Supporting Information for

Organic and Biomolecular Chemistry

The Effect of Donor-modification in Organic Light-harvesting Motifs: Triphenylamine Donors Appended with Polymerisable Thienyl Subunits

by

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General Considerations

All reagents were purchased from Aldrich except $Pd(PPh_3)_4$ (Pressure Chemical Co., Pittsburg, PA). Purification by column chromatography was carried out using silica (Silicycle: ultrapure flash silica). Analytical thin-layer chromatography was performed on aluminum-backed sheets precoated with silica 60 F254 adsorbent (0.25 mm thick; Silicycle) and visualized under UV light. IR data was collected in KBr using a Perkin Elmer Spectrum 1 Fourier Transform Infrared spectrophotometer. Melting points were determined using a Fisher-Johns Melting Point Apparatus. Cyclic voltammetry data was collected using a MetrOhm μ-Autolab Type III potentiostat/galvanostat and UV-Vis absorption profiles were collected using an Agilent Cary 5000 UV-vis-NIR spectrophotometer. Routine ^{1}H, $^{13}C\{^{1}H\}$, NMR spectra were recorded at 400 and 100 MHz, respectively, on a Bruker AV 400 instrument at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm) from low to high field and referenced to a residual nondeuterated solvent ($CHCl_3$) for ^{1}H and ^{13}C nuclei. Standard abbreviations indicating multiplicity are used as follows: s = singlet; d = doublet; m = multiplet; br = broad. DFT calculations were performed using Gaussian 09M version C. 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (***A***)[1], 2-(5-(1,3-dioxolan-2-yl)thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (***C***)[2], ethyl (2,5-dibromothiophene-3-yl)methyl(methyl)phosphinate (***D***)[3], and compounds ***1***[4], ***2a***[5], ***2b***[6] and ***9a***[7] and ***9b***[8] were prepared as previously reported.

Cell Fabrication. Photoanodes were fabricated by screen-printing methods on fluorine-doped tin-oxide [FTO; Hartford Glass; TEC8 (8 Ω cm^{-2})] using 2 layers of 18NR-T (20 nm particles, 12 μm thick), and 1 layer of WER4-O (100 nm particles, 6 μm thick) for a total thickness of 18 μm. The FTO glass was cleaned by sonication in a detergent solution for 30 min followed by subsequent rinsing with deionized water and abs. EtOH and dried under a stream of air. The TiO_2 pastes were dried between layers in an oven at 120 °C for 25 min. Once the desired thickness had been achieved, the anode was fired to 450 °C for 20 min in an ambient atmosphere and left to room temperature. The TiO_2 substrates were treated with $TiCl_4$(aq) (0.05 M) at 70 °C for 30 min and subsequently rinsed with H_2O and then dried prior to heating. The electrodes were heated to 450 °C for 20 min in an ambient atmosphere and left to cool to 80 °C prior to immersing into a $CHCl_3$ solution containing the dye (0.25 mM) and chenodeoxycholic acid (2.5 mM) for 16 h. The stained films were then rinsed with copious amounts of $CHCl_3$ and dried. The cells were fabricated using Pt-coated counter-electrode [FTO TEC-15 (15 Ω cm^{-2})] and sealed with a 30 μm Surlyn (Dupont) gasket by resistive heating. The **Z1137** electrolyte used for this study was I_3^-/I^- [1.0 M 1,3- dimethylimidazolium iodide (DMII), 60 mM I_2, 0.5 M *tert*-butylpyridine, 0.05 M NaI and 0.1 M GuNCS in a mixed solvent system of acetonitrile and valeronitrile (85:15, *v/v*)]. The electrolyte was introduced into the two-sandwiched electrodes via vacuum backfilling through a hole in the counter electrode. In the cases where the I_3^-/I^- electrolyte was used, the hole was sealed with an aluminum-backed Bynel® foil (Dyesol™). The active area of the TiO_2 was 0.26 cm^2. Silver bus bars were added to all cells after sealing. Dyes devices were made and tested in triplicate with standard deviations in device efficiency not exceeding +/- 0.2%

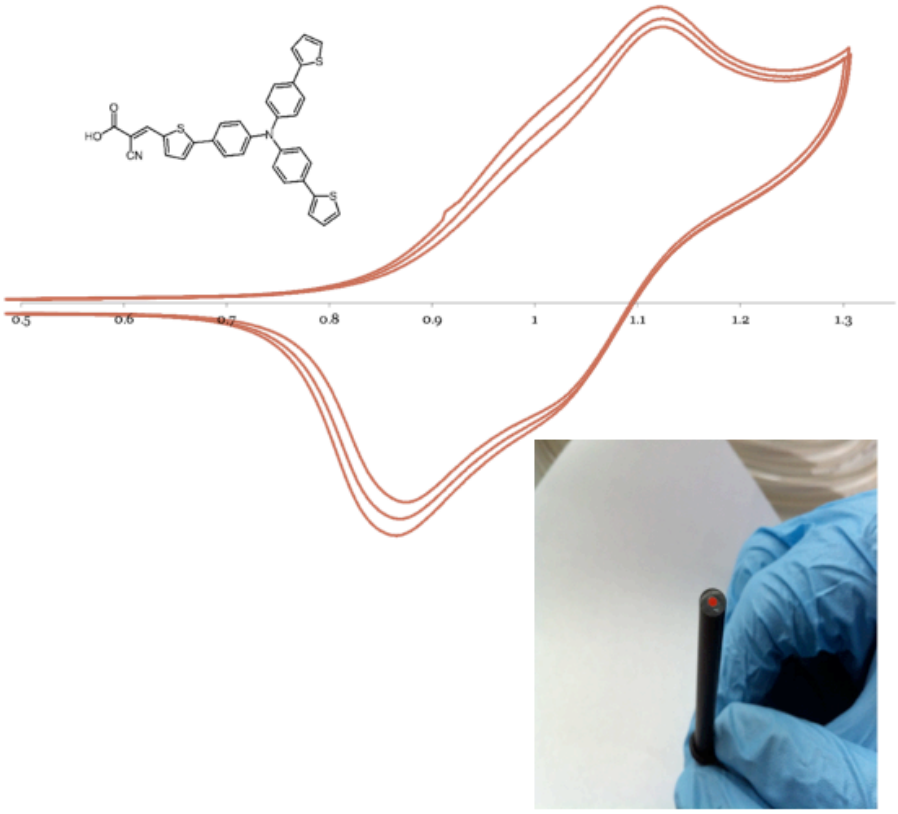


Figure S1. *Film formation at the electrode surface. Cyclic voltammetry scans 10, 11 and 12 for dye* ***4b****.*

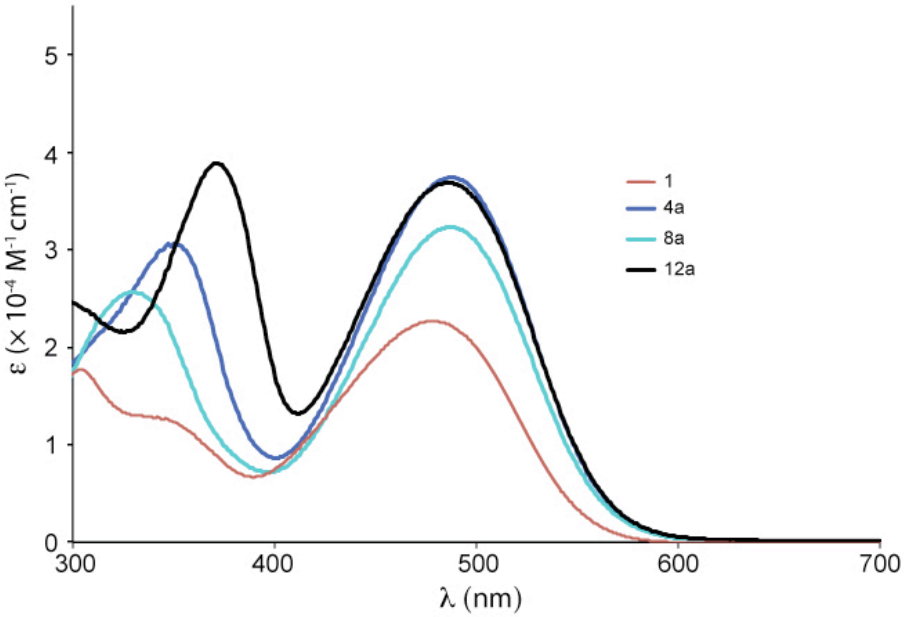
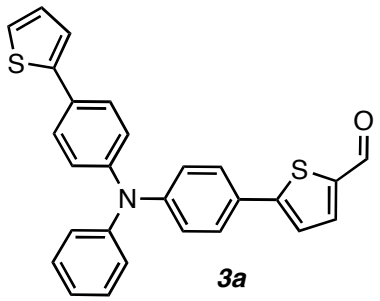


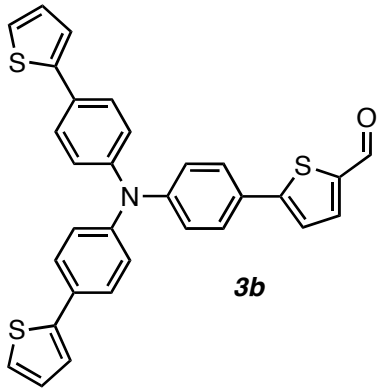
Figure S2. *UV-vis spectra in DCM for the mono-substituted TPA dyes* ***4a, 8a, 12b*** *and benchmark dye* ***1****.*

Synthetic Procedures



3a

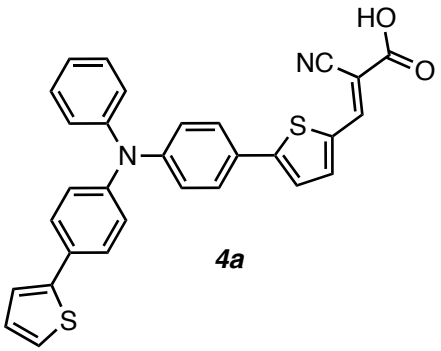
Synthesis of *3a*: Under an atmosphere of N_2, ***2a*** (160 mg, 0.37 mmol) and ***A*** (89 mg, 0.42 mmol) were dissolved in 55 mL of a mixture of THF:H_2O 9:1 and the solution was sparged 10 min with N_2. K_2CO_3 (254 mg, 1.84 mmol) and $Pd(PPh_3)_4$ (43 mg, 0.037 mmol) were added and the mixture was refluxed 12 h. After being cooled to room temperature, 50 mL of H_2O were added and the organic layer was separated. The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organic layers were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using CH_2Cl_2 as the eluent, affording the desired product as a yellow solid (110 mg, 68 %). Mp 123-124 °C; IR (KBr, cm^{-1}) 1664. ^1H NMR (400 MHz, acetone-d_6): δ = 9.91 (m, 1H), 7.94 (d, 1H, $^3J_{HH}$ = 3.9 Hz), 7.72 (d, 2H, $^3J_{HH}$ = 8.8 Hz), 7.65 (d, 2H, $^3J_{HH}$ = 8.6 Hz), 7.58 (d, 1H), 7.40 (m, 4H), 7.15 (m, 8H). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ = 183.7, 154.1, 149.7, 147.7, 147.3, 144.5, 142.7, 139.3, 130.6, 129.1, 128.3, 128.2, 128.1, 127.7, 127.6, 126.3, 126.1, 126.0, 125.8, 125.5, 125.2, 124.5, 123.8, 123.6. HRMS (DART): *m/z* 438.0994 $[(M+H)^+]$, calcd for $^{12}C_{27}{}^1H_{20}{}^{14}N^{16}O^{32}S_2{}^+$: *m/z* 438.0986.



3b

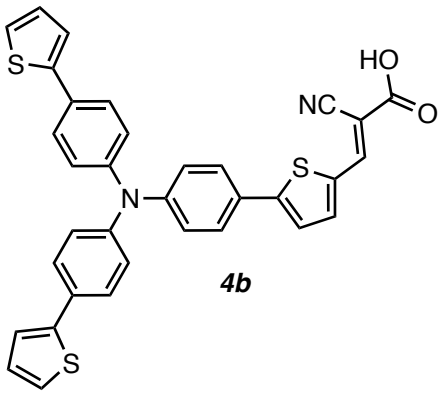
Synthesis of *3b*: Under an atmosphere of N_2, ***2b*** (294 mg, 0.57 mmol) and ***A*** (275 mg, 1.31 mmol) were dissolved in 55 mL of a mixture of THF:H_2O 9:1 and the solution was sparged 10 min with N_2. K_2CO_3 (788 mg, 5.7 mmol) and $Pd(PPh_3)_4$ (132 mg, 0.144 mmol) were added and the mixture was refluxed 12 h. After being cooled to room temperature, 25 mL of H_2O were added and the organic layer was separated. The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organic layers were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using CH_2Cl_2 as the eluent, affording the desired product as a yellow solid (192 mg, 65 %). Mp 98-100 °C; IR (KBr, cm^{-1}) 1663. ^1H

NMR (400 MHz, acetone-d_6): δ = 9.92 (s, 1H), 7.96 (d, 1H, $^3J_{HH}$ = 4.0 Hz), 7.75 (d, 2H, $^3J_{HH}$ = 8.7 Hz), 7.67 (d, 4H, $^3J_{HH}$ = 8.6 Hz), 7.60 (d, 1H), 7.43 (d, 4H), 7.19 (m, 6H), 7.12 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ = 183.7, 154.0, 149.3, 147.0, 144.4, 142.8, 139.4, 131.0, 129.2, 128.3, 128.0, 127.7, 126.1, 125.6, 124.7, 124.1, 123.9. HRMS (DART): *m/z* 520.0860 [(M+H)$^+$], calcd for $^{12}C_{31}{}^1H_{22}{}^{14}N^{16}O^{32}S_3{}^+$: *m/z* 520.0864.



