

Supporting Information

**Base-Promoted Decarboxylative Condensation of Cinnamitriles
and Phenylacetic Acids with Sulfur: Direct Access to
Azatrithiapentalenes**

Ngoc Lan Chu,^b Quang Huy Tran,^b Quynh Trang Tran,^b Thai Thanh Thu Bui,^b Dinh Hung
Mac^{b,*} Quoc Anh Ngo,^{*,c} Quoc Nghi Pham,^c Le Anh Nguyen,^{d,e} Pascal Retailleau^a

and Thanh Binh Nguyen^{a,*}

^a Institut de Chimie des Substances Naturelles, CNRS UPR 2301, Université Paris-Sud, Université Paris-Saclay, 1, av de la Terrasse, 91198 Gif-sur-Yvette France.

^b Faculty of chemistry, VNU University of Science, Vietnam National University in Hanoi, 19 Le Thanh Tong, Hanoi, Viet Nam

^c Institut de Chimie Moléculaire et des Matériaux d'Orsay, CNRS, UMR 8182, Université Paris-Saclay, 17, avenue des Sciences, 91400 Orsay, France

^d Graduate University of Science and Technology, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam

^e Institute of Chemistry, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam

Contents

General Information	S2
Representative protocol for the synthesis of 2,6-diphenyl-4H-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3a)	S2
Characterization of products	S2
Crystallographic experimental section	S14
Copies of ¹ H and ¹³ C spectra	S19

General Information

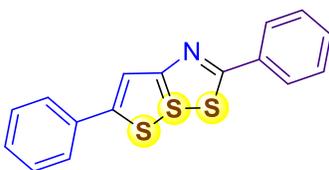
Reagents (S₈, DMSO, as well as other bases) were obtained from commercial supplier and used without further purification. Analytical thin layer chromatography (TLC) was purchased from Merck KGaA (silica gel 60 F254). Visualization of the chromatogram was performed by UV light (254 nm) or KMnO₄ or vanillin stains. Flash column chromatography was carried out using kieselgel 35-70 μm particle sized silica gel (230-400 mesh). NMR Chemical shifts are reported in (δ) ppm relative to tetramethylsilane (TMS) with the residual solvent as internal reference (CDCl₃, δ 7.26 ppm for 1 H and δ 77.0 ppm for ¹³C). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. Aluminum or copper blocks were used for heating the reaction tubes. Mass spectra were determined on an X500R-QTOF (SCIEX) machine.

Representative protocol for the synthesis of 6-phenyl-2-(pyridin-4-yl)-4 λ⁴-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3a)

A mixture of cinnamionitrile **1a** (0.5 mmol, 65 mg), elemental sulfur (2 mmol, 64 mg), phenyl acetic acid **2a** (0.6 mmol, 1.2 eq) and DABCO (1 mmol, 112 mg, 2eq) in DMSO (3 mmol, 0.2 mL) in a 7-mL test tube closed with a septum rubber (mounted with an inflated rubber balloon) was heated at 80 °C with a heating block for 16 h. The reaction mixture cooled down to room temperature was purified by column flash chromatography on silica gel (solvent hexane/ ethyl acetate: 49/1 to 19/1) to give the desired product as an orange product (orange solid, 55 mg, 35%).

Characterization of products

2,6-Diphenyl-4λ⁴-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3a)



Orange solid (55 mg, 35%).

¹H NMR (500 MHz, CDCl₃) δ 8.52 (s, 1H), 8.34 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.92 – 7.85 (m, 2H), 7.58 – 7.46 (m, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 196.2, 188.0, 177.4, 138.5, 136.52, 132.5, 131.3, 129.4 (2C), 129.3 (2C), 128.9 (2C), 127.7 (2C), 127.0.

HRMS (QTOF, ESI+) *m/z* calcd for [M+Na]⁺ C₁₆H₁₁NNaS₃⁺ 335.9951. Found: 335.9957.

Elemental Analysis Calculated for C₁₆H₁₁NS₃: C, 61.31%; H, 3.54%; N, 4.47%. Found: C, 61.40; H, 3.58; N, 4.50.

2-Phenyl-6-(*p*-tolyl)-4I4-[1,2]dithiolo[5,1-*e*][1,2,4]dithiazole (3b)



Orange solid (49 mg, 30%).

^1H NMR (500 MHz, CDCl_3) δ 8.50 (s, 1H), 8.34 (dd, $J = 8.5, 1.0$ Hz, 2H), 7.78 (d, $J = 8.2$ Hz, 2H), 7.54 (t, $J = 7.2$ Hz, 1H), 7.49 (t, $J = 7.3$ Hz, 2H), 7.30 (d, $J = 7.8$ Hz, 2H), 2.43 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 196.0, 187.8, 177.3, 141.9, 138.5, 133.6, 132.3, 130.0 (2C), 129.2 (2C), 128.8 (2C), 127.5 (2C), 126.5, 21.6.

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{17}\text{H}_{13}\text{NNaS}_3^+$ 350.0108. Found: 350.0112.

6-(4-Isopropylphenyl)-2-phenyl-4I4-[1,2]dithiolo[5,1-*e*][1,2,4]dithiazole (3c)



Orange solid (57 mg, 32%).

^1H NMR (500 MHz, CDCl_3) δ 8.50 (s, 1H), 8.34 (dd, $J = 8.5, 1.3$ Hz, 2H), 7.82 (d, $J = 8.0$ Hz, 2H), 7.54 (t, $J = 7.1$ Hz, 1H), 7.49 (t, $J = 7.5$ Hz, 2H), 2.99 (hept, $J = 7.0$ Hz, 1H), 1.30 (d, $J = 6.9$ Hz, 6H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.9, 187.6, 177.1, 152.6, 138.4, 133.8, 132.2, 129.0 (2C), 128.6 (2C), 127.5 (2C), 127.3 (2C), 126.3, 34.1, 23.7 (2C).

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{19}\text{H}_{17}\text{NNaS}_3^+$ 378.0421. Found: 378.0426.

6-(3-Methoxyphenyl)-2-phenyl-4I4-[1,2]dithiolo[5,1-*e*][1,2,4]dithiazole (3d)



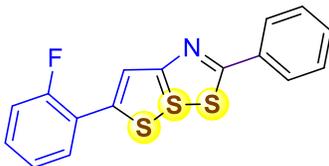
Orange solid (48 mg, 28%).

^1H NMR (500 MHz, CDCl_3) δ 8.51 (s, 1H), 8.34 (dd, $J = 8.6, 1.1$ Hz, 2H), 7.55 (t, $J = 7.3$ Hz, 1H), 7.52 – 7.44 (m, 3H), 7.44 – 7.37 (m, 2H), 7.05 (ddd, $J = 8.2, 2.6, 1.0$ Hz, 1H), 3.90 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 196.0, 187.8, 177.1, 160.2, 138.4, 137.7, 132.4, 130.3, 129.2 (2C), 128.8 (2C), 127.0, 120.0, 117.0, 112.9, 55.7.

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{15}\text{H}_{10}\text{N}_2\text{NaS}_3^+$ 366.0057. Found: 366.0062.

6-(2-Fluorophenyl)-2-phenyl-4H-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3e)



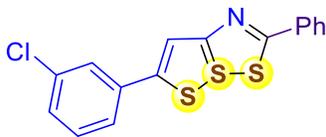
Orange solid (53 mg, 32%).

^1H NMR (500 MHz, CDCl_3) δ 8.59 (d, $J = 1.5$ Hz, 1H), 8.35 (dd, $J = 8.5, 1.5$ Hz, 2H), 7.80 (td, $J = 7.7, 1.8$ Hz, 1H), 7.54 (t, $J = 7.2$ Hz, 1H), 7.52 – 7.46 (m, 3H), 7.31 – 7.27 (m, 1H), 7.26 – 7.21 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 196.3, 187.9, 170.4 (d, $J = 2.9$ Hz, 1C), 158.9 (d, $J = 254.2$ Hz, 1C), 138.4, 132.5 (d, $J = 8.8$ Hz, 1C), 132.4, 131.5 (d, $J = 1.9$ Hz, 1C), 130.3 (d, $J = 8.6$ Hz, 1C), 129.2 (2C), 128.8 (2C), 124.9 (d, $J = 3.8$ Hz, 1C), 124.6 (d, $J = 11.5$ Hz, 1C), 117.0 (d, $J = 22.4$ Hz, 1C).

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{16}\text{H}_{10}\text{FNNaS}_3^+$ 353.9857. Found: 353.9863.

6-(3-Chlorophenyl)-2-phenyl-4H-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3f)



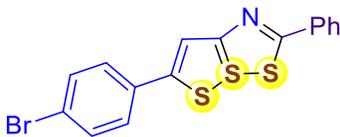
Orange solid (47 mg, 27%).

^1H NMR (500 MHz, CDCl_3) δ 8.48 (s, 1H), 8.32 (d, $J = 7.7$ Hz, 2H), 7.85 (s, 1H), 7.74 (d, $J = 7.6$ Hz, 1H), 7.55 (t, $J = 7.3$ Hz, 1H), 7.51 – 7.39 (m, 4H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.5, 188.0, 176.1, 138.4, 137.9, 135.3, 132.6, 130.9, 130.5, 129.2 (2C), 128.9 (2C), 127.6, 126.9, 125.7.

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{16}\text{H}_{10}\text{ClNNaS}_3^+$ 369.9562. Found: 369.9568.

6-(4-Bromophenyl)-2-phenyl-4H-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3g)



Orange solid (49 mg, 25%).

^1H NMR (500 MHz, CDCl_3) δ 8.49 (s, 1H), 8.32 (dd, $J = 8.5, 1.4$ Hz, 2H), 7.75 (d, $J = 8.5$ Hz, 2H), 7.63 (d, $J = 8.6$ Hz, 2H), 7.55 (t, $J = 7.3$ Hz, 1H), 7.49 (t, $J = 7.3$ Hz, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.5, 188.0, 176.5, 137.9, 135.6, 132.6, 132.5 (2C), 129.2 (2C), 129.0 (2C), 128.9 (2C), 126.6, 125.8.

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{16}\text{H}_{10}\text{BrNNaS}_3^+ 413.9056$. Found: 413.9066.

4-(2-Phenyl-4(1,2)dithiolo[5,1-e][1,2,4]dithiazol-6-yl)benzonitrile (3h)



Orange solid (54 mg, 32%).

^1H NMR (500 MHz, CDCl_3) δ 8.55 (s, 1H), 8.32 (d, $J = 7.1$ Hz, 2H), 7.98 (d, $J = 8.4$ Hz, 2H), 7.79 (d, $J = 8.4$ Hz, 2H), 7.58 (t, $J = 7.3$ Hz, 1H), 7.51 (t, $J = 7.5$ Hz, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.3, 188.2, 175.8, 141.1, 137.4, 133.0 (2C), 132.9, 129.2 (2C), 129.0 (2C), 128.2 (2C), 127.2, 118.4, 114.2.

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{17}\text{H}_{10}\text{N}_2\text{NaS}_3^+ 360.9904$. Found: 360.9910.

Methyl-4-(2-phenyl-4(1,2)dithiolo[5,1-e][1,2,4]dithiazol-6-yl)benzoate (3i)



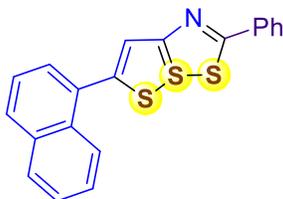
Orange solid (54 mg, 28%).

^1H NMR (500 MHz, CDCl_3) δ 8.57 (s, 1H), 8.33 (dd, $J = 8.6, 1.2$ Hz, 2H), 8.16 (d, $J = 8.5$ Hz, 2H), 7.95 (d, $J = 8.5$ Hz, 2H), 7.56 (t, $J = 7.2$ Hz, 1H), 7.50 (t, $J = 7.5$ Hz, 2H), 3.97 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.7, 188.0, 176.2, 166.5, 140.6, 137.9, 132.6, 132.1, 130.5 (2C), 129.2 (2C), 128.9 (2C), 127.6 (2C), 127.3, 52.6.

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{18}\text{H}_{13}\text{NNaO}_2\text{S}_3^+ 394.0006$. Found: 394.0012.

6-(Naphthalen-2-yl)-2-phenyl-4(1,2)dithiolo[5,1-e][1,2,4]dithiazole (3j)



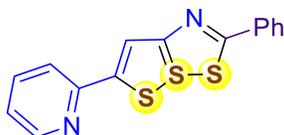
Orange solid (55 mg, 30%).

^1H NMR (500 MHz, CDCl_3) δ 8.67 (s, 1H), 8.41 (s, 1H), 8.36 (d, $J = 7$ Hz, 2H), 7.99 – 7.95 (m, 3H), 7.93 – 7.87 (m, 1H), 7.61 – 7.52 (m, 3H), 7.50 (t, $J = 7.3$ Hz, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.9, 187.8, 177.3, 138.4, 134.6, 133.7, 133.3, 132.4, 129.2, 129.2 (2C), 129.1, 128.8 (2C), 128.0 (2C), 127.9, 127.2, 127.0, 124.4.

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{20}\text{H}_{13}\text{NNaS}_3^+$ 386.0108. Found: 386.0112.

2-Phenyl-6-(pyridin-2-yl)-4I4-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3k)



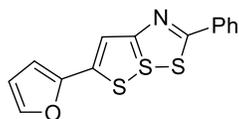
Orange solid (38 mg, 22%).

^1H NMR (500 MHz, CDCl_3) δ 9.13 (s, 1H), 8.72 (d, $J = 4.8$ Hz, 1H), 8.55 (s, 1H), 8.33 (d, $J = 7.1$ Hz, 2H), 8.15 (d, $J = 8.0$ Hz, 1H), 7.57 (t, $J = 7.2$ Hz, 1H), 7.50 (t, $J = 7.5$ Hz, 2H), 7.44 (dd, $J = 8.0, 4.8$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.2, 188.0, 175.0, 151.7, 148.1, 137.6, 135.0, 133.3, 132.8, 129.2 (2C), 129.0 (2C), 126.7, 123.9.

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{15}\text{H}_{10}\text{N}_2\text{NaS}_3^+$ 336.9904. Found: 336.9909.

6-(Furan-2-yl)-2-phenyl-4I4-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3l)



Orange solid (38 mg, 25%).

^1H NMR (500 MHz, CDCl_3) δ 8.52 (s, 1H), 8.30 (d, $J = 7.0$ Hz, 1H), 7.64 (d, $J = 1.7$ Hz, 1H), 7.55 (t, $J = 7.3$ Hz, 1H), 7.49 (t, $J = 7.4$ Hz, 1H), 7.12 (d, $J = 3.5$ Hz, 1H), 6.59 (dd, $J = 3.5, 1.7$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 193.2, 187.1, 166.3, 150.2, 145.3, 137.1, 132.4, 129.0 (2C), 128.8 (2C), 123.9, 114.1, 113.2

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{14}\text{H}_9\text{NNaOS}_3^+$ 325.9744. Found: 325.9748.

2-Phenyl-6-(thiophen-2-yl)-4I4-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3m)



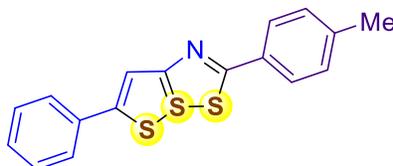
Orange solid (54 mg, 34%).

^1H NMR (500 MHz, CDCl_3) δ 8.44 (s, 1H), 8.32 (dd, $J = 8.5, 1.1$ Hz, 2H), 7.93 (dd, $J = 2.9, 1.4$ Hz, 1H), 7.58 – 7.53 (m, 2H), 7.49 (t, $J = 7.3$ Hz, 2H), 7.46 – 7.44 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.2, 187.7, 171.7, 138.9, 138.0, 132.5, 129.2 (2C), 128.9 (2C), 127.4, 126.8, 126.4, 126.3.

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{14}\text{H}_9\text{NNaS}_4^+$ 341.9515. Found: 341.9522.

6-Phenyl-2-(p-tolyl)-4I4-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3n)



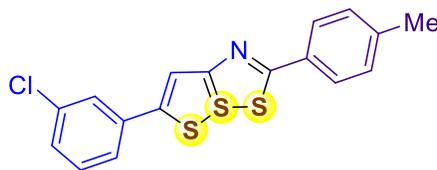
Orange solid (62 mg, 38%).

^1H NMR (500 MHz, CDCl_3) δ 8.50 (s, 1H), 8.24 (d, $J = 8.2$ Hz, 2H), 7.91 – 7.85 (m, 2H), 7.52 – 7.47 (m, 3H), 7.29 (d, $J = 8.0$ Hz, 2H), 2.43 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.8, 187.9, 177.4, 143.3, 136.6, 135.8, 131.1, 129.6 (2C), 129.3 (2C), 129.2 (2C), 127.6 (2C), 126.6, 21.8.

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{17}\text{H}_{13}\text{NNaS}_3^+$ 350.0108. Found: 350.0116.

6-(3-Chlorophenyl)-2-(p-tolyl)-4I4-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3o)



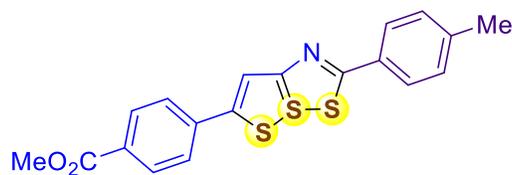
Orange solid (61 mg, 34%).

^1H NMR (500 MHz, CDCl_3) δ 8.48 (s, 1H), 8.22 (d, $J = 8.3$ Hz, 2H), 7.87 (t, $J = 1.9$ Hz, 1H), 7.76 (dt, $J = 7.4, 1.6$ Hz, 1H), 7.49 – 7.43 (m, 1H), 7.43 (t, $J = 7.7$ Hz, 1H), 7.30 (d, $J = 7.9$ Hz, 2H), 2.43 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.3, 188.0, 176.3, 143.6, 138.6, 135.3, 135.2, 130.8, 130.5, 129.7 (2C), 129.2 (2C), 127.6, 126.6, 125.7, 21.9.

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{17}\text{H}_{12}\text{ClNNaS}_3^+$ 383.9718. Found: 383.9726.

Methyl 4-(2-(p-tolyl)-4I4-[1,2]dithiolo[5,1-e][1,2,4]dithiazol-6-yl)benzoate (3p)



Orange solid (68 mg, 35%).

^1H NMR (500 MHz, CDCl_3) δ 8.53 (s, 1H), 8.23 (d, $J = 8.2$ Hz, 2H), 8.15 (d, $J = 8.4$ Hz, 2H), 7.94 (d, $J = 8.5$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 3.96 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.4, 188.0, 176.3, 166.5, 143.6, 140.8, 135.3, 132.0, 130.4 (2C), 129.7 (2C), 129.3 (2C), 127.6 (2C), 127.0, 52.6, 21.9.

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{19}\text{H}_{15}\text{NNaO}_2\text{S}_3^+$ 408.0163. Found: 408.0169.

2-(2-Fluorophenyl)-6-phenyl-4,14-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3q)



Orange solid (55 mg, 33%).

^1H NMR (500 MHz, CDCl_3) δ 8.58 (s, 1H), 8.11 (td, $J = 7.7, 1.8$ Hz, 1H), 7.91 – 7.87 (m, 2H), 7.52 – 7.48 (m, 4H), 7.28 (dd, $J = 7.7, 1.2$ Hz, 1H), 7.24 – 7.18 (m, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 190.3 (q, $J = 3.8$ Hz, 1C), 186.9, 178.4, 160.40 (d, $J = 257.0$ Hz), 136.6, 133.2 (d, $J = 9.1$ Hz, 1C), 131.3 (d, $J = 5.0$ Hz, 1C), 129.3 (2C), 127.7 (2C), 127.1, 127.0 (d, $J = 8.9$ Hz, 1C), 124.4 (d, $J = 3.7$ Hz, 1C), 117.08 (d, $J = 22.1$ Hz, 1C).

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{16}\text{H}_{10}\text{FNNaS}_3^+$ 353.9857. Found: 353.9866.

2-(4-Fluorophenyl)-6-phenyl-4,14-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3r)



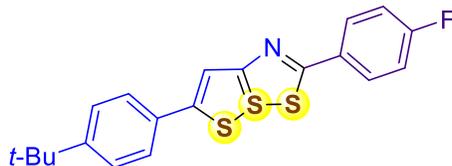
Orange solid (58 mg, 35%).

^1H NMR (500 MHz, CDCl_3) δ 8.48 (s, 1H), 8.40 – 8.33 (m, 2H), 7.91 – 7.85 (m, 2H), 7.54 – 7.48 (m, 3H), 7.16 (t, $J = 8.6$ Hz, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.1, 187.8, 176.7, 165.6 (d, $J = 253.7$ Hz, 1C), 136.1, 135.0 (d, $J = 2.9$ Hz, 1C), 131.5 (d, $J = 8.6$ Hz, 2C), 131.3, 129.2 (2C), 127.5 (2C), 127.0, 115.9 (d, $J = 21.9$ Hz, 2C).

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{16}\text{H}_{10}\text{FNNaS}_3^+$ 353.9857. Found: 353.9866.

6-(4-(*tert*-Butyl)phenyl)-2-(4-fluorophenyl)-4I4-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3s)



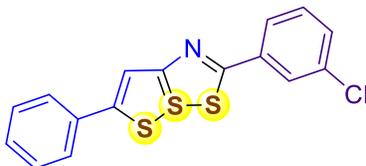
Orange solid (60 mg, 31%).

^1H NMR (500 MHz, CDCl_3) δ 8.47 (s, 1H), 8.37 (dd, $J = 8.9, 5.4$ Hz, 2H), 7.82 (d, $J = 8.5$ Hz, 2H), 7.52 (d, $J = 8.5$ Hz, 2H), 7.16 (t, $J = 8.6$ Hz, 2H), 1.37 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3) δ 194.9, 187.6, 176.4, 166.4 (d, $J = 253.7$ Hz, 1C), 155.0, 135.0 (d, $J = 3.3$ Hz, 1C), 133.0, 131.4 (d, $J = 9.1$ Hz, 2C), 129.0, 127.3 (2C), 126.4, 126.2 (2C), 126.1, 115.8 (d, $J = 21.9$ Hz, 2C), 31.1 (2C).

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{20}\text{H}_{18}\text{FNNaS}_3^+$ 410.0483. Found: 410.0492.

2-(3-Chlorophenyl)-6-phenyl-4I4-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3t)



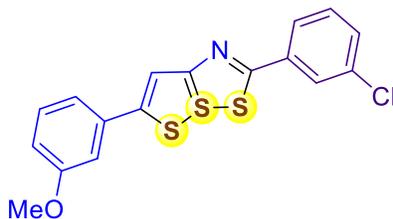
Orange solid (52 mg, 30%).

^1H NMR (500 MHz, CDCl_3) δ 8.51 (s, 1H), 8.36 (t, $J = 1.9$ Hz, 1H), 8.22 (dt, $J = 7.8, 1.4$ Hz, 1H), 7.88 (dd, $J = 6.5, 3.2$ Hz, 2H), 7.54 – 7.48 (m, 4H), 7.42 (t, $J = 7.9$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 194.8, 187.5, 176.4, 140.2, 135.7, 134.7, 131.9, 131.2, 129.8, 129.3 (2C), 128.6, 127.5 (2C), 127.4, 127.2.

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{16}\text{H}_{10}\text{ClNNaS}_3^+$ 369.9562. Found: 369.9568.

2-(3-Chlorophenyl)-6-(3-methoxyphenyl)-4I4-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3u)



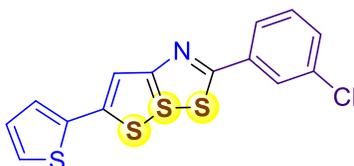
Orange solid (53 mg, 28%).

^1H NMR (500 MHz, CDCl_3) δ 8.47 (s, 1H), 8.30 (d, $J = 8.5$ Hz, 2H), 7.45 (d, $J = 8.6$ Hz, 3H), 7.41 (t, $J = 7.9$ Hz, 1H), 7.37 (s, 1H), 7.06 (dd, $J = 8.2, 2.5$ Hz, 1H), 3.90 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.1, 187.7, 176.5, 160.3, 138.7, 137.3, 137.1, 131.3, 130.4 (2C), 129.0 (2C), 127.2, 120.0, 117.1, 112.9, 55.7.

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{17}\text{H}_{12}\text{ClNNaOS}_3^+$ 399.9667. Found: 399.9676.

2-(3-Chlorophenyl)-6-(thiophen-2-yl)-4,4-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3v)



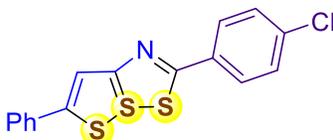
Orange solid (53 mg, 30%).

^1H NMR (500 MHz, CDCl_3) δ 8.43 (s, 1H), 8.34 (t, $J = 1.9$ Hz, 1H), 8.20 (dt, $J = 7.9, 1.3$ Hz, 1H), 7.93 (dd, $J = 3.0, 1.3$ Hz, 1H), 7.56 (dd, $J = 5.1, 1.4$ Hz, 1H), 7.52 – 7.49 (m, 1H), 7.46 (dd, $J = 5.1, 2.9$ Hz, 1H), 7.42 (t, $J = 7.9$ Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 194.2, 187.5, 170.9, 140.1, 138.3, 134.9, 132.1, 130.0, 128.8, 127.6, 127.5, 127.0, 126.8, 126.3.

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{14}\text{H}_8\text{ClNNaS}_4^+$ 375.9126. Found: 375.9132.

2-(4-Chlorophenyl)-6-phenyl-4,4-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3w)



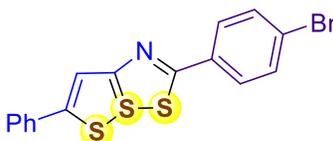
Orange solid (57 mg, 33%).

^1H NMR (500 MHz, CDCl_3) δ 8.47 (s, 1H), 8.29 (d, $J = 8.7$ Hz, 2H), 7.90 – 7.81 (m, 2H), 7.53 – 7.49 (m, 3H), 7.44 (d, $J = 8.6$ Hz, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.1, 187.7, 176.6, 138.6, 137.1, 135.9, 131.3, 130.4 (2C), 129.4 (2C), 129.0 (2C), 127.6 (2C), 127.1.

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{16}\text{H}_{10}\text{ClNNaS}_3^+$ 369.9562. Found: 369.9568.

2-(4-Bromophenyl)-6-phenyl-4,4-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3x)



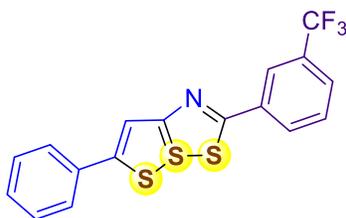
Orange solid (60 mg, 31%).

^1H NMR (500 MHz, CDCl_3) δ 8.49 (s, 1H), 8.30 (d, $J = 8.6$ Hz, 2H), 7.90 – 7.84 (m, 2H), 7.53 – 7.50 (m, 3H), 7.45 (d, $J = 8.6$ Hz, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.1, 187.8, 176.6, 138.7, 137.1, 136.0, 131.3, 130.4 (2C), 129.4 (2C), 129.0 (2C), 127.6 (2C), 127.1.

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{16}\text{H}_{10}\text{BrNNaS}_3^+$ 413.9056. Found: 413.9066.

