Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Regioselective Palladium-Catalyzed Olefination of Coumarins via Aerobic Oxidative Heck Reactions

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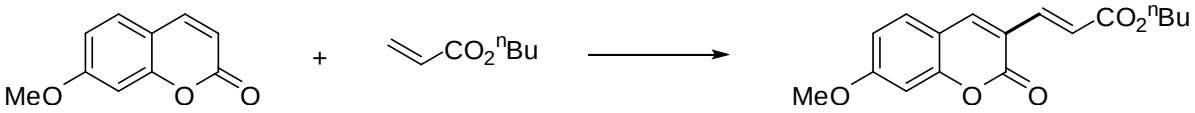
I. General Methods and Materials. Unless stated otherwise, reactions were performed in flame-dried glassware under a positive pressure of nitrogen. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F_{254} plates and visualization on TLC was achieved by UV light (254 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. Unless otherwise stated, all commercial reagents and solvents were used without additional purification.

II. Optimization Study

Table S1. Optimization of the Dehydrogenation/Alkenylations of chromanone.[a]



entry	catalyst	solvent	oxidant (equiv)	additive (equiv)	yield (%)[b]
1	$Pd(OPiv)_2$	PivOH	TEMPO (1.2)	K_2CO_3 (3)	75
2	$Pd(OPiv)_2$	PivOH	Air	K_2CO_3 (3)	76
3	$Pd(OPiv)_2$	PivOH	Ag_2CO_3 (3)	-	40
4	$Pd(OPiv)_2$	PivOH	Oxone (2)	K_2CO_3 (3)	10
5	$Pd(OPiv)_2$	PivOH	DDQ (1)	K_2CO_3 (3)	-
6	$Pd(OPiv)_2$	PivOH	$AgNO_3$ (3)	K_2CO_3 (3)	28
7	$Pd(OPiv)_2$	PivOH	Cu(OTf)2 (3)	Ag_2CO_3 (3)	-
8	$Pd(OPiv)_2$	PivOH	$Cu(OAc)_2$ (3)	Ag_2CO_3 (3)	30
9	$Pd(OPiv)_2$	Dioxane	$Cu(OAc)_2$ (3)	Ag_2CO_3 (3)	trace

10	$Pd(OPiv)_2$	DMSO	$Cu(OAc)_2$ (3)	Ag_2CO_3 (3)	-
11	$Pd(OPiv)_2$	DMA	$Cu(OAc)_2$ (3)	Ag_2CO_3 (3)	-
12	$Pd(OPiv)_2$	PivOH	HPMoV (0.1)/O_2	K_2CO_3 (3)	63
13	$Pd(OPiv)_2$	PivOH	CuF_2 (3.0)	K_2CO_3 (3)	35
14	$Pd(OPiv)_2$	PivOH	$Cu(OAc)_2$ (3.0)	-	20
15	$Pd(OPiv)_2$	PivOH	$Cu(OAc)_2$ (3.0)	K_2CO_3 (3)	40
16	$Pd(OPiv)_2$	PivOH	TEMPO (2)	Ag_2CO_3 (3)	40
17	$Pd(OPiv)_2$	PivOH	O_2	K_2CO_3 (3) TBAB (1)	trace
18	$Pd(OPiv)_2$	PivOH	O_2	Li_2CO_3 (3)	50
19	$Pd(OPiv)_2$	PivOH	O_2	CsOPiv (3)	64
20	$Pd(OPiv)_2$	PivOH	N_2	K_2CO_3 (3)	14
21	$Pd(OPiv)_2$	PivOH	O_2	K_2CO_3 (3)	81
22	$Pd(OAc)_2$	PivOH	O_2	K_2CO_3 (3)	51
23	$Pd(TFA)_2$	PivOH	O_2	K_2CO_3 (3)	61
24	$Pd(OPiv)_2$	PivOH	$Cu(OAc)_2$ (0.1)/O_2	K_2CO_3 (3)	59
25	$Pd(TFA)_2$	PivOH	HPMoV (0.1)/O_2	CsOAc (3)	38
26	$Pd(TFA)_2$	PivOH	HPMoV (0.1)/O_2	CsOPiv (3)	50
27	$Pd(TFA)_2$	Dioxane	HPMoV (0.1)/O_2	K_2CO_3 3.0 PivOH 6.0	13
28	$Pd(TFA)_2$	DMF	HPMoV (0.1)/O_2	K_2CO_3 3.0 PivOH 6.0	5
29	$Pd(OPiv)_2$	PivOH	O_2	K_2CO_3 (3) IPr-HCl (0.2)	trace
30	$Pd(OPiv)_2$	PivOH	O_2	K_2CO_3 (3) Pyridine (0.2)	48
31	$Pd(OPiv)_2$	PivOH	O_2	K_2CO_3 (3) 1,10-Phenanthroline (0.2)	-
32	$Pd(OPiv)_2$	PivOH	O_2	K_2CO_3 (3) Xantphos (0.3)	40
33	$Pd(OPiv)_2$	PivOH	O_2	K_2CO_3 (3) X-Phos (0.2)	11
34	$Pd(OPiv)_2$	PivOH	O_2	K_2CO_3 (3) PPh_3 (0.2)	44
35	$Pd(OPiv)_2$	PivOH	O_2	K_2CO_3 (3) Ethyl Nicotinate (0.2)	45

[a] Reactions were conducted with coumarin, *tert*-butyl acrylate (2.0 equiv), Pd(OPiv)2 (0.2 equiv), and base (3 equiv) in PivOH at 100 °C for 9 h. [b] Yields are reported after isolation and purification by flash silica gel chromatography.

III. Experimental Procedures

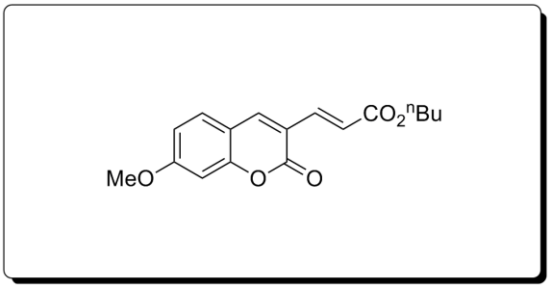
General Procedure for Coumarin Alkenylation:

Coumarin derivative (0.1 mmol), $Pd(OPiv)_2$ (0.2 equiv), K_2CO_3 (3.0 equiv) were combined in PivOH (1.0 mL) under O_2 (balloon). The alkene (2.0 equiv) was added and the reaction mixture was heated to 100 ^oC for 3–9 h. The reaction mixture was monitored by TLC using (Tetrahydrofuran:*n*-Hexane = 1:5) 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 sequentially 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.

General Procedure for the H/D Exchange Experiments:

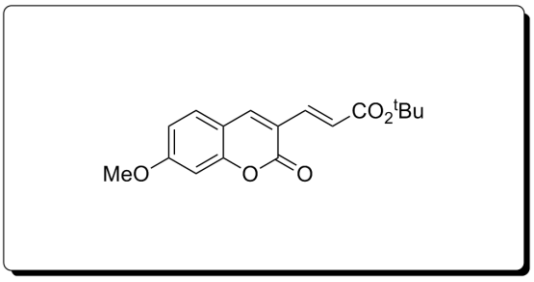
7-Methoxycoumarin (0.1 mmol), $Pd(OPiv)_2$ (0.2 equiv), K_2CO_3 (3.0 equiv) were combined in PivOH (1.0 mL) under O_2 (balloon). The D_2O (20 equiv) was added and the reaction mixture was heated to 95 ^oC. The reaction mixture was diluted with CH_2Cl_2 and the excess $NaHCO_3$ was added to neutralize PivOH. After stirring the mixture for 10 min, the residue was washed with sequentially aqueous $NaHCO_3$ and NH_4Cl. The organic layer was dried over $MgSO_4$. The residue was concentrated, and evaporated to dryness under high vacuum. The extent of H/D exchange was determined by integration of ^{1}H-NMR.

IV. Compound characterizations

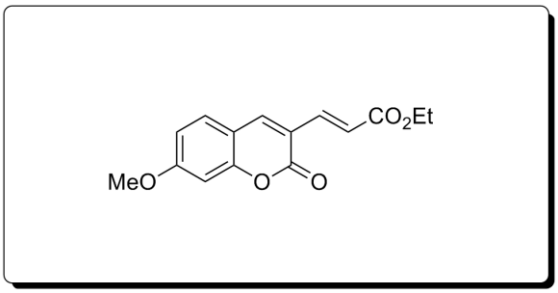


(E)-Butyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)acrylate (3a). Yield 81%. mp 120–122 ^oC. δ 7.79 (s, 1H), 7.51 (dd, *J* = 15.9, 0.6 Hz, 1H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.02 (d, *J* = 15.8 Hz, 1H), 6.86 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.81

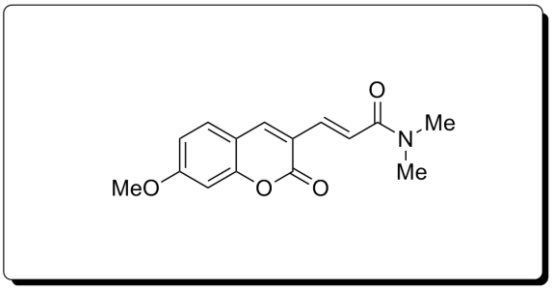
(d, *J* = 2.5 Hz, 1H), 4.18 (t, *J* = 6.6 Hz, 2H), 3.88 (s, 3H), 1.70 – 1.62 (m, 2H), 1.46 – 1.36 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 163.9, 159.3, 155.6, 143.7, 138.2, 129.6, 122.3, 118.9, 113.4, 112.7, 100.5, 64.5, 55.9, 30.8, 19.2, 13.7. HRMS (ESI+) m/z calcd. for $C_{17}H_{18}NaO_5^+$ $[M+Na]^+$: 325.1046, found: 325.1048.



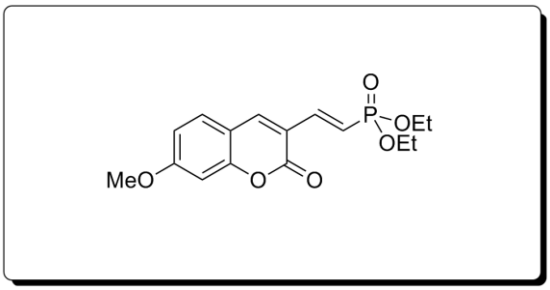
(E)-tert-Butyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)acrylate (3b). Yield 74%. mp 149–153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.44 – 7.38 (m, 2H), 6.92 (d, *J* = 15.8 Hz, 1H), 6.85 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.80 (d, *J* = 2.4 Hz, 1H), 3.87 (s, 3H), 1.50 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 163.7, 159.4, 155.5, 143.2, 137.1, 129.4, 124.2, 119.1, 113.3, 112.7, 100.5, 80.6, 55.7, 28.1. HRMS (ESI+) m/z calcd. for $C_{17}H_{18}NaO_5^+$ $[M+Na]^+$: 325.1046, found: 325.1051.



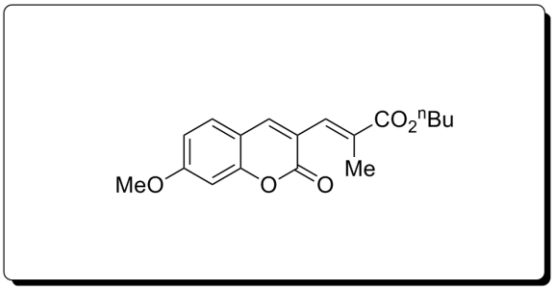
(E)-Ethyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)acrylate (3c). Yield 68%. mp 170–172 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.83 (s, 1H), 7.54 – 7.42 (m, 2H), 6.94 (s, *J* = 15.8 Hz, 1H), 6.88 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.82 (d, *J* = 2.6 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 167.2, 164.3, 159.6, 156.0, 144.1, 138.6, 130.1, 122.2, 119.0, 113.5, 113.1, 100.8, 60.9, 56.4, 14.5. HRMS (ESI+) m/z calcd. for $C_{15}H_{14}NaO_5^+$$[M+Na]^+$: 297.0733, found: 297.0742.



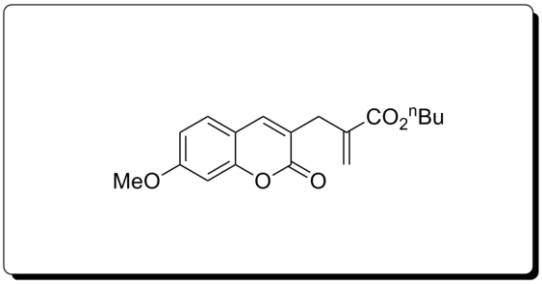
(E)-3-(7-Methoxy-2-oxo-2H-chromen-3-yl)-N,N-dimethylacrylamide (3d). Yield 50%. mp 228–231 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.80 (s, 1H), 7.61 (d, *J* = 15.2 Hz, 1H), 7.46 (d, *J* = 8.7 Hz, 1H), 7.39 (d, *J* = 15.1 Hz, 1H), 6.88 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.83 (d, *J* = 2.4 Hz, 1H), 3.88 (s, 3H), 3.15 (s, 3H), 3.00 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 166.8, 164.0, 159.9, 155.6, 144.1, 136.3, 129.8, 122.2, 119.8, 113.4, 113.3, 100.7, 56.3, 37.6, 35.9. HRMS (ESI+) m/z calcd. for $C_{15}H_{15}NNaO_4^+$[M+Na]$^+$: 296.0893, found: 296.0883.



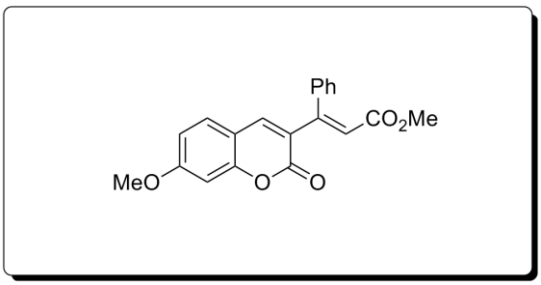
(E)-Diethyl (2-(7-methoxy-2-oxo-2H-chromen-3-yl)vinyl)phosphonate (3e). Yield 42%. mp 120–124 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.41 (d, *J* = 8.7 Hz, 1H), 7.36 – 7.25 (m, 1H), 7.01 – 6.90 (m, 1H), 6.85 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.79 (d, *J* = 2.3 Hz, 1H), 4.14 – 4.04 (m, 4H), 3.86 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 159.7, 155.9, 144.3, 142.8 (d, J_{CP} = 7.9 Hz), 130.0, 119.2 (d, J_{CP} = 186.5 Hz), 119.1 (d, J_{CP} = 23.5 Hz), 113.8, 113.0, 100.8, 62.3 (d, J_{CP} = 5.5 Hz), 56.3, 16.8 (d, J_{CP} = 6.4 Hz). HRMS (ESI+) m/z calcd. for $C_{16}H_{19}NaO_6P^+$ [M+Na]$^+$: 361.0811, found: 361.0812.



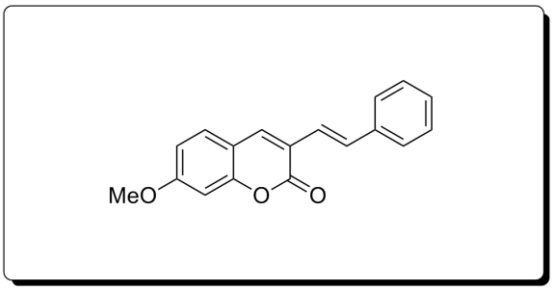
(E)-Butyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)-2-methylacrylate (3g). Yield 27% (total yield 56%). mp 101–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.63 – 7.60 (m, 1H), 7.40 (d, *J* = 8.6 Hz, 1H), 6.86 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.81 (d, *J* = 2.4 Hz, 1H), 4.19 (t, *J* = 6.7 Hz, 2H), 3.87 (s, 3H), 2.11 (d, *J* = 1.6 Hz, 3H), 1.73 – 1.63 (m, 2H), 1.48 – 1.36 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 163.6, 161.0, 155.7, 142.0, 131.8, 131.7, 129.6, 120.8, 113.4, 112.9, 101.0, 65.4, 56.2, 31.1, 19.6, 15.0, 14.1. HRMS (ESI+) m/z calcd. for $C_{18}H_{20}NaO_5^+$[M+Na]$^+$: 339.1203, found: 339.1206.



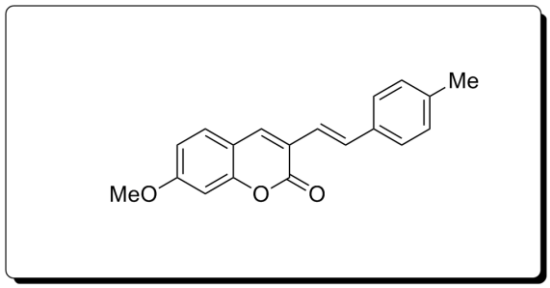
Butyl 2-((7-methoxy-2-oxo-2H-chromen-3-yl)methyl)acrylate (3g`). Yield 29% (total yield 56%). Colorless Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 6.83 – 6.76 (m, 2H), 6.31 (d, *J* = 1.3 Hz, 1H), 5.77 (d, *J* = 1.3 Hz, 1H), 4.11 (t, *J* = 6.6 Hz, 2H), 3.83 (s, 3H), 3.52 (s, 2H), 1.64 – 1.55 (m, 2H), 1.38 – 1.28 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 162.1, 161.7, 155.0, 140.2, 136.9, 128.3, 127.9, 123.0, 113.0, 112.4, 100.5, 64.8, 55.7, 32.7, 30.6, 19.2, 13.6. HRMS (ESI+) m/z calcd. for $C_{18}H_{20}NaO_5^+$[M+Na]$^+$: 339.1203, found: 339.1211.



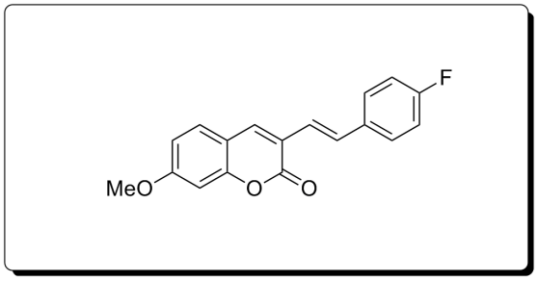
(E)-Methyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)-3-phenylacrylate (3f). Yield 52%. mp 190–194 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.44 – 7.40 (m, 3H), 7.35 (s, 1H), 7.29 – 7.20 (m, 3H), 7.13 (s, 1H), 6.85 – 6.78 (m, 2H), 3.87 (s, 3H), 3.56 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 166.8, 164.1, 159.5, 155.7, 149.6, 144.7, 138.3, 130.1, 129.2, 128.5, 123.4, 121.3, 113.3, 112.9, 100.4, 56.3, 51.4. HRMS (ESI+) m/z calcd. for $C_{20}H_{16}NaO_5^+$[M+Na]$^+$: 359.0890, found: 359.0884.



(E)-7-Methoxy-3-styryl-2H-chromen-2-one (3h). Yield 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.55 – 7.47 (m, 3H), 7.38 (d, *J* = 8.6 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.29 – 7.23 (m, 1H), 7.07 (d, *J* = 16.4 Hz, 1H), 6.83 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.80 (d, *J* = 2.5 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 160.6, 154.6, 137.1, 137.1, 132.3, 128.7, 128.6, 128.1, 126.8, 122.3, 121.5, 113.3, 112.9, 100.4, 55.7. [Ref]. *Org. Lett.* 2011, *13*, 5112-5115.

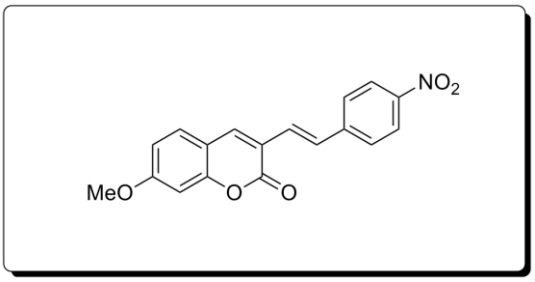


(E)-7-Methoxy-3-(4-methylstyryl)-2H-chromen-2-one (3i). Yield 56%. mp 188–191 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.50 – 7.34 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 16.3 Hz, 1H), 6.82 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.78 (d, *J* = 2.5 Hz, 1H), 3.84 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 160.7, 154.5, 138.1, 136.7, 134.2, 132.1, 129.4, 128.5, 126.7, 121.7, 121.2, 113.4, 112.8, 100.4, 55.7, 21.3. HRMS (ESI+) m/z calcd. for $C_{19}H_{16}NaO_3^+$[M+Na]$^+$: 315.0992, found: 315.0993.