4a

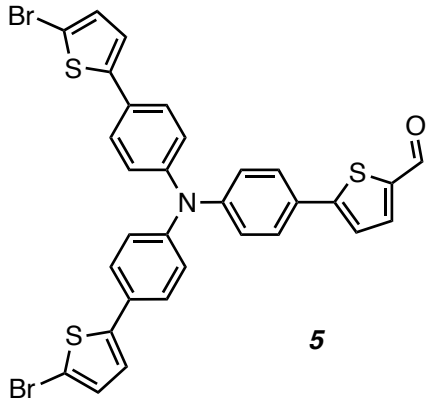
Synthesis of *4a*: ***3a*** (50 mg, 0.11 mmol) was dissolved in 25 mL of $CHCl_3$ and cyanoacetic acid (19 mg, 0.22 mmol) was added, followed by piperidine (3 μL, 0.03 mmol). The mixture was refluxed 12 h and after being cooled at room temperature, the organic layer was washed with HCl 1N (3 × 25 mL). The organic layer was dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude product was recrystallized from hexanes:CH_2Cl_2 3:1, affording the desired product as a dark red solid (49 mg, 88 %). Mp 168-171 °C; IR (KBr, cm^{-1}) 2217, 1686. ^1H NMR (400 MHz, acetone-d_6): δ = 8.42 (s, 1H), 7.97 (d, 1H, $^3J_{HH}$ = 3.9 Hz), 7.75 (d, 2H, $^3J_{HH}$ = 8.7 Hz), 7.64 (m, 3H), 7.39 (m, 4H), 7.16 (m, 8H). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ = 154.8, 149.9, 147.6, 147.4, 147.2, 144.5, 141.6, 135.0, 130.8, 130.6, 130.5, 129.1, 128.3, 127.7, 126.4, 126.2, 125.9, 125.5, 125.3, 124.6, 123.8, 123.4, 117.0, *C*=O signal not detected. HRMS (DART): *m/z* 505.1041 [(M+H)$^+$], calcd for $^{12}C_{30}{}^1H_{21}{}^{14}N_2{}^{16}O_2{}^{32}S_2{}^+$: *m/z* 505.1044.



4b

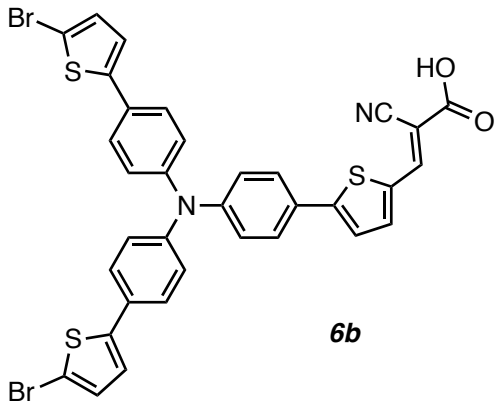
Synthesis of *4b*: ***3b*** (50 mg, 0.10 mmol) was dissolved in 25 mL of $CHCl_3$ and cyanoacetic acid (16 mg, 0.19 mmol) was added, followed by piperidine (3 μL, 0.03 mmol). The mixture was refluxed 12 h and after being cooled at room temperature, the organic layer was washed with HCl 1N (3 × 25 mL). The organic layer was dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude product was recrystallized from hexanes:CH_2Cl_2 3:1, affording the desired product as a dark red solid

(53 mg, 90 %). Mp 213-216 °C; IR (KBr, cm^{-1}) 2217, 1693. ^{1}H NMR (400 MHz, acetone-d_6): δ = 8.39 (s, 1H), 7.94 (d, 1H, $^{3}J_{HH}$ = 4.4 Hz), 7.77 (d, 2H, $^{3}J_{HH}$ = 8.6 Hz), 7.68 (d, 4H, $^{3}J_{HH}$ = 8.5 Hz), 7.63 (d, 1H), 7.44 (m, 4H), 7.20 (m, 6H), 7.13 (m, 2H). Compound was too insoluble to obtain $^{13}C\{^{1}H\}$ spectrum after 24 h. HRMS (DART): *m/z* 587.0925 [(M+H)$^{+}$], calcd for $^{12}C_{34}{}^{1}H_{23}{}^{14}N_2{}^{16}O_2{}^{32}S_3{}^{+}$: *m/z* 587.0922.



5

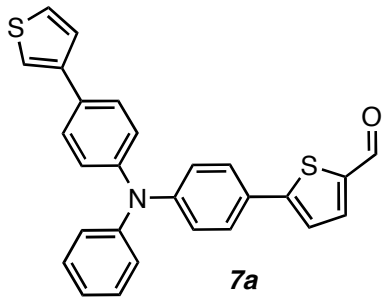
Synthesis of *5*: Under an atmosphere of N_2, ***3b*** (59 mg, 0.11 mmol) was dissolved in 50 mL of a mixture of THF:EtOAc 1:1 and N-bromosuccinimide (40 mg, 0.23 mmol) was added. The mixture was stirred at room temperature for 12 h and volatiles were removed *in vacuo*. The crude product was purified via column chromatography using CH_2Cl_2 as the eluent, affording the desired compound as an orange solid (64 mg, 83 %). Mp 157-159 °C; IR (KBr, cm^{-1}) 1667. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.87 (s, 1H), 7.73 (d, 1H, $^{3}J_{HH}$ = 3.9 Hz), 7.57 (d, 2H, $^{3}J_{HH}$ = 8.6 Hz), 7.43, (d, 4H, $^{3}J_{HH}$ = 8.6 Hz), 7.34 (d, 1H), 7.14 (d, 2H), 7.13 (d, 4H), 7.01 (m, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 182.8, 154.2, 148.3, 146.5, 145.4, 141.9, 137.8, 131.1, 129.4, 127.6, 127.5, 126.9, 125.2, 123.7, 123.4, 123.0, 111.1. HRMS (DART): *m/z* 675.9077 [(M+H)$^{+}$], (calcd for $^{12}C_{31}{}^{1}H_{20}{}^{79}Br_2{}^{14}N^{16}O^{32}S_3{}^{+}$: *m/z* 675.9074.



6b

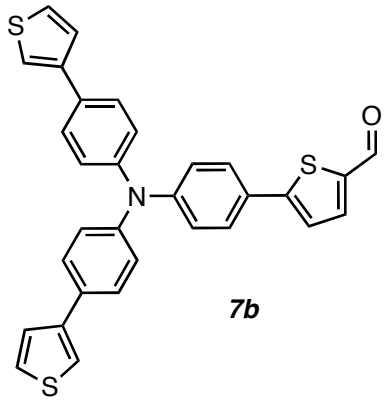
Synthesis of *6b*: ***5*** (50 mg, 0.10 mmol) was dissolved in 25 mL of $CHCl_3$ and cyanoacetic acid (16 mg, 0.19 mmol) was added, followed by piperidine (2 μL, 0.02 mmol). The mixture was refluxed 12 h and after being cooled at room temperature, the organic layer was washed with HCl 1N (3 × 25 mL). The organic layer was dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude product was

recrystallized from hexanes:CH_2Cl_2 3:1, affording a dark red solid (49 mg, 89 %). Mp 169-170 °C; IR (KBr, cm^{-1}) 2217, 1687. ^1H NMR (400 MHz, acetone-d_6): δ = 8.39 (s, 1H), 7.94 (d, 2H, $^3J_{HH}$ = 4.4 Hz), 7.77 (d, 2H, 8.6 Hz), 7.68 (d, 4H, $^3J_{HH}$ = 8.5 Hz), 7.63 (d, 1H), 7.44 (m, 3H), 7.20 (m, 6H), 7.12 (m, 2H). Compound was too insoluble to detect ^{13}C signals after 24 h. HRMS (DART): *m/z* 698.9243 [$(M+H-CO_2)^+$], calcd for $^{12}C_{33}{}^1H_{21}{}^{79}Br_2{}^{14}N_2{}^{32}S_3{}^+$: *m/z* 698.9234.



7a

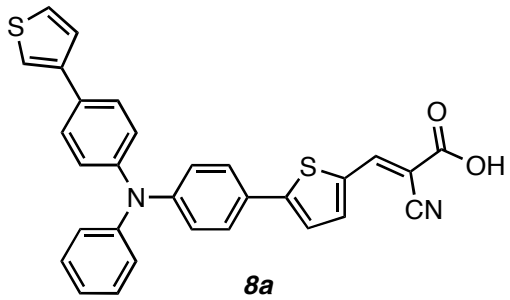
Synthesis of *7a*: Under an atmosphere of N_2, ***2a*** (200 mg, 0.46 mmol) and ***B*** (68 mg, 0.53 mmol) were dissolved in 55 mL of a mixture of THF:H_2O 9:1 and the solution was sparged 10 min with N_2. K_2CO_3 (318 mg, 2.3 mmol) and $Pd(PPh_3)_4$ (53 mg, 0.046 mmol) were added and the mixture was refluxed 12 h. After being cooled to room temperature, 50 mL of H_2O were added and the organic layer was separated. The aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organic layers were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using hexanes:CH_2Cl_2 1:1 as the eluent, affording the desired product as a yellow solid (110 mg, 68 %). Mp 94-97 °C; IR (KBr, cm^{-1}) 1662. ^1H NMR (400 MHz, acetone-d_6): δ = 9.90 (m, 1H), 7.94 (d, 1H, $^3J_{HH}$ = 4.0 Hz), 7.71 (m, 5H), 7.56 (m, 2H), 7.52 (m, 1H), 7.38 (m, 2H), 7.17 (m, 5H), 7.09 (d, 2H, $^3J_{HH}$ = 8.8 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ = 183.7, 154.2, 149.9, 147.8, 146.9, 142.6, 142.4, 139.4, 132.3, 130.6, 128.3, 128.2, 127.4, 127.3, 126.9, 126.2, 126.0, 125.1, 124.5, 123.3, 120.7. HRMS (DART): *m/z* 438.0986 [$(M+H)^+$], calcd for $^{12}C_{27}{}^1H_{20}{}^{14}N^{16}O^{32}S_2{}^+$: *m/z* 487.0986.



7b

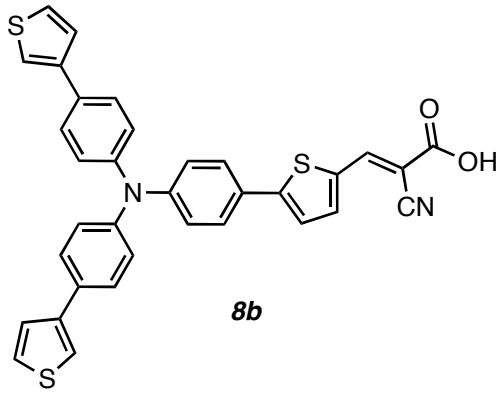
Synthesis of *7b*: Under an atmosphere of N_2, ***2b*** (250 mg, 0.49 mmol) and ***B*** (145 mg, 1.13 mmol) were dissolved in 55 mL of a mixture of THF:H_2O 9:1 and the solution was sparged 10 min with N_2. K_2CO_3 (677 mg, 4.9 mmol) and $Pd(PPh_3)_4$ (113 mg, 0.098 mmol) were added and the mixture was refluxed 12 h. After being cooled to room temperature, 25 mL of H_2O were added and the organic layer was separated. The

aqueous layer was extracted with Et_2O (3 × 25 mL) and the combined organic layers were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using CH_2Cl_2 as the eluent, affording the desired product as a yellow solid (113 mg, 44 %). Mp 112-115 °C; IR (KBr, cm^{-1}) 1661. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.86 (s, 1H), 7.72 (d, 1H, $^3J_{HH}$ = 4.0 Hz), 7.56 (d, 2H, $^3J_{HH}$ = 8.6 Hz), 7.54 (d, 4H, $^3J_{HH}$ = 8.6 Hz), 7.40 (m, 6H), 7.33 (d, 1H), 7.19 (d, 4H), 7.14 (d, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 182.8, 154.6, 148.9, 146.0, 141.8, 141.6, 137.8, 131.7, 127.6, 127.5, 126.7, 126.5, 126.3, 125.4, 123.1, 123.0, 119.9. HRMS (DART): *m/z* 520.0859 [$(M+H)^+$], calcd for $^{12}C_{31}{}^1H_{22}{}^{14}N^{16}O^{32}S_3{}^+$: *m/z* 520.0864.



