Supporting Information

Palladium(II)-Catalyzed Direct Intermolecular Alkenylation of Chromones

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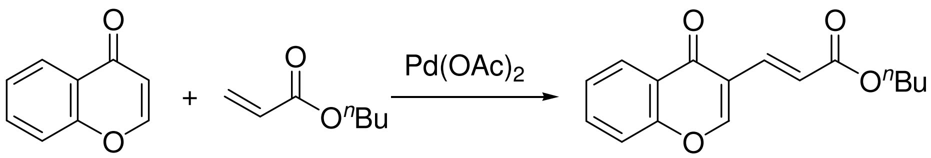
I. General Methods and Materials. Unless stated otherwise, reactions were performed in flame-dried glassware under a positive pressure of nitrogen using freshly distilled solvents. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F_{254} plates and visualization on TLC was achieved by UV light (254 and 354nm). Flash column chromatography was undertaken on silica gel (400-630 mesh). ^{1}H NMR was recorded on 400 MHz or 300 MHz and chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR was recorded on 75 MHz and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d*. Mass spectral data were obtained from the KAIST Basic Science Institute by using EI method. Commercial grade reagents and solvents were used without further purification except as indicated below. Dichloromethane was distilled from calcium hydride. THF was distilled from sodium. Unless otherwise stated, all commercial reagents and solvents were used without additional purification.

II. Optimization Study

Table S1. Screen of solvent or acid[a]



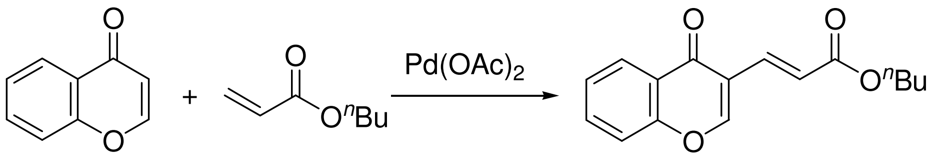
1a **5a** **2a**

Entry	Oxidant (equiv)	Solvent or acid	Base (equiv)	Yield (%)[b]
1	$Cu(OAc)_2$ (3)	DMF	K_2CO_3 (3)	trace
2	$Cu(OAc)_2$ (3)	toluene	K_2CO_3 (3)	trace
3	$Cu(OAc)_2$ (3)	acetone	K_2CO_3 (3)	nr
4	$Cu(OAc)_2$ (3)	AcOH/DMF	K_2CO_3 (3)	trace
5	$Cu(OAc)_2$ (3)	AcOH/H_2O	K_2CO_3 (3)	n.r.
6	$Cu(OAc)_2$ (3)	AcOH/MeOH	K_2CO_3 (3)	5%

7	$Cu(OAc)_2$ (3)	^{t}BuOH/AcOH/DMSO[c]	K_2CO_3 (3)	10
8	$Cu(OAc)_2$ (3)	AcOH	K_2CO_3 (3)	31
9	$Cu(OAc)_2$ (3)	TFA	K_2CO_3 (3)	18
10	$Cu(OAc)_2$ (3)	$PhCO_2H$	K_2CO_3 (3)	trace
11	$Cu(OAc)_2$ (3)	$EtCO_2H$	K_2CO_3 (3)	37
12	**$Cu(OAc)_2$ (3)**	**$^tBuCO_2H$**	**K_2CO_3 (3)**	**72**

[a] Reactions were conducted in the presence of chromone (1 equiv), n-butyl acrylate (2 equiv), $Pd(OAc)_2$ (0.1 equiv), oxidant, and base at 120°C for 24 h. [b] Yields are reported after isolation and purification by flash silica gel chromatography. DMF = *N,N*-dimethylformamide, DMSO = dimethylsulfoxide.

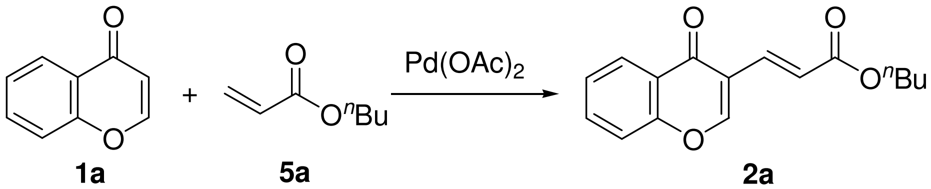
Table S2. Screen of bases.[a]



Entry	Oxidant (equiv)	Solvent or acid	Base (equiv)	Yield (%)[b]
1	$Cu(OAc)_2$ (3)	$^tBuCO_2H$	none	39
2	$Cu(OAc)_2$ (3)	$^tBuCO_2H$	K_2CO_3 (3)	72
3	$Cu(OAc)_2$ (3)	$^tBuCO_2H$	Cs_2CO_3 (3)	54
4	**$Cu(OAc)_2$ (3)**	**$^tBuCO_2H$**	**Ag_2CO_3 (3)**	**94**
5	$Cu(OAc)_2$ (3)	$^tBuCO_2H$	AgOAc (3)	25
6	$Cu(OAc)_2$ (3)	$^tBuCO_2H$	AgO_2CF_3 (3)	76
7	$Cu(OAc)_2$ (3)	$^tBuCO_2H$	AgOTf (3)	22

[a] Reactions were conducted in the presence of chromone (1 equiv), n-butyl acrylate (2 equiv), $Pd(OAc)_2$ (0.1 equiv), oxidant, and base at 120 °C for 24 h. [b] Yields are reported after isolation and purification by flash silica gel chromatography. DMF = *N,N*-dimethylformamide, DMSO = dimethylsulfoxide.

Table S3. Screen of other conditions[a]



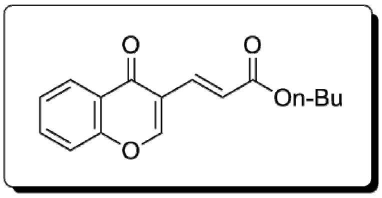
Entry	Oxidant (equiv)	Solvent or acid	Base (equiv)	Yield (%)[b]
1	$CuCl_2$ (3)	AcOH	K_2CO_3 (3)	trace
2	CuI (3)	AcOH	K_2CO_3 (3)	n.r.
3	O_2	$^tBuCO_2H$	K_2CO_3 (3)	trace
4	benzoylperoxide	$^tBuCO_2H$	K_2CO_3 (3)	trace
5	$K_3Fe(CN)_6$	$^tBuCO_2H$	K_2CO_3 (3)	trace
6	$FeCl_3$	$^tBuCO_2H$	K_2CO_3 (3)	trace
7	$Cu(OAc)_2$ (3)	$^tBuCO_2H$	K_2CO_3 (3)	72
8	$Cu(acac)_2$ (3)	$^tBuCO_2H$	Ag_2CO_3 (3)	12
9	CuO (3)	$^tBuCO_2H$	Ag_2CO_3 (3)	32
10	none	$^tBuCO_2H$	Ag_2CO_3 (3)	74
11	**$Cu(OAc)_2$ (3)**	**$^tBuCO_2H$**	**Ag_2CO_3 (3)**	**94**

[a] Reactions were conducted in the presence of chromone (2 equiv), n-butyl acrylate (1 equiv), $Pd(OAc)_2$ (0.1 equiv), oxidant, and base at 120°C for 24 h. [b] Yields are reported after isolation and purification by flash silica gel chromatography. DMF = *N,N*-dimethylformamide, DMSO = dimethylsulfoxide.

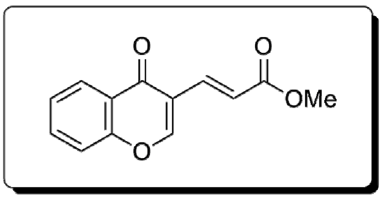
III. Experimental Procedure

General procedure (GP) for Enolone Vinylation:

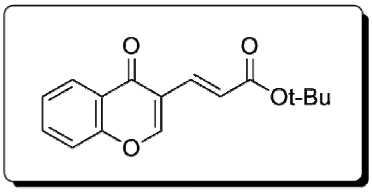
Enolone (Chromone derivatives) (1eq.), $Pd(OAc)_2$ (0.1 eq.), $Cu(OAc)_2$ (3 eq.) and Ag_2CO_3 (3 eq.) were combined in PivOH (3 ml) under N_2. The alkene (2 eq.) was added slowly and the reaction mixture was heated to 120 °C. The reaction was was monitored by TLC using 25 % EtOAc and 75 % *n*-hexane as the mobile phase. The reaction mixture was diluted with CH_2Cl_2 and the excess $NaHCO_3$ was added to neutralize PivOH. After stirring the mixture for 10 min, the residue was washed with sequencially aqueous $NaHCO_3$ and NH_4Cl. The organic layer was dried over $MgSO_4$. After removal of solvent, the residue was purified by flash chromatography on silica gel to give desired product.



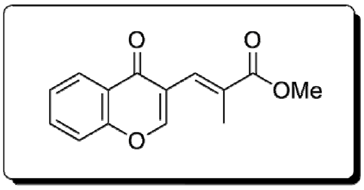
(E)-butyl-3-(4-oxo-4H-chromen-3-yl)acrylate (2a). Chromone (50 mg, 0.342 mmol) was reacted with *n*-butylacrylate (0.097 ml, 0.683 mmol) according to GP for 5 h. The residue was purified by flash column chromatography (EtOAc : *n*-hexane = 1 : 3) to produce the desired product (86.5 mg, 94%) as white solid, m.p. 71-73 °C; ^{1}H NMR δ (400 MHz, $CDCl_3$): 0.926 (t, 3H, *J* = 7.3 Hz), 1.39 (sextet, 2H, *J* = 7.6 Hz), 1.65 (quintet, 2H, *J* = 7.6 Hz), 4.16 (t, 2H, *J* = 6.4 Hz), 7.24 (d, 1H, *J* = 16 Hz), 7.35 (d, 1H, *J* = 16 Hz), 7.43 (q, 2H, 8 Hz), 7.66 (td, 1H, *J* = 7.2, 1.6 Hz), 8.08 (s, 1H), 8.23 (dd, 1H, *J* = 8.0, 1.6 Hz); ^{13}C NMR δ (100 MHz, $CDCl_3$): 13.84, 19.30, 30.86, 64.53, 118.23, 119.50, 122.42, 124.35, 125.95, 126.46, 134.11, 135.39, 155.67, 157.43, 167.60, 176.03; HRMS (EI^+) m/z calcd. for $C_{16}H_{16}NaO_4^+$ $[M+Na]^+$: 295.0941, found: 295.0952.



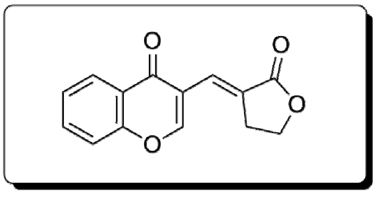
(E)-methyl-3-(4-oxo-4H-chromen-3-yl)acrylate (2b). Chromone (50 mg, 0.342 mmol) was reacted with methylacrylate (0.062 ml, 0.683 mmol) according to GP for 7 h. The residue was purified by flash column chromatography (EtOAc : *n*-hexane = 1 : 3) to produce the desired product (74 mg, 94%) as yellowish solid, m.p. 138-139 °C (lit.,[1] 139-140 °C); ^{1}H NMR δ (400 MHz, $CDCl_3$): 3.77 (s, 3H), 7.26 (d, 1H, *J* = 15.6 Hz), 7.37 (d, 1H, *J* = 15.6 Hz), 7.44 (q, 2H, *J* = 7.6 Hz), 7.67 (td, 1H, *J* = 7.2, 1.6 Hz), 8.09 (s, 1H), 8.24 (dd, 1H, *J* = 8.0, 1.6 Hz); ^{13}C NMR δ (100 MHz, $CDCl_3$): 51.83, 118.25, 119.46, 121.95, 124.37, 126.00, 126.50, 134.15, 135.77, 155.69, 157.53, 167.98, 176.04; HRMS (EI^+) m/z calcd. for $C_{13}H_{10}NaO_4^+$ $[M+Na]^+$: 253.0471, found: 253.0479.



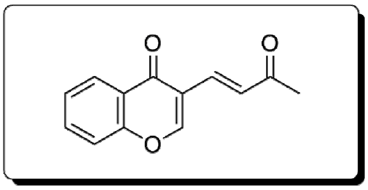
(E)-tert-butyl-3-(4-oxo-4H-chromen-3-yl)acrylate (2c). Chromone (50 mg, 0.342 mmol) was reacted with *t*-butylacrylate (0.010 ml, 0.683 mmol) according to GP for 4 h 30 min. The residue was purified by flash column chromatography (CH_2Cl_2) to produce the desired product (85 mg, 92%) as white solid, m.p. 93-95 °C; ^{1}H NMR δ (400 MHz, $CDCl_3$): 1.47 (s, 9H), 7.10 (d, 1H, *J* = 15.6 Hz), 7.24 (d, 1H, *J* = 15.6 Hz), 7.39 (q, 2H, *J* = 8.8 Hz), 7.62 (td, *J* = 7.2, 1.6 Hz), 8.04 (s, 1H), 8.19 (dd, *J* = 8.0, 1.6 Hz); ^{13}C NMR δ (100 MHz, $CDCl_3$): 28.35, 80.49, 118.16, 119.55, 124.18, 124.25, 125.80, 126.35, 133.99, 134.24, 155.60, 157.02, 166.65, 175.96; HRMS (EI^+) m/z calcd. for $C_{16}H_{16}NaO_4^+$ $[M+Na]^+$: 295.0941, found: 295.0958.



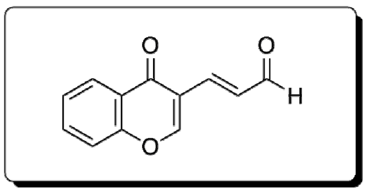
(E)-methyl-2-methyl-3-(4-oxo-4H-chromen-3-yl)acrylate (2d). Chromone (50 mg, 0.342 mmol) was reacted with methylmethacrylate (0.075 ml, 0.683 mmol) according to GP for 4 h. The residue was purified by flash column chromatography (EtOAc : *n*-hexane = 1 : 3) to produce the desired product (43 mg, 52%) as white solid, m.p. 155-158 °C; ^{1}H NMR δ (400 MHz, $CDCl_3$): 2.05 (s, 3H), 3.79 (s, 3H), 7.41 (t, 1H, *J* = 7.6 Hz), 7.44 (d, 1H, 8.4 Hz), 7.62 (s, 1H), 7.67 (td, 1H, *J* = 7.2, 1.6 Hz), 7.98 (s, 1H), 8.23 (dd, 1H, *J* = 8.0, 1.6 Hz); ^{13}C NMR δ (100 MHz, $CDCl_3$): 14.63, 52.13, 118.11, 120.84, 123.92, 125.55, 126.26, 129.00, 130.39, 133.96, 154.74, 156.08, 168.11, 176.15; HRMS (EI^+) m/z calcd. for $C_{14}H_{12}NaO_4^+$ $[M+Na]^+$: 267.0628, found: 267.0640.



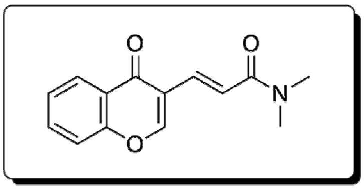
(E)-3-((2-oxodihydrofuran-3(2H)-ylidene)methyl)-4H-chromen-4-one (2e). Chromone (50 mg, 0.342 mmol) was reacted with methylvinylketone (0.056 ml, 0.683 mmol) according to GP for 2 days. The residue was purified by flash column chromatography (EtOAc : *n*-hexane = 1 : 1) to produce the desired product (53.5 mg, 65%) as white solid, m.p. 164-166 °C; ^{1}H NMR δ (400 MHz, $CDCl_3$): 3.43 (s, 2H), 4.71 (d, 4.71, *J* = 1.2 Hz), 7.34 ~ 7.42 (3H), 7.63 (td, 1H, 8.8, 2.0 Hz), 8.03 (s, 1H), 8.14 (dd, 1H, *J* = 8.0, 1.6 Hz); ^{13}C NMR δ (100 MHz, $CDCl_3$): 21.85, 70.13, 118.18, 120.19, 123.78, 125.14, 125.60, 130.55, 133.64, 146.93, 153.93, 156.48, 173.96, 177.14; HRMS (EI^+) m/z calcd. for $C_{14}H_{10}NaO_4^+$ $[M+Na]^+$: 265.0471, found:265.0513.



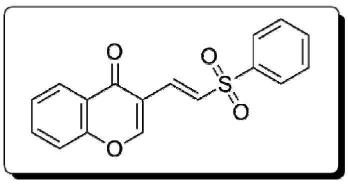
(E)-3-(3-oxobut-1-enyl)-4H-chromen-4-one (2f). Chromone (50 mg, 0.342 mmol) was reacted with methylvinylketone (0.056 ml, 0.683 mmol) according to GP for 7 h. The residue was purified by flash column chromatography (CH_2Cl_2) to produce the desired product (65 mg, 89%) as yellowish solid, m.p. 172-173 °C (lit.,[2] 173-174 °C); ^{1}H NMR δ (400 MHz, $CDCl_3$): 2.32 (s, 3H), 7.26 (d, 1H, *J* = 16 Hz), 7.39 ~ 7.46 (3H), 7.66 (td, 1H, *J* = 6.8, 1.2 Hz), 8.12 (s, 1H), 8.21 (dd, 1H, 8.0, 1.6 Hz); ^{13}C NMR δ (100 MHz, $CDCl_3$): 28.70, 118.26, 119.45, 124.18, 126.02, 126.38, 129.52, 133.69, 134.21, 155.68, 157.53, 176.03, 198.69; HRMS (EI^+) m/z calcd. for $C_{13}H_{10}NaO_3^+$ $[M+Na]^+$: 237.0522, found: 237.0529.



