Supporting Information

A Novel Enantioselective Synthesis of 6*H*-Dibenzopyran Derivatives by Combined Palladium/Norbornene and Cinchona Alkaloids Catalysis

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General

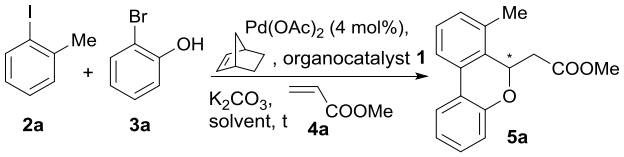
Most starting materials were commercially available and were used without further purification. 2-*i*-Propyliodobenzene, 2,3-dimethyliodobenzene were prepared by iodination of the corresponding diazonium salt according to the literature.[1] 3,4-Dimethoxy-2-methyliodobenzene[2], 4-iodo-*N*,*N*-dimethylaniline and 1-iodo-4-methoxynaphthalene[3], diethyl 2-methylenemalonate[4], nitroethene[5], quincorine and monodeazacinchona alkaloid derivatives[6] were prepared according to reported procedures.

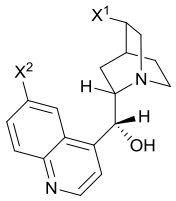
All reactions were carried out under nitrogen using standard Schlenk techniques. DMF was dried and stored over 4 Å molecular sieves under nitrogen. Gas chromatography analyses were performed with a Yonglin GC System using a 30 m SE-30 capillary column. Flash column chromatography was carried out on Liang Chen Gui Yuan Silica Gel 200–300 mesh and TLC on Yan Tai Jiang You plates. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker AVANCE-400 spectrometer. Chemical shifts are reported in ppm using the solvent as internal reference (7.26 and 77.00 ppm, respectively for ^{1}H and ^{13}C). Melting points were determined with XT4 microscope electrothermal apparatus and were uncorrected. Enantiomeric excess values were determined with a Knauer S1050 instrument. Electron impact mass spectra (*m/z*, relative intensity (%)) were determined with an Agilent Technologies instrument working at 70 eV ionization energy. Infrared spectra were recorded using a Bruker Alpha spectrophotometer with a ATR-Ge device. Elemental analyses were obtained on an Elementar Vario MICRO CUBE (Germany) elemental analyzer.

General Procedure: reaction of o-substituted aryl iodides with 2-bromophenols and terminal olefins in the presence of norbornene, $Pd(OAc)_2$, K_2CO_3 and cinchona alkaloids in DMF.

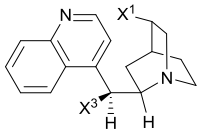
To a Schlenck-type flask, containing $Pd(OAc)_2$ (2 mg, 0.009 mmol), K_2CO_3 (98 mg, 0.714 mmol) and the cinchona alkaloid (0.056 - 0.223 mmol as indicated in table 1 and 2), was added a DMF solution (4 mL) of the *o*-substituted aryl iodide (0.223 mmol), the 2-bromophenol (0.223 mmol), the terminal olefin (0.714 mmol) and norbornene (17 mg, 0.178 mmol). The reaction mixture was allowed to stir under nitrogen at 80 ℃ for the time indicated in Table 1 and 2. After cooling to room temperature, the mixture was diluted with EtOAc (20 mL), washed with a saturated solution of NaCl (3 × 15 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography on silica gel using mixtures of petrol ether-EtOAc as eluent.

Table S1 Screening of reaction conditions[a]

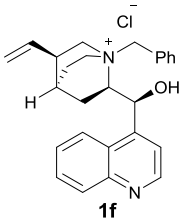




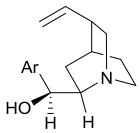
1a X^1 = CH=CH_2, X^2 = OMe, quinine
1b X^1 = CH_2CH_3, X^2 = OMe, hydroquinine
1e X^1 = CH=CH_2, X^2 = H, cinchonidine



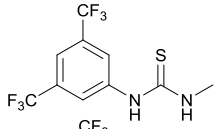
1c X^3 = OH, X^1 = CH=CH_2, cinchonine
1d X^3 = OH, X^1 = CH_2CH_3, hydrocinchonine

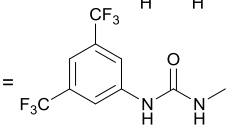


1f



1g Ar = Ph
1h Ar = 1-naphthyl
1i Ar = 9-anthryl

1j X^3 =  , X^1 = CH=CH_2

1k X^3 =  , X^1 = CH=CH_2

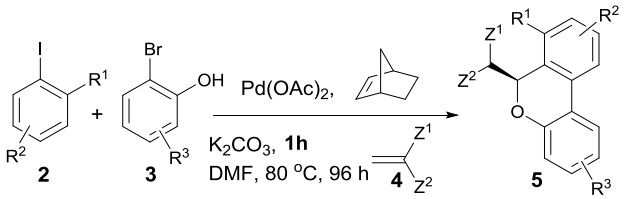
1l Y = COONa
1m Y = $C(Ph)_2OTMS$

Entry	Chiral Catalyst (mol%)	mol% of $Pd(OAc)_2$	solvent	*T* (^oC)	time (h)	yield[b] (%)	*ee*[c] (%)
1	-	4	DMF	80	24	83	0
2	**1l** (50)	4	DMF	80	24	4	n.d.[d]
3	**1m** (50)	4	DMF	80	24	10	0
4	**1a** (50)	4	DMF	80	24	32	80
5	**1b** (50)	4	DMF	80	24	5	n.d.
6	**1c** (50)	4	DMF	80	24	35	99
7	**1d** (50)	4	DMF	80	24	22	75
8	**1c** (150)	4	DMF	80	24	6	> 99
9	**1c** (50)	12	DMF	80	24	45	51
10	**1c** (150)	12	DMF	80	24	35	97
11	**1c** (25)	8	DMF	80	24	50	29
12	**1c** (25)	4	DMF	80	24	52	76
13	**1c** (50)(Cs_2CO_3)[e]	4	DMF	80	24	43	85
14	**1c** (50)	4	DMF	150	24	82	12
15	**1c** (50)	4	DMF	r.t.	24	12	>99
16	**1c** (50)	4	DMF	80	96	72	94
17	**1c** (50) + NBu_4Br (5)	4	DMF	80	96	51	85
18	**1c** (50) + NH_4Cl (5)	4	DMF	80	96	53	>99

19	**1c** (50) + Et_3NMeI (5)	4	DMF	80	96	49	n.d.
20	**1c** (50) + Et_3NMeI (50)	4	DMF	80	96	38	n.d.
21	**1e** (50)	4	DMF	80	96	69	89
22	**1f** (50)	4	DMF	80	96	75	2
23	**1g** (50)	4	DMF	80	96	77	82
24	**1h** (50)	4	DMF	80	96	75	95
25	**1i** (50)	4	DMF	80	96	74	95
26	**1j** (50)	4	DMF	80	96	43	73
27	**1k** (50)	4	DMF	80	96	42	75
28	+ pyridine (50)	4	DMF	80	24	64	0
29	+ EtOH (50)	4	DMF	80	24	82	0
30	-	4	$ClCH_2CH_2Cl$	80	24	5	0
31	**1h** (50)	4	NMP	80	96	21	62
32	**1h** (50)	4	Dioxane	80	96	33	82
33	**1h** (50)	4	DMA	80	96	56	91
34	**1h** (50)	4	THF	80	96	38	88
35	**1h** (50)	4	Toluene	80	96	23	85

[a] Unless otherwise noted, all reactions were carried out with **2a** (0.223 mmol), **3a** (0.223 mmol), **4a** (0.714 mmol), K_2CO_3 (0.714 mmol), norbornene (0.178 mmol), $Pd(OAc)_2$ (0.009 mmol), and organocatalyst **1** (0.112 mmol) in solvent (4.0 mL) at 80 °C. [b] Isolated yield. [c] Determined by chiral HPLC analysis (Daicel OD-H, hexane/*i*-propane = 95/5). [d] Not determined. [e] Cs_2CO_3 in place of K_2CO_3.

Table S2 Investigating the reaction scope[a]



Entry	Chiral catalyst. (mol%)	R^1,R^2	R^3	Z^1	Z^2	**5** Yield[b] (%)	*ee*[c] (%)
1	**1c** (50)	2-Me, 4-Me	H	COOMe	H	**5b** 25	79
2	**1c** (25)	2-Me, 4-Me	H	COOMe	H	**5b** 51	77
3	**1h** (25)	2-Me, 4-Me	H	COOMe	H	**5b** 73	92
4	**1i** (25)	2-Me, 4-Me	H	COOMe	H	**5b** 62	75
5	**1c** (25)	2-Me, 3-Me	H	COOMe	H	**5c** 59	75
6	**1h** (25)	2-Me, 3-Me	H	COOMe	H	**5c** 68	93
7	**1c** (50)	2-CF_3	H	COOMe	H	**5d** 73	43

8	**1c** (100)	2-CF_3	H	COOMe	H	**5d** 45	72
9	**1h** (100)	2-CF_3	H	COOMe	H	**5d** 59	83
10	**1i** (100)	2-CF_3	H	COOMe	H	**5d** 55	85
11	-	2-Me, 3,4-diOMe	H	COOMe	H	**5e** 89	0
12	**1c** (50)	2-Me, 3,4-diOMe	H	COOMe	H	**5e** 31	35
13	**1c** (50)+4 Å MS	2-Me, 3,4-diOMe	H	COOMe	H	**5e** 33	57
14	**1h** (50)	2-Me, 3,4-diOMe	H	COOMe	H	**5e** 61	88
15	-	2-Me, 4-NMe_2	H	COOMe	H	**5f** 85	0
16	**1c** (50)	2-Me, 4-NMe_2	H	COOMe	H	**5f** 32	79
17	**1h** (50)	2-Me, 4-NMe_2	H	COOMe	H	**5f** 56	90
18	-	4-OMe-naphthyl	H	COOMe	H	**5g** 77	0
19	**1c** (50)	4-OMe-naphthyl	H	COOMe	H	**5g** 49	86
20	**1h** (50)	4-OMe-naphthyl	H	COOMe	H	**5g** 68	91
21	**1h** (50)	2-Me	4-Me	COOMe	H	**5h** 40	97
22	**1h** (50)	2-Me	5-NO_2	COOMe	H	**5i** 63	80
23	**1h** (50)	2-Me	H	COOEt	COOEt	**5j** 52	84
24	**1h** (50)	2-Me	H	NO_2	Et	-	-

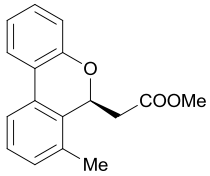
[a] Unless otherwise noted, all reactions were carried out with **2** (0.223 mmol), **3** (0.223 mmol), **4** (0.714 mmol), K_2CO_3 (0.714 mmol), norbornene (0.178 mmol), $Pd(OAc)_2$ (0.0089 mmol), and catalyst **1** in DMF (4.0 mL) at 80 ^oC. [b] Isolated yield. [c] Determined by chiral HPLC analysis (Daicel OD-H, hexane/*i*-propane = 95/5 - 99/1).

Procedure for 5k[7]

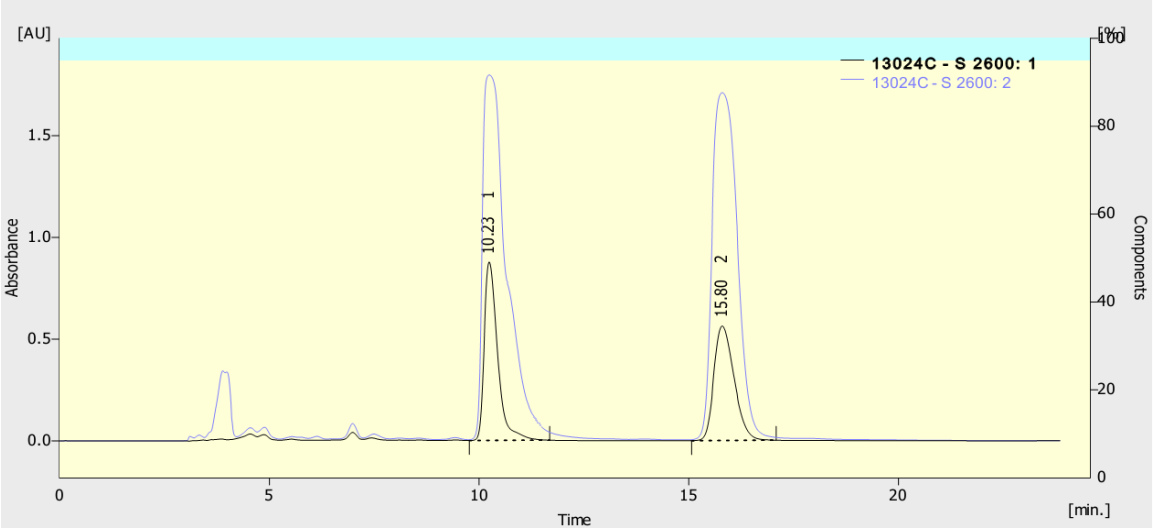
To a Schlenk flask provided with a mechanical stirrer, (*S*)-6-methoxycarbonylmethyl-8,9-dimethoxy-7-methyl-6*H*-dibenzopyran (**5e**) (150 mg, 6.46 mmol) and *N*-iodosuccinimide (97 mg, 0.43 mmol) was added. Then glacial acetic acid (4.5 mL), and concentrated sulfuric acid (0.5 mL) was added portionwise at the internal temperature ~20 ℃. The suspension was stirred overnight under nitrogen. Then the reaction mixture was slowly added to $NaHCO_3$ (10%) solution, and then extracted by CH_2Cl_2. The product was purified by chromatography (Petrol ether / EtOAc = 10/1). (*S*)-6-Methoxycarbonylmethyl-8,9-dimethoxy-2-iodo-7-methyl-6*H*-dibenzopyran (191 mg) (**5k**) was obtained as white solid (92% yield). Colorless crystal of **5k** was obtained from a solution of heptane / CCl_4 (CCDC 1027228 (**5k**) contains the crystallographic data of **5k**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ca.ac.uk/data_request/cif).

