Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Information for

Synthesis, crystal structure and reactivity of η²–thiophyne Ni complexes

Misaki Terada, Yuji Nishii,* Masahiro Miura*

Contents

1. Experimental procedures

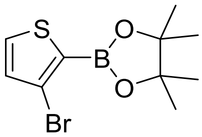
General

All manipulations were performed under N_2 either using standard Schlenk techniques or in glovebox otherwise noted. Toluene, Et_2O, and MeCN were dried and deoxygenated by Glass Counter Solvent Dispending System (Nikko Hansen & Co., Ltd.). DCM was distilled over CaH_2. Hexane, benzene, and THF (stabilizer free) were purchased from Wako Pure Chemical Industries as Super Dehydrated solvents and stored with dried MS. Silica gel column chromatography was performed using Wakosil® C-200 (64–210 μm). All other reagents were purchased from commercial resources and used without further purification.

Nuclear magnetic resonance spectra were measured with Bruker AVANCE III 400 spectrometer operating at 400 MHz (^{1}H NMR), at 100 MHz (^{13}C NMR), and at 162 MHz (^{31}F NMR) in 5 mm NMR tubes. ^{1}H NMR chemical shifts were reported in ppm relative to the resonance in TMS (δ 0.00 $CDCl_3$) or the residual solvent signals; δ 7.26 for $CDCl_3$, δ 7.16 for C_6D_6, δ 5.32 for CD_2Cl_2, and δ 3.58 for THF-d_8. ^{13}C NMR chemical shifts were reported in ppm relative to the residual solvent signals; δ 77.2 for $CDCl_3$, δ 128.1 for C_6D_6, δ 53.8 for CD_2Cl_2, and δ 67.2 for THF-d_8. Melting points were measured with Mettler Toledo MP90. High resolution mass spectra (HRMS) were recorded on Bruker micrOTOF II-H3 by APCI-TOF. GC analyses were carried out with Shimadzu GC-8A equipped with Shimadzu silicon OV-17 column (2.6 mm × 1.5 m). GC-MS spectra were recorded on Shimadzu GC-2010 Plus and GCMS-QP2010 SE with Shimadzu CBP-1 column (0.5 mm × 25 m). The DFT calculations were performed by using the GAUSSIAN 09 package. [1]

Note: Since no reliable information of integration values and coupling constants were obtained for cyclohexyl groups on dcpe ligand, NMR signals of Ni complexes are reported as appeared in the spectra.

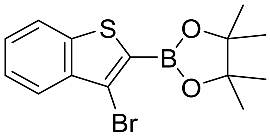
Preparation of (3-bromothiophen-2-yl)boronic acid pinacol ester (**1a**)



(3-Bromothiophen-2-yl)boronic acid was prepared from 3-bromothiophene (815 mg, 5.0 mmol) according to the literature procedure.[2] The obtained boronic acid was dissolved in toluene (20 mL) and refluxed for 3 h with pinacol (590 mg, 5.0 mmol). After removal of the solvent in vacuo, the residue was filtered through silica gel eluting with hexane/EtOAc = 20/1. The filtrate was evaporated to give the pinacol ester as white solid (1.09 g, 76% yield).

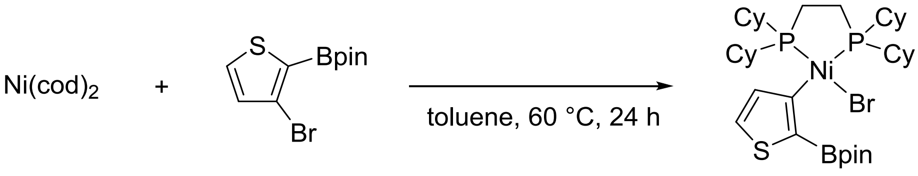
^{1}H NMR (400 MHz, $CDCl_3$, 21 °C) δ 1.36 (*methyl*, s, 12H), 7.11 (SCHC*H*, d, J = 4.9 Hz, 1H), 7.51 (SC*H*, d, J = 4.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 21 °C) δ 24.9, 84.5, 119.8, 132.6, 132.7; ^{11}B NMR (128 MHz, $CDCl_3$, 21 °C) δ 28.7.

Preparation of (3-bromobenzo[*b*]thiophen-2-yl)boronic acid pinacol ester (**1b**)



The title compound was prepared similarly to **1a** from 3-bromobenzo[*b*]thiophene. The obtained brownish crystalline solid was washed with cold hexane to give **1b** as white solid (544 mg, 80% yield). m.p. 71.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C) δ 1.40 (*methyl*, s, 12H), 7.39-7.48 (m, 2H), 7.82-7.87 (m, 1H), 7.88-7.94 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 21 °C) δ 25.0, 84.8, 117.4, 122.6, 124.3, 125.1, 126.4, 139.5, 141.8.; ^{11}B NMR (128 MHz, $CDCl_3$, 21 °C) δ 28.9; HRMS (APCI) *m/z* calcd for $C_{10}H_{14}BBrO_2S$ ($[M+H]^+$) 339.0220, found 339.0212.

Preparation of complex **2a**

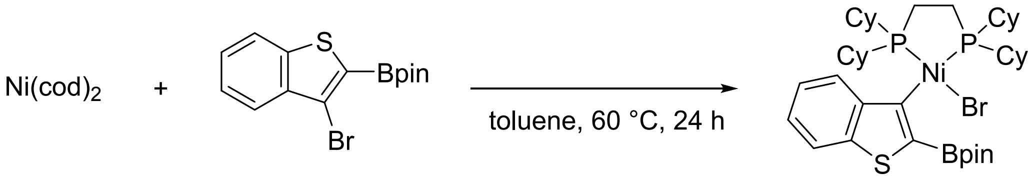


1a **2a**

A mixture of $Ni(cod)_2$ (83 mg, 0.3 mmol) and 1,2-bis(dicyclohexylphosphanyl)ethane (127 mg, 0.3 mmol) in toluene (3.0 mL) was stirred for 5 min. at room temperature. A toluene solution (1.0 mL) containing a boronic ester **1a** (87 mg, 0.3 mmol) was then added, and the mixture was heated for 24 h at 60 °C to afford a brown suspension. The precipitate was collected by filtration through a pad of Celite, and washed with toluene and THF. The solid material was dissolved (eluted out from the Celite) with DCM and the fraction was evaporated to dryness to give complex **2a** as yellow powder (60% yield). Single crystals suitable for X-ray diffraction analysis were obtained by hexane vapor diffusion into DCM solution.

m.p. 202 °C (decomp.); ^{1}H NMR (400 MHz, CD_2Cl_2, 21 °C) δ 0.28-0.44 (m, 1H), 0.94-2.23 (m, 60.3H), 2.34 (d, J = 12.9 Hz, 1H), 2.49 (br, 1H), 7.08-7.14 (m, 1H), 7.46 (dd, J = 0.5, 4.6 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2, 21°C) δ 19.9, 20.0, 20.1, 20.2, 24.0, 24.2, 24.3, 24.4, 24.9, 25.8, 25.8, 26.1, 26.4, 26.7, 26.7, 27.2, 27.3, 27.3, 27.5, 27.5, 27.6, 27.6, 27.7, 27.8, 27.9, 28.0, 28.0, 28.1, 28.6, 28.6, 29.2, 29.3, 30.1, 30.1, 30.8, 32.8, 32.8, 33.0, 33.3, 34.1, 34.4, 35.8, 36.0, 36.2, 36.5, 83.5, 127.9 (d, $J_{\text{C-P}}$ = 7.3 Hz), 135.4 (dd. $J_{\text{C-P}}$ = 2.2, 5.1 Hz), 166.4 (Ni*C*, dd, $J_{\text{C-P}}$ = 37.4, 85.5 Hz); ^{31}P NMR (162 MHz, CD_2Cl_2, 21 °C) δ 62.4 (d, *J* = 27.2 Hz), 68.5 (d, *J* = 27.2 Hz); Anal. calcd for C36H62BBrNiO2P2S: C 56.13, H 8.11; found: C 56.19, H 8.22%.

Preparation of complex **2b**



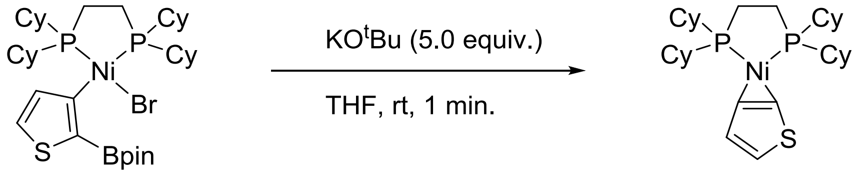
1b **2b**

The title complex was prepared similarly to **2a** from boronic ester **1b**. The precipitate was collected by filtration through a pad of Celite, eluted with toluene, THF, and DCM. The DCM fraction was evaporated to dryness to give complex **2b** as yellow powder (32% yield). Single crystals suitable for X-ray diffraction analysis were obtained from CH_2Cl_2 solution layered with MeCN.

m.p. 214 °C; ^{1}H NMR (400 MHz, CD_2Cl_2, 21 °C) δ 0.67-2.05 (m, 65.2H), 2.11-2.51 (m, 4H), 2.68 (br, 1H), 7.21–7.29 (m, 2H), 7.79 (d, *J* = 7.5 Hz, 1H), 8.55 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2, 21 °C) δ 14.2, 14.3, 19.6, 19.7, 19.8, 19.9, 22.7, 23.1, 23.3, 23.5, 23.5, 23.7, 24.3, 24.8, 25.0, 26.2, 26.4, 26.4, 26.7, 27.0, 27.1, 27.3, 27.4, 27.4, 27.5, 27.5, 27.6, 27.7, 27.9, 28.0, 28.2, 28.3, 28.9, 29.0, 29.0, 29.3, 30.1, 30.4, 30.5, 30.5, 31.4, 34.5, 34.7, 35.0, 35.3, 35.4, 35.7, 35.8, 35.9, 83.9, 122.3, 122.5, 124.3, 129.7, 143.2 (d, $J_{\text{C-P}}$ = 6.6 Hz), 149.4 (d, $J_{\text{C-P}}$ = 4.7 Hz), 168.1 (Ni*C*, dd, $J_{\text{C-P}}$ = 33.0, 86.4 Hz); ^{31}P NMR (162 MHz, CD_2Cl_2, 21 °C) δ 60.5 (d, *J* = 28.9 Hz), 63.9 (d, *J* = 28.9 Hz); Anal. calcd for C40H64BBrNiO2P2S: C 58.56, H 7.86; found: C 58.66, H 7.94%.

Note: Although the complexes **2a** and **2b** were considerably soluble in THF, it was necessary to wash with THF for the removal of Ni(dcpe)Br_2 (δ_P 85.5 ppm in THF-d_8), which might be formed though radical reactions[3] or disproportionation. Color of the eluted fraction obviously changed from deep red to yellow during the wash with THF, then the eluent was changed to DCM.

Preparation of complex **3a**

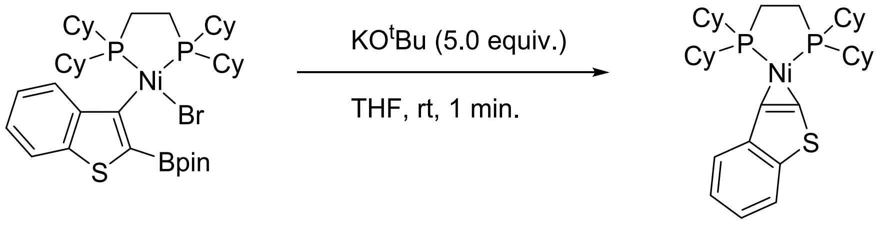


2a **3a**

A mixture of **2a** (154 mg, 0.2 mmol) and KO^{t}Bu (112 mg, 1.0 mmol) in THF (5.0 mL) was stirred at room temperature for 30 seconds under N_2. The reaction mixture was diluted with hexane and the resulting suspension was filtered through a pad of Celite. After removal of the solvent in vacuo, the obtained brown semisolid was washed with Et_2O and pentane to afford complex **3a** as pale yellow powder (86% yield). Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from Et_2O solution.

m.p. 112 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6, 21 °C) δ 0.92-1.86 (m, 59.5H), 2.10 (d, J = 11.7 Hz, 4H), 7.63 (d, J = 2.9 Hz, 1H), 7.94 (d, J = 2.9 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6, 21 °C) δ 21.4, 21.6, 21.6, 21.8, 22.5, 22.7, 22.7, 22.9, 26.4, 26.4, 27.2, 27.3, 27.3, 27.4, 27.4, 27.5, 29.4, 29.7, 29.7, 29.9, 31.5, 34.8, 35.0, 35.3, 35.3, 35.5, 35.6, 120.0 (dd, $J_{\text{C-P}}$ = 1.8, 9.7 Hz), 144,3 (d, $J_{\text{C-P}}$ = 6.2 Hz), 149.6 (Ni*C*S, dd, $J_{\text{C-P}}$ = 10.2, 78.7 Hz), 156.6 (Ni*C*CH, dd, $J_{\text{C-P}}$ = 12.4, 58.3 Hz); ^{31}P NMR (162 MHz, C_6D_6, 21 °C) δ 81.8 (d, J = 8.1 Hz), 86.6 (d, J = 8.1 Hz); Elemental analysis was unsuccessful due to considerable weight loss during combustion analysis.

Preparation of complex **3b**

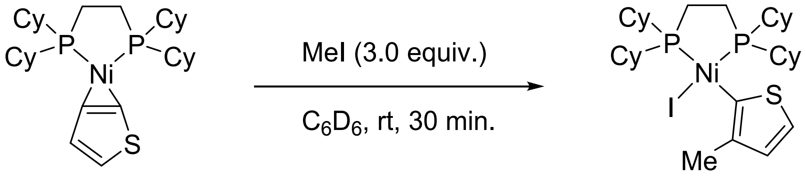


2b **3b**

The title complex was prepared similarly to **3a** from the complex **2b** (164 mg). The title complex **3b** was obtained as yellow powder (91% yield). Single crystals suitable for X-ray diffraction analysis were obtained by pentane vapor diffusion into Et_2O/THF solution.

m.p. 137 °C (decomp.); ^{1}H NMR (400 MHz, THF-d_8, 21 °C) δ 0.84-2.12 (m, 62.7H), 2.17 (d, J = 12.2 Hz, 2H), 6.94–6.98 (m, 1H), 7.07–7.11 (m, 1H), 7.62 (*d*, J = 7.9 Hz, 1H), 7.70 (*d*, J = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, THF-d_8, 21 °C) δ 21.7, 21.9, 22.0, 22.1, 22.8, 23.0, 23.1, 23.2, 26.8, 26.9, 27.7, 27.8, 27.8, 27.9, 27.9, 29.8, 29.9, 30.4, 30.4, 30.5, 30.5, 31.5, 35.3, 35.5, 36.0, 36.0, 36.2, 36.2, 121.7, 123.1, 123.7, 124.4, 135.7 (dd, $J_{C\text{-}P}$ = 8.8, 11.7 Hz), 152.6 (Ni*C*, dd, $J_{C\text{-}P}$ = 11.7, 71.8 Hz), 154.9 (Ni*C*S, dd, $J_{C\text{-}P}$ = 9.5, 87.5 Hz), 166.8 (d, $J_{C\text{-}P}$ = 4.4 Hz); ^{31}P NMR (162 MHz, THF-d_8, 21 °C) δ 83.5 (d, *J* = 6.4 Hz), 87.7 (d, *J* = 7.8 Hz); Elemental analysis was unsuccessful due to considerable weight loss during combustion analysis.

