Supporting Information

Molecular design of new organic sensitizers based on thieno[1,4]benzothiazine for dye-sensitized solar cells

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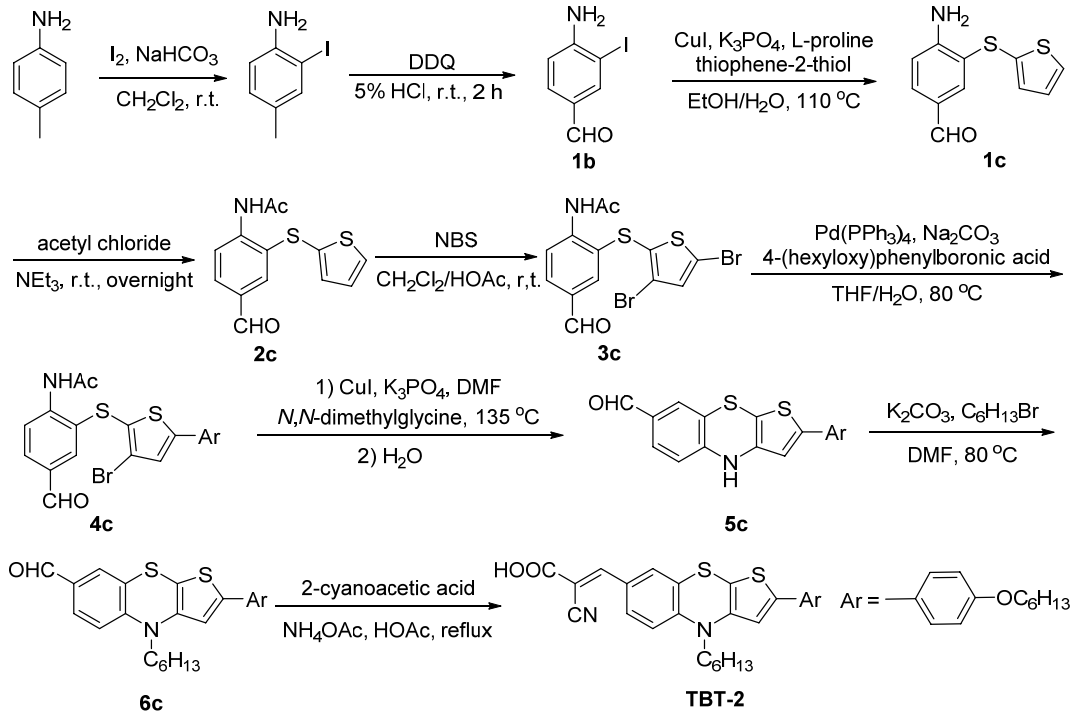
1. Synthetic procedures of TBT-2



Scheme S1. Synthetic route of **TBT-2**

2-Iodo-4-methylaniline

This compound was prepared according to the reported procedure.[1] To a solution of 4-methylaniline (10.70 g, 100 mmol) in CH_2Cl_2 (50 mL) was added the solution of $NaHCO_3$ (10.10 g, 120 mmol) in water (100 mL), and then I_2 (25.50 g, 100 mmol) was added. The mixture was stirred at room temperature overnight. Then the mixture was treated with aqueous $NaHSO_3$ and extracted with CH_2Cl_2 two times. The combined organic layers were washed with water and saturated brine, respectively, dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (20/1, v/v) as the eluent to give the product as a brown solid (22.03 g, 94% yield). M.p.: 35-37 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.21 (s, 3H), 3.94 (s, 2H), 6.66 (d, J = 8.4 Hz, 1H), 6.95 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.47 (d, J = 1.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0, 84.5, 114.8, 129.7, 130.2, 139.2, 144.4 ppm.

HRMS (ESI^+): calcd for C_7H_9IN $[M+H]^+$ 233.9780, found 233.9782.

4-Amino-3-iodobenzaldehyde (1b)

This compound was prepared according to the reported procedure.[2] 2-Iodo-4-methylaniline (3.95 g, 17.0 mmol) was added to a stirred 5% aq. HCl. After the solid was absolutely dissolved, DDQ (7.95 g, 35.0 mmol) was slowly added. The mixture was stirred at room temperature for 2 hours and then treated with dilute NaOH (pH = 10) and extracted with CH_2Cl_2 three times. The combined organic layers were washed with water and saturated brine, respectively, dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (8/1, v/v) as the eluent to give the product as a yellow solid (3.43 g, 82% yield). M.p.: 104-106 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.74 (s, 2H), 6.76 (d, J = 8.4 Hz, 1H), 7.66 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 8.15 (d, J = 2.0 Hz, 1H), 9.67 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 82.7, 113.6, 129.1, 131.5, 142.1, 152.2, 189.1 ppm. HRMS (ESI^+): calcd for C_7H_7INO $[M+H]^+$ 247.9572, found 247.9574.

4-Amino-3-(thiophen-2-ylthio)benzaldehyde (1c)

To a mixture of compound **1b** (63 mg, 0.25 mmol), CuI (9.6 mg, 0.05 mmol), L-proline (11.6 mg, 0.10 mmol), and $K_3PO_4 \cdot 7H_2O$ (127 mg, 0.38 mmol) in H_2O/EtOH (1/1, v/v, 3.0 mL) under an N_2 atmosphere, thiophene-2-thiol (25 μL, 0.26 mmol) was added slowly. The mixture was stirred and heated at 110 °C for 10 hours. After cooling the solution, EtOH was removed under vacuum. Then the mixture was quenched with water and extracted with EtOAc two times. The combined organic layers were washed with saturated Na_2CO_3 and water, respectively, dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (6/1, v/v) as the eluent to give the product as colorless oil (48 mg, yield 82%). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.00 (s, 2H), 6.75 (d, J = 8.4 Hz, 1H), 6.96 (dd, J = 5.6 Hz, 3.6 Hz, 1H), 7.17 (dd, J = 3.6 Hz, 1.2 Hz, 1H), 7.31 (dd, J = 5.2 Hz, 1.2 Hz, 1H), 7.66 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.93 (d, J = 2.0 Hz, 1H), 9.71 (s, 1H) ppm. ^{13}C NMR

(100 MHz, $CDCl_3$): δ = 114.9, 118.5, 127.8, 128.0, 129.3, 132.1, 132.4, 133.1, 138.5, 152.7, 189.9 ppm. HRMS (ESI^+): calcd for $C_{11}H_{10}NOS_2$ $[M+H]^+$ 236.0204, found 236.0204.

***N*-(4-Formyl-2-(thiophen-2-ylthio)phenyl)acetamide (2c)**

1c (1.00 g, 4.25 mmol) was diluted in 50 mL CH_2Cl_2 together with Et_3N (1.2 mL, 8.5 mmol). Acetyl chloride (0.6 mL, 8.5 mmol) was added dropwise at room temperature under strong magnetic stirring. The mixture was stirred at room temperature for 4 hours, and then quenched with water and extracted with CH_2Cl_2 two times. The combined organic layers were washed with saturated brine and water, respectively, dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (5/1, v/v) as the eluent to give the product as a white solid (1.05 g, 89% yield). M.p.: 106-108 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 3H), 7.01 (dd, J = 5.2 Hz, 3.6 Hz, 1H), 7.22 (dd, J = 3.6 Hz, 1.2 Hz, 1H), 7.38 (dd, J = 5.2 Hz, 1.2 Hz, 1H), 7.83 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 8.04 (d, J = 2.0 Hz, 1H), 8.46 (br. s, 1H), 8.56 (d, J = 8.4 Hz, 1H), 9.87 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.2, 120.6, 128.1, 130.6, 131.3, 132.2, 132.4, 133.8, 135.3, 143.4, 168.6, 190.4 ppm. HRMS (ESI^+): calcd for $C_{13}H_{12}NO_2S_2$ $[M+H]^+$ 278.0309, found 278.0306.

***N*-(2-(3,5-Dibromothiophen-2-ylthio)-4-formylphenyl)acetamide (3c)**

To a stirred solution of **2c** (0.83 g, 3.0 mmol) in the mixture of HOAc/CH_2Cl_2 (1/1, v/v, 30 mL), NBS (1.12 g, 6.3 mmol) was added slowly in portions. After this addition, the mixture was stirred at room temperature for 6 hours. Then the mixture was quenched with water and extracted with EtOAc two times. The combined organic layers were washed with water, saturated Na_2CO_3 and water, respectively, dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (5/1, v/v) as the eluent to give the product as a white solid (1.07 g, 82% yield). M.p.: 136-138 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.31 (s, 3H), 6.98 (s, 1H), 7.89 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 8.14 (d, J = 2.0 Hz, 1H), 8.56 (br. s, 1H), 8.64 (d, J = 8.8 Hz, 1H),

9.90 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.5, 116.6, 117.2, 120.6, 122.3, 130.0, 132.3, 133.0, 133.1, 136.6, 144.1, 168.8, 190.1 ppm. HRMS (ESI^+): calcd for $C_{13}H_{10}Br_2NO_2S_2$ $[M+H]^+$ 433.8520, found 433.8520.

_N_-(2-(3-Bromo-5-(4-(hexyloxy)phenyl)thiophen-2-ylthio)-4-formylphenyl)acetamide (4c)

A mixture of compound **3c** (218 mg, 0.5 mmol), 4-(hexyloxy)phenylboronic acid (133 mg, 0.6 mmol), $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) and Na_2CO_3 (212 mg, 2.0 mmol) were dissolved in THF/H_2O (4/1, v/v, 5.0 mL). Then, the mixture was heated at 80 °C for 10 hours under an N_2 atmosphere. After cooling, THF was removed under vacuum. The reaction mixture was poured into water and extracted with CH_2Cl_2 two times. The combined organic layers were washed with water and dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (6/1, v/v) as the eluent to give the product as a white solid (174 mg, 65% yield). M.p.: 126-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 6.8 Hz, 3H), 1.31-1.34 (m, 4H), 1.41-1.48 (m, 2H), 1.74-1.81 (m, 2H), 2.33 (s, 3H), 3.95 (t, J = 6.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 7.05 (s, 1H), 7.37 (d, J = 8.8 Hz, 2H), 7.87 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 8.19 (d, J = 1.6 Hz, 1H), 8.64-8.67 (m, 2H), 9.90 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 22.7, 25.5, 25.8, 29.3, 31.7, 68.3, 115.1, 118.4, 120.4, 123.1, 124.9, 125.0, 125.8, 127.1, 132.2, 132.8, 136.7, 144.1, 149.2, 160.0, 168.9, 190.3 ppm. HRMS (ESI^+): calcd for $C_{25}H_{27}BrNO_3S_2$ $[M+H]^+$ 532.0616, found 532.0625.

2-(4-(Hexyloxy)phenyl)-4*H*-benzo[*b*]thieno[3,2-*e*][1,4]thiazine-7-carbaldehyde (5c)

A mixture of compound **4c** (134 mg, 0.25 mmol), CuI (9.6 mg, 0.05 mmol), *N*,*N*-dimethylglycine hydrochloride (7.0 mg, 0.05 mmol) and K_3PO_4 (108 mg, 0.5 mmol) were dissolved in DMF (4.0 mL) under an N_2 atmosphere and heated at 135 °C for 20 hours. After cooling the solution, H_2O (2.0 mL) was added and the mixture was heated again to 80 °C for 4 hours. The reaction mixture was cooled to ambient temperature, diluted with 10 mL of water, and then filtered through a

filtration funnel to get a yellow solid. The solid was used as the substrate without further purification. HRMS (ESI^+): calcd for $C_{23}H_{24}NO_2S_2$ $[M+H]^+$ 410.1248, found 410.1241.

4-Hexyl-2-(4-(hexyloxy)phenyl)-4*H*-benzo[*b*]thieno[3,2-*e*][1,4]thiazine-7-carbaldehyde (6c)

A mixture of compound **5c** (206 mg, 0.5 mmol) and K_2CO_3 (690 mg, 5.0 mmol) were dissolved in DMF (8.0 mL) under an N_2 atmosphere and heated to 80 °C. After 30 min, *n*-$C_6H_{13}Br$ (175 μL, 1.3 mmol) was added. The mixture was kept at 80 °C for 12 h under an N_2 atmosphere. Then the mixture was quenched with water and extracted with EtOAc two times. The combined organic layers were washed with water and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (20/1, v/v) as the eluent to give the product as yellow oil (211 mg, 85% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.91 (m, 6H), 1.34-1.35 (m, 8H), 1.46 (m, 4H), 1.78-1.80 (m, 4H), 3.75 (t, *J* = 7.2 Hz, 2H), 3.96 (t, *J* = 6.8 Hz, 2H), 6.74-6.75 (m, 2H), 6.89 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.44 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 9.72 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 14.2, 22.8, 25.8, 26.6, 26.9, 29.3, 31.6, 31.7, 48.8, 68.3, 106.2, 113.0, 113.1, 115.1, 121.7, 126.5, 126.6, 128.6, 130.9, 131.1, 142.7, 143.2, 150.2, 159.2, 189.6 ppm. HRMS (ESI^+): calcd for $C_{29}H_{36}NO_2S_2$ $[M+H]^+$ 494.2187, found 494.2182.

(*E*)-2-Cyano-3-(4-hexyl-2-(4-(hexyloxy)phenyl)-4H-benzo[*b*]thieno[3,2-*e*][1,4]thiazin-7-yl)acrylic acid (TBT-2)

This material was prepared according to the reported method with some modification.[3] A mixture of compound **6c** (740 mg, 1.5 mmol) and cyanoacetic acid (631 mg, 7.5 mmol) in acetic acid (120 mL) was refluxed in the presence of ammonium acetate (1.27 g, 16.5 mmol) overnight under an N_2 atmosphere. Then, water was added and extracted with CH_2Cl_2. Next, the solvent was removed under vacuum and the crude compound was purified by column chromatography on silica gel eluting with petroleum ether/EtOAc/HOAc (100/50/1, v/v/v) to give the product

as a dark purple solid (489 mg, 58% yield). M.p.: 228-230 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.83-0.88 (m, 6H), 1.25-1.30 (m, 8H), 1.38-1.43 (m, 4H), 1.63-1.71 (m, 4H), 3.85 (t, J = 7.2 Hz, 2H), 3.96 (t, J = 6.4 Hz, 2H), 6.93-6.95 (m, 2H), 7.02 (d, J = 9.2 Hz, 1H), 7.25 (s, 1H), 7.50 (d, J = 8.8 Hz, 2H), 7.66 (d, J = 2.0 Hz, 1H), 7.87 (dd, J = 8.8 Hz, J = 2.0 Hz, 1H), 8.08 (s, 1H), 13.67 (br. s, 1H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ = 13.86, 13.91, 22.08, 22.13 25.2, 25.6, 26.3, 28.6, 30.9, 31.0, 47.5, 67.6, 98.6, 103.6, 114.0, 114.2, 114.9, 116.9, 119.4, 125.2, 125.6, 126.1, 129.5, 132.3, 141.8, 142.4, 148.0, 152.1, 158.6, 163.9 ppm. HRMS (ESI$^+$): calcd for $C_{32}H_{37}N_2O_3S_2$ $[M+H]^+$ 561.2246, found 561.2239. Anal. calcd for $C_{32}H_{36}N_2O_3S_2$ (%): C, 68.54; H, 6.47; N, 5.00; S, 11.43. found: C, 68.30; H, 6.48; N, 5.50; S, 10.69.

2. Synthetic procedures of TBT-3

4-Amino-3-(thiophen-3-ylthio)benzaldehyde (2b)

To a mixture of compound **1b** (4.94 g, 20.0 mmol), CuI (384 mg, 2.0 mmol), L-proline (464 mg, 4.0 mmol), and $K_3PO_4 \cdot 7H_2O$ (10.14 g, 30.0 mmol) in H_2O/EtOH (1/1, v/v, 100 mL) under an N_2 atmosphere, thiophene-3-thiol (2.49 g, 21.0 mmol) was added slowly. The mixture was vigorously stirred and heated at 110 °C for 10 hours. After cooling the solution, EtOH was removed under vacuum. Then the mixture was quenched with water and extracted with EtOAc two times. The combined organic layers were washed with saturated Na_2CO_3 and water, respectively, dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (6/1, v/v) as the eluent to give the product as a yellow solid (3.62g, 77% yield). M.p.: 80-82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.98 (s, 2H) , 6.79 (d, J = 8.4 Hz, 1H), 6.88 (dd, J = 4.8 Hz, 0.8 Hz, 1H) , 6.99 (d, J = 1.6 Hz, 1H), 7.31 (dd, J = 4.8 Hz, 2.8 Hz, 1H) , 7.71 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.95 (d, J = 1.6 Hz, 1H), 9.72 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 114.8, 116.3, 122.3, 127.0, 127.9, 128.3, 130.4, 132.2, 139.7, 153.3, 189.9 ppm. HRMS (ESI$^+$): calcd for $C_{11}H_{10}NOS_2$ $[M+H]^+$ 236.0204, found 236.0205.

N-(4-Formyl-2-(thiophen-3-ylthio)phenyl)acetamide (3b)

2b (3.53 g, 15 mmol) was diluted in 100 mL CH_2Cl_2 together with Et_3N (4.2 mL, 30 mmol). Acetyl chloride (2.2 mL, 30 mmol) was added dropwise at room temperature under strong magnetic stirring. The mixture was stirred at room temperature for 4 hours, then quenched with water and extracted with CH_2Cl_2 two times. The combined organic layers were washed with saturated brine and water, respectively, dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (5/1, v/v) as the eluent to give the product as a white solid (3.22 g, 78% yield). M.p.: 118-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.18 (s, 3H), 6.86 (dd, J = 4.8 Hz, 1.2 Hz, 1H), 7.10 (dd, J = 3.2 Hz, 1.6 Hz, 1H), 7.35 (dd, J = 4.8 Hz, 2.8 Hz, 1H), 7.86 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 8.05 (d, J = 1.6 Hz, 1H), 8.44 (br. s, 1H), 8.61 (d, J = 8.4 Hz, 1H), 9.87 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.1, 120.4, 122.7, 124.3, 127.8, 128.5, 128.9, 132.26, 132.29, 136.3, 144.0, 168.7, 190.4 ppm. HRMS (ESI^+): calcd for $C_{13}H_{12}NO_2S_2$ $[M+H]^+$ 278.0309, found 278.0300.

***N*-(2-(2-Bromothiophen-3-ylthio)-4-formylphenyl)acetamide (4b)**

To a stirred solution of **3b** (1.11 g, 4.0 mmol) in the mixture of HOAc-CH_2Cl_2 (1/1, v/v, 40 mL), NBS (785 mg, 4.4 mmol) was added slowly in portions. After this addition, the mixture was stirred for 6 hours. Then the mixture was quenched with water and extracted with EtOAc two times. The combined organic layers were washed with water, saturated Na_2CO_3 and water respectively, dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was crystalized by petroleum ether/EtOH to give the product as a white solid (1.07 g, 75% yield). M.p.: 132-134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3H), 6.62 (d, J = 6.0 Hz, 1H), 7.23 (d, J = 6.0 Hz, 1H), 7.87 (dd, J = 8.4 Hz, 1.2 Hz, 1H), 8.13 (s, 1H), 8.46 (br. s, 1H), 8.63 (d, J = 8.8 Hz, 1H), 9.89 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.3, 113.8, 120.3, 122.0, 127.6, 129.6, 130.5, 132.2, 132.8, 136.7, 144.4, 168.8, 190.3 ppm. HRMS (ESI^+): calcd for $C_{13}H_{11}BrNO_2S_2$ $[M+H]^+$ 355.9415, found 355.9416.

