Electronic Supplementary Material (ESI) for ChemComm.

Direct Access to Thieno[3,4-b]thiophenes via Elemental Sulfur-Promoted Sulfurative Tetramerization of Acetophenones

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Supporting information

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General information

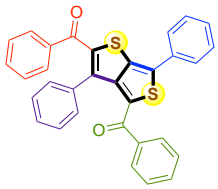
Reagents were obtained from commercial supplier and used without further purification. Thin layer chromatography (TLC) was purchased from Merck KGaA (silica gel 60 F254). Visualization of the chromatogram was performed by UV light (254 nm) or phosphomolybdic acid or vanilline stains. Flash column chromatography 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 ($CDCl_3$, δ 7.26 ppm for ^1H and δ 77.0 ppm for ^{13}C). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration.

General procedure

A mixture of acetophenone **1** (1 mmol), elemental sulfur (2 mmol), DABCO (0.5 mmol) and DMSO (0.1 mL) was heated under an argon atmosphere in a 7-mL test tube at 80-120 °C for 3-16 h (See Tables 1 and 2 of the manuscript). The reaction mixture was purified by trituration by dilution with methanol (2 mL) to a slurry which was filtered, washed with methanol (2 mL × 2) then dried in vacuo (0.01 mmHg, 80 °C) to afford the expected tetramer **2** as a bright yellow solid. Alternatively, the crude reaction mixture could be purified by chromatography.

Characterizations of Products

(3,6-Diphenylthieno[3,4-*b*]thiophene-2,4-diyl)bis(phenylmethanone) (2a)



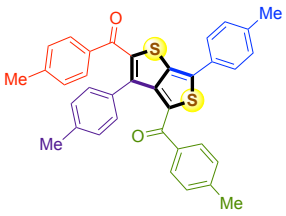
The product was purified by trituration of the crude mixture (Table 1, entry 1) with methanol, followed by filtration, dried in vacuo (0.01 mmHg, 80 ºC) to afford a bright yellow solid (90 mg, 72%).

^1H NMR (500 MHz, $CDCl_3$) δ 7.83-7.80 (m, 2H), 7.58-7.56 (m, 2H), 7.54-7.50 (m, 4H), 7.43-7.40 (m, 1H), 7.35-7.29 (m, 2H), 7.19-7.12 (m, 4H), 6.99-6.96 (m, 2H), 6.89-6.83 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.8, 187.6, 147.9, 145.2, 138.7, 136.5, 135.5, 135.1, 134.0, 132.8, 132.6, 132.2, 130.5, 129.7, 129.6, 129.5, 129.5, 128.8, 128.0, 128.0, 127.9, 126.5.

HRMS (ESI+) calcd for $C_{32}H_{21}O_2S_2$ $[M + H]^+$ 501.0983. Found 501.0976.

(3,6-Di-*p*-tolylthieno[3,4-b]thiophene-2,4-diyl)bis(p-tolylmethanone) (2b)



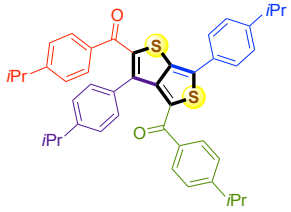
The crude mixture (Table 2, entry 2) was purified by column chromatography (CH_2Cl_2:heptane 2:1) to afford the product as a bright yellow solid (72 mg, 52%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65, 7.63 (m, 2H), 7.50, 7.48, 7.48 (m, 2H), 7.40, 7.39, 7.39 (m, 2H), 7.26, 7.24 (m, 2H), 6.94, 6.93, 6.91 (m, 4H), 6.82, 6.81 (m, 2H), 6.61, 6.59 (m, 2H), 2.36 (s, 3H), 2.25 (s, 3H), 2.22 (s, 3H), 2.04 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.4, 187.3, 147.8, 144.6, 143.9, 143.2, 138.9, 137.3, 136.4, 135.2, 135.1, 134.6, 134.0, 131.2, 130.1, 129.9, 129.3, 128.7, 128.6, 128.5, 126.4, 21.6, 21.5, 21.4, 21.1.

HRMS (ESI+) calcd for $C_{36}H_{29}O_2S_2$ $[M + H]^+$ 557.1609. Found 557.1605.

(3,6-Bis(4-isopropylphenyl)thieno[3,4-*b*]thiophene-2,4-diyl)bis((4-isopropylphenyl)methanone) (2c)



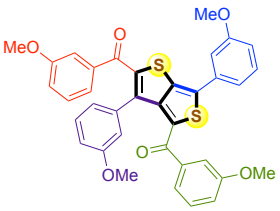
The crude mixture (Table 2, entry 4) was purified by column chromatography (CH_2Cl_2:heptane 2:1) to afford the product as a bright yellow solid (78 mg, 47%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75-7.73 (m, 2H), 7.47-7.44 (m, 2H), 7.39-7.36 (m, 2H), 7.35-7.32 (m, 2H), 6.96-6.91 (m, 4H), 6.82-6.80 (m, 2H), 6.61-6.60 (m, 2H), 3.02 (septet, J = 7.1 Hz, 1H), 2.97 (septet, J = 7.1 Hz, 1H), 2.75 (septet, J = 7.1 Hz, 1H), 2.57 (septet, J = 7.1 Hz, 1H), 1.31 (d, J = 7.1 Hz, 6H), 1.16 (d, J = 7.1 Hz, 6H), 1.12 (d, J = 7.1 Hz, 6H), 1.03 (d, J = 7.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.6, 188.1, 154.2, 153.5, 149.6, 147.9, 147.8, 144.6, 136.6, 135.3, 134.6, 134.3, 134.1, 131.6, 130.4, 130.0, 129.9, 129.4, 127.5, 126.4, 126.0, 125.9, 125.8, 34.2, 34.1, 34.0, 33.6, 23.8, 23.6, 23.6, 23.5, 23.4. (1 signal missing due to overlap).

HRMS (ESI+) calcd for $C_{44}H_{45}O_2S_2$ $[M + H]^+$ 669.2861. Found 669.2855.

(3,6-Bis(3-methoxyphenyl)thieno[3,4-*b*]thiophene-2,4-diyl)bis((3-methoxyphenyl)methanone) (2d)



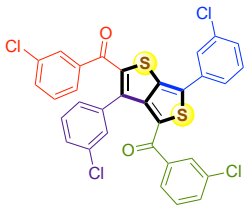
The crude mixture (Table 2, entry 5) was purified by column chromatography (CH_2Cl_2:EtOAc 99:1) to afford the product as a bright yellow solid (40 mg, 26%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53-7.47 (m, 2H), 7.42-7.41 (m, 1H), 7.34 (s, 1H), 7.26-7.24 (m, 1H), 7.16-7.15 (m, 3H), 7.06-7.03 (m, 2H), 6.95-6.92 (m, 2H), 6.87-6.83 (m, 1H), 6.66-6.64 (m, 1H), 6.49-6.47 (m, 2H), 3.99 (s, 3H), 3.81 (s, 3H), 3.77 (s, 3H), 3.63 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.6, 187.9, 160.3, 159.1, 159.0, 158.8, 147.5, 145.0, 140.0, 137.8, 135.3, 135.2, 135.1, 135.0, 133.5, 130.8, 130.6, 129.2, 129.0, 128.8, 122.6, 122.3, 121.9, 119.7, 119.2, 119.0, 114.7, 114.4, 114.3, 113.5, 113.4, 111.8, 55.5, 55.4, 55.3, 54.9.

HRMS (ESI+) calcd for $C_{36}H_{29}O_6S_2$ $[M + H]^+$ 621.1406. Found 621.1421.

(3,6-Bis(3-chlorophenyl)thieno[3,4-*b*]thiophene-2,4-diyl)bis((3-chlorophenyl)methanone) (2e)



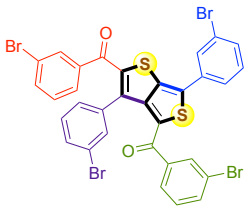
The crude mixture (Table 2, entry 6) was purified by column chromatography (CH_2Cl_2:heptane 2:1) to afford the product as a bright yellow solid (75 mg, 47%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76-7.75 (m, 1H), 7.68-7.66 (m, 1H), 7.48-7.45 (m, 2H), 7.41-7.39 (m, 3H), 7.35-7.29 (m, 4H), 7.13-7.09 (m, 2H), 6.87-6.86 (m, 3H), 6.80-6.79 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.0, 186.1, 147.1, 145.9, 139.9, 137.8, 135.7, 135.6, 135.4, 134.5, 134.4, 134.3, 134.2, 134.2, 133.5, 132.8, 132.6, 131.2, 130.8, 129.5, 129.4, 129.3, 129.2, 129.1, 128.3, 127.5, 127.4, 127.2, 126.5, 124.6.

HRMS (ESI+) calcd for $C_{32}H_{17}Cl_4O_2S_2$ $[M + H]^+$ 636.9424. Found 636.9431.

(3,6-Bis(3-bromophenyl)thieno[3,4-*b*]thiophene-2,4-diyl)bis((3-bromophenyl)methanone) (2f)



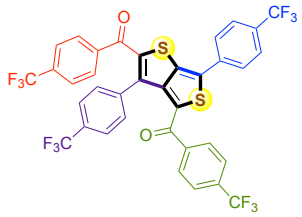
The crude mixture (Table 2, entry 7) was purified by preparative thin layer chromatography (CH_2Cl_2:heptane 2:1) to afford the product as a bright yellow solid (51 mg, 25%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94-7.93 (m, 1H), 7.74-7.72 (m, 1H), 7.59-7.56 (m, 1H), 7.52-7.51 (m, 1H), 7.48-7.44 (m, 3H), 7.43-7.37 (m, 3H), 7.08-7.02 (m, 3H), 6.93-6.90 (m, 2H), 6.82-6.78 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.0, 186.1, 147.1, 146.0, 140.1, 137.9, 135.7, 135.5, 134.2, 133.8, 132.4, 132.2, 132.2, 132.1, 132.0, 131.6, 131.3, 131.2, 131.0, 129.8, 129.7, 129.6, 129.4, 127.9, 127.8, 127.5, 127.4, 125.1, 123.7, 122.7, 122.6, 122.2.

HRMS (ESI+) calcd for $C_{32}H_{17}Br_4O_2S_2$ $[M + H]^+$ 812.7403. Found 812.7418.

(3,6-Bis(4-(trifluoromethyl)phenyl)thieno[3,4-*b*]thiophene-2,4-diyl)bis((4-(trifluoromethyl)phenyl)methanone) (2g)



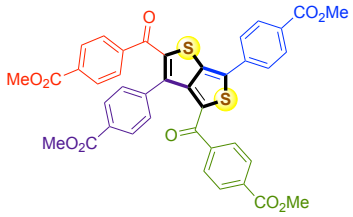
The crude mixture (Table 2, entry 8) was purified by preparative thin layer chromatography (CH_2Cl_2:heptane 2:1) to afford the product as a bright yellow solid (64 mg, 33%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94, 7.92, 7.83, 7.81, 7.58, 7.56, 7.52, 7.50, 7.43, 7.41, 7.39, 7.11, 7.09, 7.00, 6.98.

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.0, 186.3, 147.4, 146.2, 141.2, 139.2, 137.3, 136.2, 135.0, 134.6, 134.5, 134.3, 134.0, 131.6, 130.7 (q, J = 33.6 Hz) 129.9, 129.7, 129.5, 129.4, 126.7 (q, J = 4.1 Hz), 125.3 (q, J = 3.7 Hz), 123.3 (q, J = 272.3 Hz).

HRMS (ESI+) calcd for $C_{36}H_{17}F_{12}O_2S_2$ $[M + H]^+$ 773.0478. Found 773.0452.

Dimethyl 4,4'-(2,4-bis(4-(methoxycarbonyl)benzoyl)thieno[3,4-*b*]thiophene-3,6-diyl)dibenzoate (2h)



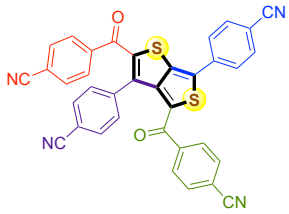
The crude mixture (Table 2, entry 9) was purified by column chromatography (CH_2Cl_2:EtOAc 95:5) to afford the product as a bright yellow solid (93 mg, 51%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19, 8.17, 7.86, 7.85, 7.84, 7.83, 7.81, 7.80, 7.60, 7.58, 7.57, 7.56, 7.54, 7.53, 7.04, 7.03, 3.96, 3.92, 3.87, 3.83.

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.6, 186.2, 166.2, 166.0, 165.9, 165.8, 147.5, 146.0, 141.8, 139.7, 138.3, 136.5, 135.9, 134.9, 134.7, 133.8, 133.6, 131.4, 130.8, 130.3, 129.7, 129.5, 129.4, 129.3, 129.2, 129.1, 126.3, 52.5, 52.4, 52.4, 52.1.

HRMS (ESI+) calcd for $C_{40}H_{29}O_{10}S_2$ $[M + H]^+$ 733.1202. Found 733.1223.

