Electronic supplementary information for

Spiro-2,2'-bichroman-Based Bisoxazoline (SPANbox) Ligands for Zn(II)-Catalyzed Enantioselective Hydroxylation of β-Keto Esters and 1,3-Diester

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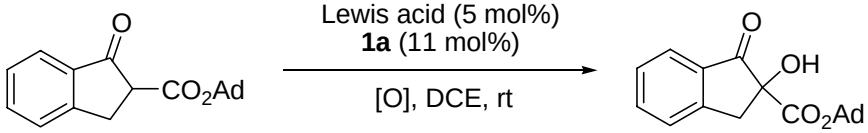
General Method: All reactions and manipulations were performed using standard Schlenk techniques. All solvents were purified and dried using standard procedures. ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury 300 MHz or 400 MHz spectrometers. Chemical shifts (δ values) were reported in ppm (residual chloroform δ = 7.26 ppm or TMS δ = 0 ppm for ^{1}H, residual chloroform δ = 77.0 ppm for ^{13}C). Melting points were measured on a SGW X-4 apparatus and uncorrected. The IR spectra were measured on a NICOLET AVATAR 330 or a BRUKER TENSOR 27 FT-IR spectrometer. MS(EI) and MS(ESI) mass spectra were obtained on AGILENT 5973N and Agilent LC/MSD SL or Shimadzu LCMS-2010EV spectrometers, respectively. HRMS(EI), HRMS(ESI) and HRMS(MALDI) were determined on Waters Micromass GCT, BRUKER DALTONICS APEX III and IonSpect 4.7 TESLA FTMS spectrometers, respectively. Optical rotations were determined using a Perkin Elmer 341 MC polarimeter. HPLC analyses were performed on JASCO 1580 or JASCO 2089 liquid chromatograph. GC analyses were performed on an Agilent 6890N gas chromatograph.

Optimization of Reaction Conditions for the Enantioselective Hydroxylation of **6a** to **7a**

Table S1. Optimization of Lewis acids for the enantioselective hydroxylation of **6a**[a]

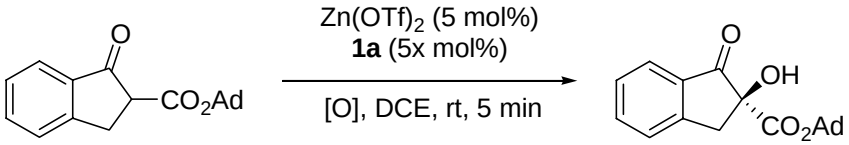


Entry	Lewis acid	Time (min)	Yield[b] (%)	Ee[c] (%)
1	$InCl_3$	5	>99	11(*R*)
2	$InBr_3$	5	>99	30(*R*)
3	$In(OTf)_3$	120	>99	Rac
4	$Sc(OTf)_3$	10	>99	Rac
5	$La(OTf)_3$	5	>99	Rac
6	$Fe(OAc)_2$	180	>99	5(*S*)
7	$FeCl_3 + AgPF_6$	90	>99	Rac
8	$Ni(ClO_4)_2{\cdot}6H_2O$	5	>99	18(*S*)
9	$CuOTf{\cdot}0.5C_6H_6$	5	>99	4(*R*)
10	$CuCl_2 + AgBF_4$	5	>99	18(*R*)
11	$CuCl_2 + AgPF_6$	5	>99	20(*R*)
12	$CuCl_2$ + NaBArF	5	>99	30(*R*)
13	$Cu(OAc)_2$	30	>99	Rac
14	$Cu(TFA)_2{\cdot}\ 0.56H_2O$	5	>99	3(*S*)
15	$Cu(ClO_4)_2 \cdot 6H_2O$	5	>99	39(*R*)
16	$Cu(OTf)_2$	5	>99	26(*R*)

17	$ZnCl_2$	5	>99	28(*S*)
18	$ZnCl_2 + AgBF_4$	5	>99	96(*S*)
19	$ZnCl_2 + AgPF_6$	5	>99	97(*S*)
20	$ZnCl_2$ + NaBArF	5	>99	96(*S*)
21	$Zn(OAc)_2$	5	>99	3(*R*)
22	$Zn(OTf)_2$	5	>99	98(*S*)

[a] Conditions: All reactions were performed in DCE (0.4 mL) at rt with **6a** (0.1 mmol), [O] = 3-(4-nitrophenyl)-2-(phenylsulfonyl)-1,2-oxaziridine, (0.12 mmol), Lewis acid (0.005 mmol) and (*S,R,S*)-**1a** (0.011 mmol). [b] Yield of isolated product. [c] Enantiomeric excess was determined by chiral HPLC on CHIRALPAK AD-H column.

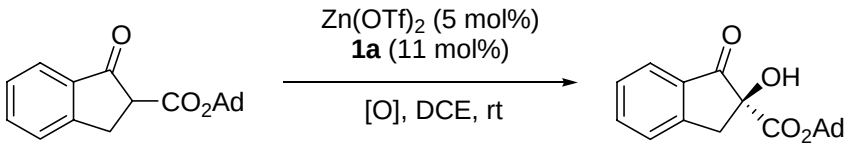
Table S2. Optimization of metal/ligand ratio for the enantioselective hydroxylation of **6a**[a]

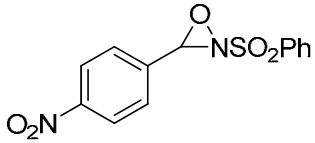


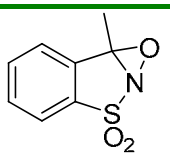
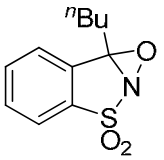
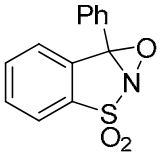
Entry	Metal/Ligand	Yield[b] (%)	Ee[c] (%)
1	1:1.2	>99	74
2	1:1.4	>99	85
3	1:1.6	>99	94
4	1:1.8	>99	96
5	1:2.0	>99	98
6	1:2.2	>99	98

[a] Conditions: All reactions were performed in DCE (0.4 mL) at rt with **6a** (0.1 mmol), [O] = 3-(4-nitrophenyl)-2-(phenylsulfonyl)-1,2-oxaziridine, (0.12 mmol), $Zn(OTf)_2$ (0.005 mmol) and (*S,R,S*)-**1a** (0.005x mmol) in 5 min. [b] Yield of isolated product. [c] Enantiomeric excess was determined by chiral HPLC on CHIRALPAK AD-H column.

Table S3. Optimization of oxidant for the enantioselective hydroxylation of **6a**[a]

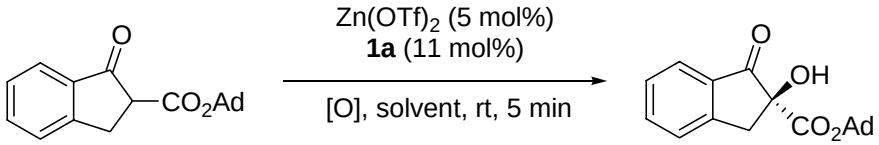


Entry	Oxidant	Time (h)	Yield[b] (%)	Ee[c] (%)
1		5 min	>99	98

2		3.5	>99	65
3		24	N.R.	N.D.
4		2.5	>99	87
5	H_2O_2	24	8	15
6	TBHP	24	11	7
7	CMHP	24	13	11
8	*m*-CPBA	0.25	>99	19

[a] Conditions: All reactions were performed in DCE (0.4 mL) at rt with **6a** (0.1 mmol), [O] (0.12 mmol), $Zn(OTf)_2$ (0.005 mmol) and (*S,R,S*)-**1a** (0.0011 mmol). [b] Yield of isolated product. [c] Enantiomeric excess was determined by chiral HPLC on CHIRALPAK AD-H column.

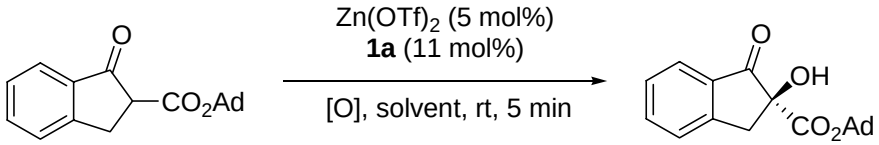
Table S4. Solvent effect on the enantioselective hydroxylation of **6a**[a]



Entry	Solvent	Yield[b] (%)	Ee[c] (%)
1[d]	Et_2O	>99	58
2	THF	>99	42
3[d]	PhMe	>99	57
4[d]	^{t}BuOH	>99	78
5	CH_2Cl_2	>99	98
6	$CHCl_3$	>99	95
7[d]	CCl_4	>99	58
8	DCE	>99	98

[a] Conditions: All reactions were performed in solvent (0.4 mL) at rt with **6a** (0.1 mmol), [O] = 3-(4-nitrophenyl)-2-(phenylsulfonyl)-1,2-oxaziridine, (0.12 mmol), $Zn(OTf)_2$ (0.005 mmol) and (*S,R,S*)-**1a** (0.0011 mmol) in 5 min. [b] Yield of isolated product. [c] Enantiomeric excess was determined by chiral HPLC on CHIRALPAK AD-H column. [d] 0.8-mL solvent was used.

Table S5. The influence of temperature on the enantioselective hydroxylation of **6a**[a]



Entry	Temp.	Time (min)	Yield[b] (%)	Ee[c] (%)
1	60	5	93	91
2	rt	5	>99	98
3	0	5	>99	98
4	-30	60	>99	98
5[d]	-78	360	>99	91

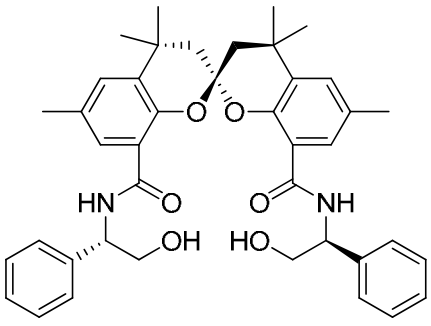
[a] Conditions: All reactions were performed in DCE (0.4 mL) at rt with **6a** (0.1 mmol), [O] = 3-(4-nitrophenyl)-2-(phenylsulfonyl)-1,2-oxaziridine, (0.12 mmol), $Zn(OTf)_2$ (0.005 mmol) and (*S,R,S*)-**1a** (0.0011 mmol). [b] Yield of isolated product. [c] Enantiomeric excess was determined by chiral HPLC on CHIRALPAK AD-H column. [d] CH_2Cl_2 (0.4 mL) was used as solvent.

Preparation of Ligands **1a-h**

2,[1] **3**,[1] **4**,[2] and **5**[3] was prepared according to the reported procedures, respectively.

Characterization data for compounds (*S*,*R*,*S*)-**5a-h** and (*S*,*S*,*S*)-**5a-h**:

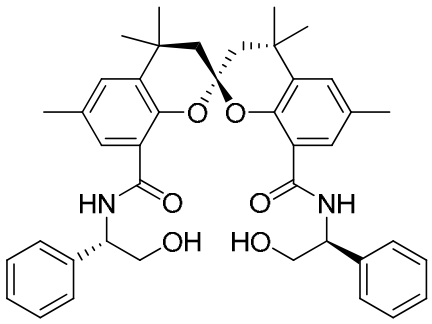
(-)-(*R*)-*N*8,*N*8'-Bis((*S*)-2-hydroxy-1-phenylethyl)-4,4,4',4',6,6'-hexamethyl-2,2'-spirobi[chroman]-8,8'-dicarboxamide ((*S,R,S*)-Ph-SPAN-diCONH, (*S,R,S*)-**5a**)



White solid, 47% yield; m.p. 210-211 °C; $[\alpha]_D^{20}$ = -63.9 (c = 0.50, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (2H, d, *J* = 6.3 Hz), 7.64 (2H, s), 7.20-7.18 (8H, m), 7.06-7.04 (4H, m), 4.86 (2H, dd, *J* = 9.9, 6.0 Hz), 3.61-3.56 (2H, m), 3.48-3.44 (2H, m), 2.32 (6H, s), 2.23 (2H, d, *J* = 14.4 Hz), 2.07 (2H, d, *J* = 14.4 Hz), 1.36 (6H, s), 1.32 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 146.1, 138.9, 132.5, 1321.6, 129.9, 129.6, 128.6, 127.5, 126.5, 122.8, 101.0, 66.3, 56.5, 46.9, 31.6, 31.4, 31.1, 20.7; IR (neat) *v* 3322, 3278,

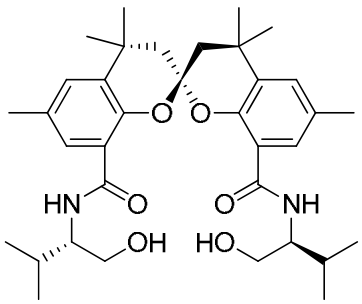
2927, 2850, 1648, 1626, 1602, 1573, 1537, 1493, 1456, 1277, 1223, 1196, 1167, 1130, 1107, 1086, 1049, 1027, 1003, 970, 892, 863, 841, 761, 742, 700, 640 cm^{-1}; ESI-MS, *m*/*z* = 685 ($[M+Na]^+$); HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{41}H_{47}N_2O_6$, 663.34286, found, 663.3443.

(+)-(*S*)-*N*8,*N*8'-Bis((*S*)-2-hydroxy-1-phenylethyl)-4,4,4',4',6,6'-hexamethyl-2,2'-spirobi[chroman]-8,8'-dicarboxamide ((*S,S,S*)-Ph-SPAN-diCONH, (*S,S,S*)-**5a**)



White solid, 45% yield; m.p. 88-89 °C; $[\alpha]_D^{20}$ = +9.6 (c = 1.01, $CHCl_3$); ^1H NMR (3400 MHz, $CDCl_3$) δ 8.03 (2H, d, *J* = 7.2 Hz), 7.74 (2H, s), 7.19-7.13 (6H, m), 6.9-6.89 (4H, m), 5.05 (2H, dd, *J* = 10.8, 6.8 Hz), 3.62-3.59 (2H, m), 3.41-3.36 (2H, m), 2.32 (6H, s), 2.22-2.15 (4H, m), 1.34 (6H, s), 1.33 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 146.8, 139.1, 133.4, 132.0, 130.1, 129.3, 128.3, 127.3, 126.7, 122.4, 103.0, 65.6, 56.2, 48.3, 31.4, 30.5, 29.8, 20.7; IR (neat) *v* 3394, 2959, 2926, 2863, 1639, 1601, 1519, 1443, 1262, 1225, 1192, 1174, 1154, 1120, 1078, 1027, 1004, 963, 953, 934, 882, 783, 755, 698 cm^{-1}; ESI-MS, *m*/*z* = 685 ($[M+Na]^+$); HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{41}H_{47}N_2O_6$, 663.34286, found, 663.3424.

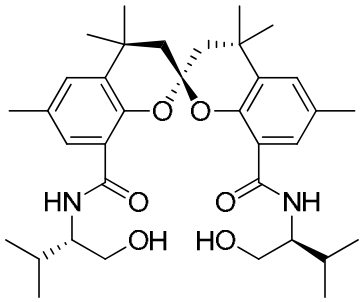
(-)-(*R*)-*N*8,*N*8'-Bis((*S*)-1-hydroxy-3-methylbutan-2-yl)-4,4,4',4',6,6'-hexamethyl-2,2'-spirobi[chroman]-8,8'-dicarboxamide ((*S,R,S*)-^{i}Pr-SPAN-diCONH, (*S,R,S*)-**5b**)



White solid, 40% yield; m.p. 105-108 °C; $[\alpha]_D^{20}$ = -76.7 (c = 0.46 $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (2H, d, *J* = 3.2 Hz), 7.25-7.24 (4H, m), 3.51-3.47 (2H, m), 3.40 (4H, t, *J* = 6.4 Hz), 2.97 (2H, t, *J* = 7.6 Hz), 2.36 (2H, d, *J* = 22.0 Hz), 2.33 (6H, s), 2.18 (2H, d, *J* = 19.2 Hz), 1.46 (6H, s), 1.39 (6H, s), 0.80 (6H, d, *J* = 9.2 Hz), 0.74 (6H, d, *J* = 9.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 146.2, 132.8, 131.6, 129.5, 129.4, 123.1, 101.2, 63.3, 57.6, 47.7, 31.3, 31.2, 31.1, 28.6, 20.5, 19.2, 18.9; IR (neat) *v* 3397, 3275, 2956, 2927, 2870, 1648, 1601, 1532, 1452, 1388, 1365, 1264, 1224, 1193, 1167, 1118, 1080, 1025,

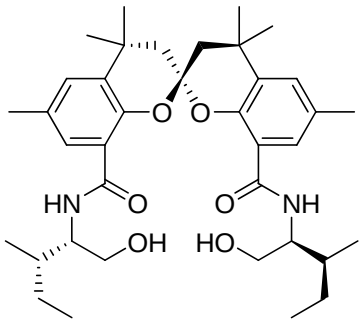
1002, 968, 936, 927, 885, 863, 784, 739 cm^{-1}; ESI-MS, *m/z* = 595 ($[M+H]^+$), 617 ($[M+Na]^+$); HRMS-ESI (*m/z*) $[M+H]^+$ calcd for $C_{35}H_{51}N_2O_6$, 595.37416, found, 595.3756.

(+)-(*S*)-*N*8,*N*8'-Bis((*S*)-1-hydroxy-3-methylbutan-2-yl)-4,4,4',4',6,6'-hexamethyl-2,2'-spirobi[chroman]-8,8'-dicarboxamide ((*S,S,S*)-^{i}Pr-SPAN-diCONH, (*S,S,S*)-**5b**)



White solid, 41% yield; m.p. 92-95 °C; $[\alpha]_D^{20}$ = +13.6 (c = 0.99, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (2H, s), 7.21 (2H, s), 3.67-3.66(2H, m), 3.45-3.41 (2H, m), 3.20-3.15 (2H, m), 2.34 (2H, d, *J* = 16.4 Hz), 2.32 (6H, s), 2.26 (2H, d, *J* = 14.4 Hz), 1.42 (6H, s), 1.38 (6H, s), 1.08-1.05 (1H, m), 0.77 (6H, d, *J* = 6.8 Hz), 0.70 (6H, d, *J* = 6.8 Hz); ^{13}C NMR (100MHz, $CDCl_3$) δ 166.5, 146.5, 133.2, 131.9, 129.9, 129.1, 123.1, 102.3, 63.0, 57.3, 48.6, 31.4, 30.8, 30.4, 28.9, 20.6, 19.1; IR (neat) *v* 3404, 3323, 3270, 2956, 2927, 2853, 1636, 1602, 1520, 1445, 1365, 1322, 1272, 1260, 1224, 1197, 1166, 1119, 1086, 1065, 1023, 1000, 959, 927, 886, 781, 742 cm^{-1}; ESI-MS, *m/z* = 595 ($[M+H]^+$); HRMS-ESI (*m/z*) $[M+Na]^+$ calcd for $C_{35}H_{50}N_2O_6Na$, 617.35611, found, 617.3561.

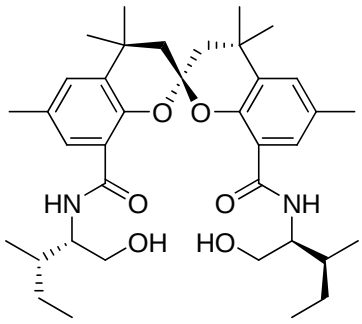
(-)-(*R*)-*N*8,*N*8'-Bis((2*S*,3*S*)-1-hydroxy-3-methylpentan-2-yl)-4,4,4',4',6,6'-hexamethyl-2,2'-spirobi[chroman]-8,8'-dicarboxamide ((*S,S,R,S,S*)-^{s}Bu-SPAN-diCONH, (*S,S,R,S,S*)-**5c**)



White solid, 53% yield; m.p. 89-90 °C; $[\alpha]_D^{20}$ = -43.3 (c = 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (2H, s), 7.20 (2H, s), 3.58-3.56 (2H, m), 3.42-3.37 (2H, m), 3.33-3.29 (2H, m), 2.30-2.26 (8H, m), 2.12 (2H, d *J* = 14.4 Hz), 1.42 (6H, s), 1.35 (6H, s), 1.10-1.04 (2H, m), 0.96-0.83 (4H, m), 0.77-0.73 (12H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 146.2, 132.9, 131.6, 129.6, 129.2, 123.1, 101.2, 63.2, 56.5, 47.7, 35.1, 33.6, 31.3, 31.1, 25.4, 20.6, 15.2, 11.1; IR (neat) *v* 3443, 3287, 2960, 2927, 2877, 1648, 1627, 1600, 1535, 1453, 1393, 1382, 1363, 1318, 1275, 1263, 1224, 1198, 1165, 1106, 1083, 1073, 1026, 1000, 974, 954, 896, 862, 815, 783, 741, 677, 665 cm^{-1}; ESI-MS, *m/z* = 623 ($[M+H]^+$); HRMS-ESI (*m/z*)

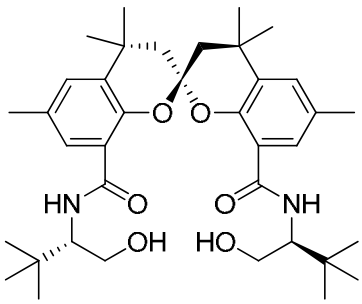
$[M+H]^+$ calcd for $C_{37}H_{55}N_2O_6$, 623.40546, found, 623.4044.

(+)-(*S*)-*N*8,*N*8'-Bis((2*S*,3*S*)-1-hydroxy-3-methylpentan-2-yl)-4,4,4',4',6,6'-hexamethyl-2,2'-spirobi[chroman]-8,8'-dicarboxamide ((*S,S,S,S,S*)-^{s}Bu-SPAN-diCONH, (*S,S,S,S,S*)-**5c**)



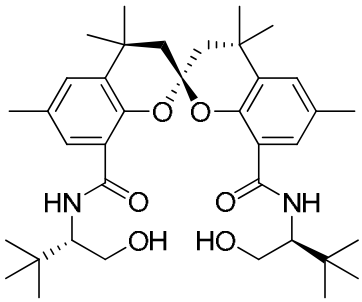
White solid, 46% yield; m.p. 55-56 °C; $[\alpha]_D^{20}$ = +13.9 (c = 0.99, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (2H, s), 7.21 (2H, s), 3.78-3.76 (2H, m), 3.48-2.44 (2H, m), 3.19-3.15 (2H, m), 2.34-2.24 (10H, m), 1.41 (6H, s), 1.38 (6H, s), 1.07-1.04 (2H, m), 0.96-0.86 (4H, m), 0.78-0.70 (12H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 146.5, 133.1, 131.8, 130.0, 129.2, 122.7, 102.4, 62.9, 56.1, 48.5, 35.4, 31.4, 30.7, 30.3, 25.4, 20.6, 15.1, 11.0; IR (neat) *v* 3420, 3231, 2960, 2929, 2872, 1650, 1620, 1602, 1560, 1513, 1445, 1393, 1357, 1286, 1224, 1174, 1158, 1118, 1081, 1048, 994, 945, 924, 913, 888, 876, 799, 781, 764, 739 cm^{-1}; ESI-MS, *m*/*z* = 623 ($[M+H]^+$); HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{37}H_{55}N_2O_6$, 623.40546, found, 623.4040.

(-)-(*R*)-*N*8,*N*8'-Bis((*S*)-1-hydroxy-3,3-dimethylbutan-2-yl)-4,4,4',4',6,6'-hexamethyl-2,2'-spirobi[chroman]-8,8'-dicarboxamide ((*S,R,S*)-^{t}Bu-SPAN-diCONH, (*S,R,S*)-**5d**)



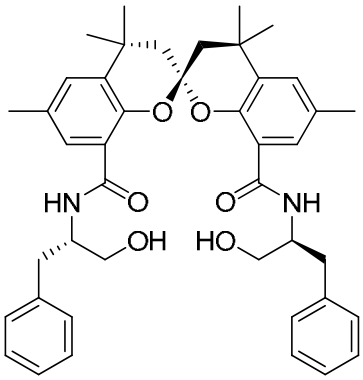
White solid, 36% yield; m.p. 156-160 °C; $[\alpha]_D^{20}$ = -64.2 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (2H, s), 7.24 (2H, s), 3.83-3.82 (2H, m), 3.57-3.54 (2H, m), 3.27-3.23 (2H, m), 2.38 (2H, d, *J* = 14.4 Hz), 2.32 (6H, s), 2.12 (2H, d, *J* = 14.4 Hz), 1.41 (6H, s), 1.40 (6H, s), 0.82 (18H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 146.2, 132.3, 131.5, 130.1, 129.8, 123.1, 100.9, 62.9, 59.8, 46.9, 33.6, 32.0, 31.7, 31.2, 27.0, 20.6; IR (neat) *v* 3325, 2927, 2851, 1647, 1602, 1518, 1455, 1364, 1262, 1221, 1195, 1166, 1083, 1026, 1002, 975, 894, 862, 799, 709, 657 cm^{-1}; ESI-MS, *m*/*z* = 623 ($[M+H]^+$); HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{37}H_{55}N_2O_6$, 623.40546, found, 623.4034.

(+)-(*S*)-*N*8,*N*8'-Bis((*S*)-1-hydroxy-3,3-dimethylbutan-2-yl)-4,4,4',4',6,6'-hexamethyl-2,2'-spirobi[chroman]-8,8'-dicarboxamide ((*S,S,S*)-^{t}Bu-SPAN-diCONH, (*S,S,S*)-**5d**)



White solid, 43% yield; m.p. 81-82 °C; $[\alpha]_D^{20}$ = +13.0 (c = 0.99 $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (2H, s), 7.19 (2H, s), 3.88-3.83 (2H, m), 3.54-3.50 (2H, m), 3.01-2.97 (2H, m), 2.25-2.30 (10H, m), 1.41 (6H, s), 1.36 (6H, s), 0.68 (18H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 146.7, 133.5, 132.0, 130.2, 128.9, 122.7, 103.0, 62.0, 59.8, 49.2, 33.5, 31.5, 30.1, 29.6, 26.7, 20.6; IR (neat) ν 3436, 3369, 3324, 2954, 2927, 2851, 1643, 1627, 1599, 1572, 1520, 1446, 1366, 1345, 1310, 1261, 1243, 1226, 1194, 1176, 1158, 1121, 1106, 1083, 1028, 1010, 971, 947, 890, 873, 782, 741, 709 cm^{-1}; ESI-MS, *m*/*z* = 623 ([M+H]$^+$); HRMS-ESI (*m*/*z*) [M+H]$^+$ calcd for $C_{37}H_{55}N_2O_6$, 623.40546, found, 623.4033.

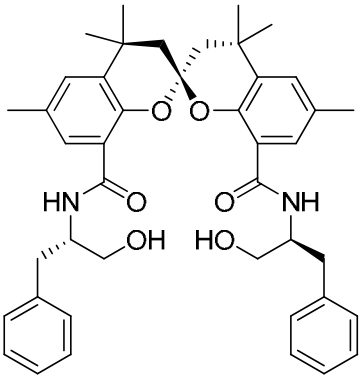
(-)-(*R*)-*N*8,*N*8'-Bis((*S*)-1-hydroxy-3-phenylpropan-2-yl)-4,4,4',4',6,6'-hexamethyl-2,2'-spirobi[chroman]-8,8'-dicarboxamide ((*S,R,S*)-Bn-SPAN-diCONH, (*S,R,S*)-**5e**)



White solid, 32% yield; m.p. 95-96 °C; $[\alpha]_D^{20}$ = -8.1 (c = 0.52, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (2H, s), 7.28-7.10 (14H, m), 3.83-3.78 (2H, m), 3.28-3.25 (3H, m), 2.57-2.52 (3H, m), 2.24 (2H, d, *J* = 11.7 Hz), 2.22 (6H, s), 2.10 (2H, d, *J* = 14.4 Hz), 1.39 (6H, s), 1.33 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 146.2, 138.1, 133.5, 131.7, 129.2, 129.1, 128.8, 128.3, 126.3, 123.7, 101.4, 62.8, 53.5, 48.2, 36.4, 31.3, 30.8, 30.8, 20.6; IR (neat) ν 3392, 3065, 3024, 2957, 2927, 2864, 1636, 1601, 1533, 1496, 1455, 1445, 1361, 1272, 1225, 1191, 1173, 1153, 1120, 1091, 1038, 956, 909, 884, 733, 700, 648 cm^{-1}; ESI-MS, *m*/*z* = 691 ([M+H]$^+$), 713 ([M+Na]$^+$); HRMS-ESI (*m*/*z*) [M+H]$^+$ calcd for $C_{43}H_{51}N_2O_6$, 691.37416, found, 691.3733.

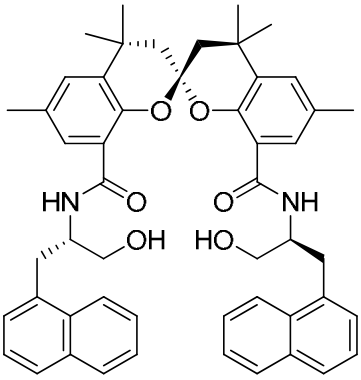
(+)-(*S*)-*N*8,*N*8'-Bis((*S*)-1-hydroxy-3-phenylpropan-2-yl)-4,4,4',4',6,6'-hexamethyl-2,2'-spirobi[chroman]-8

,8'-dicarboxamide ((*S,S,S*)-Bn-SPAN-diCONH, (*S,S,S*)-**5e**)



White solid, 22% yield; m.p. 90-91 °C; $[\alpha]_D^{20}$ = +46.3 (c = 0.56, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (2H, s), 7.50 (2H, d, *J* = 7.8 Hz), 7.26-7.07 (12H, m), 4.13-4.12 (2H, m), 3.59-3.58 (2H, m), 3.41-3.38 (2H, m), 3.11-3.08 (2H, m), 2.47-2.41 (2H, m), 2.25 (6H, s), 2.18 (2H, d, *J* = 13.8 Hz), 2.09 (2H, d, *J* = 14.4 Hz), 1.38 (6H, s), 1.35 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 146.2, 137.8, 132.8, 131.7, 129.7, 129.3, 129.0, 128.3, 126.2, 123.2, 101.4, 62.5, 52.4, 47.7, 36.3, 31.3, 31.2, 30.7, 20.6; IR (neat) *v* 3404, 2959, 2926, 2867, 1644, 1602, 1531, 1496, 1445, 1364, 1268, 1226, 1193, 1174, 1156, 1119, 1082, 1040, 1007, 990, 952, 909, 886, 732, 700, 646 cm^{-1}; ESI-MS, *m/z* = 691 ($[M+H]^+$), 713 ($[M+Na]^+$); HRMS-ESI (*m/z*) $[M+H]^+$ calcd for $C_{43}H_{51}N_2O_6$, 691.37416, found, 691.3745.

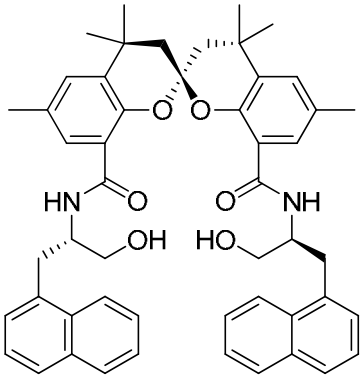
(-)-(*R*)-*N*8,*N*8'-Bis((*S*)-1-hydroxy-3-(naphthalen-1-yl)propan-2-yl)-4,4,4',4',6,6'-hexamethyl-2,2'-spirobi[chroman]-8,8'-dicarboxamide ((*S,R,S*)-1-Np-SPAN-diCONH, (*S,R,S*)-**5f**)



White solid, 35% yield; m.p. 123-124 °C; $[\alpha]_D^{20}$ = -73.1 (c = 0.52, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (2H, d, *J* = 8.0 Hz), 7.83-7.81 (2H, m), 7.70 (2H, d, *J* = 8.4 Hz), 7.53-7.43 (8H, m), 7.34-7.30 (2H, m), 7.26-7.23 (2H, m), 7.09 (2H, s), 4.16-4.14 (2H, m), 3.97-3.96 (2H, m), 3.49-3.45 (2H, m), 3.36-3.32 (2H, m), 2.92-2.86 (2H, m), 2.22 (2H, d, *J* = 14.0 Hz), 2.14 (6H, s), 2.09 (2H, d, *J* = 14.4 Hz), 1.29 (6H, s), 1.17 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 146.4, 134.6, 133.8, 133.7, 132.1, 131.8, 129.0, 128.9, 128.5, 127.5, 127.1, 126.1, 125.6, 125.3, 124.1, 123.9, 101.8, 62.6, 52.9, 48.6, 33.5, 31.3, 30.5, 30.4, 20.5; IR (neat) *v* 3324, 2927, 2850, 1625, 1573, 1535, 1439, 1310, 1269, 1243, 1225, 1087, 891, 799, 777, 732, 641 cm^{-1}; ESI-MS, *m/z* = 791 ($[M+H]^+$), 813 ($[M+Na]^+$); HRMS-ESI (*m/z*) $[M+Na]^+$ calcd

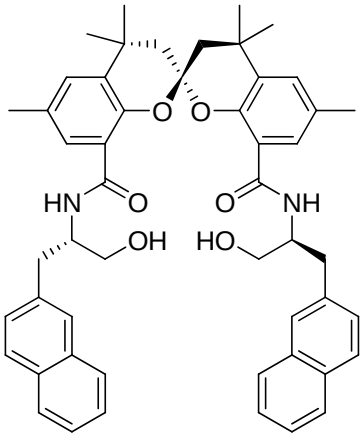
for $C_{51}H_{54}N_2O_6Na$, 813.38741, found, 813.38766.

(+)-(*S*)-*N*8,*N*8'-Bis((*S*)-1-hydroxy-3-(naphthalen-1-yl)propan-2-yl)-4,4,4',4',6,6'-hexamethyl-2,2'-spirobi[chroman]-8,8'-dicarboxamide ((*S,S,S*)-1-Np-SPAN-diCONH, (*S,S,S*)-**5f**)



White solid, 16% yield; m.p. 231-232 °C; $[\alpha]_D^{20}$ = +89.5 (c = 0.48, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (2H, d, *J* = 8.4 Hz), 7.83-7.81 (2H, m), 7.72-7.67 (6H, m), 7.56-7.52 (2H, m), 7.49-7.45 (2H, m), 7.36-7.32 (2H, m), 7.21-7.19 (2H, m), 7.13-7.12 (2H, m), 4.41-4.33 (2H, m), 3.46-3.42 (2H, m), 3.24-3.20 (2H, m), 3.09-3.04 (2H, m), 2.62-2.56 (2H, m), 2.23 (6H, s), 2.11 (2H, d, *J* = 14.4 Hz), 2.03 (2H, d, *J* = 14.4 Hz), 1.34 (6H, s), 1.27 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 146.3, 134.0, 133.7, 132.8, 132.1, 131.7, 129.6, 129.4, 128.4, 127.1, 127.0, 126.1, 125.6, 125.2, 124.1, 123.4, 101.3, 62.5, 51.4, 47.5, 33.7, 31.2, 31.2, 30.8, 20.6; IR (neat) *v* 3382, 2927, 2862, 1664, 1653, 1646, 1627, 1596, 1558, 1540, 1521, 1463, 1443, 1397, 1365, 1336, 1257, 1227, 1193, 1174, 1158, 1115, 1086, 1012, 997, 970, 949, 888, 875, 863, 798, 777, 739 cm^{-1}; ESI-MS, *m/z* = 791 ($[M+H]^+$); HRMS-ESI (*m/z*) $[M+Na]^+$ calcd for $C_{51}H_{54}N_2O_6Na$, 813.38741, found, 813.3860.

