Electronic Supplementary Information

Chiral N-Heterocyclic Carbene/Lewis Acid Cooperative Catalysis in the Reaction of 2-Aroylvinylcinnamaldehydes: A Switch of Reaction Pathway by Lewis Acid Activation

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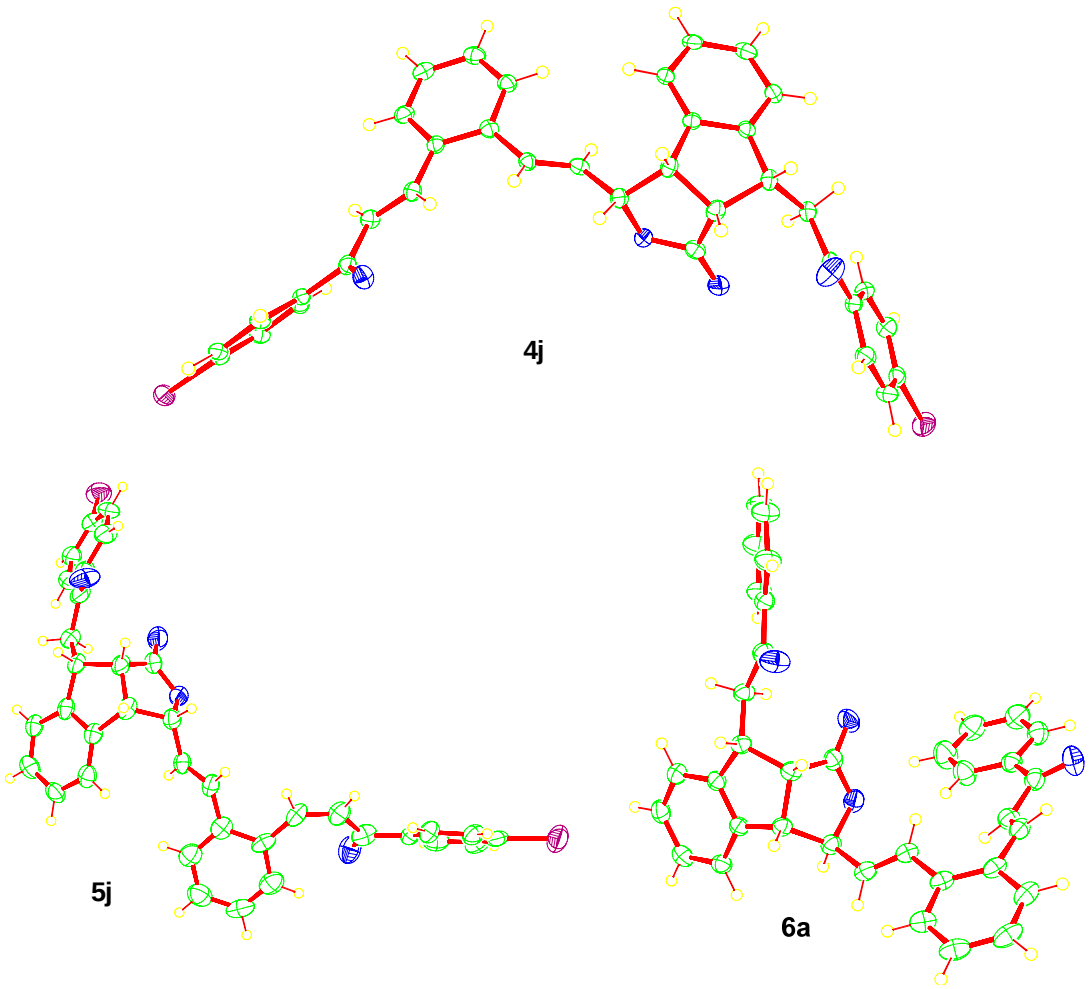


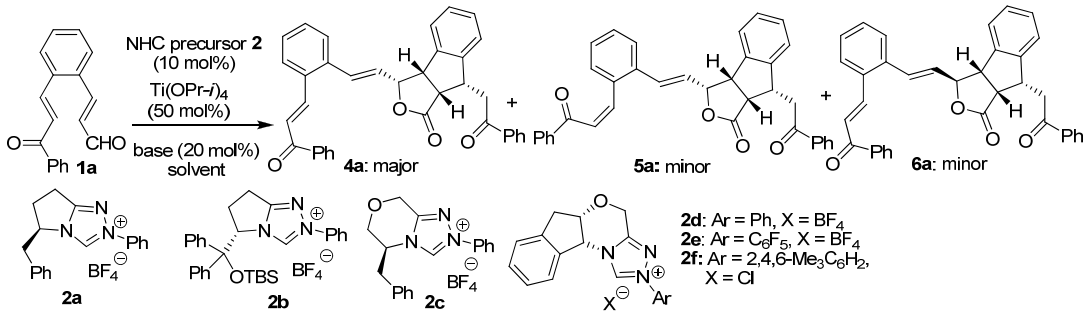
Figure S1. ORTEP drawings of X-ray structures of **4j, 5j** and **6a.**

General Information:

Commercially available chemical reagents were used without further purification. Dichloromethane was dried over CaH_2 and redistilled. Melting points are uncorrected. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded in the indicated solvents using Bruker instrument. J values are reported in Hz. IR spectra were recorded using an AVATAR 360 FT-IR spectrometer. Mass spectra were recorded on a BRUKER AUTOFLEX (MALDI-TOF) Mass spectrometer. Column chromatography was performed using 200-300 mesh silica gel. The 2-aroylvinylcinnamaldehydes **1**[1] and the chiral NHC precursor **2f**[2] were prepared according to literature method.

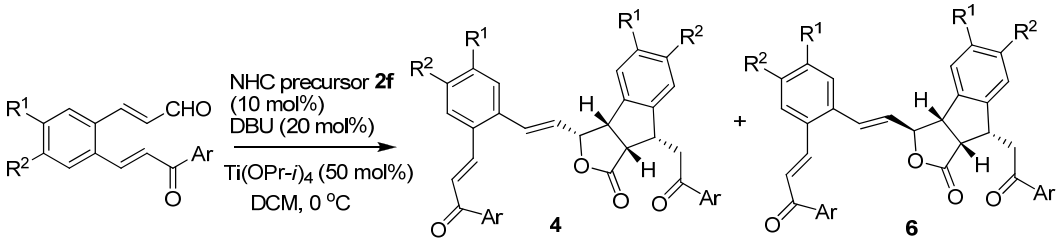
1. J. W. Yang, M. T. H. Fonseca, B. List, *J. Am. Chem. Soc*. 2005, **127**, 15036-15037.
2. J. R. Struble, J. W. Bode, *Org. Synth*. 2010, **87**, 362-376.

Table S1. Optimization of reaction conditions.



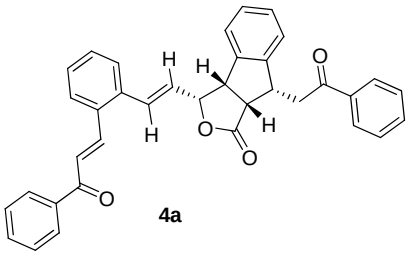
entry	**2**	base	solvent	Temp	T (h)	yield **4a+5a** (%)[a]	ee of **4a** (%)[b]	**4a**:**5a**[c]	yield **6a** (%)[a]	**4a**:**6a**[d] (dr)
1	**2a**	DIPEA	DCM	rt	21	10	-89	8:1	—	ND
2	**2b**	DIPEA	DCM	rt	12	24	99	4:1	—	ND
3	**2c**	DIPEA	DCM	rt	24	10	-85	5:1	—	ND
4	**2d**	DIPEA	DCM	rt	25	21	99	12:1	—	ND
5	**2e**	DIPEA	DCM	rt	48	mess	—	—	—	
6	**2f**	DIPEA	DCM	rt	5	63	99	7:1	6	9:1
7	**2f**	*t*-BuOK	DCM	rt	5	38	99	9:1	5	7:1
8	**2f**	Cs_2CO_3	DCM	rt	5	31	99	8:1	5	6:1
9	**2f**	NaH	DCM	rt	5	55	97	3:1	8	5:1
10	**2f**	DBU	DCM	rt	5	75	>99	9:1	8	9:1
11	**2f**	DBU	THF	rt	5	36	99	10:1	5	7:1
12	**2f**	DBU	acetone	rt	5	50	99	5:1	4	13:1
13	**2f**	DBU	toluene	rt	5	56	99	3:1	10	4:1
14	**2f**	DBU	CH_3CN	rt	5	62	99	8:1	6	9:1
15	**2f**	DBU	DCM	0 °C	2	80	>99	14:1	4	20:1
16	**2f**	DBU	DCM	reflux	5	62	98	9:1	6	9:1

[a]Isolated yields. [b]Determined by HPLC analysis on a AD-H column. [c]Determined by ^{1}H NMR. [d]Calculated based on the yields of **4a** and **6a**.

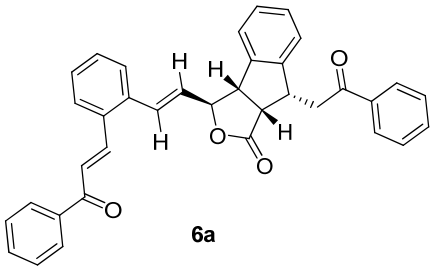


General procedure for the NHC/Ti(OPr-*i*)$_4$-catalyzed dimerization reaction of 2-aroylvinylcinnamaldehydes 1.

Under nitrogen atmosphere, 2-aroylvinylcinnamaldehydes **1** (1 mmol), *N*-mesityl-indeno[2,1-b]triazolo[4,3-d][1,4]oxazinium salt **2f** (27 mg, 0.1 mmol) and Ti(OPr-*i*)$_4$ (0.5 mmol) were mixed in dry dichloromethane (20 mL). The resulting mixture was cooled to 0 °C in an ice-bath, and then DBU (0.2 mmol) was added using a microsyringe. The reaction mixture was then stirred at 0 °C for 2-3 h. After removal of the solvent, the residue was chromatographyed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE:EA = 4:1) to give the major products indeno[1,2-*c*]furan-1-ones **4** in 67%-88% yields with 95%-99% ee. In addition, a trace amount of minor diastereoisomers **6** (4%-7%) were also isolated.

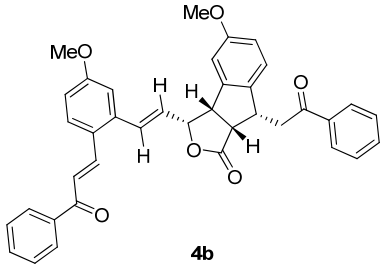


(*3R,3aS,8R,8aS*)-8-(Benzoylmethyl)-3-((*E*)-2-((*E*)-benzoylvinyl)styryl)-3,3a,8,8a-tetrahydroindeno[1,2-*c*]furan-1-one 4a: white solid, 209 mg, 80%, ee >99%, $[\alpha]^{20}_{D}$ = -55.3 ° (*c* = 0.45, CH_2Cl_2), mp 134-135 °C; IR *v* (cm^{-1}) 1763, 1682, 1599; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.16 (d, *J* = 15.5 Hz, 1H), 8.08 (d, *J* = 7.2 Hz, 2H), 8.02 (d, *J* = 7.2 Hz, 2H), 7.71 (d, *J* = 7.3 Hz, 1H), 7.56-7.61 (m, 2H), 7.47-7.53 (m, 5H), 7.36-7.47 (m, 3H), 7.26-7.30 (m, 2H), 7.18-7.23 (m, 3H), 6.22 (dd, *J* = 15.8, 8.1 Hz, 1H), 5.41 (t, *J* = 7.2 Hz, 1H), 4.32 (t, *J* = 7.3 Hz, 1H), 4.18-4.24 (m, 1H), 4.01 (dd, *J* = 18.2, 9.8 Hz, 1H), 3.91 (t, *J* = 8.3 Hz, 1H), 3.53 (dd, *J* = 18.2, 5.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.1, 190.1, 176.4, 145.3, 141.8, 138.0, 137.6, 137.1, 136.3, 133.6, 133.1, 133.0, 130.8, 130.4, 128.7, 128.6, 128.57, 128.4, 128.2, 127.5, 127.2, 127.1, 127.0, 124.8, 123.5, 81.4, 49.9, 46.4, 40.6, 38.5; HRMS (MALDI-TOF): $[M + Na]^+$ calcd for $C_{36}H_{28}O_4Na$: 547.1880; found: 547.1882.



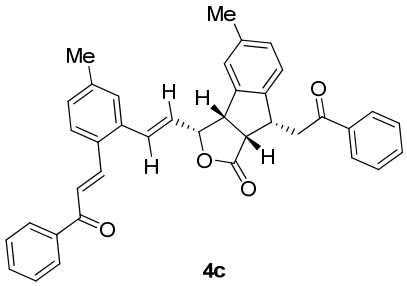
6a

(*3S,3aS,8R,8aS*)-8-(Benzoylmethyl)-3-((*E*)-2-((*E*)-benzoylvinyl)styryl)-3,3a,8,8a-tetrahydroindeno[1,2-*c*]furan-1-one 6a: white solid, 10 mg, 4%, ee >99%, $[\alpha]^{20}_{D}$ = -29.5 ^{o} (*c* = 0.5, CH_2Cl_2), mp 102-103 ^{o}C; IR *v* (cm^{-1}) 1769, 1680, 1603; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.16 (d, *J* = 15.5 Hz, 1H), 8.07 (d, *J* = 7.3 Hz, 2H), 8.03 (d, *J* = 7.1 Hz, 2H), 7.71 (d, *J* = 7.3 Hz, 1H), 7.56-7.60 (m, 2H), 7.47-7.53 (m, 6H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.31-7.41 (m, 3H), 7.22 (d, *J* = 6.2 Hz, 1H), 7.16 (d, *J* = 15.6 Hz, 1H), 6.24 (dd, *J* = 15.6, 6.8 Hz, 1H), 5.30 (d, *J* = 6.8 Hz, 1H), 4.25-4.31 (m, 1H), 4.01 (d, *J* = 7.7 Hz, 1H), 3.95 (dd, *J* = 18.3, 9.4 Hz, 1H), 3.84 (t, *J* = 8.0 Hz, 1H), 3.53 (dd, *J* = 18.3, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.1, 190.3, 176.6, 144.2, 142.2, 141.1, 138.0, 137.0, 136.4, 133.5, 133.1, 133.0, 131.3, 130.3, 130.0, 128.7, 128.59, 128.56, 128.2, 128.1, 127.7, 127.5, 124.7, 124.2, 123.4, 83.7, 51.2, 44.7, 41.0, 38.4; HRMS (MALDI-TOF): $[M + Na]^+$ calcd for $C_{36}H_{28}O_4Na$: 547.1880; found: 547.1882.



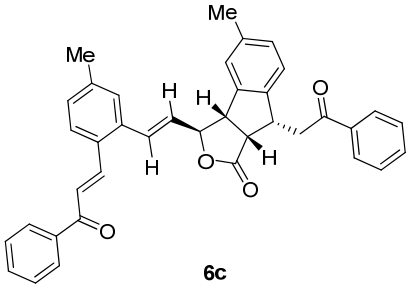
4b

(*3R,3aS,8R,8aS*)-8-(Benzoylmethyl)-5-methoxy-3-((*E*)-2-((*E*)-benzoylvinyl)-5-methoxystyryl)-3,3a,8,8a-tetrahydroindeno[1,2-*c*]furan-1-one 4b: white solid, 225 mg, 77%, ee >99%, $[\alpha]^{20}_{D}$ = +8.6 ^{o} (*c* = 0.45, CH_2Cl_2), mp 71-72 ^{o}C; IR *v* (cm^{-1}) 1763, 1684, 1659, 1584; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.13 (d, *J* = 15.4 Hz, 1H), 8.07 (d, *J* = 7.2 Hz, 2H), 8.01 (d, *J* = 7.2 Hz, 2H), 7.70 (d, *J* = 8.7 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 7.47-7.52 (m, 4H), 7.40 (d, *J* = 15.4 Hz, 1H), 7.23 (d, *J* = 16.0 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 7.03 (d, *J* = 2.6 Hz, 1H), 6.93 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.83 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.79 (d, *J* = 2.1 Hz, 1H), 6.20 (dd, *J* = 15.8, 8.2 Hz, 1H), 5.42 (t, *J* = 7.3 Hz, 1H), 4.29 (t, *J* = 7.4 Hz, 1H), 4.12-4.18 (m, 1H), 3.95 (dd, *J* = 18.2, 9.8 Hz, 1H), 3.92 (t, *J* = 8.7, 1H), 3.86 (s, 3H), 3.63 (s, 3H), 3.48 (dd, *J* = 18.2, 5.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.2, 190.1, 176.3, 161.4, 159.0, 141.2, 139.0, 138.30, 138.3, 137.3, 137.1, 133.0, 132.8, 130.6, 129.1, 129.0, 128.7, 128.6, 128.5, 128.1, 126.1, 124.1, 122.3, 115.3, 114.4, 112.5, 111.4, 81.1, 55.4, 55.3, 49.9, 46.7, 39.9, 38.8; HRMS (MALDI-TOF): $[M + Na]^+$ calcd for $C_{38}H_{32}O_6Na$: 607.2091; found: 607.2091.



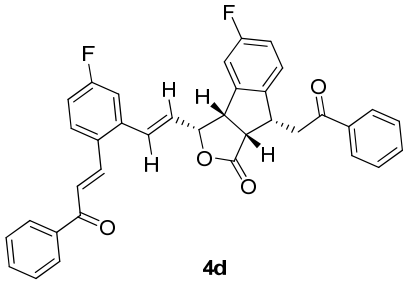
4c

(*3R,3aS,8R,8aS*)-8-(Benzoylmethyl)-5-methyl-3-((*E*)-2-((*E*)-benzoylvinyl)-5-methylstyryl)-3,3a,8,8a-tetrahydroindeno[1,2-*c*]furan-1-one 4c: white solid, 220 mg, 80%, ee 99%, $[\alpha]^{20}_{D}$ = +39 ^{o} (*c* = 0.45, CH_2Cl_2), mp 94-95 ^{o}C; IR *v* (cm^{-1}) 1765, 1684, 1597; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.13 (d, *J* = 15.5 Hz, 1H), 8.07 (d, *J* = 7.2 Hz, 2H), 8.01 (d, *J* = 7.1 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.55-7.60 (m, 2H), 7.50 (d, *J* = 7.6 Hz, 2H), 8.47 (d, *J* = 7.3 Hz, 2H), 7.44 (d, *J* = 15.5 Hz, 1H), 7.34 (s, 1H), 7.11-7.20 (m, 5H), 6.18 (dd, *J* = 15.8, 8.1 Hz, 1H), 5.39 (t, *J* = 7.2 Hz, 1H), 4.27 (t, *J* = 7.4 Hz, 1H), 4.14-4.19 (m, 1H), 3.96 (dd, *J* = 18.2, 9.9 Hz, 1H), 3.90 (t, *J* = 8.4 Hz, 1H), 3.50 (dd, *J* = 18.2, 4.9 Hz, 1H), 2.40 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.2, 190.2, 176.4, 142.4, 141.7, 140.7, 138.1, 137.8, 137.1, 136.7, 136.5, 133.0, 132.9, 130.8, 130.4, 129.5, 129.2, 128.7, 128.6, 128.5, 128.1, 127.82, 127.75, 127.5, 123.8, 123.2, 81.3, 49.9, 46.4, 40.3, 38.6, 21.5, 21.3; HRMS (MALDI-TOF): $[M + Na]^+$ calcd for $C_{38}H_{32}O_4Na$: 575.2193; found: 575.2195.



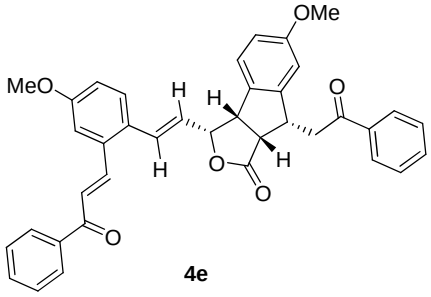
6c

(*3S,3aS,8R,8aS*)-8-(Benzoylmethyl)-5-methyl-3-((*E*)-2-((*E*)-benzoylvinyl)-5-methylstyryl)-3,3a,8,8a-tetrahydroindeno[1,2-*c*]furan-1-one 6c: white solid, 17.5 mg, 6%, ee >99%, $[\alpha]^{20}_{D}$ = -27.3 ^{o} (c = 0.50, CH_2Cl_2), mp 187-188 ^{o}C; IR *v* (cm^{-1}) 1765, 1680, 1597; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.16 (d, *J* = 15.5 Hz, 1H), 8.07 (d, *J* = 7.3 Hz, 2H), 8.03 (d, *J* = 7.1 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.55-7.60 (m, 2H), 7.51 (d, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.45 (d, *J* = 15.4 Hz, 1H), 7.33 (s, 1H), 7.08-7.20 (m, 4H), 6.22 (dd, *J* = 15.6, 7.1 Hz, 1H), 5.28 (d, *J* = 7.0 Hz, 1H), 4.20-4.25 (m, 1H), 3.96 (d, *J* = 7.4 Hz, 1H), 3.91 (t, *J* = 9.6 Hz, 1H), 3.84 (t, *J* = 7.9 Hz, 1H), 3.50 (dd, *J* = 18.3, 5.2 Hz, 1H), 2.42 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.2, 190.4, 176.7, 142.1, 141.3, 141.2, 140.8, 138.2, 138.0, 137.1, 136.5, 133.0, 132.8, 131.2, 130.8, 130.2, 129.5, 129.4, 128.7, 128.6, 128.5, 128.3, 128.2, 127.4, 124.7, 123.7, 123.1, 83.7, 51.2, 44.9, 40.7, 38.5, 21.5, 21.3; HRMS (MALDI-TOF): $[M + Na]^+$ calcd for $C_{38}H_{32}O_4Na$: 575.2193; found: 575.2195.



4d

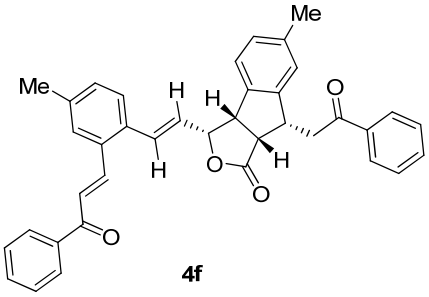
(*3R,3aS,8R,8aS*)-8-(Benzoylmethyl)-5-fluoro-3-((*E*)-2-((*E*)-benzoylvinyl)-5-fluorostyryl)-3,3a, 8,8a-tetrahydroindeno[1,2-*c*]furan-1-one 4d: white solid, 227 mg, 81%, ee >99%, $[\alpha]^{20}_{D}$ = -58.4 ^{o} (*c* = 0.45, CH_2Cl_2), mp 132-133 ^{o}C; IR *v* (cm^{-1}) 1771, 1674, 1595; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.08 (d, *J* = 15.3 Hz, 1H), 8.07 (d, *J* = 7.6 Hz, 2H), 8.02 (d, *J* = 7.5 Hz, 2H), 7.72 (dd, *J* = 8.6, 5.8 Hz, 1H), 7.57-7.62 (m, 2H), 7.48-7.53 (m, 4H), 7.42 (d, *J* = 15.4 Hz, 1H), 7.13-7.21 (m, 3H), 7.10 (dt, *J* = 8.2, 2.4 Hz, 1H), 6.99 (dt, *J* = 8.4, 2.2 Hz, 1H), 6.90 (d, *J* = 8.9 Hz, 1H), 6.20 (dd, *J* = 15.8, 7.8 Hz, 1H), 5.41 (t, *J* = 7.3 Hz, 1H), 4.30 (t, *J* = 7.3 Hz, 1H), 4.12-4.18 (m, 1H), 3.98 (dd, *J* = 18.2, 9.6 Hz, 1H), 3.94 (t, *J* = 8.4 Hz, 1H), 3.50 (dd, *J* = 18.2, 5.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.9, 189.8, 175.9, 164.2 (d, $J_{C\text{-}F}$ = 184 Hz), 161.7 (d, $J_{C\text{-}F}$ = 179 Hz), 140.8, 140.4, 139.5 (d, $J_{C\text{-}F}$ = 8 Hz), 138.4 (d, $J_{C\text{-}F}$ = 8 Hz), 137.9, 136.9, 133.1 (d, $J_{C\text{-}F}$ = 11 Hz), 133.0, 129.8, 129.77, 129.6 (d, $J_{C\text{-}F}$ = 8 Hz), 129.0, 128.7, 128.6, 128.5, 128.1, 124.6 (d, $J_{C\text{-}F}$ = 8 Hz), 124.5, 116.1 (d, $J_{C\text{-}F}$ = 22 Hz), 115.7 (d, $J_{C\text{-}F}$ = 22 Hz), 113.8 (d, $J_{C\text{-}F}$ = 19 Hz), 113.6 (d, $J_{C\text{-}F}$ = 18 Hz), 80.6, 49.7, 46.7, 40.0, 38.5; HRMS (MALDI-TOF): $[M + Na]^{+}$ calcd for $C_{36}H_{26}F_2O_4Na$: 583.1691; found: 583.1694.



4e

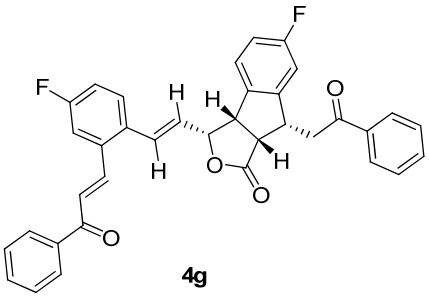
(*3R,3aS,8R,8aS*)-8-(Benzoylmethyl)-6-methoxy-3-((*E*)-2-((*E*)-benzoylvinyl)-4-methoxystyryl)-3,3a,8,8a-tetrahydroindeno[1,2-*c*]furan-1-one 4e: white solid, 222 mg, 76%, ee 99%, $[\alpha]^{20}_{D}$ = -104.7 ^{o} (*c* = 0.45, CH_2Cl_2), mp 96-97 ^{o}C; IR *v* (cm^{-1}) 1763, 1680, 1603; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.14 (d, *J* = 15.5 Hz, 1H), 8.08 (d, *J* = 7.2 Hz, 2H), 8.02 (d, *J* = 7.2 Hz, 2H), 7.56-7.61 (m, 2H), 7.47-7.53 (m, 5H), 7.43 (d, *J* = 15.5 Hz, 1H), 7.18 (d, *J* = 2.6 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 1H), 7.11 (d, *J* = 15.7 Hz, 1H), 6.99 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.75 (dd, *J* = 10.4, 2.0 Hz, 1H), 6.73 (s, 1H), 6.10 (dd, *J* = 15.7, 8.2 Hz, 1H), 5.34 (t, *J* = 7.2 Hz, 1H), 4.22 (t, *J* = 7.2 Hz, 1H), 4.13-4.19 (m, 1H), 4.01 (dd, *J* = 18.1, 9.9 Hz, 1H), 3.88-3.92 (m, 1H), 3.88 (s, 3H), 3.76 (s, 3H), 3.48 (dd, *J* = 18.1, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.1, 190.1, 176.5,

160.1, 159.7, 147.0, 141.8, 137.9, 137.1, 134.8, 133.0, 130.3, 129.6, 129.2, 128.7, 128.58, 128.57, 128.4, 128.2, 127.6, 126.5, 125.0, 116.5, 113.3, 112.0, 108.7, 81.7, 55.5, 55.4, 49.2, 47.0, 40.6, 38.4; HRMS (MALDI-TOF): $[M + Na]^+$ calcd for $C_{38}H_{32}O_6Na$: 607.2091; found: 607.2093.



4f

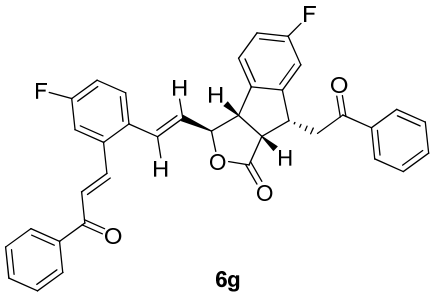
(*3R,3aS,8R,8aS*)-8-(Benzoylmethyl)-6-methyl-3-((*E*)-2-((*E*)-benzoylvinyl)-4-methylstyryl)-3,3a,8,8a-tetrahydroindeno[1,2-*c*]furan-1-one 4f: white solid, 203 mg, 73%, ee 99%, $[\alpha]^{20}_D$ = -95.3 ^{o} (*c* = 0.50, CH_2Cl_2), mp 113-114 ^{o}C; IR *v* (cm^{-1}) 1763, 1672, 1599; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.16 (d, *J* = 15.5 Hz, 1H), 8.09 (d, *J* = 7.2 Hz, 2H), 8.03 (d, *J* = 7.1 Hz, 2H), 7.57-7.62 (m, 2H), 7.45-7.53 (m, 5H), 7.43 (d, *J* = 2.7 Hz, 1H), 7.24 (d, *J* = 8.6 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 3.6 Hz, 1H), 7.02 (s, 1H), 7.01 (d, *J* = 6.0 Hz, 1H), 6.18 (dd, *J* = 15.8, 8.2 Hz, 1H), 5.38 (t, *J* = 7.2 Hz, 1H), 4.26 (t, *J* = 7.2 Hz, 1H), 4.14-4.19 (m, 1H), 4.00 (dd, *J* = 18.2, 10.0 Hz, 1H), 3.90 (t, *J* = 8.2 Hz, 1H), , 3.52 (dd, *J* = 18.2, 4.8 Hz, 1H), 2.42 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.2, 190.1, 176.5, 145.4, 141.9, 138.4, 138.2, 138.0, 137.1, 134.7, 133.6, 133.4, 133.0, 132.9, 131.4, 130.6, 128.7, 128.56, 128.55, 128.2, 128.1, 127.9, 127.5, 127.0, 126.7, 124.6, 124.0, 81.5, 49.5, 46.6, 40.4, 38.5, 21.3, 21.2; HRMS (MALDI-TOF): $[M + Na]^+$ calcd for $C_{38}H_{32}O_4Na$: 575.2193; found: 575.2194.



4g

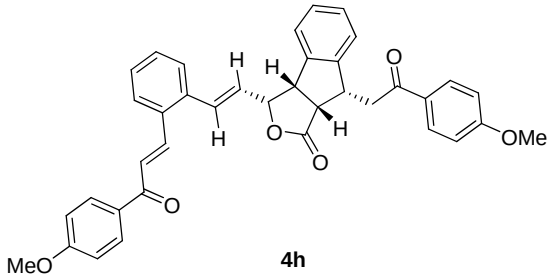
(*3R,3aS,8R,8aS*)-8-(Benzoylmethyl)-6-fluoro-3-((*E*)-2-((*E*)-benzoylvinyl)-4-fluorostyryl)-3,3a,8,8a-tetrahydroindeno[1,2-*c*]furan-1-one 4g: white solid, 188 mg, 67%, ee 95%, $[\alpha]^{20}_D$ = -54.3 ^{o} (*c* = 0.45, CH_2Cl_2), mp 181-182 ^{o}C; IR *v* (cm^{-1}) 1767, 1682, 1667, 1605; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09 (d, *J* = 16.3 Hz, 1H), 8.07 (d, *J* = 7.2 Hz, 2H), 8.03 (d, *J* = 7.3 Hz, 2H), 7.57-7.63 (m, 2H), 7.45-7.54 (m, 6H), 7.40 (dd, *J* = 9.6, 2.6 Hz, 1H), 7.13-7.19 (m, 2H), 7.13 (d, *J* = 16.1 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 1H), 6.89-6.92 (m, 1H), 6.11 (dd, *J* = 15.8, 8.0 Hz, 1H), 5.38 (t, *J* = 7.2 Hz, 1H), 4.27 (t, *J* = 7.2 Hz, 1H), 4.16-4.21 (m, 1H), 4.01 (dd, *J* = 18.2, 9.7 Hz, 1H), 3.94 (t, *J* = 8.3, 1H), , 3.48 (dd, *J* = 18.2, 5.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.7,

189.6, 176.0, 164.4 (d, $J_{C\text{-}F}$ = 59 Hz), 161.7 (d, $J_{C\text{-}F}$ = 61 Hz), 147.8 (d, $J_{C\text{-}F}$ = 8 Hz), 140.3, 137.7, 136.8, 135.4 (d, $J_{C\text{-}F}$ = 7 Hz), 133.2 (d, $J_{C\text{-}F}$ = 6 Hz), 133.0 (d, $J_{C\text{-}F}$ = 2 Hz), 132.4 (d, $J_{C\text{-}F}$ = 3.0 Hz), 130.0, 129.0 (d, $J_{C\text{-}F}$ = 8 Hz), 128.8, 128.63, 128.57, 128.2, 128.0, 127.9, 125.5, 117.6 (d, $J_{C\text{-}F}$ = 21 Hz), 114.5 (d, $J_{C\text{-}F}$ = 23 Hz), 113.7 (d, $J_{C\text{-}F}$ = 22 Hz), 110.7 (d, $J_{C\text{-}F}$ = 22 Hz), 81.2, 49.1, 46.9, 40.6, 38.2; HRMS (MALDI-TOF): $[M + Na]^+$ calcd for $C_{36}H_{26}F_2O_4Na$: 583.1691; found: 583.1693.



6g

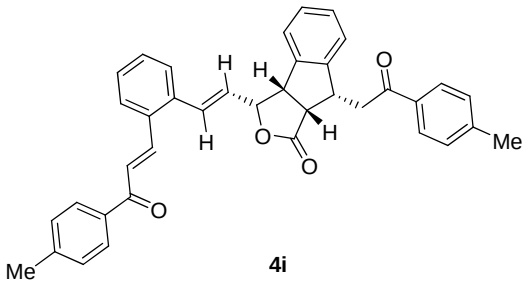
(*3S,3aS,8R,8aS*)-8-(Benzoylmethyl)-6-fluoro-3-((*E*)-2-((*E*)-benzoylvinyl)-4-fluorostyryl)-3,3a, 8,8a-tetrahydroindeno[1,2-*c*]furan-1-one 6g: white solid, 17.1 mg, 6%, ee >99%, $[\alpha]^{20}_D$ = -26.1 ^{o} (c = 0.50, CH_2Cl_2), mp 127-128 ^{o}C; IR *v* (cm^{-1}) 1765, 1682, 1667, 1597; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09 (d, *J* = 15.7 Hz, 1H), 8.07 (d, *J* = 8.9 Hz, 2H), 8.04 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.59 (dt, *J* = 7.2, 1.4 Hz, 2H), 7.47-7.54 (m, 5H), 7.44 (s, 1H), 7.36-7.41 (m, 2H), 7.13 (dt, *J* = 8.3, 2.6 Hz, 1H), 7.59 (d, *J* = 15.6 Hz, 1H), 7.02 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 1H), 6.17 (dd, *J* = 15.6, 6.8 Hz, 1H), 5.25 (d, *J* = 6.8 Hz, 1H), 4.23-4.29 (m, 1H), 3.96 (dd, *J* = 18.2, 9.2 Hz, 1H), 3.97 (d, *J* = 7.5 Hz, 1H), 3.86 (t, *J* = 8.0 Hz, 1H), 3.47 (dd, *J* = 18.3, 5.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.7, 189.8, 176.2, 146.7, 146.6, 140.8, 137.7, 136.8, 136.5, 135.4 (d, $J_{C\text{-}F}$ = 8 Hz), 133.3, 133.2, 132.5, 131.1, 129.7, 129.6, 129.2, 128.8, 128.7, 128.6, 128.2, 125.4, 125.3 (d, $J_{C\text{-}F}$ = 9 Hz), 117.5 (d, $J_{C\text{-}F}$ = 21 Hz), 115.3 (d, $J_{C\text{-}F}$ = 23 Hz), 113.7 (d, $J_{C\text{-}F}$ = 22 Hz), 110.8 (d, $J_{C\text{-}F}$ = 23 Hz), 83.5, 50.5, 45.2, 40.9, 38.2; HRMS (MALDI-TOF): [M + Na]+ calcd for $C_{36}H_{26}F_2NaO_4$: 583.1691; found: 583.1692.



4h

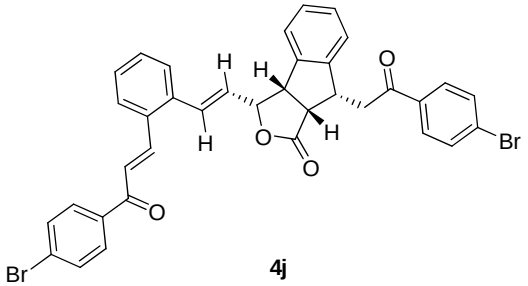
(*3R,3aS,8R,8aS*)-8-((4-Methoxybenzoyl)methyl)-3-((*E*)-2-((*E*)-(4-methoxybenzoyl)vinyl)styryl)-3,3a,8,8a-tetrahydroindeno[1,2-*c*]furan-1-one 4h: white solid, 258 mg, 88%, ee >99%, $[\alpha]^{20}_D$ = -39.4 ^{o} (*c* = 0.50, CH_2Cl_2), mp 165-166 ^{o}C; IR *v* (cm^{-1}) 1765, 1668, 1601; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.13 (d, *J* = 15.4 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 7.1 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.46 (d, *J* = 15.4 Hz, 1H), 7.35-7.42 (m, 2H), 7.18-7.28 (m, 5H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 6.22 (dd, *J* = 15.8, 8.2 Hz, 1H), 5.41 (t, *J* = 7.2 Hz, 1H), 4.30 (t, *J* = 7.3 Hz, 1H), 4.17-4.23 (m, 1H), 3.96 (dd, *J* = 18.0, 9.7

Hz, 1H), 3.90 (d, *J* = 8.4 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.49 (dd, *J* = 18.0, 5.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.6, 188.4, 176.4, 163.6, 163.4, 145.5, 140.9, 137.6, 136.1, 133.8, 130.9, 130.8, 130.4, 130.2, 130.1, 128.5, 128.3, 128.2, 127.5, 127.1, 127.03, 126.96, 124.9, 123.5, 113.9, 113.7, 81.4, 55.52, 55.46, 49.8, 46.5, 40.6, 38.0; HRMS (MALDI-TOF): $[M + Na]^+$ calcd for $C_{38}H_{32}O_6Na$: 607.2091; found: 607.2093.



4i

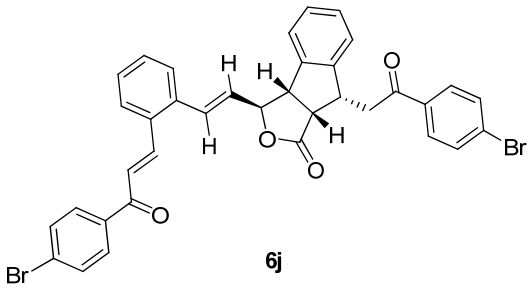
(*3R,3aS,8R,8aS*)-8-((4-Methylbenzoyl)methyl)-3-((*E*)-2-((*E*)-(4-methylbenzoyl)vinyl)styryl)-3, 3a,8,8a-tetrahydroindeno[1,2-*c*]furan-1-one 4i: white solid, 229 mg, 83%, ee >99%, $[\alpha]^{20}_D$ = -44 ^{o} (*c* = 0.45, CH_2Cl_2), mp 153-154 ^{o}C; IR *v* (cm^{-1}) 1767, 1680, 1663, 1607; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.16 (d, *J* = 15.5 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 7.3 Hz, 1H), 7.47 (d, *J* = 15.5 Hz, 1H), 7.36-7.43 (m, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.18-7.26 (m, 5H), 6.21 (dd, *J* = 15.8, 8.2 Hz, 1H), 5.41 (t, *J* = 7.3 Hz, 1H), 4.31 (t, *J* = 7.3 Hz, 1H), 4.18-4.24 (m, 1H), 3.98 (dd, *J* = 18.1, 9.7 Hz, 1H), 3.90 (t, *J* = 8.3 Hz, 1H), 3.51 (dd, *J* = 18.2, 5.0 Hz, 1H), 2.43 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.7, 189.5, 176.4, 145.4, 143.9, 143.8, 141.3, 137.6, 136.2, 135.4, 134.6, 133.7, 130.9, 130.3, 129.4, 129.3, 128.7, 128.6, 128.33, 128.29, 127.5, 127.2, 127.1, 127.0, 124.9, 123.5, 100.0, 81.4, 49.9, 46.4, 40.6, 38.3, 21.73, 21.69; HRMS (MALDI-TOF): $[M + Na]^+$ calcd for $C_{38}H_{32}O_4Na$: 575.2193; found: 575.2194.



