

Electronic Supplementary Information (ESI)

Straightforward access to aryl-substituted/fused 1,3-dithiole-2-chalcogenones by Cu-catalyzed C-S coupling between aryl iodides and zinc-thiolate complex (TBA)₂[Zn(DMIT)₂]

Jibin Sun,^a Xiaofeng Lu,^a Jiafeng Shao,^b Zili Cui,^a Yu Shao,^a Guiyang Jiang,^a Wei Yu,^a Xiangfeng Shao^{*a}

^a*State Key Laboratory of Applied Organic Chemistry and School of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China;*

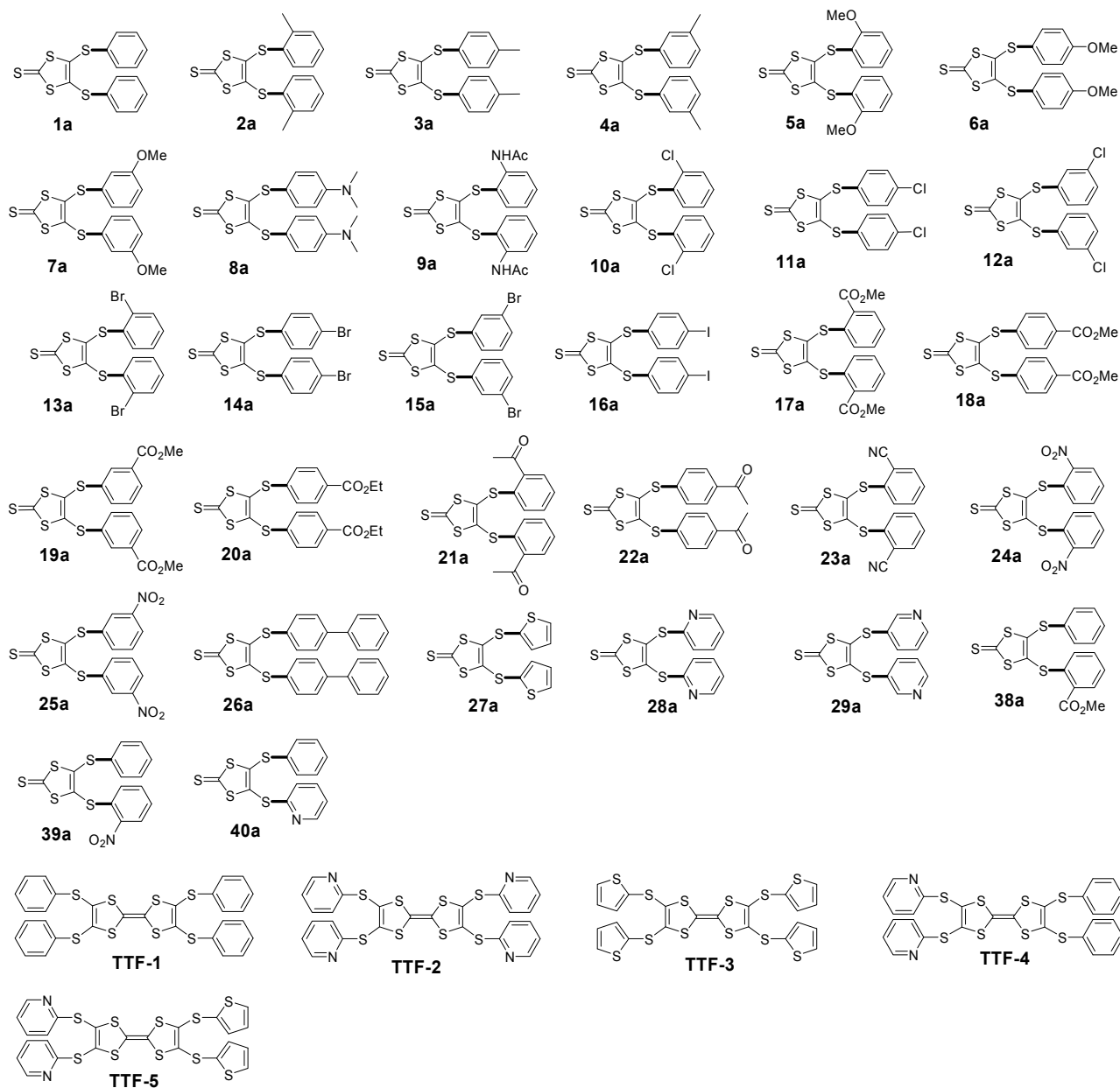
^b*School of Physical Science and Technology, Lanzhou University, Lanzhou 730000, P. R. China;*

E-mail: shaoxf@lzu.edu.cn (X. Shao)

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1. Chemical structures of the compounds in this report



2. Experimental

General methods.

The compounds in this report were identified by ^1H and ^{13}C NMR, mass spectra (EI, or ESI, or APCI, or HRMS), element analysis, and/or X-ray single crystal diffraction. Melting points were determined on WRS-2 melting point apparatus. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400MHz (100 MHz for ^{13}C) spectrometer or Agilent Inova 150 MHz for ^{13}C NMR in several cases. EI-MS was determined on Trace DSQ GC-MS spectrometer (Thermo Electron). ESI- and APCI-MS were measured on Esquire 6000 (Bruker Daltonics Inc.). High-resolution mass spectral analysis (HRMS) was carried out on maXis 4G (Bruker Daltonic Inc.) or APEX II (Bruker) type mass spectrometer. MALDI-TOF was measured on BIFLEX III (Bruker Daltonics Inc.) mass spectrometer. Element analysis (EA) was performed on Vario EL. The X-ray diffraction measurement was carried out on SMART APEX II (Bruker) or SuperNova (Agilent) type diffractometer. The crystal structure was solved by a direct method *SIR2004*^{1a} and refined by full-matrix least-square method on F^2 by means of *SHELXL-97*.^{1b}

Typical synthetic procedure.

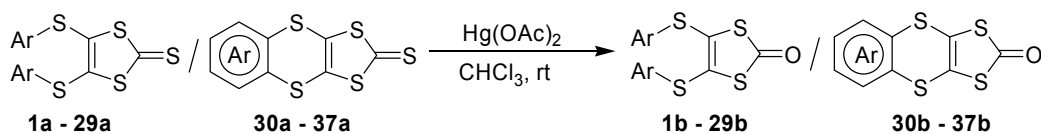
1a: (TBA)₂[Zn(DMIT)₂] (1.60 g, 1.69 mmol), iodobenzene (1.56 g, 7.44 mmol), Cu₂O (50 mg, 0.34 mmol), ethyl acetoacetate (86 μL , 0.68 mmol), and DMF (3 mL) were placed in a two-necked flask and heated to 120 °C. After stirred at 120 °C for 10 h, the reaction mixture was cooled down to room temperature (rt) and poured into 30 mL dichloromethane (DCM). The resulting mixture was washed with distilled water (3 \times 10 mL) and brine (10 mL) successively, and then dried over anhydrous Na₂SO₄. The crude product was purified by column chromatography on silica gel (eluent: v/v, DCM : petroleum ether = 1 : 5) to afford **1a** as yellow solid (0.86 g, yield 81%).

1b: To a solution of **1a** (1.78 g, 5.06 mmol) in chloroform (50 ml) was added Hg(OAc)₂ (4.84 g, 15.00 mmol), then stirred at rt for 5 h. The reaction mixture was filtered through celite column and washed with chloroform. The filtrate was rinsed with saturated NaHCO₃ (2 \times 15 mL) and brine (10 mL) successively, and then dried over anhydrous Na₂SO₄. After removing the solvent, **1b** was obtained as pale yellow solid (1.69 g, yield 99%). The synthetic approach as well as the yield for **2b** – **37b** is shown in Fig. S1.

40a: (TBA)₂[Zn(DMIT)₂] (3.2 g, 3.38 mmol), 2-iodopyridine (1.04g, 5.10mmol), iodobenzene

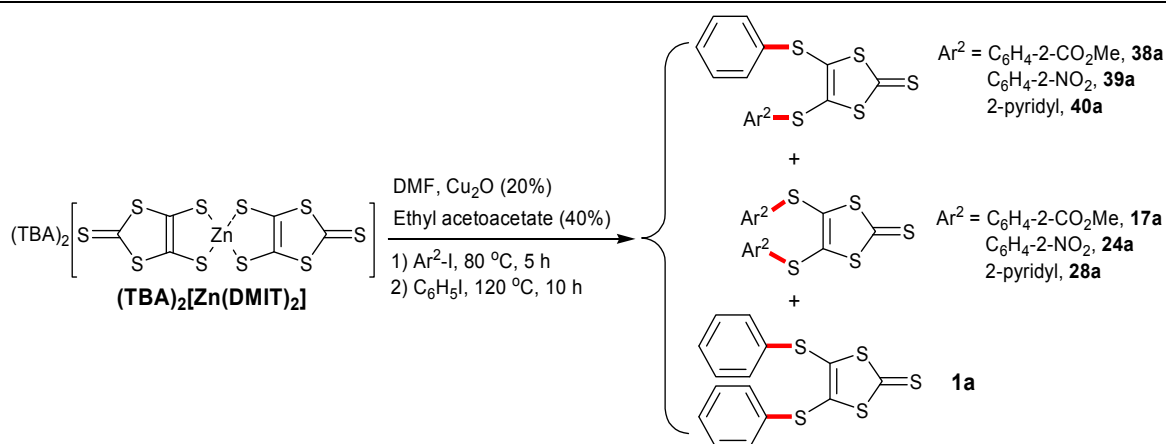
(2.07 g, 10.14 mmol), Cu₂O (97 mg, 0.68 mmol), ethyl acetoacetate (176ul, 1.36 mmol), and DMF (5 mL) were placed in a two-necked flask. The resulting mixture was heated up to 80 °C and stirred at this temperature for 5 h, then reaction temperature was increased to 120 °C and stirred for another 10 h. The reaction mixture was cooled down to room temperature (rt) and poured into 50 mL dichloromethane (DCM). The resulting mixture was washed with distilled water (3 × 10 mL) and brine (10 mL) successively, and then dried over anhydrous Na₂SO₄. The crude product was purified by column chromatography on silica gel (eluent: v/v, DCM : petroleum ether = 1 : 2) to afford **40a** as yellow oil (0.78 g, yield 44%), **1a** (0.36 g, yield 20%), and **28a** (0.33 g, 17%). The synthetic approach as well as the yield for **38a** and **39a** is shown in Table S1.

