

Tunable synthesis of benzothiophene fused pyranone and thiochromen fused furan derivatives via domino process

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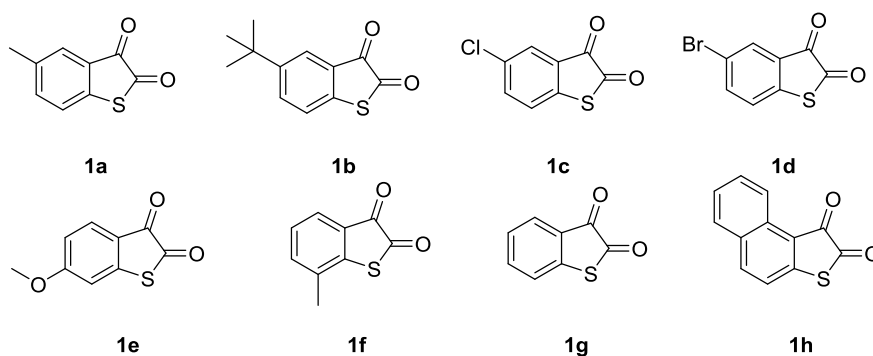
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1. General information and materials

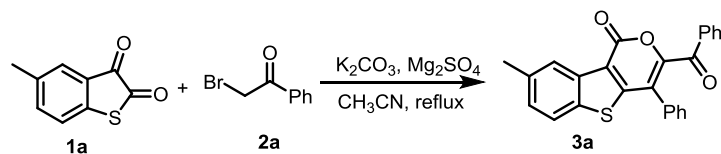
All reactions were performed under Ar atmospheres in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers (Aldrich, TCI or Alfa Aesar) and used without further purification. All solvents were purified and dried according to standard methods prior to use. TLC monitored all reactions with silica gel-coated plates. Flash column chromatography was performed using 200-300 mesh silica gel. ^1H - and ^{13}C NMR spectra were recorded at ambient temperature on Bruker 400 instruments. All spectra were referenced to CDCl_3 (^1H δ 7.26 ppm and ^{13}C NMR δ 77.00 ppm). ^{19}F NMR spectrum was recorded on Bruker 400 (376 MHz) spectrometers with CFCl_3 as external standard. HRMS were obtained on Waters Xevo Q-TOF MS with ESI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected. IR were measured on a Perkin-Elmer 983G apparatus. Compound **1a-1h** was synthesized according to the reported method¹, The characterization of compounds **5a** has been reported².

2. The structure of thioisatin 1



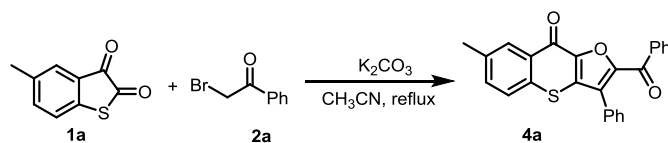
3. General procedure for the synthesis of 3 and 4

3a as an example



Under Ar atmosphere, to a solution of **1a** (134 mg, 0.75 mmol) in CH_3CN 5 mL was added **2a** (373 mg, 1.88 mmol), MgSO_4 (651 mg, 4.5 mmol) and K_2CO_3 (311 mg, 2.25 mmol). The stirred mixture was heated under reflux for several hours and the progress was monitored using TLC detection. After hydrolysis with H_2O , the combined aqueous layers were extracted with DCM (20 mL \times 4). The combined organic layers were dried over MgSO_4 and concentrated. The residue was purified by column chromatography (ethyl acetate: petroleum ether = 1:5) to give **3a** (282 mg, 95%) as yellow solid.

4a as an example



Under Ar atmosphere, to a solution of **1a** (134 mg, 0.75 mmol) in CH_3CN 5 mL was added **2a** (373 mg, 1.88 mmol) and K_2CO_3 (311 mg, 2.25 mmol). The stirred mixture was heated under reflux for several hours and the progress was monitored using TLC detection. After hydrolysis with H_2O , the combined aqueous layers were extracted with DCM (20 mL \times 4). The combined organic layers were dried over

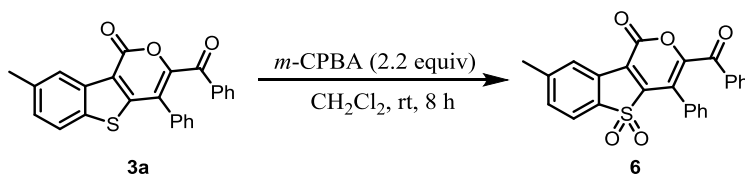
MgSO₄ and concentrated. The residue was purified by column chromatography (ethyl acetate: petroleum ether = 1:5) to give **4a** (95 mg, 32%) as yellow solid.

4. Procedure for gram-scale reaction of **3a** and **4a**

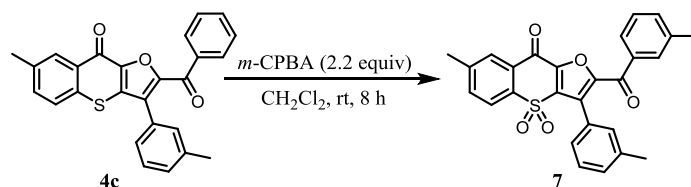
Under Ar atmosphere, to a solution of **1a** (1 g, 5.61 mmol) in CH₃CN 37 mL was added **2a** (2.79 g, 14.03 mmol), MgSO₄ (4.87 g, 33.67 mmol) and K₂CO₃ (2.33 g, 16.83 mmol). The stirred mixture was heated under reflux for several hours and the progress was monitored using TLC detection. After hydrolysis with H₂O, the combined aqueous layers were extracted with DCM (50 mL×4). The combined organic layers were dried over MgSO₄ and concentrated. The residue was purified by column chromatography (ethyl acetate: petroleum ether = 1:5) to give **3a** (1.3 g, 58%) as yellow solid.

Under Ar atmosphere, to a solution of **1a** (1 g, 5.61 mmol) in CH₃CN 37 mL was added **2a** (2.79 g, 14.03 mmol) and K₂CO₃ (2.33 g, 16.83 mmol). The stirred mixture was heated under reflux for several hours and the progress was monitored using TLC detection. After hydrolysis with H₂O, the combined aqueous layers were extracted with DCM (50 mL×4). The combined organic layers were dried over MgSO₄ and concentrated. The residue was purified by column chromatography (ethyl acetate: petroleum ether = 1:5) to give **3a** (670 mg, 30%) as yellow solid.

5. Synthetic procedure for **6**, **7** and **8**

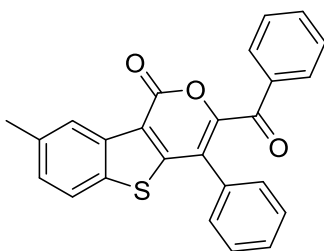


Under Ar atmosphere, to a solution of **3a** (119mg, 0.30 mmol) in DCM 3 mL was added *m*-CPBA (114 mg, 0.66 mmol). The reaction mixture was stirred at room temperature for 8 hours. After the reaction complete (monitored by TLC), the solvent was removed in vacuum. The residue was purified by column chromatography (ethyl acetate: petroleum ether = 1:2) to give **6** (78 mg, 61%) as yellow solid.



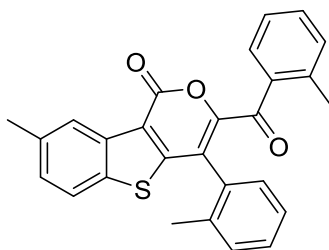
Under Ar atmosphere, to a solution of **4c** (123 mg, 0.30 mmol) in DCM 3 mL was added *m*-CPBA (114 mg, 0.66 mmol). The reaction mixture was stirred at room temperature for 8 hours. After the reaction complete (monitored by TLC), the solvent was removed in vacuum. The residue was purified by column chromatography (ethyl acetate: petroleum ether = 1:2) to give **7** (111 mg, 81%) as yellow solid.

6. Characterization of all new compounds



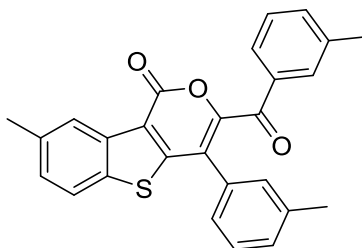
3-benzoyl-8-methyl-4-phenyl-1H-benzo[4,5]thieno[3,2-c]pyran-1-one (3a)

Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 282 mg (yield 95%); mp 171-173 °C; IR (KBr) 3436, 3056, 2919, 1728, 1659, 1448, 1278, 1254, 1012, 816, 732, 708 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.56 (s, 1H), 7.91 – 7.83 (m, 2H), 7.75 (d, J = 8.4 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 – 7.34 (m, 8H), 2.57 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 187.4, 156.0, 155.1, 148.9, 137.0, 136.5, 136.1, 135.6, 134.2, 132.4, 130.1, 129.5, 129.4, 129.1, **128.83**, **128.76**, 125.1, 121.9, 120.2, 118.9, 21.8 ppm. HRMS (ESI-TOF) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{16}\text{O}_3\text{SNa}^+$ 419.0712, found 419.0716.



8-methyl-3-(2-methylbenzoyl)-4-(o-tolyl)-1H-benzo[4,5]thieno[3,2-c]pyran-1-one (3b)

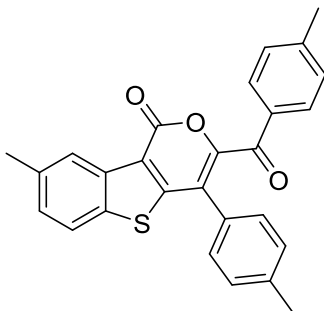
Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 240 mg (yield 75%); mp 184-186 °C; IR (KBr) 3403, 3056, 2919, 1718, 1669, 1452, 1270, 1252, 1014, 804, 767, 653 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.54 (s, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.39 – 7.27 (m, 4H), 7.21 (q, J = 8.0, 6.1 Hz, 4H), 2.56 (s, 3H), 2.39 (s, 3H), 2.25 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 189.2, 156.0, 155.5, 149.0, 139.0, 137.1, **136.84**, **136.76**, 136.0, 135.9, 132.1, 131.9, 131.6, 130.5, 130.2, 129.5, 129.4, 128.7, 126.1, 125.4, 125.0, 121.9, 120.0, 119.0, 21.6, 20.3, 19.9 ppm. HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{21}\text{O}_3\text{S}^+$ 425.1206, found 425.1208.



8-methyl-3-(3-methylbenzoyl)-4-(m-tolyl)-1H-benzo[4,5]thieno[3,2-c]pyran-1-one (3c)

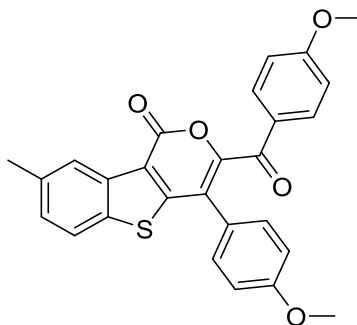
Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 266 mg (yield 84%); mp 174-176 °C; IR (KBr) 3418, 3042, 2912, 2855, 1718, 1649, 1600, 1459, 1280, 1217, 1047, 815, 767, 696 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.55 (s, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 9.6 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 7.24 (s, 2H), 7.22 – 7.15 (m,

2H), 2.56 (s, 3H), 2.36 (s, 3H), 2.33 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 187.7, 156.1, 155.2, 149.0, 138.8, 138.5, 136.9, 136.5, 136.1, 135.6, 135.0, 132.3, 130.5, 130.2, 129.9, 128.9, 128.7, 128.6, 127.4, 126.4, 125.0, 121.9, 120.2, 118.8, 21.7, 21.5, 21.4 ppm. HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{21}\text{O}_3\text{S}^+$ 425.1206, found 425.1204.



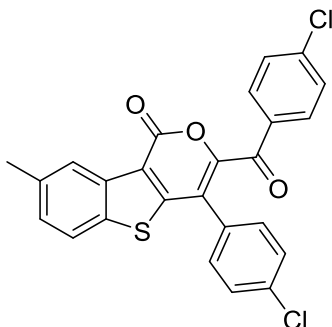
8-methyl-3-(4-methylbenzoyl)-4-(p-tolyl)-1H-benzo[4,5]thieno[3,2-c]pyran-1-one (3d)

Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 253 mg (yield 80%); mp 178-180 °C; IR (KBr) 3437, 3054, 2920, 1728, 1652, 1599, 1446, 1276, 1253, 1012, 972, 802, 768 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.53 (s, 1H), 7.80 (d, $J = 8.0$ Hz, 2H), 7.72 (d, $J = 8.0$ Hz, 1H), 7.33 (t, $J = 7.6$ Hz, 3H), 7.21 (dd, $J = 18.2, 7.8$ Hz, 4H), 2.56 (s, 3H), 2.41 (s, 3H), 2.36 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 187.0, 156.0, 155.3, 149.2, 145.2, 139.3, 136.7, 136.3, 136.1, 133.1, 130.2, 129.7, 129.4, 129.3, 129.1, 128.5, 124.9, 121.7, 119.5, 118.5, 21.8, 21.6, 21.4 ppm. HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{21}\text{O}_3\text{S}^+$ 425.1206, found 425.1207.



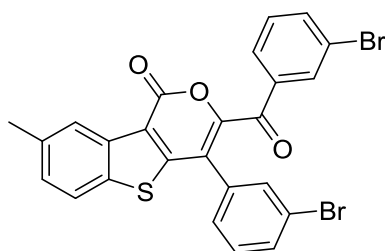
3-(3-methoxybenzoyl)-4-(4-methoxyphenyl)-8-methyl-1H-benzo[4,5]thieno[3,2-c]pyran-1-one (3e)

Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 301 mg (yield 88%); mp 198-200 °C; IR (KBr) 3422, 2934, 2838, 1724, 1648, 1597, 1512, 1258, 1172, 1022, 837, 805, 769 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.53 (s, 1H), 7.87 (d, $J = 8.8$ Hz, 2H), 7.73 (d, $J = 8.4$ Hz, 1H), 7.35 (t, $J = 8.0$ Hz, 3H), 6.90 (d, $J = 8.8$ Hz, 4H), 3.86 (s, 3H), 3.80 (s, 3H), 2.56 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 185.8, 164.4, 160.2, 156.1, 155.6, 149.3, 136.7, **136.14, 136.11**, 132.5, 130.6, 128.5, 128.4, 124.9, 124.4, 121.8, 118.8, 118.3, 114.4, 114.0, 55.6, 55.3, 21.6 ppm. HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{21}\text{O}_5\text{S}^+$ 457.1104, found 457.1106.



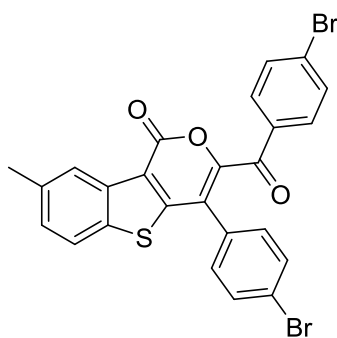
3-(4-chlorobenzoyl)-4-(4-chlorophenyl)-8-methyl-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (3f)

Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 258 mg (yield 74%); mp 239-240 °C; IR (KBr) 3448, 2917, 1716, 1654, 1491, 1273, 1255, 1150, 1090, 1011, 838, 777 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.53 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.39 (q, *J* = 8.2 Hz, 5H), 2.57 (s, 3H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 185.7, 155.4, 154.4, 148.4, 140.9, 137.1, 136.4, 135.9, 135.7, 133.7, 131.4, 130.7, 130.6, 129.4, 129.2, 129.0, 125.0, 121.9, 119.6, 119.1, 21.6 ppm. HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₂₅H₁₅Cl₂O₃S⁺ 465.0113, found 465.0117.



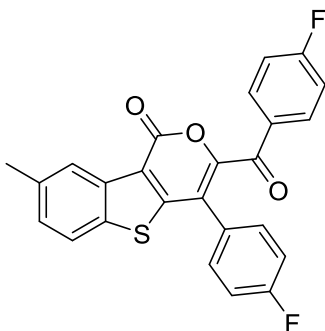
3-(3-bromobenzoyl)-4-(3-bromophenyl)-8-methyl-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (3g)

Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 313 mg (yield 75%); mp 179-181 °C; IR (KBr) 3416, 3058, 2918, 1728, 1662, 1560, 1474, 1419, 1252, 1034, 793, 761, 716 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.55 (s, 1H), 7.96 (t, *J* = 1.6 Hz, 1H), 7.82 – 7.74 (m, 2H), 7.72 – 7.68 (m, 1H), 7.61 – 7.52 (m, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.32 – 7.29 (m, 1H), 2.57 (s, 3H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 185.5, 155.3, 154.0, 148.1, 137.2, 137.1, 136.9, 136.6, 135.9, 134.2, 132.7, 132.6, 132.2, 130.5, 130.2, 129.1, 128.4, 128.1, 125.1, 123.0, 122.9, 121.9, 119.7, 119.3, 21.6 ppm. HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₂₅H₁₅Br₂O₃S⁺ 552.9103, found 552.9107.



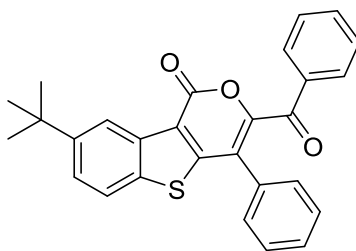
3-(4-bromobenzoyl)-4-(4-bromophenyl)-8-methyl-1*H*-benzo[4,5]thieno[3,2-*c*]pyran-1-one (3h)

Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 317 mg (yield 76%); mp 243-245 °C; IR (KBr) 3448, 2917, 1714, 1654, 1586, 1487, 1273, 1151, 1071, 1007, 769 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.57 – 8.54 (m, 1H), 7.79 (ddd, *J* = 8.3, 4.3, 2.2 Hz, 3H), 7.67 – 7.62 (m, 2H), 7.61 – 7.57 (m, 2H), 7.41 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.35 – 7.31 (m, 2H), 2.59 (s, 3H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 185.9, 155.4, 154.3, 148.3, 137.1, 136.4, 135.9, 134.1, 132.3, 132.2, 131.4, 131.1, 130.8, 129.8, 129.0, 125.0, 124.0, 121.9, 119.7, 119.1, 21.6 ppm. HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₂₅H₁₅Br₂O₃S⁺ 552.9103, found 552.9106.



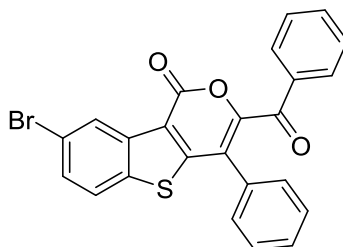
3-(4-fluorobenzoyl)-4-(4-fluorophenyl)-8-methyl-1H-benzo[4,5]thieno[3,2-c]pyran-1-one (3i)

Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 233 mg (yield 72%); mp 211-213 °C; IR (KBr) 3422, 2918, 1730, 1671, 1598, 1509, 1279, 1238, 1155, 1013, 846, 795 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.53 (s, 1H), 7.97 – 7.90 (m, 2H), 7.75 (d, J = 8.0 Hz, 1H), 7.44 – 7.36 (m, 3H), 7.12 (q, J = 8.0 Hz, 4H), 2.57 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 185.4, 167.6, 165.0, 163.2(d, J = 248.4 Hz), 155.6, 154.7, 148.6, 137.0, 136.3, 135.9, 132.8 (d, J = 9.6 Hz), 131.8 (d, J = 2.6 Hz), 131.3 (d, J = 8.4 Hz), 128.9, 128.1 (d, J = 3.5 Hz), 125.0, 121.8, 119.1 (d, J = 40.2 Hz), 116.2 (d, J = 15.8 Hz), 116.0 (d, J = 16.2 Hz), 21.6 ppm; ^{19}F NMR (376 MHz, Chloroform- d) δ -102.24 (tt, J = 8.2, 5.4 Hz), -110.91 (tt, J = 8.4, 5.2 Hz) ppm; HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{25}\text{H}_{15}\text{F}_2\text{O}_3\text{S}^+$ 433.0704, found 433.0709.



3-benzoyl-8-(tert-butyl)-4-phenyl-1H-benzo[4,5]thieno[3,2-c]pyran-1-one (j)

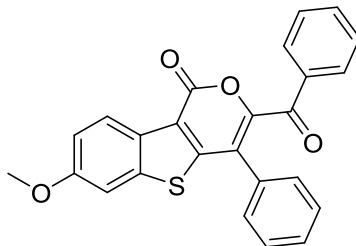
Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 276 mg (yield 84%); mp 183-185 °C; IR (KBr) 3421, 3057, 2959, 2863, 1716, 1664, 1597, 1450, 1255, 1183, 1014, 731, 696 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.76 (d, J = 2.0 Hz, 1H), 7.88 (d, J = 7.6 Hz, 2H), 7.80 (d, J = 8.8 Hz, 1H), 7.62 (dd, J = 8.6, 1.8 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 – 7.38 (m, 7H), 1.45 (s, 9H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 187.3, 155.9, 154.9, 150.3, 148.8, 136.4, 135.9, 135.5, 134.1, 132.3, 130.0, 129.4, 129.3, 129.0, 128.6, 125.3, 121.7, 121.4, 120.1, 119.2, 35.2, 31.6 ppm. HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{23}\text{O}_3\text{S}^+$ 439.1362, found 439.1363.



3-benzoyl-8-bromo-4-phenyl-1H-benzo[4,5]thieno[3,2-c]pyran-1-one (3k)

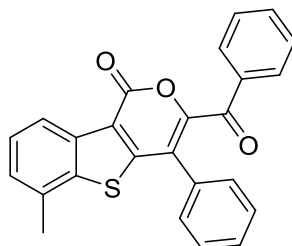
Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 235 mg (yield 68%); mp 209-211 °C; IR (KBr) 3435, 3089, 3062, 1726, 1668, 1595, 1451, 1421,

1261, 1179, 1007, 840, 777, 707 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.92 (d, *J* = 1.6 Hz, 1H), 7.95 – 7.84 (m, 2H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.50 – 7.40 (m, 7H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 187.0, 156.0, 155.5, 149.5, 137.6, 137.3, 135.3, 134.3, 131.9, 130.2, 130.0, 129.6, 129.2, 129.1, 128.7, 127.7, 123.4, 121.1, 119.6, 118.2 ppm. HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₂₄H₁₄BrO₃S⁺ 460.9842, found 460.9843.



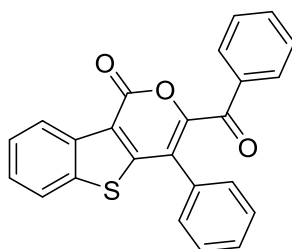
3-benzoyl-7-methoxy-4-phenyl-1H-benzo[4,5]thieno[3,2-c]pyran-1-one (3l)

Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 270 mg (yield 87%); mp 199-200 °C; IR (KBr) 3432, 3061, 2938, 2837, 1725, 1661, 1603, 1484, 1263, 1053, 1007, 837, 734 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.61 (d, *J* = 9.2 Hz, 1H), 7.87 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.38 (m, 7H), 7.31 (d, *J* = 2.0 Hz, 1H), 7.21 (dd, *J* = 9.0, 2.2 Hz, 1H), 3.91 (s, 3H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 187.1, 159.3, 155.8, 152.5, 148.2, 141.1, 135.7, 133.9, 132.4, 130.0, 129.4, 129.31, 129.26, 128.9, 128.6, 125.9, 120.4, 119.2, 116.0, 105.2, 55.7 ppm. HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₂₅H₁₇O₄S⁺ 413.0842, found 413.0844.



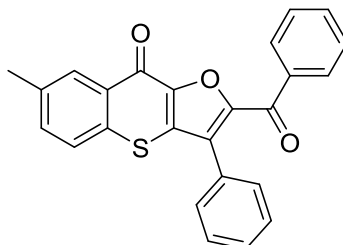
3-benzoyl-6-methyl-4-phenyl-1H-benzo[4,5]thieno[3,2-c]pyran-1-one (3m)

Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 249 mg (yield 84%); mp 172-174 °C; IR (KBr) 3422, 3060, 1728, 1673, 1597, 1471, 1447, 1271, 1008, 793, 737, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.58 (d, *J* = 8.0 Hz, 1H), 7.92 – 7.83 (m, 2H), 7.56 (dt, *J* = 12.3, 7.6 Hz, 3H), 7.46 – 7.40 (m, 6H), 7.34 (d, *J* = 7.2 Hz, 1H), 2.56 (s, 3H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 187.2, 155.9, 154.2, 148.9, 139.4, 135.6, 135.5, 134.1, 132.3, 131.8, 130.0, 129.4, 129.3, 129.0, 128.6, 127.4, 127.1, 122.7, 120.0, 119.7, 20.3 ppm. HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₂₅H₁₇O₃S⁺ 397.0893, found 397.0895.



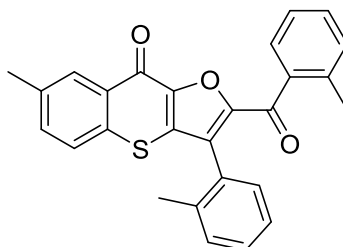
3-benzoyl-4-phenyl-1H-benzo[4,5]thieno[3,2-c]pyran-1-one (3n)

Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 221 mg (yield 77%); mp 168-170 °C; IR (KBr) 3439, 3064, 1726, 1662, 1594, 1450, 1277, 1007, 825, 781, 732, 695 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.74 (d, *J* = 8.0 Hz, 1H), 7.92 – 7.84 (m, 3H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.47 – 7.37 (m, 7H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 187.2, 155.8, 154.8, 149.1, 139.1, 135.8, 135.5, 134.1, 132.2, 130.0, 129.4, 129.3, 129.0, 128.6, 127.0, 126.6, 125.1, 122.2, 119.9, 119.1, 32.1 ppm. HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₂₄H₁₅O₃S⁺ 383.0736, found 383.0734.