Reaction of complex **3a** with MeI



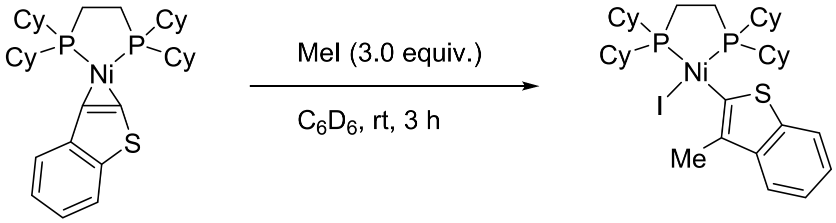
3a

4a: 75% yield (NMR)

To a solution of **3a** (5.6 mg, 0.01 mmol) in C_6D_6 (1.0 mL), MeI (1.9 μL, 0.03 mmol) and mesitylene (internal standard) were added at room temperature. The reaction was monitored by ^{1}H and ^{31}P NMR measurements, and complete consumption of **3a** and formation of **4a** (75% NMR yield) was observed within 30 minutes. Single crystals suitable for X-ray diffraction analysis were obtained from the benzene solution of NMR sample.

m.p. 202 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6, 21 °C) δ 0.64 (m, 1H), 1.01-2.47 (m, 71.7H), 2.91 (m, 1H), 6.82 (SCHC*H*, d, *J* = 4.4 Hz, 1H), 7.39 (SC*H*, d, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6, 21 °C) δ 20.4, 20.6, 20.7, 20.8, 21.0, 23.3, 23.5, 23.5, 26.1, 26.5, 27.0, 27.3, 27.4, 27.4, 27.5, 27.5, 27.6, 27.6, 27.7, 27.7, 27.8, 27.9, 28.1, 28.4, 28.5, 28.6, 29.2, 29.3, 30.1, 30.1, 30.4, 30.4, 30.6, 30.7, 32.3, 32.3, 33.7, 33.9, 36.2, 36.4, 36.9, 37.0, 37.1, 37.2, 129.8 (d, $J_{C\text{-}P}$ = 3.9 Hz), 130.7 (dd, $J_{C\text{-}P}$ = 2.2, 6.6 Hz), 137.0 (Ni*C*, dd, $J_{C\text{-}P}$ = 36.6, 86.6 Hz), 139.9 (d, $J_{C\text{-}P}$ = 2.7 Hz); ^{31}P NMR (162 MHz, C_6D_6, 21 °C) δ 67.6 (d, *J* = 29.3 Hz), 75.2 (d, *J* = 29.4 Hz); Anal. calcd for C31H53INiP2S: C 52.79, H 7.57; found: C 53.02, H 7.58%.

Reaction of complex **3b** with MeI



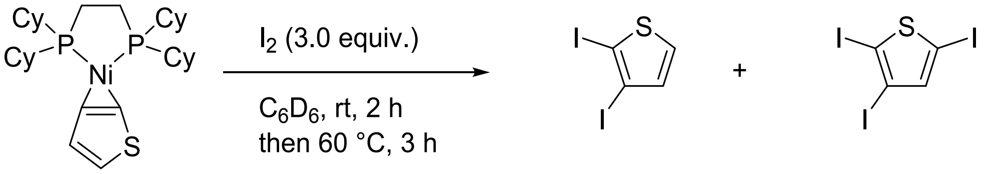
3b

4b: 48% yield (NMR)

To a solution of **3b** (6.2 mg, 0.01 mmol) in C_6D_6 (1.0 mL), MeI (1.9 μL, 0.03 mmol) and mesitylene (internal standard) were added at room temperature. The reaction was monitored by ^{1}H and ^{31}P NMR measurements, and formation of **4b** (48% NMR yield) was observed after 3 h. Single crystals suitable for X-ray diffraction analysis were obtained by Et_2O vapor diffusion into DCM solution.

m.p. 212 °C (decomp.); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 0.8-2.6 (m, 79H), 2.61 (s, 3H), 2.89 (m, 1H), 6.94 (t, *J* = 7.3 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H); ^{31}P NMR (162 MHz, CD_2Cl_2) δ 68.3 (d, *J* = 29.3 Hz), 75.7 (d, *J* = 29.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 19.4, 20.6, 20.8, 21.0, 23.3, 23.5, 23.5, 23.7, 25.6, 26.0, 26.1, 26.2, 26.4, 26.5, 26.0, 26.1, 26.2, 26.4, 26.5, 26.7, 26.8, 27.2, 27.3, 27.4, 27.5, 27.5, 27.6, 27.8, 27.8, 27.9, 28.4, 28.5, 28.8, 29.3, 29.4, 30.1, 30.5, 30.6, 31.3, 32.2, 34.2, 34.5, 36.3, 36.6, 36.9, 37.1, 37.3, 118.0, 119.2, 120.7, 122.3, 133.4, 142.7 (d, $J_{C\text{-}P}$ = 6.6 Hz), 147.0 (Ni*C*, dd, $J_{C\text{-}P}$ = 34.5, 86.4 Hz), 147.6 (d, $J_{C\text{-}P}$ = 3.7 Hz); Anal. calcd for C35H55INiP2S: C 55.65, H 7.34; found: C 55.32, H 7.74%.

Reaction of complex **3a** with iodine



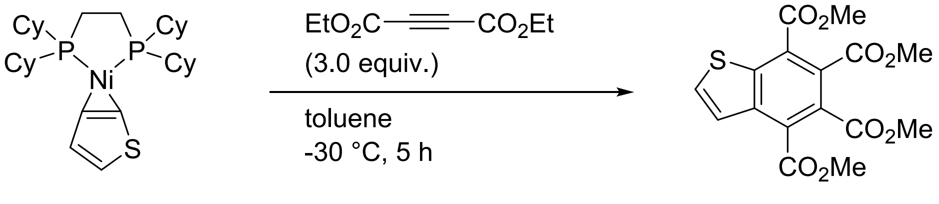
3a 32% yield (NMR) 8% yield (NMR)

To a solution of **3a** (5.6 mg, 0.01 mmol) in C_6D_6 (1.0 mL), I_2 (7.6 mg, 0.03 mmol) and mesitylene (internal standard) were added at room temperature. After heating at 60 °C for 3 h resulted in the complete consumption of **3a**, and 2,3-diiodothiophene was obtained along with 2,3-diiodothiophene in 32% and 8% NMR yield, respectively.

2,3-diiodothiophene: ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C) δ 6.95 (SCHC*H*, d, *J* = 5.5 Hz, 1H), 7.34 (SC*H*, d, *J* = 5.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 21 °C) δ 84.1, 93.9, 133.74, 135.89; HRMS (APCI) *m/z* calcd for $C_4H_2I_2S$ ($[M]^+$) 335.7971, found 335.7971.

2,3,5-triiodothiophene: ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C) δ 7.06 (s, 1H); ^{13}C NMR (100 MHz, C_6D_6, 21 °C) δ 78.8, 87.7, 94.4, 144.27; HRMS (APCI) *m/z* calcd for C_4HI_3S ($[M]^+$) 461.6928, found 461.6927.

Reaction of complex **3a** with dimethyl acetylenedicarboxylate

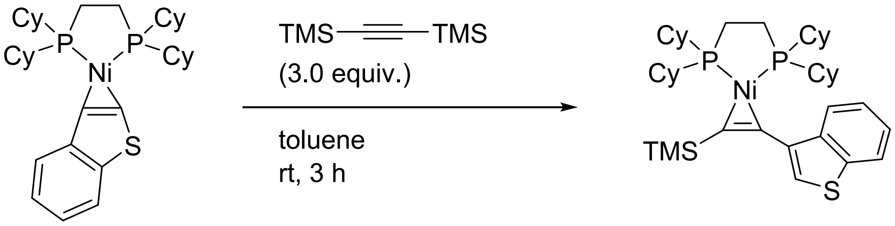


3a **5**: 40% yield

To a solution of **3a** (56 mg, 0.1 mmol) in toluene (3.0 mL), dimethyl acetylenedicarboxylate (42.6 mg, 0.3 mmol) was added at -30 °C. After stirring this temperature for 6 h, the reaction mixture was poured into H_2O, extracted with EtOAc, dried over Na_2SO_4, and concentrated in vacuo. The residue was subjected to silica gel chromatography (eluent: hexane/EtOAc = 40/1) to obtain the corresponding benzo[*b*]thiophene in 40% yield.

tetraethyl benzo[*b*]thiophene-4,5,6,7-tetracarboxylate (**5**): ^{1}H NMR (400 MHz, $CDCl_3$, 21 °C) δ 3.91 (*methyl*, s, 3H), 3.95 (*methyl*, s, 3H), 4.00 (*methyl*, s, 3H), 4.03 (*methyl*, s, 3H), 7.66 (SCHC*H*, d, *J* = 5.7 Hz, 1H), 7.80 (SC*H*, d, *J* = 5.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, 21 °C) δ 53.3, 53.3, 53.4, 53.4, 123.2, 124.9, 127.7, 130.8, 131.1, 133.8, 139.0, 143.0, 165.1, 166.7, 166.8, 167.8; HRMS (APCI) *m/z* calcd for $C_{16}H_{15}O_8S$ ($[M+H]^+$) 367.0482 found 367.0486.

Reaction of complex **3b** with bis(trimethylsilyl)acetylene



3b

6: 72% yield

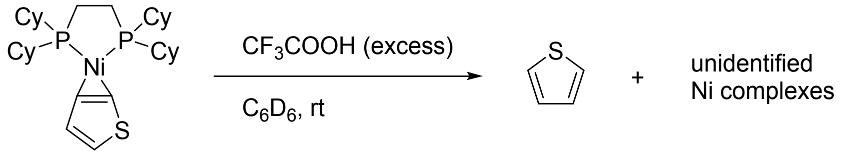
To a solution of **3b** (5.6 mg, 0.01 mmol) in C_6D_6 (1.0 mL), bis(trimethylsilyl)acetylene (5.1 mg, 0.03 mmol) was added at rt. After stirring for 3 h, the title compound formed in 72% yield. The complex **6** was also obtained by treating Ni(cod)(dcpe) (59 mg, 0.1 mmol) with the corresponding silyl alkyne (23 mg, 0.1 mmol) in C_6D_6 at room temperature, and identical NMR signals were observed. Single crystals suitable for X-ray diffraction analysis were obtained by cold pentane solution.

m.p. 71.2 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6, 21 °C) δ 0.49 (*methyl*, s, 9H), 0.86-2.25 (m, 67H), 7.07 (SC*H*, s, 1H), 7.09 (m, 1H), 7.21 (m, 1H), 7.63 (d, *J* = 7.88 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H); ^{31}P NMR (162 MHz, C_6D_6) δ 68.5; ^{13}C NMR (100 MHz, CD_2Cl_2, 21 °C) δ -0.03, 22.2, 22.4, 22.6, 22.7, 26.3, 26.7, 27.2, 27.4, 27.5, 28.7, 29.3, 29.6, 30.3, 36.3, 36.5, 36.6, 37.7, 97.5, 98.4, 118.7, 122.9, 123.2, 125.1, 125.4, 131.1, 139.0, 139.5 (signals for the carbon atoms bonded to nickel were not obtained due to decomposition during the measurement); Elemental analysis was unsuccessful due to considerable weight loss during combustion analysis.

2. NMR experiments

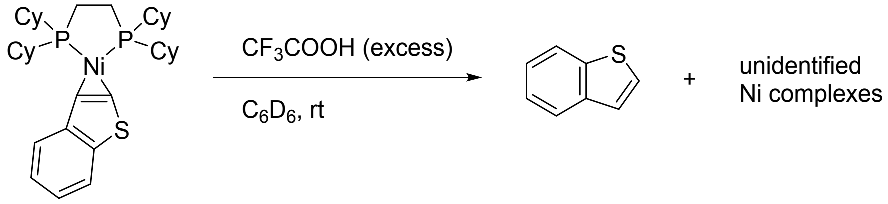
Reaction of complex **3a** and **3b** with trifluoroacetic acid

To a C_6D_6 solution of **3a** in an NMR tube, a few drops of trifluoroacetic acid was added at room temperature to give orange suspension (eq. S1). Instantaneous consumption of the complex **3a** and formation of thiophene was observed in ^{1}H NMR spectra (Figure S1, left). The precipitate was collected and washed with hexane; a peak at δ_p 78.2 ppm ($CDCl_3$) suggested the formation of Ni(dcpe)($OCOCF_3$)$_2$.[4] A similar experiment was conducted with complex **3b** (eq. S2), and the peaks correspond to **3b** disappeared in ^{1}H NMR and benzo[*b*]thiophene was detected (Figure S1, right).



3a

(S1)



3b

(S2)

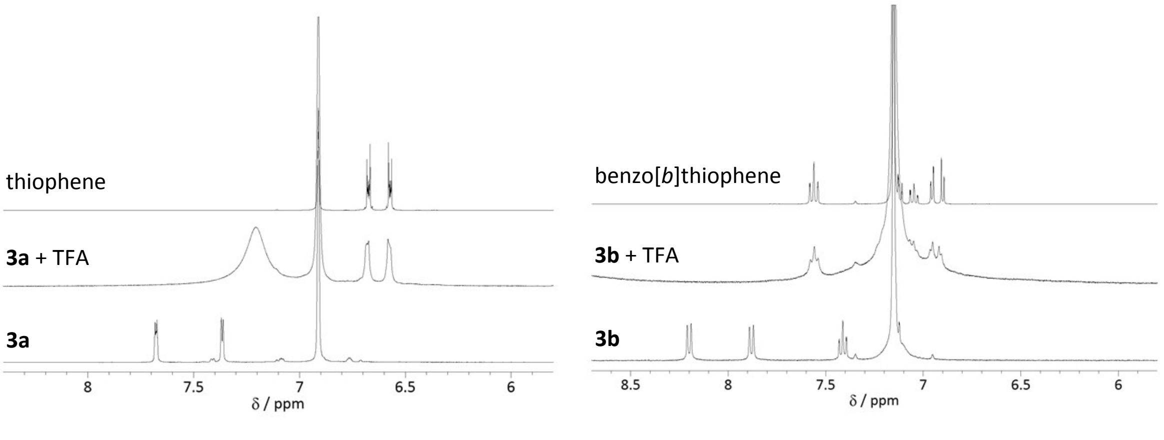


Fig. S1 ^{1}H NMR spectra in C_6D_6 for the reaction of **3a** (left) and **3b** (right) with TFA.

Stability of complexes **3a** and **3b**

Stability of Ni-aryne complexes **3a** and **3b** was examined by monitoring NMR spectra in C_6D_6. In ^1H NMR measurement, the peaks correspond to the complex **3a** slowly decreased with a half-life of approximately 60 h at room temperature (Figure S2). A new singlet at $\delta_p = 46.3$ ppm was detected after 1 day, that might be assigned to $Ni(dcpe)_2$ (Figure S3).[5] In contrast, the complex **3b** was significantly stable and no obvious spectral change was observed within 4 days at room temperature (Figure S4), and elevated temperature was required for complete consumption (Figure S5). Time course for the decomposition of complexes **3a** and **3b** is summarized in Figure S6.

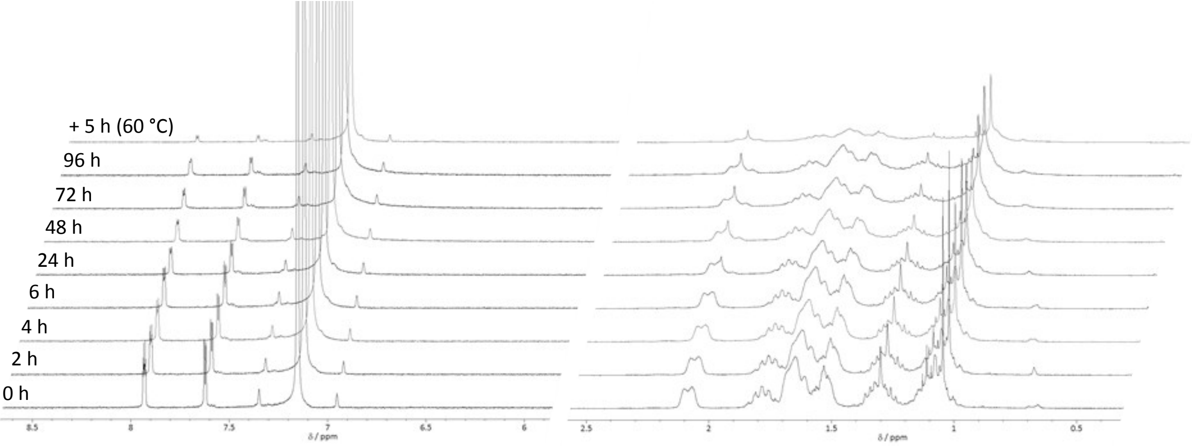


Fig. S2 ^1H NMR spectra of **3a** in C_6D_6 at 23 °C. Spectra from 2.5 ppm to 6.0 ppm were omitted for clarity.