6-Phenyl-2-(3-(trifluoromethyl)phenyl)-4,14-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3y)



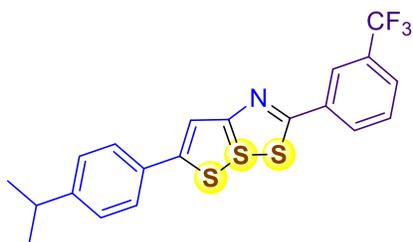
Orange solid (57 mg, 30%).

^1H NMR (500 MHz, CDCl_3) δ 8.64 (s, 1H), 8.51 (d, $J = 6.6$ Hz, 2H), 7.89 – 7.85 (m, 2H), 7.77 (d, $J = 7.8$ Hz, 1H), 7.60 (t, $J = 7.8$ Hz, 1H), 7.53 – 7.50 (m, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.0, 187.7, 176.3, 139.5, 135.6, 132.6 (d, $J = 1.4$ Hz, 1C), 131.2 (d, $J = 32.6$ Hz, 1C), 131.1, 129.4 (2C), 129.3, 128.48 (q, $J = 3.8$ Hz, 1C), 127.6 (2C), 127.5, 125.6 (q, $J = 3.6$ Hz, 1C), 124.06 (d, $J = 272.7$ Hz, 1C).

HRMS (QTOF, ESI+) m/z calcd for $[\text{M}+\text{Na}]^+ \text{C}_{17}\text{H}_{10}\text{F}_3\text{NNaS}_3^+$ 403.9825. Found: 403.9836.

6-(4-Isopropylphenyl)-2-(3-(trifluoromethyl)phenyl)-4,14-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3z)



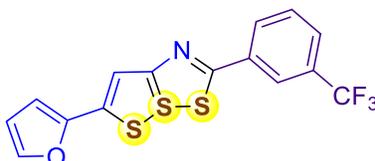
Orange solid (59 mg, 28%).

^1H NMR (500 MHz, CDCl_3) δ 8.64 (s, 1H), 8.52 (d, $J = 10.2$ Hz, 2H), 7.81 (d, $J = 8.4$ Hz, 2H), 7.77 (d, $J = 7.8$ Hz, 1H), 7.60 (t, $J = 7.8$ Hz, 1H), 7.37 (d, $J = 8.4$ Hz, 2H), 2.99 (hept, $J = 6.9$ Hz, 1H), 1.31 (d, $J = 7.0$ Hz, 6H).

^{13}C NMR (126 MHz, CDCl_3) δ 195.0, 187.6, 176.3, 153.1, 139.6, 133.1, 132.6, 131.2 (d, $J = 32.7$ Hz, 1C), 129.3, 128.4 (q, $J = 3.6$ Hz, 1C), 127.7 (2C), 127.6 (2C), 127.1, 125.6 (q, $J = 4.0$ Hz, 1C), 124.1 (d, $J = 272.9$ Hz, 1C), 34.3, 23.9 (2C).

HRMS (QTOF, ESI+) m/z calcd for $[M+Na]^+ C_{20}H_{16}F_3NNaS_3^+$ 446.0295. Found: 446.02999.

6-(furan-2-yl)-2-(3-(trifluoromethyl)phenyl)-4,4-[1,2]dithiolo[5,1-e][1,2,4] dithiazole (3aa)



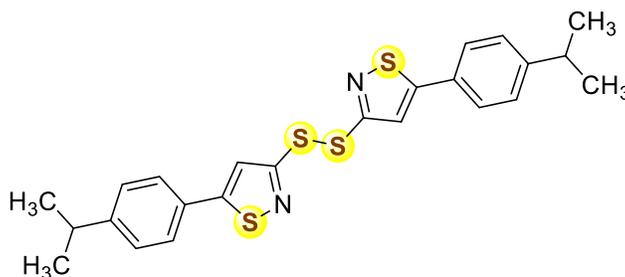
Orange solid (46 mg, 25%).

1H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.52 (s, 1H), 8.49 (d, $J = 8.0$ Hz, 1H), 7.79 (d, $J = 7.8$ Hz, 1H), 7.66 (d, $J = 1.1$ Hz, 1H), 7.62 (t, $J = 7.8$ Hz, 1H), 7.13 (d, $J = 3.5$ Hz, 1H), 6.61 (dd, $J = 3.5, 1.8$ Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.7, 187.1, 165.0, 151.2, 145.8, 138.6, 132.5, 131.4 (d, $J = 32.9$ Hz, 1C), 129.4, 128.66 (q, $J = 3.7$ Hz, 1C), 125.68 (d, $J = 3.8$ Hz, 1C), 124.8, 124.0 (d, $J = 272.9$ Hz, 1C), 114.4, 113.5.

HRMS (QTOF, ESI+) m/z calcd for $[M+Na]^+ C_{15}H_8F_3NNaOS_3^+$ 393.9618. Found: 393.9622.

1,2-Bis(5-(4-isopropylphenyl)isothiazol-3-yl)disulfane (4)



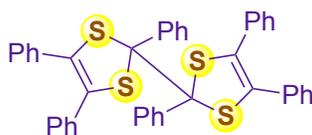
White solid (70 mg, 30%).

1H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 2H), 7.51 (d, $J = 8.0$ Hz, 4H), 7.31 (d, $J = 7.9$ Hz, 4H), 2.96 (p, $J = 6.9$ Hz, 2H), 1.29 (d, $J = 6.9$ Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1 (2C), 163.2 (2C), 151.3 (2C), 127.8 (2C), 127.4 (4C), 126.7 (4C), 118.7 (2C), 34.0 (2C), 23.8 (4C).

HRMS (QTOF, ESI+) m/z calcd for $[M+H]^+ C_{24}H_{25}N_2S_4^+$ 469.0901. Found: 469.0913.

2,2',4,4',5,5'-Hexaphenyl-2,2'-bi(1,3-dithiole) (5)¹



¹ T. B. Nguyen and P. Retailleau, *Org. Lett.*, 2019, **21**, 279.

Pale yellow solid (72 mg, 65% from 1 mmol of phenylacetic acid).

^1H NMR (300 MHz, CDCl_3) δ 7.78-7.74 (m, 4H), 7.23-7.19 (m, 6H), 7.13-7.06 (m, 12H), 6.83-6.79 (m, 8H).

Crystallographic experimental section

Thin elongated red crystals of **3a**, and colourless ones of **4** suitable for X-ray diffraction analysis were obtained in saturated solutions of each compound in dichloromethane. High resolution crystallographic data were recorded at low temperature (123K) for **3a**, or at room temperature for **4**, using a Rigaku *XtaLabPro* single-crystal diffractometer equipped with a microfocus Mo $K\alpha$ radiation and a HPAD PILATUS3 R 200K detector. *CrysAlisPro* ^[1] was used to process these data recorded from multiple ω scans, applying an absorption correction both empirical using spherical harmonics, implemented in the *SCALE3 ABSPACK* scaling algorithm, and numerical based on Gaussian integration over a multifaceted crystal model. Their respective structures were readily solved by intrinsic phasing methods (*SHELXT*) ^[2] and then refined by full-matrix least-squares methods on F^2 using *SHELXL*. ^[3] The non-hydrogen atoms were refined anisotropically, and if most of the hydrogen atoms were identified in difference Fourier maps, they were nevertheless geometrically positioned and refined using a riding model with U_{iso} set to xU_{eq} of the parent atom ($x=1.2$ for the aromatic ones and 1.5 for the methyl carbon in **4**). **3a**-was. Found: to belong to the orthorhombic polar space group, $Pna2_1$ and its absolute structure parameter was refined to the value of 0.30(3). This compound is distinct from 2,5-diphenyl-thiathiophene due to the presence of an amide nitrogen atom, which replaces a central C–H group. This may bring partial explanation why the crystallographic space group is different from $P2_12_12_1$.^[4] The **3a** structure appears as quasi-planar in its asymmetric unit (rmsd of 0.09Å) (figure S1), while the meso-compound features twisted peripheral phenyl groups, resulting in dihedral angles ranging from 27.6 to 34° relative to the central tri-sulphur ring. The two C–H groups form non-conventional hydrogen bonds with a sulphur atom of a vicinal molecule (C8–H8... S1^{#2-x, y+0.5, 1.5-z}; 3.047Å, 125.9° and C10–H10... S1^{#1-x, y+0.5, 1.5-z}; 3.34Å, 141.5°). In the present case, the single C–H group, irrespective to its position around the pseudo-twofold molecular axis parallel to the median C–S bond (which was not split during the course of the structure refinement) does not make any contact closer than 2.9Å with carbon atoms of a proximal phenyl group at 0.5-x, y-0.5, z+0.5 and the **3a**-molecule has been. Found: to better refine as a disordered flipped molecule in a 0.627(5):0.373(5) ratio. A set of restraints on rigid-bond distances and anisotropic displacement parameters (DELU, SIMU, RIGU, ISOR) were applied to the split atoms of the five-hetero-membered bicycle, which may have an effect on the precision of the conformer geometrical details, at least for the minor one (see figure S2c-d). Both studied structures were further subjected to Hirshfeld atom refinement (HAR)^[5] using aspherical scattering factors via *NoSpherA2* ^[6] partitioning in *Olex2*.^[7] This was based on electron density obtained from iterative single-determinant SCF single-point DFT calculations using *ORCA* ^[8] at the *R2SCAN/def2-TZVP* level of theory. The *NoSpherA2* software read any of these wavefunctions and the related electron-density was partitioned into Hirshfeld atoms. The Fourier transforms of these atoms are the non-spherical scattering factors, which were then tabulated in a .tsc file and provided to *olex2.refine* ^[9] for the L-M refinement. All hydrogen atoms

were refined independently and anisotropically, with the exception of few of them, which received some restraints on their ADPs, providing better descriptions of their positions, and therefore more precise hydrogen-bond length and, in fine, better model statistics, as summarized in *Table S1*.

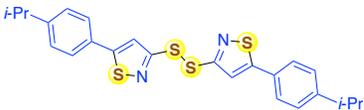
To the best of our knowledge, **4** is the first example to date of an 1,2-di(isothiazol-3-yl)disulfane derivative to be documented in the Cambridge Structural Database (CSD^[10] version 6.00, update of 04/2025).

Crystallographic data for the two X-ray structures have been deposited in the Cambridge Crystallographic Data Centre database (deposition number CCDC 2474319-2474320 for **3a**, and **4**, respectively). Copies of the data can be obtained free of charge from the CCDC at www.ccdc.cam.ac.uk.

References

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- 4 (a) Hordvik, A. (1971). *Acta Chem. Scand.* (1971), **25**, 1583-1598; (b) Wu, J., Gao, W-G., Huang, X-B., Zhou, Y-B., Liu, M-C., Wu, H-Y. (2020) *Org.Lett.*, **22**, 5555-5560.
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- 6 Kleemiss, F., Dolomanov, O. V., Bodensteiner, M., Peyerimhoff, N., Midgley, L., Bourhis, L. J., Genoni, A., Malaspina, L. A., Jayatilaka, D., Spencer, J. L., White, F., Grundkötter-Stock, B., Steinhauer, S., Lentz, D., Puschmann, H. & Grabowsky, S. (2021). *Chem. Sci.* **12**, 1675–1692; Midgley, L., Bourhis, L. J., Dolomanov, O. V., Grabowsky, S., Kleemiss, F., Puschmann, H. & Peyerimhoff, N. (2021). *Acta Cryst.* **A77**, 519–533.
- 7 Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
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- 11 CCDC RefCode VEMCEV Capuano, L., Bolz, G., Burger, R. Burkhardt, V. Huch, V. Liebigs Ann. Chem. **1990**, 239-243.

Table S1 Crystal data and structure refinement for **3a** and **4**

Identification code		3a	4
2D scheme			
Empirical formula		C ₁₆ H ₁₁ N ₃ S ₃	C ₂₄ H ₂₄ N ₂ S ₄
Formula weight		313.471	468.736
Temperature	K	123 (2)	293 (2)
Diffractionmeter,		<i>Rigaku XtaLabPro μ-Source</i> MM003, Pilatus3 R 200K	<i>Rigaku XtaLabPro μ-Source</i> MM003, Pilatus3 R 200K
Wavelength	Å	0.71073	0.71073
Crystal system, Space group		Monoclinic, P na2 ₁	Monoclinic, P 2 ₁ /c
Unit cell dimensions	a Å b Å c Å α ° β ° γ °	27.8169(10) 12.6863(6) 3.9186(2) 90 90 90	14.0690(5) 18.3904(7) 8.9706(4) 90 91.920(4) 90
Volume	Å ³	1382.85(11)	2319.70(16)
Z, Z'		4, 1	4, 1
Calculated density	Mg/m ³	1.506	1.342
Absorption coefficient	mm ⁻¹	0.523	0.424
F(000)		648	984
Crystal size	mm	0.51 x 0.11 x 0.05	0.60 x 0.11 x 0.07
θ range for data collection	°	2.17 to 30.50	2.53 to 27.1
Limiting indices		-41 ≤ h ≤ 39, -18 ≤ k ≤ 19, -5 ≤ l ≤ 5	-19 ≤ h ≤ 18, -25 ≤ k ≤ 24, -20 ≤ l ≤ 11
Refl. collected / unique R(int)		12784 / 3826 0.027	31472 / 5098 0.0305
Completeness θ _{full} =25.2°	to %	99.9	99.98
Absorption correction		Gaussian & Multi-scan	
Max. and min. transmission		1.000 and 0.743	1.000 and 0.653
Refinement method		<i>HAR least squares</i>	
Data / restraints / parameters		3826 / 406 / 344	5098 / 12 / 487
Goodness-of-fit on F ²		1.0449	1.0841
Final R indices [I > 2σ(I)]	R1, wR2	0.0213, 0.0329	0.0417, 0.0857
R indices (all data)	R1, wR2	0.0247, 0.0337	0.0521, 0.091
Largest Δ peak and hole	e.Å ⁻³	0.1691 and -0.1383	0.4654 and -0.3741
Absolute structure parameter		0.30(3)	-
CCDC deposit number		2474319	2474320

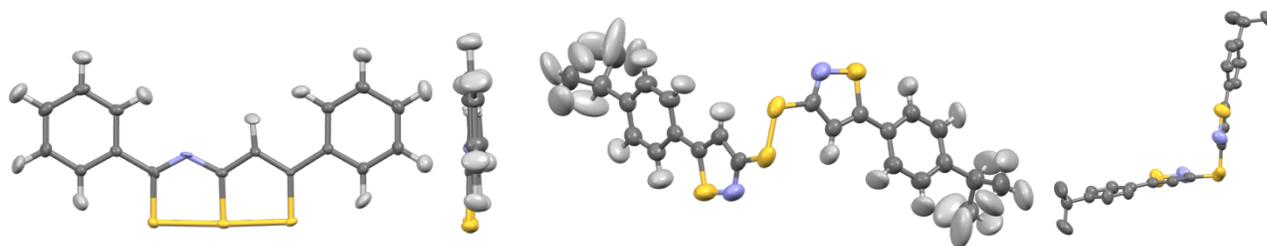


Figure S1. Ortep (orthogonal) views of the molecular structure of the major conformer of **3a** (left) and **4** (right), with atom labelling. Displacement ellipsoids are drawn at the 30% probability level.

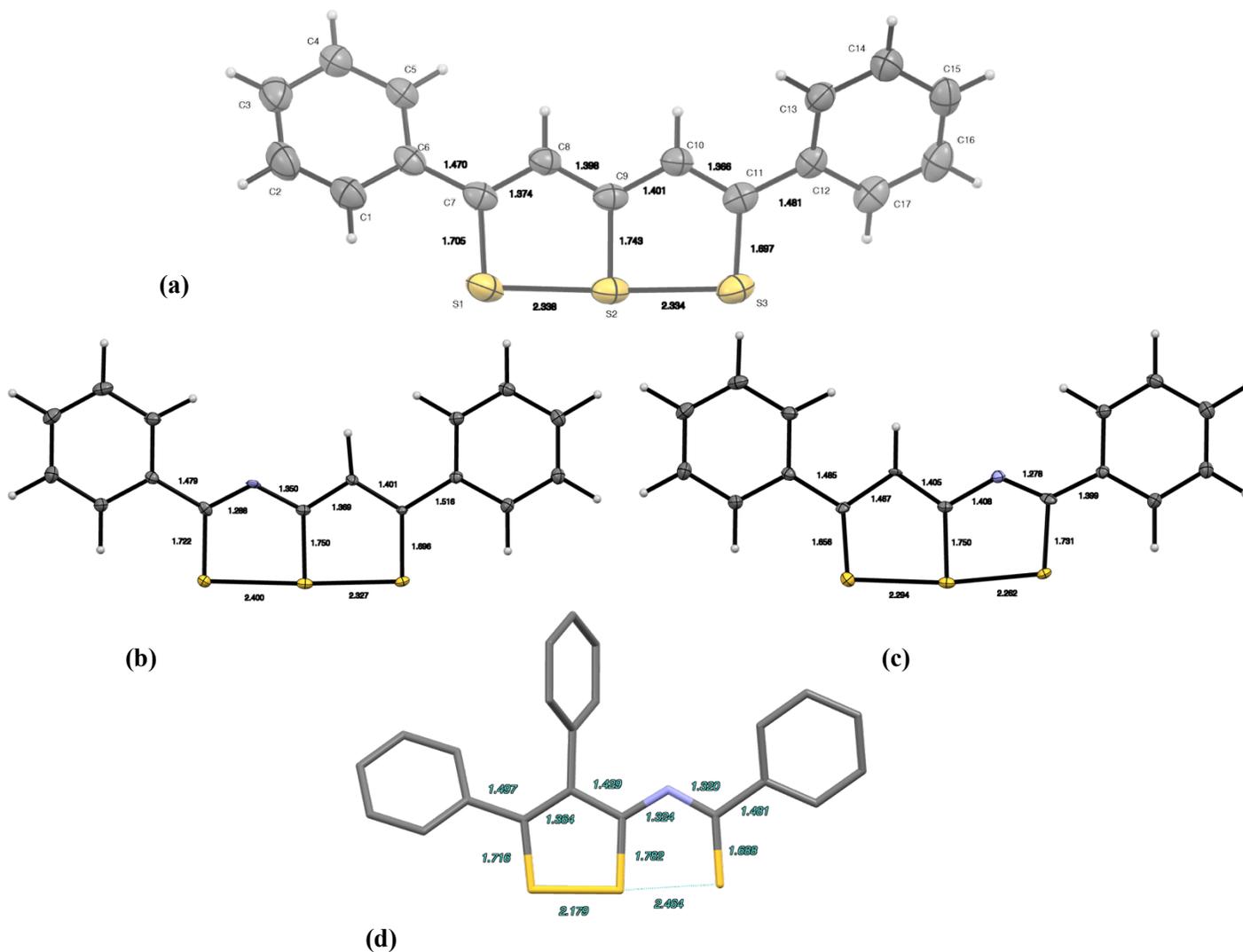


Figure S2 Selected bond distances (in Å) for CCDC Refcode DPHTPT11^[4b] (a) and **3a** conformers **1** and **2** (b-c) and CCDC Refcode VEMCEV^[11] as unique (*Z*)-1-phenyl-2-(5-phenyl-3*H*-1,2,4-dithiazol-3-ylidene)ethane-1-thione derivative structure. Found: in the CCDC database (d). Hydrogen bonds are shown as small spheres with arbitrary radius.

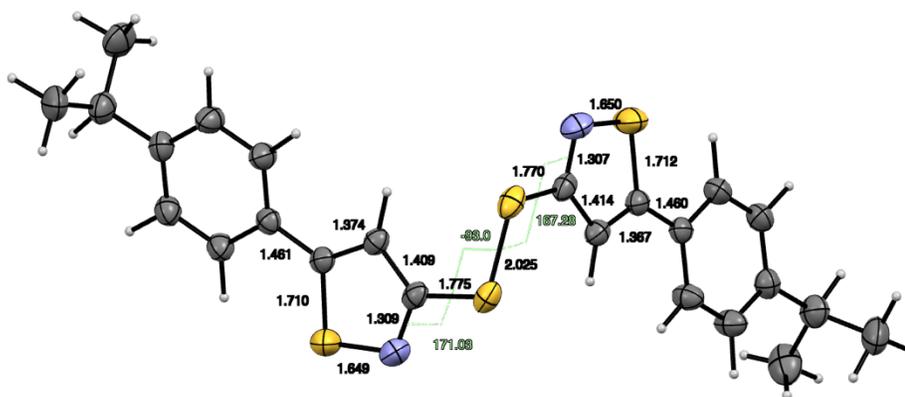
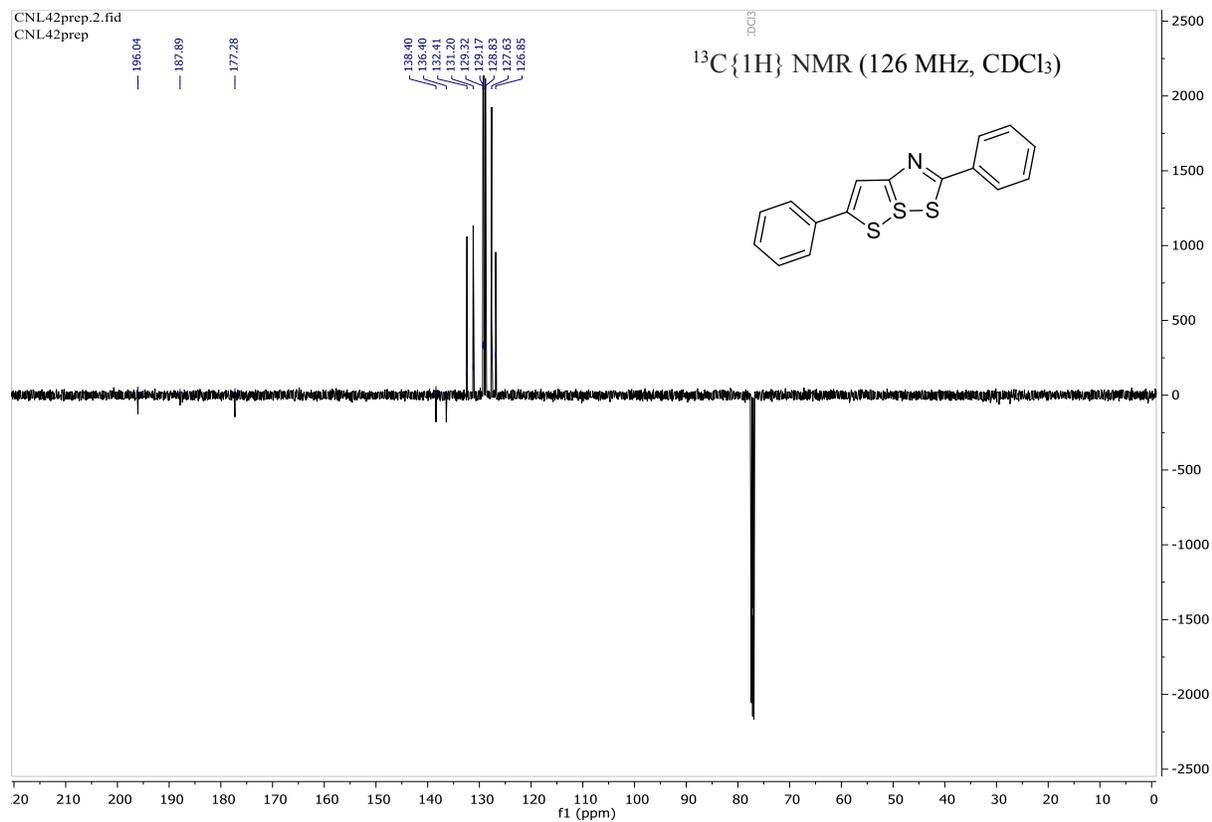
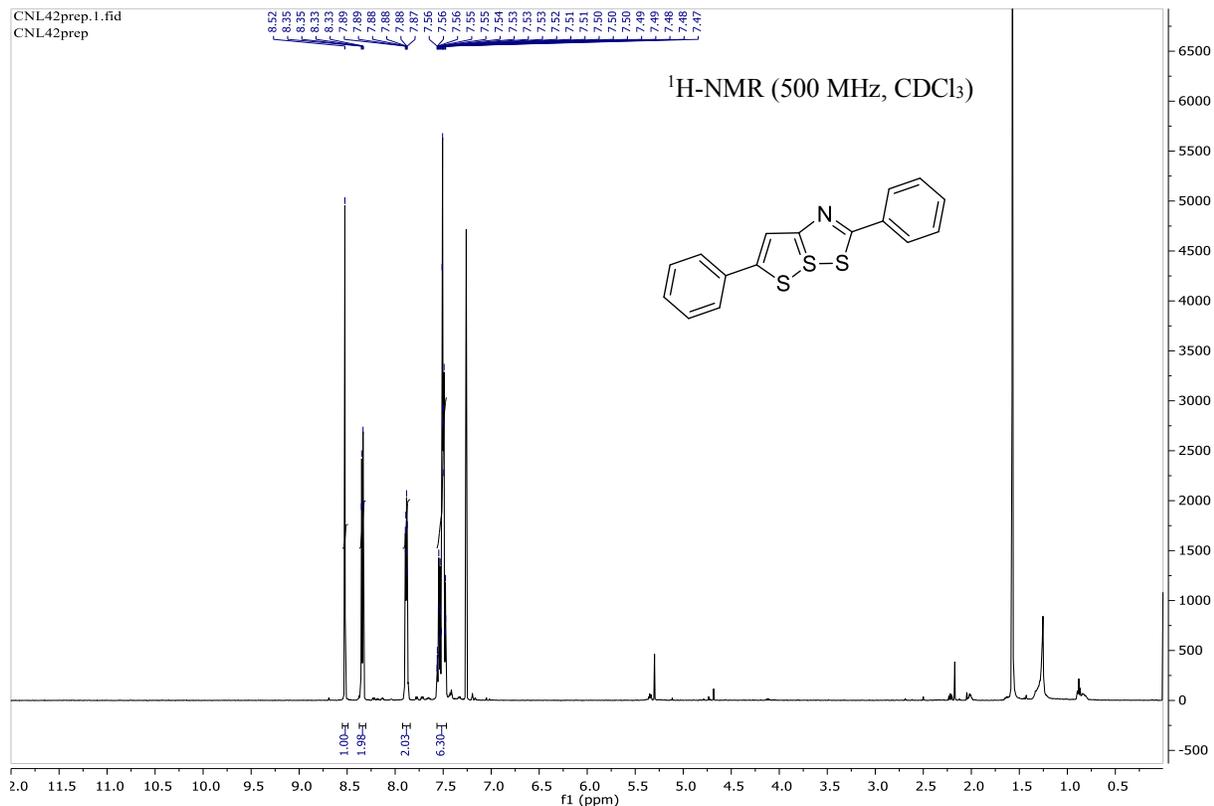


