Supporting Information

$AgSbF_6$-Controlled Diastereodivergence in Alkyne Hydroarylation: Facile Access to Z- and E-Alkenyl Arenes

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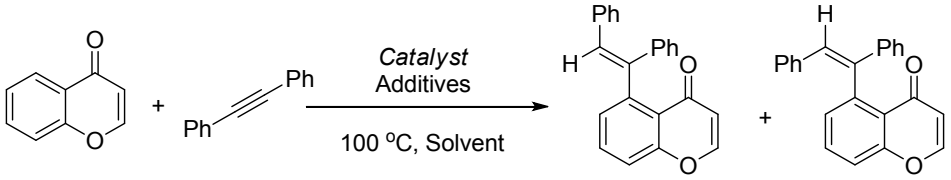
I. General Methods and Materials. Unless stated otherwise, reactions were performed in flame-dried glassware. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F^{254} plates and visualization on TLC was achieved by UV light (254 and 365 nm). Flash column chromatography was undertaken on silica gel (400-630 mesh). ^1H NMR was recorded on 400 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, td = doublet of triplet, ddd = doublet of doublet of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR was recorded on 100 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 $CDCl_3$. Mass spectral data were obtained from the KAIST Basic Science Institute by using ESI method. Commercial grade reagents and solvents were used without further purification except as indicated below. Dichloromethane was distilled from calcium hydride.

II. Optimization Study

Table S1. Representative optimization study on Ru-catalyzed hydroarylation of chromone.[a]



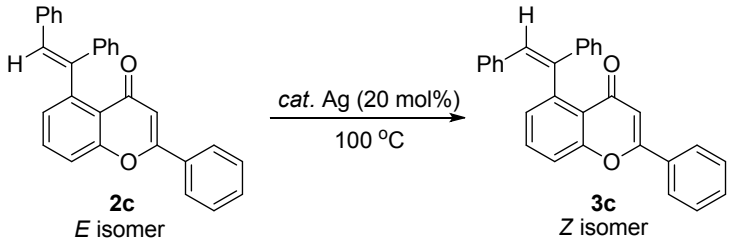
1a **2a** **3a**

Entry	Catalyst (5 mol %)	Ag Additive (mol %)	Additive (equiv)	Solvent	Yield[%] (**2a**:**3a**)[b]
1	$[RhCp^*Cl_2]_2$	$AgNTf_2$ (20)	AcOH (2.0)	1,2-DCE	-
2	$[Ru(p\text{-cymene})Cl_2]_2$	$AgNTf_2$ (20)	AcOH (2.0)	Toluene	-
3	$[Ru(p\text{-cymene})Cl_2]_2$	$AgNTf_2$ (20)	AcOH (2.0)	CH_3CN	-
4	$[Ru(p\text{-cymene})Cl_2]_2$	$AgNTf_2$ (20)	AcOH (2.0)	DMF	-
5	$[Ru(p\text{-cymene})Cl_2]_2$	$AgNTf_2$ (20)	AcOH (2.0)	DMSO	-
6	$[Ru(p\text{-cymene})Cl_2]_2$	$AgNTf_2$ (20)	AcOH (2.0)	Dioxane	< 10%
7	$[Ru(p\text{-cymene})Cl_2]_2$	$AgNTf_2$ (20)	AcOH (2.0)	EtOH	-
8	$[Ru(p\text{-cymene})Cl_2]_2$	$AgNTf_2$ (20)	AcOH (2.0)	DME	64% (84:16)
9	$[Ru(p\text{-cymene})Cl_2]_2$	$AgNTf_2$ (20)	AcOH (2.0)	*i*-PrOAc	30% (78:22)
10	$[Ru(p\text{-cymene})Cl_2]_2$	AgOAc (20)	AcOH (2.0)	1,2-DCE	-

11	[Ru(*p*-cymene)Cl_2]$_2$	$AgBF_4$ (20)	AcOH (2.0)	1,2-DCE	-
12	[Ru(*p*-cymene)Cl_2]$_2$	AgF (20)	AcOH (2.0)	1,2-DCE	24% (91:9)
13	[Ru(*p*-cymene)Cl_2]$_2$	Ag_2CO_3 (20)	AcOH (2.0)	1,2-DCE	-
14	[Ru(*p*-cymene)Cl_2]$_2$	AgOTFA (20)	AcOH (2.0)	1,2-DCE	-
15	[Ru(*p*-cymene)Cl_2]$_2$	AgOTf (20)	AcOH (2.0)	1,2-DCE	53% (64:36)
16	[Ru(*p*-cymene)Cl_2]$_2$	$AgPF_6$ (20)	AcOH (2.0)	1,2-DCE	-
17	[Ru(*p*-cymene)Cl_2]$_2$	$AgNTf_2$ (20)	AcOH (2.0)	1,2-DCE	84% (80:20)
18	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$ (20)	AcOH (2.0)	1,2-DCE	90% (76:24)
19	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$ (40)	AcOH (2.0)	1,2-DCE	58% (7:93)
20	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$ (40)	PivOH (2.0)	1,2-DCE	56% (9:91)
21	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$ (40)	AcOH (2.0) $Cu(OAc)_2$ (0.1)	1,2-DCE	71% (9:91)
22[c]	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$ (16+20)	AcOH (2.0) $Cu(OAc)_2$ (0.1)	1,2-DCE	87% (8:92)
23	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$ (20)	AcOH (2.0) $Cu(OAc)_2$ (0.1)	1,2-DCE	88% (86:14)
24	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$ (16)	AcOH (2.0) $Cu(OAc)_2$ (0.1)	1,2-DCE	94% (91:9)
25	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$ (16)	AcOH (2.0)	1,2-DCE	77% (69:31)
26	[Ru(*p*-cymene)Cl_2]$_2$	-	AcOH (2.0) $Cu(OAc)_2$ (0.1)	1,2-DCE	-
27	[Ru(*p*-cymene)Cl_2]$_2$	$AgSbF_6$ (20)	-	1,2-DCE	-

[a] Reaction conditions : **1a** (0.2 mmol), Diphenylalkyne (0.3 mmol). [b] Ratio was determined by ^{1}H NMR spectroscopy. [c] 20 mol% of $AgSbF_6$ was added to the reaction mixture after consumption of chromone.

Table S2. Optimization of the Dehydrogenation/Alkenylations of chromanone.[a]



2c
E isomer

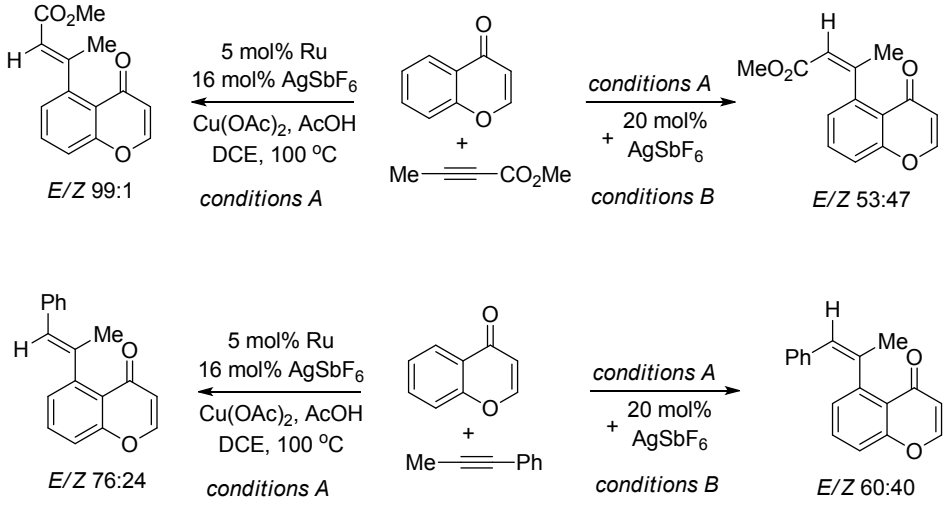
3c
Z isomer

Entry	Ag Catalyst (mol %)	Additive (equiv)	Solvent (0.1 M)	Yield [%] (*E*:*Z*)[b]
1	AgOAc (20)	AcOH (2.0)	1,2-DCE	98% (88:12)

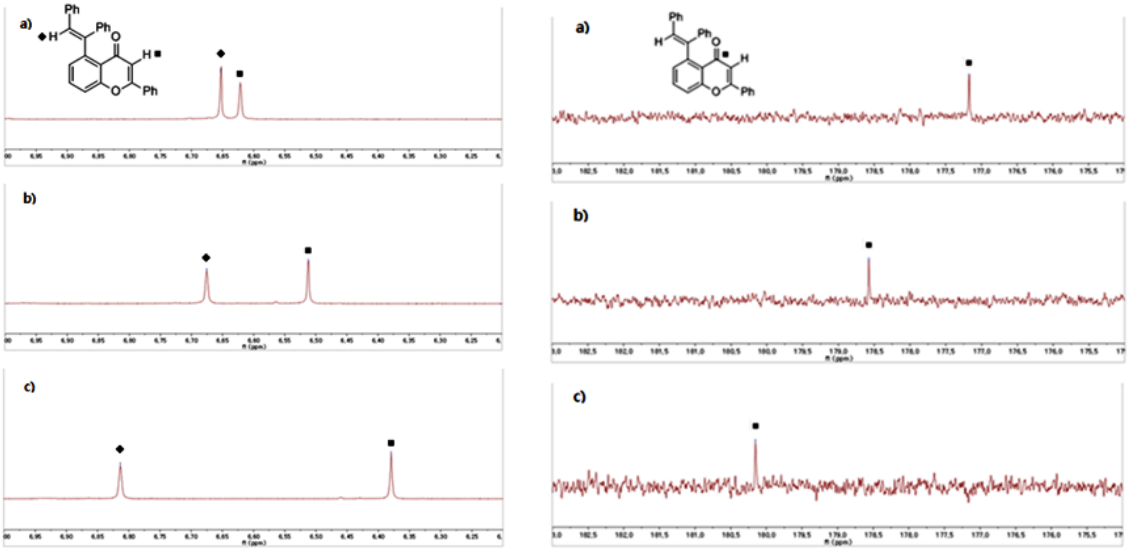
2	AgOTFA (20)	AcOH (2.0)	1,2-DCE	96% (74:26)
3	AgOTf (20)	AcOH (2.0)	1,2-DCE	95% (38:62)
4	Ag_2CO_3 (20)	AcOH (2.0)	1,2-DCE	91% (87:13)
5	AgF (20)	AcOH (2.0)	1,2-DCE	93% (64:36)
6	Ag_2O (20)	AcOH (2.0)	1,2-DCE	99% (86:14)
7	$AgPF_6$ (20)	AcOH (2.0)	1,2-DCE	86% (17:83)
8	$AgNTf_2$ (20)	AcOH (2.0)	1,2-DCE	70% (10:90)
9	$AgNO_3$ (20)	AcOH (2.0)	1,2-DCE	82% (20:80)
10	$AgSbF_6$ (20)	AcOH (2.0)	1,2-DCE	93% (9:91)
11	$AgSbF_6$ (20)	-	1,2-DCE	86% (9:91)
12	-	AcOH (2.0)	1,2-DCE	-
13[c]	$AgSbF_6$ (20)	AcOH (2.0)	CH_3CN	90% (90:10)
14[c]	$AgSbF_6$ (20)	AcOH (2.0)	dioxane	72% (77:23)
15[c]	$AgSbF_6$ (20)	AcOH (2.0)	toluene	88% (69:31)
16[c]	$AgSbF_6$ (20)	AcOH (2.0)	*i*PrOH	91% (75:25)
17[c]	$AgSbF_6$ (20)	AcOH (2.0)	DMF	-

[a] Reactions were conducted with flavone (1.0 equiv), $AgSbF_6$ (20 mol%), and additive(s) at 100 °C for 2 h. [b] Ratio was determined by ^1H NMR spectroscopy. [c] Reactions were carried out for 6 h.

Scheme S1. Ru-Catalyzed Hydroarylation of Aliphatic Alkynes



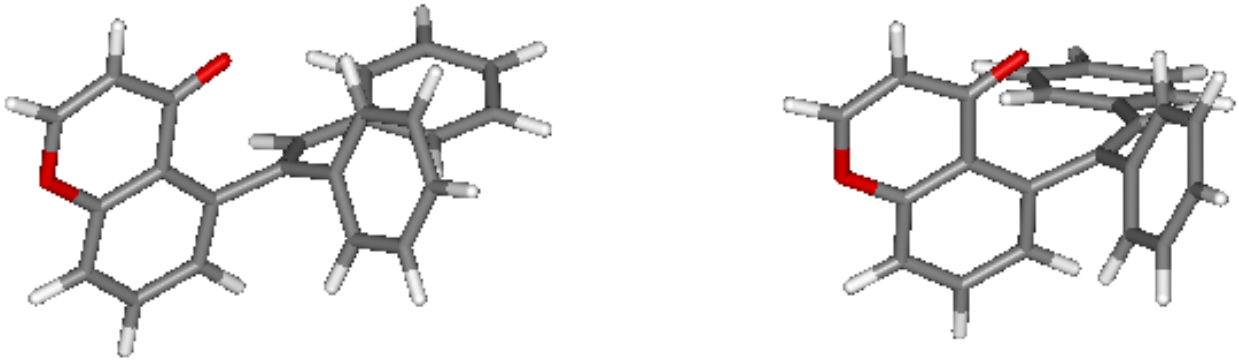
III. NMR Study



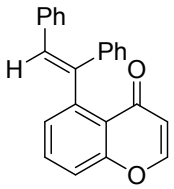
^{1}H NMR ^{13}C NMR

a) Flavone w/o $AgSbF_6$, b) with 20 mol% $AgSbF_6$, c) with 50 mol% $AgSbF_6$

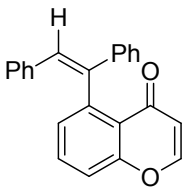
IV. Computational Study on the Thermodynamic Stability



E Z



2a
E-isomer

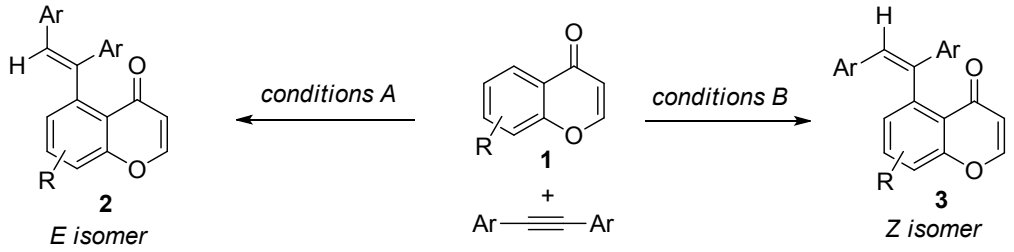


3a
Z-isomer

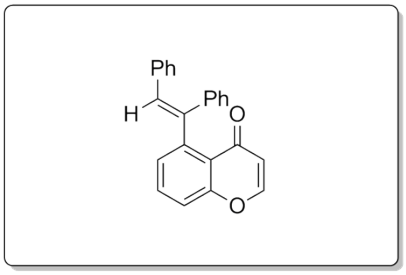
-*Z*-isomer **3a** is more stable than *E*-isomer **2a** by 1.6 kcal/mol (Hartree-Fock calculations) and 1.0 kcal/mol (Density functional theory calculations).

V. Experimental Procedures

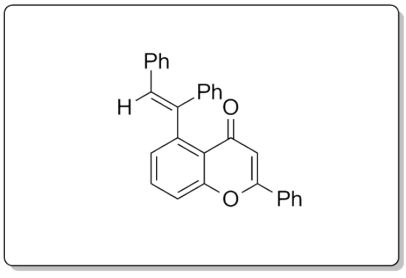
1. General Procedure for the Stereodivergent Hydroarylation of Chromones



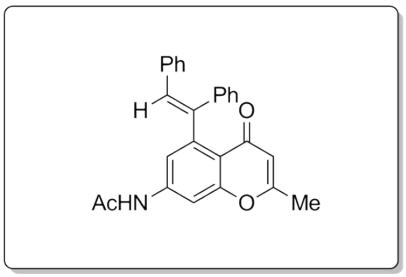
Conditions A: Reactions were conducted in Cap Test Tube. Chromone (0.2 mmol), acetylene (1.5 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol%), $AgSbF_6$ (16 mol%), $Cu(OAc)_2$ (10 mol%), AcOH (2.0 equiv) were combined in 1,2-DCE (2.0 mL). The reaction mixture was stirred at 100 ^oC for 2-4 h. The reaction mixture 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 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 (*n*-Hexane/EtOAc or *n*-Hexane/EtOAc/CH_2Cl_2) to give the *E*-selective product.



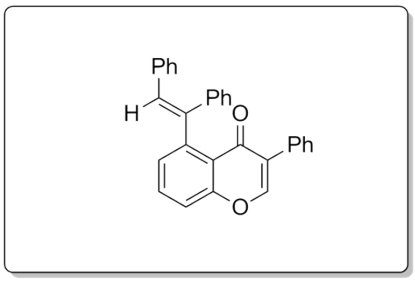
(E)-5-(1,2-diphenylvinyl)-4H-chromen-4-one (2a). Overall yield 94% (60.9 mg). White solid. mp 156 – 158 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 6.0, 0.8 Hz, 1H), 7.67 (ddd, *J* = 8.3, 7.3, 0.8 Hz, 1H), 7.47 (dt, *J* = 8.5, 1.0 Hz, 1H), 7.40 (dt, *J* = 7.4, 1.0 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.23 – 7.13 (m, 8H), 6.60 (s, 1H), 6.18 (dd, *J* = 6.0, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 157.6, 153.6, 144.8, 142.9, 139.5, 137.4, 132.5, 130.2, 129.4, 128.4, 127.9, 127.9, 127.5, 126.8, 126.6, 122.9, 117.9, 114.1. HRMS (ESI+) m/z calcd. for $C_{23}H_{16}NaO_2^+$[M+Na]$^+$: 347.1043, found : 347.1024.



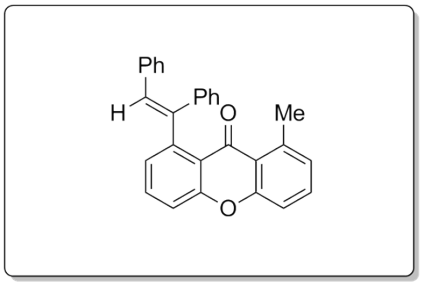
(E)-5-(1,2-diphenylvinyl)-2-phenyl-4H-chromen-4-one (2b). Overall yield 87% (69.6 mg). Pale yellow solid. mp 195 – 197 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.80 (m, 2H), 7.67 (dd, *J* = 8.4, 7.3 Hz, 1H), 7.55 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.51 – 7.44 (m, 3H), 7.38 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.29 – 7.23 (m, 2H), 7.21 – 7.11 (m, 8H), 6.63 (s, 1H), 6.60 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 161.6, 157.4, 144.7, 143.0, 139.6, 137.5, 132.6, 131.5, 131.3, 130.2, 129.4, 128.9, 128.4, 128.0, 127.9, 127.5, 126.8, 126.6, 126.1, 121.9, 117.8, 108.6. HRMS (ESI+) m/z calcd. for $[C_{29}H_{20}NaO_2]^+$: 423.1356, found : 423.1341.



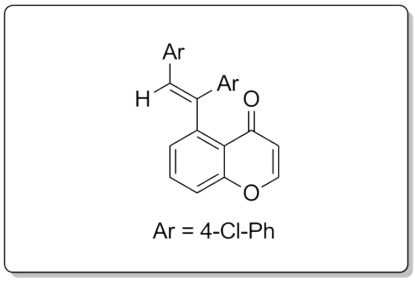
(E)-*N*-(5-(1,2-diphenylvinyl)-2-methyl-4-oxo-4H-chromen-7-yl)acetamide (2c). Overall yield 83% (65.5 mg). White solid. mp 206 – 208 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.11 (d, *J* = 2.1 Hz, 1H), 7.17 – 7.00 (m, 10H), 6.96 (d, *J* = 2.1 Hz, 1H), 6.42 (s, 1H), 5.88 (s, 1H), 2.20 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 169.4, 164.7, 158.6, 144.9, 142.6, 141.8, 139.3, 137.1, 130.0, 129.2, 127.8, 127.5, 126.9, 126.7, 119.4, 111.1, 107.1, 24.6, 19.9. HRMS (ESI+) m/z calcd. for $[C_{26}H_{21}NNaO_3]^+$: 418.1414, found : 418.1408.



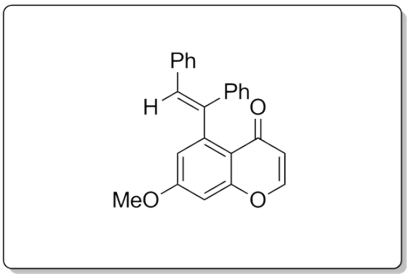
(E)-5-(1,2-diphenylvinyl)-3-phenyl-4H-chromen-4-one. (2d). Overall yield 82% (65.6 mg). Pale yellow solid. mp 82 – 85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 0.7 Hz, 1H), 7.64 (ddd, *J* = 8.3, 7.3, 0.6 Hz, 1H), 7.44 (dt, *J* = 8.4, 1.1 Hz, 1H), 7.39 (dt, *J* = 7.3, 0.9 Hz, 1H), 7.36 – 7.26 (m, 7H), 7.20 – 7.11 (m, 8H), 6.60 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 157.3, 151.3, 145.4, 143.1, 139.6, 137.4, 132.4, 132.0, 130.3, 129.4, 128.8, 128.3, 128.3, 127.9, 127.8, 127.7, 127.5, 126.8, 126.6, 126.2, 122.7, 117.7. HRMS (ESI+) m/z calcd. for $[C_{29}H_{20}NaO_2]^+$: 423.1356, found : 423.1364.



(E)-1-(1,2-diphenylvinyl)-8-methyl-9H-xanthen-9-one (2e). Overall yield 80% (62.1 mg). White solid. mp 162 – 164 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 8.4, 7.3 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.37 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.31 – 7.09 (m, 11H), 7.00 (dt, *J* = 7.4, 1.1 Hz, 1H), 6.76 (s, 1H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 156.5, 156.4, 145.7, 143.6, 141.2, 139.7, 137.6, 132.9, 132.8, 130.6, 129.5, 127.9, 127.7, 127.4, 127.1, 126.8, 126.6, 126.3, 121.6, 117.2, 115.2, 22.1. HRMS (ESI+) m/z calcd. for $[C_{28}H_{20}NaO_2]^+$: 411.1356, found : 411.1340.

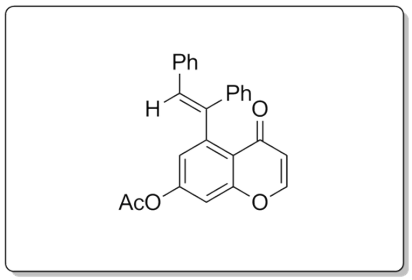


(E)-5-(1,2-bis(4-chlorophenyl)vinyl)-4H-chromen-4-one (2f). Overall yield 85% (66.6 mg). Pale yellow solid. mp 89 – 92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 5.9, 0.6 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.52 – 7.46 (m, 1H), 7.40 – 7.30 (m, 1H), 7.23 – 7.00 (m, 8H), 6.54 (s, 1H), 6.18 (d, *J* = 6.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 157.6, 153.8, 143.9, 142.6, 137.6, 135.5, 132.8, 132.7, 132.5, 131.5, 130.6, 128.3, 128.2, 127.9, 127.1, 122.7, 118.4, 114.0. HRMS (ESI+) m/z calcd. for $[C_{23}H_{14}Cl_2NaO_2]^+$: 415.0263, found : 415.0266.

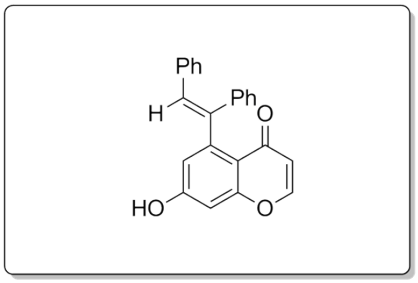


(E)-5-(1,2-diphenylvinyl)-7-methoxy-4H-chromen-4-one (2g). Overall yield 90% (63.7 mg). White solid. mp 179 – 182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 5.9 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.23 – 7.14 (m, 8H), 6.99 (d, *J* = 2.6 Hz, 1H), 6.86 (d, *J* = 2.6 Hz, 1H), 6.61 (s, 1H), 6.11 (d, *J* = 5.9 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.9, 162.5, 159.4, 153.1, 146.3, 142.9, 139.2, 137.3, 130.2, 129.4, 127.8, 127.8, 127.5,

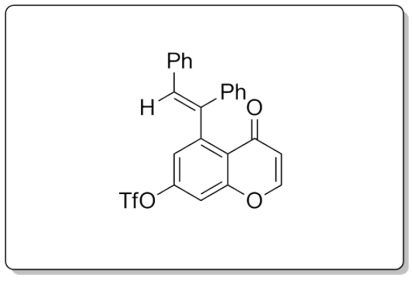
126.9, 126.6, 117.4, 116.9, 113.9, 100.1, 55.8. HRMS (ESI+) m/z calcd. for $[C_{24}H_{18}NaO_3]^+$: 377.1148, found : 377.1145.



(E)-5-(1,2-diphenylvinyl)-4-oxo-4H-chromen-7-yl acetate (2h). Overall yield 80% (61.1 mg). White solid. mp 82 – 85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 6.0 Hz, 1H), 7.30 (d, *J* = 2.3 Hz, 1H), 7.26 – 7.09 (m, 11H), 6.60 (s, 1H), 6.17 (d, *J* = 5.9 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 168.4, 158.1, 153.7, 153.0, 146.5, 142.0, 139.0, 137.1, 130.2, 129.4, 128.5, 127.9, 127.6, 127.0, 126.8, 122.3, 120.7, 114.1, 110.6, 21.1. HRMS (ESI+) m/z calcd. for $[C_{25}H_{18}NaO_4]^+$: 405.1097, found : 405.1131.

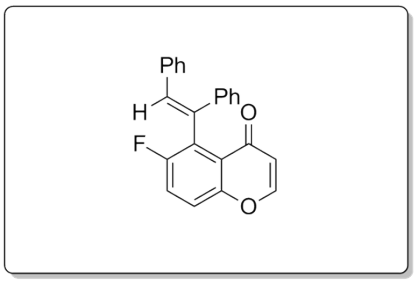


(E)-5-(1,2-diphenylvinyl)-7-hydroxy-4H-chromen-4-one (2i). Overall yield 66% (44.8 mg). Pale brown solid. mp 230 – 232 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.86 (br, 1H), 8.03 (d, *J* = 5.9 Hz, 1H), 7.27 – 7.06 (m, 10H), 6.85 (d, *J* = 2.4 Hz, 1H), 6.80 (d, *J* = 2.4 Hz, 1H), 6.47 (s, 1H), 6.03 (d, *J* = 5.9 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.9, 161.1, 158.9, 154.5, 145.7, 142.7, 139.4, 137.0, 129.7, 129.0, 127.9, 127.6, 126.9, 126.9, 126.7, 117.3, 115.2, 112.9, 102.2. HRMS (ESI+) m/z calcd. for $[C_{23}H_{16}NaO_3]^+$: 363.0992, found : 363.0965.

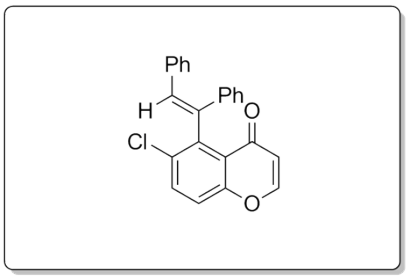


(E)-5-(1,2-diphenylvinyl)-4-oxo-4H-chromen-7-yl trifluoromethanesulfonate (2j). Overall yield 79% (74.5 mg). Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 5.9 Hz, 1H), 7.45 (d, *J* = 2.4 Hz, 1H), 7.35 – 7.10 (m, 11H), 6.62 (s, 1H), 6.22 (d, *J* = 5.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 157.9, 153.9, 150.7, 148.0,

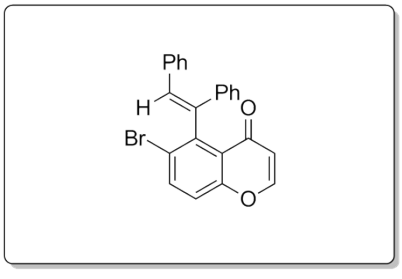
141.2, 138.4, 136.6, 130.2, 129.4, 129.2, 128.0, 127.7, 127.4, 127.1, 122.7, 121.4, 118.7 (q, J_{CF} = 321.0 Hz), 114.6, 110.9. HRMS (ESI+) m/z calcd. for $[C_{24}H_{15}F_3NaO_5S]^+$: 495.0484, found : 495.0501.



(E)-5-(1,2-diphenylvinyl)-6-fluoro-4H-chromen-4-one (2k). Overall yield 92% (62.9 mg). White solid. mp 178 – 180 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 5.9 Hz, 1H), 7.48 – 7.45 (m, 2H), 7.40 – 7.34 (m, 2H), 7.25 – 7.14 (m, 8H), 6.58 (s, 1H), 6.23 (d, J = 5.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8 (d, J_{CF} = 2.8 Hz), 156.7 (d, J_{CF} = 242.8 Hz), 153.8, 153.7 (d, J_{CF} = 1.9 Hz), 139.0, 137.0, 134.4, 130.29 (d, J_{CF} = 19.0 Hz), 130.0, 129.9 (d, J_{CF} = 1.6 Hz), 129.4, 127.9, 127.8, 127.1, 126.8, 124.0 (d, J_{CF} = 2.6 Hz), 121.5 (d, J_{CF} = 27.5 Hz), 119.2 (d, J_{CF} = 8.6 Hz), 113.6. HRMS (ESI+) m/z calcd. for $[C_{23}H_{15}FNaO_2]^+$: 365.0948, found : 365.0934.



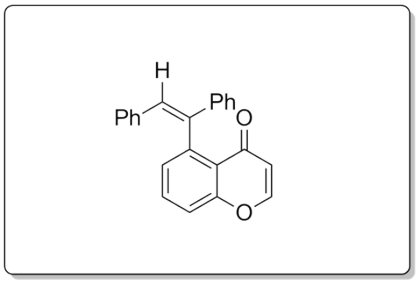
(E)-6-chloro-5-(1,2-diphenylvinyl)-4H-chromen-4-one (2l). Overall yield 90% (64.1 mg). White solid. mp 190 – 192 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.60 (m, 2H), 7.40 (d, J = 9.0 Hz, 1H), 7.28 – 7.23 (m, 4H), 7.21 – 7.08 (m, 6H), 6.46 (s, 1H), 6.22 (d, J = 5.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 156.1, 153.7, 142.1, 138.7, 137.9, 137.4, 134.3, 132.0, 130.4, 129.4, 129.2, 128.0, 127.6, 127.0, 126.8, 124.6, 119.1, 114.4. HRMS (ESI+) m/z calcd. for $[C_{23}H_{15}ClNaO_2]^+$: 381.0653, found : 381.0657.



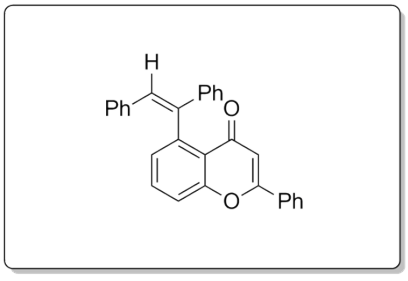
(E)-6-bromo-5-(1,2-diphenylvinyl)-4H-chromen-4-one (2m). Overall yield 90% (72.4 mg). White solid. mp 200 – 202 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 6.0 Hz, 1H), 7.38 (d, J = 9.0 Hz, 1H),

7.33 – 7.09 (m, 10H), 6.49 (s, 1H), 6.26 (d, J = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.0, 156.7, 153.6, 144.1, 140.6, 137.6, 137.4, 137.3, 130.6, 129.4, 129.3, 128.0, 127.5, 127.0, 126.8, 124.9, 122.7, 119.4, 114.4. HRMS (ESI+) m/z calcd. for $[C_{23}H_{15}BrNaO_2]^+$: 425.0148, found : 425.0127.

***Conditions B*:** Reactions were conducted in Cap Test Tube. Chromone (0.2 mmol), acetylene (1.5 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol%), $AgSbF_6$ (16 mol%), $Cu(OAc)_2$ (10 mol%), AcOH (2.0 equiv) were combined in 1,2-DCE (2.0 mL). The reaction mixture was stirred at 100 °C for 2-4 h. Additional $AgSbF_6$ (20 mol%) was added to the reaction mixture after consumption of chromone. After completion of the isomerization (~2 h), the reaction mixture was diluted with CH_2Cl_2 and 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 (*n*-Hexane/EtOAc or *n*-Hexane/EtOAc/CH_2Cl_2) to give the desired product.

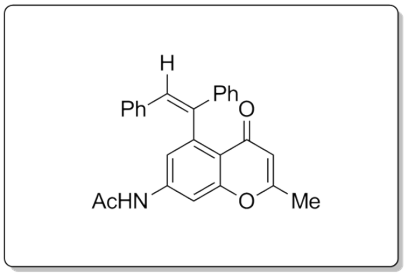


(Z)-5-(1,2-diphenylvinyl)-4H-chromen-4-one (3a). Overall yield 87% (56.3 mg). Yellow soild. mp 150 – 153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 5.8 Hz, 1H), 7.61 (dd, J = 8.6, 7.4 Hz, 1H), 7.50 (dd, J = 8.5, 1.3 Hz, 1H), 7.38 – 7.05 (m, 10H), 6.96 (ddd, J = 7.4, 1.6, 0.8 Hz, 2H), 6.17 (d, J = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 158.0, 153.9, 142.7, 142.6, 140.7, 137.4, 133.3, 129.3, 128.7, 128.0, 127.9, 127.1, 127.0, 126.5, 126.4, 124.1, 118.0, 113.9. HRMS (ESI+) m/z calcd. for $C_{23}H_{16}NaO_2^+$[M+Na]$^+$: 347.1043, found : 347.1045.

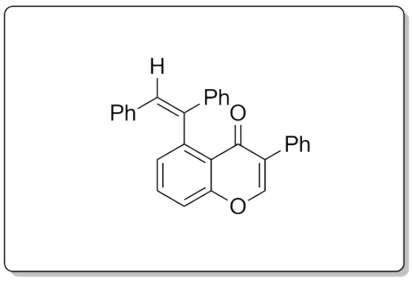


(Z)-5-(1,2-diphenylvinyl)-2-phenyl-4H-chromen-4-one (3b). Overall yield 82% (65.5 mg). Yellow solid. mp 180 – 182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.82 (m, 2H), 7.68 – 7.59 (m, 2H), 7.58 – 7.49 (m, 3H), 7.40 – 7.22 (m, 5H), 7.18 (dd, J = 6.3, 2.2 Hz, 1H), 7.15 – 7.06 (m, 4H), 7.04 – 6.95 (m, 2H), 6.67 (s, 1H). ^{13}C NMR (100 MHz,

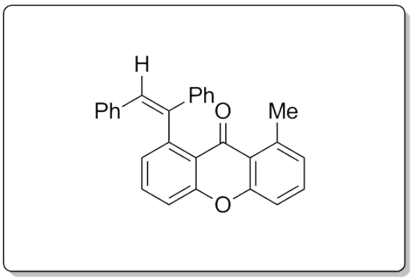
$CDCl_3$) δ 177.3, 161.9, 157.8, 142.7, 142.7, 140.6, 137.5, 133.3, 131.6, 131.4, 129.4, 129.0, 128.7, 128.0, 127.9, 127.1, 126.6, 126.4, 126.1, 123.2, 117.9, 108.5. HRMS (ESI+) m/z calcd. for $[C_{29}H_{20}NaO_2]^+$: 423.1356, found : 423.1333.



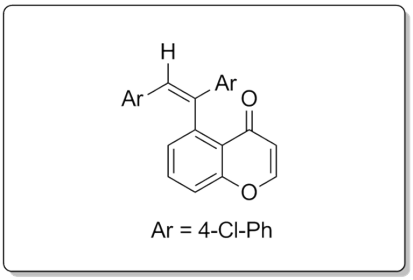
(Z)-*N*-(5-(1,2-diphenylvinyl)-2-methyl-4-oxo-4H-chromen-7-yl)acetamide (3c). Overall yield 63% (49.6 mg). White solid. mp 280 – 282 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.39 (s, 1H), 8.16 (d, *J* = 2.0 Hz, 1H), 7.33 – 7.04 (m, 9H), 6.99 (d, *J* = 2.0 Hz, 1H), 6.97 – 6.93 (m, 2H), 5.96 (s, 1H), 2.33 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 175.4, 169.4, 165.1, 158.3, 143.5, 141.8, 141.7, 140.1, 137.1, 128.9, 128.1, 128.0, 127.0, 126.6, 126.1, 125.5, 118.1, 117.5, 110.5, 105.8, 24.2, 19.5. HRMS (ESI+) m/z calcd. for $[C_{26}H_{21}NNaO_3]^+$: 418.1414, found : 418.1415.



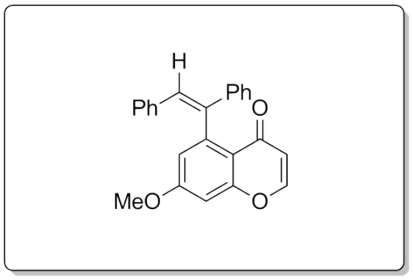
(Z)-5-(1,2-diphenylvinyl)-3-phenyl-4H-chromen-4-one (3d). Overall yield 78% (62.3 mg). Yellow soild. mp 74 – 76 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.63 (ddd, *J* = 8.3, 7.3, 0.7 Hz, 1H), 7.52 (dt, *J* = 8.3, 0.7 Hz, 1H), 7.44 – 7.20 (m, 10H), 7.19 – 7.04 (m, 5H), 7.00 – 6.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 157.6, 151.8, 142.7, 142.4, 141.3, 137.6, 133.2, 131.8, 129.3, 128.9, 128.8, 128.3, 128.0, 127.9, 127.9, 127.0, 126.8, 126.6, 126.4, 126.0, 124.0, 117.9. HRMS (ESI+) m/z calcd. for $[C_{29}H_{20}NaO_2]^+$: 423.1356, found : 423.1354.



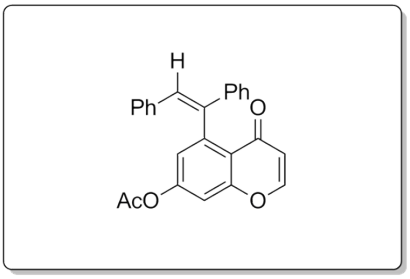
(Z)-1-(1,2-diphenylvinyl)-8-methyl-9H-xanthen-9-one (3e). Overall yield 66% (51.2 mg). Yellow solid. mp 155 – 157 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.4, 7.4 Hz, 1H), 7.54 – 7.44 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.20 (m, 4H), 7.15 – 7.06 (m, 5H), 7.05 – 6.98 (m, 3H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 156.7, 156.7, 143.2, 142.6, 141.8, 141.5, 137.6, 133.7, 133.1, 129.4, 127.9, 127.9, 127.4, 127.0, 126.8, 126.6, 126.5, 126.4, 122.4, 121.1, 117.3, 115.4, 22.8. HRMS (ESI+) m/z calcd. for $[C_{28}H_{20}NaO_2]^+$: 411.1356, found : 411.1335.



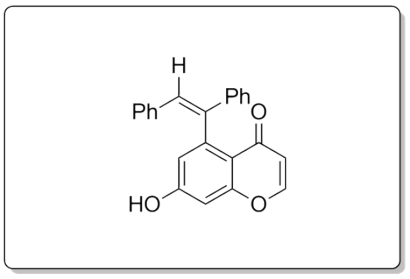
(Z)-5-(1,2-bis(4-chlorophenyl)vinyl)-4H-chromen-4-one (3f). Overall yield 71% (55.7 mg). Pale yellow solid. mp 153 – 155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 6.0 Hz, 1H), 7.63 (ddd, *J* = 8.1, 7.3, 0.7 Hz, 1H), 7.52 (dt, *J* = 8.4, 0.9 Hz, 1H), 7.31 – 7.18 (m, 4H), 7.12 – 7.03 (m, 3H), 6.96 (s, 1H), 6.89 – 6.80 (m, 2H), 6.19 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 158.1, 154.1, 142.3, 140.9, 139.8, 135.7, 133.5, 133.0, 132.3, 130.5, 128.6, 128.3, 128.2, 127.8, 126.1, 124.0, 118.5, 114.0. HRMS (ESI+) m/z calcd. for $[C_{23}H_{14}Cl_2NaO_2]^+$: 415.0263, found : 415.0260.



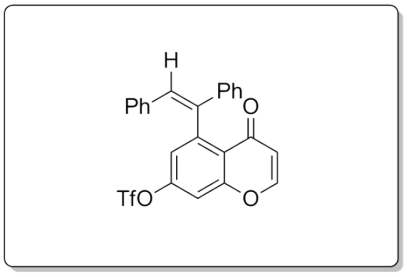
(Z)-5-(1,2-diphenylvinyl)-7-methoxy-4H-chromen-4-one (3g). Overall yield 86% (60.8 mg). White solid. mp 170 – 172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 5.9 Hz, 1H), 7.38 – 7.21 (m, 5H), 7.17 – 7.07 (m, 3H), 7.05 (s, 1H), 7.03 – 6.96 (m, 2H), 6.89 (d, *J* = 2.5 Hz, 1H), 6.74 (d, *J* = 2.6 Hz, 1H), 6.11 (d, *J* = 5.9 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 163.1, 159.7, 153.4, 142.4, 142.2, 142.1, 137.4, 129.2, 128.0, 127.9, 127.1, 127.0, 126.5, 126.4, 118.1, 117.3, 113.8, 100.4, 55.7. HRMS (ESI+) m/z calcd. for $[C_{24}H_{18}NaO_3]^+$: 377. 1148, found : 377.1134.



(Z)-5-(1,2-diphenylvinyl)-4-oxo-4H-chromen-7-yl acetate (3h). Overall yield 77% (58.8 mg). White solid. mp 183 – 185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 6.0 Hz, 1H), 7.37 (d, *J* = 2.3 Hz, 1H), 7.35 – 7.23 (m, 5H), 7.19 – 7.08 (m, 3H), 7.05 (s, 1H), 7.00 – 6.95 (m, 2H), 6.92 (d, *J* = 2.3 Hz, 1H), 6.15 (d, *J* = 6.0 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7, 168.2, 158.5, 153.9, 153.7, 142.4, 142.1, 141.7, 137.0, 129.3, 128.1, 128.0, 127.4, 127.2, 126.6, 122.4, 121.8, 114.0, 110.8, 21.1. HRMS (ESI+) m/z calcd. for $[C_{25}H_{18}NaO_4]^+$: 405.1097, found : 405.1131.

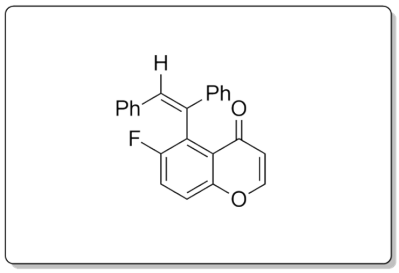


(Z)-5-(1,2-diphenylvinyl)-7-hydroxy-4H-chromen-4-one (3i). Overall yield 73% (49.6 mg). Pale brown solid. mp 238 – 240 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.79 (br, 1H), 8.08 (d, *J* = 5.9 Hz, 1H), 7.33 – 7.19 (m, 5H), 7.18 – 7.13 (m, 2H), 7.12 – 7.06 (m, 1H), 7.03 (s, 1H), 6.98 – 6.94 (m, 2H), 6.91 (d, *J* = 2.4 Hz, 1H), 6.51 (d, *J* = 2.4 Hz, 1H), 6.01 (d, *J* = 5.9 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.8, 161.8, 159.3, 154.9, 142.0, 141.7, 141.4, 137.1, 128.9, 128.1, 128.0, 126.9, 126.6, 126.1, 125.4, 117.0, 116.4, 112.7, 102.6. HRMS (ESI+) m/z calcd. for $[C_{23}H_{16}NaO_3]^+$: 363.0992, found : 363.0981.

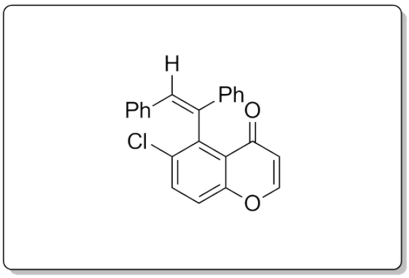


(Z)-5-(1,2-diphenylvinyl)-4-oxo-4H-chromen-7-yl trifluoromethanesulfonate (3j). Overall yield 87% (82.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 6.0 Hz, 1H), 7.42 (d, *J* = 2.5 Hz, 1H), 7.32 – 7.06 (m, 9H), 7.01 (d, *J* = 2.5 Hz, 1H), 6.93 – 6.82 (m, 2H), 6.17 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 158.2, 154.3,

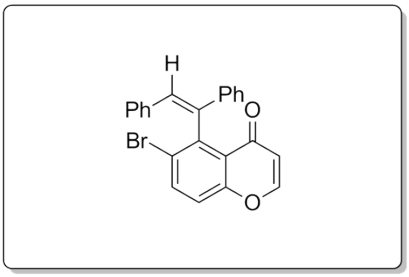
151.3, 144.3, 141.5, 141.0, 136.6, 129.2, 128.4, 128.2, 128.1, 127.5, 126.9, 126.5, 123.9, 121.8, 118.5 (q, J_{CF} = 321.3 Hz), 114.5, 111.1. HRMS (ESI+) m/z calcd. for $[C_{24}H_{15}F_3NaO_5S]^+$: 495.0484, found : 495.0496.



(Z)-5-(1,2-diphenylvinyl)-6-fluoro-4H-chromen-4-one (3k). Overall yield 91% (62.2 mg). White solid. mp 165 – 167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 5.9 Hz, 1H), 7.50 (dd, J = 9.2, 4.4 Hz, 1H), 7.43 – 7.36 (m, 3H), 7.34 – 7.30 (m, 2H), 7.29 – 7.24 (m, 1H), 7.22 (s, 1H), 7.17 – 7.08 (m, 3H), 7.03 – 6.98 (m, 2H), 6.16 (dd, J = 6.0, 0.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3 (d, J_{CF} = 2.6 Hz), 155.9 (d, J_{CF} = 245.0 Hz), 154.0 (d, J_{CF} = 2.0 Hz), 154.0, 141.5, 137.5, 134.2, 129.5 (d, J_{CF} = 1.5 Hz), 128.4, 128.2, 128.0, 127.2, 126.8, 126.4, 126.2 (d, J_{CF} = 19.2 Hz), 124.8 (d, J_{CF} = 3.2 Hz), 121.7 (d, J_{CF} = 27.4 Hz), 119.8 (d, J_{CF} = 8.5 Hz), 113.5. HRMS (ESI+) m/z calcd. for $[C_{23}H_{15}FNaO_2]^+$: 365.0948, found : 365.0933.

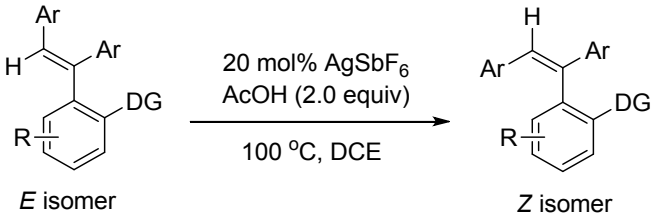


(Z)-6-chloro-5-(1,2-diphenylvinyl)-4H-chromen-4-one (3l). Overall yield 92% **(**65.8 mg). White solid. mp 169 – 171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 6.0 Hz, 1H), 7.72 (d, J = 9.0 Hz, 1H), 7.47 (d, J = 9.0 Hz, 1H), 7.41 – 7.31 (m, 4H), 7.29 – 7.23 (m, 1H), 7.21 (s, 1H), 7.17 – 7.08 (m, 3H), 7.01 – 6.90 (m, 2H), 6.17 (d, J = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.6, 156.3, 153.8, 140.7, 138.3, 138.0, 137.3, 134.5, 131.3, 128.6, 128.3, 128.2, 128.0, 127.2, 126.8, 126.4, 125.1, 119.4, 114.1. HRMS (ESI+) m/z calcd. for $[C_{23}H_{15}ClNaO_2]^+$: 381.0653, found : 381.0646.

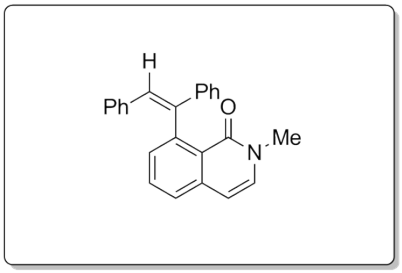


(Z)-6-bromo-5-(1,2-diphenylvinyl)-4H-chromen-4-one (3m). Overall yield 82% (65.9 mg). White solid. mp 187 – 189 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 9.0 Hz, 1H), 7.74 (d, *J* = 5.9 Hz, 1H), 7.45 – 7.22 (m, 6H), 7.19 (s, 1H), 7.16 – 7.10 (m, 3H), 6.98 – 6.91 (m, 2H), 6.18 (d, *J* = 5.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 156.9, 153.7, 140.5, 140.5, 139.8, 137.7, 137.3, 128.4, 128.2, 128.0, 127.2, 126.8, 126.5, 125.5, 122.0, 119.7, 114.1. HRMS (ESI+) m/z calcd. for $[C_{23}H_{15}BrNaO_2]^+$: 425.0148, found : 425.0150.