4,4'-(2,4-Bis(4-cyanobenzoyl)thieno[3,4-*b*]thiophene-3,6-diyl)dibenzonitrile (2i)



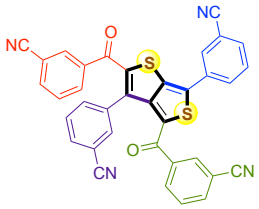
The crude mixture (Table 2, entry 10) was purified by preparative thin layer chromatography (CH_2Cl_2:EtOAc 99:1) to afford the product as a bright yellow solid (53 mg, 35%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88-7.87 (m, 2H), 7.84-7.82 (m, 2H), 7.73-7.65 (m, 6H), 7.60-7.58 (m, 2H), 7.37-7.35 (m, 2H), 7.19-7.17 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 188.8, 184.5, 147.9, 145.9, 141.4, 139.4, 138.3, 137.1, 135.5, 134.6, 134.2, 133.4, 132.5, 132.3, 132.2, 132.2, 131.8, 130.6, 130.5, 130.1, 129.8, 129.7, 129.3, 128.7, 126.9, 117.9, 117.7, 117.4, 117.3, 117.0, 116.6, 113.0, 112.5.

HRMS (ESI+) calcd for $C_{36}H_{17}N_4O_2S_2$ [M + H]+ 601.0793. Found 601.0799.

3,3'-(2,4-Bis(3-cyanobenzoyl)thieno[3,4-*b*]thiophene-3,6-diyl)dibenzonitrile (2j)



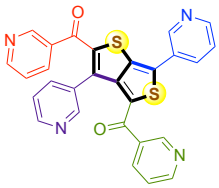
The crude mixture (Table 2, entry 11) was purified by column chromatography (CH_2Cl_2:EtOAc 99:1) to afford the product as a bright yellow solid (68 mg, 45%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04-8.01 (m, 2H), 7.87-7.82 (m, 3H), 7.78-7.74 (m, 3H), 7.71-7.68 (m, 2H), 7.50-7.44 (m, 2H), 7.38-7.35 (m, 2H), 7.25-7.22 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 188.3, 184.1, 147.7, 146.3, 139.2, 137.2, 136.1, 135.9, 135.1, 134.4, 133.9, 133.5, 133.1, 133.0, 132.9, 132.9, 132.6, 131.9, 130.7, 130.6, 130.4, 129.8, 129.6, 129.5, 129.2, 126.1, 117.7, 117.5, 117.4, 117.3, 117.2, 117.1, 114.3, 113.1, 112.9, 112.7.

HRMS (ESI+) calcd for $C_{36}H_{17}N_4O_2S_2$ [M + H]+ 601.0793. Found 601.0774.

(3,6-Di(pyridin-3-yl)thieno[3,4-*b*]thiophene-2,4-diyl)bis(pyridin-3-ylmethanone) (2k)



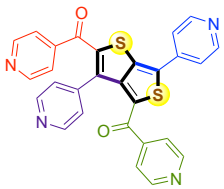
The crude mixture (Table 2, entry 12) was purified by preparative thin layer chromatography (EtOAc) to afford the product as a bright yellow solid (39 mg, 31%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.09-9.08 (m, 1H), 8.79-8.79 (m, 1H), 8.74-8.74 (m, 1H), 8.69-8.68 (m, 1H), 8.64-8.63 (m, 1H), 8.57-8.56 (m, 1H), 8.29-8.28 (m, 1H), 8.24-8.23 (m, 1H), 8.10-8.07 (m, 1H), 7.85-7.82 (m, 2H), 7.50-7.47 (m, 1H), 7.37-7.35 (m, 1H), 7.22-7.15 (m, 2H), 6.93-6.90 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 189.2, 184.7, 153.4, 153.4, 150.5, 150.4, 150.2, 149.9, 149.7, 149.6, 149.4, 149.0, 148.7, 147.9, 147.4, 146.8, 136.7, 136.7, 136.6, 136.4, 136.3, 134.2, 133.5, 133.3, 132.7, 132.1, 130.8, 130.0, 127.9, 124.2, 123.6, 123.3, 123.2, 122.8.

HRMS (ESI+) calcd for $C_{28}H_{17}N_4O_2S_2$ $[M + H]^+$ 505.0793. Found 505.0788.

(3,6-Di(pyridin-4-yl)thieno[3,4-b]thiophene-2,4-diyl)bis(pyridin-4-ylmethanone) (2l)



The crude mixture (Table 2, entry 13) was purified by preparative thin layer chromatography (EtOAc) to afford the product as a bright yellow solid (44 mg, 35%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.81-8.79 (m, 2H), 8.65-8.58 (m, 4H), 8.29-8.27 (m, 2H), 7.65-7.63 (m, 2H), 7.38-7.36 (m, 2H), 7.32-7.30 (m, 2H), 6.92-6.90 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.4, 185.3, 151.2, 150.6, 150.5, 149.7, 147.5, 145.8, 144.2, 142.7, 141.5, 138.4, 137.4, 133.6, 130.9, 123.9, 122.1, 121.8, 120.1.

HRMS (ESI+) calcd for $C_{28}H_{17}N_4O_2S_2$ $[M + H]^+$ 505.0793. Found 505.0771.

Crystallographic data collection, structure determination and refinement

Suitable crystals for single crystal X-ray diffraction (SCXRD) analyses were obtained for the five following compounds (see Table S1) in the presence of deuterated chloroform solvent.

X-ray diffraction data were measured at room temperature using a RIGAKU *XtaLabPro* diffractometer (except for **2h**) equipped with a Mo microfocus sealed tube *MM003* generator coupled to a double-bounce confocal Max-Flux® multilayer optic and a HPAD *PILATUS3R 200K* detector. *CrysAlisPro 1.171.41.122a* [1] was employed for the data processing, with a combination of absorption correction, a numerical one based on gaussian integration over a multifaceted crystal and an empirical one using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. **2h** was mounted on a RIGAKU MM007 HF rotating anode delivering copper radiation through Osmic CMF confocal optics and equipped with a Rapid II curved Image Plate. The recorded data were integrated and reduced using *Fs_process* [2] software implemented in the *CrystalClear 2.0* [2] and corrected for the radiation absorption using the multi-scan *Abscor* option.[2] The four original structures of 2,4,3,6-substituted thieno[3,4-b]thiophene derivatives (**2a**, **2f**, **2h**, and **2i***)* and that with a single thiophene core (**3i**) were readily solved by intrinsic phasing methods (*SHELXT* program),[3] and all were refined by full-matrix least-squares methods on F^2 using *SHELX-L*.[4] All non-hydrogen atoms of the molecules of interest improved by anisotropic refinement. Nevertheless residual peaks around the bromide atoms in **2f** were reduced after few runs using *Olex2.refine* [5] and an anharmonic thermal motion description (*anis -a*) for these four atoms per molecule. Additionally, if most of their H atoms could be identified in difference maps, the aromatic H atoms were positioned geometrically and refined with U_{iso} set to $1.2U_{eq}$(C) of the parent carbon atom whereas methyl H atoms in **2h** structure were allowed as rigid groups to rotate but not tip, so as to match the electron-density maxima, with U_{iso} set to $1.5U_{eq}(C_{sp3})$. Out of the four racemic monoclinic crystals, the **3i** thiophene structure is the one which has two independently refined molecules in its corresponding asymmetric unit and both molecules present a disorder in the thiophene unit corresponding approximately to a 180° rotation about the C1-C5 bond. The respective occupancies of the two sets of atomic sites are 0.857(3)/0.143(3) and 0.757(3)/0.243(3) leading to the description of four independent conformers within the crystal. In the **2f** structure, the bromophenyl group squeezed by the two Br-phenylmethanone substituents appears also disordered with a *ca* 180° rotation along the C5–C20 bond, the occupancy factors of these two sites being refined to 0.634(2)/0.366(2). Regarding the **2i** thieno[3,4-b]thiophene structure, a solvent molecule of deuterated chloroform was trapped in the crystal packing leading to the centrosymmetric triclinic space group and its disorder over two atomic sites was responsible to the loss of diffraction quality at room temperature. *SAME, DELU and SIMU* restraints were applied to smoothen the disordered molecular parts in the last three mentioned structures.

Crystal data, data collection and structure refinement details are summarized in Table S1.

CCDC 2194328-2194331 and 2194534 (compounds **2a**, **2f**, **2h**, **2i** and **3i** respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

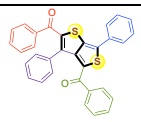
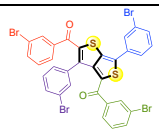
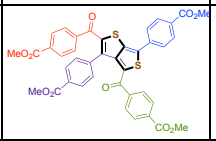
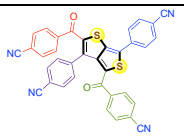
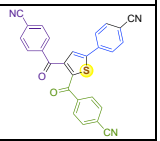
1 Rigaku OD (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, Oxfordshire, England.

2 Rigaku (2014). *CrystalClear-SM Expert 2.0 r16,* Rigaku Corporation, Tokyo, Japan.

3 Sheldrick, G. M. (2015). *Acta Crystallogr.,* **C**71, 3-8.

4 Sheldrick, G. M. (2015). *Acta Crystallogr.,* **A**71, 3-8.

Table S1 Crystal data, data collection and structure refinement details for the five thiophene derivatives.

Compound	**2a**	**2f**	**2h**	**2i**	**3i**
2D-scheme					
Chemical name	(3,6-diphenylthieno[3,4-*b*]thiophene-2,4-diyl)bis(phenylmethanone)	(3,6-bis(3-bromophenyl)thieno[3,4-*b*]thiophene-2,4-diyl)bis((3-bromophenyl)methanone)	dimethyl 4,4'-(2,4-bis(4-(methoxycarbonyl)benzoyl)thieno[3,4-*b*]thiophene-3,6-diyl)dibenzoate	4,4'-(2,4-bis(4-cyanobenzoyl) thieno[3,4-b]thiophene-3,6-diyl)dibenzonitrile, deuterated chloroform solvate	4,4'-(5-(4-cyanophenyl) thiophene-2,3-dicarbonyl) dibenzonitrile
Empirical formula	$C_{32}H_{20}O_2S_2$	$C_{32}H_{16}Br_4O_2S_2$	$C_{40}H_{28}O_{10}S_2$	$C_{36}H_{16}N_4O_2S_2{\cdot}CDCl_3$	$C_{27}H_{13}N_3O_2S$
Formula weight	500.60	816.229	732.74	721.01	443.46
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	1.54187	0.71073	0.71073
Crystal system, space group	Monoclinic, P $2_1/c$	Monoclinic, P $2_1/n$	Monoclinic, P $2_1/c$	Triclinic, P -1	Monoclinic, P $2_1/c$
Unit cell dimensions | (Å) | (°)	12.0865(6) 12.4636(6) 17.3007(8) 90 104.435(5) 90	12.9600(9) 15.6784(9) 15.0197(9) 90 110.769(7) 90	19.7293(14) 14.6779(4) 11.7861(3) 90 94.661(7) 90	11.4125(9) 12.1675(8) 12.9619(10) 77.294(6) 83.420(7) 74.234(6)	18.6659(8) 12.4099(6) 19.1062(7) 90 96.991(4) 90
Volume ($Å^3$)	2523.9(2)	2853.6(3)	3401.8(3)	1686.9(2)	4392.9(3)
Z, Calculated density (Mg/m^3)	4, 1.317	4, 1.900	4, 1.431	2, 1.418	8, 1.341
Absorption coefficient (mm^{-1})	0.239	5.818	1.951	0.436	0.177
F(000)	1040	1584	1520	732	1824
Crystal size (mm)	0.30 x 0.21 x 0.04	0.18 x 0.18 x 0.03	0.32 x 0.08 x 0.02	0.17 x 0.11 x 0.07	0.20 x 0.10 x 0.02
θ range for data collection (°)	2.387 to 27.102	2.89 to 26.02	6.755 to 63.018	2.459 to 23.012	2.291 to 25.027
Limiting indices	$-15 \le h \le 15$, $-15 \le k \le 15$, $-21 \le l \le 21$	$-17 \le h \le 17$, $-21 \le k \le 21$, $-19 \le l \le 19$	$-22 \le h \le 22$, $-16 \le k \le 11$, $-13 \le l \le 13$	$-12 \le h \le 12$, $-13 \le k \le 13$, $-14 \le l \le 14$	$-22 \le h \le 22$, $-13 \le k \le 14$, $-22 \le l \le 22$
Reflections collected / unique [R(int)	34392 / 5513 0.0360	52554 / 5603 0.0554	27560 / 5427 0.0737	21940 / 4707 0.060	48311 / 7755 0.045
Completeness to θ_{full} (%)	99.9	99.7	98.4	99.7	99.8
Absorption correction	& Gaussian	Semi-empirical from equivalents & Gaussian	-	& Gaussian	& Gaussian
Max. and min. transmission	1.000 and 0.406	1.000 and 0.321	1.000 and 0.677	1.000 and 0.584	1.000 and 0.723
Refinement method	Full-matrix least-squares on F^2 *Anharmonic refinement for the Br atoms*				
Data / restraints / parameters	5513 / 0 / 325	5603 / 260 / 500	5422 / 0 / 473	4706 / 54 / 470	7751 / 282 / 681
Goodness-of-fit on F^2	1.014	1.0836	1.007	1.110	1.025
Final R indices [$I>2\sigma(I)$] R1, wR2	0.0434, 0.1075	0.0372, 0.0898	0.0674, 0.1479	0.0753, 0.1754	0.0500, 0.1350
R indices (all data) R1, wR2	0.0588, 0.1166	0.0506, 0.0961	0.1313, 0.2094	0.1254, 0.2196	0.0853, 0.1546
Largest Δ peak and hole ($e.Å^{-3}$)	0.389 and -0.307	1.303 and -0.736	0.363 and -0.538	0.739 and -0.417	0.354 and -0.154
CCDC deposit number	2194328	2194329	2194330	2194331	2194534