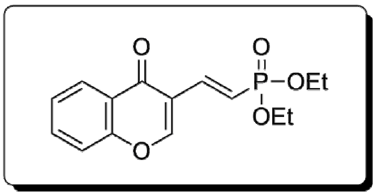
(E)-3-(4-oxo-4H-chromen-3-yl)acrylaldehyde (2g). Chromone (50 mg, 0.342 mmol) was reacted with acrolein (0.046 ml, 0.683 mmol) according to GP for 5 h. The residue was purified by flash column chromatography (EtOAc : *n*-hexane = 1 : 3) to produce the desired product (53 mg, 78%) as white solid, m.p. 135-137 °C (lit.,[3] 135-138 °C); ^{1}H NMR δ (400 MHz, $CDCl_3$): 7.23 ~ 7.34 (2H), 7.45 (t, 1H, *J* = 7.2 Hz), 7.47 (t, 1H, *J* = 8.8 Hz), 7.70 (td, 1H, *J* = 7.2, 1.6 Hz), 8.21 (s, 1H), 8.24 (dd, 1H, *J* = 8.0, 1.6 Hz), 9.63 (dd, 1H, 6.4, 0.8 Hz); ^{13}C NMR δ (100 MHz, CDCl$_3$): 118.20, 119.33, 124.03, 126.14, 126.39, 131.07, 134.31, 142.97, 155.65, 157.01, 175.32, 194.05; HRMS (EI$^+$) m/z calcd. for $C_{12}H_8NaO_3^+$ [M+Na]$^+$: 223.0366, found: 223.0360.



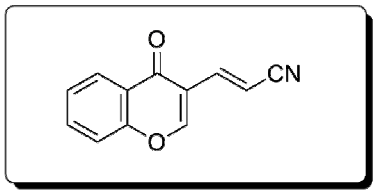
(E)-N,N-dimethyl-3-(4-oxo-4H-chromen-3-yl)acrylamide (2h). Chromone (50 mg, 0.342 mmol) was reacted with *N,N*-dimethylacrylamide (0.071 ml, 0.683 mmol) according to GP for 8 h 30 min. The residue was purified by flash column chromatography (EtOAc) to produce the desired product (68 mg, 82%) as yellowish solid, m.p. 149-150 °C; ^{1}H NMR δ (400 MHz, CDCl$_3$): 3.04 (s, 3H), 3.17 (s, 3H), 7.25 (d, 1H, *J* = 14.8 Hz), 7.42 (t, 1H, *J* = 8 Hz), 7.44 (d, 1H, *J* = 8.8 Hz), 7.66 (td, 1H, *J* = 7.2, 1.6 Hz), 8.02 (d, 1H, *J* = 14.8 Hz), 8.07 (1H, s), 8.23 (dd, 1H, *J* = 8.0, 1.6 Hz); ^{13}C NMR δ (100 MHz, CDCl$_3$): 36.00, 37.53, 118.28, 119.77, 122.14, 124.45, 125.85, 126.28, 133.22, 134.01, 155.59, 158.04, 167.29, 176.70; HRMS (EI$^+$) m/z calcd. for $C_{14}H_{13}NNaO_3^+$ [M+Na]$^+$: 266.0788, found: 266.0806.



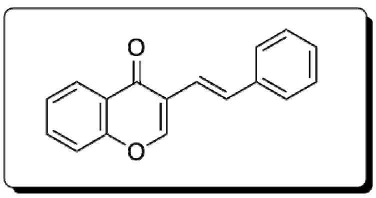
(E)-3-(2-(phenylsulfonyl)vinyl)-4H-chromen-4-one (2i). Chromone (50 mg, 0.342 mmol) was reacted with phenylvinylsulfone (115 mg, 0.683 mmol) according to GP for 21 h. Then, phenylvinylsulfone (115 mg, 0.683 mmol) was added one more time. The reaction mixture was stirred for 21 h totally. The residue was purified by flash column chromatography (EtOAc : *n*-hexane = 1 : 2) to produce the desired product (75.6 mg, 71%) as white solid, m.p. 193-194 °C (lit.,[2] 194-195 °C); ^{1}H NMR δ (400 MHz, CDCl$_3$): 7.29 (d, 1H, *J* = 14.8 Hz), 7.43 - 7.60 (m, 5H), 7.90 (d, 1H, *J* = 7.2 Hz), 8.04 (d, 1H, *J* = 14.4 Hz), 8.18 (t, 1H, 8.8 Hz); ^{13}C NMR δ (100 MHz, CDCl$_3$): 117.80, 118.34, 124.18, 126.35, 127.84, 129.41, 131.73, 133.21, 133.45, 134.50, 140.79, 155.56, 159.38, 175.80; HRMS (EI$^+$) m/z calcd. for $C_{17}H_{12}NaO_4S^+$ [M+Na]$^+$: 335.0349, found: 335.0373.



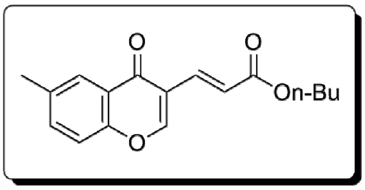
(E)-diethyl-2-(4-oxo-4H-chromen-3-yl)vinylphosphonate (2j). Chromone (50 mg, 0.342 mmol) was reacted with diethyl vinylphosphonate (0.11 ml, 0.683 mmol) according to GP for 12 h. Then, diethyl vinylphosphonate (0.11 ml, 0.683 mmol) was added one more time. The residue was purified by flash column chromatography (EtOAc). After removal of solvent, the residue was recrystallized using petroleum ether to produce the desired product (75.4 mg, 72%); ^{1}H NMR δ (400 MHz, $CDCl_3$): 1.36 (t, 6H, *J* = 7.2 Hz), 4.13 (quintet, 4H, *J* = 7.2 Hz), 7.22 (d, 1H, *J* = 16 Hz), 7.28 (d, 1H, *J* = 16 Hz), 7.48 (q, 2H), 7.71 (td, 1H, *J* = 8.0, 0.8 Hz), 8.13 (s, 1H), 8.26 (dd, 1H, *J* = 6.8, 1.2 Hz); ^{13}C NMR δ (100 MHz, $CDCl_3$): 16.44, 62.19, 118.29, 119.13, 119.34, 124.47, 125.98, 126.30, 134.17, 140.53, 155.60, 158.47, 176.31; HRMS (EI^+) m/z calcd. for $C_{15}H_{17}NaO_5P^+$ $[M+Na]^+$: 331.0706, found: 331.0769.



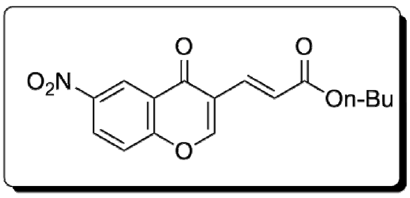
(E)-3-(4-oxo-4H-chromen-3-yl)acrylonitrile (2k). Chromone (50 mg, 0.342 mmol) was reacted with *t*-butylacrylate (0.045 ml, 0.683 mmol) according to GP for 4 h. The residue was purified by flash column chromatography (EtOAc : *n*-hexane = 1 : 3) to produce the desired product (33 mg, 49%) as as yellowish solid, m.p. 193-194 °C (lit.,[3] 194 °C) with the recovery of a starting material (23 mg, 47%); ^{1}H NMR δ (400 MHz, $CDCl_3$): 6.96 (d, 1H, *J* = 16 Hz), 7.08 (d, 1H, *J* = 16 Hz), 7.46 (q, 2H, *J* = 8.8 Hz), 7.71 (td, 1H, 7.2, 1.6 Hz), 8.05 (s, 1H), 8.22 (dd, *J* = 8.0, 1.6 Hz); ^{13}C NMR δ (100 MHz, $CDCl_3$): 101.55, 118.34, 118.46, 118.54, 124.22, 126.39, 126.42, 134.58, 141.65, 155.50, 158.05, 176.02; HRMS (EI^+) m/z calcd. for $C_{12}H_7NNaO_2^+$ $[M+Na]^+$: 220.0369, found: 220.0360.



(E)-3-styryl-4H-chromen-4-one (2l). Chromone (50 mg, 0.342 mmol) was reacted with styrene (0.080 ml, 0.683 mmol) according to GP for 4 h. The residue was purified by flash column chromatography (CH_2Cl_2 : *n*-hexane = 1 : 1) to produce the desired product (39 mg, 46%) as yellowish solid, m.p. 170-172 °C (lit.,[1] 170-171 °C); ^{1}H NMR δ (400 MHz, $CDCl_3$): 6.94 (d, 1H, *J* = 16.4 Hz), 7.24 (tt, 1H, *J* = 6.4, 1.2 Hz), 7.33 (t, 2H, *J* = 5.6 Hz), 7.40 (td, 1H, *J* = 7.2, 0.8 Hz), 7.43 (d, 1H, *J* = 8.4 Hz), 7.49 (d, 1H, *J* = 7.6 Hz), 7.59 (d, 1H, 16.4 Hz), 7.64 (td, 1H, *J* = 6.8, 1.6 Hz), 8.08 (s, 1H), 8.27 (dd, 1H, *J* = 8.0, 1.6 Hz); ^{13}C NMR δ (100 MHz, $CDCl_3$): 118.01, 118.99, 121.81, 124.09, 125.21, 126.22, 126.57, 127.82, 128.61, 131.67, 133.46, 137.34, 152.97, 155.79, 176.56; HRMS (EI^+) m/z calcd. for $C_{17}H_{12}NaO_2^+$ $[M+Na]^+$: 271.0730, found: 271.0749.

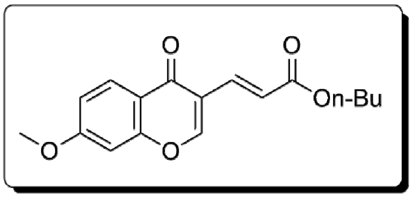


(E)-butyl-3-(6-methyl-4-oxo-4H-chromen-3-yl)acrylate (2m). 6-methylchromone (50 mg, 0.312 mmol) was reacted with *n*-butylacrylate (0.089 ml, 0.624 mmol) according to GP for 11 h. The residue was purified by flash column chromatography (CH_2Cl_2) to produce the desired product (69.4 mg, 78%) as yellowish solid m.p. 97-98 °C; ^{1}H NMR δ (400 MHz, $CDCl_3$): 0.91 (t, 3H, *J* = 7.6 Hz), 1.38 (q, 2H, *J* = 7.6 Hz), 1.64 (t, 2H, *J* = 7.6 Hz), 2.42 (s, 3H,), 4.15 (t, 2H, *J* = 7.6 Hz), 7.21 (d, 1H, *J* = 15.6 Hz), 7.31 (d, 1H, *J* = 8.4 Hz), 7.34 (d, 1H, 15.6 Hz), 7.44 (dd, 1H, *J* = 8.4, 2.0 Hz), 7.99 (d, 1H, *J* = 1.2 Hz), 8.05 (s, 1H); ^{13}C NMR δ (100 MHz, $CDCl_3$): 13.82, 19.28, 21.07, 30.86, 64.48, 117.94, 119.25, 122.09, 123.98, 125.72, 135.30, 135.58, 136.02, 153.93, 157.34, 167.62, 176.05; HRMS (EI^+) m/z calcd. for $C_{17}H_{18}NaO_4^+$ $[M+Na]^+$: 309.1097, found: 309.1235.

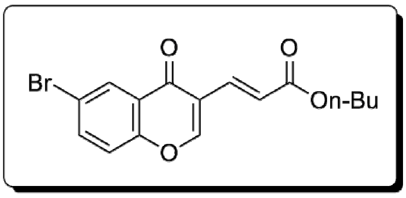


(E)-butyl-3-(6-nitro-4-oxo-4H-chromen-3-yl)acrylate (2n). 6-nitrochromone (50 mg, 0.262 mmol) was reacted with *n*-butylacrylate (0.075 ml, 0.523 mmol) according to GP for 16 h. The residue was purified by flash column chromatography (EtOAc : *n*-hexane = 1 : 2) to produce the desired product (67.3 mg, 81%) as yellowish solid, m.p. 158-160 °C; ^{1}H NMR δ (400 MHz, $CDCl_3$): 0.93 (t, 3H, *J* = 7.2 Hz), 1.40 (quintet, 2H, *J* = 7.2 Hz), 1.66 (q, 2H, *J* =

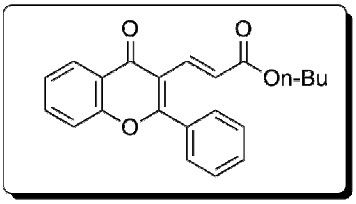
7.2 Hz), 4.18 (t, 2H, *J* = 7.2 Hz), 7.24 (d, 1H, *J* = 16 Hz), 7.33 (d, 1H, *J* = 16 Hz), 7.62 (d, 1H, *J* = 9.2 Hz), 8.14 (s, 1H), 8.48 (dd, 1H, *J* = 8.8, 2.8 Hz), 9.10 (d, 1H, *J* = 2.8 Hz); ^{13}C NMR δ (100 MHz, $CDCl_3$): 13.82, 19.27, 30.82, 64.78, 120.09, 120.22, 123.17, 124.03, 124.40, 128.41, 133.91, 145.35, 157.22, 158.33, 167.12, 174.49; HRMS (EI^+) m/z calcd. for $C_{16}H_{15}NNaO_6^+$ $[M+Na]^+$: 340.0792, found: 340.0795.



(E)-butyl-3-(7-methoxy-4-oxo-4H-chromen-3-yl)acrylate (2o). 7-methoxychromone (50 mg, 0.284 mmol) was reacted with *n*-butylacrylate (0.081 ml, 0.568 mmol) according to GP for 9 h 30 min. The residue was purified by flash column chromatography (EtOAc : *n*-hexane = 1 : 3) to produce the desired product (70.4 mg, 82%) as yellowish solid, m.p. 84-85 °C; ^{1}H NMR δ (400 MHz, $CDCl_3$): 0.90 (t, 3H, *J* = 7.2 Hz), 1.35 (quintet, 2H, *J* = 7.2 Hz), 1.58 (sextet, 2H, *J* = 7.2 Hz), 3.85 (s, 3H), 4.14 (t, 2H, *J* = 7.2 Hz), 6.78 (d, 1H, *J* = 2.4 Hz), 6.92 (dd, 1H, *J* = 2.4 Hz), 7.19 (d, 1H, *J* = 15.6 Hz), 7.30 (d, 1H, *J* = 15.6 Hz), 7.98 (s, 1H), 8.08 (d, 1H, *J* = 8.8 Hz); ^{13}C NMR δ (100 MHz, $CDCl_3$): 13.79, 19.24, 30.891, 55.96, 64.43, 100.39, 115.11, 118.08, 119.21, 122.10, 127.71, 135.52, 157.00, 157.34, 164.37, 167.58, 175.33; HRMS (EI^+) m/z calcd. for $C_{17}H_{18}NaO_5^+$ $[M+Na]^+$: 325.1046, found: 325.1060.



(E)-butyl-3-(6-bromo-4-oxo-4H-chromen-3-yl)acrylate (2p). 6-Bromochromone (50 mg, 0.222 mmol) was reacted with *n*-butylacrylate (0.065 ml, 0.444 mmol) according to GP for 11 h. The residue was purified by flash column chromatography (EtOAc : *n*-hexane = 2 : 9) to produce the desired product (72 mg, 93%) as white solid, m.p. 124-127 °C; ^{1}H NMR δ (400 MHz, $CDCl_3$): 0.92 (t, 3H, *J* = 7.2 Hz), 1.37 (sextet, 2H, *J* = 7.2 Hz), 1.63 (quintet, 2H, *J* = 7.2 Hz), 4.16 (t, 2H, *J* = 7.2 Hz), 7.20 (d, 1H, *J* = 16 Hz), 7.32 (d, 1H, *J* = 7.2 Hz), 7.32 (d, 1H, *J* = 16 Hz), 7.22 (dd, 1H, *J* = 9.2, 2.8 Hz), 8.08 (s, 1H), 8.33 (d, 1H, *J* = 2.4 Hz); ^{13}C NMR δ (100 MHz, $CDCl_3$): 13.83, 19.28, 30.84, 64.61, 119.47, 119.61, 120.18, 122.89, 125.56, 129.03, 134.83., 137.09, 154.39, 157.37, 167.39, 174.65; HRMS (EI^+) m/z calcd. for $C_{16}H_{15}BrNaO_4^+$ $[M+Na]^+$: 373.0046, found: 373.0052.