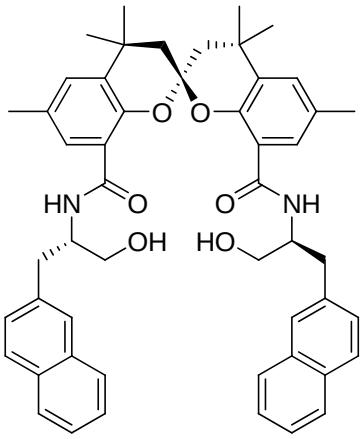
(-)-(*R*)-*N*8,*N*8'-Bis((*S*)-1-hydroxy-3-(naphthalen-2-yl)propan-2-yl)-4,4,4',4',6,6'-hexamethyl-2,2'-spirobi[chroman]-8,8'-dicarboxamide ((*S,R,S*)-2-Np-SPAN-diCONH, (*S,R,S*)-**5g**)



White solid, 39% yield; m.p. 120-123 °C; $[\alpha]_D^{20}$ = -76.6 (c = 0.57, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.67 (6H, m), 7.55 (2H, s), 7.40-7.36 (6H, m), 7.33-7.31 (2H, d, *J* = 7.2 Hz), 7.28-7.25 (2H, m), 7.14

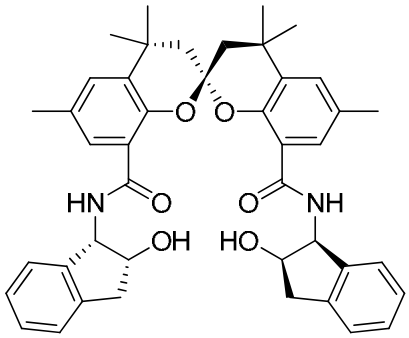
(2H, s), 3.94-3.92 (2H, m), 3.33-3.23 (4H, m), 2.72-2.66 (4H, m), 2.17-2.12 (8H, m), 1.99 (2H, d, *J* = 14.4 Hz), 1.30 (6H, s), 1.28 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 146.2, 135.7, 133.4, 133.4, 132.1, 131.7, 129.1, 128.9, 128.0, 127.5, 127.5, 127.4, 127.4, 125.9, 125.3, 123.8, 101.3, 62.8, 53.5, 48.1, 36.5, 31.2, 30.8, 30.8, 20.6; IR (neat) *v* 3386, 3324, 2927, 2850, 1627, 1599, 1574, 1530, 1442, 1364, 1310, 1269, 1242, 1224, 1192, 1172, 1154, 1120, 1087, 1045, 1025, 991, 953, 890, 861, 815, 749, 641 cm^{-1}; ESI-MS, *m*/*z* = 791 ([M+H]$^+$), 813 ([M+Na]$^+$); HRMS-ESI (*m*/*z*) [M+Na]$^+$ calcd for $C_{51}H_{54}N_2O_6Na$, 813.38741, found, 813.38335.

(+)-(*S*)-*N*8,*N*8'-Bis((*S*)-1-hydroxy-3-(naphthalen-2-yl)propan-2-yl)-4,4,4',4',6,6'-hexamethyl-2,2'-spirobi[chroman]-8,8'-dicarboxamide ((*S,S,S*)-2-Np-SPAN-diCONH, (*S,S,S*)-**5g**)



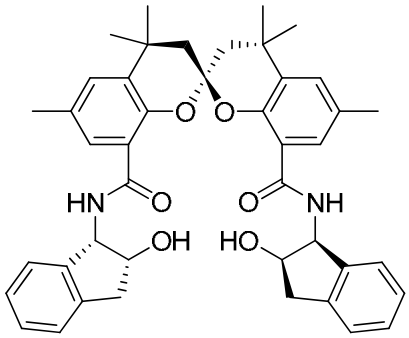
White solid, 55% yield; m.p. 101-102 °C; $[\alpha]_D^{20}$ = +13.3 (c = 0.53, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.60 (6H, m), 7.51 (2H, s), 7.43-7.38 (6H, m), 7.34-7.22 (4H, m), 7.15 (2H, s), 4.26-4.23 (2H, m), 3.44-3.40 (2H, m), 3.16-3.12 (2H, m), 2.65-2.60 (2H, m), 2.41-2.35 (2H, m), 2.20 (6H, s), 2.05 (2H, d, *J* = 14.4 Hz), 1.92 (2H, d, *J* = 14.4 Hz), 1.32 (6H, s), 1.29 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 146.2, 135.3, 133.4, 132.9, 132.1, 131.8, 129.6, 126.5, 127.9, 127.6, 127.5, 127.5, 125.9, 125.4, 123.1, 101.3, 62.4, 52.4, 47.5, 31.3, 31.1, 30.8, 24.8, 20.6; IR (neat) *v* 3388, 3325, 2927, 2851, 1627, 1599, 1531, 1446, 1391, 1379, 1359, 1270, 1225, 1190, 1159, 1107, 1046, 1026, 991, 952, 888, 861, 815, 781, 740 cm^{-1}; ESI-MS, *m*/*z* = 791 ([M+H]$^+$); HRMS-ESI (*m*/*z*) [M+Na]$^+$ calcd for $C_{51}H_{54}N_2O_6Na$, 813.38741, found, 813.3869.

(-)-(*R*)-*N*8,*N*8'-Bis((1*S*,2*R*)-2-hydroxy-2,3-dihydro-1H-inden-1-yl)-4,4,4',4',6,6'-hexamethyl-2,2'-spirobi[chroman]-8,8'-dicarboxamide ((*S,R,R,R,S*)-In-SPAN-diCONH, (*S,R,R,R,S*)-**5h**)



White solid, 37% yield; m.p. 118-120 °C; $[\alpha]_D^{20}$ = -63.8 (c = 0.48, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (2H, d, *J* = 8.0 Hz), 7.42 (2H, s), 7.22 (2H, s), 7.19-7.15 (4H, m), 7.10-7.06 (2H, m), 6.90 (2H, d, *J* = 7.6 Hz), 5.16-5.12 (2H, m), 4.37-4.36 (2H, m), 3.06-3.00 (2H, m), 2.82-2.73 (2H, m), 2.29 (6H, s), 2.21 (2H, d, *J* = 14.4 Hz), 2.08 (2H, d, *J* = 14.4 Hz), 1.44 (6H, s), 1.34 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 146.6, 140.6, 139.7, 134.0, 131.4, 129.0, 128.8, 127.8, 127.1, 125.0, 124.4, 123.8, 101.9, 73.4, 57.9, 48.5, 39.7, 31.6, 30.5, 30.4, 20.7; IR (neat) *v* 3323, 2927, 2850, 1625, 1601, 1573, 1519, 1458, 1443, 1310, 1268, 1242, 1226, 1192, 1174, 1155, 1086, 1054, 1023, 992, 967, 953, 936, 892, 818, 791, 752, 737, 725, 640 cm^{-1}; ESI-MS, *m*/*z* = 709 ([M+Na]$^+$); HRMS-ESI (*m*/*z*) [M+Na]$^+$ calcd for $C_{43}H_{46}N_2O_6Na$, 709.32481, found, 709.3254.

(+)-(*S*)-*N*8,*N*8'-Bis((1*S*,2*R*)-2-hydroxy-2,3-dihydro-1H-inden-1-yl)-4,4,4',4',6,6'-hexamethyl-2,2'-spirobi[chroman]-8,8'-dicarboxamide ((*S,R,S,R,S*)-In-SPAN-diCONH, (*S,R,S,R,S*)-**5h**)



White solid, 36% yield; m.p. 92-94 °C; $[\alpha]_D^{20}$ = +26.2 (c = 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (2H, d, *J* = 8.0 Hz), 7.67 (2H, s), 7.19-7.08 (8H, m), 7.01 (2H, m), 5.37-5.34 (2H, m), 4.48-4.45 (2H, m), 3.04-2.98 (2H, m), 2.47-2.70 (2H, m), 2.20 (6H, s), 2.11 (2H, d, *J* = 14.0 Hz), 1.99 (2H, d, *J* = 14.0 Hz), 1.32 (6H, s), 1.17 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 146.3, 140.4, 139.8, 131.5, 131.3, 130.1, 130.0, 127.8, 126.6, 125.0, 124.7, 121.5, 101.1, 73.2, 58.0, 46.2, 39.2, 32.0, 31.3, 31.1, 20.7; IR (neat) *v* 3388, 2925, 2860, 1633, 1599, 1517, 1443, 1390, 1365, 1341, 1299, 1263, 1224, 1191, 1175, 1154, 1121, 1084, 1054, 1025, 1004, 972, 956, 896, 879, 818, 783, 741, 726 cm^{-1}; ESI-MS, *m*/*z* = 687 ([M+H]$^+$); HRMS-ESI (*m*/*z*) [M+Na]$^+$ calcd for $C_{43}H_{46}N_2O_6Na$, 709.32481, found, 709.3239

Typical procedure for preparation of ligand **1a-h** from **5a-h**

Method A[4a] (for **5a** and **5d**):

To a suspension of **5** (0.5 mmol) in dry CH_2Cl_2 (5.0 mL) was slowly added (diethylamino)sulfur trifluoride (DAST, 0.16 mL, 1.1 mmol) at -78°C. After stirring for 6 h at -78°C and overnight at r.t., 4 *N* NH_4OH, aq. (1 mL) was added. Water (10 mL) was added to the solution and the aqueous layer was extracted with CH_2Cl_2 for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate/Net_3 as the eluent to afford **1**.

Method B[4b] (for **5b-c** and **5e-g**):

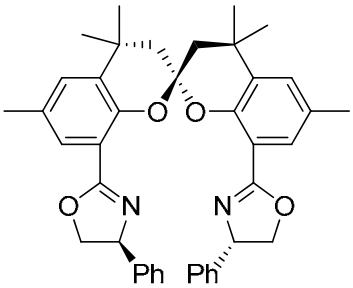
To a mixture of **5** (0.5 mmol), 4-dimethylaminopyridine (DMAP, 5.0 mg, 0.04 mmol), and NEt_3 (0.6 mL, 4.0 mmol) in dry CH_2Cl_2 (5.0 mL) was added methanesulfonyl chloride (0.32 mL, 4.0 mmol) at 0°C, and the solution was stirred for 2 h at this temperature. Then another portion of NEt_3 (3.3 mL, 24.0 mmol) was added to the solution, and it was stirred at r.t. until the initially formed mesylate disappeared (checked by TLC). The reaction mixture was diluted with CH_2Cl_2 and washed with an aqueous $NaHCO_3$ solution. The organic layer was dried over anhydrous Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate/Net_3 as the eluent to afford **1**.

Method C[4c] (for (*S,R,S*)-**5h**):

A mixture of (*S,R,S*)-**5h** (274.0 mg, 0.4 mmol) and $Ti(OiPr)_4$ (1.0 mL, 3.2 mmol) was stirred for 145 ^oC for 18 h. The reaction was cooled to r.t and 1,2-propanediol (0.4 mL, 3.8 mol) was added. After 30 min, EtOAc and water were added and the reaction mixture was stirred for an additional 30-60 min. The aqueous layer was extracted with EtOAc for 3 times. The combined organic layers were dried over anhydrous Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate/Net_3 as the eluent to afford (*S,R,S*)-**1h** (127.0 mg, yield 49%).

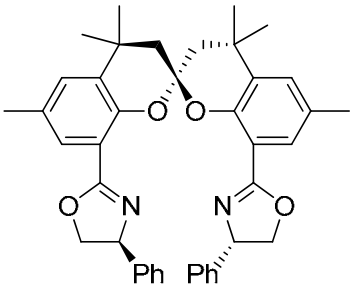
Characterization data for ligands (*S*,*R*,*S*)-**1a-h** and (*S*,*S*,*S*)-**1a-g**

(-)-(4*S*,4'*S*)-2,2'-((*R*)-4,4,4',4',6,6'-Hexamethyl-2,2'-spirobi[chroman]-8,8'-diyl)bis(4-phenyl-4,5-dihydroxazole) ((*S,R,S*)-Ph-SPANbox, (*S,R,S*)-**1a**)



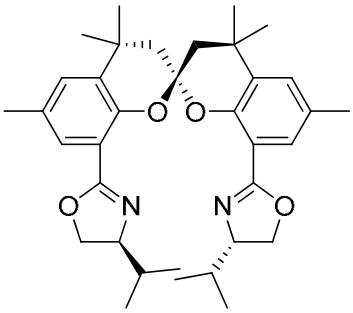
White solid, 77% yield; m.p. 184-185 °C; $[\alpha]_D^{20}$ = -3.9 (c = 0.53, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.30-7.21 (10H, m), 7.12-7.09 (4H, m), 5.07 (2H, t, J = 9.3 Hz), 4.35 (2H, dd, J = 10.2, 8.4 Hz), 3.82 (2H, t, J = 8.4 Hz),2.27 (6H, s), 2.22 (2H, d, J = 14.4 Hz), 2.12 (2H, d, J = 14.1 Hz), 1.61 (6H, s), 1.34 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 147.3, 142.4, 133.4, 130.1, 129.5, 129.2, 128.5, 127.2, 126.7, 117.8, 98.4, 69.5, 46.9, 33.0, 31.7, 30.8, 20.6; IR (neat) v 3026, 2958, 2920, 2895, 2860, 1645, 1630, 1492, 1451, 1356, 1316, 1267, 1228, 1197, 1181, 1163, 1099, 1079, 1029, 1002, 977, 924, 902, 886, 872, 816, 761, 701, 612 cm^{-1}; ESI-MS, m/z = 627 ($[M+H]^+$), 649 ($[M+Na]^+$); HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{41}H_{43}N_2O_4$, 627.32173, found, 627.3234.

(-)-(4*S*,4'*S*)-2,2'-((*S*)-4,4,4',4',6,6'-Hexamethyl-2,2'-spirobi[chroman]-8,8'-diyl)bis(4-phenyl-4,5-dihydroox azole) ((*S,S,S*)-Ph-SPANbox, (*S,S,S*)-**1a**)



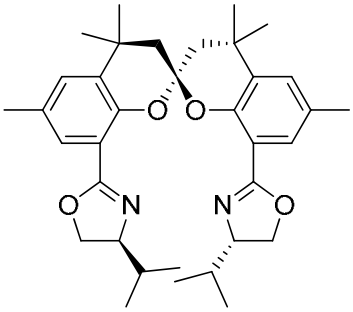
White solid, 81% yield; m.p. 98-99 °C; $[\alpha]_D^{20}$ = -14.4 (c = 0.99, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.38 (2H, s), 7.24-7.19 (8H, m), 7.13-7.10 (4H, m), 5.07 (2H, dd, J = 10.2, 8.7 Hz), 4.28 (2H, dd, J = 10.2, 8.7 Hz), 3.81 (2H, t, J = 8.7 Hz),2.30 (6H, s), 2.26 (2H, d, J = 14.1 Hz), 2.14 (2H, d, J = 14.1 Hz), 1.50 (6H, s), 1.32 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 147.8, 142.5, 130.1, 129.3, 129.2, 128.3, 127.1, 126.6, 126.4, 117.6, 99.3, 74.2, 69.4, 68.0, 47.8, 32.1, 31.0, 31.0, 20.5; IR (neat) v 3060, 3027, 2957, 2922, 2864, 1644, 1603, 1492, 1454, 1356, 1265, 1229, 1217, 1183, 1164, 1116, 1088, 1026, 997, 957, 937, 921, 891, 871, 753, 698, 613 cm^{-1}; ESI-MS, m/z = 627 ($[M+H]^+$), 649 ($[M+Na]^+$); HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{41}H_{43}N_2O_4$, 627.32173, found, 627.3227.

(-)-(4*S*,4'*S*)-2,2'-((*R*)-4,4,4',4',6,6'-Hexamethyl-2,2'-spirobi[chroman]-8,8'-diyl)bis(4-*iso*-propyl-4,5-dihydr ooxazole) ((*S,R,S*)-^{i}Pr-SPANbox, (*S,R,S*)-**1b**)



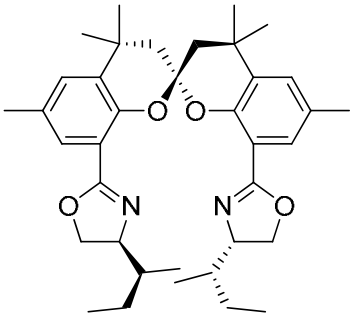
White solid, 58% yield; m.p. 112-113 °C; $[\alpha]_D^{20}$ = -11.8 (c = 0.49, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.14 (2H, s), 7.10 (2H, s), 3.98-3.92 (2H, m), 3.81-3.71 (4H, m), 2.25 (6H, s), 2.17 (2H, d, J = 14.1 Hz), 2.09 (2H, d, J = 14.1 Hz), 1.88-1.86 (2H, m), 1.61 (6H, s), 1.31 (6H,), 0.85 (6H, d, J = 6.9 Hz), 0.73 (6H, d, J = 6.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 762.9, 146.8, 133.0, 130.0, 129.1, 128.8, 118.4, 98.0, 72.1, 69.6, 46.7, 33.2, 32.4, 31.9, 30.7, 20.6, 19.0, 17.9; IR (neat) ν 2954, 2921, 2868, 1642, 1611, 1592, 1480, 1452, 1356, 1317, 1267, 1228, 1215, 1189, 1162, 1116, 1097, 1029, 1002, 976, 939, 887, 815, 802, 764 cm^{-1}; ESI-MS, m/z = 559 ($[M+H]^+$), 581 ($[M+Na]^+$); HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{35}H_{47}N_2O_4$, 559.35503, found, 559.3544.

(-)-(4*S*,4'*S*)-2,2'-((*S*)-4,4,4',4',6,6'-Hexamethyl-2,2'-spirobi[chroman]-8,8'-diyl)bis(4-*iso*-propyl-4,5-dihydrooxazole) ((*S,S,S*)-^{i}Pr-SPANbox, (*S,S,S*)-**1b**)



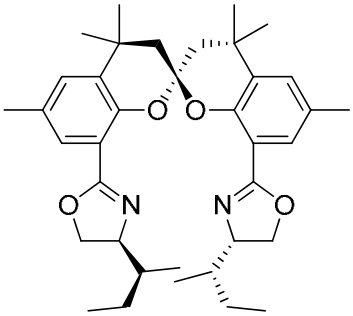
White solid, 51% yield; m.p. 89-90 °C; $[\alpha]_D^{20}$ = -30.5 (c = 0.99, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (2H, s), 7.16 (2H, s), 3.99-3.94 (2H, m), 3.73-3.65 (4H, m), 2.27 (6H, s), 2.21 (2H, d, J = 14.0 Hz), 2.12 (2H, d, J = 14.4 Hz), 1.57 (6H, s), 1.32 (6H, s), 1.12-1.06 (2H, m), 0.87 (6H, d, J = 6.8 Hz), 0.78 (6H, d, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 147.1, 133.7, 130.2, 129.2, 128.8, 118.2 99.0, 71.9, 69.8, 47.5, 33.0, 32.5, 31.4, 30.9, 20.5, 18.8, 18.1; IR (neat) ν 2957, 2928, 2868, 1732, 1644, 1602, 1529, 1461, 1447, 1362, 1325, 1257, 1226, 1193, 1173, 1153, 1084, 1024, 990, 966, 910, 890, 801, 785, 731, 644 cm^{-1}; ESI-MS, m/z = 577 ($[M+H_2O+H]^+$); HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{35}H_{47}N_2O_4$, 559.35503, found, 559.3523.

(-)-(4*S*)-4-*sec*-Butyl-2-((2*R*)-8'-((4*S*)-4-*sec*-butyl-4,5-dihydrooxazol-2-yl)-4,4,4',4',6,6'-hexamethyl-2,2'-spirobi[chroman]-8-yl)-4,5-dihydrooxazole ((*S,S,R,S,S*)-^{s}Bu-SPANbox, (*S,S,R,S,S*)-**1c**)



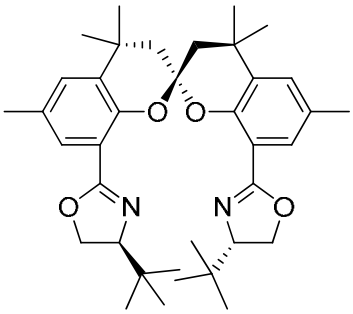
White solid, 68% yield; m.p. 109-110 °C; $[\alpha]_D^{20}$ = -8.6 (c = 0.99, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (2H, s), 7.11(2H, s), 3.91-3.89 (4H, m), 3.73-3.71 (2H, m), 2.25 (6H, s), 2.17 (2H, d, J = 14.0 Hz), 2.09 (2H, d, J = 14.0 Hz), 1.61 (6H, s), 1.45-4.42 (2H, m), 1.31-1.26 (8H, m), 1.12-1.08 (2H, m), 0.89-0.85 (6H, t, J = 7.2 Hz), 0.64 (6H, d, J = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 146.8, 133.0, 129.9, 129.0, 128.7, 118.2, 97.9, 70.4, 68.8, 46.7, 38.4, 33.1, 30.6, 26.0, 20.5, 13.8, 11.4; IR (neat) ν 2956, 2917, 2875, 1642, 1594, 1455, 1380, 1353, 1314, 1261, 1227, 1214, 1188, 1163, 1115, 1099, 1028, 1000, 978, 935, 888, 868, 791, 765, 706 cm^{-1}; ESI-MS, m/z = 587 ($[M+H]^+$); HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{37}H_{51}N_2O_4$, 587.38433, found, 587.3829.

(-)-(4*S*)-4-*sec*-Butyl-2-((2*S*)-8'-((4*S*)-4-*sec*-butyl-4,5-dihydrooxazol-2-yl)-4,4,4',4',6,6'-hexamethyl-2,2'-spirobi[chroman]-8-yl)-4,5-dihydrooxazole ((*S,S,S,S,S*)-^{s}Bu-SPANbox, (*S,S,S,S,S*)-**1c**)



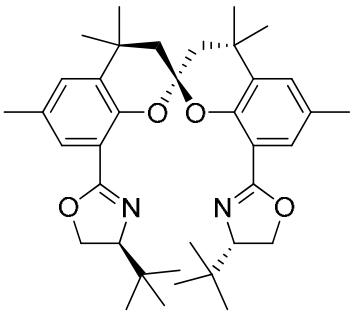
White solid, yield 63%; m.p. 32-34 °C; $[\alpha]_D^{20}$ = -78.1 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (2H, s), 7.14 (2H, s), 3.93-3.89 (2H, m), 3.82-3.76 (2H, m), 3.68 (2H, t, J = 8.0 Hz), 2.25 (6H, s), 2.2.20 (2H, d, J = 14.4 Hz), 2.10 (2H, d, J = 14.0 Hz), 1.55 (6H, s), 1.49-1.41 (4H, m), 1.32 (6H, m), 1.08-1.04 (2H, m), 0.84 (6H, t, J = 7.2 Hz), 0.68 (6H, d, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 147.2, 133.6, 130.1, 129.1, 128.8, 118.1, 98.9, 70.4, 69.2, 47.6, 38.7, 32.5, 31.4, 30.9, 25.8, 20.5, 14.1, 11.4; IR (neat) ν 2958, 2924, 2873, 1949, 1606, 1458, 1356, 1259, 1229, 1189, 1163, 1115, 1087, 1025, 979, 937, 892, 870, 806, 769, 732 cm^{-1}; ESI-MS, m/z = 587 ($[M+H]^+$), 619 ($[M+Na]^+$); HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{37}H_{51}N_2O_4$, 587.38433, found, 587.38452.

(-)-(4*S*,4'*S*)-2,2'-((*R*)-4,4,4',4',6,6'-Hexamethyl-2,2'-spirobi[chroman]-8,8'-diyl)bis(4-*tert*-butyl-4,5-dihydrooxazole) ((*S,R,S*)-^{t}Bu-SPANbox, (*S,R,S*)-**1d**)



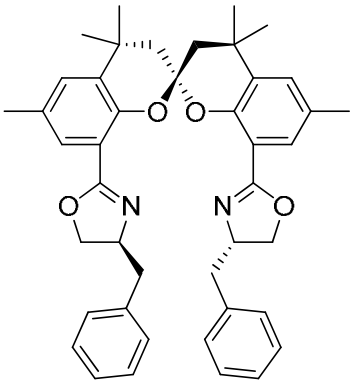
White solid, 64% yield; m.p. 203-204 °C; $[\alpha]_D^{20}$ = -25.6 (c = 1.00, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.07 (2H, s), 7.01 (2H, s), 3.84-3.62 (6H, m), 2.18 (6H, s), 2.09 (2H, d, J = 14.4 Hz), 2.00 (2H, d, J = 14.4 Hz), 1.52 (6H, s), 1.24 (6H, s), 0.71 (18H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 146.8, 133.0, 129.9, 129.0, 128.7, 118.2, 97.9, 70.4, 68.8, 46.6, 38.4, 33.1, 31.7, 30.6, 26.0, 20.5, 13.8, 11.4; IR (neat) ν 3013, 2952, 2866, 1645, 1611, 1478, 1451, 1392, 1357, 1316, 1281, 1260, 1228, 1214, 1187, 1163, 1116, 1103, 1029, 1003, 979, 966, 939, 886, 815, 771 cm^{-1}; ESI-MS, m/z = 587 ($[M+H]^+$); HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{37}H_{51}N_2O_4$, 587.38433, found, 587.3829.

(-)-(4*S*,4'*S*)-2,2'-((*S*)-4,4,4',4',6,6'-Hexamethyl-2,2'-spirobi[chroman]-8,8'-diyl)bis(4-*tert*-butyl-4,5-dihydr ooxazole) ((*S,S,S*)-^{t}Bu-SPANbox, (*S,S,S*)-**1d**)



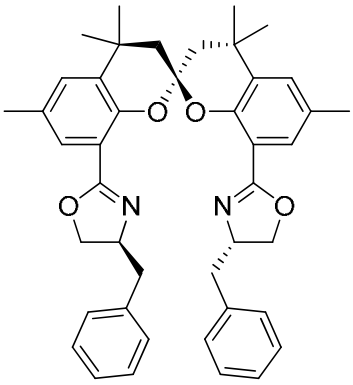
White solid, yield 42%; m.p. 190-191 °C; $[\alpha]_D^{20}$ = -16.5 (c = 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.14 (2H, s), 7.09 (2H, s), 3.90-3.79 (4H, m), 3.74-3.70 (2H, m), 2.25 (6H, s), 2.16 (2H, d, J = 14.0 Hz), 2.07 (2H, d, J = 14.4 Hz), 1.59 (6H, s), 1.31 (6H, s), 0.78 (18H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 146.8, 132.9, 130.0, 129.1, 128.8, 118.4, 98.1, 77.3, 77.0, 76.7, 75.7, 68.3, 46.8, 33.4, 32.9, 31.8, 30.7, 25.8, 20.5; IR (neat) ν 2953, 2866, 1645, 1591, 1451, 1392, 1357, 1317, 1281, 1260, 1228, 1214, 1187, 1163, 1102, 1029, 1003, 978, 939, 886, 815, 767, 730 cm^{-1}; ESI-MS, m/z = 587 ($[M+H]^+$); HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{37}H_{51}N_2O_4$, 587.38433, found, 587.38434.

(-)-(4*S*,4'*S*)-2,2'-((*R*)-4,4,4',4',6,6'-Hexamethyl-2,2'-spirobi[chroman]-8,8'-diyl)bis(4-benzyl-4,5-dihydroo xazole) ((*S,R,S*)-Bn-SPANbox, (*S,R,S*)-**1e**)



White solid, 81% yield; m.p. 104-105 °C; $[\alpha]_D^{20}$ = -40.8 (c = 0.49, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.32-7.14 (12H, m), 7.09 (2H, s), 4.24-4.22 (2H, m), 3.89 (2H, t, J = 9.0 Hz), 3.76 (2H, t, J = 7.8 Hz), 3.06-3.00 (2H, m), 2.35-2.28 (2H, m), 2.23-2.19 (8H, m), 2.13 (2H, d, J = 14.1 Hz), 1.64 (6H, s), 1.34 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 146.7, 138.3, 133.4, 130.3, 129.2, 129.0, 128.8, 128.5, 126.3, 118.4, 98.2, 71.6, 67.3, 46.7, 41.6, 33.3, 32.0, 30.7, 20.6; IR (neat) v 3386, 3026, 2957, 2923, 2860, 1731, 1648, 1631, 1602, 1495, 1451, 1359, 1314, 1301, 1266, 1187, 1160, 1115, 1092, 1026, 996, 981, 943, 891, 872, 844, 817, 791, 775, 747, 736, 699 cm^{-1}; ESI-MS, m/z = 655 ($[M+H]^+$), 677 ($[M+Na]^+$); HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{43}H_{47}N_2O_4$, 655.35303, found, 655.3522.

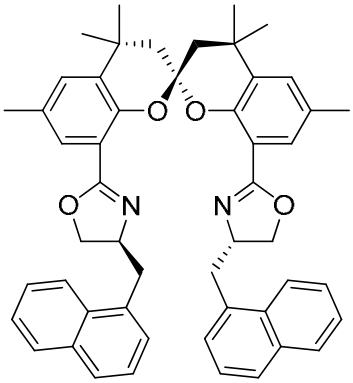
(+)-(4*S*,4'*S*)-2,2'-((*S*)-4,4,4',4',6,6'-Hexamethyl-2,2'-spirobi[chroman]-8,8'-diyl)bis(4-benzyl-4,5-dihydroo xazole) ((*S,S,S*)-Bn-SPANbox, (*S,S,S*)-**1e**)



White solid, 25% yield; m.p. 58-59 °C; $[\alpha]_D^{20}$ = +50.0 (c = 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.30-7.11 (14H, m), 4.25-4.22 (2H, m), 3.92 (2H, t, J = 8.8 Hz), 3.77 (2H, t, J = 7.6 Hz), 3.05-3.00 (2H, m), 2.29-2.11 (12H, m), 1.66 (6H, s), 1.35 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 146.5, 138.2, 133.2, 130.3, 129.2, 128.9, 128.9, 128.4, 126.2, 118.3, 98.1, 71.5, 67.1, 46.6, 41.4, 33.2, 31.9, 30.6, 20.5; IR (neat) v 2956, 2924, 2863, 1649, 1602, 1495, 1454, 1358, 1263, 1217, 1188, 1163, 1097, 1026, 997, 975, 940, 890, 870, 816, 749, 699 cm^{-1}; ESI-MS, m/z = 655 ($[M+H]^+$), 673 ($[M+H_2O+H]^+$); HRMS-ESI (m/z) $[M+H]^+$ calcd for $C_{43}H_{47}N_2O_4$, 655.35303, found, 655.3532.

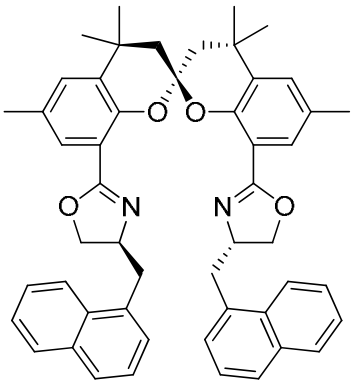
(+)-(4*S*,4'*S*)-2,2'-((*R*)-4,4,4',4',6,6'-Hexamethyl-2,2'-spirobi[chroman]-8,8'-diyl)bis(4-(naphthalen-1-ylmet

hyl)-4,5-dihydrooxazole) ((*S,R,S*)-1-Np-SPANbox, (*S,R,S*)-**1f**)



White solid, 44% yield; m.p. 86-86 °C; $[\alpha]_D^{20}$ = +94.8 (c = 0.62, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (2H, d, *J* = 8.0 Hz), 7.87 (2H, d, *J* = 7.6 Hz), 7.76 (2H, d, *J* = 8.4 Hz), 7.57-7.49 (4H, m), 7.42 (2H, t, *J* = 7.6 Hz), 7.27 (2H, d, *J* = 7.6 Hz), 7.20 (2H, s), 7.16 (2H, s), 4.45-4.42 (2H, m), 3.89-3.81 (4H, m), 3.67-3.62 (2H, m), 2.65-2.59 (2H, m), 2.65 (2H, d, *J* = 14.0 Hz), 2.18-2.15 (8H, m), 1.70 (6H, s), 1.26 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 146.8, 134.4, 133.9, 133.5, 131.9, 130.4, 129.3, 128.9, 128.7, 127.3, 126.6, 126.0, 125.7, 125.4, 123.8, 118.3, 98.3, 71.8, 66.2, 46.8, 39.1, 33.3, 32.0, 30.8, 20.5; IR (neat) *v* 3044, 2954, 2923, 2861, 1645, 1595, 1509, 1455, 1395, 1357, 1312, 1260, 1227, 1217, 1189, 1162, 1115, 1087, 1025, 998, 975, 940, 891, 870, 776, 733, 609 cm^{-1}; ESI-MS, *m*/*z* = 755 ($[M+H]^+$), 777 ($[M+Na]^+$); HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{51}H_{51}N_2O_4$, 755.38433 found, 755.38484.

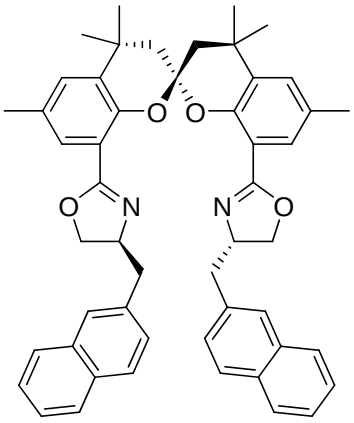
(-)-(4*S*,4'*S*)-2,2'-((*S*)-4,4,4',4',6,6'-Hexamethyl-2,2'-spirobi[chroman]-8,8'-diyl)bis(4-(naphthalen-1-ylmeth yl)-4,5-dihydrooxazole) ((*S,S,S*)-1-Np-SPANbox, (*S,S,S*)-**1f**)



White solid, 46% yield; m.p. 64-64 °C; $[\alpha]_D^{20}$ = -44.4 (c = 1.01, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (2H, d, *J* = 8.4 Hz), 7.84-7.84 (2H, m), 7.74 (2H, d, *J* = 8.4 Hz), 7.56-7.47 (4H, m), 7.42-7.38 (2H, m), 7.26-7.24 (4H, m), 7.16 (2H, s), 4.45-4.42 (2H, m), 3.82-3.80 (4H, m), 3.69-3.65 (2H, m), 2.75-2.69 (2H, m), 2.25 (2H, d, *J* = 14.0 Hz), 2.19 (6H, s), 2.15 (2H, d, *J* = 14.4 Hz), 1.64 (6H, s), 1.34 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 147.4, 134.2, 133.9, 133.7, 131.9, 130.3, 129.2, 129.1, 128.7, 126.7, 126.0, 125.6, 125.4, 123.8, 117.9, 98.9, 71.5, 66.3, 47.5, 39.0, 32.8, 31.8, 30.9, 20.5; IR (neat) *v* 3044, 2923, 2859, 1645, 1595, 1510, 1455, 1395, 1357, 1260, 1228, 1188, 1162, 1087, 1024, 998, 977, 940, 891,

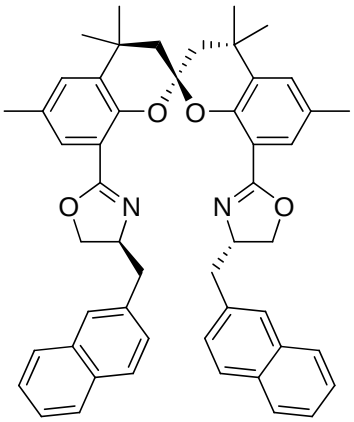
870, 777, 730 cm^{-1}; ESI-MS, *m*/*z* = 755 ($[M+H]^+$); HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{51}H_{51}N_2O_4$, 755.38433 found, 755.38656.

(+)-(4*S*,4'*S*)-2,2'-((*R*)-4,4,4',4',6,6'-Hexamethyl-2,2'-spirobi[chroman]-8,8'-diyl)bis(4-(naphthalen-2-ylmethyl)-4,5-dihydrooxazole) ((*S,R,S*)-2-Np-SPANbox, (*S,R,S*)-**1g**)



White solid, 62% yield; m.p. 84-85 °C; $[\alpha]_D^{20}$ = +57.4 (c = 1.15, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81-7.76 (6H, m), 7.58 (2H, s), 7.48-7.41 (4H, m), 7.32-7.29 (2H, m), 7.22-7.21 (2H, m), 7.07-7.06 (2H, m), 4.36-4.33 (2H, m), 3.90 (2H, t, *J* = 8.8 Hz), 3.84-3.80 (2H, m), 3.19-3.14 (2H, m), 2.51-2.46 (2H, m), 2.22 (2H, d, *J* = 14.4 Hz), 1.18 (6H, s), 2.14 (2H, d, *J* = 14.0 Hz), 1.67 (6H, s), 1.36 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 146.7, 135.8, 133.4, 132.1, 130.3, 129.2, 128.8, 128.1, 127.5, 127.4, 127.3, 126.0, 125.4, 118.4, 98.2, 71.6, 67.2, 41.7, 33.2, 32.0, 31.4, 30.7, 20.6; IR (neat) *v* 3324, 3051, 2924, 2851, 1731, 1627, 1599, 1536, 1507, 1456, 1358, 1311, 1265, 1218, 1188, 1163, 1115, 1087, 1025, 998, 975, 940, 891, 869, 815, 748, 639, 620 cm^{-1}; ESI-MS, *m*/*z* = 755 ($[M+H]^+$), 777 ($[M+Na]^+$); HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{51}H_{51}N_2O_4$, 755.38433 found, 755.38471.