Characterization data

(S)-6-Methoxycarbonylmethyl-7-methyl-6H-dibenzopyran (**5a**)

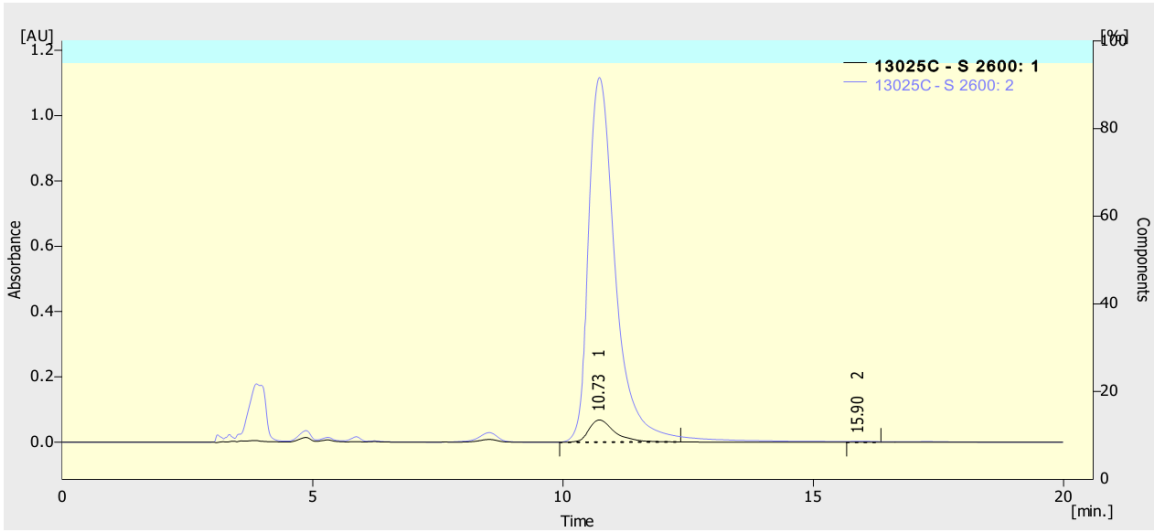


Following the general procedure (*S*)-6-methoxycarbonylmethyl-7-methyl-6*H*-dibenzopyran was isolated in 75% yield (90 mg) by flash column chromatography (96:4 petrol ether/EtOAc). M.p. (petrol ether): 84 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (1H, dd, *J* = 7.7, 1.6 Hz), 7.57 (1H, br d, *J* = 7.8 Hz), 7.29 and 7.24 (2H, t, *J* = 7.7 Hz and td, *J* = 7.7, 1.6 Hz), 7.13 (1H, br d, *J* = 7.6 Hz), 7.04 (1H, td, *J* = 7.6, 1.2 Hz), 6.96 (1H, dd, *J* = 8.0, 1.2 Hz), 5.95 (1H, dd, *J* = 10.7, 2.8 Hz), 3.75 (3H, s), 2.89 (1H, dd, *J* = 15.2, 10.7 Hz), 2.4 and 2.36 (4H, dd, *J* = 15.2, 2.8 Hz and s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 151.1, 132.9, 131.5, 129.9, 129.7, 128.8, 128.3, 123.7, 122.2, 122.1, 120.2, 118.5, 71.4, 51.9, 38.0, 18.2; IR (KBr, cm^{-1}): ν 1726; MS (EI, 70eV): M^+ 268 (9), *m/z* 195 (100), 165 (11), 152 (7). Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 75.79; H, 6.10. $[\alpha]_D^{20}$ = +44.5 (*c* 1.0, MeOH). HPLC (Daicel OD-H, hexane/*i*PrOH = 95/5, 1.0 mL/min, 215 nm) t_1 = 10.7 min (major), t_2 = 15.9 min (minor).



Result Table (Uncal - 13024C - S 2600: 1)

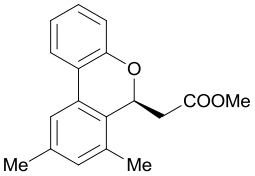
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Peak Purity [-]
1	10.233	19527.878	876.535	50.9	60.9	0.35	776
2	15.800	18850.837	562.962	49.1	39.1	0.55	944
	Total	38378.715	1439.497	100.0	100.0		



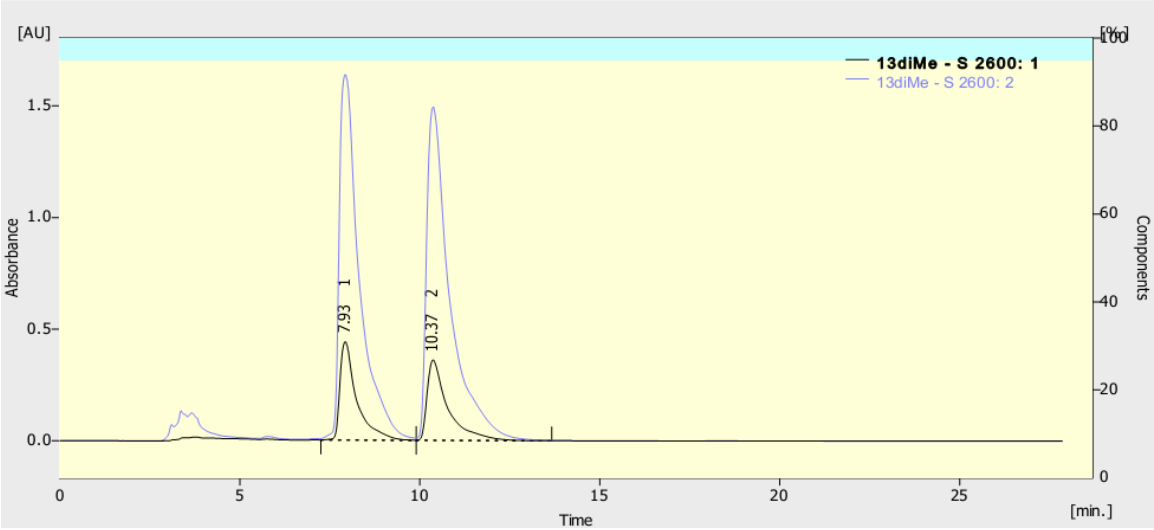
Result Table (Uncal - 13025C - S 2600: 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Peak Purity [-]
1	10.733	2436.354	67.865	99.8	99.7	0.53	916
2	15.900	4.241	0.176	0.2	0.3	0.37	998
	Total	2440.594	68.041	100.0	100.0		

(S)-6-Methoxycarbonylmethyl-7,9-dimethyl-6H-dibenzopyran (**5b**)

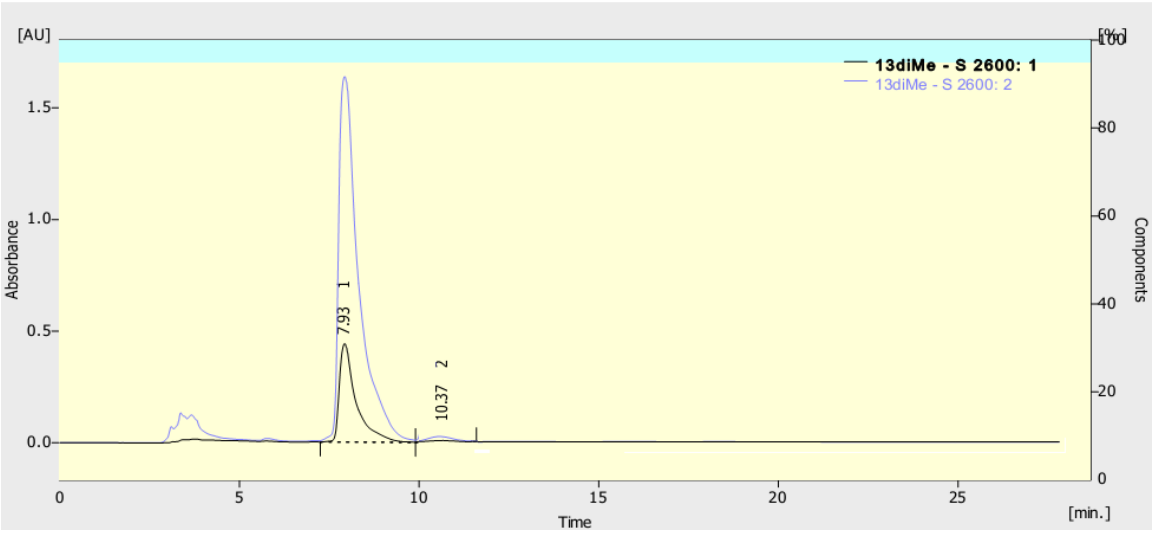


Following the general procedure (*S*)-6-methoxycarbonylmethyl-7,9-dimethyl-6*H*-dibenzopyran was isolated in 73% yield (92 mg) by flash column chromatography (98:2 petrol ether/EtOAc). M.p. (petrol ether): 98 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (1H, dd, *J* = 7.8, 1.6 Hz), 7.42 (1H, br s), 7.25 (1H, m), 7.06 (1H, td, *J* = 7.5, 1.3 Hz), 6.98 and 6.97 (2H, dd, *J* = 8.0, 1.3 Hz and s furt her split), 5.94 (1H, dd, *J* = 10.7, 2.8 Hz), 3.76 (3H, s), 2.88 (1H, dd, *J* = 15.2, 10.7 Hz), 2.38 and 2.37 (4H, dd, *J* = 15.2, 2.8 Hz and s), 2.32 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 151.1, 137.8, 132.7, 130.7, 129.4, 128.6, 128.5, 123.0, 122.2, 122.1, 120.8, 118.4, 71.3, 51.8, 38.2, 21.2, 18.0; IR (KBr, cm^{-1}): ν 1734; MS (EI, 70eV): M^+ 282 (8), *m/z* 195 (100), 209 (100), 178 (6), 165 (10). Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.49; H, 6.66. HPLC (Daicel OD-H, hexane/*i*PrOH = 95/5, 1.0 mL/min, 215 nm) t_1 = 7.9 min (major), t_2 = 10.4 min (minor).



Result Table (Uncal - 13diMe - S 2600: 1)

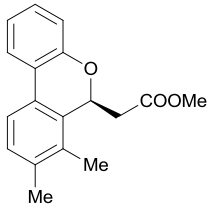
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Peak Purity [-]
1	7.933	14284.933	440.956	49.9	55.1	0.43	968
2	10.367	14345.120	359.997	50.1	44.9	0.52	958
	Total	28630.053	800.954	100.0	100.0		



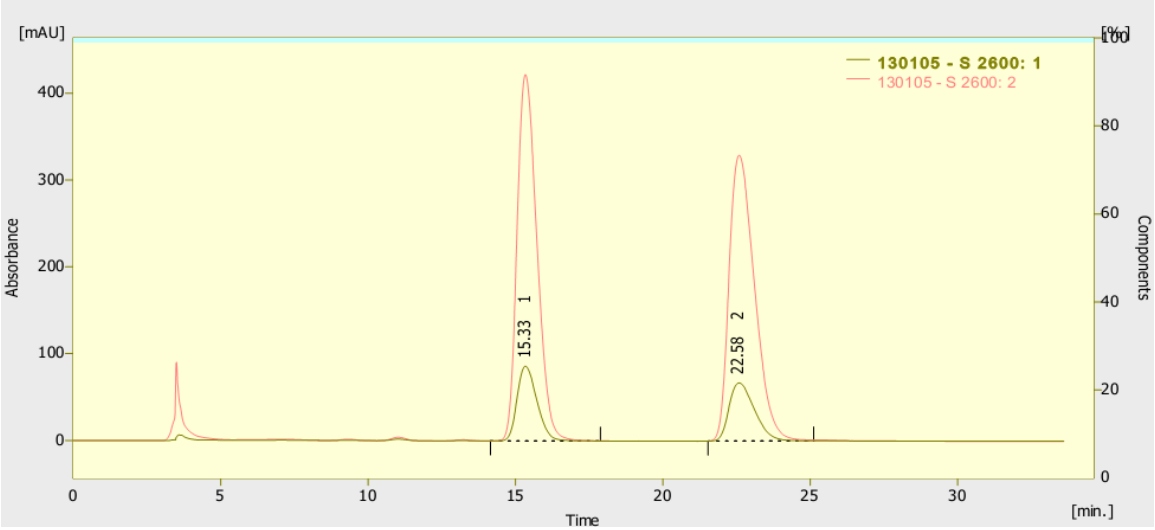
Result Table (Uncal - diMe cat-2 - S 2600: 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Peak Purity [-]
1	7.930	8.534	0.137	95.9	88.1	1.07	636
2	10.365	0.365	0.019	4.1	11.9	0.08	961
	Total	8.899	0.156	100.0	100.0		

(S)-6-Methoxycarbonylmethyl-7,8-dimethyl-6H-dibenzopyran (**5c**)



Following the general procedure (*S*)-6-methoxycarbonylmethyl-7,8-dimethyl-6*H*-dibenzopyran was isolated in 68% yield (86 mg) by flash column chromatography (98:2 petrol ether/EtOAc). M.p. (petrol ether): 93 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (1H, dd, *J* = 7.8, 1.6 Hz), 7.42 (1H, br s), 7.32 (1H, td, *J* = 7.5, 1.3 Hz), 7.19 (1H, td, *J* = 7.7, 1.6 Hz), 7.15 and 7.12 (2H, dd, *J* = 8.0, 1.3 Hz and s further split), 5.83 (1H, dd, *J* = 10.7, 2.8 Hz), 3.74 (3H, s), 2.99-2.96 (1H, m), 2.72-2.70 (1H, m), 2.33 (3H,s), 2.07 (3H,s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.0, 152.8, 132.3, 129.9, 128.1, 127.0, 126.8, 125.8, 125.4, 122.9, 121.5, 114.9, 68.5, 51.8, 39.5, 19.9, 18.4; IR (KBr, cm^{-1}): ν 1730; MS (EI, 70eV): M^+ 282 (7), *m/z* 195 (100), 209 (100), 178 (5), 165 (9). Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.47; H, 6.58. HPLC (Daicel OD-H, hexane/*i*PrOH = 99/1, 1.0 mL/min, 215 nm) t_1 = 15.7 min (major), t_2 = 22.0 min (minor).



