Supporting Information

Dynamic Kinetic Asymmetric Cross-Benzoin Additions of β-Stereogenic α-Keto Esters

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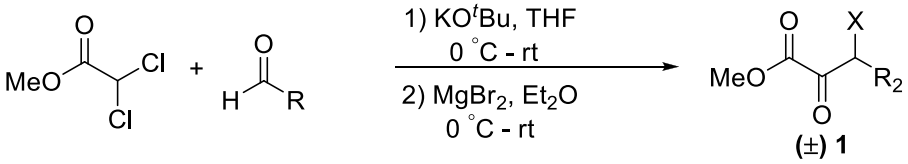
General Information:

Methods: Infrared (IR) spectra were obtained using an ASI ReactIR 1000 Fourier transform infrared spectrometer. Proton and carbon magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Bruker model DRX 400 or 600 (^{1}H NMR at 400 MHz or 600 MHz and ^{13}C NMR at 100 MHz or 150 MHz) spectrometer with solvent resonance as the internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, dd = doublet of doublet, t = triplet, dt = doublet of triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. Supercritical fluid chromatography was performed on a Berger SFC system equipped with Chiracel AD, AS, OD, and WO columns as well as Regis Industries RegisPack (RP) column (φ 4.6 mm x 250 mm). Samples were eluted with SFC grade CO_2 at the indicated percentage of methanol with an oven temperature of 40 °C. HPLC analysis was performed on an Agilent Technologies 1200 system equipped with Chiralpak IA, IB, and IC columns (constant flow at 1.00 mL/min). Samples were eluted with the indicated percentages of HPLC grade isopropanol in hexanes. Optical rotations were measured using a 2 mL cell with a 1 dm path length on a Jasco DIP 1000 digital polarimiter. Mass spectra were obtained using a Micromass Quattro II (triple quad) instrument with nanoelectrospray ionization. Samples were prepared via diluted with either Methanol (MeOH), 0.1 M ammonium formate (MeOH), or 0.1 M formic acid (MeOH). Analytical thin layer chromatography (TLC) was performed on Sorbtec 0.25 mm silica gel 60 plates. Visualization was accomplished with UV light and/or either aqueous potassium permanganate $KMnO_4$ or aqueous ceric ammonium molybdate (CAM) solution followed by heating. Product purification was accomplished using Siliaflash-P60 silica gel (40-63 μm) purchased from Silicycle. Unless otherwise noted all reactions were carried out in flame-dried glassware with magnetic stirring. Yields and diastereomeric ratios (dr) are reported for a specific experiment and as a result may differ slightly from those found in the reported tables, which represent an average of at least two trials. In order to overlay the SFC traces for the chiral and racemic samples two separate integrations of the peaks must be taken. This results in slight discrepancies between the integration values shown in the report and seen on the trace itself.

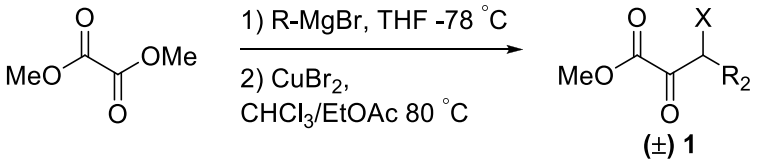
Materials: NHC catalysts **A**-**C,**[1-3] **E,**[4] β-halo α-keto esters **1a**,[5] and 1-tosyl-1*H*-indole-3-carbaldehyde[6] were all prepared according to literature procedures. Potassium carbonate was purchased from Sigma Aldrich and dried under vacuum (5 torr) for 3 h at 110 °C. Methanol (MeOH) was distilled from 3 Å molecular sieves prior to use. HPLC grade chloroform ($CHCl_3$), ethyl acetate (EtOAc) and ethanol (EtOH) were used directly from the bottle. Dichloromethane (DCM) and tetrahydrofuran (THF) were passed through a column of neutral alumina under nitrogen prior to use. Methyl *t*butyl ether (MTBE) was distilled prior to use and stored over 4 Å molecular sieves. Benzaldehyde, *o*-tolualdehyde, *m*-tolualdehyde, *p*-tolualdehyde, *p*-anisaldehyde, furfural, and isobutyraldehyde were all purchased from Sigma Aldrich and distilled before use. All other reagents were purchased from commercial sources and were used as received unless otherwise noted. All racemic products were obtained via General Procedure B, Method 1 using Rovis's achiral triazolium catalyst.[2]

General Procedure A: Preparation of α-keto esters.



Method 1:

The following protocol was adopted from a literature procedure.[5] A 100 mL round-bottomed flask equipped with a magnetic stir bar was charged with aldehyde (10.0 mmol, 1.0 equiv), methyl dichloroacetate (13.0 mmol, 1.3 equiv), and THF (20 mL, 0.5 M). This solution was cooled to 0 °C and potassium tert-butoxide (13.0 mmol, 1.3 equiv) was added in one portion. The mixture was warmed slowly to room temperature and stirred for 18 h, followed by dilution with Et_2O (60 mL) and H_2O (60 mL). The layers were separated and the organic layer was further washed with H_2O (1 x 60 mL) and brine (1 x 60 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was then dissolved in Et_2O (30 mL, 0.33 M) and cooled to 0 °C. To the resulting solution, magnesium bromide (10.0 mmol, 1.0 equiv) was added in one portion. The reaction was warmed slowly to room temperature and stirred for 2 h followed by dilution with Et_2O (60 mL) and H_2O (60 mL). The layers were separated and the organic layer was further washed with H_2O (1 x 60 mL) and brine (1 x 60 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography using a gradient of 10-15% EtOAc/hexanes.

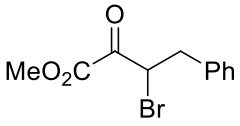


Method 2:

The following protocol was adopted from a literature procedure.[7] A 50 mL round-bottomed flask equipped with a magnetic stir bar was charged with dimethyl oxalate (10.0 mmol, 1.0 equiv) and THF (10 mL, 1.0 M). This solution was cooled to -78 °C and the required Grignard reagent (1.0 M solution in THF, 11 mL, 1.1 equiv) was added dropwise The resulting mixture was stirred at -78 °C for 2 h, quenched with saturated ammonium chloride, then diluted with Et_2O (60 mL) and 1 M HCl (60 mL). The layers were separated and the organic layer was further washed with H_2O (2 x 60 mL) and brine (1 x 60 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was then dissolved in EtOAc (130 mL, 0.075M) and $CHCl_3$ (67 mL, 0.15 M). Copper(II) bromide (30 mmol, 3.0 equiv) was added in one portion and the reaction was heated at reflux for 12 h. The reaction was then cooled to room temperature and filtered through celite with Et_2O. The filtrate was concentrated *in vacuo* and the crude residue was purified by column chromatography using a gradient of 10-15% EtOAc/hexanes.

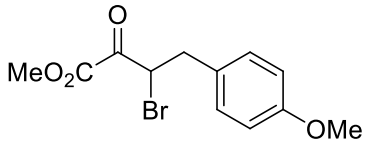
Grignard reagents were prepared according to the following procedure: a 50 mL 2-neck round-bottomed flask fitted with a reflux condenser and septa were charged with magnesium turnings (12.0 mmol, 1.2 equiv). The apparatus was flame-dried under vacuum (<5 torr). After cooling to room temperature, THF (9 mL) was added. A small portion of alkyl bromide (11.0 mmol, 1.1 equiv) dissolved in THF (2 mL) was then added to this solution.

This solution was stirred until color change was observed, indicating reaction initiation. The remainder of the alkyl bromide was then added at a rate that maintained gentle reflux of the reaction mixture. After the addition was complete, the reaction was then aged for 1-2 h at room temperature; and used in the subsequent reaction.



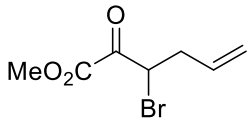
1b

Methyl 3-bromo-2-oxo-4-phenylbutanoate (1b): The title compound was prepared according to General Procedure A (Method 1) using phenylacetaldehyde (2.2 mL, 10.0 mmol), affording **1b** (2.5 g, 4.62 mmol, 47% yield) as a yellow oil. Analytical data for **1b:** ^{1}**H NMR** (600 MHz, $CDCl_3$): δ 7.36-7.33 (m, 2H), 7.30-7.27 (m, 3H), 5.30 (t, *J* = 7.8 Hz, 1H), 3.92 (s, 3H), 3.56 (dd, *J* = 14.4, 7.8 Hz, 1H) 3.28 (dd, *J* = 14.4, 7.8 Hz, 1H); ^{13}**C NMR** (150 MHz, $CDCl_3$): δ 184.8, 160.4, 136.3, 129.3, 128.7, 127.3, 53.4, 47.3, 38.1; **IR** (thin film): 3031, 1733,1455, 1260, 1068, 1027, 699 cm^{-1}; **TLC** (15% EtOAc/hexane): R_f = 0.17; **LRMS** (ESI): Calcd. for $C_{11}H_{11}BrO_3$: ([M+H]): 271.00, Found: 271.12.



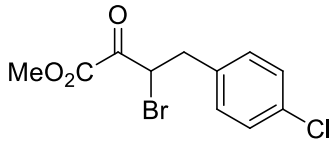
1c

Methyl 3-bromo-4-(4-methoxyphenyl)-2-oxobutanoate (1c): The title compound was prepared according to General Procedure A (Method 2) using dimethyl oxalate (0.76 g, 5.7 mmol), affording **1c** (2.5 g, 3.27 mmol, 57% yield) as a yellow oil. Analytical data for **1c:** ^{1}**H NMR** (600 MHz, $CDCl_3$): δ 7.16 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 5.22 (t, *J* = 7.8 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 3.48 (dd, *J* = 14.4, 7.8 Hz, 1H) 3.20 (dd, *J* = 14.4, 7.8 Hz, 1H); ^{13}**C NMR** (150 MHz, $CDCl_3$): δ 184.9, 160.4, 158.8, 130.4, 128.4, 114.1, 55.2, 53.4, 47.5, 37.3; **IR** (thin film): 3436, 1731, 1665, 1514, 1249, 1036 cm^{-1}; **TLC** (15% EtOAc/hexane): R_f = 0.17; **LRMS** (ESI): Calcd. for $C_{12}H_{13}BrO_4$: ([M+NH_4]): 318.03, Found: 318.09.



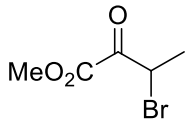
1d

Methyl 3-bromo-2-oxohex-5-enoate (1d): The title compound was prepared according to General Procedure A (Method 2) using dimethyl oxalate (0.660 g, 5.0 mmol), affording **1d** (0.320 g, 1.55 mmol, 31% yield) as a yellow oil. Analytical data for **1d:** ^{1}**H NMR** (600 MHz, $CDCl_3$): δ 5.79-5.74 (m, 1H), 5.21-5.16 (m, 2H), 5.06-5.04 (t, *J* = 7.8 Hz, 1H), 3.91 (s, 3H), 2.92-2.87 (m, 1H) 2.75-2.70 (m, 1H); ^{13}**C NMR** (150 MHz, $CDCl_3$): δ 184.9, 160.7, 132.6, 119.5, 53.4, 46.2, 36.0; **IR** (thin film): 3480, 1736, 1644, 1438, 1258, 1163, 1077 cm^{-1}; **TLC** (15% EtOAc/hexane): R_f = 0.17; **LRMS** (ESI): Calcd. for $C_7H_9BrO_3$: ([M+Na]): 239.08, Found: 239.16.



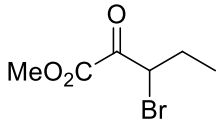
1e

Methyl 3-bromo-4-(4-chlorophenyl)-2-oxobutanoate (1e): The title compound was prepared according to General Procedure A (Method 2) using dimethyl oxalate (0.951 g, 7.2 mmol), affording **1e** (0.66 g, 2.16 mmol, 30% yield) as a yellow oil. Analytical data for **1d: ^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.27 (d, J = 8.4 Hz, 1H), 7.17 (d, J = 8.4 Hz, 1H), 5.21 (t, J = 7.8 Hz, 1H), 3.88 (s, 3H), 3.47 (dd, J = 14.4, 7.8 Hz, 1H), 3.20 (dd, J = 14.4, 7.8 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 184.5, 160.3, 134.7, 133.1, 130.6, 128.7, 53.4, 46.9, 37.2; **IR** (thin film): 2955, 1735, 1493, 1255, 1081, 1016 cm^{-1}; **TLC** (15% EtOAc/hexane): R_f = 0.17; **LRMS** (ESI): Calcd. for $C_6H_7BrO_3$: ([M+NH_4]): 321.98, Found: 322.12.



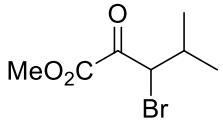
1f

Methyl 3-bromo-2-oxobutanoate (1f): The title compound was prepared according to General Procedure A (Method 1) using acetaldehyde (0.56 mL, 10.0 mmol) and affording **1f** (0.5 g, 2.58 mmol, 26% yield) as a yellow oil whose spectral properties matched those previously reported. [8]



1g

Methyl 3-bromo-2-oxopentanoate (1g): The title compound was prepared according to General Procedure A (Method 1) using propanal (0.72 mL, 10.0 mmol), affording **1g** (0.34 g, 1.62 mmol, 16% yield) as a yellow oil whose spectral properties matched those previously reported. [9]



1h

Methyl 3-bromo-4-methyl-2-oxopentanoate (1h): The title compound was prepared according to General Procedure A (Method 1) using isobutyraldehyde (0.912 mL, 10.0 mmol), affording **1b** (0.60 g, 2.70 mmol, 27% yield) as a yellow oil whose spectral properties matched those previously reported. [10]

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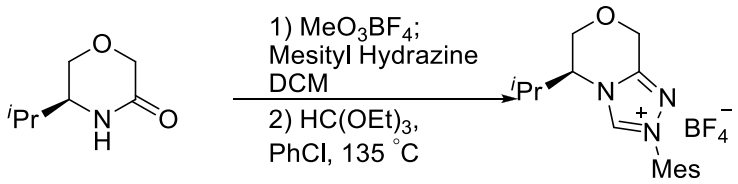
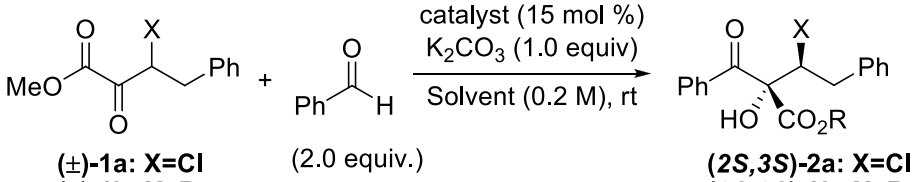
Preparation of Catalyst D.