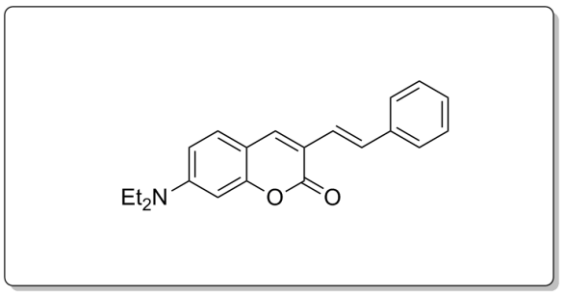


(E)-3-(4-Fluorostyryl)-7-methoxy-2H-chromen-2-one (3j). Yield 60%. mp 147–150 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.71 (s, 1H), 7.54 – 7.47 (m, 3H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.08 – 7.02 (m, 2H), 6.96 (d, *J* = 16.4 Hz,

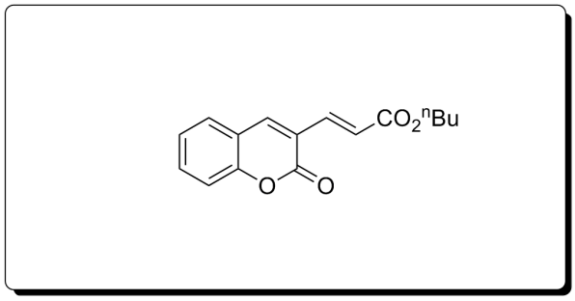
1H), 6.85 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.79 (d, *J* = 2.4 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 164.2, 163.0, 161.7, 160.6, 155.0, 137.9, 133.9, 133.9, 131.1, 129.1, 128.7, 128.6, 122.8, 122.8, 121.5, 116.0, 115.8, 113.6, 113.1, 100.7, 56.2. HRMS (ESI+) m/z calcd. for $C_{18}H_{13}FNaO_3^+$[M+Na]$^+$: 319.0741, found: 319.0740.



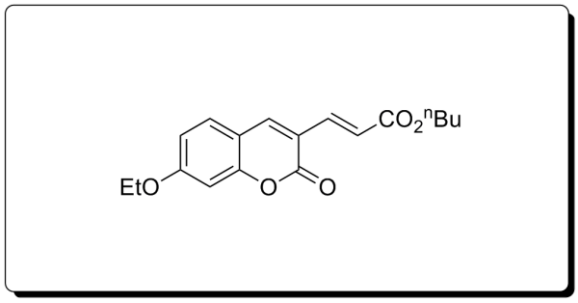
(E)-7-Methoxy-3-(4-nitrostyryl)-2H-chromen-2-one (3k). Yield 47%. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.20 – 8.18 (m, 2H), 7.83 (s, 1H), 7.71 – 7.64 (m, 3H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.21 (dd, *J* = 16.3, 0.7 Hz, 1H), 6.89 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.84 (d, *J* = 2.5 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) 163.7, 160.3, 155.5, 147.4, 144.2, 140.3, 130.1, 129.6, 127.7, 127.5, 124.4, 120.7, 113.5, 113.4, 100.8, 56.3. [Ref]. *Org. Lett.* 2011, *13*, 5112-5115.



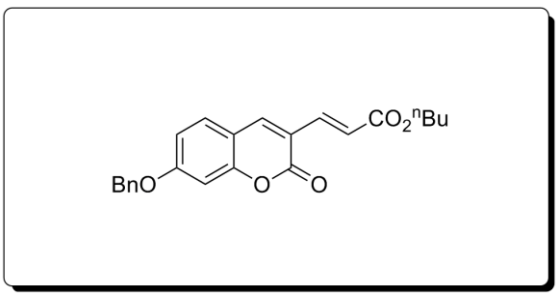
(E)-7-(Diethylamino)-3-styryl-2H-chromen-2-one (3l). Yield 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.52 – 7.48 (m, 2H), 7.44 (d, *J* = 16.3 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.27 (d, *J* = 8.8 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.08 (d, *J* = 16.3 Hz, 1H), 6.57 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.49 (d, *J* = 2.5 Hz, 1H), 3.40 (q, *J* = 7.1 Hz, 4H), 1.20 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 155.6, 150.4, 137.9, 137.6, 130.0, 128.7, 128.6, 127.5, 126.5, 123.1, 117.8, 109.1, 97.2, 44.8, 12.5. [Ref]. *Org. Lett.* 2011, *13*, 5112-5115.



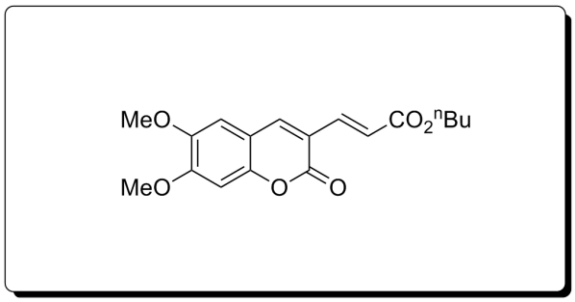
(E)-Butyl 3-(2-oxo-2H-chromen-3-yl)acrylate (3m). Yield 53%. mp 105–108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.57 – 7.49 (m, 3H), 7.33 – 7.26 (m, 2H), 7.07 (d, *J* = 15.9 Hz, 1H), 4.18 (t, *J* = 6.7 Hz, 2H), 1.70 – 1.61 (m, 2H), 1.45 – 1.35 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 159.0, 153.5, 143.4, 137.7, 132.8, 128.4, 124.8, 123.8, 122.4, 118.9, 116.6, 64.6, 30.7, 19.1, 13.7. HRMS (ESI+) m/z calcd. for $C_{16}H_{16}NaO_4^+$ $[M+Na]^+$: 295.0941, found: 295.0948.



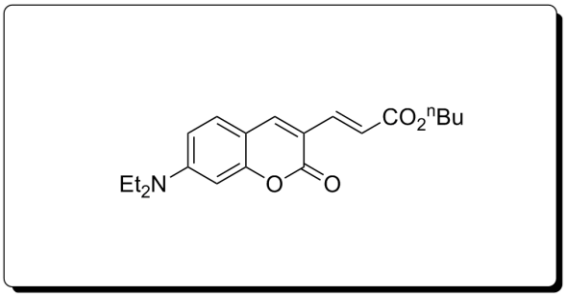
(E)-Butyl 3-(7-ethoxy-2-oxo-2H-chromen-3-yl)acrylate (3n). Yield 74%. mp 149–151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.49 (d, *J* = 15.7 Hz, 1H), 7.40 (d, *J* = 8.7 Hz, 1H), 7.00 (d, *J* = 15.8 Hz, 1H), 6.83 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.77 (d, *J* = 2.4 Hz, 1H), 4.17 (t, *J* = 6.7 Hz, 2H), 4.08 (q, *J* = 7.0 Hz, 2H), 1.69 – 1.61 (m, 2H), 1.46 – 1.33 (m, 5H), 0.93 (t, *J* = 7.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 163.7, 159.8, 156.0, 144.1, 138.6, 129.9, 122.5, 119.0, 114.1, 112.9, 101.3, 64.9, 64.8, 31.1, 19.5, 14.9, 14.1. HRMS (ESI+) m/z calcd. for $C_{18}H_{20}NaO_5^+$ $[M+Na]^+$: 339.1203, found: 339.1208.



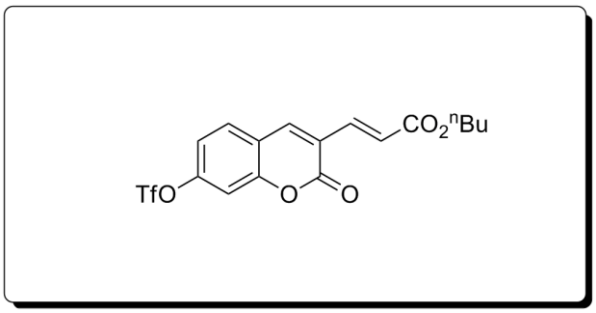
(E)-Butyl 3-(7-(benzyloxy)-2-oxo-2H-chromen-3-yl)acrylate (3o). Yield 75%. mp 155–159 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.84 (s, 1H), 7.53 – 7.33 (m, 7H), 7.00 – 6.88 (m, 3H), 5.15 (s, 2H), 4.17 (t, *J* = 6.6 Hz, 2H), 1.72 – 1.62 (m, 2H), 1.49 – 1.37 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 167.3, 163.3, 159.6, 155.9, 144.1, 138.5, 136.2, 130.1, 129.0, 128.7, 128.0, 122.3, 119.2, 114.1, 113.3, 101.7, 71.0, 64.8, 31.1, 19.6, 13.9. HRMS (ESI+) m/z calcd. for $C_{23}H_{22}NaO_5^+$[M+Na]$^+$: 401.1359, found: 401.1360.



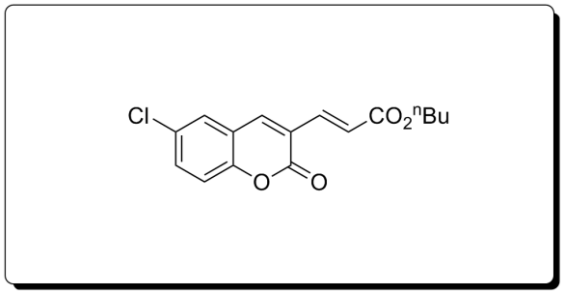
(E)-Butyl 3-(6,7-dimethoxy-2-oxo-2H-chromen-3-yl)acrylate (3p). Yield 77%. mp 152–155 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.81 (s, 1H), 7.50 (dd, *J* = 15.9, 0.7 Hz, 1H), 6.96 (dd, *J* = 15.9, 0.4 Hz, 1H), 6.87 (d, *J* = 26.9 Hz, 2H), 4.17 (t, *J* = 6.7 Hz, 2H), 3.92 (s, 3H), 3.87 (s, 3H), 1.71 – 1.63 (m, 2H), 1.48 – 1.37 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) 167.4, 159.8, 154.8, 150.4, 147.3, 144.1, 138.7, 122.1, 119.3, 112.1, 108.8, 100.0, 64.8, 56.8, 56.7, 31.2, 19.6, 13.9. HRMS (ESI+) m/z calcd. for $C_{18}H_{20}NaO_6^+$[M+Na]$^+$: 355.1152, found: 355.1147.



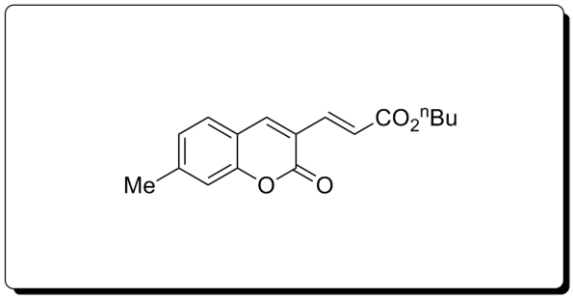
(E)-Butyl 3-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)acrylate (3q). Yield 66%. mp 111–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.50 (d, *J* = 15.8 Hz, 1H), 7.27 (d, *J* = 8.9 Hz, 1H), 6.92 (d, *J* = 15.8 Hz, 1H), 6.57 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.46 (d, *J* = 2.5 Hz, 1H), 4.16 (t, *J* = 6.7 Hz, 2H), 3.41 (q, *J* = 7.1 Hz, 4H), 1.68 – 1.61(m, 2H), 1.46 – 1.34 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 6H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 160.2, 156.5, 151.7, 144.2, 139.3, 129.8, 119.5, 114.7, 109.4, 108.6, 97.0, 64.2, 45.0, 30.8, 19.2, 13.7, 12.5. HRMS (ESI+) m/z calcd. for $C_{20}H_{25}NNaO_4^+$ [M+Na]$^+$: 366.1676, found: 366.1662.



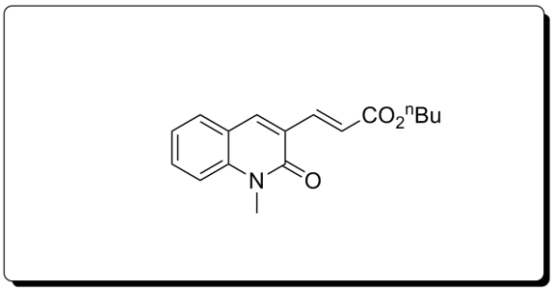
(E)-Butyl 3-(2-oxo-7-(((trifluoromethyl)sulfonyl)oxy)-2H-chromen-3-yl)acrylate (3r). Yield 51%. mp 163–166 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.91 (s, 1H), 7.68 (d, *J* = 8.6 Hz, 1H), 7.52 (dd, *J* = 15.9, 0.7 Hz, 1H), 7.32 (d, *J* = 2.4 Hz, 1H), 7.27 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.04 (d, *J* = 15.9 Hz, 1H), 4.19 (t, *J* = 6.6 Hz, 2H), 1.73 – 1.63 (m, 2H), 1.49 – 1.40 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 166.7, 158.3, 154.3, 151.6, 142.1, 137.2, 130.6, 125.1, 123.7, 119.4, 119.0 (q, J_{CF} = 318.9 Hz), 118.4, 110.5, 65.0, 31.1, 19.5, 13.8. HRMS (ESI+) m/z calcd. for $C_{17}H_{15}F_3NaO_7S^+[M+Na]^+$: 443.0383, found: 443.0377.



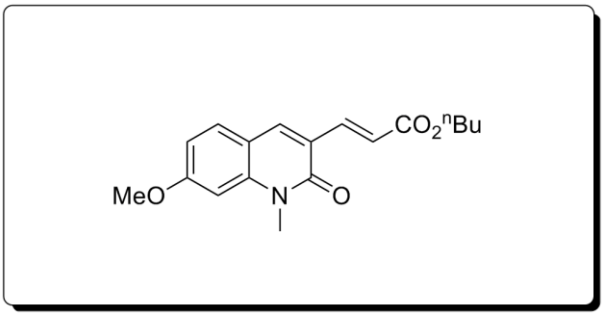
(E)-Butyl 3-(6-chloro-2-oxo-2H-chromen-3-yl)acrylate (3s). Yield 43%. mp 161–164 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.83 (s, 1H), 7.58 – 7.49 (m, 3H), 7.30 (dd, *J* = 8.7, 0.6 Hz, 1H), 7.03 (d, *J* = 15.9 Hz, 1H), 4.19 (t, *J* = 6.6 Hz, 2H), 1.72 – 1.63 (m, 2H), 1.49 – 1.35 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) 166.9, 158.8, 152.3, 142.3, 137.5, 132.9, 130.2, 128.0, 124.7, 123.8, 120.5, 118.4, 65.0, 31.1, 19.6, 13.9. HRMS (ESI+) m/z calcd. for $C_{16}H_{15}ClNaO_4^+[M+Na]^+$: 329.0551, found: 329.0545.



(E)-Butyl 3-(7-methyl-2-oxo-2H-chromen-3-yl)acrylate (3t). Yield 70%. mp 127–130 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.86 (s, 1H), 7.55 – 7.42 (m, 2H), 7.16 – 7.11 (m, 2H), 6.99 (d, *J* = 15.9 Hz, 1H), 4.17 (t, *J* = 6.6 Hz, 2H), 2.45 (s, 3H), 1.73 – 1.61 (m, 2H), 1.49 – 1.37 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 167.2, 159.6, 154.1, 145.1, 144.0, 138.3, 128.6, 126.4, 123.1, 121.4, 117.0, 116.9, 64.8, 31.1, 22.1, 19.6, 13.9. HRMS (ESI+) m/z calcd. for $C_{17}H_{18}NaO_4^+$[M+Na]$^+$: 309.1097, found: 309.1103.

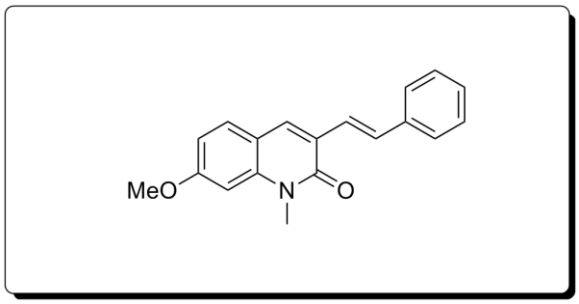


(E)-Butyl 3-(1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acrylate (3u). Yield 52%. mp 77–81 °C. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.91 (s, 1H), 7.71 (dd, *J* = 16.0, 0.6 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.38 – 7.33 (m, 1H), 7.28 – 7.22 (m, 1H), 7.05 (d, *J* = 15.9 Hz, 1H), 4.18 (t, *J* = 6.7 Hz, 2H), 3.71 (s, 3H), 1.72 – 1.63 (m, 2H), 1.51 – 1.38 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 167.5, 161.0, 140.4, 139.9, 139.7, 132.0, 129.8, 126.1, 122.7, 122.1, 120.3, 114.5, 64.7, 31.2, 29.9, 19.6, 13.9. HRMS (ESI+) m/z calcd. for $C_{17}H_{19}NNaO_3^+$[M+Na]$^+$: 308.1257, found: 308.1253.



(E)-Butyl 3-(7-methoxy-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acrylate (3v). Yield 59%. mp 83–87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.71 (dd, *J* = 15.9, 0.7 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 1H), 7.01 (d, *J* = 15.9 Hz, 1H), 6.82 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.73 (d, *J* = 2.3 Hz, 1H), 4.17 (t, *J* = 6.6 Hz, 2H), 3.91 (s, 3H), 3.69 (s, 3H), 1.70 – 1.61 (m, 2H), 1.47 – 1.35 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 162.8,

161.1, 141.7, 139.9, 139.3, 131.0, 122.7, 120.6, 114.3, 110.5, 98.4, 64.2, 55.7, 30.7, 29.7, 19.2, 13.7. HRMS (ESI+) m/z calcd. for $C_{18}H_{21}NNaO_4^+$[M+Na]$^+$: 338.1363, found: 338.1366.



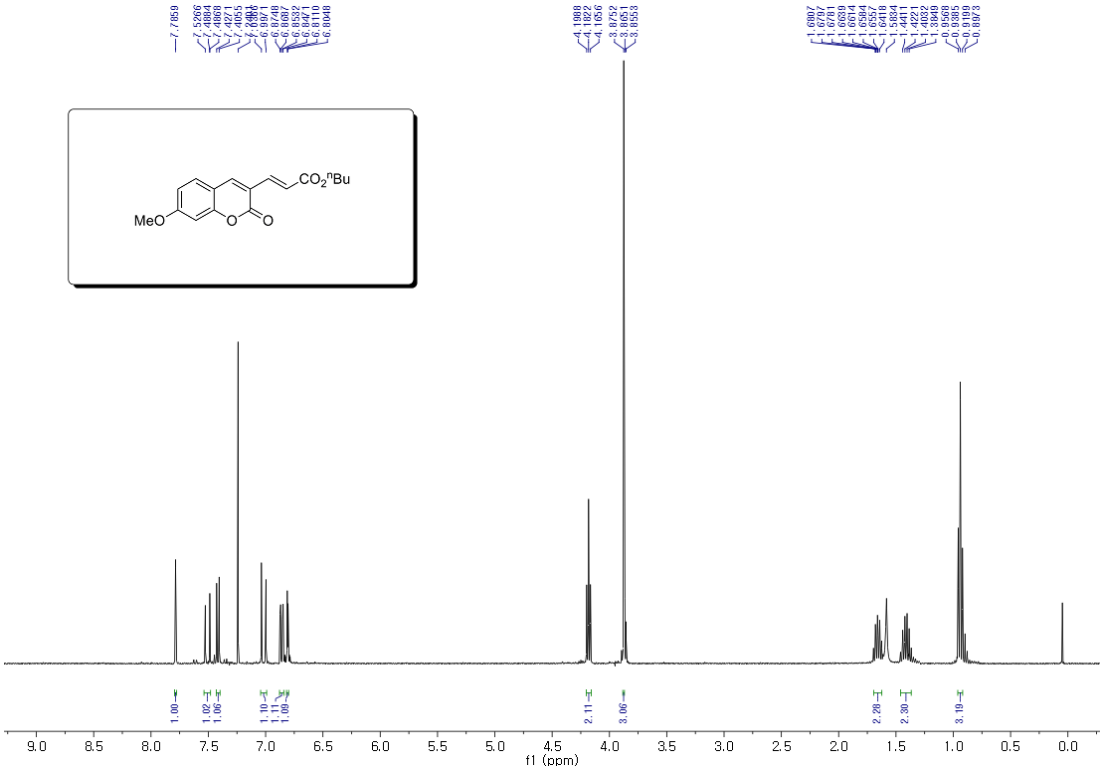
(E)-7-Methoxy-1-methyl-3-styrylquinolin-2(1H)-one. Yield 71%. Yellow Oil. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.80 (s, 1H), 7.58 – 7.47 (m, 4H), 7.39 – 7.23 (m, 4H), 6.83 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.75 (d, *J* = 2.3 Hz, 1H), 3.90 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 162.0, 161.9, 141.3, 138.1, 133.8, 130.5, 130.4, 129.0, 128.0, 127.0, 125.6, 124.4, 115.2, 110.3, 98.7, 55.9, 30.0. HRMS (ESI+) m/z calcd. for $C_{19}H_{17}NNaO_2^+$[M+Na]$^+$: 314.1151, found: 314.1161.