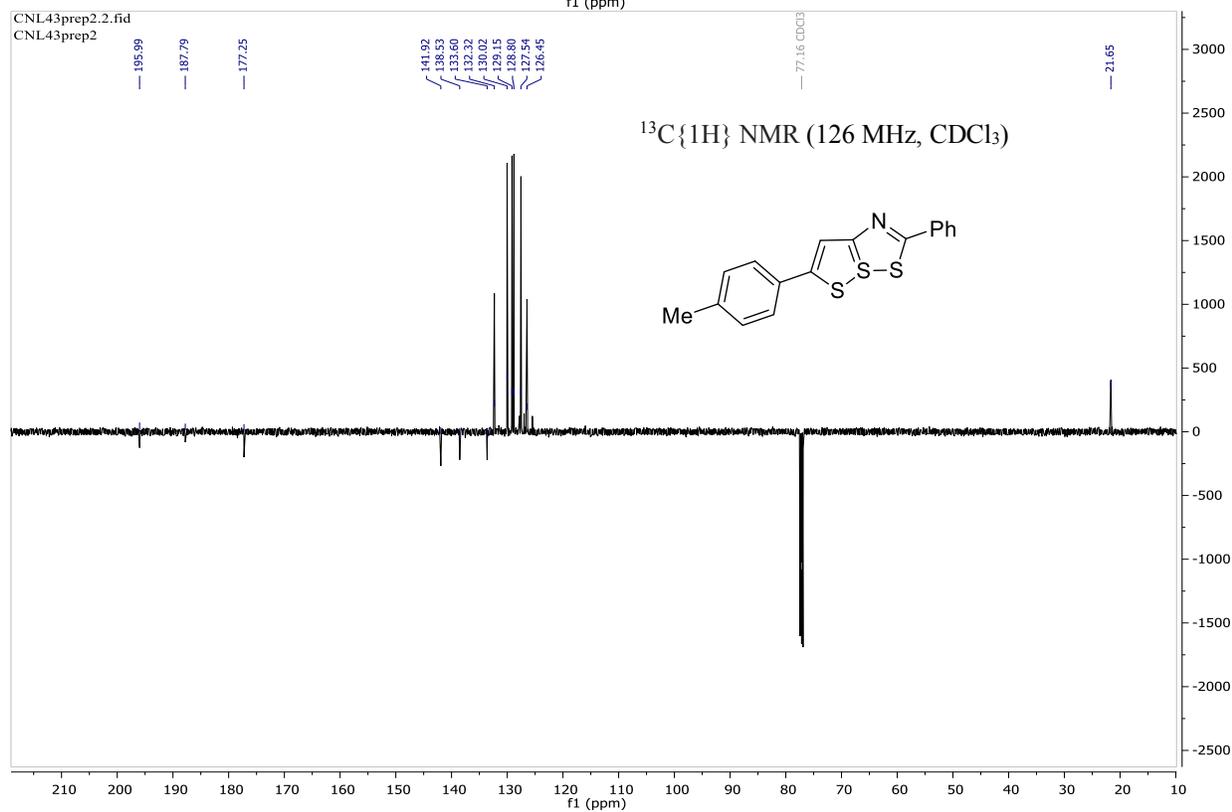
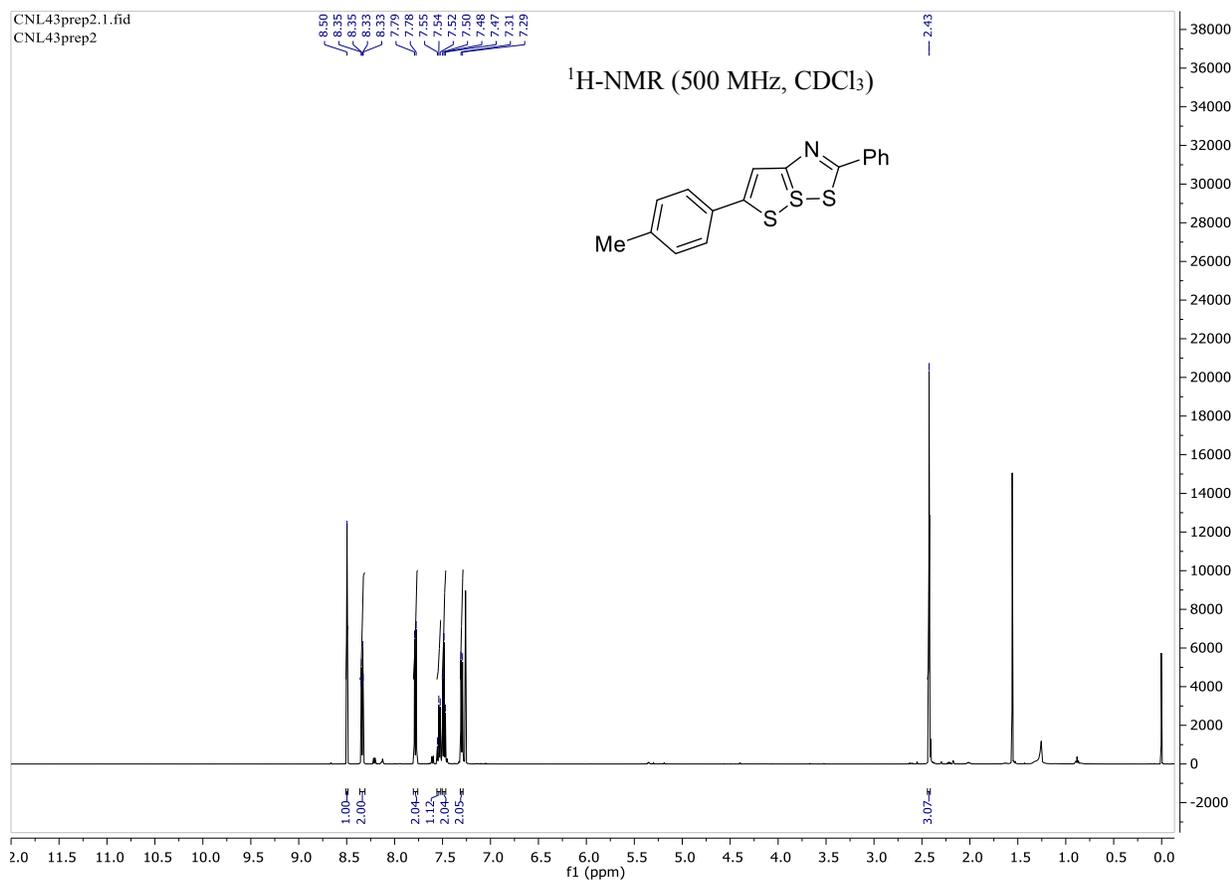
Figure S3 Selected bond distances (Å) and torsion angles (°) labelled in green for **4**. Hydrogen bonds are shown as small spheres with arbitrary radius.

Copies of ^1H and ^{13}C spectra

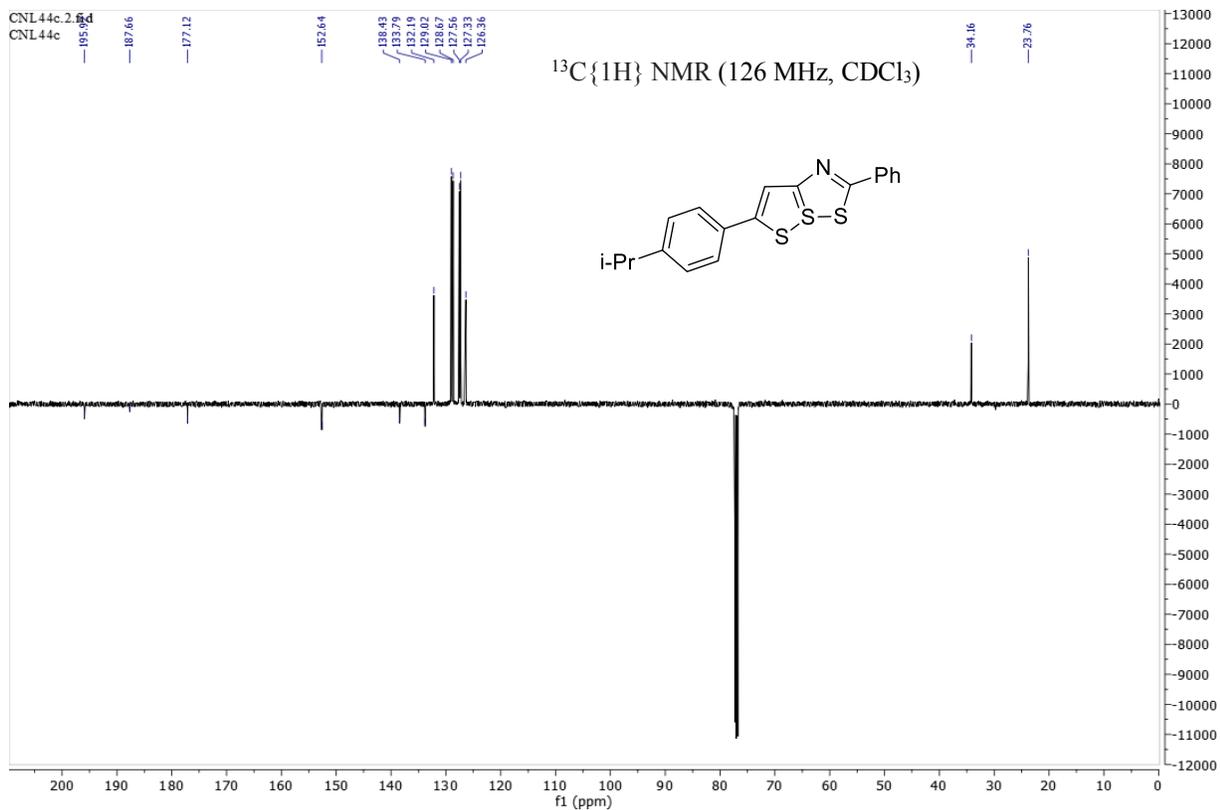
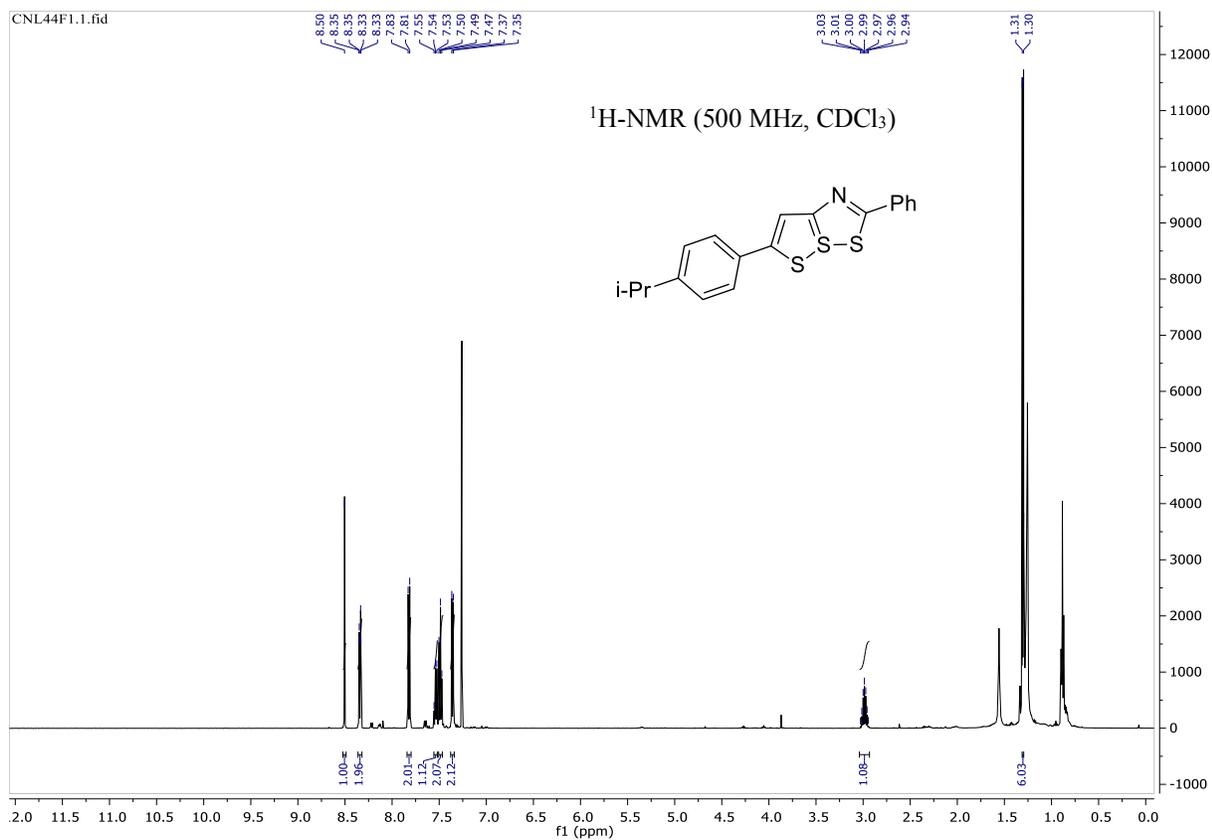
2,6-Diphenyl-4(1,2)dithiolo[5,1-e][1,2,4]dithiazole (3a)



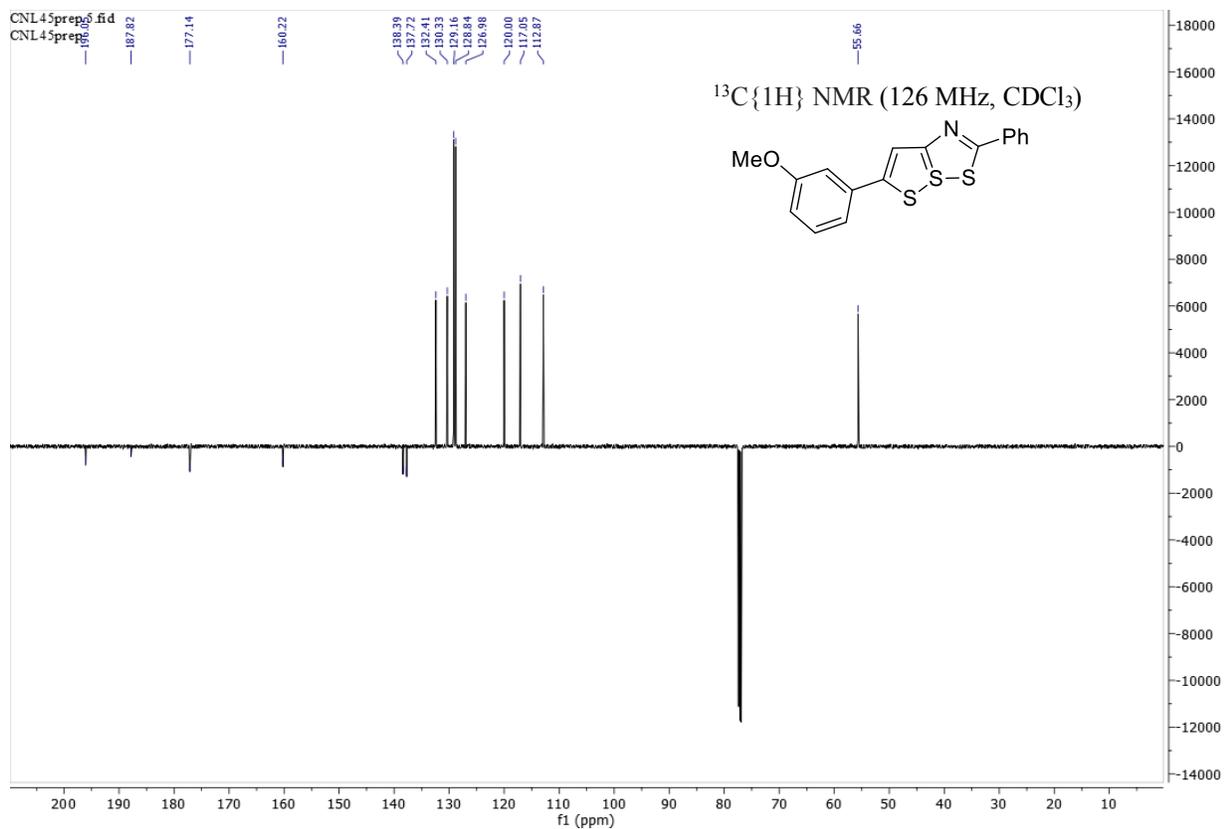
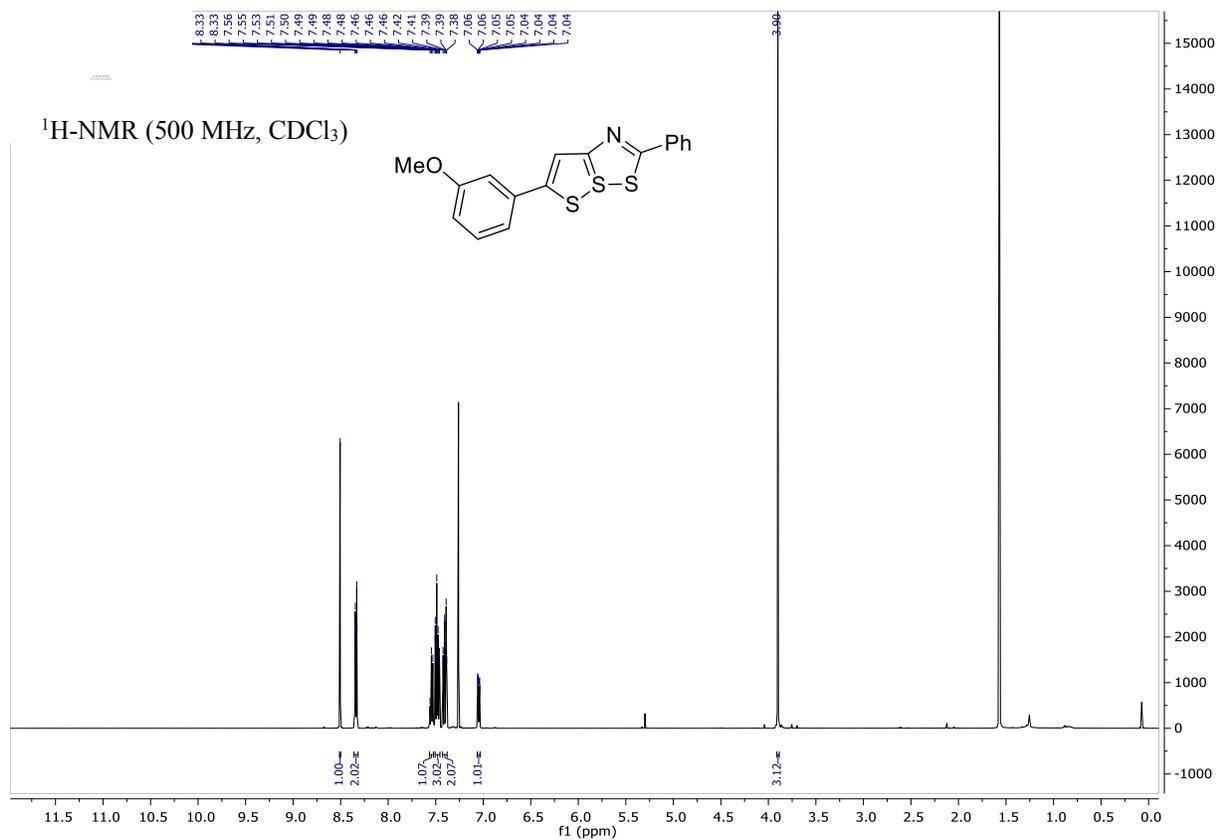
2-Phenyl-6-(p-tolyl)-4[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3b)



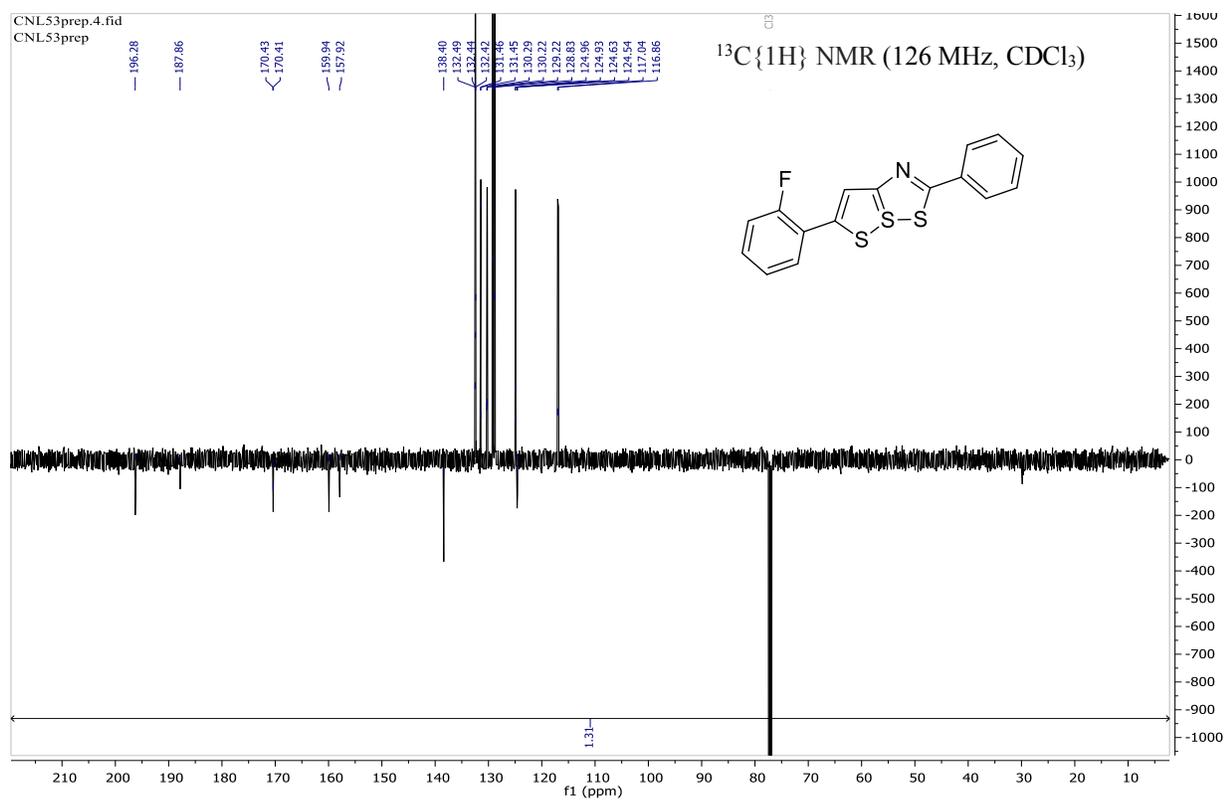
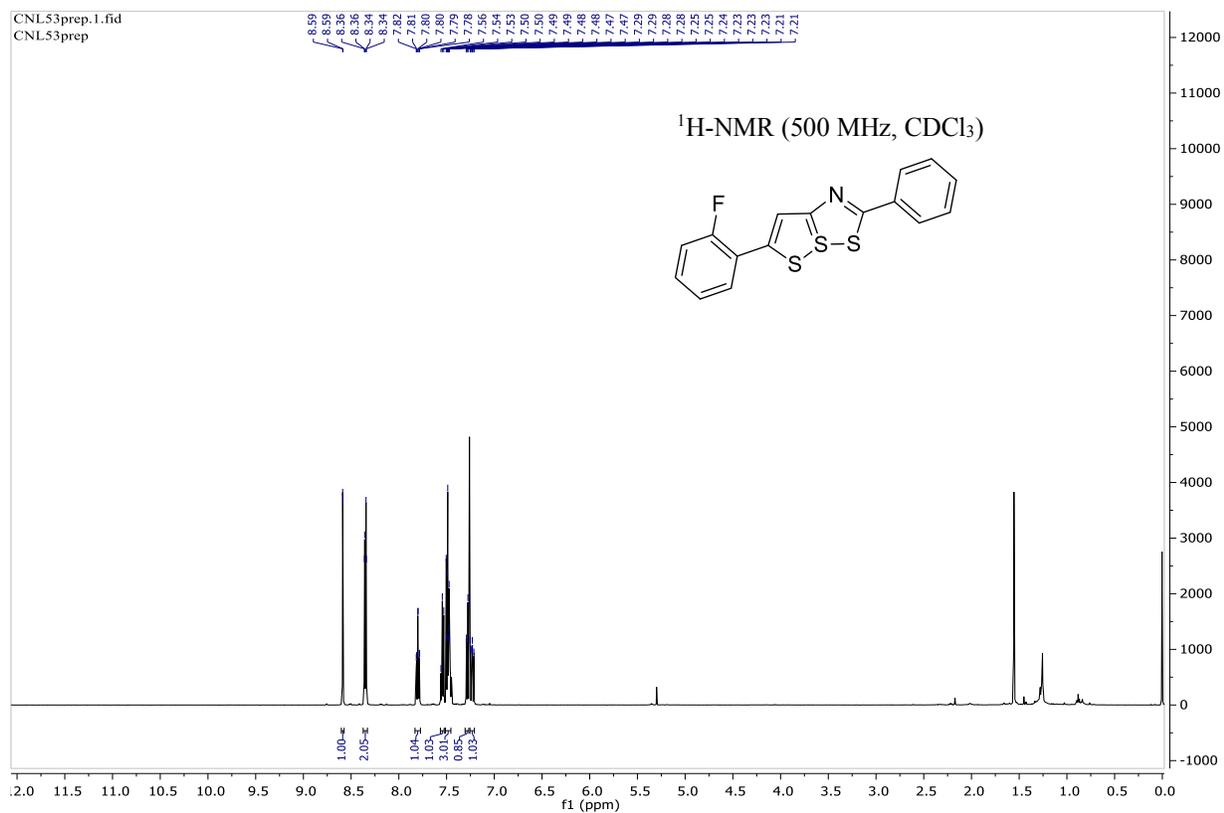
6-(4-Isopropylphenyl)-2-phenyl-4H-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3c)



