Electronic Supplementary Material (ESI) for Chemical Communications

Catalytic Asymmetric Cross-Dehydrogenative Coupling: Activation of C-H Bonds by a Cooperative Bimetallic Catalyst System**

Weidi Cao, Xiaohua Liu, Ruixue Peng, Peng He, Lili Lin and Xiaoming Feng *

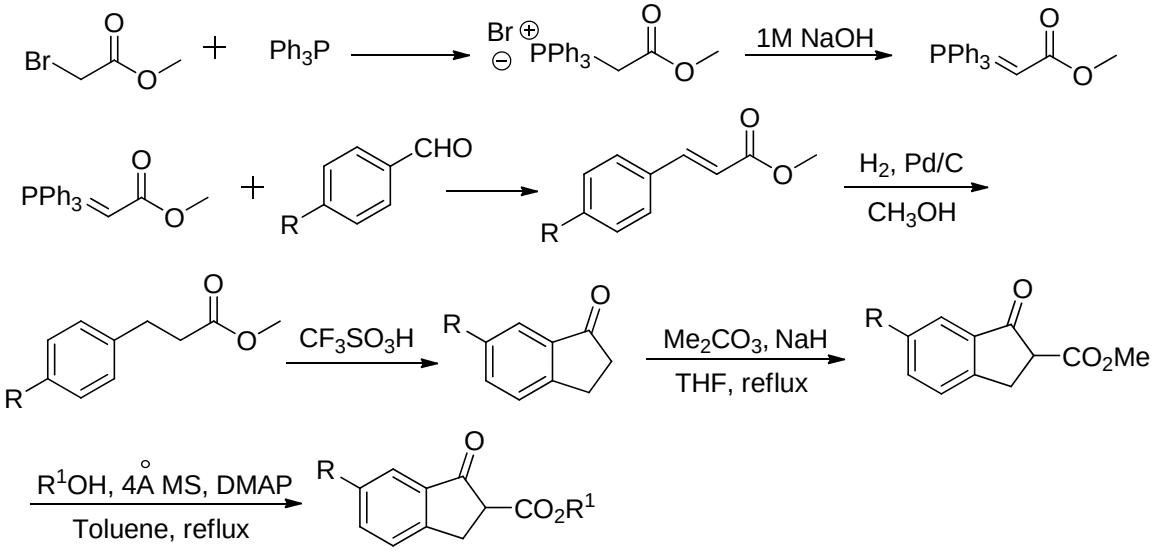
Supporting Information

CONTENTS:

(A) General remarks

^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}C NMR spectra were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0). Melting points (m.p.) were measured on electrothermal digital melting point apparatus and were uncorrected. Enantiomeric excesses (ee) were determined by HPLC analysis using the corresponding commercial chiral column as stated in the experimental procedures at 25 ^{o}C. Optical rotations were reported as follows: $[\alpha]^{T}_{D}$ (c g/100 mL, in CH_2Cl_2). HRMS was recorded on a commercial apparatus (ESI Source). All catalytic reactions were run in dried glassware using standard techniques. THF was distilled from sodium benzophenone ketyl. $CHCl_2CHCl_2$ was distilled after dried over K_2CO_3. MeOH was distilled over magnesium rod. **1b**、**1c**、**1d** and **1e** were prepared following a literature procedure,[1] xanthene was used after recrystallized, ^{t}BuOOH was 5.0-6.0 M in decane. All of racemic samples were prepared by using 10 mol% (DL)-pipecolic acid derived **L**-$Fe(BF_4)_2{\cdot}6H_2O$ complex as the catalyst.

(B) Typical procedure for substrates preparation.



1) The synthesis of phosphorus ylide

To a solution of triphenylphosphine in toluene, methyl bromoacetate was added. The mixture was stirred at room temperature for 2 h, then filtrated. The residue was washed with toluene. 1M NaOH was used to all the solid dissolved, CH_2Cl_2 extracted for three times, dried by $MgSO_4$, removing CH_2Cl_2 in vacuum.

2) The synthesis of *α,β*-unsaturated esters

To a solution of phosphorus ylide in toluene, aldehyde was added. The reaction was stirred at room temperature for 3 h, removing CH_2Cl_2 in vacuum without further purification.

3) The synthesis of esters

The α,*β*-unsaturated esters was reducing to esters under H_2 atmosphere in MeOH with palladium 10% on carbon as the catalyst. filtrated, removing MeOH in vacuum, the residue was purified by flash chromatography on silica gel, formed pure products.

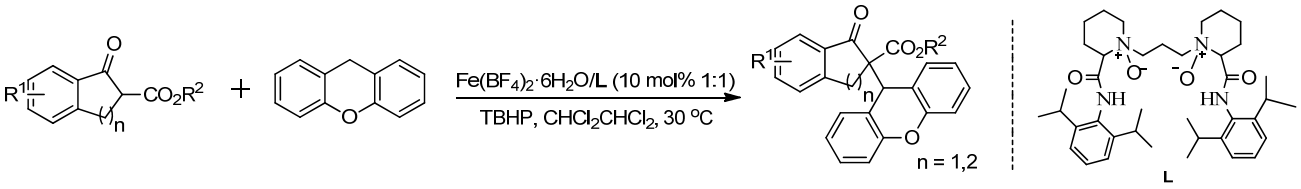
4) The synthesis of substituted indenone

To ice-cooled TFSA (100 equiv) was slowly added esters, and the solution was stirred at 25 °C for 96 h. To the solution was added CH_2Cl_2 and the mixture was poured into ice-water, which was extracted with CH_2Cl_2. The organic phase was washed with brine and dried over Na_2SO_4, and the solvent was evaporated under reduced pressure to give a residue, which was purified via column chromatography on silica gel and to give pure substituted indenone.

2) The synthesis of *β*-ketoesters

To a solution of NaH in THF was slowly added indenone under N_2 atmosphere. After 20 min, dimethyl carboxylate was added and warmed to reflux. The reaction was monitored by TLC. The solvent was evaporated under reduced pressure, and 1 M HCl was added making pH to 4, extracted with CH_2Cl_2, the organic phase was washed with brine and dried over Na2SO4, and the solvent was evaporated under reduced pressure to give a residue, which was purified via column chromatography on silica gel and to give *β*-ketoesters.

(C) Typical procedure for the preparation of the racemic products



A mixture of (±)-**L** (0.01 mmol), $Fe(BF_4)_2.6H_2O$ (0.01 mmol), *β*-ketoesters (0.1 mmol), xanthene (0.1mmol) and ^{t}BuOOH (20 μL) were stirred in $CHCl_2CHCl_2$ (0.5 mL) at 30 ^{o}C for 10 h. The residue was purified by flash chromatography on silica gel (prtroleum ether/ethyl acetate = 20/1) to afford the pure racemic product.

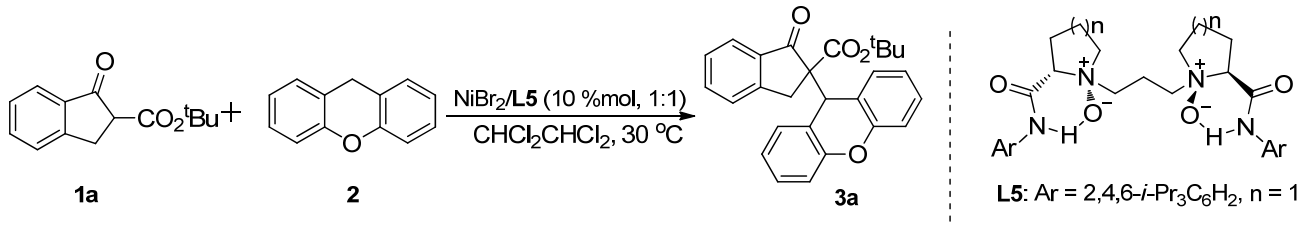
(D) Typical procedure for catalytic asymmetric CDC reaction

To a dry volumetlric flask (1.0 mL), **L2** or **L5** (0.02 mmol), $Fe(BF_4)_2{\cdot}6H_2O$ (0.02 mmol, 6.8 mg) and

THF (1.0 mL) were added and stirred at 30 °C for 0.5 h. Then the catalyst solution (100 μL) was added to a dry reaction tube. After removing THF in vacuum, additional **L2** or **L5** (0.01 mmol), $NiBr_2$ (0.01 mmol, 2.2 mg), *β*-ketoesters (0.1 mmol) were added under N_2 atmosphere, and stirred at 30 °C for 0.5 h. Next, xanthene (0.11-0.2 mmol) and ^{t}BuOOH (20 μL) were added, and the mixture continued stirring at 30 °C for the indicated time. The residue was purified by flash chromatography on silica gel (0-5 °C) to afford the corresponding products.

(E) Optimization of the Oxidant

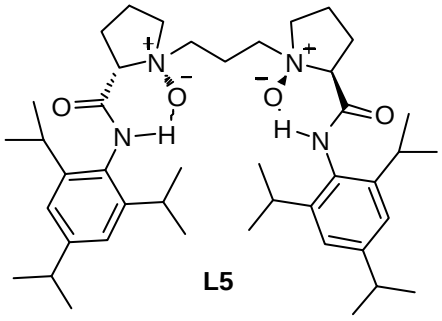
Table 1 : Optimization of the Oxidant.[a]



Entry	oxidant	Yield of **3a** (%)[b]	*ee* of **3a** (%)[c]
1	H_2O_2	NR[d]	-
2[e]	DDQ	85	0
3[f]	*m*-CPBA	trace	-
4	TBHP	51	99

a Unless otherwise noted, all reactions were performed with $NiBr_2$/**L5** (10 mol%, 1:1), **1a** (0.10 mmol), **2** (0.11 mmol), oxidant (0.10 mmol) at 30 °C for 24 h. *b* Isolated yield. *c* Determined by chiral HPLC analysis of ID column. *d* NR = no reaction. *e* DDQ = 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone. *f* *m*-CPBA = 3-Chloroperoxybenzoic acid.

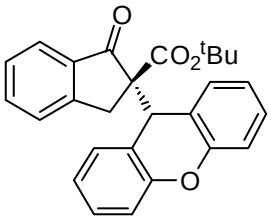
(F) The analytical and spectral characterization data of catalyst the L5 and products



White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.44 (S, 2H), 7.01 (S, 4H), 3.88 – 3.59 (m, 6H), 3.54 – 3.32 (m, 4H), 3.12 – 2.96 (m, 4H), 2.95 – 2.78 (m, 4H), 2.76 – 2.44 (m, 6H), 2.22 – 1.88 (m, 4H), 1.24 (d, J = 6.8 Hz, 22H), 1.18 (d, J = 6.8 Hz, 12H). ^{13}C

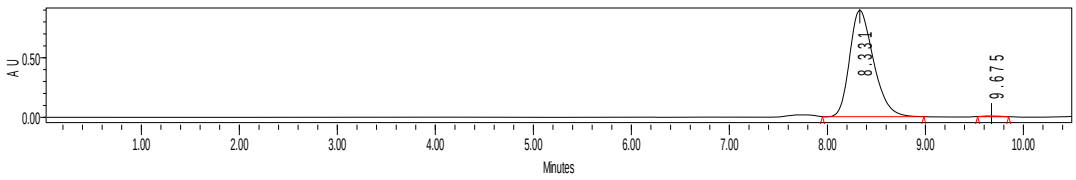
NMR (101 MHz, $CDCl_3$) δ = 166.40, 148.06, 144.53, 128.67, 121.37, 68.21, 64.05, 34.29, 29.06, 27.57, 24.09, 23.28, 20.33, 19.80; HRMS (ESI-TOF) calcd for $C_{43}H_{68}N_4O_4$ ([M+H^+]) = 705.5319, Found 705.5320.

(*R*)-tert-butyl 1-oxo-2-(9H-xanthen-9-yl)-2,3-dihydro-1H-indene-2-carboxylate



3a

White solid, m.p. 98 –100 °C, 90% yield, 99% ee; $[\alpha]_D^{25}$ = −188.57 (c = 0.70 in CH_2Cl_2); the ee was determined by HPLC analysis using a chiral ID column (hexane/^{i}PrOH = 95/5, 1.0 mL/min, 254 nm) t_r (major) = 8.33 min, t_r (minor) = 9.67 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.28 (m, 5H), 7.25 – 7.23 (m, 1H), 7.21 – 7.13 (m, 2H), 7.12 – 7.05 (m, 1H), 7.04 – 6.97 (m, 1H), 6.96 – 6.91 (m, 1H), 6.87 – 6.76 (m, 1H), 5.36 (s, 1H), 3.48 (d, J = 17.6 Hz, 1H), 3.10 (d, J = 17.6 Hz, 1H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.40, 167.34, 154.35, 153.58, 153.46, 134.98, 134.91, 130.83, 129.79, 128.46, 128.20, 127.06, 125.77, 124.32, 123.44, 123.30, 122.32, 120.77, 116.73, 116.44, 82.69, 71.39, 42.97, 31.61, 27.86; HRMS (ESI-TOF) calcd for $C_{27}H_{24}O_4$ ([M+Na^+]) = 435.1572, Found 435.1576.



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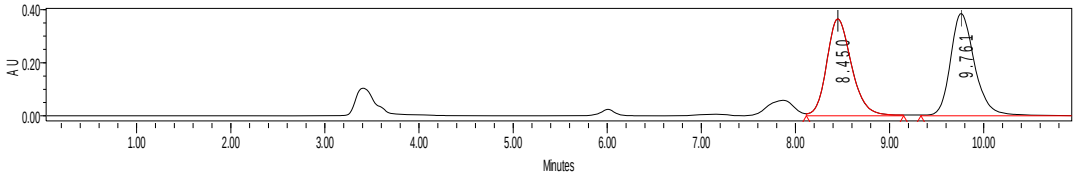
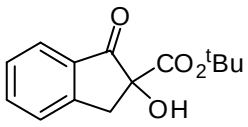
1	8.331	15127139	99.55
2	9.675	68992	0.45



	Retention Time	Area	% Area

1	8.450	6709734	49.27
2	9.761	6908165	50.73

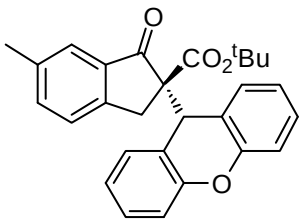
tert-butyl 2-hydroxy-1-oxo-2,3-dihydro-1H-indene-2-carboxylate



3a'

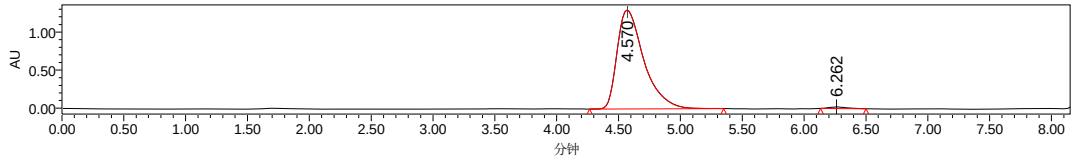
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 4.02 (s, 1H), 3.65 (d, *J* = 17.1 Hz, 1H), 3.22 (d, *J* = 17.1 Hz, 1H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ =200.37, 169.53, 151.31, 134.85, 132.89, 126.92, 125.26, 124.05, 82.93, 79.51, 38.42, 26.66.

(*R*)-tert-butyl 6-methyl-1-oxo-2-(9H-xanthen-9-yl)-2,3-dihydro-1H-indene-2-carboxylate

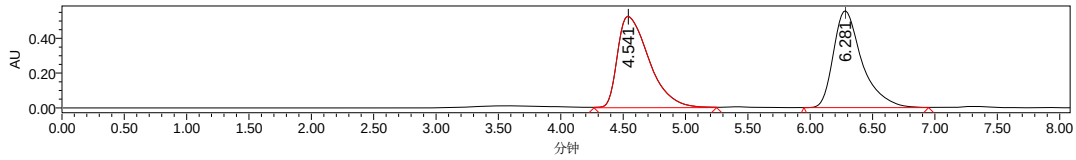


3b

White solid, m.p. 168 –170 °C, 71% yield, 98% ee; $[\alpha]_D^{25}$ = −173.93 (c = 0.56 in CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IC column (hexane/^{i}PrOH = 90/10, 1.0 mL/min, 254 nm) t_r (major) = 4.57 min, t_r (minor) = 6.26 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.38 (s, 1H), 7.30 – 7.27 (m, 1H), 7.26 – 7.10 (m, 4H), 7.09 – 7.00 (m, 2H), 6.97 – 6.92 (m, 1H), 6.87 – 6.80 (m, 1H), 5.36 (s, 1H), 3.41 (d, *J* = 17.4 Hz, 1H), 3.04 (d, *J* = 17.4 Hz, 1H), 2.28 (s, 3H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.36, 167.42, 153.59, 153.49, 151.81, 136.93, 136.27, 135.13, 130.91, 129.78, 128.40, 128.16, 125.44, 124.22, 123.40, 123.32, 122.40, 120.94, 116.71, 116.40, 82.60, 71.79, 42.86, 31.21, 27.86, 20.95; HRMS (ESI-TOF) calcd for $C_{28}H_{26}O_4$ ([M+Na^+]) = 449.1729, Found 449.1728.

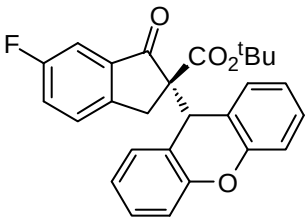


	Retention Time	Area	% Area
1	4.570	19414238	99.09
2	6.262	177620	0.91



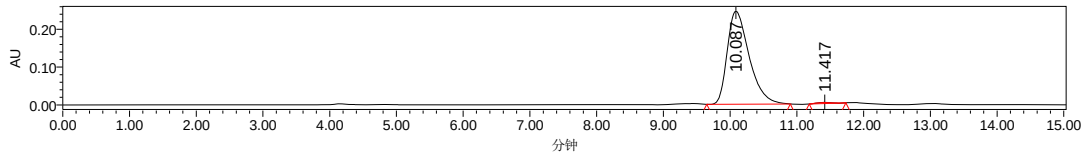
	Retention Time	Area	% Area
1	4.541	9164244	50.71
2	6.281	8907311	49.29

(*R*)-tert-butyl 6-fluoro-1-oxo-2-(9H-xanthen-9-yl)-2,3-dihydro-1H-indene-2-carboxylate

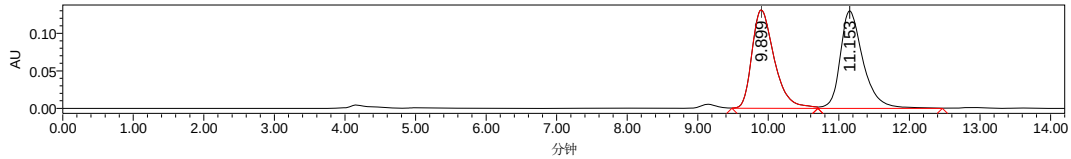


3c

White solid, m.p. 90 –92 °C, 71% yield, 99% ee; $[\alpha]_D^{25}$ = −111.21 (c = 0.66 in CH_2Cl_2); the ee was determined by HPLC analysis using a chiral ID column (hexane/^{i}PrOH = 78/2, 0.8 mL/min, 254 nm) t_r (major) = 10.08 min, t_r (minor) = 11.42 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.23 – 7.19 (m, 2H), 7.19 – 7.13 (m, 2H), 7.13 – 7.06 (m, 2H), 7.05 – 7.00 (m, 1H), 6.97 – 6,93 (m, 1H), 6.85 (dd, *J* = 7.5, 1.2 Hz, 1H), 5.34 (s, 1H), 3.43 (d, *J* = 17.4 Hz, 1H), 3.06 (d, *J* = 17.4 Hz, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 198.59, 165.98, 152.51, 152.42, 148.75, 129.69, 128.72, 127.54, 127.31, 126.15, 126.07, 122.47, 122.36, 121.76, 121.53, 121.06, 119.54, 115.76, 115.48, 109.02, 108.80, 81.92, 71.23, 42.08, 30.08, 26.83; HRMS (ESI-TOF) calcd for $C_{27}H_{23}FO_4$ ([M+Na$^+$]) = 453.1478, Found 453.1475.



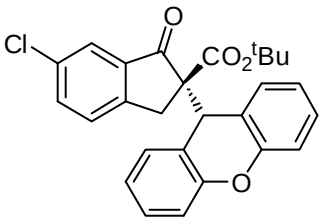
	Retention Time	Area	% Area
1	10.087	5604891	99.71
2	11.417	16112	0.29



	Retention Time	Area	% Area

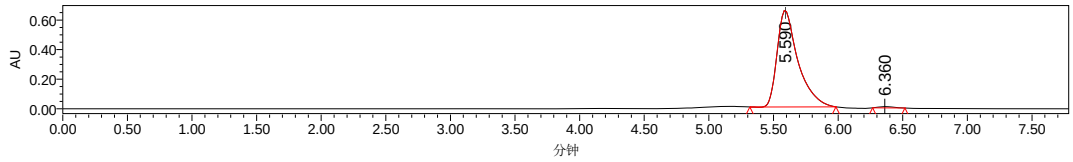
1	9.899	2882781	49.77
2	11.153	2908982	50.23

(*R*)-tert-butyl 6-chloro-1-oxo-2-(9H-xanthen-9-yl)-2,3-dihydro-1H-indene-2-carboxylate

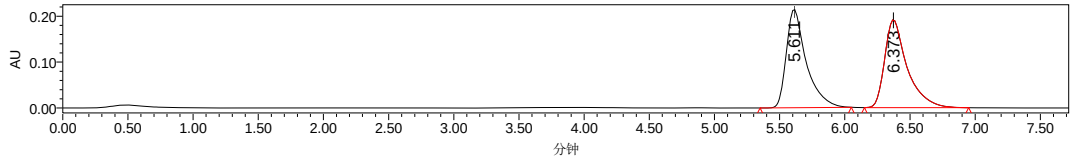


3d

White solid, m.p. 120 –122 °C, 75% yield, 98% ee; $[\alpha]_D^{25}$ = −164.58 (c = 0.24 in CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IC column (hexane/^{i}PrOH = 95/5, 0.8 mL/min, 254 nm) t_r (major) = 5.59 min, t_r (minor) = 6.36 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.50 (m, 2H), 7.35 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.21 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.19 – 7.13 (m, 2H), 7.11 – 7.02 (m, 2H), 6.98 – 6.92 (m, 1H), 6.88 – 6.82 (m, 1H), 5.34 (s, 1H), 3.43 (d, *J* = 17.8 Hz, 1H), 3.06 (d, *J* = 17.8 Hz, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 198.23, 165.88, 152.51, 152.42, 151.40, 135.40, 133.91, 132.39, 129.71, 128.71, 127.56, 127.37, 125.98, 122.96, 122.49, 122.43, 121.02, 119.52, 115.77, 115.51, 82.00, 70.95, 42.02, 30.25, 26.83; HRMS (ESI-TOF) calcd for $C_{27}H_{23}{}^{34.9689}ClO_4$ ([M+Na$^+$]) = 469.1183, Found 469.1185.