TTF-1: 1b (1.50 g, 4.48 mmol) was suspended in freshly distilled P(OEt)₃ (20 ml) under N₂ atmosphere and stirred at 80 °C for 6 h. After cooling down to rt, 20 mL CH₃OH was added to the reaction mixture and kept at around 5 °C overnight. The resulting orange-red solid (**TTF-1**) was collected by suction, washed with CH₃OH, then dried in vacuo (1.33 g, 2.08 mmol, 92%), which was enough pure for elemental analysis. Note that reaction conditions for the synthesis of **TTF-2** and **TTF-3** were same as for **TTF-1**. For the synthesis of **TTF-4**, the reactants were **1b** (1 mmol) + **28a** (2.5 mmol) and the other reaction conditions were same to that for the synthesis of **TTF-1**. **TTF-5** was obtained by the combination of **27 b** (1.5 mmol) + **28a** (1 mmol).



Scheme S1. Preparation of aryl substituted/fused 1,3-dithiole-2-one *via* C-S bond connection. Reaction conditions: 1,3-dithiole-2-thiones (5.0 mmol), Hg(OAc)₂ (15.0 mmol), CHCl₃ (50 mL), room temperature, 5 h. The isolated yields (%) of the corresponding 1,3-dithiole-2-ones: **1b**, 99; **2b**, 89; **3b**, 99; **4b**, 97; **8b**, 72; **9b**, 91; **10b**, 91; **11b**, 100; **12b**, 98; **13b**, 99; **14b**, 100; **15b**, 100; **16b**, 98; **17b**, 99; **18b**, 99; **19b**, 97; **20b**, 99; **21b**, 98; **22b**, 100; **23b**, 90; **24b**, 96; **25b**, 99; **26b**, 100; **27b**, 92; **28b**, 98; **29b**, 100; **30b**, 96; **31b**, 94; **32b**, 100; **33b**, 98; **34b**, 75; **35b**, 100; **36b**, 80; **37b**, 75.

Table S1. Synthesis of asymmetric 1,3-dithiole-2-thiones *via* the three component tandem method.

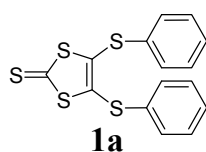


(TBA) ₂ [Zn(DMIT) ₂]	Ar ² -I	C ₆ H ₅ I	1a
3.2 g (3.38 mmol)	Ar ² C ₆ H ₄ -2-CO ₂ Me (1.34g, 5.1 mmol)	2.07 g (10.1 mmol)	38a , 41 % ^a 17a , 18% 20 %
3.2 g (3.38 mmol)	Ar ² C ₆ H ₄ -2-NO ₂ (1.27 g, 5.1 mmol)	2.07 g (10.1 mmol)	39a , 38% 24a , 14% 21%
3.2 g (3.38 mmol)	Ar ² 2-pyridyl (1.04g, 5.1 mmol)	2.07 g (10.1 mmol)	40a , 44% 28a , 17% 20%

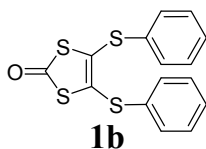
^a Isolated yield

3. Characterisation data

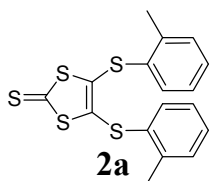
The following are the appearance, yield, melting point (Mp), ^1H NMR, ^{13}C NMR, mass spectra (MS), and elemental analysis results for the compounds reported in this work. In the case of compounds **36a** and **37a**, which don't contain hydrogen atoms, the ^{13}C NMR of them cannot be measured due to the poor solubility. The compositions for **36a** and **37a** are characterized by Mp, EI-MS, and elemental analysis. When **36a** and **37a** are converted into the corresponding ketone form, **36b** and **37b**, the solubility of which are highly improved and their characterization by ^{13}C NMR are available as reported in the following.



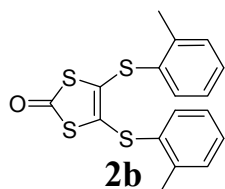
Yellow solid (Yield = 77%); Mp: 77-78 °C; ^1H NMR (CDCl_3): δ 7.51-7.48 (m, 4H), 7.42-7.39 (m, 6H). ^{13}C NMR (CDCl_3): δ 211.31, 135.91, 132.71, 131.73, 129.75, 129.11; EI-MS, m/z (I %): 350 (M^+ , 56); Anal. Calcd. for $\text{C}_{15}\text{H}_{10}\text{S}_5$ (MW 350.56): C, 51.39; H, 2.88; Found: C, 51.22; H, 2.91.



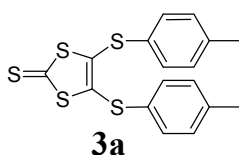
Pale yellow solid (Yield = 99%); Mp: 120-122 °C; ^1H NMR (CDCl_3): δ 7.48-7.45 (m, 4H), 7.42-7.36 (m, 6H); ^{13}C NMR (CDCl_3): δ 189.34, 132.80, 131.28, 129.58, 128.70, 127.61; EI-MS, m/z (I %): 334 (M^+ , 96); Anal. Calcd. for $\text{C}_{15}\text{H}_{10}\text{OS}_4$ (MW 334.50): C, 53.86; H, 3.01; Found: C, 53.63; H, 2.95.



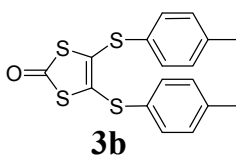
Yellow solid (Yield = 66%); Mp: 101-103 °C. ^1H NMR (CDCl_3): δ 7.48 (d, J = 7.6 Hz, 2H), 7.33-7.22 (m, 6H), 2.50 (s, 6H); ^{13}C NMR (CDCl_3): δ 211.46, 140.06, 134.51, 132.70, 131.20, 131.15, 129.56, 127.25, 20.61; EI-MS, m/z (I %): 378 (M^+ , 100). Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{S}_5$ (MW 378.62): C, 53.93; H, 3.73; Found: C, 54.09; H, 3.59.



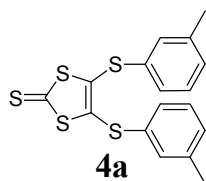
White solid (Yield = 89%); Mp: 103-105 °C; ^1H NMR (CDCl_3): δ 7.43 (d, J = 7.6 Hz, 2H), 7.29-7.19 (m, 6H), 2.47 (s, 6H); ^{13}C NMR (CDCl_3): δ 189.60, 139.75, 132.17, 131.84, 130.99, 129.12, 127.08, 126.06, 20.55. EI-MS, m/z (I %): 362 (M^+ , 100); Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{OS}_4$ (MW 362.55): C, 56.32; H, 3.89; Found: C, 56.53; H, 3.65.



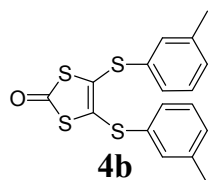
Yellow solid (Yield = 70%); Mp: 92 -93 °C. ^1H NMR (CDCl_3): δ 7.41 (d, J = 8.1 Hz, 4H), 7.21 (d, J = 8.1 Hz, 4H), 2.39 (s, 6H); ^{13}C NMR (CDCl_3): δ 211.44, 139.68, 135.75, 132.29, 130.49, 128.58, 21.21; EI-MS, m/z (I %): 378 (M^+ , 100); Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{S}_5$ (MW 378.62): C, 53.93; H, 3.73; Found: C, 54.09; H, 3.59.



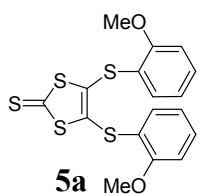
White solid (Yield = 99%); Mp: 78-80 °C. ^1H NMR (CDCl_3): δ 7.39 (d, J = 8.1 Hz, 4H), 7.20 (d, J = 8.1 Hz, 4H), 2.39 (s, 6H); ^{13}C NMR (CDCl_3): δ 189.46, 139.20, 131.88, 130.31, 129.20, 127.29, 21.18; MS (ESI): 363.1(M^+); Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{OS}_4$ (MW 362.55): C, 56.32; H, 3.89; Found: C, 56.09; H, 3.73.



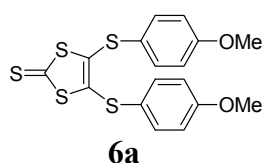
Yellow solid (Yield = 67%); Mp: 94-96 °C; ^1H NMR (CDCl_3): δ 7.30-7.26 (m, 6H), 7.19 (d, J = 6.5 Hz, 2H), 2.38 (s, 6H); ^{13}C NMR (CDCl_3): δ 211.54, 139.77, 135.99, 132.26, 131.91, 129.95, 129.51, 128.80, 21.32; EI-MS, m/z (I %): 378 (M^+ , 100); Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{S}_5$ (MW 378.62): C, 53.93; H, 3.73; Found: C, 54.16; H, 3.55.



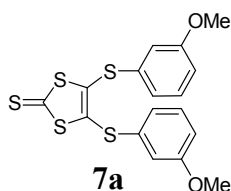
Pale yellow oil (Yield = 97%); $^1\text{H NMR}$ (CDCl_3): δ 7.31-7.29 (m, 6H), 7.20-7.18 (m, 2H), 2.39 (s, 6H); $^{13}\text{C NMR}$ (CDCl_3): δ 189.23, 139.40, 132.49, 131.70, 129.42, 129.24, 128.23, 127.55, 21.23; HRMS Calcd. for $\text{C}_{17}\text{H}_{14}\text{OS}_4\text{Na}$: 384.9820; Found: 384.9818.



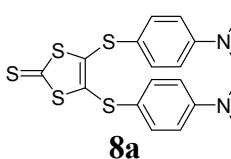
Yellow solid (Yield = 56%); Mp: 105-106 °C; $^1\text{H NMR}$ (CDCl_3): δ 7.44 (d, J = 7.6 Hz, 2H), 7.37 (t, J = 7.8 Hz, 2H), 6.97 (q, J = 7.5 Hz, 4H), 3.92 (s, 6H); $^{13}\text{C NMR}$ (CDCl_3): δ 212.50, 158.14, 135.72, 133.02, 130.78, 121.44, 120.15, 111.45, 55.96; EI-MS, m/z (I %): 410 (M^+ , 63); Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{O}_2\text{S}_5$ (MW 410.62): C, 49.73; H, 3.44; Found: C, 49.67; H, 3.27.



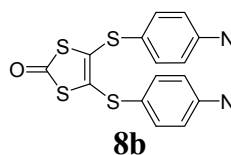
Yellow solid (Yield = 75%); Mp: 75 -76 °C; $^1\text{H NMR}$ (CDCl_3): δ 7.49 (d, J = 8.8 Hz, 4H), 6.92 (d, J = 8.8 Hz, 4H), 3.84 (s, 6H). $^{13}\text{C NMR}$ (CDCl_3): δ 211.36, 160.92, 135.64, 134.96, 122.44, 115.35, 55.51. EI-MS, m/z (I %): 410 (M^+ , 68); Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{O}_2\text{S}_5$ (MW 410.62): C, 49.73; H, 3.44; Found: C, 49.85; H, 3.27.



