_4)(\text{PMe}_2\text{Ph})_2]$	$[\text{Pt}(\text{C}_2\text{H}_4)(\text{PMe}_2\text{Ph})_2]$
			
M-P	2.201	2.391	2.343, 2.353
M-C	1.990	2.210	2.146, 2.154
C-C	1.412	1.395	1.430
P-M-P	115.1	112.3	106.6

**Table S1.** Calculated  $\Delta G$  energies (kcal/mol, gas-phase) for the reaction of  $[M(\text{PMe}_2\text{Ph})_2]$  complexes ( $M = \text{Ni}, \text{Pd}, \text{Pt}$ ) with ethylene.

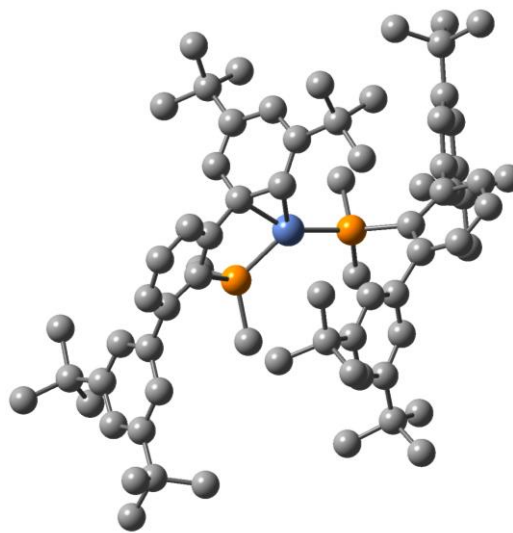
$\text{R}_3\text{P}-\text{M}-\text{PR}_3 \xrightarrow{\text{C}_2\text{H}_4} \text{R}_3\text{P}-\overset{\equiv}{\text{C}}-\text{M}-\text{PR}_3$	Ni	Pd	Pt
	-10.6	5.6	7.6



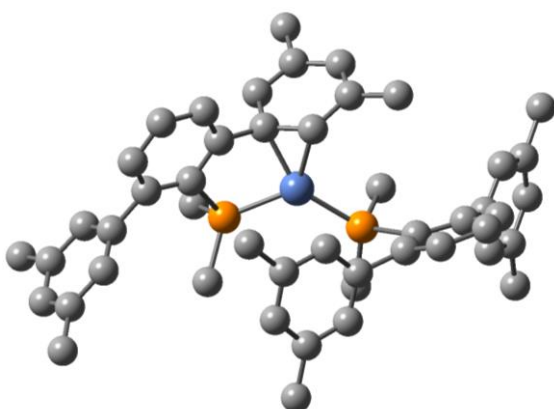
**Figure S2.** Optimized structures of complexes  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{Ph}_2})_2]$ , **1**,  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{Dtbp}_2})_2]$ , **2**,  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{m-Xil}_2})_2]$ , **3**, and  $[\text{Ni}(\text{P}(\text{OPh})_2\text{Ar}^{\text{Ph}_2})_2]$ , **4** (hydrogen atoms omitted for clarity).



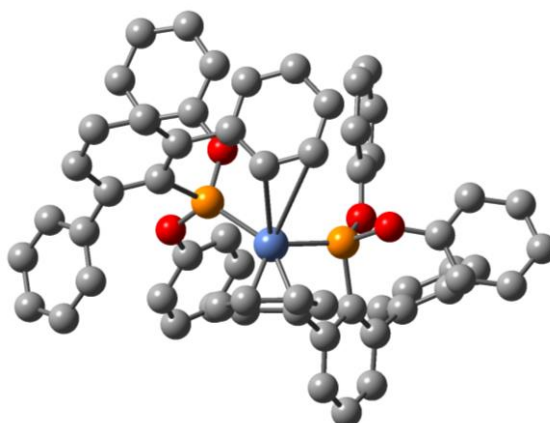
$[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{Ph}_2})_2]$ , **1**



$[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{Dtbp}_2})_2]$ , **2**



$[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{m-Xil}_2})_2]$ , **3**

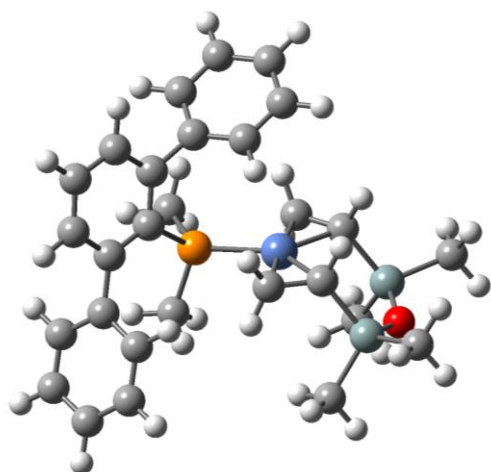


$[\text{Ni}(\text{P}(\text{OPh})_2\text{Ar}^{\text{Ph}_2})_2]$ , **4**

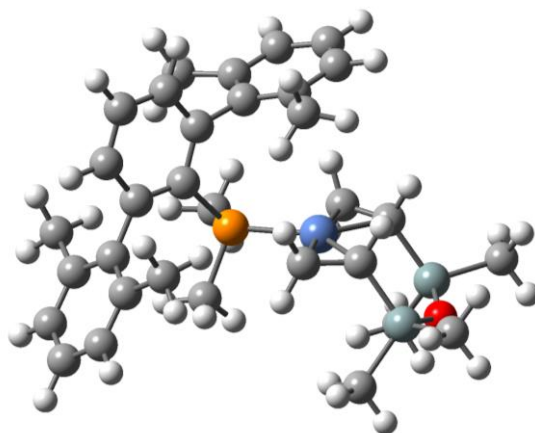
**Table S2.** Comparison of selected structural parameters of experimental and calculated complexes  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{Ph}_2})_2]$ , **1**,  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{Dtbp}_2})_2]$ , **2**,  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{m-Xil}_2})_2]$ , **3**, and  $[\text{Ni}(\text{P}(\text{OPh})_2\text{Ar}^{\text{Ph}_2})_2]$ , **4**.

Bond distances (Å) and angles (°)	1		2		3	4	
	X-ray	DFT	X-ray	DFT	DFT	X-ray	DFT
Ni-P	2.1978(7),	2.198,	2.137(2),	2.180,	2.175,	2.1074(5),	2.156,
	2.1700(7)	2.215	2.220	2.207	2.195	2.1253(5)	2.161
Ni-C	2.058(2),	2.018,		1.964,	1.970,	2.086(2),	2.083,
	2.186(3),	2.063,	2.142(5),	2.045,	2.014,	2.211(2),	2.088,
	2.322(3),	3.499,	2.292(7)	3.740,	3.526,	2.461(2),	3.024,
	2.403(3)	4.201		3.754	3.576	2.614(2)	3.638
P-Ni-P	112.5	116.3	115.37(7)	116.2	121.0	115.4	125

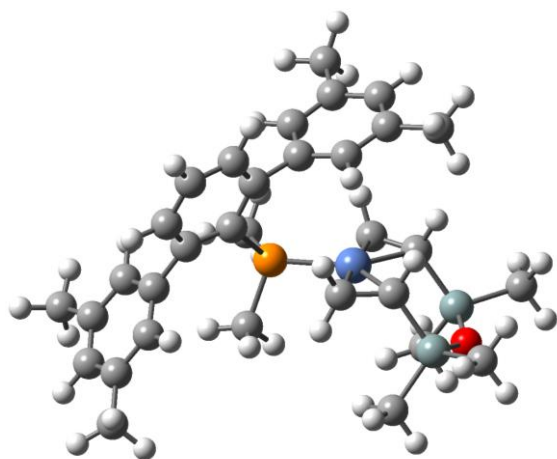
**Figure S3.** Optimized structures of divinyldisiloxane  $[\text{Ni}(\text{PR}_2\text{Ar}')(\text{DVDS})]$  complexes 5-9.



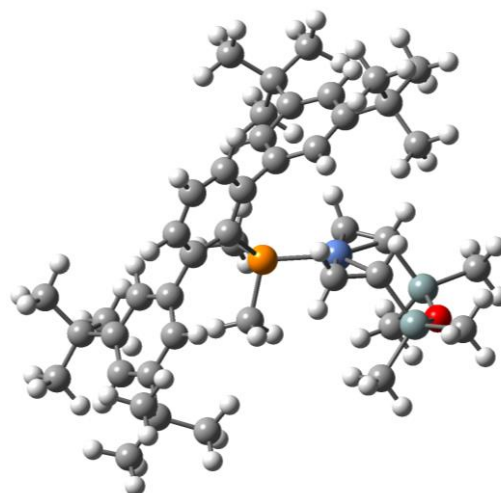
5



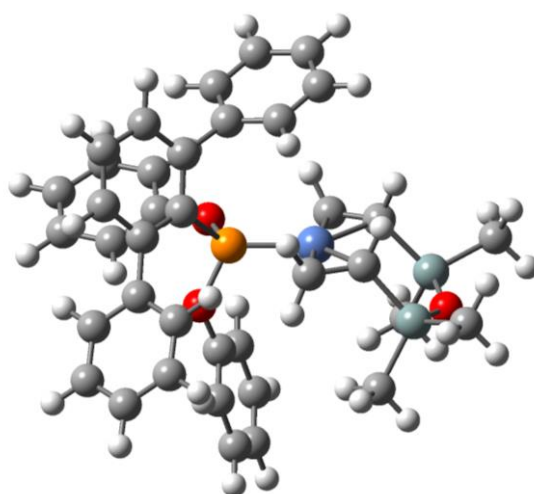
6



7

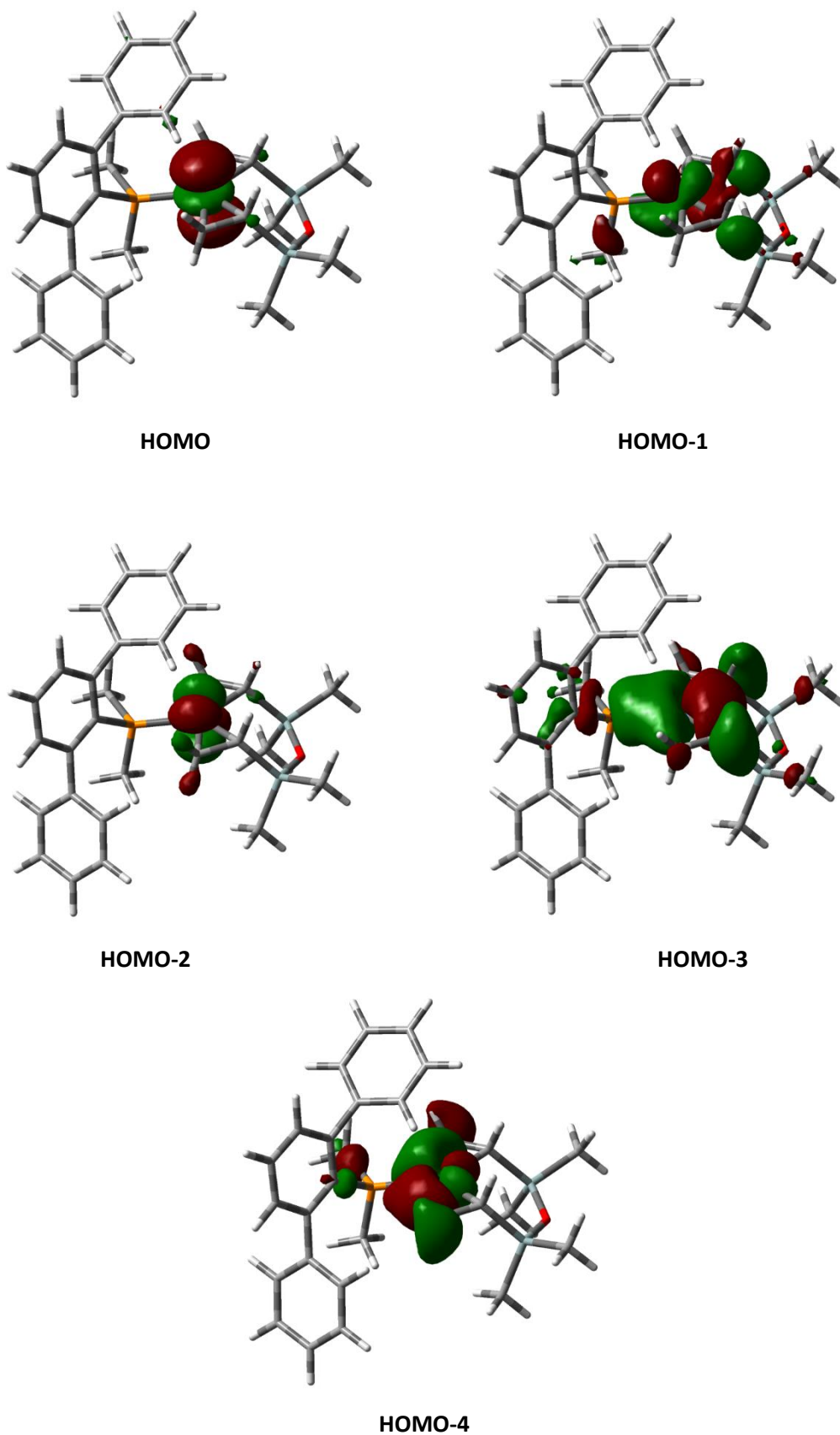


8



9

**Figure S4.** Selected molecular orbitals of complex **5** (isovalue = 0.03).



**Table S3.** Comparison of selected structural parameters of experimental and calculated divinylidisiloxane [Ni(PR<sub>2</sub>Ar')(DVDS)] complexes **5-9**.

Bond distances (Å) and angles (°)	5		6	7		8	9
	X-ray	DFT	DFT	X-ray	DFT	DFT	DFT
Ni-P	2.162(1)	2.228	2.209	2.1669(8)	2.210	2.206	2.146
Ni-C	1.995(3)	1.990	1.987	1.990(2)	1.987	1.983	1.993
	1.986(4)	1.996	1.990	1.998(2)	1.989	1.993	2.002
	2.000(4)	2.017	2.018	2.008(2)	2.017	2.018	2.022
	2.019(3)	2.030	2.024	2.017(2)	2.022	2.018	2.043
C-C	1.293(5)	1.403	1.406	1.406(3)	1.406	1.407	1.399
	1.398(6)	1.409	1.409	1.411(4)	1.409	1.408	1.407
P-Ni-C	92.1(1)	92.6	91.0	91.67(8)	92.0	91.2	91.6
	93.2(1)	93.6	93.4	92.70(7)	92.8	94.1	94.5

**Table S4.** Thermodynamic data (kcal·mol<sup>-1</sup>) for the synthesis of complexes **5-9**.<sup>a</sup>

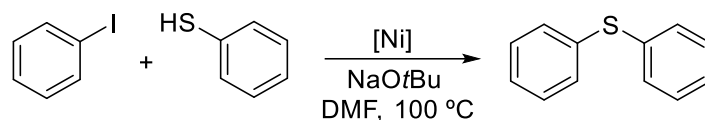
Reaction	Complex	$\Delta G$	$\Delta H$
$\text{Ni}(\text{PR}_2\text{Ar}')_2 + \text{DVDS} \longrightarrow \begin{array}{c} \text{PR}_2\text{Ar}' \\   \\ \text{Ni} \\   \\ \text{Si} \text{---} \text{O} \text{---} \text{Si} \\ / \quad \backslash \\ \text{---} \quad \text{---} \end{array} + \text{PR}_2\text{Ar}'$ <p> <math>\text{PR}_2\text{Ar}' = \text{PMe}_2\text{Ar}^{\text{Ph}2}</math>, <b>5</b>  <math>= \text{PMe}_2\text{Ar}^{\text{o-Xyl}2}</math>, <b>6</b>  <math>= \text{PMe}_2\text{Ar}^{\text{m-Xyl}2}</math>, <b>7</b>  <math>= \text{PMe}_2\text{Ar}^{\text{Dtbp}2}</math>, <b>8</b>  <math>= \text{P}(\text{OPh})_2\text{Ar}^{\text{Ph}2}</math>, <b>9</b> </p>	<b>5</b>	-14.7	-18.9
	<b>6</b>	-9.3	-5.1
	<b>7</b>	-18.3	-20.3
	<b>8</b>	-22.3	-23.0
	<b>9</b>	-17.7	-20.8
$\text{Ni}(\text{COD})_2 + \text{PR}_2\text{Ar}' + \text{DVDS} \longrightarrow \begin{array}{c} \text{PR}_2\text{Ar}' \\   \\ \text{Ni} \\   \\ \text{Si} \text{---} \text{O} \text{---} \text{Si} \\ / \quad \backslash \\ \text{---} \quad \text{---} \end{array} + 2 \text{COD}$ <p> <math>\text{PR}_2\text{Ar}' = \text{PMe}_2\text{Ar}^{\text{Ph}2}</math>, <b>5</b>  <math>= \text{PMe}_2\text{Ar}^{\text{o-Xyl}2}</math>, <b>6</b>  <math>= \text{PMe}_2\text{Ar}^{\text{m-Xyl}2}</math>, <b>7</b>  <math>= \text{PMe}_2\text{Ar}^{\text{Dtbp}2}</math>, <b>8</b>  <math>= \text{P}(\text{OPh})_2\text{Ar}^{\text{Ph}2}</math>, <b>9</b> </p>	<b>5</b>	-11.5	-12.8
	<b>6</b>	-7.1	-9.8
	<b>7</b>	-11.3	-13.7
	<b>8</b>	-7.9	-12.2
	<b>9</b>	-9.4	-12.6

<sup>a</sup> DFT, B3LYP/6-311G\*, gas-phase.

## 5. C-S coupling reactions catalyzed by Ni(0) complexes.

### 5.1. Screening of precatalysts

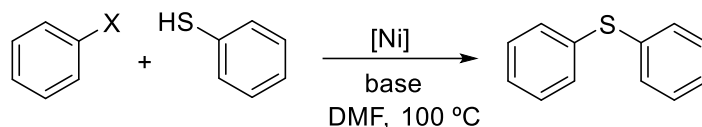
**Table S5.** Optimization of reaction conditions for the arylation of thiophenol with phenyl iodide using complexes **1-9** as precatalysts.<sup>a</sup>



	Entry	[Ni] (mol%)	Time/h	Conversion/% <sup>b</sup>
<b>NiP<sub>2</sub></b>	1	<b>1</b> (3)	24	21
	2	<b>1</b> (5)	24	43
	3	<b>1</b> ( <b>10</b> )	<b>24</b>	<b>100 (93)<sup>c</sup></b>
	4	<b>1</b> (10)	12	77
	5	<b>2</b> (3)	24	43
	6	<b>2</b> (5)	24	56
	7	<b>2</b> (10)	24	(80) <sup>c</sup>
	8	<b>3</b> (3)	24	11
	9	<b>3</b> (5)	24	26
	10	<b>3</b> (10)	24	69
	11	<b>4</b> (3)	24	-
	12	<b>2</b> (5)	24	15
<b>NiP(DVDS)</b>	13	<b>5</b> (3)	6	100
	14	<b>5</b> (1)	6	99
	15	<b>5</b> (0.5)	6	51
	16	<b>5</b> ( <b>1</b> )	<b>4</b>	<b>100 (93)<sup>c</sup></b>
	17	<b>5</b> (1)	2	78
	18	<b>5</b> (0.5)	12	83
	19	<b>5</b> (0.5)	24	100
	20	<b>6</b> ( <b>1</b> )	<b>4</b>	<b>97 (95)<sup>c</sup></b>
	21	<b>7</b> (1)	4	77
	22	<b>9</b> (1)	4	41

<sup>a</sup> Reaction conditions: iodobenzene (1.0 mmol), thiophenol (1.1 mmol), NaOtBu (1.2 mmol), DMF (1 mL), T = 100 °C. <sup>b</sup> Conversion determined by GC using dodecane as an internal standard (average of two runs). <sup>c</sup> Isolated yield of product.