This catalyst was synthesized according to the literature procedure.[2] Under N_2, a 50 mL flame-dried round-bottomed flask equipped with a magnetic stir bar was charged with trimethyloxonium tetrafluoroborate (3.6 mmol, 1.0 equiv) and capped with a septum. DCM

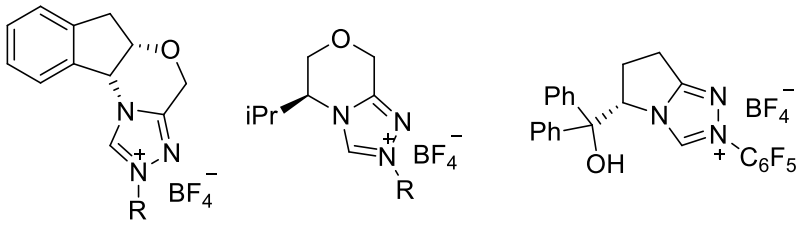
(20 mL, 0.2 M) was added under an atmosphere of N_2. The septum was removed and (*S*)-5-isopropylmorpholin-3-one[11] was added in a single portion. The flask was capped, put under N_2, and stirred vigorously for 14 h or until homogenous. Mesityl hydrazine[12] was then added in a single portion and the reaction mixture was stirred for an additional 6 h. The reaction was then concentrated *in vacuo* and dried under high vacuum for 15 min. The crude reaction mixture was dissolved in chlorobenzene (20 mL, 0.2 M) and triethyl orthoformate (18.0 mmol, 5.0 equiv) was added. The reaction flask was equipped with a reflux condenser and heated to open to the atmosphere at 135 °C for 12 h. A second portion of triethyl orthoformate (18.0 mmol, 5.0 equiv) was added and the reaction mixture was heated for an additional 24 h at 135 °C. The flask was then cooled to room temperature, diluted with 200 mL of toluene, and concentrated *in vacuo*. The crude residue was purified by column chromatography using 5% MeOH/DCM. The resultant solid was stirred in Et_2O (100 mL) for 2 h then filtered, providing **D** (0.62 g, 1.66 mmol, 46% yield) as a tan solid. Analytical data for **2a: mp** 165.2-166.2 °C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 9.76 (s, 1H), 6.99 (s, *1*H), 5.09 (d, *J* = 16.2 Hz, 1H) 4.99 (d, *J* = 16.2 Hz, 1H) 4.29-4.20 (m, 2H), 2.48-2.43 (m, 1H), 2.37 (s, 3H), 2.03 (s, 6H) 1.07 (d, *J* = 6.6 Hz, 3H) 0.98 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 150.3, 143.6, 143.5, 142.0, 131.0, 129.7, 63.7, 61.6, 60.3, 31.8, 21.2, 18.7, 17.5, 17.1; **IR** (thin film): 3507, 2927, 1796, 1692, 1599, 1226, 1151 cm^{-1}; **TLC** (5% MeOH/DCM): R_f = 0.21; **LRMS** (ESI): Calcd. for $C_{17}H_{24}N_3O$: ([M+H-BF_4]): 287.20, Found: 287.23.

Optimization data for the Asymmetric Cross Benzoin of 1a/1b with benzaldehyde.



(±)-1a: X=Cl
(±)-1b: X=Br

(*2S,3S*)-2a: X=Cl
(*2S,3S*)-2b: X=Br



A: R = C_6F_5
B: R = Mes

C: R = C_6F_5
D: R = Mes

E

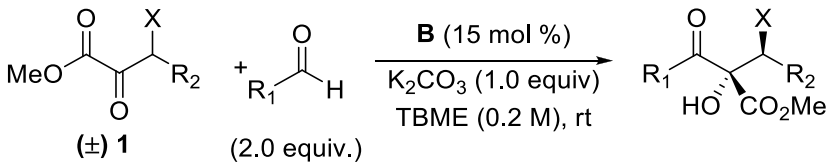
General procedure B for the asymmetric cross benzoin addition: To a flame dried 1-dram vial was added catalyst, (0.03 mmol, 0.15 equiv) β-halo α-keto ester **1** (0.2 mmol, 1.0 equiv), TBME (1 mL, 0.2 M) and aldehyde (0.4 mmol, 2.0 equiv). This solution was stirred for 5 min followed by the addition of potassium carbonate (0.2 mmol, 1.0 equiv). This reaction mixture was then stirred (rate of stirring should be >800 rpm) for 14 h, filtered through a short plug of silica gel, and concentrated *in vacuo.* The crude product was purified by column chromatography using EtOAc/hexanes.

Catalyst, **base and solvent optimization table**

Trial	X	catalyst	base	solvent	T (°C)	conversion (%)	dr	er
1	Cl	**C**	NEt_3	DCM	rt	100	12:1	78:22
2	Cl	**A**	NEt_3	DCM	rt	100	12:1	78:22
3	Cl	**C**	NEt_3	DCM	0	100	10:1	70:30
4	Cl	**A**	NEt_3	DCM	0	100	7:1	88:12
5	Cl	**C**	NEt_3	DCM	-40	45	1.4:1	99:1
6	Cl	**A**	NEt_3	DCM	-40	50	5.5:1	99:1
7	Cl	**E**	NEt_3	DCM	rt	<10	5.5:1	--
8	Br	**C**	K_2CO_3	THF	rt	<5	--	--
9	Br	**A**	K_2CO_3	THF	rt	<5	--	--
10	Br	**E**	K_2CO_3	THF	rt	<5	--	--
11	Cl	**C**	K_2CO_3	THF	rt	40	1.5:1	98:2
12	Cl	**A**	K_2CO_3	THF	rt	25	4.5:1	96:4
13	Br	**D**	K_2CO_3	THF	rt	30	--	--
14	Br	**B**	K_2CO_3	THF	rt	>95	>20:1	94:6
15	Br	**B**	K_2CO_3	THF	0	60	7:1	96:4
16	Cl	**D**	K_2CO_3	THF	rt	100	>20:1	90:10
17	Cl	**B**	K_2CO_3	THF	rt	100	14:1	95:5
18	Br	**B**	K_2CO_3	2-Me	rt	72	>20:1	95:5
19	Br	**B**	K_2CO_3	DCM	rt	23	>20:1	--
20	Br	**B**	K_2CO_3	$CHCl_3$	rt	16	>20:1	--
21	Br	**B**	K_2CO_3	$PhCH_3$	rt	78	>20:1	92:8
22	Br	**B**	K_2CO_3	MeOH	rt	100	*	--
23	Br	**B**	K_2CO_3	EtOAc	rt	100	>20:1	95:5
24	Br	**B**	K_2CO_3	Et_2O	rt	100	>20:1	95:5
25	Br	**B**	K_2CO_3	CH_3CN	rt	100	*	--
26	Br	**B**	K_2CO_3	CPME	rt	100	>20:1	95.5:4.5
27	Br	**B**	K_2CO_3	TBME	rt	100	>20:1	96:4
28	Cl	**B**	K_2CO_3	Et_2O	rt	100	15:1	96.5:4.5
29	Cl	**B**	K_2CO_3	CPME	rt	100	15:1	97:3
30	Cl	**B**	K_2CO_3	TBME	rt	100	14:1	97.5:2.5
31	Cl	**B**	NEt_3	TBME	rt	50	20:1	97:3
32	Cl	**B**	DBU	TBME	rt	100	*	--
33	Cl	**B**	Hunig's	TBME	rt	0	--	--
34	Cl	**B**	Pyridine	TBME	rt	50	8:1	97.5:2.5
35	Cl	**B**	Cs_2CO_3	TBME	rt	100	>20:1	96:4
36	Cl	**B**	DMAP	TBME	rt	100	17:1	97:3
37	Br	**B**	NaOAc	TBME	rt	6	--	--
38	Br	**B**	$NaHCO_3$	TBME	rt	0	--	--
39	Br	**B**	Na_2CO_3	TBME	rt	10	--	--

* Reaction mixture did not contain any desired Cross-Benzoin product.

General procedure B for the Asymmetric Cross Benzoin Procedure.

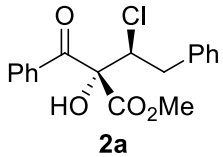


Method 1:

To a flame-dried 1-dram vial was added catalyst **B**, (0.03 mmol, 0.15 equiv) β-halo α-keto ester **1** (0.2 mmol, 1.0 equiv), TBME (1 mL, 0.2 M) and aldehyde (0.4 mmol, 2.0 equiv). This solution was stirred for 5 min followed by the addition of potassium carbonate (0.2 mmol, 1.0 equiv). This reaction mixture was then stirred (rate of stirring should be >800 rpm) for 14 h, filtered through a short plug of silica gel, and concentrated *in vacuo.* The crude product was purified by column chromatography using EtOAc/hexanes. In certain instances minor impurities remained after purification, in these cases a ^{1}H NMR yield utilizing ferrocene (20 mg, 0.108 mmol) as an internal standard is provided.

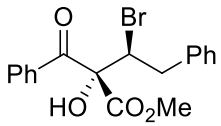
Method 2:

To a flame dried 1-dram vial was added catalyst **B,** (0.03 mmol, 0.15 equiv) β-halo α-keto ester **1** (0.2 mmol, 1.0 equiv), and TBME (.5 mL, 0.4 M) followed by potassium carbonate (0.4 mmol, 2.0 equiv). This reaction mixture was then stirred (rate of stirring should be >800 rpm) while a 0.8 M solution of aldehyde in TBME (0.5 mL, 2.0 equiv) was added in 50 μL portions every 30 min for 5 h. Upon complete aldehyde addition the reaction was stirred an additional 9 h then filtered through a short plug of silica gel with Et_2O, and concentrated *in vacuo*. The crude residue was then purified by column chromatography using between 2.5% EtOAc/hexanes.



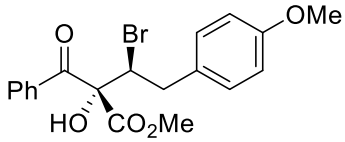
2a

Methyl (2*S*,3*S*)-2-benzoyl-3-chloro-2-hydroxy-4-phenylbutanoate (2a): The title compound was prepared according to General Procedure B (Method 1) using α-keto ester **1a** (0.045 g, 0.20 mmol), and benzaldehyde (0.04 mL, 0.40 mmol) affording **2a** (0.064 g, 0.19 mmol, 96% yield, 12:1 dr) as a colorless oil. Analytical data for **2a: ^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.8 Hz, 2H), 7.60-7.58 (m, 1H), 7.48-7.45 (m, 2H), 7.35-7.33 (m, 5H), 7.28-7.26 (m, 1H), 5.15 (dd, *J* = 10.7, 2.1 Hz, 1H) 4.30 (s, 1H), 3.82 (s, 3H), 3.24 (dd, *J* = 14.4, 2.2 Hz, 1H) 2.91 (dd, *J* = 14.4, 10.7 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 193.6, 170.4, 137.7, 134.6, 133.8, 129.8, 129.5, 128.5, 128.4, 126.9, 86.3, 67.1, 54.4, 39.1; **IR** (thin film): 3507, 2927, 1796, 1692, 1599, 1226, 1151 cm^{-1}; **TLC** (10% EtOAc/hexane): R_f = 0.26; **LRMS** (ESI): Calcd. for $C_{18}H_{17}ClO_4$: ([M+H]): 333.09, Found: 333.21; **SFC:** Regis RP, 5% MeOH, flow rate = 3.0 mL/min, λ = 210 nm, $t_{R\ (major)}$ = 3.7 min $t_{R\ (minor)}$ = 4.3 min, 96:4 er; **[α]$_D$** = +45.8 (*c* = 0.03, DCM)



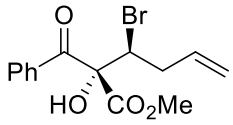
2b

Methyl (2*S*,3*S*)-2-benzoyl-3-bromo-2-hydroxy-4-phenylbutanoate (2b): The title compound was prepared according to General Procedure B (Method 1) using α-keto ester **1b** (0.054 g, 0.20 mmol), and benzaldehyde (0.04 mL, 0.40 mmol) affording **2b** (0.071 g major product + minor impurity, 78% ^{1}H NMR yield, >20:1 dr) as a colorless oil. Analytical data for **2a: ^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.8 Hz, 2H), 7.61-7.58 (m, 1H), 7.47-7.45 (m, 2H), 7.34-7.19 (m, 5H), 5.22-5.20 (m, 1H) 4.37 (s,1H), 3.85 (s, 3H), 3.32-3.31 (m, 1H) 3.04-2.98 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 193.4, 170.5, 138.2, 134.7, 133.8, 129.8, 129.4, 128.5, 128.3, 126.9, 86.5, 60.9, 54.4, 39.9; **IR** (thin film): 3066, 2089, 2699, 1746, 1692, 1421, 1244 cm^{-1}; **TLC** (10% EtOAc/hexane): R_f = 0.26; **LRMS** (ESI): Calcd. for $C_{18}H_{17}BrO_4$: ([M+H]): 377.23, Found: 377.15; **SFC:** Regis RP, 5% MeOH, flow rate = 3.0 mL/min, λ = 210 nm, $t_{R\ (major)}$ = 4.5 min $t_{R\ (minor)}$ = 5.0 min, 96:4 er; **[α]$_D$** = +39.8 (*c* = 0.03, DCM)



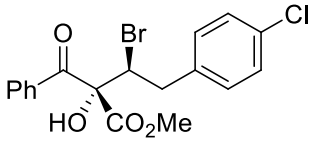
2c

Methyl (2*S*,3*S*)-2-benzoyl-3-bromo-2-hydroxy-4-(4-methoxyphenyl)butanoate (2c): The title compound was prepared according to General Procedure B (Method 2) using α-keto ester **1c** (0.060 g, 0.20 mmol), and benzaldehyde (0.04 mL, 0.40 mmol) affording **2c** (0.050g, major product + homo-benzoin impurity 83 % ^{1}H NMR yield, >20:1 dr) as a colorless oil. Analytical data for **2a: ^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.8 Hz, 2H), 7.60-7.57 (m, 1H), 7.47-7.44 (m, 2H), 7.26-7.23 (m, 2H) 6.87 (d, *J* = 8.4 Hz, 2H), 5.16 (dd, *J* = 10.8, 2.3 Hz, 1H) 4.35 (s,1H), 3.82-3.81 (m, 6H), 3.24 (dd, *J* = 15.0, 2.3 Hz, 1H) 2.95 (dd, *J* = 15.0, 10.8 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 193.4, 170.5, 158.5, 134.7, 133.8, 130.4, 130.3, 129.8, 128.5, 113.7, 86.5, 61.5, 55.2, 54.4, 39.0; **IR** (thin film): 3059, 2989, 2306, 1715, 1429, 1267, 896 cm^{-1}; **TLC** (10% EtOAc/hexane): R_f = 0.14; **LRMS** (ESI): Calcd. for $C_{19}H_{19}BrO_5$: ([M+H]): 407.05, Found: 407.08; **SFC:** Regis RP, 5% MeOH, flow rate = 3.0 mL/min, λ = 210 nm, **2c** could not be directly analyzed via SFC, see compound **4c** for enantiomeric analysis; **[α]$_D$** = +39.8 (*c* = 0.03, DCM)



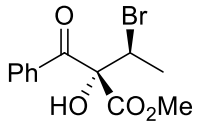
2d

Methyl (2*S*,3*S*)-2-benzoyl-3-bromo-2-hydroxyhex-5-enoate (2d): The title compound was prepared according to General Procedure B (Method 1) using α-keto ester **1d** (0.044 g, 0.20 mmol), and benzaldehyde (0.04 mL, 0.40 mmol) affording **2d** (0.046g, 0.15 mmol, 74% yield, 17:1 dr) as a white solid. Analytical data for **2d: mp** 68.6-70.0 °C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.01-8.00 (m, 2H), 7.58-7.57 (m, 1H), 7.45-7.42 (m, 2H), 5.89-5.83 (m, 1H) 5.17-5.14 (m, 2H) 5.02 (dd, *J* = 10.8, 3 Hz, 1H), 4.22 (s,1H), 3.83 (s, 3H), 2.68-2.65 (m, 1H) 2.64-2.56 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 193.4, 170.5, 134.72, 134.70, 133.7, 129.8, 128.5, 118.2, 86.4, 58.9, 54.4, 37.8; **IR** (thin film): 3059, 2989, 2306, 1715, 1614, 1420, 1267 cm^{-1}; **TLC** (10% EtOAc/hexane): R_f = 0.22; **LRMS** (ESI): Calcd. for $C_{14}H_{15}BrO_4$: ([M+Na]): 350.16, Found: 350.16; **2d** could not be directly analyzed via SFC, see compound **4d** for enantiomeric analysis; **[α]$_D$** = +14.8 (*c* = 0.01, DCM).