4j

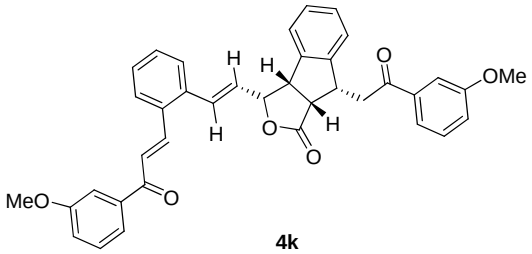
(*3R,3aS,8R,8aS*)-8-((4-Bromobenzoyl)methyl)-3-((*E*)-2-((*E*)-(4-bromobenzoyl)vinyl)styryl)-3, 3a,8,8a-tetrahydroindeno[1,2-*c*]furan-1-one 4j: white solid, 265 mg, 78%, ee >99%, $[\alpha]^{20}_D$ = -28.3 ^{o} (*c* = 0.40, CH_2Cl_2), mp 192-193 ^{o}C; IR *v* (cm^{-1}) 1767, 1684, 1663, 1585; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06 (d, *J* = 15.5 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 7.4 Hz, 1H), 7.28-7.38 (m, 2H), 7.45 (d, *J* = 15.5 Hz, 1H), 7.08-7.22 (m, 5H), 6.15 (dd, *J* = 15.8, 7.8 Hz, 1H), 5.35 (t, *J* = 7.2 Hz, 1H), 4.24 (t, *J* = 7.3 Hz, 1H), 4.10-4.16 (m, 1H), 3.88 (dd, *J* = 18.2, 10.1

Hz, 1H), 3.83 (t, *J* = 8.3, 1H), 3.41 (dd, *J* = 18.2, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.1, 188.9, 176.3, 145.1, 142.3, 137.6, 136.7, 136.4, 135.8, 133.4, 132.0, 131.9, 130.7, 130,5, 130.0, 129.7, 128.6, 128.4, 128.3, 128.15, 128.1, 127.7, 127.2, 127.0, 124.3, 123.4, 81.3, 49.8, 46.3, 40.5, 38.4; HRMS (MALDI-TOF): $[M + Na]^+$ calcd for $C_{36}H_{26}Br_2O_4Na$: 703.0090; found: 703.0093.



6j

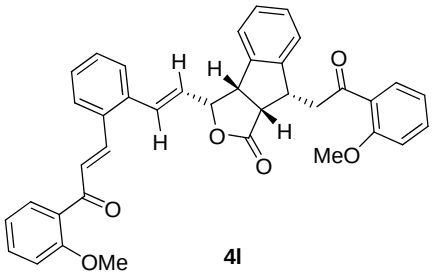
(*3S,3aS,8R,8aS*)-8-((4-Bromobenzoyl)methyl)-3-((*E*)-2-((*E*)-(4-bromobenzoyl)vinyl)styryl)-3, 3a,8,8a-tetrahydroindeno[1,2-*c*]furan-1-one 6j: white solid, 24 mg, 7%, ee >99%, $[\alpha]^{20}_D$ = -20.6 ^{o} (c = 0.45, CH_2Cl_2), mp 176-177 ^{o}C; IR *v* (cm^{-1}) 1763, 1684, 1587; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.16 (d, *J* = 15.5 Hz, 1H), 7.93 (d, *J* = 8.7 Hz, 2H), 7.90 (d, *J* = 9.6 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.33-7.44 (m, 6H), 7.21 (d, *J* = 6.5 Hz, 1H), 7.15 (d, *J* = 15.6 Hz, 1H), 6.24 (dd, *J* = 15.6, 6.7 Hz, 1H), 5.30 (d, *J* = 6.7 Hz, 1H), 4.24-4.30 (m, 1H), 4.02 (d, *J* = 7.7 Hz, 1H), 3.89 (dd, *J* = 18.2, 9.8 Hz, 1H), 3.84 (t, *J* = 8.0 Hz, 1H), 3.47 (dd, *J* = 18.2, 5.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.1, 189.0, 176.6, 144.0, 142.7, 141.1, 136.7, 136.5, 135.8, 133.4, 132.1, 131.9, 131.4, 130.5, 130.1, 130.0, 129.7, 128.6, 128.3, 128.1, 127.8, 127.7, 124.19, 124.17, 123.4, 83.6, 51.2, 44.6, 41.0, 38.4; HRMS (MALDI-TOF): [M + Na]+ calcd for $C_{36}H_{26}Br_2O_4Na$: 703.0090; found: 703.0091.



4k

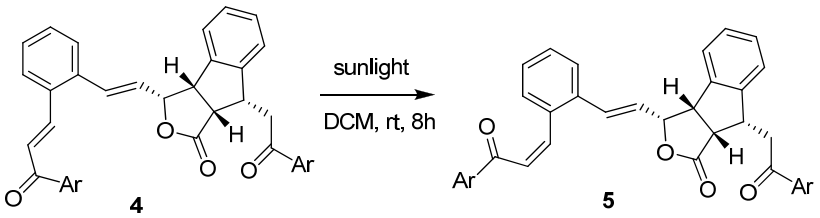
(*3R,3aS,8R,8aS*)-8-((3-Methoxybenzoyl)methyl)-3-((*E*)-2-((*E*)-(3-methoxybenzoyl)vinyl)styryl)-3,3a,8,8a-tetrahydroindeno[1,2-*c*]furan-1-one 4k: white solid, 233.7 mg, 80%, ee >99%, $[\alpha]^{20}_D$ = -53.1 ^{o} (*c* = 0.45, CH_2Cl_2), mp 86-87 ^{o}C; IR *v* (cm^{-1}) 1761, 1670, 1585; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.16 (d, *J* = 15.5 Hz, 1H), 7.70 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.53-7.61 (m, 3H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 14.2 Hz, 1H), 7.36-7.43 (m, 4H), 7.26-7.30 (m, 2H), 7.18-7.23 (m, 3H), 7.11-7.15 (m, 2H), 6.21 (dd, *J* = 15.8, 8.2 Hz, 1H), 5.41 (t, *J* = 7.2 Hz, 1H), 4.32 (t, *J* = 7.3 Hz, 1H), 4.17-4.23 (m, 1H), 3.98 (dd, *J* = 18.2, 9.9 Hz, 1H), 3.91 (t, *J* = 8.4 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.53 (dd, *J* = 18.2, 4.9 Hz, 1H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ (ppm) 198.9, 189.8, 176.3, 160.0, 159.8, 145.3, 141.8, 139.4, 138.4, 137.6, 136.3, 133.6, 130.8, 130.4, 129.7, 129.6, 128.6, 128.4, 128.35, 127.5, 127.2, 127.1, 127.0, 124.9, 123.5, 121.1, 120.9, 119.6, 119.5, 112.9, 112.3, 81.4, 55.5, 55.4, 49.9, 46.3, 40.6, 38.6; HRMS (MALDI-TOF): $[M + Na]^+$ calcd for $C_{38}H_{32}O_6Na$: 607.2091; found: 607.2094.



4l

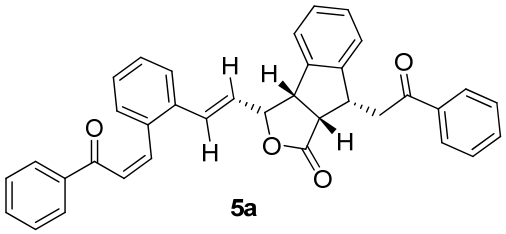
(*3R,3aS,8R,8aS*)-8-((2-Methoxybenzoyl)methyl)-3-((*E*)-2-((*E*)-(2-methoxybenzoyl)vinyl)styryl)-3,3a,8,8a-tetrahydroindeno[1,2-*c*]furan-1-one 4l: white solid, 225 mg, 77%, ee >99%, $[\alpha]^{20}_D$ = -41.2 ° (*c* = 0.55, CH_2Cl_2), mp 76-77 °C; IR *v* (cm^{-1}) 1765, 1665, 1595; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.00 (d, *J* = 15.7 Hz, 1H), 7.89 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.63-7.66 (m, 2H), 7.46-7.49 (m, 3H), 7.33-7.40 (m, 4H), 7.32 (d, *J* = 15.7 Hz, 1H), 7.20-7.28 (m, 4H), 7.15 (d, *J* = 15.8 Hz, 1H), 7.04 (dt, *J* = 7.7, 2.3 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.17 (dd, *J* = 15.8, 8.2 Hz, 1H), 5.38 (t, *J* = 7.5 Hz, 1H), 4.29 (t, *J* = 7.4 Hz, 1H), 4.15-4.21 (m, 1H), 3.93 (s, 3H), 3.88 (s, 3H), 3.86-3.92 (m, 2H), 3.69 (dd, *J* = 19.0, 5.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 200.8, 192.5, 176.3, 158.7, 158.3, 145.8, 139.9, 137.7, 136.2, 133.8, 133.4, 133.2, 130.7, 130.6, 130.5, 130.1, 129.6, 129.1, 128.5, 128.4, 128.2, 128.1, 127.4, 127.0, 126.9, 123.6, 120.8, 120.7, 111.70, 111.65, 81.4, 55.8, 55.6, 49.9, 46.4, 43.8, 41.0; HRMS (MALDI-TOF): $[M + Na]^+$ calcd for $C_{38}H_{32}O_6Na$: 607.2091; found: 607.2090.



4 **5**

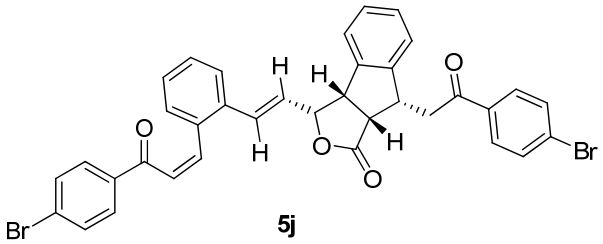
The preparation of 8-(aroylmethyl)-3-((*E*)-2-((*Z*)-aroylvinyl)styryl)-tetrahydroindeno[1,2-*c*]furan-1-one 5 from photoisomerization of 8-(aroylmethyl)-3-((*E*)-2-((*E*)-aroylvinyl)styryl)tetrahydroindeno[1,2-*c*]furan-1-one 4:

A solution of **4a** or **4j** (50 mg) in dichloromethane (10 mL) was irradiated under sunlight for 8h (summertime). Then the solvent was removed and the residue was chromatographyed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (5:1). **5a** and **5j** were isolated in 58% and 64% yield, respectively, along with the recovered **4a** (13%) and **4j** (10%).



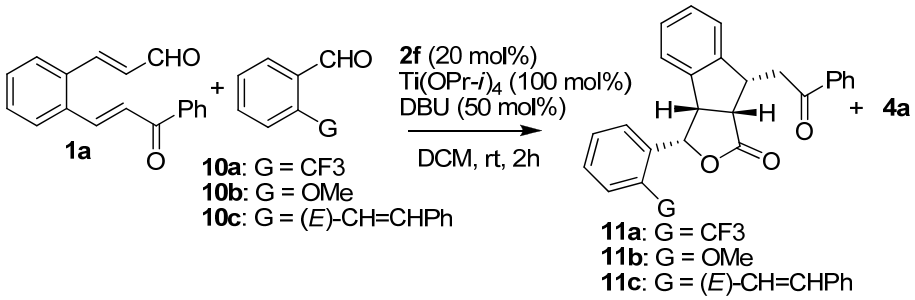
5a

(*3R,3aS,8R,8aS*)-8-(Benzoylmethyl)-3-((*E*)-2-((*Z*)-benzoylvinyl)styryl)-3,3a,8,8a-tetrahydroindeno[1,2-*c*]furan-1-one 5a: 29 mg, 58%, white solid, ee 98%, $[\alpha]^{20}_{D}$ = -114.8 ^{o} (c = 0.50, CH_2Cl_2), mp 82-83 ^{o}C; IR *v* (cm^{-1}) 1763, 1684, 1597; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.07 (d, *J* = 7.1 Hz, 2H), 7.87 (d, *J* = 7.1 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 3H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.21-7.30 (m, 7H), 7.13 (t, *J* = 7.0 Hz, 1H), 6.96 (d, *J* = 15.8 Hz, 1H), 6.81 (d, *J* = 12.3 Hz, 1H), 6.18 (dd, *J* = 15.8, 7.9 Hz, 1H), 5.28 (t, *J* = 7.0 Hz, 1H), 4.10-4.21 (m, 1H), 4.12 (t, *J* = 7.3 Hz, 1H), 3.98 (dd, *J* = 18.2, 9.9 Hz, 1H), 3.85 (t, *J* = 8.3 Hz, 1H), 3.51 (dd, *J* = 18.2, 5.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.2, 193.4, 176.6, 145.3, 139.4, 137.7, 137.3, 137.1, 134.9, 134.3, 133.2, 133.1, 131.4, 129.8, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 128.0, 127.23, 127.17, 126.2, 123.5, 81.6, 49.8, 46.4, 40.6, 38.6; HRMS (MALDI-TOF): $[M + Na]^+$ calcd for $C_{36}H_{28}O_4Na$: 547.1880; found: 547.1880.



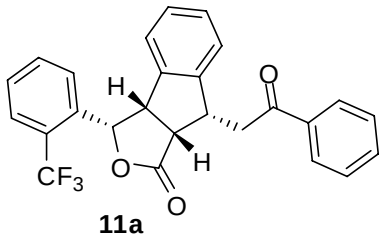
5j

(*3R,3aS,8R,8aS*)-8-((4-Bromobenzoyl)methyl)-3-((*E*)-2-((*Z*)-(4-bromobenzoyl)vinyl)styryl)-3,3a,8,8a-tetrahydroindeno[1,2-*c*]furan-1-one 5j: 32 mg, 64%, white solid, ee >99%, $[\alpha]^{20}_{D}$ = -58.9 ^{o} (c = 0.50, CH_2Cl_2), mp 101-102 ^{o}C; IR *v* (cm^{-1}) 1765, 1686, 1584; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.93 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.20-7.31 (m, 6H), 7.11-7.17 (m, 2H), 6.93 (d, *J* = 15.8 Hz, 1H), 6.72 (d, *J* = 12.3 Hz, 1H), 6.18 (dd, *J* = 15.8, 7.7 Hz, 1H), 5.33 (t, *J* = 6.9 Hz, 1H), 4.21 (t, *J* = 7.1 Hz, 1H), 4.15-4.19 (m, 1H), 3.92 (dd, *J* = 18.1, 10.1 Hz, 1H), 3.87 (t, *J* = 8.3, 1H), 3.47 (dd, *J* = 18.2, 4.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.2, 192.5, 176.5, 145.1, 139.9, 137.7, 136.0, 135.9, 134.6, 134.3, 131.9, 131.8, 131.1, 130.3, 129.7, 129.0, 128.4, 128.24, 128.17, 128.0, 127.30, 127.26, 127.2, 126.2, 123.5, 81.6, 49.8, 46.3, 40.6, 38.5; HRMS (MALDI-TOF): $[M + Na]^+$ calcd for $C_{36}H_{26}Br_2O_4Na$: 703.0090; found: 703.0091.



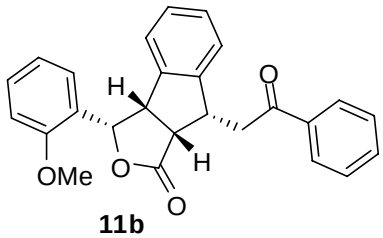
General procedure for the NHC/Ti(OPr-*i*)$_4$-catalyzed reaction between 2-benzoylvinylcinnamaldehyde 1a and another different aldehyde.

Under nitrogen atmosphere, a mixture of *N*-mesityl-indeno[2,1-b]triazolo[4,3-d][1,4]oxazinium salt **2f** (27 mg, 0.1 mmol) and DBU (0.25 mmol) in dry dichloromethane (5 mL) was stirred for 0.5h at room temperature. After that, the solution of 2-benzoylvinylcinnamaldehyde **1a** (0.5 mmol), *o*-trifluoromethyl, *o*-methoxy or *o*-styrylbenzaldehyde **10a-10c** (0.5 mmol) and Ti(OPr-*i*)$_4$ (0.5 mmol) in DCM (5 mL) was added dropwise in 0.5h to this mixture of catalyst **2f** and DBU in DCM. The resulting mixture was then stirred at room temperature for 2h. After removal of the solvent, the residue was chromatographyed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE:EA = 4:1) to give the major products indeno[1,2-*c*]furan-1-ones **11** in 42%-54% yields with 97%->99% ee. In addition, dimer **4a** was also isolated in 13%-18% yields.



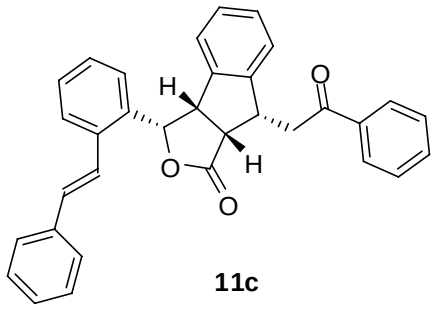
11a

(*3S,3aS,8R,8aS*)-8-(Benzoylmethyl)-3-(2-(trifluoromethyl)phenyl)-3,3a,8,8a-tetrahydroinden o[1,2-*c*]furan-1-one 11a: pale yellow solid, 109 mg, 50%, ee 97%, $[\alpha]^{20}_{D}$ = -150.1 ^{o} (*c* = 0.45, CH_2Cl_2), mp 137-138 ^{o}C; IR *v* (cm^{-1}) 1771, 1686; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (d, *J* = 7.5 Hz, 2H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.47-7.61 (m, 3H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.16-7.17 (m, 3H), 6.79-6.83 (m, 3H), 6.23 (d, *J* = 6.4 Hz, 1H), 5.65 (d, *J* = 7.7 Hz, 1H), 4.47 (t, *J* = 6.9 Hz, 1H), 4.15-4.21 (m, 1H), 3.99-4.08 (m, 2H), 3.56 (dd, *J* = 18.0, 4.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.0, 176.2, 145.2, 137.1, 137.0, 134.5, 133.0, 131.7, 129.0, 128.6, 128.5, 128.2, 128.1, 127.1 (q, *J* = 30.5 Hz), 126.7, 126.6, 125.9, 125.8, 123.0, 77.9, 50.5, 46.9, 40.4, 38.4; HRMS (TOF-ESI): $[M + H]^+$ calcd for $C_{26}H_{20}F_3O_3$: 437.1356; found: 437.1365.



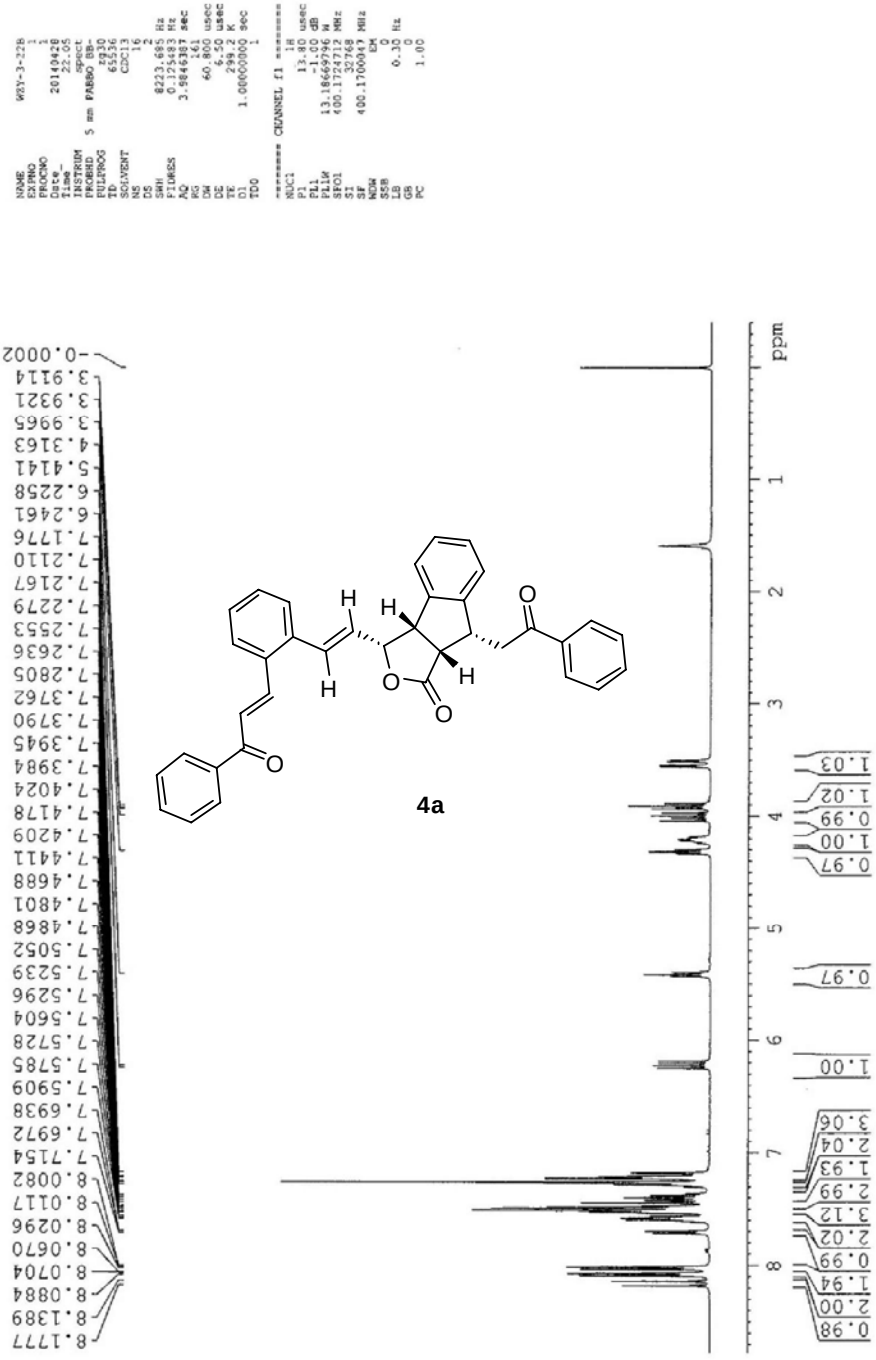
11b

(3S,3aS,8R,8aS)-8-(Benzoylmethyl)-3-(2-methoxyphenyl)-3,3a,8,8a-tetrahydroindeno[1,2-*c*]furan-1-one 11b: white solid, 84 mg, 42%, ee >99%, $[\alpha]^{20}_{D}$ = -242.2 ^{o} (*c* = 0.50, CH_2Cl_2), mp 170-171 ^{o}C; IR *v* (cm^{-1}) 1769, 1682; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (dd, *J* = 8.1, 1.5 Hz, 2H), 7.59 (tt, *J* = 7.3, 1.3 Hz, 1H), 7.50 (dt, *J* = 7.8, 1.4 Hz, 2H), 7.35 (dt, *J* = 8.7, 1.6 Hz, 1H), 7.12-7.16 (m, 2H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.81-6.86 (m, 1H), 6.06 (d, *J* = 6.0 Hz, 1H), 5.84 (d, *J* = 7.6 Hz, 1H), 4.49 (t, *J* = 6.8 Hz, 1H), 4.14-4.19 (m, 1H), 4.05 (dd, *J* = 18.0, 9.8 Hz, 1H), 3.91-3.95 (m, 1H), 3.94 (s, 3H), 3.53 (dd, *J* = 18.0, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.4, 176.7, 155.9, 145.3, 138.1, 137.2, 133.0, 129.2, 128.6, 128.2, 127.9, 126.8, 126.7, 126.5, 124.4, 122.8, 120.6, 109.7, 78.0, 55.5, 48.6, 47.2, 40.3, 38.4; HRMS (TOF-ESI): $[M + H]^{+}$ calcd for $C_{26}H_{23}O_4$: 421.1416; found: 421.1413.