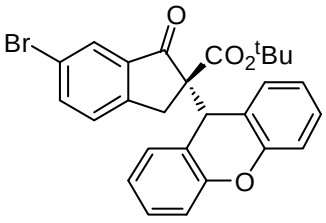


	Retention Time	Area	% Area
1	5.590	7295757	99.05
2	6.360	70237	0.95



	Retention Time	Area	% Area
1	5.611	2270812	49.88
2	6.373	2282099	50.12

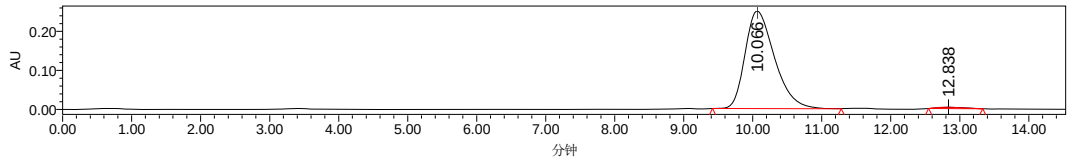
(*R*)-tert-butyl 6-bromo-1-oxo-2-(9H-xanthen-9-yl)-2,3-dihydro-1H-indene-2-carboxylate



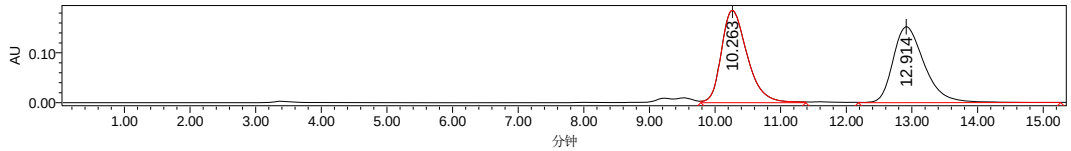
3e

White solid, m.p. 80–82 °C, 80% yield, 97% ee; $[\alpha]_D^{25}$ = −216.30 (c =

0.46 in CH_2Cl_2); the ee was determined by HPLC analysis using a chiral ID column (hexane/^{i}PrOH = 98/2, 1.0 mL/min, 254 nm) t_r (major) = 10.06 min, t_r (minor) = 12.83 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.53 (m, 2H), 7.38 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.25 – 7.23 (m, 1H), 7.22 – 7.18 (m, 1H), 7.16 – 7.14 (m, 1H), 7.09 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.99 (dd, *J* = 7.1, 1.5 Hz, 1H), 6.97 – 6.91 (m, 1H), 6.83 (dd, *J* = 7.5, 1.2 Hz, 1H), 5.36 (s, 1H), 3.47 (d, *J* = 17.6 Hz, 1H), 3.10 (d, *J* = 17.6 Hz, 1H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 199.34, 166.32, 153.32, 152.56, 152.44, 133.97, 133.87, 129.81, 128.77, 127.43, 127.17, 126.03, 124.74, 123.30, 122.41, 122.28, 121.30, 119.75, 115.71, 115.40, 81.66, 70.37, 41.95, 30.60, 26.84; HRMS (ESI-TOF) calcd for $C_{27}H_{23}{}^{78.9183}BrO_4$ ([M+Na$^+$]) = 513.0677, Found 513.0684.

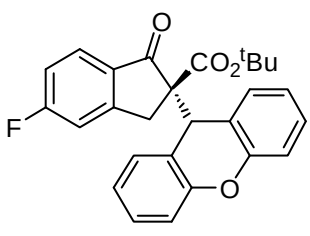


	Retention Time	Area	% Area
1	10.066	7383258	98.75
2	12.838	93542	1.25



	Retention Time	Area	% Area
1	10.263	5059426	50.08
2	12.914	5043285	49.92

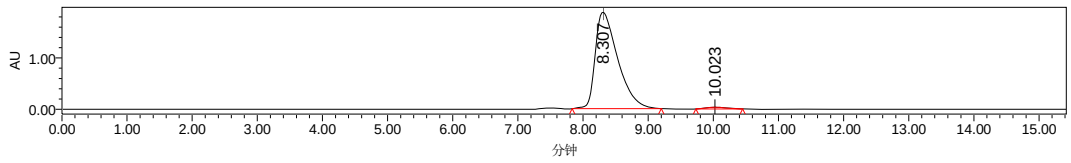
(*R*)-tert-butyl 5-fluoro-1-oxo-2-(9H-xanthen-9-yl)-2,3-dihydro-1H-indene-2-carboxylate



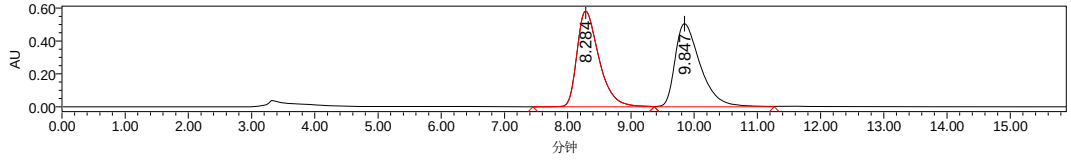
3f

White solid, m.p. 126 –128 °C, 81% yield, 97% ee; $[\alpha]_D^{25}$ = −189.16 (c = 0.48 in CH_2Cl_2); the ee was determined by HPLC analysis using a chiral ID column (hexane/^{i}PrOH = 98/2, 1.0 mL/min, 254 nm) t_r (major) = 8.31 min, t_r (minor) = 10.02 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.51 (m,

2H), 7.33 – 7.26 (m, 1H), 7.23 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.18 – 7.12 (m, 1H), 7.11 – 7.06 (m, 1H), 7.04 – 6.93 (m, 2H), 6.92 – 6.79 (m, 3H), 5.34 (s, 1H), 3.47 (d, *J* = 17.9 Hz, 1H), 3.09 (d, *J* = 17.9 Hz, 1H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 198.53, 167.11, 153.54, 153.44, 130.75, 129.76, 128.56, 128.34, 126.70, 126.59, 123.52, 123.34, 122.13, 120.56, 116.79, 116.53, 115.66, 115.42, 112.60, 112.38, 82.91, 71.60, 42.99, 31.58, 27.87; HRMS (ESI-TOF) calcd for $C_{27}H_{23}FO_4$ ([M+Na^+]) = 453.1478, Found 453.1479.

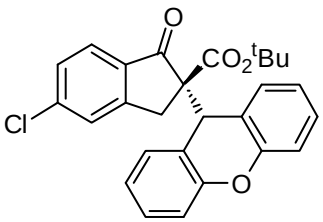


	Retention Time	Area	% Area
1	8.307	45115899	98.46
2	10.023	706470	1.54



	Retention Time	Area	% Area
1	8.284	14011828	50.02
2	9.847	14001076	49.98

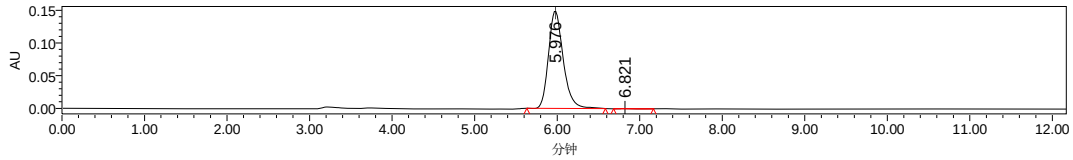
(*R*)-tert-butyl 5-chloro-1-oxo-2-(9H-xanthen-9-yl)-2,3-dihydro-1H-indene-2-carboxylate



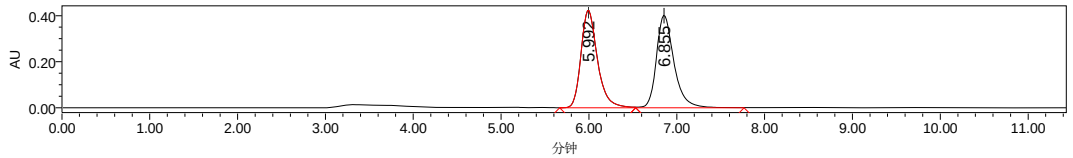
3g

White solid, m.p. 172 –174 °C, 68% yield, 99% ee; $[\alpha]_D^{25}$ = −187.04 (c = 0.54 in CH_2Cl_2); the ee was determined by HPLC analysis using a chiral ID column (hexane/^{i}PrOH = 95/5, 1.0 mL/min, 254 nm) t_r (major) = 5.97 min, t_r (minor) = 6.82 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.25 – 7.20 (m, 2H), 7.19 – 7.13 (m, 2H), 7.11 – 7.01 (m, 2H), 6.99 – 6.94 (m, 2H), 6.87 – 6.79 (m, 1H), 5.34 (s, 1H), 3.45 (d, *J* = 17.8 Hz, 1H), 3.08 (d, *J* = 17.8 Hz, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 199.02, 166.98,

155.71, 153.54, 153.44, 141.52, 133.43, 130.73, 129.74, 128.58, 128.39, 128.00, 126.01, 125.38, 123.52, 123.37, 122.07, 120.55, 116.81, 116.58, 82.99, 71.51, 43.01, 31.42, 27.86; HRMS (ESI-TOF) calcd for $C_{27}H_{23}{}^{34.9689}ClO_4$ ([M+Na$^+$]) = 469.1183, Found 469.1183.

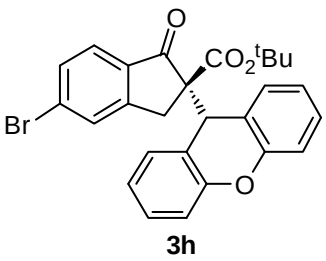


	Retention Time	Area	% Area
1	5.975	1890952	99.86
2	6.821	2664	0.14



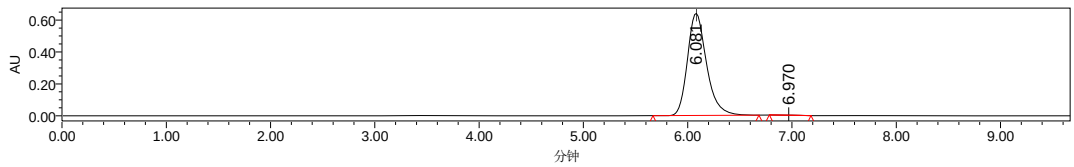
	Retention Time	Area	% Area
1	5.992	5511095	49.78
2	6.855	5560752	50.22

(*R*)-tert-butyl 5-bromo-1-oxo-2-(9H-xanthen-9-yl)-2,3-dihydro-1H-indene-2-carboxylate

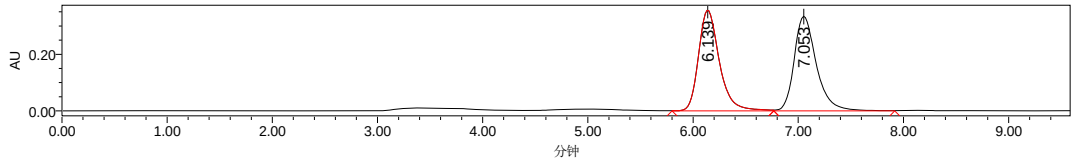


3h

White solid, m.p. 177 –179 ^{o}C, 76% yield, 99% ee; $[\alpha]_D^{25}$ = −193.93 (c = 0.56 in CH_2Cl_2); the ee was determined by HPLC analysis using a chiral ID column (hexane/^{i}PrOH = 95/5, 1.0 mL/min, 254 nm) t_r (major) = 6.08 min, t_r (minor) = 6.75 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 1H), 7.48 – 7.38 (m, 2H), 7.36 – 7.26 (m, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.11 – 7.02 (m, 2H), 7.00 – 6.93 (m, 1H), 6.88 – 6.78 (m, 1H), 5.34 (s, 1H), 3.46 (d, *J* = 17.9 Hz, 1H), 3.08 (d, *J* = 17.9 Hz, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 199.26, 166.92, 155.81, 153.53, 153.44, 133.80, 130.82, 130.72, 130.48, 129.72, 129.09, 128.58, 128.40, 125.44, 123.51, 123.38, 122.05, 120.54, 116.81, 116.59, 83.00, 71.43, 42.99, 31.36, 27.86; HRMS (ESI-TOF) calcd for $C_{27}H_{23}{}^{78.9183}BrO_4$ ([M+Na$^+$]) = 513.0677, Found 513.0684.

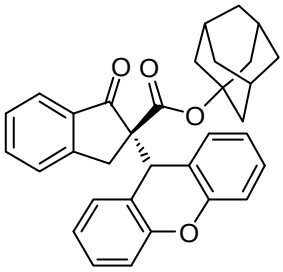


	Retention Time	Area	% Area
1	6.081	8178647	99.88
2	6.750	9557	0.12



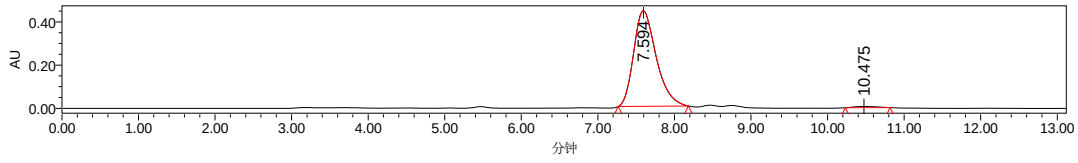
	Retention Time	Area	% Area
1	6.139	4876283	49.95
2	7.053	4885133	50.05

(*R*)-adamantan-1-yl 1-oxo-2-(9H-xanthen-9-yl)-2,3-dihydro-1H-indene-2-carboxylate



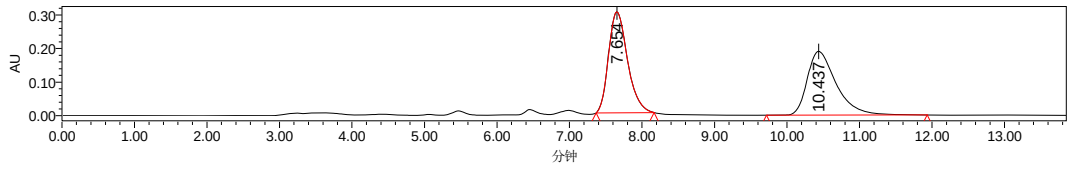
3i

White solid, m.p. 176 –178 °C, 72% yield, 99% ee; $[\alpha]_D^{25}$ = −105.12 (c = 0.52 in CH_2Cl_2); the ee was determined by HPLC analysis using a chiral ID column (hexane/^{i}PrOH = 90/10, 1.0 mL/min, 254 nm) t_r (major) = 7.59 min, t_r (minor) = 10.47 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.54 (m, 2H), 7.42 – 7.36 (m, 1H), 7.32 – 7.26 (m, 1H), 7.26 – 7.12 (m, 4H), 7.17 – 7.12 (m, 1H), 7.05 – 6.98 (m, 1H), 6.97 – 6.92 (m, 1H), 6.86 – 6.78 (m, 1H), 5.36 (s, 1H), 3.47 (d, *J* = 17.6 Hz, 1H), 3.08 (d, *J* = 17.6 Hz, 1H), 2.20 – 2.10 (m, 4H), 2.19 – 2.14 (m, 5H), 1.64 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 200.44, 166.98, 154.35, 153.56, 153.47, 135.03, 134.89, 130.89, 129.83, 128.43, 128.18, 127.04, 125.78, 124.32, 123.47, 123.30, 122.33, 120.83, 116.69, 116.42, 82.83, 71.56, 42.88, 41.05, 36.09, 31.63, 30.88; HRMS (ESI-TOF) calcd for $C_{33}H_{30}O_4$ ([M+Na$^+$]) = 513.2042, Found 513.2036.



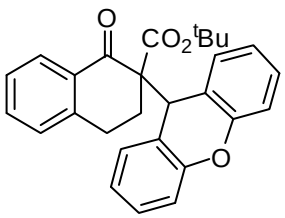
	Retention Time	Area	% Area

1	7.594	9380158	98.66
2	10.475	127479	1.34



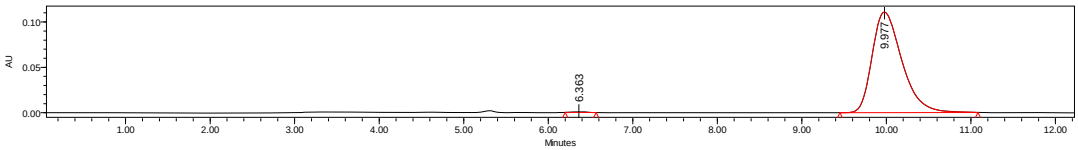
	Retention Time	Area	% Area
1	7.654	5455484	50.69
2	10.437	5306205	49.31

tert-butyl 1-oxo-2-(9H-xanthen-9-yl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate

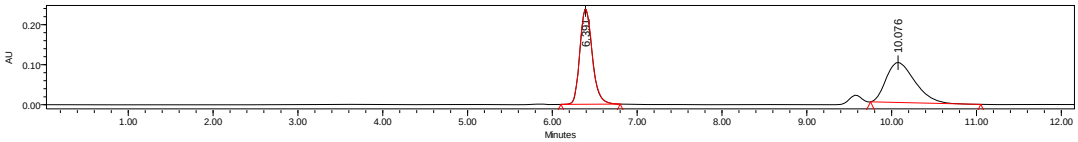


5a

Viscous oil, 70% yield, 99% ee; $[\alpha]_D^{25} = -53.88$ (c = 0.18 in CH_2Cl_2); the ee was determined by HPLC analysis using a chiral ID column (hexane/^{i}PrOH = 80/20, 1.0 mL/min, 254 nm) t_r (minor) = 6.36 min, t_r (major) = 9.97 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.9 Hz, 1H), 7.46 – 7.33 (m, 3H), 7.32 – 7.26 (m, 1H), 7.25 – 7.22 (m, 1H), 7.21 – 7.13 (m, 2H), 7.12 – 7.01 (m, 3H), 6.98 (t, *J* = 7.5 Hz, 1H), 5.47 (s, 1H), 3.13 – 3.00 (m, 1H), 2.74 – 2.63 (m, 1H), 2.23 – 2.35 (m, 1H), 1.81 – 1.67 (m, 1H), 1.21 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.22, 167.63, 154.58, 154.27, 142.92, 133.25, 132.64, 130.83, 130.29, 128.57, 128.28, 128.10, 128.09, 126.40, 123.37, 123.02, 122.38, 122.14, 116.49, 116.33, 82.68, 65.91, 42.46, 27.66, 25.90, 25.76; HRMS (ESI-TOF) calcd for $C_{28}H_{26}O_4$ ([M+Na$^+$]) = 449.1729, Found 449.1725.

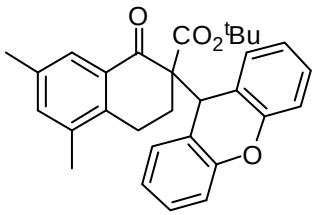


	Retention Time	Area	% Area
1	6.363	8363	0.31
2	9.977	2705291	99.69



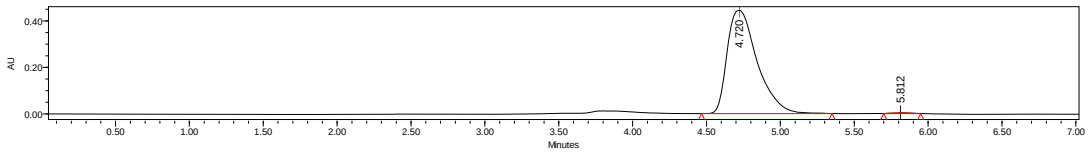
	Retention Time	Area	% Area
1	6.391	2414269	50.63
2	10.076	2354573	49.37

tert-butyl
5,7-dimethyl-1-oxo-2-(9H-xanthen-9-yl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate

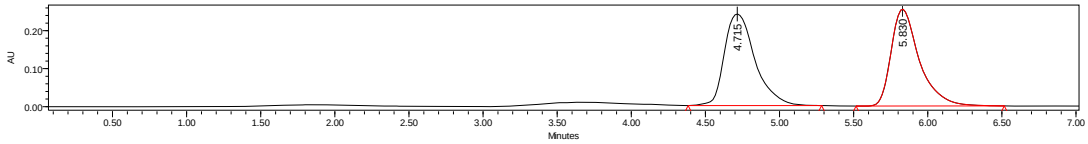


5b

Viscous oil, 36% yield, 99% ee; $[\alpha]_D^{25} = -46.00$ (c = 0.10 in CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IC column (hexane/^{i}PrOH = 90/10, 1.0 mL/min, 254 nm) t_r (major) = 4.72 min, t_r (minor) = 5.81 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.47 (d, *J* = 6.6 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.28 (s, 1H), 7.25 – 7.15 (m, 2H), 7.14 – 7.07 (m, 1H), 7.08 (s, 1H), 7.07 – 7.02 (m, 1H), 6.99 (t, *J* = 7.4 Hz, 1H), 5.46 (s, 1H), 2.83 – 2.71 (m, 1H), 2.64 – 2.54 (m, 1H), 2.38 – 2.31 (m, 1H), 2.30 (s, 3H), 2.11 (s, 3H), 1.72 – 1.64 (m, 1H), 1.26 – 1.10 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.74, 167.72, 154.62, 154.29, 138.28, 136.11, 135.66, 135.56, 132.71, 130.91, 130.29, 128.21, 128.05, 125.98, 123.34, 123.01, 122.49, 122.32, 116.47, 116.27, 82.46, 65.28, 42.14, 27.63, 25.19, 23.21, 20.81, 18.97; HRMS (ESI-TOF) calcd for $C_{30}H_{30}O_4$ ([M+Na$^+$]) = 477.2042, Found 477.2040.

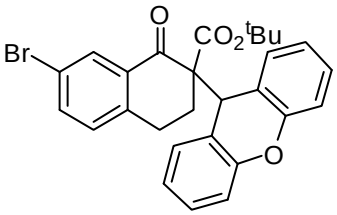


	Retention Time	Area	% Area
1	4.720	6266511	99.50
2	5.812	31217	0.50



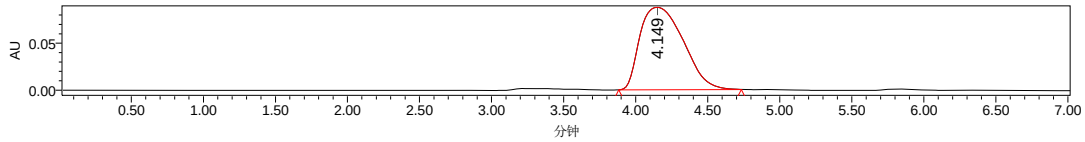
	Retention Time	Area	% Area
1	4.715	3457259	50.61
2	5.830	3374100	49.39

tert-butyl 7-bromo-1-oxo-2-(9H-xanthen-9-yl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate

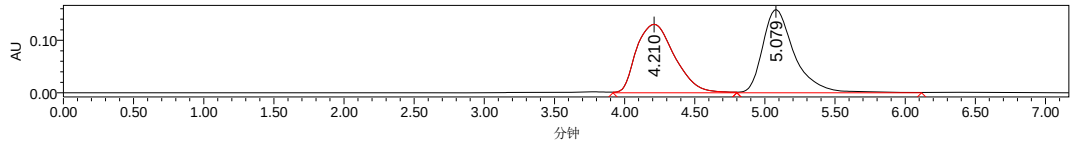


5c

Viscous oil, 60% yield, 99% ee; $[\alpha]_D^{25}$ = −56.89 (c = 0.58 in CH_2Cl_2); the ee was determined by HPLC analysis using a chiral IC column (hexane/^{i}PrOH = 90/10, 1.0 mL/min, 254 nm) t_r (major) = 4.15 min, t_r (minor) = 5.07 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.1 Hz, 1H), 7.48 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.38 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.33 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.22 – 7.13 (m, 2H), 7.12 – 7.03 (m, 2H), 7.02 – 6.93 (m, 2H), 5.44 (s, 1H), 3.06 – 2.85 (m, 1H), 2.72 – 2.55 (m, 1H), 2.37 – 2.23 (m, 1H), 1.78 – 1.66 (m, 1H), 1.25 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 191.99, 167.29, 154.57, 154.25, 141.68, 136.06, 134.03, 130.76, 130.70, 130.41, 130.26, 128.40, 128.24, 123.46, 123.07, 122.14, 121.85, 120.45, 116.55, 116.40, 83.00, 65.80, 42.53, 27.70, 25.65, 25.50; HRMS (ESI-TOF) calcd for $C_{28}H_{25}{}^{78.9183}BrO_4$ ([M+Na$^+$]) = 527.0834, Found 527.0830.

