Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Rh(III)-catalyzed C-H activation-cyclization of benzamides and diazo compounds to form isocoumarins and α-pyrones

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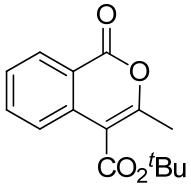
1. General information

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were dehydrated and distilled under nitrogen. Phenyl(pyrrolidin-1-yl)methanone and its dervitives,[1] diazo compounds[2,3] and $[Cp^*RhCl_2]_2$[4] were prepared according to the literature methods. Other chemicals were purchased from Adams-beta, TCI, Alfa-Aesar, J&K and other commercial places, and were used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz Spectrometer at 298 K. Chemical shifts (δ, ppm) in the ^1H NMR spectra were recorded using TMS as internal standard. Chemical shifts in ^{13}C $\{^1H\}$ NMR spectra were internally referenced to $CHCl_3$ (δ = 77.16 ppm). Chemical shift of water in ^1H NMR was found in 1.54-1.56 ppm. HRMS were obtained by EI-TOF or ESI-TOF mass spectrometer.

2. Typical procedure for the synthesis of isocoumarins and *α*-pyrones

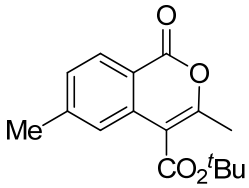
To a mixture of $[Cp^*RhCl_2]_2$ (4.6 mg, 0.0075 mmol, 2.5 mol%) and $AgSbF_6$ (10.3 mg, 0.03 mmol, 10 mol%) in 1, 2-dichloroethane (2 mL) was added phenyl(pyrrolidin-1-yl)methanone **1** (0.6 mmol), diazo compounds **2** (0.3 mmol), HOAc (10.8 mg, 0.18 mmol, 0.6 equiv) and Ac_2O (42.9 mg, 0.42 mmol, 1.4 equiv). The reaction mixture was stirred at 60 ^oC for 12 hours and the progress was monitored using TLC detection. After completion of present reaction, the solvent was evaporated under reduced pressure and the residue passed through flash column chromatography on silica gel to afford the desired products **3**.

3. Analytical data for the products

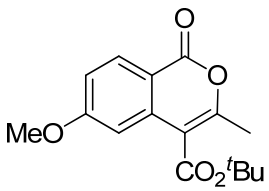


***tert*-Butyl 3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3a).** The compound was prepared from phenyl(pyrrolidin-1-yl)methanone **1a** (105.1 mg, 0.6 mmol) and

tert-butyl 2-diazo-3-oxobutanoate **2a** (55.3 mg, 0.3 mmol) following the typical procedure. The product **3a** was obtained in 84% yield (65 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 83.0-85.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64 (s, 9H), 2.44 (s, 3H), 7.49-7.52 (m, 1H), 7.70-7.72 (m, 2H), 8.28 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.1, 28.3, 83.2, 111.8, 119.7, 123.9, 128.1, 129.8, 135.0, 135.1, 156.4, 161.5, 165.1; HRMS (EI, TOF) calcd for $C_{15}H_{16}O_4^+$ $[M]^+$: 260.1049, found: 260.1050.

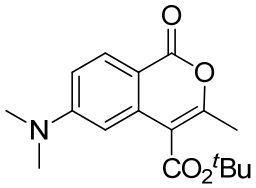


***tert*-Butyl 3,6-dimethyl-1-oxo-1*H*-isochromene-4-carboxylate (3b).** The compound was prepared from pyrrolidin-1-yl(*p*-tolyl)methanone **1b** (113.6 mg, 0.6 mmol) and *tert*-butyl 2-diazo-3-oxobutanoate **2a** (55.3 mg, 0.3 mmol) following the typical procedure. The product **3b** was obtained in 85% yield (70 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 113.0-114.8 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64 (s, 9H), 2.42 (s, 3H), 2.48 (s, 3H), 7.30-7.33 (m, 1H), 7.45 (s, 1H), 8.17 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.1, 22.4, 28.4, 83.1, 111.7, 117.3, 123.9, 129.5, 129.7, 135.0, 146.3, 156.3, 161.6, 165.3; HRMS (ESI, TOF) calcd for $C_{16}H_{19}O_4$, $[M+H]^+$: 275.1283, found: 275.1287.

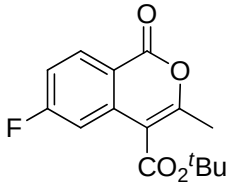


***tert*-Butyl 6-methoxy-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3c).** The compound was prepared from (4-methoxyphenyl)(pyrrolidin-1-yl)methanone **1c** (123.2 mg, 0.6 mmol) and *tert*-butyl 2-diazo-3-oxobutanoate **2a** (55.3 mg, 0.3 mmol) following the typical procedure. The product **3c** was obtained in 93% yield (81 mg) as

white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 144.5-146.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64 (s, 9H), 2.42 (s, 3H), 3.91 (s, 3H), 7.03 (dd, J_1 = 2.4 Hz, J_2 = 8.8 Hz, 1H), 7.16 (d, J = 2.4 Hz, 1H), 8.20 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.3, 28.4, 55.7, 83.0, 106.7, 111.5, 112.7, 116.2, 132.0, 137.2, 157.4, 161.2, 164.9, 165.2; HRMS (ESI, TOF) calcd for $C_{16}H_{19}O_5$, $[M+H]^+$: 291.1232, found: 291.1233.

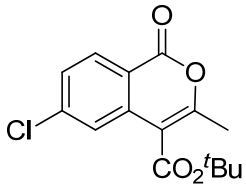


***t*ert-Butyl 6-(dimethylamino)-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3d).** The compound was prepared from (4-(dimethylamino)phenyl)(pyrrolidin-1-yl) methanone **1d** (131.0 mg, 0.6 mmol) and *tert*-butyl 2-diazo-3-oxobutanoate **2a** (55.3 mg, 0.3 mmol) following the typical procedure. The product **3d** was obtained in 83% yield (75 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 145.4-148.2 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63 (s, 9H), 2.37 (s, 3H), 3.10 (s, 6H), 6.73 (d, J = 2.5 Hz, 1H), 6.80 (dd, J_1 = 2.5 Hz, J_2 = 9.0 Hz, 1H), 8.08 (d, J = 9.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.1, 28.4, 40.2, 82.6, 103.5, 107.5, 111.9, 112.6, 131.5, 136.6, 154.4, 156.2, 161.9, 165.9; HRMS (ESI, TOF) calcd for $C_{17}H_{22}NO_4$, $[M+H]^+$: 304.1549, found: 304.1546.

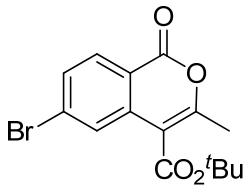


***tert*-Butyl 6-fluoro-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3e).** The compound was prepared from (4-fluorophenyl)(pyrrolidin-1-yl)methanone **1e** (115.9 mg, 0.6 mmol) and *tert*-butyl 2-diazo-3-oxobutanoate **2a** (55.3 mg, 0.3 mmol) following the typical procedure. The product **3e** was obtained in 83% yield (69 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1

v/v). Mp: 137.3-139.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64 (s, 9H), 2.46 (s, 3H), 7.19 (td, J_1 = 2.4 Hz, J_2 = 8.4 Hz, 1H), 7.48 (dd, J_1 = 2.4 Hz, J_2 = 10.4 Hz, 1H), 8.30 (dd, J_1 = 5.8 Hz, J_2 = 8.8 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.5, 28.3, 83.5, 110.5 (d, J = 25.0 Hz), 111.0 (d, J = 2.8 Hz), 116.1 (d, J = 23.4 Hz), 133.0 (d, J = 10.4 Hz), 137.8 (d, J = 11.1 Hz), 158.7, 160.5, 164.6, 165.7, 168.2; HRMS (ESI, TOF) calcd for $C_{15}H_{16}O_4F$, $[M+H]^+$: 279.1033, found: 279.1031.

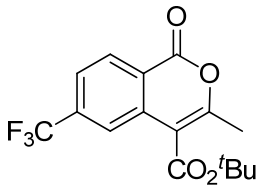


***tert*-Butyl 6-chloro-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3f).** The compound was prepared from (4-chlorophenyl)(pyrrolidin-1-yl)methanone **1f** (125.8 mg, 0.6 mmol) and *tert*-butyl 2-diazo-3-oxobutanoate **2a** (55.3 mg, 0.3 mmol) following the typical procedure. The product **3f** was obtained in 90% yield (79 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 115.2-117.3 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64 (s, 9H), 2.46 (s, 3H), 7.46 (dd, J_1 = 2.0 Hz, J_2 = 8.5 Hz, 1H), 7.79 (d, J = 1.9 Hz 1H), 8.21 (d, J = 8.5 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.5, 28.4, 83.5, 110.7, 118.0, 124.1, 128.6, 131.3, 136.4, 142.0, 158.5, 160.6, 164.5; HRMS (ESI, TOF) calcd for $C_{15}H_{16}O_4Cl$, $[M+H]^+$: 295.0737, found: 295.0742.

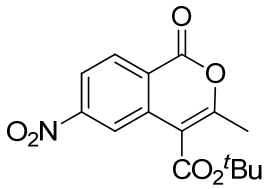


***tert*-Butyl 6-bromo-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3g).** The compound was prepared from (4-bromophenyl)(pyrrolidin-1-yl)methanone **1g** (152.5 mg, 0.6 mmol) and *tert*-butyl 2-diazo-3-oxobutanoate **2a** (55.3 mg, 0.3 mmol) following the typical procedure. The product **3g** was obtained in 78% yield (79 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1

v/v). Mp: 114.2-115.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64 (s, 9H), 2.46 (s, 3H), 7.62 (dd, J_1 = 1.8 Hz, J_2 = 8.5 Hz, 1H), 7.97 (d, J = 1.8 Hz 1H), 8.12 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.5, 28.4, 83.6, 110.6, 118.3, 127.2, 130.9, 131.2, 131.5, 136.4, 158.5, 160.8, 164.5; HRMS (EI, TOF) calcd for $C_{15}H_{15}O_4Br^+$ $[M]^+$: 340.0133, found: 340.0136.

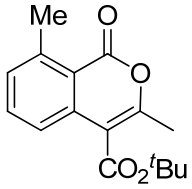


***tert*-Butyl 3-methyl-1-oxo-6-(trifluoromethyl)-1*H*-isochromene-4-carboxylate (3h).** The compound was prepared from pyrrolidin-1-yl(4-(trifluoromethyl)phenyl)-methanone **1h** (145.9 mg, 0.6 mmol) and *tert*-butyl 2-diazo-3-oxobutanoate **2a** (55.3 mg, 0.3 mmol) following the typical procedure. The product **3h** was obtained in 64% yield (63 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 111.4-113.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 (s, 9H), 2.50 (s, 3H), 7.72 (d, J = 8.3 Hz, 1H), 8.12 (s, 1H), 8.40 (d, J = 8.3 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.5, 28.4, 83.8, 111.1, 121.7 (q, J = 4.1 Hz), 122.1, 123.4 (q, J = 273.1 Hz), 124.4 (q, J = 3.5 Hz), 130.7, 135.5, 136.4 (q, J = 32.8 Hz), 159.1, 160.3, 164.4; HRMS (ESI, TOF) calcd for $C_{16}H_{16}O_4F_3$, $[M+H]^+$: 329.1001, found: 329.1006.

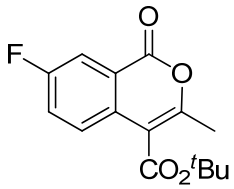


***tert*-Butyl 3-methyl-6-nitro-1-oxo-1*H*-isochromene-4-carboxylate (3i).** The compound was prepared from (4-nitrophenyl)(pyrrolidin-1-yl)methanone **1i** (132.1 mg, 0.6 mmol) and *tert*-butyl 2-diazo-3-oxobutanoate **2a** (55.3 mg, 0.3 mmol) following the typical procedure. The product **3i** was obtained in 63% yield (58 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 149.9-153.3°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.68 (s, 9H), 2.53 (s, 3H),

8.27 (dd, J_1 = 2.1 Hz, J_2 = 8.7 Hz, 1H), 8.77 (d, J = 2.1 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.7, 28.4, 84.2, 110.9, 120.1, 122.0, 123.6, 131.6, 136.4, 151.8, 159.7, 160.3, 164.0; HRMS (EI, TOF) calcd for $C_{15}H_{15}NO_6^+$ $[M]^+$: 305.0899, found: 305.0892.

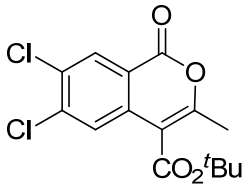


***tert*-Butyl 3,8-dimethyl-1-oxo-1*H*-isochromene-4-carboxylate (3j).** The compound was prepared from pyrrolidin-1-yl(*o*-tolyl)methanone **1j** (113.6 mg, 0.6 mmol) and *tert*-butyl 2-diazo-3-oxobutanoate **2a** (55.3 mg, 0.3 mmol) following the typical procedure. The product **3j** was obtained in 80% yield (66 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 105.0-107.1 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63 (s, 9H), 2.42 (s, 3H), 2.46 (s, 3H), 7.55 (dd, J_1 = 1.6 Hz, J_2 = 8.3 Hz, 1H), 7.62 (d, J = 8.3 Hz 1H), 8.09 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.0, 21.3, 28.4, 83.1, 111.7, 119.6, 123.9, 129.5, 132.5, 136.4, 138.4, 155.6, 161.8, 165.3; HRMS (ESI, TOF) calcd for $C_{16}H_{19}O_4$, $[M+H]^+$: 275.1283, found: 275.1287.

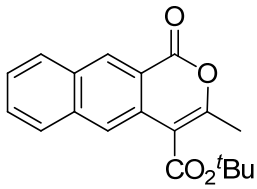


***tert*-Butyl 7-fluoro-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3k).** The compound was prepared from (3-fluorophenyl)(pyrrolidin-1-yl)methanone **1k** (115.9 mg, 0.6 mmol) and *tert*-butyl 2-diazo-3-oxobutanoate **2a** (55.3 mg, 0.3 mmol) following the typical procedure. The product **3k** was obtained in 68% yield (57 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 87.2-89.0 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60 (s, 9H), 2.34 (s, 3H), 7.41-7.50 (m, 2H), 8.09-8.12 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 17.8, 27.9,

83.3, 108.6, 121.6 (d, J = 21.2 Hz), 121.6 (d, J = 3.8 Hz), 123.7 (d, J = 14.0 Hz), 125.9 (d, J = 3.7 Hz), 129.0 (d, J = 8.2 Hz), 154.0, 155.1, 157.6, 160.4 (J = 3.5 Hz), 165.4; HRMS (ESI, TOF) calcd for $C_{15}H_{16}O_4F$, $[M+H]^+$: 279.1033, found: 279.1034.

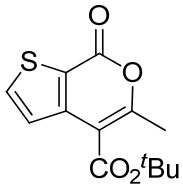


***tert*-Butyl 6,7-dichloro-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3l).** The compound was prepared from (3,4-dichlorophenyl)(pyrrolidin-1-yl)methanone **1l** (146.5 mg, 0.6 mmol) and *tert*-butyl 2-diazo-3-oxobutanoate **2a** (55.3 mg, 0.3 mmol) following the typical procedure. The product **3l** was obtained in 22% yield (22 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 10:1 v/v). Mp: 134.9-137.8 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 1.64 (s, 9H), 2.47 (s, 3H), 7.97 (s, 1H), 8.33 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.7, 28.4, 83.8, 110.1, 119.2, 126.4, 131.1, 132.7, 134.4, 140.4, 159.1, 159.7, 164.2; HRMS (ESI, TOF) calcd for $C_{15}H_{15}O_4Cl_2$, $[M+H]^+$: 329.0347, found: 329.0347.

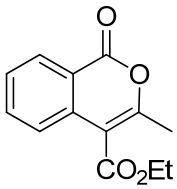


***tert*-Butyl 3-methyl-1-oxo-1*H*-benzo[*g*]isochromene-4-carboxylate (3m).** The compound was prepared from naphthalen-2-yl(pyrrolidin-1-yl)methanone **1m** (135.2 mg, 0.6 mmol) and *tert*-butyl 2-diazo-3-oxobutanoate **2a** (55.3 mg, 0.3 mmol) following the typical procedure. The product **3m** was obtained in 78% yield (73 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 140.3-142.7 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 1.69 (s, 9H), 2.46 (s, 3H), 7.54-7.58 (m, 1H), 7.63-7.67 (m, 1H), 7.93 (d, J = 8.3 Hz, 1H), 8.01 (d, J = 8.2 Hz, 1H), 8.14 (s, 1H), 8.92 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.1, 28.4, 83.1, 111.6, 118.0, 122.8, 127.0, 128.4, 129.5, 129.5, 129.6, 132.0, 132.1, 136.6, 154.8,

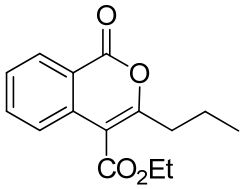
161.7, 165.4; HRMS (EI, TOF) calcd for $C_{19}H_{18}O_4^+$ $[M]^+$: 310.1205, found: 310.1206.



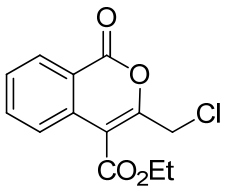
***tert*-Butyl 5-methyl-7-oxo-7*H*-thieno[2,3-c]pyran-4-carboxylate (3n).** The compound was prepared from pyrrolidin-1-yl(thiophen-2-yl)methanone **1n** (108.8 mg, 0.6 mmol) and *tert*-butyl 2-diazo-3-oxobutanoate **2a** (55.3 mg, 0.3 mmol) following the typical procedure. The product **3n** was obtained in 64% yield (51 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 107.0-108.8 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 1.63 (s, 9H), 2.42 (s, 3H), 7.70 (d, J = 5.2 Hz, 1H), 7.83 (d, J = 5.2 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 20.0, 28.4, 83.0, 109.7, 122.3, 126.1, 136.6, 145.7, 157.3, 163.4, 164.1; HRMS (ESI, TOF) calcd for $C_{13}H_{15}O_4S$, $[M+H]^+$: 267.0691, found: 267.0691.



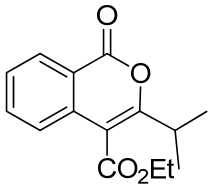
Ethyl 3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3o). The compound was prepared from phenyl(pyrrolidin-1-yl)methanone **1a** (105.1 mg, 0.6 mmol) and ethyl 2-diazo-3-oxobutanoate **2b** (46.8 mg, 0.3 mmol) following the typical procedure. The product **3o** was obtained in 75% yield (52 mg) as colorless oil after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 1.45 (d, J = 7.1 Hz, 3H), 2.46 (s, 3H), 4.46 (d, J = 7.1 Hz, 2H), 7.50-7.54 (m, 1H), 7.72-7.78 (m, 2H), 8.28-8.30 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.3, 19.4, 61.8, 110.4, 119.6, 124.2, 128.3, 129.8, 134.7, 135.2, 157.8, 161.3, 165.9; HRMS (ESI, TOF) calcd for $C_{13}H_{13}O_4$, $[M+H]^+$: 233.0814, found: 233.0813.



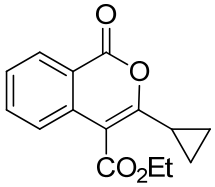
Ethyl 1-oxo-3-propyl-1*H*-isochromene-4-carboxylate (3p). The compound was prepared from phenyl(pyrrolidin-1-yl)methanone **1a** (105.1 mg, 0.6 mmol) and ethyl 2-diazo-3-oxohexanoate **2c** (55.3 mg, 0.3 mmol) following the typical procedure. The product **3p** was obtained in 81% yield (63 mg) as colorless oil after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00 (t, *J* = 7.4 Hz, 3H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.76-1.85 (m, 2H), 2.66-2.70 (m, 2H), 4.45 (d, *J* = 7.2 Hz, 2H), 7.50-7.54 (m, 1H), 7.68-7.76 (m, 2H), 8.21-8.31 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.8, 14.3, 21.2, 34.6, 61.8, 110.5, 119.7, 124.2, 128.3, 129.8, 134.7, 135.2, 160.4, 161.5, 166.0; HRMS (EI, TOF) calcd for $C_{15}H_{16}O_4^+$ $[M]^+$: 260.1049, found: 260.1050.



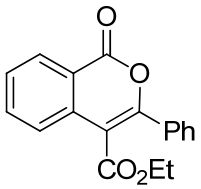
Ethyl 3-(chloromethyl)-1-oxo-1*H*-isochromene-4-carboxylate (3q). The compound was prepared from phenyl(pyrrolidin-1-yl)methanone **1a** (105.1 mg, 0.6 mmol) and ethyl 4-chloro-2-diazo-3-oxobutanoate **2d** (57.2 mg, 0.3 mmol) following the typical procedure. The product **3q** was obtained in 34% yield (21 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 55.6-58.1 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ1.47 (t, *J* = 7.2 Hz, 3H), 4.51 (q, *J* = 7.2 Hz, 2H), 4.59 (s, 2H), 7.59-7.63 (m, 1H), 7.77-7.86 (m, 2H), 8.33-8.35 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.3, 40.3, 62.6, 112.6, 120.6, 125.3, 129.7, 130.1, 133.7, 135.4, 154.0, 160.3, 164.6; HRMS (ESI, TOF) calcd for $C_{13}H_{12}O_4Cl$, $[M+H]^+$: 267.0424, found: 267.0423.



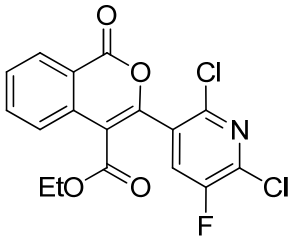
Ethyl 3-isopropyl-1-oxo-1*H*-isochromene-4-carboxylate (3r). The compound was prepared from phenyl(pyrrolidin-1-yl)methanone **1a** (105.1 mg, 0.6 mmol) and ethyl 2-diazo-4-methyl-3-oxopentanoate **2e** (55.3 mg, 0.3 mmol) following the typical procedure. The product **3r** was obtained in 83% yield (65 mg) as colorless oil after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (s, 3H), 1.33 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H), 3.09-3.19 (m, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 7.49-7.53 (m, 1H), 7.59-7.61 (m, 1H), 7.71-7.75 (m, 1H), 8.29-8.31 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.3, 20.2, 31.6, 61.9, 109.2, 119.8, 124.0, 128.2, 129.8, 134.8, 135.1, 161.5, 163.2, 166.1; HRMS (ESI, TOF) calcd for $C_{15}H_{17}O_4$, $[M+H]^+$: 261.1127, found: 261.1122.



Ethyl 3-cyclopropyl-1-oxo-1*H*-isochromene-4-carboxylate (3s). The compound was prepared from phenyl(pyrrolidin-1-yl)methanone **1a** (105.1 mg, 0.6 mmol) and ethyl 3-cyclopropyl-2-diazo-3-oxopropanoate **2f** (54.7 mg, 0.3 mmol) following the typical procedure. The product **3s** was obtained in 74% yield (57 mg) as colorless oil after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00-1.05 (m, 2H), 1.26-1.30 (m, 2H), 1.44 (t, *J* = 7.2 Hz, 3H), 2.26-2.33 (m, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 7.44-7.48 (m, 1H), 7.67-7.74 (m, 2H), 8.23-8.26 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 8.6, 12.6, 14.4, 61.8, 109.5, 119.2, 123.7, 127.7, 129.7, 135.1, 135.2, 160.4, 160.9, 166.3; HRMS (ESI, TOF) calcd for $C_{15}H_{15}O_4$, $[M+H]^+$: 259.0970, found: 259.0978.

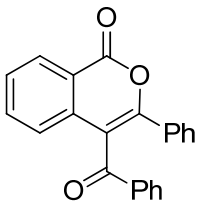


Ethyl 1-oxo-3-phenyl-1*H*-isochromene-4-carboxylate (3t). The compound was prepared from phenyl(pyrrolidin-1-yl)methanone **1a** (105.1 mg, 0.6 mmol) and ethyl 2-diazo-3-oxo-3-phenylpropanoate **2g** (65.5 mg, 0.3 mmol) following the typical procedure. The product **3t** was obtained in 85% yield (75 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 85.0-88.2 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (t, *J* = 7.1 Hz, 3H), 4.20 (q, *J* = 7.2 Hz, 3H), 7.43-7.49 (m, 3H), 7.56-7.61 (m, 1H), 7.64-7.66 (m, 2H), 7.74-7.82 (m, 2H), 8.36-8.38 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.7, 62.0, 111.1, 119.9, 124.3, 128.3, 128.6, 128.9, 130.0, 130.7, 132.7, 134.8, 135.4, 155.5, 161.2, 166.4; HRMS (ESI, TOF) calcd for $C_{18}H_{15}O_4$, $[M+H]^+$: 295.0970, found: 295.0966.

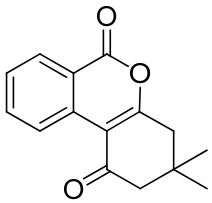


Ethyl 3-(2,6-dichloro-5-fluoropyridin-3-yl)-1-oxo-1*H*-isochromene-4-carboxylate (3u). The compound was prepared from phenyl(pyrrolidin-1-yl)methanone **1a** (105.1 mg, 0.6 mmol) and ethyl 2-diazo-3-(2,6-dichloro-5-fluoropyridin-3-yl)-3-oxopropanoate **2h** (92.0 mg, 0.3 mmol) following the typical procedure. The product **3u** was obtained in 94% yield (108 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 95.8-97.6 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08 (t, *J* = 7.1 Hz, 3H), 4.22 (q, *J* = 7.2 Hz, 3H), 7.67-7.71 (m, 2H), 7.85-7.89 (m, 1H), 8.14-8.36 (m, 1H), 8.39-8.41 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.8, 62.2, 113.5, 120.4, 125.7, 127.9 (d, *J* = 21.8 Hz), 129.7 (d, *J* = 3.1 Hz), 130.1 (d, *J* = 7.4 Hz), 133.4, 135.7, 139.1 (d, *J* = 21.1 Hz), 143.2 (d, *J* = 3.6 Hz), 151.2, 152.4, 155.0, 160.0, 163.9; HRMS (ESI, TOF) calcd for $C_{17}H_{11}O_4NFCl_2$,

$[M+H]^+$: 382.0049, found: 382.0047.