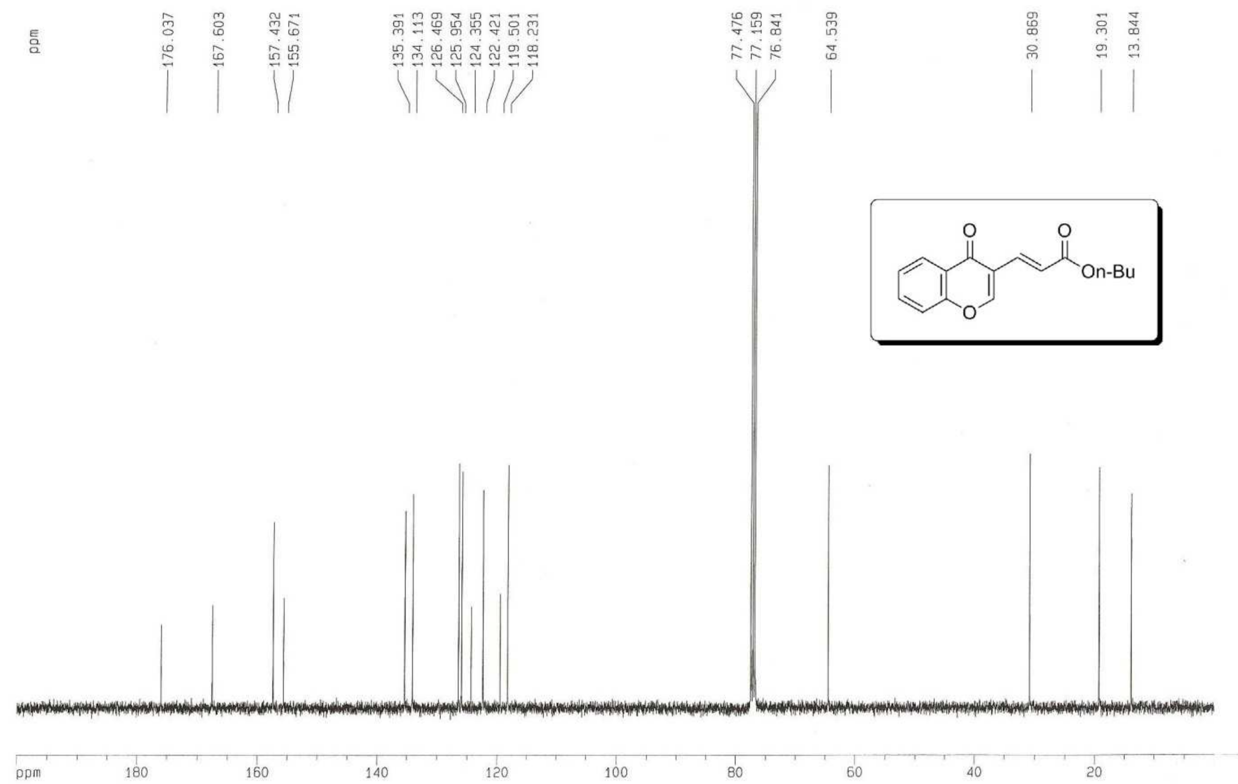


(E)-butyl-3-(4-oxo-2-phenyl-4H-chromen-3-yl)acrylate (2q). Flavone (50 mg, 0.225 mmol) was reacted with *n*-butylacrylate (0.065 ml, 0.450 mmol) according to GP for 18 h. The residue was purified by flash column chromatography (CH_2Cl_2 → EtOAc : *n*-hexane = 1 : 7) to produce the desired product (40.4 mg, 52 %) as white solid, m.p. 66-68 °C; ^{1}H NMR δ (400 MHz, $CDCl_3$): 7.40 - 7.48 (4H), 7.53 - 7.58 (3H), 7.63 (dd, 2H, *J* = 6.0, 2.0 Hz), 7.68 (td, 1H, *J* = 8.0, 1.6 Hz), 8.27 (dd, 1H, *J* = 8.0, 1.6 Hz); ^{13}C NMR δ (100 MHz, $CDCl_3$): 13.70, 19.16, 30.72, 64.17, 115.58, 117.90, 123.49, 125.59, 126.37, 128.44, 128.71, 129.88, 131.40, 132.18, 133.91, 135.97, 155.32, 166.84, 167.93, 176.86; HRMS (EI^+) m/z calcd. for $C_{22}H_{20}NaO_4^+$ $[M+Na]^+$: 371.1254, found: 371.1315.

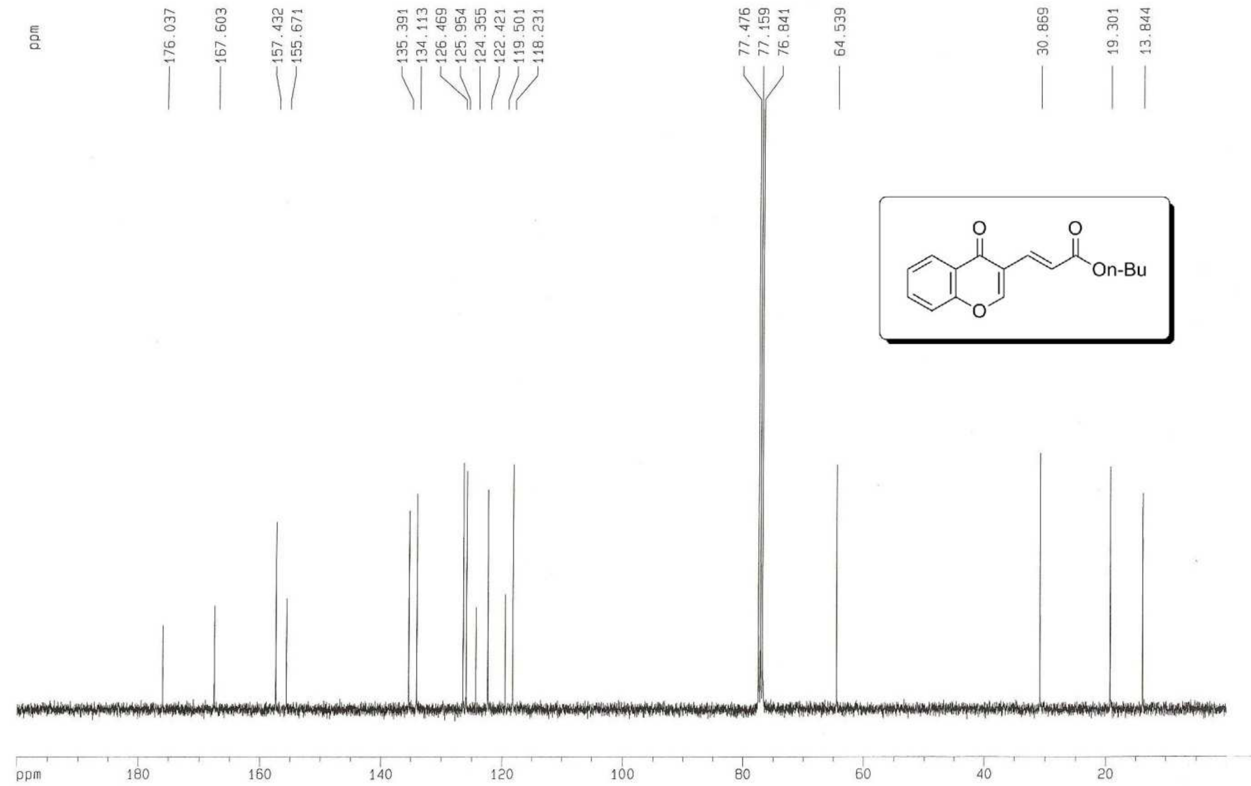
References

1. Davies, S. G.; Mobbs, B. E.; Goodwin, C. J. *J. Chem. Soc., Perkin Trans. 1* **1987**, *1*, 2597.
2. Dang, A.-T.; Miller, D. O.; Dawe, L. N.; Bodwell, G. J. *Org. Lett.* **2008**, *10*, 233.
3. Patonay, T.; Vasas, A; Kiss-Szikszai, A.; Silva, A. M. S.; Cavaleiro, J. A. S. *Aust. J. Chem.* **2010**, *63*, 1582.

4. **(E)-butyl-3-(4-oxo-4H-chromen-3-yl)acrylate (2a)**

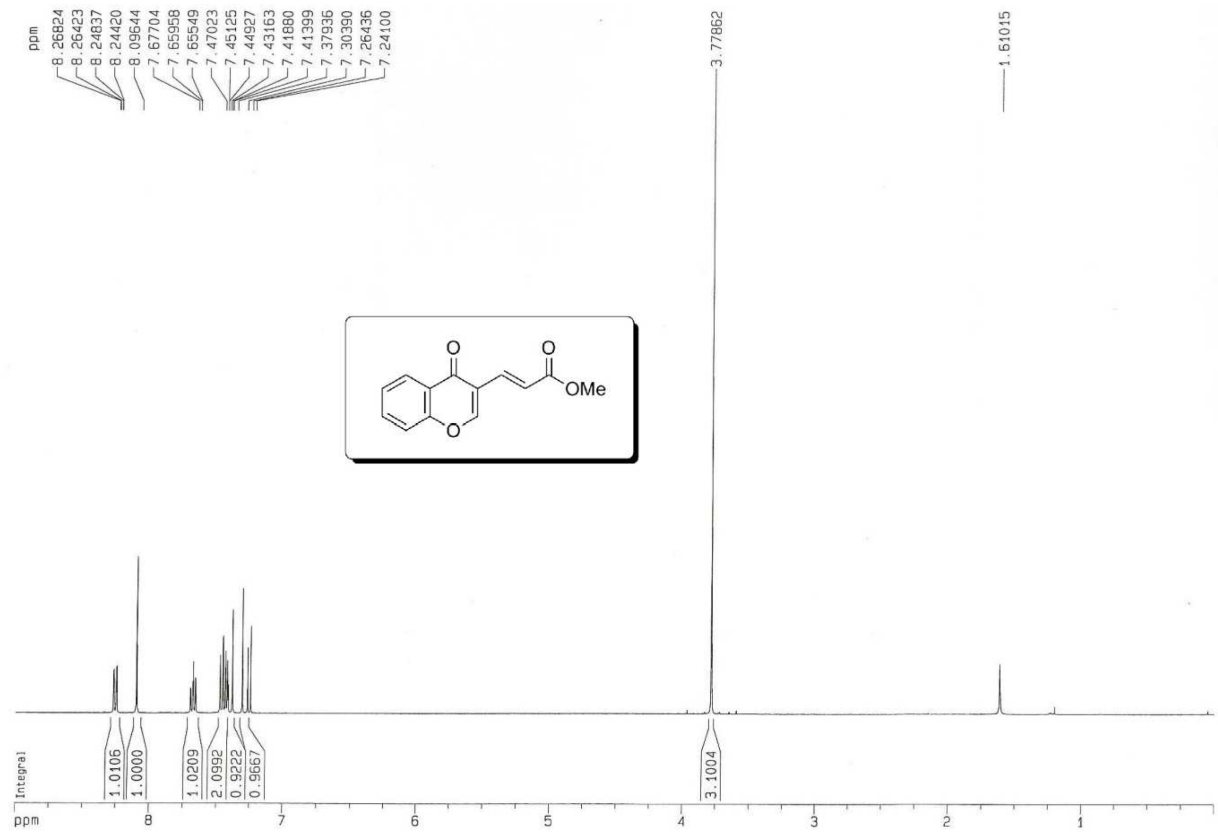


400 MHz, ^{1}H NMR in $CDCl_3$

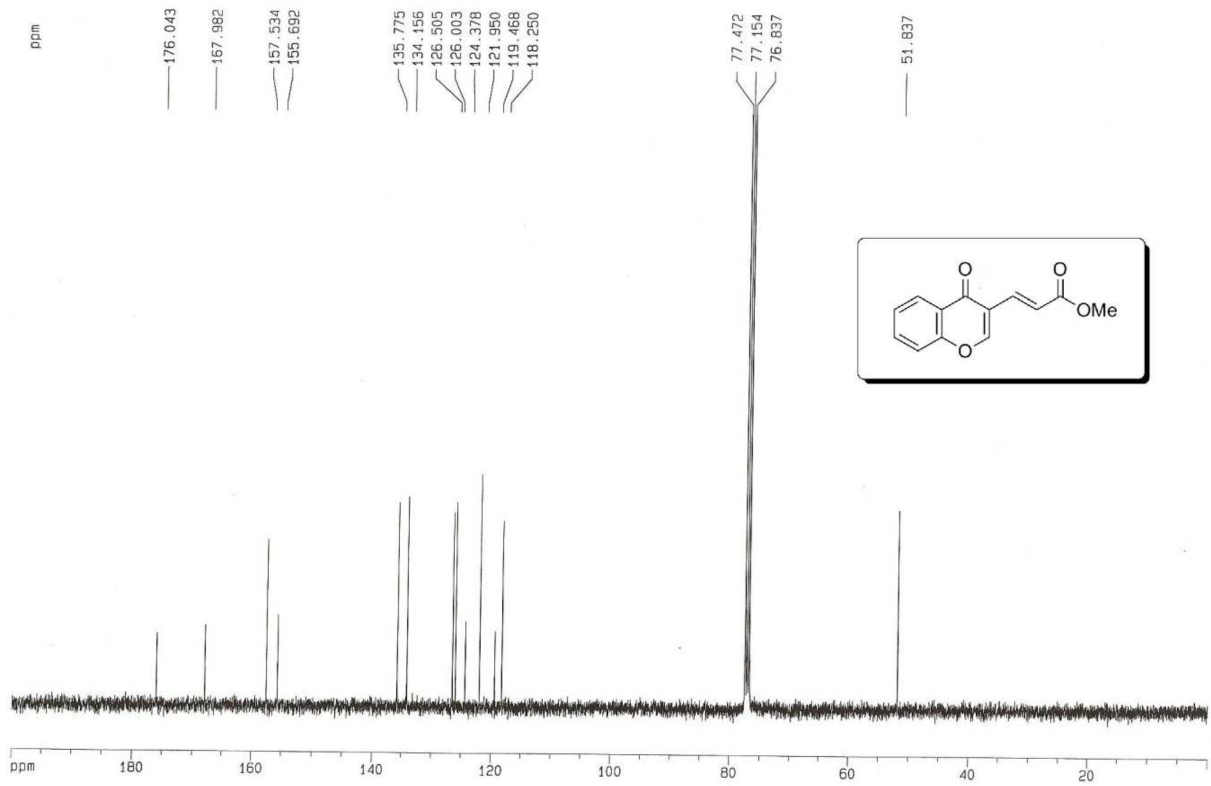


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-methyl-3-(4-oxo-4H-chromen-3-yl)acrylate (2b)