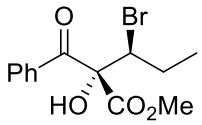
2e

Methyl (*2S,3S*)-2-benzoyl-3-bromo-4-(4-chlorophenyl)-2-hydroxybutanoate (2e): The title compound was prepared according to General Procedure B (Method 1) using α-keto ester **1e** (0.061 g, 0.20 mmol), and benzaldehyde (0.04 mL, 0.40 mmol) affording **2e** (0.050 g, 0.12 mmol, 61% yield, 12:1 dr) as a colorless oil. Analytical data for **2e: ^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.07 (d, *J* = 4.2 Hz, 2H), 7.63-7.61 (m, 1H), 7.50-7.47 (m, 2H), 7.36-7.28 (m, 4H), 5.16-5.14 (m, 1H) 4.36 (s,1H), 3.85 (s, 3H), 3.30 (d, *J* = 15.0 Hz, 1H) 3.00 (dd, *J* = 15.0, 10.8 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 193.3, 170.4, 136.7, 134.5, 133.9, 132.7, 130.7, 129.8, 128.5, 128.5, 86.3, 60.5, 54.5, 39.3; **IR** (thin film): 3507, 3059, 2309, 1748, 1692, 1228, 1151 cm^{-1}; **TLC** (10% EtOAc/hexane): R_f = 0.21; **LRMS** (ESI): Calcd. for $C_{18}H_{16}BrClO_4$: ([M+H]):411.00, Found: 411.14; **2e** could not be directly analyzed via SFC, see compound **4e** for enantiomeric analysis; **[α]$_D$** = +44.9 (*c* = 0.02, DCM).



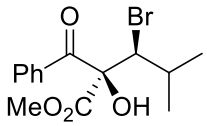
2f

Methyl (2*S*,3*S*)-2-benzoyl-3-bromo-2-hydroxybutanoate (2f): The title compound was prepared according to General Procedure B (Method 1) using α-keto ester **1f** (0.039 g, 0.20 mmol), and benzaldehyde (0.04 mL, 0.40 mmol) affording **2f** (0.042g, 0.14 mmol, 70% yield, 14:1 dr) as a colorless oil. Analytical data for **2f: ^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.58-7.55 (m, 1H), 7.44-7.42 (m, 2H), 5.16 (*q*, *J* = 6.6 Hz, 1H) 4.17 (s,1H), 3.83 (s, 3H), 1.72 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 193.0, 170.7, 134.6, 133.8, 129.8, 128.5, 86.2, 54.3, 53.4, 20.6; **IR** (thin film): 3507, 2936, 2309, 1746, 1692, 1166, 1050 cm^{-1}; **TLC** (10% EtOAc/hexane): R_f = 0.24; **LRMS** (ESI): Calcd. for $C_{12}H_{13}BrO_4$: ([M+H]): 301.01, Found: 300.99; **SFC:** Chiracel AD, 5% MeOH, flow rate = 1.5 mL/min, λ = 210 nm, $t_{R\ (major)}$ = 5.7 min $t_{R\ (minor)}$ = 6.1 min, 93:7 er; **[α]$_D$** = +26.1 (*c* = 0.02, DCM)



2g

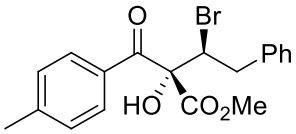
Methyl (2*S*,3*S*)-2-benzoyl-3-bromo-2-hydroxypentanoate (2g): The title compound was prepared according to General Procedure B (Method 1) using α-keto ester **1g** (0.042 g, 0.20 mmol), and benzaldehyde (0.04 mL, 0.40 mmol) affording **2g** (0.046g, 0.15 mmol, 73% yield, >20:1 dr) as a white solid. Analytical data for **2g: ^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.01-8.00 (m, 2H), 7.58-7.55 (m, 1H), 7.44-7.42 (m, 2H), 4.92 (dd, *J* = 9, 4.2 Hz, 1H) 4.17 (s,1H), 3.83 (s, 3H), 1.87-1.82 (m, 2H), 1.11 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 193.7, 170.6, 134.8, 133.7, 129.8, 128.5, 86.8, 62.8, 54.4, 26.9, 12.8; **IR** (thin film): 3507, 2935, 1748, 1692, 1228, 1189 cm^{-1}; **TLC** (10% EtOAc/hexane): R_f = 0.24; **LRMS** (ESI): Calcd. for $C_{13}H_{15}BrO_4$: ([M+H]): 315.02, Found: 315.06; **SFC:** Chiracel AD, 5% MeOH, flow rate = 1.5 mL/min, λ = 210 nm, $t_{R\ (major)}$ = 5.9 min $t_{R\ (minor)}$ = 6.4 min, 94:6 er; **[α]$_D$** = +12.5 (*c* = 0.02, DCM)



2h

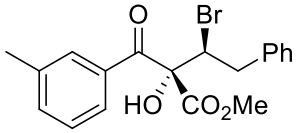
Methyl (2*R*,3*S*)-2-benzoyl-3-bromo-2-hydroxy-4-methylpentanoate (2h): The title compound was prepared according to General Procedure B

(Method 1) using α-keto ester **1h** (0.044 g, 0.20 mmol), benzaldehyde (0.04 mL, 0.40 mmol) and mesitylene as an internal standard (0.028 mL, 0.20 mmol) affording **2h** (0.026g, 0.08 mmol, 65% ^{1}H NMR yield, 40% isolated yield, >20:1 dr) as a colorless oil. Analytical data for **2h: ^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.57-7.55 (m, 1H), 7.44-7.42 (m, 2H), 5.08 (d, *J* = 3 Hz, 1H) 4.22 (s,1H), 3.83 (s, 3H), 2.09-2.05 (m, 1H), 1.06 (d, *J* = 6.6 Hz, 3H) 1.00 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 193.5, 170.7, 135.0, 133.5, 129.8, 128.4, 88.0, 67.2, 54.4, 31.5, 23.1, 19.8; **IR** (thin film): 3507, 2966, 1740, 1692, 1159, 409 cm^{-1}; **TLC** (10% EtOAc/hexane): R_f = 0.29; **LRMS** (ESI): Calcd. for $C_{14}H_{17}BrO_4$: ([M+H]): 329.03, Found: 329.13; **SFC:** Regis RP, 5% MeOH, flow rate = 1.5 mL/min, λ = 210 nm, $t_{R\ (major)}$ = 4.0 min $t_{R\ (minor)}$ = 4.3 min, 94:6 er; **$[\alpha]_D$** = +18.3 (*c* = 0.01, DCM)



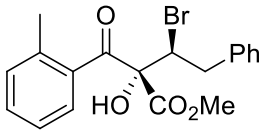
2i

Methyl (2*S*,3*S*)-3-bromo-2-hydroxy-2-(4-methylbenzoyl)-4-phenylbutanoate (2i): The title compound was prepared according to General Procedure B (Method 1) using α-keto ester **1b** (0.054 g, 0.20 mmol), and *p*-tolualdehyde (0.05 mL, 0.40 mmol) affording **2i** (0.060g, 0.15 mmol, 77% yield, >20:1 dr) as a colorless oil. Analytical data for **2i: ^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.36-7.28 (m, 7H), 5.23 (dd, *J* = 10.7, 2.3 Hz, 1H) 4.36 (s, 1H), 3.84 (s, 3H), 3.34 (dd, *J* = 14.6, 2.3 Hz, 1H) 3.02 (dd, *J* = 14.6, 10.7 Hz, 1H), 2.45 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 192.7, 170.6, 145.0, 138.3, 132.0, 130.0, 129.4, 129.2, 128.3, 126.8, 86.4, 61.1, 54.3, 39.9, 21.7; **IR** (thin film): 3507, 2927, 1746, 1684, 1607, 1151 cm^{-1}; **TLC** (10% EtOAc/hexane): R_f = 0.24; **LRMS** (ESI): Calcd. for $C_{19}H_{19}BrO_4$: ([M+H]): 391.05, Found: 391.15; **SFC:** Regis RP, 10% MeOH, flow rate = 1.5 mL/min, λ = 210 nm, $t_{R\ (major)}$ = 9.7 min $t_{R\ (minor)}$ = 11.1 min, 97:3 er; **$[\alpha]_D$** = +20.7 (*c* = 0.02, DCM)



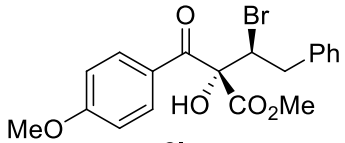
2j

Methyl (2*S*,3*S*)-3-bromo-2-hydroxy-2-(3-methylbenzoyl)-4-phenylbutanoate (2j): The title compound was prepared according to General Procedure B (Method 1) using α-keto ester **1b** (0.054 g, 0.20 mmol), and *m*-tolualdehyde (0.05 mL, 0.40 mmol) affording **2j** (0.066g, 0.17 mmol, 85% yield, >20:1 dr) as a colorless oil. Analytical data for **2j: ^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.87-7.84 (m, 2H), 7.41-7.40 (m, 1H), 7.35-7.26 (m, 6H), 5.22 (m, 1H) 4.31 (s,1H), 3.82 (s, 3H), 3.31-3.28 (d, *J* = 12.6 Hz, 1H) 3.02-2.97 (dd, *J* = 14.4, 11.4 Hz, 1H), 2.41 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$, two coincident aromatic resonances): δ 193.7, 170.5, 138.4, 138.2, 134.7, 134.6, 130.2, 129.4, 128.4, 127.0, 126.9, 86.5, 70.0, 54.4, 39.9, 21.4 (two coincident resonances); **IR** (thin film): 3507, 2927, 1746, 1692, 1607, 1143 cm^{-1}; **TLC** (10% EtOAc/hexane): R_f = 0.24; **LRMS** (ESI): Calcd. for $C_{19}H_{19}BrO_4$: ([M+Na]): 413.04, Found: 413.12; **HPLC:** Chiralpak IC, 5% ^{i}PrOH, flow rate = 1.0 mL/min, λ = 230 nm, $t_{R\ (major)}$ = 5.1 min $t_{R\ (minor)}$ = 5.7 min, 96:4 er; **$[\alpha]_D$** = +39.8 (*c* = 0.03, DCM)



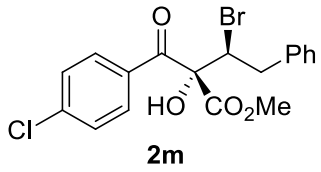
2k

Methyl (2*S*,3*S*)-3-bromo-2-hydroxy-2-(2-methylbenzoyl)-4-phenylbutanoate (2k): No reaction was observed using General Procedure B (Method 1) with α-keto ester **1b** (0.054 g, 0.20 mmol), and *o*-tolualdehyde (0.05 mL, 0.40 mmol).



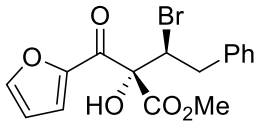
2l

Methyl (2*S*,3*S*)-3-bromo-2-hydroxy-2-(4-methoxybenzoyl)-4-phenylbutanoate (2l): The title compound was prepared according to General Procedure B (Method 1) using α-keto ester **1b** (0.054 g, 0.20 mmol), *p*-anisaldehyde (0.05 mL, 0.40 mmol), and mesitylene as an internal standard (0.028 mL, 0.20 mmol) resulting in 50% conversion of **1b** and affording **2l** (0.040 g, 0.10 mmol, 49% yield, >20:1 dr) as a colorless oil. Analytical data for **2l: ^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.8 Hz, 2H), 7.33-7.32 (m, 5H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.20 (dd, *J* = 10.7, 2.2 Hz, 1H) 4.33 (s,1H), 3.88 (s, 3H), 3.80 (s, 3H), 3.33 (dd, *J* = 14.8, 2.2 Hz, 1H) 2.99 (dd, *J* = 14.8, 10.7 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 191.1, 107.8, 164.2, 138.3, 132.6, 129.4, 128.3, 127.3, 126.8, 113.8, 86.4, 61.3, 55.5, 54.3, 39.9; **IR** (thin film): 3066, 2989, 2309, 1746, 1684, 1599, 1420, 1159 cm^{-1}; **TLC** (10% EtOAc/hexane): R_f = 0.15; **LRMS** (ESI): Calcd. for $C_{19}H_{19}BrO_5$: ([M+Na]): 429.03, Found: 429.18; **SFC:** Regis RP, 10% MeOH, flow rate = 1.5 mL/min, λ = 210 nm, $t_{R\ (major)}$ = 9.7 min $t_{R\ (minor)}$ = 12.1 min, 98:2 er; **[α]$_D$** = +8.23 (*c* = 0.02, DCM)