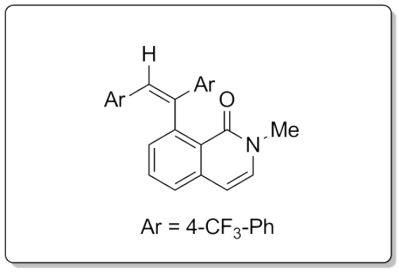
2. General Procedure for the Silver-Catalyzed Isomerization of E-Alkenyl Arenes



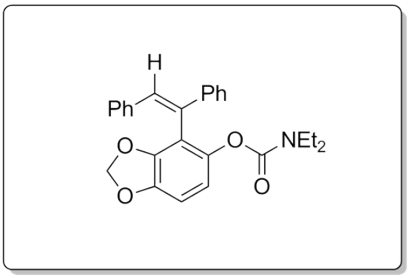
Reactions were conducted in Cap Test Tube. E Alkene (0.1 mmol), $AgSbF_6$ (20 mol%), AcOH (2.0 equiv) were combined in 1,2-DCE (1.0 mL). The reaction mixture was stirred at 100 °C for specified time. The reaction mixture was diluted with CH_2Cl_2 and washed with sequentially aqueous $NaHCO_3$ and NH_4Cl. The organic layer was dried over $MgSO_4$. After removal of solvent, the residue was purified by flash chromatography on silica gel (*n*-Hexane/EtOAc or *n*-Hexane/EtOAc/CH_2Cl_2) to give the desired product.



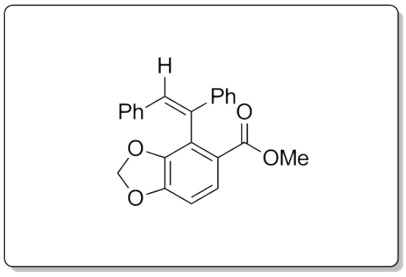
(Z)-8-(1,2-diphenylvinyl)-2-methylisoquinolin-1(2H)-one (4a). Overall yield 95% (32.2 mg). Reaction time: 40 min. White solid. mp 180 – 182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.48 (m, 2H), 7.40 – 7.16 (m, 6H), 7.13 – 7.01 (m, 5H), 6.95 – 6.88 (m, 2H), 6.50 (d, *J* = 7.3 Hz, 1H), 3.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 144.3, 143.2, 141.6, 139.2, 137.7, 132.9, 131.9, 130.5, 129.4, 128.0, 127.8, 126.8, 126.4, 126.1, 126.0, 125.7, 125.3, 105.5, 37.2. HRMS (ESI+) m/z calcd. for $[C_{24}H_{19}NNaO]^+$: 360.1359, found : 360.1348.



(Z)-8-(1,2-bis(4-(trifluoromethyl)phenyl)vinyl)-2-methylisoquinolin-1(2H)-one (4b). Overall yield 95% (44.9 mg). Reaction time: 1 h 30 min. Pale yellow solid. mp 174 – 176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.53 – 7.47 (m, 2H), 7.44 – 7.36 (m, 2H), 7.33 – 7.25 (m, 2H), 7.14 (dd, *J* = 5.0, 3.5 Hz, 1H), 7.09 – 7.03 (m, 2H), 7.02 – 6.96 (m, 2H), 6.50 (d, *J* = 7.3 Hz, 1H), 3.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 146.1, 145.6, 140.8, 140.7, 140.0, 139.5, 133.2, 132.2, 130.2, 129.5, 129.4, 129.1, 128.8, 128.7, 128.4, 128.0, 126.7, 126.7, 125.8, 125.6, 125.5, 125.1, 125.1, 125.1, 125.0, 124.9, 124.9, 124.8, 124.8, 122.9, 122.8, 105.7, 37.2. HRMS (ESI+) m/z calcd. for $[C_{26}H_{17}F_6NNaO]^+$: 496.1107, found : 496.1121.

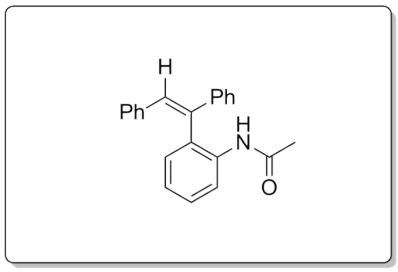


(Z)-4-(1,2-diphenylvinyl)benzo[d][1,3]dioxol-5-yl diethylcarbamate (4c). Overall yield 92% (38.2 mg). Reaction time: 46 h. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 2H), 7.37 – 7.26 (m, 5H), 7.25 – 7.09 (m, 4H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 5.80 (s, 1H), 5.45 (s, 1H), 3.17 (q, *J* = 7.1 Hz, 2H), 2.92 – 2.55 (m, 2H), 1.00 (t, *J* = 7.1 Hz, 3H), 0.85 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 146.0, 144.6, 144.3, 141.2, 137.5, 131.8, 131.7, 128.7, 128.2, 128.0, 127.5, 127.2, 126.5, 116.4, 115.8, 107.3, 101.4, 41.7, 41.1, 13.7, 13.1. HRMS (ESI+) m/z calcd. for $[C_{26}H_{25}NNaO_4]^+$: 438.1676, found : 438.1687.

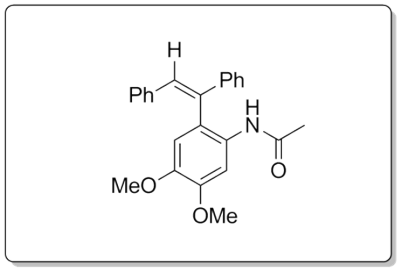


(Z)-methyl 4-(1,2-diphenylvinyl)benzo[d][1,3]dioxole-5-carboxylate (4d). Overall yield 95% (33.9 mg). Reaction time: 16 h. Yellow solid. mp 128 – 130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.2, 0.6 Hz, 1H),

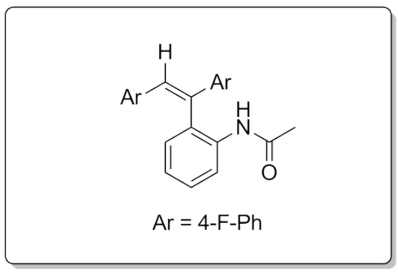
7.38 – 7.25 (m, 5H), 7.21 – 7.05 (m, 6H), 6.86 (dd, J = 8.2, 0.6 Hz, 1H), 5.91 (s, 1H), 5.62 (s, 1H), 3.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 150.6, 146.1, 141.6, 137.6, 135.3, 129.2, 128.5, 128.3, 128.0, 127.4, 127.0, 126.7, 126.3, 124.9, 122.9, 107.3, 101.6, 51.7. HRMS (ESI+) m/z calcd. for $[C_{23}H_{18}NaO_4]^+$: 381.1097, found : 381.1080.



(Z)-*N*-(2-(1,2-diphenylvinyl)phenyl)acetamide (4e). Overall yield 94% (29.7 mg). Reaction time: 10 h. Pale orange solid. mp 143 – 145 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.3 Hz, 1H), 7.48 – 7.32 (m, 6H), 7.24 – 6.99 (m, 9H), 1.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 141.7, 137.6, 136.2, 135.5, 130.7, 130.3, 129.5, 128.9, 128.9, 128.7, 128.5, 128.2, 127.9, 126.8, 124.6, 121.5, 24.4. HRMS (ESI+) m/z calcd. for $[C_{22}H_{19}NNaO]^+$: 336.1359, found : 336.1335.

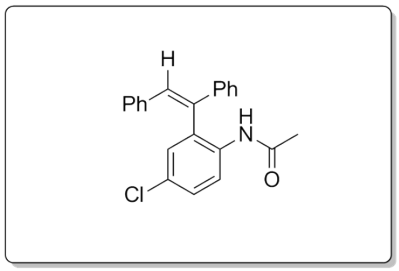


(Z)-*N*-(2-(1,2-diphenylvinyl)-4,5-dimethoxyphenyl)acetamide (4f). Overall yield 92% (34.2 mg). Reaction time: 10 h. Pale brown soild. mp 198 – 200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.45 – 7.33 (m, 5H), 7.24 – 7.06 (m, 6H), 7.02 (br, 1H), 6.62 (s, 1H), 3.97 (s, 3H), 3.74 (s, 3H), 1.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 148.7, 145.8, 141.8, 137.4, 136.2, 130.1, 129.1, 128.8, 128.7, 128.5, 128.3, 127.9, 126.9, 121.2, 112.8, 105.7, 56.0, 55.9, 24.3. HRMS (ESI+) m/z calcd. for $[C_{24}H_{23}NNaO_3]^+$: 396.1570, found : 396.1576.

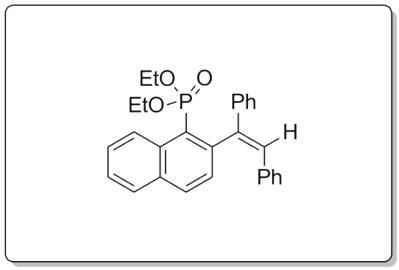


(Z)-N-(2-(1,2-bis(4-fluorophenyl)vinyl)phenyl)acetamide (4g). Overall yield 86% (30.0 mg). Reaction time: 10 h. Pale yellow soild. mp 149 – 151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.3 Hz, 1H), 7.43 (ddd, J = 8.4, 7.1,

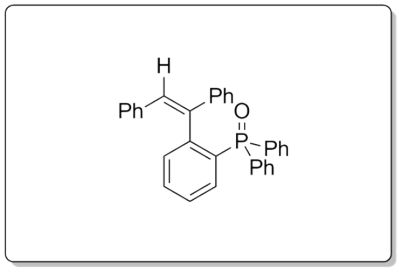
1.9 Hz, 1H), 7.35 – 7.25 (m, 2H), 7.21 – 6.98 (m, 8H), 6.94 – 6.80 (m, 2H), 1.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 162.7 (d, J_{CF} = 248.6 Hz) ,162.1 (d, J_{CF} = 247.9 Hz), 137.6 (d, J_{CF} = 3.3 Hz), 136.3, 135.3, 132.2 (d, J_{CF} = 3.5 Hz), 130.6, 130.5, 129.1, 128.7, 128.5, 128.4, 124.8, 121.8, 115.6 (d, J_{CF} = 21.5 Hz), 115.5 (d, J_{CF} = 21.4 Hz), 24.4. HRMS (ESI+) m/z calcd. for $[C_{22}H_{17}F_2NNaO]^+$: 372.1170, found : 372.1154.



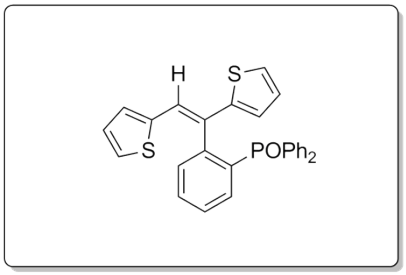
(Z)-*N*-(4-chloro-2-(1,2-diphenylvinyl)phenyl)acetamide (4h). Overall yield 87% (30.1 mg). Reaction time: 10 h. White solid. mp 151 – 153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 8.8 Hz, 1H), 7.45 – 7.31 (m, 6H), 7.25 – 7.20 (m, 4H), 7.17 (d, J = 2.5 Hz, 1H), 7.15 (br, 1H), 7.10 – 7.04 (m, 2H), 1.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 141.1, 136.2, 135.7, 134.1, 131.1, 130.9, 130.3, 129.4, 128.9, 128.8, 128.8, 128.6, 128.4, 128.3, 126.8, 122.6, 24.4. HRMS (ESI+) m/z calcd. for $[C_{22}H_{18}ClNNaO]^+$: 370.0969, found : 370.0956.



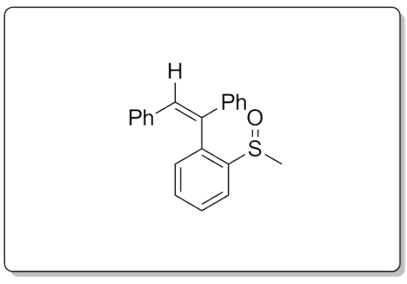
(Z)-diethyl (2-(1,2-diphenylvinyl)naphthalen-1-yl)phosphonate (4i). Overall yield 89% (39.4 mg). Reaction time: 20 min. White solid. mp 114 – 116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, J = 8.8 Hz, 1H), 8.07 – 8.00 (m, 1H), 7.96 – 7.89 (m, 1H), 7.72 – 7.54 (m, 2H), 7.41 – 7.20 (m, 6H), 7.17 – 7.02 (m, 6H), 4.39 – 3.25 (m, 4H), 1.31 – 0.53 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 145.8, 143.6, 143.4, 143.4, 137.2, 134.5, 134.4, 133.6, 133.6, 133.0, 132.9, 130.1, 129.9, 129.5, 128.6, 128.5, 127.3, 127.0, 126.9, 126.9, 126.6, 126.3, 125.7, 123.9, 61.7, 61.7, 61.5, 61.4, 16.2, 16.1, 16.1. HRMS (ESI+) m/z calcd. for $[C_{28}H_{27}NaO_3P]^+$ 465.1590, found : 465.1628.



(Z)-(2-(1,2-diphenylvinyl)phenyl)diphenylphosphine oxide (4j). Overall yield 84% (38.2 mg). Reaction time: 60 h. White solid. mp 198 – 200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.31 (m, 10H), 7.31 – 7.17 (m, 4H), 7.16 – 7.03 (m, 8H), 7.00 – 6.92 (m, 2H), 6.89 – 6.83 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 144.8, 142.0, 141.0, 141.0, 137.2, 134.8, 134.7, 133.8, 133.3, 133.2, 133.1, 132.8, 132.3, 132.1, 132.0, 131.9, 131.8, 131.7, 131.6, 131.3, 131.3, 131.3, 131.0, 131.0, 129.7, 129.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.2, 127.1, 127.0, 126.9, 126.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.4. HRMS (ESI+) m/z calcd. for $[C_{32}H_{25}NaOP]^+$:479.1535, found : 479.1551.

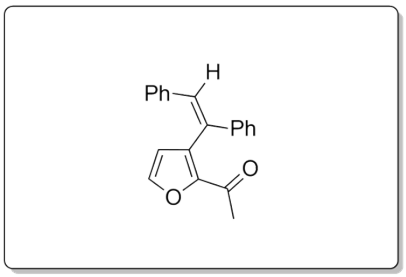


(E)-(2-(1,2-di(thiophen-2-yl)vinyl)phenyl)diphenylphosphine oxide (4k). Overall yield 92% (43.1 mg). Reaction time: 5 h. Pale yellow solid. mp 98 – 100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (ddd, *J* = 13.2, 7.6, 1.3 Hz, 1H), 7.63 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.56 – 7.48 (m, 3H), 7.47 – 7.30 (m, 5H), 7.28 – 7.21 (m, 2H), 7.16 (td, *J* = 7.7, 3.0 Hz, 2H), 7.04 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.01 (d, *J* = 5.1 Hz, 1H), 6.81 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.78 (s, 1H), 6.71 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.66 (d, *J* = 3.5 Hz, 1H), 6.37 (d, *J* = 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 142.1, 142.1, 140.6, 135.5, 135.3, 133.0, 132.9, 132.0, 131.9, 131.9, 131.9, 131.8, 131.3, 131.3, 129.1, 128.4, 128.3, 127.9, 127.8, 127.8, 127.6, 127.2, 126.5, 126.5, 126.2, 124.3, 120.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.6. HRMS (ESI+) m/z calcd. for $[C_{28}H_{21}NaOPS_2]^+$: 491.0664, found : 491.0690.

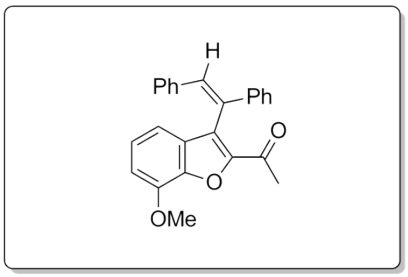


(Z)-(1-(2-(methylsulfinyl)phenyl)ethene-1,2-diyl)dibenzene (4l). Overall yield 91% (28.9 mg). Reaction time: 24 h. White soild. mp 121 – 123 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99 (d, *J* = 7.9 Hz, 1H), 7.71 (td, *J* = 7.6, 1.4 Hz, 1H), 7.62 (td, *J* = 7.4, 1.4 Hz, 1H), 7.40 – 7.21 (m, 7H), 7.18 – 7.07 (m, 3H), 7.00 – 6.83 (m, 2H), 2.17 (s, 3H).

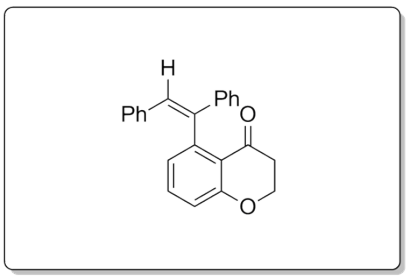
^{13}C NMR (100 MHz, DMSO-d_6) δ 144.9, 140.6, 136.7, 135.8, 135.7, 131.2, 130.4, 129.3, 128.7, 128.3, 127.9, 127.6, 127.3, 126.1, 124.0, 41.6. HRMS (ESI+) m/z calcd. for $[C_{21}H_{18}NaOS]^+$: 341.0971, found : 341.0962.



(Z)-1-(3-(1,2-diphenylvinyl)furan-2-yl)ethanone (4m). Overall yield 93% (26.8 mg). Reaction time: 1 h. Pale yellow solid. mp 98 – 100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 1.7 Hz, 1H), 7.49 – 7.32 (m, 5H), 7.28 – 7.14 (m, 6H), 6.45 (d, *J* = 1.7 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.4, 148.5, 146.0, 140.8, 136.4, 132.6, 131.4, 130.8, 128.9, 128.5, 128.2, 127.8, 127.5, 126.4, 115.5, 26.9. HRMS (ESI+) m/z calcd. for $[C_{20}H_{16}NaO_2]^+$: 311.1043, found : 311.1016.

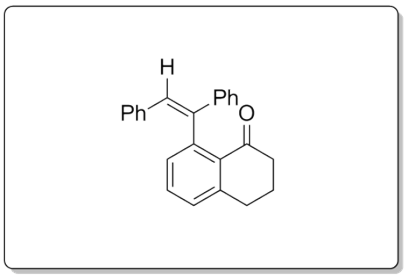


(Z)-1-(3-(1,2-diphenylvinyl)-7-methoxybenzofuran-2-yl)ethanone (4n). Overall yield 97% (35.7 mg). Reaction time: 1 h. White solid. mp 148 – 150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.37 – 7.28 (m, 4H), 7.16 – 7.06 (m, 6H), 7.00 – 6.92 (m, 2H), 4.08 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 148.4, 145.9, 144.4, 140.9, 136.4, 132.0, 131.1, 129.8, 128.7, 128.5, 128.3, 127.9, 127.6, 126.4, 124.6, 114.4, 109.6, 56.0, 27.6. HRMS (ESI+) m/z calcd. for $[C_{25}H_{20}NaO_3]^+$: 391.1305, found : 391.1290.

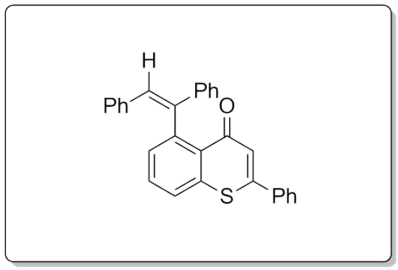


(Z)-5-(1,2-diphenylvinyl)chroman-4-one (4o). Overall yield 90% (29.3 mg). Reaction time: 15 min. White solid. mp 147 – 149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.42 (m, 1H), 7.42 – 7.24 (m, 5H), 7.22 – 7.03 (m, 4H), 7.03 – 6.96 (m, 3H), 6.91 – 6.80 (m, 1H), 4.61 – 4.38 (m, 2H), 2.88 – 2.55 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

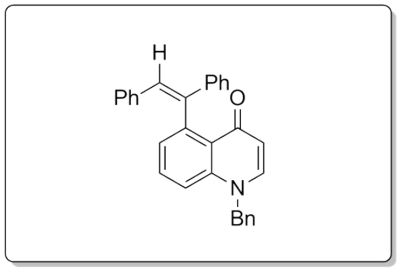
190.1, 163.1, 142.7, 142.4, 141.9, 137.4, 135.2, 129.1, 128.0, 127.9, 127.1, 126.7, 126.5, 126.4, 125.2, 120.4, 117.6, 66.7, 38.3. HRMS (ESI+) m/z calcd. for $[C_{23}H_{18}NaO_2]^+$: 349.1199, found : 349.1183.



(Z)-8-(1,2-diphenylvinyl)-3,4-dihydronaphthalen-1(2H)-one (4p). Overall yield 94% (30.3 mg). Reaction time: 15 min. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (t, *J* = 7.6 Hz, 1H), 7.36 – 7.23 (m, 6H), 7.16 – 7.06 (m, 4H), 6.96 – 6.85 (m, 3H), 3.02 (td, *J* = 5.9, 2.2 Hz, 2H), 2.45 (dd, *J* = 7.5, 5.9 Hz, 2H), 2.06 (p, *J* = 6.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 145.9, 143.9, 142.9, 141.6, 137.7, 132.7, 132.4, 130.8, 129.2, 128.4, 128.0, 127.8, 127.0, 126.7, 126.2, 126.0, 39.7, 30.6, 23.0. HRMS (ESI+) m/z calcd. for $[C_{24}H_{20}NaO]^+$: 347.1406, found : 347.1396.

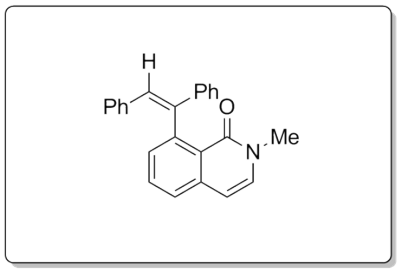


(Z)-5-(1,2-diphenylvinyl)-2-phenyl-4H-thiochromen-4-one (4q). Overall yield 84% (34.8 mg). Reaction time: 4 h 30 min. Pale brown solid. mp 103 – 105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.64 (m, 3H), 7.61 – 7.44 (m, 4H), 7.38 – 7.21 (m, 6H), 7.16 – 6.94 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 150.3, 144.5, 143.1, 142.9, 139.6, 137.6, 136.1, 132.2, 131.2, 130.6, 130.3, 129.4, 129.2, 128.0, 127.9, 127.0, 126.7, 126.5, 126.4, 126.2, 125.7, 124.4. HRMS (ESI+) m/z calcd. for $[C_{29}H_{20}NaOS]^+$: 439.1127, found : 439.1129.



(Z)-1-benzyl-5-(1,2-diphenylvinyl)quinolin-4(1H)-one (4r). Overall yield 68% **(**27.9 mg). Reaction time: 48 h. Pale yellow solid. mp 130 – 132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.26 (m, 10H), 7.24 – 7.14 (m, 3H), 7.12

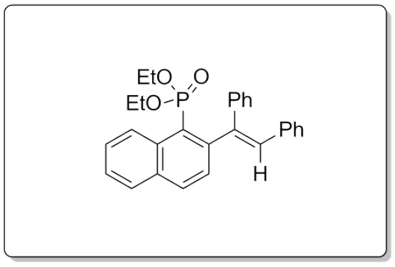
– 6.85 (m, 7H), 6.13 (d, J = 7.7 Hz, 1H), 5.30 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.4, 144.7, 143.2, 142.6, 141.8, 141.3, 137.9, 135.3, 131.7, 129.3, 129.1, 128.2, 127.9, 127.7, 127.3, 126.7, 126.5, 126.5, 126.1, 125.9, 125.4, 115.9, 111.5, 56.7. HRMS (ESI+) m/z calcd. for $[C_{30}H_{23}NNaO]^+$: 436.1672, found : 436.1667.



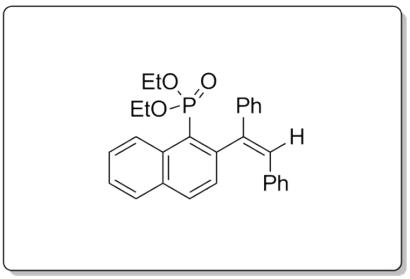
Scheme 3. Hydroarylation of Aryl Phosphonates

*E Selective Hydroarylation***:** Reactions were conducted in screw cap test tube. Aryl Phosphonate (0.2 mmol), Diphenylacetylene (2.0 equiv), $[RhCp^*Cl_2]_2$ (3 mol%), $AgSbF_6$ (10 mol%), $Cu(OAc)_2$ (10 mol%), PivOH (1.0 equiv) were combined in 1,2-DCE (1.0 mL). The reaction mixture was stirred at 110 ^oC for 12 h. The reaction mixture was monitored by TLC using 50% EtOAc and 50% *n*-Hexane as the mobile phase. The reaction mixture was diluted with CH_2Cl_2 and 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 (*n*-Hexane/EtOAc) to give the desired product.

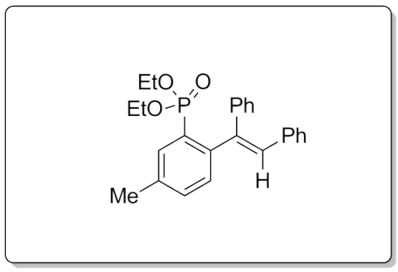
*Z Selective Hydroarylation***:** Reactions were conducted in screw cap test tube. Aryl Phosphonate (0.2 mmol), Diphenylacetylene (2.0 equiv), $[RhCp^*Cl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), $Cu(OAc)_2$ (10 mol%), PivOH (1.0 equiv) were combined in 1,2-DCE (1.0 mL). The reaction mixture was stirred at 110 ^oC for 12 h. Additional $AgSbF_6$ (20 mol%) was added to the reaction mixture after 12 h. After completion of the isomerization, the reaction mixture was diluted with CH_2Cl_2 and 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 (*n*-Hexane/EtOAc) to give the desired product.



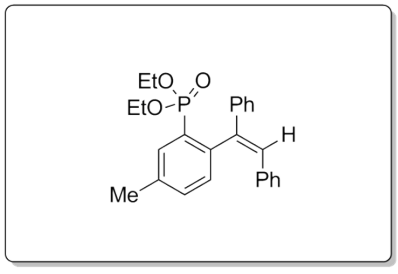
(E)-diethyl (2-(1,2-diphenylvinyl)naphthalen-1-yl)phosphonate. Overall yield 82% (72.3 mg). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 8.8, 1.1 Hz, 1H), 7.95 – 7.80 (m, 2H), 7.63 (ddd, *J* = 8.6, 6.9, 1.5 Hz, 1H), 7.55 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 7.43 – 7.33 (m, 2H), 7.32 – 7.17 (m, 9H), 6.67 (s, 1H), 4.07 (s, 4H), 1.24 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 150.3, 143.0, 143.0, 139.9, 137.4, 134.1, 134.0, 132.6, 132.5, 132.0, 131.9, 131.3, 131.3, 130.7, 129.5, 128.8, 128.5, 128.3, 128.3, 128.0, 128.0, 127.8, 127.8, 127.7, 127.2, 127.1, 126.9, 126.0, 124.1, 122.3, 61.8, 61.7, 16.3, 16.3. [Ref] *Org. Lett*. **2013**, *15*, 4504.



(Z)-diethyl (2-(1,2-diphenylvinyl)naphthalen-1-yl)phosphonate. Overall yield 81% (71.6 mg). White solid. mp 114 – 116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 8.8 Hz, 1H), 8.07 – 8.00 (m, 1H), 7.96 – 7.89 (m, 1H), 7.72 – 7.54 (m, 2H), 7.41 – 7.20 (m, 6H), 7.17 – 7.02 (m, 6H), 4.39 – 3.25 (m, 4H), 1.31 – 0.53 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 145.8, 143.6, 143.4, 143.4, 137.2, 134.5, 134.4, 133.6, 133.6, 133.0, 132.9, 130.1, 129.9, 129.5, 128.6, 128.5, 127.3, 127.0, 126.9, 126.9, 126.6, 126.3, 125.7, 123.9, 61.7, 61.7, 61.5, 61.4, 16.2, 16.1, 16.1. HRMS (ESI+) m/z calcd. for $[C_{28}H_{27}NaO_3P]^+$ 465.1590, found : 465.1628.



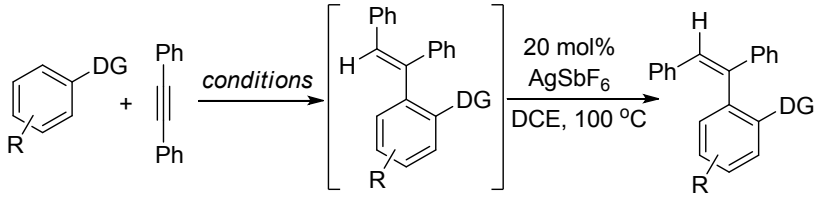
(E)-diethyl (2-(1,2-diphenylvinyl)-5-methylphenyl)phosphonate. Overall yield 61% (49.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 14.3, 1.8 Hz, 1H), 7.37 – 7.06 (m, 12H), 6.72 (s, 1H), 4.22 – 3.87 (m, 4H), 2.42 (s, 3H), 1.23 (t, *J* = 7.0 Hz, 6H). [Ref] *Org. Lett*. **2013**, *15*, 4504.

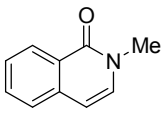
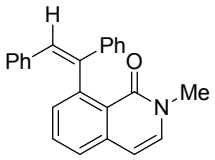
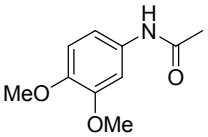
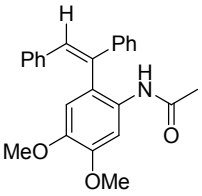
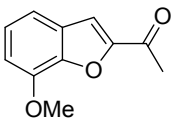
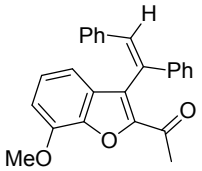


(Z)-diethyl (2-(1,2-diphenylvinyl)-5-methylphenyl)phosphonate. Overall yield 80% (64.5 mg). δ 8.04 (dd, *J* = 14.9, 1.9 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.07 (m, 10H), 7.01 – 6.90 (m, 2H), 3.97 – 3.35 (m, 4H), 2.49 (s, 3H), 0.97 (t, *J* = 7.0 Hz, 3H), 0.84 (t, *J* = 7.0 Hz, 3H). [Ref] *Org. Lett*. **2013**, *15*, 4504.

As mentioned in the text, DCE proved to be the most suitable solvent for the $AgSbF_6$-catalyzed isomerization, and the tandem hydroarylation/isomerization process was sluggish in other solvents (e.g., dioxane, *i*PrOH, and toluene). We envisaged that the resulting *E*-isomers would be prone to isomerization upon the addition of $AgSbF_6$ in DCE without solvent exchange. Indeed, a convenient one-pot procedure was found to proceed through the hydroarylation and subsequent isomerization to deliver the *Z*-selective alkene products (Table 3S).

Table 3S. One-pot sequence for the hydroarylation/isomerization process.



Entry	substrate	Yield[a] (E:Z)
1		 **4a**, 80% (*E/Z* 6:94)
2		 **4f**, 76% (*E/Z* 6:94)
3		 **4n**, 78% (*E/Z* 10:90)

(Z)-8-(1,2-diphenylvinyl)-2-methylisoquinolin-1(2H)-one (4a). Overall yield 80% (26.9 mg). Reactions were conducted in screw cap test tube. 2-methylisoquinolin-1(2H)-one (0.1 mmol), diphenylacetylene (1.5 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol%), $AgSbF_6$ (20 mol%), AcOH (4.0 equiv) were combined in 1,4-Dioxane (0.4 mL). The reaction mixture was stirred at 100 ^oC for 2 h. $AgSbF_6$ (20 mol%) and 1,2-DCE (2.0 mL) were added to the reaction mixture. After 1 h, the reaction mixture was diluted with CH_2Cl_2 and 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 (*n*-Hexane : EtOAc = 2 : 1) to give the desired product **(4a)** as white solid.

(Z)-*N*-(2-(1,2-diphenylvinyl)-4,5-dimethoxyphenyl)acetamide (4f). Overall yield 76% (28.3 mg). Reactions were conducted in screw cap test tube. N-(3,4-dimethoxyphenyl)acetamide (0.1 mmol), diphenylacetylene (1.2 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (5 mol%), $AgSbF_6$ (20 mol%), PivOH (5.0 equiv) were combined in *i*PrOH (0.2 mL). The reaction mixture was stirred at 100 ^oC for 6 h. $AgSbF_6$ (20 mol%) and 1,2-DCE (2.0 mL) were added to the reaction mixture. After 12 h, the reaction mixture was diluted with CH_2Cl_2 and 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 (*n*-Hexane : EtOAc = 1 : 1) to give the desired product **(4f)** as pale brown solid.

(Z)-1-(3-(1,2-diphenylvinyl)-7-methoxybenzofuran-2-yl)ethanone (4n). Overall yield 78% (28.6 mg). Reactions were conducted in screw cap test tube. 1-(7-methoxybenzofuran-2-yl)ethanone (0.1 mmol), diphenylacetylene (2.0 equiv), $RuH_2(CO)(PPh_3)_3$ (10 mol%) were combined in toluene (0.2 mL). The reaction mixture was stirred at 135 ^oC for 30 min. $AgSbF_6$ (20 mol%), AcOH (2.0 equiv) and 1,2-DCE (2.0 mL) were added to the reaction mixture. After 2 h, the reaction mixture was diluted with CH_2Cl_2 and 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 (*n*-Hexane : EtOAc = 6 : 1) to give the desired product **(4n)** as white solid.

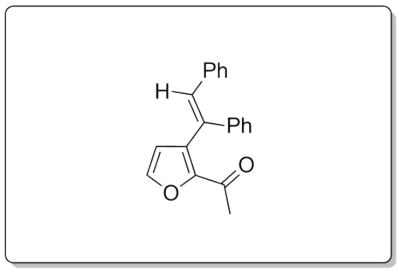
3. Preparation of Starting Materials

Starting materials (4a[1], 4b[1], 4c[2], 4d[3], 4e[3], 4f[3], 4g[3], 4h[3], 4i[4], 4j[5], 4k[5], 4l[6]) were prepared by the reported method.

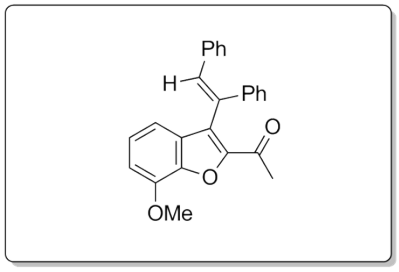
General Procedure for the Preparation of *E*-Alkenyl Arenes (4m – 4r)[7]

Reactions were conducted in screw cap test tube. Substrate (2 mmol), diphenylacetylene (4 mmol), $RuH_2(CO)(PPh_3)_3$ (6 mol%) were combined in toluene (4 mL). The reaction mixture was stirred at 135 °C for 1 h. Toluene was removed under the reduced pressure and the residue was purified by flash chromatography on silica gel to give desired product.

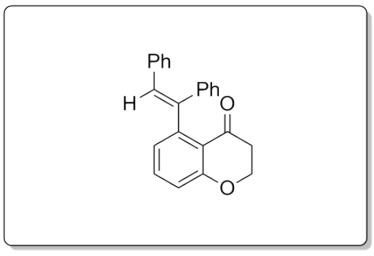
Compound Characterizations:



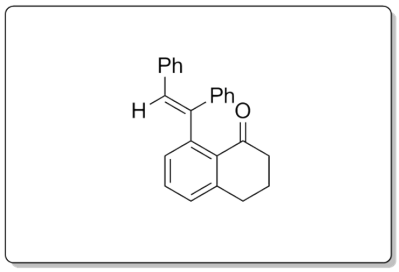
(E)-1-(3-(1,2-diphenylvinyl)furan-2-yl)ethanone. Pale yellow solid. mp 103 – 105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 1.7 Hz, 1H), 7.33 – 7.25 (m, 5H), 7.21 – 7.11 (m, 6H), 6.36 (d, *J* = 1.7 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 148.0, 144.2, 139.2, 136.4, 136.0, 132.9, 132.5, 129.7, 129.6, 128.4, 127.9, 127.5, 127.3, 115.2, 27.7. HRMS (ESI+) m/z calcd. for $[C_{20}H_{16}NaO_2]^+$: 311.1043, found : 311.1021.



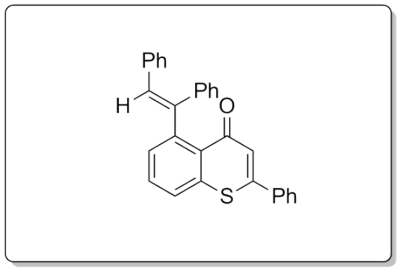
(E)-1-(3-(1,2-diphenylvinyl)-7-methoxybenzofuran-2-yl)ethanone. Yellow solid. mp 121 – 123 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.31 – 7.22 (m, 8H), 7.19 – 7.12 (m, 1H), 7.05 (dd, *J* = 7.8, 1.0 Hz, 1H), 6.98 (s, 1H), 6.96 (dd, *J* = 7.8, 1.0 Hz, 1H), 4.07 (s, 3H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.0, 148.2, 145.8, 143.7, 138.6, 136.3, 133.3, 131.6, 130.3, 130.0, 129.7, 129.5, 128.2, 128.0, 127.6, 127.4, 124.3, 114.3, 109.3, 56.0, 28.1. HRMS (ESI+) m/z calcd. for $[C_{25}H_{20}NaO_3]^+$: 391.1305, found : 391.1290.



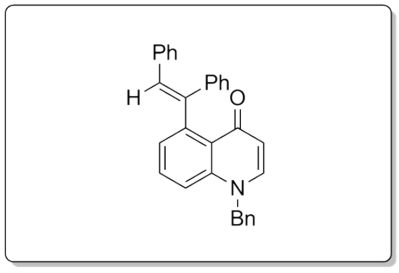
(E)-5-(1,2-diphenylvinyl)chroman-4-one. Dark brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.4, 7.4 Hz, 1H), 7.33 – 7.16 (m, 10H), 7.09 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.04 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.62 (s, 1H), 4.47 (t, *J* = 6.4 Hz, 2H), 2.70 (t, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 162.8, 146.3, 143.3, 139.4, 137.4, 134.3, 130.1, 129.3, 127.8, 127.5, 127.4, 126.8, 126.5, 125.0, 119.5, 117.5, 66.5, 38.5. HRMS (ESI+) m/z calcd. for $[C_{23}H_{18}NaO_2]^+$: 349.1199, found : 349.1199.



(E)-8-(1,2-diphenylvinyl)-3,4-dihydronaphthalen-1(2H)-one. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, *J* = 7.6 Hz, 1H), 7.33 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.29 – 7.07 (m, 11H), 6.56 (s, 1H), 2.98 (t, *J* = 6.1 Hz, 2H), 2.51 (t, *J* = 6.7 Hz, 2H), 2.08 (q, *J* = 6.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 145.9, 145.5, 144.2, 139.9, 137.7, 131.8, 131.7, 130.5, 130.3, 129.3, 128.2, 127.8, 127.5, 127.1, 126.8, 126.4, 39.9, 30.5, 22.9. HRMS (ESI+) m/z calcd. for $[C_{24}H_{20}NaO]^+$: 347.1406, found : 347.1424.



(E)-5-(1,2-diphenylvinyl)-2-phenyl-4H-thiochromen-4-one. Pale brown solid. mp 124 – 126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.58 (m, 4H), 7.58 – 7.44 (m, 4H), 7.34 – 7.27 (m, 2H), 7.25 – 7.14 (m, 8H), 7.06 (s, 1H), 6.58 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 149.9, 147.0, 144.5, 139.7, 139.2, 137.7, 136.1, 131.7, 130.6, 130.4, 130.3, 129.4, 129.2, 129.2, 127.9, 127.5, 126.8, 126.8, 126.7, 126.5, 126.2, 124.4. HRMS (ESI+) m/z calcd. for $[C_{29}H_{20}NaOS]^+$: 439.1127, found : 439.1128.



(E)-1-benzyl-5-(1,2-diphenylvinyl)quinolin-4(1H)-one. Pale yellow solid. mp 113 – 115 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 1H), 7.44 – 7.26 (m, 8H), 7.24 – 7.09 (m, 10H), 6.55 (s, 1H), 6.12 (d, *J* = 7.7 Hz, 1H), 5.21 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 145.3, 144.8, 142.4, 141.4, 140.0, 137.8, 135.2, 130.8, 130.2, 129.3, 129.0, 128.0, 127.6, 127.3, 127.0, 126.4, 126.1, 126.1, 125.8, 125.1, 115.7, 111.6, 56.6. HRMS (ESI+) m/z calcd. for $[C_{30}H_{23}NNaO]^+$: 436.1672, found : 436.1668.

Reference

(1) P. Zhao, R. Niu, F. Wang, K. Han, X. Li, *Org. Lett.* **2012**, *14*, 4166.

(2) M. C. Reddy, M. Jeganmohan, *Chem. Commun.* **2013**, *49*, 481.

(3) R. Manikandan, M. Jeganmohan, *Org. Lett.* **2014**, *16*, 912.

(4) D. Zhao, C. Nimphius, M. Lindale, F. Glorius, *Org. Lett*. **2013**, *15*, 4504.

(5) M. Itoh, Y. Hashimoto, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2013**, *78*, 8098.

(6) K. Nobushige, K. Hirano, T. Satoh, M. Miura, *Org. Lett*. **2014**, *16*, 1188.

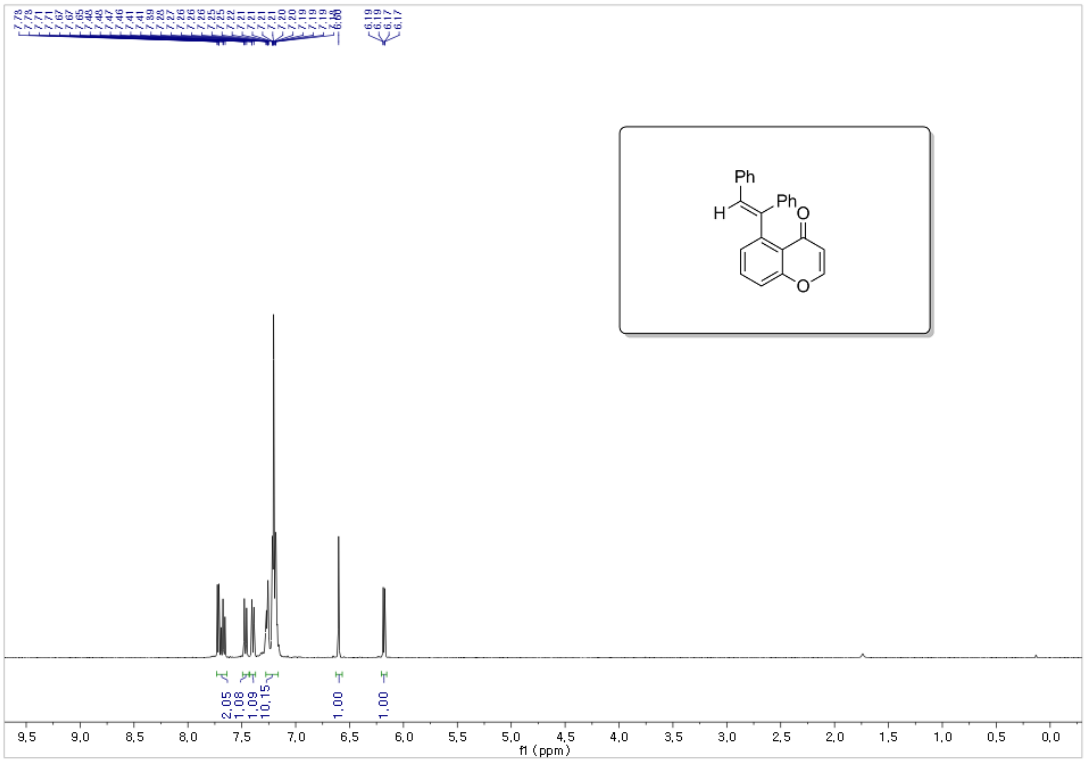
(7) F. Kakiuchi, Y. Yamamoto, N. Chatani, S. Murai, *Chem. Lett*. **1995**, 681.

Appendix I

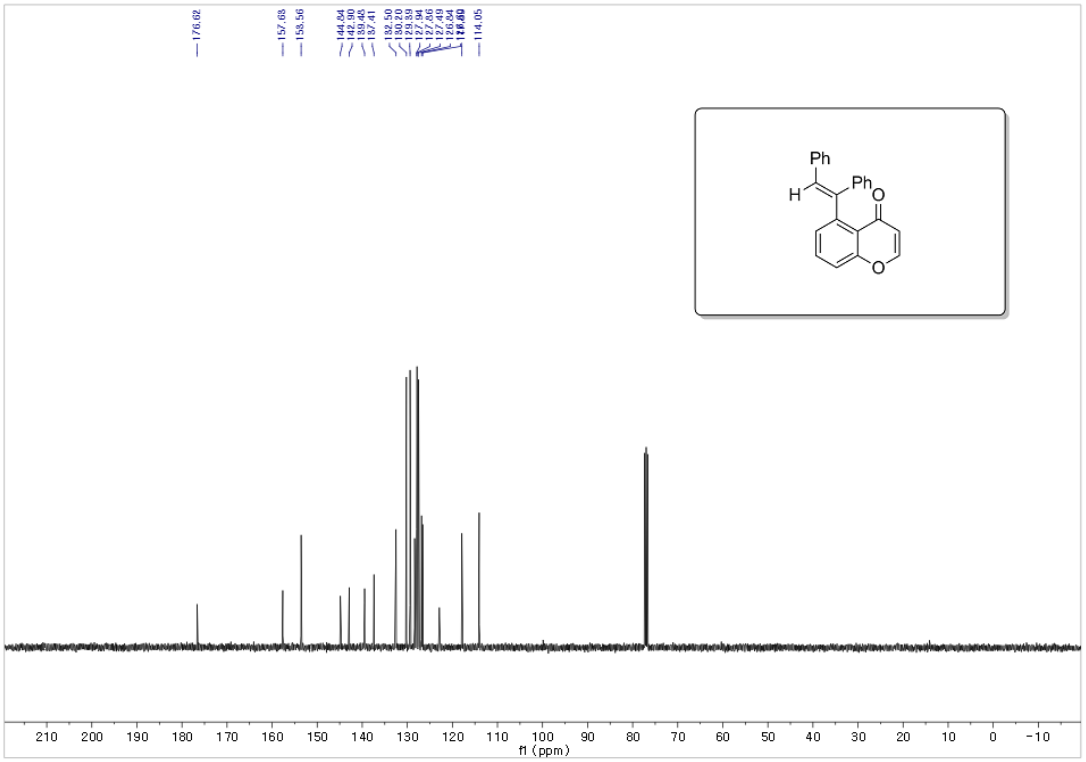
Spectral Copies of ^{1}H and ^{13}C NMR Data

Obtained in this Study

(E)-5-(1,2-diphenylvinyl)-4H-chromen-4-one (2a).