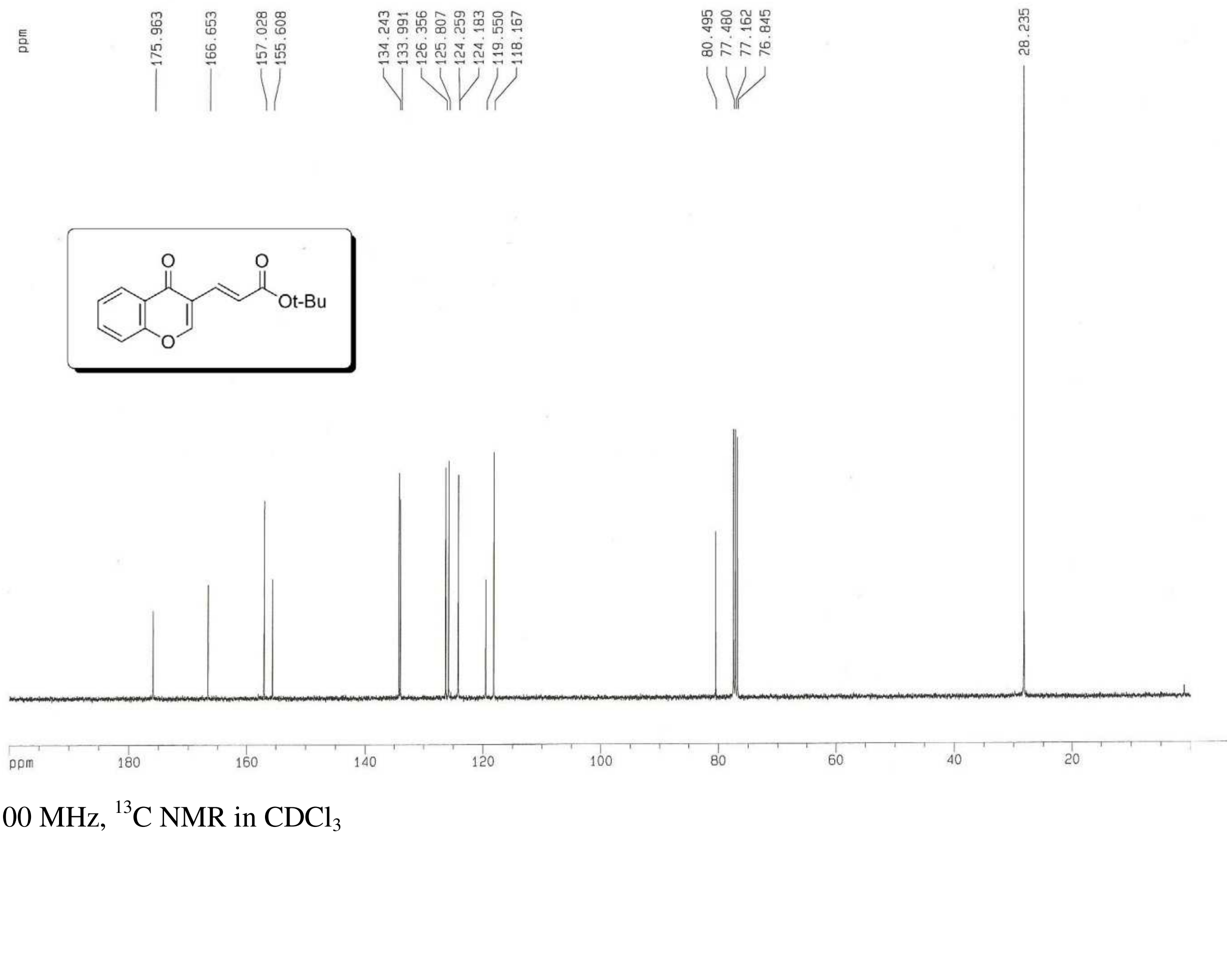
400 MHz, ^{1}H NMR in $CDCl_3$



100 MHz, ^{13}C NMR in $CDCl_3$

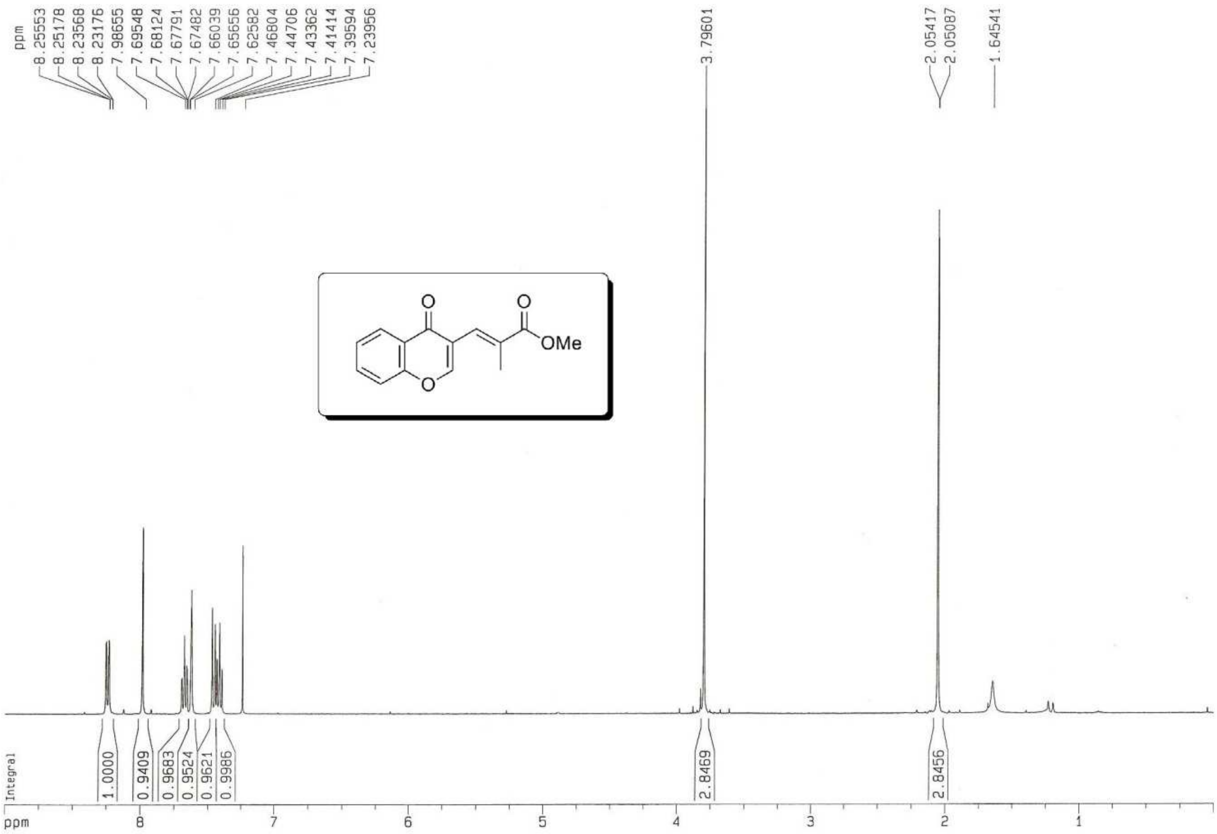
(E)-tert-butyl-3-(4-oxo-4H-chromen-3-yl)acrylate (2c)

400 MHz, ^{1}H NMR in $CDCl_3$

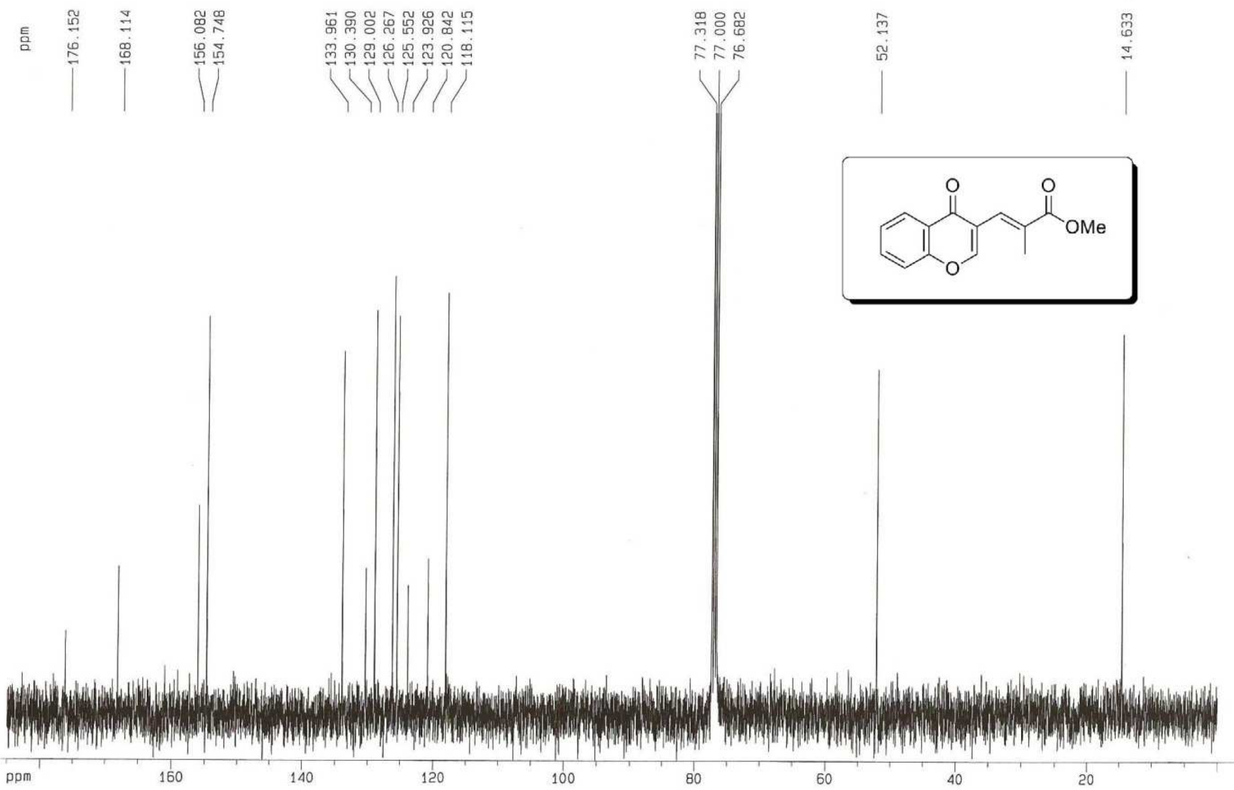


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-methyl-2-methyl-3-(4-oxo-4H-chromen-3-yl)acrylate (2d)

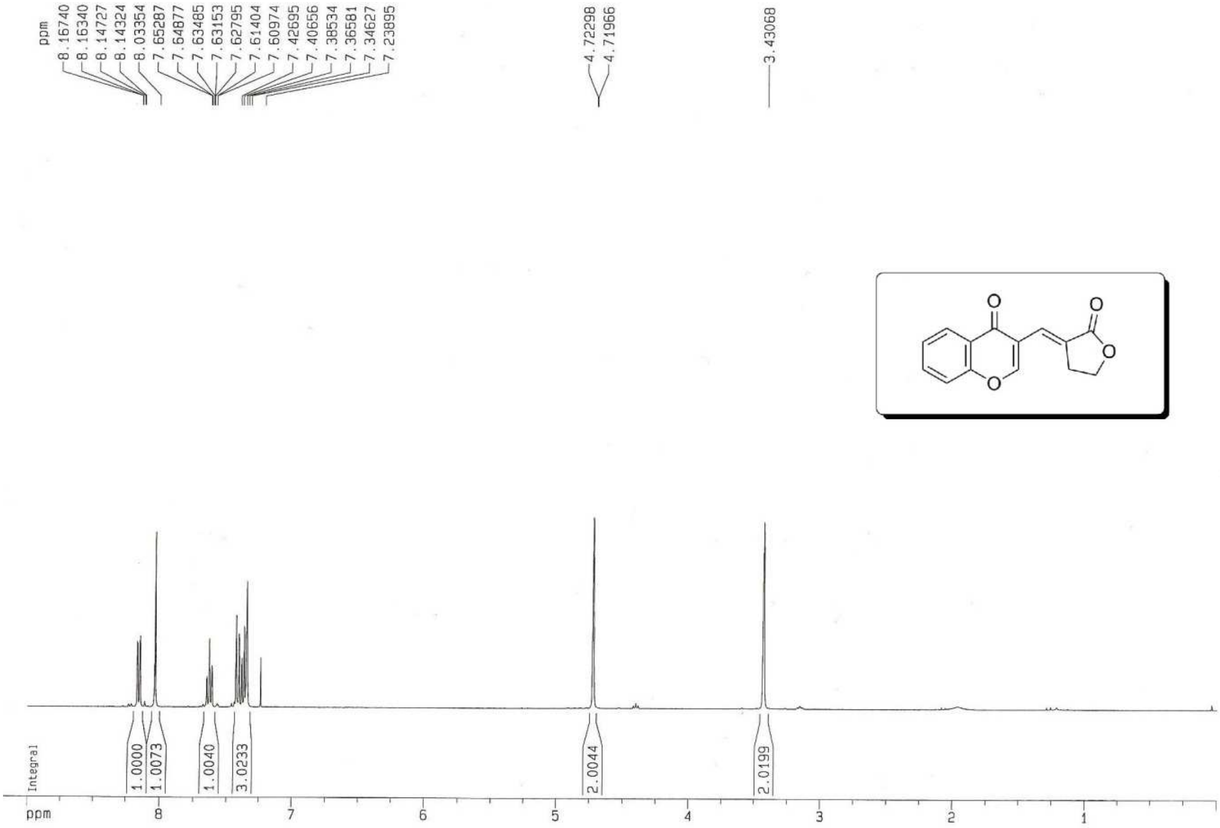


400 Mhz, ^{1}H NMR in $CDCl_3$

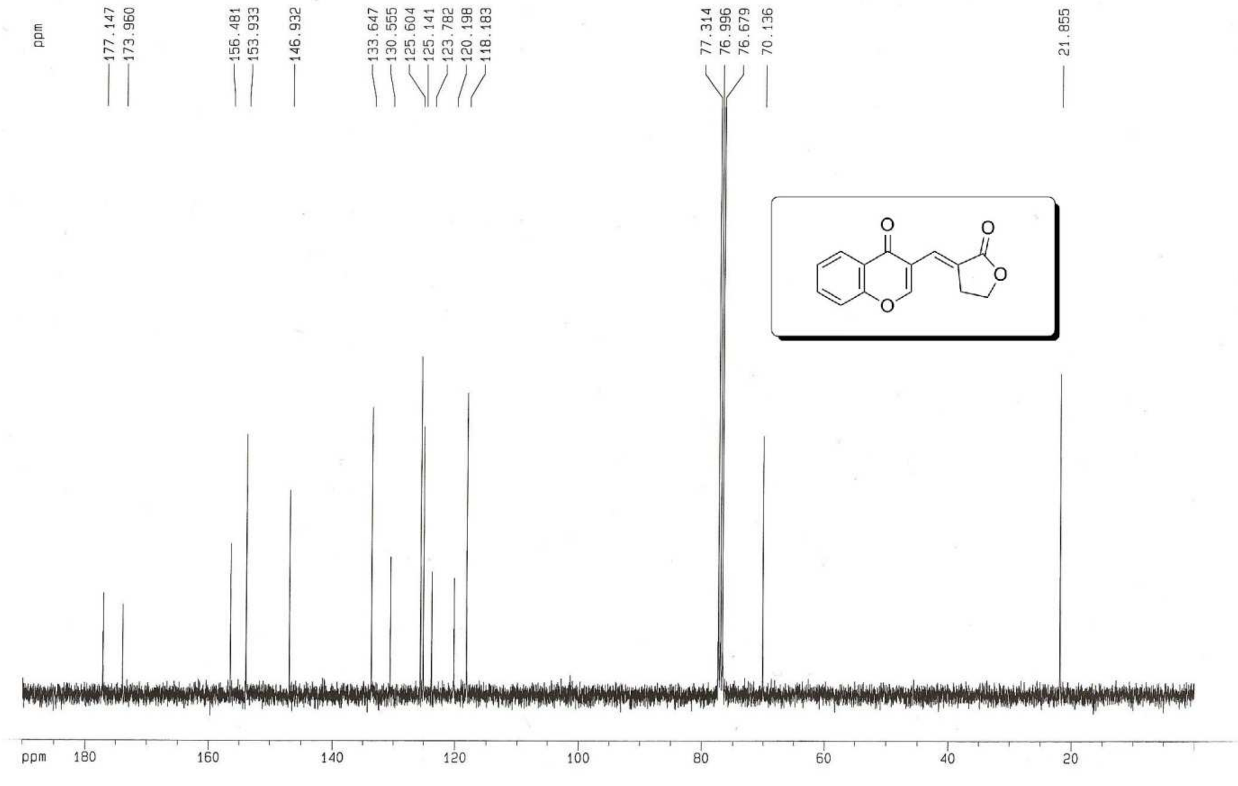


100 Mhz, ^{13}C NMR in $CDCl_3$

(E)-3-((2-oxodihydrofuran-3(2H)-ylidene)methyl)-4H-chromen-4-one (2e)



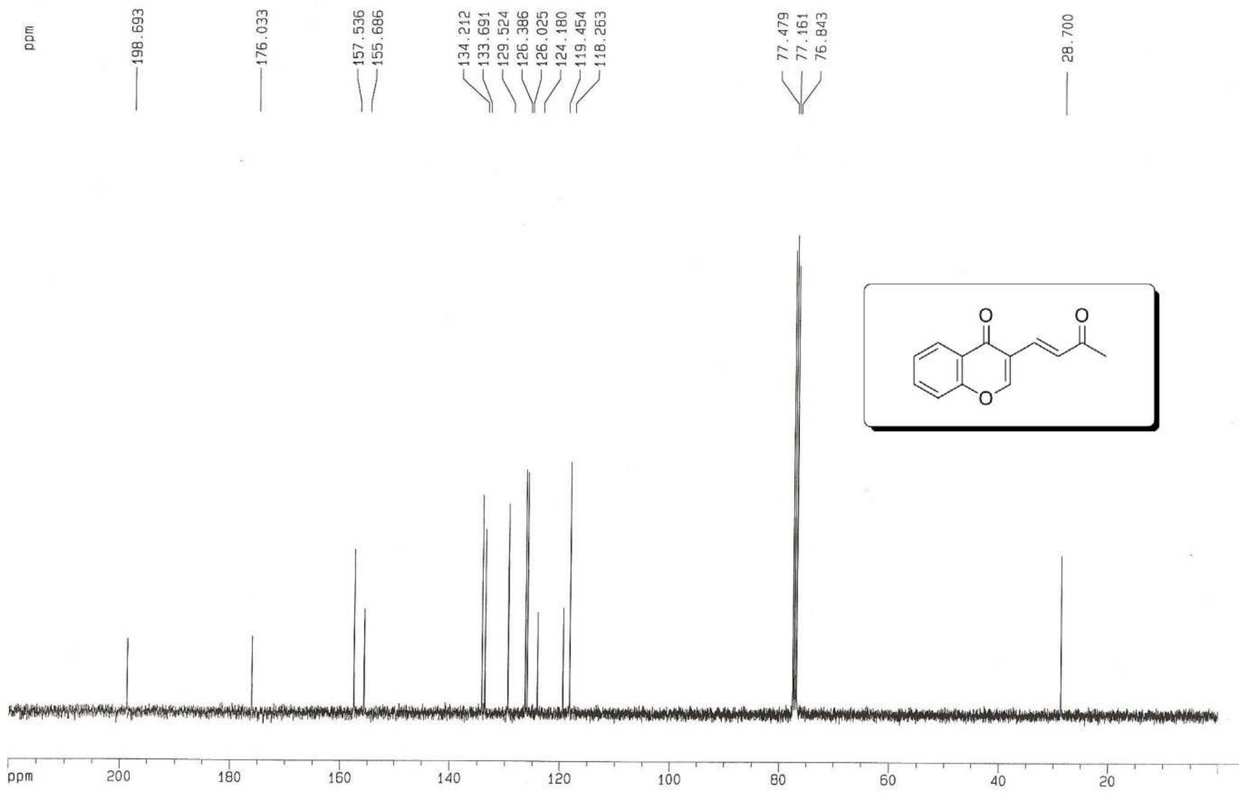
400 MHz, ^{1}H NMR in $CDCl_3$



100 MHz, ^{13}C NMR in $CDCl_3$

(E)-3-(3-oxobut-1-enyl)-4H-chromen-4-one (2f)