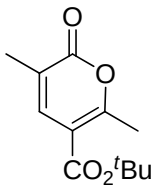


4-Benzoyl-3-phenyl-1*H*-isochromen-1-one (3v). The compound was prepared from phenyl(pyrrolidin-1-yl)methanone **1a** (105.1 mg, 0.6 mmol) and 2-diazo-1,3-diphenylpropane-1,3-dione **2i** (49.9 mg, 0.3 mmol) following the typical procedure. The product **3v** was obtained in 38% yield (37 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 136.2-139.1 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.23-7.29 (m, 3H), 7.33 (t, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 1H), 7.46-7.50 (m, 1H), 7.56-7.59 (m, 3H), 7.67-7.71 (m, 1H), 7.84-7.86 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 115.7, 120.2, 124.6, 128.6, 128.7, 128.9, 129.0, 129.7, 130.1, 130.6, 132.0, 134.3, 135.4, 136.0, 137.0, 153.0, 161.6, 194.9; HRMS (EI, TOF) calcd for $C_{22}H_{14}O_3^+$ $[M]^+$: 326.0943, found: 326.0944.

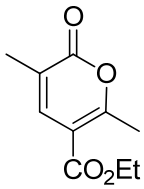


3,3-Dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6(2*H*)-dione (3w). The compound was prepared from phenyl(pyrrolidin-1-yl)methanone **1a** (105.1 mg, 0.6 mmol) and 2-diazo-5,5-dimethylcyclohexane-1,3-dione **2j** (49.9 mg, 0.3 mmol) following the typical procedure. The product **3w** was obtained in 93% yield (80 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 143.2-144.9 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 1.18 (s, 6H), 2.53 (s, 2H), 2.81 (s, 2H), 7.52-7.56 (m, 1H), 7.78-7.82 (m, 1H), 8.29 (dd, J_1 = 1.5 Hz, J_2 = 8.0 Hz, 1H), 9.05 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 28.2, 32.1, 42.6, 52.9, 110.7, 119.9, 125.9, 128.5, 129.7, 133.9, 135.7, 160.8, 168.1, 197.0;

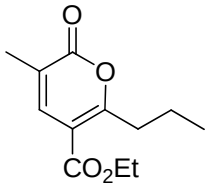
HRMS (ESI, TOF) calcd for $C_{15}H_{15}O_3$, $[M+H]^+$: 243.1021, found: 243.1026.



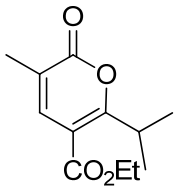
***tert*-Butyl-3,6-dimethyl-2-oxo-2*H*-pyran-5-carboxylate (4a).** The compound was prepared from 2-methyl-1-(pyrrolidin-1-yl)prop-2-en-1-one **1o** (83.5 mg, 0.6 mmol) and *tert*-butyl 2-diazo-3-oxobutanoate **2a** (55.3 mg, 0.3 mmol) following the typical procedure. The product **4a** was obtained in 76% yield (51 mg) as colorless oil after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.56 (s, 9H), 2.10 (s, 3H), 2.60 (s, 3H), 7.55 (d, J = 0.9 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.3, 20.1, 28.3, 82.4, 110.6, 121.6, 140.3, 162.7, 163.5, 167.2; HRMS (ESI, TOF) calcd for $C_{12}H_{16}O_4Na$, $[M+Na]^+$: 247.0946, found: 247.0949.



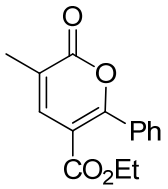
Ethyl-3,6-dimethyl-2-oxo-2*H*-pyran-5-carboxylate (4b). The compound was prepared from 2-methyl-1-(pyrrolidin-1-yl)prop-2-en-1-one **1o** (83.5 mg, 0.6 mmol) and ethyl 2-diazo-3-oxobutanoate **2b** (46.8 mg, 0.3 mmol) following the typical procedure. The product **4b** was obtained in 68% yield (40 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 45.7-47.8 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (t, J = 7.2 Hz, 3H), 2.11 (s, 3H), 2.63 (s, 3H), 4.32 (q, J = 7.1 Hz, 2H), 7.62 (d, J = 1.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.4, 16.4, 20.1, 61.4, 109.3, 121.8, 139.8, 162.5, 164.4, 168.0; HRMS (EI, TOF) calcd for $C_{10}H_{12}O_4$, $[M]^+$: 196.0736, found:196.0737.



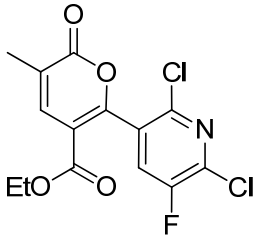
Ethyl-3-methyl-6-propyl-2-oxo-2*H*-pyran-5-carboxylate (4c). The compound was prepared from 2-methyl-1-(pyrrolidin-1-yl)prop-2-en-1-one **1o** (83.5 mg, 0.6 mmol) and ethyl ethyl 2-diazo-3-oxohexanoate **2c** (55.3 mg, 0.3 mmol) following the typical procedure. The product **4c** was obtained in 82% yield (55 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 30.2-31.9 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (t, *J* = 7.1 Hz, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.69-1.79 (m, 2H), 2.10 (s, 3H), 2.94-2.98 (m, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 7.61 (d, *J* = 1.1 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.9, 14.3, 16.4, 21.4, 34.7, 61.4, 109.1, 121.9, 139.9, 162.6, 164.3, 171.5; HRMS (EI, TOF) calcd for $C_{12}H_{16}O_4$, $[M]^+$: 224.1049, found: 224.1048.



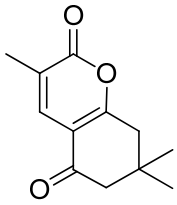
Ethyl-6-isopropyl-3-methyl-2-oxo-2*H*-pyran-5-carboxylate (4d). The compound was prepared from 2-methyl-1-(pyrrolidin-1-yl)prop-2-en-1-one **1o** (83.5 mg, 0.6 mmol) and ethyl 2-diazo-4-methyl-3-oxopentanoate **2e** (55.3 mg, 0.3 mmol) following the typical procedure. The product **4d** was obtained in 73% yield (49 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 71.6-73.8 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (s, 3H), 1.27 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 2.10 (d, *J* = 1.2 Hz, 3H), 3.92-4.02 (m, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 7.59 (d, *J* = 1.2 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 14.3, 16.4, 20.1, 30.4, 61.4, 107.8, 121.7, 140.1, 162.5, 164.4, 175.0; HRMS (EI, TOF) calcd for $C_{12}H_{16}O_4$, $[M]^+$: 224.1049, found: 224.1052.



Ethyl-3-methyl-2-oxo-6-phenyl-2*H*-pyran-5-carboxylate (4e). The compound was prepared from 2-methyl-1-(pyrrolidin-1-yl)prop-2-en-1-one **1o** (83.5 mg, 0.6 mmol) and ethyl 2-diazo-3-oxo-3-phenylpropanoate **2g** (65.5 mg, 0.3 mmol) following the typical procedure. The product **4e** was obtained in 61% yield (47 mg) as colorless oil after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08 (t, *J* = 7.2 Hz, 3H), 2.18 (d, *J* = 1.2 Hz, 3H), 4.14 (q, *J* = 7.1 Hz, 2H), 7.40-7.53 (m, 5H), 7.64 (d, *J* = 1.2 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.8, 16.6, 61.6, 110.0, 123.3, 128.1, 129.1, 130.9, 132.4, 140.1, 162.2, 164.4, 165.1; HRMS (EI, TOF) calcd for $C_{15}H_{14}O_4$, $[M]^+$: 258.0892, found: 258.0893.



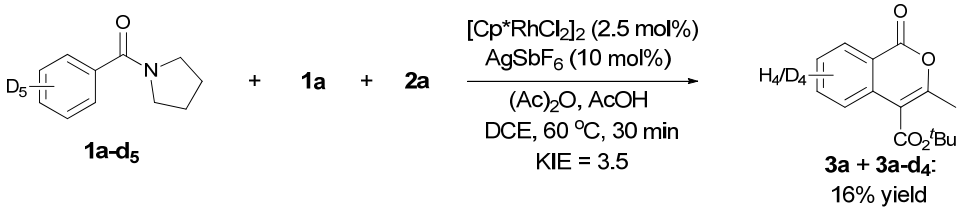
Ethyl-6-(2,6-dichloro-5-fluoropyridin-3-yl)-3-methyl-2-oxo-2H-pyran-5-carboxylate (4f). The compound was prepared from 2-methyl-1-(pyrrolidin-1-yl)prop-2-en-1-one **1o** (83.5 mg, 0.6 mmol) and ethyl 2-diazo-3-(2,6-dichloro-5-fluoropyridin-3-yl)-3-oxopropanoate **2h** (92.0 mg, 0.3 mmol) following the typical procedure. The product **4f** was obtained in 86% yield (89 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 10:1 v/v). Mp: 116.2-118.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (t, *J* = 7.1 Hz, 3H), 2.22 (d, *J* = 1.2 Hz, 3H), 4.19 (q, *J* = 7.1 Hz, 2H), 7.59 (d, *J* = 7.1 Hz, 1H), 7.73 (d, *J* = 1.2 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.9, 16.8, 62.2, 112.4, 126.0, 127.5 (d, *J* = 21.9 Hz), 129.2 (d, *J* = 3.5 Hz), 138.6, 139.2 (d, *J* = 20.8 Hz), 142.9 (d, *J* = 3.7 Hz), 152.4, 155.0, 157.4, 160.9, 162.7; HRMS (EI, TOF) calcd for $C_{14}H_{10}O_4ClNF$, $[M\text{-}Cl]^+$: 310.0277, found: 310.0277.



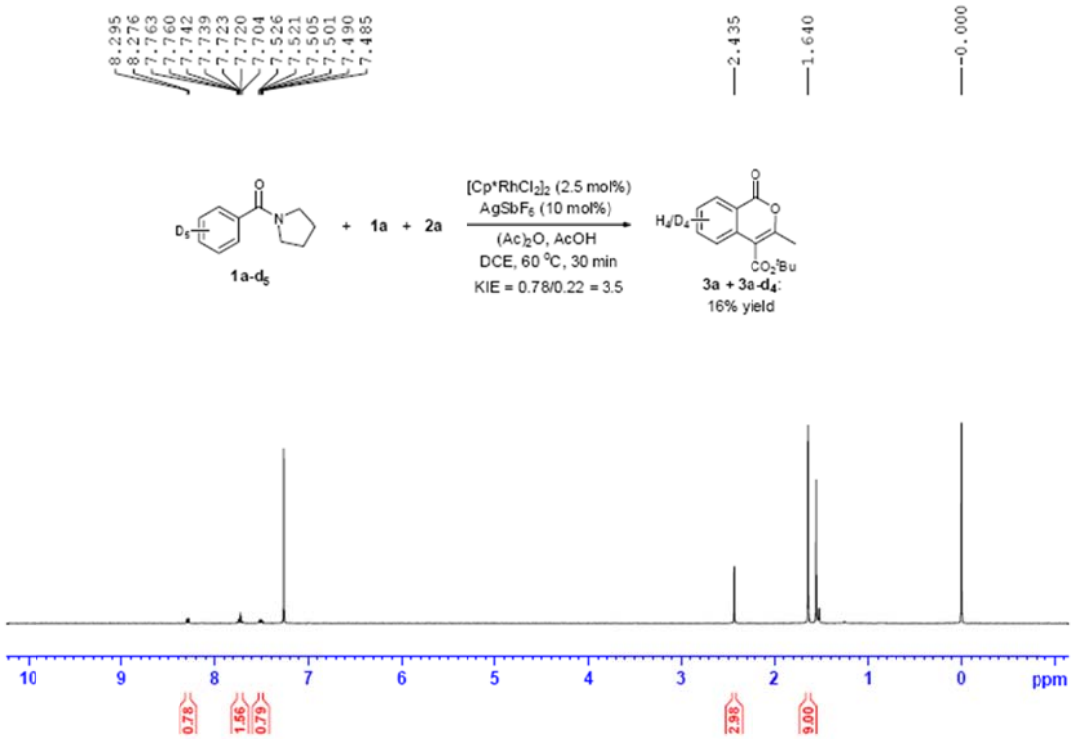
3,7,7-Trimethyl-7,8-dihydro-2*H*-chromene-2,5(6*H*)-dione (4g). The compound was prepared from 2-methyl-1-(pyrrolidin-1-yl)prop-2-en-1-one **1o** (83.5 mg, 0.6 mmol) and 2-diazo-1,3-diphenylpropane-1,3-dione **2i** (49.9 mg, 0.3 mmol) following the typical procedure. The product **4g** was obtained in 87% yield (54 mg) as white solid after column chromatography (eluent = petroleum ether/ethyl acetate 15:1 v/v). Mp: 109.3-111.6 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (s, 6H), 2.12 (s, 3H), 2.40 (s, 2H), 2.70 (s, 2H), 7.62 (d, *J* = 1.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.7, 28.4, 32.8, 41.5, 50.6, 113.7, 123.4, 135.2, 162.2, 170.6, 194.2; HRMS (EI, TOF) calcd for $C_{12}H_{14}O_3$, $[M]^+$: 206.0943, found: 206.0946.

4. Compete experiments and mechanistic studies

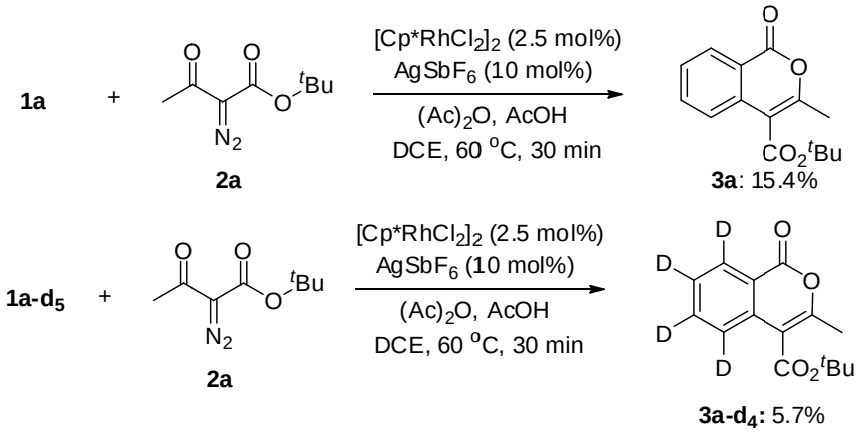
Kinetic isotope effect experiment



To a mixture of $[Cp^*RhCl_2]_2$ (4.6 mg, 0.0075 mmol, 2.5 mol%) and $AgSbF_6$ (10.3 mg, 0.03 mmol, 10 mol%) in 1, 2-dichloroethane (2 mL) was added **1a** (105.1 mg, 0.6 mmol), **1a-d$_5$** (108.2 mg, 0.6 mmol) and *tert*-butyl 2-diazo-3-oxobutanoate **2a** (55.3 mg, 0.3 mmol), HOAc (10.8 mg, 0.18 mmol, 0.6 equiv) and Ac_2O (42.9 mg, 0.42 mmol, 1.4 equiv). The reaction mixture was stirred at 60 ^{o}C for 30 min. After cooling to ambient temperature by the ice-water bath, the solvent was evaporated under reduced pressure and the residue passed through flash column chromatography on silica gel to afford the mixture of products **3a** and **3a-d$_4$** with 13.0 mg (16 % yield).

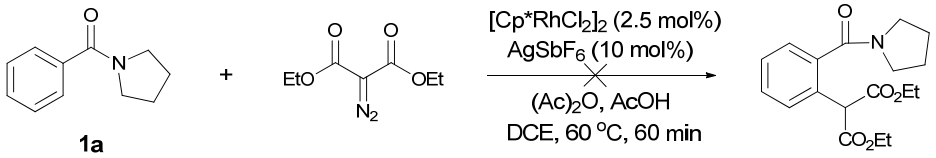


Parallel reactions using 1a and 1a-d_5 under the optimal conditions for 30 min



To a mixture of $[Cp^*RhCl_2]_2$ (4.6 mg, 0.0075 mmol, 2.5 mol%) and $AgSbF_6$ (10.3 mg, 0.03 mmol, 10 mol%) in 1, 2-dichloroethane (2 mL) was added **1a** (105.1 mg, 0.6 mmol) or **1a-d_5** (108.2 mg, 0.6 mmol) and *tert*-butyl 2-diazo-3-oxobutanoate **2a** (55.3 mg, 0.3 mmol), HOAc (10.8 mg, 0.18 mmol, 0.6 equiv) and Ac_2O (42.9 mg, 0.42 mmol, 1.4 equiv). The reaction mixture was stirred at 60 °C for 30 min. After cooling to ambient temperature by the ice-water bath, the solvent was evaporated under reduced pressure and the residue passed through flash column chromatography on silica gel to afford the product **3a** (4.5 mg, 5.7%) or **3a-d_4** (12.0 mg, 15.4%).

Reaction of 1a and diethyl 2-diazomalonate under standard conditions



To a mixture of $[Cp^*RhCl_2]_2$ (4.6 mg, 0.0075 mmol, 2.5 mol%) and $AgSbF_6$ (10.3 mg, 0.03 mmol, 10 mol%) in 1, 2-dichloroethane (2 mL) was added **1a** (105.1 mg, 0.6 mmol) and diethyl 2-diazomalonate (55.9 mg, 0.3 mmol), HOAc (10.8 mg, 0.18 mmol, 0.6 equiv) and Ac_2O (42.9 mg, 0.42 mmol, 1.4 equiv). The reaction mixture was stirred at 60 °C and the progress was monitored using TLC detection.

5. Crystal data and structure refinement of product 3a

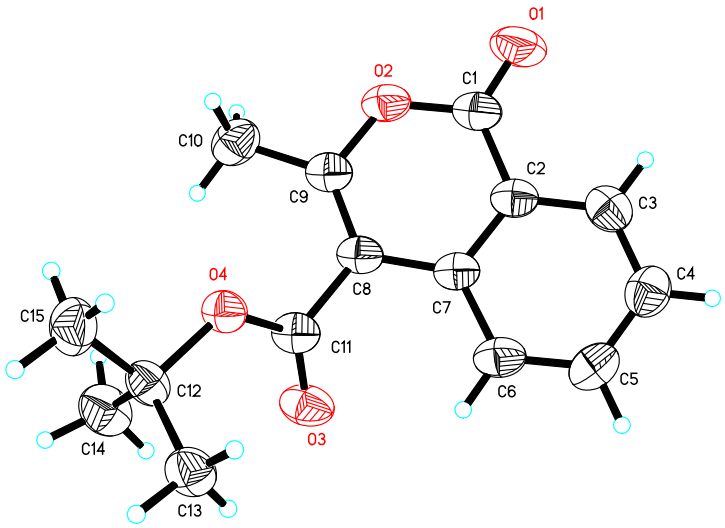


Table 1. Crystal data and structure refinement for **3a**.

CCDC number	1035334	
Empirical formula	$C_{15}\ H_{16}\ O_4$	
Formula weight	260.28	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.153(9) Å	a= 86.72(3)°.
	b = 8.436(8) Å	b= 72.91(2)°.
	c = 10.959(10) Å	g = 72.86(2)°.

Volume	688.1(12) $Å^3$
Z	2
Density (calculated)	1.256 Mg/m^3
Absorption coefficient	0.091 mm^{-1}
F(000)	276
Crystal size	0.211 x 0.156 x 0.112 mm^3
Theta range for data collection	1.945 to 25.998°.
Index ranges	-10<=h<=9, -10<=k<=7, -13<=l<=12
Reflections collected	4021
Independent reflections	2687 [R(int) = 0.0238]
Completeness to theta = 25.242°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.6689
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2687 / 0 / 176
Goodness-of-fit on F^2	0.898
Final R indices [I>2sigma(I)]	R1 = 0.0468, wR2 = 0.1120
R indices (all data)	R1 = 0.1073, wR2 = 0.1336
Extinction coefficient	n/a
Largest diff. peak and hole	0.127 and -0.116 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-3892(2)	6853(3)	12132(2)	114(1)
O(2)	-2952(2)	7917(2)	10291(2)	75(1)

O(3)	2567(2)	8959(2)	8490(2)	87(1)
O(4)	1458(2)	7887(2)	7177(1)	65(1)
C(1)	-2621(3)	7104(3)	11342(2)	76(1)
C(2)	-783(3)	6635(3)	11415(2)	64(1)
C(3)	-399(4)	5780(3)	12470(2)	78(1)
C(4)	1300(4)	5335(3)	12575(3)	86(1)
C(5)	2642(3)	5733(3)	11646(3)	87(1)
C(6)	2301(3)	6571(3)	10597(2)	76(1)
C(7)	558(3)	7044(3)	10440(2)	59(1)
C(8)	73(3)	7895(3)	9363(2)	60(1)
C(9)	-1632(3)	8301(3)	9322(2)	67(1)
C(10)	-2460(3)	9254(3)	8355(2)	88(1)
C(11)	1493(3)	8339(3)	8317(2)	66(1)
C(12)	2770(3)	8169(3)	5994(2)	66(1)
C(13)	4651(3)	7125(3)	5995(2)	79(1)
C(14)	2588(3)	10017(3)	5870(3)	96(1)
C(15)	2194(3)	7519(3)	4967(2)	93(1)

Table 3. Bond lengths [Å] and angles [°] for **3a**.

O(1)-C(1)	1.204(3)
O(2)-C(1)	1.361(3)
O(2)-C(9)	1.373(3)
O(3)-C(11)	1.206(3)
O(4)-C(11)	1.338(3)
O(4)-C(12)	1.477(3)
C(1)-C(2)	1.459(3)
C(2)-C(3)	1.392(3)
C(2)-C(7)	1.396(3)
C(3)-C(4)	1.362(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.367(3)
C(4)-H(4)	0.9300
C(5)-C(6)	1.370(3)
C(5)-H(5)	0.9300
C(6)-C(7)	1.417(3)
C(6)-H(6)	0.9300

C(7)-C(8)	1.441(3)
C(8)-C(9)	1.345(3)
C(8)-C(11)	1.490(3)
C(9)-C(10)	1.492(3)
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(12)-C(14)	1.524(4)
C(12)-C(15)	1.524(3)
C(12)-C(13)	1.527(3)
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600

C(1)-O(2)-C(9)	122.50(19)
C(11)-O(4)-C(12)	120.58(18)
O(1)-C(1)-O(2)	116.3(2)
O(1)-C(1)-C(2)	126.1(3)
O(2)-C(1)-C(2)	117.6(2)
C(3)-C(2)-C(7)	121.1(2)
C(3)-C(2)-C(1)	118.8(2)
C(7)-C(2)-C(1)	120.1(2)
C(4)-C(3)-C(2)	120.4(2)
C(4)-C(3)-H(3)	119.8
C(2)-C(3)-H(3)	119.8
C(3)-C(4)-C(5)	120.2(3)
C(3)-C(4)-H(4)	119.9
C(5)-C(4)-H(4)	119.9
C(4)-C(5)-C(6)	120.6(2)
C(4)-C(5)-H(5)	119.7
C(6)-C(5)-H(5)	119.7
C(5)-C(6)-C(7)	121.2(2)

C(5)-C(6)-H(6)	119.4
C(7)-C(6)-H(6)	119.4
C(2)-C(7)-C(6)	116.5(2)
C(2)-C(7)-C(8)	118.0(2)
C(6)-C(7)-C(8)	125.4(2)
C(9)-C(8)-C(7)	120.3(2)
C(9)-C(8)-C(11)	121.2(2)
C(7)-C(8)-C(11)	118.5(2)
C(8)-C(9)-O(2)	121.5(2)
C(8)-C(9)-C(10)	129.7(2)
O(2)-C(9)-C(10)	108.7(2)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
O(3)-C(11)-O(4)	125.1(2)
O(3)-C(11)-C(8)	124.1(2)
O(4)-C(11)-C(8)	110.7(2)
O(4)-C(12)-C(14)	109.91(18)
O(4)-C(12)-C(15)	102.06(19)
C(14)-C(12)-C(15)	111.5(2)
O(4)-C(12)-C(13)	109.19(18)
C(14)-C(12)-C(13)	113.1(2)
C(15)-C(12)-C(13)	110.5(2)
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5

C(12)-C(15)-H(15A)	109.5
C(12)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(12)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5

Symmetry transformations used to generate equivalent atoms:

6. References

[1] K. D. Hesp, R. G. Bergman and J. A. Ellman, *Org. Lett.*, 2012, **14**, 2304.

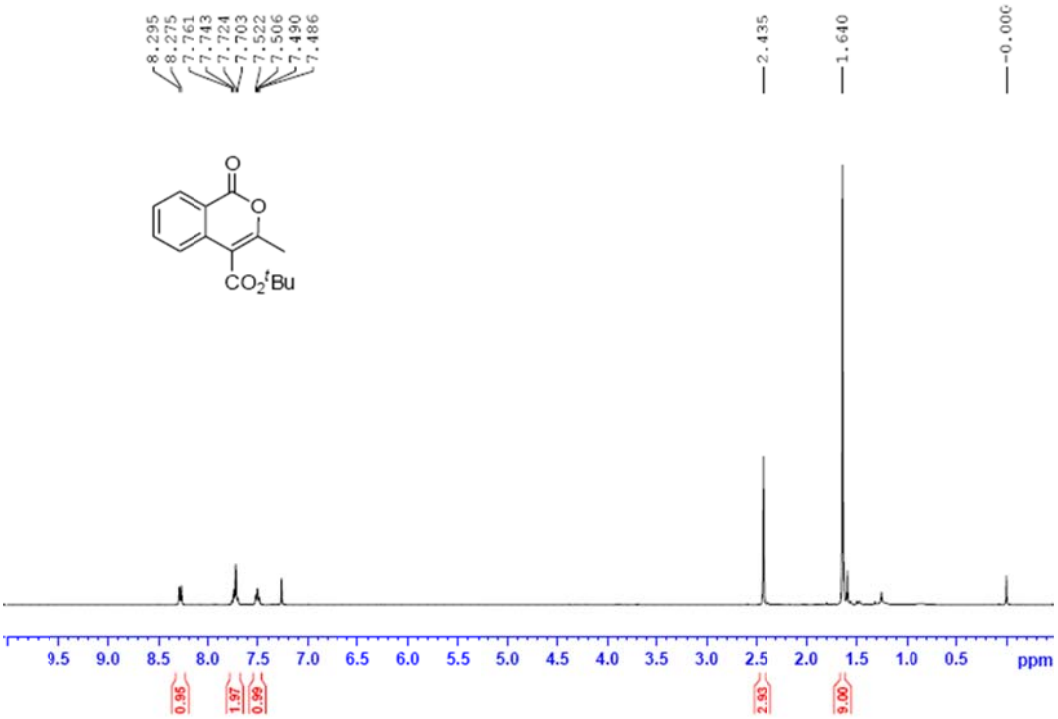
[2] N. D. Koduri, H. Scott, B. Hileman, J. D. Cox, M. Coffin, L. Glicksberg and S. R. Hussaini, *Org. Lett.*, 2012, **14**, 440.