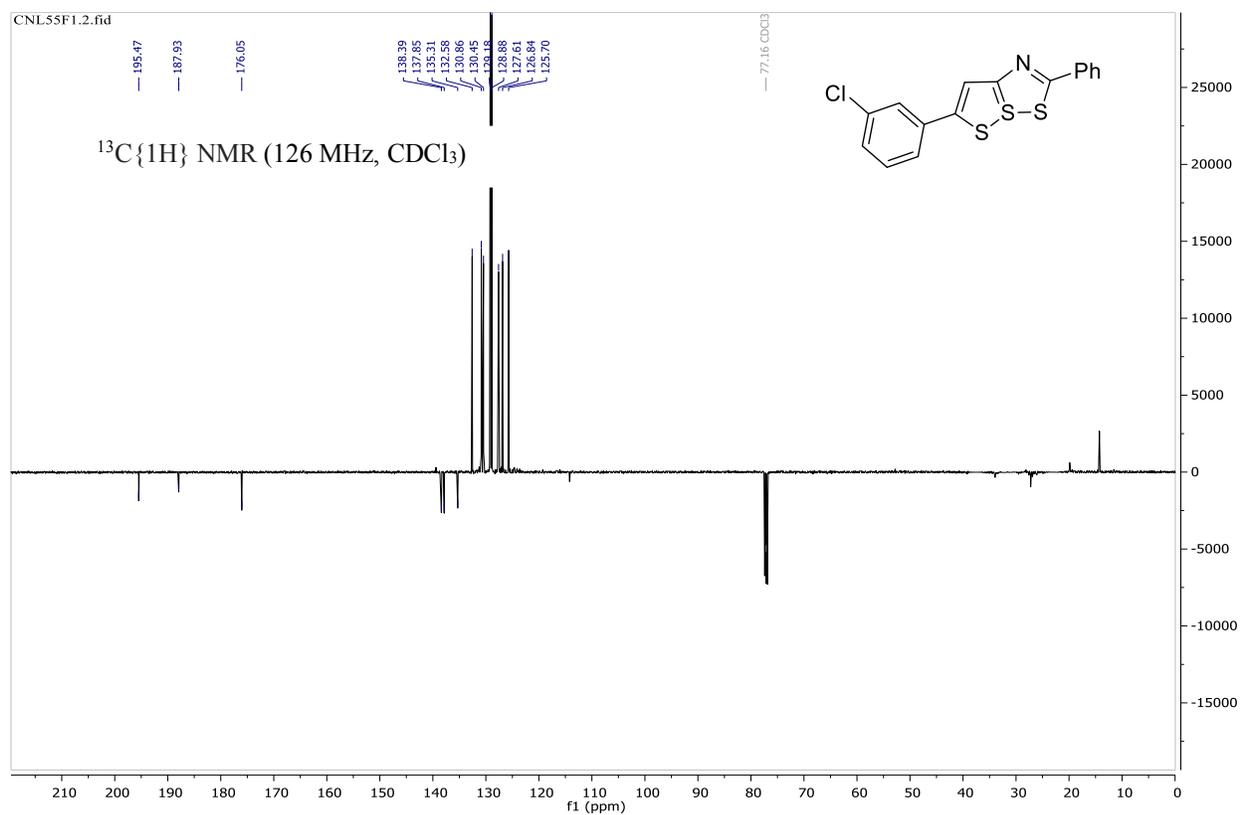
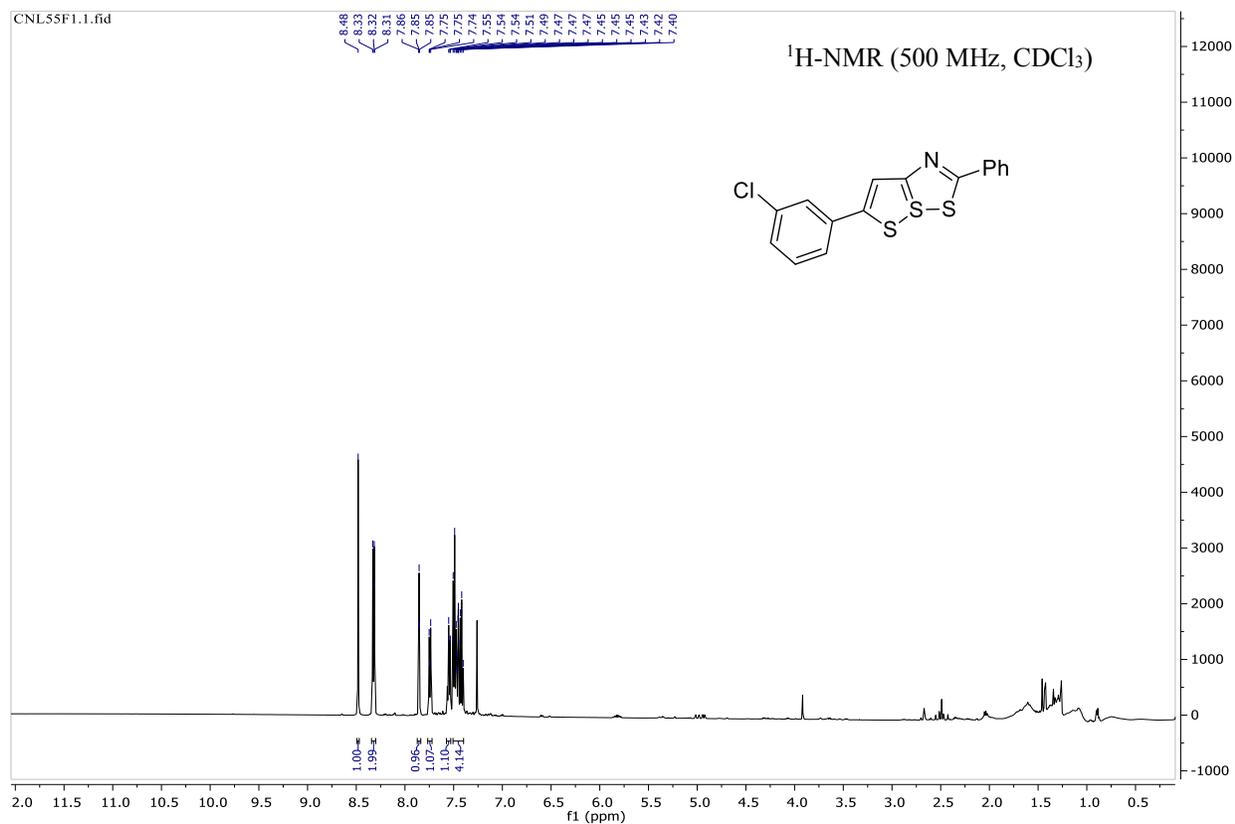
6-(3-Methoxyphenyl)-2-phenyl-4H-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3d)



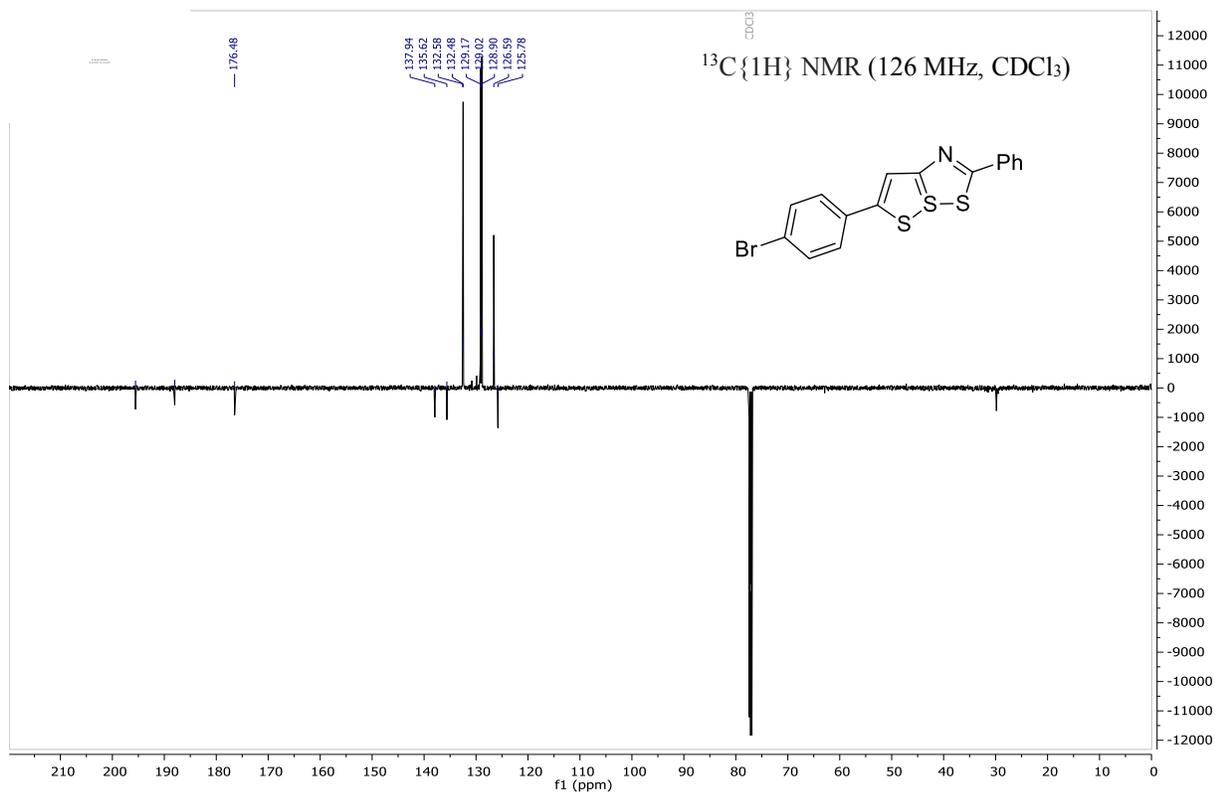
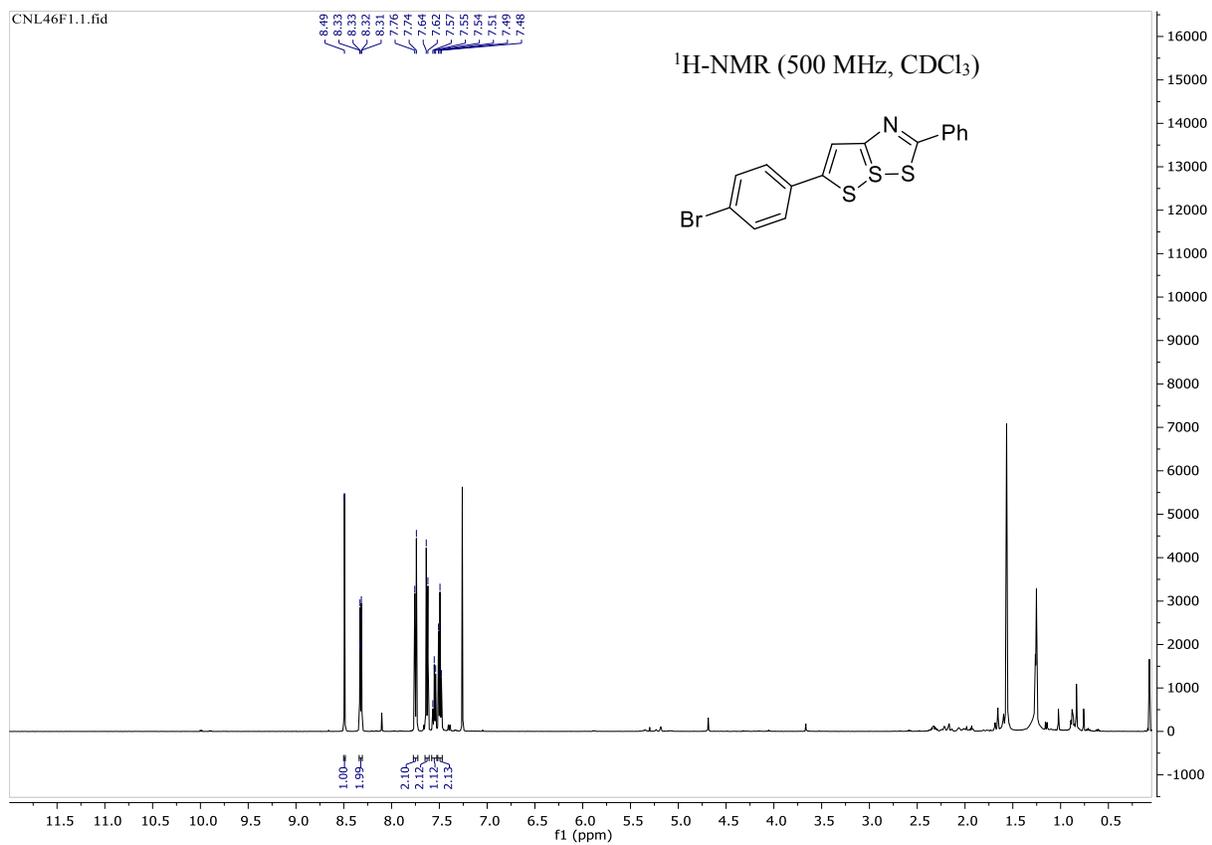
6-(2-Fluorophenyl)-2-phenyl-4H-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3e)



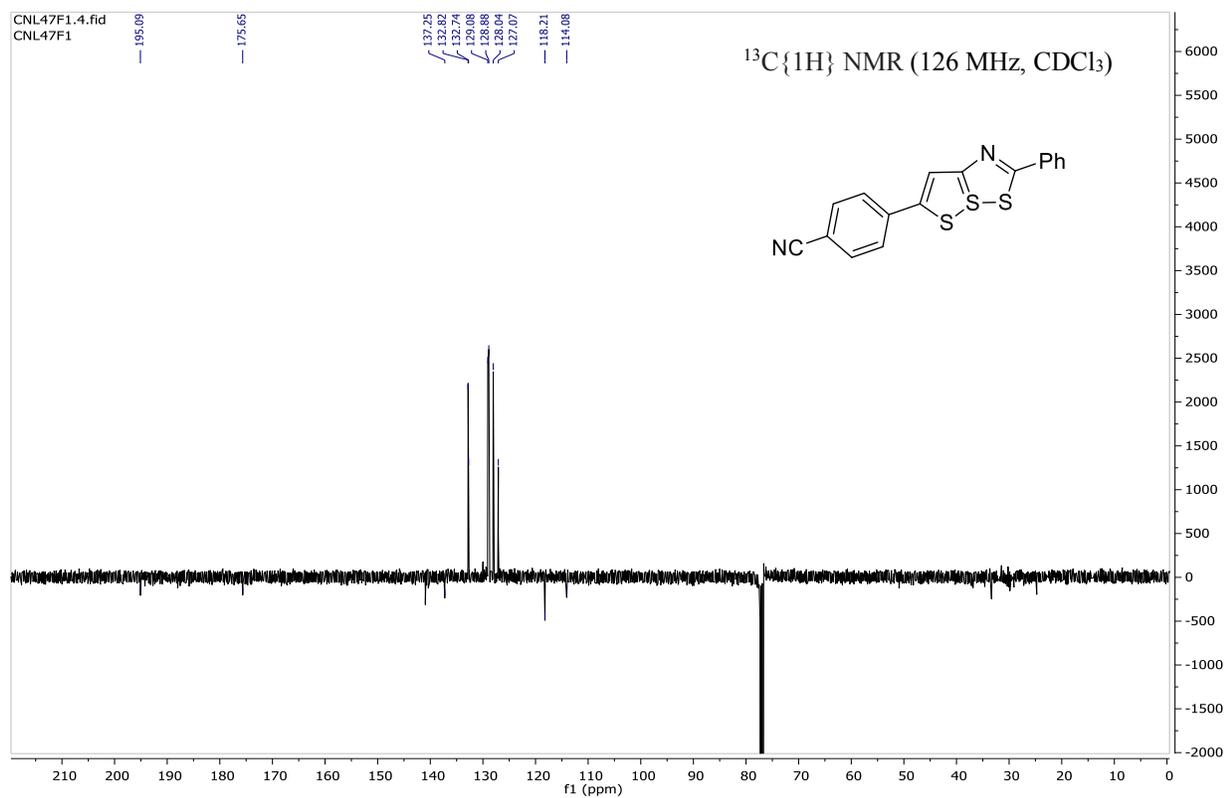
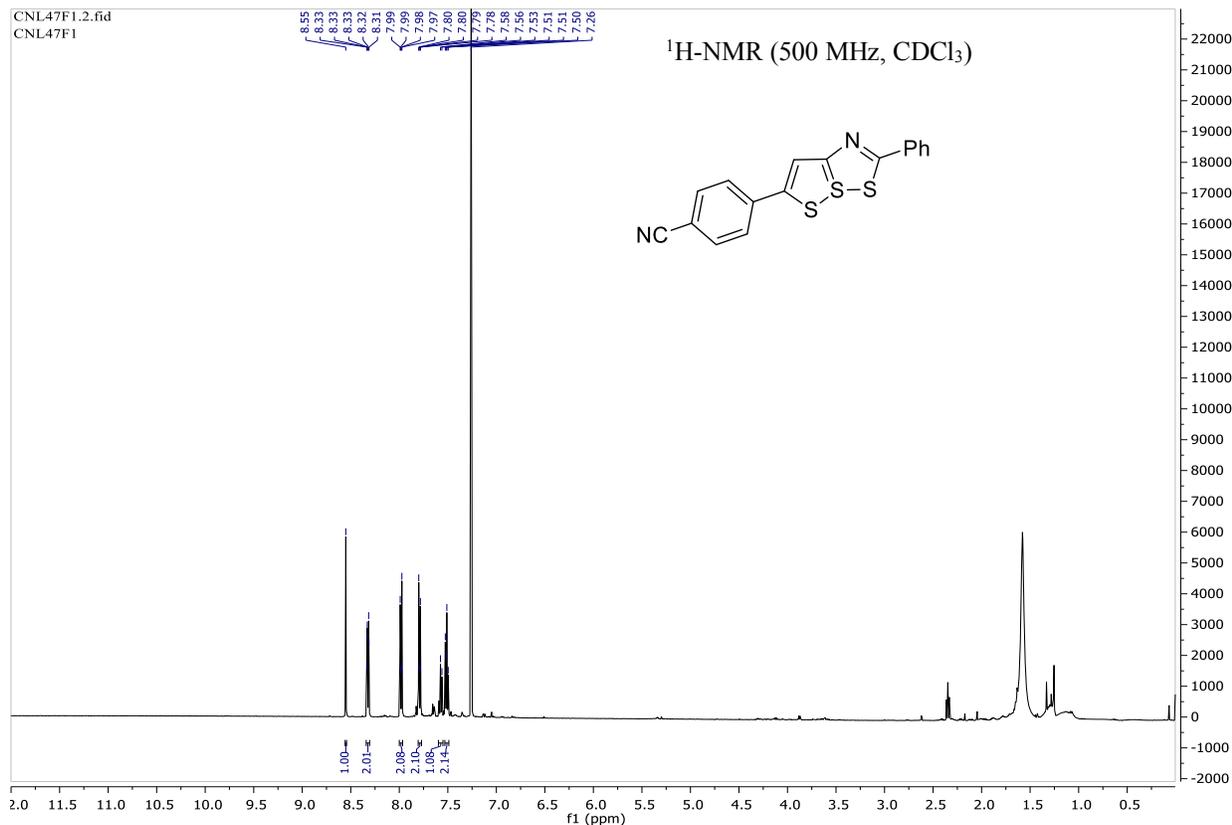
6-(3-Chlorophenyl)-2-phenyl-4,4-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3f)



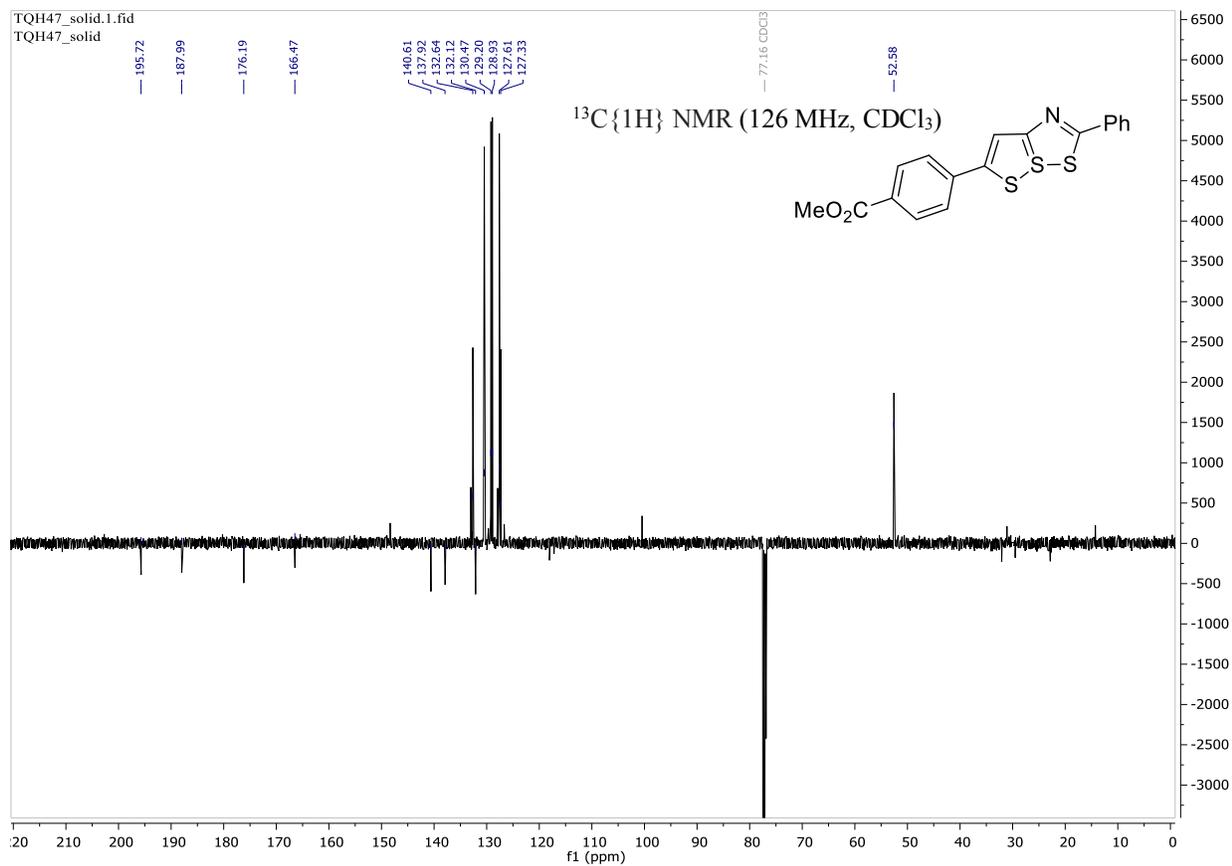
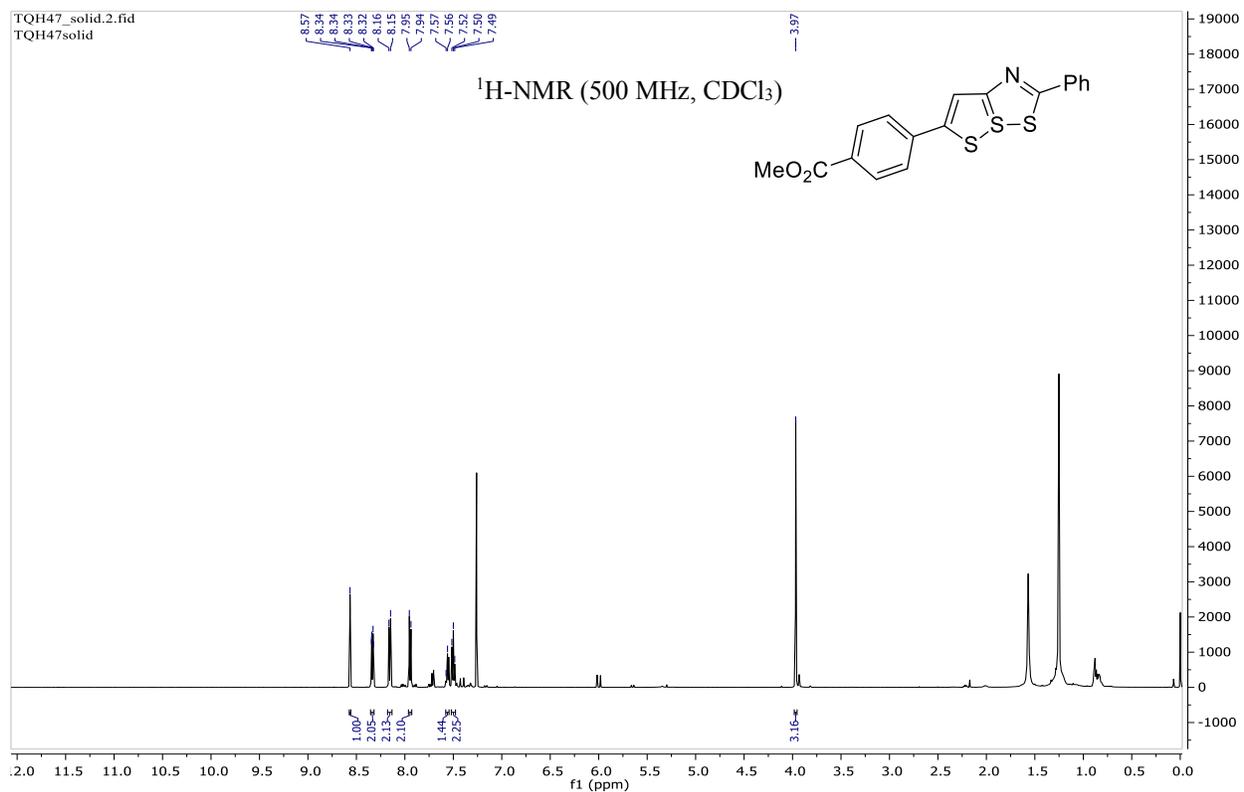
6-(4-Bromophenyl)-2-phenyl-4,4-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3g)