2m

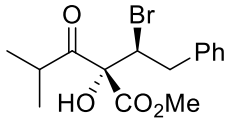
Methyl (2*S*,3*S*)-3-bromo-2-(4-chlorobenzoyl)-2-hydroxy-4-phenylbutanoate (2m): The title compound was prepared according to General Procedure B (Method 1) using α-keto ester **1b** (0.054 g, 0.20 mmol), 4-Chlorobenzaldehyde (0.056 g, 0.40 mmol) and mesitylene as an internal standard (0.028 mL, 0.20 mmol) resulting in 71% conversion of **1b** and affording **2m** (0.036 g, 0.09 mmol, 44% yield >20:1 dr) as a colorless oil. With 20 mol % of catalyst **1b** went to full conversion and **2m** was obtained with identical selectivity but higher isolated yield (0.066 g, 0.16 mmol, 80% yield >20:1 dr). Analytical data for **2m: ^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.34-7.33 (m, 4H), 7.29-7.26 (m, 1H), 5.17 (dd, *J* = 10.8, 1.8 Hz, 1H) 4.27 (s,1H), 3.82 (s, 3H), 3.30 (dd, *J* = 15.0, 1.8 Hz, 1H) 3.00 (dd, *J* = 15.0, 10.8 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 192.1, 170.4, 140.5, 138.1, 132.9, 131.4, 129.4, 128.8, 128.4, 127.0, 86.6, 60.8, 54.5, 39.9; **IR** (thin film): 3630, 3507, 3059, 2958, 2308, 1746, 1692, 1591, 1097, 1026 cm^{-1}; **TLC** (10% EtOAc/hexane): R_f = 0.28; **LRMS** (ESI): Calcd. for $C_{18}H_{16}BrClO_4$: ([M+Na]): 411.00, Found: 411.14; **2m** could not be directly analyzed via SFC, see compound **4m** for enantiomeric analysis; **[a]$_D$** = +24.6 (*c* = 0.03, DCM)



2n

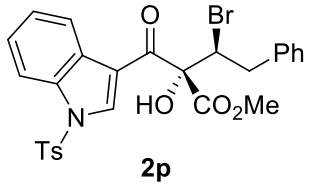
Methyl (2*S*,3*S*)-3-bromo-2-(furan-2-carbonyl)-2-hydroxy-4-phenylbutanoate (2n): The title compound was prepared according to General Procedure B (Method 1) using α-keto ester **1b** (0.054 g,

0.20 mmol), and furfural (0.03 mL, 0.40 mmol) affording **2n** (0.052g, 0.14 mmol, 71% yield, >20:1 dr) as a colorless oil. Analytical data for **2n:** **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.69 (d, *J* = 1.2 Hz, 1H), 7.64 (d, *J* = 3.6 Hz, 1H), 7.32-7.29 (m, 4H), 6.58 (dd, *J* = 3.6, 1.2 Hz, 1H), 5.15 (dd, *J* = 11.4, 2.4 Hz, 1H) 4.47 (s,1H), 3.81 (s, 3H), 3.28 (dd, *J* = 15.0, 2.4 Hz, 1H) 3.00 (dd, *J* = 14.4, 10.8 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 180.9, 169.8, 149.5, 148.2, 138.0, 129.4, 128.3, 126.9, 123.1, 112.6, 85.8, 59.7, 54.4, 39.6; **IR** (thin film): 3507, 1746, 167, 1466, 1159, 1027, 818, 617 cm^{-1}; **TLC** (10% EtOAc/hexane): R_f = 0.35; **LRMS** (ESI): Calcd. for $C_{16}H_{15}BrO_5$: ([M+H]): 367.02, Found: 367.02; **SFC:** Regis RP, 5% MeOH, flow rate = 3.0 mL/min, λ = 210 nm, $t_{R\ (major)}$ = 4.3 min $t_{R\ (minor)}$ = 7.0 min, 75.5:25.5 er; **$[\alpha]_D$** = +4.7 (*c* = 0.02, DCM)



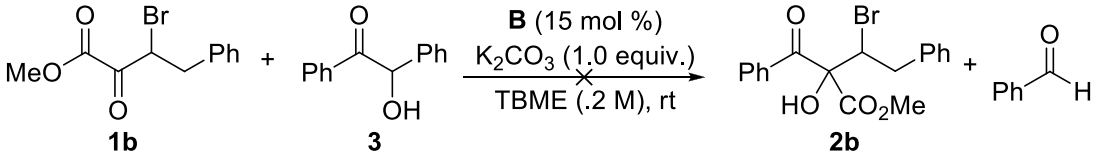
2o

Methyl (*S*)-2-((*S*)-1-bromo-2-phenylethyl)-2-hydroxy-4-methyl-3-oxopentanoate (2o): The title compound was prepared according to General Procedure B (Method 2) using α-keto ester **1b** (0.054 g, 0.20 mmol), and isobutyraldehyde (0.02 mL, 0.40 mmol) affording **2o** (0.039 g, 0.12 mmol, 59% yield 10:1 dr) as a colorless oil. Analytical data for **2n:** **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.33-7.30 (m, 2H), 7.27-7.25 (m, 3H), 5.75 (dd, *J* = 9.0, 4.5 Hz, 1H) 3.86 (s, 3H), 3.25 (dd, *J* = 14.1, 4.5 Hz, 1H) 3.07 (dd, *J* = 14.1, 9.0 Hz, 1H) 2.61-2.57 (m, 1H), 1.15 (d, *J* = 7.2 Hz, 3H), 1.11 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 189.5, 176.3, 160.2, 135.3, 129.4, 128.5, 127.2, 75.7, 53.1, 36.2, 33.4, 18.64, 18.60; **IR** (thin film): 3059, 2989, 2688, 2410, 2308, 1760, 1429, 1267, 896 cm^{-1}; **TLC** (10% EtOAc/hexane): R_f = 0.15; **LRMS** (ESI): Calcd. for $C_{15}H_{19}BrO_4$: ([M+H]): 343.05, Found: 343.04; **HPLC:** Chiralpak IC, 5% ^{i}PrOH, flow rate = 1.0 mL/min, λ = 230 nm, $t_{R\ (major)}$ = 9.1 min $t_{R\ (minor)}$ = 9.9 min, 58:42 er; **$[\alpha]_D$** = +2.3 (*c* = 0.02, DCM)



2p

Methyl (*2S,3S*)-3-bromo-2-hydroxy-4-phenyl-2-(1-tosyl-1H-indole-3-carbonyl)butanoate (2p): The title compound was prepared according to General Procedure B (Method 1) using α-keto ester **1b** (0.054 g, 0.20 mmol), and 1-tosyl-1*H*-indole-3-carbaldehyde (0.119 g, 0.40 mmol). **2a** was not isolable from 1-tosyl-1*H*-indole-3-carbaldehyde and was reduced with $NaBH_4$ **4p** (0.074 g, 0.13 mmol, 65% yield, 10:1 dr), was isolated by column chromatography using 15% EtOAc/hexanes. See compound **4p** for all characterization data.



1b **3** **2b**

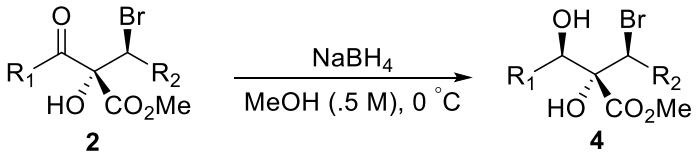
Attempting the Cross Benzoin Reaction Using Homo-Benzoin Product 3.

To a flame dried 1-dram vial was added catalyst **B,** (0.03 mmol, 0.15 equiv) β-halo α -keto ester **1** (0.2 mmol, 1.0 equiv), TBME (1 mL, 0.2 M) and benzoin product **3** (0.2 mmol, 1.0 equiv). This solution stirred for 5 minutes followed by the addition of potassium carbonate (0.2 mmol, 1.0 equiv). This reaction was stirred for 14 h, filtered through a short plug of silica gel with Et_2O, and concentrated *in vacuo* for analysis by ^1H NMR.

Procedure for the Gram Scale Asymmetric Cross Benzoin.

To a flame dried 50 mL round bottom flask was added catalyst **B,** (0.55 mmol, 0.15 equiv) β-halo α-keto ester **1** (3.7 mmol, 1.0 equiv), TBME (19 mL, 0.2 M) and benzaldehyde (7.4 mmol, 2.0 equiv). This solution stirred for 5 minutes followed by the addition of potassium carbonate (3.7 mmol, 1.0 equiv). This reaction was stirred (rate of stirring should be >800 rpm) for 14 h, filtered through celite with DCM, and concentrated *in vacuo*. The resulting precipitate was dissolved in MeOH and quenched with (1.1 mmol, 0.3 equiv conc. HCl). The solvent was removed *in vacuo* and the crude residue was purified by column chromatography with 5% EtOAc/hexanes until **2b** (1.26 g, 91% yield, >20:1 dr, 95.5:4.5 er) had eluted from the column (TLC analysis). At this point the eluent was changed to 2.5% MeOH/DCM in order to recover the HCl salt of catalyst **B** (0.15 g, 74% recovery based on the HCl salt).

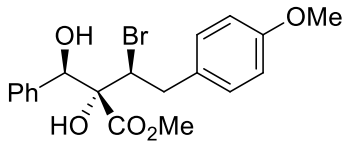
General Procedure C for the Reduction of Cross Benzoin Products.



2 **4**

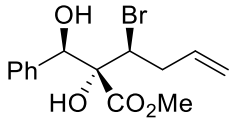
A flame dried scintillation vial was charged with cross-benzoin product **2**, diluted with MeOH (to 0.5 M), and cooled to 0 °C. $NaBH_4$ (5.0 equiv) was added and the reaction was stirred at 0 °C for 7 min, then quenched with saturated NH_4Cl and diluted with Et_2O (15 mL)

and H_2O (10 mL). The layers were separated and the organic layer was further washed with brine (1 x 10 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. In general no further purification was required but if necessary diols **4** could be purified by column chromatography using an eluent of 15% EtOAc/hexanes.



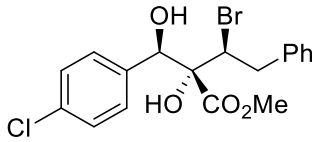
4c

Methyl (2*S*,3*S*)-3-bromo-2-hydroxy-2-((*R*)-hydroxy(phenyl)methyl)-4-(4-methoxyphenyl)butanoate (4c): The title compound was prepared according to General Procedure C using **2c** (0.030 g, 0.074 mmol), affording **4c** (0.027 g, 0.66 mmol, 91% yield, >20:1 dr) as a white solid. Analytical data for **4c: mp** 124.5-125.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42-7.40 (m, 2H), 7.38-7.32 (m, 3H), 7.26-7.19 (m, 2H) 6.87-6.85 (m, 2H), 5.07 (d, *J* = 7.6, Hz, 1H) 4.79 (dd, *J* = 11.4, 2.0 Hz, 1H), 3.84-3.79 (m, 4H), 3.72 (s, 3H), 3.60 (s, 1H), 3.52 (d, *J* = 14.4 Hz, 1H) 2.99 (dd, *J* = 14.4, 11.4 Hz, 1H), 2.85 (d, *J* = 8.1 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.5, 158.5, 138.7, 130.31, 130.29, 128.6, 128.2, 126.7, 113.7, 75.4, 82.7, 60.8, 55.2, 53.2, 37.2; **IR** (thin film): 2927, 2866, 1738, 1514, 803, 602 cm^{-1}; **TLC** (15% EtOAc/hexane): R_f = 0.21; **LRMS** (ESI): Calcd. for $C_{19}H_{21}BrO_5$: ([M+H]): 409.07, Found: 409.17; **SFC:** Regis RP, 15% MeOH, flow rate = 3.0 mL/min, λ = 210 nm, $t_{R\ (major)}$ = 5.5 min $t_{R\ (minor)}$ = 10.8 min, 96:4 er; **[α]$_D$** = -24.8 (*c* = 0.005, DCM)



4d

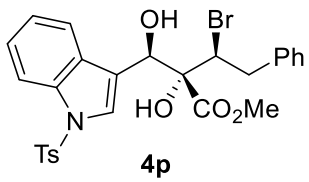
Methyl (2*S*,3*S*)-3-bromo-2-hydroxy-2-((*R*)-hydroxy(phenyl)methyl)hex-5-enoate (4d): The title compound was prepared according to General Procedure C using **2d** (0.040 g, 0.13 mmol), affording **4d** (0.039 g, 0.13 mmol, 98% yield, >20:1 dr) as a white solid. Analytical data for **4c mp** 72.1-73.0 °C;**: ^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.38-7.30 (m, 5H), 5.92-5.85 (m, 1H), 5.19-5.15 (m, 2H) 4.99 (d, *J* = 8.4, Hz, 1H) 4.57 (dd, *J* = 10.8, 2.4 Hz, 1H), 3.73 (s, 3H), 3.55 (s, 1H), 3.55 (s, 1H), 2.91-2.86 (m, 2H), 2.66-2.60 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.6, 138.6, 134.9, 128.6, 128.2, 126.8, 118.0, 75.4, 82.5, 58.1, 53.2, 36.2; **IR** (thin film): 2924, 1731, 1454, 1242, 1024, 701 cm^{-1}; **TLC** (15% EtOAc/hexane): R_f = 0.12; **LRMS** (ESI): Calcd. for $C_{14}H_{17}BrO_4$: ([M+NH_4]): 347.22, Found: 347.22; **SFC:** Regis RP, 5% MeOH, flow rate = 3.0 mL/min, λ = 210 nm, $t_{R\ (major)}$ = 7.7 min $t_{R\ (minor)}$ = 8.7 min, 95.5:4.5 er; **[α]$_D$** = -20.1 (*c* = 0.007, DCM)



4m

Methyl (2*S*,3*S*)-3-bromo-2-((*R*)-(4-chlorophenyl)(hydroxy)methyl)-2-hydroxy-4-phenylbutanoate (4m): The title compound was prepared according to General Procedure C using **2m** (0.031 g, 0.075 mmol), affording **4m** (0.030 g, 0.073 mmol, 97% yield, >20:1 dr) as a white solid. This solid was then recrystallized from 5% EtOAc/hexanes. Analytical data for **4m: mp** 149.2-150.0 °C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.38-7.26 (m, 9H), 5.06 (d, *J* = 8.2 Hz, 1H), 4.78 (dd, *J* = 11.3, 2.6 Hz, 1H), 3.72 (s, 3H), 3.64 (s, 1H), 3.58 (dd, *J* = 14.6, 2.6 Hz, 1H), 3.03 (dd, *J* = 22.4, 14.6 Hz, 1H) 2.98 (d, *J* = 8.2 Hz, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ

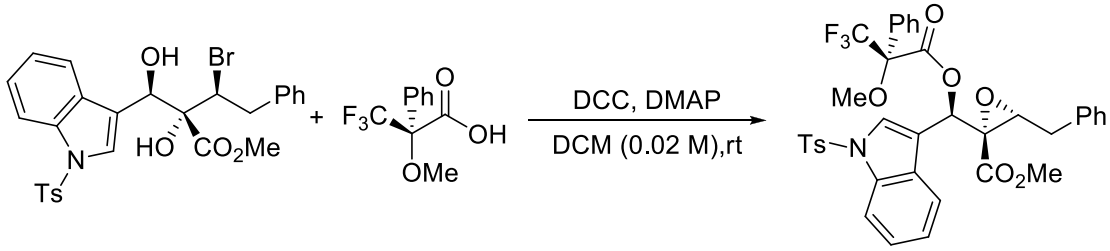
172.4, 138.1, 137.2, 134.5, 131.0, 129.3, 128.4, 128.2, 126.9, 82.6, 74.7, 60.0, 53.4, 38.1; **IR** (thin film): 3059, 2989, 2688, 2309, 1738, 1429, 1267 cm^{-1}; **TLC** (15% EtOAc/hexane): R_f = 0.41; **LRMS** (ESI): Calcd. for $C_{18}H_{18}BrClO_4$: ([M+Na]): 435.00, Found: 435.09; **SFC:** Regis RP, 15% MeOH, flow rate = 3.0 mL/min, λ = 210 nm, $t_{R\ (major)}$ = 4.4 min $t_{R\ (minor)}$ = 8.2 min, 98:2 er (>99.9:0.1 recrystallized); $[\alpha]_D$ = -56.3 (*c* = 0.004, DCM)