[3] F. Nanteuil and J. Waser, *Angew. Chem. Int. Ed.*, 2011, **50**, 12075.

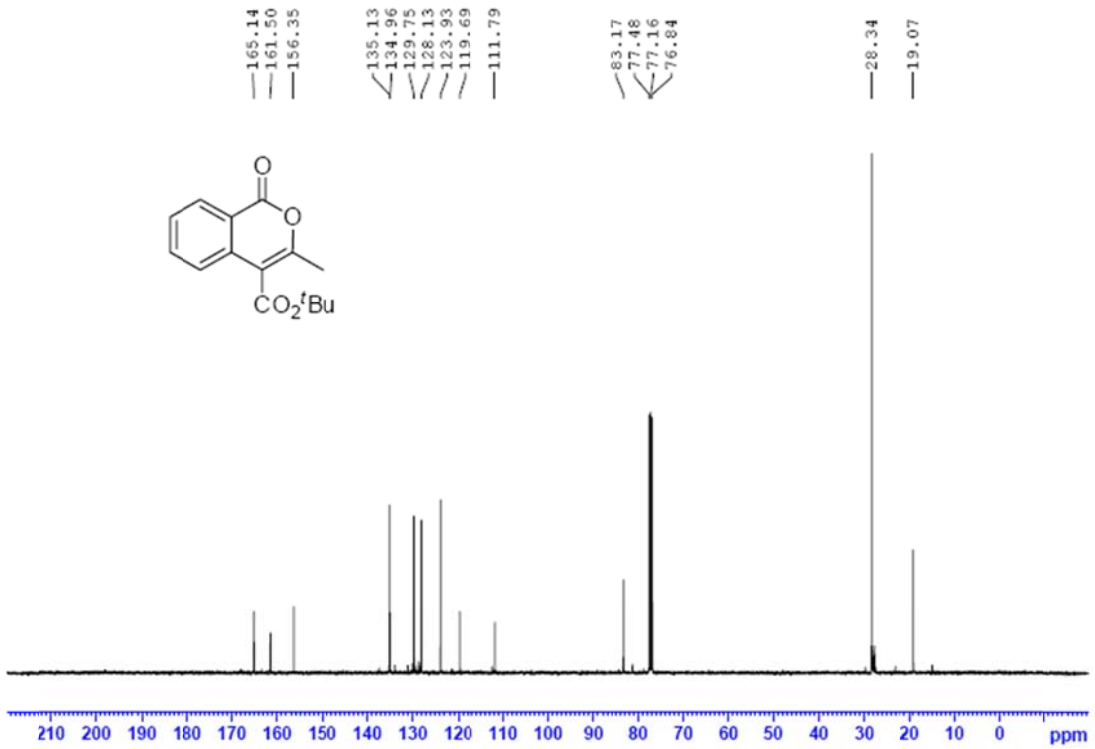
[4] C. White, A. Yates and P. M. Maitlis, *Inorg. Synth.*, 1974, **29**, 228.

7. Copies of ^{1}H NMR, ^{13}C NMR for the products

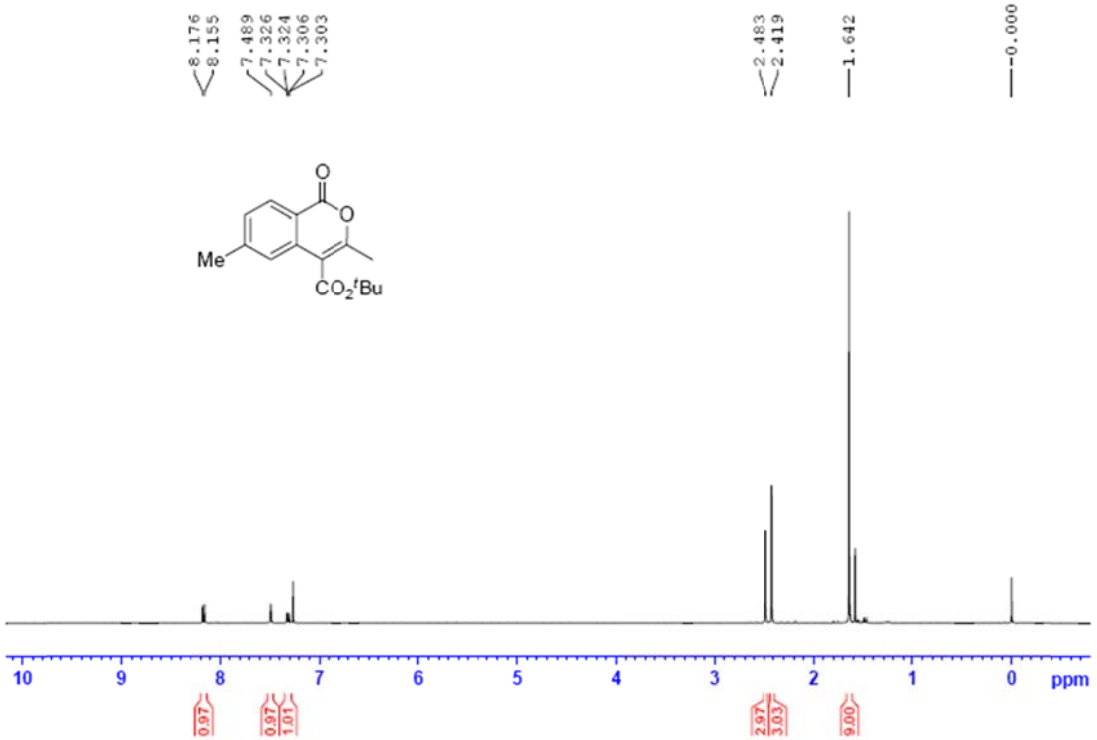
^{1}H NMR spectra of *tert*-Butyl 3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3a).



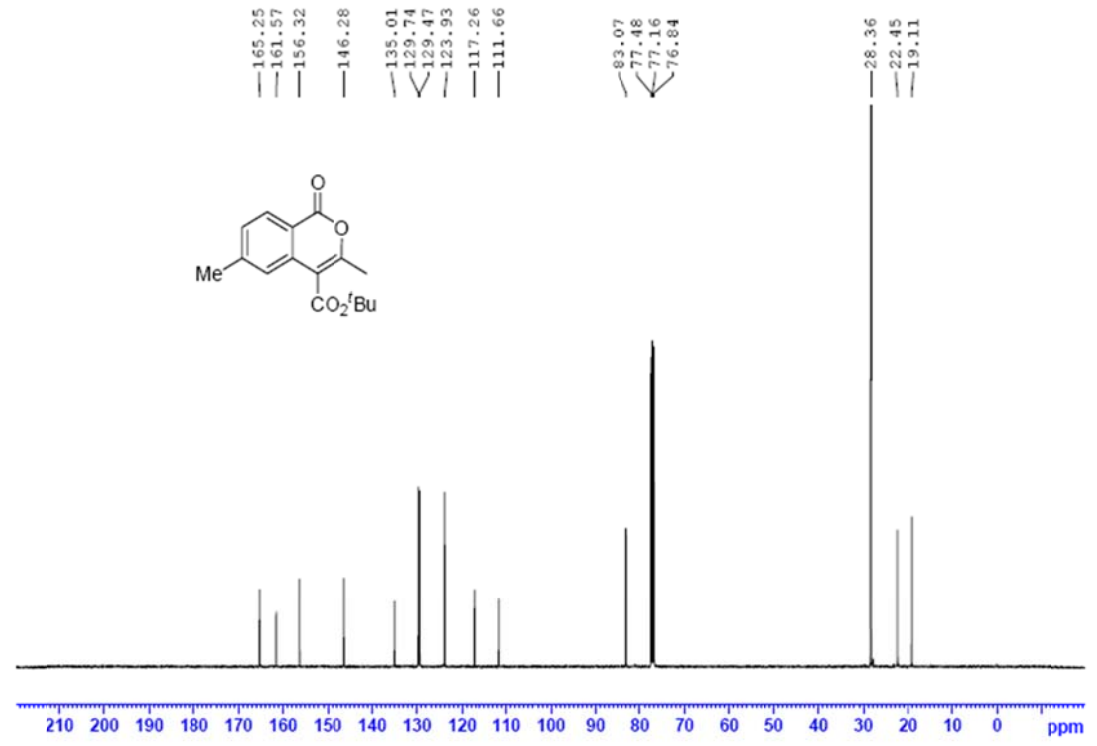
^{13}C NMR spectra of *tert*-Butyl 3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3a).



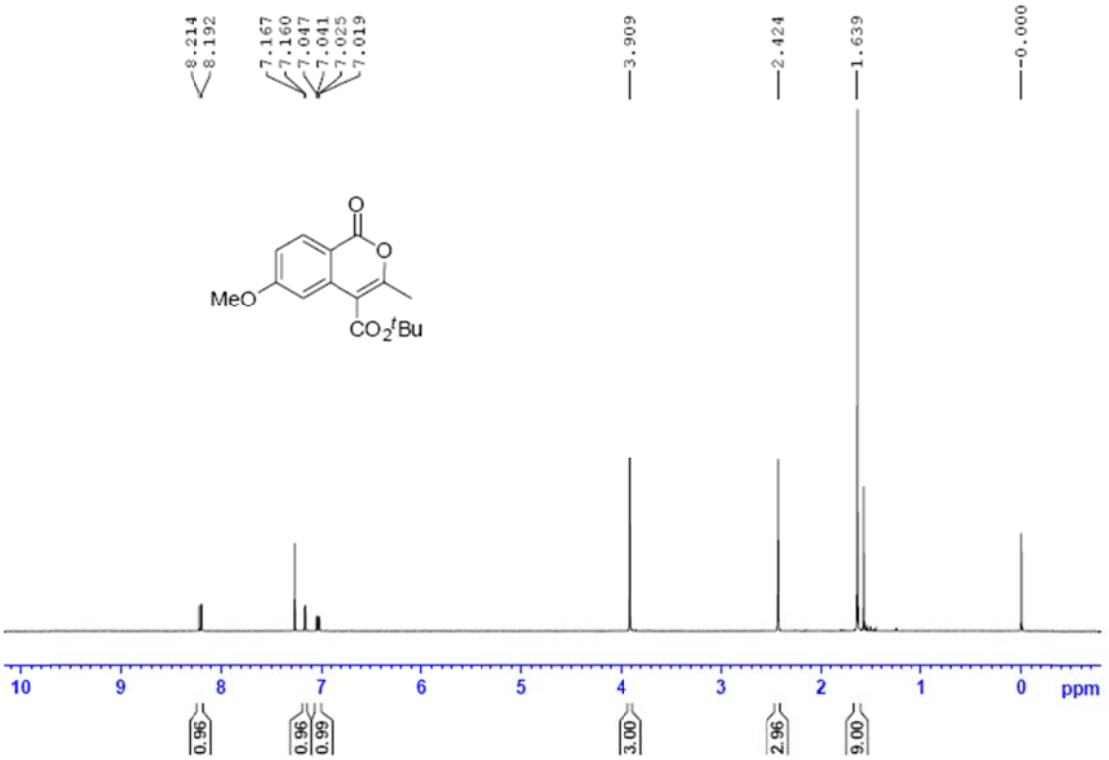
^{1}H NMR spectra of *tert*-Butyl 3,6-dimethyl-1-oxo-1*H*-isochromene-4-carboxylate (3b).



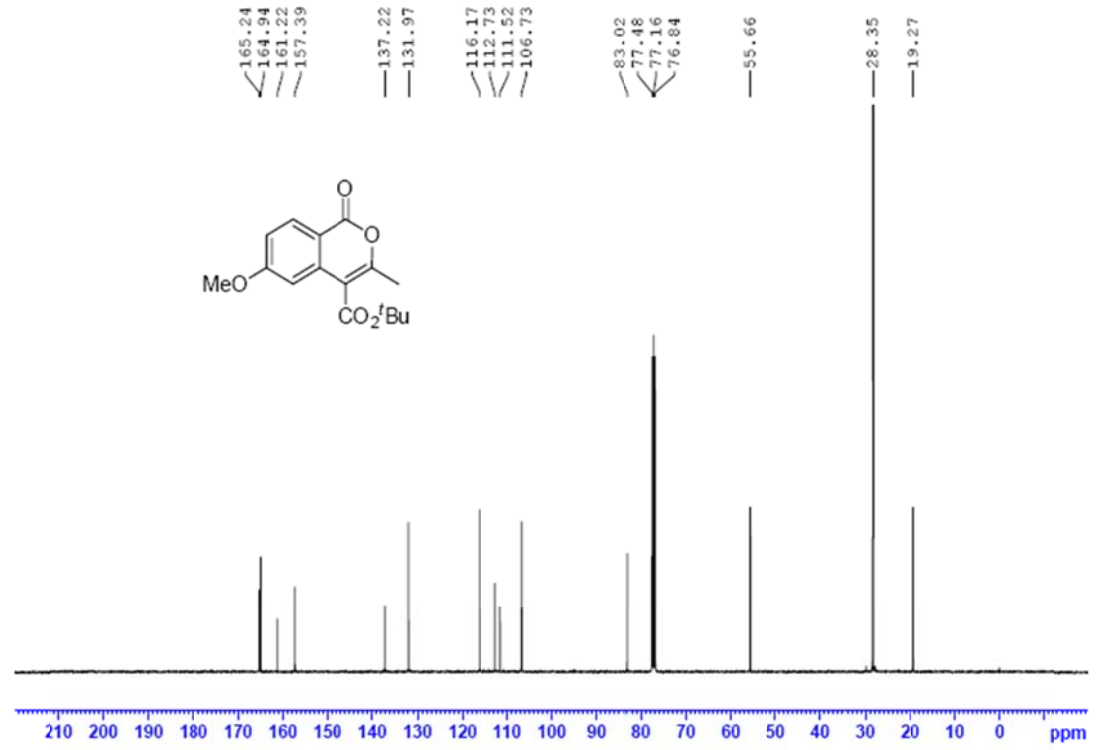
^{13}C NMR spectra of *tert*-Butyl 3,6-dimethyl-1-oxo-1*H*-isochromene-4-carboxylate (3b).



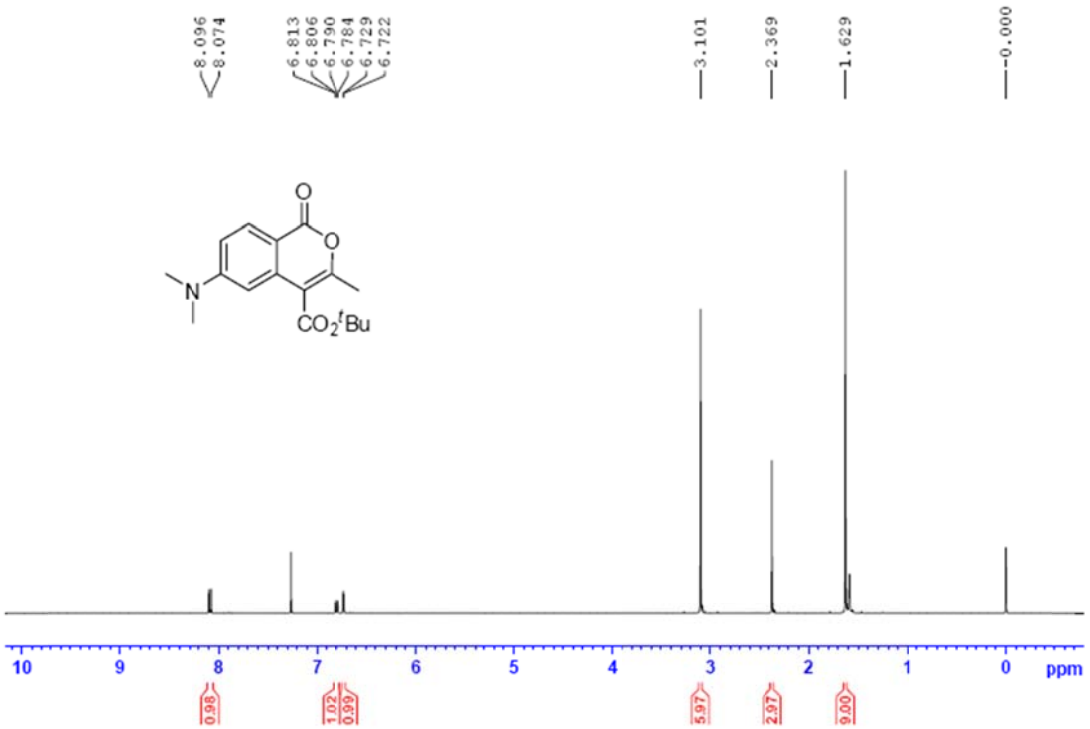
^{1}H NMR spectra of *tert*-Butyl 6-methoxy-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3c).



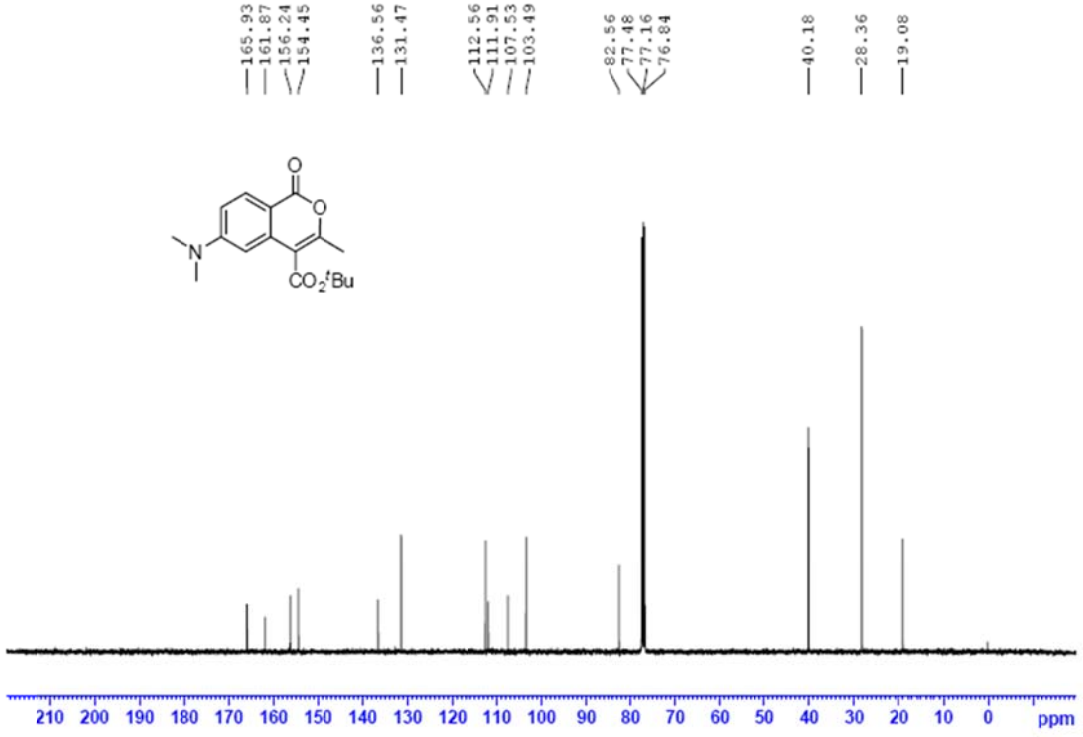
^{13}C NMR spectra of *tert*-Butyl 6-methoxy-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3c).



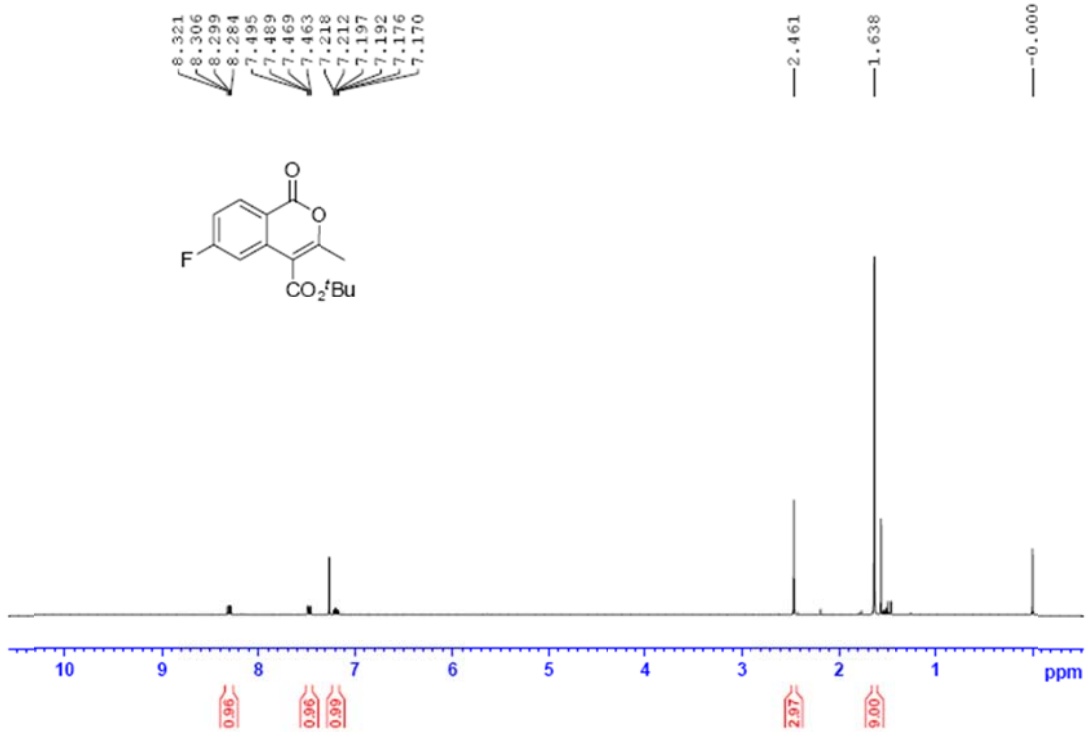
^{1}H NMR spectra of *t*ert-Butyl 6-(dimethylamino)-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3d).



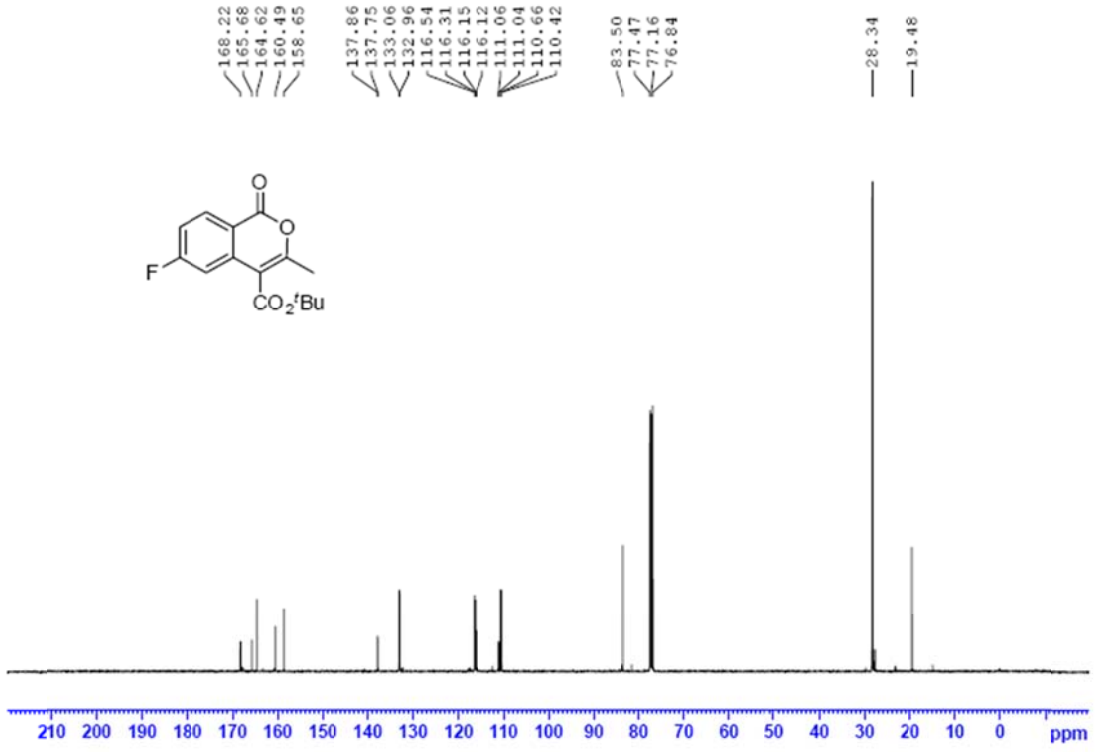
^{13}C NMR spectra of *t*ert-Butyl 6-(dimethylamino)-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3d).