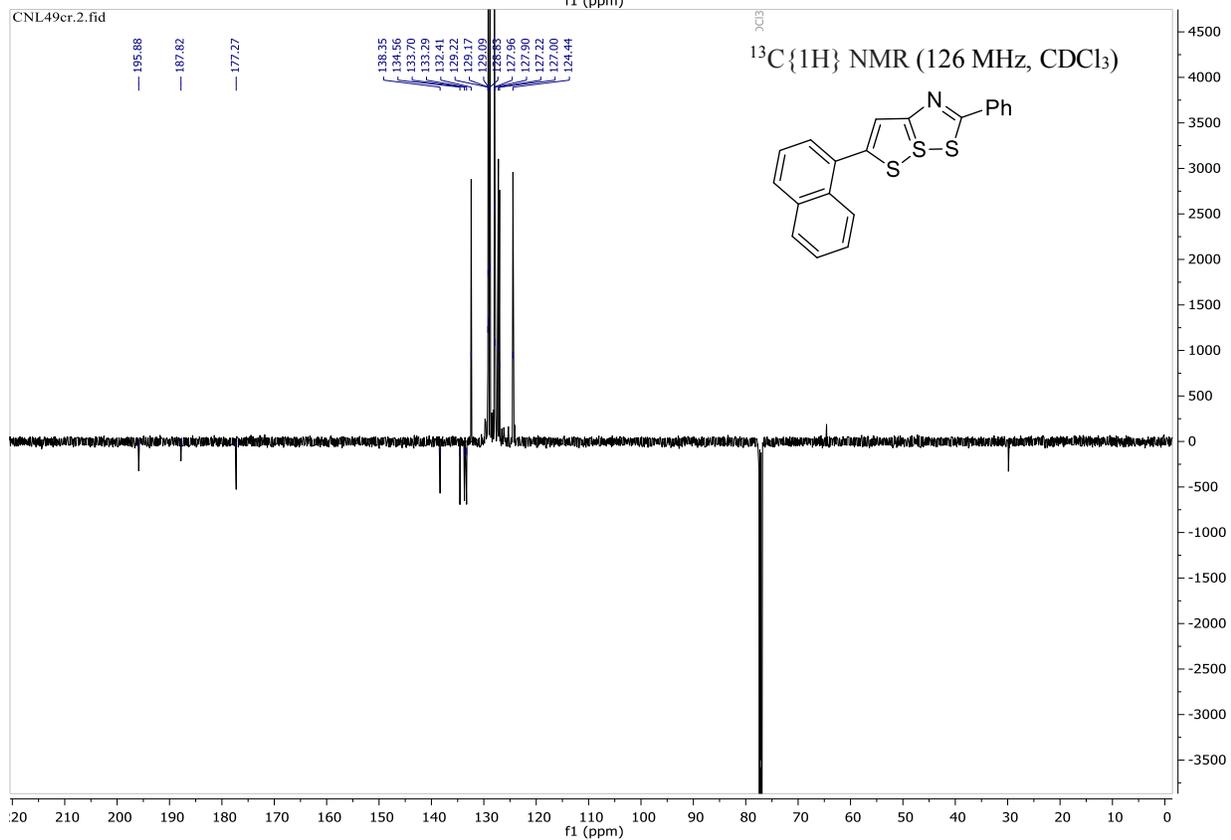
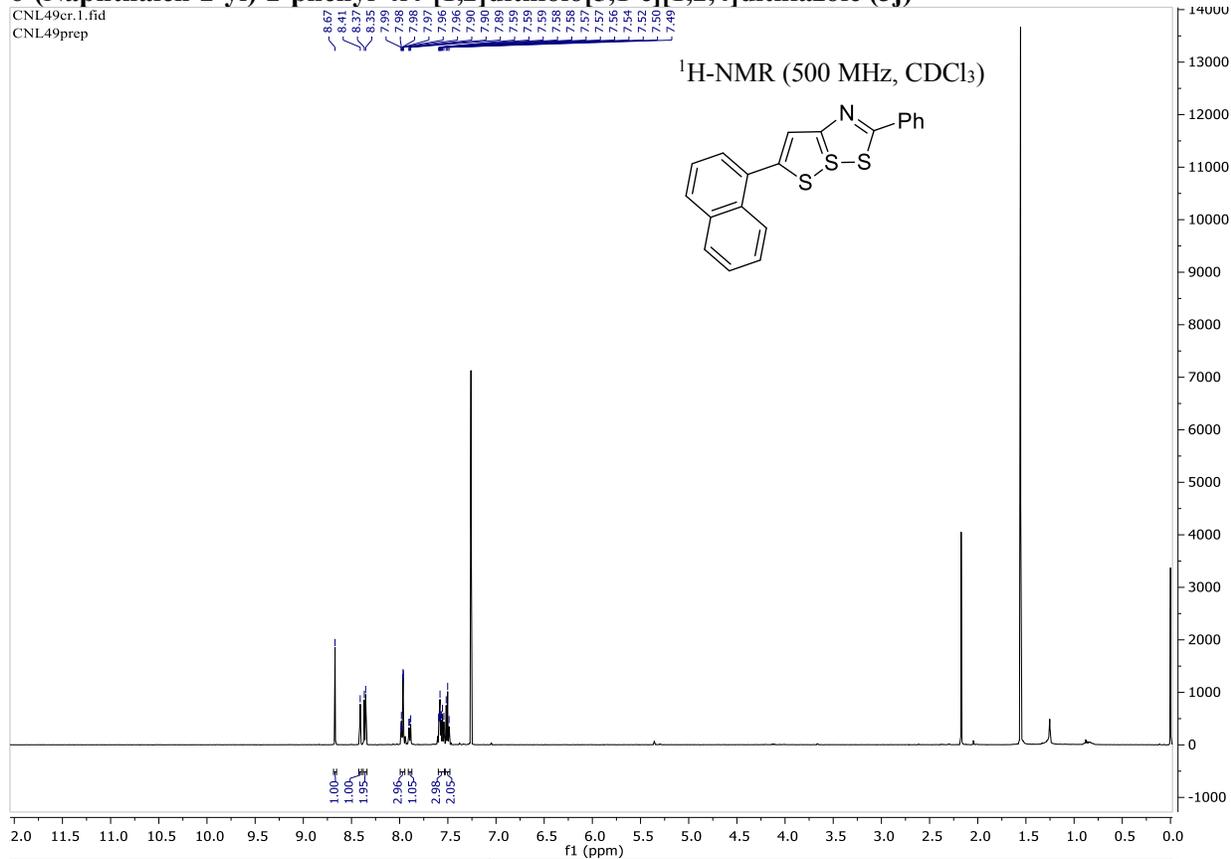
4-(2-Phenyl-1,2-dithiolo[5,1-e][1,2,4]dithiazol-6-yl)benzonitrile (3h)



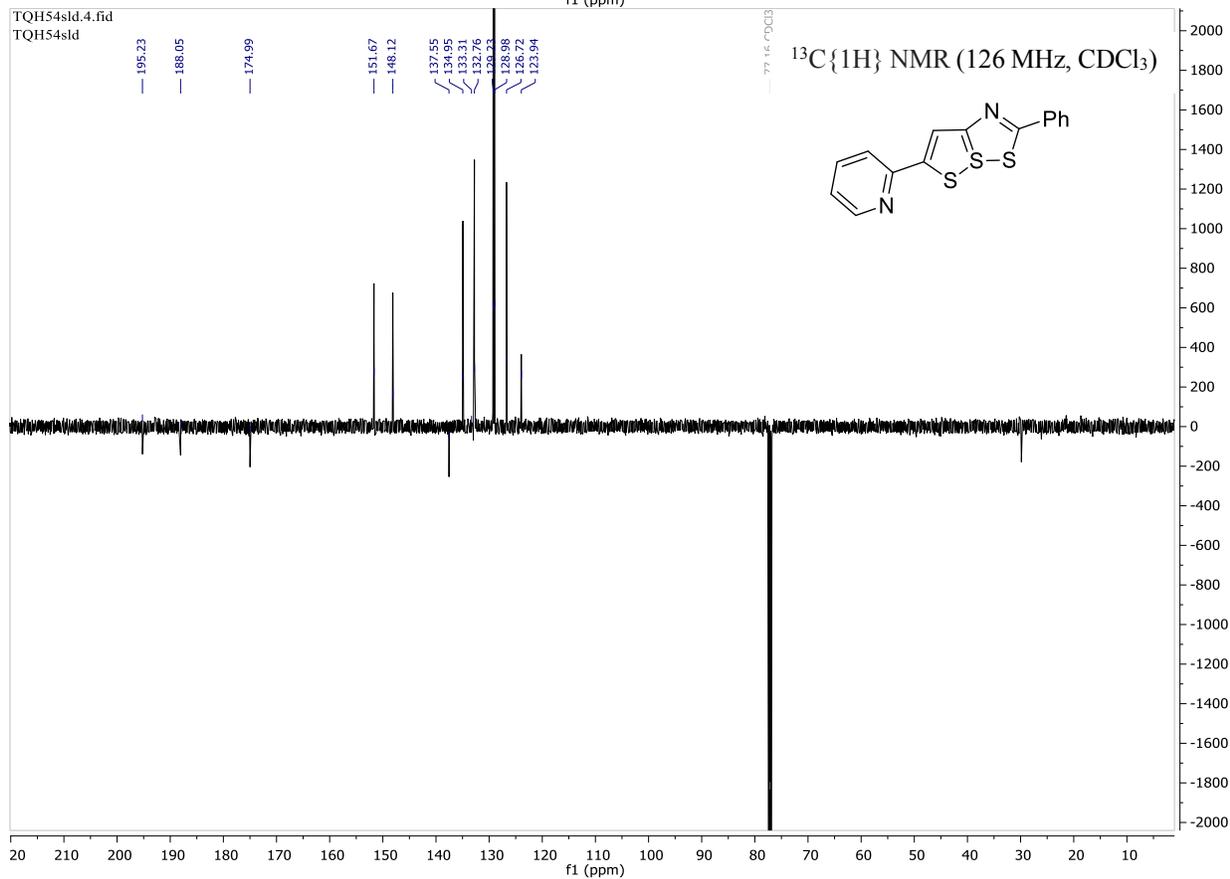
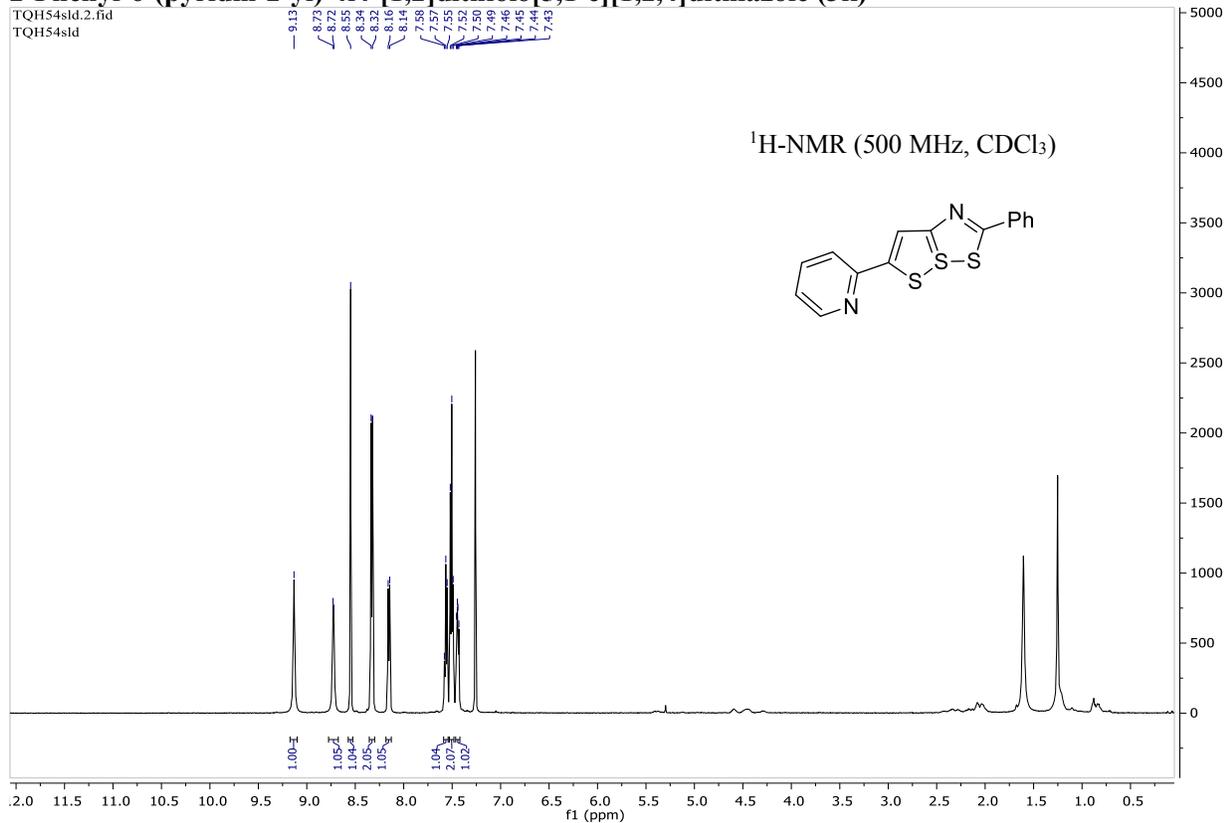
Methyl-4-(2-phenyl-1,2-dithiolo[5,1-e][1,2,4]dithiazol-6-yl)benzoate (3i)



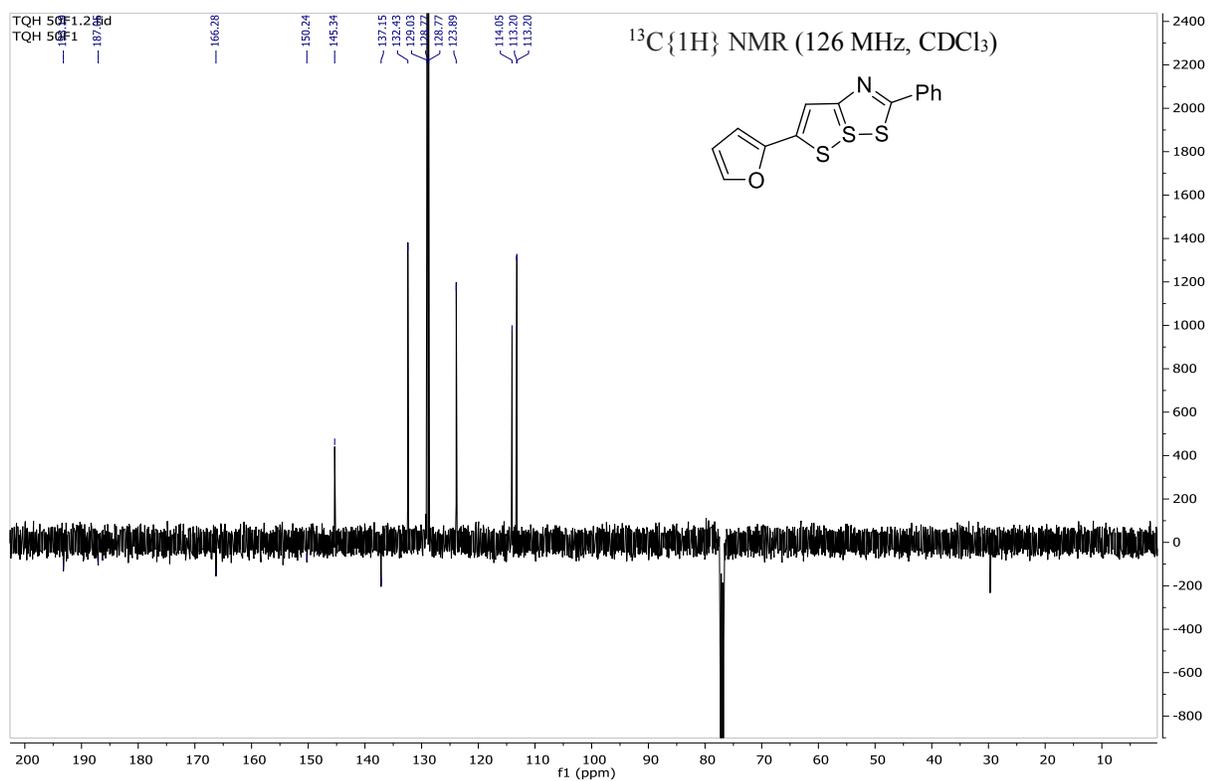
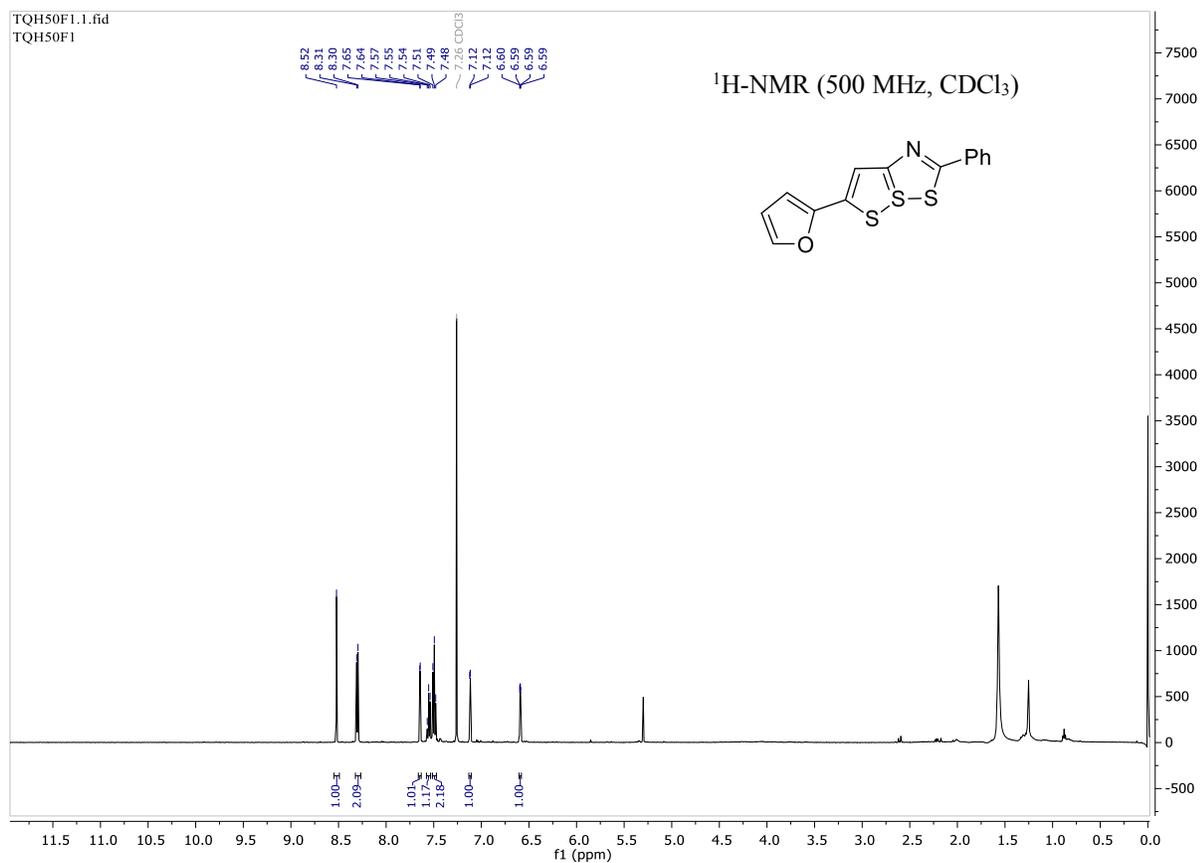
6-(Naphthalen-2-yl)-2-phenyl-4,4-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3j)



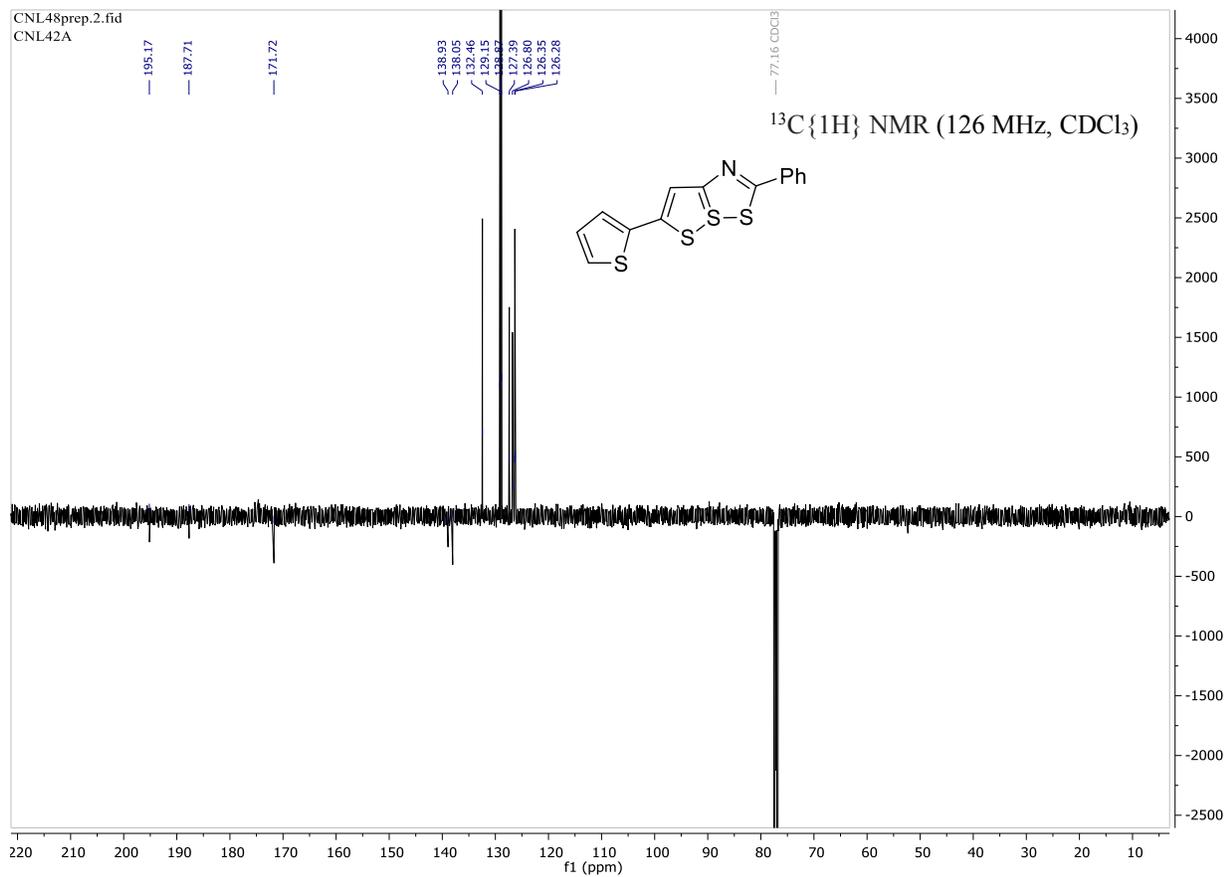
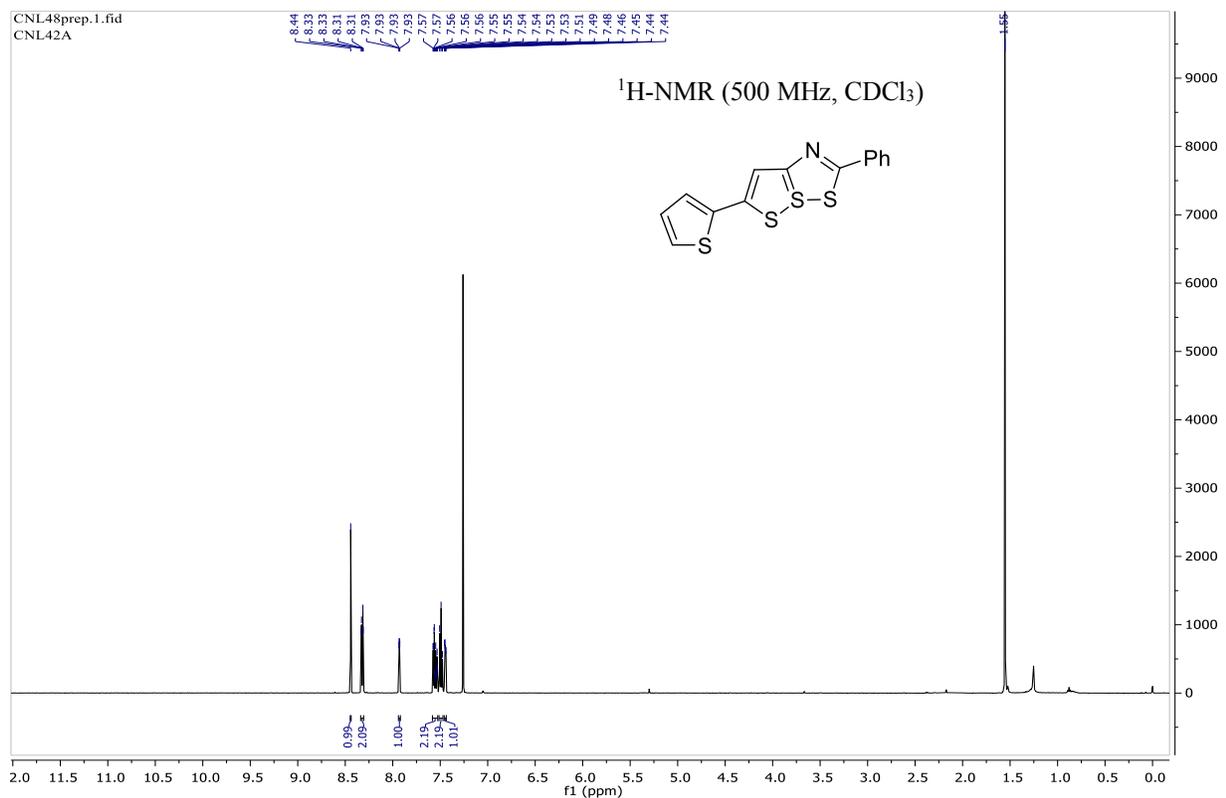
2-Phenyl-6-(pyridin-2-yl)-4H-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3k)



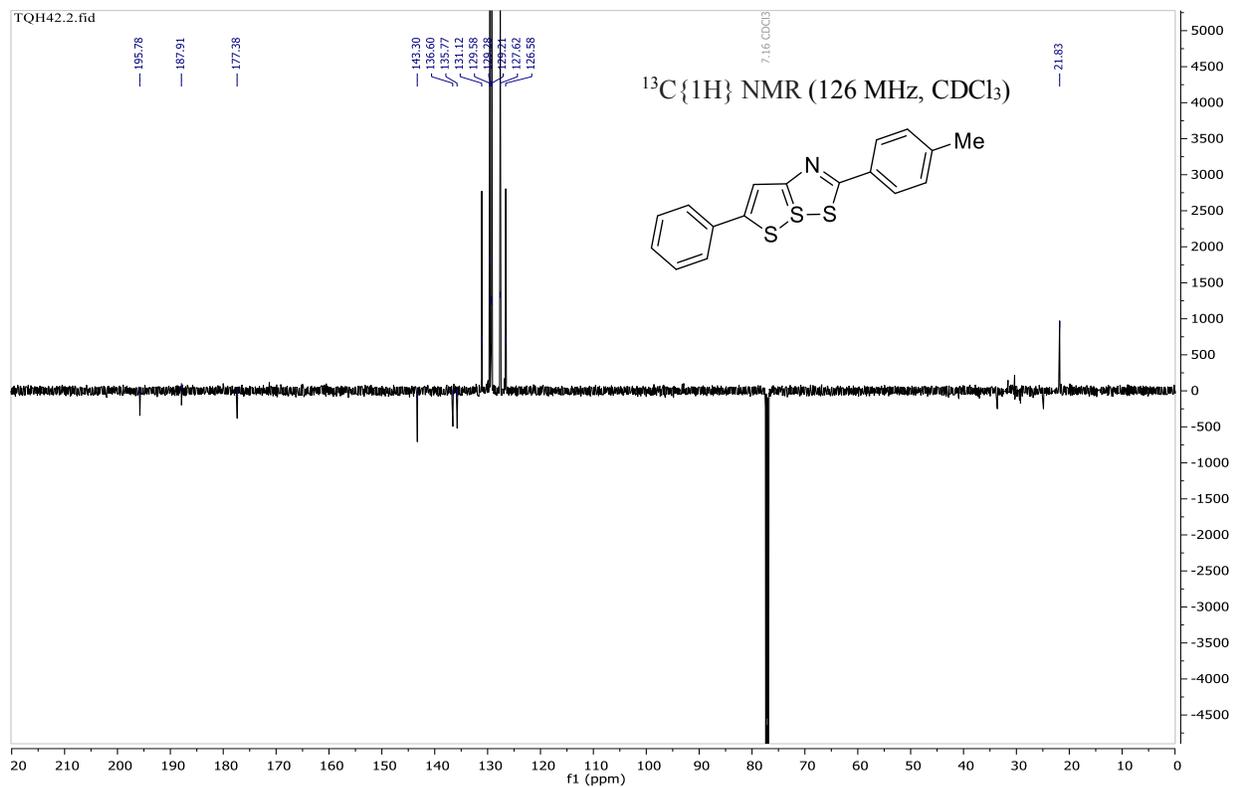
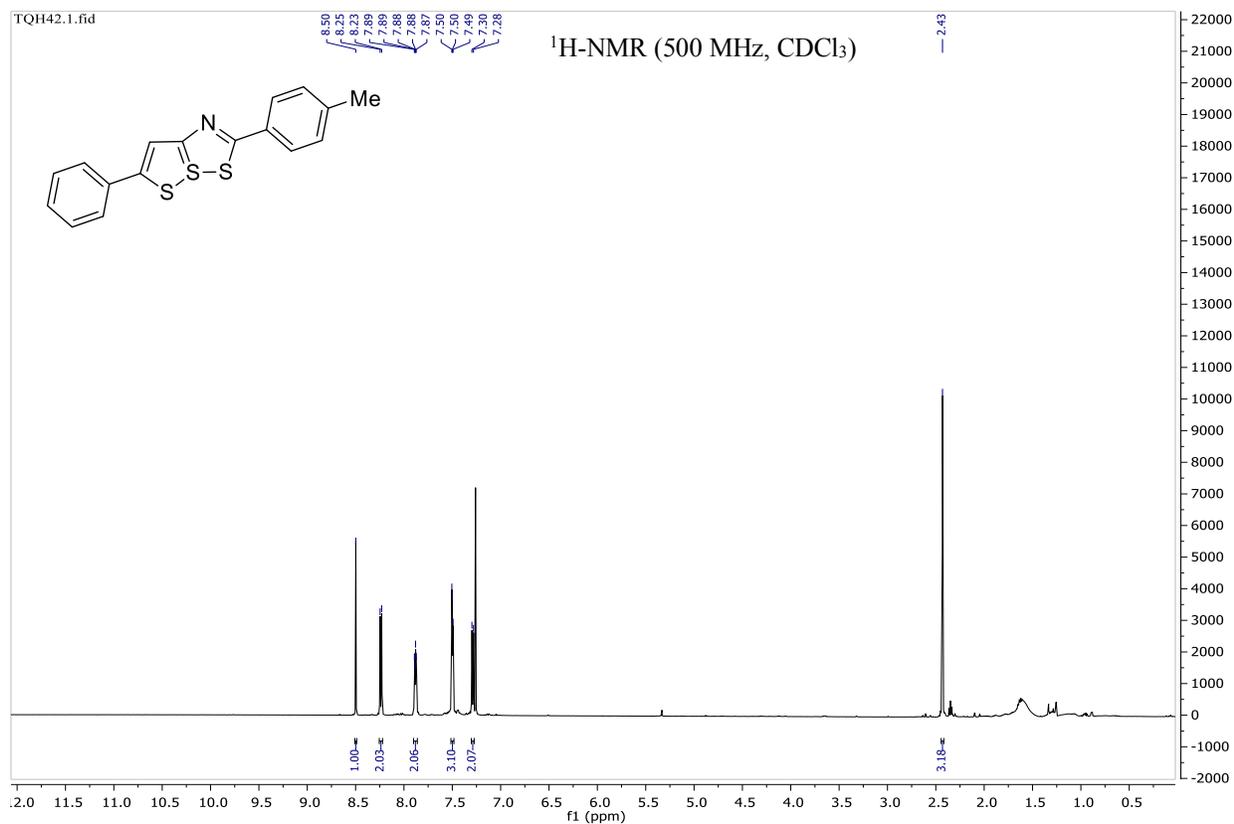
6-(Furan-2-yl)-2-phenyl-4H-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3I)