**Table S6.** Optimization of reaction conditions for the arylation of thiophenol with phenyl bromide and phenyl tosylate using complexes **5-9** as precatalysts.<sup>a</sup>



Entry	X	[Ni] (mol%)	Base	Time/h	Conversion <sup>b</sup> /%
1	Br	<b>5</b> (5)	NaOtBu	6	100
2	Br	<b>5</b> (3)	NaOtBu	6	100
3	Br	<b>5</b> (1)	NaOtBu	6	48
4	<b>Br</b>	<b>5</b> ( <b>3</b> )	NaOtBu	<b>4</b>	<b>99 (92)<sup>c</sup></b>
5	Br	<b>5</b> (1)	NaOtBu	24	97
6	<b>Br</b>	<b>6</b> ( <b>3</b> )	NaOtBu	<b>4</b>	<b>94 (91)<sup>c</sup></b>
7	Br	<b>7</b> (3)	NaOtBu	4	69
8	Br	<b>9</b> (3)	NaOtBu	4	26
9	OTs	<b>5</b> (5)	LiOtBu	6	100
10	OTs	<b>5</b> (3)	LiOtBu	6	100
11	OTs	<b>5</b> (1)	LiOtBu	6	21
12	<b>OTs</b>	<b>5</b> ( <b>3</b> )	LiOtBu	<b>4</b>	<b>92 (79)<sup>c</sup></b>
13	OTs	<b>5</b> (3)	LiOtBu	2	78
14	OTs	<b>5</b> (1)	LiOtBu	24	100
15	<b>OTs</b>	<b>6</b> ( <b>3</b> )	LiOtBu	<b>4</b>	<b>88 (77)<sup>c</sup></b>
16	OTs	<b>7</b> (3)	LiOtBu	4	41
17	OTs	<b>9</b> (3)	LiOtBu	4	16

<sup>a</sup> Reaction conditions: aryl halide (1.0 mmol), thiophenol (1.1 mmol), NaOtBu (1.2 mmol), DMF (1 mL) T = 100 °C. <sup>b</sup> Conversion determined by GC using dodecane as an internal standard (average of two runs). <sup>c</sup> Optimized conditions found for the coupling of bromobenzene with thiophenol catalyzed by Ni(II)-allyl (see ref. 2). <sup>d</sup> Isolated yield of product. <sup>e</sup> Optimized conditions found for the coupling of bromobenzene with thiophenol catalyzed by Ni(II)-allyl (see ref. 2).

## 5.2. Catalytic procedures for the C-S coupling of aryl iodides and bromides with aromatic and aliphatic thiols

The catalyst **5** or **6** (0.01 or 0.03 mmol) and NaOtBu (1.2 mmol) were dissolved in DMF (1 mL) into a vial equipped with a J Young tap containing a magnetic bar. The thiol (1.1 mmol) and the aryl halide (1 mmol) were added in turn under a nitrogen atmosphere. The mixture was stirred at 100 °C for 4 h in an oil bath. The reaction mixture was allowed to cool to room temperature, diluted with ethyl acetate (10 mL) and filtered through Celite plug. The conversion was determined by GC analysis. Pure products were obtained after purification by flash chromatography on silica gel with petroleum ether (unless otherwise indicated).



### 5.3. General catalytic procedures for the C-S coupling of aryl tosylates with aromatic and aliphatic thiols

The catalyst **5** or **6** (0.03 mmol) and LiOtBu (1.2 mmol) were dissolved in DMF (1 mL) into a vial equipped with a J Young tap containing a magnetic bar. The thiol (1.1 mmol) and the aryl halide (1 mmol) were added in turn under a nitrogen atmosphere. The mixture was stirred at 100 °C for 4 h in an oil bath. The reaction mixture was allowed to cool to room temperature, diluted with ethyl acetate (10 mL) and filtered through Celite plug. The conversion was determined by GC analysis. Pure products were obtained after purification by flash chromatography on silica gel with petroleum ether (unless otherwise indicated).

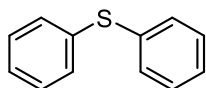
### 5.4. General catalytic procedures for the C-S coupling of aryl chlorides with aliphatic thiols

The catalyst **6** (0.025 mmol) and NaOtBu (1.2 mmol) were dissolved in NMP (1 mL) into a vial equipped with a J Young tap containing a magnetic bar. The thiol (0.5 mmol) and the aryl chloride (0.55 mmol) were added in turn under a nitrogen atmosphere. The mixture was stirred at 120 °C for 16 h in an oil bath. The reaction mixture was allowed to cool to room temperature, diluted with ethyl acetate (10 mL) and filtered through Celite plug. Pure products were obtained after purification by flash chromatography on silica gel with petroleum ether (unless otherwise indicated).

### 5.5. Characterization data for C-S coupling products

All C-S coupling products have been described in the literature. However, <sup>1</sup>H NMR spectra of these compounds used to identify them have been included herein along with the references where their spectroscopic characterization appeared.

#### Diphenylsulfane<sup>11</sup> (Scheme 5, **10a**)

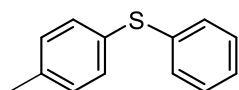


Colorless oil. Yield with catalyst **5**: 176.7 mg, 93% (X = I); 174.8 mg, 92% (X = Br); 146.9 mg, 79% (X = OTs). Yield with catalyst **6**: 176.6 mg, 95% (X = I); 169.2 mg, 91% (X = Br); 146.8mg, 77% (X=OTs).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.51-7.32 (m, 10 H).

<sup>11</sup> C. Bates, R. K. Gujadhur and D. Venkataraman, *Org. Lett.*, 2002, **4**, 2803-2806.

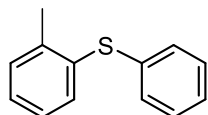
### Phenyl(4-methylphenyl)sulfane<sup>11</sup> (Scheme 5, 10b)



Colorless oil. Yield with catalyst **5**: 182.1 mg, 90% (X = I); 177.8 mg, 88% (X = Br); 174.1 mg, 87% (X = OTs). Yield with catalyst **6**: 177.9 mg, 89% (X = I); 177.8 mg, 89% (X = Br); 165.8 mg, 83% (X = OTs).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.42-7.39 (m, 1H), 7.23-7.03 (m, 8H), 2.25 (s, 3H).

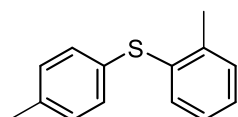
### Phenyl(2-methylphenyl)sulfane<sup>11</sup> (Scheme 5, 10c)



Colorless oil. Yield with catalyst **5**: 165.8 mg, 83% (X = I); 162.1 mg, 81% (X = Br). Yield with catalyst **6**: 165.7 mg, 83% (X = I); 153.8 mg, 77% (X = Br).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.27-7.01 (m, 9H), 2.29 (s, 3H).

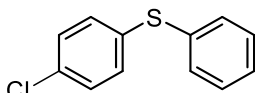
### (2-Methylphenyl)(4-methylphenyl)sulfane<sup>12</sup> (Scheme 5, 10d)



Colorless oil. Yield with catalyst **5**: 184.1 mg, 84% (X = I); 173.4 mg, 81% (X = Br); 151.9 mg, 71% (X = OTs). Yield with catalyst **6**: 173.3 mg, 81% (X = I); 171.2 mg, 80% (X = Br); 154.1 mg, 72% (X = OTs).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.30-7.14 (m, 8H), 2.50 (s, 3H), 2.40 (s, 3H).

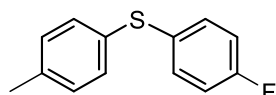
### (4-Chlorophenyl)(phenyl)sulfane<sup>13</sup> (Scheme 5, 10e)



Colorless oil. Yield with catalyst **5**: 187.1 mg, 83% (X = I); 180.4 mg, 80% (X = Br); 162.6 mg, 74% (X = OTs). Yield with catalyst **6**: 173.7 mg, 79% (X = I); 169.4 mg, 77% (X = Br); 156.2 mg, 71% (X = OTs).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.29-7.16 (m, 9H).

### (4-fluorophenyl)(p-tolyl)sulfane<sup>14</sup> (Scheme 5, 10f)



Colorless oil. Yield with catalyst **5**: 196.3 mg, 89% (X = I); 185.4 mg, 86% (X = Br); 165.6 mg, 76% (X = OTs). Yield with catalyst **6**: 185.5 mg, 85% (X = I); 174.6 mg, 80% (X = Br); 157.1 mg, 72% (X = OTs).

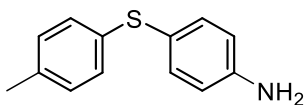
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 278 K): δ 7.24-7.17 (m, 2H), 7.14 (d, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 7.6 Hz, 2H), 6.99-6.86 (m, 2H), 2.23 (s, 3H).

<sup>12</sup> B. C. Ranu, A. Saha and R. Jana, *Adv. Synth. Catal.*, 2007, **349**, 2690–2696.

<sup>13</sup> W. Deng, Y. Zou, Y. F. Wang, L. Liu and Q. X. Guo, *Synlett* 2004, **7**, 1254–1258.

<sup>14</sup> P. Malik and D. Chakraborty, *Appl. Organomet. Chem.*, 2012, **26**, 557–561.

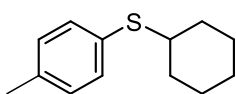
#### 4-(4-Methylphenylthio)aniline<sup>15</sup> (Scheme 5, **10g**)



Colorless oil. Purification by column chromatography in silica gel with a mixture 1:20 ethyl acetate/petroleum ether. Yield with catalyst **5**: 185.1 mg, 84% (X = I); 180.6 mg, 82% (X = Br); 176.9 mg, 74% (X = OTs). Yield with catalyst **6**: 176.4 mg, 82% (X = I); 178.5 mg, 81% (X = Br); 148.3 mg, 69% (X = OTs).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.21-7.14 (m, 2H), 7.06-6.94 (m, 4H), 6.59-6.51 (m, 2H), 3.67 (bs, 2H), 2.21 (s, 3H).

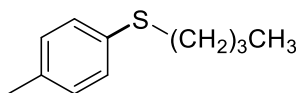
#### Cyclohexyl(2-methylphenyl)sulfane<sup>16</sup> (Scheme 5, **10h**; Scheme 6, **11d**)



Colorless oil. Purification by column chromatography in silica gel with a mixture 1:50 ethyl acetate/petroleum ether. Yield with catalyst **5**: 187.6 mg, 93% (X = I); 179.3 mg, 88% (X = Br), 154.5mg, 75% (X = Cl). Yield with catalyst **6**: 181.4 mg, 88% (X = I); 179.3 mg, 87% (X = Br).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.24 (d, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 2H), 2.99- 2.89 (m, 1H), 2.25 (s, 3H), 1.99-1.82 (m, 3H), 1.75-1.65 (m, 2H), 1.56-1.50 (m, 2H), 1.30-1.16(m, 2H).

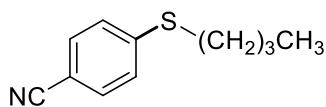
#### Butyl(*p*-tolyl)sulfane<sup>11</sup> (Scheme 6, **11a**)



Colorless oil. Purification by column chromatography in silica gel with petroleum ether. Yield with catalyst **5**: 63 mg, 70 %.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.30-7.25 (m, 2H), 7.13-7.10 (m, 2H), 2.93-2.88 (m, 2H), 2.34 (s, 3H), 1.70-1.57 (m, 2H), 1.52-1.40 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

#### 4-(butylthio)benzonitrile<sup>17</sup> (Scheme 6, **11b**)



Colorless oil. Purification by column chromatography in silica gel with a mixture 1:50 ethyl acetate/petroleum ether. Yield with catalyst **5**: 170.1 mg, 89%.

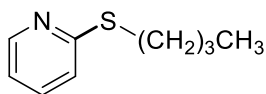
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.53-7.49 (m, 2H), 7.31-7.27 (m, 2H), 2.97 (t, *J* = 7.9 Hz, 2H), 1.73-1.63 (m, 2H), 1.54-1.42 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

<sup>15</sup> W. Zhang, M. Huang, Z. Zou, Z. Wu, S. Ni, L. Kong, Y. Zheng, Y. Wang and Y. Pan, *Chem. Sci.*, 2021, **12**, 2509–2514

<sup>16</sup> H. L. Kao, C. K. Chen, Y. J.; Wang and C. F. Lee, *Eur. J. Org. Chem.*, 2011, **9**, 1776–1781.

<sup>17</sup> Z. Qiao, J. Wei and X. Jiang, *Org. Lett.*, 2014, **16**, 1212–1215.

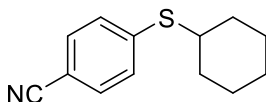
#### 2-(butylthio)pyridine<sup>18</sup> (Scheme 6, 11c)



Colorless oil. Purification by column chromatography in silica gel with a mixture 1:50 ethyl acetate/petroleum ether. Yield with catalyst **5**: 132 mg, 79%.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.42 (ddd, *J* = 4.9; 1.9; 0.9 Hz, 1H), 7.45(ddd, *J* = 8.0; 7.3; 1.9 Hz, 1H), 7.16 (dt, *J* = 8.1; 0.9 Hz, 1H), 6.95 (ddd, *J* = 7.3; 4.9; 1.0 Hz, 1H), 3.17 (t, *J* = 7.2 Hz, 2H), 1.75-1.65 (m, 2H), 1.54-1.42 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H).

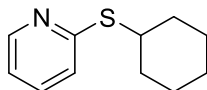
#### 4-(Cyclohexylthio)benzonitrile<sup>19</sup> (Scheme 6, 11e)



Colorless oil. Purification by column chromatography in silica gel with a mixture 1:50 ethyl acetate/petroleum ether. Yield with catalyst **5**: 175.8 mg, 81%.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.50 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 3.32-3.24 (m, 1H), 2.04-2.00 (m, 2H), 1.80-1.76 (m, 2H), 1.66-1.61 (m, 1H), 1.45-1.32(m, 5H).

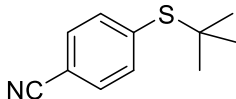
#### 2-(Cyclohexylthio)pyridine<sup>20</sup> (Scheme 6, 11f)



Colorless oil. Purification by column chromatography in silica gel with a mixture 1:50 ethyl acetate/petroleum ether. Yield with catalyst **5**: 173.8 mg, 90%.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.41 (ddd, *J* = 4.9; 1.9; 0.9 Hz, 1H), 7.44(ddd, *J* = 8.0; 7.4; 1.9 Hz, 1H), 7.15 (ddd, *J* = 7.4; 4.9; 1.1 Hz, 1H), 6.94 (ddd, *J* = 8.0; 1.1; 0.9 Hz, 1H), 3.86-3.77 (m, 1H), 2.12-2.05 (m, 2H), 1.79-1.73 (m, 2H), 1.51-1.41 (m, 6H).

#### 4-(tert-Butylthio)benzonitrile<sup>21</sup> (Scheme 6, 11g)



Colorless oil. Purification by column chromatography in silica gel with a mixture 1:50 ethyl acetate/petroleum ether. Yield with catalyst **5**: 164 mg, 86%.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.63-7.57 (m, 4H), 1.31(s, 9H).

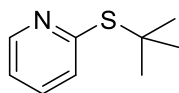
<sup>18</sup> A. R. Martínez, G. D. Gonzalo, D. E. T. Pazmiño, M. W. Fraaije and V. Gotor, *Eur. J. Org. Chem.*, 2010, **33**, 6409-6416.

<sup>19</sup> M. A. Fernandez-Rodriguez, Q. Shen and J. F. Hartwig, *Chem. Eur.*, 2006, **12**, 7782-7796.

<sup>20</sup> D. H. R. Barton, C. Y. Chern and J. C. Jaszberenyi, *Tetrahedron* 1995, **51**, 1867-1886.

<sup>21</sup> M. Jouffroy, C. B. Kelly, and G. A. Molander, *Org. Lett.*, 2016, **18**, 876-879.

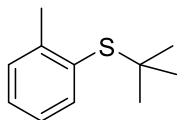
**2-(tert-butylthio)pyridine**<sup>22</sup> (Scheme 6, **11h**)



Colorless oil. Purification by column chromatography in silica gel with a mixture 1:50 ethyl acetate/petroleum ether. Yield with catalyst **5**: 137 mg, 82%.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.50 (ddd, *J* = 7.4; 4.9; 1.1 Hz, 1H), 7.49 (td, *J* = 7.9; 1.9 Hz, 1H), 7.32 (dt, *J* = 7.9; 1.0 Hz, 1H), 7.06 (ddd, *J* = 4.9; 1.9; 0.8 Hz, 1H), 1.50 (s, 9H).

**tert-butyl(o-tolyl)sulfane**<sup>23</sup> (Scheme 6, **11i**)



Colorless oil. Purification by column chromatography in silica gel with petroleum ether. Yield with catalyst **5**: 106 mg, 59%.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.57-7.54 (m, 1H), 7.32-7.25 (m, 2H), 7.20-7.14 (m, 1H), 2.55 (s, 3H), 1.33 (s, 9H).

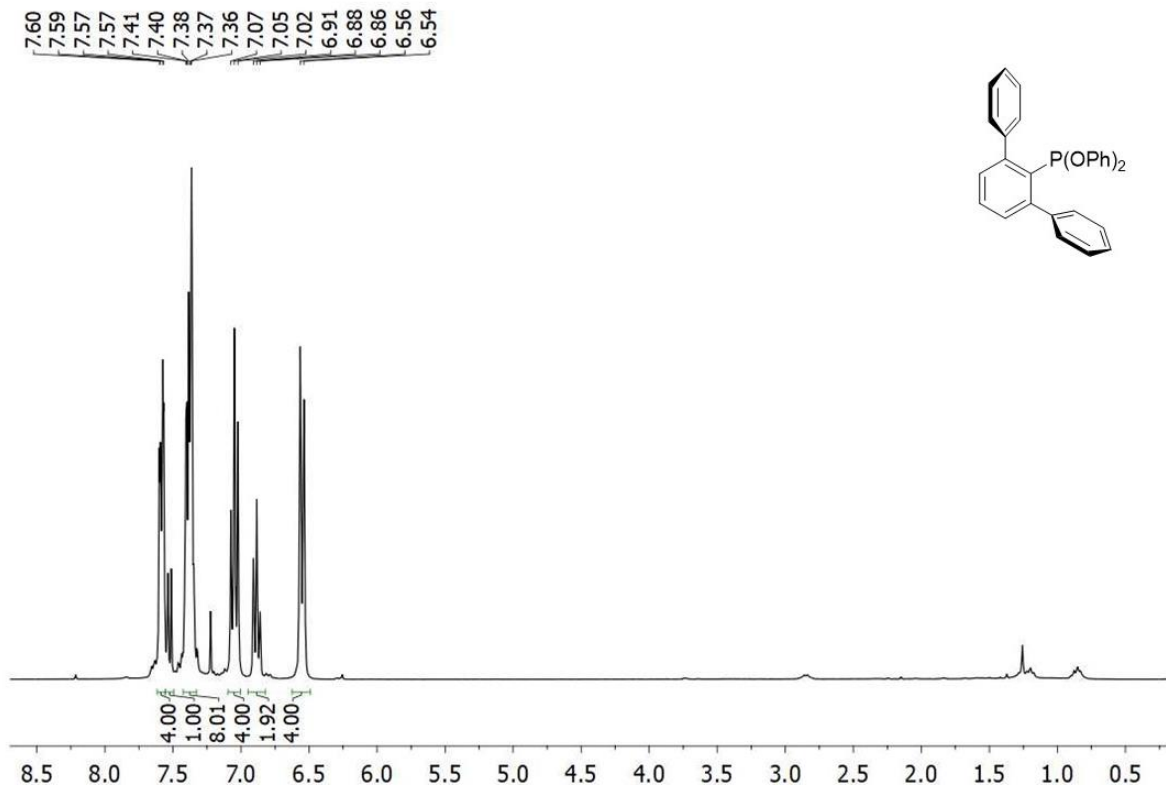
---

<sup>22</sup> C. C. Eichman and J. P. Stambuli, *J. Org. Chem.*, 2009, **74**, 4005-4008.