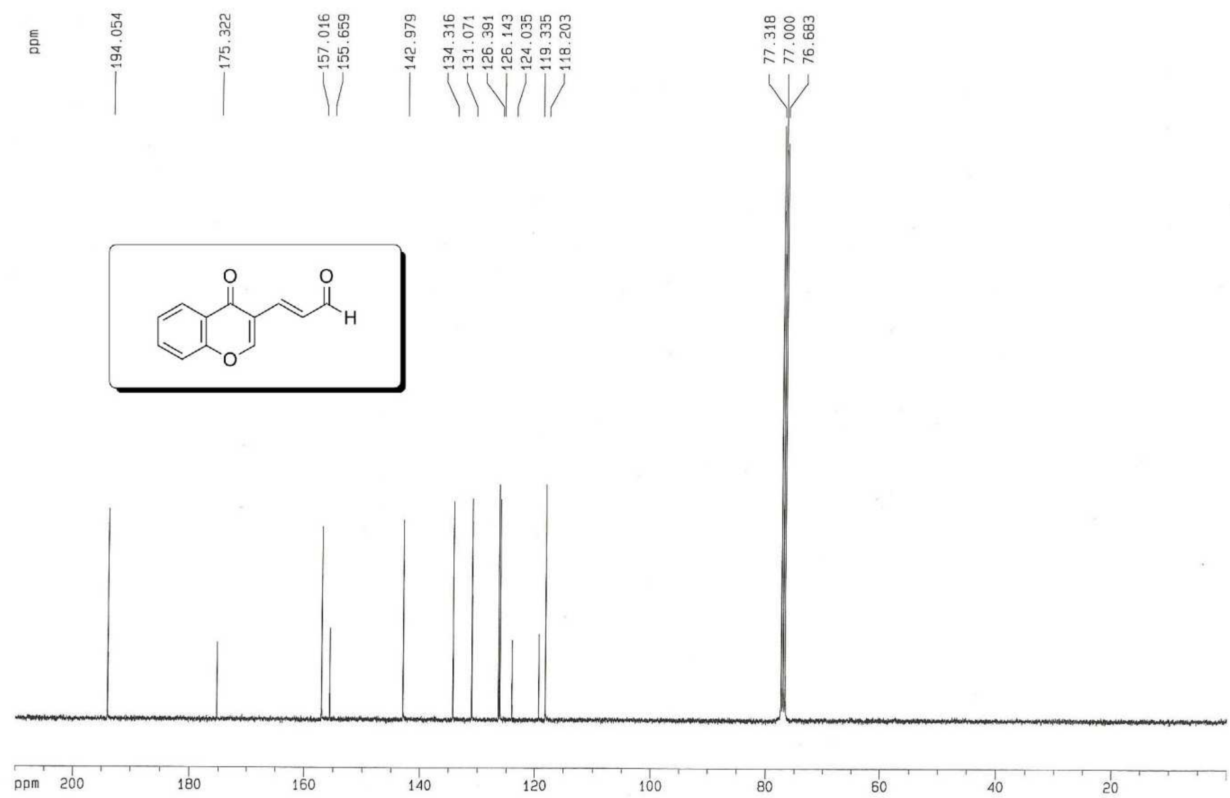
400 MHz, ^{1}H NMR in $CDCl_3$



100 MHz, ^{13}C NMR in $CDCl_3$

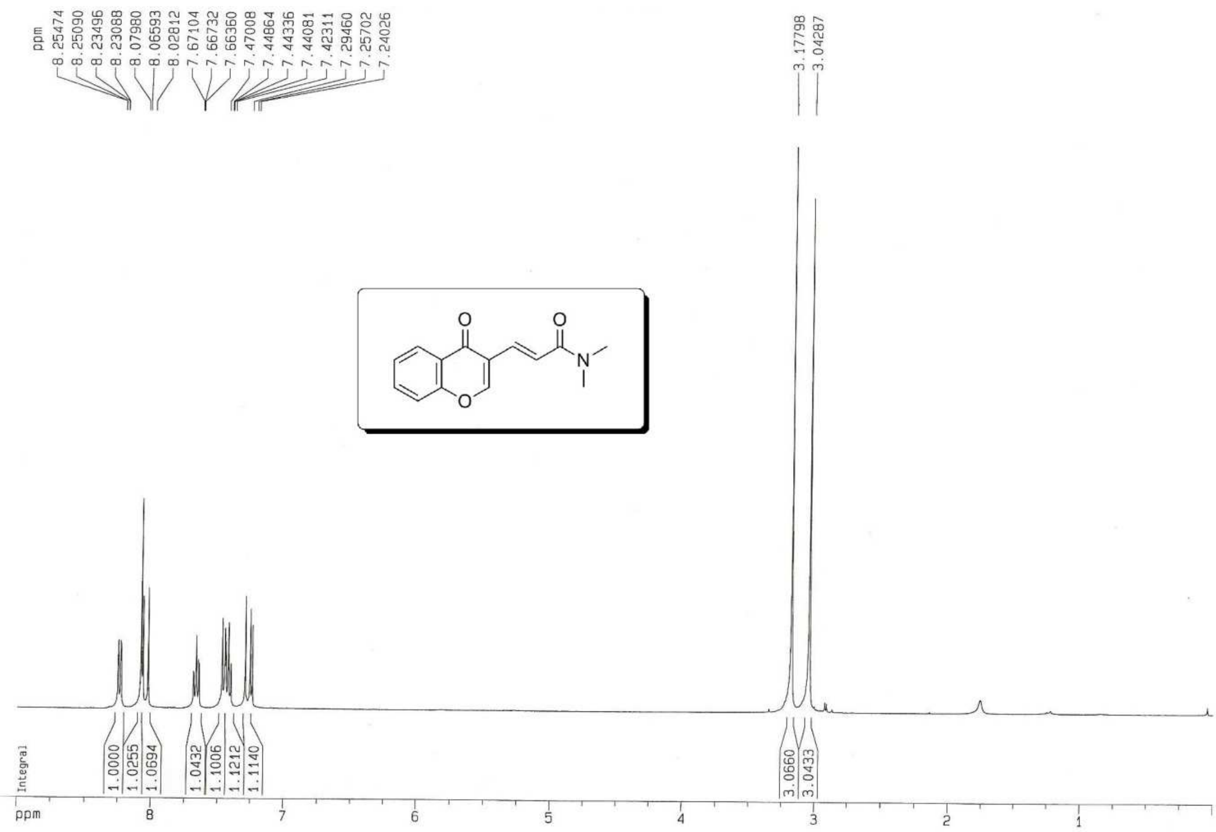
(E)-3-(4-oxo-4H-chromen-3-yl)acrylaldehyde (2g)

400 MHz, ^{1}H NMR in $CDCl_3$

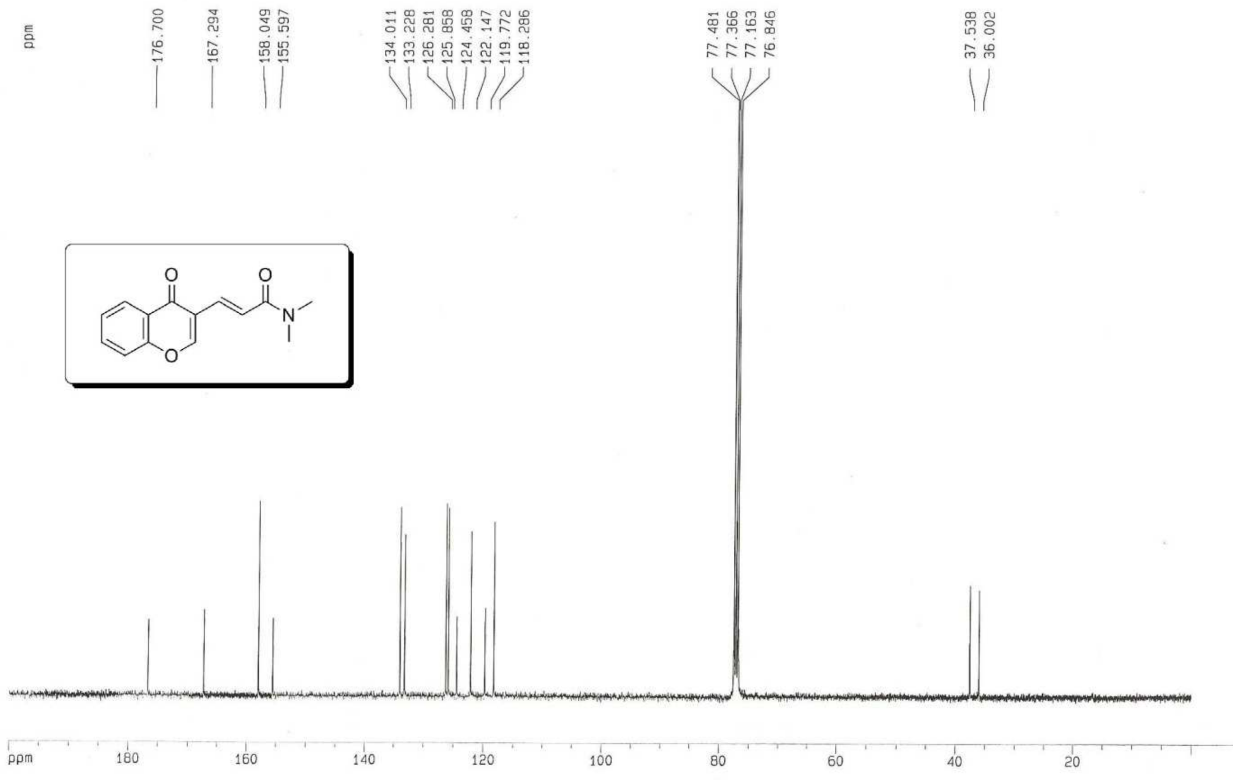


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-N,N-dimethyl-3-(4-oxo-4H-chromen-3-yl)acrylamide (2h)

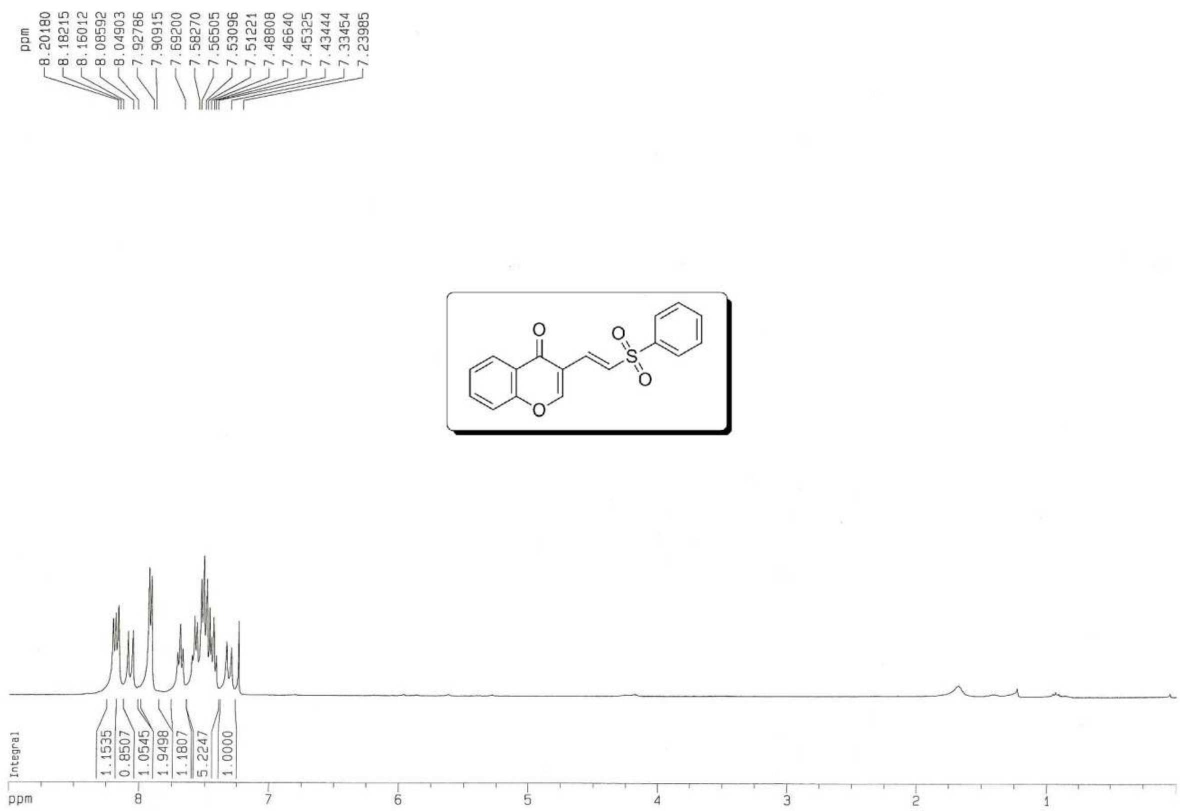


400 MHz, ^{1}H NMR in $CDCl_3$

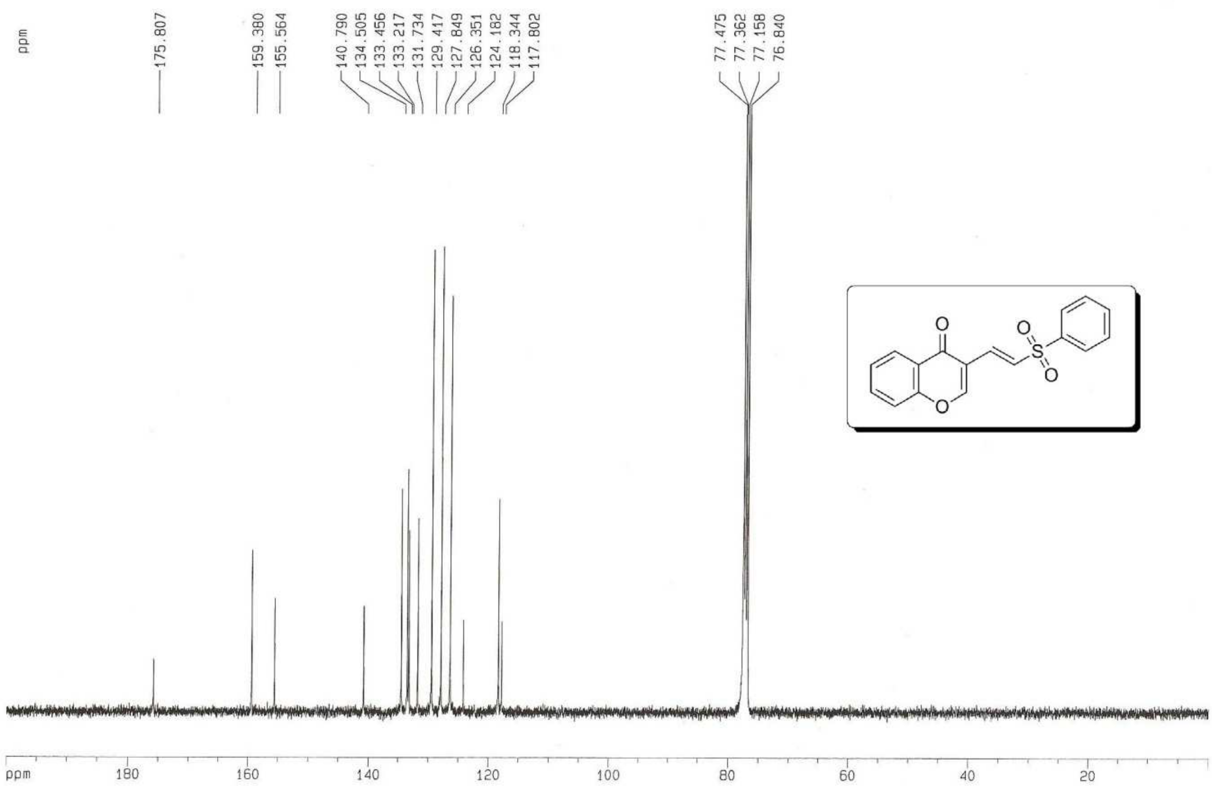


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-3-(2-(phenylsulfonyl)vinyl)-4H-chromen-4-one (2i)