11c

(*3S,3aS,8R,8aS*)-8-(Benzoylmethyl)-3-((*E*)-2-styrylphenyl)-3,3a,8,8a-tetrahydroindeno[1,2-*c*]furan-1-one 11c: white solid, 128 mg, 54%, ee >99%, $[\alpha]^{20}_{D}$ = -208.8 ^{o} (*c* = 0.45, CH_2Cl_2), mp 167-168 ^{o}C; IR *v* (cm^{-1}) 1767, 1686; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.08 (d, *J* = 7.3 Hz, 2H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.37-7.42 (m, 4H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.04-7.16 (m, 4H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.18 (d, *J* = 6.2 Hz, 1H), 5.72 (d, *J* = 7.8 Hz, 1H), 4.38 (t, *J* = 6.8 Hz, 1H), 4.10-4.15 (m, 1H), 3.96-4.05 (m, 2H), 3.50 (dd, *J* = 17.9, 4.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.3, 176.4, 145.2, 137.4, 137.2, 137.0, 135.1, 133.6, 133.1, 132.6, 128.9, 128.6, 128.5, 128.3, 128.2, 128.1, 127.8, 126.8, 126.6, 126.4, 126.2, 124.6, 122.8, 79.4, 49.6, 47.3, 40.3, 38.4; HRMS (TOF-ESI): $[M + H]^{+}$ calcd for $C_{33}H_{27}O_3$: 471.1960; found: 471.1955.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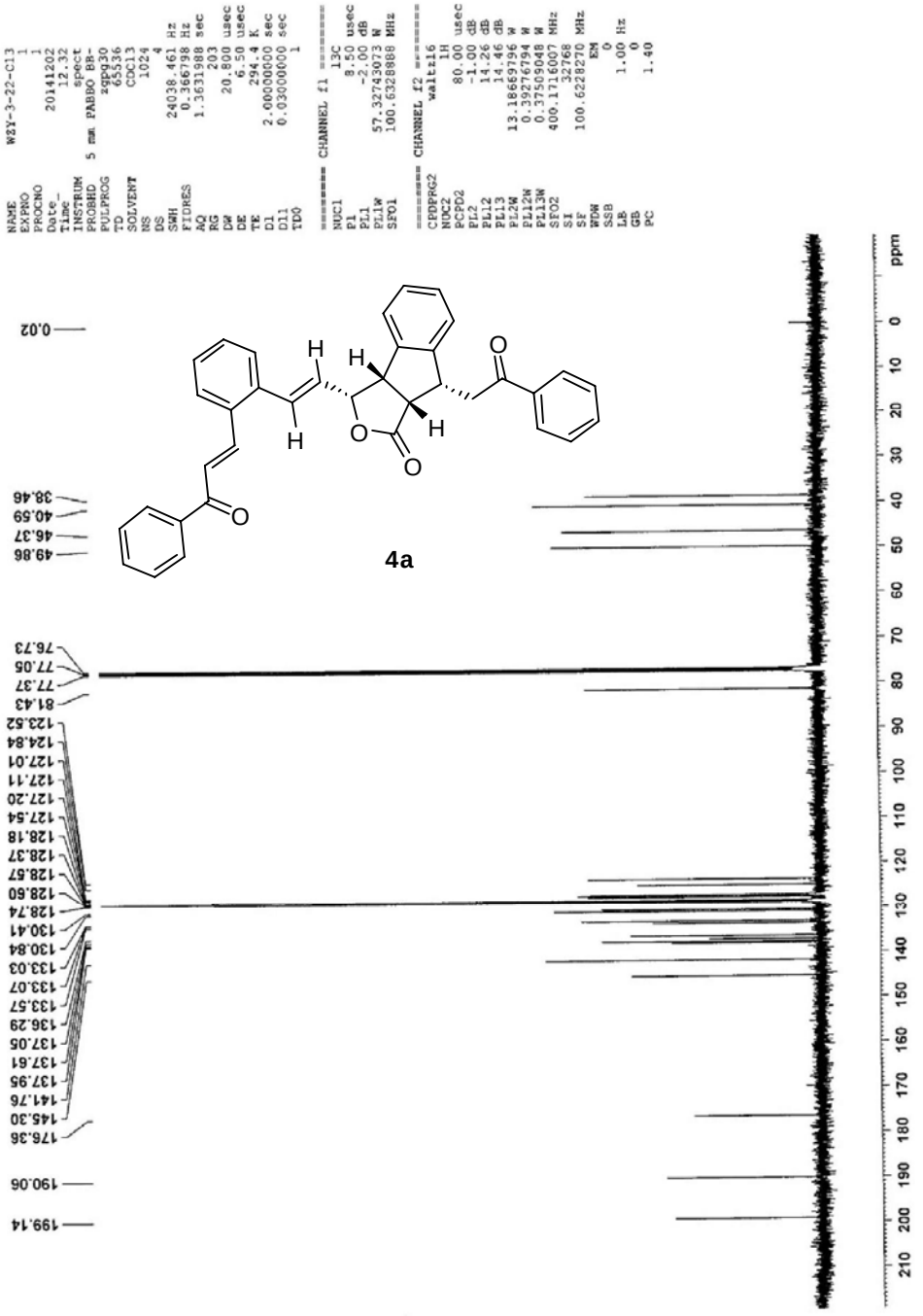
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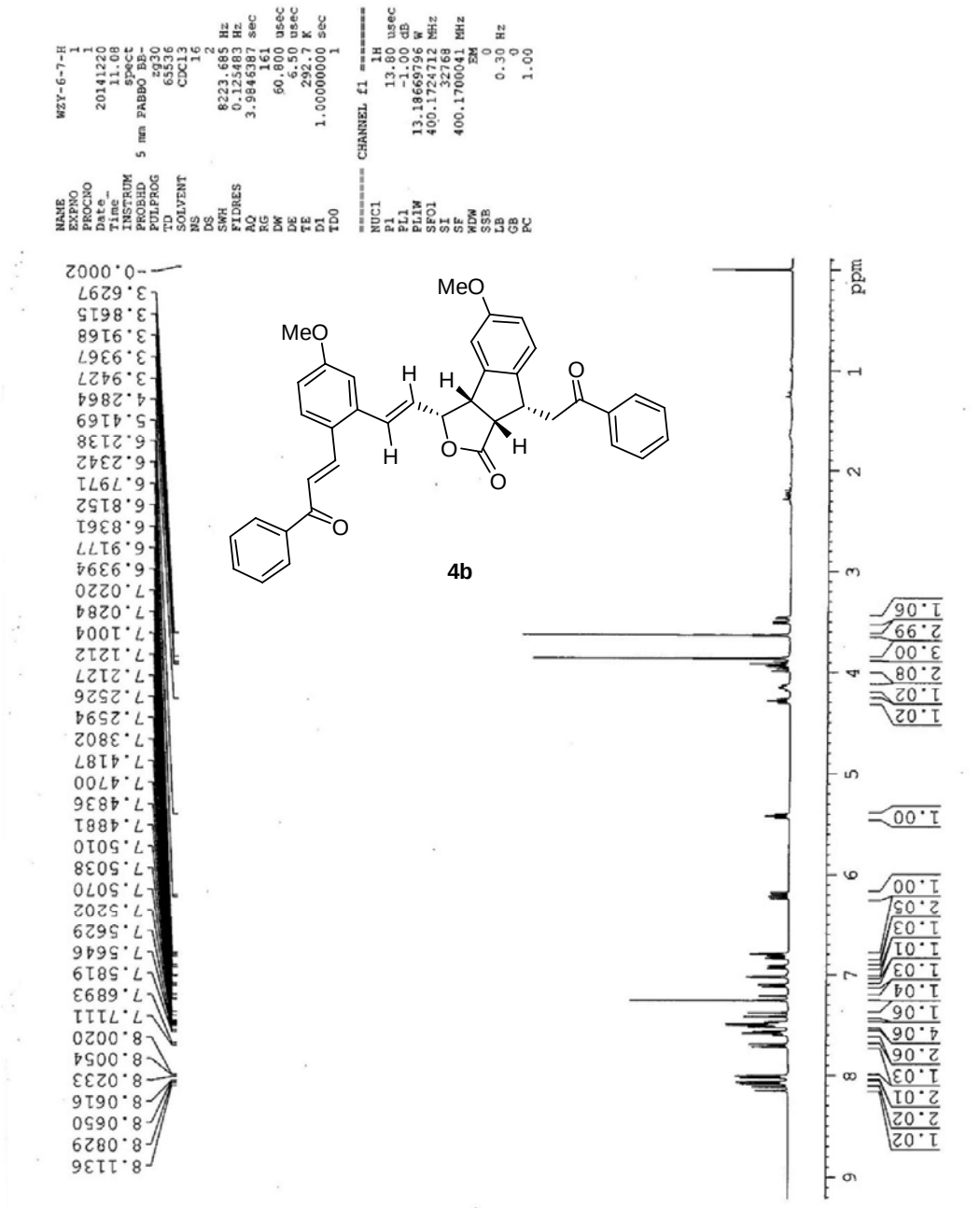
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SSB 0
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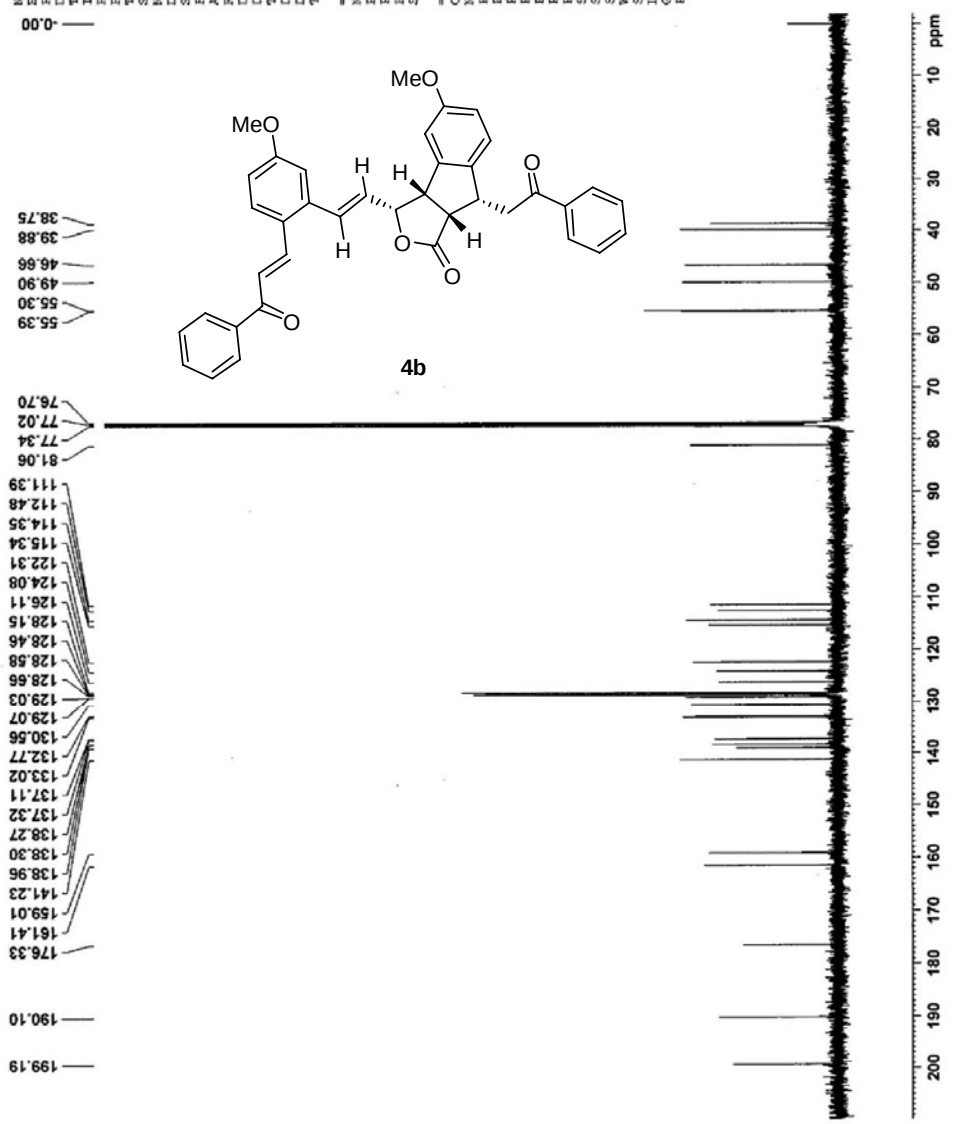
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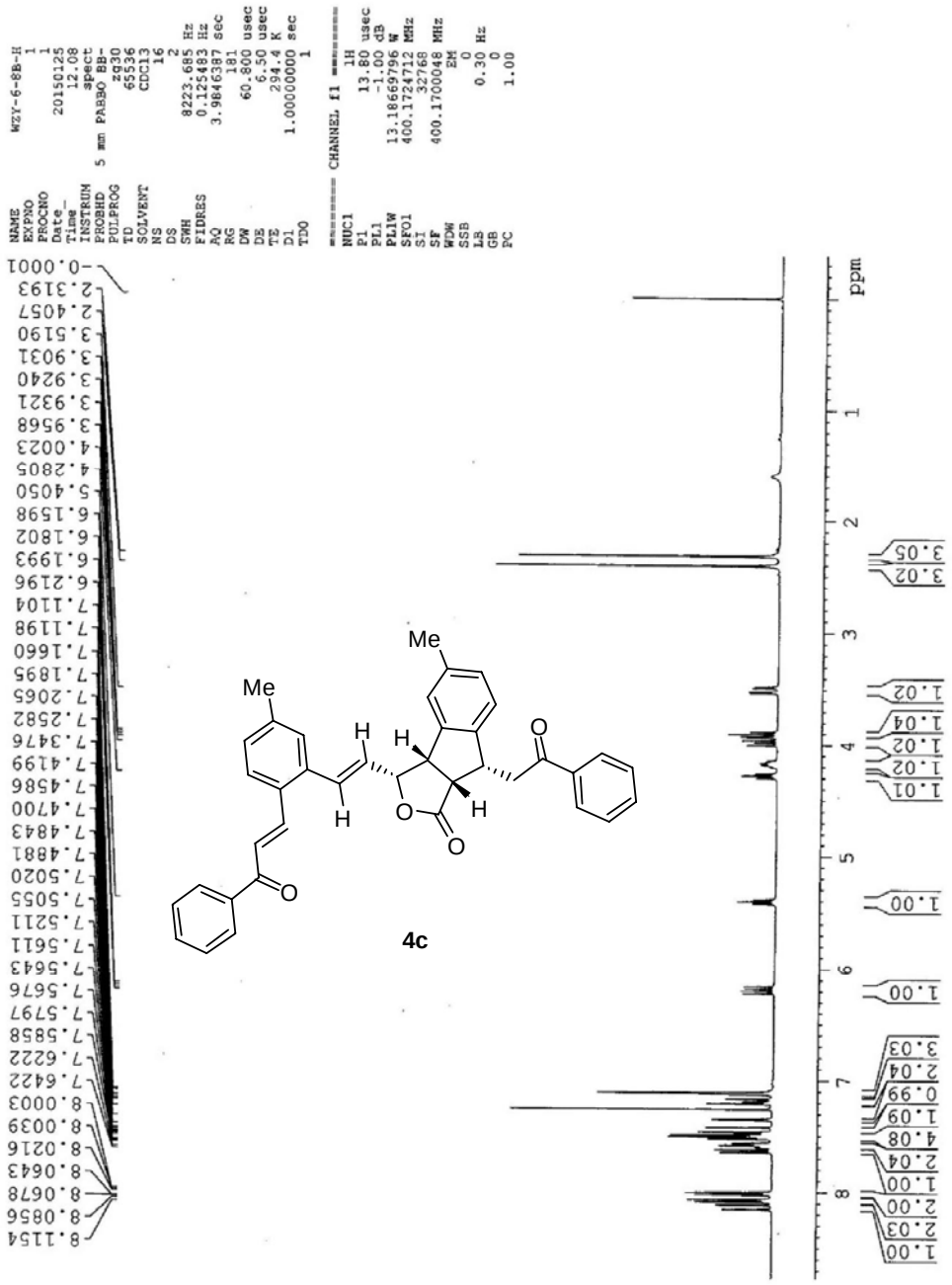
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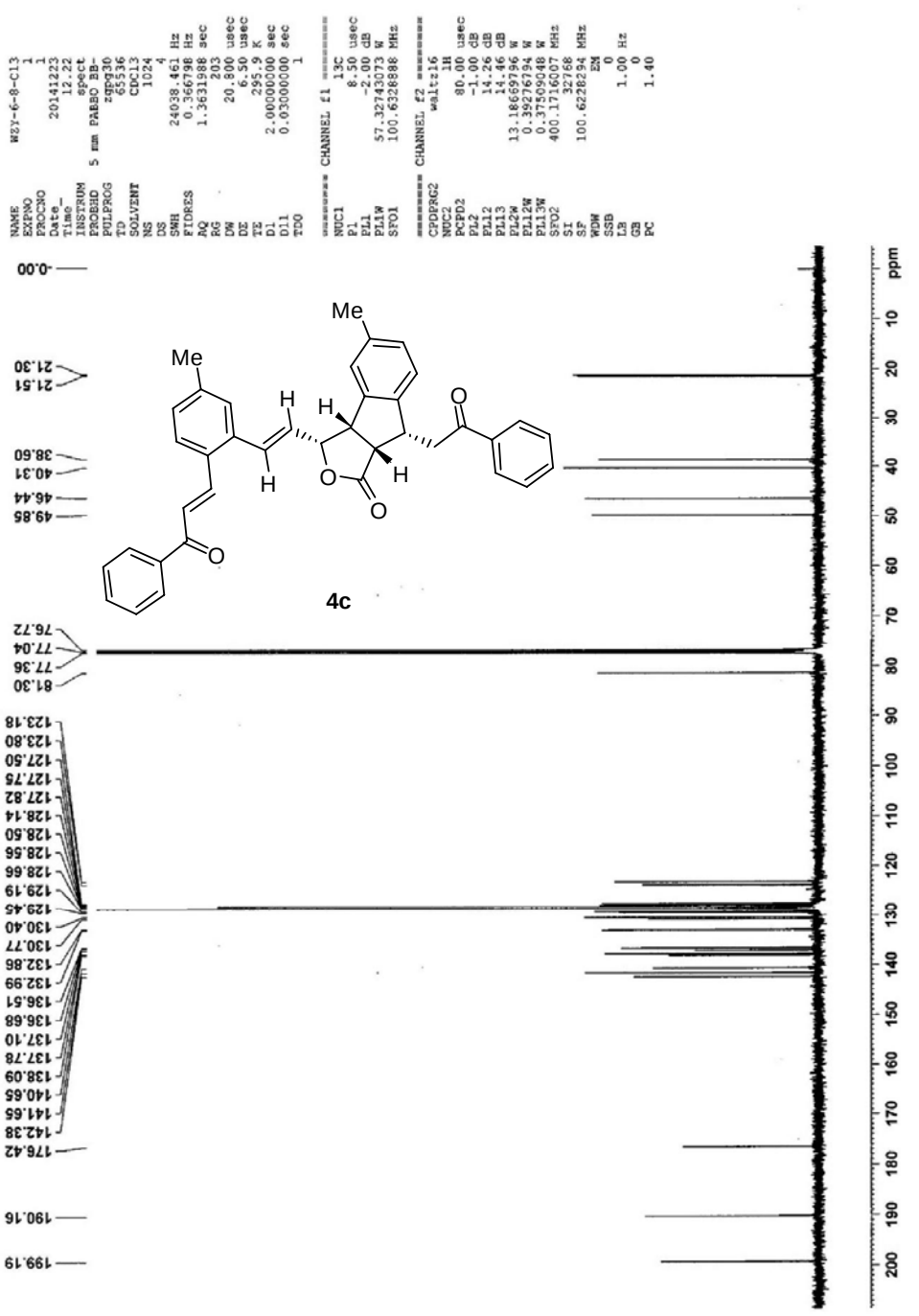
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132.86
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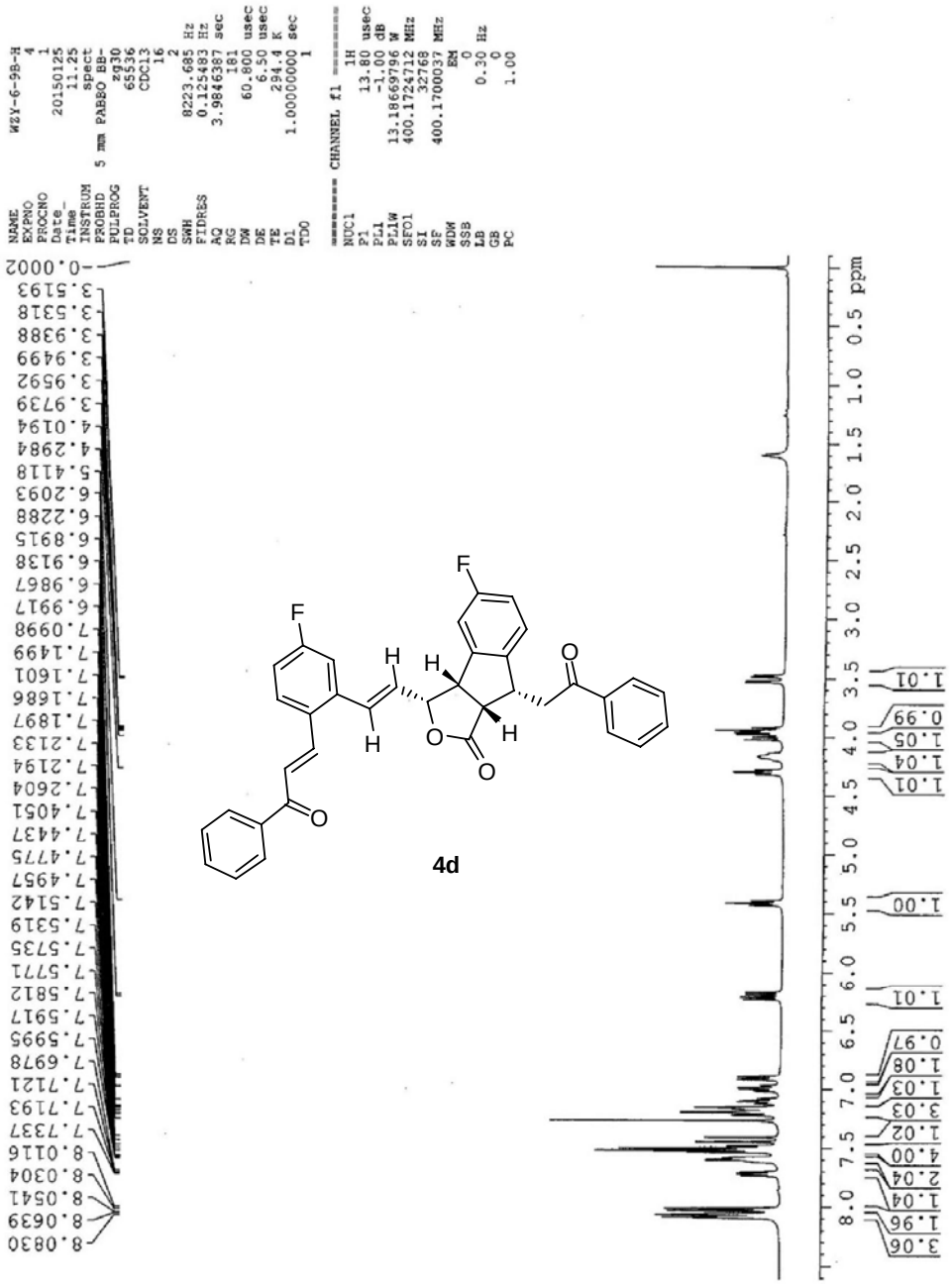
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TE 294.4 K
D1 1.00000000 sec
TD0 1
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NUC1 1H
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LB 0.30 Hz
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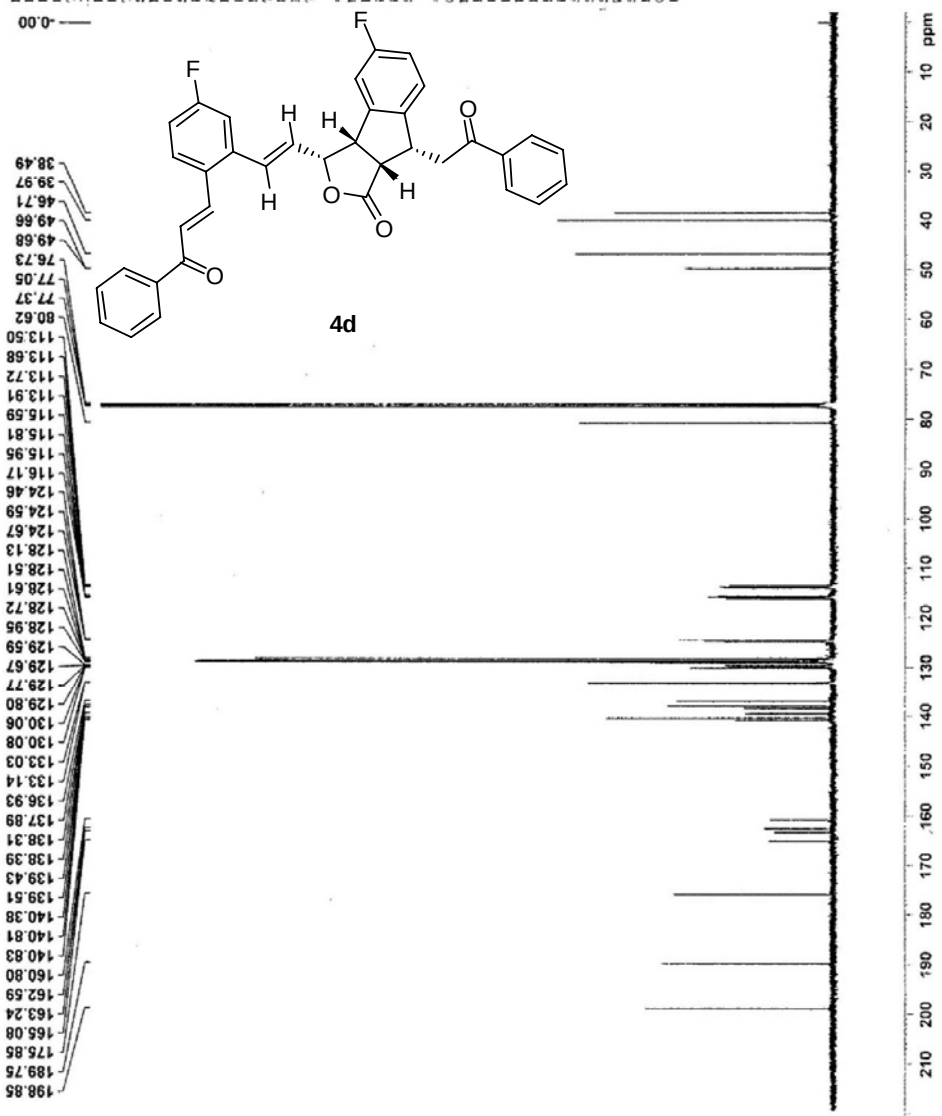
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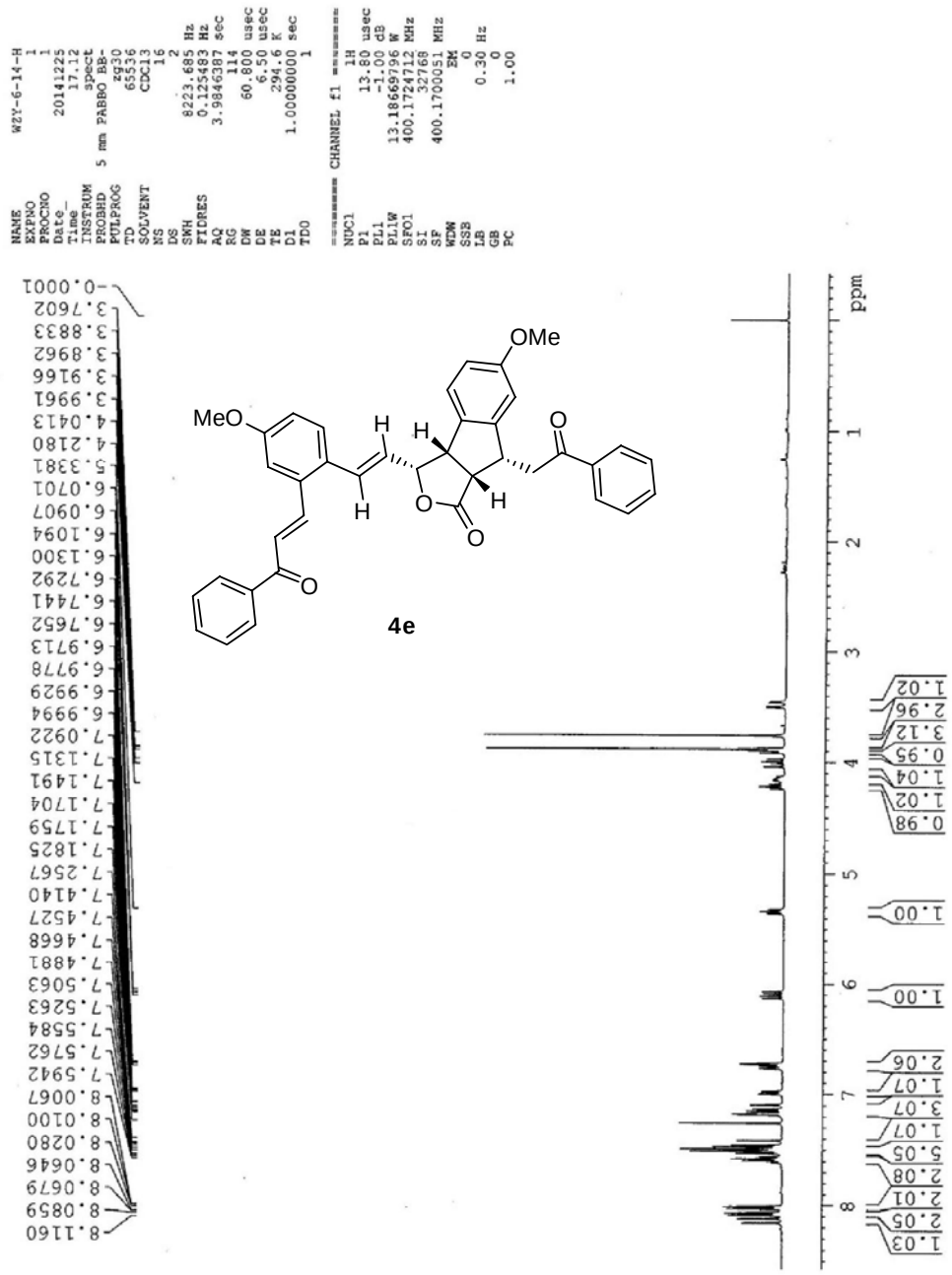
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TD0 1
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PL1 -1.00 dB
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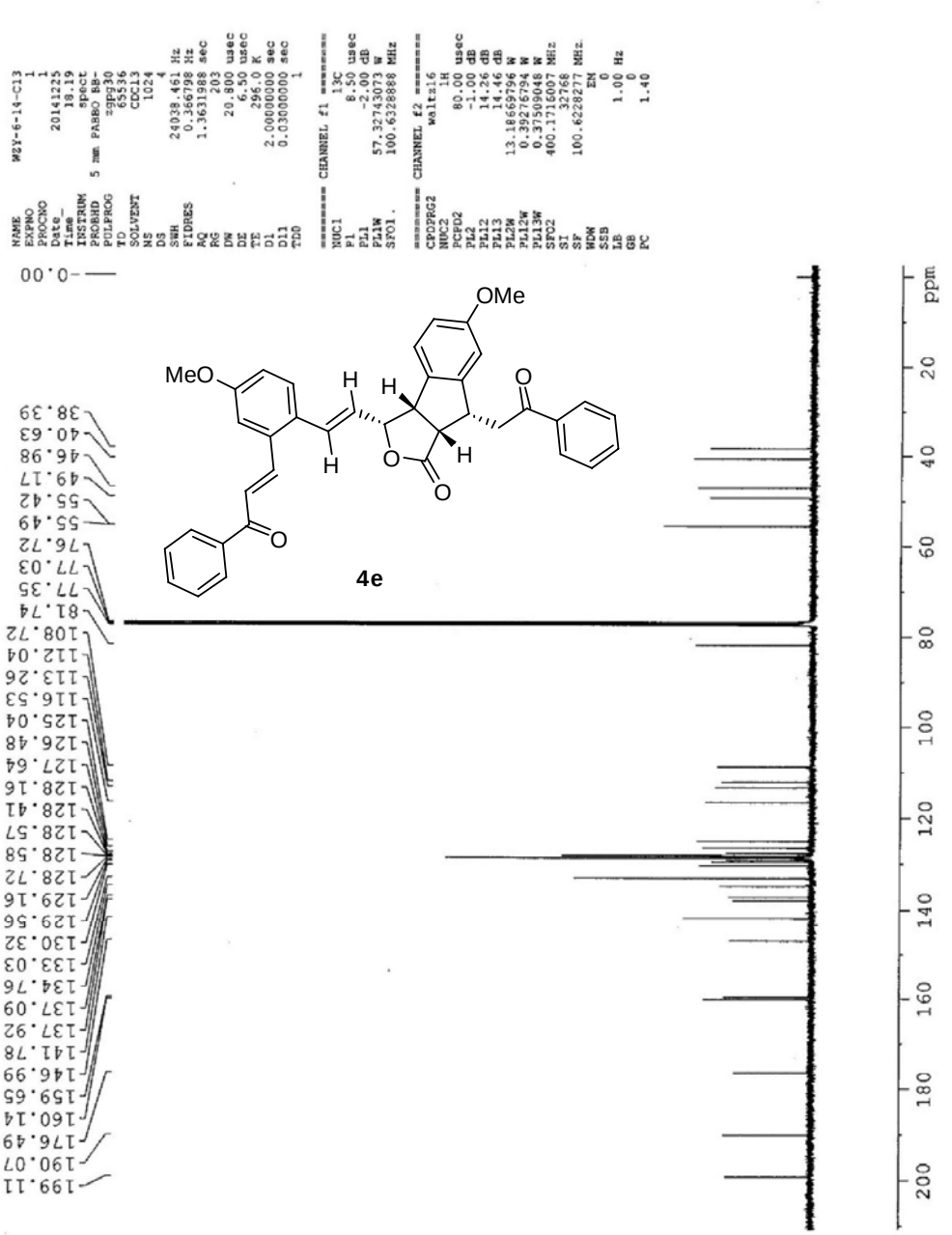
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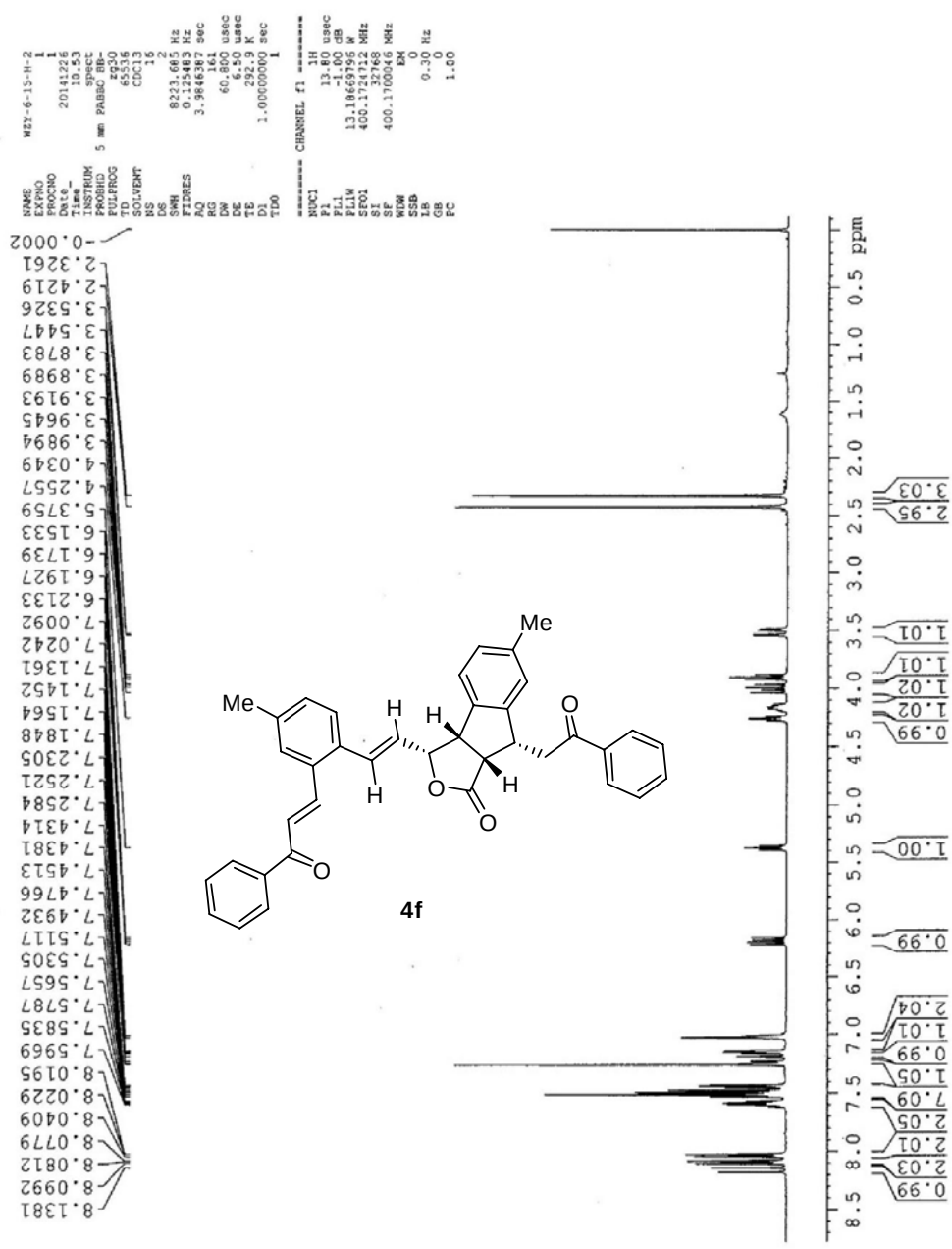
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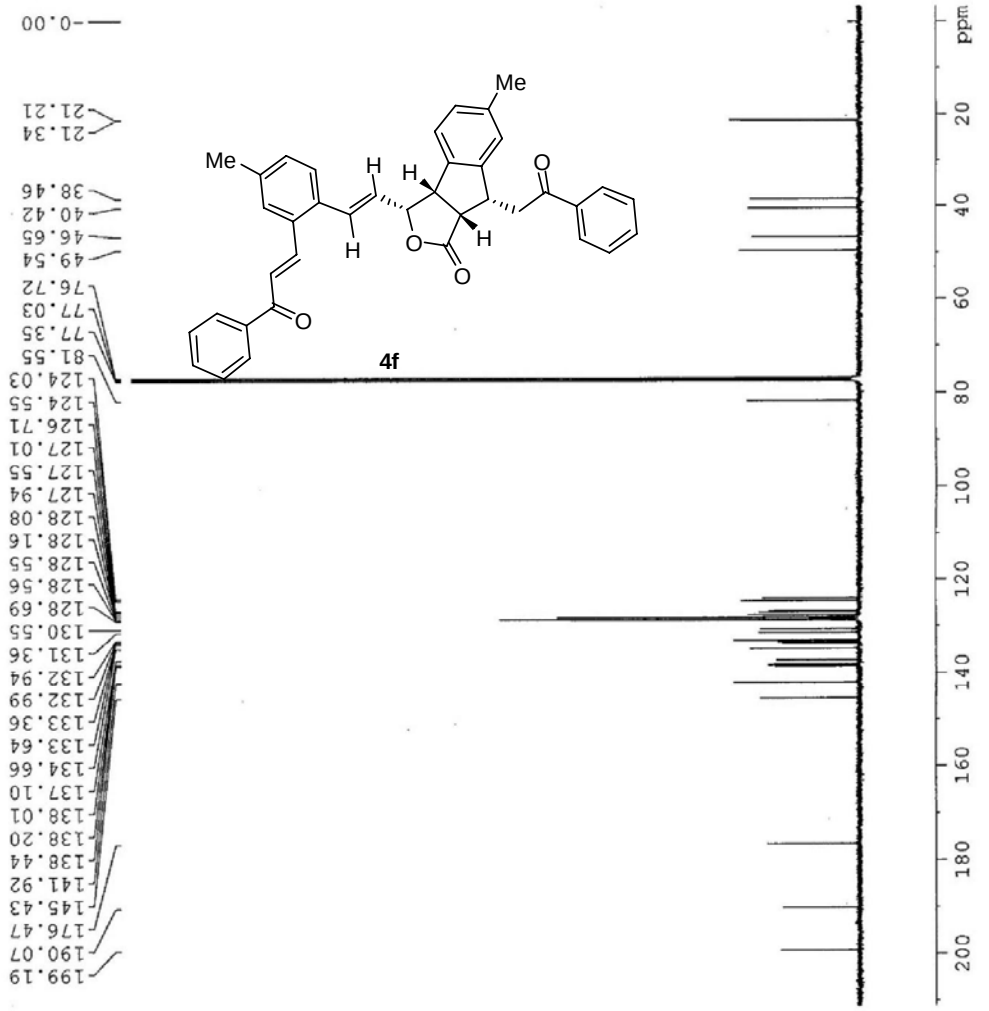
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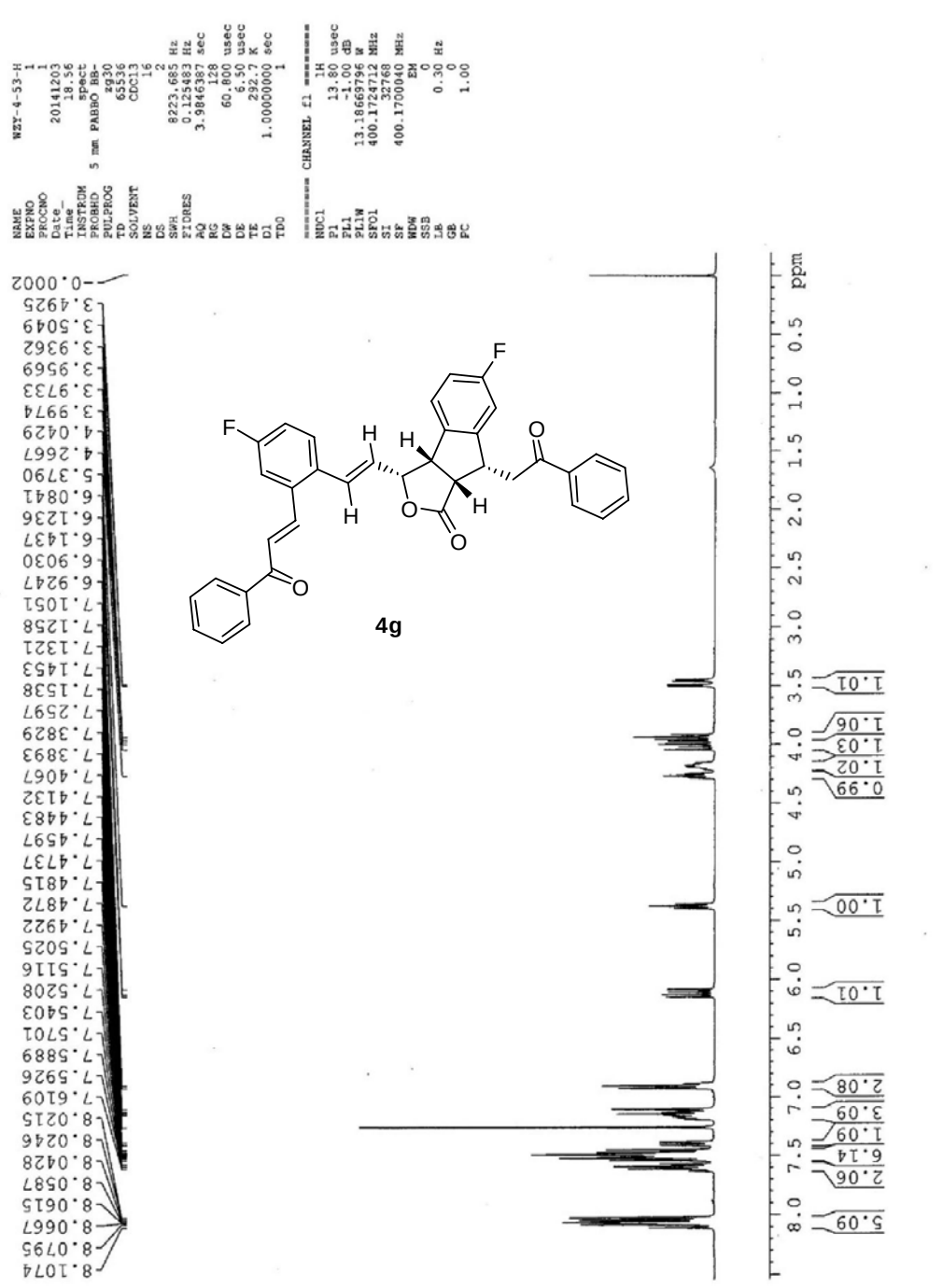
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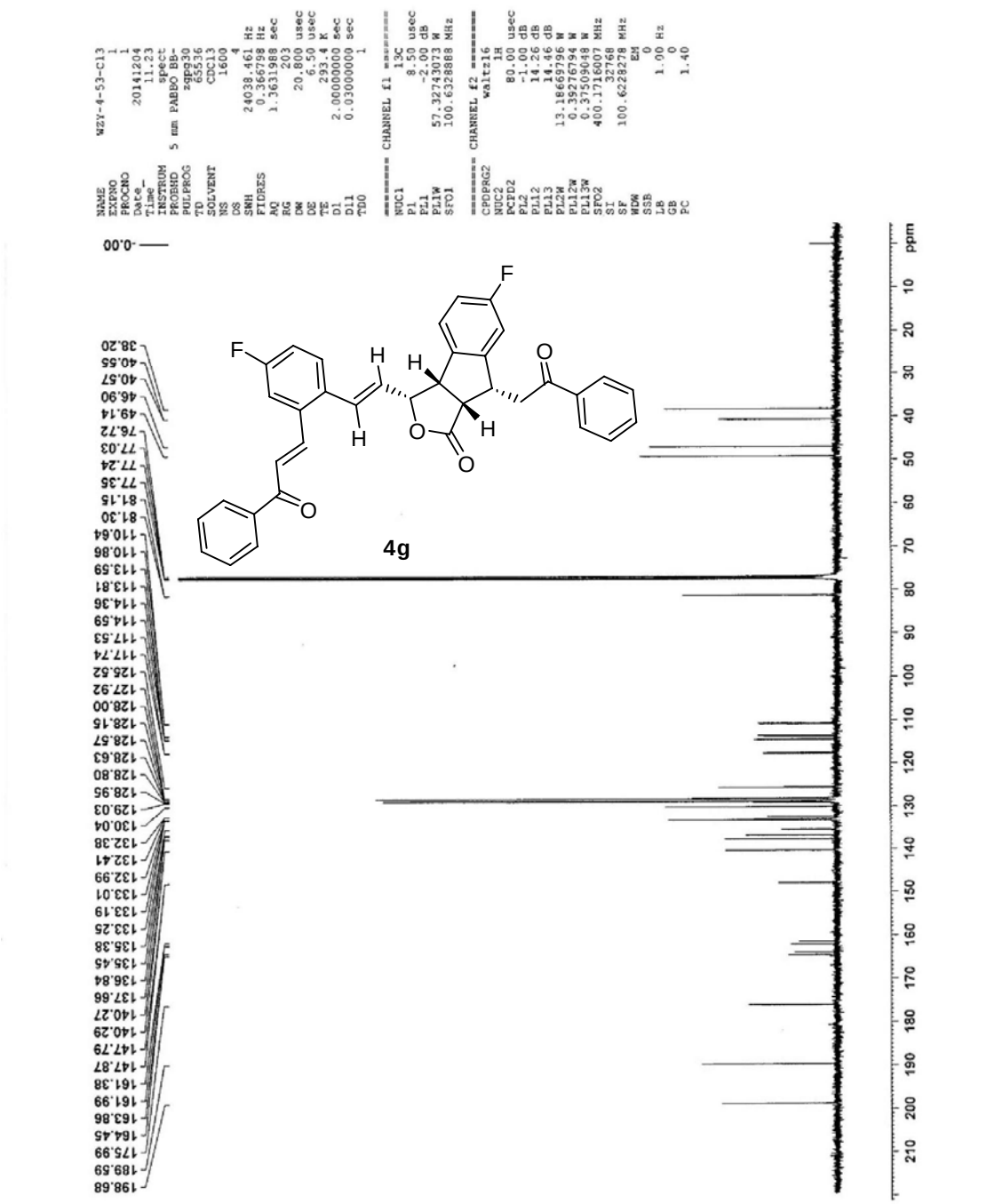
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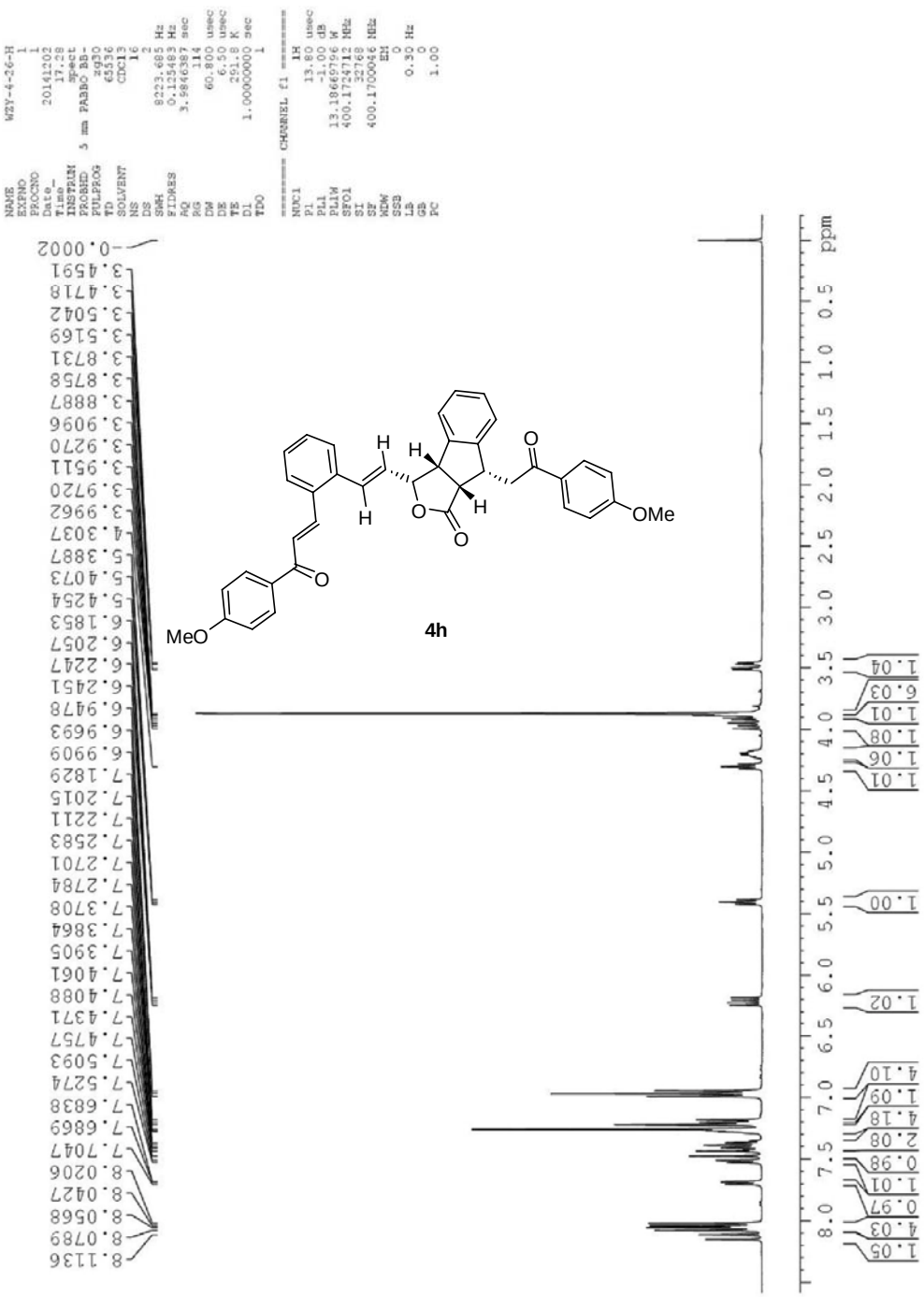
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4h
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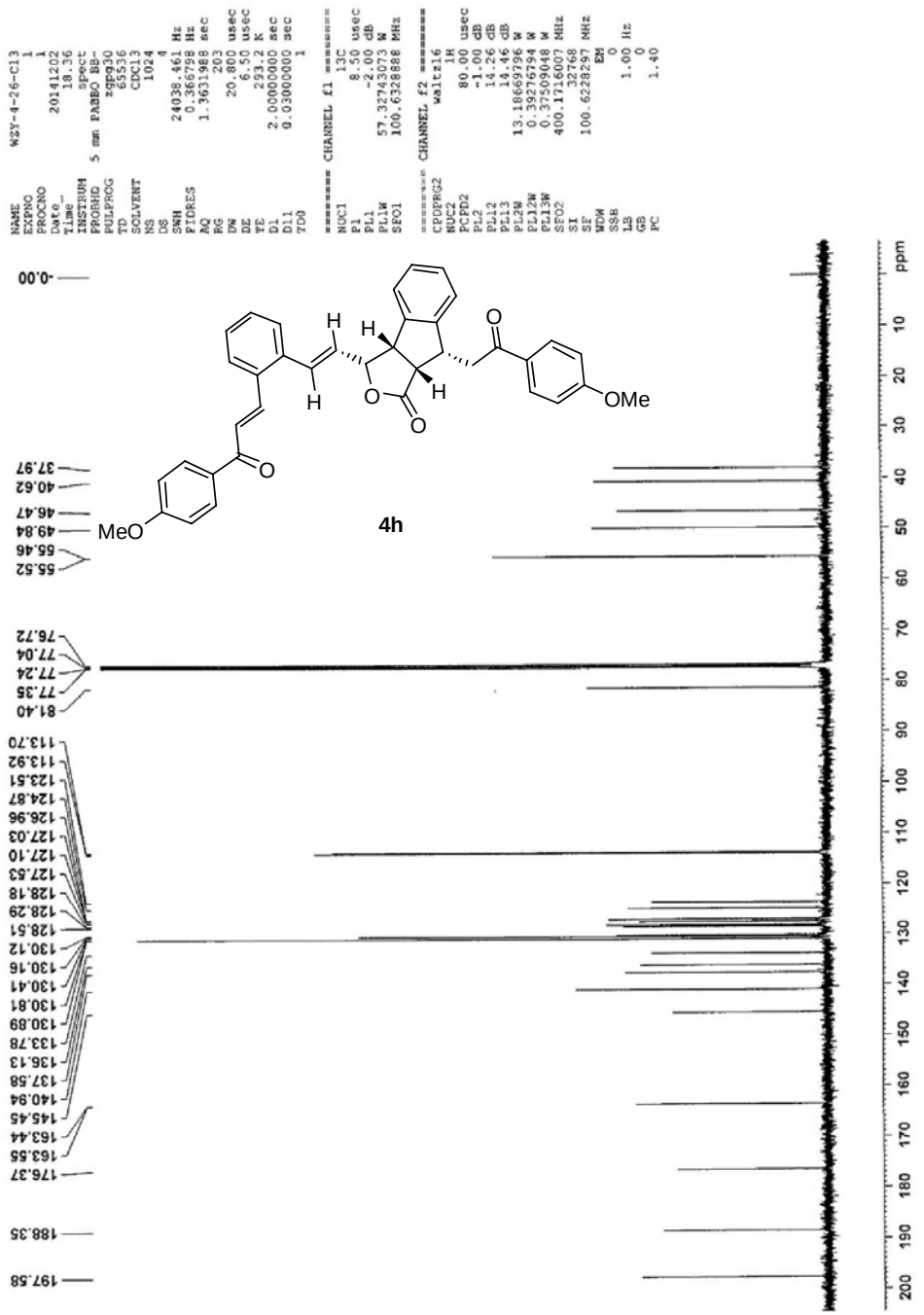
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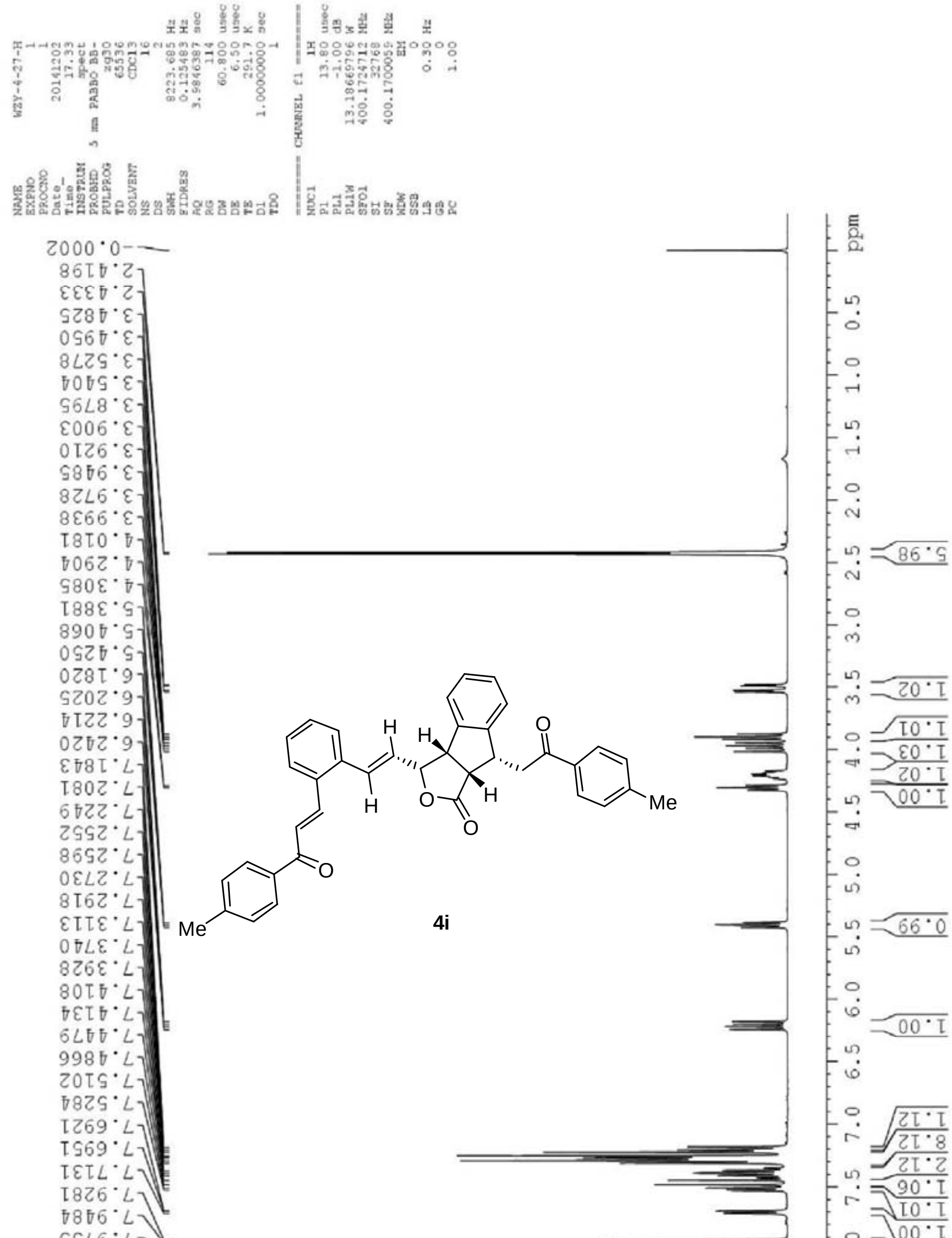
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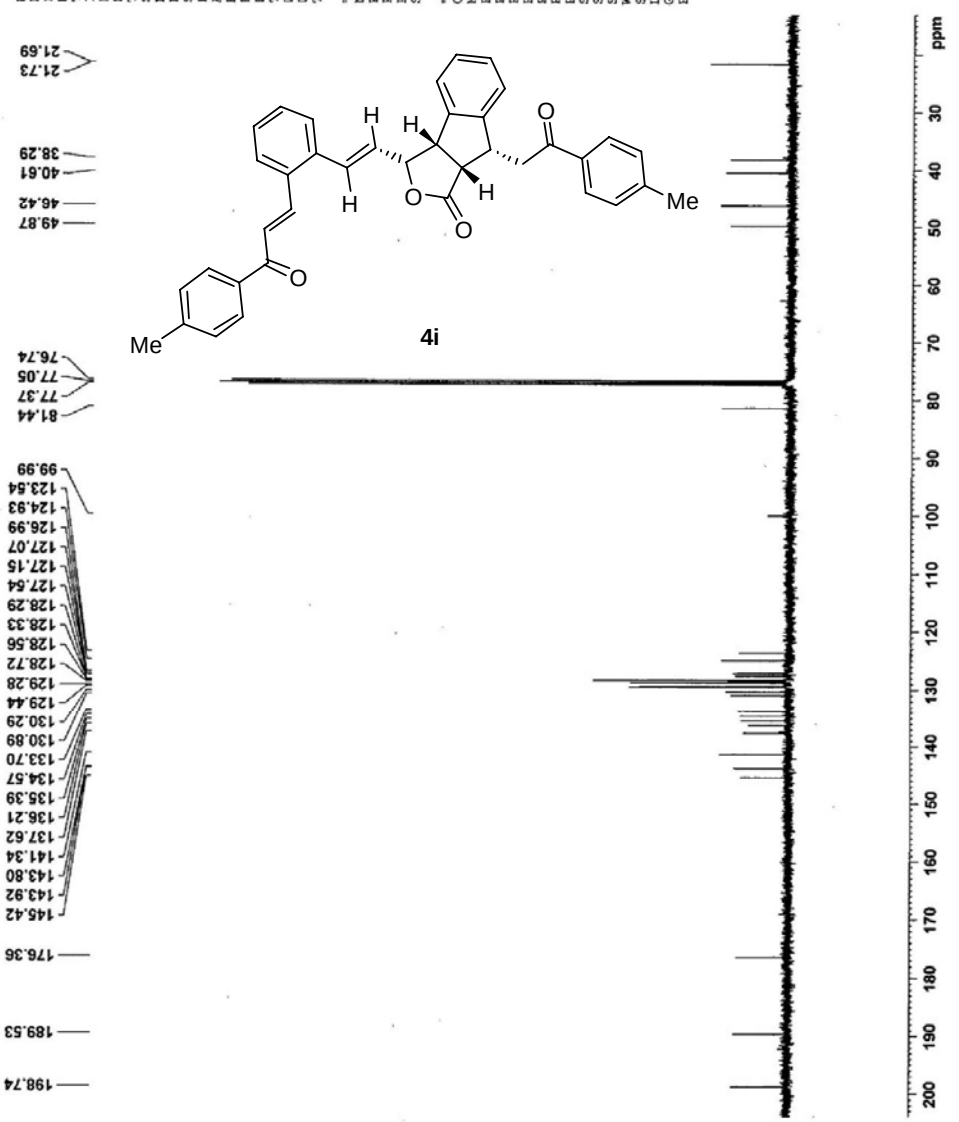
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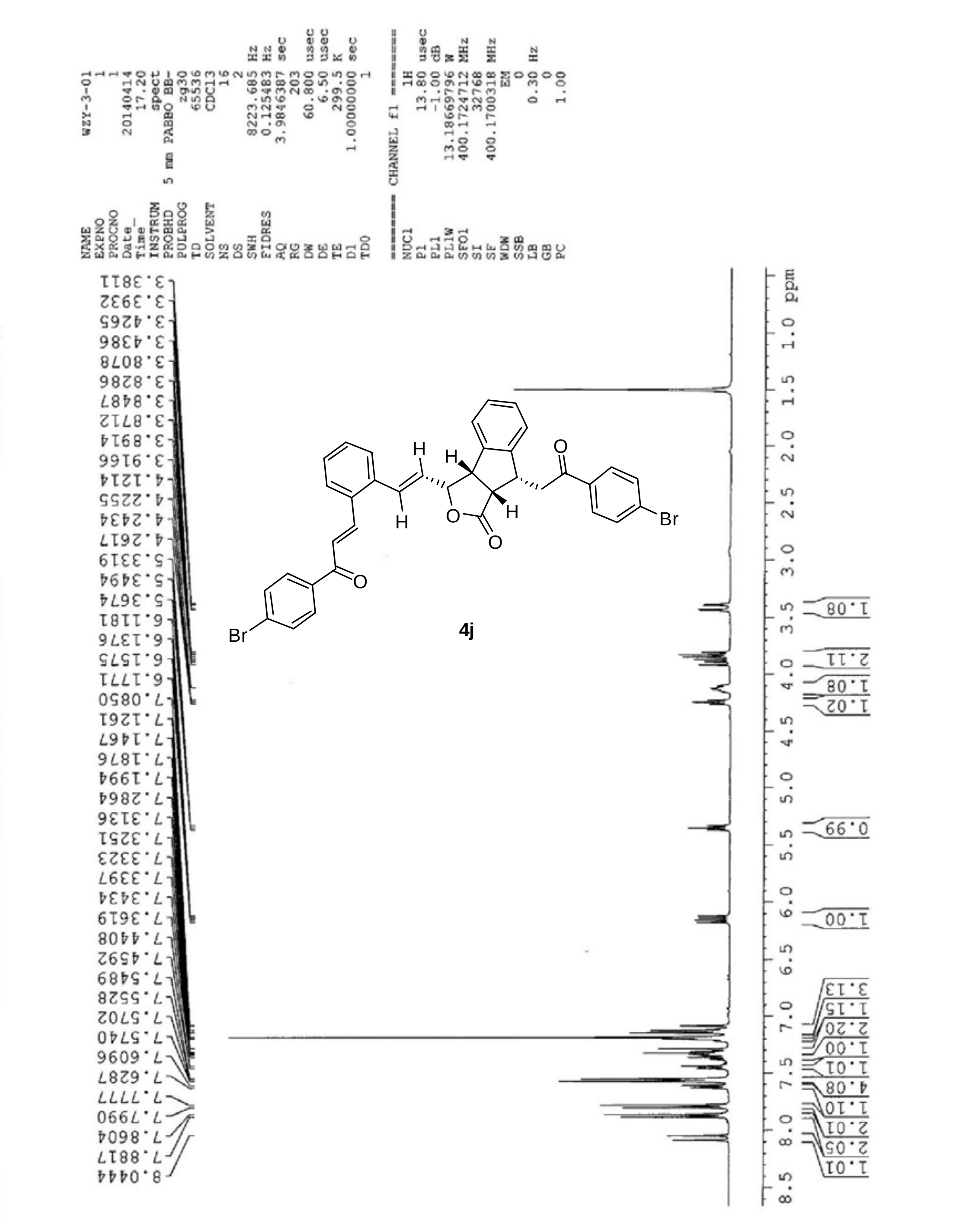
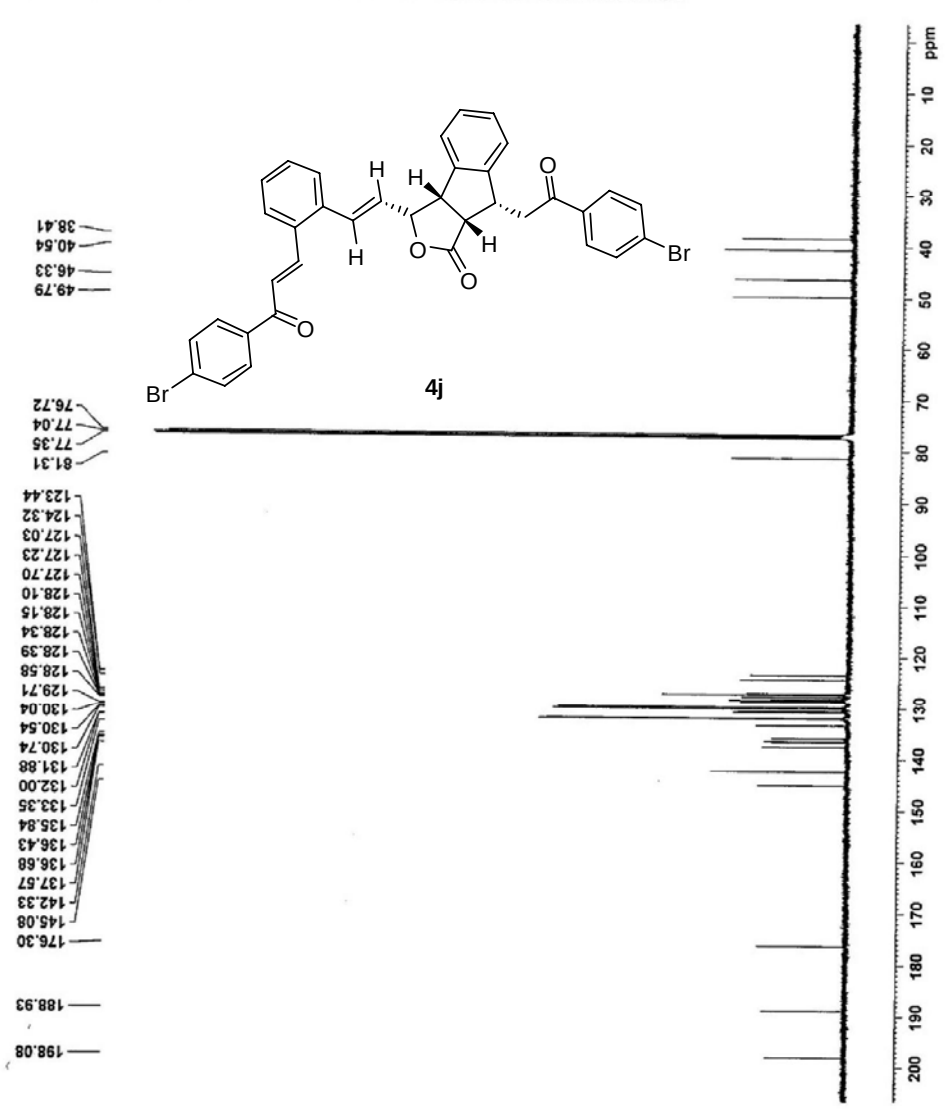
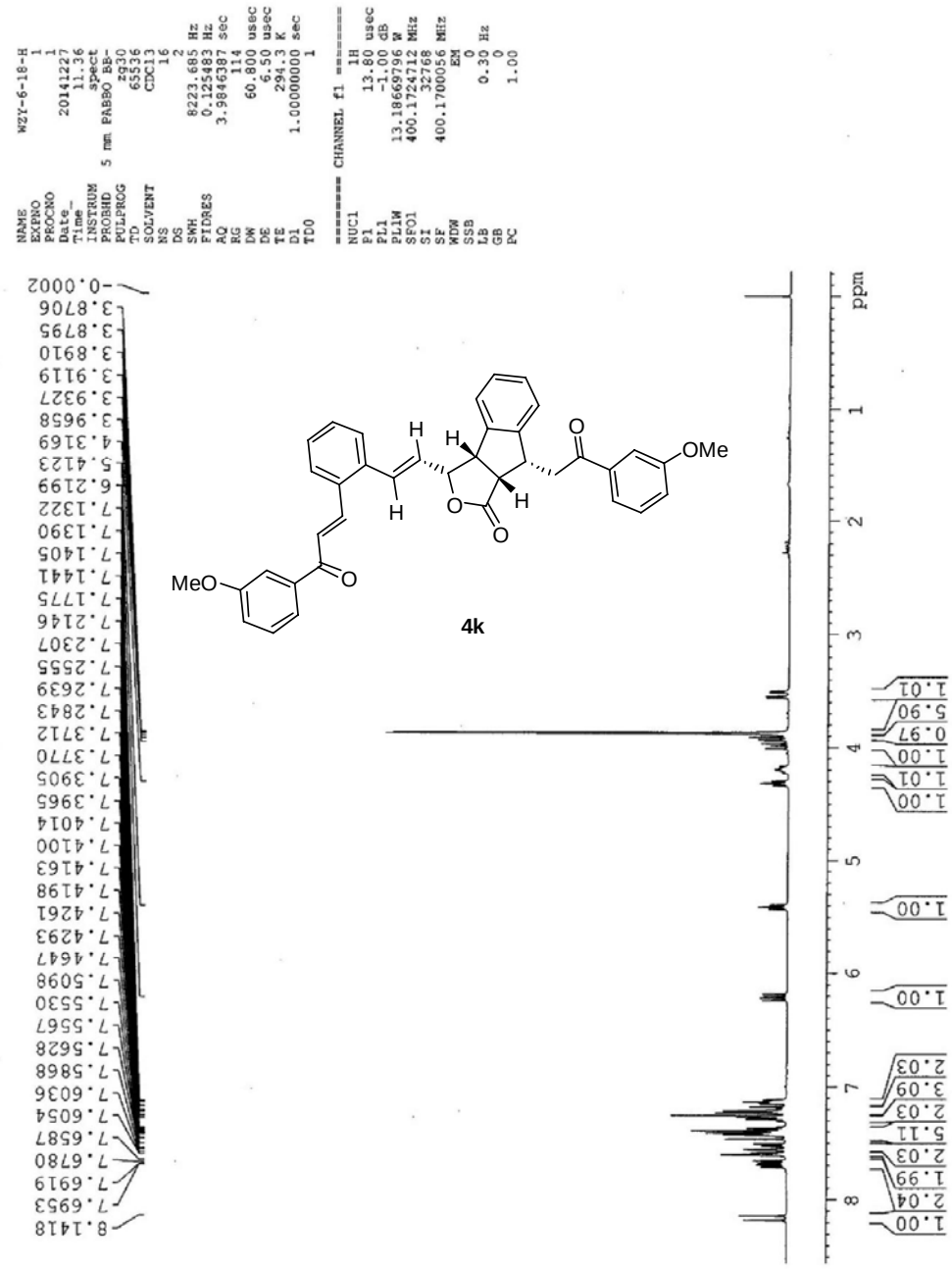
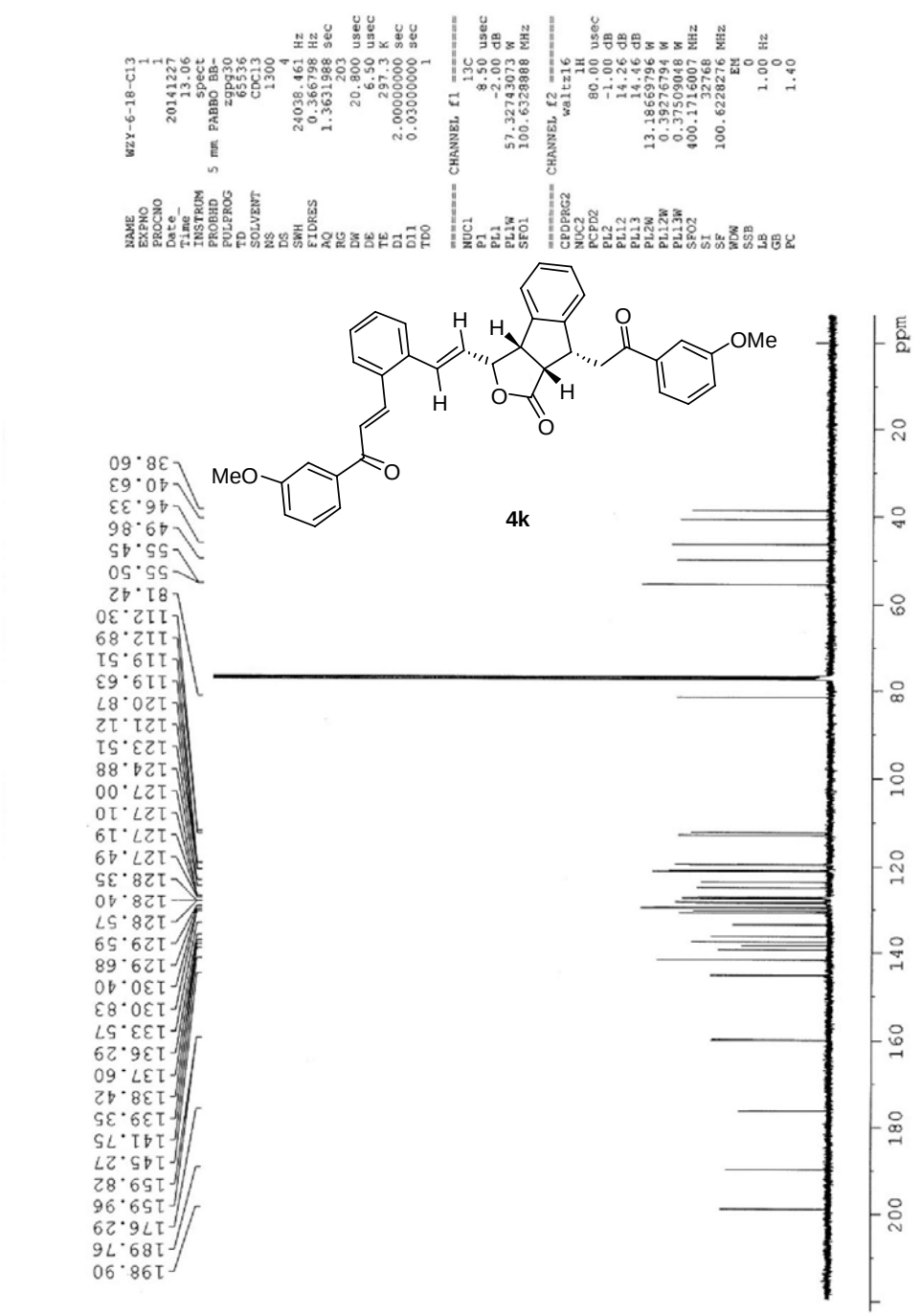
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2.25
DW 20.800 usec
DE 6.50 usec
TE 293.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 57.32743073 W
SFO1 100.6328888 MHz
CHANNEL f2
waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.26 dB
PL13 14.46 dB
PL2W 13.18669796 W
PL12W 0.39276794 W
PL13W 0.37509048 W
SFO2 400.1716007 MHz
SI 32768
SF 100.6228270 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
21.69
21.73
38.29
40.61
46.42
49.87
76.74
77.05
77.37
81.44
99.99
123.64
124.93
126.99
127.07
127.15
127.64
128.29
128.33
128.56
128.72
129.28
129.44
130.29
130.89
133.70
134.57
135.39
136.21
137.62
141.34
143.80
143.92
145.42
176.36
189.53
198.74
H
H
H
O
O
O
O
Me
Me
4i
ppm