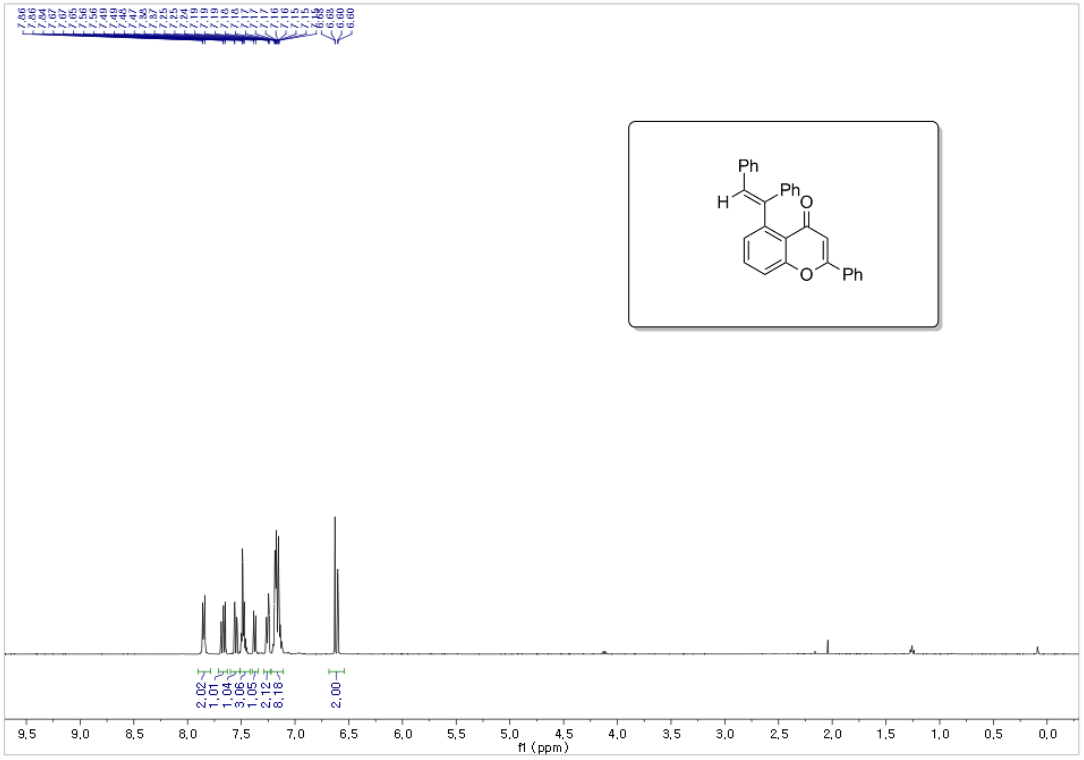


400 MHz, ^{1}H NMR in $CDCl_3$

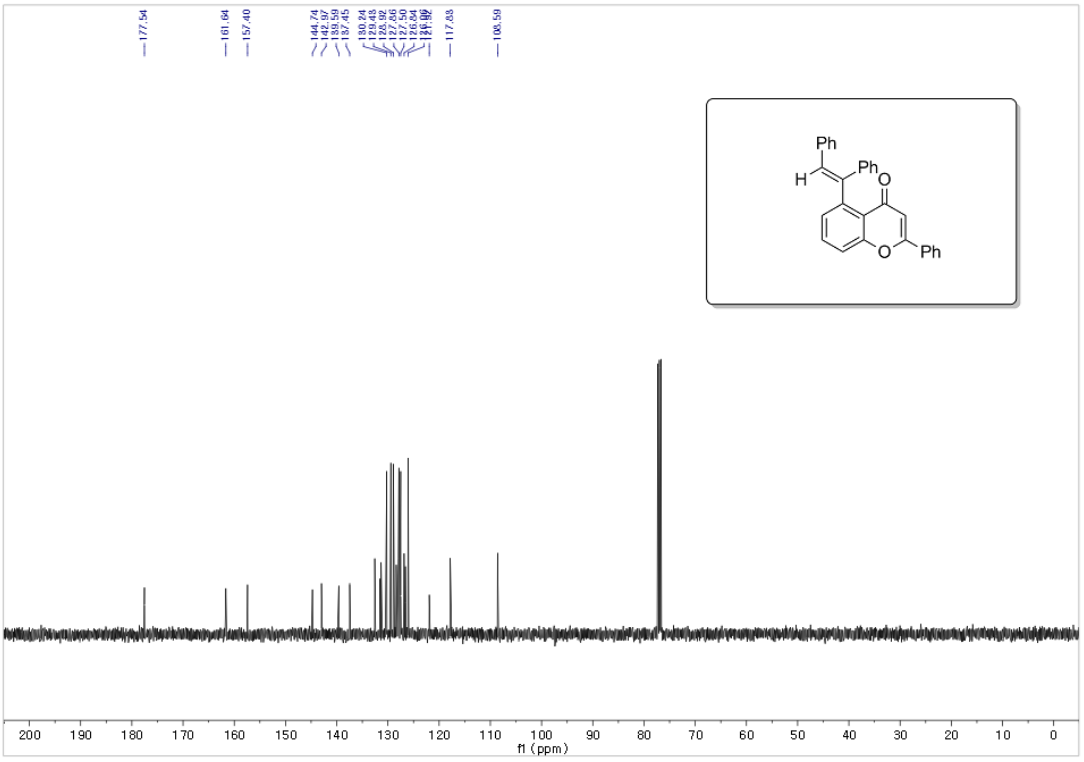


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-5-(1,2-diphenylvinyl)-2-phenyl-4H-chromen-4-one (2b).

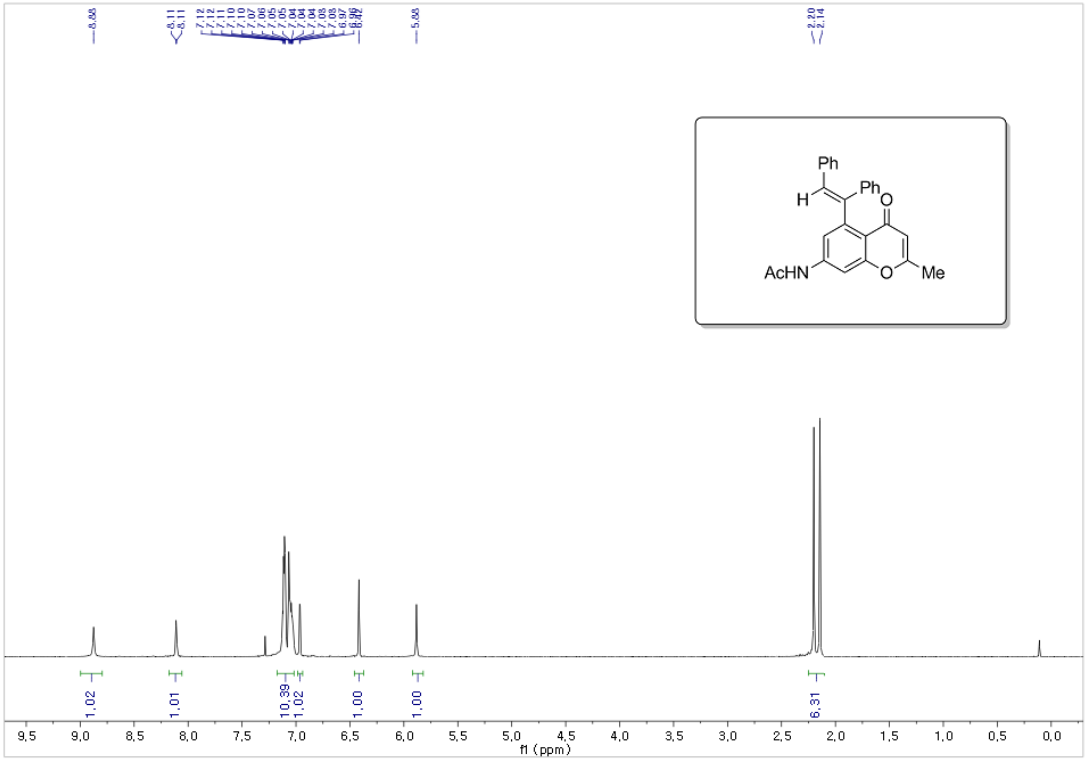


400 MHz, ^{1}H NMR in $CDCl_3$

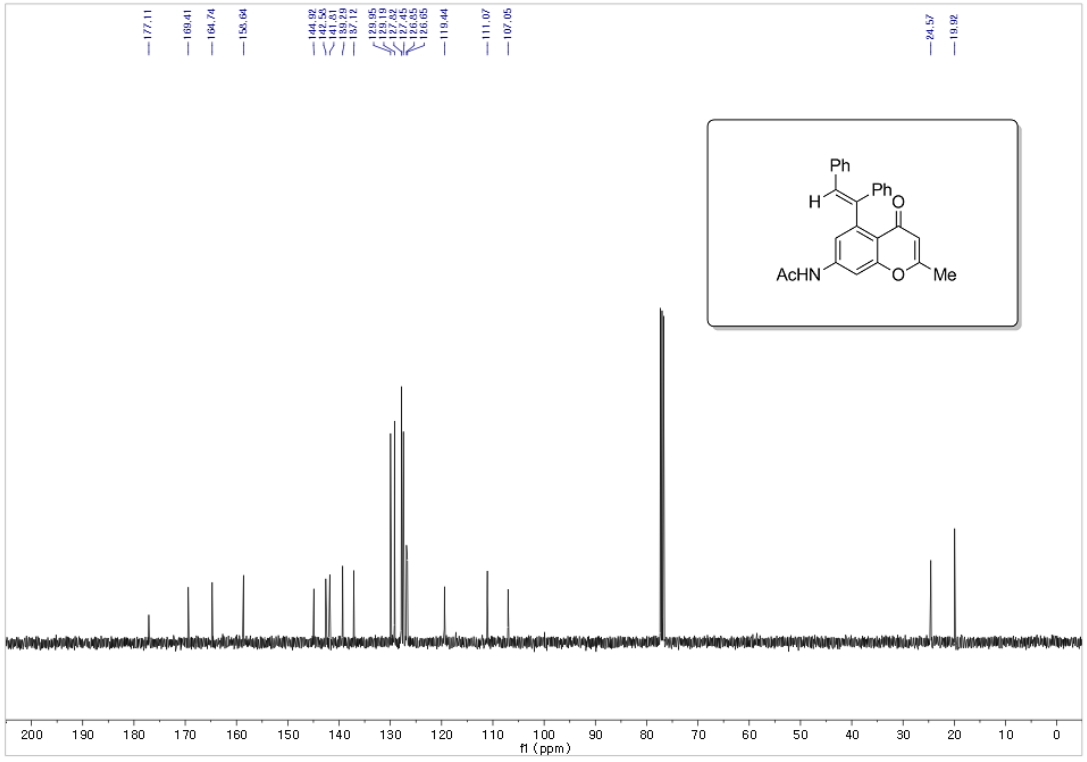


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-N-(5-(1,2-diphenylvinyl)-2-methyl-4-oxo-4H-chromen-7-yl)acetamide (2c).

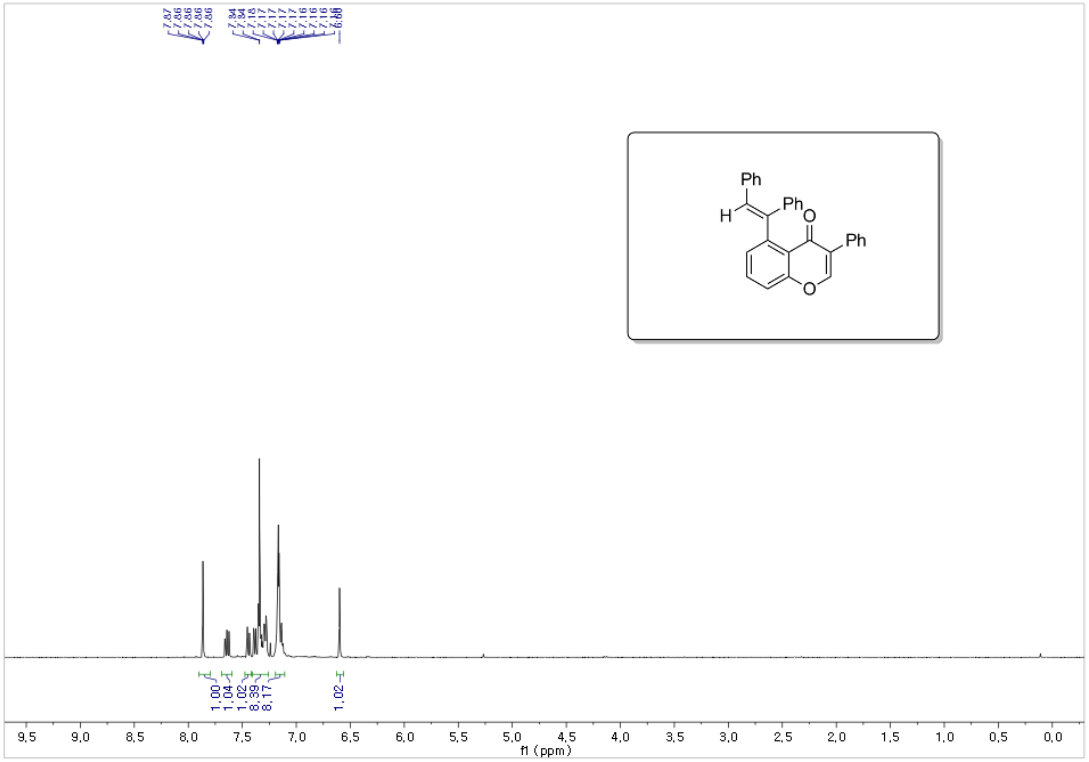


400 MHz, ^{1}H NMR in $CDCl_3$

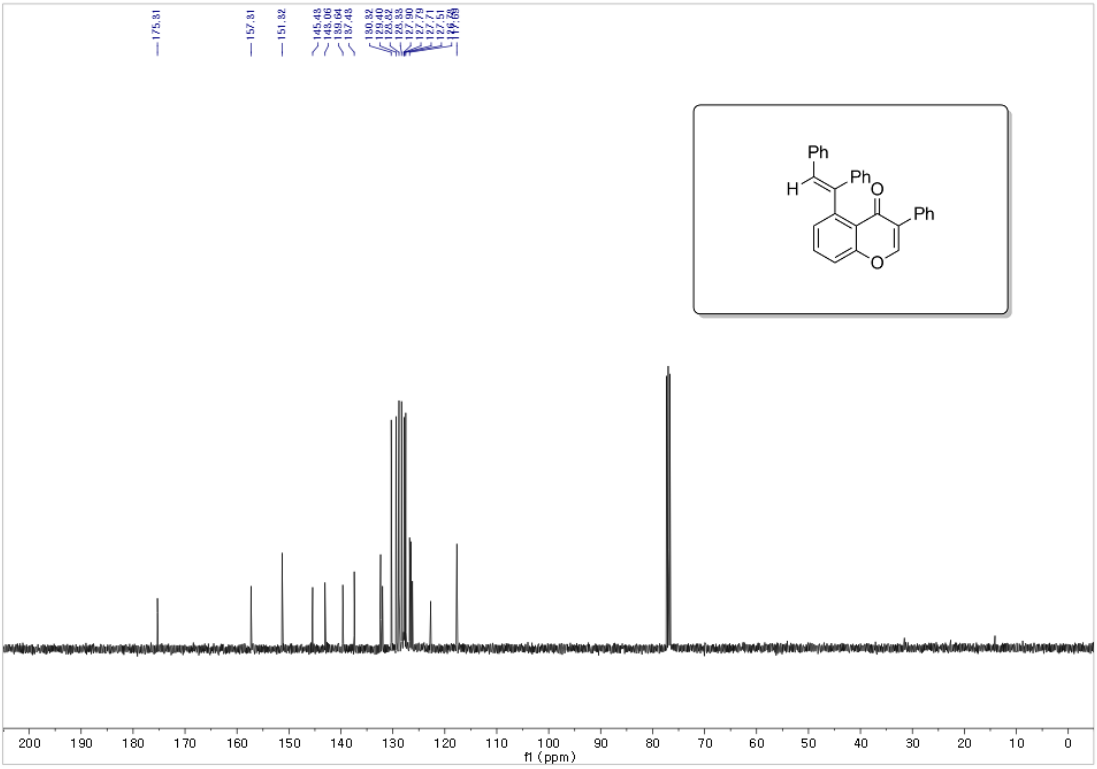


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-5-(1,2-diphenylvinyl)-3-phenyl-4H-chromen-4-one (2d).

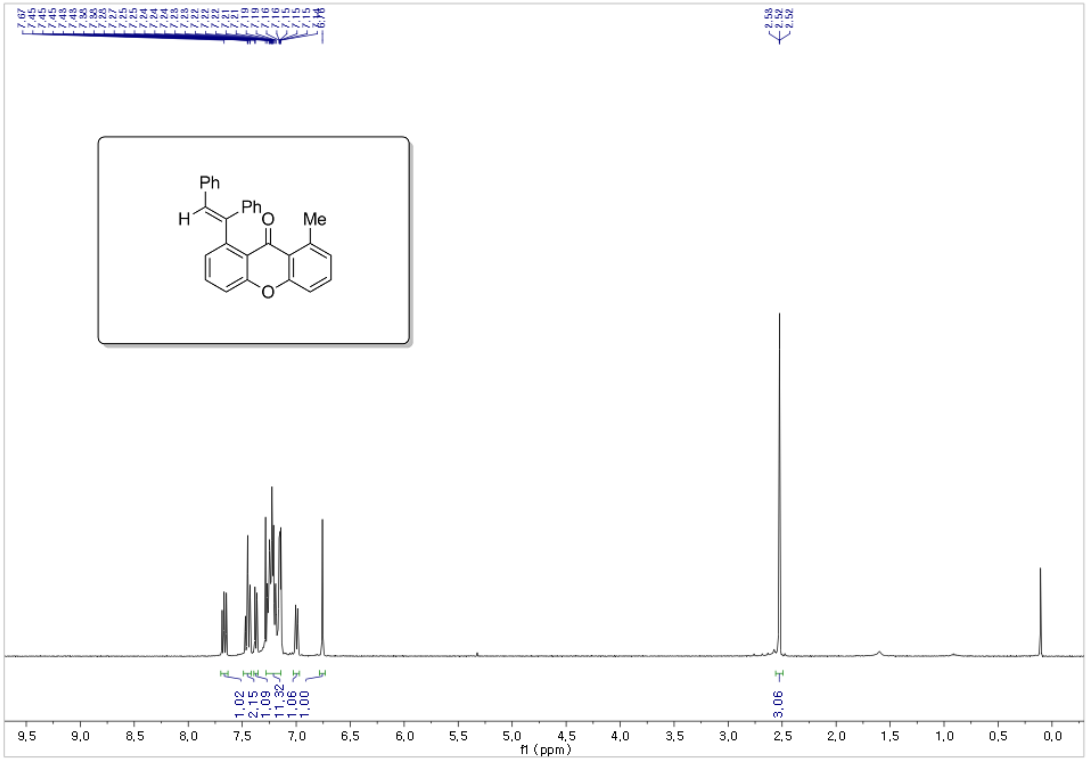


400 MHz, ^{1}H NMR in $CDCl_3$

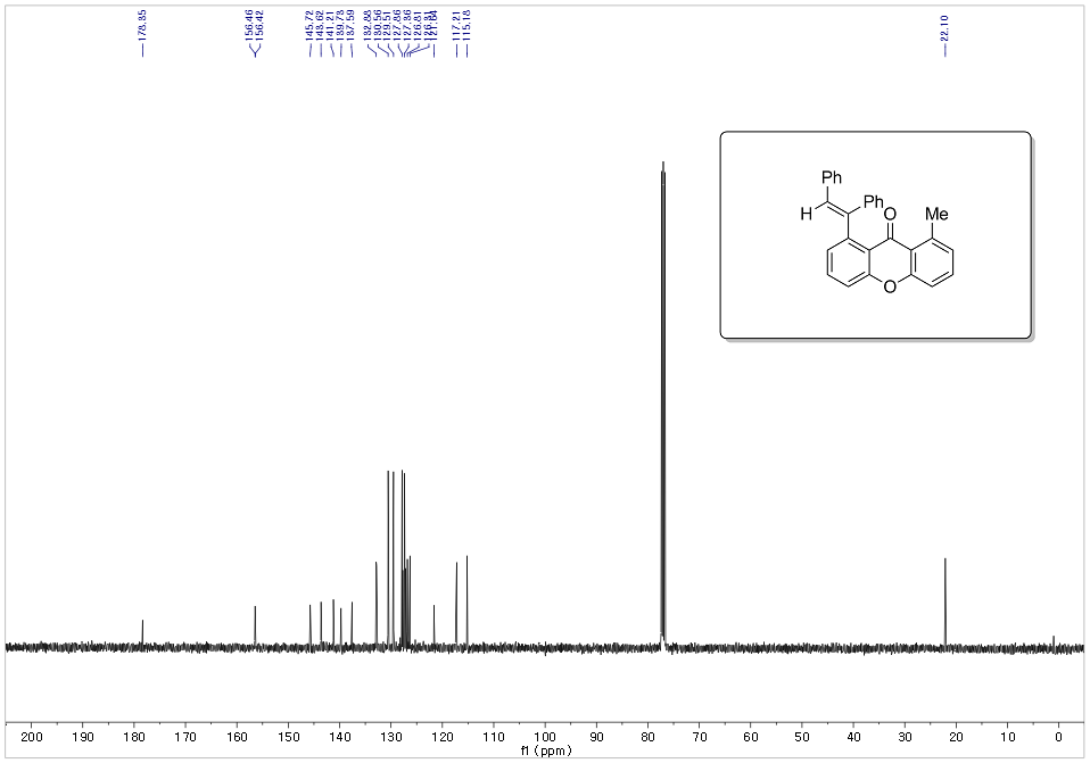


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-1-(1,2-diphenylvinyl)-8-methyl-9H-xanthen-9-one (2e).

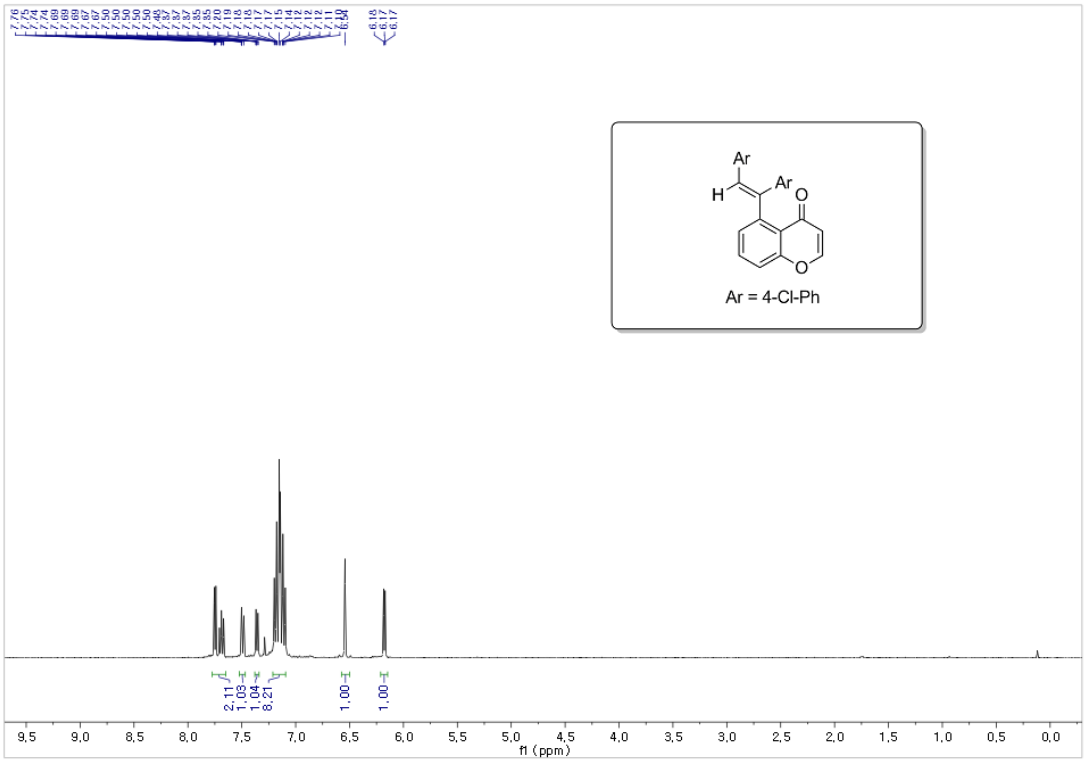


400 MHz, ^{1}H NMR in $CDCl_3$

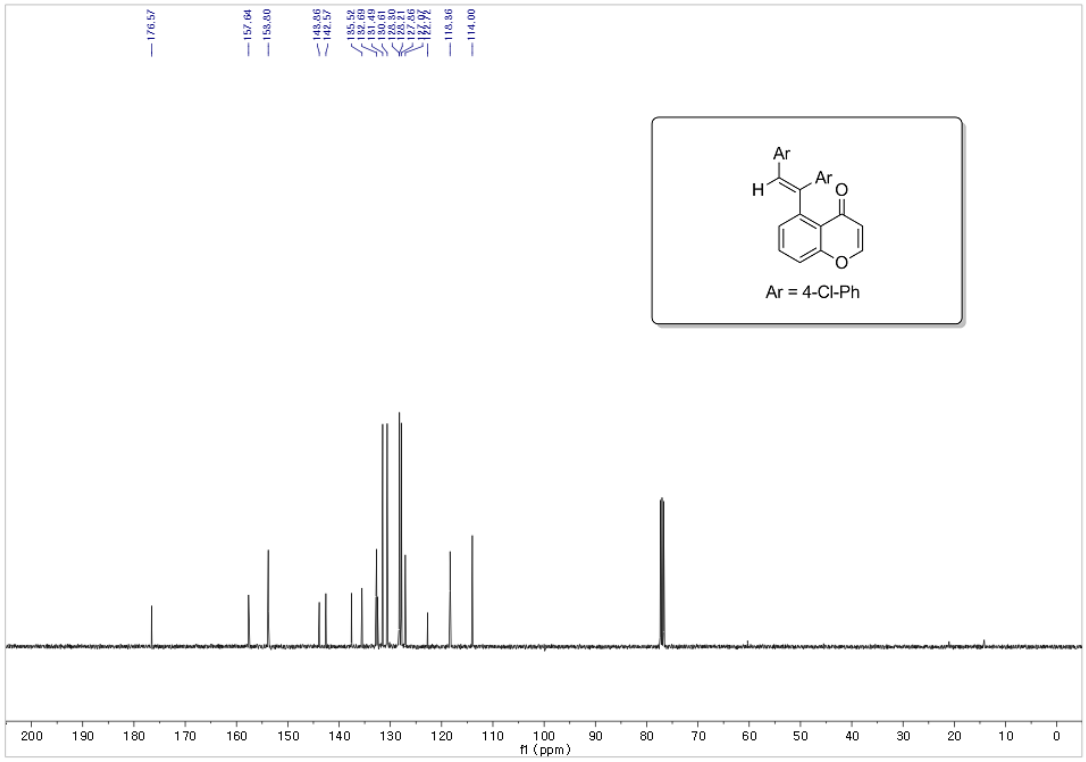


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-5-(1,2-bis(4-chlorophenyl)vinyl)-4H-chromen-4-one (2f).

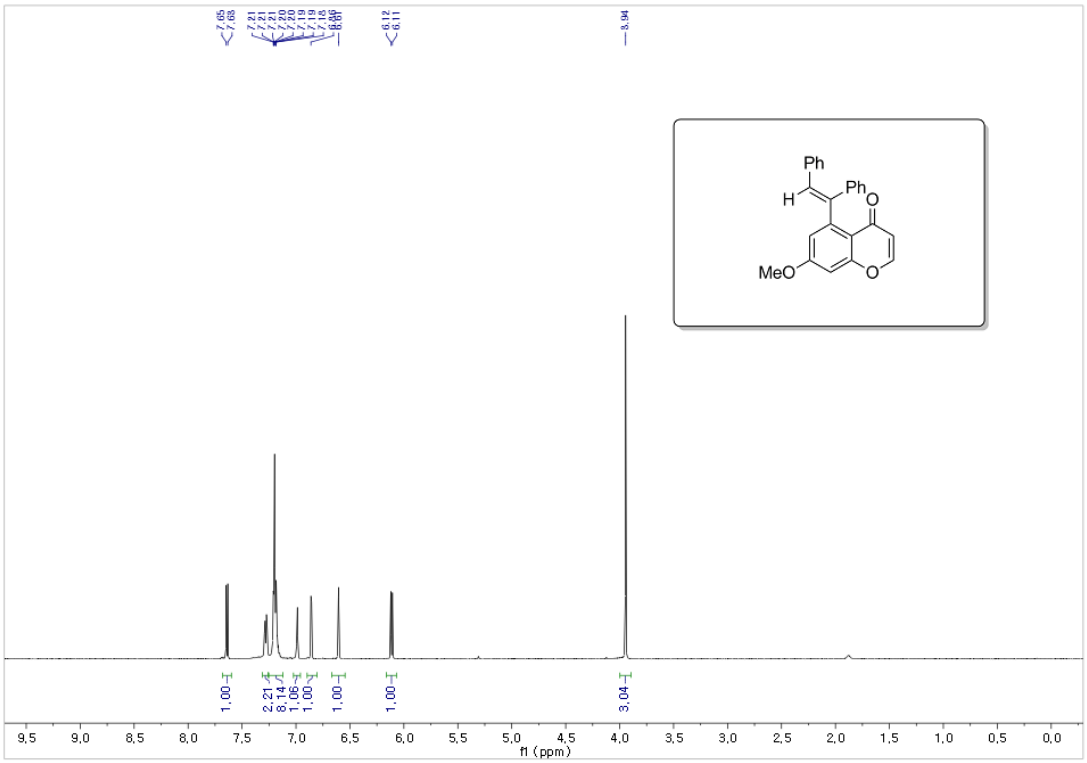


400 MHz, ^{1}H NMR in $CDCl_3$

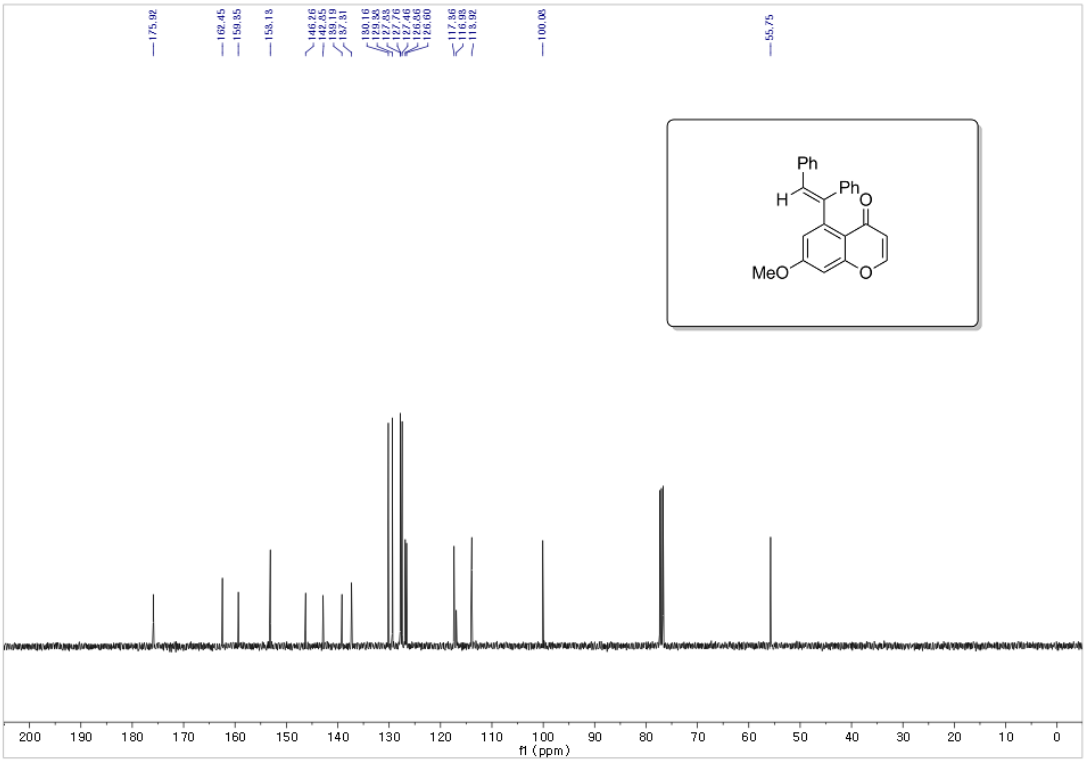


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-5-(1,2-diphenylvinyl)-7-methoxy-4H-chromen-4-one (2g).

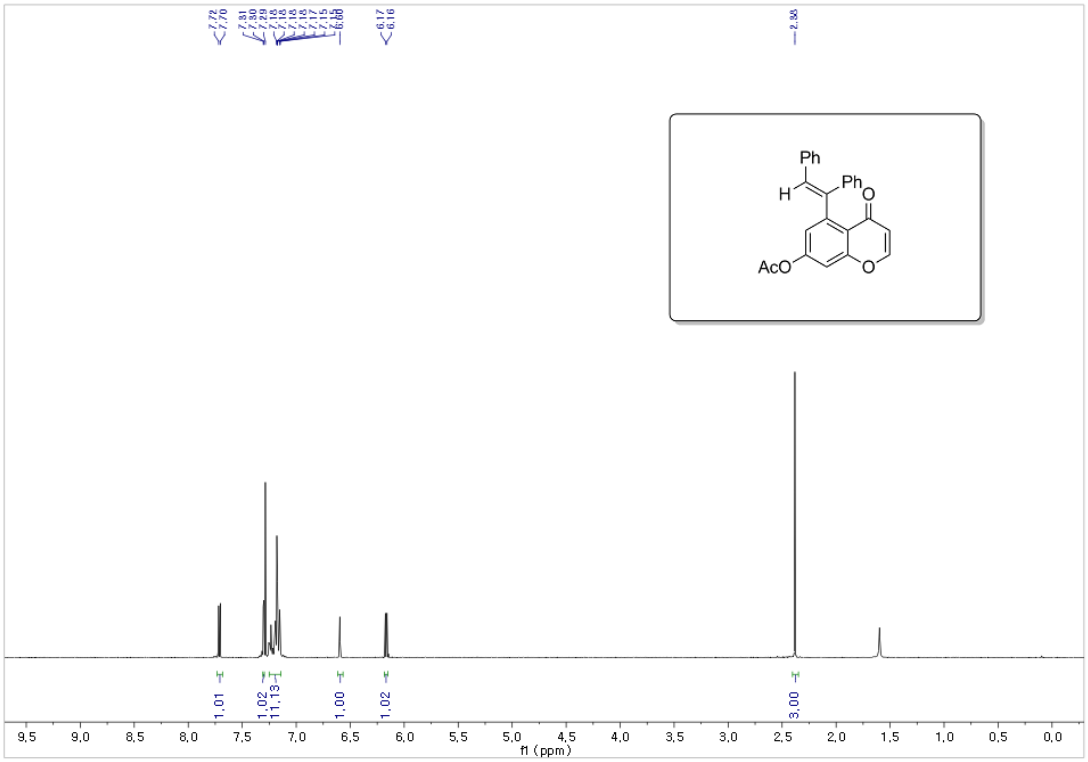


400 MHz, ^{1}H NMR in $CDCl_3$

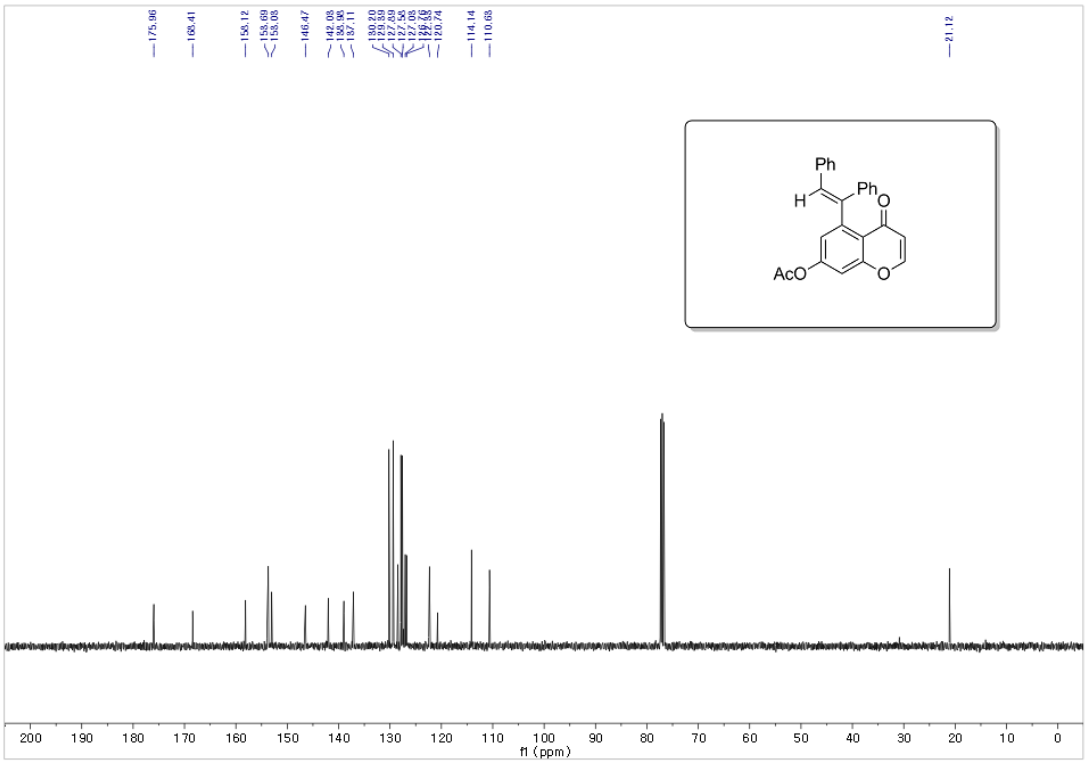


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-5-(1,2-diphenylvinyl)-4-oxo-4H-chromen-7-yl acetate (2h).

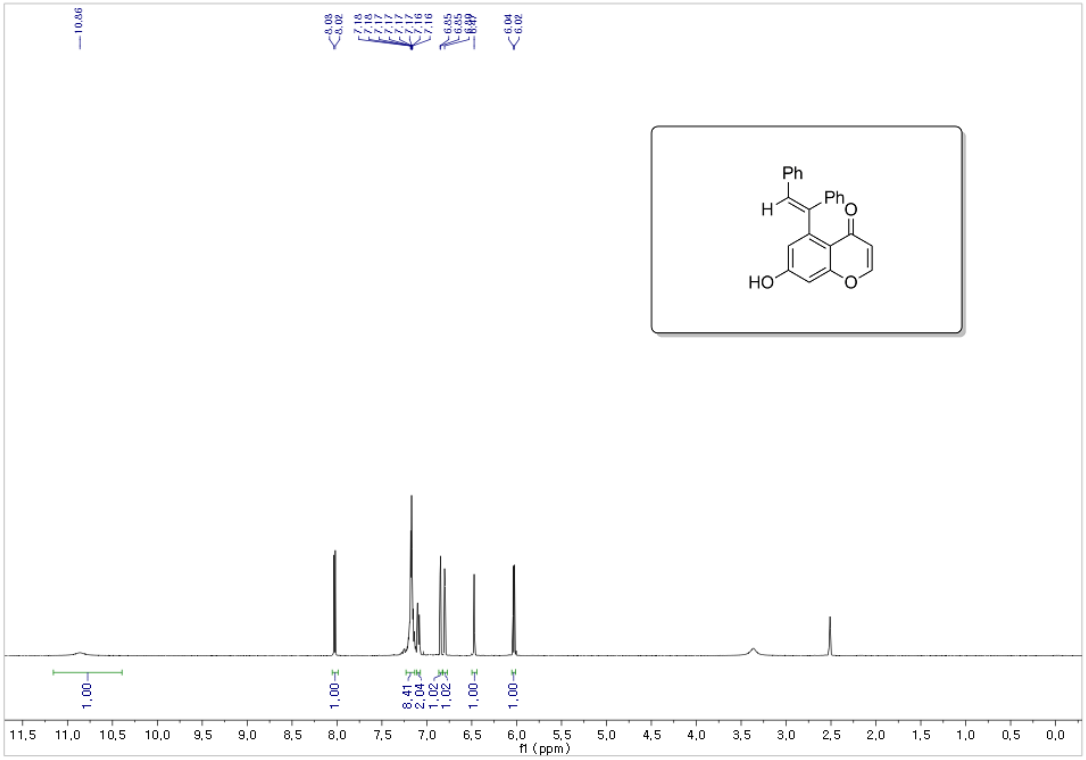


400 MHz, ^{1}H NMR in $CDCl_3$

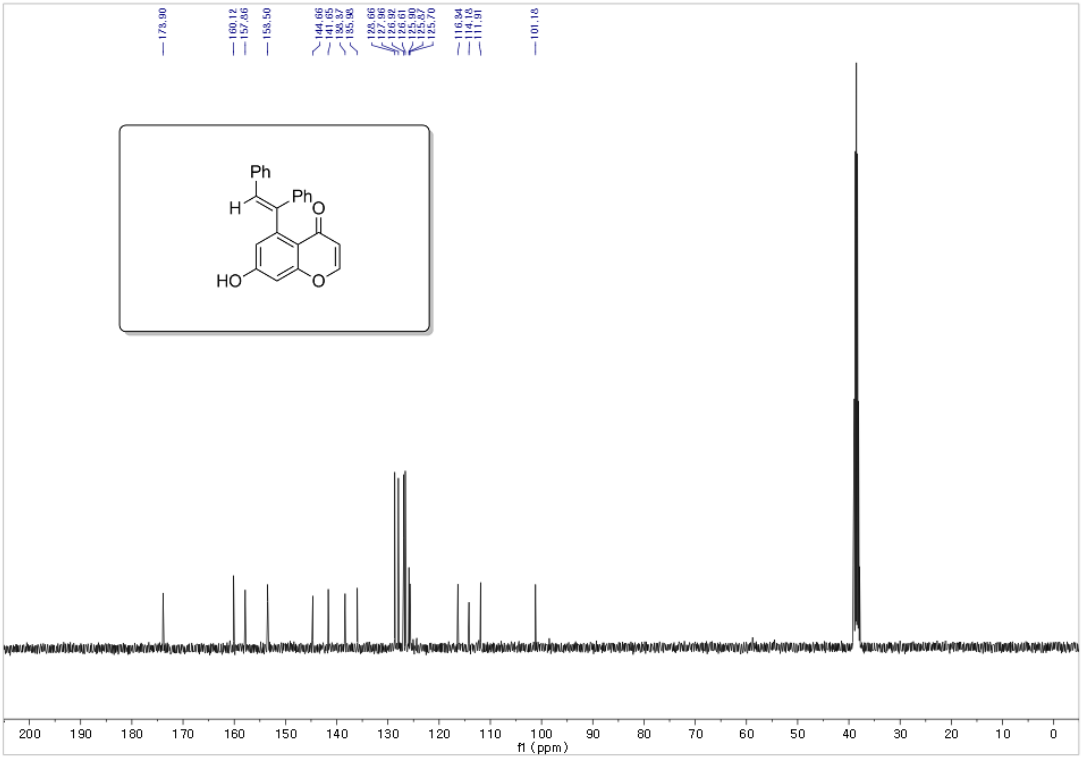


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-5-(1,2-diphenylvinyl)-7-hydroxy-4H-chromen-4-one (2i).

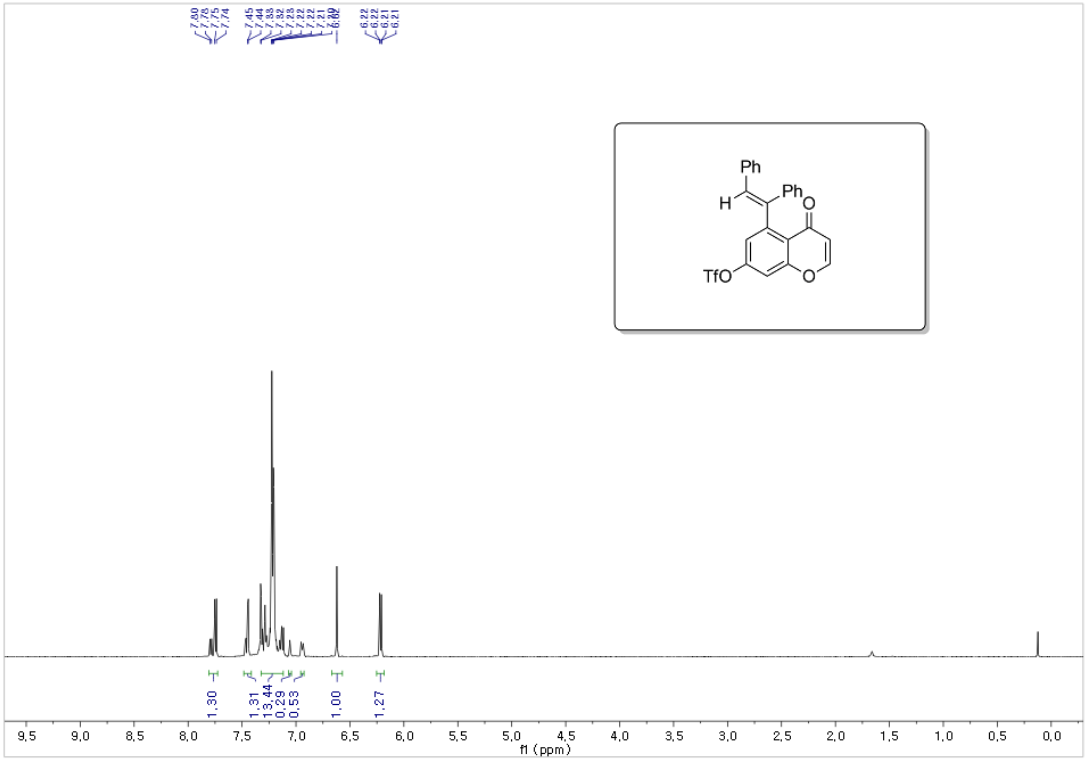


400 MHz, ^{1}H NMR in DMSO-d$_6$

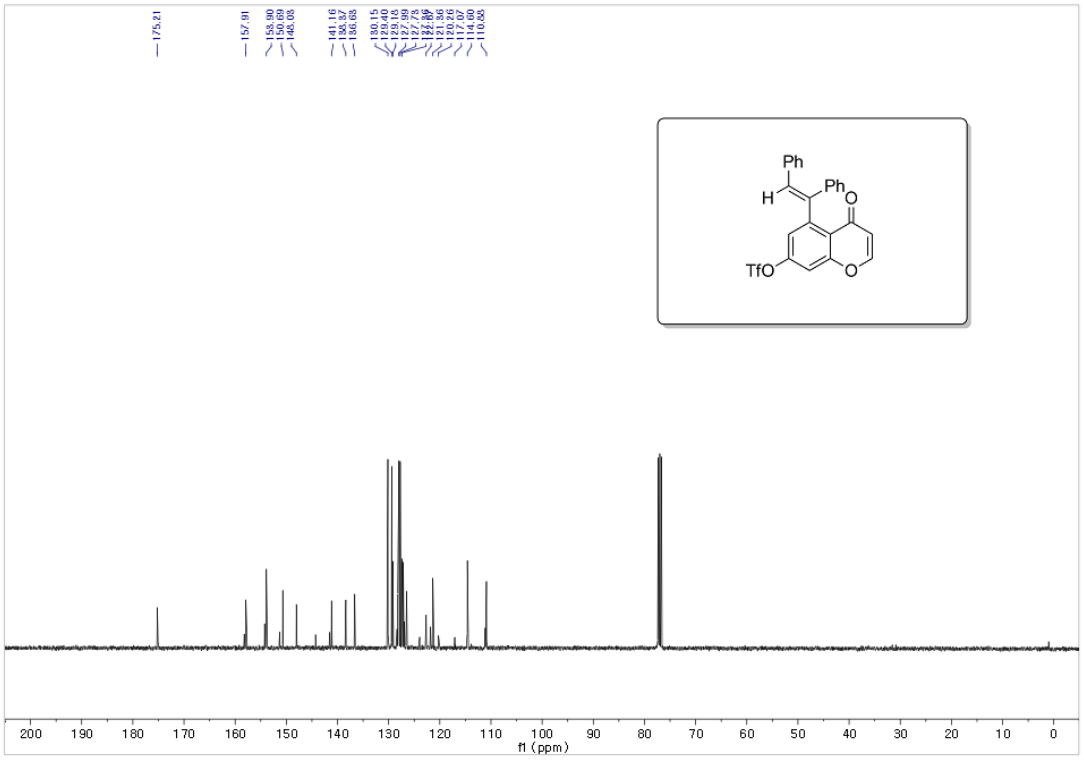


100 MHz, ^{13}C NMR in DMSO-d$_6$

(E)-5-(1,2-diphenylvinyl)-4-oxo-4H-chromen-7-yl trifluoromethanesulfonate (2j).

