Electronic Supplementary Information

Modular access to furo[3,2-*c*]chromen-4-ones *via* $Yb(OTf)_3$-catalyzed [3 + 2] annulation of 4-hydroxycoumarins with *β*-nitroalkenes

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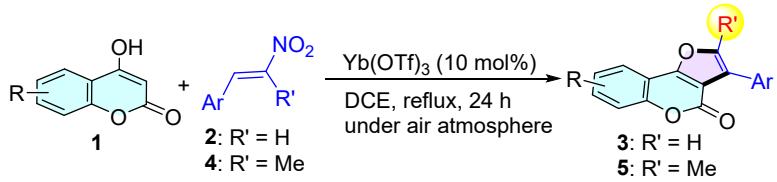
1. General comments

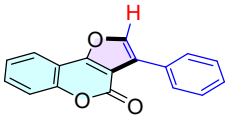
General comments. Unless otherwise noted, all commercially available reagents and solvents were used without further purification unless noted otherwise. The *β*-nitroalkenens 2 were prepared from benzaldehyde and nitroalkanes.[1] Infrared spectra were obtained on a FTIR spectrometer. ^{1}H NMR spectra were recorded on 400 MHz or 500MHz spectrometer in $CDCl_3$ solution and the chemical shifts were reported relative to internal standard TMS (0 ppm). The following abbreviations are used to describe peak patterns where appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants are reported in Hertz (Hz). ^{13}C NMR were recorded on 100 MHz or 125 MHz and referenced to the internal solvent signals (central peak is 77.00 ppm in $CDCl_3$). HRMS analysis with a quadrupole time-of-flight mass spectrometer yielded ion mass/charge (*m/z*) ratios in atomic mass units. Melting points were measured with micro melting point apparatus.

2. General procedure for the synthesis of furo[3,2-*c*]chromen-4-ones 3 and 5.

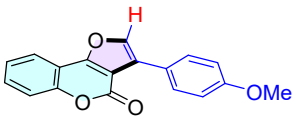


A solution of 4-hydroxycoumarin **1** (0.5 mmol), *β*-nitrostyrenes **2** (0.5 mmol) or *β*-2-nitrophenylpropenes **4** (0.5 mmol), and $Yb(OTf)_3$ (0.05 mmol) in 1,2-DCE (5 mL) was stirred under air atmosphere at reflux for 24 h. After being cooled down to room temperature, the mixture was diluted with ethyl acetate (50 mL), washed with saturated NaCl solution (10 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1:10, v/v) to afforded the desired product **3** or **5**.

3. Characterization data for all compounds

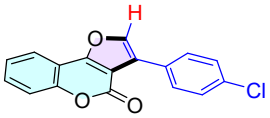


3-Phenyl-4*H*-furo[3,2-*c*]chromen-4-one (3a).[2] White solid (81 mg, 62% *vs* 79% as prvious reported); m.p. 173-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 7.8, 1.0 Hz, 1H), 7.81 – 7.71 (m, 3H), 7.56 – 7.49 (m, 1H), 7.49 – 7.42 (m, 3H), 7.41 – 7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.71, 157.77, 152.52, 141.18, 130.88, 129.00, 128.59, 128.50, 128.31, 126.64, 124.42, 120.90, 117.05, 112.68, 108.39; IR (KBr) ν 3157, 3053, 1740, 1497, 755, 696 cm^{-1}; HRMS (ESI): *m/z* calcd. for ($[C_{17}H_{10}O_3+H]^+$): 263.0703; found: 263.0704.

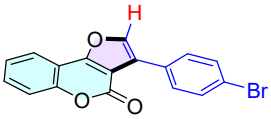


3-(4-Methoxyphenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3b).[2] White solid (95 mg, 65% *vs* 54% as prvious reported); m.p. 189-190 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.5 Hz, 1H), 7.72 (d, J = 8.7 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.43 (d, J = 8.1 Hz, 1H), 7.36 (t,

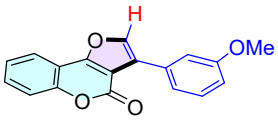
J = 7.4 Hz, 1H), 7.12 – 6.88 (m, 3H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.30, 158.34, 156.70, 156.31, 152.36, 130.27, 126.06, 124.48, 121.70, 120.59, 117.27, 114.40, 112.76, 112.52, 100.85, 55.37; IR (KBr) ν 3080, 2843, 1746, 1505, 1264, 1178, 748 cm^{-1}; HRMS (ESI): *m/z* calcd. for ($[C_{18}H_{12}O_4+H]^+$): 293.0808; found: 293.0809.



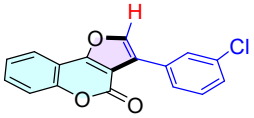
3-(4-Chlorophenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3c).[2] White solid (89 mg, 60% *vs* 88% as prvious reported); m.p. 188-189 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.3 Hz, 1H), 7.77 (s, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.92, 157.82, 152.58, 141.22, 134.36, 131.10, 129.92, 128.75, 127.50, 125.66, 124.56, 120.99, 117.14, 112.61, 108.25; IR (KBr) ν 3439, 1746, 1632, 1092, 1328, 971, 752 cm^{-1}; HRMS (ESI): *m/z* calcd. for ($[C_{17}H_9ClO_3+H]^+$): 297.0313; found: 297.0314.



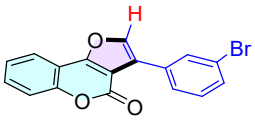
3-(4-Bromophenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3d).[2] Brown solid (106 mg, 62% *vs* 84% as prvious reported); m.p. 192-193 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.77 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.60 – 7.51 (m, 3H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.93, 157.79, 152.57, 141.20, 131.70, 131.11, 130.19, 127.97, 125.69, 124.56, 122.58, 120.98, 117.13, 112.58, 108.19; IR (KBr) ν 3055, 1746, 1484, 1105, 970, 750 cm^{-1}; HRMS (ESI): *m/z* calcd. for ($[C_{17}H_9BrO_3+H]^+$): 340.9808; found: 340.9810.



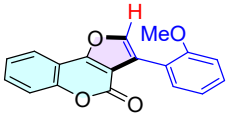
3-(3-Methoxyphenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3e).[2] White solid (73 mg, 50% *vs* 53% as prvious reported); m.p. 189-190 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.77 (s, 1H), 7.56 – 7.48 (m, 1H), 7.47 – 7.39 (m, 2H), 7.38– 7.28 (m, 3H), 6.97 – 6.88 (m, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.57, 158.75, 157.75, 152.53, 141.32, 130.90, 130.26, 129.47, 126.54, 124.42, 120.91, 120.71, 117.03, 114.24, 114.13, 112.67, 108.37, 55.29; IR (KBr) ν 3127, 3000, 1747, 1499, 1026, 754, 700 cm^{-1}; HRMS (ESI): *m/z* calcd. for ($[C_{18}H_{12}O_4+H]^+$): 293.0808; found: 293.0809.



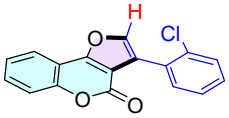
3-(3-Chlorophenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3f).[3] White solid (83 mg, 56% *vs* 69% as prvious reported); m.p. 177-178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.78 (s, 1H), 7.76 – 7.66 (m, 2H), 7.60 – 7.51 (m, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.43 – 7.32 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.92, 157.67, 152.60, 141.55, 134.32, 131.13, 130.81, 129.80, 128.40, 128.38, 126.99, 125.51, 124.56, 120.99, 117.15, 112.57, 108.20; IR (KBr) ν 3149, 1736, 1628, 1497, 983, 750 cm^{-1}; HRMS (ESI): *m/z* calcd. for ($[C_{17}H_9ClO_3+H]^+$): 297.0313; found: 297.0314.



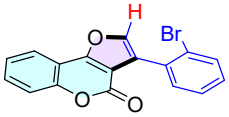
3-(3-Bromophenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3g).[3] Brown solid (85 mg, 50% *vs* 66% as prvious reported); m.p. 195-196 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.85 (m, 2H), 7.82 – 7.73 (m, 2H), 7.59 – 7.44 (m, 3H), 7.41 – 7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.96, 157.68, 152.66, 141.56, 131.33, 131.25, 131.16, 131.13, 130.09, 127.53, 125.45, 124.57, 122.47, 121.02, 117.19, 112.61, 108.25; IR (KBr) ν 3066, 1735, 1496, 1323, 1049, 760 cm^{-1}; HRMS (ESI): *m/z* calcd. for ($[C_{17}H_9BrO_3+H]^+$): 340.9808; found: 340.9809.



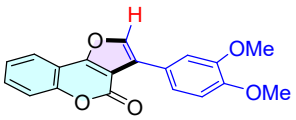
3-(2-Methoxyphenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3h).[4] White solid (66 mg, 45% *vs* 28% as prvious reported); m.p. 133-134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 7.8, 1.4 Hz, 1H), 7.83 (s, 1H), 7.62 (dd, J = 7.5, 1.6 Hz, 1H), 7.56 – 7.48 (m, 1H), 7.47 – 7.30 (m, 3H), 7.11 – 6.97 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.77, 157.57, 157.06, 152.53, 142.89, 131.39, 130.58, 129.75, 124.29, 121.73, 120.83, 120.45, 118.06, 117.02, 112.93, 110.88, 109.64, 55.57; IR (KBr) ν 3160, 2837, 1747, 1499, 1328, 1129, 743 cm^{-1}; HRMS (ESI): *m/z* calcd. for ($[C_{18}H_{12}O_4+H]^+$): 293.0808; found: 293.0810.



3-(2-Chlorophenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3i). White solid (67 mg, 45%); m.p. 196-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 7.8, 1.3 Hz, 1H), 7.78 (s, 1H), 7.59 – 7.48 (m, 3H), 7.45 (d, J = 8.2 Hz, 1H), 7.42 – 7.31 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.88, 157.31, 152.68, 142.97, 133.77, 132.08, 130.91, 129.79, 129.76, 128.08, 126.59, 124.46, 122.73, 120.91, 117.21, 112.77, 109.62; IR (KBr) ν 3129, 1740, 1508, 1039, 755 cm^{-1}; HRMS (ESI): *m/z* calcd. for ($[C_{17}H_9ClO_3+H]^+$): 297.0313; found: 297.0314.

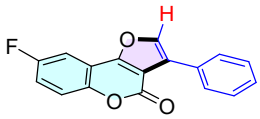


3-(2-Bromophenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3j). White solid (94 mg, 55%); m.p. 197-198 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.8 Hz, 1H), 7.75 (s, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.59 – 7.50 (m, 1H), 7.50 – 7.42 (m, 2H), 7.38 (q, J = 7.7 Hz, 2H), 7.32 – 7.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.74, 157.23, 152.68, 142.81, 132.97, 132.02, 130.89, 130.15, 129.96, 127.15, 124.45, 123.99, 120.91, 117.21, 112.78, 109.63; IR (KBr) ν 3128, 1741, 1497, 1036, 930, 754 cm^{-1}; HRMS (ESI): *m/z* calcd. for ($[C_{17}H_9BrO_3+H]^+$): 340.9808; found: 340.9809.

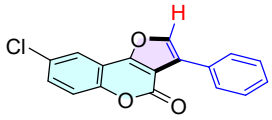


3-(3,4-Dimethoxyphenyl)-4*H*-furo[3,2-*c*]chromen-4-one (3k). White solid (108 mg, 67%); m.p. 229-230 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 7.7 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.44 (d, J = 8.2 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.25 (d, J = 1.5 Hz, 1H), 7.04 (s,

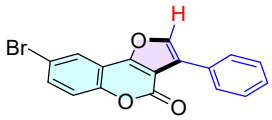
1H), 6.95 (d, J = 8.4 Hz, 1H), 3.99 (s, 3H), 3.95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.25, 156.63, 156.36, 152.40, 149.97, 149.27, 130.32, 124.46, 121.87, 120.62, 117.68, 117.30, 112.71, 112.54, 111.35, 107.50, 101.23, 56.00, 55.97; IR (KBr) ν 3112, 2991, 2827, 1747, 1508, 1139, 745 cm^{-1}; HRMS (ESI): *m/z* calcd. for ([$C_{19}H_{14}O_5$+H]$^+$): 323.0914; found: 323.0915.



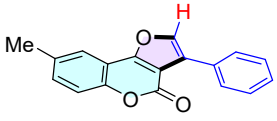
8-Fluoro-3-phenyl-4*H*-furo[3,2-*c*]chromen-4-one (3l). White solid (85 mg, 61%); m.p. 190-191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.77 – 7.72 (m, 2H), 7.58 (dd, J = 7.7, 2.9 Hz, 1H), 7.51 – 7.37 (m, 4H), 7.30 – 7.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.93 (d, $J_{C\text{-}F}$ = 243.4 Hz), 157.88 (d, $J_{C\text{-}F}$ = 2.8 Hz), 157.40, 148.72(d, $J_{C\text{-}F}$ = 2.1 Hz), 141.71, 128.76, 128.63 (d, $J_{C\text{-}F}$ = 8.7 Hz), 128.50, 126.94, 118.93, 118.85, 118.26(d, $J_{C\text{-}F}$ = 24.4 Hz), 113.54, 113.44, 109.17, 106.80 (d, $J_{C\text{-}F}$ = 25.7 Hz); IR (KBr) ν 3433, 2868, 1739, 1513, 1072, 755 cm^{-1}; HRMS (ESI): *m/z* calcd. for ([$C_{17}H_9FO_3$+H]$^+$): 281.0608; found: 281.0606.



8-Chloro-3-phenyl-4*H*-furo[3,2-*c*]chromen-4-one (3m).[5] Yellow solid (83 mg, 56% *vs* 54% as prvious reported); m.p. 181-182 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 2.3 Hz, 1H), 7.77 (s, 1H), 7.73 (d, J = 7.4 Hz, 2H), 7.51 – 7.42 (m, 3H), 7.39 (t, J = 8.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.41, 157.15, 150.85, 141.74, 130.87, 129.99, 128.67, 128.62, 128.56, 128.49, 126.89, 120.45, 118.56, 113.77, 109.14; IR (KBr) ν 3446, 2879, 1746, 1502, 1071, 746 cm^{-1}; HRMS (ESI): *m/z* calcd. for ([$C_{17}H_9ClO_3$+H]$^+$): 297.0313; found: 297.0316.

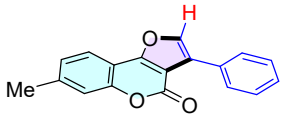


8-Bromo-3-phenyl-4*H*-furo[3,2-*c*]chromen-4-one (3n).[5] Yellow solid (75 mg, 44% *vs* 71% as prvious reported); m.p. 187-188 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 2.3 Hz, 1H), 7.78 (s, 1H), 7.77 – 7.71 (m, 2H), 7.62 (dd, J = 8.8, 2.3 Hz, 1H), 7.50 – 7.37 (m, 3H), 7.33 (d, J = 8.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.30, 157.12, 151.35, 141.76, 133.71, 128.69, 128.65, 128.59, 128.52, 126.93, 123.51, 118.87, 117.28, 114.28, 109.17; IR (KBr) ν 3442, 2985, 1746, 1502, 1157, 746 cm^{-1}; HRMS (ESI): *m/z* calcd. for ([$C_{17}H_9BrO_3$+H]$^+$): 340.9808; found: 340.9810.