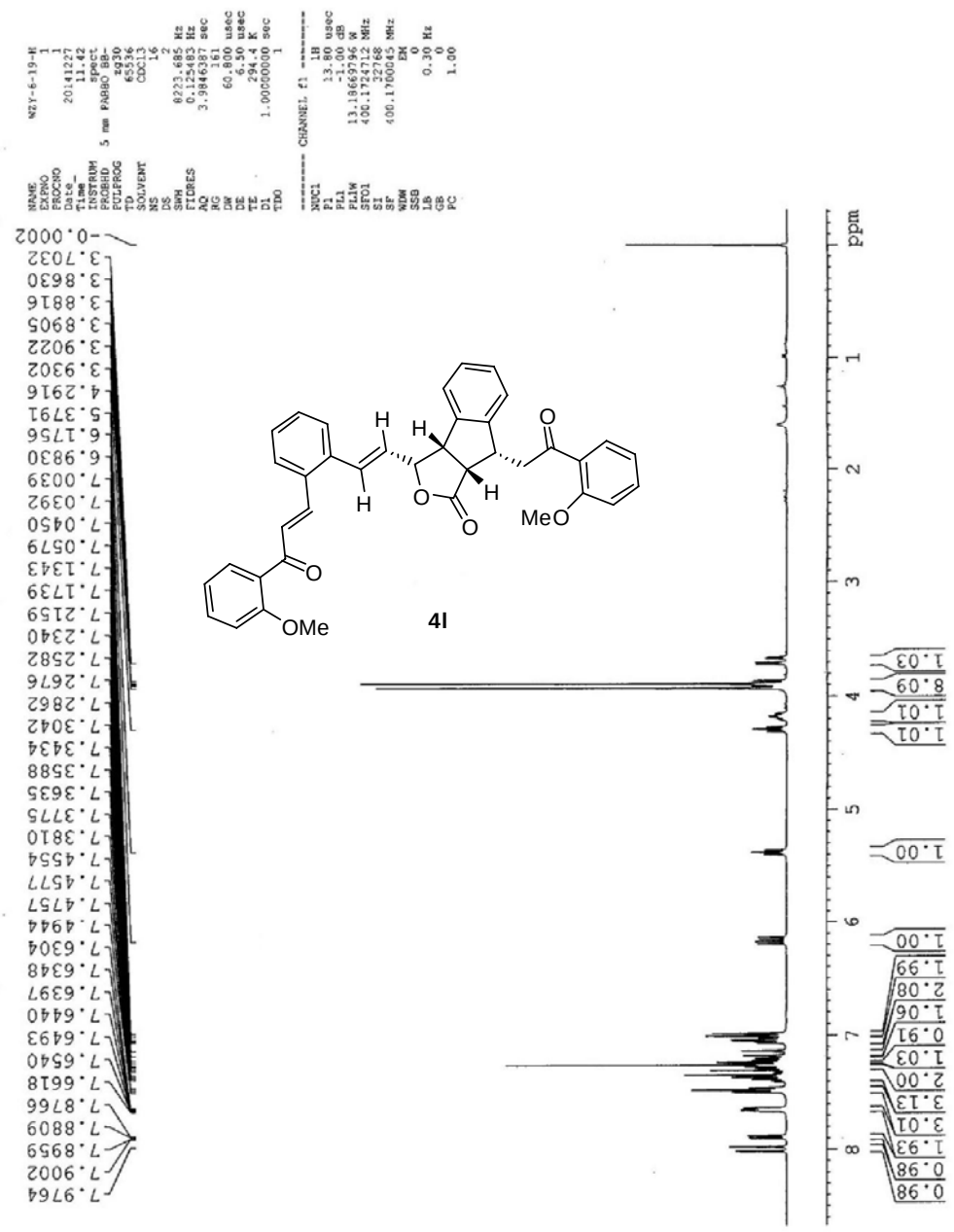

NAME WZY-3-01
EXPNO 1
PROCNO 1
Date_ 20140414
Time 17.20
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 299.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700318 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Br
Br
4j
ppm

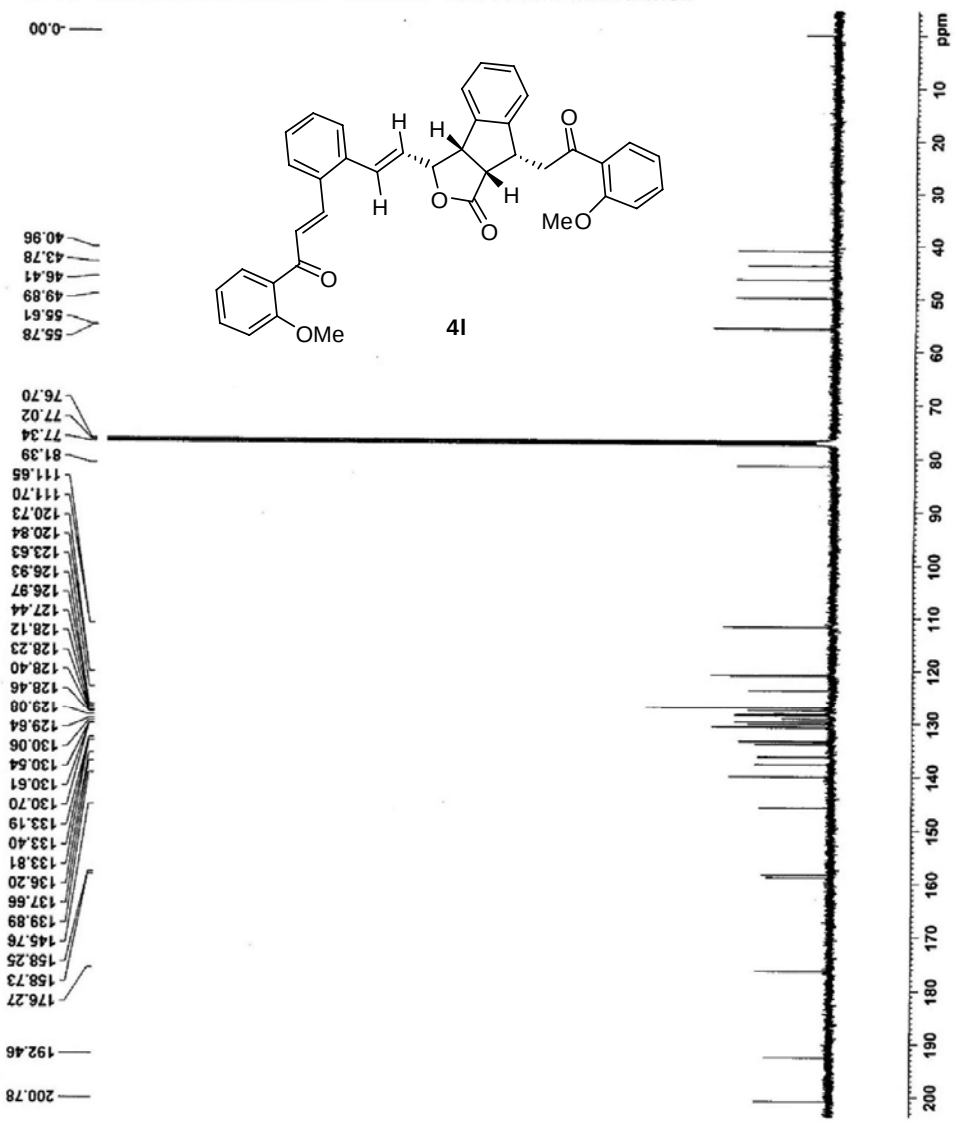

NAME WZY-3-01C
EXPNO 1
PROCNO 1
Date_ 20140414
Time_ 21.27
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 916
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 300.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 57.32743073 W
SFO1 100.6328898 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.26 dB
PL13 14.46 dB
PL2W 13.18669796 W
PL12W 0.39676794 W
PL13W 0.37509048 W
SFO2 400.1716007 MHz
SI 32768
SF 100.6228270 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
H
H
H
O
O
O
Br
Br
4j
38.41
40.54
46.33
49.79
76.72
77.04
77.35
81.31
123.44
124.32
127.03
127.23
127.70
128.10
128.15
128.34
128.39
128.58
129.71
130.04
130.54
130.74
131.88
132.00
133.35
135.84
136.43
136.68
137.67
142.33
145.08
176.30
188.93
198.08
ppm

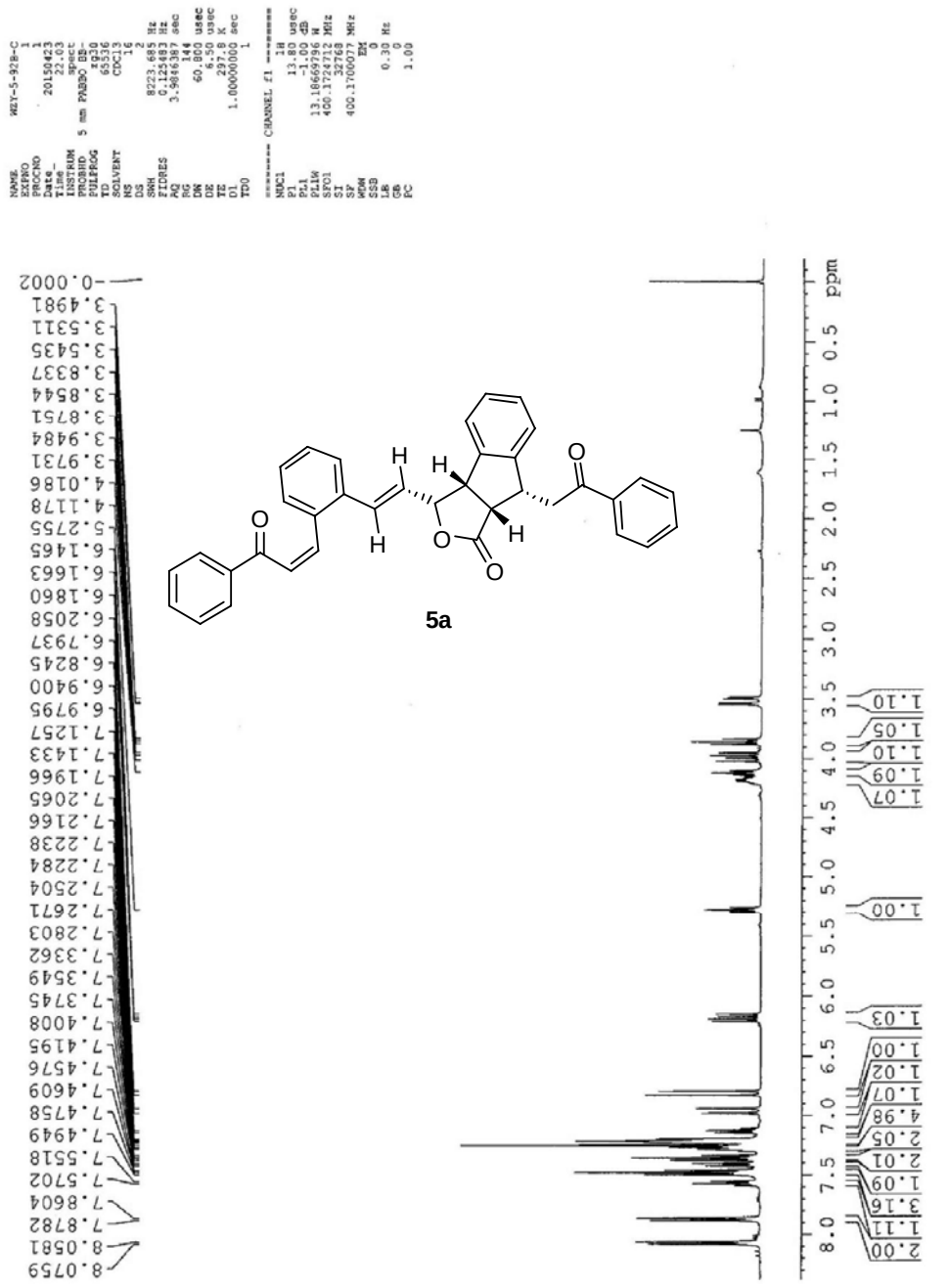

NAME WZY-6-18-H
EXPNO 1
PROCNO 1
Date_ 20141227
Time 11.36
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 114
DW 60.800 usec
DE 6.50 usec
TE 294.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700056 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
MeO
OMe
O
H
4k
ppm