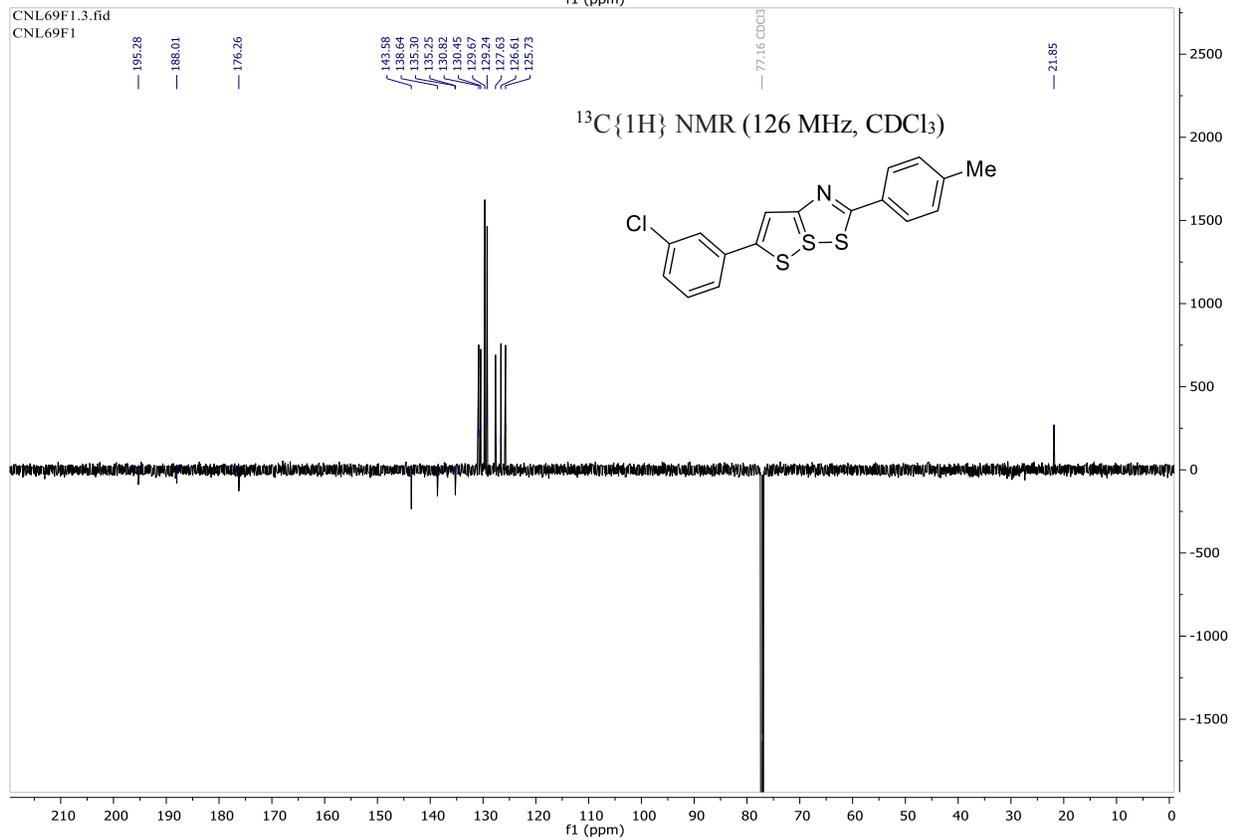
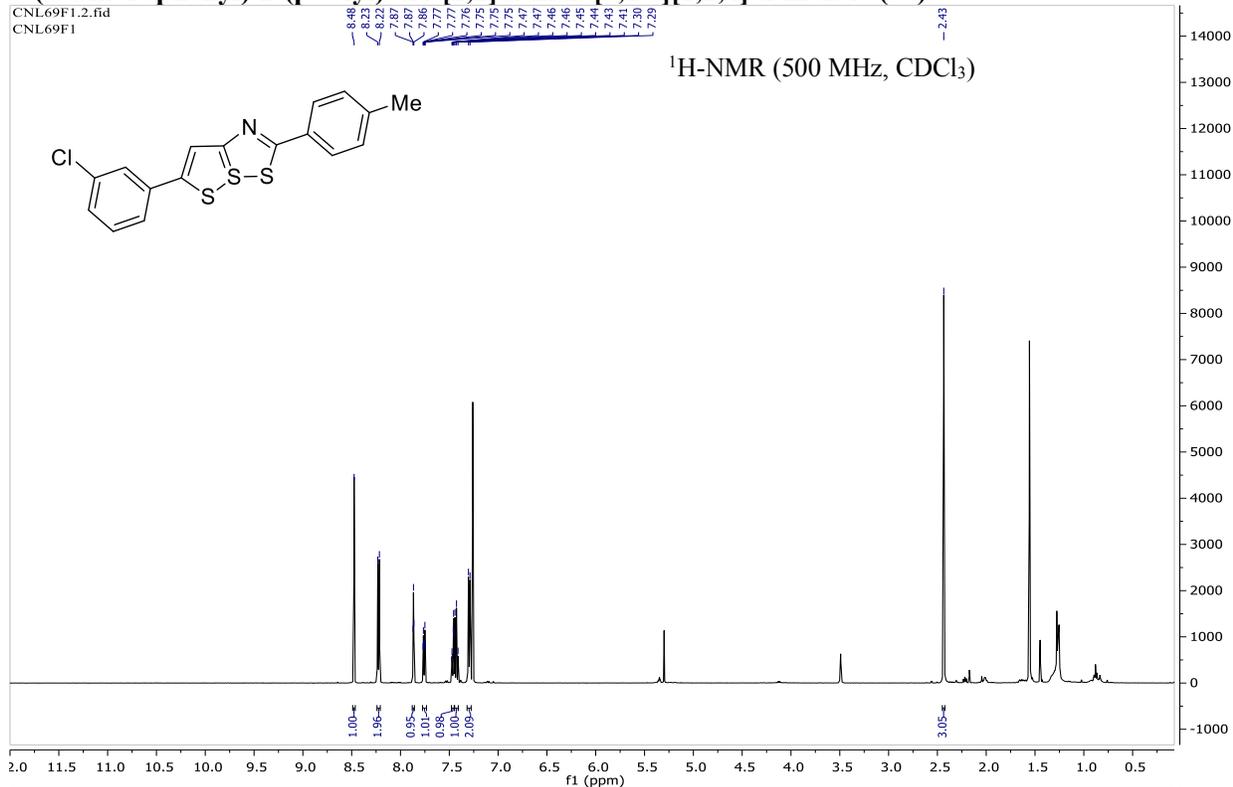
2-Phenyl-6-(thiophen-2-yl)-4H-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3m)



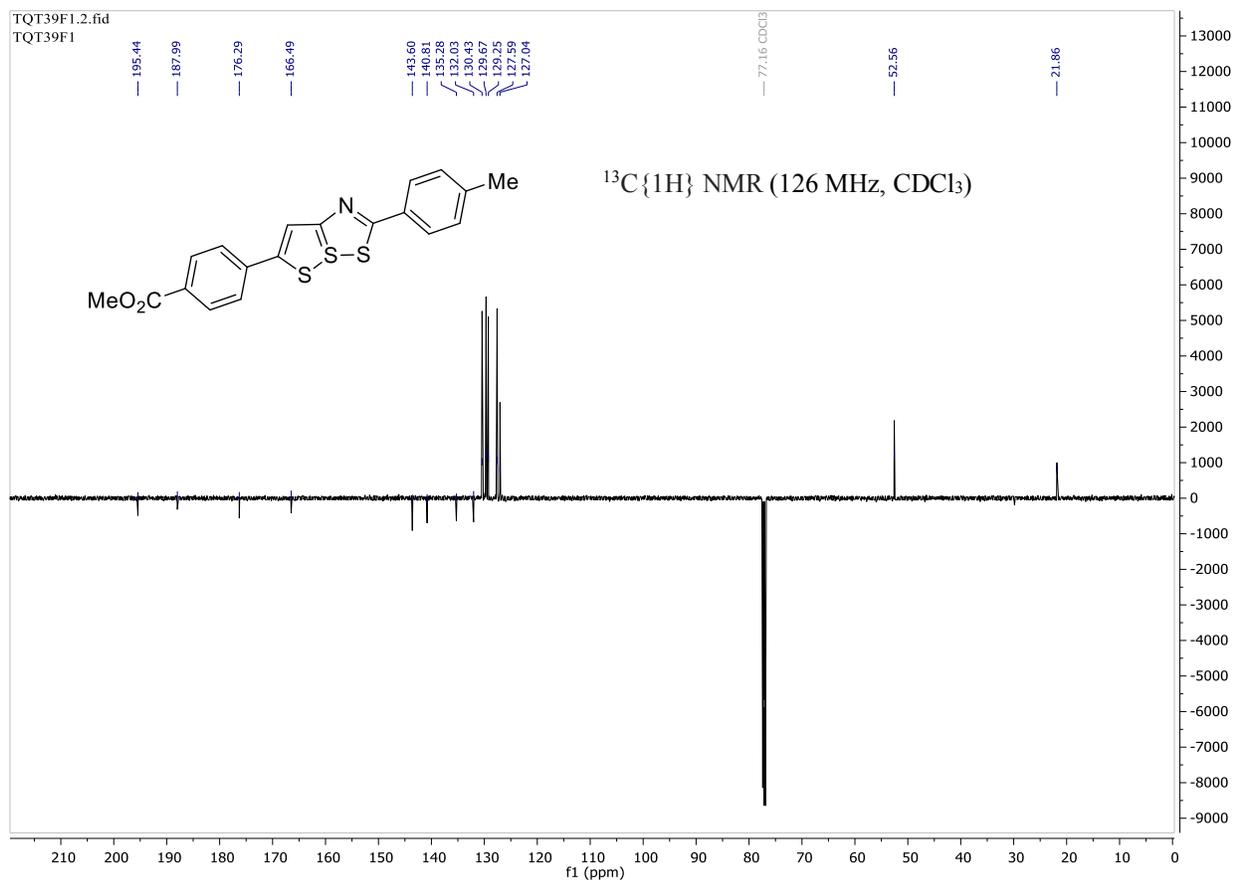
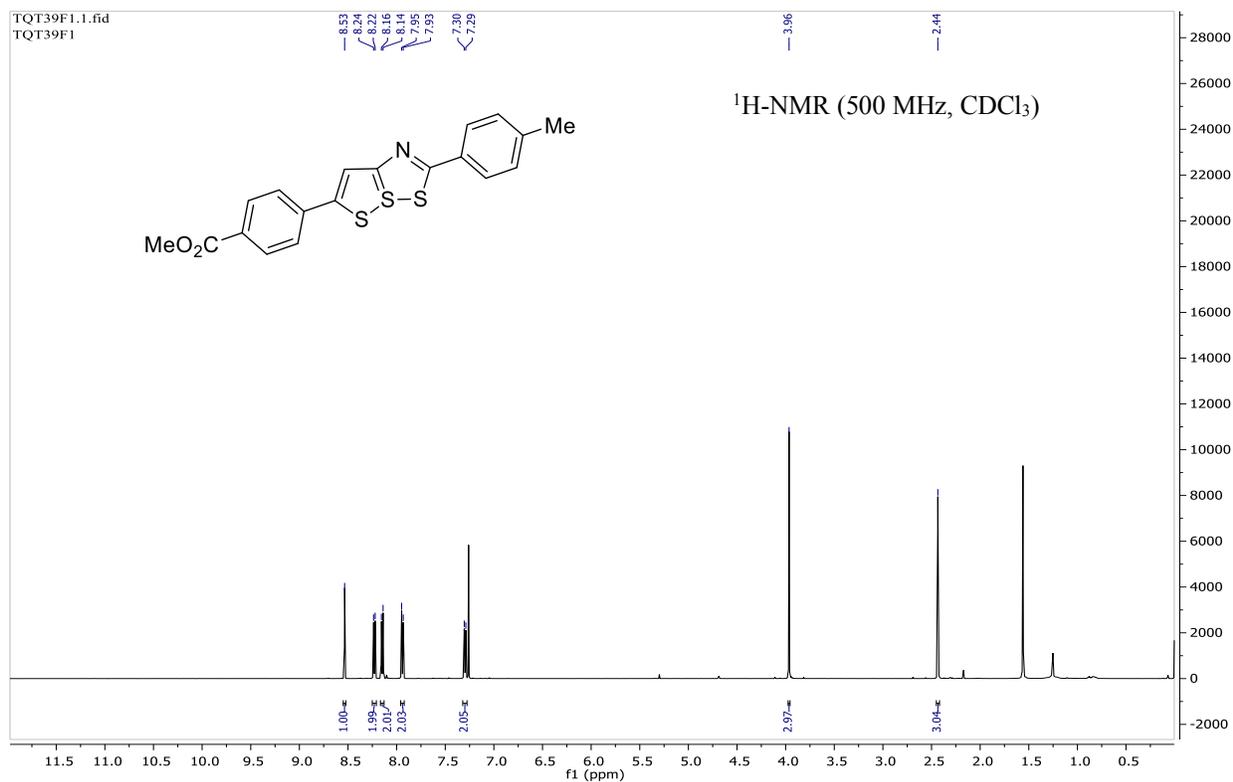
6-Phenyl-2-(p-tolyl)-4[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3n)



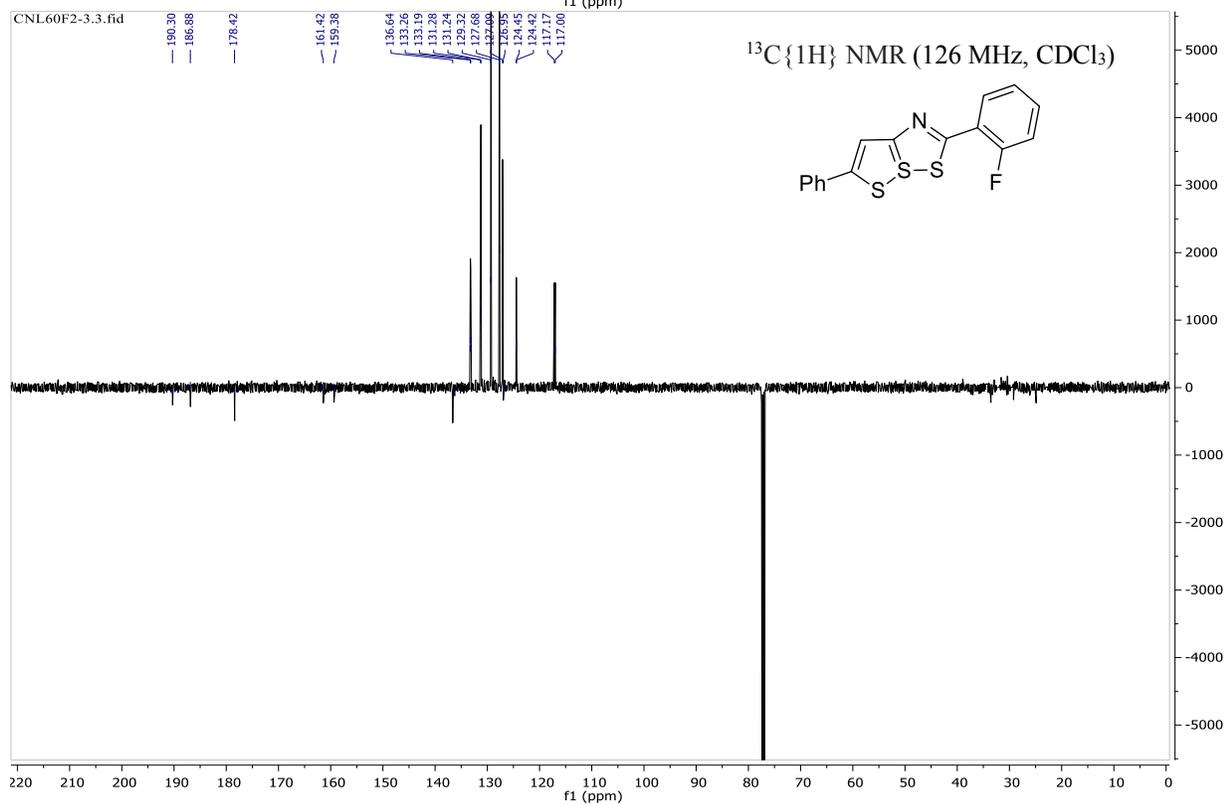
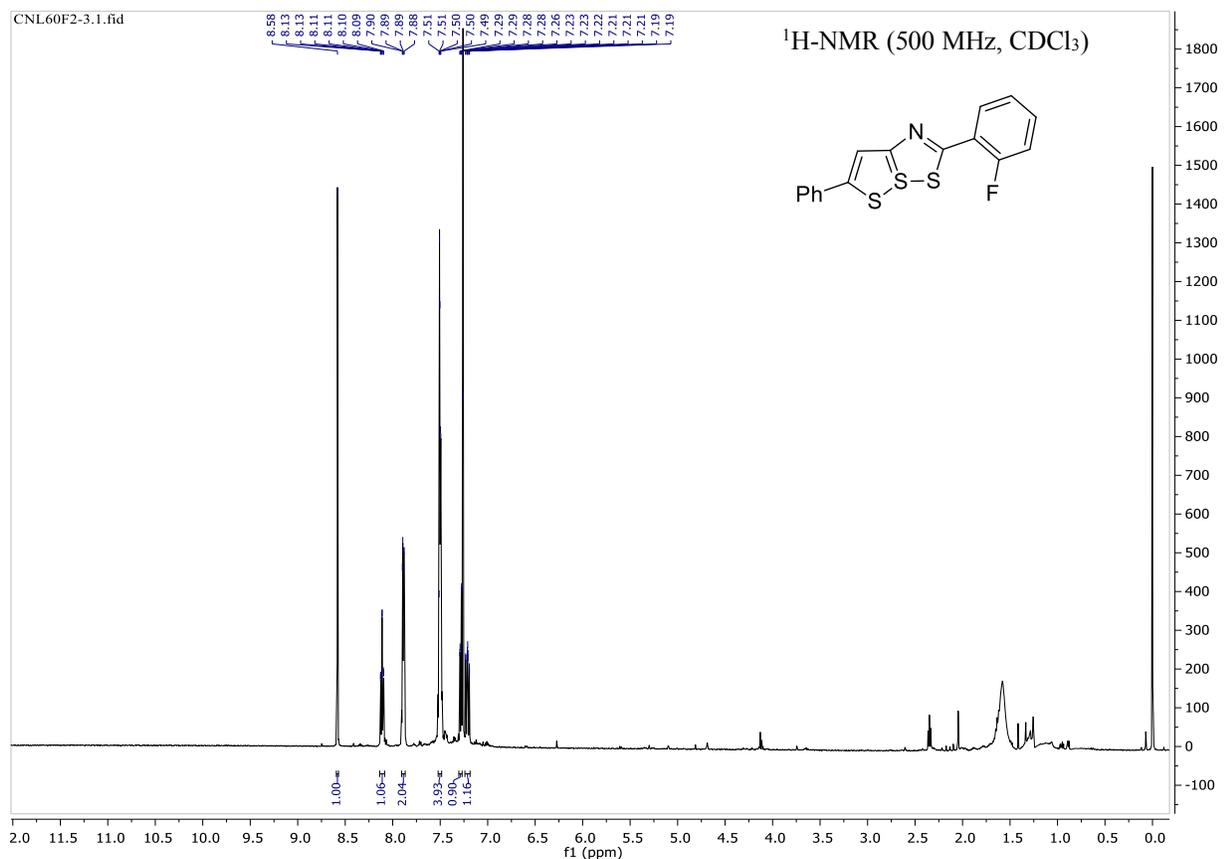
6-(3-Chlorophenyl)-2-(p-tolyl)-4H-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3o)



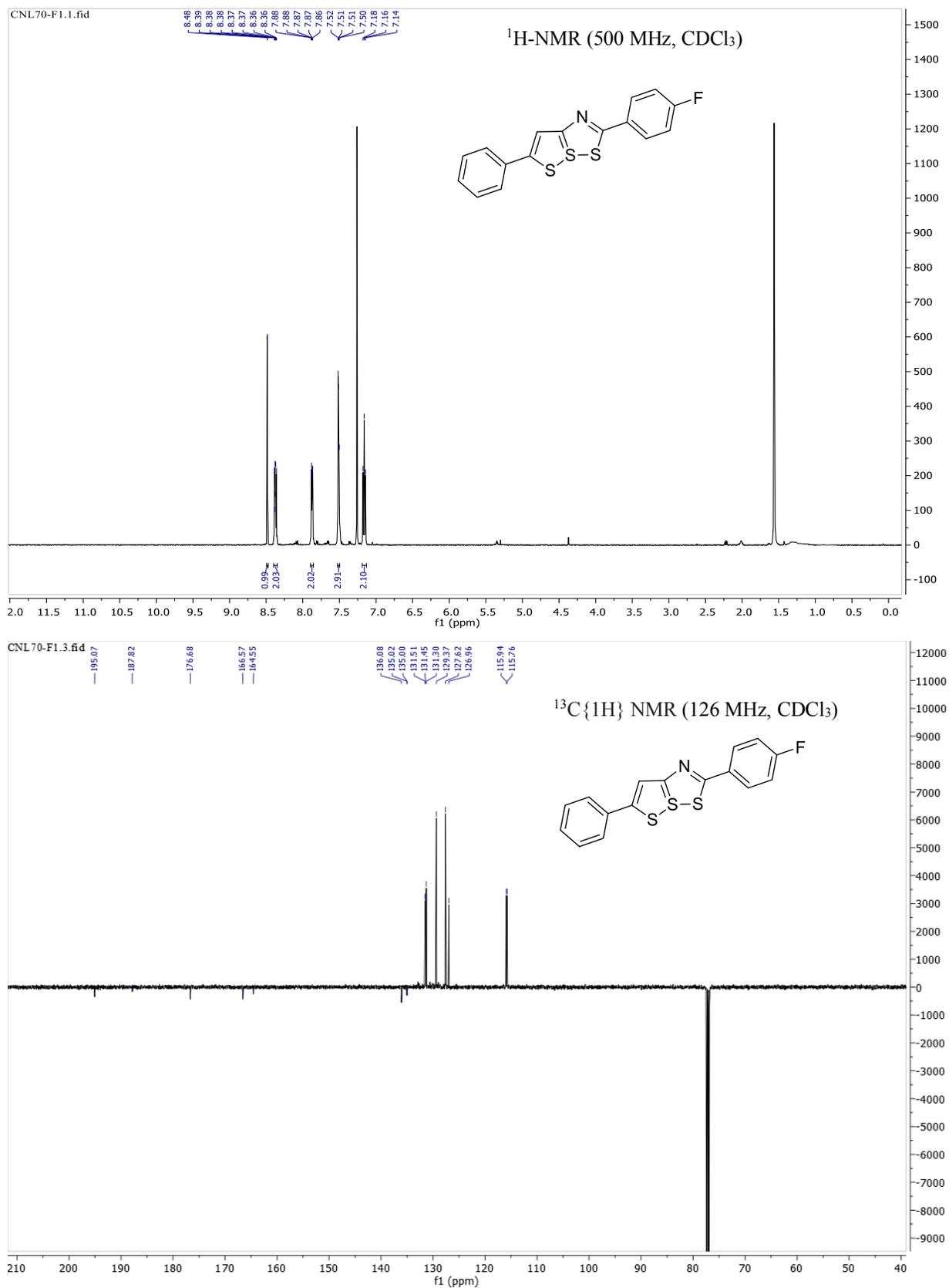
Methyl 4-(2-(p-tolyl)-4-[1,2]dithiolo[5,1-e][1,2,4]dithiazol-6-yl)benzoate (3p)



2-(2-Fluorophenyl)-6-phenyl-4,4-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3q)