Appendix I

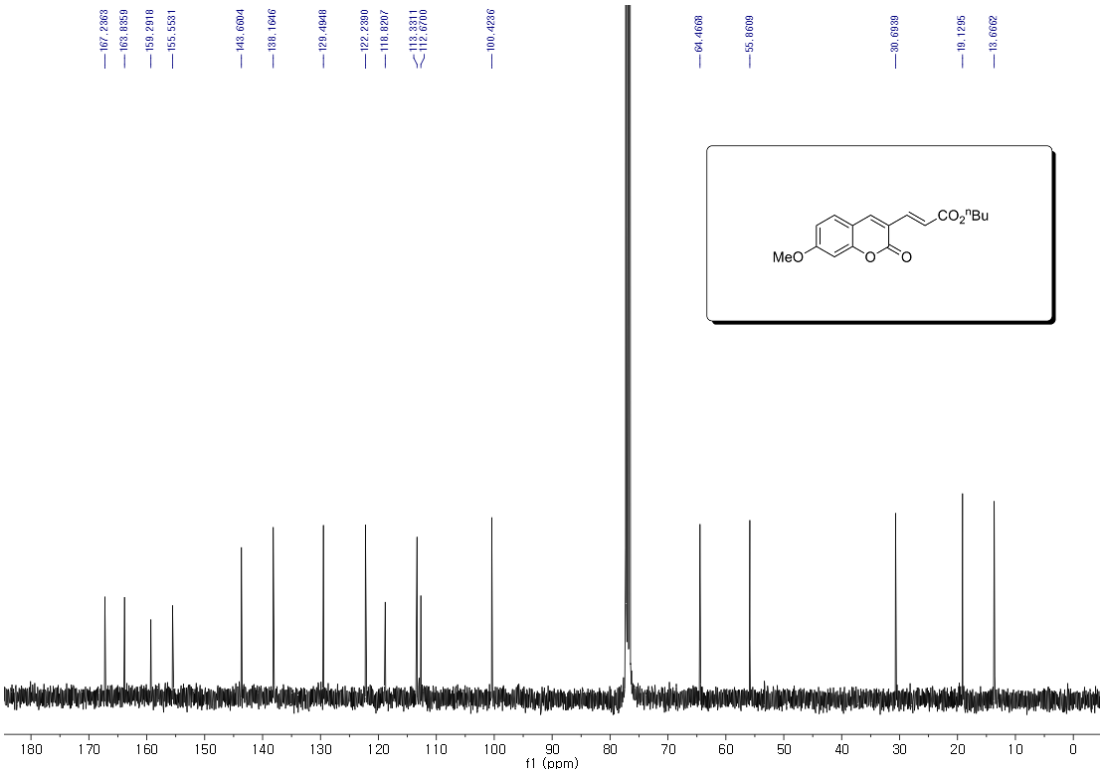
Spectral Copies of ^{1}H and ^{13}C NMR Data

Obtained in this Study

(E)-Butyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)acrylate (3a).

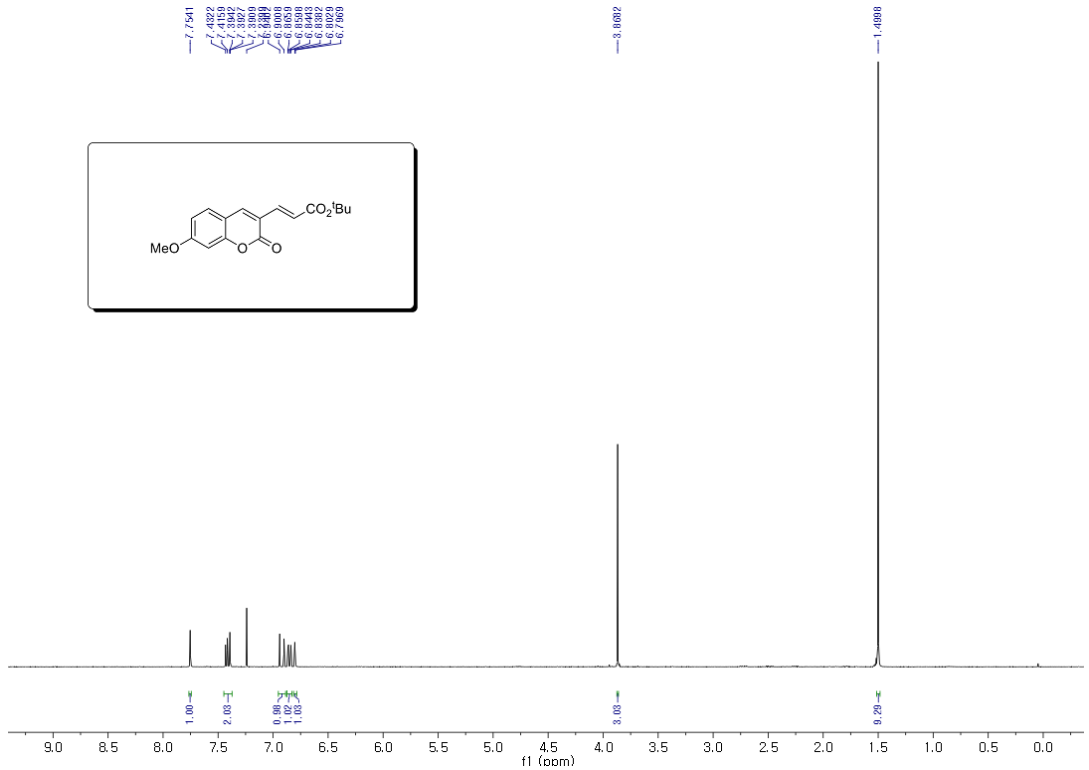


400 MHz, ^{1}H NMR in $CDCl_3$

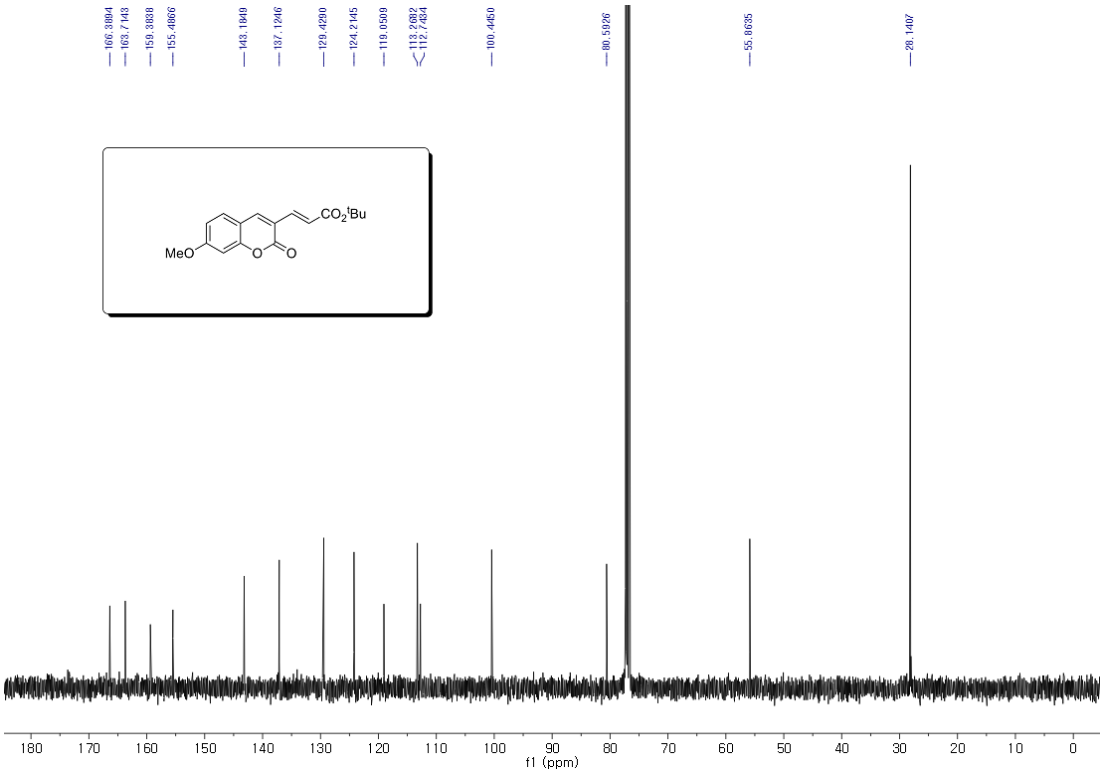


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-tert-Butyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)acrylate (3b).

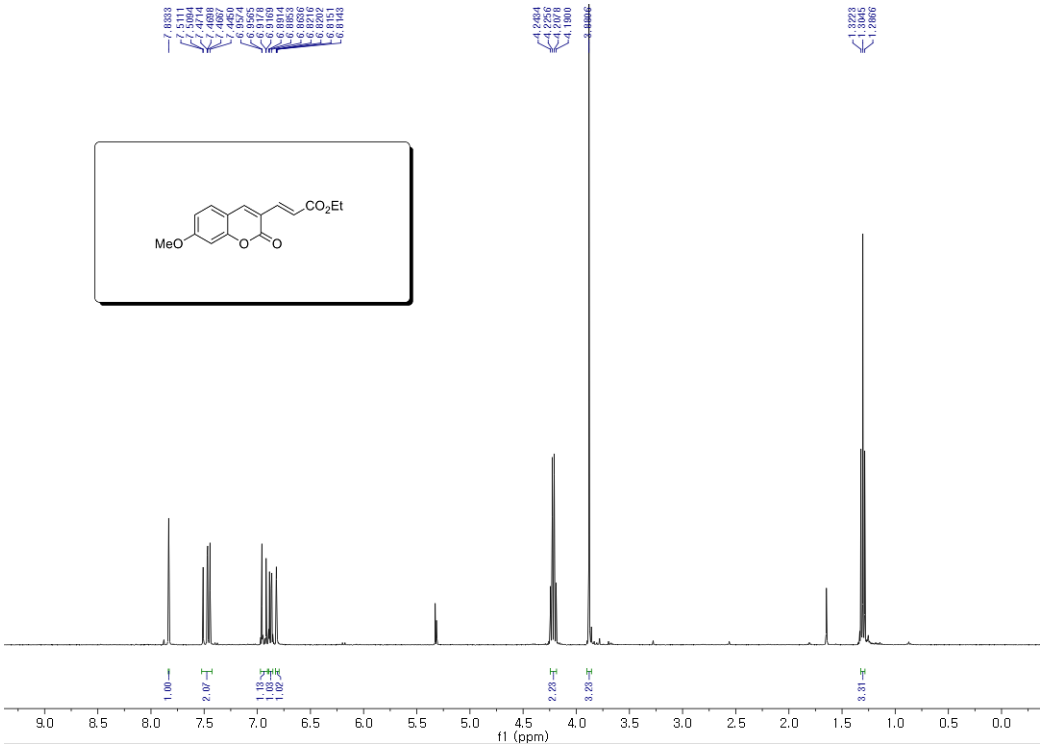


400 MHz, ^{1}H NMR in $CDCl_3$

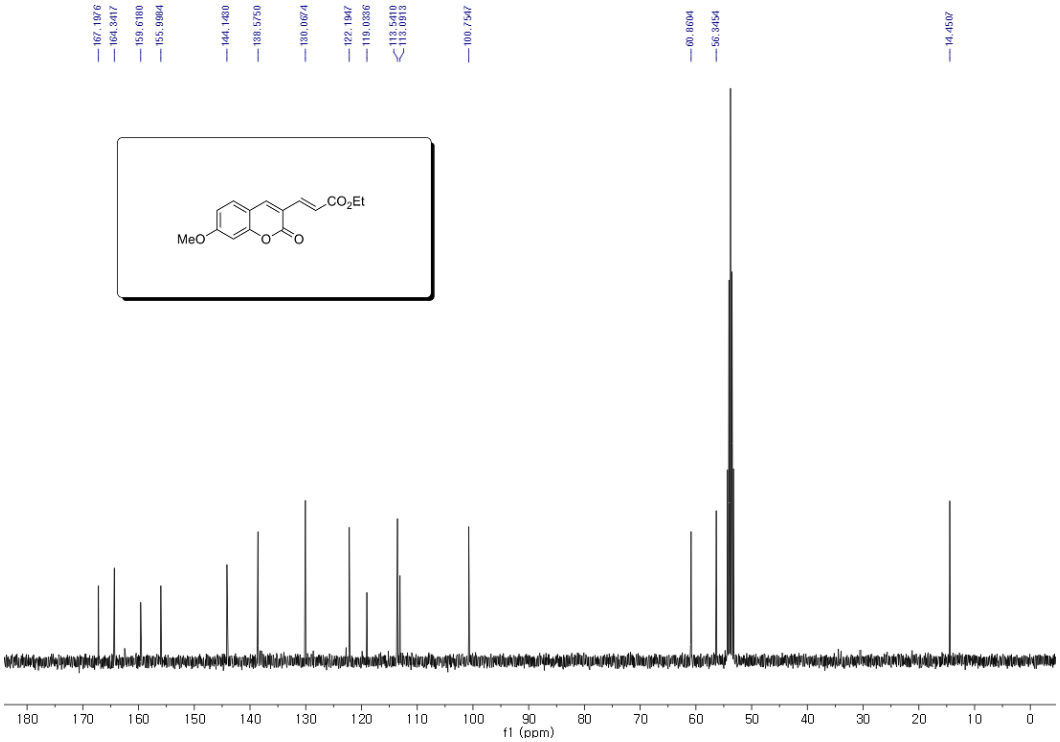


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-Ethyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)acrylate (3c).

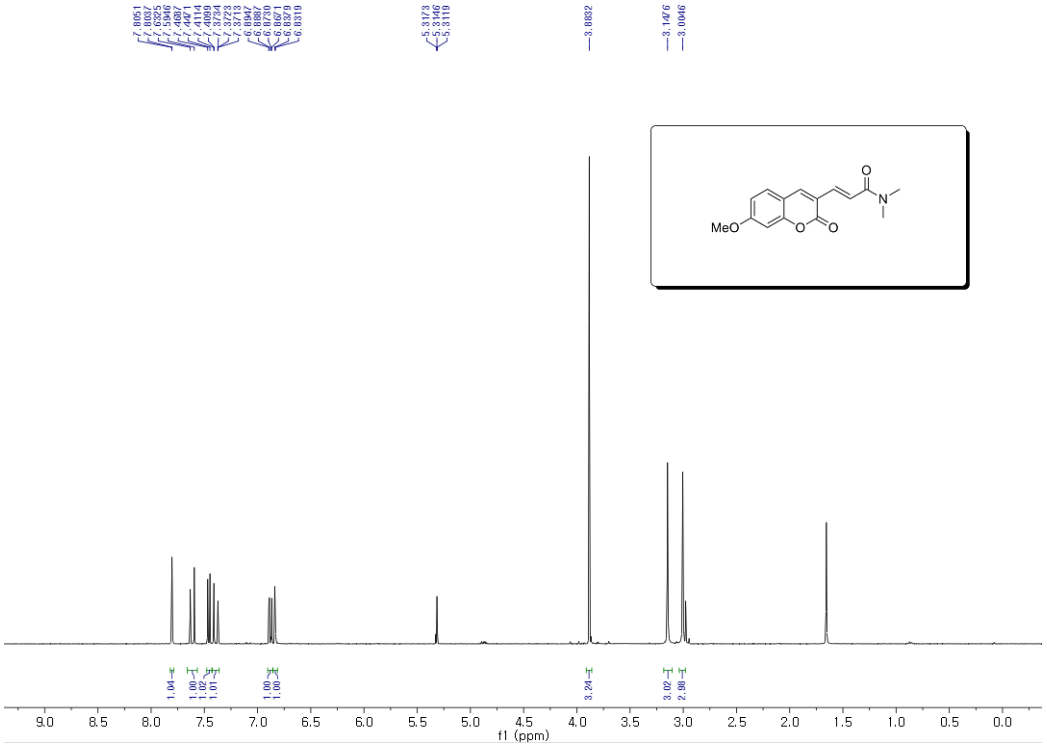


400 MHz, ^{1}H NMR in CD_2Cl_2

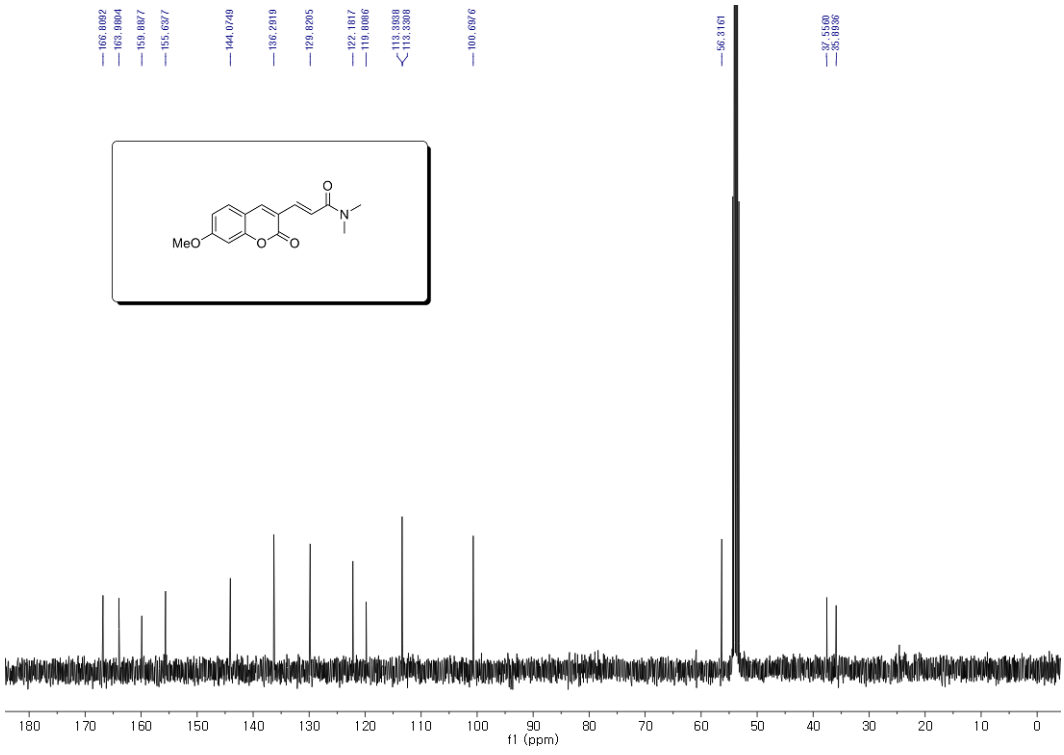


100 MHz, ^{13}C NMR in CD_2Cl_2

(E)-3-(7-Methoxy-2-oxo-2H-chromen-3-yl)-N,N-dimethylacrylamide (3d).

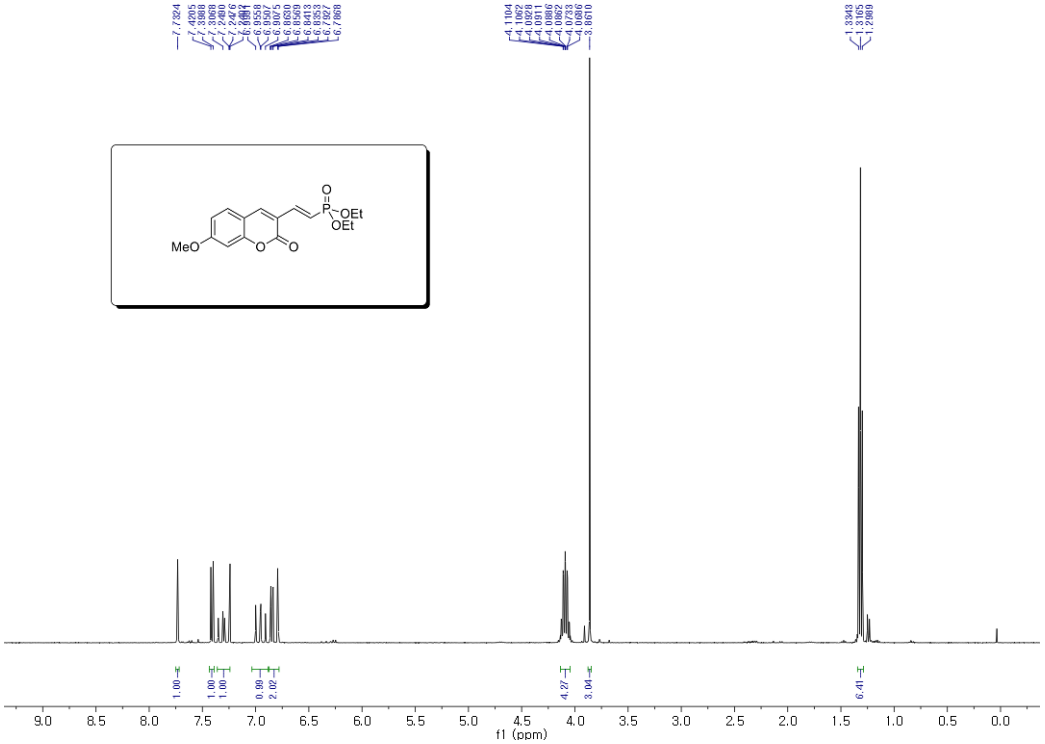


400 MHz, ^{1}H NMR in CD_2Cl_2

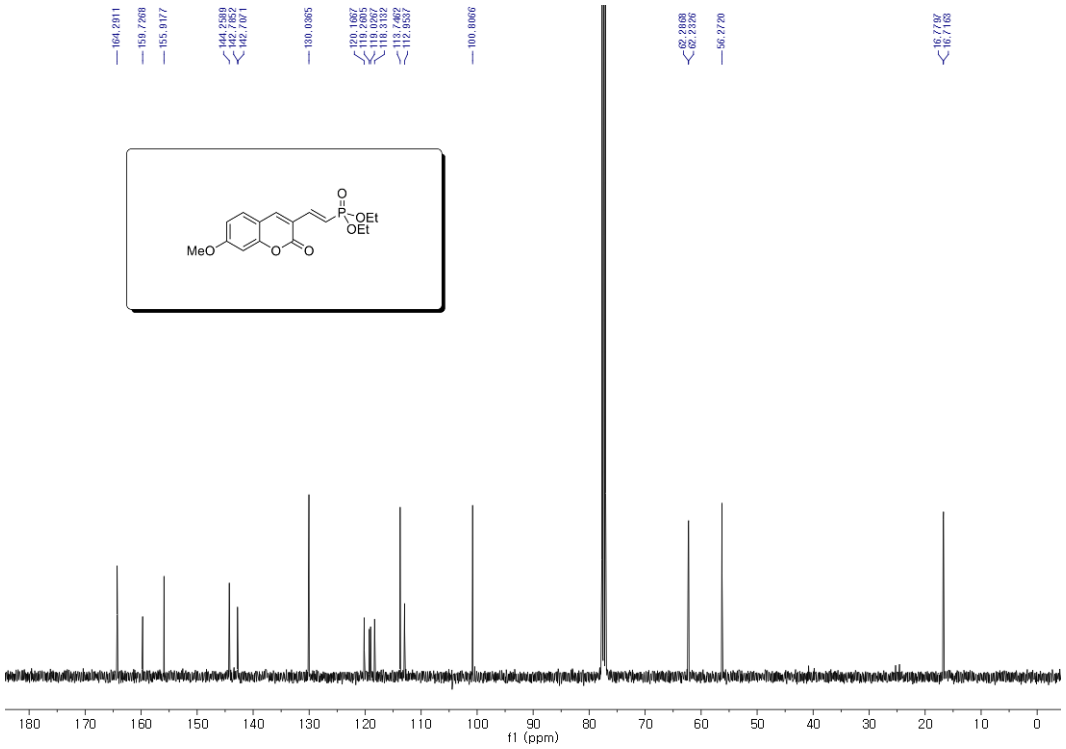


100 MHz, ^{13}C NMR in CD_2Cl_2

(E)-3-(7-Methoxy-2-oxo-2H-chromen-3-yl)-N,N-dimethylacrylamide (3e).