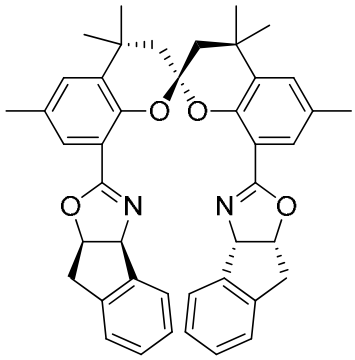
(-)-(4*S*,4'*S*)-2,2'-((*S*)-4,4,4',4',6,6'-Hexamethyl-2,2'-spirobi[chroman]-8,8'-diyl)bis(4-(naphthalen-2-ylmethyl)-4,5-dihydrooxazole) ((*S,S,S*)-2-Np-SPANbox, (*S,S,S*)-**1g**)



White solid, yield 57%; m.p. 65-66 °C; $[\alpha]_D^{20}$ = -28.7 (c = 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.80-7.75 (6H, m), 7.58 (2H, s), 7.47-7.41 (4H, m), 7.30 (2H, d, *J* = 8.8 Hz), 7.25 (2H, s), 7.17 (2H, s),

4.35-4.32 (2H, m), 3.89 (2H, t, *J* = 8.8 Hz), 3.76 (2H, t, *J* = 8.0 Hz), 3.26-3.22 (2H, m), 2.64-2.59 (2H, m), 2.24 (6H, s), 2.19 (2H, d, *J* = 14.0 Hz), 2.10 (2H, d, *J* = 14.4 Hz), 1.58 (6H, s), 1.35 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 147.3, 135.7, 133.6, 133.4, 131.1, 130.2, 129.1, 129.1, 128.0, 127.5, 127.4, 127.4, 125.9, 125.3, 117.9, 98.8, 71.3, 67.1, 47.4, 41.7, 32.7, 31.4, 30.8, 20.6; IR (neat) *v* 2924, 2852, 1730, 1649, 1599, 1508, 1455, 1359, 1315, 1263, 1227, 1189, 1170, 1090, 1024, 998, 976, 941, 891, 867, 816, 790, 749, 642, 620 cm^{-1}; ESI-MS, *m*/*z* = 755 ([M+H]$^+$); HRMS-ESI (*m*/*z*) [M+H]$^+$ calcd for $C_{51}H_{51}N_2O_4$, 755.38433 found, 755.38458.

(-)-(3a*S*,3a'*S*,8a*R*,8a'*R*)-2,2'-((*R*)-4,4,4',4',6,6'-Hexamethyl-2,2'-spirobi[chroman]-8,8'-diyl)bis(8,8a-dihydro-3aH-indeno[1,2-d]oxazole) ((*S,R,R,R,S*)-In-SPANbox, (*S,R,R,R,S*)-**1h**)



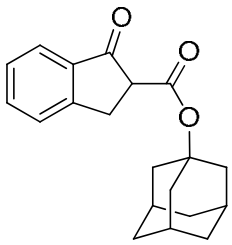
White solid, 40% yield; m.p. 246-247 °C; $[\alpha]_D^{20}$ = -188.7 (c = 0.44, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.42 (2H, m), 7.19-7.15 (8H, m), 7.04 (2H, s), 5.38 (2H, d, *J* = 8.4 Hz), 4.88 (2H, t, *J* = 7.5 Hz), 3.21-3.13 (2H, m), 2.87 (2H, d, *J* = 17.7 Hz), 2.25-2.18 (8H, m), 2.10 (2H, d, *J* = 14.1 Hz), 1.65 (6H, s), 1.32 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 147.3, 142.1, 140.0, 133.3, 129.6, 129.0, 128.7, 128.0, 127.0, 125.6, 125.0, 118.0, 98.3, 82.3, 46.8, 39.5, 33.1, 31.9, 30.8, 20.6; IR (neat) *v* 2953, 2922, 2855, 1662, 1458, 1353, 1315, 1264, 1228, 1215, 1186, 1165, 1113, 1092, 1022, 999, 951, 937, 894, 871, 855, 843, 754, 741, 709 cm^{-1}; ESI-MS, *m*/*z* = 651 ([M+H]$^+$); HRMS-ESI (*m*/*z*) [M+H]$^+$ calcd for $C_{43}H_{43}N_2O_4$, 651.32173, found, 651.3227.

Preparation of β-Keto Esters and 1,3-Diester.

All 1-admantyl esters were prepared by transesterification[5] of methyl ester which was prepared according to the reported procedures.[6] The *tert*-butyl ester **6b**[7] and **6k**[8] was prepared according to the reported procedures, respectively. The β-keto esters **6a-c**,[9, 7, 6] **6i-k**,[10, 5, 6] and α-hydroxy-β-keto esters **7a-b**,[10] **7c**,[11-12] **7i**,[10] **7k**,[13] are known compounds and their ^{1}H NMR data are consistent with the literature data.

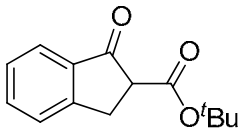
Characterization data for substrates **6a-m**:

1-Adamantyl 1-oxo-indan-2-carboxylate (**6a**)[9]



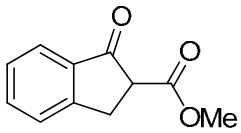
White solid, m.p. 109-111 °C (lit. m.p. 103 °C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (1H, d, *J* = 7.8 Hz), 7.61 (1H, t, *J* = 7.2 Hz), 7.49 (1H, d, *J* = 7.5 Hz), 7.38 (1H, t, *J* = 7.2 Hz), 3.61 (1H, dd, *J* = 8.1, 3.9 Hz), 3.53-3.46 (1H, m), 3.32 (1H, dd, *J* = 17.1, 8.1 Hz), 2.23-2.14 (9H, m), 1.71-1.61 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 167.8, 153.6, 135.3, 135.0, 127.5, 126.4, 124.4, 81.9, 54.4, 41.1, 36.0, 30.7, 30.2; IR (neat) ν 2911, 2852, 1734, 1713, 1642, 1572, 1457, 1353, 1258, 1207, 1162, 1055, 966, 763, 720 cm^{-1}; ESI-MS, *m*/*z* = 333 $[M+Na]^+$.

tert-Butyl 1-oxo-indan-2-carboxylate (**6b**)[7]



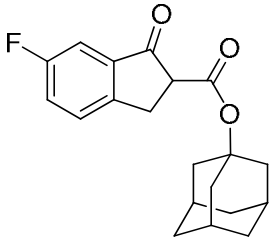
Pink solid, m.p. 41-43 °C (lit. m.p. 44-46 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (1H, d, *J* = 7.6 Hz), 7.61 (1H, t, *J* = 8.0 Hz), 7.49 (1H, d, *J* = 7.2 Hz), 7.38 (1H, t, *J* = 7.2 Hz), 3.63 (1H, dd, *J* = 8.0, 4.0 Hz), 3.52-3.47 (1H, m), 3.33 (1H, dd, *J* = 17.2, 8.4 Hz), 1.49 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 168.3, 153.6, 135.4, 135.2, 127.6, 126.5, 124.5, 82.0, 54.3, 30.3, 28.0; IR (neat) ν 2969, 1713, 1645, 1626, 1595, 1574, 1456, 1367, 1255, 1147, 1130, 760, 723 cm^{-1}; ESI-MS, *m*/*z* = 255 $[M+Na]^+$, 287$[M+MeOH+Na]^+$.

Methyl 1-oxo-indan-2-carboxylate (**6c**)[6]



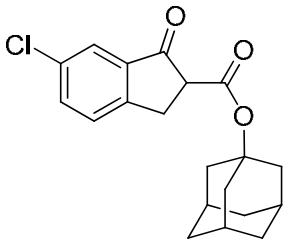
White solid, m.p. 51-53 °C (lit. m.p. 51-60 °C); ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.78 (1H, d, *J* = 6.6 Hz), 7.63 (1H, t, *J* = 7.5 Hz), 7.51 (1H, d, *J* = 7.5 Hz), 7.40 (1H, t, *J* = 7.5 Hz), 3.80 (3H, s), 3.75 (1H, dd, *J* = 8.1, 4.2 Hz), 3.58 (1H, dd, *J* = 17.4, 3.9 Hz), 3.39 (1H, dd, *J* = 17.1, 7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) *δ* 199.3, 169.4, 153.4, 135.3, 135.0, 127.6, 126.4, 124.5, 52.9, 52.6, 30.1; IR (neat) *ν* 3413, 3031, 2953, 2845, 1744, 1713, 1655, 1609, 1573, 1436, 1326, 1209, 1155, 989, 763, 680 cm^{-1}; ESI-MS, *m*/*z* = 191 $[M+H]^+$.

1-Adamantyl 6-flroro-1-oxo-indan-2-carboxylate (**6d**)



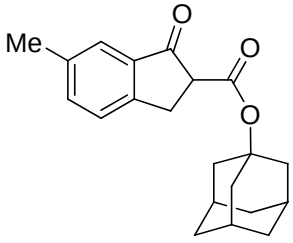
White solid, m.p. 139-141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.05 (3H, m), 3.68-3.26 (3H, m), 2.22-2.14 (9H, m), 1.74-1.62 (6H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.0, 167.4, 163.6, 161.1, 149.0, 138.1, 137.1, 127.9, 122.9, 116.0, 110.3, 110.1, 82.2, 55.3, 55.1, 41.6, 41.5, 41.1, 36.1, 36.0, 32.3, 30.8, 30.7, 29.8, 29.7, 29.6; IR (neat) *v* 2983, 2917, 2852, 2795, 2896,1724, 1632, 1580, 1475, 1403, 1352, 1301, 1259, 1197, 1139, 1052, 969, 898, 864, 807, 780, 734 cm^{-1}; EI-MS, *m*/*z* = 328 ([M]$^{+}$), 194, 177, 149,135,121, 101, 93, 79, 67, 55, 41; HRMS-EI (*m*/*z*) [M]$^{+}$ calcd for $C_{20}H_{21}O_3F$, 328.1475, found, 328.1474.

1-Adamantyl 6-chloro-1-oxo-indan-2-carboxylate (**6e**)



White solid, m.p. 172-174 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.35 (3H, m), 3.67-3.25 (3H, m), 2.22-2.13 (9H, m), 1.71-1.61 (6H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.6, 167.3, 151.6, 140.9, 138.8, 136.8, 135.0, 133.9, 132.7, 128.8, 127.6, 125.5, 124.1, 120.4, 105.4, 82.2, 81.3, 54.8, 41.6, 41.0, 36.0, 35.9, 32.4, 30.8, 30.7, 29. 8; IR (neat) *v* 2936, 2904, 2842, 1760, 1632, 1404, 1303, 1256, 1217, 1056, 872, 817, 774, 738 cm^{-1}; ESI-MS, *m*/*z* = 367 [M+Na]$^{+}$; HRMS-EI (*m*/*z*) [M]$^{+}$ calcd for $C_{20}H_{21}O_3Cl$, 344.1179, found, 344.1183.

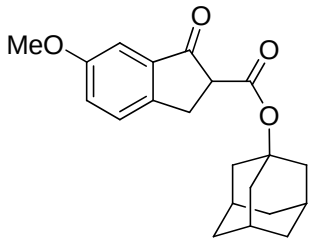
1-Adamantyl 6-methyl-1-oxo-indan-2-carboxylate (**6f**)



White solid, m.p. 110-112 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (1H, s), 7.43-7.35 (2H, m), 3.60 (1H, dd, *J* = 8.1, 3.9 Hz), 3.43 (1H, dd, *J* = 16.2, 3.6 Hz), 3.27 (1H, dd, *J* = 17.4, 8.1 Hz), 2.41-2.14 (9H, s), 1.70-1.61 (6H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.0, 167.9, 151.0, 137.4, 136.3, 135.5, 126.0, 124.2, 81.8, 54.7, 41.0, 36.1, 36.0, 30.7, 29.9; IR (neat) *v* 2910, 2852, 1731, 1710, 1642, 1584, 1573, 1493, 1456,

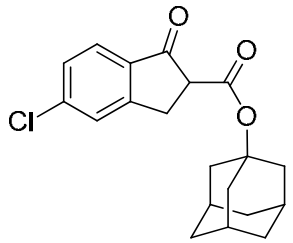
1278, 1148, 1054, 966, 866, 813, 736 cm^{-1}; ESI-MS, *m*/*z* = 347 $[M+Na]^+$; HRMS-ESI (*m*/*z*) $[M+Na]^+$ calcd for $C_{21}H_{24}NaO_3$, 347.1628, found, 347.1617.

1-Adamantyl 6-methoxy-1-oxo-indan-2-carboxylate (**6g**)



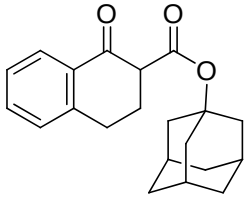
White solid, m.p. 126-128 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.30 (1H, d, *J* = 7.8 Hz), 7.14-7.11 (2H, m), 3.75 (3H, s), 3.55 (1H, dd, *J* = 8.1, 4.2 Hz), 3.32 (1H, dd, *J* = 15.3, 3.6 Hz), 3.17 (1H, dd, *J* = 17.1, 7.8 Hz), 2.15-2.07 (9H, m), 1.63-1.58 (6H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.0, 167.9, 159.5, 146.5, 136.6, 127.1, 124.6, 105.5, 82.0, 55.5, 55.2, 41.1, 36.0, 30.8, 29.6; IR (neat) *v* 2912, 2852, 1710, 1641, 1573, 1492, 1457, 1275, 1213, 1156, 1055, 1028, 865 cm^{-1}; ESI-MS, *m*/*z* = 363 $[M+Na]^+$; HRMS-ESI (*m*/*z*) $[M+Na]^+$ calcd for $C_{21}H_{24}NaO_4$, 363.1566, found, 362.1585.

1-Adamantyl 5-chloro1-oxo-indan-2-carboxylate (**6h**)



White solid, m.p. 124-126 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.67 (1H, d, *J* = 8.1 Hz), 7.48 (1H, s), 7.35 (1H, d, *J* = 8.1 Hz), 3.62 (1H, dd, *J* = 7.8, 3.6 Hz), 3.51-3.44 (1H, m), 3.30 (1H, dd, J = 17.4, 8.1 Hz), 2.21-2.14 (9H, m), 1.70-1.65 (6H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.4, 167.4, 155.0, 141.6, 133.8, 128.4, 126.6, 125.5, 82.2, 54.4, 41.0, 36.0, 30.7, 29.9; IR (neat) *v* 2911, 2852, 1733, 1714, 1646, 1599, 1565, 1421, 1353, 1257, 1183, 1102, 1054, 967, 814, 766 cm^{-1}; EI-MS, *m*/*z* = 344 ($[M]^+$), 309, 192, 152, 135, 119, 95, 79, 67; HRMS-EI (*m*/*z*) $[M]^+$ calcd for $C_{11}H_9O_3F$, 344.1179, found, 344.1181.

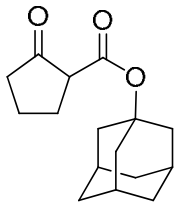
1-Adamantyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**6i**)[10]



White solid, m.p. 89-92 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 12.6 (0.79H, br, HO of enol), 8.03-7.76 (1H,

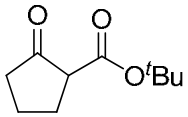
m), 7.48-7.14 (3H, m), 3.50-3.47 (0.21H, m, HC of ketone), 3.04-2.76 (2H, m), 2.52-2.30 (2H, m), 2.20-2.13 (9H, m), 1.73-1.65 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 172.4, 169.1, 164.4, 143.5, 139.3, 133.6, 130.3, 130.1, 128.7, 127.5, 127.2, 126.7, 126.4, 124.1, 98.3, 81.8, 81.3, 55.4, 41.5 41.2, 36.2, 36.1, 30.9, 30.8, 27.8, 27.5, 26.5, 20.9; IR (neat) ν 2909, 2858, 1630, 1568, 1452, 1378, 1349, 1326, 1263, 1210, 1083, 1046, 845, 769, 750, 731 cm^{-1}; EI-MS, m/z = 324 ([M]$^+$), 173, 144, 135, 115, 107, 93, 79.

1-Adamantyl 2-oxocyclopentanecarboxylate (**6j**)[5]



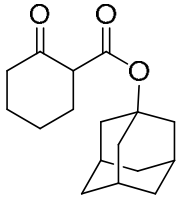
Pink oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.04 (1H, t, J = 9.0 Hz), 2.31-2.07 (13H, m), 1.91-1.61 (8H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.9, 168.3, 81.6, 55.7, 41.1, 38.0, 36.0, 30.7, 27.4, 20.8; IR (neat) ν 3376, 2911, 2852, 1753, 1720, 1455, 1405, 1350, 1251, 1188, 1053, 931, 834, 814 cm^{-1}; ESI-MS, m/z = 285 ([M+Na]$^+$), 317 ([M+MeOH+Na]$^+$).

tert-Butyl 2-oxocyclopentanecarboxylate (**6k**)[8]



Colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.04 (1H, t, J = 9.0 Hz), 2.31-2.21 (4H, m), 2.17-2.07 (1H, m), 1.89-1.79 (1H, m), 1.47 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.9, 168.6, 81.6, 55.6, 38.0, 27.9, 27.3, 20.8; IR (neat) ν 2977, 2884, 1755, 1722, 1652, 1455, 1369, 1341, 1256, 1157, 1110, 983, 844 cm^{-1}; ESI-MS, m/z = 207 ([M+Na]$^+$), 239 ([M+MeOH+Na]$^+$).

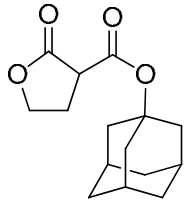
1-Adamantyl 2-oxocyclohexanecarboxylate (**6l**)



White solid, m.p. 69-70 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.3 (0.75 H, br), 3.51-3.49 (0.25H, m), 2.26-2.16 (13H, m), 1.67-1.55 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 171.2, 98.8, 80.6, 41.4, 36.1, 30.7, 29.0, 22.7, 22.4, 21.9; IR (neat) ν 2912, 2854, 1736, 1717, 1649, 1613, 1456, 1390, 1259, 1219, 1175, 1062, 967, 920, 836, 814 cm^{-1}; ESI-MS, m/z = 299 [M+Na]$^+$; HRMS-ESI (m/z) [M+Na]$^+$ calcd for $C_{17}H_{24}NaO_3$, 299.1621, found, 299.1617; Anal. cacld for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C,

73.93; H, 9.17.

1-Adamantyl 2-oxotetrahydrofuran-3-carboxylate (**6m**)



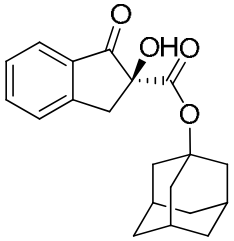
White solid, m.p. 79-82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.47-4.41 (1H, m), 4.33-4.27 (1H, m), 3.43 (1H, dd, J = 9.2, 7.2 Hz), 2.65-2.56 (1H, m), 2.51-2.42 (1H, m), 2.19-14 (9H, m), 1.72-1.58 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 166.5, 83.0, 67.2, 47.0, 41.1, 36.0, 30.8, 26.5; IR (neat) ν 2911, 2853, 1773, 1726, 1456, 1349, 1257, 1147, 1050, 1017,967, 802, 687 cm^{-1}; ESI-MS, m/z = 264 $[M]^+$, 134, 92, 95, 79, 41; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{15}H_{20}O_4$, 264.1362, found, 264.1364.

A Typical Procedure for Enantioselective Hydroxylation of β-Keto Esters or 1,3-Diester:

$Zn(OTf)_2$ (0.9 mg, 0.0025 mmol) and (*S,R,S*)-**1** (0.0055 mmol) were weighed in a nitrogen-filled glovebox and transferred into a pre-dried Schlenk tube equipped with a Teflon-coated magnetic stirring bar. The Schlenk tube was further vacuumized for 2 h before dry 1,2-dichloroethane (1.0 mL) was added under argon atmosphere. The resultant solution was stirred for 1 h and the substrate β-keto ester or 1,3-diester (0.25 mmol) was added to the solution. After stirring for additional 30 min, the oxidant (0.30 mmol) was added to the solution in one portion. The mixture was stirred at the defined temperature and the reaction process was monitored by TLC. The reaction was quenched by addition of saturated aqueous $NaHSO_3$ solution when the conversion of starting material was completed. The mixture was then extracted with dichloromethane, the combined organic phase was washed with brine and then dried over Na_2SO_4. After removal of the solvent under vacuum evaporation, the residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as the eluent to afford **7**. The enantiomeric excess of the obtained hydroxylation product **7** was determined by HPLC or GC on a chiral stationary phase.

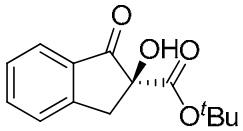
Characterization Data for Hydroxylation Products.

(*S*)-(+)-1-Adamantyl 2-hydroxy-1-oxo-indan-2-carboxylate (**7a**) [10]



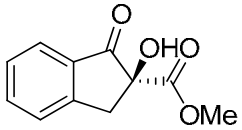
Colorless oil, >99% yield, 98% *ee*; $[\alpha]_D^{20}$ = +19.7 (c = 0.89, $CHCl_3$) [lit. $[\alpha]_D^{20}$ = +19.7 (c = 0.60, $CHCl_3$) for 91% *ee* (*S*)]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (1H, d, *J* = 7.8 Hz), 7.67-7.62 (1H, m), 7.48-7.38 (2H, m), 4.03 (1H, br), 3.65 (1H, d, *J* = 17.4 Hz), 3.22 (1H, d, *J* = 17.1 Hz), 2.11 (3H, s), 1.97-1.95 (6H, m), 1.60-1.59 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 170.1, 152.3, 135.7, 133.9, 127.8, 126.2, 125.0, 83.8, 80.5, 40.8, 39.5, 35.8, 30.7; IR (neat) *v* 3476, 2912, 2852, 1740, 1608, 1457, 1249, 1196, 1103, 1049, 964, 881, 754, 695, 669 cm^{-1}; EI-MS, *m*/*z* = 243, 195, 179, 152, 135, 103, 95, 76, 51. The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 90: 10, flow rate: 1.0 mL/min, 254 nm, t_{R1} = 15.6 min (major), t_{R2} = 24.6 min (minor).

(*S*)-(+)-*tert*-Butyl 2-hydroxy-1-oxo-indan-2-carboxylate (**7b**) [10]



White solid, >99% yield, 94% *ee*; m.p. 63-66 °C; $[\alpha]_D^{20}$ = +37.8 (c = 1.09, $CHCl_3$) [lit. $[\alpha]_D^{20}$ = +34.1 (c = 0.42, $CHCl_3$) for 89% *ee* (*S*)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (1H, d, *J* = 8.0 Hz), 7.64 (1H, t, *J* = 7.2 Hz), 7.48 (1H, d, *J* = 7.6 Hz), 7.40 (1H, t, *J* = 7.2 Hz), 4.22 (1H, br), 3.66 (1H, d, *J* = 17.2 Hz), 3.22 (1H, d, *J* = 17.2 Hz), 1.36 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 170.4, 152.2, 135.7, 133.7, 127.7, 126.1, 124.8, 83.6, 80.4, 39.3, 27.5; IR (neat) *v* 3409, 2924, 2852, 1735, 1708, 1603, 1465, 1369, 1290, 1252, 1210, 1150, 1127, 1102, 924, 836, 816, 765, 744, 721, 694, 678 cm^{-1}; EI-MS, *m*/*z* = 205, 192, 164, 147, 136, 130, 118, 91, 65, 57, 41. The enantiomeric excess was determined by HPLC on Chiralpak OJ column, hexane: isopropanol = 90: 10, flow rate: 1.0 mL/min, 254 nm, t_{R1} = 7.7 min (major), t_{R2} = 12.2 min (minor).

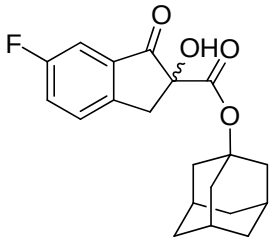
(*S*)-(+)-Methyl 2-hydroxy-1-oxo-indan-2-carboxylate (**7c**) [11]



White solid, >99% yield, 90% *ee*; m.p. 135-137 °C [lit.[12] m.p. 131-132 °C]; $[\alpha]_D^{20}$ = +44.9 (c = 1.01, $CHCl_3$) [lit. $[\alpha]_D^{25}$ = +52.1 (c = 1.0, $CHCl_3$) for >98% *ee* (*S*)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (1H, d, *J* = 7.6 Hz), 7.68 (1H, t, *J* = 7.6 Hz), 7.50 (1H, d, *J* = 7.6 Hz), 7.44 (1H, t, J = 7.6 Hz), 4.06 (1H, b), 3.74 (1H, d, *J* = 17.2 Hz), 3.74 (3H, s), 3.26 (1H, d, *J* = 17.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 171.9,

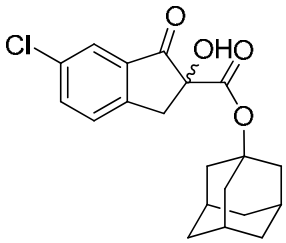
152.2, 136.2, 133.5, 128.1, 126.5, 125.3, 80.3, 53.4, 39.2; IR (neat) *v* 3404, 2958, 2923, 2853, 1746, 1706, 1605, 1463, 1258, 1202, 1187, 1116, 1103, 801, 754, 693 cm^{-1}; EI-MS, *m*/*z* = 206 ($[M]^+$), 147, 118, 97, 91, 83, 70, 57, 55, 41. The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 90: 10, flow rate: 1.0 mL/min, 254 nm, t_{R1} = 20.2 min (major), t_{R2} = 21.9 min (minor).

(+)-1-Adamantyl 6-fluoro-2-hydroxy-1-oxo-indan-2-carboxylate (**7d**)



White solid, >99% yield, 93% *ee*; m.p. 64-65 °C; $[\alpha]_D^{20}$ = +20.6 (c = 1.00, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 7.47-7.33 (3H, m), 4.08 (1H, br), 3.61 (1H, d, *J* = 17.4 Hz), 3.18 (1H, d, *J* = 16.8 Hz), 2.12 (3H, s), 1.97-1.96 (6H, m), 1.60 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 169.7, 160.6, 147.7, 135.6, 127.7, 123.4; 110.6, 84.2, 81.1, 40.8, 38.9, 35.7, 30.7; IR (neat) *v* 3473, 3066, 2913, 2853, 1743, 1613, 1487, 1440, 1368, 1257, 1158, 1049, 964, 882, 817, 768 cm^{-1}; EI-MS, *m*/*z* = 344 ($[M]^+$), 288, 259, 243, 229, 212, 195, 184, 179, 165, 152; HRMS-EI (*m*/*z*) $[M]^+$ calcd for $C_{20}H_{21}O_4F$, 344.1424, found, 344.1425. The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 90: 10, flow rate: 1.0 mL/min, 254 nm, t_{R1} = 13.3 min (major), t_{R2} = 26.0 min (minor).

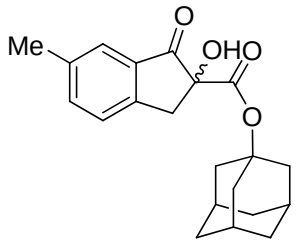
(+)-1-Adamantyl 6-chloro-2-hydroxy-1-oxo-indan-2-carboxylate (**7e**)



Yellow solid, >99% yield, 95% *ee*; m.p. 91-93 °C; $[\alpha]_D^{20}$ = +2.1 (c = 1.02, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 7.74 (1H, s), 7.60 (1H, d, *J* = 8.1 Hz), 7.42 (1H, d, *J* = 8.1 Hz), 4.09 (1H, br), 3.62 (1H, d, *J* = 16.8 Hz), 3.18 (1H, d, *J* = 16.8 Hz), 2.12 (3H, s), 1.95 (6H, s), 1.60 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 169.7, 150.3, 135.7, 135.4, 134.1, 127.4, 124.6, 84.2, 80.8, 40.8, 39.1, 35.7, 30.7; IR (neat) *v* 3471, 2912, 1853, 1750, 1720, 1600, 1467, 1429, 1368, 1242, 1201, 1120, 1048, 964, 880, 815, 754, 696 cm^{-1}; EI-MS, *m*/*z* = 181, 169, 152, 135, 125, 107, 93, 79, 77, 67, 55; HRMS-EI (*m*/*z*) $[M]^+$ calcd for $C_{20}H_{21}O_4Cl$, 360.1128, found, 360.1132. The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 90: 10, flow rate: 1.0 mL/min, 254 nm, t_{R1} = 12.9 min (major), t_{R2}

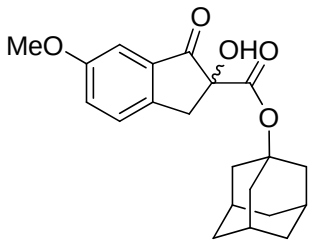
= 24.4 min (minor).

(+)-1-Adamantyl 2-hydroxy-6-methyl-1-oxo-indan-2-carboxylate (**7f**)



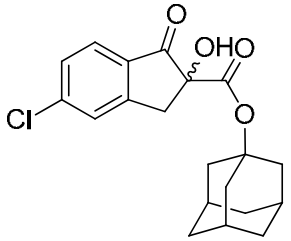
White solid, >99% yield, 97% *ee*; m.p. 86-88 °C; $[\alpha]_D^{20}$ = +13.0 (c = 0.98, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (1H, s), 7.45 (1H, d, *J* = 7.8 Hz), 7.34 (1H, d, *J* = 8.1 Hz), 4.02 (1H, br), 3.60 (1H, d, *J* = 17.1 Hz), 3.15 (1H, d, *J* = 16.8 Hz), 2.41 (3H, s), 2.17 (3H, s), 1.96 (6H, s), 1.59 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 170.3, 149.7, 137.8, 137.0, 134.0, 125.8, 124.8, 83.7, 80.7, 40.8, 39.1, 35.8, 30.7, 21.0; IR (neat) *v* 3464, 2912, 2852, 1716, 1615, 1492, 1456, 1367, 1278, 1189, 1129, 1049, 964, 884, 766 cm^{-1}; EI-MS, *m*/*z* = 340 ($[M]^+$), 176, 161, 144, 135, 117, 107, 93, 79, 67, 55; HRMS-EI (*m*/*z*) $[M]^+$ calcd for $C_{21}H_{24}O_4$, 340.1675, found, 340.1676. Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 73.97; H, 6.96. The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 90: 10, flow rate: 1.0 mL/min, 254 nm, t_{R1} = 15.8 min (major), t_{R2} = 30.8 min (minor).

(+)-1-Adamantyl 2-hydroxy-6-methoxy-1-oxo-indan-2-carboxylate (**7g**)



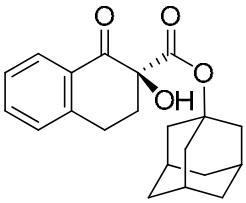
White solid, >99% yield, 96% *ee*; m.p. 87-89 °C; $[\alpha]_D^{20}$ = +5.8 (c = 1.01, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (1H, d, *J* = 8.4 Hz), 7.25-7.21 (2H, m), 4.05 (1H, br), 3.85 (3H, s), 3.57 (1H, d, *J* = 16.8 Hz), 3.13 (1H, d, *J* = 16.5 Hz), 2.17 (3H, s), 1.96 (6H, s), 1.71 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 170.2, 159.5, 145.3, 135.0, 126.9, 125.1, 105.9, 83.8, 81.1, 55.5, 40.8, 38.9, 35.8, 30.7; IR (neat) *v* 3480, 2912, 2852, 1740, 1717, 1616, 1493, 1456, 1254, 1195, 1104, 1049, 964, 884 cm^{-1}; EI-MS, *m*/*z* = 356 ($[M]^+$), 338, 300, 243, 204, 179 152, 135, 120, 95, 93, 77, 67, 51; HRMS-EI (*m*/*z*) $[M]^+$ calcd for $C_{21}H_{24}O_5$, 356.1624, found, 356.1628. The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 90: 10, flow rate: 1.0 mL/min, 254 nm, t_{R1} = 20.3 min (major), t_{R2} = 35.8 min (minor).

(+)-1-Adamantyl 5-chloro-2-hydroxy-1-oxo-indan-2-carboxylate (**7h**)



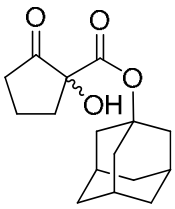
White solid, 98% yield, 96% *ee*; m.p. 124-126 °C; $[\alpha]_D^{20}$ = +51.2 (c = 1.02, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 7.72 (1H, d, *J* = 8.4 Hz), 7.47 (1H, s), 7.39 (1H, d, *J* = 8.4 Hz), 4.09 (1H, br), 3.63 (1H, d, *J* = 17.4 Hz), 3.19 (1H, d, *J* = 17.4 Hz), 2.12 (3H, s), 1.97 (6H, s), 1.60 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.9, 169.7, 153.6, 142.3, 132.3, 128.7, 126.4, 126.0, 84.1, 80.4, 40.9, 39.1, 35.7, 30.7; IR (neat) *v* 3346, 2912, 2850, 1742, 1734, 1599, 1577, 1417, 1261, 1198, 1065, 927, 792, 678 cm^{-1}; EI-MS, *m*/*z* = 360 ($[M]^+$), 224, 207, 196, 181, 169, 163, 135, 93, 79; HRMS-EI (*m*/*z*) $[M]^+$ calcd for $C_{20}H_{21}O_4Cl$, 360.1128, found, 360.1117. The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 90:10, flow rate: 1.0 mL/min, 254 nm, t_{R1} = 15.6 min (major), t_{R2} = 25.2 min (minor).

(*S*)-(-)-1-Adamantyl 2-hydroxy-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (**7i**)[10]



White solid, >99% yield, 94% *ee*; m.p. 106-108 °C; $[\alpha]_D^{20}$ = -4.6 (c = 1.02, $CHCl_3$) [lit. $[\alpha]_D^{26}$ = -3.7 (c = 0.4, $CHCl_3$) for 82% ee (*S*)]; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (1H, d, *J* = 8.0 Hz), 7.52 (1H, t, *J* = 7.6 Hz), 7.34 (1H, t, *J* = 7.6 Hz), 7.60 (1H, d, *J* = 8.4 Hz), 4.26 (1H, br), 3.12 (2H, t, *J* = 7.4 Hz), 2.67-2.61 (1H, m), 2.26-2.19 (1H, m), 2.12 (3H, s), 2.01 (6H, s), 1.61 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 169.6, 143.8, 134.0, 130.7, 128.7, 127.9, 126.8, 83.4, 77.7, 40.9, 35.9, 32.8, 30.7, 25.7; IR (neat) *v* 3459, 2921, 2892, 2853, 1727, 1681, 1454, 1255, 1195, 1128, 1108, 1048, 964, 921, 865, 826, 799, 734, 719 cm^{-1}; ESI-MS, *m*/*z* = 363 ($[M+Na]^+$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 90: 10, flow rate: 1.0 mL/min, 254 nm, t_{R1} = 13.1 min (major), t_{R2} = 20.1 min (minor).

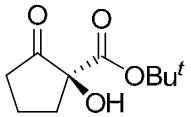
(-)-1-Adamantyl 1-hydroxy-2-oxocyclopentanecarboxylate (**7j**)



White solid, >99% yield, 97% *ee*; m.p. 77-78 °C; $[\alpha]_D^{20}$ = -10.4 (c = 1.00, $CHCl_3$). ^1H NMR (300 MHz,

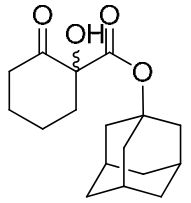
$CDCl_3$) δ 3.71 (1H, br), 2.45-2.43 (3H, m), 2.34-2.10 (12H, m), 1.66 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.0, 170.4, 83.9, 79.7, 41.0, 35.8, 35.6, 34.8, 30.8, 18.3; IR (neat) ν 3487, 2912, 2854, 1756, 1727, 1457, 1255, 1173, 1103, 1052, 965, 887 cm^{-1}; ESI-MS, m/z = 301 $[M+Na]^+$; Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.00; H, 7.86. The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 90: 10, flow rate: 1.0 mL/min, 227 nm, t_{R1} = 9.0 min (major), t_{R2} = 11.0 min (minor).