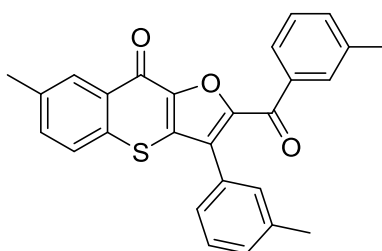
2-benzoyl-7-methyl-3-phenyl-9H-thiochromeno[3,2-b]furan-9-one (4a)

Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 95 mg (yield 32%); mp 149-151 °C; IR (KBr) 3051, 1640, 1606, 1330, 1262, 1176, 904, 737, 717, 694 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.56 (s, 1H), 8.08 (d, *J* = 7.5 Hz, 2H), 7.65 – 7.58 (m, 4H), 7.50 (qt, *J* = 9.4, 4.1 Hz, 6H), 2.56 (s, 3H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 183.9, 169.7, 149.0, 144.0, 137.3, 136.2, 133.7, 133.4, 133.3, 132.6, 130.8, 130.5, 130.2, 129.33, 129.29, 129.0, 128.8, 128.8, 128.6, 127.0, 21.2 ppm. HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₂₅H₁₇O₃S⁺ 397.0893, found 397.0892.



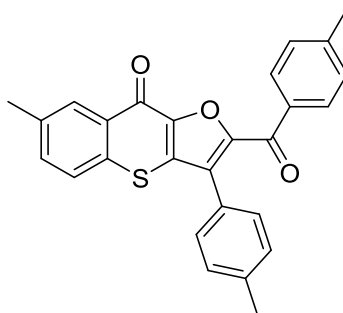
7-methyl-2-(2-methylbenzoyl)-3-(*o*-tolyl)-9H-thiochromeno[3,2-b]furan-9-one (4b)

Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 88 mg (yield 27%); mp 165-167 °C; IR (KBr) 2921, 1656, 1634, 1606, 1329, 1272, 1167, 916, 749 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.53 (s, 1H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.47 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.38 – 7.26 (m, 5H), 7.24 – 7.14 (m, 2H), 2.52 (s, 3H), 2.41 (s, 3H), 2.24 (s, 3H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 186.4, 169.7, 149.8, 144.0, 138.2, 137.3, 136.8, 136.2, 133.34, 133.26, 132.8, 131.8, 131.7, 131.3, 130.5, 129.9, 129.7, 129.44, 129.39, 129.1, 128.3, 127.0, 126.1, 125.4, 21.2, 20.2, 19.9 ppm. HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₂₇H₂₁O₃S⁺ 425.1206, found 425.1208.



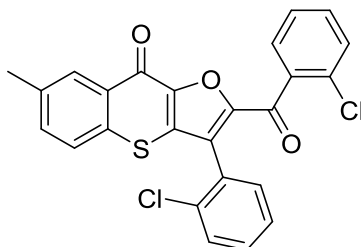
7-methyl-2-(3-methylbenzoyl)-3-(*m*-tolyl)-9*H*-thiochromeno[3,2-*b*]furan-9-one (4c)

Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 105 mg (yield 33%); mp 156-158 °C; IR (KBr) 2961, 2920, 1650, 1604, 1544, 1330, 1258, 1169, 1083, 817, 748, 692 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.57 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.80 (s, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.52 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.43 – 7.33 (m, 5H), 7.26 (dt, *J* = 5.0, 2.9 Hz, 1H), 2.55 (s, 3H), 2.41 (s, 3H), 2.39 (s, 3H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 184.3, 169.7, 149.1, 144.0, 138.6, 138.3, 137.2, 136.2, 134.4, 133.3, 132.6, 130.7, 130.5, 130.4, 130.1, 129.9, 129.0, 128.8, 128.7, 128.4, 127.5, 127.0, 126.3, 21.5, 21.3, 21.2 ppm. HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₂₇H₂₁O₃S⁺ 425.1206, found 425.1210.



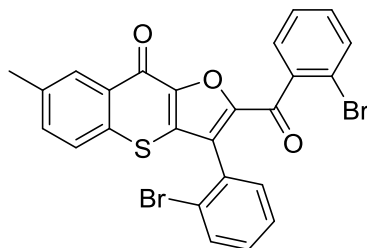
7-methyl-2-(4-methylbenzoyl)-3-(*p*-tolyl)-9*H*-thiochromeno[3,2-*b*]furan-9-one (4d)

Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 129 mg (yield 40%); mp 177-179 °C; IR (KBr) 2918, 1643, 1605, 1329, 1256, 1174, 907, 817, 756 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.54 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.44 (m, 3H), 7.32 – 7.27 (m, 4H), 2.53 (s, 3H), 2.45 – 2.40 (m, 6H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 183.5, 169.7, 149.2, 144.7, 143.8, 139.4, 137.2, 133.7, 133.4, 133.2, 132.6, 130.9, 130.4, 130.3, 129.5, 129.3, 129.1, 129.0, 127.0, 125.9, 21.8, 21.5, 21.3 ppm. HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₂₇H₂₁O₃S⁺ 425.1206, found 425.1202.



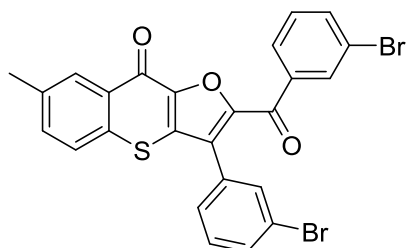
2-(2-chlorobenzoyl)-3-(2-chlorophenyl)-7-methyl-9*H*-thiochromeno[3,2-*b*]furan-9-one (4e)

Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 280 mg (yield 80%); mp 196-198 °C; IR (KBr) 3052, 2921, 1670, 1631, 1468, 1331, 1247, 1166, 908, 771, 749 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.51 (s, 1H), 7.55 – 7.40 (m, 5H), 7.38 – 7.26 (m, 5H), 2.51 (s, 3H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 183.5, 169.7, 149.3, 144.4, 137.3, 136.4, 133.7, 133.4, 133.2, 132.7, 132.5, 132.3, 131.4, 131.2, 130.8, 130.2, 130.02, 129.95, 129.1, 127.9, 127.7, 127.0, 126.9, 126.7, 21.3 ppm. HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₂₅H₁₅Cl₂O₃S⁺ 465.0113, found 465.0114.



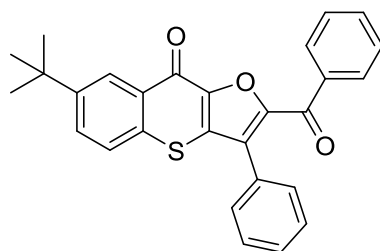
2-(2-bromobenzoyl)-3-(2-bromophenyl)-7-methyl-9H-thiochromeno[3,2-b]furan-9-one (4f)

Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 326 mg (yield 79%); mp 199-201 °C; IR (KBr) 3052, 2920, 1670, 1630, 1467, 1411, 1330, 1246, 1166, 906, 823, 770, 747 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.52 (s, 1H), 7.68 – 7.60 (m, 1H), 7.58 – 7.44 (m, 4H), 7.43 – 7.26 (m, 5H), 2.51 (s, 3H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 184.1, 169.7, 148.8, 144.4, 138.4, 137.3, 133.4, 133.3, 133.2, 133.1, 132.7, 132.4, 131.4, 131.2, 130.9, 129.9, 129.8, 129.1, 127.6, 127.2, 126.9, 123.6, 120.5, 21.2 ppm. HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₂₅H₁₅Br₂O₃S⁺ 552.9103, found 552.9100.



2-(3-bromobenzoyl)-3-(3-bromophenyl)-7-methyl-9H-thiochromeno[3,2-b]furan-9-one (4g)

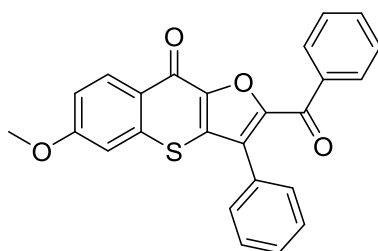
Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 143 mg (yield 34%); mp 211-213 °C; IR (KBr) 2919, 1649, 1602, 1543, 1326, 1269, 1248, 1169, 750, 731 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.53 (s, 1H), 8.18 – 8.09 (m, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.79 – 7.69 (m, 2H), 7.64 – 7.57 (m, 2H), 7.56 – 7.48 (m, 2H), 7.38 (q, *J* = 7.7 Hz, 2H), 2.54 (s, 3H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 182.1, 169.6, 148.5, 144.2, 137.7, 137.6, 136.6, 133.6, 133.1, 132.9, 132.6, 132.5, 132.1, 130.6, 130.5, 130.4, 130.3, 129.7, 129.1, 128.8, 128.0, 127.0, 122.9, 122.8, 21.3 ppm. HRMS (ESI-TOF) *m/z* [M + H]⁺ calcd for C₂₅H₁₅Br₂O₃S⁺ 552.9103, found 552.9102.



2-benzoyl-7-(tert-butyl)-3-phenyl-9H-thiochromeno[3,2-b]furan-9-one (4h)

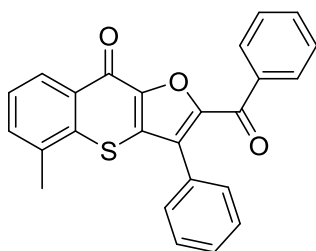
Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 65 mg (yield 20%); mp 188-190 °C; IR (KBr) 2960, 2870, 1641, 1597, 1335, 1252, 1197, 904, 736, 699 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.74 (d, *J* = 2.0 Hz, 1H), 8.08 – 8.04 (m, 2H), 7.74 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.62 – 7.57 (m, 3H), 7.47 (dtd, *J* = 6.0, 4.1, 1.9 Hz, 5H), 1.43 (s, 9H) ppm. ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 183.9, 169.9, 150.6, 149.0, 144.0, 136.2, 133.7, 133.5, 132.4, 130.6, 130.5, 130.2, 130.0, 129.33, 129.31, 128.83, 128.81, 128.61, 128.57, 128.1, 126.9,

125.4, 35.1, 31.2 ppm. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{28}H_{23}O_3S^+$ 439.1362, found 439.1363.



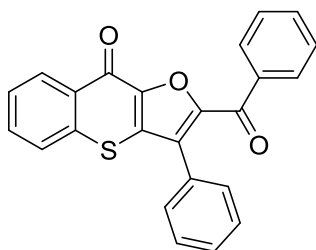
2-benzoyl-6-methoxy-3-phenyl-9H-thiochromeno[3,2-b]furan-9-one (4i)

Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 120 mg (yield 39%); mp 203-205 °C; IR (KBr) 3055, 2972, 1635, 1598, 1331, 1241, 1211, 1010, 301, 698 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, $J = 9.2$ Hz, 1H), 8.13 – 7.98 (m, 2H), 7.64 – 7.55 (m, 3H), 7.52 – 7.42 (m, 5H), 7.13 (dd, $J = 9.2, 2.4$ Hz, 1H), 7.07 (d, $J = 2.4$ Hz, 1H), 3.92 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 183.8, 169.2, 162.1, 148.8, 143.9, 138.8, 136.2, 133.6, 131.1, 130.6, 130.2, 129.8, 129.31, 129.29, 128.9, 128.8, 128.6, 126.5, 115.7, 109.4, 55.8 ppm. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{25}H_{17}O_4S^+$ 413.0842, found 413.0842.



2-benzoyl-5-methyl-3-phenyl-9H-thiochromeno[3,2-b]furan-9-one (4j)

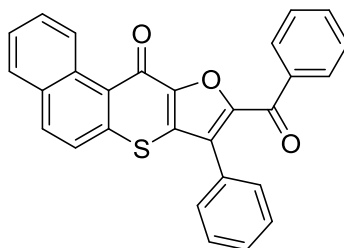
Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 95 mg (yield 32%); mp 177-199 °C; IR (KBr) 2973, 1635, 1336, 1260, 1231, 1010, 908, 733, 697 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, $J = 9.2$ Hz, 1H), 8.06 (d, $J = 8.4$ Hz, 2H), 7.63 – 7.58 (m, 3H), 7.56 – 7.45 (m, 7H), 2.58 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 183.9, 170.0, 149.1, 143.9, 136.2, 136.0, 135.2, 133.7, 133.2, 133.1, 130.8, 130.2, 130.1, 129.4, 129.3, 129.0, 128.8, 128.6, 127.3, 126.5, 20.1 ppm. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{25}H_{17}O_3S^+$ 397.0893, found 397.0897.



2-benzoyl-3-phenyl-9H-thiochromeno[3,2-b]furan-9-one (4k)

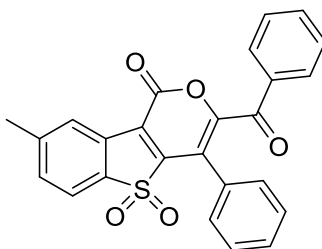
Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 109 mg (yield 38%); mp 129-131 °C; IR (KBr) 3066, 1636, 1593, 1446, 1339, 1268, 1198, 1070, 897, 748 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, $J = 8.8$ Hz, 1H), 8.12 – 8.00 (m, 2H), 7.74 – 7.58 (m, 6H), 7.53 – 7.45 (m, 5H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 183.8, 169.7, 149.1, 143.9,

136.4, 136.2, 133.7, 132.8, 131.8, 130.8, 130.5, 130.2, 129.4, 129.3, 128.83, 128.75, 128.6, 127.1, 126.9 ppm. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{24}H_{15}O_3S^+$ 383.0736, found 383.0735.



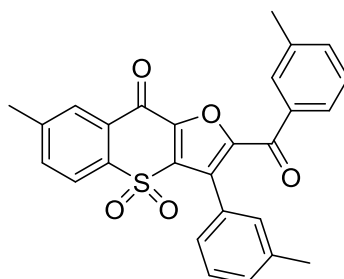
9-benzoyl-8-phenyl-11H-benzo[5,6]thiopheno[3,2-b]furan-11-one (4)

Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v). Yellow solid: 97 mg (yield 30%); mp 205-207 °C; IR (KBr) 3052, 1645, 1620, 1596, 1338, 1261, 1185, 1107, 899, 815, 718 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 10.33 (d, $J = 8.8$ Hz, 1H), 8.13 (d, $J = 7.2$ Hz, 2H), 8.04 (d, $J = 8.8$ Hz, 1H), 7.95 (d, $J = 8.0$ Hz, 1H), 7.84 – 7.78 (m, 1H), 7.71 – 7.59 (m, 5H), 7.54 – 7.45 (m, 5H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 183.8, 172.1, 148.7, 145.9, 139.9, 136.3, 133.6, 133.4, 133.2, 132.1, 130.4, 130.3, 129.4, 129.3, 128.9, 128.6, 128.5, 127.40, 127.35, 127.3, 127.2, 124.4 ppm. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{28}H_{17}O_3S^+$ 433.0893, found 433.0896.



3-benzoyl-8-methyl-4-phenyl-1H-benzo[4,5]thieno[3,2-c]pyran-1-one 5,5-dioxide (6)

Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 1:1 (v/v). Yellow solid: 78 mg (yield 61%); mp 178-180 °C; IR (KBr) 1743, 1670, 1327, 1317, 1250, 1173, 567 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.84 – 7.77 (m, 2H), 7.65 (d, $J = 7.8$ Hz, 1H), 7.58 (tt, $J = 7.0$, 1.1 Hz, 1H), 7.48 – 7.38 (m, 5H), 7.33 (qd, $J = 4.4$, 1.6 Hz, 3H), 2.52 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 186.0, 155.9, 155.7, 149.1, 145.9, 134.7, 134.5, 133.8, 131.9, 130.3, 129.9, 128.8, 128.7, 127.2, 126.5, 126.3, 121.8, 119.5, 117.0, 22.0 ppm. HRMS (ESI-TOF) m/z $[M + H]^+$ calcd for $C_{25}H_{17}O_5S^+$ 429.0791, found 429.0787.

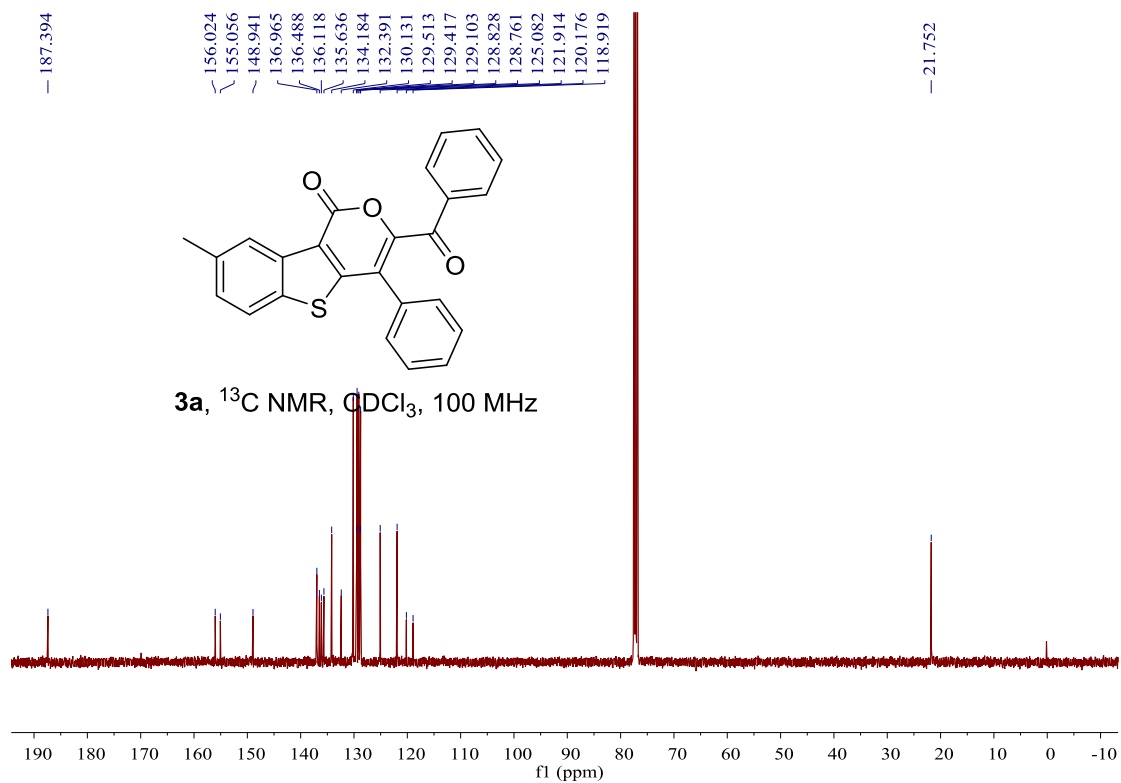
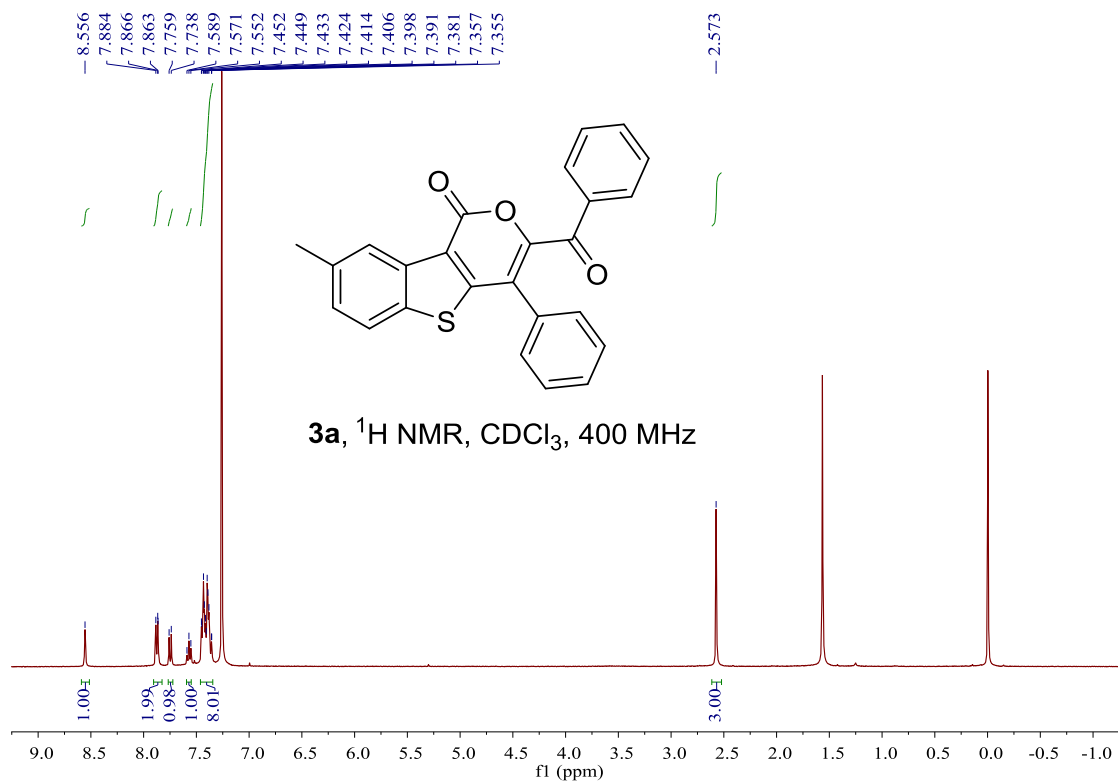


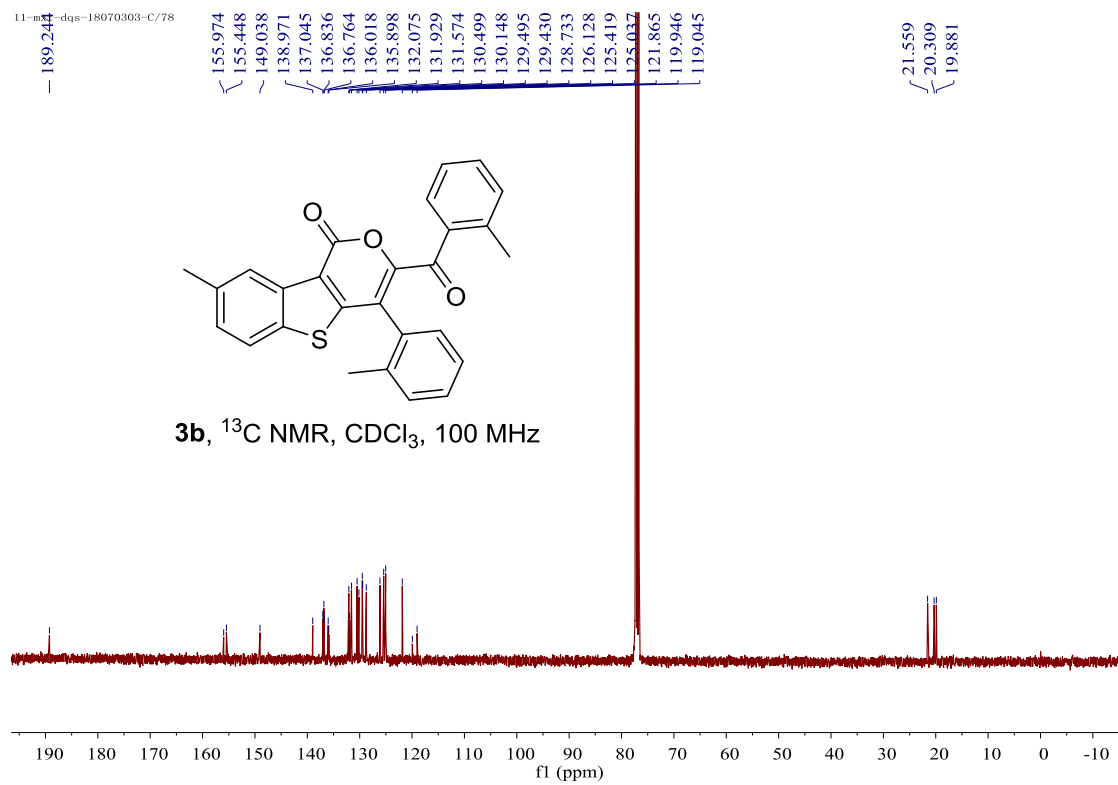
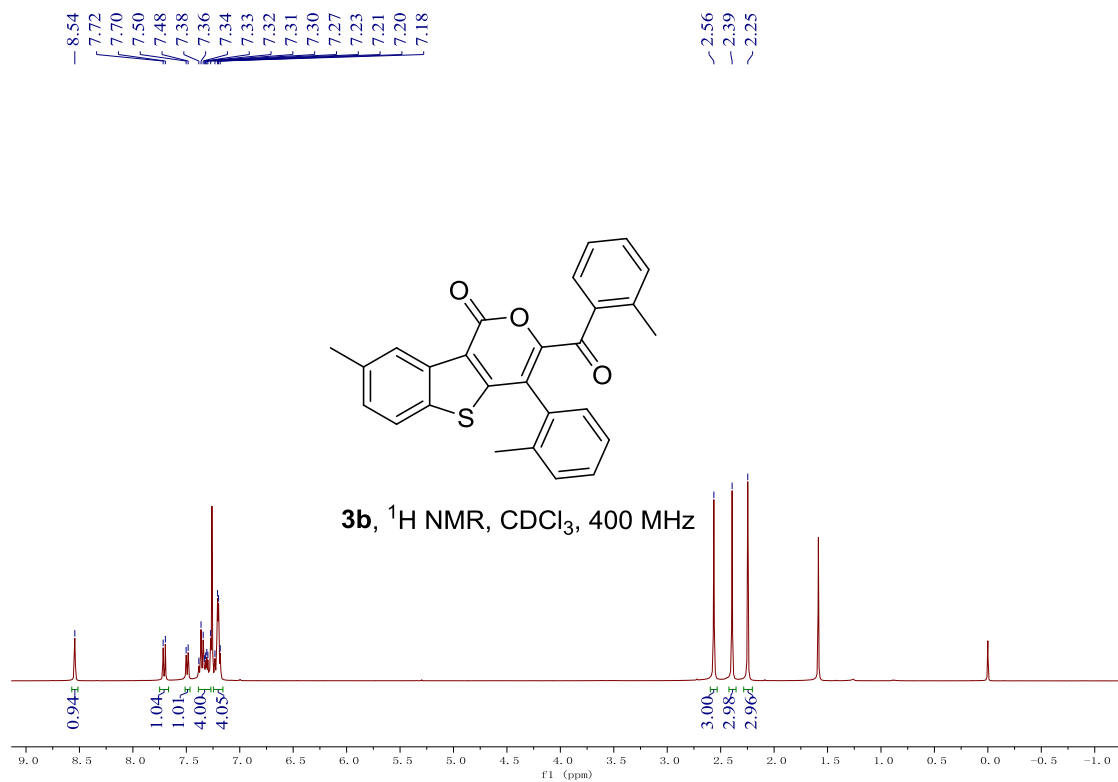
7-methyl-2-(3-methylbenzoyl)-3-(m-tolyl)-9H-thiopheno[3,2-b]furan-9-one 4,4-dioxide (7)

