Electronic Supplementary Information (ESI)

Highly enantioselective construction of carbazole derivatives *via* [4+2] cycloaddition of silyloxyvinylindoles and β,γ-unsaturated α-ketoesters

Xiaohu Zhao, Hongjiang Mei, Qian Xiong, Kai Fu, Lili Lin*, Xiaohua Liu and Xiaoming Feng*

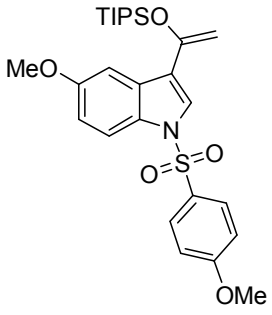
Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, (China)

xmfeng@scu.edu.cn

1. General remarks

^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz), integration. ^{13}C NMR data 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. Enantiomer excesses were determined by chiral HPLC analysis on Daicel Chiralcel IA, ID and AD-H in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: g/100 mL, in solvent). HRMS was recorded on a commercial apparatus (ESI Source). All the solvents were purified by usual methods before use. Silica gel for Thin-layer chromatography (HG/T2354-92) made in Qingdao Haiyang Chemical Co., Ltd. The compounds **1a-c** were synthesized by the procedure in the literature.[1], and the compounds **2** were synthesized by the procedure in the literature. [2]

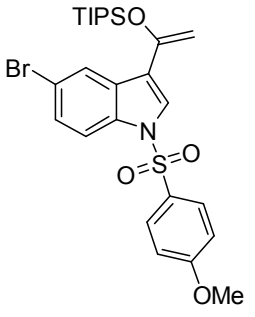
5-methoxy-1-((4-methoxyphenyl)sulfonyl)-3-(1-((triisopropylsilyl)oxy)vinyl)-1H-indole (1b)



($C_{27}H_{37}NO_5SSi$) White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 9.2 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.63 (s, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 6.86 (dd, *J* = 9.2, 2.4 Hz, 1H), 6.80 – 6.73 (m, 2H), 4.68 (d, *J* = 1.2 Hz, 1H), 4.47 (d, *J* = 1.6 Hz, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 1.25 – 1.16 (m, 3H), 1.04 (d, *J* = 7.2 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.75, 156.53, 150.97, 130.23, 129.49, 129.05, 128.97, 125.62, 121.65, 114.59, 114.40, 113.44, 103.90, 92.48, 55.64, 18.09, 12.77.

HRMS (ESI-TOF) calcd for $C_{27}H_{37}NO_5SSi$ ([M+Na^+]) = 538.2054, Found 538.2055.

5-bromo-1-((4-methoxyphenyl)sulfonyl)-3-(1-((triisopropylsilyl)oxy)vinyl)-1H-indole (1c)

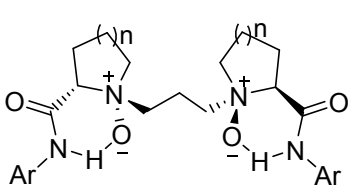


($C_{26}H_{34}BrNO_4SSi$) White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 2H), 7.74 (s, 1H), 7.41 (d, *J* = 8.8 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 2H), 4.76 (s, 1H), 4.56 (s, 1H), 3.80 (s, 3H), 1.34 – 1.23 (m, 3H), 1.12 (d, *J* = 7.2 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.01, 150.32, 134.20, 129.60, 129.18, 129.13, 127.52, 125.85, 123.96, 120.98, 117.19, 115.14, 114.57, 92.82, 55.69, 18.07, 12.75.

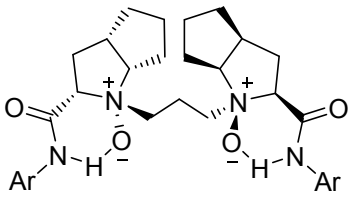
HRMS (ESI-TOF) calcd for $C_{26}H_{34}Br^{78.9183}NO_4SSi$ ([M+Na^+]) = 586.1053, Found 586.1054. HRMS (ESI-TOF) calcd for $C_{26}H_{34}Br^{80.9163}NO_4SSi$ ([M+Na^+]) = 588.1033, Found 588.1036.

2. General procedure for *N,N′*-dioxide preparation

The *N,N′*-dioxide ligands **L** were synthesized by the same procedure in the literature.[3]

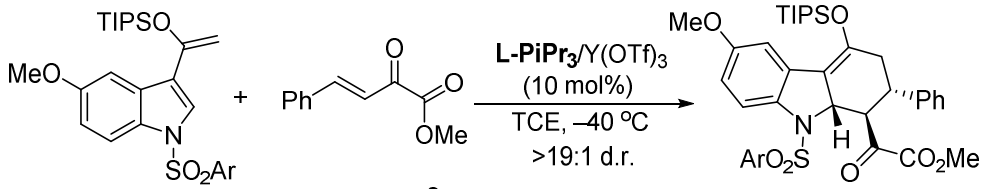


L-PrPr$_2$: Ar = 2,6-*i*Pr$_2$C$_6$H$_3$, n = 1
L-PiPr$_2$: Ar = 2,6-*i*Pr$_2$C$_6$H$_3$, n = 2
L-PiEt$_2$: Ar = 2,6-Et$_2$C$_6$H$_3$, n = 2
L-PiPr$_3$: Ar = 2,4,6-*i*Pr$_3$C$_6$H$_2$, n = 2



L-RaPr$_2$: Ar = 2,6-*i*Pr$_2$C$_6$H$_3$

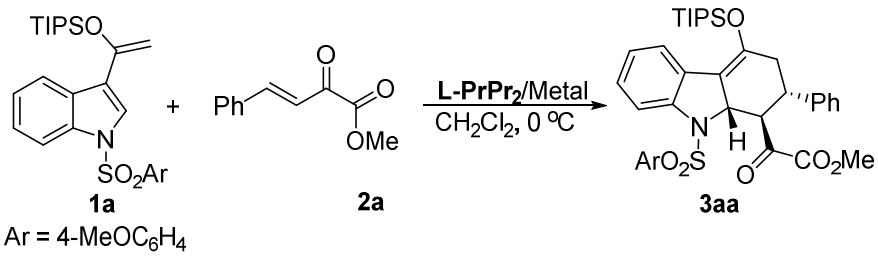
3. Typical procedure for the asymmetric reaction 1b to 2a



$Y(OTf)_3$ (0.01 mmol, 10 mol%), *N,N′*-dioxide ligand **L-PrPr$_3$** (0.01 mmol, 10 mol%), and β,γ-unsaturated α-ketoester **2a** (0.10 mmol) were stirred in $Cl_2CHCHCl_2$ (1.0 mL) at 35 °C for 0.5 h under nitrogen atmosphere. Subsequently, 5-methoxy-1-((4-methoxyphenyl)sulfonyl)-3-(1-((triisopropylsilyl)oxy)vinyl)-1H-indole **1b** (0.12 mmol) was added at −40 °C. The reaction was stirred at −40 °C for 96 h, and then directly purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1) to afford the desired product **3ba** (98% yield, 92% *ee* and >19:1 d.r.).

4. Optimization of the reaction conditions.

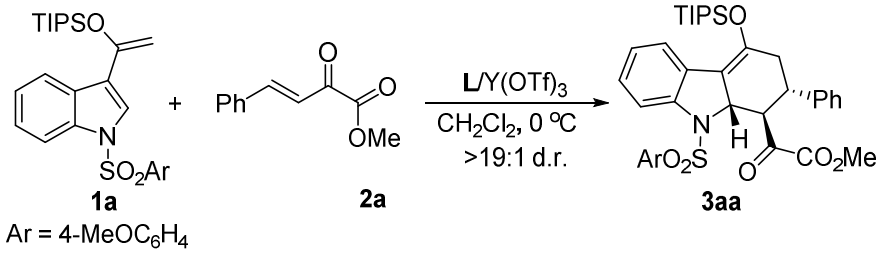
4.1 Screening of the metal salts[a]



Entry[a]	Ligand	Metal salt	Yield [%][b]	d.r.[c]	ee of **3aa**[%][c]
1	**L-PrPr$_2$**	$Fe(acac)_3$	trace	>95:5	19 (–)
2	**L-PrPr$_2$**	$Co(BF_4)_2$•$6H_2O$	11	>95:5	37 (–)
3	**L-PrPr$_2$**	$Ni(OTf)_2$	6	>95:5	30 (–)
4	**L-PrPr$_2$**	$Cu(OTf)_2$	trace	>95:5	19 (–)
5	**L-PrPr$_2$**	$Zn(OTf)_2$	trace	>95:5	42 (–)
6	**L-PrPr$_2$**	$Mg(OTf)_2$	trace	>95:5	7(–)
7	**L-PrPr$_2$**	$Y(OTf)_3$	95	>95:5	65
8	**L-PrPr$_2$**	$La(OTf)_3$	89	>95:5	12 (–)
9	**L-PrPr$_2$**	$Yb(OTf)_3$	95	>95:5	56
10	**L-PrPr$_2$**	$Er(OTf)_3$	90	>95:5	60

[a] Reaction conditions: metal salt/**L-PrPr$_2$** (1:1, 10 mol%), **1a** (0.12 mmol), **2a** (0.10 mmol) in CH_2Cl_2 (1.0 mL) at 0 °C for 4 h, and the products were purified by silica gel column chromatography. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

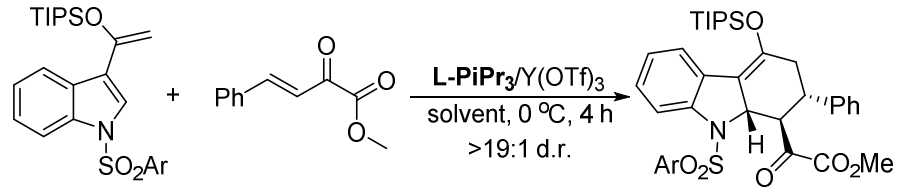
4.2 Screening of the Ligands[a]



Entry[a]	**L**	Yield [%][b]	ee of **3aa**[%][c]
1	**L-PrPr$_2$**	95	65
2	**L-PiPr$_2$**	95	82
3	**L-RaPr$_2$**	93	78
4	**L-PiPr$_3$**	93	85
5	**L-PiEt$_2$**	94	6 (–)
6	**L-PiMe$_2$**	87	45 (–)

[a] Reaction conditions: $Y(OTf)_3$/**L** (1:1, 10 mol%), **1a** (0.12 mmol), **2a** (0.10 mmol) in CH_2Cl_2 (1.0 mL) at 0 °C for 4 h, and the products were purified by silica gel column chromatography.[b] Isolated yield. [c] Determined by chiral HPLC analysis.

4.3 Screening of the solvents[a]

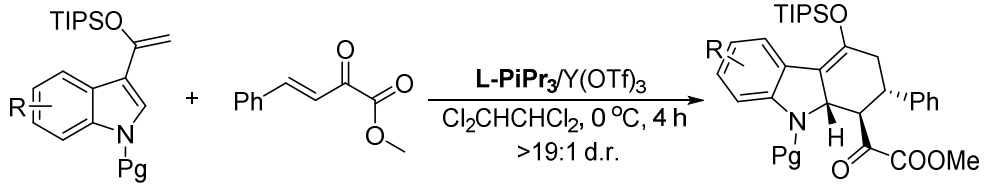


1a Ar = 4-$MeOC_6H_4$ **2a** **3aa**

Entry[a]	solvent	Yield [%][b]	ee of **3aa**[%][c]
1	CH_2Cl_2	93	85
2	$ClCH_2CH_2Cl$	81	82
3	$CHCl_3$	43	85
4	$ClCH_2CHCl_2$	61	84
5	CH_3CCl_3	Trace	---
6	$Cl_2CHCHCl_2$	80	87
7	Toluene	<5	12
8	THF	6	55
9	EtOAc	6	18
10	CH_3CN	10	0

[a] Reaction conditions: $Y(OTf)_3$/**L-PiPr$_3$** (1:1, 10 mol%), **1a** (0.12 mmol), **2a** (0.10 mmol) in solvent (1.0 mL) at 0 °C for 4 h, and the products were purified by silica gel column chromatography. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

4.4 Screening of the electronic nature of substrate **1**[a]

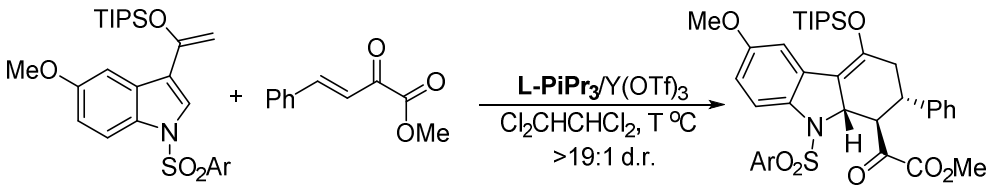


1 **2a** **3**

Entry[a]	R	Pg	Yield [%][b]	ee of **3** [%][c]
1	H	4-$MeOC_6H_4SO_2$	80	87
2	H	3,4-$(MeO)_2C_6H_3SO_2$	94	77
3	5-MeO	4-$MeOC_6H_4SO_2$	96	87

[a] Reaction conditions: $Y(OTf)_3$/**L-PiPr$_3$** (1:1, 10 mol%), **1** (0.12 mmol), **2a** (0.10 mmol) in $Cl_2CHCHCl_2$ (1.0 mL) at 0 °C for 4 h, and the products were purified by silica gel column chromatography. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

4.5 Screening of the reaction tepmerature [a]

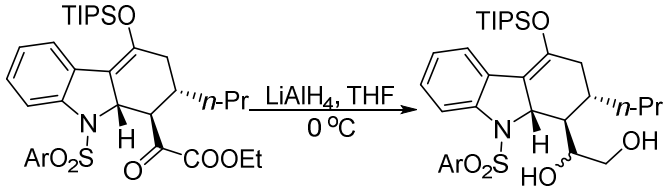


1b Ar = 4-$MeOC_6H_4$ **2a** **3ba**

Entry[a]	T °C	t (h)	Yield [%][b]	ee of **3ba**[%][c]
1	0	4	96	87
2	−30.	17	85	90
3	−40	17	63	92
4	−40	96	98	92

[a] Reaction conditions: $Y(OTf)_3$/**L-PiPr$_3$** (1:1, 10 mol%), **1b** (0.12 mmol), **2a** (0.10 mmol) in $Cl_2CHCHCl_2$ (1.0 mL) at T °C, and the products were purified by silica gel column chromatography. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

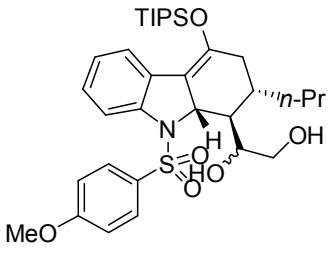
5. The transformation of the product 3au



3au (Ar = 4-$MeOC_6H_4$-) **4au**

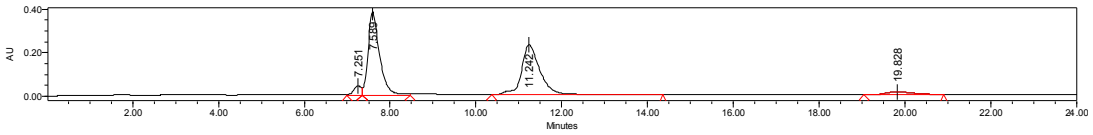
Lithium aluminum hydride (30.0 mg, 6 equiv) was added to **3au** (85.5 mg, 0.13 mmol) inTHF (3.5 mL) at 0 ºC. Then, the mixture was stirred for 2.5 h at room temperature. Subquently, the reaction was quenched with saturated NH_4Cl(*aq*). The aqueous layer was extracted with CH_2Cl_2 three times. The organic phases were dried over Na_2SO_4 and the solvents evaporated. The residue was purified by flash chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 2/1) to afford the desired product **4au** as a white foam (46% yield, 98% ee, >19:1 d.r.).

1-((1R,2S,9aS)-9-((4-methoxyphenyl)sulfonyl)-2-propyl-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)ethane-1,2-diol (4au)

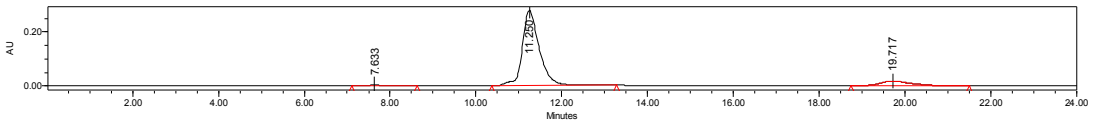


4au: ($C_{33}H_{49}NO_6SSi$) white foam, 46% yield, 98% ee, 9:1 d.r. by ^1H NMR, HPLC DAICEL CHIRALCEL AD-H, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.63 min, 11.25 min, 19.72 min.

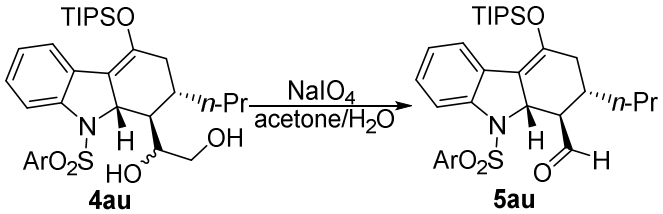
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.36 – 7.28 (m, 2H), 7.20 – 7.07 (m, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 4.26 (d, *J* = 10 Hz, 1H), 4.22 (d, *J* = 10.4 Hz, 1H), 3.98 (t, *J* = 8.8 Hz, 1H), 3.81 – 3.72 (m, 4H), 3.68 (d, *J* = 10.0 Hz, 1H), 2.29 (dd, *J* = 15.2, 7.6 Hz, 2H), 2.08 (d, *J* = 15.6 Hz, 1H), 1.07 – 1.88 (m, 1H), 1.34 – 1.21 (m, 4H), 1.19 – 1.11 (m, 4H), 0.98 (t, *J* = 7.6 Hz, 18H), 0.85 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.49, 145.92, 141.79, 130.83, 129.67, 126.34, 126.26, 126.18, 123.02, 120.04, 114.07, 113.87, 74.88, 66.06, 64.01, 55.41, 50.06, 39.01, 35.08, 34.99, 20.44, 17.67, 17.56, 14.02, 13.18. HRMS (ESI-TOF) calcd for $C_{33}H_{49}NO_6SSi$ ([M+Na^+]) = 638.2942, Found 638.2946.



	Retention Time	Area	% Area
1	7.251	537564	3.50
2	7.589	7110471	46.26
3	11.242	7126889	46.36
4	19.828	597403	3.89



	Retention Time	Area	% Area
1	7.633	58987	0.69
2	11.250	7726596	90.39
3	19.717	762756	8.92

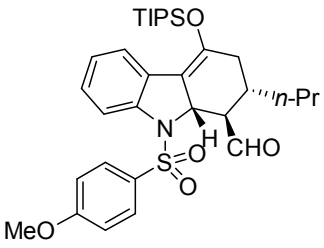


The compound **4au** (35.7 mg, 0.058 mmol) was stirred in acetone/H_2O (3 mL, 1:1, v:v), then $NaIO_4$ (50 mg, 4 equiv) was added slowly to the mixture at room temperature, and the mixture was stirred for 3 h at room temperature, After the aqueous layer was extracted with CH_2Cl_2 and solvent evaporation, the residue was purified by flash chromatography (SiO_2, eluent: petroleum ether/ethyl acetate = 5/1) to afford the desired product **5au** as a white foam (86 yield, 98% ee, >19:1 d.r.)

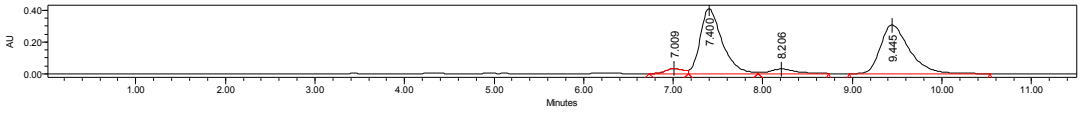
(1R,2S,9aS)-9-((4-methoxyphenyl)sulfonyl)-2-propyl-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazole-1-carbaldehyde (5au)

5au: ($C_{32}H_{45}NO_5SSi$) white foam, 86% yield, 98% ee, >19:1 d.r. by HNMR, $[\alpha]_D^{27.2}$ = +274.8 (c = 0.44, CH_2Cl_2). HPLC DAICEL CHIRALCEL AD-H, *n*-hexane/2-propanol = 90/10, flow rate = 1.0 mL/min,

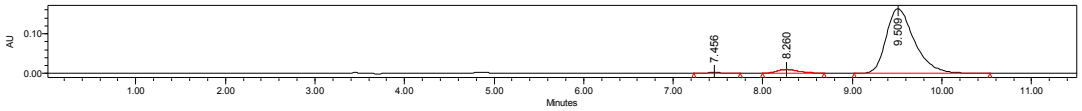
λ = 254 nm, retention time: 7.46 min, 8.26 min, 9.51 min.



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (d, *J* = 2.4 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 3H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.79 (d, *J* = 8.0 Hz, 1H), 3.79 (s, 3H), 2.77 (t, *J* = 5.2 Hz, 1H), 2.41 (dd, *J* = 16.0, 6.0 Hz, 1H), 2.24 – 1.99 (m, 2H), 1.47 – 1.34 (m, 2H), 1.33 – 1.25 (m, 2H), 1.24 – 1.14 (m, 3H), 1.07 (d, *J* = 7.2 Hz, 18H), 0.89 (t, *J* = 6.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.95, 163.48, 144.34, 141.94, 130.06, 128.74, 127.74, 126.96, 124.25, 123.42, 115.93, 114.09, 111.25, 62.69, 57.56, 55.51, 55.49, 36.95, 34.99, 32.95, 19.96, 17.89, 13.90, 13.51. HRMS (ESI-TOF) calcd for $C_{32}H_{45}NO_5SSi$ ([M+Na$^+$]) = 606.2680, Found 606.2683.



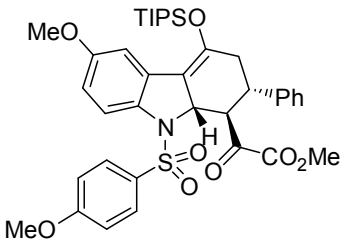
	Retention Time	Area	% Area
1	7.009	433585	2.95
2	7.400	6903947	47.03
3	8.206	541557	3.69
4	9.445	6799995	46.32



	Retention Time	Area	% Area
1	7.456	23915	0.63
2	8.260	167657	4.43
3	9.509	3590135	94.93

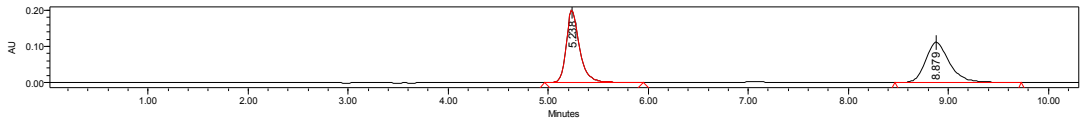
6. The analytical and spectral characterization data of the reaction products 3

Methyl 2-((1R,2S,9aS)-6-methoxy-9-((4-methoxyphenyl)sulfonyl)-2-phenyl-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3ba)

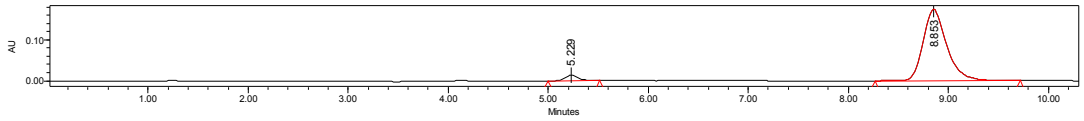


($C_{38}H_{47}NO_8SSi$**)** white foam, 98% yield, 92% *ee*. $[\alpha]_D^{16.9}$ = +108.9 (c = 1.09, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.23 min, 8.85 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.30 – 7.02 (m, 7H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.63 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.79 (d, *J* = 9.2 Hz, 1H), 4.26 (t, *J* = 9.6 Hz, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 3.61 (s, 3H), 3.36 – 3.17 (m, 1H), 2.69 – 2.44 (m, 2H), 1.11 – 1.03 (m, 3H), 0.97 (dd, *J* = 7.2, 4.4 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.18, 163.59, 160.14, 156.61, 144.63, 140.39, 135.64, 130.29, 129.69, 128.82, 128.41, 127.50, 126.56, 116.12, 114.15, 113.38, 111.23, 108.76, 65.77, 55.53, 55.49, 52.90, 51.47, 44.32, 38.58, 17.90, 13.65. HRMS (ESI-TOF) calcd for $C_{38}H_{47}NO_8SSi$ ([M+Na$^+$]) = 728.2684, Found 728.2689.

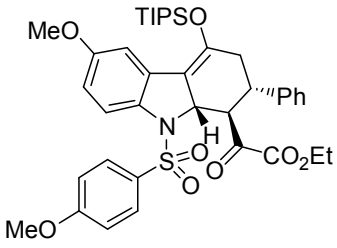


	Retention Time	Area	% Area
1	5.238	1873081	50.51
2	8.879	1835299	49.49



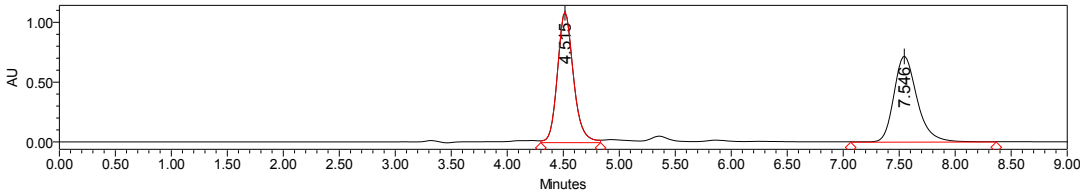
	Retention Time	Area	% Area
1	5.229	120947	4.06
2	8.853	2858371	95.94

Ethyl 2-((1R,2S,9aS)-6-methoxy-9-((4-methoxyphenyl)sulfonyl)-2-phenyl-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3bb)

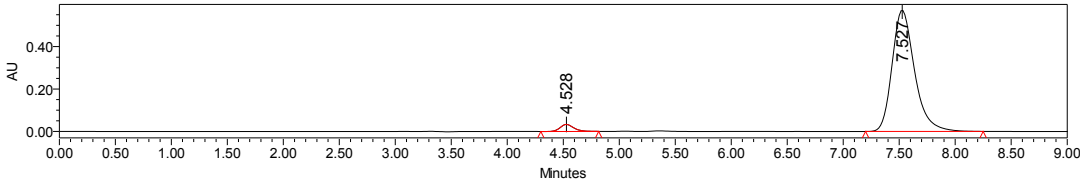


($C_{39}H_{49}NO_8SSi$) white foam, 98% yield, 93% *ee*, $[\alpha]_D^{14.6}$ = +110.8 (c = 1.16, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 4.53 min, 7.53 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 9.2 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.23 – 7.12 (m, 4H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.71 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.88 (d, *J* = 8.8 Hz, 1H), 4.34 (t, *J* = 9.2 Hz, 1H), 4.25 – 4.05 (m, 2H), 3.80 (s, 3H), 3.76 (s, 3H), 3.37 (dd, *J* = 17.2, 9.6 Hz, 1H), 2.70 – 2.56 (m, 2H), 1.22 – 1.12 (m, 6H), 1.04 (dd, *J* = 7.2, 3.6 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.54, 163.56, 159.55, 156.58, 144.60, 140.44, 135.70, 130.30, 129.69, 128.81, 128.49, 127.45, 126.65, 116.10, 114.12, 113.37, 111.26, 108.76, 65.75, 62.24, 55.53, 55.50, 51.39, 44.34, 38.54, 17.90, 13.91, 13.66. HRMS (ESI-TOF) calcd for $C_{39}H_{49}NO_8SSi$ ([M+Na$^+$]) = 742.2840, Found 742.2838.



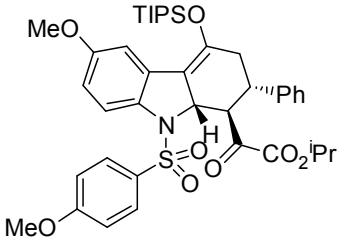
	Retention Time	Area	% Area
1	4.515	10852977	51.02
2	7.546	10421053	48.98



	Retention Time	Area	% Area

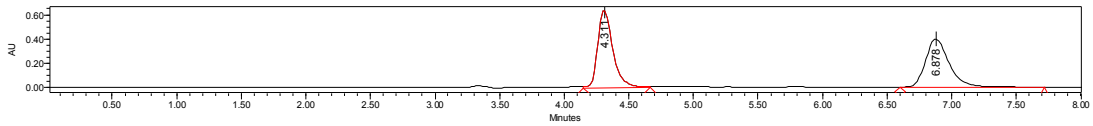
1	4.528	272730	3.32
2	7.527	7952343	96.68

Isopropyl 2-((1R,2S,9aS)-6-methoxy-9-((4-methoxyphenyl)sulfonyl)-2-phenyl-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3bc)

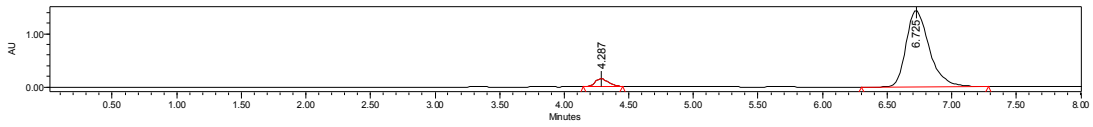


(**$C_{40}H_{51}NO_8SSi$**) white foam, 95% yield, 89% *ee*. $[\alpha]_D^{14.7}$ = +108.2 (c = 1.12, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 4.29 min, 6.72 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 9.2 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.22 – 7.14 (m, 4H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.71 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.00 – 4.91 (m, 1H), 4.87 (d, *J* = 8.8 Hz, 1H), 4.34 (t, *J* = 8.8 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.49 – 3.29 (m, 1H), 2.73 – 2.52 (m, 2H), 1.23 (d, *J* = 6.0 Hz, 3H), 1.18 – 1.12 (m, 6H), 1.04 (dd, *J* = 7.2, 3.2 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.78, 163.53, 158.98, 156.56, 144.57, 140.54, 135.75, 130.32, 129.69, 128.81, 128.51, 127.40, 126.73, 116.09, 114.10, 113.36, 111.28, 108.74, 70.24, 65.76, 55.52, 55.49, 51.27, 44.32, 38.51, 21.43, 17.90, 13.66. HRMS (ESI-TOF) calcd for $C_{40}H_{51}NO_8SSi$ ([M+Na$^+$]) = 756.2997, Found 756.2999.

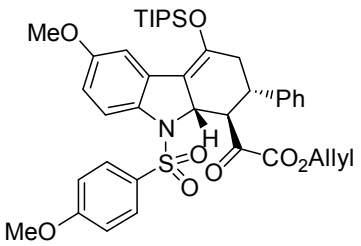


	Retention Time	Area	% Area
1	4.311	5206683	50.81
2	6.878	5040626	49.19



	Retention Time	Area	% Area
1	4.287	1048416	5.57
2	6.725	17762414	94.43

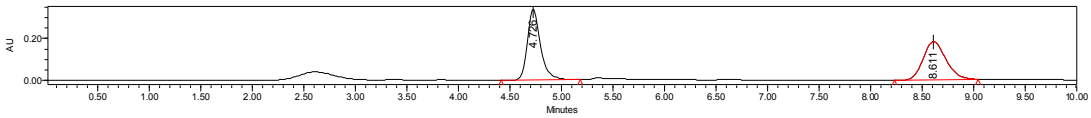
Allyl 2-((1R,2S,9aS)-6-methoxy-9-((4-methoxyphenyl)sulfonyl)-2-phenyl-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3bd)



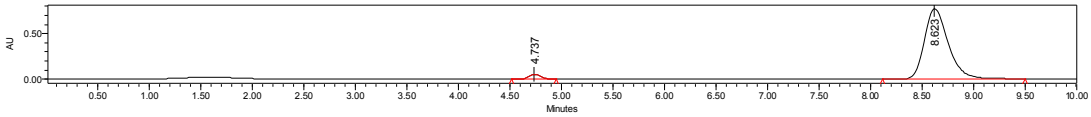
(**$C_{40}H_{49}NO_8SSi$**) white foam, 95% yield, 93% *ee*, $[\alpha]_D^{22.1}$ = +110.4 (c = 1.09, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 4.74 min, 8.62 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.8 Hz, 1H), 7.58 – 7.48 (m, 2H), 7.22 – 7.16 (m, 2H), 7.15 – 7.07 (m, 4H), 6.81 (d, *J* = 9.2 Hz, 2H), 6.63 (dd, *J* = 8.8, 2.8 Hz, 1H), 5.86 – 5.60 (m, 1H), 5.23 – 5.02 (m, 2H), 4.80 (d, *J* = 8.8 Hz, 1H), 4.58 – 4.42 (m, 2H), 4.27 (t, *J* = 9.6 Hz, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 3.40 – 3.22 (m, 1H), 2.64 – 2.46 (m, 2H), 1.01 – 1.03 (m, 3H), 0.97 (dd, *J* = 7.2, 4.0 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.17, 163.57, 159.22, 156.58, 144.60, 140.35, 135.68, 131.08, 130.31, 129.67, 128.85, 128.48, 127.48, 126.62, 118.96, 116.09, 114.13, 113.38, 111.23, 108.77, 66.63, 65.76,

55.53, 55.49, 51.41, 44.37, 38.57, 17.90, 13.66. HRMS (ESI-TOF) calcd for $C_{40}H_{49}NO_8SSi$ ([M+Na$^+$]) = 754.2840, Found 754.2844.

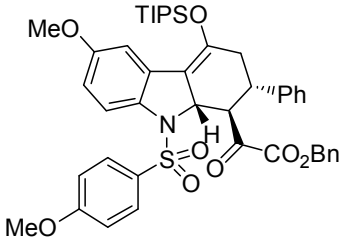


	Retention Time	Area	% Area
1	4.726	2963981	51.69
2	8.611	2769983	48.31



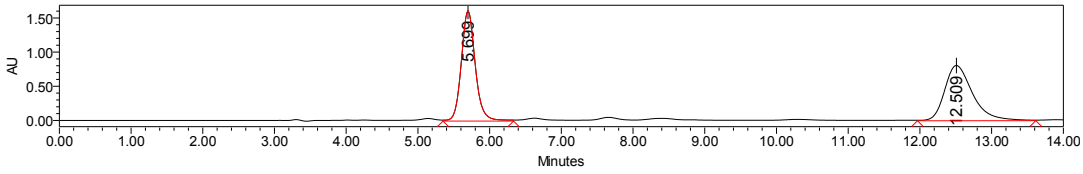
	Retention Time	Area	% Area
1	4.737	440545	3.40
2	8.623	12499368	96.60

Benzyl 2-((1R,2S,9aS)-6-methoxy-9-((4-methoxyphenyl)sulfonyl)-2-phenyl-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3be)

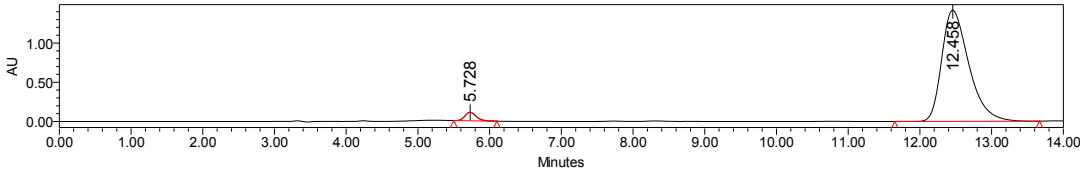


($C_{44}H_{51}NO_8SSi$) white foam, 92% yield, 94% *ee*, $[\alpha]_D^{17.3}$ = +92.2 (c = 0.51, CH_2Cl_2); HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.73 min, 12.46 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.38 – 7.05 (m, 12H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.71 (dd, *J* = 8.8, 2.0 Hz, 1H), 5.13 (q, *J* = 12.4 Hz, 2H), 4.89 (d, *J* = 8.4 Hz, 1H), 4.33 (t, *J* = 8.4 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.46 – 3.27 (m, 1H), 2.70 – 2.49 (m, 2H), 1.18 – 1.09 (m, 3H), 1.03 (d, *J* = 4.8 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.01, 163.58, 159.37, 156.63, 144.60, 140.38, 135.71, 134.93, 130.32, 129.69, 128.81, 128.47, 128.38, 128.29, 128.25, 127.43, 126.66, 116.12, 114.15, 113.40, 111.28, 108.80, 67.68, 65.76, 55.52, 51.74, 44.25, 38.60, 17.91, 13.66. HRMS (ESI-TOF) calcd for $C_{44}H_{51}NO_8SSi$ ([M+Na$^+$]) = 804.2997, Found 804.2997.