9-Acetyl-9*H*-benzo[*b*]thieno[2,3-*e*][1,4]thiazine-6-carbaldehyde (5b)

A mixture of compound **4b** (45 mg, 0.125 mmol), CuI (4.8 mg, 0.025 mmol),

N,N-dimethylglycine hydrochloride (3.6 mg, 0.025 mmol) and K_3PO_4 (108 mg, 0.5 mmol) were dissolved in dioxane (4.0 mL) under an N_2 atmosphere and heated at 105 °C for 20 hours. After cooling, water was added and extracted with CH_2Cl_2 two times. The combined organic layers were washed with water and dried over anhydrous Na_2SO_4. Next, the solvent was removed under vacuum and the crude compound was purified by column chromatography on silica gel using petroleum ether/EtOAc (5/1, v/v) as the eluent to give the product as a white solid (22 mg, 64% yield). M.p.: 138-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 6.82 (d, J = 5.6 Hz, 1H), 7.21 (d, J = 6.0 Hz, 1H), 7.52 (d, J = 7.2 Hz, 1H), 7.79 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.86 (d, J = 1.6 Hz, 1H), 9.96 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.5, 123.4, 124.0, 127.2, 128.3, 129.2, 134.0, 134.7, 135.7, 143.6, 169.3, 190.4 ppm. HRMS (ESI^+): calcd for $C_{13}H_{10}NO_2S_2$ $[M+H]^+$ 276.0153, found 276.0158.

9-Acetyl-2-bromo-9*H*-benzo[*b*]thieno[2,3-*e*][1,4]thiazine-6-carbaldehyde (6b)

To a stirred solution of **5b** (138 mg, 0.5 mmol) in the mixture of HOAc-CH_2Cl_2 (1:1, v/v, 10.0 mL), NBS (98 mg, 0.55 mmol) was added slowly in portions. After this addition the mixture was stirred at room temperature for 6 hours. Then the mixture was quenched with water and extracted with EtOAc two times. The combined organic layers were washed with water, saturated Na_2CO_3 and water, respectively, dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was crystalized by ether/EtOH to give the product as a white solid (135 mg, 76% yield). M.p.: 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 6.82 (s, 1H), 7.44 (d, J = 5.6 Hz, 1H), 7.80 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.85 (d, J = 1.6 Hz, 1H), 9.97 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.3, 110.6, 125.5, 126.6, 128.5, 129.3, 133.4, 134.9, 135.0, 143.0, 169.0, 190.2 ppm. HRMS (ESI^+): calcd for $C_{13}H_9BrNO_2S_2$ $[M+H]^+$ 353.9258, found 353.9259.

9-Acetyl-2-(4-(hexyloxy)phenyl)-9*H*-benzo[*b*]thieno[2,3-*e*][1,4]thiazine-6-carbald ehyde (7b)

A mixture of compound **6b** (213 mg, 0.6 mmol), 4-(hexyloxy)phenylboronic acid (167 mg, 0.75 mmol), $Pd(PPh_3)_4$ (35 mg, 0.03 mmol) and Na_2CO_3 (255 mg, 2.4 mmol)

were dissolved in THF/H_2O (4/1, v/v, 10.0 mL). Then, the mixture was heated at 85 °C for 10 hours under an N_2 atmosphere. After cooling, the solvent was removed under vacuum. The reaction mixture was diluted with water and extracted with CH_2Cl_2 two times. The combined organic layers were washed with water and dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (6/1, v/v) as the eluent to give the product as a white solid (249 mg, 92% yield). M.p.: 74-76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.2 Hz, 3H), 1.32-1.35 (m, 4H), 1.42-1.50 (m, 2H), 1.75-1.82 (m, 2H), 2.45 (s, 3H), 3.97 (t, J = 6.4 Hz, 2H), 6.89-6.91 (m, 3H), 7.42-7.44 (m, 2H), 7.56 (d, J = 6.8 Hz, 1H), 7.80 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 7.88 (d, J = 1.6 Hz, 1H), 9.97 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.2, 22.7, 23.6, 25.8, 29.3, 31.7, 68.3, 115.1, 117.9, 125.8, 127.1, 127.3, 128.3, 129.3, 133.5, 133.9, 134.7, 143.0, 143.6, 159.6, 169.4, 190.4 ppm. HRMS (ESI^+): calcd for $C_{25}H_{26}NO_3S_2$ $[M+H]^+$ 452.1354, found 452.1360.

9-Hexyl-2-(4-(hexyloxy)phenyl)-9*H*-benzo[*b*]thieno[2,3-*e*][1,4]thiazine-6-carbalde hyde (8b)

A mixture of compound **7b** (720 mg, 1.6 mmol) and K_2CO_3 (2.21 g, 16 mmol) were dissolved in DMF/H_2O (v/v, 4/1, 15.0 mL) under an N_2 atmosphere and heated to 85 °C overnight. After cooling, the solvent was removed under vacuum. Then, the residue was dissolved in anhydrous DMF under an N_2 atmosphere and followed by the addition of n-$C_6H_{13}Br$ (560 μL, 4.0 mmol). The mixture was kept at 85 °C for 12 hours under an N_2 atmosphere. Then the mixture was quenched with water and extracted with EtOAc two times. The combined organic layers were washed with water and dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc (20/1, v/v) as the eluent to give the product as an orange red solid (640 mg, 81% yield). M.p.: 68-70 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, J = 6.8 Hz, 6H), 1.34-1.36 (m, 8H), 1.46-1.47 (m, 4H), 1.76-1.89 (m, 4H), 3.71 (t, J = 7.6 Hz, 2H), 3.96 (t, J = 6.8 Hz, 2H), 6.57 (s, 1H), 6.69 (d, J = 8.4 Hz, 1H), 6.87 (d, J = 8.4

Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 7.41 (d, J = 1.6 Hz, 1H), 7.52 (dd, J = 8.4 Hz, 2.0 Hz, 1H), 9.72 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1, 14.2, 22.7, 22.8, 25.9, 26.5, 26.7, 29.3, 31.5, 31.7, 51.1, 68.3, 108.6, 112.9, 115.0, 118.9, 122.4, 126.2, 126.4, 128.5, 130.7, 131.5, 135.0, 140.6, 148.9, 158.8, 189.7 ppm. HRMS (ESI^+): calcd for $C_{29}H_{36}NO_2S_2$ $[M+H]^+$ 494.2187, found 494.2180.

(*E*)-2-Cyano-3-(9-hexyl-2-(4-(hexyloxy)phenyl)-9H-benzo[*b*]thieno[2,3-*e*][1,4]thiazin-6-yl)acrylic acid (TBT-3)

To a stirred solution of **8b** (59 mg, 0.12 mmol) and cyanoacetic acid (32 mg, 0.36 mmol) in $CHCl_3$ (10.0 mL) was added piperidine (80 μL, 0.84 mmol). The resulting mixture was refluxed for 20 hours under an N_2 atmosphere, then cooled to room temperature and acidified with 2 M hydrochloric acid aqueous solution. The solution was extracted with $CHCl_3$. Then the organic phase was washed with water and dried over anhydrous Na_2SO_4. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel using petroleum ether/EtOAc/HOAc (100:50:1, v/v/v) to give the product as a blue solid (44 mg, 65% yield). M.p.: 214-216 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.84-0.88 (m, 6H), 1.23-1.30 (m, 8H), 1.36-1.41 (m, 4H), 1.65-1.76 (m, 4H), 3.75 (t, J = 6.8 Hz, 2H), 3.95 (t, J = 6.4 Hz, 2H), 6.90-6.92 (m, 3H), 7.01 (d, J = 8.8 Hz, 1H), 7.41 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 1.6 Hz, 1H), 7.82 (d, J = 9.6 Hz, 1H), 8.06 (s, 1H) ppm. Clear ^{13}C NMR spectrum was not obtained even after overnight collection of data due to the poor solubility of the compound. HRMS (ESI^+): calcd for $C_{32}H_{37}N_2O_3S_2$ $[M+H]^+$ 561.2246, found 561.2244. Anal. calcd for $C_{32}H_{36}N_2O_3S_2$ (%): C, 68.54; H, 6.47; N, 5.00; S, 11.43. found: C, 67.90; H, 6.40; N, 5.55; S, 11.18.

II. Electrochemical properties

The electrochemical properties were recorded by cyclic voltammetry (CV) in CH_2Cl_2 using 0.1 M tetrabutylammonium hexa-fluorophosphate as supporting electrolyte, Pt as the counter electrode, $Ag/AgNO_3$ as a reference electrode, ferrocene/ferricenium (Fc/Fc^+) redox couple as an internal standard at 0.63 V (*vs* NHE).[4] The ground oxidation potential (E_{ox}) corresponding to the highest occupied

molecular orbital (HOMO) and the zero–zero band gaps (E_{0-0}) estimated from the onset of the UV-vis absorption spectra. The excited-state oxidation potential (E_{ox}^{*}) corresponding to the lowest unoccupied molecular orbital (LUMO), calculated from $E_{ox}-E_{0-0}$.

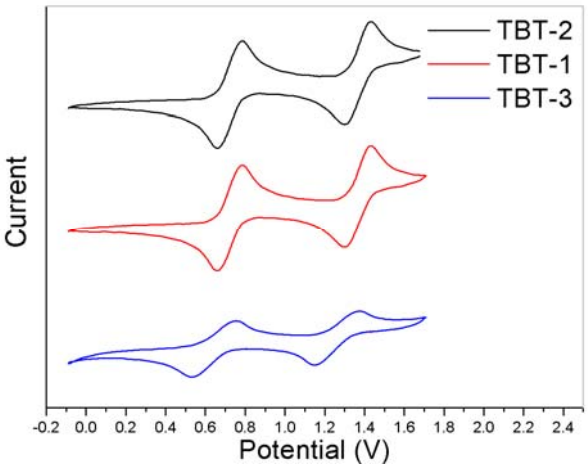


Figure S1. CV curves of three thieno[1,4]-benzothiazine-based dyes.

III. Photophysical and photovoltaic parameters

1) *J–V* curves of TBT-1–3 and PT-C_6 based DSSCs with CDCA

The TiO_2 photoanode was dipped into the solution containing 0.5 mM dye sensitizers in THF with 2.5 mM chenodeoxycholic acid (CDCA) as co-adsorbent for 36 h.

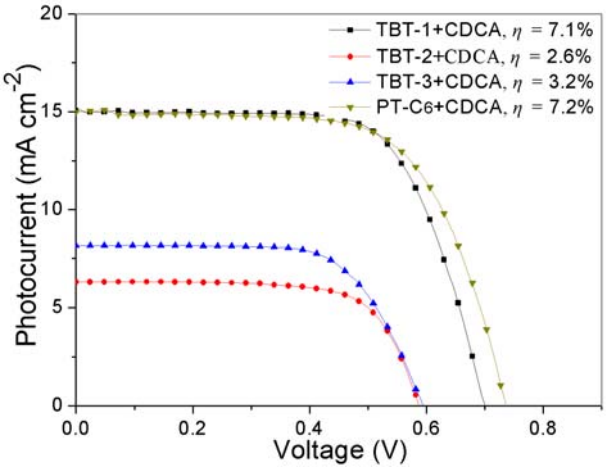


Figure S2. *J–V* curves of **TBT-1–3** and **PT-C_6**-based DSSCs with CDCA

2) The absorption spectra of the dyes desorbed from the TiO_2 photoanodes

Dye adsorption amounts on TiO_2 photoanodes were obtained by using 0.1 M NaOH aqueous-THF (1:1) mixture solutions to desorb the dye on photoanode for 10 min and measuring their UV-vis spectra. The **TBT-1−3** and **PT-C$_6$** standard sample were prepared into 1×10^{-5} M by using 0.1 M NaOH aqueous-THF (1:1) mixture solutions as solvent.

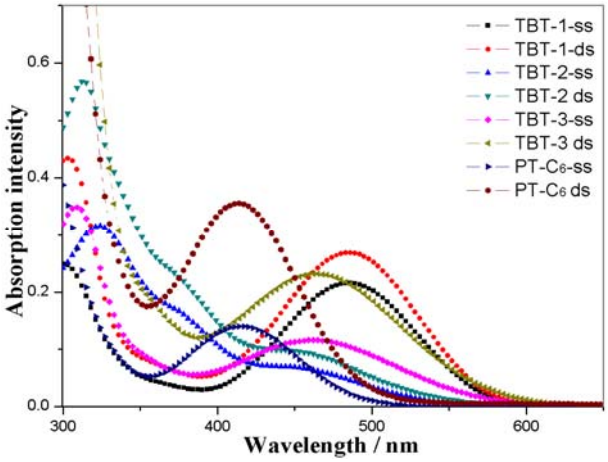


Figure S3. The absorption spectra of the dyes desorbed from the TiO_2 photoanodes (ss = standard sample, ds = desorbed sample)

3) LHE of TBT-1–3 and PT-C$_6$

The light harvesting efficiency (LHE) was calculated from the absorption spectra of dyes loaded on 7 μm TiO_2 films through the relation of LHE = $1-10^{-\alpha}$, where α is the intensity of light absorption on the nanoporous TiO_2 film.[5]

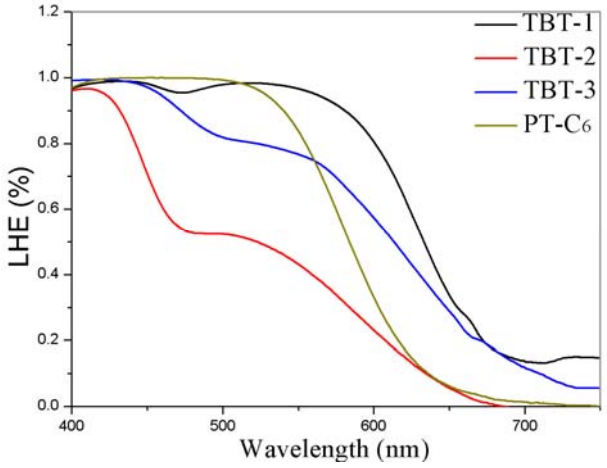


Figure S4. LHE of **TBT-1–3** and **PT-C$_6$**

IV. References

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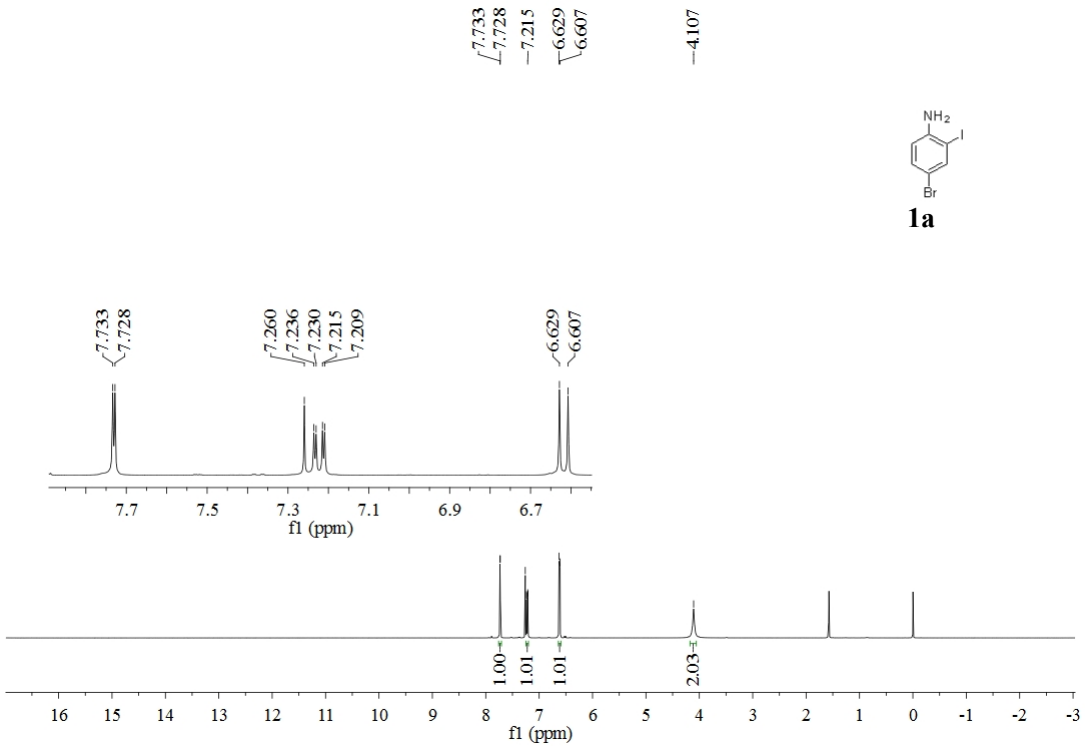
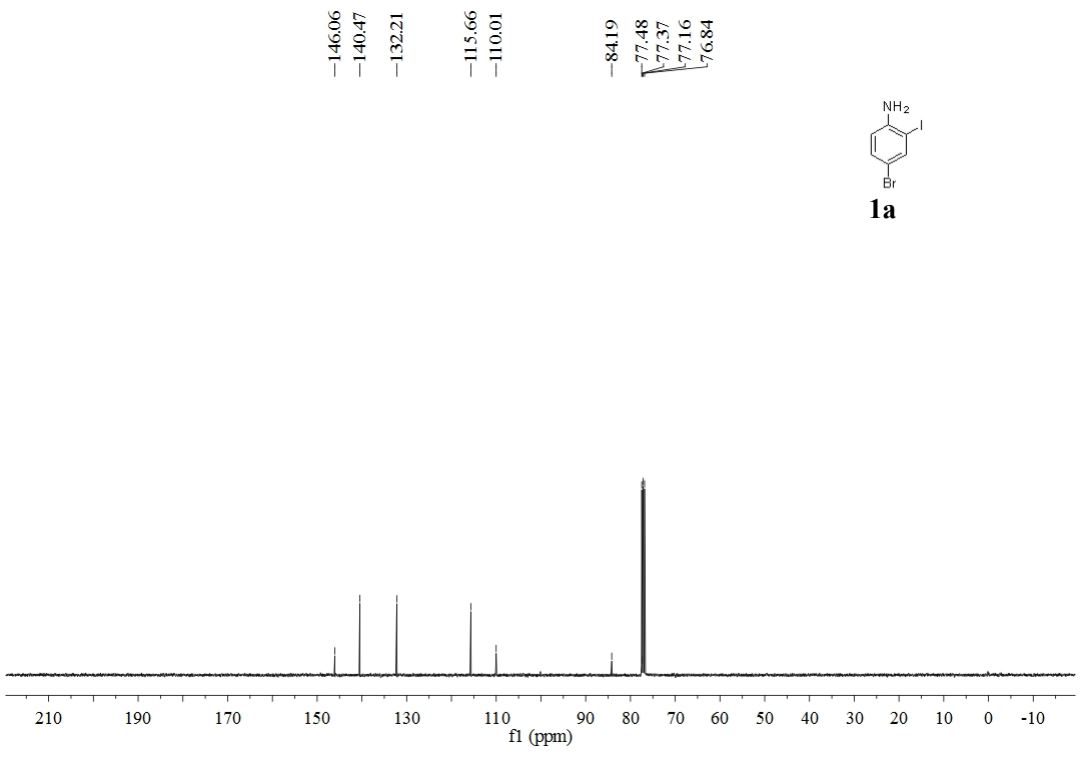
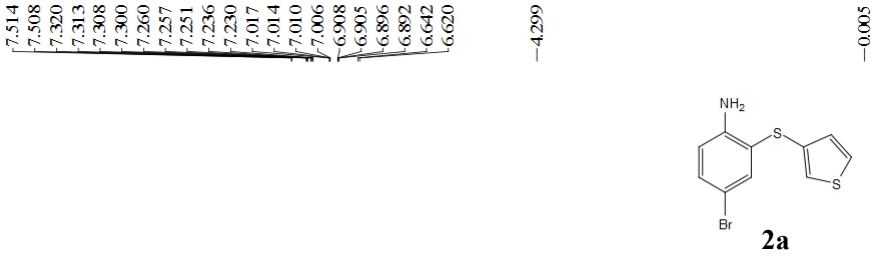
V. Copies of ^{1}H, and ^{13}C NMR spectra