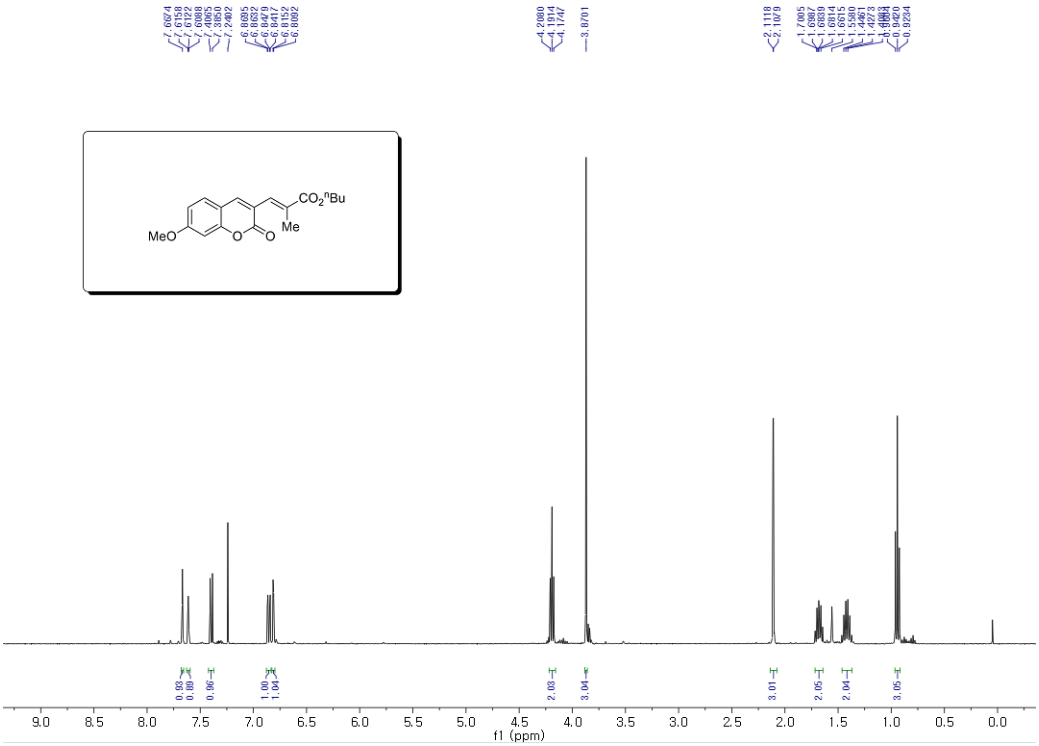


400 MHz, ^{1}H NMR in $CDCl_3$

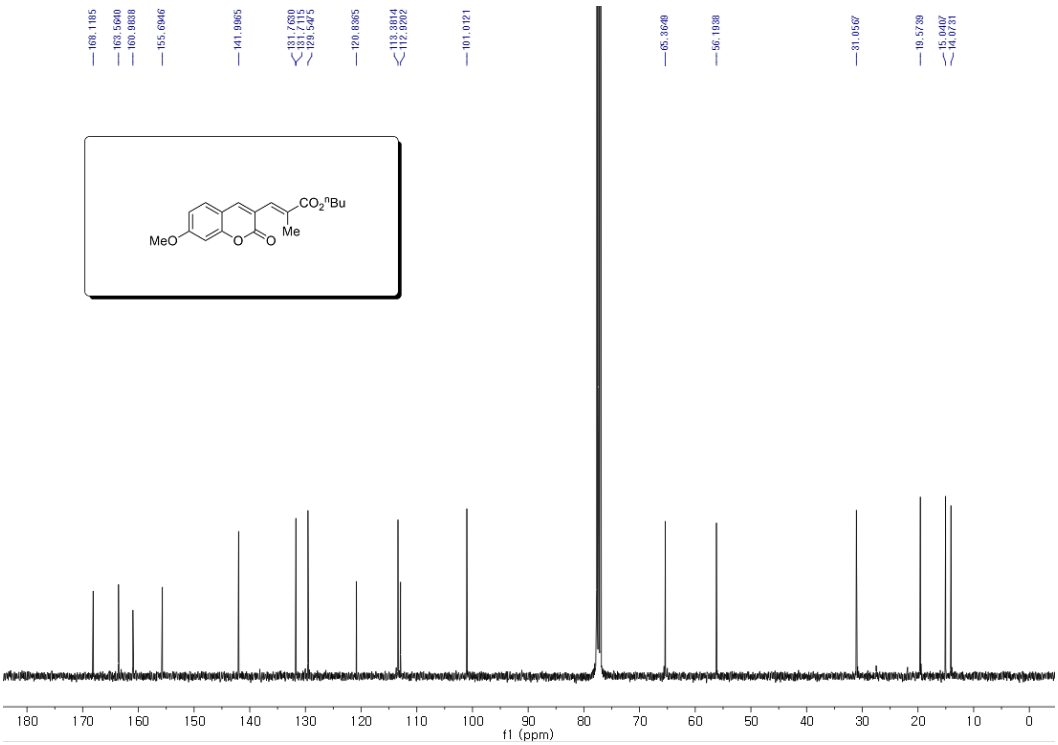


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-Butyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)-2-methylacrylate (3g).

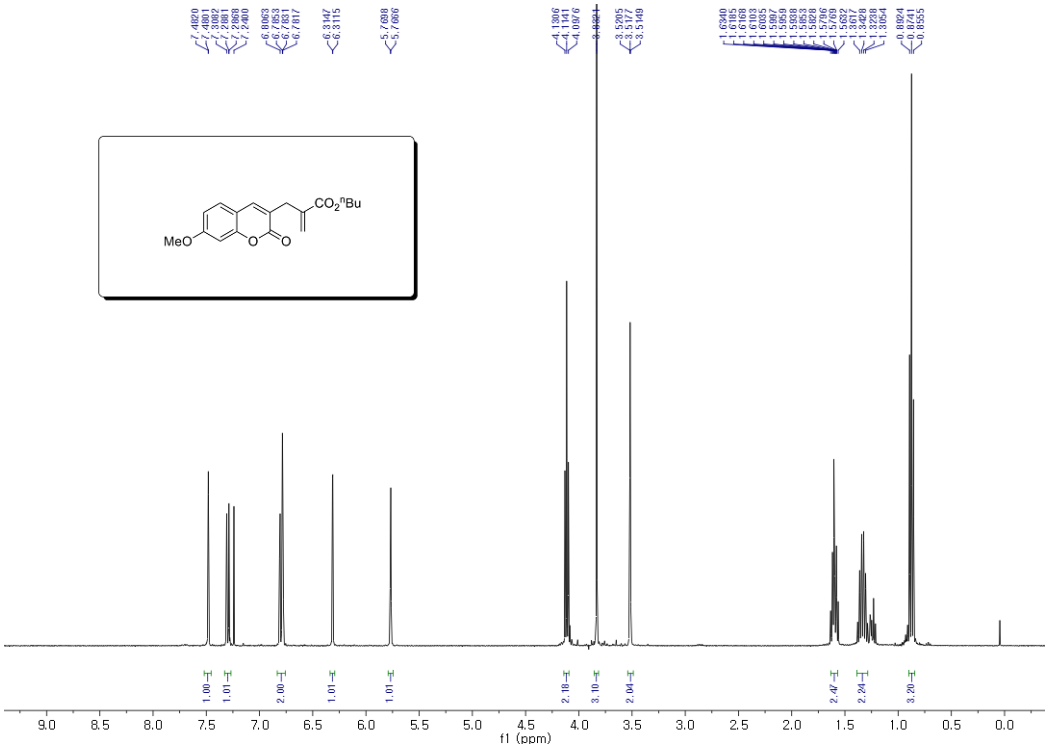


400 MHz, ^{1}H NMR in $CDCl_3$

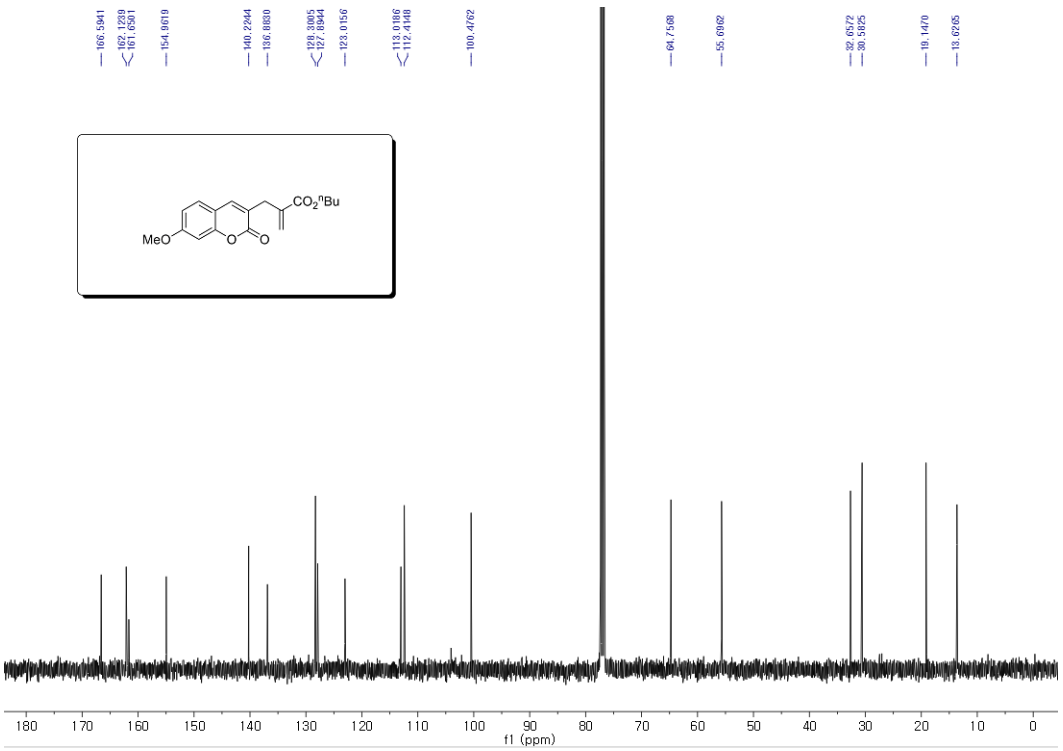


100 MHz, ^{13}C NMR in $CDCl_3$

Butyl 2-((7-methoxy-2-oxo-2H-chromen-3-yl)methyl)acrylate (3g`).

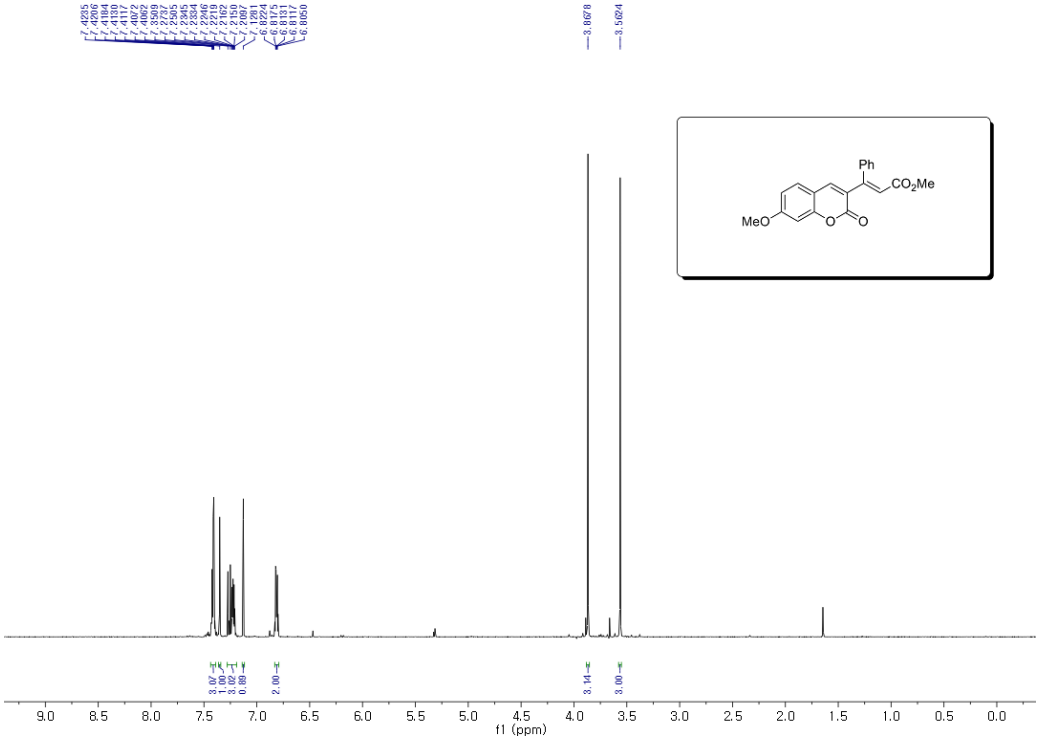


400 MHz, ^{1}H NMR in $CDCl_3$

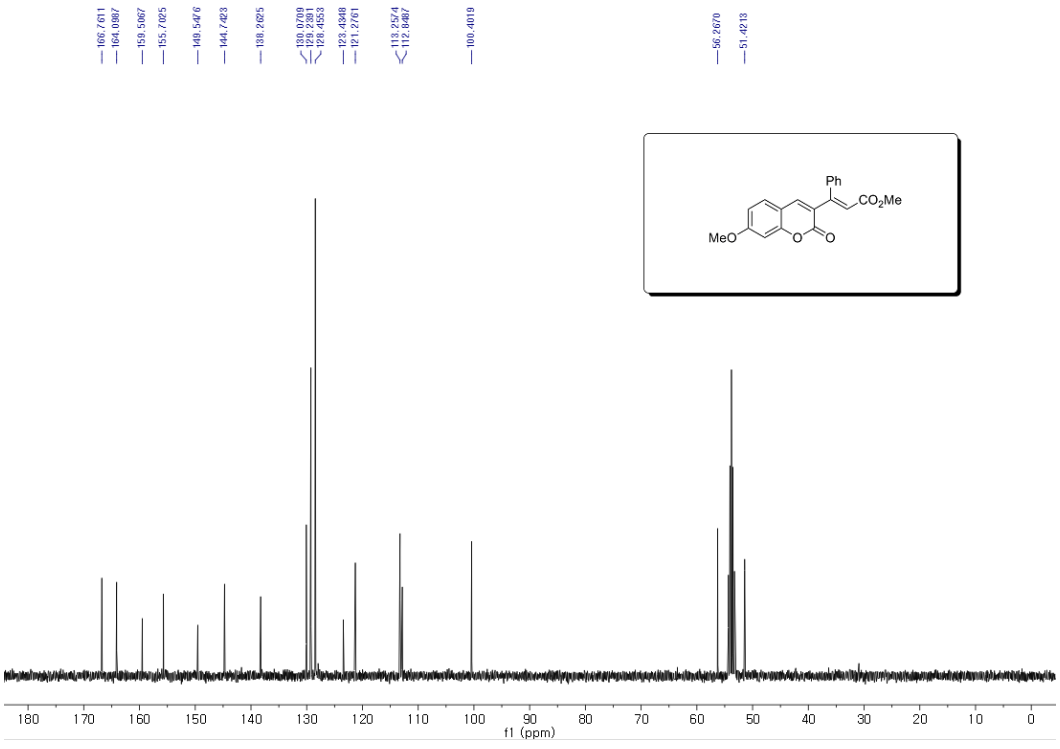


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-Methyl 3-(7-methoxy-2-oxo-2H-chromen-3-yl)-3-phenylacrylate (3f).

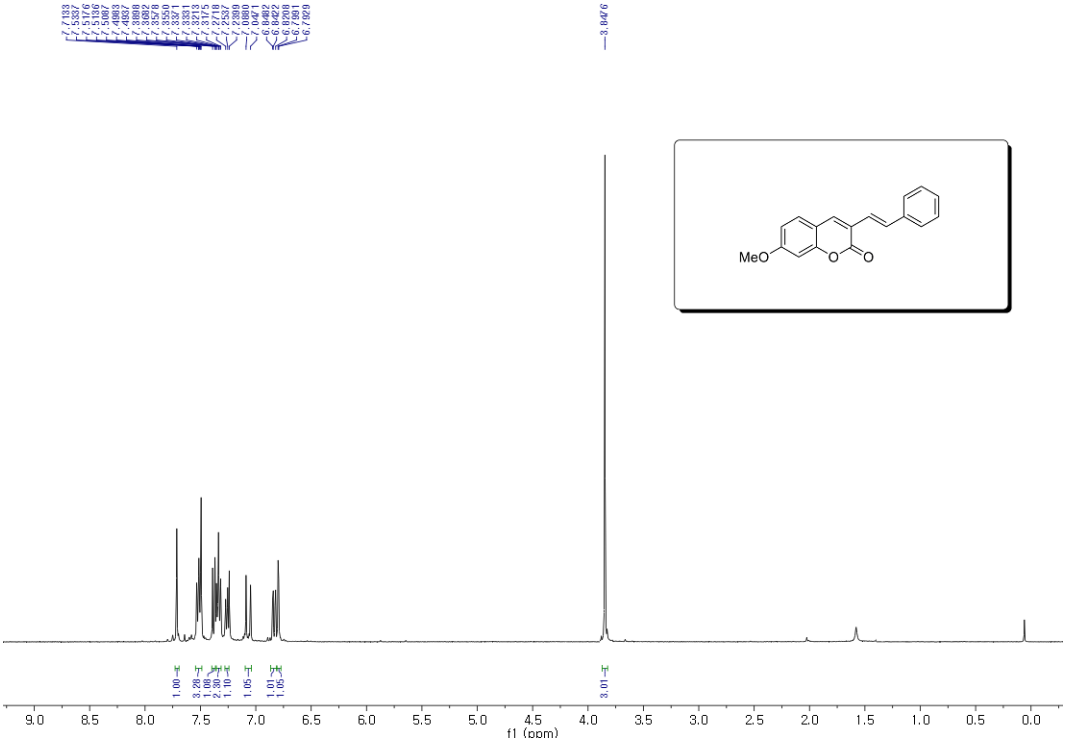


400 MHz, ^{1}H NMR in CD_2Cl_2

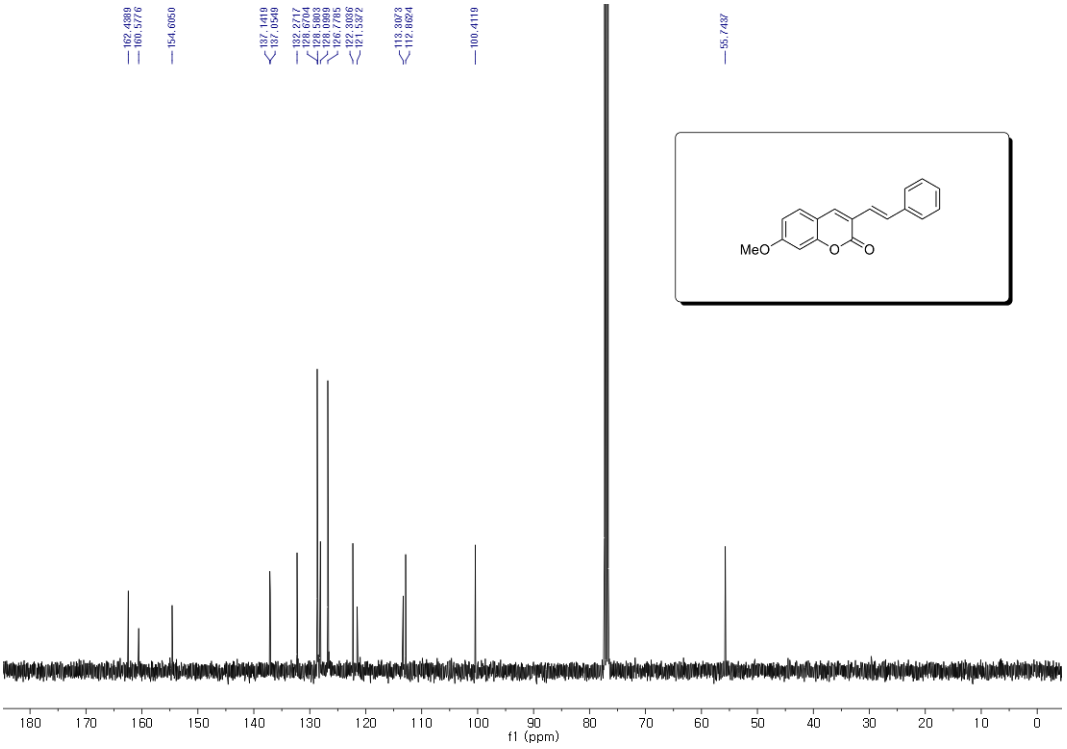


100 MHz, ^{13}C NMR in CD_2Cl_2

(E)-7-Methoxy-3-styryl-2H-chromen-2-one (3h).