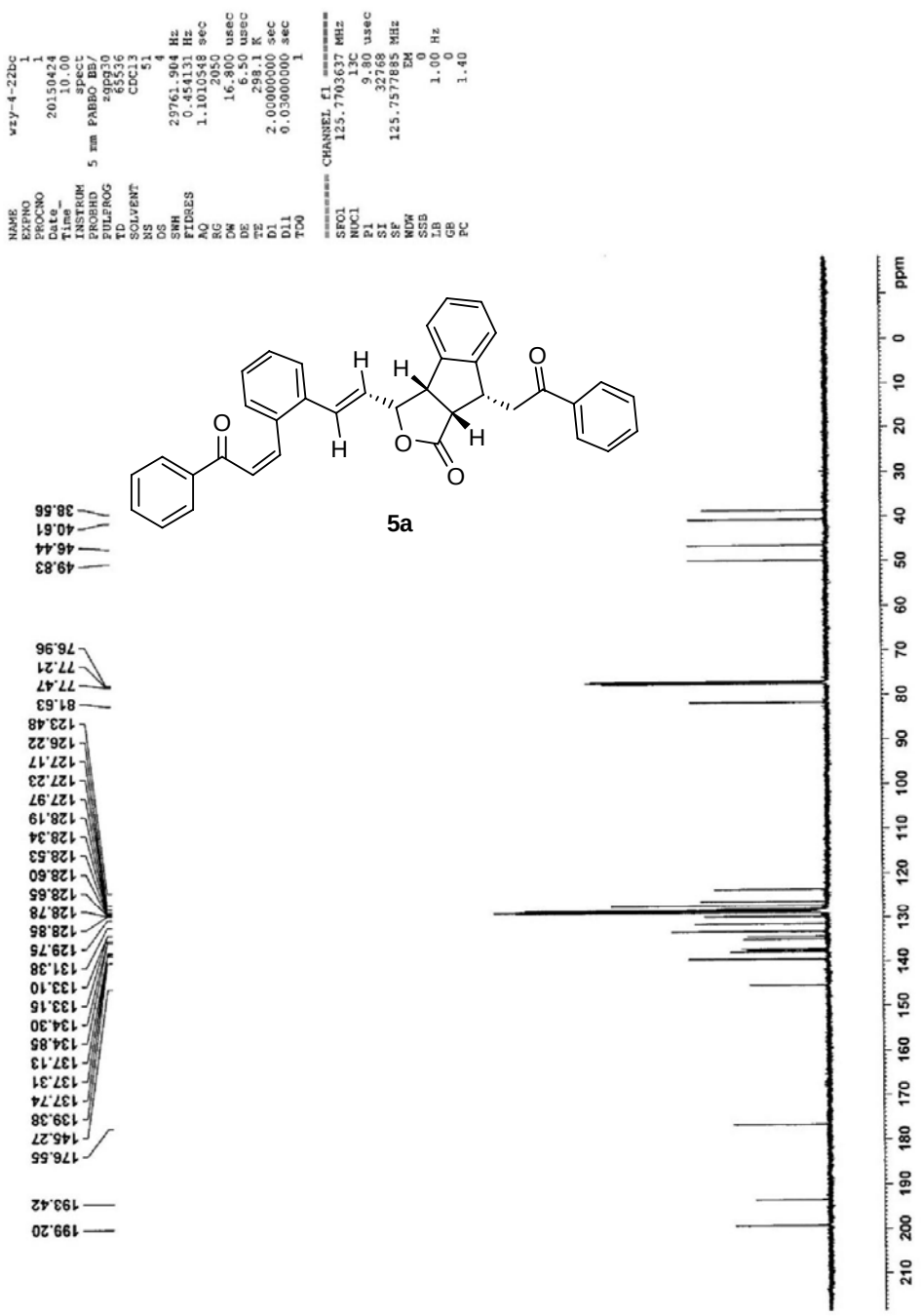

NAME WZY-6-18-C13
EXPNO 1
PROCNO 1
Date_ 20141227
Time_ 13.06
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1300
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 297.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 57.32743073 W
SFO1 100.6328888 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.26 dB
PL13 14.46 dB
PL2W 13.18669796 W
PL12W 0.39276794 W
PL13W 0.37509048 W
SFO2 400.1716007 MHz
SI 32768
SF 100.6228276 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
MeO
O
H
H
H
O
O
H
O
OMe
4k
38.60
40.63
46.33
49.86
55.45
55.50
81.42
112.30
112.89
119.51
119.63
120.87
121.12
123.51
124.88
127.00
127.10
127.19
127.49
128.35
128.40
128.57
129.59
129.68
130.40
130.83
133.57
136.29
137.60
138.42
139.35
141.75
145.27
159.82
159.96
176.29
189.76
198.90
ppm
200
180
160
140
120
100
80
60
40
20

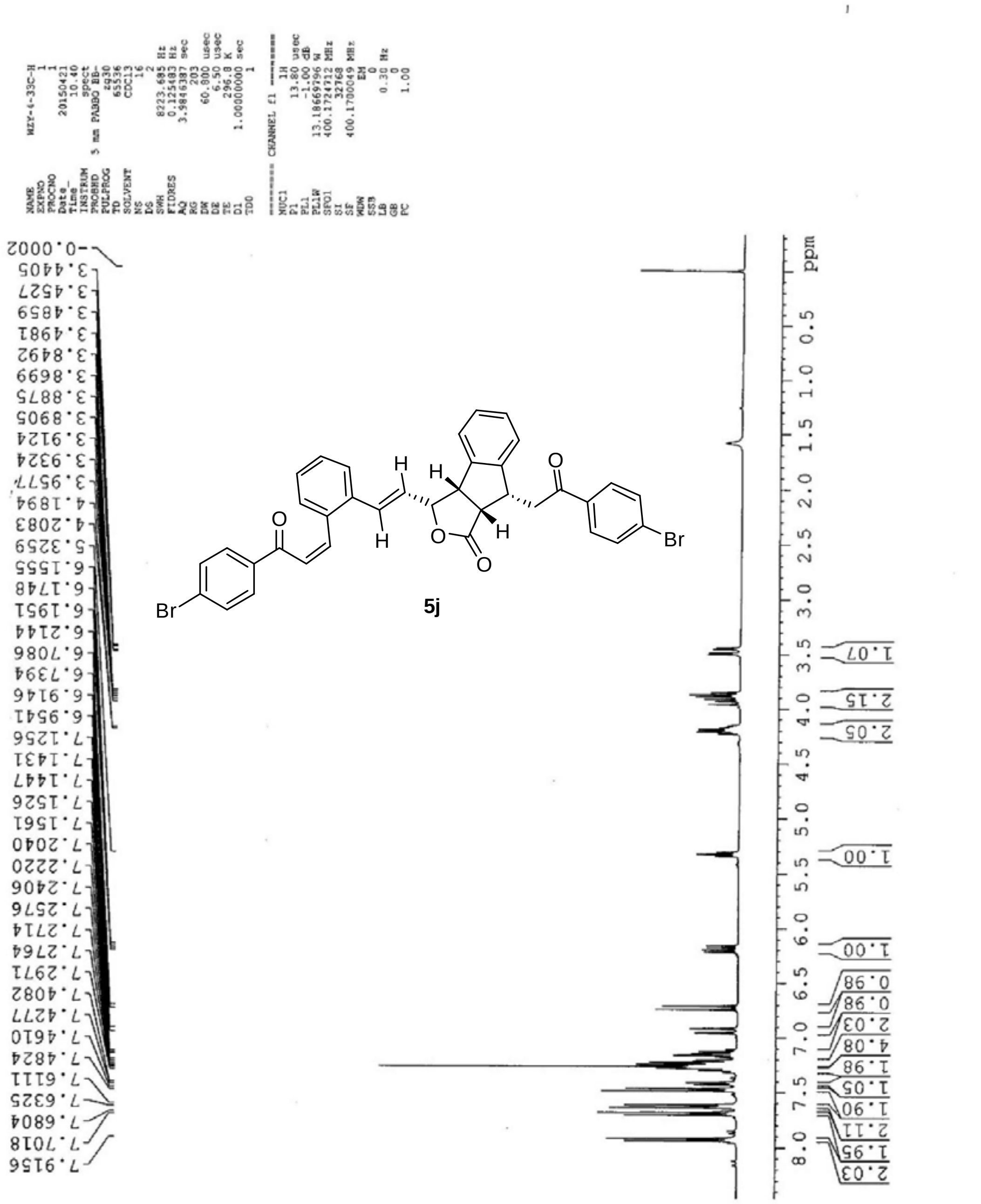
c

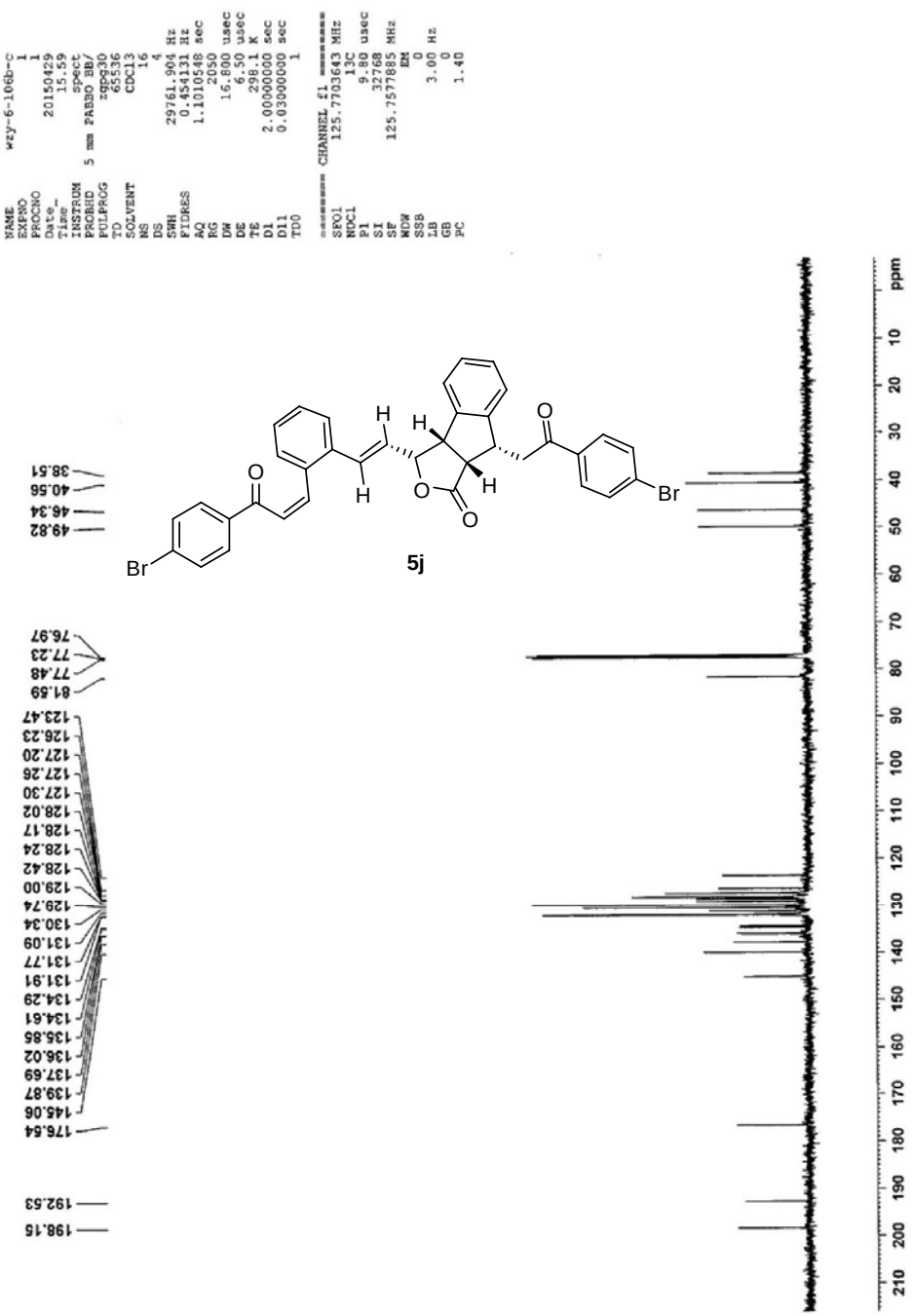

4l
OMe
MeO
ppm

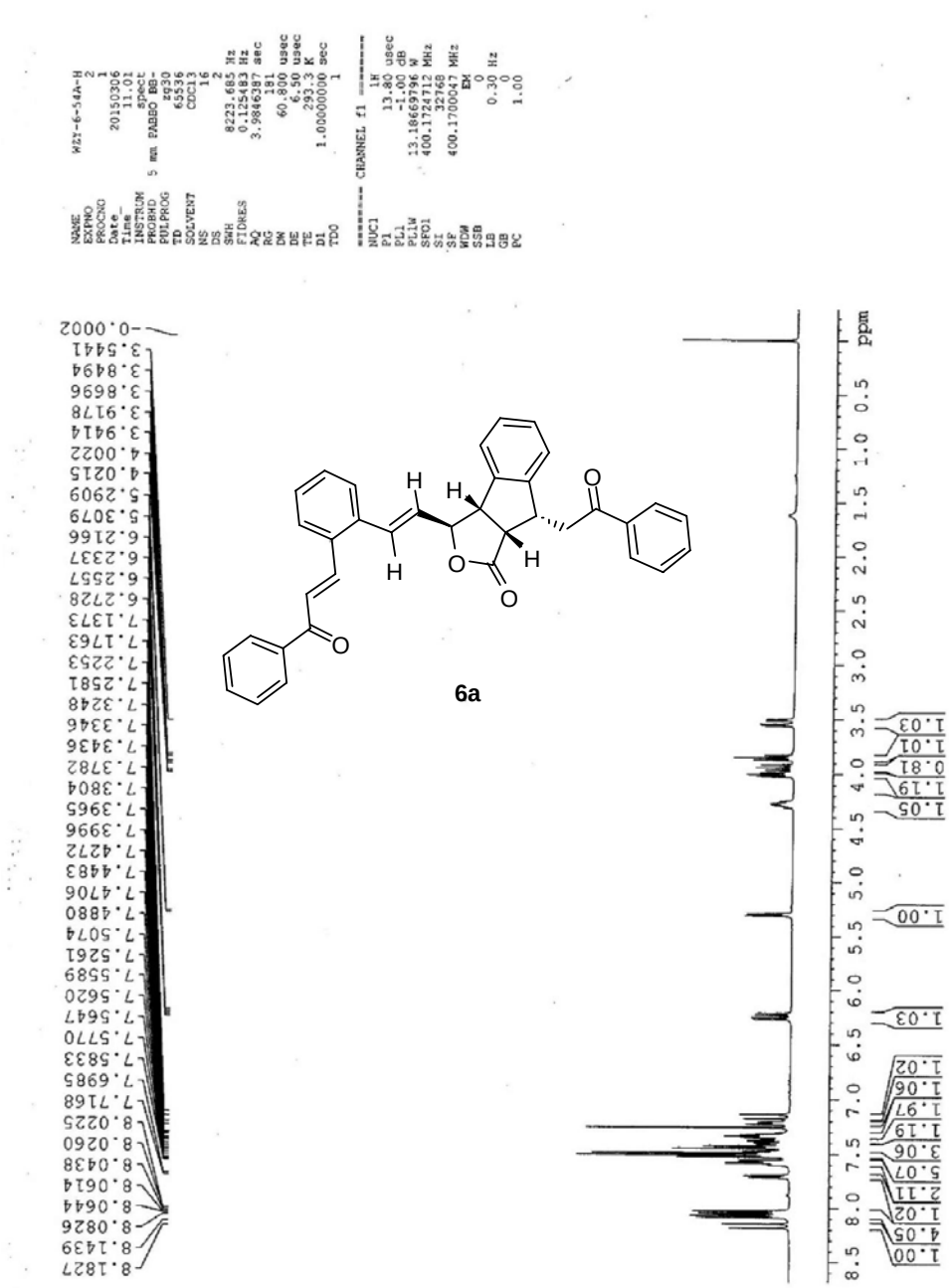

wzy-6-19-c13
NAME
EXPNO
PROCNO
Date_
Time
INSTRUM
PROBHD
PULPROG
TD
SOLVENT
NS
DS
SWH
FIDRES
AQ
RG
DW
DE
TE
D1
D11
TD0
CHANNEL f1
NUC1
P1
PL1
PL1W
SFO1
CHANNEL f2
CPDPRG2
NUC2
PCPD2
PL2
PL12
PL13
PL2W
PL12W
PL13W
SFO2
SI
SF
WDW
SSB
LB
GB
PC
OMe
MeO
4l
ppm

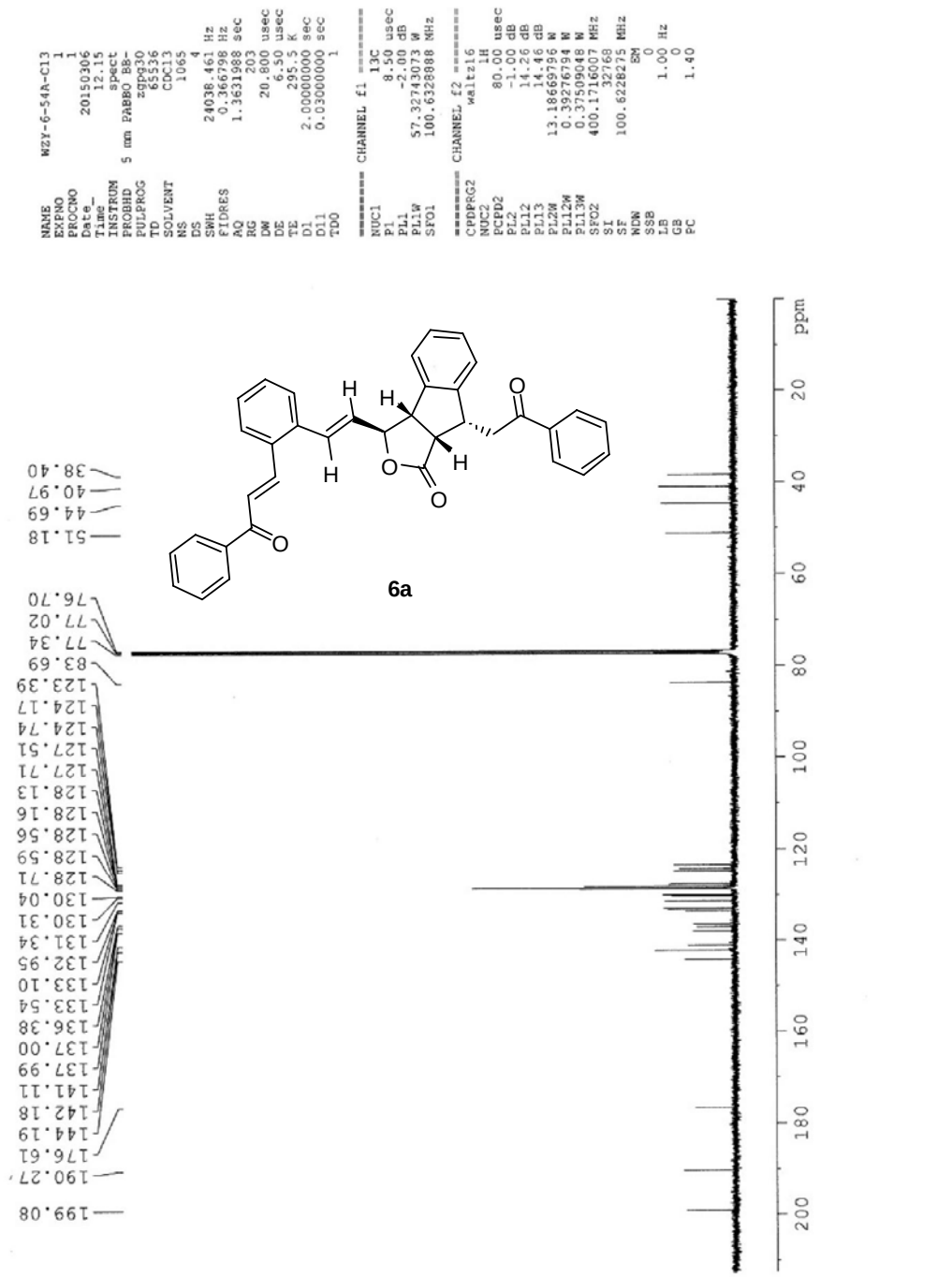

NAME KEY-5-92B-C
EXPNO 1
PROCNO 1
Date_ 20150423
Time 22.03
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 144
DW 60.800 usec
DE 6.50 usec
TE 297.8 K
D1 1.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.16663456 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700077 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
5a
ppm


NAME wzy-4-22bc
EXPNO 1
PROCNO 1
Date_ 20150424
Time 10.00
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 51
DS 4
SWH 29761.904 Hz
FIDRES 0.454113 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703637 MHz
NUC1 13C
P1 9.80 usec
SI 32768
SF 125.7577885 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
38.56
40.61
46.44
49.83
76.96
77.21
77.47
81.63
123.48
126.22
127.17
127.23
127.97
128.19
128.34
128.53
128.60
128.65
128.78
128.86
129.75
131.38
133.10
133.15
134.30
134.85
137.13
137.31
137.74
139.38
146.27
176.55
193.42
199.20
ppm
5a




NAME wzy-6-106b-c
EXPNO 1
PROCNO 1
Date_ 20150429
Time 15.59
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 16
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010548 sec
RG 2050
DW 16.800 usec
DE 6.50 usec
TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703643 MHz
NUC1 13C
P1 9.80 usec
SI 32768
SF 125.7577885 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
38.51
40.56
46.34
49.82
76.97
77.23
77.48
81.59
123.47
126.23
127.20
127.26
127.30
128.02
128.17
128.24
128.42
129.00
129.74
130.34
131.09
131.77
131.91
134.29
134.61
135.85
136.02
137.69
139.87
145.06
176.64
192.53
198.15
O
H
H
H
O
O
H
O
Br
Br
5j
ppm


NAME wzt-6-54A-H
EXPNO 2
PROCNO 1
Date_ 20150306
Time 11.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 181
DW 60.800 usec
DE 6.50 usec
TE 293.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700047 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
6a
ppm


NAME WZY-6-54A-C13
EXPNO 1
PROCNO 1
Date_ 20150306
Time 12.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1065
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.36319888 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 295.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 57.32743073 W
SFO1 100.6328888 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.26 dB
PL13 14.46 dB
PL2W 13.18669796 W
PL12W 0.39276794 W
PL13W 0.37509048 W
SFO2 400.1716007 MHz
SI 32768
SF 100.6228275 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
6a
38.40
40.97
44.69
51.18
76.70
77.02
77.34
83.69
123.39
124.17
124.74
127.51
127.71
128.13
128.16
128.56
128.59
128.71
130.04
130.31
131.34
132.95
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136.38
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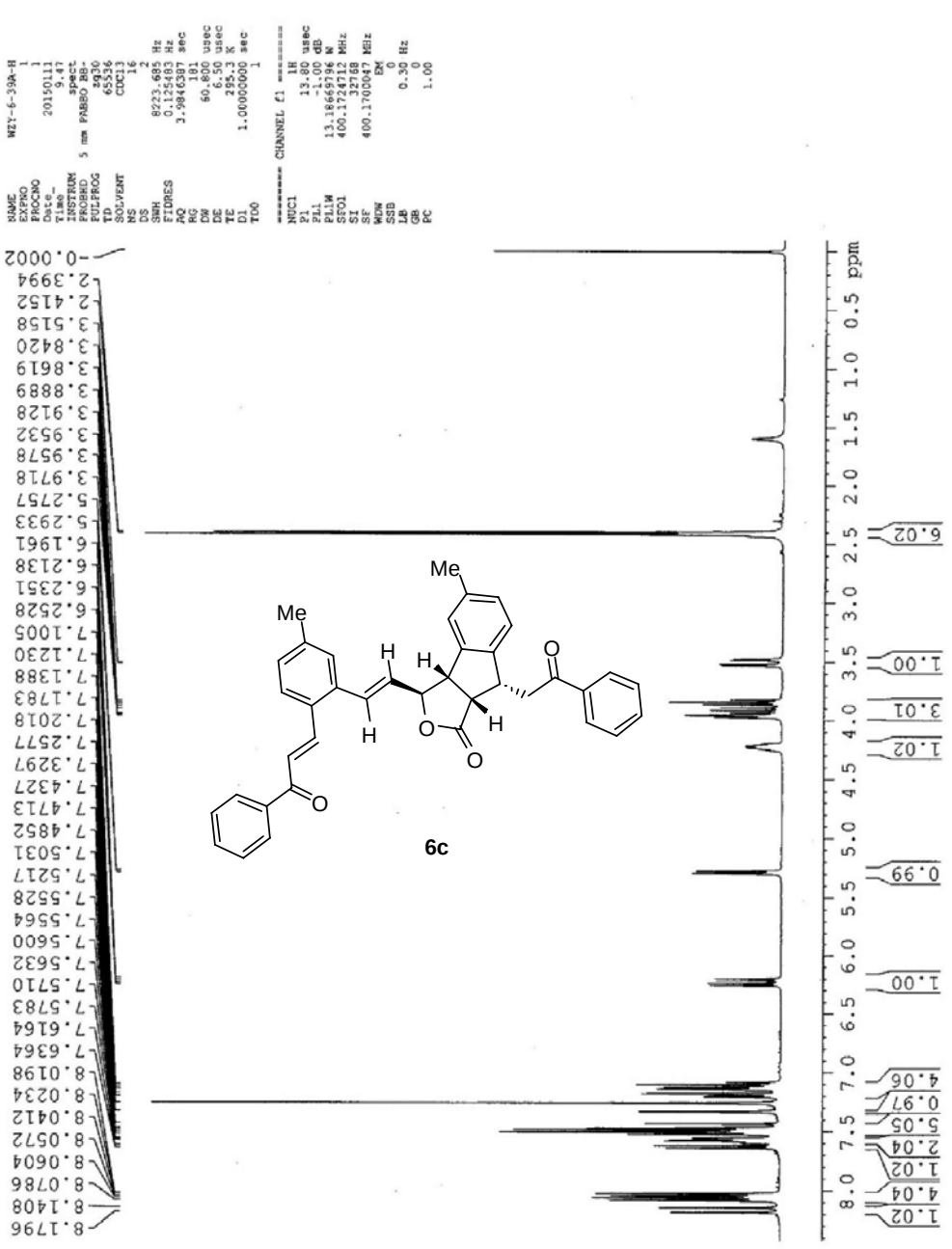
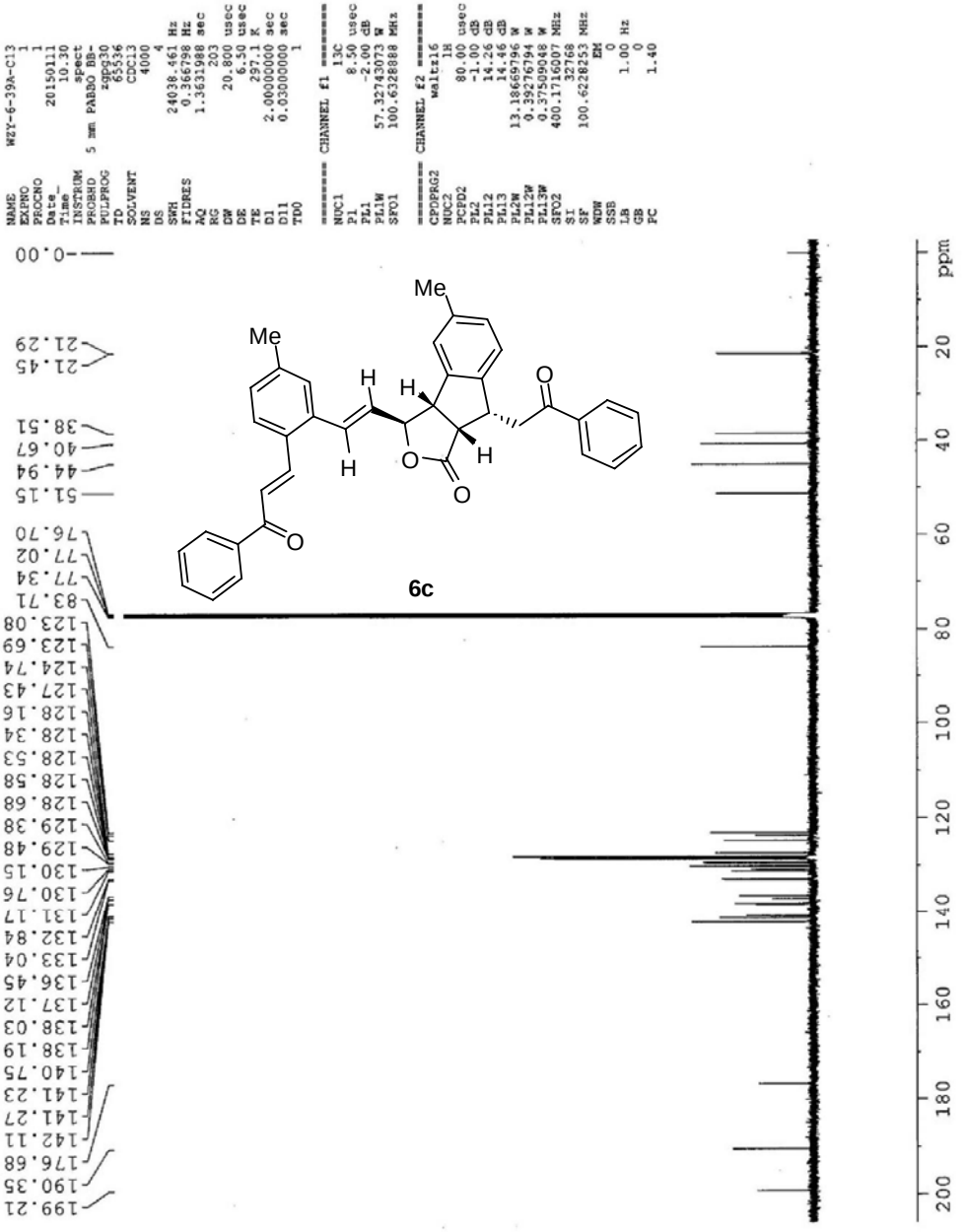
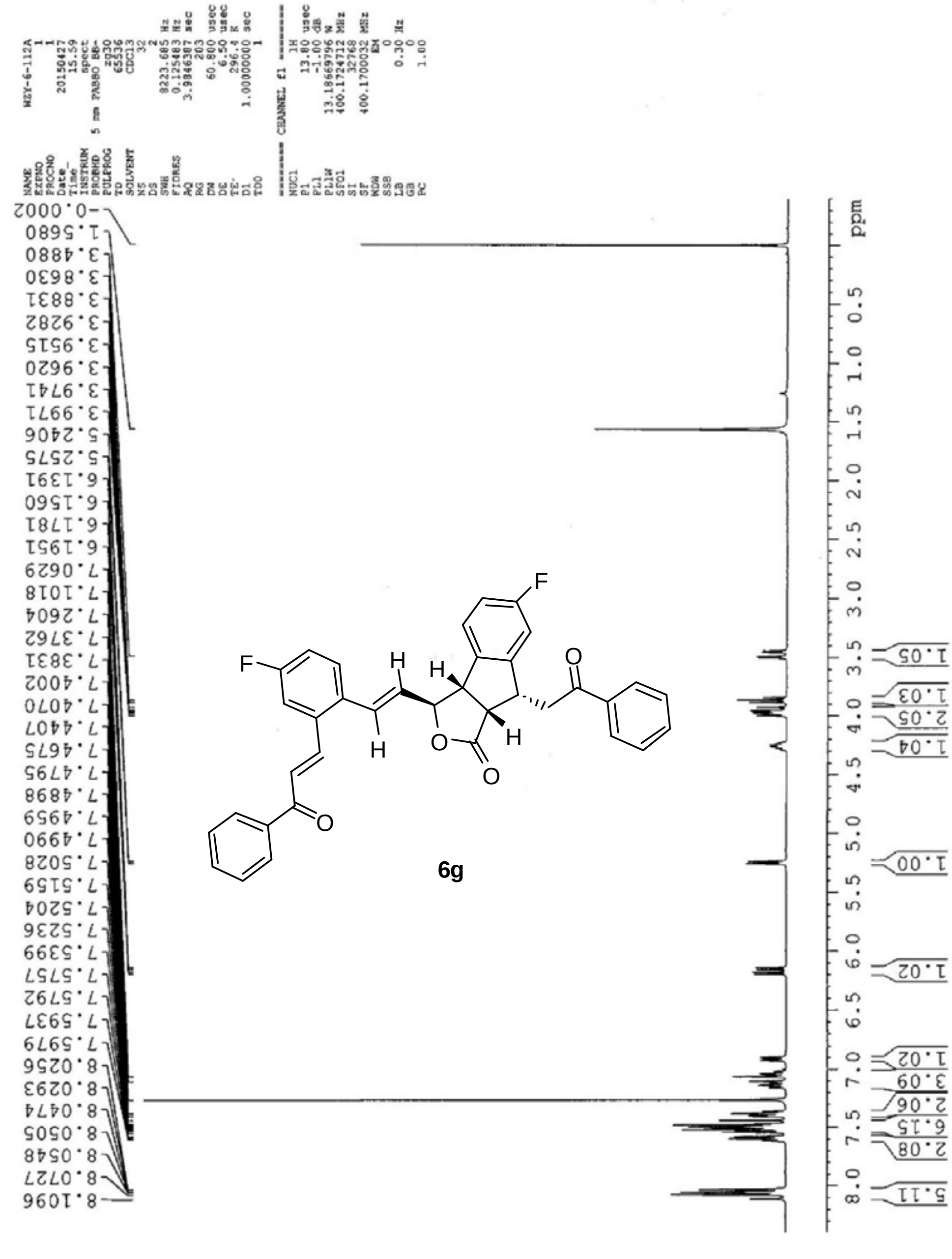
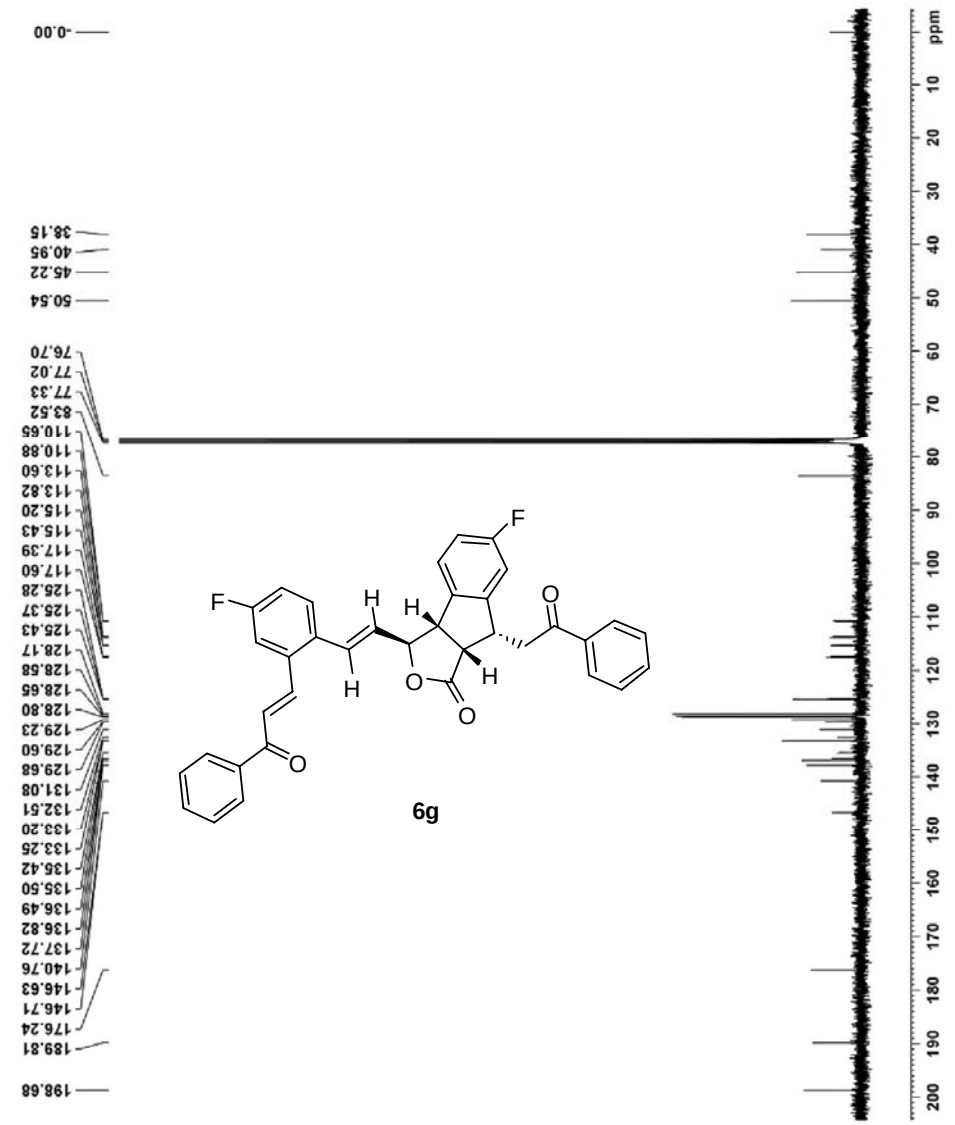
142.18
144.19
176.61
190.27
199.08
ppm