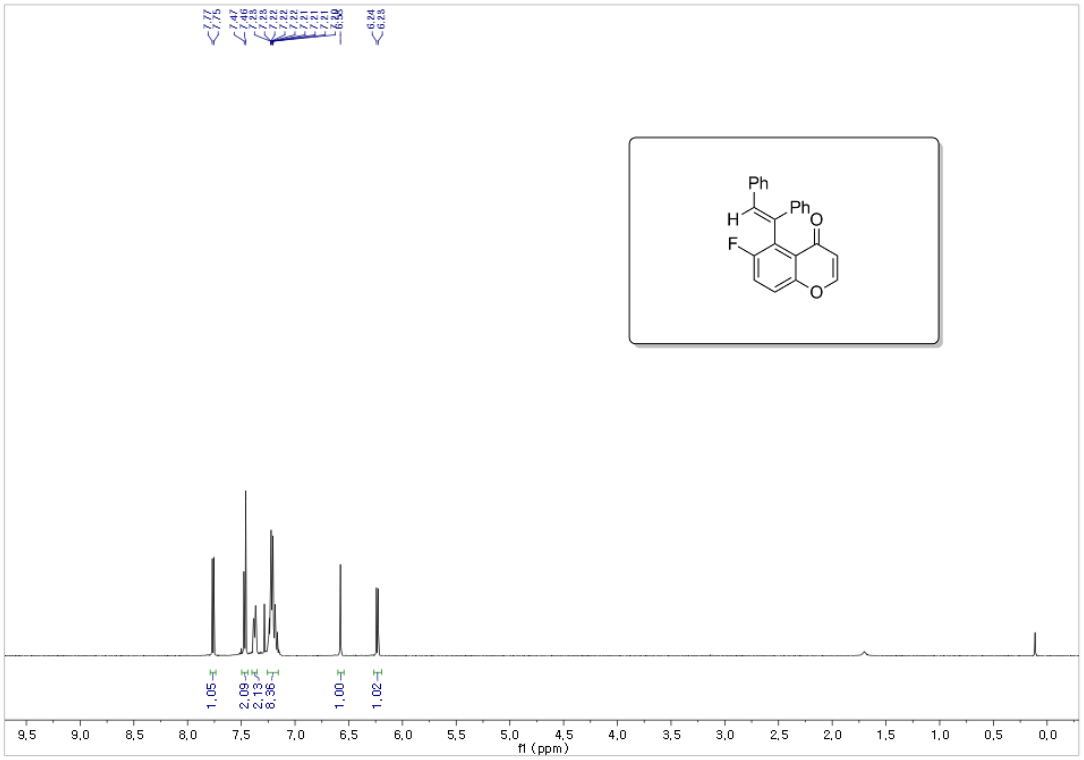


400 MHz, ^{1}H NMR in $CDCl_3$ (*E/Z* Mixture 81:19)

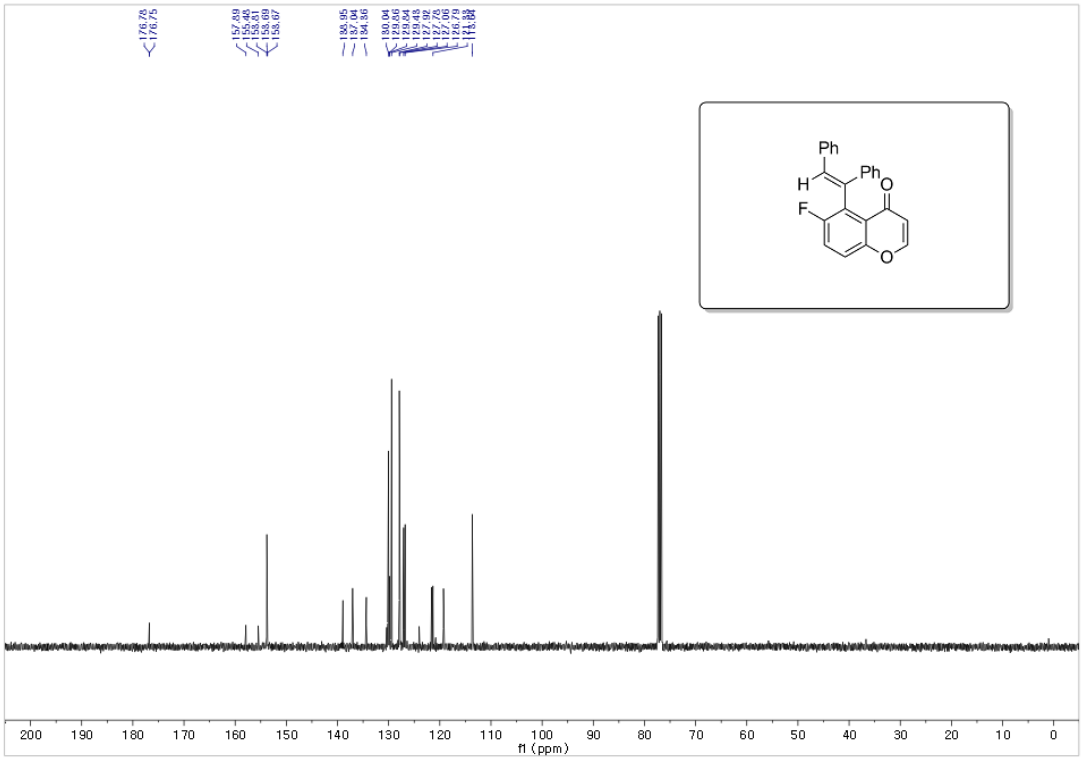


100 MHz, ^{13}C NMR in $CDCl_3$ (*E/Z* Mixture 81:19)

(E)-5-(1,2-diphenylvinyl)-6-fluoro-4H-chromen-4-one (2k).

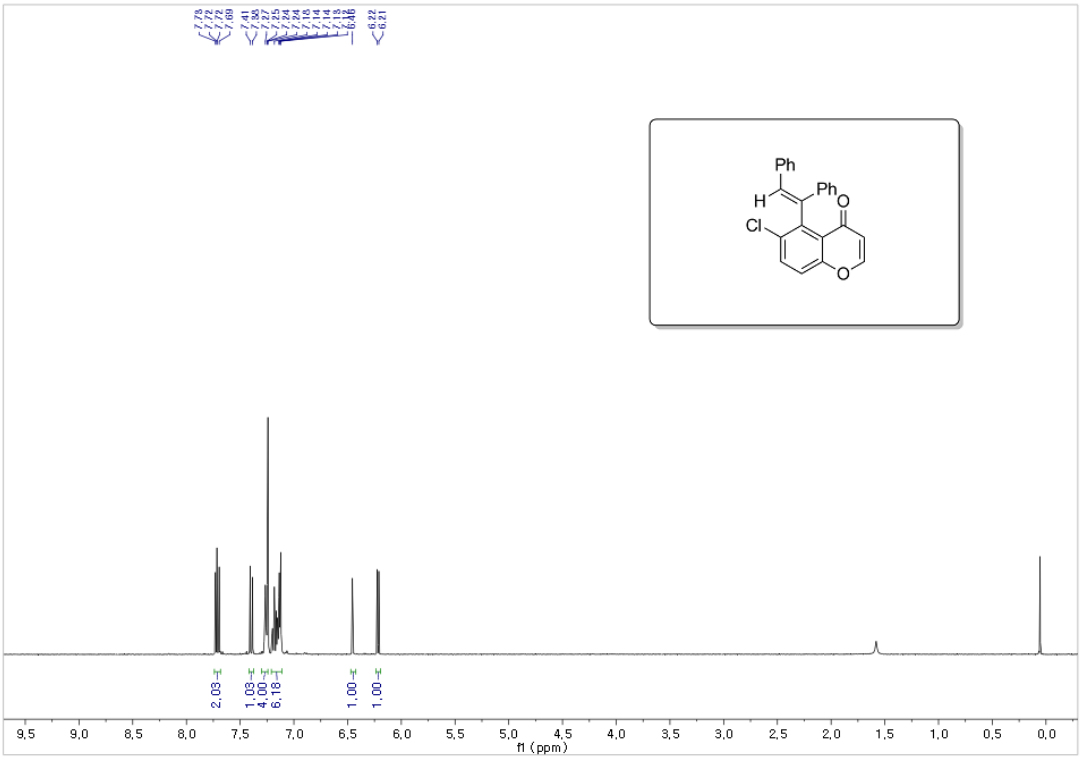


400 MHz, ^{1}H NMR in $CDCl_3$

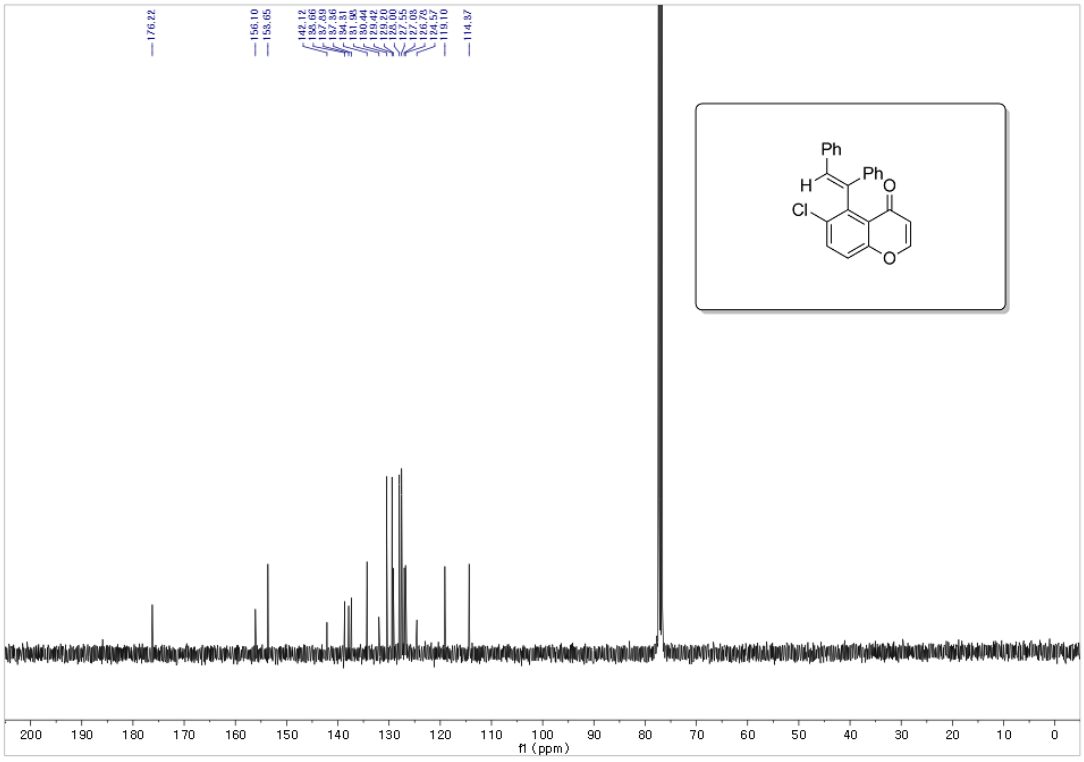


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-6-chloro-5-(1,2-diphenylvinyl)-4H-chromen-4-one (2l).

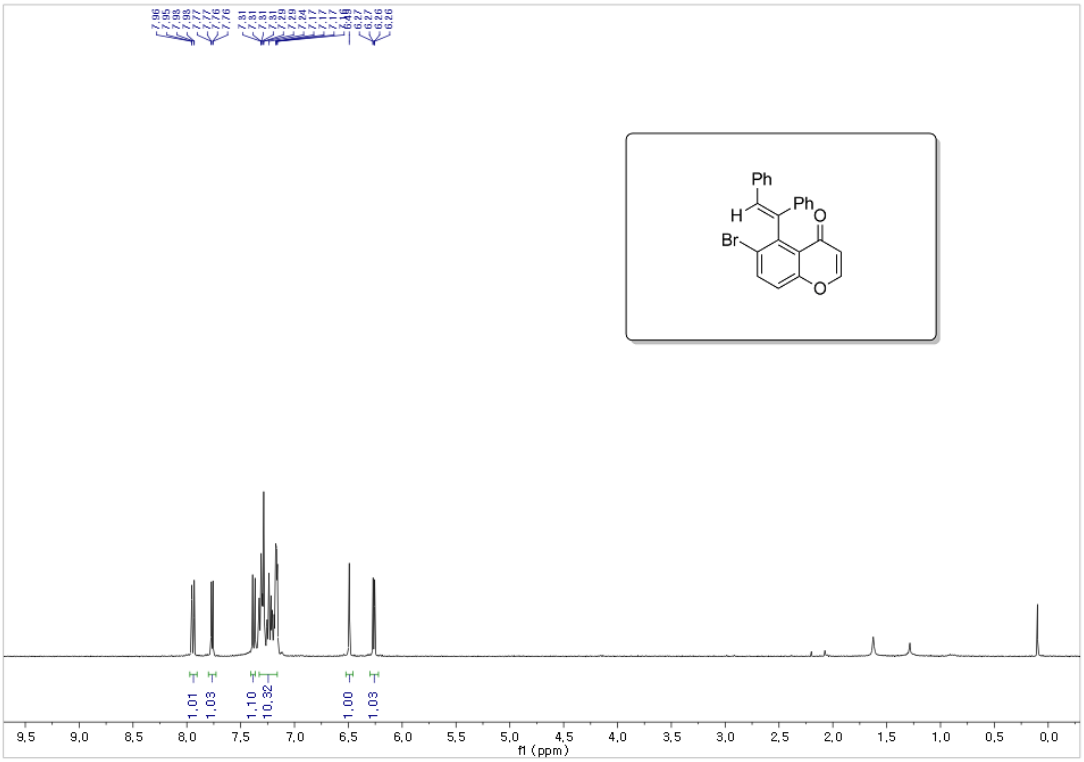


400 MHz, ^{1}H NMR in $CDCl_3$

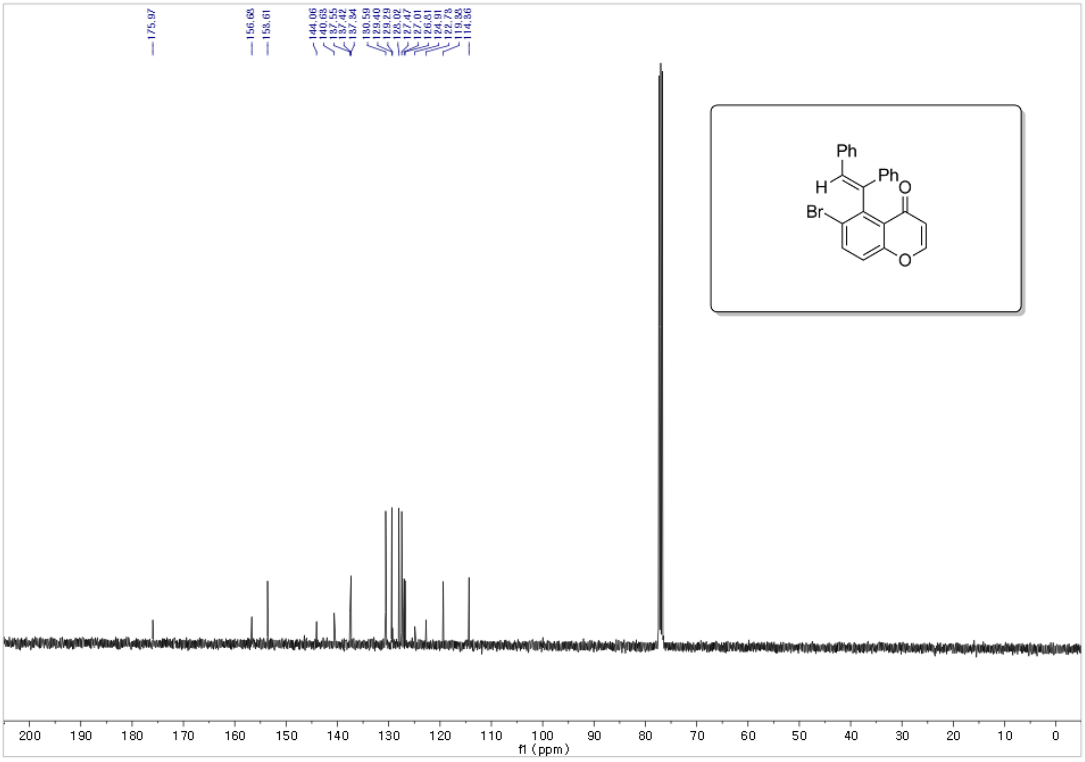


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-6-bromo-5-(1,2-diphenylvinyl)-4H-chromen-4-one (2m).

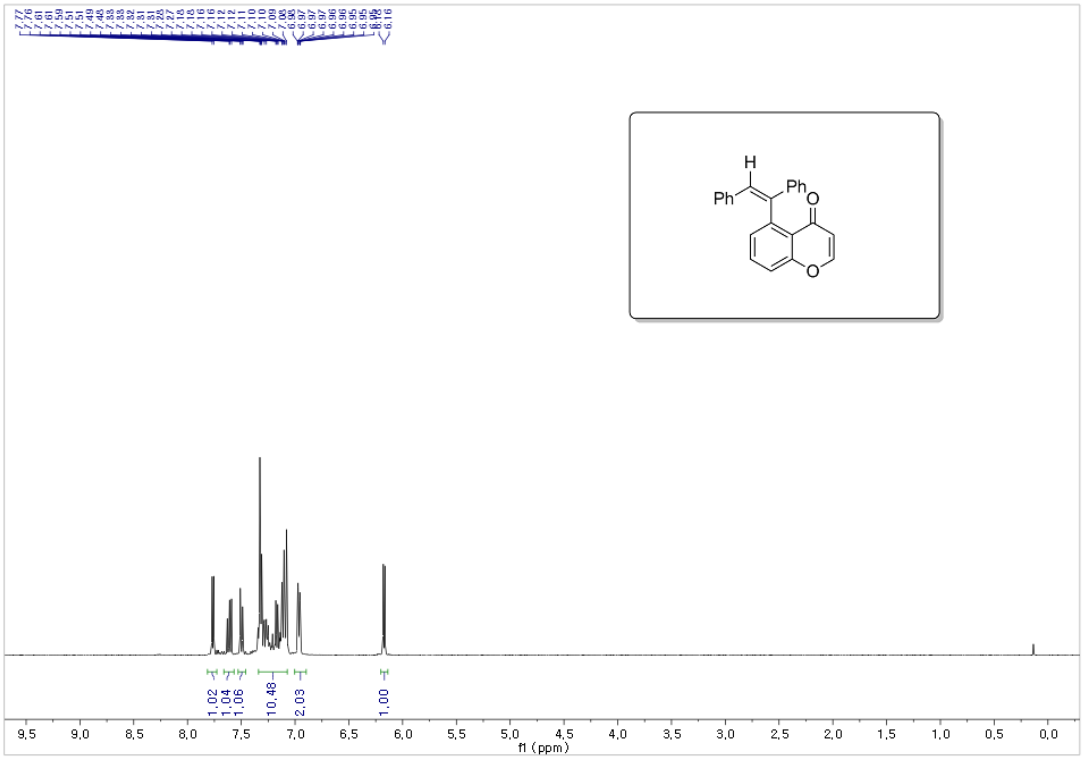


400 MHz, ^{1}H NMR in $CDCl_3$

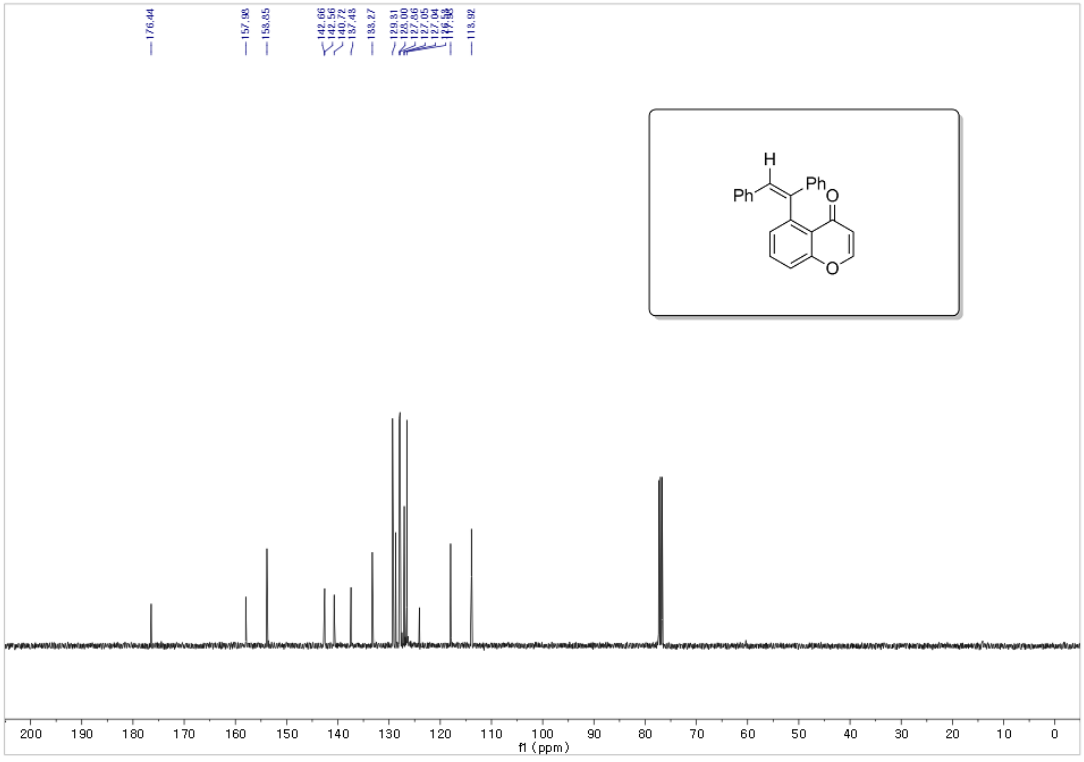


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-5-(1,2-diphenylvinyl)-4H-chromen-4-one (3a).

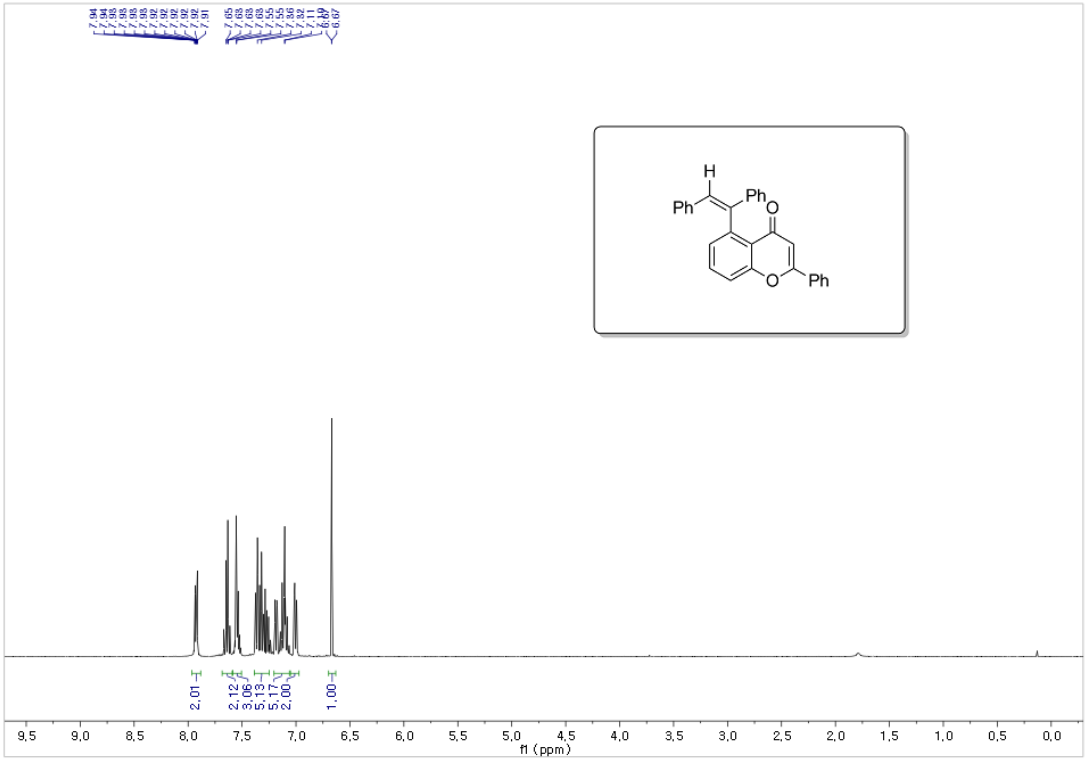


400 MHz, ^{1}H NMR in $CDCl_3$

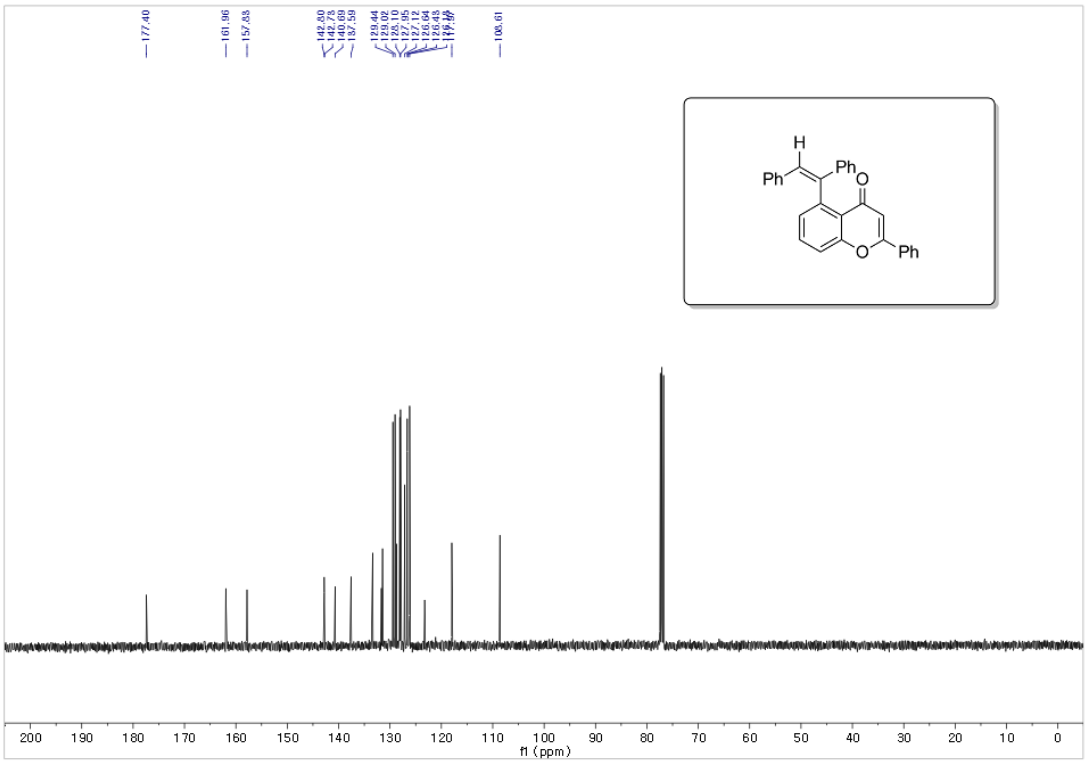


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-5-(1,2-diphenylvinyl)-2-phenyl-4H-chromen-4-one (3b).

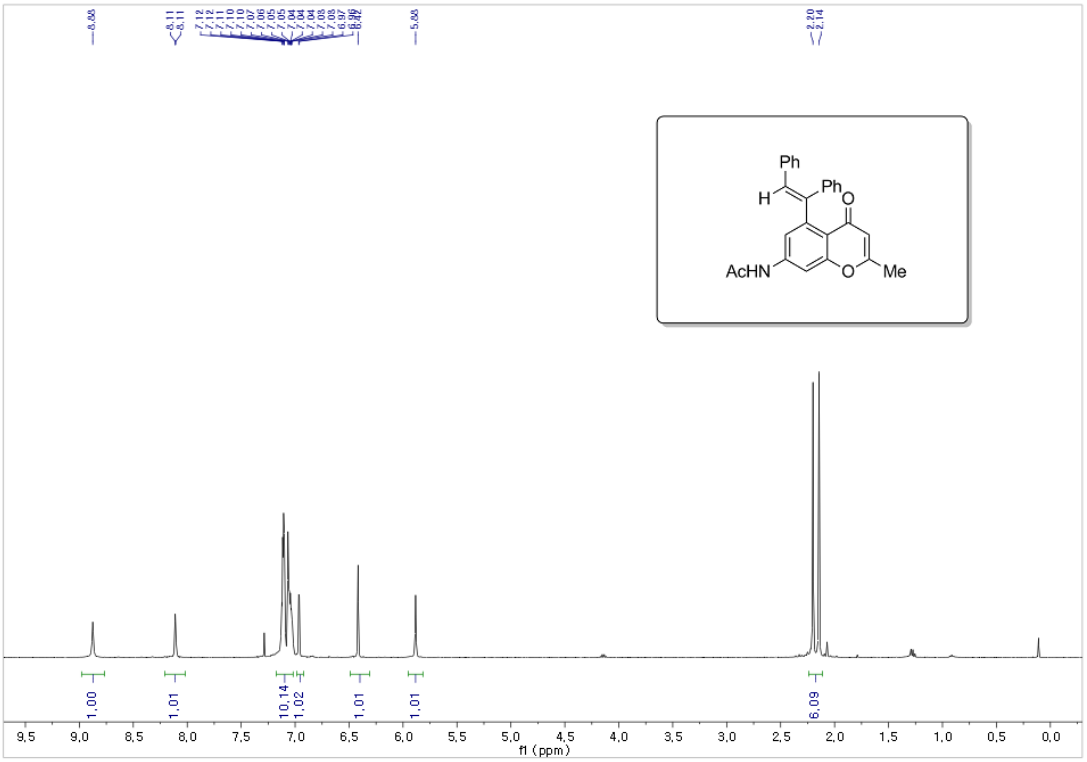


400 MHz, ^{1}H NMR in $CDCl_3$

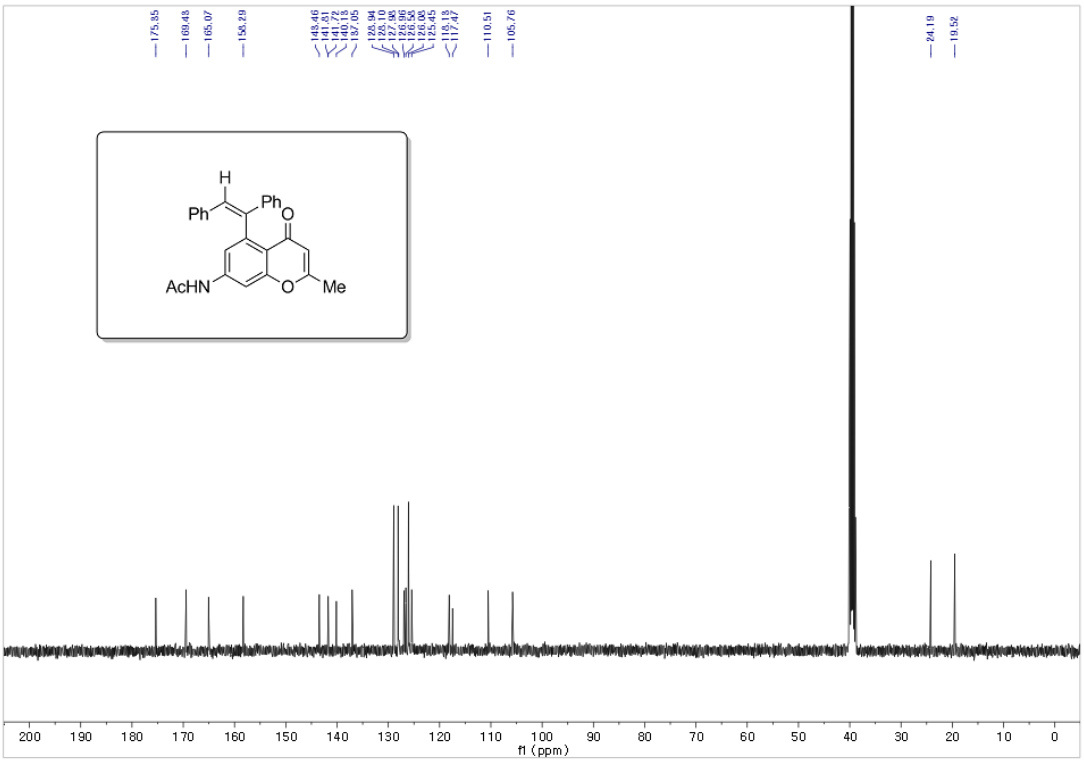


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-*N*-(5-(1,2-diphenylvinyl)-2-methyl-4-oxo-4H-chromen-7-yl)acetamide (3c).

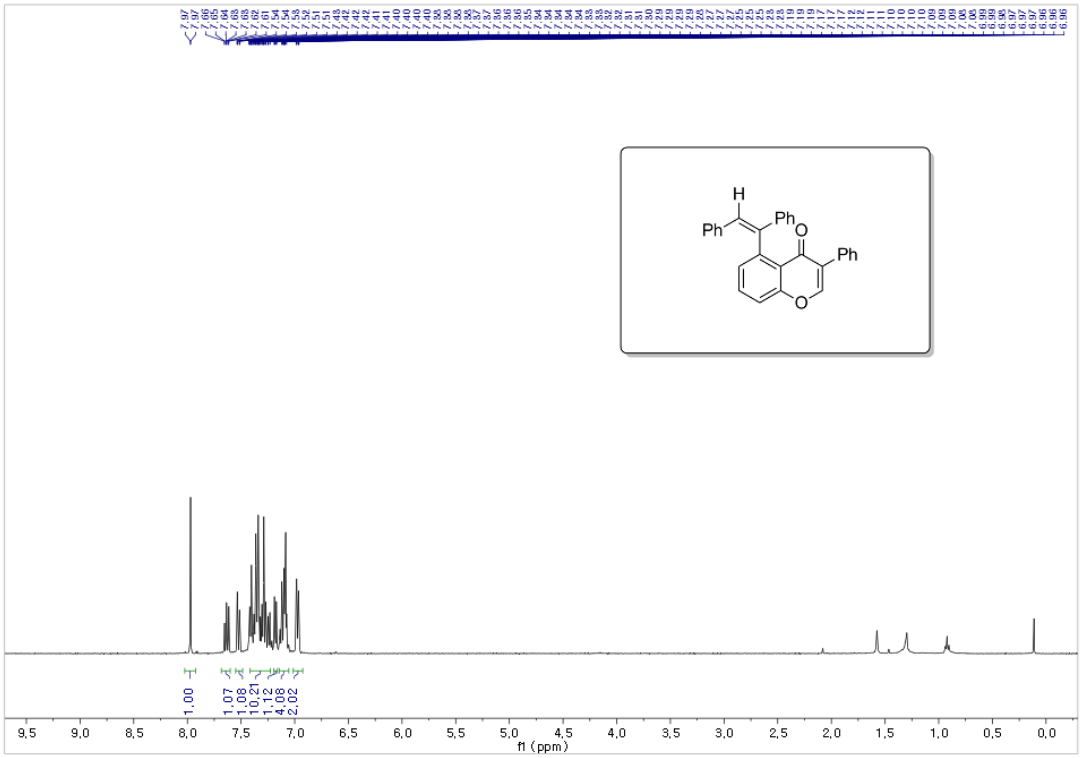


400 MHz, ^{1}H NMR in DMSO-d$_6$

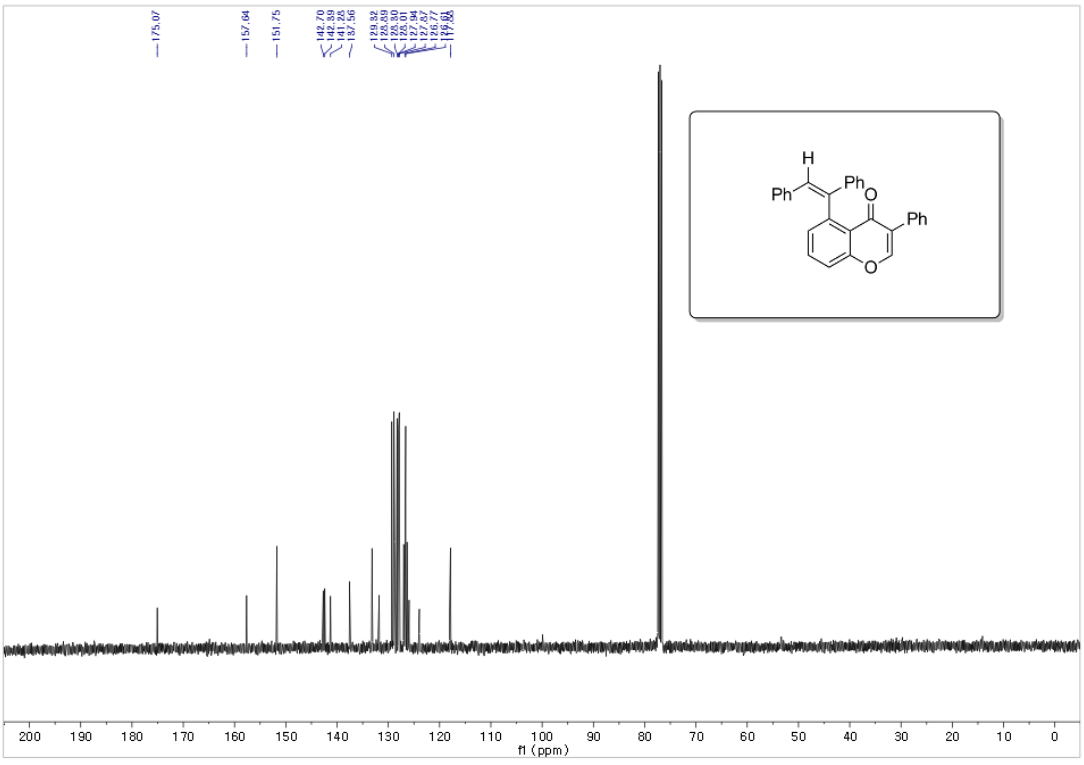


100 MHz, ^{13}C NMR in DMSO-d$_6$

(Z)-5-(1,2-diphenylvinyl)-3-phenyl-4H-chromen-4-one (3d).

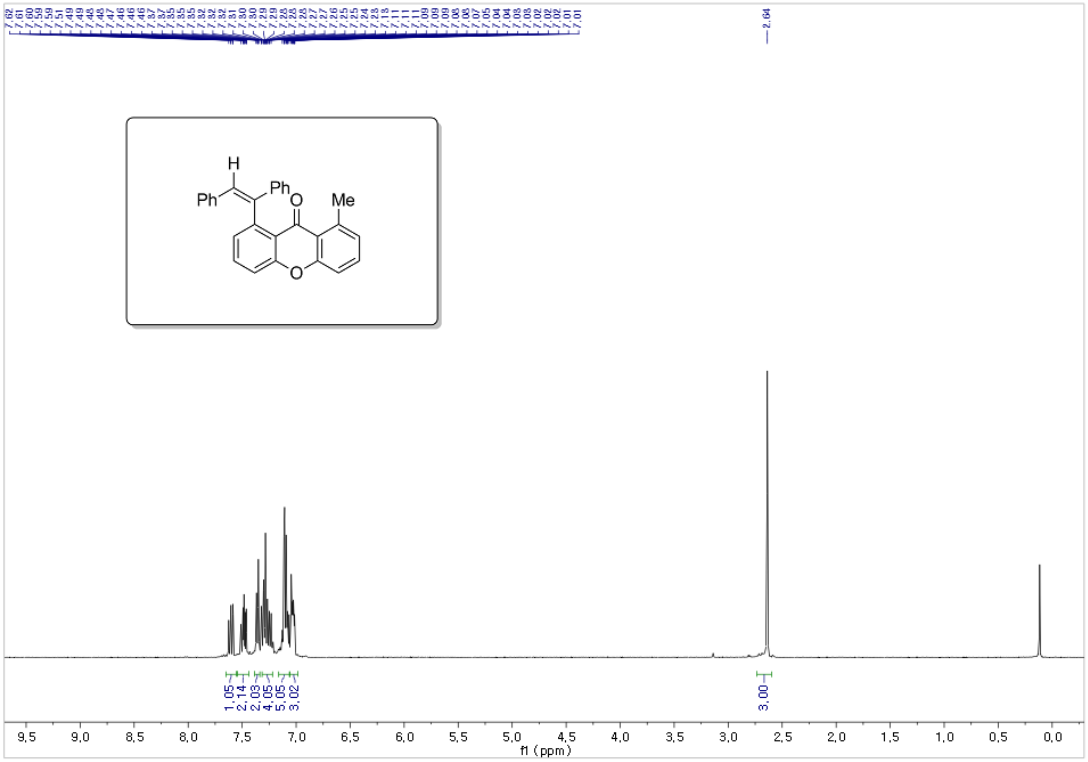


400 MHz, ^{1}H NMR in $CDCl_3$

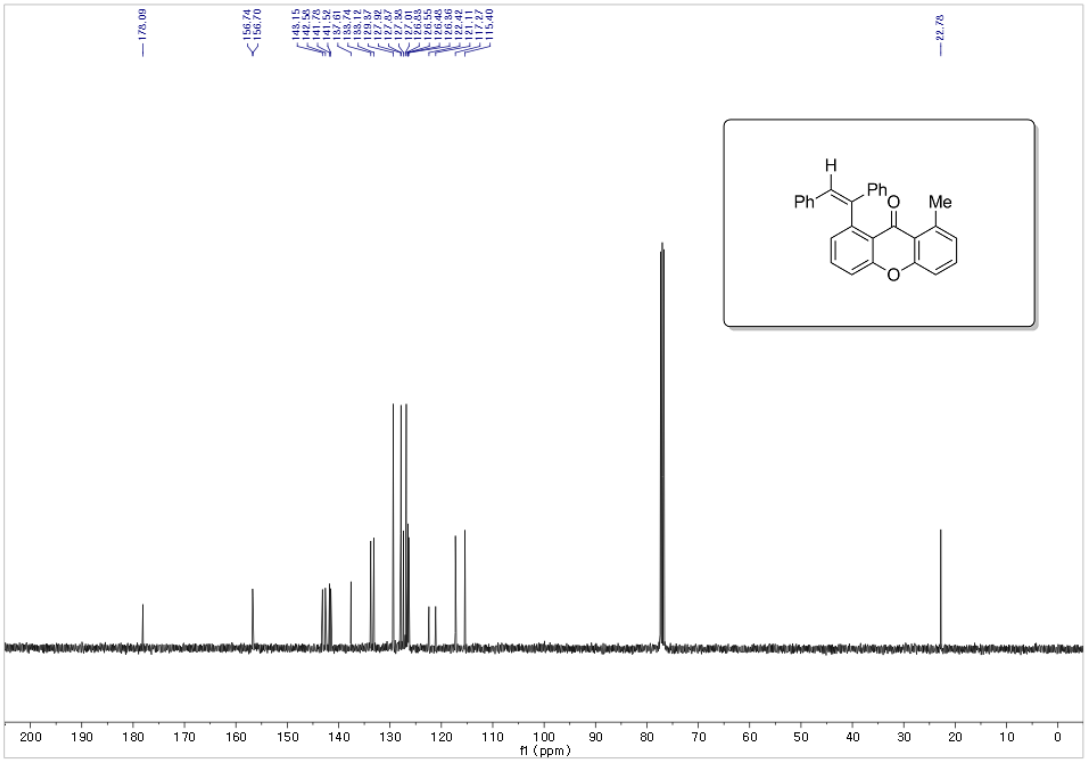


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-1-(1,2-diphenylvinyl)-8-methyl-9H-xanthen-9-one (3e).

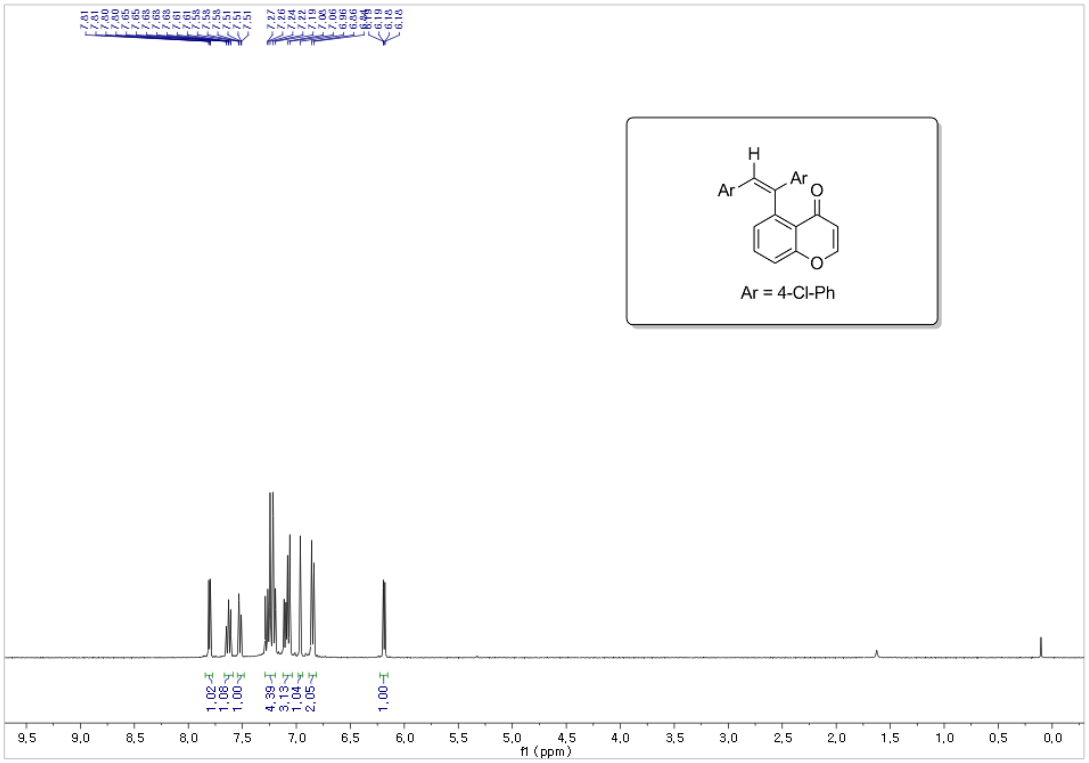


400 MHz, ^{1}H NMR in $CDCl_3$

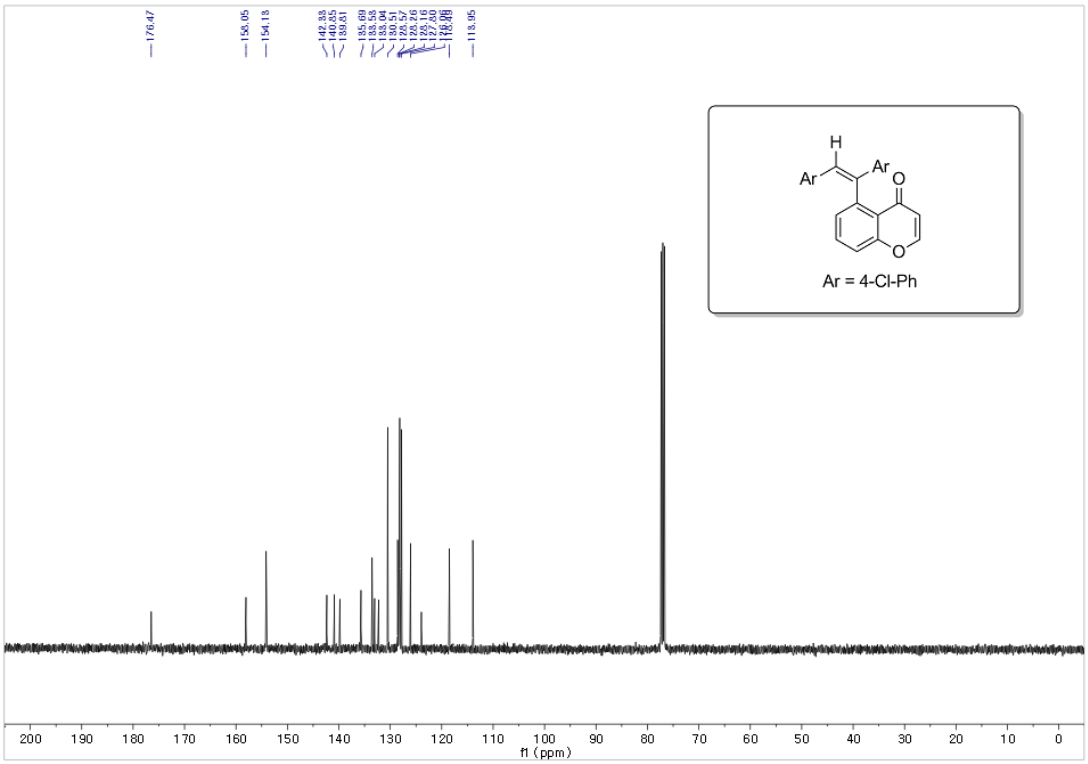


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-5-(1,2-bis(4-chlorophenyl)vinyl)-4H-chromen-4-one (3f).