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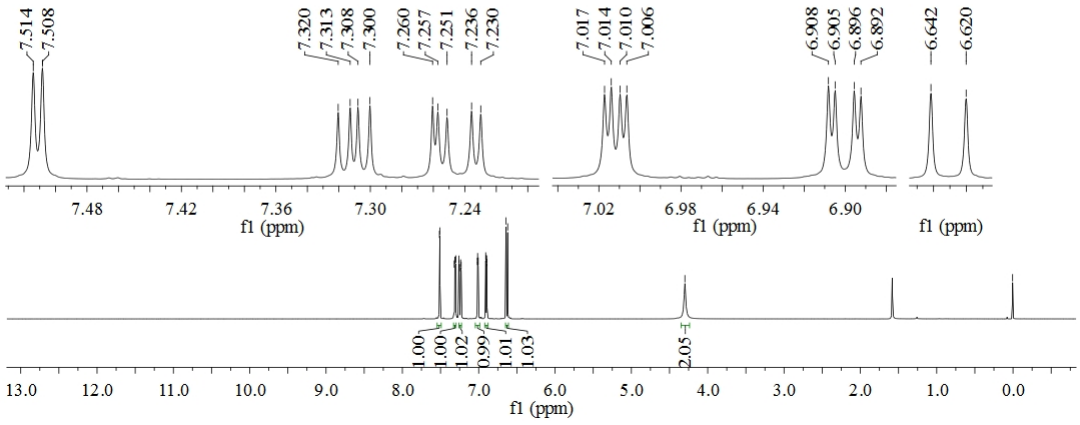
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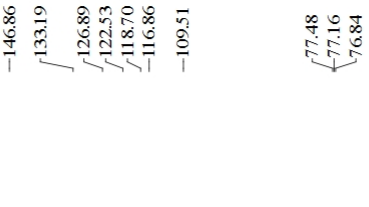
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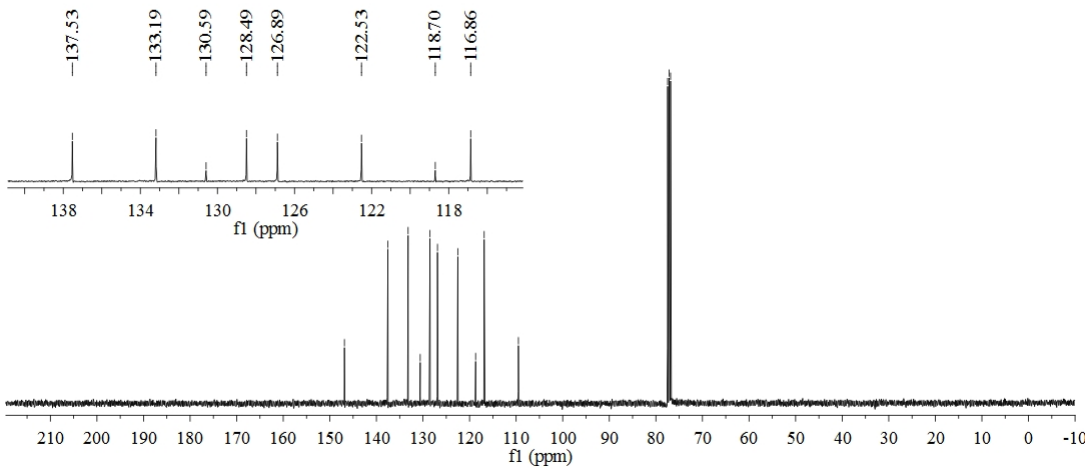
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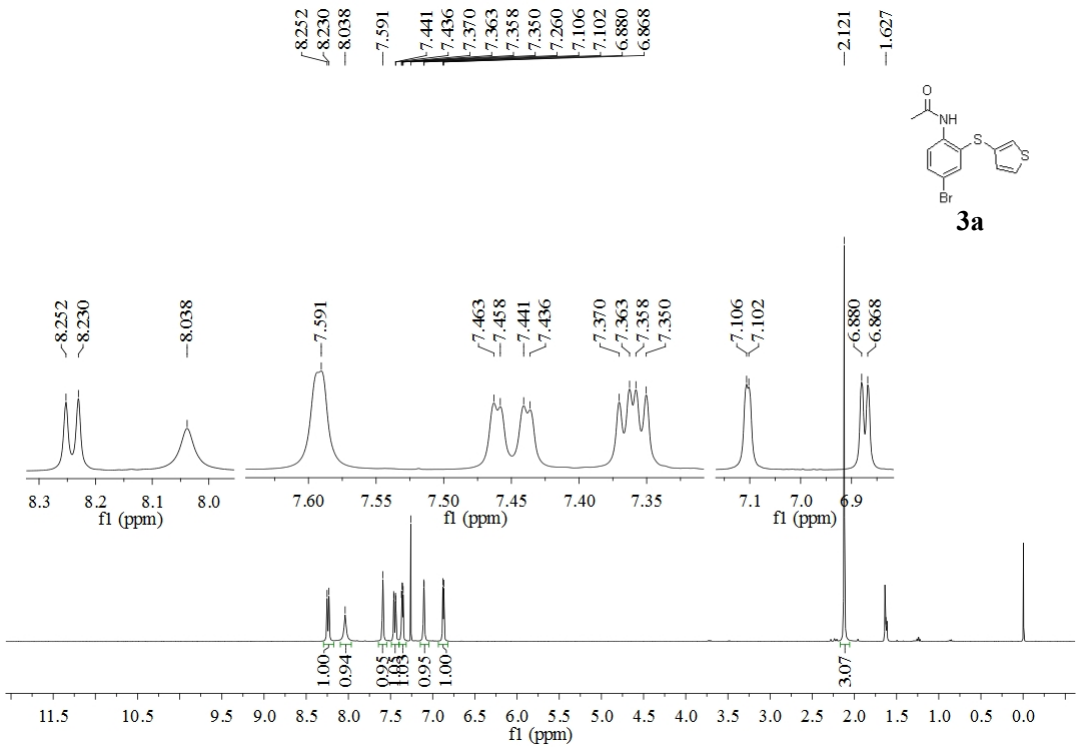
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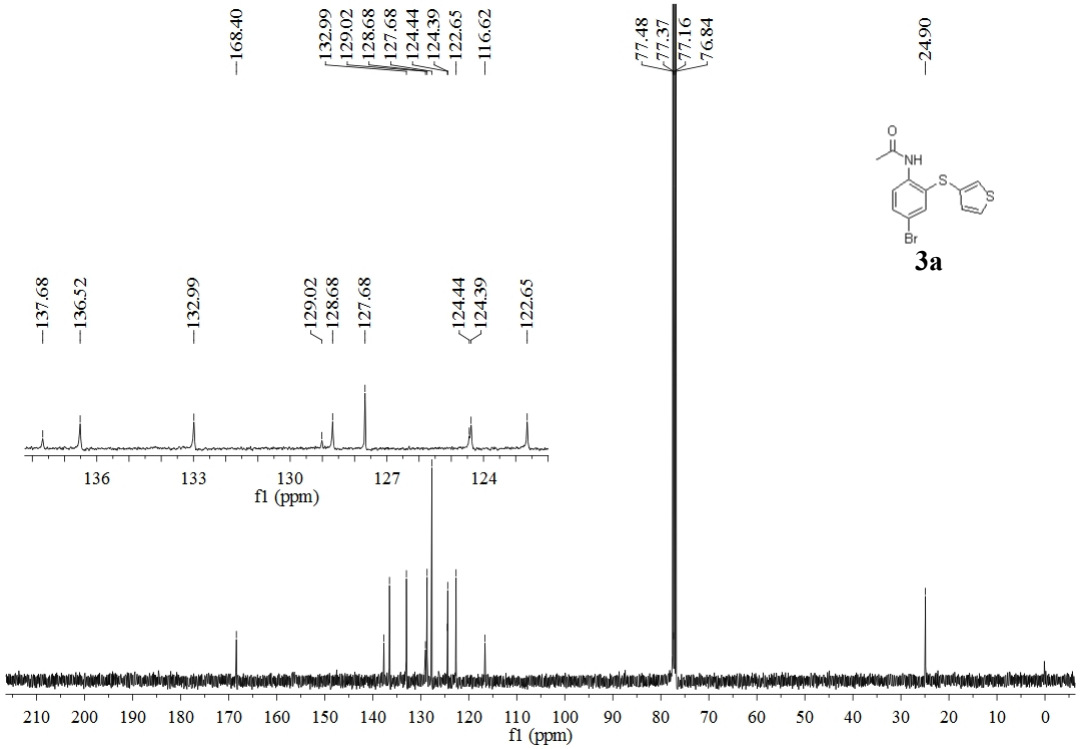
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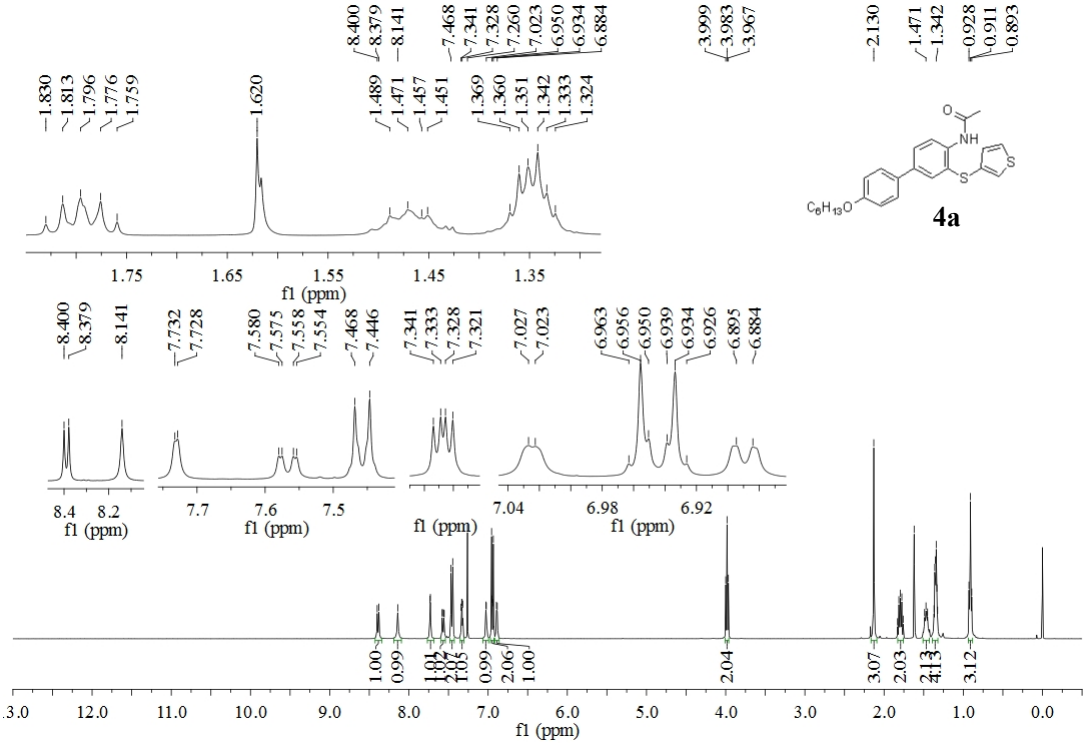
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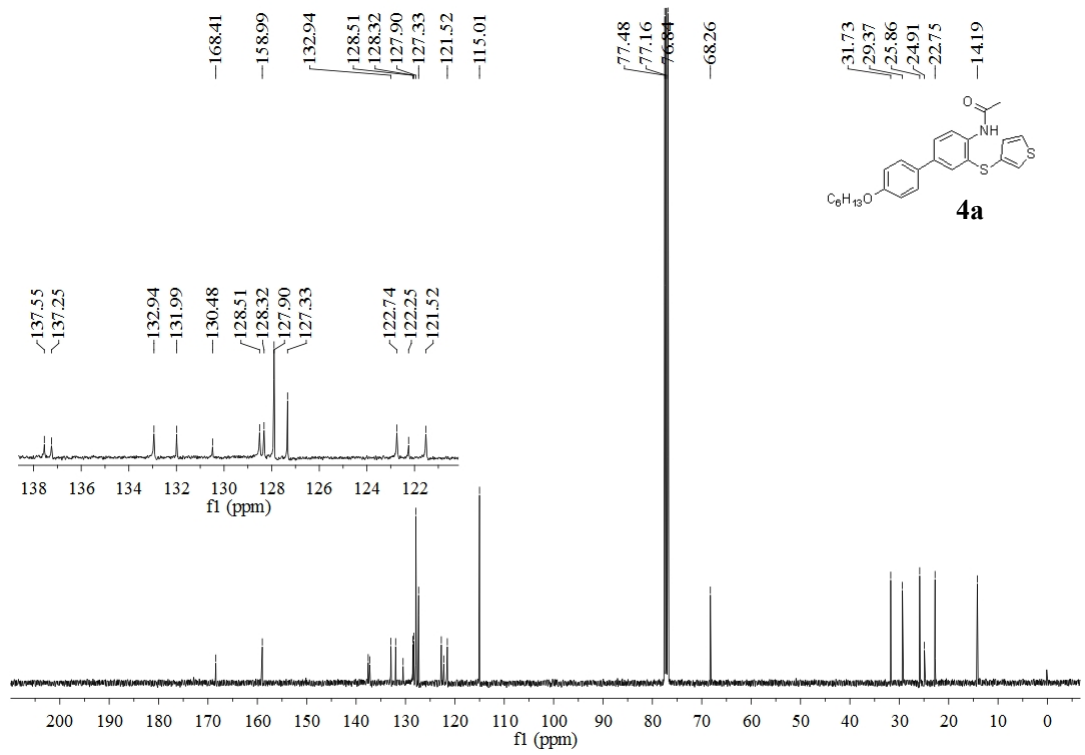
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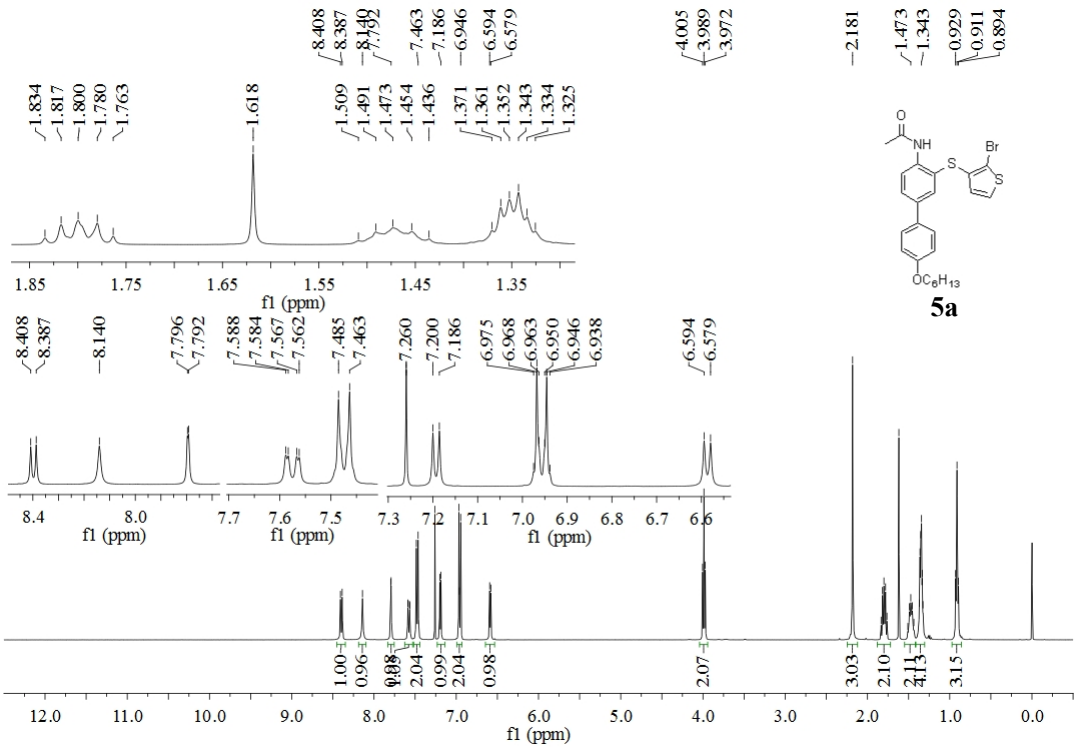