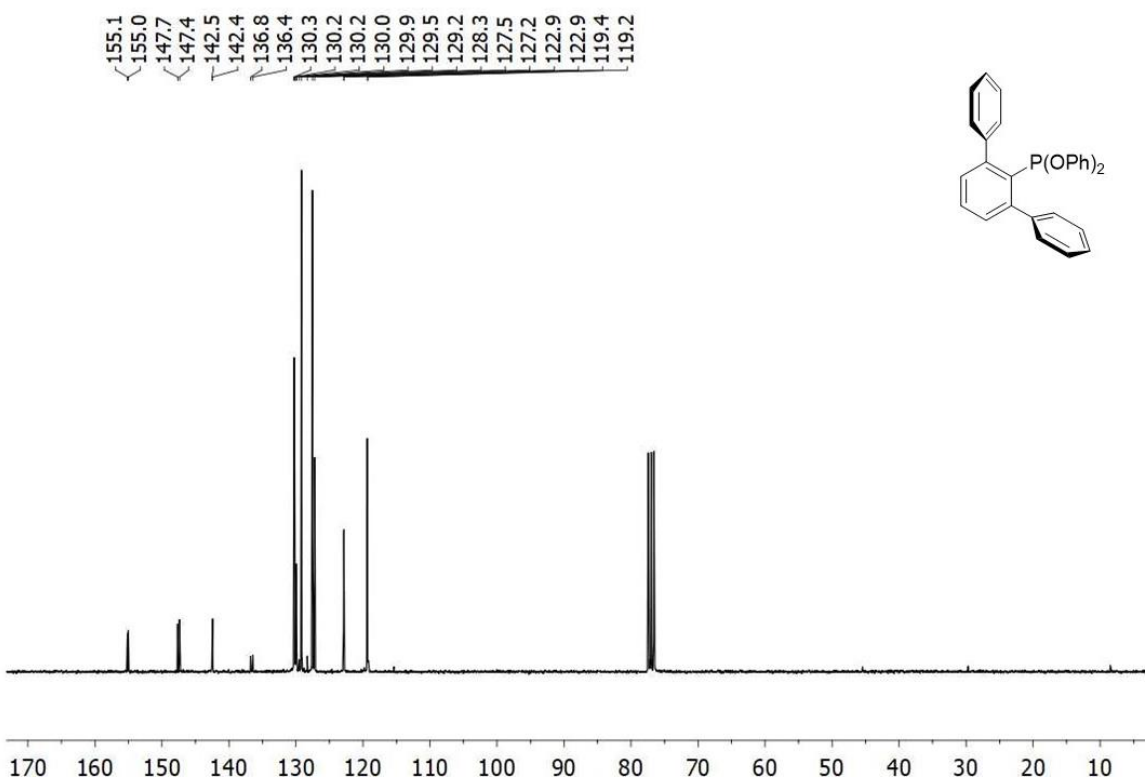
<sup>23</sup> M. Sayah and M. G. Organ, *Chem. Eur. J.*, 2011, **17**, 11719-11722.

## 6 NMR spectra of compounds

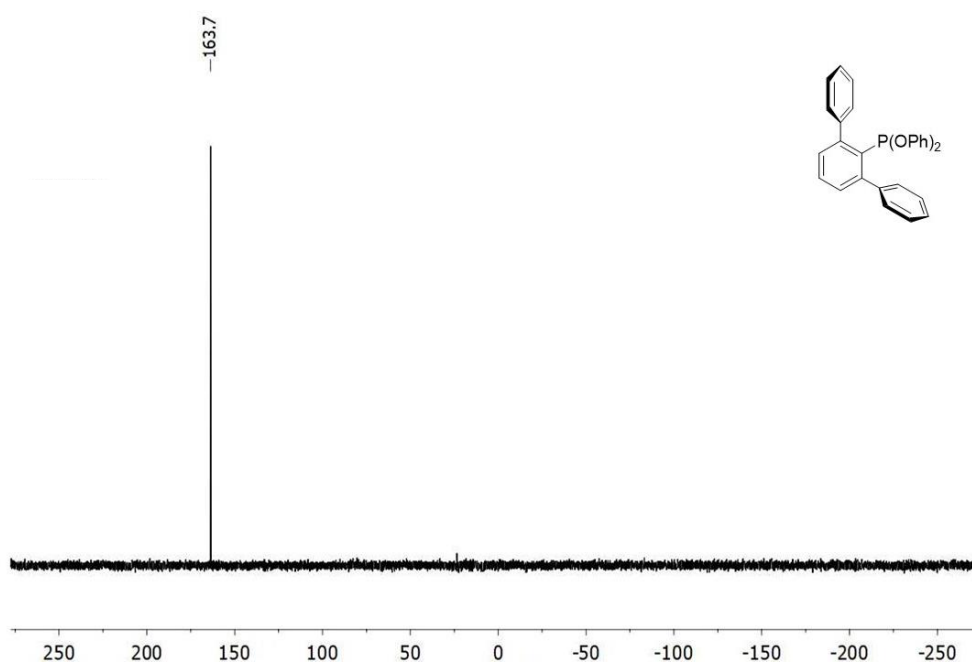
$^1\text{H}$  NMR spectrum of  $\text{P}(\text{OPh})_2\text{Ar}^{\text{Ph}_2}$ , (300 MHz,  $\text{CDCl}_3$ , 298 K)



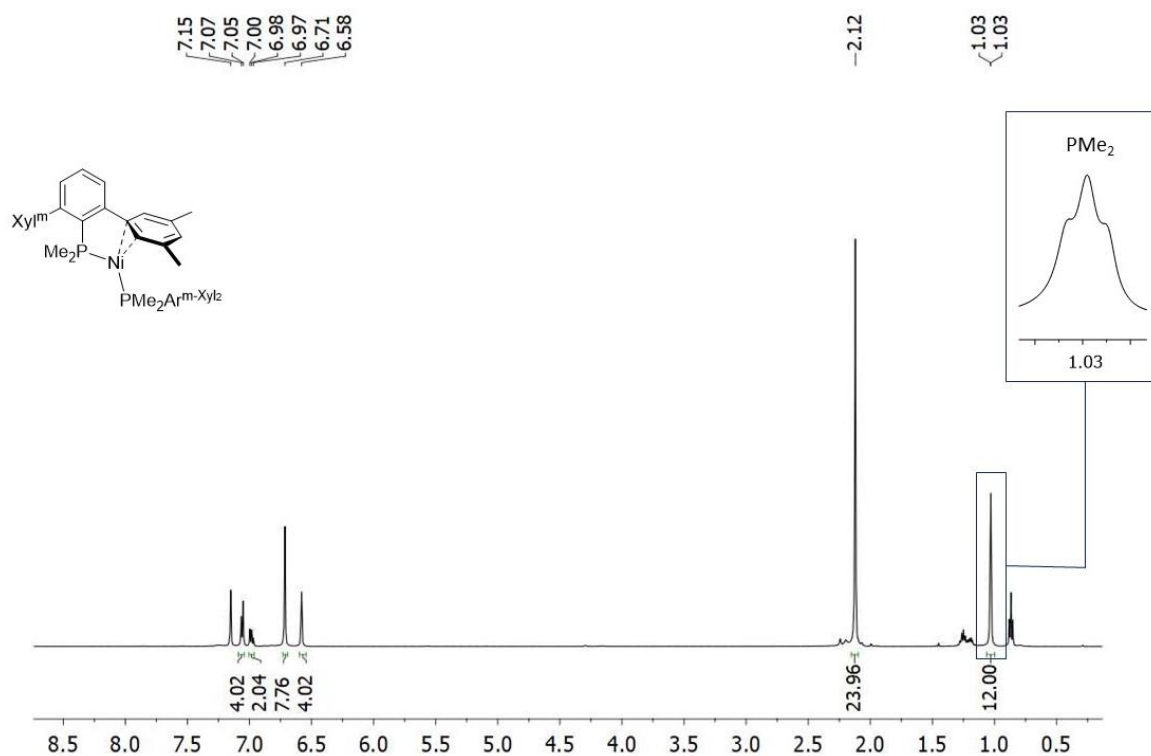
$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $\text{P}(\text{OPh})_2\text{Ar}^{\text{Ph}_2}$ , (75 MHz,  $\text{CDCl}_3$ , 298 K)



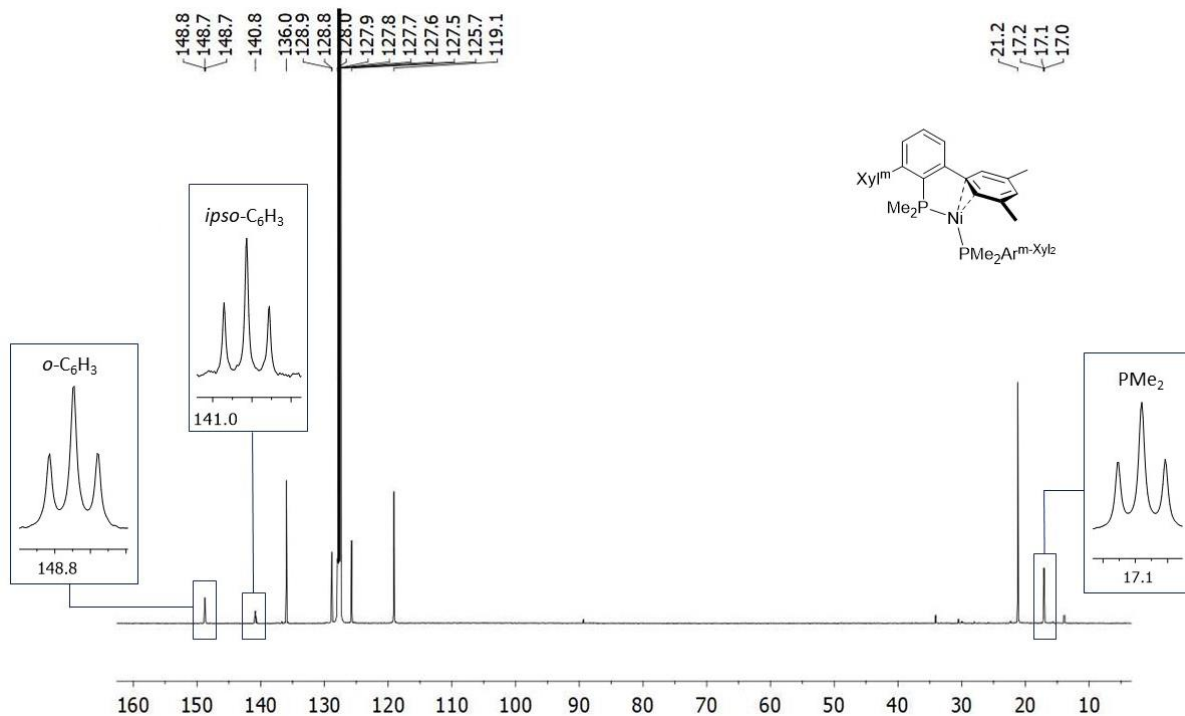
$^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{P}(\text{OPh})_2\text{Ar}^{\text{Ph}_2}$ , (121 MHz,  $\text{CDCl}_3$ , 298 K)



$^1\text{H}$  NMR spectrum of  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{m-Xyl}2})_2]$ , **3**, (500 MHz,  $\text{C}_6\text{D}_6$ , 298 K)

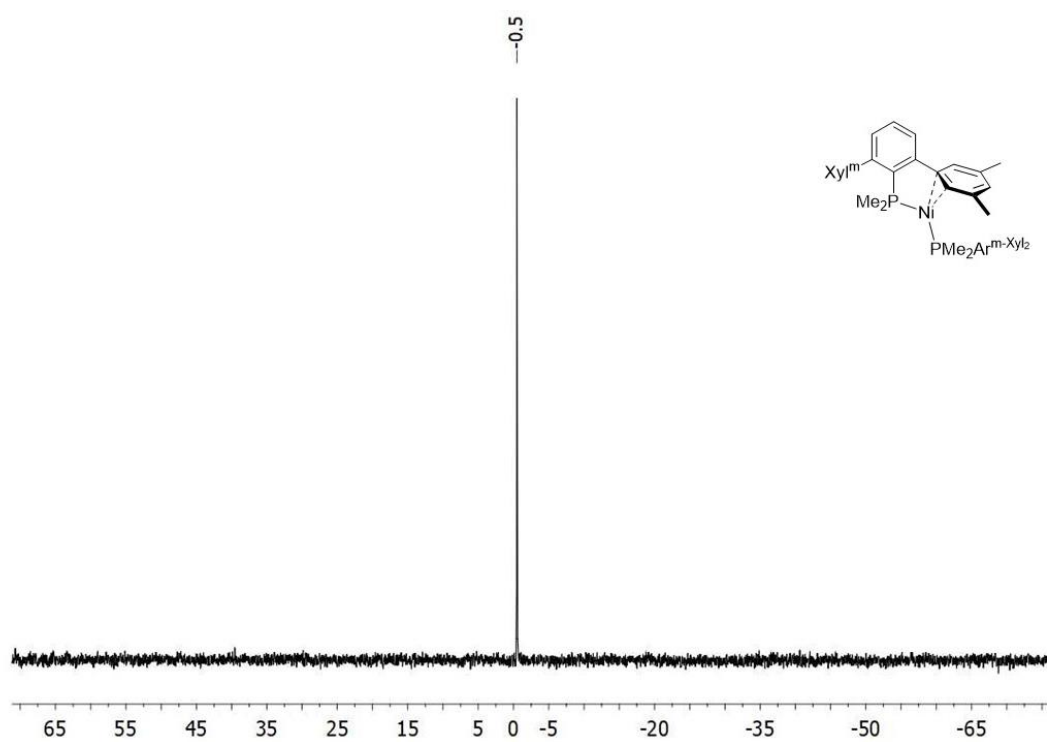


$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{m-Xyl}2})_2]$ , **3**, (125 MHz,  $\text{C}_6\text{D}_6$ , 298 K)

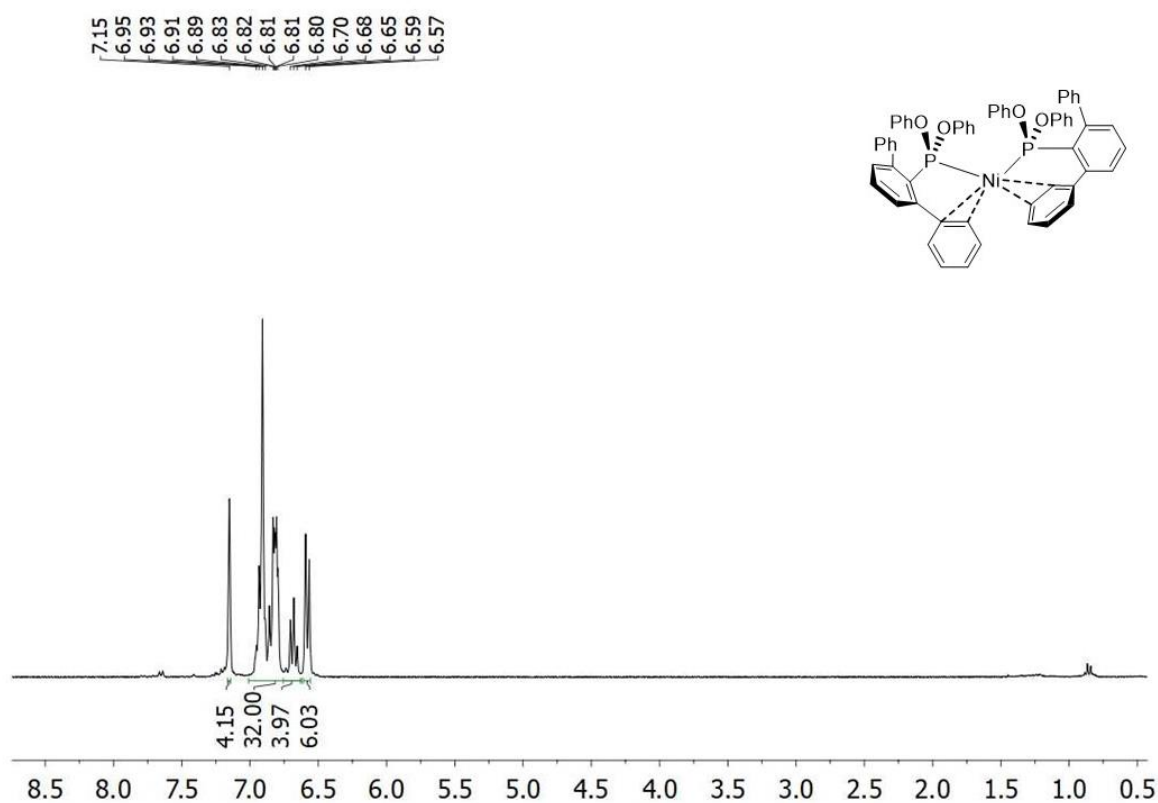




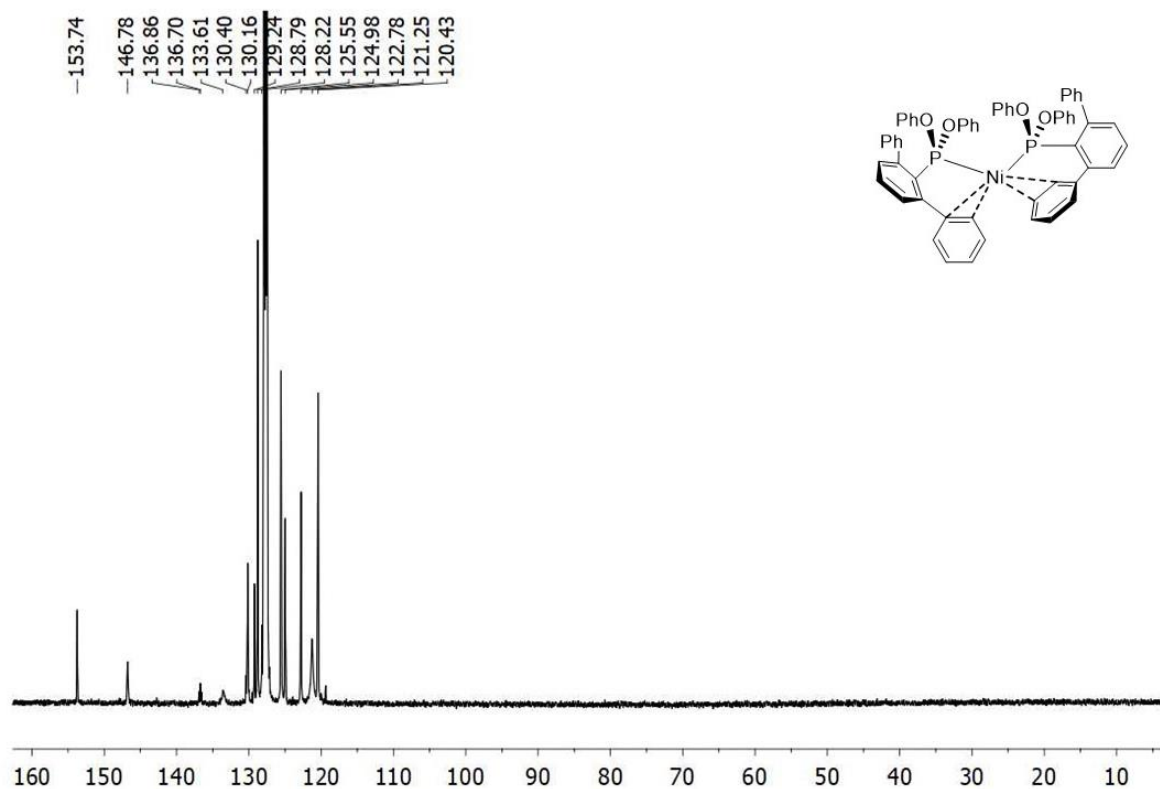
$^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{m-Xyl}^2})_2]$ , **3**, (202 MHz,  $\text{C}_6\text{D}_6$ , 298 K)