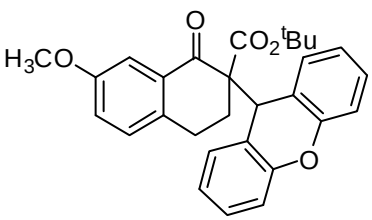


	Retention Time	Area	% Area
1	4.149	1851192	100.00



	Retention Time	Area	% Area
1	4.210	2470483	49.73
2	5.079	2497535	50.27

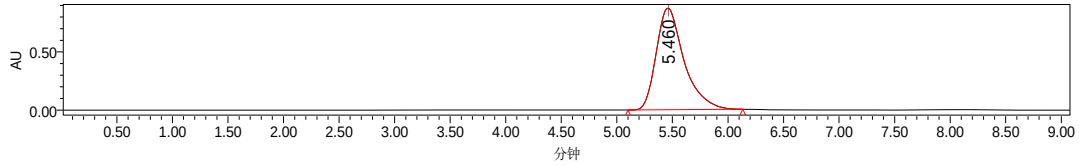
tert-butyl 7-methoxy-1-oxo-2-(9H-xanthen-9-yl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate



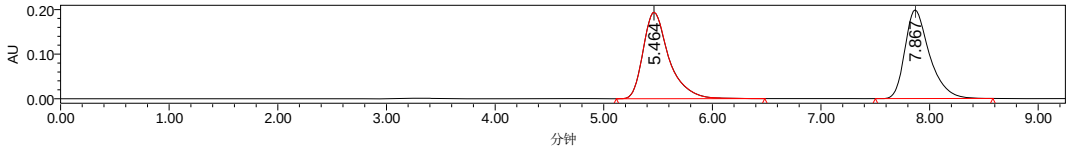
5d

White solid, m.p. 113 –115 °C, 71% yield, 99% ee; $[\alpha]_D^{25}$ = −31.36 (c = 0.66 in CH_2Cl_2); the ee was determined by HPLC analysis using a

chiral IC column (hexane/^{i}PrOH = 90/10, 1.0 mL/min, 254 nm) t_r (major) = 5.46 min, t_r (minor) = 7.86 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.45 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.34 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.23 – 7.19 (m, 1H), 7.19 – 7.13 (m, 2H), 7.12 – 7.07 (m, 1H), 7.07 – 7.02 (m, 1H), 7.01 – 6.96 (m, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 5.45 (s, 1H), 3.77 (s, 3H), 2.86 – 2.76 (m, 1H), 2.75 – 2.64 (m, 1H), 2.36 – 2.27 (m, 1H), 1.71 – 1.61 (m, 1H), 1.18 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.47, 167.62, 156.59, 154.61, 154.27, 133.70, 132.03, 130.82, 130.32, 128.23, 128.06, 126.67, 123.31, 122.99, 122.44, 122.26, 119.63, 116.49, 116.31, 113.85, 82.52, 65.46, 55.57, 42.16, 27.62, 25.20, 19.99; HRMS (ESI-TOF) calcd for $C_{29}H_{28}O_5$ ([M+Na^+]) = 479.1834, Found 479.1837.

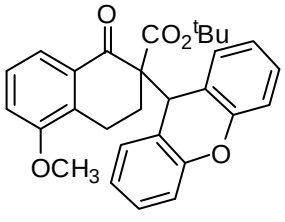


	Retention Time	Area	% Area
1	5.460	15162973	100.00



	Retention Time	Area	% Area
1	5.464	3191697	50.53
2	7.867	3124635	49.47

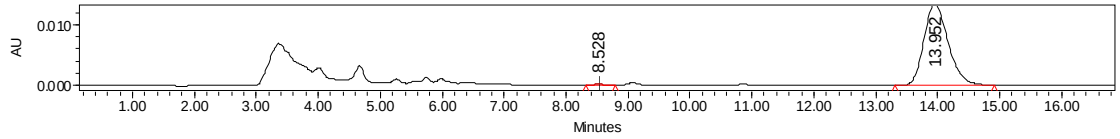
tert-butyl 5-methoxy-1-oxo-2-(9H-xanthen-9-yl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate



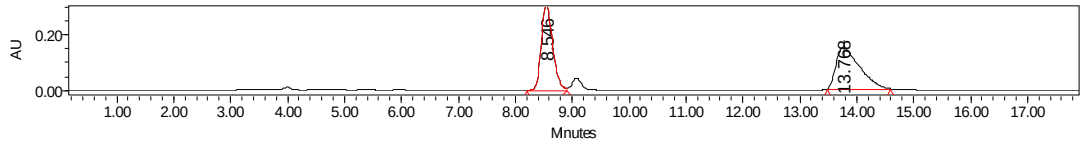
5e

Viscous oil, 34% yield, 99% ee; $[\alpha]_D^{25}$ = −7.92 (c = 0.24 in CH_2Cl_2); the ee was determined by HPLC analysis using a chiral ID column (hexane/^{i}PrOH = 80/20, 1.0 mL/min, 254 nm) t_r (minor) = 8.93 min, t_r (major) = 13.95 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.26 d, *J* = 7.7 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.15 – 7.05 (m, 2H), 7.04 – 6.95 (m, 2H), 6.95 – 6.84 (m, 3H),

5.38 (s, 1H), 3.76 (s, 3H), 2.97 – 2.82 (m, 1H), 2.61 – 2.50 (m, 1H), 2.28 – 2.11 (m, 1H), 1.75 – 1.58 (m, 1H), 1.15 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 193.11, 167.17, 158.15, 154.59, 154.28, 135.48, 133.37, 130.77, 130.33, 129.79, 128.27, 128.11, 123.35, 123.01, 122.41, 122.13, 121.89, 116.50, 116.34, 109.82, 82.68, 65.77, 55.49, 42.51, 27.69, 26.07, 25.13; HRMS (ESI-TOF) calcd for $C_{29}H_{28}O_5$ ([M+Na$^+$]) = 479.1834, Found 479.1835.

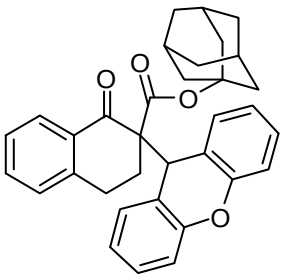


	Retention Time	Area	% Area
1	8.528	1586	0.43
2	13.952	363534	99.57



	Retention Time	Area	% Area
1	8.546	4345859	50.43
2	13.768	4272058	49.57

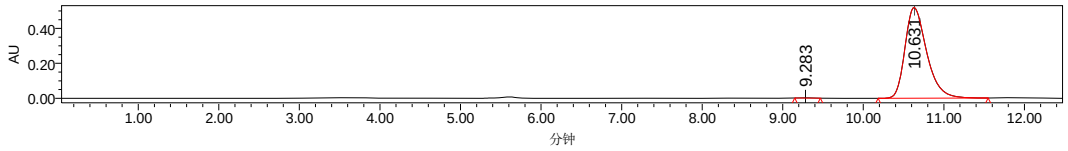
adamantan-1-yl 1-oxo-2-(9H-xanthen-9-yl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate



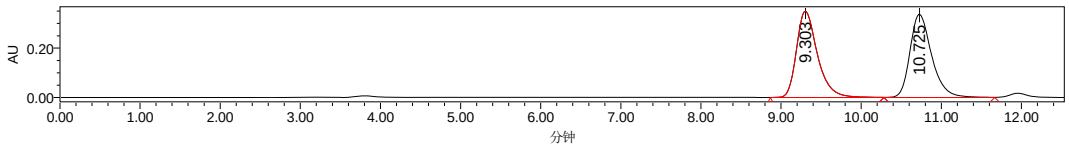
5f

White solid, m.p. 165 –167 °C, 72% yield, 99% ee; $[\alpha]_D^{25}$ = −17.14 (c = 0.14 in CH_2Cl_2); the ee was determined by HPLC analysis using a chiral ID column (hexane/^{i}PrOH = 90/10, 1.0 mL/min, 254 nm) t_r (minor) = 9.28 min, t_r (major) = 10.63 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.31 – 7.26 (m, 1H), 7.25 – 7.21 (m, 1H), 7.20 – 7.12 (m, 2H), 7.12 – 7.02 (m, 3H), 6.98 (t, *J* = 7.4 Hz, 1H), 5.47 (s, 1H), 3.13 – 3.01 (m, 1H), 2.76 – 2.61 (m, 1H), 2.35 – 2.24 (m, 1H), 2.05 (s, 3H), 1.85 (dd, *J* = 30.4, 11.3 Hz, 6H), 1.77 – 1.62 (m, 2H), 1.55 (s, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 192.09, 166.16, 153.56, 153.23, 141.98, 132.21,

131.56, 129.82, 129.30, 127.55, 127.23, 127.10, 127.05, 125.35, 122.35, 122.00, 121.37, 121.11, 115.39, 115.27, 81.72, 65.08, 41.48, 39.91, 34.95, 29.73, 24.91, 24.64; HRMS (ESI-TOF) calcd for $C_{34}H_{32}O_4$ ([M+Na$^+$]) = 527.2189, Found 527.2200.

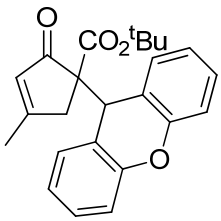


	Retention Time	Area	% Area
1	9.283	16880	0.17
2	10.631	9662276	99.83

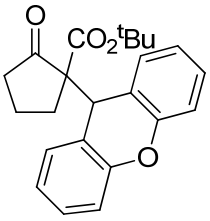


	Retention Time	Area	% Area
1	9.303	6329854	49.98
2	10.725	6333878	50.02

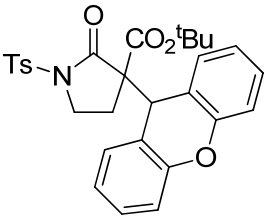
The results of other *β*-ketoesters substrates



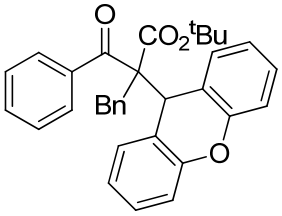
56% yield, 57% ee



trace

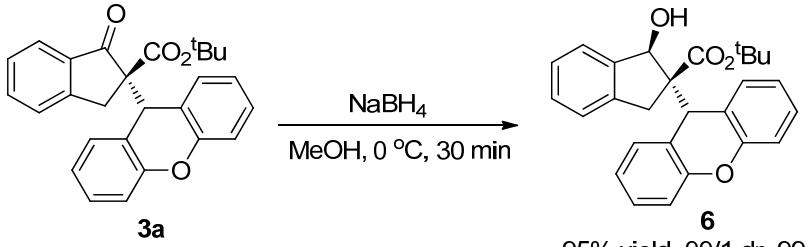


trace



trace

(G) Typical procedure for the reduction of 3a



3a **6**

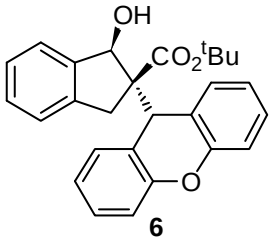
95% yield, 99/1 dr, 99% ee

To a solution of **3a** (0.02 mmol) in 1 mL MeOH, $NaBH_4$ (1.5 eq) was added at 0 °C, the reaction was

stirred at this temperature for 30 min. 1 M HCl was added making pH to 5, CH_2Cl_2 extracted for three times, dried by $MgSO_4$, removing CH_2Cl_2 in vacuum. The residue was purified by flash chromatography on silica gel (0-5 ^oC) to afford the product **6**.

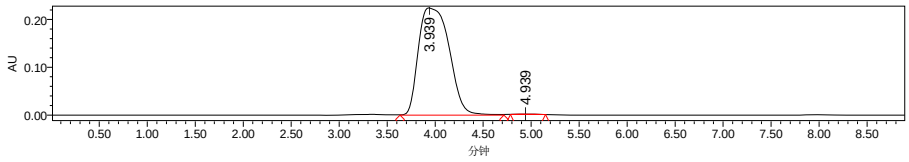
(H) The analytical and spectral characterization data of 6

(*1R,2R*)-tert-butyl 1-hydroxy-2-(9H-xanthen-9-yl)-2,3-dihydro-1H-indene-2-carboxylate

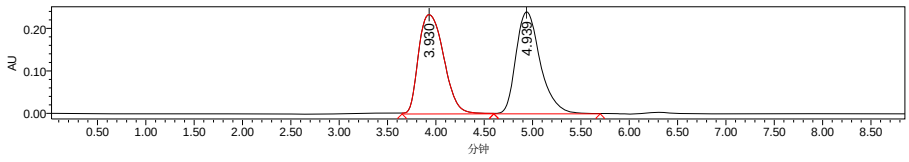


6

White solid, 95% yield, 99/1 dr, 99% ee; $[\alpha]_D^{25}$ = 11.38 (c = 0.36 in CH_2Cl_2); the dr determined was by ^1H NMR; the ee was determined by HPLC analysis using a chiral IC column (hexane/^{i}PrOH = 90/10, 1.0 mL/min, 254 nm) t_r (major) = 3.94 min, t_r (minor) = 4.94 min; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.6 Hz, 1H), 7.26 – 7.16 (m, 4H), 7.10 (t, *J* = 7.7 Hz, 1H), 7.07 – 6.98 (m, 4H), 6.97 – 6.94 (m, 2H), 6.89 (t, *J* = 7.4 Hz, 1H), 5.19 (s, 1H), 4.78 (s, 1H), 3.17 (d, *J* = 15.5 Hz, 1H), 2.95 (d, *J* = 15.5 Hz, 1H), 0.97 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.94, 153.99, 153.64, 143.28, 141.80, 130.06, 129.95, 128.64, 127.98, 127.85, 126.76, 124.62, 123.85, 123.13, 123.09, 122.53, 122.48, 116.47, 116.25, 81.00, 77.87, 67.22, 40.71, 37.59, 27.22; HRMS (ESI-TOF) calcd for $C_{27}H_{26}O_4$ ([M+Na^+]) = 437.1729, Found 437.1724.



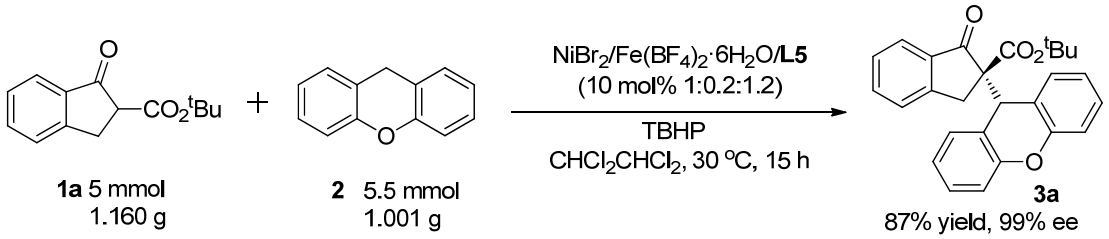
	Retention Time	Area	% Area
1	3.939	5013392	99.77
2	4.939	11423	0.23



	Retention Time	Area	% Area

1	3.930	4248313	50.25
2	4.939	4206416	49.75

(I) Typical procedure for the scale-up reaction

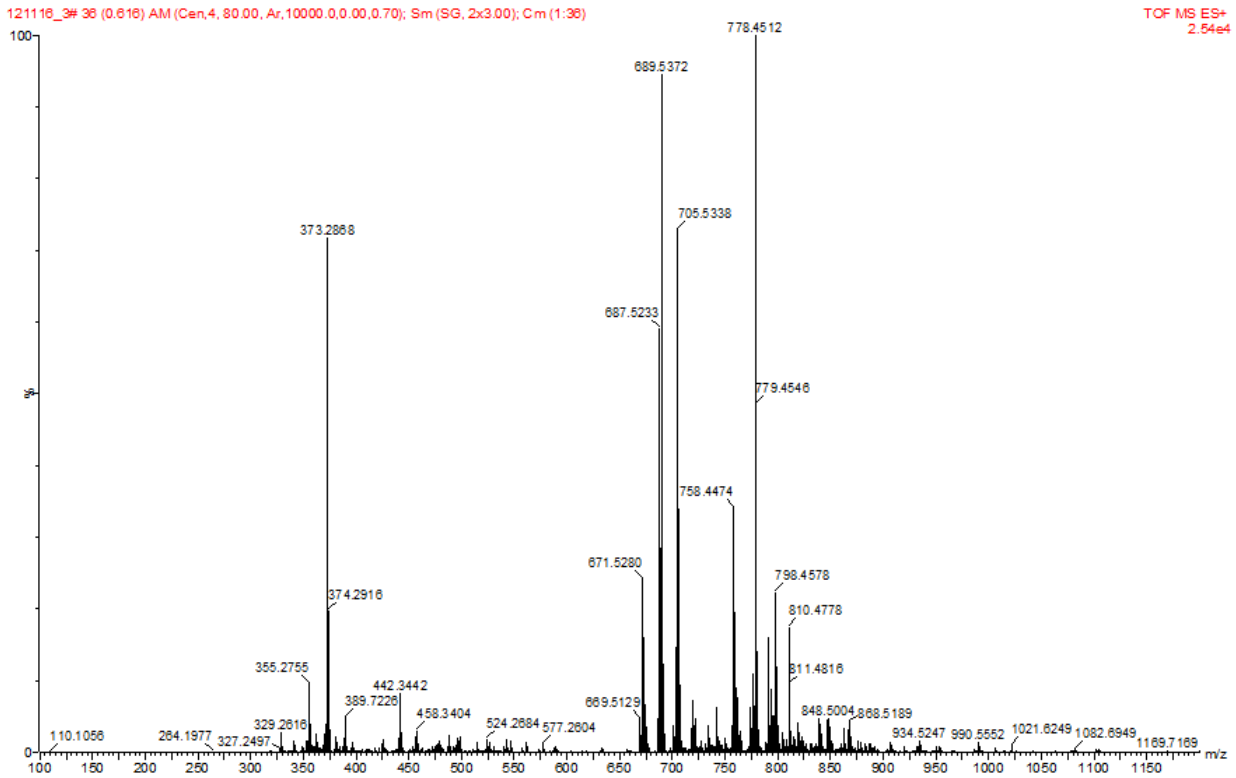


1a 5 mmol
1.160 g

2 5.5 mmol
1.001 g

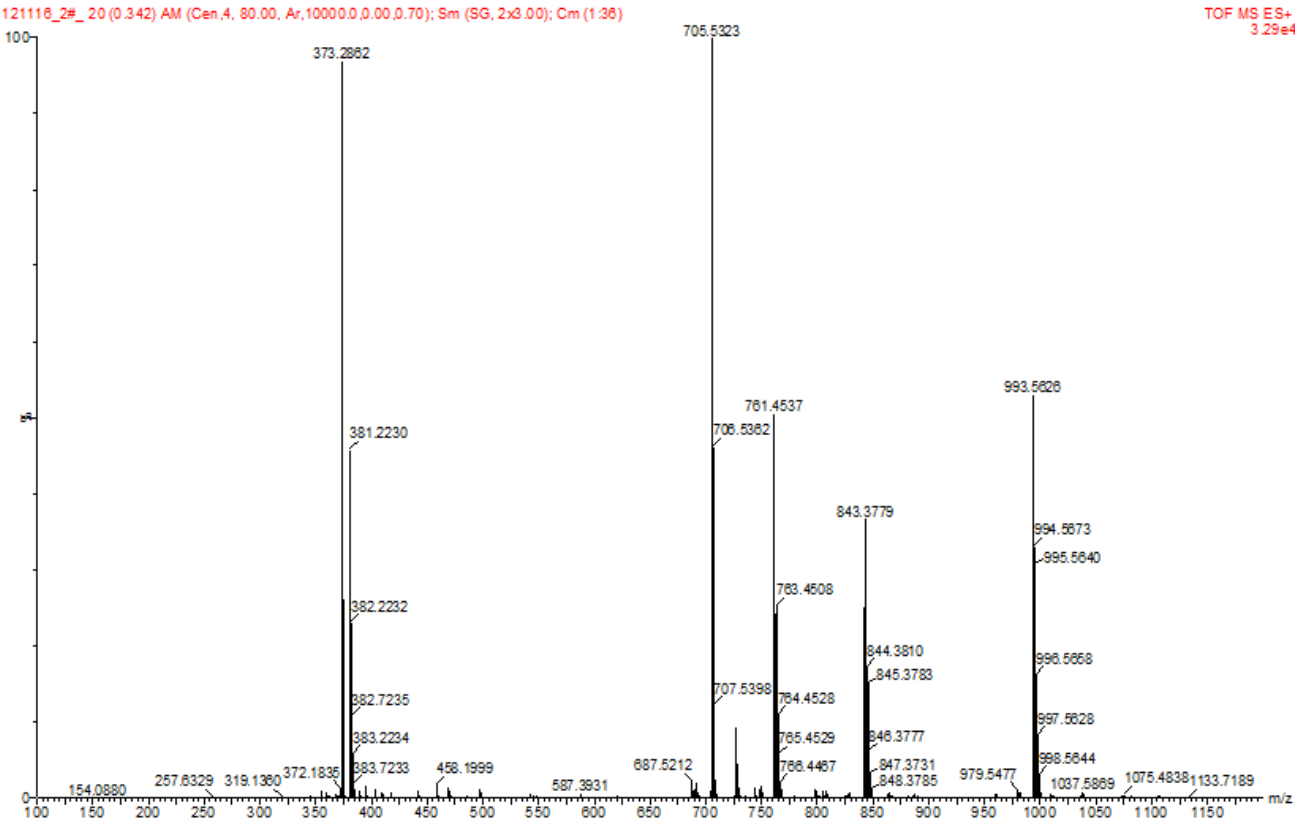
To a dried round flash, **L5** (0.1 mmol, 71.0 mg), $Fe(BF_4)_2{\cdot}6H_2O$ (0.1 mmol, 34 mg) and THF (5 mL) were added and stirred at 30 °C for 2.5 h. After removing THF in vacuum, **L5** (0.5 mmol, 355.0 mg), $NiBr_2$ (0.5 mmol, 108.5 mg), and β-ketoester (5.0 mmol) were added under N_2 atmosphere, and continued stirring at 30 °C for 2.5 h. Next, xanthene (5.5 mmol) and ^{t}BuOOH (1.0 mL) were added, the reaction was stirred at 30 °C for 15 h. The residue was purified by flash chromatography on silica gel (0-5 °C) to afford the product **3a**.

(J) The electrospray ionization mass spectrometry (ESI-MS) analysis



$Fe(BF_4)_2{\cdot}6H_2O$ + **L5** + TBHP

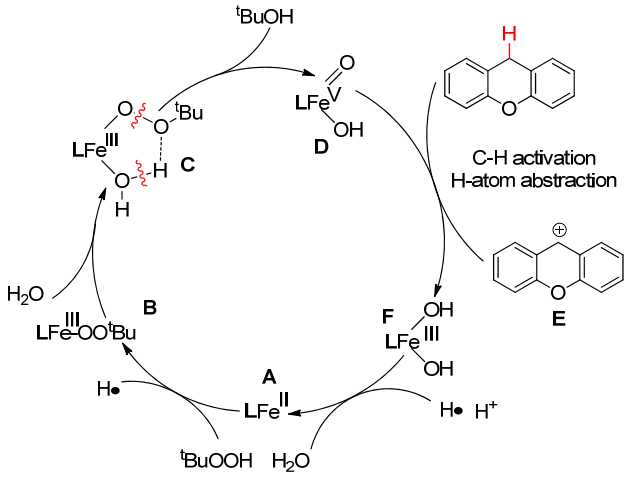
[(**L5**-O) + H^+] Calcd for $C_{43}H_{69}N_4O_3^+$ 689.5370, found: 689.5372; [Fe^{III} + **L5** – $2H^+$] Calcd for : 758.4433 found : 758.4474; [Fe^{III} + (**L5**-O) + $2OH^-]^+$ Calcd for : 778.4696 found : 778.4512; [O=Fe^V + **L5** + $2OH^-]^+$ Calcd for : 810.4594 found : 810.4778.



$NiBr_2$ + **L5** + **1a**

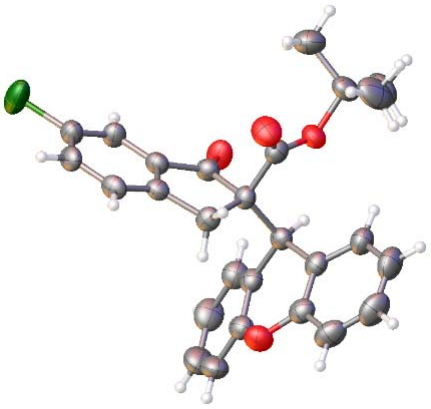
[Ni^{II} + (**L5** – H^+) + **1a**] Calcd for : 993.5615 found : 993.5626.