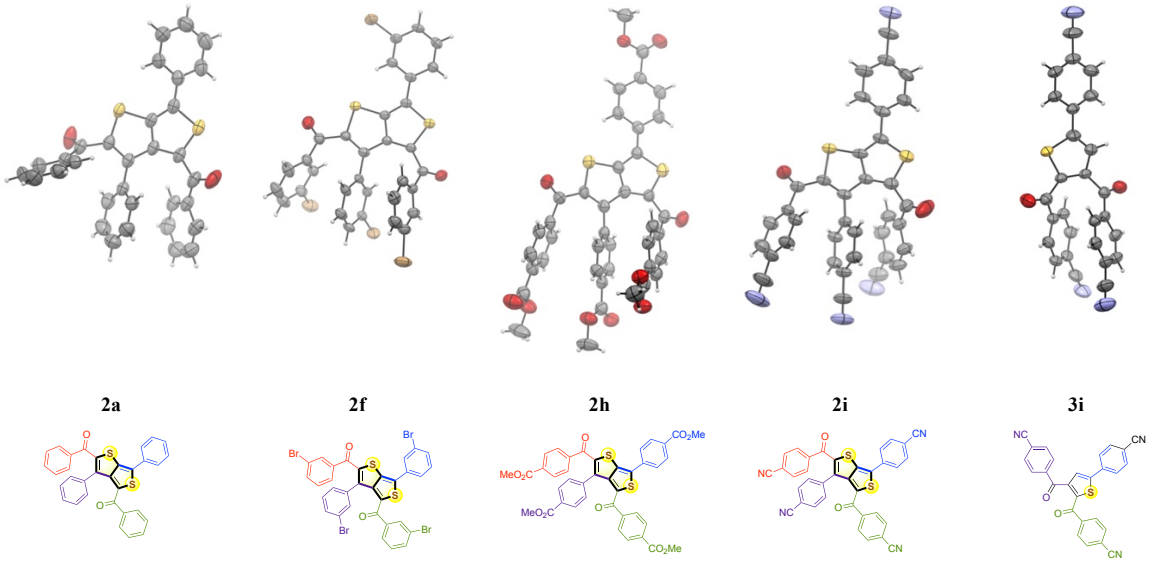


Figure 1 Ortep views of the molecular structures. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms with an arbitrary radius size. From left to right **2a, 2f**, **2h**, **2i** and **3i**. For clarity, only major conformers are shown for the **2f** and **2i** derivatives and the disordered solvent is omitted in **2i**.

Yellow plate-like single salt crystals of **4c**, alias 1,4-diazabicyclo[2.2.2]octan-1-ium 2-(4-isopropylphenyl)-2-oxoethanedithioate were obtained in methanol and one of dimension 0.29 x 0.22 x 0.02 mm served for X-ray diffraction analysis at 293(2) K using the Rigaku Mo microsource.

The crystal was found to be twinned by a 180° rotation about the direct *c* crystallographic axis, data were processed by *Crysalispro* accordingly, and the structure solved by Intrinsic Phasing methods and refined against a hklf 5 formatted datafile, led to a twin ratio equal to 0.628(1):0.372(1). Main statistics related to the crystal structure determination of **4c** are as follows : Crystal Data for $[C_{11}H_{11}OS_2]^-$, $[C_6H_{13}N_2]^+$ (M =336.50 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 14.9171(10) Å, b = 11.5193(10) Å, c = 10.7037(8) Å, β = 98.827(7)°, V = 1817.5(2) $Å^3$, Z = 4, T = 293(2) K, μ(Mo Kα) = 0.296 mm^{-1}, D_{calc} = 1.230 g/cm^3, 7441 reflections measured (4.488° ≤ 2θ ≤ 53.464°), 7441 unique (Rint = ?, Rsigma = 0.0247) which were used in all calculations. The final R1 was 0.0415 (I > 2σ(I)) and wR2 was 0.1173 (all data). CCDC 2195876 contains the supplementary crystallographic data for compound **4c**.

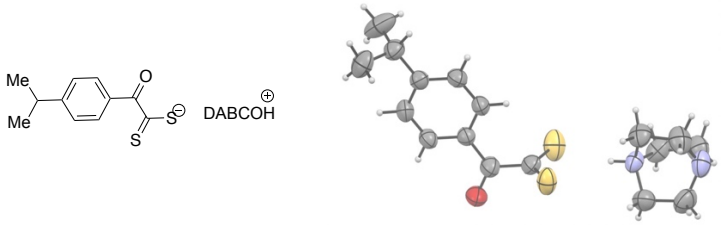
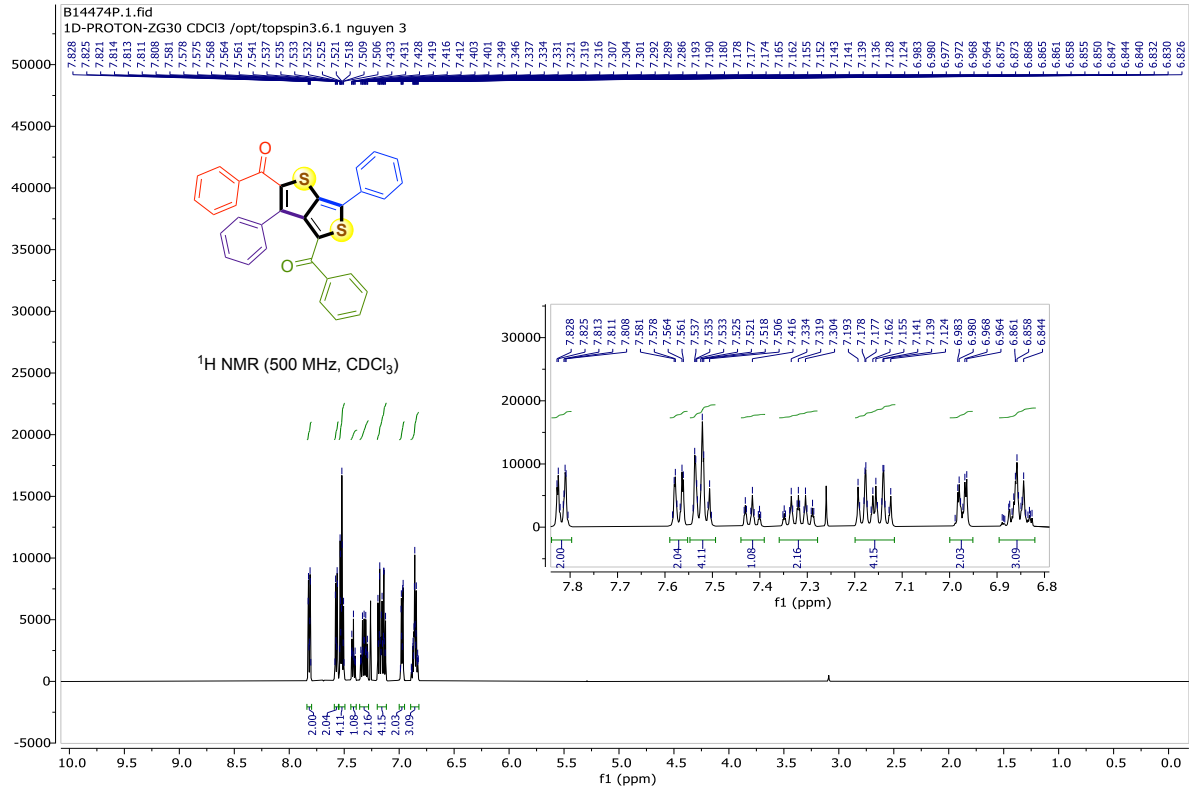
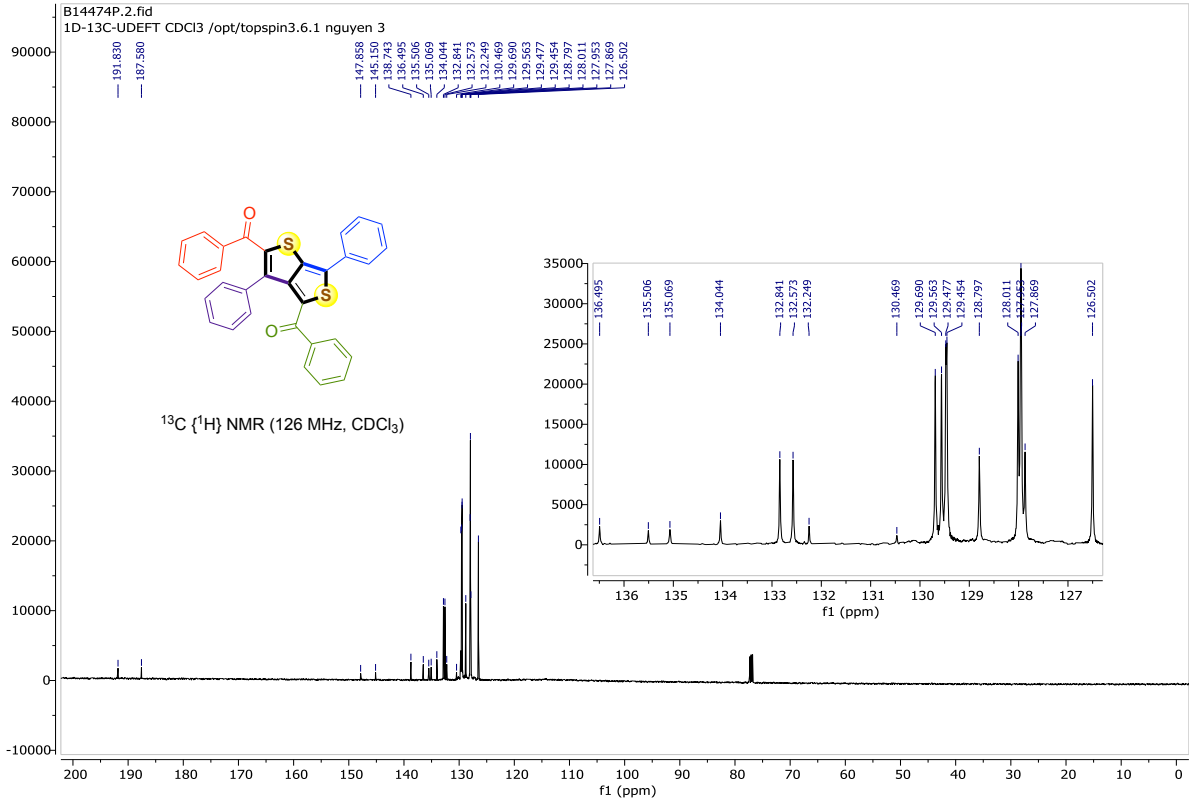


Figure S2. Ortep view for **4c**. Disorder at the level of ethanedithioate group is not shown, only the major conformer (60%) for clarity.