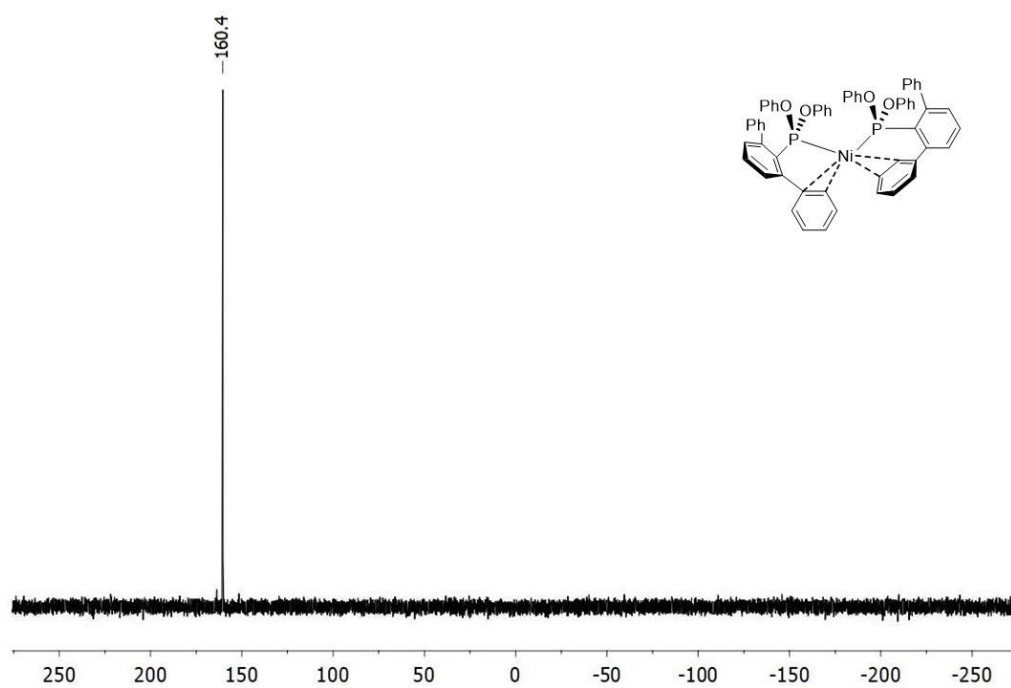
$^1\text{H}$  NMR spectrum of  $[\text{Ni}(\text{P}(\text{O}Ph)_2\text{Ar}^{\text{Ph}_2})_2]$ , **4**, (500 MHz,  $\text{C}_6\text{D}_6$ , 298 K)



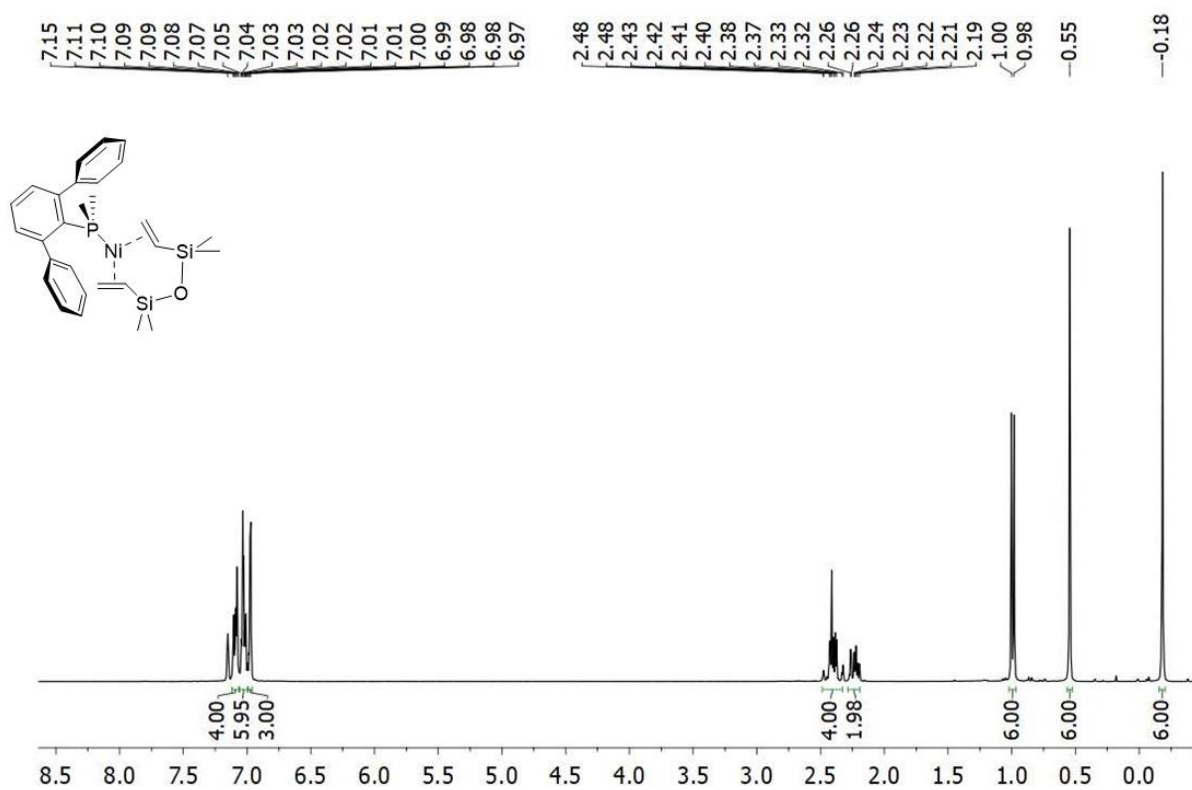
$^{13}\text{C}$  NMR spectrum of  $[\text{Ni}(\text{P}(\text{O}Ph)_2\text{Ar}^{\text{Ph}_2})_2]$ , **4**, (125 MHz,  $\text{C}_6\text{D}_6$ , 298 K)



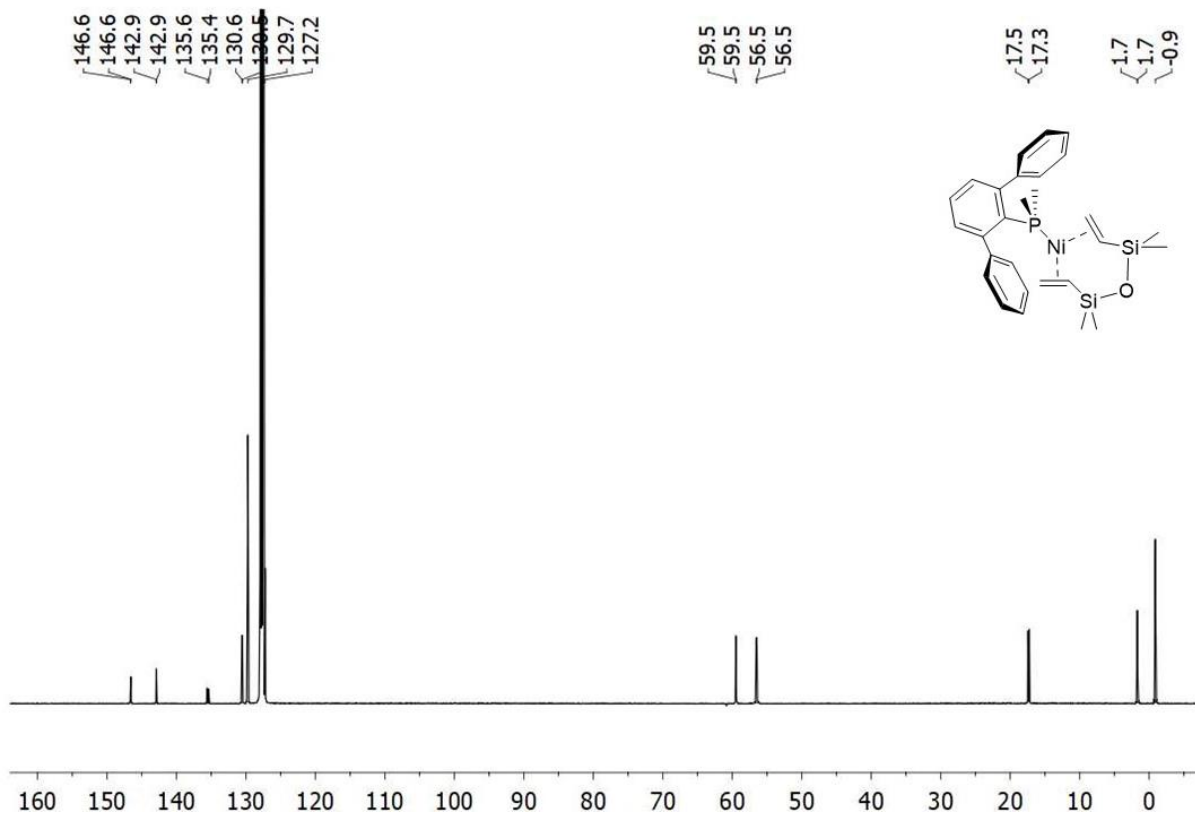
$^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ni}(\text{P}(\text{OPh})_2\text{Ar}^{\text{Ph}_2})_2]$ , **4**, (202 MHz,  $\text{C}_6\text{D}_6$ , 298 K)



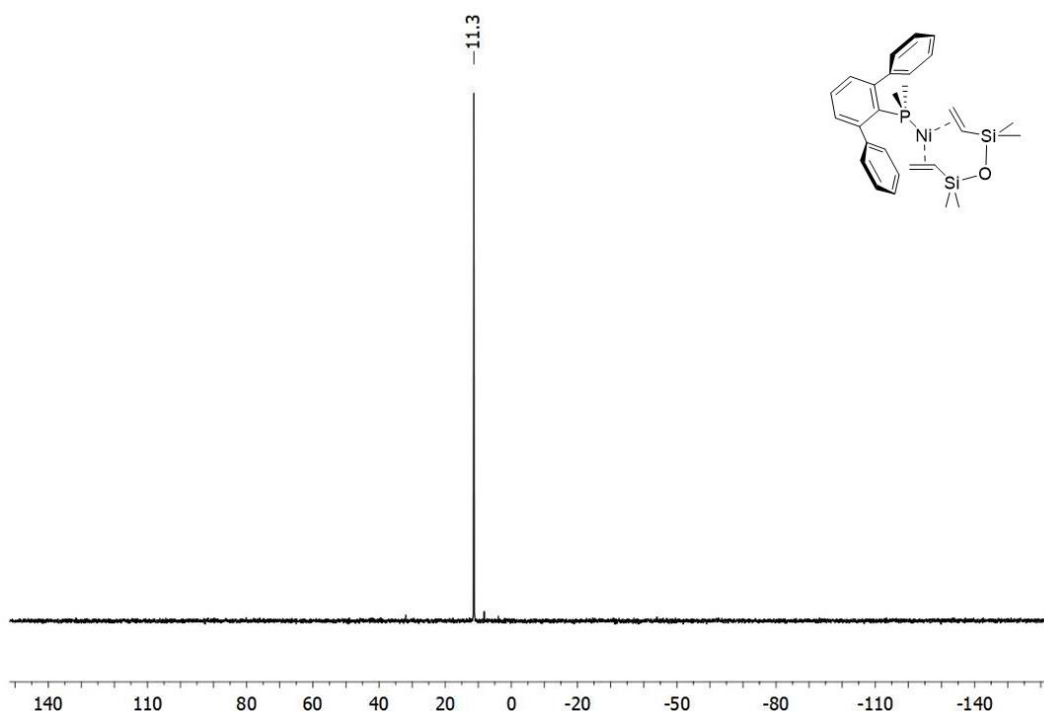
$^1\text{H}$  NMR spectrum of  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{Ph}_2})(\text{DVDS})]$ , **5**, (500 MHz,  $\text{C}_6\text{D}_6$ , 298 K)



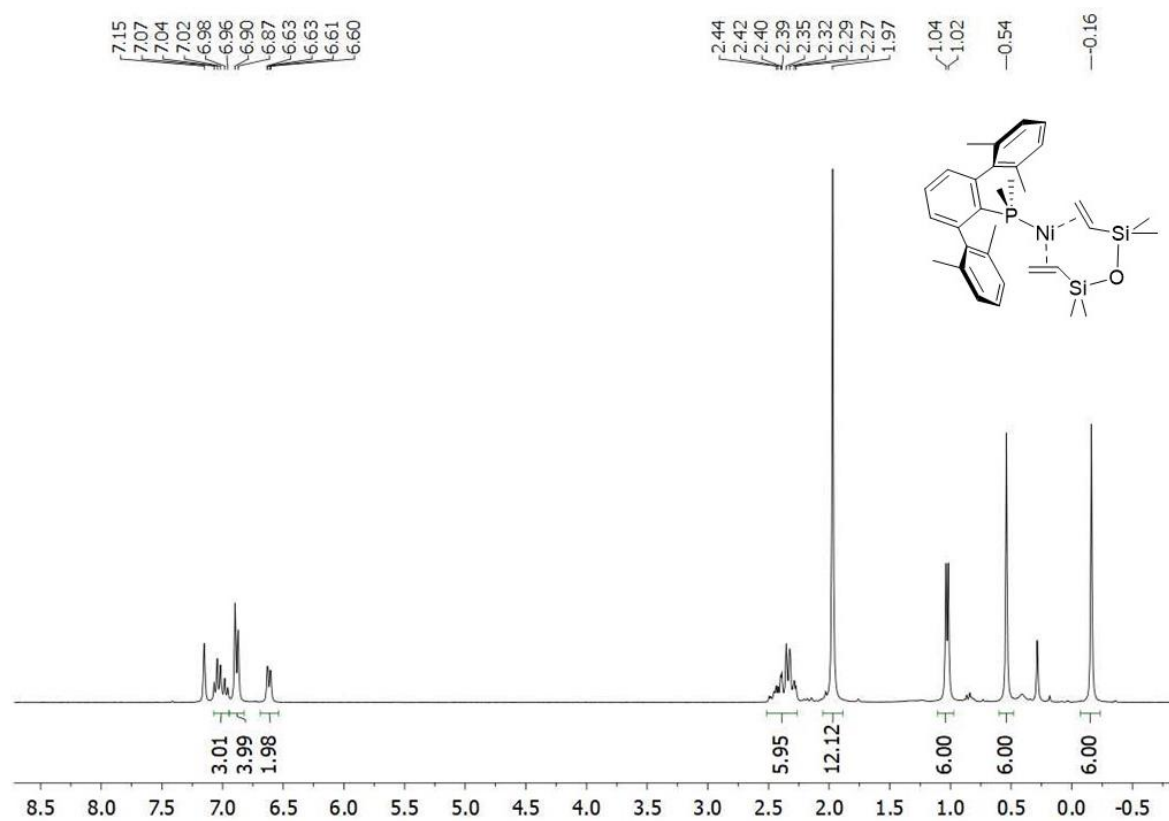
$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{Ph}_2})(\text{DVDS})]$ , **5**, (125 MHz,  $\text{C}_6\text{D}_6$ , 298 K)



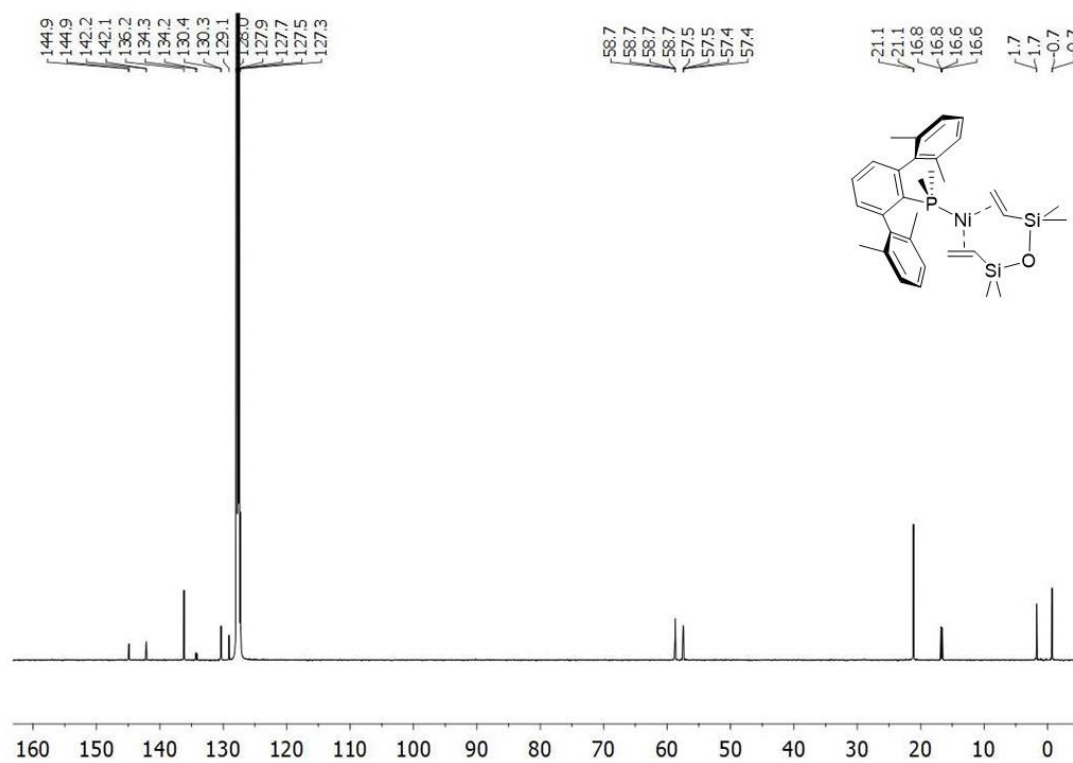
$^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{Ph}_2})(\text{DVDS})]$ , **5**, (202 MHz,  $\text{C}_6\text{D}_6$ , 298 K)