Me
Me
H
H
H
O
O
O
O
6c
ppm


Me
Me
H
H
H
O
O
O
O
6c
ppm


6g


NAME W2Y-6-99A-C13
EXPNO 1
PROCNO 1
Date_ 20150415
Time 14.12
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1646
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 296.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 57.32743073 W
SFO1 100.6328888 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.26 dB
PL13 14.46 dB
PL2W 13.18669796 W
PL12W 0.39276794 W
PL13W 0.37509048 W
SFO2 400.1716007 MHz
SI 32768
SF 100.6228259 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
-0.00
38.15
40.95
45.22
50.54
76.70
77.02
77.33
83.52
110.65
110.88
113.60
113.82
115.20
115.43
117.39
117.60
126.28
126.37
126.43
128.17
128.58
128.65
128.80
129.23
129.60
129.68
131.08
132.61
133.20
133.25
136.42
135.50
136.49
136.82
137.72
140.76
146.63
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176.24
189.81
198.68
F
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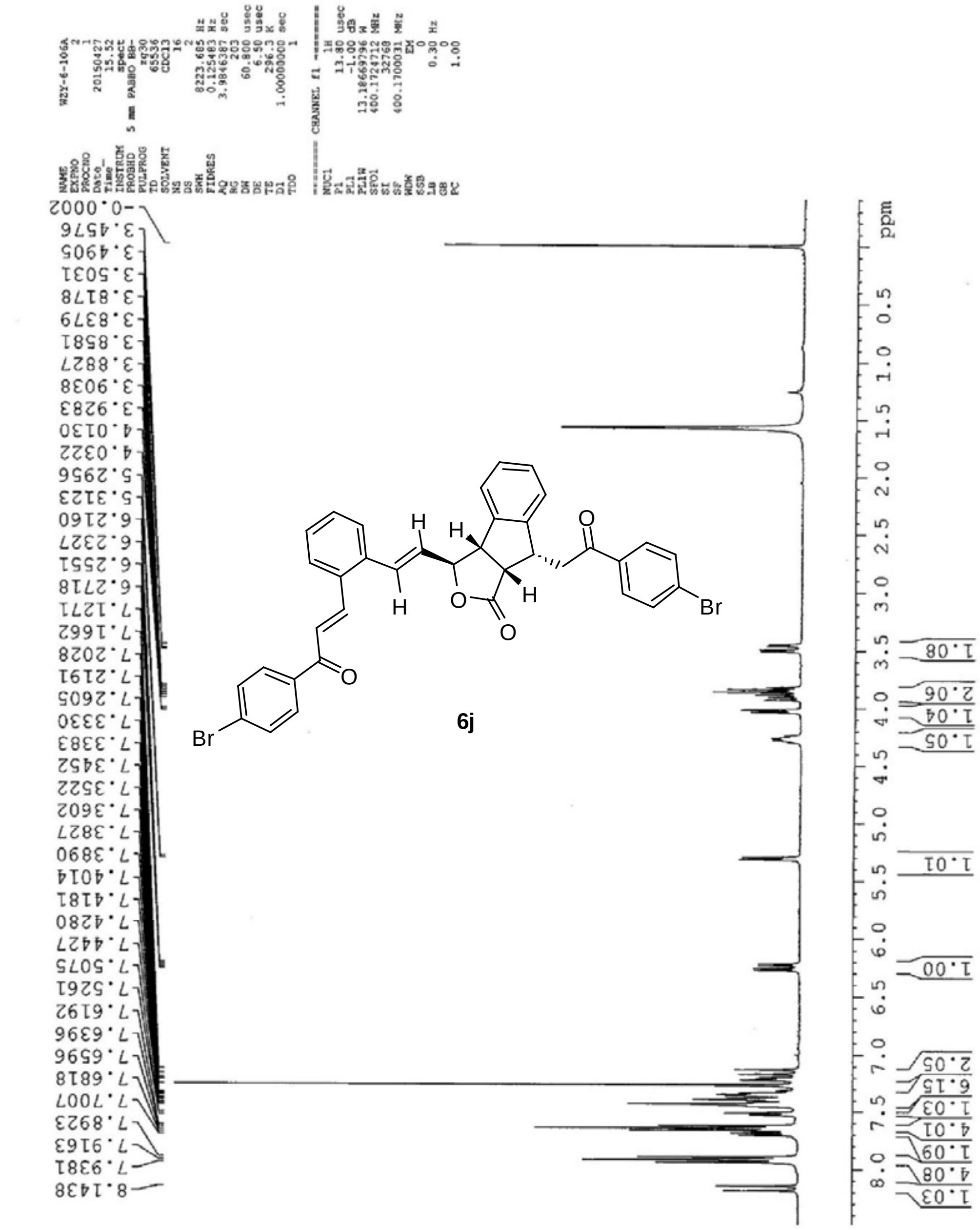
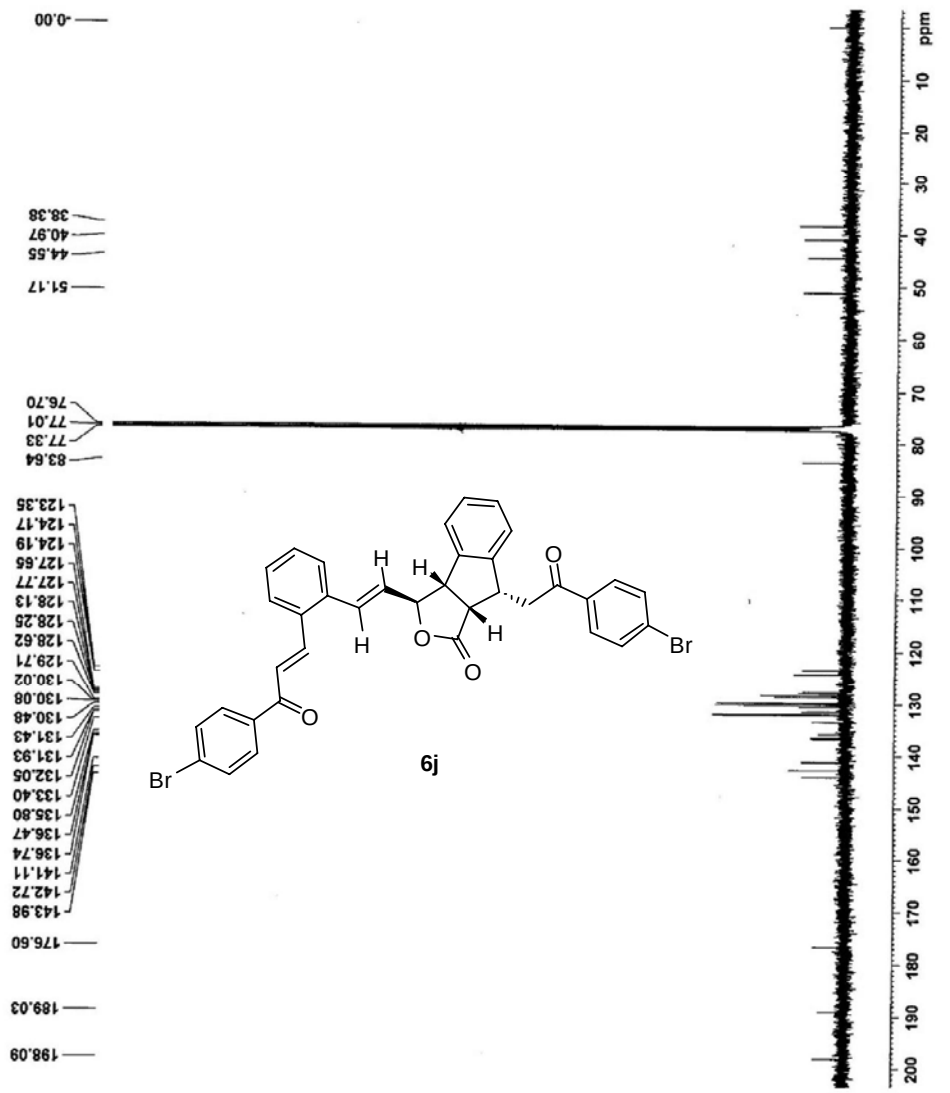
H
H
O
O
O
F
6g
ppm


6j


NAME WZY-6-106A-C13
EXPNO 1
PROCNO 1
Date_ 20150427
Time_ 19.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2000
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 300.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 57.32743073 W
SFO1 100.6328888 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.26 dB
PL13 14.46 dB
PL2W 13.18669796 W
PL12W 0.39276794 W
PL13W 0.37509048 W
SFO2 400.1716007 MHz
SI 32768
SF 100.6228245 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
-0.00
38.38
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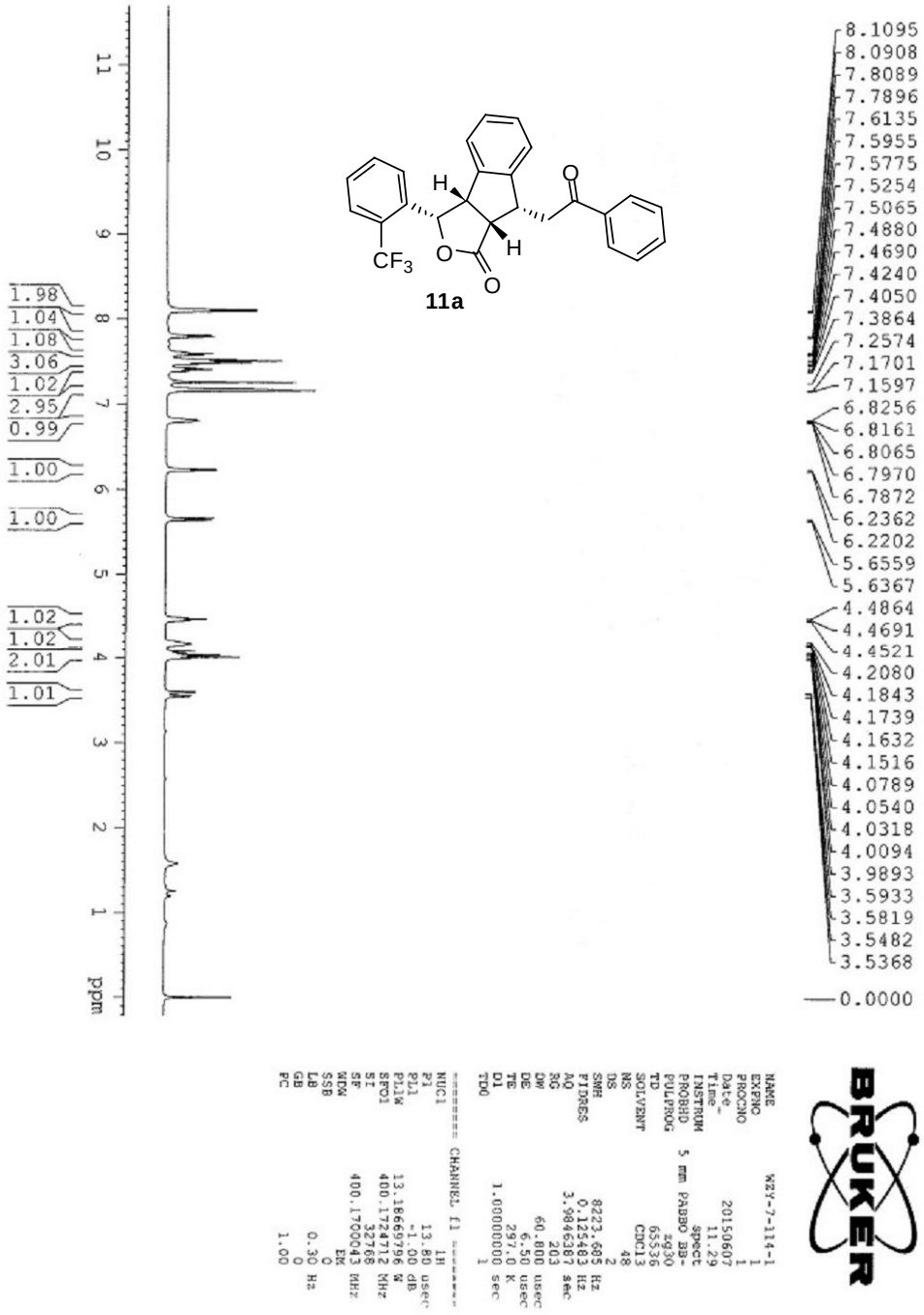
44.55
51.17
76.70
77.01
77.33
83.64
123.35
124.17
124.19
127.66
127.77
128.13
128.25
128.62
129.71
130.02
130.08
130.48
131.43
131.93
132.05
133.40
135.80
136.47
136.74
141.11
142.72
143.98
176.60
189.03
198.09
ppm
O
H
H
H
O
O
Br
O
Br

6j


11a
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1.08
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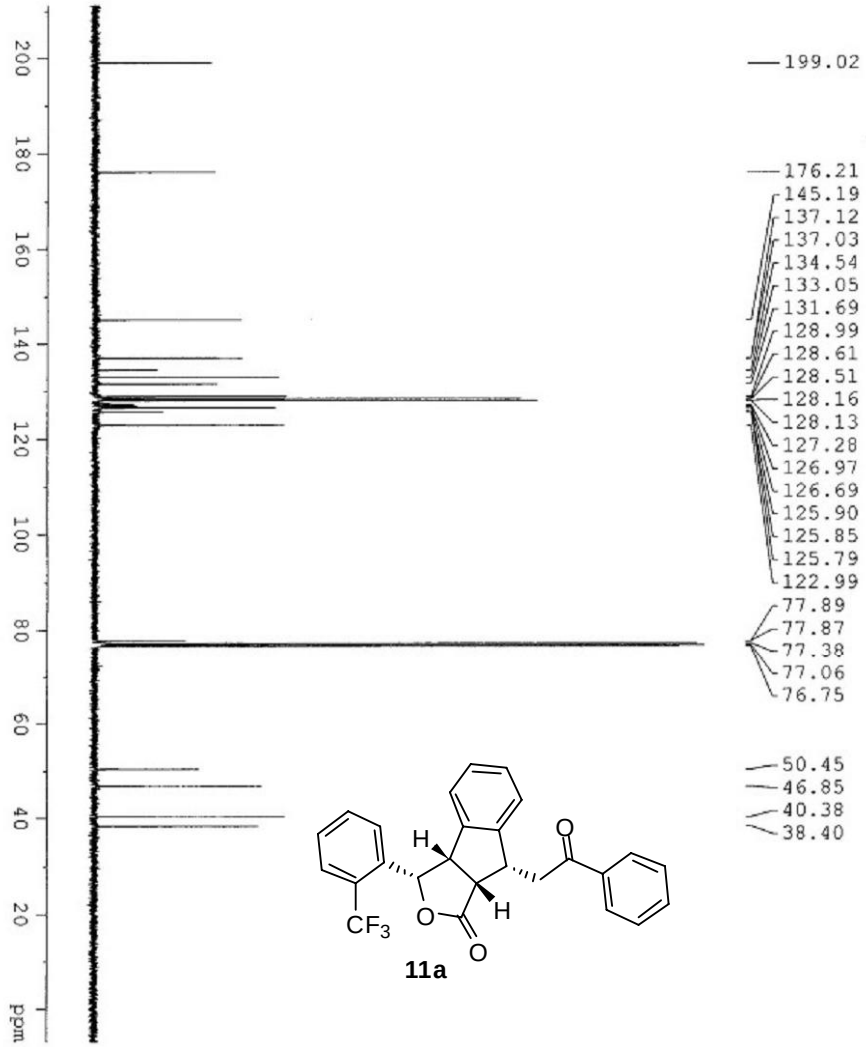
1.02
2.95
0.99
1.00
1.00
1.02
1.02
2.01
1.01
ppm
8.1095
8.0908
7.8089
7.7896
7.6135
7.5955
7.5775
7.5254
7.5065
7.4880
7.4690
7.4240
7.4050
7.3864
7.2574
7.1701
7.1597
6.8256
6.8161
6.8065
6.7970
6.7872
6.2362
6.2202
5.6559
5.6367
4.4864
4.4691
4.4521
4.2080
4.1843
4.1739
4.1632
4.1516
4.0789
4.0540
4.0318
4.0094
3.9893
3.5933
3.5819
3.5482
3.5368
0.0000
NAME W2Y-7-114-1
EXPNO 1
PROCNO 1
Date_ 20150607
Time_ 11.29
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 48
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 297.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.17247712 MHz
SI 32768
SF 400.1700043 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

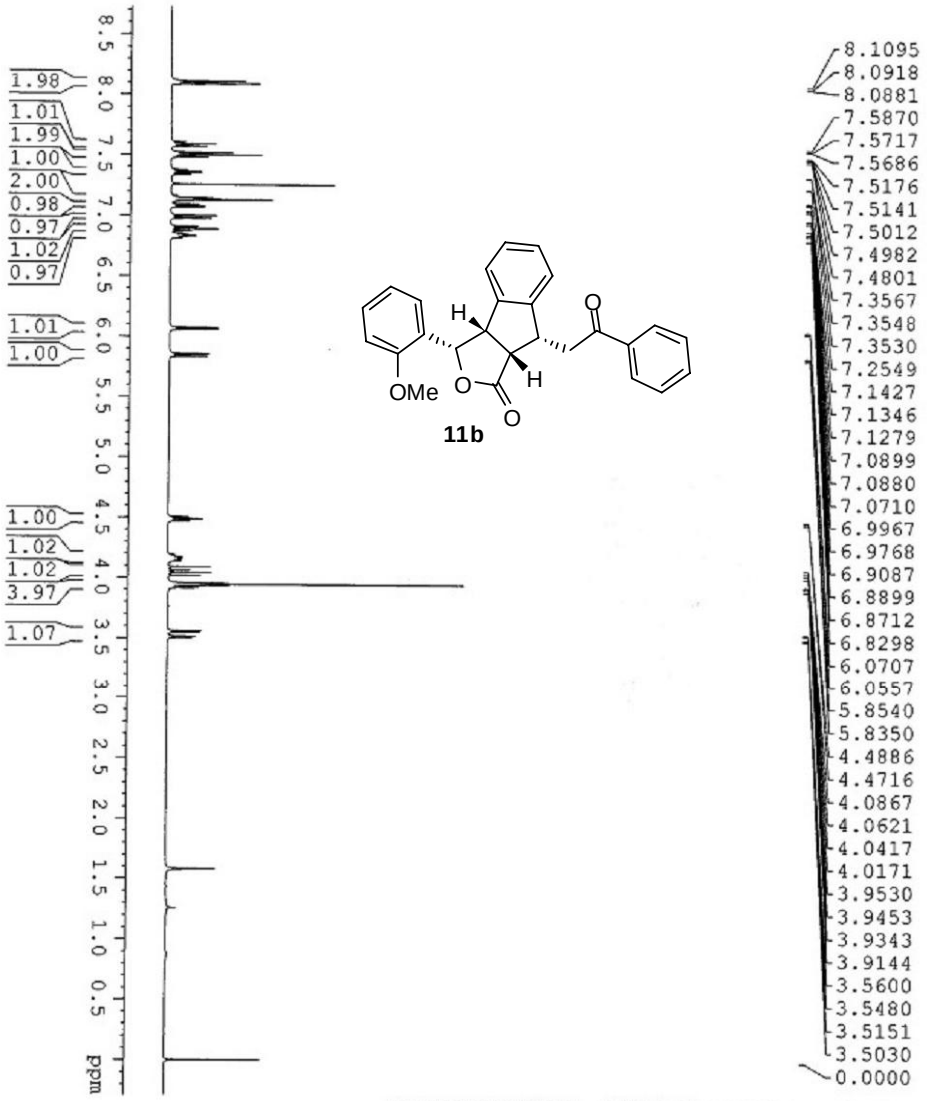


11a

```
NAME                  WZY-7-114-c13
EXPNO                           11
PROCNO                           1
Date_               20150607
Time_                   12.39
INSTRUM                   spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                        1047
DS                           4
SWH                  24038.461 Hz
FIDRES                0.366798 Hz
AQ                    1.3631988 sec
RG                         203
DW                      20.800 usec
DE                       6.50 usec
TE                      296.8 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                             1

======== CHANNEL f1 ========
NUC1                       13C
P1                        8.50 usec
PL1                      -2.00 dB
PL1W                57.32743073 W
SFO1               100.6328888 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                    80.00 usec
PL2                      -1.00 dB
PL12                     14.26 dB
PL13                     14.46 dB
PL2W                13.18669796 W
PL12W                0.39276794 W
PL13W                0.37509048 W
SFO2               400.1716007 MHz
SI                        32768
SF                 100.6228270 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```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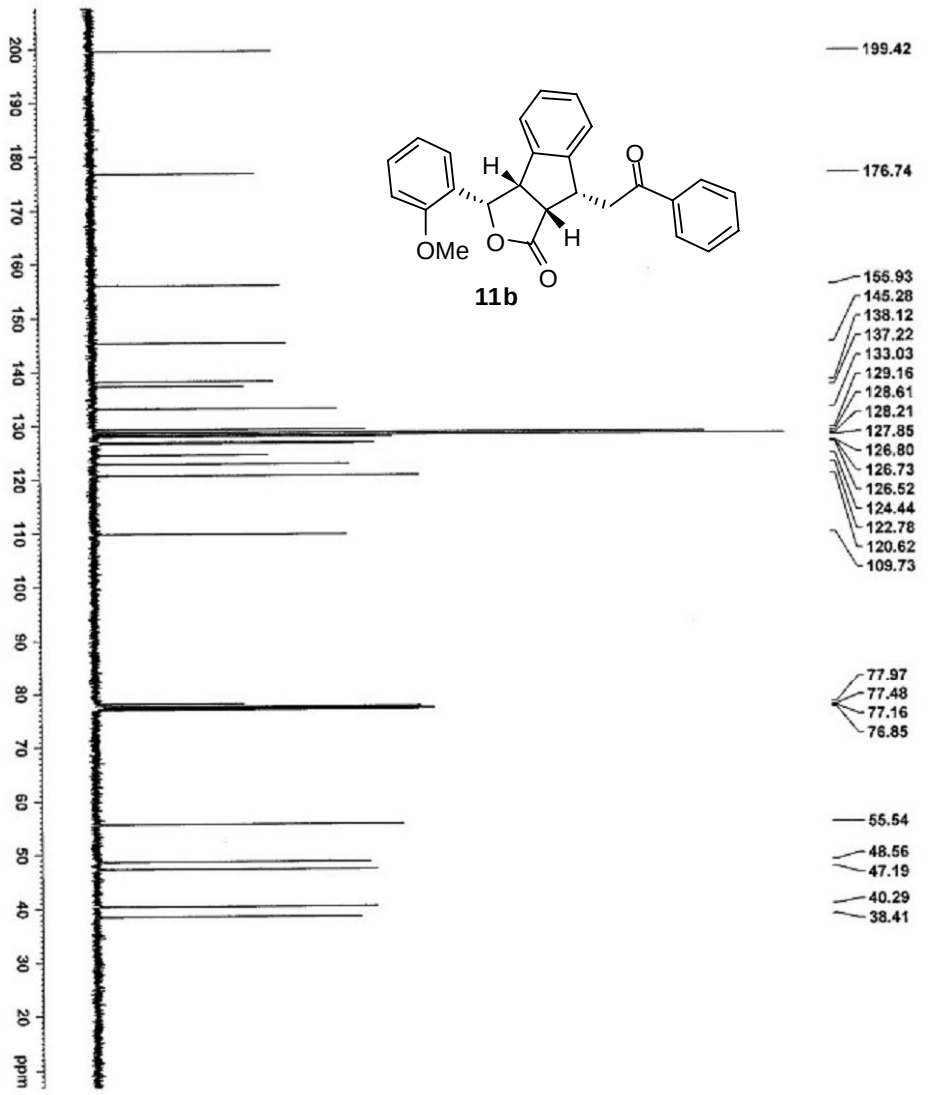
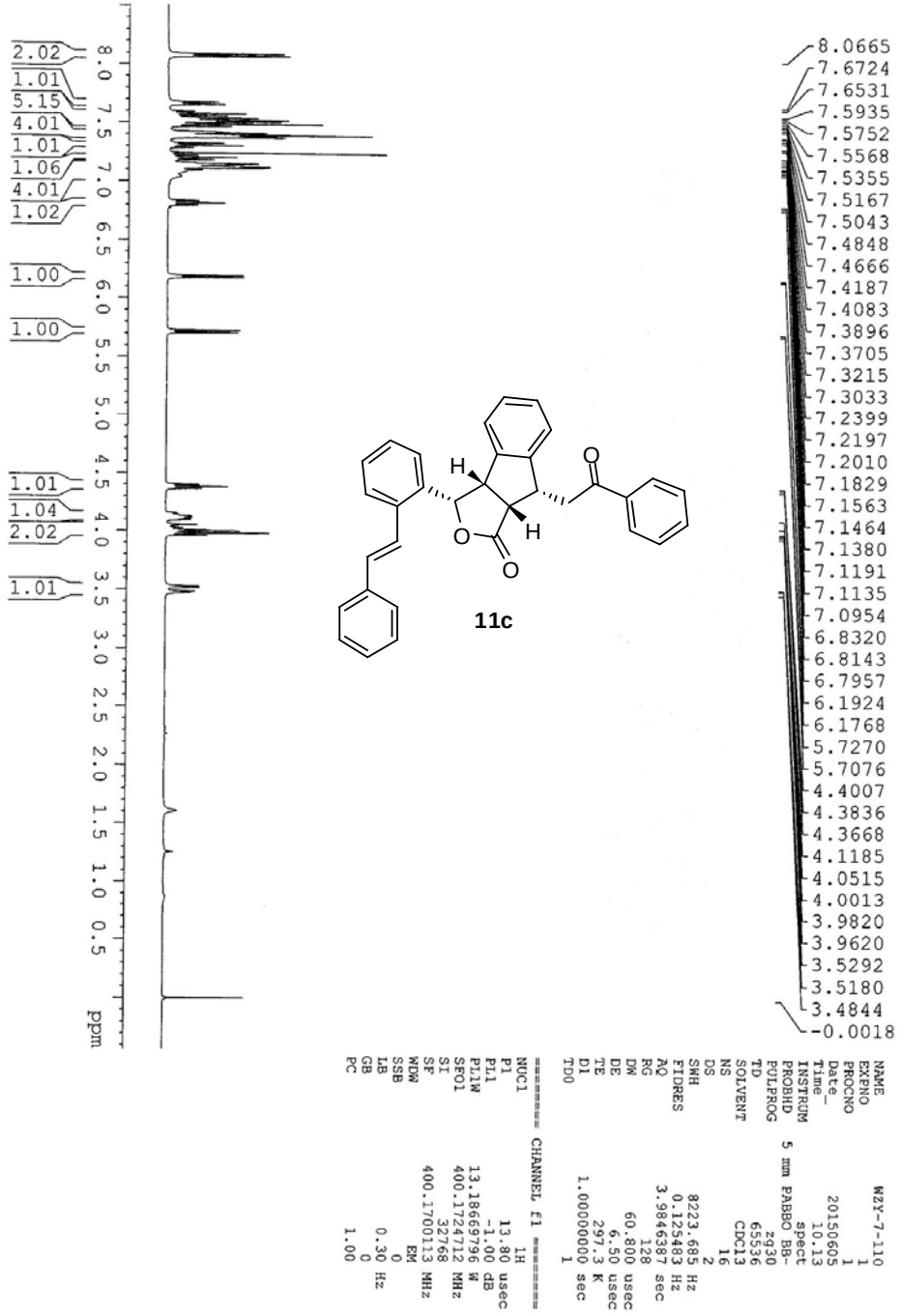
1.99
1.00
2.00
0.98
0.97
1.02
0.97
1.01
1.00
1.00
1.02
1.02
3.97
1.07
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
H
O
OMe
O
H
O
11b
8.1095
8.0918
8.0881
7.5870
7.5717
7.5686
7.5176
7.5141
7.5012
7.4982
7.4801
7.3567
7.3548
7.3530
7.2549
7.1427
7.1346
7.1279
7.0899
7.0880
7.0710
6.9967
6.9768
6.9087
6.8899
6.8712
6.8298
6.0707
6.0557
5.8540
5.8350
4.4886
4.4716
4.0867
4.0621
4.0417
4.0171
3.9530
3.9453
3.9343
3.9144
3.5600
3.5480
3.5151
3.5030
0.0000
NAME WZY-7-119
EXPNO 1
PROCNO 1
Date_ 20150610
Time 10.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125493 Hz
AQ 3.9846387 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 297.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PLW1 13.18669796 W
SFO1 400.1324712 MHz
SI 32768
SF 400.1700053 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



NAME wzx-7-119-c13
EXPNO 1
PROCNO 1
Date_ 20150610
Time 11.00
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 122
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 297.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 -2.00 dB
PL1W 57.32743073 W
SFO1 100.6328000 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.26 dB
PL13 14.46 dB
PL2W 13.18669796 W
PL12W 0.39276794 W
PL13W 0.37509048 W
SFO2 400.1716007 MHz
SI 32768
SF 100.6228270 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40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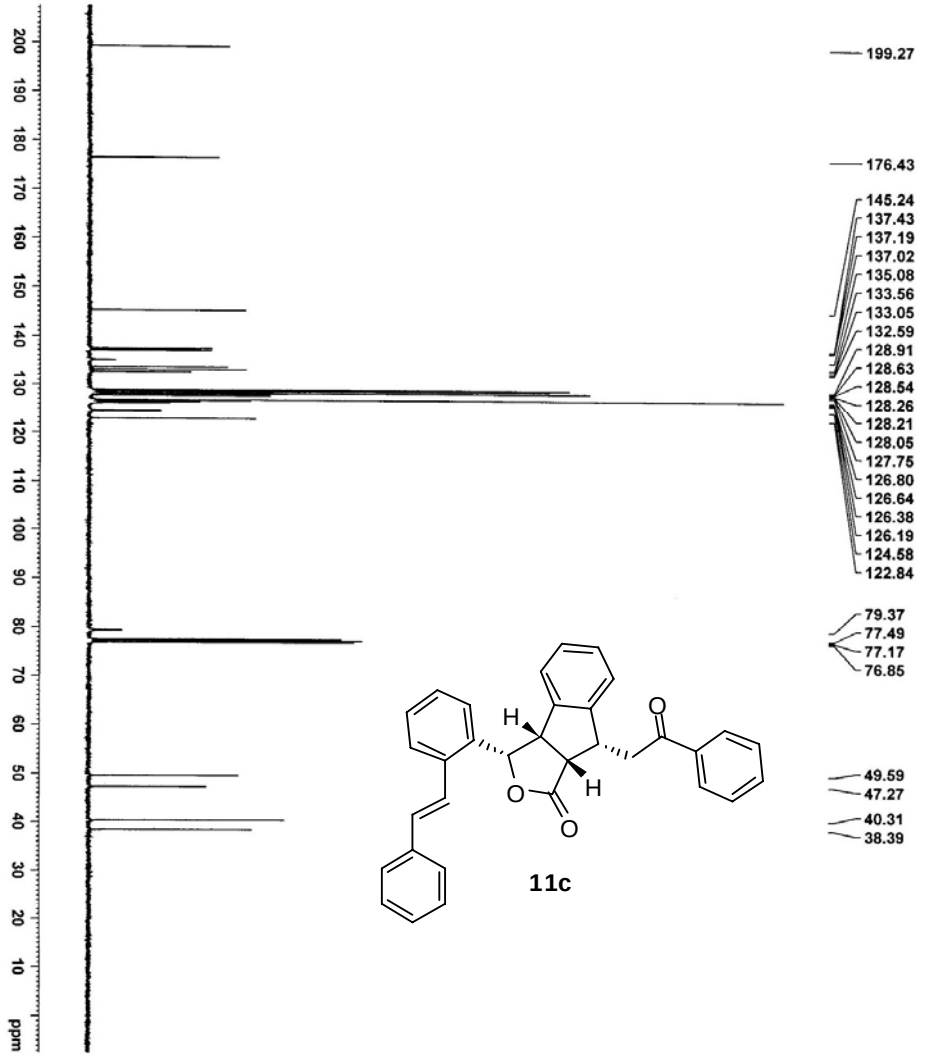
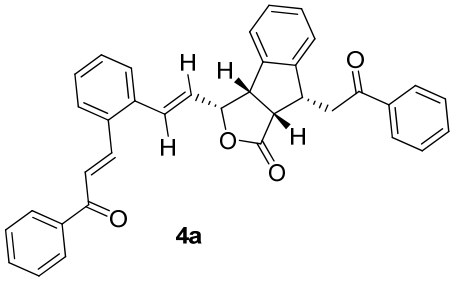
7.4848
7.4666
7.4187
7.4083
7.3896
7.3705
7.3215
7.3033
7.2399
7.2197
7.2010
7.1829
7.1563
7.1464
7.1380
7.1191
7.1135
7.0954
6.8320
6.8143
6.7957
6.1924
6.1768
5.7270
5.7076
4.4007
4.3836
4.3668
4.1185
4.0515
4.0013
3.9820
3.9620
3.5292
3.5180
3.4844
-0.0018
NAME W2Y-7-110
EXPNO 1
PROCNO 1
Date_ 20150605
Time_ 10.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 128
DW 60.800 usec
DE 6.50 usec
TE 297.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.80 usec
PL1 -1.00 dB
PL1W 13.18669796 W
SFO1 400.1724712 MHz
SI 32768
SF 400.1700113 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
H
H
O
O
O
11c
2.02
1.01
5.15
4.01
1.01
1.06
4.01
1.02
1.00
1.00
1.01
1.04
2.02
1.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

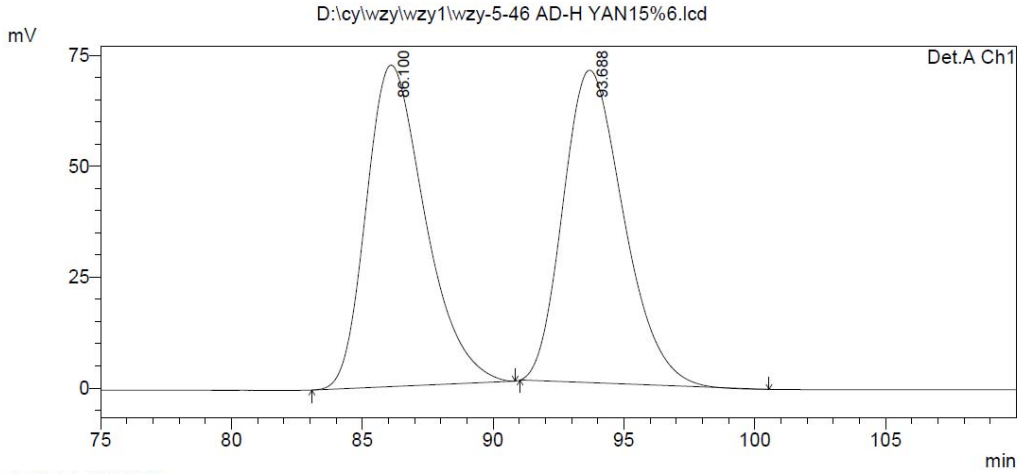



```
NAME                 WZY-7-110-c13
EXPNO                           1
PROCNO                          1
Date_                    20150605
Time_                       12.00
INSTRUM                      spect
PROBHD     5 mm PABBO BB-
PULPROG                  zgpg30
TD                            65536
SOLVENT                     CDCl3
NS                              200
DS                                4
SWH                       24038.461 Hz
FIDRES                        0.366798 Hz
AQ                        1.3631988 sec
RG                              203
DW                           20.800 usec
DE                            6.50 usec
TE                           297.4 K
D1                        2.00000000 sec
D11                       0.03000000 sec
TD0                               1

======== CHANNEL f1 ========
NUC1                            13C
P1                             8.50 usec
PL1                           -2.00 dB
PL1W                    57.32743073 W
SFO1                   100.6328888 MHz