Result Table (Uncal - 130105 - S 2600: 1)

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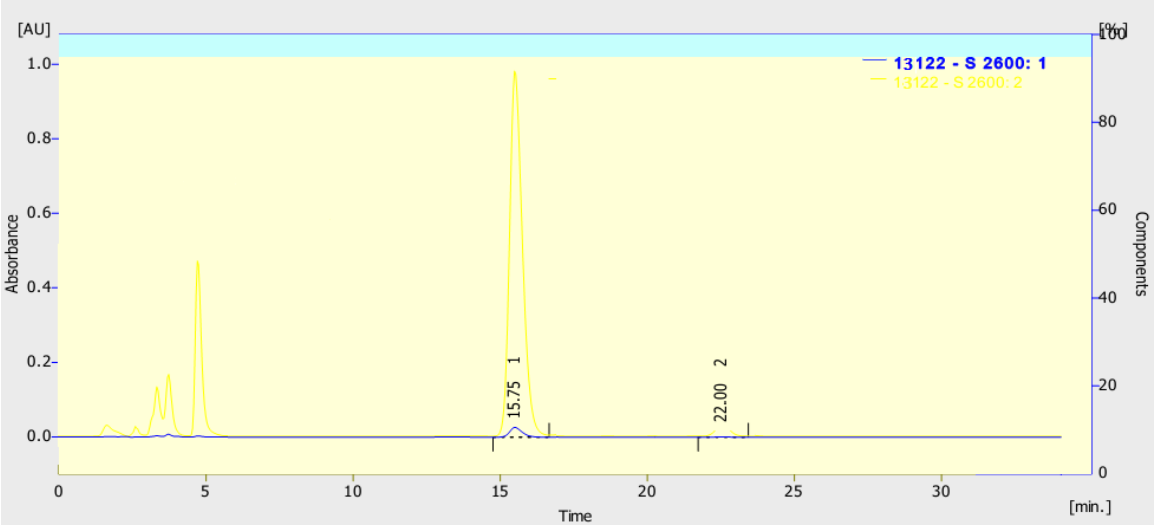
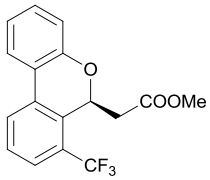
1	15.333	4030.931	86.121	50.2	56.3	0.75	866
2	22.583	3997.852	66.920	49.8	43.7	0.95	941
	Total	8028.783	153.041	100.0	100.0		



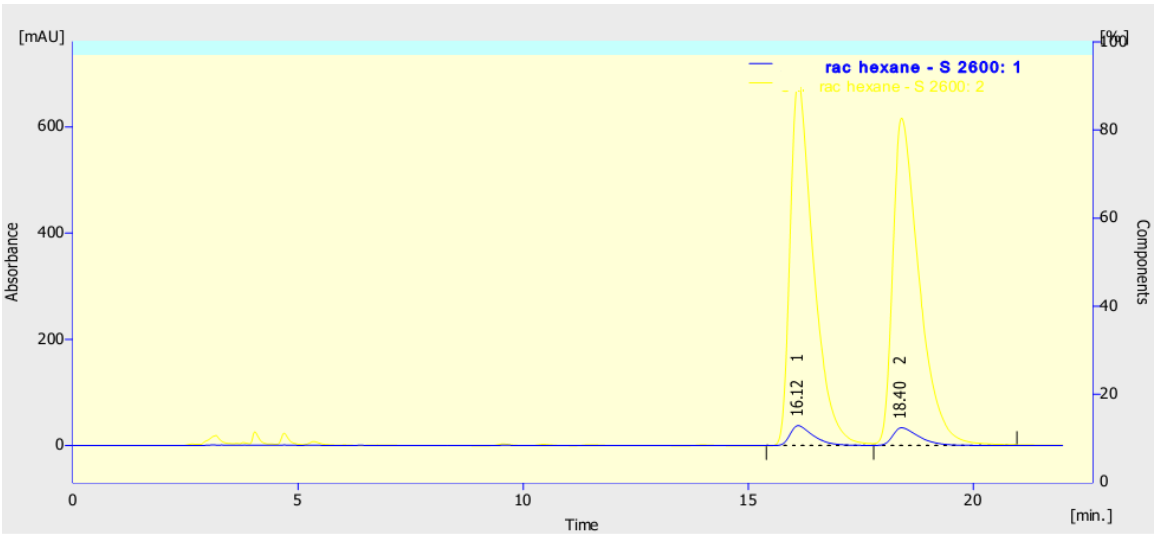
Result Table (Uncal - 13122 - S 2600: 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Peak Purity [-]
1	15.750	318.970	26.377	96.4	96.6	0.20	919
2	22.000	11.840	0.919	3.6	3.4	0.22	914
	Total	330.810	27.295	100.0	100.0		

(S)-6-Methoxycarbonylmethyl-7-trifluoromethyl-6H-dibenzopyran (**5d**)

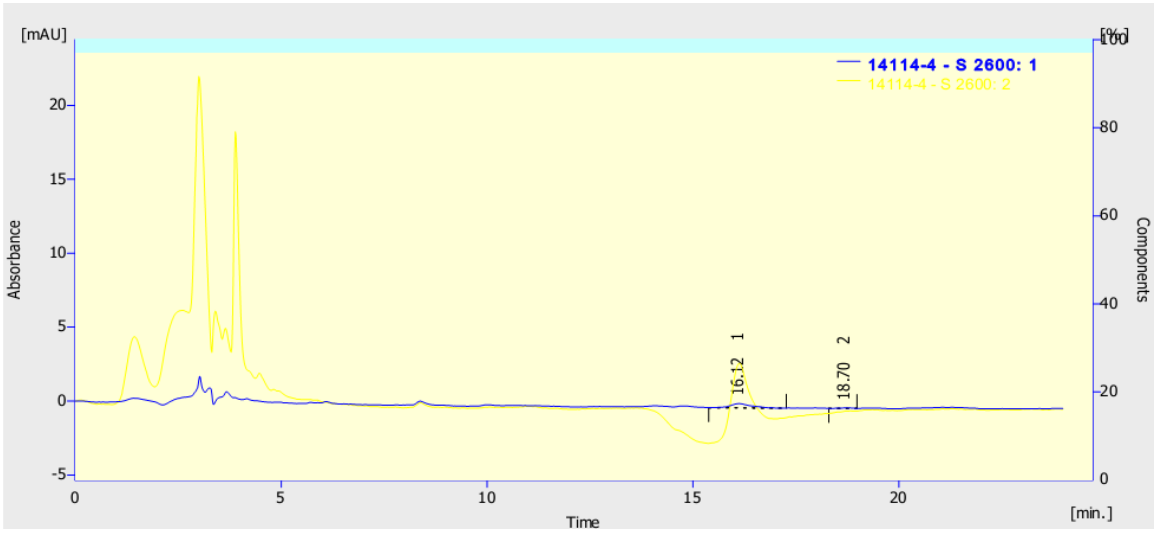


Following the general procedure (*S*)-6-methoxycarbonylmethyl-7-trifluoromethyl-6*H*-dibenzopyran was isolated in 59% yield (85 mg) by flash column chromatography (97:3 petrol ether/EtOAc). M.p. (petrol ether): 83 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (1H, br d, J = 7.8 Hz), 7.74 (1H, dd, J = 7.8, 1.6 Hz), 7.62 (1H, d, J = 7.7 Hz), 7.51 (1H, t, J = 7.8 Hz), 7.30 (1H, td, J = 7.7, 1.6 Hz), 7.14 (1H, td, J = 7.6, 1.2 Hz), 7.02 (1H, dd, J = 8.1, 1.2 Hz), 6.17 (1H, d further split, J = 11.0 Hz, H6), 3.74 (3H, s), 2.90 (1H, dd, J = 15.6, 11.0 Hz), 2.51 (1H, dd, J = 15.6, 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.0, 150.9, 130.9, 130.8, 128.5, 126.4, 126.0 (quart, $J_{C,F}$ = 30.4 Hz), 125.2 (quart, $J_{C,F}$ = 5.8 Hz), 123.9 (quart, $J_{C,F}$ = 273.6 Hz), 123.2, 122.6, 121.2, 118.8, 70.5 (quart, $J_{C,F}$ = 2.7 Hz), 51.9, 38.0; IR (KBr, cm^{-1}): ν 1741; MS: M^+ 322 (7), *m/z* 249 (100), 201 (11), 165 (8), 152 (6). Anal. Calcd for $C_{17}H_{13}F_3O_3$: C, 63.36; H, 4.07. Found: C, 63.23; H, 4.39. HPLC (Daicel OD-H, hexane/*i*PrOH = 97/3, 1.0 mL/min, 215 nm) t_1 = 16.1 min (major), t_2 = 18.7 min (minor).



Result Table (Uncal - rac hexane - S 2600: 1)

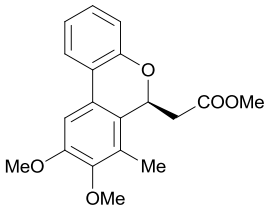
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Peak Purity [-]
1	16.117	1351.671	37.679	49.8	53.0	0.55	925
2	18.400	1363.583	33.478	50.2	47.0	0.63	948
	Total	2715.254	71.157	100.0	100.0		



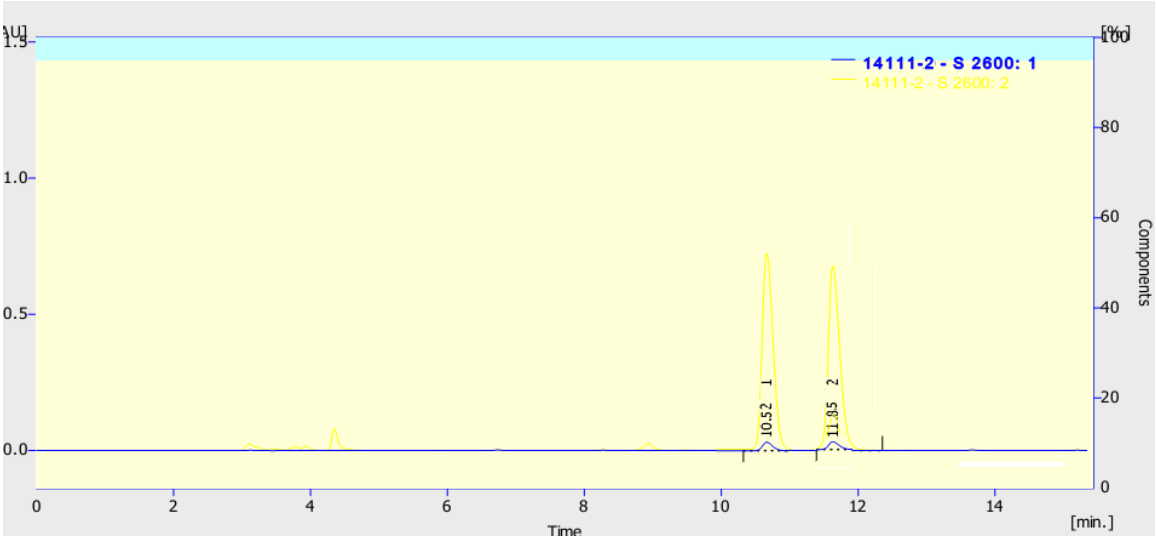
Result Table (Uncal - 14114-4 - S 2600: 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Peak Purity [-]
1	16.117	10.378	0.290	92.5	88.9	0.52	600
2	18.700	0.840	0.036	7.5	11.1	0.43	999
	Total	11.218	0.326	100.0	100.0		

(S)-6-Methoxycarbonylmethyl-8,9-dimethoxy-7-methyl-6H-dibenzopyran (**5e**)

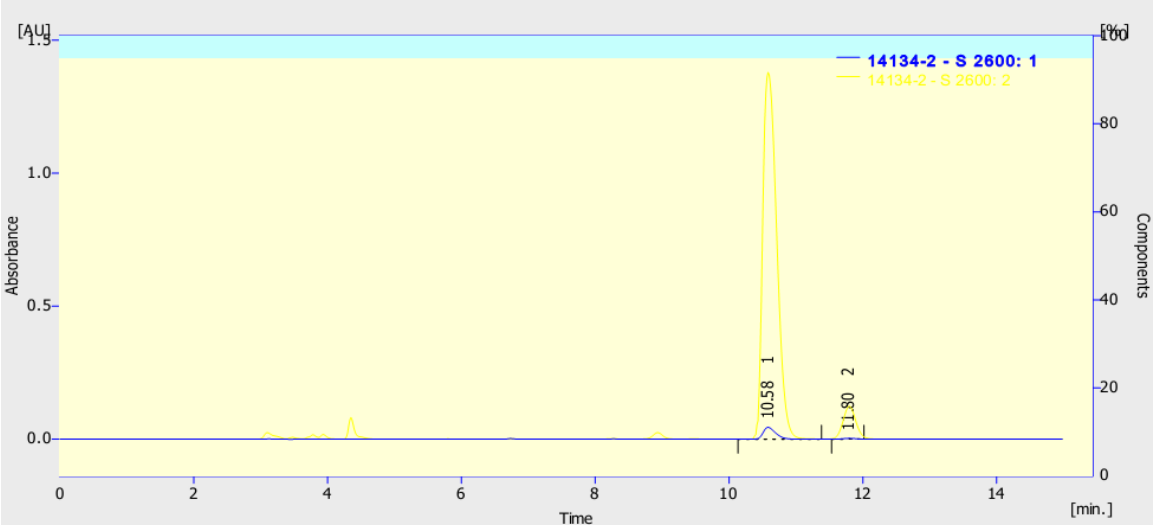


Following the general procedure (*S*)-6-methoxycarbonylmethyl-8,9-dimethoxy-7-methyl-6*H*-dibenzopyran was isolated in 61% yield (89 mg) by flash column chromatography (90:10 petrol ether/EtOAc). M.p. (petrol ether): 105 ℃. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (1H, d, J = 7.7 Hz), 7.22 (1H, t, J = 7.6 Hz), 7.13 (1H, s), 7.05 (1H, t, J = 7.6 Hz), 6.95 (1H, d, J = 8.0 Hz), 5.87 (1H, dd, J = 10.6, 2.6 Hz), 3.94 (3H, s), 3.82 (3H, s), 3.75 (3H, s), 2.85 (1H, dd, J = 15.2, 10.8 Hz), 2.35 (1H, dd, J = 15.3, 2.7 Hz), 2.26 (3H s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 152.8, 150.9, 147.5, 129.4, 127.4, 124.9, 124.8, 122.8, 122.2, 122.2, 118.6, 104.2, 71.5, 60.5, 55.8, 51.9, 38.4, 10.9; IR (KBr, cm^{-1}): ν 1720; MS: (*m*/*z*): 328.3 $(M+H)^+$. Anal. Calcd for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.61; H, 6.22. HPLC (Daicel OD-H, hexane/*i*PrOH = 97/3, 1.0 mL/min, 215 nm) t_1 = 10.6 min (major), t_2 = 11.8 min (minor).