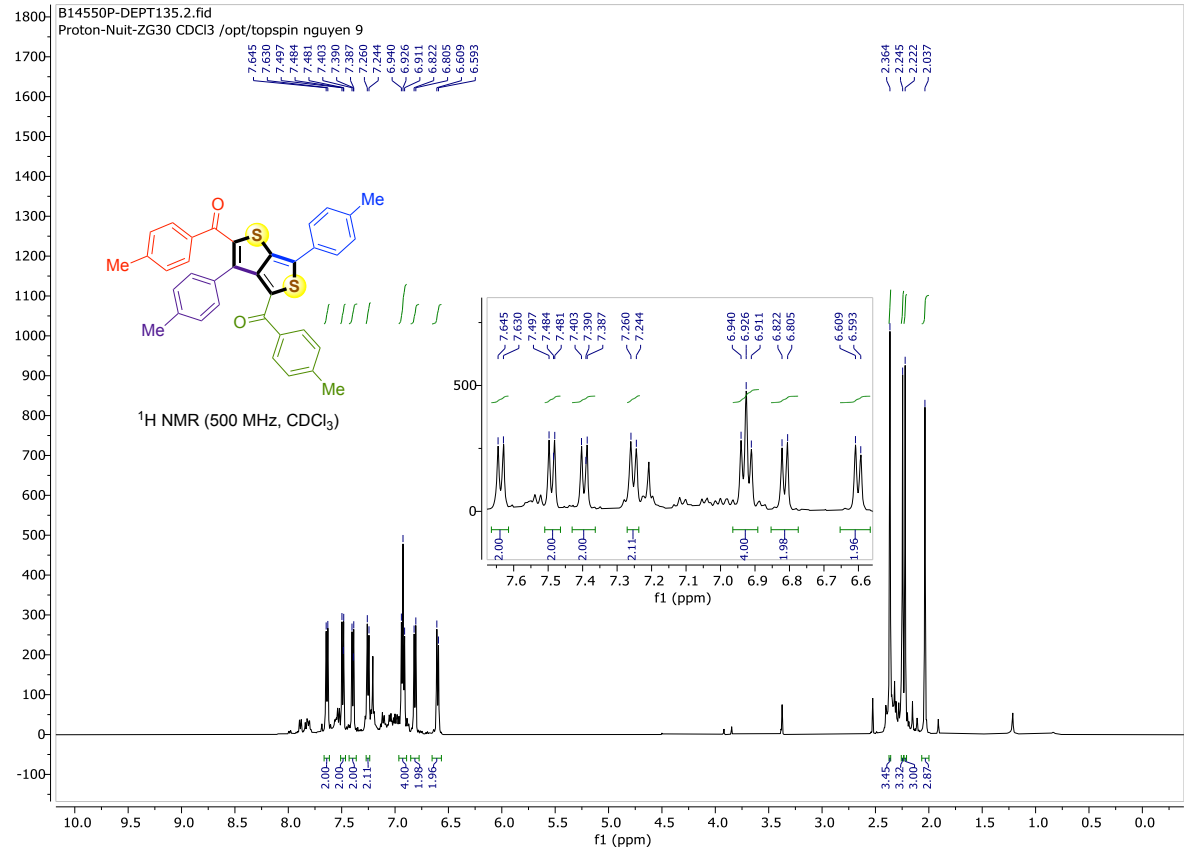
Copies of ^{1}H and ^{13}C NMR spectra

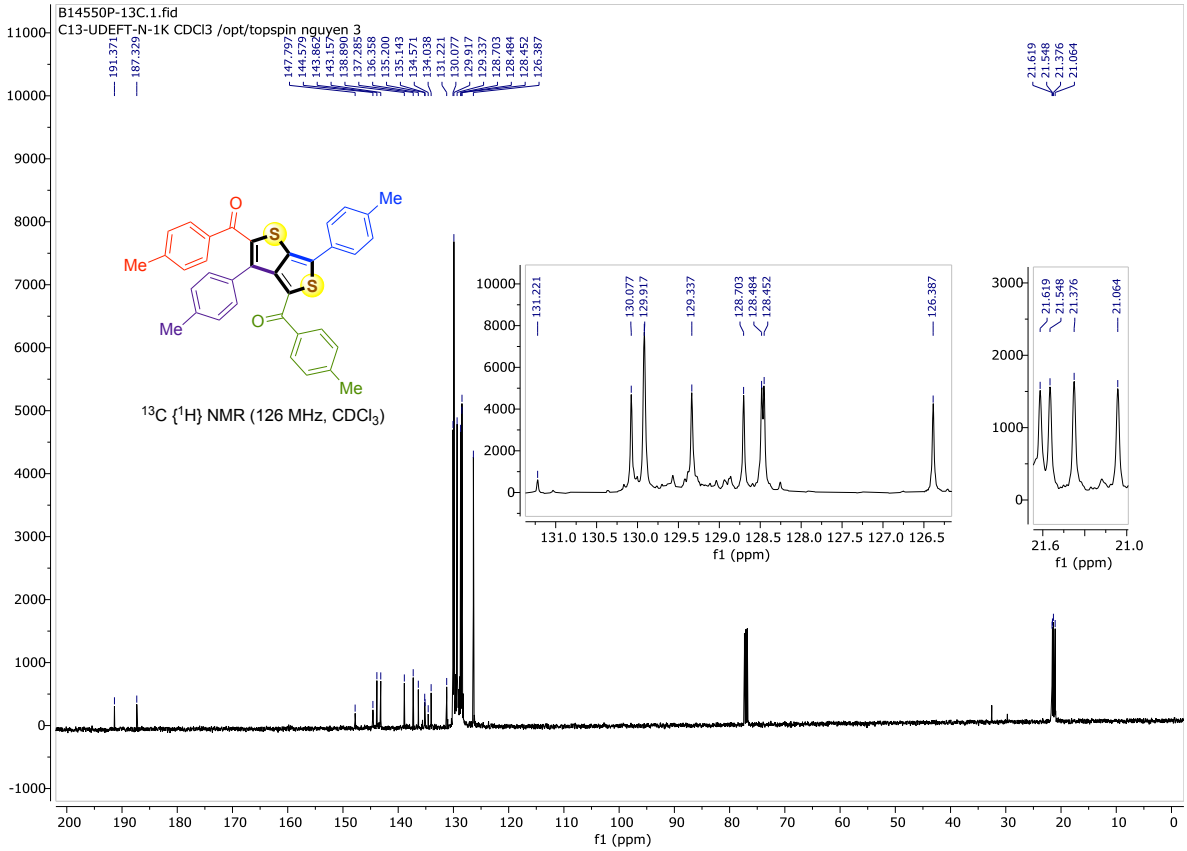
(3,6-Diphenylthieno[3,4-*b*]thiophene-2,4-diyl)bis(phenylmethanone) (2a)



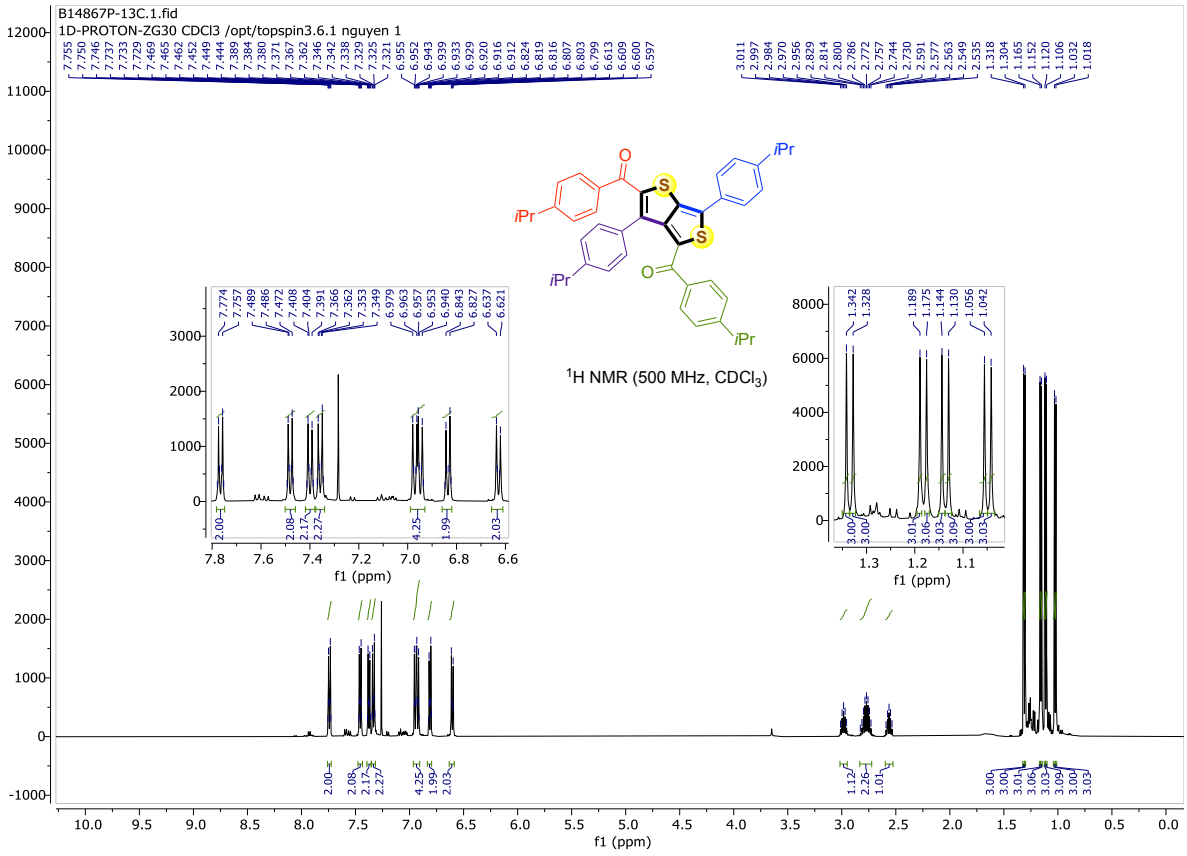


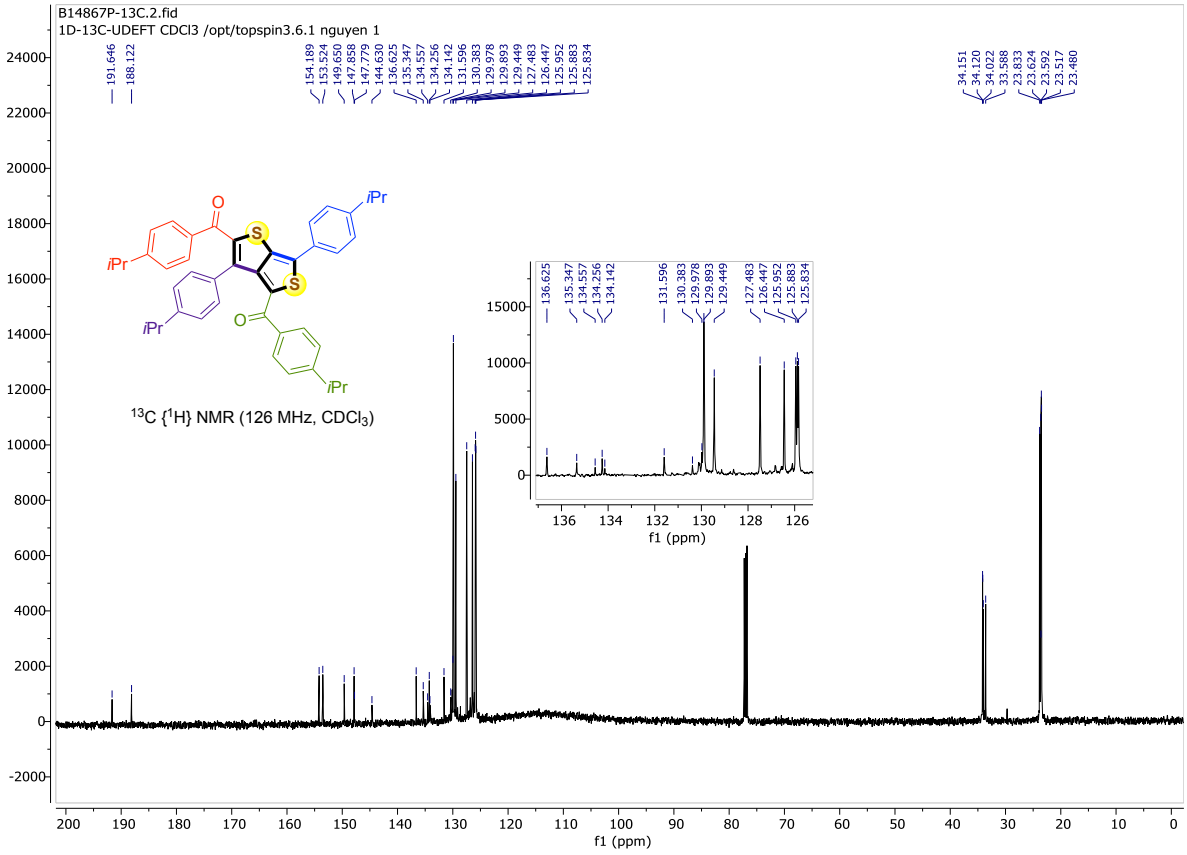
(3,6-Di-p-tolylthieno[3,4-b]thiophene-2,4-diyl)bis(p-tolylmethanone) (2b)