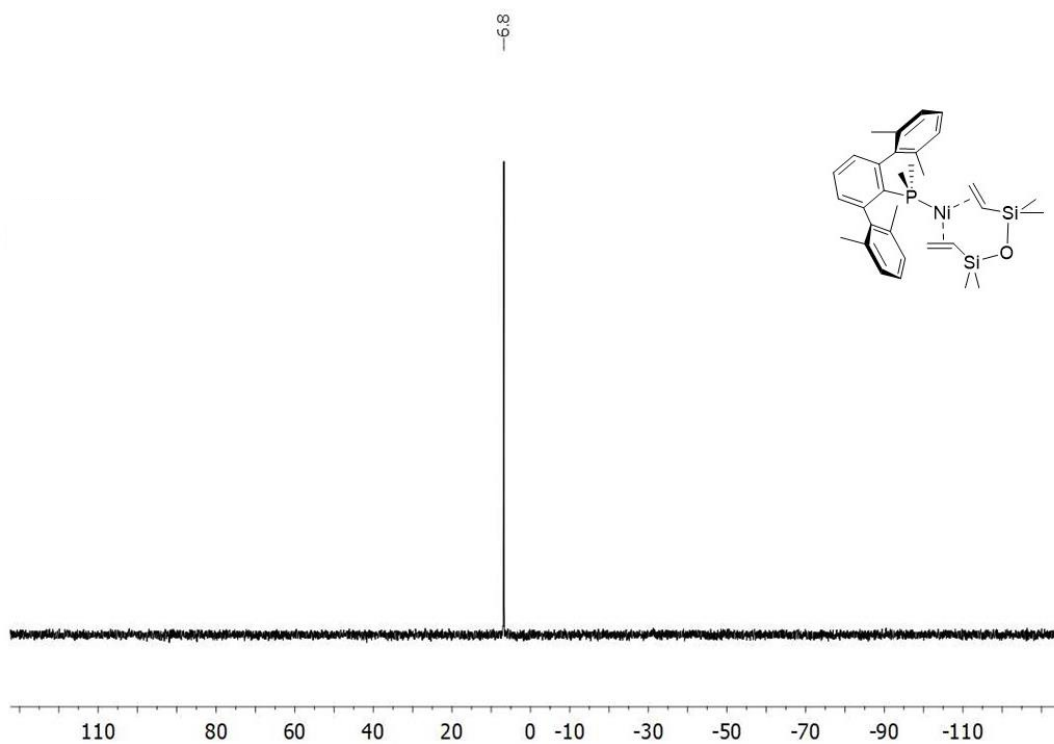
$^1\text{H}$  NMR spectrum of  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{Xyl}2})(\text{DVDS})]$ , **6**, (500 MHz,  $\text{C}_6\text{D}_6$ , 298 K)



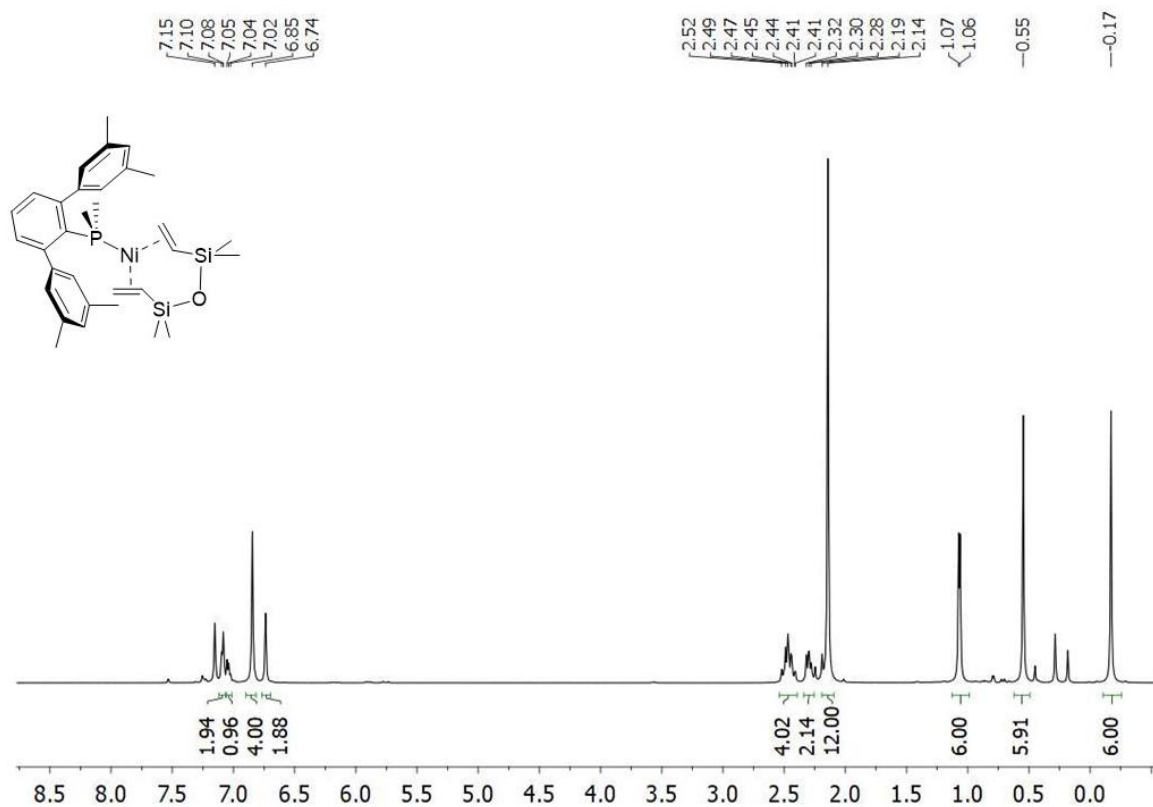
$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{Xyl}2})(\text{DVDS})]$ , **6**, (125 MHz,  $\text{C}_6\text{D}_6$ , 298 K)



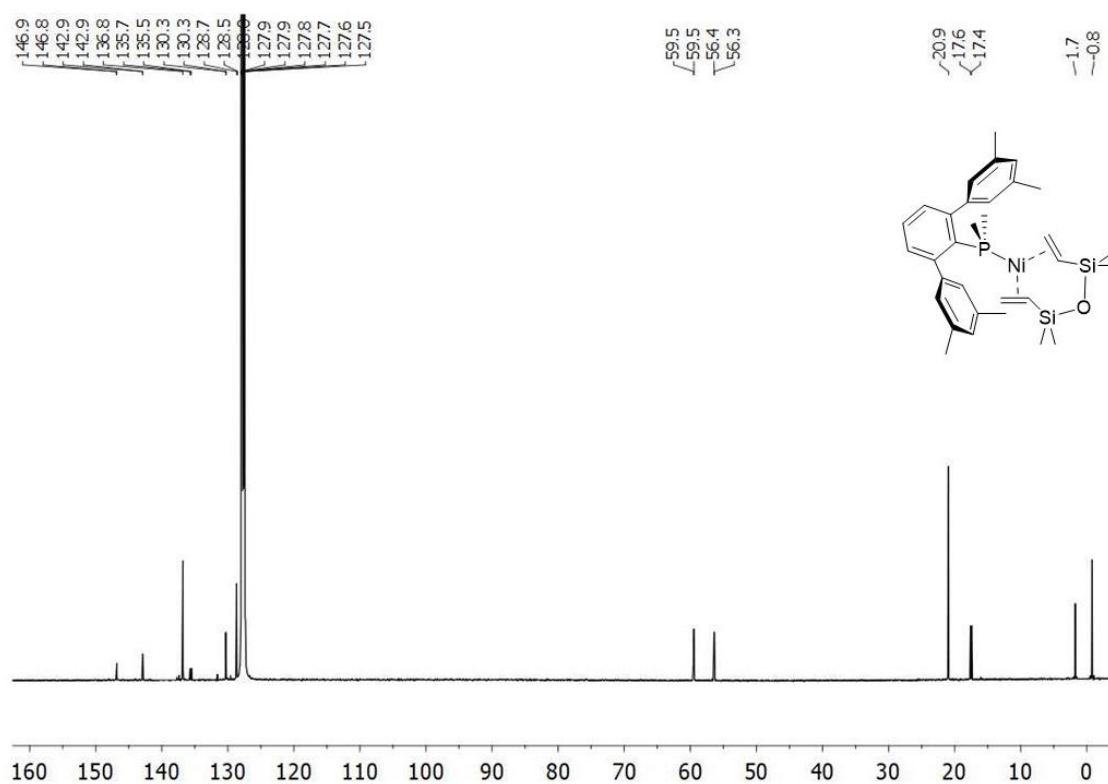
$^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{Xyl}2})(\text{DVDS})]$ , **6**, (202 MHz,  $\text{C}_6\text{D}_6$ , 298 K)



$^1\text{H}$  NMR spectrum of  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{m-Xyl}2})(\text{DVDS})]$ , **7**, (500 MHz,  $\text{C}_6\text{D}_6$ , 298 K)

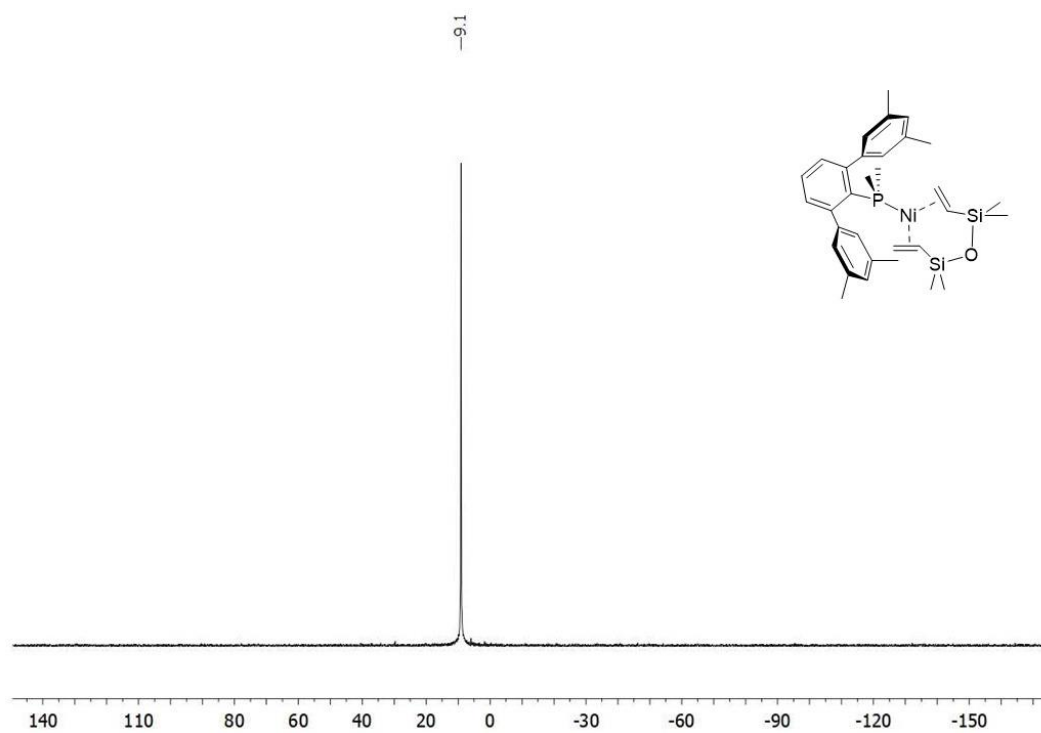


$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{m-Xyl}2})(\text{DVDS})]$ , **6**, (125 MHz,  $\text{C}_6\text{D}_6$ , 298 K)

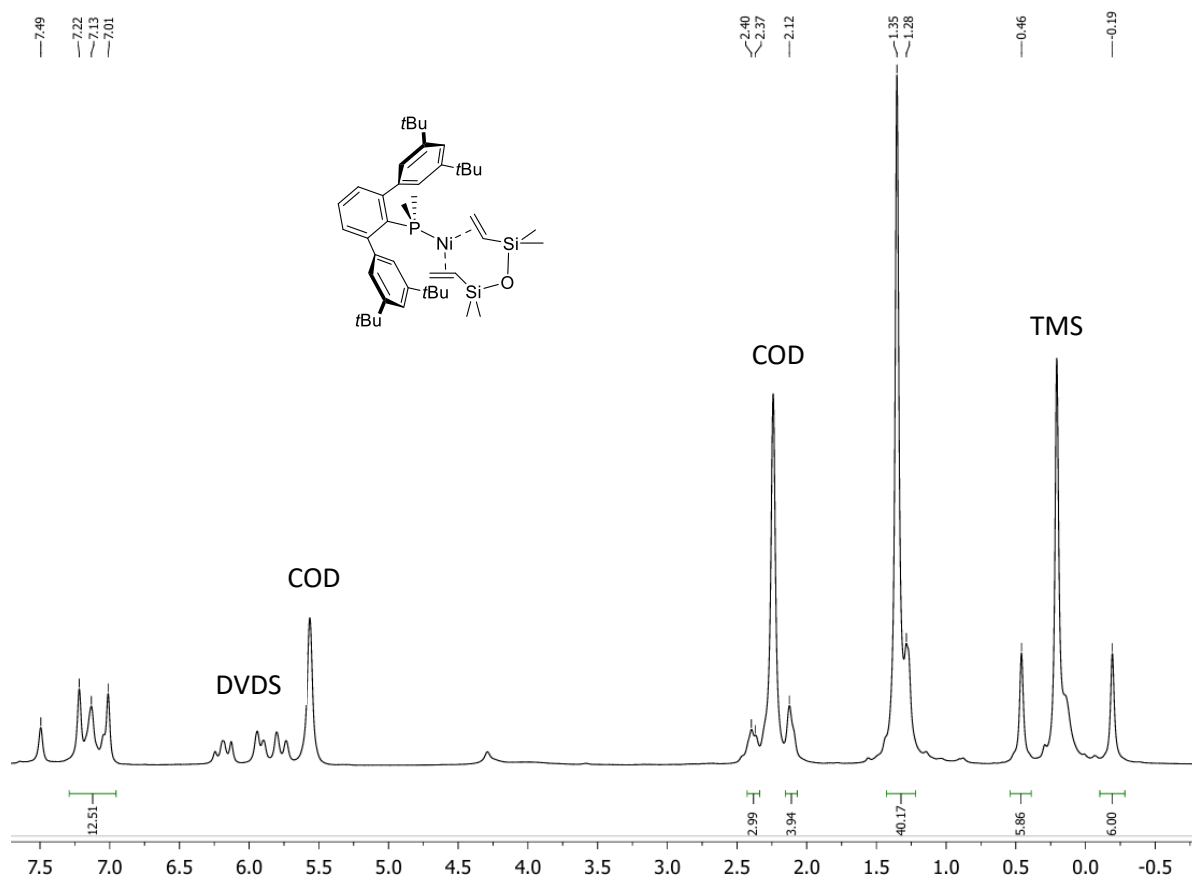




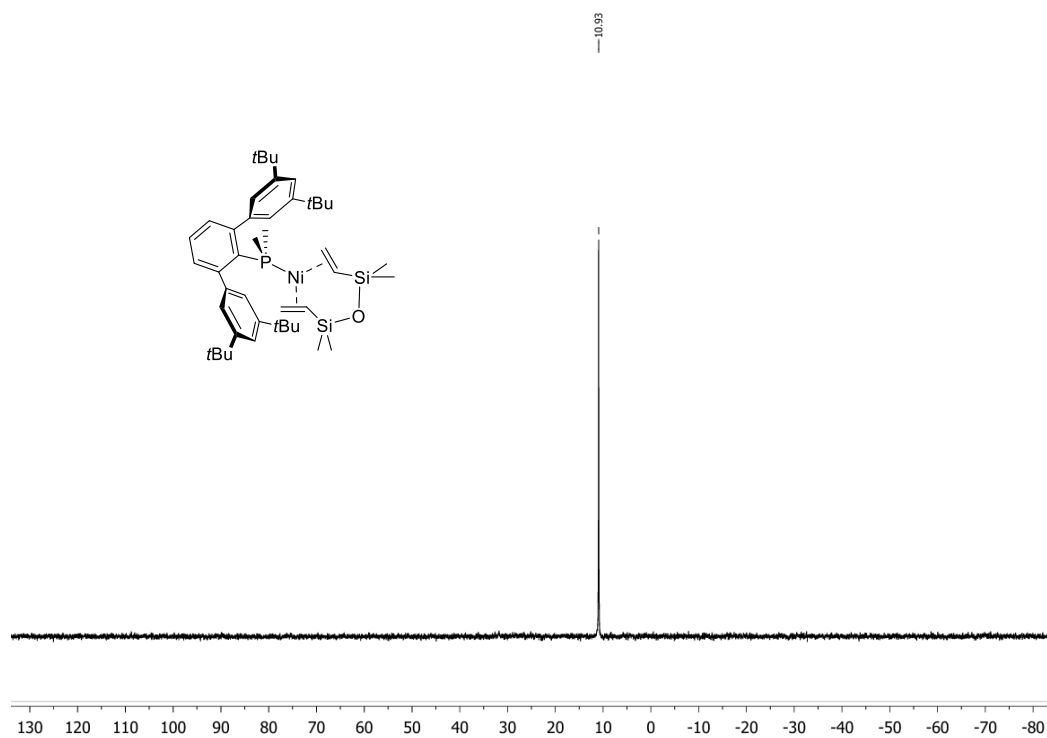
$^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{m-Xyl}2})(\text{DVDS})]$ , **7**, (202 MHz,  $\text{C}_6\text{D}_6$ , 298 K)



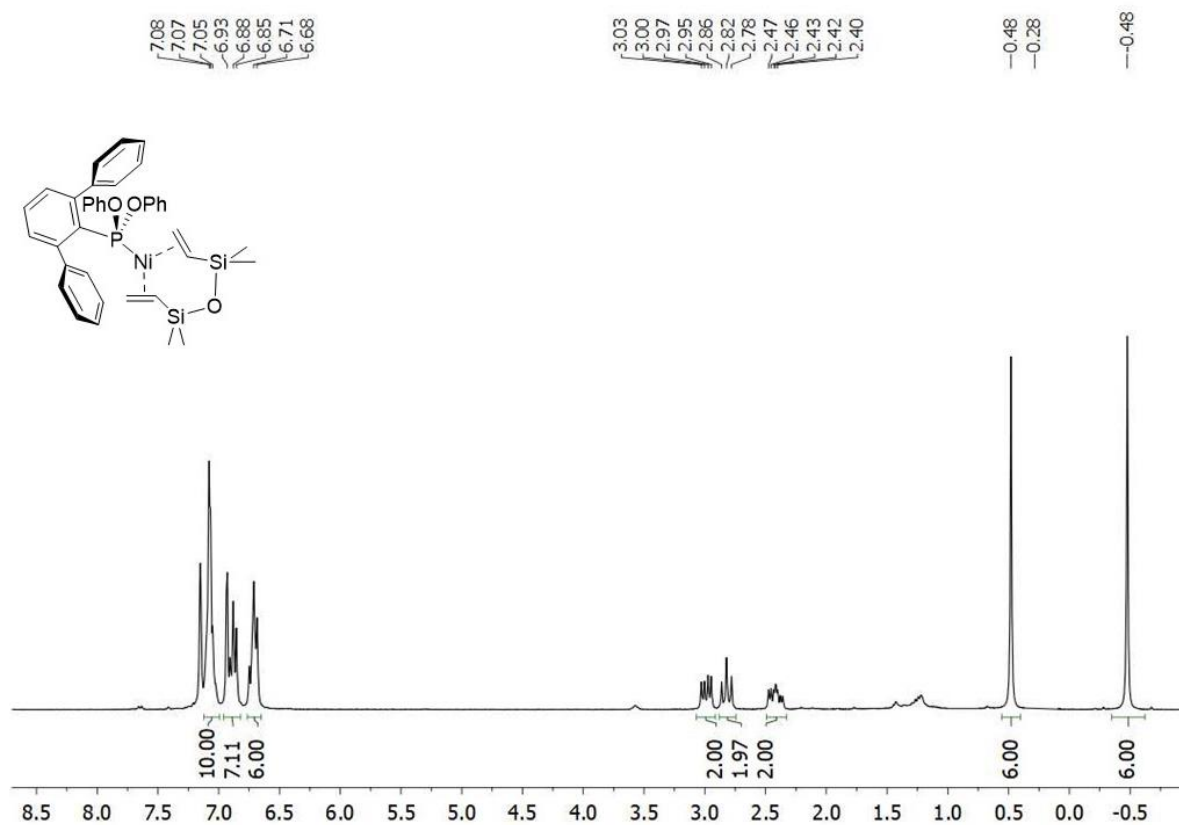
$^1\text{H}$  NMR spectrum of  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{Dtbp}2})(\text{DVDS})]$ , **8** (300 MHz,  $\text{C}_6\text{D}_6$ , 298 K)