Result Table (Uncal - 14111-2 - S 2600: 1)

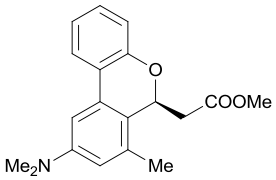
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Peak Purity [-]
1	10.522	375.357	24.357	50.7	52.2	0.25	982
2	11.853	364.890	22.286	49.3	47.8	0.27	981
	Total	740.247	46.642	100.0	100.0		



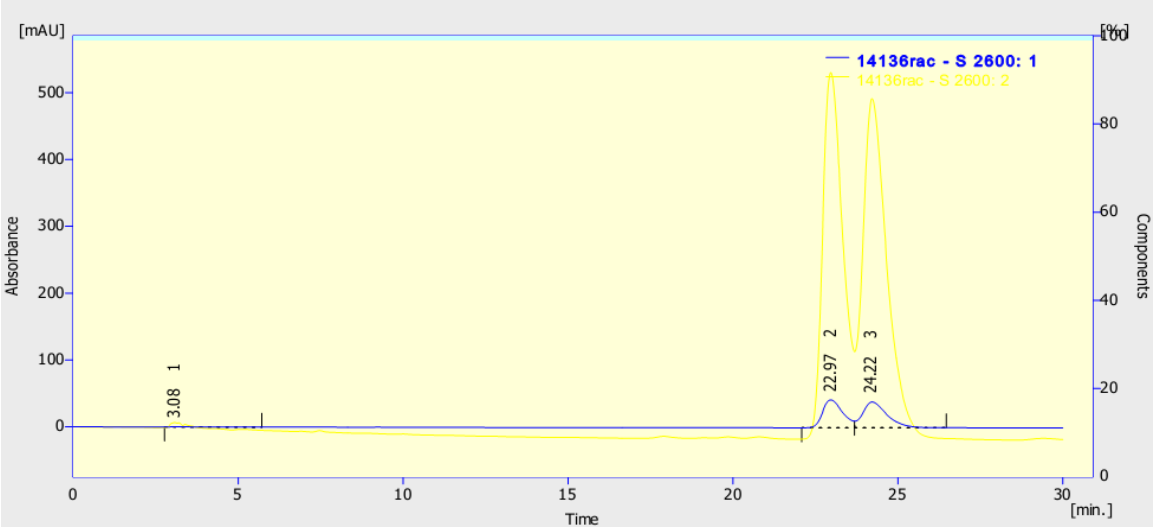
Result Table (Uncal - 14134-2 - S 2600: 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Peak Purity [-]
1	10.583	578.642	44.895	93.9	93.7	0.22	763
2	11.800	37.638	3.030	6.1	6.3	0.22	974
	Total	616.280	47.925	100.0	100.0		

(S)-6-Methoxycarbonylmethyl-9-(dimethylamino)-7-methyl-6H-dibenzopyran (**5f**)

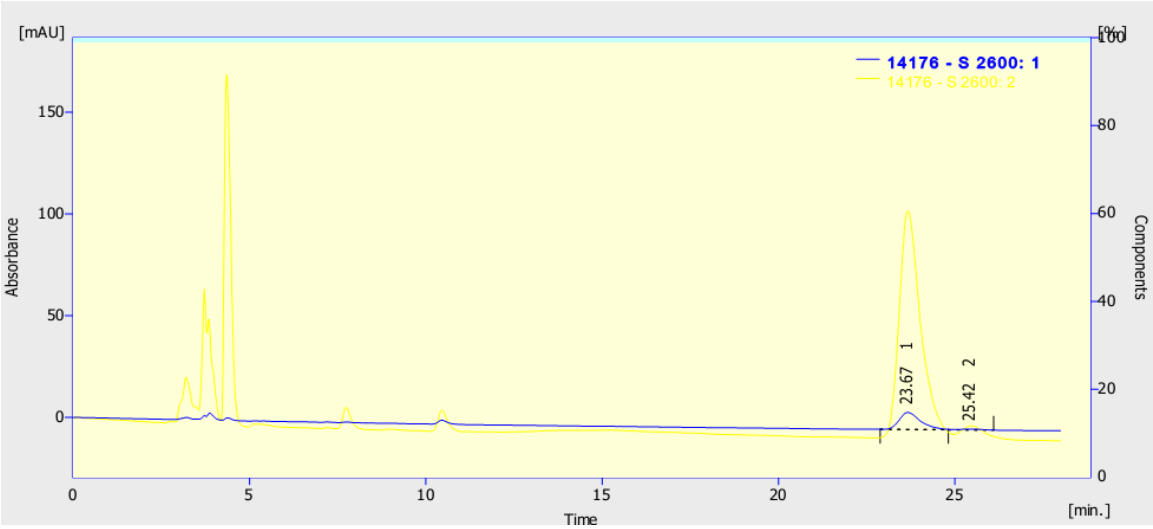


Following the general procedure (*S*)-6-methoxycarbonylmethyl-9-(dimethylamino)-7-methyl-6*H*-dibenzopyran was isolated in 56% yield (78 mg) by flash column chromatography (95:5 petrol ether/EtOAc). Mp (petrol ether): 78 ℃. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (1H, dd, J = 7.8, 1.5 Hz), 7.25 – 7.16 (1H, m), 7.04 (1H, td, J = 7.6, 1.3 Hz), 6.98 – 6.89 (2H, m), 6.54 (1H, d, J = 2.4 Hz), 5.87 (1H, dd, J = 10.7, 2.8 Hz), 3.75 (3H, s), 3.00 (6H, s), 2.85 (1H, dd, J = 15.1, 10.8 Hz), 2.41 – 2.33 (1H, m), 2.32 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 151.5, 150.9, 150.4, 133.8, 129.4, 123.1, 122.8, 122.0, 120.4, 118.6, 114.4, 104.1, 71.5, 51.8, 40.7, 38.8, 29.7, 18.7. IR (KBr, cm^{-1}): ν 1723; MS: (*m*/*z*): 312.4 $(M+H)^+$. Anal. Calcd for $C_{19}H_{21}NO_3$: C, 73.29; H, 6.80; N, 4.50. Found: C, 73.11; H, 6.72; N, 4.57. HPLC (Daicel OD-H, hexane/*i*PrOH = 99/1, 1.0 mL/min, 215 nm) t_1 = 23.7 min (major), t_2 = 25.4 min (minor).



Result Table (Uncal - 14136rac - S 2600: 1)

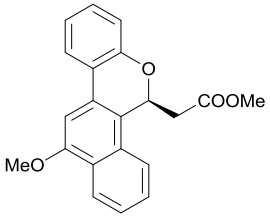
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Peak Purity [-]
1	3.083	25.719	0.545	0.7	0.7	0.13	942
2	22.967	1759.609	41.711	46.7	51.6	0.68	927
3	24.217	1982.147	38.619	52.6	47.8	0.77	869
	Total	3767.474	80.875	100.0	100.0		



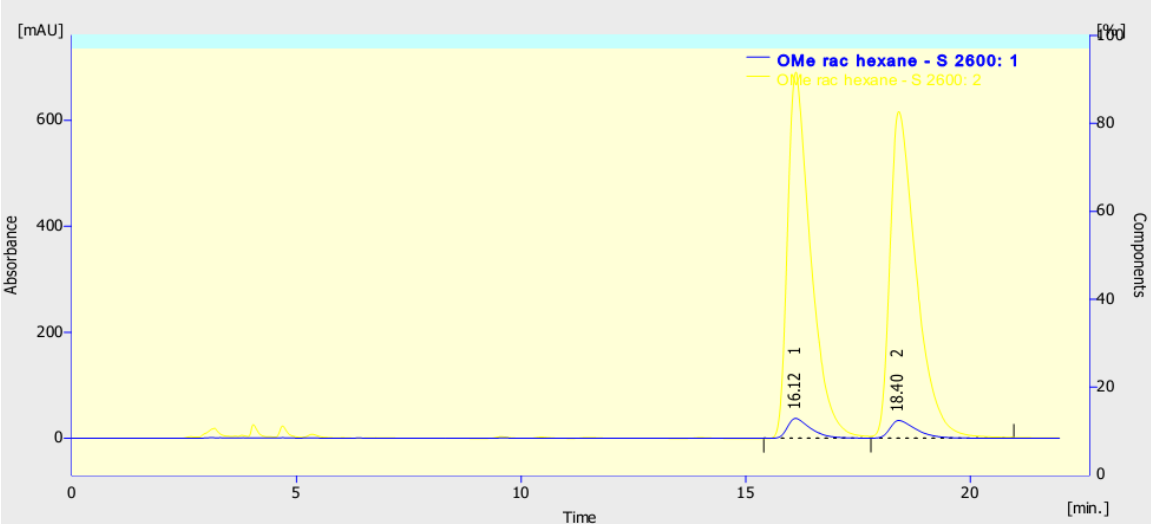
Result Table (Uncal - 14176 - S 2600: 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Peak Purity [-]
1	23.667	356.777	8.394	95.0	95.1	0.65	798
2	25.417	18.858	0.434	5.0	4.9	0.67	873
	Total	375.634	8.828	100.0	100.0		

(S)-12-Methoxy-5-methoxycarbonylmethyl-5H-Benzo[b]naphtho[2,1-d]pyran (**5g**)

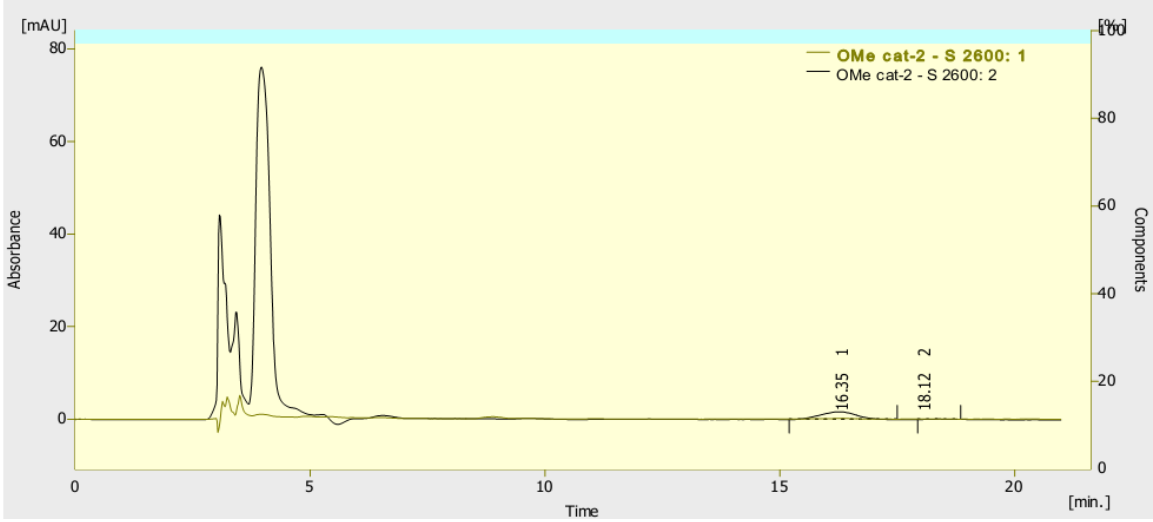


Following the general procedure (*S*)-12-methoxy-5-methoxycarbonylmethyl-5*H*-benzo[*b*]naphtho[2,1-*d*]pyran was isolated in 68% yield (96 mg) by flash column chromatography (96:4 petrol ether/EtOAc). M.p. (petrol ether): 96 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (1H, br d, J = 8.4 Hz), 7.91-7.86 (3H, m), 7.82(1H, dd, J = 7.7, 1.6 Hz), 7.61-7.60 (1H, m), 7.52-7.51 (1H, m), 7.31 (1H, td, J = 7.6, 1.6 Hz), 7.12 (1H, td, J = 7.6, 1.2 Hz), 7.05 (1H, dd, J = 8.0, 1.2 Hz), 6.61 (1H, dd, J = 10.7, 2.8 Hz), 3.91 (3H, s), 3.80 (3H, s), 3.03 (1H, dd, J = 15.3, 10.7 Hz), 2.61 (1H, dd, J = 15.3, 2.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 154.0, 151.0, 129.9, 128.9, 128.9, 128.5, 127.3, 127.3, 126.1, 125.9, 123.3, 122.3, 122.0, 121.9, 120.3, 118.3, 71.3, 58.0, 52.0, 38.4; IR (KBr, cm^{-1}): ν 1728; MS: M^+ 328 (13), *m/z* 245 (100), 229 (9), 216 (22). Anal. Calcd for $C_{21}H_{18}O_4$: C, 75.43; H, 5.43. Found: C, 75.38; H, 5.46. HPLC (Daicel OD-H, hexane/*i*PrOH = 97/3, 1.0 mL/min, 215 nm) t_1 = 16.3 min (major), t_2 = 18.1 min (minor).



Result Table (Uncal - OMe rac hexane - S 2600: 1)

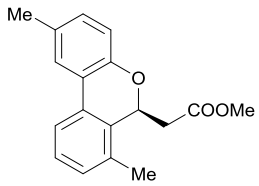
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Peak Purity [-]
1	16.117	1351.671	37.679	49.8	53.0	0.55	925
2	18.400	1363.583	33.478	50.2	47.0	0.63	948
	Total	2715.254	71.157	100.0	100.0		



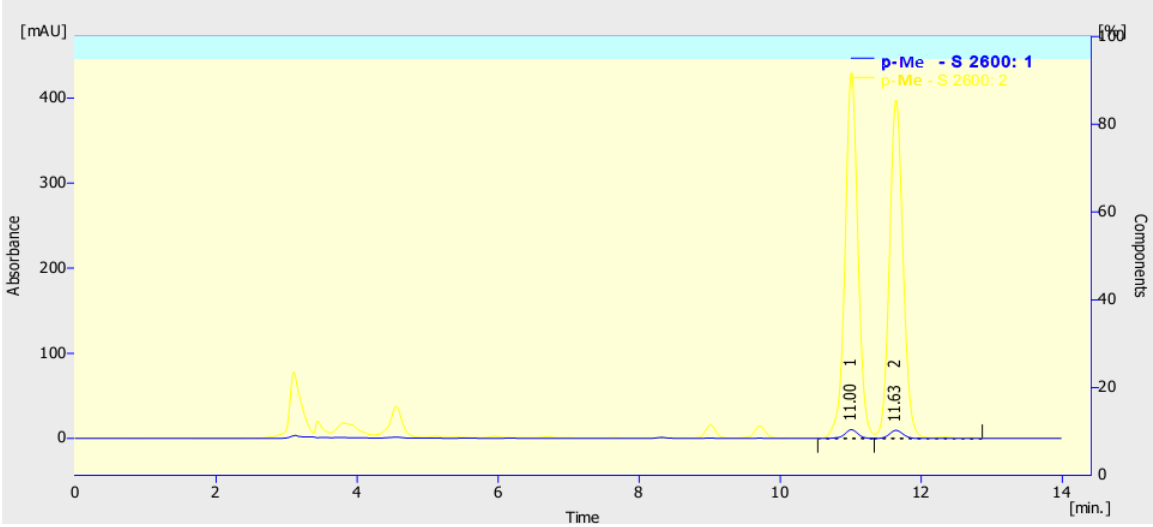
Result Table (Uncal - OMe cat-2 - S 2600: 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Peak Purity [-]
1	16.350	8.534	0.137	95.9	88.1	1.07	636
2	18.117	0.365	0.019	4.1	11.9	0.08	961
	Total	8.899	0.156	100.0	100.0		

(S)-2,7-Dimethyl-6-methoxycarbonylmethyl-6H-dibenzopyran (**5h**)