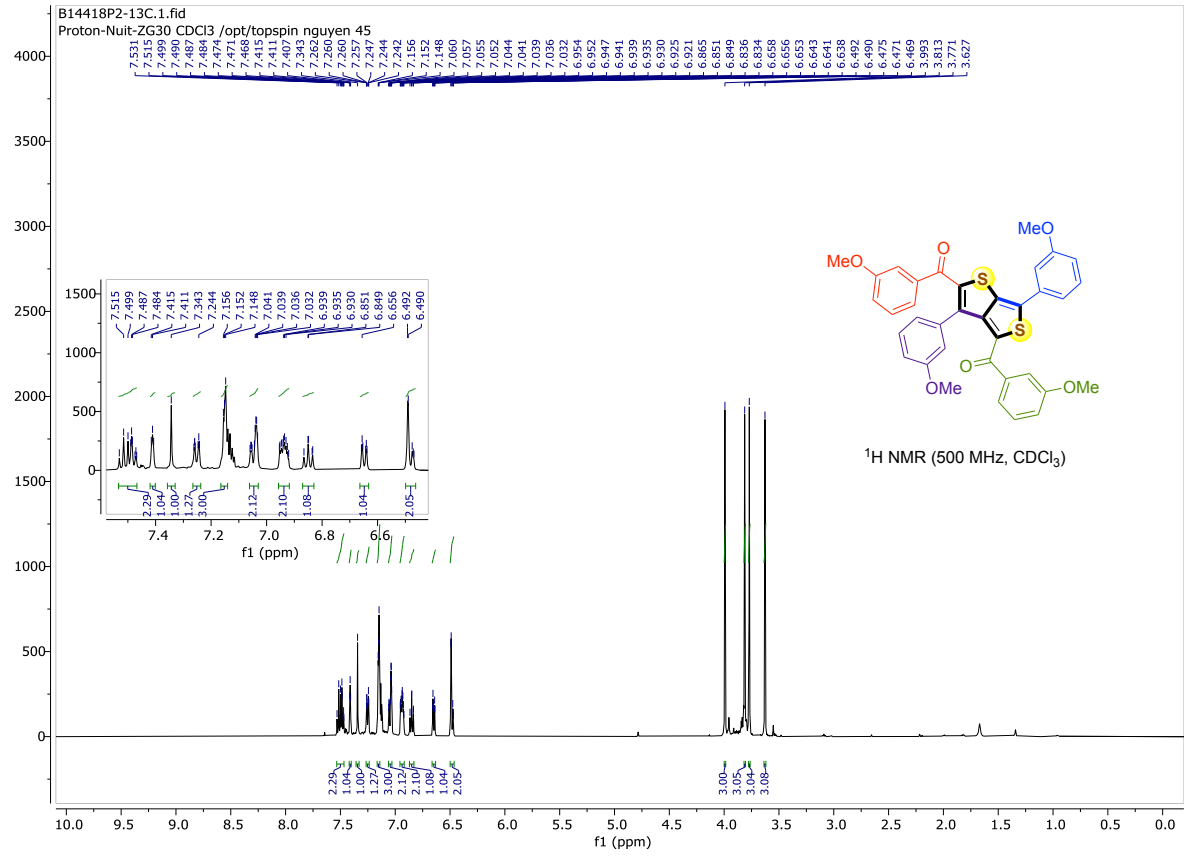
(3,6-Bis(4-isopropylphenyl)thieno[3,4-*b*]thiophene-2,4-diyl)bis((4-isopropylphenyl)methanone) (2c)

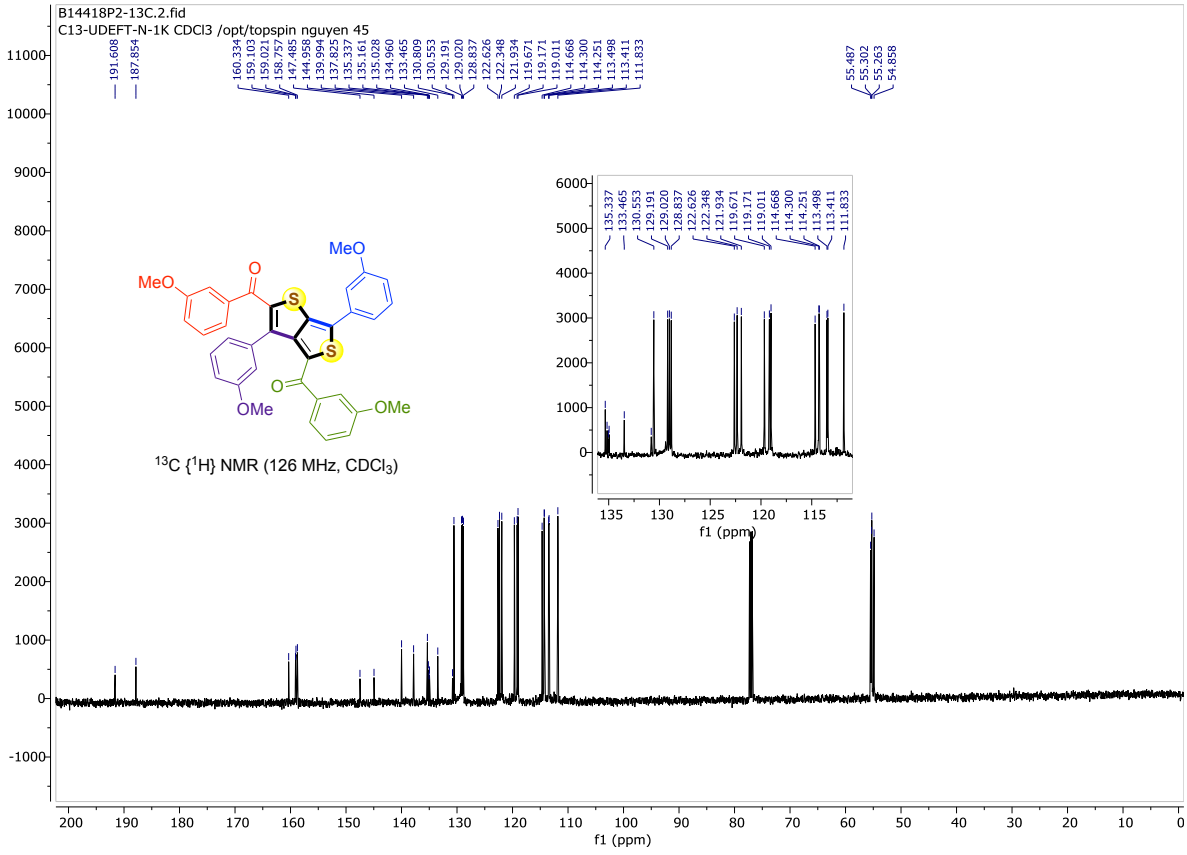




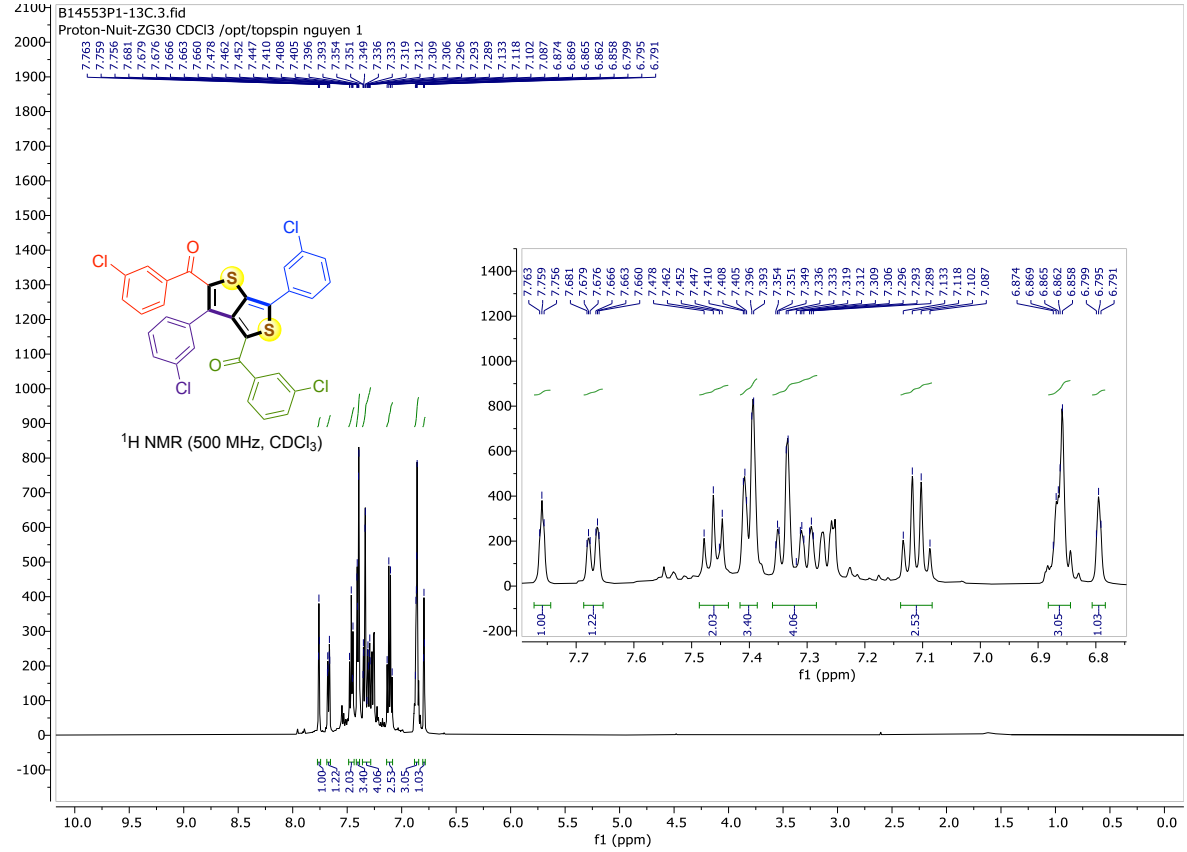
(3,6-Bis(3-methoxyphenyl)thieno[3,4-*b*]thiophene-2,4-diyl)bis((3-methoxyphenyl)methanone)

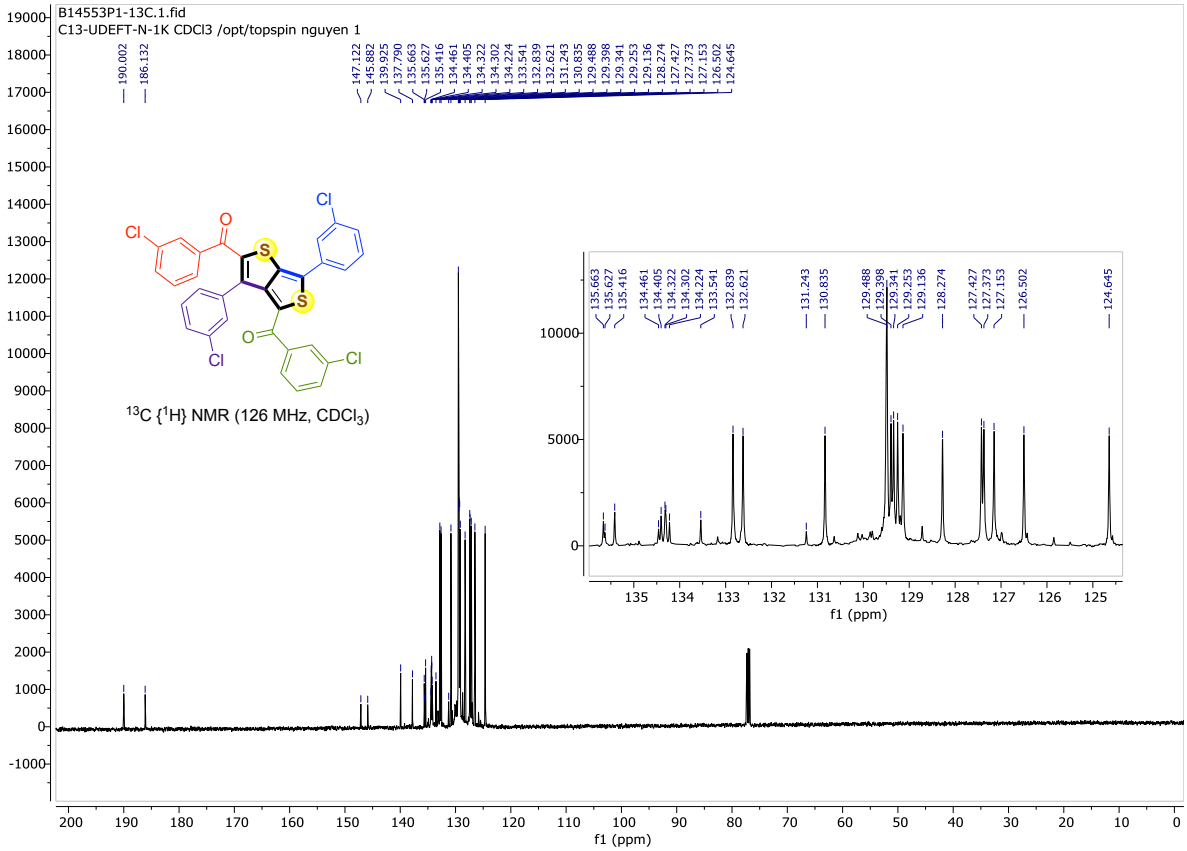
(2d)