(*S*)-(-)-*tert*-butyl 1-hydroxy-2-oxocyclopentanecarboxylate (**7k**)[13]



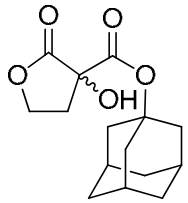
Yellow oil, >99% yield, 95% *ee*; $[\alpha]_D^{20}$ = -8.9 (c = 1.00, $CHCl_3$) [lit. $[\alpha]_D$ = -4.3 (c = 1.9, CH_2Cl_2) for 93% ee (*S*)]; ^1H NMR (300 MHz, $CDCl_3$) δ 3.68 (1H, br), 2.48-2.38 (3H, m), 2.13-2.03 (3H, m), 1.47 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.9, 170.7, 83.8, 79.6, 35.8, 34.8, 27.7, 18.3; IR (neat) ν 3484, 2963, 2928, 2855, 1757, 1729, 1459, 1371, 1260, 1148, 1098, 844, 802 cm^{-1}; ESI-MS, m/z = 223 $[M+Na]^+$ The enantiomeric excess was determined by GC on Chiralcel beta-120 column, temperatue program: 120 °C, Flow rate: 1.0 mL/min, t_{R1} = 27.0 min (major), t_{R2} = 28.3 min (minor).

(-)-1-Adamantyl 1-hydroxy-2-oxocyclohexanecarboxylate (**7l**)



White solid, 98% yield, 93% *ee*; m.p. 74-75 °C; $[\alpha]_D^{20}$ = -79.9 (c = 1.02, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 4.27 (1H, br), 2.68-2.49 (3H, m), 2.18-2.02 (9H, m), 1.85-1.56 (11H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.6, 168.7, 83.1, 81.1, 41.0, 38.9, 37.4, 35.9, 30.8, 26.9, 22.1; IR (neat) ν 3462, 2913, 2855, 1721, 1453, 1439, 1355, 1263, 1210, 1114, 1050, 966, 877, 736 cm^{-1}; ESI-MS, m/z = 315 $[M+Na]^+$; HRMS-ESI (m/z) $[M+Na]^+$ calcd for $C_{17}H_{24}O_4Na$, 315.1566, found, 315.1566. The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 95: 5, flow rate: 0.7 mL/min, 210 nm, t_{R1} = 10.6 min (minor), t_{R2} = 11.3 min (major).

(+)-1-Adamantyl 3-hydroxy-2-oxotetrahydrofuran-3-carboxylate (**7m**)



White solid, >99% yield, 99% *ee*; m.p. 117-120 °C; $[\alpha]_D^{20}$ = +14.3 (c = 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 4.49-4.40 (2H, m), 4.01 (1H, br), 2.72-2.66 (1H, m), 2.51-2.44 (1H, m), 2.21 (3H, s), 2.13 (6H, s), 1.67 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 168.6, 85.3, 75.6, 65.8, 41.0, 35.7, 34.2, 30.8; IR (neat) ν 3497, 2918, 2852, 1775, 1727, 1256, 1217, 1180, 1155, 1057, 1046, 1057, 1046, 1016, 897, 846, 733, 665 cm^{-1}; EI-MS, *m*/*z* = 135, 107, 93, 91, 79, 77, 67, 55; HRMS-EI (*m*/*z*) $[M]^+$ calcd for $C_{15}H_{20}O_5$, 280.1311, found, 280.1308. The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 90: 10, flow rate: 1.0 mL/min, 216 nm, t_{R1} = 16.0 min (major), t_{R2} = 23.7 min (minor).

Reference

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Crystal Data and Structure Refinement for (*S,R,S*)-**1a**

Identification code	cd28543
Empirical formula	C41 H42 N2 O4
Formula weight	626.77
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 11.0978(11) A alpha = 90 deg. b = 10.0421(10) A beta = 99.529(2) deg. c = 15.8898(16) A gamma = 90 deg.
Volume	1746.4(3) A^3
Z, Calculated density	2, 1.192 Mg/m^3
Absorption coefficient	0.076 mm^-1
F(000)	668
Crystal size	0.346 x 0.327 x 0.086 mm
Theta range for data collection	1.86 to 27.00 deg.
Limiting indices	-14<=h<=14, -12<=k<=12, -12<=l<=20
Reflections collected / unique	10343 / 4006 [R(int) = 0.0571]
Completeness to theta = 27.00	99.3 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.79262
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4006 / 1 / 430
Goodness-of-fit on F^2	1.100
Final R indices [I>2sigma(I)]	R1 = 0.0608, wR2 = 0.1302
R indices (all data)	R1 = 0.0750, wR2 = 0.1373
Absolute structure parameter	-10(10)
Largest diff. peak and hole	0.177 and -0.157 e.A^-3

The crystal data have been deposited at the Cambridge Crystallographic Data Centre (CCDC), deposition number: CCDC 787243. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ UK (http://www.ccdc.cam.ac.uk/).

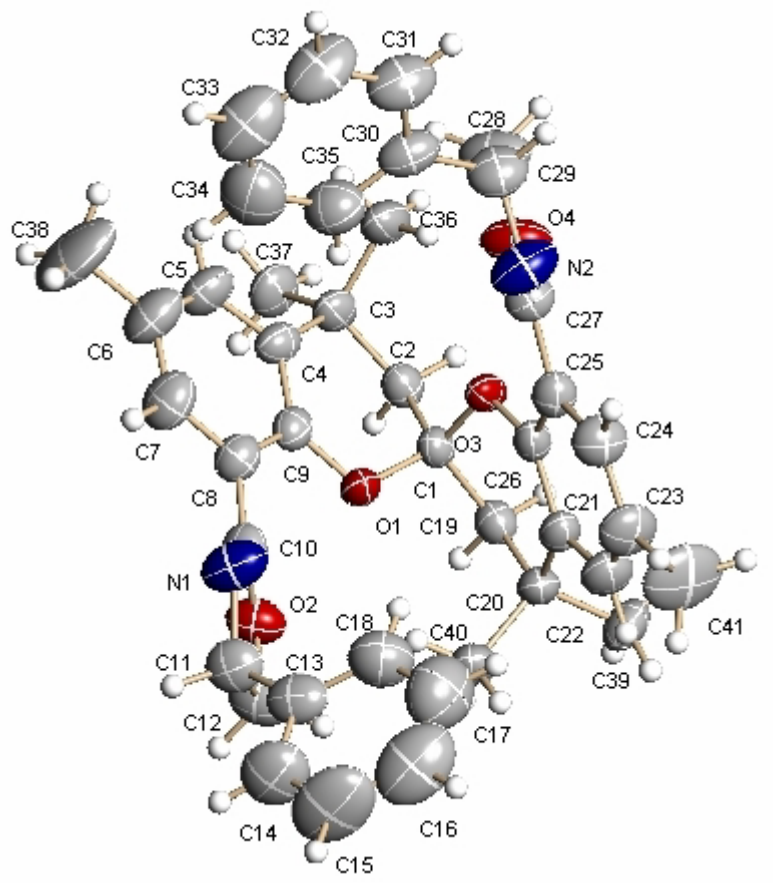


Figure S1. The molecular structure of (*S,R,S*)-**1a**

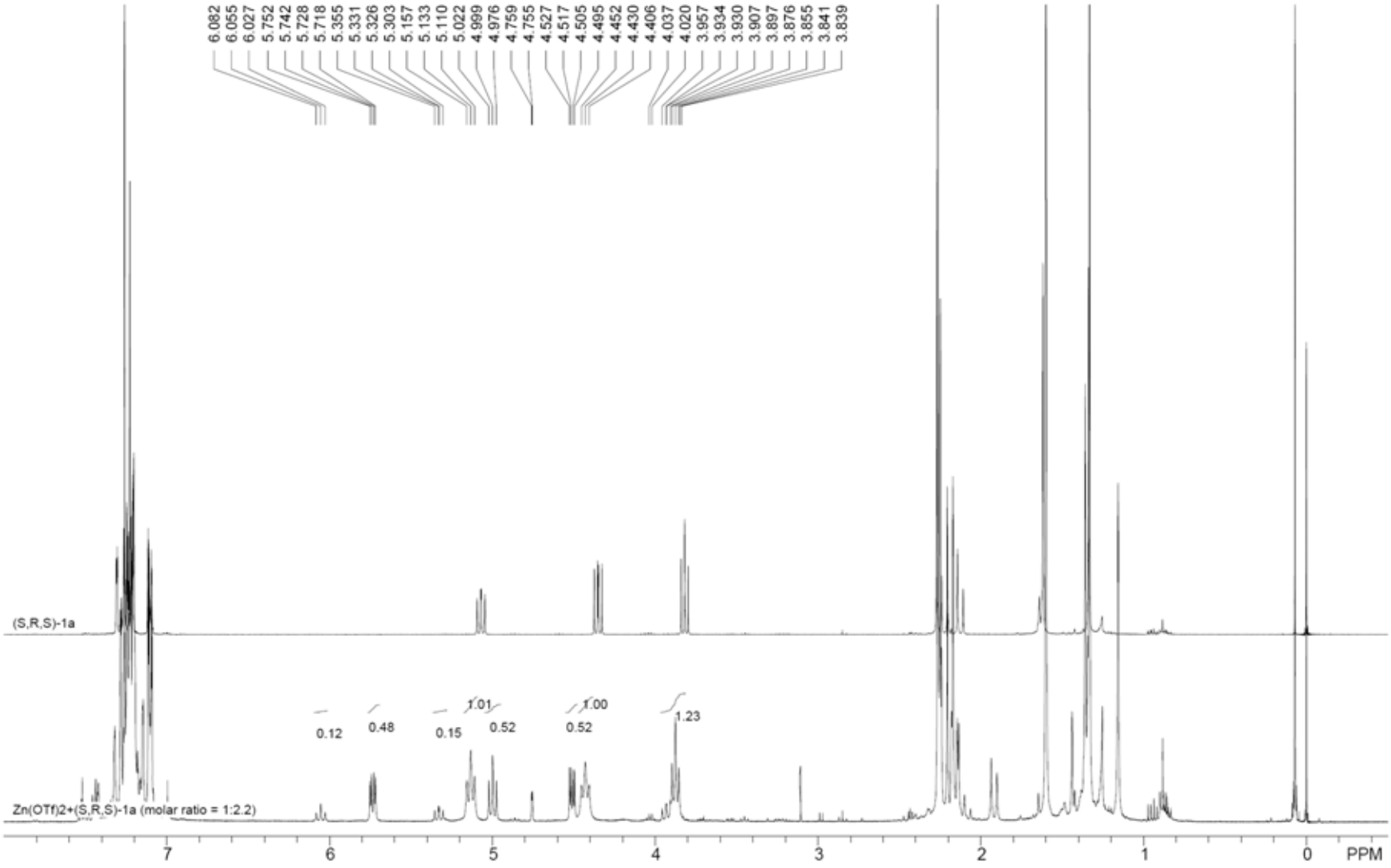


Figure S2. ^{1}H NMR spectra of (*S*,*R*,*S*)-**1a** (upper) and its in-situ prepared $Zn(OTf)_2$ complex [(*S*,*R*,*S*)-**1a**/$Zn(OTf)_2$ = 2.2/1] (lower) in $CDCl_3$.

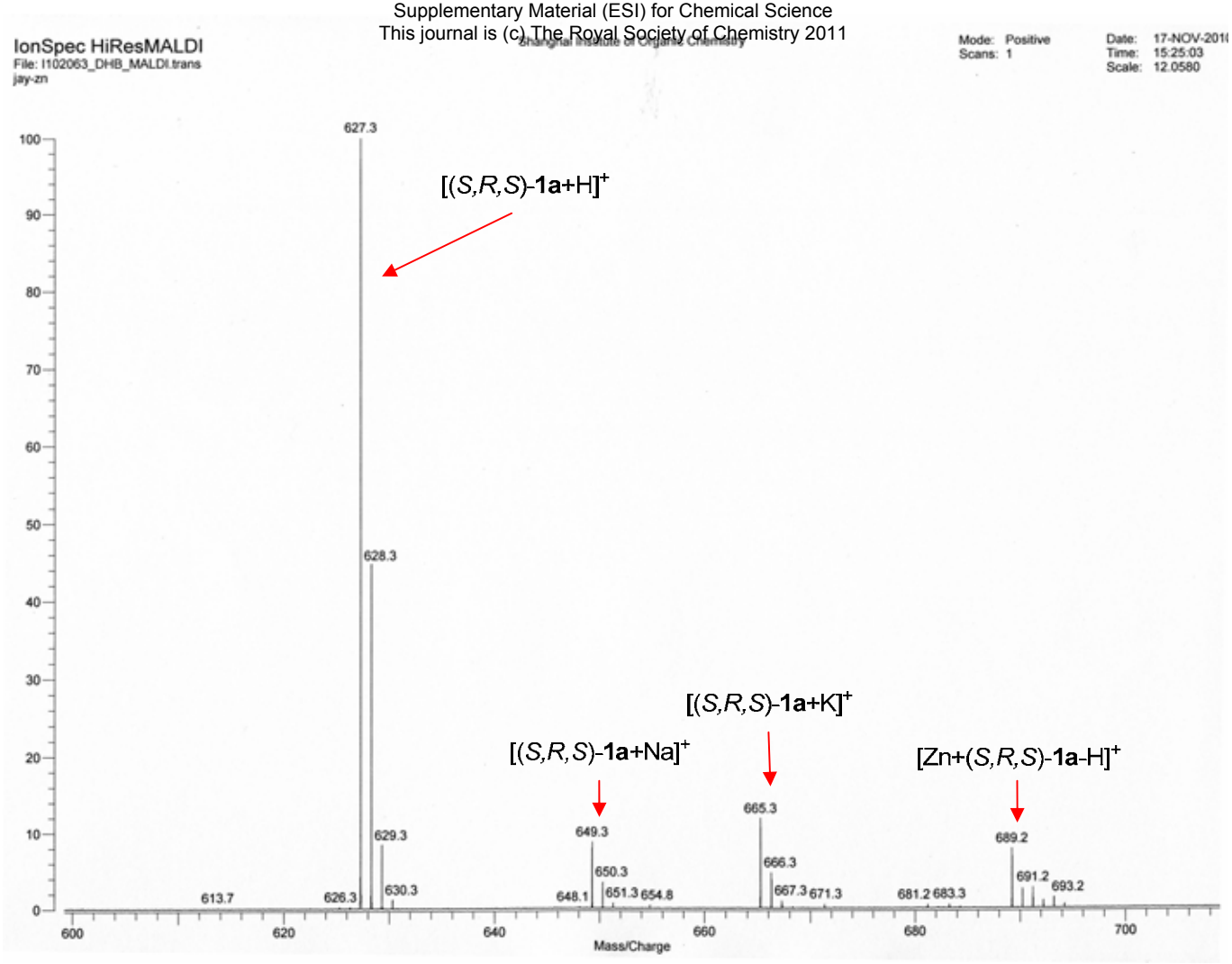
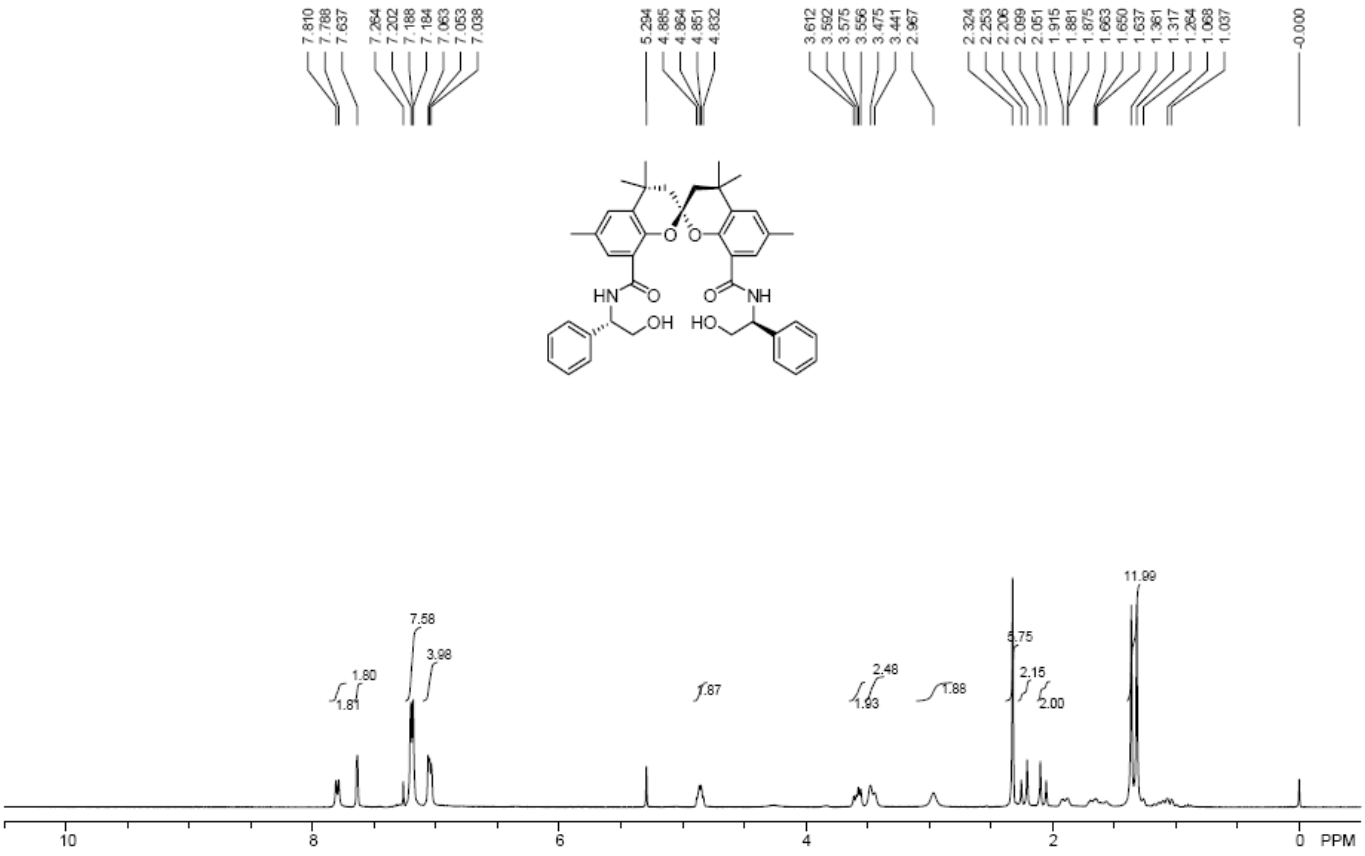
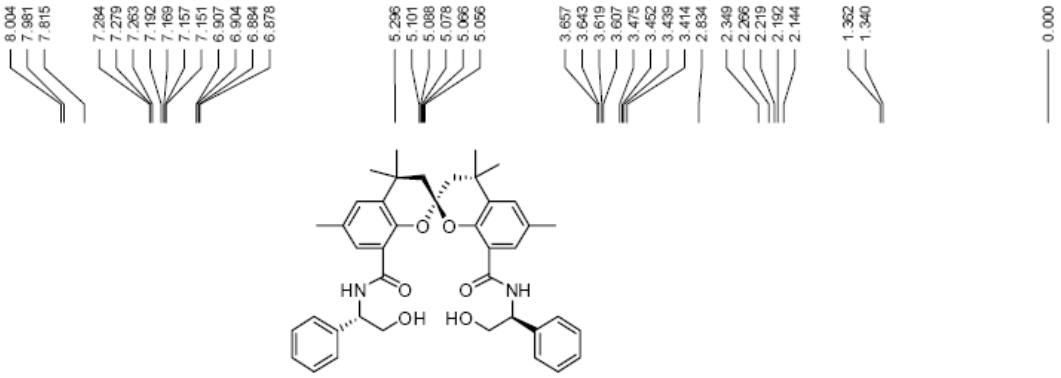


Figure S3. MALDI-TOF-MS (DHB) spectra of (*S*,*R*,*S*)-**1a**/Zn(OTf)$_2$ complex prepared in-situ in $CDCl_3$ [(*S*,*R*,*S*)-**1a**/Zn(OTf)$_2$ = 2.2/1].

HRMS [MALDI-TOF (DHB)] (*m/z*): [Zn + (*S*,*R*,*S*)-**1a** – H]$^+$ calcd for $C_{41}H_{41}N_2O_4{}^{64}Zn$, 689.23523, found, 689.2349.

^{1}H NMR spectra

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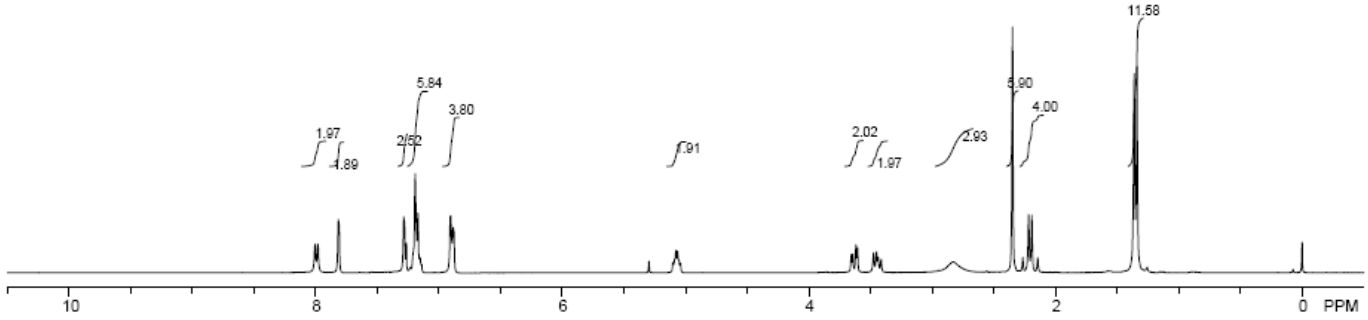
NH
HO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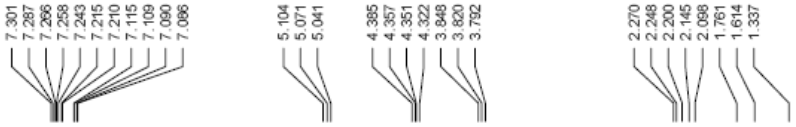
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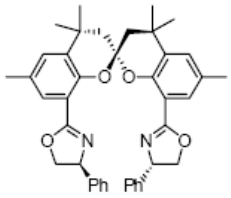
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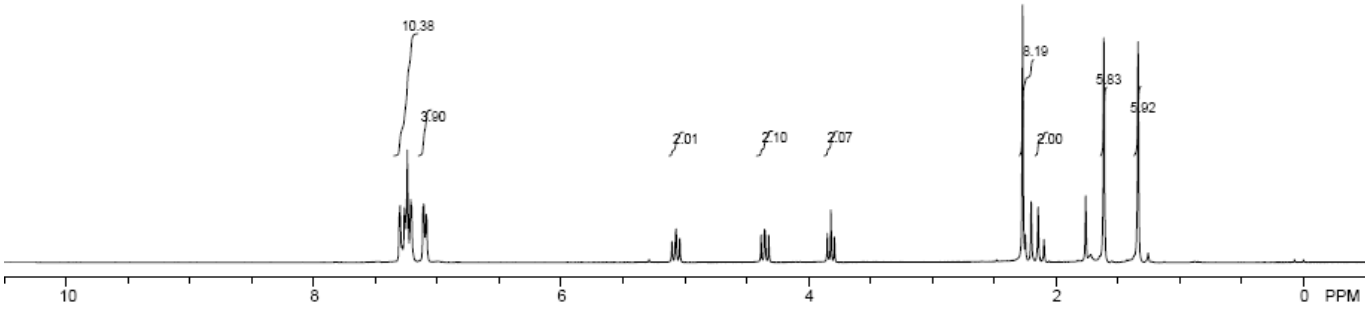
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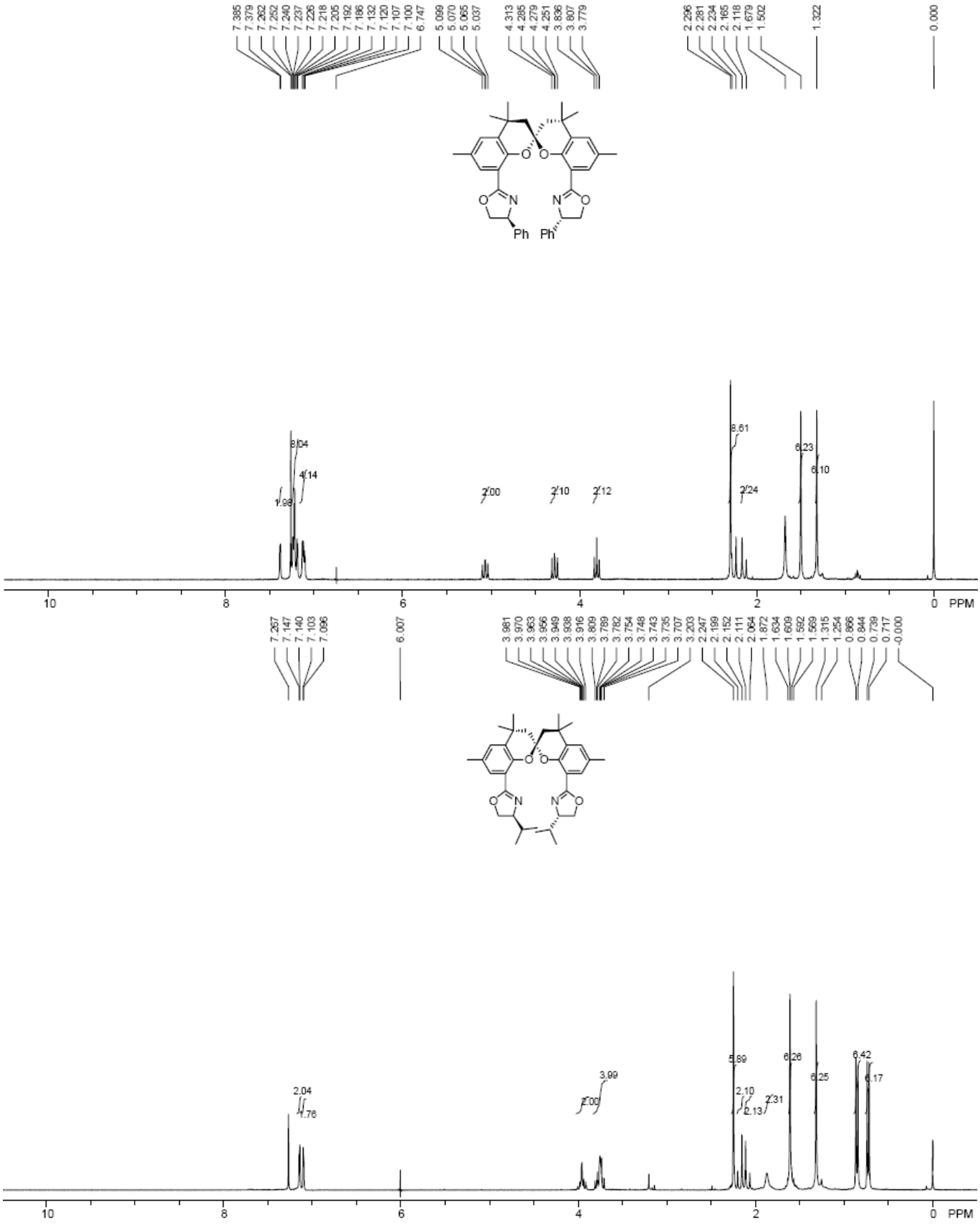
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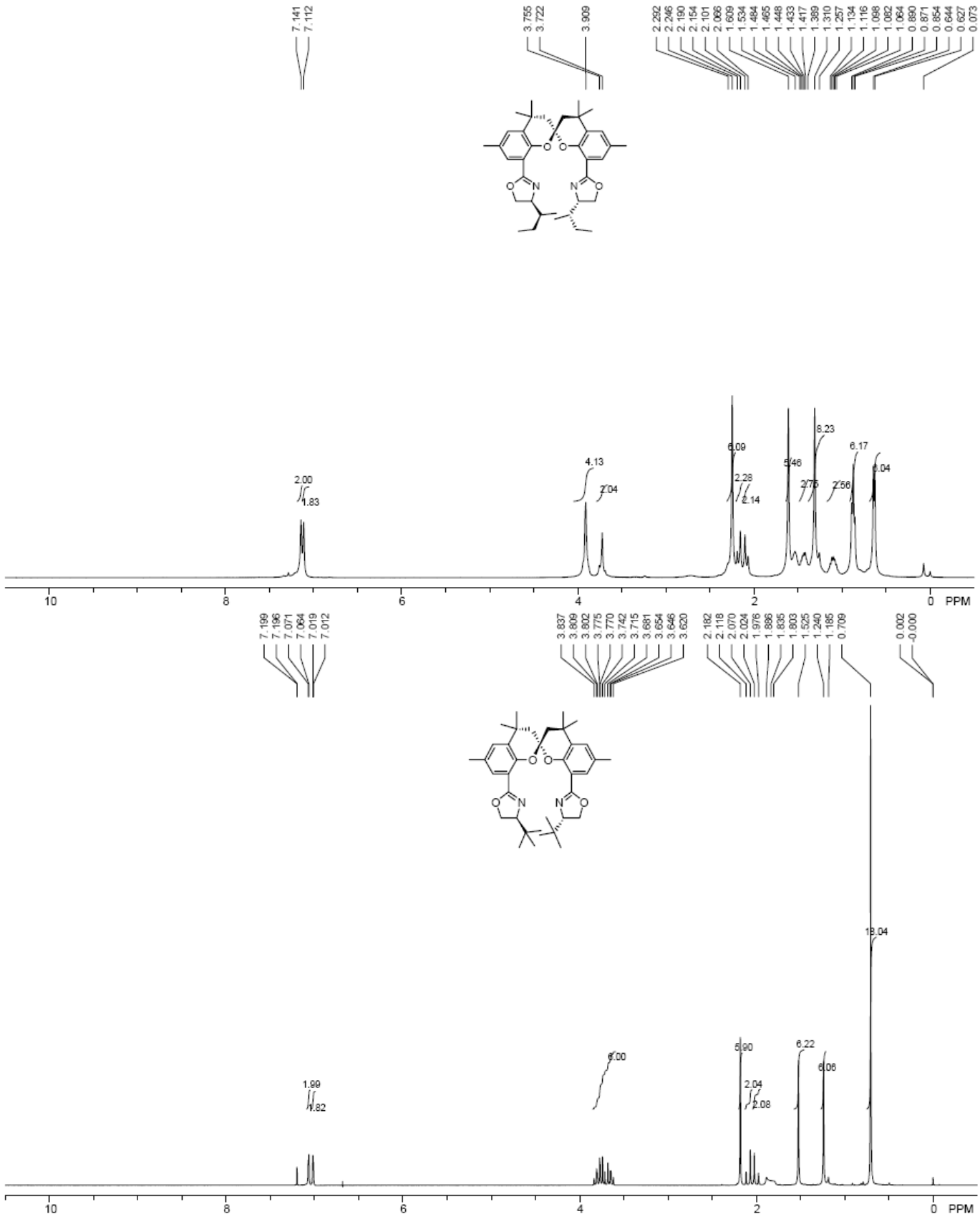
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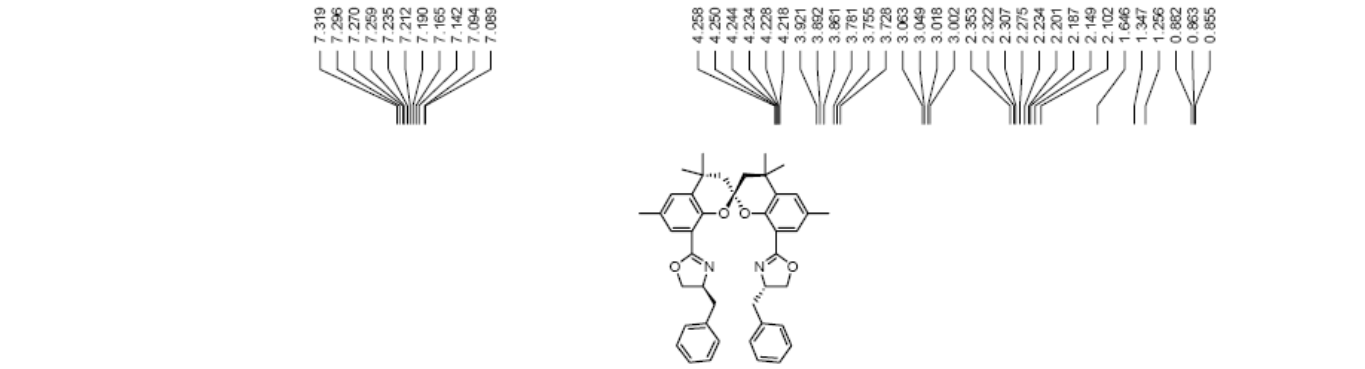
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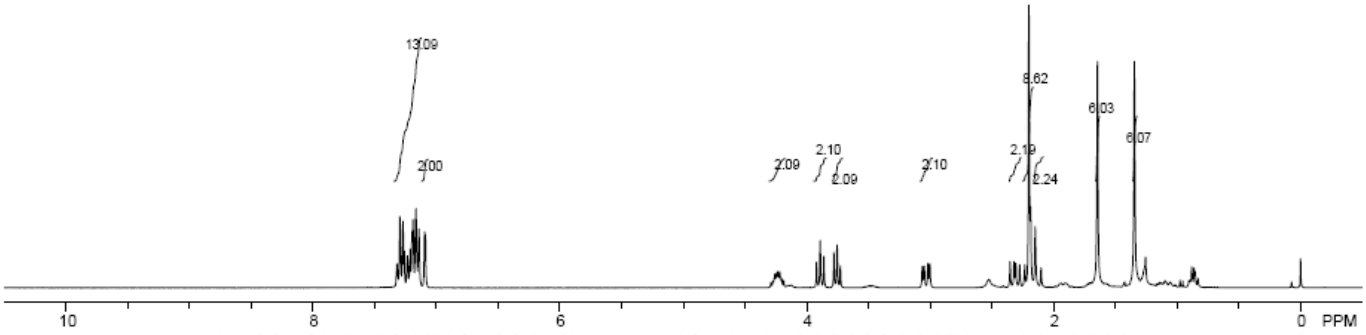
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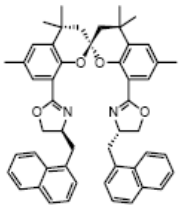

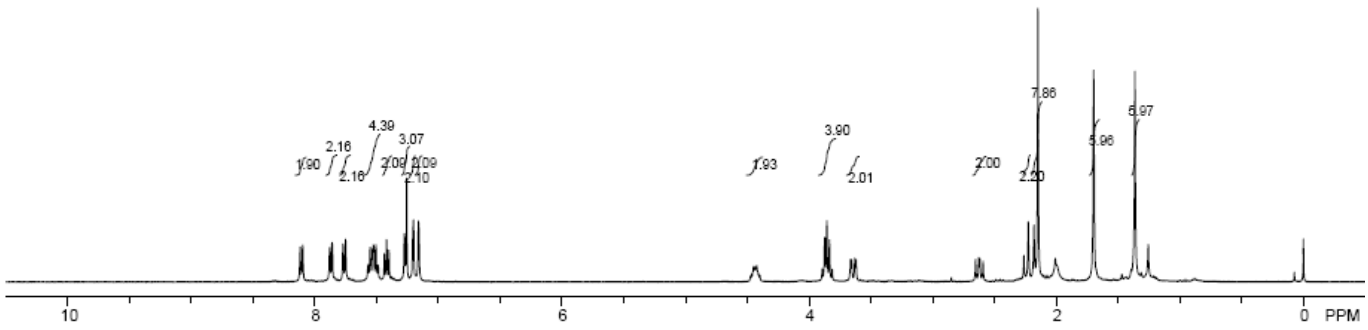
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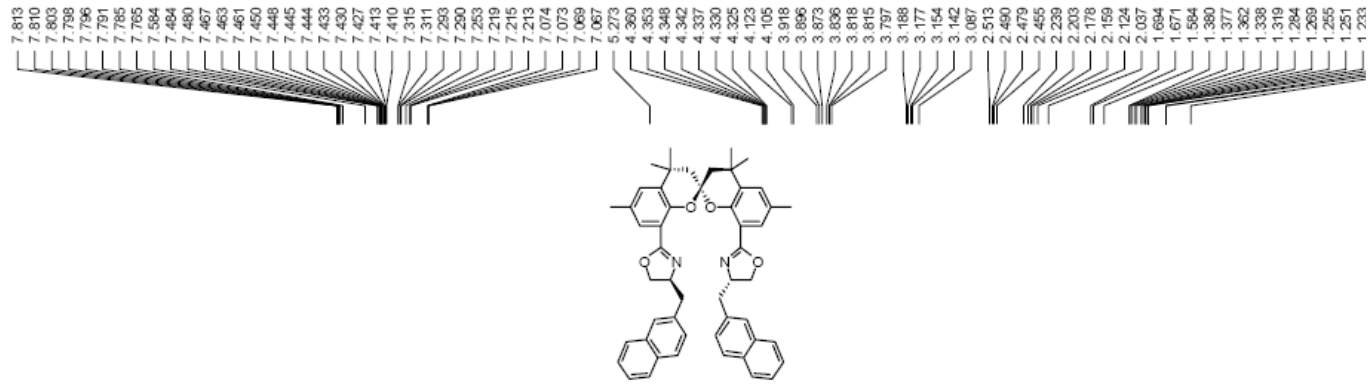