4p

Methyl (2*S*,3*S*)-3-bromo-2-hydroxy-2-((*R*)-hydroxy(1-tosyl-1H-indol-3-yl)methyl)-4-phenylbutanoate (4p): The title compound was prepared according to General Procedure C using **2p** affording **4p** (0.074 g, 0.13 mmol, 65% yield, 10:1 dr) as a white solid. Analytical data for **4p: mp** 74.8-75.2 °C; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.73-7.68 (m, 3H), 7.35-7.25 (m, 7H), 7.18 (d, *J* = 7.8 Hz, 2H), 5.42-5.41 (m, 1H), 4.71 (d, *J* = 10.8 Hz, 1H), 3.83 (s, 1H), 3.77 (s, 3H), 3.56 (d, *J* = 14.4 Hz, 1H), 3.02-2.97 (m, 1H) 2.33 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 172.8, 145.1, 138.0, 135.0, 134.9, 129.9, 128.4, 126.9, 126.8, 126.7, 125.1, 124.3, 123.3, 121.4, 121.1, 113.5, 83.0, 74.7, 69.7, 59.4, 53.4, 38.3, 21.5; **IR** (thin film): 3059, 2989, 2306, 1738, 1429, 1267, 896 cm^{-1}; **TLC** (15% EtOAc/hexane): R_f = 0.21; **LRMS** (ESI): Calcd. for $C_{27}H_{26}BrNO_6S$: ([M+Na]): 594.06, Found: 594.06; **4p** could not be directly analyzed via SFC, see compound **5** for enantiomeric analysis; $[\alpha]_D$ = -24.8 (*c* = 0.007, DCM)

Synthesis of the Mosher ester of 2p



4p **5**

A flame dried scintillation vial was loaded with cross-benzoin diol **4p** (0.035 mmol, 1.0 equiv)**,** (R)- α-methoxy- α-trifluoromethylphenylacetic acid (0.042 mmol, 1.2 equiv) and DCM (2.0 mL, 0.02 M). To this was added *N,N*-dicyclohexylcarboimide (0.07 mmol, 2.0 equiv) and 4-dimethylaminopyridine (0.035 mmol, 1.0 equiv) This reaction mixture was stirred at rt for 18 h then filtered through celite. The filtrate was then diluted with 1M HCl (10 mL) and EtOAc (10 mL). The layers were separated and the organic layer was further washed with 1 M NaOH (2 x 10 mL) and brine (1 x 10 mL). The organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The reaction mixture was purified by column chromatography using an eluent of 10% EtOAc/hexanes providing **5** as a colorless oil (22 mg, 0.031 mmol, 89% yield, 98:2 er).

Analytical data for **(2*S*,3*R*)-methyl 3-benzyl-2-((*R*)-(1-tosyl-1*H*-indol-3-yl)((*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyloxy)methyl)oxirane-2-carboxylate (5): ^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.88 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.57 (s, 1H), 7.40-7.39 (d, *J* = 7.8 Hz, 1H), 7.28-7.21 (m, 4H), 7.09-7.00 (m, 9H), 6.96 (s, 1H), 3.82 (s, 3H), 3.42 (s, 3H), 2.90-2.86 (m, 1H), 2.76-2.72 (m, 2H) 2.25 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 167.8, 165.3, 145.2, 135.6, 134.7, 134.5, 131.3, 129.8, 129.5, 128.8, 128.7, 128.4, 128.0, 127.5, 127.1, 126.9, 126.7, 125.0, 123.6, 121.0, 114.2, 113.4, 71.0, 63.2, 60.3, 55.5, 52.9, 33.9, 29.7 21.5 (two coincident peaks); **^{19}F NMR** (376 MHz, $CDCl_3$): δ_{major} 71.85 δ_{minor} 71.6, 98:2 er; **IR** (thin film): 3059, 2989, 2306, 1738, 1429, 1267, 896 cm^{-1}; **TLC** (15% EtOAc/hexane): R_f = 0.21; **LRMS** (ESI): Calcd. for $C_{37}H_{32}NO_8S$: ([M+Na]): 730.17, Found: 730.31; **$[a]_D$** = 39.0 (*c* = 0.007, DCM).

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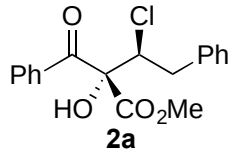
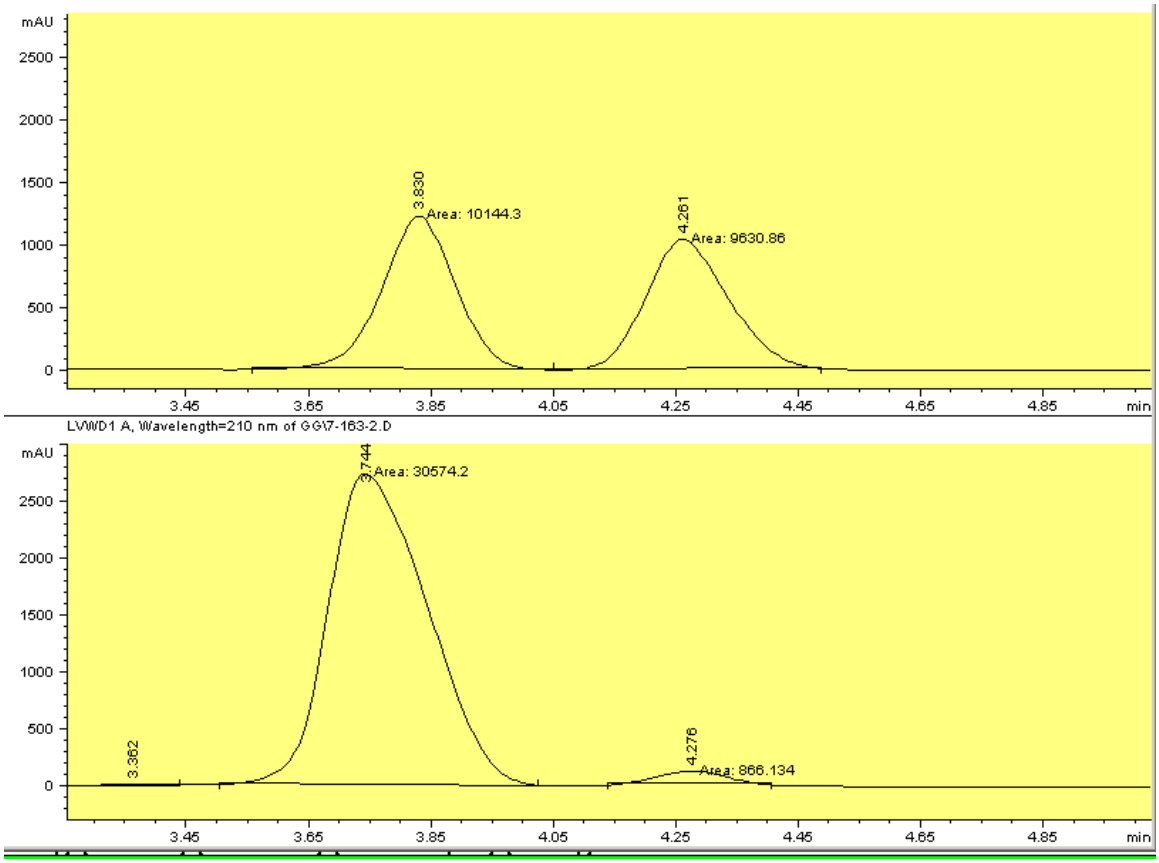
SFC and HPLC traces



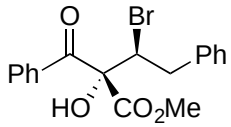
2a



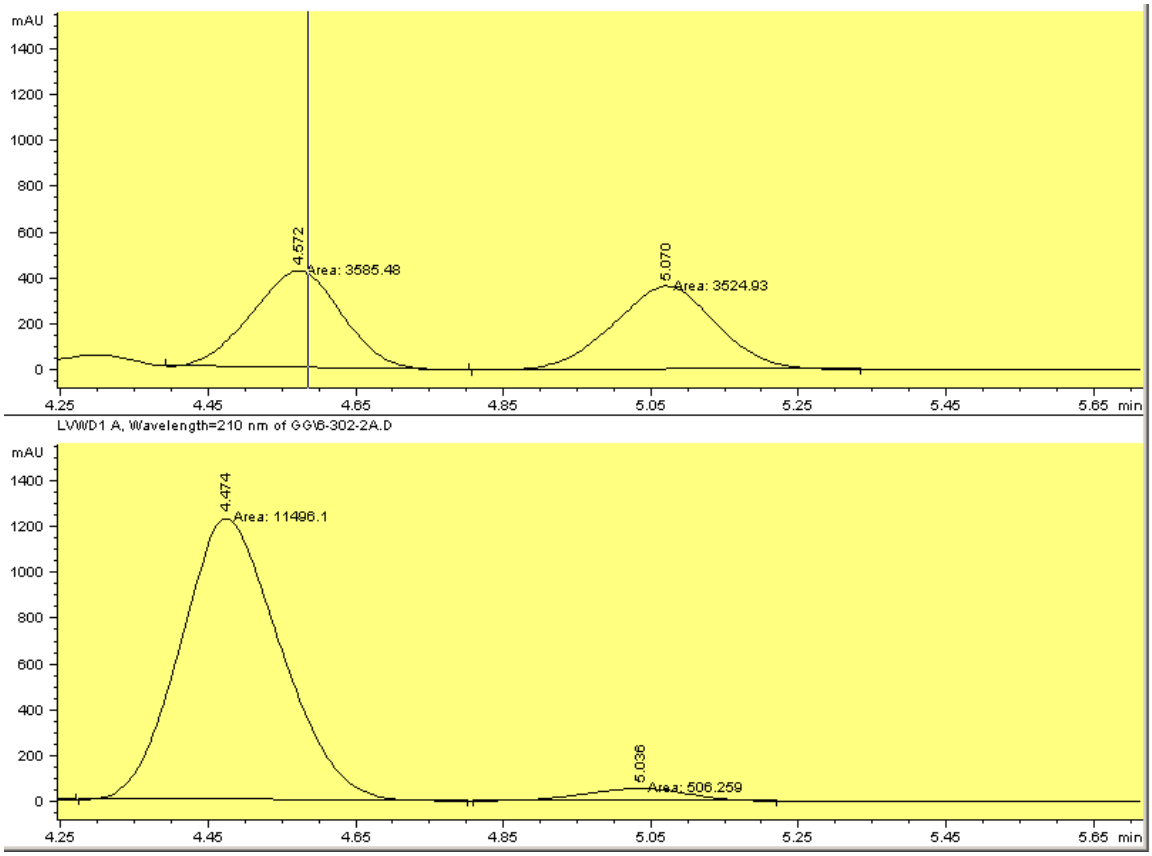
Signal 1: LVWD1 A, Wavelength=210 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	3.744	MM	0.189	31127.66406	2745.94067	96.3080
2	4.276	MM	0.147	1193.30249	135.02567	3.6920
Totals :				32320.96680	2880.96631	

*** End of Report ***



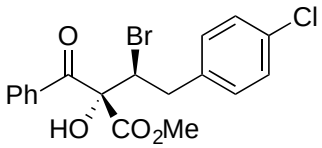
2b



Signal 1: LVWD1 A, Wavelength=210 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	3.744	MM	0.189	31127.66406	2745.94067	96.3080
2	4.276	MM	0.147	1193.30249	135.02567	3.6920
Totals :				32320.96680	2880.96631	

*** End of Report ***



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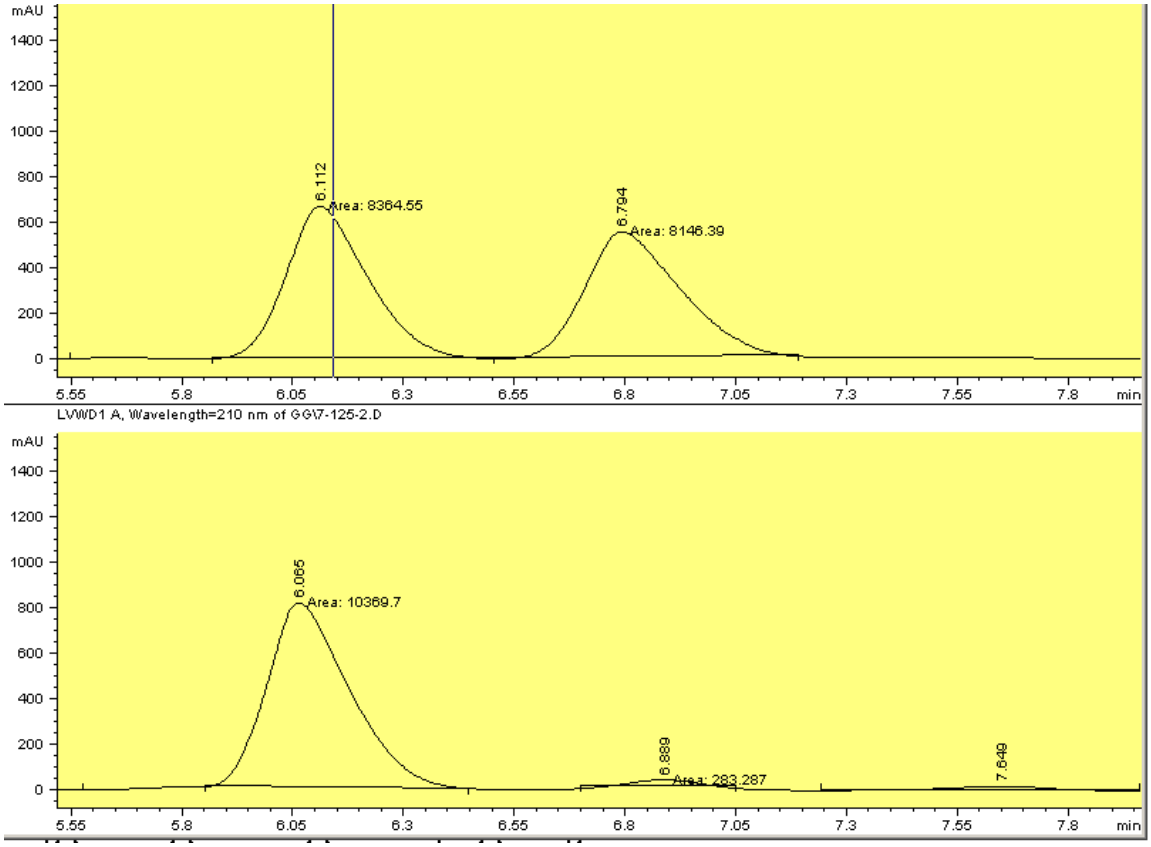
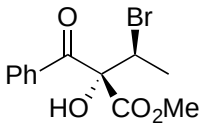