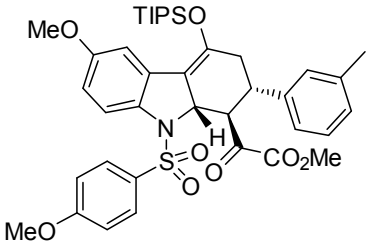
	Retention Time	Area	% Area
1	5.699	21937258	50.08
2	12.509	21865253	49.92



	Retention Time	Area	% Area

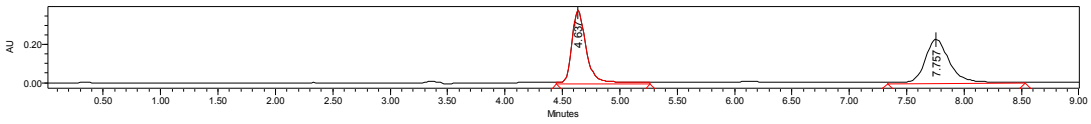
1	5.728	1194497	3.11
2	12.458	37163786	96.89

Methyl 2-((1R,2S,9aS)-6-methoxy-9-((4-methoxyphenyl)sulfonyl)-2-(m-tolyl)-4-((triisopropylsilyl) oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3bf)

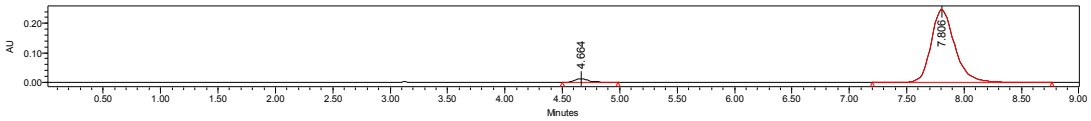


($C_{39}H_{49}NO_8SSi$) white foam, 98% yield, 94% *ee*. $[\alpha]_D^{18.9}$ = +112.3 (c = 1.32, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 4.66 min, 7.81 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.13 – 7.04 (m, 2H), 6.97 – 6.87 (m, 3H), 6.81 (d, *J* = 9.2 Hz, 2H), 6.63 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.78 (d, *J* = 9.2 Hz, 1H), 4.23 (t, *J* = 9.6 Hz, 1H), 3.73 (s, 3H), 3.68 (s, 3H), 3.62 (s, 3H), 3.33 – 3.19 (m, 1H), 2.62 – 2.47 (m, 2H), 2.21 (s, 3H), 1.12 – 1.04 (m, 3H), 0.97 (dd, *J* = 7.2, 4.4 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.21, 163.58, 160.12, 156.60, 144.74, 140.32, 138.41, 135.65, 130.29, 129.73, 129.32, 128.72, 128.19, 126.56, 125.19, 116.13, 114.13, 113.36, 111.24, 108.73, 65.82, 55.53, 55.29, 52.87, 51.53, 44.24, 38.62, 21.40, 17.90, 13.66. HRMS (ESI-TOF) calcd for $C_{39}H_{49}NO_8SSi$ ([M+Na$^+$]) = 742.2840, Found 742.2839.

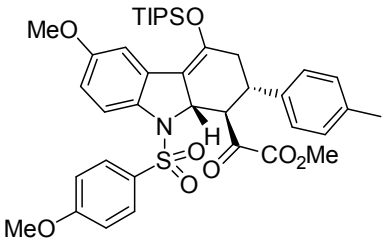


	Retention Time	Area	% Area
1	4.637	3575790	49.30
2	7.757	3676895	50.70



	Retention Time	Area	% Area
1	4.664	107380	2.96
2	7.806	3516010	97.04

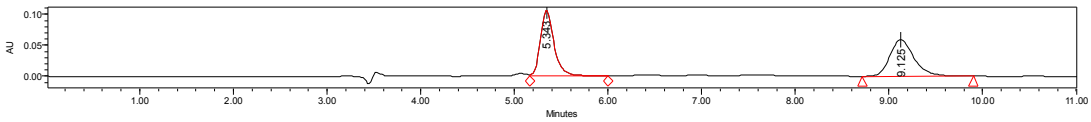
Methyl 2-((1R,2S,9aS)-6-methoxy-9-((4-methoxyphenyl)sulfonyl)-2-(p-tolyl)-4-((triisopropylsilyl) oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3bg)



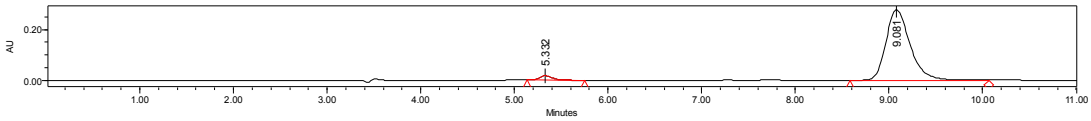
($C_{39}H_{49}NO_8SSi$) white foam, 94% yield, 93% *ee*. $[\alpha]_D^{17.0}$ = +122.8 (c = 1.14, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.33 min, 9.08 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.8 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 2.6 Hz, 1H), 7.10 – 7.03 (m, 4H), 6.89 (d, *J* = 9.2 Hz, 2H), 6.70 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.87 (d, *J* = 8.8 Hz, 1H), 4.29 (t, *J* = 9.6 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.69 (s, 3H), 3.47 – 3.28 (m, 1H), 2.73 – 2.52 (m, 2H), 2.29 (s, 3H), 1.19 – 1.11 (m, 3H), 1.08 – 0.99 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.18, 163.57, 160.12, 156.59, 144.76, 137.24, 137.13, 135.65, 130.31, 129.74, 129.48,

128.27, 126.57, 116.12, 114.13, 113.35, 111.21, 108.76, 65.85, 55.53, 55.49, 52.88, 51.60, 43.95, 38.73, 21.05, 17.91, 13.67. HRMS (ESI-TOF) calcd for $C_{39}H_{49}NO_8SSi$ ([M+Na) = 742.2840, Found 742.2841

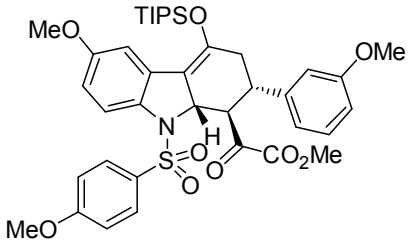


	Retention Time	Area	% Area
1	5.343	1096977	50.91
2	9.125	1057887	49.09



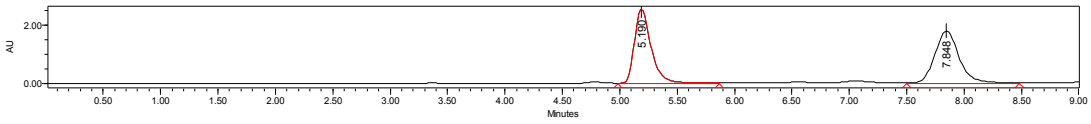
	Retention Time	Area	% Area
1	5.332	168867	3.30
2	9.081	4951275	96.70

Methyl 2-((1R,2S,9aS)-6-methoxy-2-(3-methoxyphenyl)-9-((4-methoxyphenyl)sulfonyl)-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3bh)

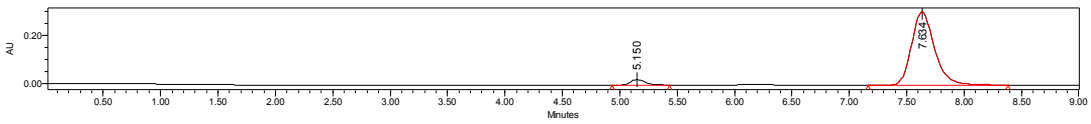


($C_{39}H_{49}NO_9SSi$) white foam, 96% yield, 90% *ee*. $[\alpha]_D^{17.2}$ = +115.6 (c = 1.35, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.15 min, 7.63 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.73 – 6.58 (m, 4H), 4.78 (d, *J* = 8.8 Hz, 1H), 4.25 (t, *J* = 9.6 Hz, 1H), 3.73 (s, 3H), 3.68 (s, 3H), 3.66 (s, 3H), 3.65 (s, 3H), 3.37 – 3.21 (m, 1H), 2.65 – 2.43 (m, 2H), 1.10 – 1.03 (m, 3H), 0.96 (dd, *J* = 7.2, 2.8 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.03, 163.59, 160.22, 159.76, 156.63, 144.58, 142.19, 135.59, 130.29, 129.85, 129.71, 126.51, 120.49, 116.16, 114.15, 113.69, 113.40, 113.20, 111.26, 108.69, 65.66, 55.53, 55.49, 55.13, 52.96, 51.55, 44.06, 38.58, 17.89, 13.64. HRMS (ESI-TOF) calcd for $C_{39}H_{49}NO_9SSi$ ([M+Na^+]) = 758.2790, Found 758.2789.



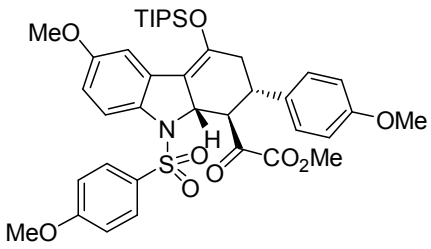
	Retention Time	Area	% Area
1	5.190	26305030	49.75
2	7.848	26564176	50.25



	Retention Time	Area	% Area
1	5.150	206508	4.71

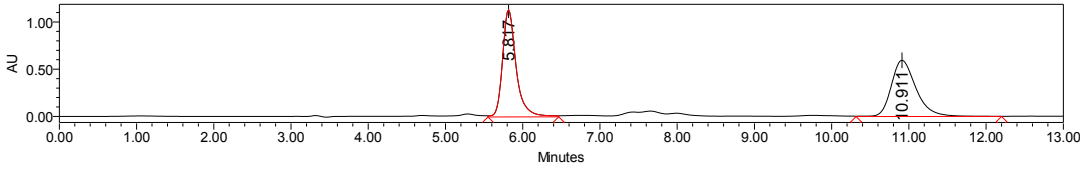
2	7.634	4178101	95.29

Methyl 2-((1R,2S,9aS)-6-methoxy-2-(4-methoxyphenyl)-9-((4-methoxyphenyl)sulfonyl)-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3bi)

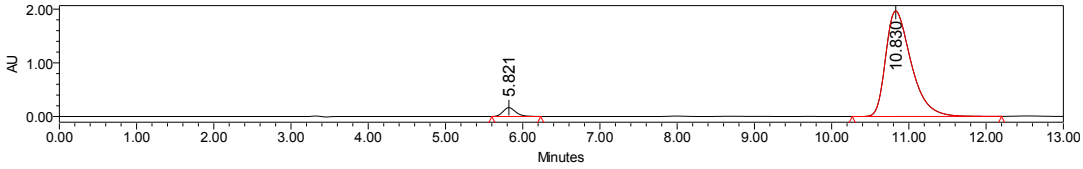


($C_{39}H_{49}NO_9SSi$) white foam, 97% yield, 92% *ee*. $[\alpha]_D^{17.4}$ = +109.6 (c = 1.17, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.82 min, 10.83 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 9.2 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.18 (d, *J* = 2.8 Hz, 1H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.70 (dd, *J* = 9.2, 2.4 Hz, 1H), 4.87 (d, *J* = 9.2 Hz, 1H), 4.29 (t, *J* = 9.6 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 6H), 3.71 (s, 3H), 3.41 – 3.27 (m, 1H), 2.66 – 2.52 (m, 2H), 1.19 – 1.11 (m, 3H), 1.08 – 1.01 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.27, 163.57, 160.11, 158.79, 156.58, 144.75, 135.65, 132.19, 130.30, 129.71, 129.49, 126.57, 116.07, 114.14, 113.34, 111.18, 108.78, 65.79, 55.53,55.49, 55.24, 52.91, 51.67, 43.58, 38.86, 17.91, 13.66. HRMS (ESI-TOF) calcd for $C_{39}H_{49}NO_9SSi$ ([M+Na$^+$]) = 758.2790, Found 758.2790.

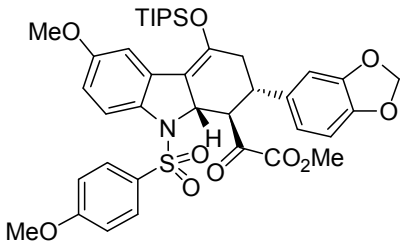


	Retention Time	Area	% Area
1	5.817	13897359	51.18
2	10.911	13255068	48.82



	Retention Time	Area	% Area
1	5.821	1878082	4.01
2	10.830	44947860	95.99

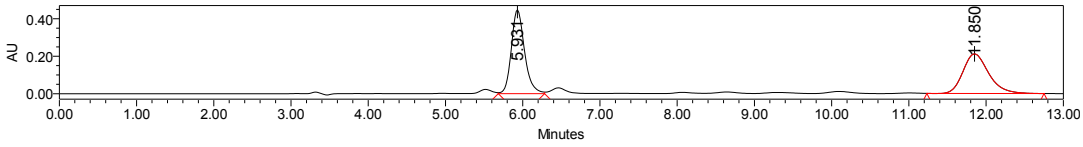
Methyl 2-((1R,2S,9aS)-2-(benzo[d][1,3]dioxol-5-yl)-6-methoxy-9-((4-methoxyphenyl)sulfonyl)-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3bj)



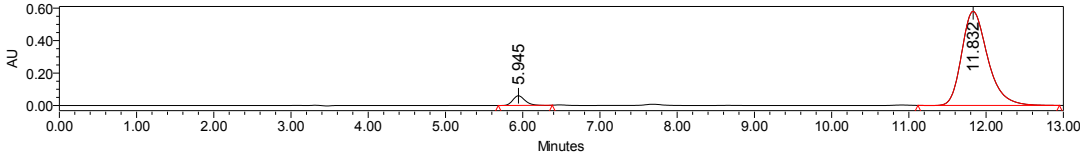
($C_{39}H_{47}NO_{10}SSi$) white foam, 97% yield, 91% *ee*. $[\alpha]_D^{14.3}$ = +119.4 (c = 1.25, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.94 min, 11.83 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 9.2 Hz, 2H), 7.17 (d, *J* = 2.8 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.74 – 6.65 (m, 3H), 6.62 (d, *J* = 8.0 Hz, 1H), 5.92 (s, 2H), 4.85 (d, *J* = 8.8 Hz, 1H), 4.24 (d, *J* = 9.6 Hz, 1H), 3.80 (s, 3H), 3.76 (d, *J* = 4.0 Hz, 6H), 3.44 – 3.25 (m, 1H), 2.73 – 2.41 (m, 2H), 1.20 – 1.12 (m, 3H), 1.05 (dd, *J* = 7.2, 4.0 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.95, 163.59, 160.17, 156.63, 147.90, 146.81, 144.57, 135.60, 134.26, 130.30, 129.68,

126.48, 121.66, 116.20, 114.14, 113.39, 111.28, 108.73, 108.49, 108.44, 101.10, 65.81, 55.53, 55.49, 53.00, 51.89, 43.87, 38.98, 17.91, 13.66. HRMS (ESI-TOF) calcd for $C_{39}H_{47}NO_{10}SSi$ ([M+Na$^+$]) = 772.2582, Found: 772.2595.

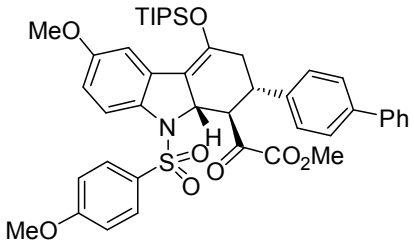


	Retention Time	Area	% Area
1	5.931	5321715	52.17
2	11.850	4878284	47.83



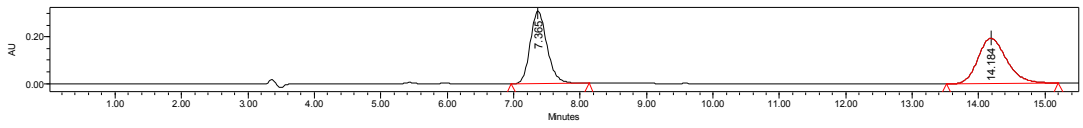
	Retention Time	Area	% Area
1	5.945	653906	4.60
2	11.832	13547884	95.40

Methyl 2-((1R,2S,9aS)-2-([1,1'-biphenyl]-4-yl)-6-methoxy-9-((4-methoxyphenyl)sulfonyl)-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3bk)

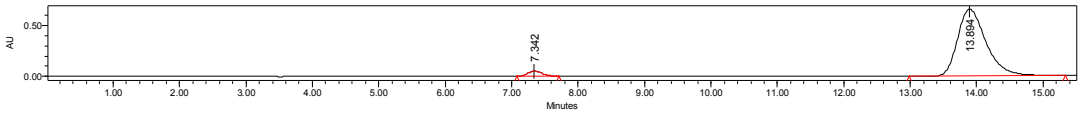


($C_{44}H_{51}NO_8SSi$) white foam, 94% yield, 92% *ee*. $[\alpha]_D^{17.4}$ = +146.5 (c = 1.34, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 7.34 min, 13.89 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 9.2 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 2.4 Hz, 1H), 6.90 (d, *J* = 9.2 Hz, 2H), 6.72 (dd, *J* = 9.2, 2.8 Hz, 1H), 4.89 (d, *J* = 8.8 Hz, 1H), 4.37 (t, *J* = 9.6 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.69 (s, 3H), 3.52 – 3.33 (m, 1H), 2.79 – 2.55 (m, 2H), 1.20 – 1.12 (m, 3H), 1.05 (dd, *J* = 7.2, 2.8 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.22, 163.61, 160.24, 156.65, 144.57, 140.47, 140.31, 139.57, 135.64, 130.31, 129.70, 128.82, 127.48, 127.41, 126.98, 126.58, 116.15, 114.17, 113.42, 111.29, 108.76, 65.68, 55.55, 55.51, 52.99, 51.61, 43.83, 38.55, 17.92, 13.67. HRMS (ESI-TOF) calcd for $C_{44}H_{51}NO_8SSi$ ([M+Na$^+$]) = 804.2994, Found. 804.3008.

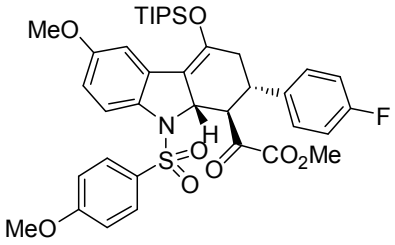


	Retention Time	Area	% Area
1	7.365	5489213	48.42
2	14.184	5847441	51.58



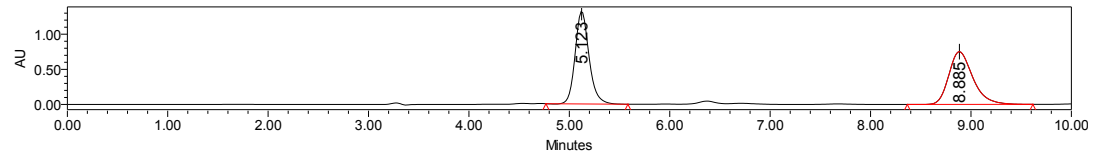
	Retention Time	Area	% Area
1	7.342	812359	3.95
2	13.894	19742909	96.05

Methyl 2-((1R,2S,9aS)-2-(4-fluorophenyl)-6-methoxy-9-((4-methoxyphenyl)sulfonyl)-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3bl)

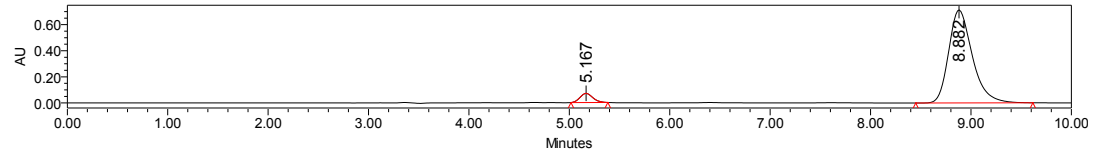


(C$_{38}$H$_{46}$FNO$_8$SSi) white foam, 95% yield, 90% *ee*. $[\alpha]_D^{14.4}$ = +99.7 (c = 1.06, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.17 min, 8.88 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.21 – 7.09 (m, 3H), 6.96 (t, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.71 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.84 (d, *J* = 8.8 Hz, 1H), 4.30 (t, *J* = 9.2 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.73 (s, 3H), 3.46 – 3.28 (m, 1H), 2.74 – 2.33 (m, 2H), 1.18 – 1.09 (m, 3H), 1.04 (d, *J* = 5.6 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.10, 163.62, 163.17, 160.72, 160.24, 156.64, 144.34, 136.39, 136.36, 135.58, 130.27, 129.98, 129.90, 129.57, 126.48, 116.13, 115.82, 115.61, 114.16, 113.45, 111.29, 108.75, 65.60, 55.54, 55.49, 53.05, 51.59, 43.39, 38.73, 17.88, 13.63. HRMS (ESI-TOF) calcd for C$_{38}$H$_{46}$FNO$_8$SSi ([M+Na$^+$]) = 746.2590, Found 746.2588.

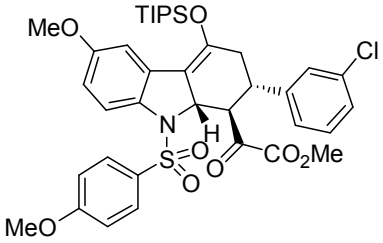


	Retention Time	Area	% Area
1	5.123	12693702	50.50
2	8.885	12441460	49.50



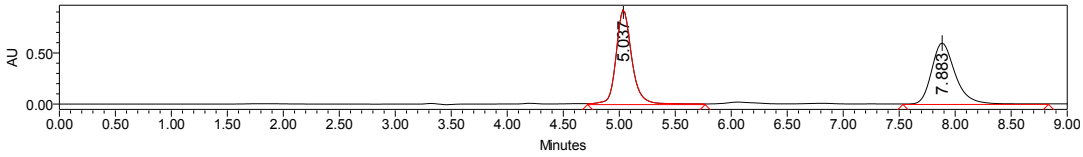
	Retention Time	Area	% Area
1	5.167	616195	5.03
2	8.882	11644344	94.97

Methyl 2-((1R,2S,9aS)-2-(3-chlorophenyl)-6-methoxy-9-((4-methoxyphenyl)sulfonyl)-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3bm)

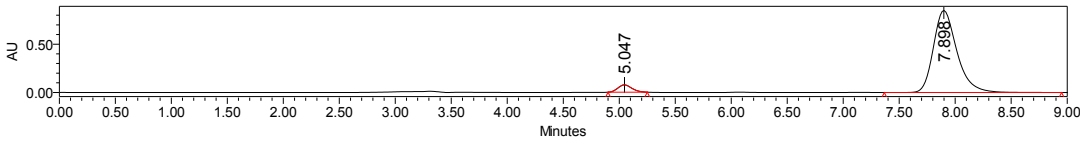


(C$_{38}$H$_{46}$ClNO$_8$SSi) white foam, 84% yield, 90% *ee*, $[\alpha]_D^{14.8}$ = +131.6 (c = 0.87, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.05 min, 7.90 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 9.2 Hz, 2H), 7.23 – 7.11 (m, 4H), 7.10 – 7.02 (m, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.72 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.83 (d, *J* = 8.8 Hz, 1H), 4.29 (t, *J* = 9.2 Hz, 1H), 3.81 (s, 3H), 3.77 (d, *J* = 3.8 Hz, 6H), 3.42 – 3.32 (m, 1H), 2.73 – 2.44 (m, 2H), 1.18 – 1.10 (m, 3H), 1.04 (d, *J* = 6.8 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.86, 163.63, 160.23, 156.69, 144.16, 142.94, 135.55, 134.52, 130.26, 13021, 129.54, 128.61, 127.69, 126.33, 116.23, 114.17, 113.53, 111.45, 108.68, 65.56, 55.55, 55.50, 53.12, 51.57, 43.59, 38.45, 17.88, 17.87, 13.63. HRMS (ESI-TOF) calcd for $C_{38}H_{46}Cl^{34.9689}NO_8SSi$ ([M+Na^+]) = 762.2294, Found. 762.2306. HRMS (ESI-TOF) calcd for $C_{38}H_{46}Cl^{36.9659}NO_8SSi$ ([M+Na^+]) = 764.2265, Found. 764.2293.

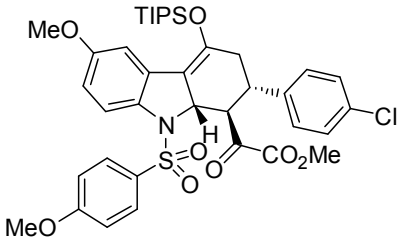


	Retention Time	Area	% Area
1	5.037	9214542	50.71
2	7.883	8955500	49.29



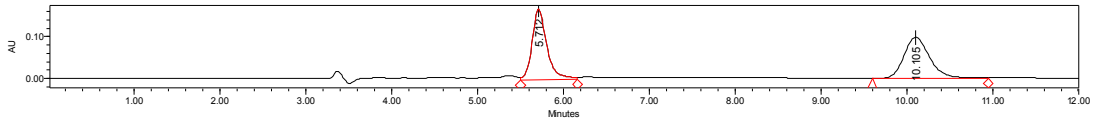
	Retention Time	Area	% Area
1	5.047	659999	5.06
2	7.898	12380951	94.94

Methyl 2-((1R,2S,9aS)-2-(4-chlorophenyl)-6-methoxy-9-((4-methoxyphenyl)sulfonyl)-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3bn)

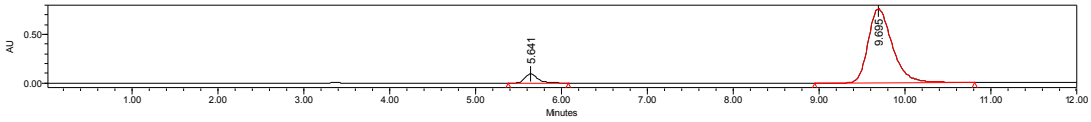


($C_{38}H_{46}ClNO_8SSi$**)** white foam, 85% yield, 87% *ee*, $[\alpha]_D^{18.0}$ = +123.6 (c = 1.07, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.64 min, 9.69 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.8 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 2.8 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.64 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.76 (d, *J* = 9.2 Hz, 1H), 4.22 (t, *J* = 9.2 Hz, 1H), 3.73 (s, 3H), 3.68 (s, 3H), 3.67 (s, 3H), 3.39 – 3.21, 2.63 – 2.36 (m, 2H), 1.08 – 1.01 (m, 3H), 0.96 (d, *J* = 6.4 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.96, 163.63, 160.29, 156.67, 144.22, 139.30, 135.54, 133.26, 130.27, 129.63,129.55, 129.02, 126.42, 116.19, 114.17, 113.49, 111.36, 108.71, 65.57, 55.50, 55.49, 53.10, 51.51, 43.36, 38.58, 17.88, 13.63. HRMS (ESI-TOF) calcd for $C_{38}H_{46}Cl^{34.9689}NO_8SSi$ ([M+Na^+]) = 762.2294, Found 762.2294. HRMS (ESI-TOF) calcd for $C_{38}H_{46}Cl^{36.9659}NO_8SSi$ ([M+Na^+]) = 764.2265, Found 764.2181.

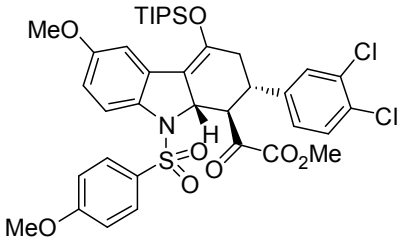


	Retention Time	Area	% Area
1	5.712	2062556	50.06
2	10.105	2057900	49.94



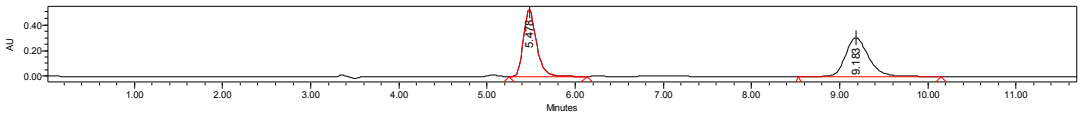
	Retention Time	Area	% Area
1	5.641	990429	6.31
2	9.695	14717479	93.69

Methyl 2-((1R,2S,9aS)-2-(3,4-dichlorophenyl)-6-methoxy-9-((4-methoxyphenyl)sulfonyl)-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3bo)

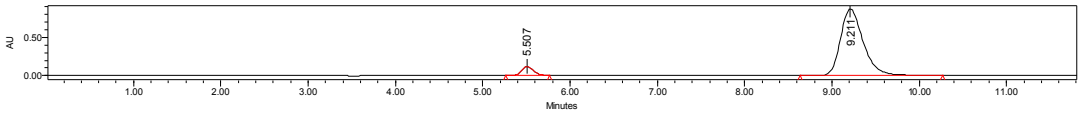


(**$C_{38}H_{45}Cl_2NO_8SSi$**) white foam, 85% yield, 86% *ee*, $[\alpha]_D^{21.4}$ = +126.4 (c = 1.23, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.51 min, 9.21 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 9.2 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.19 (d, *J* = 1.2 Hz, 1H), 7.08 (d, *J* = 2.4 Hz, 1H), 6.95 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.65 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.73 (d, *J* = 8.8 Hz, 1H), 4.18 (t, *J* = 9.2 Hz, 1H), 3.73 (s, 6H), 3.68 (s, 3H), 3.35 – 3.21 (m, 1H), 2.64 – 2.50 (ddd, *J* = 17.2, 6.1, 2.1 mHz, 1H), 2.44 – 2.31 (m, 1H), 1.09 – 1.01 (m, 3H), 0.96 (dd, *J* = 7.2, 1.6 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.72, 163.66, 160.36, 156.75, 143.86, 141.43, 135.48, 132.78, 131.54, 130.90, 130.37, 130.25, 129.44, 127.27, 126.31, 116.29, 114.19, 113.62, 111.58, 108.64, 65.40, 55.55, 55.50, 53.25, 51.64, 42.80, 38.40, 17.86, 17.84, 13.61. HRMS (ESI-TOF) calcd for $C_{38}H_{45}Cl_2^{34.9689}NO_8SSi$ ([M+Na$^+$]) = 796.1904, Found 796.1901. HRMS (ESI-TOF) calcd for $C_{38}H_{45}Cl_2^{36.9659}NO_8SSi$ ([M+Na$^+$]) = 798.1875, Found 798.1787.

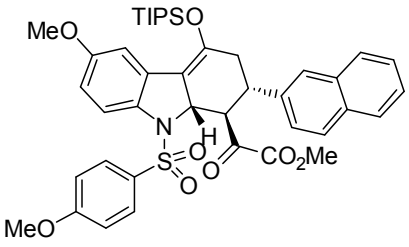


	Retention Time	Area	% Area
1	5.478	5346889	49.04
2	9.183	5556398	50.96



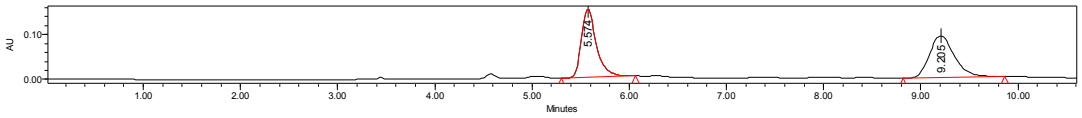
	Retention Time	Area	% Area
1	5.507	1146915	6.81
2	9.211	15689297	93.19

Methyl 2-((1R,2S,9aS)-6-methoxy-9-((4-methoxyphenyl)sulfonyl)-2-(naphthalen-2-yl)-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3bp)

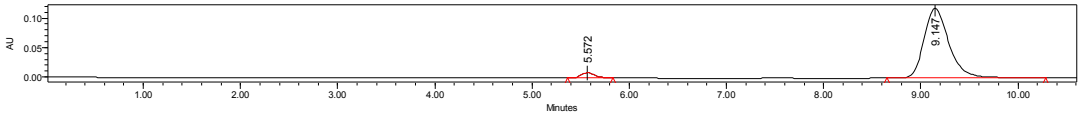


(**$C_{42}H_{49}NO_8SSi$**) white foam, 91% yield, 92% *ee*. $[\alpha]_D^{22.2}$ = +138.2 (c = 1.04, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA,

n-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.57 min, 9.15 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.62 (m, 4H), 7.54 (d, *J* = 8.8 Hz, 3H), 7.42 – 7.33 (m, 2H), 7.27 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.12 (d, *J* = 2.4 Hz, 1H), 6.82 (d, *J* = 9.2 Hz, 2H), 6.65 (dd, *J* = 9.2, 2.8 Hz, 1H), 4.84 (d, *J* = 9.2 Hz, 1H), 4.37 (t, *J* = 9.6 Hz, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 3.57 – 3.46 (m, 1H), 3.49 (s, 3H), 2.72 – 2.54 (m, 2H), 1.09 – 1.02 (m, 3H), 0.95 (dd, *J* = 7.2, 2.4 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.17, 163.57, 159.22, 156.58, 144.60, 140.35, 135.68, 131.08, 130.31, 129.67, 128.85, 128.48, 127.48, 126.62, 118.96, 116.09, 114.13, 113.38, 111.23, 108.77, 66.63, 65.76, 55.53, 55.49, 51.41, 44.37, 38.57, 17.90, 13.66. HRMS (ESI-TOF) calcd for $C_{42}H_{49}NO_8SSi$ ([M+Na$^+$]) = 778.2840, Found 778.2848.

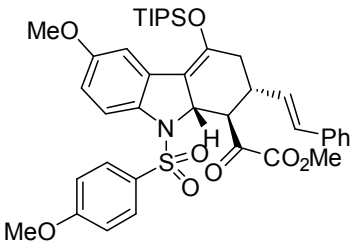


	Retention Time	Area	% Area
1	5.574	1616871	49.42
2	9.205	1655101	50.58



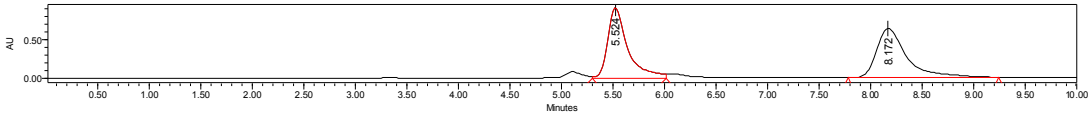
	Retention Time	Area	% Area
1	5.572	87315	4.00
2	9.147	2096511	96.00

Methyl 2-((1R,2R,9aS)-6-methoxy-9-((4-methoxyphenyl)sulfonyl)-2-((E)-styryl)-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3bq)



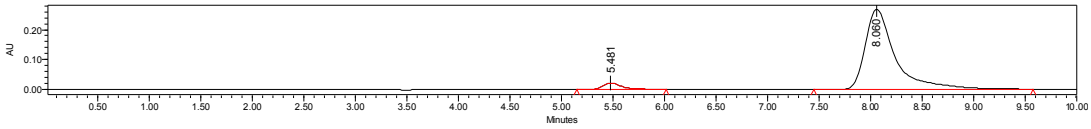
($C_{40}H_{49}NO_8SSi$) white foam, 82% yield, 90% *ee*. $[\alpha]_D^{16.5}$ = +180.3 (c = 0.58, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.48 min, 8.06 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 12.4, 8.8 Hz, 3H), 7.21 (d, *J* = 4.4 Hz, 4H), 7.18 – 7.13 (m, 1H), 7.09 (d, *J* = 2.4 Hz, 1H), 6.83 (d, *J* = 9.2 Hz, 2H), 6.62 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.27 (d, *J* = 15.6 Hz, 1H), 5.93 (dd, *J* = 15.6, 9.6 Hz, 1H), 4.79 (d, *J* = 8.8 Hz, 1H), 4.01 (t, *J* = 9.6 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 3.68 (s, 3H), 2.91 – 2.77 (m, 1H), 2.46 – 2.27 (m, 2H), 1.18 – 1.10 (m, 3H), 1.00 (t, *J* = 7.2 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.30, 163.54, 160.87, 156.52, 144.14, 136.23, 135.46, 133.03, 130.17, 129.66, 129.01, 128.57, 127.90, 127.01, 126.36, 115.84, 114.15, 113.35, 110.89, 108.87, 64.92, 55.52, 53.17, 50.26, 42.72, 36.50, 17.96, 17.95, 13.70. HRMS (ESI-TOF) calcd for $C_{40}H_{49}NO_8SSi$ ([M+Na$^+$]= 754.2840, Found 754.2843.