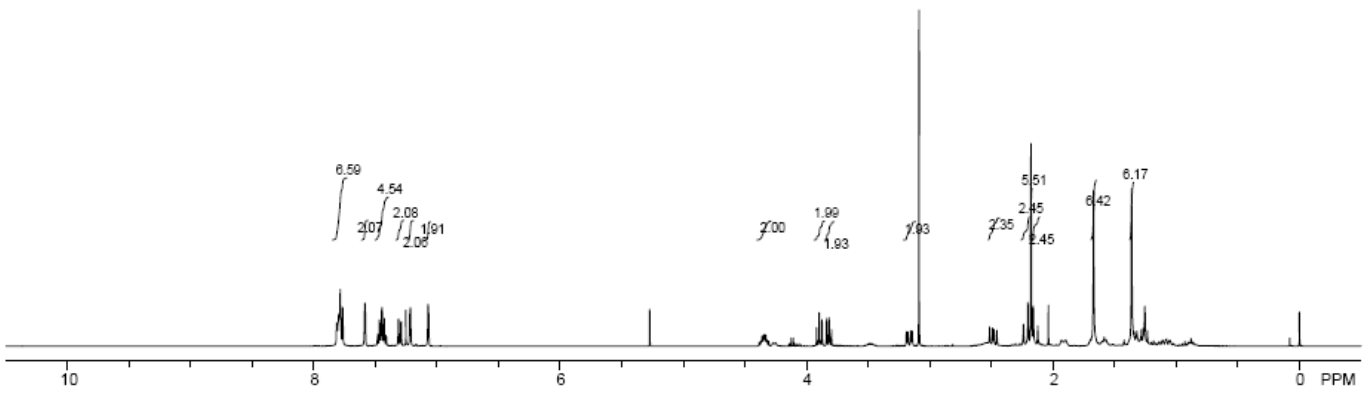
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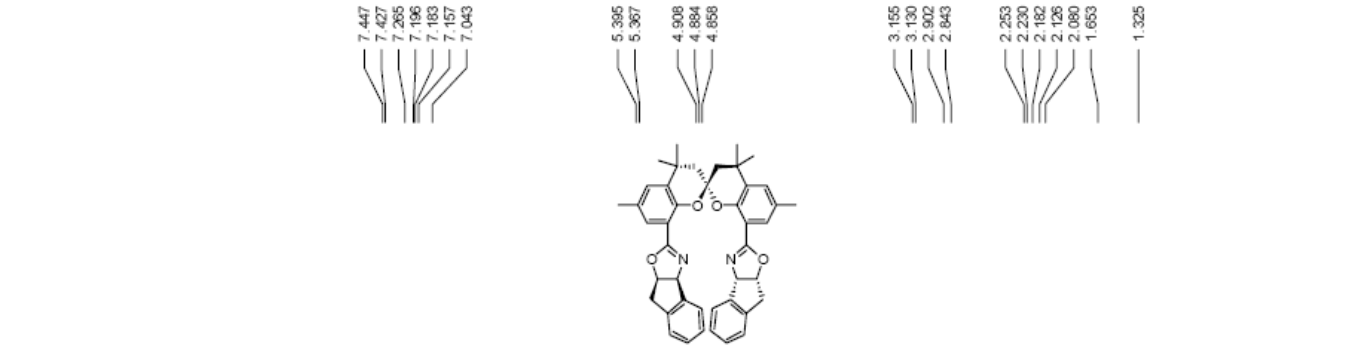