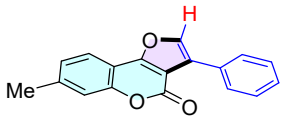


8-Methyl-3-phenyl-4*H*-furo[3,2-*c*]chromen-4-one (3o).[5] White solid (94 mg, 68% *vs* 72% as prvious reported); m.p. 202-203 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.71 (m, 3H), 7.70 – 7.65 (m, 1H), 7.45 (t, J = 7.4 Hz, 2H), 7.38 (t, J = 7.3 Hz, 1H), 7.33 (s, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.83, 157.97, 150.82, 141.06, 134.27, 131.97, 129.14, 128.64, 128.51, 128.29, 126.71, 120.61, 116.83, 112.42, 108.36, 20.94; IR (KBr) ν

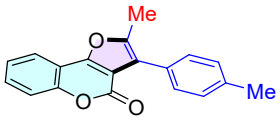
3072, 1730, 1447, 1100, 969, 745 cm^{-1}; HRMS (ESI): *m/z* calcd. for ($[C_{18}H_{12}O_3+H]^+$): 277.0859; found: 277.0859.



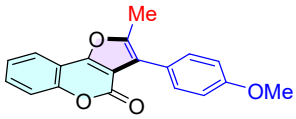
7-Methyl-3-phenyl-4*H*-furo[3,2-*c*]chromen-4-one (3p). White solid (72 mg, 52%); m.p. 194-195 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.74 (m, 3H), 7.73 (s, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.1 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.83, 157.98, 150.82, 141.06, 134.28, 131.97, 129.14, 128.64, 128.51, 128.29, 126.72, 120.61, 116.83, 112.42, 108.36, 20.94; IR (KBr) *v* 3062, 1738, 1445, 1096, 963, 747 cm^{-1}; HRMS (ESI): *m/z* calcd. for ($[C_{18}H_{12}O_3+H]^+$): 277.0859; found: 277.0862.



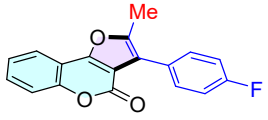
2-Methyl-3-phenyl-4*H*-furo[3,2-*c*]chromen-4-one (5a).[3] White solid (73 mg, 53% *vs* 78% as prvious reported); m.p. 194-195 °C; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.86 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.45 (m, 5H), 7.43 (d, *J* = 4.4 Hz, 1H), 7.42 – 7.30 (m, 2H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 157.68, 156.24, 152.29, 151.65, 130.23, 129.95, 129.85, 128.18, 127.74, 124.25, 120.54, 120.43, 117.04, 112.74, 109.60, 12.57; IR (KBr) *v* 3067, 1735, 1443, 1103, 963, 750 cm^{-1}; HRMS (ESI): *m/z* calcd. for ($[C_{18}H_{12}O_3+H]^+$): 277.0859; found: 277.0860.



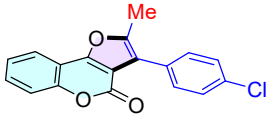
2-Methyl-3-(p-tolyl)-4*H*-furo[3,2-*c*]chromen-4-one (5b).[6] White solid (83 mg, 57% *vs* 76% as prvious reported); m.p. 162-163 °C; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.85 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.28 (t, *J* = 12.3 Hz, 3H), 2.51 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 157.73, 156.15, 152.26, 151.41, 137.51, 130.14, 129.69, 128.93, 126.92, 124.21, 120.50, 120.34, 117.01, 112.78, 109.67, 21.27, 12.54; IR (KBr) *v* 3027, 2922, 1736, 1499, 1320, 1115, 750 cm^{-1}; HRMS (ESI): *m/z* calcd. for ($[C_{19}H_{14}O_3+H]^+$): 291.1016; found: 291.1017.



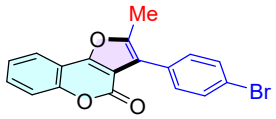
3-(4-Methoxyphenyl)-2-methyl-4*H*-furo[3,2-*c*]chromen-4-one (5c).[6] White solid (89 mg, 58% *vs* 72% as prvious reported); m.p. 168-169 °C; ^1H NMR (400 MHz, $CDCl_3$) *δ* 7.87 (d, *J* = 7.8 Hz, 1H), 7.53 – 7.40 (m, 4H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 2H), 3.86 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 159.16, 157.87, 156.15, 152.29, 151.22, 131.04, 130.16, 124.25, 122.17, 120.54, 120.08, 117.06, 113.73, 112.84, 109.71, 55.26, 12.57; IR (KBr) *v* 3446, 2935, 2839, 1739, 1515, 1174, 756 cm^{-1}; HRMS (ESI): *m/z* calcd. for ($[C_{19}H_{14}O_4+H]^+$): 307.0965; found: 307.0966.



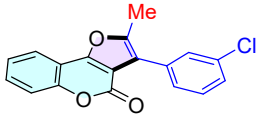
3-(4-Fluorophenyl)-2-methyl-4*H*-furo[3,2-*c*]chromen-4-one (5d).[2] White solid (59 mg, 40% *vs* 76% as prvious reported); m.p. 198-199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 7.8, 0.9 Hz, 1H), 7.53 – 7.41 (m, 4H), 7.35 (t, J = 7.5 Hz, 1H), 7.15 (t, J = 8.7 Hz, 2H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.38 (d, $J_{C\text{-}F}$ = 245.6 Hz), 157.76, 156.31, 152.31, 151.59, 131.59 (d, $J_{C\text{-}F}$ = 8.2 Hz), 130.36, 125.92 (d, $J_{C\text{-}F}$ = 3.5 Hz), 124.35, 120.59, 119.53, 117.10, 115.26 (d, $J_{C\text{-}F}$ = 21.5 Hz), 112.70, 109.52, 12.52; IR (KBr) ν 3437, 2867, 1730, 1512, 1076, 758 cm^{-1}; HRMS (ESI): *m/z* calcd. for ([$C_{18}H_{11}FO_3$+H]$^+$): 295.0765; found: 295.0766.



3-(4-Chlorophenyl)-2-methyl-4*H*-furo[3,2-*c*]chromen-4-one (5e).[7] White solid (78 mg, 50% *vs* 77% as prvious reported); m.p. 176-177 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.8 Hz, 1H), 7.50 (t, J = 7.8 Hz, 1H), 7.47 – 7.39 (m, 5H), 7.34 (t, J = 7.5 Hz, 1H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.69, 156.40, 152.31, 151.77, 133.79, 131.15, 130.43, 128.46, 128.42, 124.37, 120.60, 119.43, 117.09, 112.63, 109.40, 12.57; IR (KBr) ν 3443, 2877, 1749, 1502, 1070, 744 cm^{-1}; HRMS (ESI): *m/z* calcd. for ([$C_{18}H_{11}ClO_3$+H]$^+$): 311.0469; found: 311.0470.



3-(4-Bromophenyl)-2-methyl-4*H*-furo[3,2-*c*]chromen-4-one (5f).[7] White solid (66 mg, 52% *vs* 61% as prvious reported); m.p. 162-163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 7.2 Hz, 1H), 7.45 – 7.32 (m, 4H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.69, 156.44, 152.33, 151.74, 131.46, 131.42, 130.45, 128.91, 124.39, 122.04, 120.61, 119.48, 117.11, 112.63, 109.36, 12.58; IR (KBr) ν 3444, 2988, 1749, 1500, 1156, 745 cm^{-1}; HRMS (ESI): *m/z* calcd. for ([$C_{18}H_{11}BrO_3$+H]$^+$): 354.9964; found: 354.9965.



3-(3-Chlorophenyl)-2-methyl-4*H*-furo[3,2-*c*]chromen-4-one (5g).[3] White solid (56 mg, 36% *vs* 47% as prvious reported); m.p. 139-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 7.8, 1.2 Hz, 1H), 7.54 – 7.33 (m, 7H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.59, 156.44, 152.38, 152.07, 134.02, 131.83, 130.49, 129.70, 129.48, 128.27, 127.93, 124.39, 120.64, 119.33, 117.16, 112.65, 109.42, 12.61; IR (KBr) ν 3437, 2986, 1736, 1500, 1103, 756 cm^{-1}; HRMS (ESI): *m/z* calcd. for ([$C_{18}H_{11}ClO_3$+H]$^+$): 311.0469; found: 311.0470.

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Adv., 2020, **10**, 44332-44338.
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4. X-ray crystallographic data of compound 5d

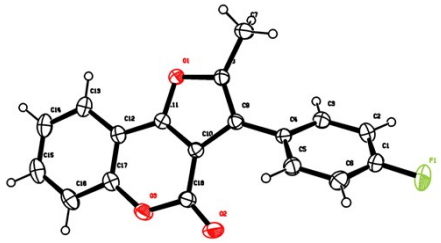


Figure S1. ORTEP drawing of compound **5d** (30% probability for the thermal ellipsoid).

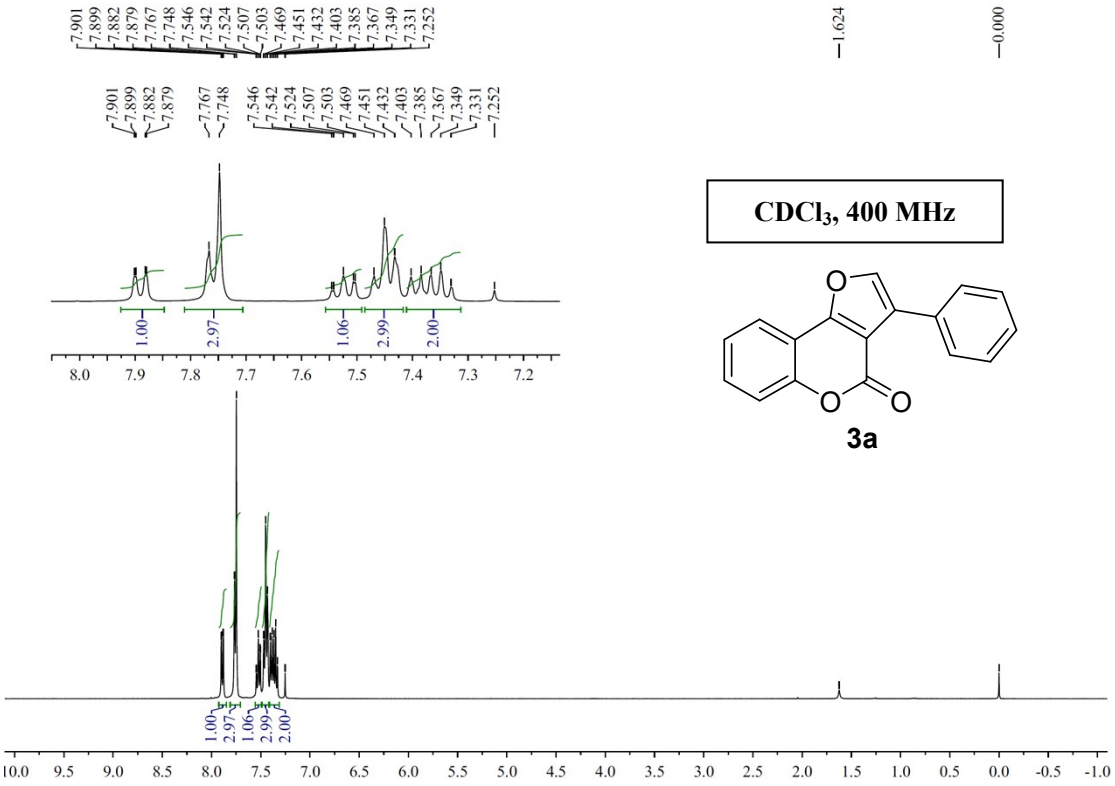
The purified compound **5d** is dissolved in a mixed solvent of dichloromethane and *n*-hexane, and placed in a dark cabinet to slowly evaporate. After several days, a colourless bulk crystal is obtained. The X-ray crystal-structure determinations were obtained on a Bruker Smart CCDC APEX-2 diffractometer (graphite- monochromated Mo *Kα* radiation, λ=0.71073 nm) at 300 K.

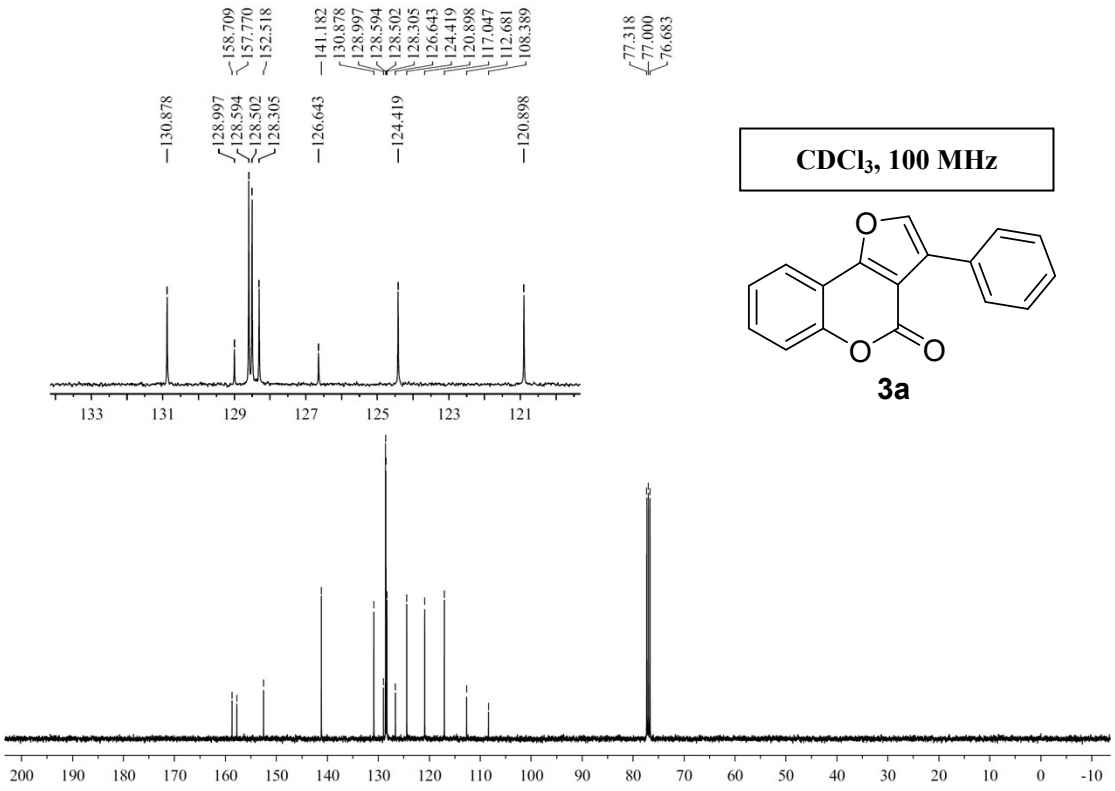
Table S1. Crystal data and structure refinement for compound **5d**.