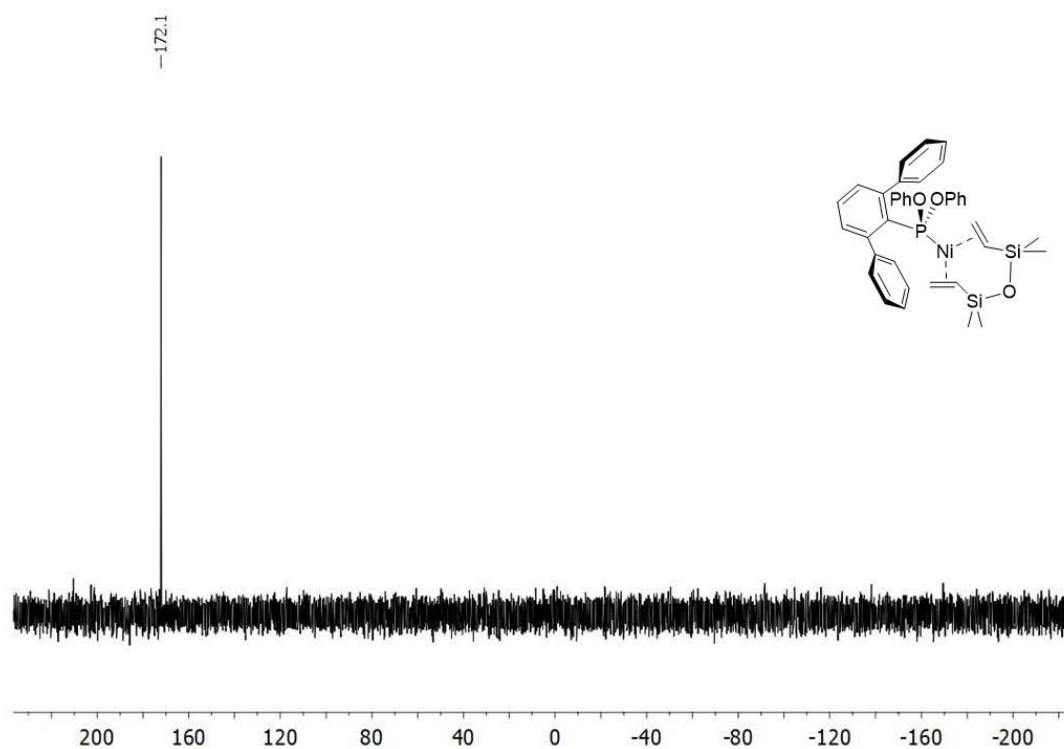
$^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ni}(\text{PMe}_2\text{Ar}^{\text{Dtbp}2})(\text{DVDS})]$ , **8** (121 MHz,  $\text{C}_6\text{D}_6$ , 298 K)



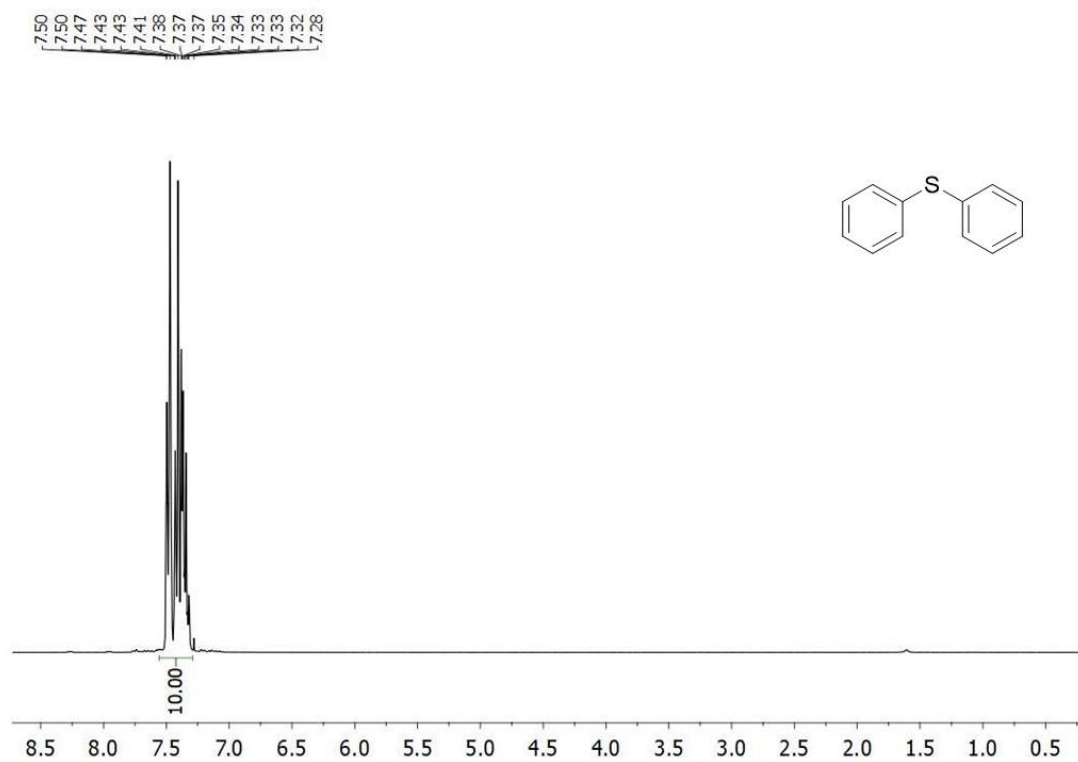
$^1\text{H}$  NMR spectrum of  $[\text{Ni}(\text{P}(\text{O}Ph)_2\text{Ar}^{\text{Ph}_2})(\text{DVDS})]$ , **9**, (500 MHz,  $\text{C}_6\text{D}_6$ , 298 K)



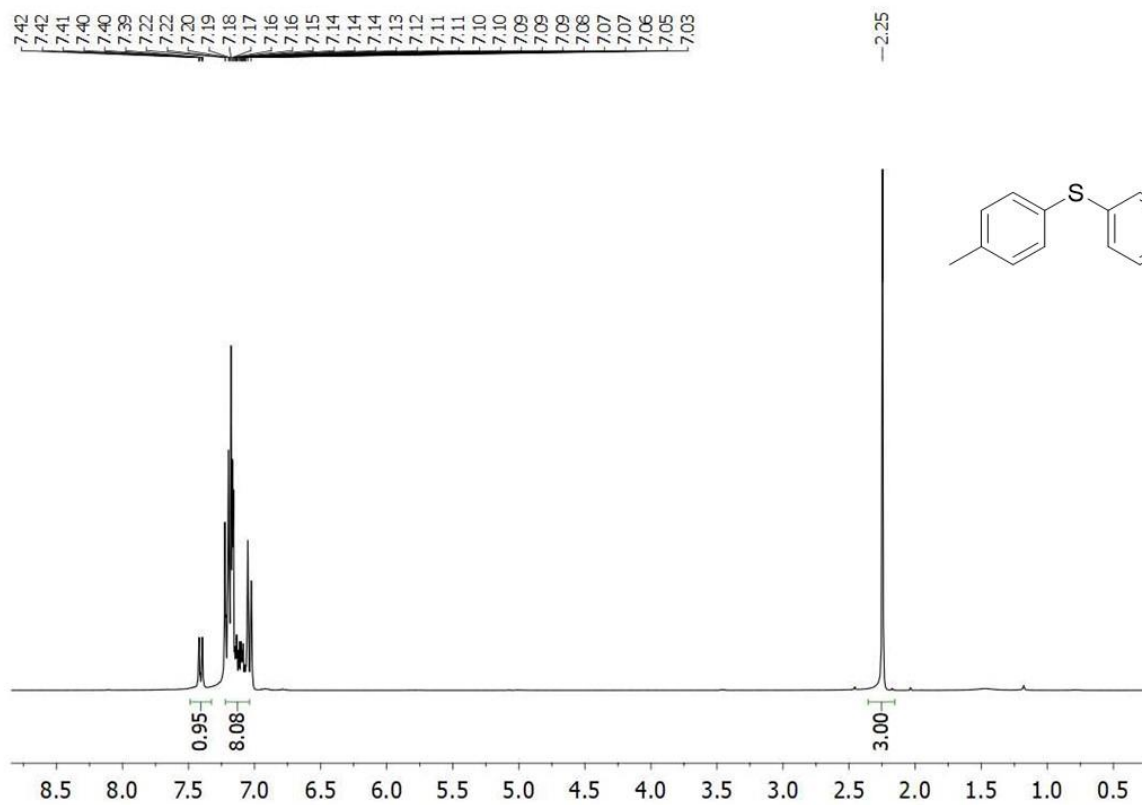
$^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ni}(\text{P}(\text{O}Ph)_2\text{Ar}^{\text{Ph}_2})(\text{DVDS})]$ , **9**, (270 MHz,  $\text{C}_6\text{D}_6$ , 298 K)



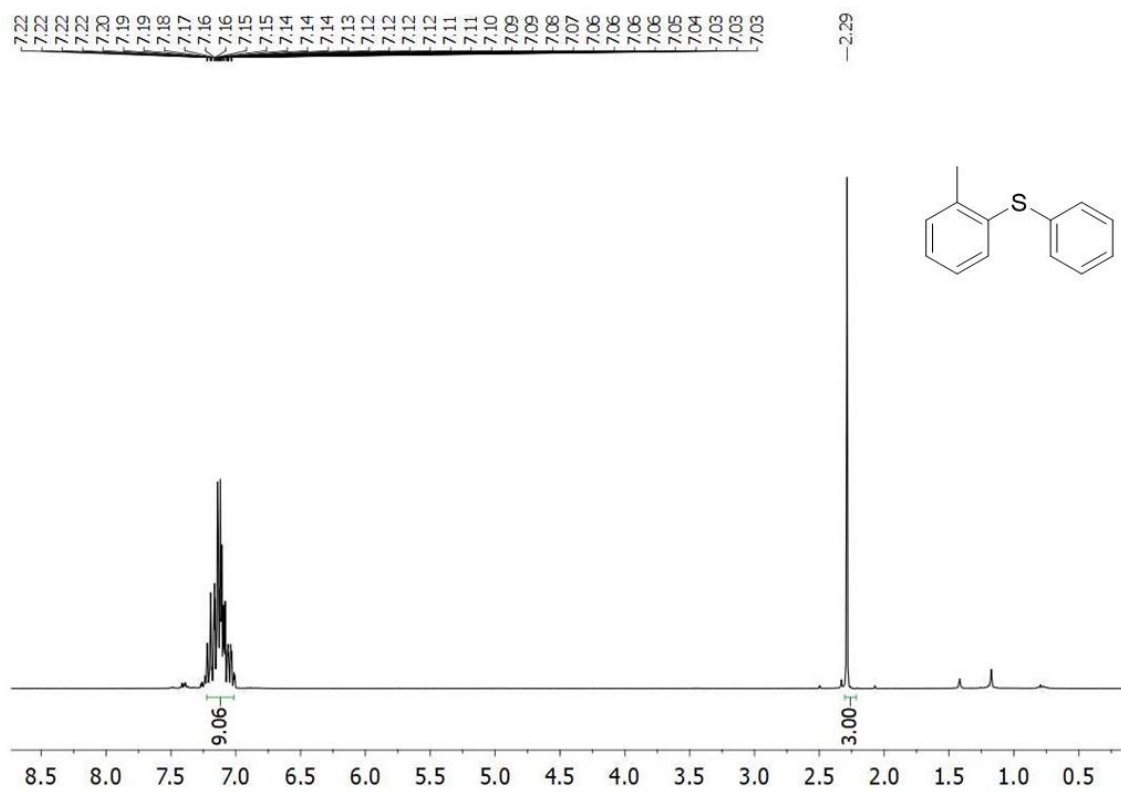
$^1\text{H}$  NMR spectrum of diphenylsulfane, **10a**, (300 MHz,  $\text{CDCl}_3$ , 298 K)



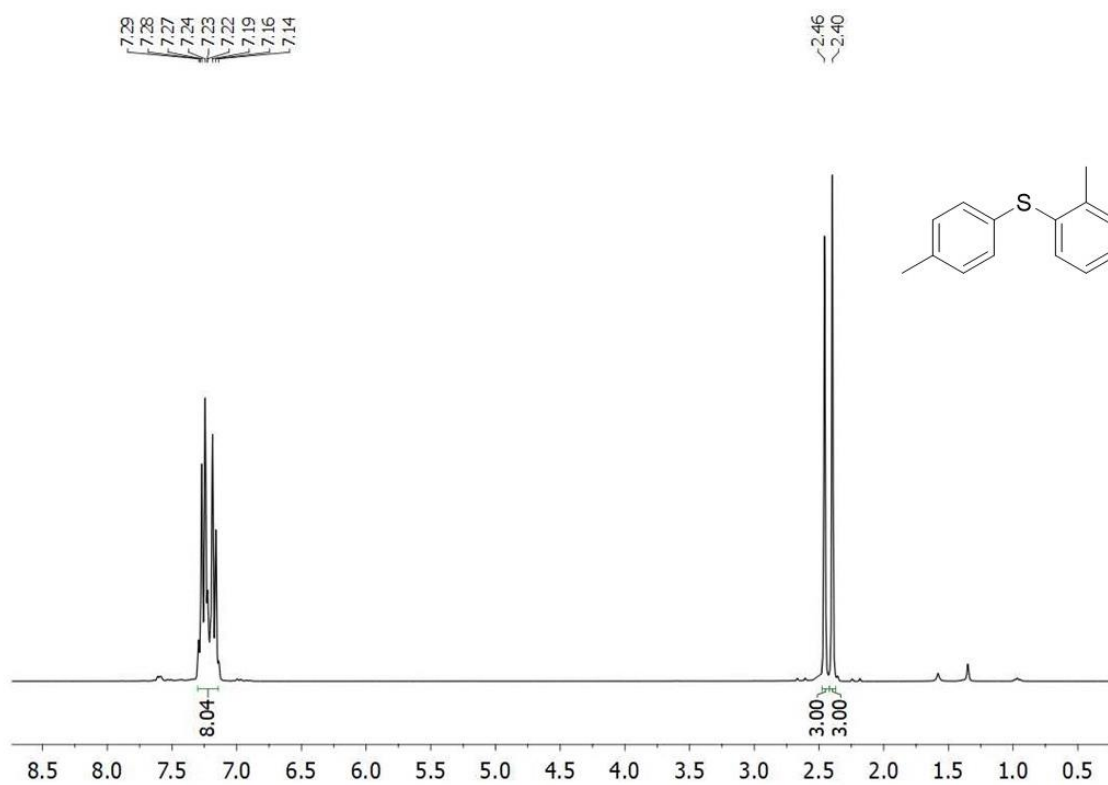
$^1\text{H}$  NMR spectrum of phenyl(4-methylphenyl)sulfane, **10b**, (300 MHz,  $\text{CDCl}_3$ , 298 K)



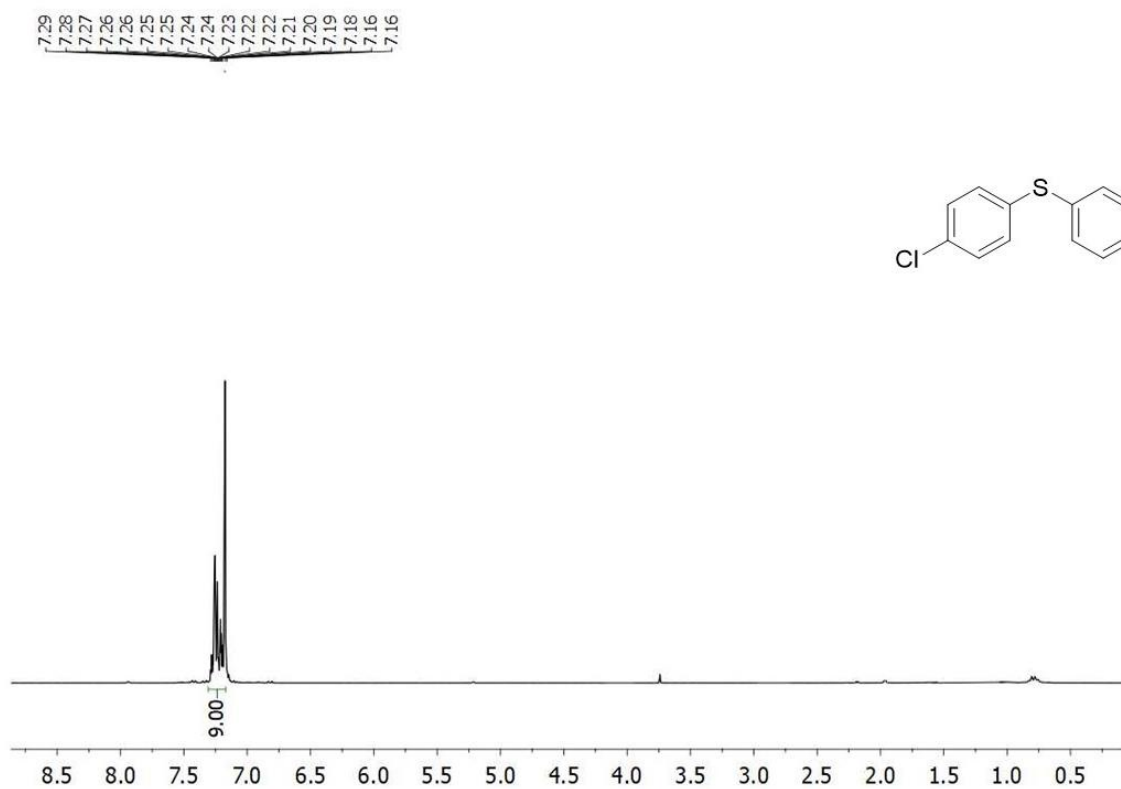
$^1\text{H}$  NMR spectrum of phenyl(2-methylphenyl)sulfane, **10c**, (300 MHz,  $\text{CDCl}_3$ , 298 K)