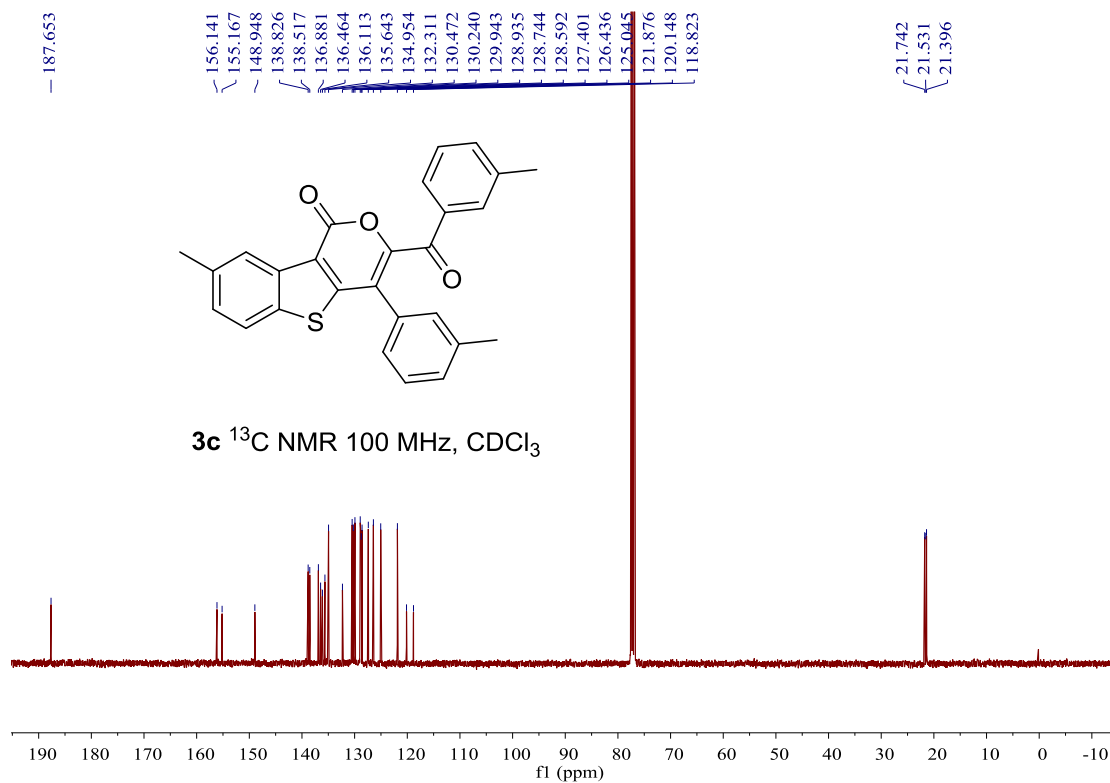
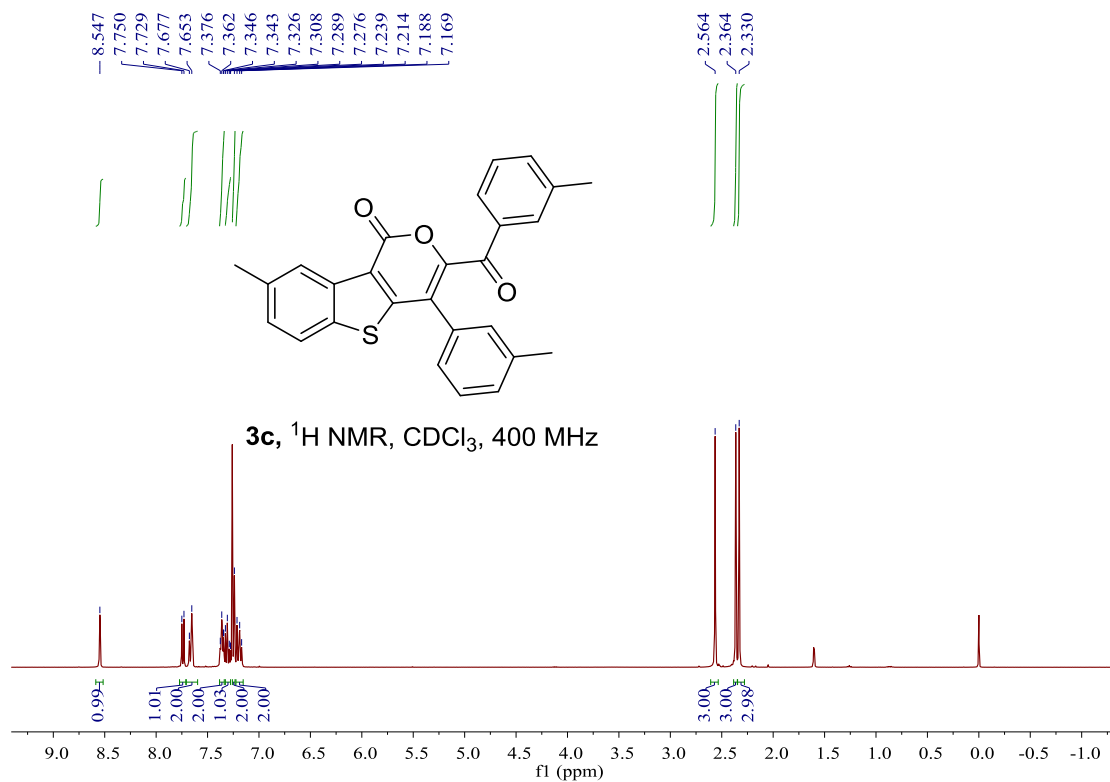
Purified by chromatography on silica gel, eluting with petroleum ether/ethyl acetate 1:1 (v/v). Yellow solid: 111 mg (yield 81%); mp 166-168 °C; IR (KBr) 2920, 1685, 1664, 1303, 1154, 822, 752, 697 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.99 (d, $J = 8.4$ Hz, 1H), 7.71 (d, $J = 8.0$ Hz, 1H), 7.66 (d, $J = 8.0$ Hz, 1H), 7.61 (s, 1H), 7.46 (d, $J = 7.6$ Hz, 1H), 7.38 (s, 1H), 7.35 (d, $J = 8.0$ Hz, 1H), 7.29 (dd,

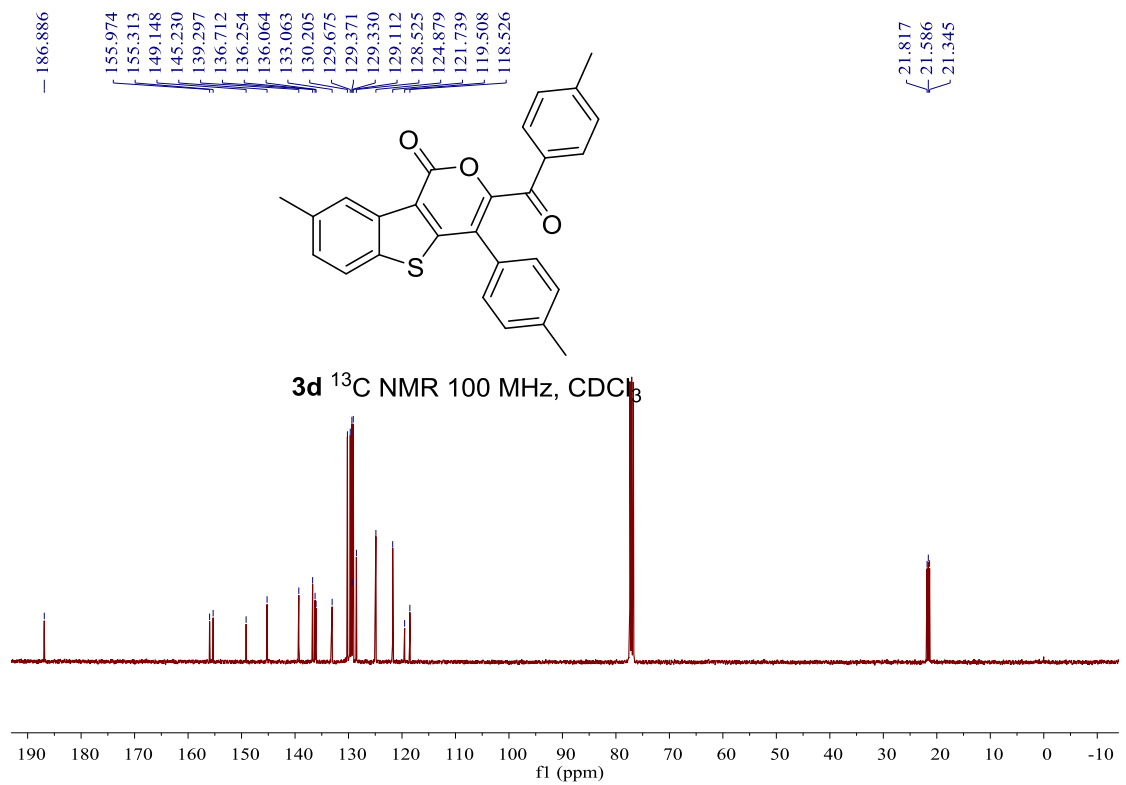
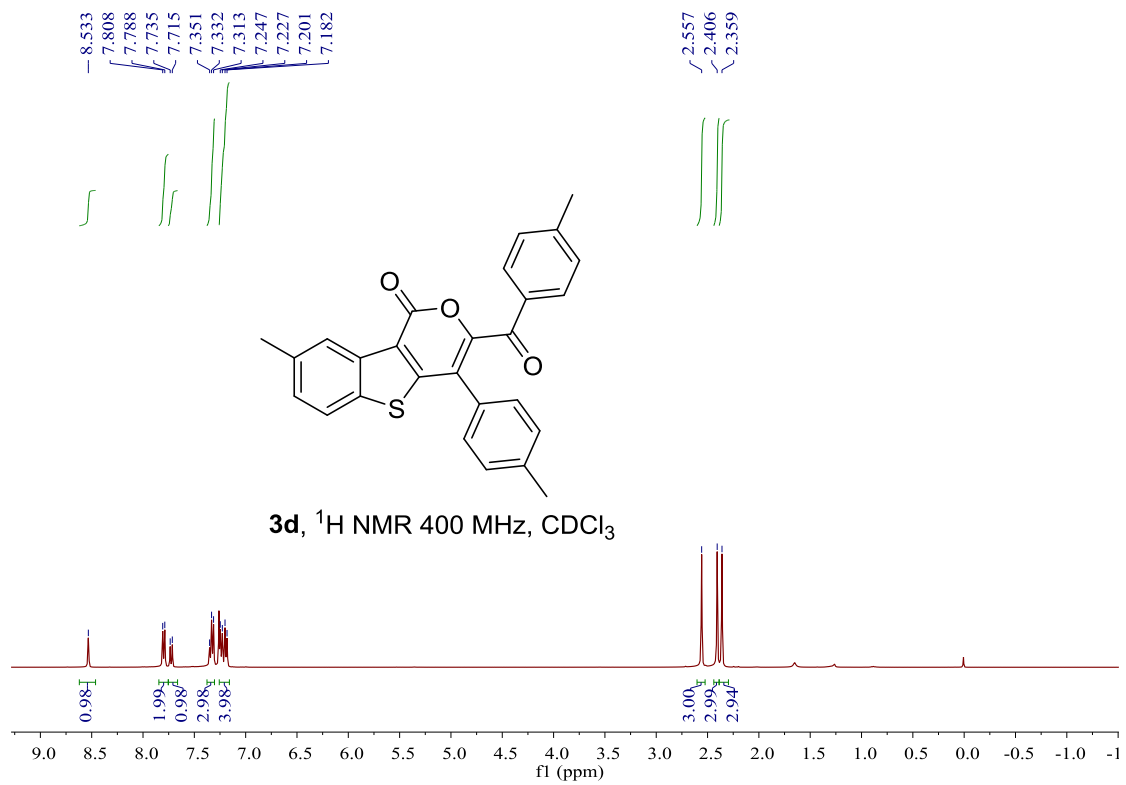
$J = 7.6, 4.8$ Hz, 2H), 7.18 (d, $J = 7.6$ Hz, 1H), 2.56 (s, 3H), 2.32 (s, 3H), 2.31 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 183.5, 169.8, 149.9, 145.1, 144.5, 141.3, 138.4, 138.2, 135.9, 135.5, 134.8, 132.7, 130.7, 130.6, 130.5, 130.4, 128.8, 128.5, 128.4, 127.3, 127.12, 127.10, 126.7, 124.0, 21.6, 21.3, 21.12 ppm. HRMS (ESI-TOF) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{21}\text{O}_5\text{S}^+$ 457.1104, found 457.1116.

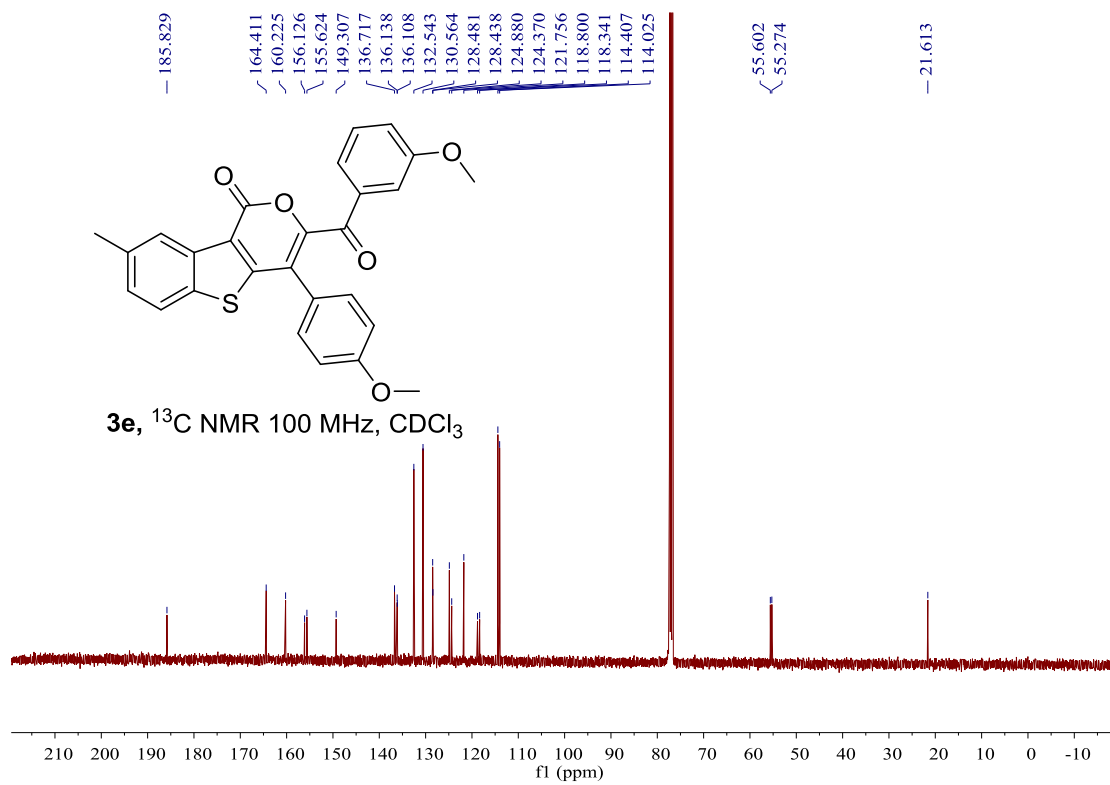
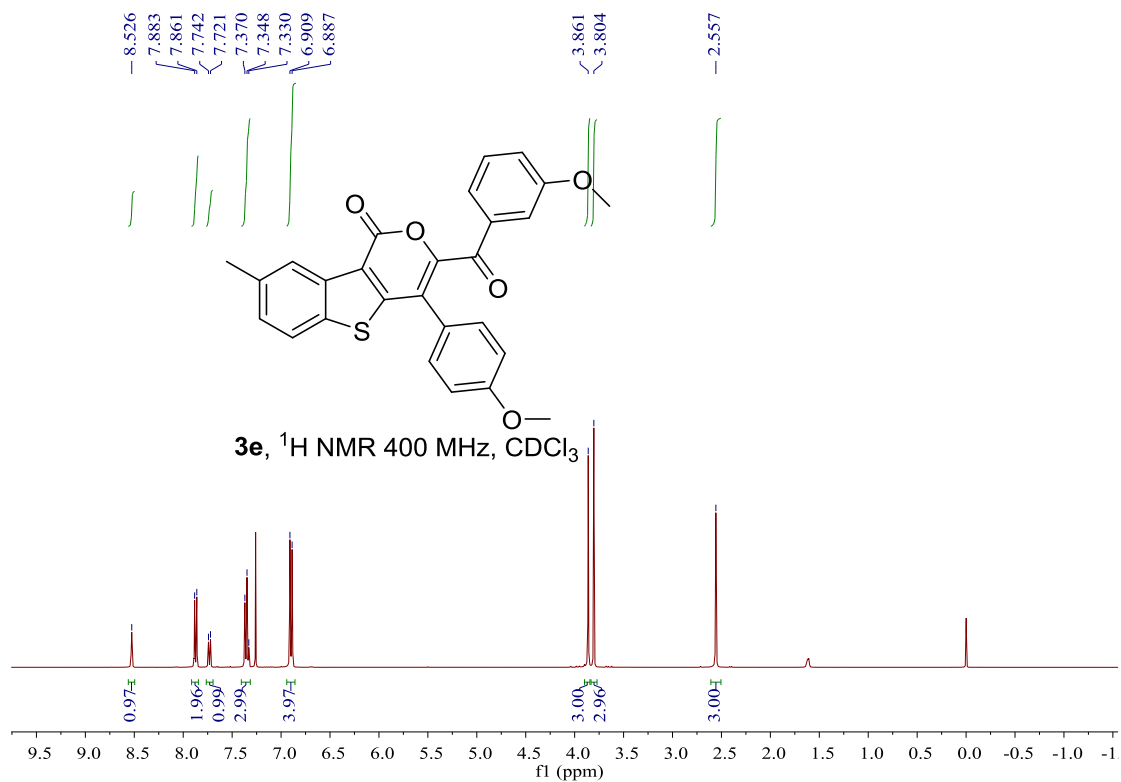
7. NMR spectra of all new compounds

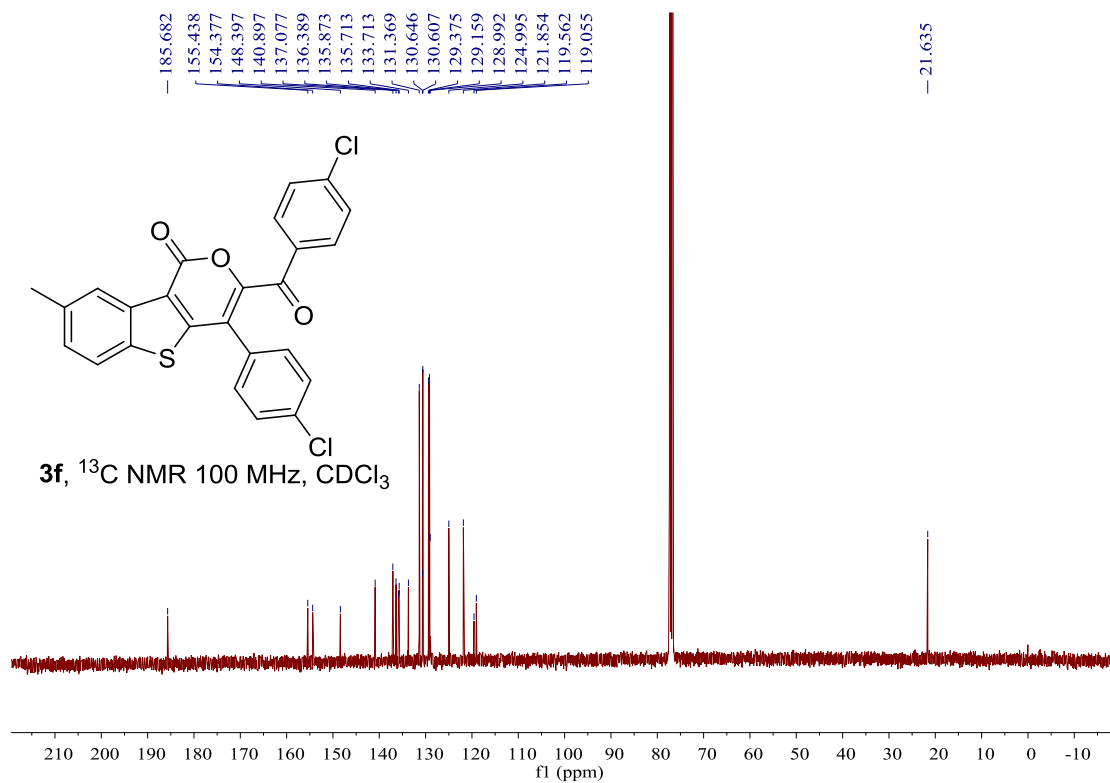
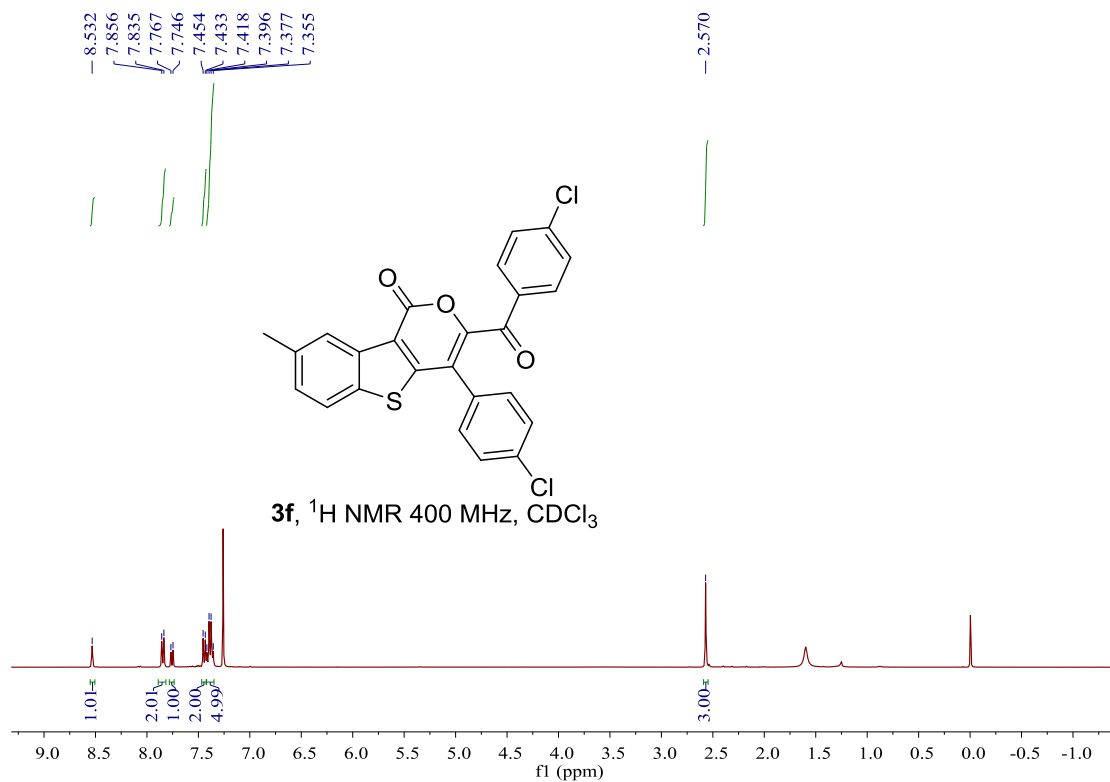