CCDC number	2354856
Identification code	mo_20210121a_0m_a
Empirical formula	$C_{18}H_{11}FO_3$
Formula weight	294.27
Temperature	300(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 6.9643(8) Å α= 90°. b = 17.995(2) Å β= 104.494(4)°. c = 11.2480(13) Å γ= 90°.
Volume	1364.7(3) $Å^3$
Z	4
Density (calculated)	1.432 Mg/m^3
Absorption coefficient	0.106 mm^{-1}
F(000)	608.0
Crystal size	0.230 × 0.210 × 0.200 mm^3
2Θ range for data collection/°	5.874 to 55.046°.
Index ranges	$-9 \le h \le 8$, $-23 \le k \le 23$, $-14 \le l \le 14$
Reflections collected	26551
Independent reflections	3123 [R_{int} = 0.0455, R_{sigma} = 0.0257]
Data/restraints/parameters	3123/0/200
Goodness-of-fit on F^2	1.089
Final R indices [I>2sigma(I)]	R1 = 0.0607, wR2 = 0.2102
R indices (all data)	R1 = 0.0886, wR2 = 0.2349
Largest diff. peak and hole	0.21 and -0.30 $e.Å^{-3}$

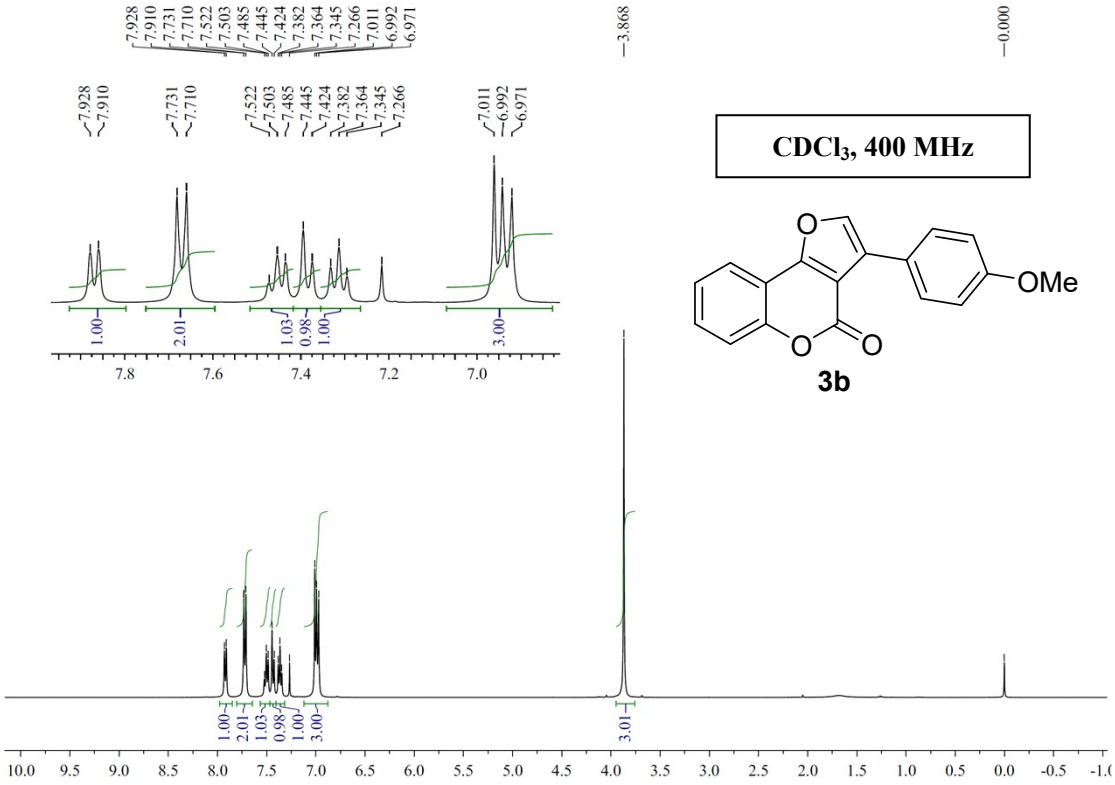
5. ^{1}H, ^{13}C NMR spectra for all compounds

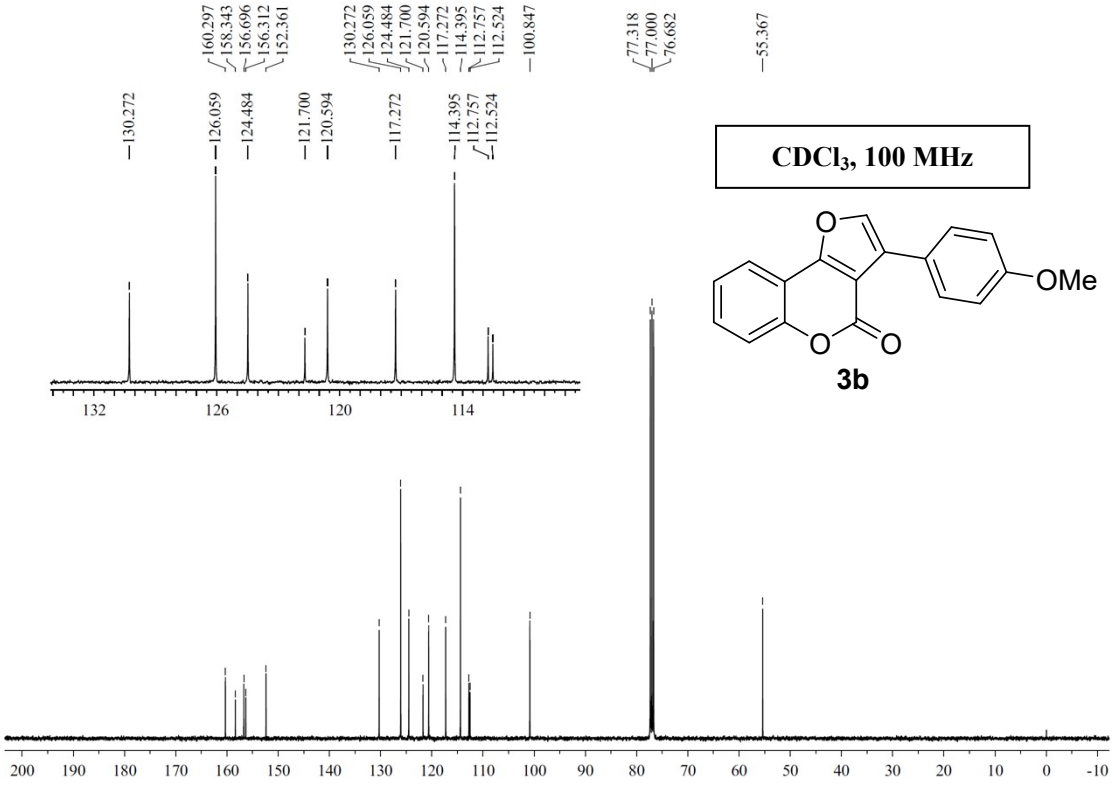
3-Phenyl-4H-furo[3,2-c]chromen-4-one **(Table 2, compound 3a)**



