Supplementary Information for

Synthesis, crystal structure and reactivity of $\eta^2$–thiophyne Ni complexes

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1. Experimental procedures

General

All manipulations were performed under N\textsubscript{2} either using standard Schlenk techniques or in glovebox otherwise noted. Toluene, Et\textsubscript{2}O, and MeCN were dried and deoxygenated by Glass Counter Solvent Dispensing System (Nikko Hansen & Co., Ltd.). DCM was distilled over CaH\textsubscript{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 (\textsuperscript{1}H NMR), at 100 MHz (\textsuperscript{13}C NMR), and at 162 MHz (\textsuperscript{31}F NMR) in 5 mm NMR tubes. \textsuperscript{1}H NMR chemical shifts were reported in ppm relative to the resonance in TMS (δ 0.00 CDCl\textsubscript{3}) or the residual solvent signals; δ 7.26 for CDCl\textsubscript{3}, δ 7.16 for C\textsubscript{6}D\textsubscript{6}, δ 5.32 for CD\textsubscript{2}Cl\textsubscript{2}, and δ 3.58 for THF-d\textsubscript{8}. \textsuperscript{13}C NMR chemical shifts were reported in ppm relative to the residual solvent signals; δ 77.2 for CDCl\textsubscript{3}, δ 128.1 for C\textsubscript{6}D\textsubscript{6}, δ 53.8 for CD\textsubscript{2}Cl\textsubscript{2}, and δ 67.2 for THF-d\textsubscript{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. \textsuperscript{1}

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

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

![Chemical structure](image)

(3-Bromothiophen-2-yl)boronic acid was prepared from 3-bromothiophene (815 mg, 5.0 mmol) according to the literature procedure.\textsuperscript{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 (SCHCH, d, $J$ = 4.9 Hz, 1H), 7.51 (SCH, 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)

![Structure](image)

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$_2$S ([M+H]$^+$) 339.0220, found 339.0212.

Preparation of complex 2a

![Complex](image)

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$_2$Cl$_2$, 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$_2$Cl$_2$, 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, $J_{C-P} = 7.3$ Hz), 135.4 (dd, $J_{C-P} = 2.2, 5.1$ Hz), 166.4 (NiC, dd, $J_{C-P} = 37.4, 85.5$ Hz); $^{31}$P NMR (162 MHz, CD$_2$Cl$_2$, 21 °C) $\delta$ 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

\[
\begin{align*}
\text{Ni(cod)$_2$} & + \begin{array}{c}
\text{Ni-C-P} \\
\text{Br} \\
\text{Bpin}
\end{array} \\
toluene, 60 ^\circ C, 24 h
\end{align*}
\]

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$_2$Cl$_2$ solution layered with MeCN.

m.p. 214 °C; $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 21 °C) $\delta$ 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$_2$Cl$_2$, 21 °C) $\delta$ 14.2, 14.3, 19.6, 19.7, 19.8, 19.9, 22.7, 23.1, 23.3, 23.5, 23.7, 24.3, 24.8, 25.0, 26.2, 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, $J_{C-P} = 6.6$ Hz), 149.4 (d, $J_{C-P} = 4.7$ Hz), 168.1 (NiC, dd, $J_{C-P} = 33.0, 86.4$ Hz); $^{31}$P NMR (162 MHz, CD$_2$Cl$_2$, 21 °C) $\delta$ 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$_2$ ($\delta_P$ 85.5 ppm in THF-$d_8$), which might be formed through 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

A mixture of 2a (154 mg, 0.2 mmol) and KOtBu (112 mg, 1.0 mmol) in THF (5.0 mL) was stirred at room temperature for 30 seconds under N2. 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 Et2O 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 Et2O solution.

m.p. 112 °C (decomp.); 1H NMR (400 MHz, C6D6, 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); 13C NMR (100 MHz, C6D6, 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, JCP = 1.8, 9.7 Hz), 144.3 (d, JCP = 6.2 Hz), 149.6 (NiCS, dd, JCP = 10.2, 78.7 Hz), 156.6 (NiCCH, dd, JCP = 12.4, 58.3 Hz); 31P NMR (162 MHz, C6D6, 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

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 Et2O/THF solution.