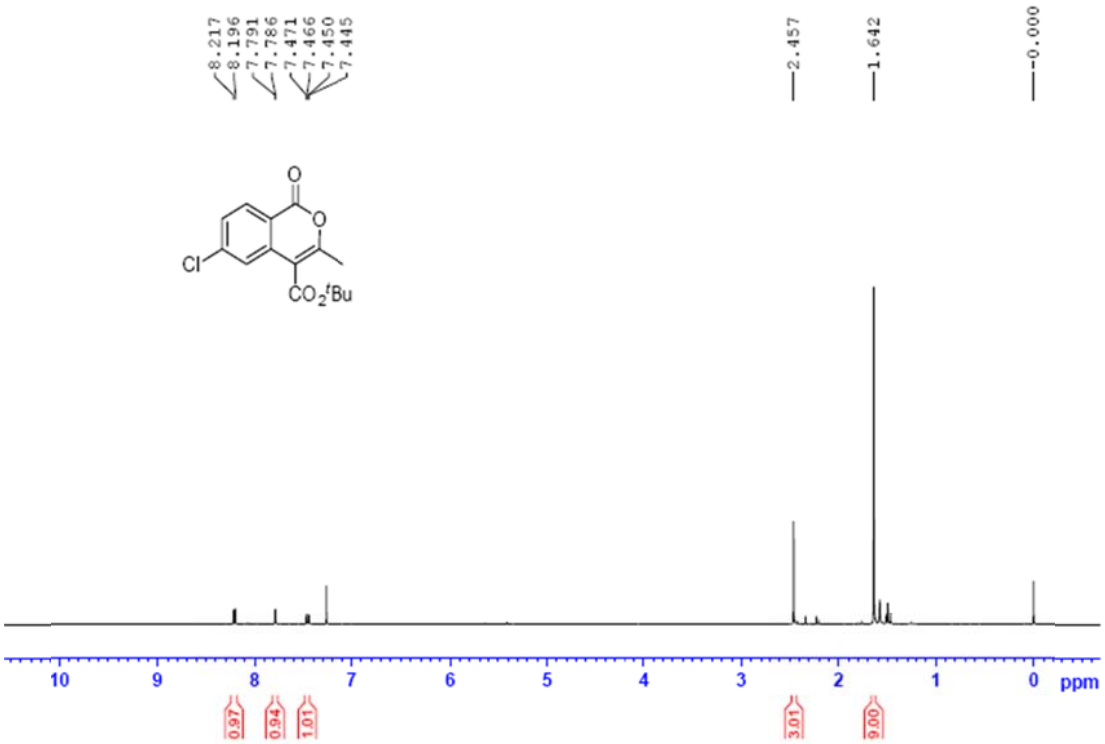
^{1}H NMR spectra of *tert*-Butyl 6-fluoro-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3e).



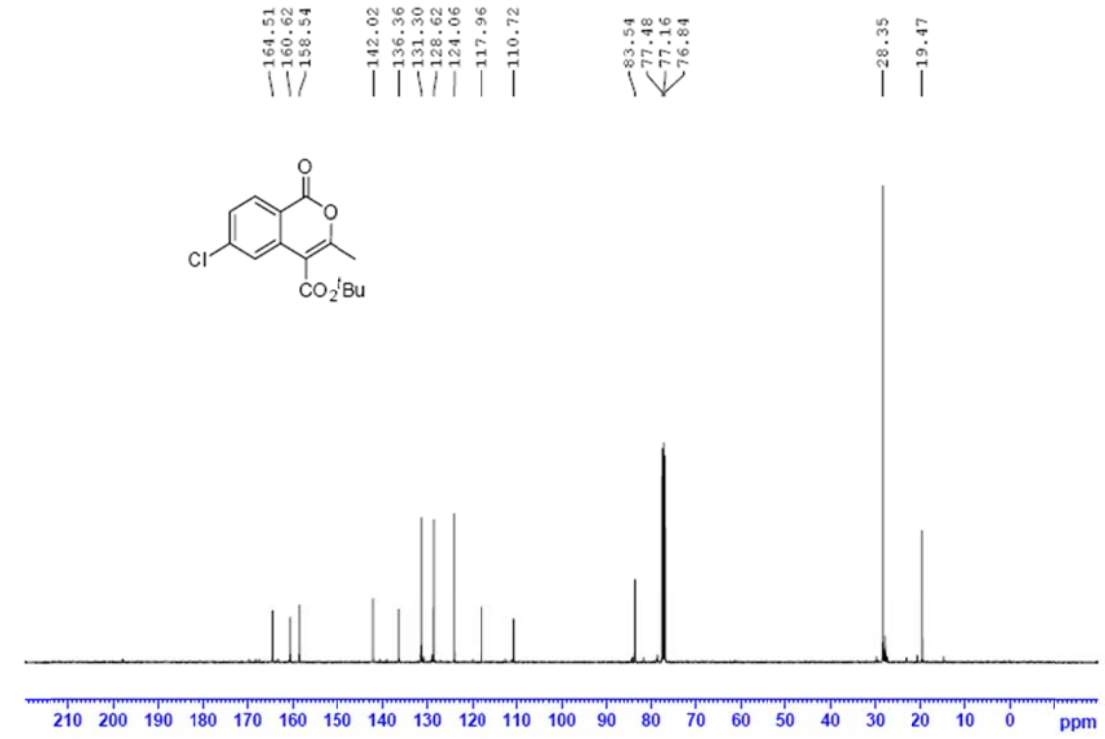
^{13}C NMR spectra of *tert*-Butyl 6-fluoro-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3e).



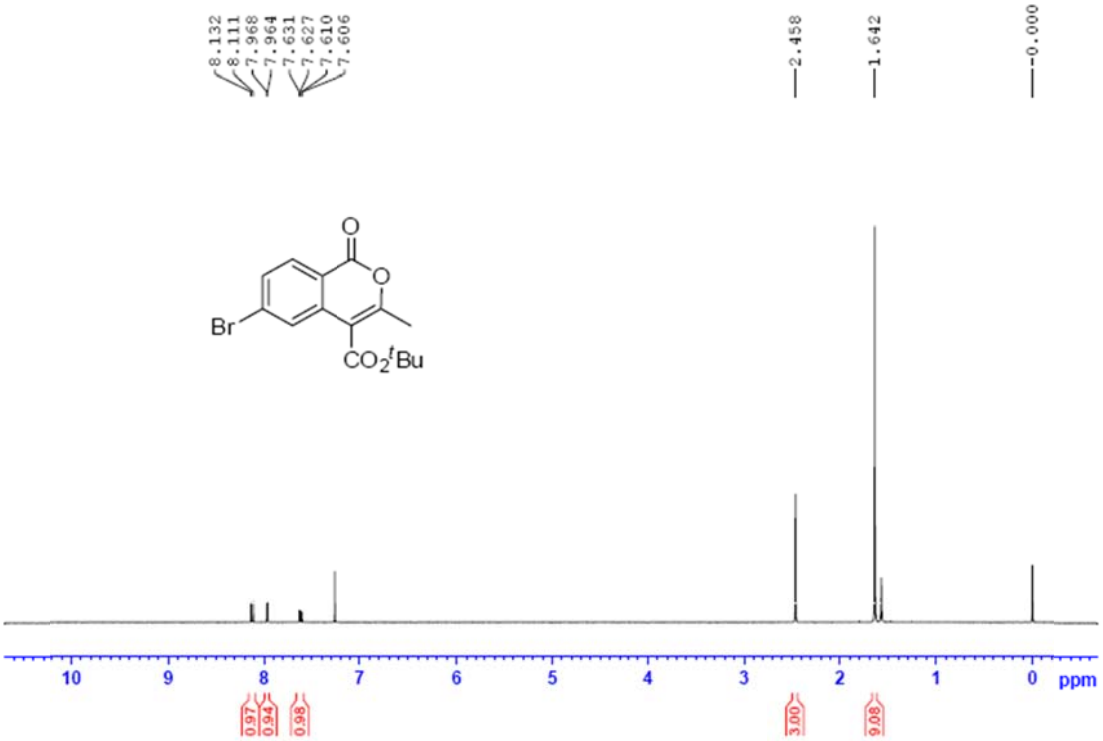
^{1}H NMR spectra of *tert*-Butyl 6-chloro-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3f).



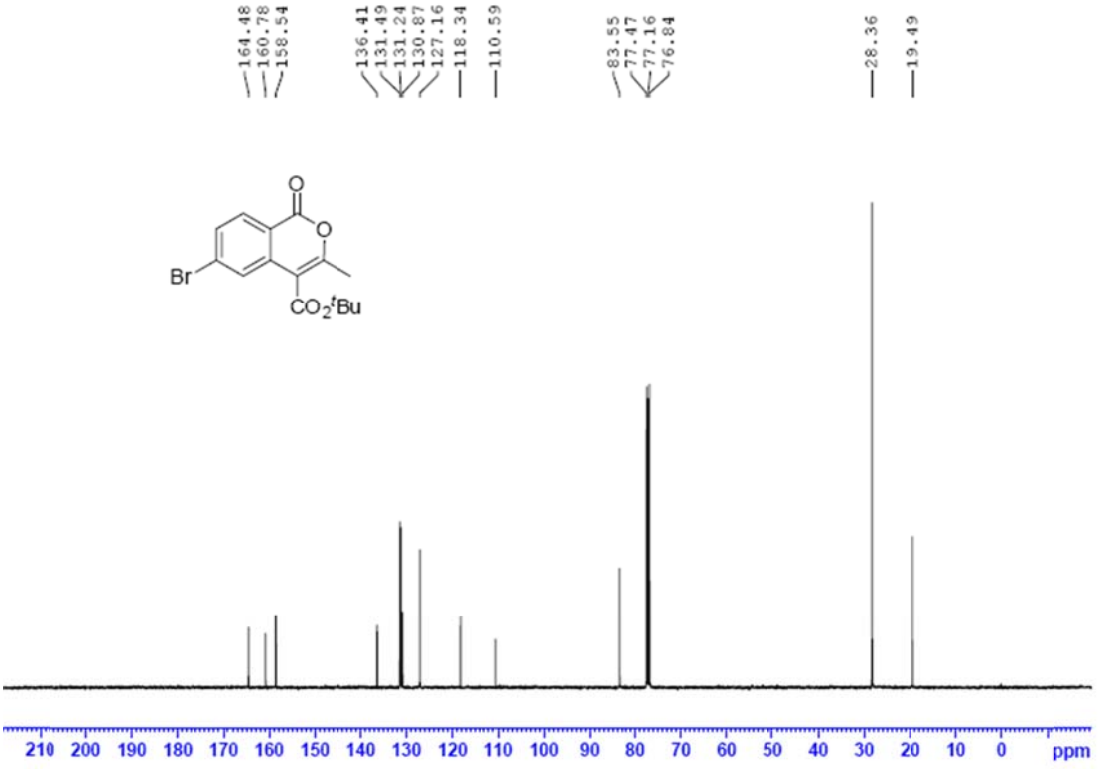
^{13}C NMR spectra of *tert*-Butyl 6-chloro-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3f).



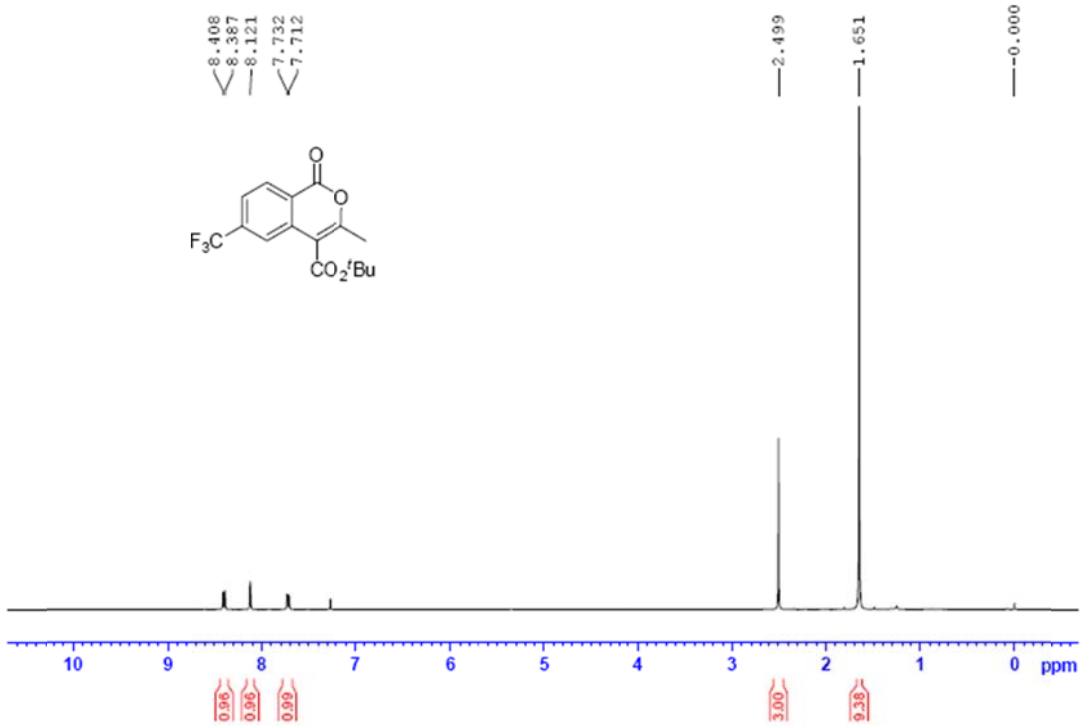
^{1}H NMR spectra of *tert*-Butyl 6-bromo-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3g).



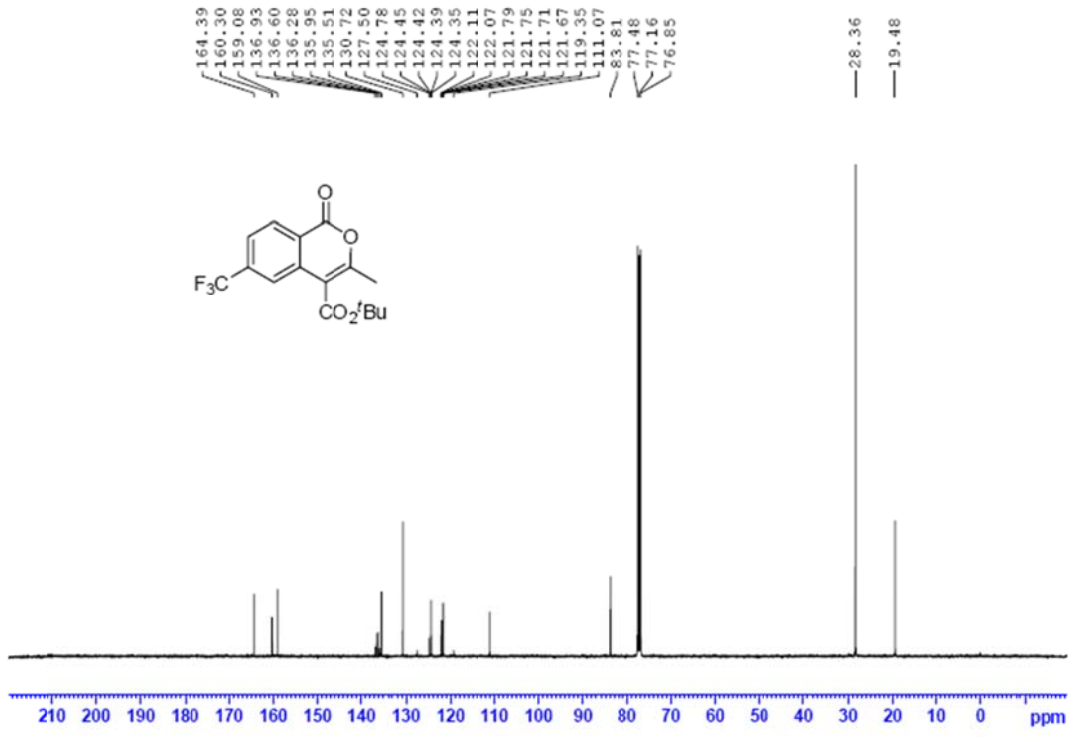
^{13}C NMR spectra of *tert*-Butyl 6-bromo-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3g).



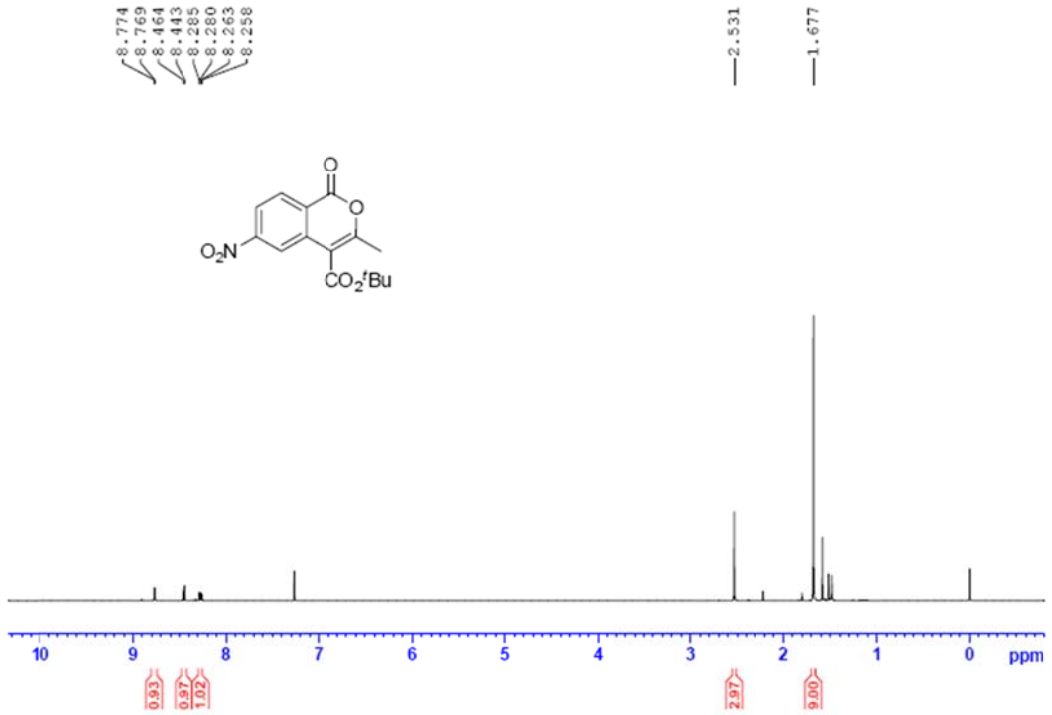
^{1}H NMR spectra of *tert*-Butyl 3-methyl-1-oxo-6-(trifluoromethyl)-1*H*-isochromene-4-carboxylate (3h).



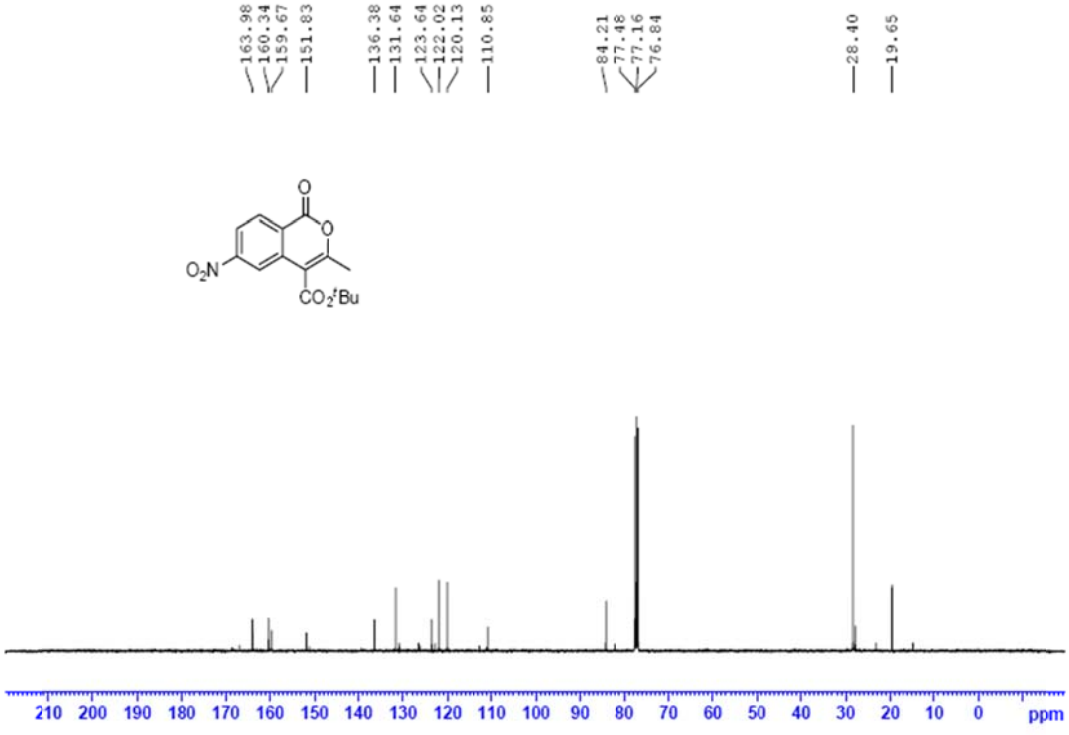
^{13}C NMR spectra of *tert*-Butyl 3-methyl-1-oxo-6-(trifluoromethyl)-1*H*-isochromene-4-carboxylate (3h).



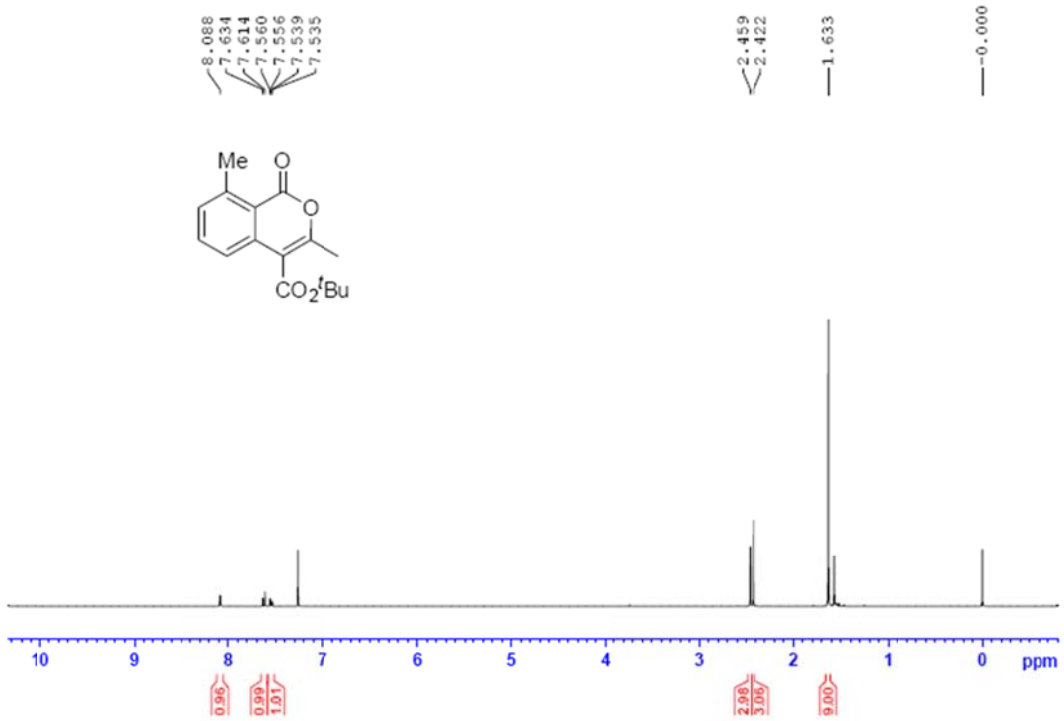
^{1}H NMR spectra of *tert*-Butyl 3-methyl-6-nitro-1-oxo-1*H*-isochromene -4-carboxylate (3i).



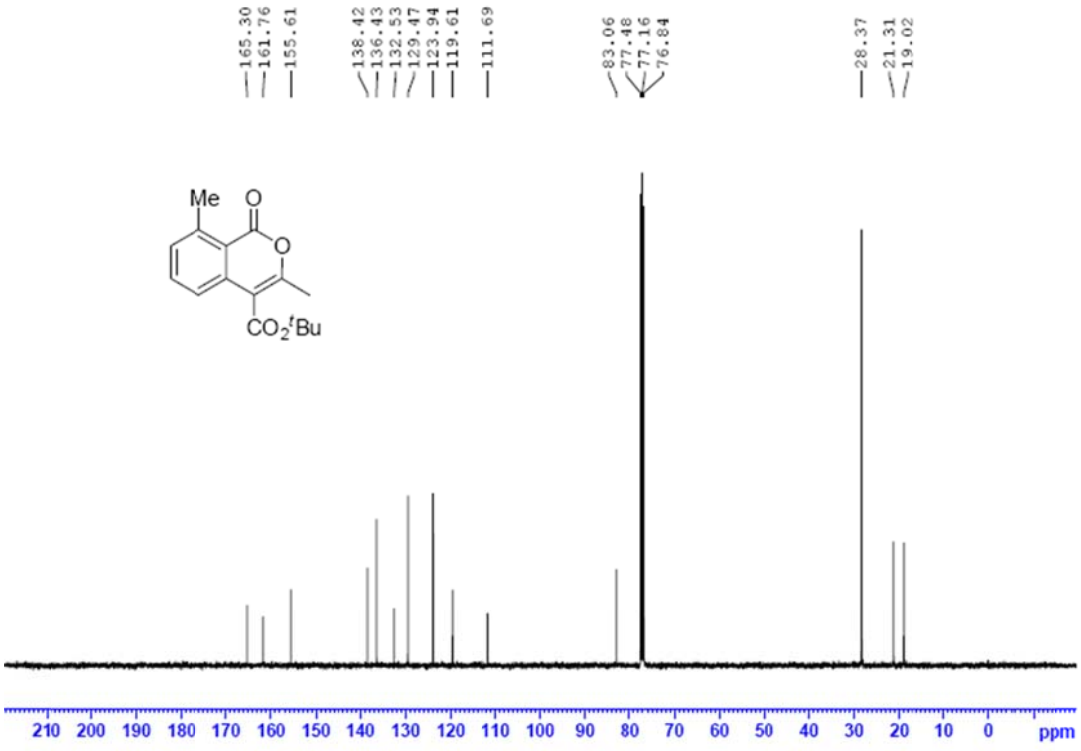
^{13}C NMR spectra of *tert*-Butyl 3-methyl-6-nitro-1-oxo-1*H*-isochromene -4-carboxylate (3i).