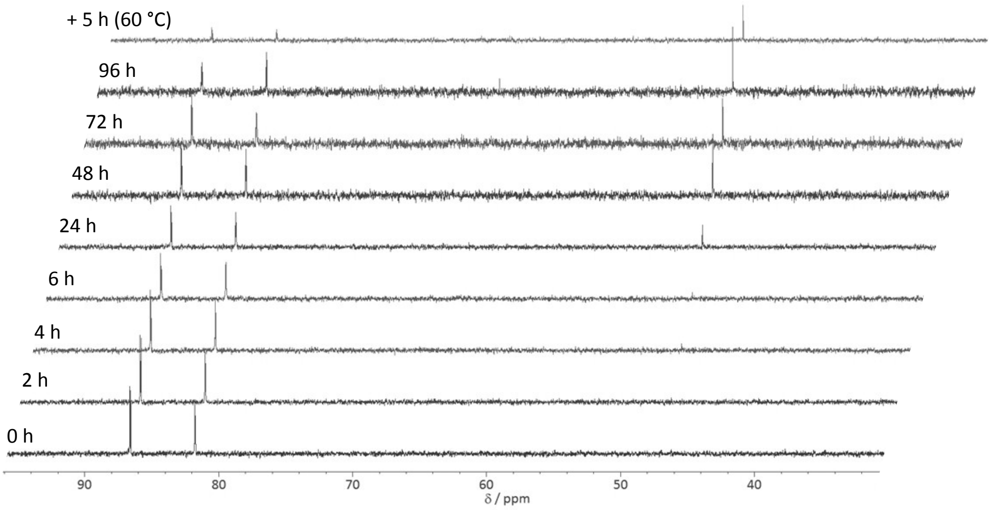


Fig. S3 ^{31}P NMR spectra of **3a** in C_6D_6 at 23 °C.

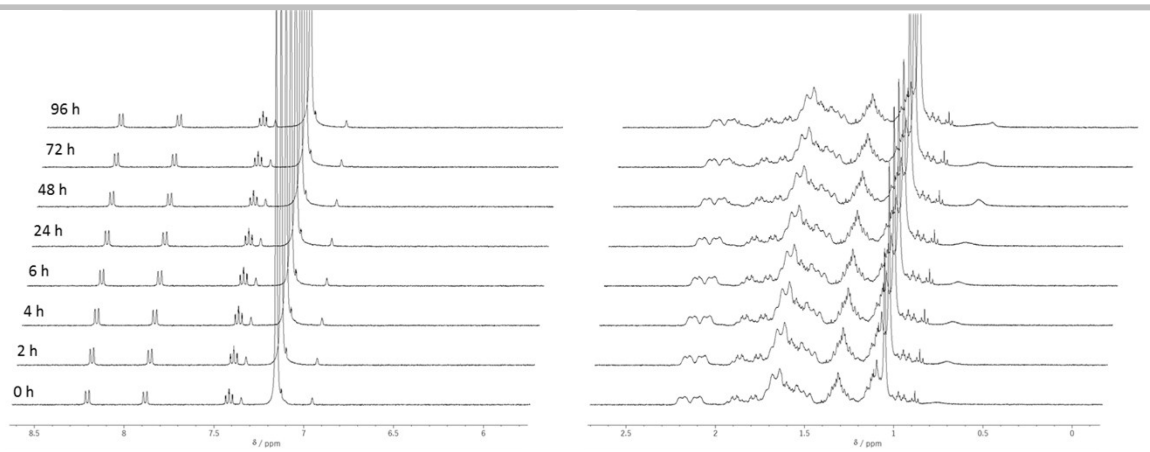


Fig. S4 ^{1}H NMR spectra of **3b** in C_6D_6 at 23 °C. Spectra from 2.5 ppm to 6.0 ppm were omitted for clarity.

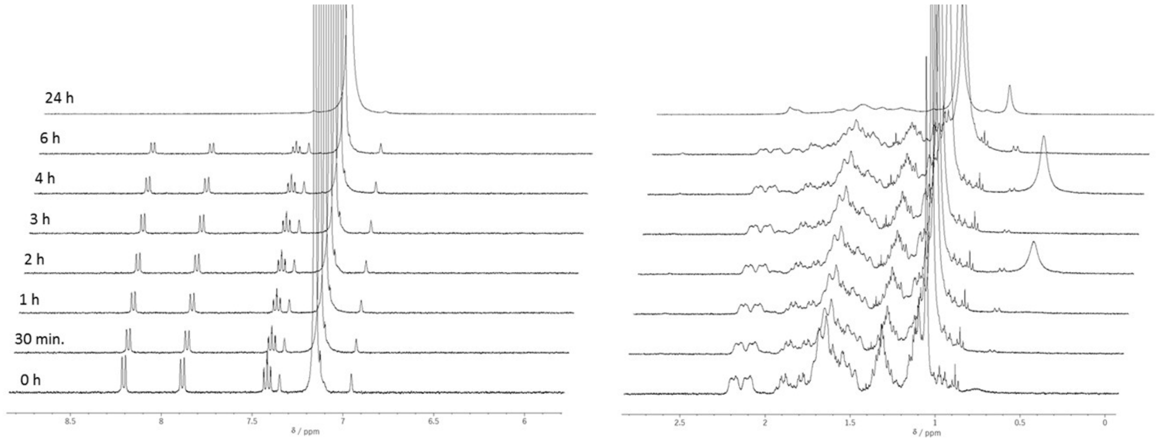


Fig. S5 ^{1}H NMR spectra of **3b** in C_6D_6 at 60 °C. Spectra from 2.5 ppm to 6.0 ppm were omitted for clarity.

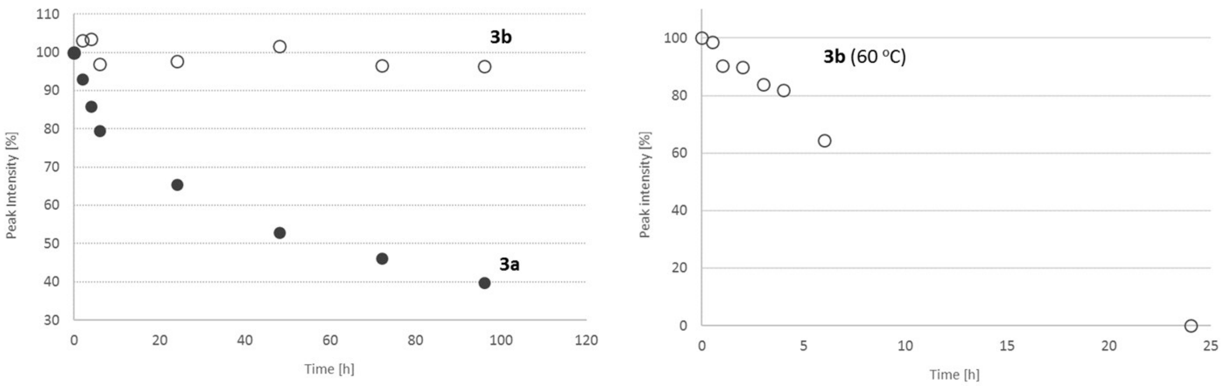


Fig. S6 Time course for peak intensity of **3a** (Figure S2) and **3b** (Figure S4 and S5).

3. Crystallographic data

X-ray diffraction measurements were carried out with Rigaku XtaLAB, Rigaku XtaLAB P200, or Rigaku XtaLAB Synergy. The structures were refined on F^2 by full-matrix least-squares method, using SHELXL-2016/6.[6] Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The ORTEP-3 program was used to draw the molecule.[7] The CCDC numbers for the complexes are 1523690 (**2a**), 1523691 (**2b**), 1529001 (**3a**), 1529002 (**3d**), 1529003 (**4a**), 1540560 (**4b**), and 1817952 (**6**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

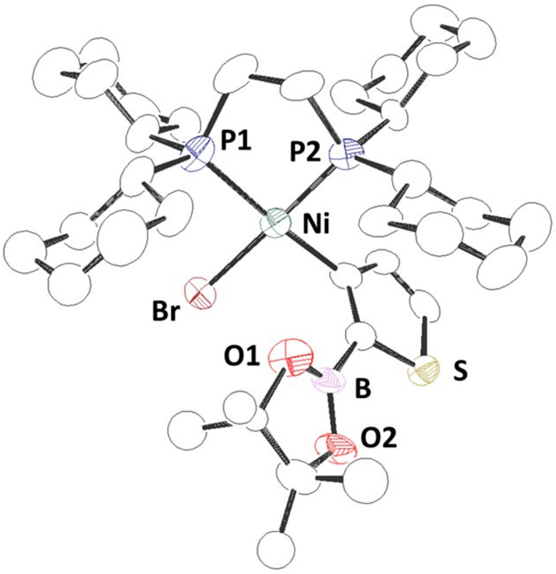


Fig. S7 ORTEP drawing of **2a** with 50% thermal probability. Only major orientation of the disordered groups is shown. Solvent molecules and hydrogen atoms are omitted for clarity.

Table S1 Crystal data and collection parameters for complex **2a**

Empirical formula	$C_{37.5}H_{65}BBrCl_3NiO_2P_2S$
Formula weight	897.67
Measurement temperature [K]	173(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$ (No. 19)
Unit cell parameter [Å]	a = 8.752(13)
	b = 21.67(3)
	c = 22.43(3)
Cell volume [Å^3]	4254(10)
Z	4
Crystal size [mm]	0.210 × 0.160 × 0.070
R factor ($I > 2.0\sigma(I)$)	$R1 = 0.0955$, $wR2 = 0.1770$
R factor (all data)	$R1 = 0.1337$, $wR2 = 0.2013$
Goodness of fit on F^2	1.076

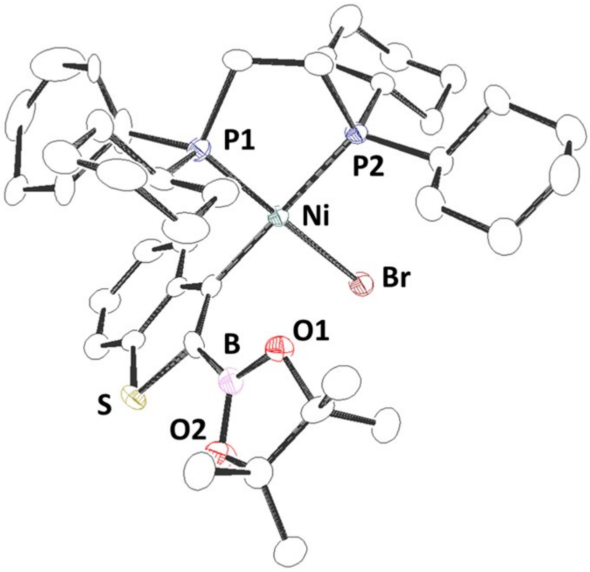


Fig. S8 ORTEP drawing of **2b** with 50% thermal probability. Only major orientation of the disordered groups is shown. Solvent molecules and hydrogen atoms are omitted for clarity.

Table S2 Crystal data and collection parameters for complex **2b**

Empirical formula	$C_{41}H_{66}BBrCl_2NiO_2P_2S$
Formula weight	905.84
Measurement temperature [K]	113(2)
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell parameter [Å, deg.]	a = 23.717(6)
	b = 11.746(2) β = 105.722(5)
	c = 16.282(4)
Cell volume [Å^3]	4366.1(17)
Z	4
Crystal size [mm]	0.190 × 0.040 × 0.020
R factor ($I > 2.0\sigma(I)$)	$R1 = 0.0766$, $wR2 = 0.1297$
R factor (all data)	$R1 = 0.1724$, $wR2 = 0.1660$
Goodness of fit on F^2	1.059

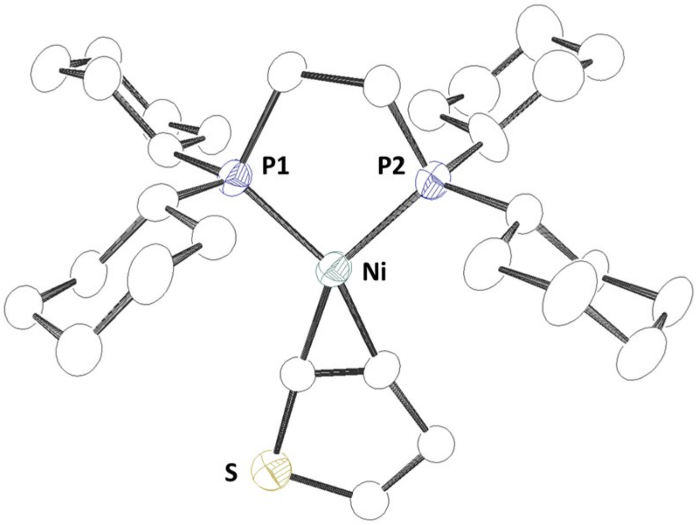


Fig. S9 ORTEP drawing of **3a** with 50% thermal probability. Only major orientation of the disordered groups is shown. Hydrogen atoms are omitted for clarity.

Table S3 Crystal data and collection parameters for complex **3a**

Empirical formula	$C_{30}H_{50}NiP_2S$
Formula weight	563.41
Measurement temperature [K]	173(2)
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
Unit cell parameter [Å, deg.]	a = 9.9110(16)
	b = 16.711(3) β = 92.402(10)
	c = 18.048(2)
Cell volume [Å^3]	2986.6(8)
Z	4
Crystal size [mm]	0.080 × 0.070 × 0.060
R factor ($I > 2.0\sigma(I)$)	$R1 = 0.0950$, $wR2 = 0.1638$
R factor (all data)	$R1 = 0.1856$, $wR2 = 0.2047$
Goodness of fit on F^2	1.047

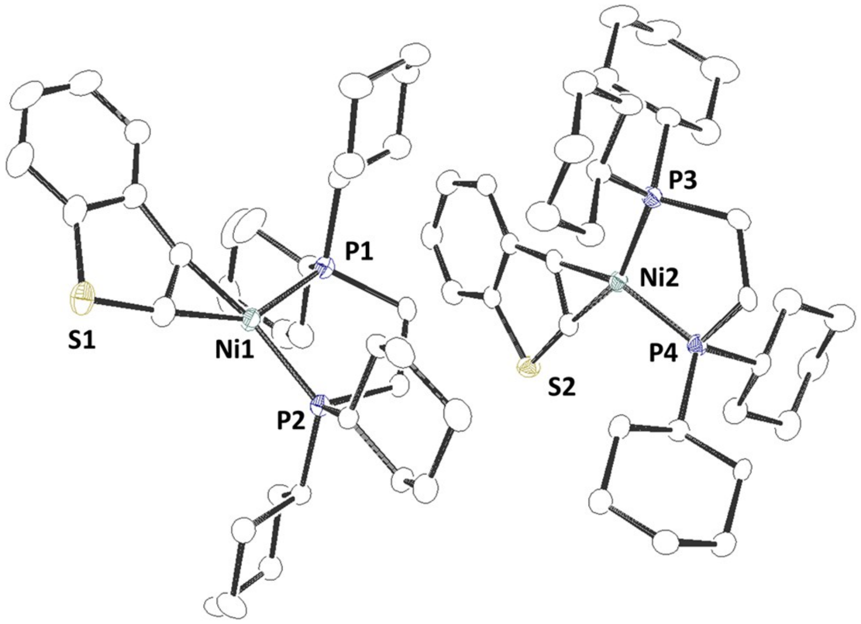


Fig. S10 ORTEP drawing of **3b** with 50% thermal probability. Solvent molecules and hydrogen atoms are omitted for clarity.