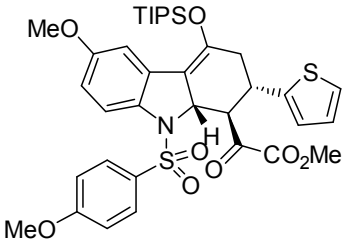
	Retention Time	Area	% Area
1	5.524	12673879	49.38

2	8.172	12992950	50.62



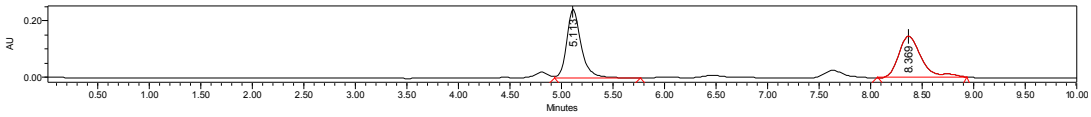
	Retention Time	Area	% Area
1	5.481	263002	4.62
2	8.060	5427579	95.38

Methyl 2-((1R,2S,9aS)-6-methoxy-9-((4-methoxyphenyl)sulfonyl)-2-(thiophen-2-yl)-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3br)

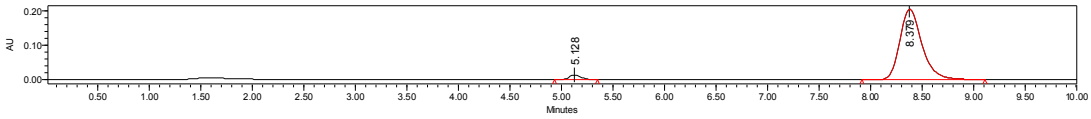


($C_{36}H_{45}NO_8S_2Si$) white foam, 94% yield, 92% *ee*. $[\alpha]_D^{21.9}$ = +106.6 (c = 1.11, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.13 min, 8.38 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 2.7 Hz, 1H), 7.06 (d, *J* = 4.4 Hz, 1H), 6.81 (d, *J* = 9.2 Hz, 2H), 6.77 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.70 (d, *J* = 2.8 Hz, 1H), 6.63 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.79 (d, *J* = 8.8 Hz, 1H), 4.16 (t, *J* = 8.8 Hz, 1H), 3.72 (d, *J* = 4.0 Hz, 6H), 3.68 (s, 3H), 2.73 – 2.49 (m, 2H), 1.13 – 1.05 (m, 3H), 0.98 (d, *J* = 6.8 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.89, 163.60, 160.12, 156.65, 144.30, 144.05, 135.54, 130.23, 129.58, 126.67,126.60, 126.13, 124.67, 116.10, 114.16, 113.49, 111.27, 108.66, 64.99, 55.53, 55.49, 53.44, 53.07, 39.02, 38.85, 17.89, 17.86, 13.60. HRMS (ESI-TOF) calcd for $C_{36}H_{45}NO_8S_2Si$ ([M+Na^+]) = 734.2248, Found 734.2251.

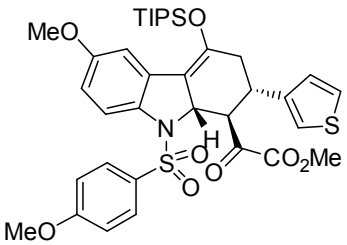


	Retention Time	Area	% Area
1	5.113	2353995	51.66
2	8.369	2202273	48.34



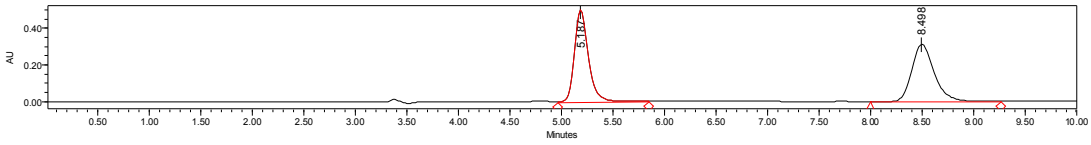
	Retention Time	Area	% Area
1	5.128	120210	3.77
2	8.379	3064289	96.23

Methyl 2-((1R,2S,9aS)-6-methoxy-9-((4-methoxyphenyl)sulfonyl)-2-(thiophen-3-yl)-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3bs)

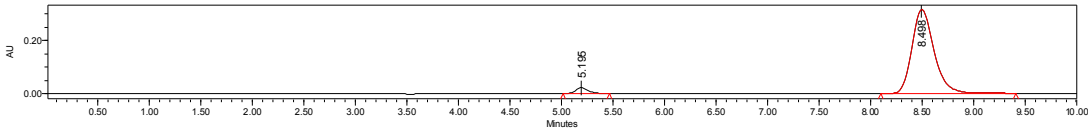


($C_{36}H_{45}NO_8S_2Si$) white foam, 92% yield, 92% *ee*. $[\alpha]_D^{17.5}$ = +107.6 (c = 1.22, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 5.19 min, 8.50 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.8 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.17 (dd, *J* = 4.8, 2.8 Hz, 1H), 7.10 (d, *J* = 2.8 Hz, 1H), 6.94 – 6.89 (m, 1H), 6.86 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.82 (d, *J* = 9.2 Hz, 2H), 6.63 (dd, *J* = 9.2, 2.8 Hz, 1H), 4.81 – 4.72 (m, 1H), 4.18 (t, *J* = 9.2 Hz, 1H), 3.73 (s, 3H), 3.68 (s, 6H), 3.52 – 3.39 (m, 1H), 2.63 – 2.42 (m, 2H), 1.15 – 1.05 (m, 3H), 0.98 (dd, *J* = 7.2, 3.2 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.27, 163.58, 160.11, 156.60, 144.42, 141.28, 135.54, 130.23, 129.59, 126.94, 126.64, 126.42, 122.81, 116.02, 114.15, 113.41, 111.16, 108.73, 65.23, 55.54, 55.49, 53.00, 51.87, 39.29, 37.79, 17.89, 13.64. HRMS (ESI-TOF) calcd for $C_{36}H_{45}NO_8S_2Si$ ([M+Na$^+$]) = 734.2248, Found 734.2247.

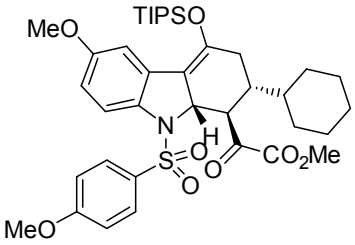


	Retention Time	Area	% Area
1	5.187	4725783	49.63
2	8.498	4795985	50.37



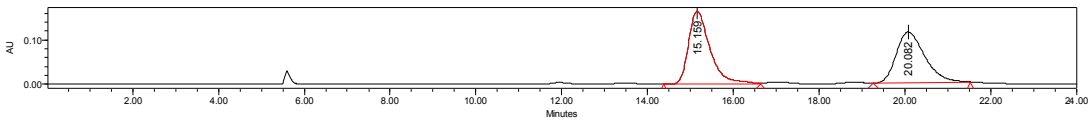
	Retention Time	Area	% Area
1	5.195	200764	4.06
2	8.498	4743548	95.94

Methyl 2-((1R,2R,9aS)-2-cyclohexyl-6-methoxy-9-((4-methoxyphenyl)sulfonyl)-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3bt)

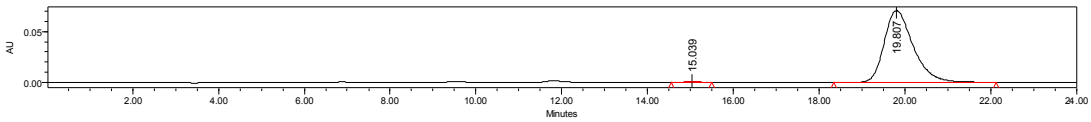


($C_{38}H_{53}NO_8SSi$) white foam, 78% yield, 99% *ee*. $[\alpha]_D^{18.9}$ = +183.4 (c = 0.57, CH_2Cl_2). HPLC DAICEL CHIRALCEL ID, *n*-hexane/2-propanol = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 15.04 min, 19.81 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.8 Hz, 1H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 2.4 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.62 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.65 (d, *J* = 8.4 Hz, 1H), 3.90 (s, 3H), 3.72 (s, 3H), 3.68 (s, 3H), 3.58 (t, *J* = 7.6 Hz, 1H), 2.28 – 2.12 (m, 2H), 2.09 – 1.99 (m, 1H), 1.65 – 1.51 (m, 5H), 1.22 – 1.06 (m, 6H), 0.99 (dd, *J* = 7.2, 1.2 Hz, 18H), 0.94 – 0.76 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.16, 163.43, 160.69, 156.91, 145.35, 135.45, 129.97, 129.82, 126.77, 117.01, 114.02, 113.25, 111.60, 108.02, 65.25, 55.48, 55.46, 53.18, 51.62, 41.60, 41.44, 31.61, 31.10, 28.37, 26.48, 26.34, 26.29, 17.86, 13.49. HRMS (ESI-TOF) calcd for $C_{38}H_{53}NO_8SSi$ ([M+Na$^+$]) = 734.3153, Found 734.3156.

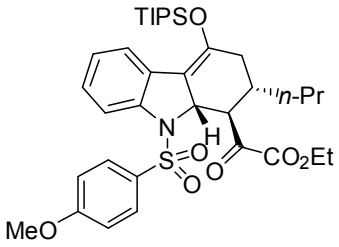


	Retention Time	Area	% Area
1	15.159	5720321	52.06
2	20.082	5268514	47.94

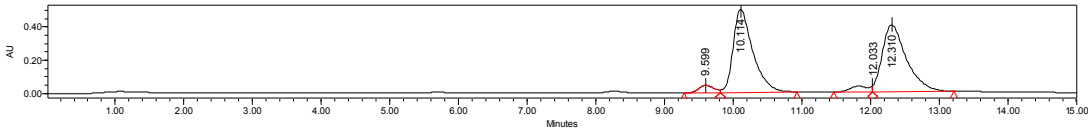


	Retention Time	Area	% Area
1	15.039	10385	0.31
2	19.807	3311727	99.69

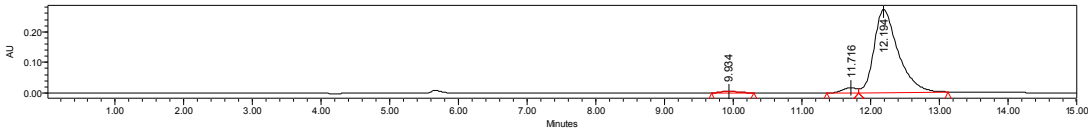
Ethyl 2-((1R,2S,9aS)-9-((4-methoxyphenyl)sulfonyl)-2-propyl-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3au)



($C_{35}H_{49}NO_7SSi$) white foam, 47 yield, 97% ee. >19:1 by ^{1}H NMR, $[\alpha]_D^{25.0}$ = +207.3 (c = 0.44, CH_2Cl_2). HPLC DAICEL CHIRALCEL ID, *n*-hexane/2-propanol = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 9.93 min, 11.72 min, 12.19 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.59 (dd, *J* = 15.6, 8.0 Hz, 3H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.82 (d, *J* = 7.6 Hz, 1H), 4.43 (q, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 3.74 (t, *J* = 7.2 Hz, 1H), 2.48 – 2.35 (m, 1H), 2.17 – 2.03 (m, 2H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.33 (s, 4H), 1.25 – 1.16 (m, 3H), 1.08 (d, *J* = 6.8 Hz, 18H), 0.85 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.39, 163.54, 160.40, 144.65, 141.77, 130.03, 128.44, 127.29, 127.00, 123.93, 123.52, 115.12, 114.13, 110.42, 64.35, 62.59, 55.49, 52.64, 37.00, 36.55, 34.91, 20.05, 17.92, 14.05, 13.84, 13.53. HRMS (ESI-TOF) calcd for $C_{35}H_{49}NO_7SSi$ ([M+Na^+]) = 678.2891, Found 678.2893

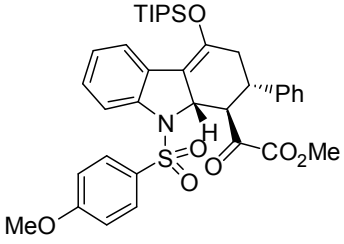


	Retention Time	Area	% Area
1	9.599	685911	3.26
2	10.114	9884903	47.03
3	12.033	647716	3.08
4	12.310	9800572	46.63



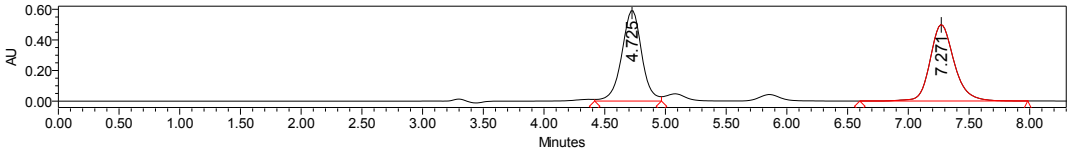
	Retention Time	Area	% Area
1	9.934	108527	1.56
2	11.716	253187	3.65
3	12.194	6574461	94.79

Methyl 2-((1R,2S,9aS)-9-((4-methoxyphenyl)sulfonyl)-2-phenyl-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3aa)

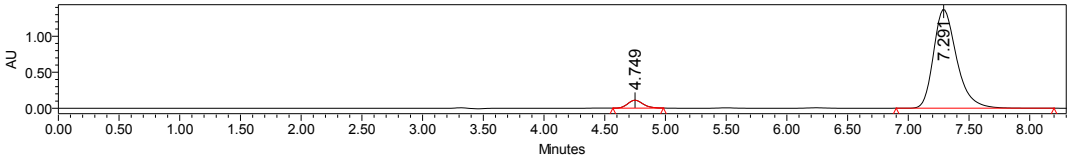


($C_{37}H_{45}NO_7SSi$**)** white foam, 85% yield, 90% *ee*, $[\alpha]_D^{17.2}$ = +155.6 (c = 0.96, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 4.75 min, 7.29 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 1H), 7.63 (t, *J* = 6.4 Hz, 3H), 7.31 – 7.12 (m, 7H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.93 (d, *J* = 9.2 Hz, 1H), 4.37 (t, *J* = 9.6 Hz, 1H), 3.80 (s, 3H), 3.67 (s, 3H), 3.44 – 3.31 (m, 1H), 2.73 – 2.56 (m, 2H), 1.18 – 1.10 (m, 3H), 1.04 (t, *J* = 7.2 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.27, 163.66, 160.11, 144.54, 142.02, 140.17, 130.24, 128.81, 128.52, 128.43, 127.54, 127.33, 126.82, 123.88, 123,85, 115.07, 114.19, 111.02, 65.60, 55.55, 52.89, 51.21, 44.63, 38.53, 17.93, 17.91, 13.60. HRMS (ESI-TOF) calcd for $C_{37}H_{45}NO_7SSi$ ([M+Na^+]) = 698.2578, Found 698.2582.

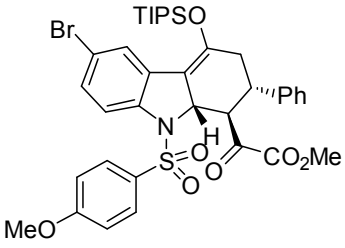


	Retention Time	Area	% Area
1	4.725	6779864	49.66
2	7.271	6872279	50.34



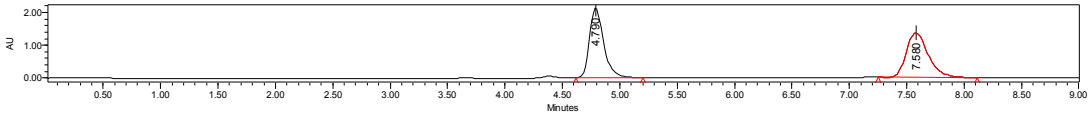
	Retention Time	Area	% Area
1	4.749	952010	4.98
2	7.291	18165946	95.02

Methyl 2-((1R,2S,9aS)-6-bromo-9-((4-methoxyphenyl)sulfonyl)-2-phenyl-4-((triisopropylsilyl)oxy)-2,3,9,9a-tetrahydro-1H-carbazol-1-yl)-2-oxoacetate (3ca)



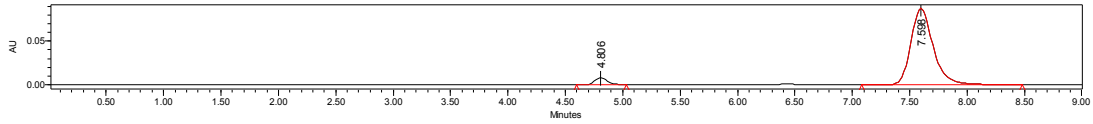
($C_{37}H_{44}BrNO_7SSi$) white foam, 91% yield, 90% *ee*. $[\alpha]_D^{21.8}$ = +59.4 (c = 1.01, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 4.81 min, 7.60 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 2.0 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 9.2 Hz, 2H), 7.23 – 7.14 (m, 4H), 7.12 – 7.06 (m, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.84 (d, *J* = 9.2 Hz, 1H), 4.29 (t, *J* = 9.6 Hz, 1H), 3.75 (s, 3H), 3.59 (s, 3H), 3.35 – 3.21 (m, 1H), 2.62 – 2.49 (m, 2H), 1.13 – 1.04 (m, 3H), 0.98 (dd, *J* = 7.2, 4.8 Hz, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.15, 163.84, 160.04, 145.96, 141.09, 139.80, 130.54, 130.24, 129.75, 128.88, 128.48, 127.66, 126.67, 126.44, 116.94, 116.39, 114.33, 109.88, 65.83, 55.61, 52.93, 50.95, 44.61, 38.49, 17.93 17.89, 13.53. HRMS (ESI-TOF) calcd for $C_{37}H_{44}Br^{78.9183}NO_7SSi$ ([M+Na^+]) = 776.1683, Found 776.1685. HRMS (ESI-TOF) calcd for $C_{37}H_{44}Br^{80.9163}NO_7SSi$ ([M+Na^+]) = 778.1663, Found 778.1659.



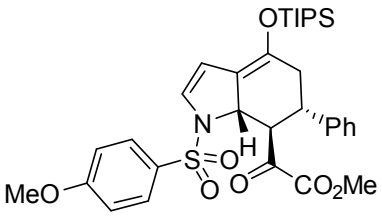
	Retention Time	Area	% Area
1	4.790	18291106	50.35

2	7.580	18037573	49.65



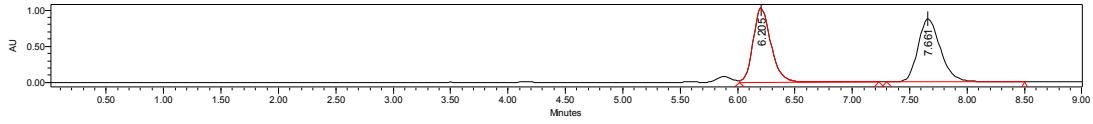
	Retention Time	Area	% Area
1	4.806	62396	5.02
2	7.598	1179383	94.98

Methyl 2-((6S,7R,7aS)-1-((4-methoxyphenyl)sulfonyl)-6-phenyl-4-((triisopropylsilyl)oxy)-5,6,7,7a-tetrahydro-1H-indol-7-yl)-2-oxoacetate (3da)

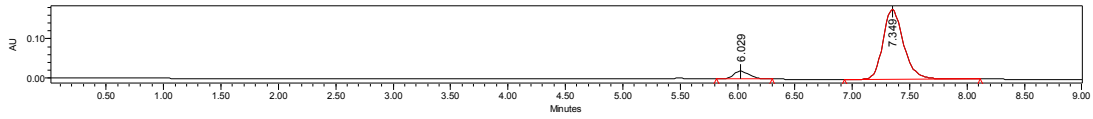


($C_{33}H_{43}NO_7SSi$) white foam, 93% yield, 84% *ee*. $[\alpha]_D^{17.9}$ = +422.6 (c = 0.67, CH_2Cl_2). HPLC DAICEL CHIRALCEL IA, *n*-hexane/2-propanol = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: 6.03 min, 7.35 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.8 Hz, 2H), 7.22-7.16 (dd, *J* = 8.1, 6.2 m, 2H), 7.15 – 7.08 (m, 3H), 6.99 – 6.88 (m, 2H), 6.44 (d, *J* = 4.0 Hz, 1H), 5.86 (d, *J* = 4.0 Hz, 1H), 4.31 (d, *J* = 8.0 Hz, 2H), 3.81 (s, 3H), 3.57 (s, 3H), 3.20 – 3.05 (m, 1H), 2.57 – 2.33 (m, 2H), 1.03 – 0.91 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.43, 163.56, 159.82, 139.81, 139.08, 132.02, 130.41, 128.79, 128.36, 127.54, 126.05, 117.28, 114.30, 110.75, 64.08, 55.63, 52.92, 49.42, 45.53, 38.47, 17.91, 12.94. HRMS (ESI-TOF) calcd for $C_{33}H_{43}NO_7SSi$ ([M+Na$^+$]) = 648.2422, Found 648.2418.

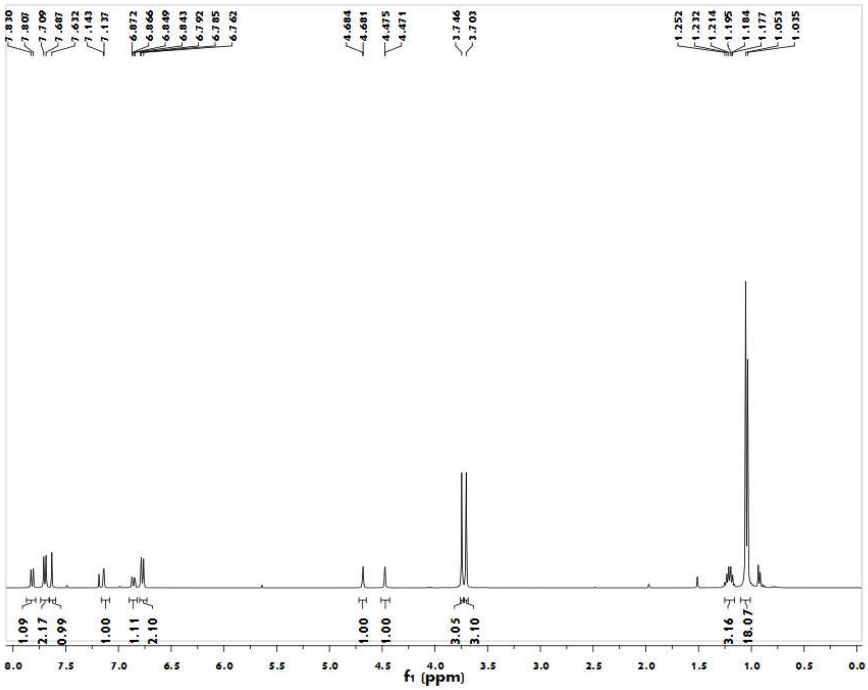


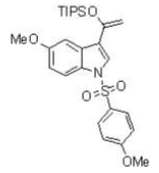
	Retention Time	Area	% Area
1	6.205	11184166	48.29
2	7.661	11978201	51.71



	Retention Time	Area	% Area
1	6.029	191615	7.93
2	7.349	2225682	92.07

7. Copies of NMR spectra for the reaction products



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AQ: undefined
TE: 0 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
Ph0: 93.15
Ph1: 21.86
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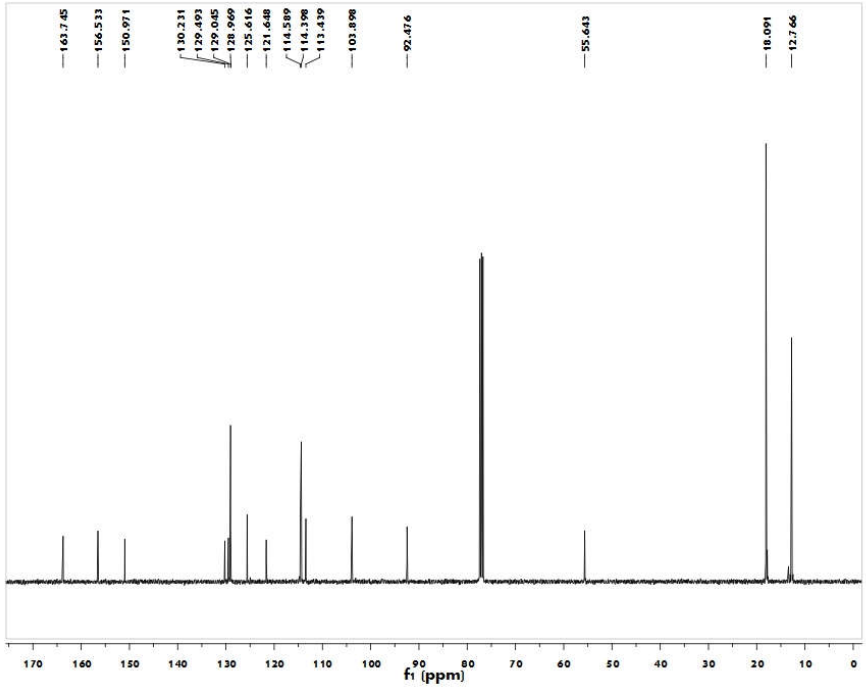

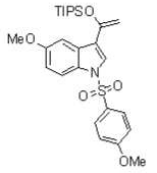


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NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== 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: -67.50
Ph1: 58.72
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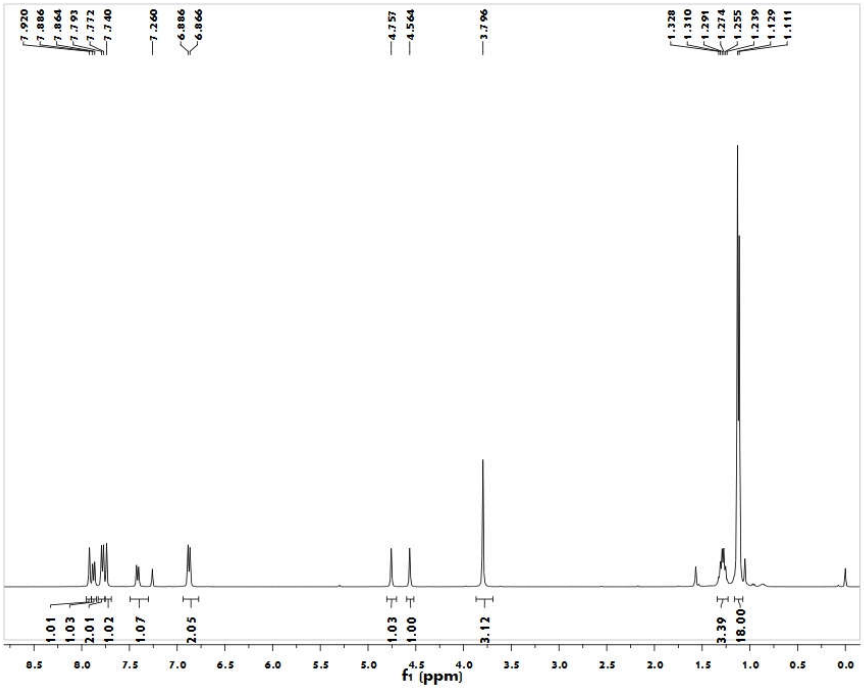

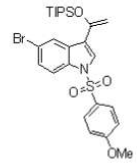

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PULPROG: zg30
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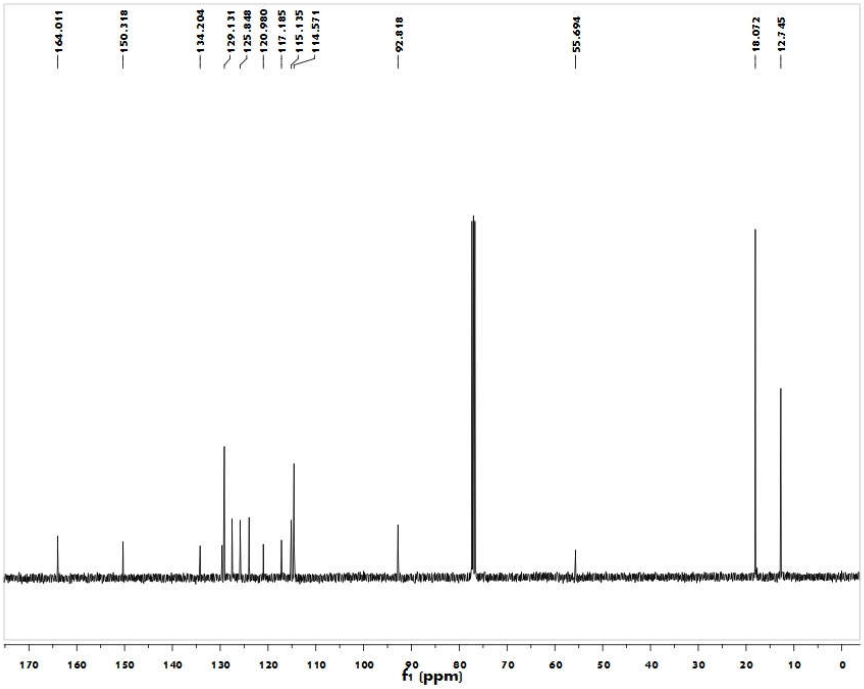
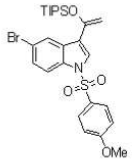
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 295.1 C

======== 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: 90.10
Ph1: 21.79





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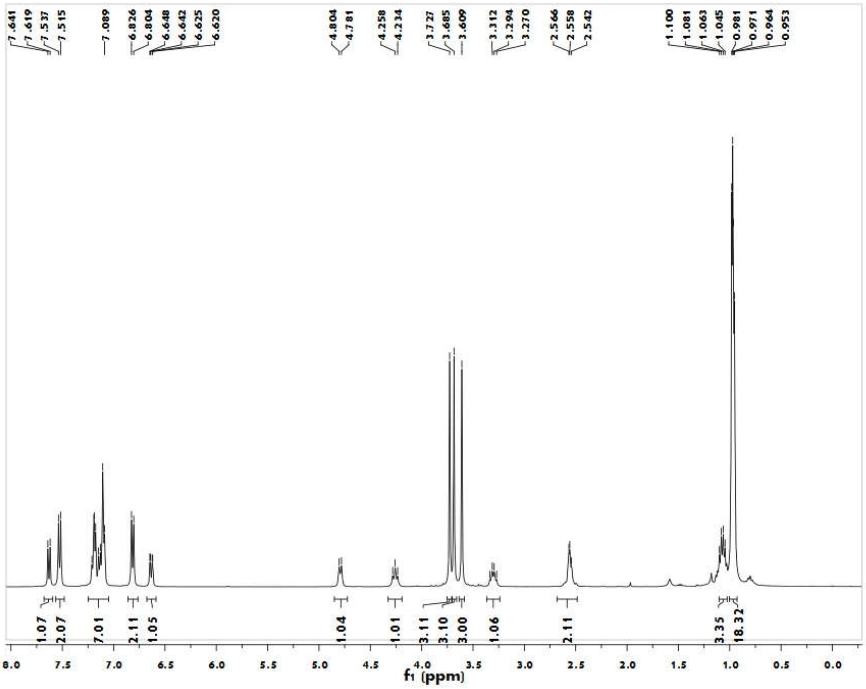
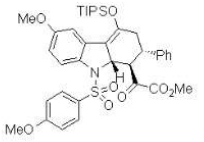
AQ: undefined
TE: 295.4 C

======== 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: -73.10
Ph1: 67.12





Current Data Parameters

F2 - Acquisition Parameters
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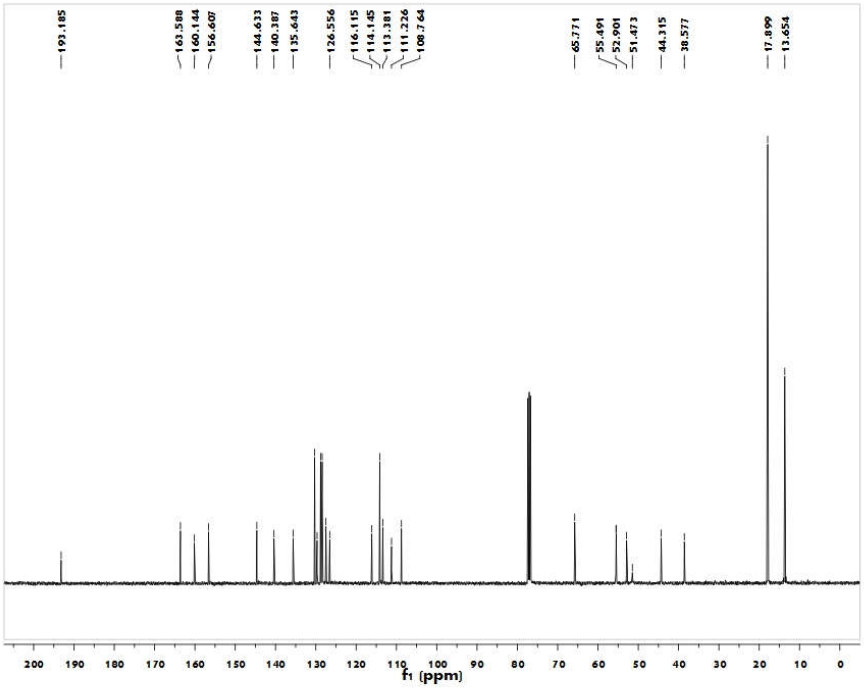
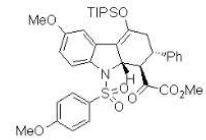
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== 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: 96.81
Ph1: 17.47





Current Data Parameters

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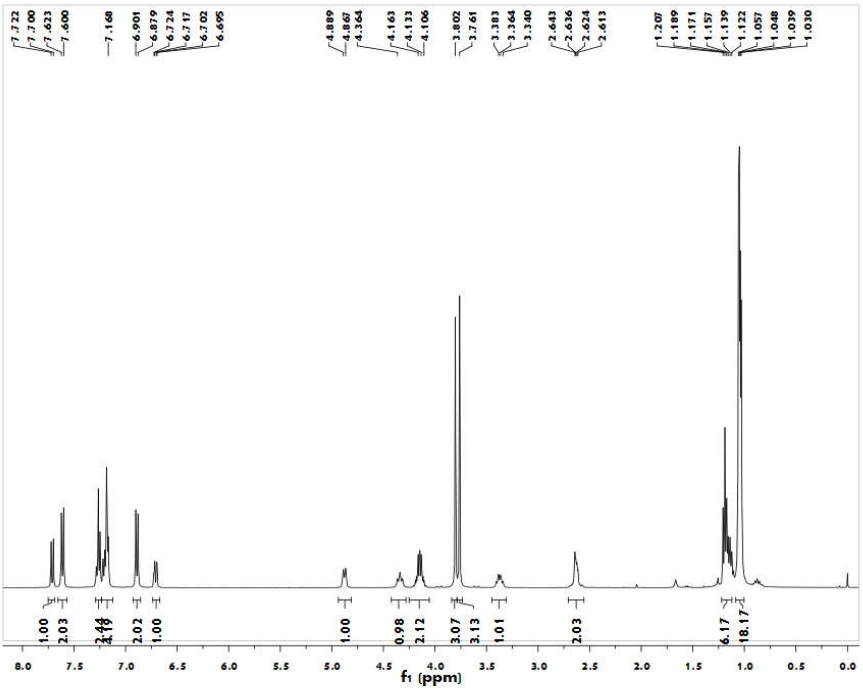
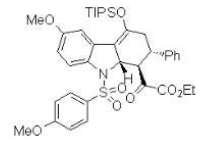
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