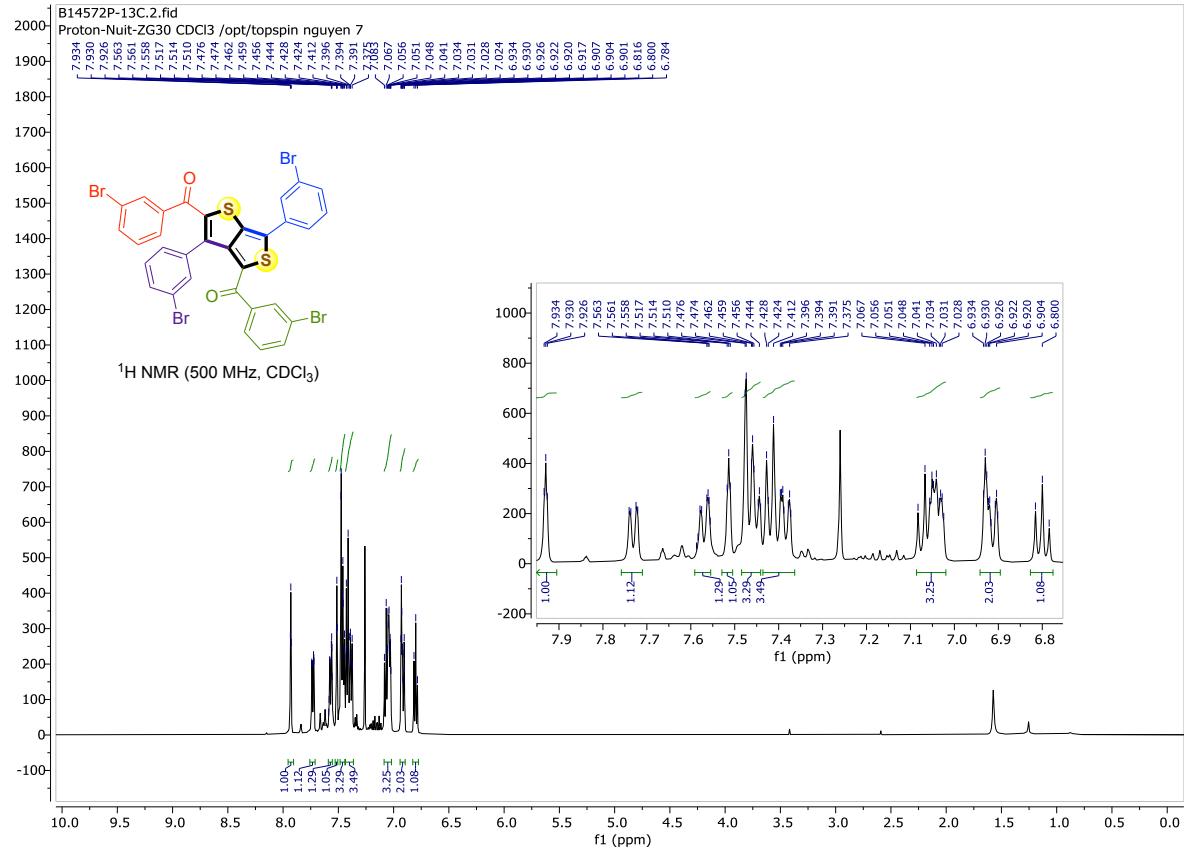


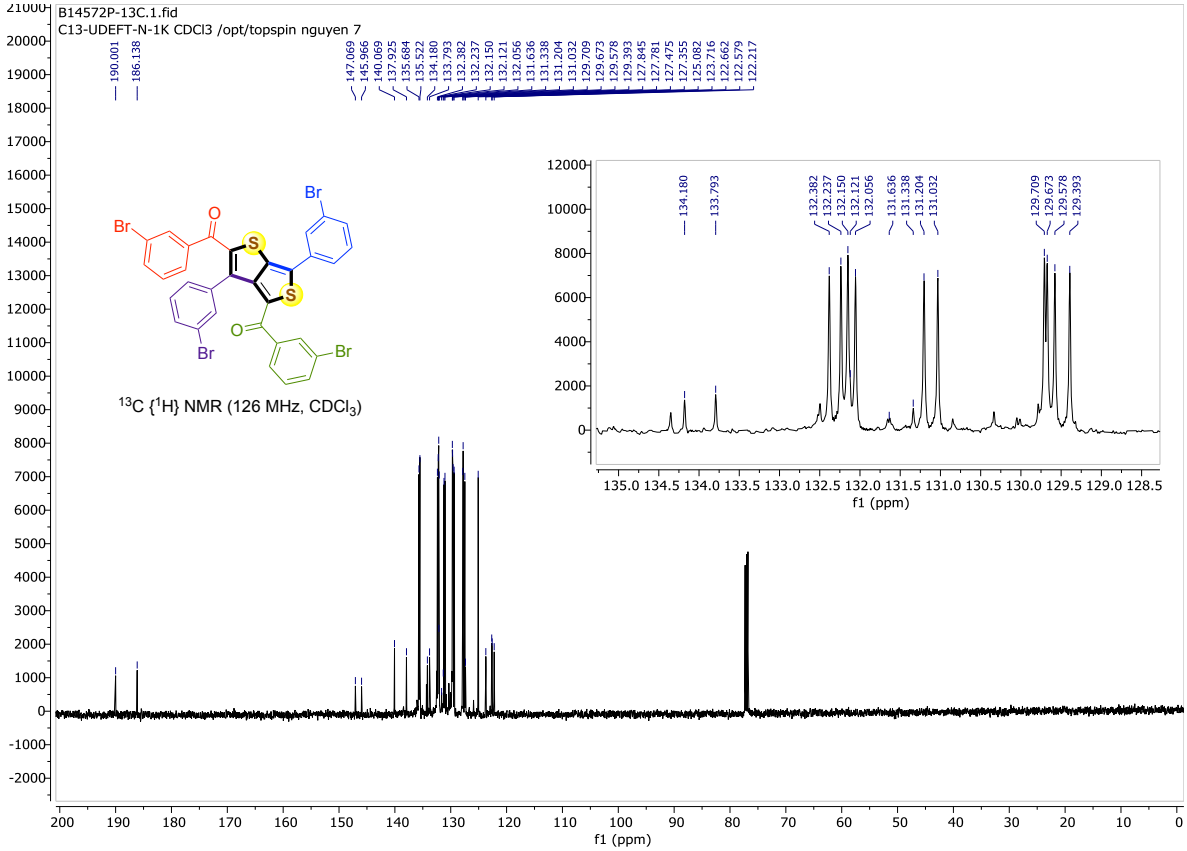
(3,6-Bis(3-chlorophenyl)thieno[3,4-*b*]thiophene-2,4-diyl)bis((3-chlorophenyl)methanone) (2e)



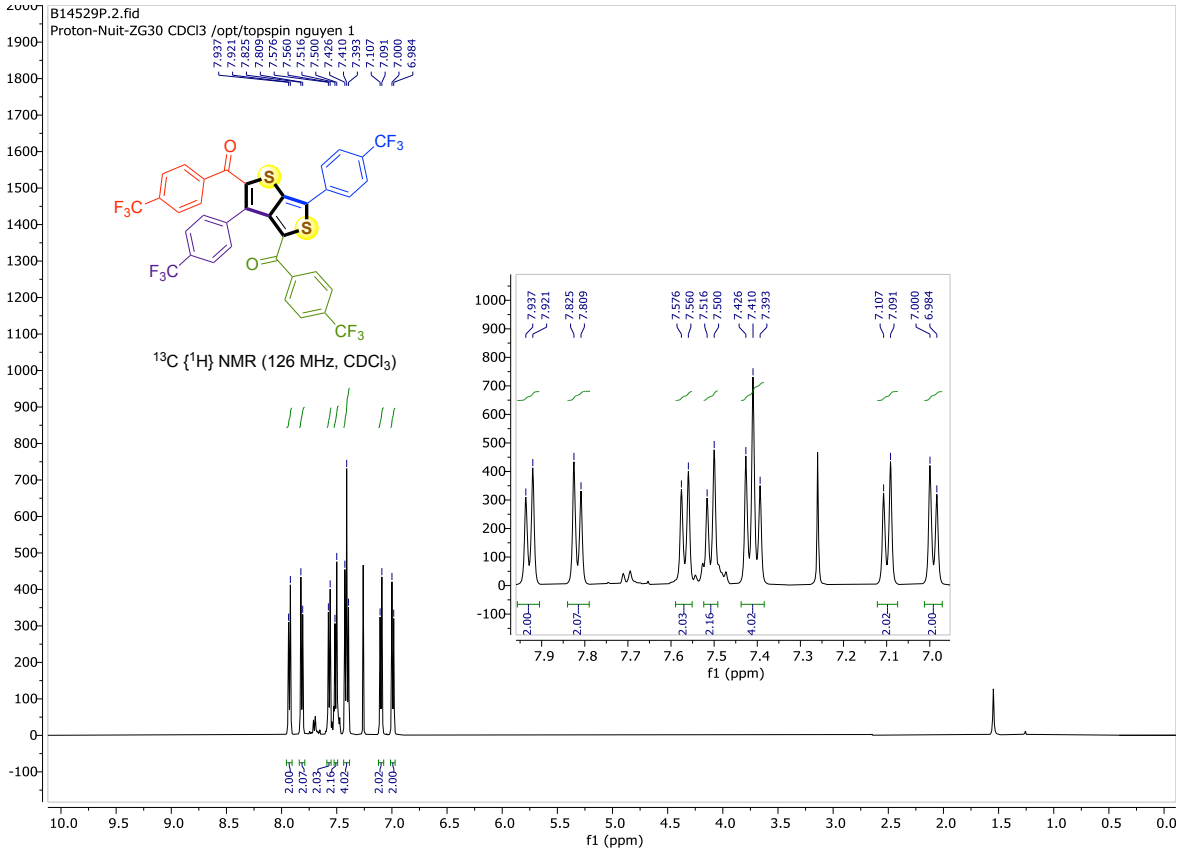


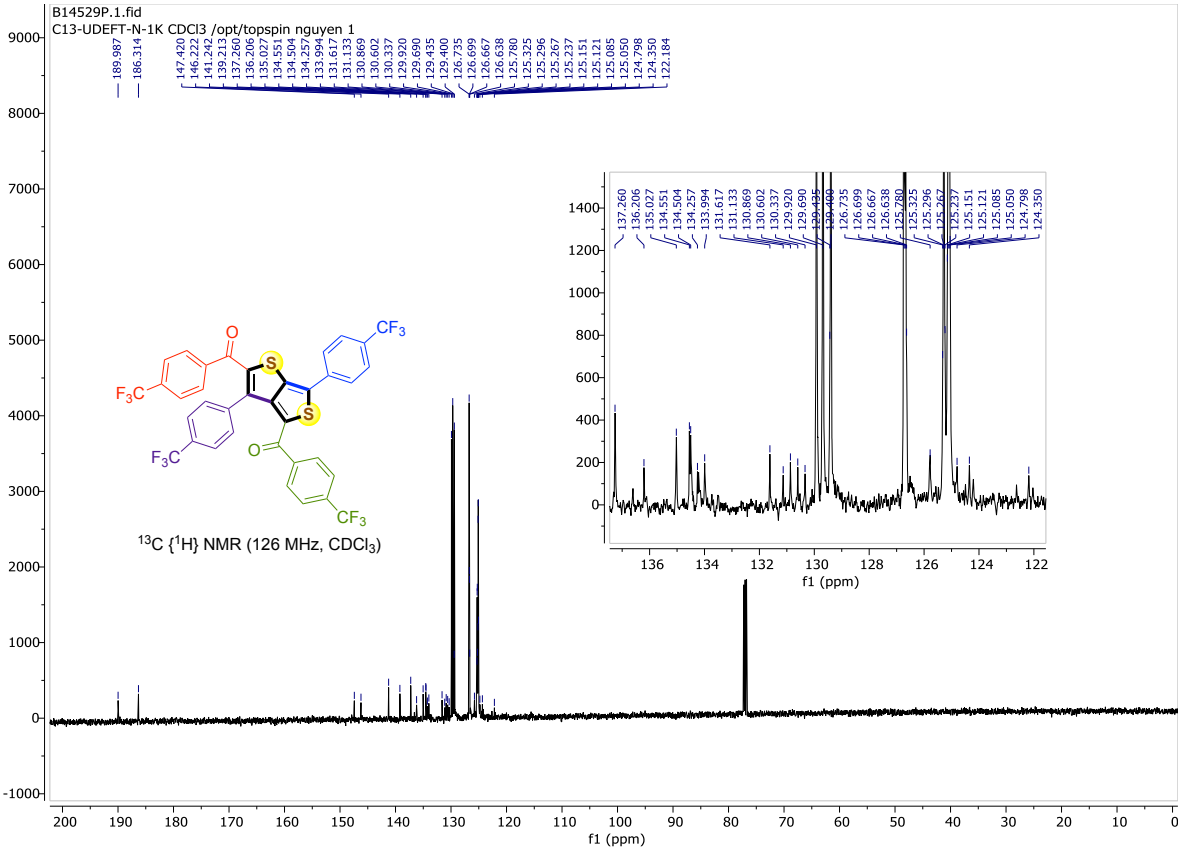
(3,6-Bis(3-bromophenyl)thieno[3,4-*b*]thiophene-2,4-diyl)bis((3-bromophenyl)methanone) (2f)