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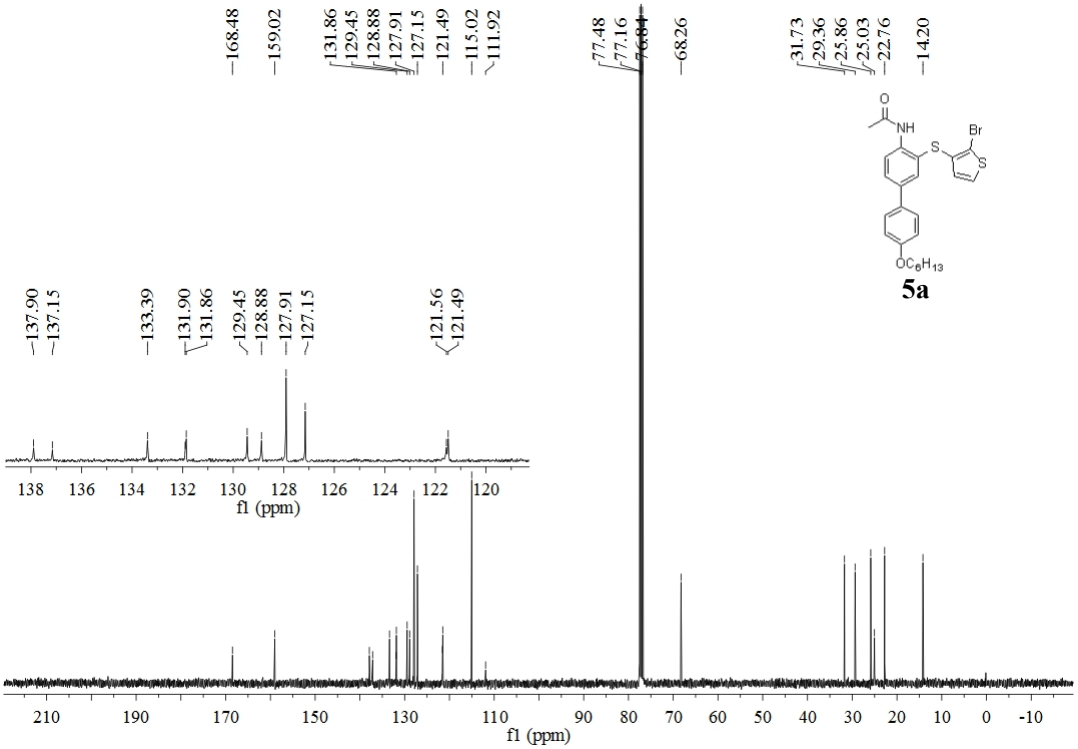
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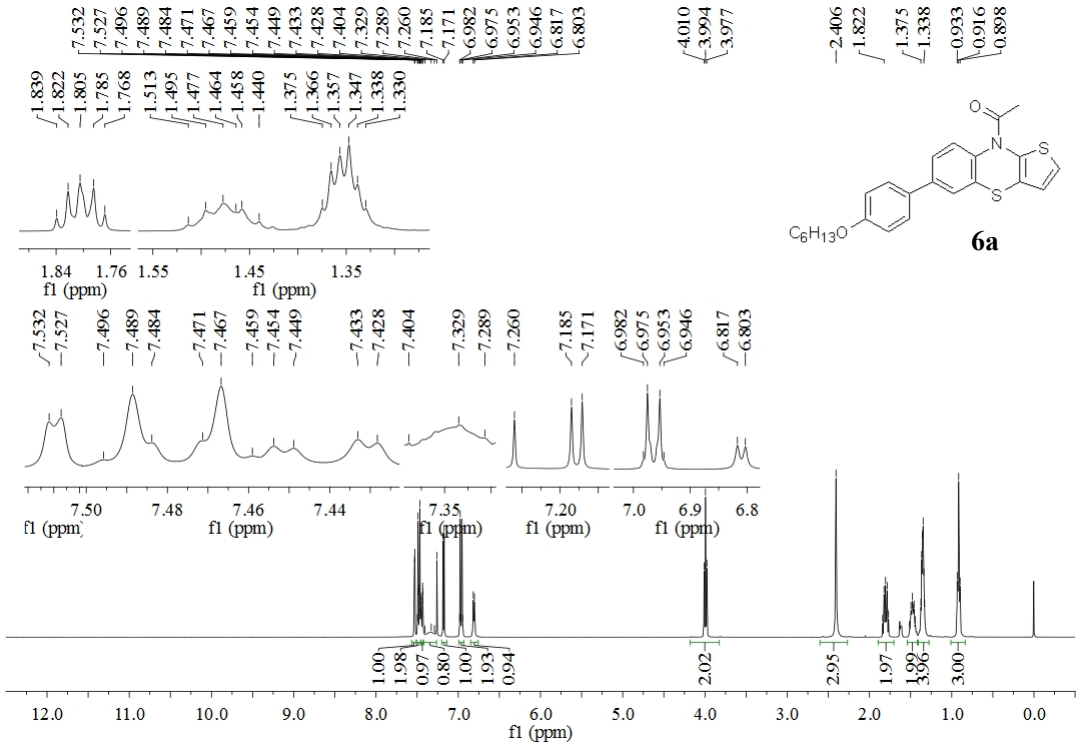
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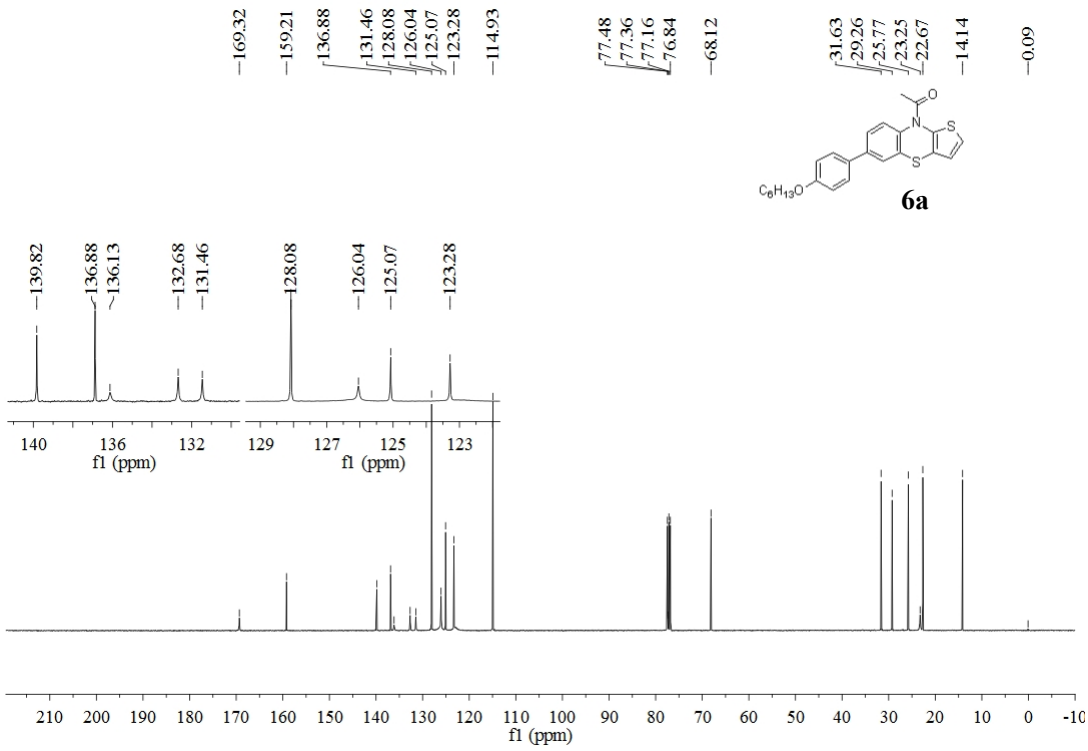
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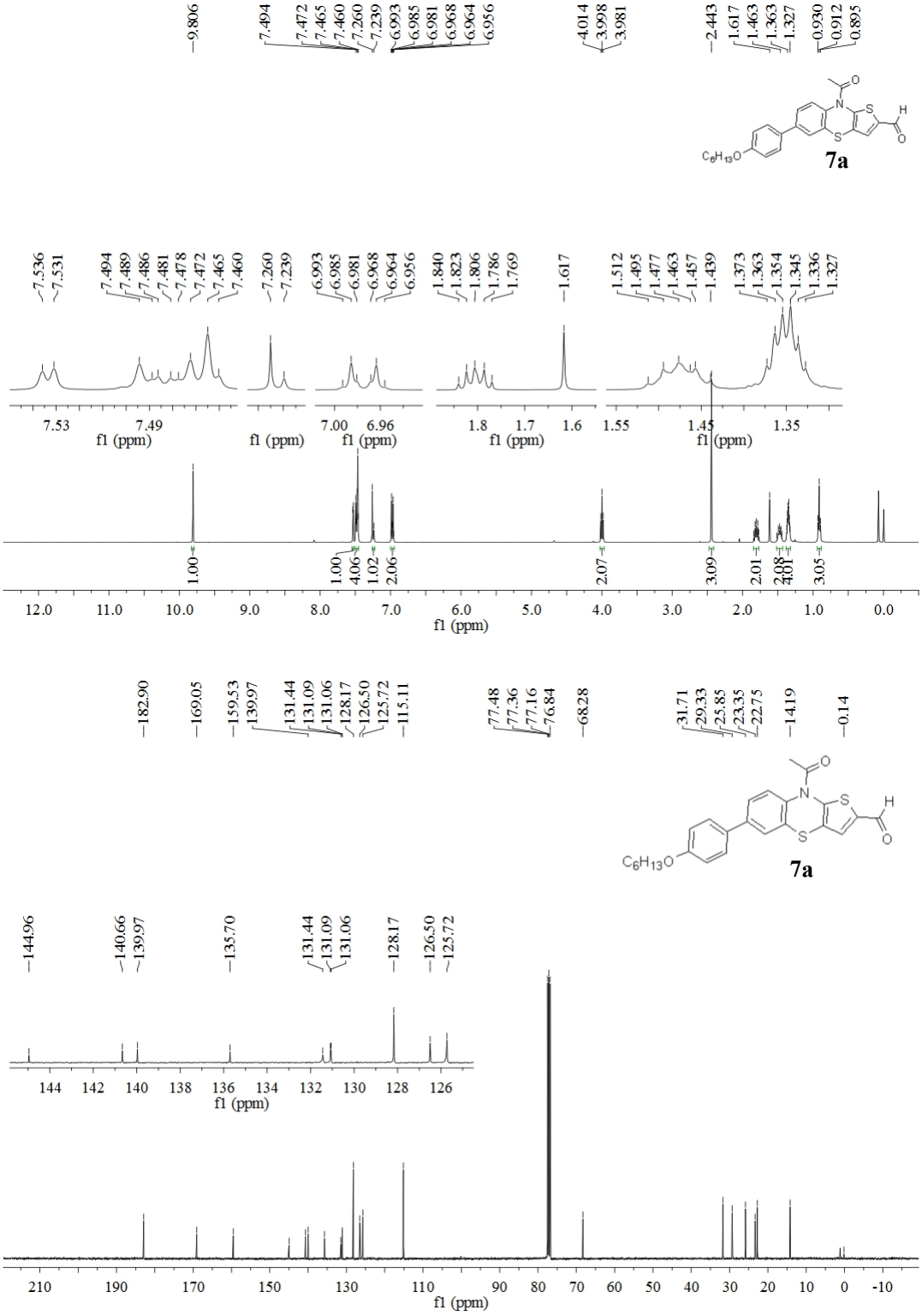
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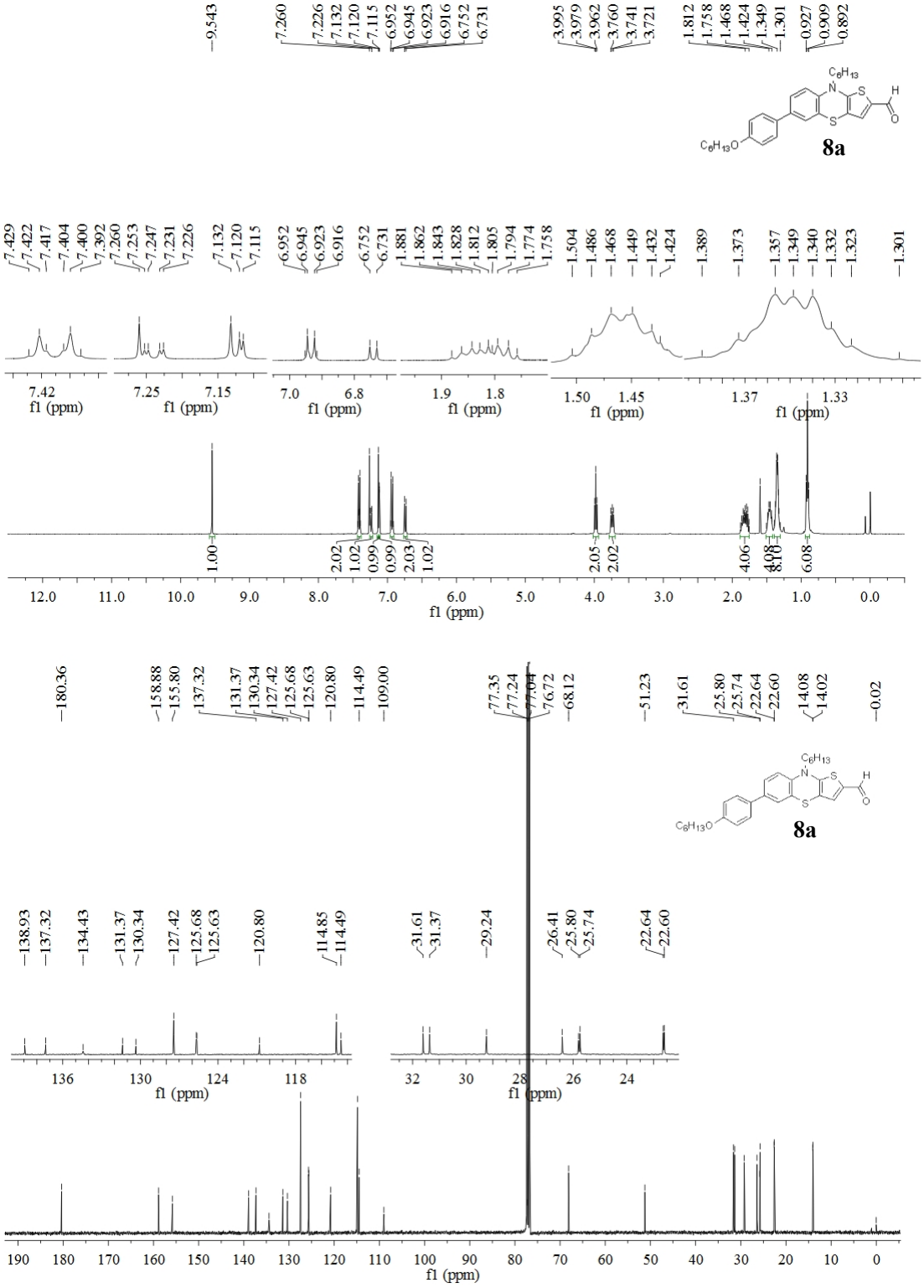
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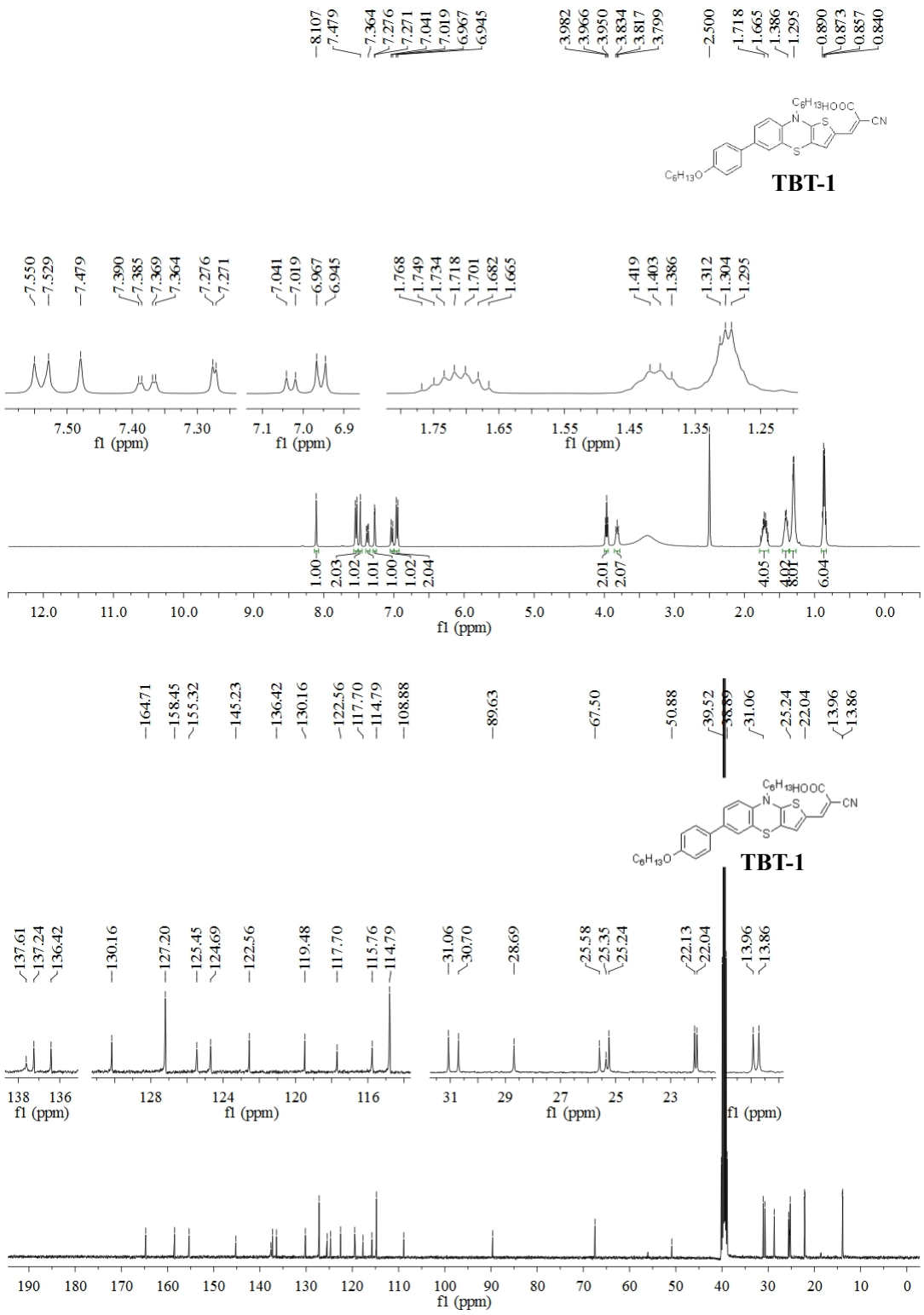
138.93
137.32
134.43
131.37
130.34
127.42
125.68
125.63
120.80
114.85
114.49
31.61
31.37
29.24
26.41
25.80
25.74
22.64
22.60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7.479
7.364
7.276
7.271
7.041
7.019
6.967
6.945
3.982
3.966
3.950
3.834
3.817
3.799
2.500