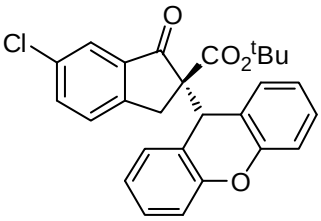
(K) The possible catalytic cycle of iron complex



Firstly, **L5**–Fe^{II} combined to ^{t}BuOOH to generate **L5**–Fe^{III}–OO^{t}Bu. In the presence of H_2O, the intermediate **C** undergoes heterolytic O–O bond and O–H cleavage, giving active high-valent **L5**–Fe^V(O)(OH) **D**. At the same time, a molecular of ^{t}BuOH left up. High-valent iron(V)–oxo specie **D** activatied sp^3 benzylic C-H bond of xanthene, and then H-atom abstraction would afford carbocation **E**.

(L) X-ray structures of 3d

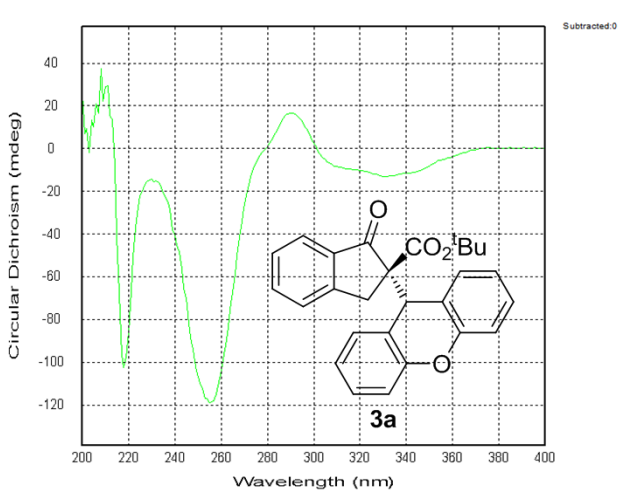


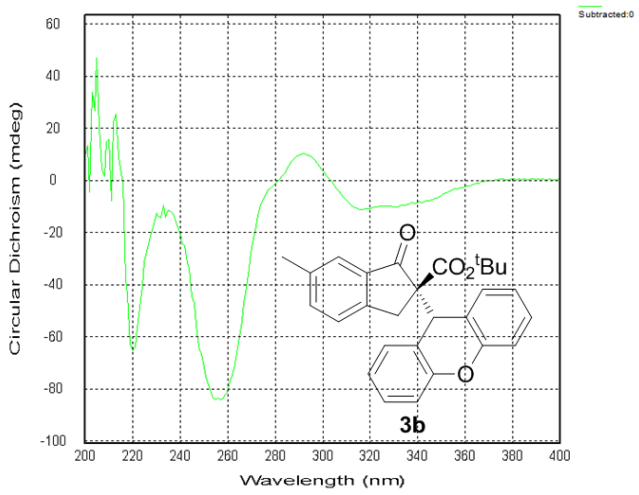


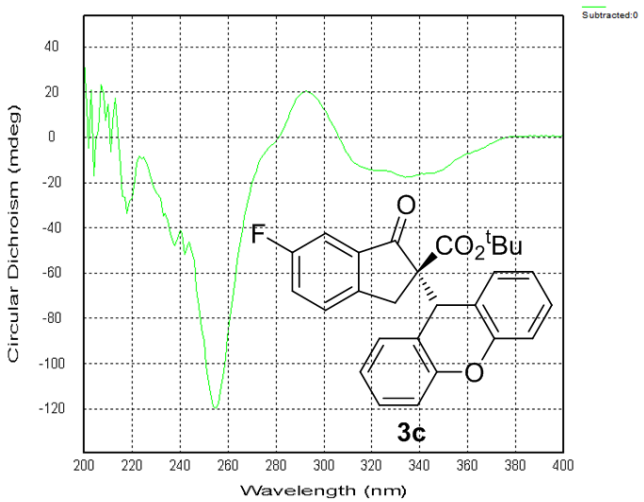
3d

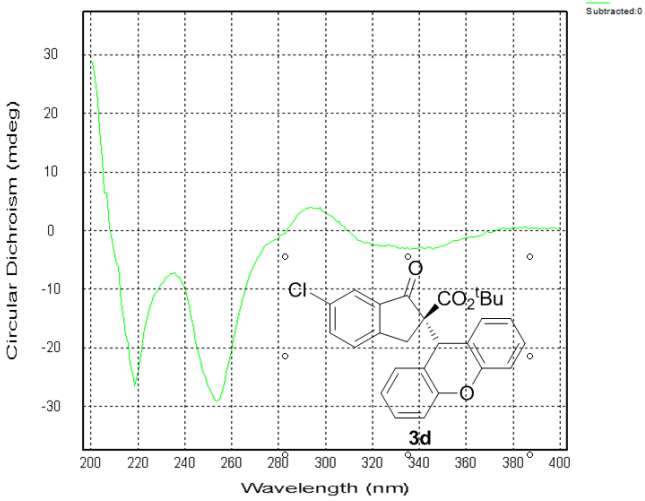
CCDC 910798 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambrige Crystallographic Data Centere via www.ccdc.cam.ac.uk/data_request/cif

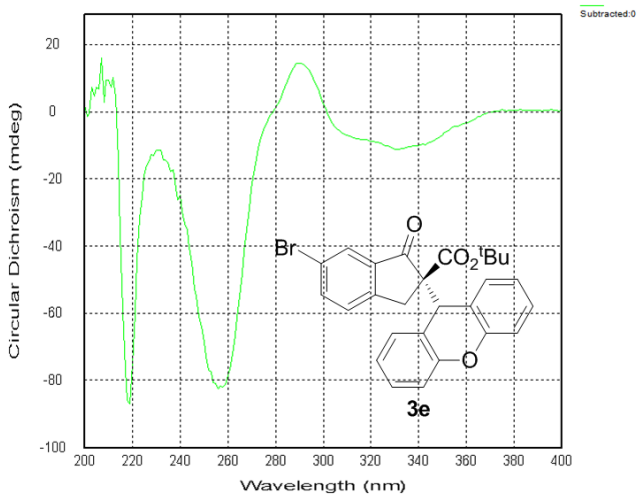
(M) Copy of CD spectras for products

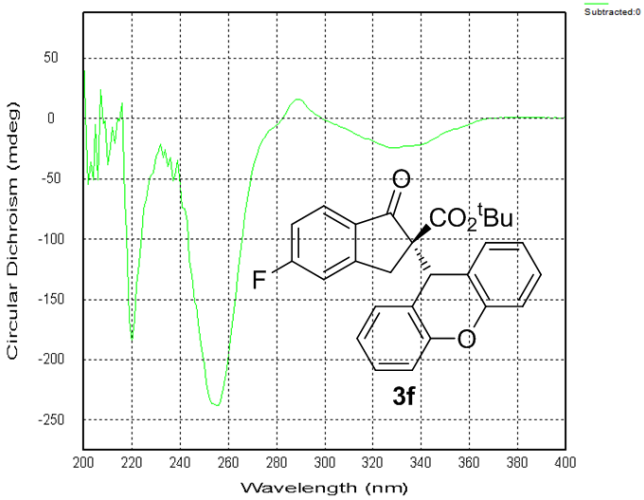


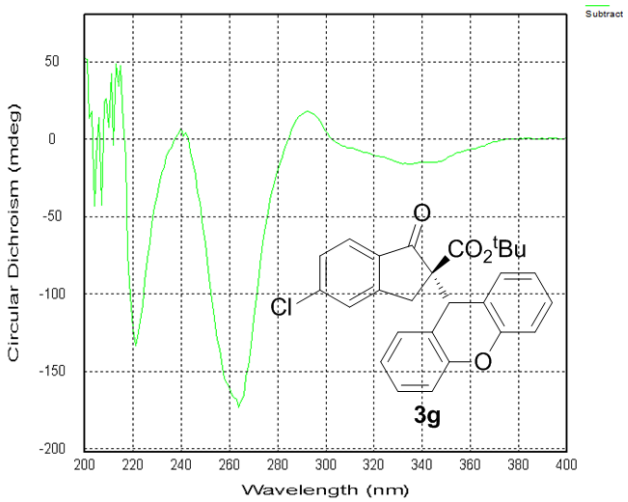


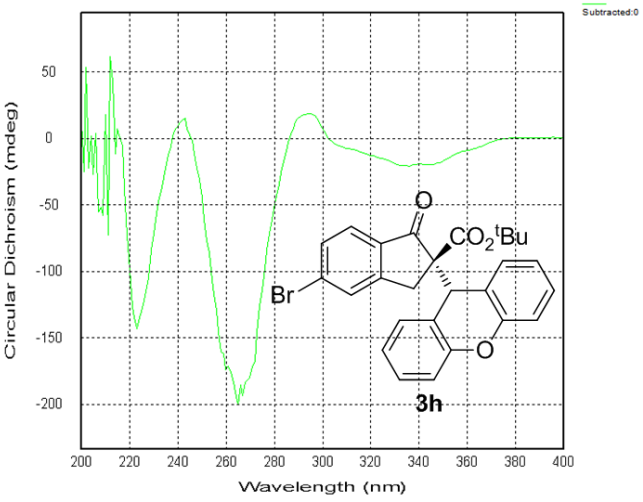


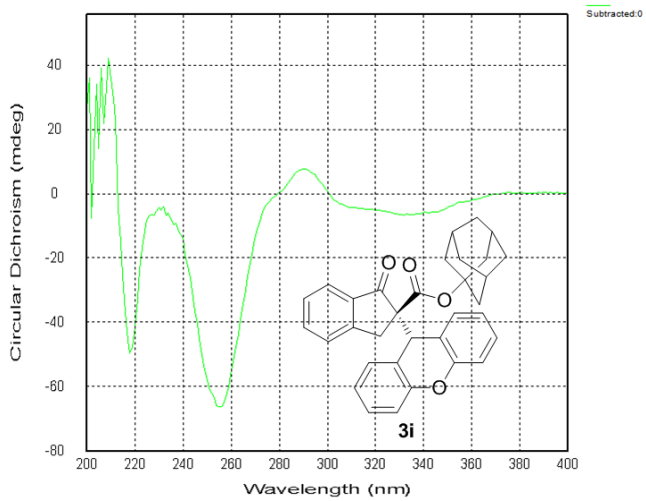



Subtracted:0
Circular Dichroism (mdeg)
Wavelength (nm)
Br
O
CO2tBu
O
3e


Subtracted:0
Circular Dichroism (mdeg)
Wavelength (nm)
O
CO2tBu
F
O
3f


Subtract
Circular Dichroism (mdeg)
Wavelength (nm)
O
CO2tBu
Cl
O
3g


Subtracted:0
Circular Dichroism (mdeg)
Wavelength (nm)
O
CO2tBu
Br
O
3h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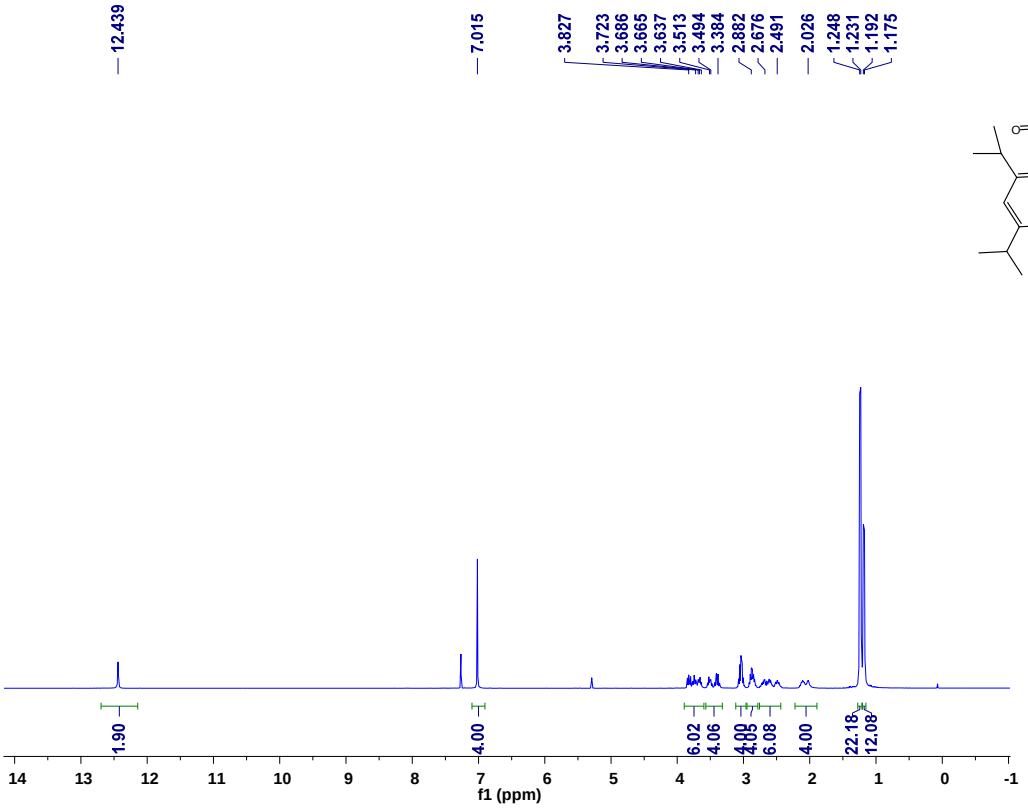
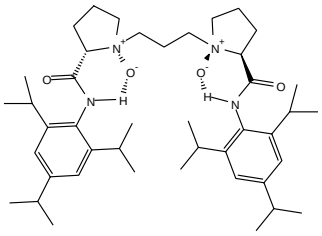
Circular Dichroism (mdeg)
Wavelength (nm)
O
O
O
O
3i

(N) Copy of ^{1}H NMR and ^{13}C NMR spectra for products





Current Data Parameters

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PULPROG: zg30
TD: 32768
Solvent: CDCl3
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SWH: 8223.7 Hz
AQ: undefined
TE: 298.2 C

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NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
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LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
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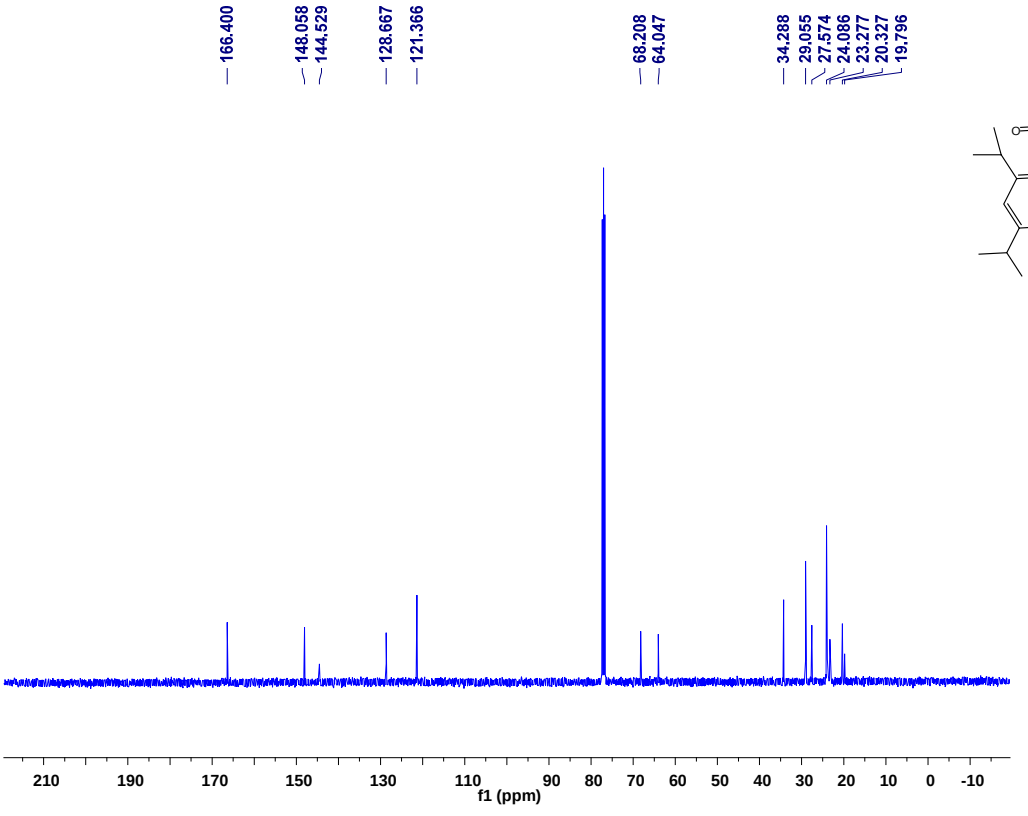
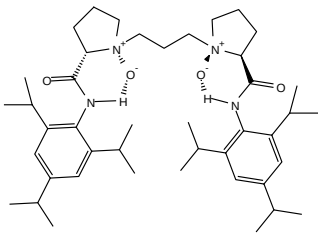
Ph1: 12.57





Current Data Parameters

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SWH: 24038.5 Hz
AQ: undefined
TE: 298.5 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
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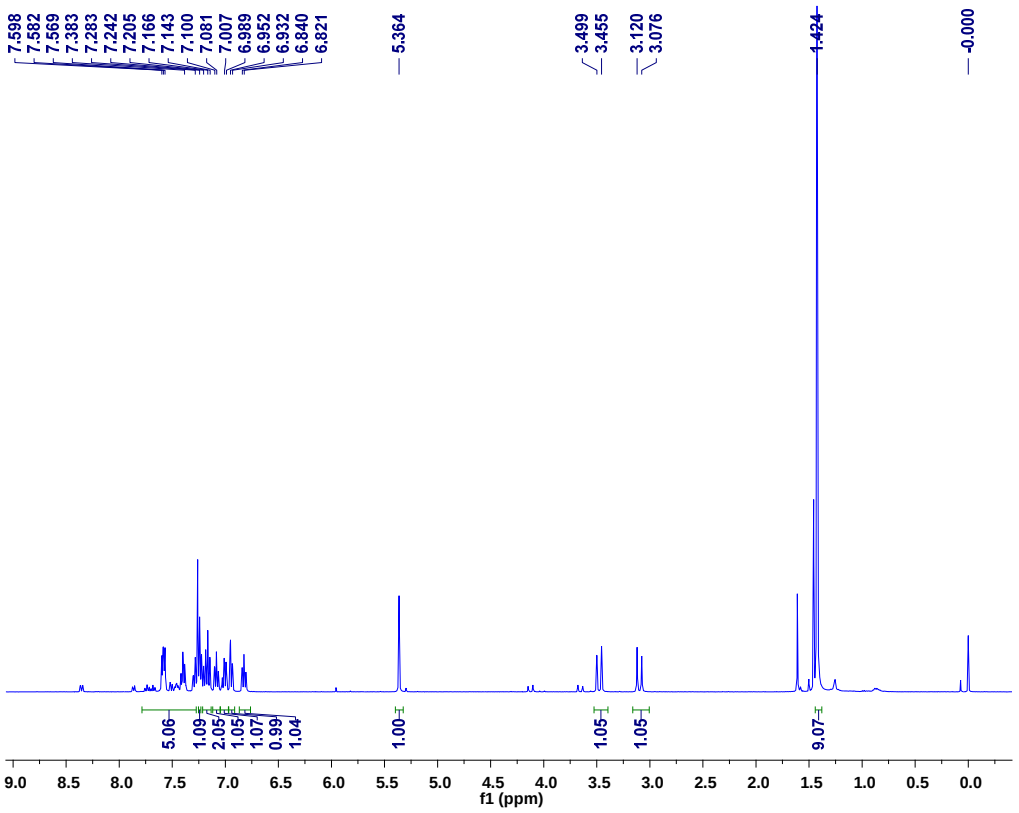
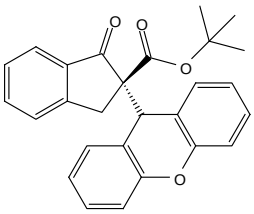
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -76.53
Ph1: 68.20





Current Data Parameters

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NS: 4
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AQ: undefined
TE: 294.2 C

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NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
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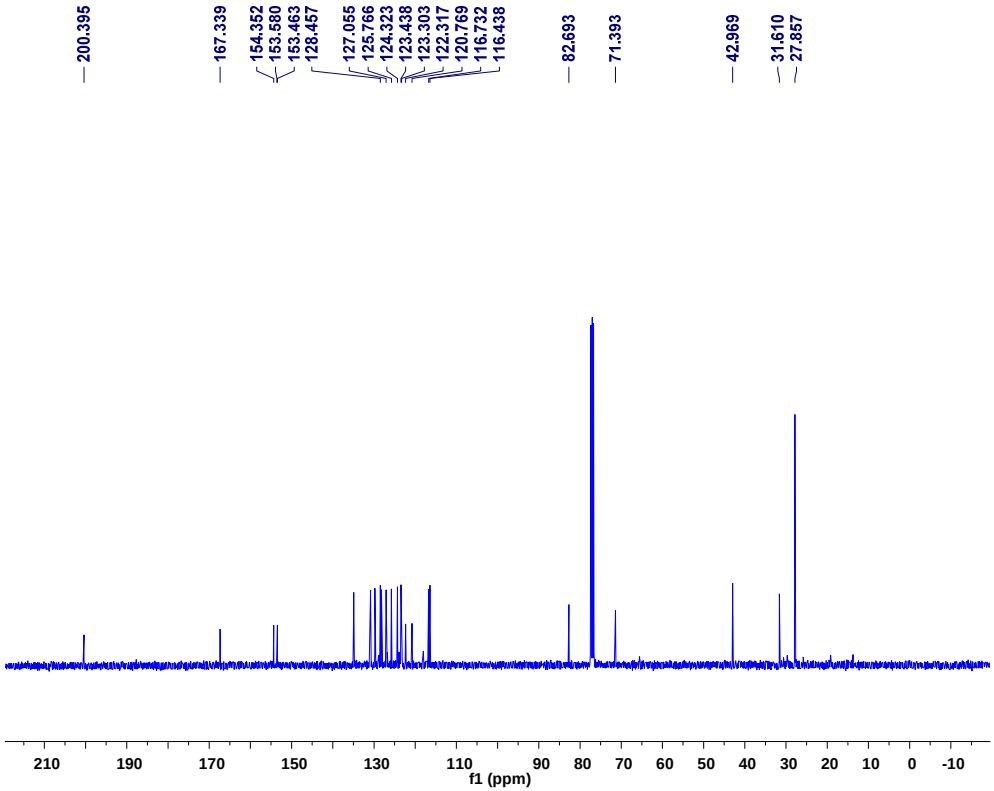
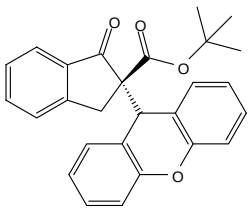
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 82.28
Ph1: 17.83