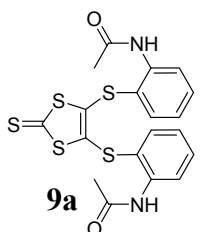
Yellow oil (Yield = 58%); $^1\text{H NMR}$ (CDCl_3): δ 7.31 (t, J = 8.0 Hz, 2H), 7.07 (d, J = 7.8 Hz, 2H), 7.01 (t, J = 2.2 Hz, 2H), 6.92 (dd, J = 2.5, 8.3 Hz, 2H), 3.83 (s, 6H); $^{13}\text{C NMR}$ (CDCl_3): δ 211.31, 160.25, 135.88, 133.14, 130.53, 123.68, 116.92, 114.76, 55.42; HRMS Calcd. for $\text{C}_{17}\text{H}_{14}\text{O}_2\text{S}_5+\text{Na}$: 432.9490; Found: 432.9483.



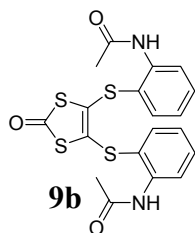
Yellow solid (Yield = 64%); Mp: 138-141 °C; $^1\text{H NMR}$ (CDCl_3): δ 7.43 (d, J = 8.9 Hz, 4H), 6.67 (d, J = 8.9 Hz, 4H), 3.01 (s, 12H); $^{13}\text{C NMR}$ (CDCl_3): δ 212.06, 151.23, 135.82, 135.32, 116.32, 112.77, 40.20; MS (APCI), m/z : 437.3 (M^+); Anal. Calcd. for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{S}_5$ (MW 436.70): C, 52.26; H, 4.62; N, 6.41; Found: C, 52.32; H, 4.46; N, 6.21.



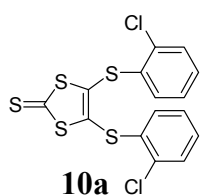
Pale yellow solid (Yield = 72%); Mp: 124-126 °C; $^1\text{H NMR}$ (CDCl_3): δ 7.43 (d, J = 9.0 Hz, 4H), 6.67 (d, J = 8.9 Hz, 4H), 3.00 (s, 12H); $^{13}\text{C NMR}$ (CDCl_3): δ 190.34, 151.05, 135.09, 126.76, 117.03, 112.61, 40.19; HRMS Calcd. for $\text{C}_{19}\text{H}_{20}\text{N}_2\text{OS}_4$: 421.0531; Found: 421.0533.



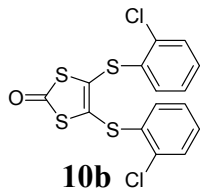
Yellow solid (Yield = 70%); Mp: 214-216 °C; $^1\text{H NMR}$ (CDCl_3): δ 8.31 (d, J = 6.8 Hz, 2H), 8.12 (br s, 2H), 7.58 (dd, J = 1.2, 7.8 Hz, 2H); 7.48 (dt, J = 1.2, 8.4 Hz, 2H); 7.17 (t, J = 7.6 Hz, 2H), 2.23 (s, 6H); $^{13}\text{C NMR}$ ($\text{DMSO}-d_6$): δ 210.83, 168.86, 137.87, 136.05, 132.58, 129.94, 127.45, 126.91, 126.32, 23.05; EI-MS, m/z (I %): 464 (M^+ , 54); Anal. Calcd. for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_2\text{S}_5$ (MW 464.67): C, 49.11; H, 3.47; N, 6.03; Found: C, 49.18; H, 3.27; N, 5.89.



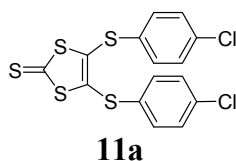
White solid (Yield = 91%); Mp: 176-177 °C; $^1\text{H NMR}$ (CDCl_3): δ 8.32 (d, J = 7.1 Hz, 2H), 8.14 (br s, 2H), 7.57 (d, J = 7.8 Hz, 2H), 7.47 (t, J = 7.3 Hz, 2H), 7.16 (t, J = 7.5 Hz, 2H), 2.22 (s, 6H); $^{13}\text{C NMR}$ (CDCl_3): δ 187.60, 168.58, 139.12, 135.09, 131.81, 126.23, 125.23, 122.39, 120.31, 24.75; EI-MS, m/z (I %): 448 (M^+ , 18); Anal. Calcd. for $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_3\text{S}_4$ (MW 448.67): C, 50.87; H, 3.59; N, 6.24; Found: C, 50.95; H, 3.36; N, 6.04.



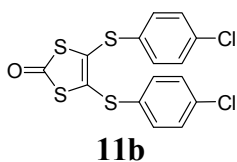
Yellow solid (Yield = 75%); Mp: 116-117 °C; ^1H NMR (CDCl_3): δ 7.50-7.46 (m, 4H), 7.34-7.28 (m, 4H); ^{13}C NMR (CDCl_3): δ 211.03, 135.61, 135.25, 132.43, 131.27, 130.53, 130.14, 127.87; MS (APCI), m/z : 419.3(M^+); Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{Cl}_2\text{S}_5$ (MW 419.46): C, 42.95; H, 1.92; Found: C, 42.75; H, 1.96.



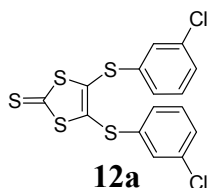
Pale yellow solid (Yield: 91%); Mp: 107-110 °C. ^1H NMR (CDCl_3): δ 7.47-7.42 (m, 4H), 7.31-7.27 (m, 4H); ^{13}C NMR (CDCl_3): δ 188.94, 135.18, 131.90, 131.86, 130.38, 129.68, 127.72, 127.23; EI-MS, m/z (I %): 403 (M^+ , 17); Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{Cl}_2\text{OS}_4$ (MW 403.39): C, 44.66; H, 2.00; Found: C, 44.91; H, 1.98.



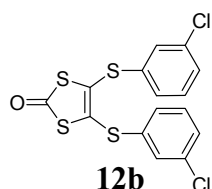
Yellow solid (Yield = 60%); Mp: 118-119 °C; ^1H NMR (CDCl_3): δ 7.42-7.36 (m, 8H); ^{13}C NMR (CDCl_3): δ 210.37, 135.65, 135.52, 132.97, 130.41, 129.99; EI-MS, m/z (I %): 419 (M^+ , 9); Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{Cl}_2\text{S}_5$ (MW 419.46): C, 42.95; H, 1.92; Found: C, 42.36; H, 1.87.



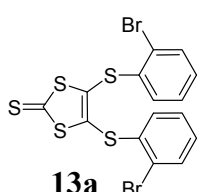
Pale yellow solid (Yield = 100%); Mp: 97-98 °C; ^1H NMR (CDCl_3): δ 7.40-7.34 (m, 8H); ^{13}C NMR (CDCl_3): δ 188.45, 135.23, 132.57, 131.06, 129.84, 127.51; EI-MS, m/z (I %): 403 (M^+ , 14); Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{Cl}_2\text{OS}_4$ (MW 403.39): C, 44.66; H, 2.00; Found: C, 44.79; H, 1.98.



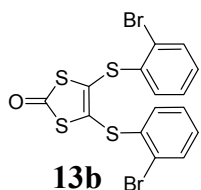
Yellow solid (Yield = 70%); Mp: 88-89 °C; ^1H NMR (CDCl_3): δ 7.44 (d, J = 1.8 Hz, 2H), 7.37-7.31 (m, 6H); ^{13}C NMR (CDCl_3): δ 210.31, 135.75, 135.49, 133.82, 130.94, 129.31, 129.27; EI-MS, m/z (I %): 419 (M^+ , 13); Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{Cl}_2\text{S}_5$ (MW 419.46): C, 42.95; H, 1.92; Found: C, 42.90; H, 1.77.



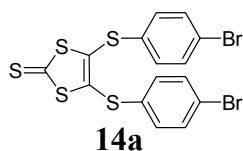
White solid (Yield = 98%); Mp: 59-60 °C; ^1H NMR (CDCl_3): δ 7.41 (d, J = 1.0 Hz, 2H), 7.34-7.30 (m, 6H); ^{13}C NMR (CDCl_3): δ 188.28, 135.31, 134.45, 130.56, 130.46, 128.84, 128.83, 127.80; EI-MS, m/z (I %): 403 (M^+ , 17); Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{Cl}_2\text{OS}_4$ (MW 403.39): C, 44.66; H, 2.00; Found: C, 44.54; H, 2.04.



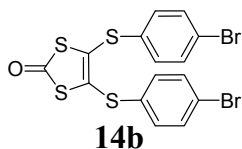
Yellow solid (Yield = 68%); Mp: 126-128 °C; ^1H NMR (CDCl_3): δ 7.64 (dd, J = 1.3, 8.0 Hz, 2H), 7.49 (dd, J = 1.5, 7.8 Hz, 2H), 7.35 (dt, J = 1.3, 7.5 Hz, 2H), 7.23 (dt, J = 1.6 Hz, 7.8 Hz, 2H); ^{13}C NMR (CDCl_3): δ 211.11, 135.57, 133.81, 133.42, 132.21, 130.12, 128.51, 125.62; EI-MS, m/z (I %): 508 (M^+ , 33); Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{Br}_2\text{S}_5$ (MW 508.36): C, 35.44; H, 1.59; Found: C, 35.26; H, 1.63.



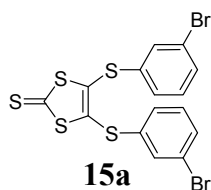
Pale yellow solid (Yield = 99%); Mp: 119-120 °C; ^1H NMR (CDCl_3): δ 7.62 (dd, J = 1.2, 8.0 Hz, 2H), 7.45 (dd, J = 1.6, 7.9 Hz, 2H), 7.34 (dt, J = 1.3, 7.5 Hz, 2H); 7.20 (dt, J = 1.6, 7.9 Hz, 2H); ^{13}C NMR (CDCl_3): δ 188.97, 134.07, 133.66, 131.66, 129.67, 128.36, 127.62, 125.13; EI-MS, m/z (I %): 492 (M^+ , 52); Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{Br}_2\text{OS}_4$ (MW 492.29): C, 36.60; H, 1.64; Found: C, 36.65; H, 1.66.



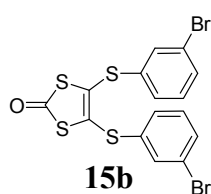
Yellow solid (Yield = 55%); Mp: 130-131 °C; ^1H NMR (CDCl_3): δ 7.54-7.51 (m, 4H), 7.35-7.32 (m, 4H); ^{13}C NMR (CDCl_3): δ 210.34, 135.49, 133.06, 132.95, 131.09, 123.07; EI-MS, m/z (I %): 508 (M^+ , 29); Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{Br}_2\text{S}_5$ (MW 508.36): C, 35.44; H, 1.59; Found: C, 35.46; H, 1.53.