8a

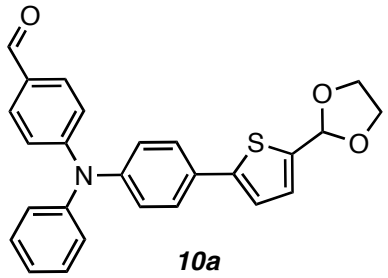
Synthesis of *8a*: ***7a*** (49 mg, 0.11 mmol) was dissolved in 25 mL of $CHCl_3$ and cyanoacetic acid (19 mg, 0.22 mmol) was added, followed by piperidine (3 μL, 0.03 mmol). The mixture was refluxed 12 h and after being cooled at room temperature, the organic layer was washed with HCl 1N (3 × 25 mL). The organic layer was dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude product was recrystallized from hexanes:CH_2Cl_2 3:1, affording the desired product as a dark red solid (52 mg, 94 %). Mp 210-212 °C; IR (KBr, cm^{-1}) 2217, 1687. ^1H NMR (400 MHz, acetone-d_6): δ = 8.42 (s, 1H), 7.96 (d, 1H, $^3J_{HH}$ = 4.1 Hz), 7.72 (m, 5H), 7.62 (d, 1H), 7.56 (m, 1H), 7.53 (m, 1H), 7.39 (m, 2H), 7.18 (m, 5H), 7.11 (d, 2H, $^3J_{HH}$ = 8.8 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, acetone-d_6): δ = 164.0, 154.9, 150.1, 147.7, 147.4, 146.8, 146.6, 142.4, 141.6, 134.9, 132.5, 130.6, 128.3, 127.4, 127.0, 126.9, 126.3, 126.2, 125.2, 124.6, 123.4, 123.1, 120.8, 117.0. HRMS (DART): *m/z* 505.1056 [$(M+H)^+$], calcd for $^{12}C_{30}{}^1H_{21}{}^{14}N_2{}^{16}O_2{}^{32}S_2{}^+$: *m/z* 505.1044.



8b

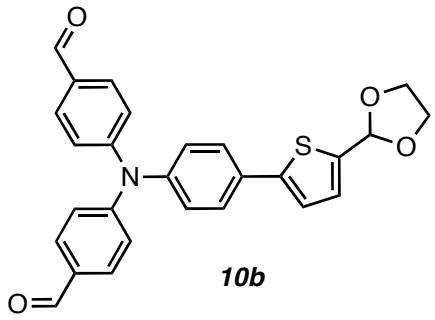
Synthesis of *8b*: ***7b*** (53 mg, 0.10 mmol) was dissolved in 25 mL of $CHCl_3$ and cyanoacetic acid (17 mg, 0.20 mmol) was added, followed by piperidine (3 μL, 0.03 mmol). The mixture was refluxed 12 h and after being cooled at room temperature, the

organic layer was washed with HCl 1N (3 × 25 mL). The organic layer was dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude product was recrystallized from hexanes:CH_2Cl_2 3:1, affording the desired product as a dark red solid (68 mg, quantitative). Mp 164-168 °C (decomp); IR (KBr, cm^{-1}) 2218, 1689. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.32 (s, 1H), 7.78 (d, 1H, $^3J_{HH}$ = 4.2 Hz), 7.58 (d, 2H, $^3J_{HH}$ = 8.8 Hz), 7.55 (d, 4H, $^3J_{HH}$ = 8.6 Hz), 7.41 (m, 6H), 7.36 (d, 1H), 7.19 (d, 4H), 7.14 (d, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 149.3, 147.9, 145.8, 141.8, 140.4, 140.4, 137.4, 134.0, 131.9, 127.7, 127.6, 126.5, 126.3, 126.1, 125.6, 125.5, 123.6, 122.6, 120.0, *C*=O signal not detected. HRMS (DART): *m/z* 587.0918 [$(M+H)^+$], calcd for $^{12}C_{34}{}^1H_{23}{}^{14}N_2{}^{16}O_2{}^{32}S_3{}^+$: *m/z* 587.0922.



10a

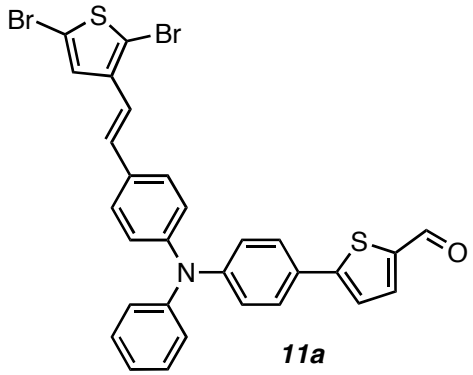
Synthesis of *10a*: Under an atmosphere of N_2, ***9a*** (700 g, 2.0 mmol) and ***C*** (846 mg, 3.0 mmol) were dissolved in 70 mL of a mixture of THF:H_2O 9:1 and the solution was sparged 10 min with N_2. K_2CO_3 (1.27 g, 10.0 mmol) and $Pd(PPh_3)_4$ (208 mg, 0.20 mmol) were added and the mixture was refluxed 12 h. After being cooled to room temperature, 50 mL of H_2O were added and the organic layer was separated. The aqueous layer was extracted with Et_2O (3 × 50 mL) and the combined organic layers were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using CH_2Cl_2 as the eluent, affording the desired product as a yellow oil (455 mg, 53 %), which was used as is. IR (KBr, cm^{-1}) 1686. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.83 (s, 1H), 7.70 (d, 2H, $^3J_{HH}$ = 8.4 Hz), 7.53 (d, 2H, $^3J_{HH}$ = 8.8 Hz), 7.36 (m, 2H), 7.16 (m, 7H), 7.06 (m, 2H), 6.09 (s, 1H), 4.10 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 190.6, 153.2, 146.1, 145.8, 144.7, 141.0, 131.5, 130.0, 129.7, 127.4, 127.2, 127.1, 126.5, 126.2, 125.5, 122.6, 120.1, 100.5, 65.4. HRMS (DART): *m/z* 428.1328 [$(M+H)^+$], calcd for $^{12}C_{26}{}^1H_{22}{}^{14}N^{16}O_3{}^{32}S^+$: *m/z* 428.1320.



10b

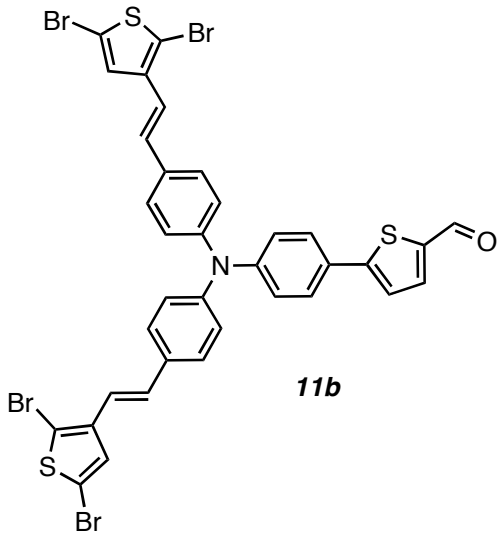
Synthesis of *10b*: Under an atmosphere of N_2, ***9b*** (1.0 g, 2.63 mmol) and ***C*** (1.11 g, 3.95 mmol) were dissolved in 90 mL of a mixture of THF:H_2O 9:1 and the solution was sparged 10 min with N_2. K_2CO_3 (1.82 g, 13.2 mmol) and $Pd(PPh_3)_4$ (300 mg, 0.26 mmol) were added and the mixture was refluxed 12 h. After being cooled to room temperature,

75 mL of H_2O were added and the organic layer was separated. The aqueous layer was extracted with Et_2O (3 × 50 mL) and the combined organic layers were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude material was purified via column chromatography using CH_2Cl_2 as the eluent, affording the desired product as a yellow solid (1.114 g, 93 %). Mp 84-89 °C; IR (KBr, cm^{-1}) 1693. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.91 (s, 1H), 7.80 (d, 4H, $^3J_{HH}$ = 8.6 Hz), 7.59 (d, 2H, $^3J_{HH}$ = 8.5 Hz), 7.22 (d, 4H), 7.16 (m, 4H), 6.10 (s, 1H), 4.11 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 190.6, 151.9, 145.1, 141.5, 132.3, 131.7, 131.5, 127.6, 127.5, 127.1, 123.7, 123.2, 123.1, 100.4, 65.5. HRMS (DART): *m/z* 456.1278 [$(M+H)^+$], calcd for $^{12}C_{27}{}^1H_{22}{}^{14}N^{16}O_4{}^{32}S^+$: *m/z* 456.1270.



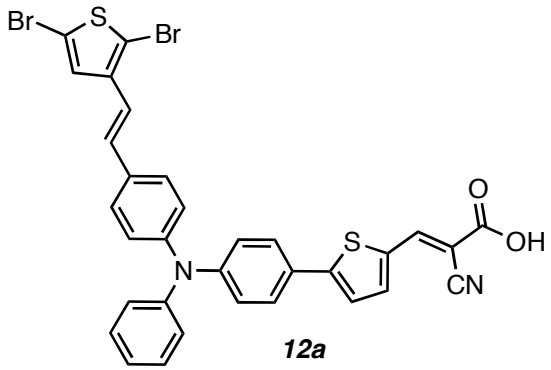
11a

Synthesis of *11a*: Under an atmosphere of N_2, ***10a*** (414 mg, 0.97 mmol) and ***D*** (419 mg, 1.07 mmol) were solubilized in 25 mL of dry THF and *t*BuOK (130 mg, 1.16 mmol) was added in one portion. The mixture was refluxed 24 h and cooled to room temperature. Volatiles were removed *in vacuo* and the crude product was purified via column chromatography using CH_2Cl_2:hexanes 2:1 as the eluent, affording a mixture of the desired compound and its corresponding protected aldehyde. This mixture was then refluxed in 60 mL of glacial AcOH:H_2O 2:1 for 1 h. After being cooled to room temperature, the solution was diluted with 150 mL of H_2O and extracted using CH_2Cl_2 (3 × 50 mL). The combined organic fractions were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*, affording the desired product as a yellow solid (252 mg, 39 %). Mp 95-98 °C; IR (KBr, cm^{-1}) 1662. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.86 (s, 1H), 7.72 (d, 1H, $^3J_{HH}$ = 4.0 Hz), 7.54 (d, 2H, $^3J_{HH}$ = 8.7 Hz), 7.41 (d, 2H), 7.32 (m, 3H), 7.21 (s, 1H), 7.16 (d, 2H), 7.11 (m, 4H), 6.92 (d, 1H, $^3J_{HH}$ = 16.3 Hz), 6.86 (d, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 182.8, 154.5, 148.8, 147.1, 146.8, 141.7, 139.4, 137.8, 131.9, 130.7, 129.8, 127.5, 127.4, 126.9, 125.6, 124.6, 124.5, 123.2, 123.2, 119.1, 112.0, 109.8. HRMS (DART): *m/z* 619.9362 [$(M+H)^+$], calcd for $^{12}C_{29}{}^1H_{20}{}^{79}Br_{21}{}^{14}N^{16}O^{32}S_2{}^+$: *m/z* 619.9353.



11b

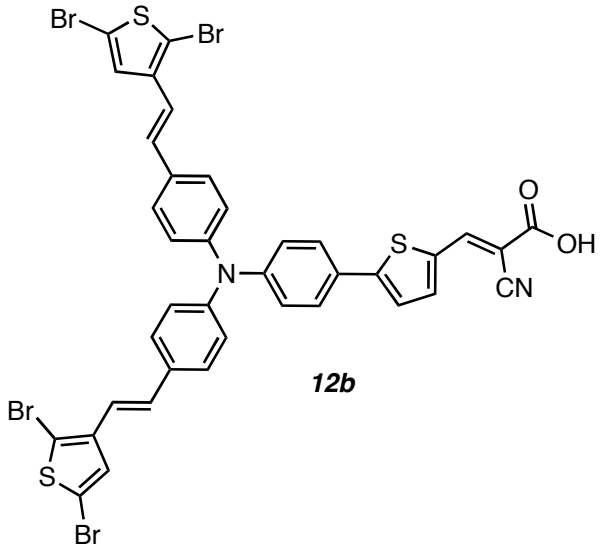
Synthesis of *11b*: Under an atmosphere of N_2, ***10b*** (439 mg, 0.96 mmol) and ***D*** (808 mg, 2.06 mmol) were solubilized in 30 mL of dry THF and *t*BuOK (255 mg, 2.27 mmol) was added in one portion. The mixture was refluxed 24 h and cooled to room temperature. Volatiles were removed *in vacuo* and the crude product was purified via column chromatography using CH_2Cl_2:hexanes 3:1 as the eluent, affording a mixture of the desired compound and its corresponding protected aldehyde. This mixture was then refluxed in 60 mL of glacial AcOH:H_2O 2:1 for 1 h. After being cooled to room temperature, the solution was diluted with 150 mL of H_2O and extracted using CH_2Cl_2 (3 × 50 mL). The combined organic fractions were dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*, affording the desired product as an orange solid (158 mg, 19 %). Mp 147-149 °C; IR (KBr, cm^{-1}) 1655. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.87 (s, 1H), 7.72 (d, 1H, $^3J_{HH}$ = 4.0 Hz), 7.56 (d, 2H, $^3J_{HH}$ = 8.6 Hz), 7.43 (d, 4H, $^3J_{HH}$ = 8.6 Hz), 7.33 (d, 1H), 7.21 (s, 2H), 7.13 (m, 6H), 6.93 (d, 2H, $^3J_{HH}$ = 16.2 Hz), 6.86 (d, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 154.3, 148.4, 146.7, 141.8, 139.3, 137.8, 132.3, 131.9, 130.7, 130.6, 130.2, 127.9, 127.6, 127.5, 124.9, 124.5, 123.8, 123.4, 121.5, 119.4, 112.0, 110.0. HRMS (DART): *m/z* 887.7532 [$(M+H)^+$], calcd for $^{12}C_{35}{}^1H_{22}{}^{79}Br_2{}^{81}Br_2{}^{14}N^{16}O^{32}S_3{}^+$: *m/z* 887.7556.