======== 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: -65.64
Ph1: 67.58





Current Data Parameters

F2 - Acquisition Parameters
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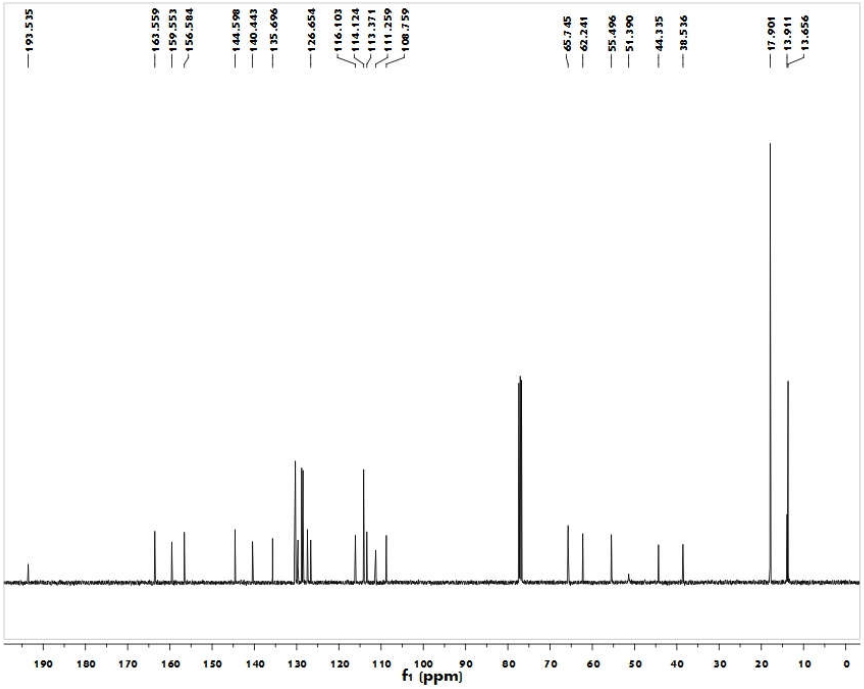
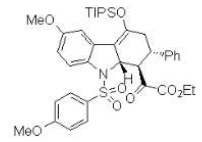
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======= 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: -263.85
Ph1: 18.15



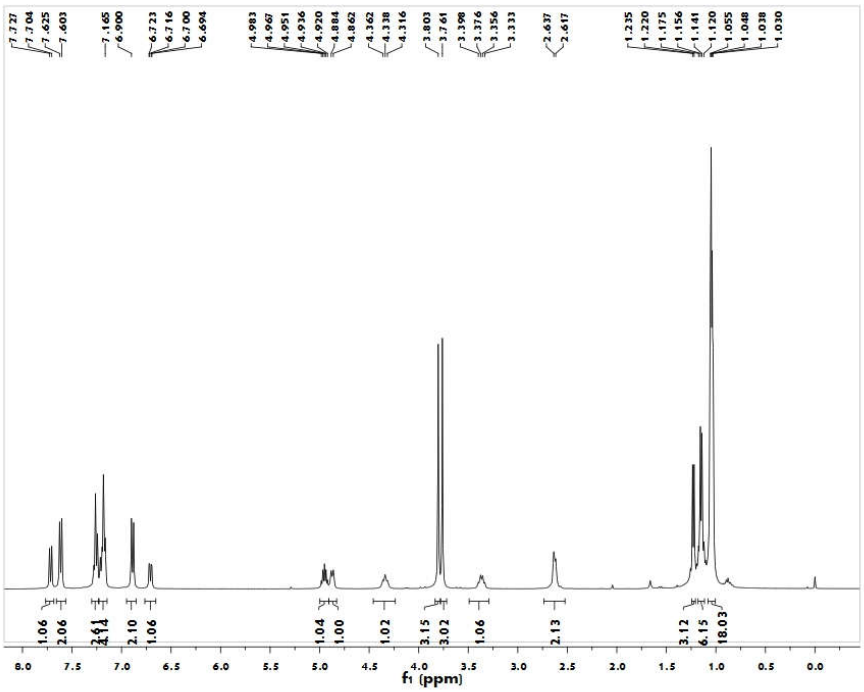


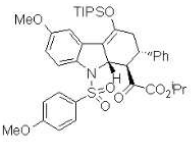
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-26T23:14:19
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -62.66
Ph1: 68.60



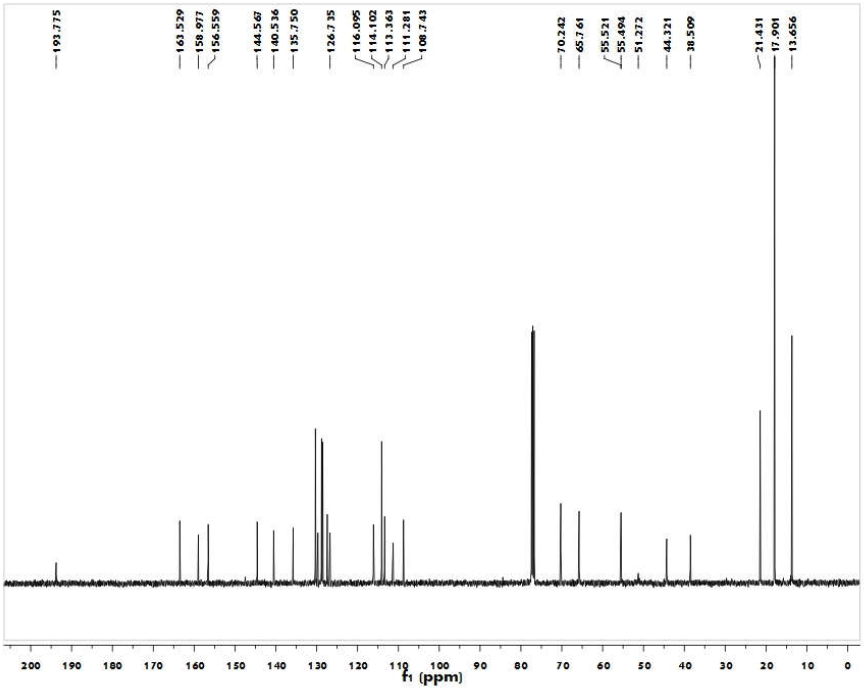


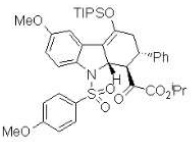

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-26T23:18:15
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: 93.99
Ph1: 20.43
```



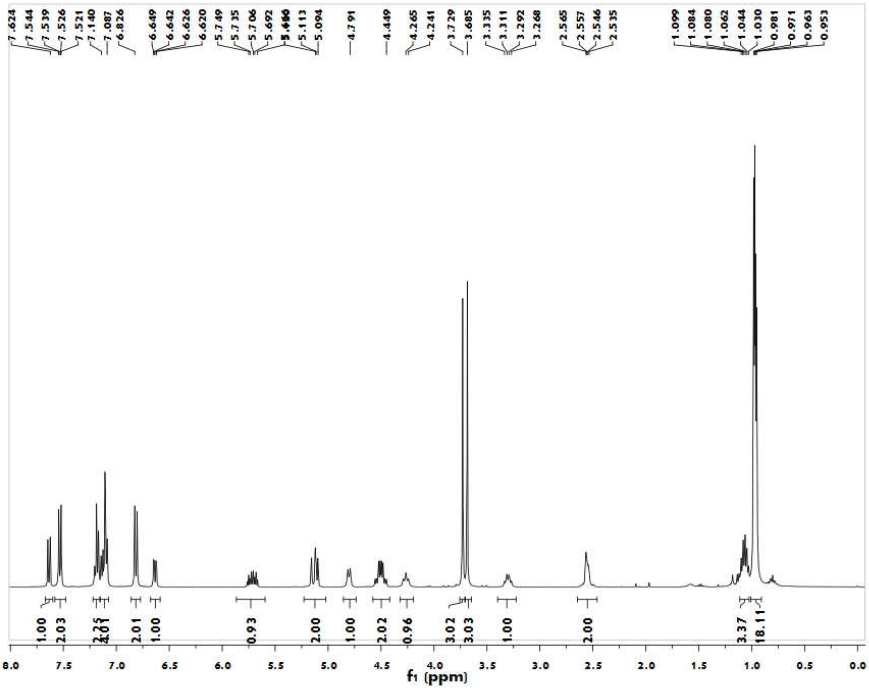


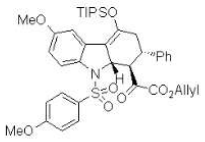