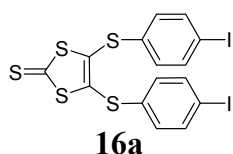
Pale yellow solid (Yield = 100%); Mp: 99-100 °C; ^1H NMR (CDCl_3): δ 7.52-7.50 (m, 4H), 7.32-7.29 (m, 4H); ^{13}C NMR (CDCl_3): δ 188.41, 132.80, 132.67, 131.75, 127.51, 123.25; EI-MS, m/z (I %): 492 (M^+ , 46); Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{Br}_2\text{OS}_4$ (MW 492.29): C, 36.60; H, 1.64; Found: C, 36.34; H, 1.56.



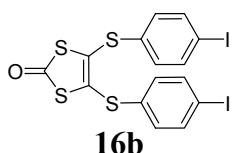
Yellow solid (Yield = 65%); Mp: 94-96 °C; ^1H NMR (CDCl_3): δ 7.60 (t, J = 1.8 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.4 Hz, 2H), 7.27 (t, J = 7.8 Hz, 2H); ^{13}C NMR (CDCl_3): δ 210.36, 135.80, 134.09, 133.82, 132.24, 131.05, 129.83, 123.48; EI-MS, m/z (I %): 508 (M^+ , 100); Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{Br}_2\text{S}_5$ (MW 508.36): C, 35.44; H, 1.59; Found: C, 35.13; H, 1.49.



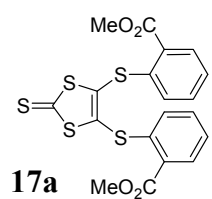
White solid (Yield = 100%); Mp: 73-74 °C; ^1H NMR (CDCl_3): δ 7.55 (t, J = 1.6 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.24 (t, J = 7.9 Hz, 2H); ^{13}C NMR (CDCl_3): δ 188.34, 134.74, 133.35, 131.81, 130.87, 129.35, 127.87, 123.34; EI-MS, m/z (I %): 492 (M^+ , 95); Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{Br}_2\text{OS}_4$ (MW 492.29): C, 36.60; H, 1.64. Found: C, 36.61; H, 1.69.



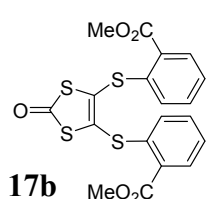
Yellow solid (Yield = 53%); Mp: 136-137 °C; ^1H NMR (CDCl_3): δ 7.72 (d, J = 8.4 Hz, 4H), 7.18 (d, J = 8.4 Hz, 4H); ^{13}C NMR (CDCl_3): δ 210.40, 138.88, 135.52, 132.99, 131.99, 95.11; HRMS Calcd. for $\text{C}_{15}\text{H}_9\text{I}_2\text{S}_5$: 602.7392; Found: 602.7384.



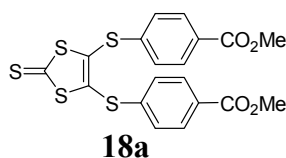
Pale yellow solid (Yield = 98%); Mp: 116-118 °C; ^1H NMR (CDCl_3): δ 7.70 (d, J = 8.4 Hz, 4H), 7.15 (d, J = 8.4 Hz, 4H). ^{13}C NMR (CDCl_3): δ 188.36, 138.62, 132.55, 132.52, 127.45, 94.60; HRMS Calcd. for $\text{C}_{15}\text{H}_9\text{I}_2\text{OS}_4$: 586.7620; Found: 586.7619.



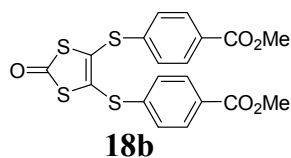
Yellow solid (Yield: 85%); Mp: 136-138 °C; ^1H NMR (CDCl_3): δ 8.03 (dd, J = 1.4, 7.8 Hz, 2H), 7.53 (dt, J = 1.5, 8.2 Hz, 2H), 7.33 (q, J = 7.8 Hz, 4H), 3.93 (s, 6H); ^{13}C NMR (CDCl_3): δ 212.51, 166.35, 140.38, 137.84, 133.21, 131.47, 128.07, 127.91, 126.50, 52.45; EI-MS, m/z (I %): 466 (M^+ , 47); Anal. Calcd. for $\text{C}_{19}\text{H}_{14}\text{O}_4\text{S}_5$ (MW 466.64): C, 48.90; H, 3.02; Found: C, 48.93; H, 2.99.



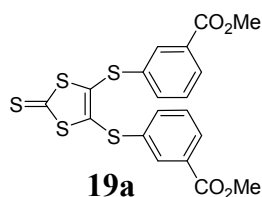
White solid (Yield = 99%); Mp: 153-154 °C; ^1H NMR (CDCl_3): δ 8.02 (d, J = 7.8 Hz, 2H), 7.52 (q, J = 7.3 Hz, 2H), 7.31 (q, J = 7.9 Hz, 4H), 3.93 (s, 6H); ^{13}C NMR (CDCl_3): δ 212.51, 166.35, 140.38, 137.84, 133.21, 131.47, 128.07, 127.91, 126.50, 52.45; EI-MS, m/z (I %): 450 (M^+ , 17); Anal. Calcd. for $\text{C}_{19}\text{H}_{14}\text{O}_5\text{S}_4$ (MW 450.57): C, 50.65; H, 3.13; Found: C, 50.64; H, 3.20.



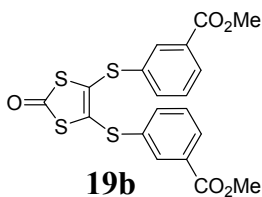
Yellow solid (Yield = 50%); Mp: 123-125 °C; ^1H NMR (CDCl_3): δ 8.03 (dd, J = 1.9, 6.7 Hz, 4H), 7.46 (dd, J = 1.9, 6.8 Hz, 4H), 3.94 (s, 6H); ^{13}C NMR (CDCl_3): δ 210.29, 166.01, 138.14, 136.00, 130.75, 130.23, 129.86, 52.36; HRMS Calcd. for $\text{C}_{19}\text{H}_{14}\text{NaO}_4\text{S}_5$: 488.9388; Found: 488.9394.



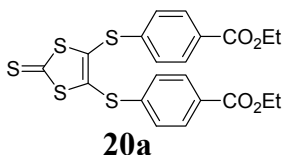
White solid (Yield = 99%); Mp: 175-176 °C; $^1\text{H NMR}$ (CDCl_3): δ 8.02 (d, $J = 8.3$ Hz, 4H), 7.43 (d, $J = 8.3$ Hz, 4H), 3.94 (s, 6H); $^{13}\text{C NMR}$ (CDCl_3): δ 188.31, 166.12, 138.83, 130.64, 129.86, 129.39, 128.21, 52.36; HRMS Calcd. for $\text{C}_{19}\text{H}_{14}\text{O}_5\text{S}_4\text{Na}$: 472.9616 [(M + Na) $^+$]; Found: 472.9617 [(M + Na) $^+$].



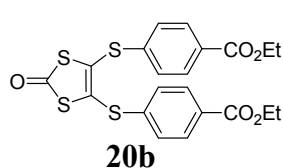
Yellow solid (Yield = 50%); Mp: 94-95 °C; $^1\text{H NMR}$ (CDCl_3): δ 8.16 (t, $J = 1.6$ Hz, 2H), 8.05 (td, $J = 1.2, 7.8$ Hz, 2H), 7.68-7.65 (m, 2H), 7.49 (t, $J = 7.8$ Hz, 2H), 3.96 (s, 6H); $^{13}\text{C NMR}$ (CDCl_3): δ 210.49, 165.76, 135.72, 135.63, 132.76, 132.54, 131.81, 130.17, 129.86, 52.49; EI-MS, m/z (I %): 466 (M^+ , 100); Anal. Calcd. for $\text{C}_{19}\text{H}_{14}\text{O}_4\text{S}_5$ (MW 466.64): C, 48.90; H, 3.02; Found: C, 48.98; H, 2.95.



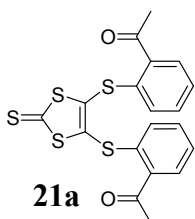
Yellow solid (Yield = 97%); Mp: 75-77 °C; $^1\text{H NMR}$ (CDCl_3): δ 8.13 (t, $J = 1.6$ Hz, 2H), 8.02 (td, $J = 1.1, 7.8$ Hz, 2H), 7.64 (td, $J = 1.1, 7.8$ Hz, 2H), 7.47 (t, $J = 7.8$ Hz, 2H), 3.95 (s, 6H); $^{13}\text{C NMR}$ (CDCl_3): δ 188.60, 165.88, 135.20, 133.42, 132.06, 131.64, 129.79, 129.70, 127.73, 52.47; EI-MS, m/z (I %) : 450 (M^+ , 100); Anal. Calcd. for $\text{C}_{19}\text{H}_{14}\text{O}_5\text{S}_4$ (MW 450.57): C, 50.65; H, 3.13; Found: C, 50.51; H, 2.91.



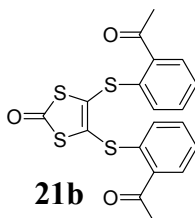
Yellow solid (Yield = 70%); Mp: 106-107 °C; $^1\text{H NMR}$ (CDCl_3): δ 8.03 (dd, $J = 1.7, 6.8$ Hz, 4H), 7.46 (dd, $J = 1.7, 6.8$ Hz, 4H), 4.40 (q, $J = 7.1$ Hz, 4H), 1.41 (t, $J = 7.1$ Hz, 6H); $^{13}\text{C NMR}$ (CDCl_3): δ 210.22, 165.46, 137.90, 135.88, 130.66, 130.53, 129.83, 61.28, 14.23; EI-MS, m/z (I %): 494 (M^+ , 100); Anal. Calcd. for $\text{C}_{21}\text{H}_{18}\text{O}_4\text{S}_5$ (MW 494.69): C, 50.99; H, 3.67; Found: C, 51.00; H, 3.45.



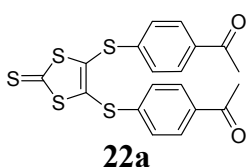
White solid (Yield: 99%); Mp: 91-92 °C; $^1\text{H NMR}$ (CDCl_3): δ 8.03 (d, $J = 8.4$ Hz, 4H), 7.44 (d, $J = 8.4$ Hz, 4H), 4.40 (q, $J = 7.1$ Hz, 4H), 1.41 (t, $J = 7.1$ Hz, 6H); $^{13}\text{C NMR}$ (CDCl_3): δ 188.34, 165.64, 138.64, 130.61, 130.26, 129.44, 128.15, 61.30, 14.28; EI-MS, m/z (I %): 478 (M^+ , 100); Anal. Calcd. for $\text{C}_{21}\text{H}_{18}\text{O}_5\text{S}_4$ (MW 478.62): C, 52.70; H, 3.79; Found: C, 52.84; H, 3.60.