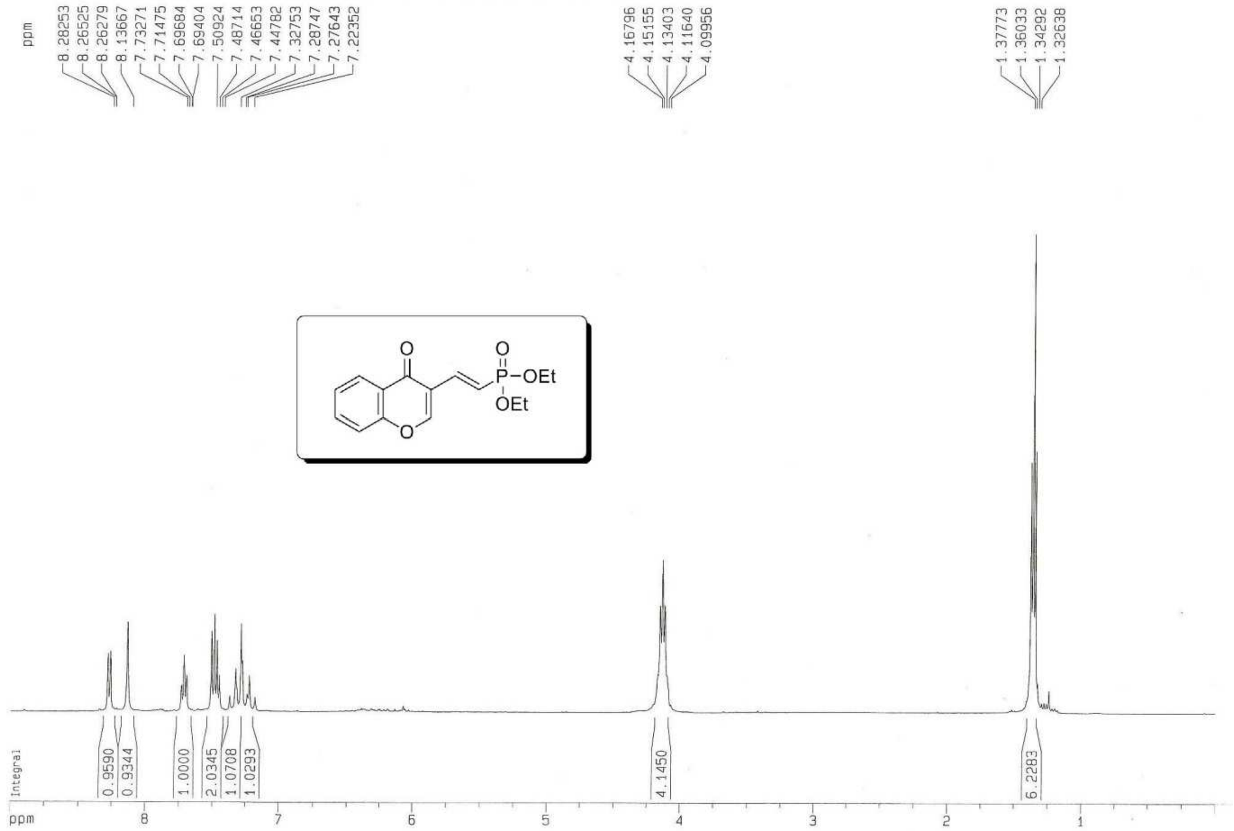


400 MHz, ^{1}H NMR in $CDCl_3$

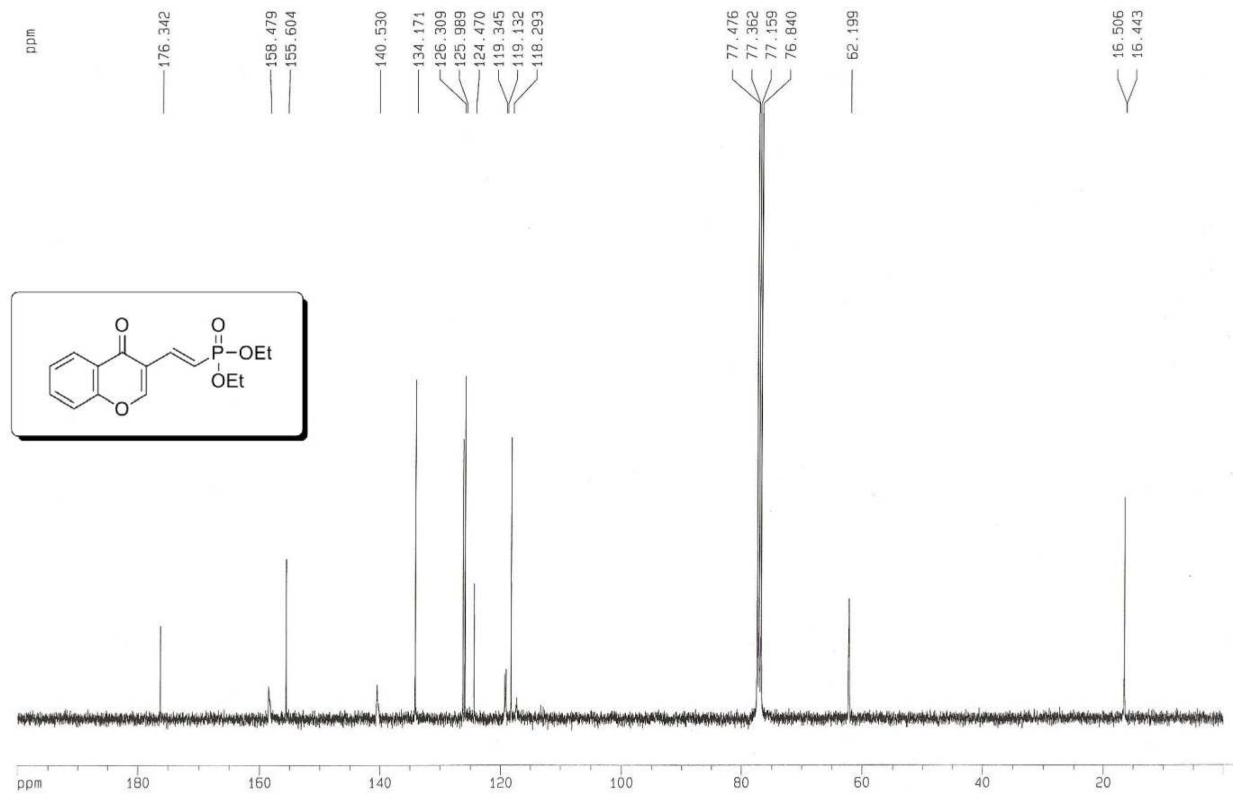


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-diethyl-2-(4-oxo-4H-chromen-3-yl)vinylphosphonate (2j)

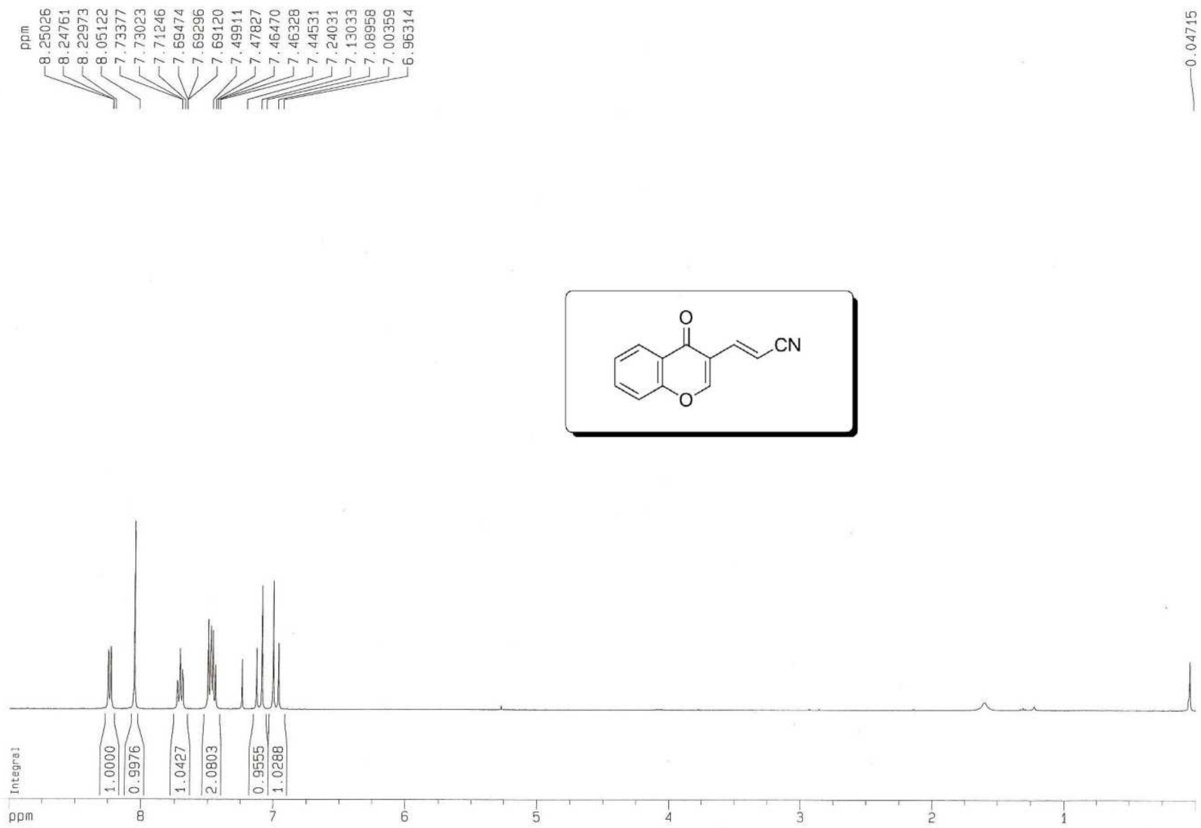


400 MHz, ^{1}H NMR in $CDCl_3$

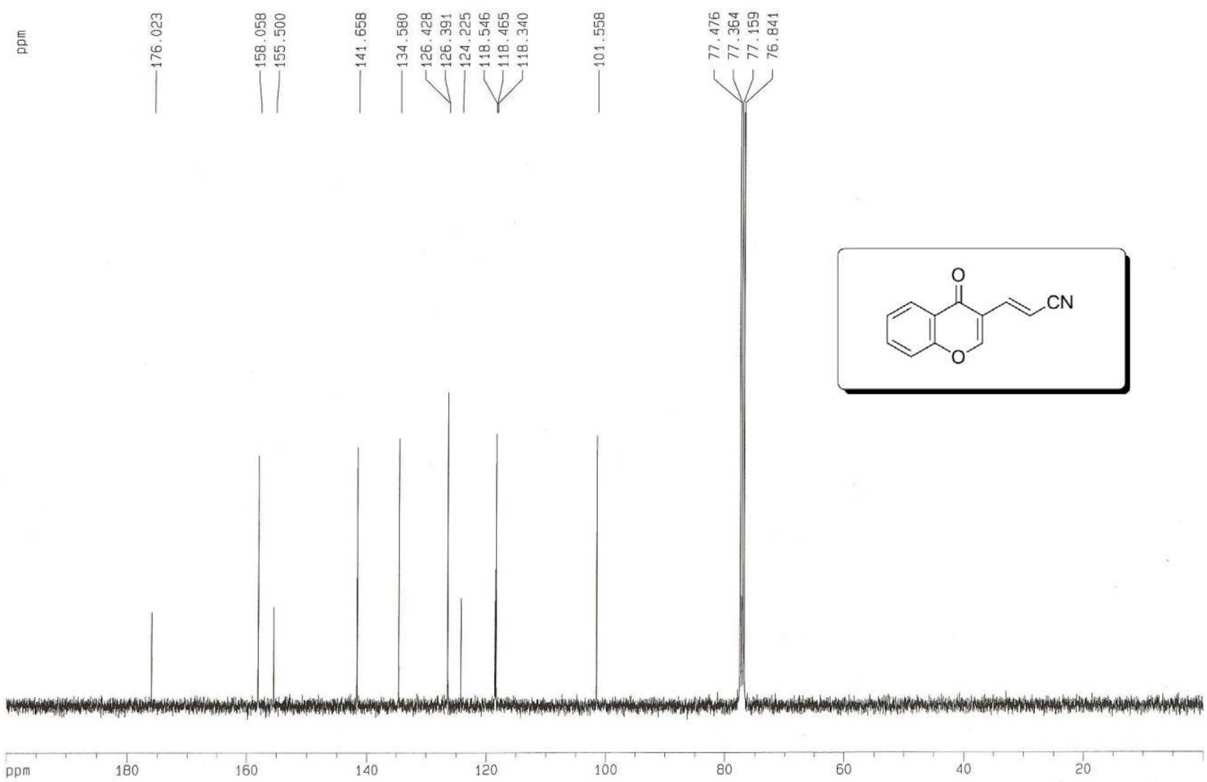


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-3-(4-oxo-4H-chromen-3-yl)acrylonitrile (2k)

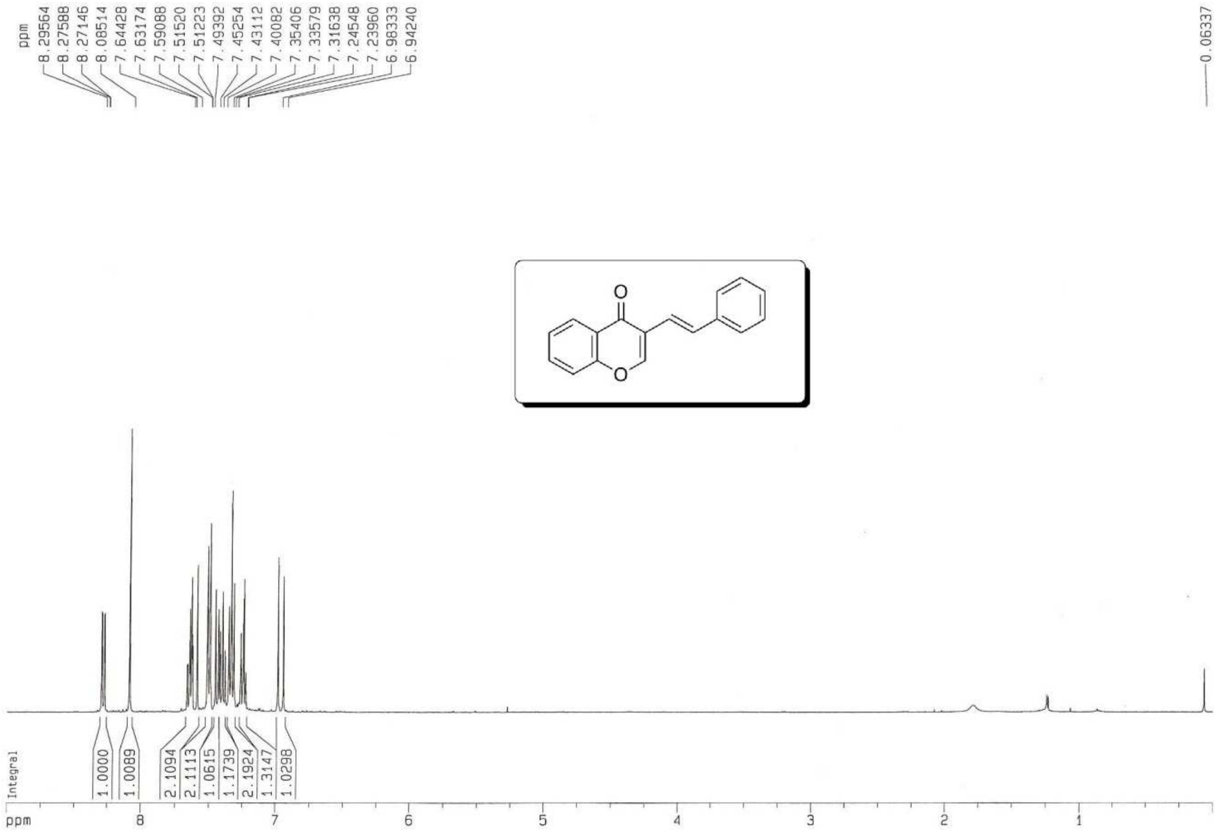


400 MHz, ^1H NMR in $CDCl_3$

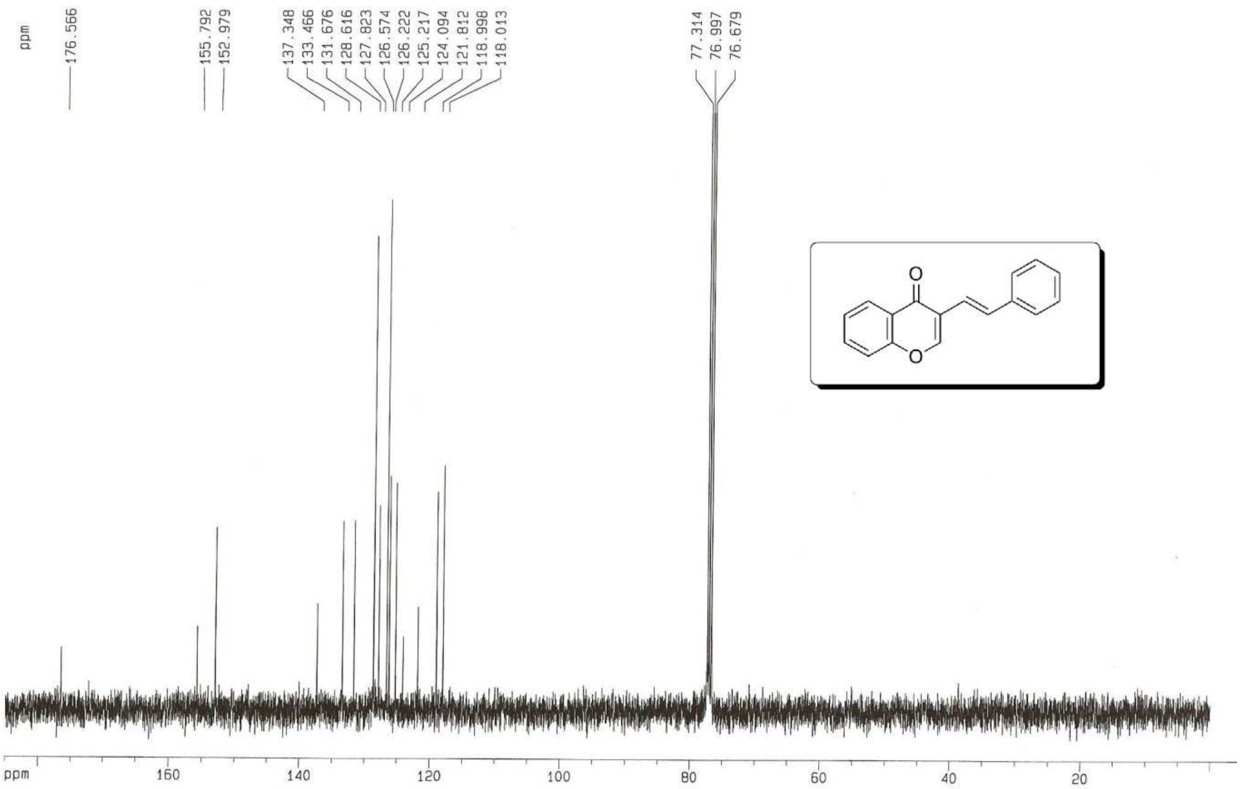


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-3-styryl-4H-chromen-4-one (2l)