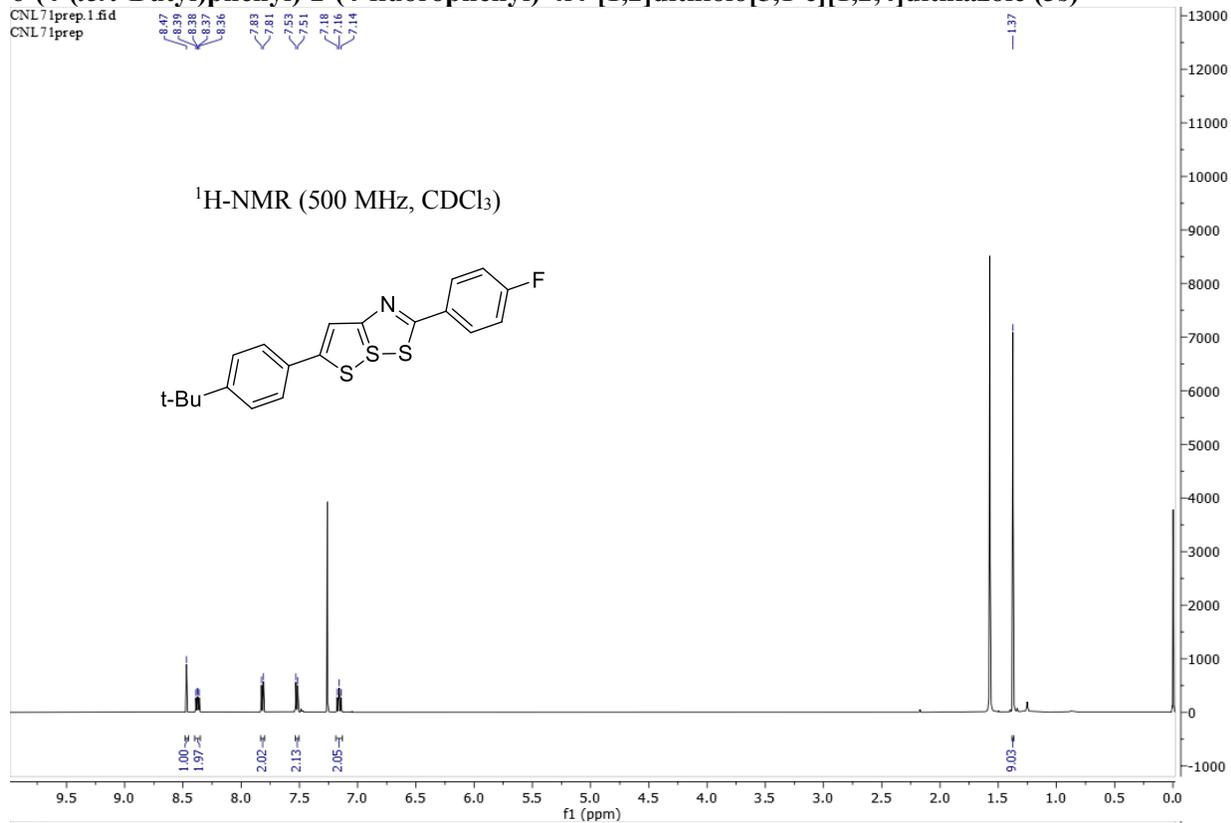


2-(4-Fluorophenyl)-6-phenyl-4,4-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3r)

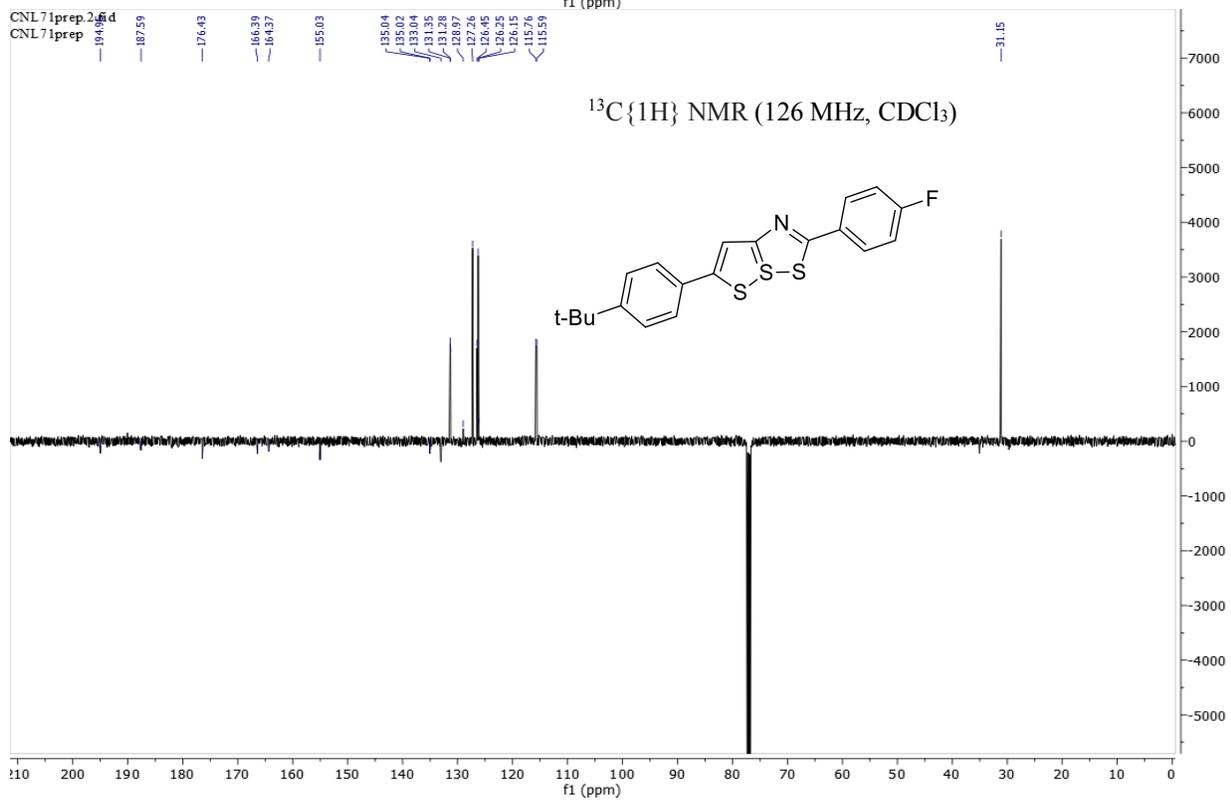


6-(4-(*tert*-Butyl)phenyl)-2-(4-fluorophenyl)-4,4-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3s)

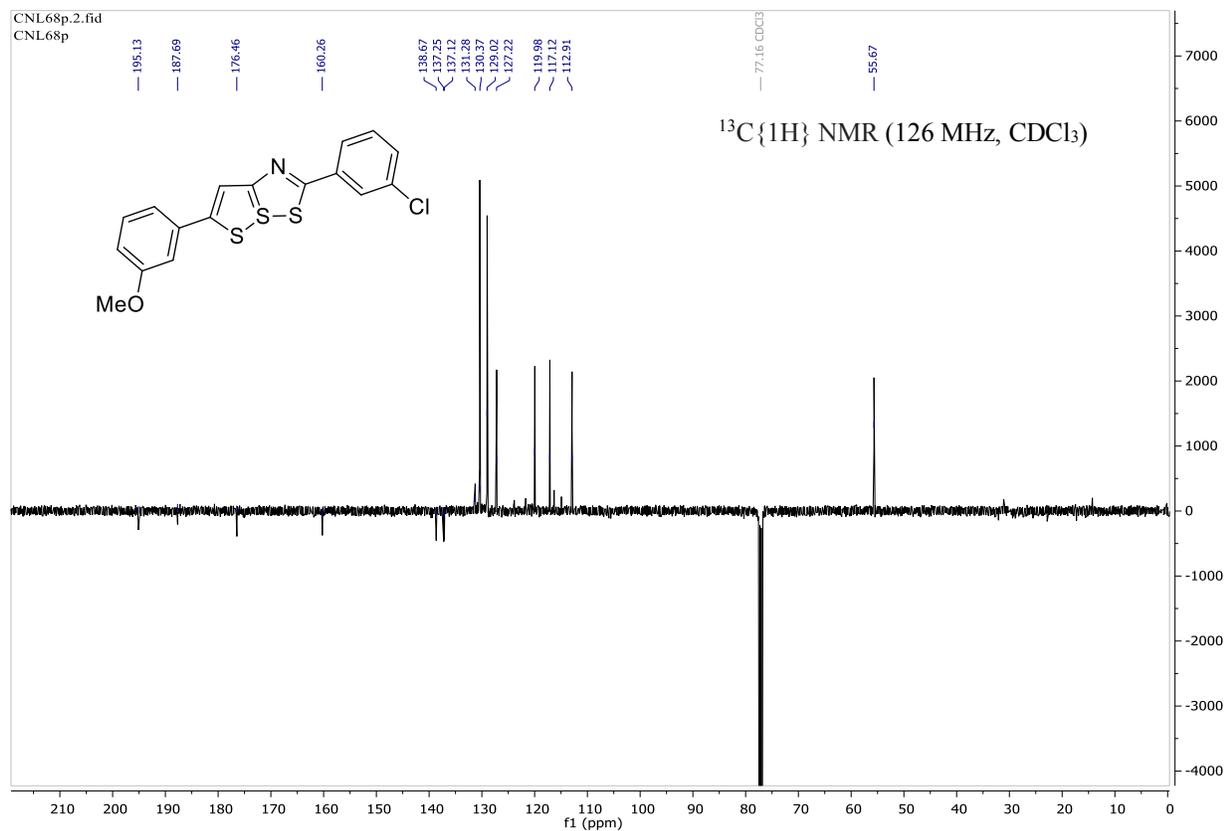
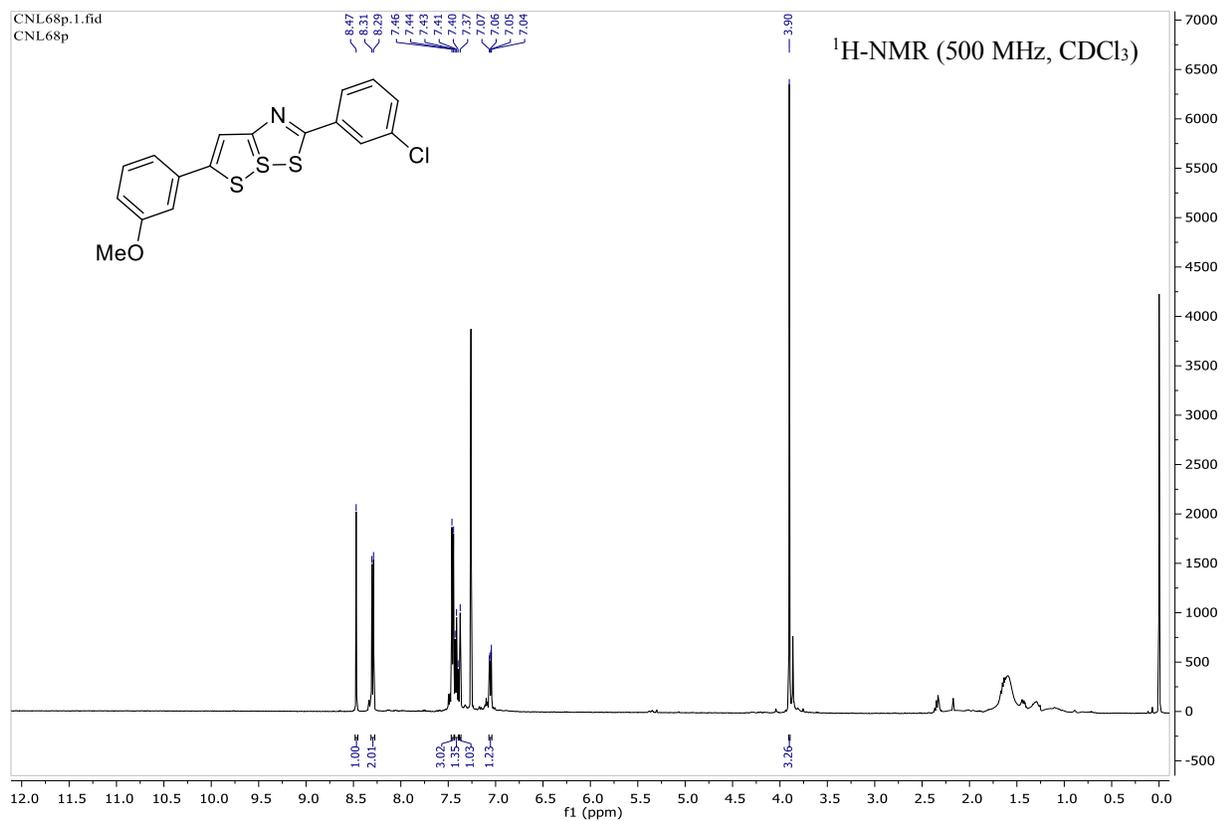
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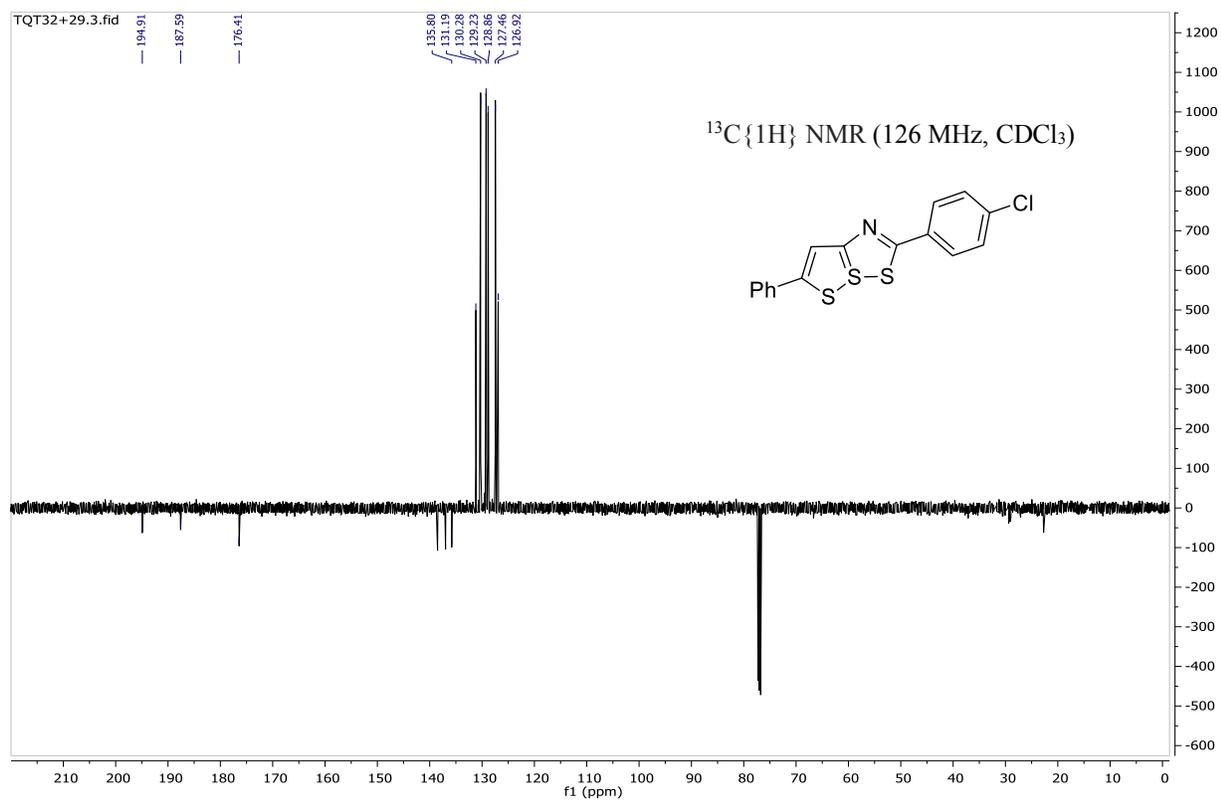
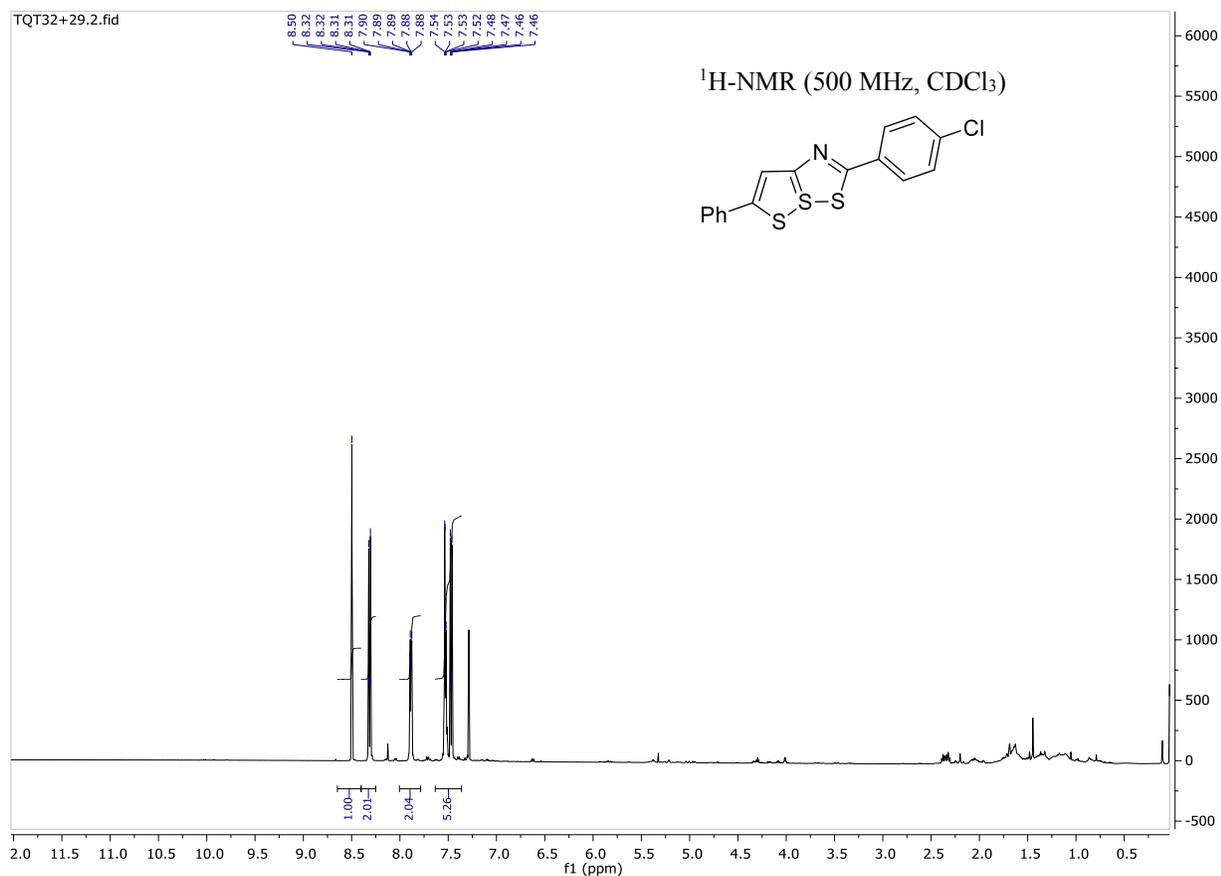
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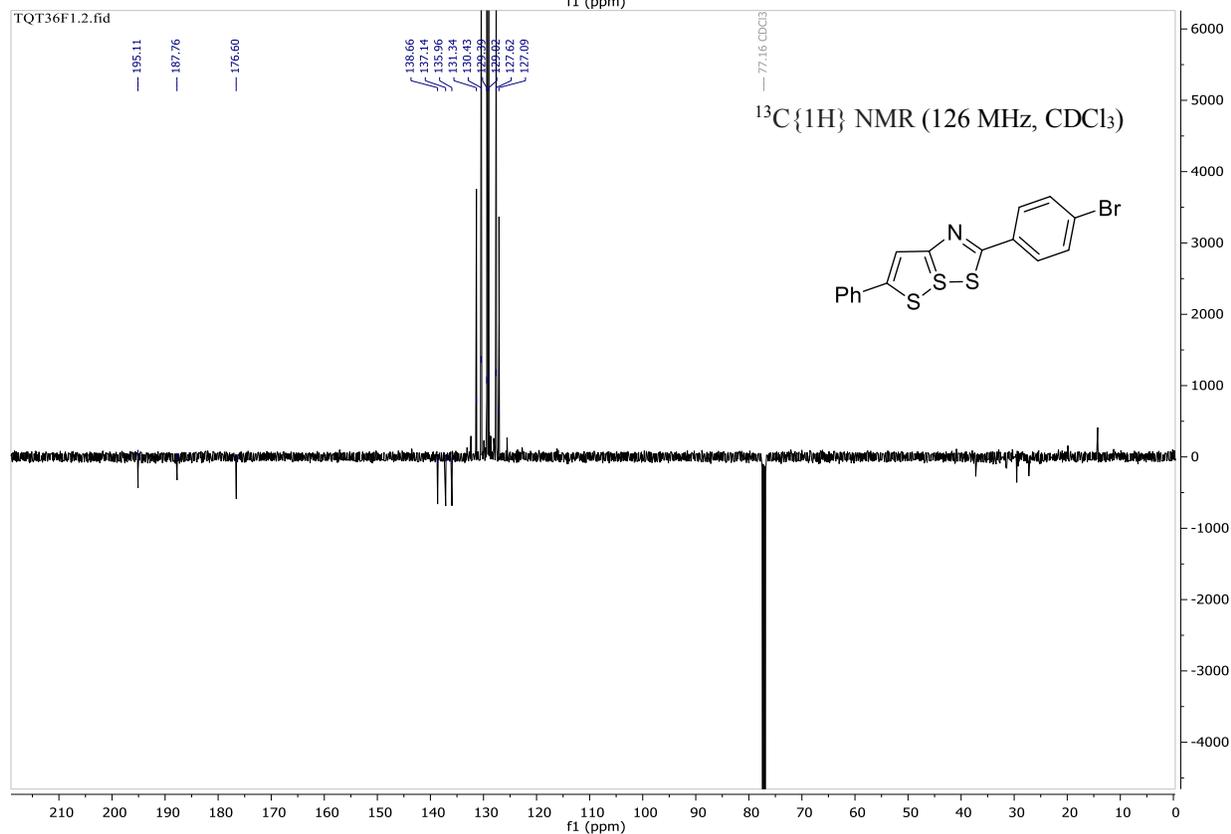
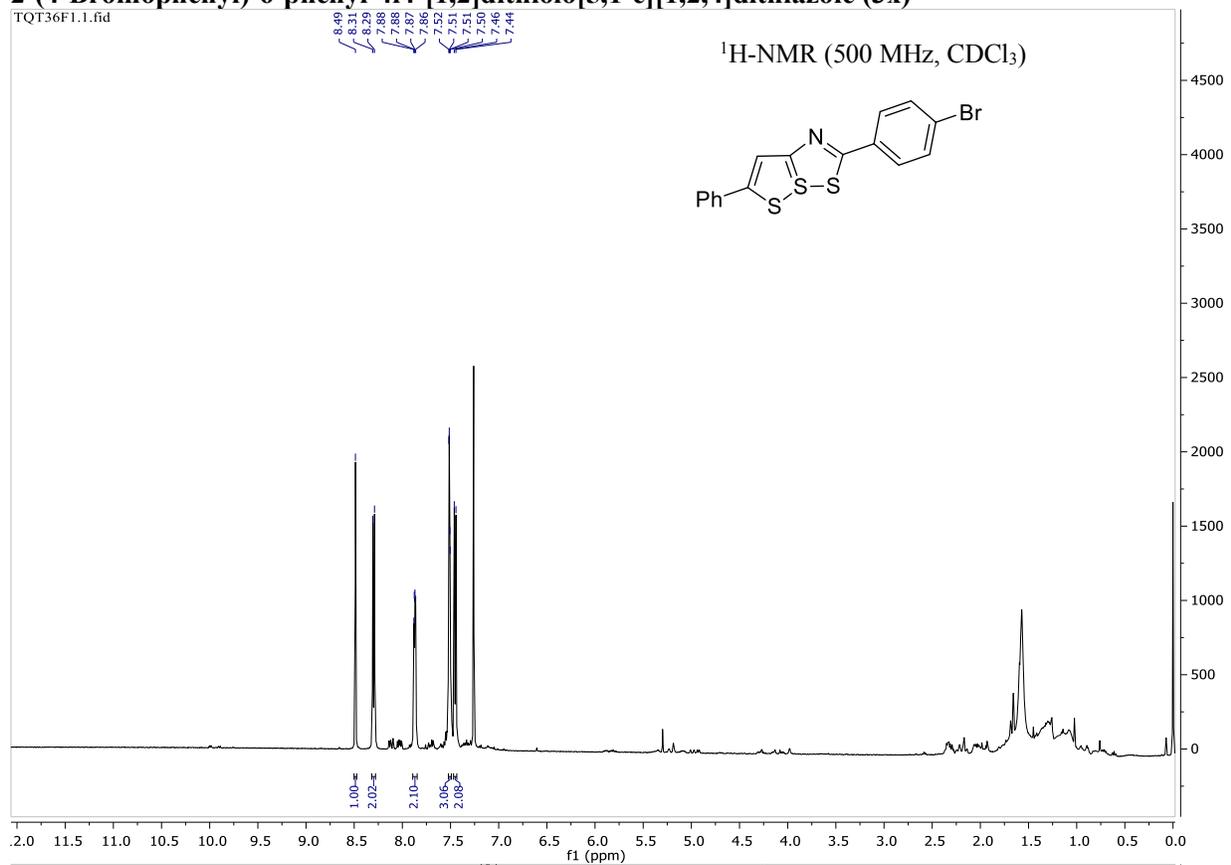
2-(3-Chlorophenyl)-6-(3-methoxyphenyl)-4H-[1,2]dithiolo[5,1e][1,2,4]dithiazole (3u)