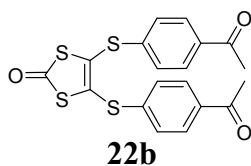
Yellow solid (Yield = 76%); Mp: 192-194 °C; $^1\text{H NMR}$ (CDCl_3): δ 7.90 (d, $J = 6.7$ Hz, 2H), 7.53 (dt, $J = 1.3, 8.5$ Hz, 2H), 7.37-7.33 (m, 4H), 2.63 (s, 6H); $^{13}\text{C NMR}$ (CDCl_3): δ 213.01, 198.58, 141.54, 137.80, 134.59, 133.19, 131.19, 128.06, 126.23, 27.46; EI-MS, m/z (I %): 434 (M^+ , 28); Anal. Calcd. for $\text{C}_{19}\text{H}_{14}\text{O}_2\text{S}_5$ (MW 434.64): C, 52.50; H, 3.25; Found: C, 52.37; H, 3.04.



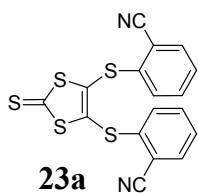
White solid (Yield = 98%); Mp: 198-200 °C; $^1\text{H NMR}$ (CDCl_3): δ 7.90 (dd, $J = 0.94, 7.6$ Hz, 2H), 7.53 (dt, $J = 1.3, 8.4$ Hz, 2H), 7.36-7.31 (m, 4H), 2.62 (s, 6H); $^{13}\text{C NMR}$ (CDCl_3): δ 198.55, 190.09, 138.27, 134.32, 133.13, 133.08, 131.19, 127.78, 125.91, 27.43; EI-MS, m/z (I %): 418 (M^+ , 27); Anal. Calcd. for $\text{C}_{19}\text{H}_{14}\text{O}_3\text{S}_4$ (MW 418.57): C, 54.52; H, 3.37; Found: C, 54.82; H, 3.01.



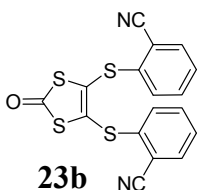
Yellow solid (Yield = 51%); Mp: 111-112 °C; $^1\text{H NMR}$ (CDCl_3): δ 7.95 (d, $J = 8.4$ Hz, 4H), 7.49 (d, $J = 8.3$ Hz, 4H), 2.61 (s, 6H); $^{13}\text{C NMR}$ (CDCl_3): δ 210.19, 196.69, 138.38, 136.81, 135.98, 129.96, 129.47, 26.57; MS (APCI), m/z : 435.3 (M^+); Anal. Calcd. for $\text{C}_{19}\text{H}_{14}\text{O}_2\text{S}_5$ (MW 434.64): C, 52.50; H, 3.25; Found: C, 52.12; H, 3.09.



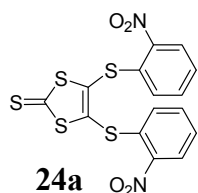
White solid (Yield = 100%); Mp: 128-130 °C; ^1H NMR (CDCl_3): δ 7.94 (d, J = 8.4 Hz, 4H), 7.46 (d, J = 8.4 Hz, 4H), 2.61 (s, 6H); ^{13}C NMR (CDCl_3): δ 196.75, 188.16, 139.05, 136.45, 129.43, 129.35, 128.20, 26.56; EI-MS, m/z (I %): 418 (M^+ , 87); Anal. Calcd. for $\text{C}_{19}\text{H}_{14}\text{O}_3\text{S}_4$ (MW 418.57): C, 54.52; H, 3.37; Found: C, 54.76; H, 3.14.



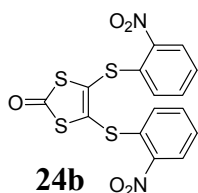
Yellow solid (Yield = 78%); Mp: 163-165 °C; ^1H NMR (CDCl_3): δ 7.77-7.64 (m, 6H), 7.51 (dt, J = 1.2, 7.6 Hz, 2H); ^{13}C NMR (CDCl_3): δ 209.33, 135.49, 134.41, 133.87, 133.02, 129.66, 116.17, 115.64; EI-MS, m/z (I %): 400 (M^+ , 59); Anal. Calcd. for $\text{C}_{17}\text{H}_8\text{N}_2\text{S}_5$ (MW 400.58): C, 50.97; H, 2.01; N, 6.99; Found: C, 50.77; H, 1.89; N, 6.71.



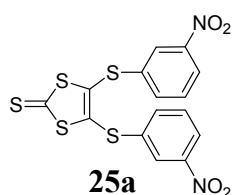
White solid (Yield = 90%); Mp: 163-166 °C; ^1H NMR (CDCl_3): δ 7.74 (d, J = 6.6 Hz, 2H), 7.69-7.62 (m, 4H), 7.49 (dt, J = 1.4, 7.5 Hz, 2H); ^{13}C NMR (CDCl_3): δ 187.51, 136.09, 134.27, 133.70, 132.56, 129.27, 126.63, 116.19, 115.25; EI-MS, m/z (I %): 284 (M^+ , 46); Anal. Calcd. for $\text{C}_{17}\text{H}_8\text{N}_2\text{OS}_4$ (MW 384.52): C, 53.10; H, 2.10; N, 7.29; Found: C, 53.20; H, 2.10; N, 7.35.



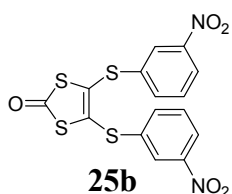
Yellow solid (Yield = 91%); Mp: 225-226 °C; ^1H NMR (CDCl_3): δ 8.30 (dd, J = 1.3, 8.2 Hz, 2H), 7.70 (dt, J = 1.4, 8.1 Hz, 2H), 7.49-7.42 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3): δ 210.76, 145.84, 140.43, 134.66, 133.26, 128.45, 127.54, 126.43; EI-MS, m/z (I %): 440 (M^+ , 12); Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{N}_2\text{O}_4\text{S}_5$ (MW 440.56): C, 40.89; H, 1.83; N, 6.36; Found: C, 41.04; H, 1.91; N, 6.51.



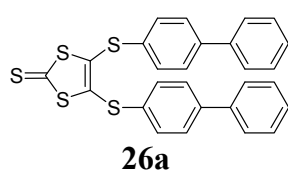
Yellow solid (Yield = 96%); Mp: 108-110 °C; ^1H NMR (CDCl_3): δ 8.30 (d, J = 8.2 Hz, 2H), 7.69 (t, J = 7.3 Hz, 2H), 7.47-7.40 (m, 4H); ^{13}C NMR (CDCl_3): δ 188.19, 145.72, 134.55, 133.69, 132.70, 128.25, 127.28, 126.39; EI-MS, m/z (I %): 424 (M^+ , 5); Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{N}_2\text{O}_5\text{S}_4$ (MW 424.49): C, 42.44; H, 1.90; N, 6.60; Found: C, 42.66; H, 1.88; N, 6.39.



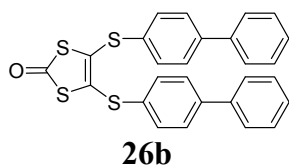
Yellow solid (Yield = 50%); Mp: 118-119 °C; ^1H NMR (CDCl_3): δ 8.29 (s, 2H), 8.23 (d, J = 8.2 Hz, 2H), 7.79 (dd, J = 0.6, 7.8 Hz, 2H), 7.62 (t, J = 8.0 Hz, 2H); ^{13}C NMR (CDCl_3): δ 209.03, 148.80, 136.36, 135.66, 134.51, 130.77, 125.53, 123.79; EI-MS, m/z (I %): 440 (M^+ , 100); Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{N}_2\text{O}_4\text{S}_5$ (MW 440.56): C, 40.89; H, 1.83; N, 6.36; Found: C, 40.67; H, 1.66; N, 6.22.



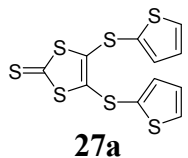
Pale yellow solid (Yield = 99%); Mp: 123-124 °C; ^1H NMR (CDCl_3): δ 8.25 (t, J = 1.9 Hz, 2H), 8.24-8.18 (m, 2H), 7.77-7.74 (m, 2H), 7.60 (t, J = 8.1 Hz, 2H); ^{13}C NMR (CDCl_3): δ 187.16, 148.71, 135.92, 135.09, 130.58, 128.09, 125.01, 123.39; EI-MS, m/z (I %): 424 (M^+ , 100); Anal. Calcd. for $\text{C}_{15}\text{H}_8\text{N}_2\text{O}_5\text{S}_4$ (MW 424.29): C, 42.44; H, 1.90; N, 6.60; Found: C, 42.20; H, 1.74; N, 6.43.



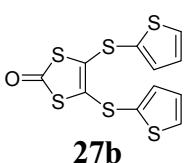
Yellow solid (Yield = 56%); Mp: 160-161 °C. ^1H NMR (CDCl_3): δ 7.63-7.56 (m, 12H), 7.47 (t, J = 7.2 Hz, 4H), 7.42-7.38 (m, 2H); ^{13}C NMR (CDCl_3): δ 211.25, 142.22, 139.72, 135.99, 132.14, 130.98, 128.95, 128.40, 127.96, 127.10; EI-MS, m/z (I %): 502 (M^+ , 50); Anal. Calcd. for $\text{C}_{27}\text{H}_{18}\text{S}_5$ (MW 502.76): C, 64.50; H, 3.61; Found: C, 64.75; H, 3.54.



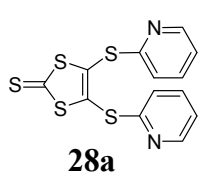
White solid (Yield = 100%); Mp: 160-162 °C; ^1H NMR (CDCl_3): δ 7.60 (t, J = 8.4 Hz, 8H), 7.54 (d, J = 8.4 Hz, 4H), 7.47 (t, J = 7.2 Hz, 4H), 7.39 (t, J = 7.4 Hz, 2H); ^{13}C NMR (CDCl_3): δ 189.33, 141.89, 139.91, 131.79, 131.76, 129.03, 128.34, 127.97, 127.84, 127.17; EI-MS, m/z (I %): 486 (M^+ , 61); Anal. Calcd. for $\text{C}_{27}\text{H}_{18}\text{OS}_4$ (MW 486.69): C, 66.63; H, 3.73; Found: C, 66.46; H, 3.56.