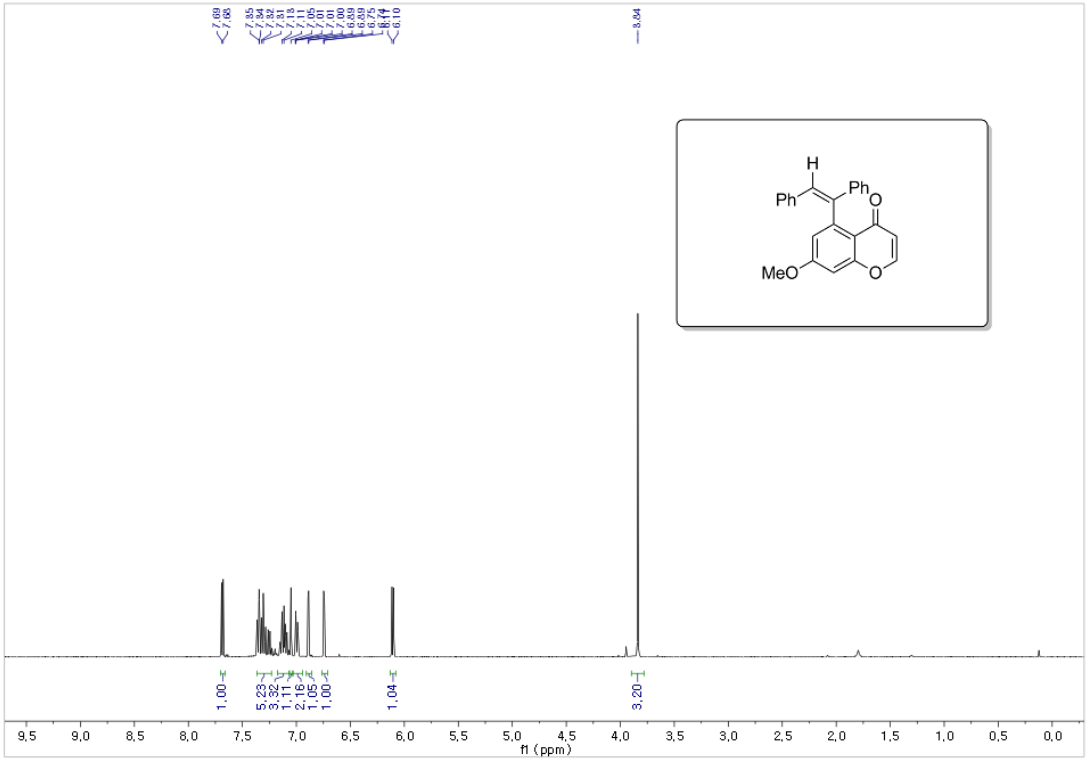


400 MHz, ^{1}H NMR in $CDCl_3$

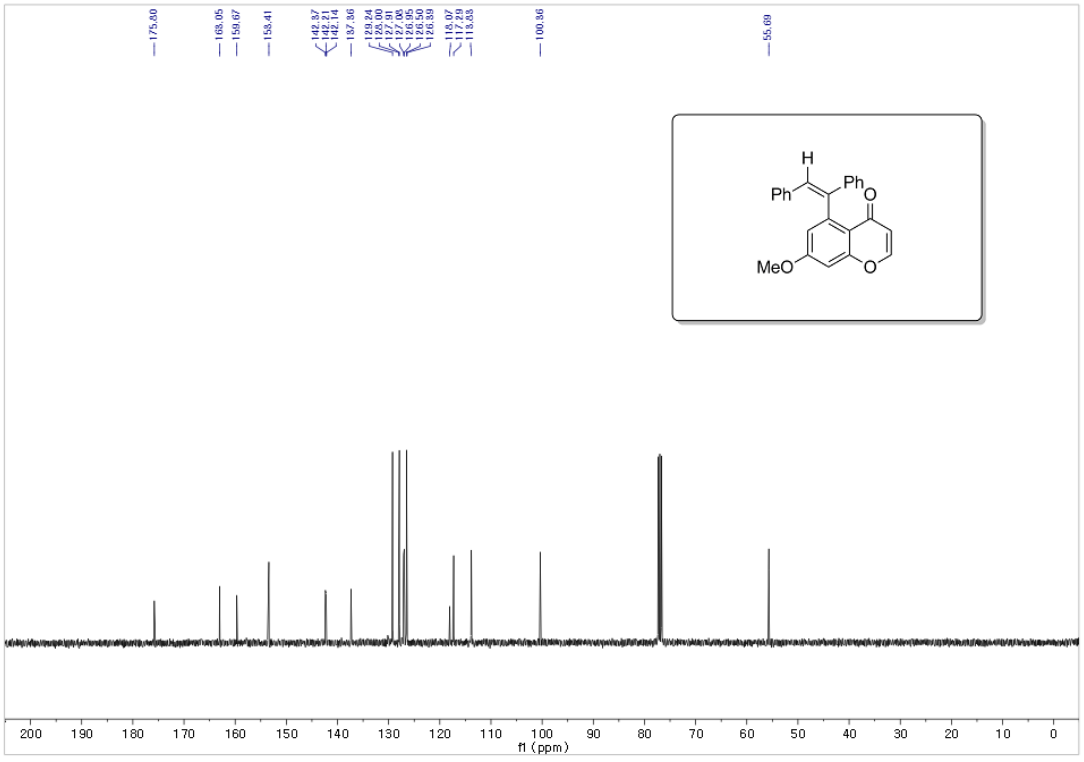


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-5-(1,2-diphenylvinyl)-7-methoxy-4H-chromen-4-one (3g).

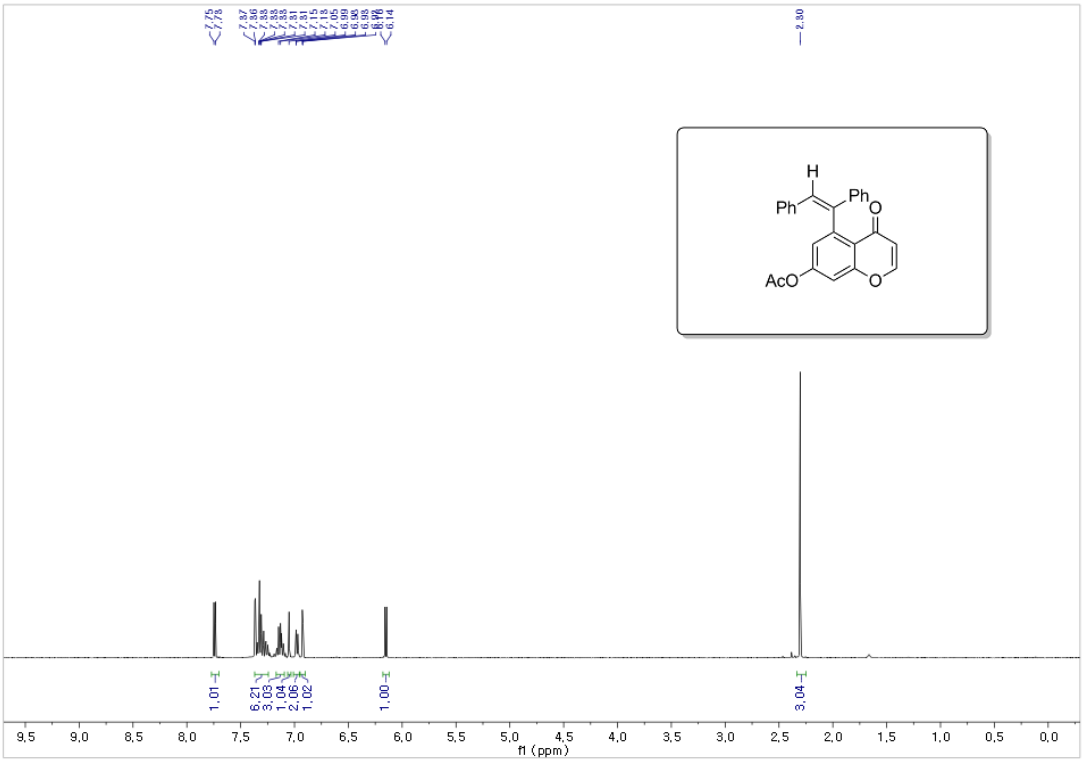


400 MHz, ^{1}H NMR in $CDCl_3$

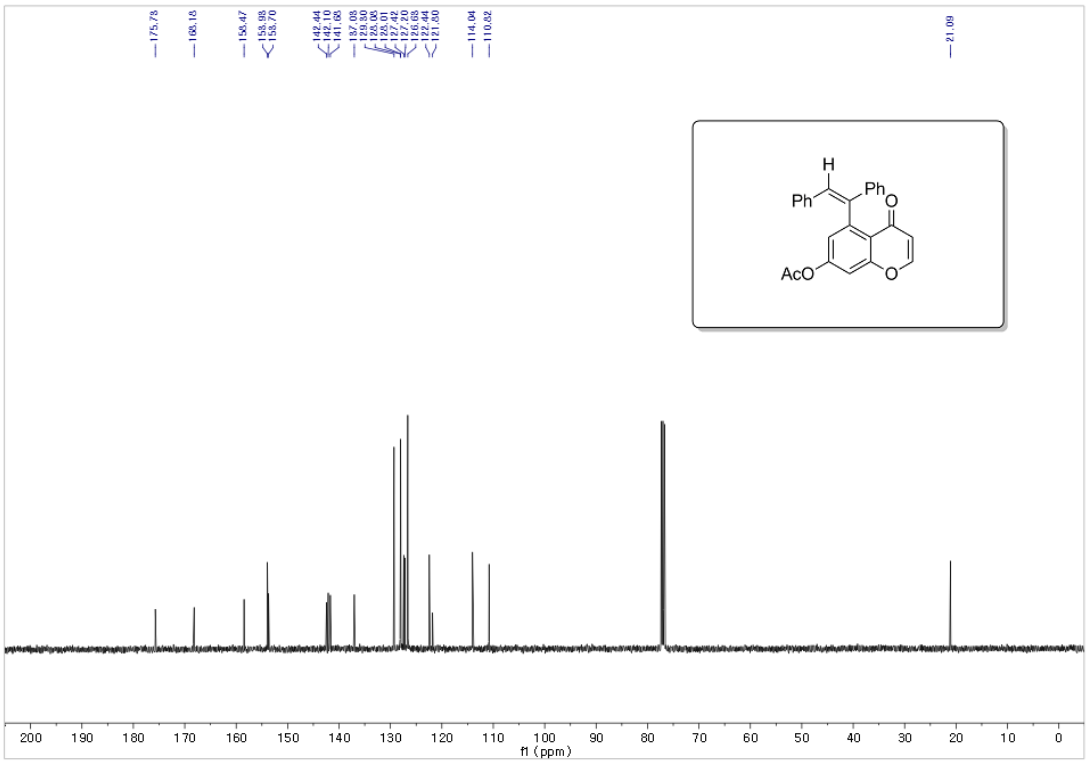


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-5-(1,2-diphenylvinyl)-4-oxo-4H-chromen-7-yl acetate (3h).

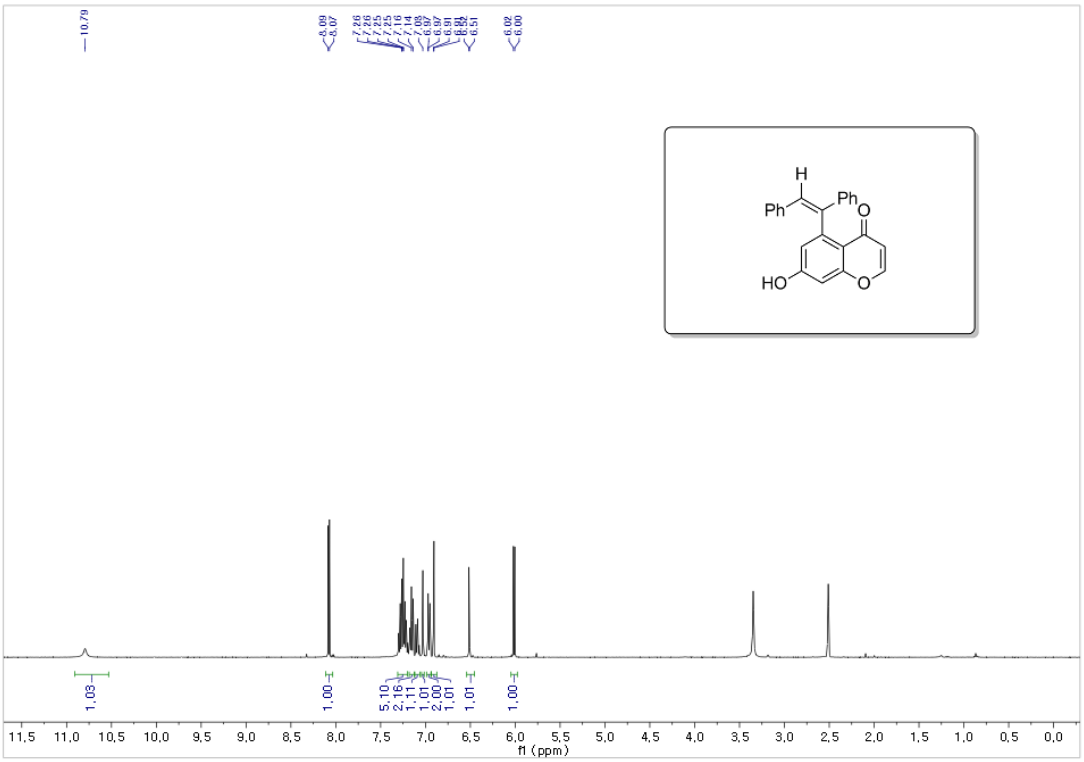


400 MHz, ^{1}H NMR in $CDCl_3$

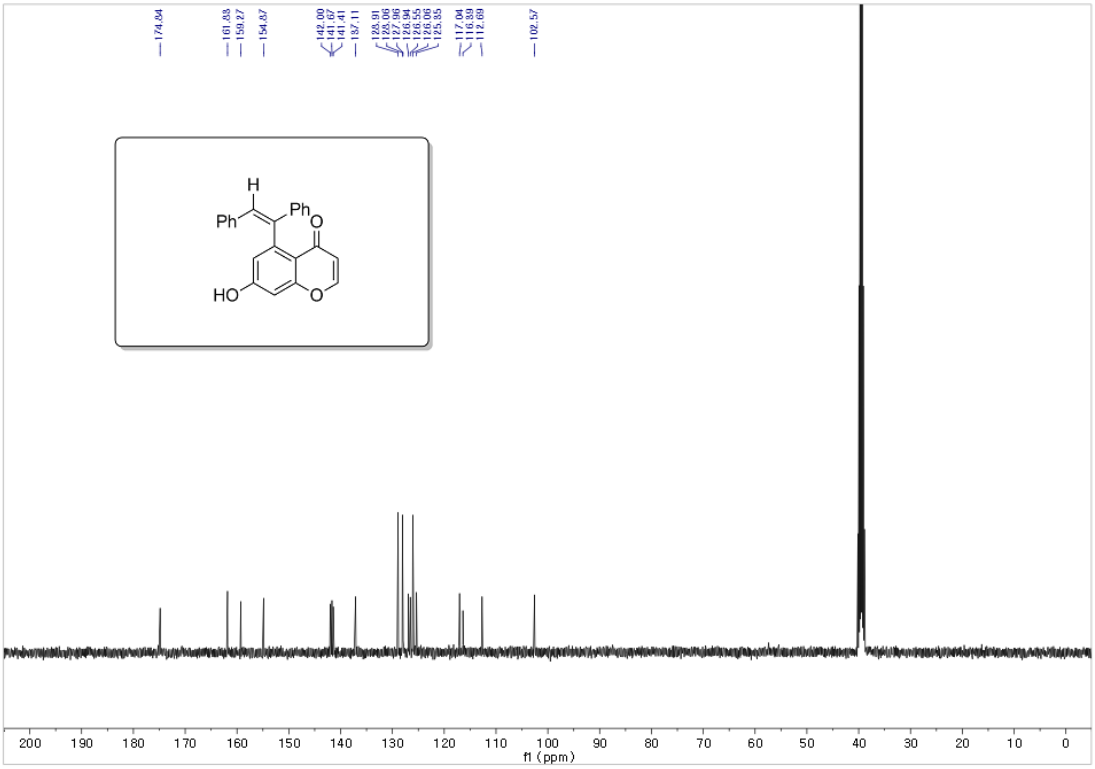


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-5-(1,2-diphenylvinyl)-7-hydroxy-4H-chromen-4-one (3i).

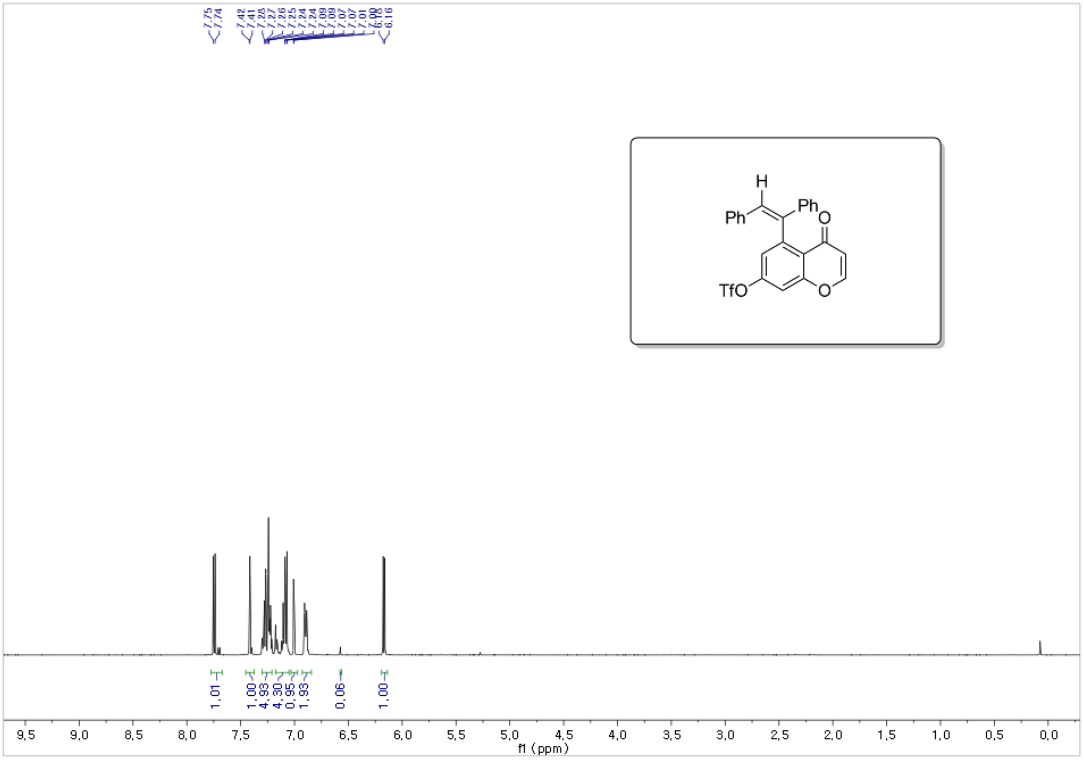


400 MHz, ^{1}H NMR in DMSO-d$_6$

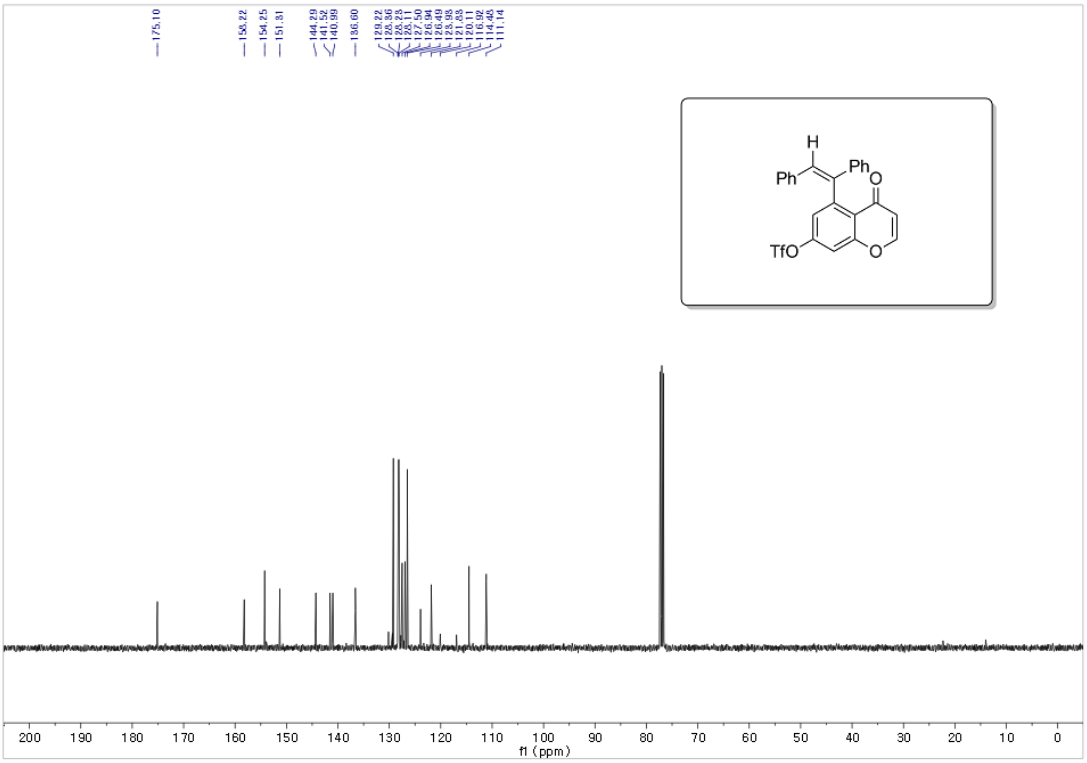


100 MHz, ^{13}C NMR in DMSO-d$_6$

(Z)-5-(1,2-diphenylvinyl)-4-oxo-4H-chromen-7-yl trifluoromethanesulfonate (3j).

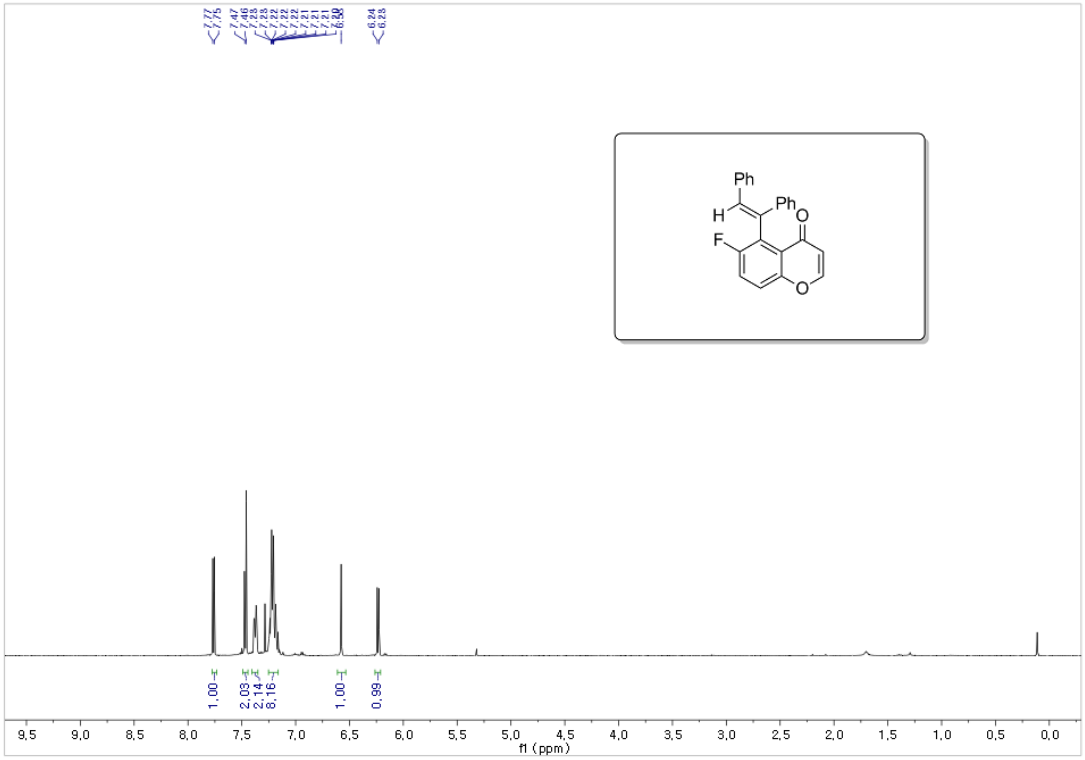


400 MHz, ^{1}H NMR in $CDCl_3$ (*E/Z* Mixture 5:95)

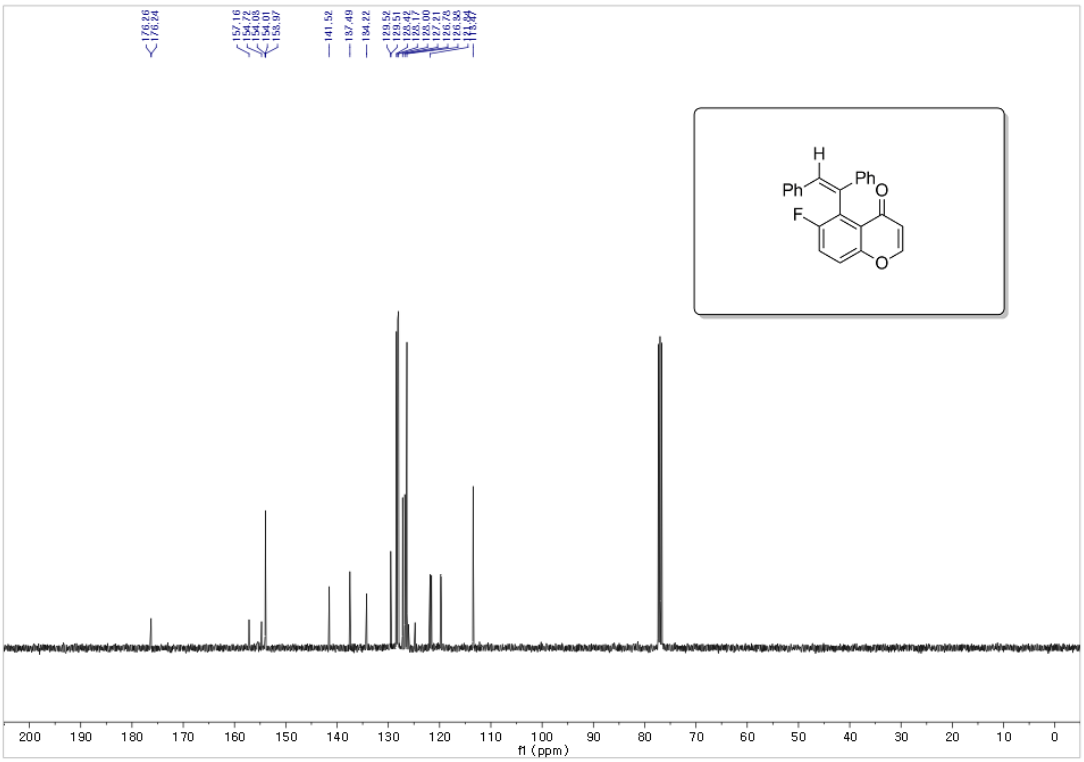


100 MHz, ^{13}C NMR in $CDCl_3$ (*E/Z* Mixture 5:95)

(Z)-5-(1,2-diphenylvinyl)-6-fluoro-4H-chromen-4-one (3k).

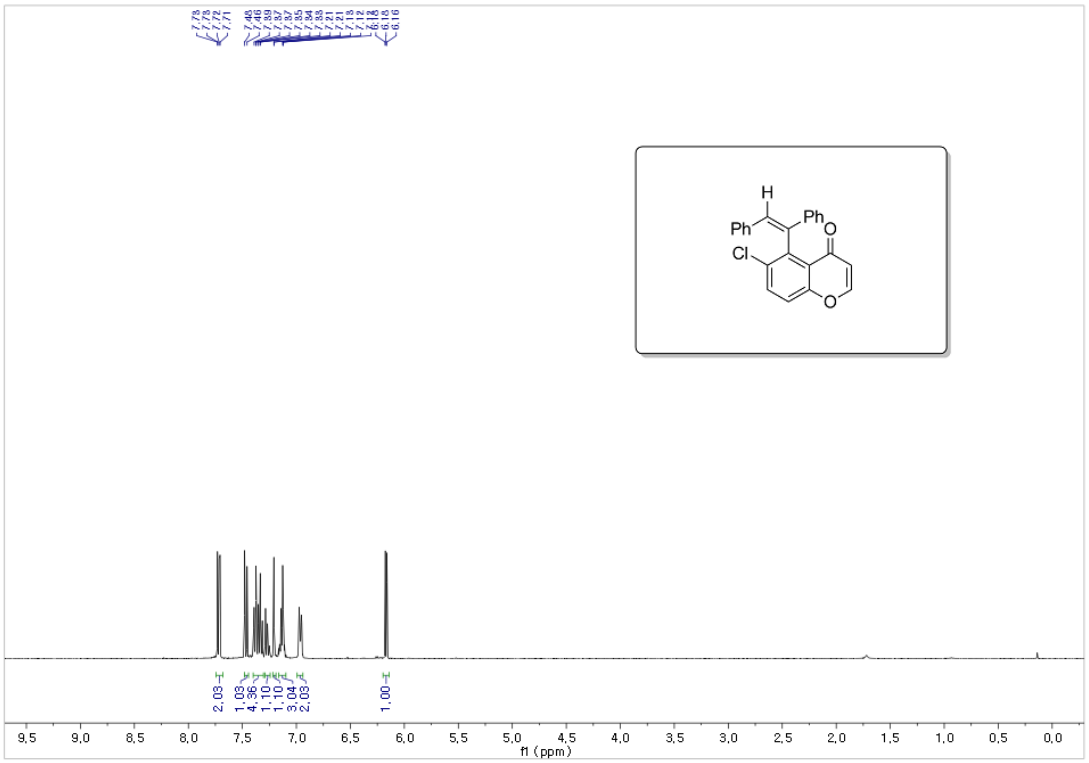


400 MHz, ^{1}H NMR in $CDCl_3$

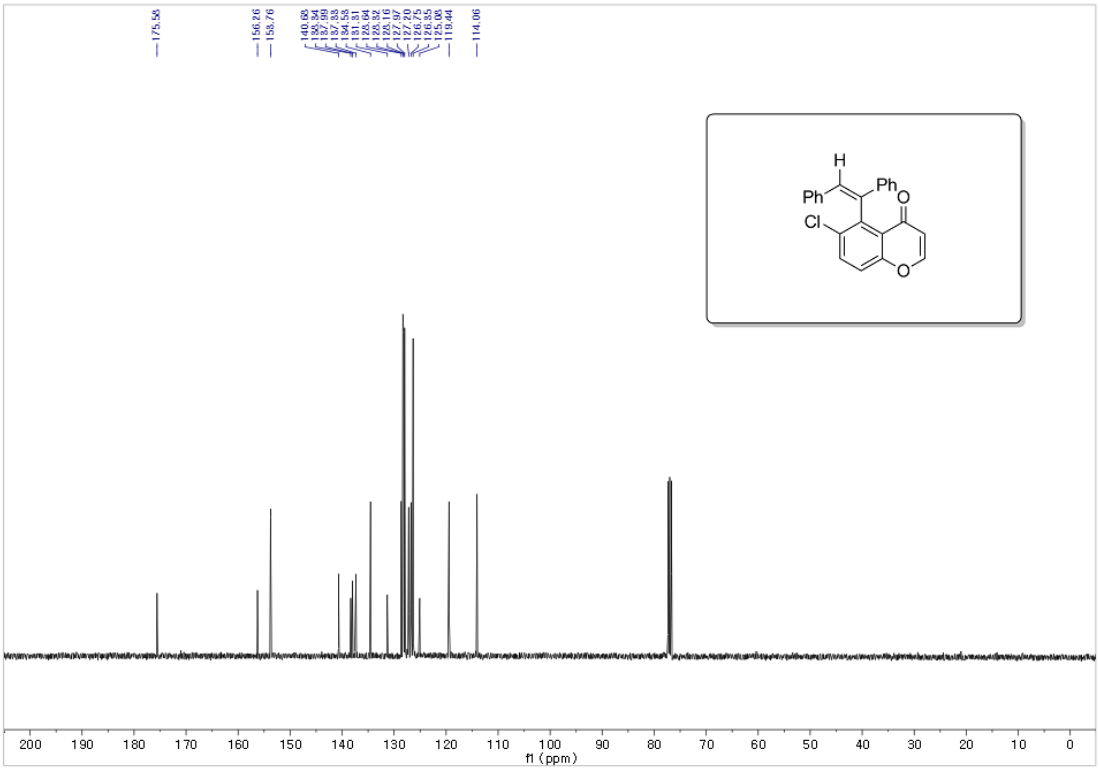


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-6-chloro-5-(1,2-diphenylvinyl)-4H-chromen-4-one (3l).

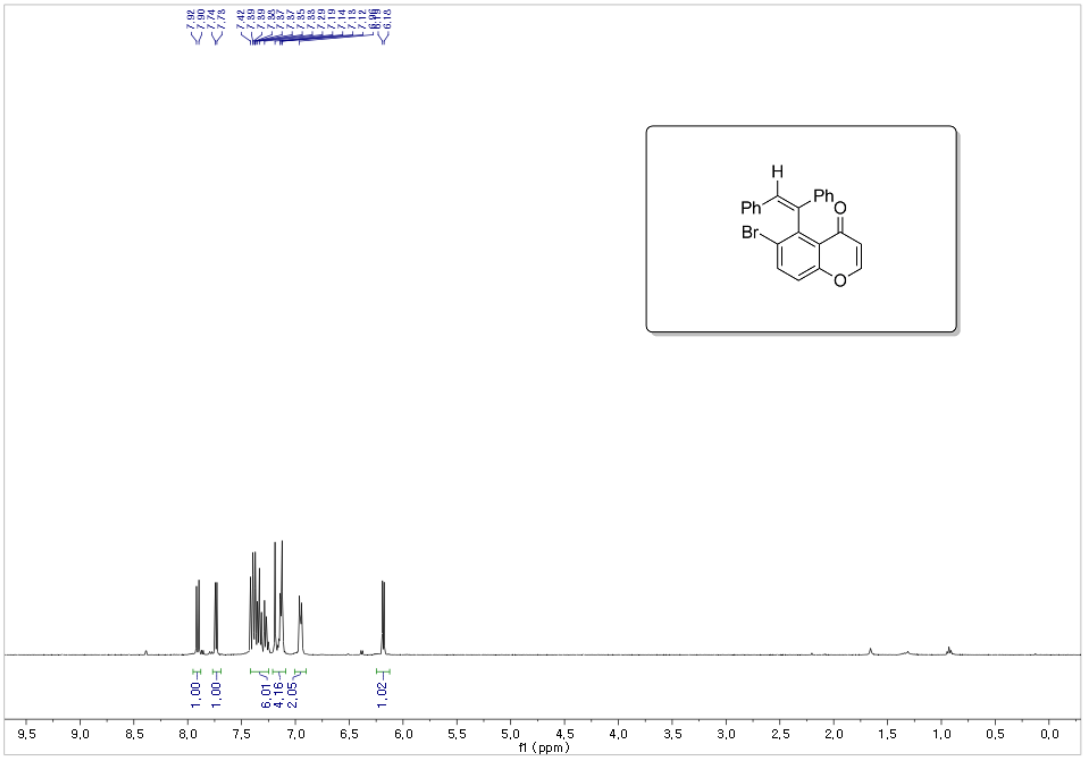


400 MHz, ^{1}H NMR in $CDCl_3$

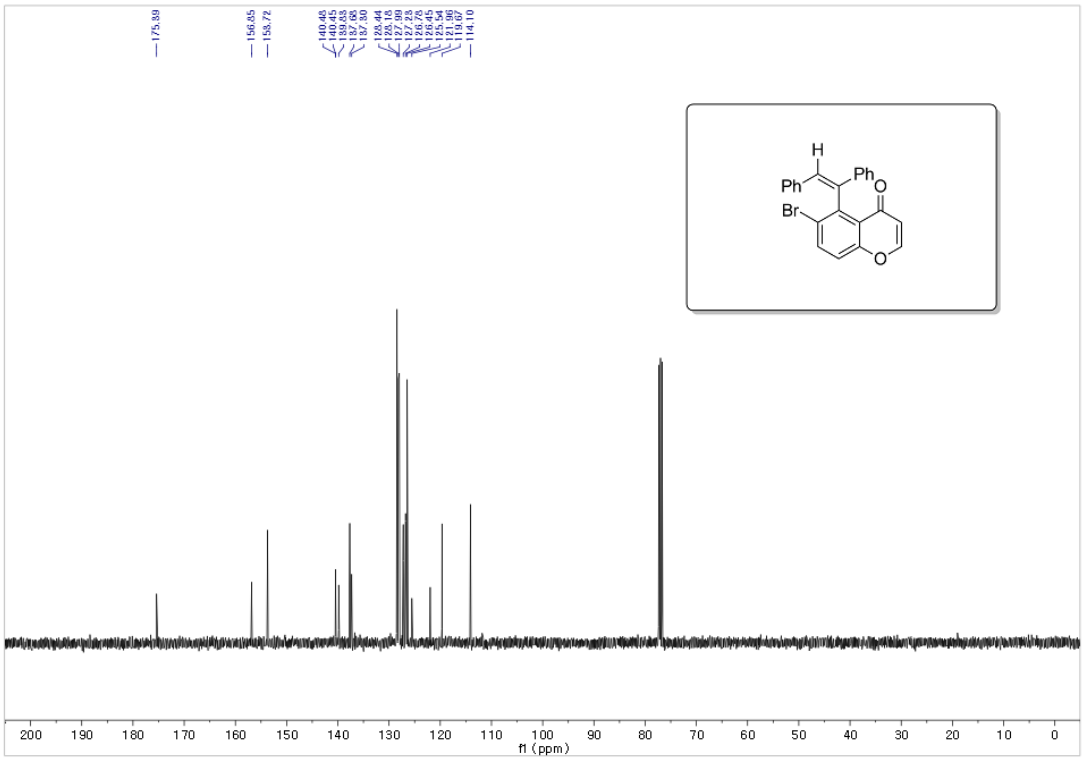


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-6-bromo-5-(1,2-diphenylvinyl)-4H-chromen-4-one (3m).

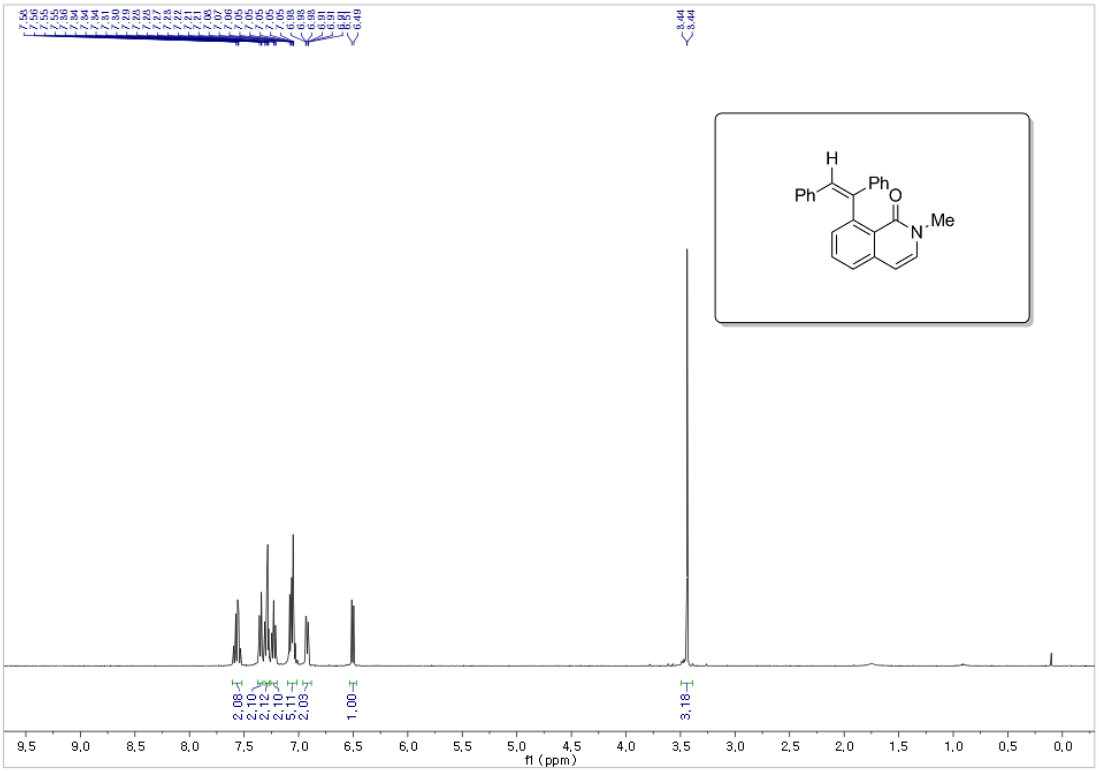


400 MHz, ^{1}H NMR in $CDCl_3$

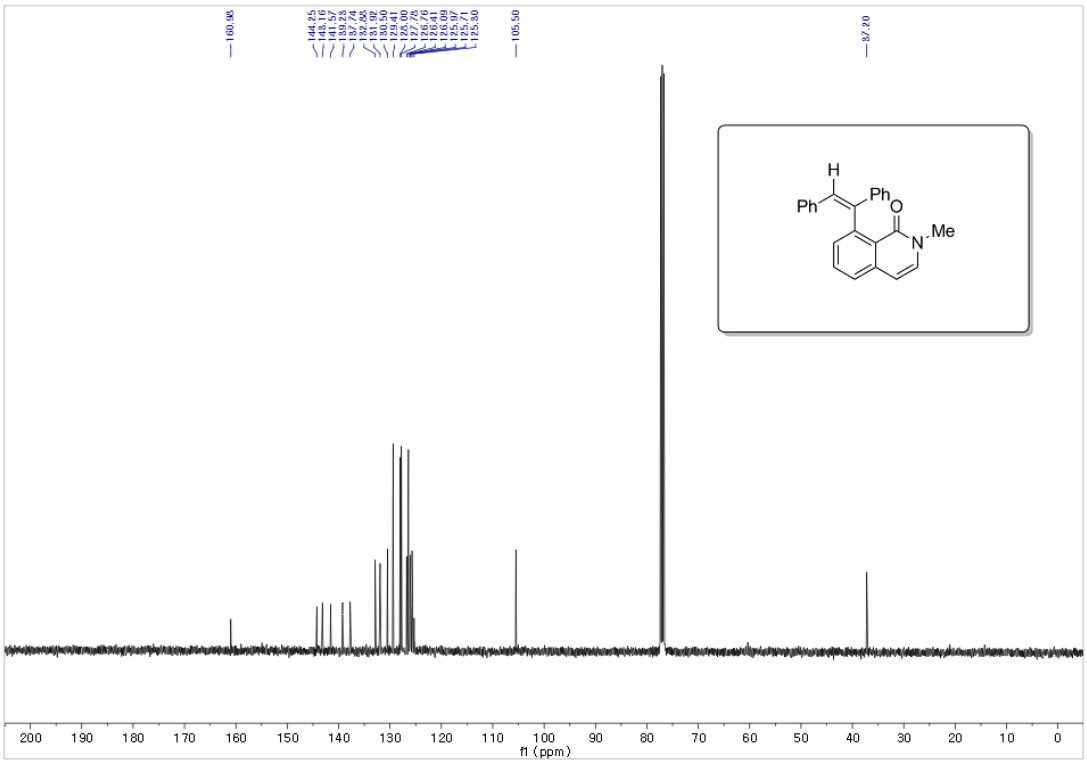


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-8-(1,2-diphenylvinyl)-2-methylisoquinolin-1(2H)-one (4a).

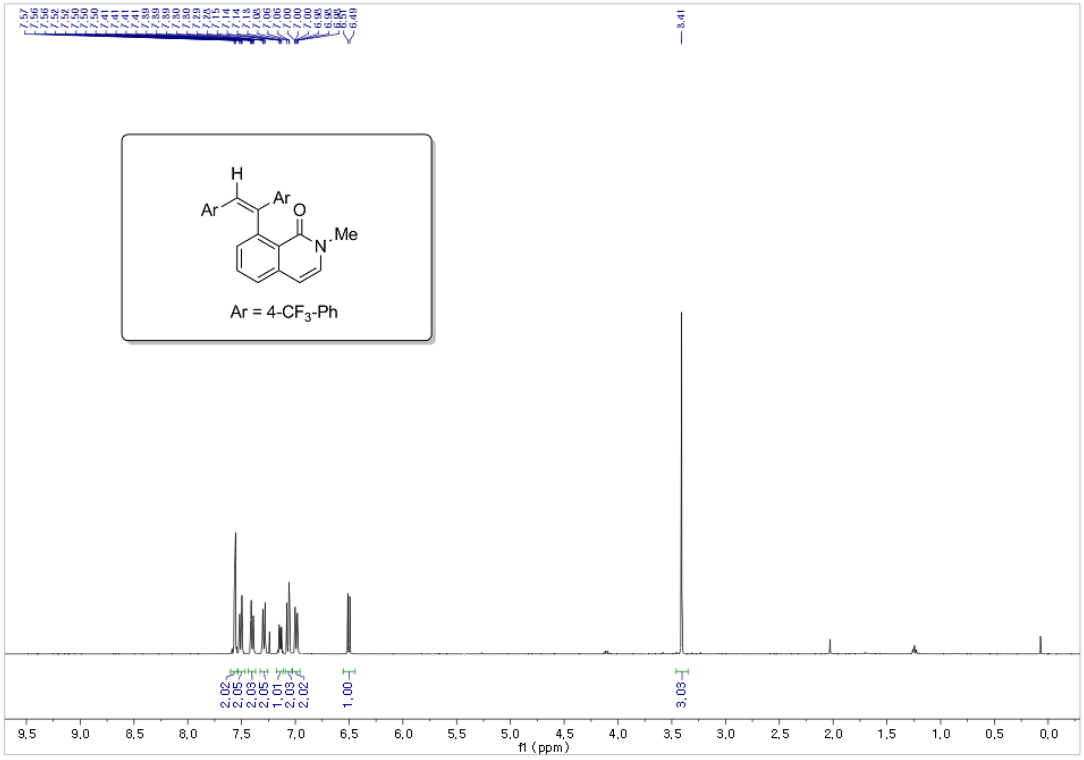


400 MHz, ^{1}H NMR in $CDCl_3$

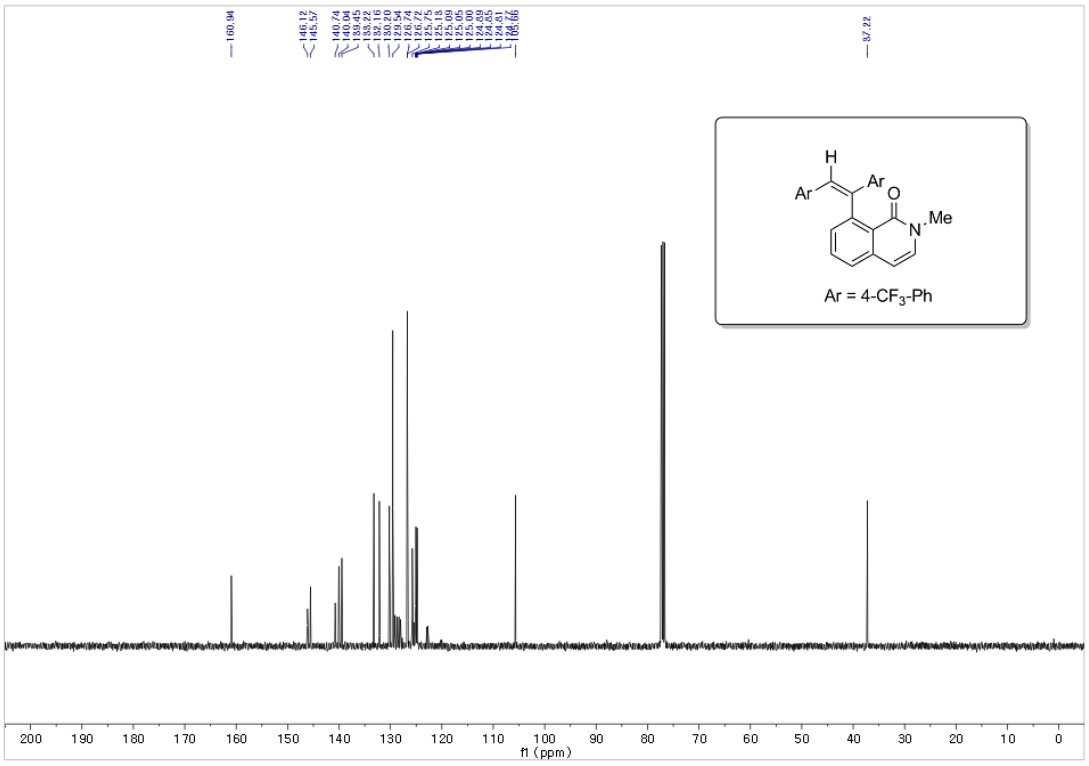


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-8-(1,2-bis(4-(trifluoromethyl)phenyl)vinyl)-2-methylisoquinolin-1(2H)-one (4b).