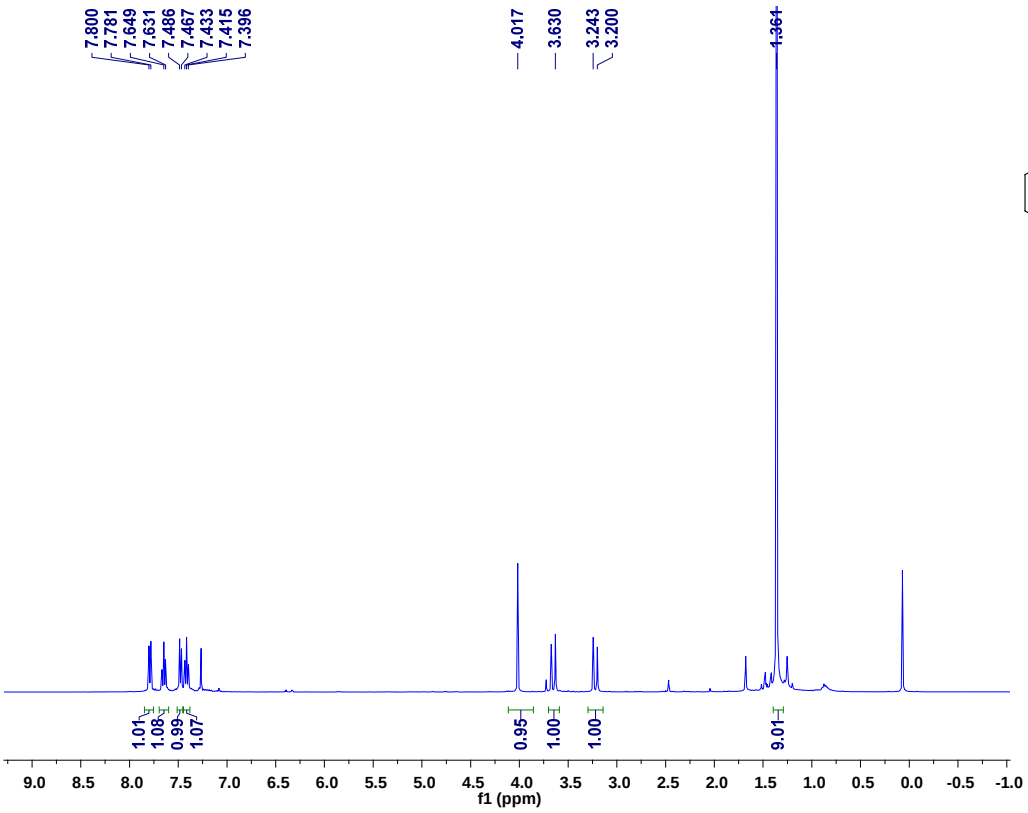


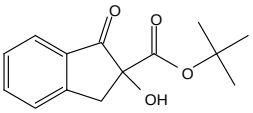
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-07-25T11:34:09
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 299.3 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -58.53
Ph1: 47.94



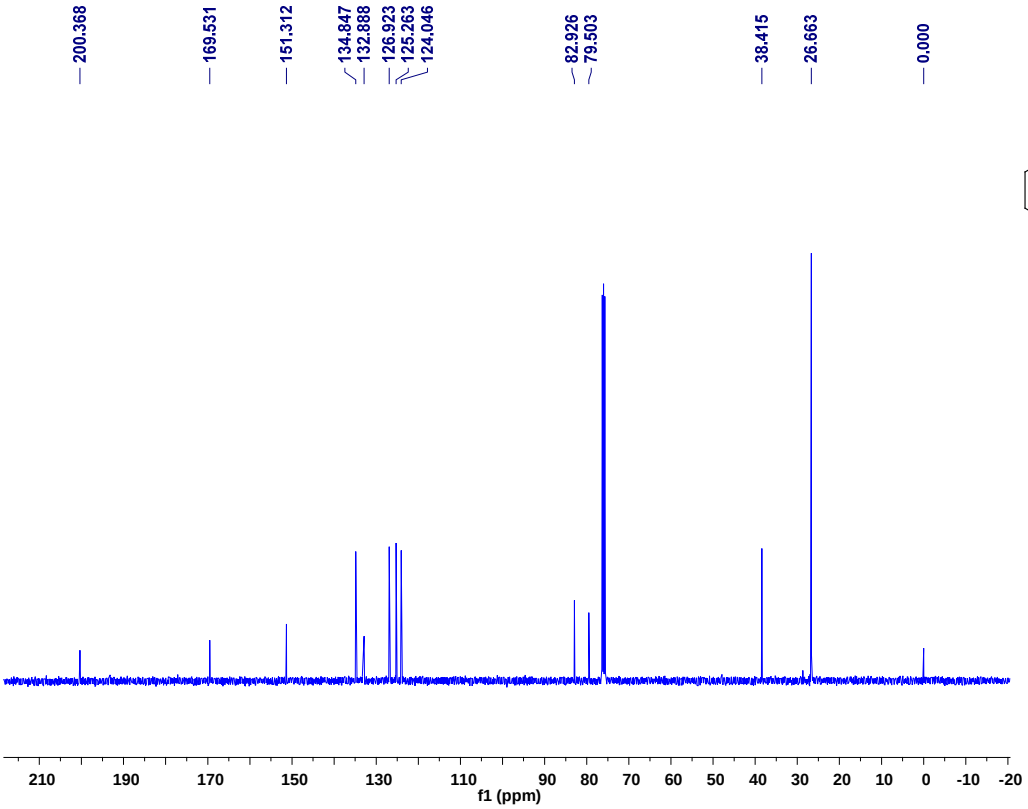


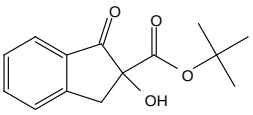
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-11-17T15:18:21
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 295.3 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 87.19
Ph1: 15.37



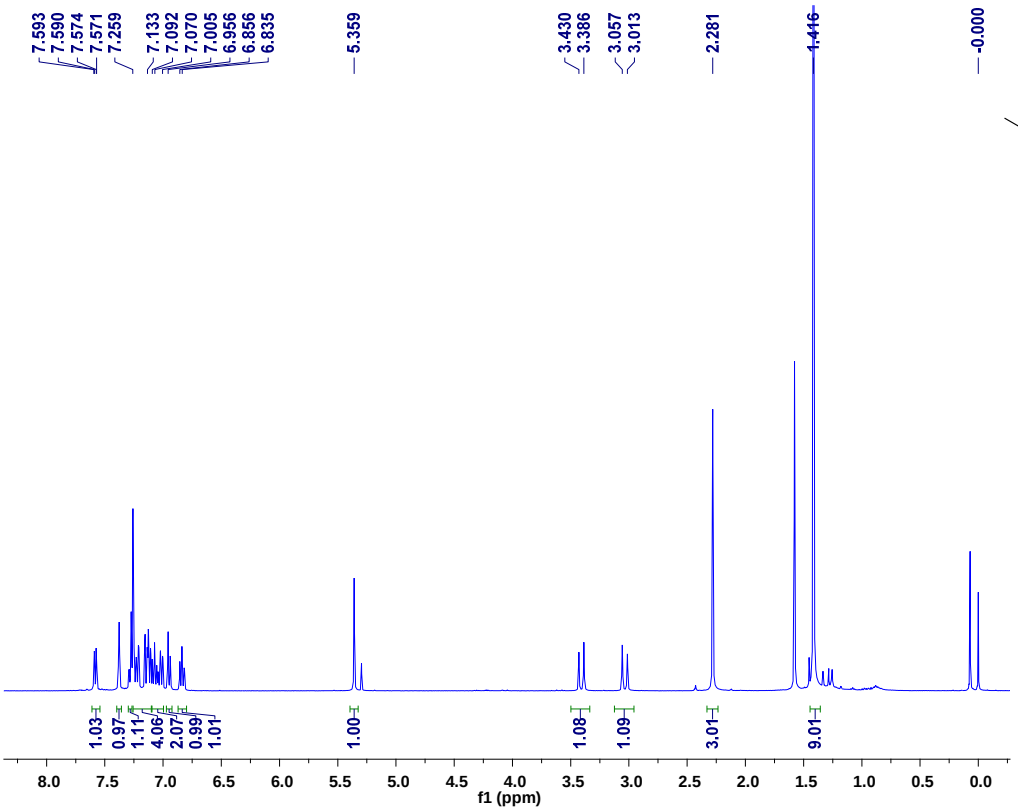


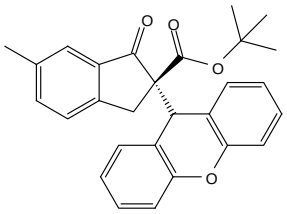
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-11-17T15:33:55
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 295.6 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -61.62
Ph1: 52.07



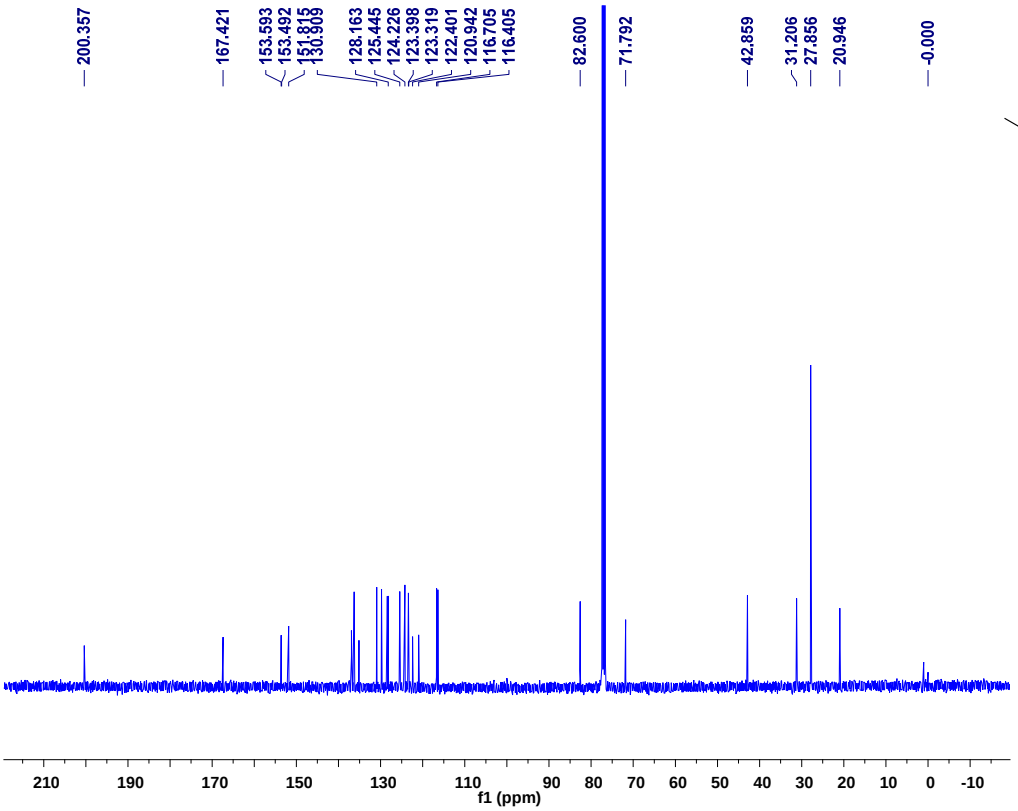


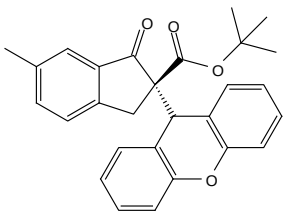
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-08-22T23:22:22
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 299.9 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 79.29
Ph1: 14.81



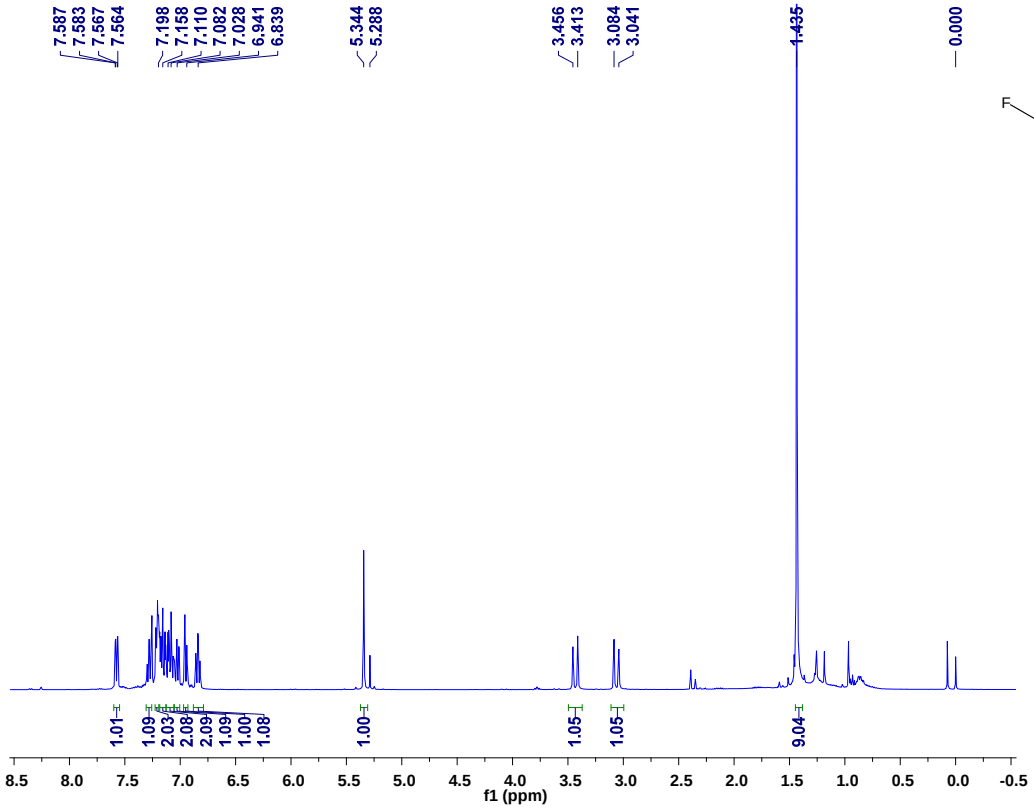


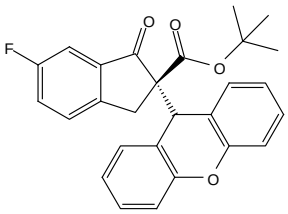
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-08-23T00:21:48
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 1024
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 300.2 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -57.72
Ph1: 32.21



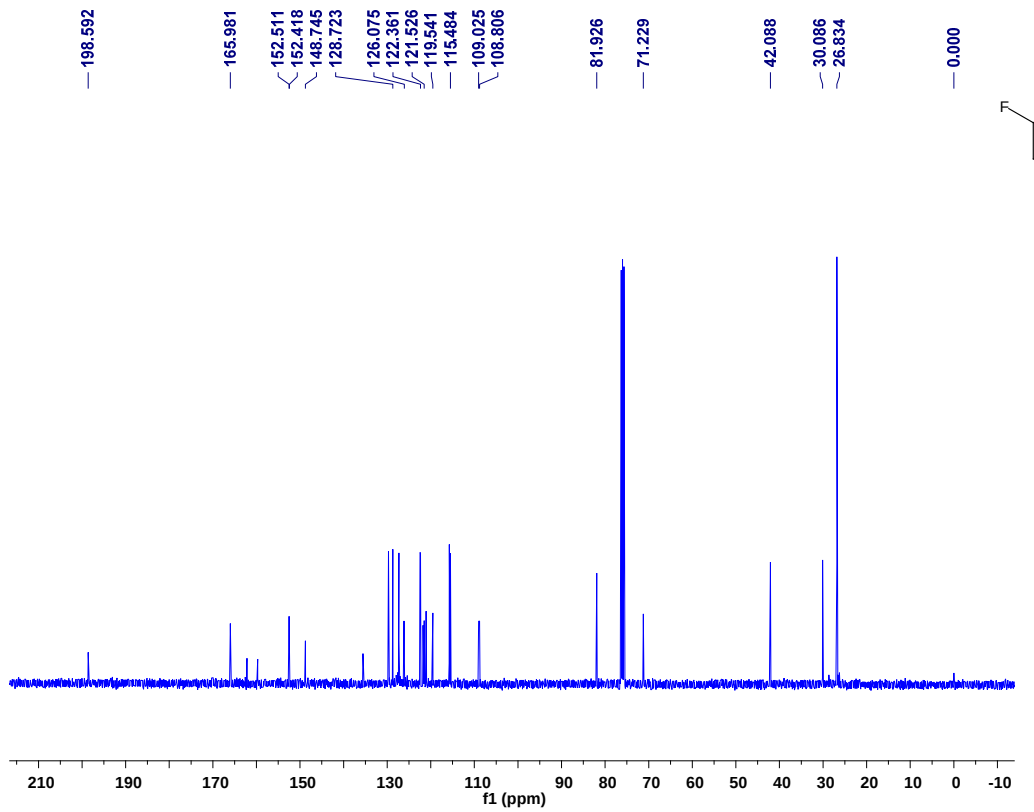


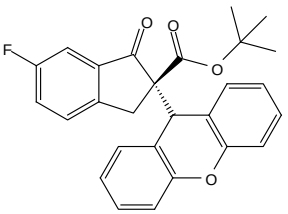
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-08-29T01:23:09
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 300.4 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 78.63
Ph1: 13.98



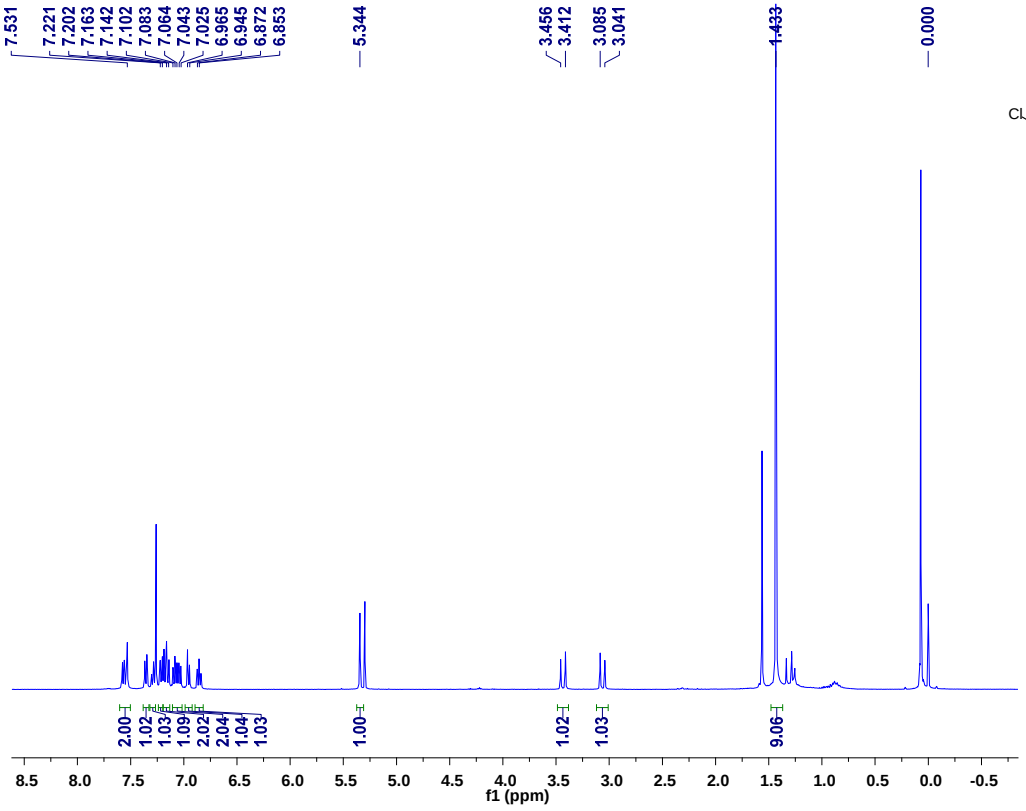


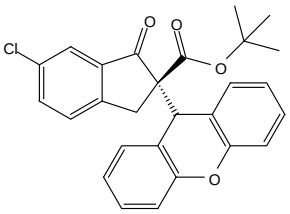
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-08-29T01:38:44
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 300.7 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -71.34
Ph1: 71.03



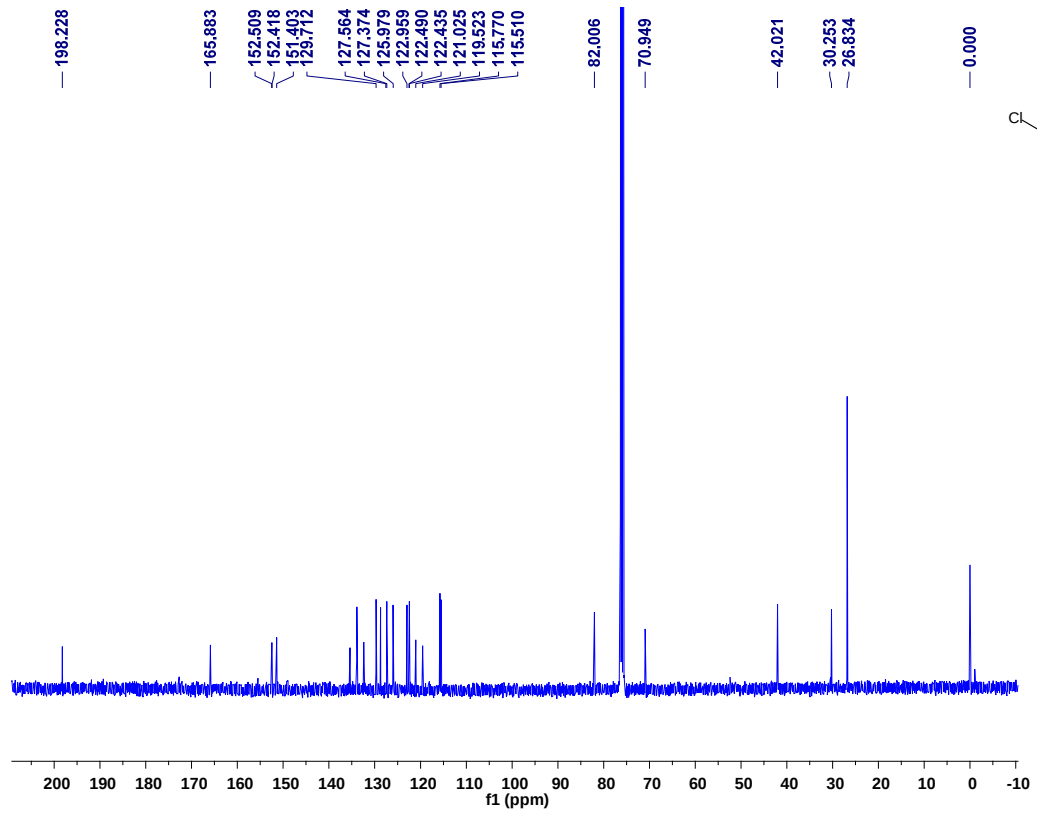


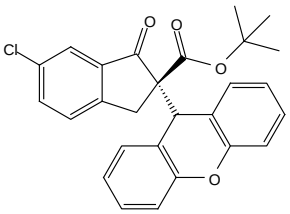
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-08-23T11:57:38
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 299.7 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 79.46
Ph1: 13.55



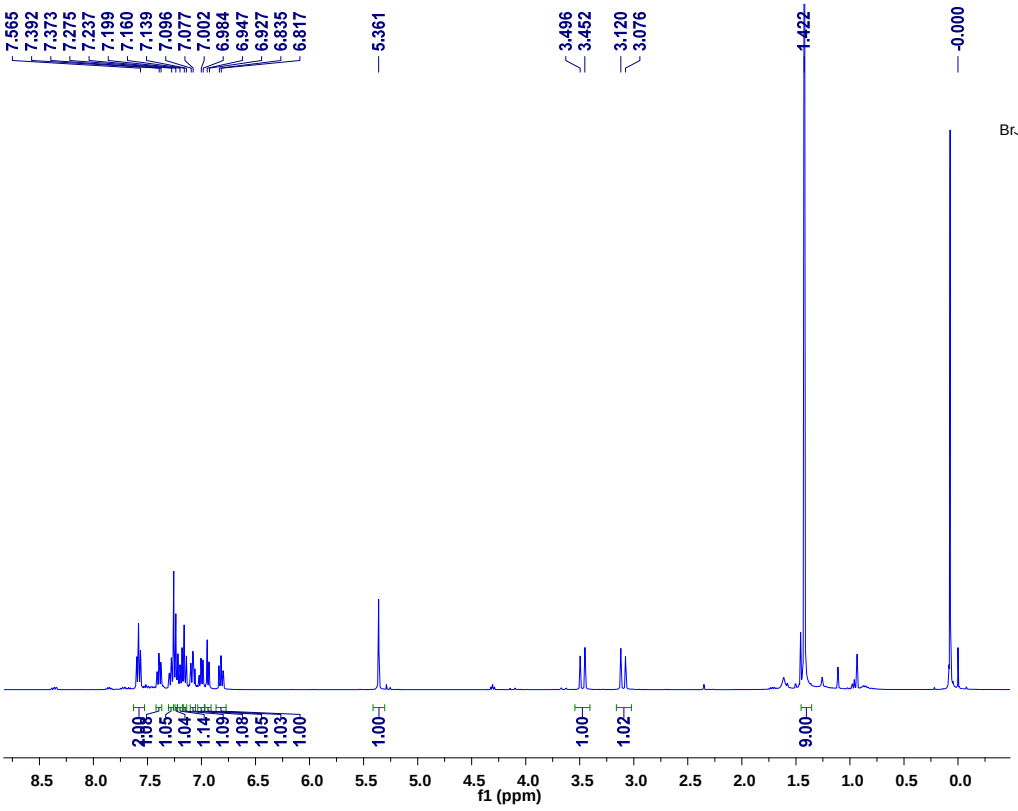


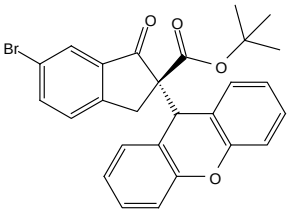
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-08-23T02:28:16
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 1024
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 300.2 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -72.39
Ph1: 59.63