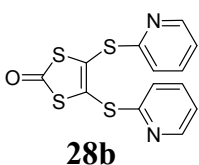
Yellow solid (Yield = 70%); Mp: 107-109 °C; ^1H NMR (CDCl_3): δ 7.55 (d, J = 5.4 Hz, 2H), 7.38 (d, J = 3.6 Hz, 2H), 7.08 (q, J = 4.1 Hz, 2H); ^{13}C NMR (CDCl_3): δ 210.41, 136.74, 135.40, 132.65, 128.55, 128.08; EI-MS, m/z (I %): 362 (M^+ , 32); Anal. Calcd. for $\text{C}_{11}\text{H}_6\text{S}_7$ (MW 362.62): C, 36.43; H, 1.67; Found: C, 36.25; H, 1.51.



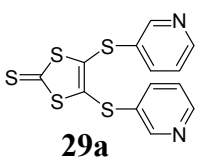
White solid (Yield = 92%); Mp: 67-68 °C; ^1H NMR (CDCl_3): δ 7.53 (dd, J = 1.1, 5.4 Hz, 2H), 7.37 (dd, J = 1.1, 3.6 Hz, 2H), 7.07 (q, J = 3.7 Hz, 2H); ^{13}C NMR (CDCl_3): δ 188.59, 136.43, 132.30, 129.36, 127.94, 127.15; EI-MS, m/z (I %): 346 (M^+ , 81); Anal. Calcd. for $\text{C}_{11}\text{H}_6\text{OS}_6$ (MW 346.55): C, 38.12; H, 1.75; Found: C, 37.89; H, 1.67.



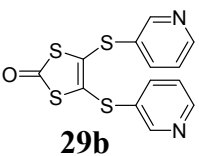
Yellow solid (Yield = 90%); Mp: 104-105 °C; ^1H NMR (CDCl_3): δ 8.49 (d, J = 4.9 Hz, 2H), 7.62 (dt, J = 1.9, 7.9 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.16 (q, J = 4.9 Hz, 2H); ^{13}C NMR (CDCl_3): δ 213.41, 155.55, 150.03, 137.33, 135.89, 122.44, 121.73; MS (ESI): 353.0 (M^+); Anal. Calcd. for $\text{C}_{13}\text{H}_8\text{N}_2\text{S}_5$ (352.54): C, 44.29; H, 2.29; N 7.95; Found: C, 44.00; H, 2.18; N, 7.77.



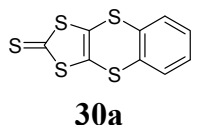
Pale yellow oil (Yield = 98%); ^1H NMR (CDCl_3): δ 8.47 (m, J = 4.9 Hz, 2H), 7.61 (dt, J = 1.9, 7.7 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.13 (m, J = 4.9 Hz, 2H); ^{13}C NMR (CDCl_3): δ 190.46, 156.24, 150.00, 137.21, 128.32, 122.41, 121.51; HRMS Calcd. for $\text{C}_{13}\text{H}_9\text{N}_2\text{OS}_4$: 336.9592. Found: 336.9593.



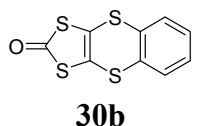
Tan solid (Yield = 60%); Mp: 98-100 °C; ^1H NMR (CDCl_3): δ 8.73 (d, J = 2.0 Hz, 2H), 8.63 (dd, J = 1.4, 4.8 Hz, 2H), 7.82-7.79 (m, 2H), 7.36 (q, J = 4.6 Hz, 2H); ^{13}C NMR (CDCl_3): δ 209.47, 151.97, 150.20, 139.21, 135.10, 129.41, 124.44; EI-MS, m/z (I %): 352 (M^+ , 67); Anal. Calcd. for $\text{C}_{13}\text{H}_8\text{N}_2\text{S}_5$ (MW 352.54): C, 44.29; H, 2.29; N, 7.95; Found: C, 44.22; H, 2.22; N, 7.82.



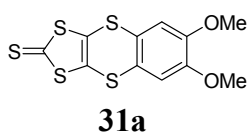
Pale brown solid (Yield = 100%); ^1H NMR (CDCl_3): δ 8.70 (d, J = 1.7 Hz, 2H), 8.62 (d, J = 4.5 Hz, 2H), 7.78 (d, J = 7.9 Hz, 2H), 7.34 (q, J = 4.8 Hz, 2H); ^{13}C NMR (CDCl_3): 187.50, 151.43, 149.67, 138.75, 129.80, 127.06, 124.20; HRMS Calcd. for $\text{C}_{13}\text{H}_9\text{N}_2\text{OS}_4$: 336.9592. Found: 336.9593.



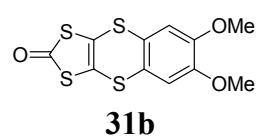
Yellow solid (Yield = 70%); Mp: 181-183 °C; ^1H NMR (CDCl_3): δ 7.51-7.49 (m, 2H), 7.38-7.36 (m, 2H); ^{13}C NMR (CDCl_3): δ 212.37, 133.87, 130.56, 129.29, 128.88. EI-MS, m/z (I %): 272 (M^+ , 100); Anal. Calcd. for $\text{C}_9\text{H}_4\text{S}_5$ (MW 272.45): C, 39.68; H, 1.48; Found: C, 39.93; H, 1.56.



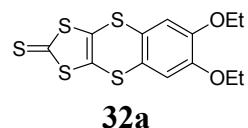
White solid (Yield = 96%); Mp: 173-175 °C; ^1H NMR (CDCl_3): δ 7.52-7.50 (m, 2H), 7.39-7.36 (m, 2H); ^{13}C NMR (CDCl_3): δ 191.14, 134.15, 129.03, 128.80, 120.92; EI-MS, m/z (I %): 256 (M^+ , 99); Anal. Calcd. for $\text{C}_9\text{H}_4\text{OS}_4$ (MW 256.39): C, 42.16; H, 1.57; Found: C, 42.20; H, 1.44.



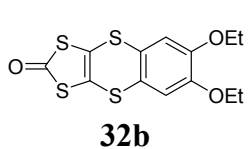
Yellow solid (Yield = 77%); Mp: 262-263 °C; ^1H NMR (CDCl_3): δ 6.96 (s, 2H), 3.90 (s, 6H); ^{13}C NMR (CDCl_3): δ 212.62, 149.66, 131.78, 125.31, 111.92, 56.32; EI-MS, m/z (I %): 332 (M^+ , 100); Anal. Calcd. for $\text{C}_{11}\text{H}_8\text{O}_2\text{S}_5$ (MW 332.51): C, 39.73; H, 2.43; Found: C, 39.50; H, 2.27.



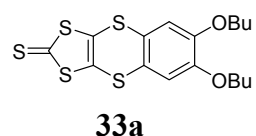
White solid (Yield = 94%); Mp: 299-301 °C; ^1H NMR (CDCl_3): δ 6.98 (s, 2H), 3.90 (s, 6H); ^{13}C NMR (CDCl_3): δ 191.27, 149.72, 125.59, 121.95, 111.69, 56.29; EI-MS, m/z (I %): 316 (M^+ , 75); Anal. Calcd. for $\text{C}_{11}\text{H}_8\text{O}_3\text{S}_4$ (MW 316.44): C, 41.75; H, 2.55; Found: C, 41.80; H, 2.58.



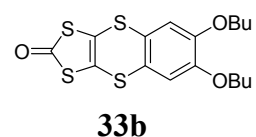
Yellow solid (Yield: 81%); Mp: 212-213 °C; ^1H NMR (CDCl_3): δ 6.95 (s, 2H), 4.09 (q, J = 7.0 Hz, 4H), 1.47 (t, J = 7.0 Hz, 6H); ^{13}C NMR (CDCl_3): δ 212.66, 149.27, 131.84, 125.01, 113.51, 65.01, 14.61; EI-MS, m/z (I %): 360 (M^+ , 20); Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{O}_2\text{S}_5$ (MW 360.56): C, 43.30; H, 3.35; Found: C, 43.43; H, 3.17.



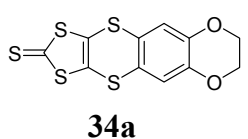
Gray solid (Yield = 100%); Mp: 138-140 °C; ^1H NMR (CDCl_3): δ 6.96 (s, 2H), 4.09 (q, J = 7.0 Hz, 4H), 1.47 (t, J = 7.0 Hz, 6H); ^{13}C NMR (CDCl_3): δ 191.42, 149.28, 125.28, 121.93, 113.20, 64.95, 14.61; EI-MS, m/z (I %): 344 (M^+ , 94); Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{O}_3\text{S}_4$ (MW 344.49): C, 45.32; H, 3.51; Found: C, 45.06; H, 3.39.



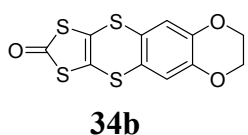
Yellow solid (Yield = 71%); Mp: 165-166 °C; ^1H NMR (CDCl_3): δ 6.95 (s, 2H), 4.00 (t, J = 6.6 Hz, 4H), 1.82 (m, J = 6.7 Hz, 4H), 1.50 (m, J = 7.5 Hz, 4H), 0.99 (t, J = 7.4 Hz, 6H); ^{13}C NMR (CDCl_3): δ 212.60, 149.68, 131.86, 124.95, 113.82, 69.29, 31.03, 19.11, 13.77; EI-MS, m/z (I %): 416 (M^+ , 60); Anal. Calcd. for $\text{C}_{17}\text{H}_{20}\text{O}_2\text{S}_5$ (MW 416.66): C, 49.00; H, 4.84; Found: C, 48.71; H, 4.72.



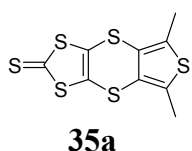
Gray solid (Yield = 98%); Mp: 127-128 °C; ^1H NMR (CDCl_3): δ 6.97 (s, 2H), 4.00 (t, J = 6.6 Hz, 4H), 1.83-1.79 (m, J = 6.7 Hz, 4H), 1.53-1.47 (m, J = 7.5 Hz, 4H), 0.99 (t, J = 7.4 Hz, 6H); ^{13}C NMR (CDCl_3): δ 191.40, 149.76, 125.28, 121.98, 113.60, 69.29, 31.06, 19.13, 13.78; EI-MS, m/z (I %): 400 (M^+ , 46); Anal. Calcd. for $\text{C}_{17}\text{H}_{20}\text{O}_3\text{S}_4$ (MW 400.60): C, 50.97; H, 5.03; Found: C, 50.75; H, 4.89.



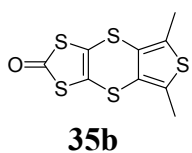
Yellow solid (Yield = 65%); Mp: 289-291 °C; ^1H NMR (CDCl_3): δ 7.01 (s, 2H), 4.27 (s, 4H); ^{13}C NMR (CDCl_3): δ 212.47, 144.11, 131.81, 125.68, 117.95, 64.31; EI-MS, m/z (I %): 330 (M^+ , 100); Anal. Calcd. for $\text{C}_{11}\text{H}_6\text{O}_2\text{S}_5$ (MW 330.49): C, 39.98; H, 1.83; Found: C, 39.98; H, 1.71.