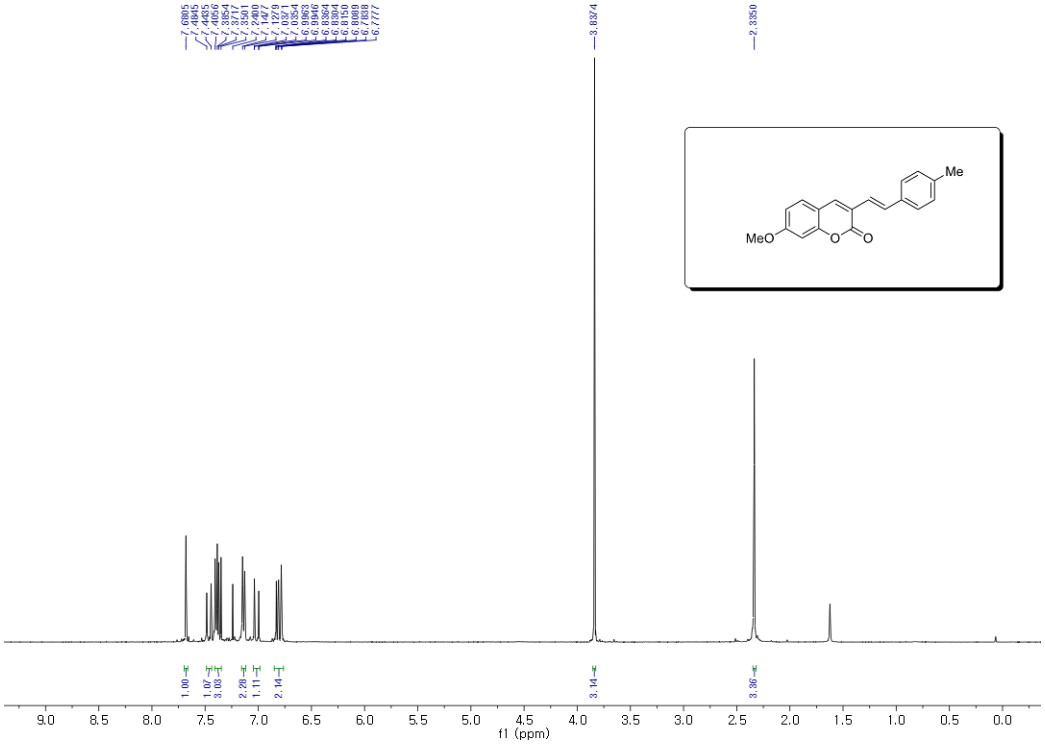


400 MHz, ^{1}H NMR in $CDCl_3$

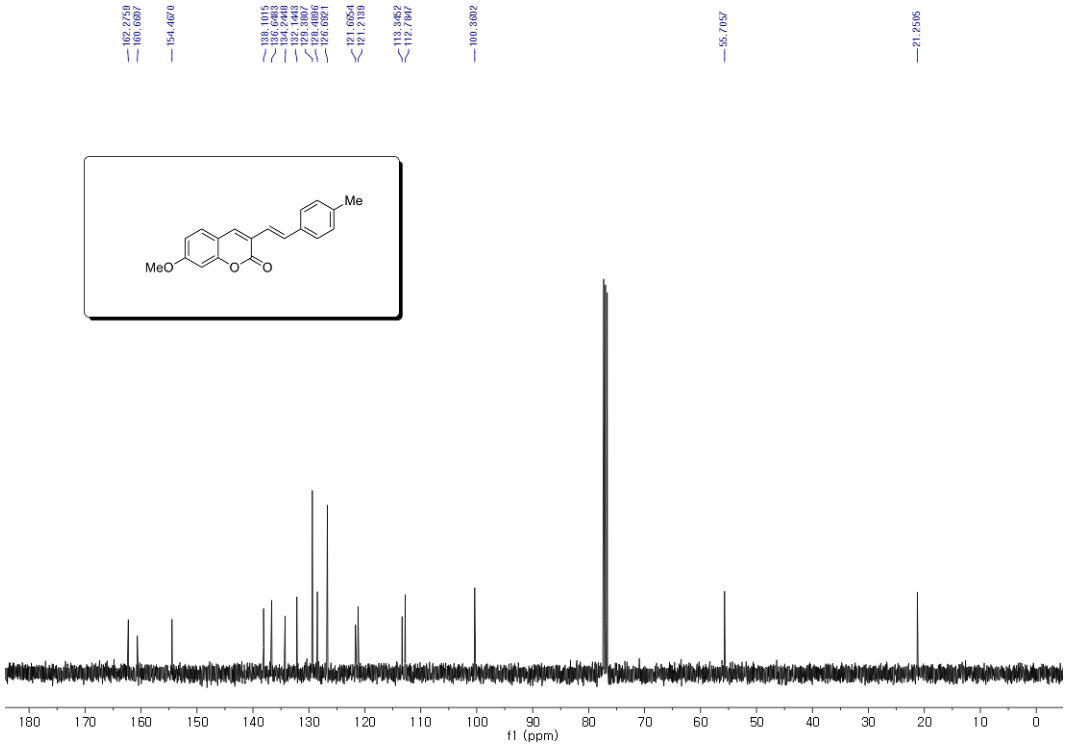


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-7-Methoxy-3-(4-methylstyryl)-2H-chromen-2-one (3i).

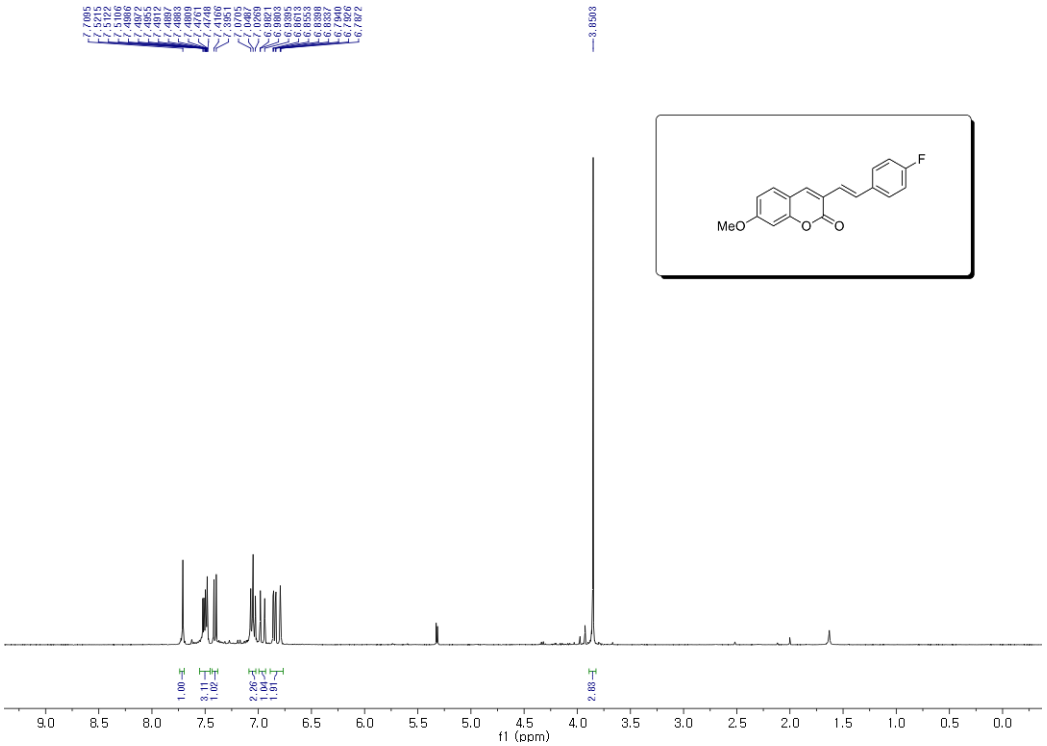


400 MHz, ^{1}H NMR in $CDCl_3$

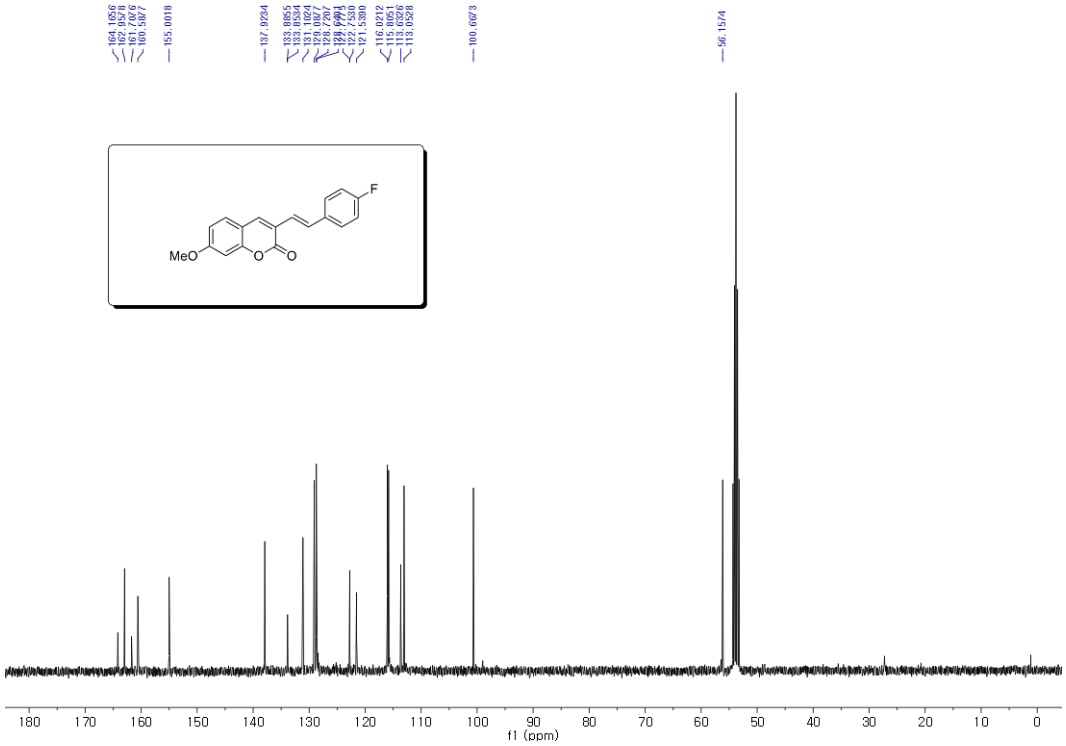


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-3-(4-Fluorostyryl)-7-methoxy-2H-chromen-2-one (3j).

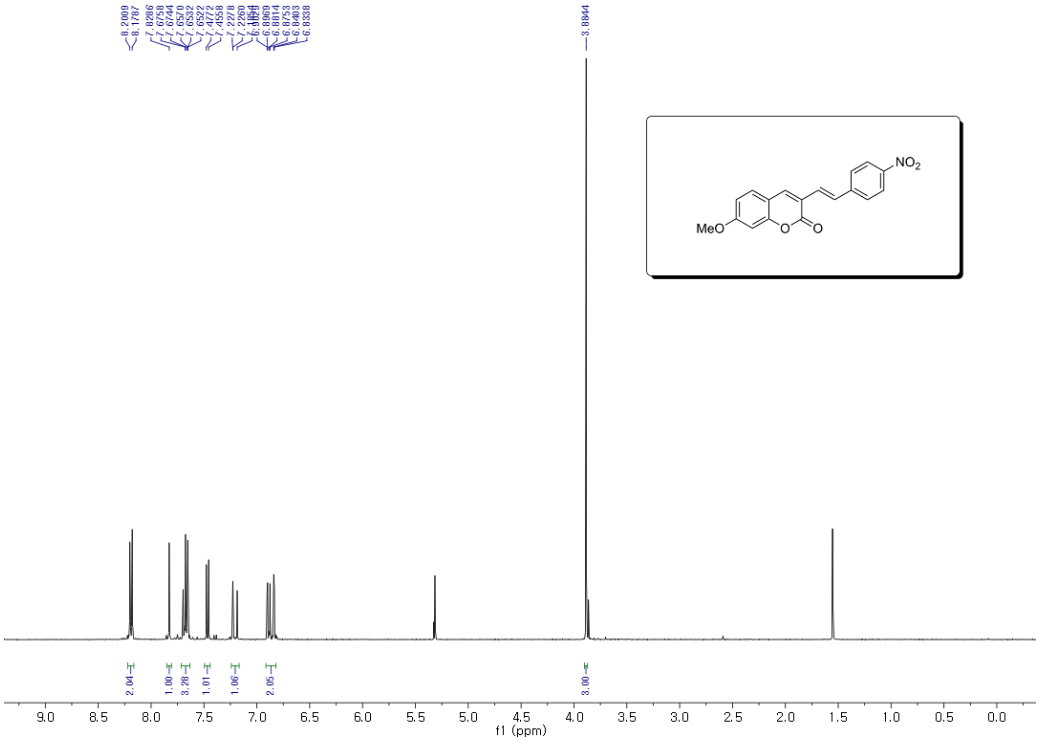


400 MHz, ^{1}H NMR in CD_2Cl_2

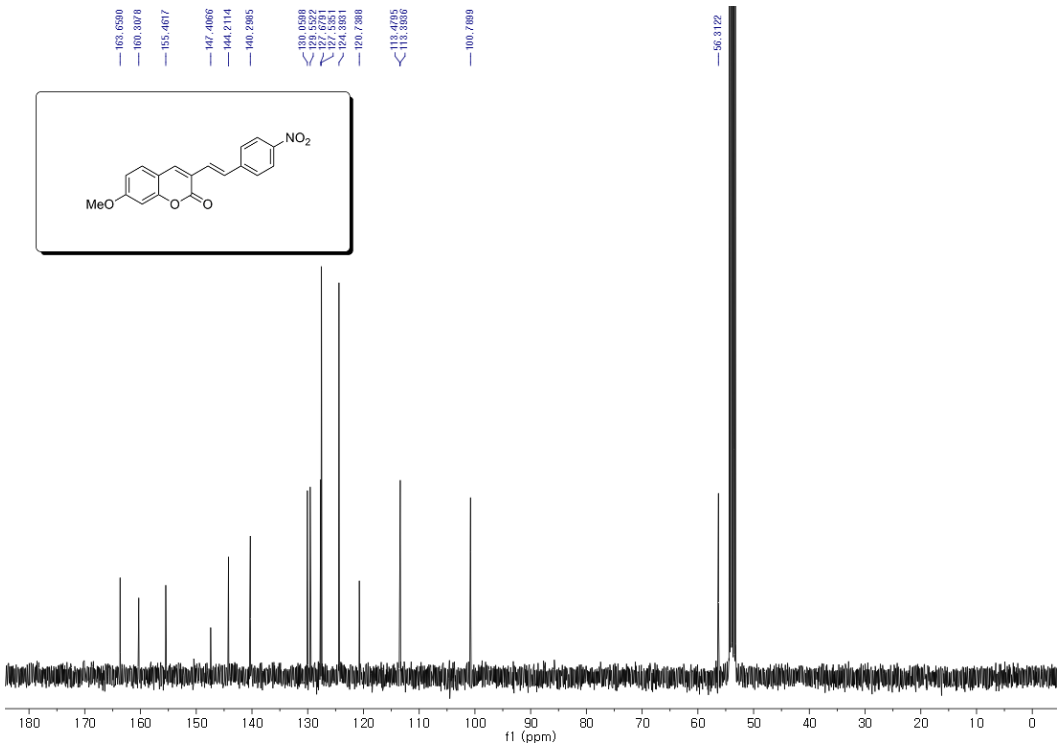


100 MHz, ^{13}C NMR in CD_2Cl_2

(E)-7-Methoxy-3-(4-nitrostyryl)-2H-chromen-2-one (3k).

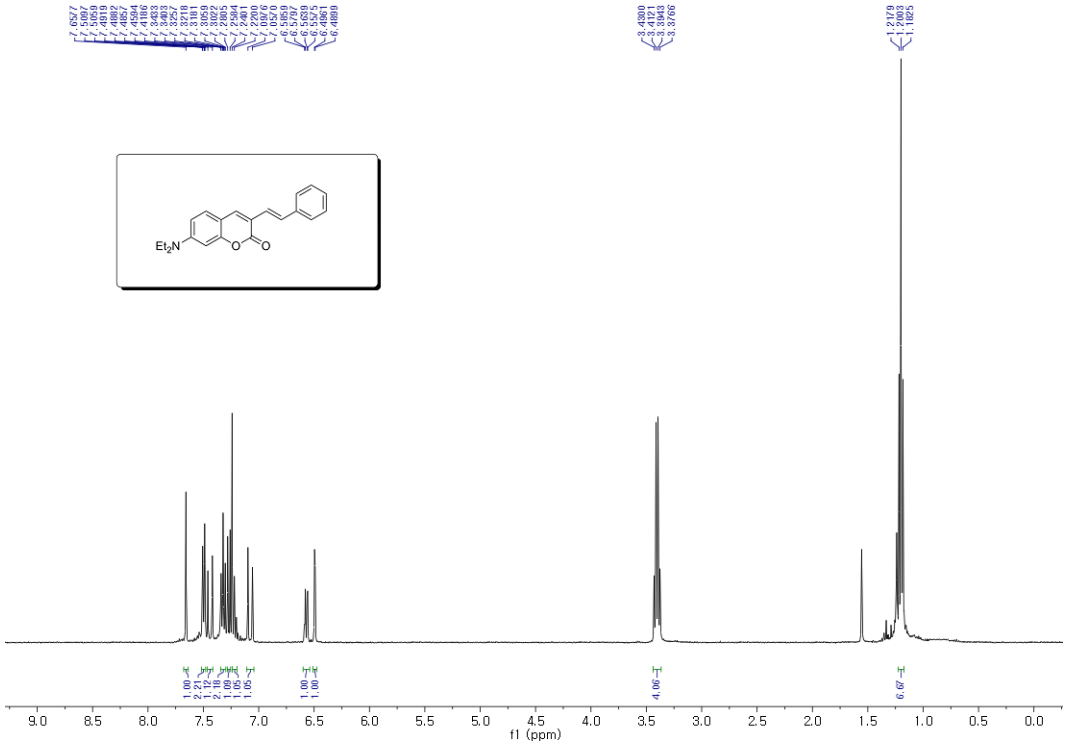


400 MHz, ^{1}H NMR in CD_2Cl_2

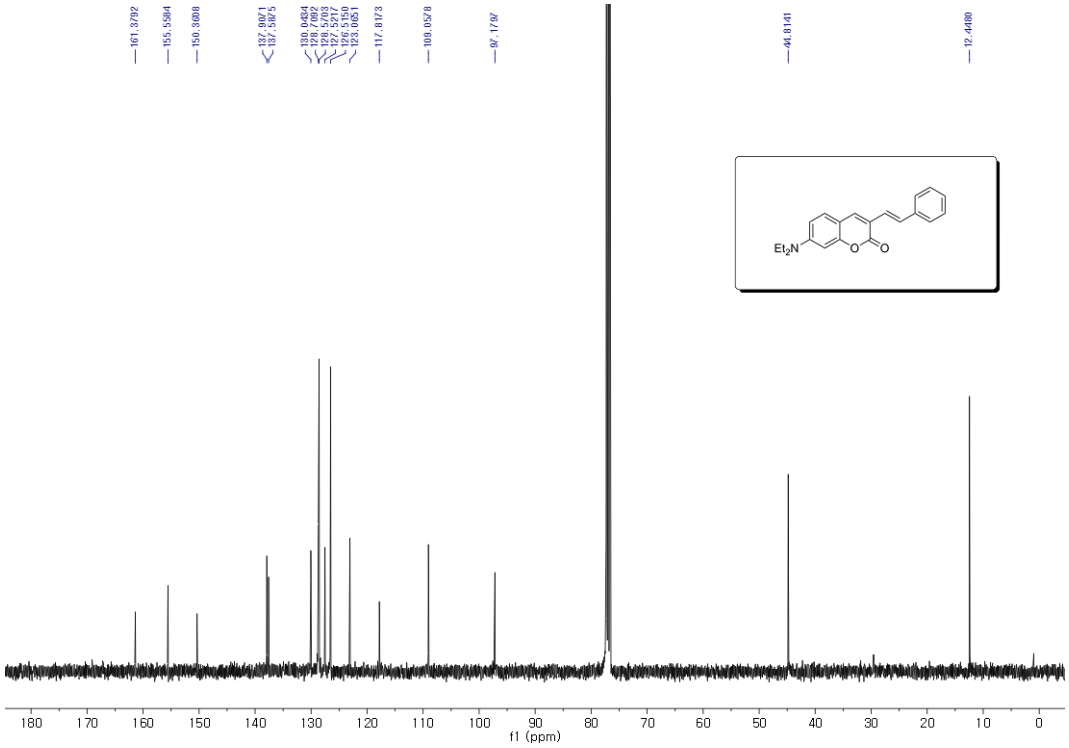


100 MHz, ^{13}C NMR in CD_2Cl_2

(E)-7-(Diethylamino)-3-styryl-2H-chromen-2-one (3l).