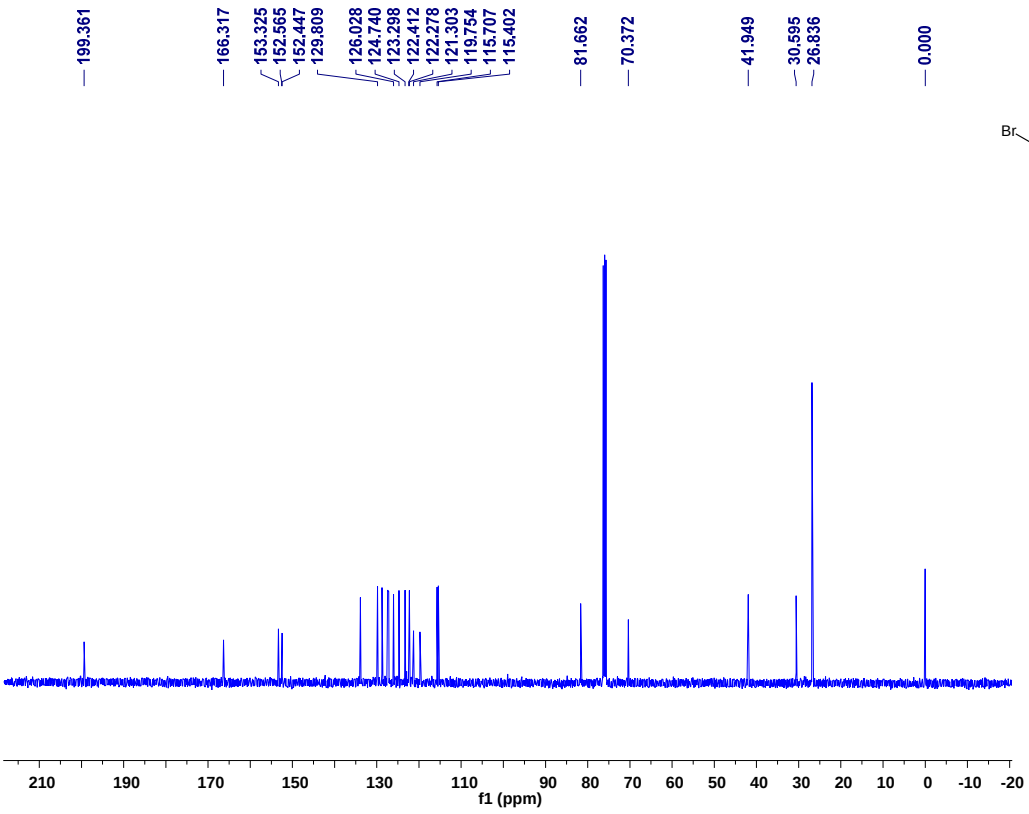


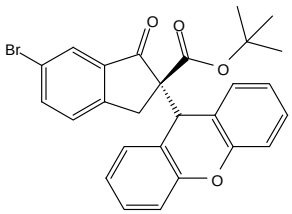
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-08-29T01:42:42
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 300.2 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 75.18
Ph1: 17.67



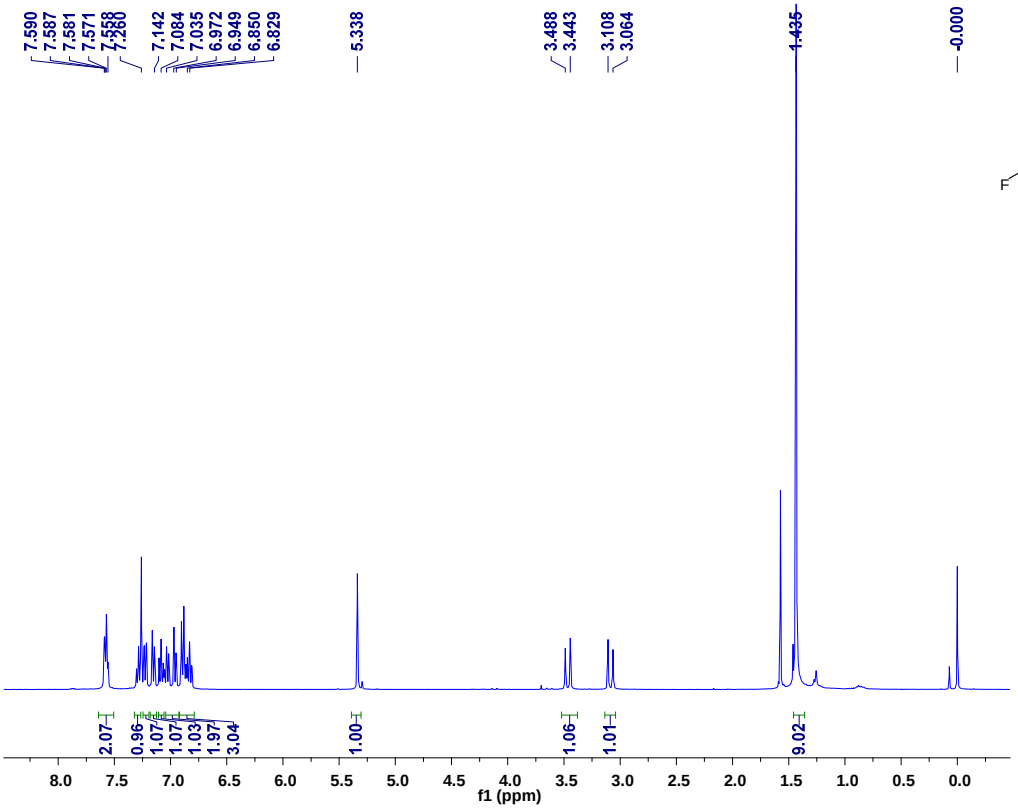


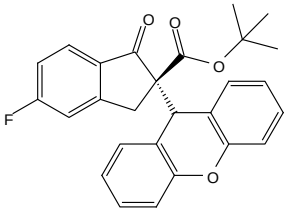
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-08-29T01:58:16
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 300.5 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -62.42
Ph1: 52.19



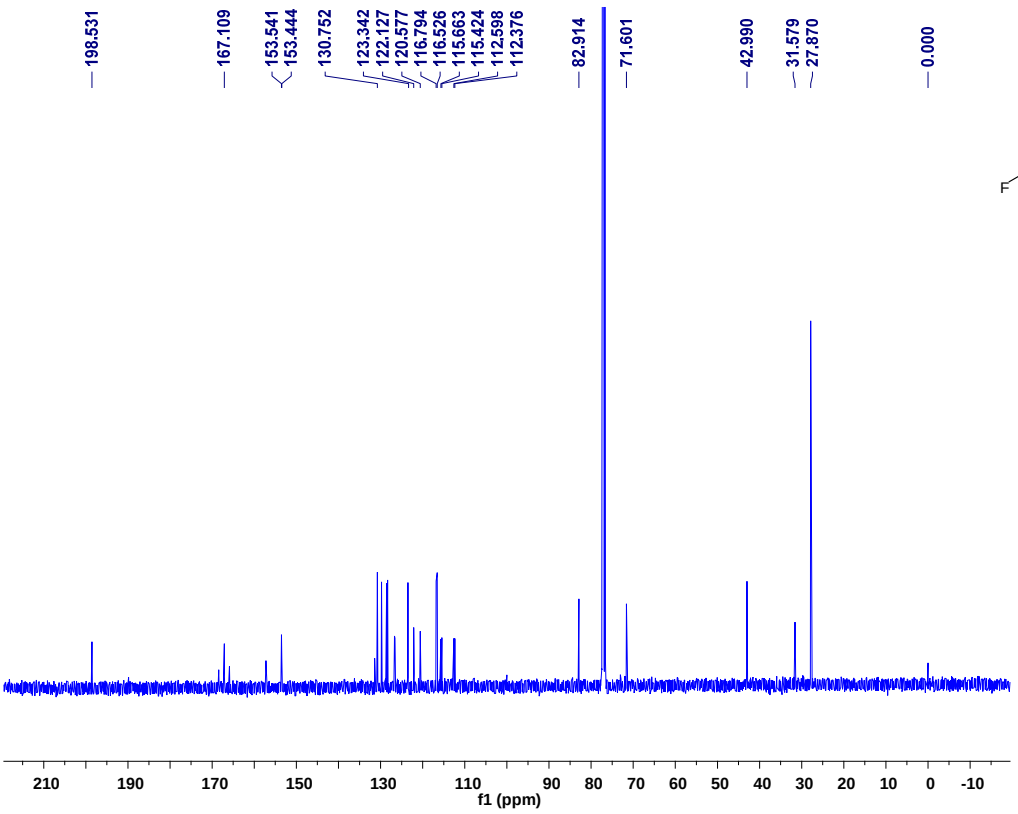


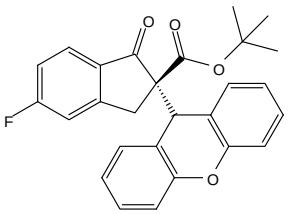
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-07-06T04:12:17
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 299.5 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 82.31
Ph1: 15.49



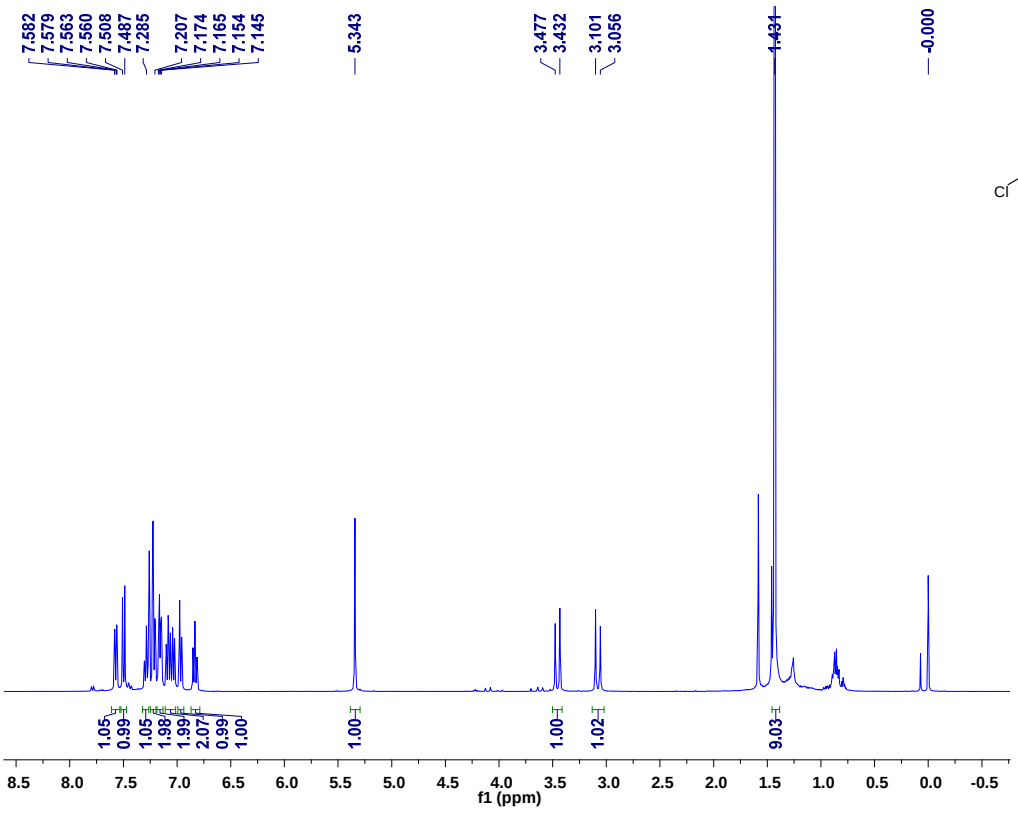


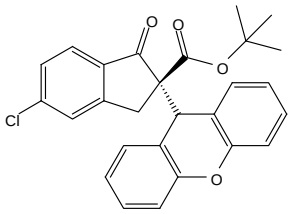
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-07-06T04:42:29
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 299.8 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -54.76
Ph1: 38.60



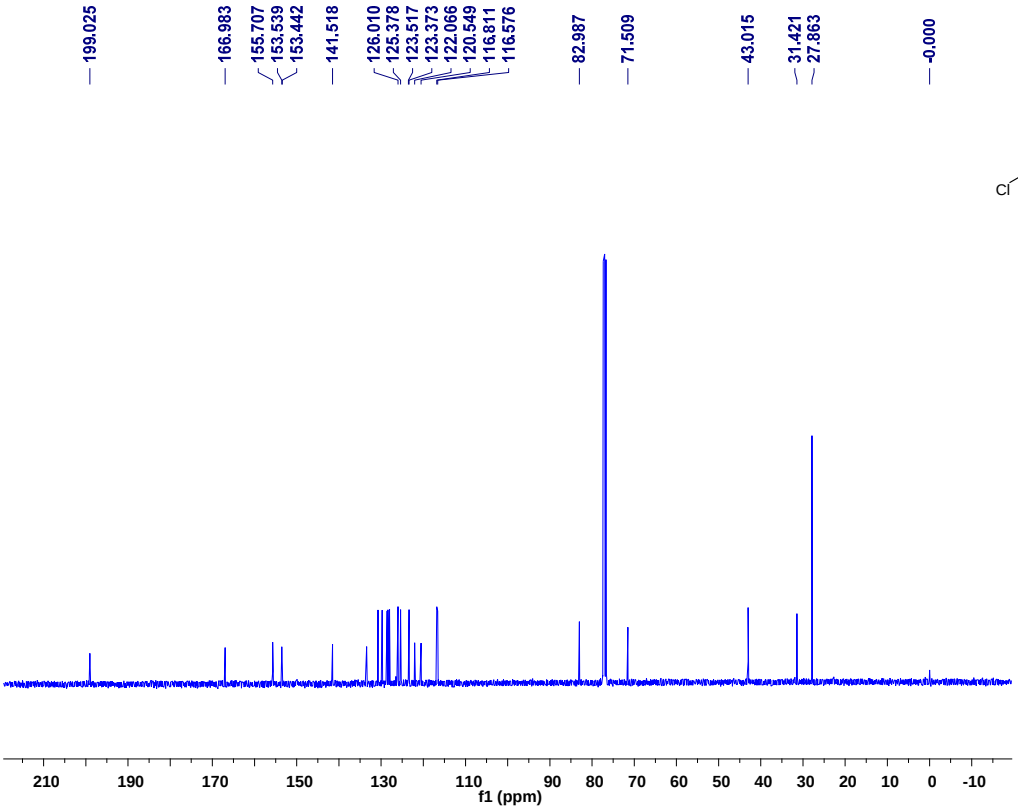


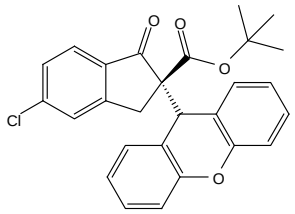
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-07-06T04:46:31
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 299.5 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 81.64
Ph1: 17.85



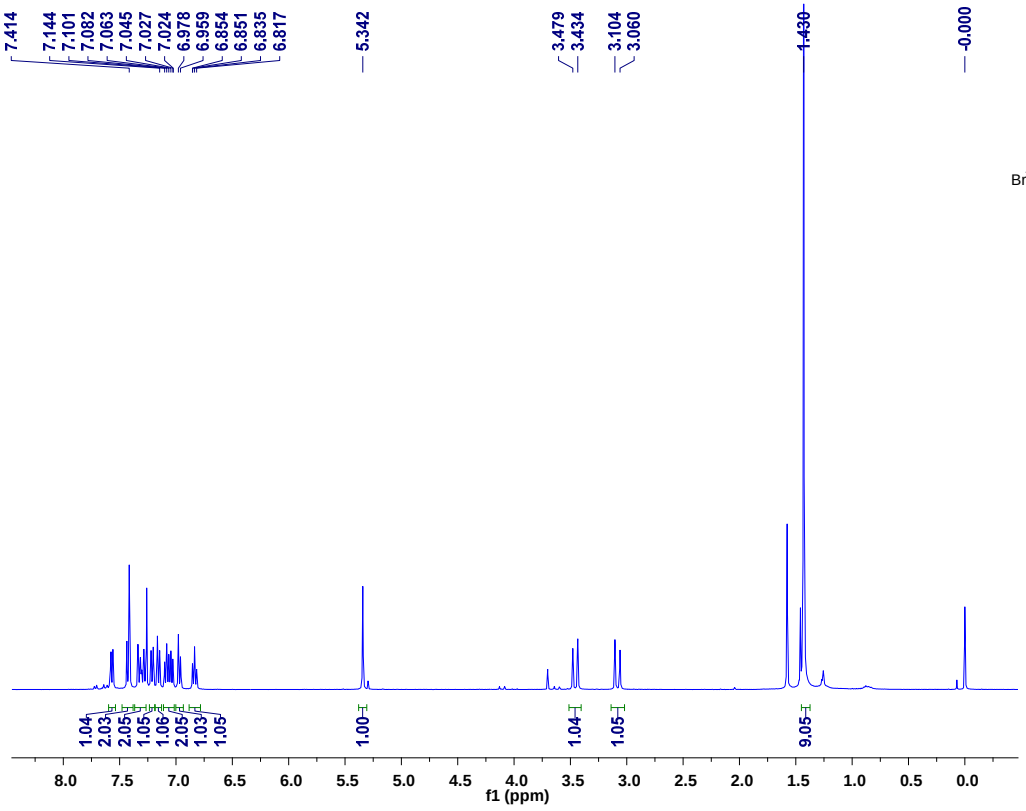


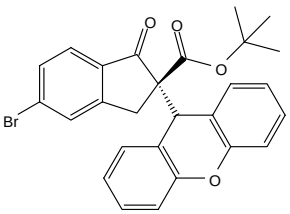
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-07-06T05:16:43
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 299.8 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -71.80
Ph1: 63.23



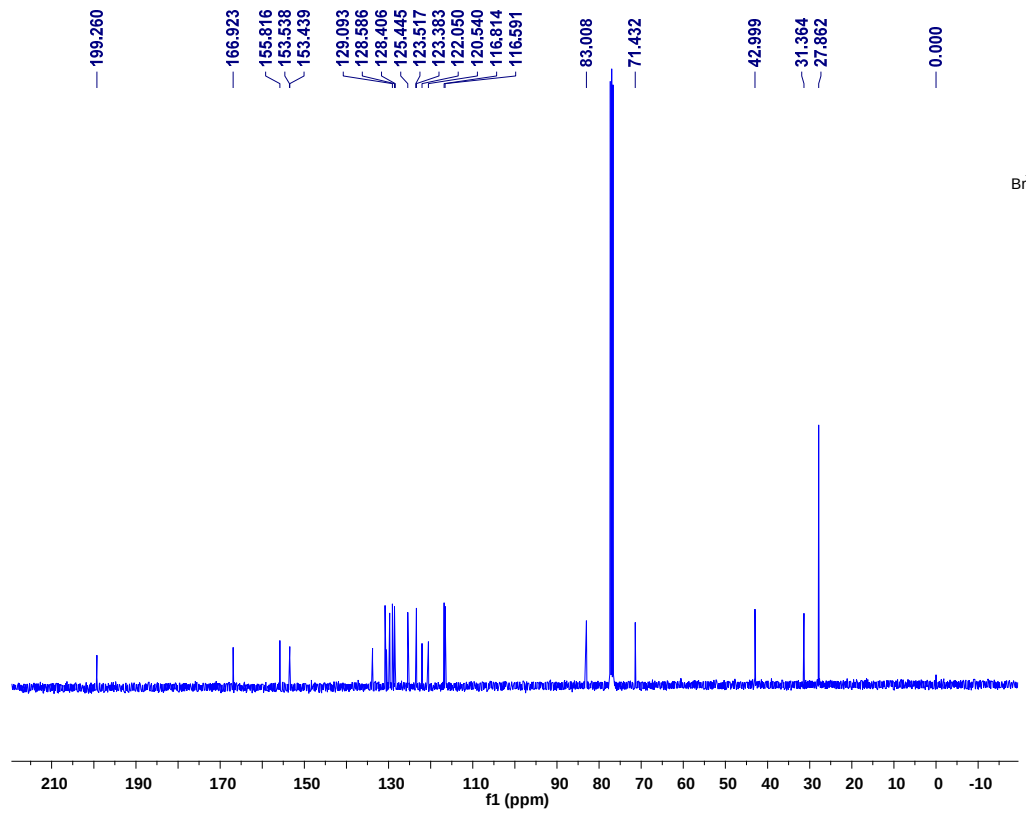


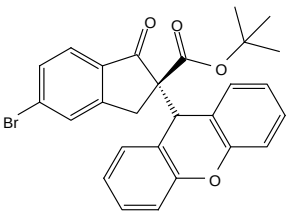
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-07-06T05:21:12
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 299.5 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 81.11
Ph1: 17.08



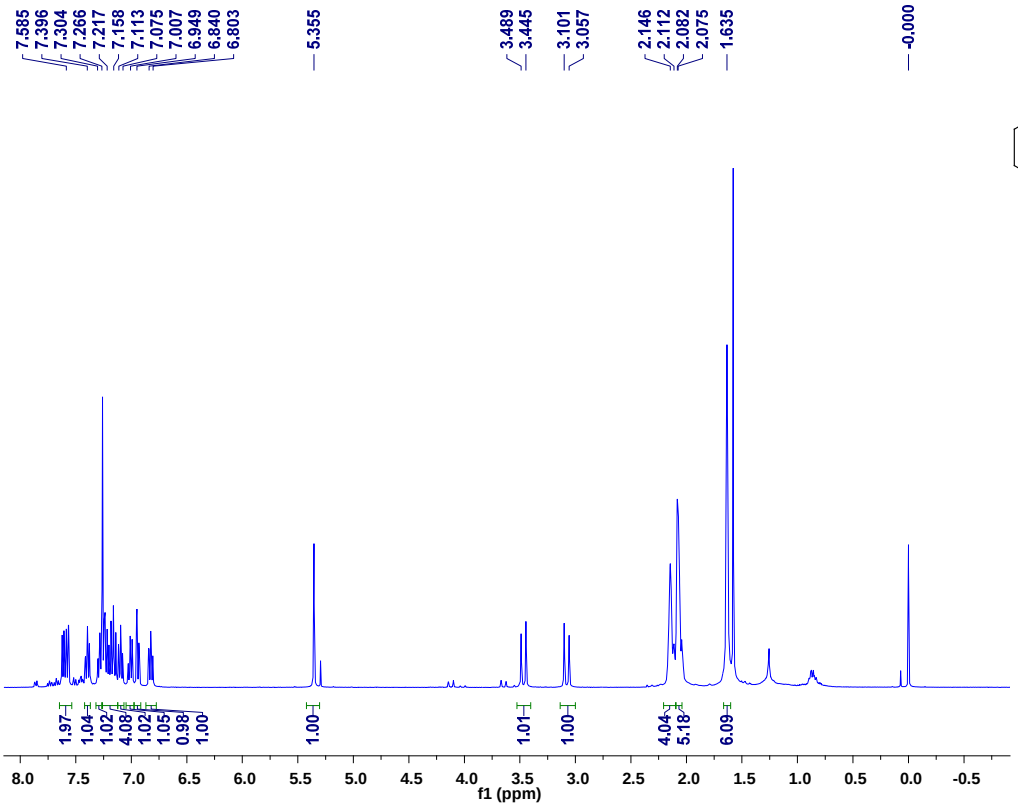


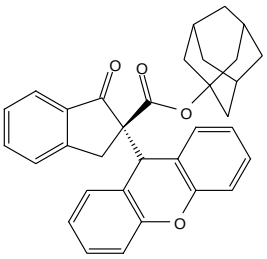
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-07-06T05:51:24
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 299.8 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -73.74
Ph1: 62.36