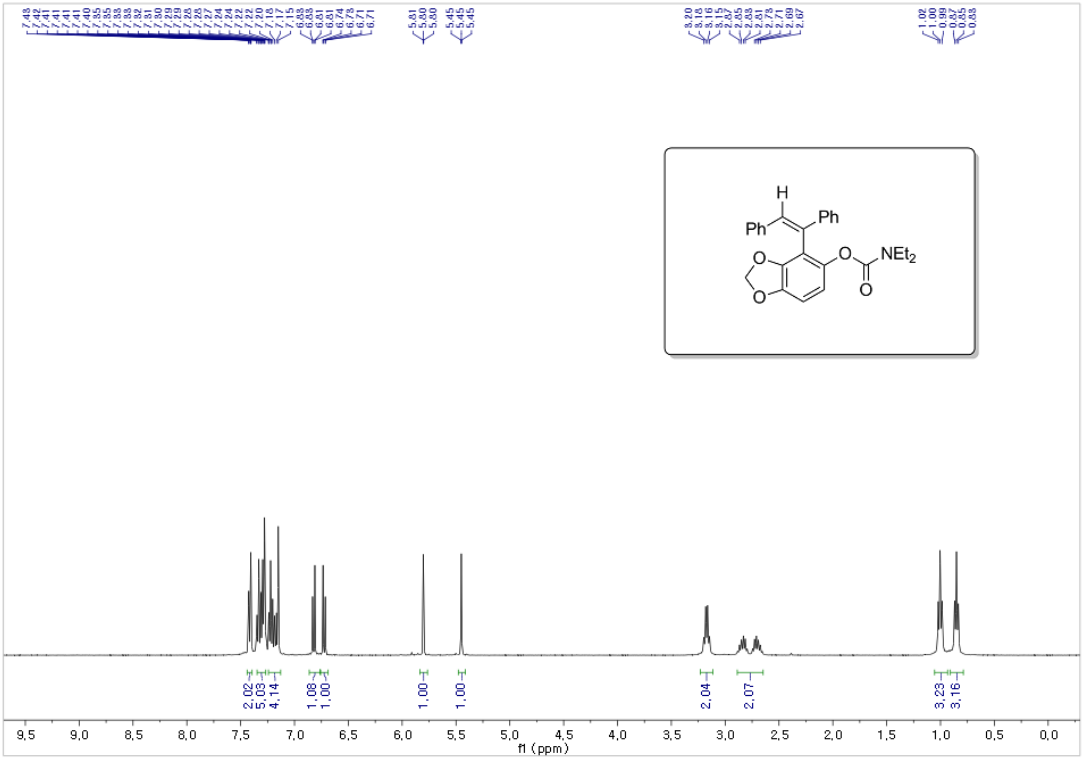


400 MHz, ^{1}H NMR in $CDCl_3$

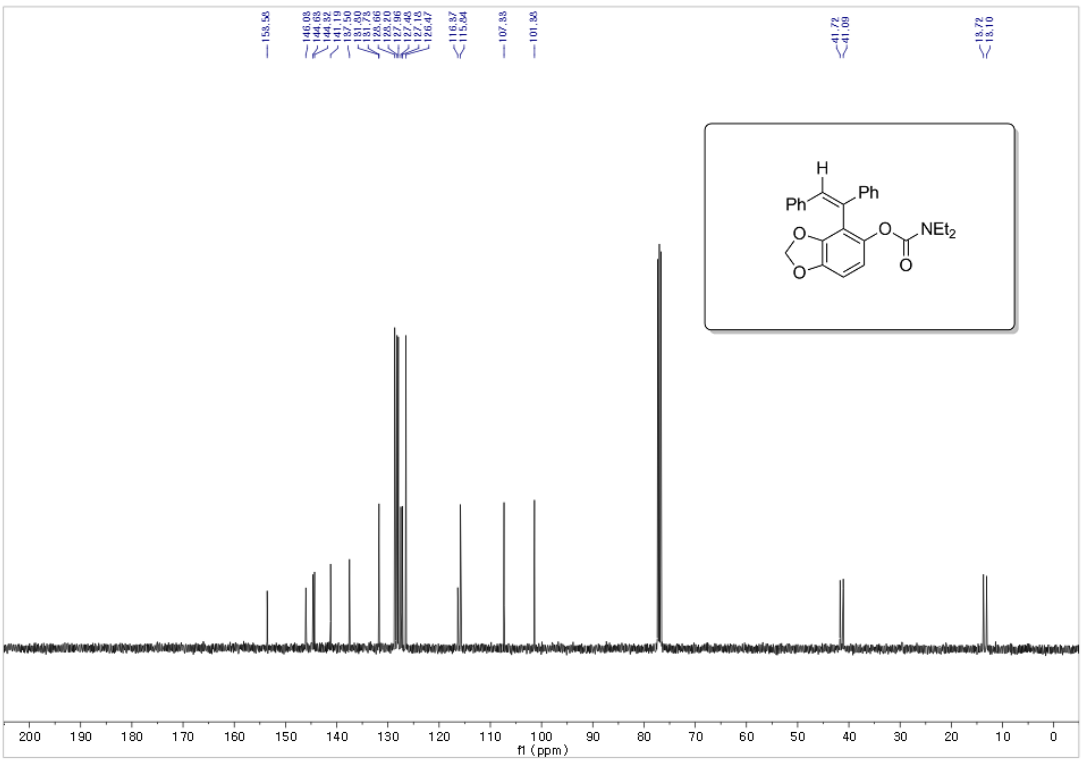


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-4-(1,2-diphenylvinyl)benzo[d][1,3]dioxol-5-yl diethylcarbamate (4c).

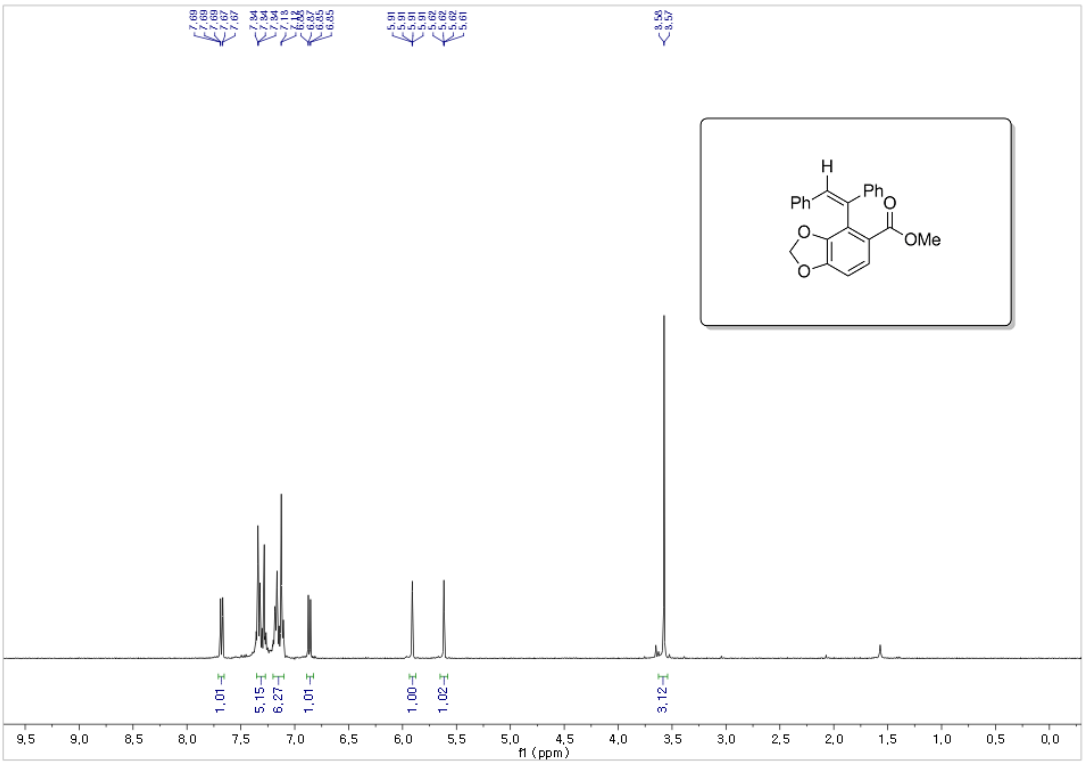


400 MHz, ^{1}H NMR in $CDCl_3$

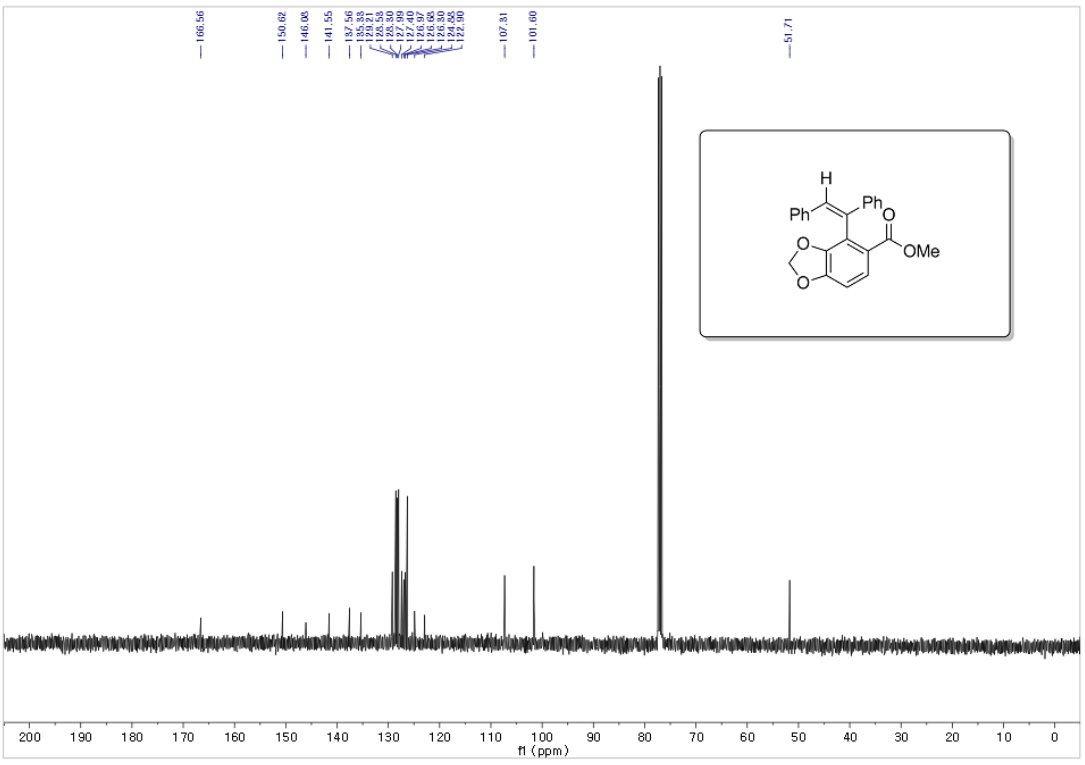


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-methyl 4-(1,2-diphenylvinyl)benzo[d][1,3]dioxole-5-carboxylate (4d).

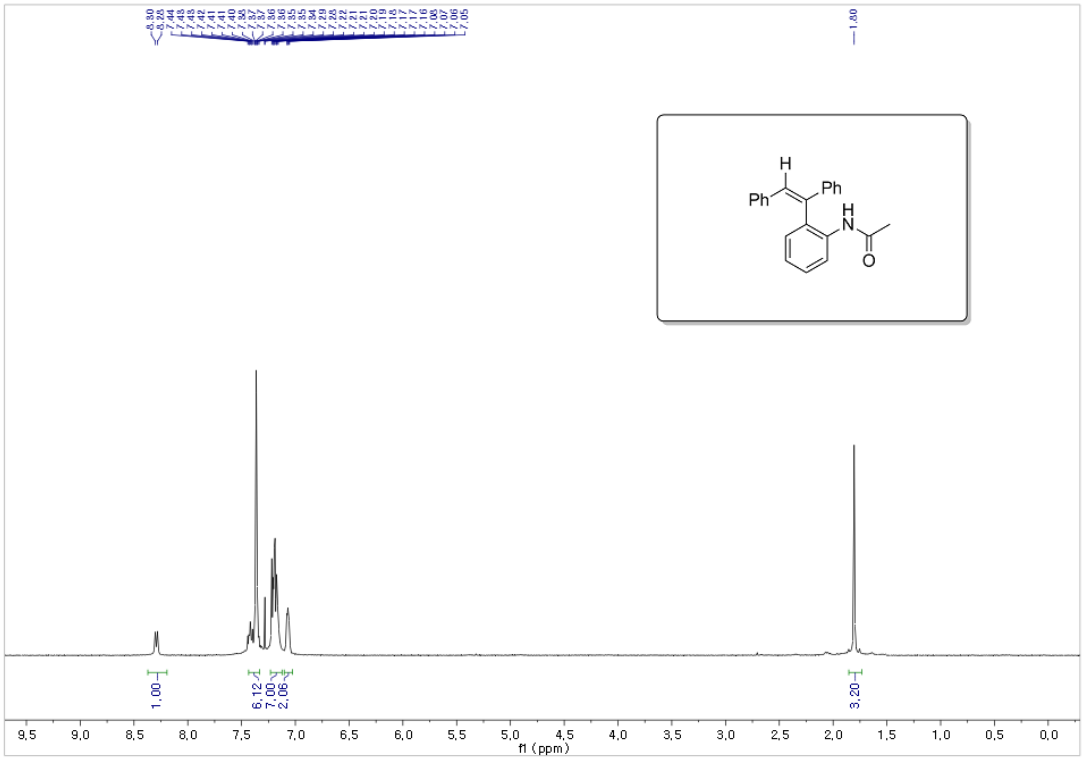


400 MHz, ^{1}H NMR in $CDCl_3$

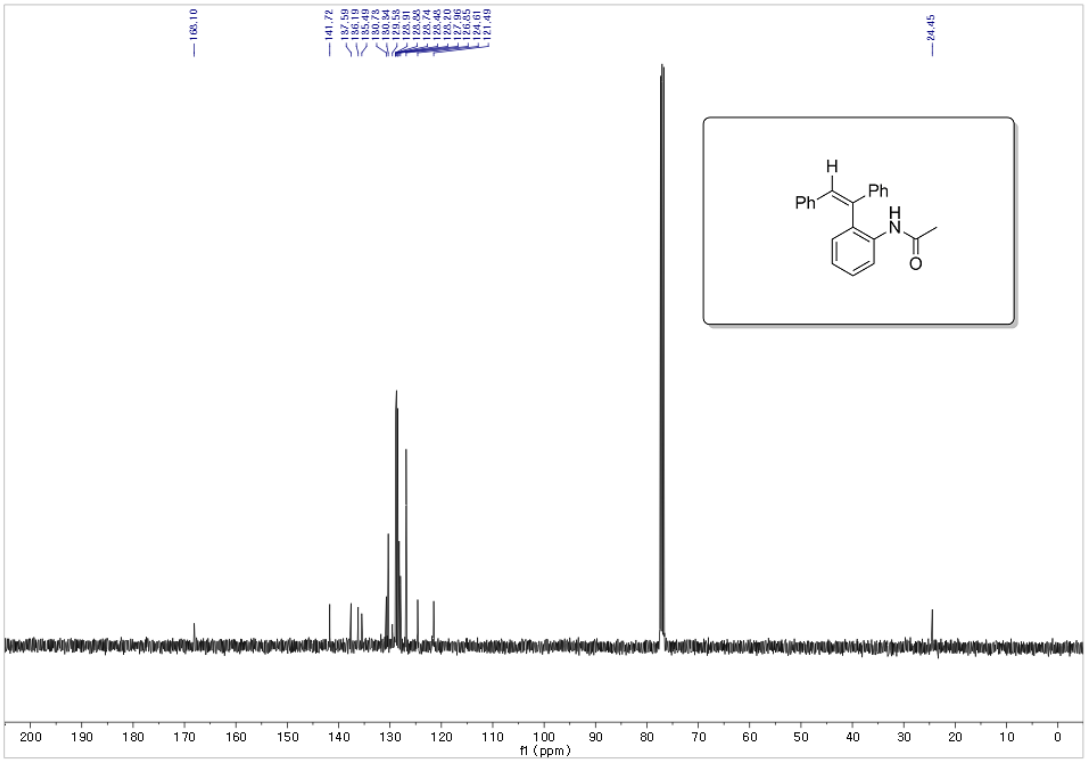


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-*N*-(2-(1,2-diphenylvinyl)phenyl)acetamide (4e).

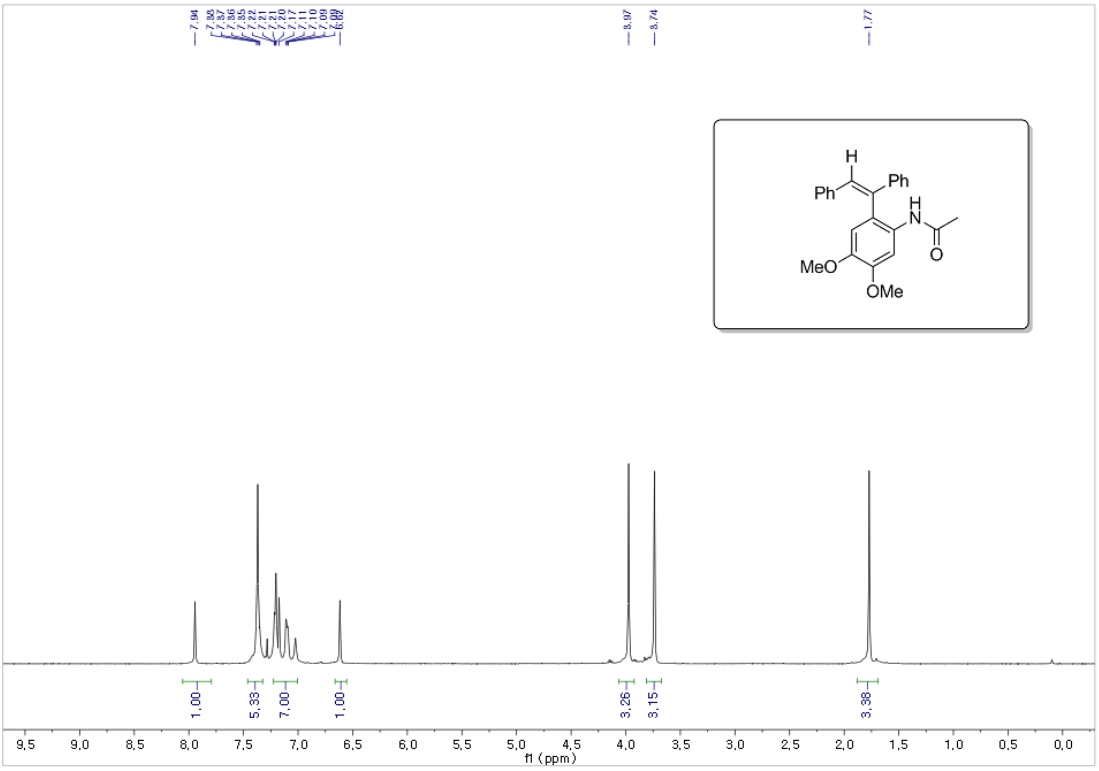


400 MHz, ^{1}H NMR in $CDCl_3$

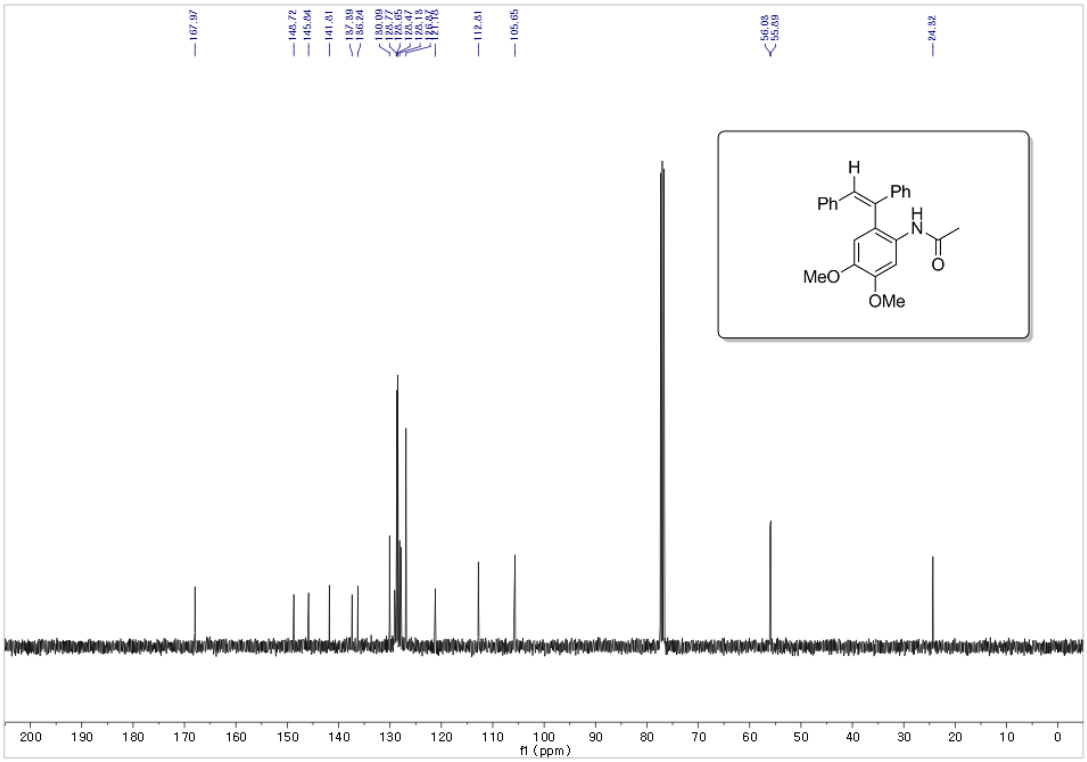


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-*N*-(2-(1,2-diphenylvinyl)-4,5-dimethoxyphenyl)acetamide (4f).

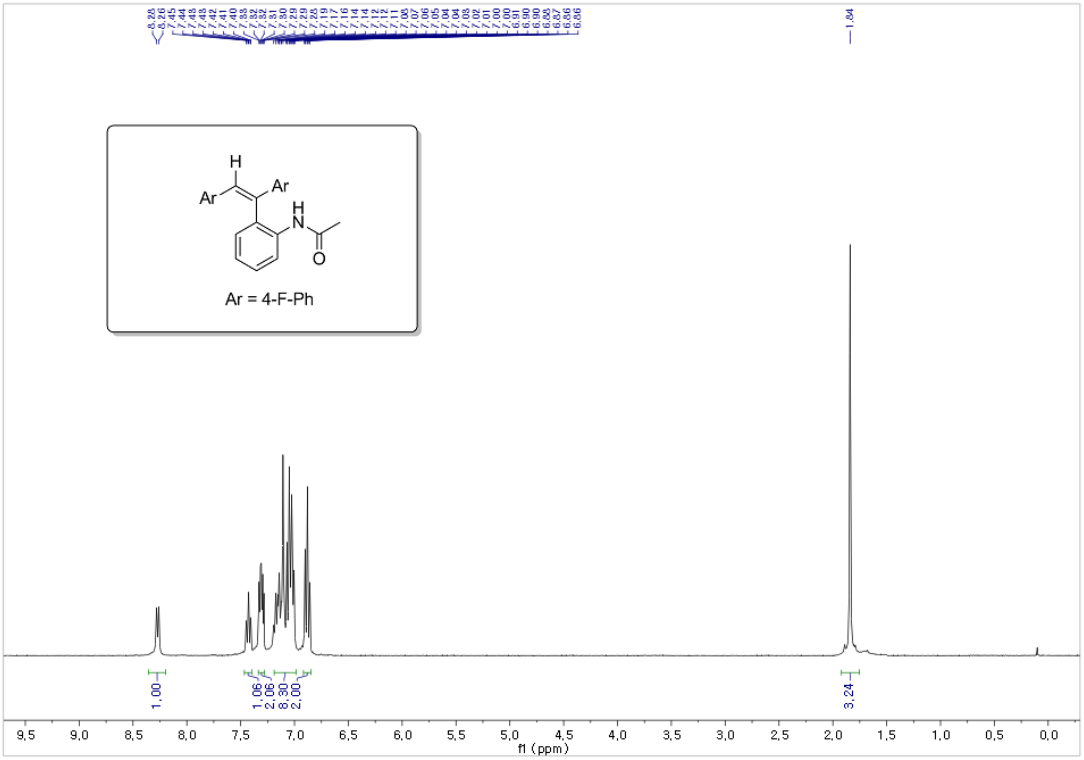


400 MHz, ^{1}H NMR in $CDCl_3$

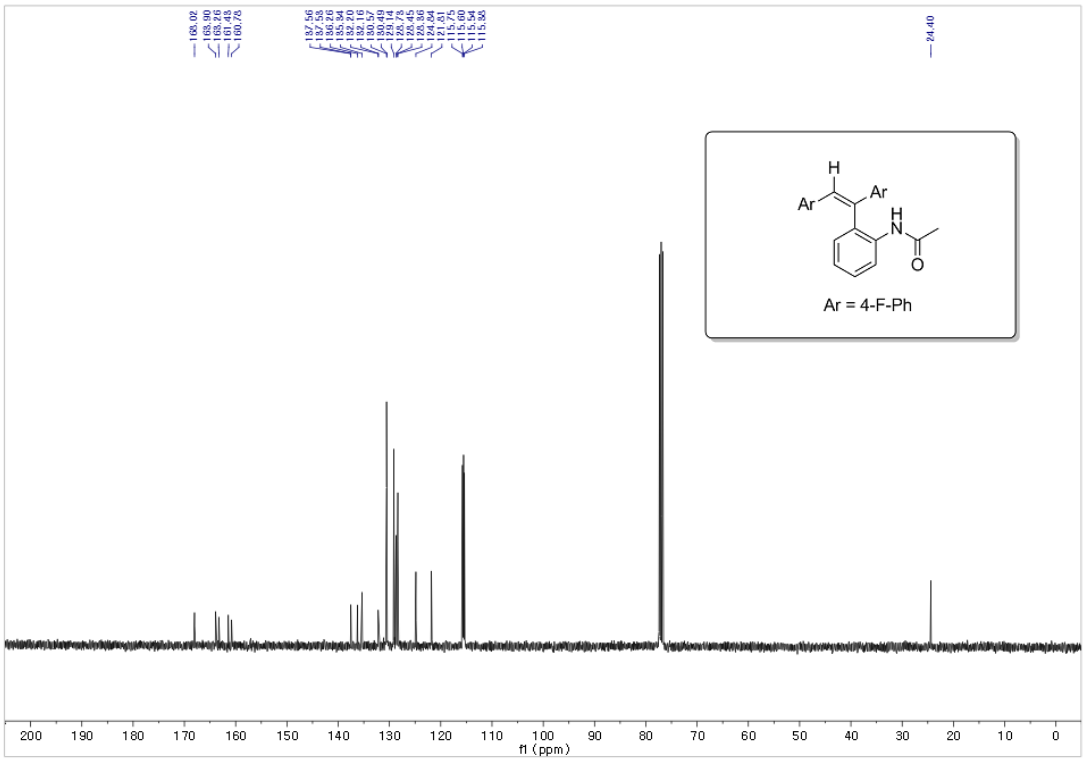


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-*N*-(2-(1,2-bis(4-fluorophenyl)vinyl)phenyl)acetamide (4g).

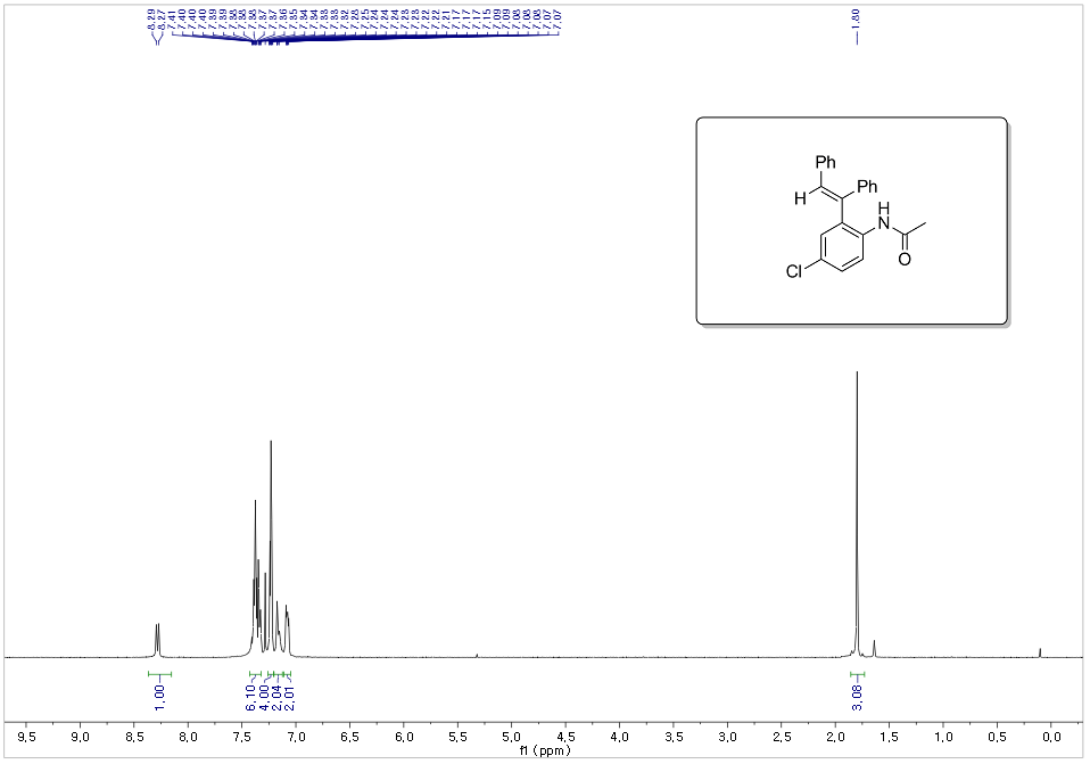


400 MHz, ^{1}H NMR in $CDCl_3$

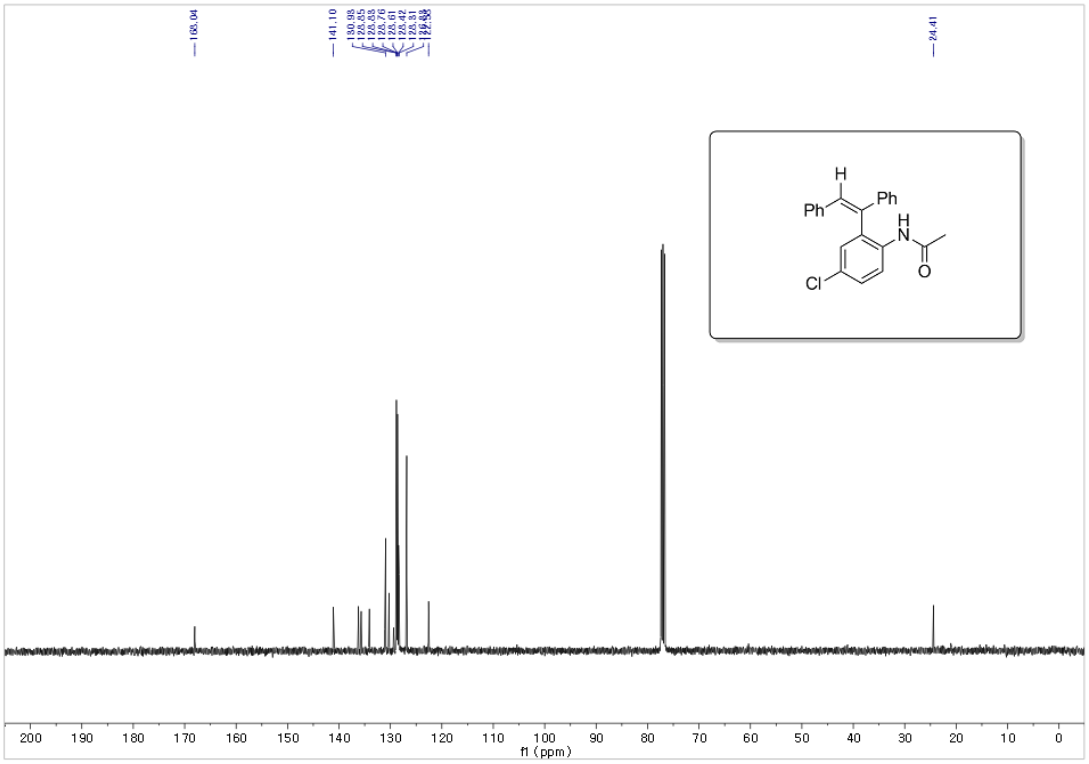


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-*N*-(4-chloro-2-(1,2-diphenylvinyl)phenyl)acetamide (4h).

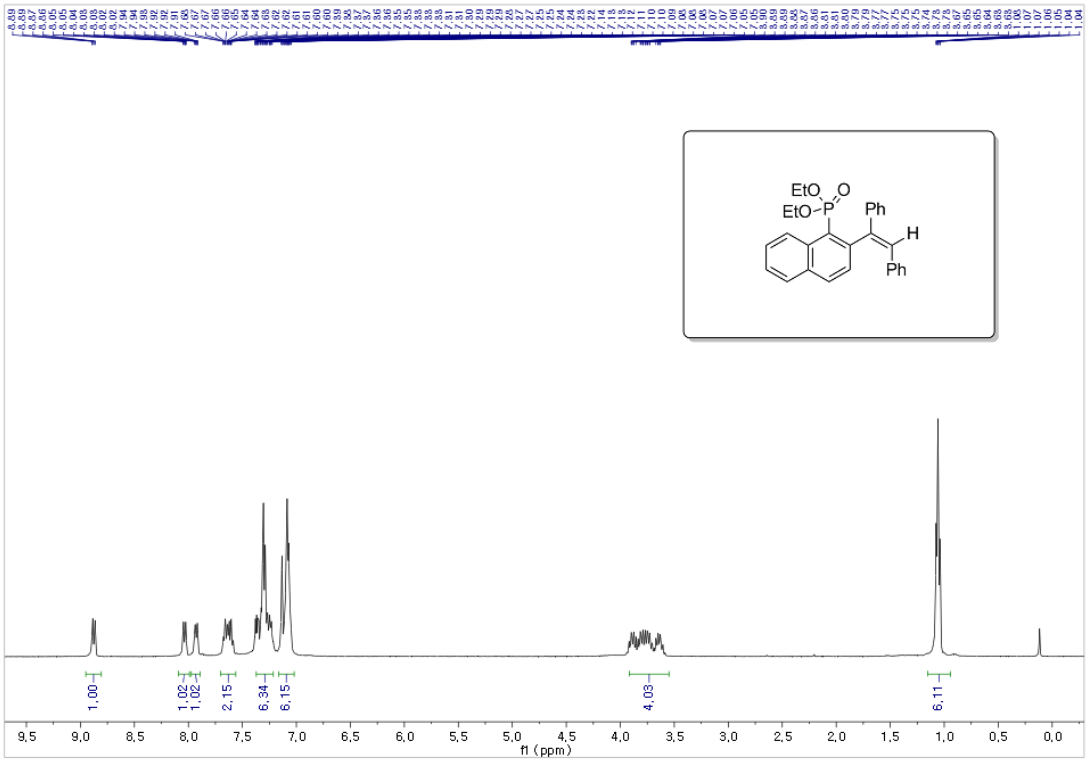


400 MHz, ^{1}H NMR in $CDCl_3$

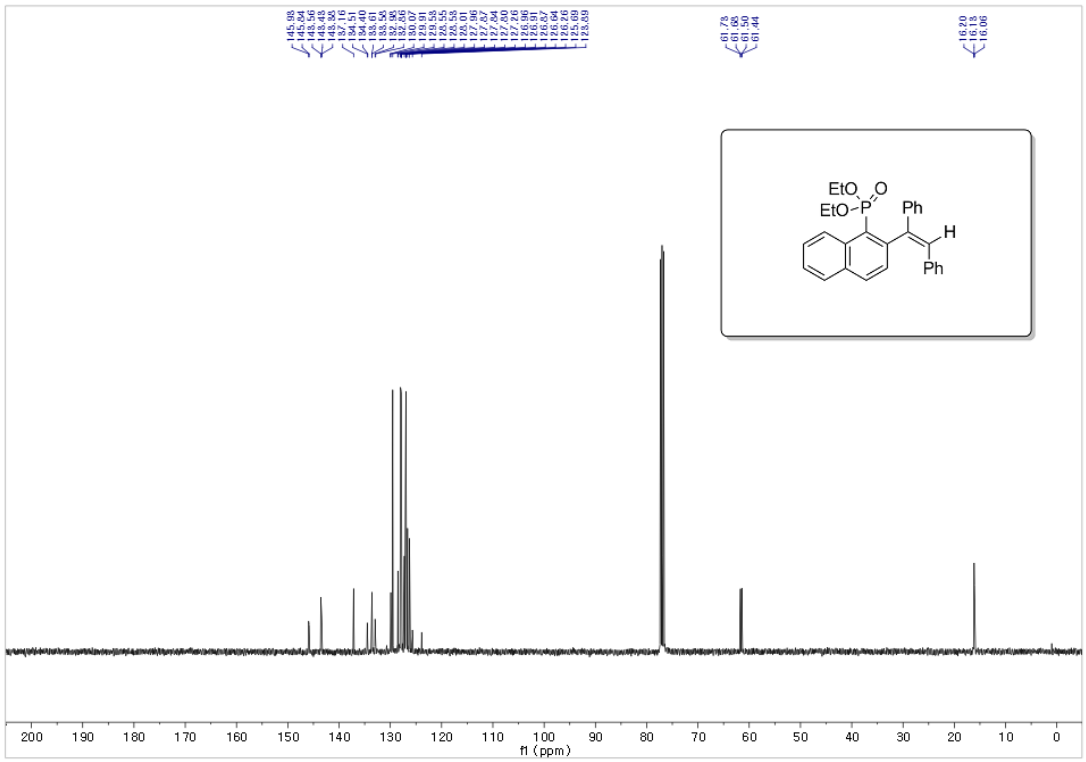


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-diethyl (2-(1,2-diphenylvinyl)naphthalen-1-yl)phosphonate (4i).

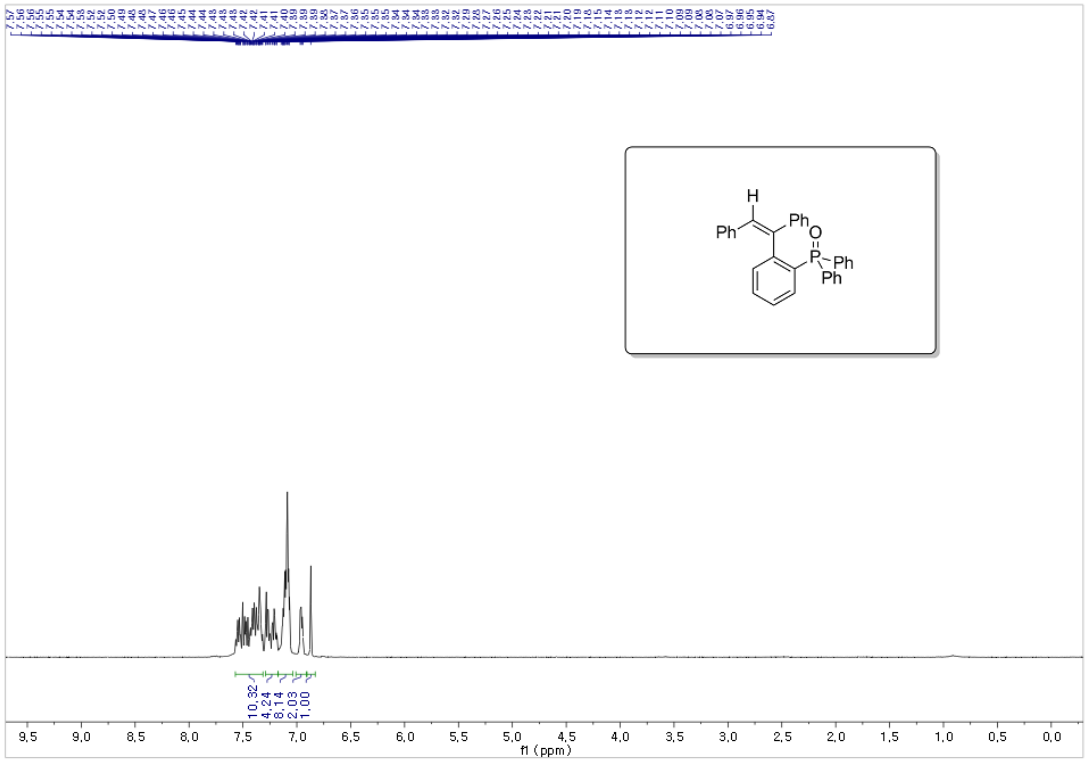


400 MHz, ^{1}H NMR in $CDCl_3$

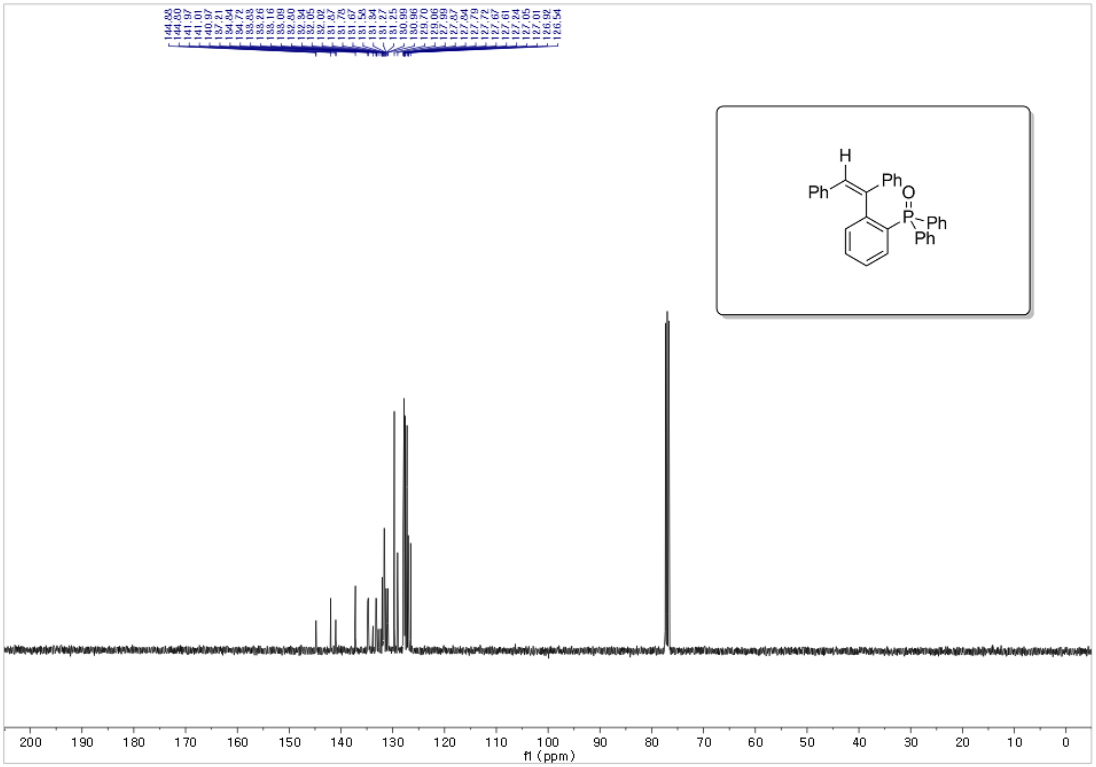


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-(2-(1,2-diphenylvinyl)phenyl)diphenylphosphine oxide (4j).

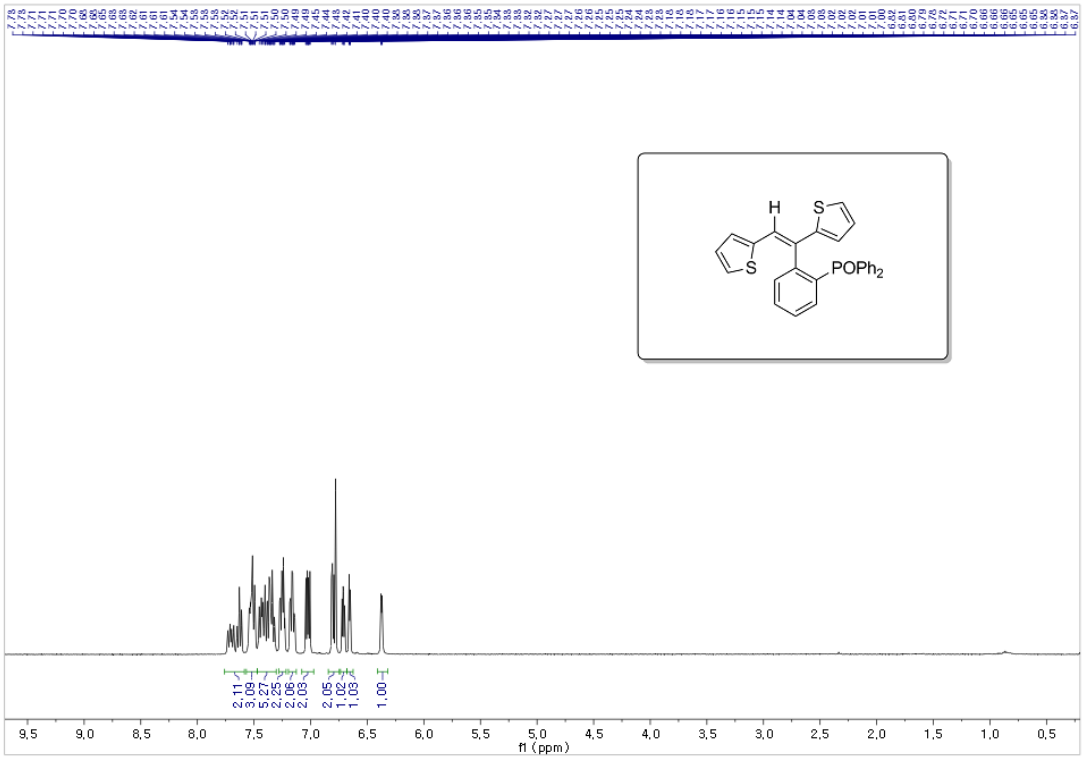


400 MHz, ^{1}H NMR in $CDCl_3$

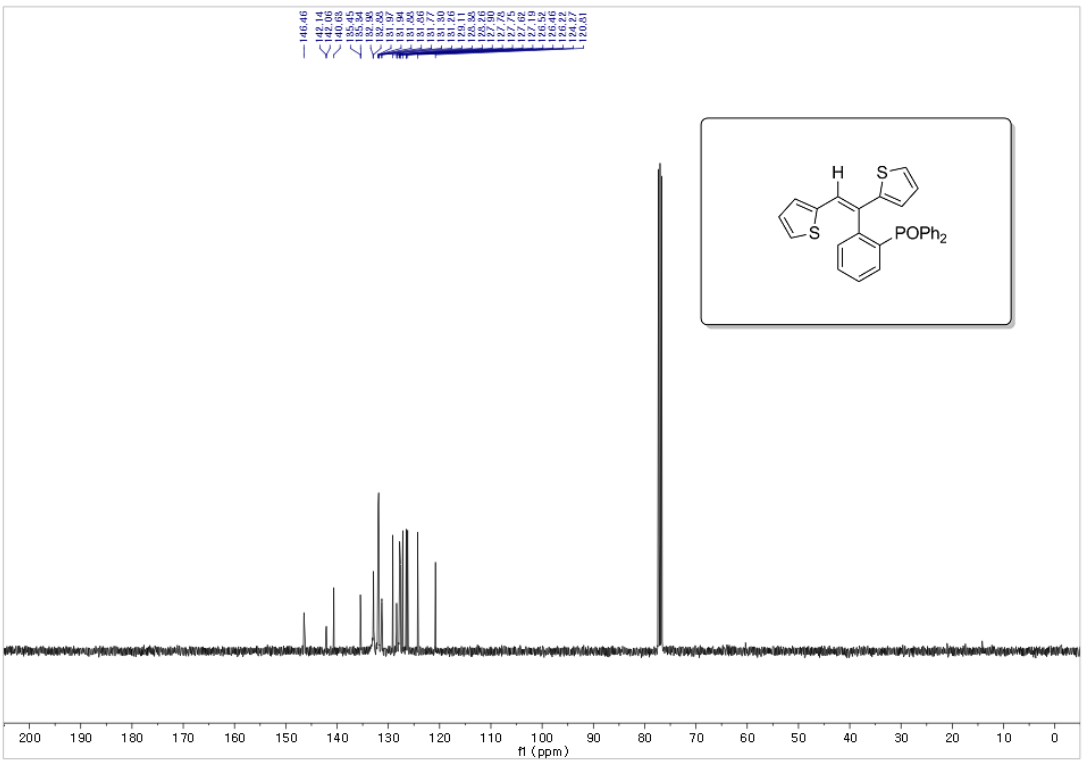


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-(2-(1,2-di(thiophen-2-yl)vinyl)phenyl)diphenylphosphine oxide (4k).