======== CHANNEL f2 ========
CPDPRG2                     waltz16
NUC2                             1H
PCPD2                        80.00 usec
PL2                           -1.00 dB
PL12                          14.26 dB
PL13                          14.46 dB
PL2W                    13.18669796 W
PL12W                    0.39276794 W
PL13W                    0.37509048 W
SFO2                   400.1716007 MHz
SI                            32768
SF                     100.6228270 MHz
WDW                              EM
SSB                               0
LB                             1.00 Hz
GB                                0
PC                             1.40
```



4a

HPLC data of compound **4a**: AD-H column, 85:15 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, >99% ee.

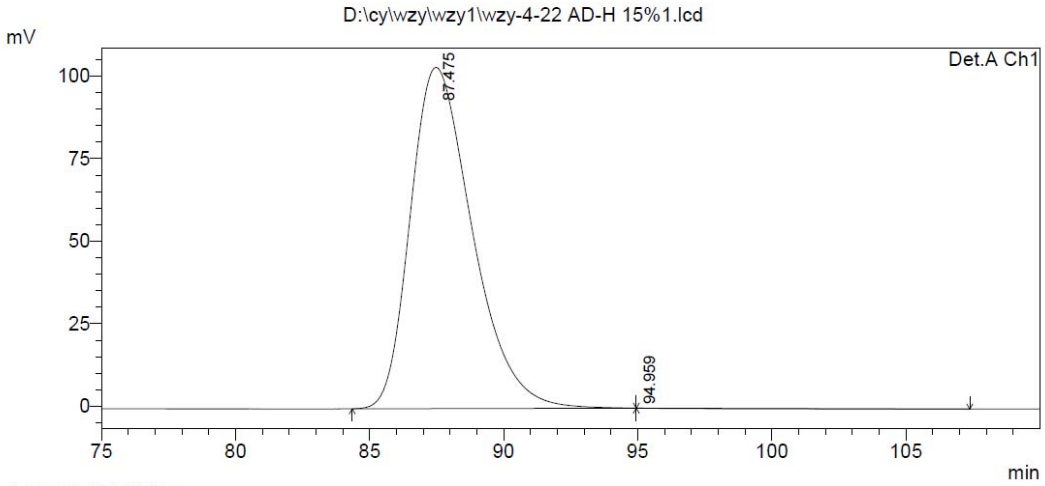


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	86.100	11322285	72436	49.935	50.708
2	93.688	11351551	70415	50.065	49.292
Total		22673836	142851	100.000	100.000

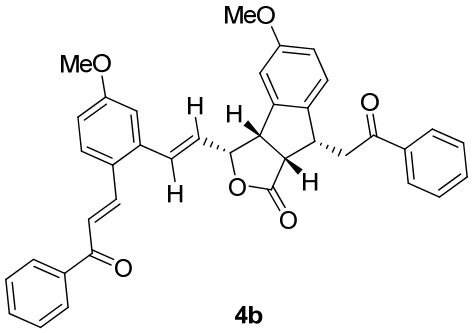


1 Det.A Ch1/254nm

PeakTable

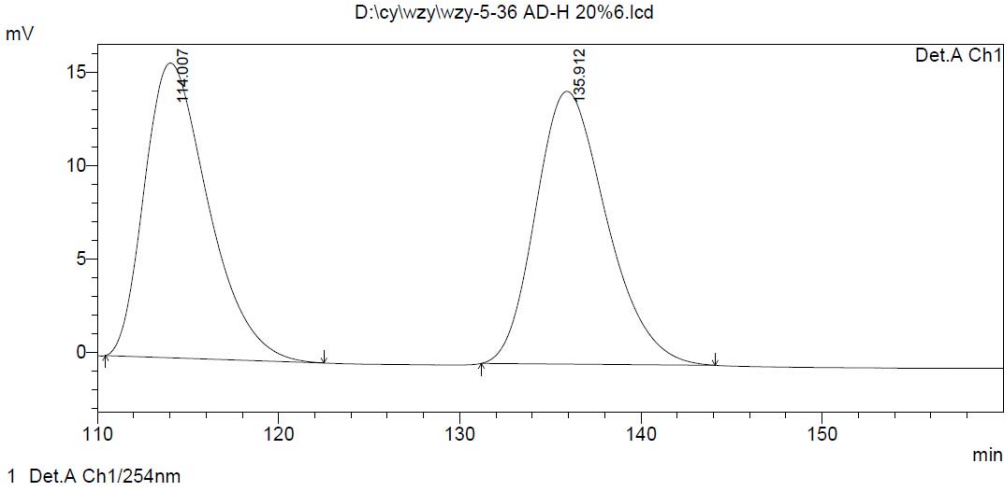
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	87.475	16608426	103274	100.281	100.000
2	94.959	-46463	0	-0.281	0.000
Total		16561963	103274	100.000	100.000



4b

HPLC data of compound **4b**: AD-H column, 80:20 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, >99% ee.

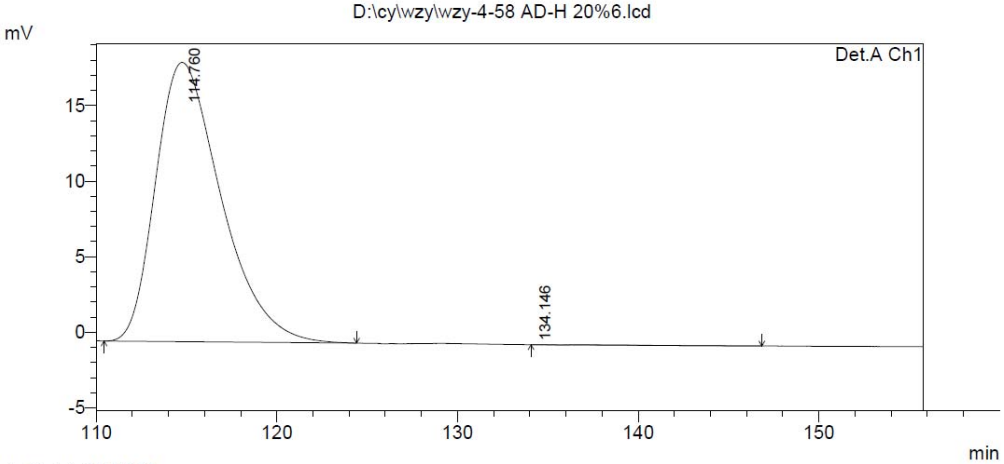


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	114.007	3868849	15789	49.274	51.937
2	135.912	3982852	14611	50.726	48.063
Total		7851702	30400	100.000	100.000

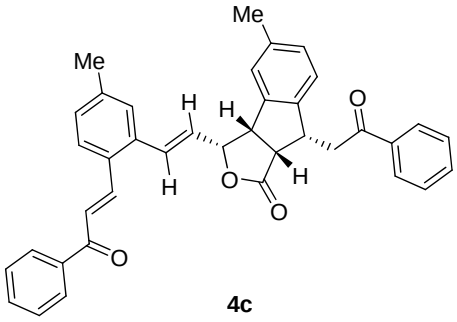


1 Det.A Ch1/254nm

PeakTable

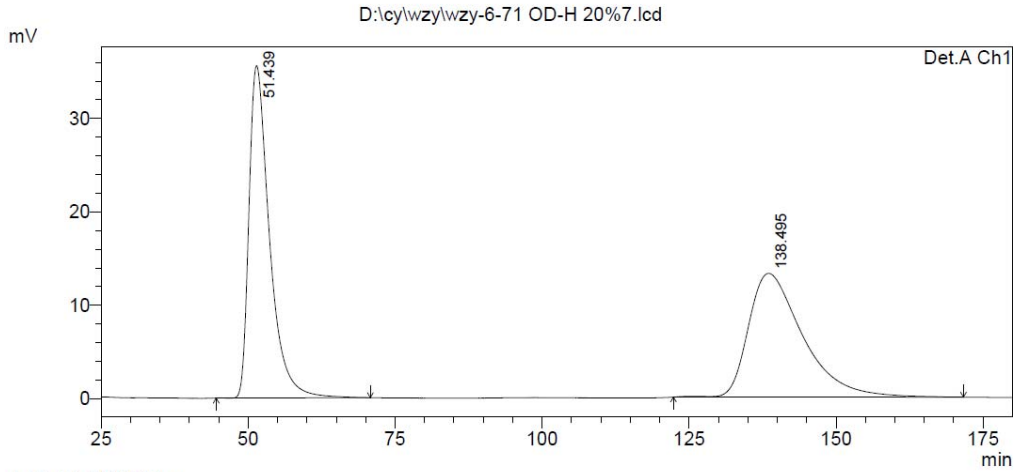
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	114.760	4652802	18477	99.904	99.991
2	134.146	4466	2	0.096	0.009
Total		4657268	18479	100.000	100.000



4c

HPLC data of compound **4c**: OD-H column, 80:20 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, 99% ee.

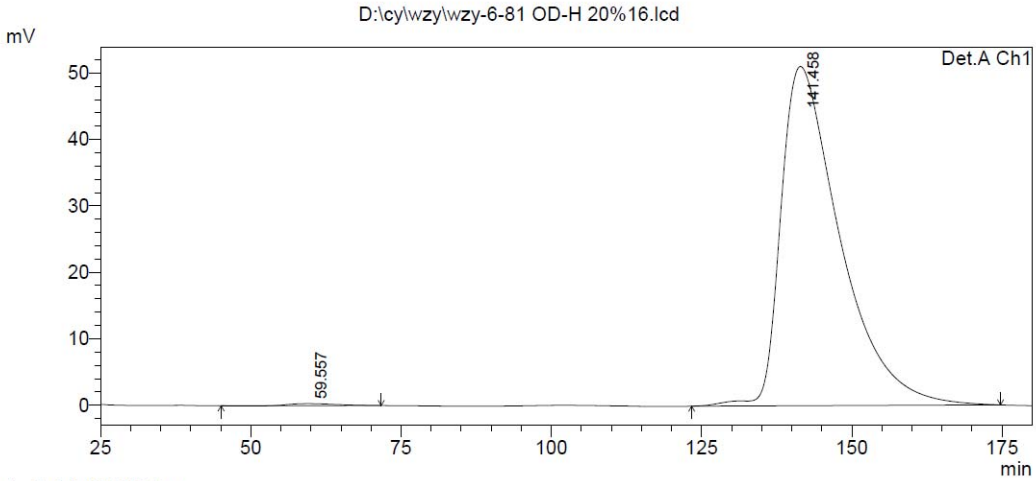


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	51.439	8634660	35610	50.348	72.879
2	138.495	8515371	13252	49.652	27.121
Total		17150032	48861	100.000	100.000

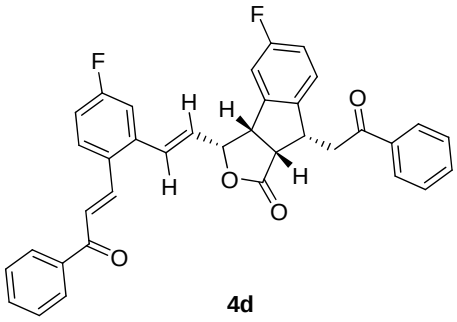


1 Det.A Ch1/254nm

PeakTable

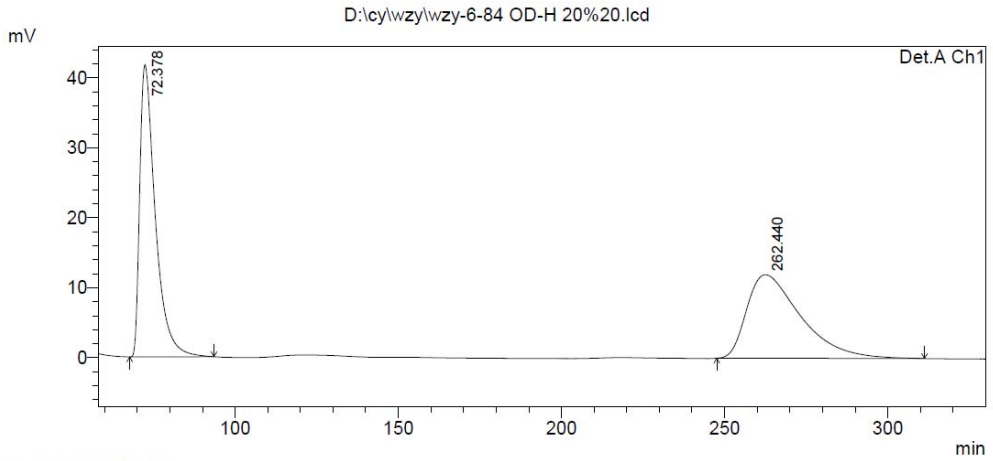
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	59.557	161846	318	0.461	0.619
2	141.458	34939361	51059	99.539	99.381
Total		35101207	51377	100.000	100.000



4d

HPLC data of compound **4d**: OD-H column, 80:20 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, >99% ee.

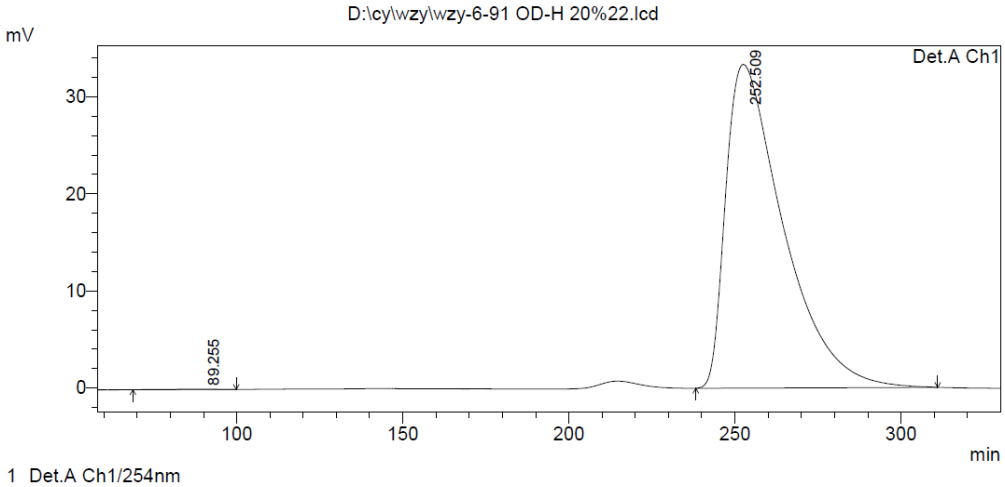


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	72.378	13835974	41778	50.182	77.746
2	262.440	13735603	11959	49.818	22.254
Total		27571577	53737	100.000	100.000

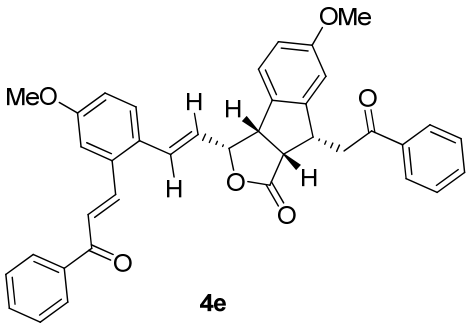


1 Det.A Ch1/254nm

PeakTable

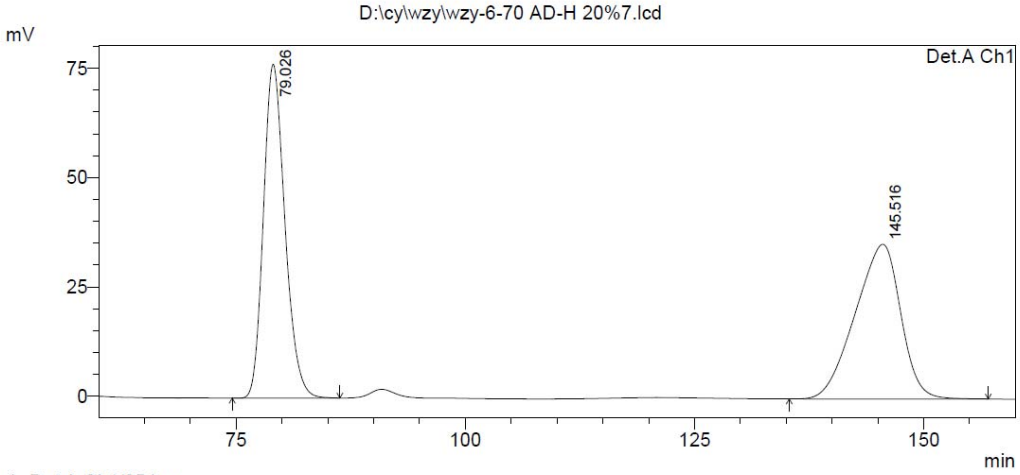
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	89.255	21258	27	0.053	0.081
2	252.509	40213275	33364	99.947	99.919
Total		40234534	33392	100.000	100.000



4e

HPLC data of compound **4e**: AD-H column, 80:20 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, 99% ee.

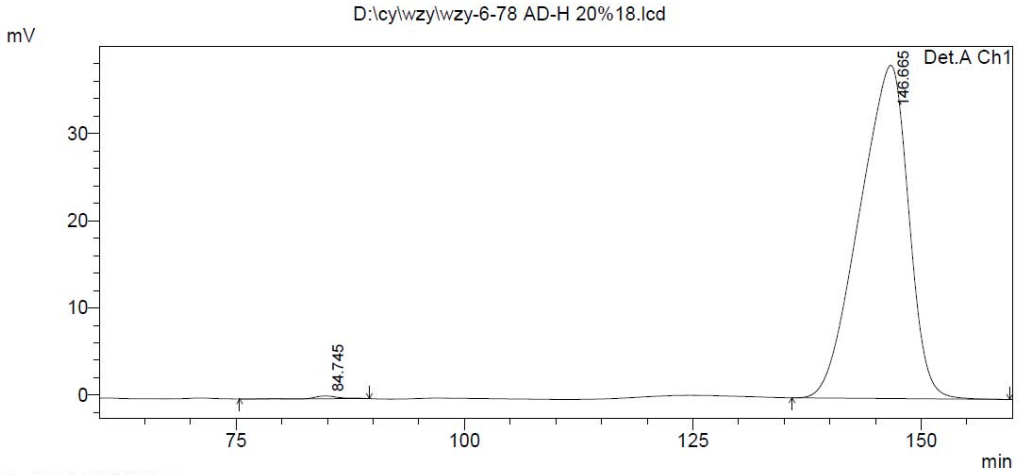


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	79.026	12451190	76332	50.419	68.331
2	145.516	12244318	35377	49.581	31.669
Total		24695508	111709	100.000	100.000

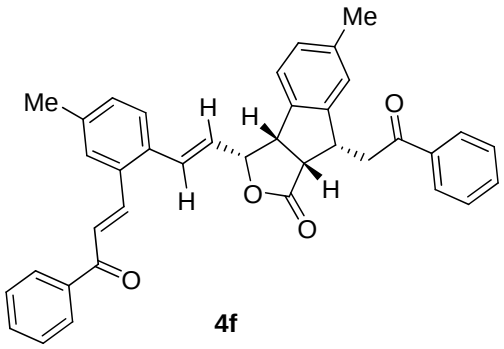


1 Det.A Ch1/254nm

PeakTable

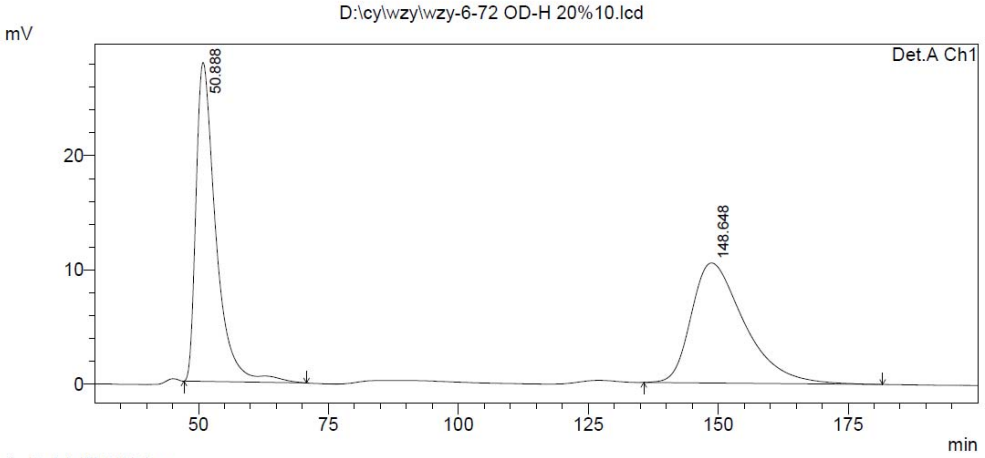
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	84.745	48525	318	0.339	0.824
2	146.665	14260716	38211	99.661	99.176
Total		14309241	38528	100.000	100.000



4f

HPLC data of compound **4f**: OD-H column, 80:20 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, 99% ee.

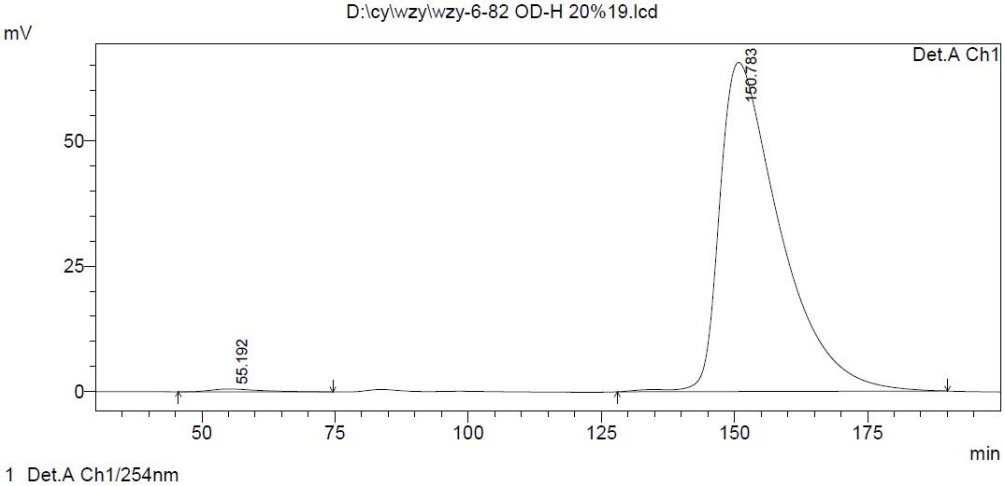


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	50.888	7420781	27915	49.841	72.658
2	148.648	7468260	10505	50.159	27.342
Total		14889041	38420	100.000	100.000

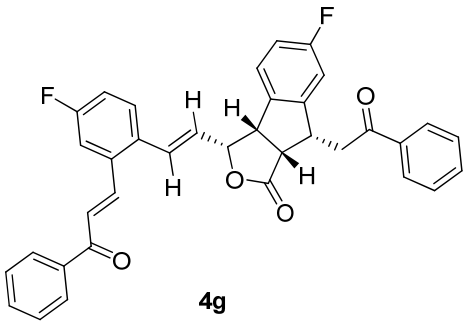


1 Det.A Ch1/254nm

PeakTable

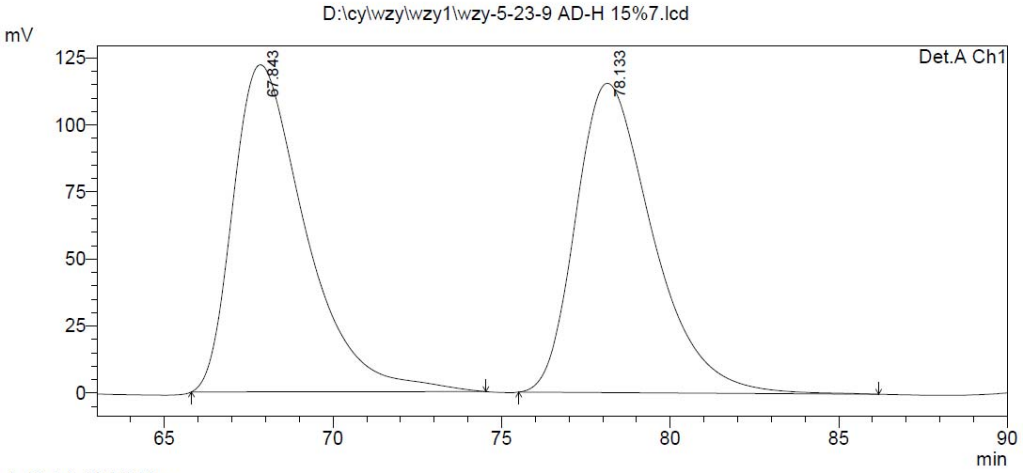
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	55.192	355795	575	0.683	0.868
2	150.783	51749496	65651	99.317	99.132
Total		52105291	66226	100.000	100.000



4g

HPLC data of compound **4g**: AD-H column, 85:15 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, 95% ee.

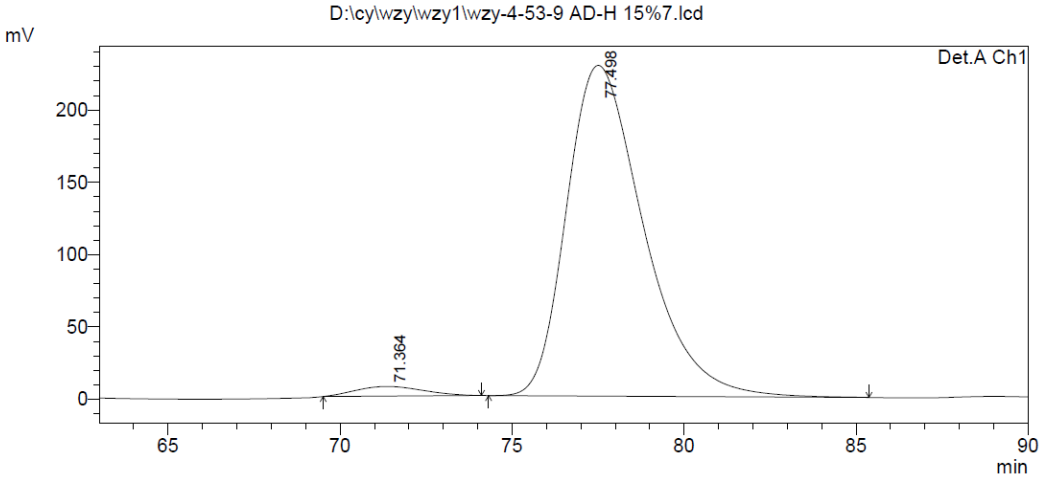


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	67.843	18300671	121963	49.956	51.394
2	78.133	18332966	115348	50.044	48.606
Total		36633637	237311	100.000	100.000

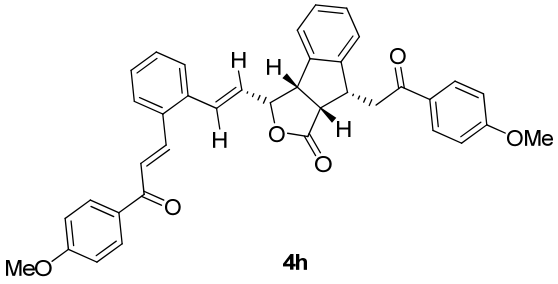


1 Det.A Ch1/254nm

PeakTable

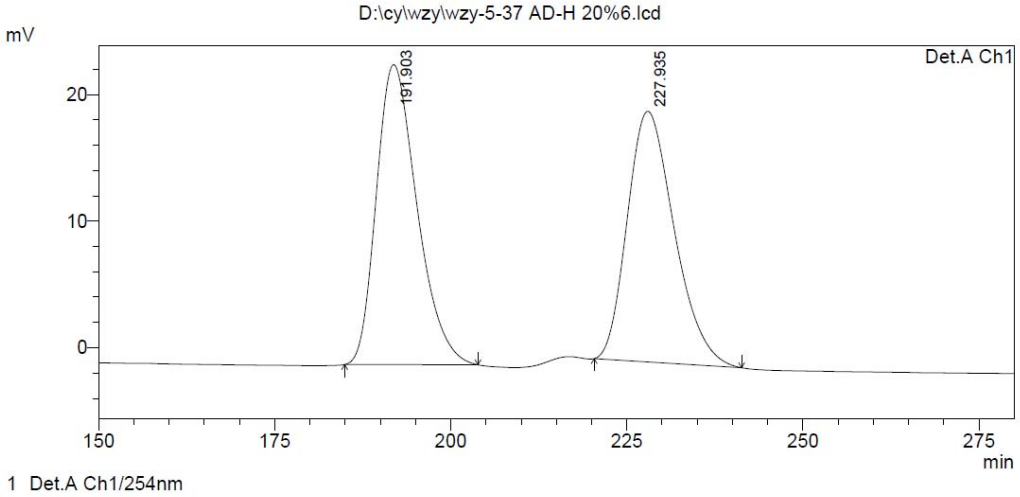
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	71.364	908331	6672	2.488	2.836
2	77.498	35605489	228629	97.512	97.164
Total		36513820	235301	100.000	100.000



4h

HPLC data of compound **4h**: AD-H column, 80:20 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, >99% ee.

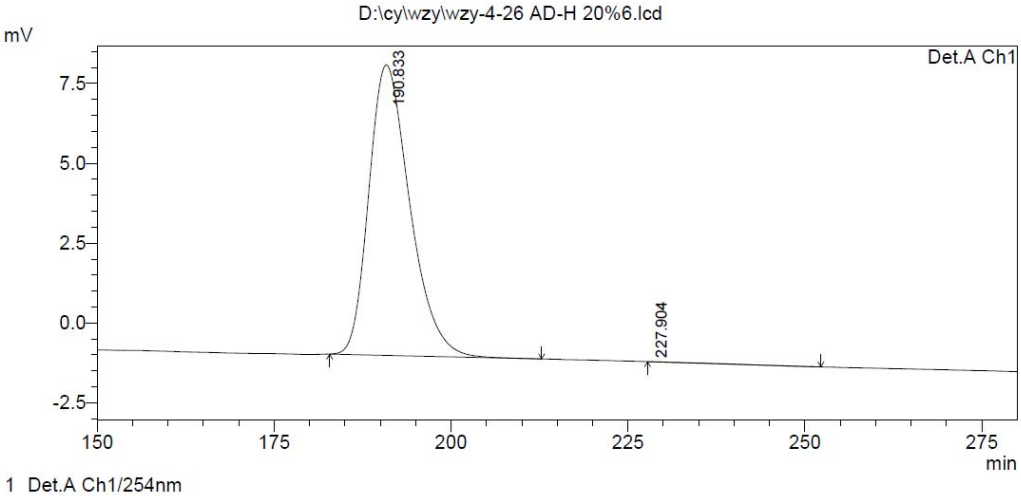


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	191.903	9518024	23686	50.898	54.481
2	227.935	9182244	19790	49.102	45.519
Total		18700267	43476	100.000	100.000

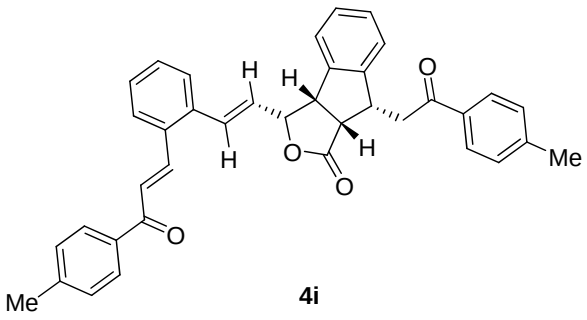


1 Det.A Ch1/254nm

PeakTable

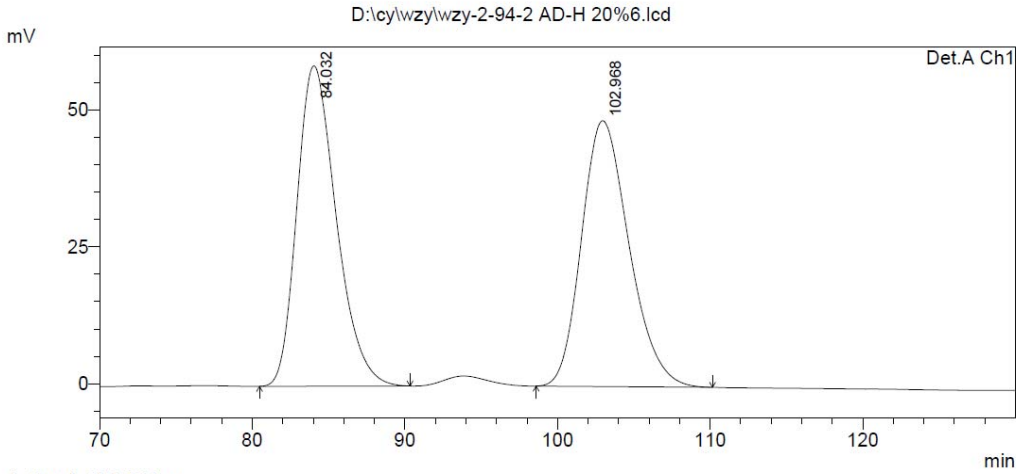
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	190.833	3666784	9090	99.923	99.985
2	227.904	2825	1	0.077	0.015
Total		3669609	9091	100.000	100.000



4i

HPLC data of compound **4i**: AD-H column, 80:20 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, >99% ee.

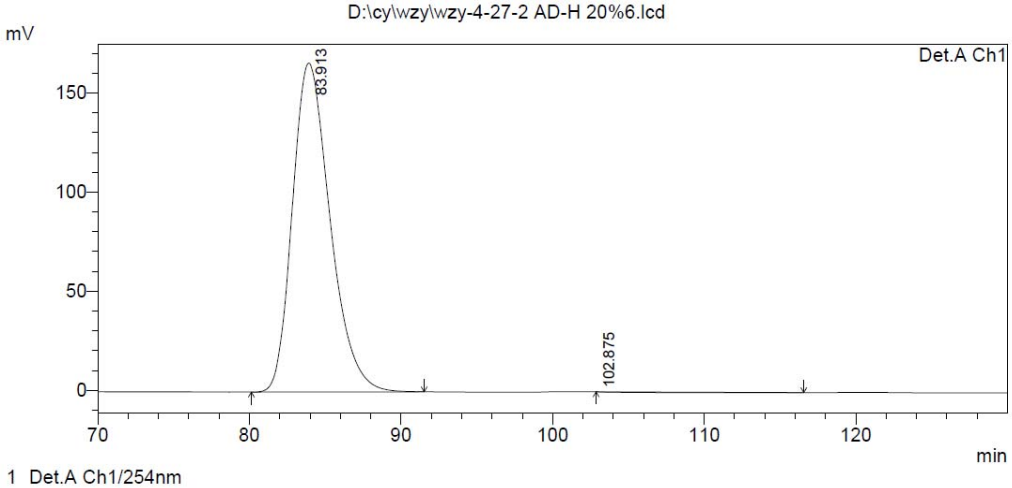


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	84.032	10508072	58524	49.979	54.653
2	102.968	10516930	48558	50.021	45.347
Total		21025002	107082	100.000	100.000

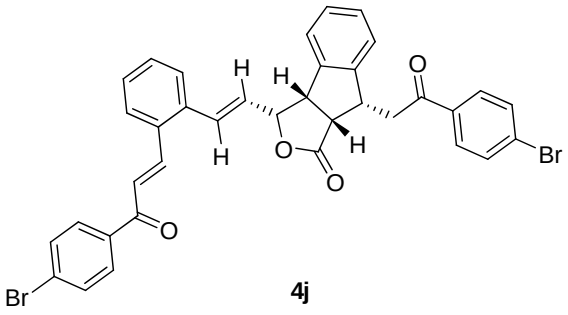


1 Det.A Ch1/254nm

PeakTable

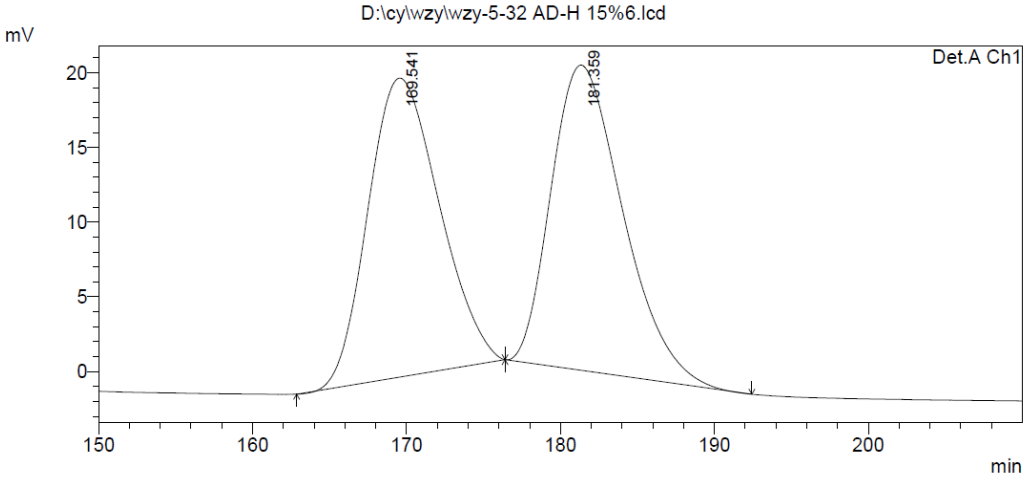
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	83.913	28685256	165954	100.415	100.001
2	102.875	-118619	-1	-0.415	-0.001
Total		28566637	165953	100.000	100.000



4j

HPLC data of compound **4j**: AD-H column, 85:15 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, >99% ee.

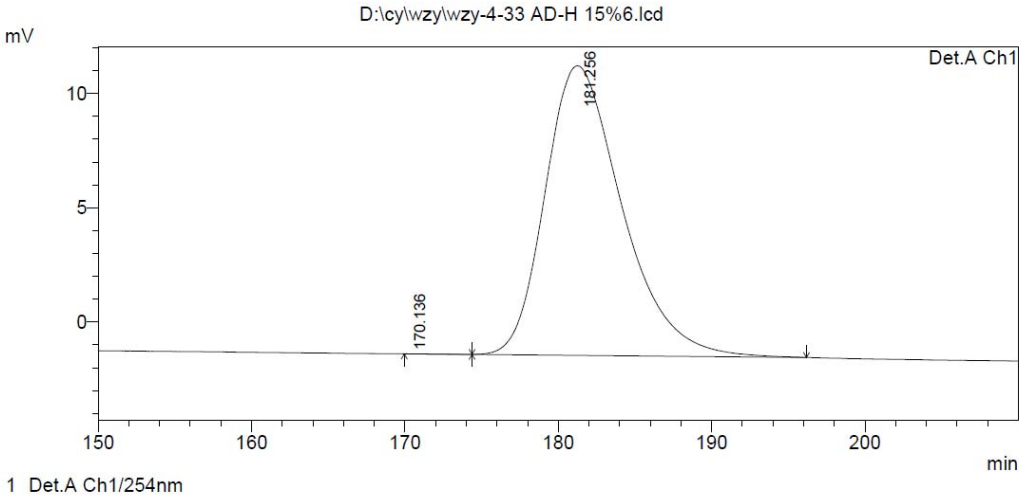


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	169.541	6423909	20023	49.200	49.487
2	181.359	6632712	20439	50.800	50.513
Total		13056621	40462	100.000	100.000

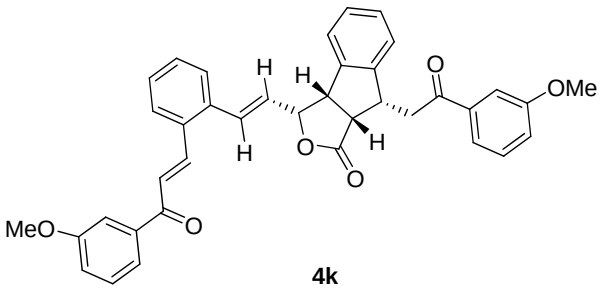


1 Det.A Ch1/254nm

PeakTable

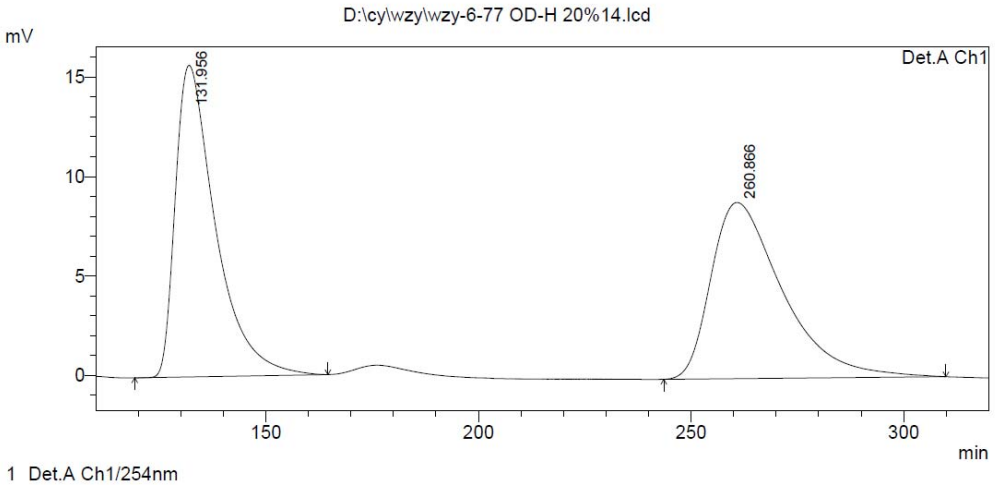
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	170.136	-627	3	-0.014	0.022