12a

Synthesis of *12a*: ***11a*** (70 mg, 0.11 mmol) was dissolved in 25 mL of $CHCl_3$ and cyanoacetic acid (19 mg, 0.23 mmol) was added, followed by piperidine (3 μL, 0.03 mmol). The mixture was refluxed 12 h and after being cooled at room temperature, the organic layer was washed with HCl 1N (3 × 25 mL). The organic layer was dried over

$MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude product was recrystallized from hexanes:CH_2Cl_2 3:1, affording the desired product as a dark red solid (59 mg, 78 %). Mp 211-215 °C (decomp.); IR (KBr, cm^{-1}) 2217, 1688. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 1H), 7.77 (d, 1H, $^3J_{HH}$ = 3.9 Hz), 7.57 (d, 2H, $^3J_{HH}$ = 8.5 Hz), 7.42 (d, 2H), 7.33 (m, 3H), 7.21 (s, 1H), 7.16 (m, 3H), 7.10 (m, 4H), 6.92 (d, 1H, $^3J_{HH}$ = 16.2 Hz), 6.86 (d, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 166.6, 156.2, 149.2, 147.9, 146.9, 146.3, 140.4, 139.4, 134.0, 132.2, 130.7, 129.8, 127.9, 127.8, 127.7, 127.5, 126.3, 125.8, 124.8, 124.7, 123.7, 122.9, 119.3, 116.1, 112.0, 109.9. HRMS (DART): *m/z* 642.9525 $[(M+H-CO_2)^+]$, calcd for $^{12}C_{31}{}^1H_{21}{}^{79}Br_2{}^{14}N_2{}^{32}S_2{}^+$: *m/z* 642.9513.



12b

Synthesis of *12b*: ***11b*** (70 mg, 0.08 mmol) was dissolved in 25 mL of $CHCl_3$ and cyanoacetic acid (13 mg, 0.16 mmol) was added, followed by piperidine (2 μL, 0.02 mmol). The mixture was refluxed 12 h and after being cooled at room temperature, the organic layer was washed with HCl 1N (3 × 25 mL). The organic layer was dried over $MgSO_4$, filtered and volatiles were removed *in vacuo*. The crude product was recrystallized from hexanes:CH_2Cl_2 3:1, affording the desired product as a dark red solid (70 mg, 92 %). Mp 183-184 °C; IR (KBr, cm^{-1}) 2217, 1686. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 1H), 7.77 (d, 1H, $^3J_{HH}$ = 4.0 Hz), 7.59 (d, 2H, $^3J_{HH}$ = 8.6 Hz), 7.44 (d, 4H, $^3J_{HH}$ = 8.5 Hz), 7.37 (d, 1H), 7.22 (s, 2H), 7.13 (m, 6H), 6.94 (d, 2H, $^3J_{HH}$ = 16.2 Hz), 6.87 (d, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 155.9, 148.8, 147.9, 147.8, 146.5, 140.4, 139.3, 134.2, 132.6, 130.6, 127.0, 127.8, 127.5, 126.8, 125.1, 123.8, 123.5, 119.5, 116.1, 112.1, 110.0, *C*=O signal not detected. HRMS (DART): *m/z* 910.7727 $[(M+H-CO_2)^+]$, calcd for $^{12}C_{37}H_{23}{}^{79}Br_2{}^{81}Br_2{}^{14}N_2{}^{32}S_4{}^+$: *m/z* 910.7716.

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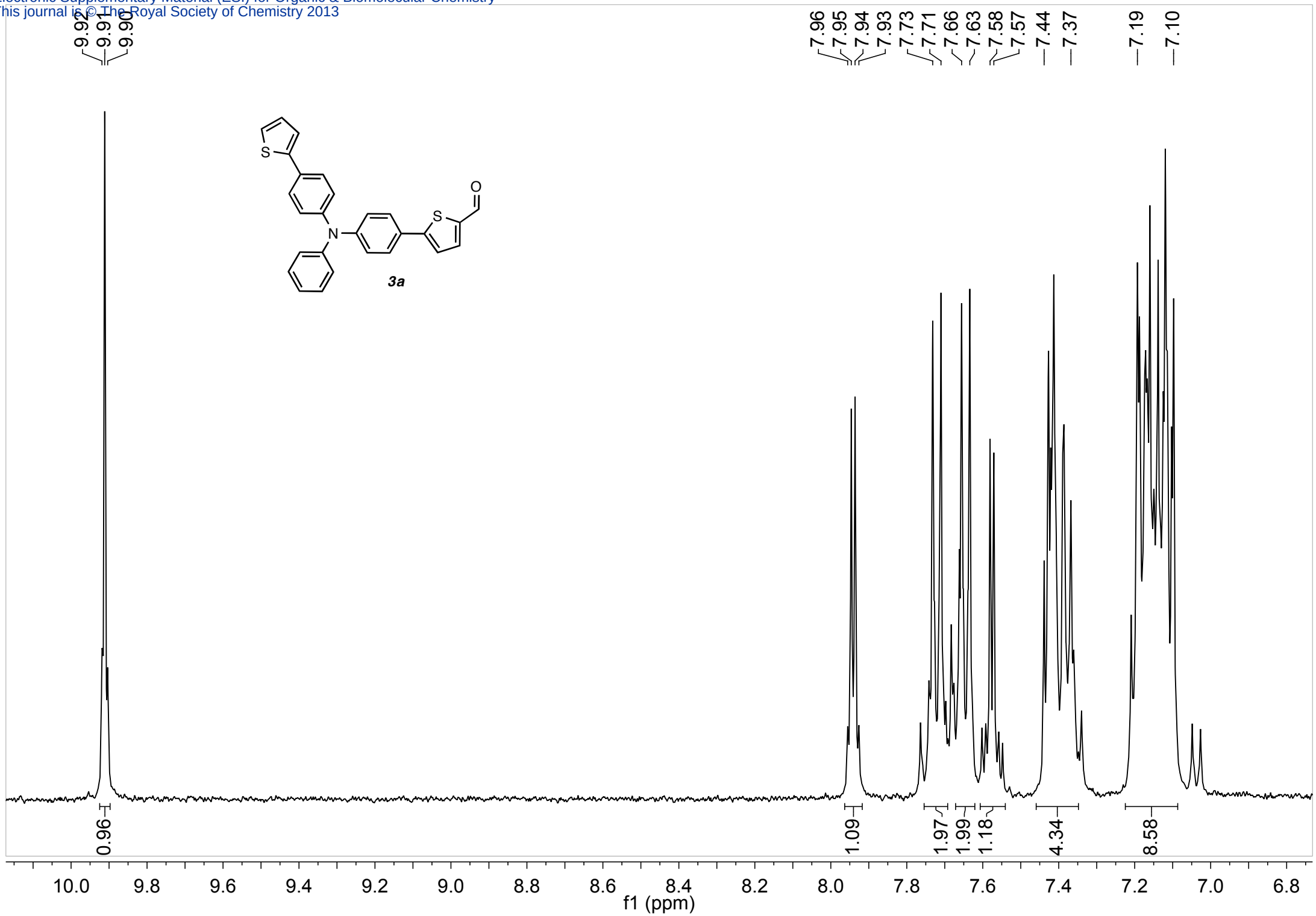