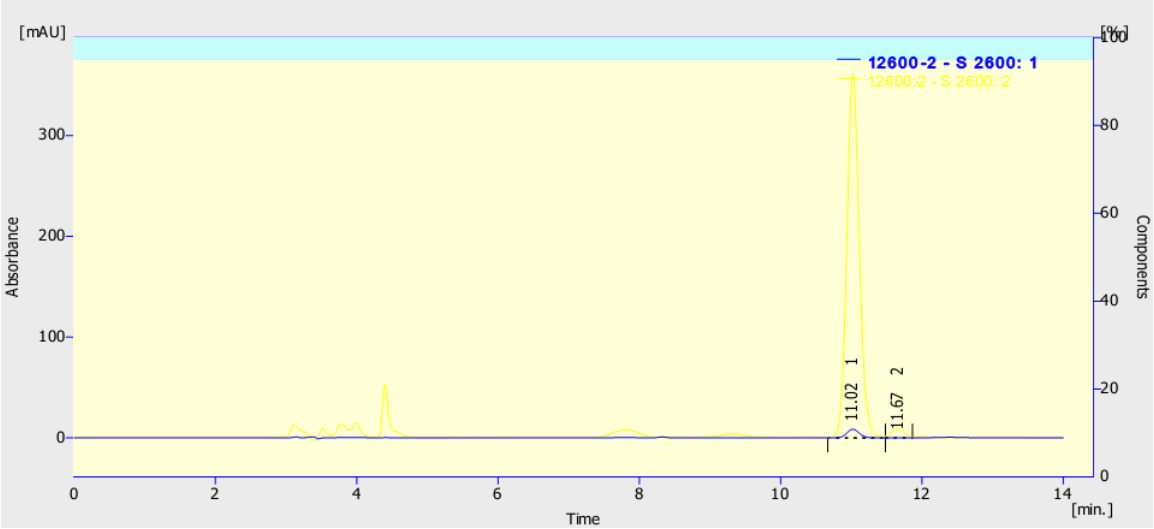


Following the general procedure (*S*)-2,7-Dimethyl-6-methoxycarbonylmethyl-6*H*-dibenzopyran was isolated in 40% yield (50 mg) by flash column chromatography (97:3 petrol ether/EtOAc). M.p. (petrol ether): 43 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (1H, br d, J = 7.7 Hz), 7.55 (1H, d, J = 2.1 Hz), 7.29 (1H, t, J = 7.7 Hz), 7.12 (1H, br d, J = 7.6 Hz), 7.06 (1H, dd, J = 8.2, 2.1 Hz), 6.87 (1H, d, J = 8.2 Hz), 5.93 (1H, dd, J = 10.8, 2.8 Hz), 3.76 (3H, s), 2.91 (1H, dd, J = 15.2, 10.9 Hz), 2.38 (7H, dd J = 15.2, 2.8 Hz), 2.37 (s), 2.36 (s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.8, 148.8, 132.8, 131.5, 131.3, 130.2, 129.8, 128.7, 128.1, 123.5, 121.8, 120.0, 118.2, 71.2, 51.8, 37.7, 20.9, 18.2; IR (KBr, cm^{-1}): ν 1738; MS: M^+ 282 (8), *m/z* 209 (100), 178 (8), 165 (22). Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.51; H, 6.39. HPLC (Daicel OD-H, hexane/*i*PrOH = 95/5, 1.0 mL/min, 215 nm) t_1 = 11.0 min (major), t_2 = 11.6 min (minor).



Result Table (Uncal - p-Me - S 2600: 1)

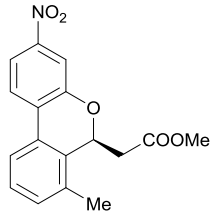
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Peak Purity [-]
1	11.000	135.868	10.326	50.9	52.0	0.22	848
2	11.633	131.294	9.541	49.1	48.0	0.22	884
	Total	267.161	19.867	100.0	100.0		



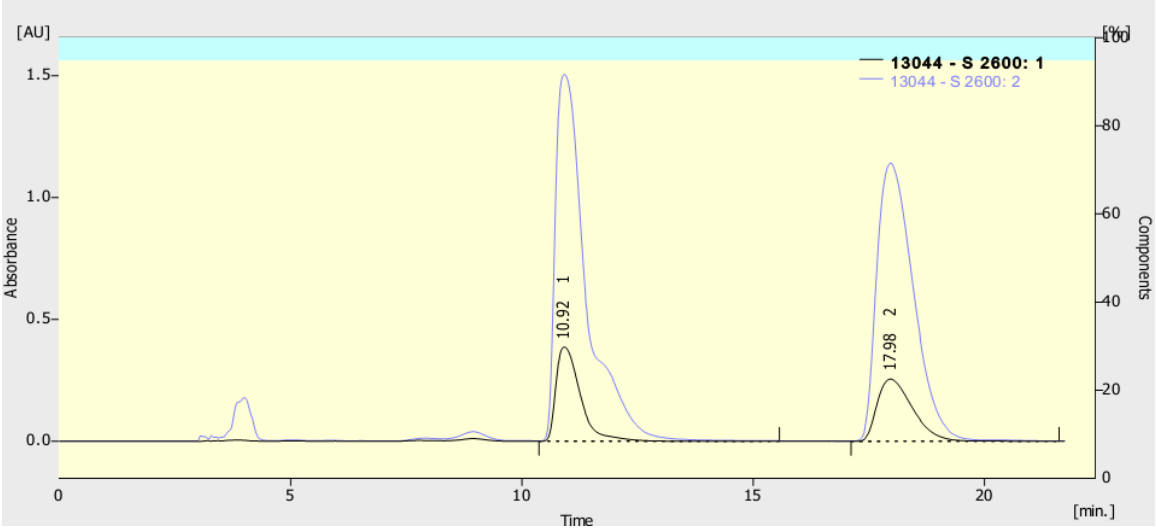
Result Table (Uncal - 12600-2 - S 2600: 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Peak Purity [-]
1	11.017	107.263	8.691	98.4	98.1	0.22	975
2	11.667	1.752	0.168	1.6	1.9	0.18	998
	Total	109.016	8.859	100.0	100.0		

(S)-6-Methoxycarbonylmethyl-7-methyl-3-nitro-6H-dibenzopyran (**5i**)

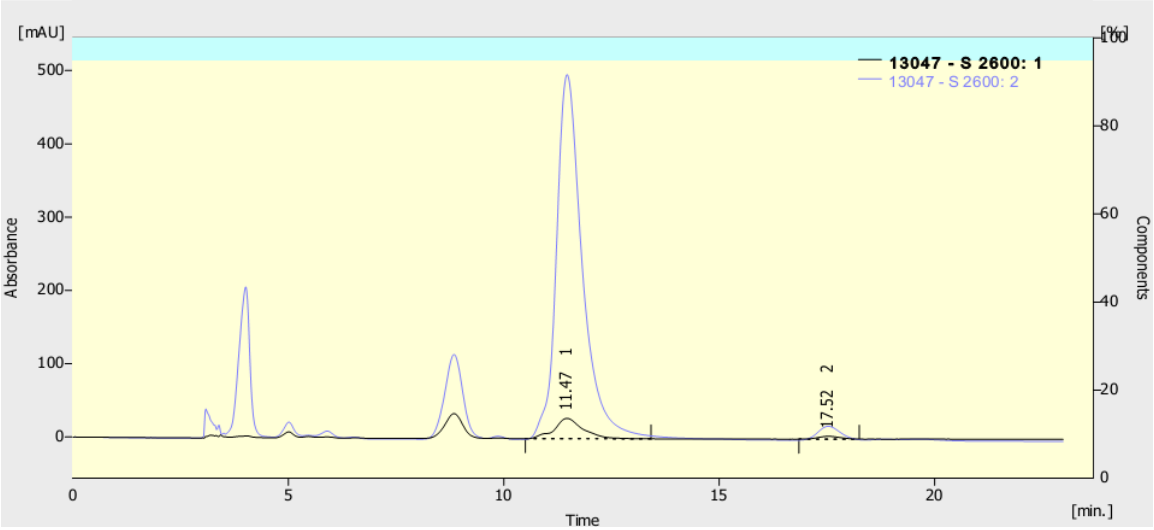


Following the general procedure (*S*)-6-Methoxycarbonylmethyl-7-methyl-3-nitro-6*H*-dibenzopyran was isolated in 63% yield (44 mg) by flash column chromatography (92:8 petrol ether/EtOAc). M.p. (petrol ether): 118 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (1H, dd, J = 8.6, 2.2 Hz), 7.83 (1H, d, J = 8.6 Hz), 7.78 (1H, br d, J = 2.2 Hz), 7.62 (1H, br d, J = 7.6 Hz), 7.34 (1H, t, J = 7.7 Hz), 7.24 (1H, br d, J = 7.6 Hz), 6.01 (1H, dd, J = 10.8, 2.7 Hz), 3.76 (3H, s), 2.81 (1H, dd, J = 15.4, 10.8 Hz), 2.42 (1H, dd, J = 15.4, 2.7 Hz), 2.36 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 151.4, 148.2, 133.4, 132.1, 131.8, 128.7, 128.3, 126.6, 123.6, 121.2, 117.4, 113.9, 72.3, 52.1, 38.4, 18.2; IR (KBr, cm^{-1}): ν 1747; MS: M^+ 313 (14), *m*/*z* 240 (100), 194 (33), 165 (15). Anal. Calcd for $C_{17}H_{15}NO_5$: C, 65.17; H, 4.83; N, 4.47. Found: C, 65.24; H, 4.79; N, 4.58. HPLC (Daicel OD-H, hexane/*i*PrOH = 95/5, 1.0 mL/min, 215 nm) t_1 = 11.4 min (major), t_2 = 17.5 min (minor).



Result Table (Uncal - 13044 - S 2600: 1)

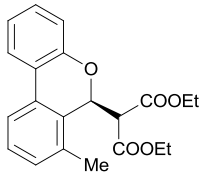
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Peak Purity [-]
1	10.917	14111.824	386.243	51.0	60.2	0.57	781
2	17.983	13566.681	255.470	49.0	39.8	0.85	864
	Total	27678.505	641.712	100.0	100.0		



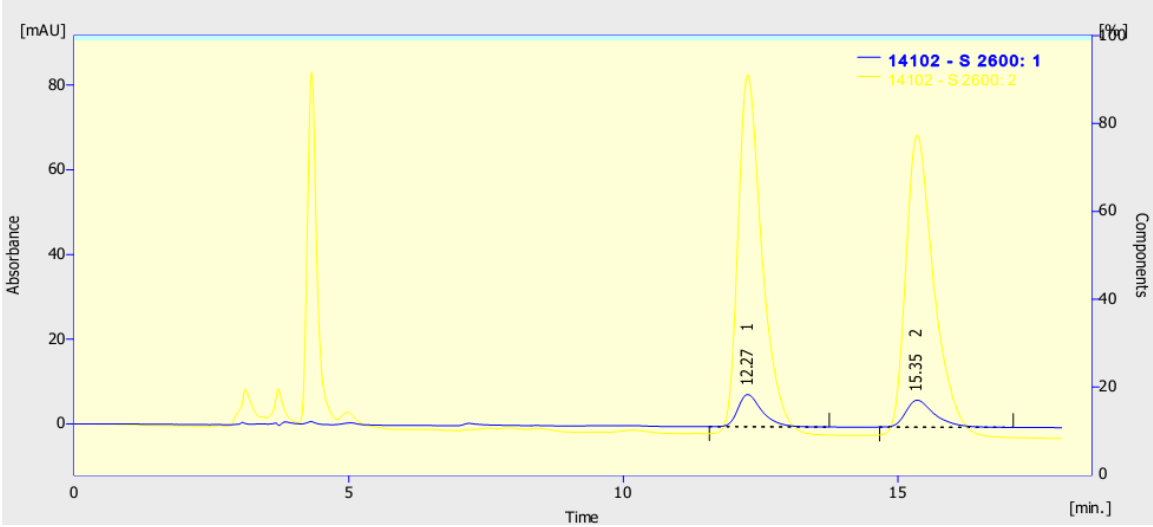
Result Table (Uncal - 13047 - S 2600: 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Peak Purity [-]
1	11.467	1293.123	27.810	90.3	87.7	0.63	854
2	17.517	138.633	3.903	9.7	12.3	0.57	695
	Total	1431.756	31.713	100.0	100.0		

(S)-6-Diethoxycarbonylmethyl-7-methyl-6H-dibenzopyran (**5j**)

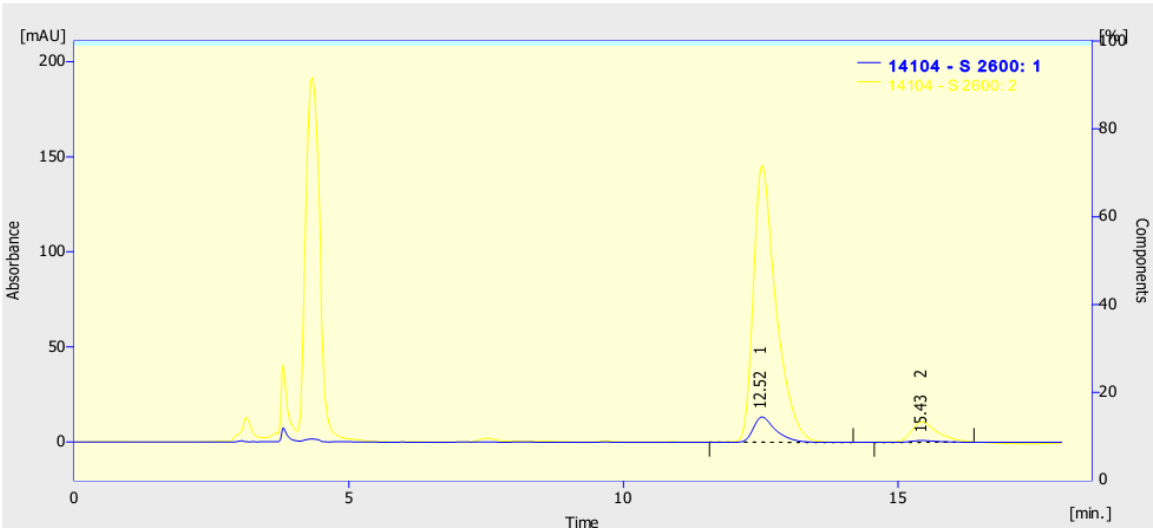


Following the general procedure (*S*)-6-Diethoxycarbonylmethyl-7-methyl-6*H*-dibenzopyran was isolated in 52% yield (82 mg) by flash column chromatography (97:3 petrol ether/EtOAc). M.p. (petrol ether): 96 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (1H, dd, *J* = 7.5, 1.4 Hz), 7.58 (1H, dd, *J* = 7.5, 1.4 Hz), 7.45 – 7.33 (2H, m), 7.30 – 7.20 (2H, m), 7.17 (1H, dd, *J* = 7.4, 1.5 Hz), 6.24 (1H, d, *J* = 0.8 Hz), 4.17 (4H, q, *J* = 5.9 Hz), 4.03 (1H, s), 2.33 (3H, s), 1.37 (6H, t, *J* = 5.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.7 (2C), 152.5, 135.8, 132.5, 130.7, 130.2, 128.9, 128.8, 125.8, 125.0, 123.0, 121.6, 115.2, 72.5, 62.0 (2C), 51.8, 19.7, 14.7 (2C). IR (KBr, cm^{-1}): ν 1726; MS: (*m*/*z*): 354.5 $(M+H)^+$. Anal. Calcd for $C_{21}H_{22}O_5$: C, 71.17; H, 6.26; Found: C, 71.08; 6.31.