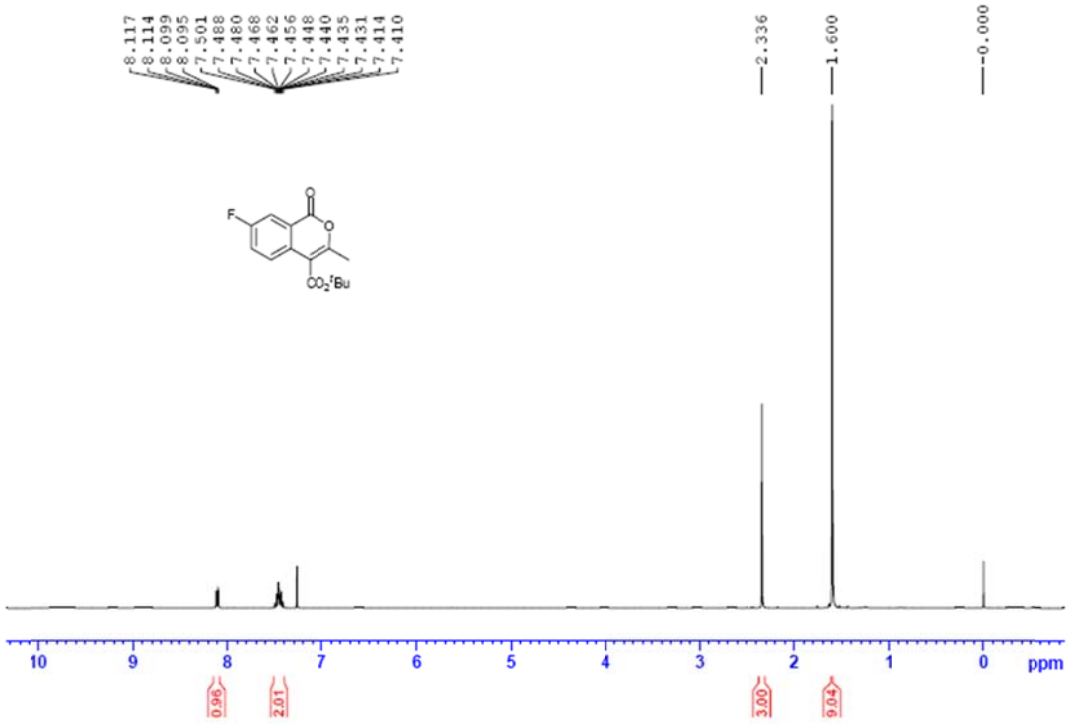
^{1}H NMR spectra of *tert*-Butyl 3,8-dimethyl-1-oxo-1*H*-isochromene-4-carboxylate (3j).



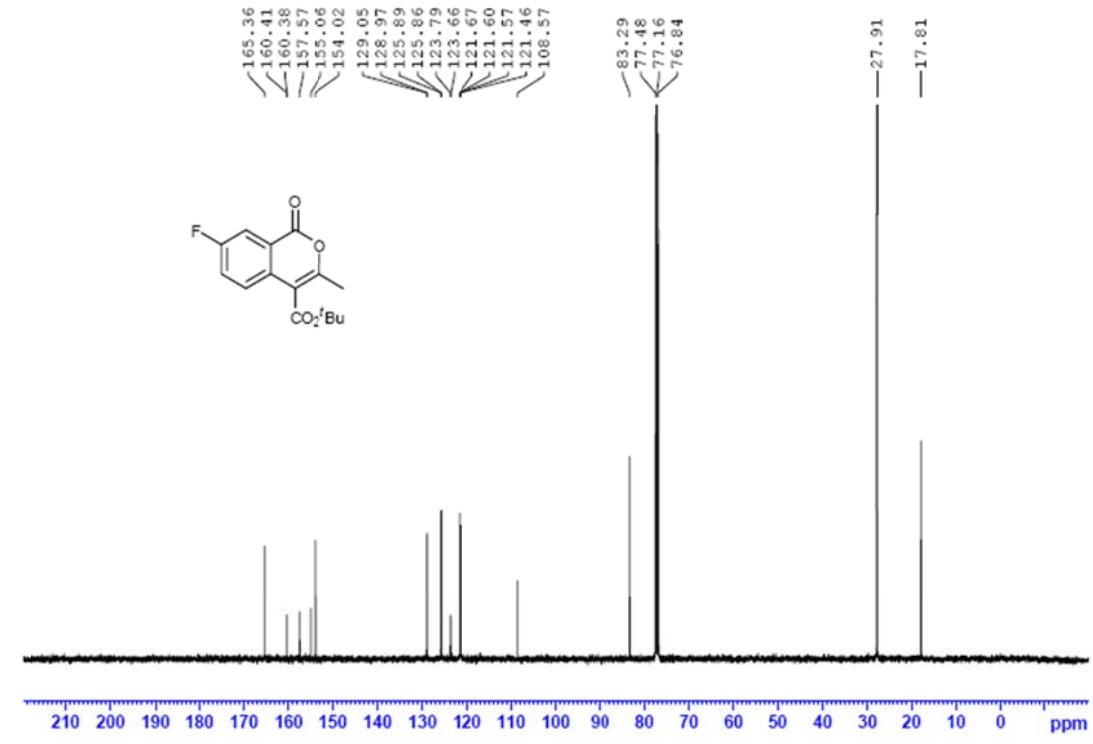
^{13}C NMR spectra of *tert*-Butyl 3,8-dimethyl-1-oxo-1*H*-isochromene-4-carboxylate (3j).



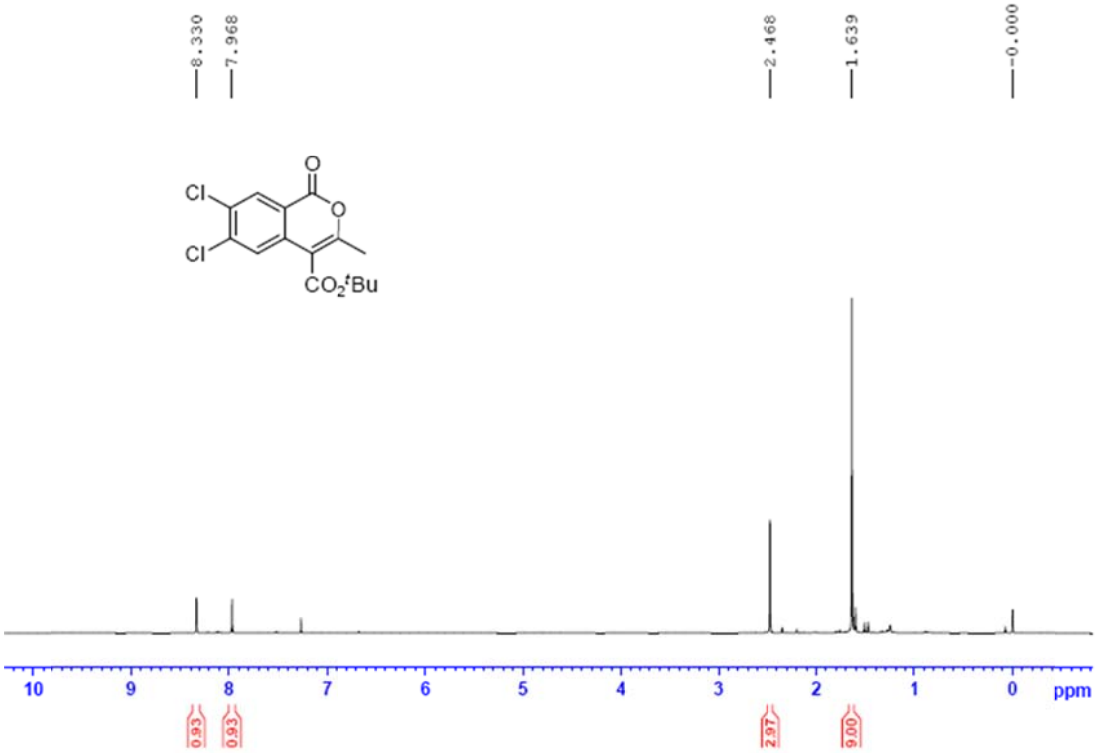
^{1}H NMR spectra of *tert*-Butyl 7-fluoro-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3k).



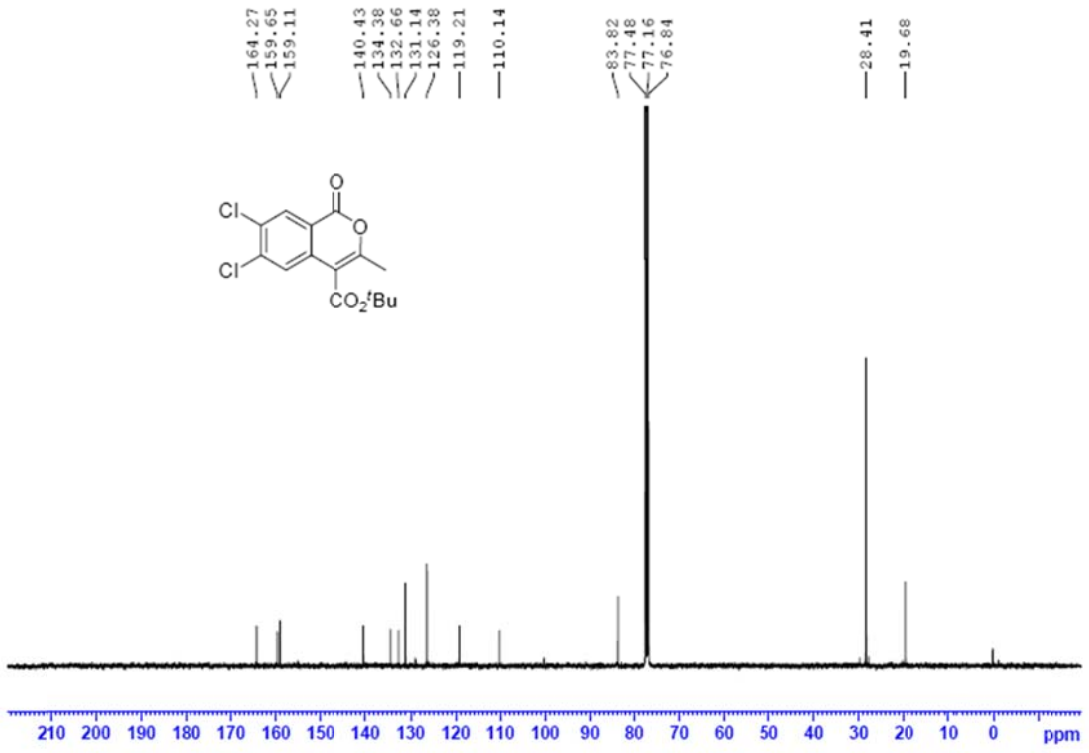
^{13}C NMR spectra of *tert*-Butyl 7-fluoro-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3k).



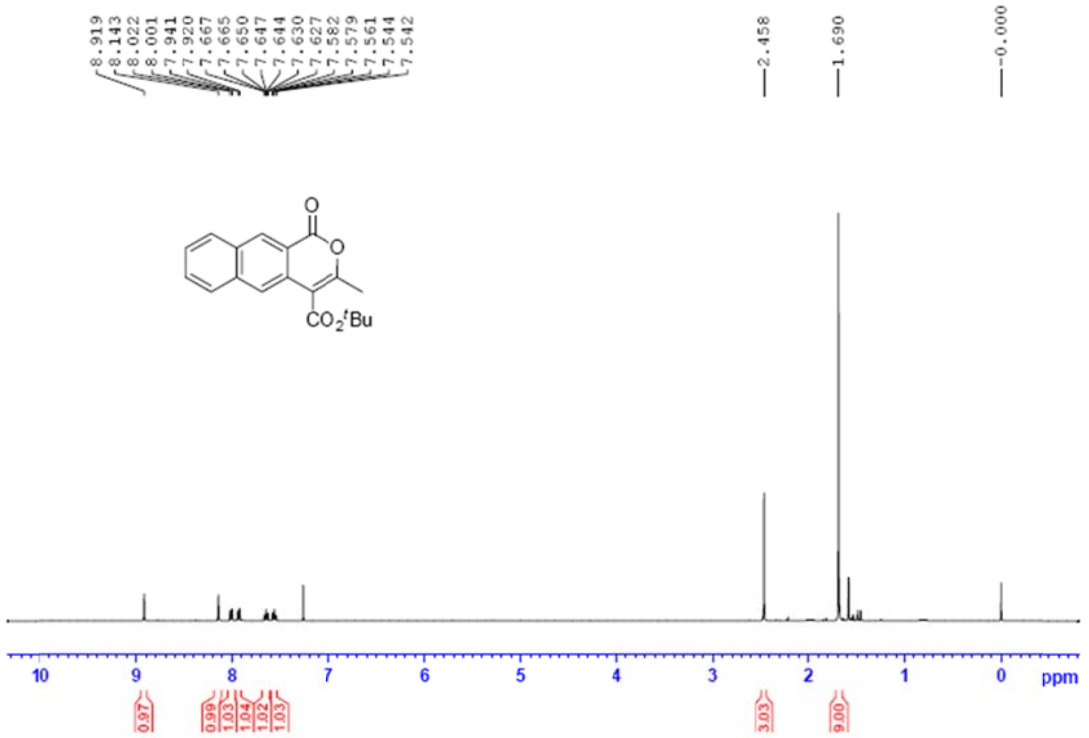
^{1}H NMR spectra of *tert*-Butyl 6,7-dichloro-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3l).



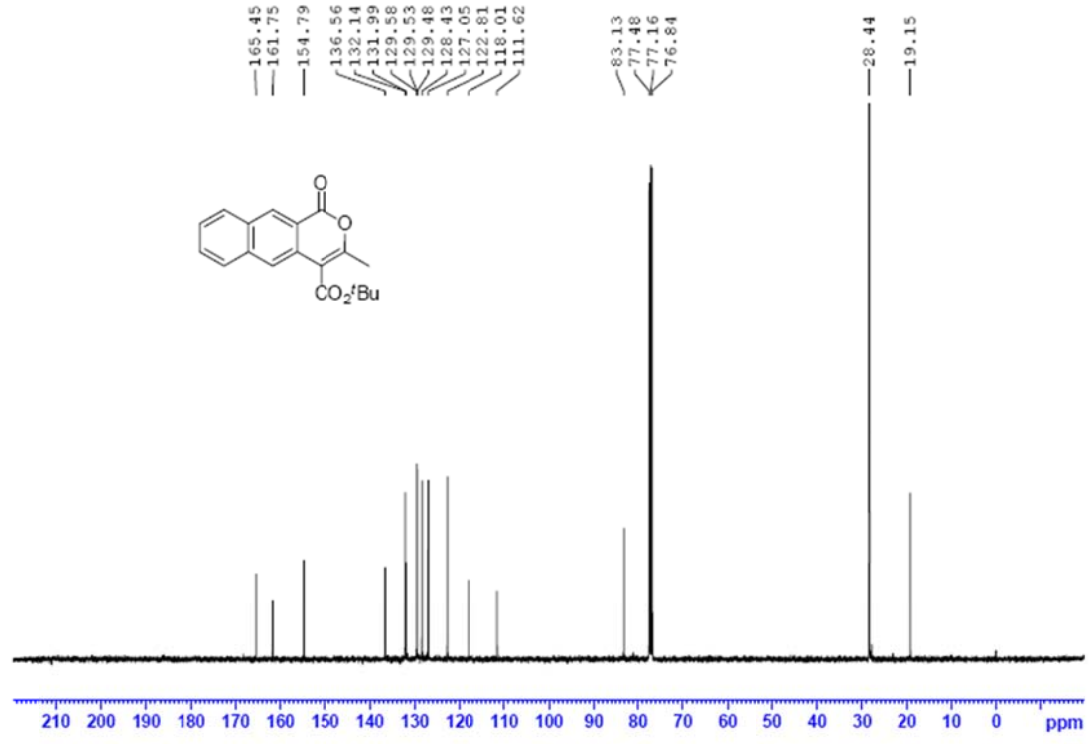
^{13}C NMR spectra of *tert*-Butyl 6,7-dichloro-3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3l).



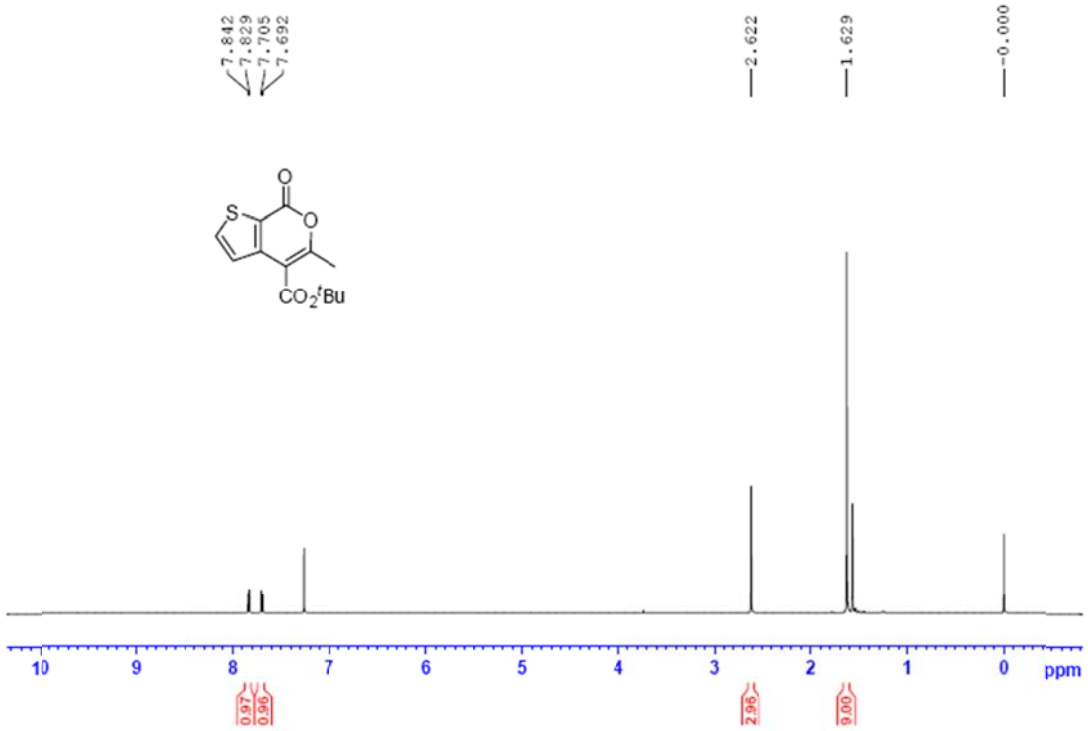
^{1}H NMR spectra of *tert*-Butyl 3-methyl-1-oxo-1*H*-benzo[*g*]isochromene-4 -carboxylate (3m).



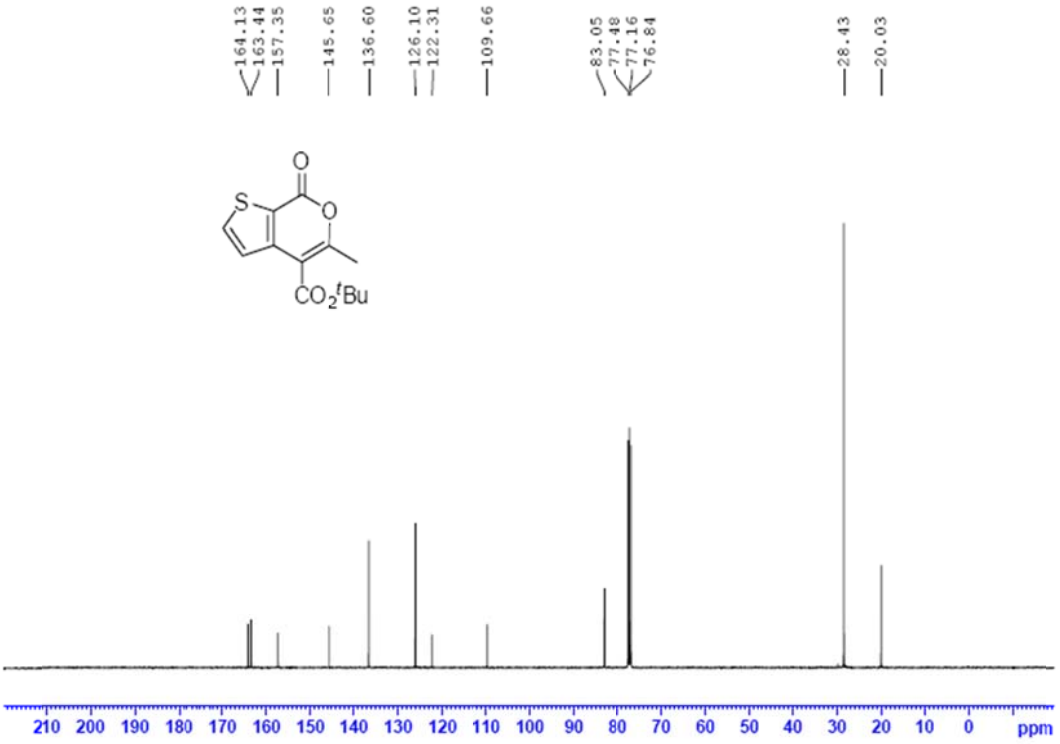
^{13}C NMR spectra of *tert*-Butyl 3-methyl-1-oxo-1*H*-benzo[*g*]isochromene-4 -carboxylate (3m).



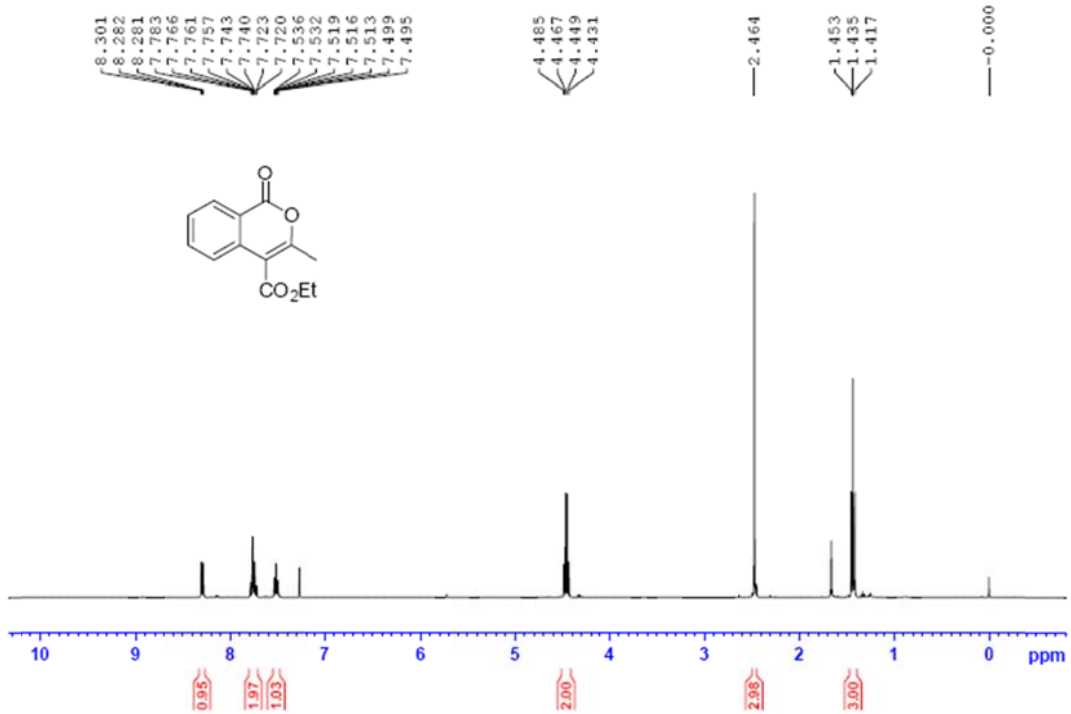
^{1}H NMR spectra of *tert*-Butyl 5-methyl-7-oxo-7*H*-thieno[2,3-c]pyran-4 -carboxylate (3n).



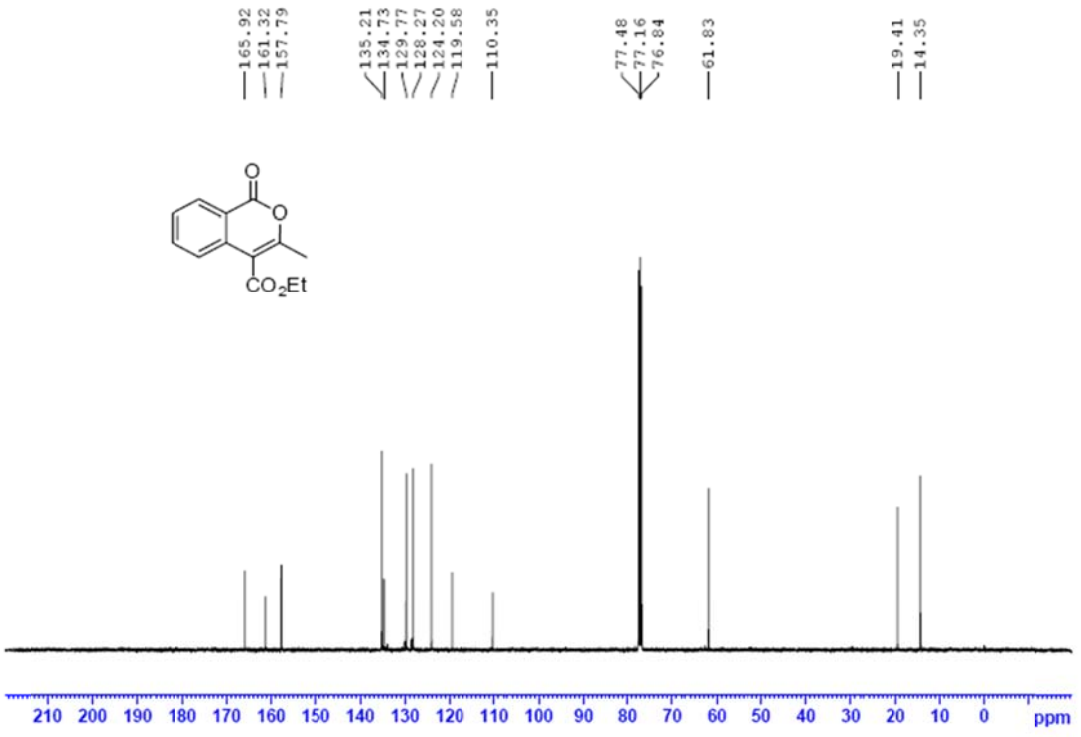
^{13}C NMR spectra of *tert*-Butyl 5-methyl-7-oxo-7*H*-thieno[2,3-c]pyran-4 -carboxylate (3n).