m.p. 137 °C (decomp.); 1H NMR (400 MHz, THF-d8, 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); 13C NMR (100 MHz, THF-d8, 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, $J_{CP} = 8.8, 11.7$ Hz), 152.6 (NiC, dd, $J_{CP} = 11.7, 71.8$ Hz), 154.9 (NiCS, dd, $J_{CP} = 9.5, 87.5$ Hz), 166.8 (d, $J_{CP} = 4.4$ Hz); $^{31}$P NMR (162 MHz, THF-$d_8$, 21 °C) $\delta$ 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**

![Chemical structure](image)

To a solution of 3a (5.6 mg, 0.01 mmol) in C$_6$D$_6$ (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$_6$D$_6$, 21 °C) $\delta$ 0.64 (m, 1H), 1.01-2.47 (m, 71.7H), 2.91 (m, 1H), 6.82 (SCHCH, d, $J = 4.4$ Hz, 1H), 7.39 (SCH, d, $J = 3.6$ Hz, 1H); $^{13}$C NMR (100 MHz, C$_6$D$_6$, 21 °C) $\delta$ 20.4, 20.6, 20.7, 20.8, 21.0, 23.3, 23.5, 26.1, 26.5, 27.0, 27.3, 27.4, 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, 30.4, 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, $J_{CP} = 3.9$ Hz), 130.7 (dd, $J_{CP} = 2.2, 6.6$ Hz), 137.0 (NiC, dd, $J_{CP} = 36.6, 86.6$ Hz), 139.9 (d, $J_{CP} = 2.7$ Hz); $^{31}$P NMR (162 MHz, C$_6$D$_6$, 21 °C) $\delta$ 67.6 (d, $J = 29.3$ Hz), 75.2 (d, $J = 29.4$ Hz); Anal. calcd for C$_{31}$H$_{53}$INiP$_2$S: C 52.79, H 7.57; found: C 53.02, H 7.58%.

**Reaction of complex 3b with MeI**

![Chemical structure](image)

To a solution of 3b (6.2 mg, 0.01 mmol) in C$_6$D$_6$ (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$_2$O vapor diffusion into DCM solution.
m.p. 212 °C (decomp.); 1H NMR (400 MHz, CD2Cl2) 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); 31P NMR (162 MHz, CD2Cl2) δ 68.3 (d, J = 29.3 Hz), 75.7 (d, J = 29.3 Hz); 13C NMR (100 MHz, CD2Cl2) δ 19.4, 20.6, 20.8, 21.0, 23.3, 23.5, 23.7, 25.6, 26.0, 26.1, 26.2, 26.4, 26.5, 26.6, 26.1, 26.2, 26.4, 26.5, 26.7, 26.8, 27.2, 27.3, 27.4, 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 = 6.6 Hz), 147.0 (NiC, dd, J = 34.5, 86.4 Hz), 147.6 (d, J = 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

To a solution of 3a (5.6 mg, 0.01 mmol) in C6D6 (1.0 mL), I2 (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: 1H NMR (400 MHz, CDCl3, 21 °C) δ 6.95 (SCHC, d, J = 5.5 Hz, 1H), 7.34 (SCH, d, J = 5.5 Hz, 1H); 13C NMR (100 MHz, CDCl3, 21 °C) δ 84.1, 93.9, 133.74, 135.89; HRMS (APCI) m/z calcd for C4H2I2S ([M]+) 335.7971, found 335.7971.

2,3,5-triiodothiophene: 1H NMR (400 MHz, CDCl3, 21 °C) δ 7.06 (s, 1H); 13C NMR (100 MHz, CD6, 21 °C) δ 78.8, 87.7, 94.4, 144.27; HRMS (APCI) m/z calcd for C4H1I3S ([M]+) 461.6928, found 461.6927.

Reaction of complex 3a with dimethyl acetylenedicarboxylate

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 H2O, extracted with EtOAc, dried over Na2SO4, 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.

tenethyl benzo[b]thiophene-4,5,6,7-tetracarboxylate (5): $^1$H NMR (400 MHz, CDCl$_3$, 21 °C) $\delta$ 3.91 (methyl, s, 3H), 3.95 (methyl, s, 3H), 4.00 (methyl, s, 3H), 4.03 (methyl, s, 3H), 7.66 (SCHCH, d, $J = 5.7$ Hz, 1H), 7.80 (SCH, d, $J = 5.7$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, 21 °C) $\delta$ 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$_8$S ([M+H]$^+$) 367.0482 found 367.0486.