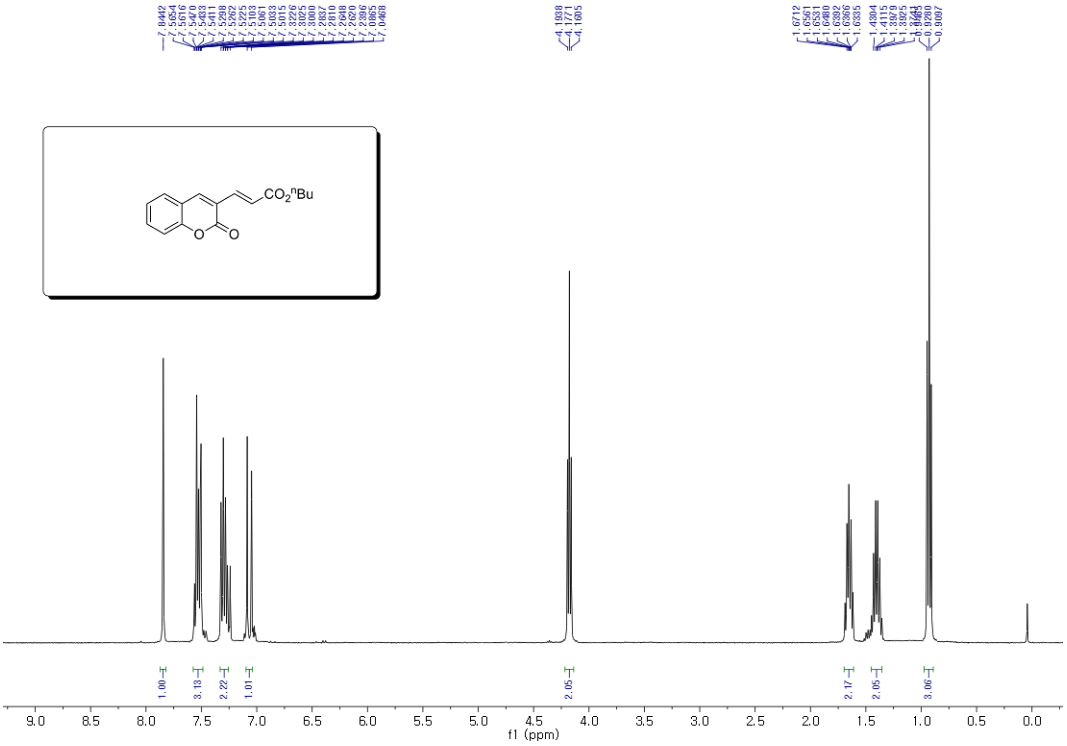


400 MHz, ^{1}H NMR in $CDCl_3$

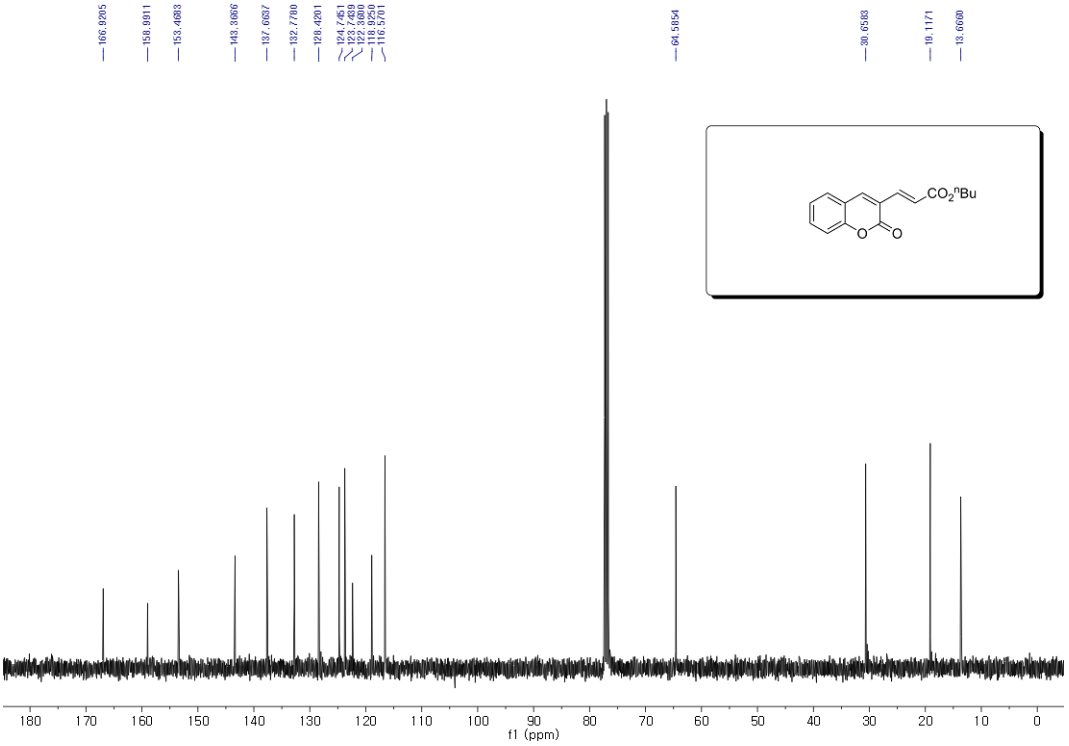


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-Butyl 3-(2-oxo-2H-chromen-3-yl)acrylate (3m).

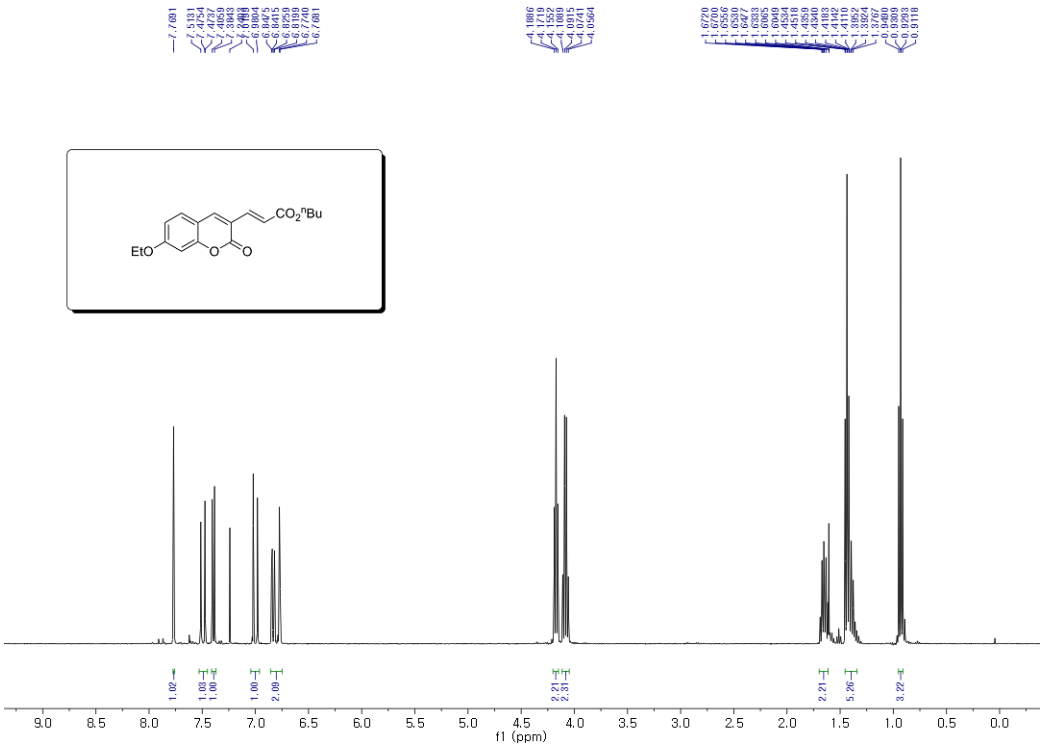


400 MHz, ^{1}H NMR in $CDCl_3$

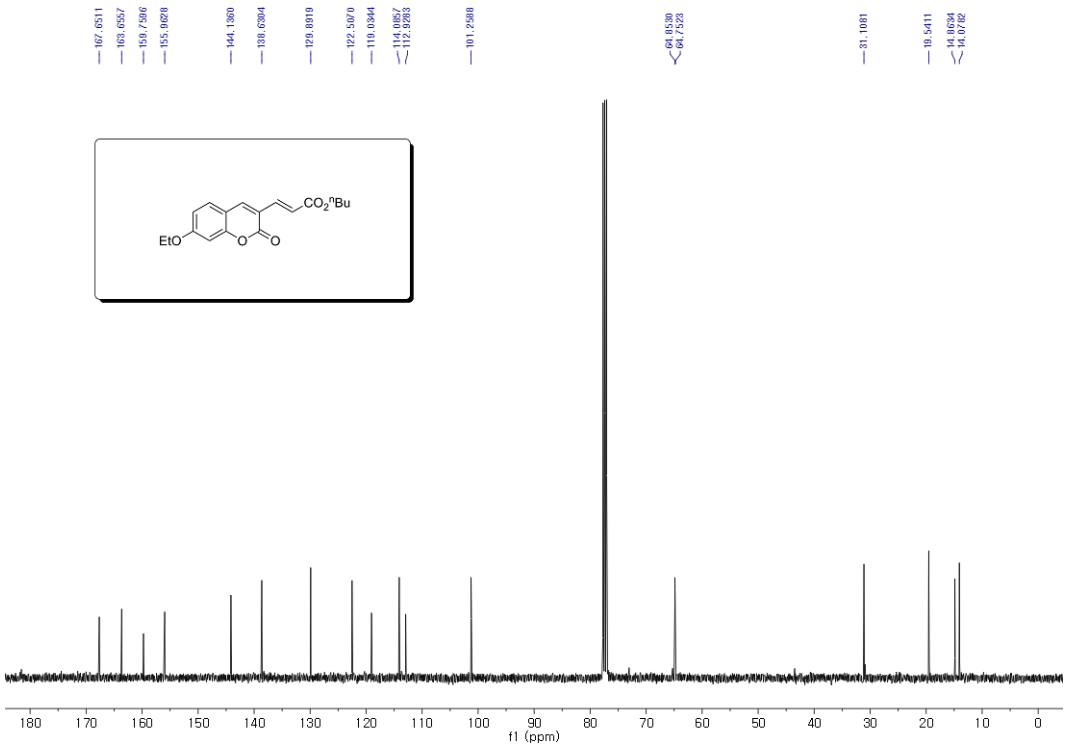


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-Butyl 3-(7-ethoxy-2-oxo-2H-chromen-3-yl)acrylate (3n).

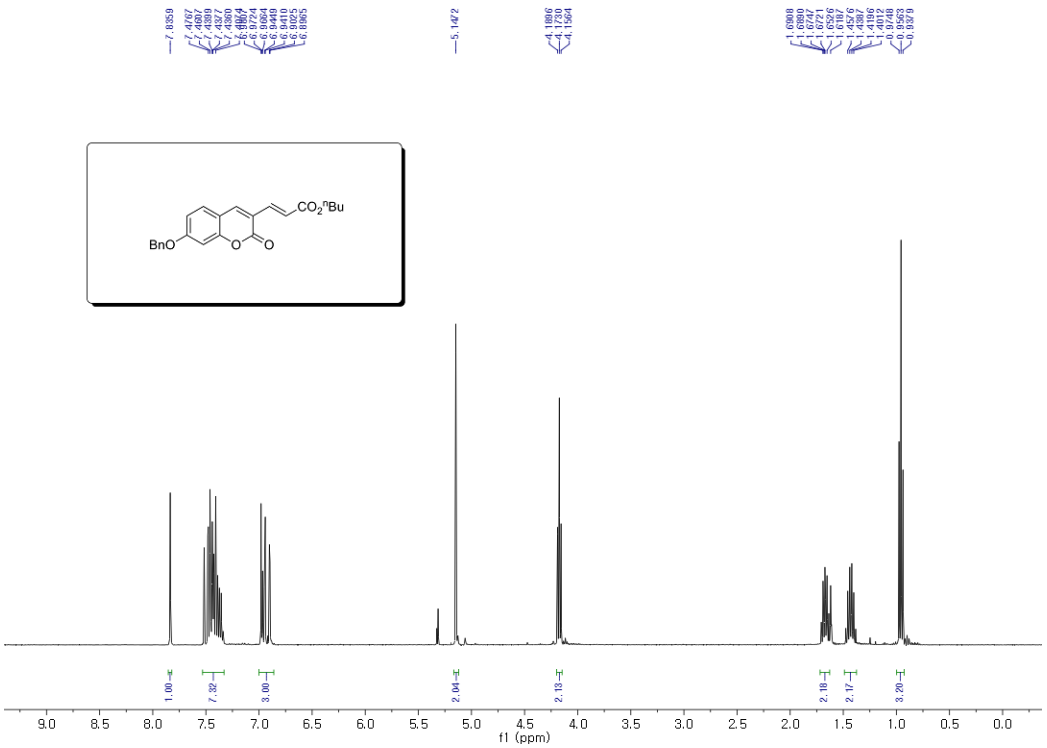


400 MHz, ^{1}H NMR in $CDCl_3$

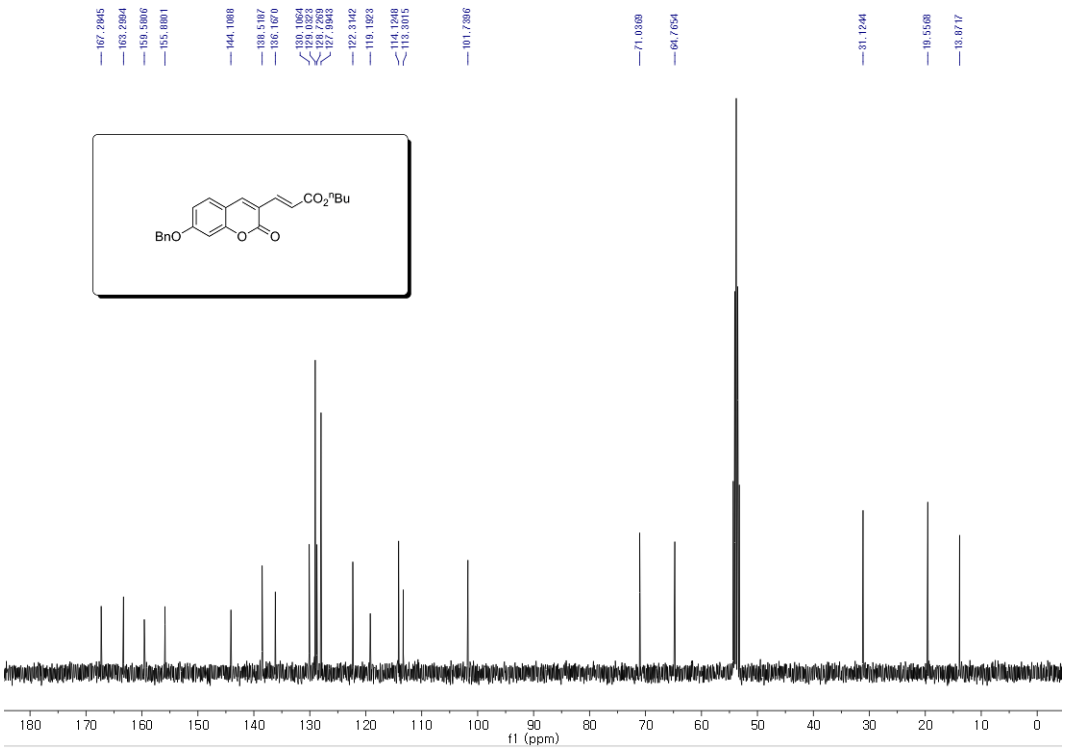


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-Butyl 3-(7-(benzyloxy)-2-oxo-2H-chromen-3-yl)acrylate (3o).

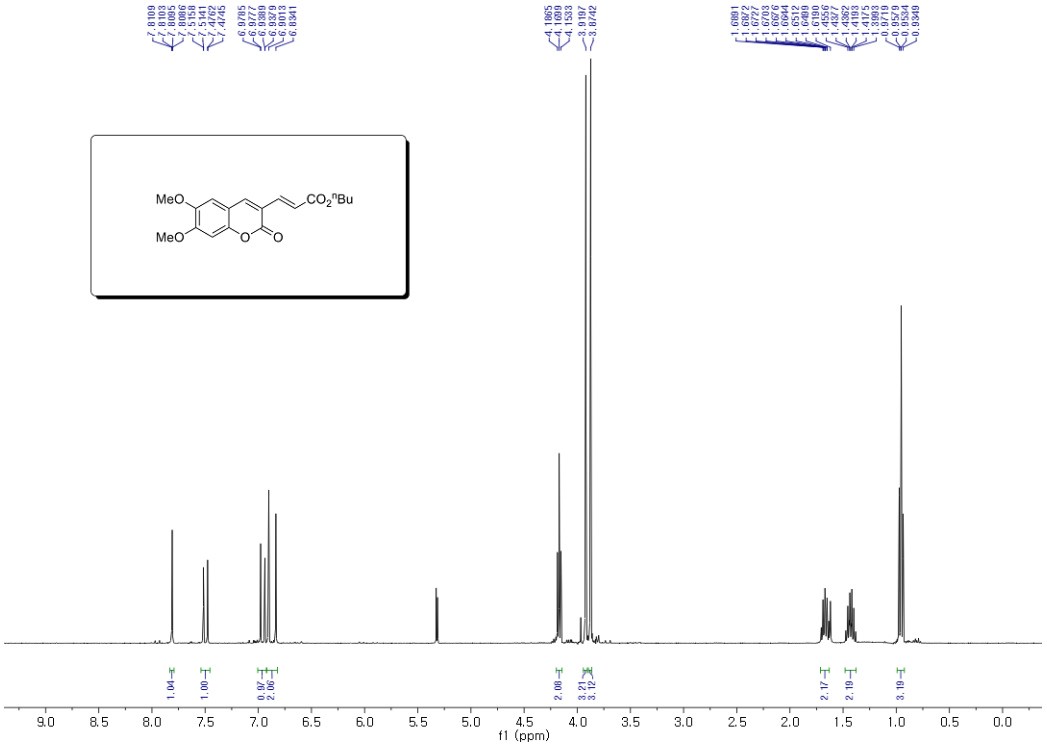


400 MHz, ^{1}H NMR in CD_2Cl_2

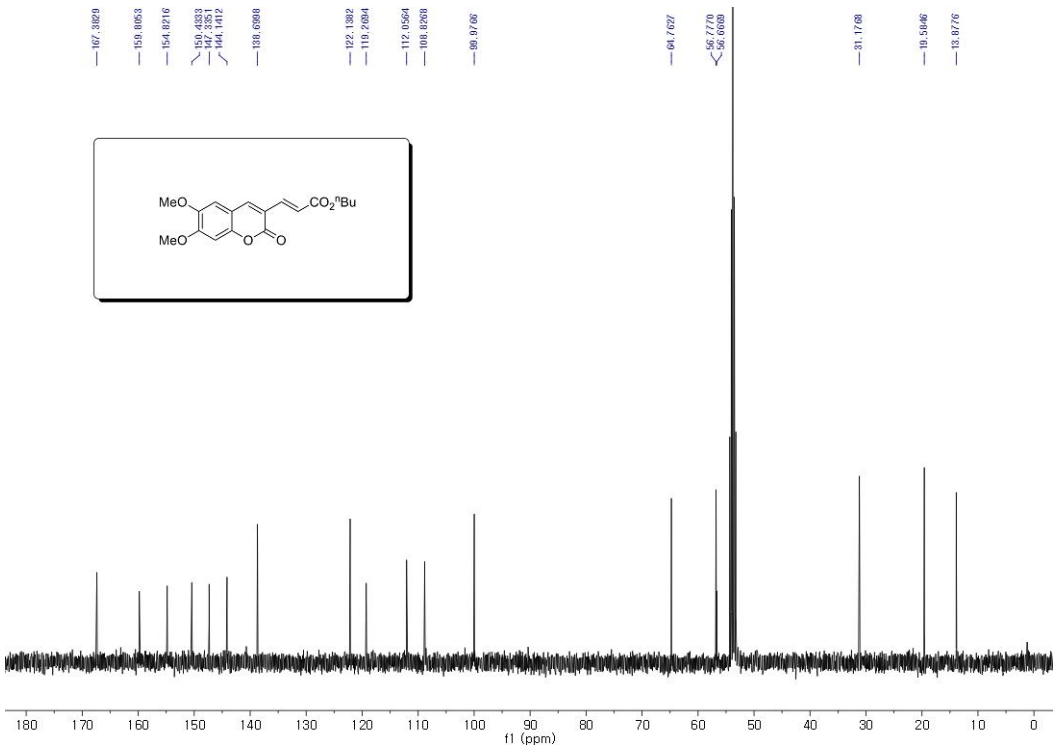


100 MHz, ^{13}C NMR in CD_2Cl_2

(E)-Butyl 3-(6,7-dimethoxy-2-oxo-2H-chromen-3-yl)acrylate (3p).