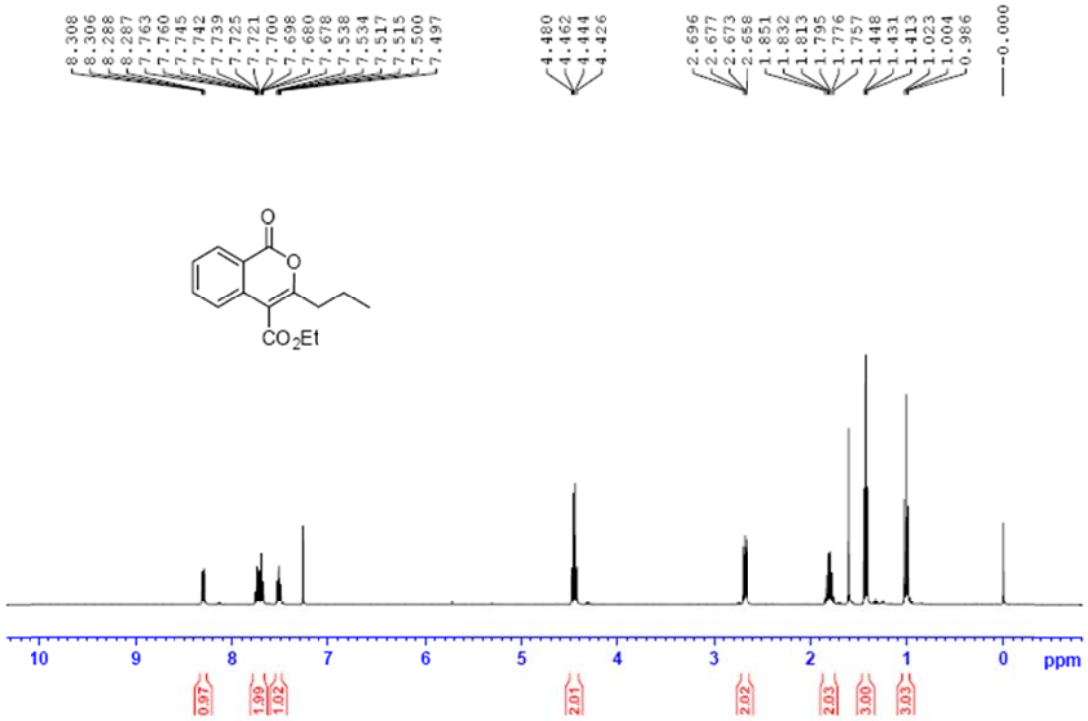
^{1}H NMR spectra of Ethyl 3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3o).



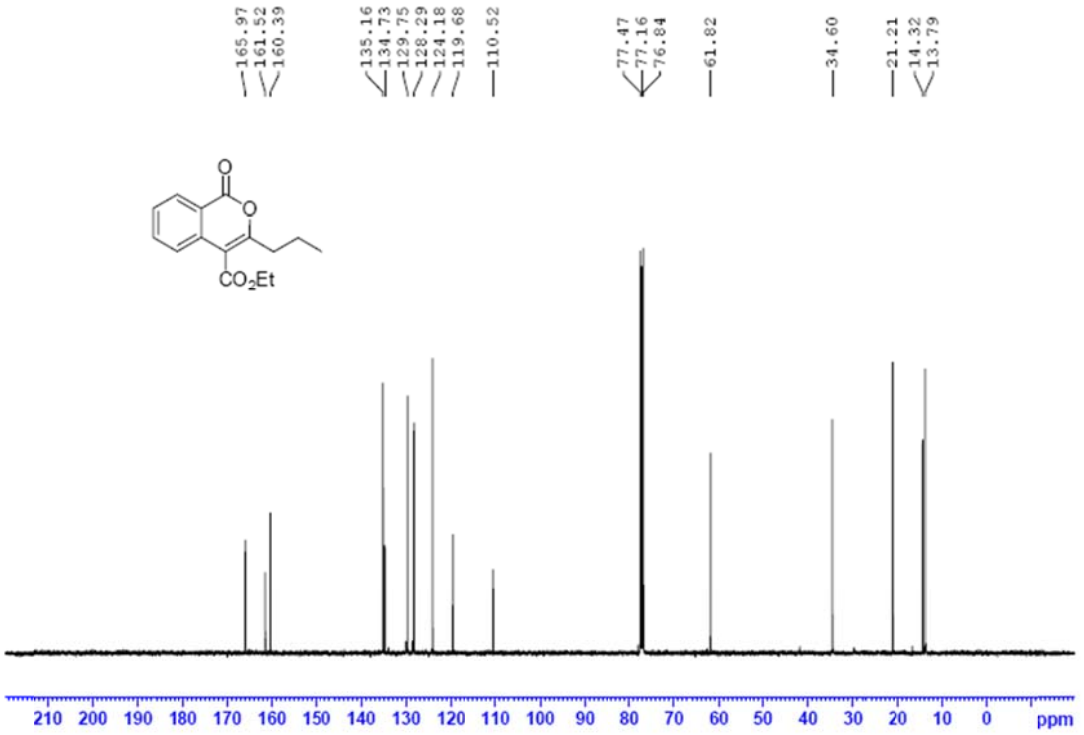
^{13}C NMR spectra of Ethyl 3-methyl-1-oxo-1*H*-isochromene-4-carboxylate (3o).



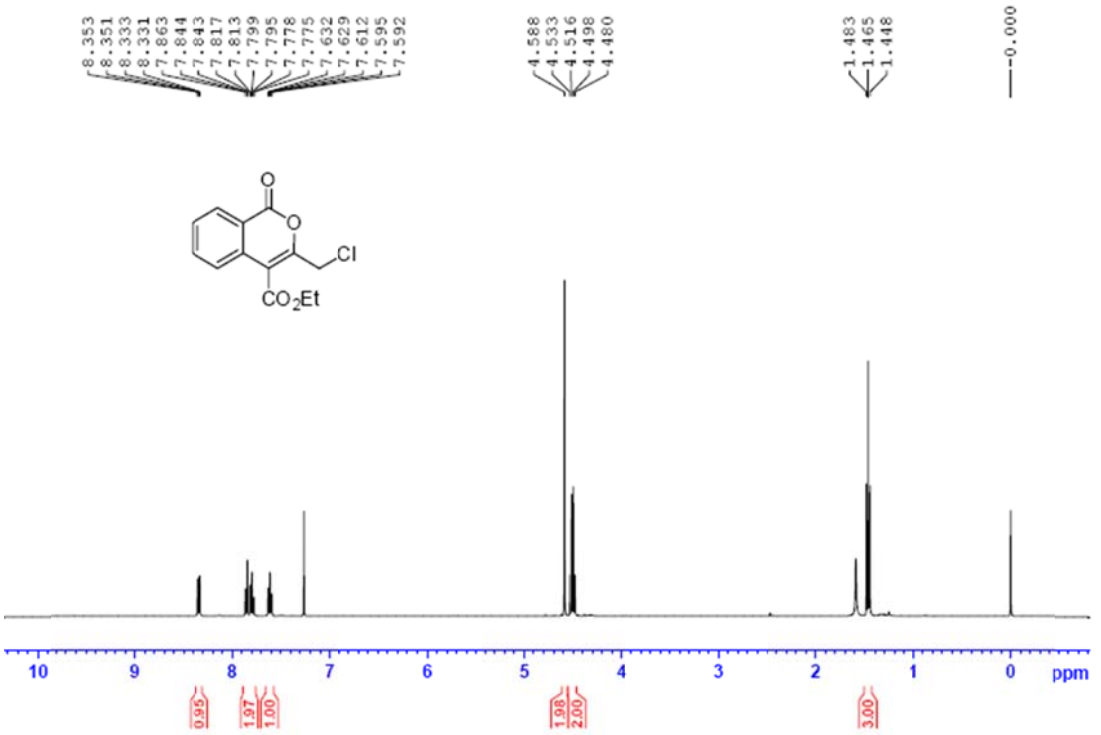
^{1}H NMR spectra of Ethyl 1-oxo-3-propyl-1*H*-isochromene-4-carboxylate (3p).



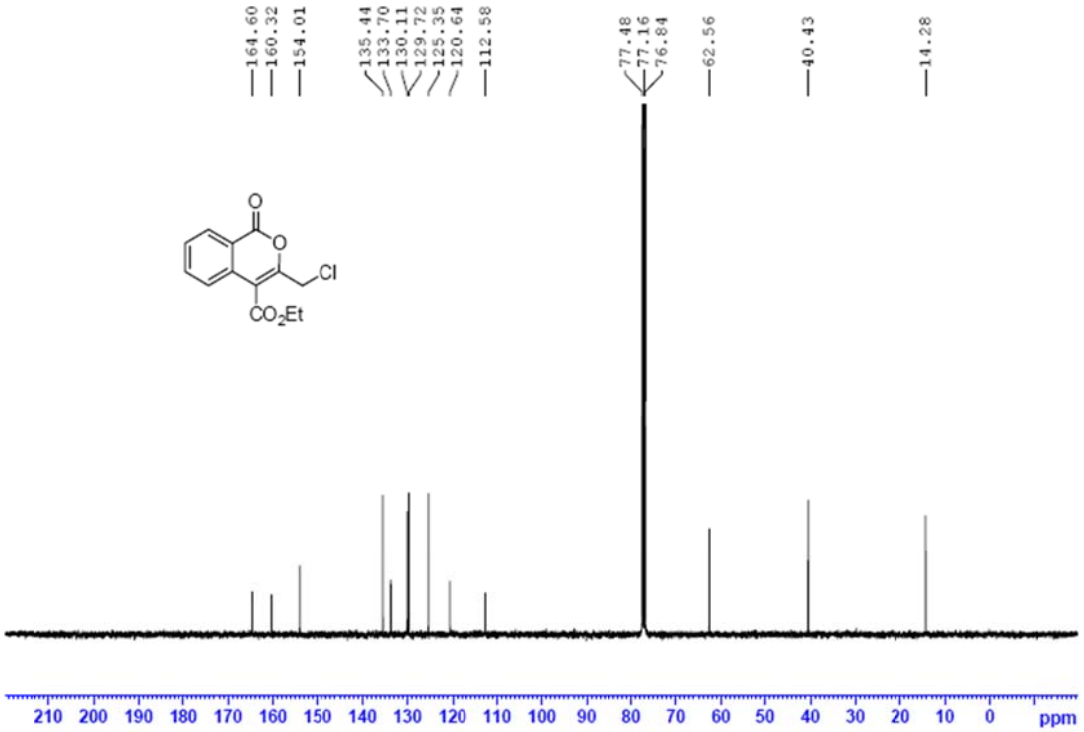
^{13}C NMR spectra of Ethyl 1-oxo-3-propyl-1*H*-isochromene-4-carboxylate (3p).



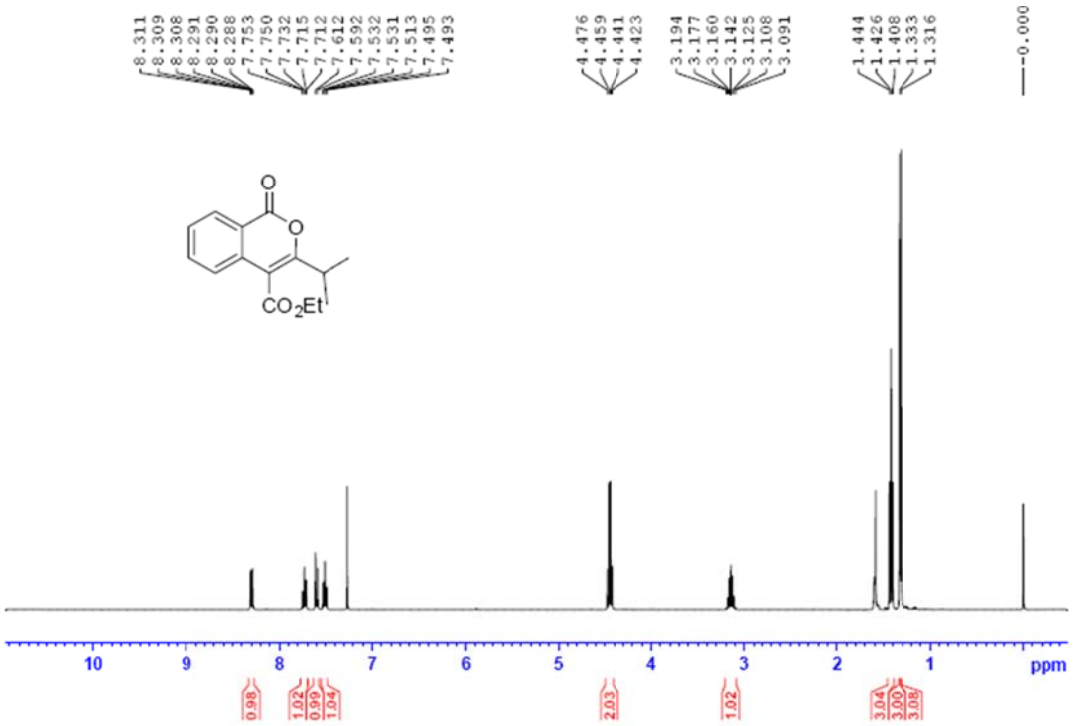
^{1}H NMR spectra of Ethyl 3-(chloromethyl)-1-oxo-1*H*-isochromene-4-carboxylate (3q).



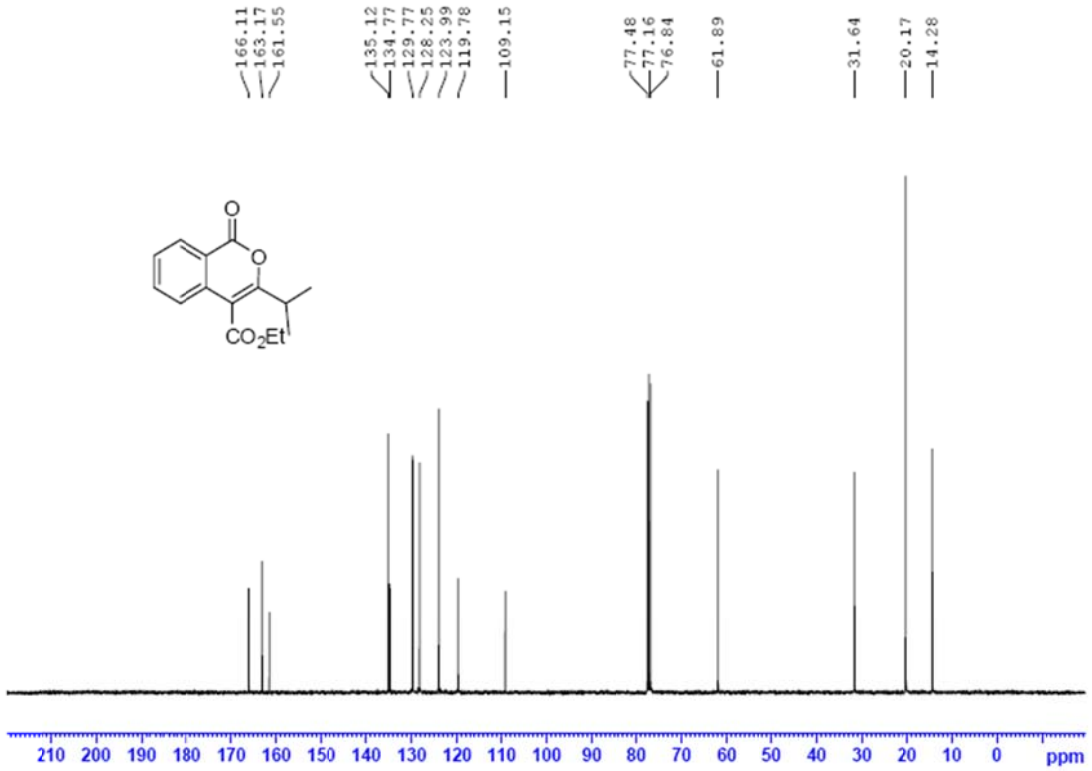
^{13}C NMR spectra of Ethyl 3-(chloromethyl)-1-oxo-1*H*-isochromene-4-carboxylate (3q).



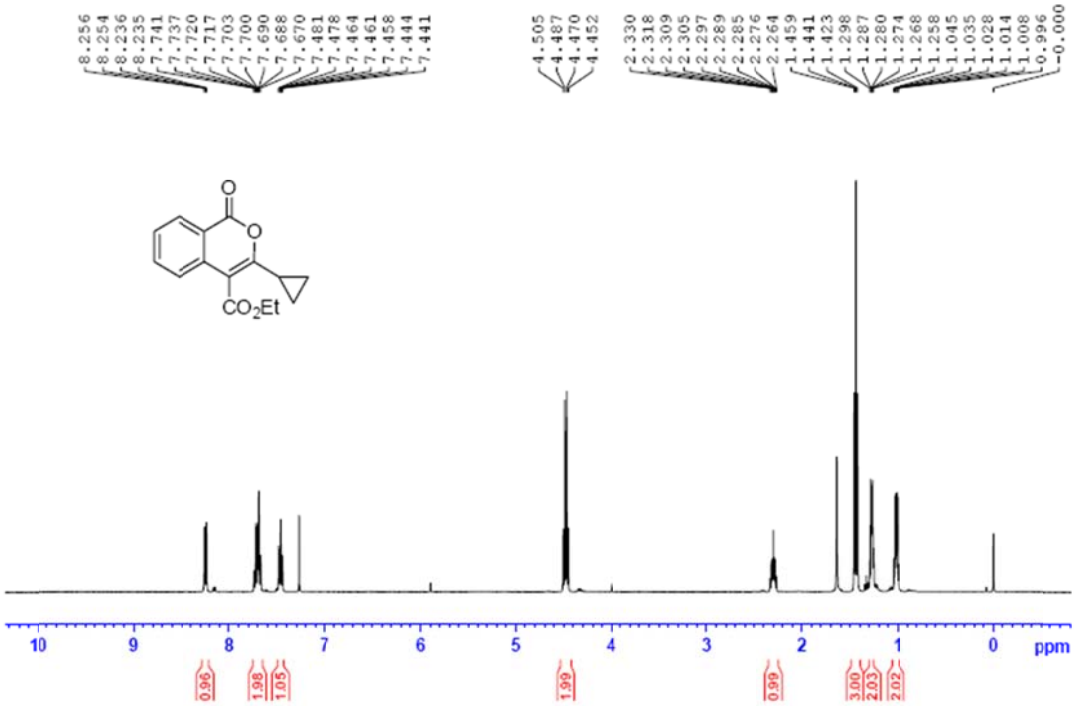
^{1}H NMR spectra of Ethyl-3-isopropyl-1-oxo-1*H*-isochromene-4-carboxylate (3r).



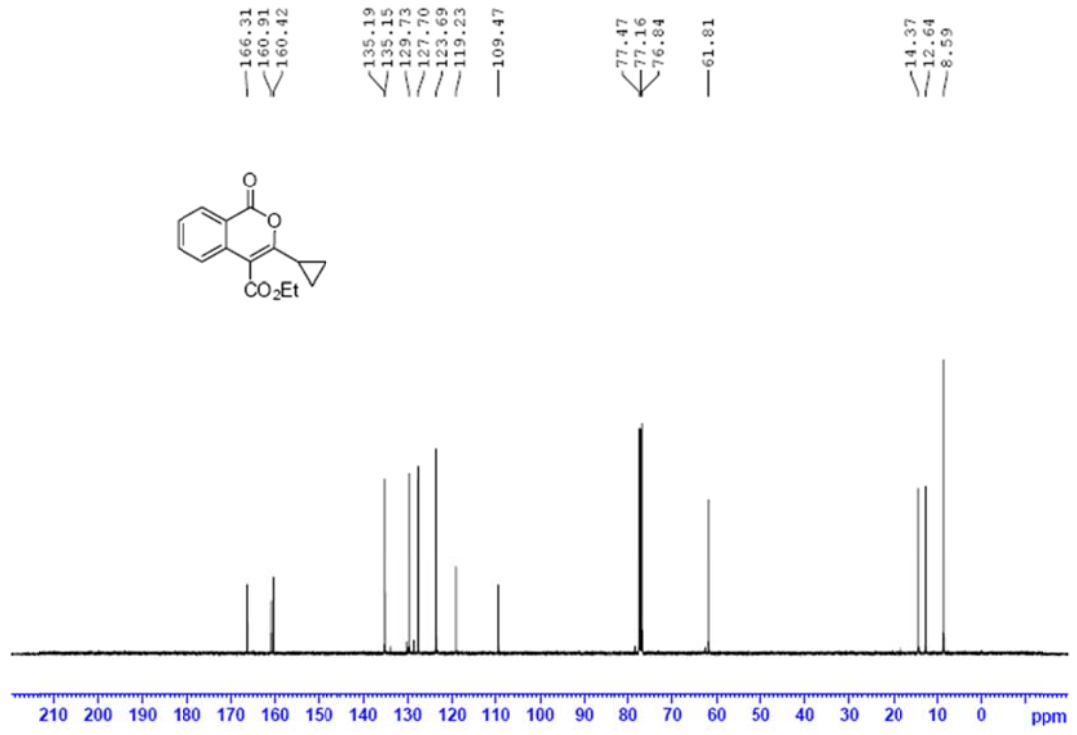
^{13}C NMR spectra of Ethyl-3-isopropyl-1-oxo-1*H*-isochromene-4-carboxylate (3r).



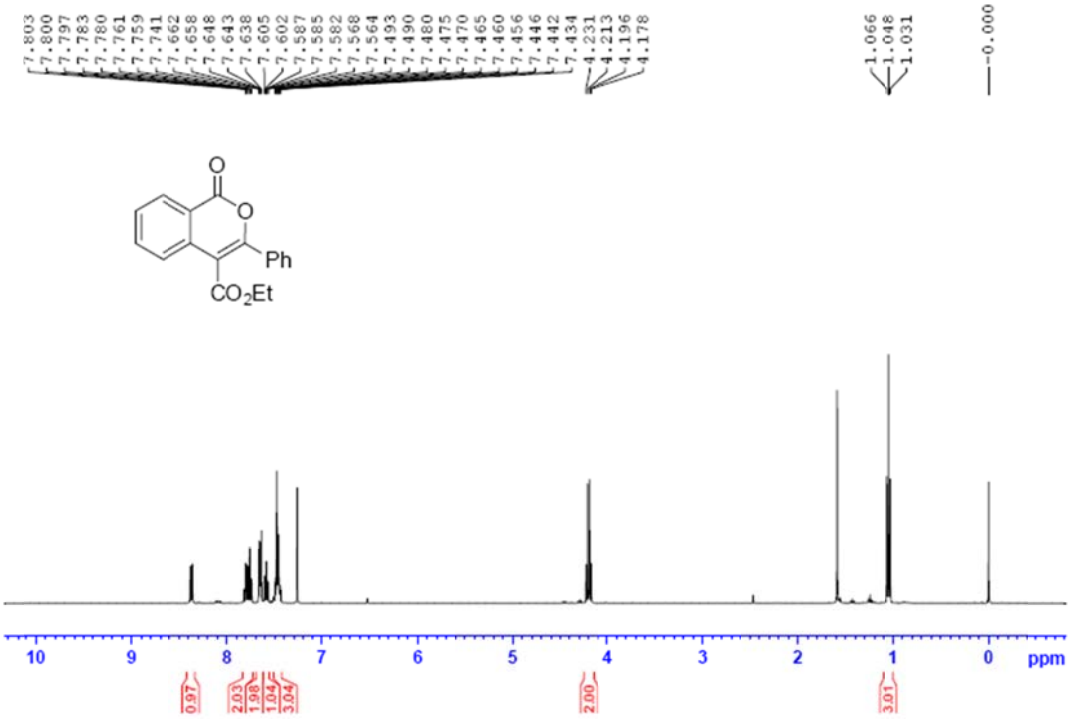
^{1}H NMR spectra of Ethyl-3-cyclopropyl-1-oxo-1*H*-isochromene-4-carboxylate (3s).



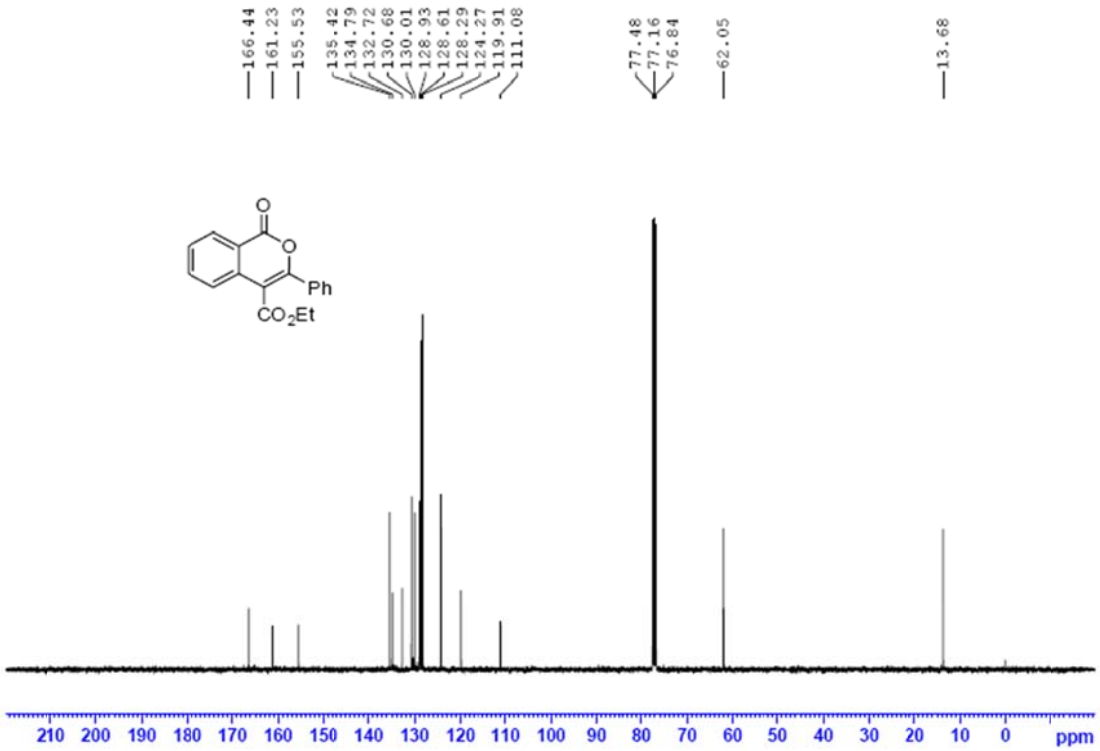
^{13}C NMR spectra of Ethyl 3-cyclopropyl-1-oxo-1*H*-isochromene-4-carboxylate (3s).