1.718
1.665
1.386
1.295
0.890
0.873
0.857
0.840
TBT-1
7.550
7.529
7.479
7.390
7.385
7.369
7.364
7.276
7.271
7.041
7.019
6.967
6.945
1.768
1.749
1.734
1.718
1.701
1.682
1.665
1.419
1.403
1.386
1.312
1.304
1.295
f1 (ppm)
1.00
2.03
1.02
1.01
1.00
1.02
2.04
2.01
2.07
4.05
4.02
8.01
6.04
164.71
158.45
155.32
145.23
136.42
130.16
122.56
117.70
114.79
108.88
89.63
67.50
50.88
39.52
31.06
25.24
22.04
13.96
13.86
TBT-1
137.61
137.24
136.42
130.16
127.20
125.45
124.69
122.56
119.48
117.70
115.76
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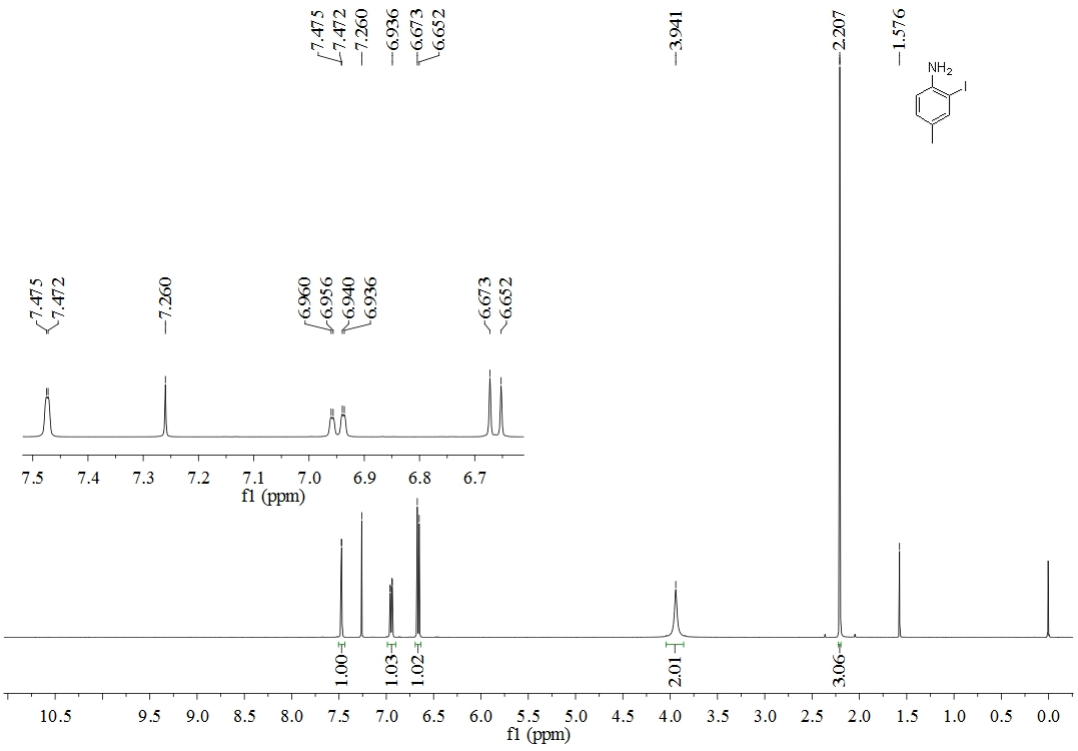
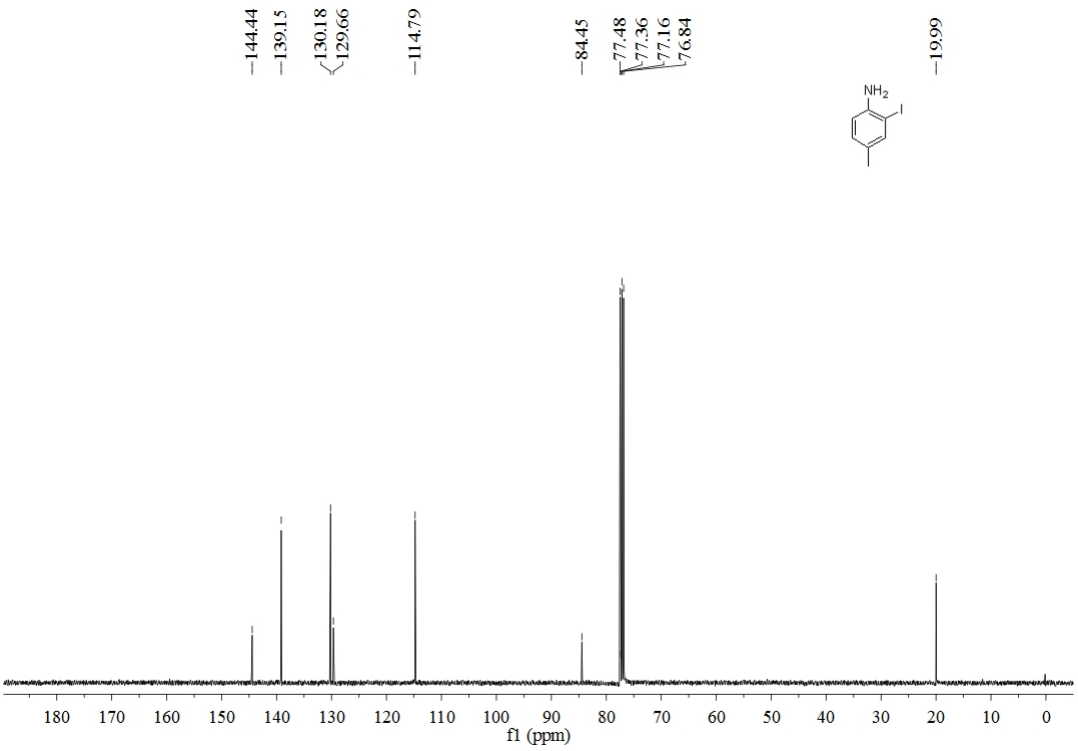
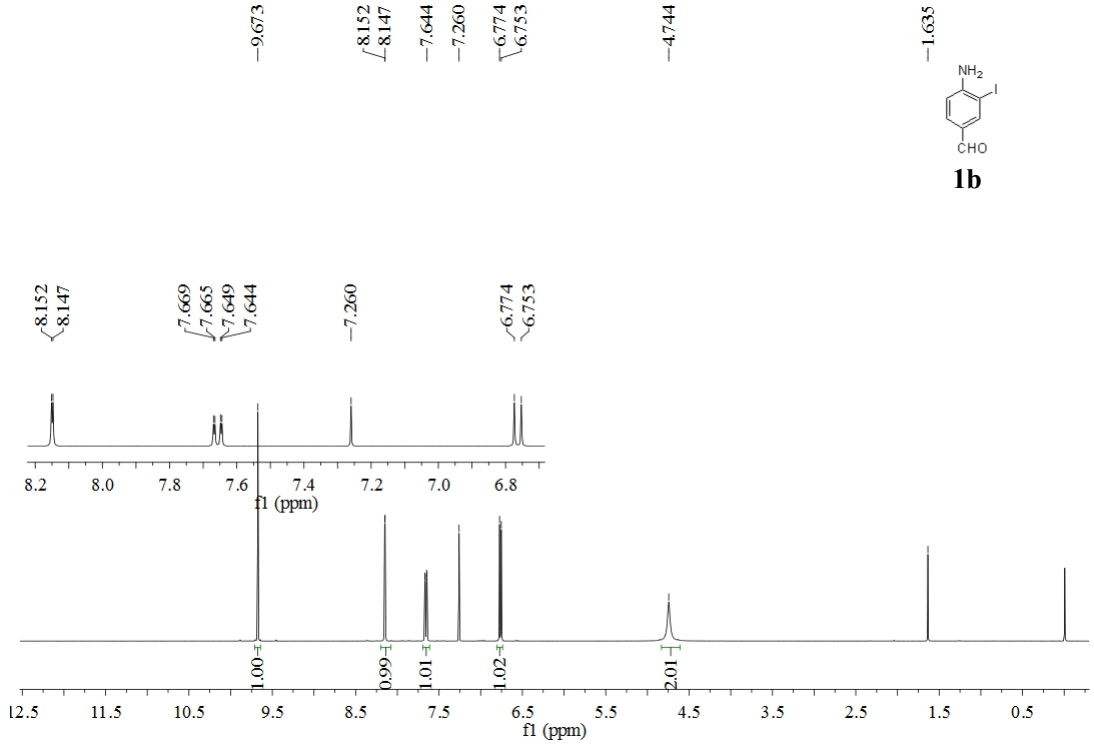
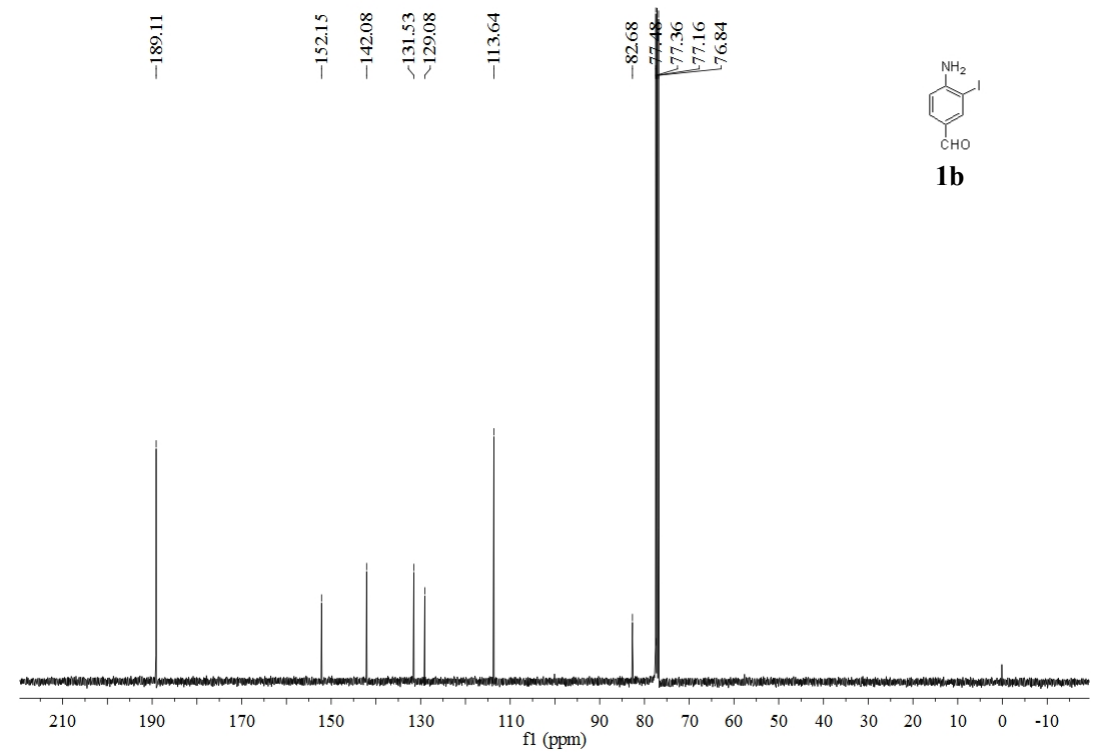
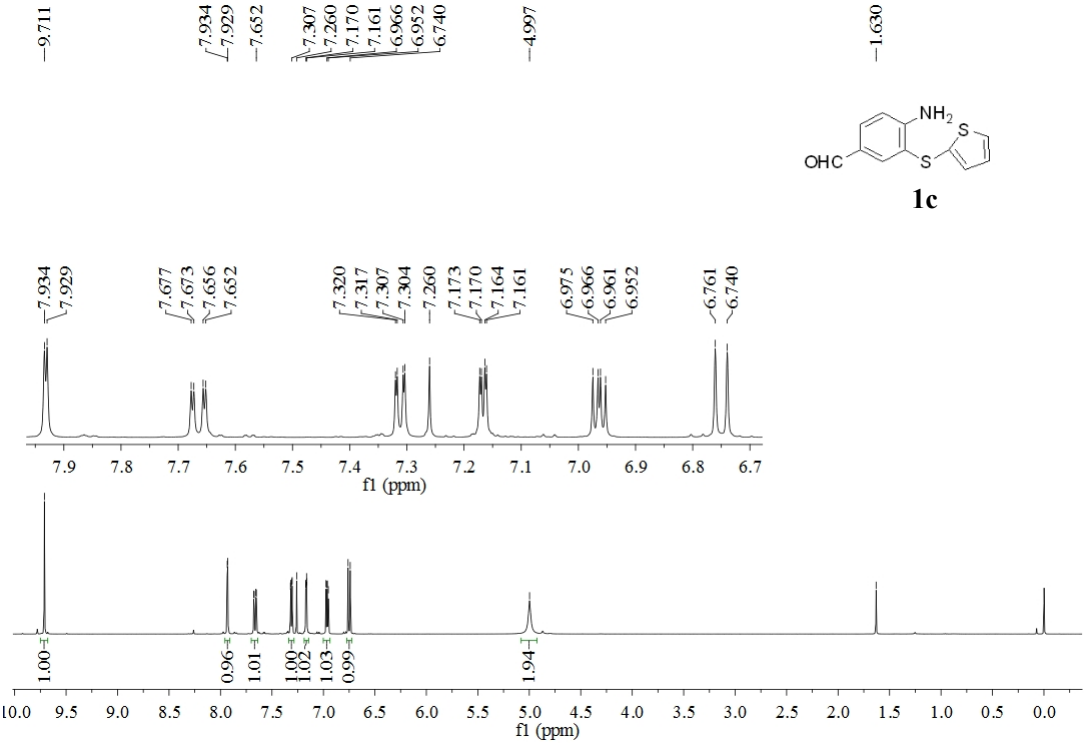
25.58
25.35
25.24
22.13
22.04
13.96
13.86