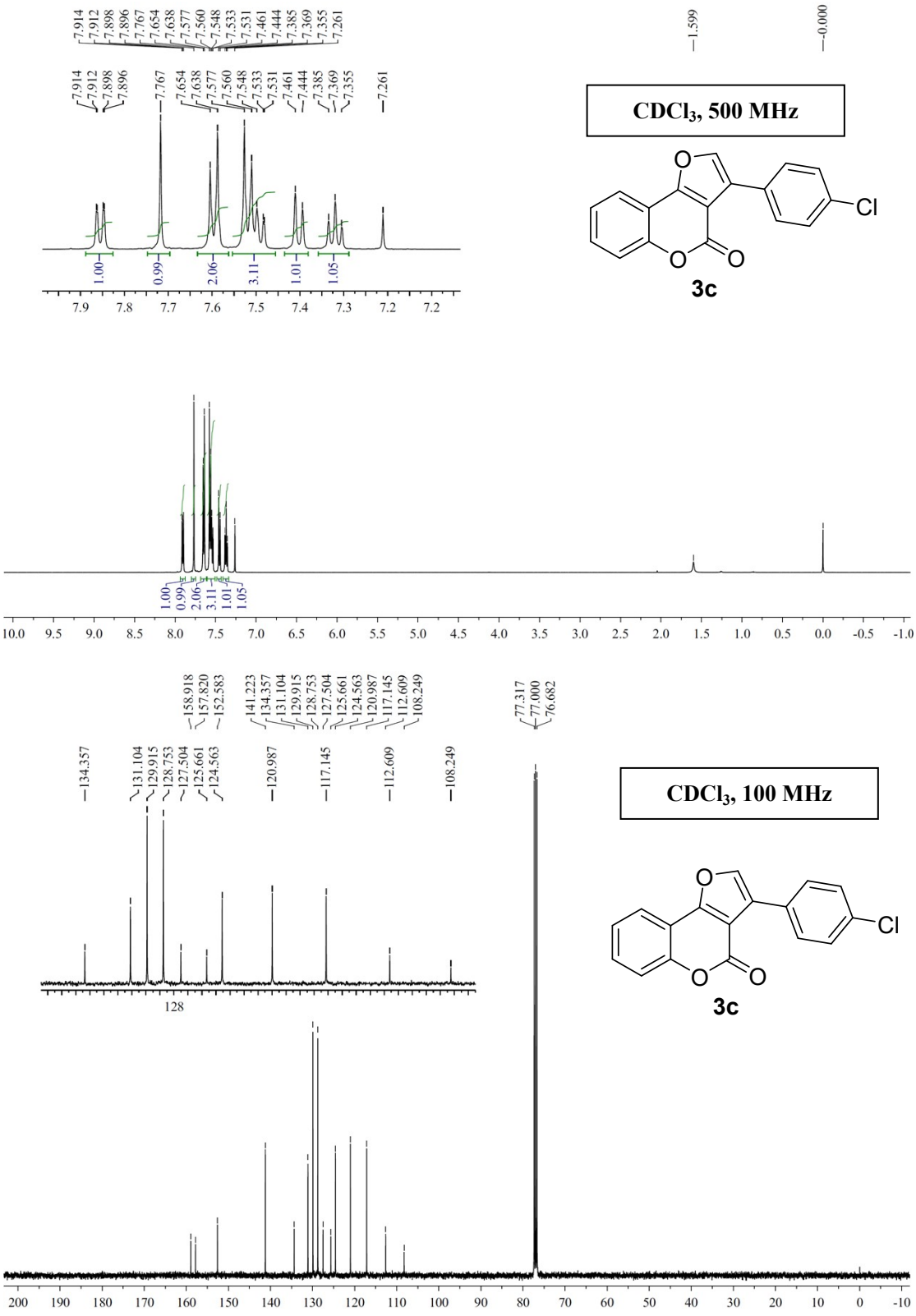


3-(4-Methoxyphenyl)-4H-furo[3,2-c]chromen-4-one **(Table 2, compound 3b)**

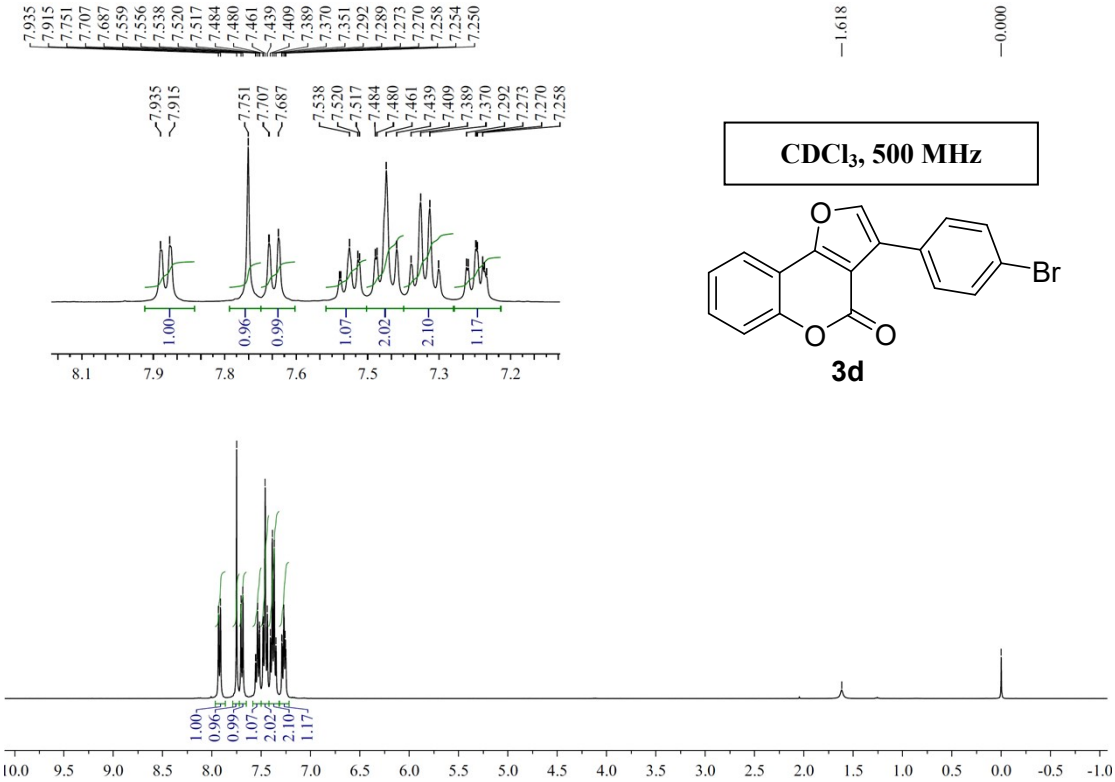


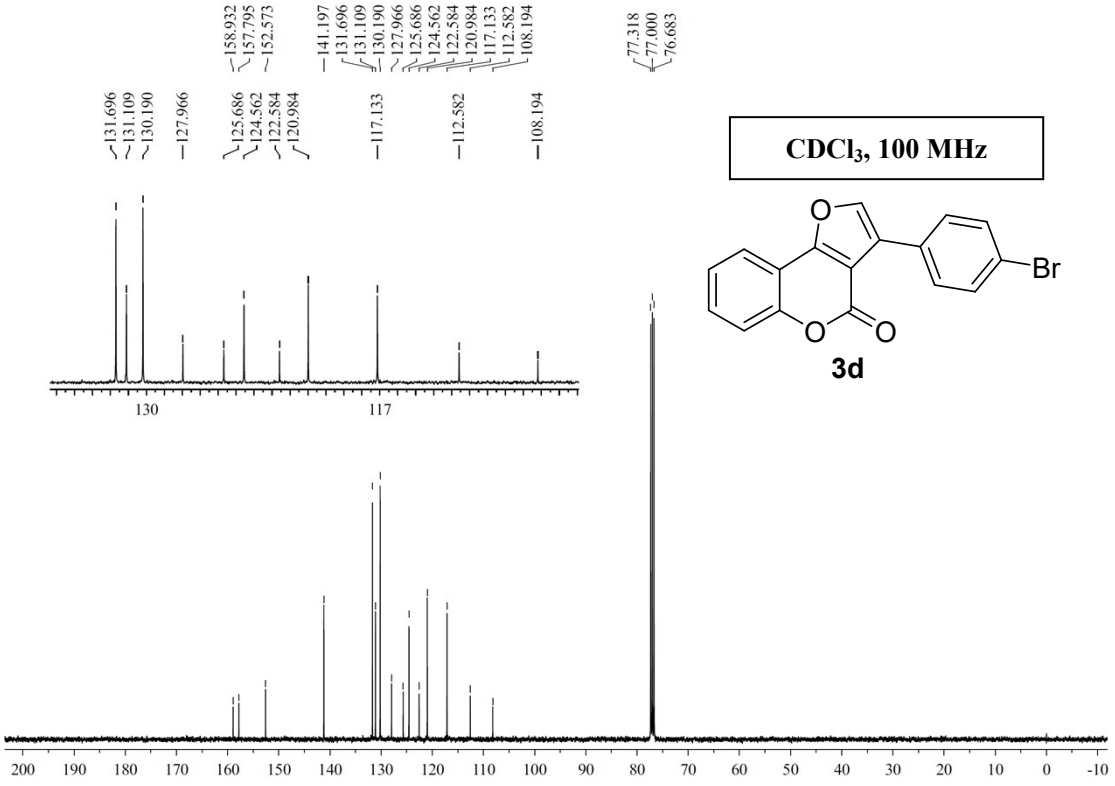


3-(4-Chlorophenyl)-4H-furo[3,2-c]chromen-4-one **(Table 2, compound 3c)**

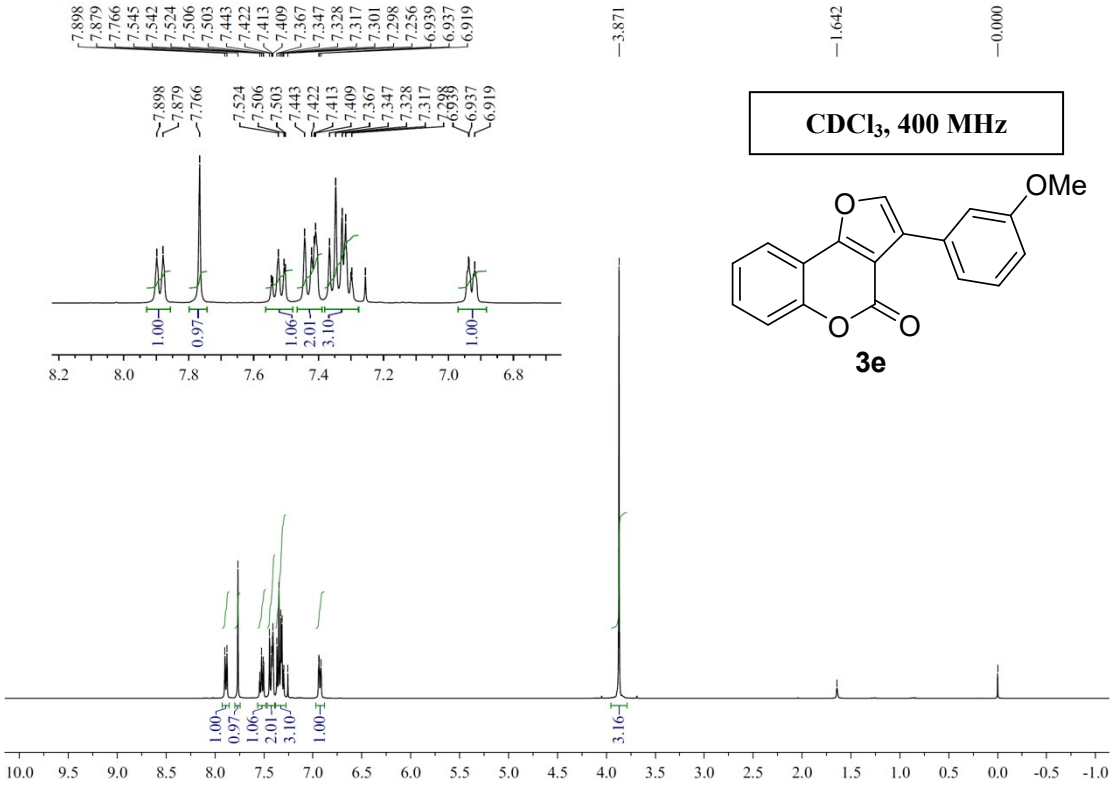


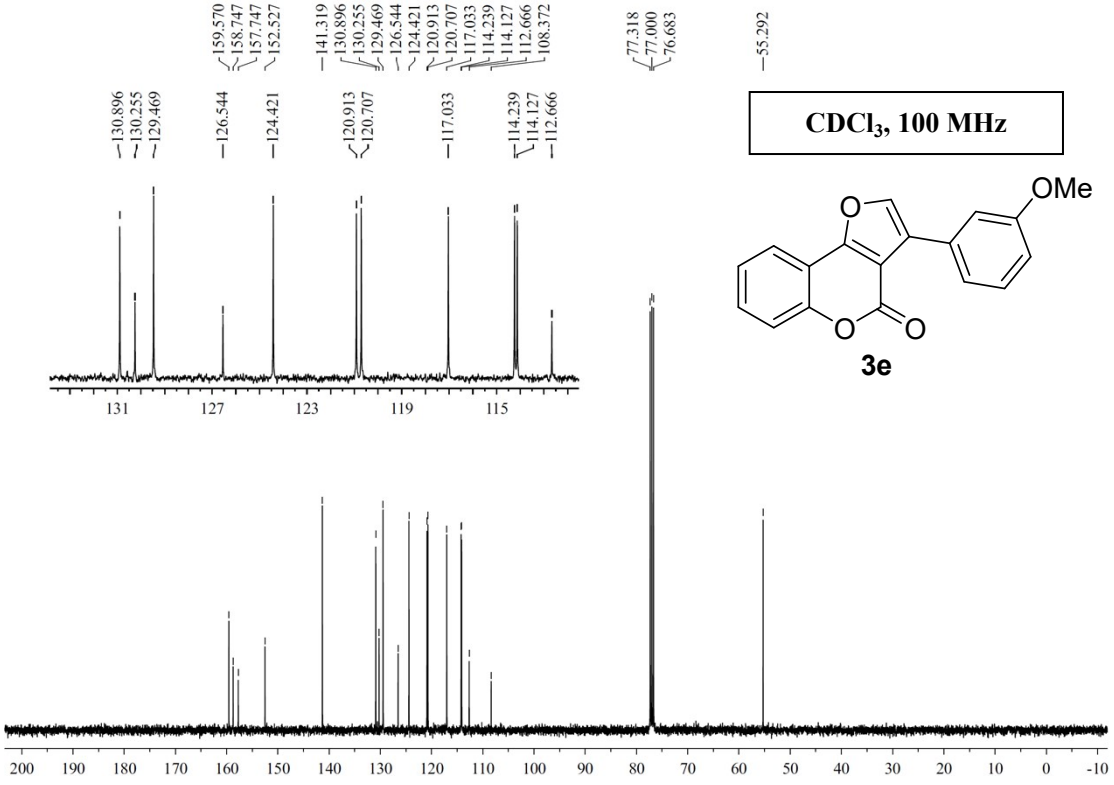
3-(4-Bromophenyl)-4H-furo[3,2-c]chromen-4-one **(Table 2, compound 3d)**



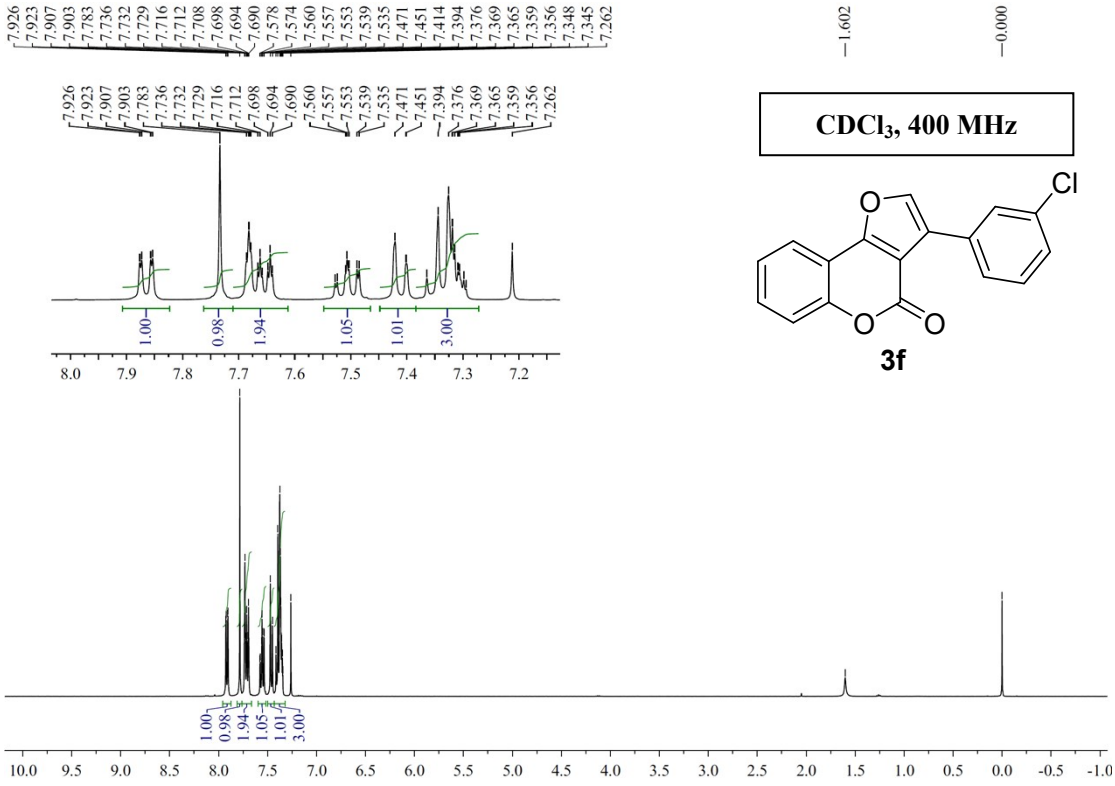


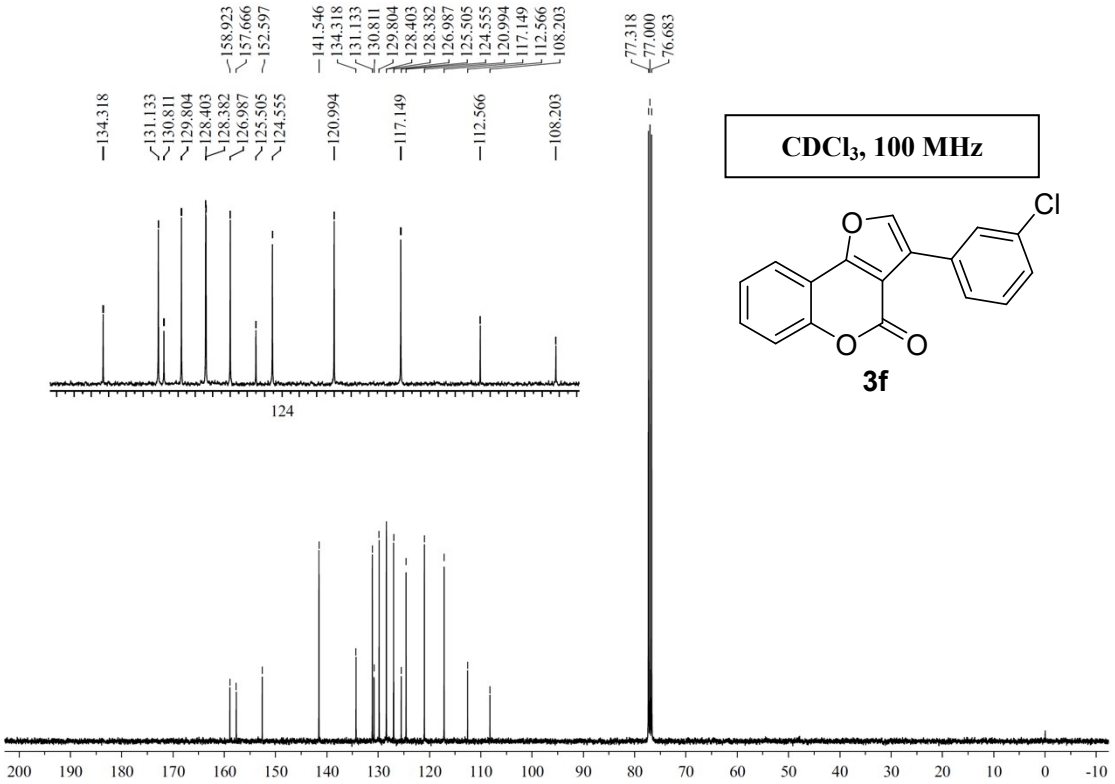
3-(3-Methoxyphenyl)-4H-furo[3,2-c]chromen-4-one **(Table 2, compound 3e)**



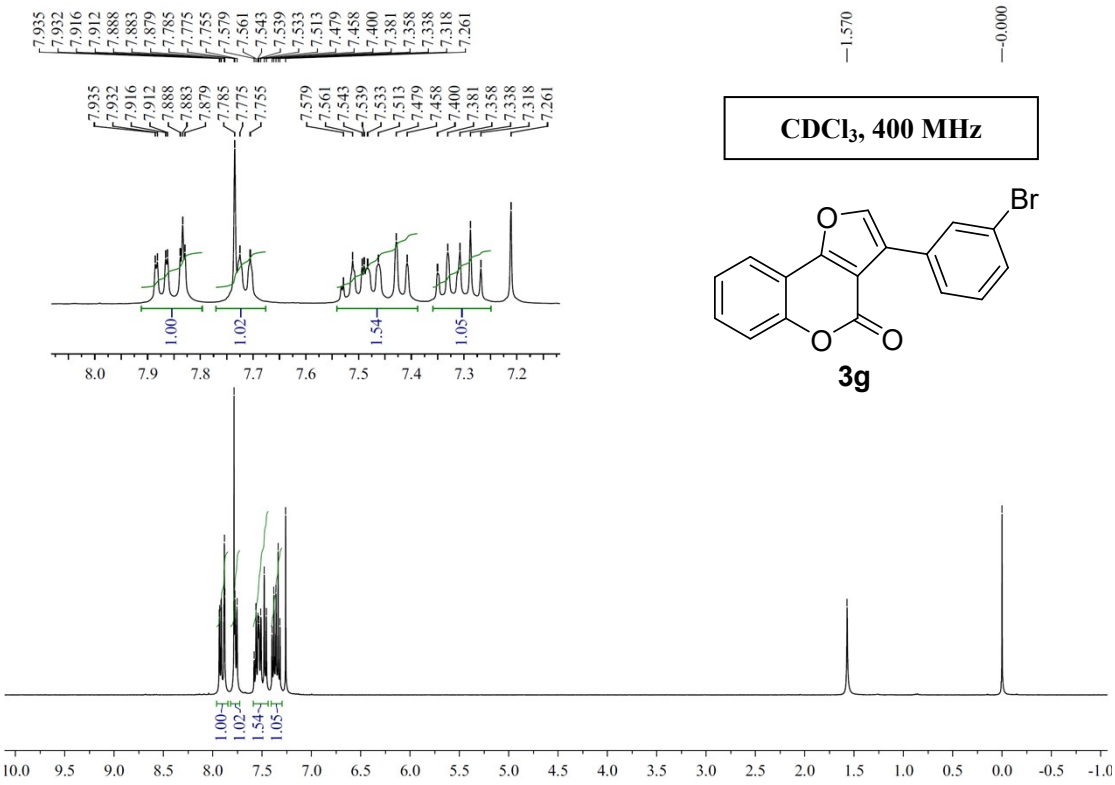


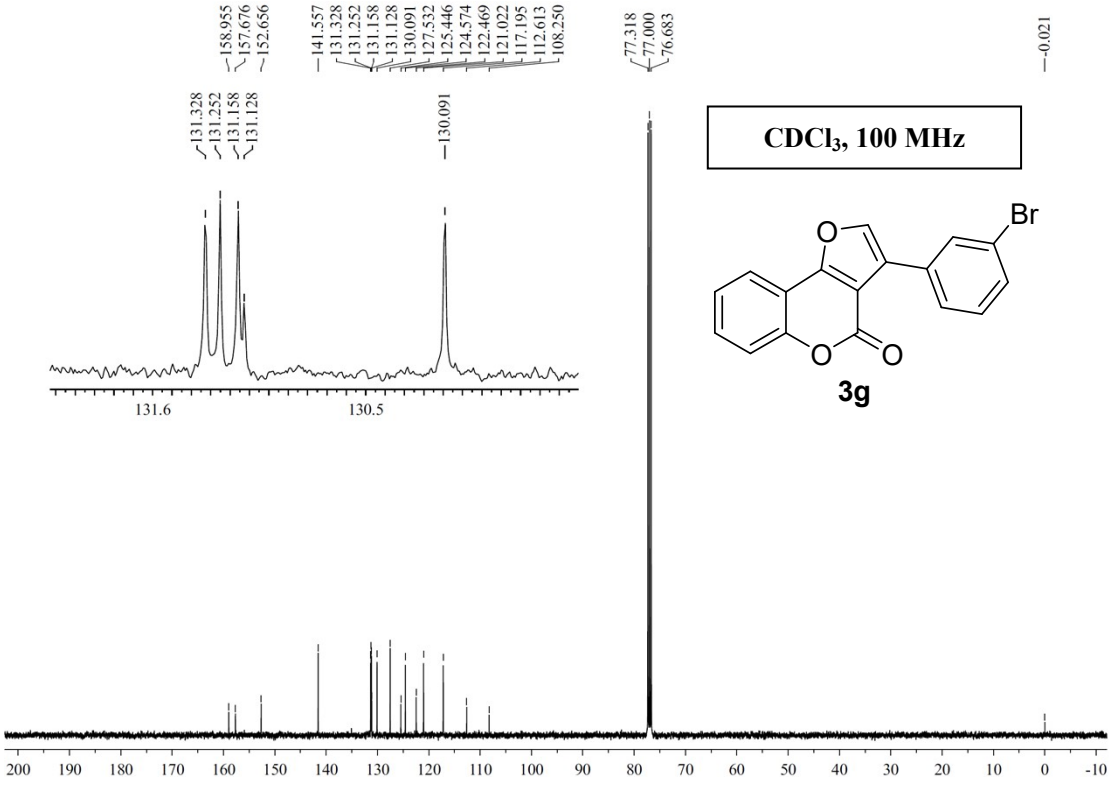
3-(3-Chlorophenyl)-4H-furo[3,2-c]chromen-4-one **(Table 2, compound 3f)**