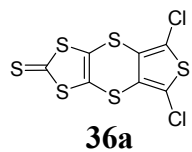
White solid (Yield = 73%); Mp: 244-247 °C; ^1H NMR (CDCl_3): δ 7.02 (s, 2H), 4.27 (s, 4H); ^{13}C NMR (CDCl_3): δ 191.21, 144.19, 126.11, 121.99, 117.58, 64.32; EI-MS, m/z (I %): 314 (M^+ , 95); Anal. Calcd. for $\text{C}_{11}\text{H}_6\text{O}_3\text{S}_4$ (MW 314.42): C, 42.02; H, 1.92; Found: C, 42.17; H, 1.83.



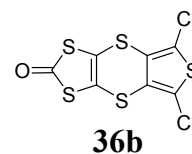
Yellow solid (Yield = 65%); Mp: 207-208 °C; ^1H NMR (CDCl_3): δ 2.35 (s, 6H); ^{13}C NMR (CDCl_3): δ 210.54, 131.27, 131.05, 125.71, 13.80; EI-MS, m/z (I %): 306 (M^+ , 100); Anal. Calcd. for $\text{C}_9\text{H}_6\text{S}_6$ (MW 306.53): C, 35.26; H, 1.97; Found: C, 35.36; H, 1.82.



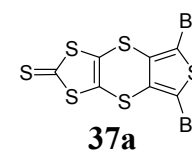
White solid (Yield = 100%); Mp: 169-171 °C; ¹H NMR (CDCl₃): δ 2.35 (s, 6H); ¹³C NMR (CDCl₃): δ 190.07, 130.72, 126.46, 121.23, 13.76; EI-MS, m/z (I %): 290 (M⁺, 100); Anal. Calcd. for C₉H₆OS₅ (MW 290.47): C, 37.21; H, 2.08; Found: C, 37.14; H, 2.00.



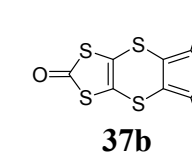
Tan solid (Yield = 72%); Mp: 227-229 °C; EI-MS, m/z (I %): 346 (M⁺, 7); Anal. Calcd. for C₇Cl₂S₆ (MW 347.37): C, 24.20; Found: C, 23.85.



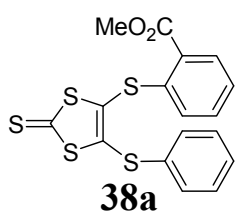
White solid (Yield = 90%); Mp: 222-224 °C; ¹³C NMR (CDCl₃): δ 188.95, 128.17, 121.03, 119.31; EI-MS, m/z (I %): 331 (M⁺, 11); Anal. Calcd. for C₇Cl₂OS₅ (MW 331.31): C, 25.38; Found: C, 25.04.



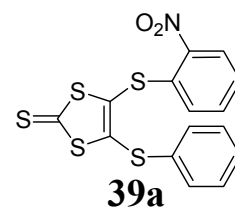
Yellow solid (Yield = 88%); Mp: 276-278 °C; EI-MS, m/z (I %): 436 (M⁺, 38); Anal. Calcd. for C₇Br₂S₆ (MW 436.27): C, 19.27; Found: C, 19.20.



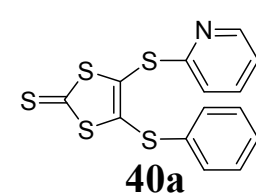
White solid (Yield = 75%); Mp: 230-233 °C; ¹³C NMR (CDCl₃): δ 189.07, 131.53, 119.55, 106.93; EI-MS, m/z (I %): 420 (M⁺, 78); Anal. Calcd. for C₇Br₂OS₅ (MW 420.21): C, 20.01; Found: C, 20.47.



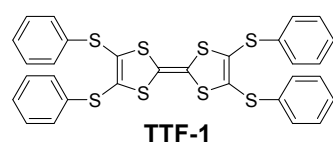
Yellow solid (Yield = 43%); Mp: 96-97°C; ¹H NMR (600 MHz, CDCl₃): δ 8.09 (dd, *J* = 1.4, 7.8 Hz, 1H), 7.55-7.53 (m, 3H), 7.41-7.38 (m, 3H), 7.33-7.28 (m, 2H), 3.98 (s, 3H); ¹³C NMR (CDCl₃): δ 211.81, 166.48, 138.60, 133.46, 133.27, 131.09, 131.77, 131.59, 129.94, 129.83, 127.17, 126.58, 125.98, 52.47; EIMS, m/z (I %): 408 (M⁺, 100); Anal. Calcd. for C₁₇H₁₂O₂S₅ (MW 408.60): C, 49.97; H, 2.96; Found: C, 50.03; H, 2.91.



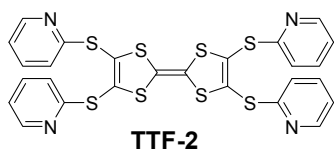
Yellow solid (Yield = 38%); Mp: 142-143°C; ¹H NMR (600 MHz, CDCl₃): δ 8.35 (dd, *J* = 1.4, 8.3 Hz, 1H), 7.67 (dt, *J* = 1.5, 8.2 Hz, 1H), 7.55-7.54 (m, 2H), 7.44-7.38 (m, 5H); ¹³C NMR (CDCl₃): δ 210.86, 145.44, 134.49, 134.31, 133.83, 130.36, 129.97, 127.36, 126.75, 126.50, 126.36, 124.48; EIMS, m/z (I %) : 395 (M⁺, 65); Anal. Calcd. for C₁₅H₉NO₂S₅ (MW 395.56): C, 45.55; H, 2.29; Found: C, 45.32; H, 2.16.



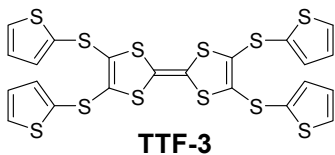
Pale yellow oil (Yield = 44%); ¹H NMR (600 MHz, CDCl₃): δ 8.52 (m, *J* = 0.9, 4.9 Hz, 1H), 7.65 (dt, *J* = 1.9, 7.6 Hz, 1H), 7.52-7.51 (m, 2H), 7.39-7.37 (m, 3H), 7.28-7.26 (m, 2H), 7.18-7.16 (m, 1H); ¹³C NMR (CDCl₃): δ 211.17, 155.00, 149.46, 142.25, 136.86, 131.75, 131.20, 129.22, 128.83, 121.39, 121.13; EIMS, m/z (I %): 351 (M⁺, 8); Anal. Calcd. for C₁₄H₉NS₅ (MW 351.55): C, 47.83; H, 2.58; Found: C, 48.01; H, 2.62.



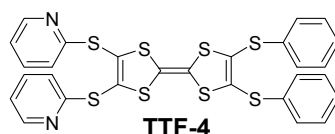
Dark red solid (Yield = 92%); Mp: 169-170 °C (lit.² 167-169 °C); ¹H NMR (CDCl₃): δ 7.41-7.39 (m, 8H), 7.36-7.30 (m, 12H); ¹³C NMR (CDCl₃): δ 133.16, 130.59, 129.28, 128.64, 1128.05, 109.66; MS(APCI), m/z: 637.2 (M⁺); Anal. Calcd. for C₃₀H₂₀S₈ (MW 637.00): C, 56.57; H, 3.16; Found: C, 56.35; H, 2.93.



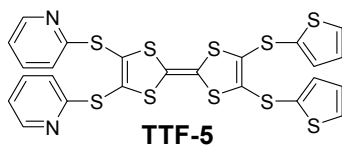
Orange solid (Yield = 80%); Mp: 158-159 °C; ^1H NMR (CDCl_3): δ 8.46 (dd, J = 0.8, 4.8 Hz, 4H), 7.59 (td, J = 1.6, 7.8 Hz, 4H), 7.32 (d, J = 8.0 Hz, 4H), 7.09 (q, J = 4.9 Hz, 4H); ^{13}C NMR (CDCl_3): δ 156.87, 149.87, 137.08, 129.41, 122.41, 121.22, 110.47; MS (APCI), m/z : 641.0 (M^+); Anal. Calcd. for $\text{C}_{26}\text{H}_{16}\text{N}_4\text{S}_8$ (MW 640.95): C, 48.72; H, 2.52; N, 8.74; Found: C, 48.52; H, 2.34; N, 8.48.



Red-orange solid (Yield = 93%); Mp: 204-205 °C; ^1H NMR (CDCl_3): δ 7.47 (d, J = 5.3 Hz, 4H), 7.28 (d, J = 4.2 Hz, 4H), 7.03-7.01 (q, J = 3.7 Hz, 4H); ^{13}C NMR (CDCl_3): δ 135.79, 131.62, 129.75, 128.01, 127.68, 109.19; MS (APCI), m/z : 661.1 (M^+); Anal. Calcd. for $\text{C}_{22}\text{H}_{12}\text{S}_{12}$ (MW 661.11): C, 39.97; H, 1.83; Found: C, 40.26; H, 1.62.



Orange solid (Yield = 80%); Mp: 101-102 °C; ^1H NMR (CDCl_3): δ 8.40 (d, J = 3.9 Hz, 2H), 7.57 (td, J = 1.7, 7.7 Hz, 2H), 7.44 (d, J = 8.2 Hz, 4H), 7.37-7.28 (m, 8H), 7.09 (q, J = 4.9 Hz, 2H); ^{13}C NMR (CDCl_3): δ 157.04, 149.96, 137.15, 133.26, 130.85, 129.60, 129.41, 128.66, 128.25, 122.45, 121.27, 110.38, 109.96; MS (APCI), m/z : 638.9 (M^+); Anal. Calcd. for $\text{C}_{28}\text{H}_{18}\text{N}_2\text{S}_8$ (MW 638.98): C, 52.63; H, 2.87; N, 4.38; Found: C, 52.80; H, 2.62; N, 4.12.



Orange solid (Yield = 75%); Mp: 112-114 °C; ^1H NMR (CDCl_3): δ 8.43 (d, J = 3.9 Hz, 2H), 7.56 (td, J = 1.8, 7.6 Hz, 2H), 7.49 (d, J = 5.4 Hz, 2H), 7.32 (d, J = 3.6 Hz, 2H), 7.27-7.26 (m, 2H), 7.08 (q, J = 4.9 Hz, 2H), 7.03 (q, J = 3.7 Hz, 2H); ^{13}C NMR (CDCl_3): δ 157.03, 149.82, 137.06, 136.05, 131.77, 129.72, 129.64, 127.73, 122.24, 121.12, 109.96, 109.78; MS (ESI), m/z : 650.6 (M^+); Anal. Calcd. for $\text{C}_{24}\text{H}_{14}\text{N}_2\text{S}_{10}$ (MW 651.03): C, 44.28; H, 2.17; N, 4.30; Found: C, 44.04; H, 1.97; N, 4.11.