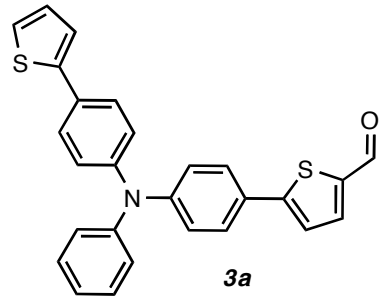

3a

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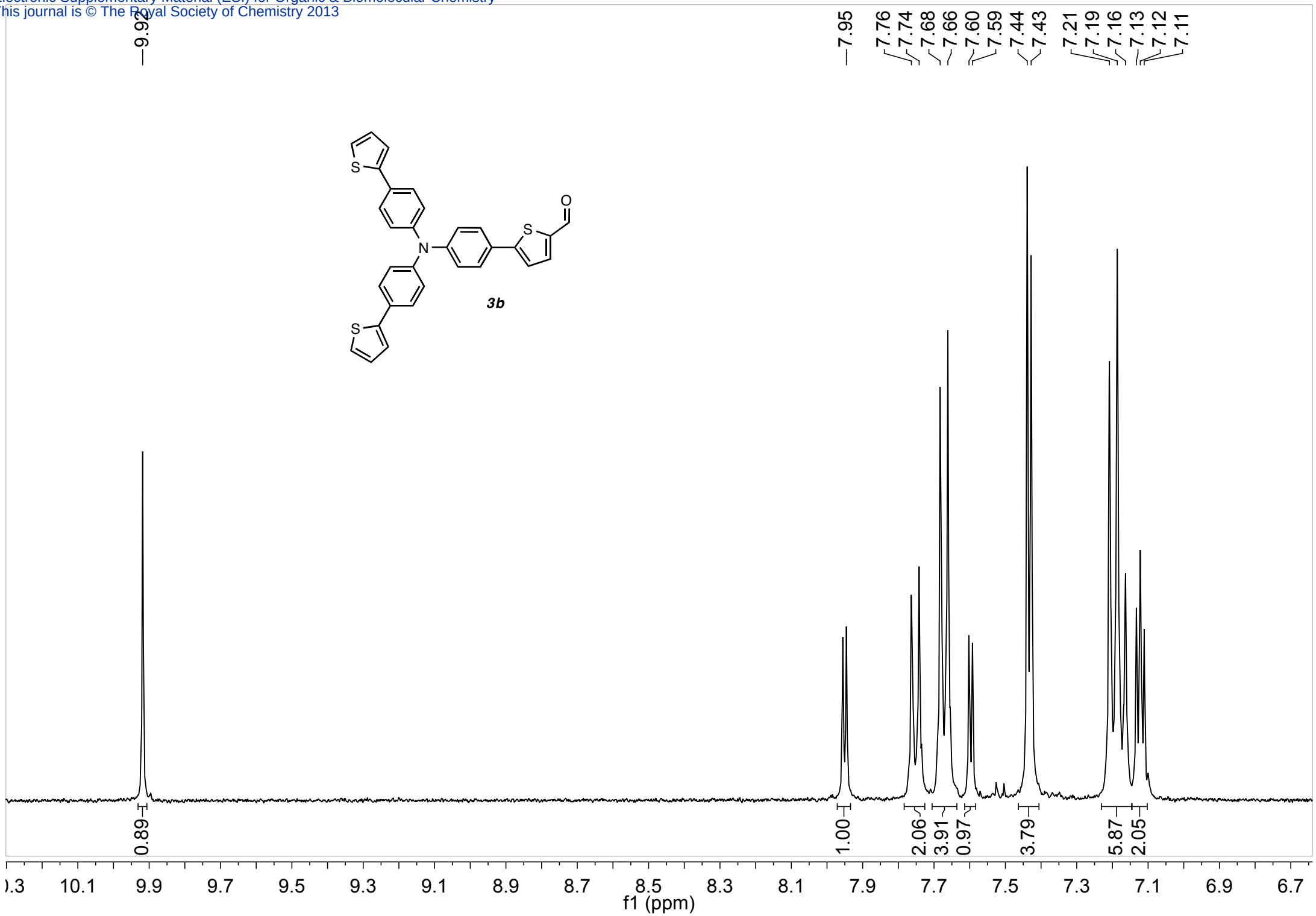
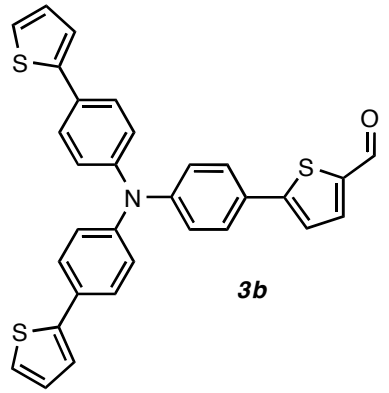
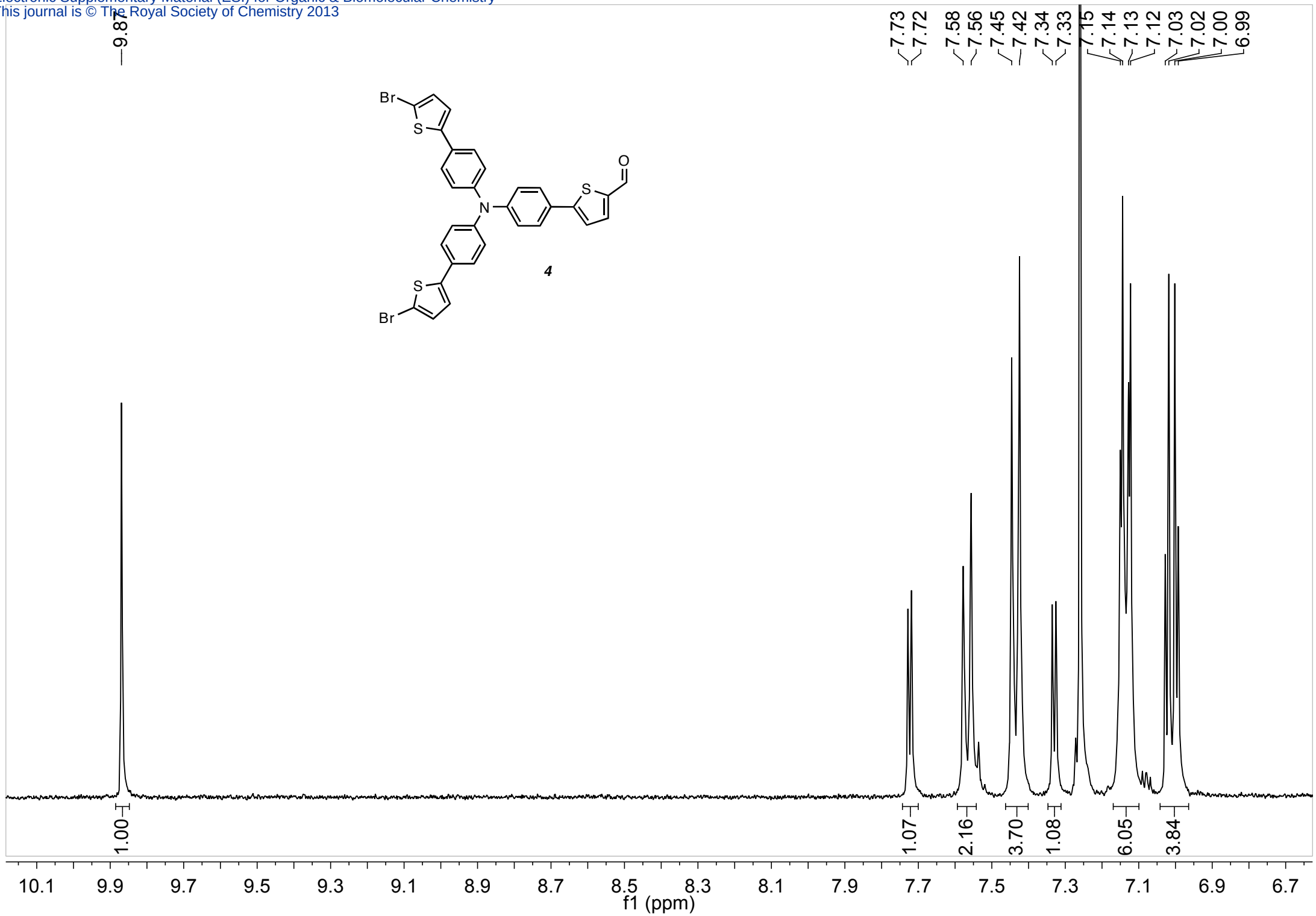
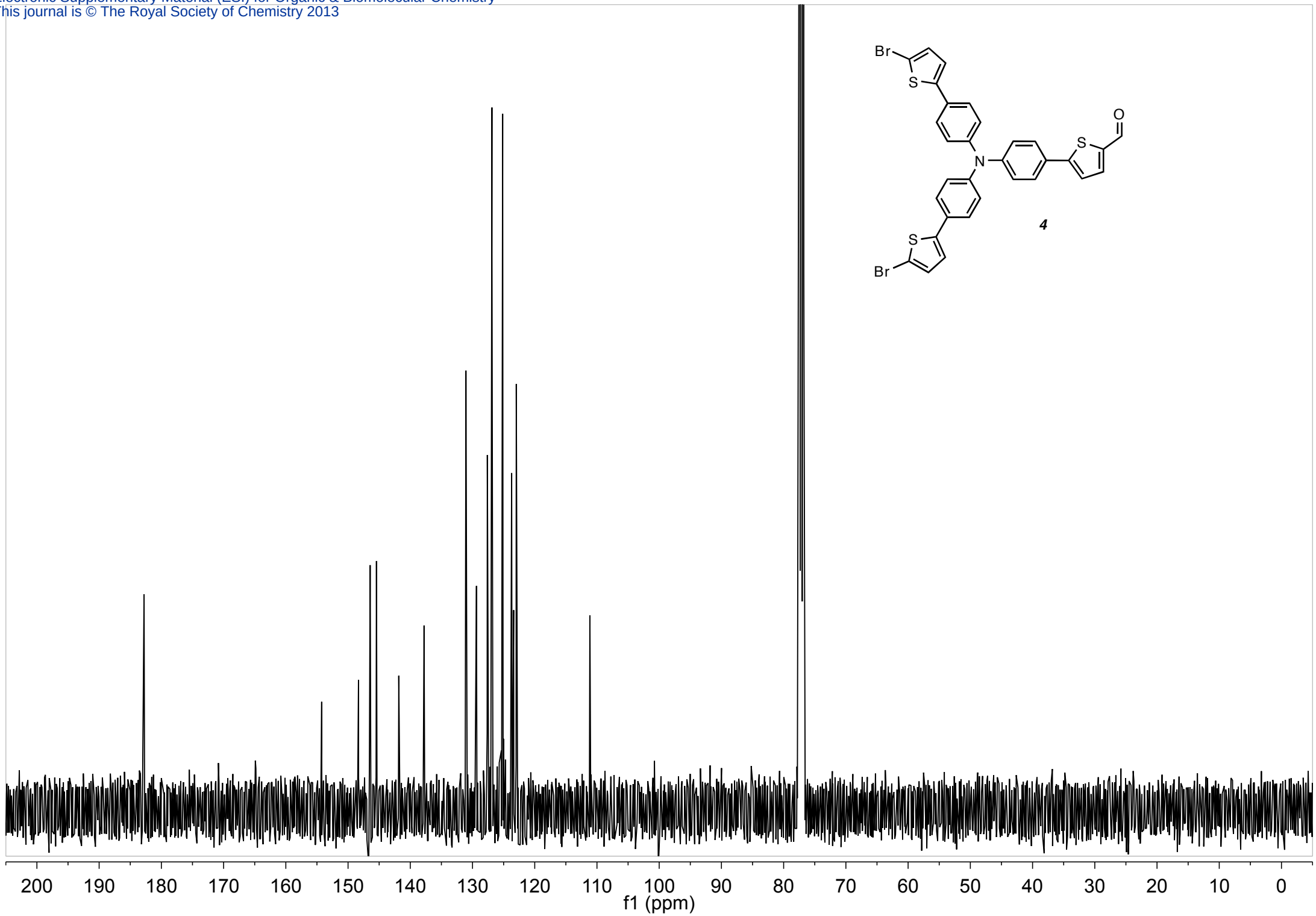
f1 (ppm)