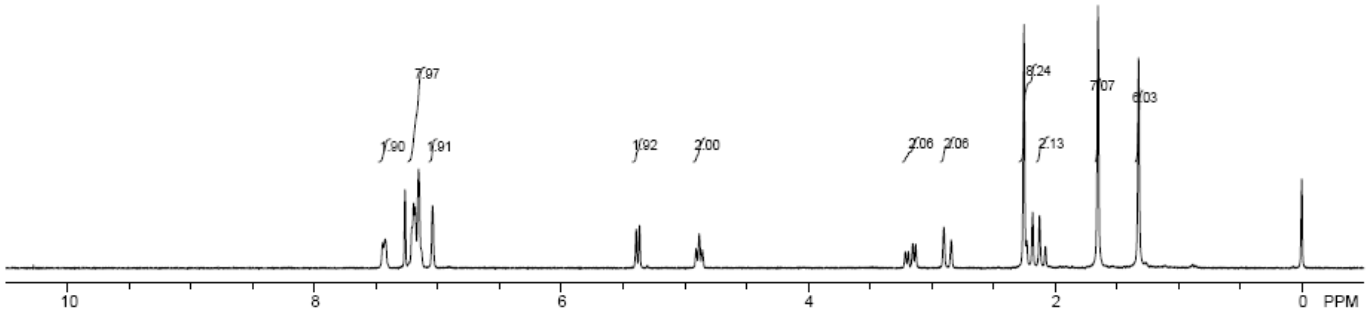
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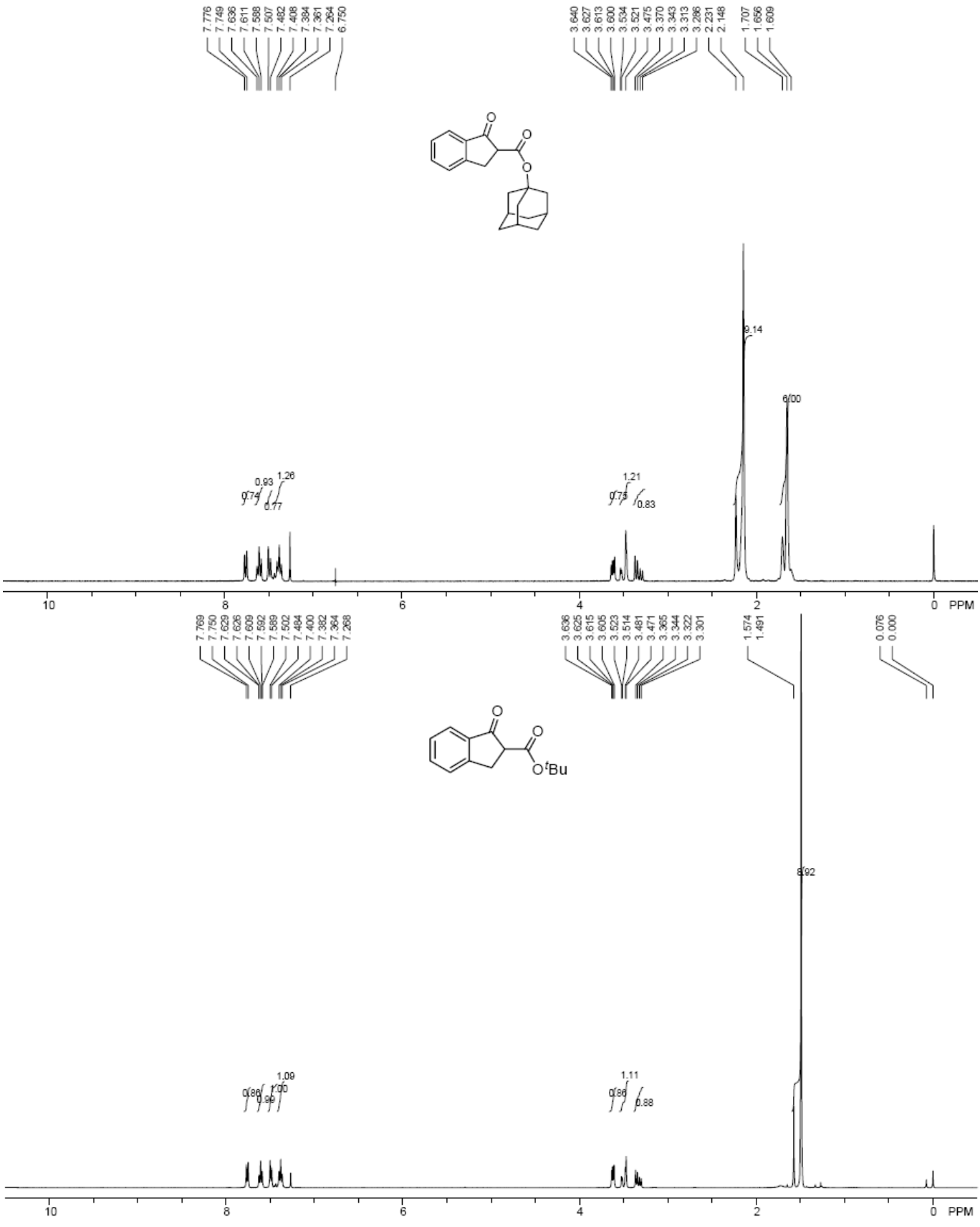
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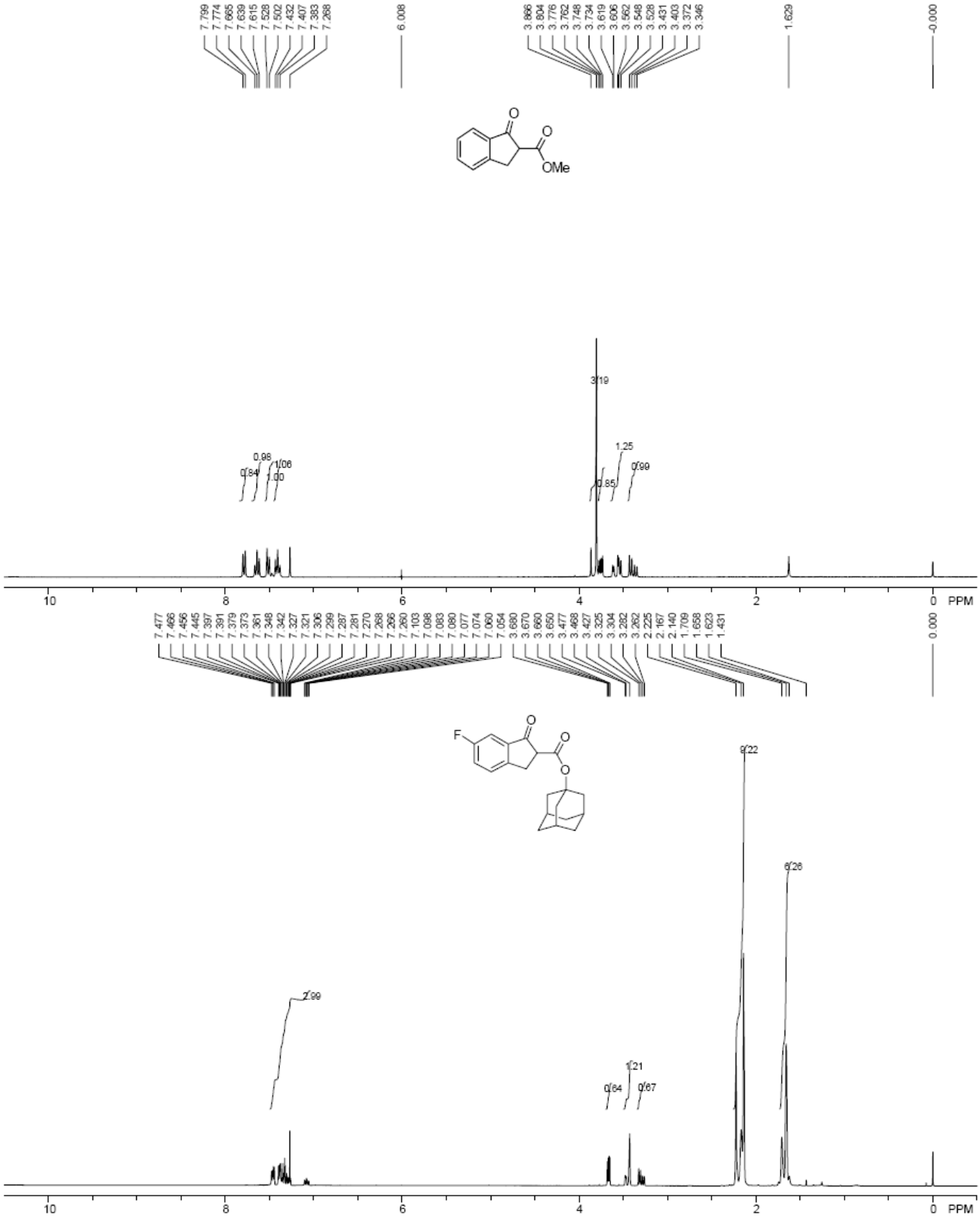
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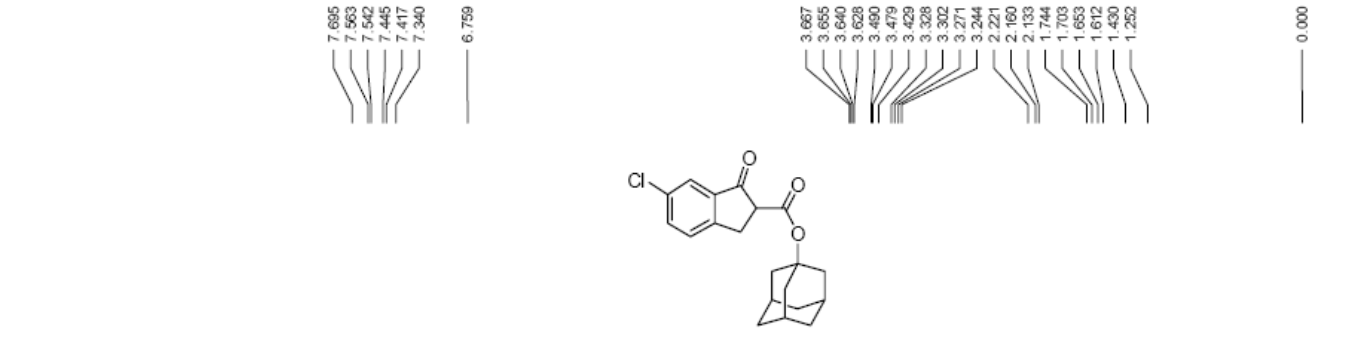
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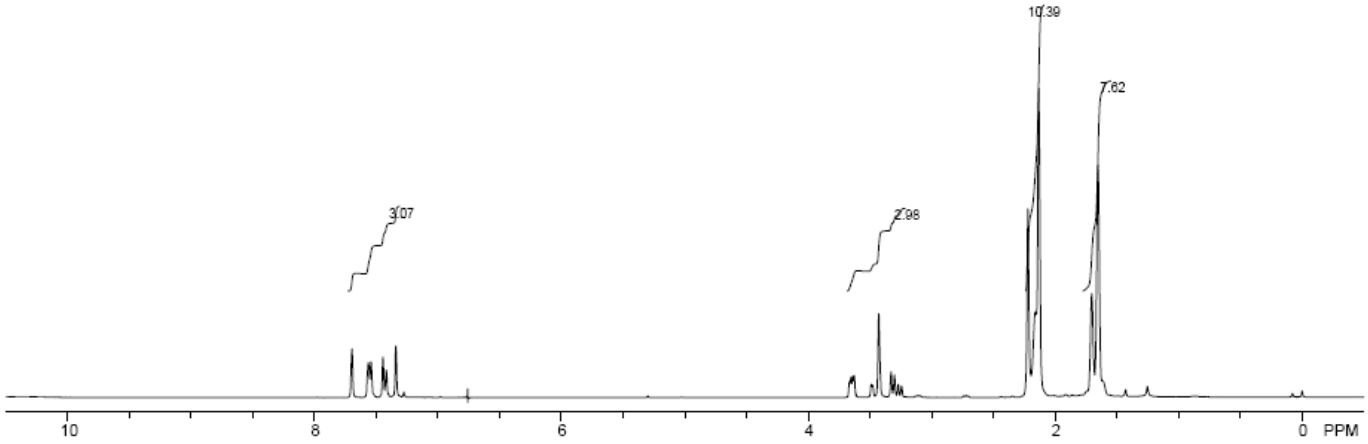
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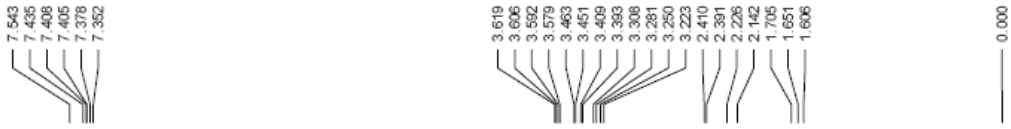
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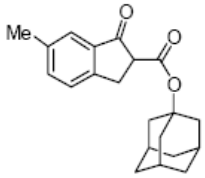
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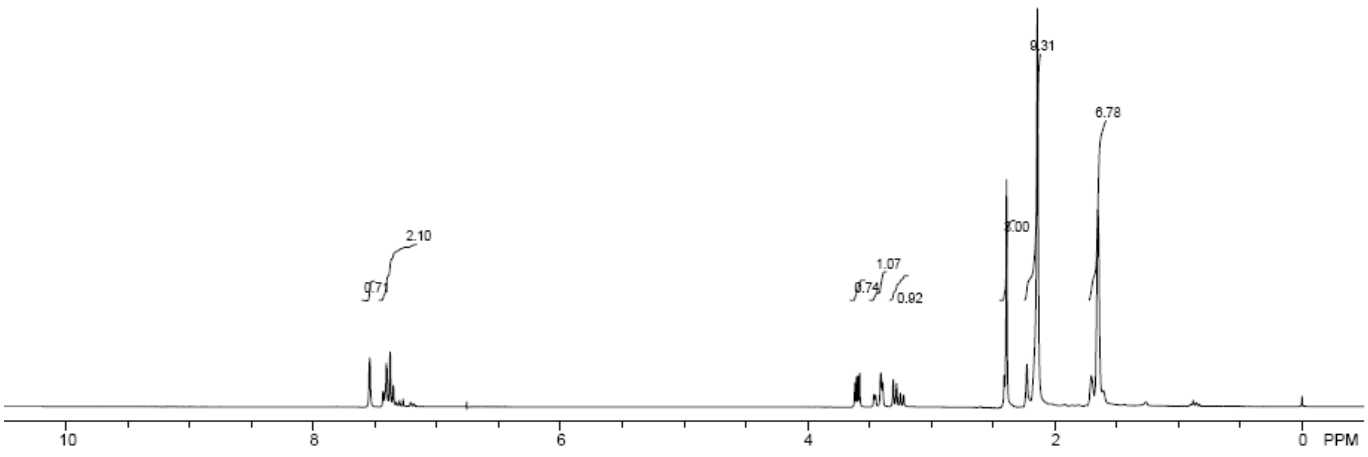
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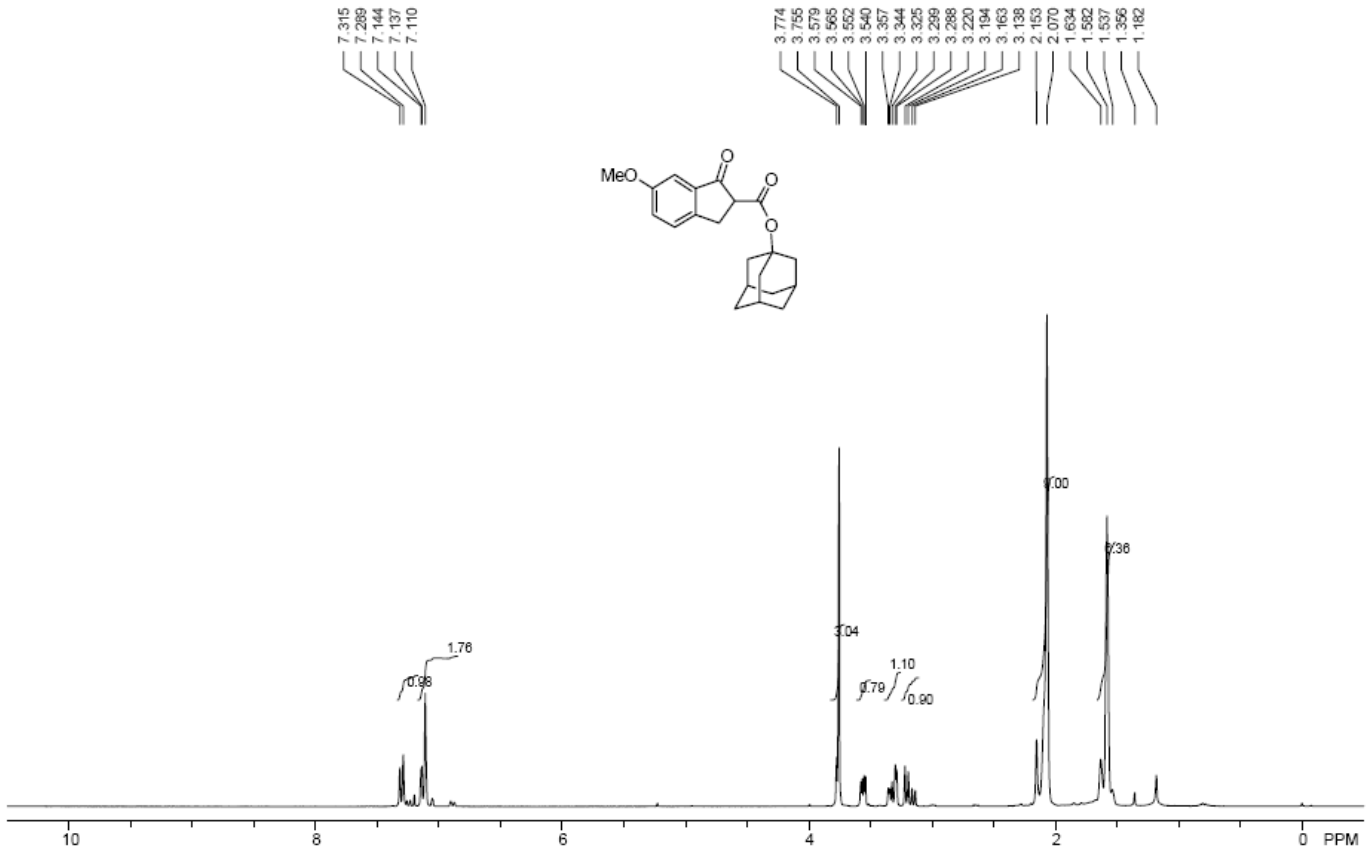
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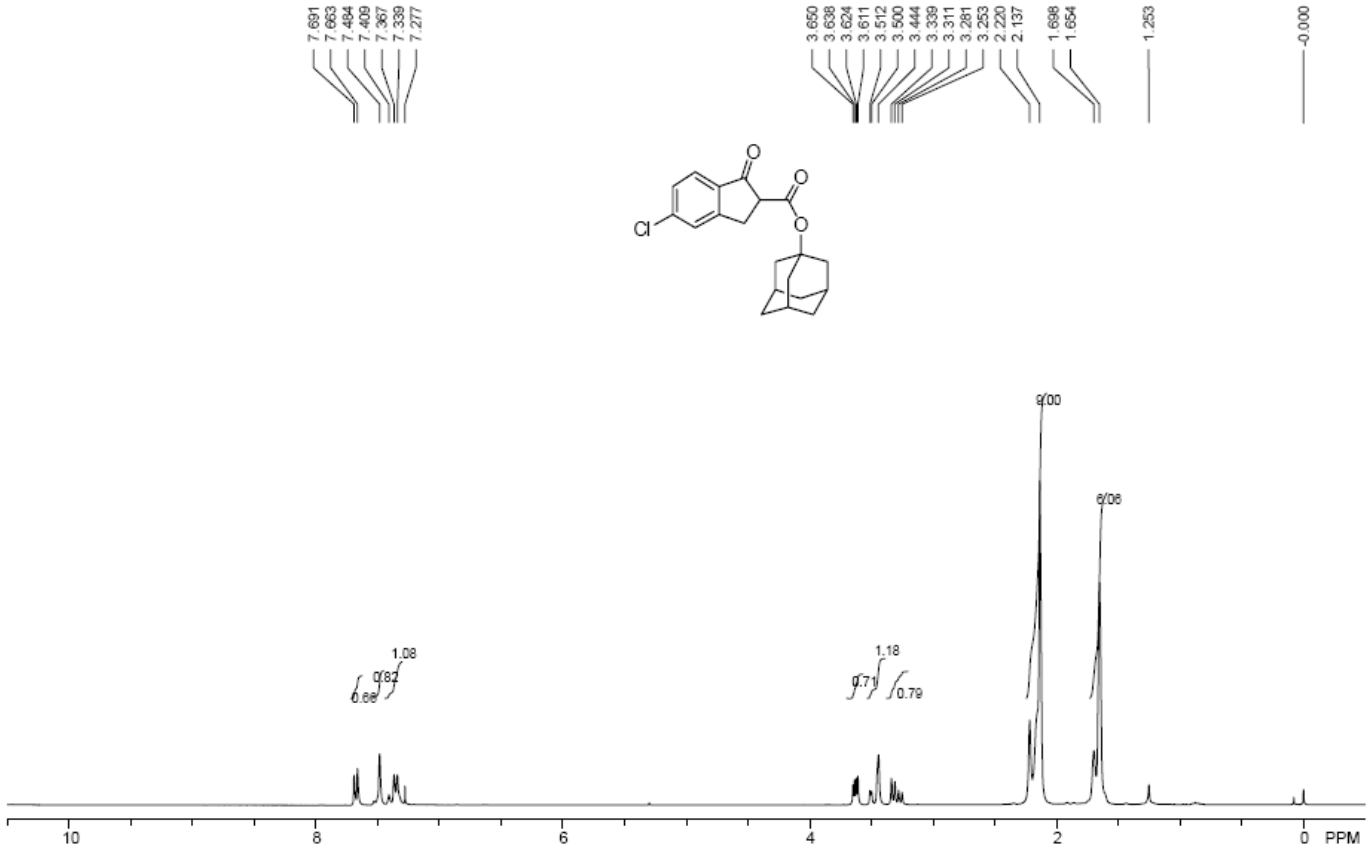
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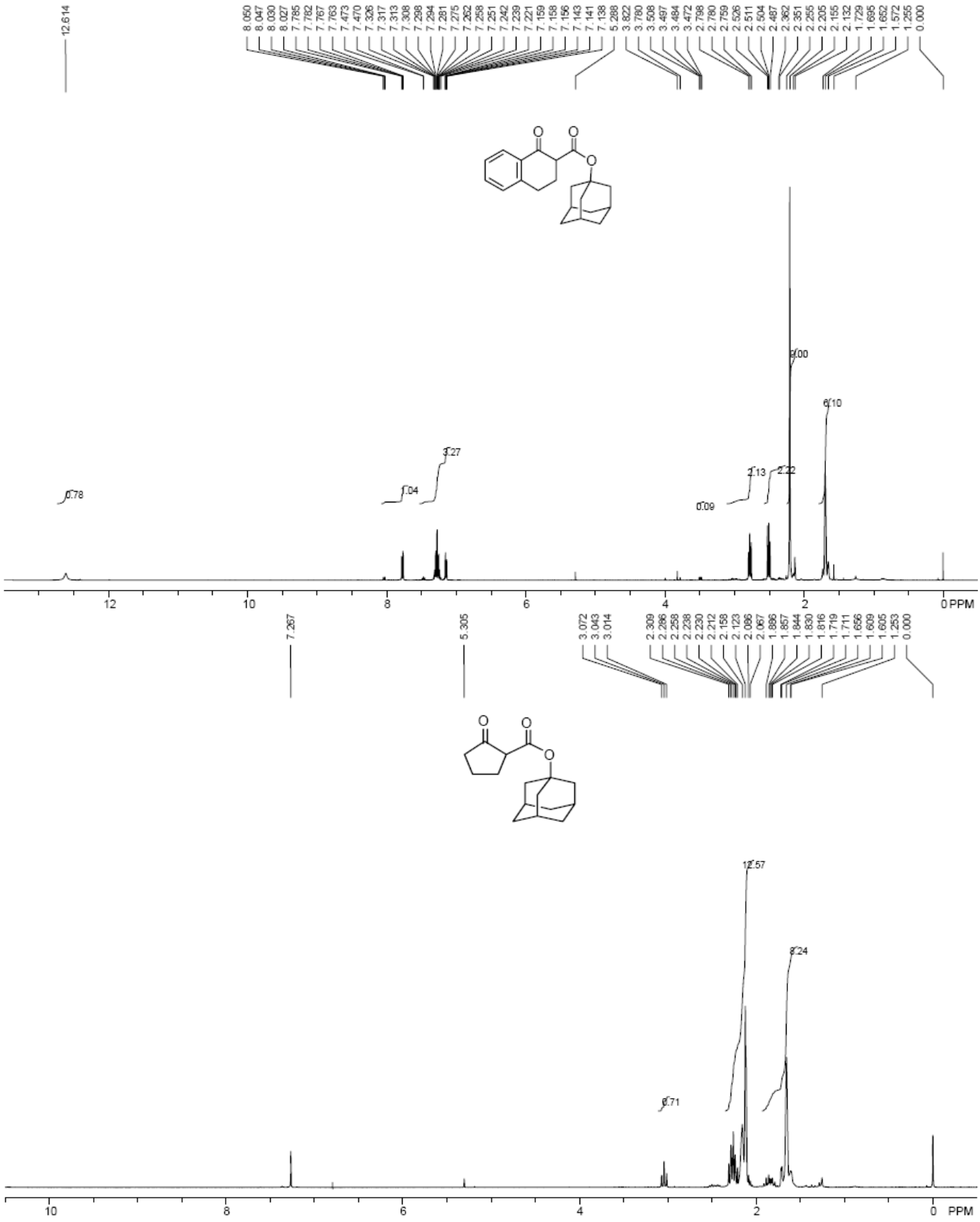
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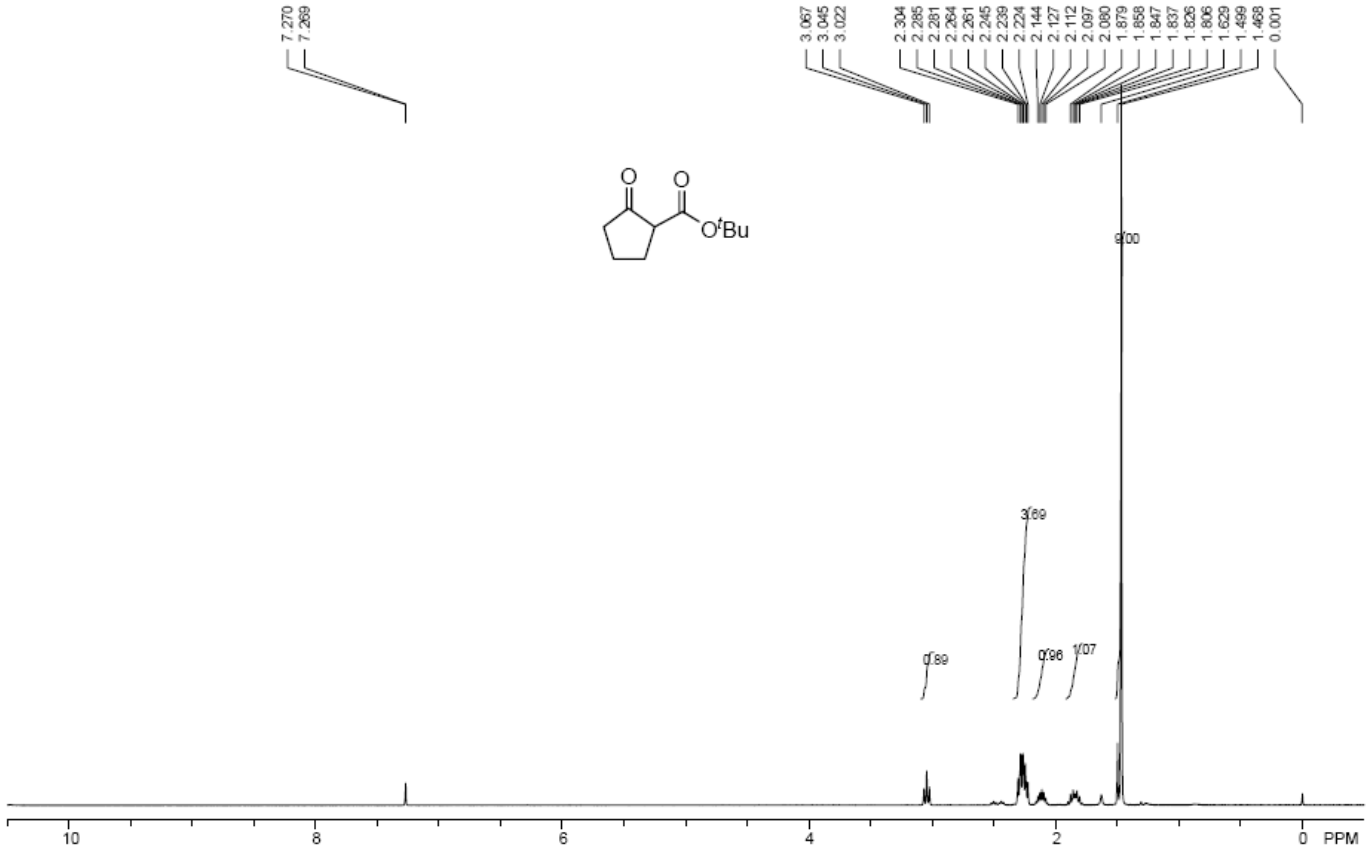
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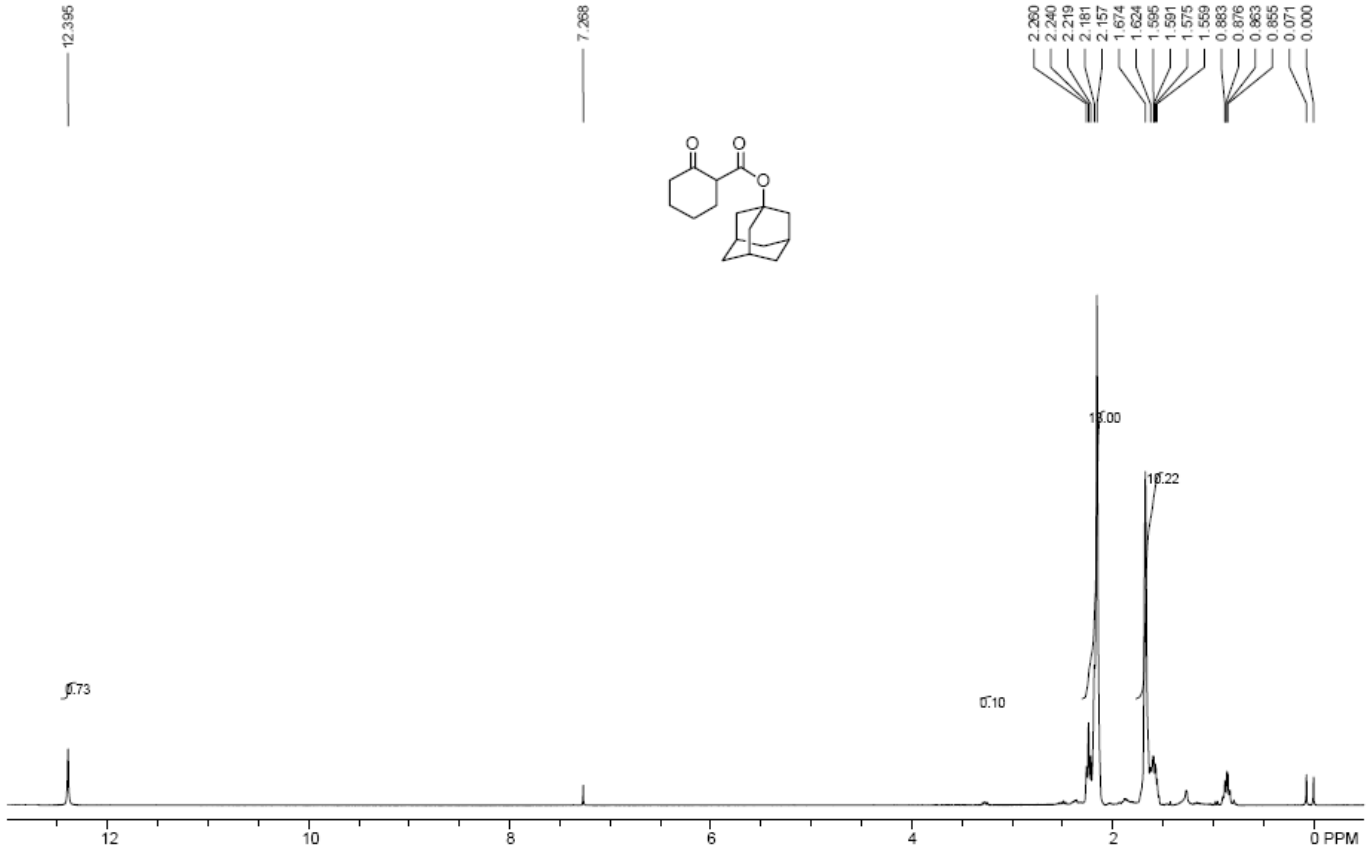
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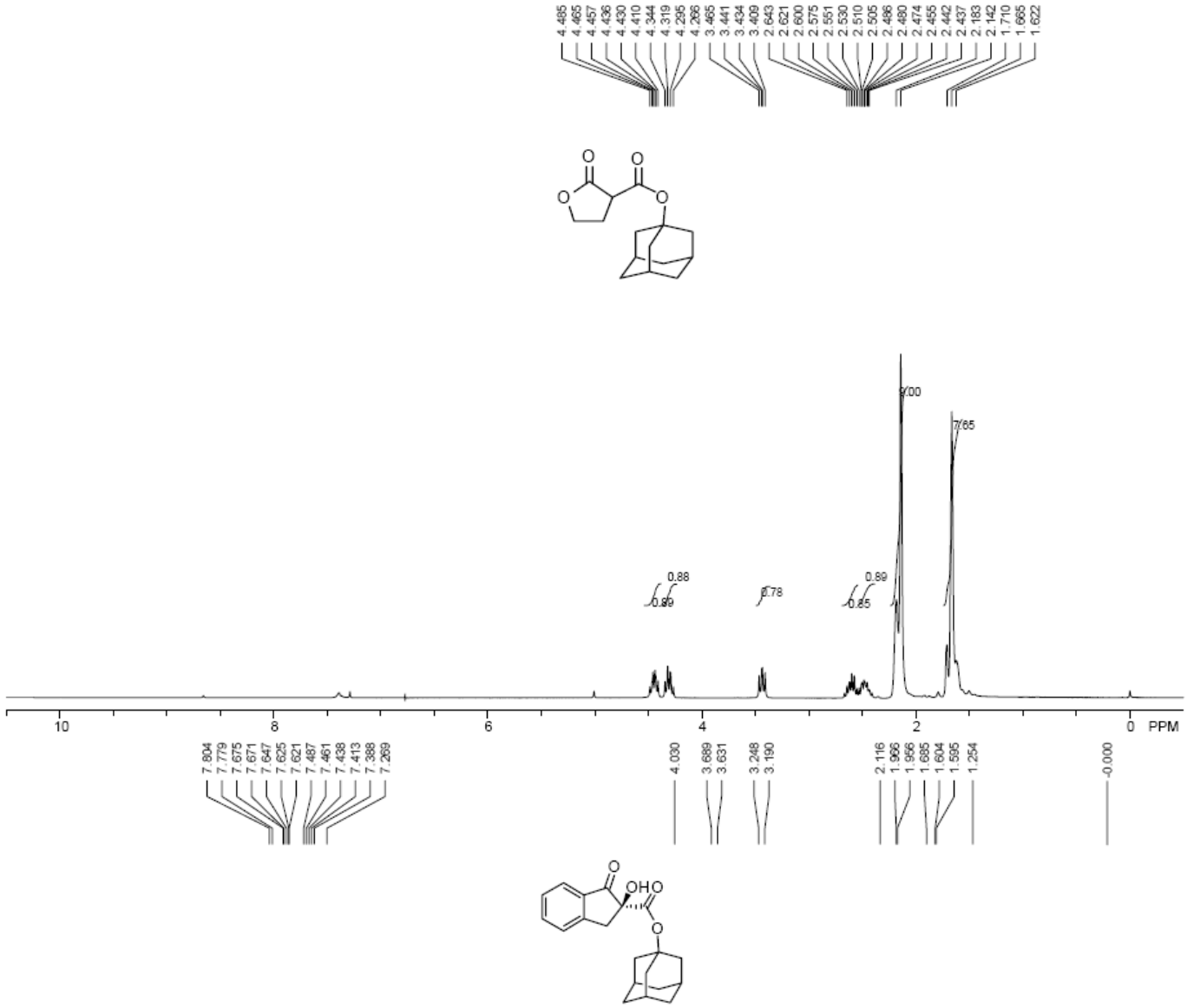
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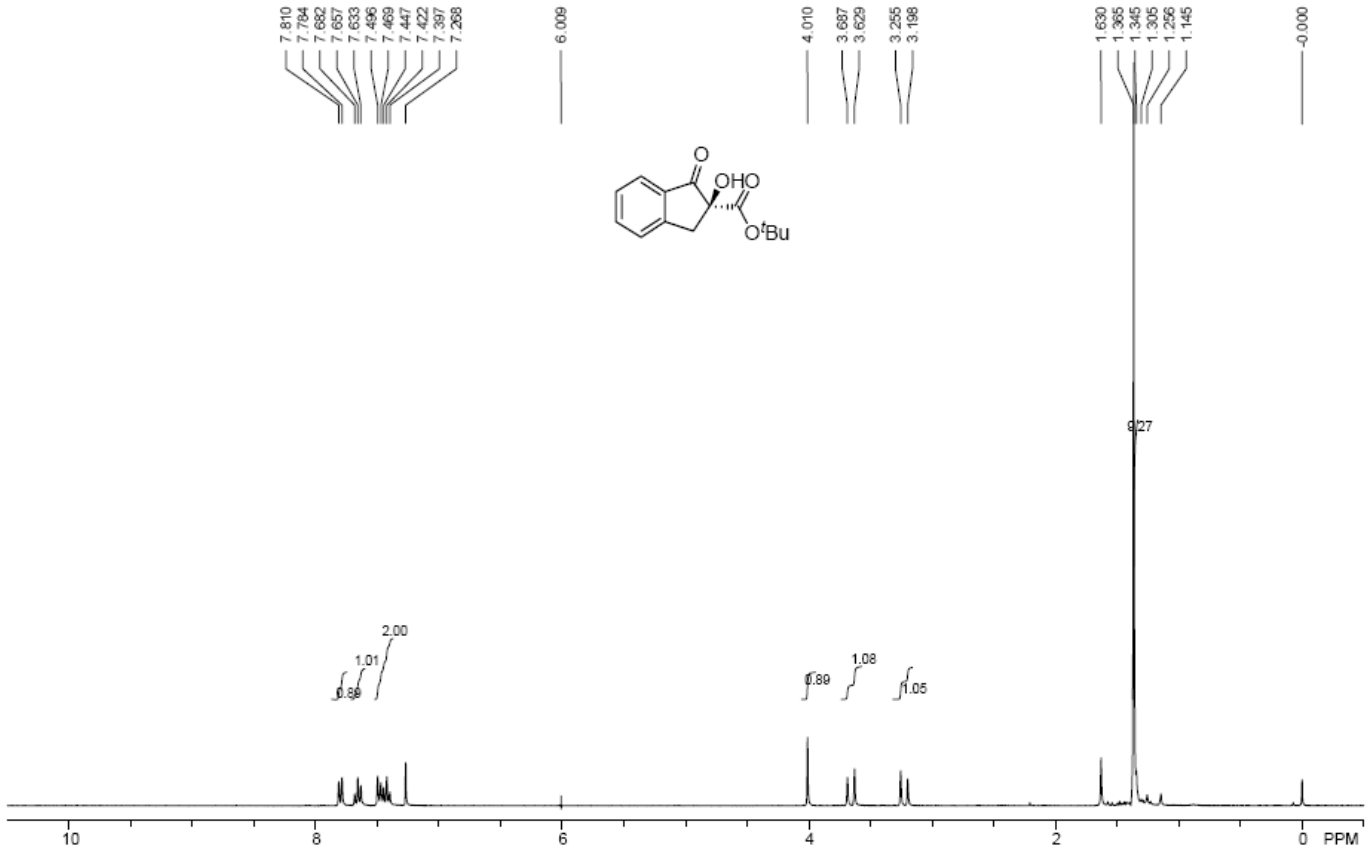
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O^{t}Bu
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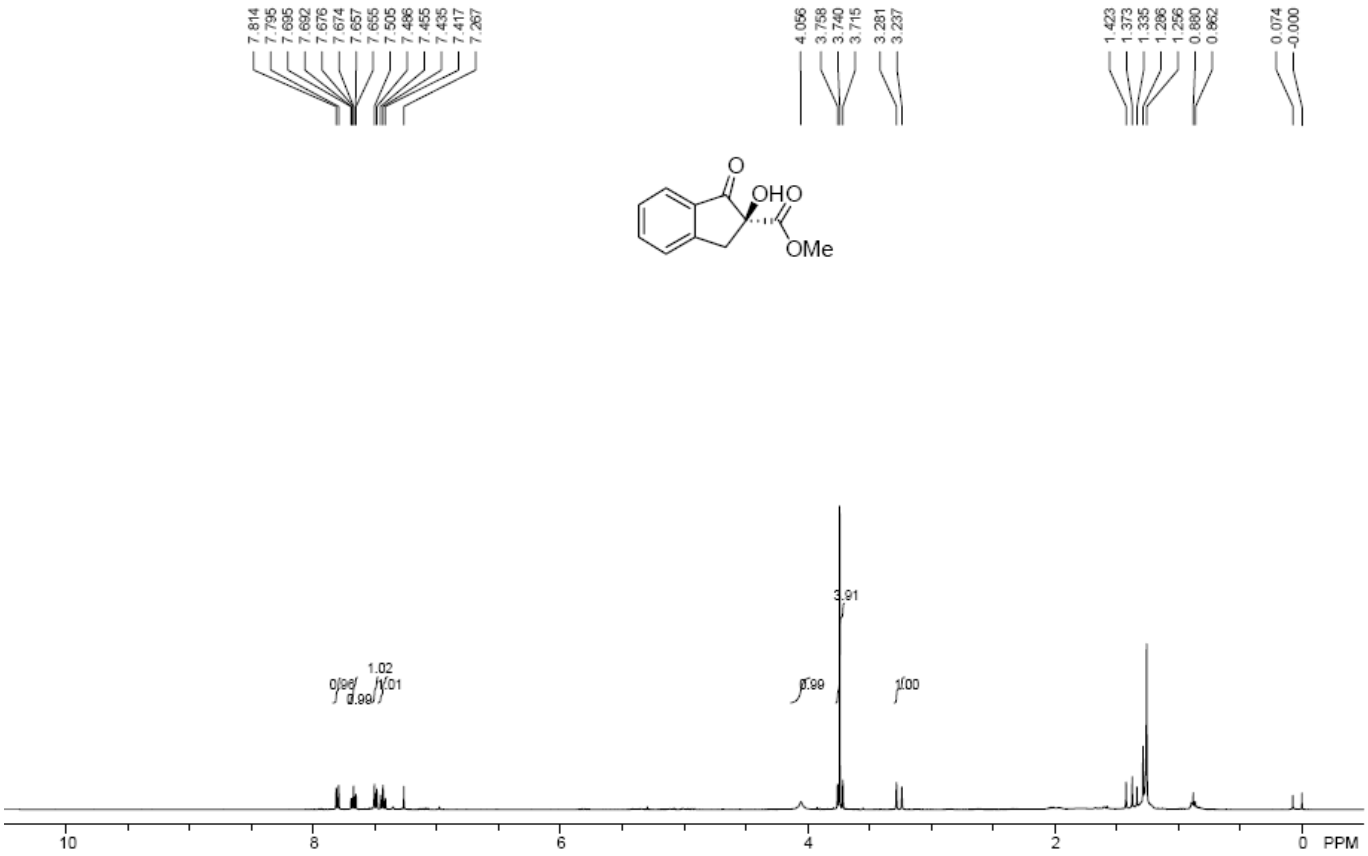
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OHO
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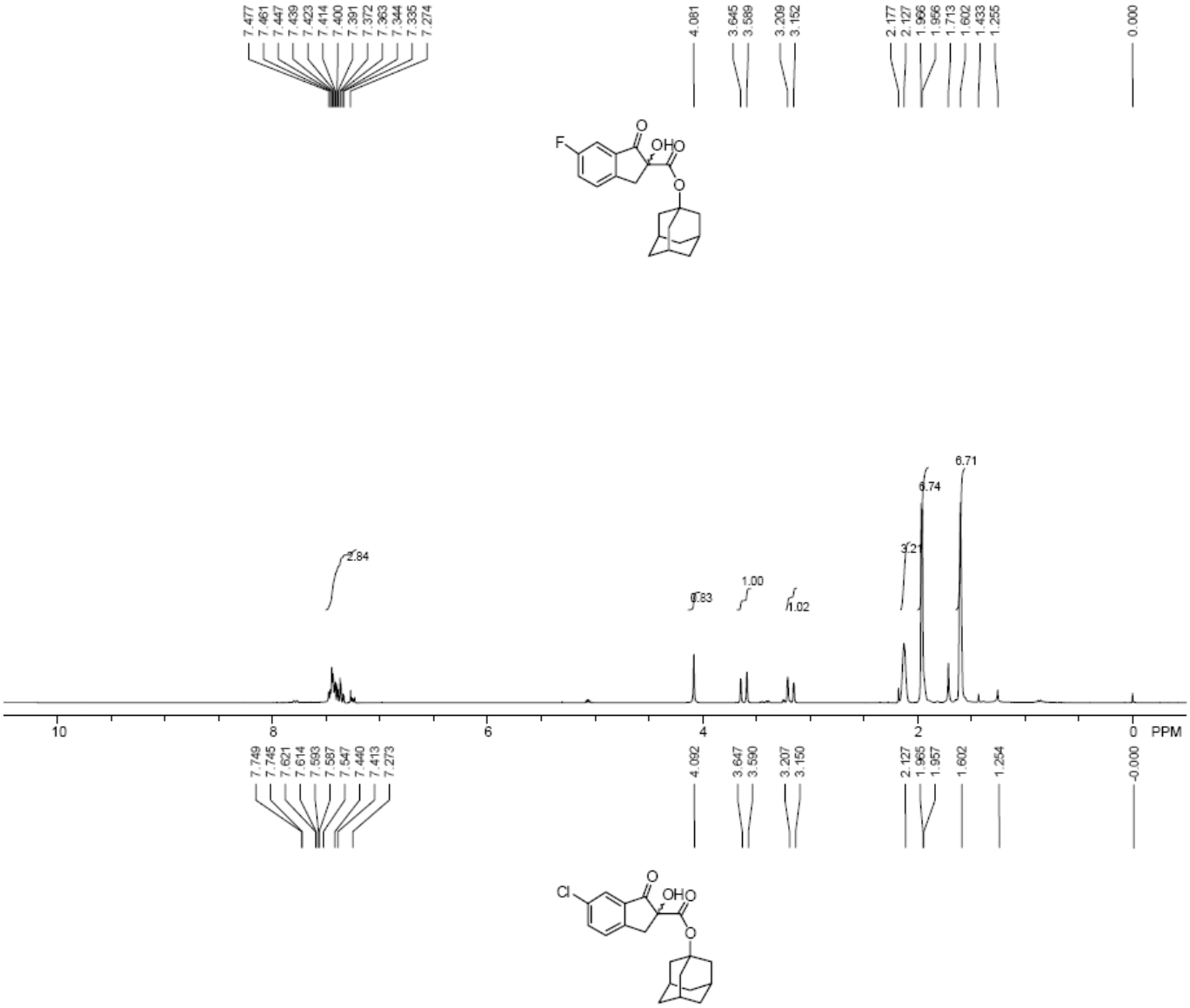
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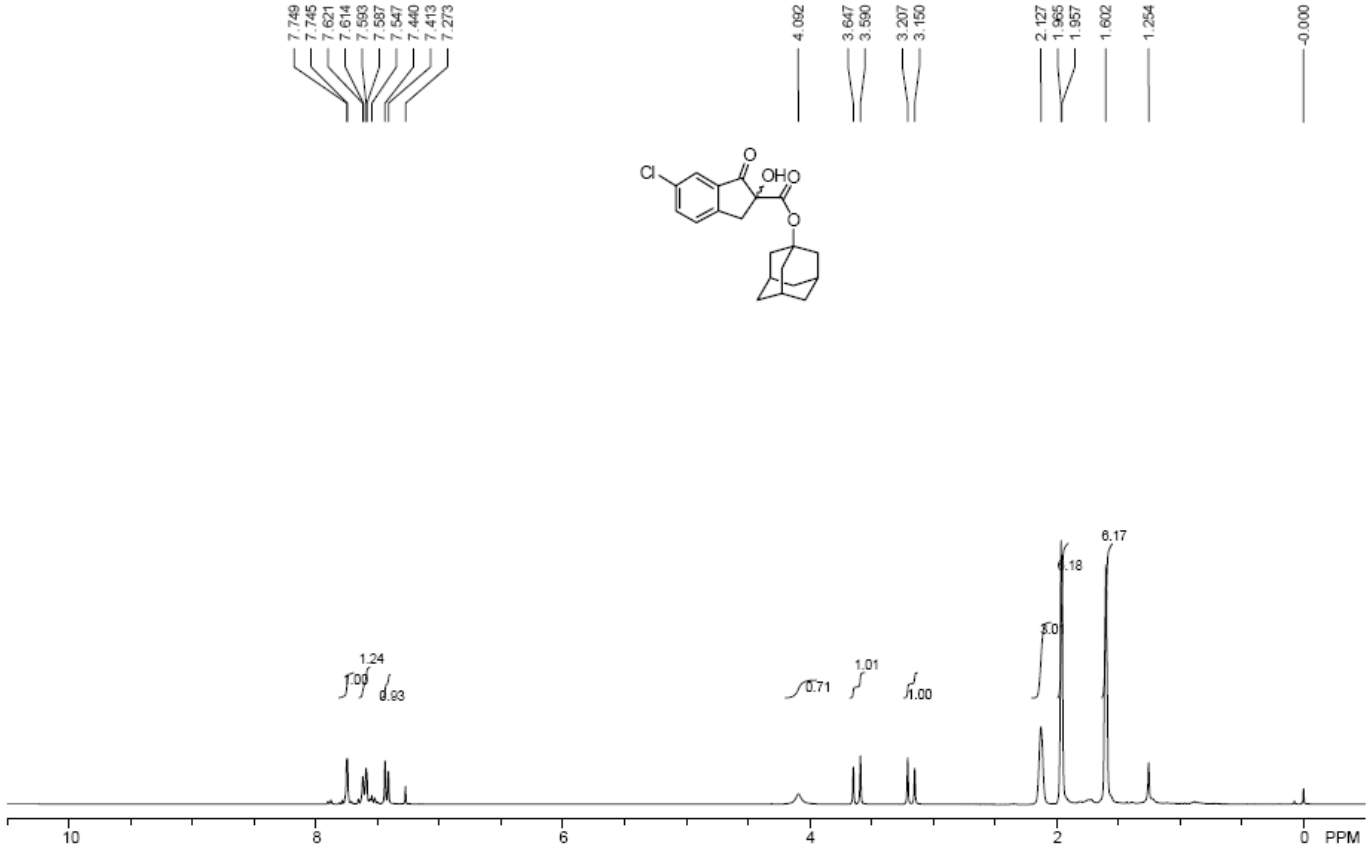
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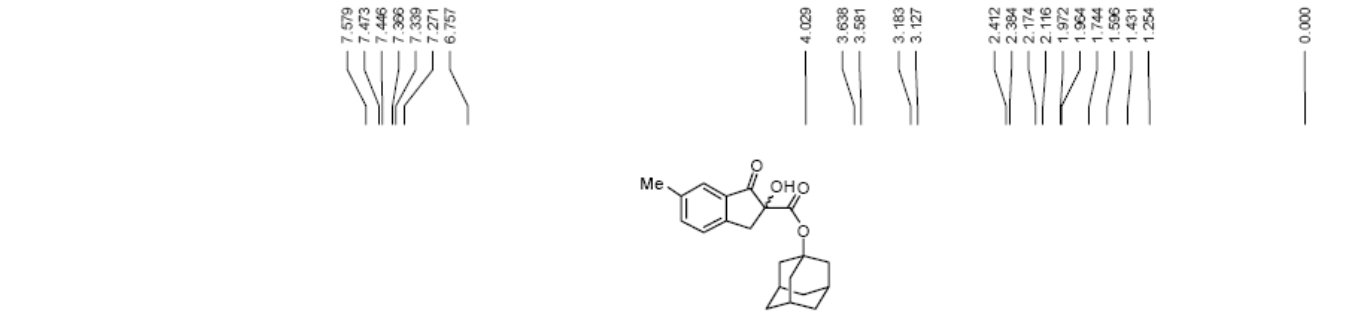
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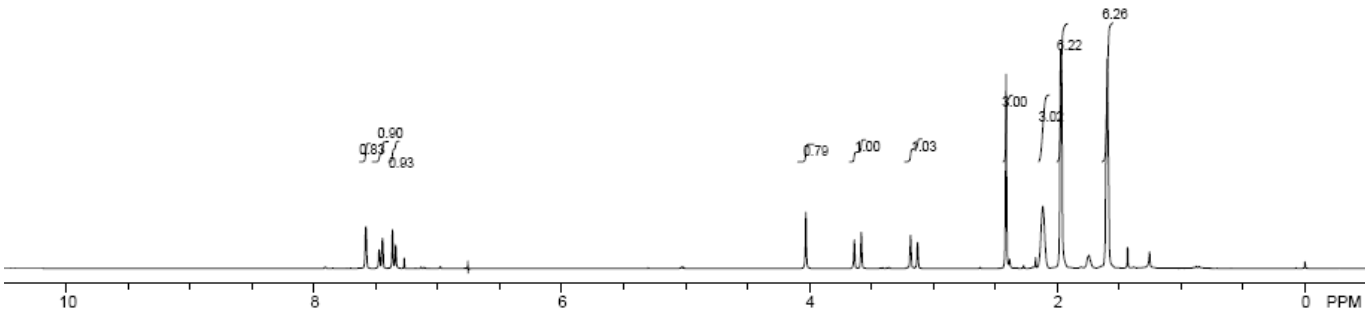
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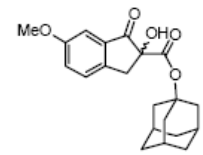
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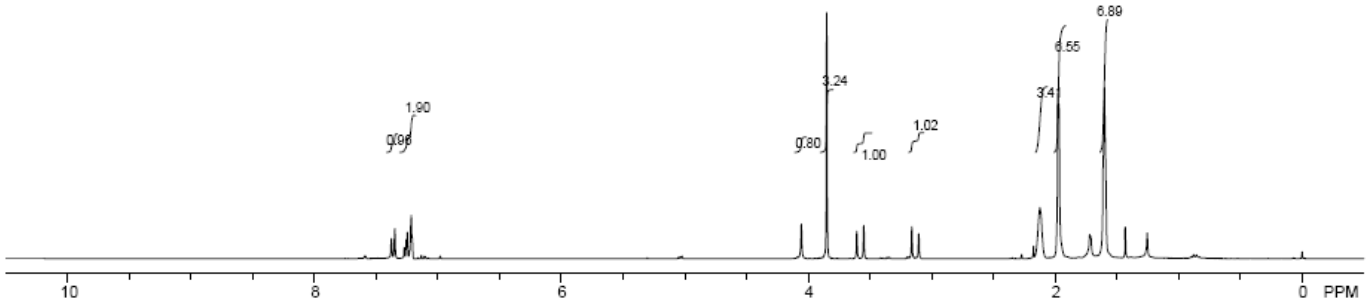
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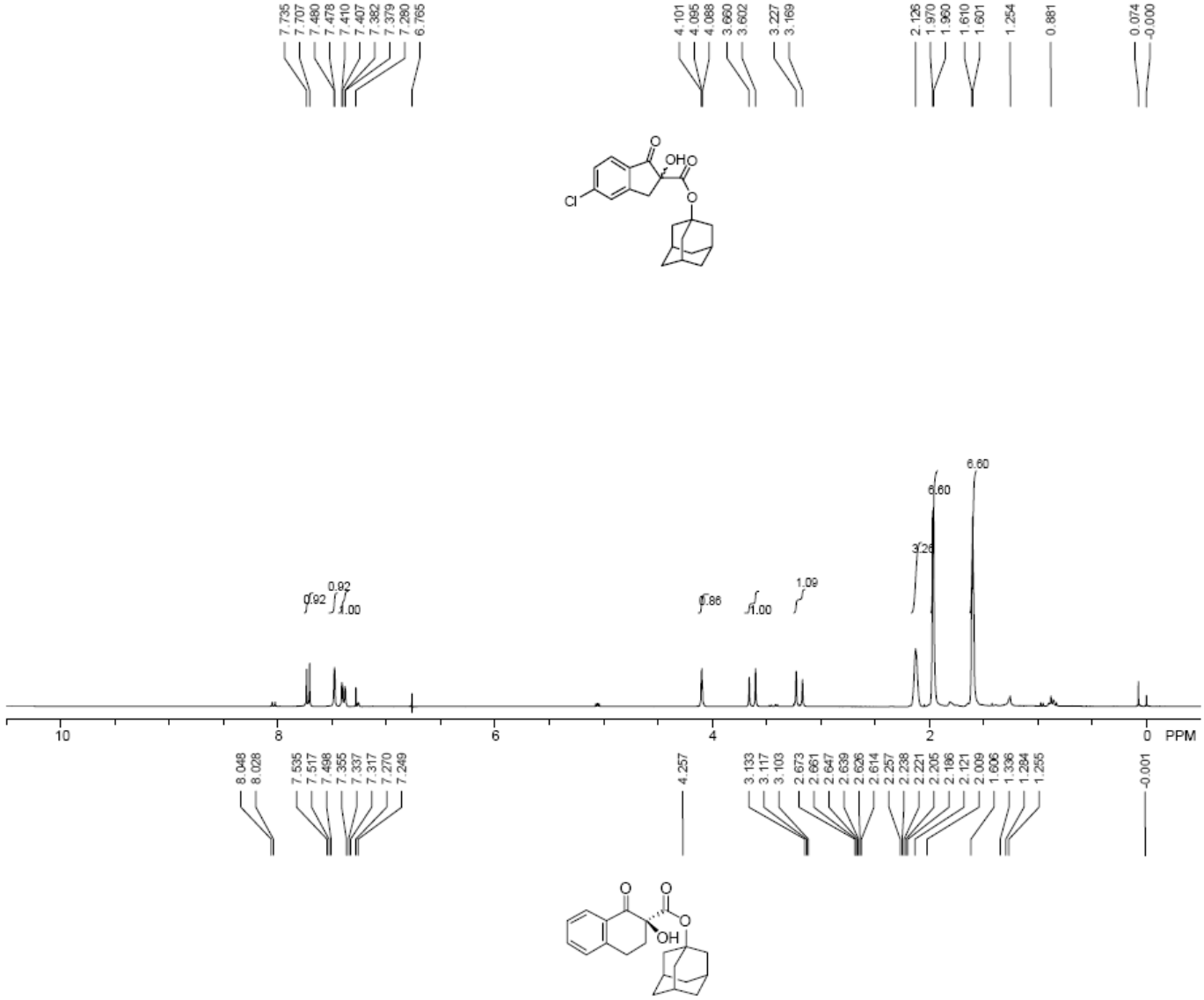
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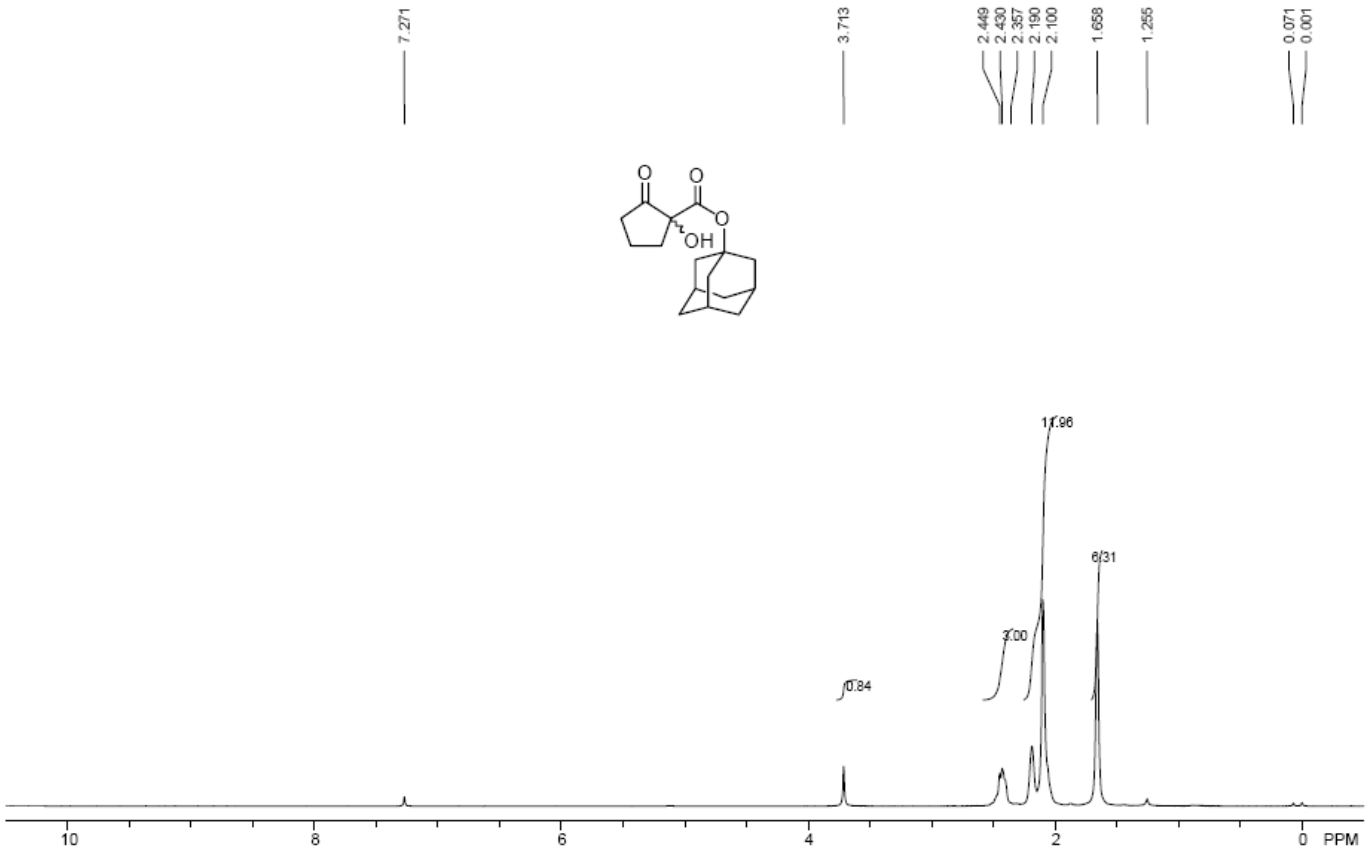
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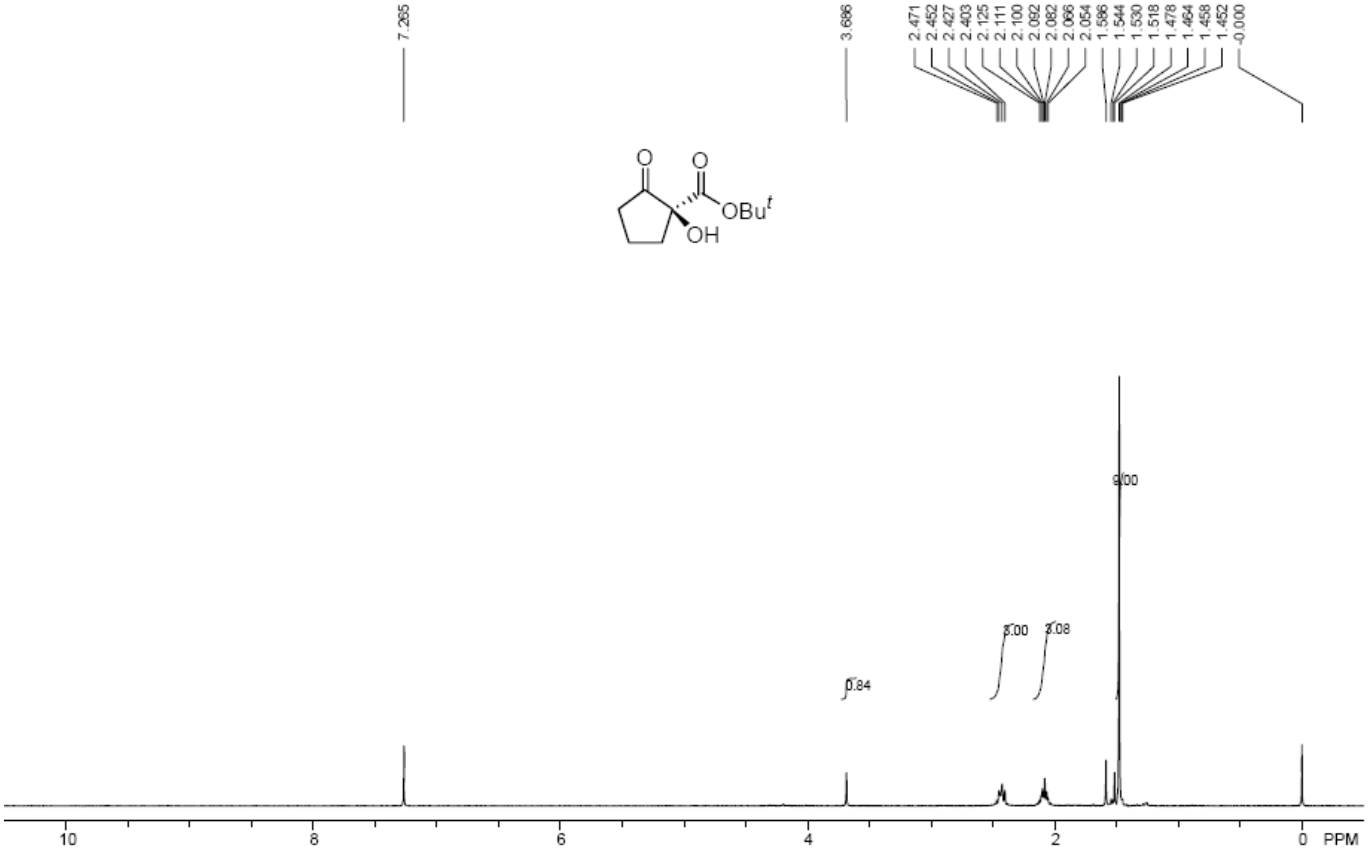
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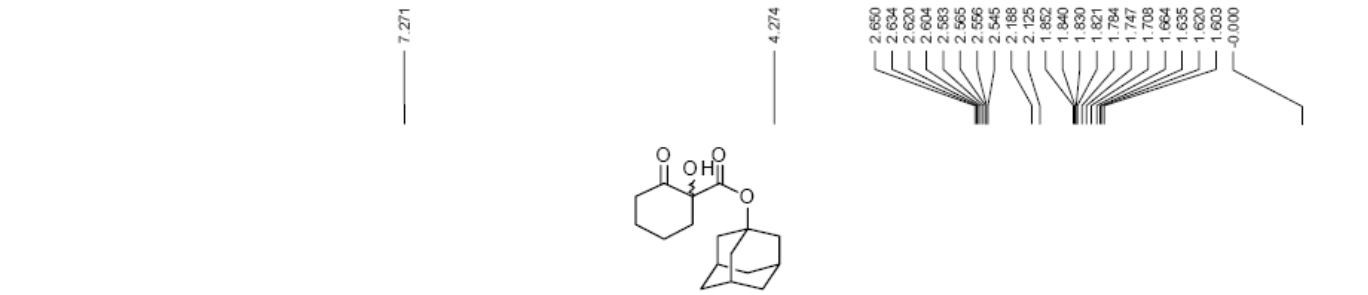
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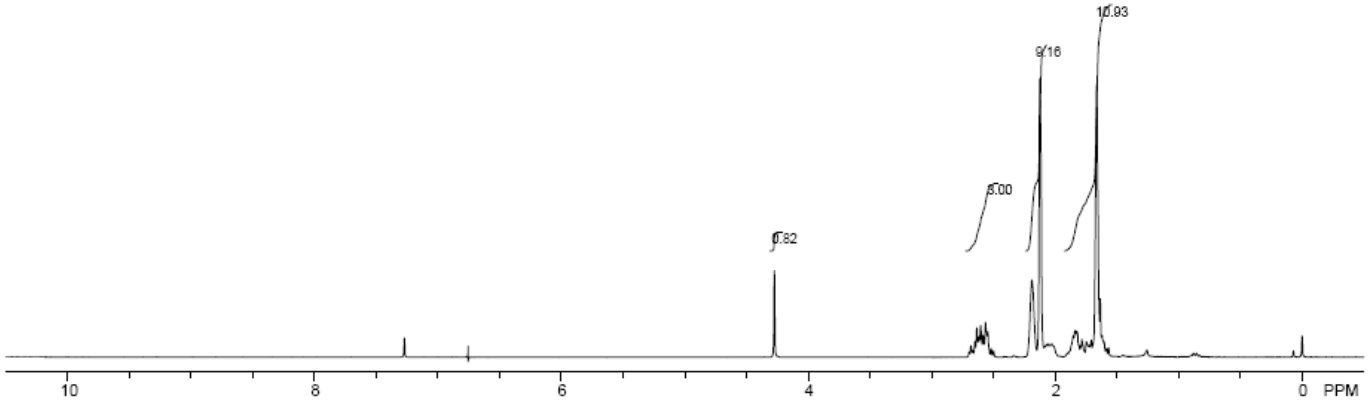
1.664
1.635
1.620
1.603
-0.000
O
OH
O
O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0.82
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8
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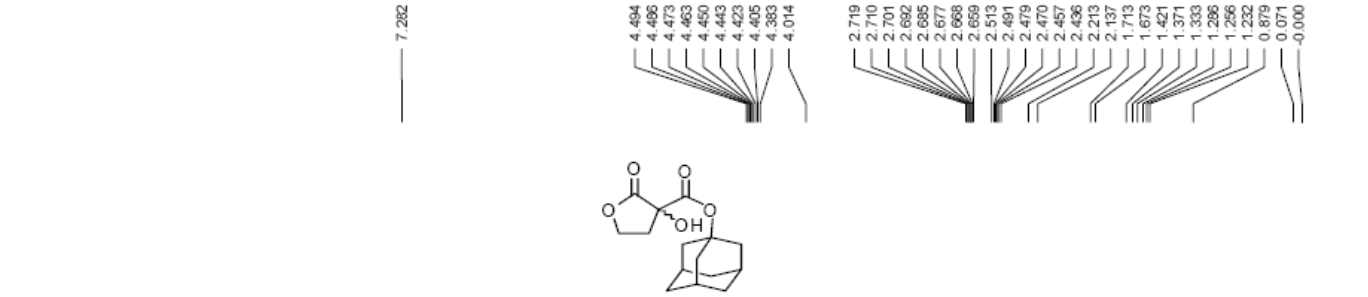
0
PPM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4.486
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4.463
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4.443
4.423
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4.383
4.014
2.719
2.710
2.701
2.692
2.685
2.677
2.668
2.659
2.513
2.491
2.479
2.470
2.457
2.436
2.213
2.137
1.713
1.673
1.421
1.371
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1.256
1.232
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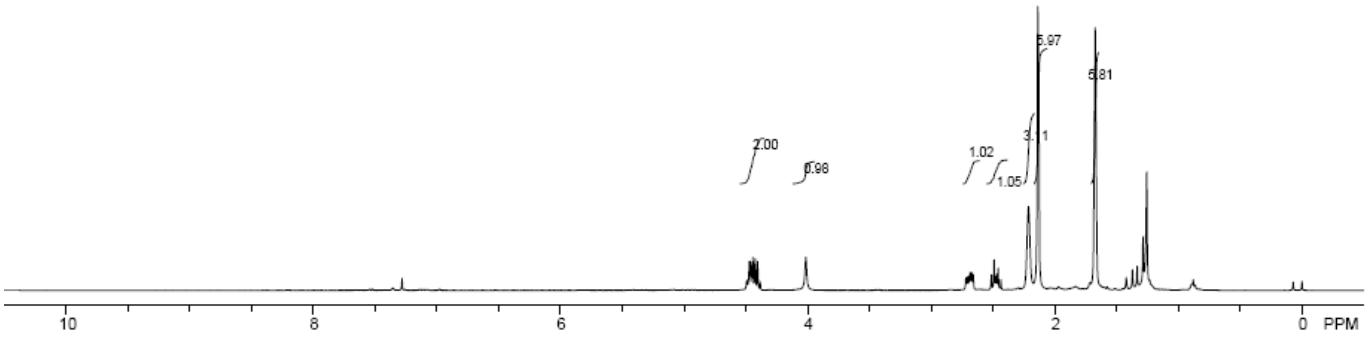
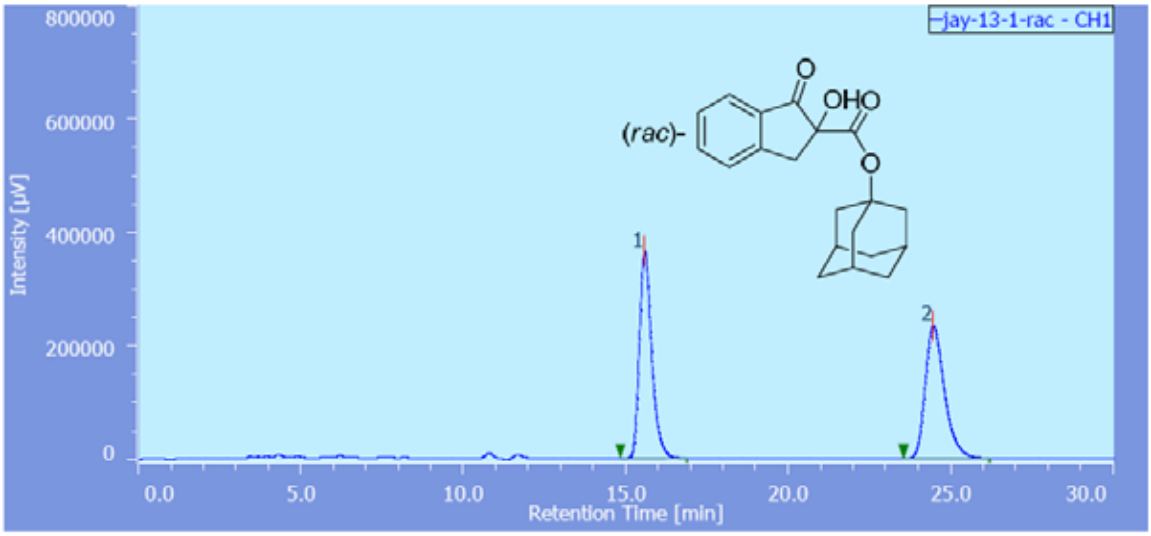
0.071
-0.000
O
O
O
O
OH