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

![Reaction of complex 3b with bis(trimethylsilyl)acetylene](image)

To a solution of 3b (5.6 mg, 0.01 mmol) in C$_6$D$_6$ (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$_6$D$_6$ 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$_6$D$_6$, 21 °C) $\delta$ 0.49 (methyl, s, 9H), 0.86-2.25 (m, 67H), 7.07 (SCH, 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$_6$D$_6$) $\delta$ 68.5; $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$, 21 °C) $\delta$ -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 C₆D₆ 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 ¹H NMR spectra (Figure S1, left). The precipitate was collected and washed with hexane; a peak at δₚ 78.2 ppm (CDCl₃) suggested the formation of Ni(dcpe)(OCOCF₃)₂.⁴

A similar experiment was conducted with complex 3b (eq. S2), and the peaks correspond to 3b disappeared in ¹H NMR and benzo[b]thiophene was detected (Figure S1, right).

\[ \text{3a} + \text{TFA} \rightarrow \text{thiophene} \]

\[ \text{3b} + \text{TFA} \rightarrow \text{benzo[b]thiophene} \]

Fig. S1 ¹H NMR spectra in C₆D₆ 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 C₆D₆. 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 δₚ = 46.3 ppm was detected after 1 day, that might be assigned to Ni(dcpe)₂ (Figure S3). 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 C₆D₆ at 23 °C. Spectra from 2.5 ppm to 6.0 ppm were omitted for clarity.](image1)

![Fig. S3 ³¹P NMR spectra of 3a in C₆D₆ at 23 °C.](image2)
Fig. S4 $^1$H NMR spectra of 3b in C$_6$D$_6$ 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$_6$D$_6$ 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. 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. 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

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<td>c</td>
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<td>R factor (I &gt; 2.0σ(I))</td>
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<td>R factor (all data)</td>
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<td>Goodness of fit on F^2</td>
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**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

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<td>c = 16.282(4)</td>
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<td>Z</td>
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</tr>
<tr>
<td>Crystal size [mm]</td>
<td>0.190 × 0.040 × 0.020</td>
</tr>
<tr>
<td>R factor (I &gt; 2.0σ(I))</td>
<td>R1 = 0.0766, wR2 = 0.1297</td>
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<tr>
<td>R factor (all data)</td>
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<tr>
<td>Goodness of fit on F^2</td>
<td>1.059</td>
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</table>
**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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Empirical formula</td>
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<tr>
<td>Formula weight</td>
<td>563.41</td>
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<tr>
<td>Measurement temperature [K]</td>
<td>173(2)</td>
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<tr>
<td>Crystal system</td>
<td>monoclinic</td>
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<tr>
<td>Space group</td>
<td>P2_1/n (No. 14)</td>
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<tr>
<td>Unit cell parameter [Å, deg.]</td>
<td>a = 9.9110(16)</td>
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<tr>
<td></td>
<td>b = 16.711(3) β = 92.402(10)</td>
</tr>
<tr>
<td></td>
<td>c = 18.048(2)</td>
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<tr>
<td>Cell volume [Å^3]</td>
<td>2986.6(8)</td>
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<tr>
<td>Z</td>
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<tr>
<td>Crystal size [mm]</td>
<td>0.080 × 0.070 × 0.060</td>
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<td>R factor (I &gt; 2.0σ(I))</td>
<td>R1 = 0.0950, wR2 = 0.1638</td>
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<tr>
<td>R factor (all data)</td>
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<tr>
<td>Goodness of fit on F^2</td>
<td>1.047</td>
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**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

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<td>1354.98</td>
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<tr>
<td>Crystal system</td>
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</tr>
<tr>
<td>Space group</td>
<td>C2/c (No. 15)</td>
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<tr>
<td>Unit cell parameter [Å, deg.]</td>
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<td></td>
<td>b = 12.095(2)</td>
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<td></td>
<td>c = 26.019(5)</td>
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<td>Cell volume [Å³]</td>
<td>14328(4)</td>
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<td>Z</td>
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<tr>
<td>Crystal size [mm]</td>
<td>0.190 × 0.110 × 0.010</td>
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<tr>
<td>R factor (I &gt; 2.0σ(I))</td>
<td>R1 = 0.0619, wR2 = 0.0973</td>
</tr>
<tr>
<td>R factor (all data)</td>
<td>R1 = 0.1460, wR2 = 0.1335</td>
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<tr>
<td>Goodness of fit on F^2</td>
<td>1.122</td>
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</table>
**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