7.475
7.472
7.260
6.936
6.673
6.652
3.941
2.207
1.576
NH2
I
6.960
6.956
6.940
6.936
f1 (ppm)
1.00
1.03
1.02
2.01
3.06


144.44
139.15
130.18
129.66
114.79
84.45
77.48
77.36
77.16
76.84
19.99
NH2
I
f1 (ppm)


9.673
8.152
8.147
7.644
7.260
6.774
6.753
4.744
1.635
NH2
I
CHO
1b
8.152
8.147
7.669
7.665
7.649
7.644
7.260
6.774
6.753
f1 (ppm)
1.00
0.99
1.01
1.02
2.01
f1 (ppm)


189.11
152.15
142.08
131.53
129.08
113.64
82.68
77.48
77.36
77.16
76.84
NH2
I
CHO
1b
f1 (ppm)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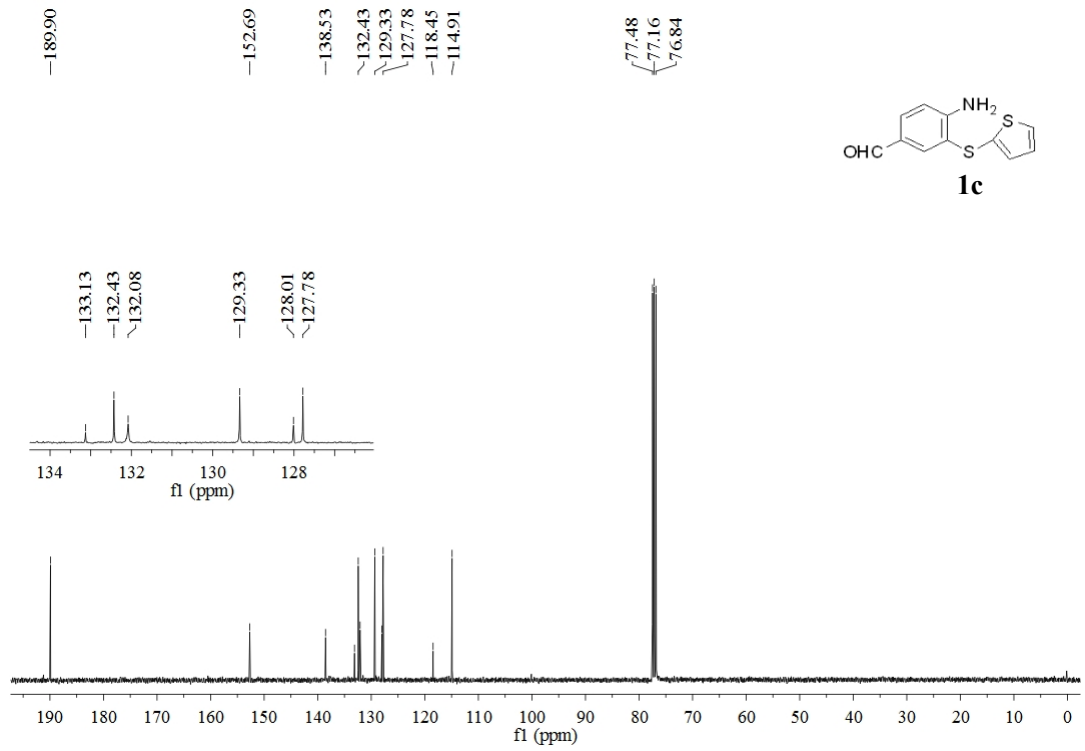
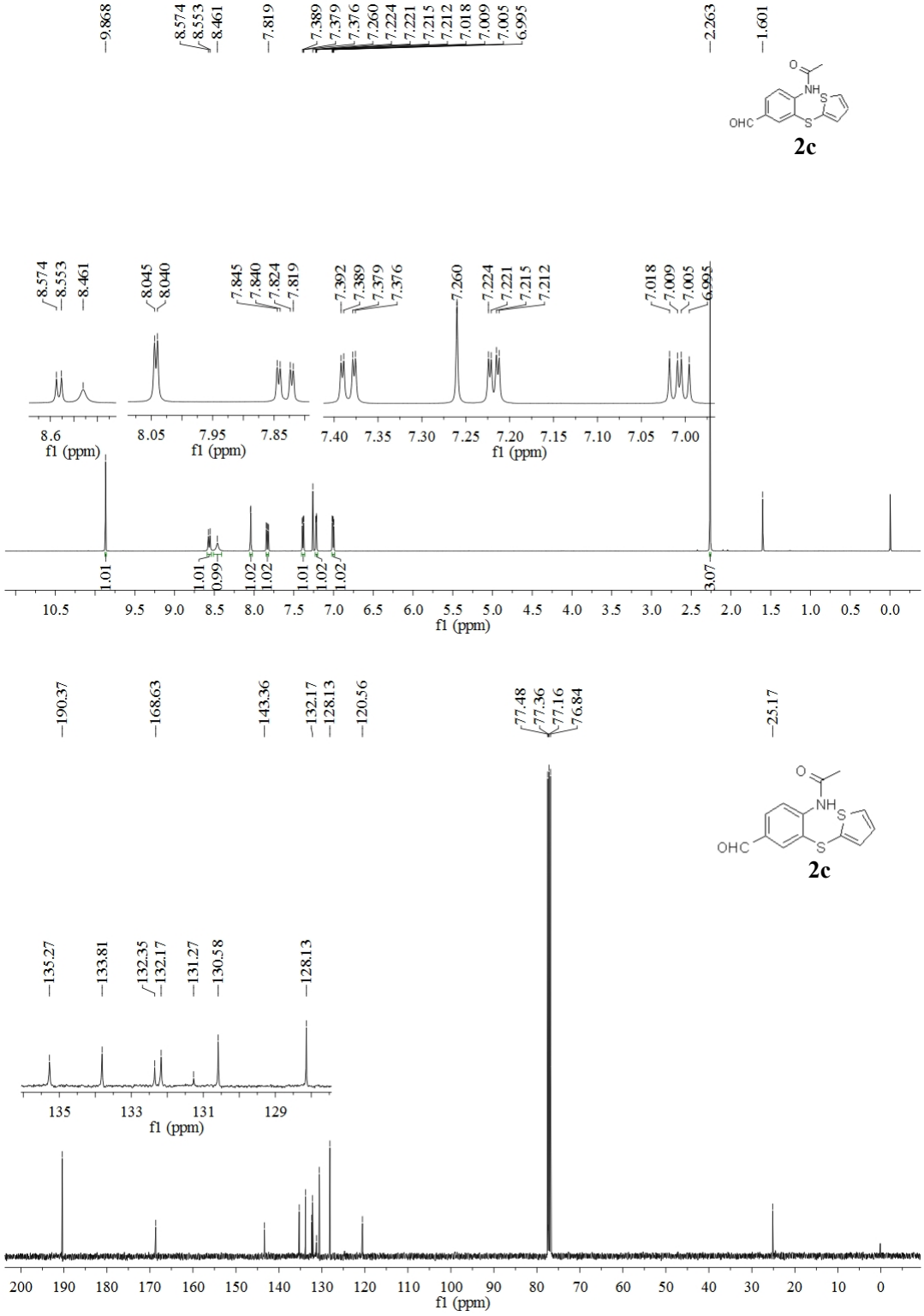
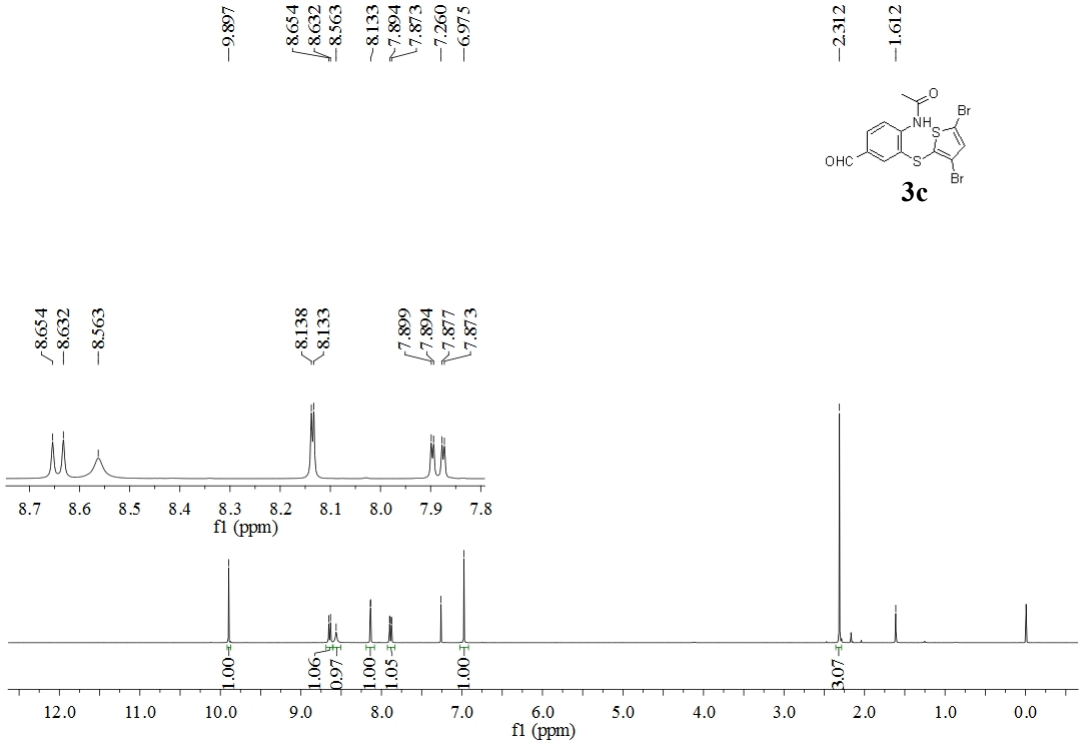
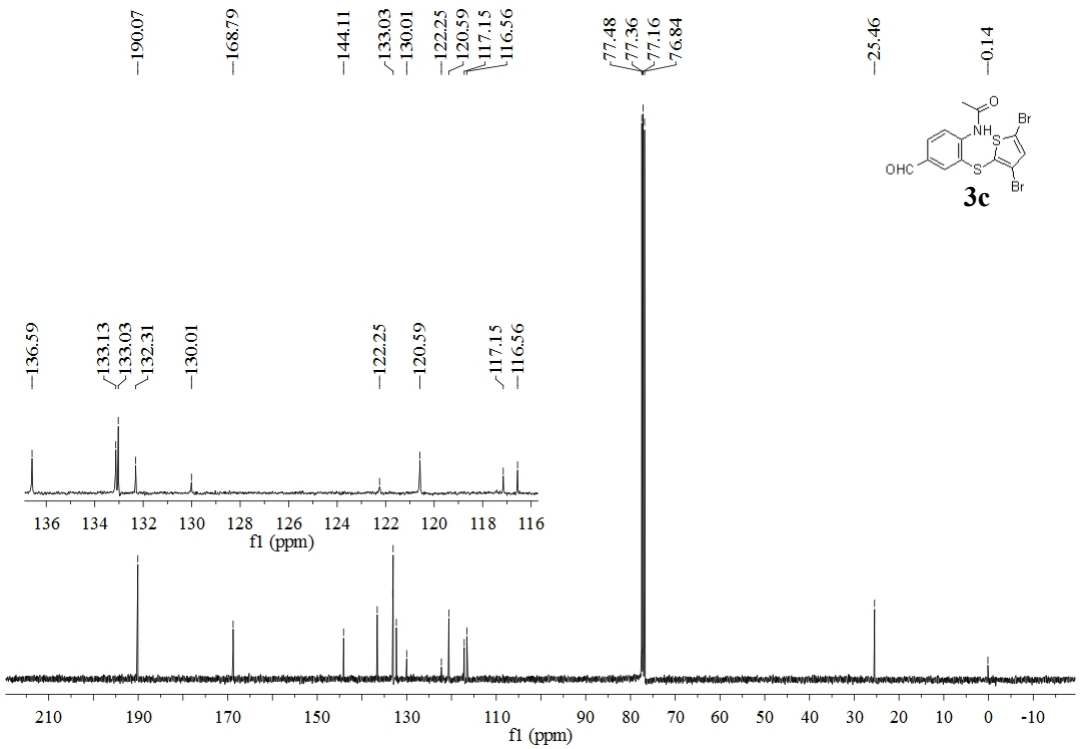
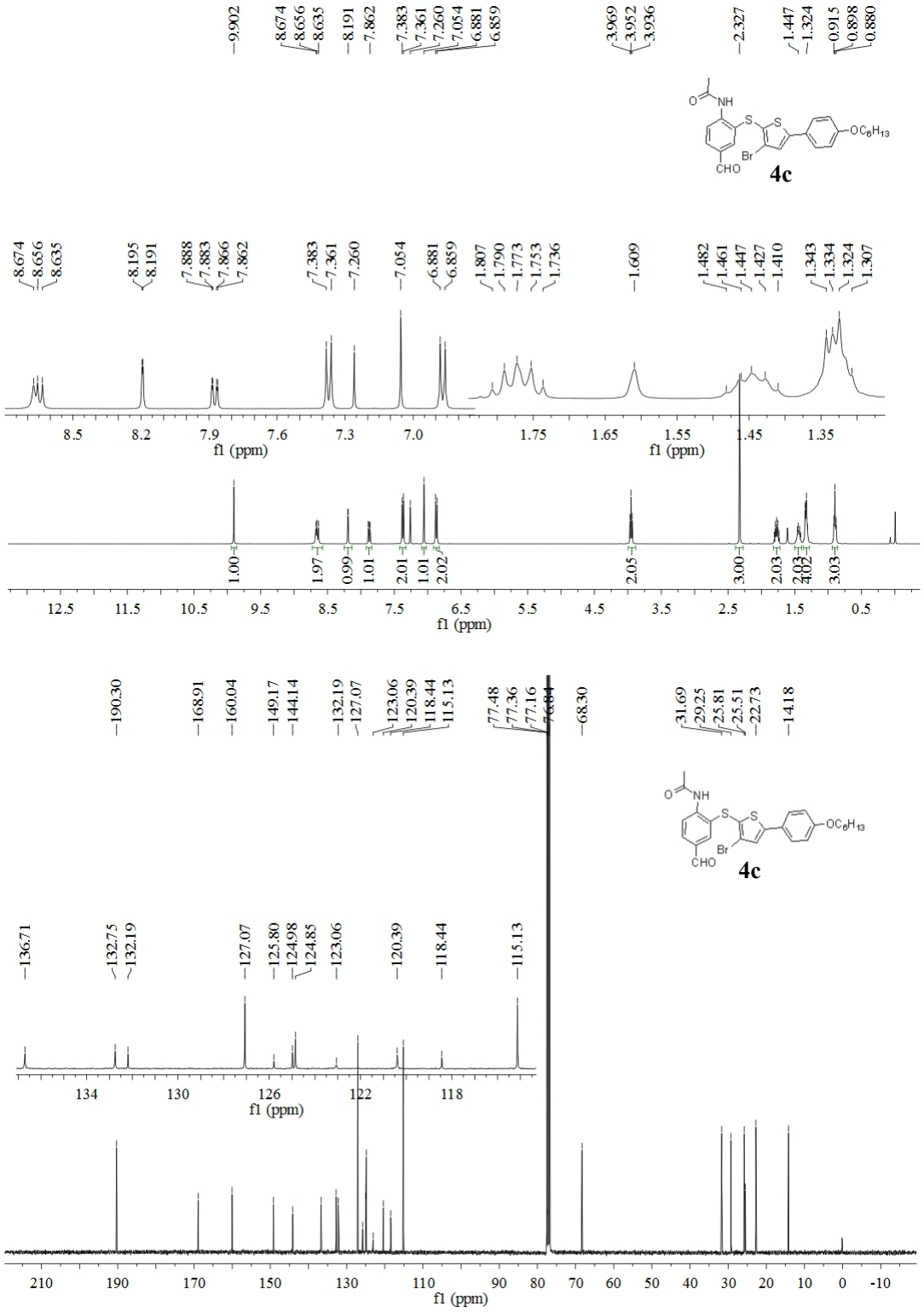
7.934
7.929
7.652
7.307
7.260
7.170
7.161
6.966
6.952
6.740
4.997
1.630
NH2
S
S
OHC
1c
7.934
7.929
7.677
7.673
7.656
7.652
7.320
7.317
7.307
7.304
7.260
7.173
7.170
7.164
7.161
6.975
6.966
6.961
6.952
6.761
6.740
f1 (ppm)
1.00
0.96
1.01
1.00
1.02
1.03
0.99
1.94
f1 (ppm)

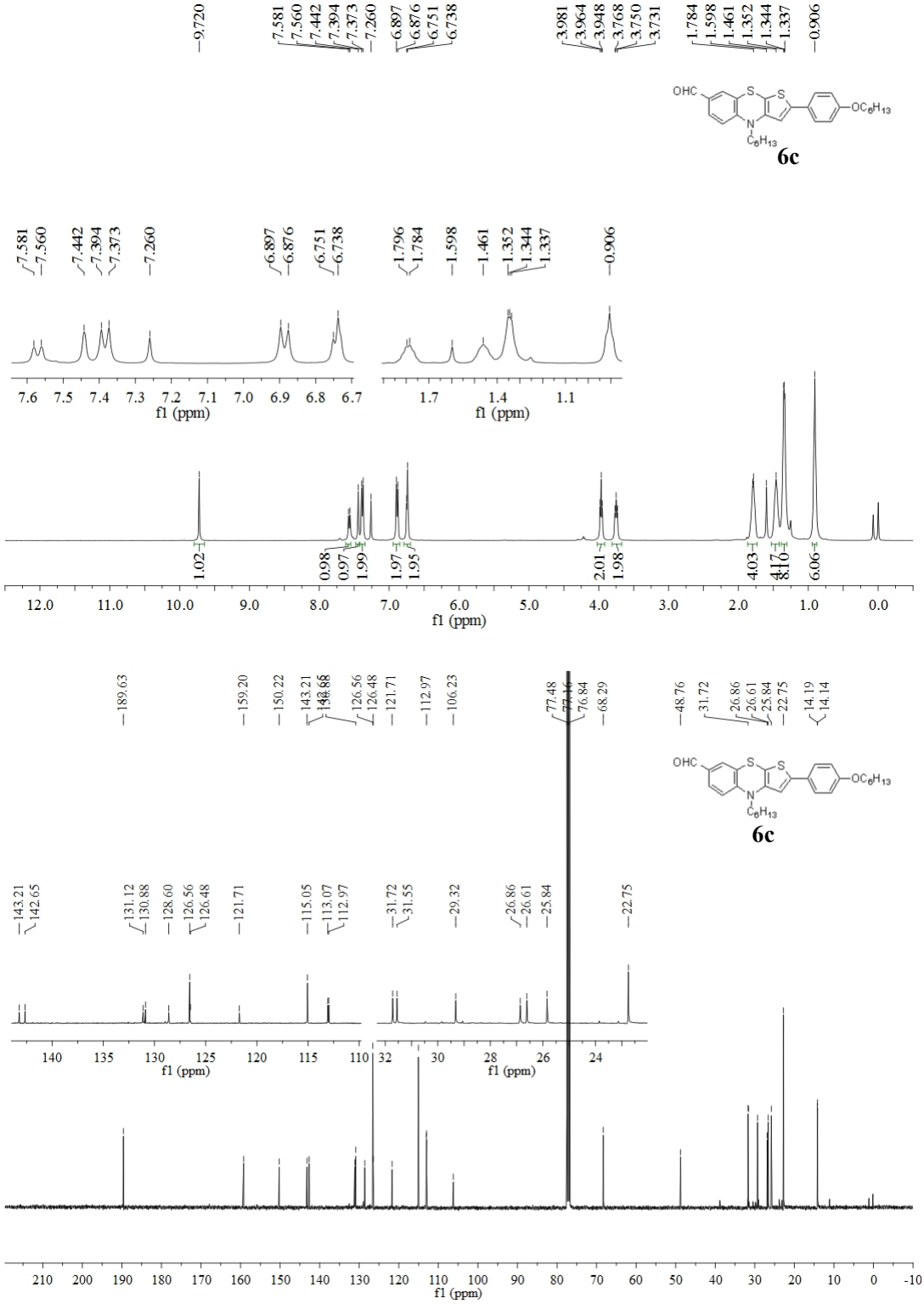

189.90
152.69
138.53
132.43
129.33
127.78
118.45
114.91
77.48
77.16
76.84
NH2
S
S
OHC
1c
133.13
132.43
132.08
129.33
128.01
127.78
f1 (ppm)
f1 (ppm)

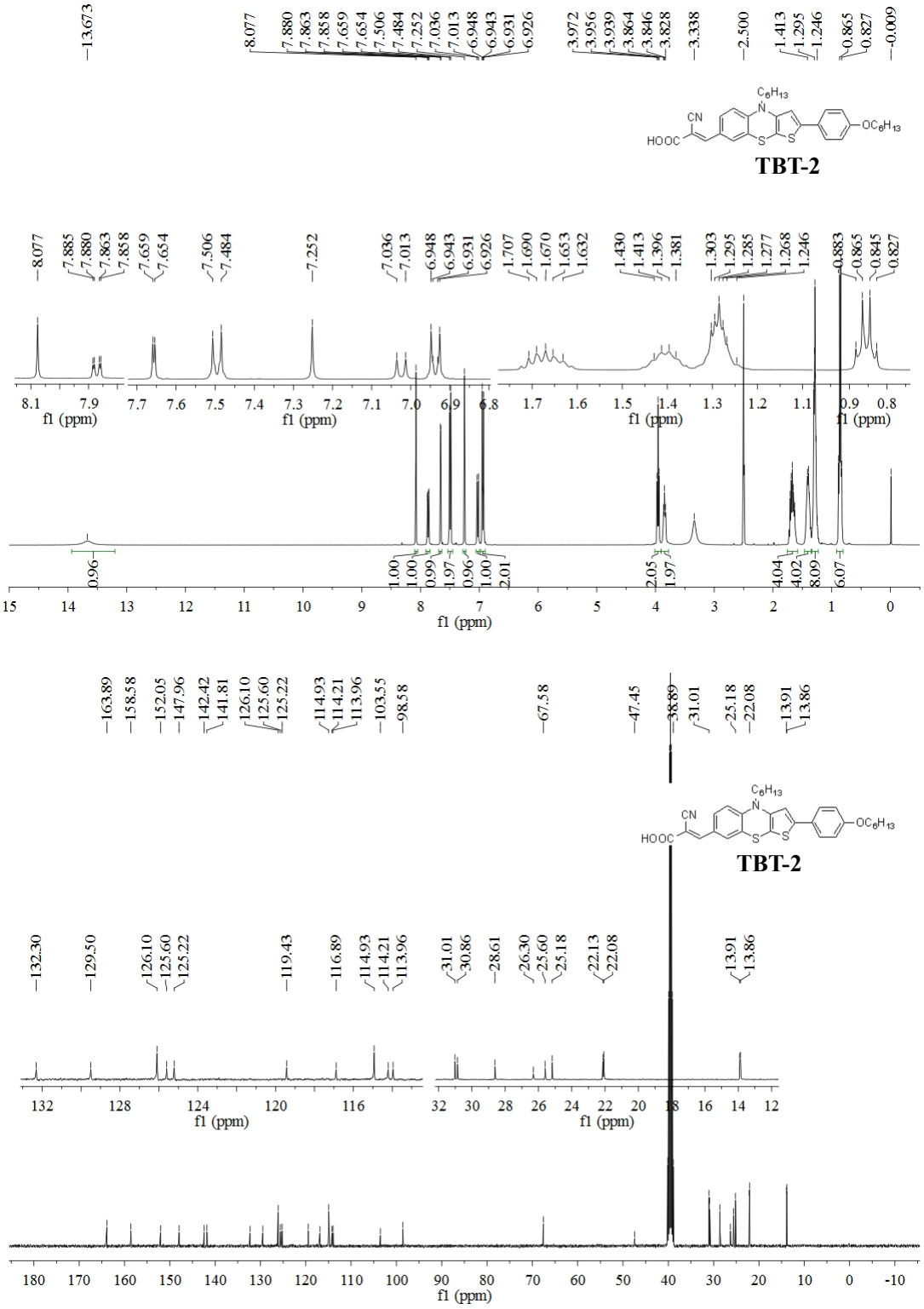

9.868
8.574
8.553
8.461
7.819
7.389
7.379
7.376
7.260
7.224
7.221
7.215
7.212
7.018
7.009
7.005
6.995
2.263
1.601
2c
f1 (ppm)
1.01
1.01
0.99
1.02
1.02
1.01
1.02
1.02
3.07
190.37
168.63
143.36
132.17
128.13
120.56
77.48
77.36
77.16
76.84
25.17
135.27
133.81
132.35
132.17
131.27
130.58
128.13
2c
f1 (ppm)

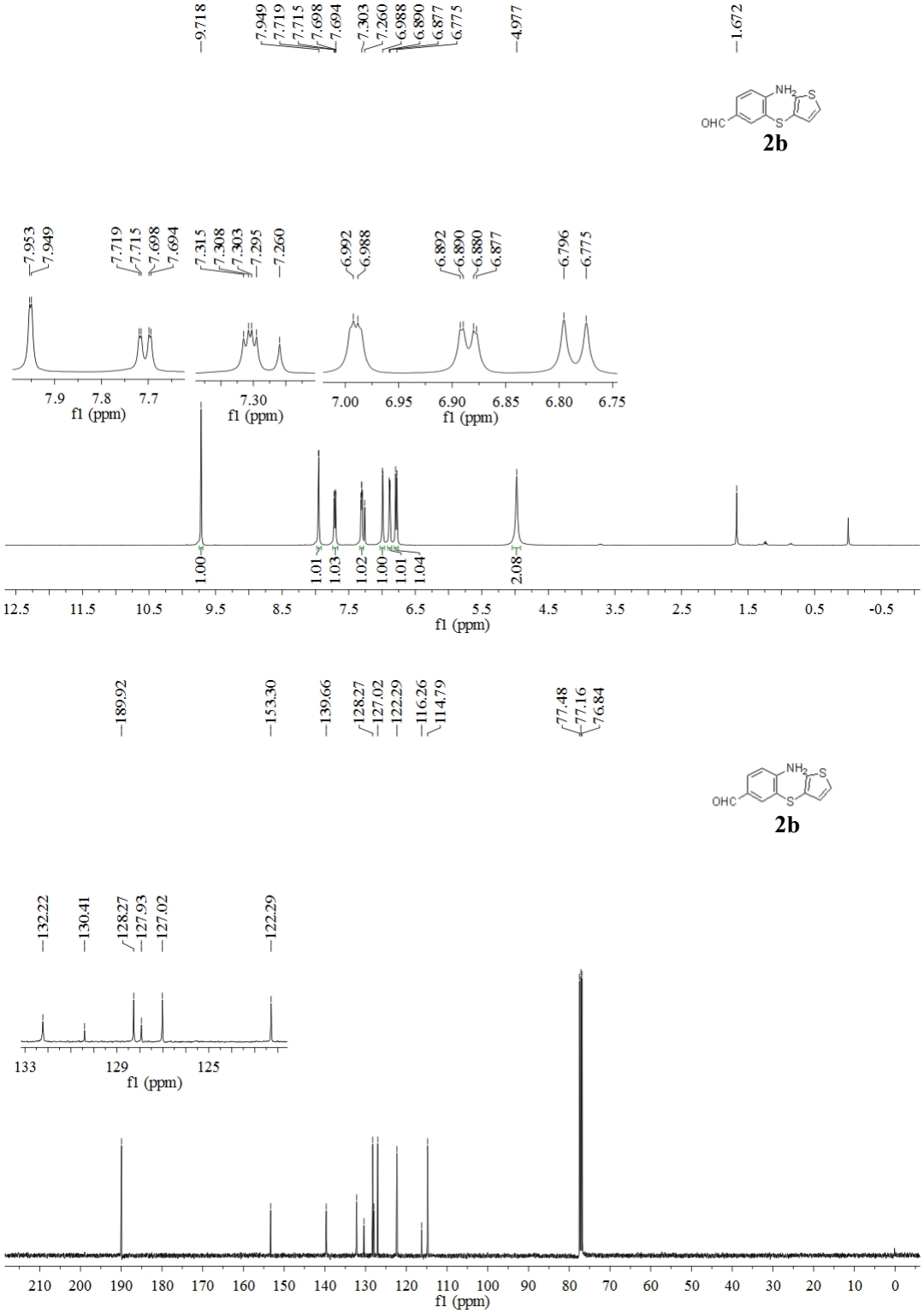

9.897
8.654
8.632
8.563
8.133
7.894
7.873
7.260
6.975
2.312
1.612
3c
8.654
8.632
8.563
8.138
8.133
7.899
7.894
7.877
7.873
f1 (ppm)
1.00
1.06
0.97
1.00
1.05
1.00
3.07
f1 (ppm)