5.97
5.81
3.11
2.00
1.02
0.98
1.05
10
8
6
4
2
0
PPM

GC or HPLC Chromatograms for the Hydroxylation Products **7a-m**

Chromatogram



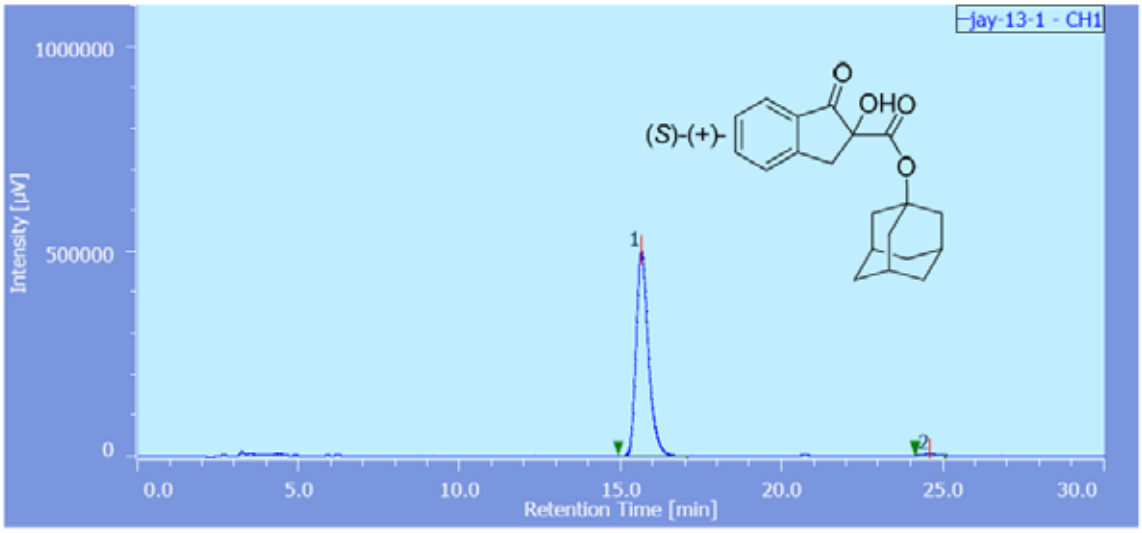
Chromatogram Information	
User Name	Administrator
Date Modified	2010-7-24 18:09:26
Description	
HPLC System Name	HPLC
Injection Date	2010-7-24 17:34:33
Volume	6.00 [μL]
Sample Number	1
Project Name	Jay
Acquisition Time	89.0 [min]
Acquisition Sequence	Hydroxylation of benzo-beta-keto Ad ester
Control Method	Hydroxylation of benzo-beta-keto Ad ester
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	jay-13-1-rac-CH1
Sample Name	
Channel Name	CH1
Sampling Interval	500 [msec]
Peak Method	(Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	15.583	9483049	365347	49.712	60.945	N/A	8975	10.483	1.315	
2	Unknown	1	24.458	9592822	234127	50.288	39.055	N/A	8854	N/A	1.341	

Chromatogram



Chromatogram Information

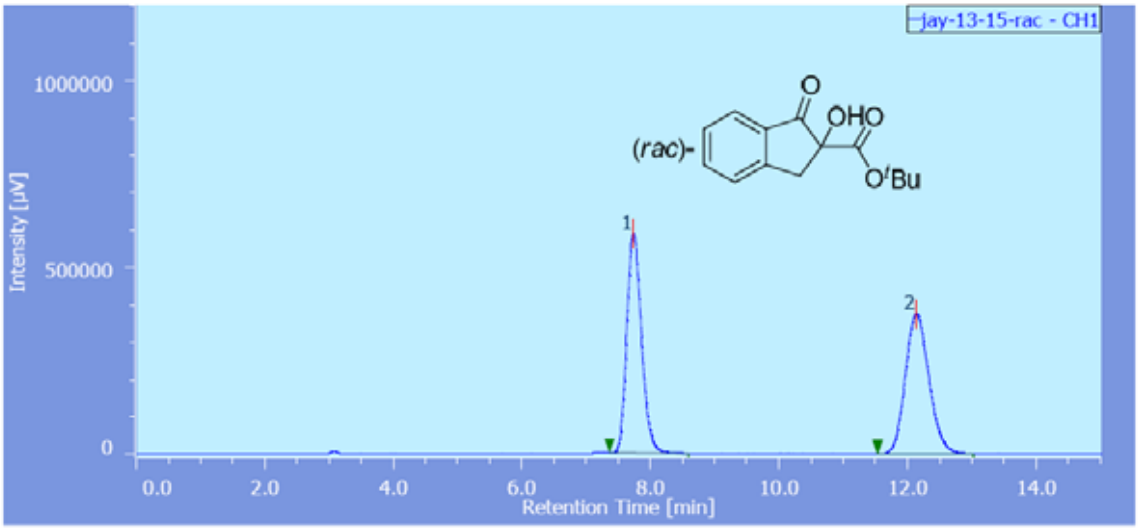
User Name	Administrator
Date Modified	2010-7-24 18:54:12
Description	
HPLC System Name	HPLC
Injection Date	2010-7-24 18:13:12
Volume	2.00 [μL]
Sample Number	1
Project Name	Jay
Acquisition Time	89.0 [min]
Acquisition Sequence	Hydroxylation of benzo-beta-keto Ad ester
Control Method	Hydroxylation of benzo-beta-keto Ad ester
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	jay-13-1-CH1
Sample Name	
Channel Name	CH1
Sampling Interval	500 [msec]
Peak Method	(Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	15.642	13136123	500474	99.159	99.276	N/A	8719	11.714	1.326	
2	Unknown	1	24.608	111474	3651	0.841	0.724	N/A	12952	N/A	0.996	

Chromatogram



Chromatogram Information

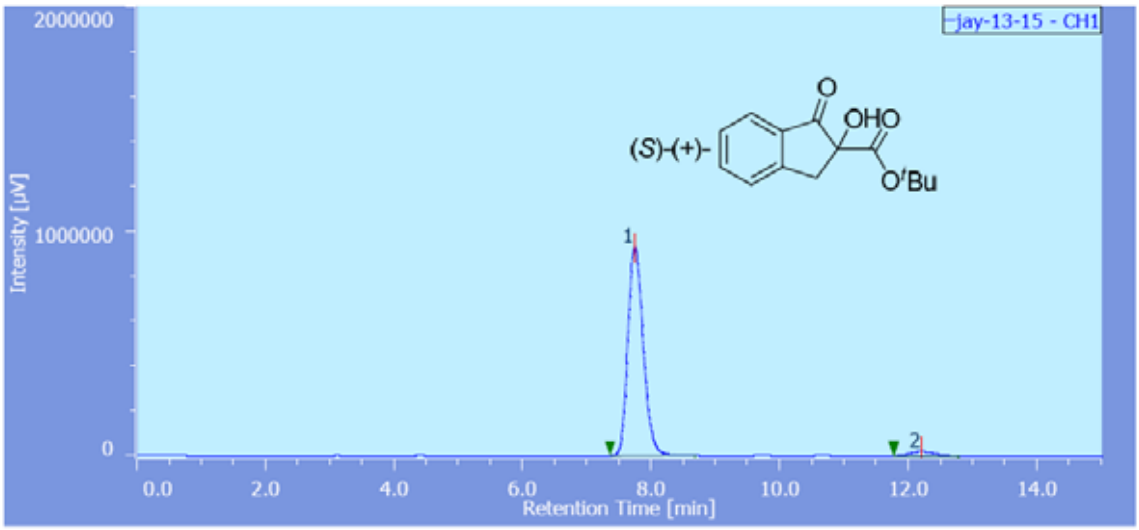
User Name	Administrator
Date Modified	2010-7-25 0:42:59
Description	
HPLC System Name	HPLC
Injection Date	2010-7-25 0:20:07
Volume	2.00 [μL]
Sample Number	1
Project Name	Jay
Acquisition Time	59.0 [min]
Acquisition Sequence	Hydroxylation of benzo-beta-keto tBu ester
Control Method	Hydroxylation of benzo-beta-keto tBu ester
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	jay-13-15-rac-CH1
Sample Name	
Channel Name	CH1
Sampling Interval	500 [msec]
Peak Method	(Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	7.733	9411552	587787	49.495	61.109	N/A	5474	8.063	1.195	
2	Unknown	1	12.125	9603518	374078	50.505	38.891	N/A	5175	N/A	1.163	

Chromatogram



Chromatogram Information

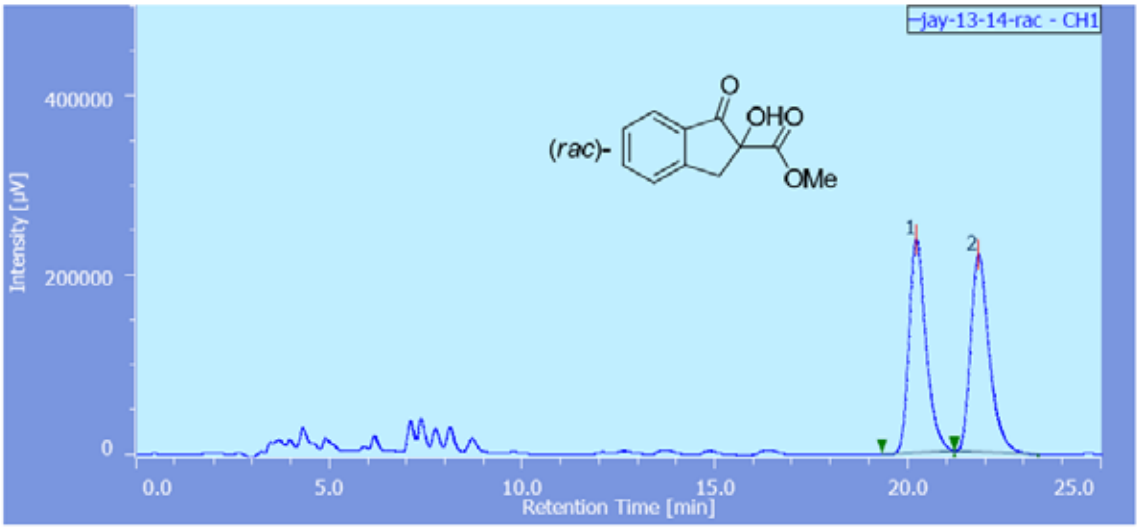
User Name	Administrator
Date Modified	2010-7-25 1:50:23
Description	
HPLC System Name	HPLC
Injection Date	2010-7-25 1:23:29
Volume	0.50 [μL]
Sample Number	1
Project Name	Jay
Acquisition Time	59.0 [min]
Acquisition Sequence	Hydroxylation of benzo-beta-keto tBu ester
Control Method	Hydroxylation of benzo-beta-keto tBu ester
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	jay-13-15-CH1
Sample Name	
Channel Name	CH1
Sampling Interval	500 [msec]
Peak Method	(Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	7.742	15445241	926946	97.163	98.079	N/A	5070	8.144	1.220	
2	Unknown	1	12.200	451029	18158	2.837	1.921	N/A	5420	N/A	1.129	

Chromatogram



Chromatogram Information

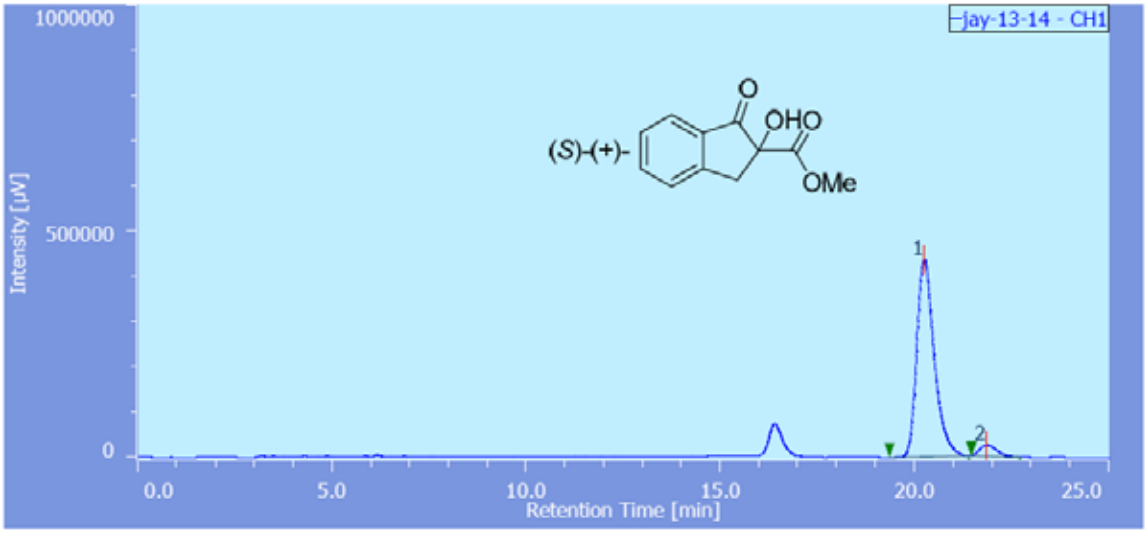
User Name	Administrator
Date Modified	2010-7-24 16:27:37
Description	
HPLC System Name	HPLC
Injection Date	2010-7-24 15:22:01
Volume	20.00 [μL]
Sample Number	1
Project Name	Jay
Acquisition Time	89.0 [min]
Acquisition Sequence	Hydroxylation of benzo-beta-keto Me ester
Control Method	Hydroxylation of benzo-beta-keto Me ester
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	jay-13-14-rac-CH1
Sample Name	
Channel Name	CH1
Sampling Interval	500 [msec]
Peak Method	(Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV*sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	20.217	7297357	238047	49.879	51.897	N/A	10673	1.982	1.302	
2	Unknown	1	21.825	7332695	220640	50.121	48.103	N/A	10687	N/A	1.359	

Chromatogram



Chromatogram Information

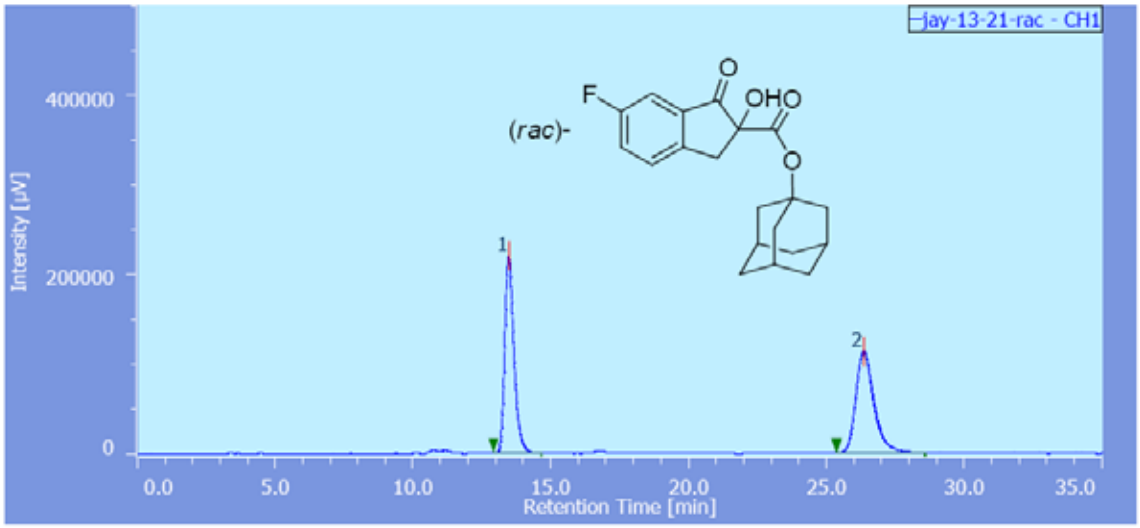
User Name	Administrator
Date Modified	2010-7-24 16:29:27
Description	
HPLC System Name	HPLC
Injection Date	2010-7-24 16:01:24
Volume	2.00 [μL]
Sample Number	1
Project Name	Jay
Acquisition Time	89.0 [min]
Acquisition Sequence	Hydroxylation of benzo-beta-keto Me ester
Control Method	Hydroxylation of benzo-beta-keto Me ester
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	jay-13-14-CH1
Sample Name	
Channel Name	CH1
Sampling Interval	500 [msec]
Peak Method	(Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	20.250	13605773	436291	95.086	94.841	N/A	10441	2.039	1.335	
2	Unknown	1	21.858	703105	23734	4.914	5.159	N/A	12276	N/A	1.333	

Chromatogram



Chromatogram Information

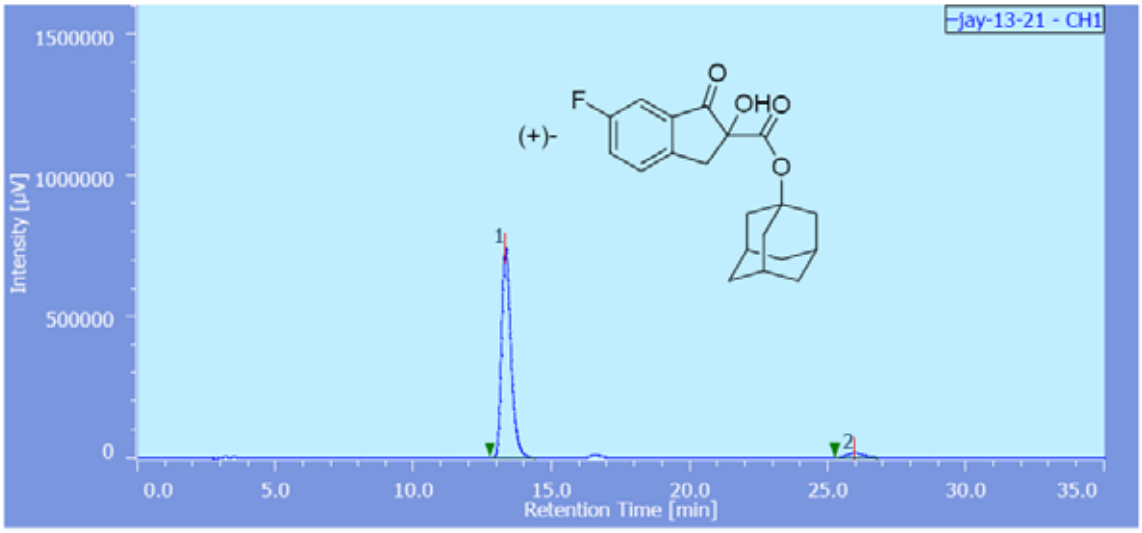
User Name	Administrator
Date Modified	2010-4-29 15:21:07
Description	
HPLC System Name	HPLC
Injection Date	2010-4-29 14:33:26
Volume	1.00 [μL]
Sample Number	1
Project Name	Jay
Acquisition Time	89.0 [min]
Acquisition Sequence	Hydroxylation of 5-F-benzo-beta-keto Ad ester
Control Method	Hydroxylation of 5-F-benzo-beta-keto Ad ester
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	jay-13-21-rac-CH1
Sample Name	
Channel Name	CH1
Sampling Interval	500 [msec]
Peak Method	(Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	13.475	5036502	220040	49.653	66.073	N/A	8614	15.003	1.313	
2	Unknown	1	26.333	5106850	112983	50.347	33.927	N/A	8568	N/A	1.360	

Chromatogram



Chromatogram Information

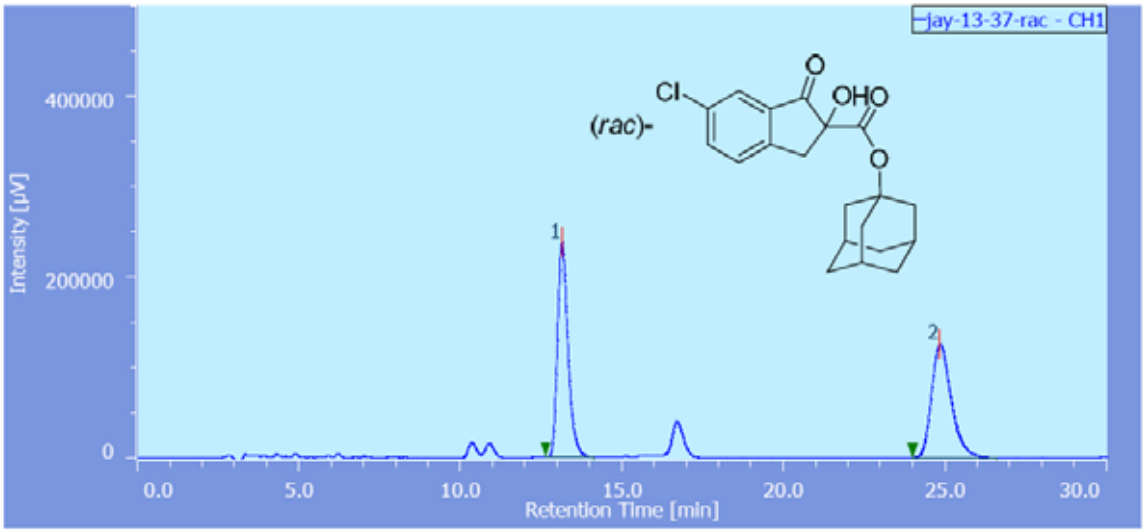
User Name	Administrator
Date Modified	2010-4-29 16:12:14
Description	
HPLC System Name	HPLC
Injection Date	2010-4-29 15:23:12
Volume	1.00 [μL]
Sample Number	1
Project Name	Jay
Acquisition Time	89.0 [min]
Acquisition Sequence	Hydroxylation of 5-F-benzo-beta-keto Ad ester
Control Method	Hydroxylation of 5-F-benzo-beta-keto Ad ester
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	jay-13-21-CH1
Sample Name	
Channel Name	CH1
Sampling Interval	500 [msec]
Peak Method	(Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	13.333	17329870	742894	96.684	97.977	N/A	7980	15.479	1.346	
2	Unknown	1	25.967	594299	15341	3.316	2.023	N/A	9979	N/A	1.076	

Chromatogram



Chromatogram Information

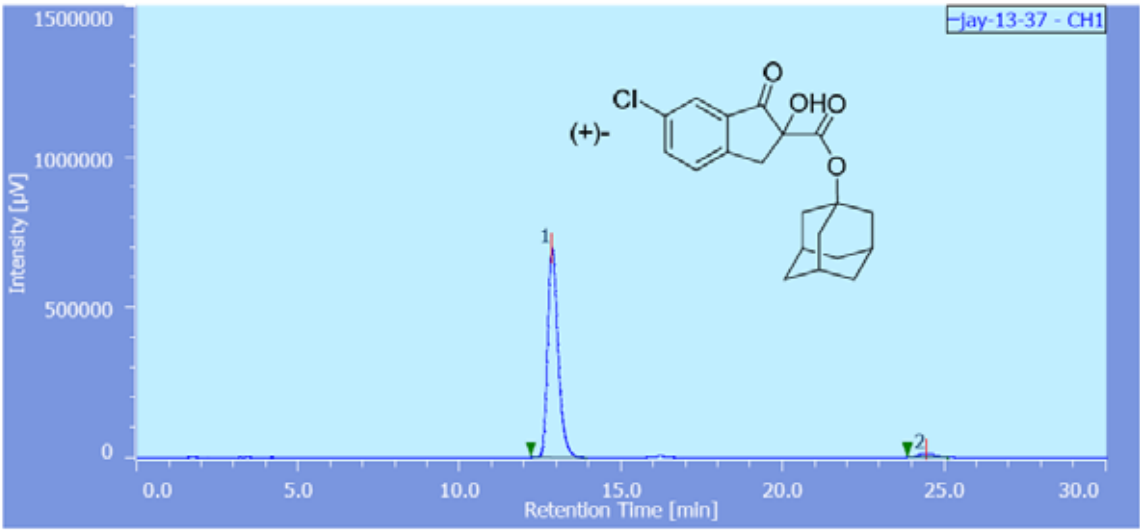
User Name	Administrator
Date Modified	2010-7-24 20:55:30
Description	
HPLC System Name	HPLC
Injection Date	2010-7-24 20:19:42
Volume	2.00 [μL]
Sample Number	1
Project Name	Jay
Acquisition Time	59.0 [min]
Acquisition Sequence	Hydroxylation of 5-Cl-benzo-beta-keto Ad ester
Control Method	Hydroxylation of 5-Cl-benzo-beta-keto Ad ester
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	jay-13-37-rac-CH1
Sample Name	
Channel Name	CH1
Sampling Interval	500 [msec]
Peak Method	(Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	13.142	5243384	236893	49.967	65.361	N/A	8654	14.374	1.331	
2	Unknown	1	24.833	5250408	125546	50.033	34.639	N/A	8682	N/A	1.317	

Chromatogram



Chromatogram Information

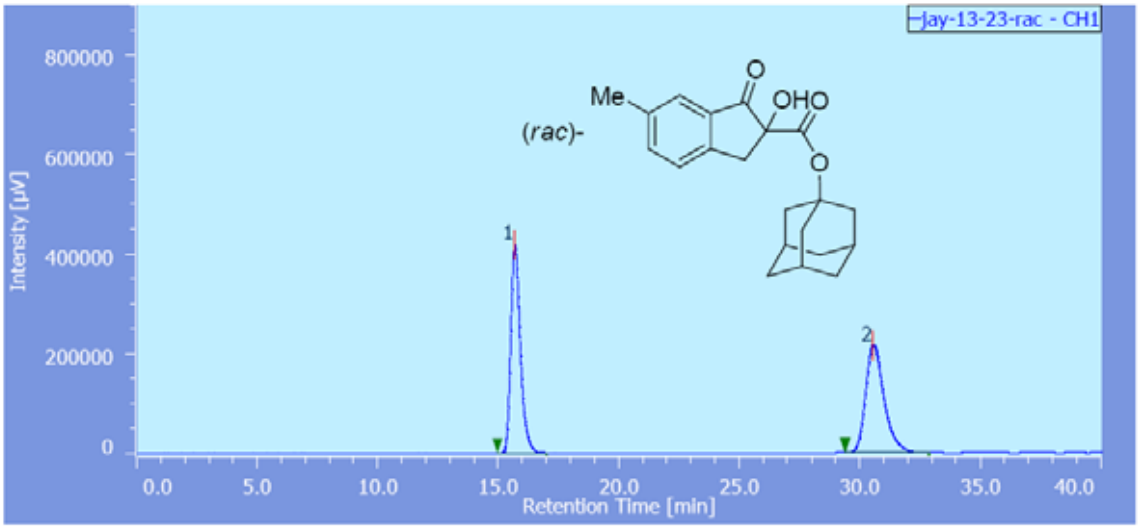
User Name	Administrator
Date Modified	2010-5-17 17:42:45
Description	
HPLC System Name	HPLC
Injection Date	2010-5-17 17:02:17
Volume	0.50 [μL]
Sample Number	1
Project Name	Jay
Acquisition Time	89.0 [min]
Acquisition Sequence	Hydroxylation of 5-Cl-benzo-beta-keto Ad ester
Control Method	Hydroxylation of 5-Cl-benzo-beta-keto Ad ester
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	jay-13-37-CH1
Sample Name	
Channel Name	CH1
Sampling Interval	500 [msec]
Peak Method	(Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	12.867	15468952	694026	97.556	98.468	N/A	8133	14.840	1.323	
2	Unknown	1	24.433	387545	10799	2.444	1.532	N/A	9700	N/A	1.092	

Chromatogram



Chromatogram Information

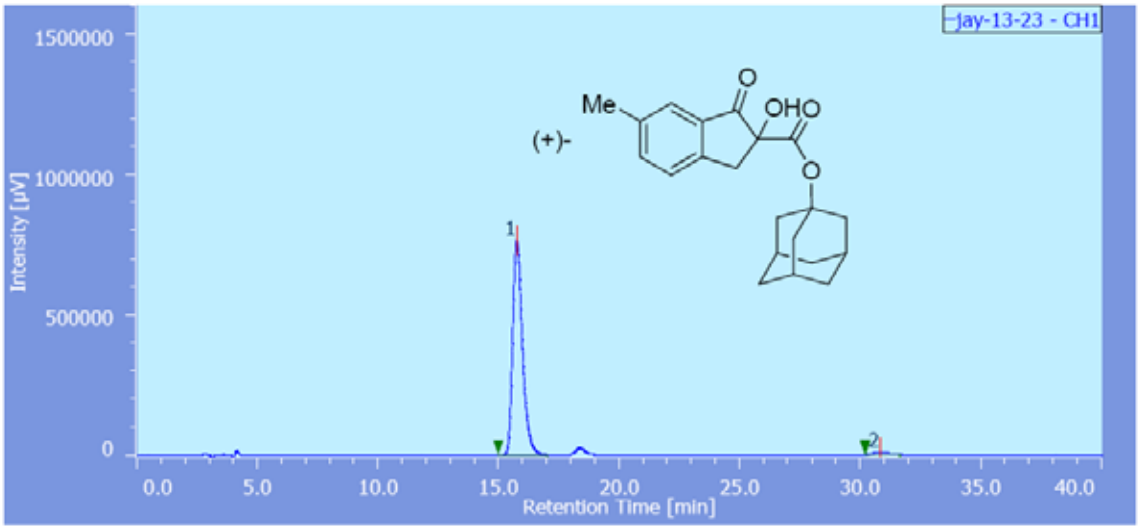
User Name	Administrator
Date Modified	2010-4-29 21:57:16
Description	
HPLC System Name	HPLC
Injection Date	2010-4-29 20:48:17
Volume	1.00 [μL]
Sample Number	1
Project Name	Jay
Acquisition Time	89.0 [min]
Acquisition Sequence	Hydroxylation of 5-Me-benzo-beta-keto Ad ester
Control Method	Hydroxylation of 5-Me-benzo-beta-keto Ad ester
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	jay-13-23-rac-CH1
Sample Name	
Channel Name	CH1
Sampling Interval	500 [msec]
Peak Method	(Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	15.692	11373100	418040	49.711	66.032	N/A	8188	14.506	1.314	
2	Unknown	1	30.550	11505383	215052	50.289	33.968	N/A	8068	N/A	1.333	