```
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-26T23:33:50
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -57.93
Ph1: 50.76
```





Current Data Parameters

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DATE: 2015-12-28T20:54:15
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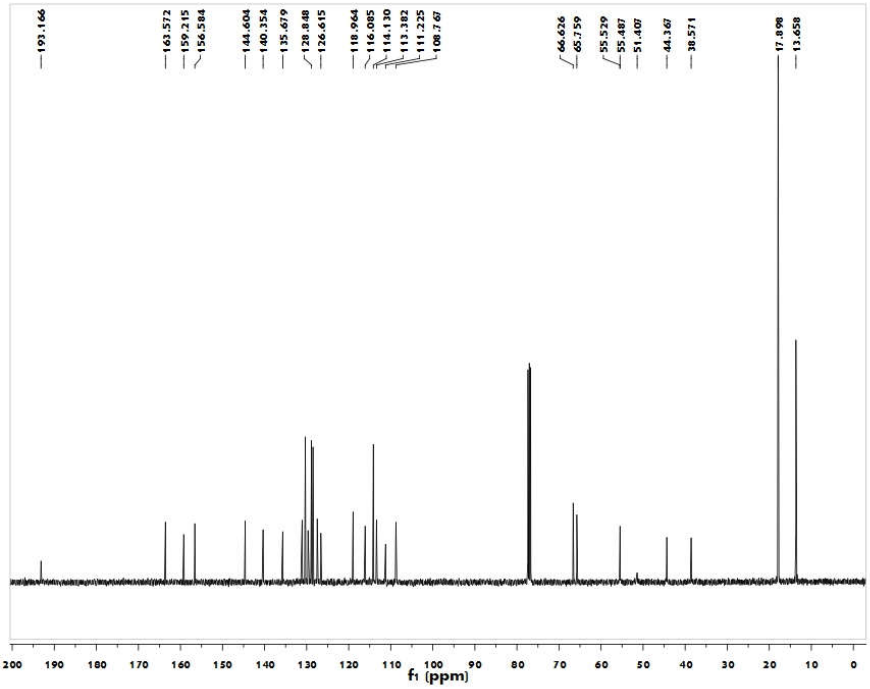
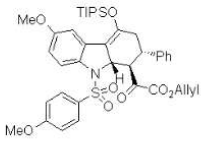
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 C

======== 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: 97.07
Ph1: 15.03



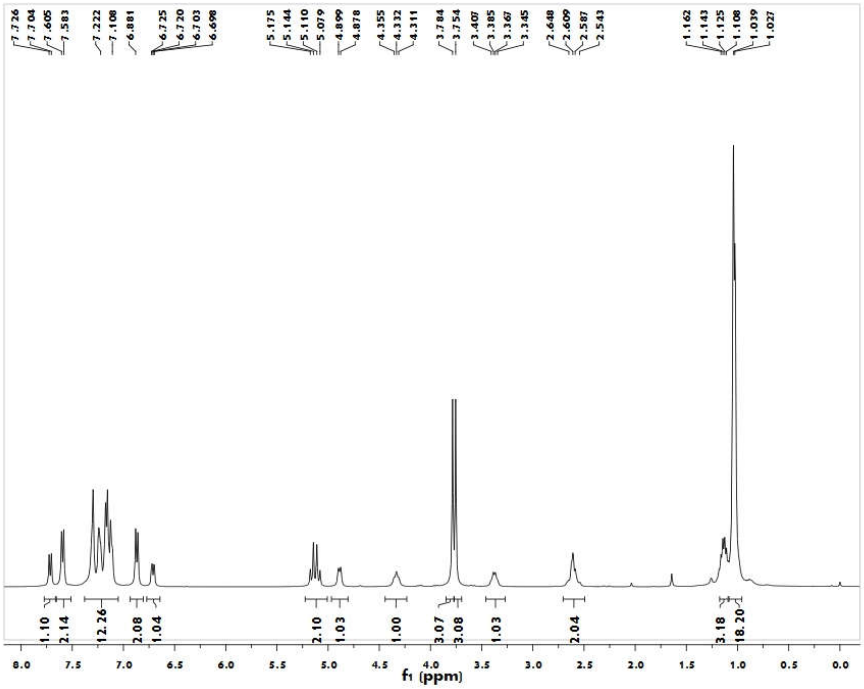


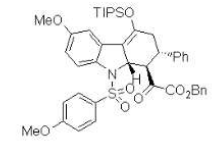
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-28T21:09:49
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -53.40
Ph1: 54.94



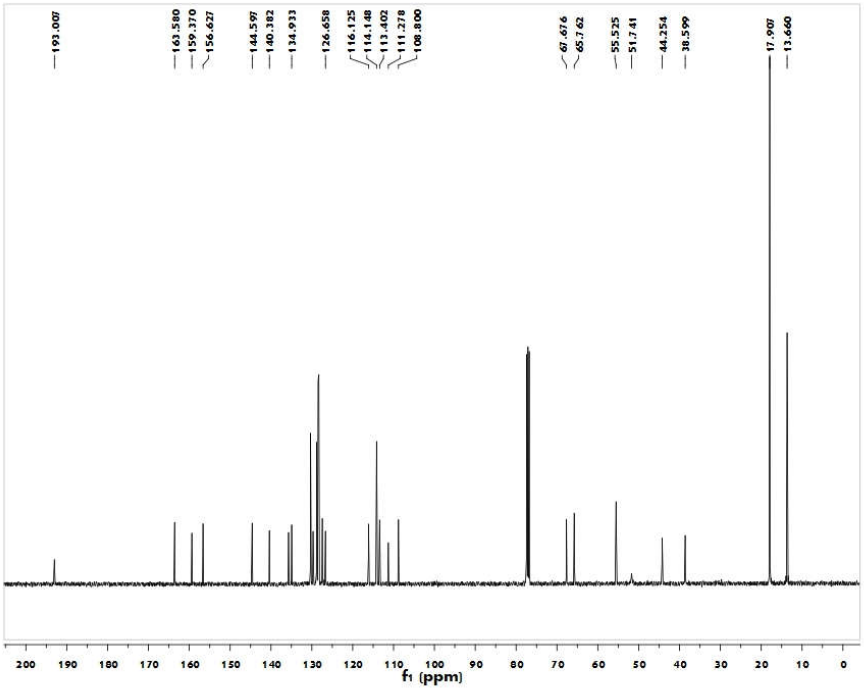


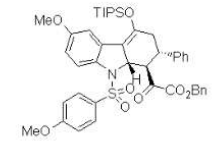
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-04-20T17:28:01
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: 91.50
Ph1: 15.51



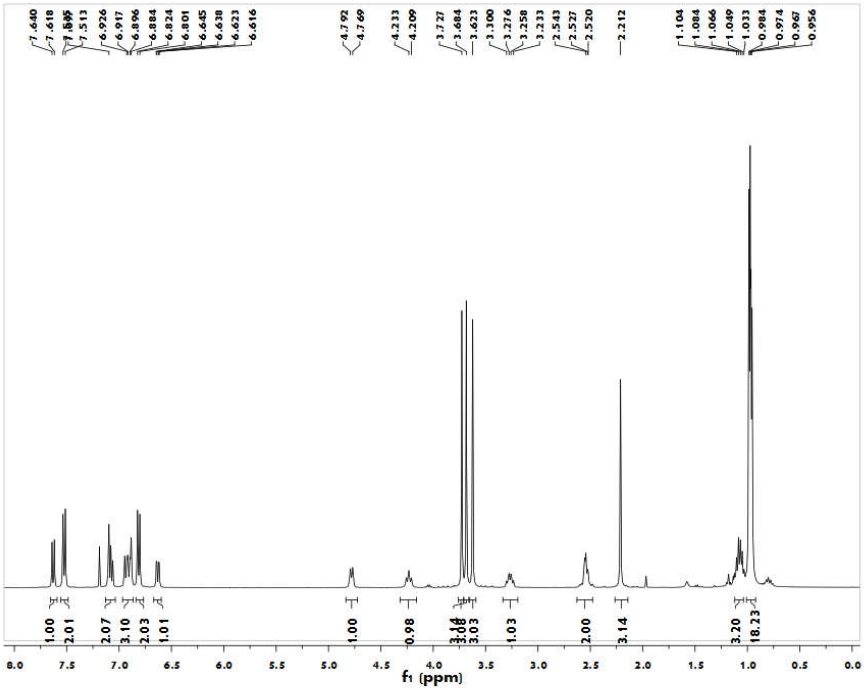


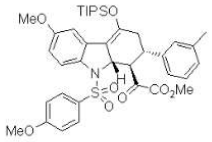
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-04-20T17:58:13
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -62.03
Ph1: 60.18



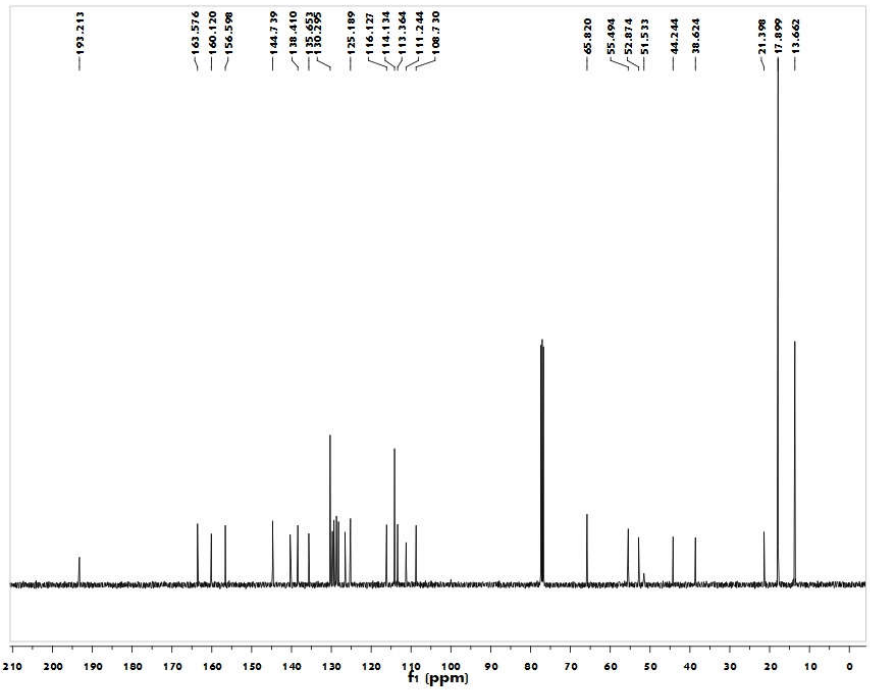


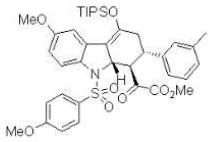
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-29T17:57:56
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: 95.08
Ph1: 17.54



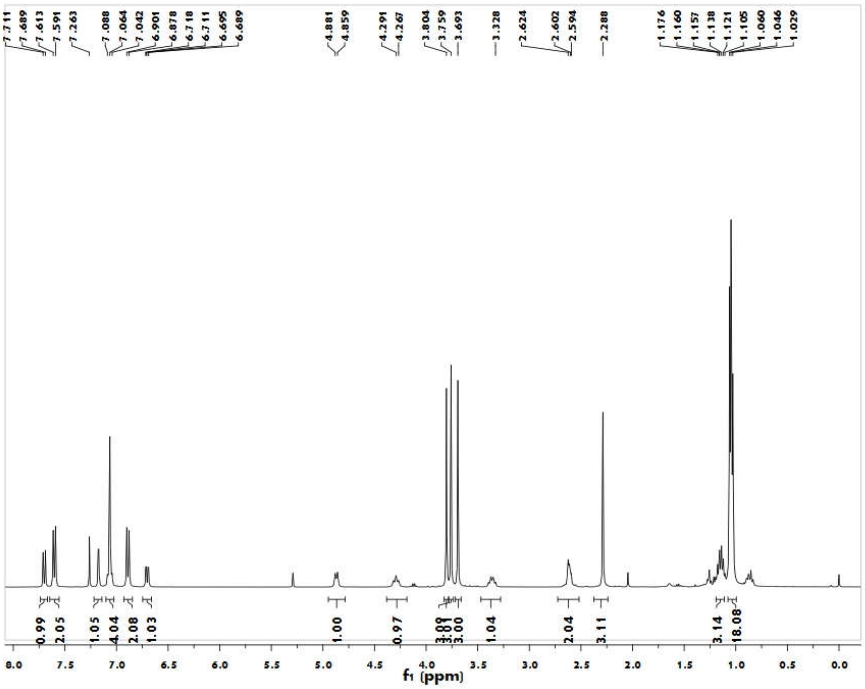


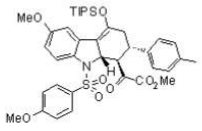
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-29T18:13:30
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -53.56
Ph1: 55.97



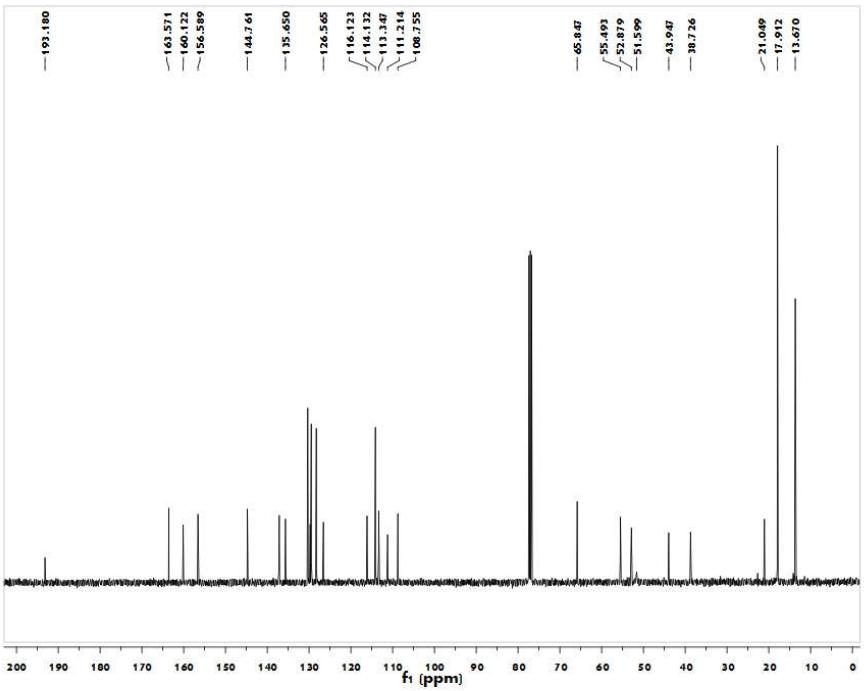


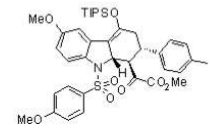
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-25T17:25:58
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: 93.47
Ph1: 19.29



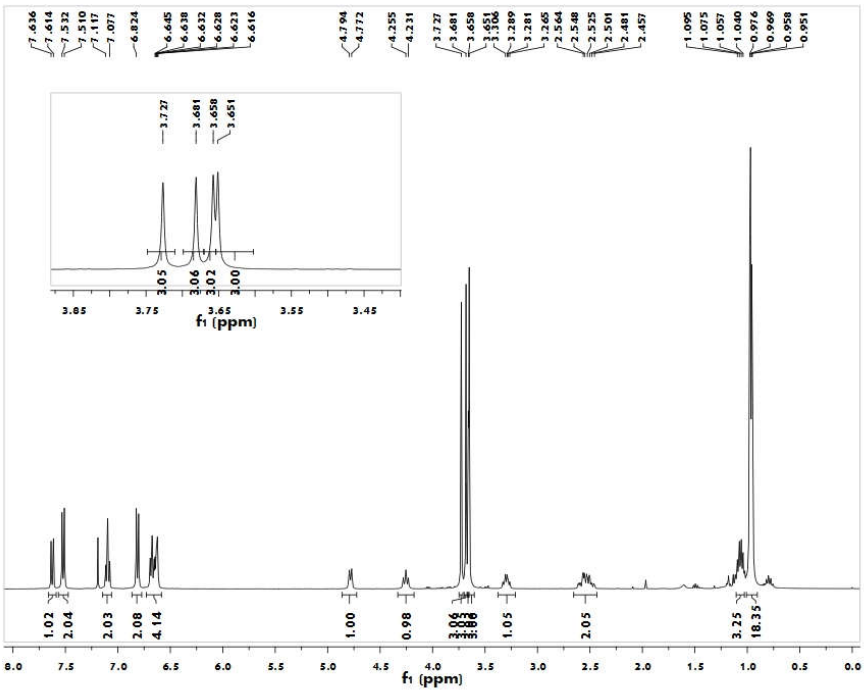


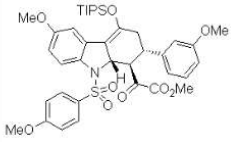
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-25T17:41:33
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -60.82
Ph1: 68.80



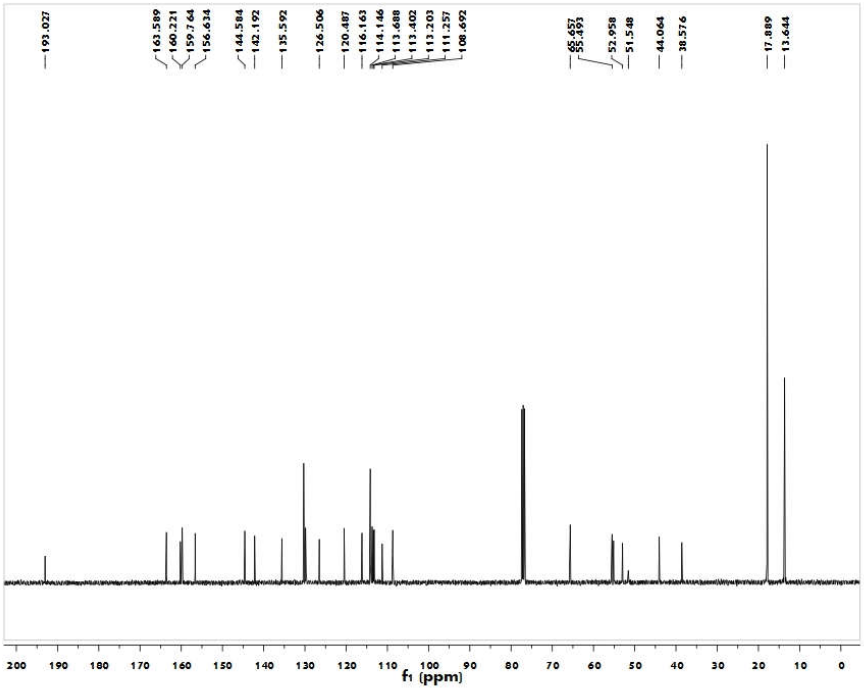


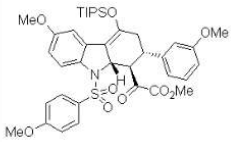
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-29T18:17:25
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: 95.04
Ph1: 18.10



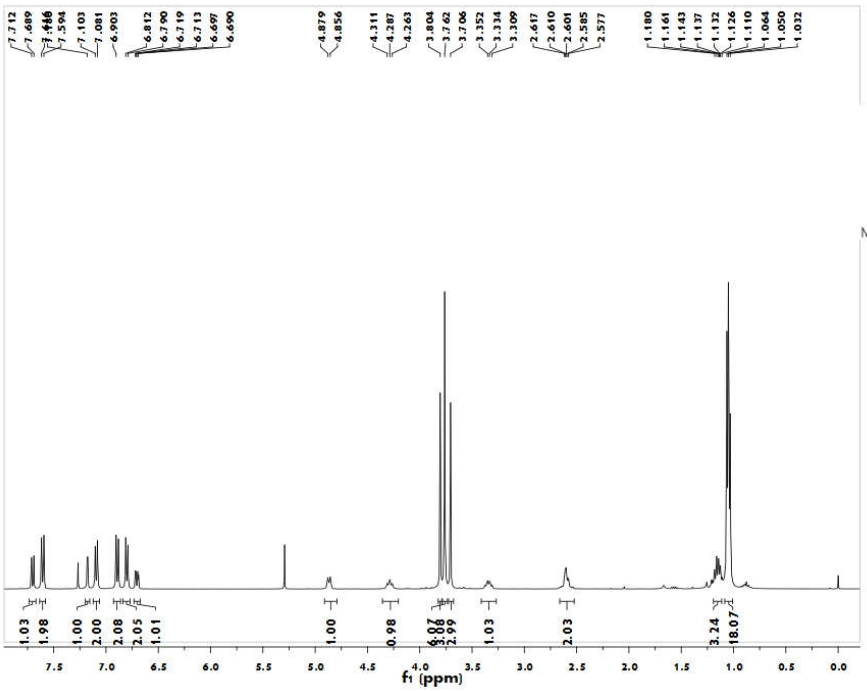


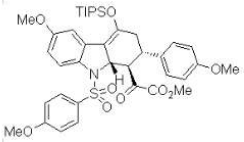
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-29T18:33:00
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -66.62
Ph1: 69.29



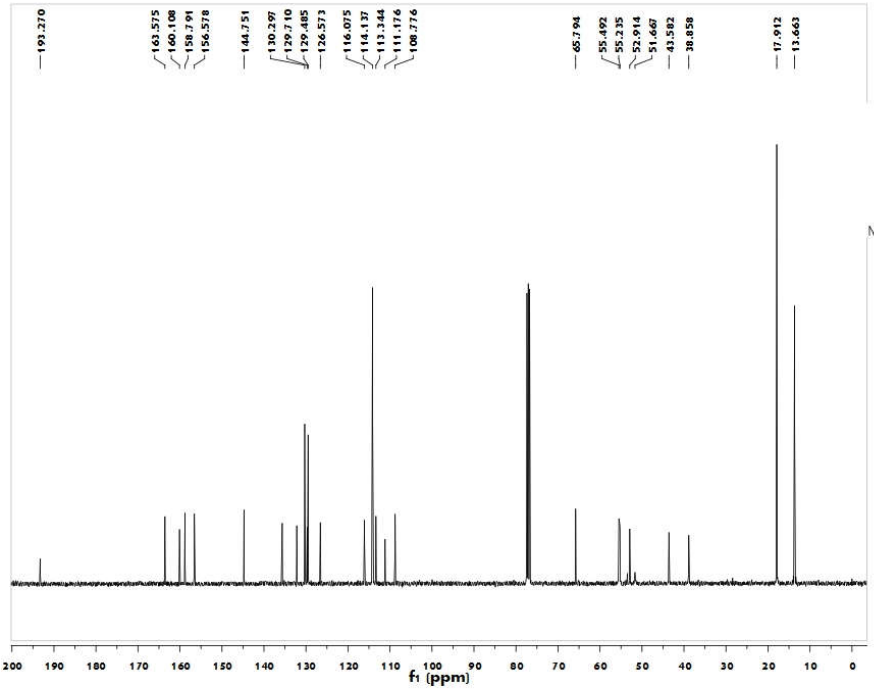


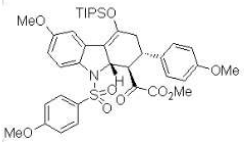
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-25T19:22:58
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: 95.46
Ph1: 17.44



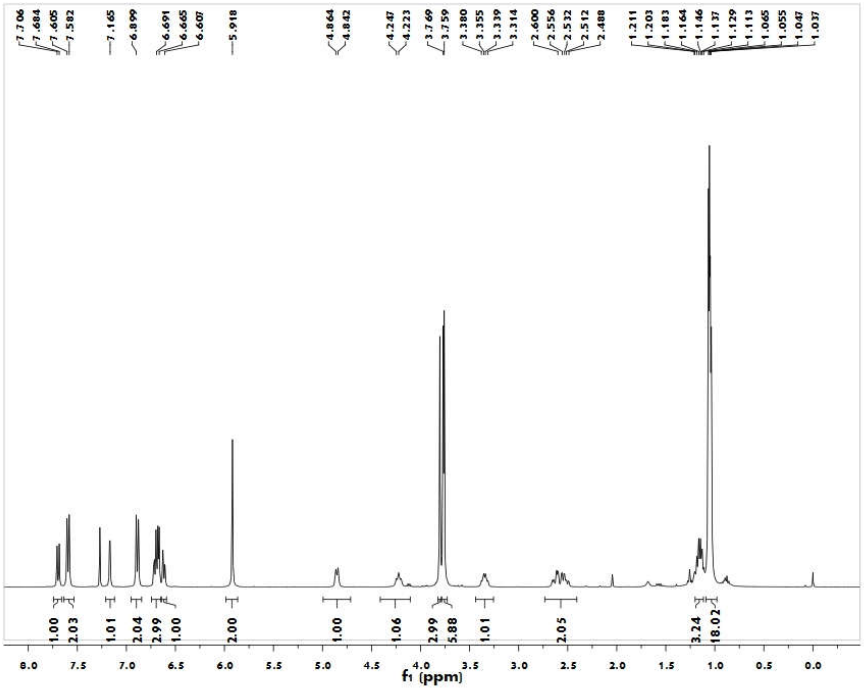


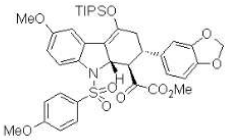
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-25T19:53:10
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -63.33
Ph1: 65.93



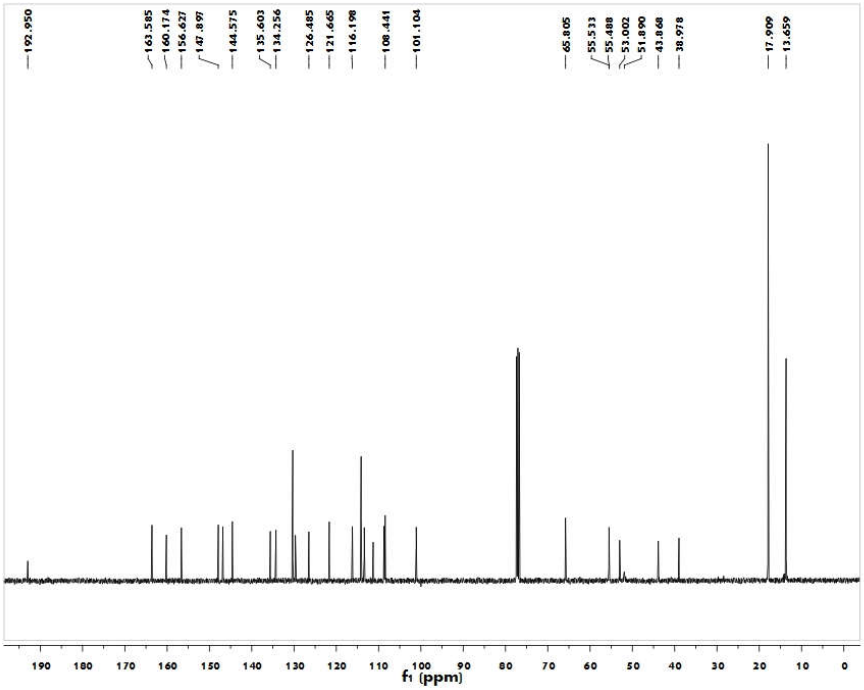


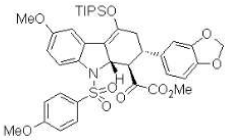
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-26T22:05:10
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: 95.77
Ph1: 19.32



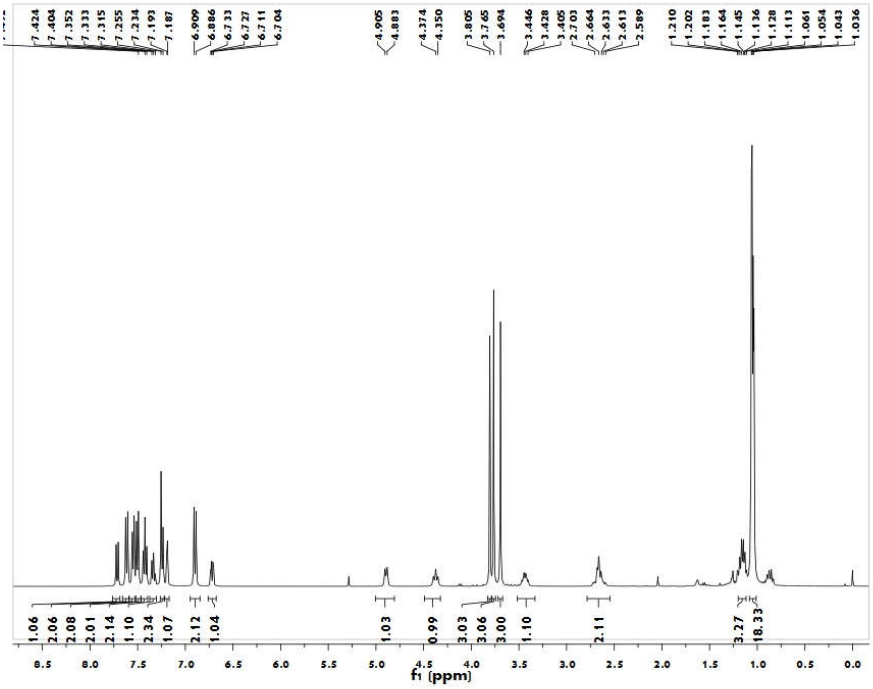


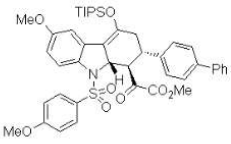
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-26T22:20:45
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -53.64
Ph1: 56.86



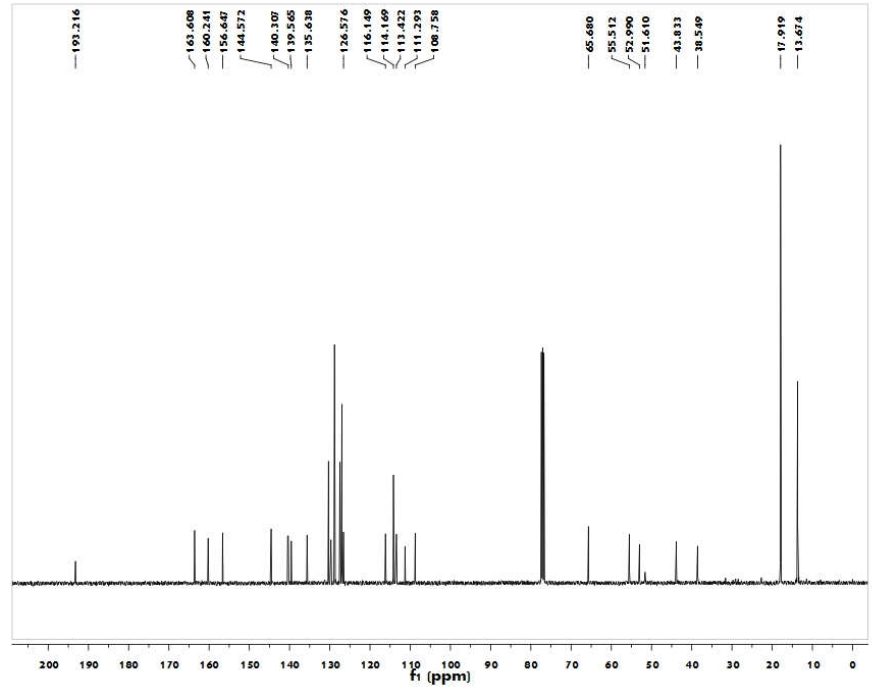


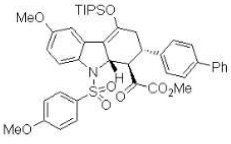
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-25T19:57:03
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: -267.21
Ph1: 19.07



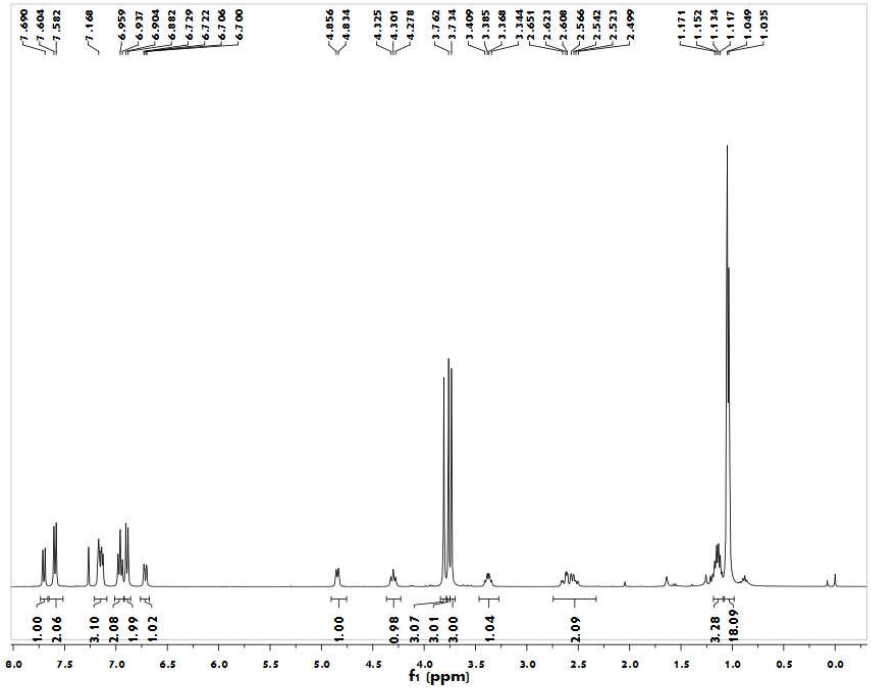


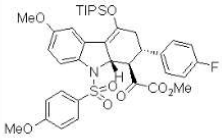
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-25T20:27:14
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -69.20
Ph1: 60.60



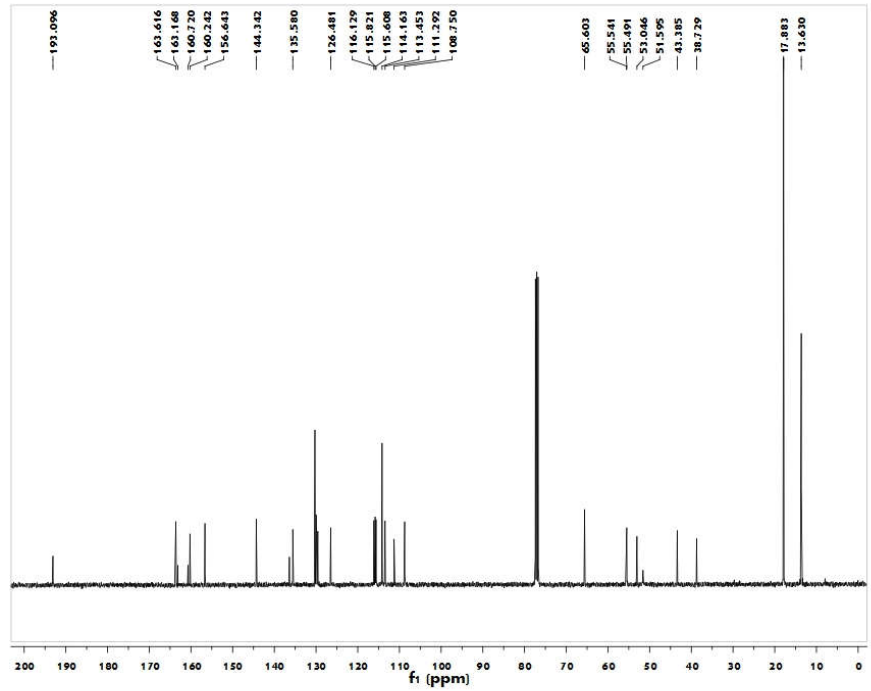


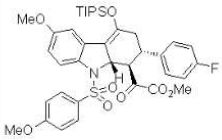
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-26T22:24:38
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: 96.04
Ph1: 17.49



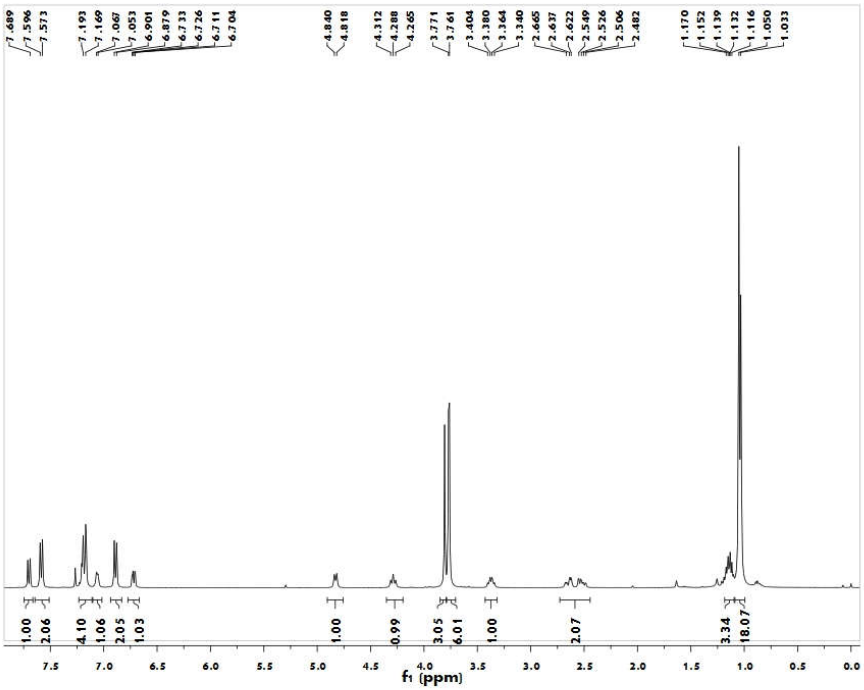


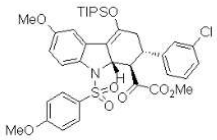