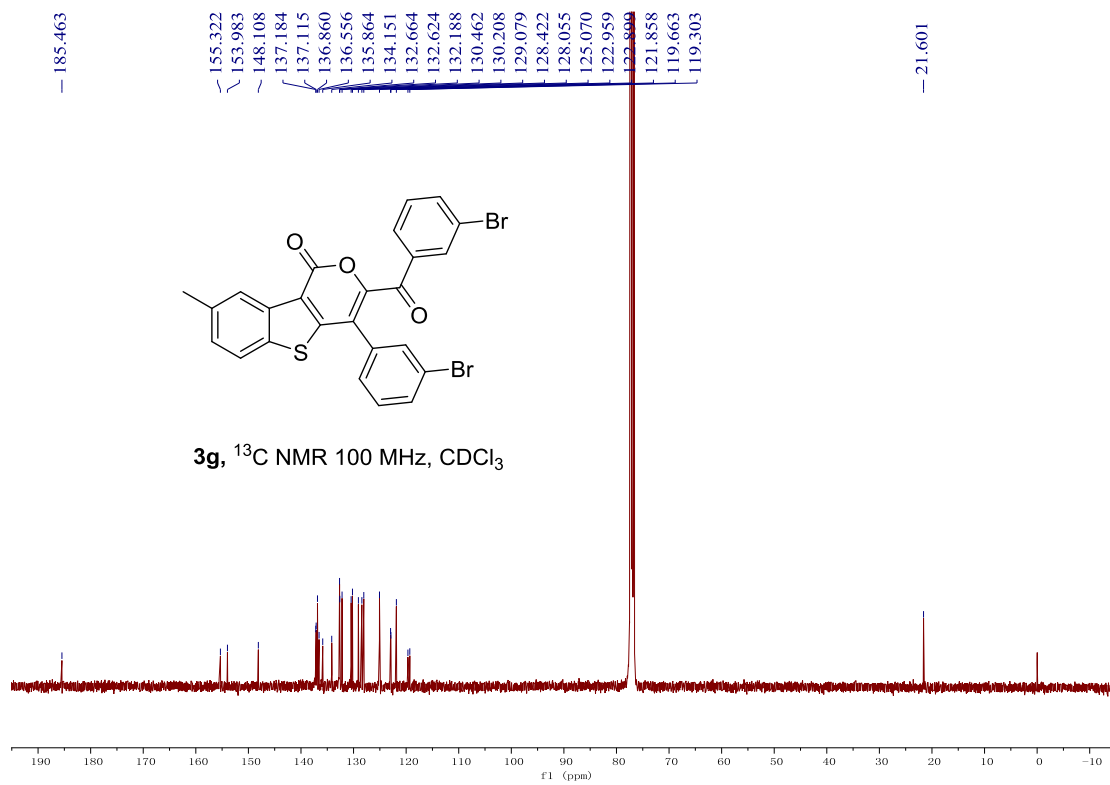
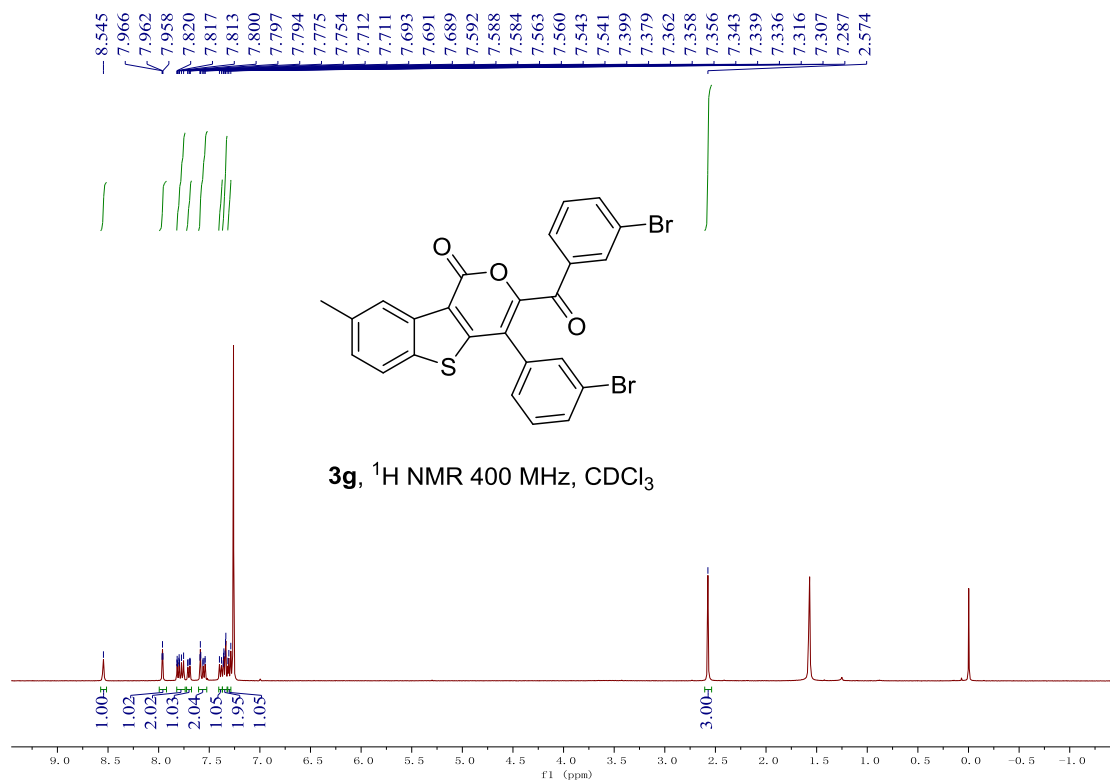


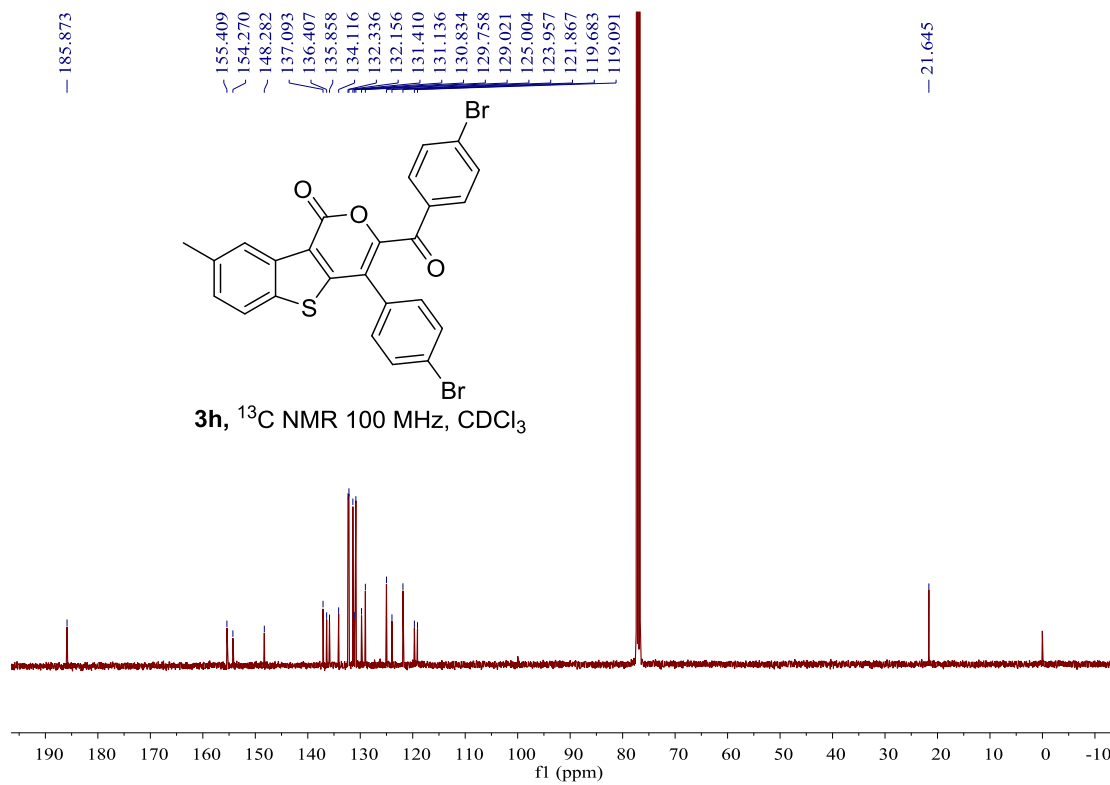
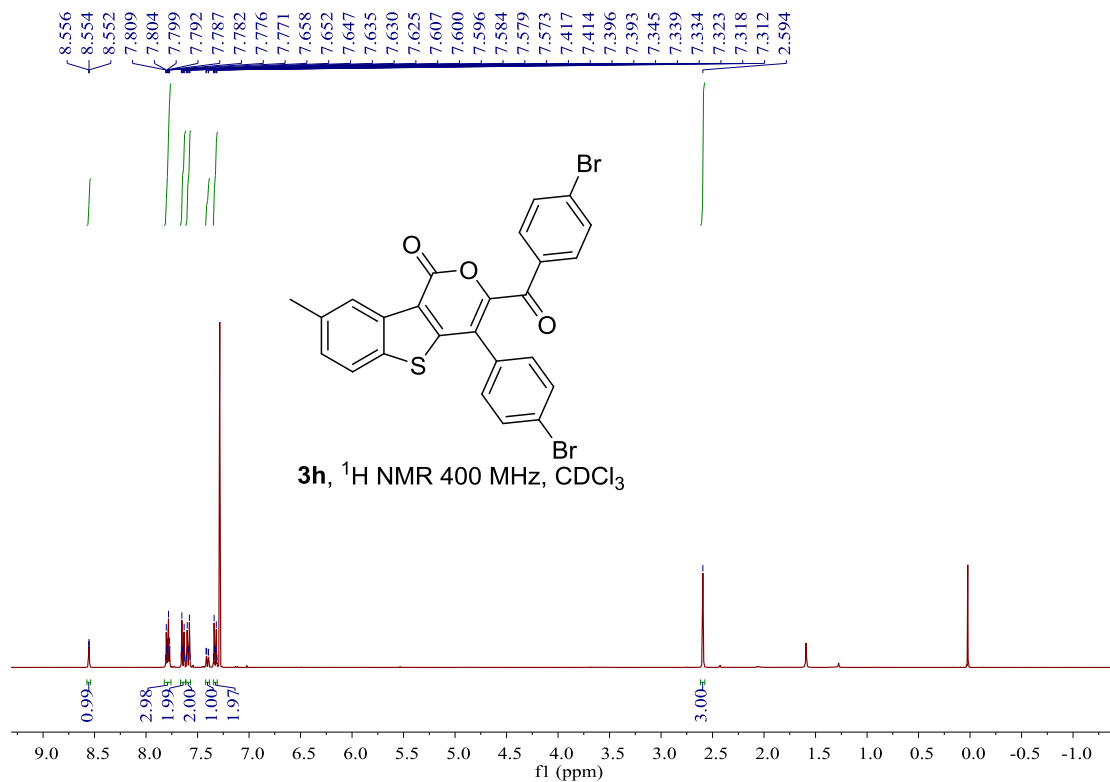


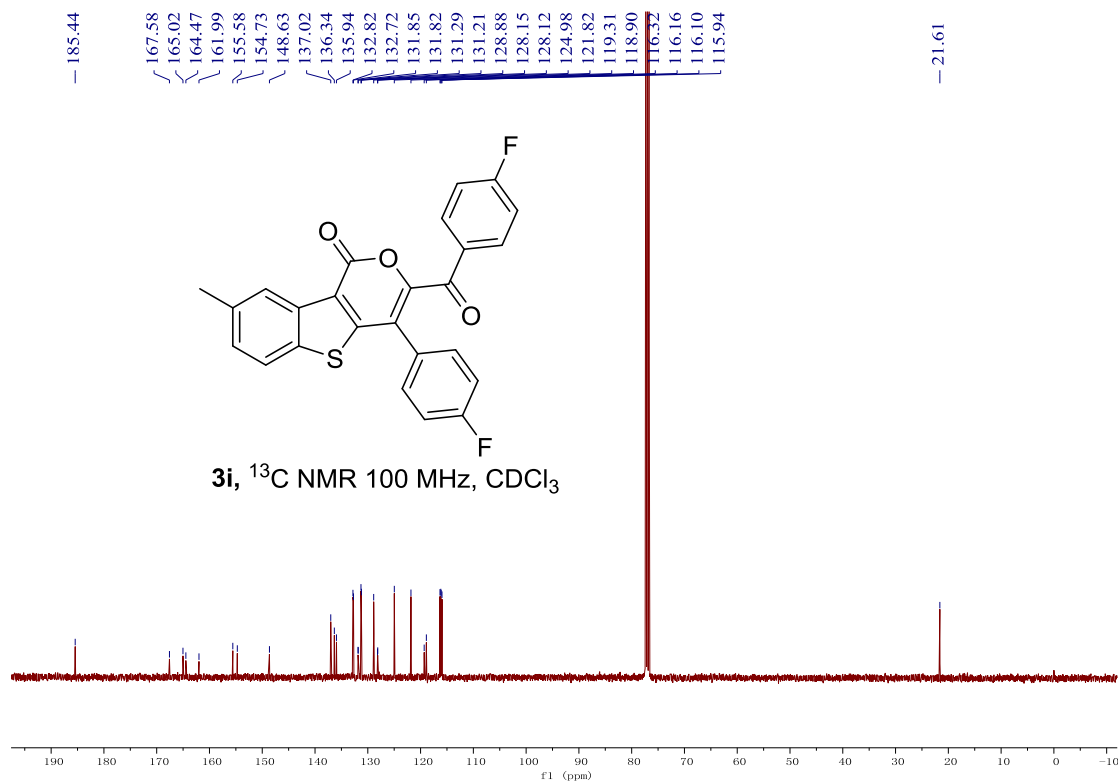
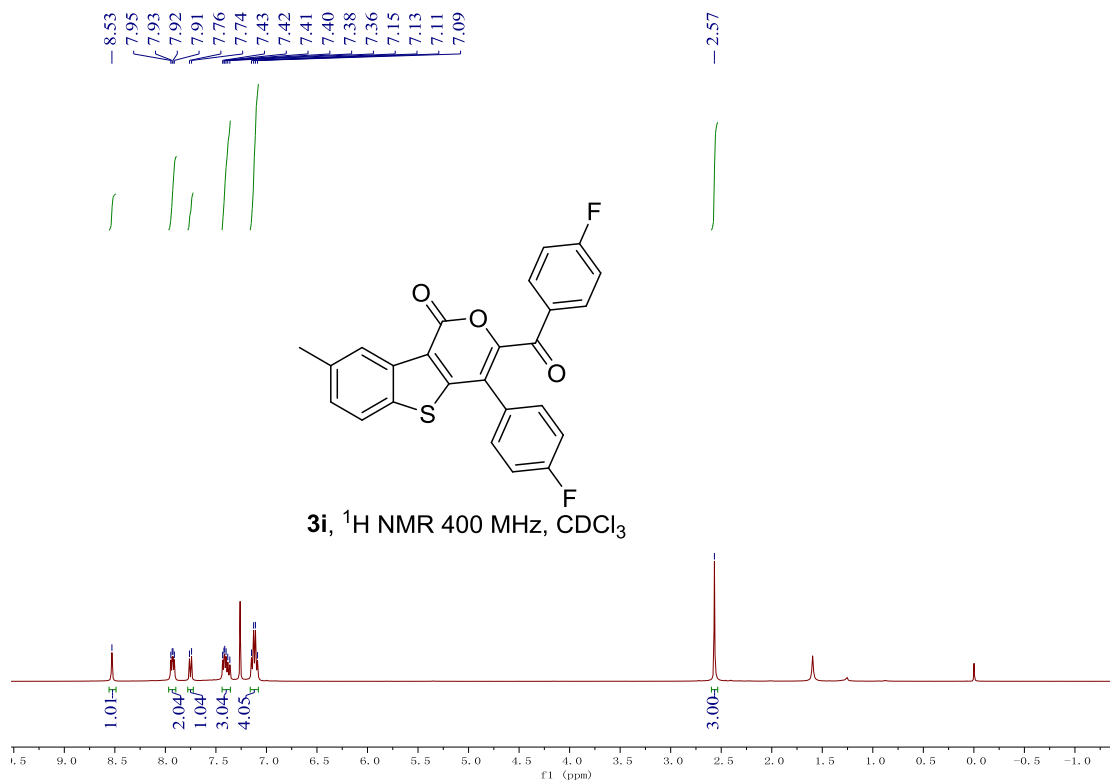


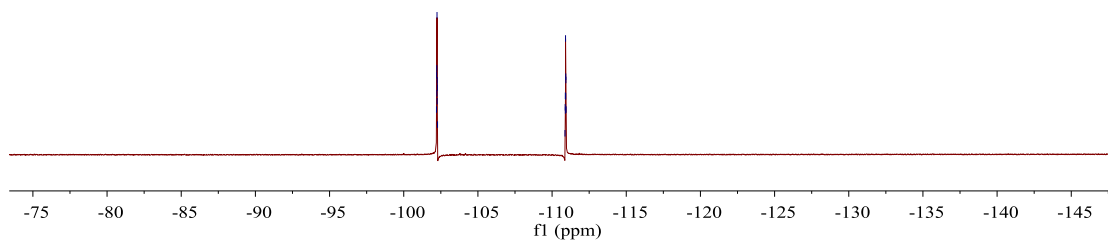
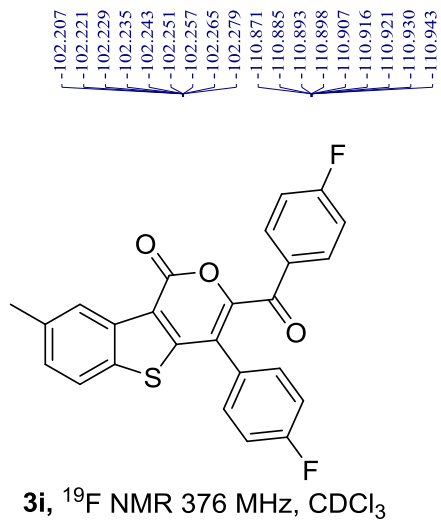




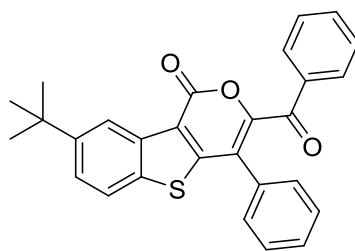




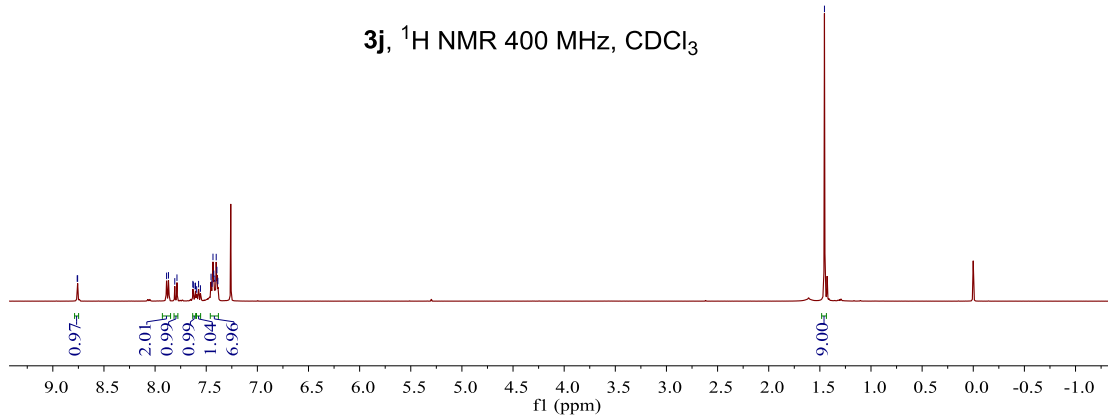


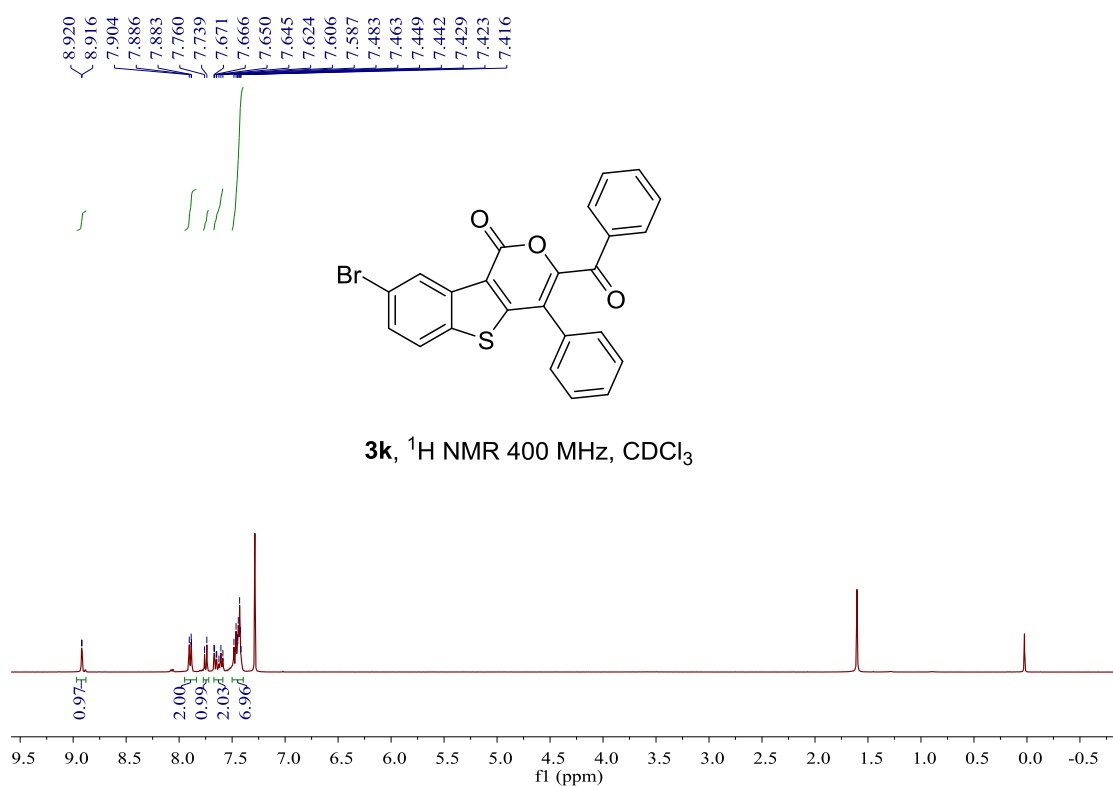
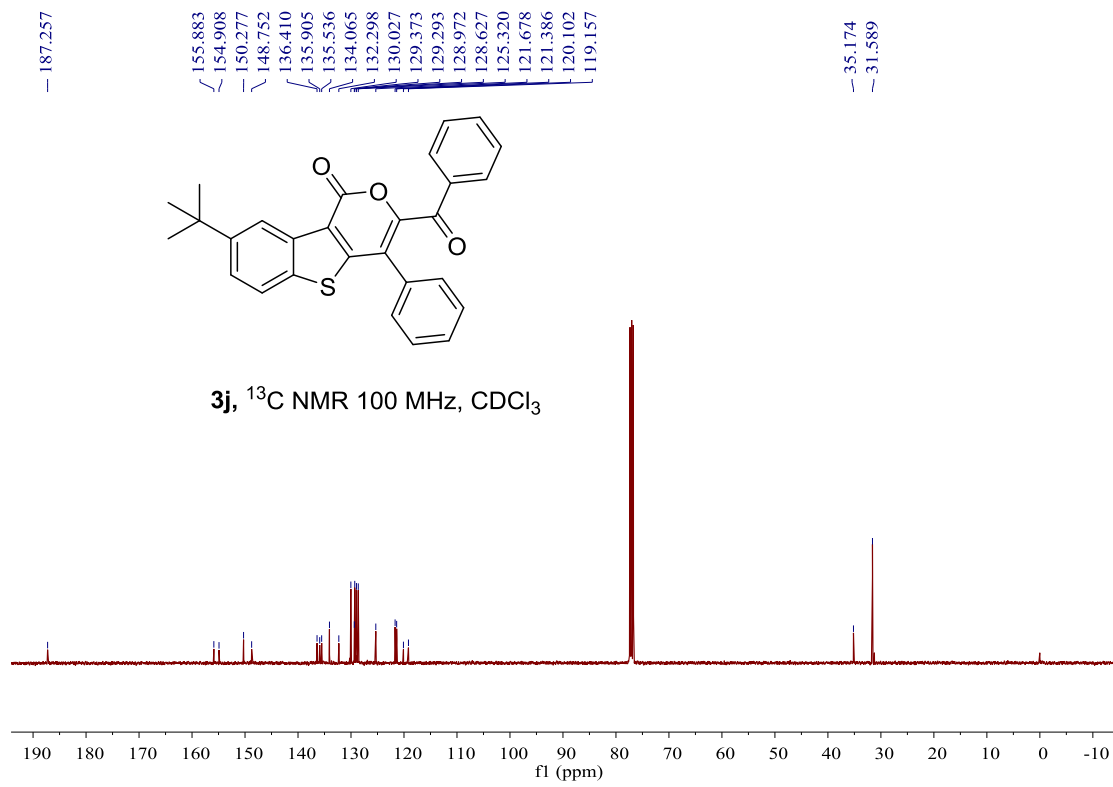