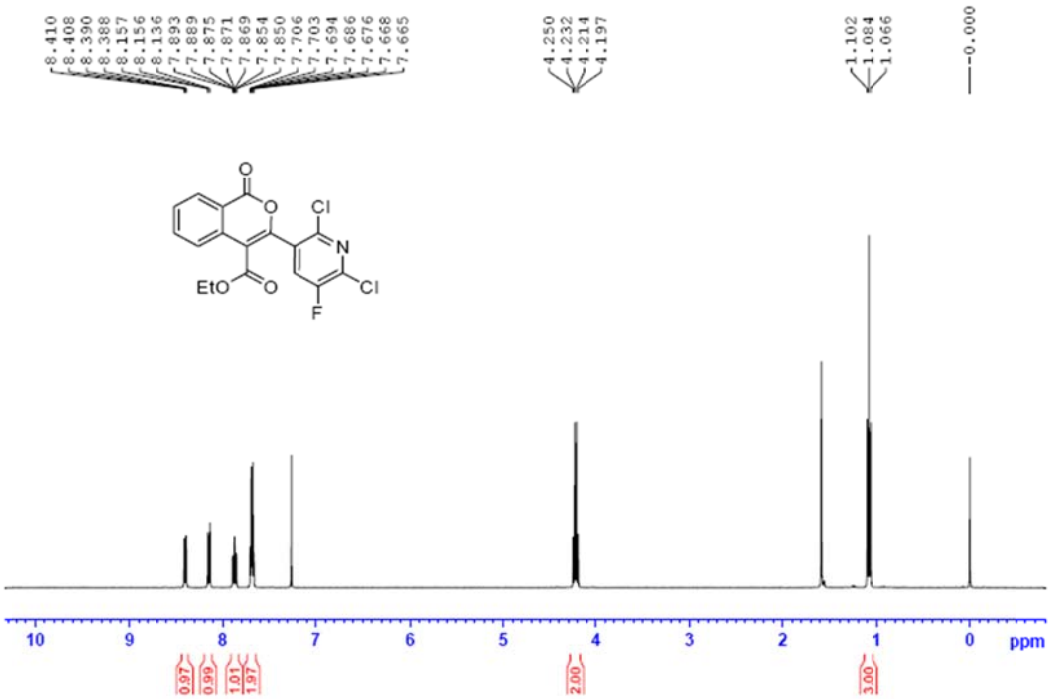
^{1}H NMR spectra of Ethyl 1-oxo-3-phenyl-1*H*-isochromene-4-carboxylate (3t).



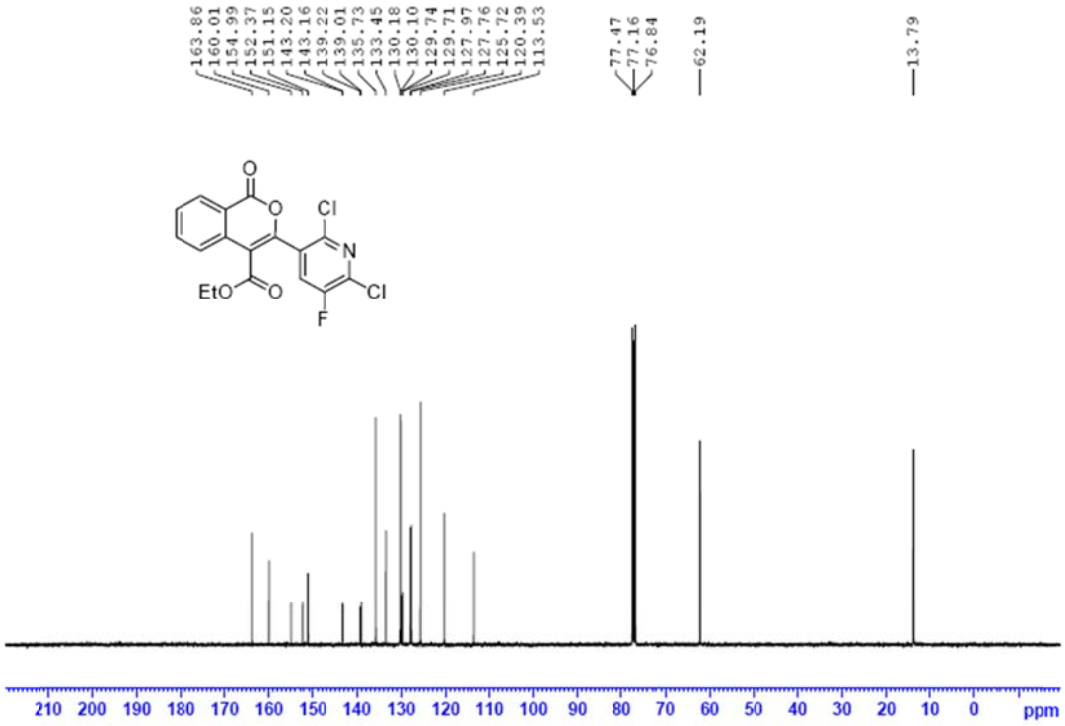
^{13}C NMR spectra of Ethyl 1-oxo-3-phenyl-1*H*-isochromene-4-carboxylate (3t).



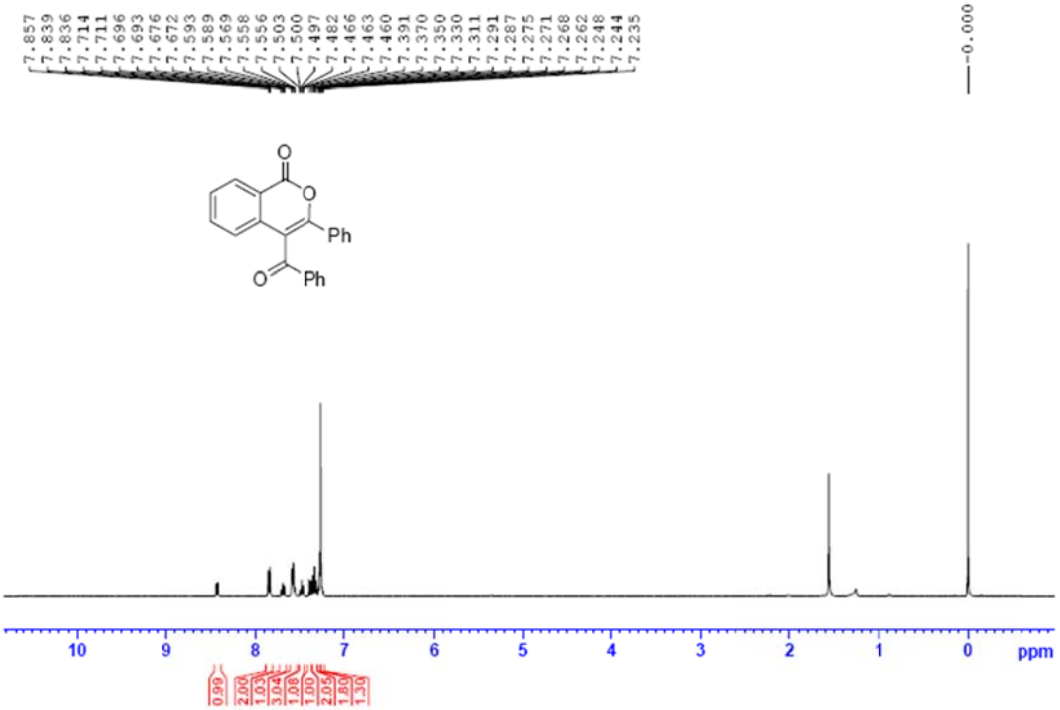
^{1}H NMR spectra of Ethyl 3-(2,6-dichloro-5-fluoropyridin-3-yl)-1-oxo-1*H*-isochromene-4-carboxylate (3u).



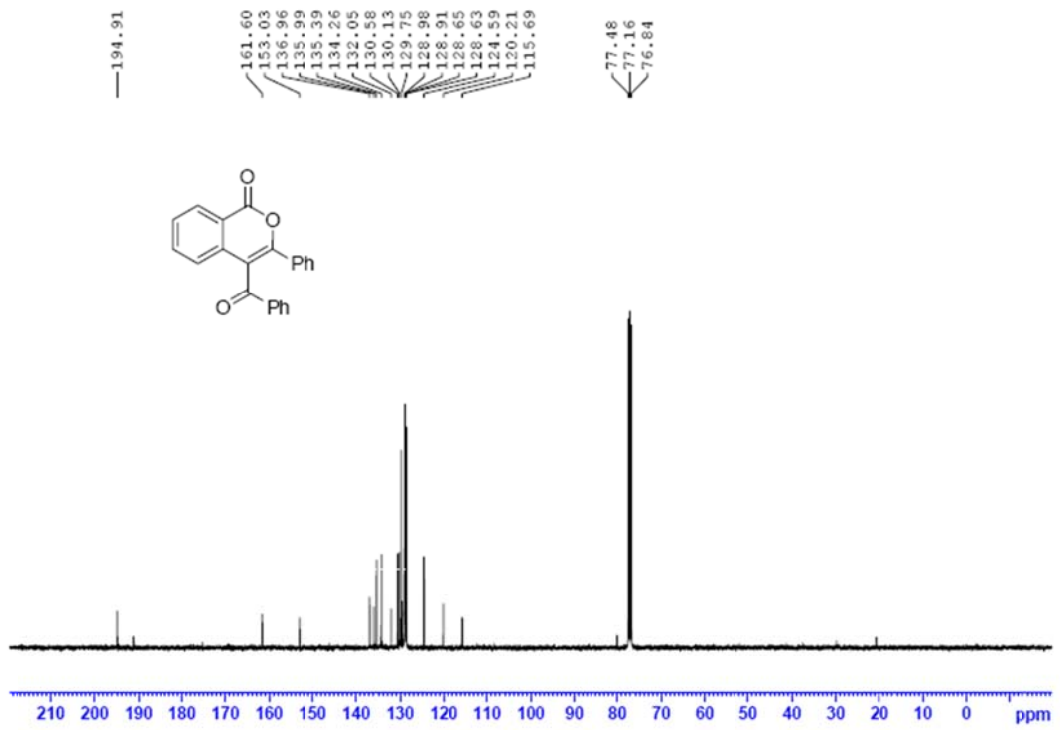
^{13}C NMR spectra of Ethyl 3-(2,6-dichloro-5-fluoropyridin-3-yl)-1-oxo-1*H*-isochromene-4-carboxylate (3u).



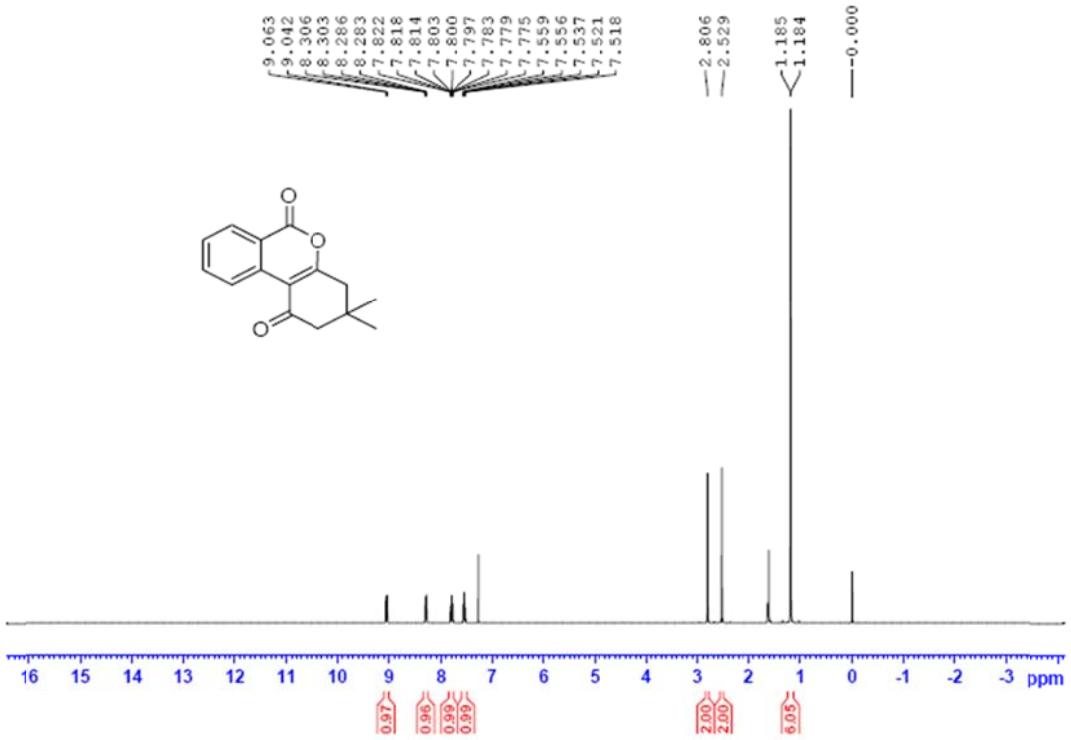
^{1}H NMR spectra of 4-Benzoyl-3-phenyl-1*H*-isochromen-1-one (3v).



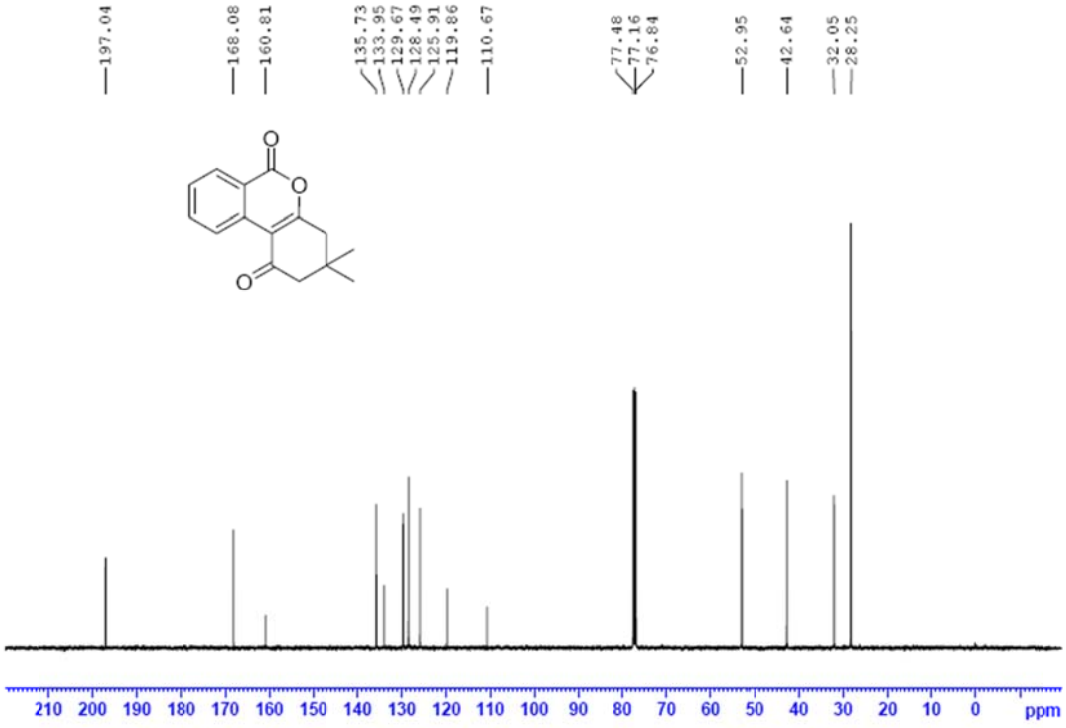
^{13}C NMR spectra of 4-Benzoyl-3-phenyl-1*H*-isochromen-1-one (3v).



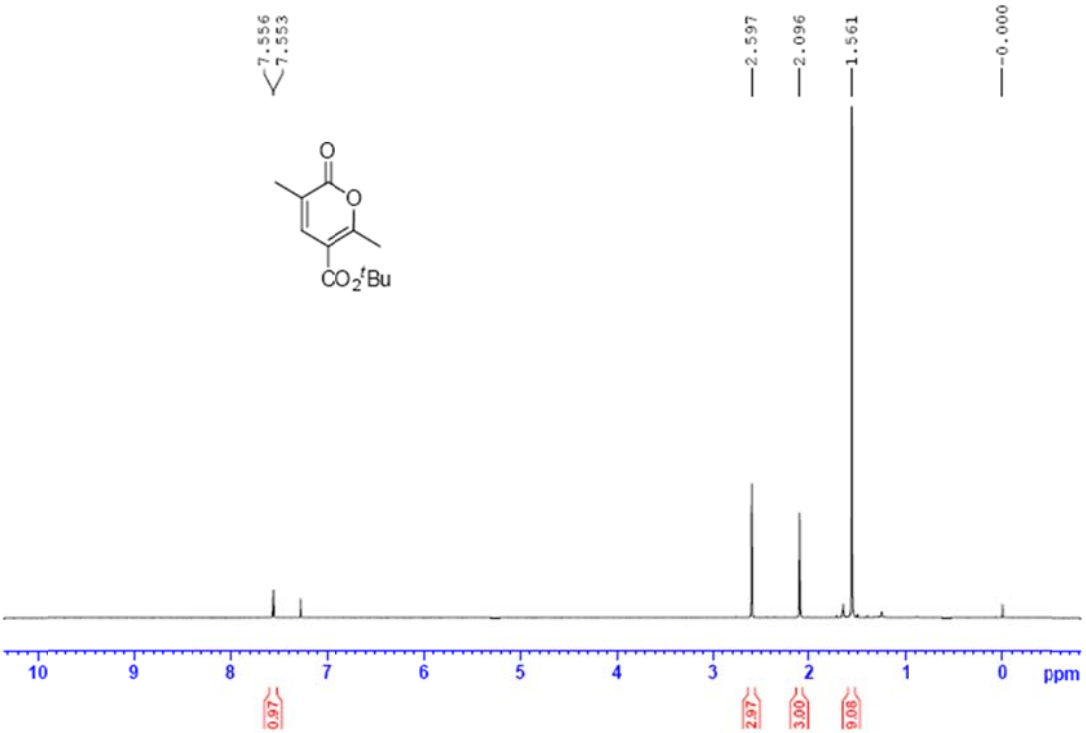
^{1}H NMR spectra of 3,3-Dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6-(2*H*)-dione (3w).



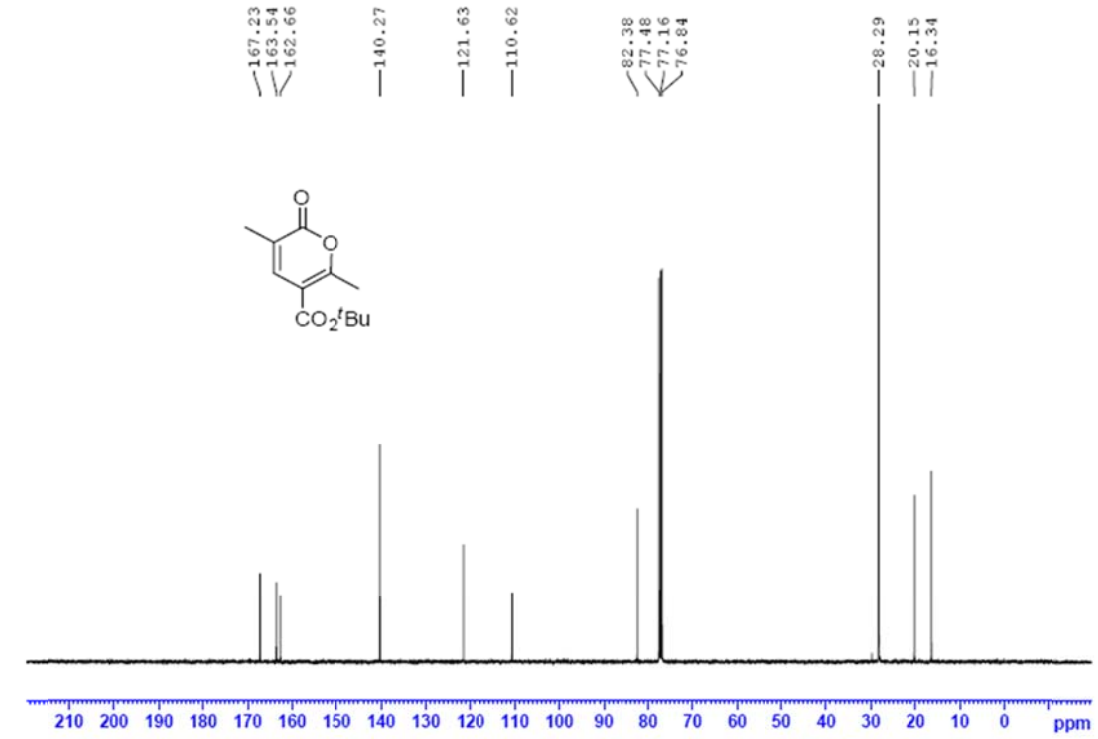
^{13}C NMR spectra of 3,3-Dimethyl-3,4-dihydro-1*H*-benzo[*c*]chromene-1,6-(2*H*)-dione (3w).



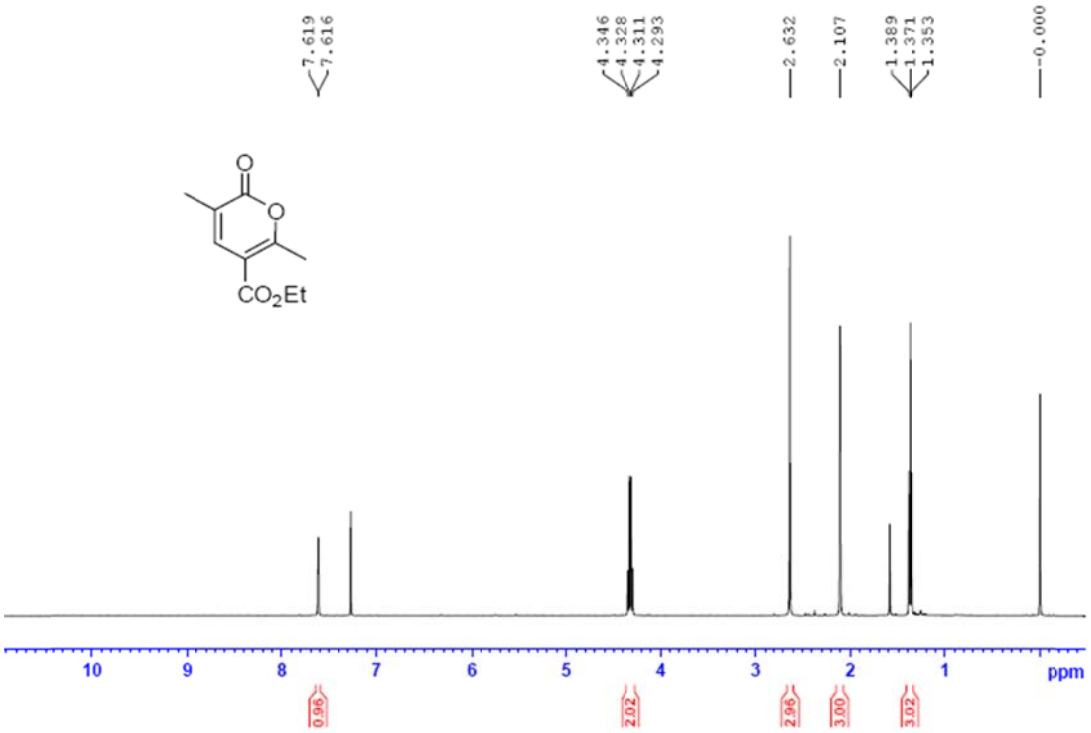
^{1}H NMR spectra of *tert*-Butyl 3,6-dimethyl-2-oxo-2*H*-pyran-5-carboxylate (4a).



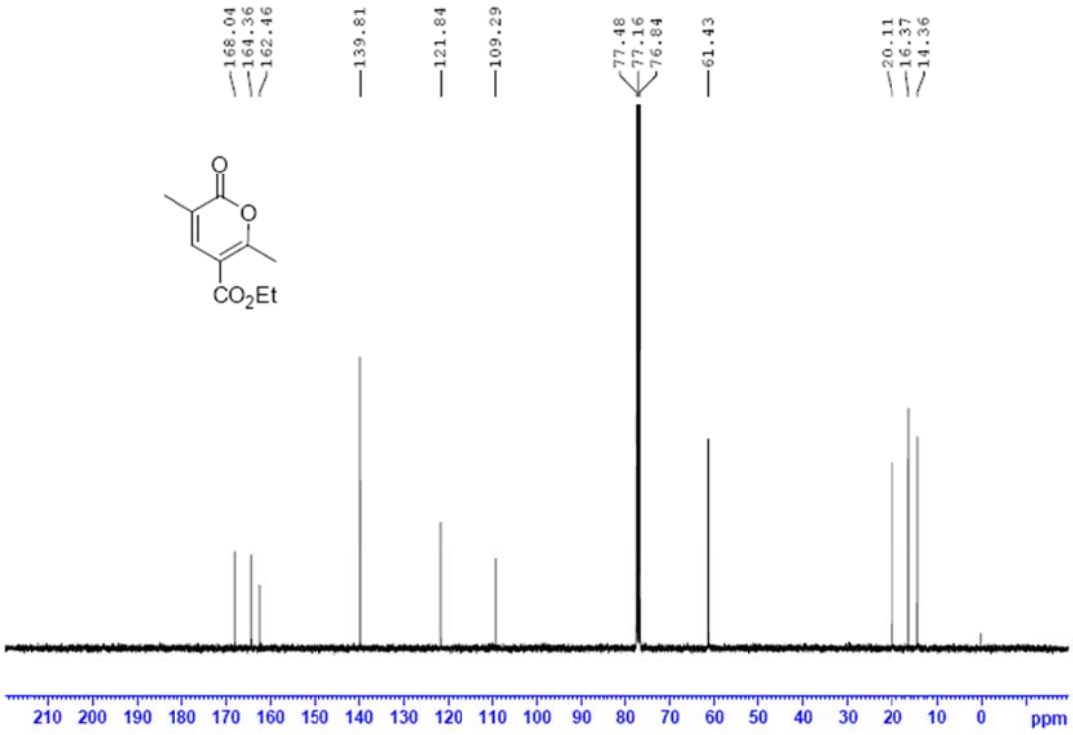
^{13}C NMR spectra of *tert*-Butyl 3,6-dimethyl-2-oxo-2*H*-pyran-5-carboxylate (4a).