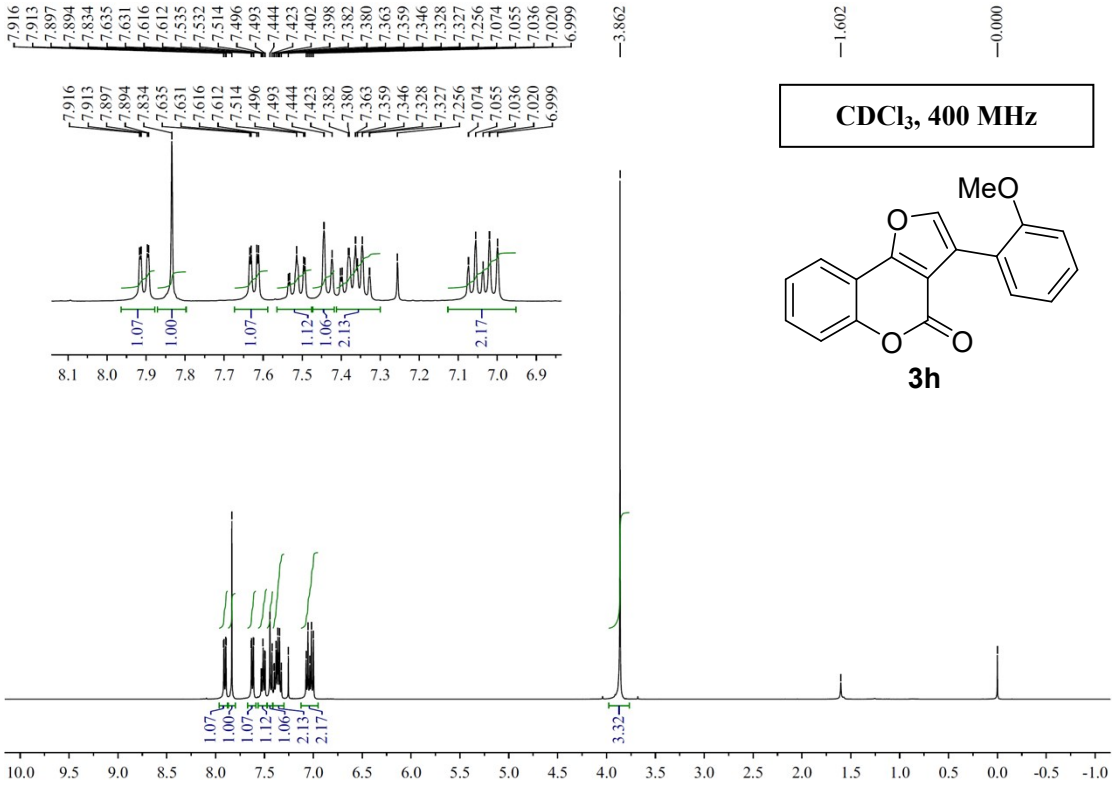


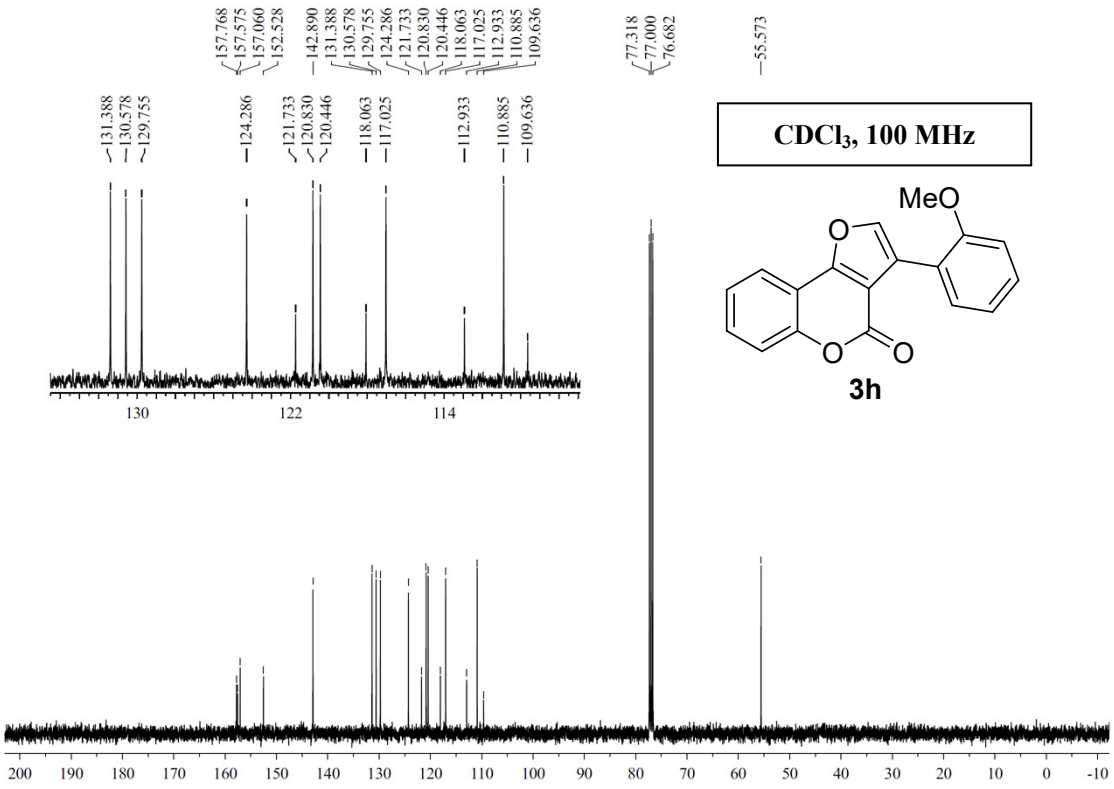
3-(3-Bromophenyl)-4H-furo[3,2-c]chromen-4-one **(Table 2, compound 3g)**



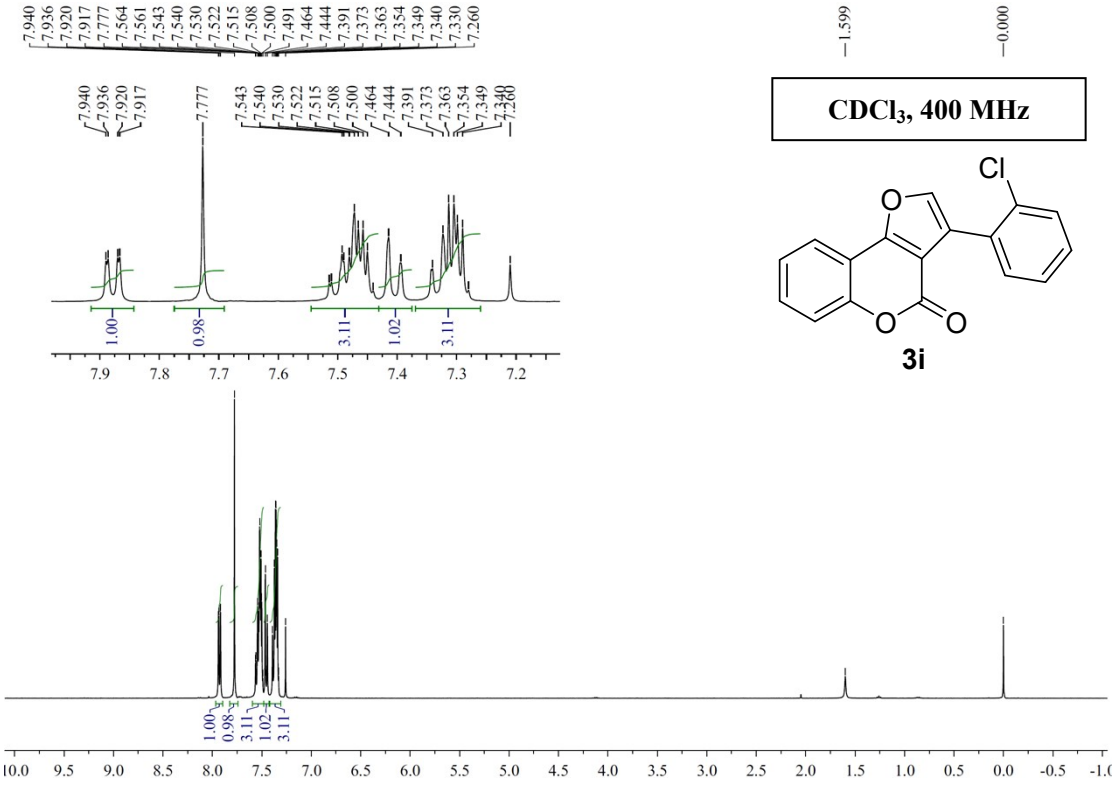


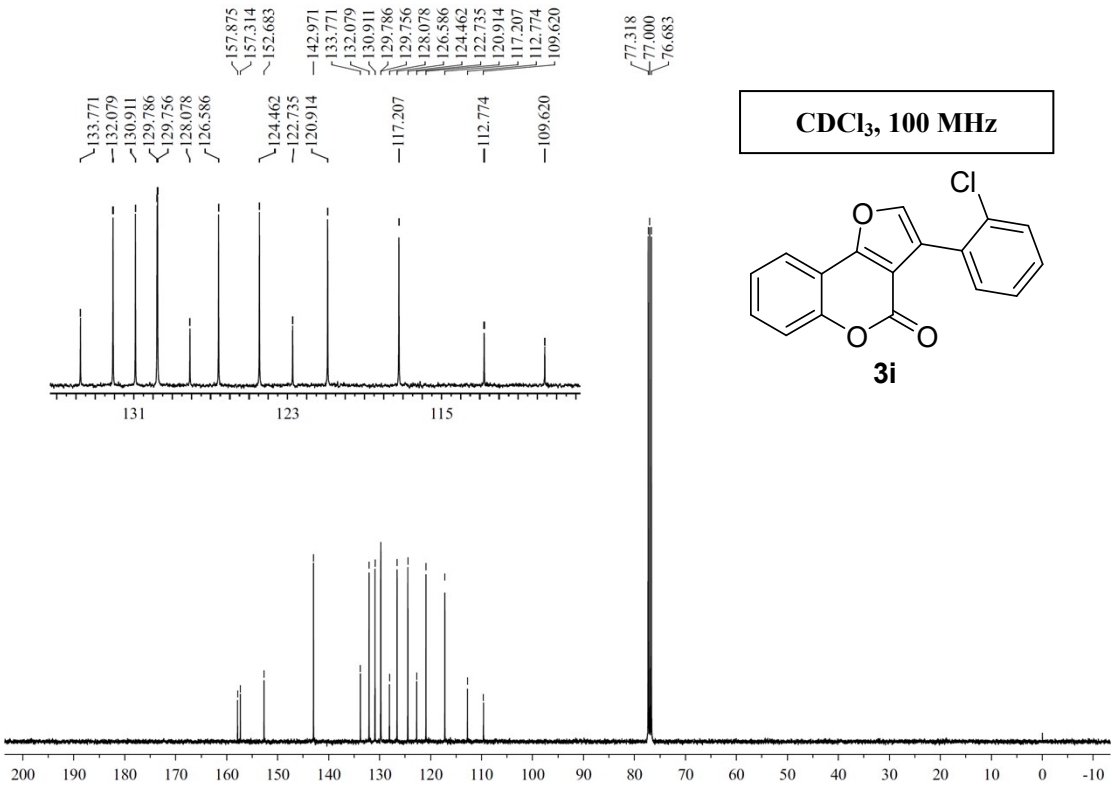
3-(2-Methoxyphenyl)-4H-furo[3,2-c]chromen-4-one **(Table 2, compound 3h)**