Table S4 Crystal data and collection parameters for complex **3b**

Empirical formula	$C_{76}H_{104}Ni_2O_2P_4S_2$	
Formula weight	1354.98	
Measurement temperature [K]	113(2)	
Crystal system	monoclinic	
Space group	$C2/c$ (No. 15)	
Unit cell parameter [Å, deg.]	a = 48.534(8)	
	b = 12.095(2)	β = 110.276(4)
	c = 26.019(5)	
Cell volume [Å^3]	14328(4)	
Z	8	
Crystal size [mm]	0.190 × 0.110 × 0.010	
R factor ($I > 2.0\sigma(I)$)	$R1 = 0.0619$, $wR2 = 0.0973$	
R factor (all data)	$R1 = 0.1460$, $wR2 = 0.1335$	
Goodness of fit on F^2	1.122	

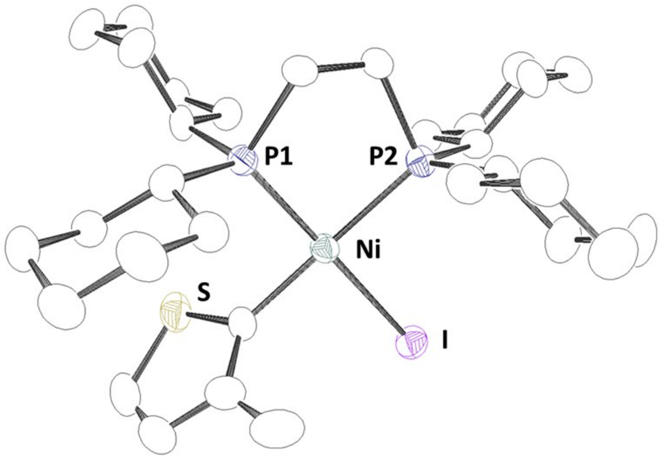


Fig. S11 ORTEP drawing of **4a** with 50% thermal probability. Solvent molecules and hydrogen atoms are omitted for clarity.

Table S5 Crystal data and collection parameters for complex **4a**

Empirical formula	$C_{37}H_{59}INiP_2S$	
Formula weight	783.49	
Measurement temperature [K]	173(2)	
Crystal system	triclinic	
Space group	*P*−1 (No. 2)	
Unit cell parameter [Å, deg.]	a = 8.481(11)	α = 96.001(14)
	b = 11.052(15)	β = 91.24(3)
	c = 21.03(3)	γ = 101.865(19)
Cell volume [$Å^3$]	1917(5)	
Z	2	
Crystal size [mm]	0.200 × 0.200 × 0.140	
R factor ($I > 2.0\sigma(I)$)	$R1$ = 0.0549, $wR2$ = 0.1183	
R factor (all data)	$R1$ = 0.0775, $wR2$ = 0.1380	
Goodness of fit on F^2	1.087	

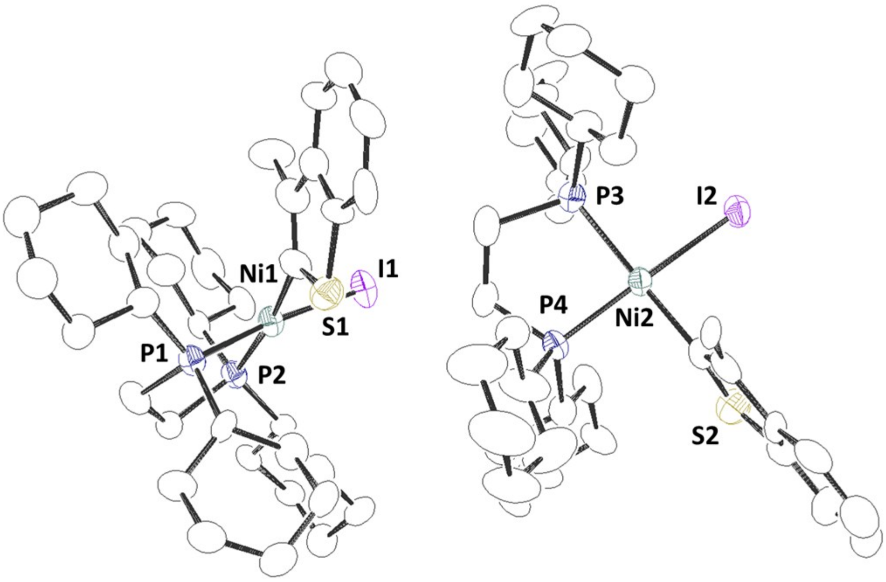


Fig. S12 ORTEP drawing of **4b** with 50% thermal probability. Solvent molecules and hydrogen atoms are omitted for clarity.

Table S6 Crystal data and collection parameters for complex **4b**

Empirical formula	$C_{35}H_{55}INiP_2S$	
Formula weight	755.40	
Measurement temperature [K]	173(2)	
Crystal system	triclinic	
Space group	$P-1$ (No. 2)	
Unit cell parameter [Å, deg.]	$a = 12.354(9)$	$\alpha = 75.82(2)$
	$b = 16.268(11)$	$\beta = 88.78(3)$
	$c = 20.938(14)$	$\gamma = 78.187(16)$
Cell volume [Å^3]	3992(5)	
Z	4	
Crystal size [mm]	0.130 × 0.120 × 0.100	
R factor ($I > 2.0\sigma(I)$)	$R1 = 0.0882$, $wR2 = 0.1597$	
R factor (all data)	$R1 = 0.1921$, $wR2 = 0.2153$	
Goodness of fit on F^2	1.028	

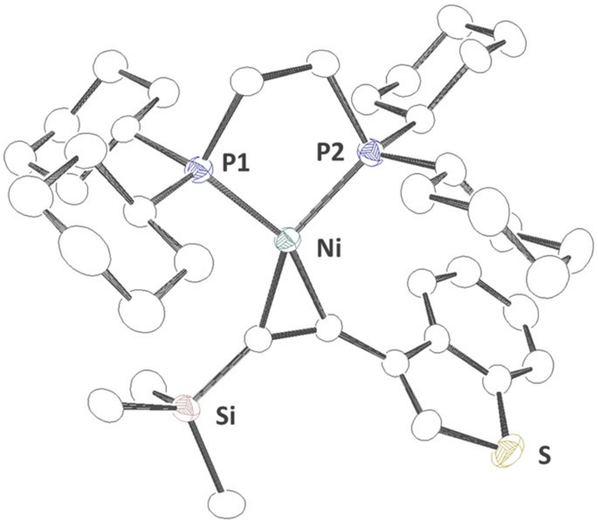


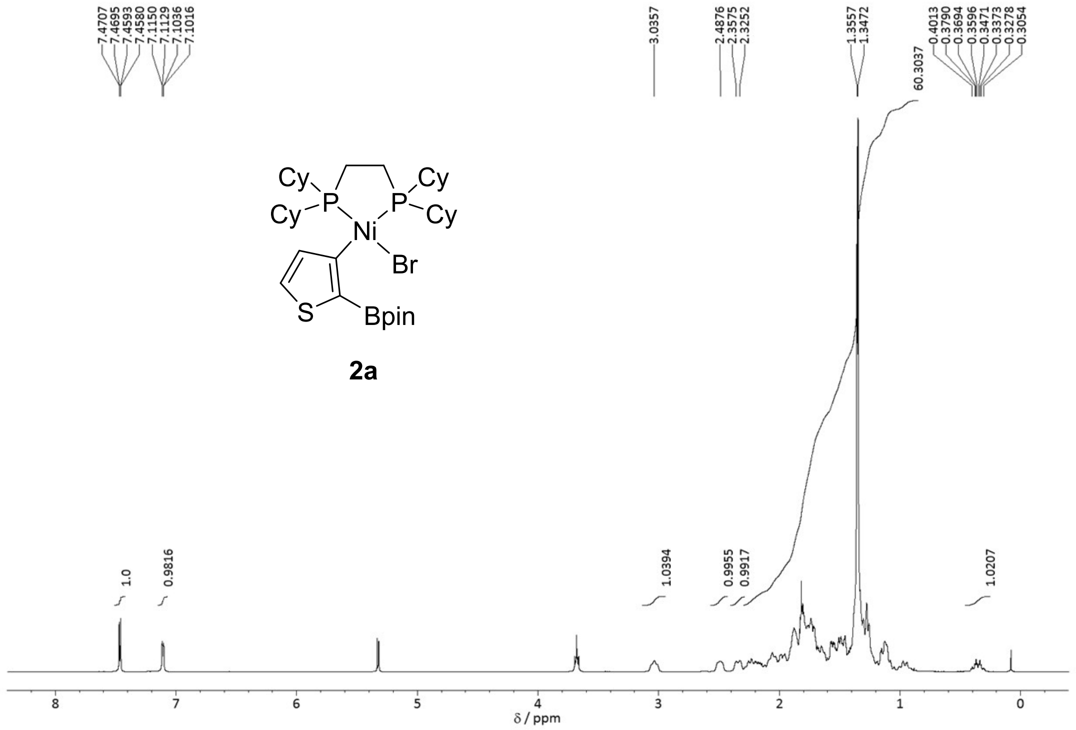
Fig. S13 ORTEP drawing of **4b** with 50% thermal probability. Solvent molecules and hydrogen atoms are omitted for clarity.

Table S7 Crystal data and collection parameters for complex **4b**

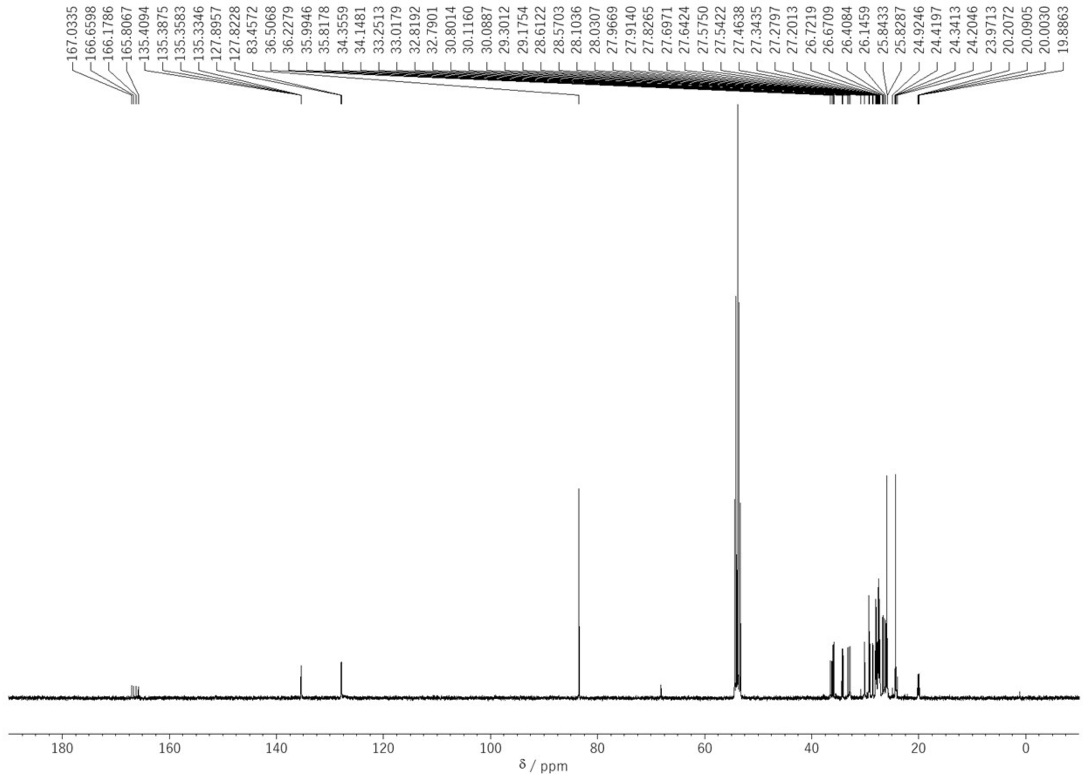
Empirical formula	$C_{39}H_{62}NiP_2SiS$	
Formula weight	711.25	
Measurement temperature [K]	173(2)	
Crystal system	triclinic	
Space group	$P-1$ (No. 2)	
Unit cell parameter [Å, deg.]	a = 10.9627(2)	α = 82.1370(10)
	b = 15.9681(3)	β = 82.6670(10)
	c = 35.1062(4)	γ = 83.181(2)
Cell volume [$Å^3$]	6005.73(17)	
Z	6	
Crystal size [mm]	0.146 × 0.093 × 0.037	
R factor ($I > 2.0\sigma(I)$)	$R1 = 0.0632$, $wR2 = 0.1585$	
R factor (all data)	$R1 = 0.0838$, $wR2 = 0.1722$	
Goodness of fit on F^2	1.010	

4. Copy of NMR spectra

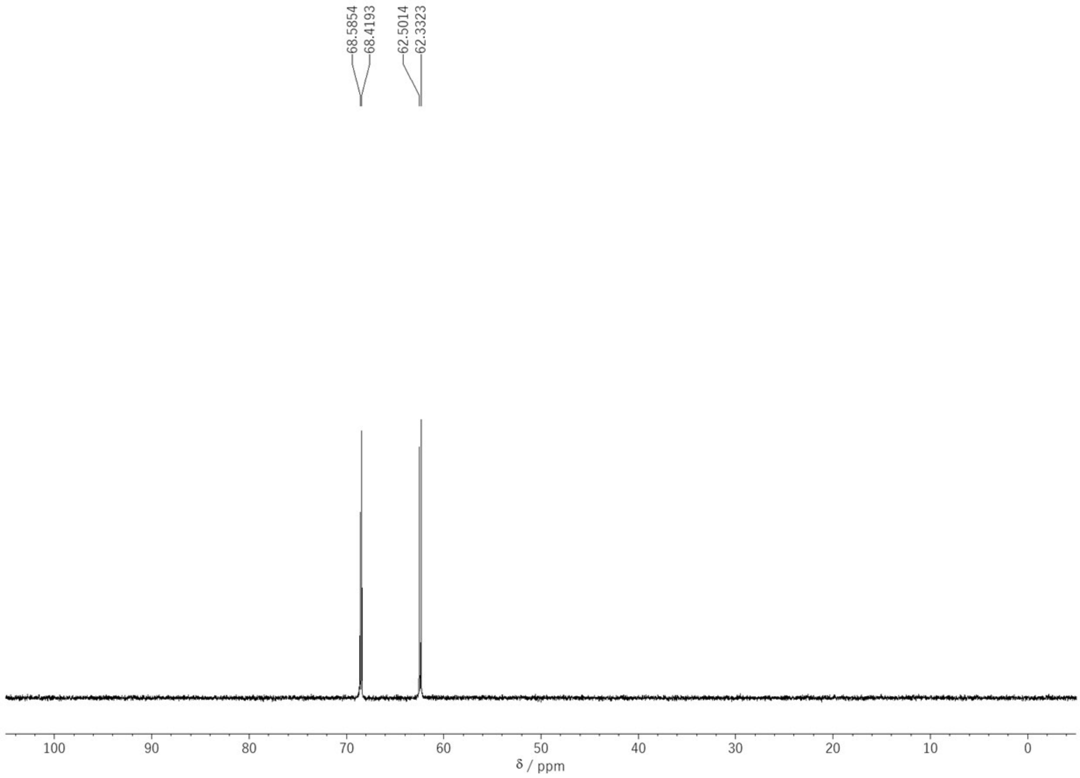
^{1}H NMR (**2a**)