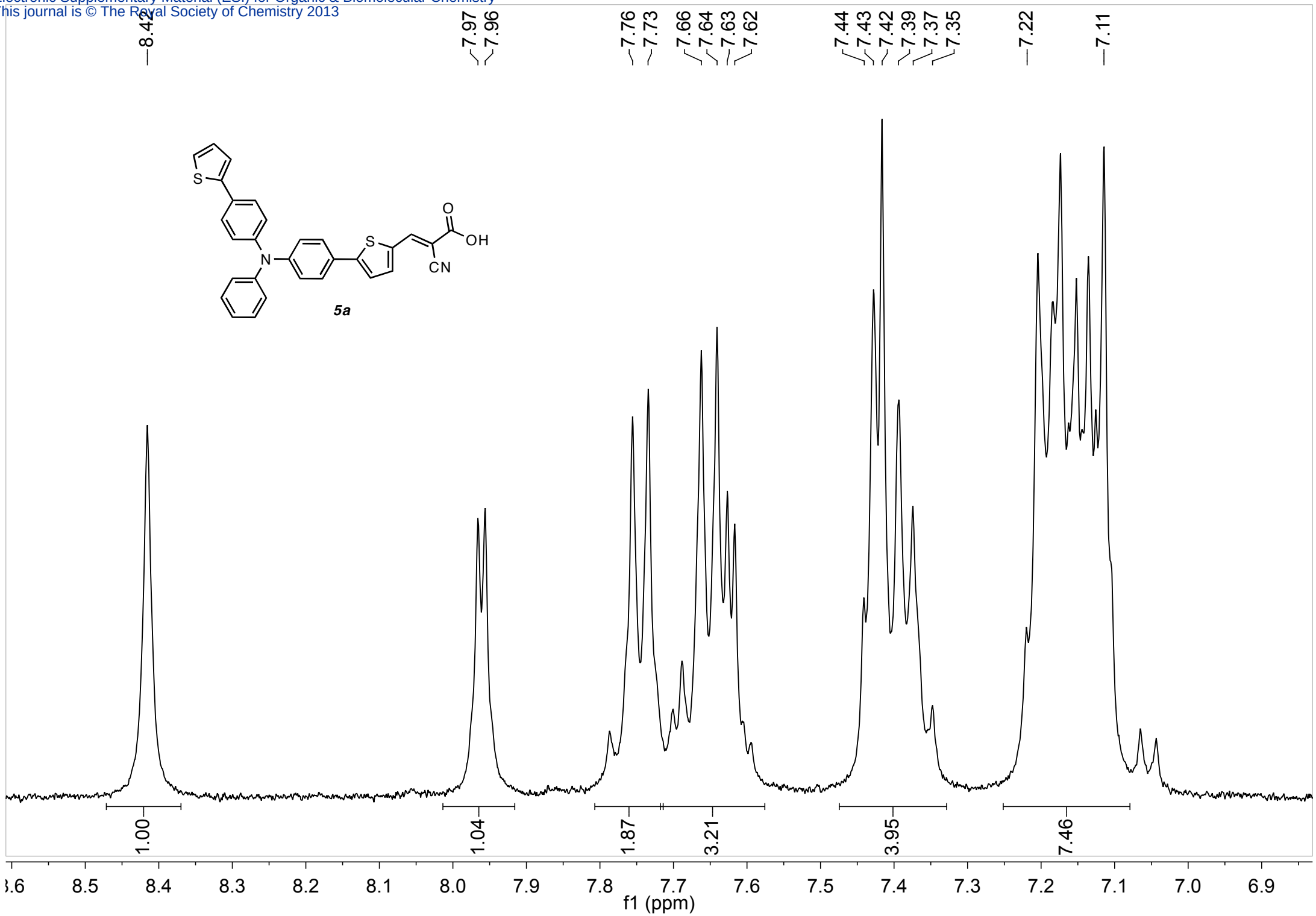


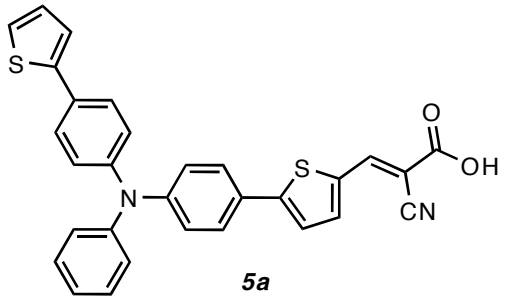


3b









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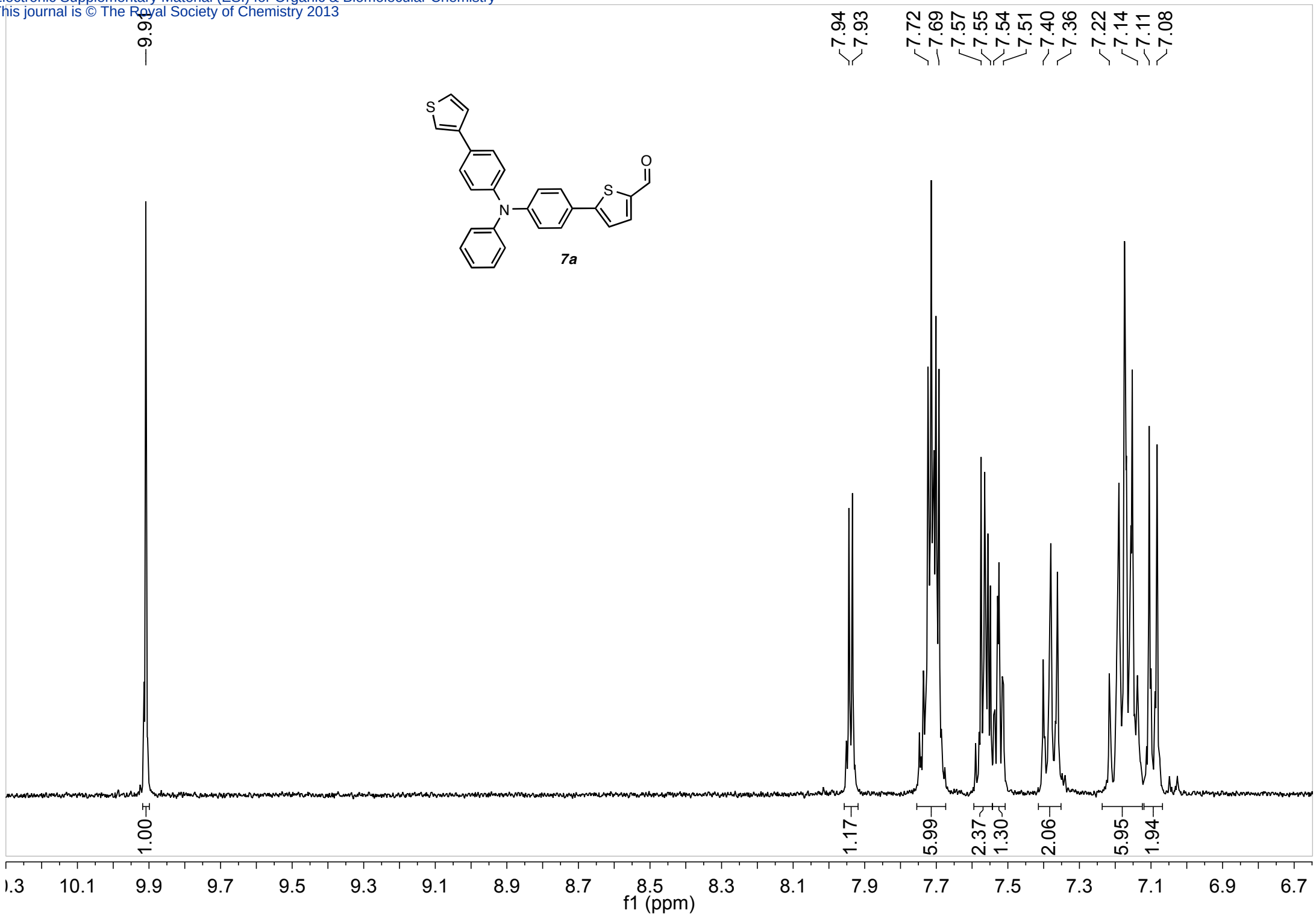

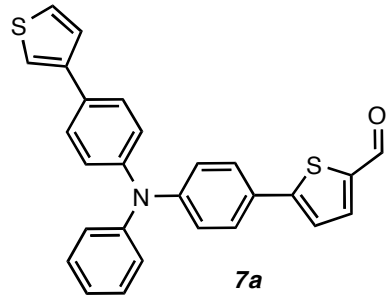

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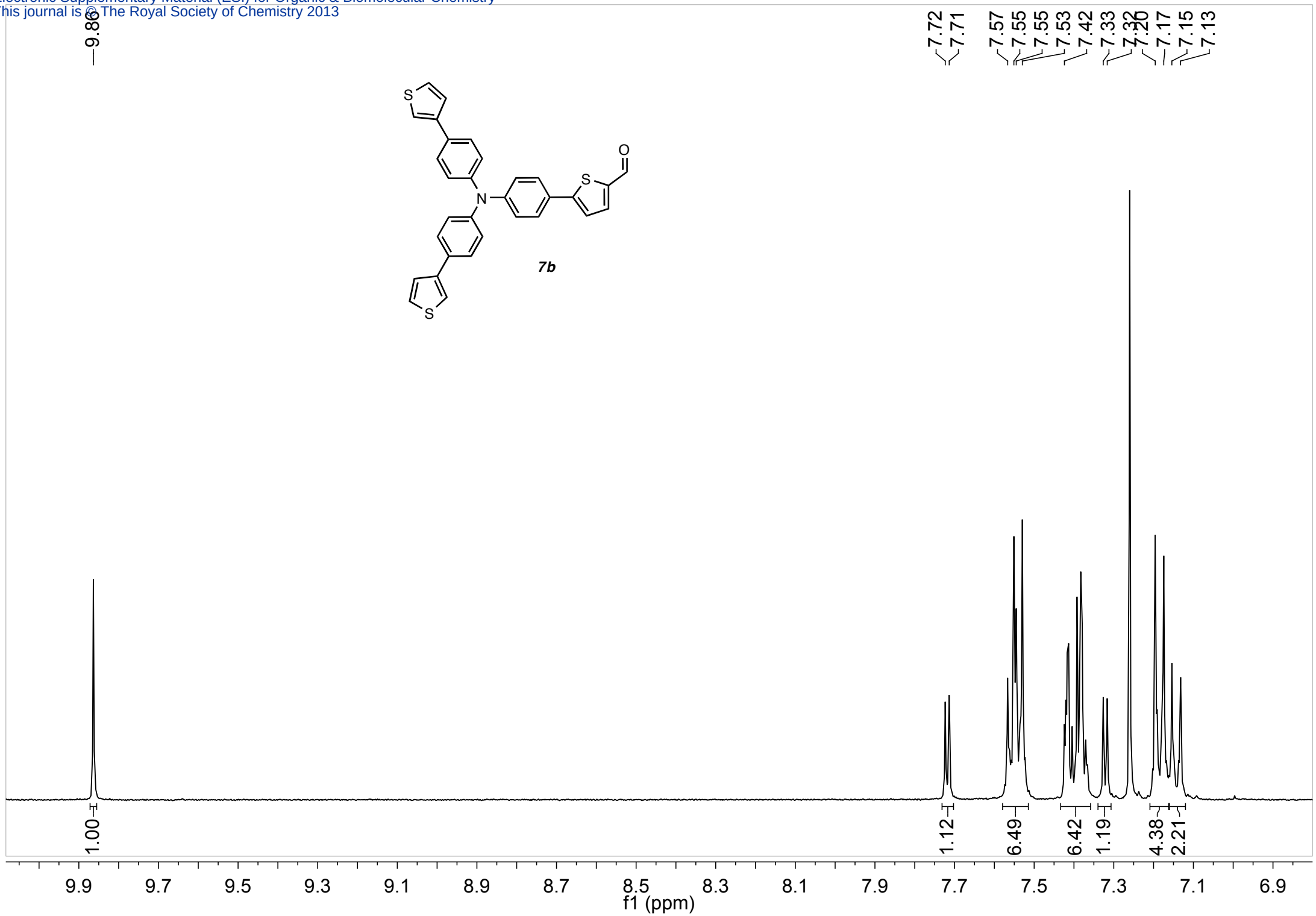

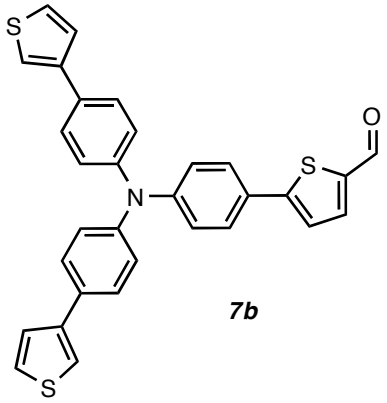

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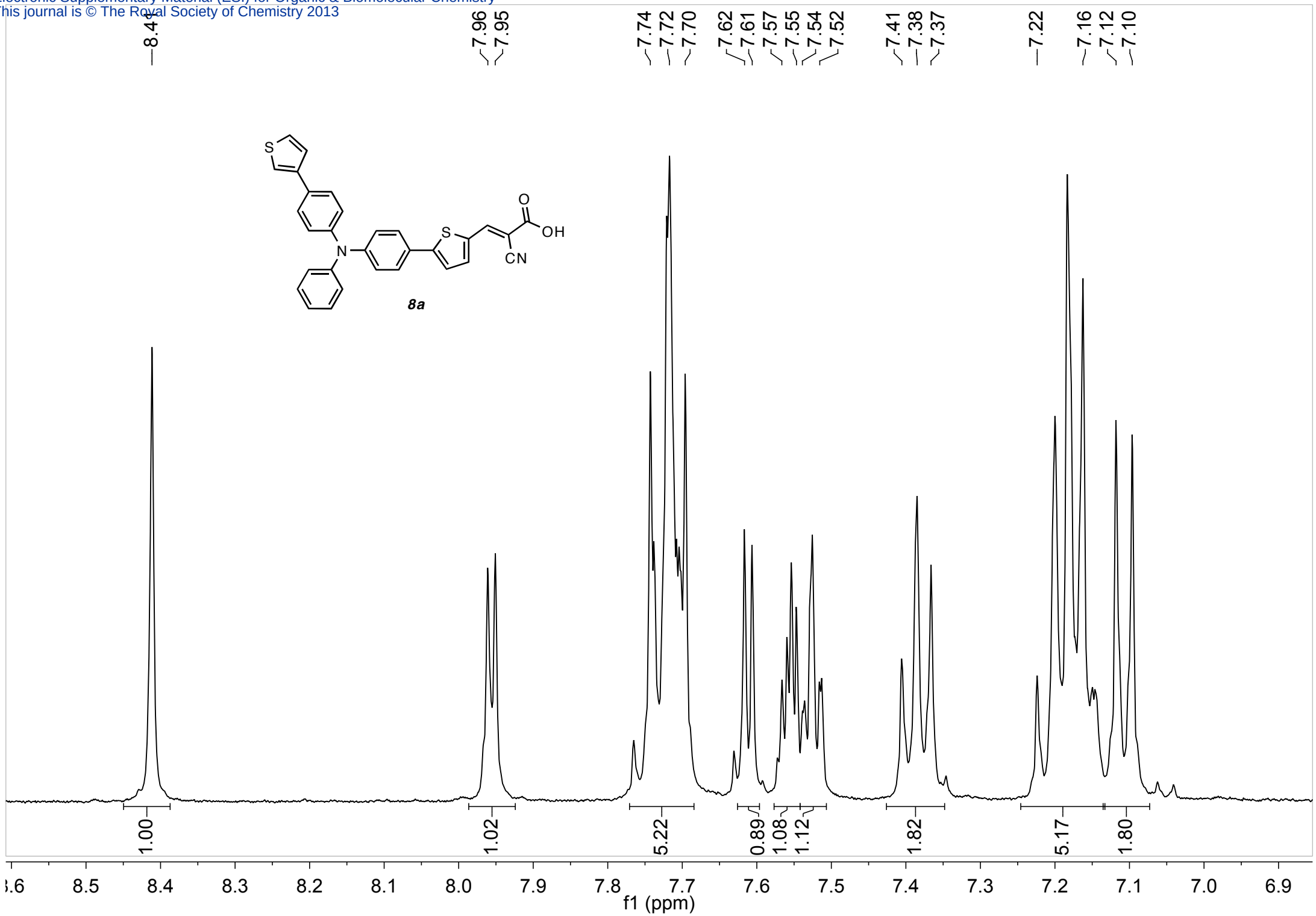