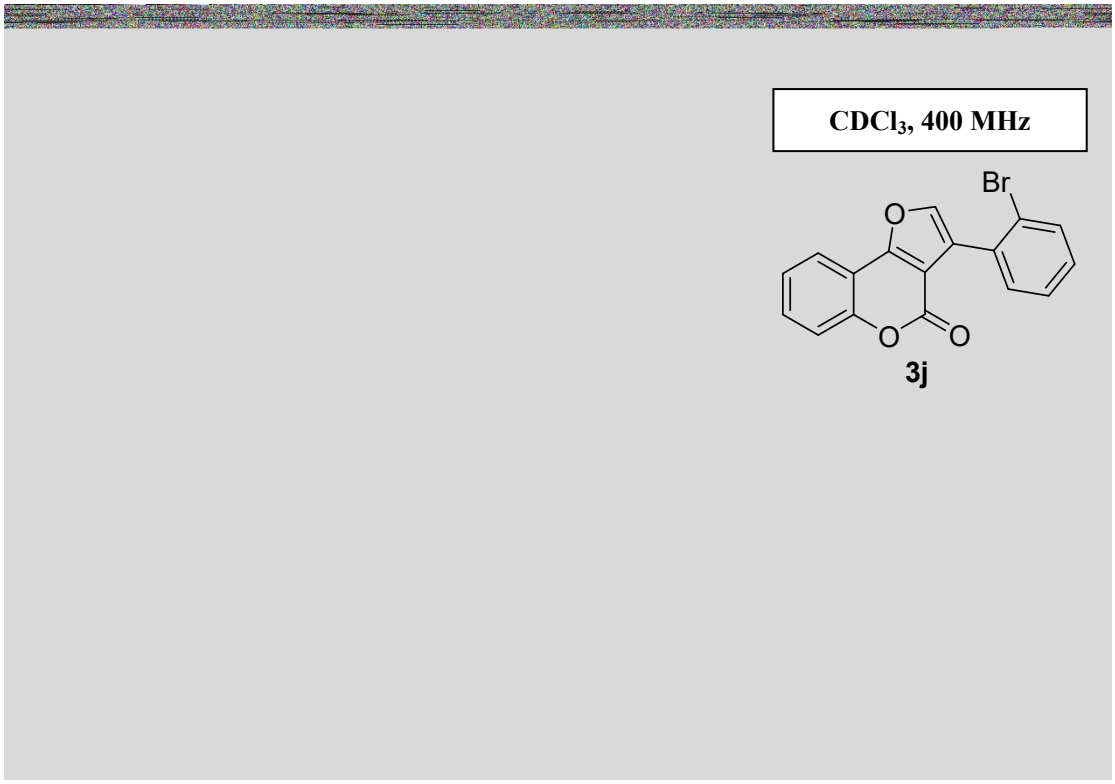


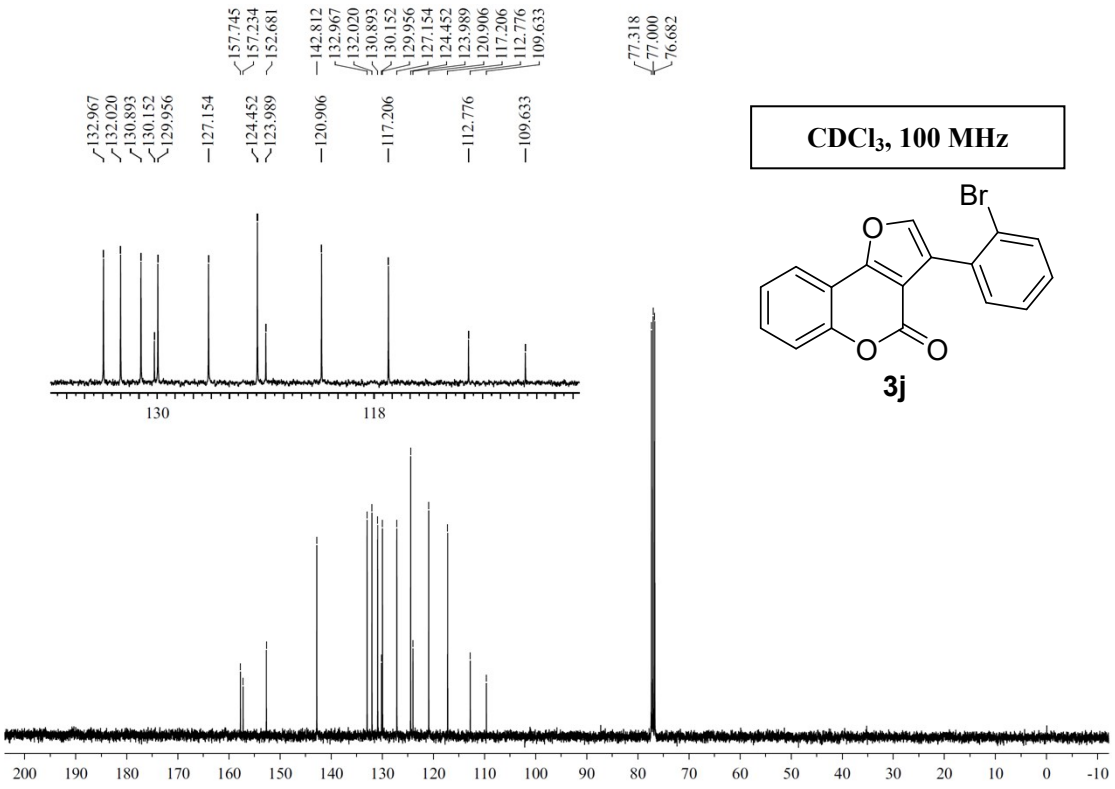
3-(2-Chlorophenyl)-4H-furo[3,2-c]chromen-4-one **(Table 2, compound 3i)**



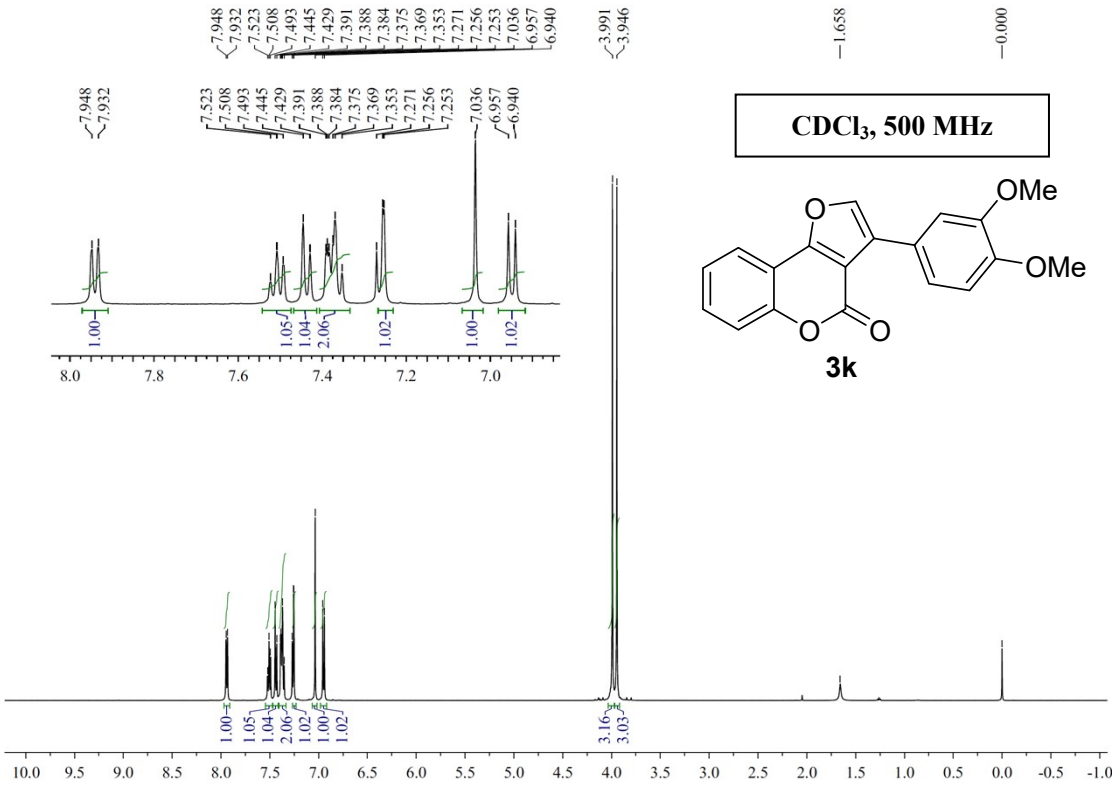


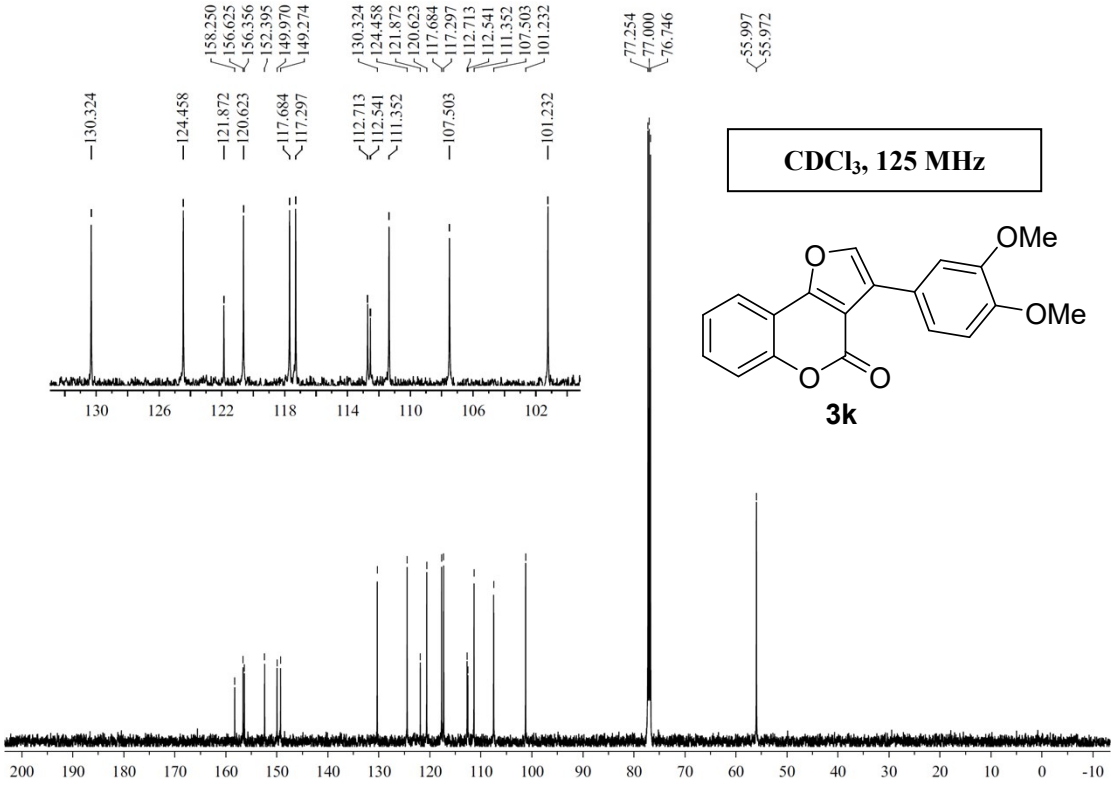
3-(2-Bromophenyl)-4H-furo[3,2-c]chromen-4-one **(Table 2, compound 3j)**



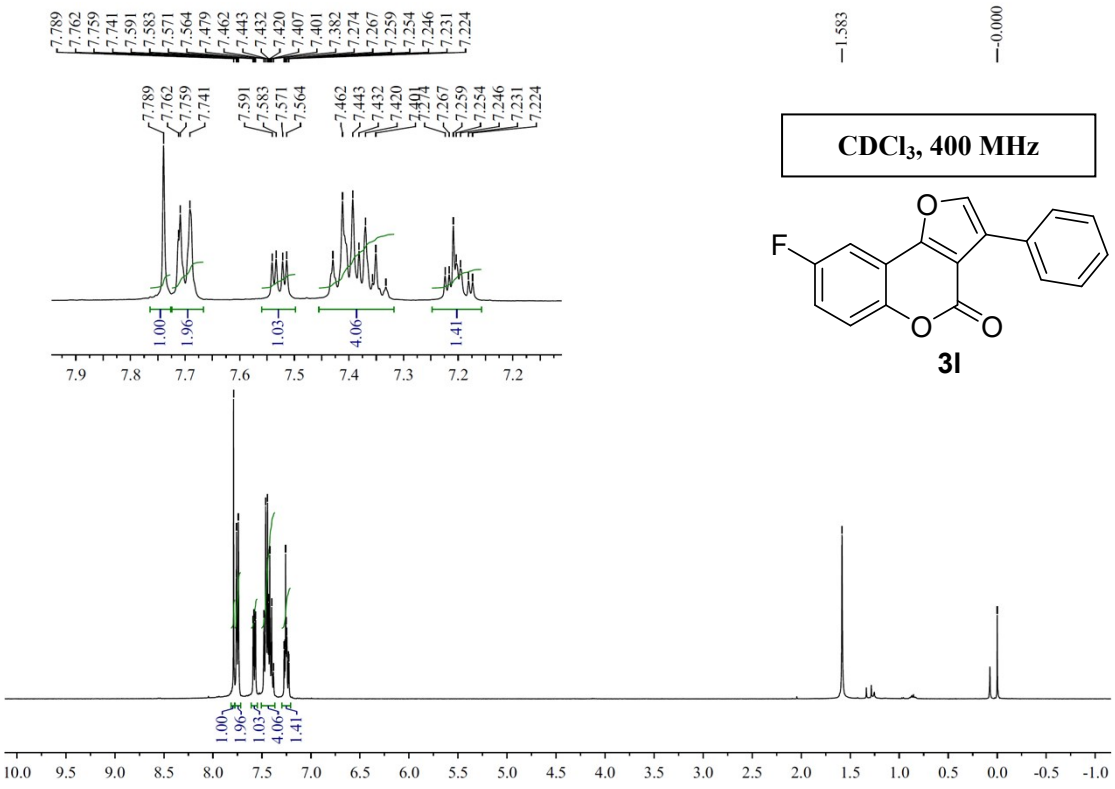


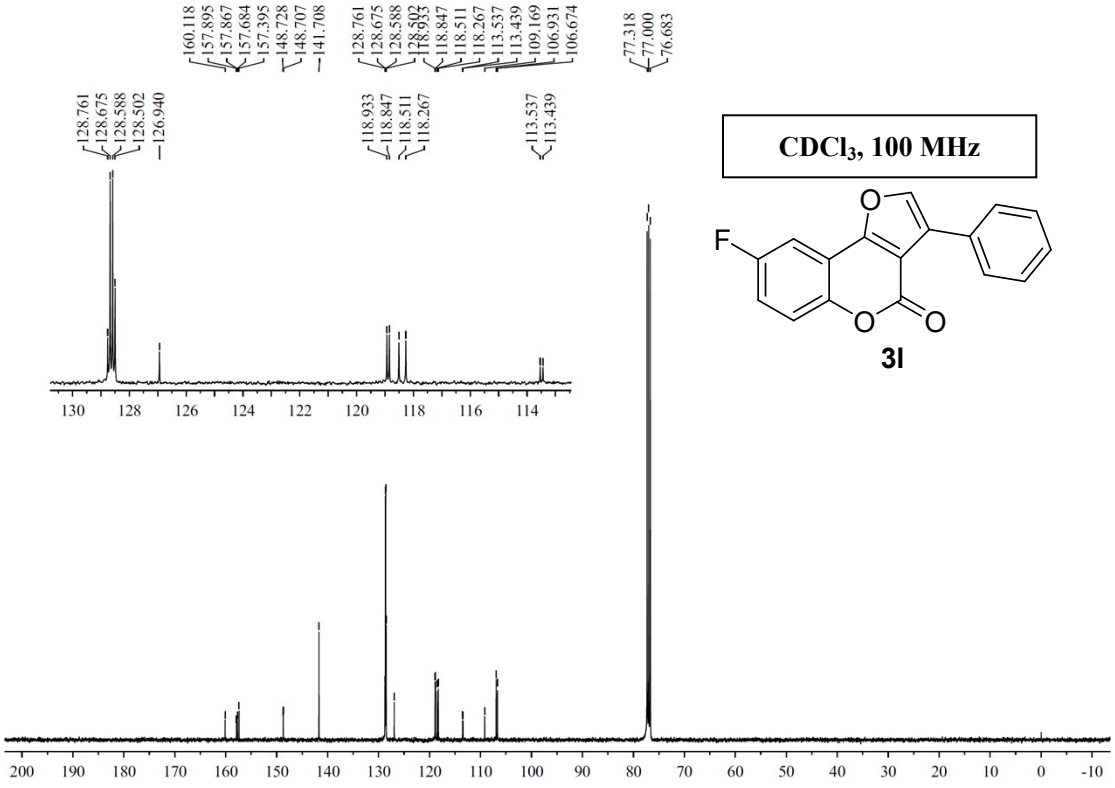
3-(3,4-Dimethoxyphenyl)-4H-furo[3,2-c]chromen-4-one **(Table 2, compound 3k)**