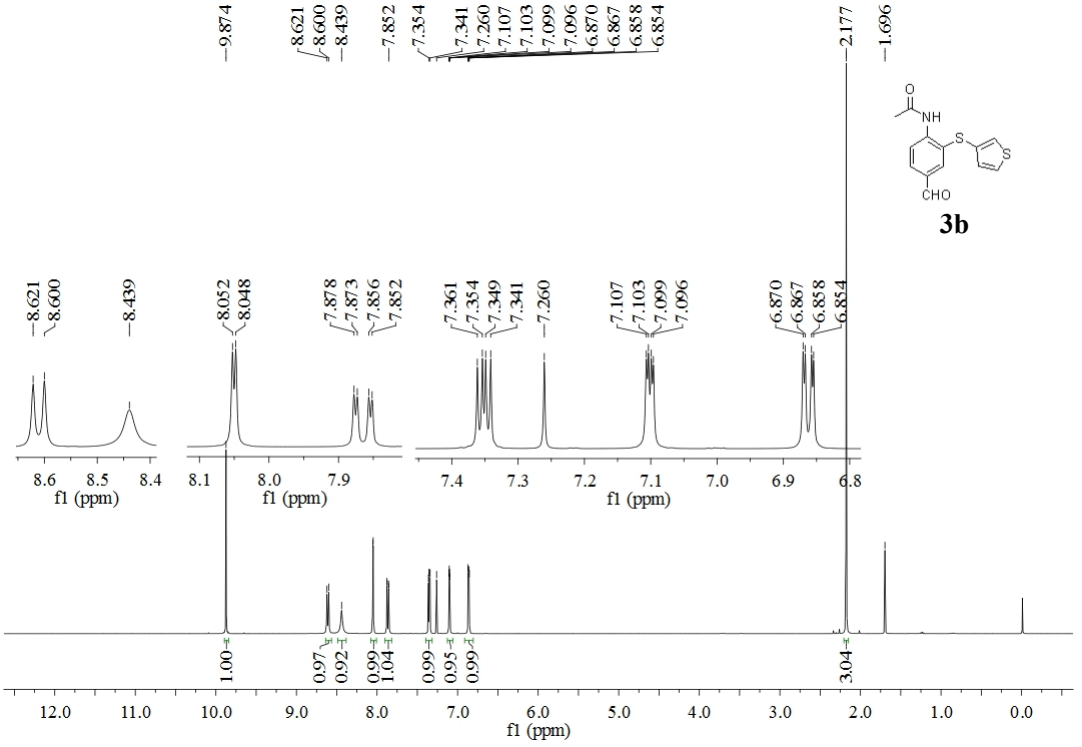

190.07
168.79
144.11
133.03
130.01
122.25
120.59
117.15
116.56
77.48
77.36
77.16
76.84
25.46
0.14
3c
136.59
133.13
133.03
132.31
130.01
122.25
120.59
117.15
116.56
f1 (ppm)
f1 (ppm)


9.902
8.674
8.656
8.635
8.191
7.862
7.383
7.361
7.260
7.054
6.881
6.859
3.969
3.952
3.936
2.327
1.447
1.324
0.915
0.898
0.880
4c
f1 (ppm)
1.00
1.97
0.99
1.01
2.01
1.01
2.02
2.05
3.00
2.03
2.03
4.02
3.03
190.30
168.91
160.04
149.17
144.14
132.19
127.07
123.06
120.39
118.44
115.13
77.48
77.36
77.16
76.84
68.30
31.69
29.25
25.81
25.51
22.73
14.18
136.71
132.75
132.19
127.07
125.80
124.98
124.85
123.06
120.39
118.44
115.13


9.720
7.581
7.560
7.442
7.394
7.373
7.260
6.897
6.876
6.751
6.738
3.981
3.964
3.948
3.768
3.750
3.731
1.784
1.598
1.461
1.352
1.344
1.337
0.906
OHC
S
S
N
OC6H13
C6H13
6c
f1 (ppm)
1.02
0.98
0.97
1.99
1.97
1.95
2.01
1.98
4.03
4.17
4.10
6.06
189.63
159.20
150.22
143.21
142.65
131.12
130.88
128.60
126.56
126.48
121.71
115.05
113.07
112.97
106.23
77.48
77.16
76.84
68.29
48.76
31.72
31.55
29.32
26.86
26.61
25.84
22.75
14.19
14.14


TBT-2
f1 (ppm)


9.718
7.949
7.719
7.715
7.698
7.694
7.303
7.260
6.988
6.890
6.877
6.775
4.977
1.672
NH2
S
OHC
S
2b
7.953
7.949
7.719
7.715
7.698
7.694
7.315
7.308
7.303
7.295
7.260
6.992
6.988
6.892
6.890
6.880
6.877
6.796
6.775
f1 (ppm)
1.00
1.01
1.03
1.02
1.00
1.01
1.04
2.08
189.92
153.30
139.66
128.27
127.02
122.29
116.26
114.79
77.48
77.16
76.84
2b
132.22
130.41
128.27
127.93
127.02
122.29


9.874
8.621
8.600
8.439
7.852
7.354
7.341
7.260
7.107
7.103
7.099
7.096
6.870
6.867
6.858
6.854
2.177
1.696
NH
S
S
CHO
3b
f1 (ppm)
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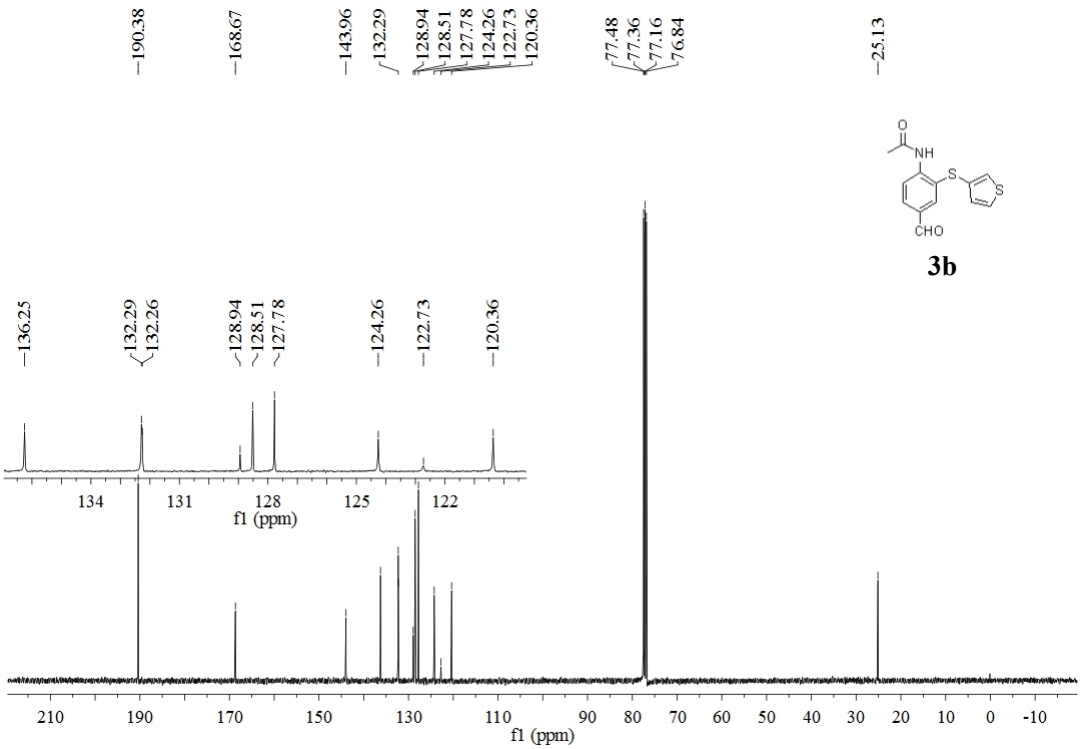
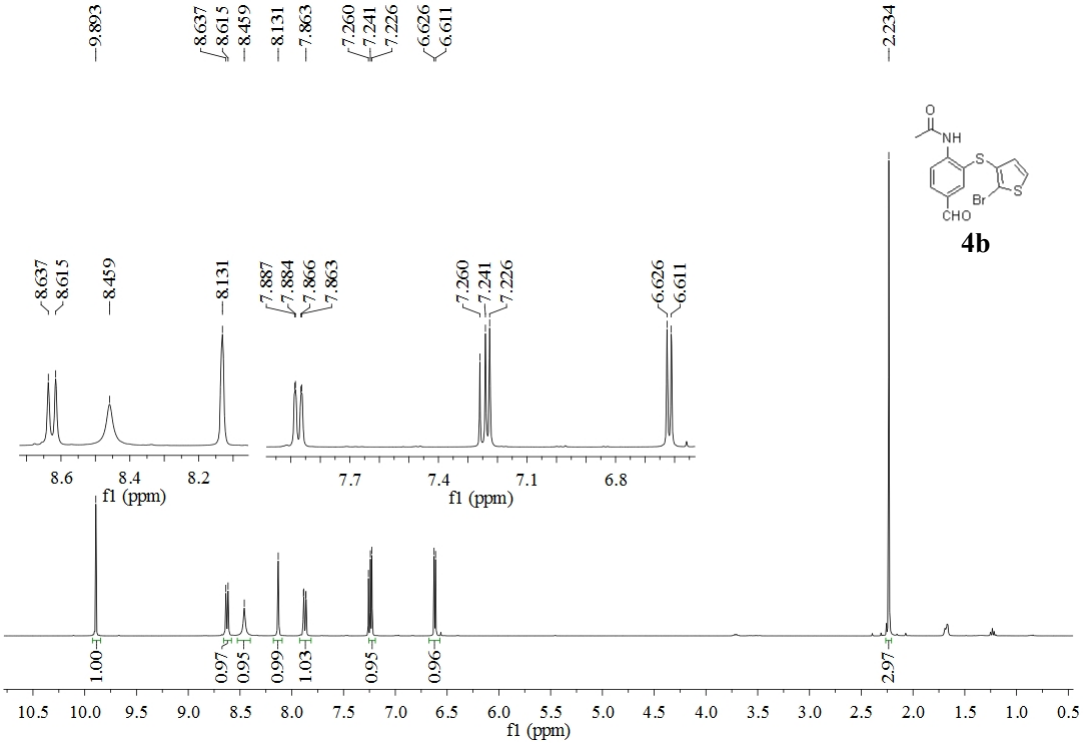
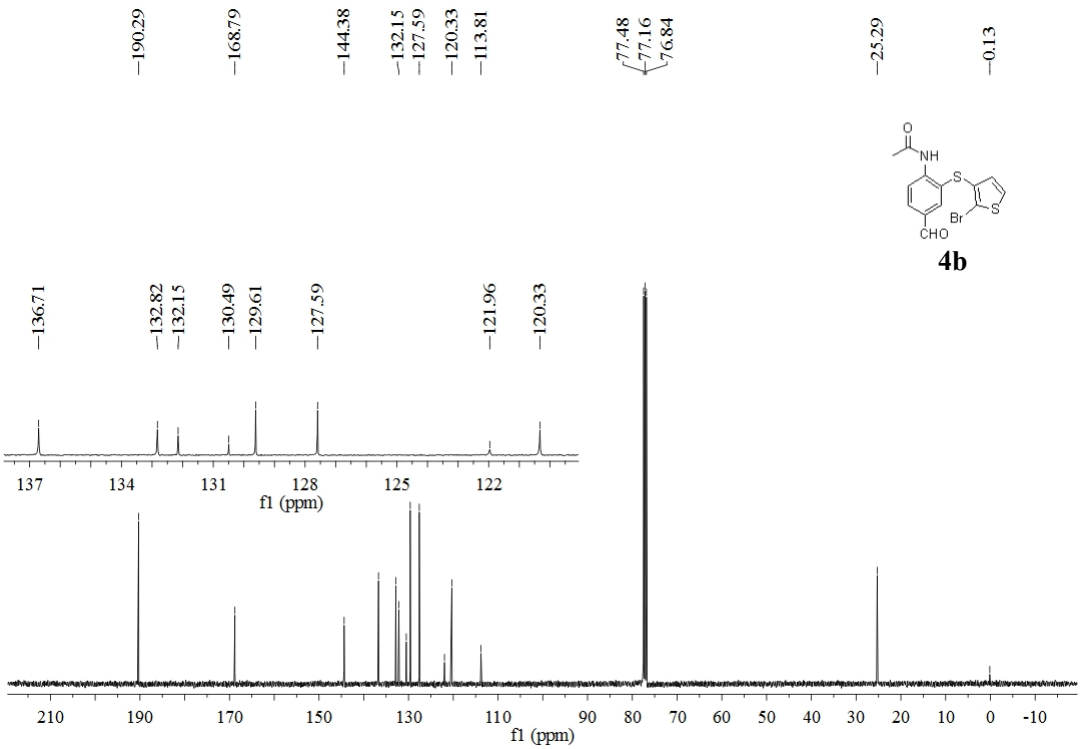
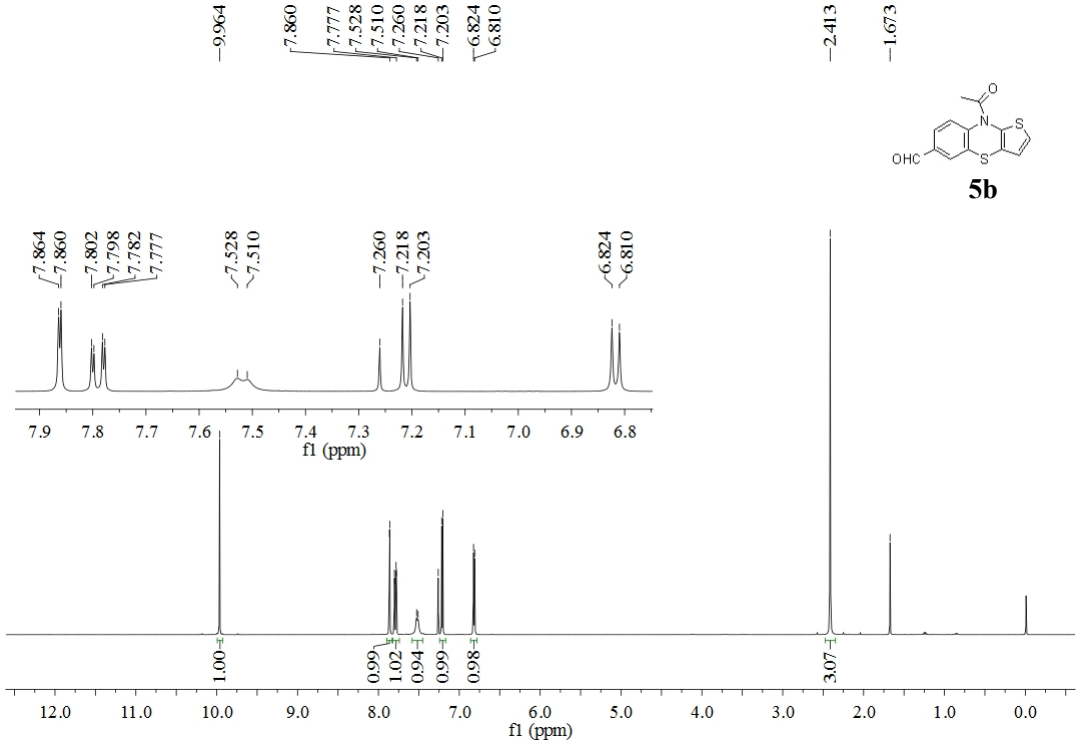
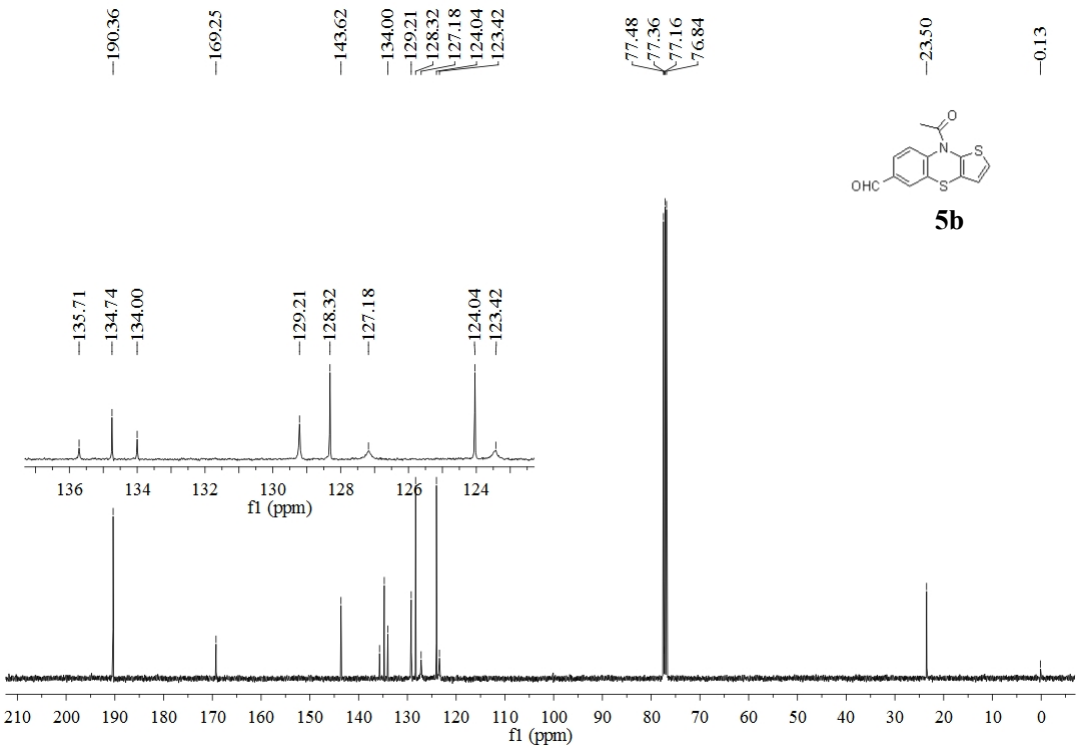
0.97
0.92
0.99
1.04
0.99
0.95
0.99
3.04