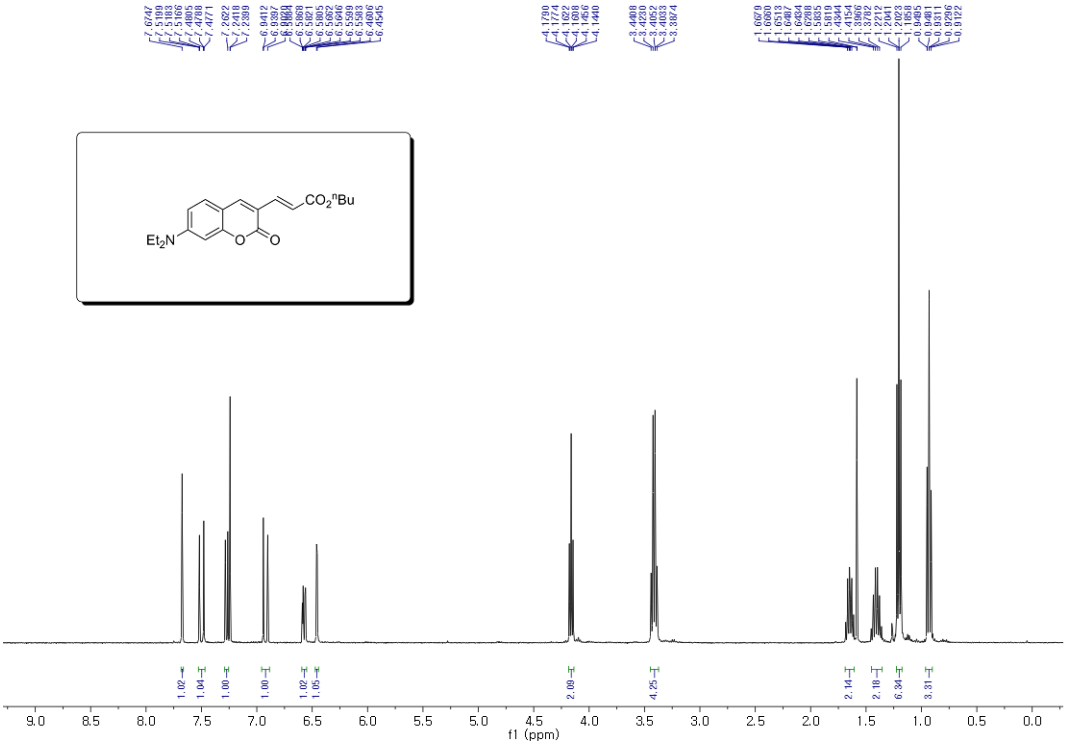


400 MHz, ^{1}H NMR in CD_2Cl_2

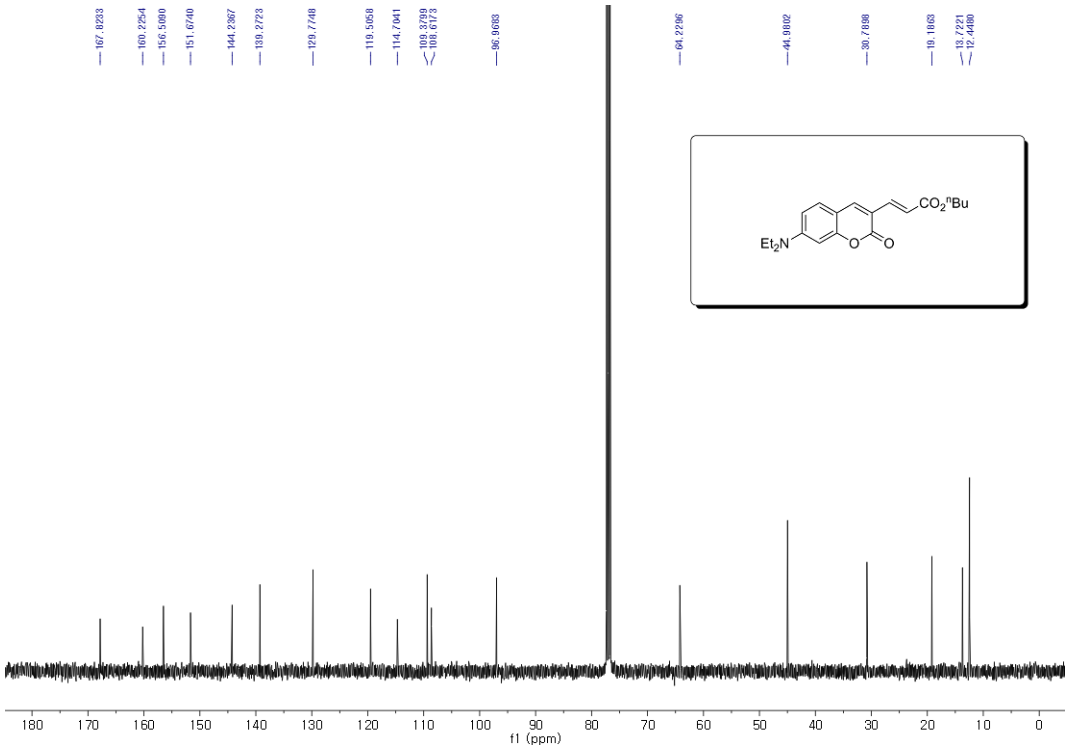


100 MHz, ^{13}C NMR in CD_2Cl_2

(E)-Butyl 3-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)acrylate (3q).

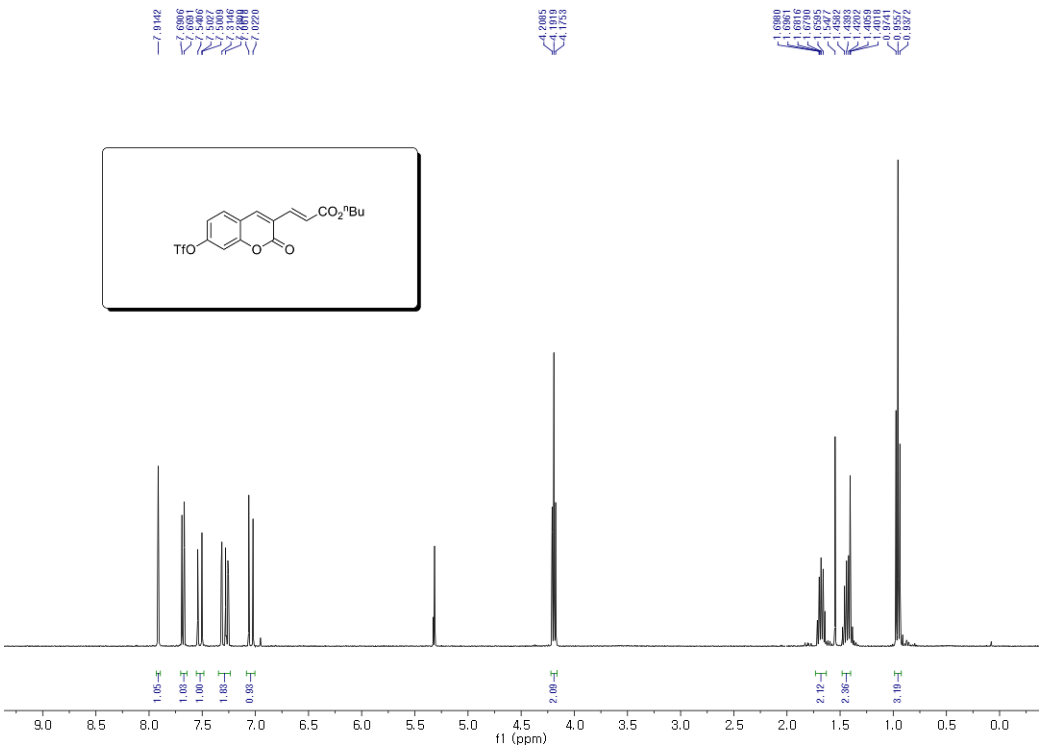


400 MHz, ^{1}H NMR in $CDCl_3$

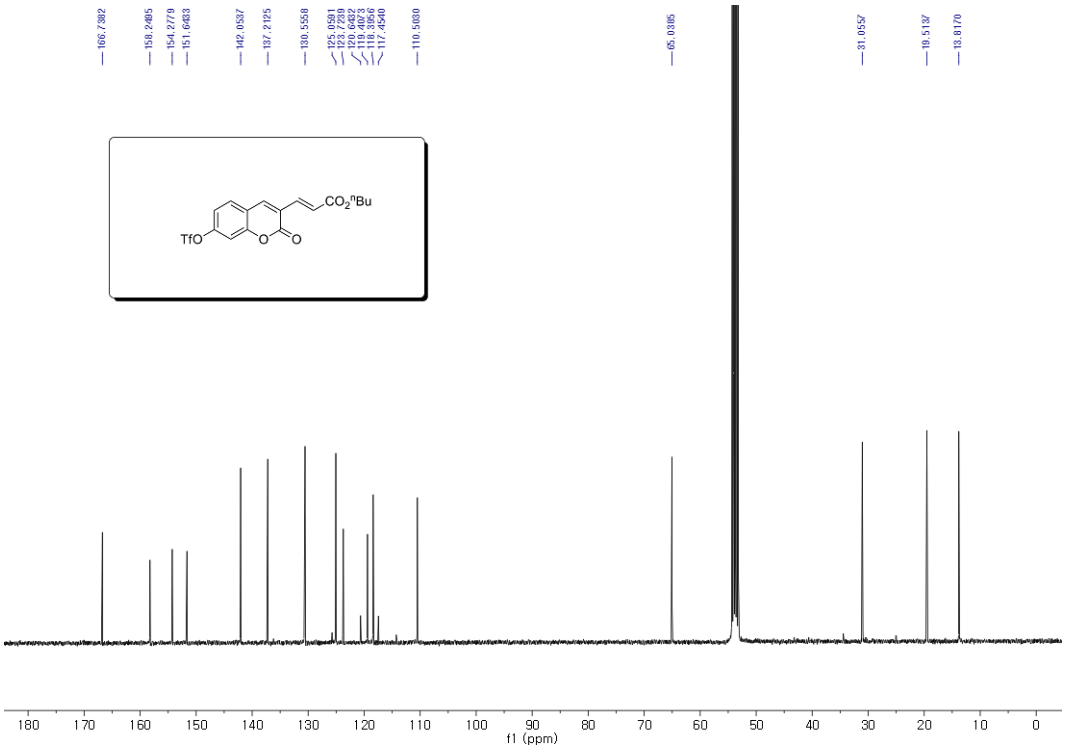


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-Butyl 3-(2-oxo-7-(((trifluoromethyl)sulfonyl)oxy)-2H-chromen-3-yl)acrylate (3r).

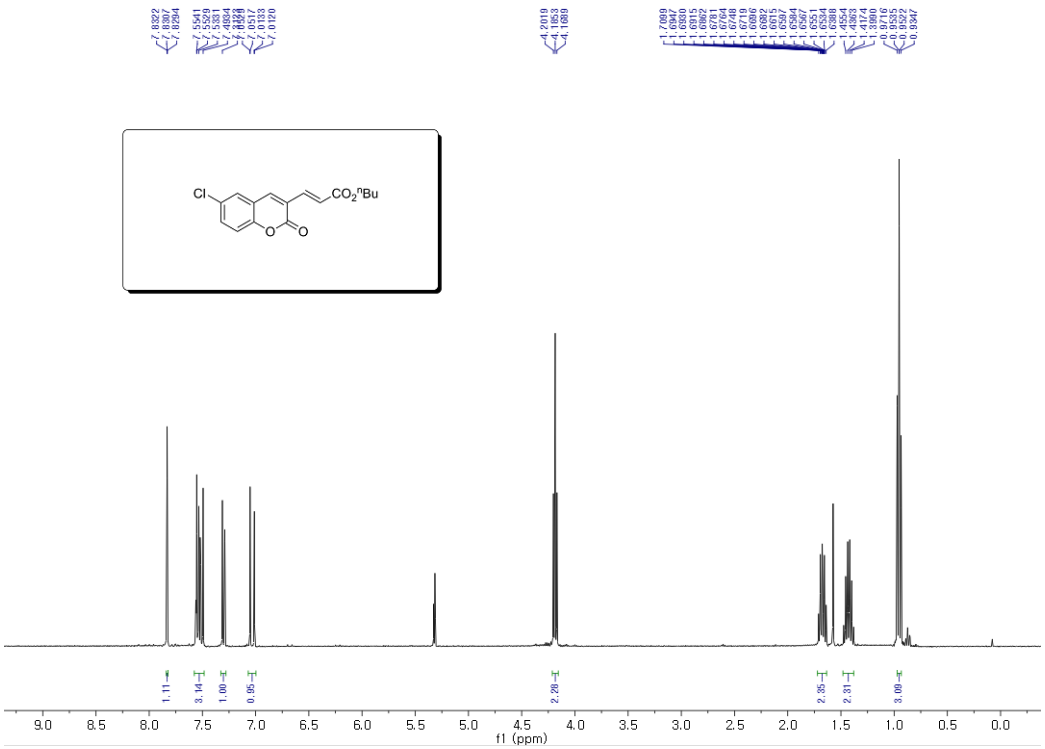


400 MHz, ^{1}H NMR in CD_2Cl_2

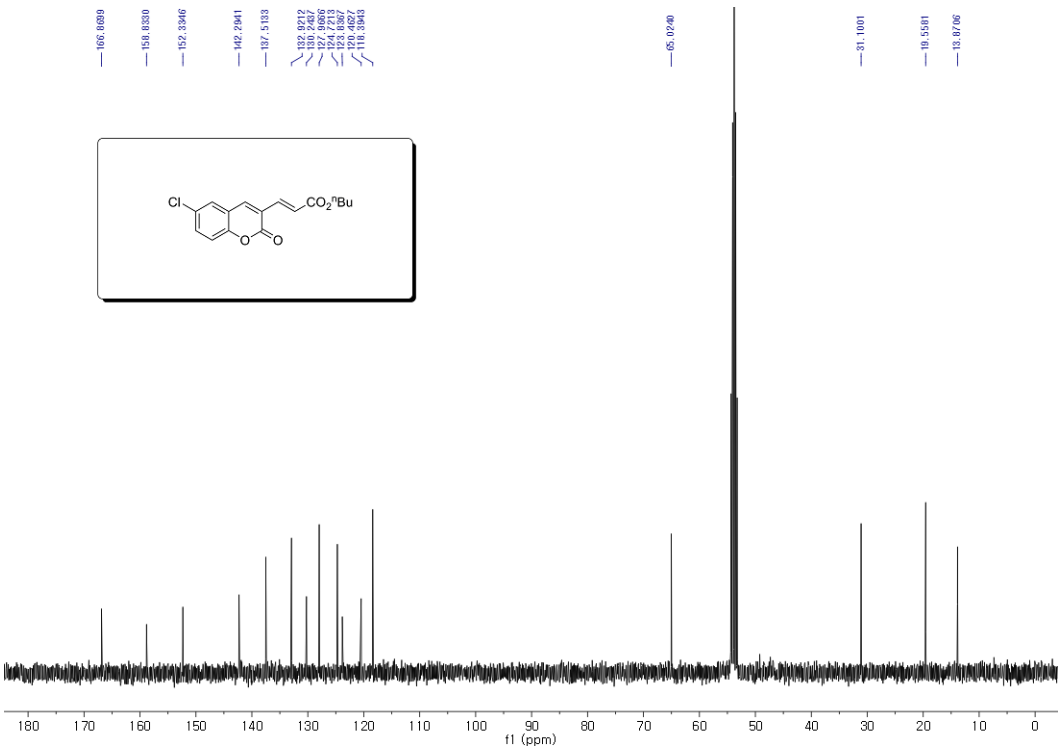


100 MHz, ^{13}C NMR in CD_2Cl_2

(E)-Butyl 3-(6-chloro-2-oxo-2H-chromen-3-yl)acrylate (3s).

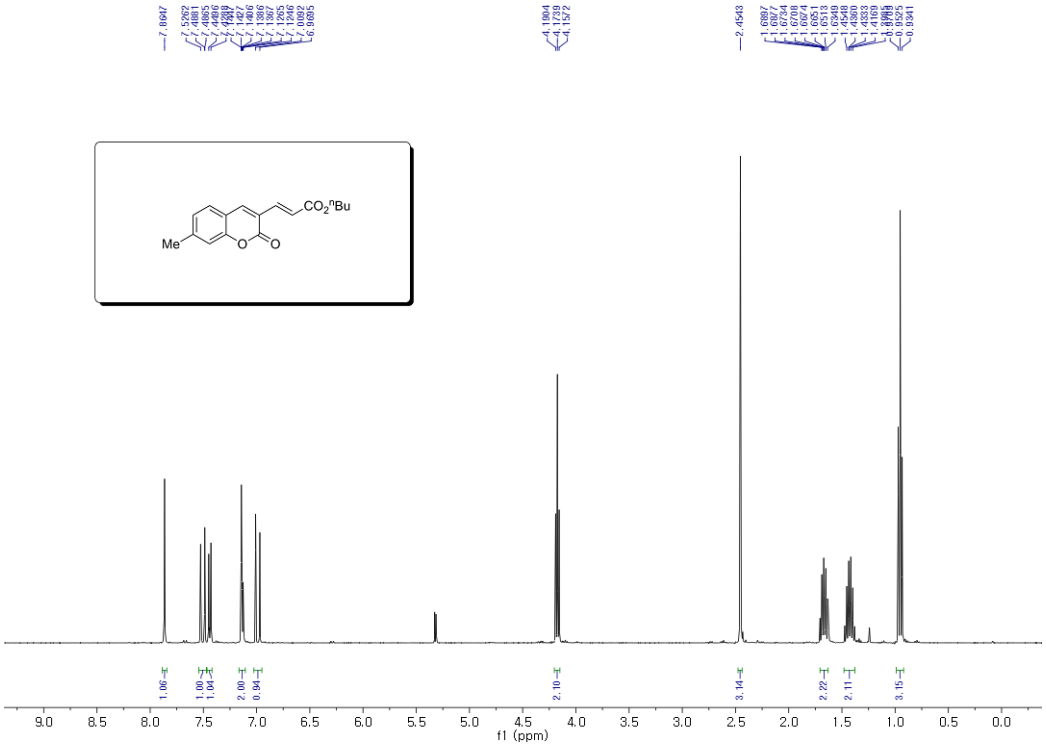


400 MHz, ^{1}H NMR in CD_2Cl_2

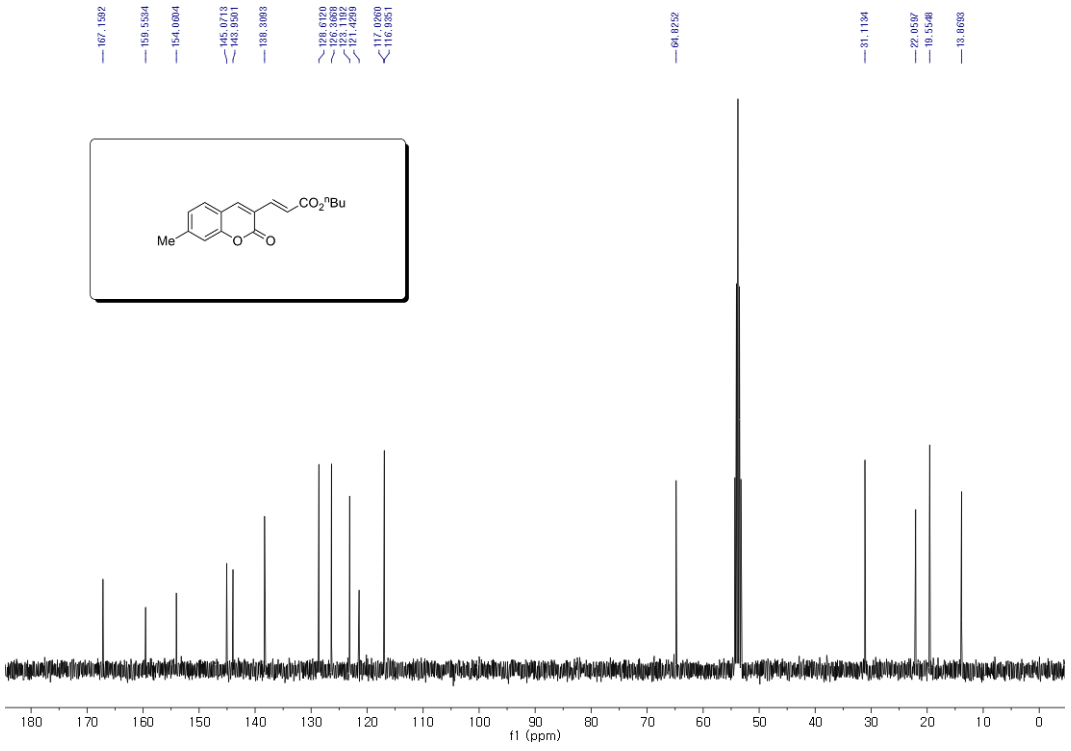


100 MHz, ^{13}C NMR in CD_2Cl_2

(E)-Butyl 3-(7-methyl-2-oxo-2H-chromen-3-yl)acrylate (3t).