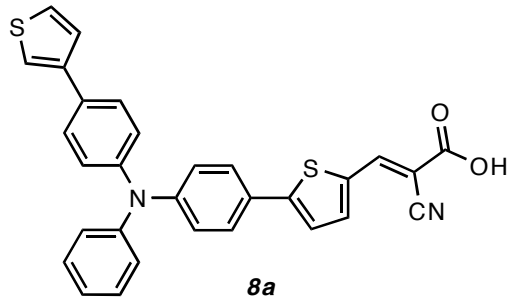

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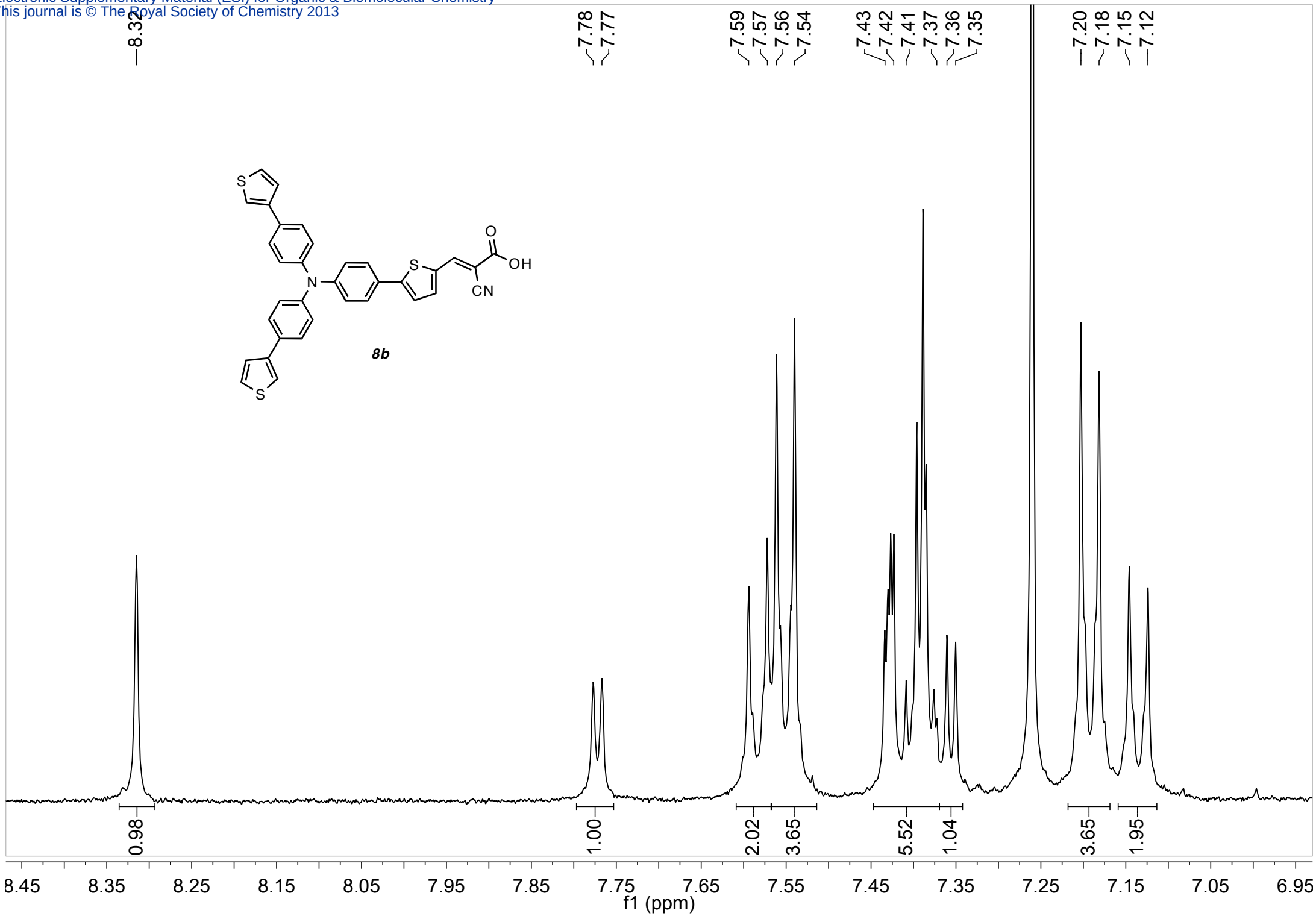

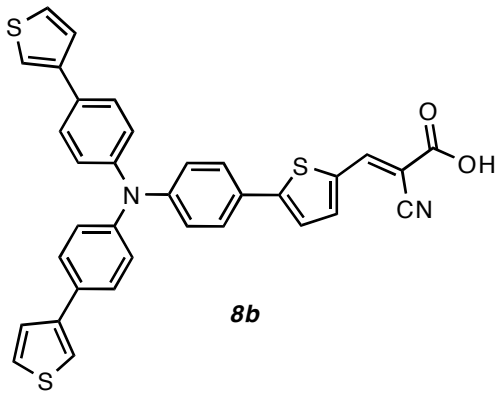

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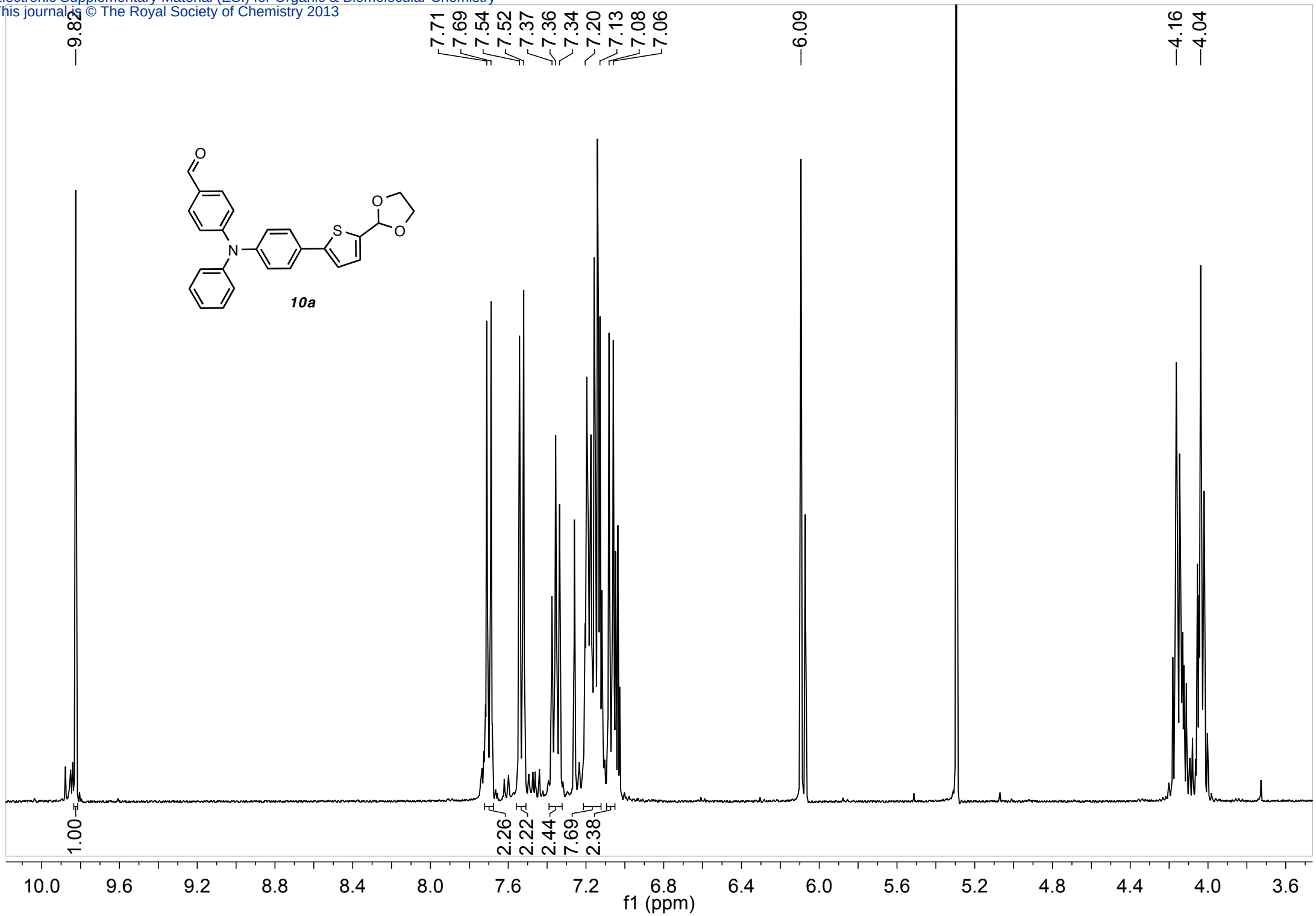

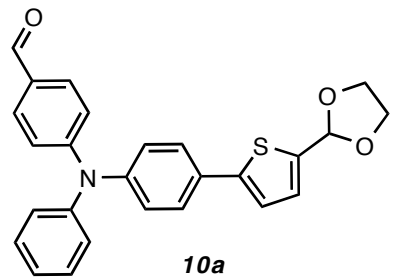

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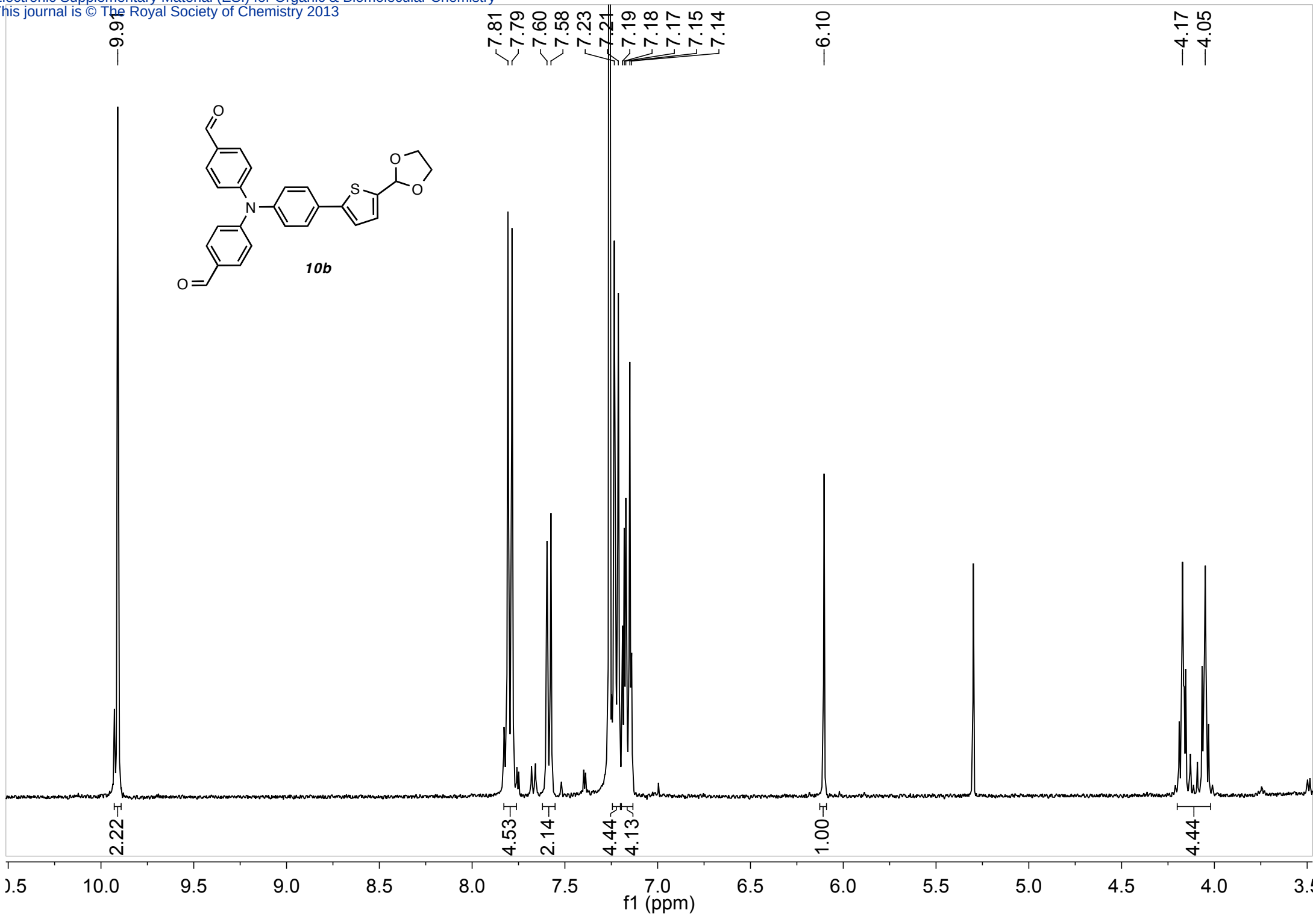