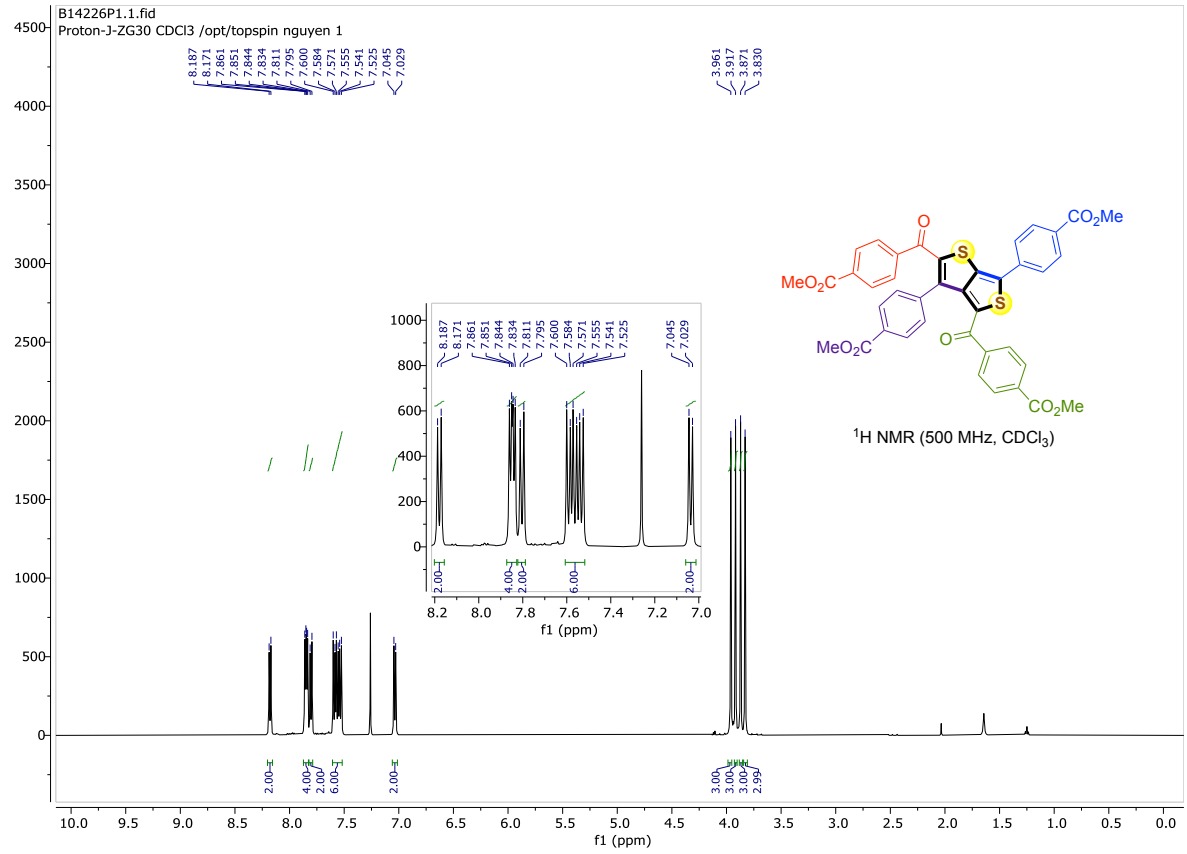


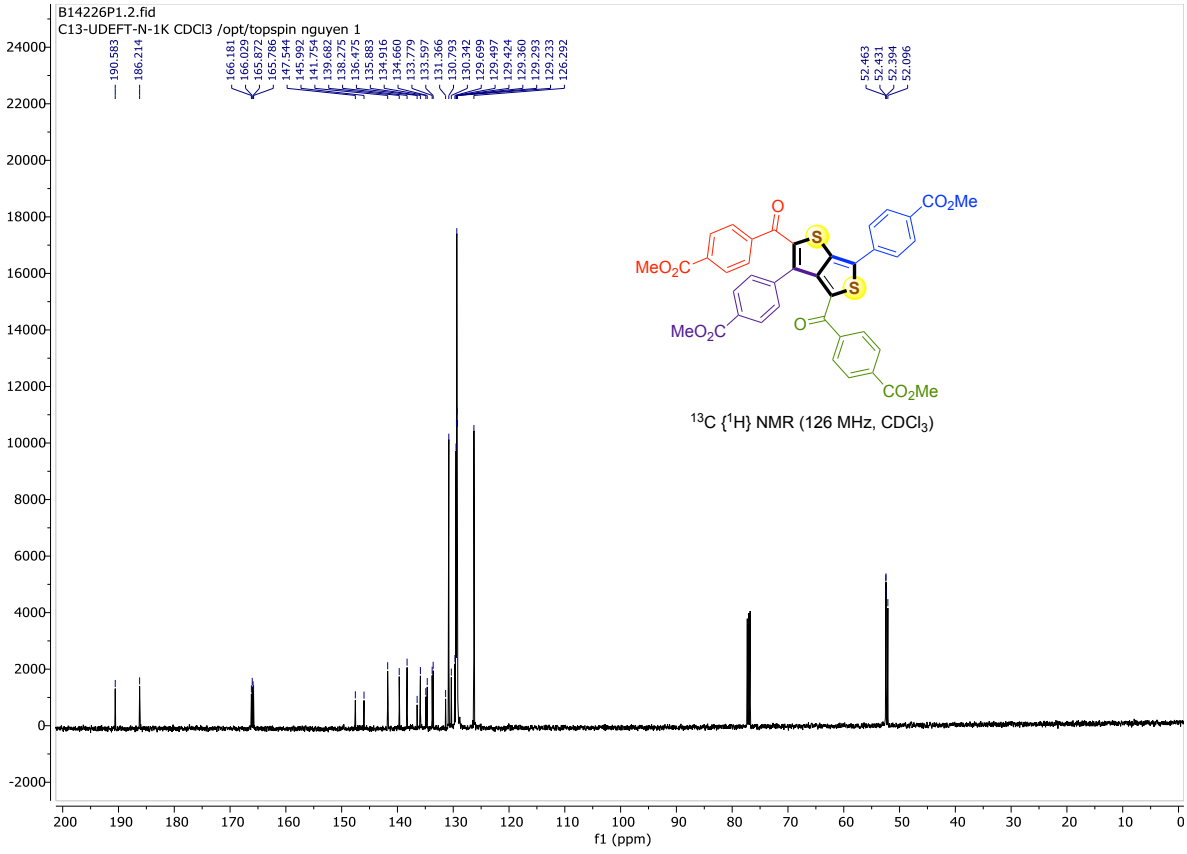
(3,6-Bis(4-(trifluoromethyl)phenyl)thieno[3,4-*b*]thiophene-2,4-diyl)bis((4-(trifluoromethyl)phenyl)methanone) (2g)



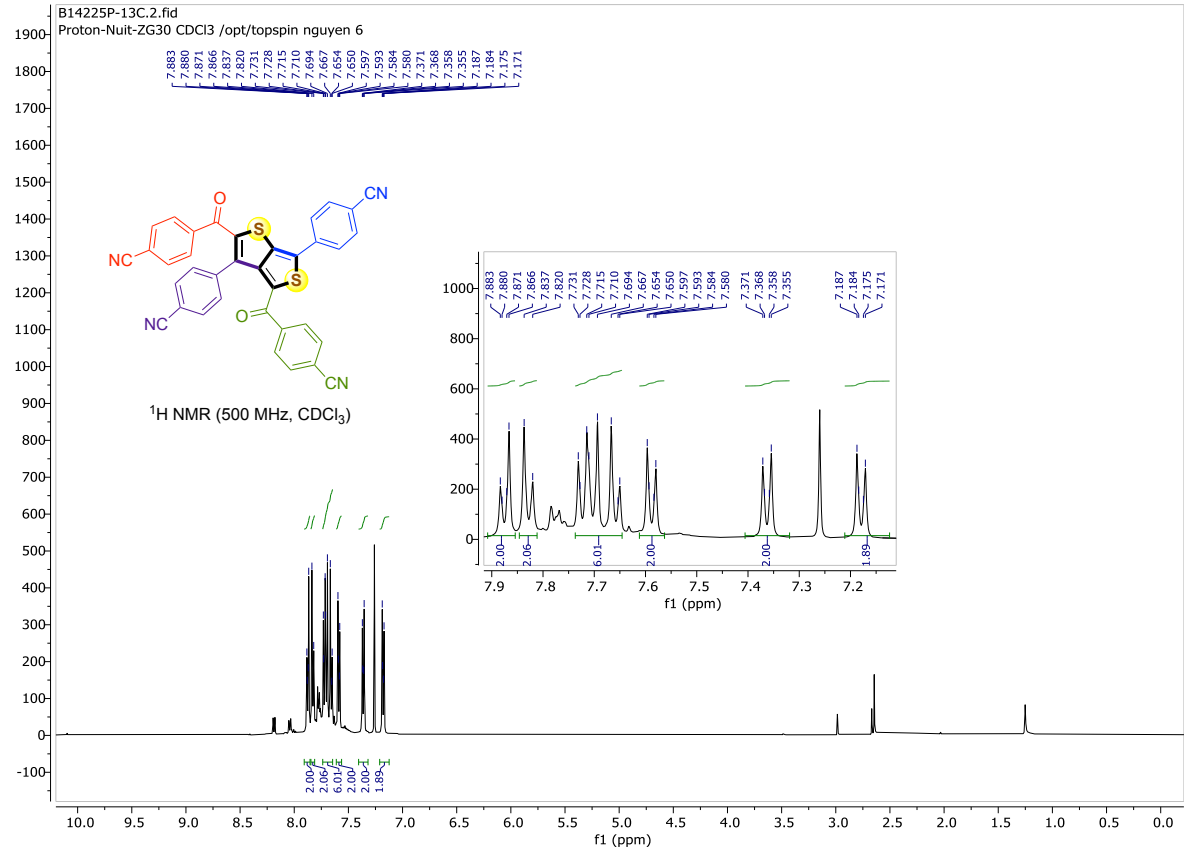


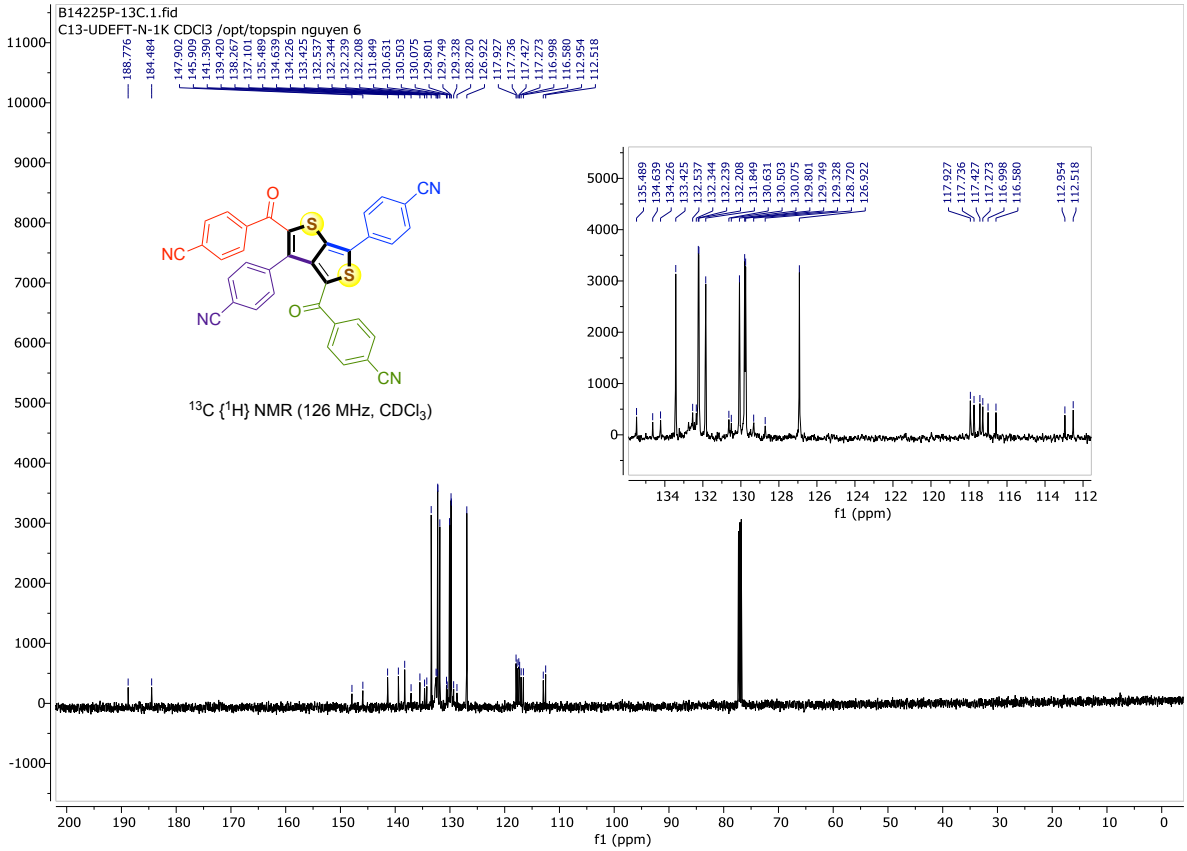
Dimethyl 4,4'-(2,4-bis(4-(methoxycarbonyl)benzoyl)thieno[3,4-*b*]thiophene-3,6-diyl)dibenzoate (2h)