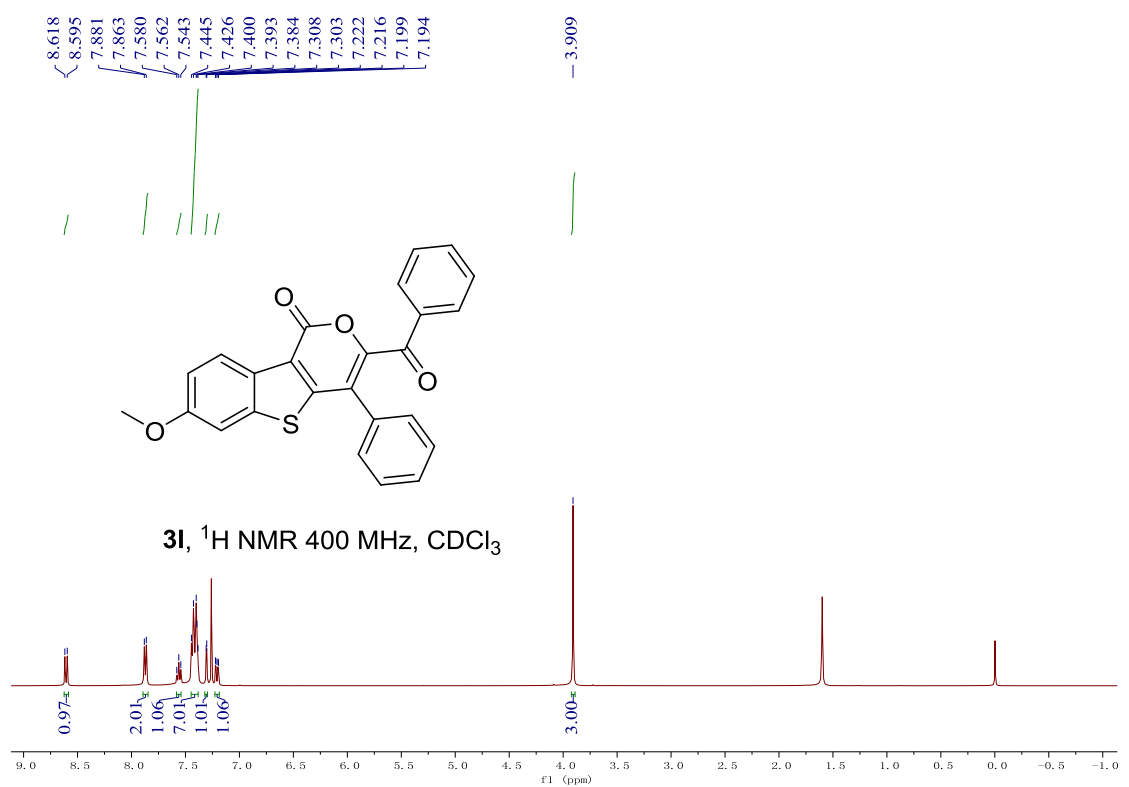
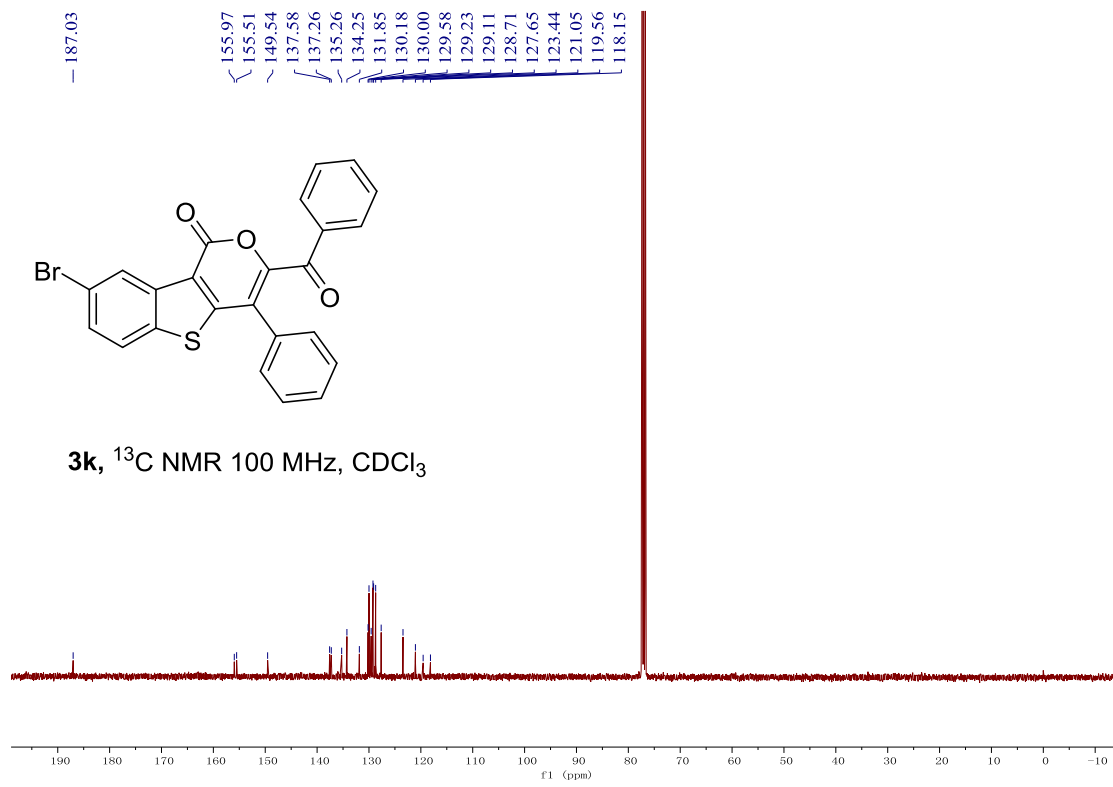
¹H NMR chemical shifts (ppm):
 8.762, 8.757, 7.888, 7.869, 7.808, 7.786, 7.631, 7.626, 7.609, 7.605, 7.593, 7.575, 7.556, 7.453, 7.443, 7.434, 7.426, 7.415, 7.402, 7.395, 7.386

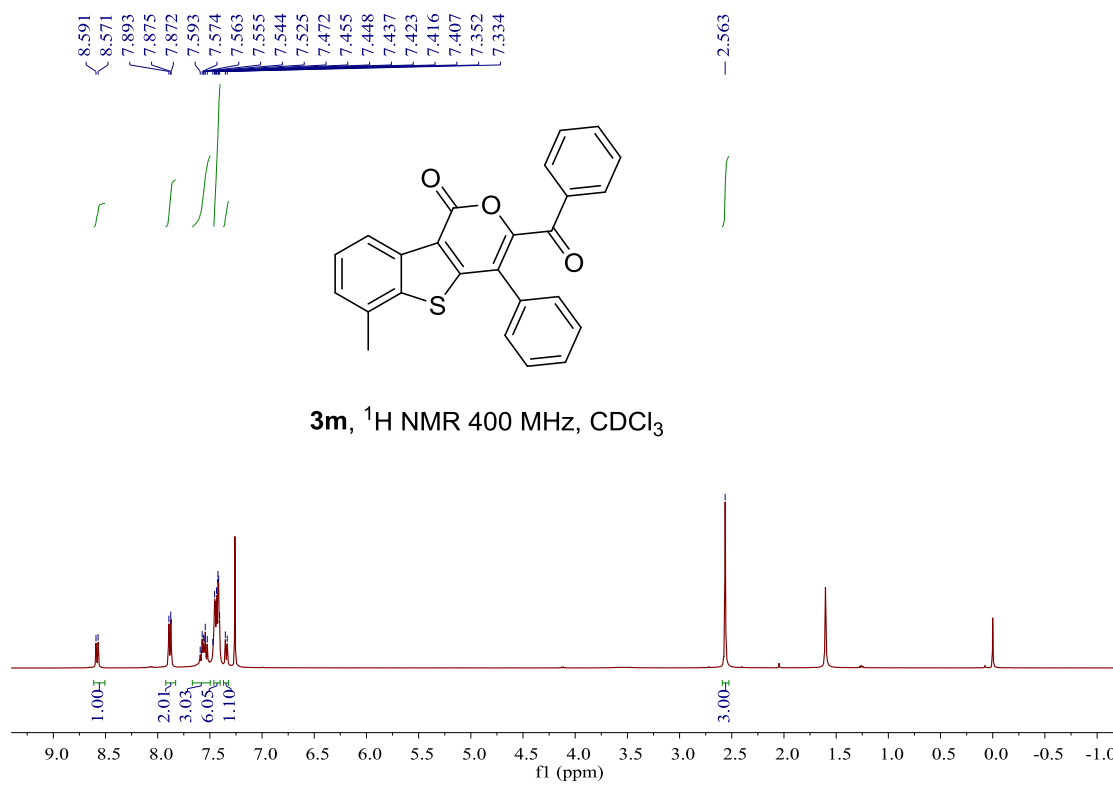
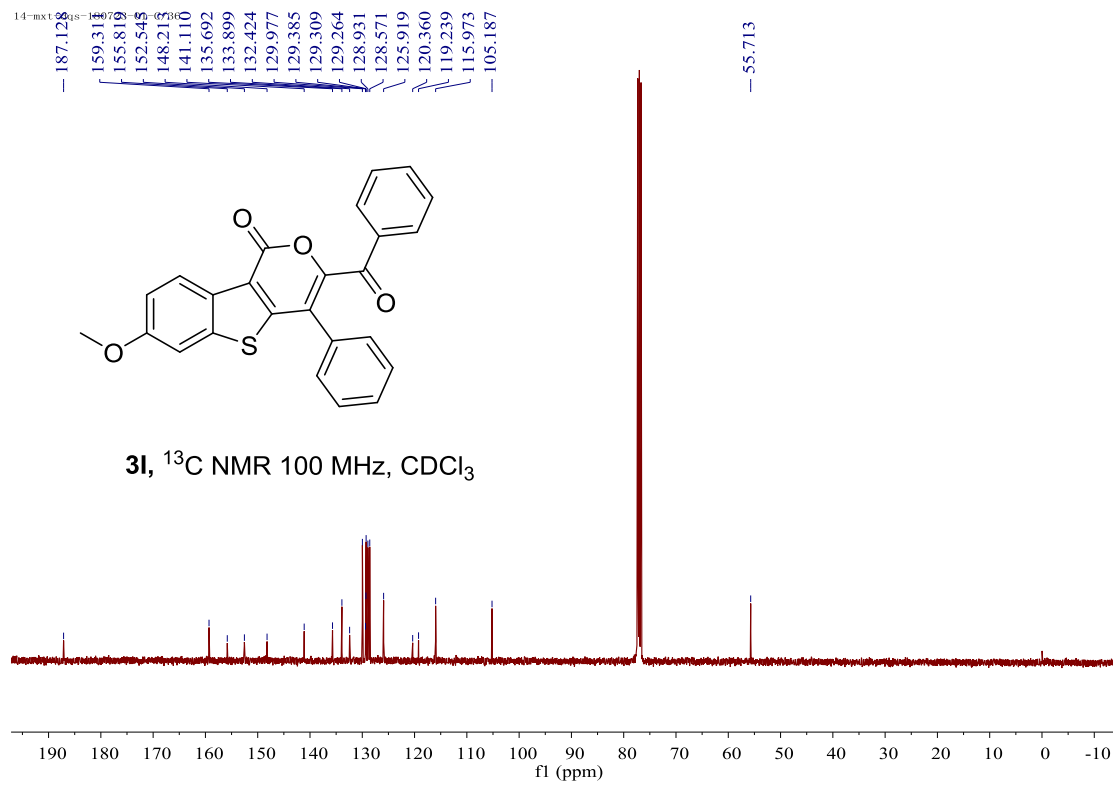


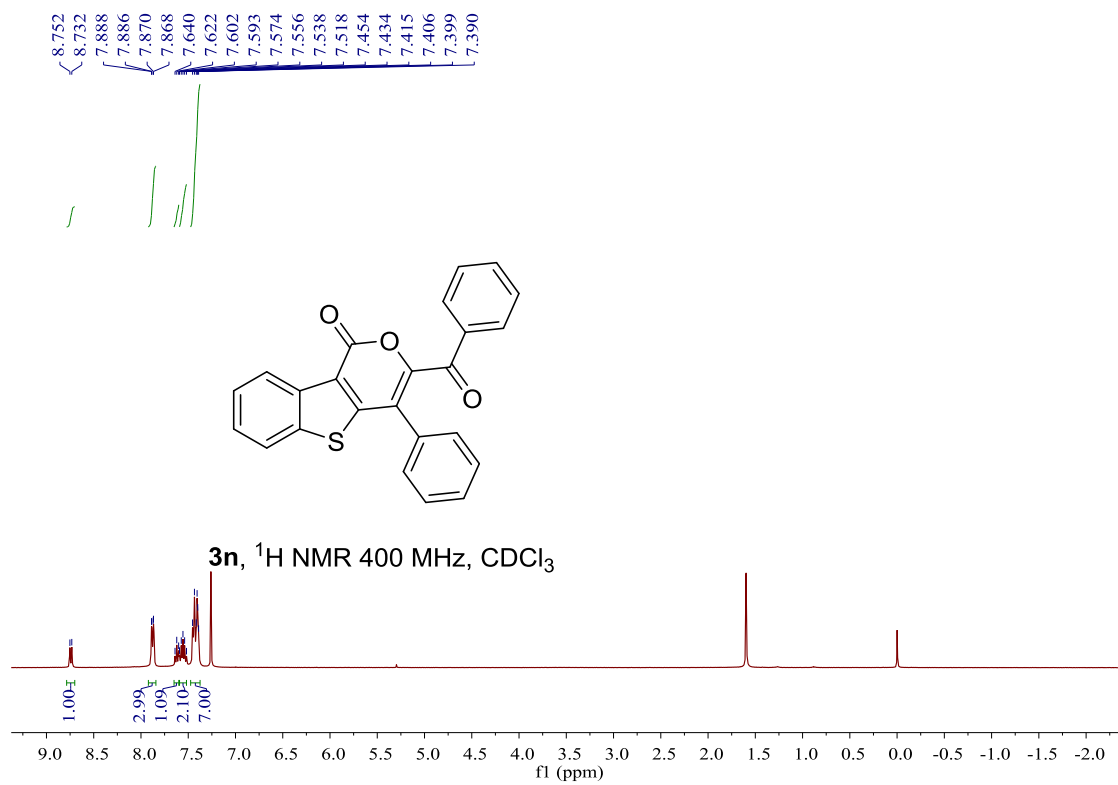
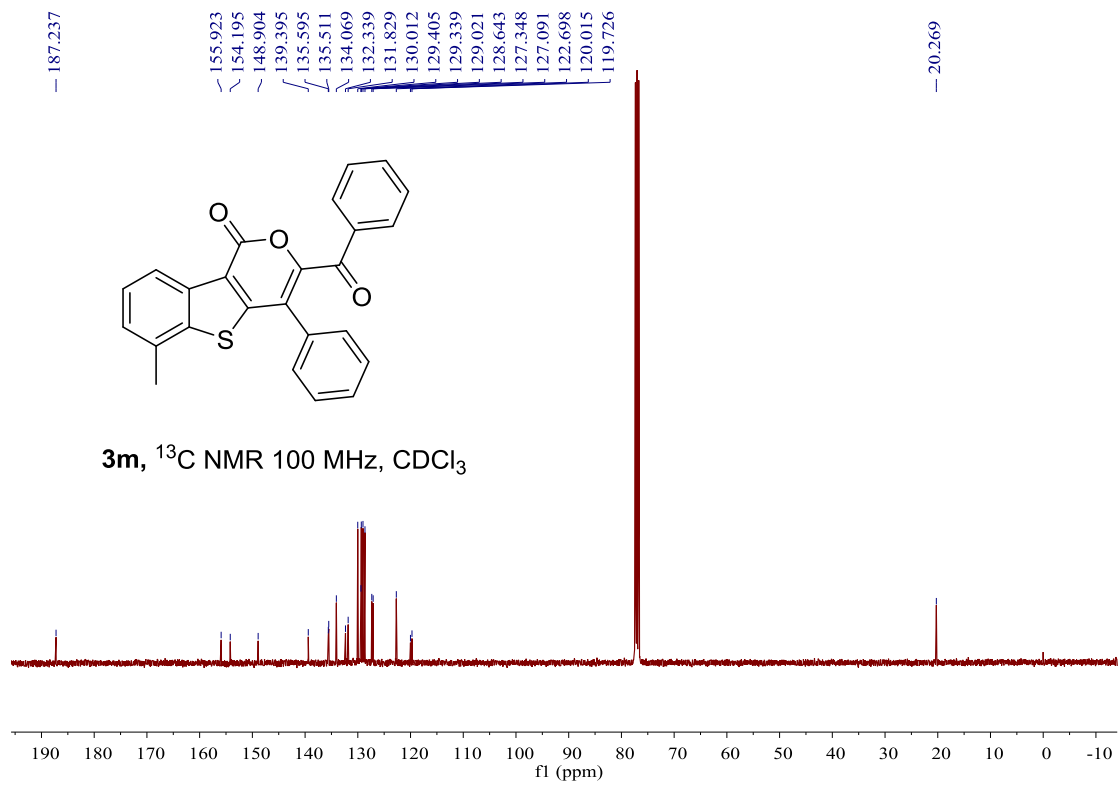
3j, ¹H NMR 400 MHz, CDCl₃

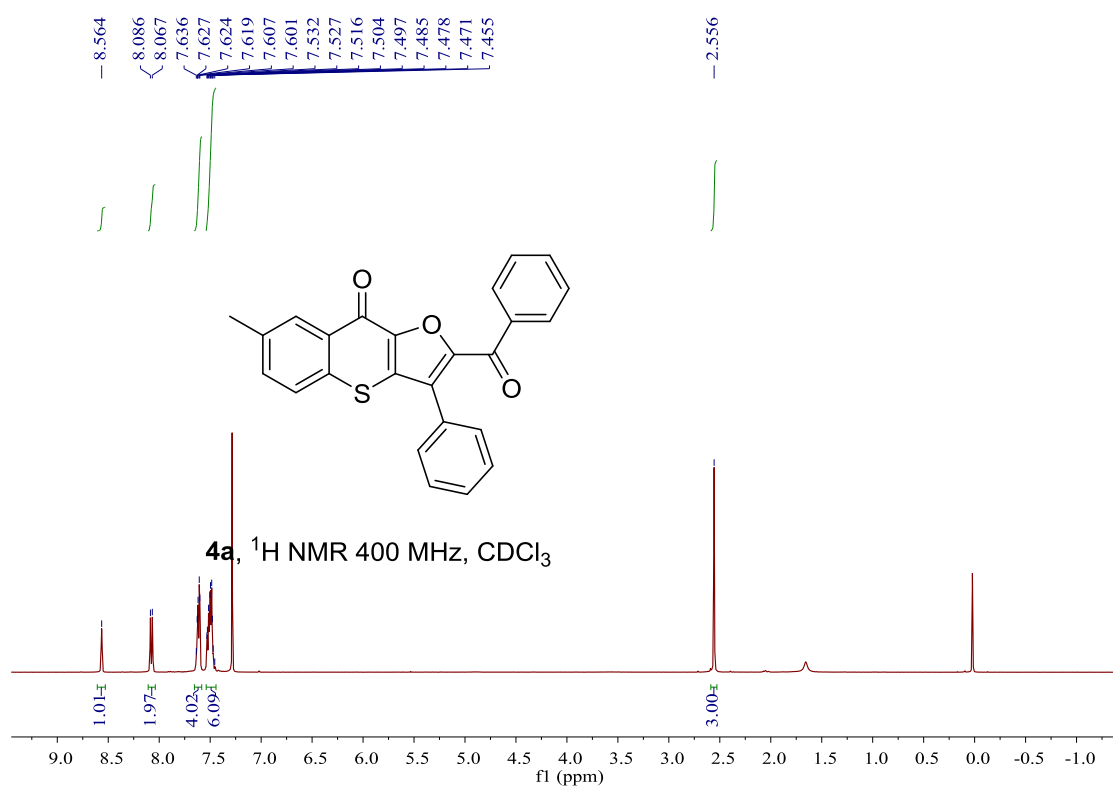
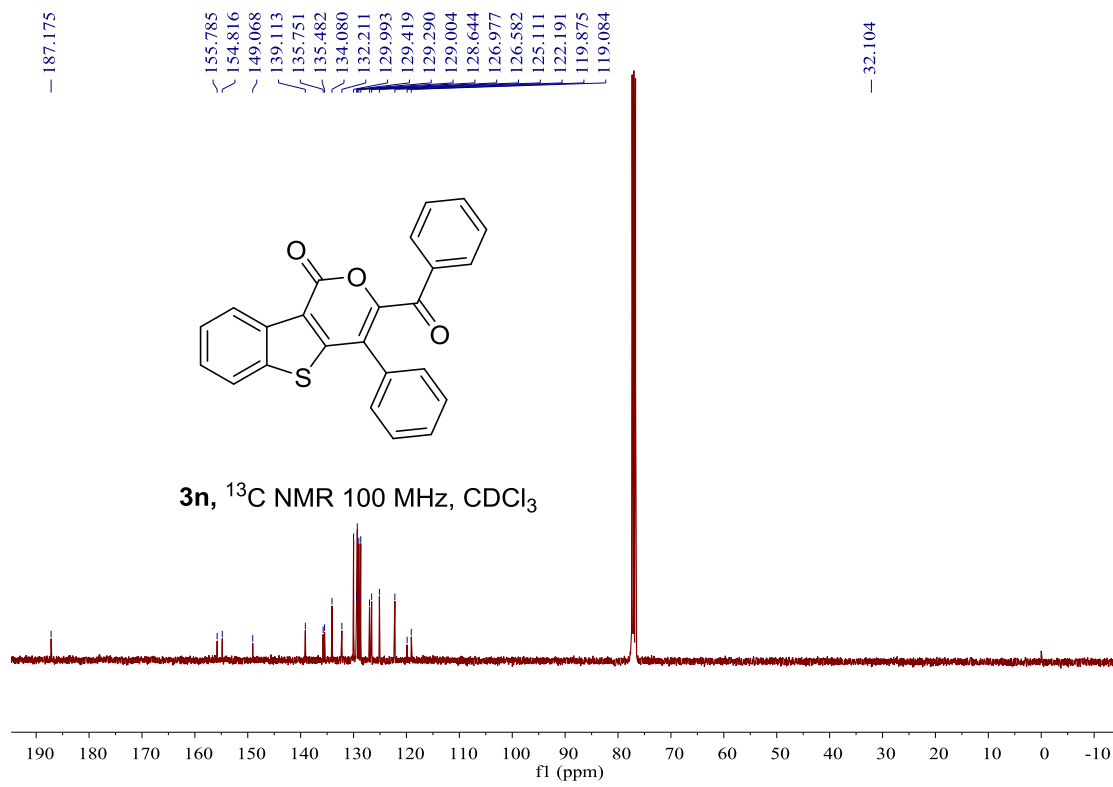


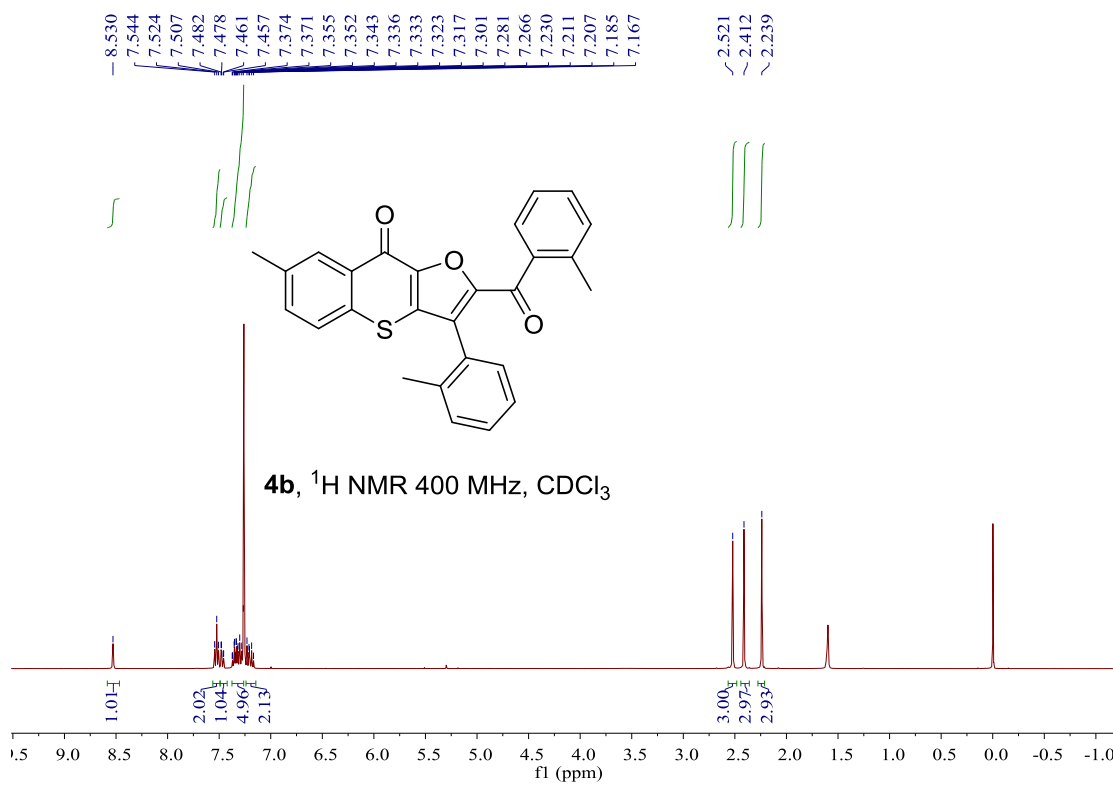
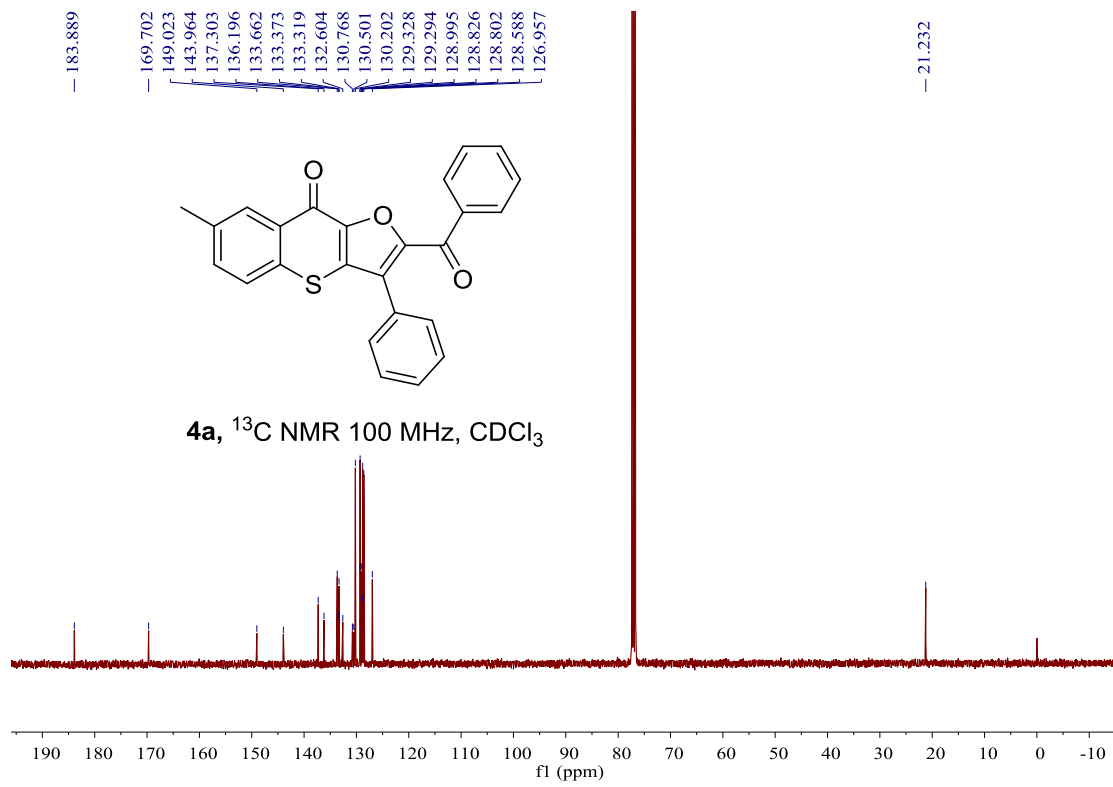