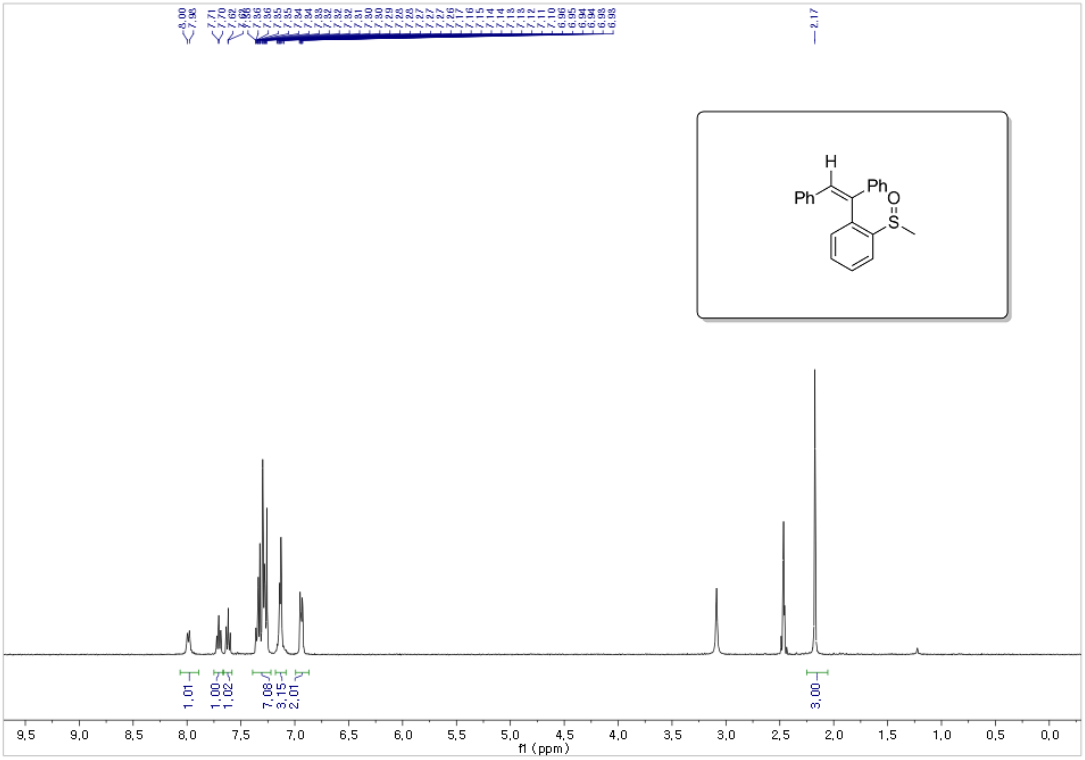


400 MHz, ^{1}H NMR in $CDCl_3$

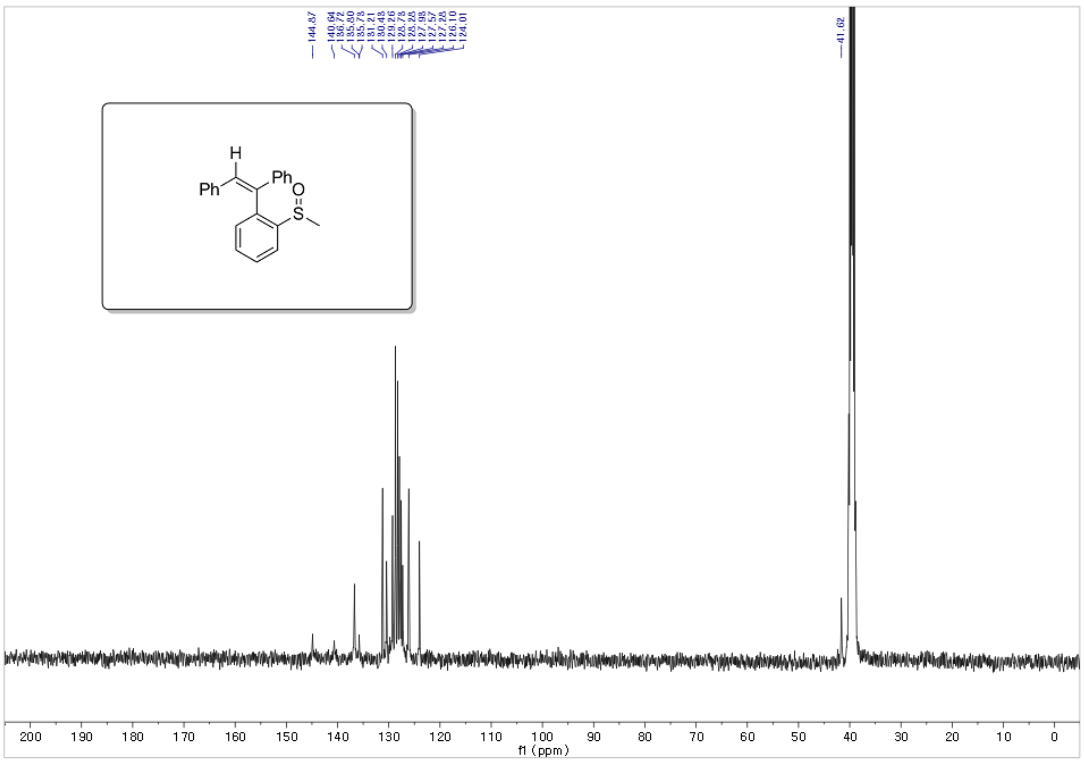


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-(1-(2-(methylsulfinyl)phenyl)ethene-1,2-diyl)dibenzene (4l)

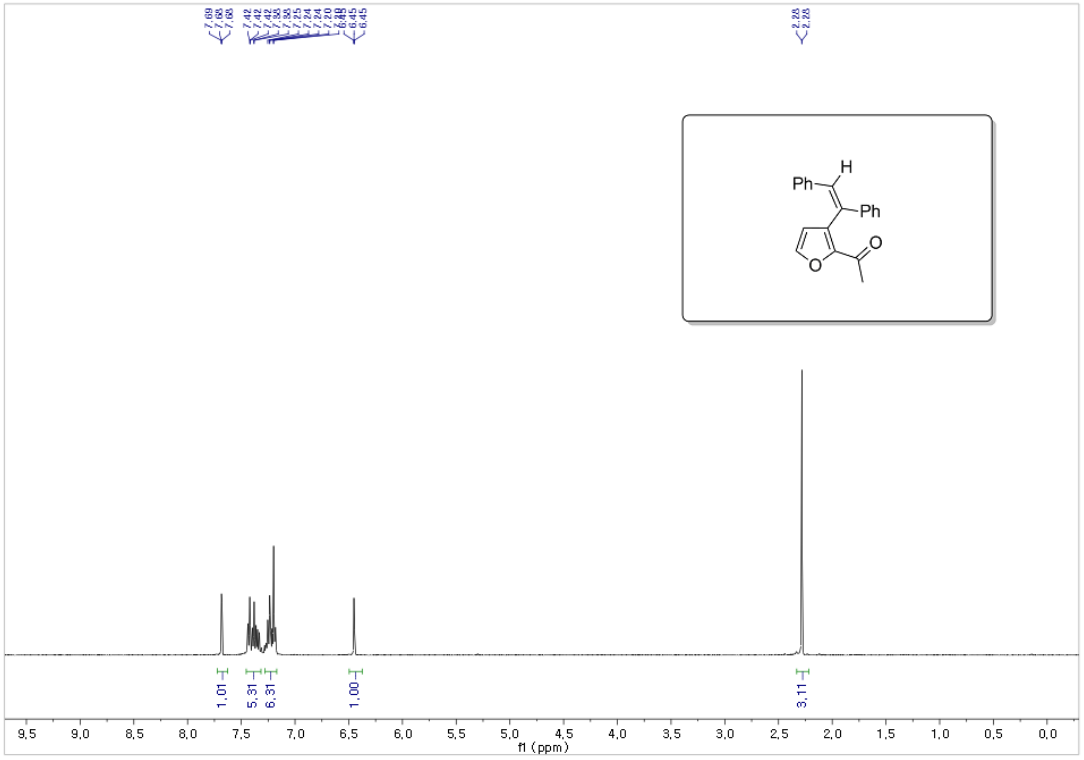


400 MHz, ^{1}H NMR in DMSO-d$_6$ (60 ^{o}C)

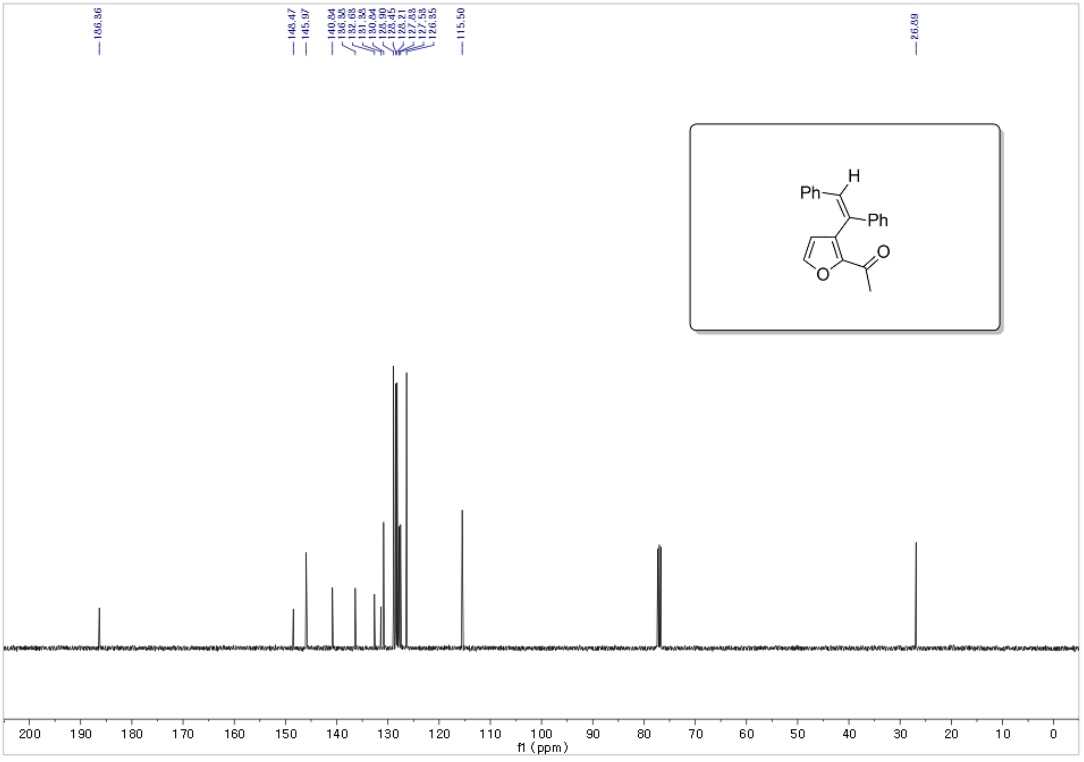


100 MHz, ^{13}C NMR in DMSO-d$_6$ (60 ^{o}C)

(Z)-1-(3-(1,2-diphenylvinyl)furan-2-yl)ethanone (4m).

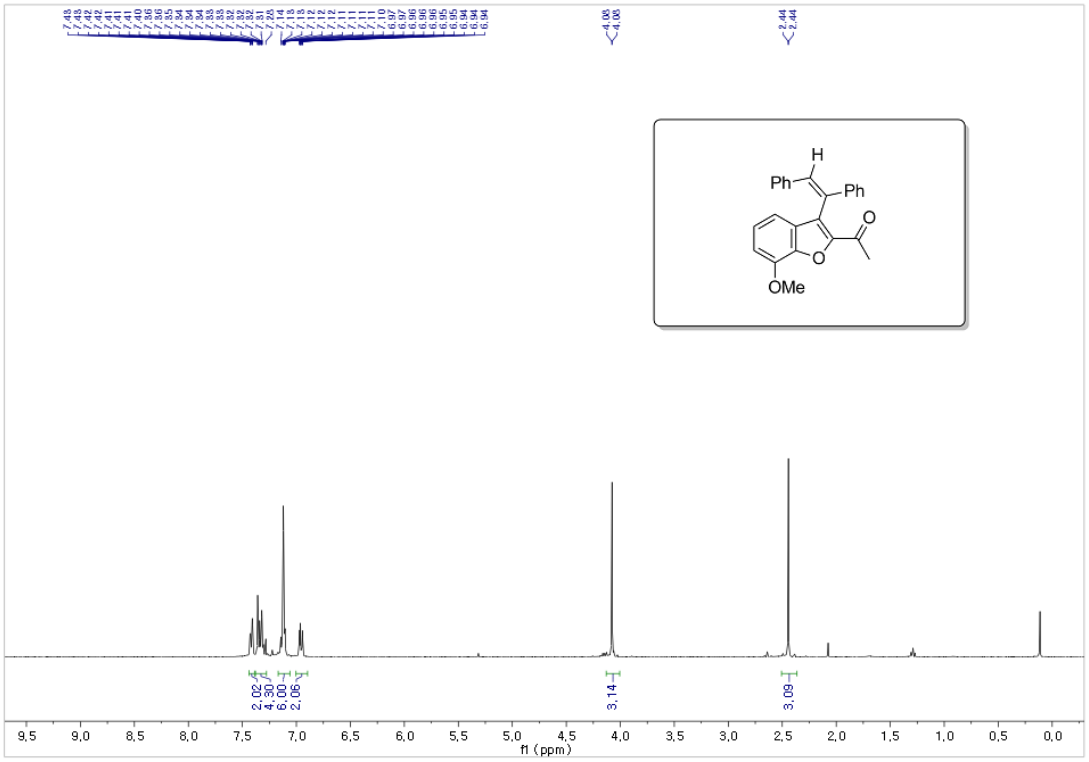


400 MHz, ^{1}H NMR in $CDCl_3$

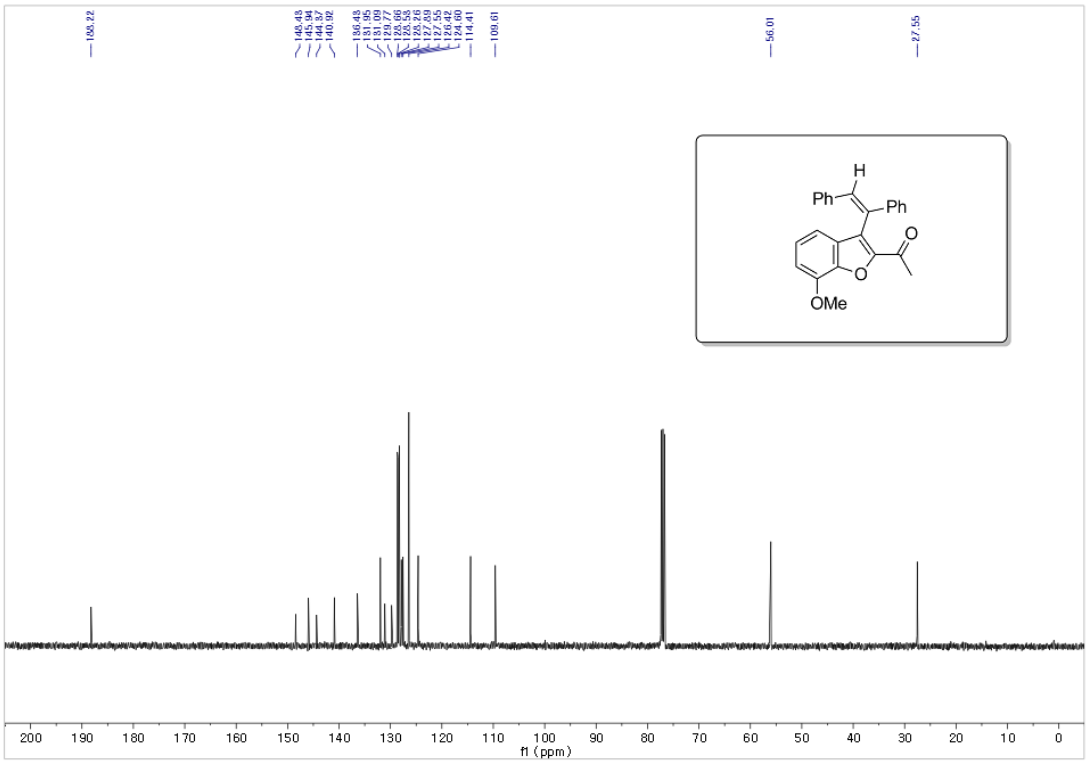


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-1-(3-(1,2-diphenylvinyl)-7-methoxybenzofuran-2-yl)ethanone (4n).

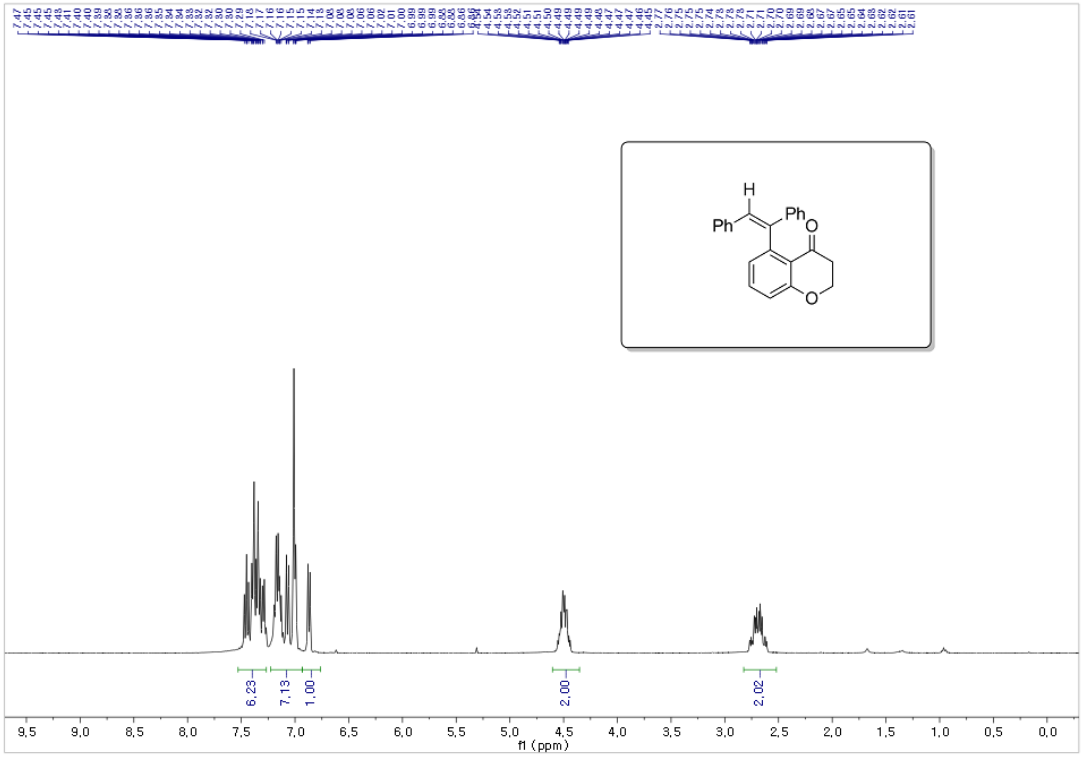


400 MHz, ^{1}H NMR in $CDCl_3$

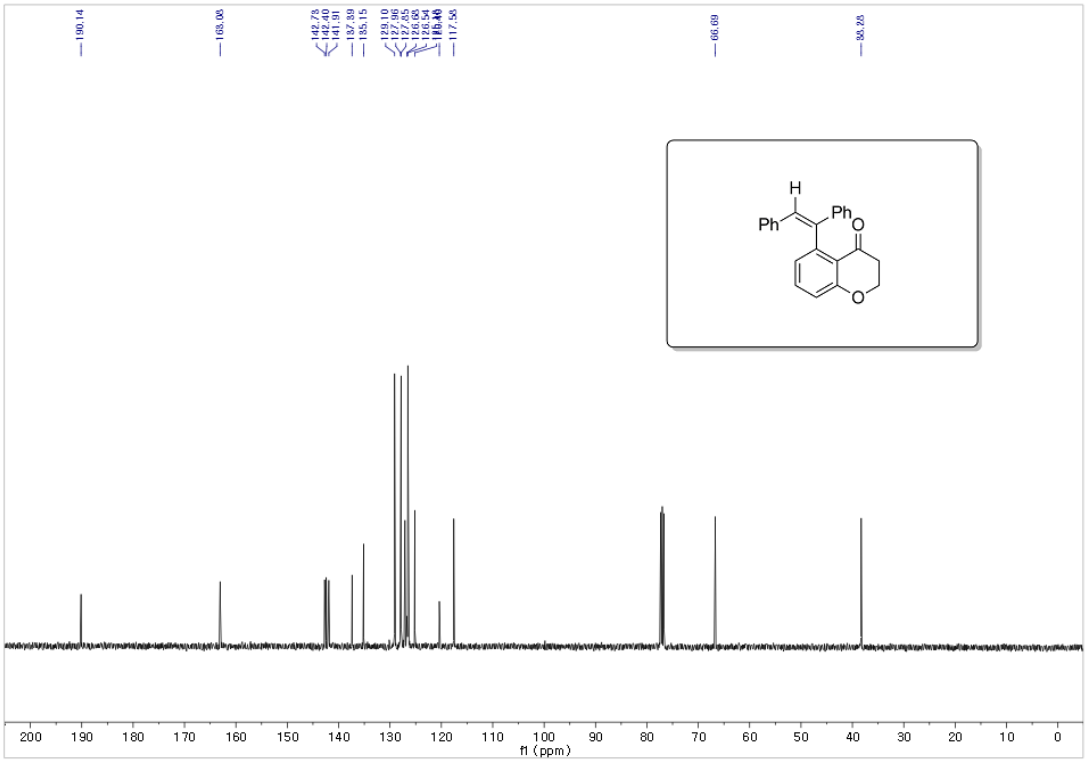


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-5-(1,2-diphenylvinyl)chroman-4-one (4o).

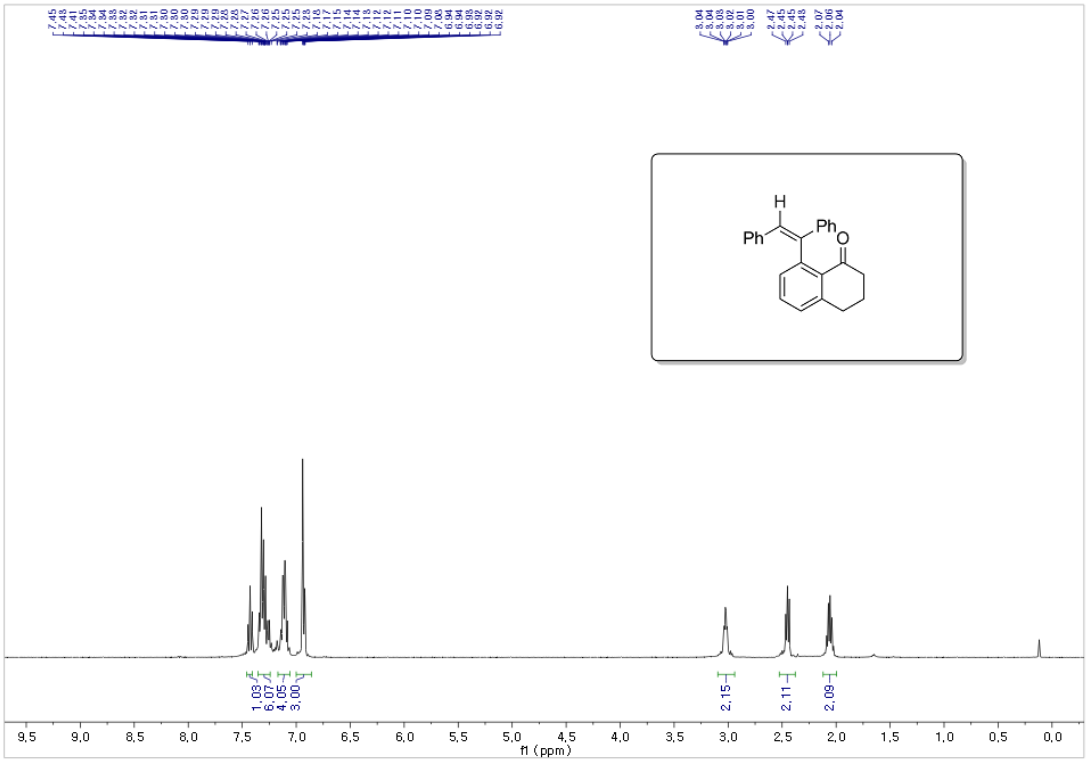


400 MHz, ^{1}H NMR in $CDCl_3$

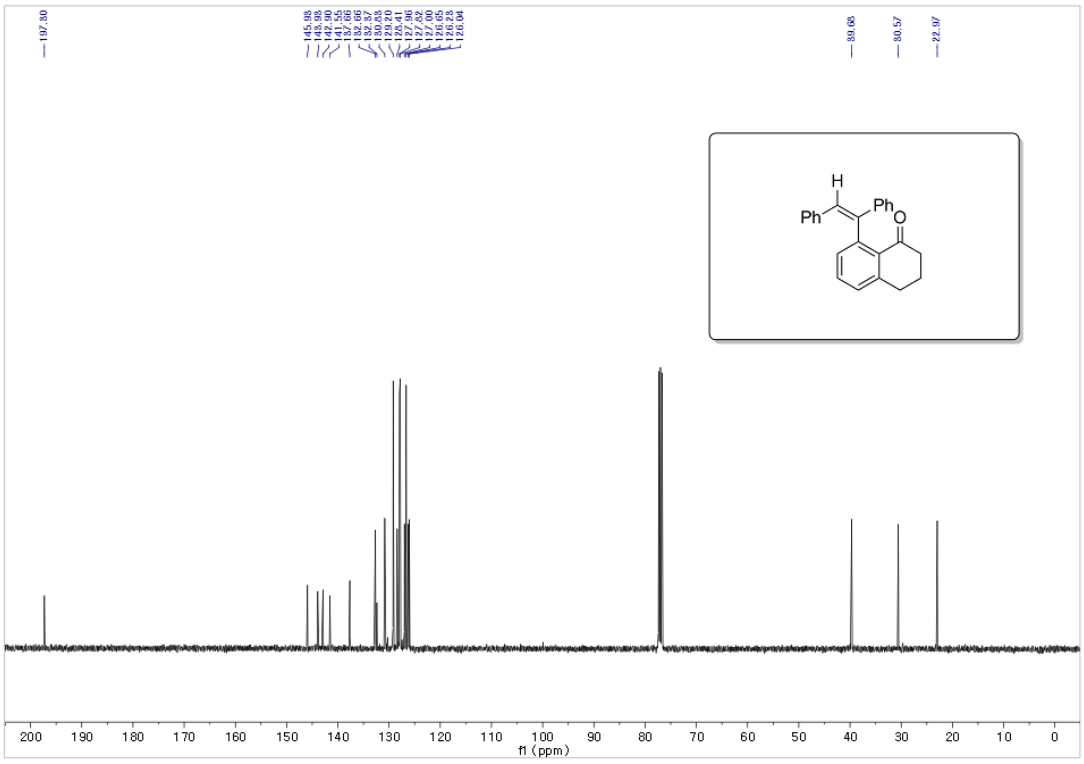


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-8-(1,2-diphenylvinyl)-3,4-dihydronaphthalen-1(2H)-one (4p).

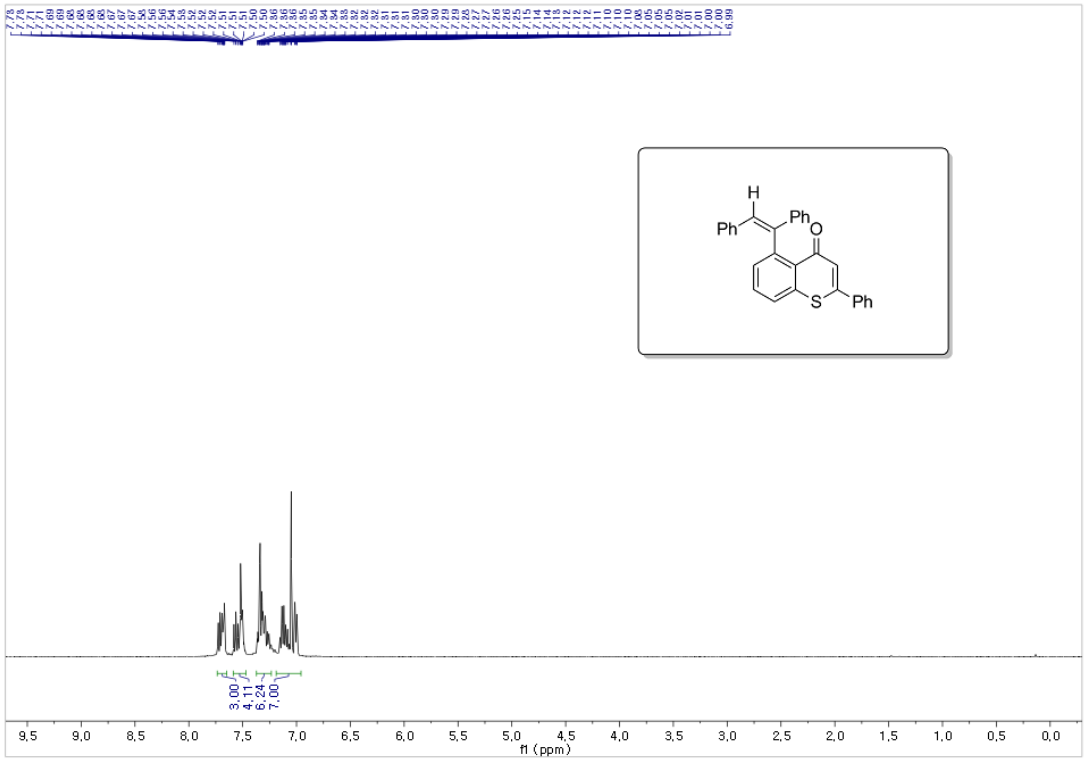


400 MHz, ^{1}H NMR in $CDCl_3$

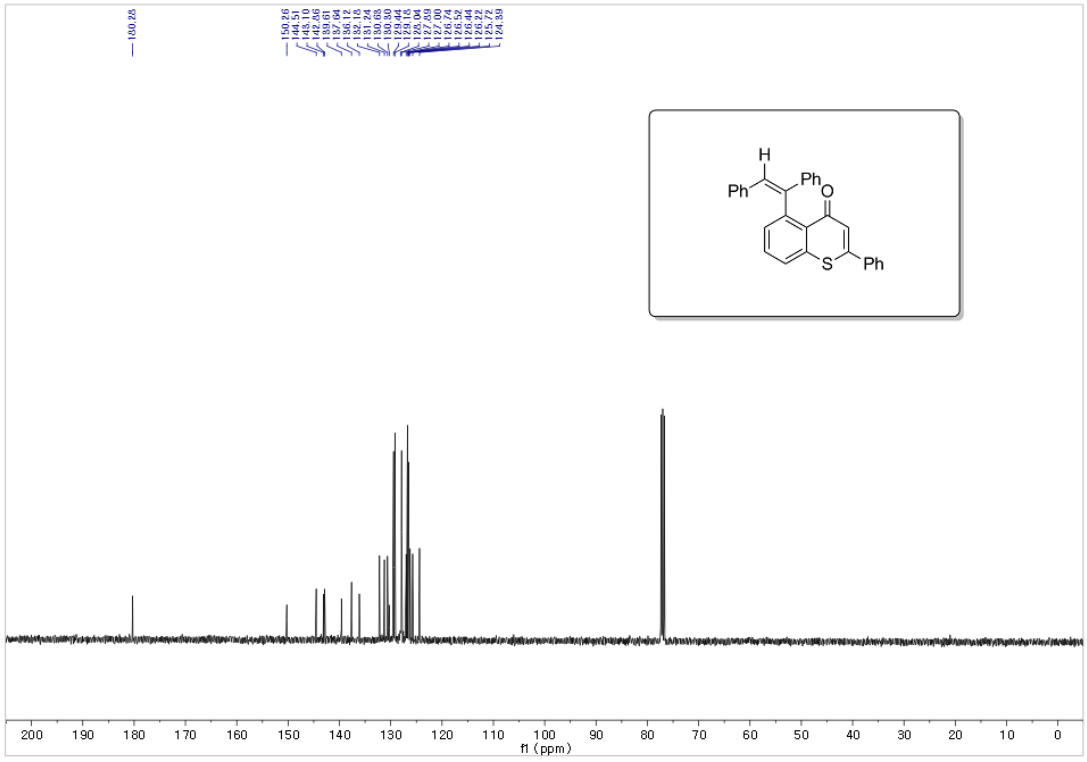


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-5-(1,2-diphenylvinyl)-2-phenyl-4H-thiochromen-4-one (4q).

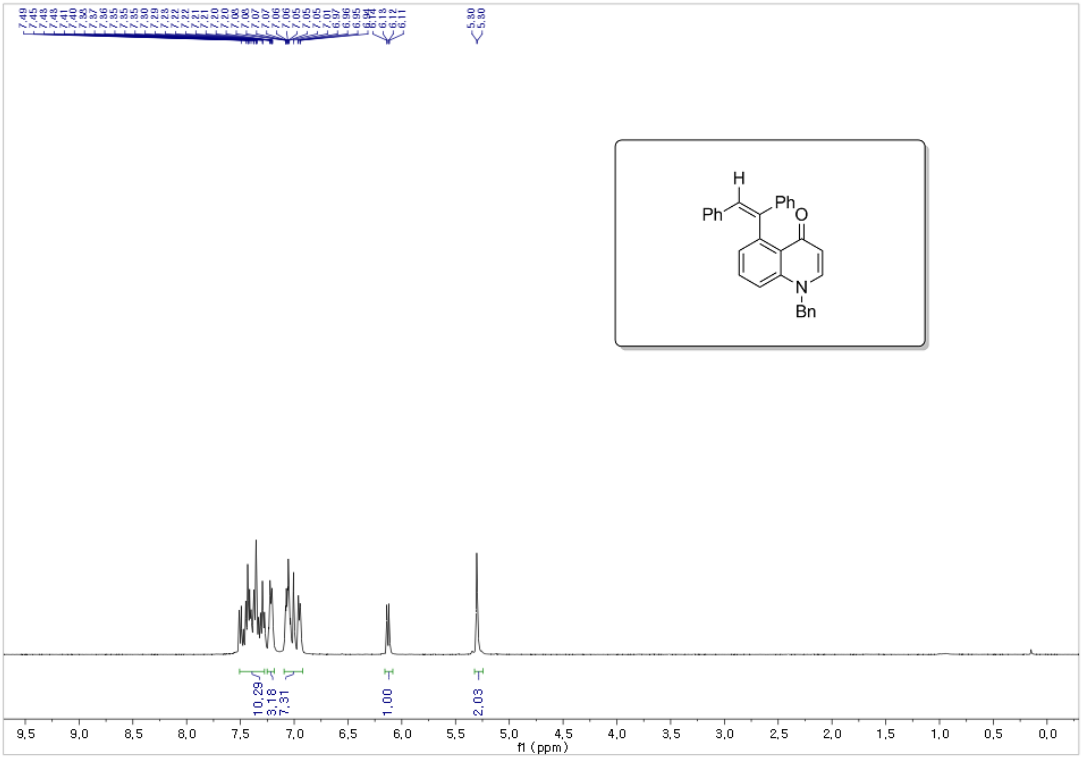


400 MHz, ^{1}H NMR in $CDCl_3$

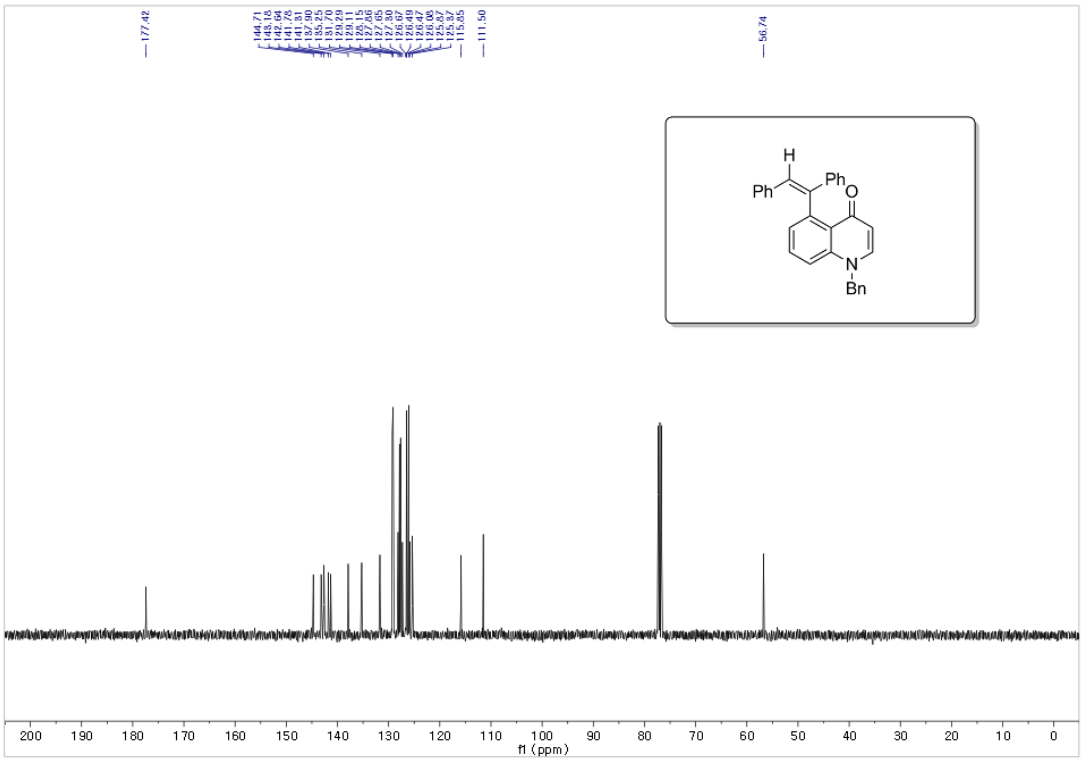


100 MHz, ^{13}C NMR in $CDCl_3$

(Z)-1-benzyl-5-(1,2-diphenylvinyl)quinolin-4(1H)-one (4r).



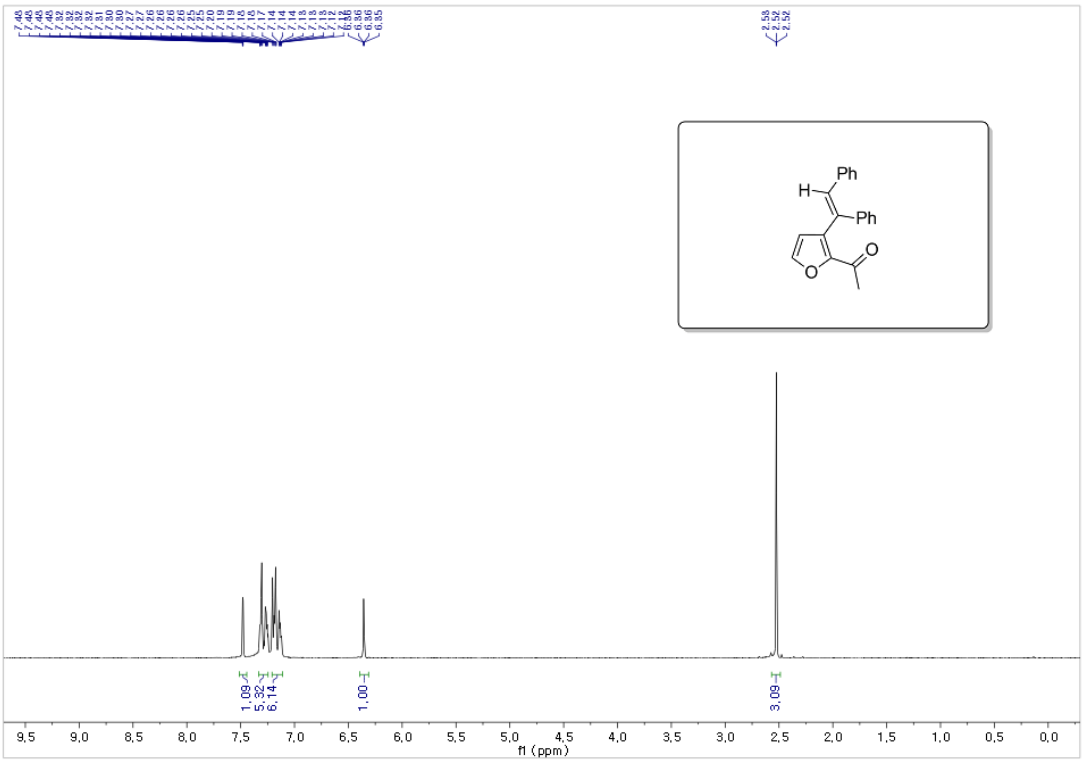
400 MHz, ^{1}H NMR in $CDCl_3$



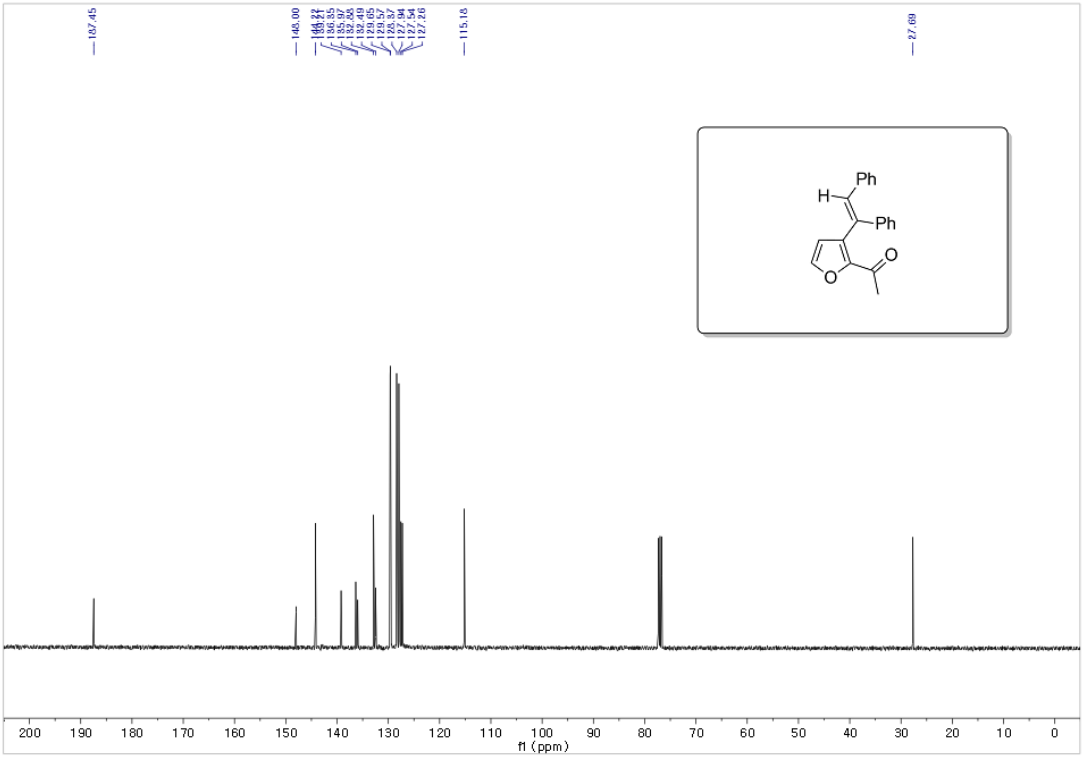
100 MHz, ^{13}C NMR in $CDCl_3$

Preparation of Starting Materials (*E*-Isomer)

(E)-1-(3-(1,2-diphenylvinyl)furan-2-yl)ethanone.

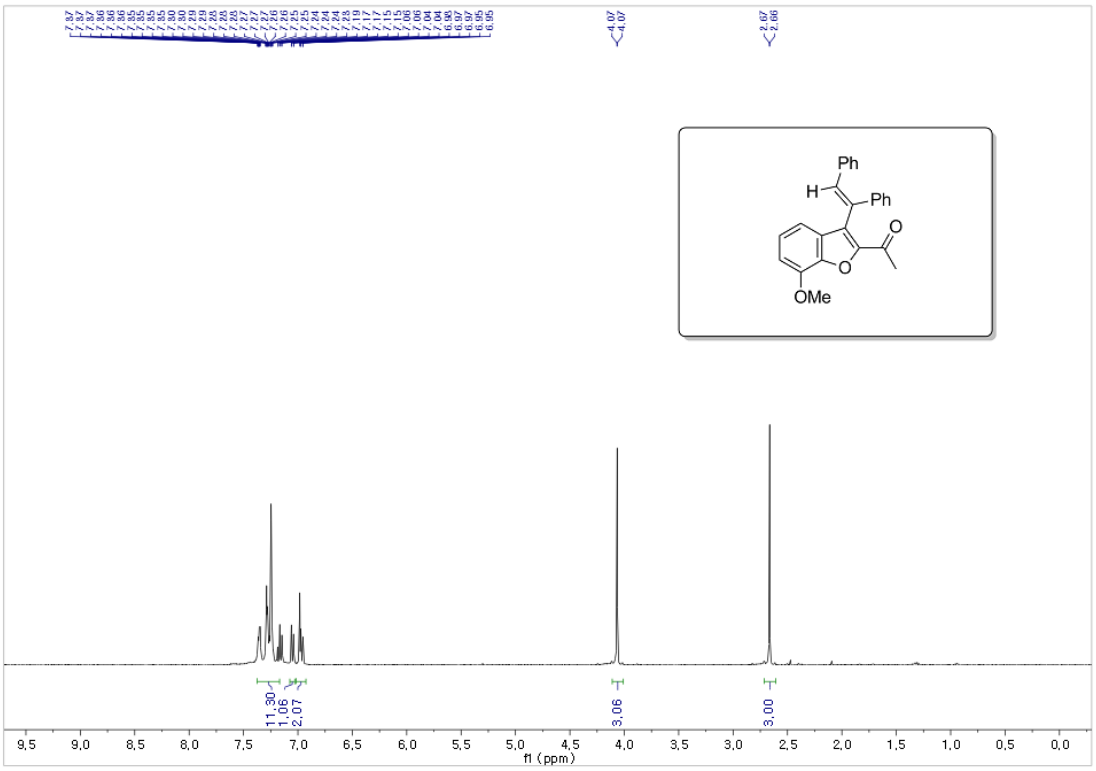


400 MHz, ^{1}H NMR in $CDCl_3$

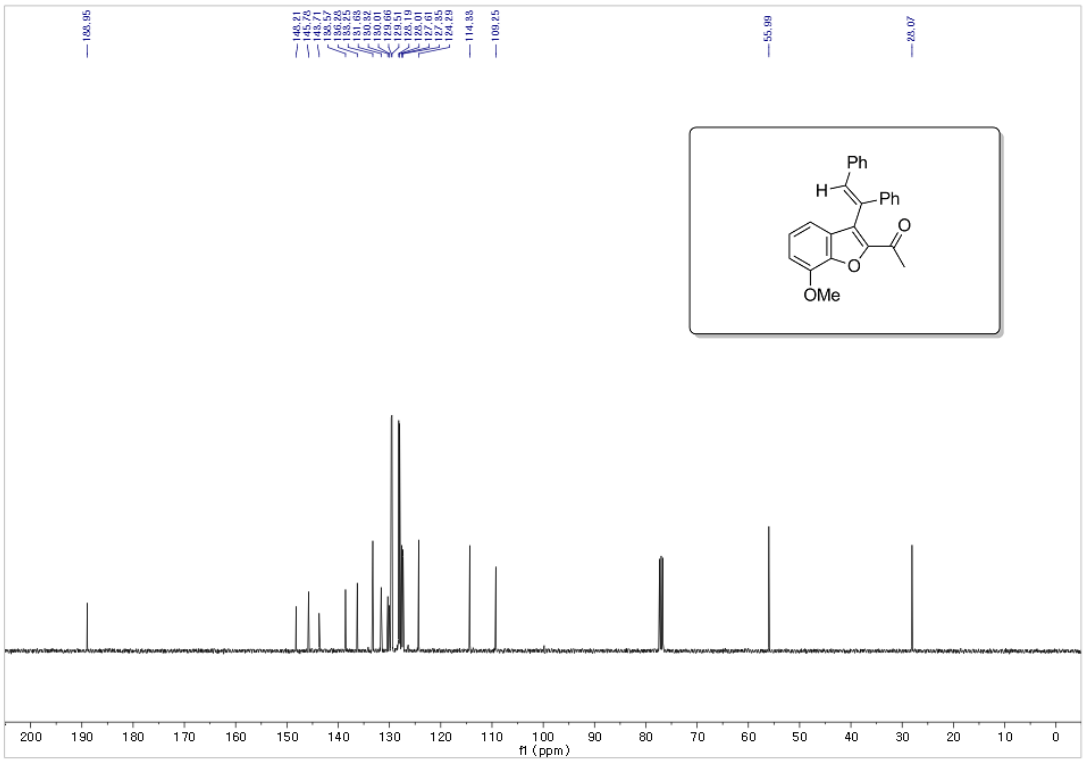


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-1-(3-(1,2-diphenylvinyl)-7-methoxybenzofuran-2-yl)ethanone.