4. Crystallographic data

	17b	24b	34a	35a
CCDC number	922049	922050	922051	922052
Empirical formula	C ₁₉ H ₁₄ O ₅ S ₄	C ₁₅ H ₈ N ₂ O ₅ S ₄	C ₁₁ H ₆ O ₂ S ₅	C ₉ H ₆ S ₆
Formula weight	450.58	424.19	330.49	306.53
Temperature / K	293(2)	293(2)	293(2)	293(2)
λ / Å	0.71073	0.71073	0.71073	0.71073
Crystal size / mm ³	0.15 × 0.10 × 0.05	0.10 × 0.05 × 0.05	0.10 × 0.10 × 0.05	0.50 × 0.20 × 0.10
Crystal system	Monoclinic	Triclinic	Orthorhombic	Orthorhombic
Space group	C 2/c (# 15)	P -1 (# 2)	P mnb (#62)	Pbca (#61)
<i>a</i> / Å	12.696(9)	11.066(12)	10.892(3)	11.411(3)
<i>b</i> / Å	17.151(12)	11.928(13)	8.013(2)	11.3850(17)
<i>c</i> / Å	10.238(7)	13.426(14)	14.444(3)	19.507(3)
α / °	90	78.033(10)	90	90
β / °	114.694(5)	89.127(10)	90	90
γ / °	90	86.984(9)	90	90
<i>V</i> / Å ³	2025(2)	1731(3)	1260.6(5)	2534.2(8)
<i>Z</i>	4	4	4	8
<i>d</i> _{calc} / g·cm ⁻³	1.478	1.629	1.741	1.607
μ / mm ⁻¹	0.502	0.579	0.906	1.041
2 θ _{max} / °	52.98	52.92	52.76	52.64
Limiting indices	-15 ≤ <i>h</i> ≤ 15 -18 ≤ <i>k</i> ≤ 21 -12 ≤ <i>l</i> ≤ 12	-12 ≤ <i>h</i> ≤ 13 -14 ≤ <i>k</i> ≤ 14 -16 ≤ <i>l</i> ≤ 16	-13 ≤ <i>h</i> ≤ 13 -10 ≤ <i>k</i> ≤ 8 -17 ≤ <i>l</i> ≤ 18	-14 ≤ <i>h</i> ≤ 12 -15 ≤ <i>k</i> ≤ 10 -26 ≤ <i>l</i> ≤ 10
Data / restraints / parameters	2085 / 0 / 128	6901 / 0 / 424	1356 / 0 / 95	2770 / 0 / 136
<i>Goof</i>	1.018	1.036	1.046	1.072
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.043	0.065	0.035	0.042
<i>wR</i> ₂	0.0916	0.1516	0.0814	0.0927

5. Crystal structures for 17b, 24b, and 35a.

In the following figures (Figures S1 – S3), the black, green, red, blue, and cyan circles represent carbon, sulfur, oxygen, nitrogen, and hydrogen atoms, respectively.

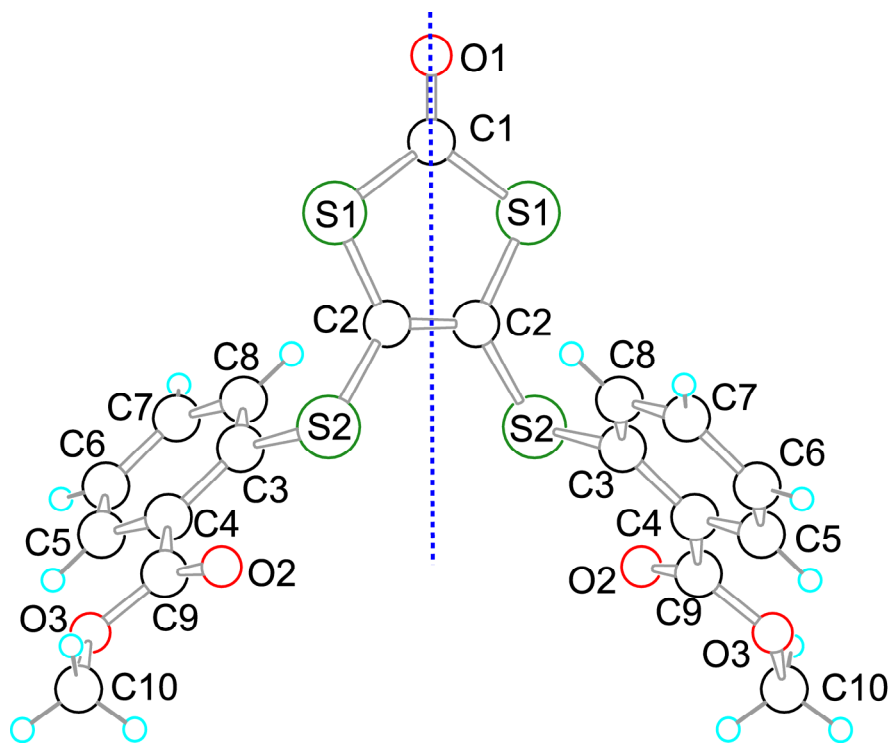


Figure S1. Crystal structure of **17b**. In the crystal of this compound, half of the molecule is crystallographically unique. Atoms O1 and C1 are located on the two-fold axis (blue dashed line), and the structure of whole molecule is generated by the symmetry operation $(1-x, y, 1.5-z)$

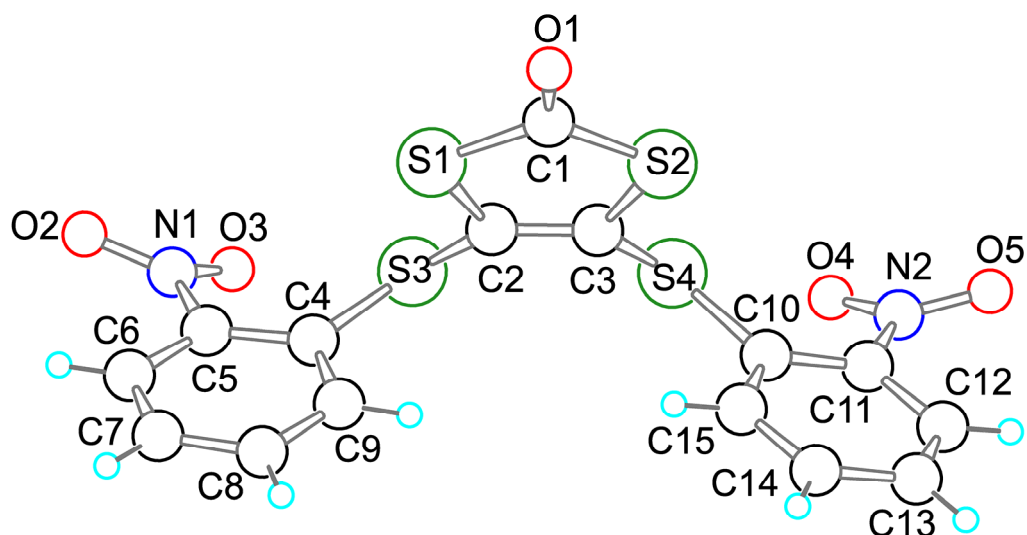


Figure S2. Crystal structure of **24b**. In the crystal of this compound, two molecules are crystallographically unique while they have almost the same configuration. The present figure depicts the structure of **molecule 1**.

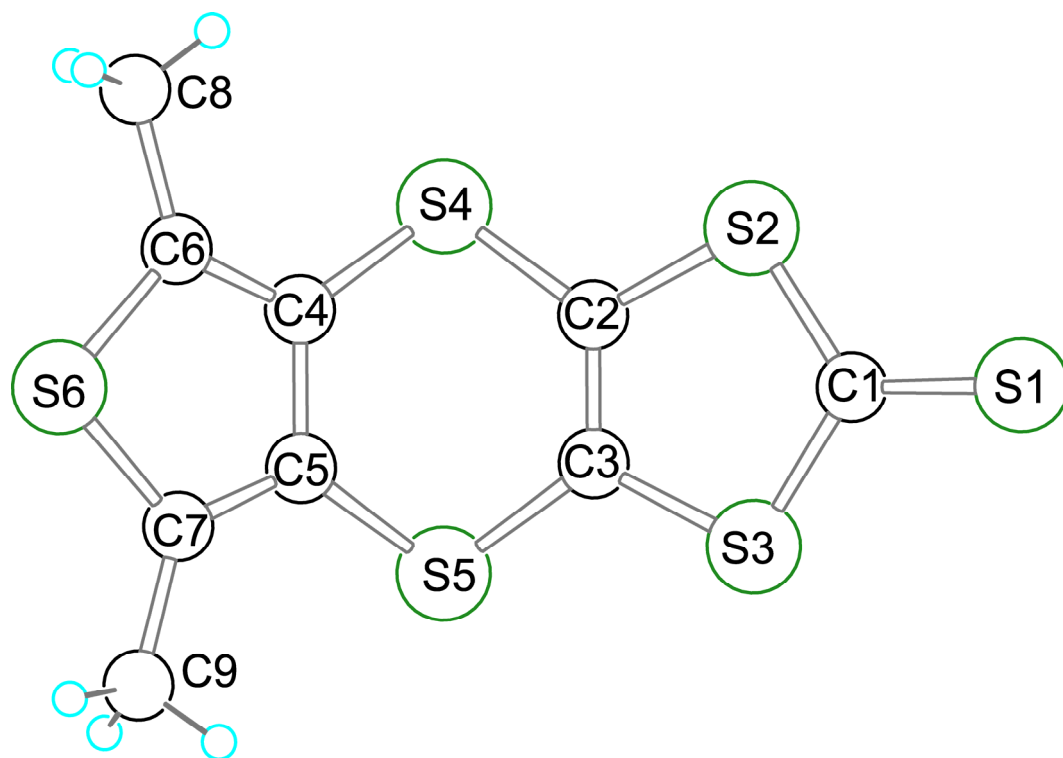


Figure S3. Crystal structure of **35a**.

6. References

1. (a) M. C. Burla, R. Caliendo, M. Camalli, B. Carrozzini, G. L. Casciaro, L. de Caro, C. Giacovazzo, G. Polidori and R. Spagna, *J. Appl. Cryst.*, 2005, **38**, 381. (b) G. M. Sheldrick, *SHELXL-97, A Program for Crystal Structure Refinement*; University of Göttingen, Göttingen, Germany, 1997, Release 97-2.
2. S. Y. Hsu and L. Y. Chiang, *L. Y. J. Org. Chem.*, 1987, **52**, 3444.