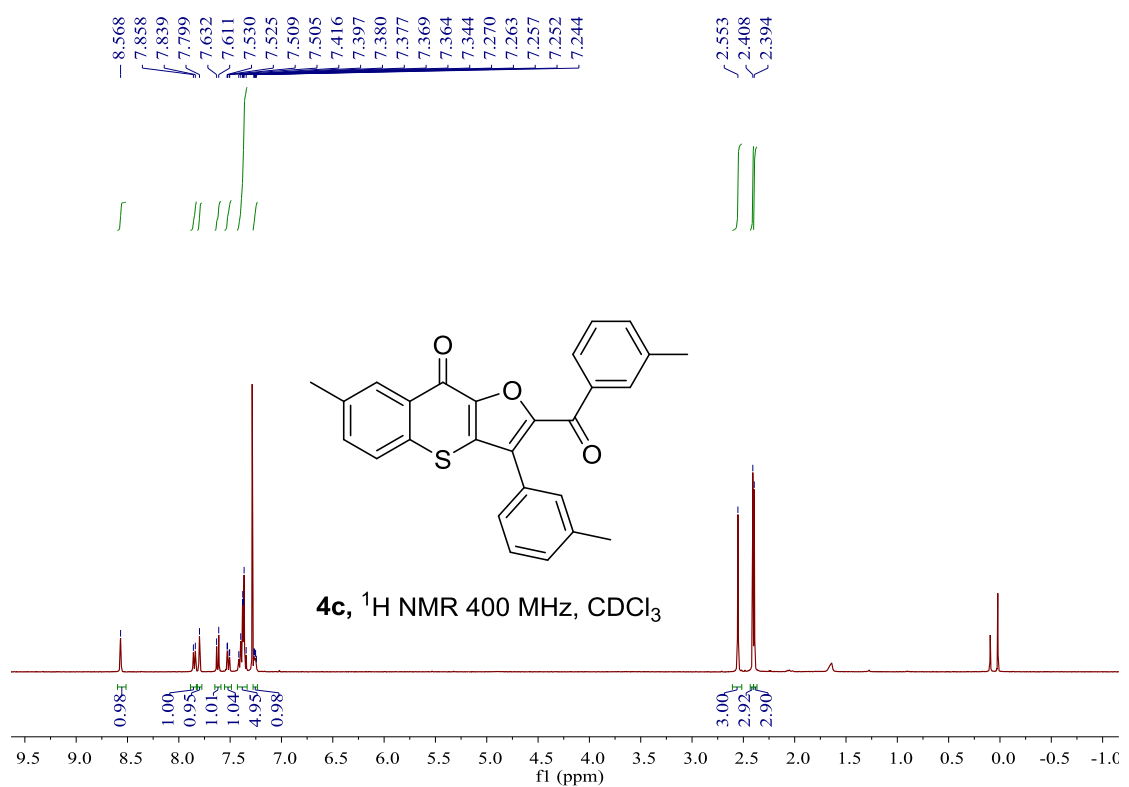
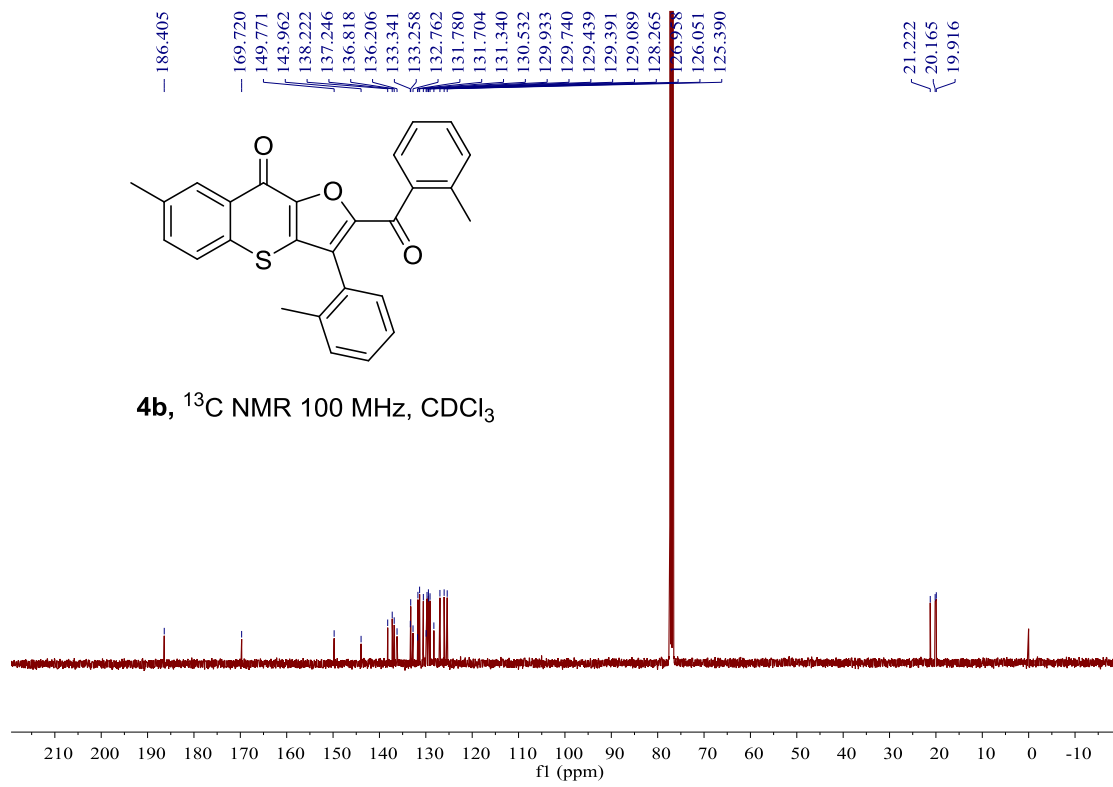


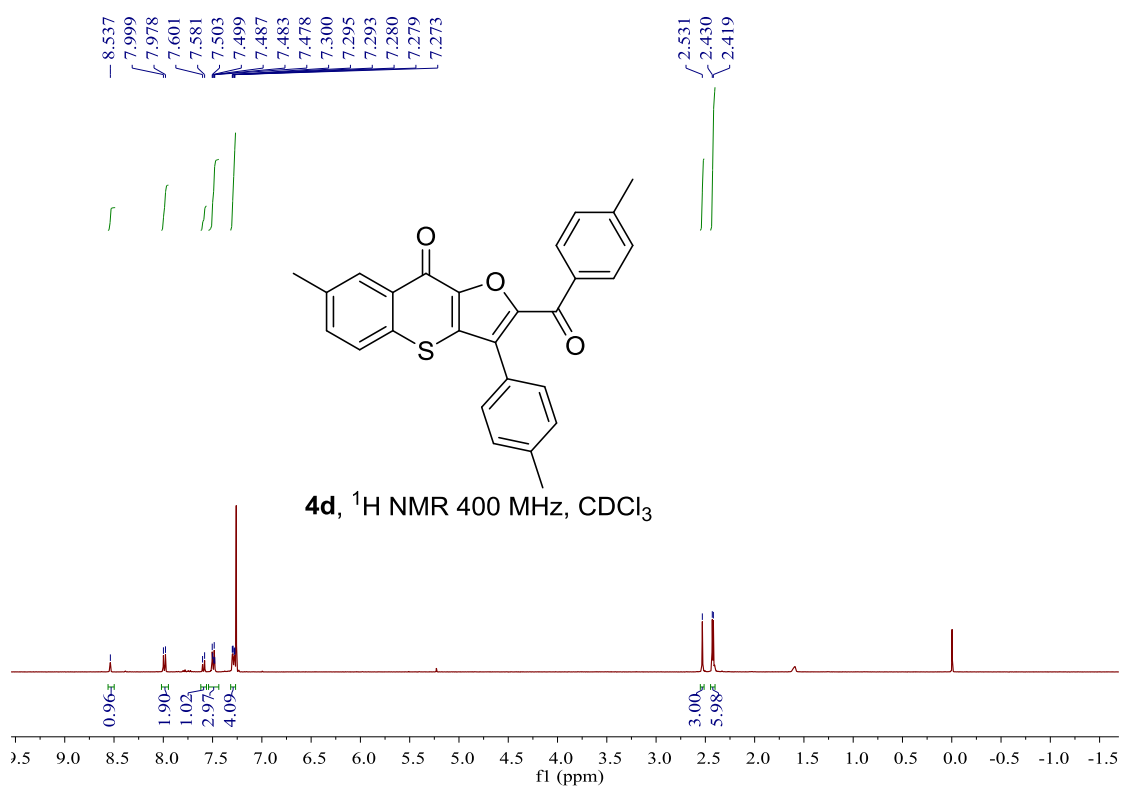
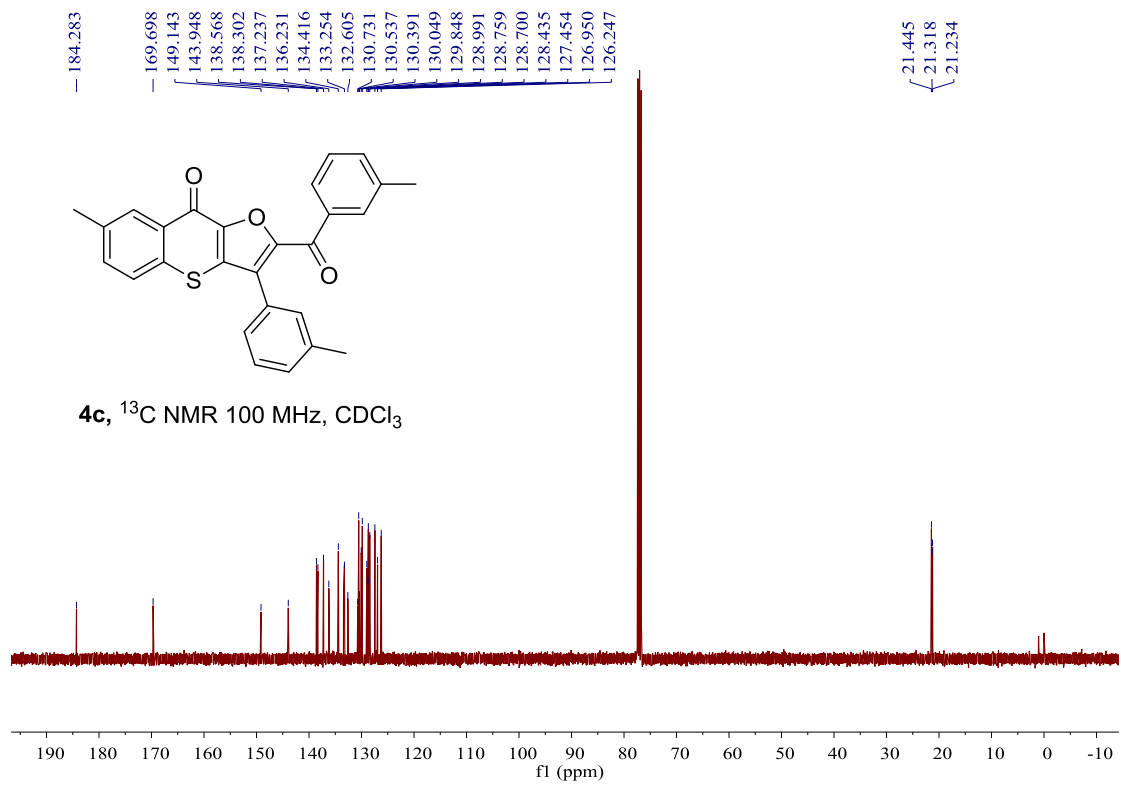


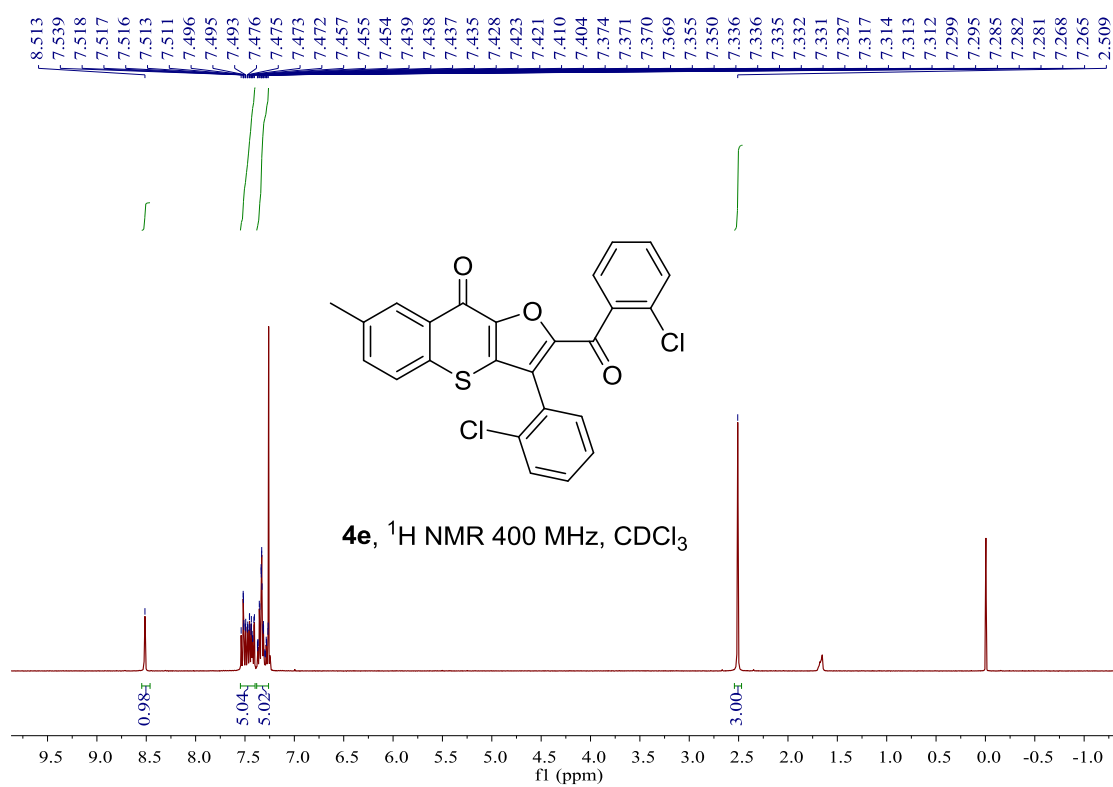
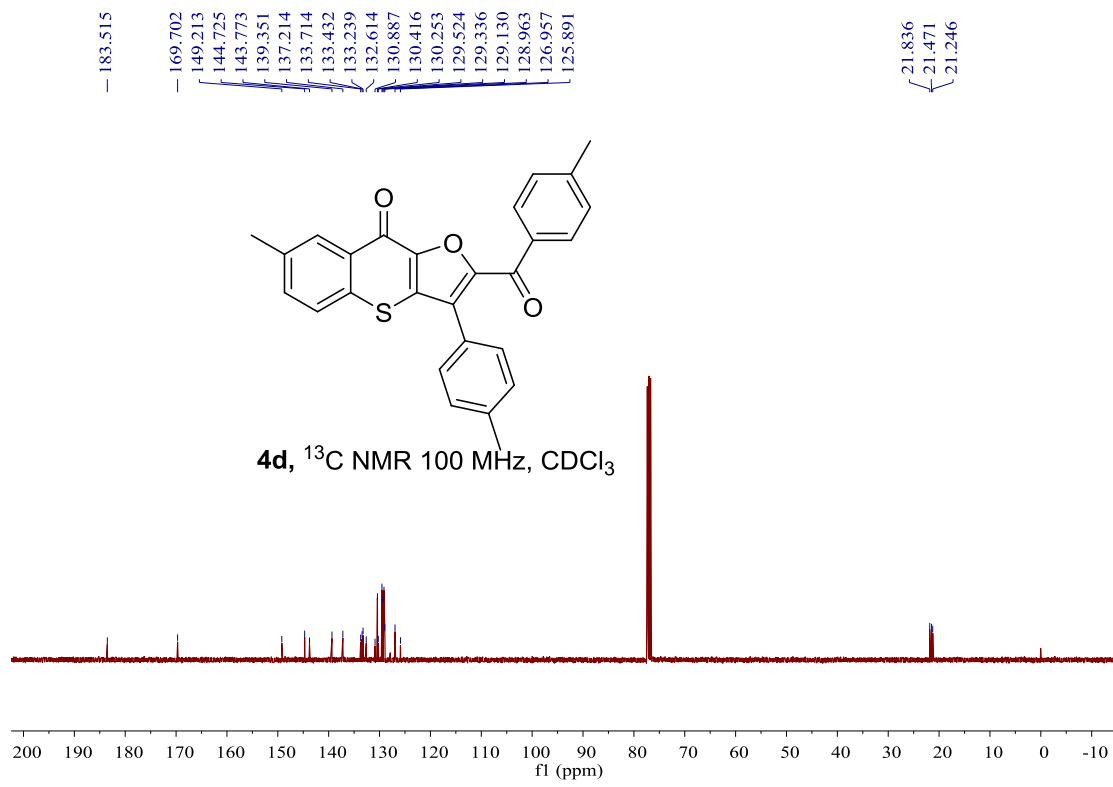


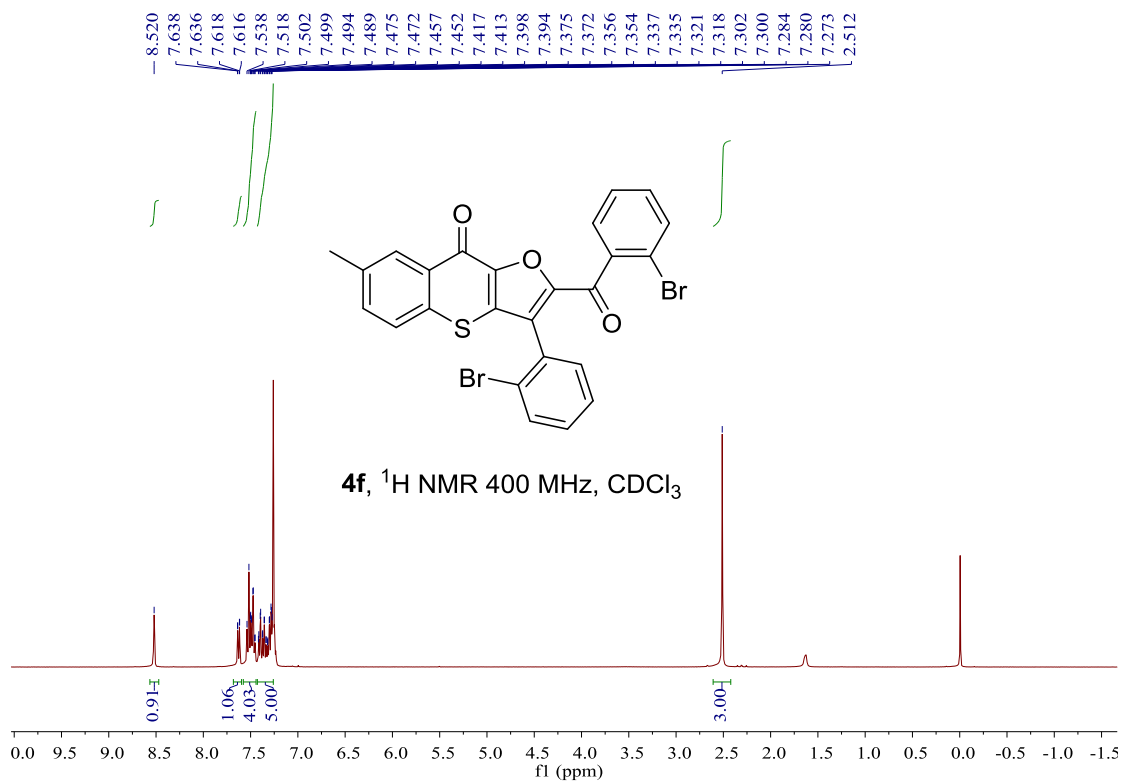
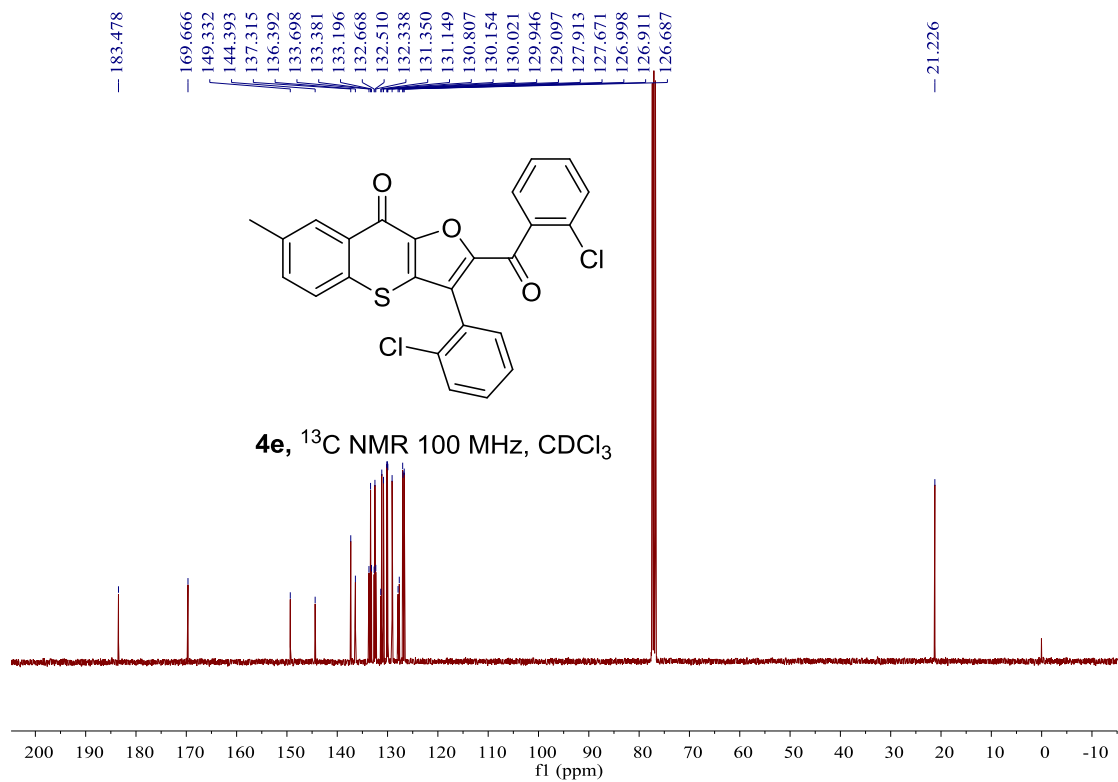