Result Table (Uncal - 14102 - S 2600: 1)

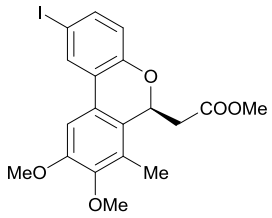
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Peak Purity [-]
1	12.267	232.301	7.608	49.8	54.4	0.47	727
2	15.350	234.081	6.374	50.2	45.6	0.55	727
	Total	466.381	13.982	100.0	100.0		



Result Table (Uncal - 14104 - S 2600: 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Peak Purity [-]
1	12.517	379.050	13.337	92.2	93.4	0.43	849
2	15.433	32.060	0.942	7.8	6.6	0.52	897
	Total	411.110	14.279	100.0	100.0		

(S)-methyl 2-(2-iodo-8,9-dimethoxy-7-methyl-6H-benzo[c]chromen-6-yl)acetate **(5k)**



Following the procedure described above, (*S*)-6-methoxycarbonylmethyl-8,9-dimethoxy-2-iodo-7-methyl-6*H*-dibenzopyran was isolated in 92% yield (191 mg). M.p. (petrol ether): 134 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92 (1H, d, *J* = 1.6 Hz), 7.50 (1H, dd, *J* = 8.5, 1.7 Hz), 6.73 (1H, d, *J* = 8.5 Hz), 5.87 (1H, dd, *J* = 10.8, 2.5 Hz), 3.96 (3H, s), 3.86 (3H, s), 3.76 (3H, s), 2.82 (1H, dd, *J* = 15.3, 10.9 Hz), 2.36 (1H, dd, *J* = 15.3, 2.6 Hz), 2.27 (3H, s); ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.5, 152.9, 150.8, 148.0, 138.7, 137.9, 131.5, 127.5, 124.8, 123.3, 120.8, 104.2, 84.8, 71.7, 60.5, 56.0, 52.0, 38.5, 10.8. IR (KBr, cm^{-1}): ν 1721; MS: M^+ 454 (100), *m/z* 433 (9), 393 (10), 375 (17), 326 (11). Anal. Calcd for $C_{19}H_{19}IO_5$: C, 50.24; H, 4.22; Found: C, 50.18; C, 50.33.

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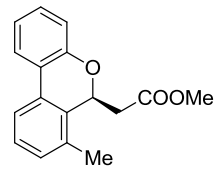
NMR Spectra (^{1}H, ^{13}C) of Products



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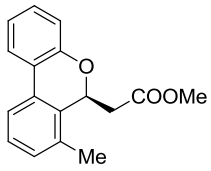

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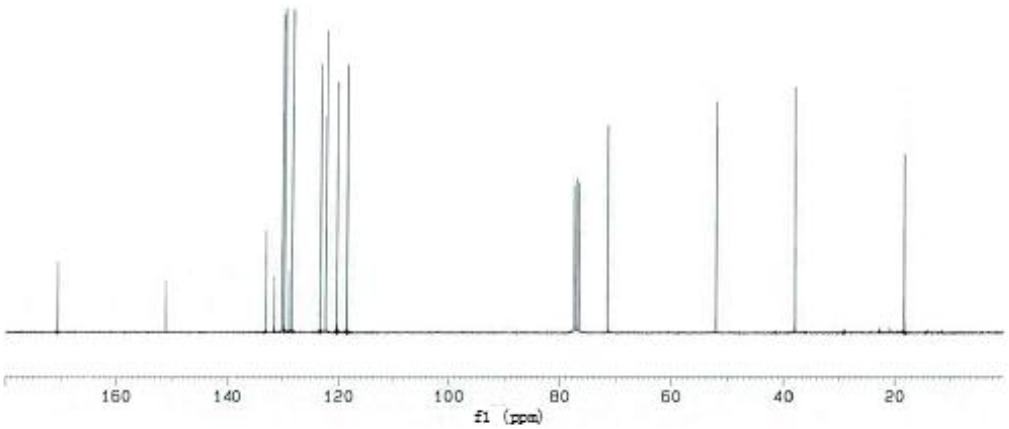

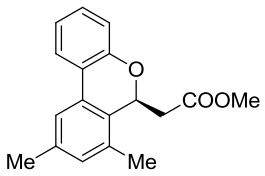
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Me
Me

5b

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5.0
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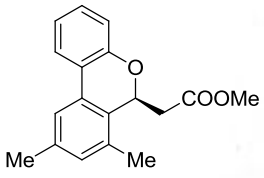
2.0
1.0
f1 (ppm)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5b

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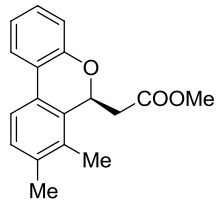
0
f1 (ppm)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Me

5c

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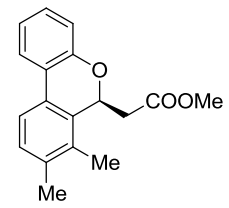
f1 (ppm)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5c

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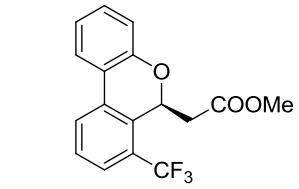
f1 (ppm)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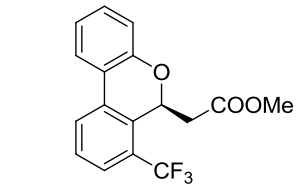
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CF3

5d

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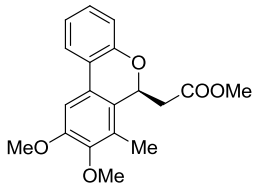
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Me
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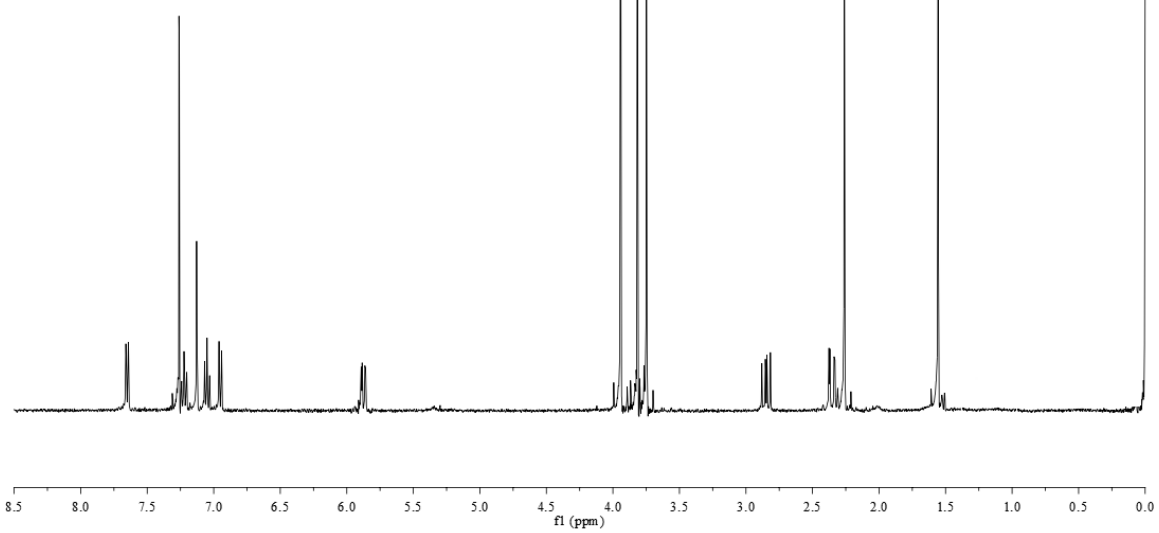
5e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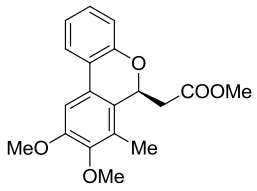
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5e

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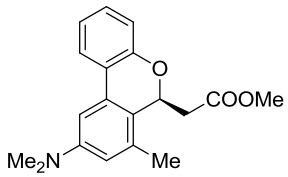
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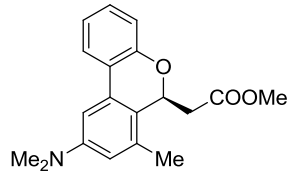
f1 (ppm)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Me2N
Me

5f

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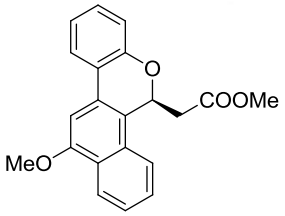
f1 (ppm)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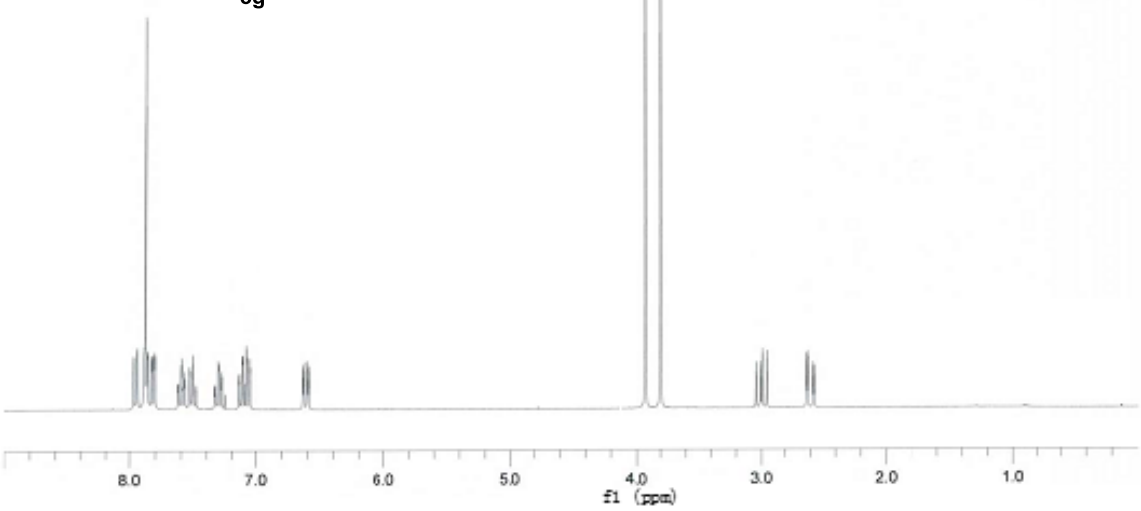
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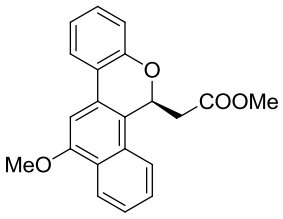
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5g