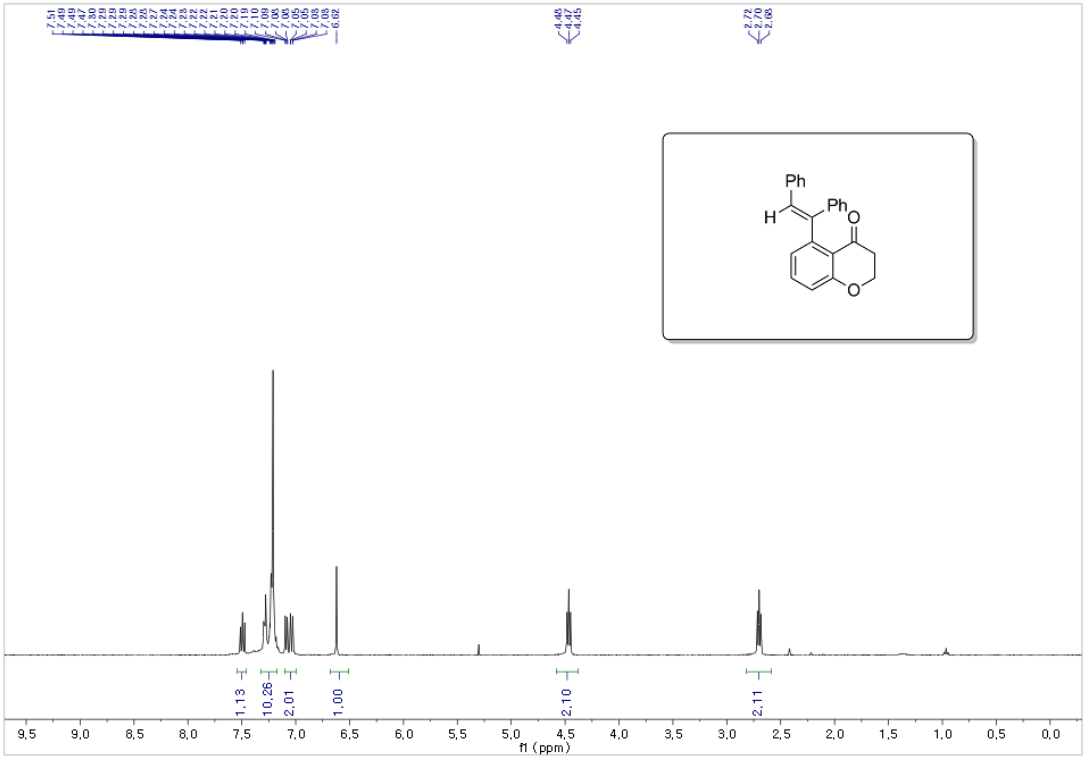


400 MHz, ^{1}H NMR in $CDCl_3$

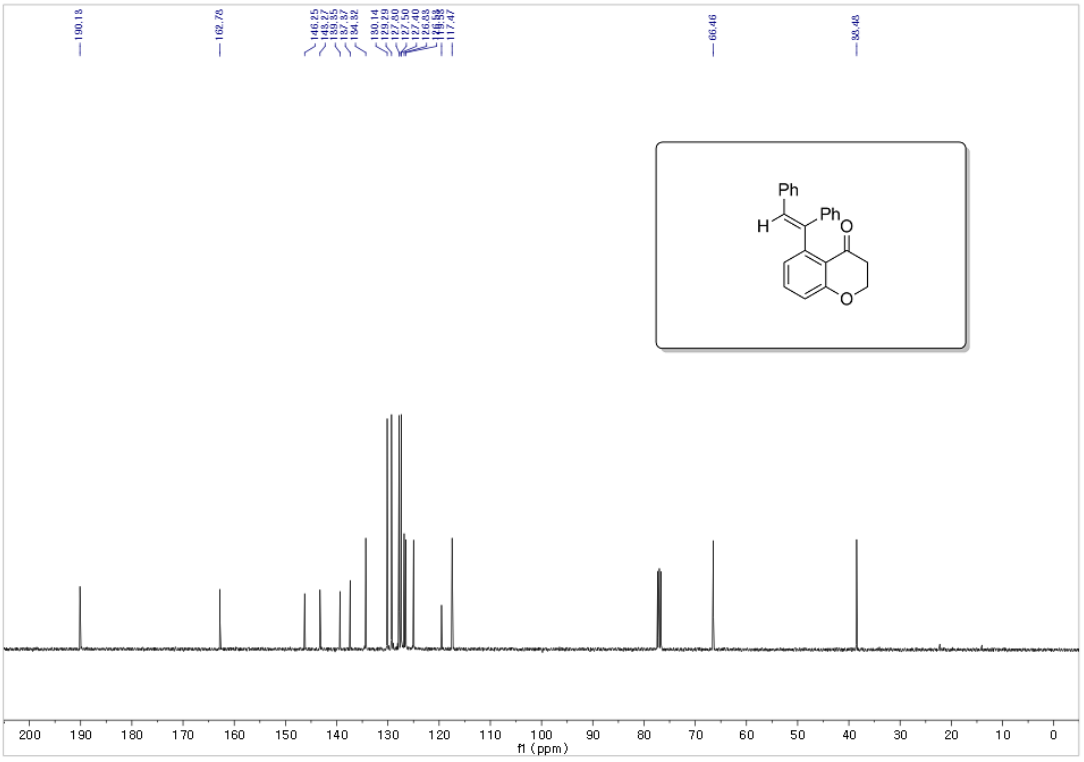


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-5-(1,2-diphenylvinyl)chroman-4-one.

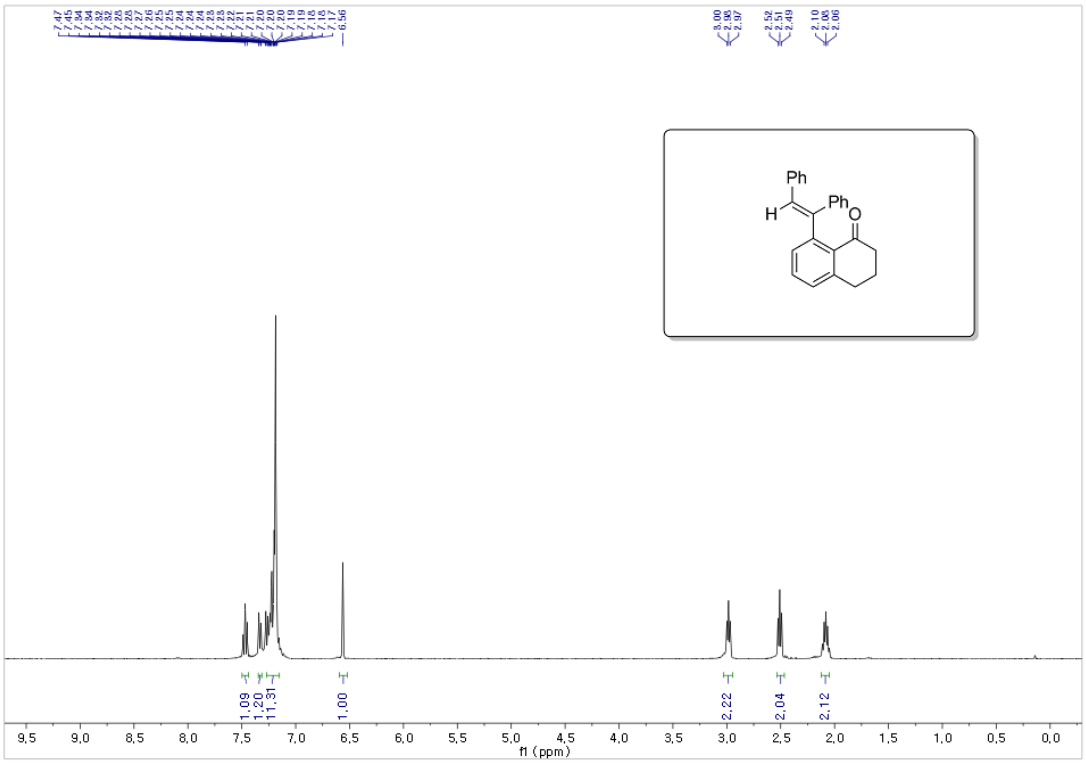


400 MHz, ^{1}H NMR in $CDCl_3$

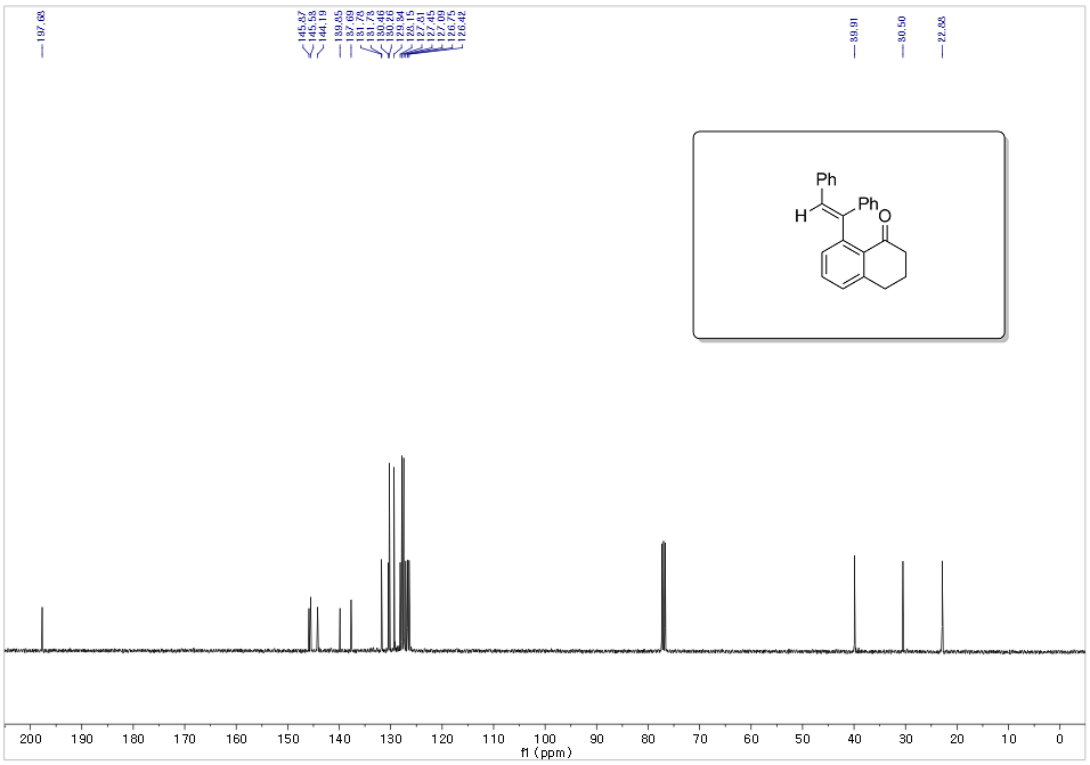


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-8-(1,2-diphenylvinyl)-3,4-dihydronaphthalen-1(2H)-one.

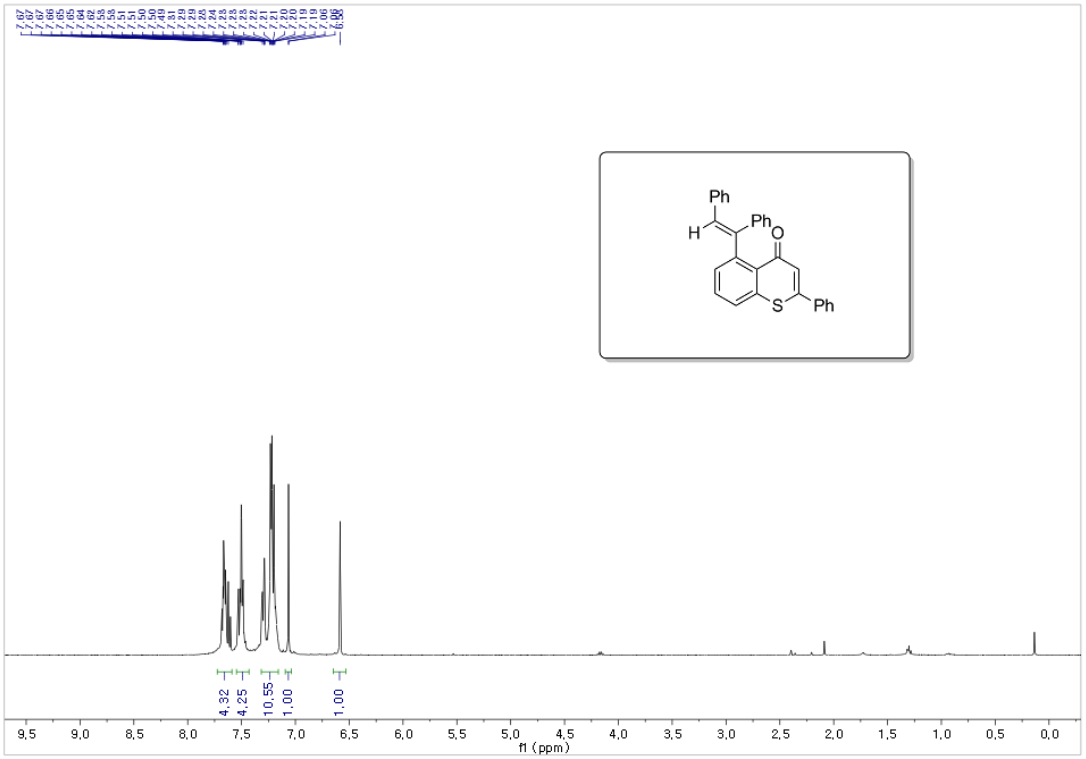


400 MHz, ^{1}H NMR in $CDCl_3$

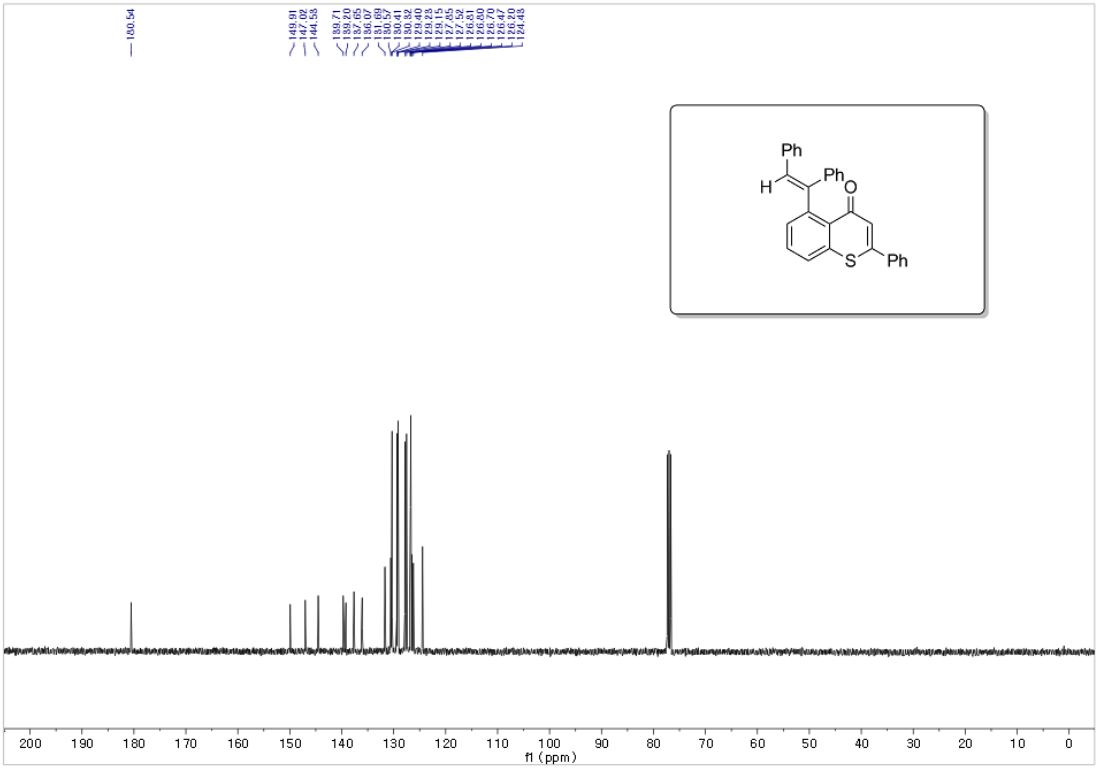


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-5-(1,2-diphenylvinyl)-2-phenyl-4H-thiochromen-4-one.

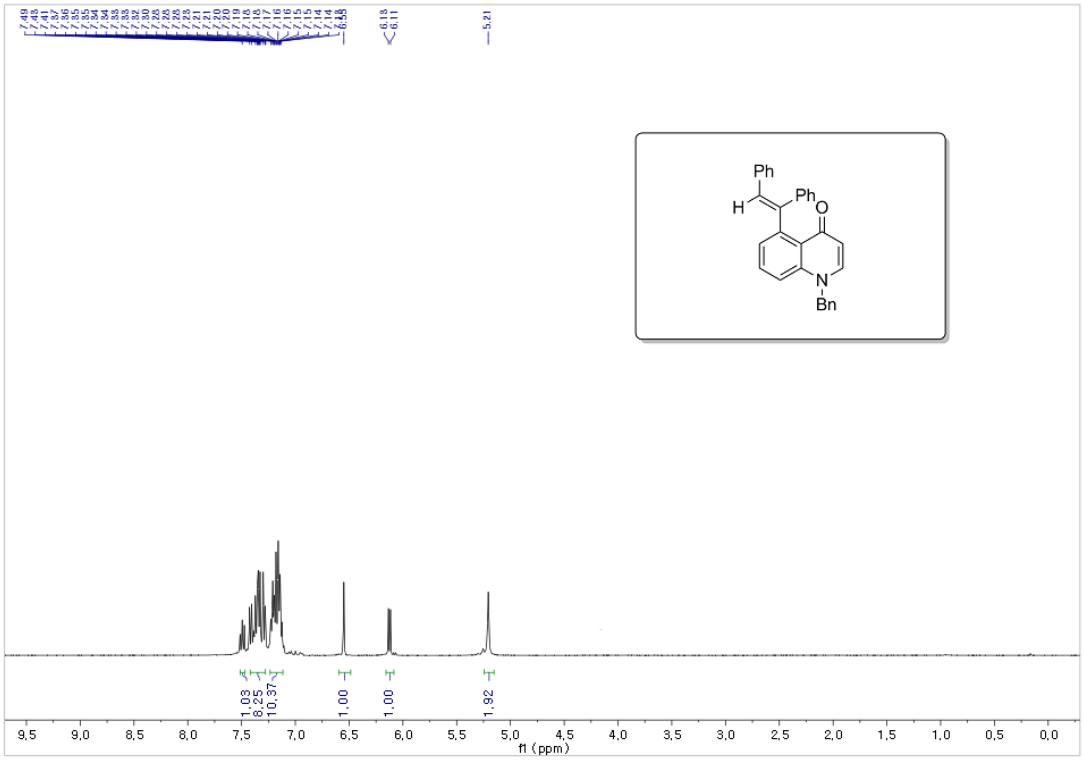


400 MHz, ^{1}H NMR in $CDCl_3$

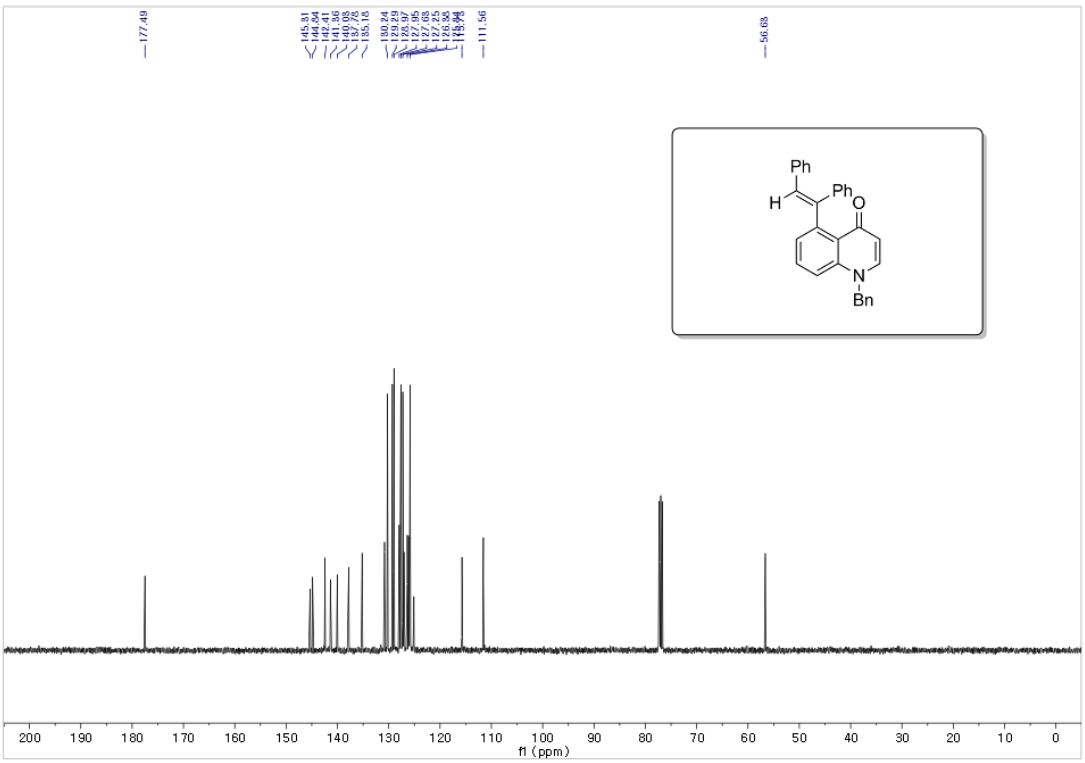


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-1-benzyl-5-(1,2-diphenylvinyl)quinolin-4(1H)-one.

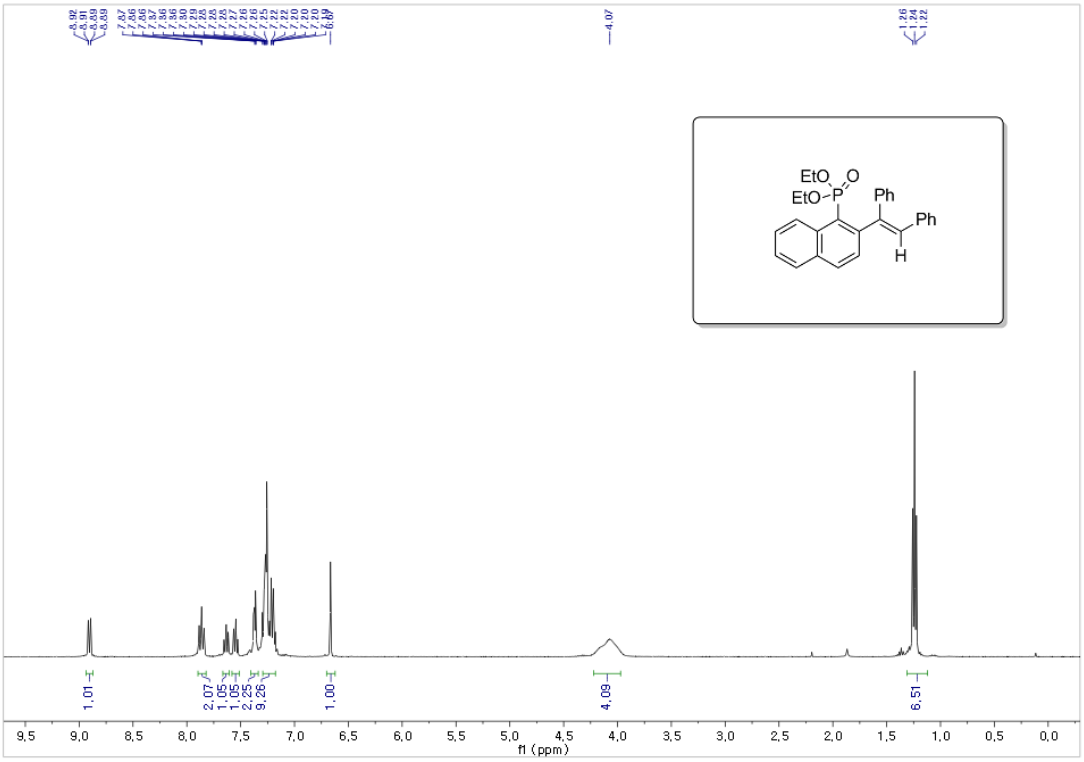


400 MHz, ^{1}H NMR in $CDCl_3$

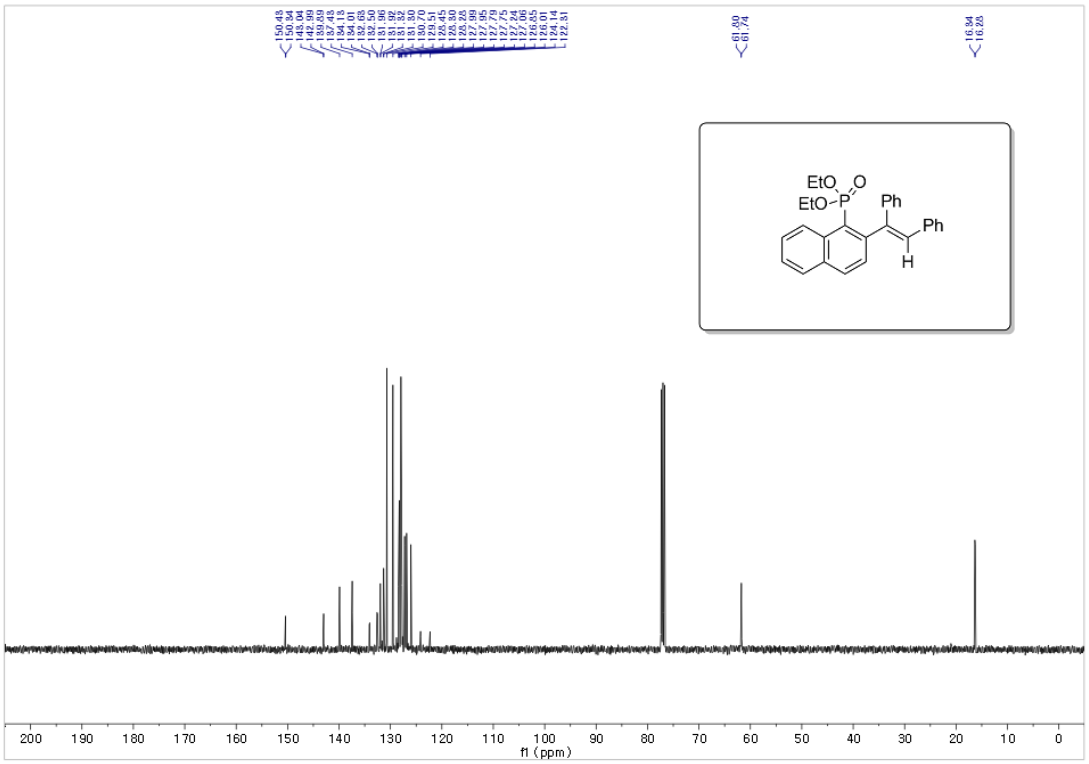


100 MHz, ^{13}C NMR in $CDCl_3$

(E)-diethyl (2-(1,2-diphenylvinyl)naphthalen-1-yl)phosphonate.



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



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

Appendix II

Crystallographic Data for 3b

Crystallographic Data for 3b

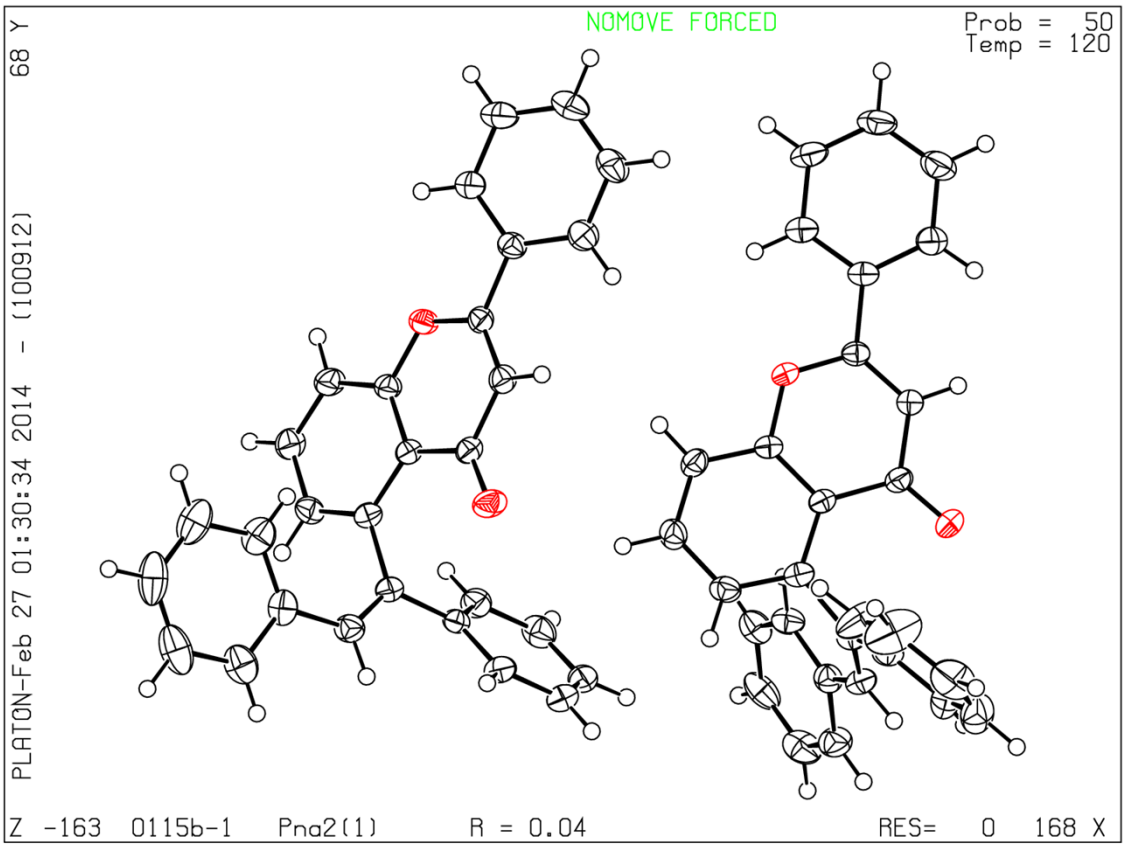


Table 1. Crystal data and structure refinement for **3b**.

Identification code	0115b-1	
Empirical formula	C29 H20 O2	
Formula weight	400.45	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pna2(1)	
Unit cell dimensions	a = 7.9125(4) Å	α= 90°.
	b = 17.8240(9) Å	β= 90°.
	c = 29.6276(16) Å	γ = 90°.
Volume	4178.5(4) $Å^3$	
Z	8	
Density (calculated)	1.273 Mg/m^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	1680	
Crystal size	0.43 x 0.33 x 0.30 mm^3	
Theta range for data collection	1.33 to 30.27°.	
Index ranges	-10<=h<=10, -25<=k<=11, -41<=l<=34	

Reflections collected	43042
Independent reflections	10984 [R(int) = 0.0243]
Completeness to theta = 25.00	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9768 and 0.9670
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10984 / 1 / 559
Goodness-of-fit on F^2	1.097
Final R indices [I>2sigma(I)]	R1 = 0.0429, wR2 = 0.1135
R indices (all data)	R1 = 0.0497, wR2 = 0.1254
Largest diff. peak and hole	0.355 and -0.221 $e.^{-3}$

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

	x	y	z	U(eq)
O(1)	9158(2)	4946(1)	4014(1)	36(1)
O(2)	7788(2)	6828(1)	4710(1)	29(1)
O(3)	3988(2)	5249(1)	1502(1)	40(1)
O(4)	5799(1)	6609(1)	2495(1)	26(1)
C(1)	8454(3)	8245(1)	4421(1)	36(1)
C(2)	8497(3)	8983(1)	4266(1)	45(1)
C(3)	8460(3)	9132(1)	3810(1)	42(1)
C(4)	8361(2)	8545(1)	3503(1)	39(1)
C(5)	8313(2)	7809(1)	3657(1)	33(1)
C(6)	8371(2)	7653(1)	4114(1)	27(1)
C(7)	8336(2)	6868(1)	4277(1)	24(1)
C(8)	8806(2)	6252(1)	4045(1)	28(1)
C(9)	8705(2)	5501(1)	4231(1)	25(1)
C(10)	8058(2)	5466(1)	4697(1)	23(1)
C(11)	7665(2)	6138(1)	4918(1)	25(1)
C(12)	7121(3)	6169(1)	5362(1)	33(1)
C(13)	6964(2)	5509(1)	5600(1)	34(1)
C(14)	7328(2)	4824(1)	5391(1)	29(1)
C(15)	7854(2)	4792(1)	4946(1)	25(1)
C(16)	8079(2)	4035(1)	4733(1)	25(1)
C(17)	9321(2)	3557(1)	4843(1)	30(1)
C(18)	10774(2)	3672(1)	5145(1)	33(1)
C(19)	11402(2)	4370(1)	5285(1)	41(1)
C(20)	12766(3)	4422(2)	5576(1)	50(1)
C(21)	13534(3)	3779(2)	5732(1)	56(1)
C(22)	12959(3)	3083(2)	5595(1)	55(1)
C(23)	11600(2)	3027(1)	5299(1)	43(1)
C(24)	6709(2)	3803(1)	4415(1)	25(1)
C(25)	7051(2)	3321(1)	4058(1)	32(1)
C(26)	5802(3)	3117(1)	3758(1)	36(1)
C(27)	4176(2)	3392(1)	3807(1)	35(1)
C(28)	3796(2)	3860(1)	4167(1)	38(1)
C(29)	5062(2)	4065(1)	4468(1)	32(1)
C(30)	5470(2)	8121(1)	2513(1)	31(1)
C(31)	5518(2)	8899(1)	2507(1)	38(1)

C(32)	5157(3)	9291(1)	2117(1)	42(1)
C(33)	4714(3)	8905(1)	1730(1)	46(1)
C(34)	4659(3)	8126(1)	1732(1)	37(1)
C(35)	5049(2)	7725(1)	2122(1)	26(1)
C(36)	5037(2)	6897(1)	2122(1)	23(1)
C(37)	4378(2)	6456(1)	1800(1)	26(1)
C(38)	4524(2)	5644(1)	1809(1)	27(1)
C(39)	5355(2)	5341(1)	2215(1)	23(1)
C(40)	5908(2)	5842(1)	2547(1)	23(1)
C(41)	6596(2)	5603(1)	2954(1)	28(1)
C(42)	6756(2)	4846(1)	3032(1)	30(1)
C(43)	6252(2)	4332(1)	2705(1)	30(1)
C(44)	5553(2)	4562(1)	2300(1)	26(1)
C(45)	5014(2)	3970(1)	1967(1)	30(1)
C(46)	3599(2)	3574(1)	2026(1)	31(1)
C(47)	2312(2)	3631(1)	2381(1)	29(1)
C(48)	2130(2)	4203(1)	2701(1)	30(1)
C(49)	928(2)	4163(1)	3038(1)	35(1)
C(50)	-134(2)	3550(1)	3065(1)	40(1)
C(51)	-26(2)	2992(1)	2753(1)	43(1)
C(52)	1167(2)	3024(1)	2412(1)	37(1)
C(53)	6231(2)	3787(1)	1592(1)	30(1)
C(54)	5803(3)	3353(1)	1225(1)	41(1)
C(55)	6947(3)	3197(1)	888(1)	51(1)
C(56)	8550(3)	3472(1)	903(1)	56(1)
C(57)	9051(4)	3905(2)	1275(1)	73(1)
C(58)	7891(3)	4052(2)	1619(1)	57(1)

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

O(1)-C(9)	1.2337(19)
O(2)-C(7)	1.356(2)
O(2)-C(11)	1.3795(19)
O(3)-C(38)	1.227(2)
O(4)-C(36)	1.357(2)
O(4)-C(40)	1.3788(18)
C(1)-C(2)	1.393(3)
C(1)-C(6)	1.394(2)
C(2)-C(3)	1.379(3)
C(3)-C(4)	1.388(3)
C(4)-C(5)	1.389(3)
C(5)-C(6)	1.385(3)
C(6)-C(7)	1.481(2)
C(7)-C(8)	1.349(2)
C(8)-C(9)	1.450(2)
C(9)-C(10)	1.473(2)
C(10)-C(11)	1.399(2)
C(10)-C(15)	1.419(2)
C(11)-C(12)	1.386(2)
C(12)-C(13)	1.376(2)
C(13)-C(14)	1.399(3)
C(14)-C(15)	1.382(2)
C(15)-C(16)	1.501(2)
C(16)-C(17)	1.340(2)
C(16)-C(24)	1.496(2)
C(17)-C(18)	1.471(2)
C(18)-C(23)	1.399(3)
C(18)-C(19)	1.402(3)
C(19)-C(20)	1.384(3)
C(20)-C(21)	1.377(4)
C(21)-C(22)	1.382(4)
C(22)-C(23)	1.391(3)
C(24)-C(25)	1.388(2)
C(24)-C(29)	1.394(2)
C(25)-C(26)	1.377(3)
C(26)-C(27)	1.385(3)
C(27)-C(28)	1.387(3)
C(28)-C(29)	1.391(3)

C(30)-C(31)	1.387(2)
C(30)-C(35)	1.398(3)
C(31)-C(32)	1.380(3)
C(32)-C(33)	1.381(3)
C(33)-C(34)	1.389(3)
C(34)-C(35)	1.392(3)
C(35)-C(36)	1.477(2)
C(36)-C(37)	1.341(2)
C(37)-C(38)	1.452(2)
C(38)-C(39)	1.473(2)
C(39)-C(40)	1.398(2)
C(39)-C(44)	1.421(2)
C(40)-C(41)	1.390(2)
C(41)-C(42)	1.376(2)
C(42)-C(43)	1.391(3)
C(43)-C(44)	1.383(3)
C(44)-C(45)	1.507(2)
C(45)-C(46)	1.335(2)
C(45)-C(53)	1.505(3)
C(46)-C(47)	1.466(3)
C(47)-C(48)	1.401(2)
C(47)-C(52)	1.414(2)
C(48)-C(49)	1.381(3)
C(49)-C(50)	1.381(3)
C(50)-C(51)	1.361(3)
C(51)-C(52)	1.383(3)
C(53)-C(54)	1.378(3)
C(53)-C(58)	1.398(3)
C(54)-C(55)	1.377(3)
C(55)-C(56)	1.361(4)
C(56)-C(57)	1.403(4)
C(57)-C(58)	1.395(3)

C(7)-O(2)-C(11)	119.41(13)
C(36)-O(4)-C(40)	119.52(12)
C(2)-C(1)-C(6)	120.09(19)
C(3)-C(2)-C(1)	120.3(2)
C(2)-C(3)-C(4)	119.84(18)
C(3)-C(4)-C(5)	119.95(19)
C(6)-C(5)-C(4)	120.61(18)

C(5)-C(6)-C(1)	119.20(16)
C(5)-C(6)-C(7)	120.50(15)
C(1)-C(6)-C(7)	120.30(16)
C(8)-C(7)-O(2)	121.95(14)
C(8)-C(7)-C(6)	126.74(15)
O(2)-C(7)-C(6)	111.30(13)
C(7)-C(8)-C(9)	122.75(16)
O(1)-C(9)-C(8)	121.61(16)
O(1)-C(9)-C(10)	123.79(15)
C(8)-C(9)-C(10)	114.59(14)
C(11)-C(10)-C(15)	117.08(15)
C(11)-C(10)-C(9)	118.60(14)
C(15)-C(10)-C(9)	124.28(14)
O(2)-C(11)-C(12)	114.21(14)
O(2)-C(11)-C(10)	122.62(15)
C(12)-C(11)-C(10)	123.17(15)
C(13)-C(12)-C(11)	118.67(16)
C(12)-C(13)-C(14)	120.06(17)
C(15)-C(14)-C(13)	121.28(16)
C(14)-C(15)-C(10)	119.72(14)
C(14)-C(15)-C(16)	118.20(14)
C(10)-C(15)-C(16)	121.94(15)
C(17)-C(16)-C(24)	120.59(15)
C(17)-C(16)-C(15)	123.82(15)
C(24)-C(16)-C(15)	115.35(13)
C(16)-C(17)-C(18)	129.20(16)
C(23)-C(18)-C(19)	117.78(18)
C(23)-C(18)-C(17)	116.70(18)
C(19)-C(18)-C(17)	125.51(17)
C(20)-C(19)-C(18)	121.4(2)
C(21)-C(20)-C(19)	119.9(2)
C(20)-C(21)-C(22)	120.1(2)
C(21)-C(22)-C(23)	120.3(2)
C(22)-C(23)-C(18)	120.5(2)
C(25)-C(24)-C(29)	118.42(16)
C(25)-C(24)-C(16)	120.71(15)
C(29)-C(24)-C(16)	120.87(15)
C(26)-C(25)-C(24)	120.98(17)
C(25)-C(26)-C(27)	120.43(18)
C(26)-C(27)-C(28)	119.60(17)

C(27)-C(28)-C(29)	119.73(17)
C(28)-C(29)-C(24)	120.81(17)
C(31)-C(30)-C(35)	119.99(18)
C(32)-C(31)-C(30)	120.71(19)
C(31)-C(32)-C(33)	119.72(16)
C(32)-C(33)-C(34)	120.2(2)
C(33)-C(34)-C(35)	120.61(19)
C(34)-C(35)-C(30)	118.81(14)
C(34)-C(35)-C(36)	120.84(16)
C(30)-C(35)-C(36)	120.35(16)
C(37)-C(36)-O(4)	122.00(13)
C(37)-C(36)-C(35)	125.95(16)
O(4)-C(36)-C(35)	112.05(14)
C(36)-C(37)-C(38)	122.67(16)
O(3)-C(38)-C(37)	122.10(16)
O(3)-C(38)-C(39)	123.34(15)
C(37)-C(38)-C(39)	114.56(14)
C(40)-C(39)-C(44)	117.73(15)
C(40)-C(39)-C(38)	118.64(13)
C(44)-C(39)-C(38)	123.56(14)
O(4)-C(40)-C(41)	115.16(13)
O(4)-C(40)-C(39)	122.37(14)
C(41)-C(40)-C(39)	122.47(14)
C(42)-C(41)-C(40)	118.89(15)
C(41)-C(42)-C(43)	120.13(17)
C(44)-C(43)-C(42)	121.59(15)
C(43)-C(44)-C(39)	119.18(15)
C(43)-C(44)-C(45)	118.32(14)
C(39)-C(44)-C(45)	122.50(15)
C(46)-C(45)-C(53)	121.29(16)
C(46)-C(45)-C(44)	121.39(16)
C(53)-C(45)-C(44)	117.01(15)
C(45)-C(46)-C(47)	129.80(16)
C(48)-C(47)-C(52)	116.53(16)
C(48)-C(47)-C(46)	127.39(15)
C(52)-C(47)-C(46)	116.04(16)
C(49)-C(48)-C(47)	121.52(16)
C(50)-C(49)-C(48)	120.14(19)
C(51)-C(50)-C(49)	120.03(19)
C(50)-C(51)-C(52)	120.61(18)

C(51)-C(52)-C(47)	121.12(19)
C(54)-C(53)-C(58)	117.65(18)
C(54)-C(53)-C(45)	123.18(17)
C(58)-C(53)-C(45)	119.15(17)
C(55)-C(54)-C(53)	121.7(2)
C(56)-C(55)-C(54)	121.1(2)
C(55)-C(56)-C(57)	119.1(2)
C(58)-C(57)-C(56)	119.4(2)
C(57)-C(58)-C(53)	121.0(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **3b**. The anisotropic displacement factor exponent takes the form : $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	47(1)	28(1)	32(1)	-8(1)	9(1)	0(1)
O(2)	41(1)	21(1)	25(1)	1(1)	6(1)	-1(1)
O(3)	59(1)	29(1)	31(1)	-7(1)	-14(1)	-1(1)
O(4)	33(1)	19(1)	26(1)	-5(1)	-3(1)	-1(1)
C(1)	51(1)	26(1)	31(1)	0(1)	-2(1)	-3(1)
C(2)	62(1)	24(1)	50(1)	1(1)	1(1)	-4(1)
C(3)	45(1)	29(1)	52(1)	12(1)	3(1)	-3(1)
C(4)	41(1)	39(1)	36(1)	13(1)	4(1)	-5(1)
C(5)	35(1)	34(1)	31(1)	3(1)	4(1)	-4(1)
C(6)	26(1)	25(1)	29(1)	3(1)	1(1)	-3(1)
C(7)	26(1)	25(1)	21(1)	1(1)	1(1)	-4(1)
C(8)	30(1)	30(1)	23(1)	0(1)	3(1)	-3(1)
C(9)	26(1)	26(1)	23(1)	-3(1)	1(1)	-5(1)
C(10)	24(1)	22(1)	24(1)	-2(1)	0(1)	-2(1)
C(11)	30(1)	22(1)	24(1)	0(1)	2(1)	-2(1)
C(12)	47(1)	27(1)	25(1)	-4(1)	8(1)	-1(1)
C(13)	42(1)	35(1)	24(1)	-1(1)	8(1)	-6(1)
C(14)	32(1)	26(1)	29(1)	5(1)	1(1)	-5(1)
C(15)	24(1)	23(1)	27(1)	-2(1)	0(1)	-2(1)
C(16)	26(1)	22(1)	28(1)	-1(1)	0(1)	-3(1)
C(17)	28(1)	27(1)	35(1)	0(1)	-2(1)	1(1)
C(18)	23(1)	45(1)	31(1)	-1(1)	1(1)	4(1)
C(19)	27(1)	50(1)	45(1)	-5(1)	-3(1)	1(1)
C(20)	31(1)	75(2)	43(1)	-15(1)	-1(1)	-5(1)
C(21)	29(1)	102(2)	35(1)	2(1)	-6(1)	2(1)
C(22)	33(1)	82(2)	48(1)	19(1)	-2(1)	19(1)
C(23)	34(1)	51(1)	43(1)	6(1)	2(1)	11(1)
C(24)	27(1)	20(1)	27(1)	3(1)	-2(1)	-1(1)
C(25)	34(1)	25(1)	37(1)	-4(1)	-1(1)	-1(1)
C(26)	44(1)	27(1)	38(1)	-4(1)	-7(1)	-5(1)
C(27)	39(1)	28(1)	40(1)	4(1)	-13(1)	-10(1)
C(28)	29(1)	36(1)	49(1)	7(1)	-6(1)	1(1)
C(29)	31(1)	30(1)	35(1)	-1(1)	-2(1)	4(1)
C(30)	34(1)	23(1)	38(1)	-3(1)	1(1)	-1(1)
C(31)	37(1)	23(1)	53(1)	-11(1)	-5(1)	-1(1)

C(32)	38(1)	20(1)	69(1)	1(1)	-14(1)	2(1)
C(33)	50(1)	28(1)	60(2)	10(1)	-18(1)	0(1)
C(34)	42(1)	28(1)	42(1)	1(1)	-11(1)	-2(1)
C(35)	24(1)	20(1)	35(1)	-1(1)	2(1)	-1(1)
C(36)	23(1)	21(1)	26(1)	-1(1)	3(1)	-1(1)
C(37)	32(1)	22(1)	25(1)	0(1)	-1(1)	-1(1)
C(38)	32(1)	23(1)	25(1)	-4(1)	0(1)	-2(1)
C(39)	24(1)	21(1)	23(1)	-3(1)	3(1)	-3(1)
C(40)	23(1)	18(1)	26(1)	-2(1)	3(1)	-1(1)
C(41)	29(1)	28(1)	26(1)	-6(1)	-2(1)	2(1)
C(42)	29(1)	31(1)	29(1)	0(1)	-3(1)	6(1)
C(43)	28(1)	23(1)	38(1)	1(1)	-2(1)	3(1)
C(44)	25(1)	22(1)	33(1)	-4(1)	0(1)	-1(1)
C(45)	35(1)	22(1)	32(1)	-2(1)	0(1)	1(1)
C(46)	37(1)	24(1)	33(1)	-5(1)	-1(1)	-3(1)
C(47)	27(1)	29(1)	31(1)	2(1)	-3(1)	2(1)
C(48)	25(1)	24(1)	40(1)	1(1)	2(1)	0(1)
C(49)	29(1)	37(1)	37(1)	5(1)	3(1)	10(1)
C(50)	27(1)	44(1)	49(1)	21(1)	6(1)	8(1)
C(51)	27(1)	40(1)	62(1)	14(1)	-4(1)	-8(1)
C(52)	34(1)	33(1)	45(1)	-1(1)	-7(1)	-5(1)
C(53)	35(1)	22(1)	32(1)	-1(1)	4(1)	2(1)
C(54)	42(1)	47(1)	34(1)	-5(1)	-7(1)	5(1)
C(55)	61(1)	55(1)	36(1)	-11(1)	-2(1)	18(1)
C(56)	66(2)	51(1)	51(2)	-1(1)	28(1)	23(1)
C(57)	52(1)	78(2)	90(2)	-29(2)	35(2)	-14(1)
C(58)	45(1)	59(1)	68(2)	-34(1)	21(1)	-18(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **3b**.

	x	y	z	U(eq)
H(1A)	8481	8146	4736	43
H(2A)	8552	9385	4476	54
H(3A)	8501	9636	3705	50
H(4A)	8327	8646	3188	46
H(5A)	8240	7409	3446	40
H(8A)	9221	6312	3746	33
H(12A)	6861	6636	5500	40
H(13A)	6608	5518	5906	40
H(14A)	7211	4372	5558	35
H(17A)	9255	3076	4706	36
H(19A)	10882	4816	5178	49
H(20A)	13171	4900	5667	60
H(21A)	14461	3814	5935	67
H(22A)	13494	2641	5703	65
H(23A)	11230	2547	5201	51
H(25A)	8163	3131	4019	38
H(26A)	6058	2785	3517	44
H(27A)	3325	3261	3595	42
H(28A)	2676	4040	4207	46
H(29A)	4800	4387	4714	38
H(30A)	5722	7858	2784	38
H(31A)	5803	9166	2774	45
H(32A)	5212	9823	2114	51
H(33A)	4446	9173	1462	55
H(34A)	4352	7864	1465	45
H(37A)	3792	6685	1556	32
H(41A)	6950	5957	3174	33
H(42A)	7211	4673	3310	36
H(43A)	6391	3811	2762	35
H(46A)	3394	3199	1805	38
H(48A)	2849	4629	2686	36
H(49A)	832	4557	3252	41
H(50A)	-941	3517	3302	48
H(51A)	-778	2577	2768	52
H(52A)	1218	2632	2195	45

H(54A)	4691	3156	1204	49
H(55A)	6611	2893	640	61
H(56A)	9321	3372	664	67
H(57A)	10170	4095	1293	88
H(58A)	8234	4336	1874	69