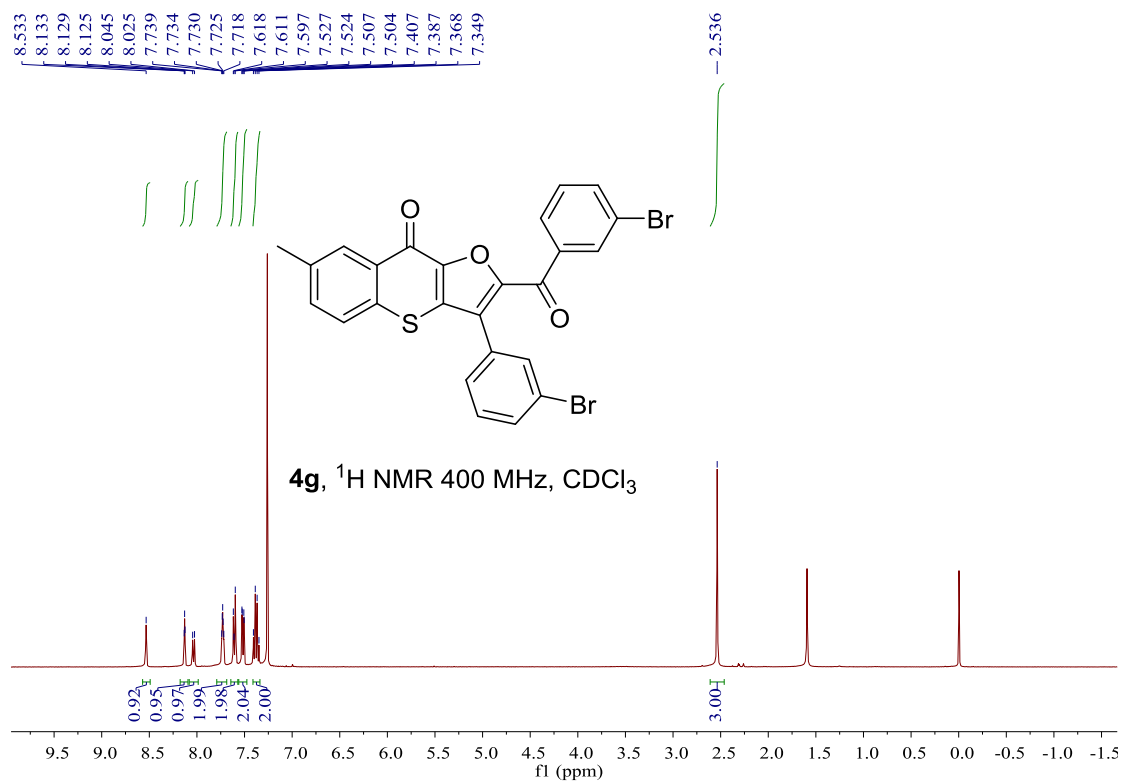
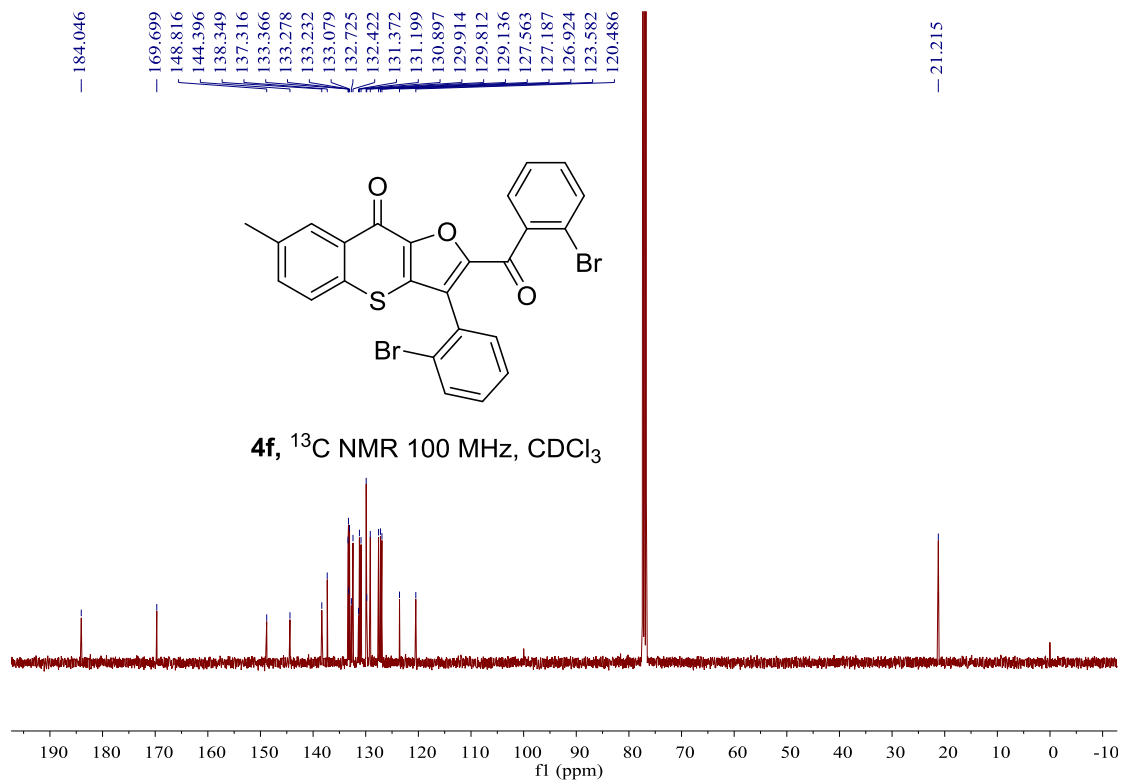


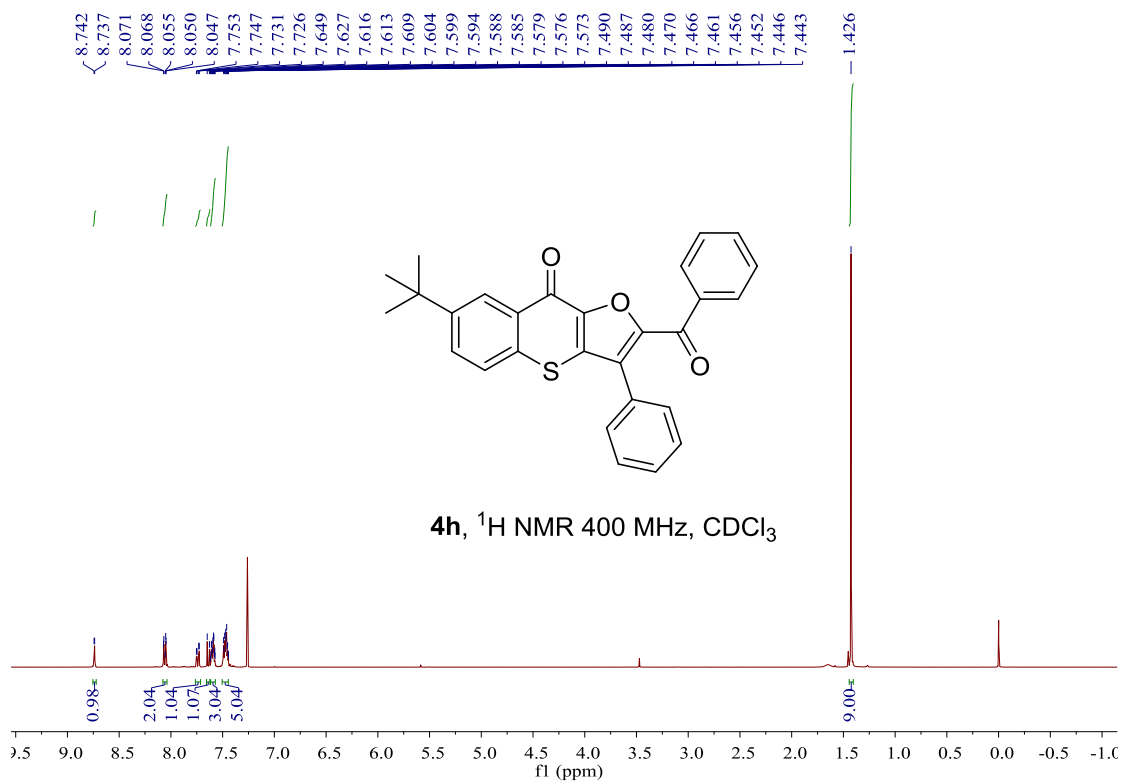
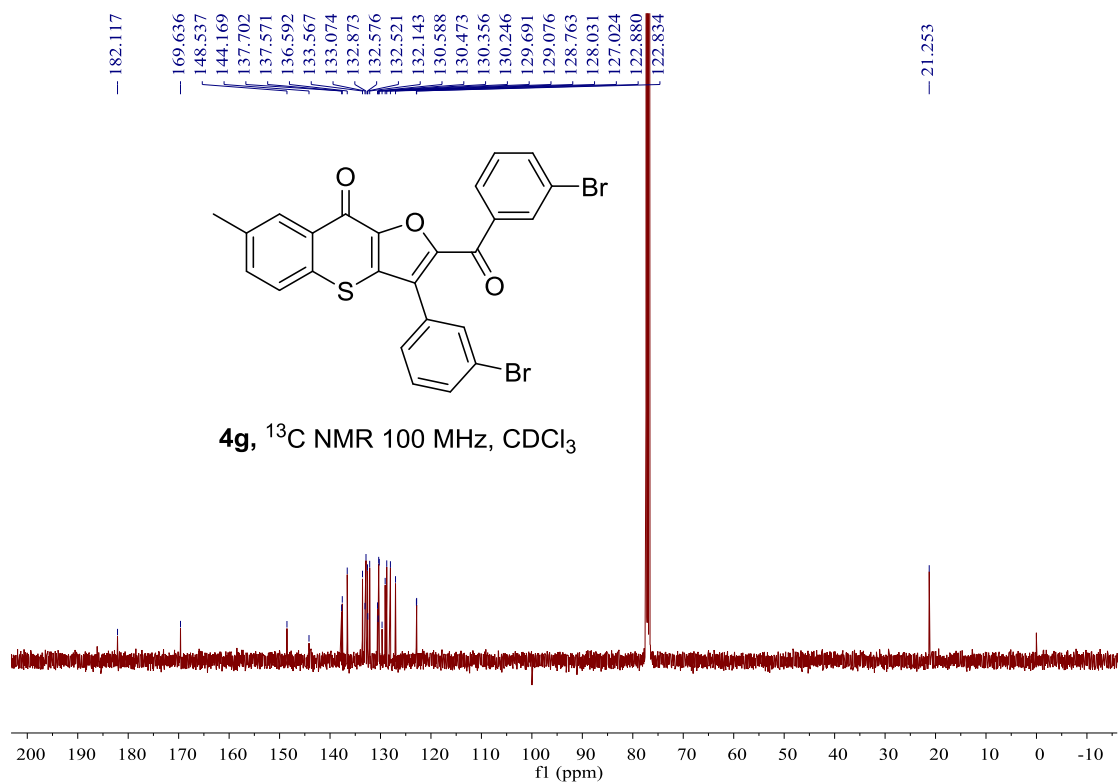


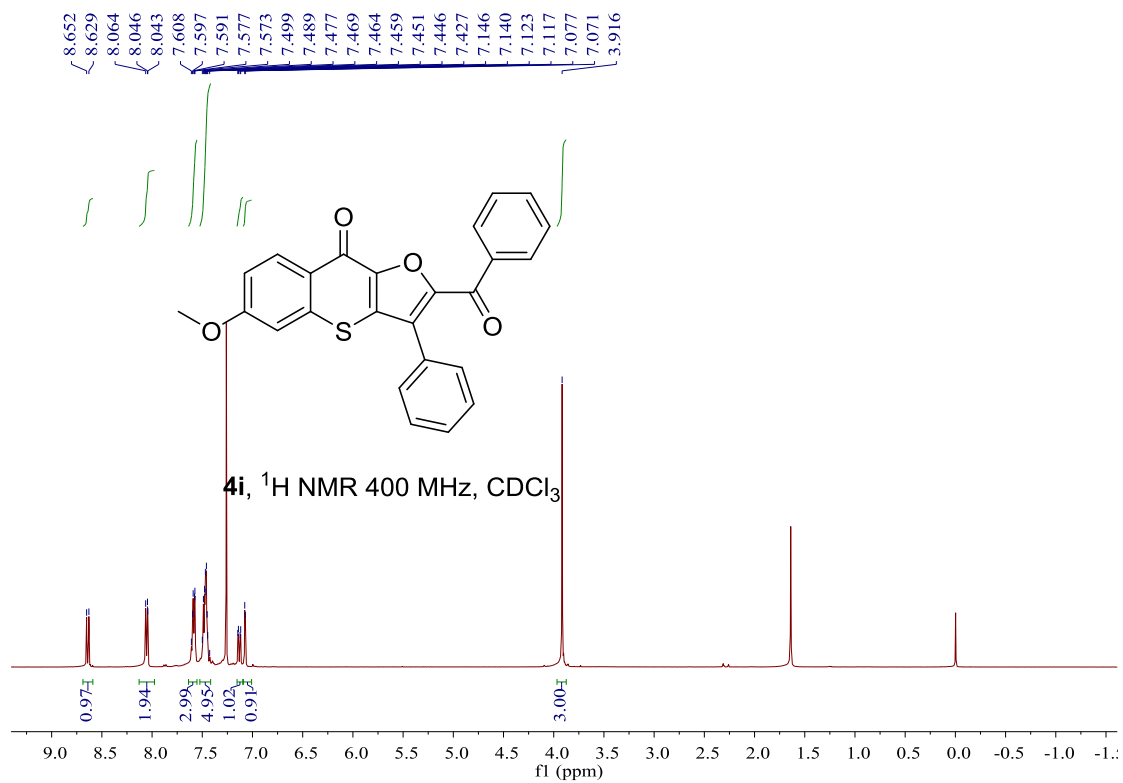
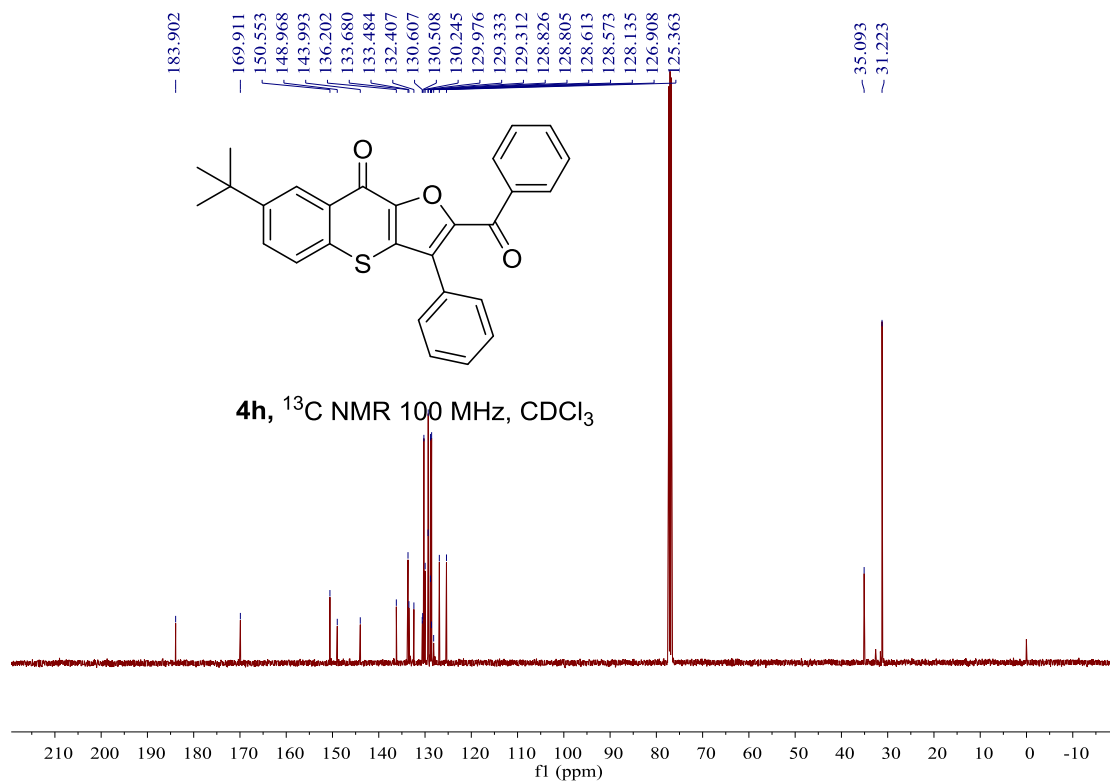


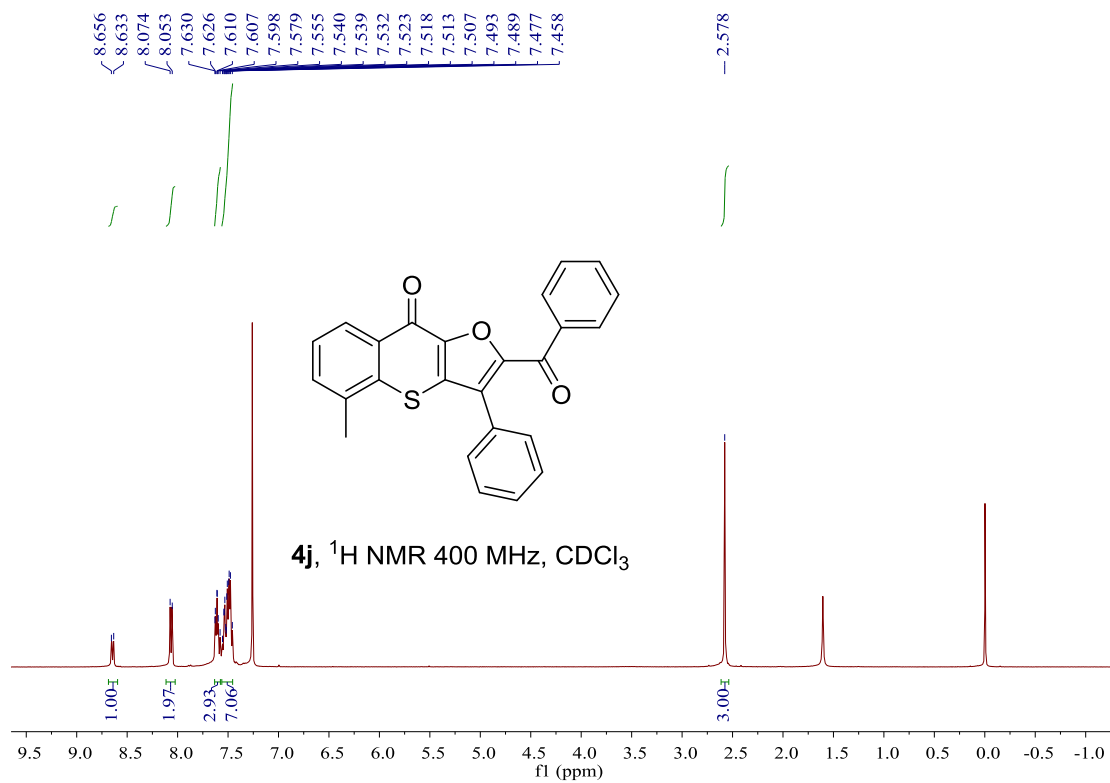
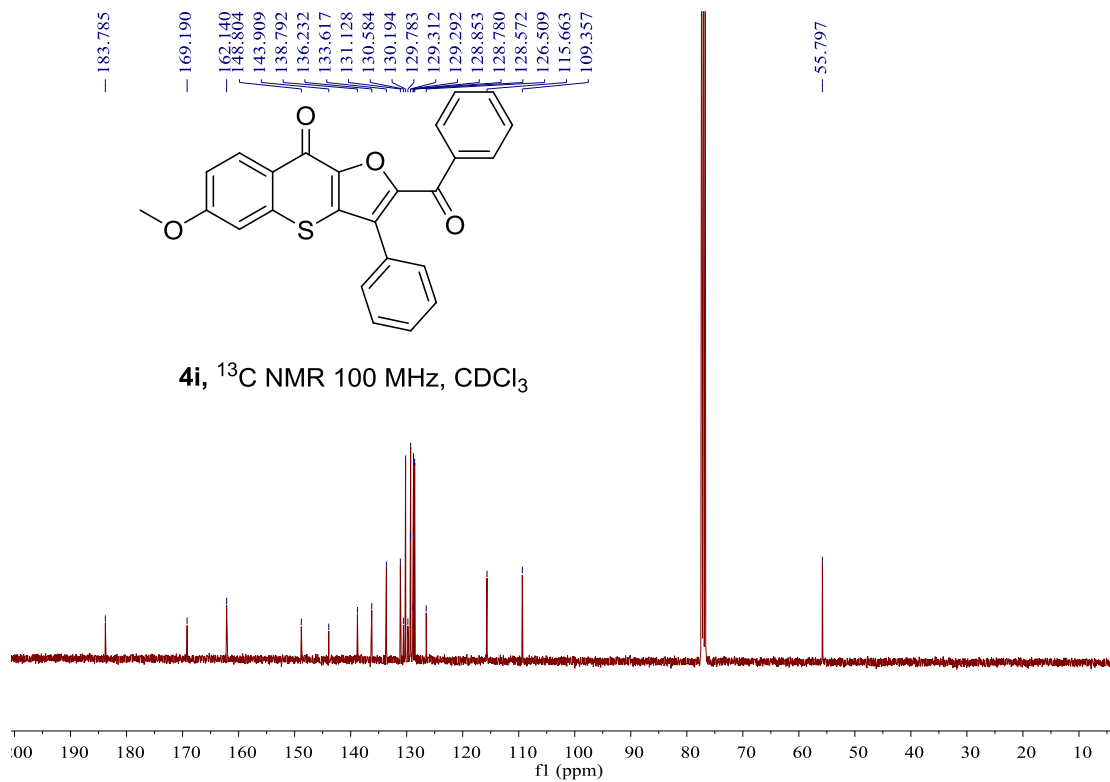


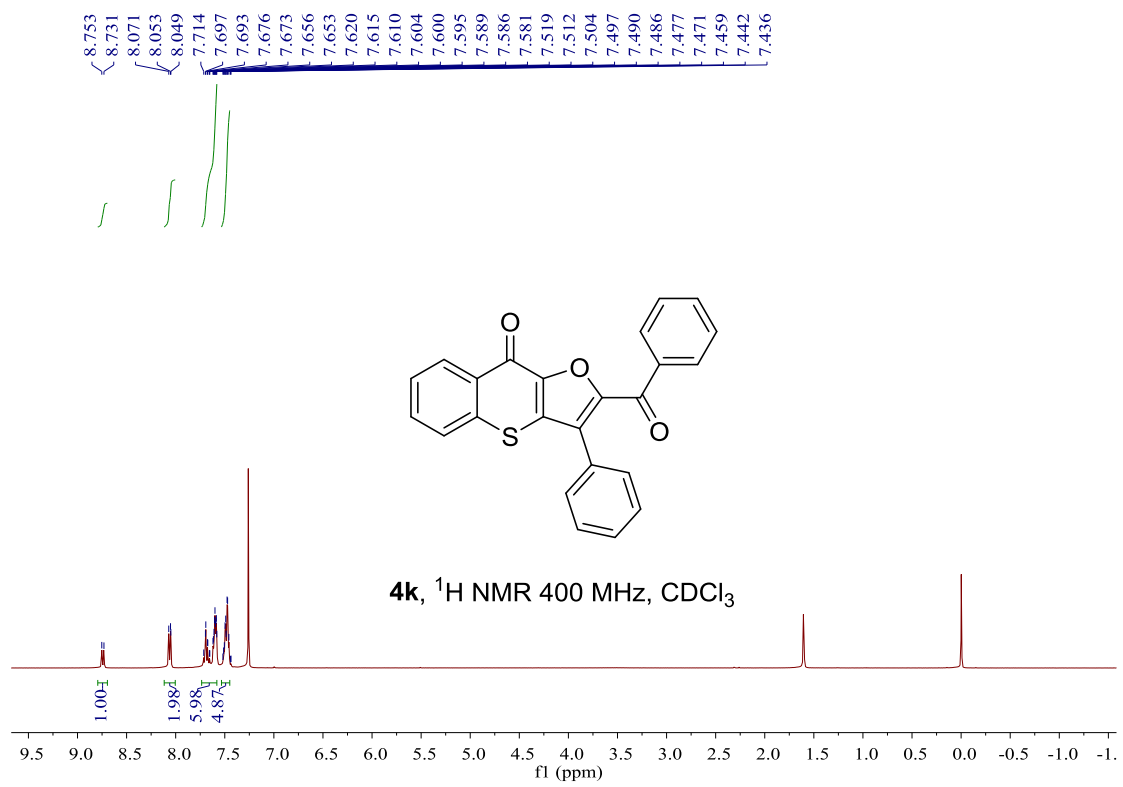
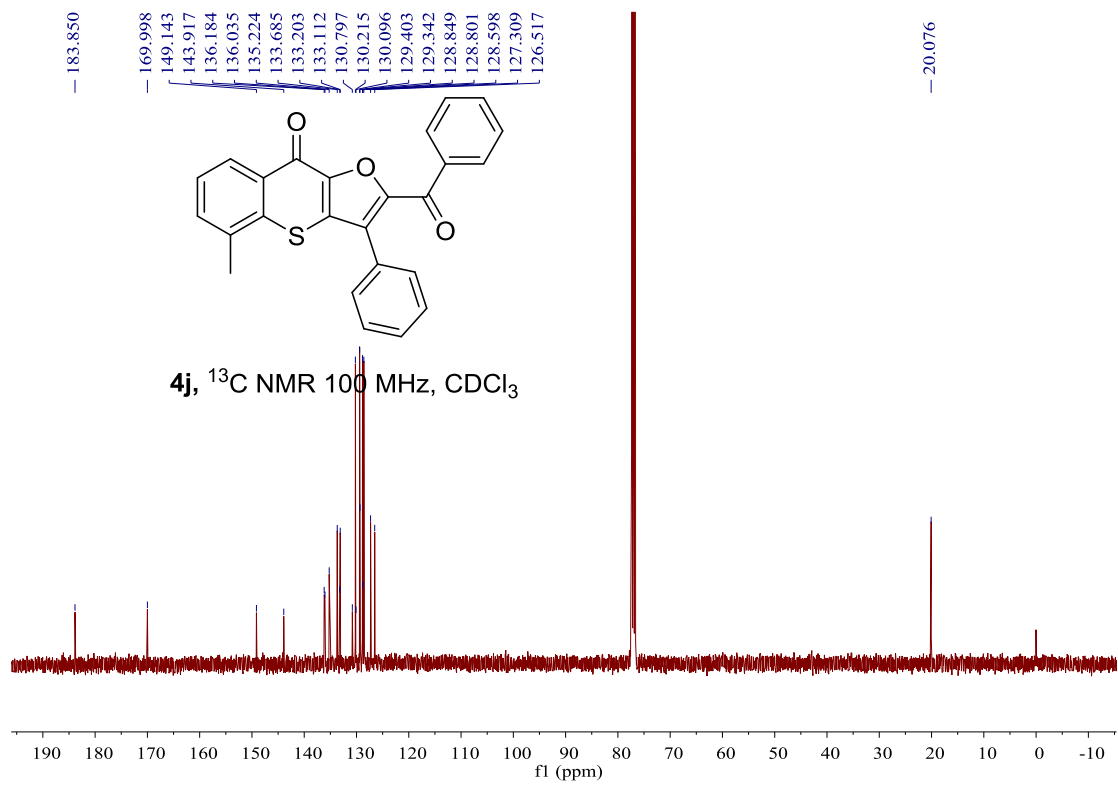