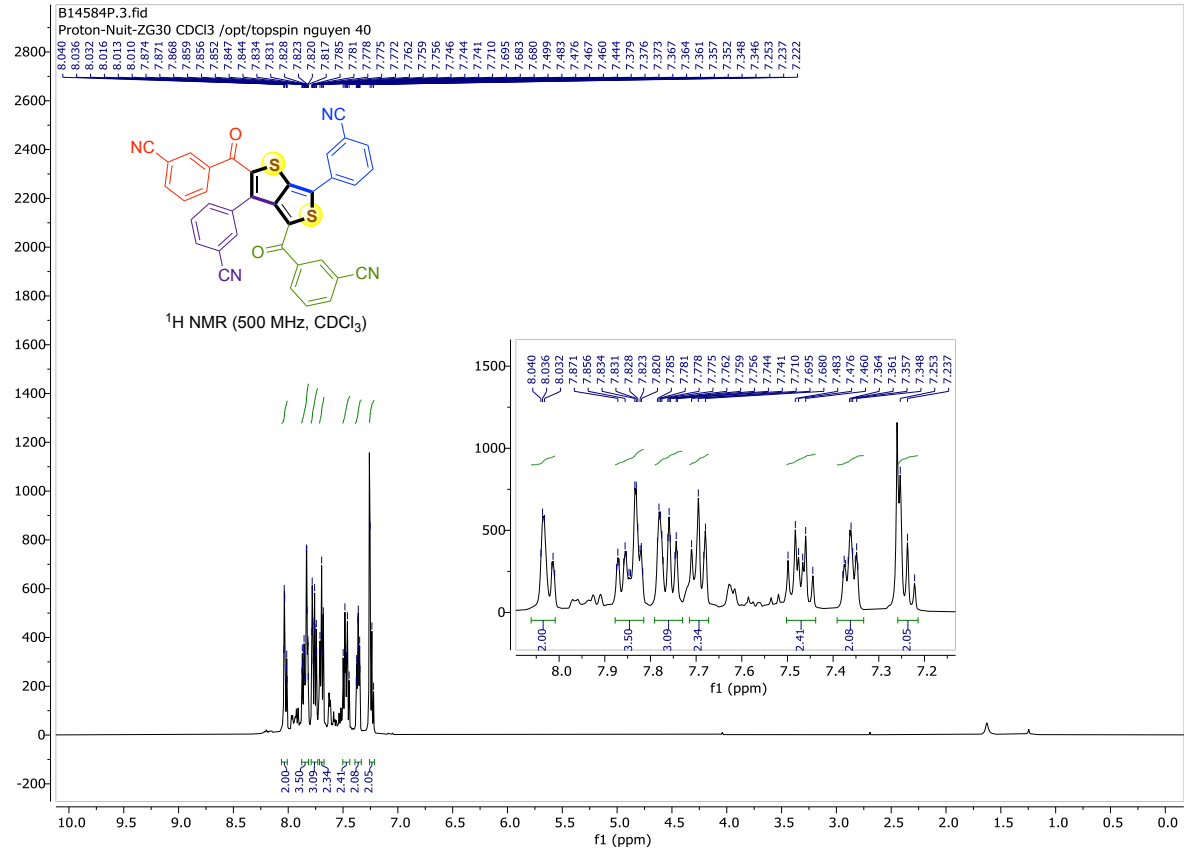


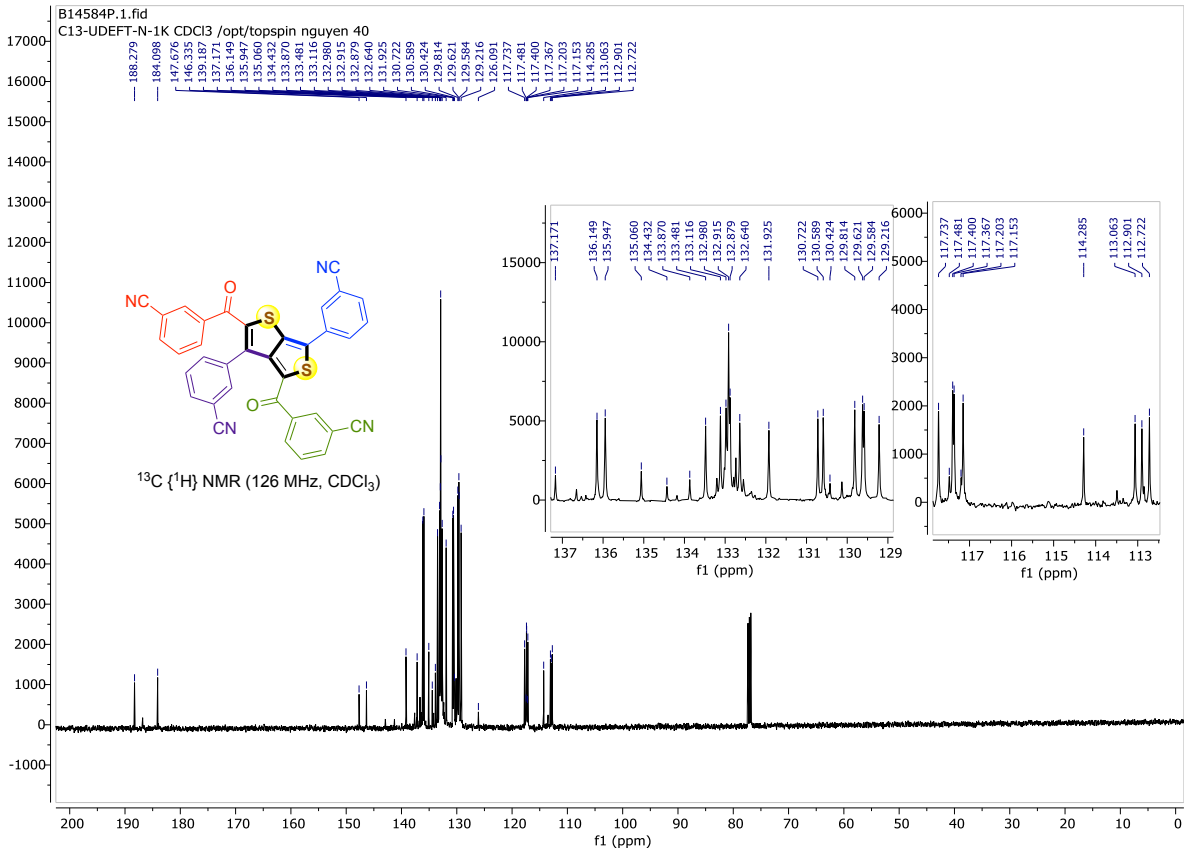
4,4'-(2,4-Bis(4-cyanobenzoyl)thieno[3,4-*b*]thiophene-3,6-diyl)dibenzonitrile (2i)



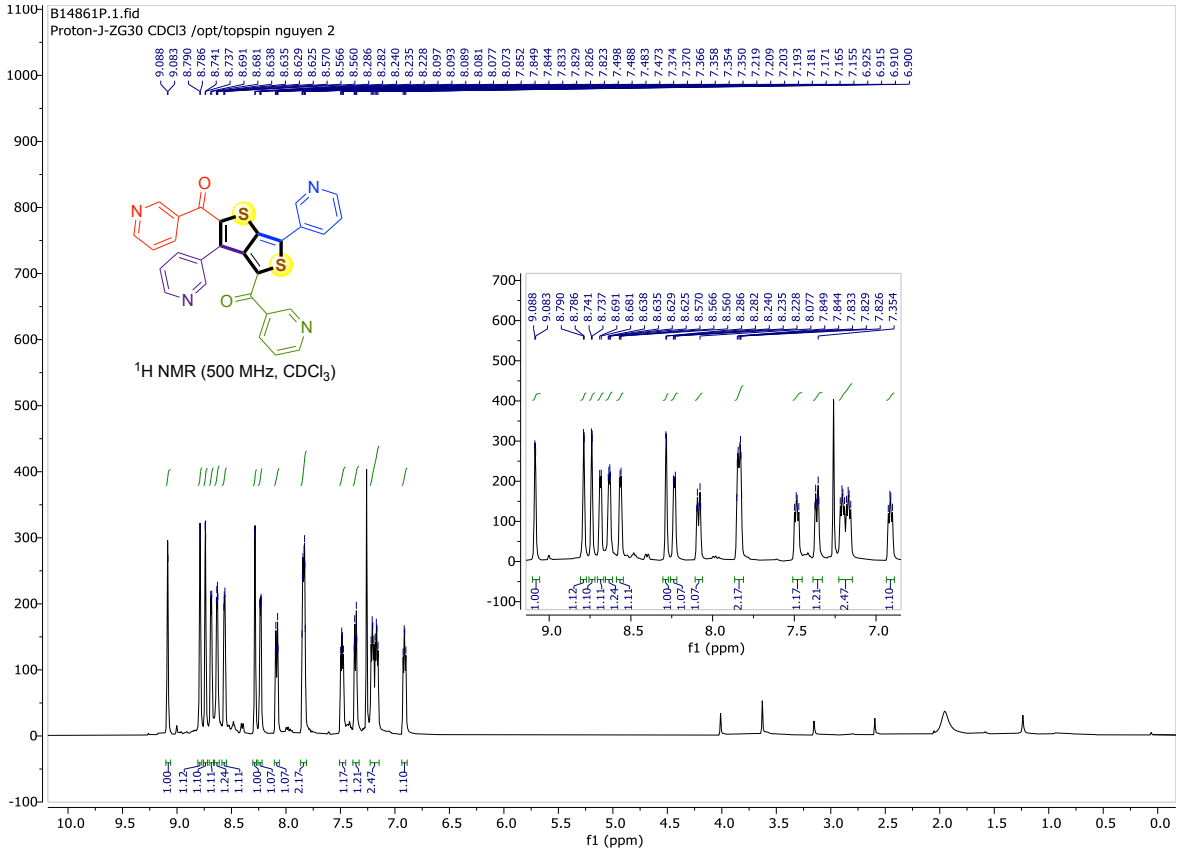


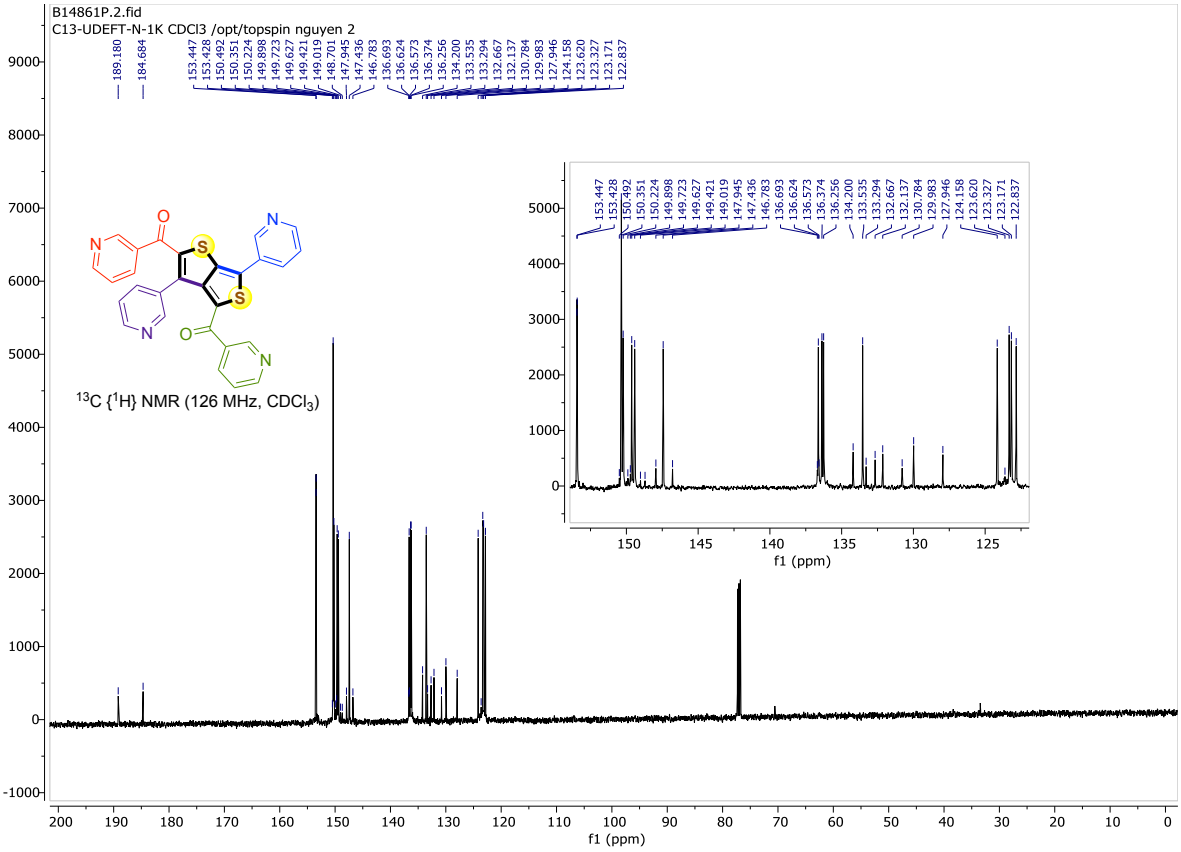
3,3'-(2,4-Bis(3-cyanobenzoyl)thieno[3,4-*b*]thiophene-3,6-diyl)dibenzonitrile (2j)





(3,6-Di(pyridin-3-yl)thieno[3,4-*b*]thiophene-2,4-diyl)bis(pyridin-3-ylmethanone) (2k)





(3,6-Di(pyridin-4-yl)thieno[3,4-b]thiophene-2,4-diyl)bis(pyridin-4-ylmethanone) (2l)