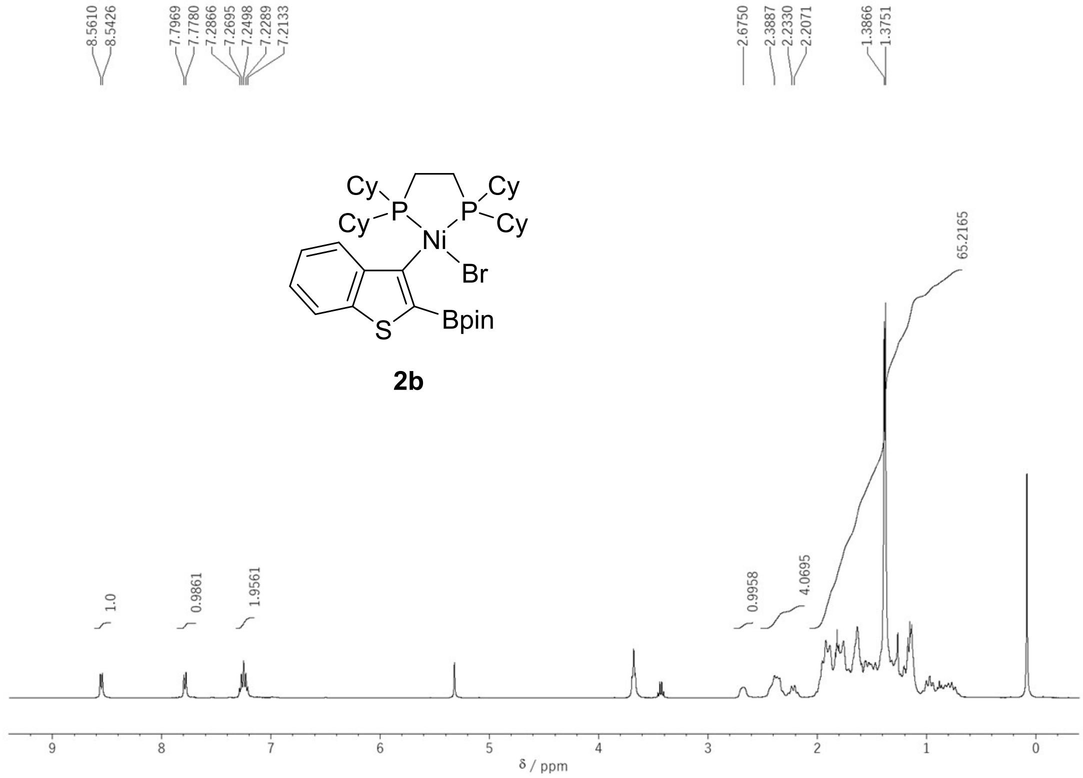
^{13}C NMR (**2a**)



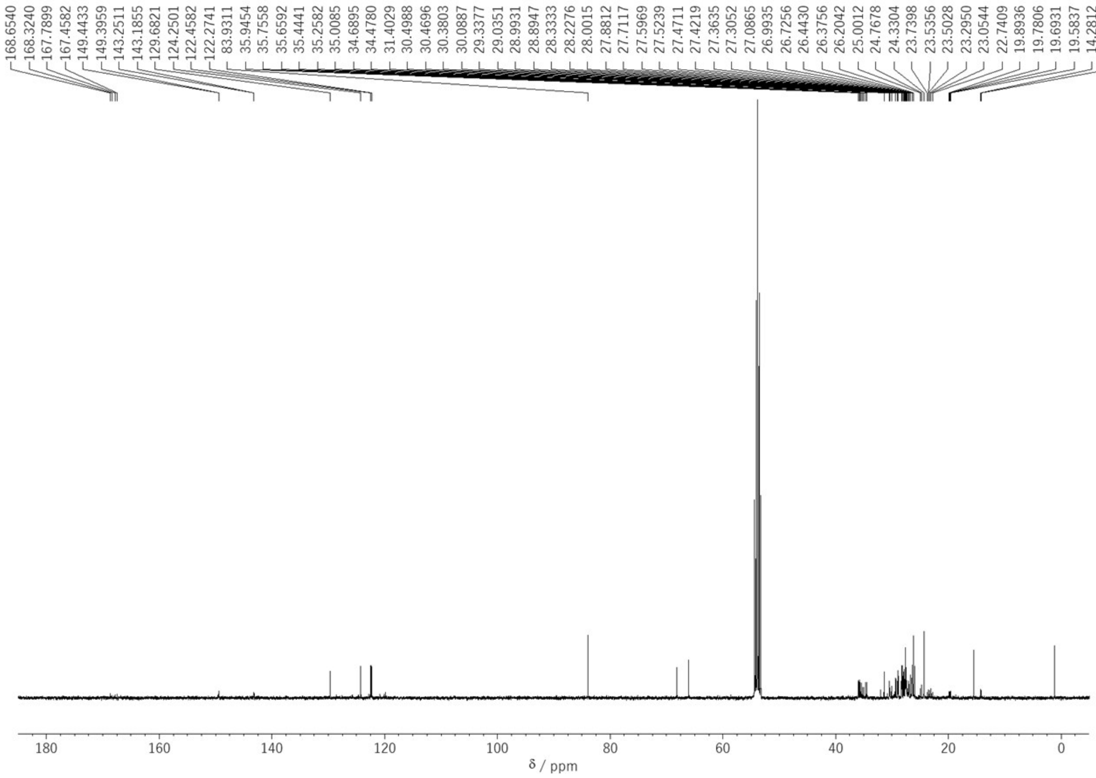
^{31}P NMR (**2a**)


68.5854
68.4193
62.5014
62.3323
100
90
80
70
60
50
40
30
20
10
0
δ / ppm

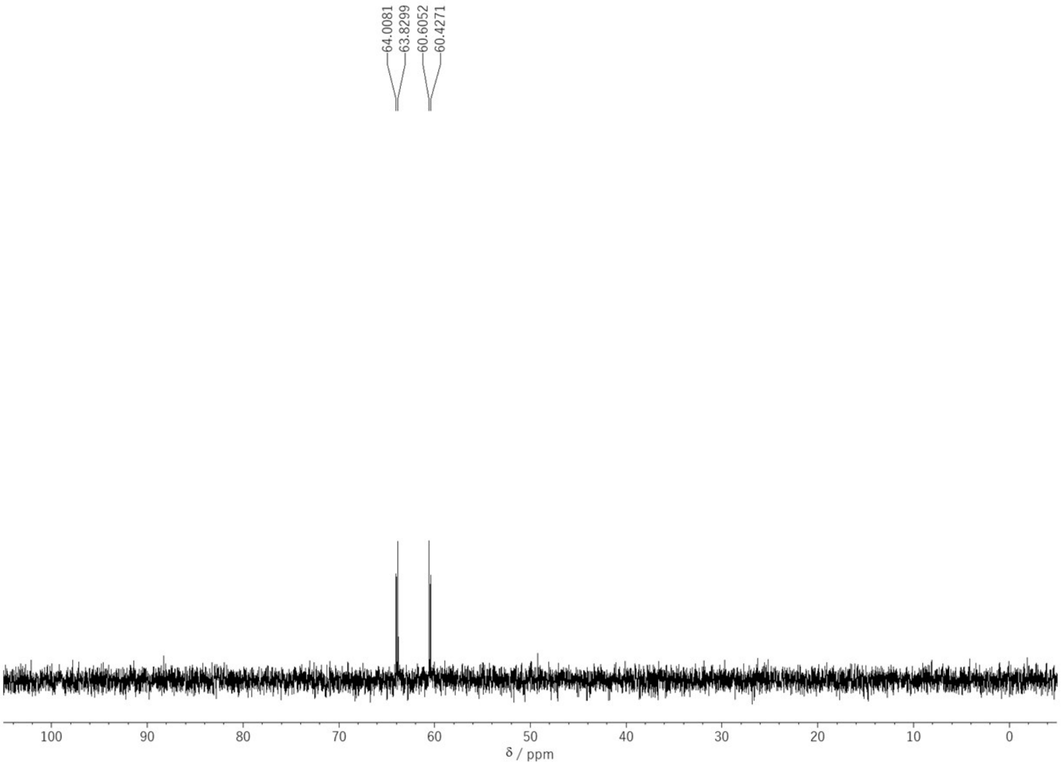
^{1}H NMR (**2b**)



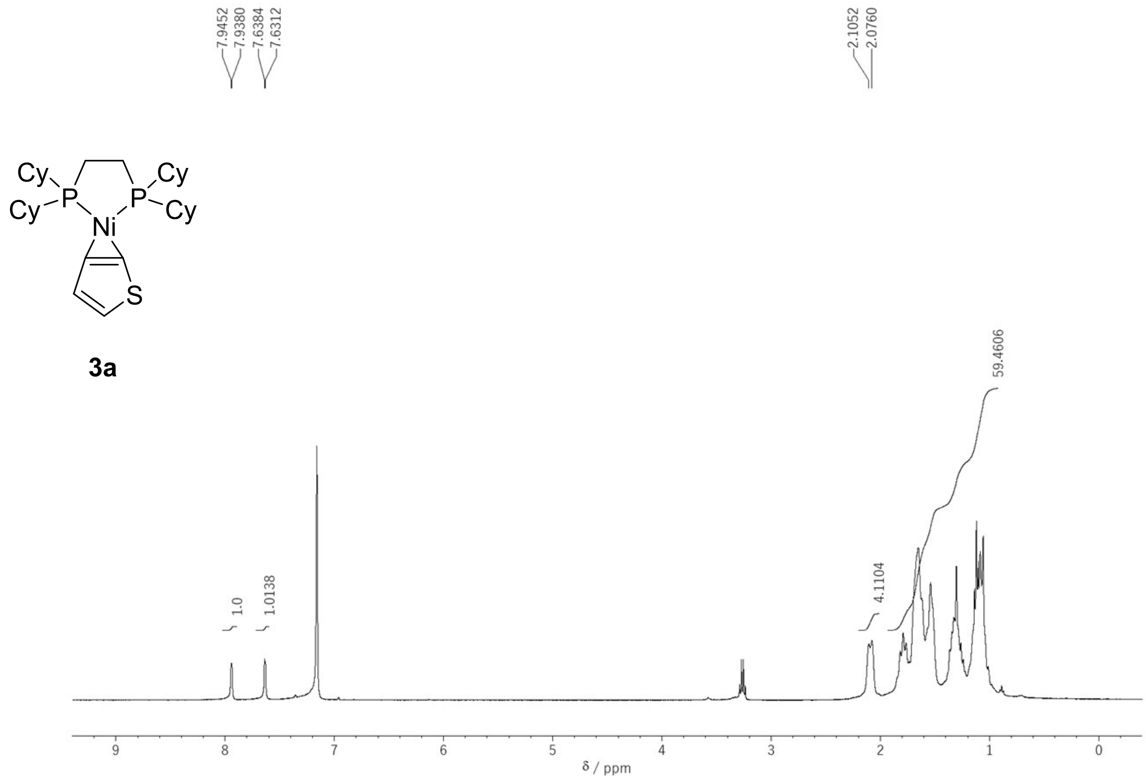
^{13}C NMR (**2b**)



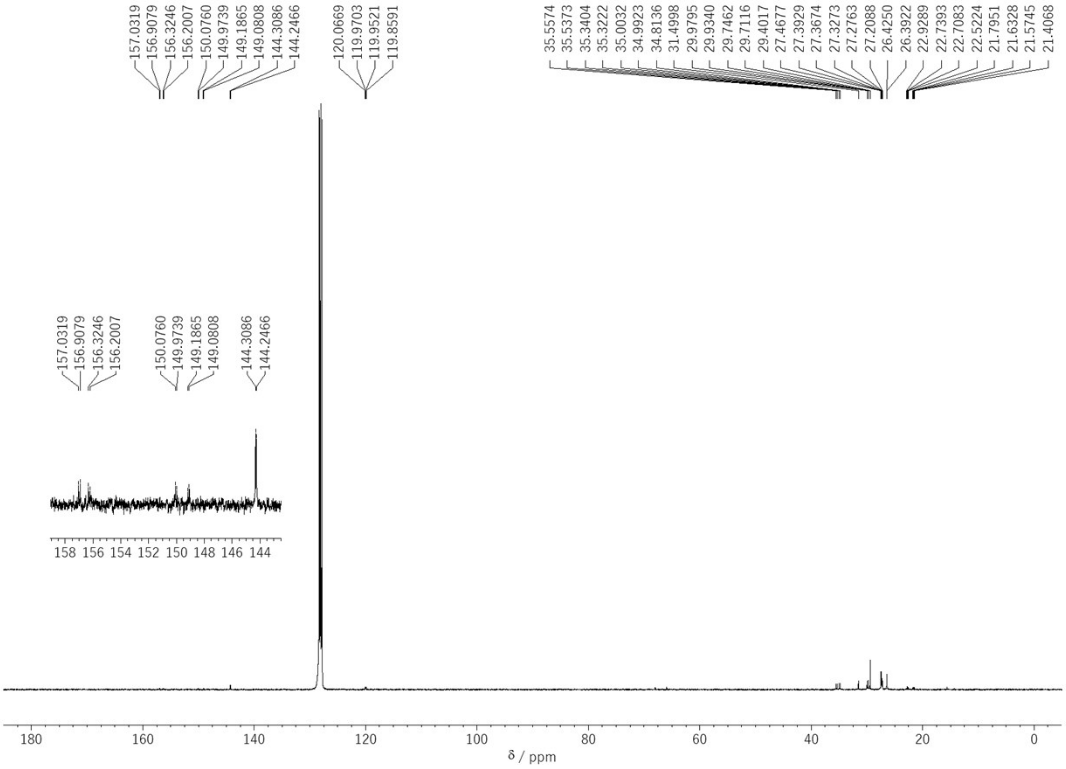
^{31}P NMR (**2b**)


64.0081
63.8299
60.6052
60.4271
100
90
80
70
60
50
40
30
20
10
0
δ / ppm

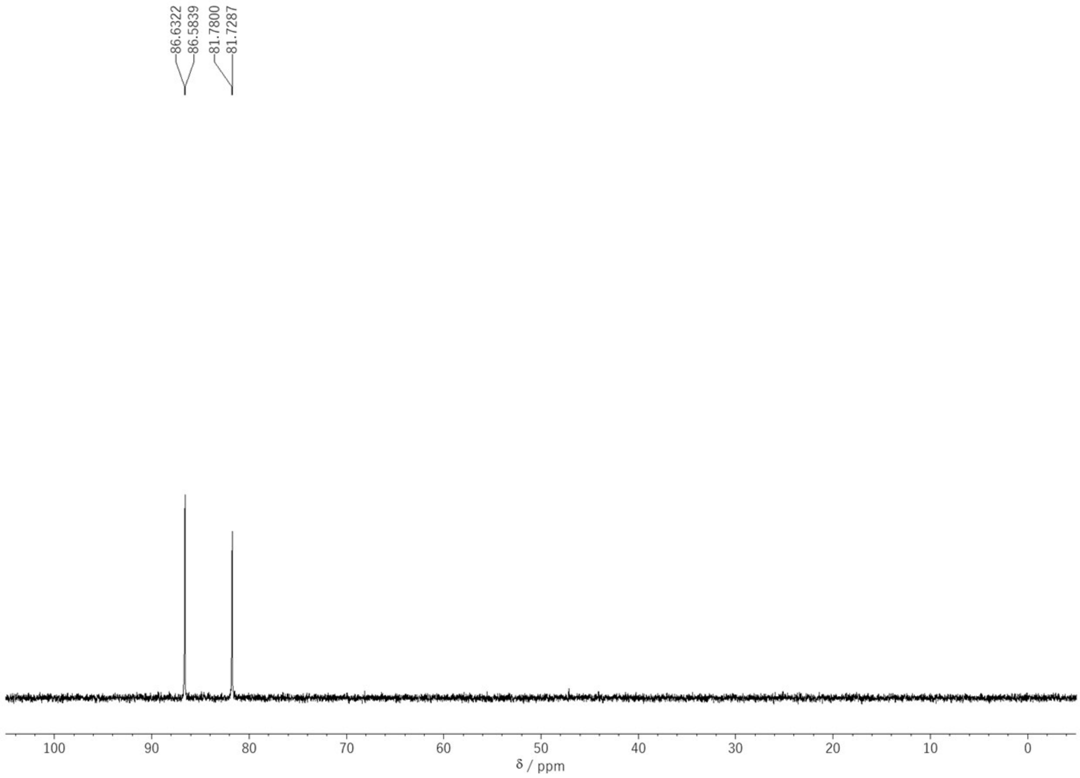
^{1}H NMR (**3a**)