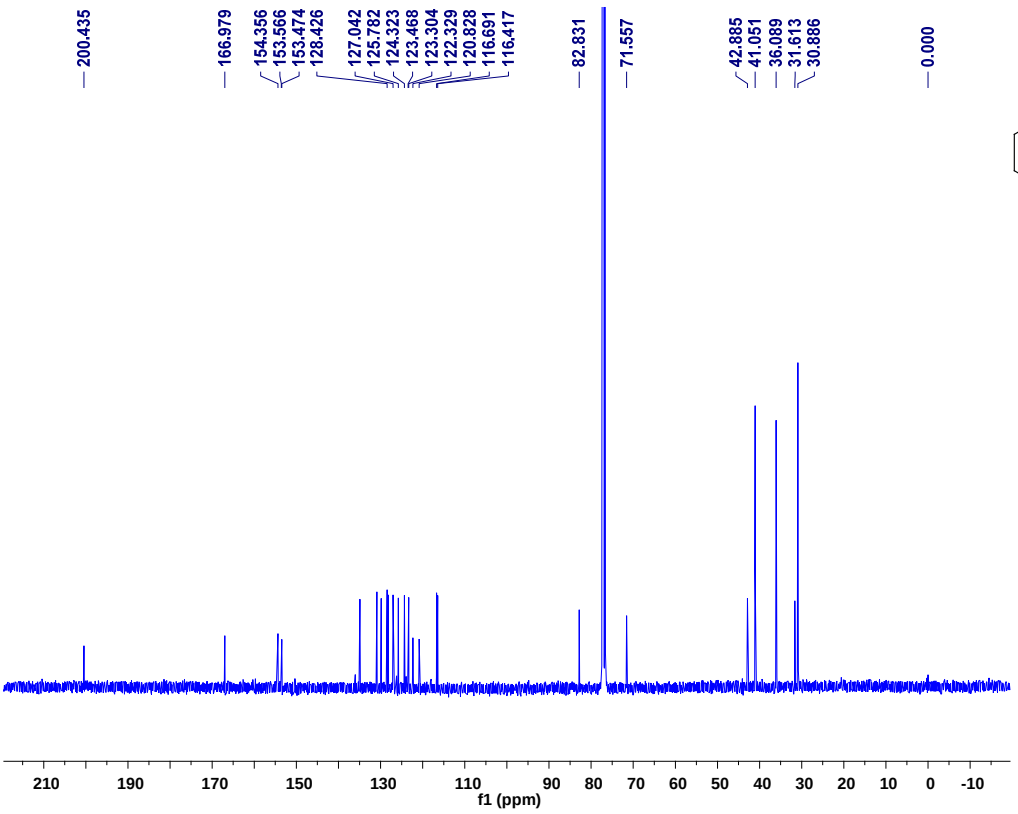


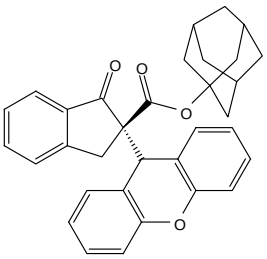
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-08-23T03:38:23
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 299.9 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 78.10
Ph1: 16.23



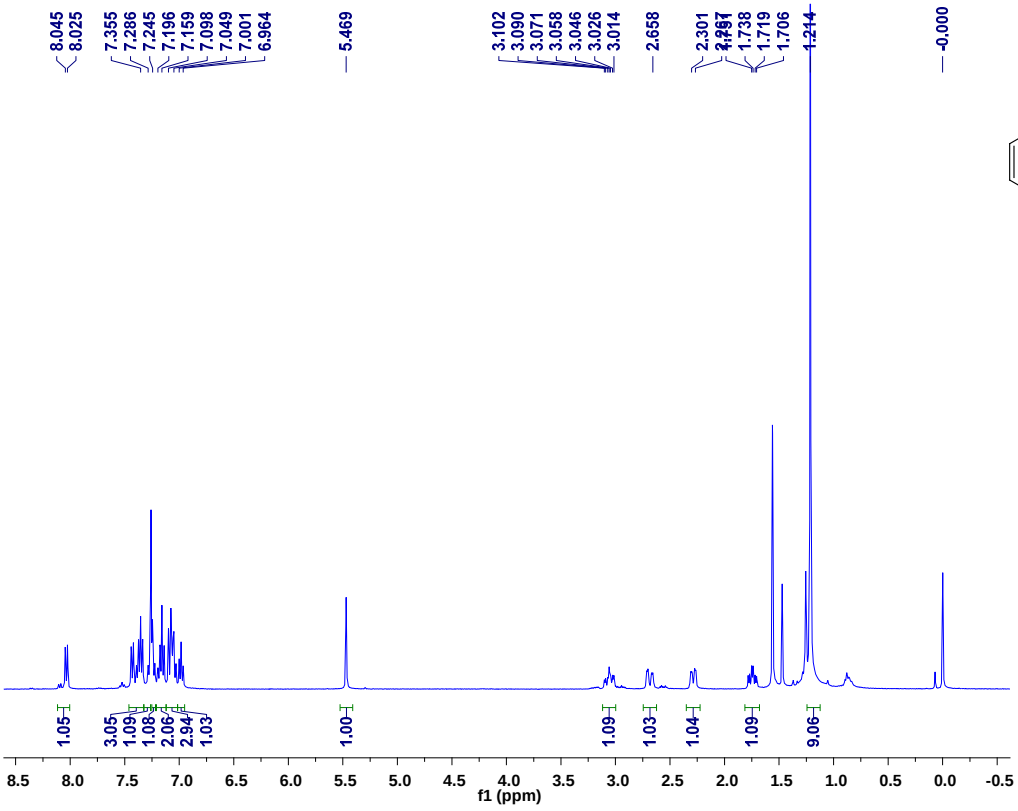


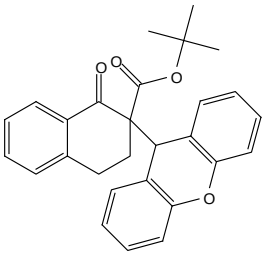
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-08-23T04:37:49
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 1024
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 300.2 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -58.65
Ph1: 29.41



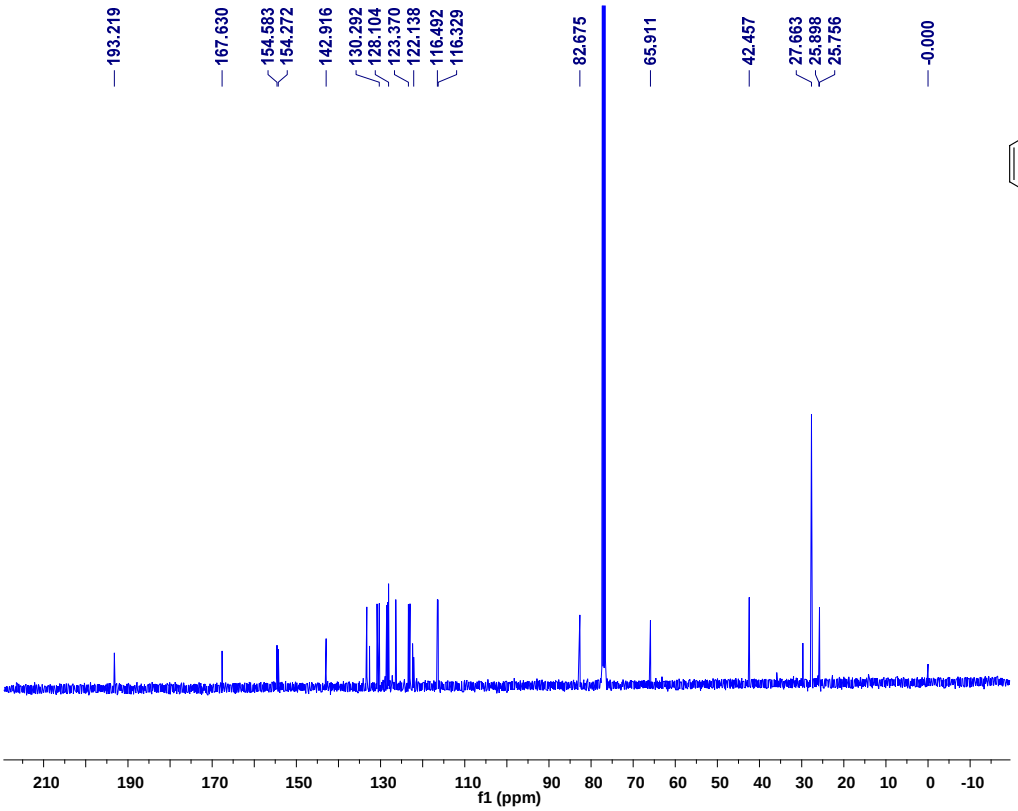


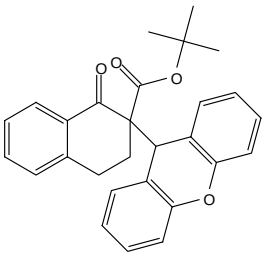
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-08-06T15:57:37
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 298.8 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 87.46
Ph1: 12.62



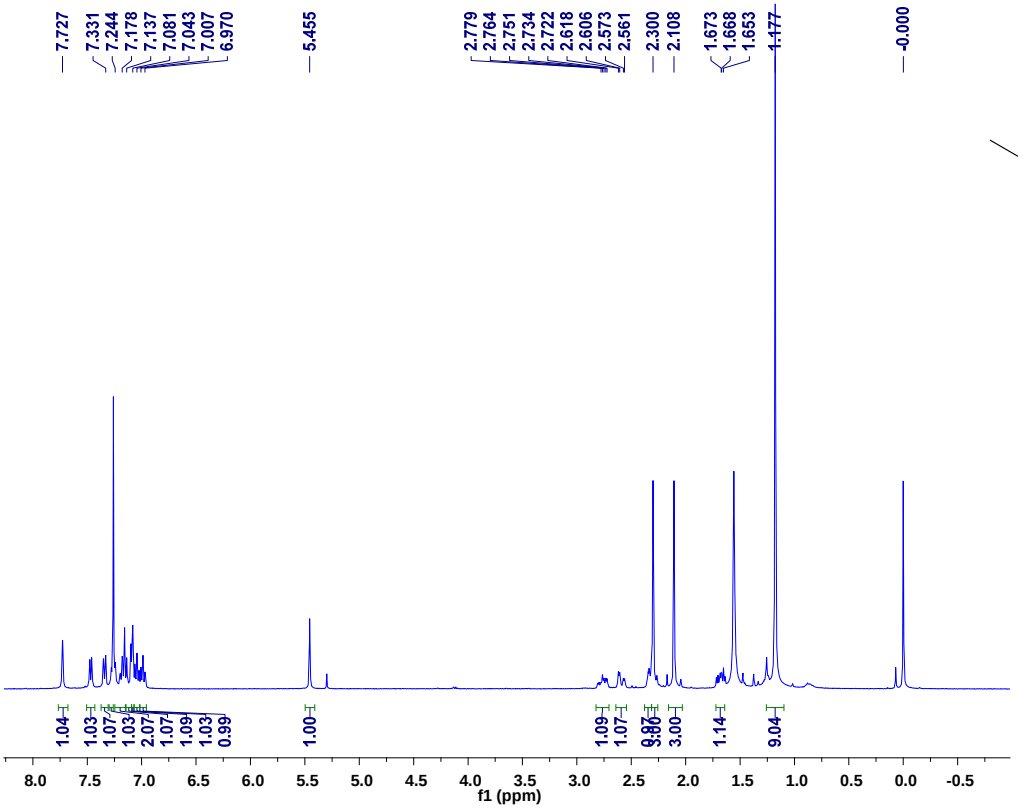


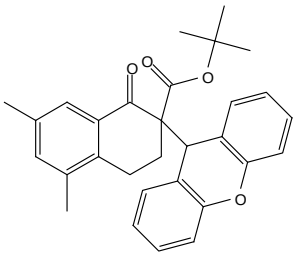
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-07-28T18:21:51
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 1024
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 299.2 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -79.04
Ph1: 75.70



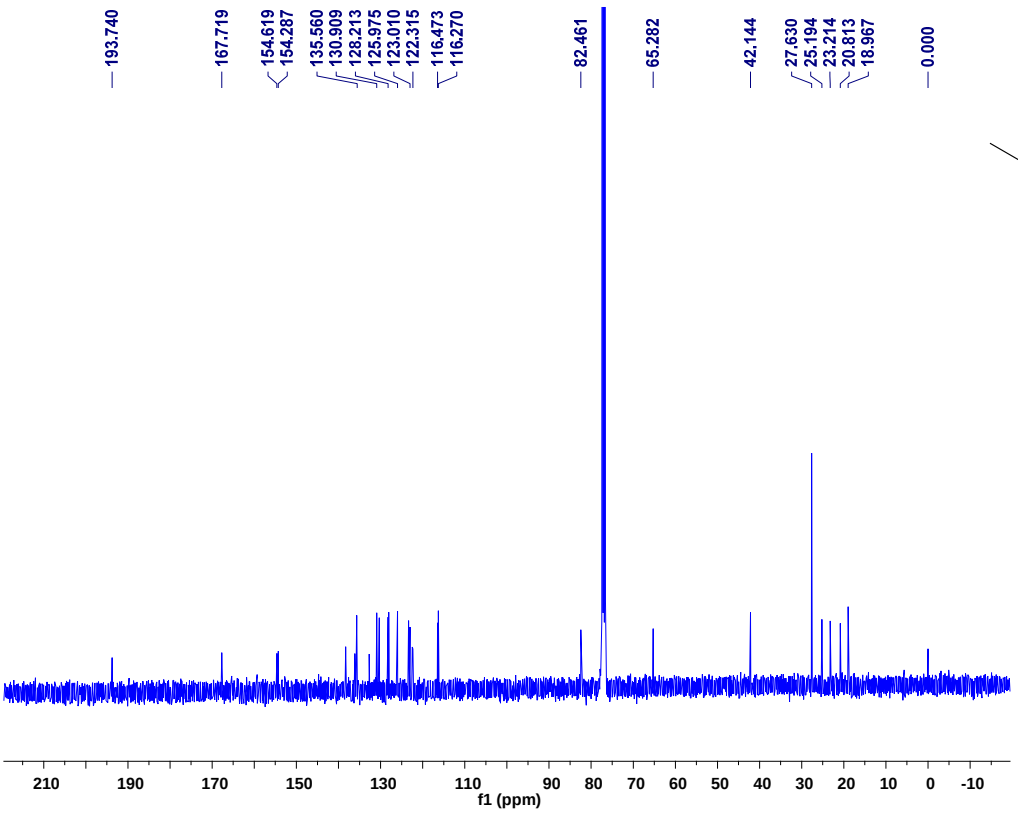


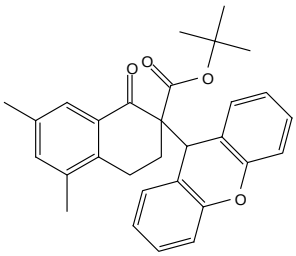
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-09-11T04:13:26
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 299.2 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 79.98
Ph1: 13.07



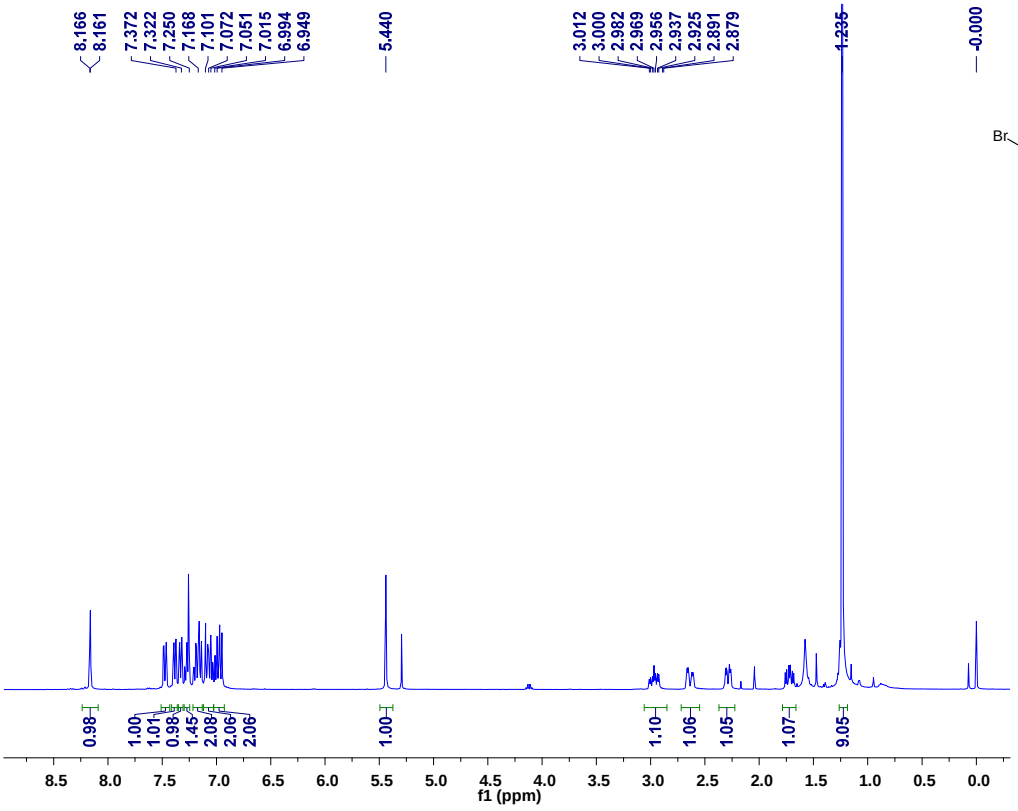


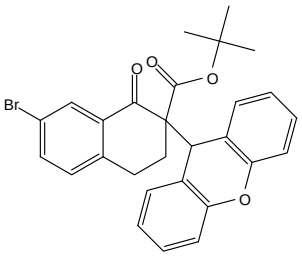
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-09-11T13:47:13
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 2048
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 299.9 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -56.87
Ph1: 30.25



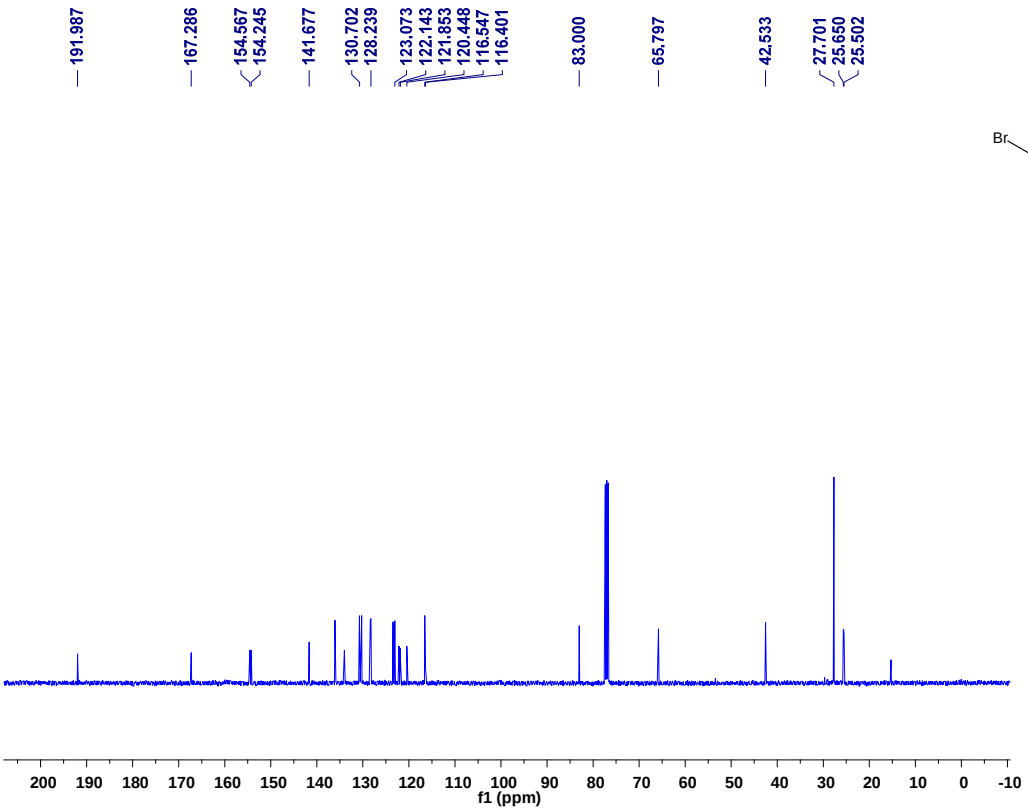


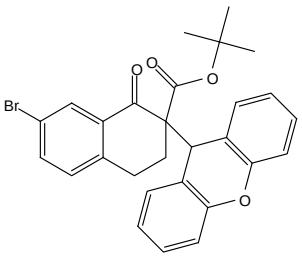
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-09-11T04:49:01
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 299.3 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 78.49
Ph1: 14.19



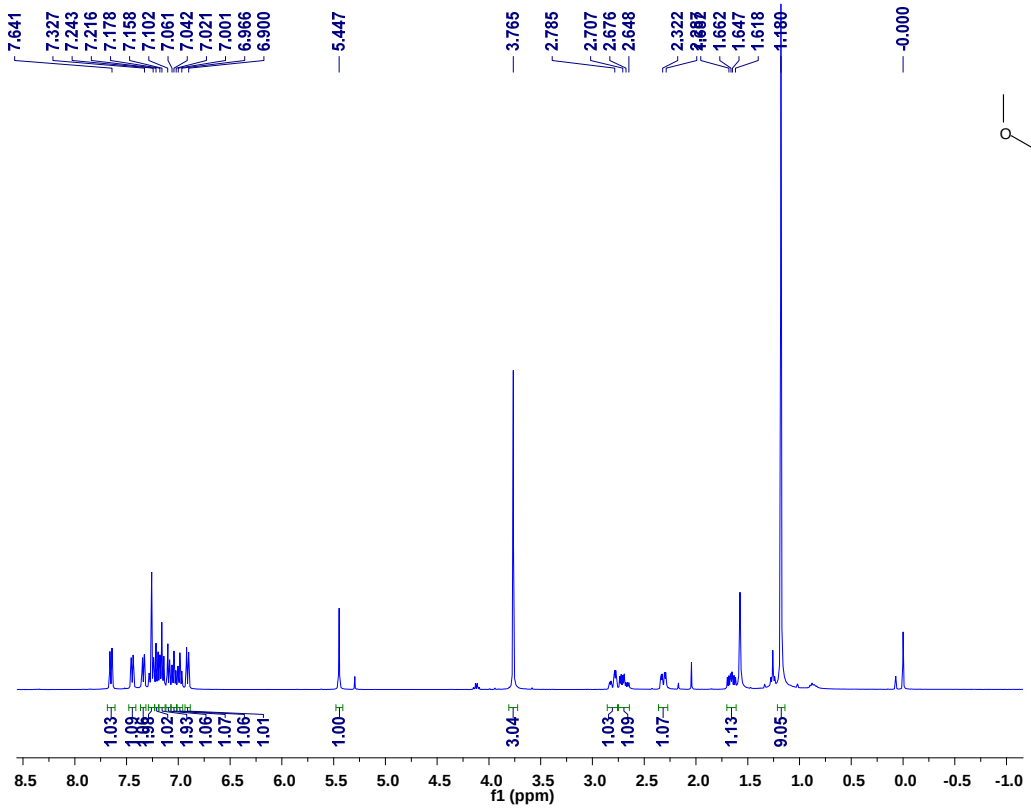


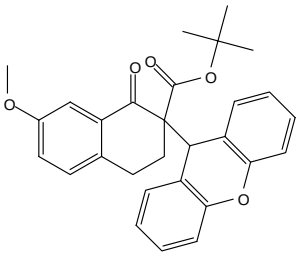
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-09-04T19:25:50
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 300.8 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -84.09
Ph1: 72.43