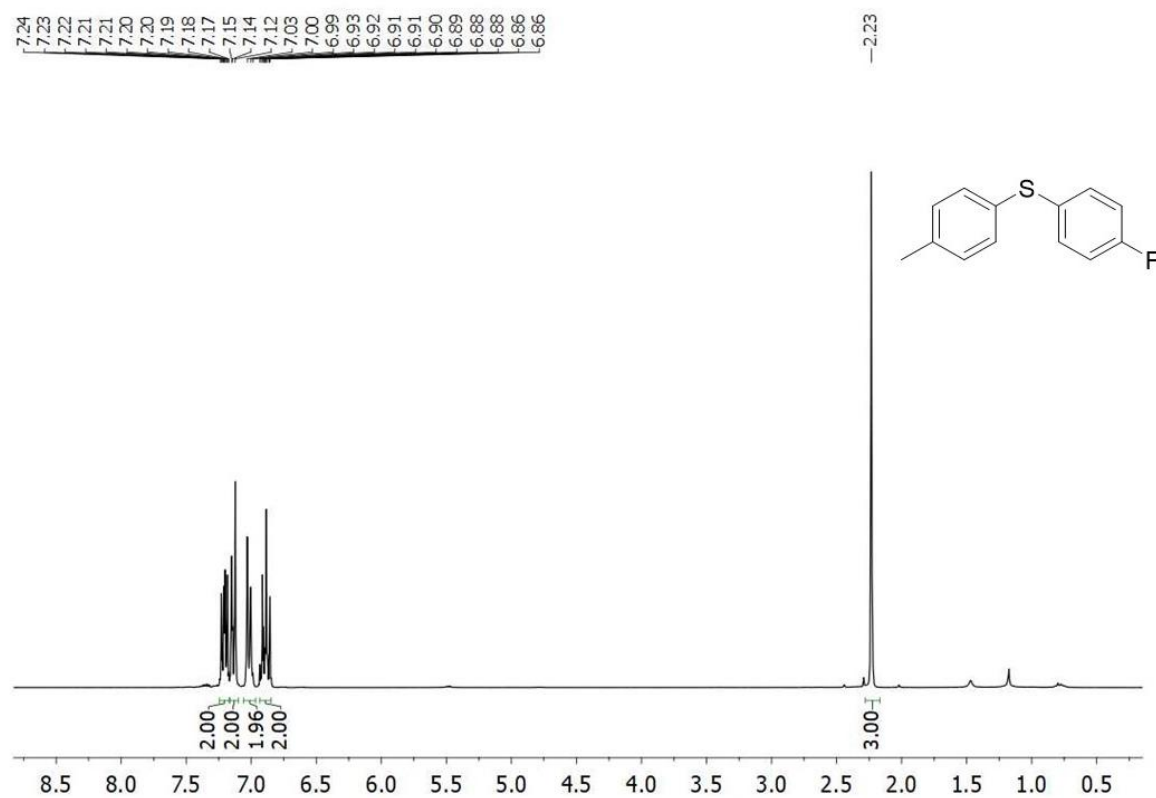
$^1\text{H}$  NMR spectrum of (2-Methylphenyl)(4-methylphenyl)sulfane, **10d**, (300 MHz,  $\text{CDCl}_3$ , 298 K)



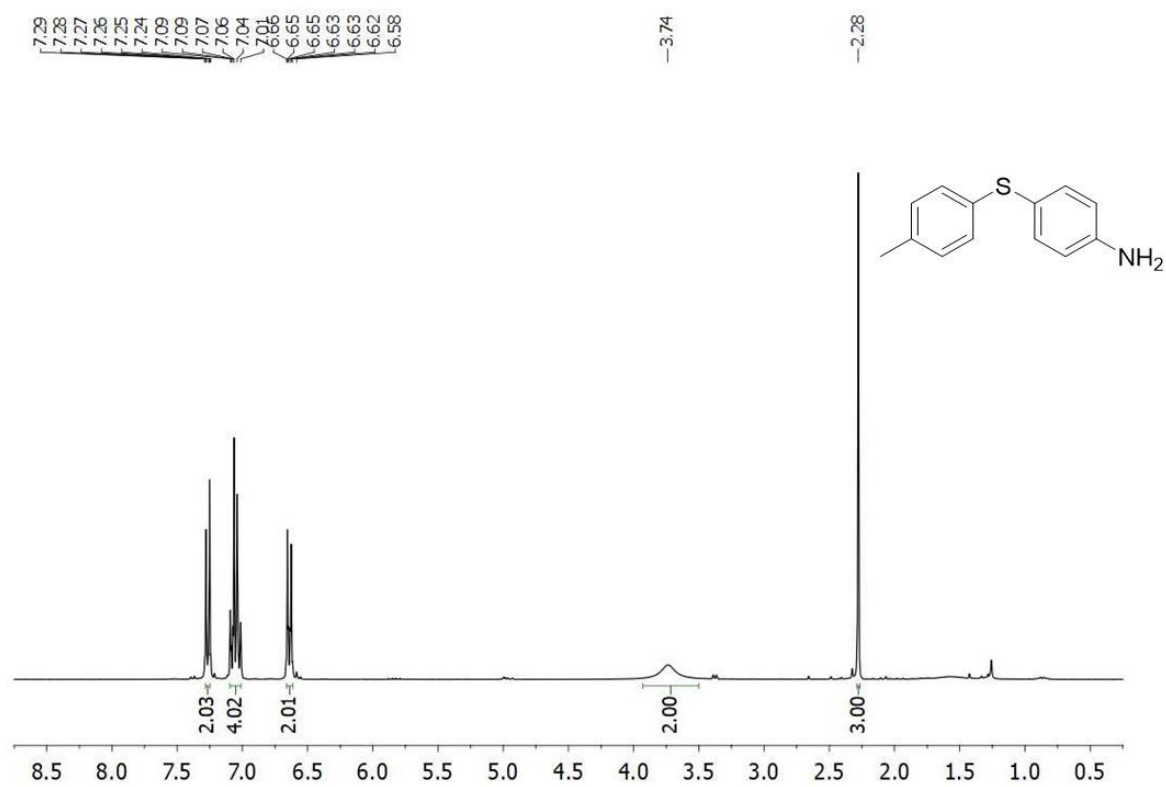
$^1\text{H}$  NMR spectrum of (4-Chlorophenyl)(phenyl)sulfane, **10e**, (300 MHz,  $\text{CDCl}_3$ , 298 K)



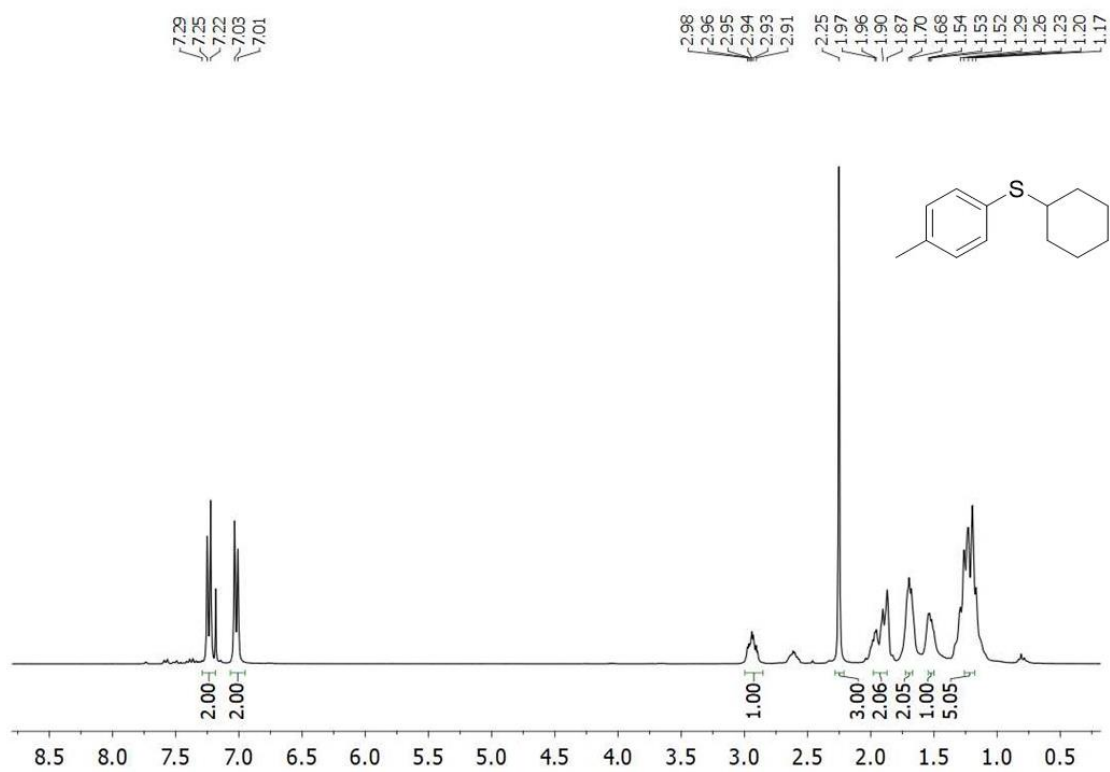
$^1\text{H}$  NMR spectrum of (4-fluorophenyl)(p-tolyl)sulfane, **10f**, (300 MHz,  $\text{CDCl}_3$ , 298 K)



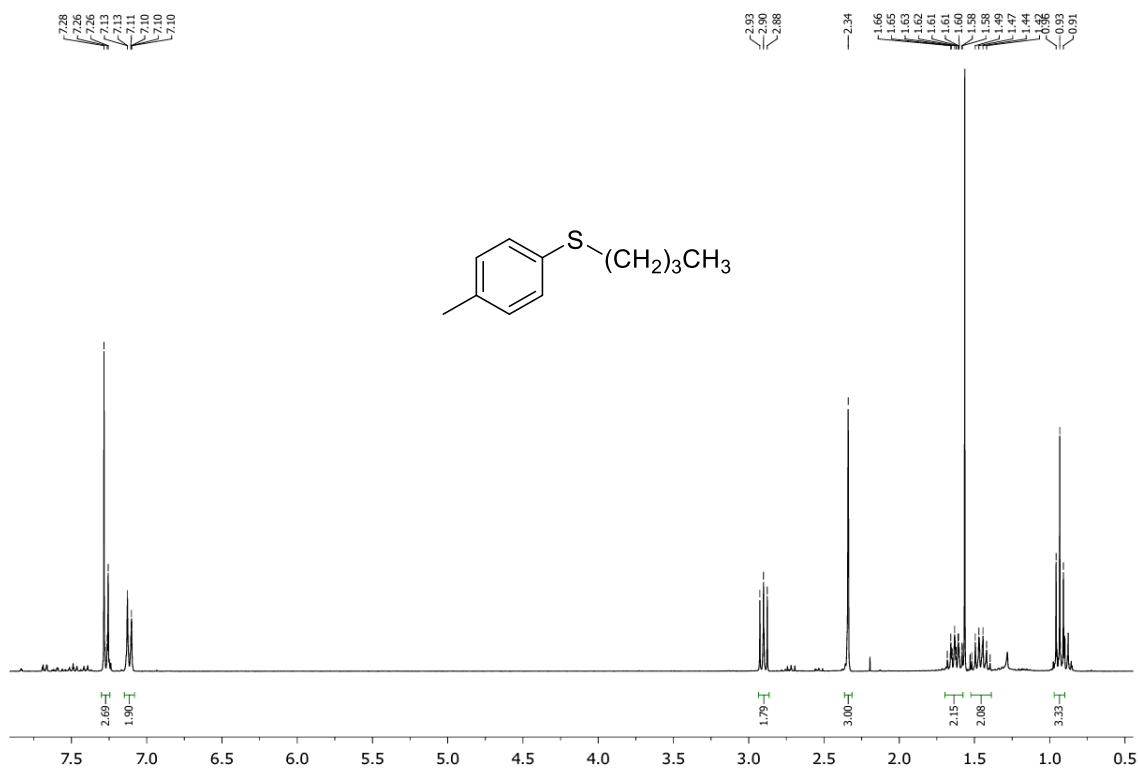
$^1\text{H}$  NMR spectrum of 4-(4-methylphenylthio)aniline, **10g**, (300 MHz,  $\text{CDCl}_3$ , 298 K)



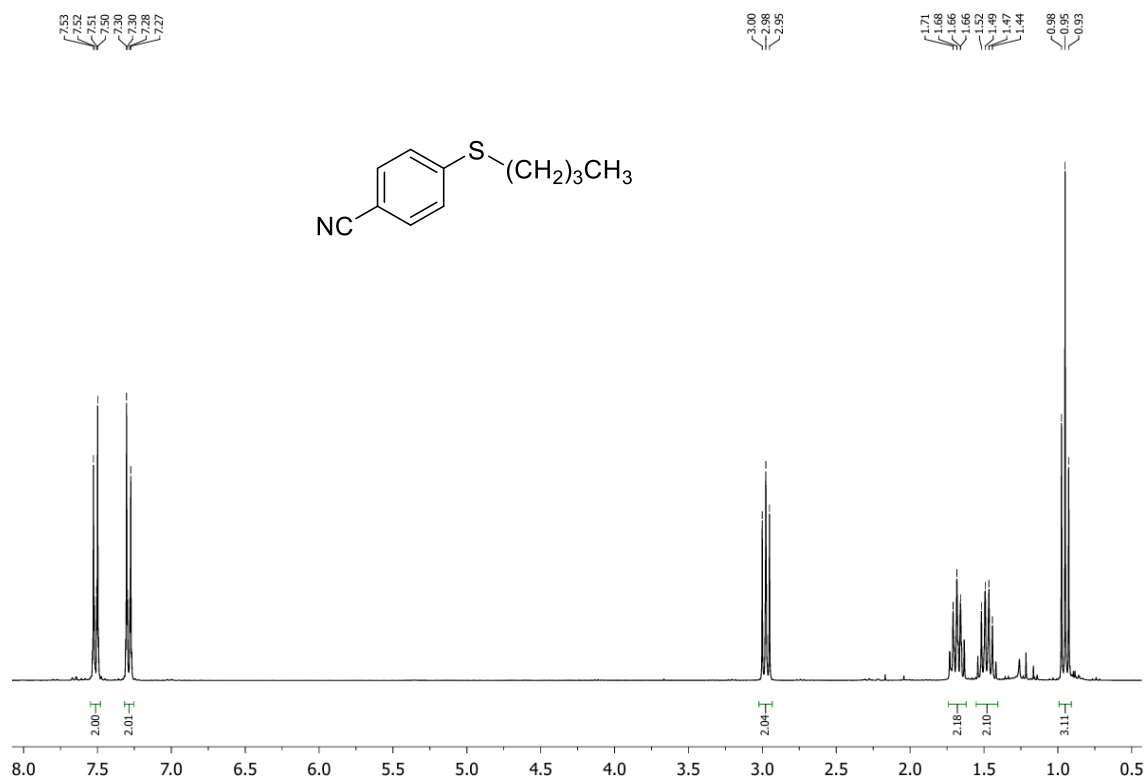
$^1\text{H}$  NMR spectrum of cyclohexyl(4-methylphenyl)sulfane, **10h**, (300 MHz,  $\text{CDCl}_3$ , 298 K)



$^1\text{H}$  NMR spectrum of butyl(*p*-tolyl)sulfane, **11a**, (300 MHz,  $\text{CDCl}_3$ , 298 K)

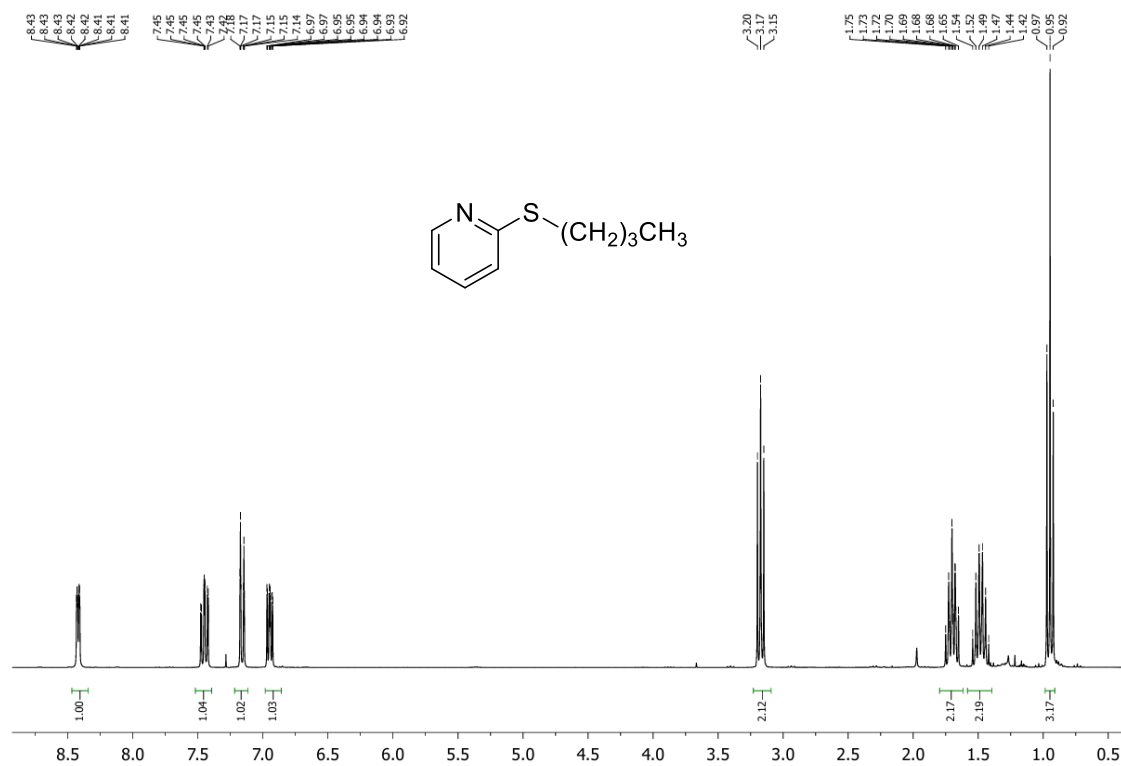


$^1\text{H}$  NMR spectrum of 4-(butylthio)benzonitrile, **11b**, (300 MHz,  $\text{CDCl}_3$ , 298 K)