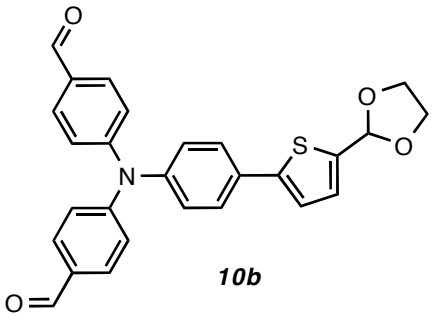

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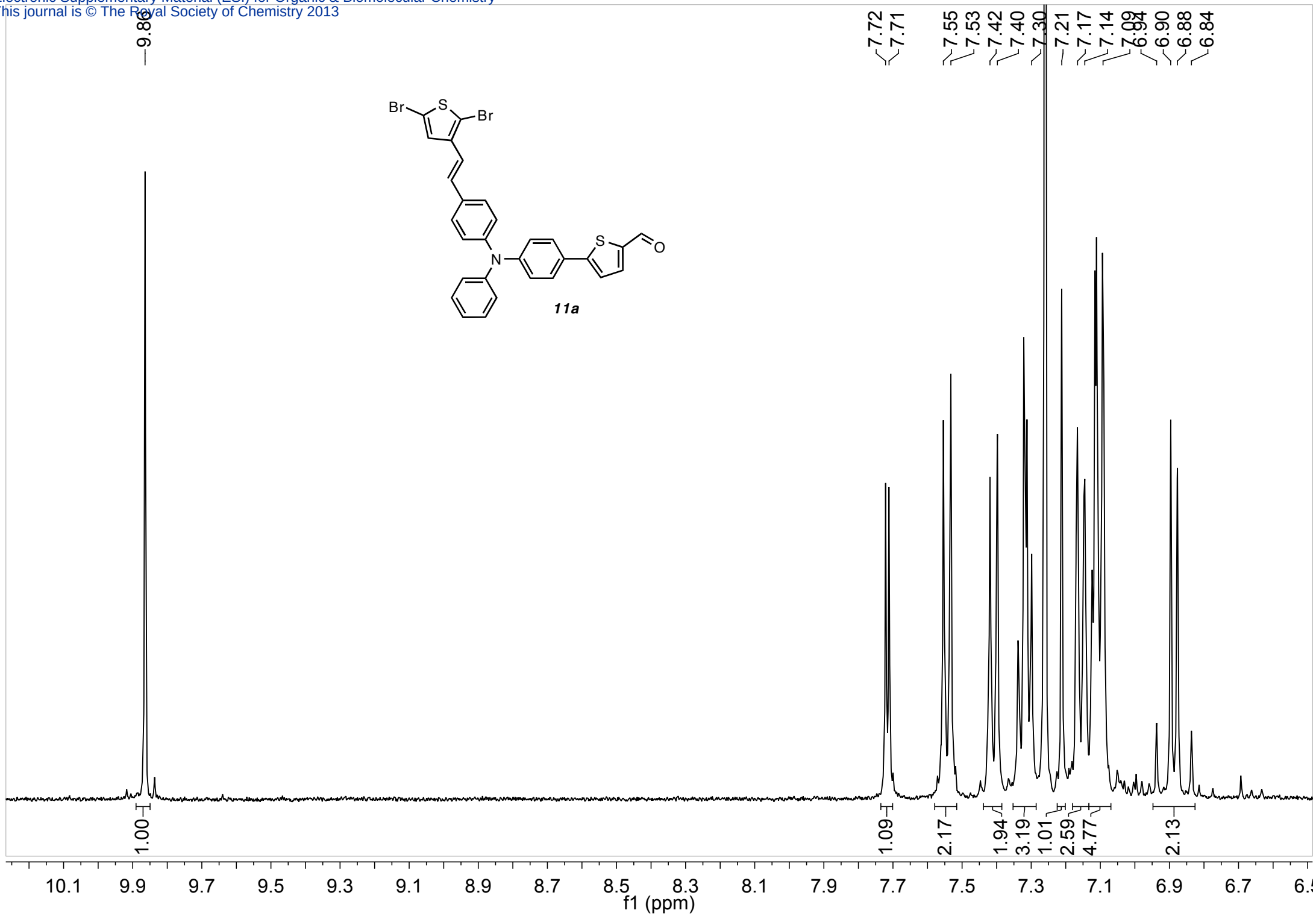

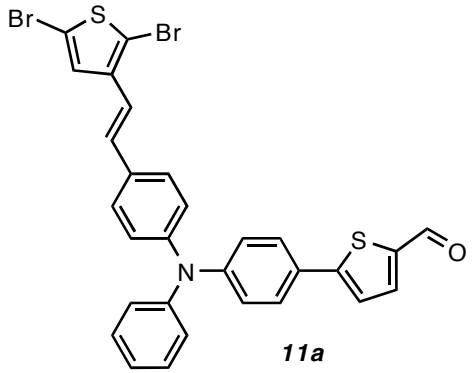

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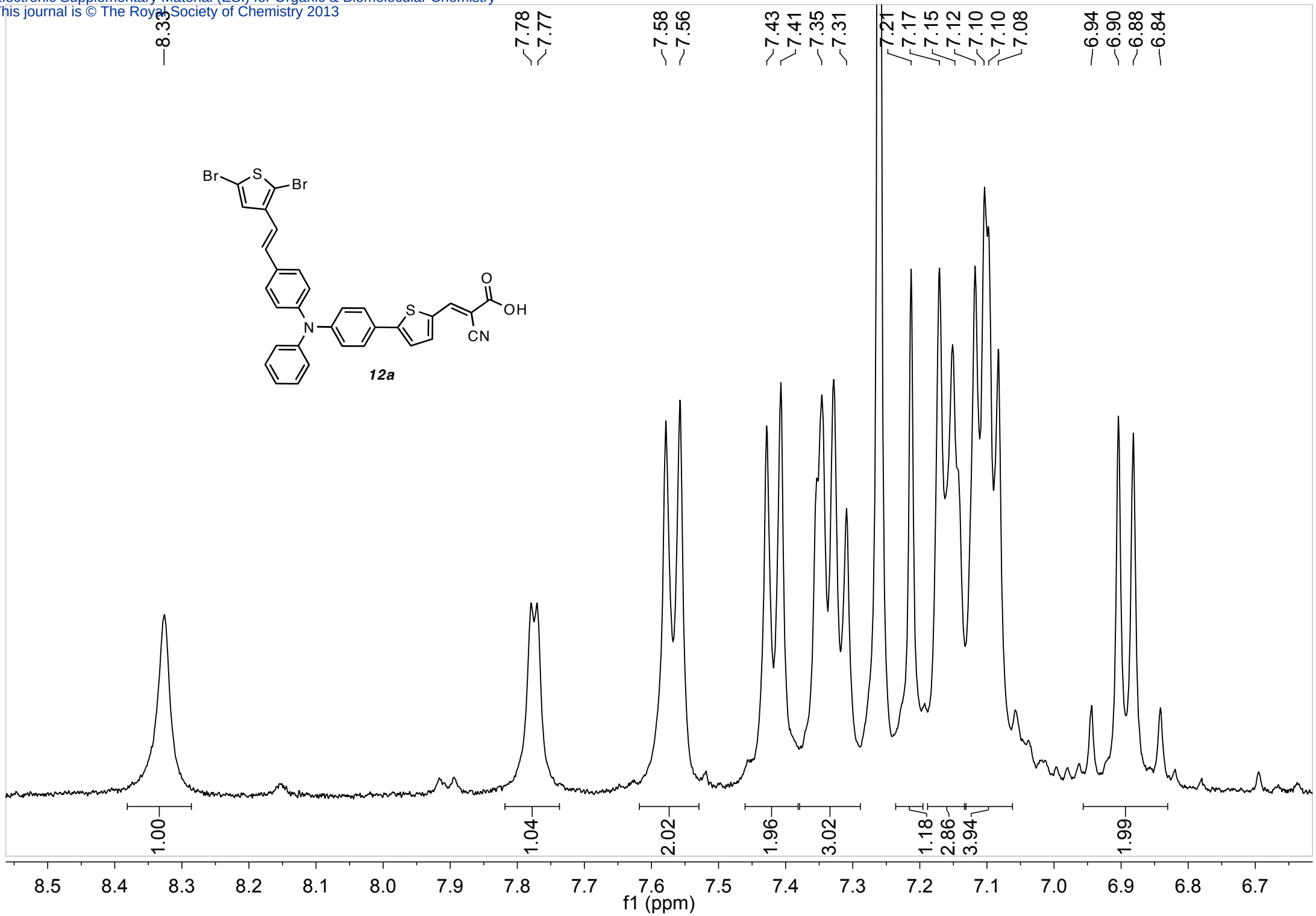

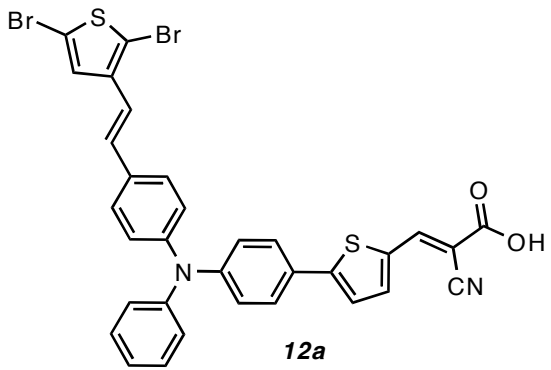

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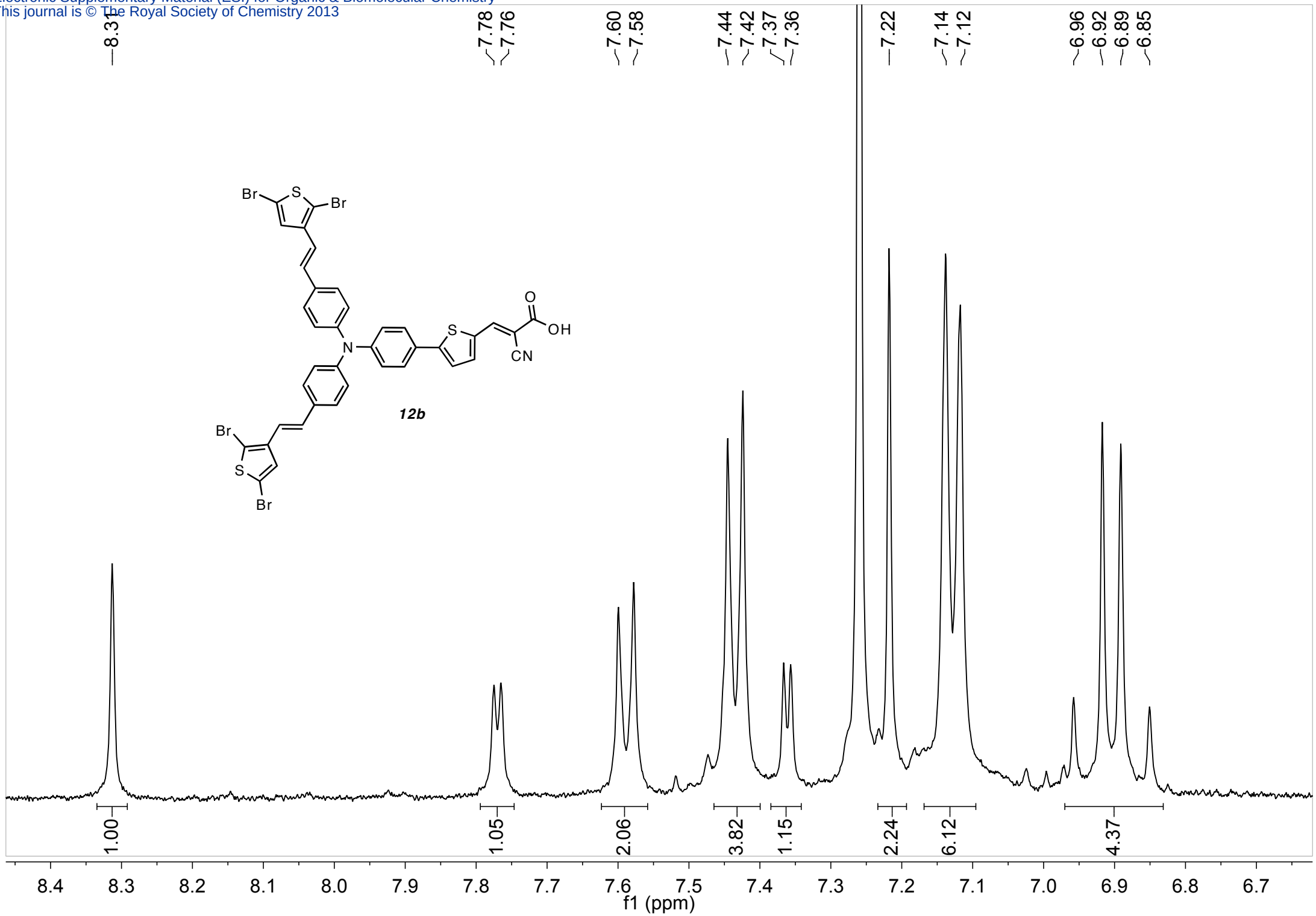

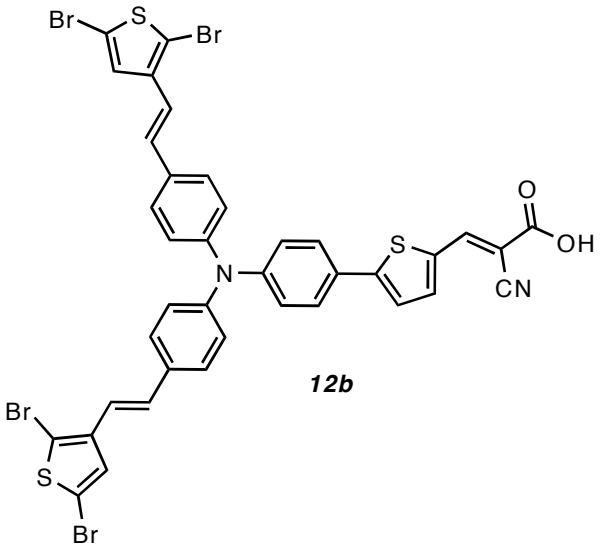

12b