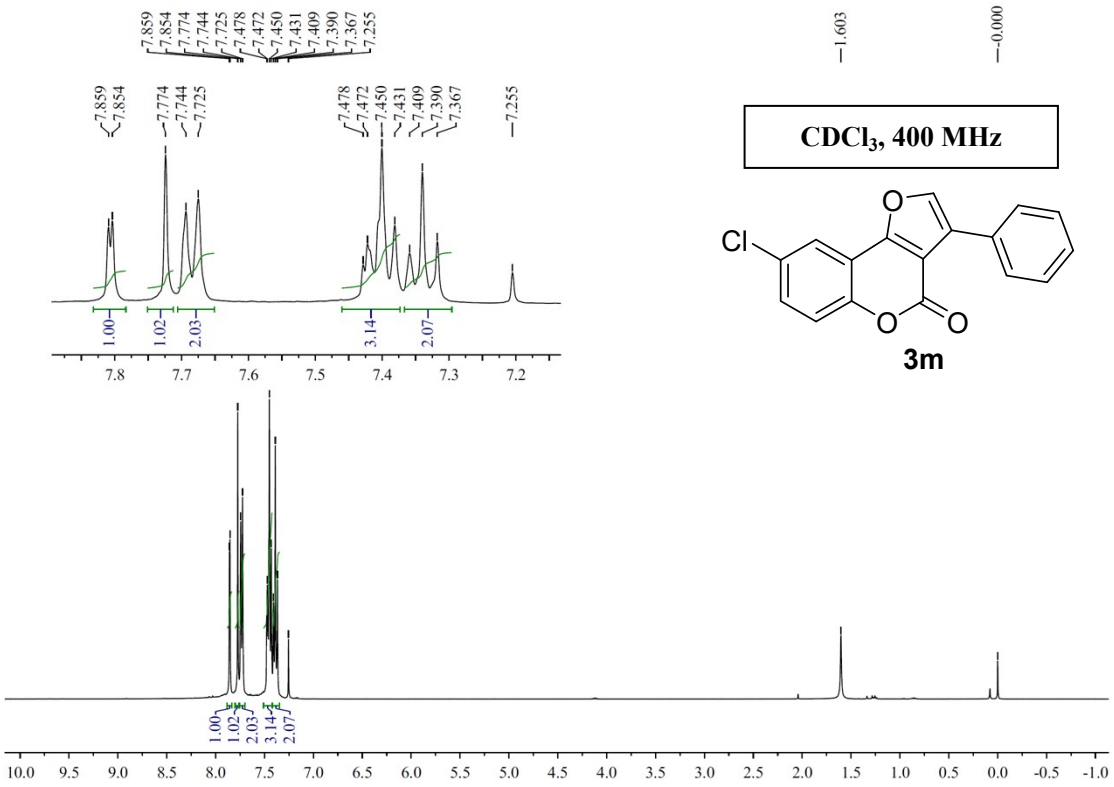


8-Fluoro-3-phenyl-4H-furo[3,2-c]chromen-4-one **(Table 2, compound 3l)**





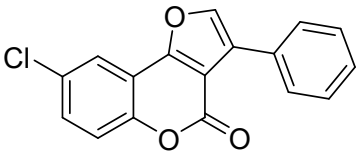
8-Chloro-3-phenyl-4H-furo[3,2-c]chromen-4-one **(Table 2, compound 3m)**



$CDCl_3$, 400 MHz

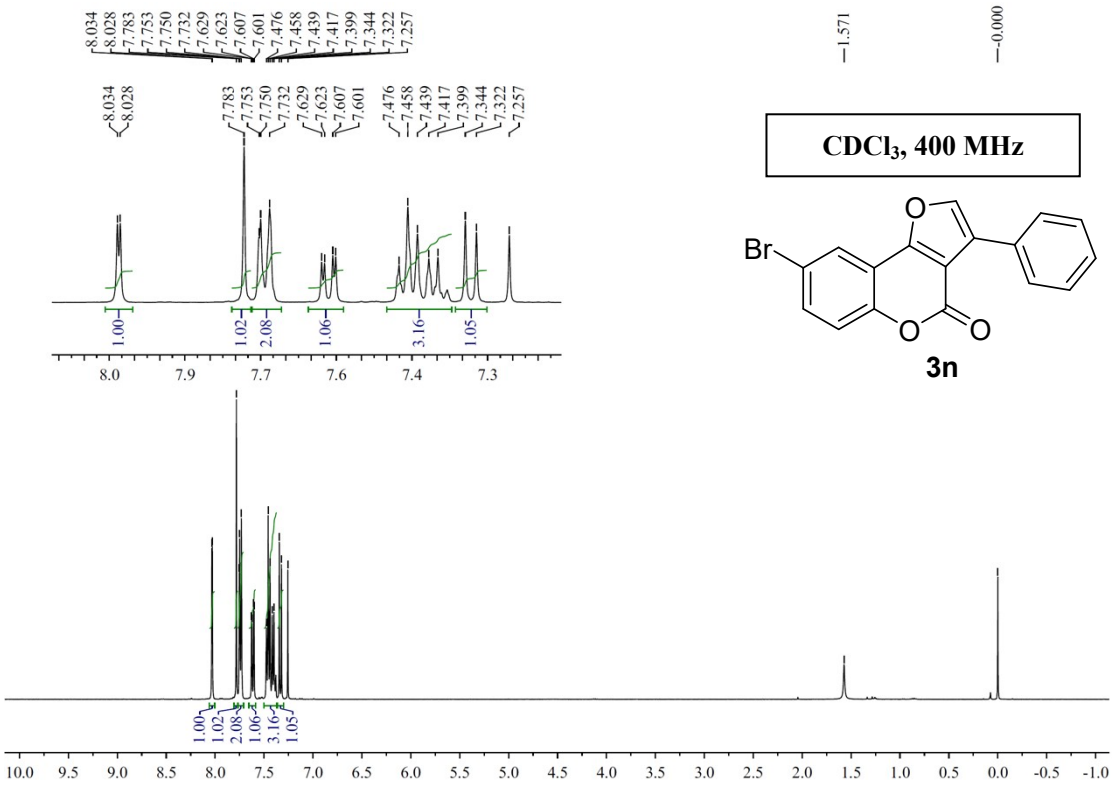
3m

$CDCl_3$, 100 MHz



3m

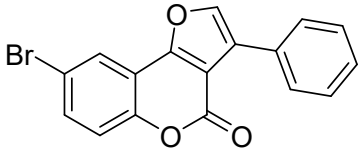
8-Bromo-3-phenyl-4H-furo[3,2-c]chromen-4-one **(Table 2, compound 3n)**



$CDCl_3$, 400 MHz

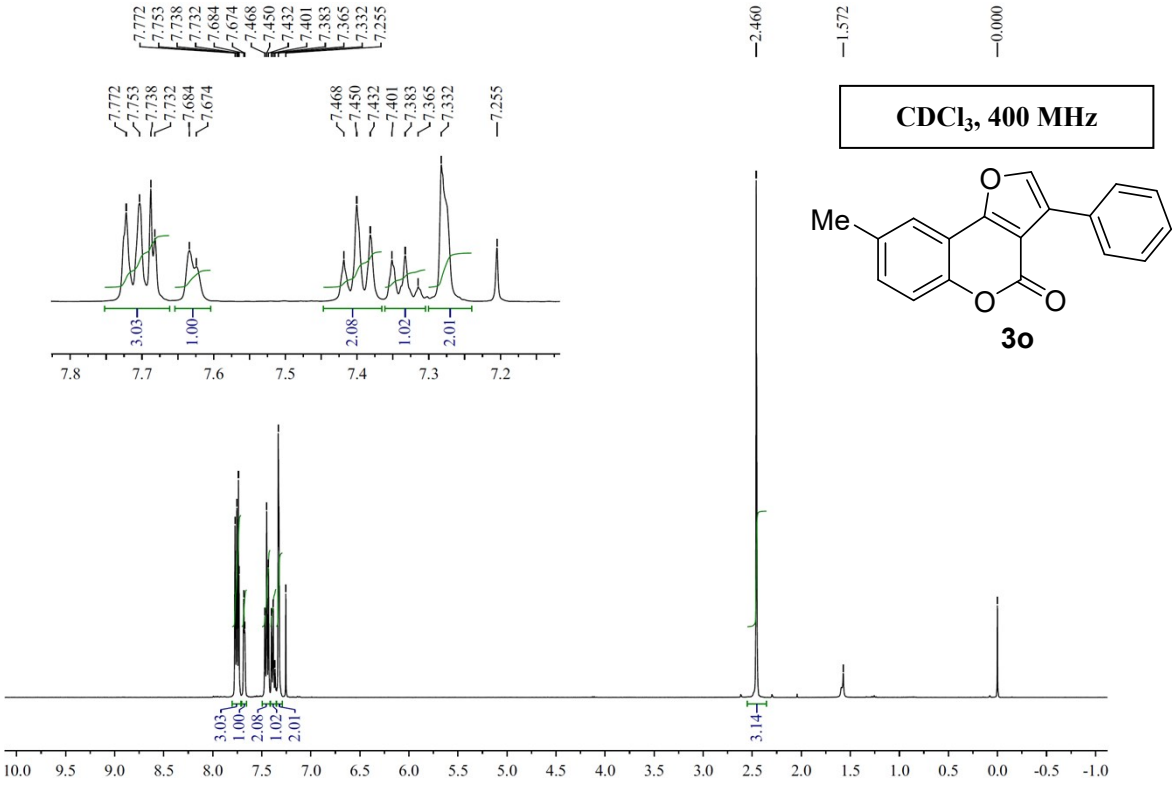
3n

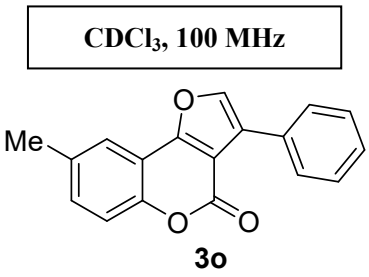
$CDCl_3$, 100 MHz



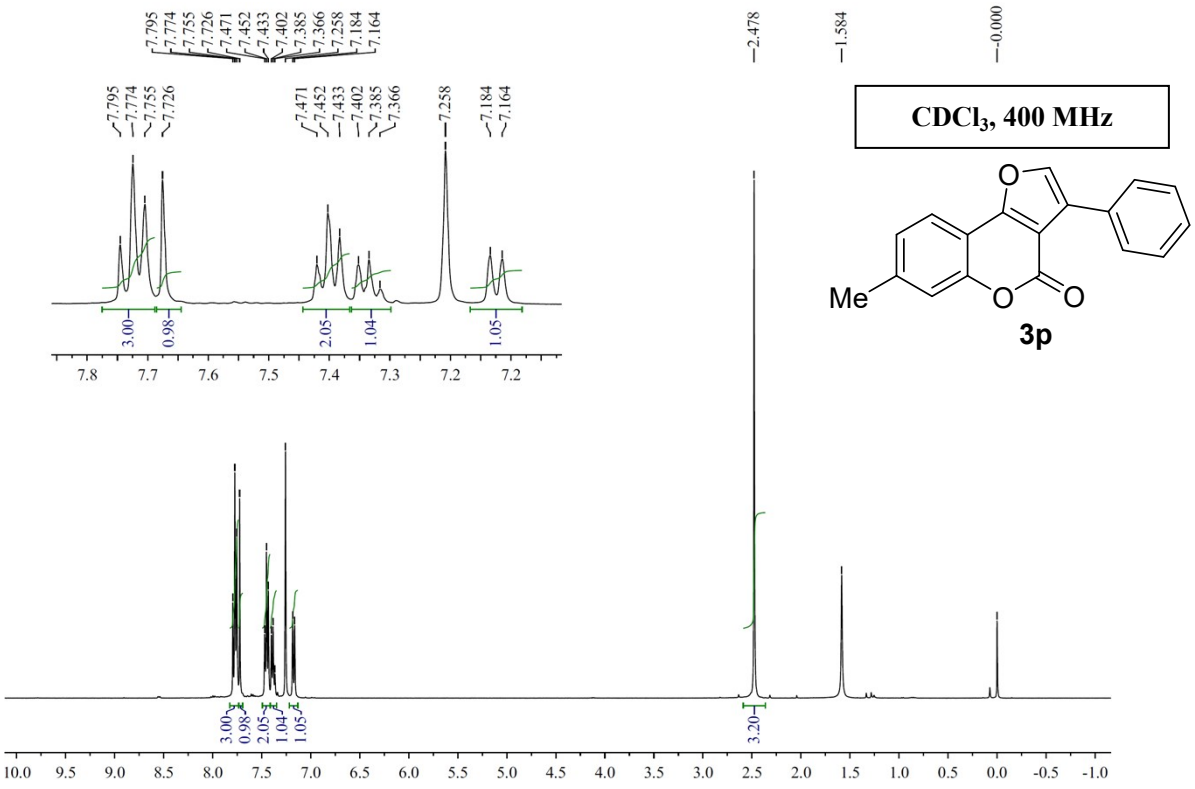
3n

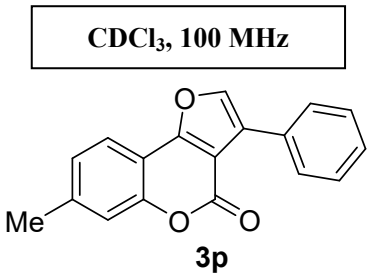
8-Methyl-3-phenyl-4H-furo[3,2-c]chromen-4-one **(Table 2, compound 3o)**



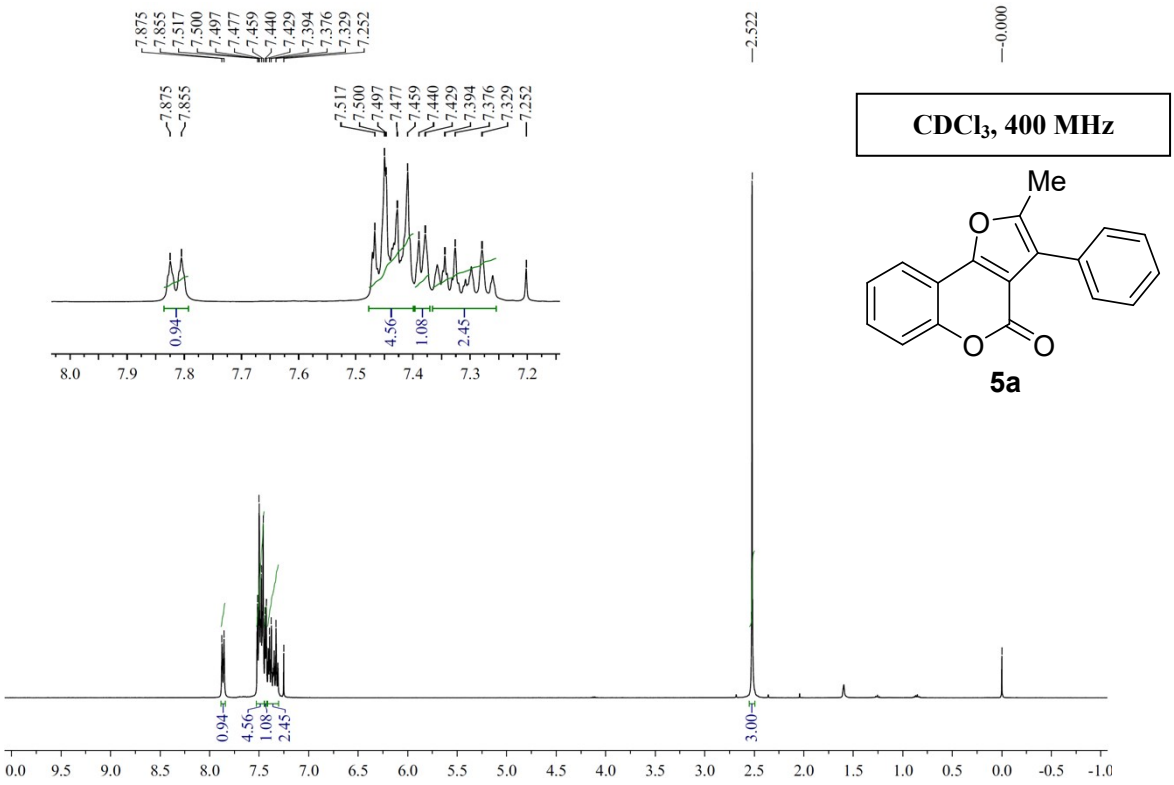


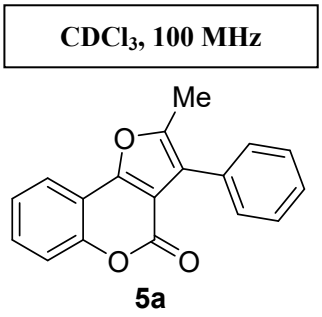
7-Methyl-3-phenyl-4H-furo[3,2-c]chromen-4-one **(Table 2, compound 3p)**





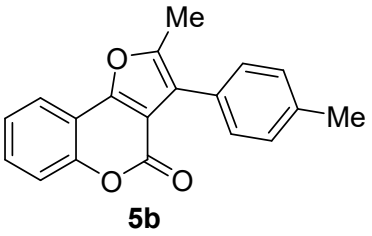
2-Methyl-3-phenyl-4H-furo[3,2-c]chromen-4-one **(Table 3, compound 5a)**