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-26T22:54:50
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -64.50
Ph1: 65.36



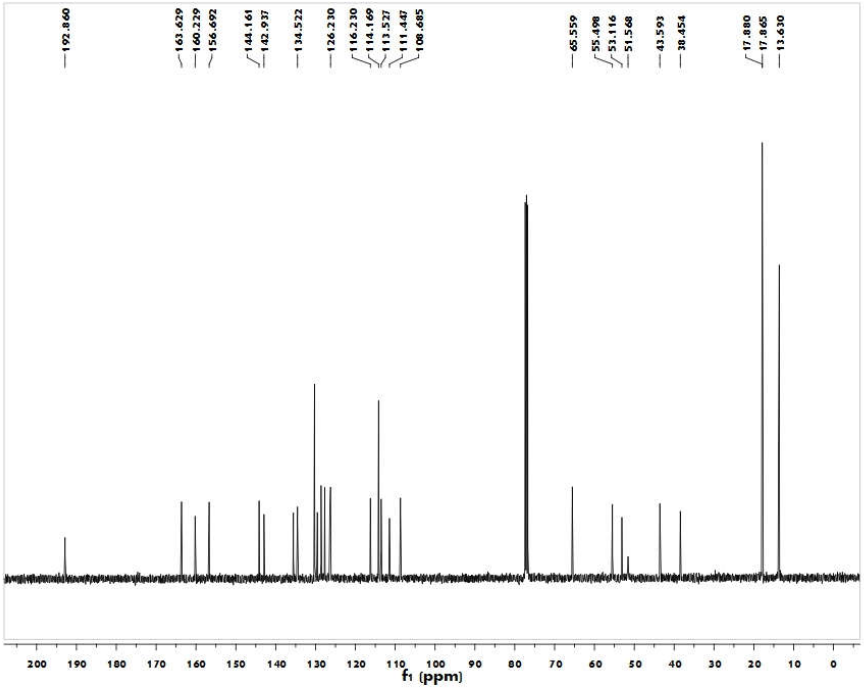


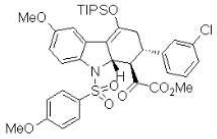
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-26T23:37:46
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: 95.58
Ph1: 19.33



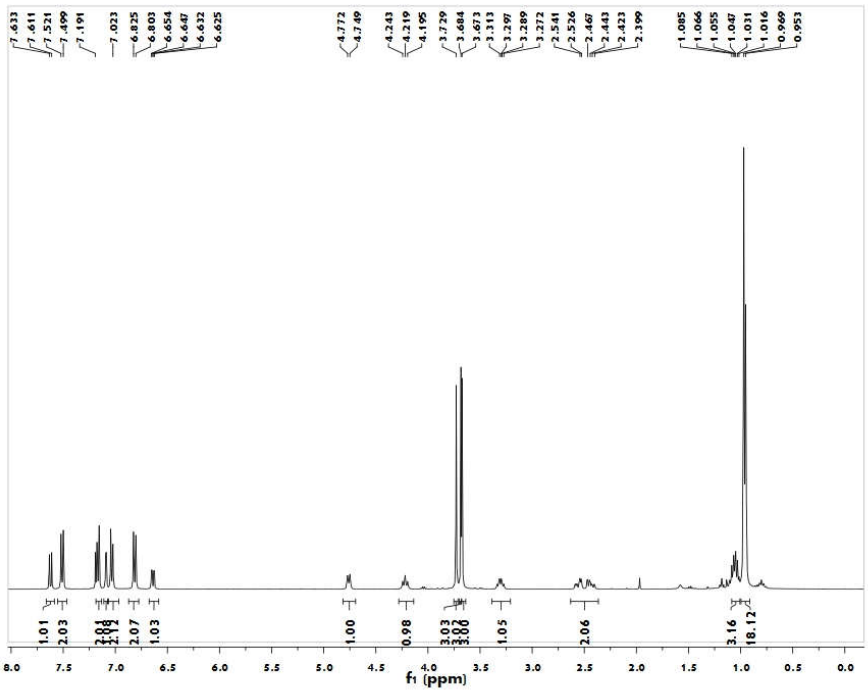


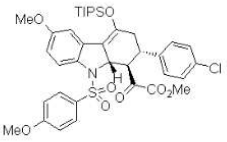
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-26T23:53:20
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -76.12
Ph1: 77.10



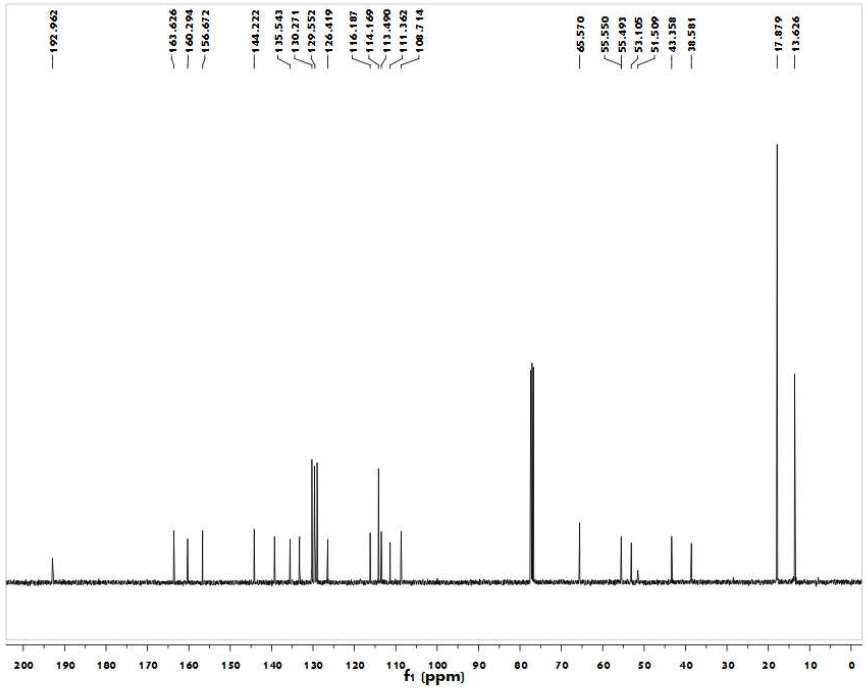


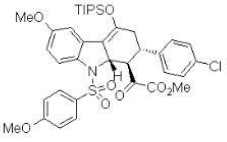
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-29T19:31:13
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: 94.48
Ph1: 19.60



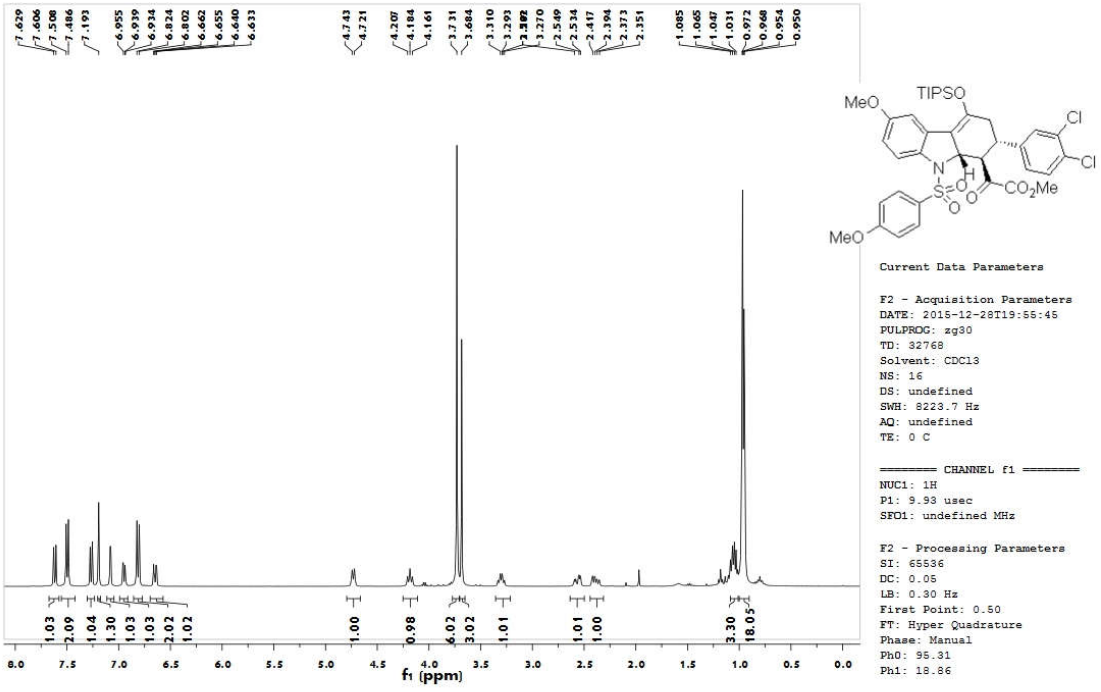


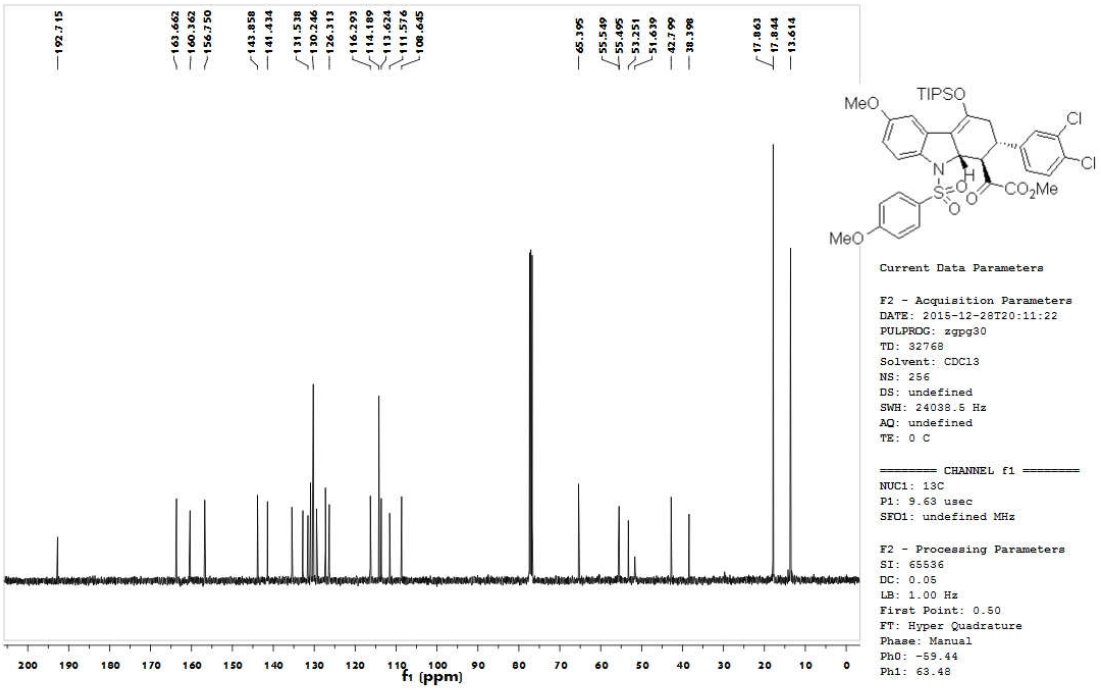
Current Data Parameters

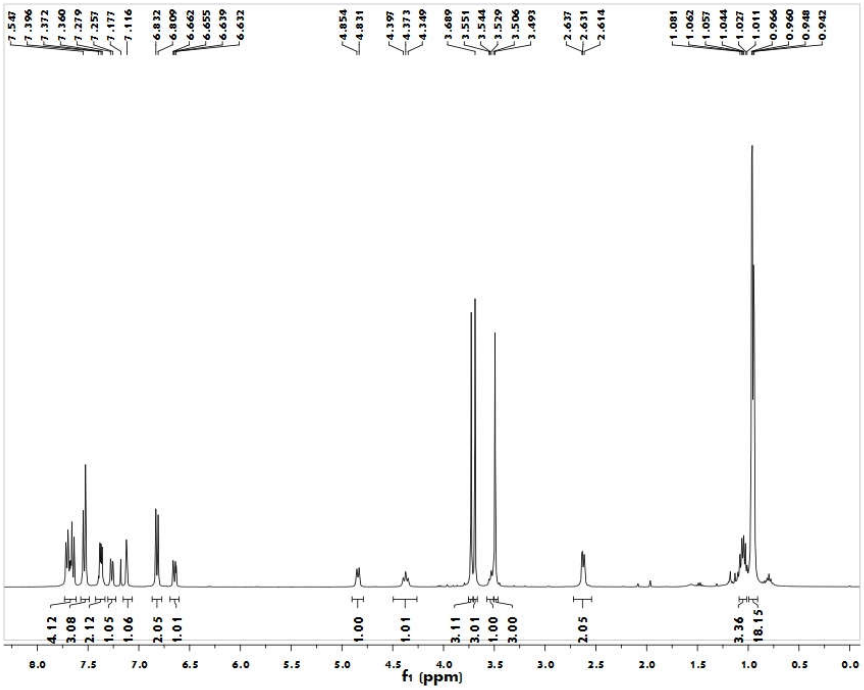
F2 - Acquisition Parameters
DATE: 2015-12-29T19:46:48
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

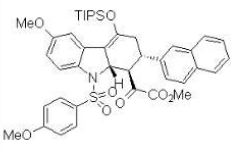
======== CHANNEL f1 ========
NUC1: 13C
P1: 9.63 usec
SFO1: undefined MHz

F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -66.15
Ph1: 68.75


7.629
7.606
7.508
7.486
7.193
6.955
6.939
6.934
6.824
6.802
6.662
6.655
6.640
6.633
4.743
4.721
4.207
4.184
4.161
3.731
3.684
3.310
3.293
3.270
2.549
2.534
2.417
2.394
2.373
2.351
1.085
1.065
1.047
1.031
0.972
0.968
0.954
0.950
1.03
2.09
1.04
1.30
1.03
1.03
2.02
1.02
1.00
0.98
6.02
3.02
1.01
1.01
1.00
3.30
18.05
f1 (ppm)
MeO
TIPSO
Cl
Cl
N
H
S
O
O
O
CO2Me
MeO
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2015-12-28T19:55:45
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: 95.31
Ph1: 18.86


192.715
163.662
160.362
156.750
143.858
141.434
131.538
130.246
126.313
116.293
114.189
113.624
111.576
108.645
65.395
55.549
55.495
53.251
51.639
42.799
38.398
17.863
17.844
13.614
f1 (ppm)
MeO
TIPSO
Cl
Cl
N
H
S
O
O
O
CO2Me
MeO
Current Data Parameters
F2 - Acquisition Parameters
DATE: 2015-12-28T20:11:22
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -59.44
Ph1: 63.48



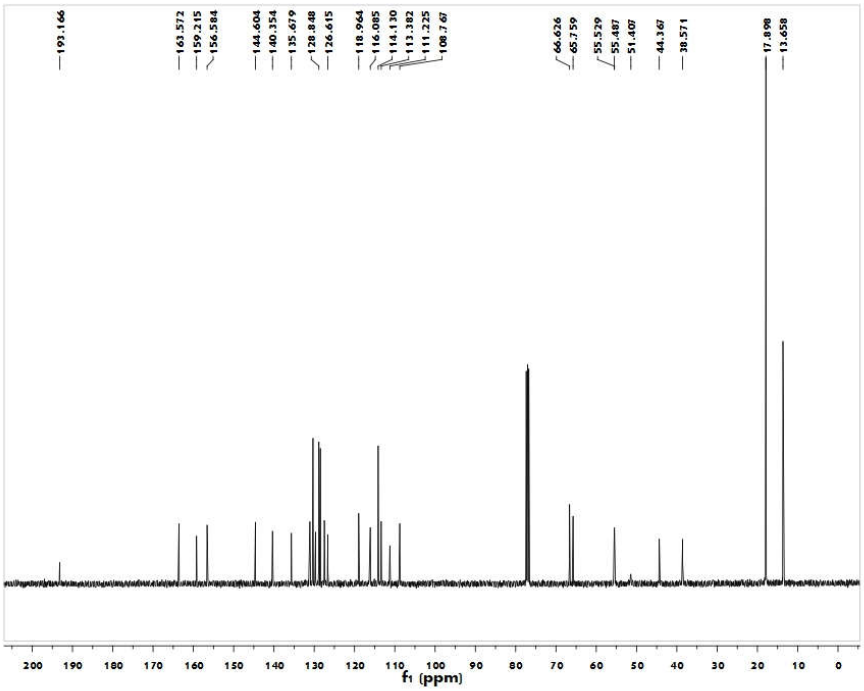


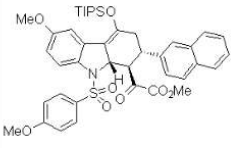
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-28T21:14:02
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: 96.77
Ph1: 17.20



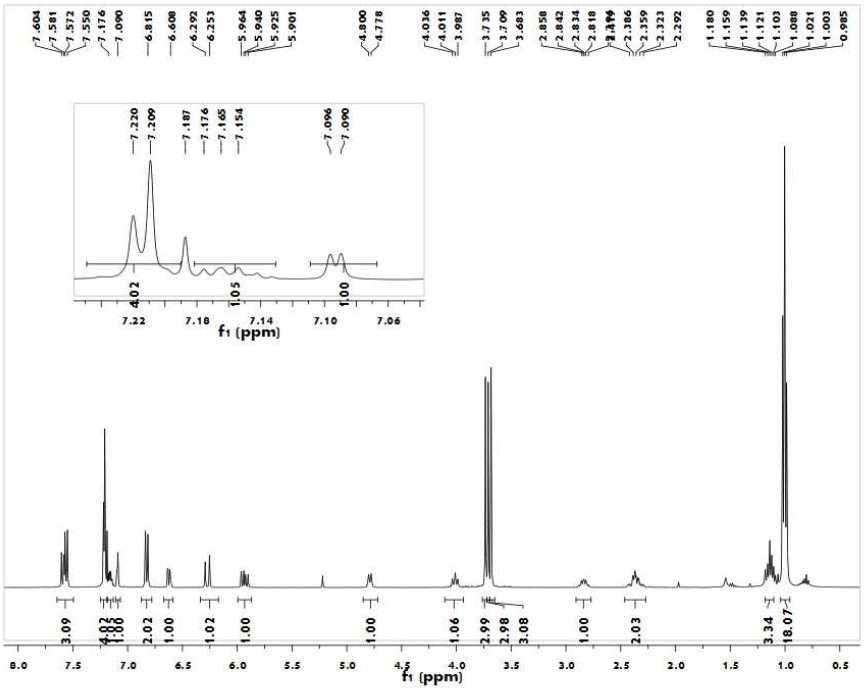


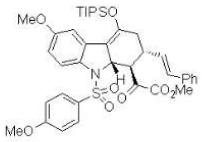
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-28T21:09:49
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -53.40
Ph1: 54.94



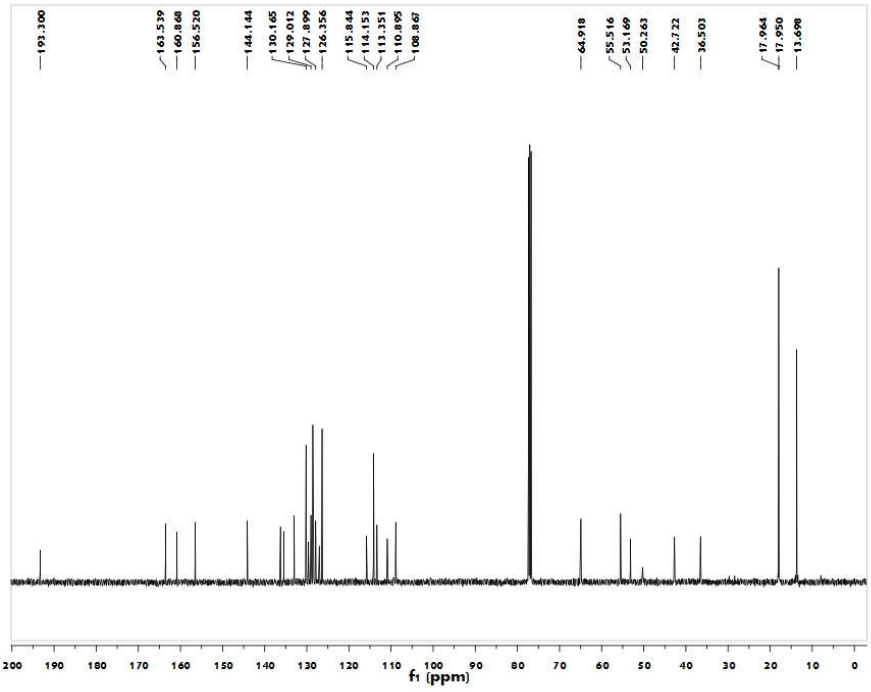


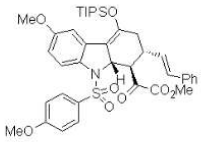
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-01-12T18:01:46
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: 98.22
Ph1: 14.68



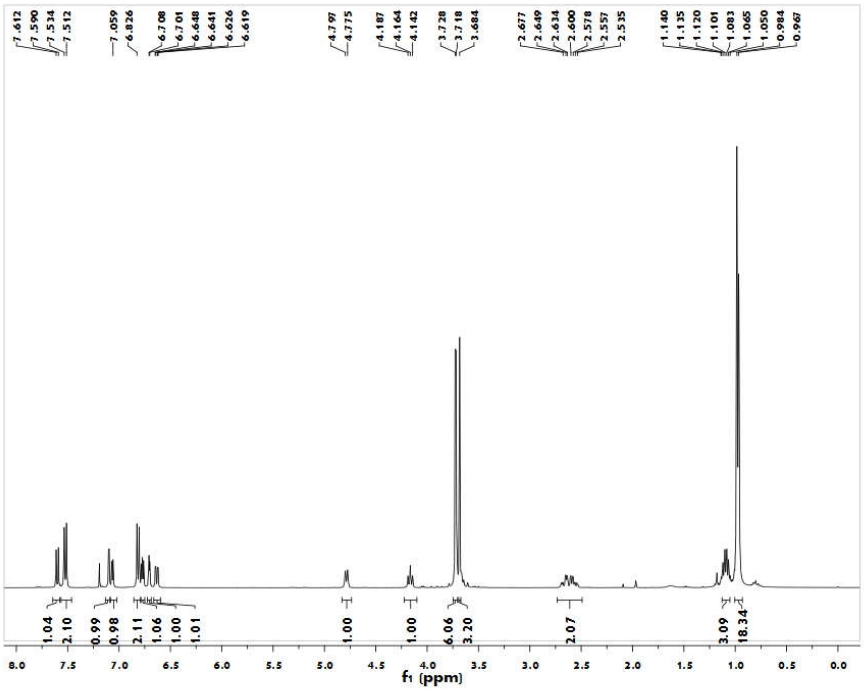


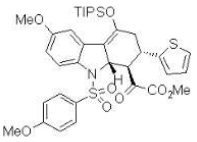
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-01-12T18:31:58
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -60.68
Ph1: 68.89



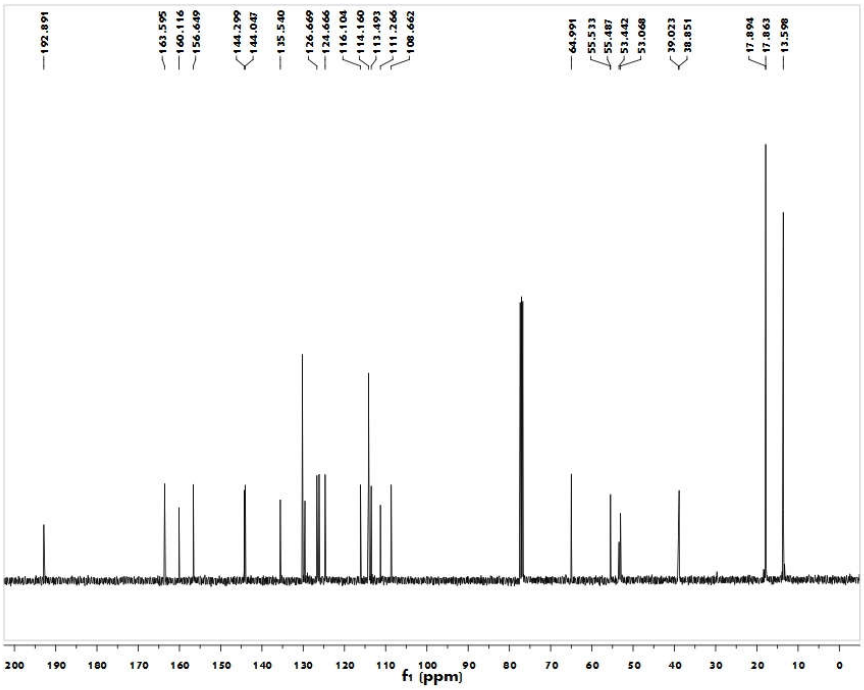


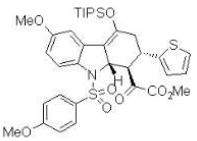
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-28T20:34:47
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: -261.73
Ph1: 14.21



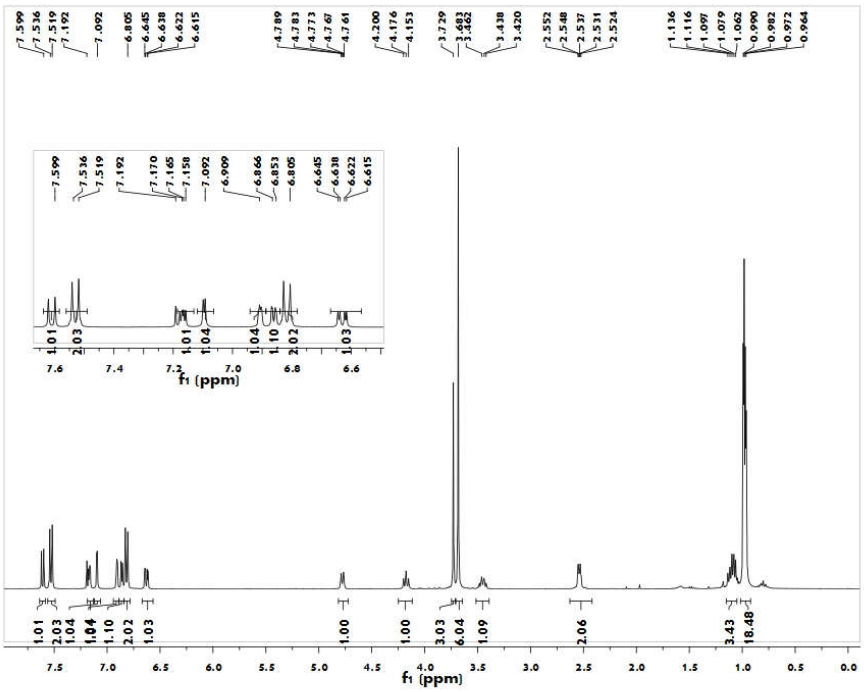


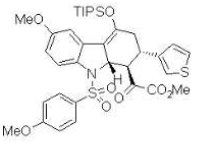
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-28T20:50:21
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -65.20
Ph1: 67.01



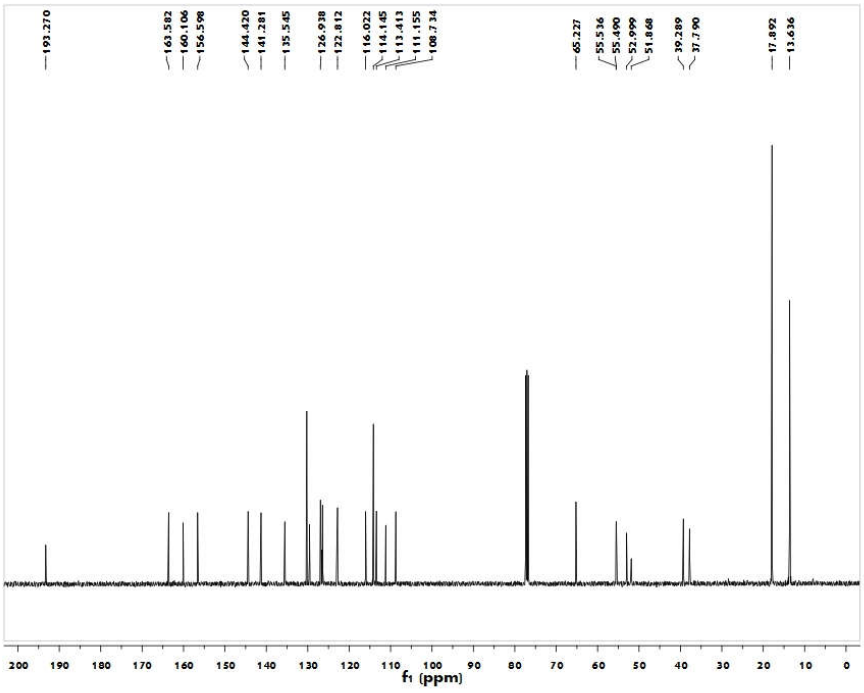


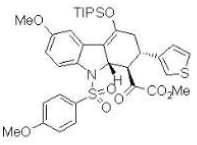
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-29T18:37:17
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: 96.63
Ph1: 17.01



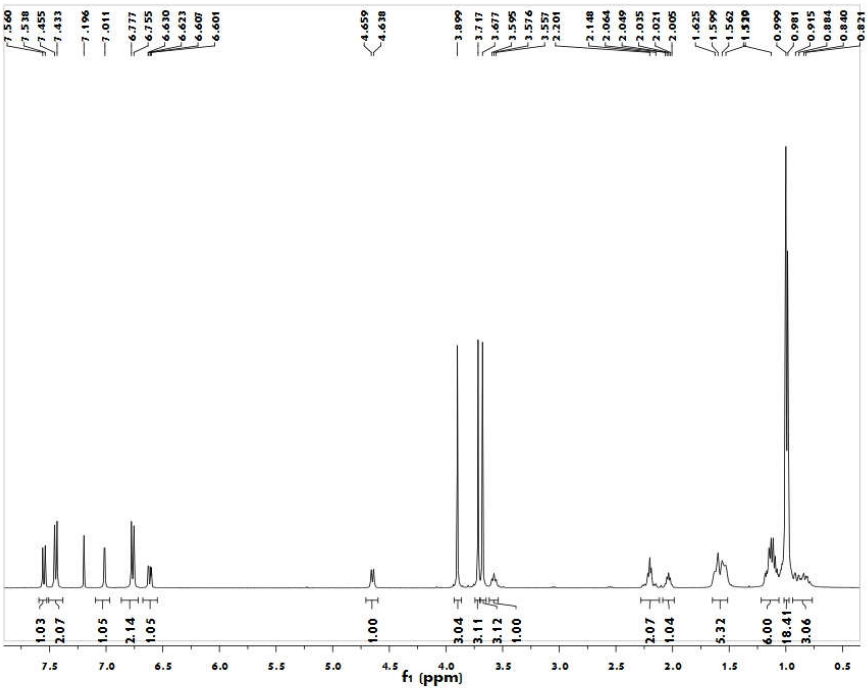


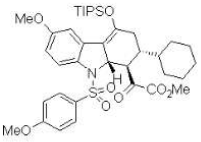
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-29T19:07:31
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -61.37
Ph1: 62.83



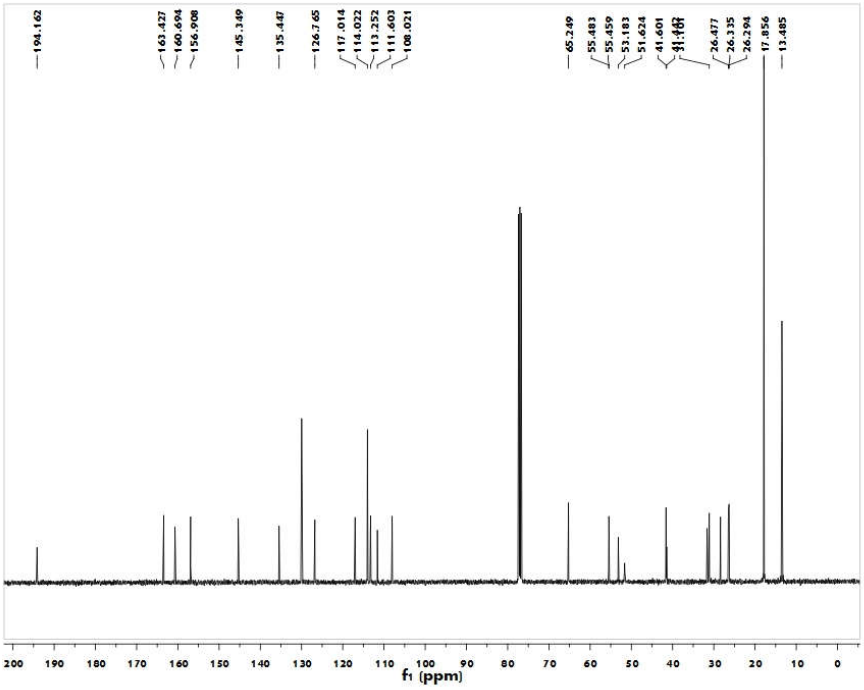


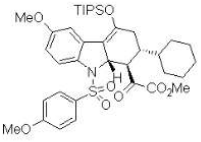
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-29T19:50:50
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: -265.58
Ph1: 20.25



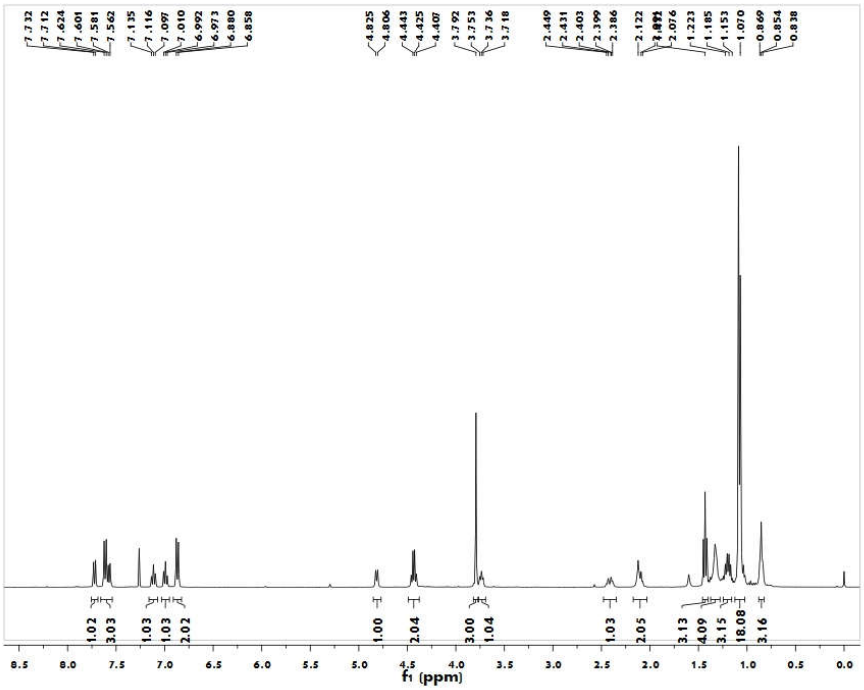