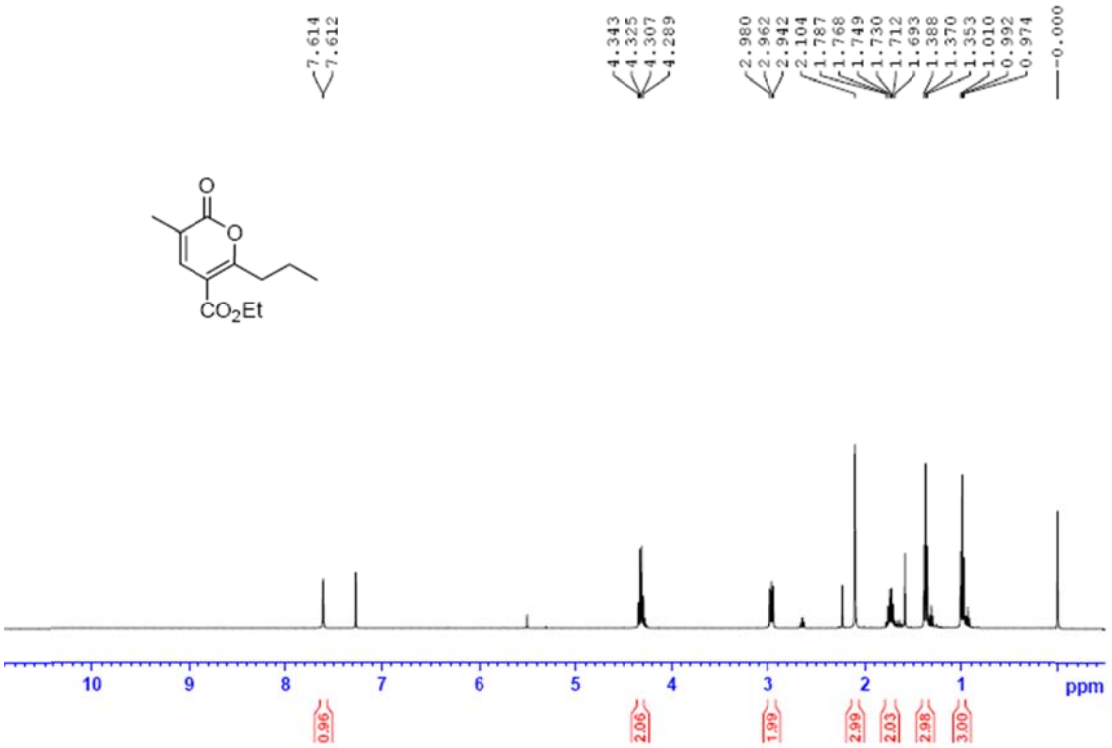
^{1}H NMR spectra of Ethyl-3,6-dimethyl-2-oxo-2*H*-pyran-5-carboxylate (4b).



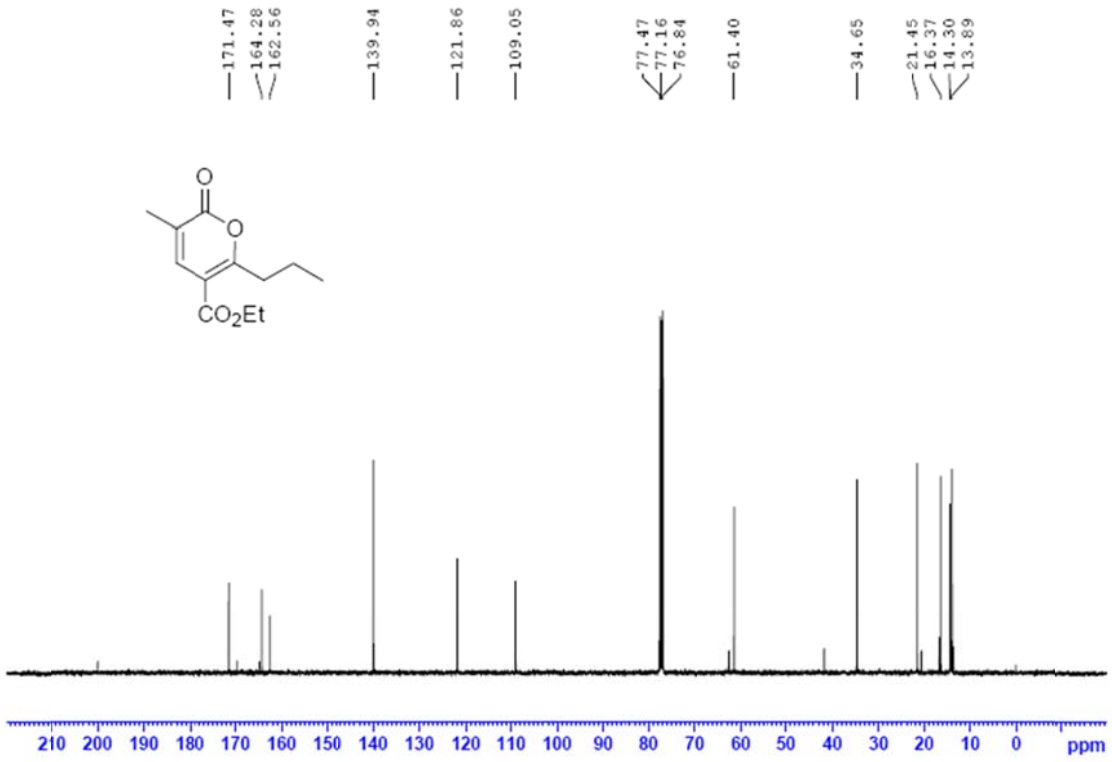
^{13}C NMR spectra of Ethyl 3,6-dimethyl-2-oxo-2*H*-pyran-5-carboxylate (4b).



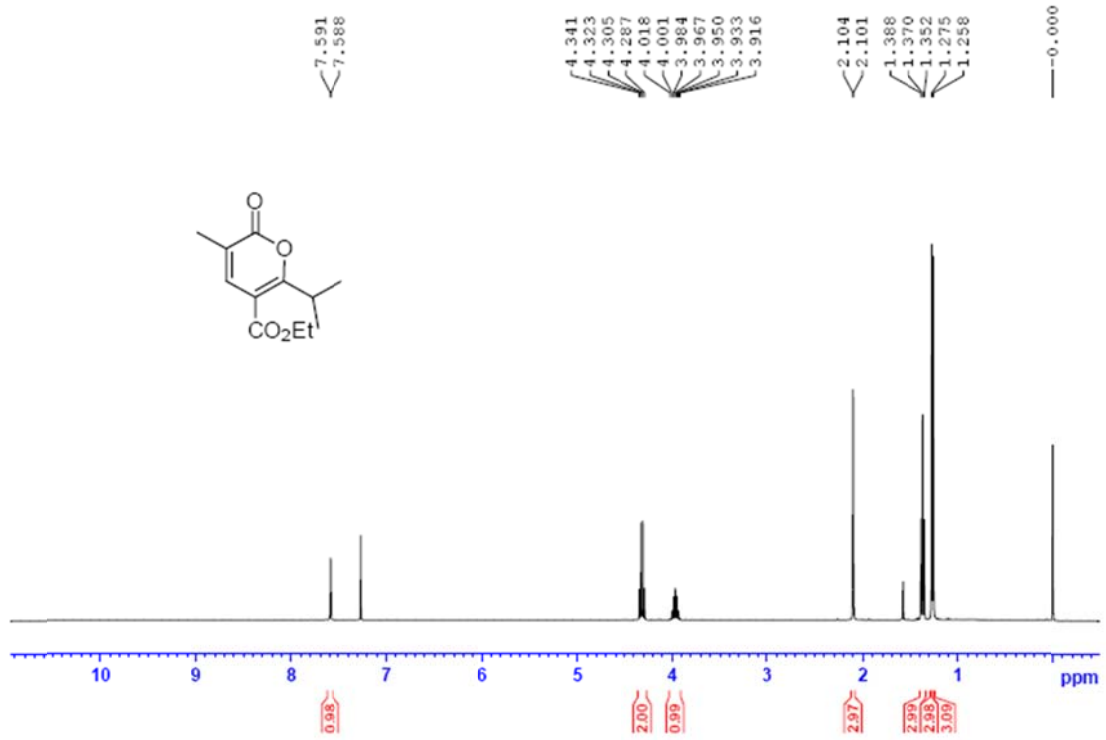
^{1}H NMR spectra of Ethyl-3-methyl-6-propyl-2-oxo-2*H*-pyran-5-carboxylate (4c).



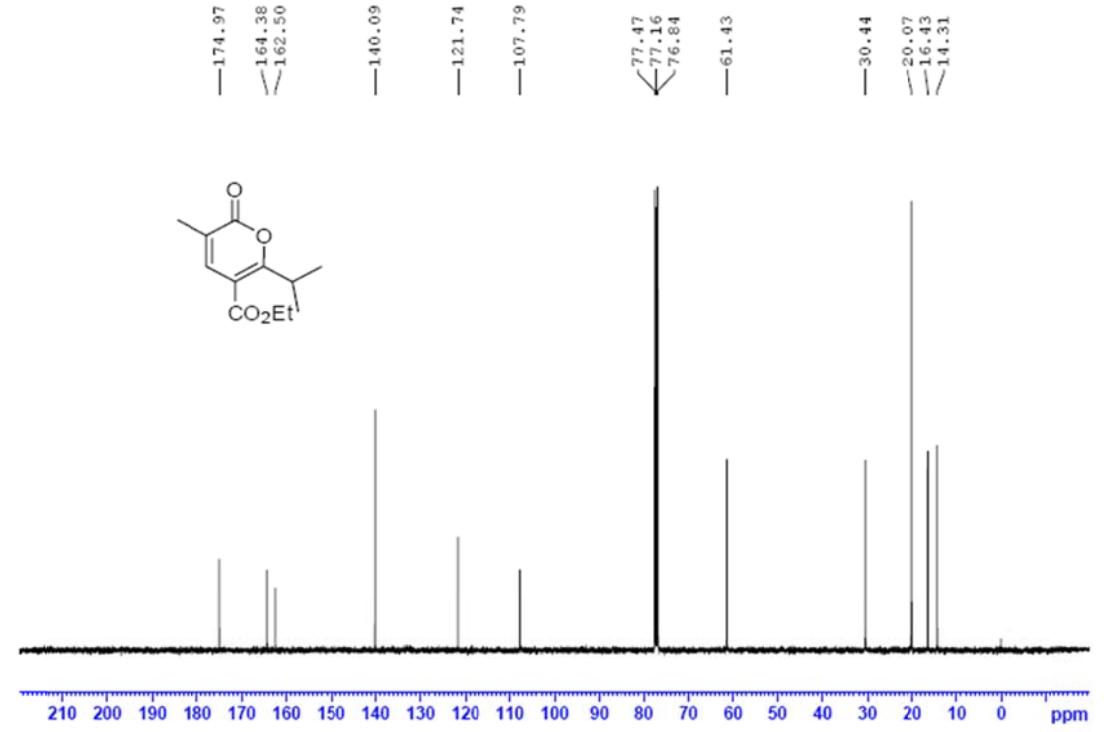
^{13}C NMR spectra of Ethyl-3-methyl-6-propyl-2-oxo-2*H*-pyran-5-carboxylate (4c).



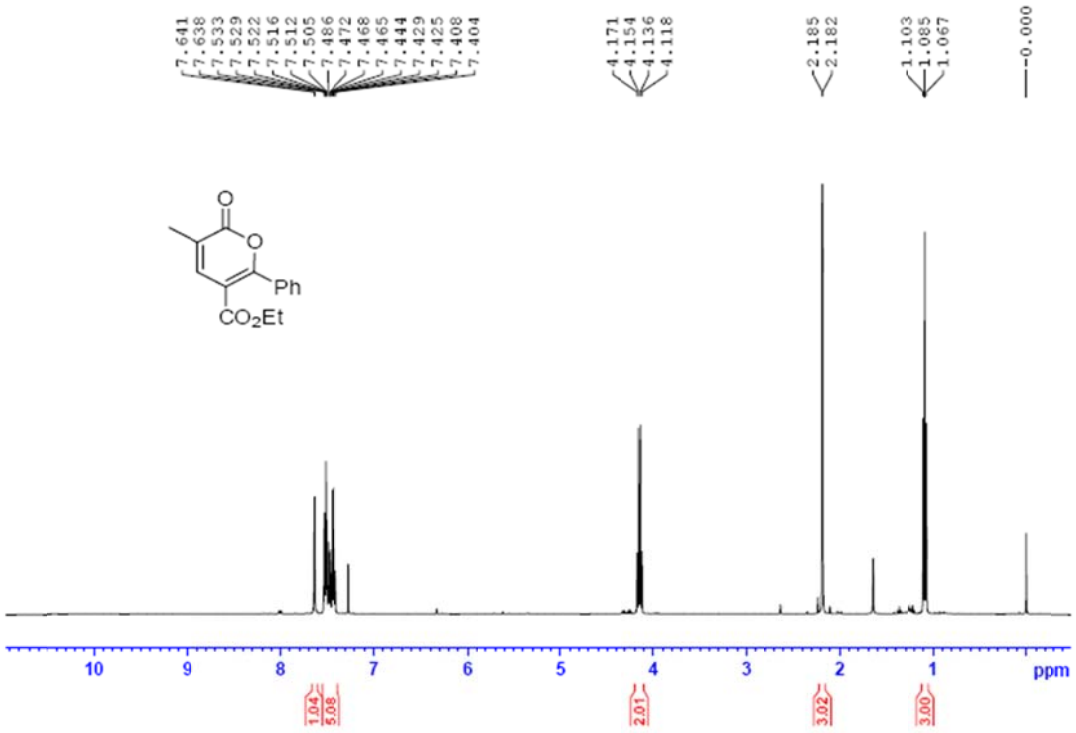
^{1}H NMR spectra of Ethyl-6-isopropyl-3-methyl-2-oxo-2*H*-pyran-5-carboxylate (4d).



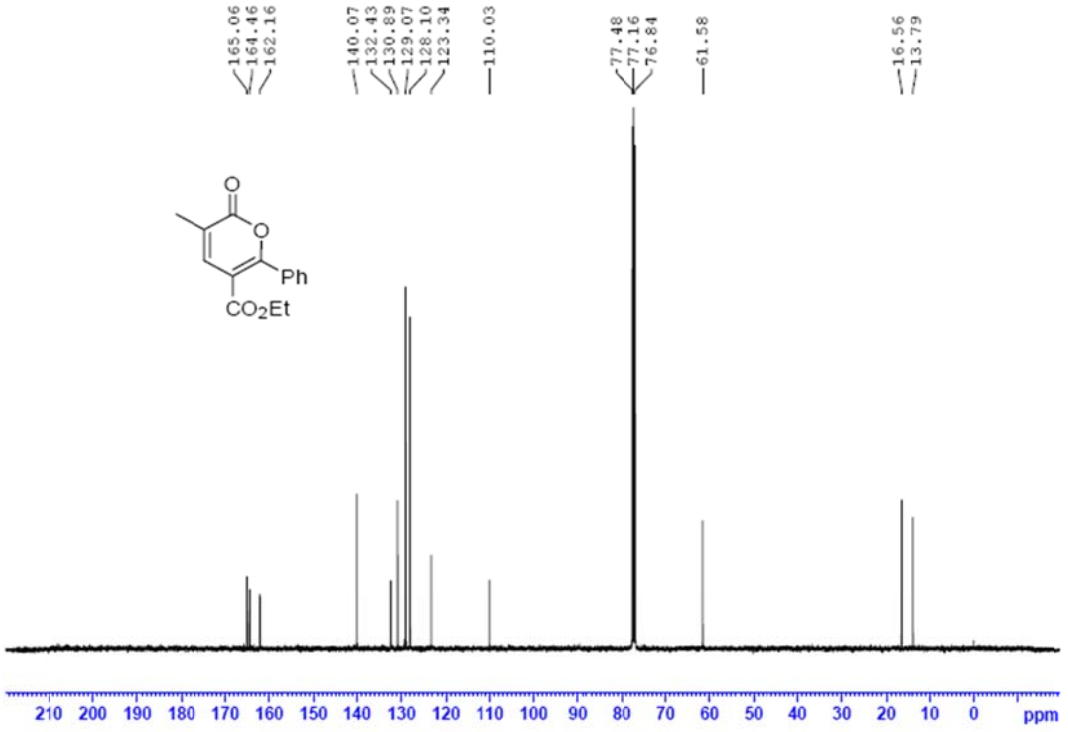
^{13}C NMR spectra of Ethyl-6-isopropyl-3-methyl-2-oxo-2*H*-pyran-5-carboxylate (4d).



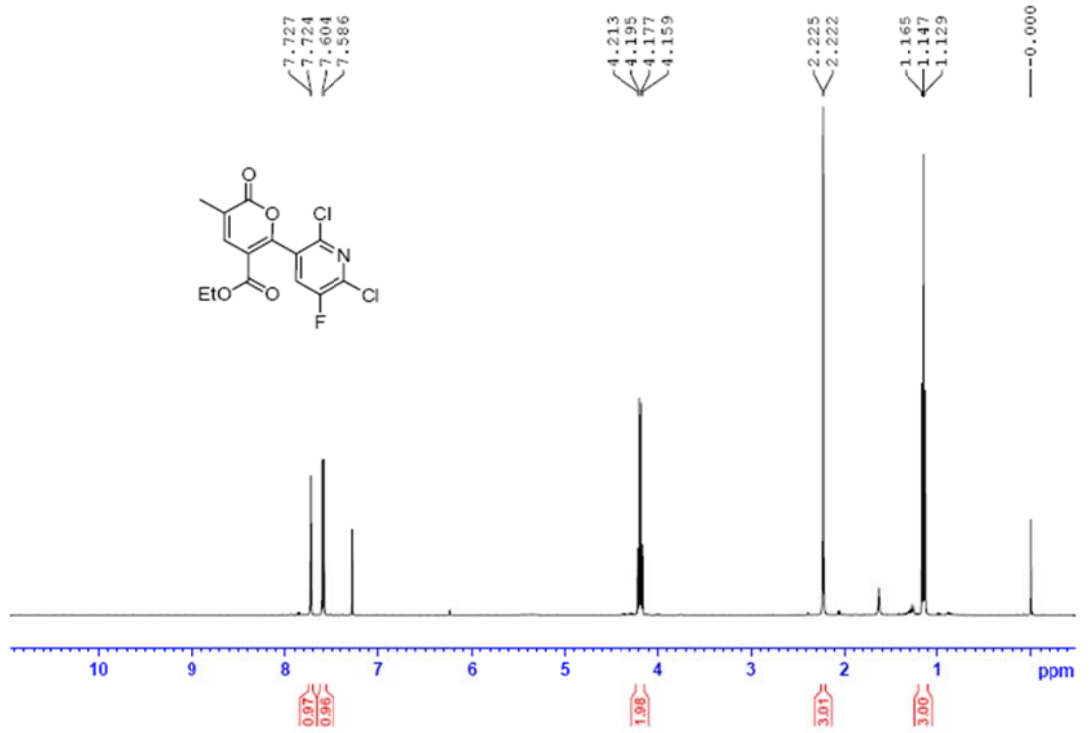
^{1}H NMR spectra of Ethyl-3-methyl-2-oxo-6-phenyl-2*H*-pyran-5-carboxylate (4e).



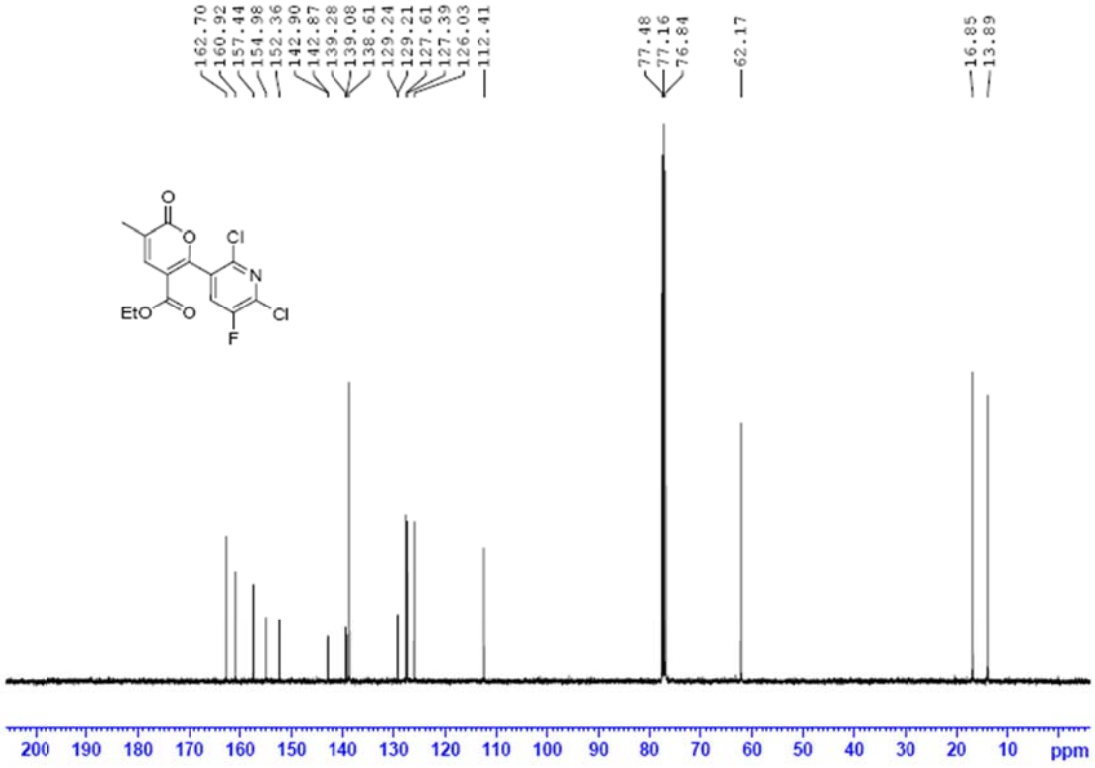
^{13}C NMR spectra of Ethyl-3-methyl-2-oxo-6-phenyl-2*H*-pyran-5-carboxylate (4e).



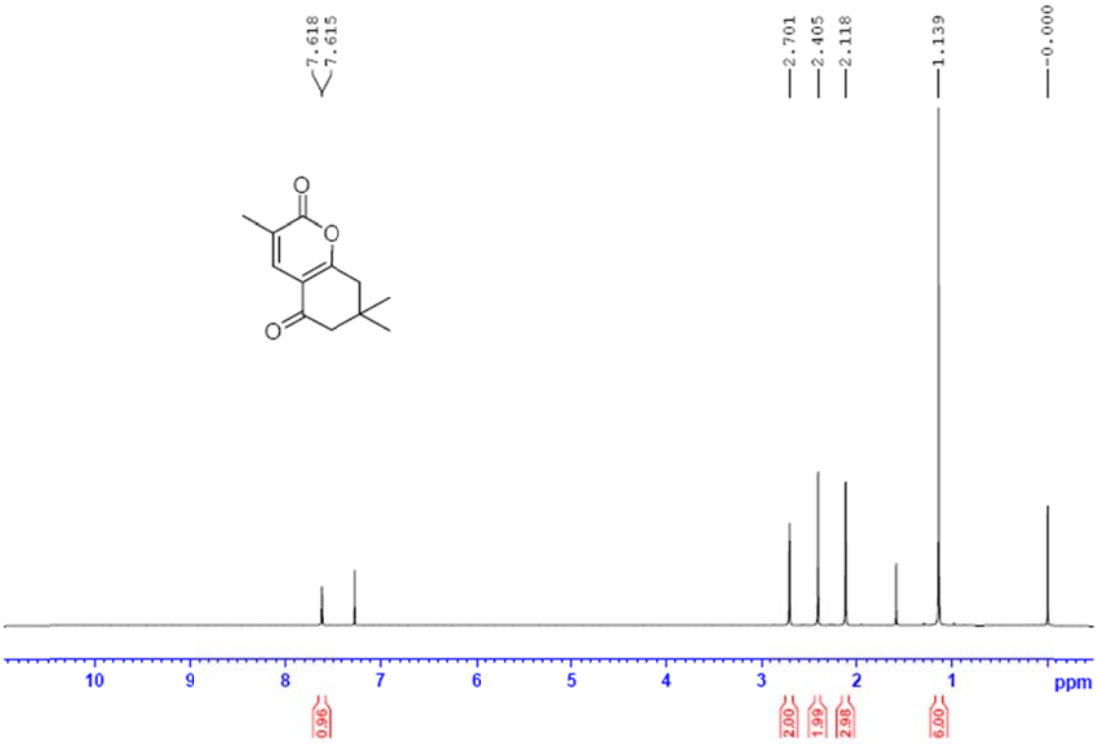
^{1}H NMR spectra of Ethyl-6-(2,6-dichloro-5-fluoropyridin-3-yl)-3-methyl-2-oxo-2*H*-pyran-5-carboxylate (4f).



^{13}C NMR spectra of Ethyl-6-(2,6-dichloro-5-fluoropyridin-3-yl)-3-methyl-2-oxo-2*H*-pyran-5-carboxylate (4f).



^{1}H NMR spectra of 3,7,7-trimethyl-7,8-dihydro-2*H*-chromene-2,5-(6*H*)-dione (4g).



^{13}C NMR spectra of 3,7,7-trimethyl-7,8-dihydro-2*H*-chromene-2,5-(6*H*)-dione (4g).