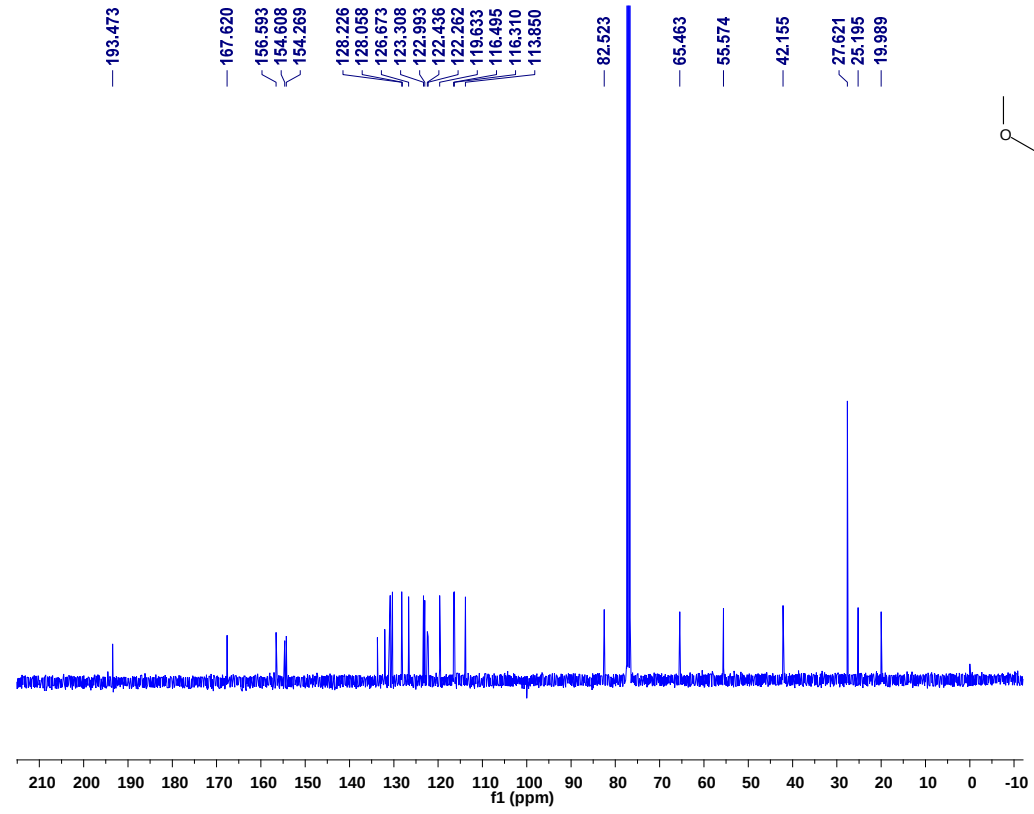


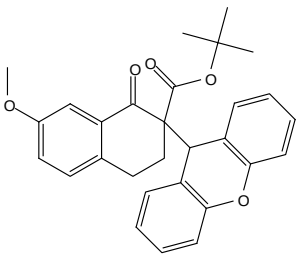
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-09-11T06:00:03
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 299.3 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 80.33
Ph1: 12.69



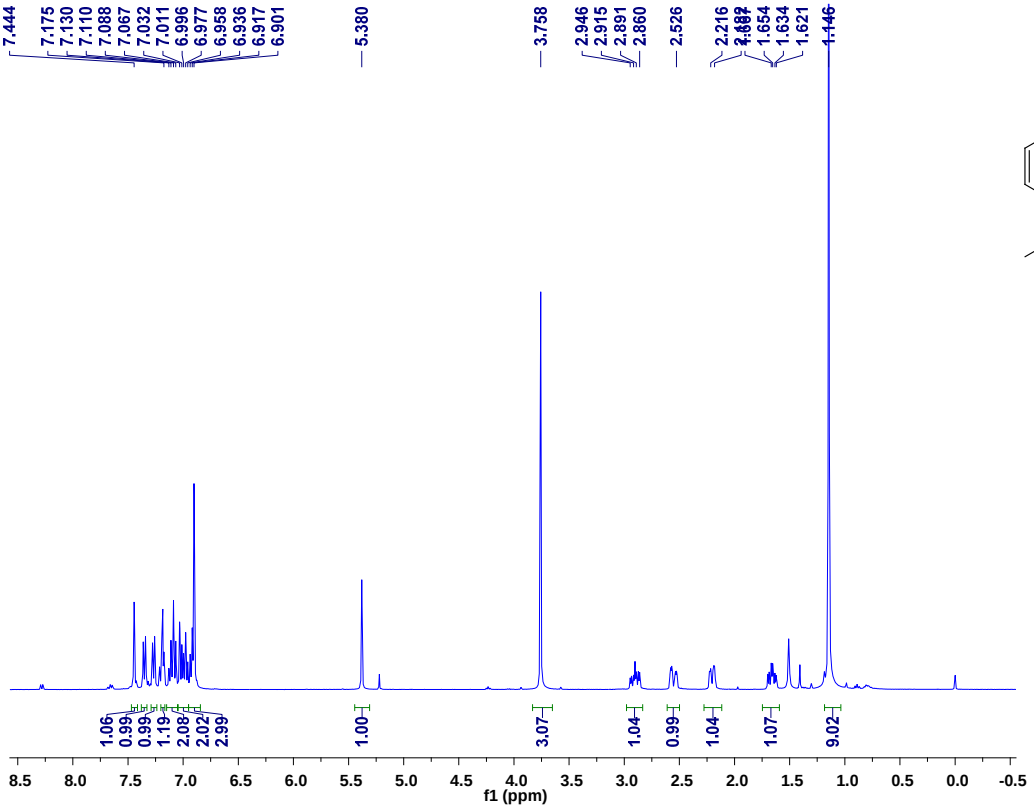


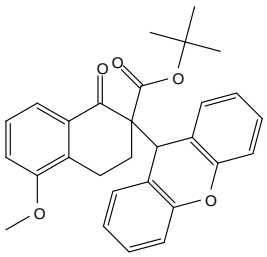
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-09-11T06:30:15
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 299.6 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -60.07
Ph1: 36.32



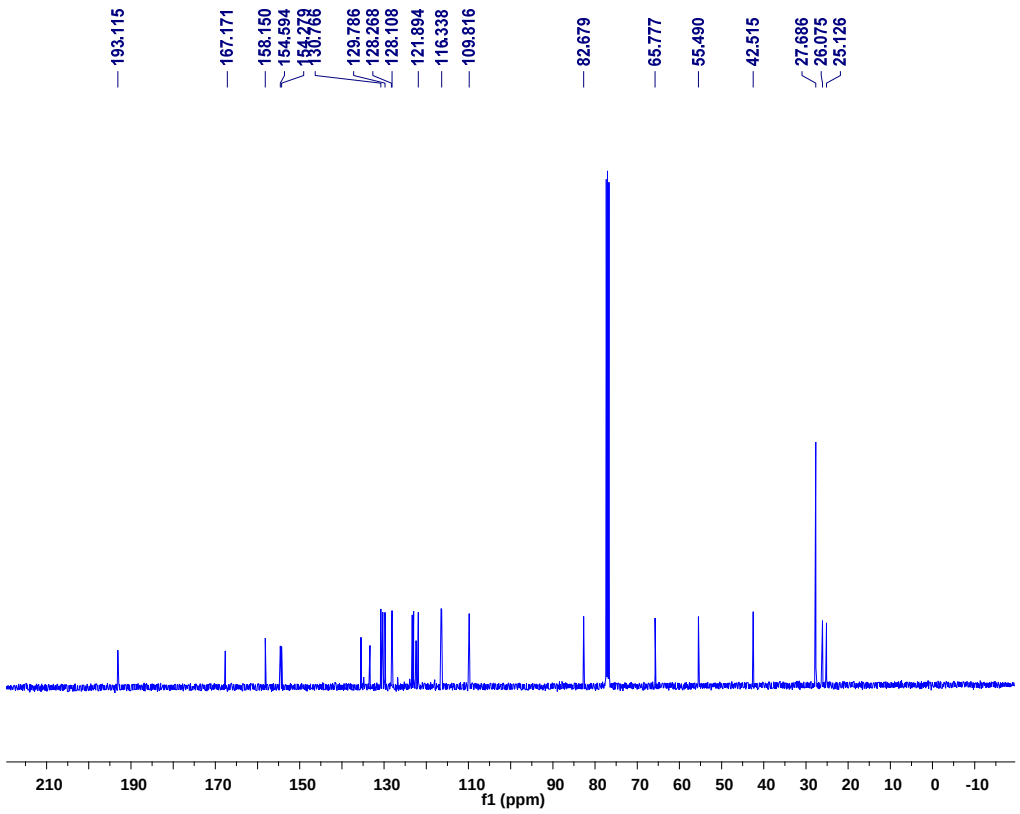


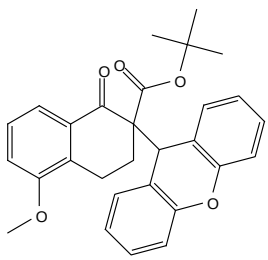
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-10-04T20:23:14
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 298.9 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 82.16
Ph1: 16.78



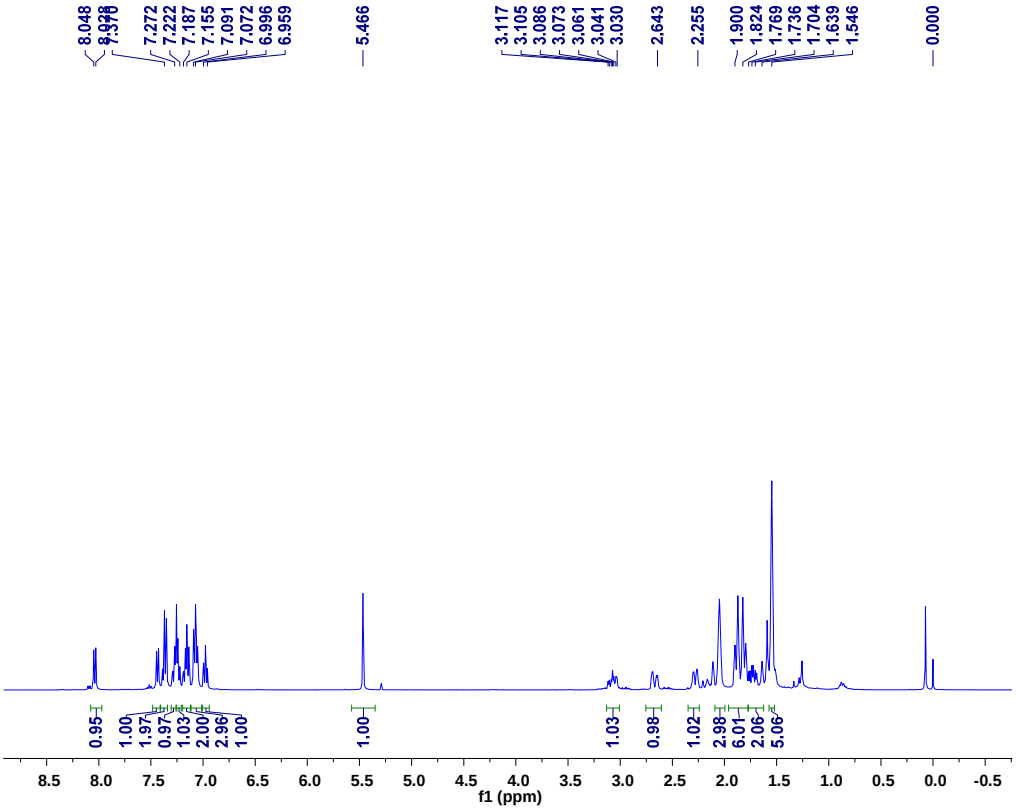


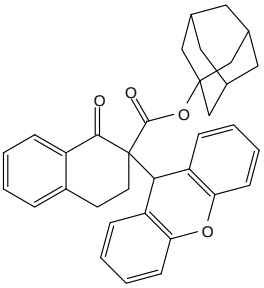
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-10-04T20:53:26
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 299.4 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -83.44
Ph1: 81.80



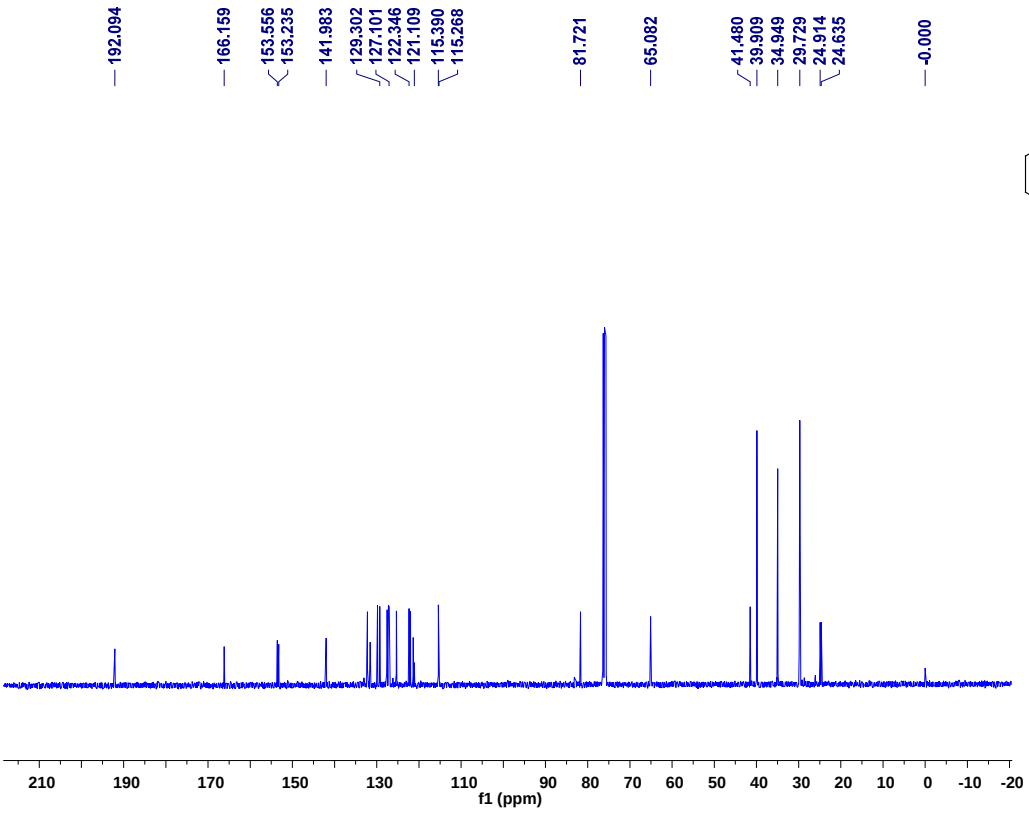


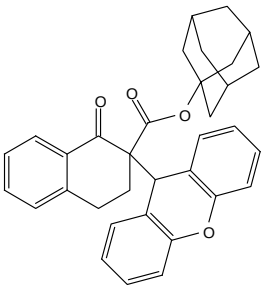
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-09-11T06:35:35
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 299.3 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 78.02
Ph1: 20.28



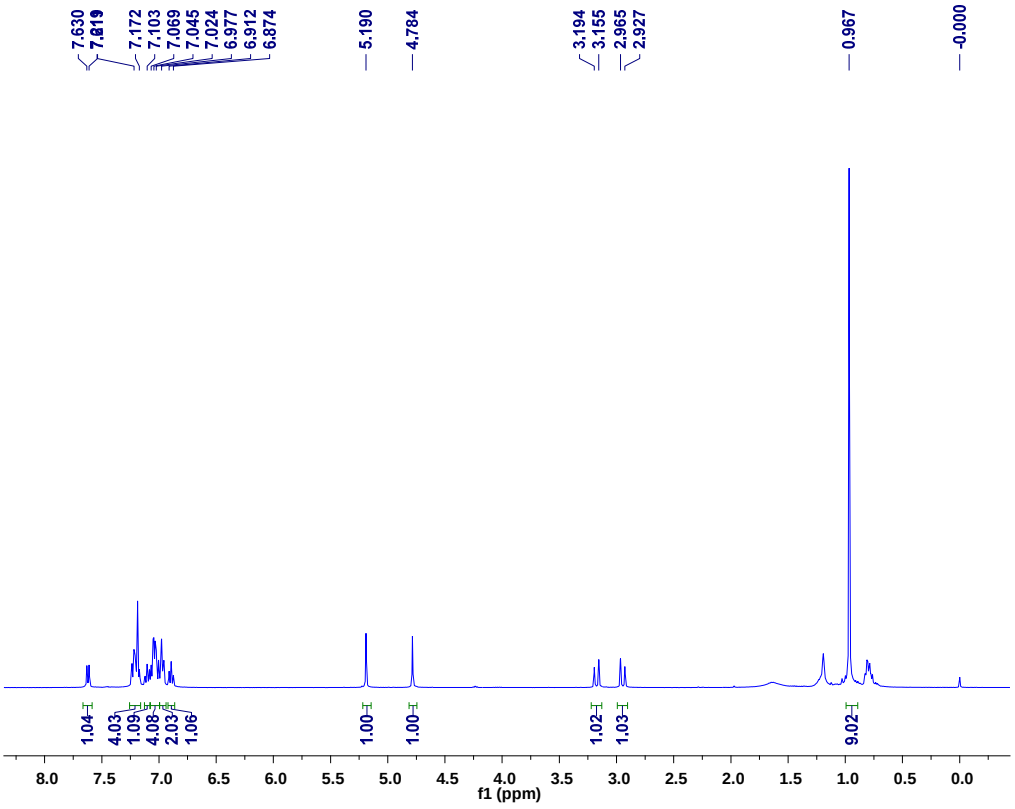


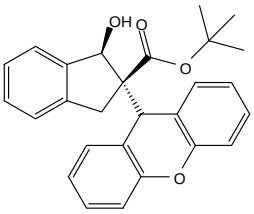
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-09-11T07:05:48
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 299.6 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -65.32
Ph1: 43.92



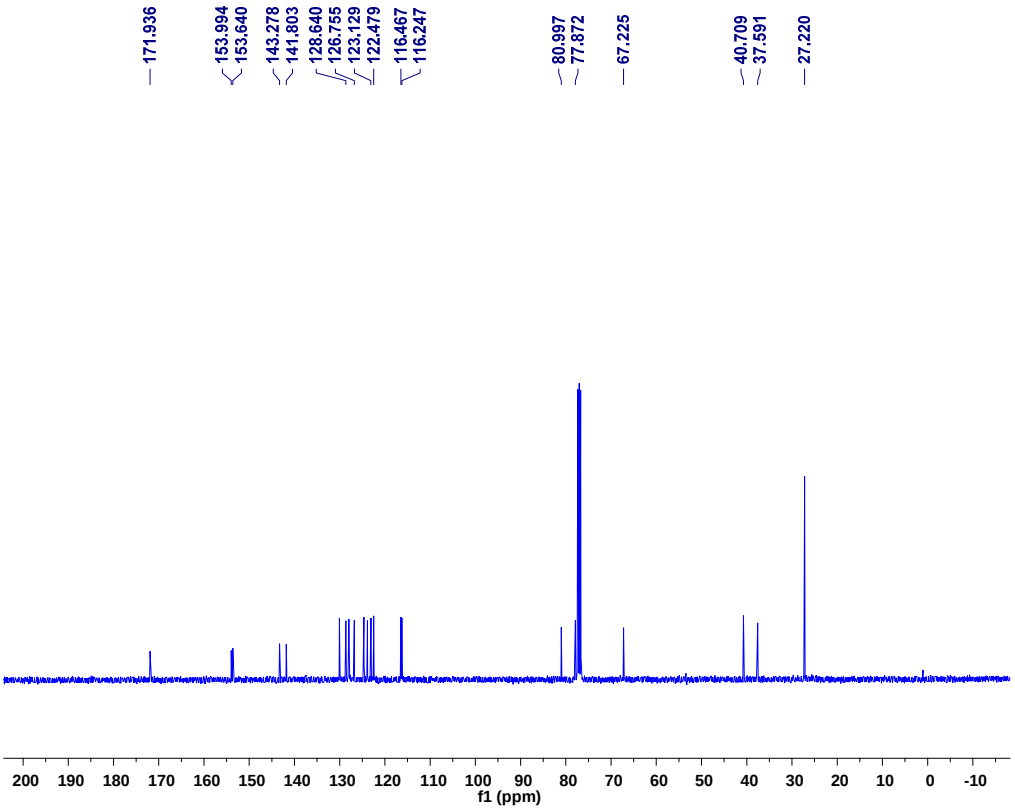


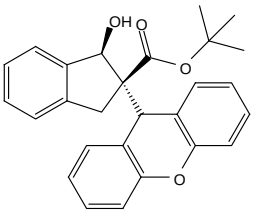
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-09-26T21:49:01
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 32
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 298.6 C

======== CHANNEL f1 ========
NUC1: 1H
P1: 9.93 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 0.30 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: 80.33
Ph1: 15.24





Current Data Parameters

F2 - Acquisition Parameters
DATE: 2012-09-21T12:09:15
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 298.8 C

======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -76.16
Ph1: 70.52

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 120904_s2_cwd

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 120904_s2_cwd

```
Bond precision:  C-C = 0.0043 A          Wavelength=0.71070

Cell:            a=8.0885(4)     b=16.7224(5)         c=9.1381(5)
                 alpha=90        beta=113.440(6)      gamma=90
Temperature:     293 K
```

	Calculated	Reported
Volume	1134.01(10)	1134.01(8)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C27 H23 Cl O4	C27 H23 Cl O4
Sum formula	C27 H23 Cl O4	C27 H23 Cl O4
Mr	446.90	446.90
Dx,g cm-3	1.309	1.309
Z	2	2
Mu (mm-1)	0.200	0.200
F000	468.0	468.0
F000’	468.51	
h,k,lmax	10,20,11	10,20,11
Nref	2394[4622]	3886
Tmin,Tmax	0.944,0.951	0.968,1.000
Tmin’	0.944	

```
Correction method= MULTI-SCAN

Data completeness= 1.62/0.84      Theta(max)= 26.370

R(reflections)= 0.0427( 3213)     wR2(reflections)= 0.0896( 3886)

S = 1.047                 Npar= 292
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
CELLV02_ALERT_1_C  The supplied cell volume s.u. differs from that
           calculated from the cell parameter s.u.’s by > 2
           Calculated cell volume su =      10.39
           Cell volume su given      =       8.00
```

```
PLAT242_ALERT_2_C Check Low       Ueq as Compared to Neighbors for        C24
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ..............     0.0043 Ang
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd.  #          1
              C27 H23 Cl O4
```

Alert level G

```
PLAT005_ALERT_5_G No _iucr_refine_instructions_details  in the CIF          ?
PLAT152_ALERT_1_G The Supplied and Calc. Volume s.1. Differ by ...          2 Units
PLAT199_ALERT_1_G Check the Reported _cell_measurement_temperature        293 K
PLAT200_ALERT_1_G Check the Reported   _diffrn_ambient_temperature        293 K
PLAT791_ALERT_4_G Note: The Model has Chirality at C8     (Verify)          R
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   4 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   5 ALERT level G = General information/check it is not something unexpected

   4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   1 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   2 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 05/11/2012; check.def file version of 05/11/2012

Datablock 120904_s2_cwd - ellipsoid plot