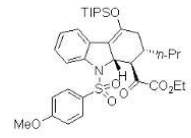
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-29T20:50:16
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 1024
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -66.82
Ph1: 65.91



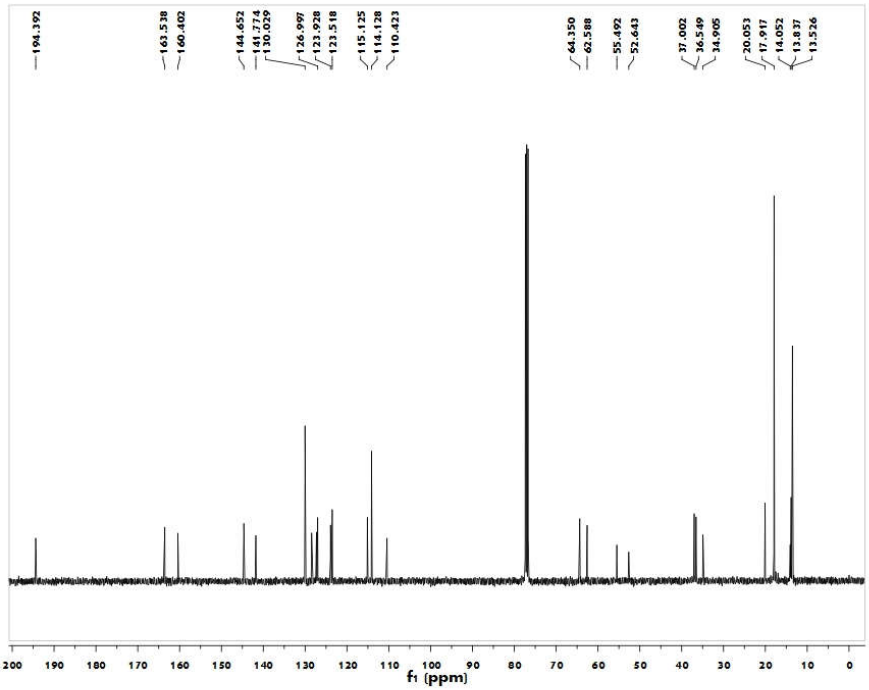


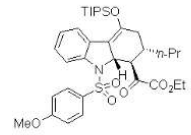
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-05-03T15:03:17
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: 81.83
Ph1: 18.04



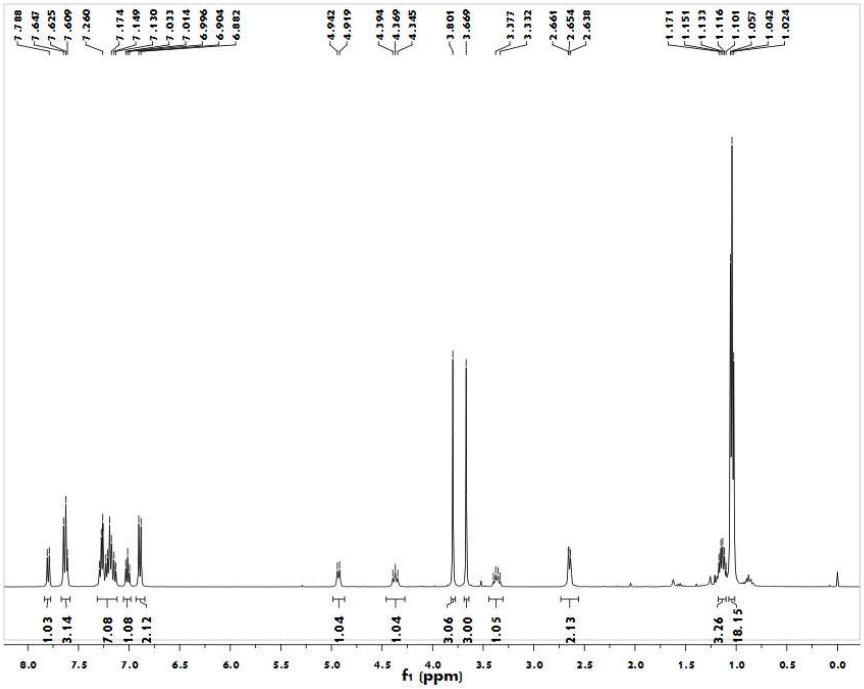


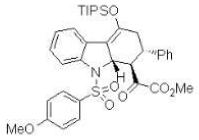
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-05-03T15:33:28
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -69.52
Ph1: 61.71



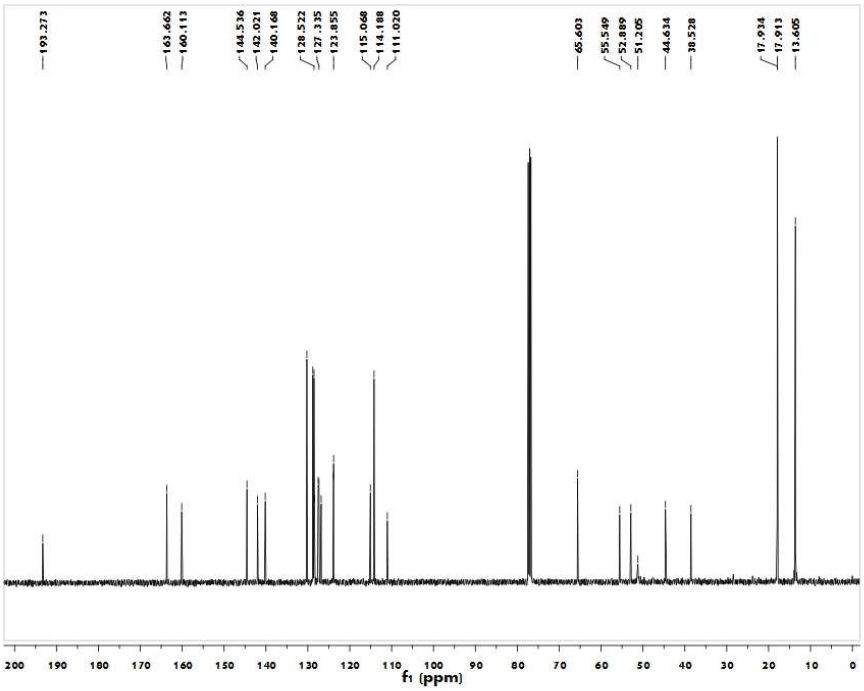


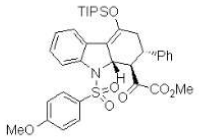
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-25T17:45:26
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: 94.74
Ph1: 18.59



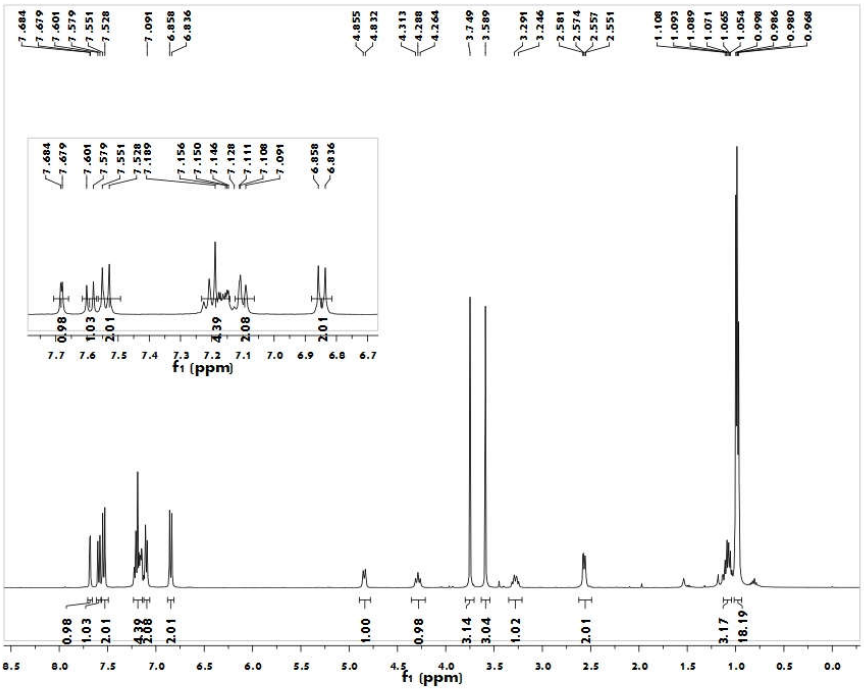


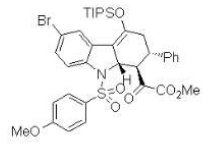
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-25T18:15:38
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -67.51
Ph1: 64.32



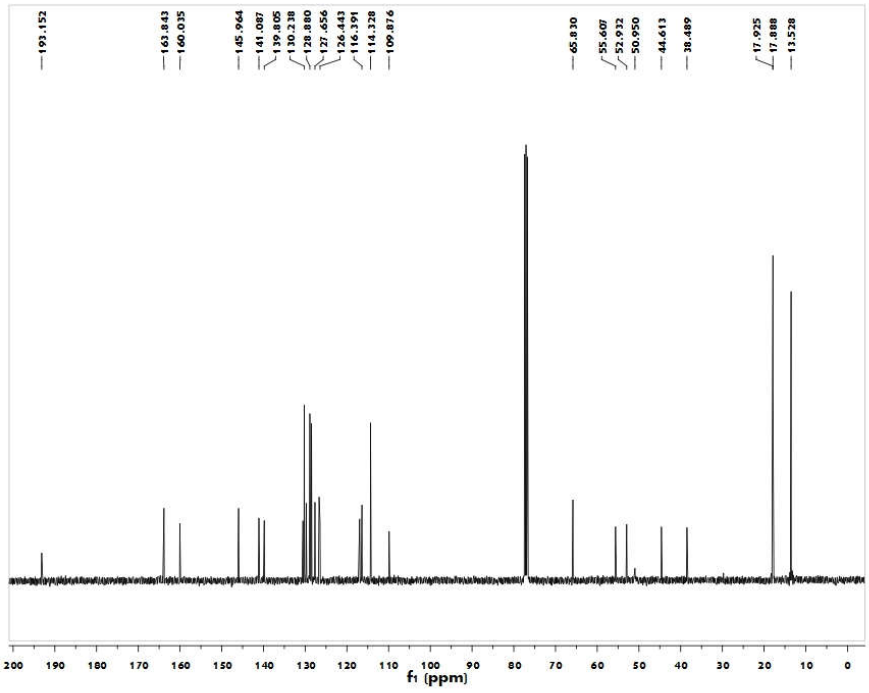


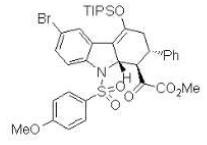
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-28T20:15:15
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: 94.73
Ph1: 18.43



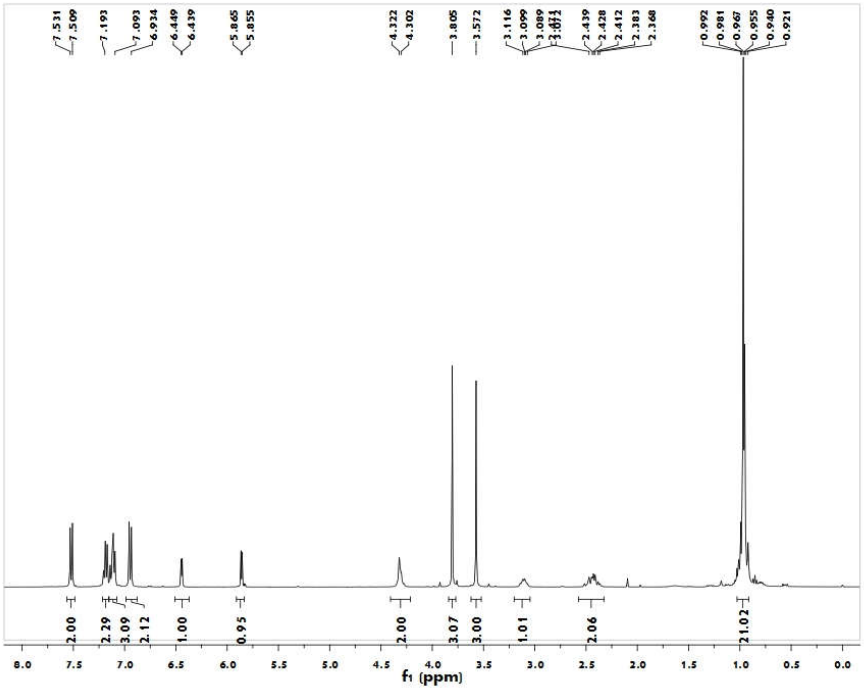


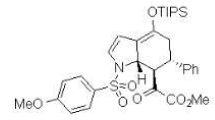
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2015-12-28T20:30:52
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -65.73
Ph1: 56.27



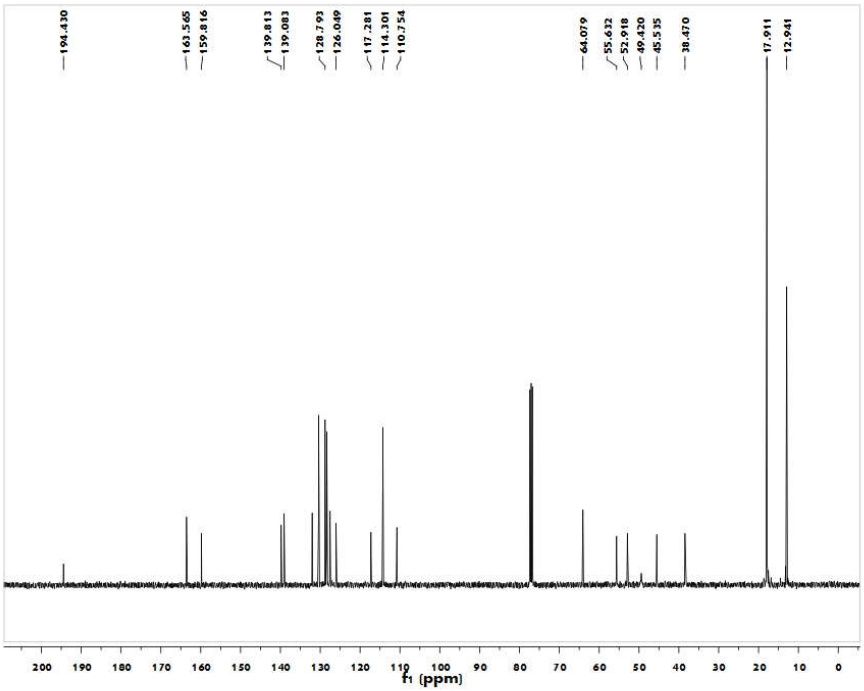


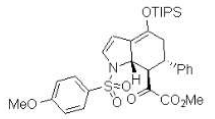
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-01-19T21:12:12
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 0 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: -264.10
Ph1: 13.20



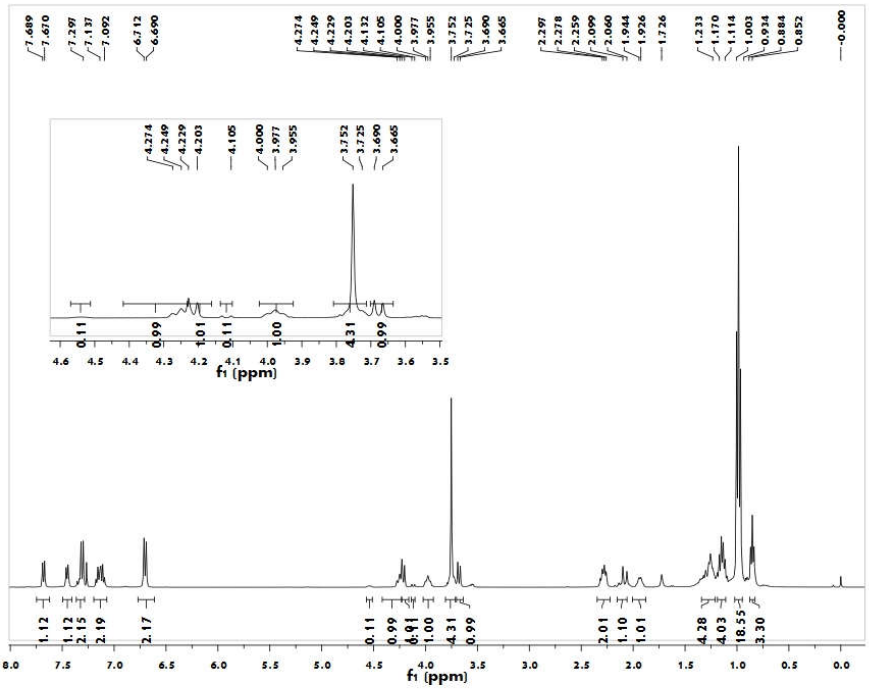


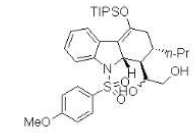
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-01-19T21:27:48
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 256
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 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: -61.69
Ph1: 65.15



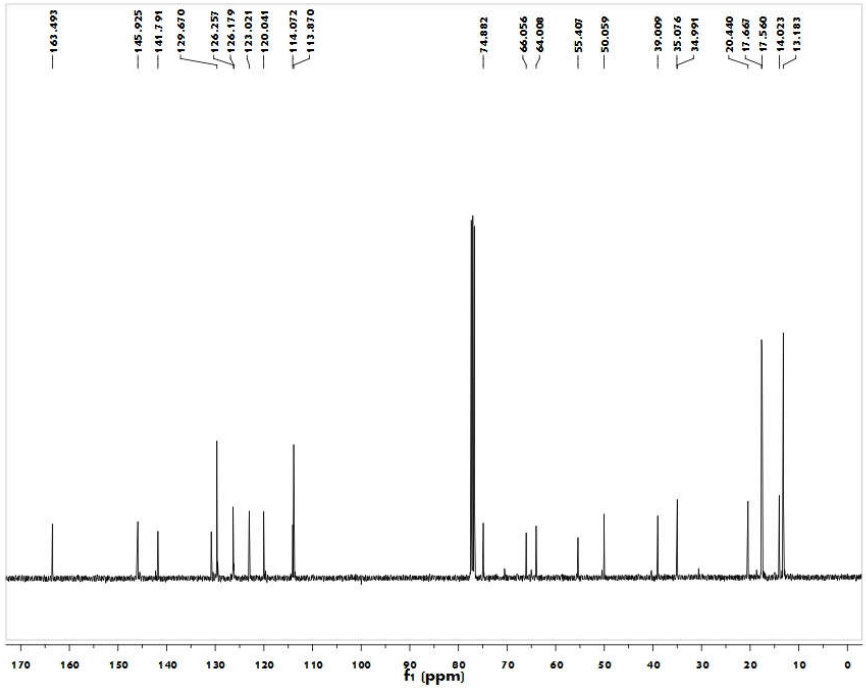


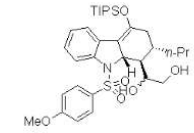
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-05-04T01:34:29
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 301 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: 84.14
Ph1: 18.94



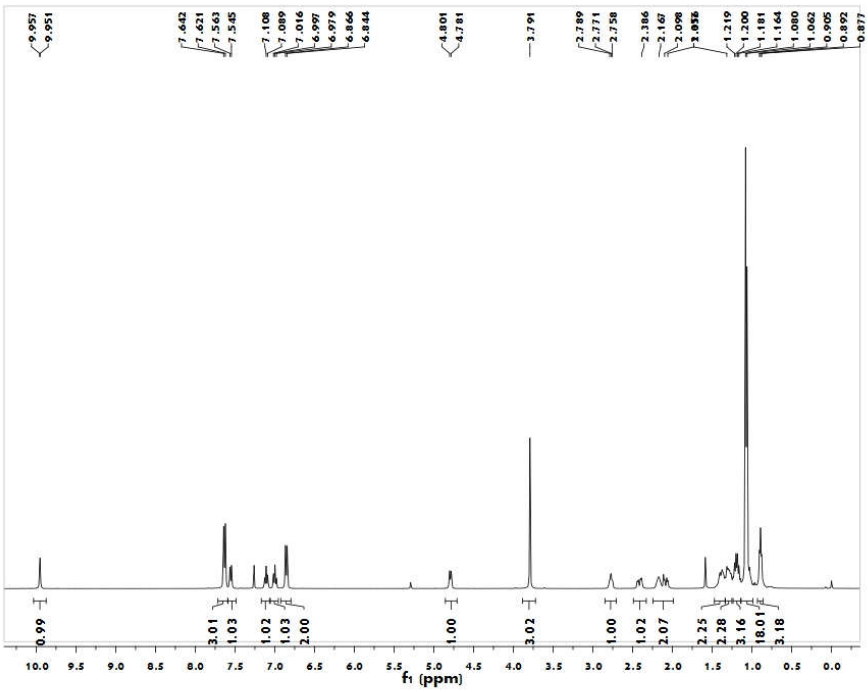


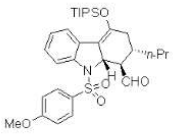
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-05-04T02:04:40
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 301 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: -62.29
Ph1: 57.25



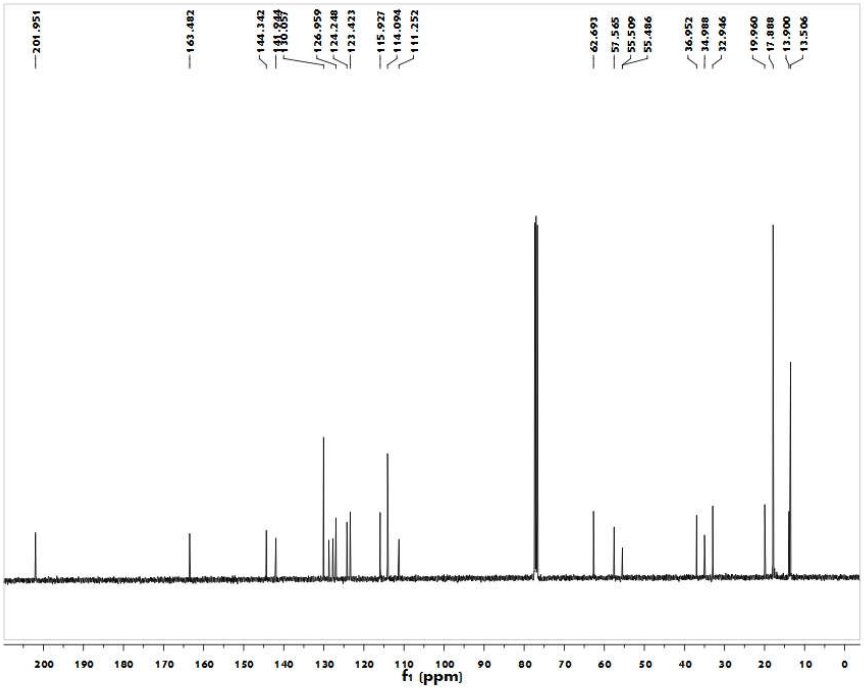


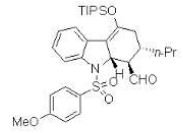
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-05-04T17:33:49
PULPROG: zg30
TD: 32768
Solvent: CDCl3
NS: 16
DS: undefined
SWH: 8223.7 Hz
AQ: undefined
TE: 645.3 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: 74.40
Ph1: 19.34





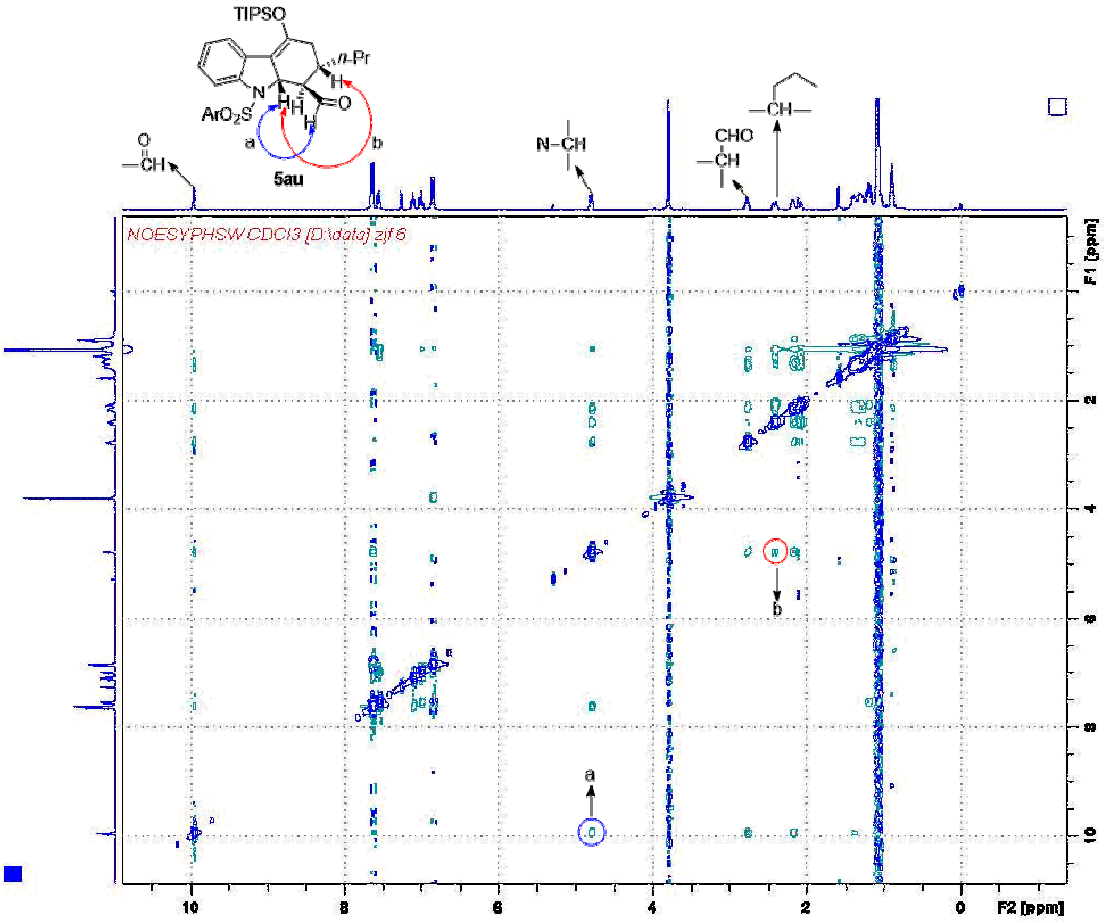
Current Data Parameters

F2 - Acquisition Parameters
DATE: 2016-05-04T18:04:01
PULPROG: zgpg30
TD: 32768
Solvent: CDCl3
NS: 512
DS: undefined
SWH: 24038.5 Hz
AQ: undefined
TE: 0 C

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

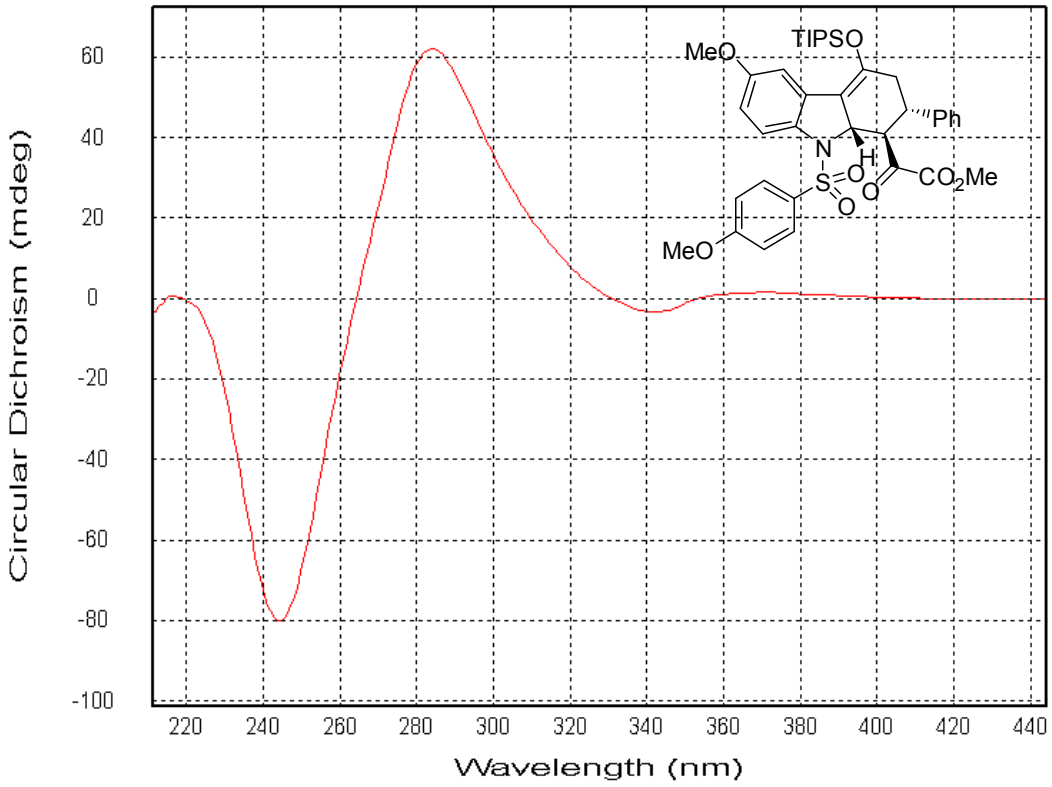
F2 - Processing Parameters
SI: 65536
DC: 0.05
LB: 1.00 Hz
First Point: 0.50
FT: Hyper Quadrature
Phase: Manual
Ph0: -77.03
Ph1: 66.97

8. NOESY spectra for the compound 5au

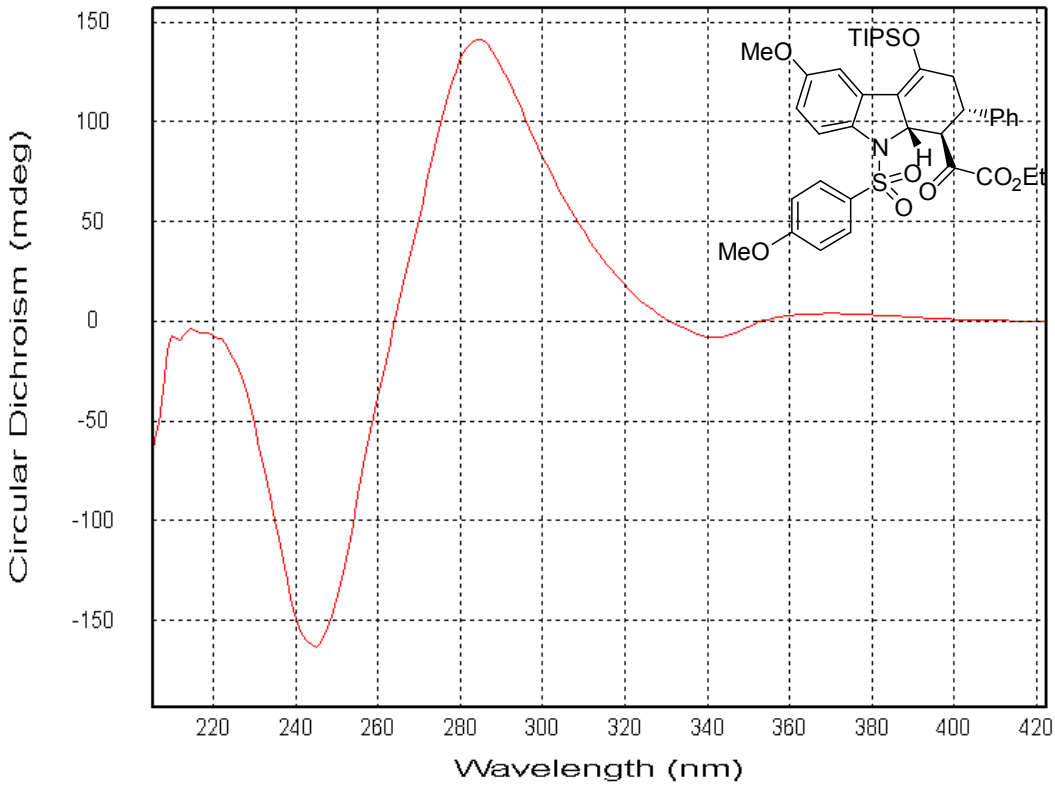


9. CD datas

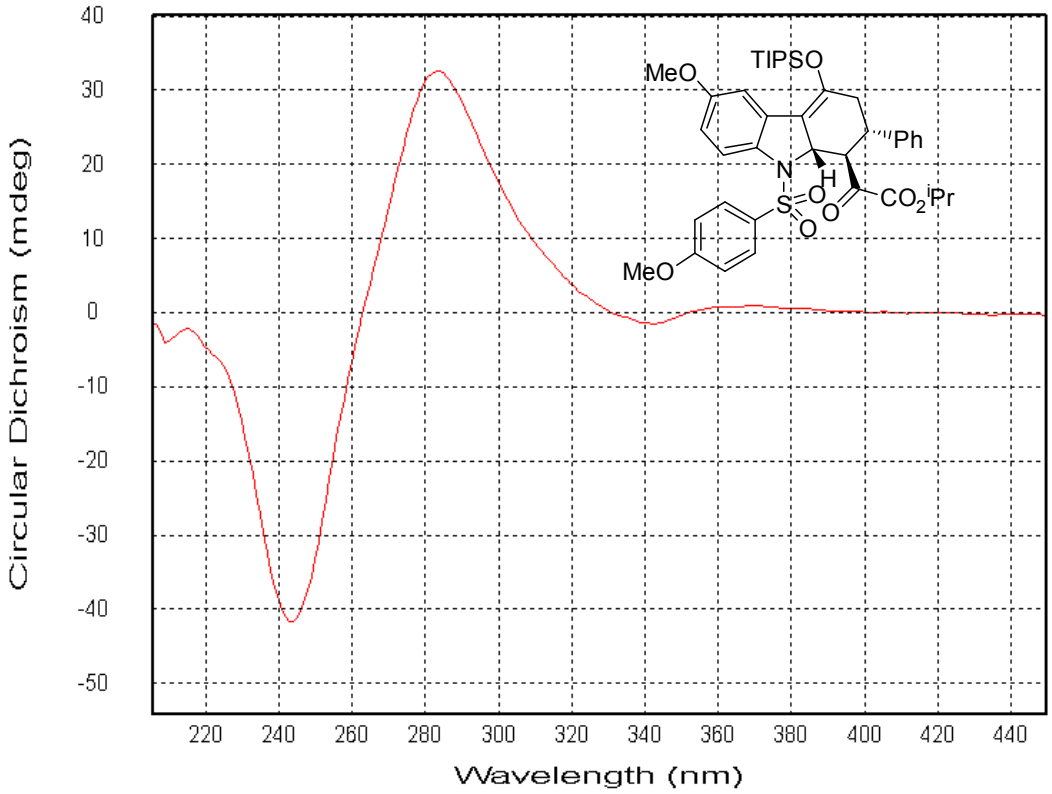
3ba



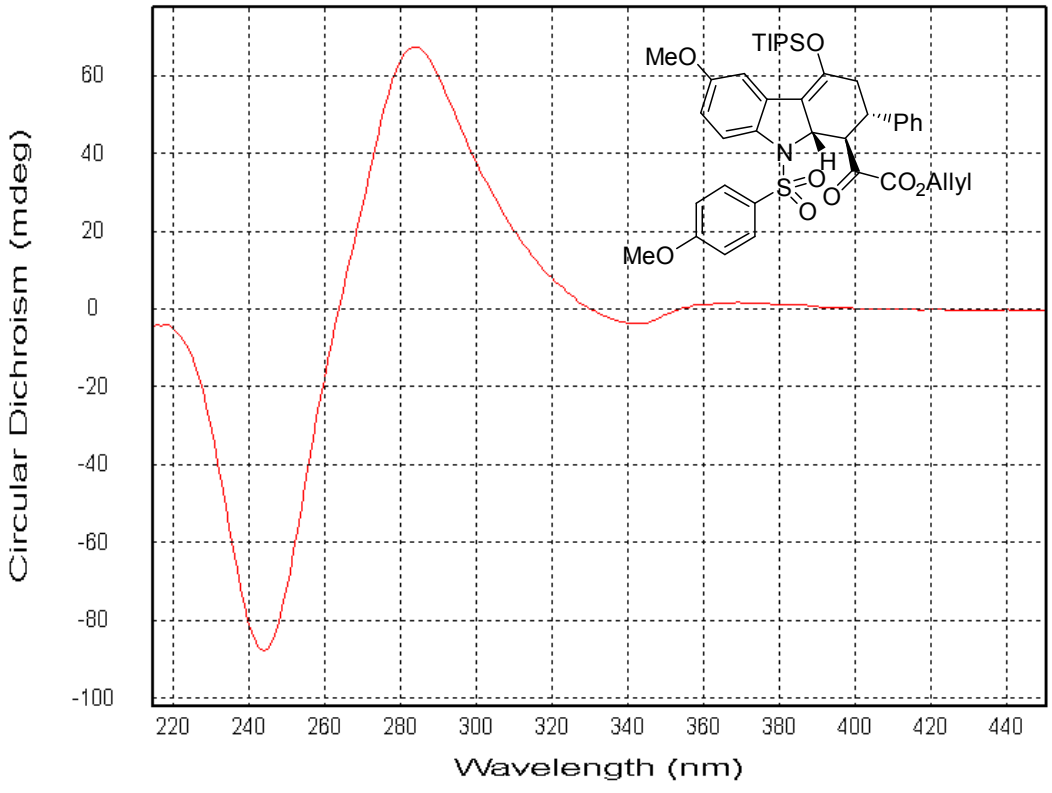
3bb



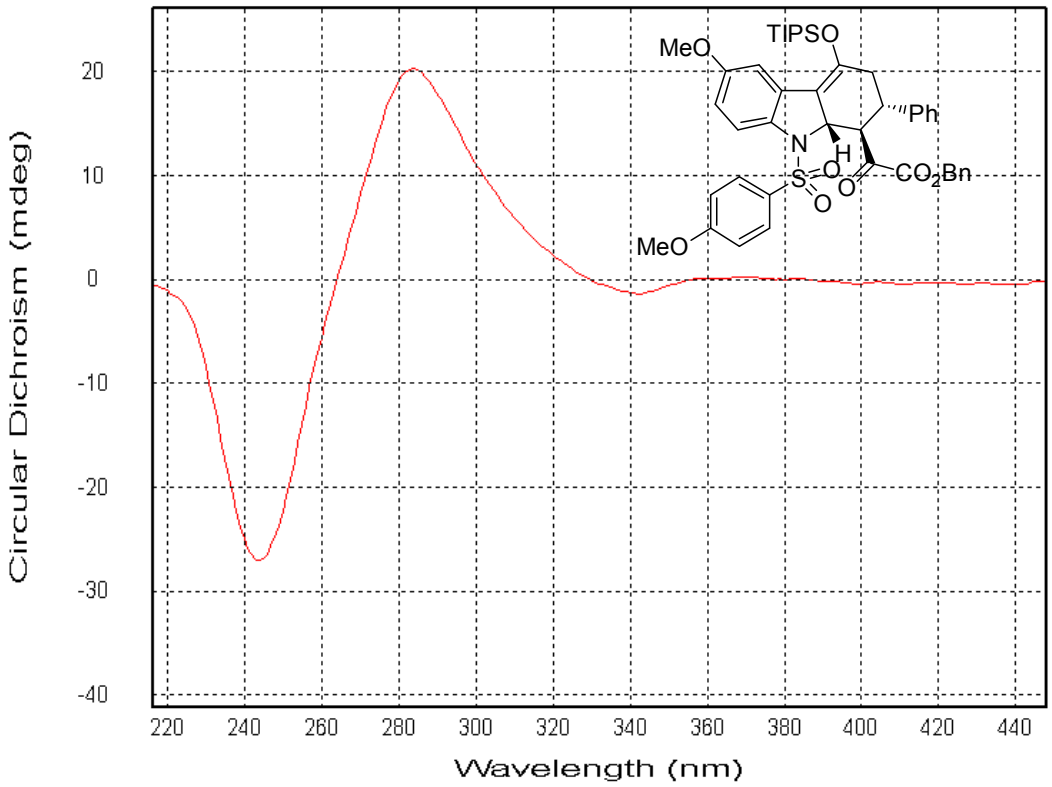
3bc


Circular Dichroism (mdeg)
40
30
20
10
0
-10
-20
-30
-40
-50
220
240
260
280
300
320
340
360
380
400
420
440
Wavelength (nm)
MeO
TIPSO
Ph
N
H
S
O
O
O
CO2iPr
MeO

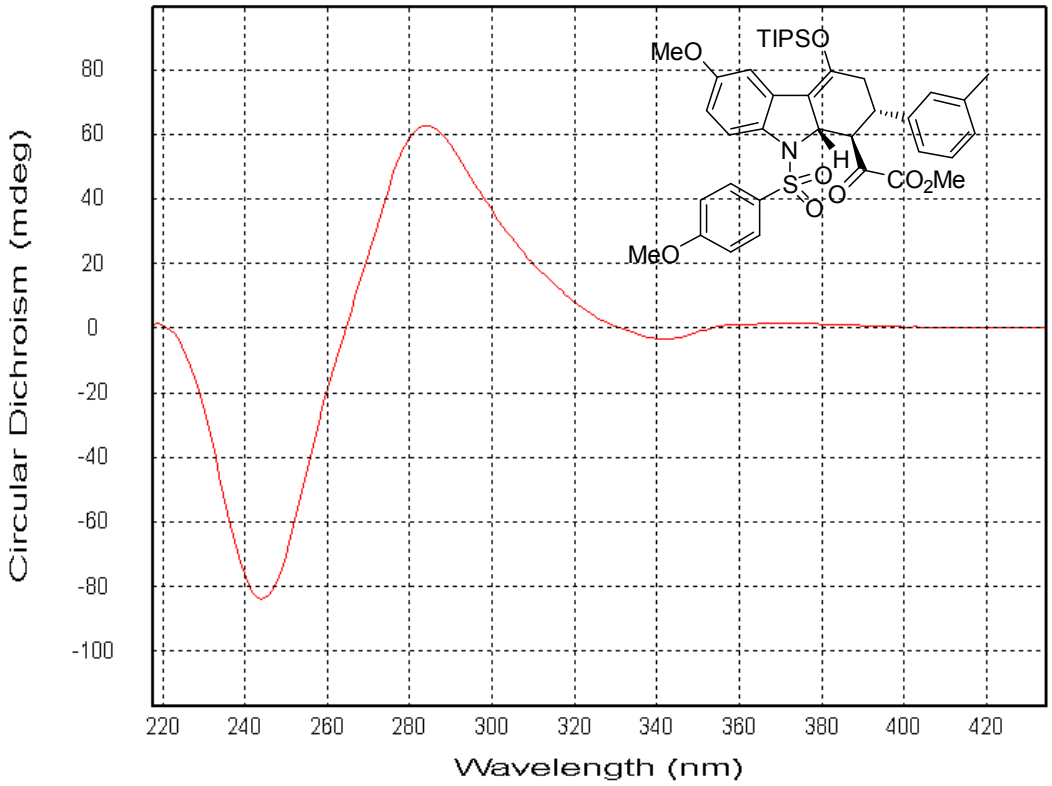
3bd


Circular Dichroism (mdeg)
60
40
20
0
-20
-40
-60
-80
-100
220
240
260
280
300
320
340
360
380
400
420
440
Wavelength (nm)
MeO
TIPSO
Ph
N
H
S
O
O
O
CO2Allyl
MeO

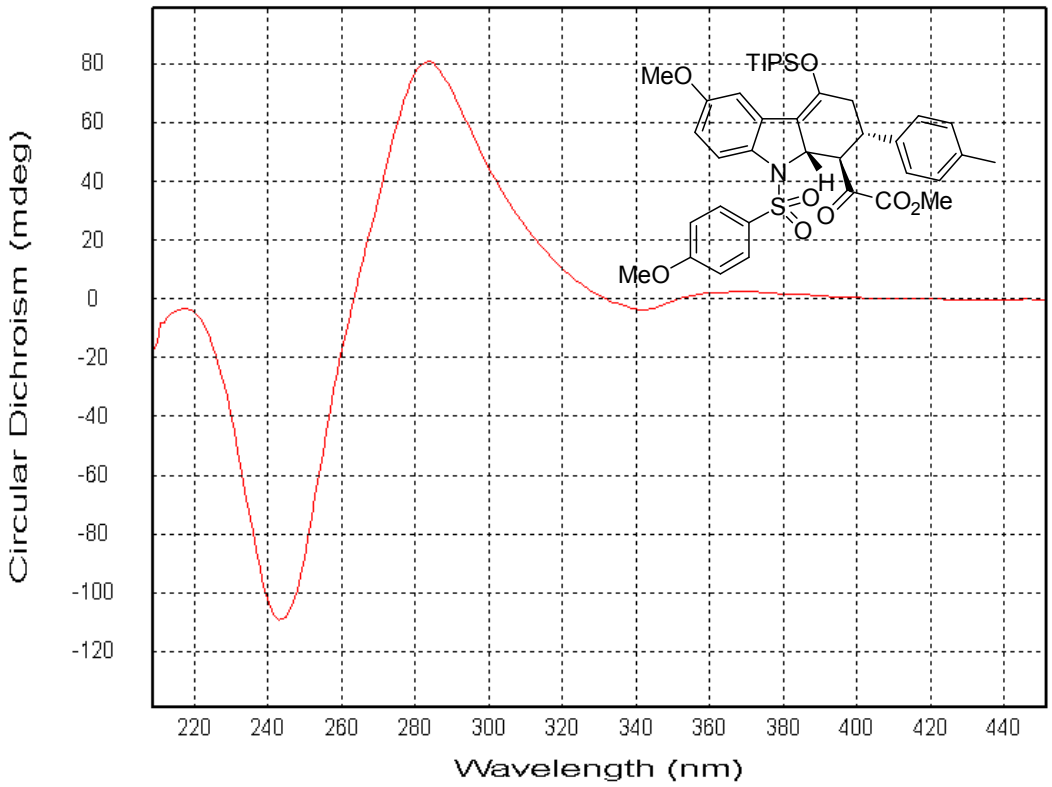
3be