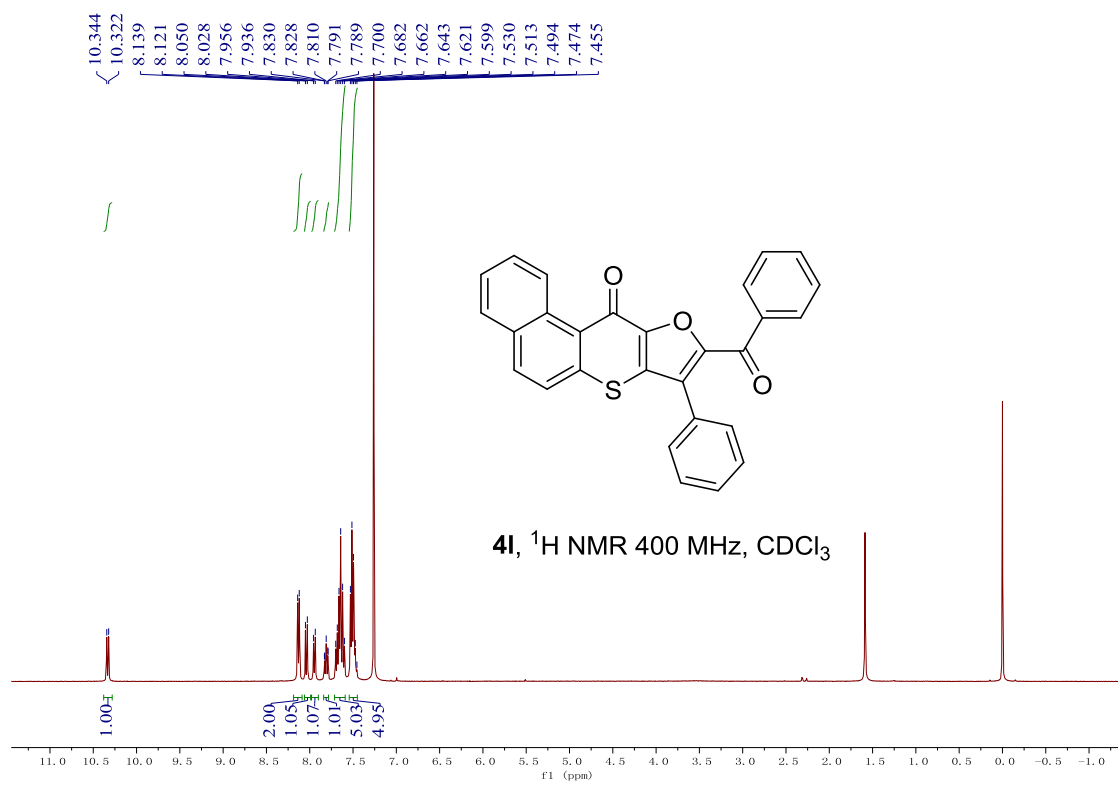
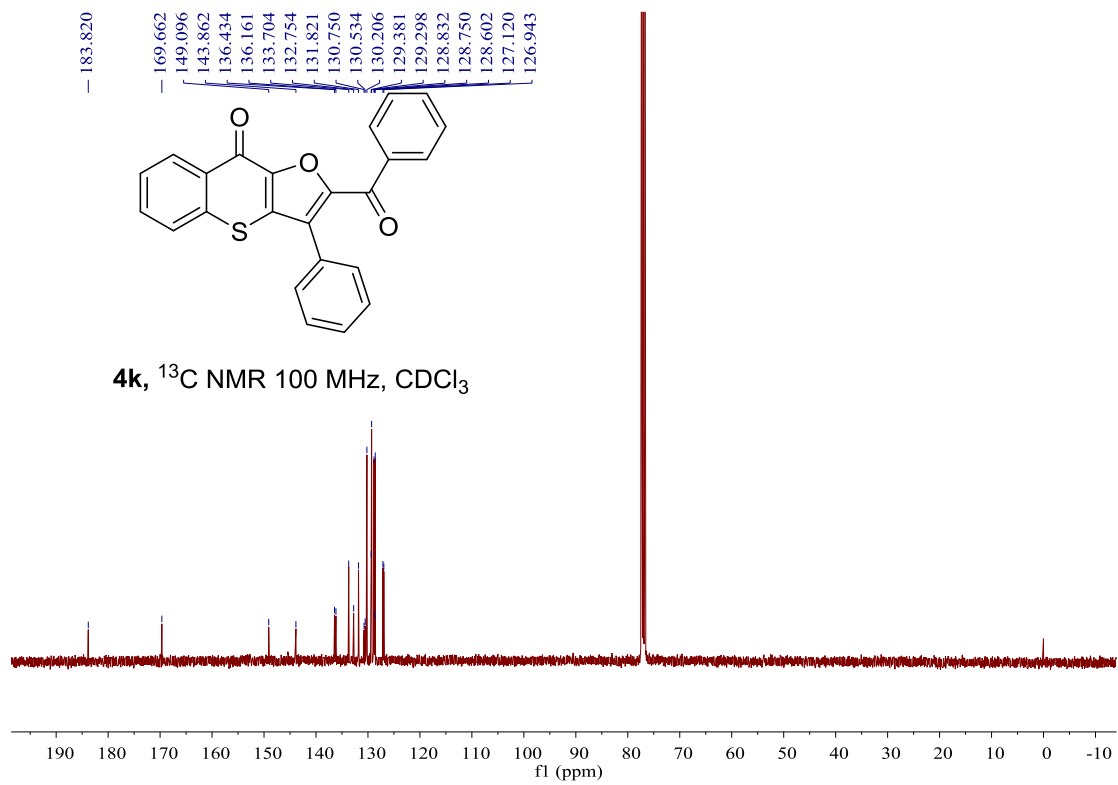


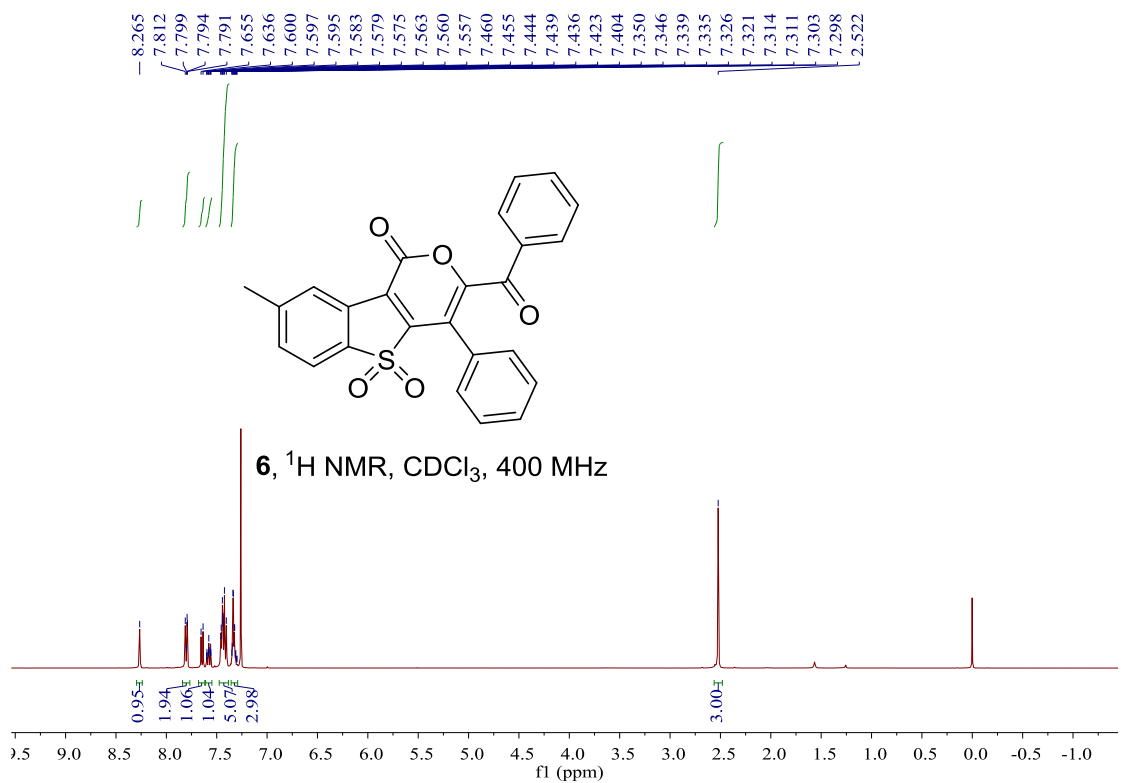
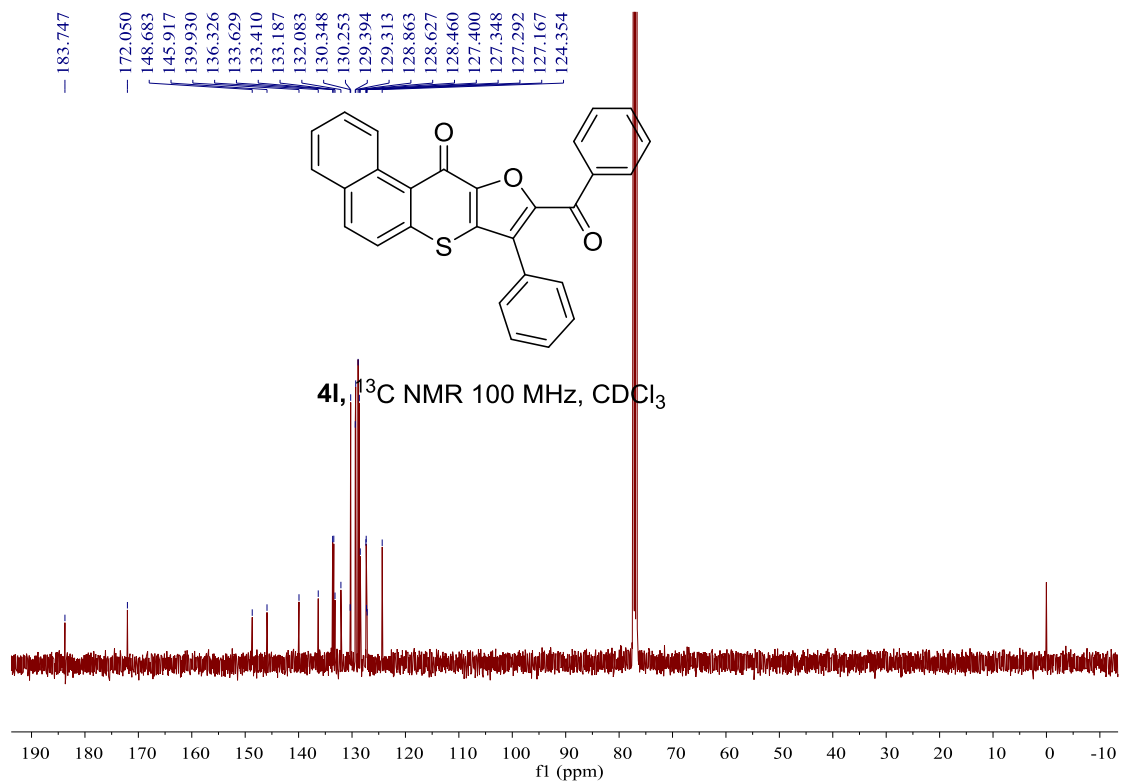


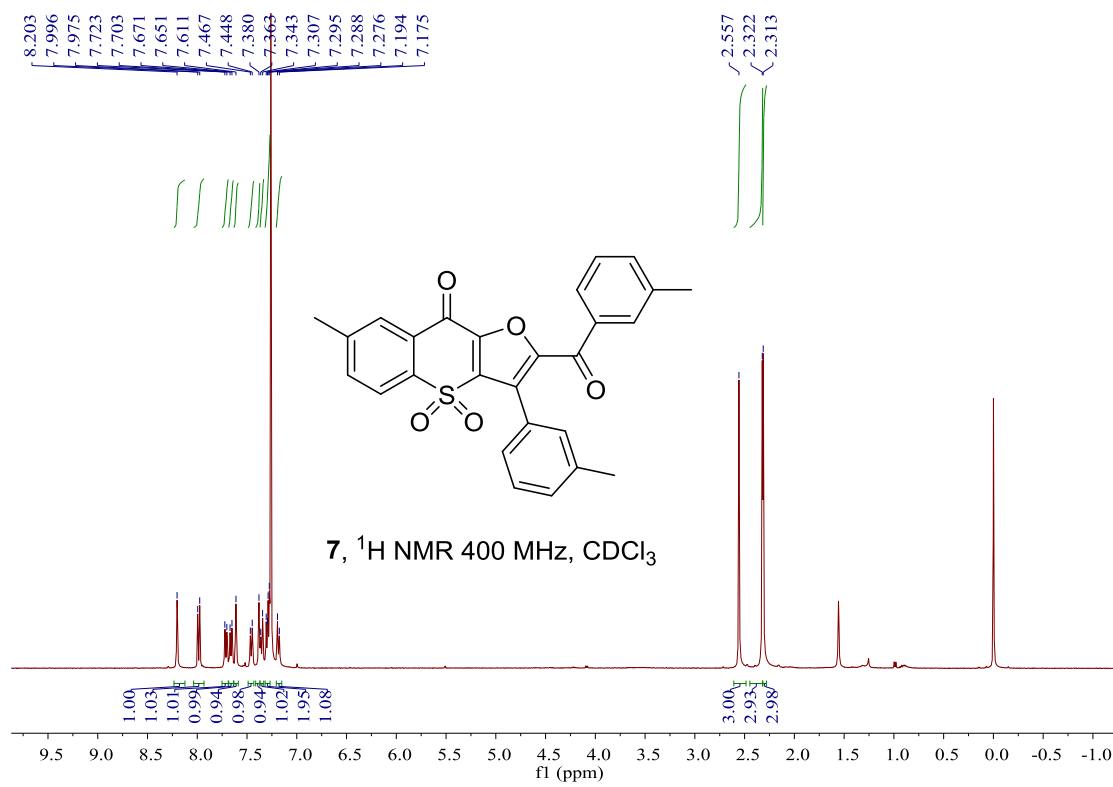
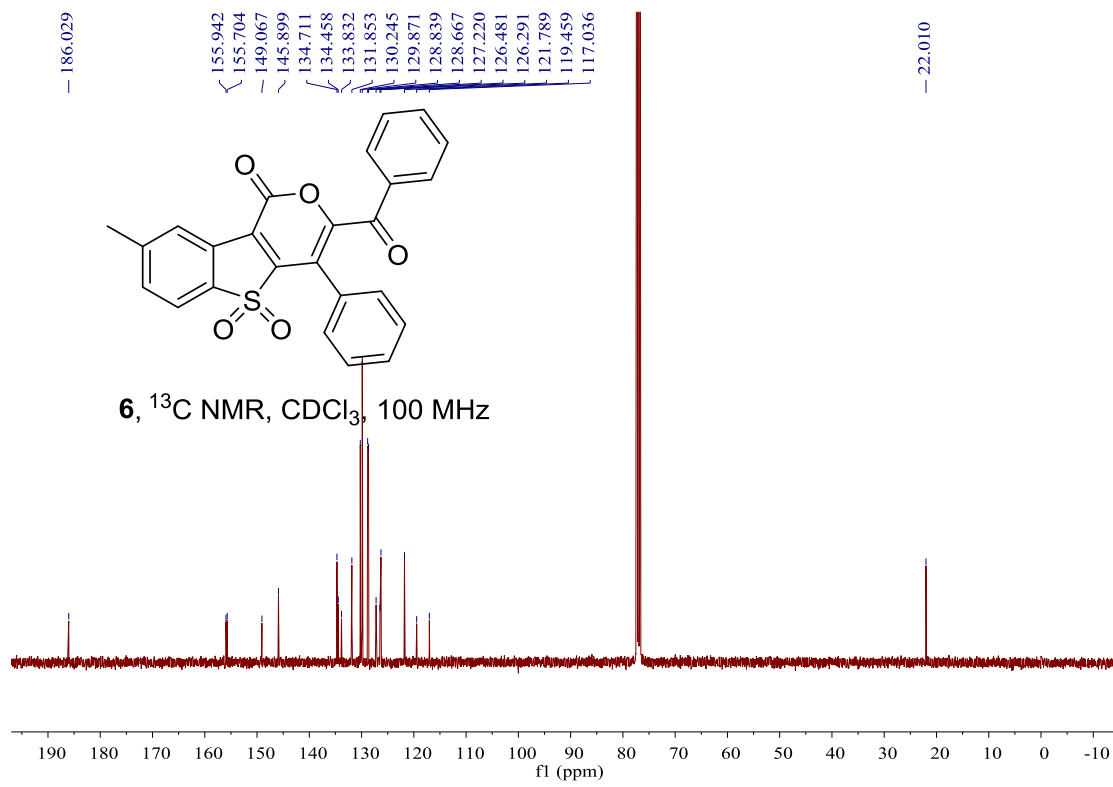


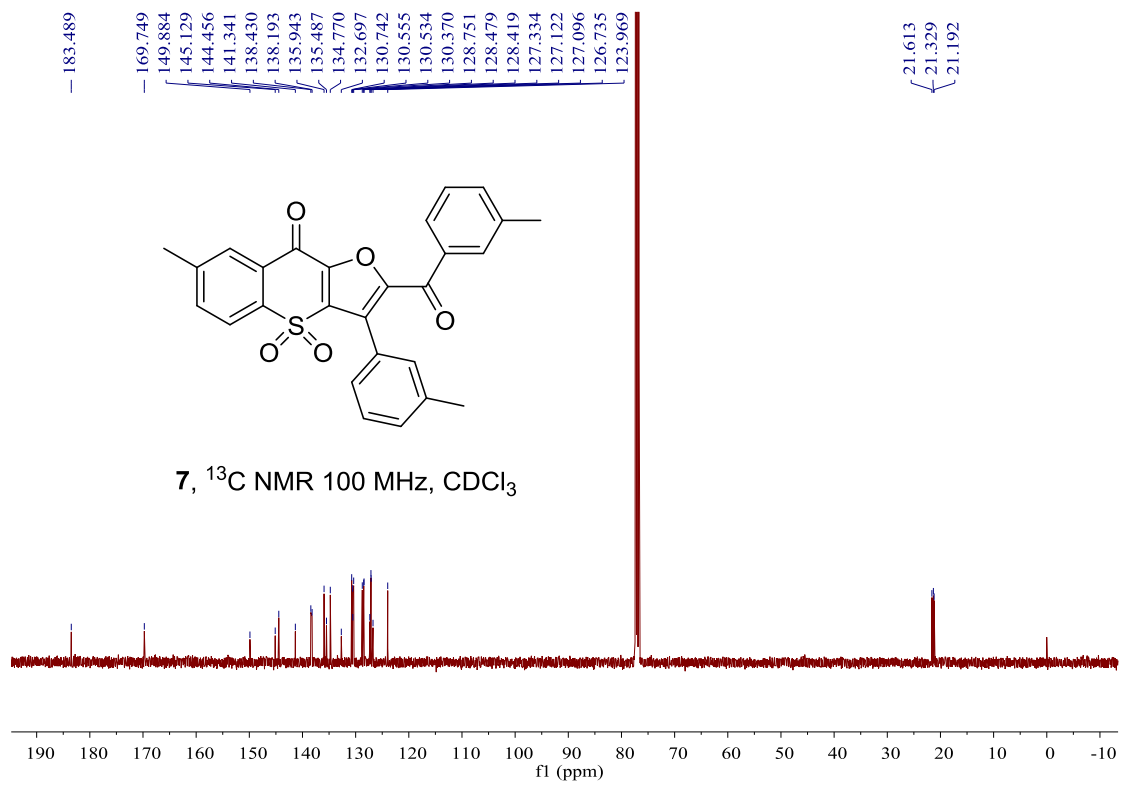












8. Table Crystal Data and Structure Refinements for **3e**, **3f**, **4e**, **4k**

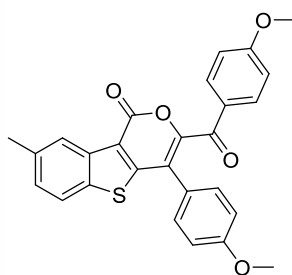
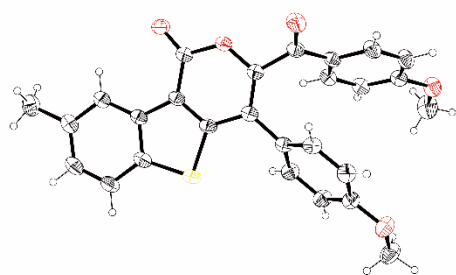
	3e	3f
Chemical formula	C ₂₇ H ₂₀ O ₅ S	C ₂₅ H ₁₄ Cl ₂ O ₃ S
Formula weight	456.49	465.32
Crystal system	triclinic	monoclinic
Space group	P 21/c	C 1 2/c 1
<i>a</i> (Å)	13.4747(3)	24.412(2)
<i>b</i> (Å)	9.9600(2)	11.9331(12)
<i>c</i> (Å)	17.0946(4)	14.5838(15)
<i>V</i> (Å ³)	2259.05(9)	4247.7(7)
α (°)	90	90
β (°)	100.047(2)	91.041(8)
γ (°)	90	90
<i>Z</i>	4	8
F(000)	952.0	1904.0
<i>GOF</i>	1.121	1.397
<i>D</i> /g cm ⁻³	1.342	1.455
μ (mm ⁻¹)	1.581	0.430
<i>T</i> /K	293	293
<i>R</i> ^{<i>a</i>} / <i>R</i> ^{<i>b</i>}	0.0513/0.1629	0.0747/0.2836

^{*a*}*R* = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{*b*}*R*_w = $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

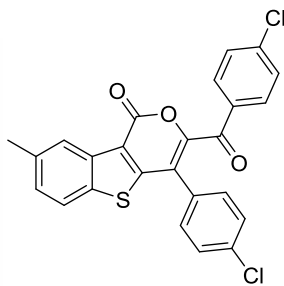
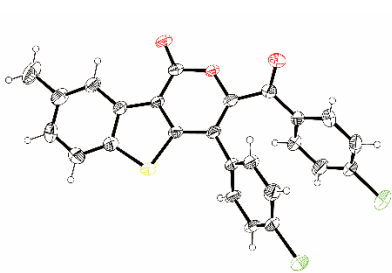
	4e	4k
Chemical formula	C ₂₅ H ₁₄ Cl ₂ O ₃ S	C ₂₄ H ₁₄ O ₃ S
Formula weight	465.32	382.41
Crystal system	triclinic	monoclinic
Space group	P 1 21/n 1	P 1 21/c 1
<i>a</i> (Å)	11.2168(14)	9.5944(2)
<i>b</i> (Å)	16.0869(15)	19.6642(4)
<i>c</i> (Å)	11.7492(13)	10.0633(2)
<i>V</i> (Å ³)	2079.6(4)	1798.08(7)
α (°)	90	90
β (°)	101.206(11)	108.728(2)
γ (°)	90	90
<i>Z</i>	4	4
F(000)	952.0	792.0
<i>GOF</i>	1.134	1.052
<i>D/g cm</i> ⁻³	1.486	1.413
μ (mm ⁻¹)	0.439	1.791
<i>T/K</i>	293	140
<i>R</i> ^{<i>a</i>} / <i>R</i> ^{<i>b</i>}	0.0479/0.1784	0.0552/0.1449

^{*a*}*R* = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{*b*}*R*_w = $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

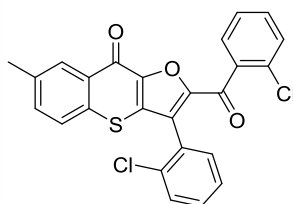
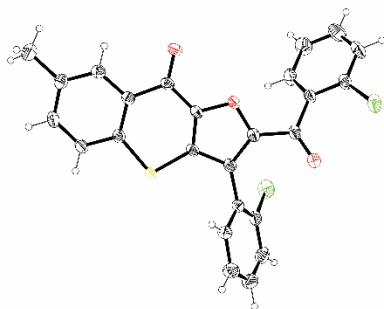
9. X-ray Crystal Structures (30% thermal ellipsoid probability levels)



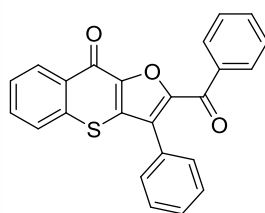
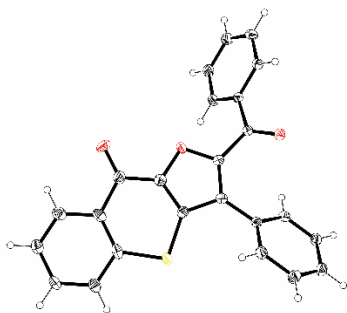
3e (CCDC 2027104)



3f (CCDC 2027105)



4e (CCDC 2027106)



4k (CCDC 2027107)

10. References

- (1) T. Inami, T. Kurahashi and S. Matsubara, Nickel-catalyzed reaction of thioisatins and alkynes: a facile synthesis of thiochromones, *Org. Lett.*, 2014, **16**, 5660.
- (2) J. Shen, Y. Yang, X. Hou, W. Zeng, A. Yu, X. Zhao and X. Meng, Darzens reaction of thioisatins and sulfonium salts: approach to the synthesis of thiochromenone derivatives with anticancer potency, *Org. Biomol. Chem.*, 2018, **16**, 3487.