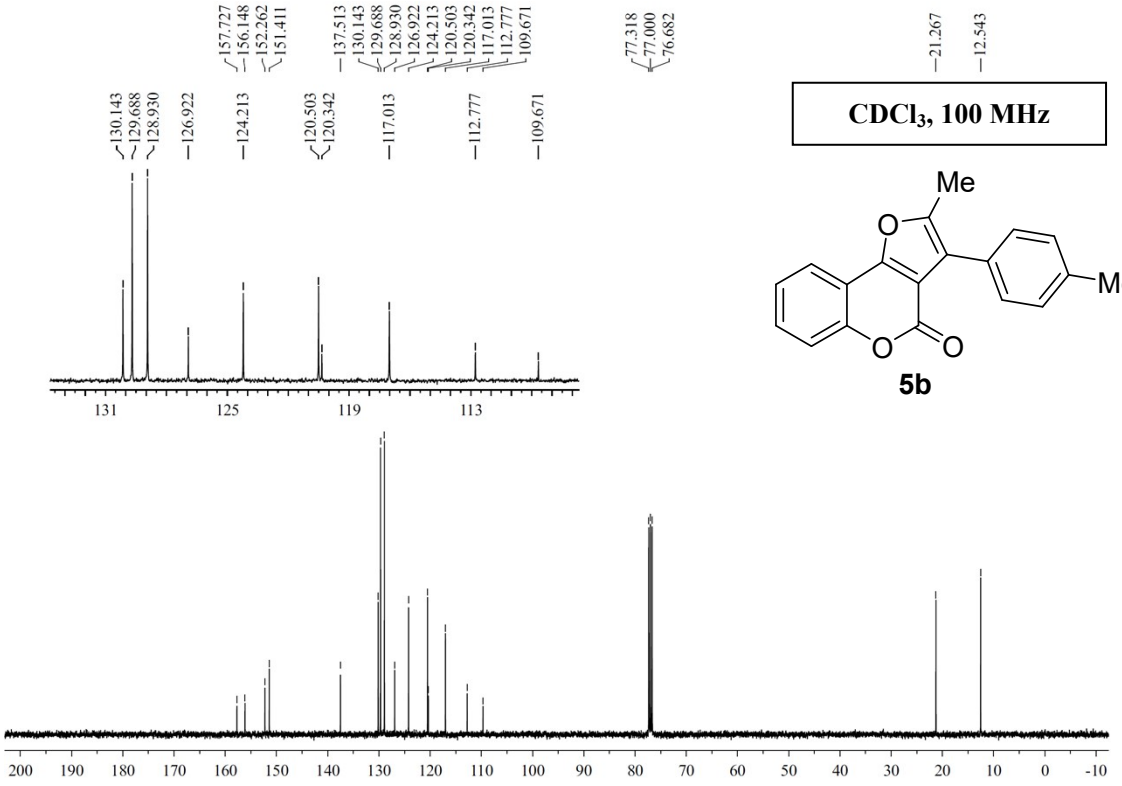


2-Methyl-3-(p-tolyl)-4H-furo[3,2-c]chromen-4-one **(Table 3, compound 5b)**

$CDCl_3$, 400 MHz



5b

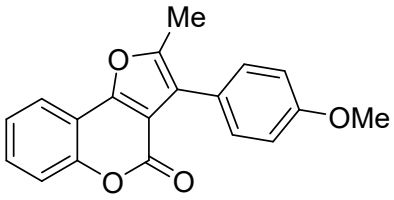


$CDCl_3$, 100 MHz

5b

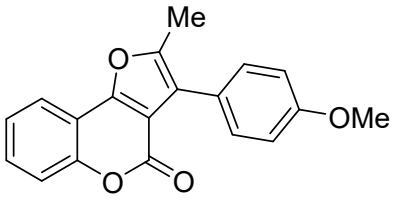
3-(4-Methoxyphenyl)-2-methyl-4H-furo[3,2-c]chromen-4-one **(Table 3, compound 5c)**

$CDCl_3$, 400 MHz



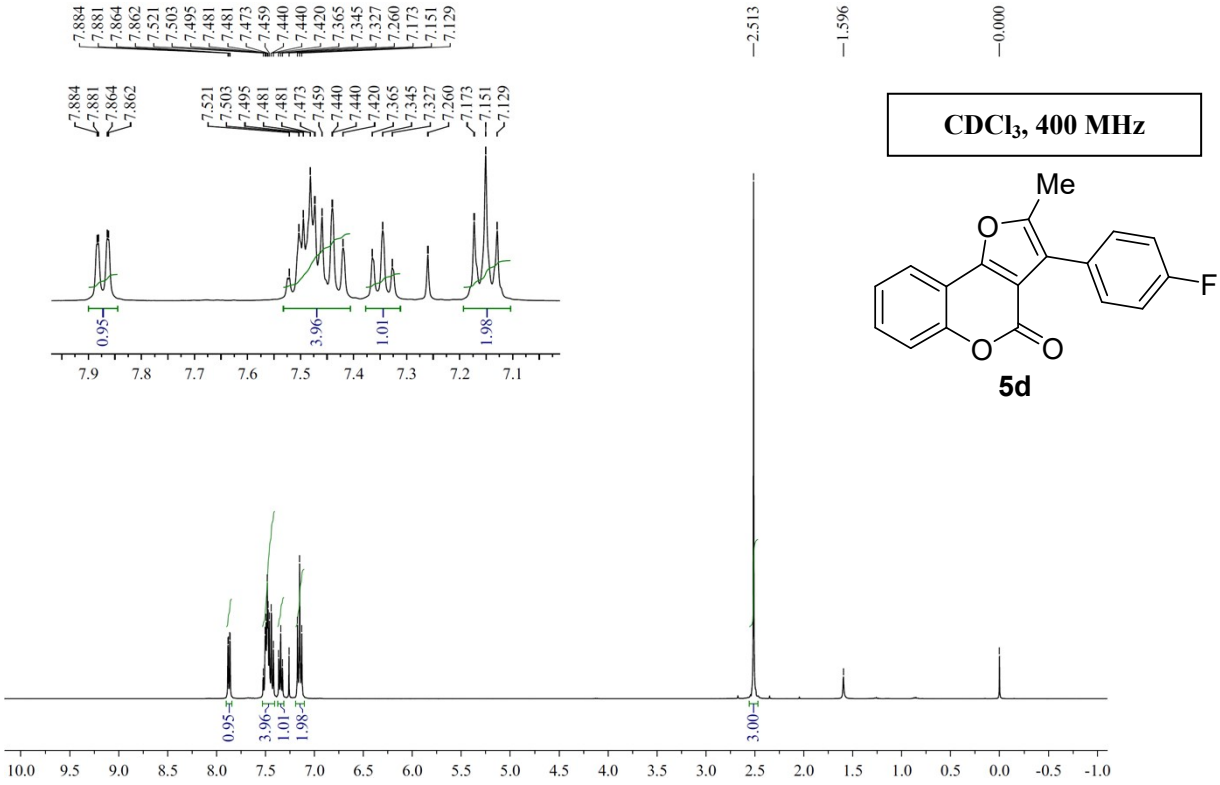
5c

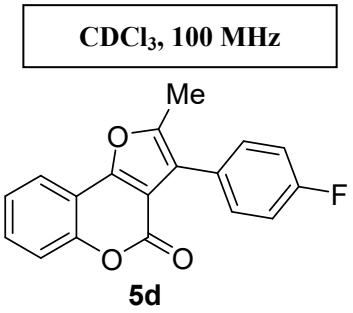
$CDCl_3$, 100 MHz



5c

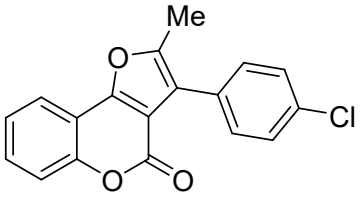
3-(4-Fluorophenyl)-2-methyl-4H-furo[3,2-c]chromen-4-one **(Table 3, compound 5d)**





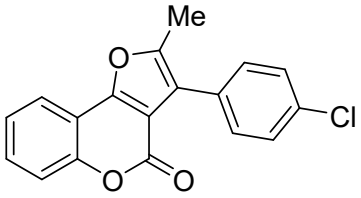
3-(4-Chlorophenyl)-2-methyl-4H-furo[3,2-c]chromen-4-one **(Table 3, compound 5e)**

$CDCl_3$, 400 MHz



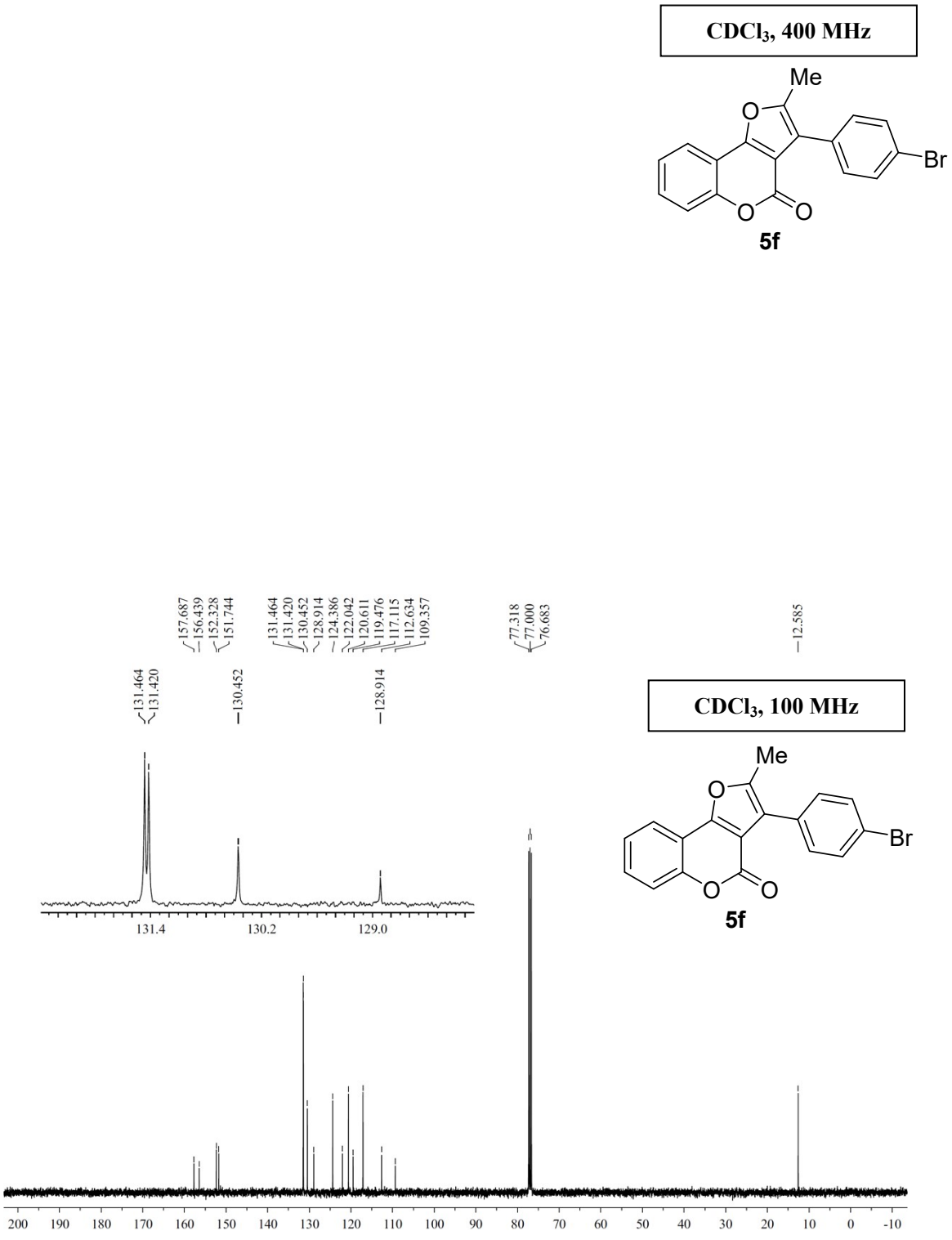
5e

$CDCl_3$, 100 MHz



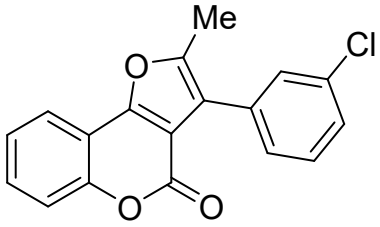
5e

3-(4-Bromophenyl)-2-methyl-4H-furo[3,2-c]chromen-4-one **(Table 3, compound 5f)**

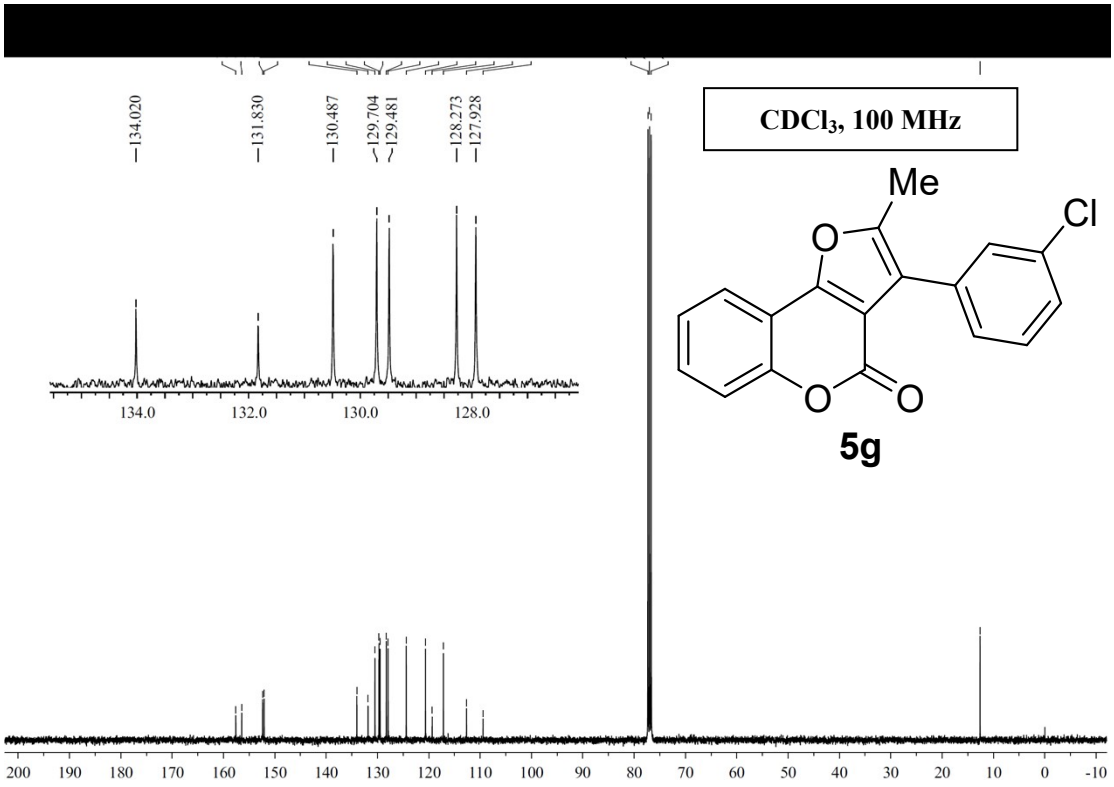


3-(3-Chlorophenyl)-2-methyl-4H-furo[3,2-c]chromen-4-one **(Table 3, compound 5g)**

$CDCl_3$, 400 MHz



5g



$CDCl_3$, 100 MHz

5g