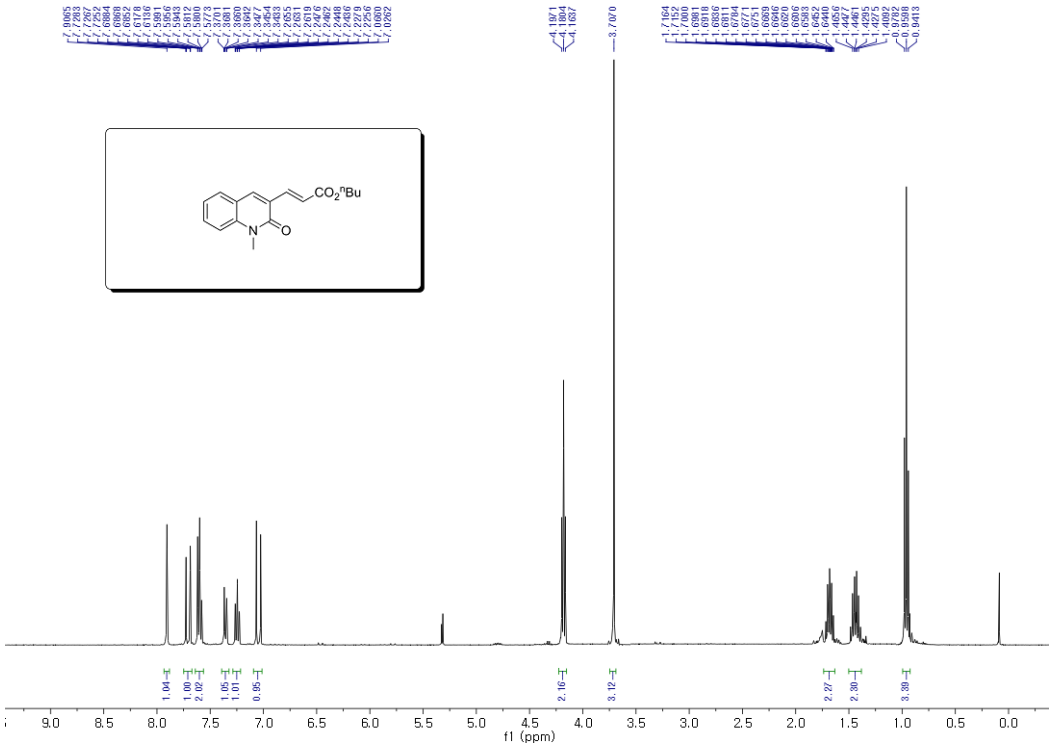


400 MHz, ^{1}H NMR in CD_2Cl_2

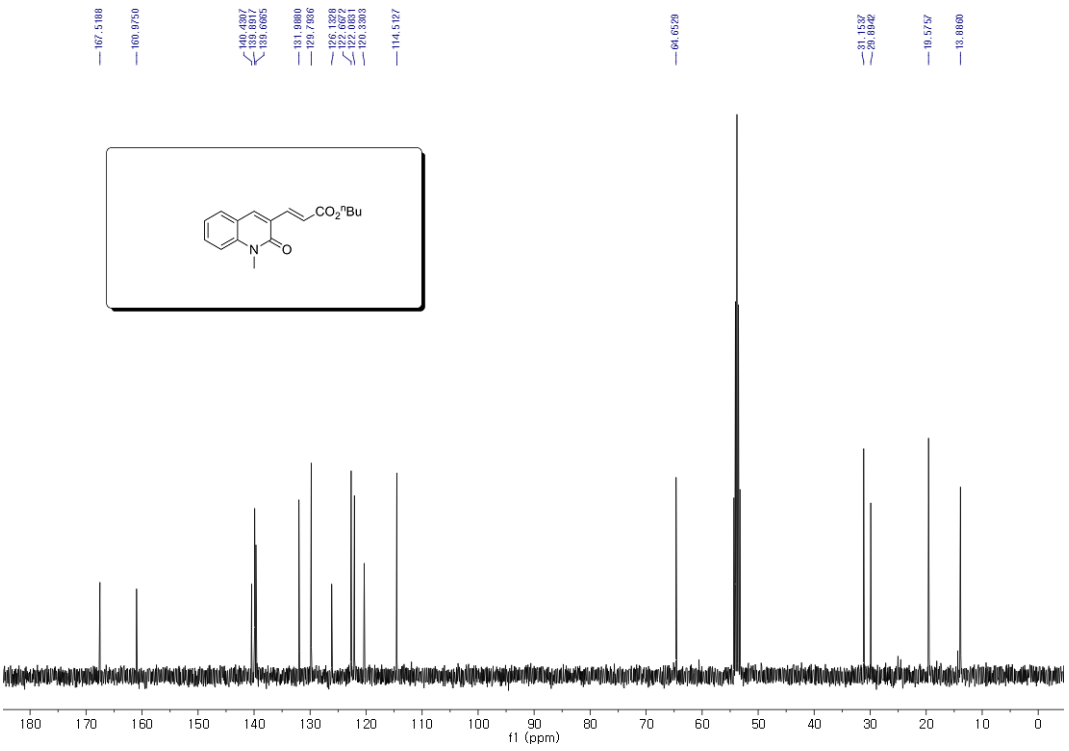


100 MHz, ^{13}C NMR in CD_2Cl_2

(E)-Butyl 3-(1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acrylate (3u).

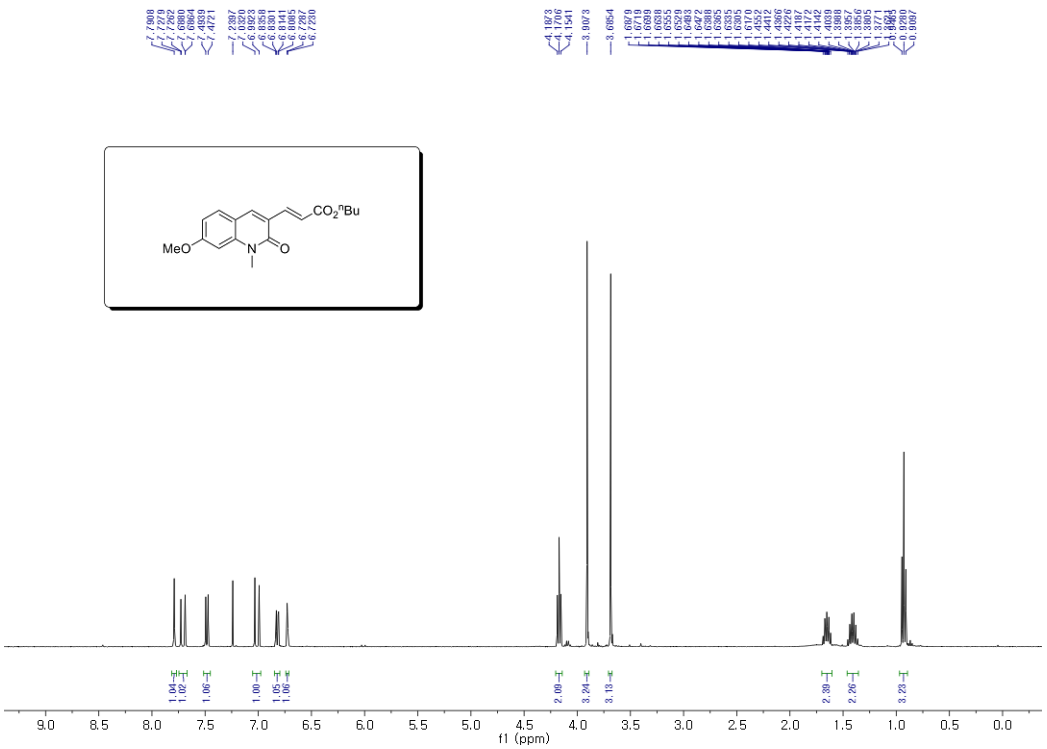


400 MHz, ^{1}H NMR in CD_2Cl_2

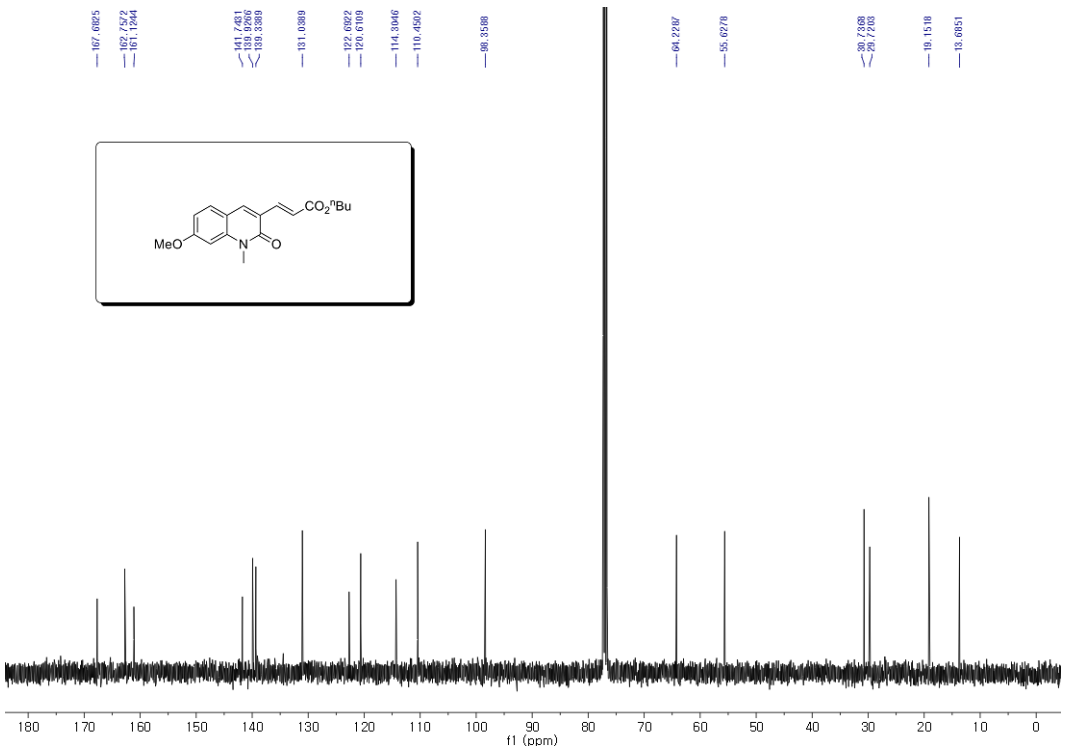


100 MHz, ^{13}C NMR in CD_2Cl_2

(E)-Butyl 3-(7-methoxy-1-methyl-2-oxo-1,2-dihydroquinolin-3-yl)acrylate (3v).

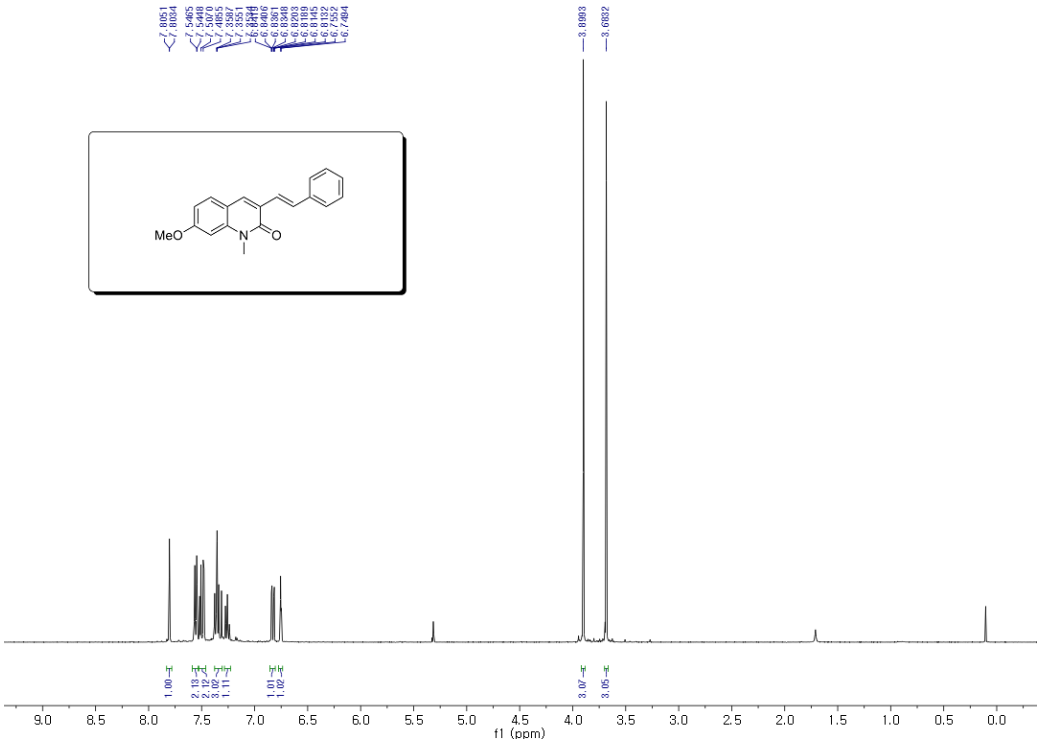


400 MHz, ^{1}H NMR in $CDCl_3$

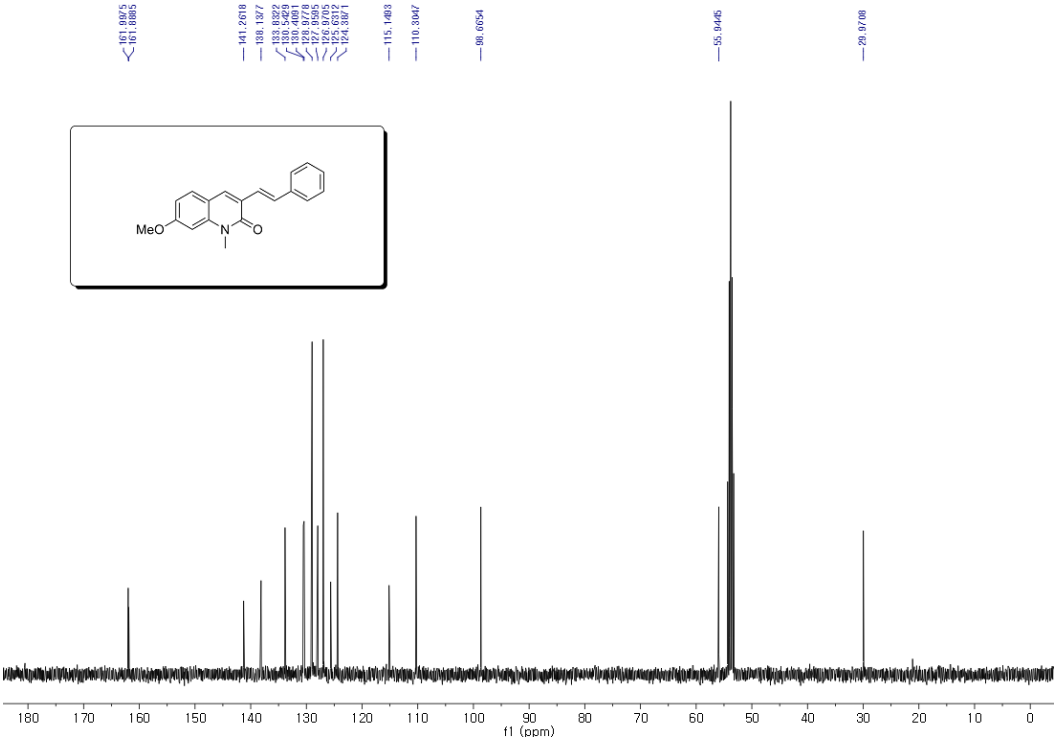


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-7-Methoxy-1-methyl-3-styrylquinolin-2(1H)-one (3w).

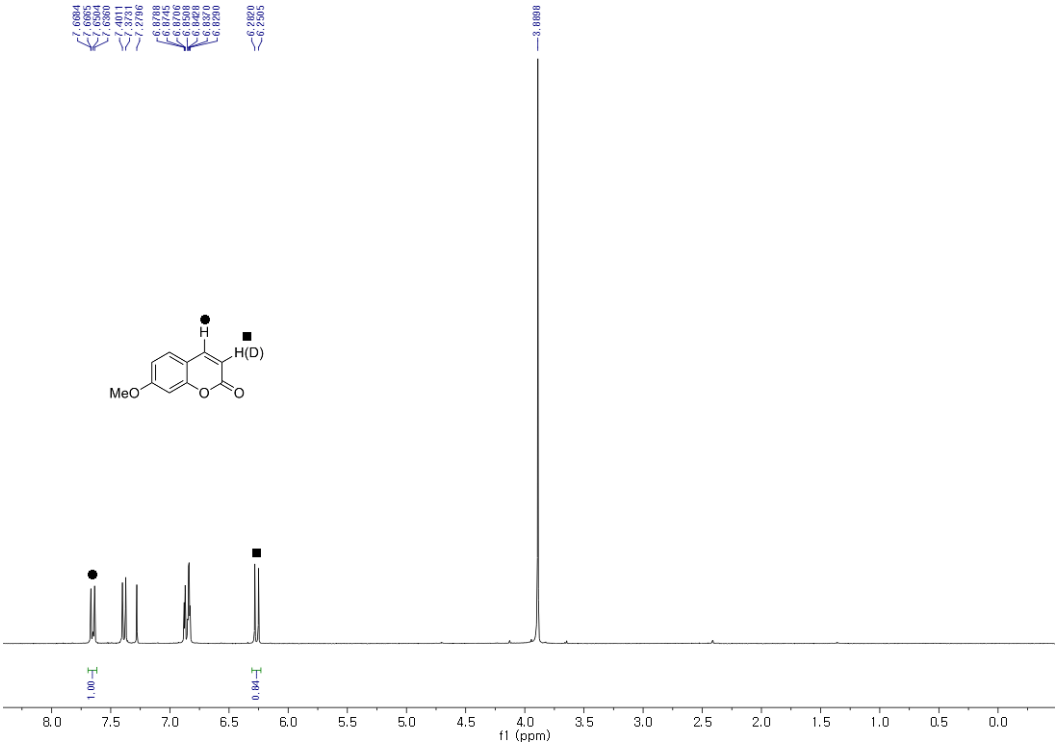


400 MHz, ^{1}H NMR in CD_2Cl_2

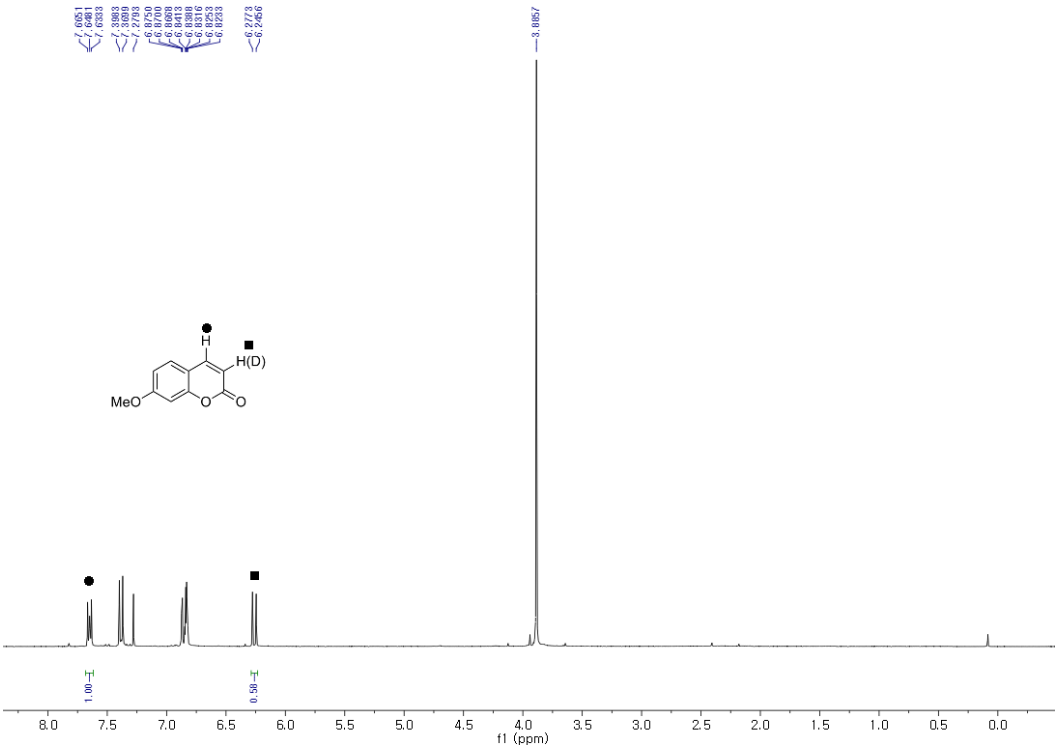


100 MHz, ^{13}C NMR in CD_2Cl_2

H/D Exchange Experiment:



^{1}H-NMR spectra observed from H/D exchange experiment (after 3h)



^{1}H-NMR spectra observed from H/D exchange experiment (after 12h)