<table>
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<tr>
<th>Property</th>
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<tr>
<td>Empirical formula</td>
<td>C$<em>{37}$H$</em>{59}$NiP$_2$S</td>
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<tr>
<td>Formula weight</td>
<td>783.49</td>
</tr>
<tr>
<td>Measurement temperature [K]</td>
<td>173(2)</td>
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<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P\bar{1}$ (No. 2)</td>
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<tr>
<td>Unit cell parameter [Å, deg.]</td>
<td>$a = 8.481(11)$</td>
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<td></td>
<td>$\alpha = 96.001(14)$</td>
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<tr>
<td></td>
<td>$b = 11.052(15)$</td>
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<tr>
<td></td>
<td>$\beta = 91.24(3)$</td>
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<td></td>
<td>$c = 21.03(3)$</td>
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<td></td>
<td>$\gamma = 101.865(19)$</td>
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<td>Cell volume [Å$^3$]</td>
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<td>$R$ factor ($I &gt; 2.0\sigma(I)$)</td>
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<td>$R$ factor (all data)</td>
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<tr>
<td>Goodness of fit on $F^2$</td>
<td>1.087</td>
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</table>
**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

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</tr>
<tr>
<td>Space group</td>
<td>P-1 (No. 2)</td>
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<tr>
<td>Unit cell parameter [Å, deg.]</td>
<td>a = 12.354(9)  ( \alpha = 75.82(2) )</td>
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<tr>
<td></td>
<td>b = 16.268(11) ( \beta = 88.78(3) )</td>
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<tr>
<td></td>
<td>c = 20.938(14) ( \gamma = 78.187(16) )</td>
</tr>
<tr>
<td>Cell volume [Å³]</td>
<td>3992(5)</td>
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<td>Z</td>
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<td>Crystal size [mm]</td>
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<tr>
<td>R factor ((I &gt; 2.0\sigma(I)))</td>
<td>( R1 = 0.0882, wR2 = 0.1597 )</td>
</tr>
<tr>
<td>R factor (all data)</td>
<td>( R1 = 0.1921, wR2 = 0.2153 )</td>
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<tr>
<td>Goodness of fit on ( F^2 )</td>
<td>1.028</td>
</tr>
</tbody>
</table>
**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

<table>
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<th>Value</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
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</tr>
<tr>
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<td>173(2)</td>
</tr>
<tr>
<td>Crystal system</td>
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</tr>
<tr>
<td>Space group</td>
<td>P−1 (No. 2)</td>
</tr>
<tr>
<td>Unit cell parameter [Å, deg.]</td>
<td>(a = 10.9627(2)) (\alpha = 82.1370(10)) (b = 15.9681(3)) (\beta = 82.6670(10)) (c = 35.1062(4)) (\gamma = 83.181(2))</td>
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<tr>
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<td>Crystal size [mm]</td>
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<td>(R) factor ((I &gt; 2.0\sigma(I)))</td>
<td>(R1 = 0.0632, wR2 = 0.1585)</td>
</tr>
<tr>
<td>(R) factor (all data)</td>
<td>(R1 = 0.0838, wR2 = 0.1722)</td>
</tr>
<tr>
<td>Goodness of fit on (F^2)</td>
<td>1.010</td>
</tr>
</tbody>
</table>
4. Copy of NMR spectra

$^1$H NMR (2a)

$^{13}$C NMR (2a)
$^{31}$P NMR (2a)
$^1$H NMR (2b)

$^{13}$C NMR (2b)
$^{31}\text{P NMR (2b)}$
\( ^1H \text{NMR (3a)} \)
$^{31}$P NMR (3a)
$^1$H NMR (3b)

$^{13}$C NMR (3b)
$^{31}$P NMR (3b)
$^1$H NMR (4a)

$^{13}$C NMR (4a)
$^{31}$P NMR (4a)
$^1$H NMR (4b)

$^{13}$C NMR (4b)
$^{31}$P NMR (4b)
2,3-diiodothiophene (\(^1\)H NMR)

\[ \text{S} \quad \text{I} \quad \text{I} \]

\(^{13}\)C NMR
2,3,5-triiodothiophene (\(^1\)H NMR)

\[
\begin{array}{c}
\text{I} \\
\text{S} \\
\text{I} \\
\end{array}
\]

\(^1\)C NMR

\[
\begin{array}{c}
\text{I} \\
\text{S} \\
\text{I} \\
\end{array}
\]
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))

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References