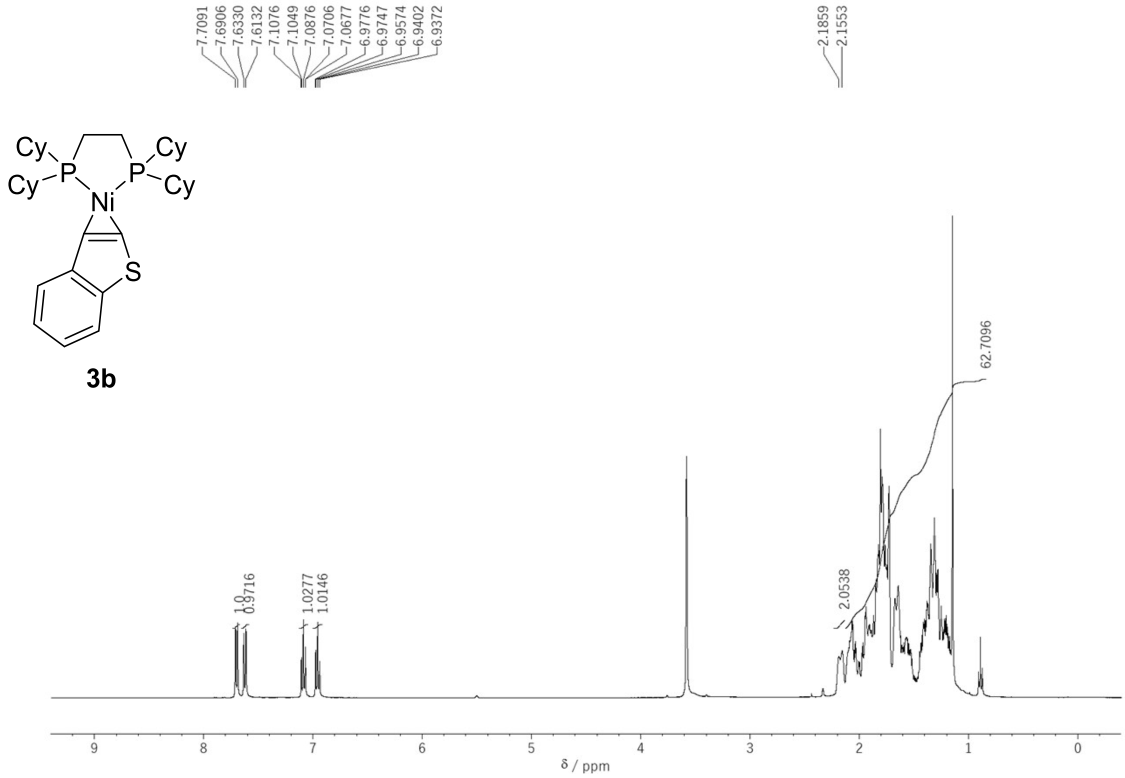
^{1}H NMR (**3a**)



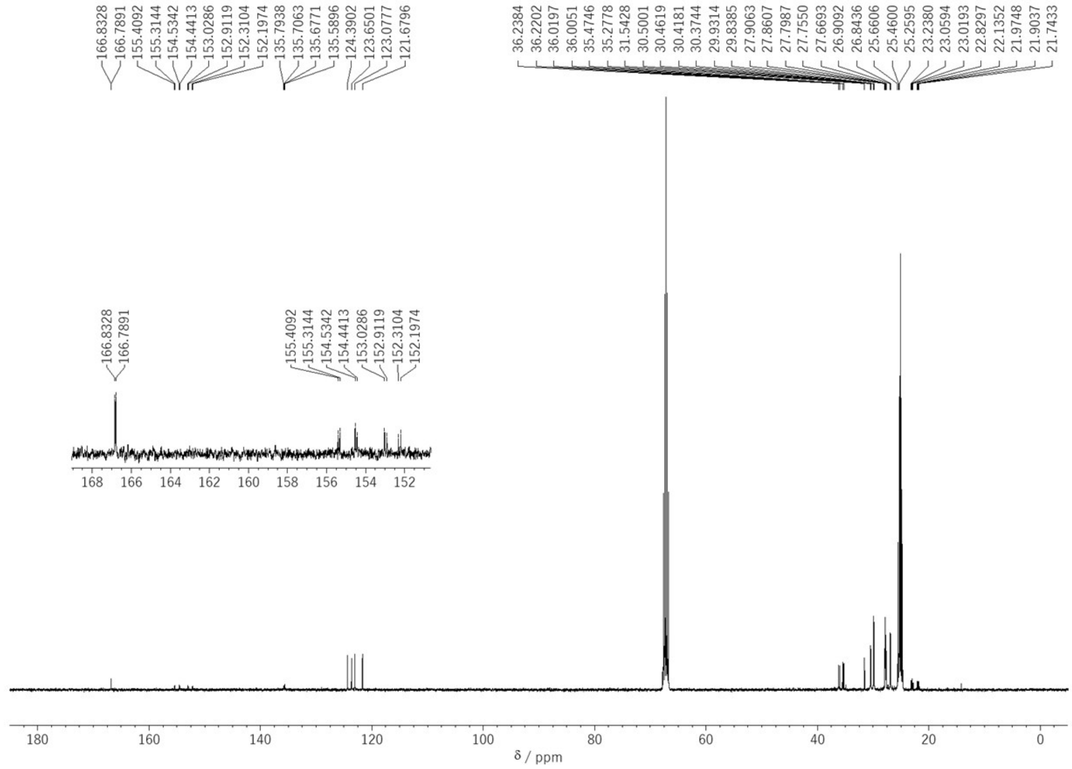
^{31}P NMR (**3a**)


86.6322
86.5839
81.7800
81.7287
100
90
80
70
60
50
40
30
20
10
0
δ / ppm

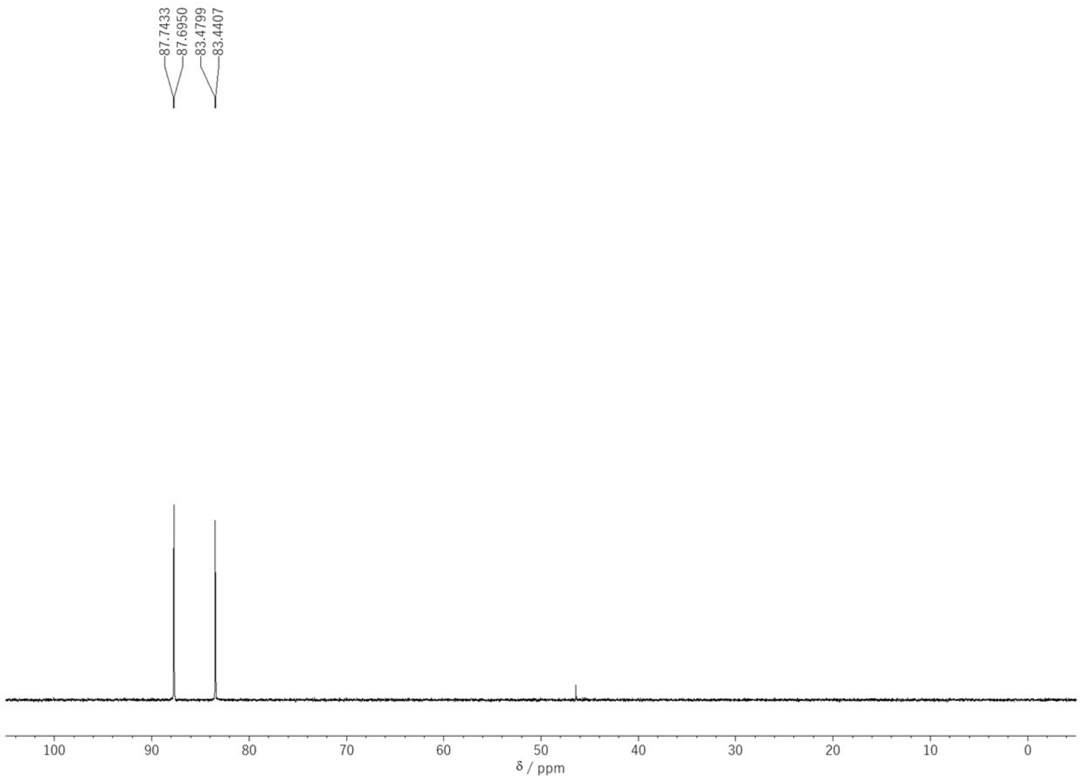
^{1}H NMR (**3b**)



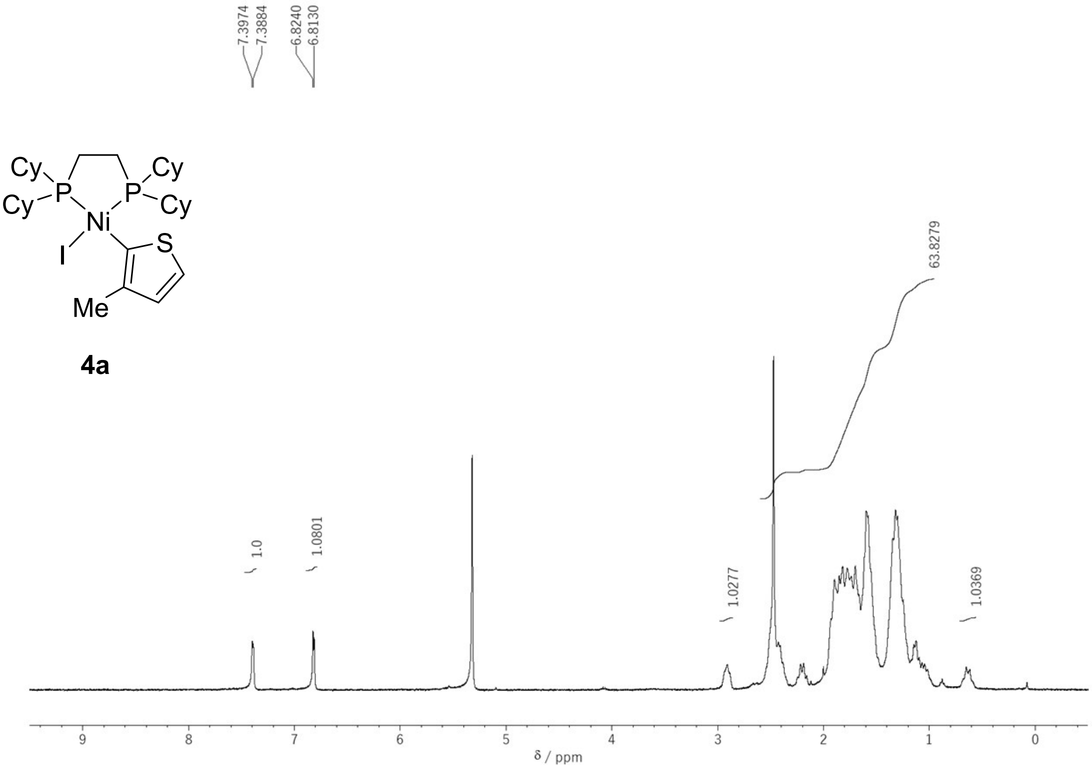
^{13}C NMR (**3b**)



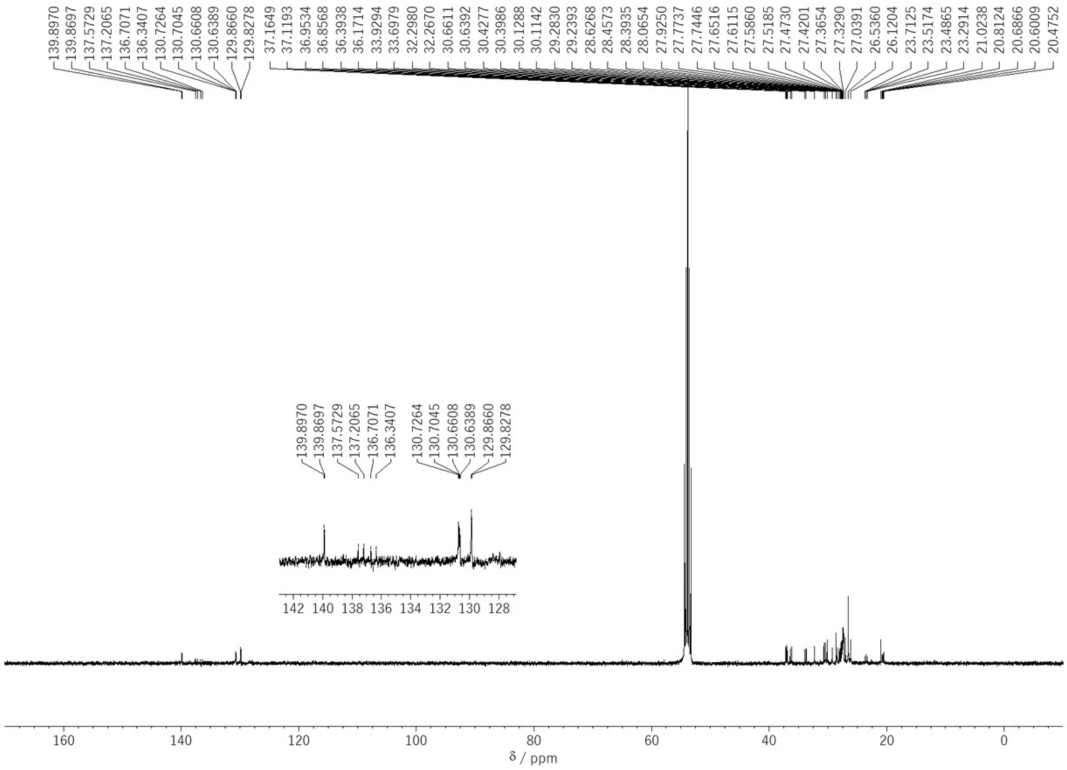
^{31}P NMR (**3b**)


87.7433
87.6950
83.4799
83.4407
100
90
80
70
60
50
40
30
20
10
0
δ / ppm

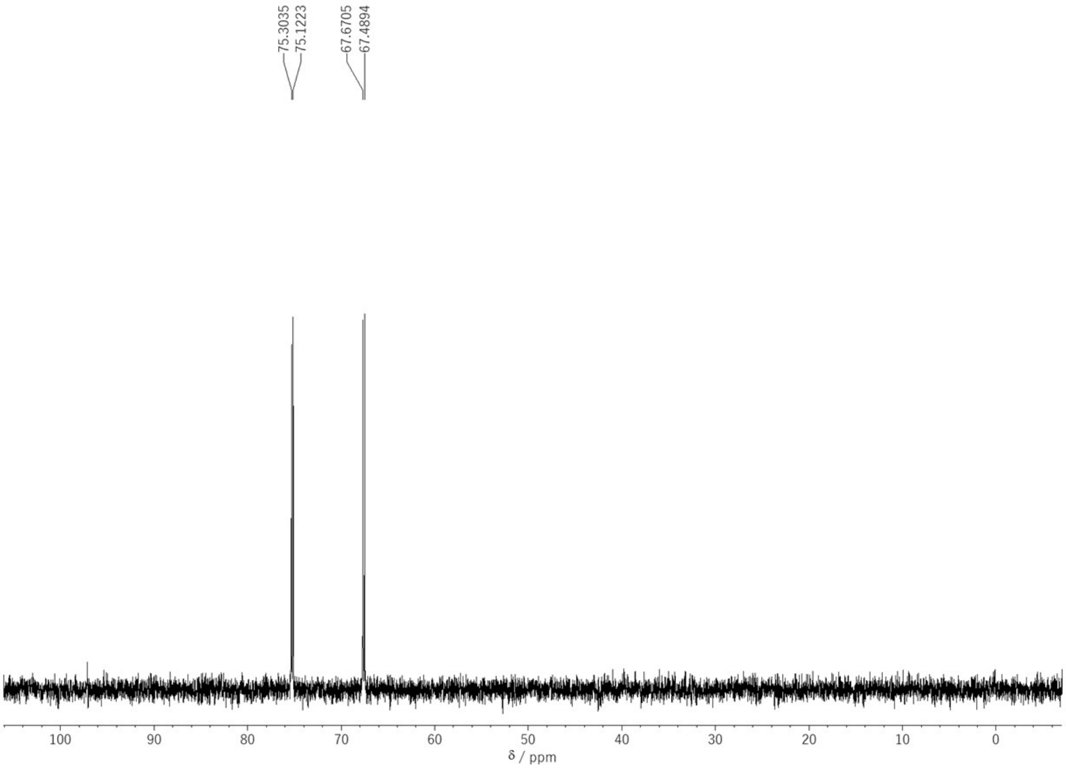
^{1}H NMR (**4a**)