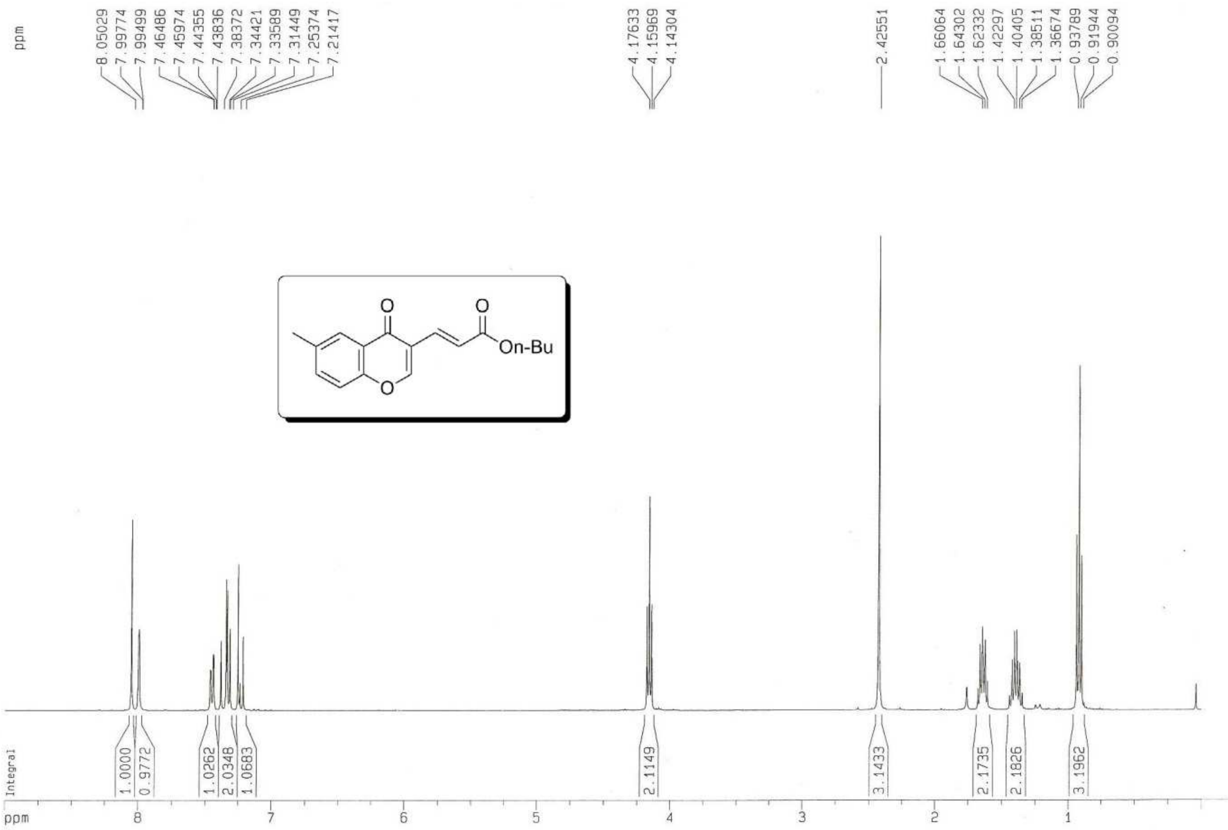


400 MHz, ^{1}H NMR in $CDCl_3$

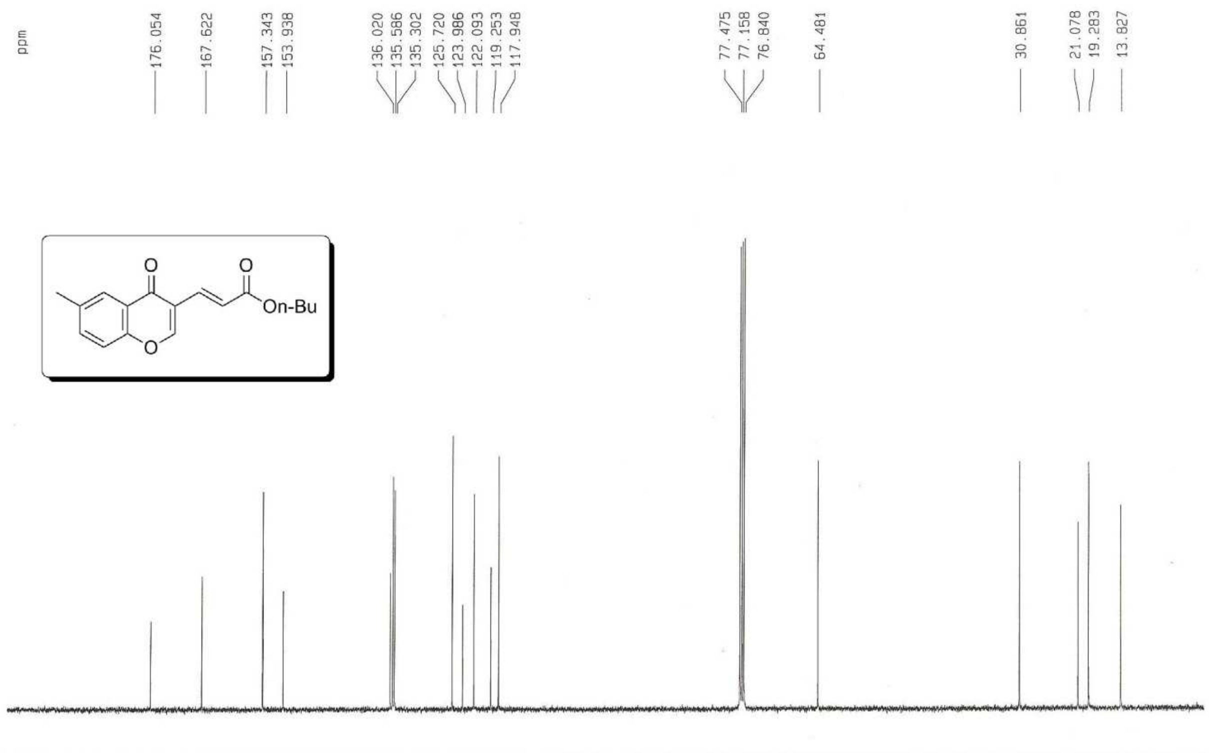


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-butyl-3-(6-methyl-4-oxo-4H-chromen-3-yl)acrylate (2m)

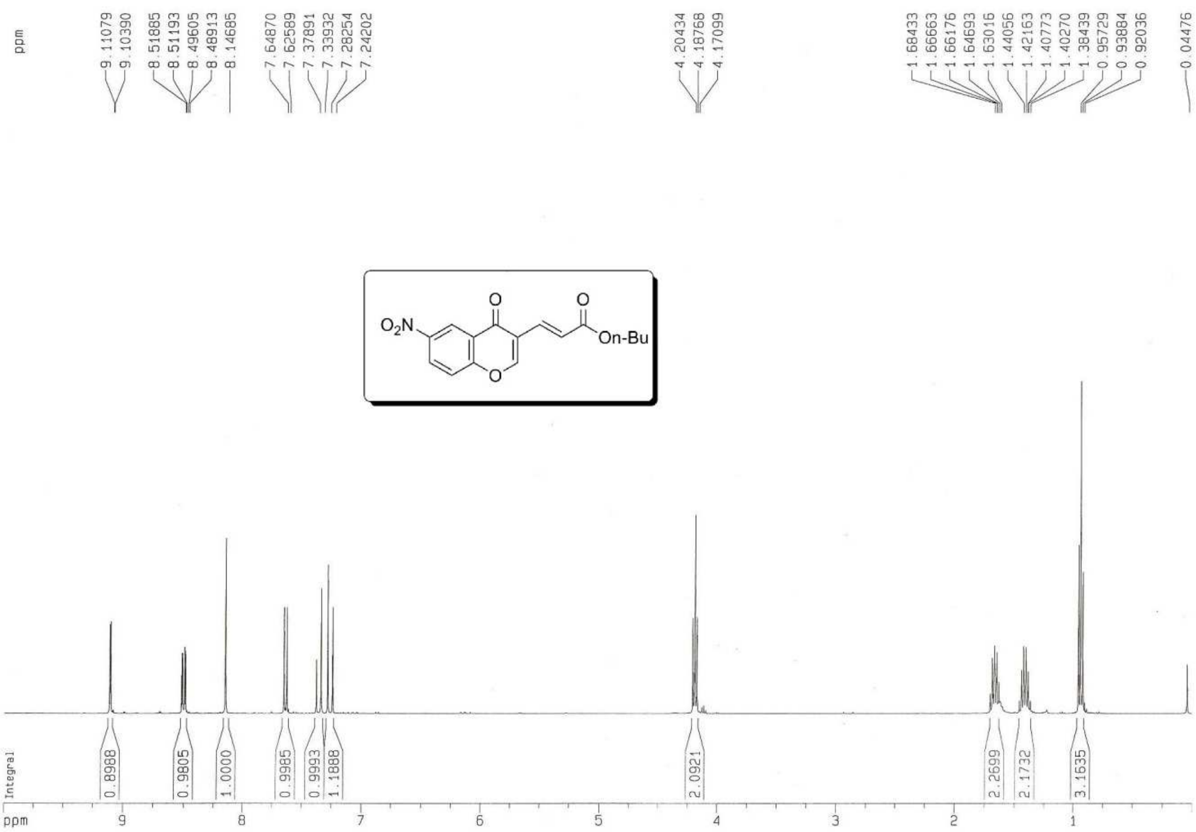


400 MHz, ^{1}H NMR in $CDCl_3$

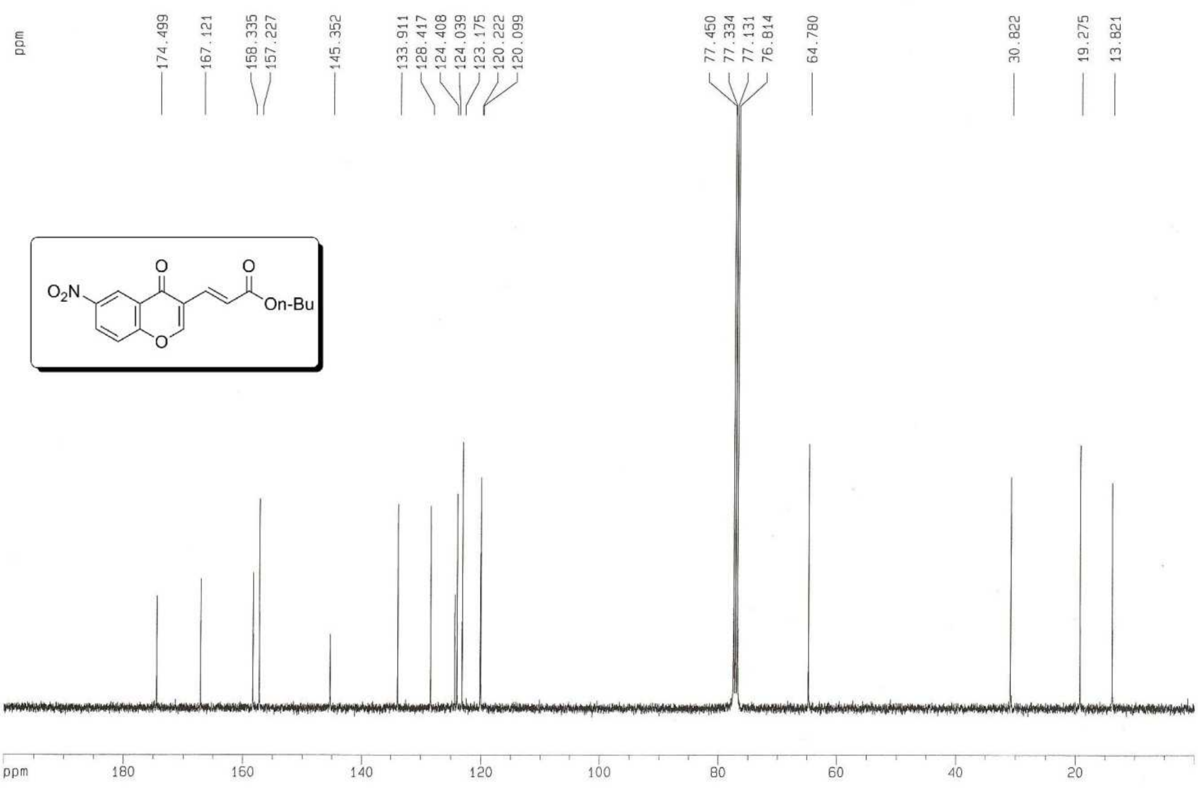


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-butyl-3-(6-nitro-4-oxo-4H-chromen-3-yl)acrylate (2n)