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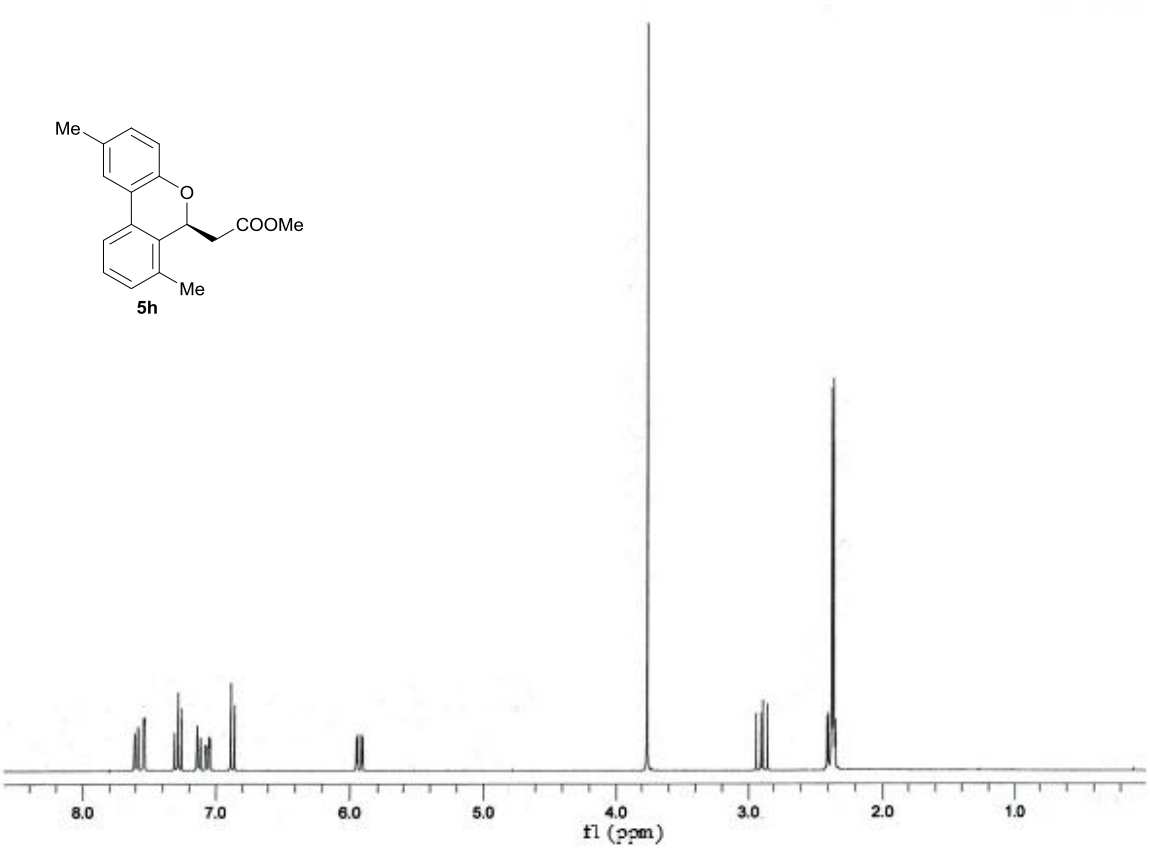
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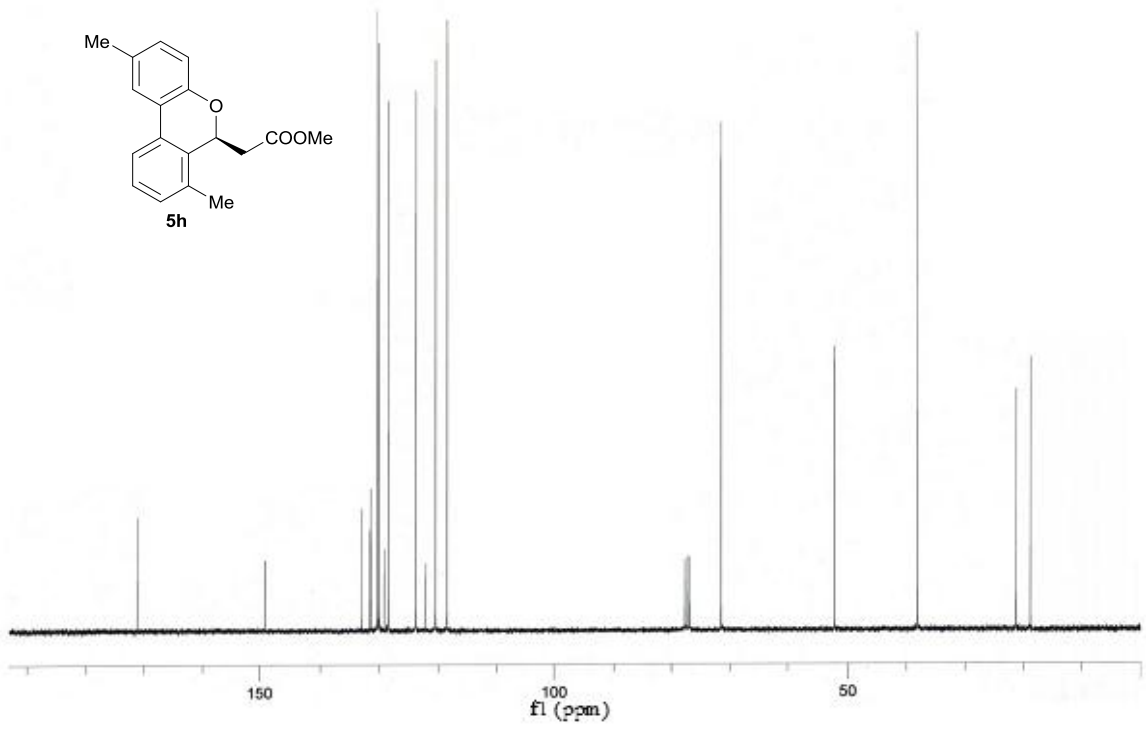
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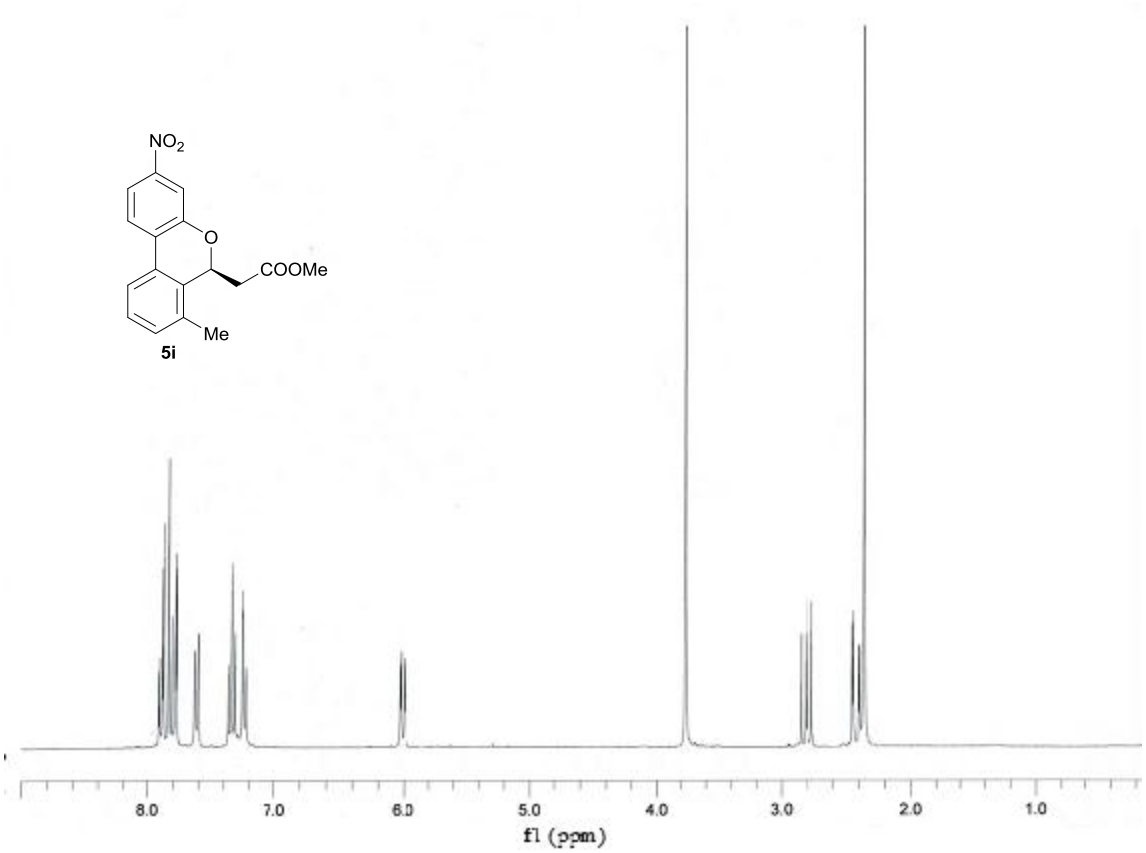
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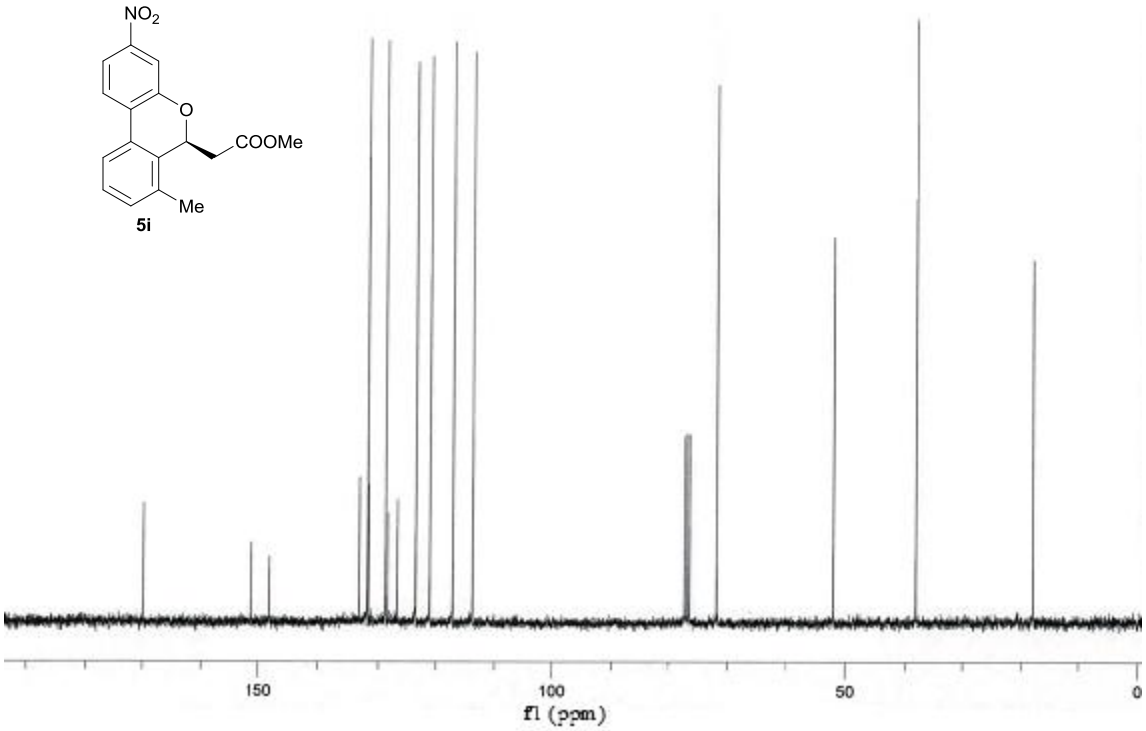
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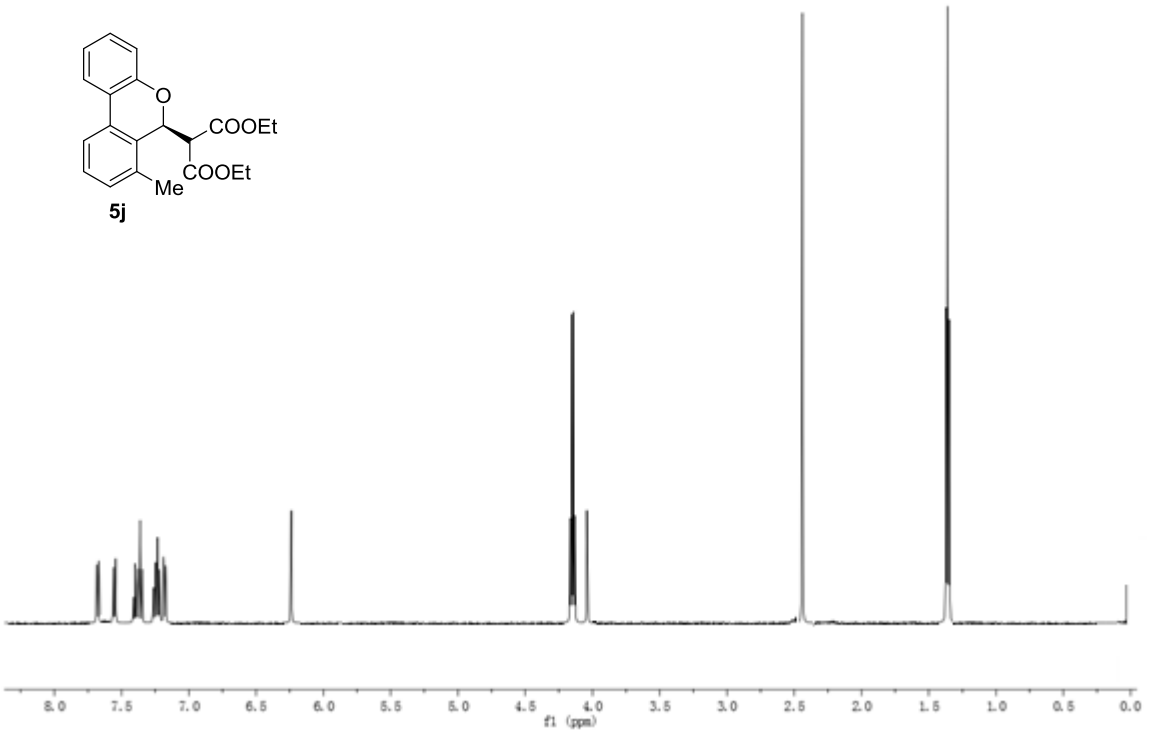
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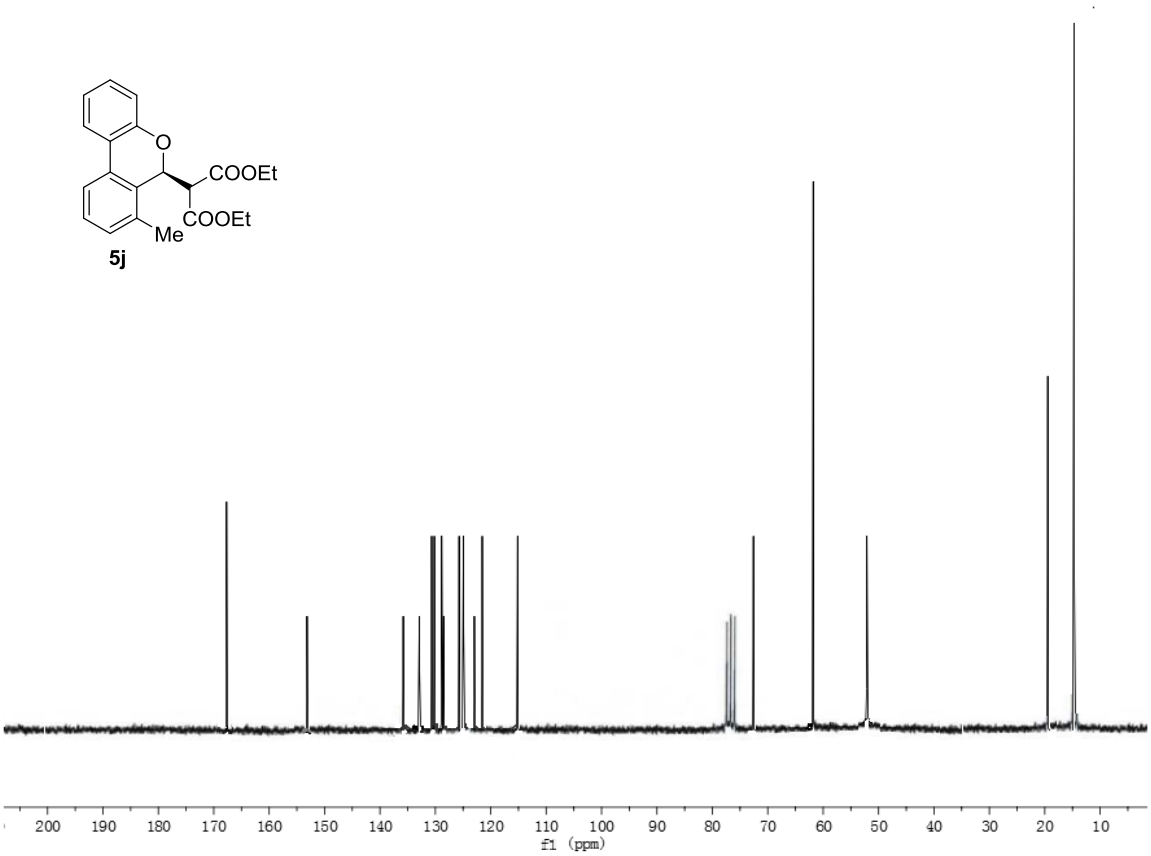
f1 (ppm)

5j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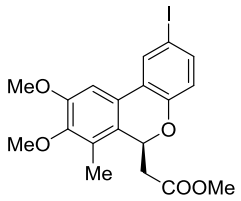
5j


I
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MeO
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O
COOMe

5k

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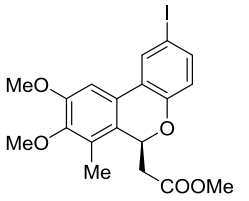
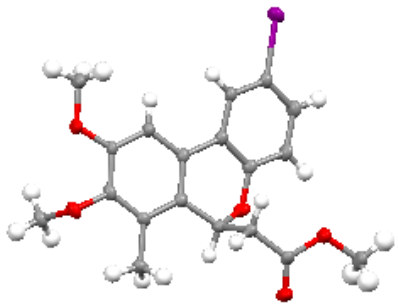
f1 (ppm)