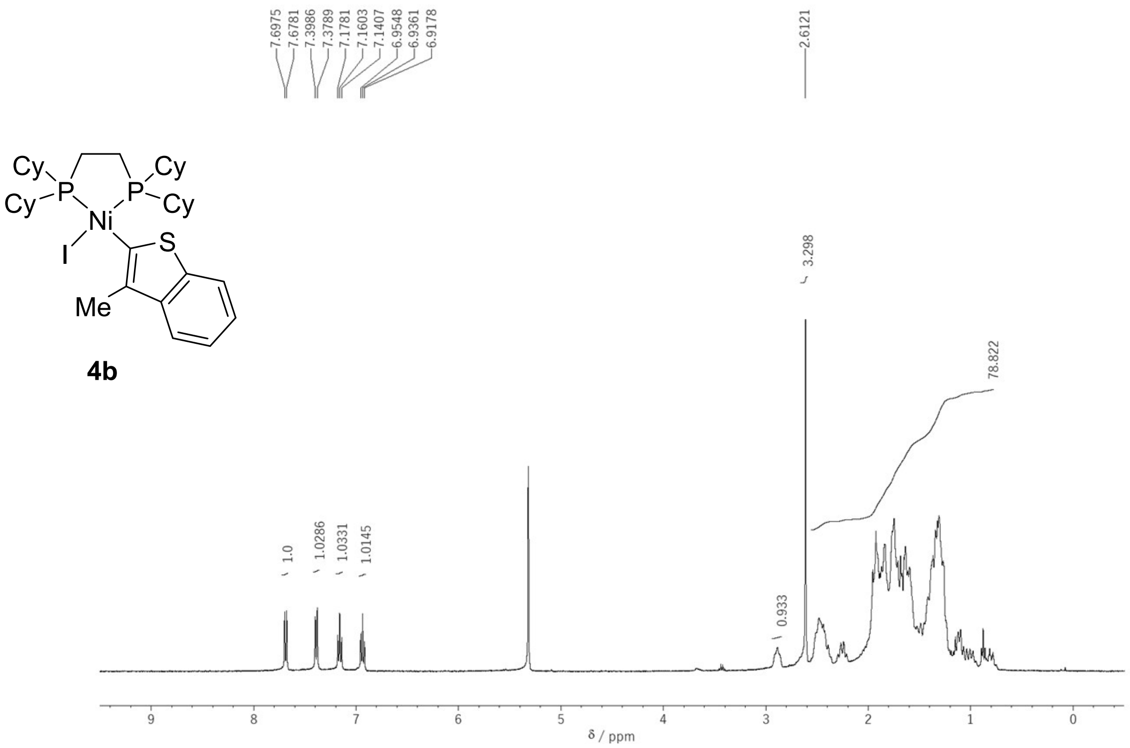
^{13}C NMR (**4a**)



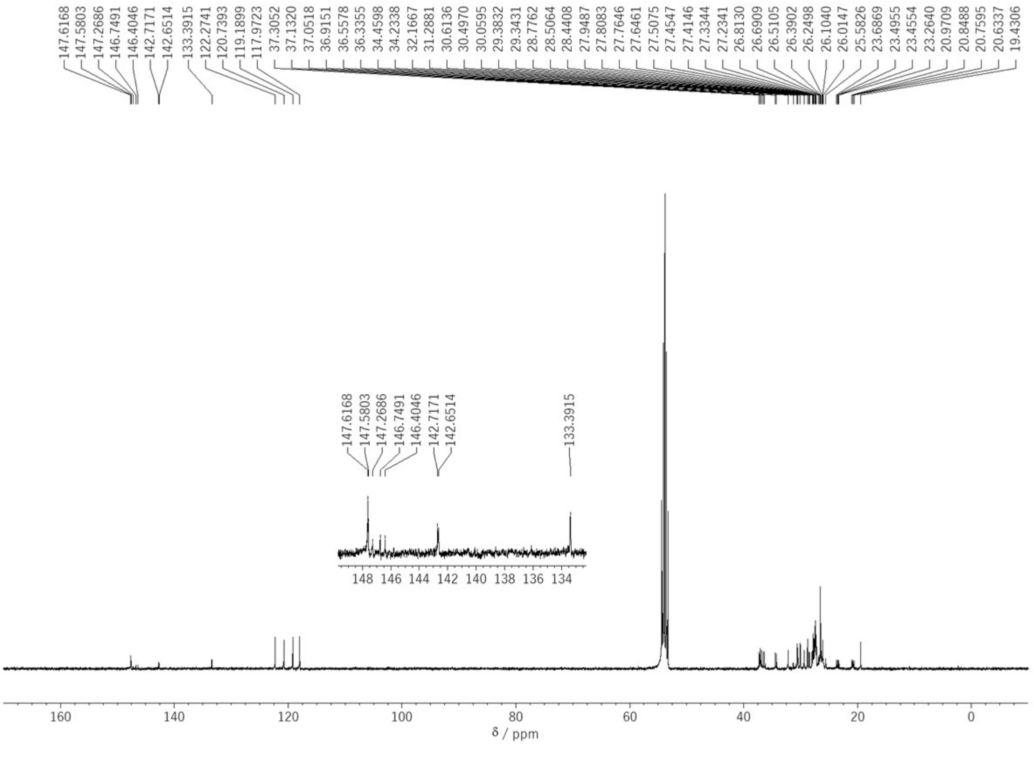
^{31}P NMR (**4a**)


75.3035
75.1223
67.6705
67.4894
100
90
80
70
60
50
40
30
20
10
0
δ / ppm

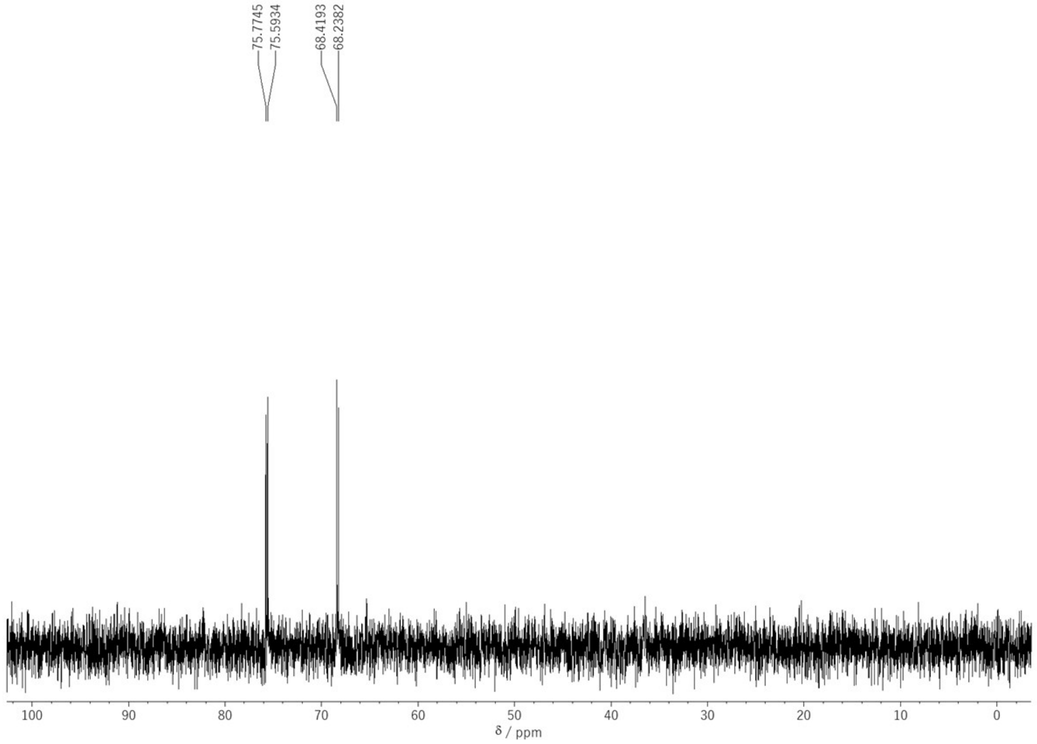
^{1}H NMR (**4b**)



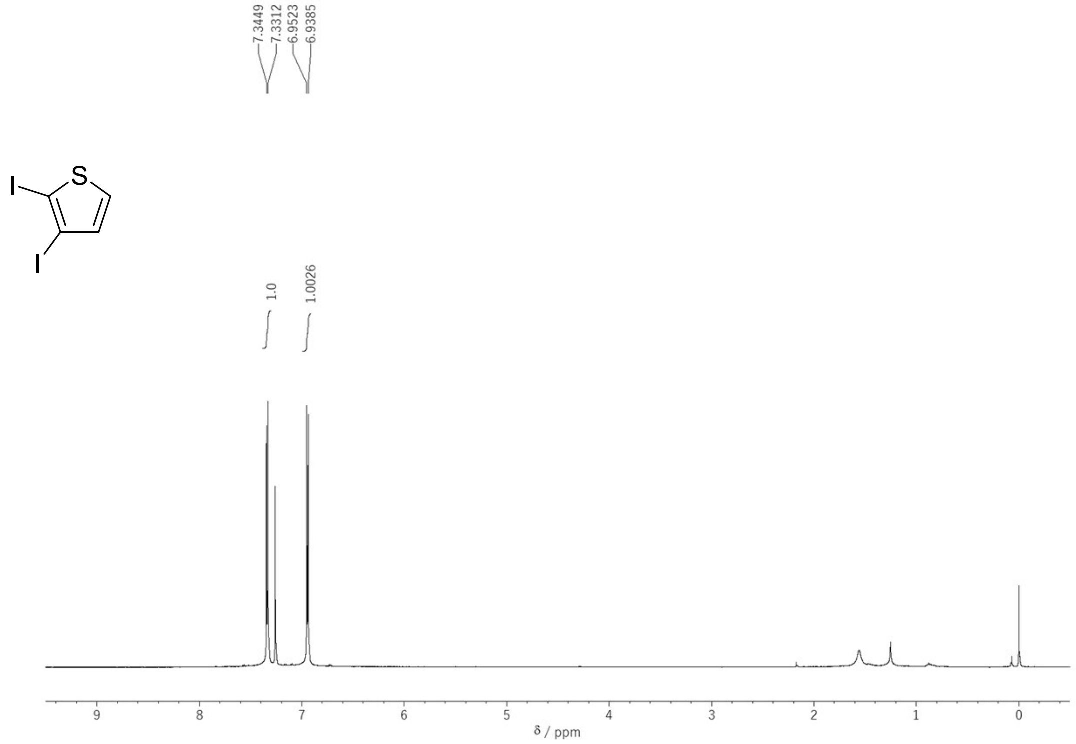
^{13}C NMR (**4b**)



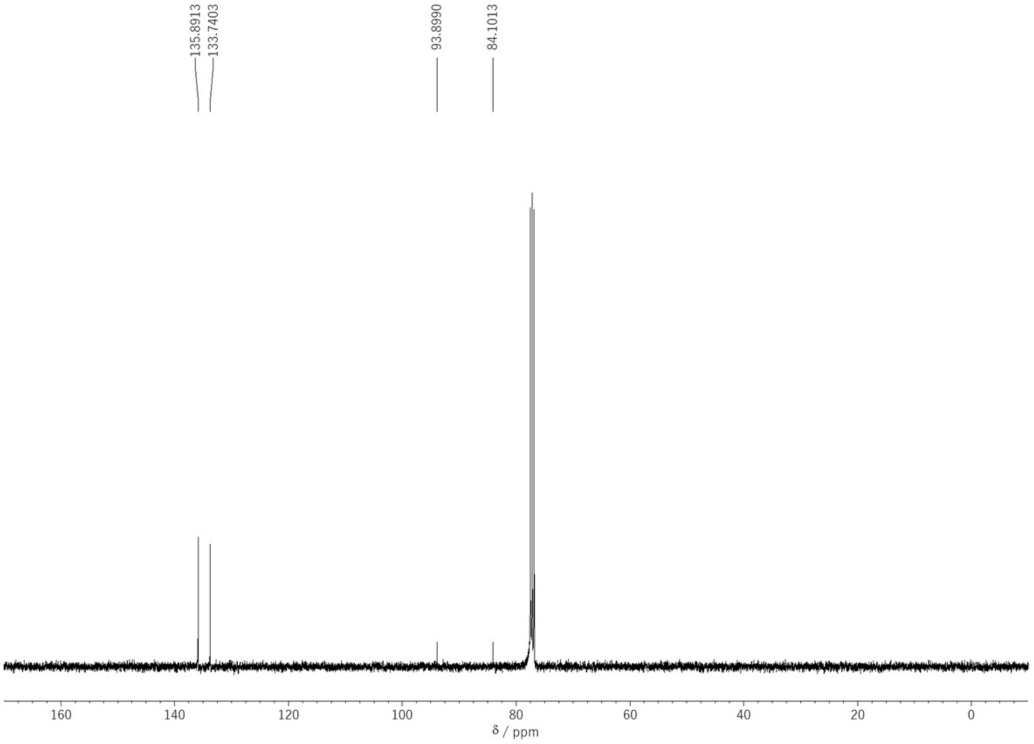
^{31}P NMR (**4b**)


75.7745
75.5934
68.4193
68.2382
100
90
80
70
60
50
40
30
20
10
0
δ / ppm

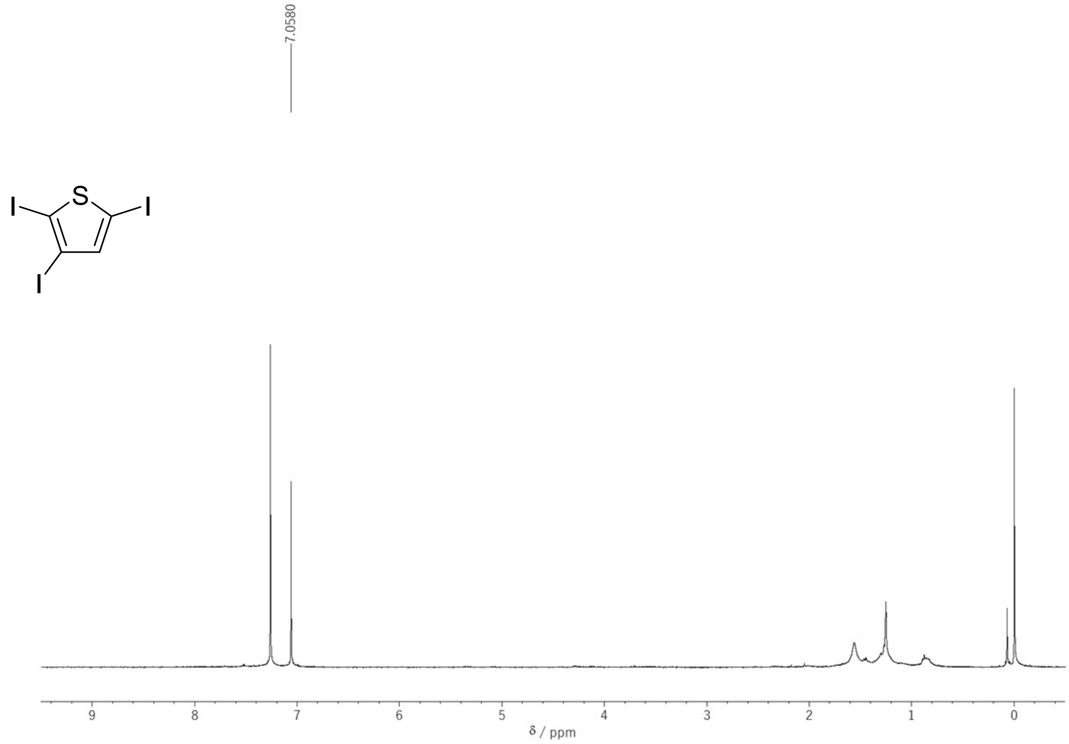
2,3-diiodothiophene (^{1}H NMR)