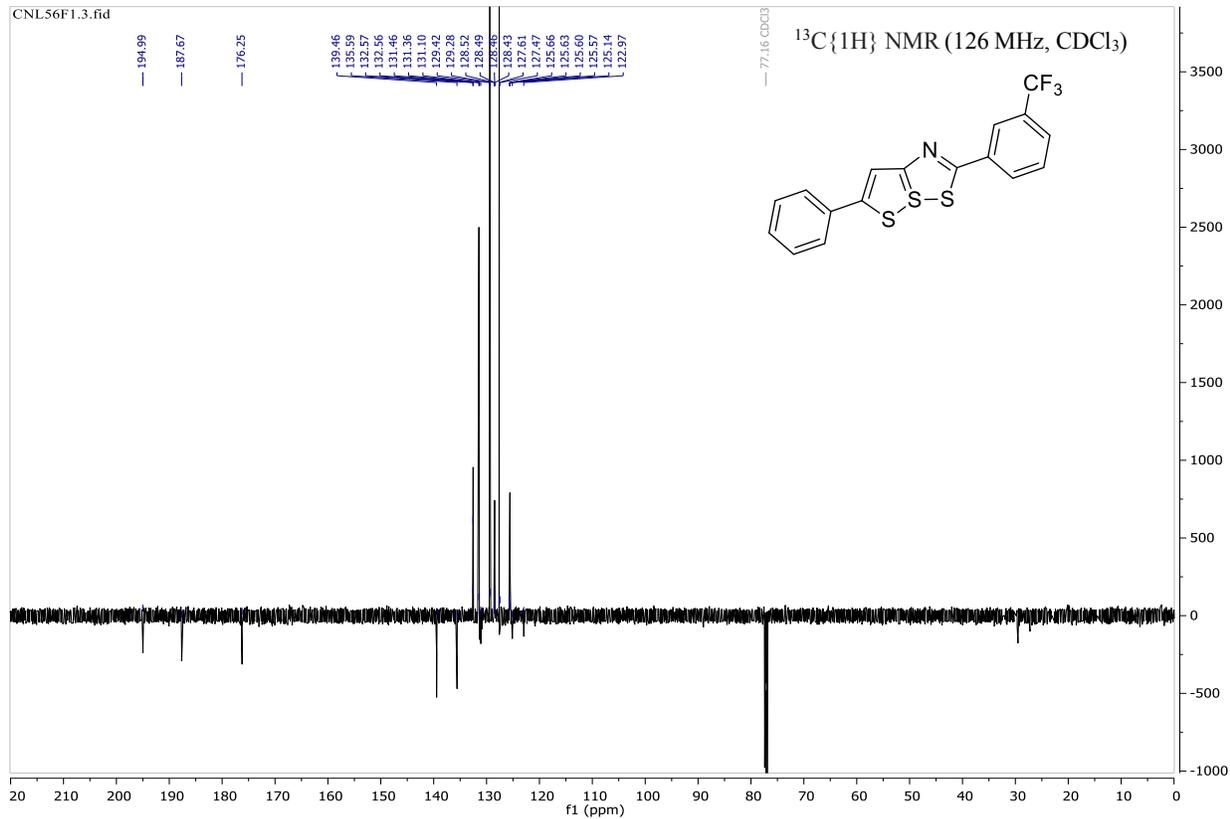
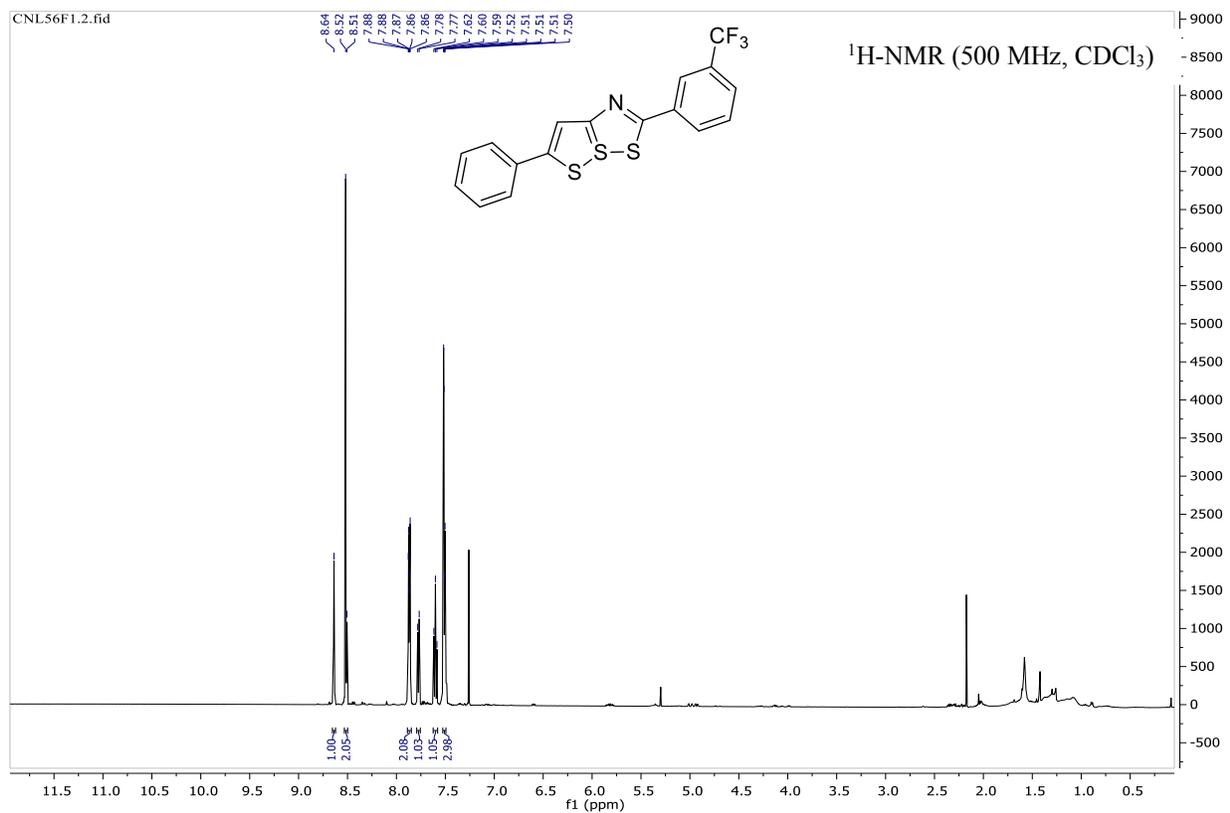
2-(4-Chlorophenyl)-6-phenyl-4H-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3w)



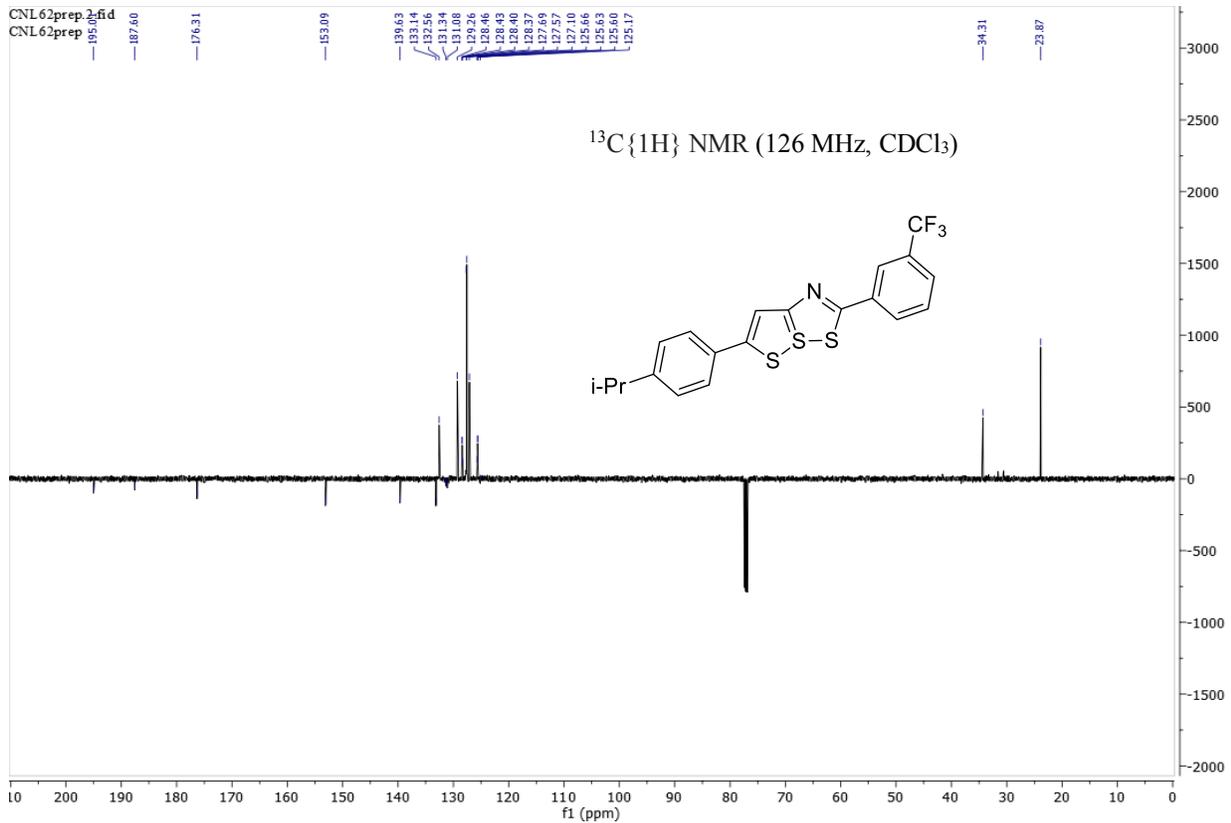
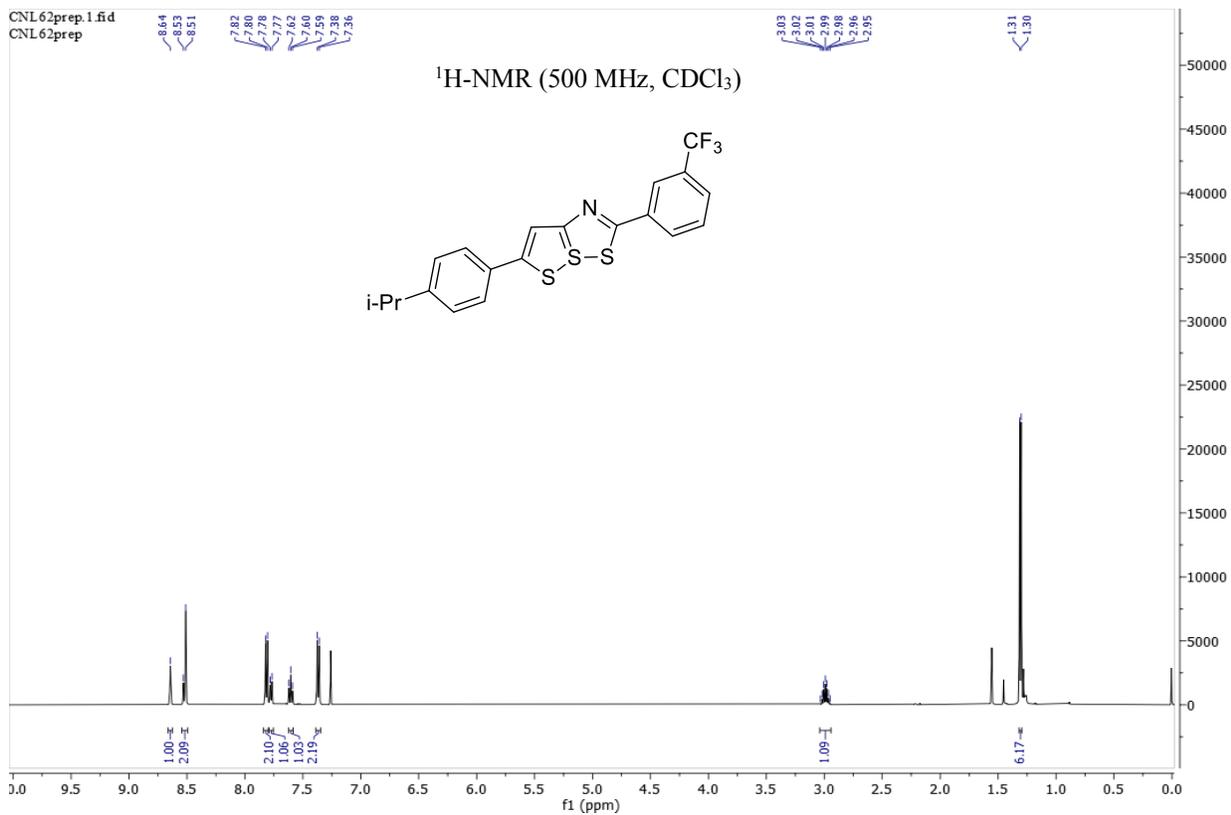
2-(4-Bromophenyl)-6-phenyl-4,4-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3x)



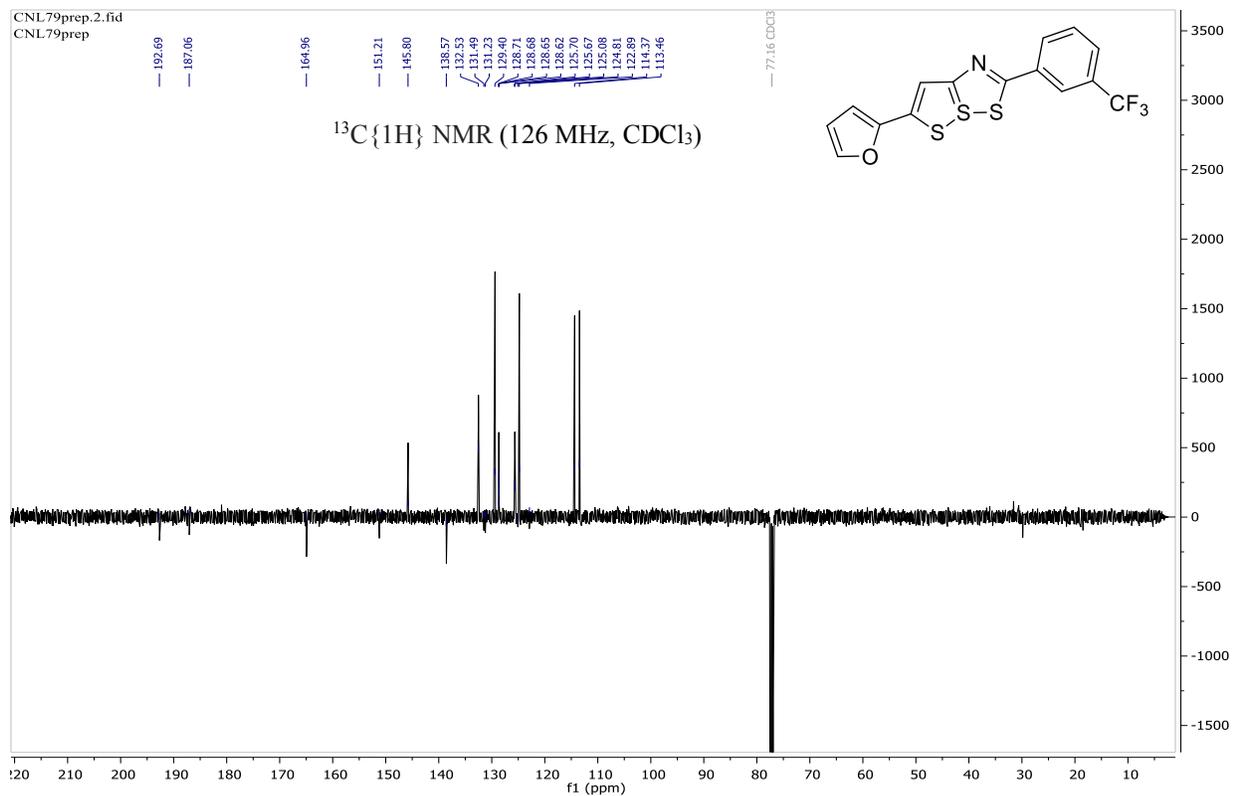
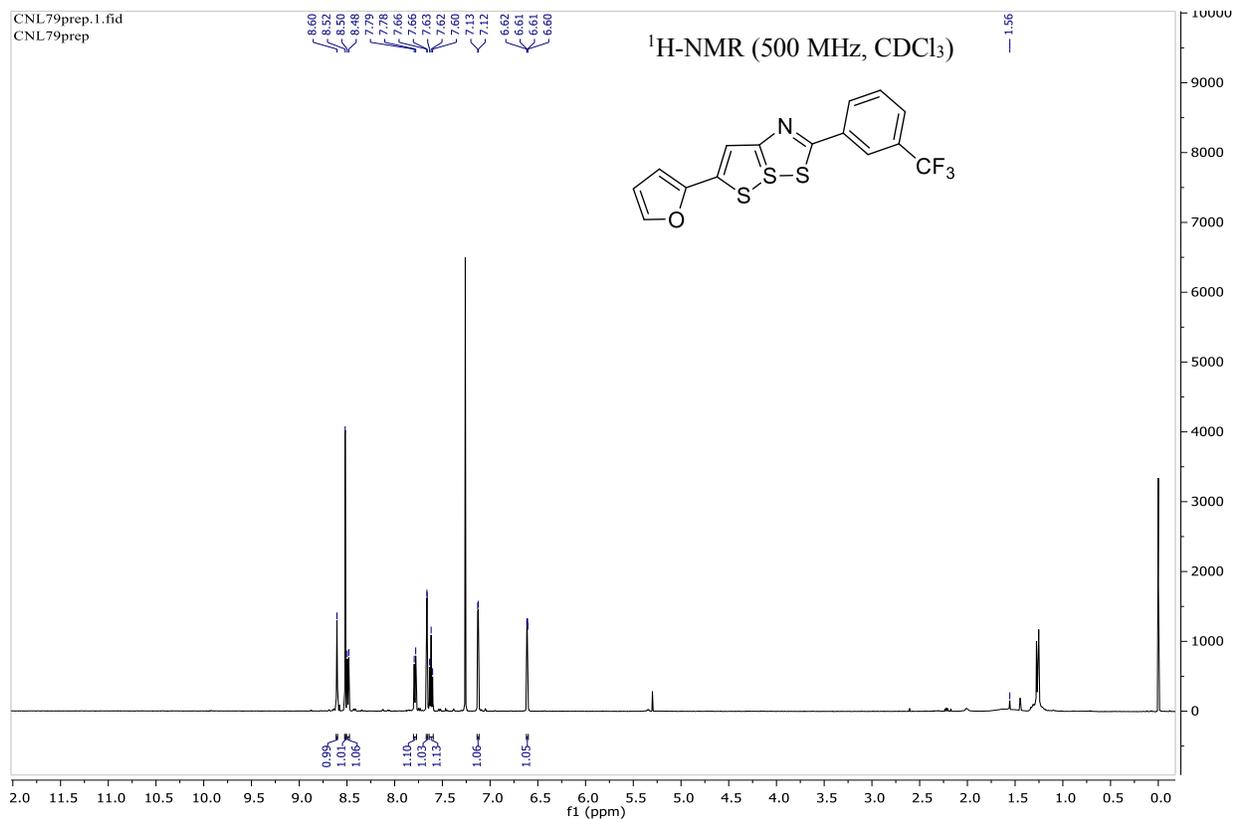
6-Phenyl-2-(3-(trifluoromethyl)phenyl)-4,4-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3y)



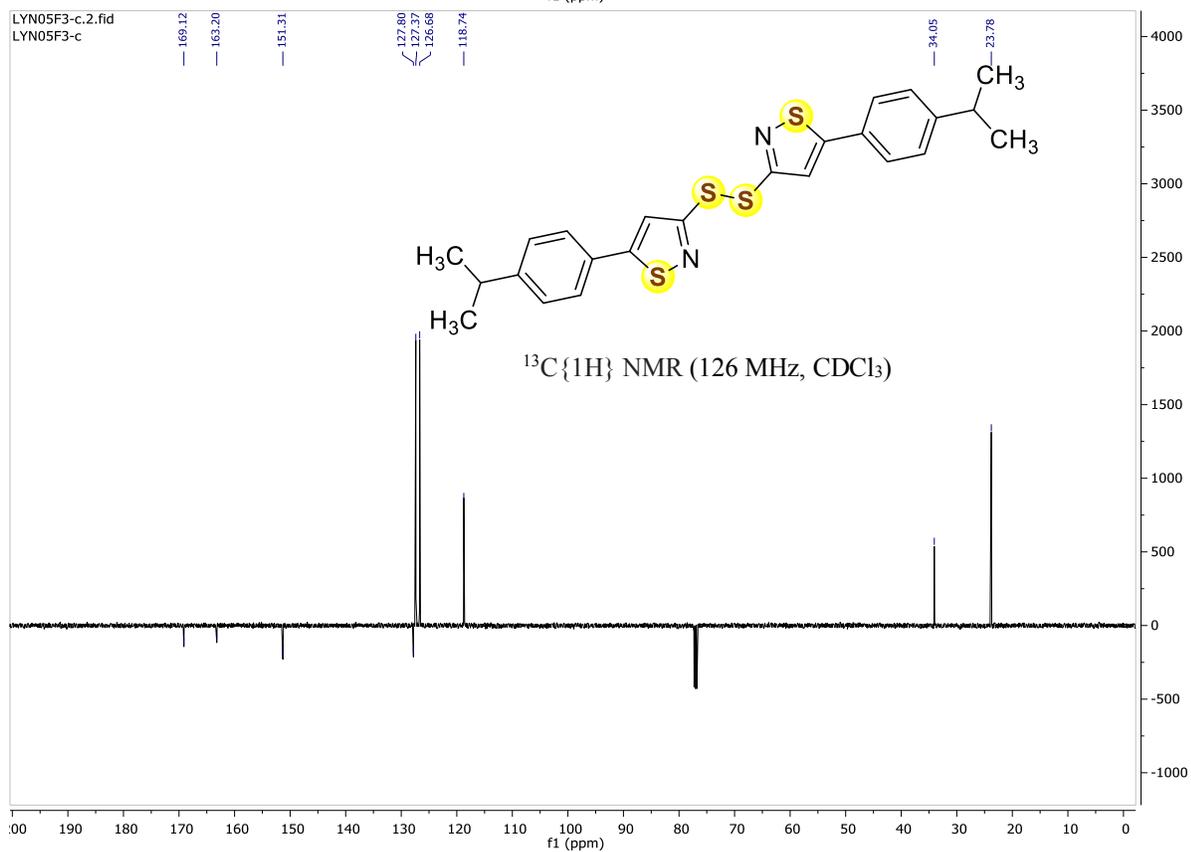
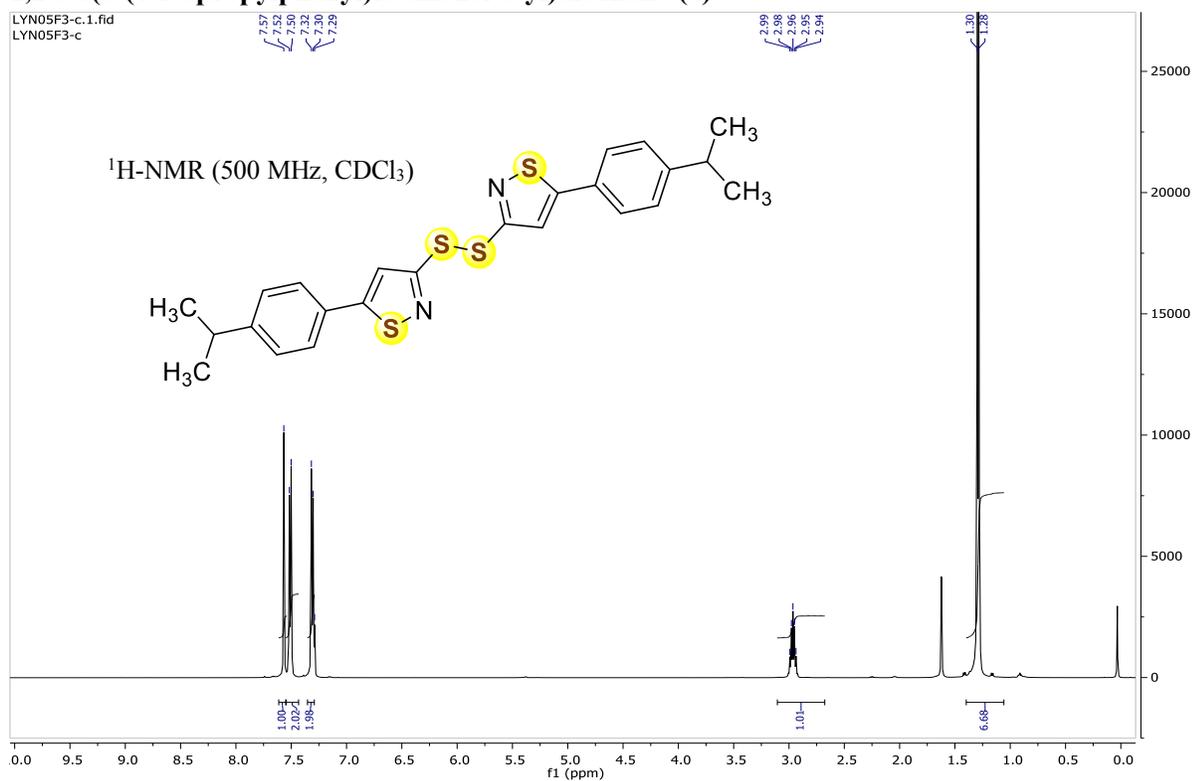
6-(4-Isopropylphenyl)-2-(3-(trifluoromethyl)phenyl)-4,4-[1,2]dithiolo[5,1-e][1,2,4]dithiazole (3z)



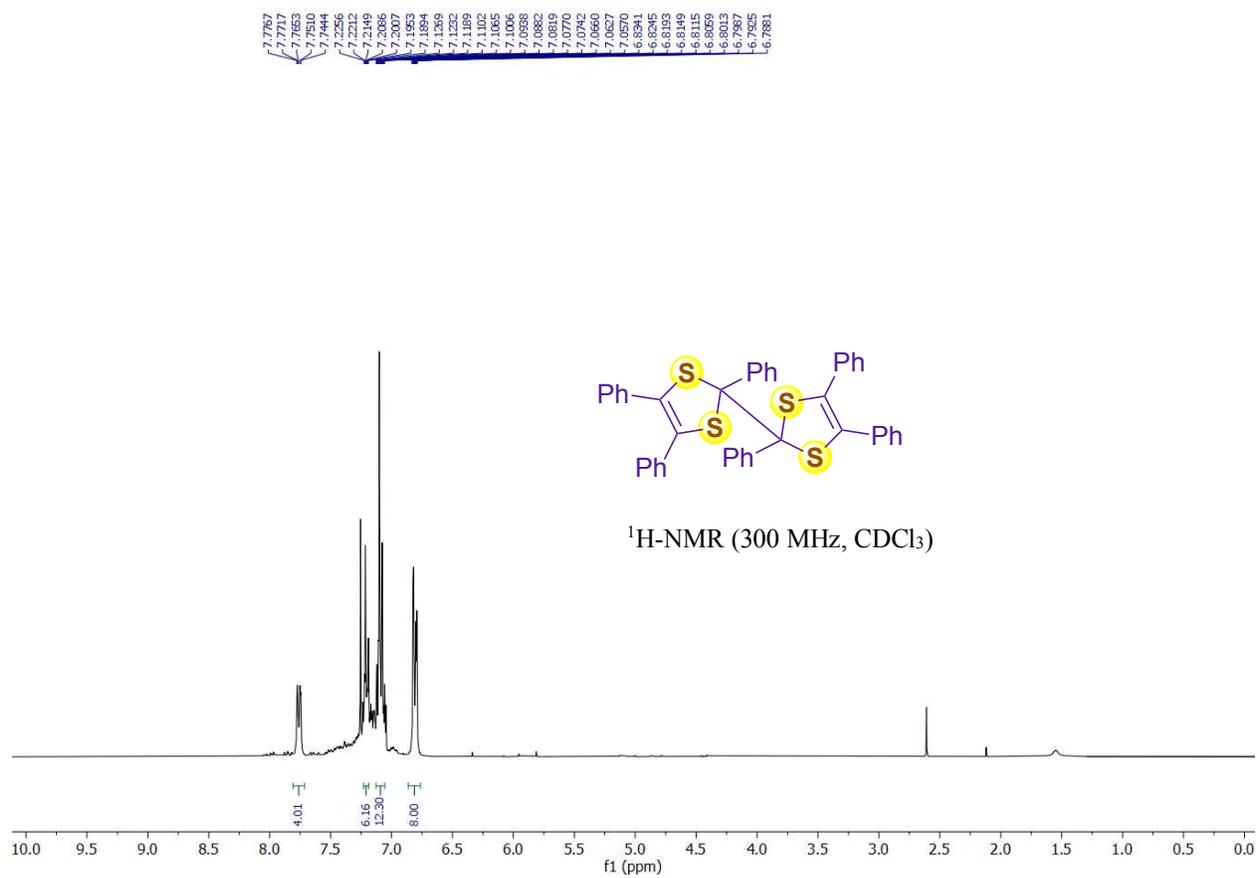
6-(Furan-2-yl)-2-(3-(trifluoromethyl)phenyl)-1,2-dithiazole (3aa)



1,2-bis(5-(4-Isopropylphenyl)isothiazol-3-yl)disulfane (4)



2,2',4,4',5,5'-Hexaphenyl-2,2'-bi(1,3-dithiole) (5)²



² T. B. Nguyen and P. Retailleau, *Org. Lett.*, 2019, **21**, 279.