2	181.256	4423198	12679	100.014	99.978
Total		4422571	12682	100.000	100.000



4k

HPLC data of compound **4k**: OD-H column, 80:20 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, >99% ee.

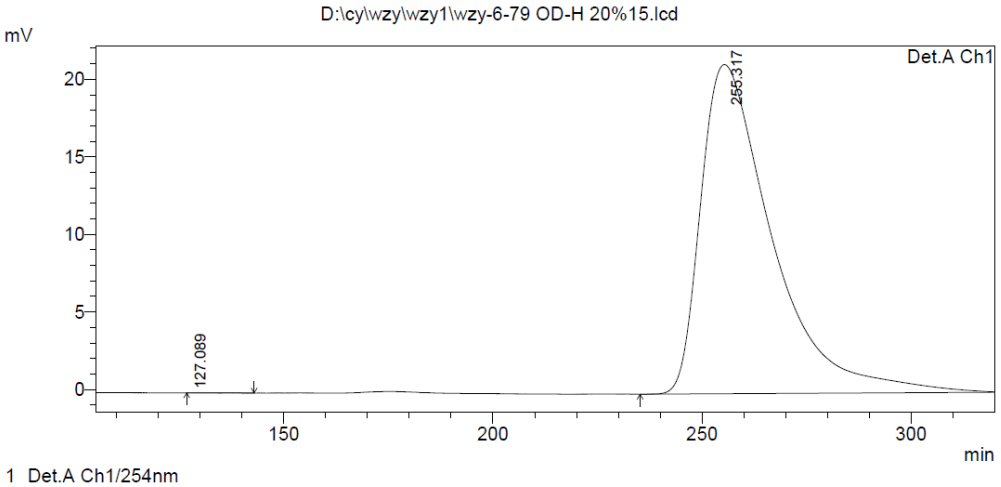


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	131.956	10280531	15672	49.802	63.890
2	260.866	10362168	8858	50.198	36.110
Total		20642700	24530	100.000	100.000

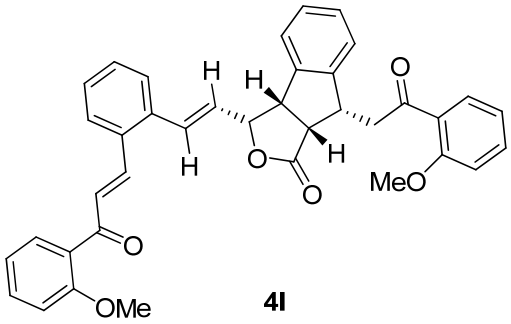


1 Det.A Ch1/254nm

PeakTable

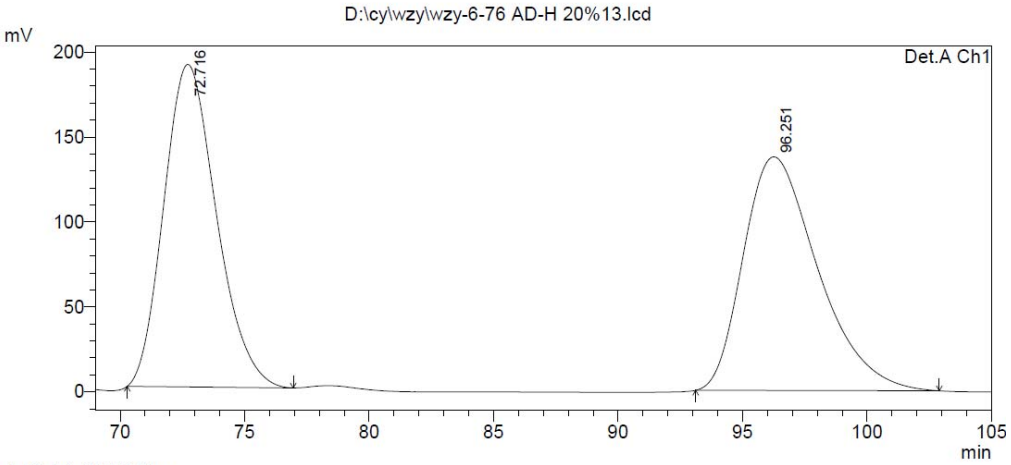
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	127.089	-2170	-0	-0.009	-0.000
2	255.317	25161528	21218	100.009	100.000
Total		25159357	21218	100.000	100.000



4l

HPLC data of compound **4l**: AD-H column, 80:20 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, >99% ee.

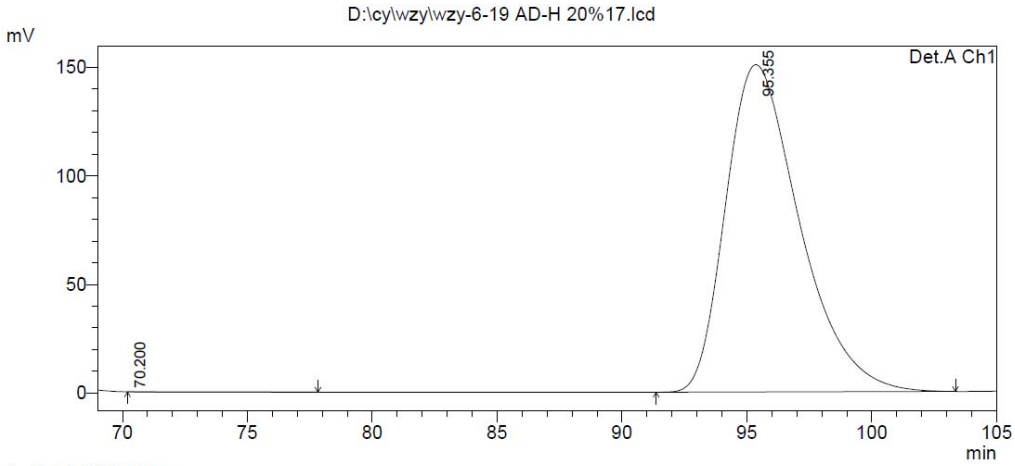


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	72.716	27921328	189839	49.395	57.988
2	96.251	28605063	137540	50.605	42.012
Total		56526390	327380	100.000	100.000

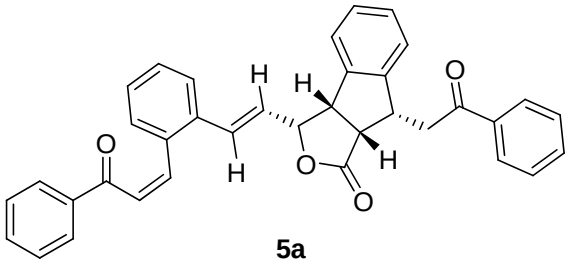


1 Det.A Ch1/254nm

PeakTable

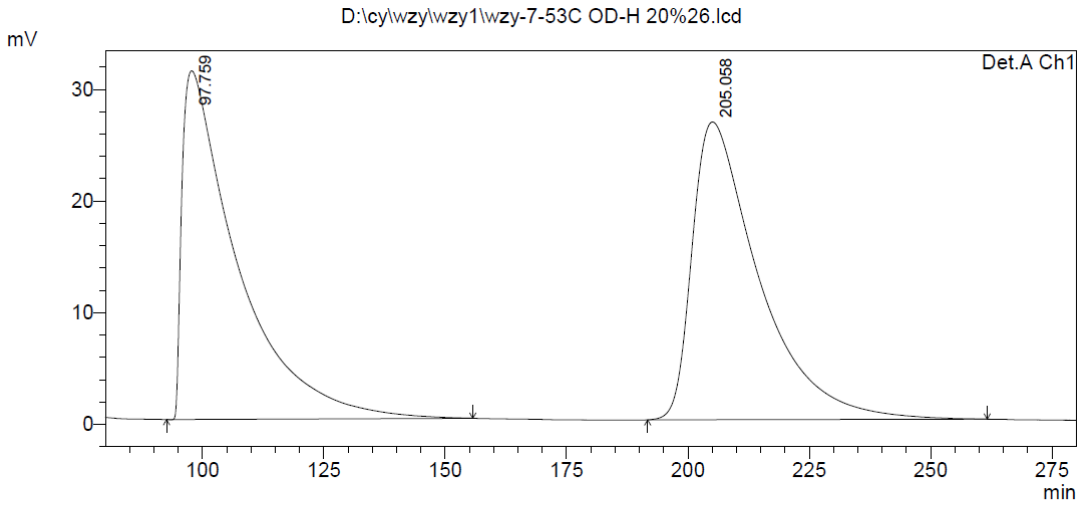
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	70.200	-22560	0	-0.073	0.000
2	95.355	31012019	150835	100.073	100.000
Total		30989459	150835	100.000	100.000



5a

HPLC data of compound **5a**: OD-H column, 80:20 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, 99% ee.

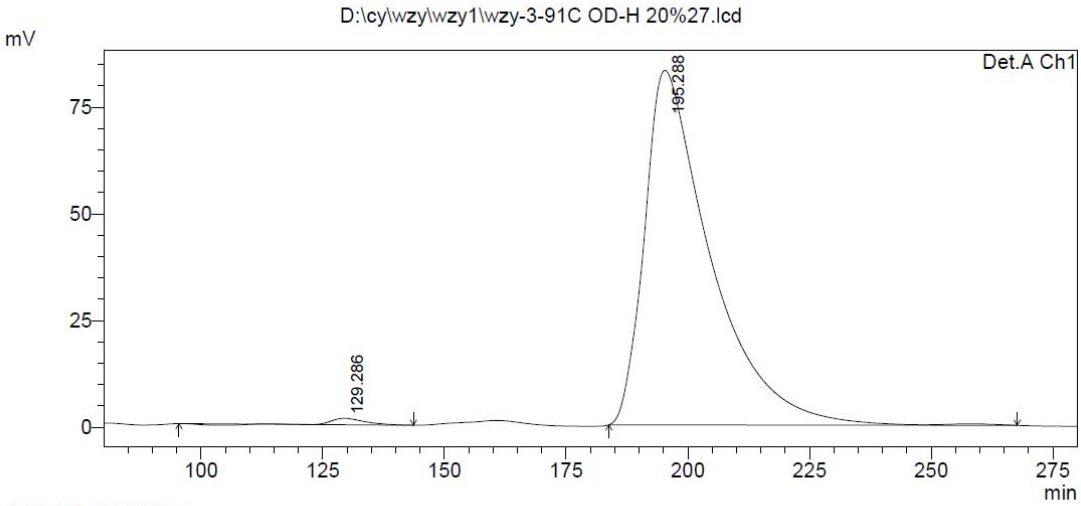


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	97.759	24823944	31235	49.246	53.939
2	205.058	25584477	26673	50.754	46.061
Total		50408421	57908	100.000	100.000

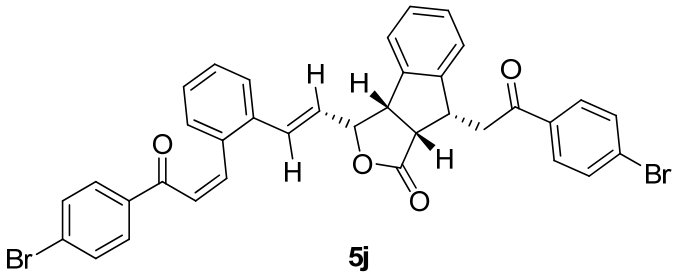


1 Det.A Ch1/254nm

PeakTable

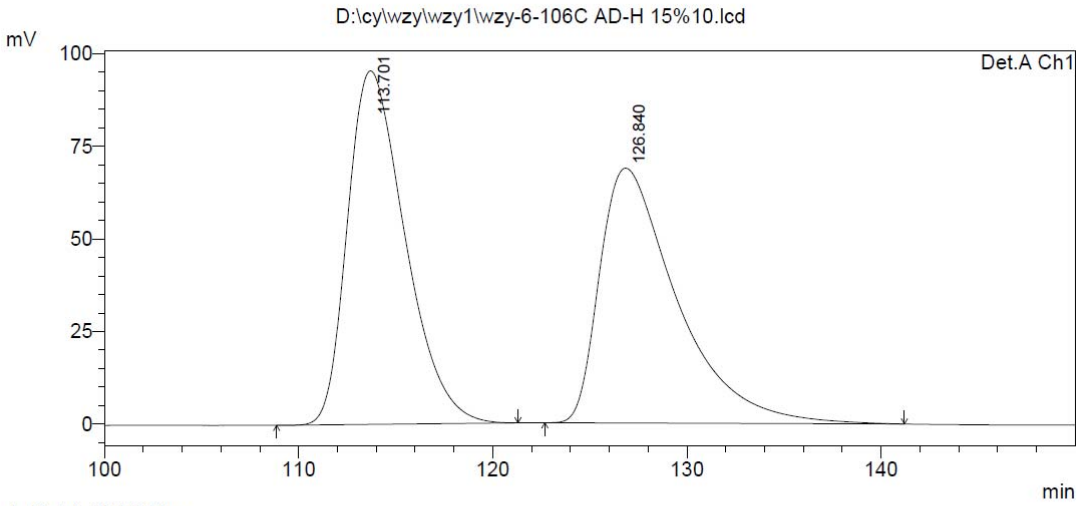
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	129.286	571358	1516	0.722	1.793
2	195.288	78522719	83038	99.278	98.207
Total		79094077	84554	100.000	100.000



5j

HPLC data of compound **5j**: AD-H column, 85:15 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, >99% ee.

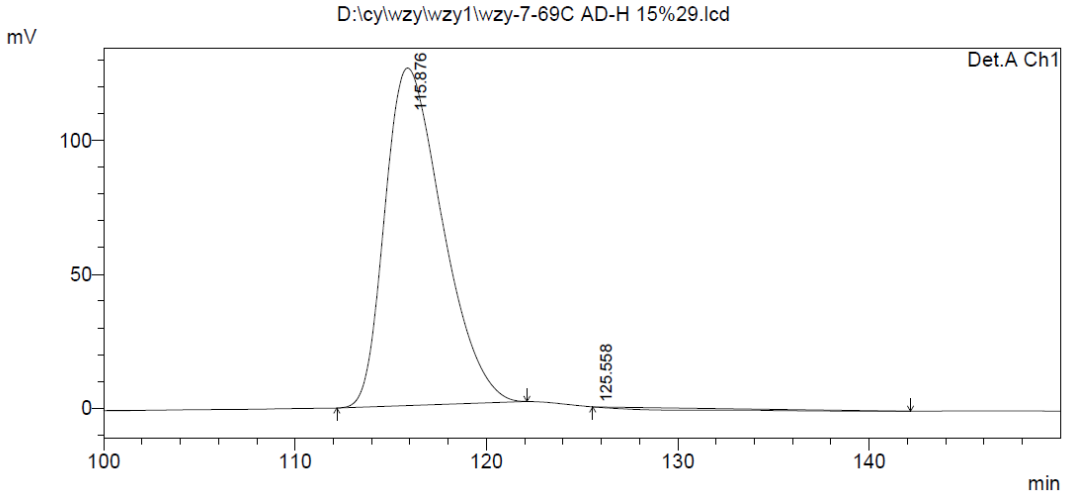


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	113.701	19650001	95412	50.754	58.105
2	126.840	19066377	68794	49.246	41.895
Total		38716378	164206	100.000	100.000

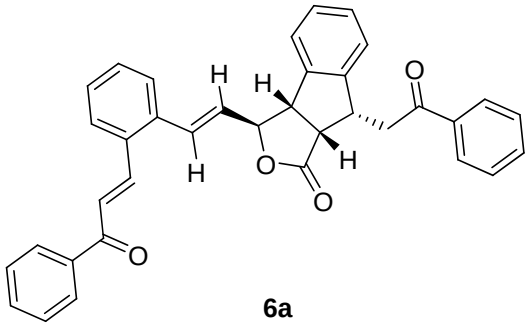


1 Det.A Ch1/254nm

PeakTable

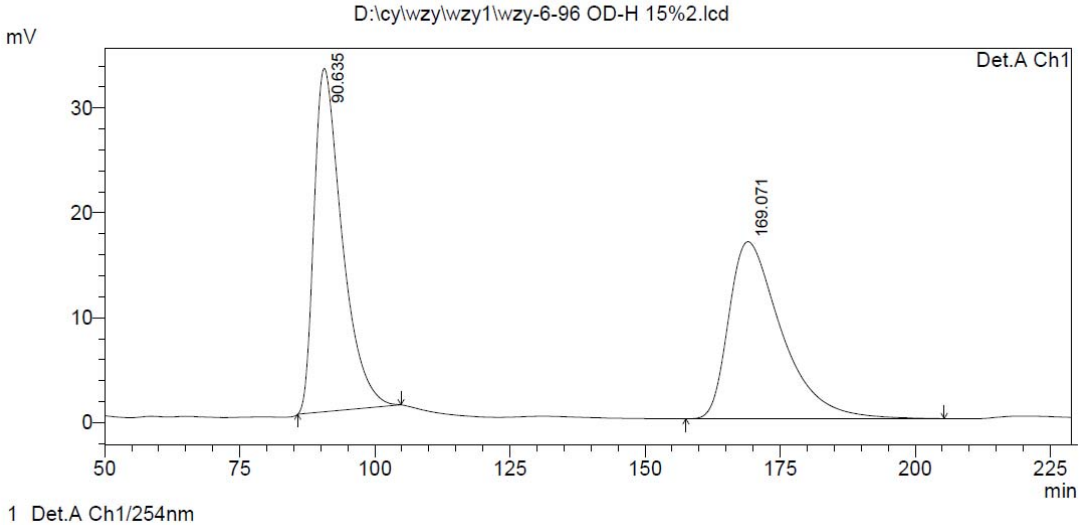
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	115.876	26378126	126108	101.792	100.004
2	125.558	-464469	-5	-1.792	-0.004
Total		25913658	126103	100.000	100.000



6a

HPLC data of compound **6a**: OD-H column, 85:15 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, >99% ee.

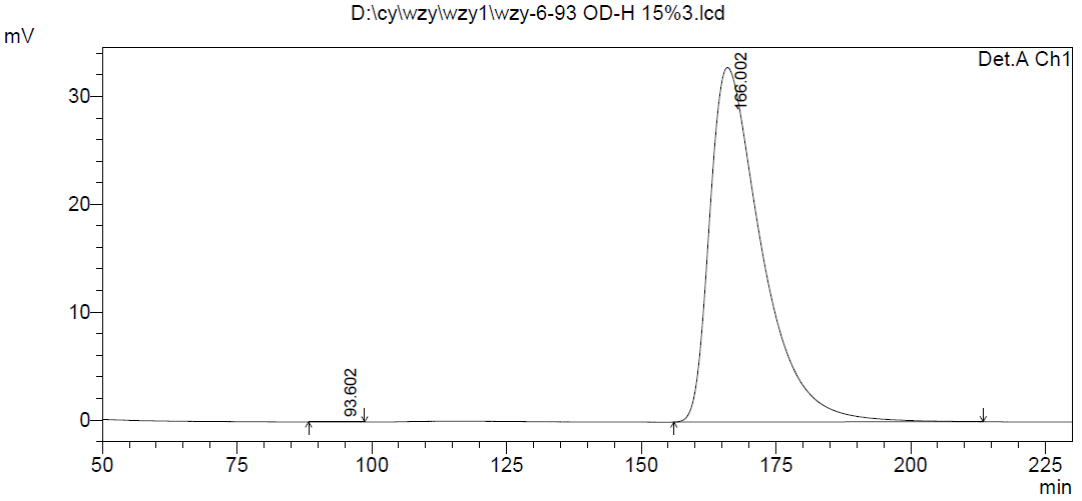


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	90.635	11829538	32733	50.758	65.965
2	169.071	11476202	16888	49.242	34.035
Total		23305740	49621	100.000	100.000

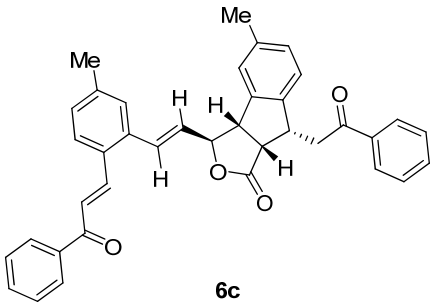


1 Det.A Ch1/254nm

PeakTable

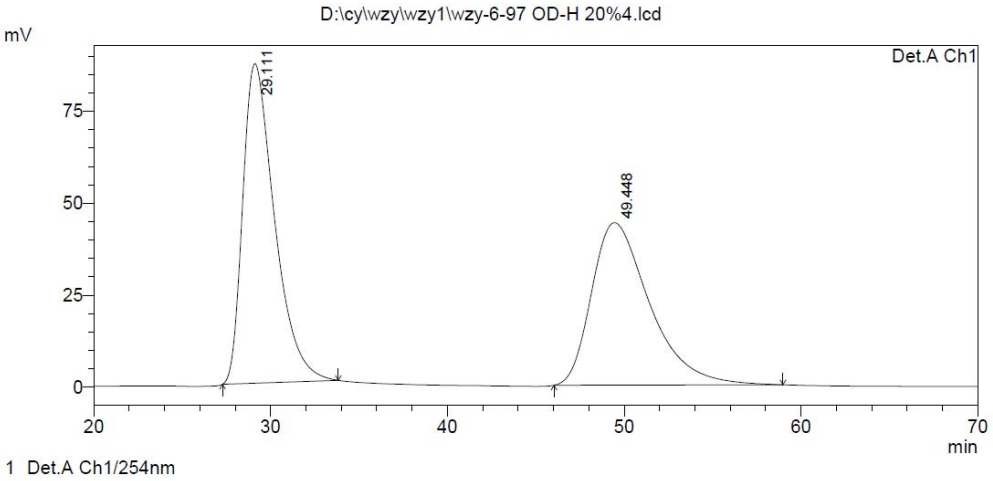
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	93.602	888	5	0.004	0.014
2	166.002	21984428	32857	99.996	99.986
Total		21985316	32862	100.000	100.000



6c

HPLC data of compound **6c**: OD-H column, 80:20 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, >99% ee.

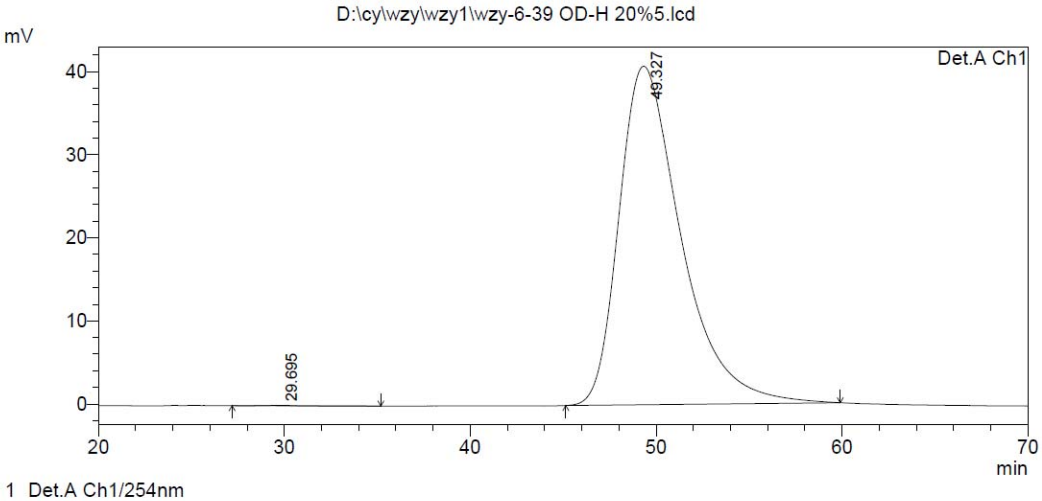


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.111	10862567	86758	51.863	66.280
2	49.448	10082361	44139	48.137	33.720
Total		20944928	130896	100.000	100.000

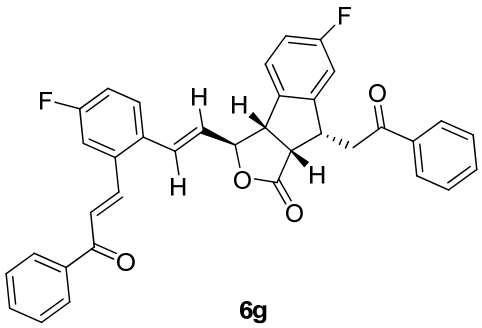


1 Det.A Ch1/254nm

PeakTable

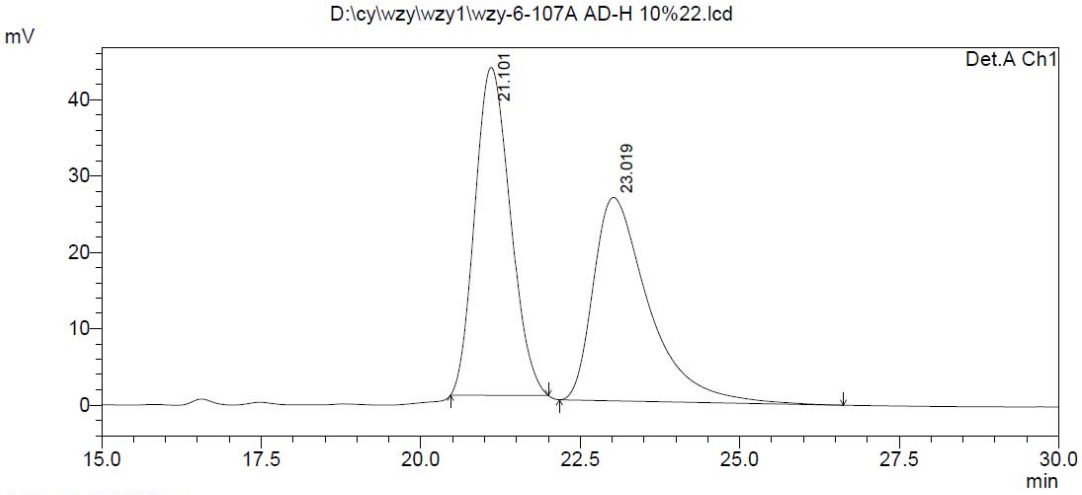
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.695	1668	44	0.018	0.108
2	49.327	9438510	40727	99.982	99.892
Total		9440178	40771	100.000	100.000



6g

HPLC data of compound **6g**: AD-H column, 90:10 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, >99% ee.

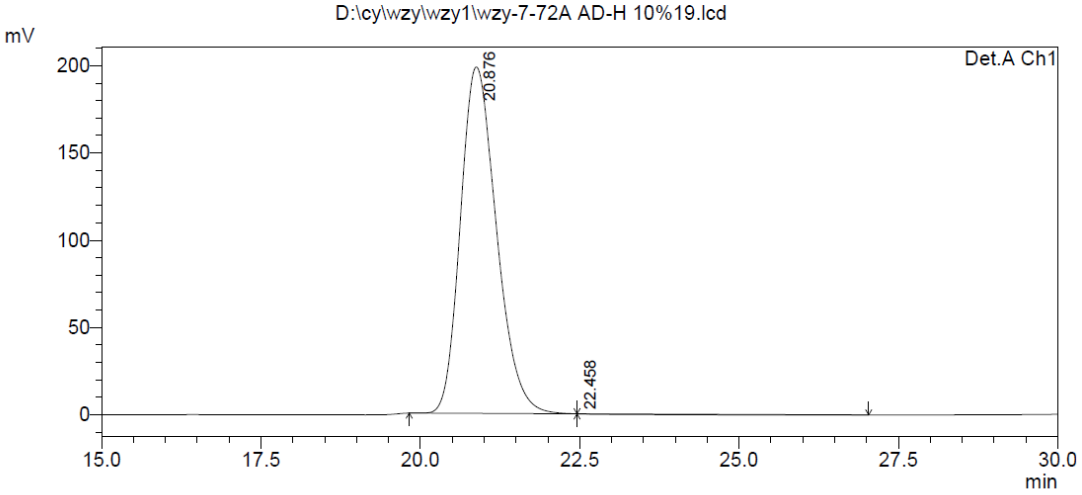


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.101	1658559	42929	50.761	61.722
2	23.019	1608844	26623	49.239	38.278
Total		3267403	69552	100.000	100.000

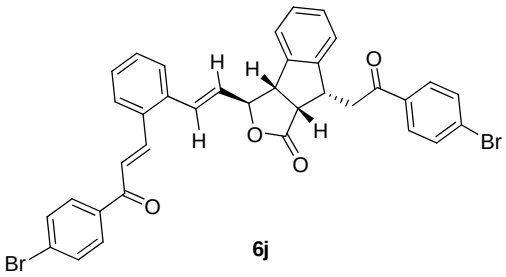


1 Det.A Ch1/254nm

PeakTable

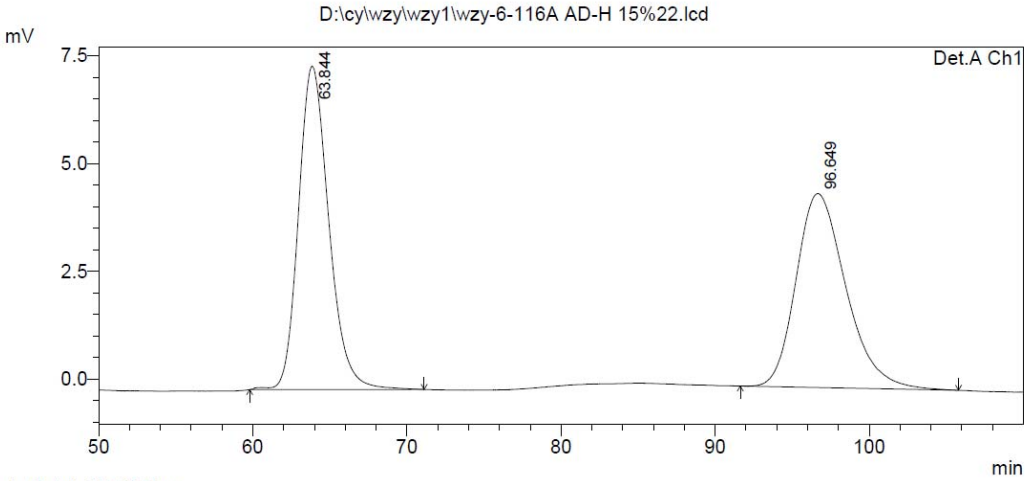
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.876	7799719	198483	100.719	100.000
2	22.458	-55650	0	-0.719	0.000
Total		7744069	198483	100.000	100.000



6j

HPLC data of compound **6j**: AD-H column, 85:15 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, >99% ee.

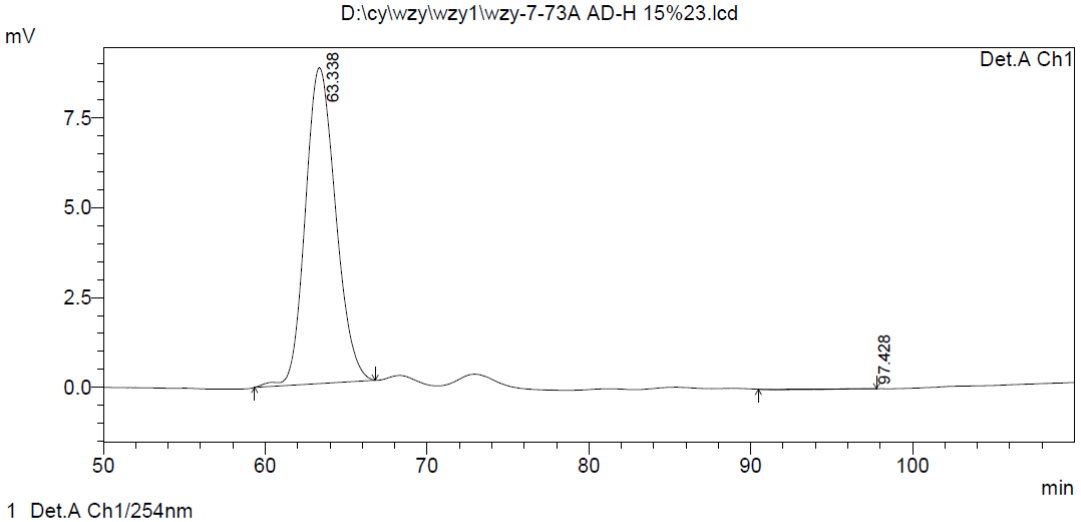


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	63.844	1026971	7496	50.388	62.496
2	96.649	1011167	4498	49.612	37.504
Total		2038138	11995	100.000	100.000

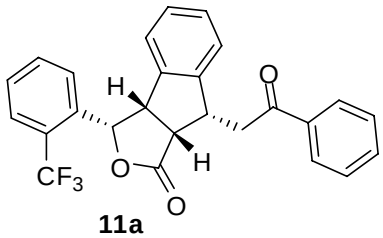


1 Det.A Ch1/254nm

PeakTable

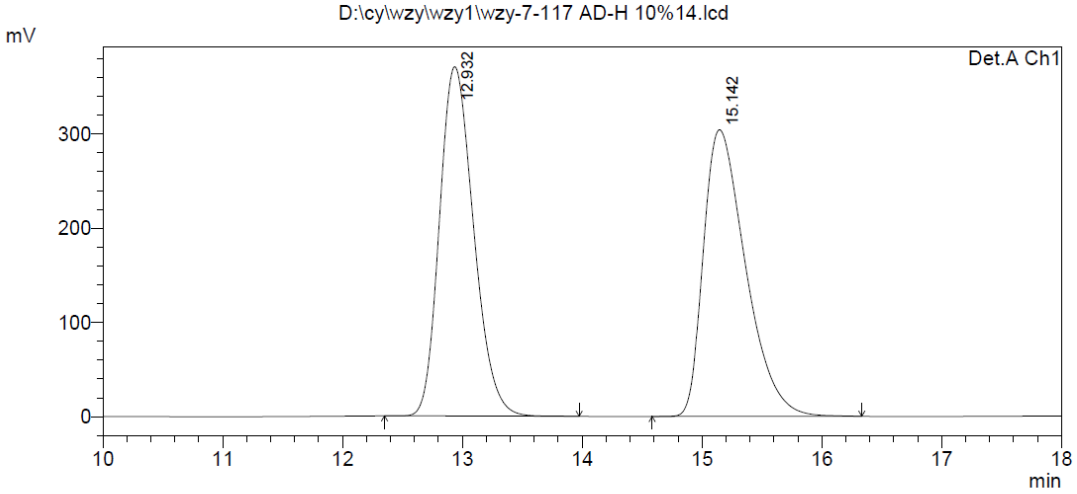
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	63.338	1147053	8795	100.290	99.961
2	97.428	-3322	3	-0.290	0.039
Total		1143731	8799	100.000	100.000



11a

HPLC data of compound **11a**: AD-H column, 90:10 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, 97% ee.

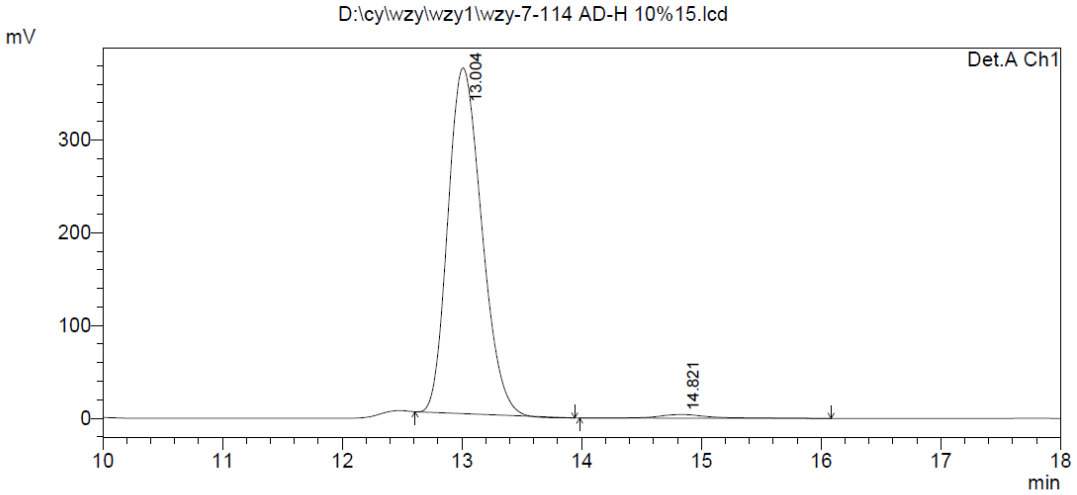


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.932	7354648	370786	49.714	54.931
2	15.142	7439408	304216	50.286	45.069
Total		14794056	675002	100.000	100.000

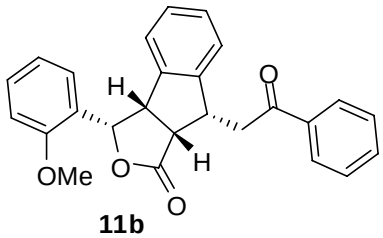


1 Det.A Ch1/254nm

PeakTable

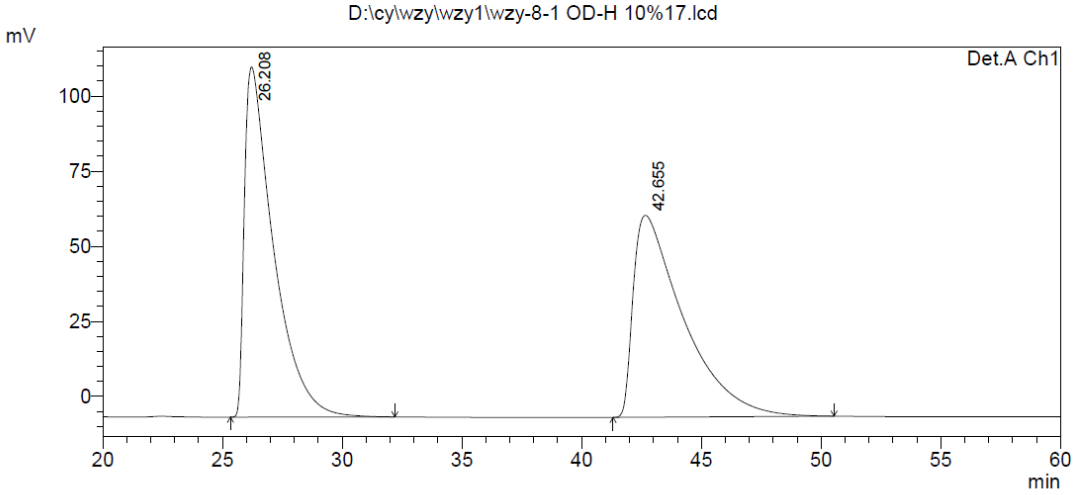
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.004	7304399	372512	98.598	98.958
2	14.821	103829	3921	1.402	1.042
Total		7408228	376433	100.000	100.000



11b

HPLC data of compound **11b**: OD-H column, 90:10 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, >99% ee.

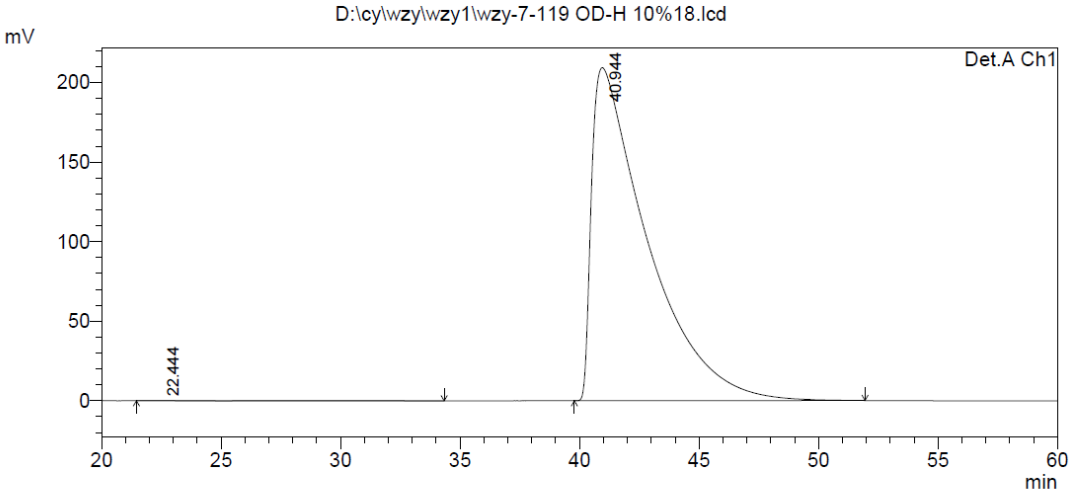


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.208	9835877	116612	50.047	63.433
2	42.655	9817307	67223	49.953	36.567
Total		19653183	183835	100.000	100.000

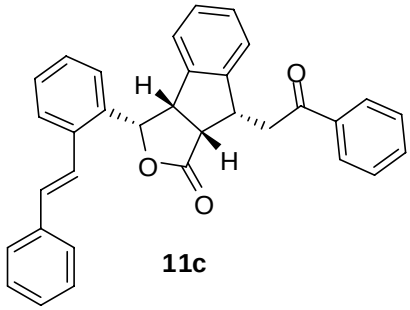


1 Det.A Ch1/254nm

PeakTable

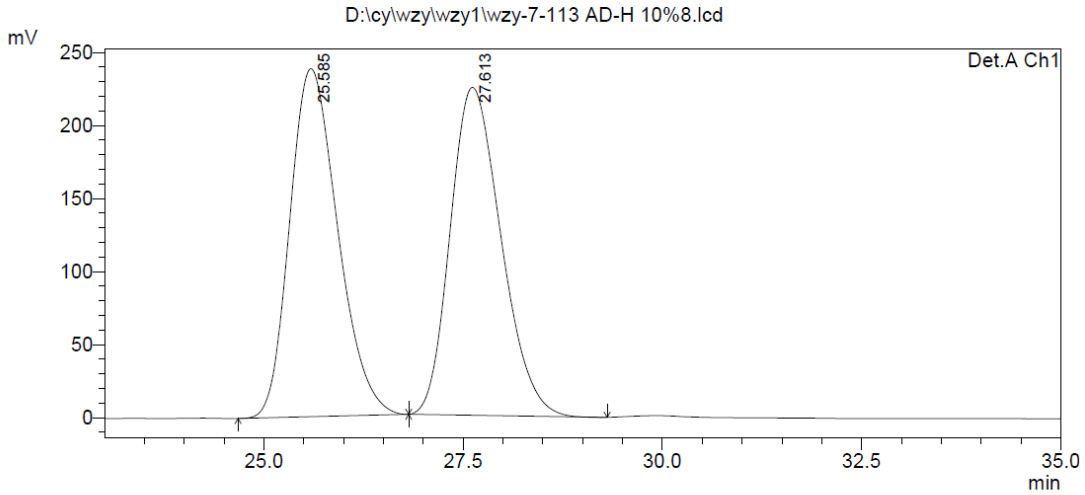
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.444	2661	19	0.008	0.009
2	40.944	33956662	209311	99.992	99.991
Total		33959322	209330	100.000	100.000



11c

HPLC data of compound **11c**: AD-H column, 90:10 hexane:IPA, flow rate 1 mL/min, 254 nm, 25 °C, >99% ee.

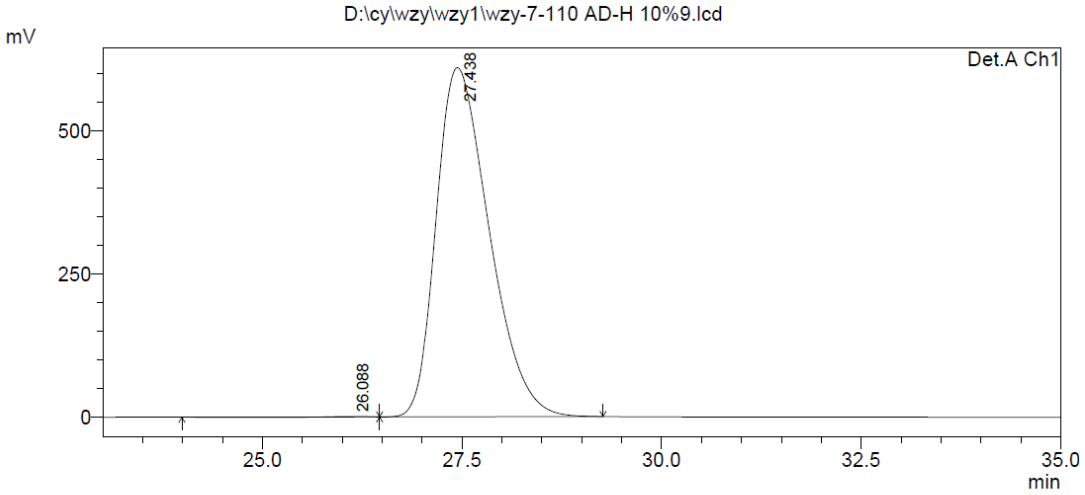


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.585	9958948	238352	50.039	51.486
2	27.613	9943463	224589	49.961	48.514
Total		19902411	462941	100.000	100.000



1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.088	-16759	891	-0.060	0.146
2	27.438	28097969	609560	100.060	99.854
Total		28081211	610451	100.000	100.000