I
MeO
MeO
Me
O
COOMe

5k

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

X-Ray Structure of **5k**



Formula	$C_{19}H_{19}IO_5$
Formula weight	454.24
Temperature / K	163(2)
Wavelength / Å	0.71073
Crystal system	Monoclinic
space group	*P2(1)/c*
Unit cell dimensions	*a* = 18.304(5) Å *α* = 90 ° *b* = 4.5035(12) Å *β* = 95.318(3) ° *c* = 21.714(6) Å *γ* = 90 °
Volume / Å^3	1782.2(8)
Z	4
Calculated density / Mg ṁ$^{-3}$	1.693
Absorption coefficient / mm^{-1}	1.823
F (000)	904
Crystal size / mm	0.64 × 0.42 × 0.17
θ range for data collection	2.28 to 31.00 °
Limiting indices	-24<=h<=26, -6<=k<=6, -31<=l<=29
Reflections collected / unique	19004 / 5623 [Rint) = 0.0403]
Completeness to theta = 29.14	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7409 and 0.3883
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5623/0/231
Goodness-of-fit on F^2	1.002
Final *R* indices [I > 2σ(I)]	R^1 = 0.0393, wR^2 = 0.1136
R indices (all data)	R^1 = 0.0506, wR^2 = 0.1261
Extinction coefficient	0.0065(7)
Largest diff. peak and hole / e.Å^{-3}	0.711 and -0.953

Atomic parameters

Atom	Ox.	Wyck.	Site	S.O.F.	x/a	y/b	z/c	U [Å^2]
I1		4e	1		0.00900(1)	-0.00361(4)	0.34245(1)	
O1		4e	1		0.28780(9)	0.6564(4)	0.27271(8)	
O2		4e	1		0.40652(10)	0.3542(5)	0.37560(8)	
O3		4e	1		0.47226(11)	0.6284(5)	0.31523(9)	
O4		4e	1		0.17268(12)	-0.0112(4)	0.02516(9)	
O5		4e	1		0.30393(9)	0.2202(4)	0.01172(7)	
C1		4e	1		0.10711(12)	0.1940(5)	0.32052(10)	

C2	4e	1	0.14299(14)	0.3911(6)	0.36191(11)	
H2	4e	1	0.12510	0.42640	0.40100	0.0320
C3	4e	1	0.20497(16)	0.5358(5)	0.34585(12)	
H3	4e	1	0.23050	0.66900	0.37410	0.0310
C4	4e	1	0.23002(15)	0.4859(4)	0.28799(12)	
C5	4e	1	0.19470(11)	0.2843(5)	0.24578(9)	
C6	4e	1	0.13295(12)	0.1372(5)	0.26353(10)	
H6	4e	1	0.10830	-0.00340	0.23640	0.0260
C7	4e	1	0.22258(12)	0.2571(5)	0.18448(9)	
C8	4e	1	0.18158(13)	0.1199(5)	0.13473(10)	
H8	4e	1	0.13540	0.03290	0.14040	0.0260
C9	4e	1	0.20854(13)	0.1114(5)	0.0770(1)	
C10	4e	1	0.27684(12)	0.2416(5)	0.06887(10)	
C11	4e	1	0.31789(12)	0.3811(5)	0.11763(10)	
C12	4e	1	0.29052(12)	0.3827(5)	0.1759(1)	
C13	4e	1	0.33443(15)	0.5173(4)	0.23135(12)	
H13	4e	1	0.36680	0.67430	0.21600	0.0250
C14	4e	1	0.38376(12)	0.2888(5)	0.26743(10)	
H14A	4e	1	0.35330	0.12900	0.28320	0.0260
H14B	4e	1	0.41770	0.19820	0.23990	0.0260
C15	4e	1	0.42685(14)	0.4422(6)	0.32067(12)	
C16	4e	1	0.4426(2)	0.5065(7)	0.42848(15)	
H16A	4e	1	0.49480	0.45410	0.43290	0.0490
H16B	4e	1	0.42020	0.44730	0.46590	0.0490
H16C	4e	1	0.43740	0.72140	0.42260	0.0490
C17	4e	1	0.39019(16)	0.5279(5)	0.10699(14)	
H17A	4e	1	0.40090	0.49480	0.06410	0.0330
H17B	4e	1	0.42950	0.44210	0.13520	0.0330
H17C	4e	1	0.38690	0.74160	0.11470	0.0330
C18	4e	1	0.10704(14)	-0.1717(7)	0.03321(12)	
H18A	4e	1	0.11750	-0.32630	0.06460	0.0400
H18B	4e	1	0.08860	-0.26380	-0.00610	0.0400
H18C	4e	1	0.07000	-0.03530	0.04670	0.0400
C19	4e	1	0.27845(18)	0.4514(6)	-0.03034(13)	
H19A	4e	1	0.22490	0.44000	-0.03820	0.0350
H19B	4e	1	0.30070	0.42730	-0.06940	0.0350
H19C	4e	1	0.29230	0.64500	-0.01220	0.0350

Anisotropic displacement parameters, in Å^2

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I1	0.02502(14)	0.03613(14)	0.02967(13)	0.00044(6)	0.01025(8)	0.00059(6)
O1	0.0229(8)	0.0186(7)	0.0300(8)	-0.0007(6)	0.0028(6)	-0.0059(6)
O2	0.0332(10)	0.0459(12)	0.0221(8)	-0.0125(9)	0.0029(7)	-0.0030(8)
O3	0.0354(11)	0.0587(14)	0.0304(9)	-0.0248(11)	0.0022(8)	-0.0038(10)
O4	0.0308(11)	0.0373(11)	0.0166(8)	-0.0091(7)	0.0037(7)	-0.0054(6)
O5	0.0312(9)	0.0267(8)	0.0213(7)	0.0037(7)	0.0097(7)	0.0024(6)
C1	0.0208(10)	0.0253(11)	0.0208(10)	0.0035(9)	0.0024(8)	0.0005(8)
C2	0.0277(12)	0.0322(12)	0.0208(10)	0.0051(10)	0.0045(9)	-0.0058(9)
C3	0.0264(13)	0.0276(12)	0.0226(11)	0.0019(9)	0.0021(10)	-0.0086(8)

C4	0.0212(12)	0.0194(10)	0.0229(11)	0.0036(7)	0.0017(9)	-0.0033(7)
C5	0.0193(10)	0.0211(10)	0.0193(9)	0.0031(8)	0.0010(8)	-0.0007(8)
C6	0.0208(10)	0.0247(10)	0.0184(9)	0.0018(9)	0.0010(8)	-0.0008(8)
C7	0.0232(10)	0.0194(9)	0.0178(9)	0.0028(8)	0.0004(8)	-0.0007(7)
C8	0.0217(10)	0.0257(11)	0.0182(9)	-0.0011(9)	0.0025(8)	-0.0007(8)
C9	0.0266(11)	0.0253(11)	0.0150(9)	0.0005(9)	0.0004(8)	0.0005(8)
C10	0.0262(11)	0.0236(10)	0.0199(10)	0.0043(9)	0.0056(8)	0.0011(8)
C11	0.0198(10)	0.0222(10)	0.0243(10)	0.0025(8)	0.0027(8)	0.0033(8)
C12	0.0223(10)	0.0174(9)	0.0224(10)	0.0002(8)	0.0008(8)	0.0004(8)
C13	0.0200(12)	0.020(1)	0.0225(11)	-0.0026(7)	0.0025(9)	-0.0017(7)
C14	0.0204(10)	0.0203(10)	0.0231(10)	-0.0007(8)	-0.0001(8)	-0.0025(8)
C15	0.0188(11)	0.0313(12)	0.0217(11)	-0.0004(9)	0.0008(9)	-0.0010(9)
C16	0.0370(18)	0.065(2)	0.0221(13)	-0.0108(13)	0.0048(12)	-0.0095(11)
C17	0.0218(13)	0.0336(13)	0.0288(13)	-0.0030(9)	0.0059(10)	0.0027(9)
C18	0.0342(13)	0.0417(15)	0.0237(11)	-0.0119(12)	0.001(1)	-0.0052(10)
C19	0.0339(15)	0.0303(12)	0.0229(12)	0.0022(10)	0.0069(11)	0.0034(9)

Selected geometric informations

Atoms 1,2	d 1,2 [?]	Atoms 1,2	d 1,2 [?]
I1—C1	2.098(2)	C8—H8	0.9500
O1—C4	1.372(3)	C9—C10	1.407(3)
O1—C13	1.439(3)	C10—C11	1.390(3)
O2—C15	1.342(3)	C11—C12	1.403(3)
O2—C16	1.444(3)	C11—C17	1.516(4)
O3—C15	1.194(3)	C12—C13	1.511(3)
O4—C9	1.366(3)	C13—C14	1.535(3)
O4—C18	1.427(3)	C13—H13	1.0000
O5—C10	1.382(3)	C14—C15	1.505(3)
O5—C19	1.434(3)	C14—H14A	0.9900
C1—C2	1.385(3)	C14—H14B	0.9900
C1—C6	1.389(3)	C16—H16A	0.9800
C2—C3	1.381(4)	C16—H16B	0.9800
C2—H2	0.9500	C16—H16C	0.9800
C3—C4	1.395(4)	C17—H17A	0.9800
C3—H3	0.9500	C17—H17B	0.9800
C4—C5	1.404(3)	C17—H17C	0.9800
C5—C6	1.395(3)	C18—H18A	0.9800
C5—C7	1.474(3)	C18—H18B	0.9800
C6—H6	0.9500	C18—H18C	0.9800
C7—C12	1.394(3)	C19—H19A	0.9800
C7—C8	1.401(3)	C19—H19B	0.9800
C8—C9	1.390(3)	C19—H19C	0.9800

Atoms 1,2,3	Angle 1,2,3 [¡ã]	Atoms 1,2,3	Angle 1,2,3 [¡ã]
C4—O1—C13	114.97(17)	O1—C13—C12	111.7(2)
C15—O2—C16	115.0(2)	O1—C13—C14	109.2(2)
C9—O4—C18	116.7(2)	C12—C13—C14	112.45(17)
C10—O5—C19	113.50(19)	O1—C13—H13	107.800
C2—C1—C6	121.1(2)	C12—C13—H13	107.800

C2—C1—I1	119.27(17)	C14—C13—H13	107.800
C6—C1—I1	119.56(16)	C15—C14—C13	109.02(19)
C3—C2—C1	119.3(2)	C15—C14—H14A	109.900
C3—C2—H2	120.300	C13—C14—H14A	109.900
C1—C2—H2	120.300	C15—C14—H14B	109.900
C2—C3—C4	119.9(2)	C13—C14—H14B	109.900
C2—C3—H3	120.100	H14A—C14—H14B	108.300
C4—C3—H3	120.100	O3—C15—O2	123.2(2)
O1—C4—C3	116.9(2)	O3—C15—C14	124.5(2)
O1—C4—C5	121.5(2)	O2—C15—C14	112.2(2)
C3—C4—C5	121.5(2)	O2—C16—H16A	109.500
C6—C5—C4	117.6(2)	O2—C16—H16B	109.500
C6—C5—C7	124.54(19)	H16A—C16—H16B	109.500
C4—C5—C7	117.8(2)	O2—C16—H16C	109.500
C1—C6—C5	120.7(2)	H16A—C16—H16C	109.500
C1—C6—H6	119.700	H16B—C16—H16C	109.500
C5—C6—H6	119.700	C11—C17—H17A	109.500
C12—C7—C8	119.8(2)	C11—C17—H17B	109.500
C12—C7—C5	118.34(19)	H17A—C17—H17B	109.500
C8—C7—C5	121.8(2)	C11—C17—H17C	109.500
C9—C8—C7	119.9(2)	H17A—C17—H17C	109.500
C9—C8—H8	120.100	H17B—C17—H17C	109.500
C7—C8—H8	120.100	O4—C18—H18A	109.500
O4—C9—C8	124.8(2)	O4—C18—H18B	109.500
O4—C9—C10	115.5(2)	H18A—C18—H18B	109.500
C8—C9—C10	119.7(2)	O4—C18—H18C	109.500
O5—C10—C11	120.1(2)	H18A—C18—H18C	109.500
O5—C10—C9	118.7(2)	H18B—C18—H18C	109.500
C11—C10—C9	121.1(2)	O5—C19—H19A	109.500
C10—C11—C12	118.4(2)	O5—C19—H19B	109.500
C10—C11—C17	119.9(2)	H19A—C19—H19B	109.500
C12—C11—C17	121.7(2)	O5—C19—H19C	109.500
C7—C12—C11	121.1(2)	H19A—C19—H19C	109.500
C7—C12—C13	118.1(2)	H19B—C19—H19C	109.500
C11—C12—C13	120.8(2)		

Atoms 1,2,3,4	Tors. an. 1,2,3,4 [¡ã]	Atoms 1,2,3,4	Tors. an. 1,2,3,4 [¡ã]
C6—C1—C2—C3	0.8(4)	C8—C9—C10—O5	177.5(2)
I1—C1—C2—C3	-175.87(19)	O4—C9—C10—C11	178.2(2)
C1—C2—C3—C4	1.0(4)	C8—C9—C10—C11	-0.4(4)
C13—O1—C4—C3	150.7(2)	O5—C10—C11—C12	-176.2(2)
C13—O1—C4—C5	-33.4(3)	C9—C10—C11—C12	1.7(3)
C2—C3—C4—O1	174.2(2)	O5—C10—C11—C17	4.0(3)
C2—C3—C4—C5	-1.7(4)	C9—C10—C11—C17	-178.1(2)
O1—C4—C5—C6	-175.1(2)	C8—C7—C12—C11	1.7(3)
C3—C4—C5—C6	0.6(3)	C5—C7—C12—C11	-175.8(2)
O1—C4—C5—C7	1.1(3)	C8—C7—C12—C13	-177.5(2)
C3—C4—C5—C7	176.9(2)	C5—C7—C12—C13	4.9(3)
C2—C1—C6—C5	-1.9(3)	C10—C11—C12—C7	-2.3(3)
I1—C1—C6—C5	174.73(16)	C17—C11—C12—C7	177.4(2)

C4—C5—C6—C1	1.2(3)	C10—C11—C12—C13	176.9(2)
C7—C5—C6—C1	-174.8(2)	C17—C11—C12—C13	-3.3(3)
C6—C5—C7—C12	-171.0(2)	C4—O1—C13—C12	49.0(2)
C4—C5—C7—C12	13.1(3)	C4—O1—C13—C14	-76.0(2)
C6—C5—C7—C8	11.5(3)	C7—C12—C13—O1	-35.3(3)
C4—C5—C7—C8	-164.4(2)	C11—C12—C13—O1	145.5(2)
C12—C7—C8—C9	-0.4(3)	C7—C12—C13—C14	87.9(3)
C5—C7—C8—C9	177.0(2)	C11—C12—C13—C14	-91.4(3)
C18—O4—C9—C8	-7.8(4)	O1—C13—C14—C15	-56.9(2)
C18—O4—C9—C10	173.7(2)	C12—C13—C14—C15	178.5(2)
C7—C8—C9—O4	-178.7(2)	C16—O2—C15—O3	1.3(4)
C7—C8—C9—C10	-0.2(3)	C16—O2—C15—C14	-176.3(2)
C19—O5—C10—C11	-95.6(3)	C13—C14—C15—O3	-65.4(3)
C19—O5—C10—C9	86.5(3)	C13—C14—C15—O2	112.1(2)
O4—C9—C10—O5	-3.9(3)		