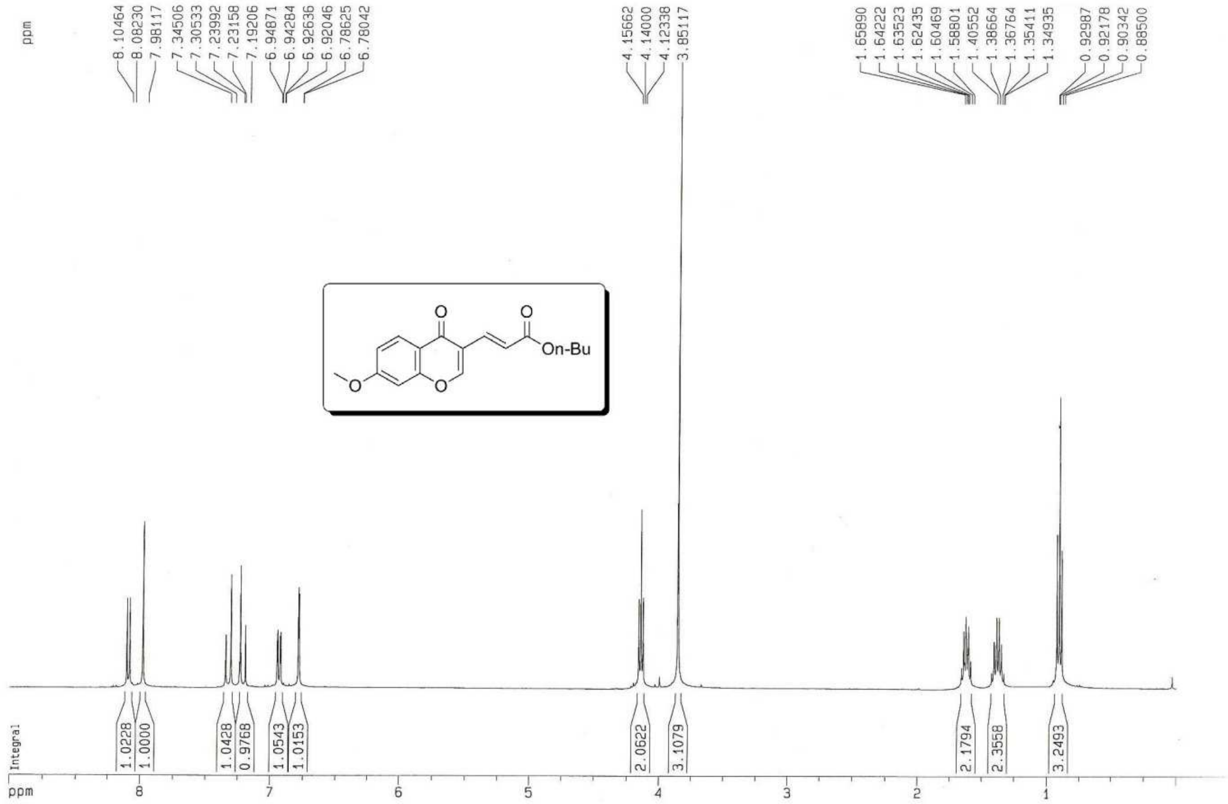


400 MHz, ^1H NMR in $CDCl_3$

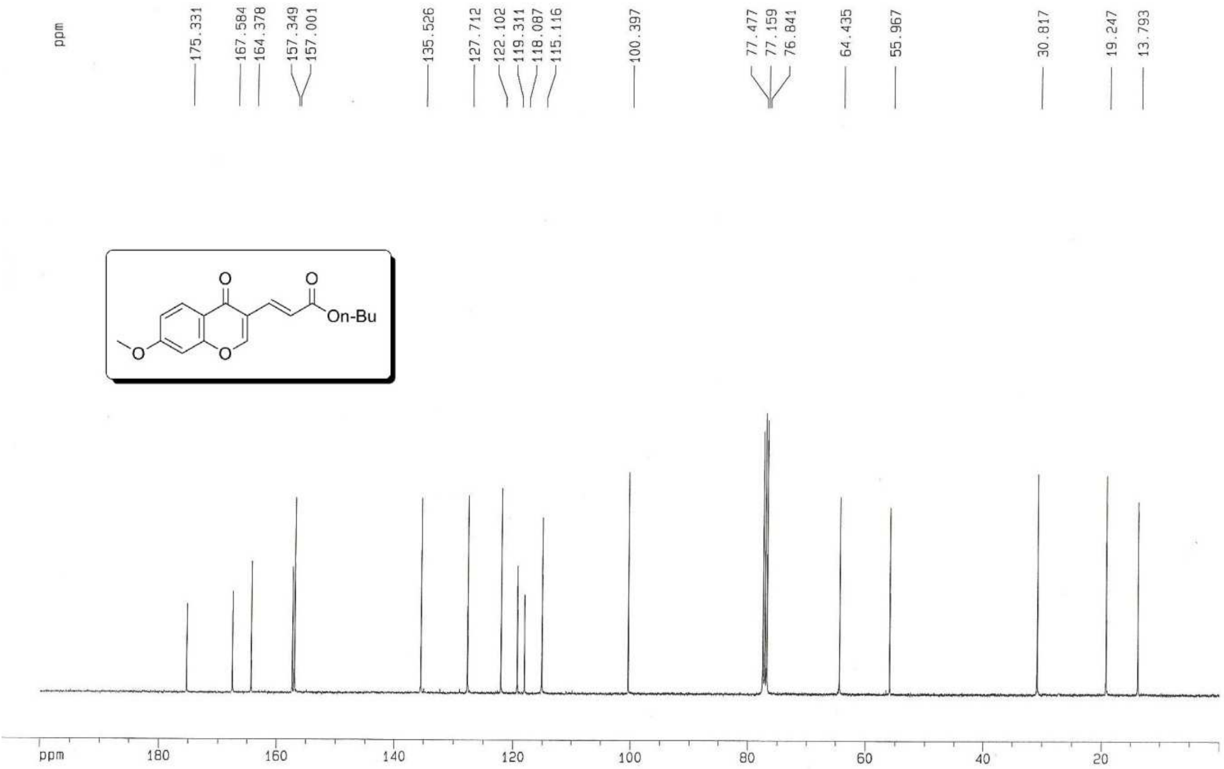


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-butyl-3-(7-methoxy-4-oxo-4H-chromen-3-yl)acrylate (2o)

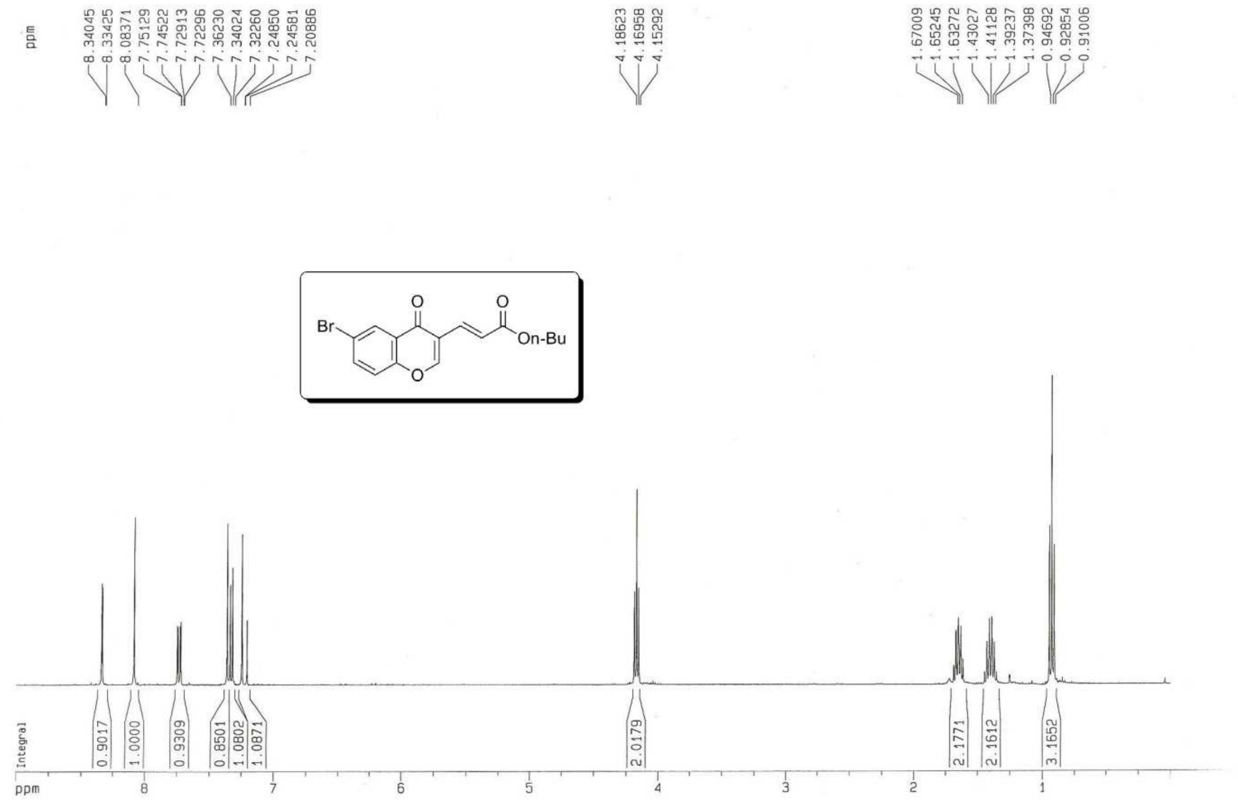


400 MHz, ^{1}H NMR in $CDCl_3$

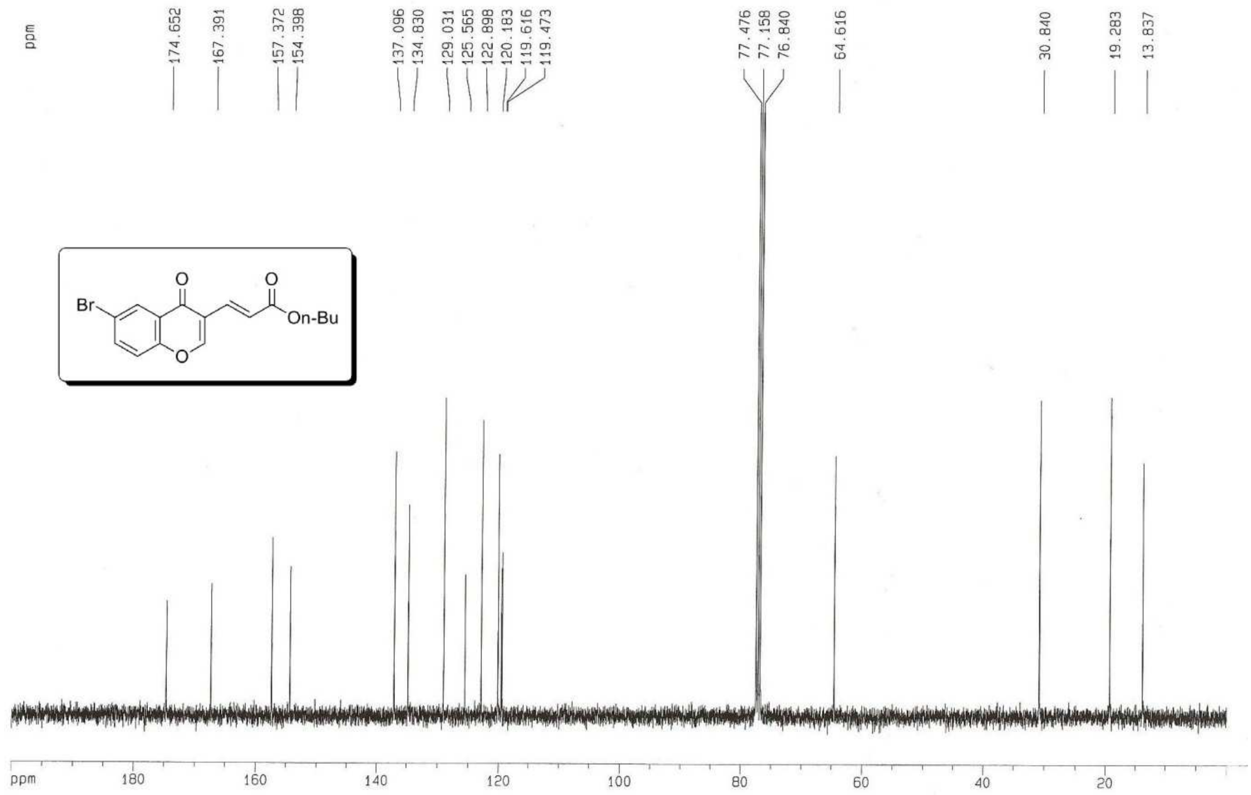


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-butyl-3-(6-bromo-4-oxo-4H-chromen-3-yl)acrylate (2p)

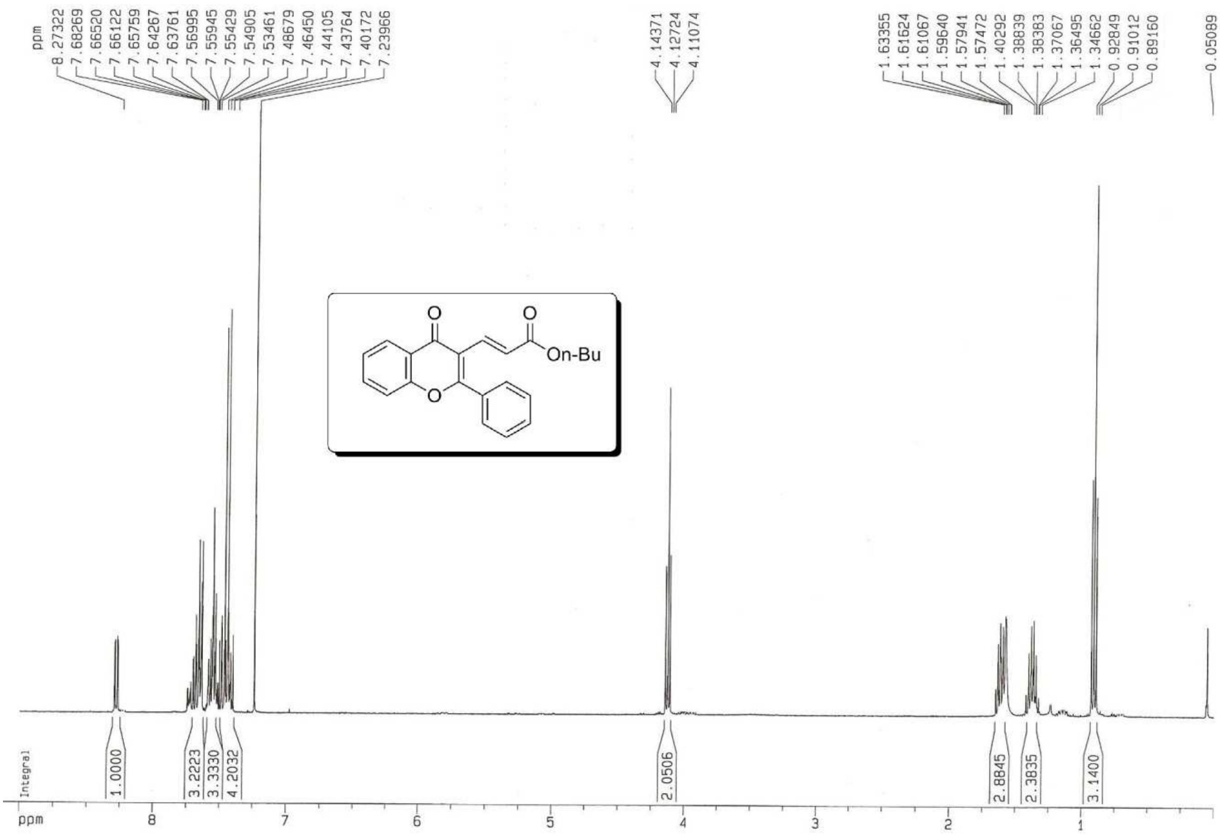


400 MHz, ^{1}H NMR in $CDCl_3$

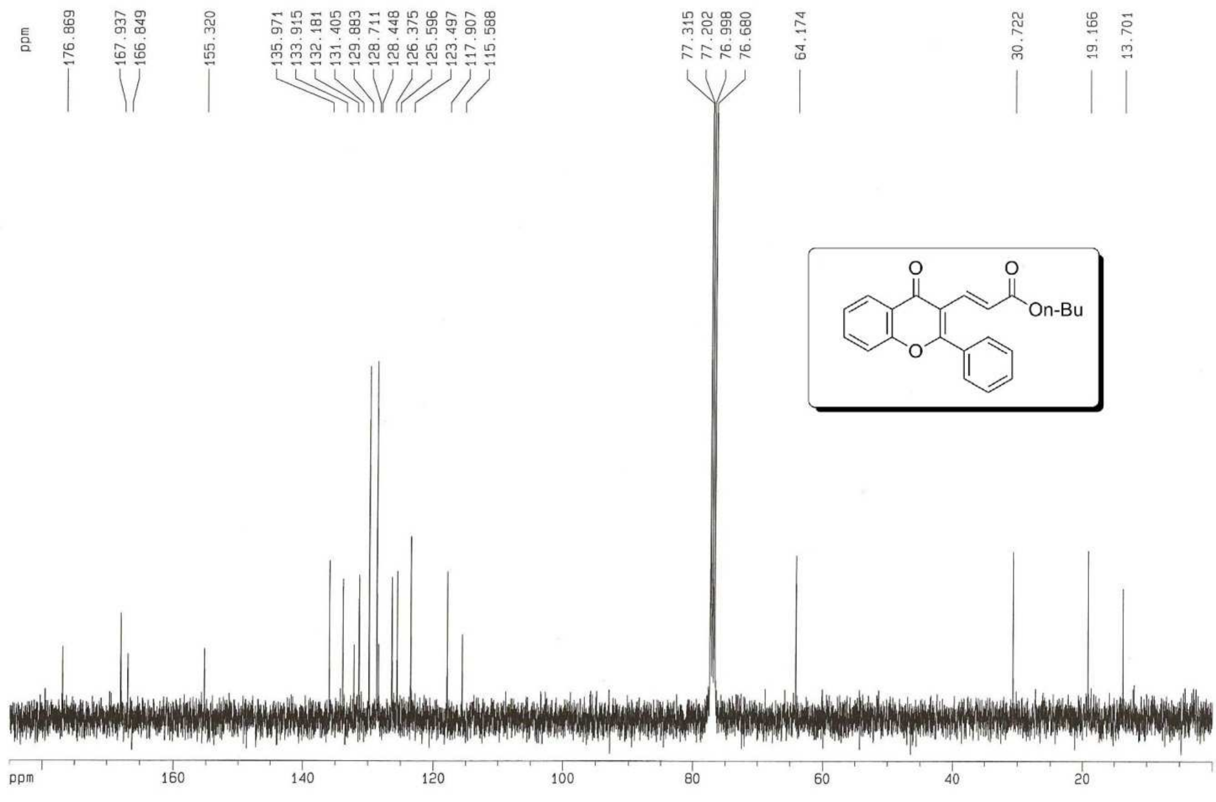


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-butyl-3-(4-oxo-2-phenyl-4H-chromen-3-yl)acrylate (2q)



400 Mhz, ^{1}H NMR in $CDCl_3$



100 Mhz, ^{13}C NMR in $CDCl_3$