Chromatogram



Chromatogram Information

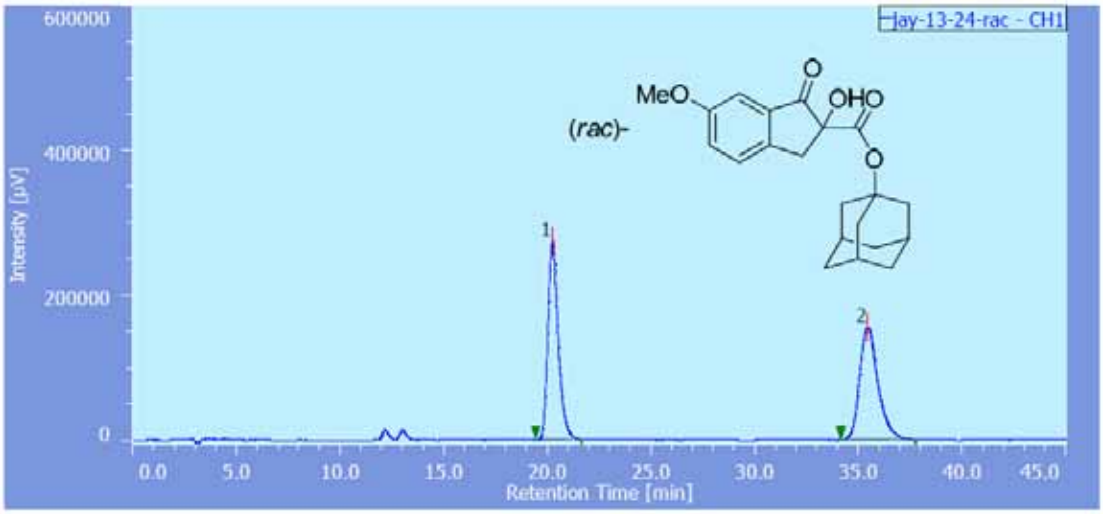
User Name	Administrator
Date Modified	2010-4-29 22:54:59
Description	
HPLC System Name	HPLC
Injection Date	2010-4-29 22:01:20
Volume	1.00 [μL]
Sample Number	1
Project Name	Jay
Acquisition Time	89.0 [min]
Acquisition Sequence	Hydroxylation of 5-Me-benzo-beta-keto Ad ester
Control Method	Hydroxylation of 5-Me-benzo-beta-keto Ad ester
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	jay-13-23-CH1
Sample Name	
Channel Name	CH1
Sampling Interval	500 [msec]
Peak Method	(Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	15.758	21182447	762736	98.579	99.096	N/A	7857	15.630	1.341	
2	Unknown	1	30.825	305304	6956	1.421	0.904	N/A	10182	N/A	1.156	

Chromatogram



Chromatogram Information

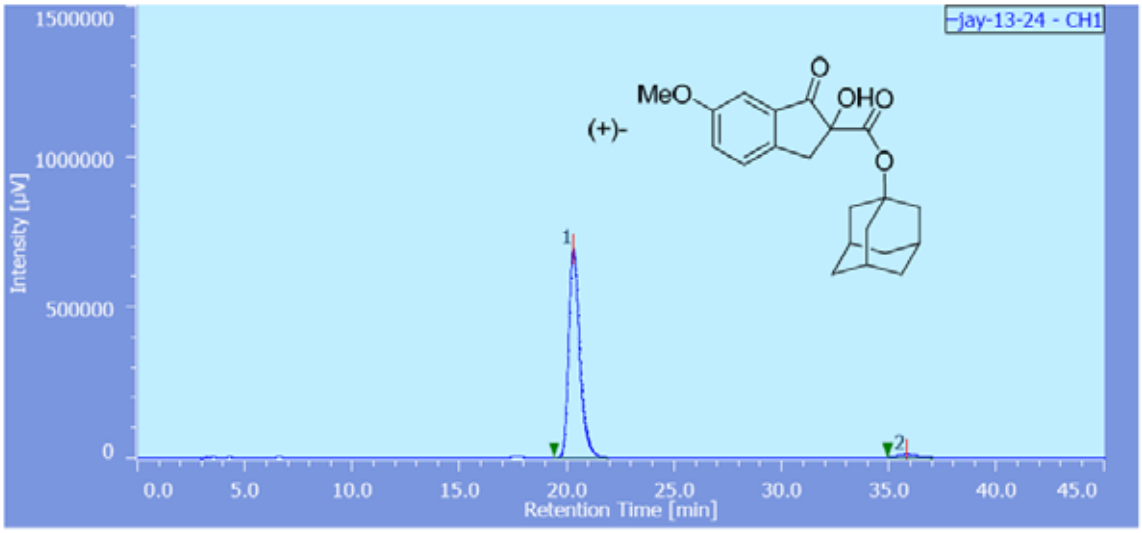
User Name	Administrator
Date Modified	2010-4-29 17:03:50
Description	
HPLC System Name	HPLC
Injection Date	2010-4-29 16:16:02
Volume	1.00 [μL]
Sample Number	1
Project Name	Jay
Acquisition Time	88.0 [min]
Acquisition Sequence	Hydroxylation of 5-MeO-benzo-beta-keto Ad ester
Control Method	Hydroxylation of 5-MeO-benzo-beta-keto Ad ester
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	jay-13-24-rac-CH1
Sample Name	
Channel Name	CH1
Sampling Interval	500 [msec]
Peak Method	(Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	20.233	9473079	274713	49.835	63.806	N/A	8489	12.512	1.314	
2	Unknown	1	35.425	9535992	155828	50.165	36.194	N/A	8290	N/A	1.297	

Chromatogram



Chromatogram Information

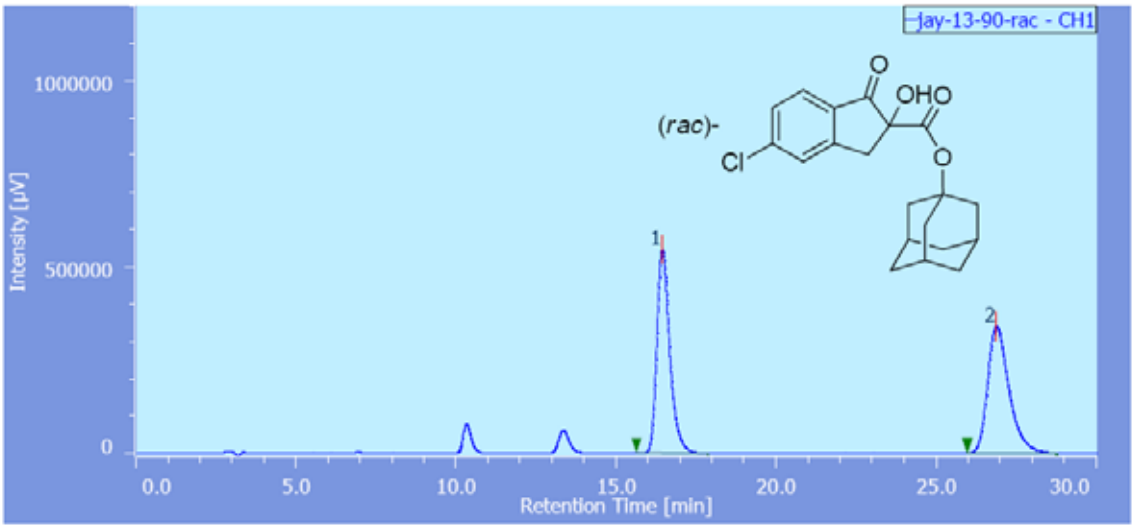
User Name	Administrator
Date Modified	2010-4-29 18:09:33
Description	
HPLC System Name	HPLC
Injection Date	2010-4-29 17:05:54
Volume	1.00 [μL]
Sample Number	1
Project Name	Jay
Acquisition Time	89.0 [min]
Acquisition Sequence	Hydroxylation of 5-MeO-benzo-beta-keto Ad ester
Control Method	Hydroxylation of 5-MeO-benzo-beta-keto Ad ester
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	jay-13-24-CH1
Sample Name	
Channel Name	CH1
Sampling Interval	500 [msec]
Peak Method	(Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	20.292	24685580	691270	98.078	98.794	N/A	7925	12.525	1.363	
2	Unknown	1	35.792	483752	8436	1.922	1.206	N/A	8316	N/A	1.183	

Chromatogram



Chromatogram Information

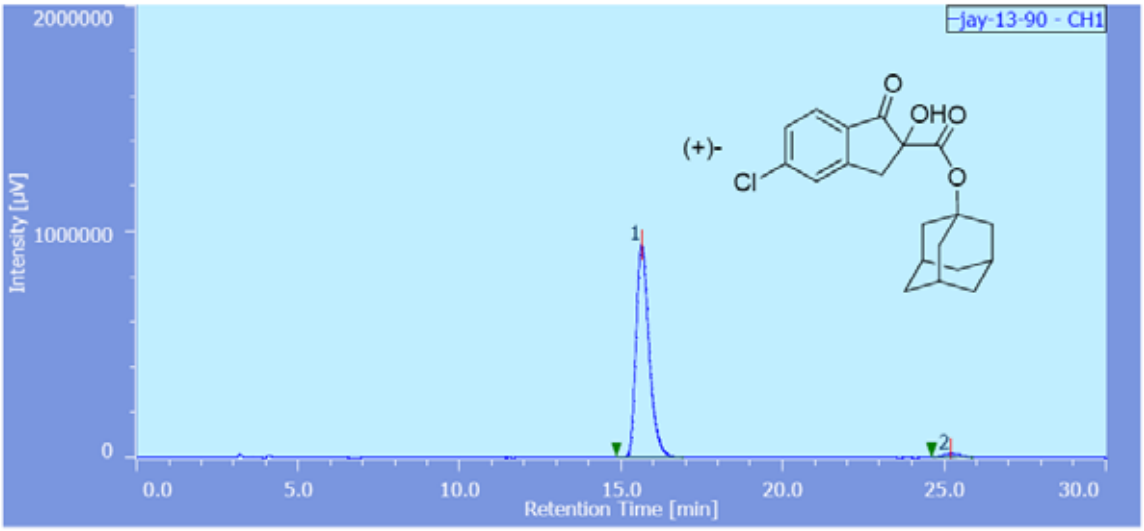
User Name	Administrator
Date Modified	2010-7-24 20:16:13
Description	
HPLC System Name	HPLC
Injection Date	2010-7-24 19:38:28
Volume	2.00 [μL]
Sample Number	1
Project Name	Jay
Acquisition Time	59.0 [min]
Acquisition Sequence	Hydroxylation of 4-Cl-benzo-beta-keto Ad ester
Control Method	Hydroxylation of 4-Cl-benzo-beta-keto Ad ester
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	jay-13-90-rac-CH1
Sample Name	
Channel Name	CH1
Sampling Interval	500 [msec]
Peak Method	(Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV*sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	16.442	15397876	544840	49.596	61.688	N/A	8291	11.005	1.331	
2	Unknown	1	26.875	15648474	338373	50.404	38.312	N/A	8315	N/A	1.365	

Chromatogram



Chromatogram Information

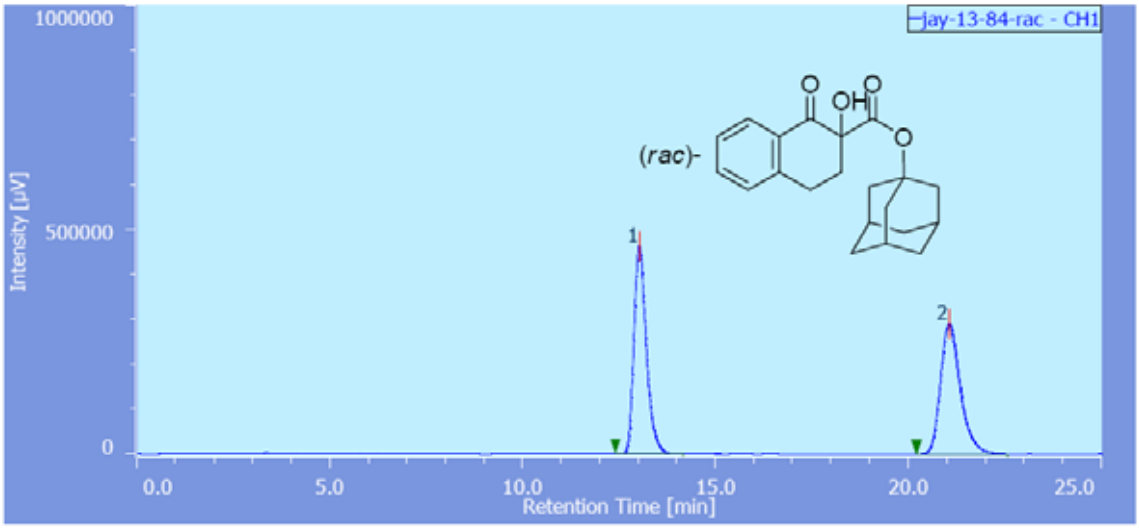
User Name	Administrator
Date Modified	2010-6-19 0:41:20
Description	
HPLC System Name	HPLC
Injection Date	2010-6-18 23:38:29
Volume	1.00 [μL]
Sample Number	1
Project Name	Jay
Acquisition Time	59.0 [min]
Acquisition Sequence	Hydroxylation of 4-Cl-benzo-beta-keto Ad ester
Control Method	Hydroxylation of 4-Cl-benzo-beta-keto Ad ester
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	jay-13-90-CH1
Sample Name	
Channel Name	CH1
Sampling Interval	500 [msec]
Peak Method	(Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	15.625	26057583	939049	98.051	98.493	N/A	7633	11.290	1.368	
2	Unknown	1	25.200	518052	14365	1.949	1.507	N/A	10465	N/A	1.060	

Chromatogram



Chromatogram Information

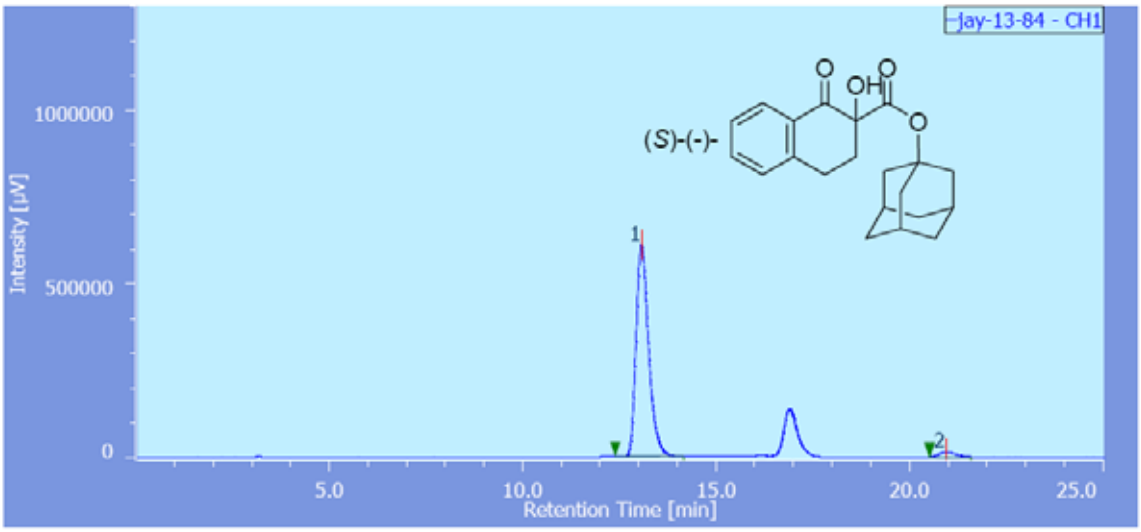
User Name	Administrator
Date Modified	2010-5-10 22:52:39
Description	
HPLC System Name	HPLC
Injection Date	2010-5-10 22:10:07
Volume	3.00 [μL]
Sample Number	1
Project Name	Jay
Acquisition Time	89.0 [min]
Acquisition Sequence	Hydroxylation of benzo-6-ring Ad ester
Control Method	Hydroxylation of benzo-6-ring Ad ester
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	jay-13-84-rac-CH1
Sample Name	
Channel Name	CH1
Sampling Interval	500 [msec]
Peak Method	(Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	13.025	10257490	461826	49.736	61.435	N/A	8447	10.900	1.321	
2	Unknown	1	21.050	10366214	289907	50.264	38.565	N/A	8571	N/A	1.311	

Chromatogram



Chromatogram Information

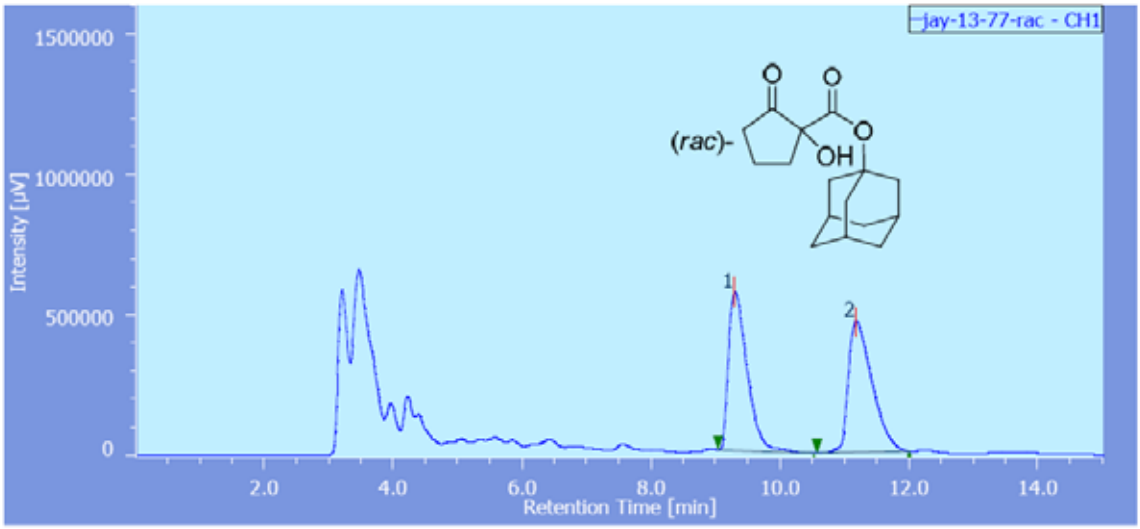
User Name	Administrator
Date Modified	2010-7-24 20:41:16
Description	
HPLC System Name	HPLC
Injection Date	2010-6-11 15:46:56
Volume	1.00 [μL]
Sample Number	1
Project Name	Jay
Acquisition Time	59.0 [min]
Acquisition Sequence	Hydroxylation of benzo-6-ring Ad ester
Control Method	Hydroxylation of benzo-6-ring Ad ester
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	jay-13-84-CH1
Sample Name	
Channel Name	CH1
Sampling Interval	500 [msec]
Peak Method	(Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	13.067	13634788	609904	97.096	97.860	N/A	8360	11.252	1.335	
2	Unknown	1	20.933	407734	13335	2.904	2.140	N/A	10170	N/A	1.214	

Chromatogram



Chromatogram Information

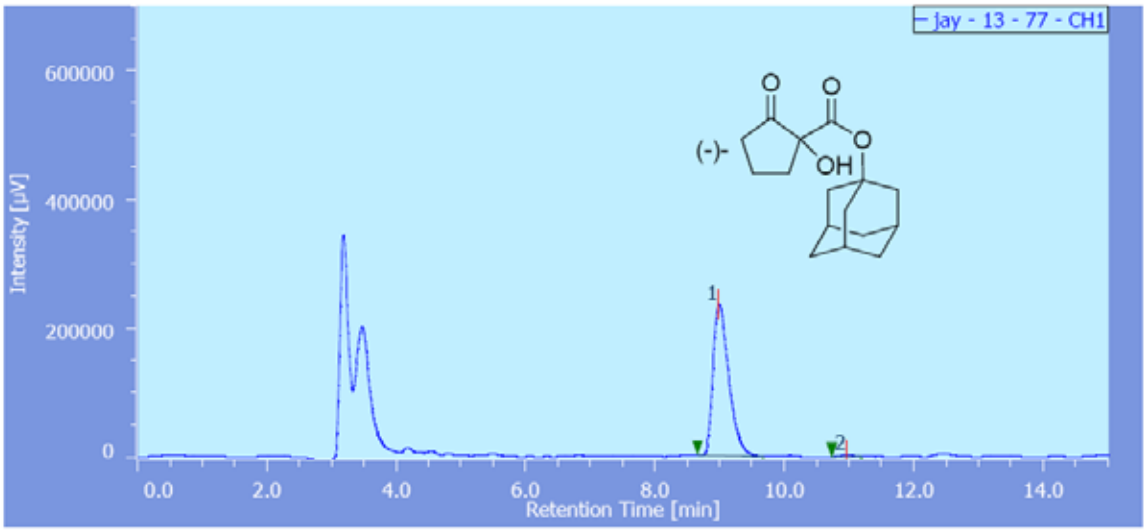
User Name	Administrator
Date Modified	2010-7-25 16:29:50
Description	
HPLC System Name	HPLC
Injection Date	2010-7-25 16:08:14
Volume	30.00 [μL]
Sample Number	1
Project Name	Jay
Acquisition Time	59.0 [min]
Acquisition Sequence	Hydroxylation of 5-ring Ad ester
Control Method	Hydroxylation of 5-ring Ad ester
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

Chromatogram Name	jay-13-77-rac-CH1
Sample Name	
Channel Name	CH1
Sampling Interval	500 [msec]
Peak Method	(Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	9.292	11381649	564795	48.797	54.772	N/A	5053	3.168	1.823	
2	Unknown	1	11.175	11942718	466380	51.203	45.228	N/A	4460	N/A	1.749	

Chromatogram



Chromatogram Information

User Name	Administrator
Date Modified	2010-6-4 0:06:53
Description	
HPLC System Name	HPLC
Injection Date	2010-6-3 23:49:18
Volume	5.00 [μL]
Sample Number	1
Project Name	Jay
Acquisition Time	59.0 [min]
Acquisition Sequence	Hydroxylation of 5-ring Ad ester
Control Method	Hydroxylation of 5-ring Ad ester
Peak ID Table	
Calibration Method	
Additional Information	

Channel & Peak Information Table

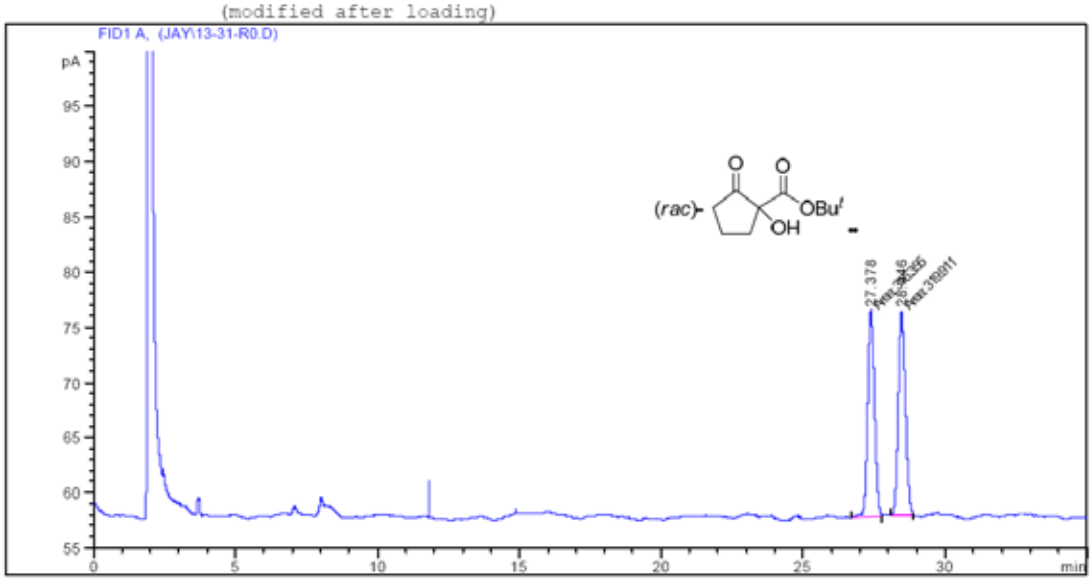
Chromatogram Name	jay-13-77-rac-CH1
Sample Name	
Channel Name	CH1
Sampling Interval	500 [msec]
Peak Method	(Manual)
Formula	
Decision	

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	1	8.983	3995532	235371	98.813	98.582	N/A	6575	4.777	1.547	
2	Unknown	1	10.958	47977	3385	1.187	1.418	N/A	12897	N/A	0.973	

Data File D:\HPCHEM\1\DATA\JAY\13-76-R0.D Sample Name: jay-13-76-rac

beta-120

```
Injection Date  : 5/14/2010 5:09:26 AM
Sample Name     : jay-13-76-rac                  Location : Vial 1
Acq. Operator   : Jay                               Inj :   1
                                                 Inj Volume : External
Acq. Method     : D:\HPCHEM\1\METHODS\JAY\HYDOXY~1.M
Last changed    : 5/14/2010 4:16:14 AM by Jay
Analysis Method : D:\HPCHEM\1\METHODS\OFFGC2.M
Last changed    : 7/23/2010 3:17:44 PM by wujiang
                  (modified after loading)
```



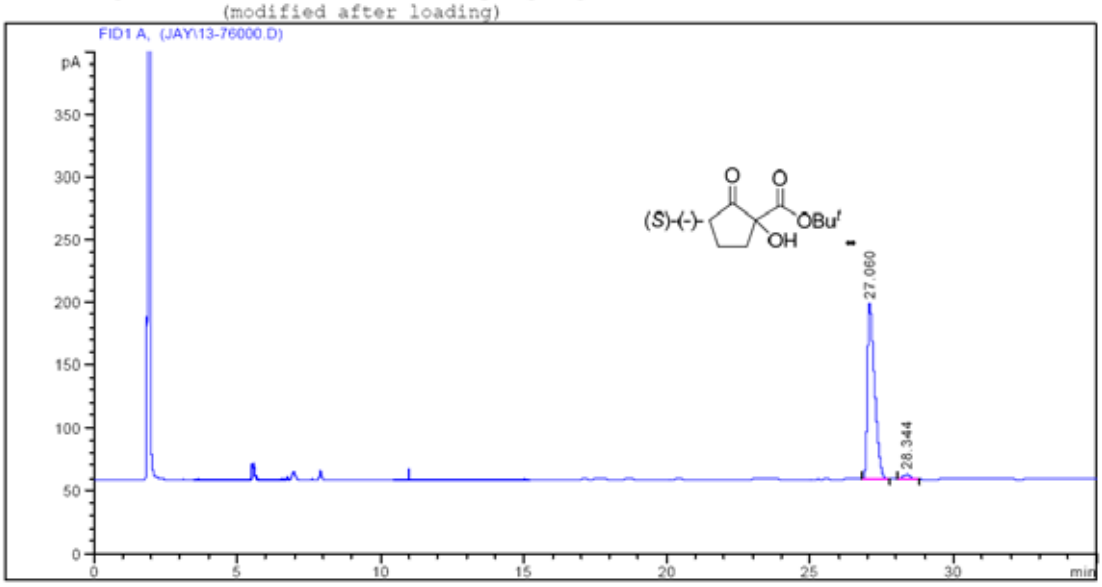

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|---------|---------|--------|
   1  27.378 MM    0.2819  316.35504   18.70178 49.72052
   2  28.446 MM    0.2895  319.91147   18.41654 50.27948

Totals :                   636.26651   37.11832

 Results obtained with enhanced integrator!

                          *** End of Report ***
```

Instrument 1 7/23/2010 3:18:35 PM wujiang Page 1 of 1

Data File D:\HPCHEM\1\DATA\JAY\13-76000.D Sample Name: jay-13-76

beta120

```
==========================================================================
Injection Date  : 6/4/2010 12:25:50 AM
Sample Name     : jay-13-76                    Location : Vial 1
Acq. Operator   : jay                             Inj :   1
                                               Inj Volume : External
Acq. Method     : D:\HPCHEM\1\METHODS\JAY\HYDOXY~1.M
Last changed    : 5/28/2010 8:53:29 AM by wujiang
Analysis Method : D:\HPCHEM\1\METHODS\OFFGC2.M
Last changed    : 7/23/2010 3:13:32 PM by wujiang
                  (modified after loading)
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  27.060 BB    0.2412 2444.23779  139.61880 97.52278
   2  28.344 PB    0.2245   62.08709    3.70458  2.47722

Totals :                  2506.32488  143.32338

 Results obtained with enhanced integrator!
==========================================================================
```

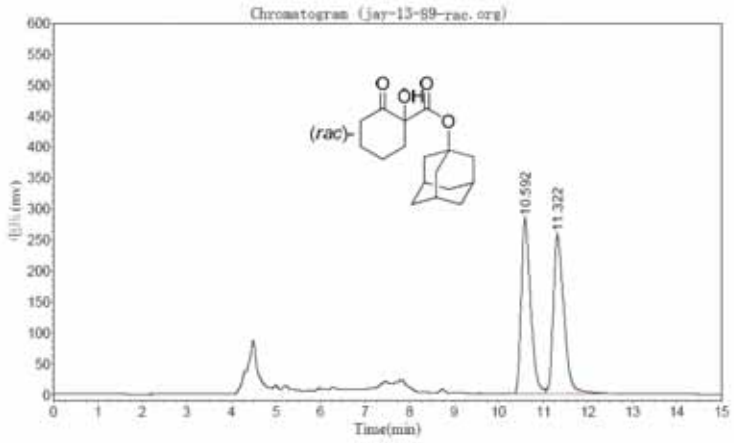
Instrument 1 7/23/2010 3:16:19 PM wujiang Page 1 of 1

HPLC Report

Date/Time: 2010-06-18,0:22:04
Data File: D:\HPLC\Jay\data\jay-13-89-rac.org

Date/Time: 2010-06-18,0:23:41
Quantification: Area/Area%

Sample Description:
AS-H, 95/5, 0.7 ml/min, 210nm



Results

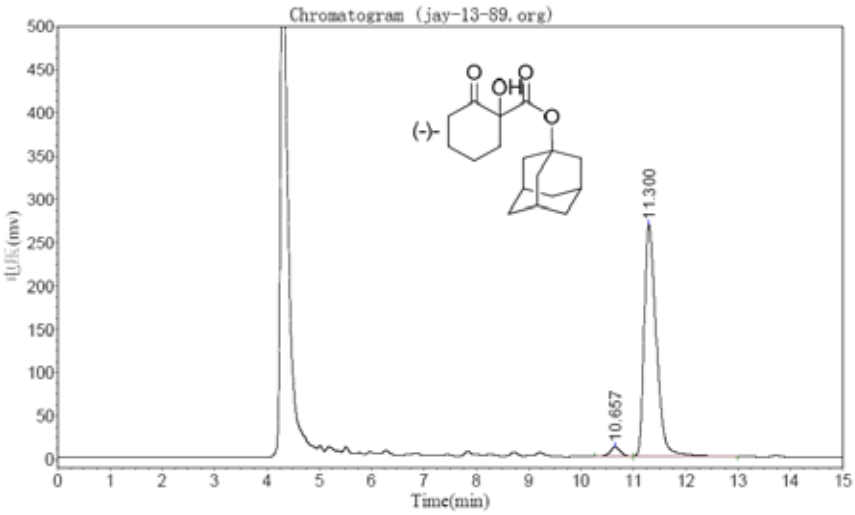
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.592	281094.438	4088707.750	49.3265
2		11.322	255228.406	4200368.000	50.6735
Total			536322.844	8289075.750	100.0000

HPLC Report

Date/Time: 2010-06-18,0:02:20
Data File: D:\HPLC\Jay\data\jay-13-89.org

Date/Time: 2010-06-18,0:05:24
Quantification: Area/Area%

Sample Description:
AS-H, 95/5, 0.7 ml/min, 210nm



Results

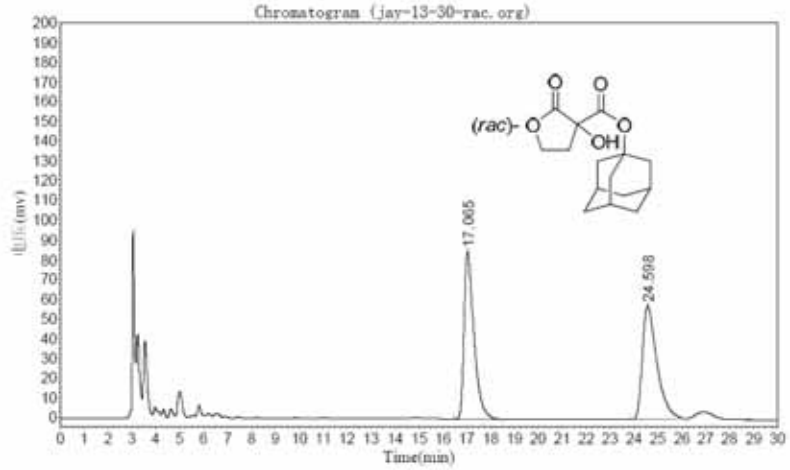
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.657	11509.521	151184.703	3.4064
2		11.300	267650.188	4287092.000	96.5936
Total			279159.708	4438276.703	100.0000

HPLC Report

Date/Time: 2010-07-24,10:35:59
Data File: D:\HPLC\Jay\data\jay-13-30-rac.org

Date/Time: 2010-07-24,10:39:05
Quantification: Area/Area%

Sample Description:
AD-H, 90/10, 1.0 ml/min, 216nm



Results

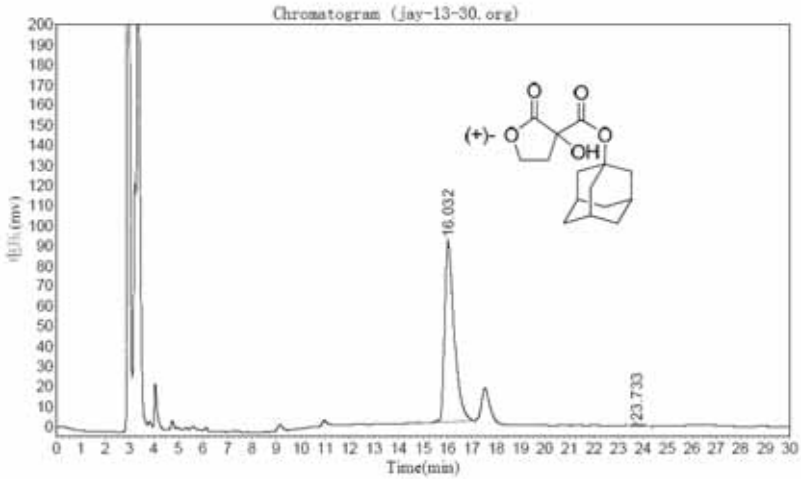
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.065	84687.813	2437963.500	49.5033
2		24.598	57539.000	2486889.500	50.4967
Total			142226.813	4924853.000	100.0000

HPLC Report

Date/Time: 2010-5-12,11:51:49
Data File: D:\HPLC\Jay\data\jay-13-30.org

Date/Time: 2010-5-12,11:54:54
Quantification: Area/Area%

Sample Description:
AD-H, 90/10, 1.0 ml/min, 216nm



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.032	89344.758	2413847.500	99.5786
2		23.733	343.115	10214.751	0.4214
Total			89687.873	2424062.251	100.0000