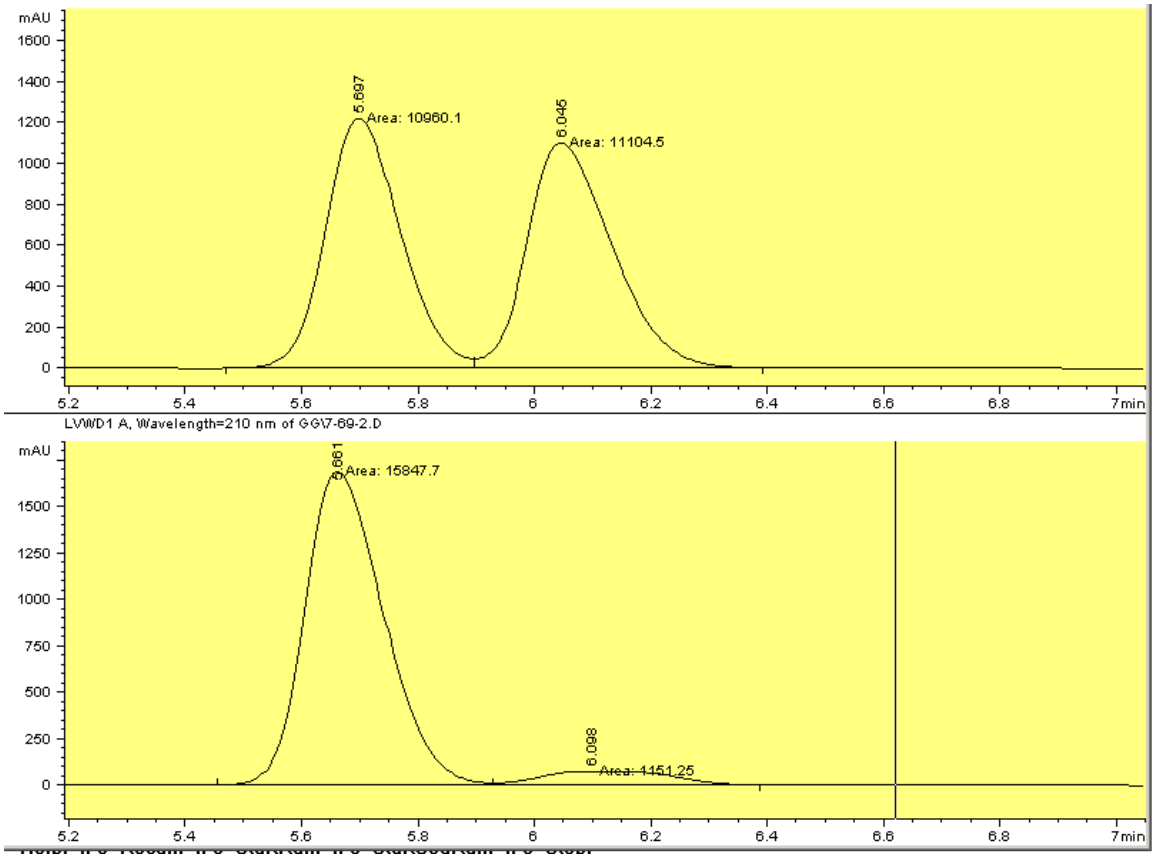
Signal 1: LVWD1 A, Wavelength=210 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	6.065	MM	0.223	10944.87598	819.77118	94.9026
2	6.888	MM	0.221	587.86420	44.27318	5.0974
Totals :				11532.74023	864.04437	

*** End of Report ***



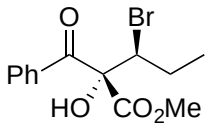
2f



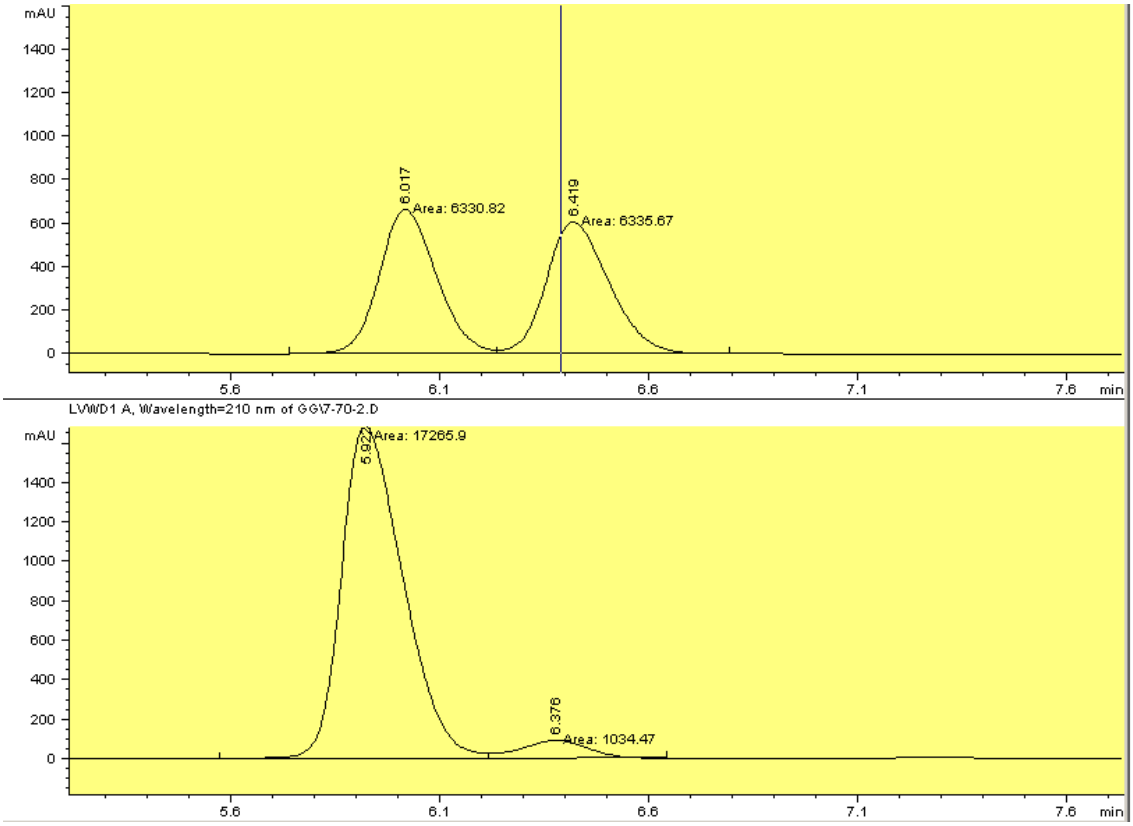
Signal 1: LVWD1 A, Wavelength=210 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	5.661	MF	0.156	15865.81836	1695.28894	93.0649
2	6.097	FM	0.262	1182.31006	75.20283	6.9351
Totals :				17048.12891	1770.49182	

*** End of Report ***



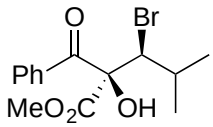
2g



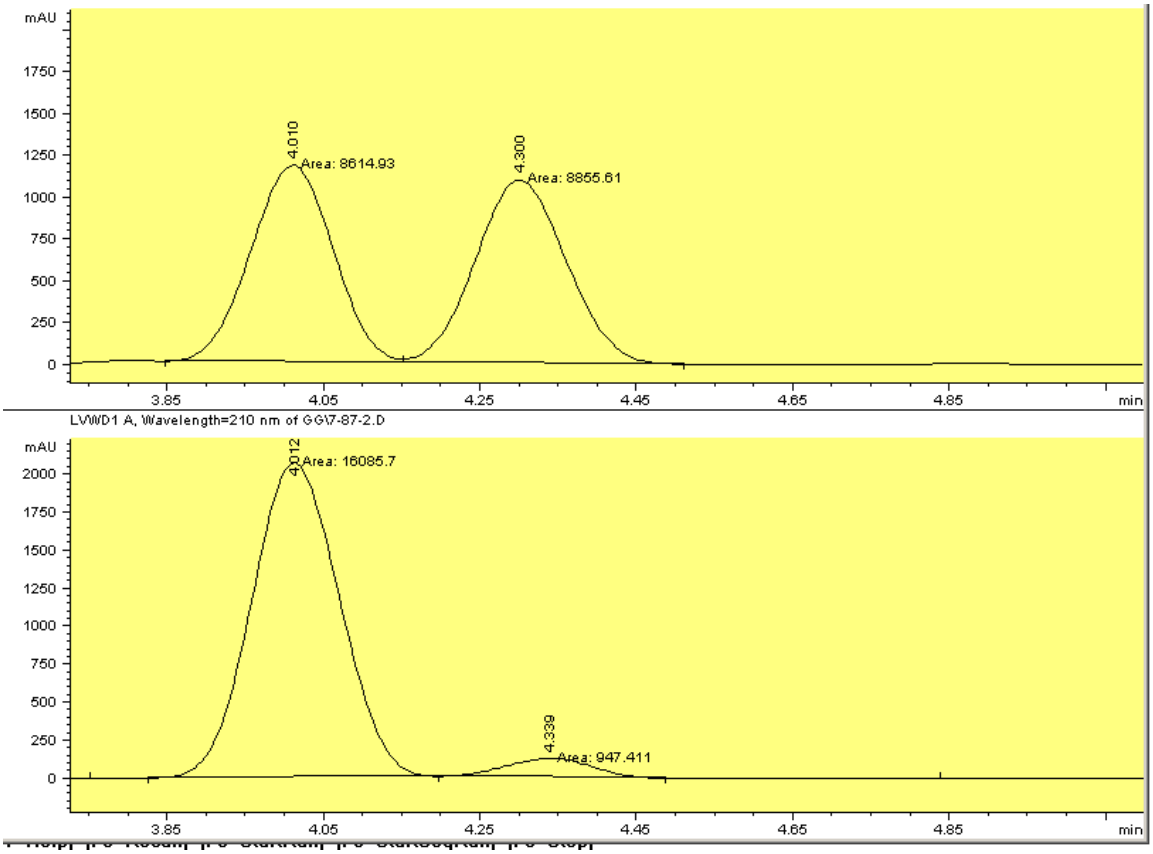
Signal 1: LVWD1 A, Wavelength=210 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	5.921	MF	0.169	17286.55859	1702.33911	94.0402
2	6.376	FM	0.195	1095.52734	93.69172	5.9598
Totals :				18382.08594	1796.03088	

*** End of Report ***



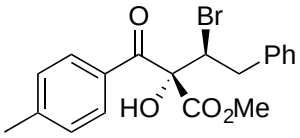
2h



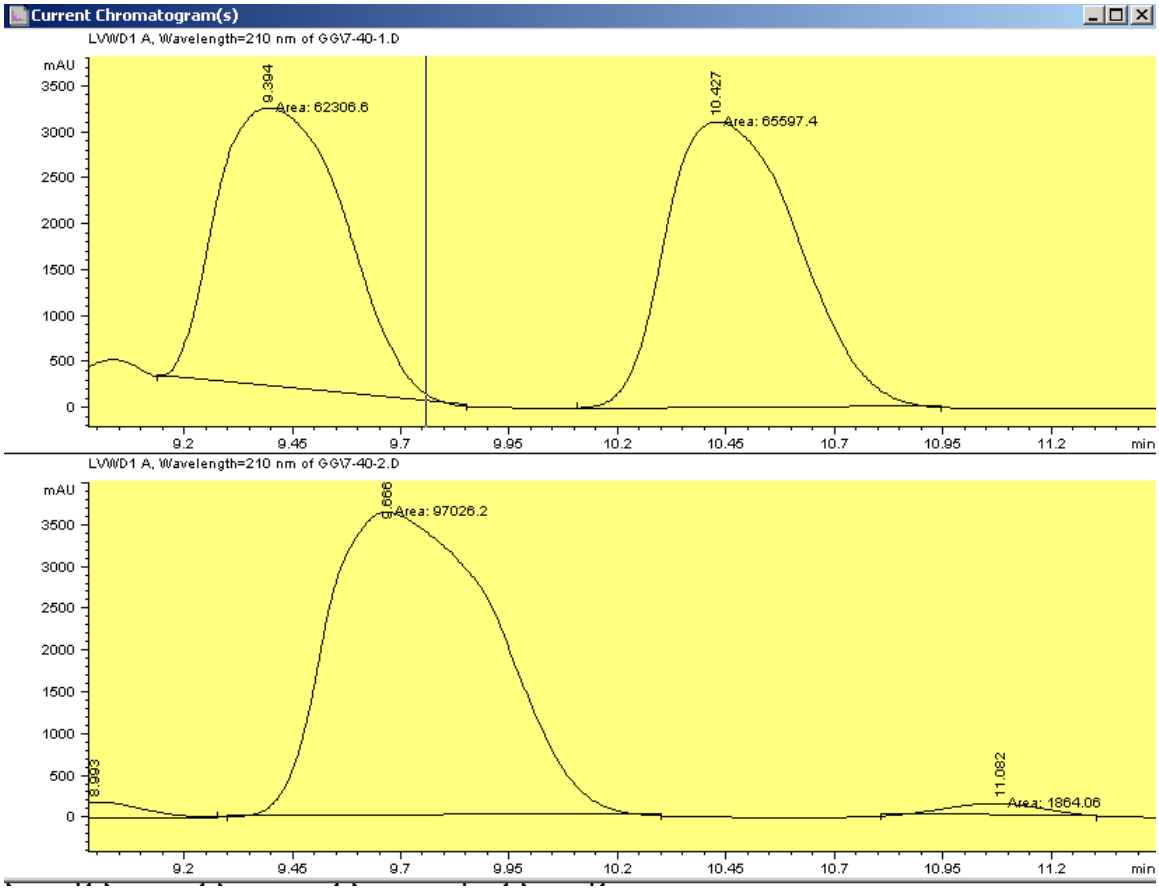
Signal 1: LVWD1 A, Wavelength=210 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	4.012	MF	0.130	16241.34668	2086.26978	93.7932
2	4.339	FM	0.136	1074.78687	132.16475	6.2069
Totals :				17316.13281	2218.43457	

*** End of Report ***



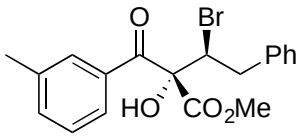
2i



Signal 1: LVWD1 A, Wavelength=210 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	9.666	MM	0.450	98423.57813	3647.09424	97.0284
2	11.070	MM	0.302	3014.31030	166.53088	2.9716
Totals :				101437.89062	3813.62500	