Circular Dichroism (mdeg)
20
10
0
-10
-20
-30
-40
220
240
260
280
300
320
340
360
380
400
420
440
Wavelength (nm)
MeO
TIPSO
Ph
N
H
S
O
O
O
CO2Bn
MeO

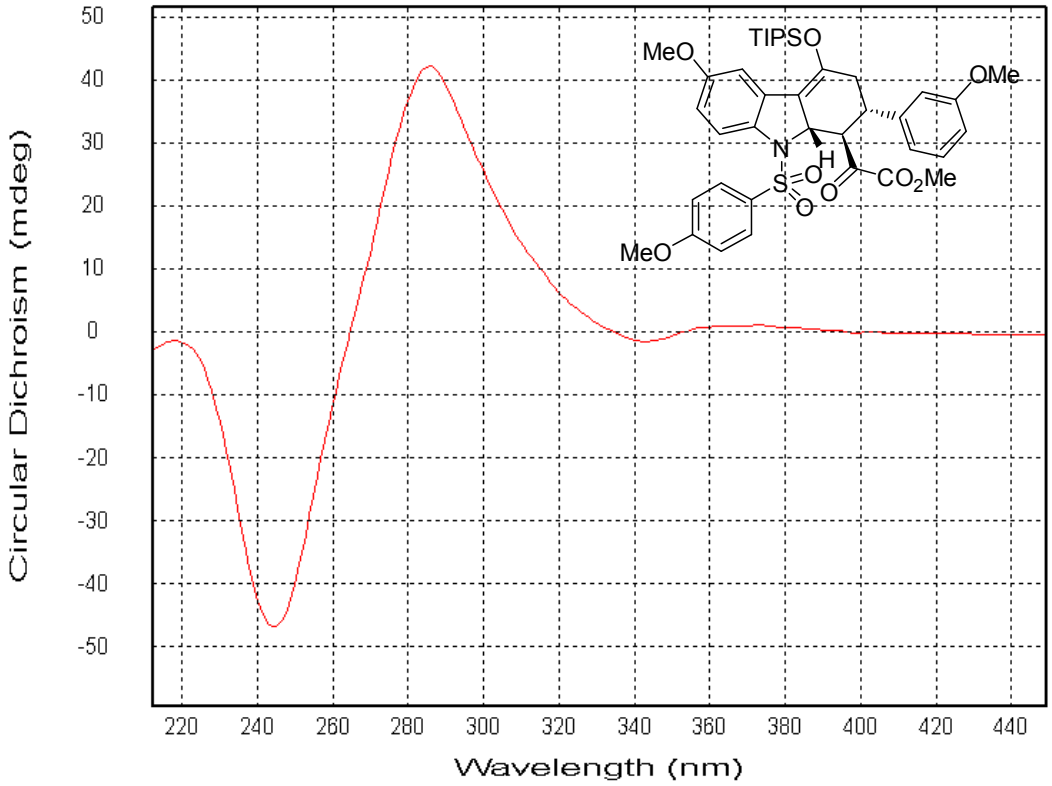
3bf


Circular Dichroism (mdeg)
80
60
40
20
0
-20
-40
-60
-80
-100
220
240
260
280
300
320
340
360
380
400
420
Wavelength (nm)
MeO
TIPSO
N
H
S
O
O
O
CO2Me
MeO

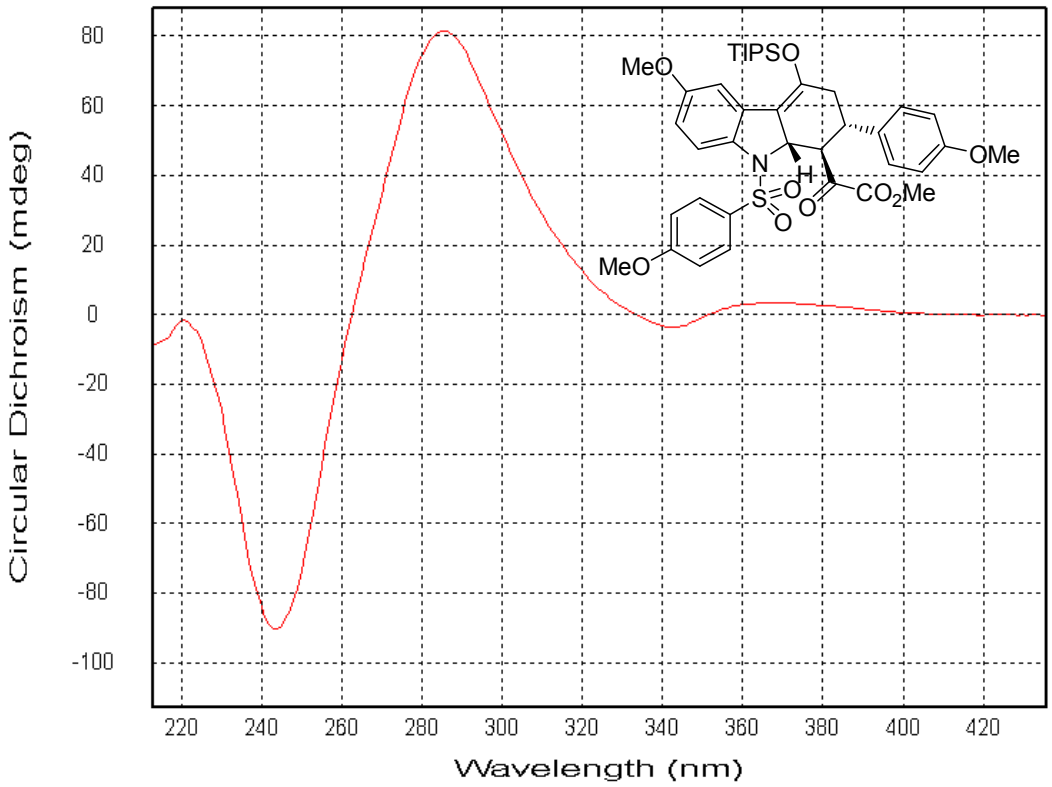
3bg


Circular Dichroism (mdeg)
80
60
40
20
0
-20
-40
-60
-80
-100
-120
220
240
260
280
300
320
340
360
380
400
420
440
Wavelength (nm)
MeO
TIPSO
N
H
S
O
O
O
CO2Me
MeO

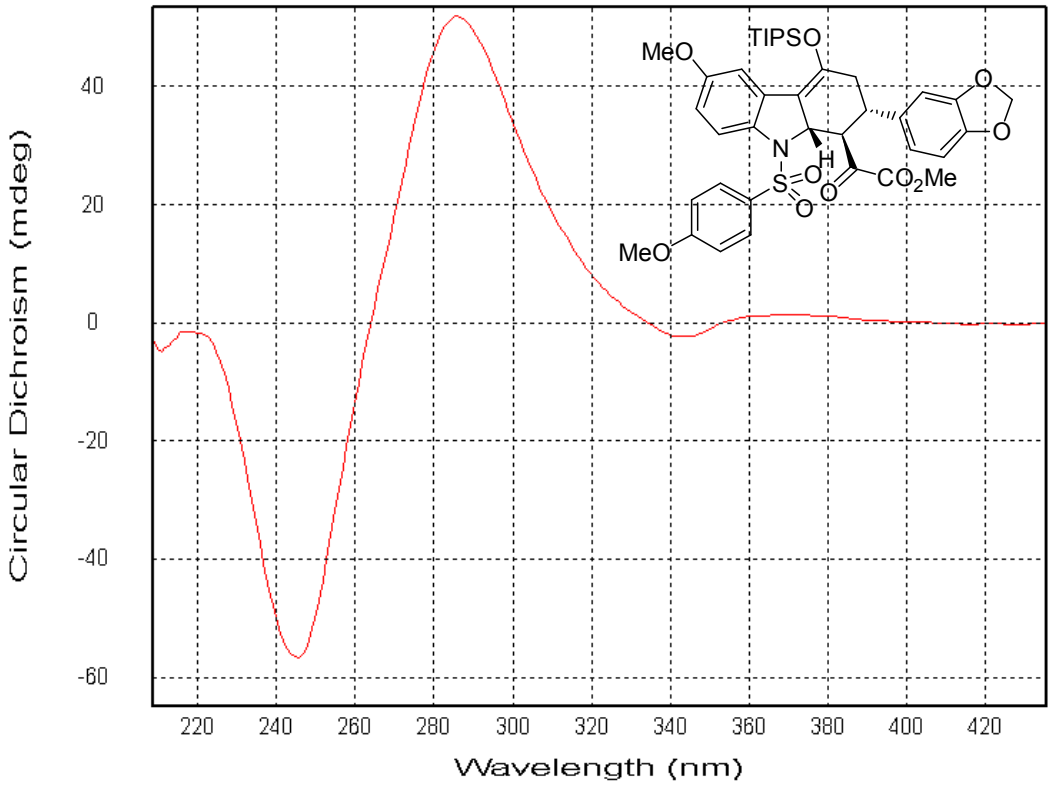
3bh


Circular Dichroism (mdeg)
50
40
30
20
10
0
-10
-20
-30
-40
-50
220
240
260
280
300
320
340
360
380
400
420
440
Wavelength (nm)
MeO
TIPSO
OMe
N
H
S
O
O
O
CO2Me
MeO

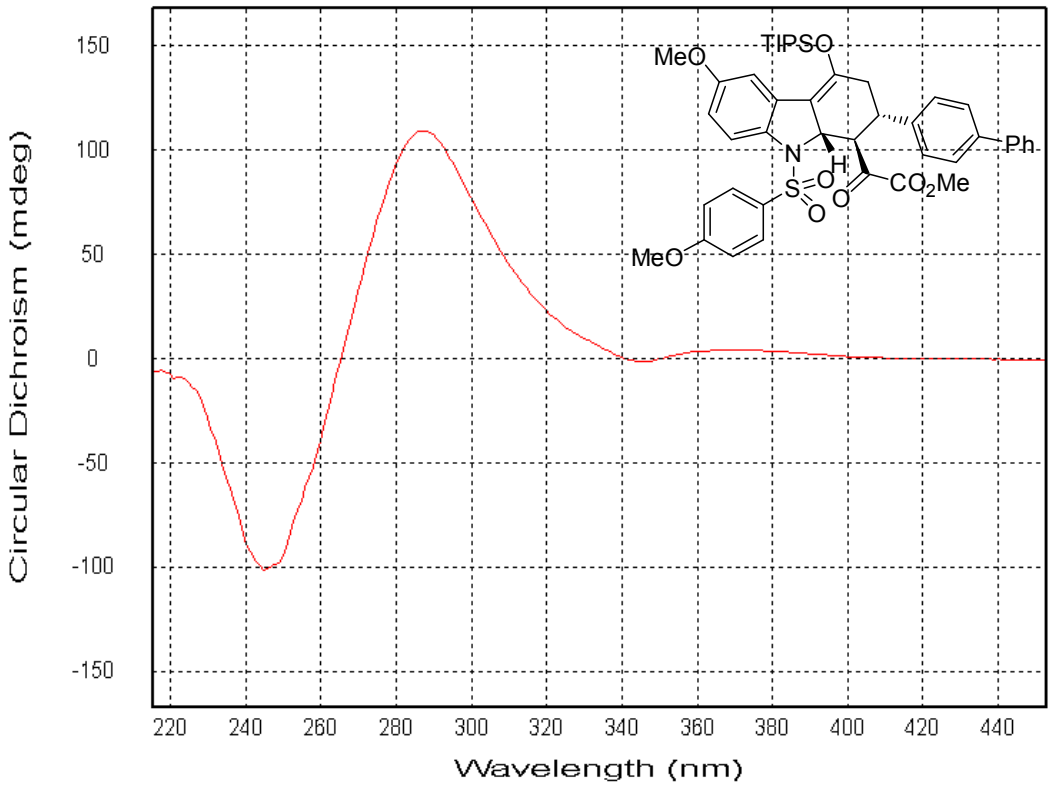
3bi


Circular Dichroism (mdeg)
80
60
40
20
0
-20
-40
-60
-80
-100
220
240
260
280
300
320
340
360
380
400
420
Wavelength (nm)
MeO
TIPSO
OMe
N
H
S
O
O
O
CO2Me
MeO

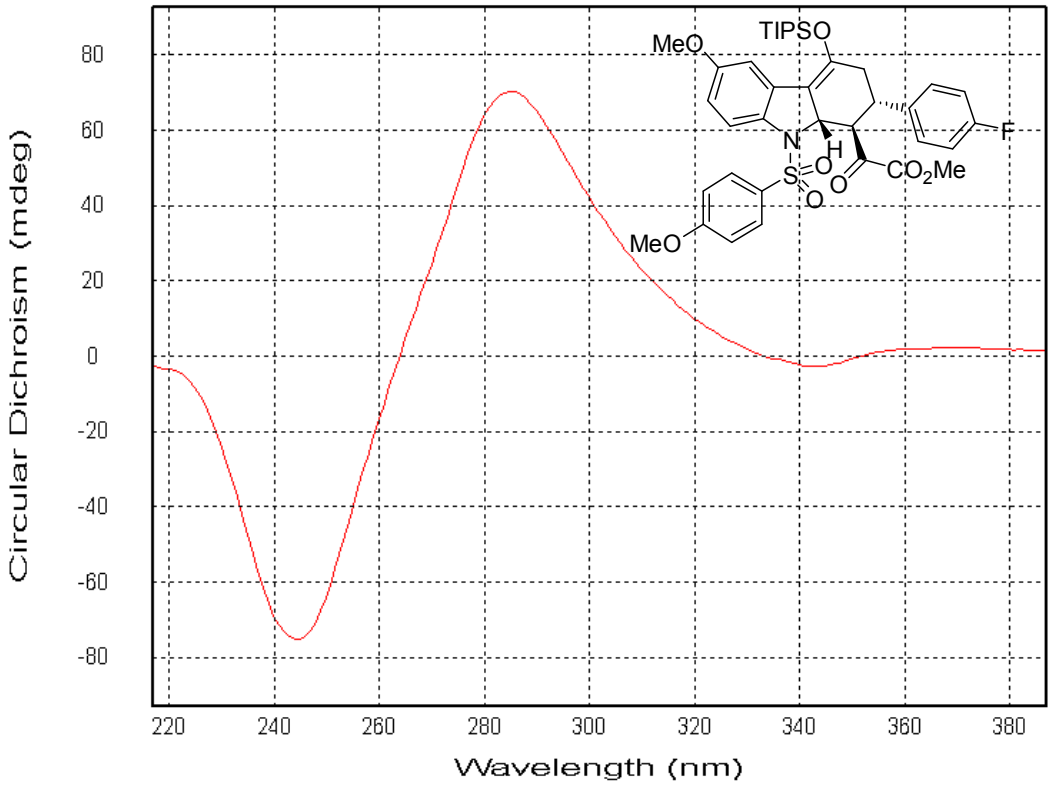
3bj


Circular Dichroism (mdeg)
40
20
0
-20
-40
-60
220
240
260
280
300
320
340
360
380
400
420
Wavelength (nm)
MeO
TIPSO
O
O
N
H
S
O
O
O
CO2Me
MeO

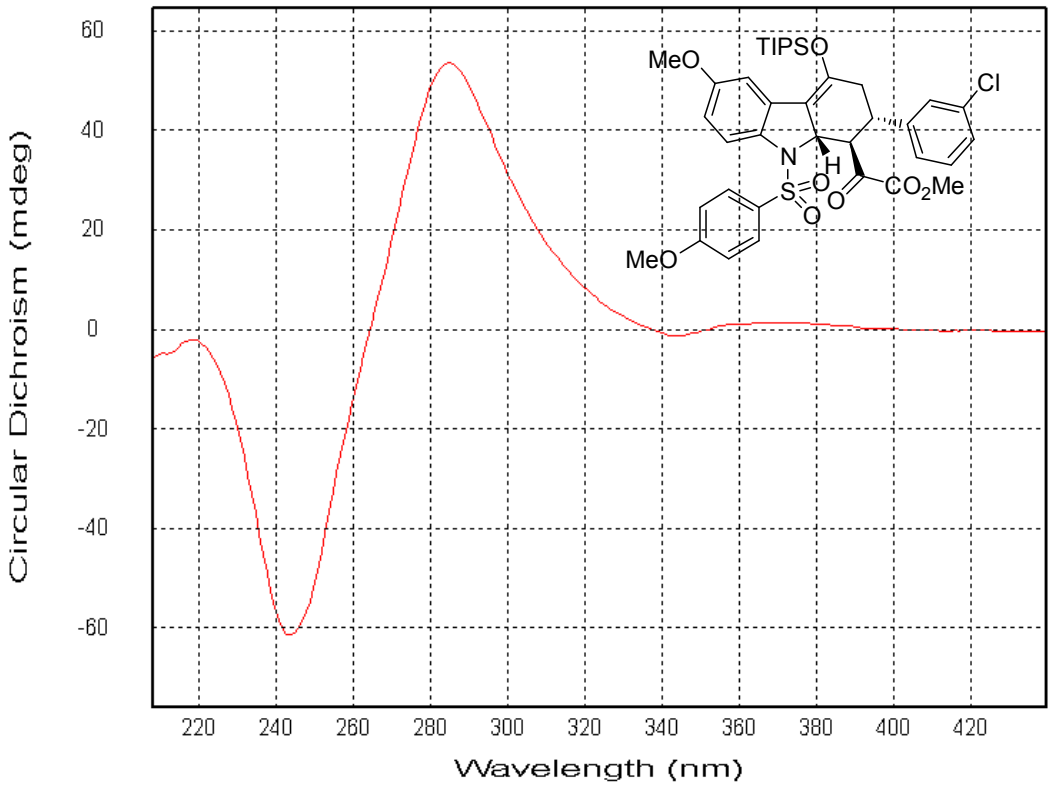
3bk


Circular Dichroism (mdeg)
150
100
50
0
-50
-100
-150
220
240
260
280
300
320
340
360
380
400
420
440
Wavelength (nm)
MeO
TIPSO
Ph
N
H
S
O
O
O
CO2Me
MeO

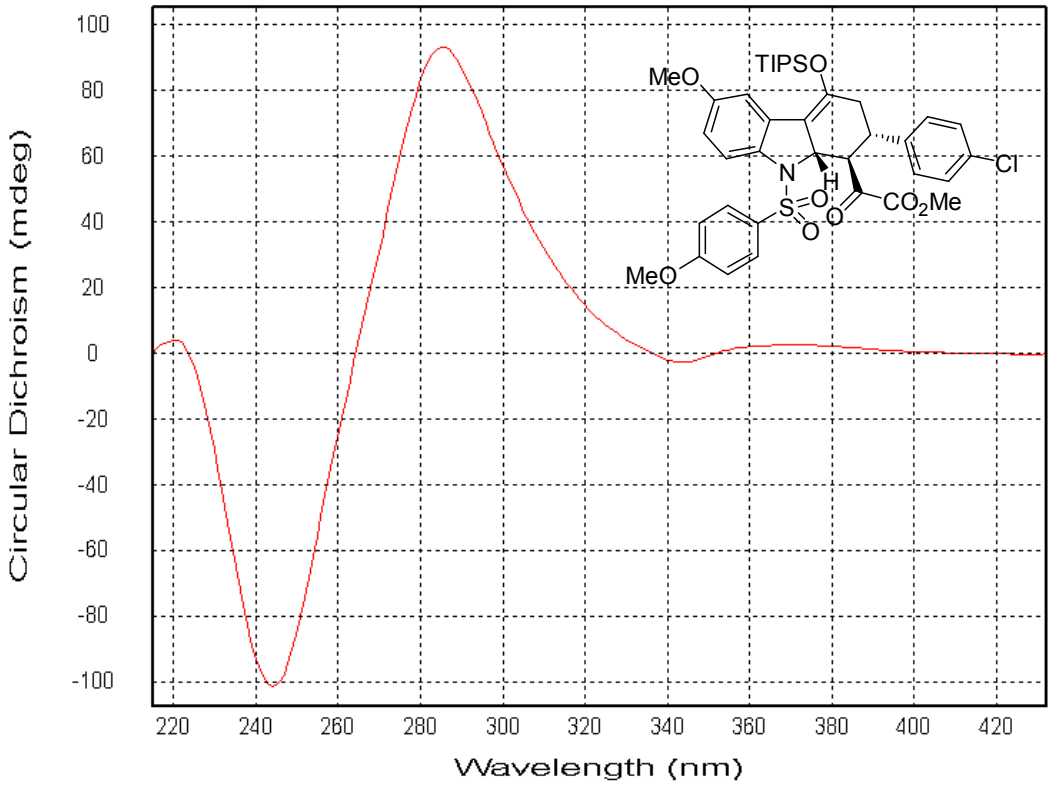
3bl


Circular Dichroism (mdeg)
80
60
40
20
0
-20
-40
-60
-80
220
240
260
280
300
320
340
360
380
Wavelength (nm)
MeO
TIPSO
F
N
H
S
O
O
O
CO2Me
MeO

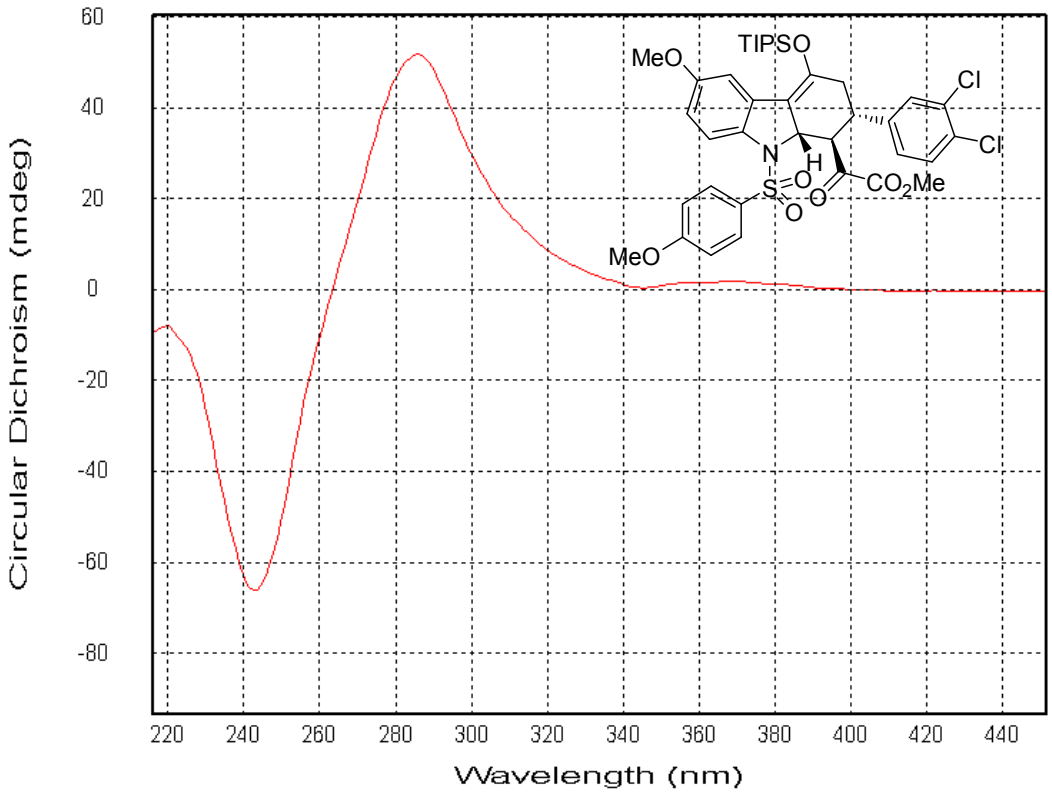
3bm


Circular Dichroism (mdeg)
60
40
20
0
-20
-40
-60
220
240
260
280
300
320
340
360
380
400
420
Wavelength (nm)
MeO
TIPSO
Cl
N
H
S
O
O
O
CO2Me
MeO

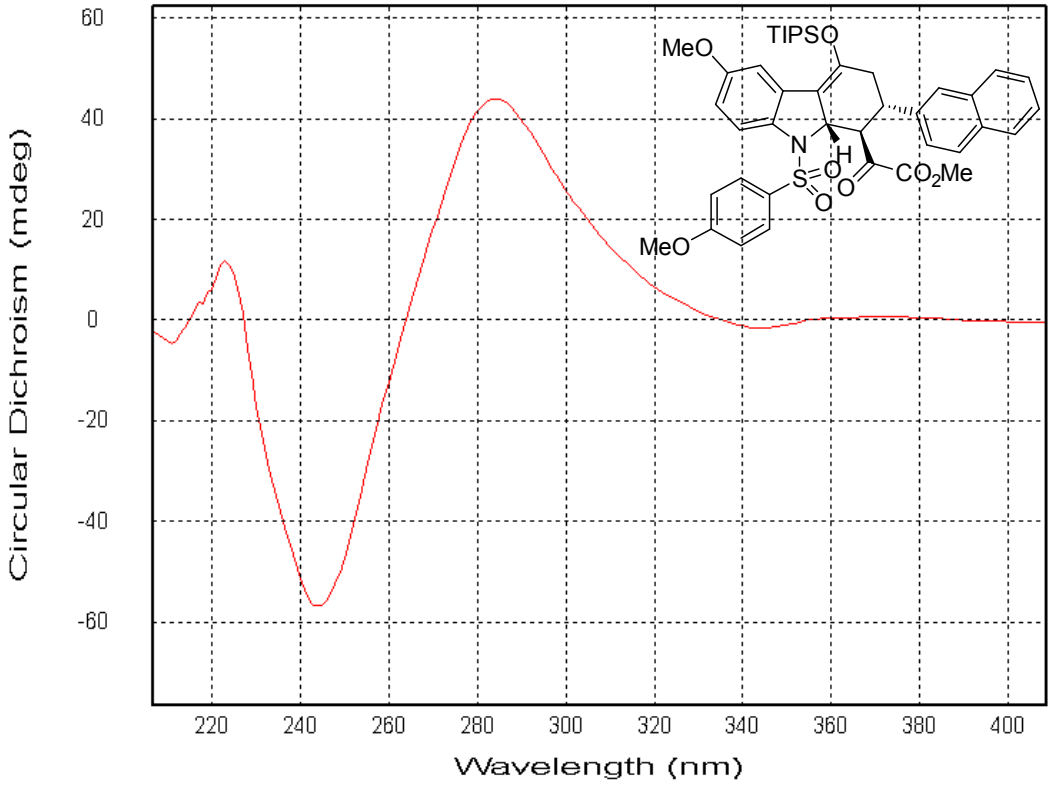
3bn


Circular Dichroism (mdeg)
100
80
60
40
20
0
-20
-40
-60
-80
-100
220
240
260
280
300
320
340
360
380
400
420
Wavelength (nm)
MeO
TIPSO
Cl
N
H
S
O
O
O
CO2Me
MeO

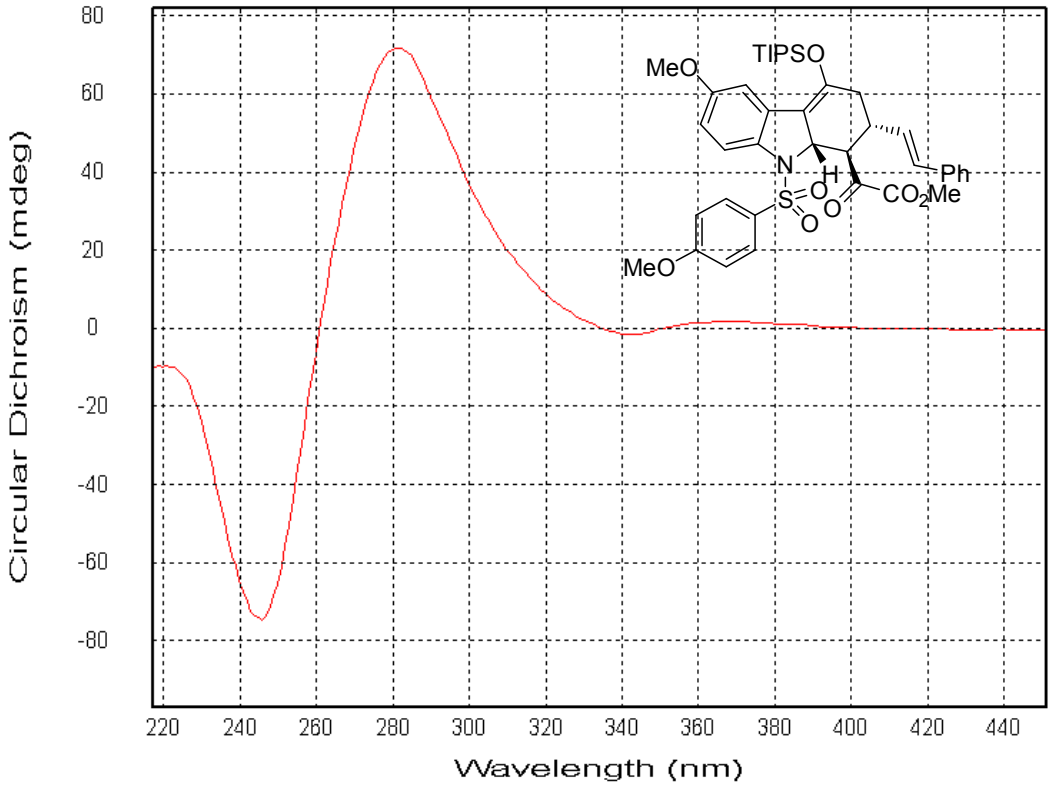
3bo


Circular Dichroism (mdeg)
60
40
20
0
-20
-40
-60
-80
220
240
260
280
300
320
340
360
380
400
420
440
Wavelength (nm)
MeO
TIPSO
Cl
Cl
N
H
S
O
O
O
CO2Me
MeO

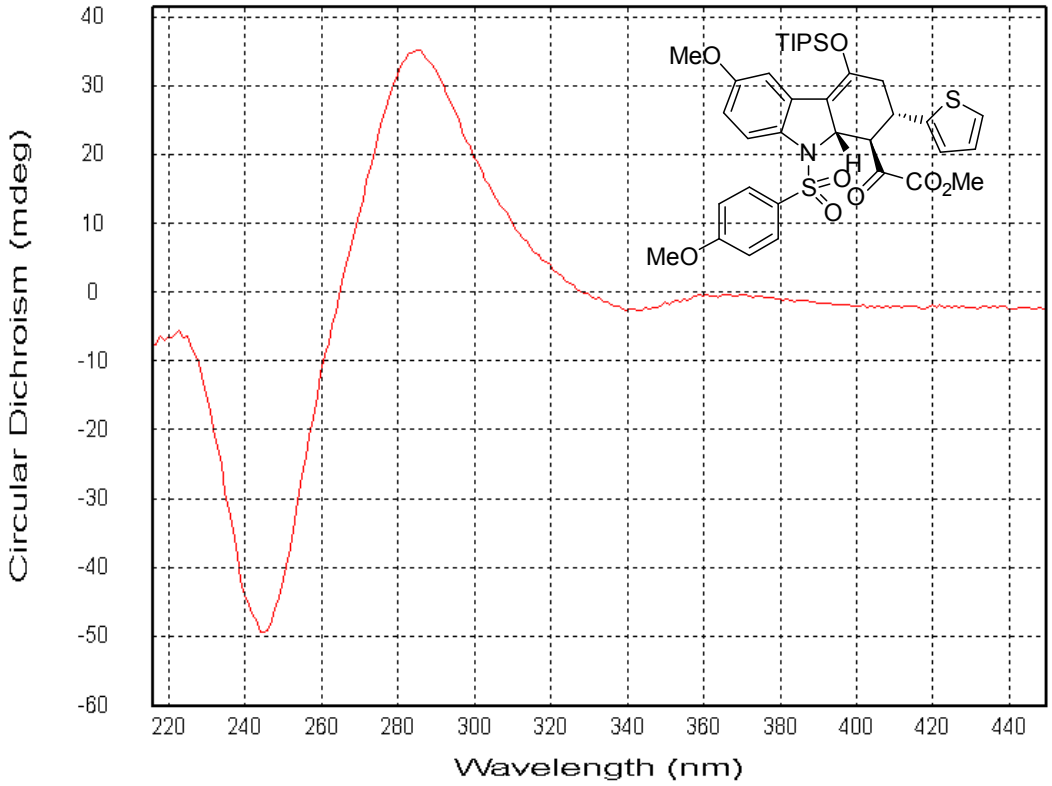
3bp


Circular Dichroism (mdeg)
60
40
20
0
-20
-40
-60
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)
MeO
TIPSO
N
H
S
O
O
O
CO2Me
MeO

3bq


Circular Dichroism (mdeg)
80
60
40
20
0
-20
-40
-60
-80
220
240
260
280
300
320
340
360
380
400
420
440
Wavelength (nm)
MeO
TIPSO
N
H
Ph
S
O
O
O
CO2Me
MeO

3br


Circular Dichroism (mdeg)
40
30
20
10
0
-10
-20
-30
-40
-50
-60
220
240
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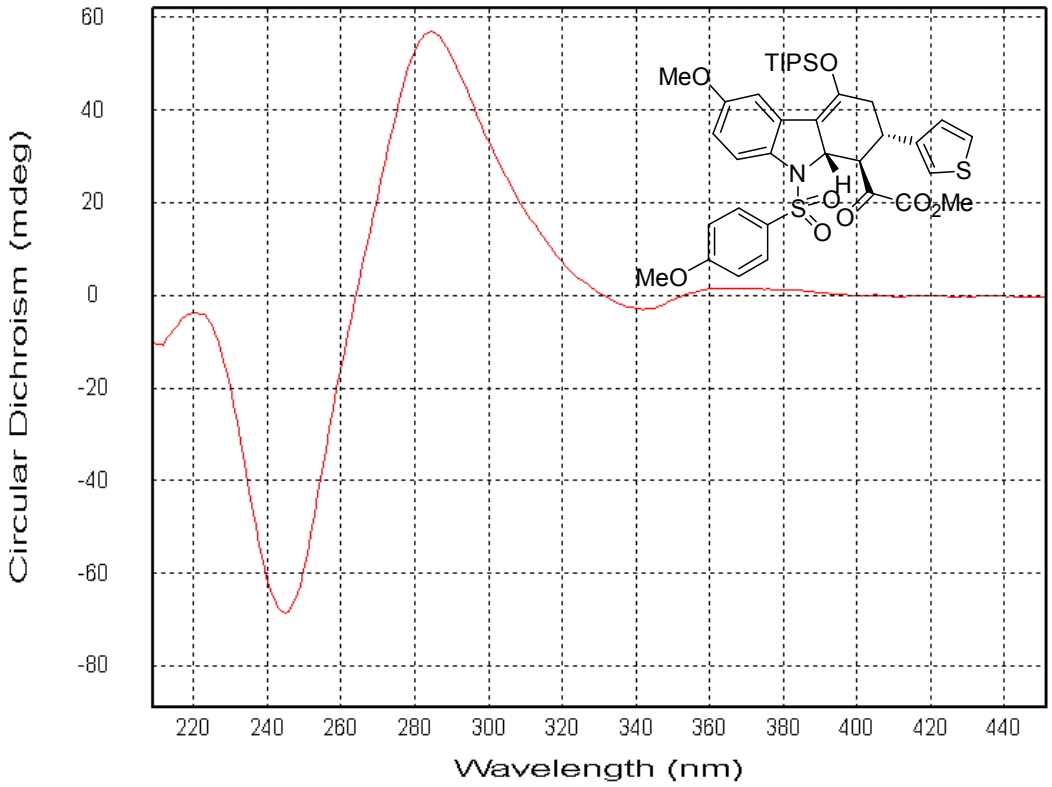
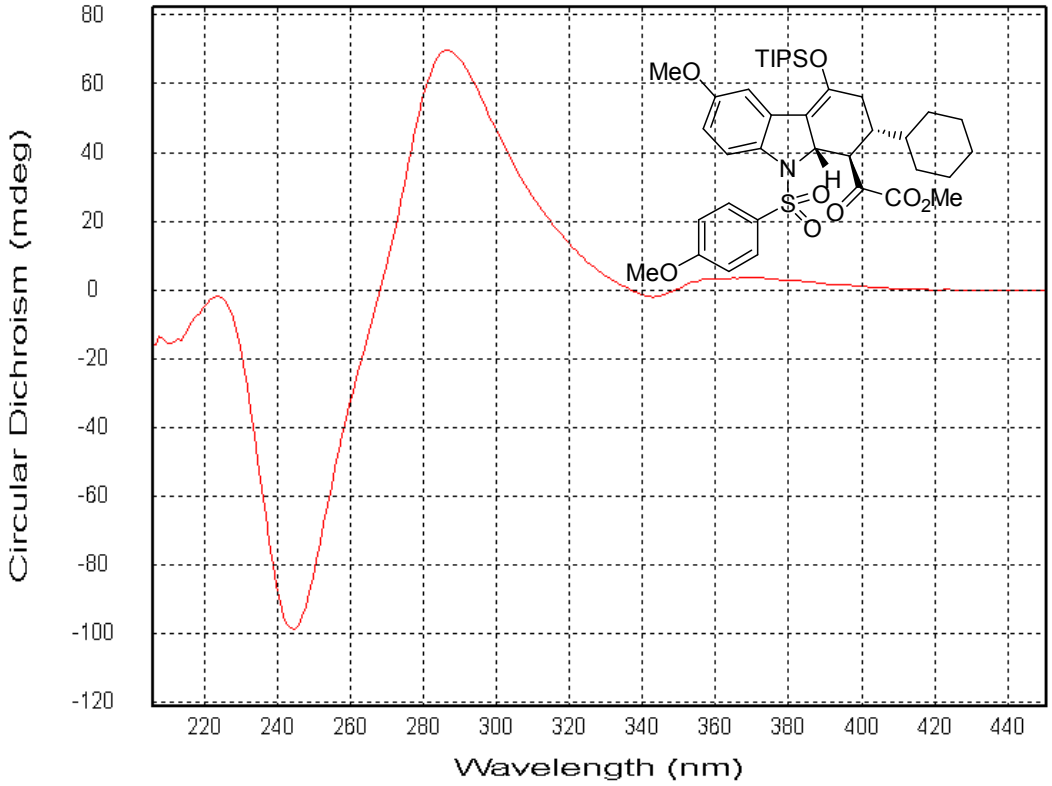
280
300
320
340
360
380
400
420
440
Wavelength (nm)
MeO
TIPSO
S
N
H
S
O
O
O
CO2Me
MeO

3bs


Circular Dichroism (mdeg)
60
40
20
0
-20
-40
-60
-80
220
240
260
280
300
320
340
360
380
400
420
440
Wavelength (nm)
MeO
TIPSO
N
H
S
O
O
O
CO2Me
S
MeO

3bt


Circular Dichroism (mdeg)
80
60
40
20
0
-20
-40
-60
-80
-100
-120
220
240
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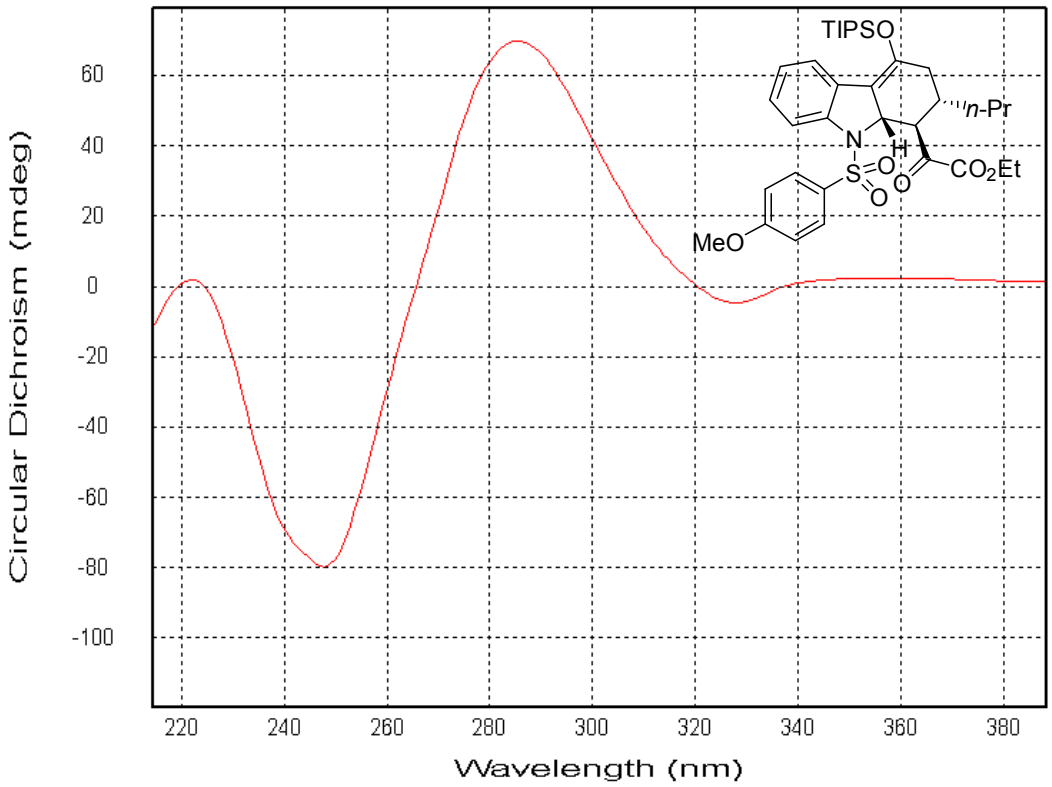
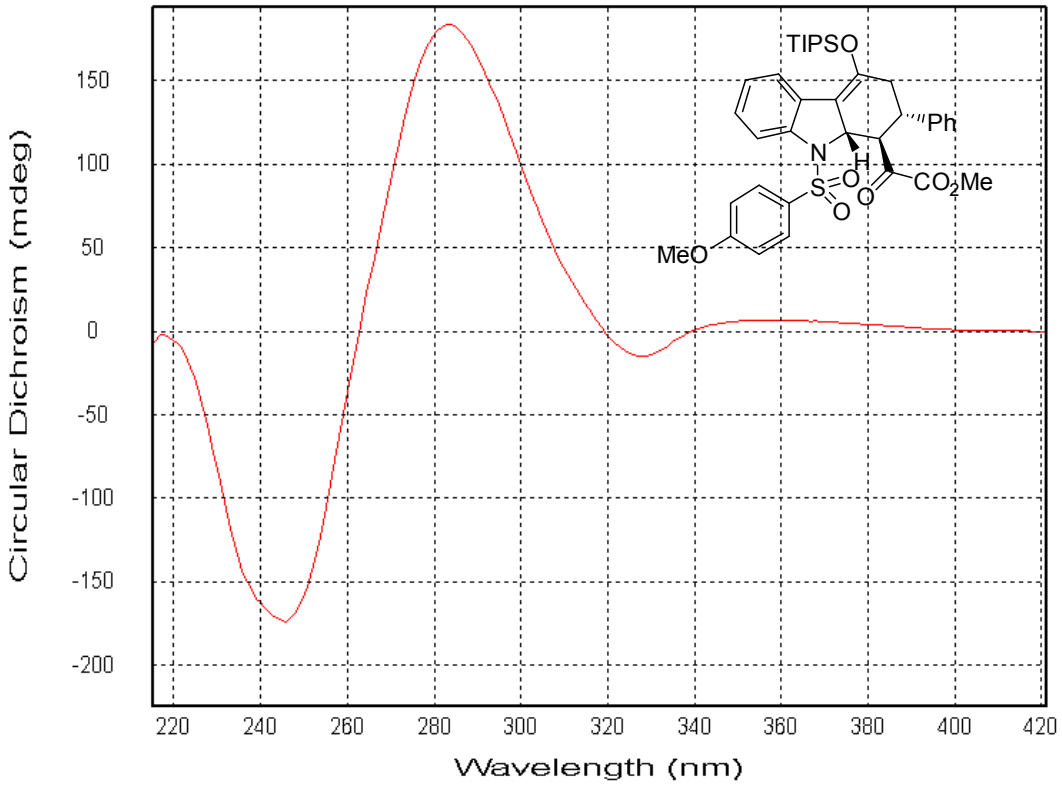
280
300
320
340
360
380
400
420
440
Wavelength (nm)
MeO
TIPSO
N
H
S
O
O
O
CO2Me
MeO

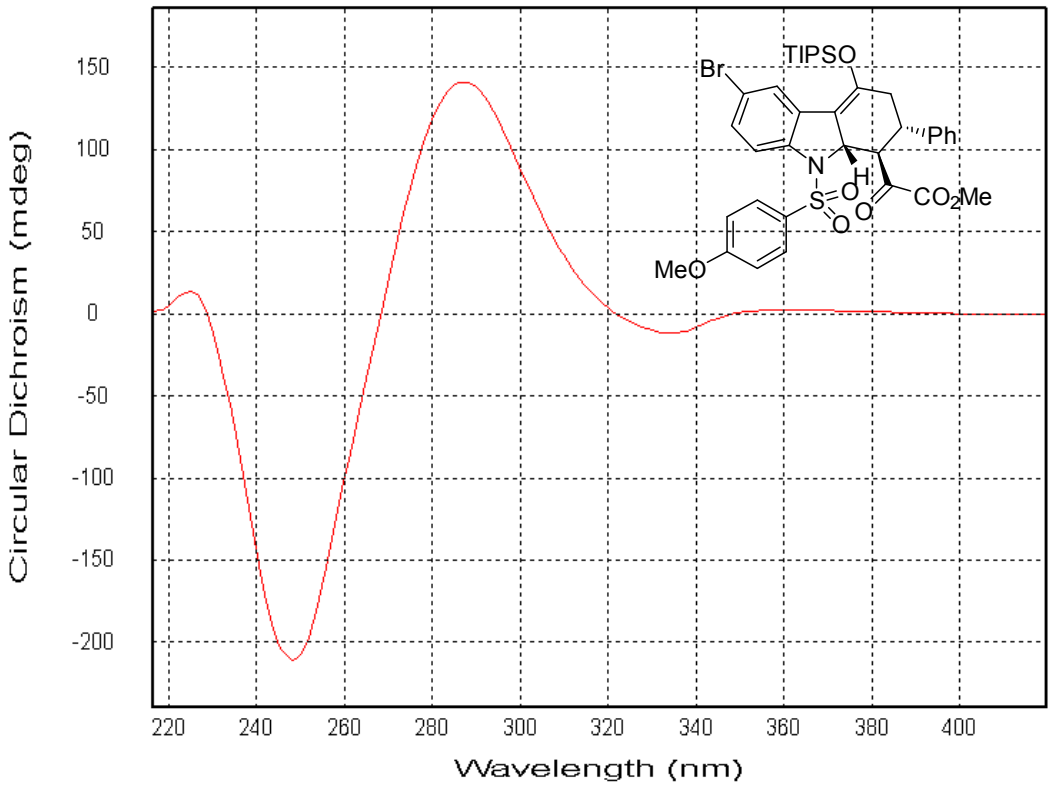
3au


Circular Dichroism (mdeg)
60
40
20
0
-20
-40
-60
-80
-100
220
240
260
280
300
320
340
360
380
Wavelength (nm)
TIPSO
n-Pr
N
H
S
O
O
O
CO2Et
MeO

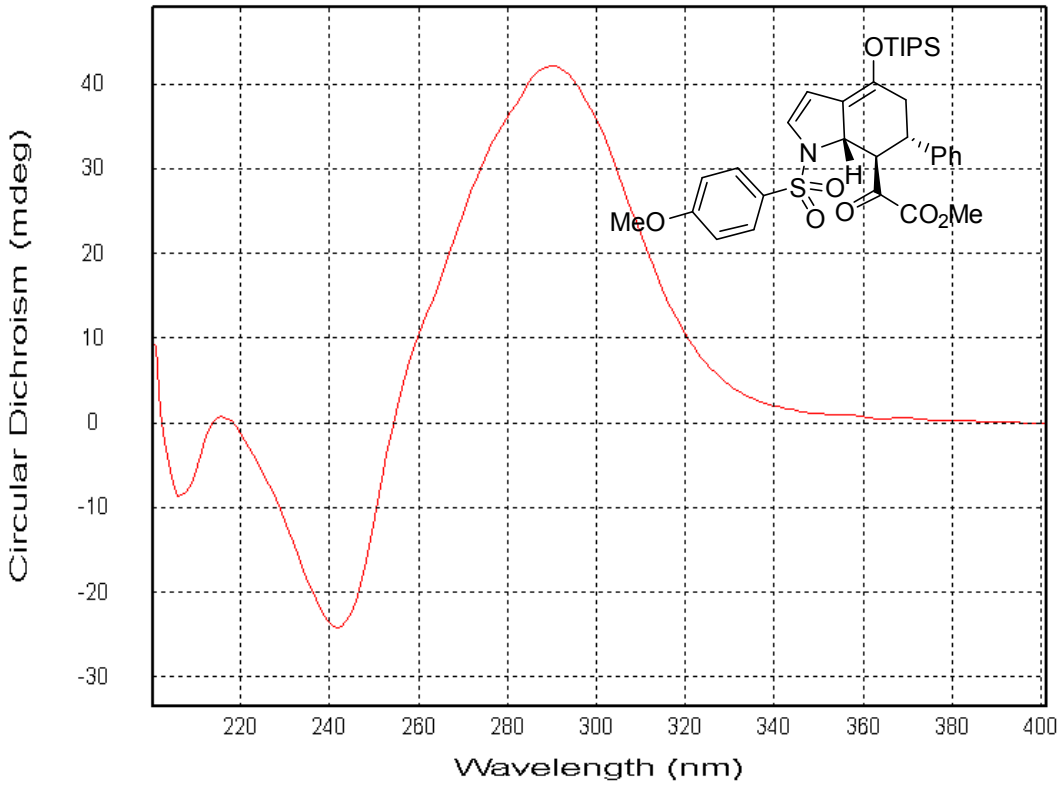
3aa


Circular Dichroism (mdeg)
150
100
50
0
-50
-100
-150
-200
220
240
260
280
300
320
340
360
380
400
420
Wavelength (nm)
TIPSO
Ph
N
H
S
O
O
O
CO2Me
MeO

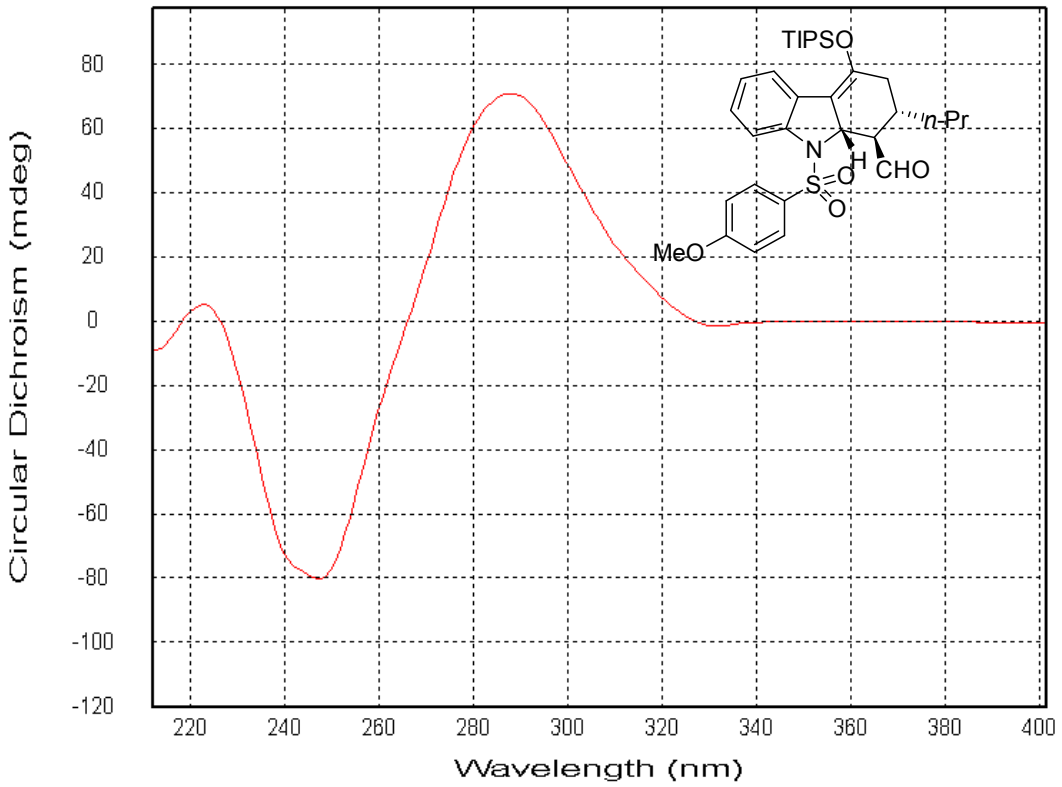
3ca


Circular Dichroism (mdeg)
150
100
50
0
-50
-100
-150
-200
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)
Br
TIPSO
Ph
N
H
S
O
O
O
O
CO2Me
MeO

3da


Circular Dichroism (mdeg)
40
30
20
10
0
-10
-20
-30
220
240
260
280
300
320
340
360
380
400
Wavelength (nm)
OTIPS
N
H
Ph
S
O
O
O
O
CO2Me
MeO

5au



10. References

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2. J. H. Feng, X. Fu, Z. L. Chen, L. L. Lin, X. H. Liu and X. M. Feng, *Org. Lett*., 2013, **15**, 2640-2643.

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