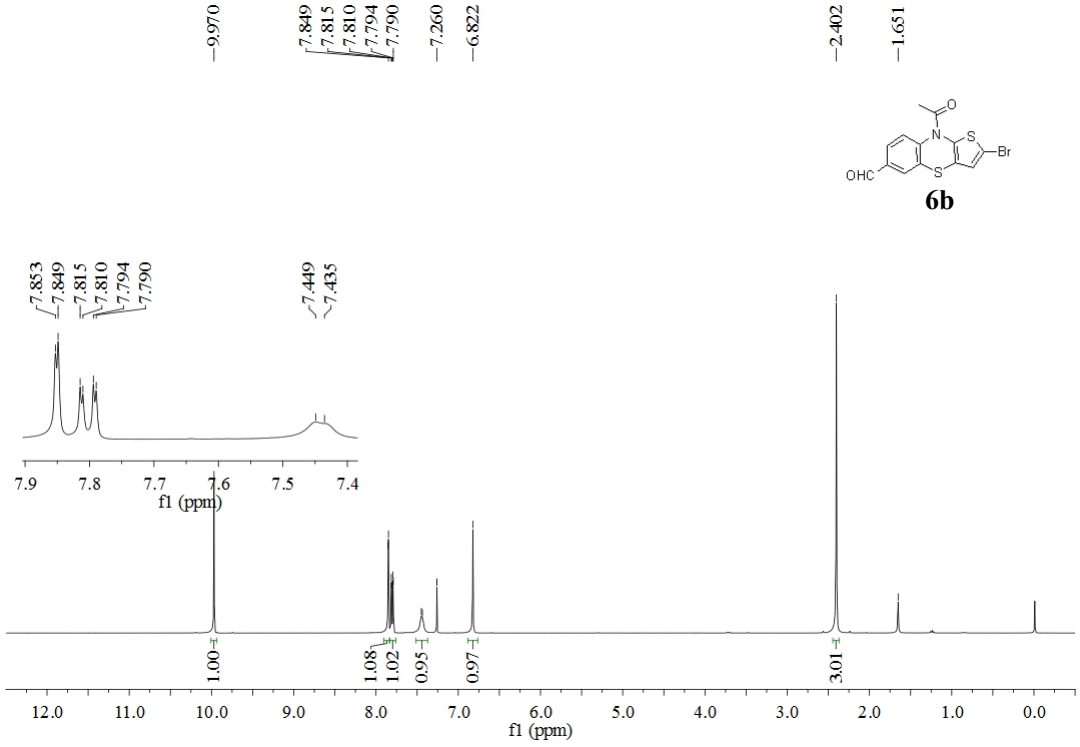

190.38
168.67
143.96
132.29
128.94
128.51
127.78
124.26
122.73
120.36
77.48
77.36
77.16
76.84
25.13
NH
S
S
CHO
3b
136.25
132.29
132.26
128.94
128.51
127.78
124.26
122.73
120.36
f1 (ppm)


9.893
8.637
8.615
8.459
8.131
7.863
7.260
7.241
7.226
6.626
6.611
2.234
4b
f1 (ppm)
1.00
0.97
0.95
0.99
1.03
0.95
0.96
2.97

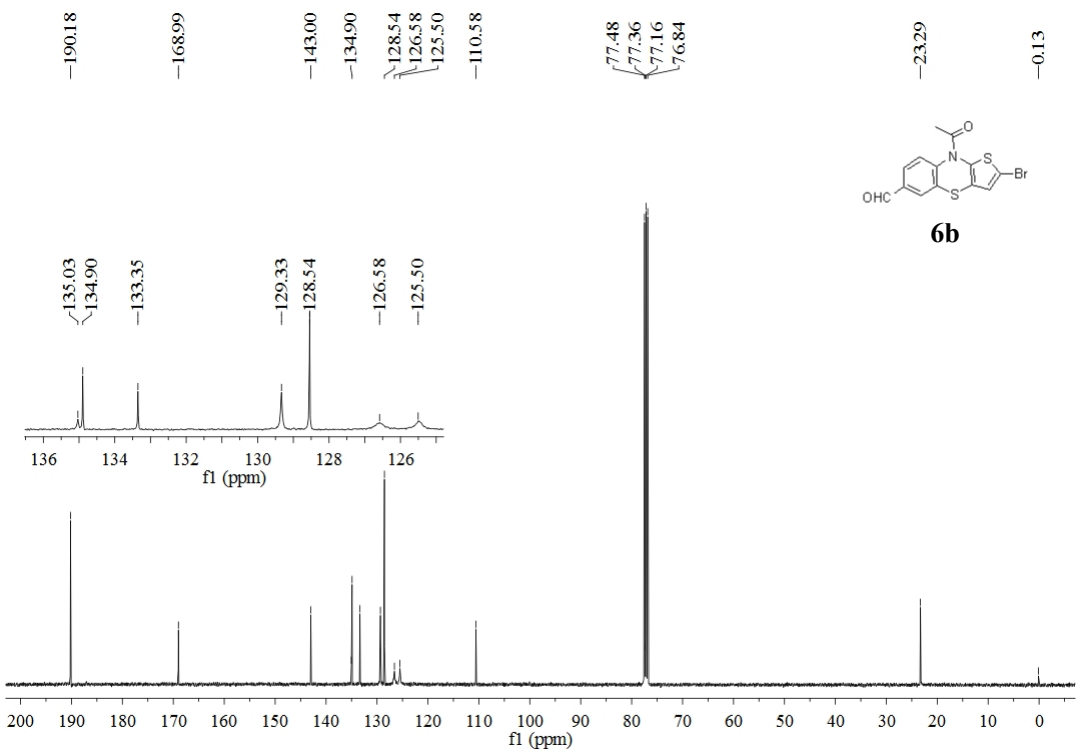

190.29
168.79
144.38
132.15
127.59
120.33
113.81
77.48
77.16
76.84
25.29
0.13
4b
136.71
132.82
132.15
130.49
129.61
127.59
121.96
120.33
f1 (ppm)


9.964
7.860
7.777
7.528
7.510
7.260
7.218
7.203
6.824
6.810
2.413
1.673
OHC
5b
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
1.00
0.99
1.02
0.94
0.99
0.98
3.07
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

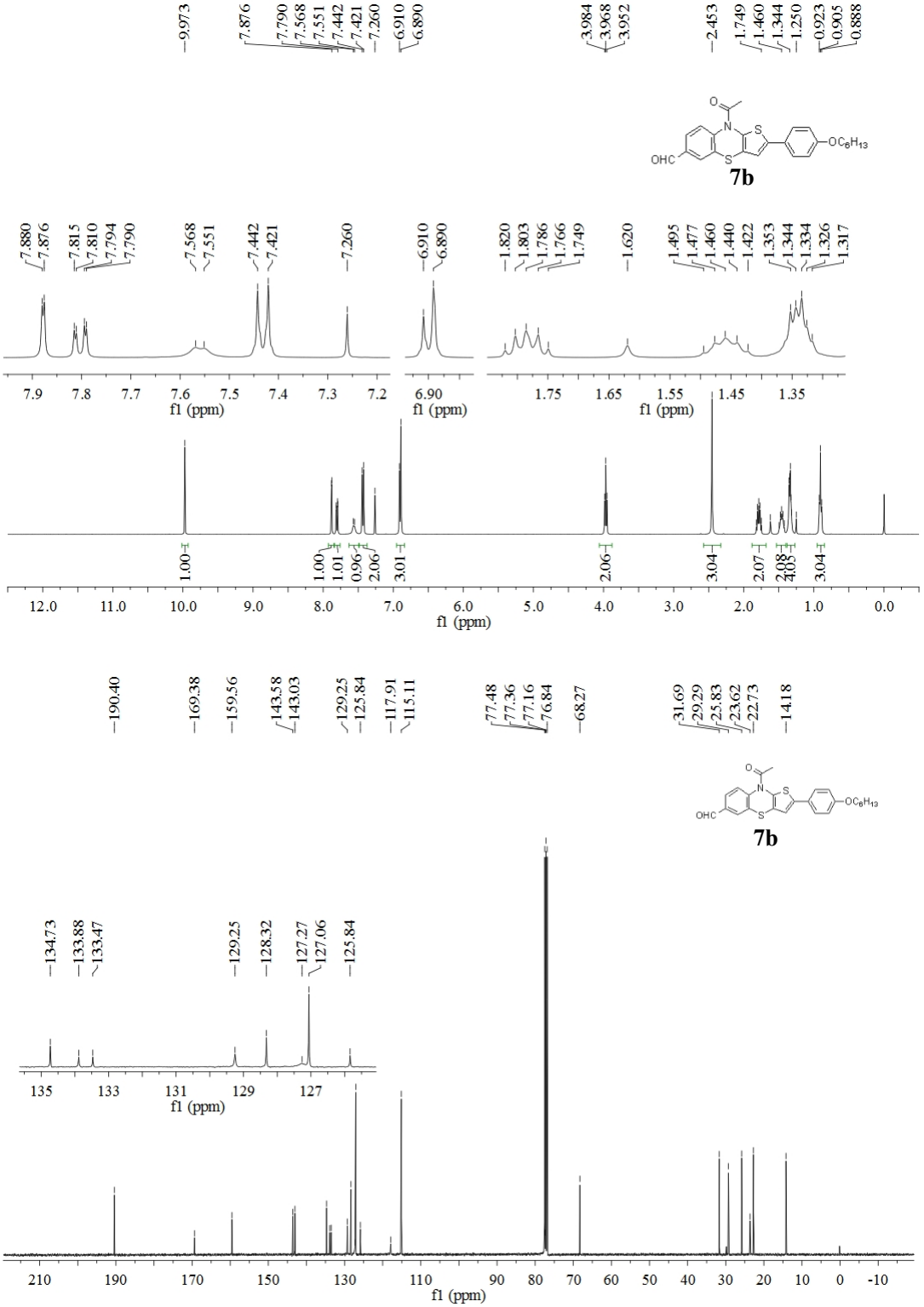

190.36
169.25
143.62
134.00
129.21
128.32
127.18
124.04
123.42
77.48
77.36
77.16
76.84
23.50
0.13
OHC
5b
135.71
134.74
134.00
129.21
128.32
127.18
124.04
123.42
136
134
132
130
128
126
124
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.970
7.849
7.815
7.810
7.794
7.790
7.260
6.822
2.402
1.651
7.853
7.849
7.815
7.810
7.794
7.790
7.449
7.435
1.00
1.08
1.02
0.95
0.97
3.01
f1 (ppm)

6b


190.18
168.99
143.00
134.90
128.54
126.58
125.50
110.58
77.48
77.36
77.16
76.84
23.29
0.13
135.03
134.90
133.35
129.33
128.54
126.58
125.50
f1 (ppm)

6b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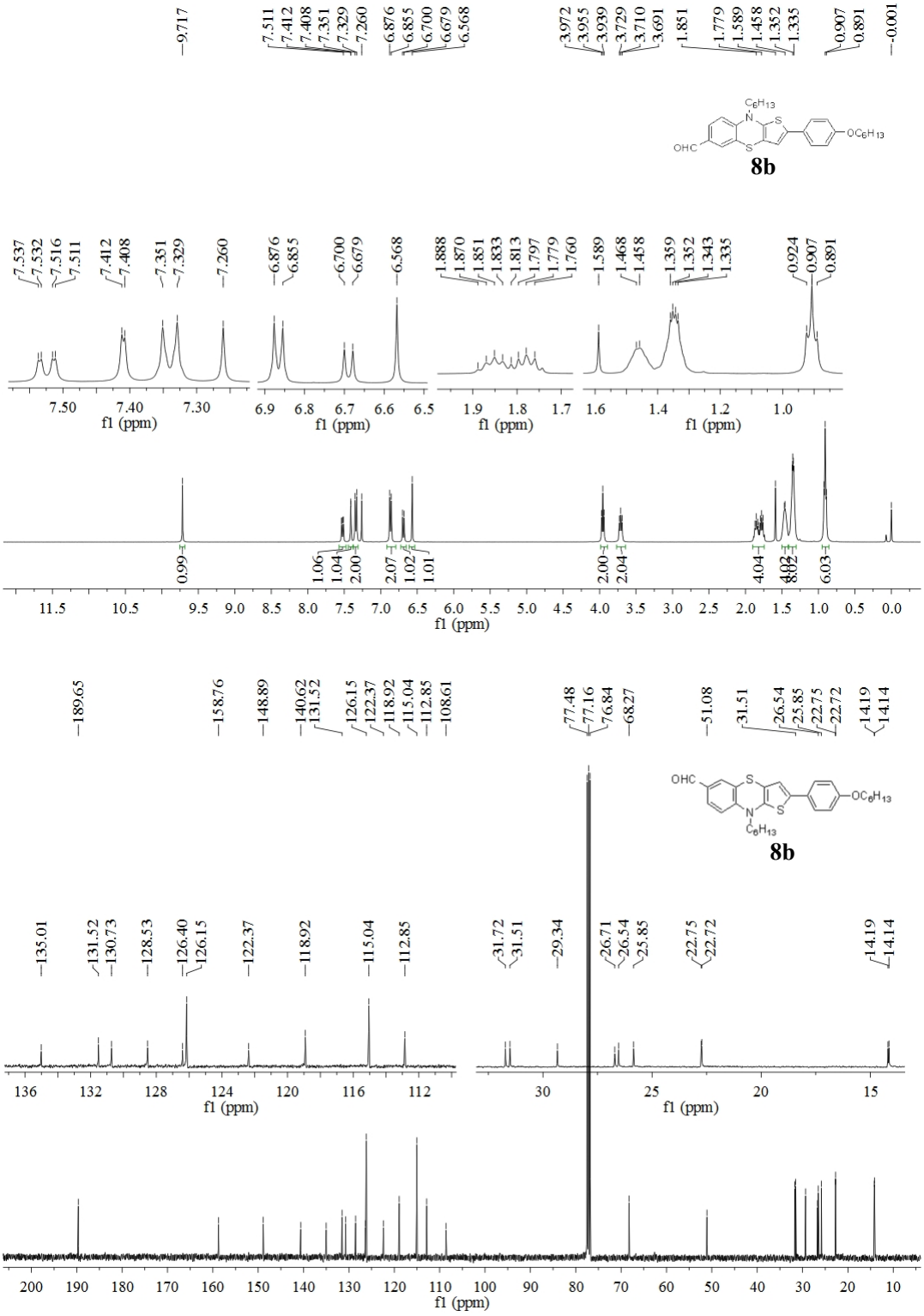
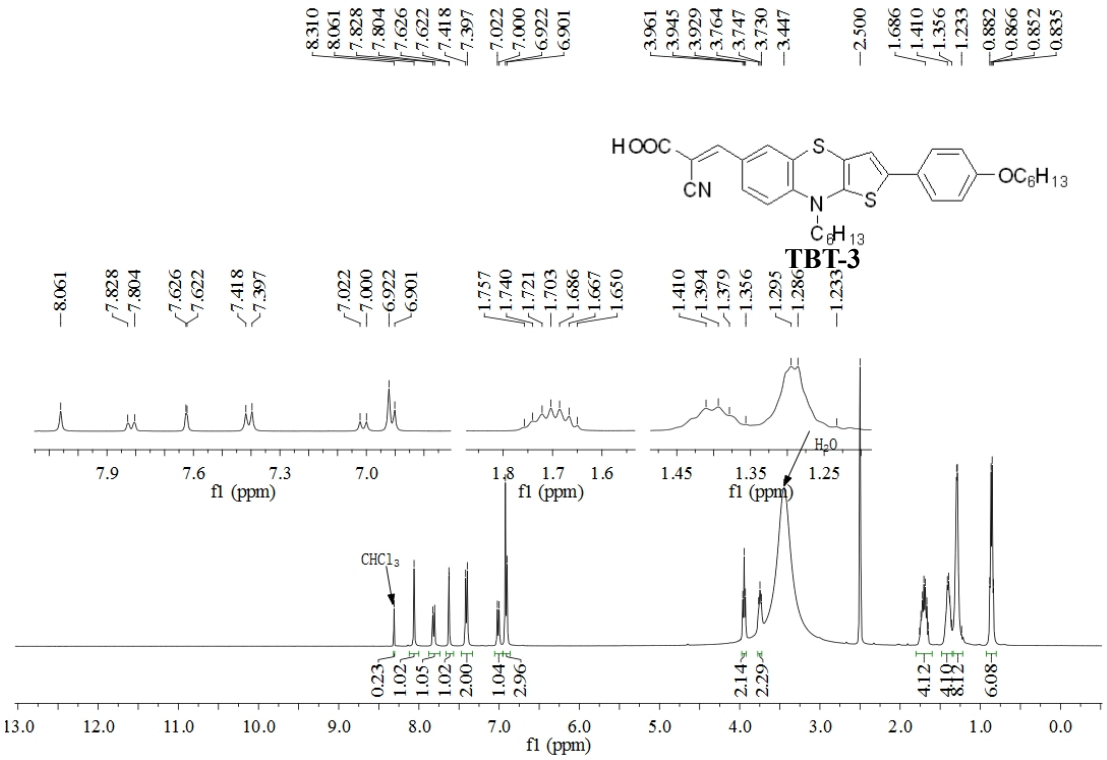
7.876
7.790
7.568
7.551
7.442
7.421
7.260
6.910
6.890
3.984
3.968
3.952
2.453
1.749
1.460
1.344
1.250
0.923
0.905
0.888
OHC
OC6H13
7b
7.880
7.876
7.815
7.810
7.794
7.790
7.568
7.551
7.442
7.421
7.260
6.910
6.890
1.820
1.803
1.786
1.766
1.749
1.620
1.495
1.477
1.460
1.440
1.422
1.353
1.344
1.334
1.326
1.317
f1 (ppm)
1.00
1.00
1.01
0.96
2.06
3.01
2.06
3.04
2.07
2.08
4.05
3.04
190.40
169.38
159.56
143.58
143.03
129.25
125.84
117.91
115.11
77.48
77.36
77.16
76.84
68.27
31.69
29.29
25.83
23.62
22.73
14.18
134.73
133.88
133.47
129.25
128.32
127.27
127.06
125.84
f1 (ppm)


9.717
7.511
7.412
7.408
7.351
7.329
7.260
6.876
6.855
6.700
6.679
6.568
3.972
3.955
3.939
3.729
3.710
3.691
1.851
1.779
1.589
1.458
1.352
1.335
0.907
0.891
-0.001
8b
f1 (ppm)
189.65
158.76
148.89
140.62
131.52
126.15
122.37
118.92
115.04
112.85
108.61
77.48
77.16
76.84
68.27
51.08
31.51
26.54
25.85
22.75
22.72
14.19
14.14
8b
f1 (ppm)


8.310
8.061
7.828
7.804
7.626
7.622
7.418
7.397
7.022
7.000
6.922
6.901
3.961
3.945
3.929
3.764
3.747
3.730
3.447
2.500
1.686
1.410
1.356
1.233
0.882
0.866
0.852
0.835
HOOC
CN
S
N
S
OC6H13
C6H13
TBT-3
f1 (ppm)
CHCl3
H2O
0.23
1.02
1.05
1.02
2.00
1.04
2.96
2.14
2.29
4.12
4.10
4.12
6.08