*** End of Report ***



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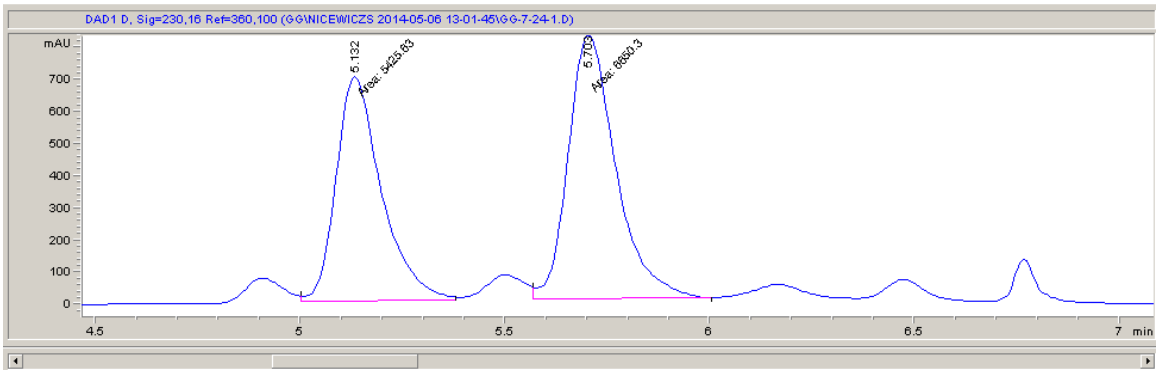
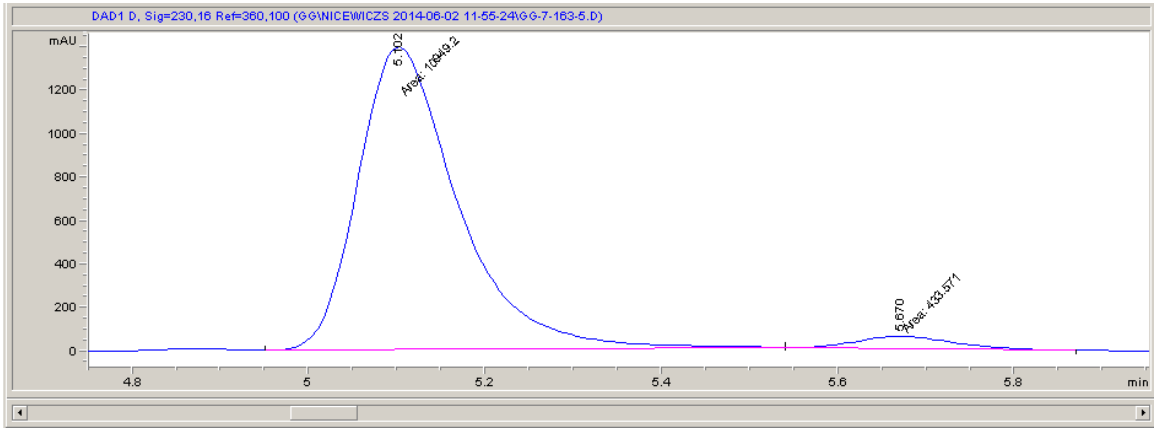
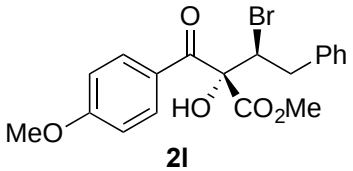
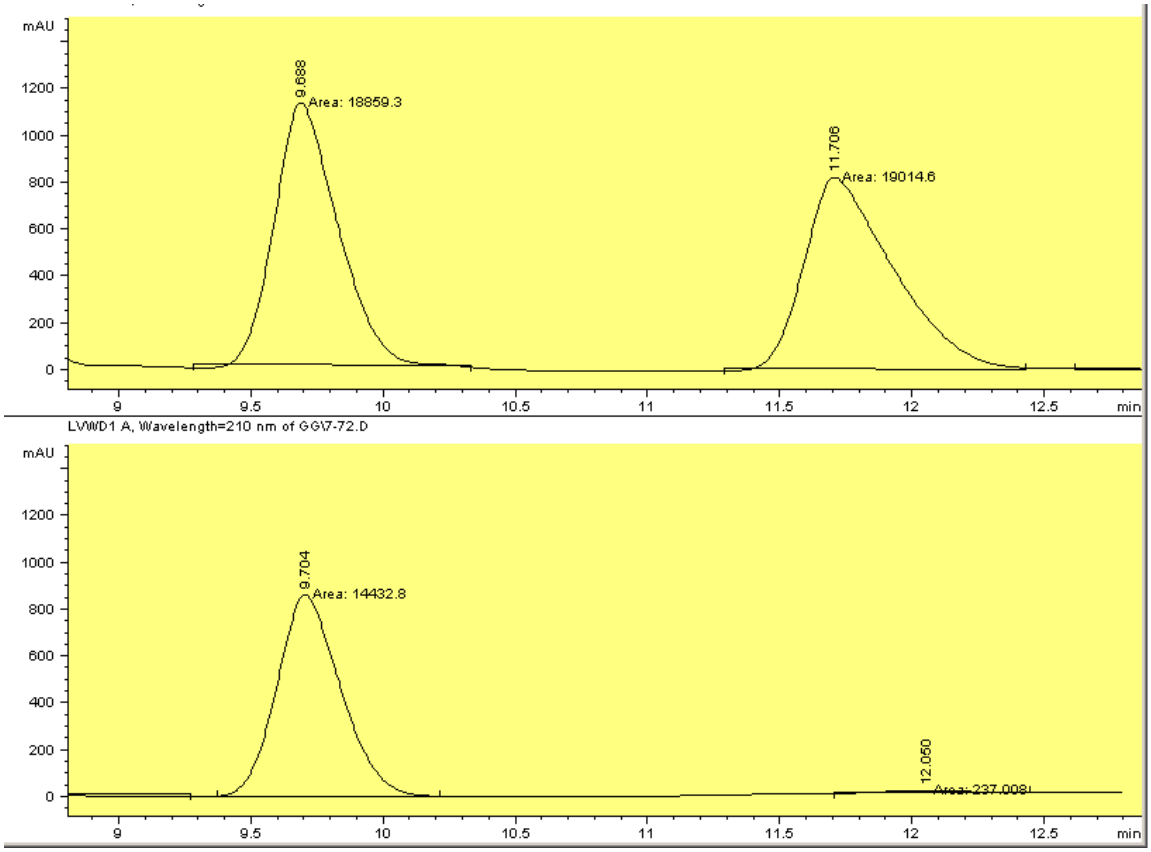




#	Time	Area	Height	Width	Area%	Symmetry
1	5.102	10949.2	1393.8	0.1309	96.191	0.662
2	5.67	433.6	56.4	0.1282	3.809	0.787



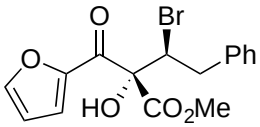
2l



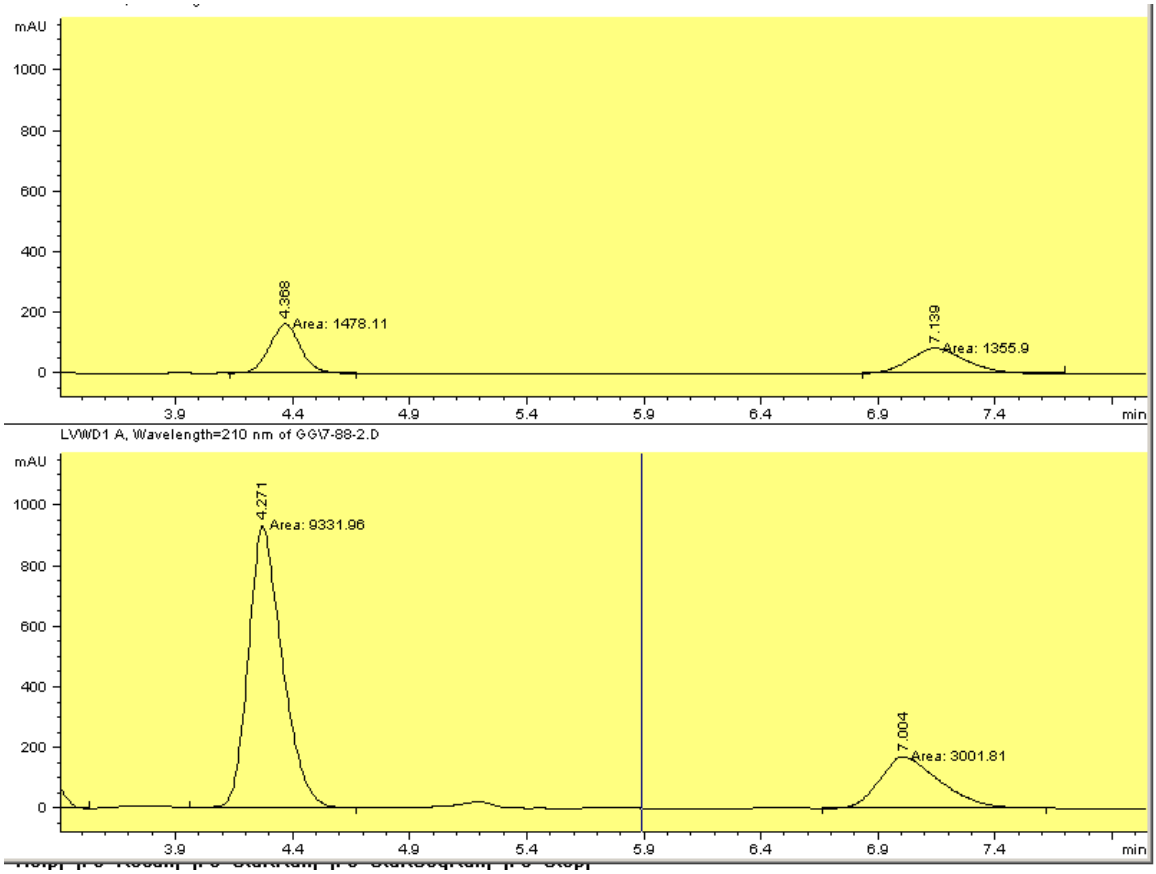
Signal 1: LVWD1 A, Wavelength=210 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	9.704	MM	0.279	14473.55078	865.08984	97.8602
2	12.050	MM	0.377	316.48083	13.99325	2.1398
Totals :				14790.03125	879.08307	

*** End of Report ***



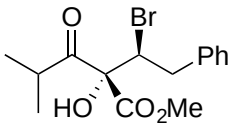
2n



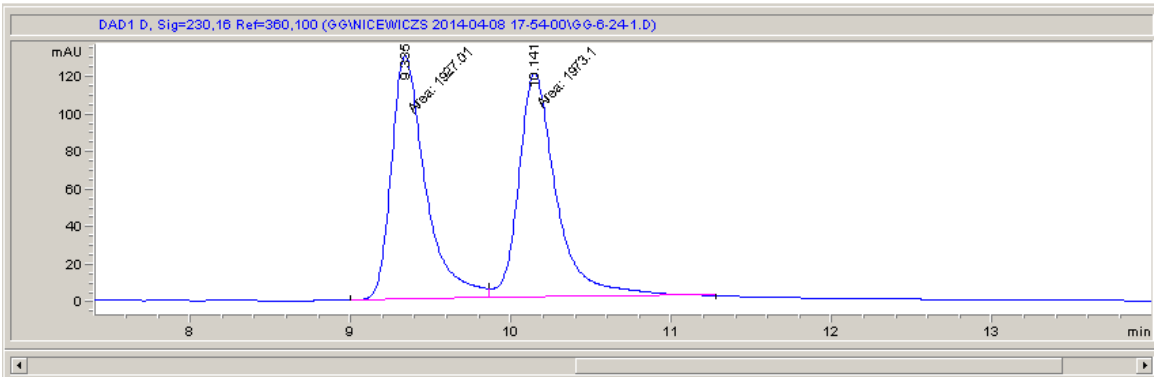
Signal 1: LVWD1 A, Wavelength=210 nm

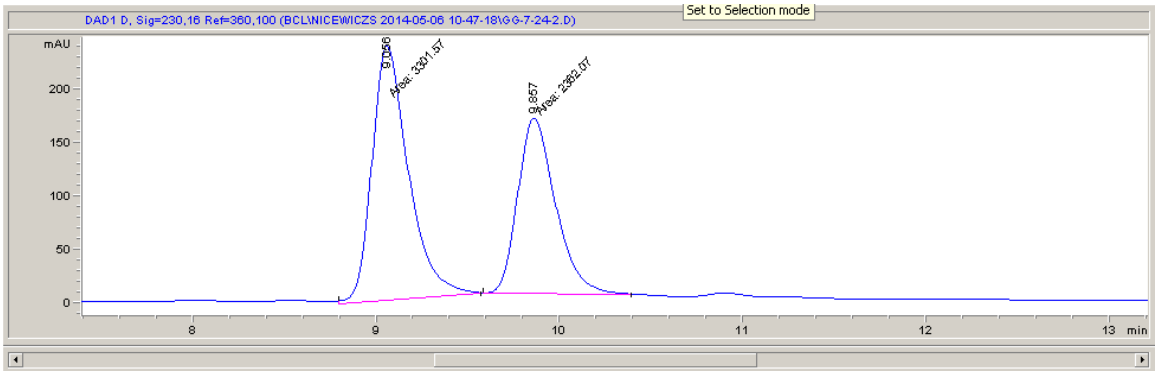
Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	4.271	MM	0.166	9333.30957	935.76410	75.5034
2	7.004	FM	0.297	3028.13525	170.21275	24.4966
Totals :				12361.44531	1105.97681	