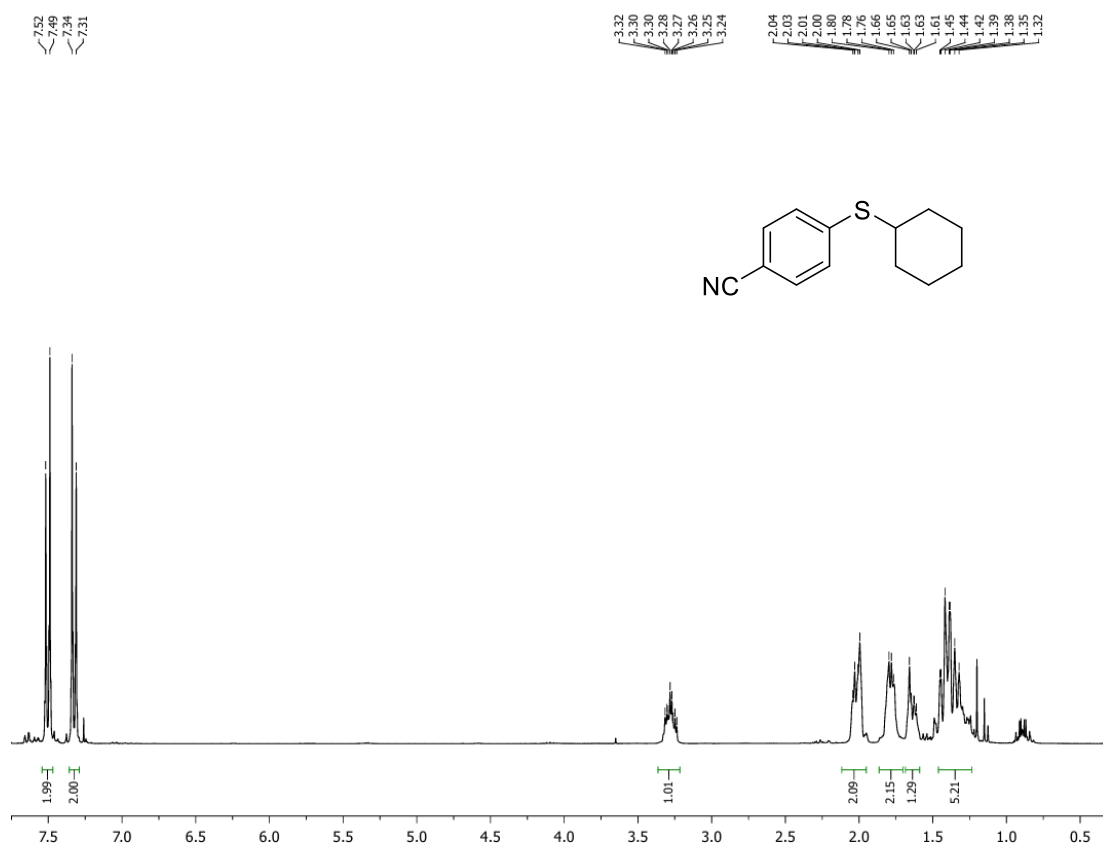




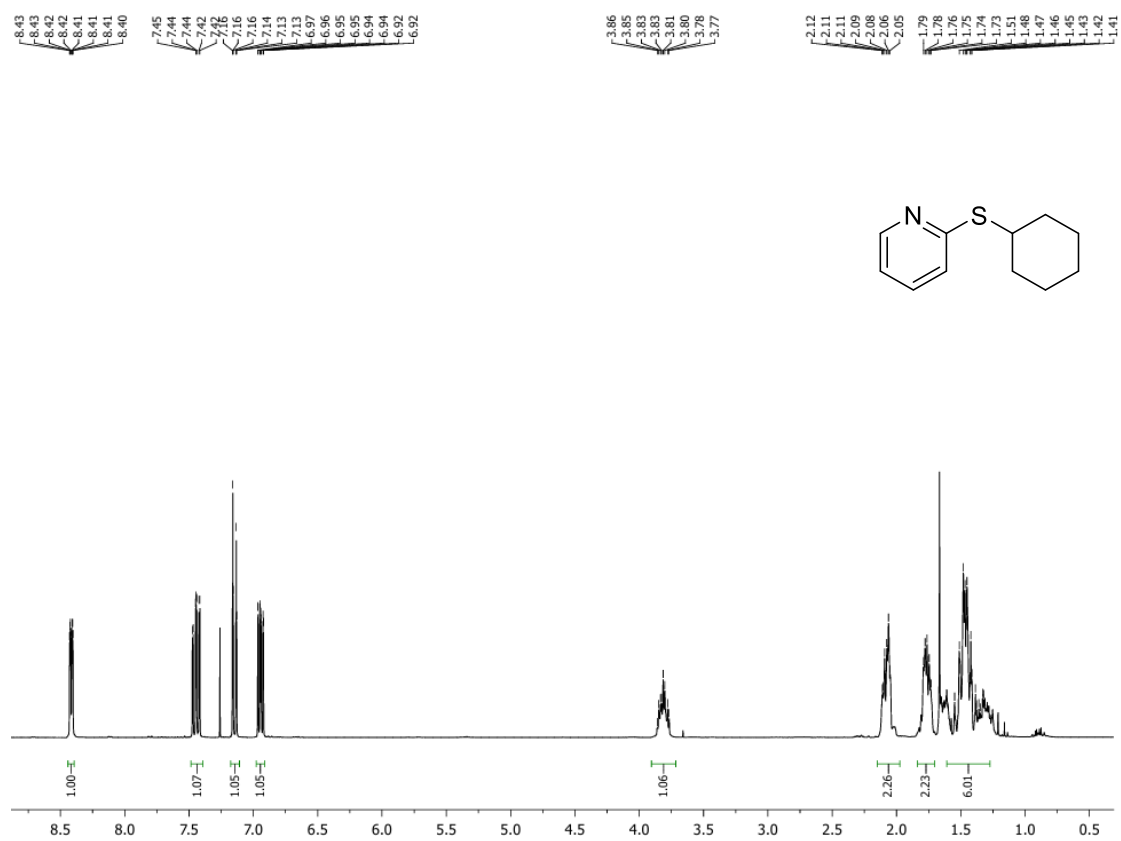
<sup>1</sup>H NMR spectrum of 2-(butylthio)pyridine, **11c**, (300 MHz, CDCl<sub>3</sub>, 298 K)



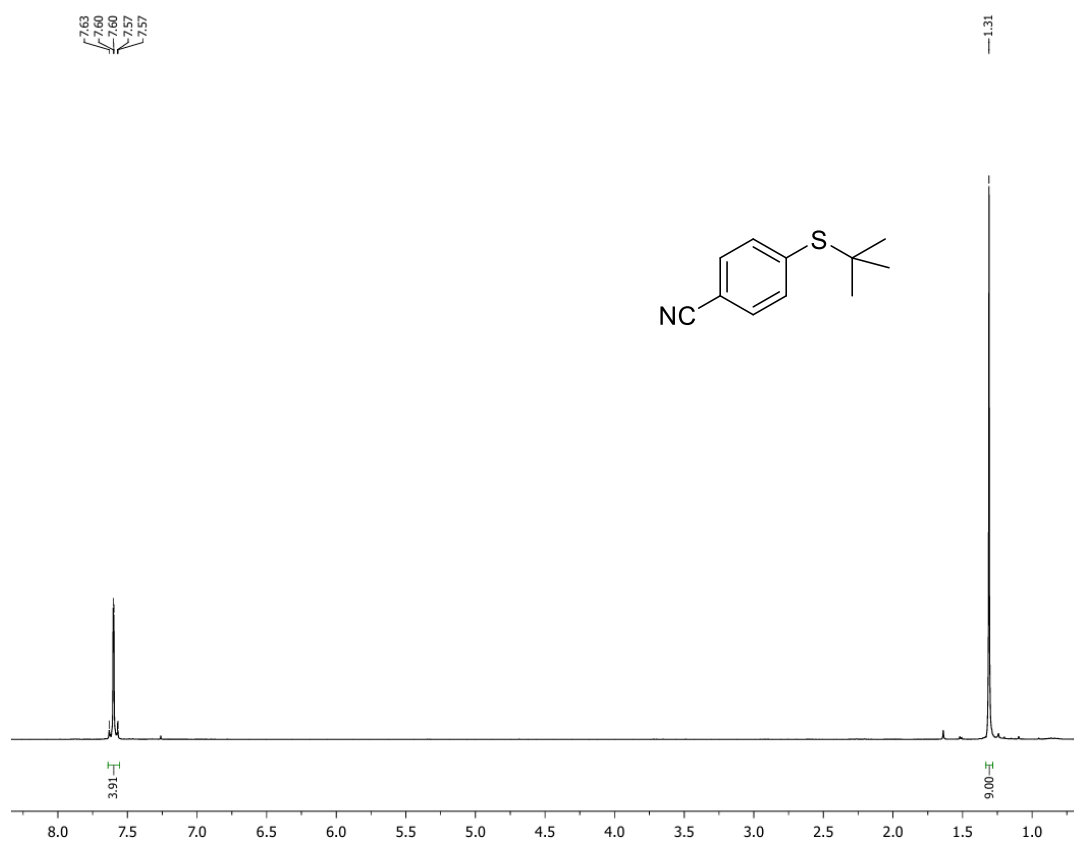
<sup>1</sup>H NMR spectrum of 4-(cyclohexylthio)benzonitrile, **11e**, (300 MHz, CDCl<sub>3</sub>, 298 K)



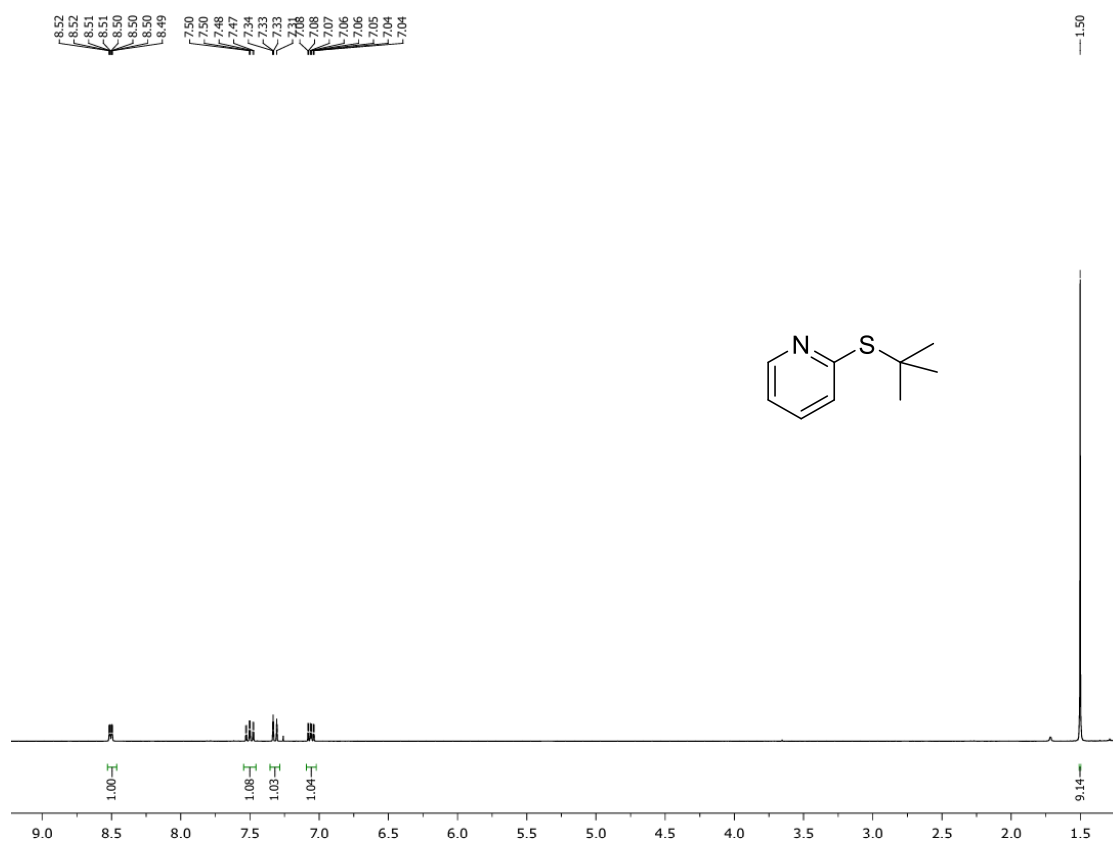
$^1\text{H}$  NMR spectrum of 2-(cyclohexylthio)pyridine, **11f**, (300 MHz,  $\text{CDCl}_3$ , 298 K)



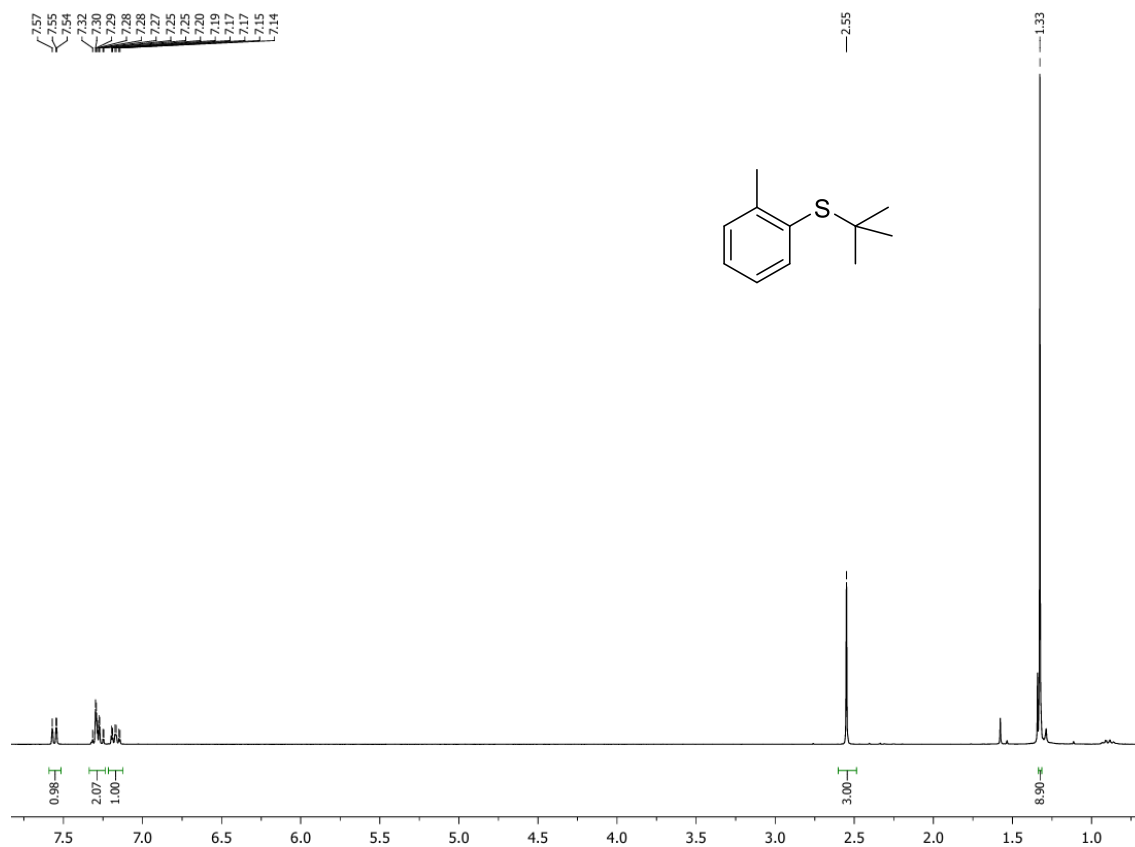
$^1\text{H}$  NMR spectrum of 4-(tert-butylthio)benzotrile, **11g**, (300 MHz,  $\text{CDCl}_3$ , 298 K)



$^1\text{H}$  NMR spectrum of 2-(*tert*-butylthio)pyridine, **11h**, (300 MHz,  $\text{CDCl}_3$ , 298 K)



$^1\text{H}$  NMR spectrum of *tert*-butyl(*o*-tolyl)sulfane, **11i**, (300 MHz,  $\text{CDCl}_3$ , 298 K)



## 7. X-ray structural data of Ni(0) complexes.

Single crystals for X-ray diffraction analysis were obtained by slow diffusion of petroleum ether into a solution of complex **4** in benzene at -20 °C, and by recrystallization from solutions of **5** and **6** in petroleum ether : tetrahydrofuran (4:1) at -20 °C. Crystals of suitable size were selected and coated with FOMBLIN oil, mounted on a loop and fixed in a cold nitrogen stream (T = 100 K or 193 K) to the goniometer head. Data collection have been performed on two diffractometers: on a D8 Quest APEX-III single crystal diffractometer with a Photon III detector and a  $\mu$ S 3.0 microfocus X-ray source (used with **4**) and a Bruker AXSX8Kappa diffractometer equipped with an Apex-II CCD area detector using monochromatic radiation  $\lambda(\text{Ag K}\alpha 1) = 0.56086 \text{ \AA}$ . (used with **5** and **6**).

Data collections were processed with APEX-W2D-ND (Bruker, 2004), cell refinement and data reduction with SAINT-Plus (Bruker, 2004) and the absorption was corrected by multi-scan method applied by SADABS. The space-group assignment was based upon systematic absences, E statistics, and successful refinement of the structure. Using Olex2<sup>24</sup>, all structures were solved with SHELXT and were refined against  $F^2$  on all data by full-matrix least squares with SHELXL.<sup>25</sup> Thermal parameters for all non-hydrogen atoms were refined anisotropically while hydrogen atoms were included in calculated positions and allowed to ride on the attached atoms with the isotropic temperature factors (Uiso values) fixed at 1.2 times (1.5 times for methyl groups) those Ueq values of the corresponding attached atoms.

A summary of the cell parameters, data collection, structures solution, and the refinement of crystal structures are provided in Table S7. Atomic coordinates, anisotropic displacement parameters and bond lengths and angles can be found in the cif files which have been deposited the Cambridge Crystallographic Data Center and FIZ Karlsruhe Access Structures service with no. 2405003 (**4**), 2405002 (**5**), and 2405004 (**6**). These data can be obtained free for charge from The Cambridge Crystallographic Data Centre via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

---

<sup>24</sup> (a) L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Acta Cryst.* 2015, **A71**, 59-75. (b) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341. (c) G.M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

<sup>25</sup> G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.

Table S7. Crystal data and structure refinement for **4**, **5** and **6**.

Identification code	<b>4</b>	<b>5</b>	<b>6</b>
Empirical formula	C <sub>60</sub> H <sub>46</sub> NiO <sub>4</sub> P <sub>2</sub>	C <sub>28</sub> H <sub>37</sub> NiOPSi <sub>2</sub>	C <sub>36</sub> H <sub>55</sub> NiO <sub>2</sub> PSi <sub>2</sub>
Formula weight	951.62	535.43	665.66
Temperature	193(2) K	100 (2) K	100 (2) K
Wavelength	0.71073 Å	0.56086 Å	0.56086 Å
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2 <sub>1</sub> /n	C2/c	P2 <sub>1</sub> /n
Unit cell dimensions	a = 11.9594(3) Å b = 29.1507(7) Å c = 13.3094(3) Å α = 90° β = 93.9410(10)° γ = 90°	a = 29.534(2) Å b = 9.7686(7) Å c = 21.7530(18) Å α = 90° β = 115.859(5)° γ = 90°	a = 12.527(3) Å b = 23.642(6) Å c = 14.134(3) Å α = 90° β = 112.336(8)° γ = 90°
Volume	4629.02(19) Å <sup>3</sup>	5647.5(8) Å <sup>3</sup>	3871.7(16) Å <sup>3</sup>
Z	4	8	4
Density (calculated)	1.365 Mg/m <sup>3</sup>	1.259 Mg/m <sup>3</sup>	1.142 Mg/m <sup>3</sup>
Absorption coefficient	0.539 mm <sup>-1</sup>	0.443 mm <sup>-1</sup>	0.332 mm <sup>-1</sup>
F(000)	1984	2272	1432
Crystal size	0.23 x 0.19 x 0.12	0.24 x 0.21 x 0.10	0.21 x 0.12 x 0.08
Theta range for data collection	4.15 to 55.004°	3.116 to 44.202°	2.81 to 40.998°
Index ranges	-15 ≤ h ≤ 15, -37 ≤ k ≤ 37, -17 ≤ l ≤ 17	-31 ≤ h ≤ 38, -11 ≤ k ≤ 13, -29 ≤ l ≤ 13	-15 ≤ h ≤ 15, -29 ≤ k ≤ 29, -17 ≤ l ≤ 17
Reflections collected	75363	13264	208312
Independent reflections	10633 [R(int) = 0.0471]	6349 [R(int) = 0.0425]	7899 [R(int) = 0.1256]
Completeness to theta = 22.00°	99.9 %	89.1%	99.8%
Absorption correction	Multi scan	Multi scan	Multi scan
Max. and min. transmission	0.6968 and 0.7456	0.5485 and 0.7447	0.6682 and 0.7285
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	10633 / 0 / 604	6349 / 0 / 304	7899 / 0 / 377
Goodness-of-fit on F <sup>2</sup>	1.061	1.011	1.054
Final R indices [I>2σ(I)]	R1= 0.0397 wR2= 0.0890	R1= 0.0456 wR2= 0.1034	R1= 0.0347 wR2= 0.0873
R indices (all data)	R1= 0.0494 wR2= 0.0936	R1= 0.0953 wR2= 0.1276	R1= 0.0428 wR2= 0.0914
Largest diff. peak and hole	0.86 and -0.89 e.Å <sup>-3</sup>	0.39 and -0.40 e.Å <sup>-3</sup>	0.30 and -0.34 e.Å <sup>-3</sup>