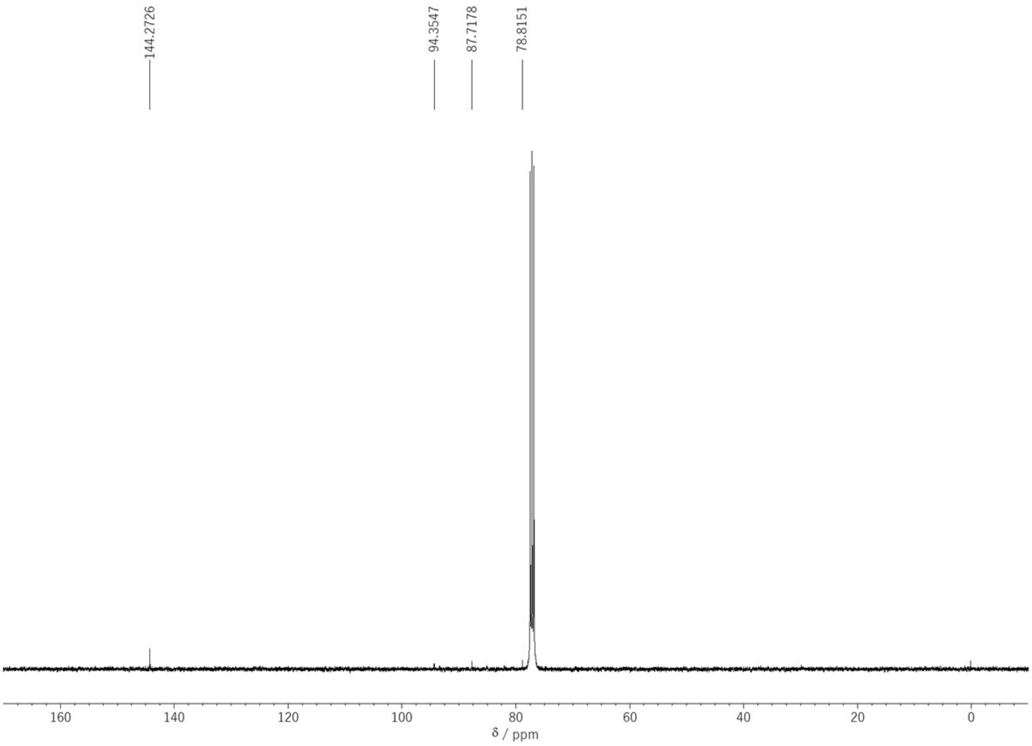
^{13}C NMR



2,3,5-triiodothiophene (^{1}H NMR)

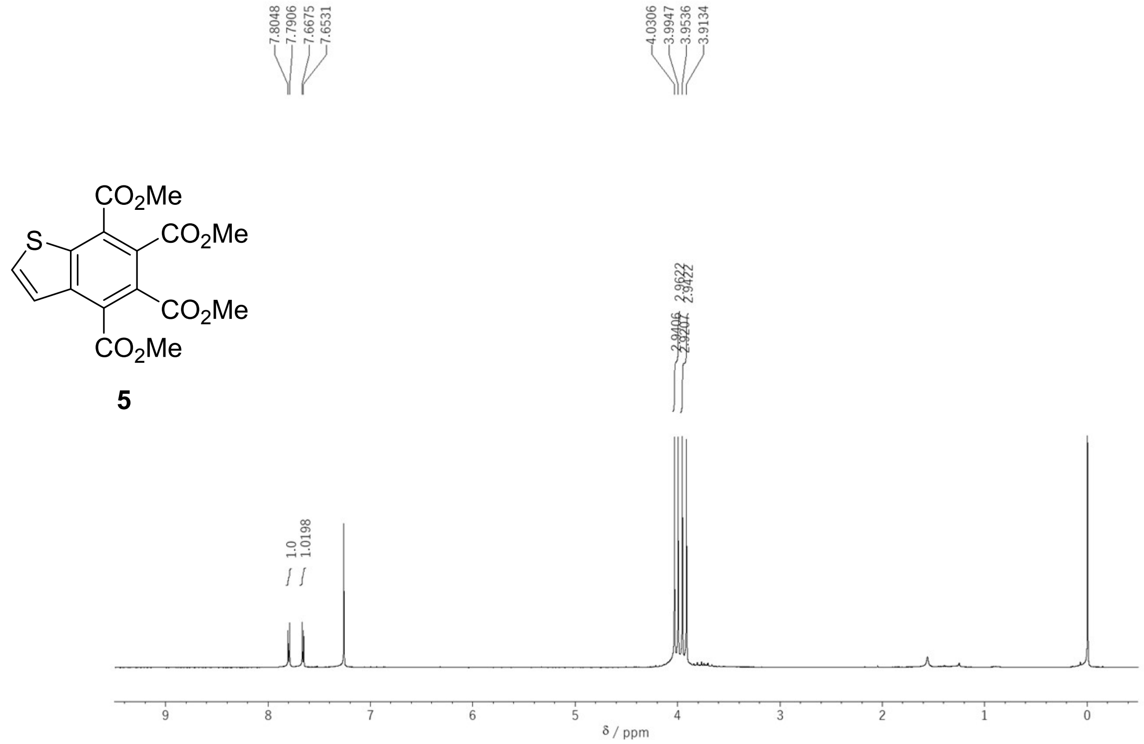


^{13}C NMR

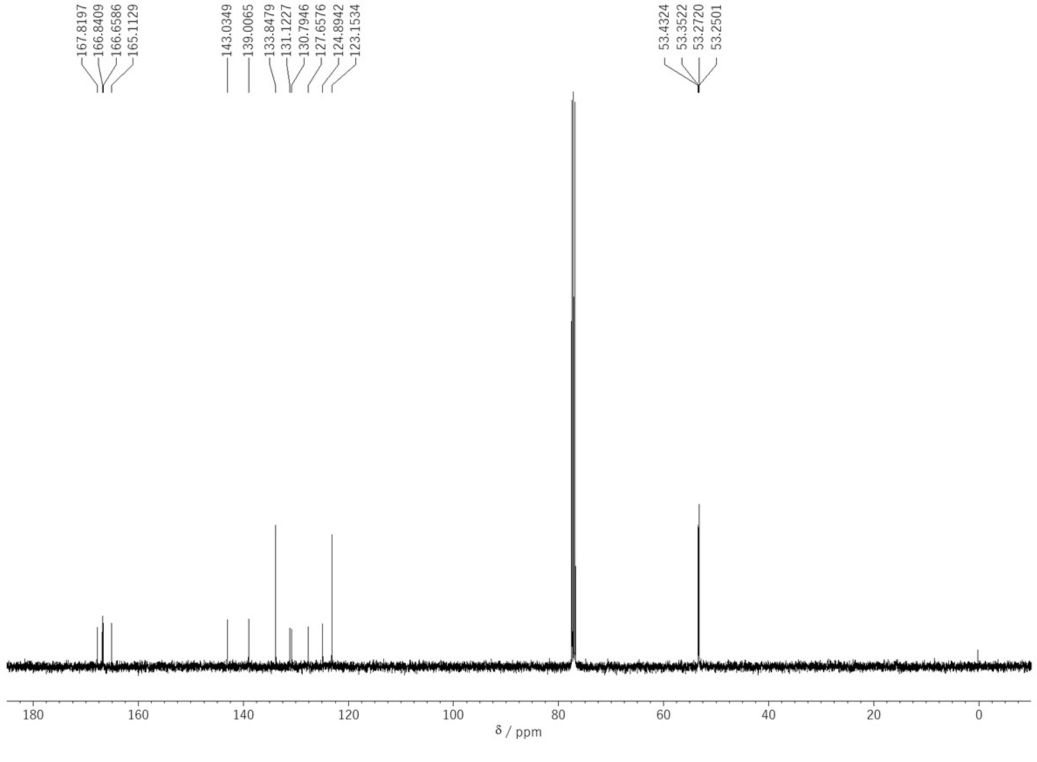


tetramethyl benzo[*b*]thiophene-4,5,6,7-tetracarboxylate (**5**)

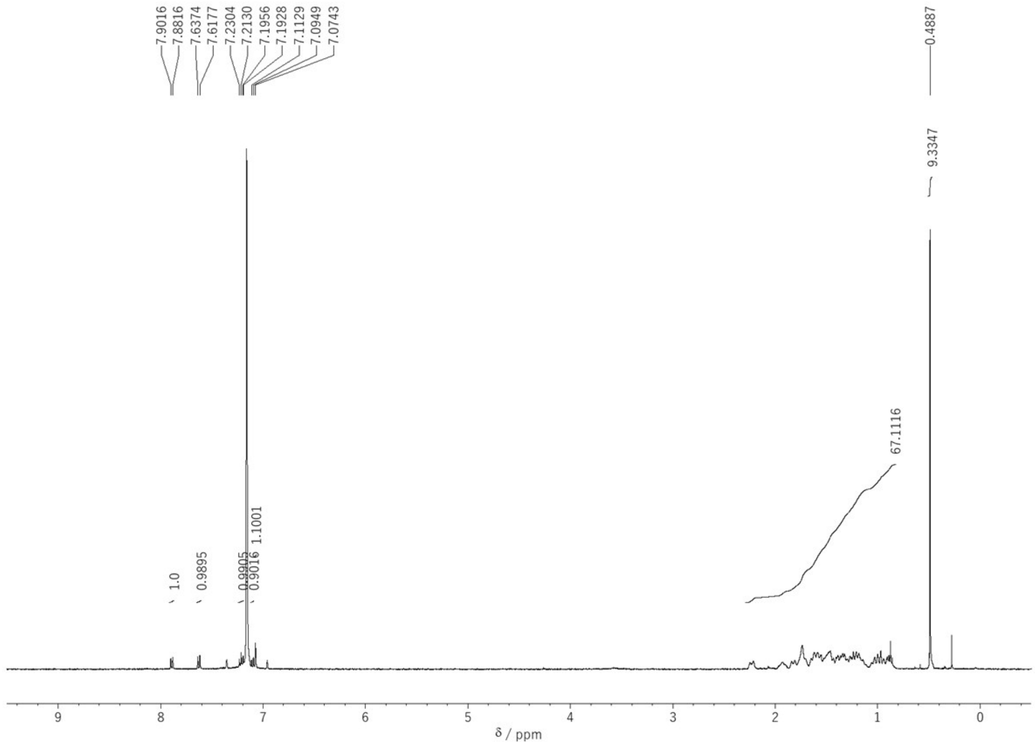
^{1}H NMR



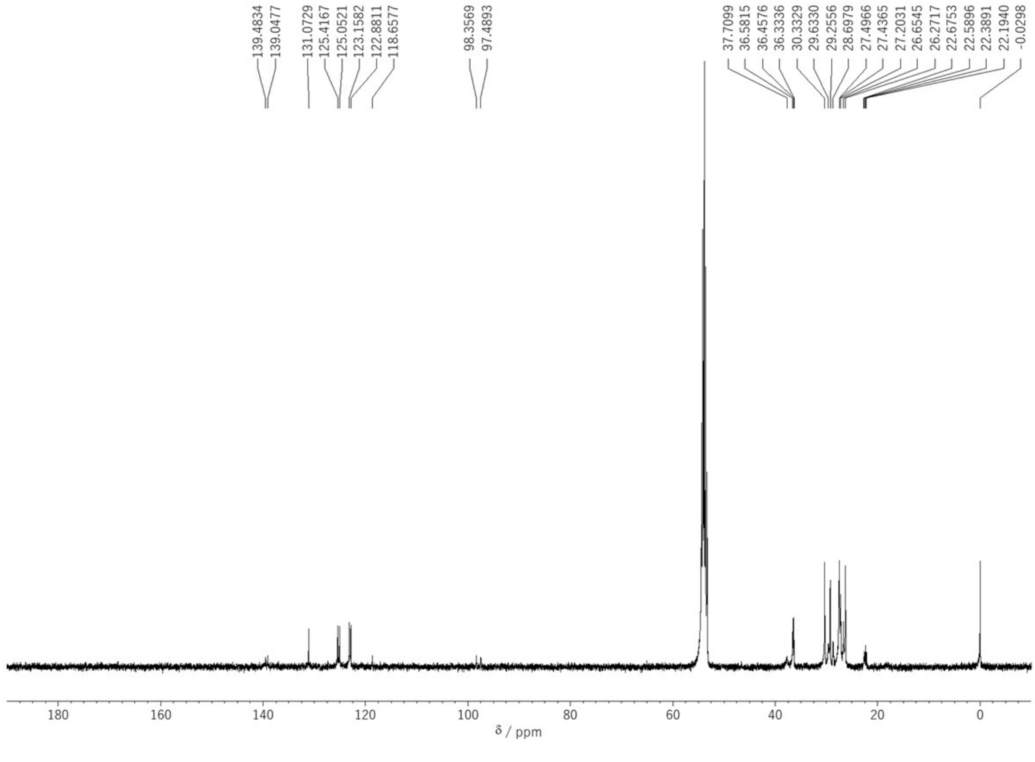
^{13}C NMR



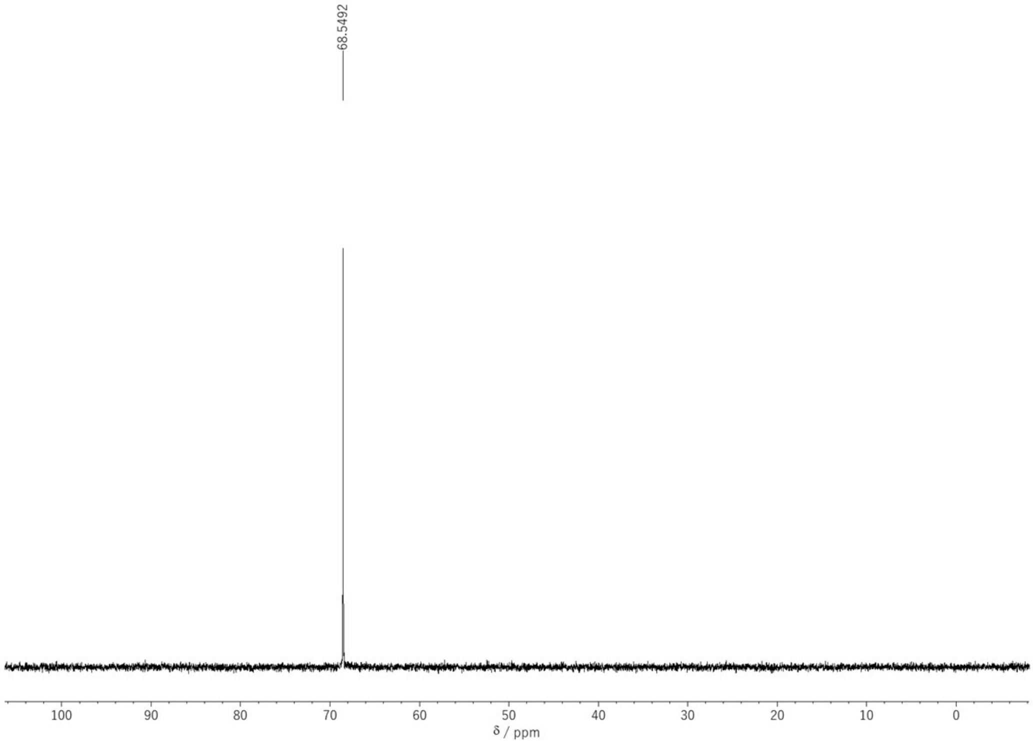
^{1}H NMR (**6**)



^{13}C NMR (**6**)



^{31}P NMR (**6**)



5. DFT study

Cartesian coordinates of all optimized structures (B3LYP 6-31G(d))

Thiophene			
C	0.012	1.244	0.000
C	1.273	0.715	0.000
C	1.273	-0.715	0.000
C	0.012	-1.244	0.000
S	-1.200	0.000	0.000
H	-0.281	2.285	0.000
H	2.173	1.320	0.000
H	2.173	-1.320	0.000
H	-0.281	-2.285	0.000

2,3-Thiophyne			
C	-0.565	-1.065	0.000
C	-1.515	-0.072	0.000
C	-0.718	1.088	0.000
C	0.518	1.328	0.000
S	1.062	-0.335	0.000
H	-0.715	-2.140	0.000
H	-2.591	-0.173	0.000

References

1 Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, 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, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

2 J. I. Tietz, A. J. Seed and P. Sampson, *Org. Lett.,* 2012, **14**, 5058.

3 M. A. Bennett and E. Wenger, *Organometallics,* 1995, **14**, 1267.

4 M. A. Bennett, T. W. Hambley, N. K. Roberts and G. B. Robertson, *Organometallics,* 1985, **4**, 1992.

5 M. A. Bennett, J. A. Johnson and A. C. Willis, *Organometallics,* 1996, **15**, 68.

6 G. M. Sheldrick, *Acta Crystallogr. Sect. A,* 2008, **64**, 112.

7 L. J. J. Farrugia, *Appl. Cryst.,* 2012, **45**, 849.