*** End of Report ***

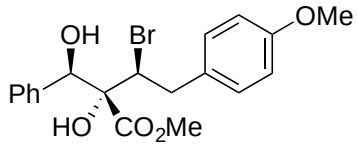


2o

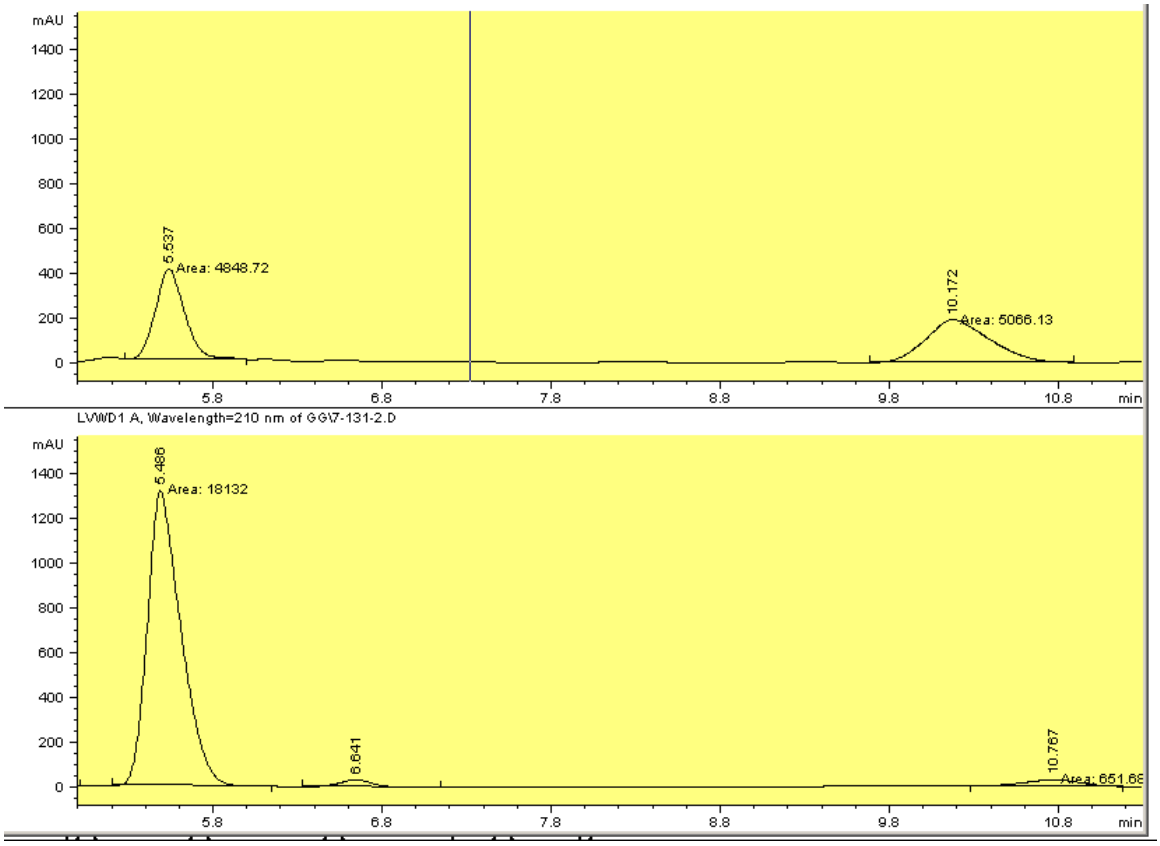




#	Time	Area	Height	Width	Area%	Symmetry
1	9.056	3301.6	239	0.2303	58.294	0.674
2	9.857	2362.1	164.9	0.2387	41.706	0.719



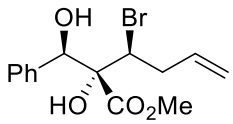
4c



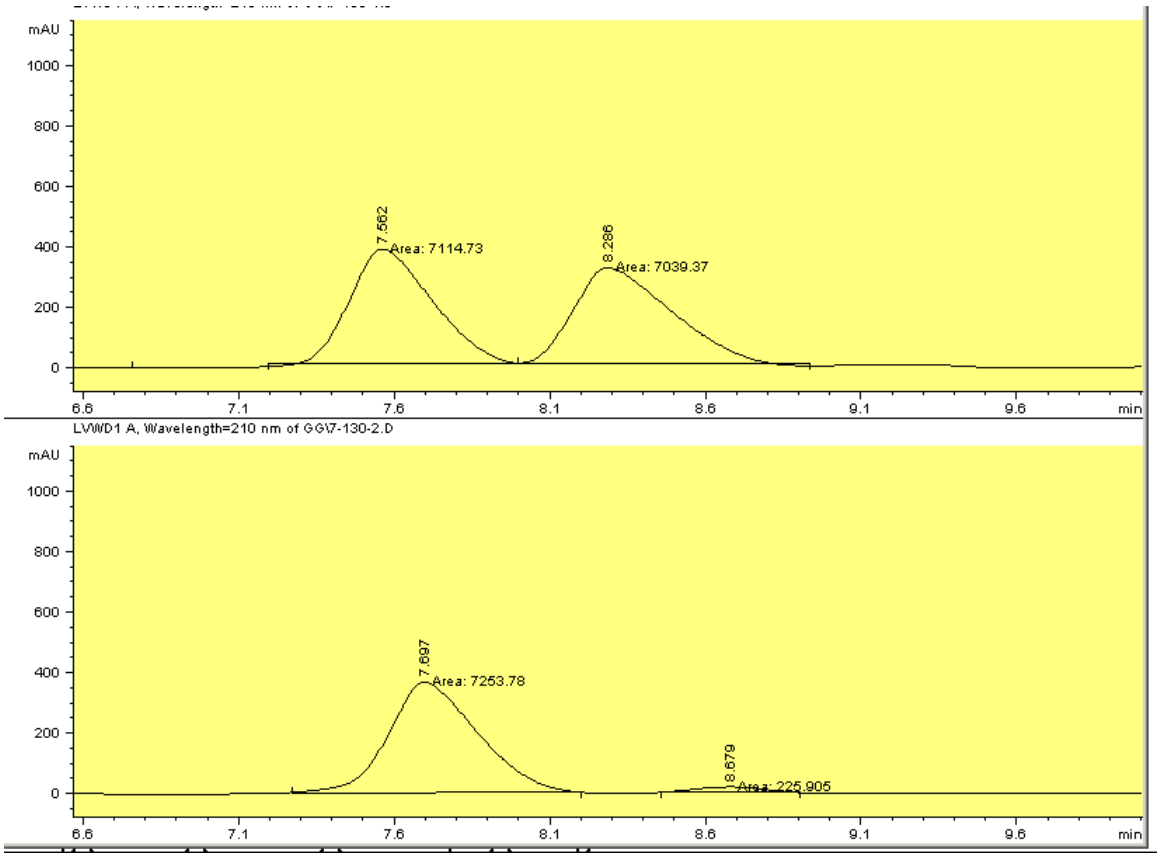
Signal 1: LVWD1 A, Wavelength=210 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	5.485	MM	0.230	18337.21484	1326.79773	96.0879
2	10.767	MM	0.416	746.57886	29.89055	3.9121
Totals :				19083.79297	1356.68823	

*** End of Report ***



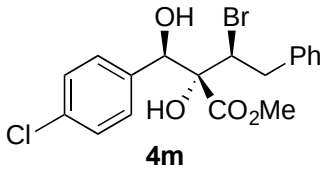
4d



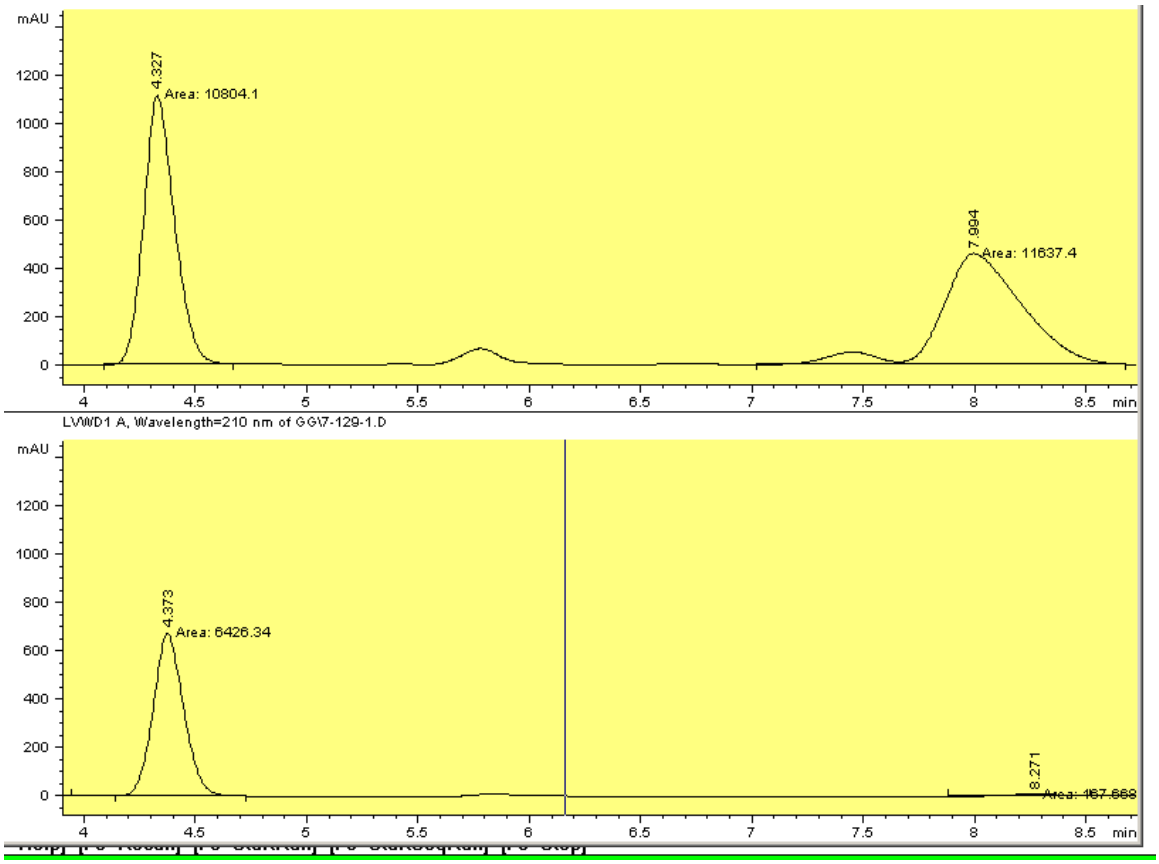
Signal 1: LVWD1 A, Wavelength=210 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	7.697	MF	0.340	7553.62842	370.17178	94.5033
2	8.679	FM	0.311	439.34650	23.54018	5.4967
Totals :				7992.97510	393.71198	

*** End of Report ***

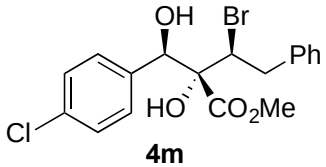


4m



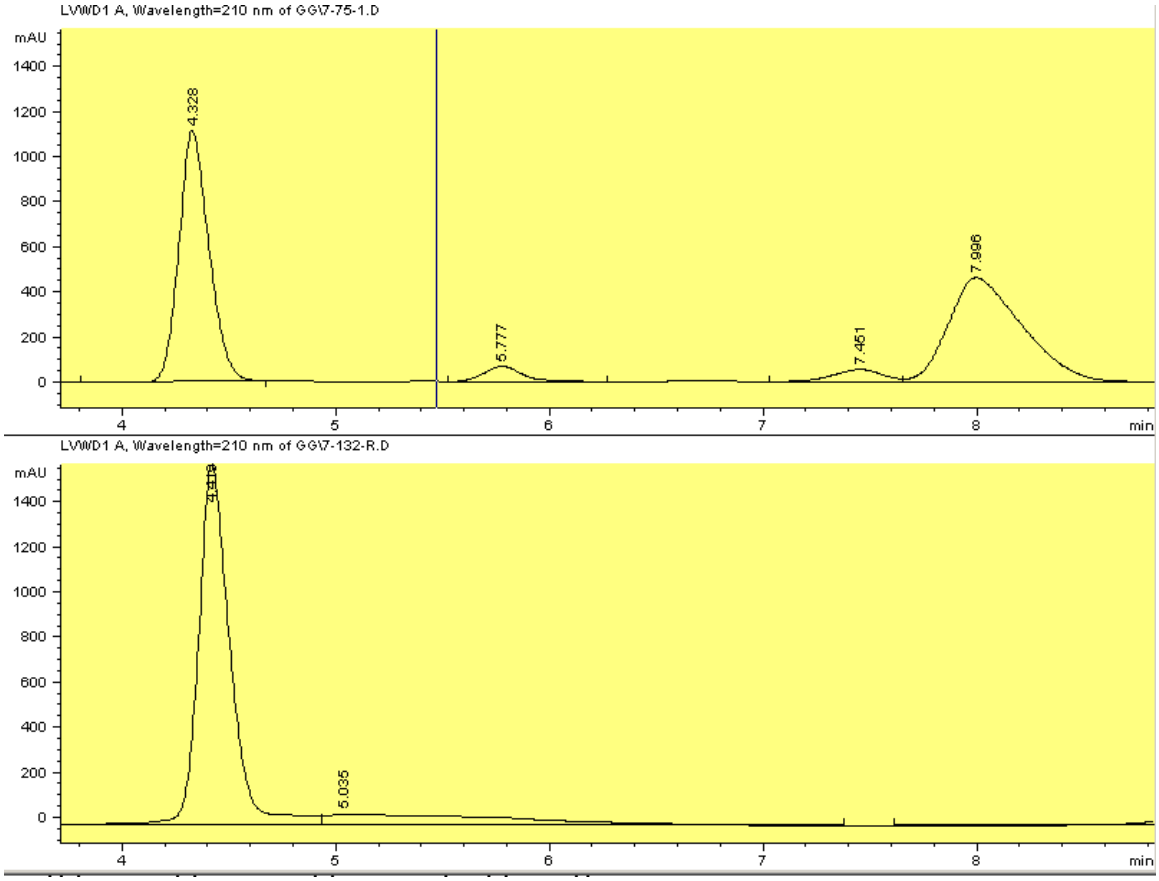
Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	4.373	MM	0.159	6445.78369	677.54773	97.7366
2	8.271	MM	0.287	149.27110	8.67632	2.2634
Totals :				6595.05469	686.22406	

*** End of Report ***

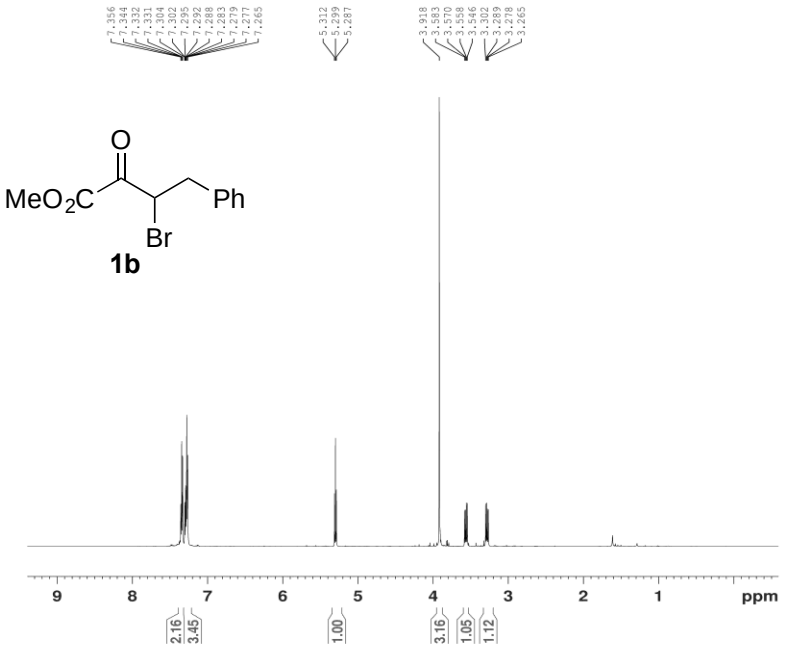


4m

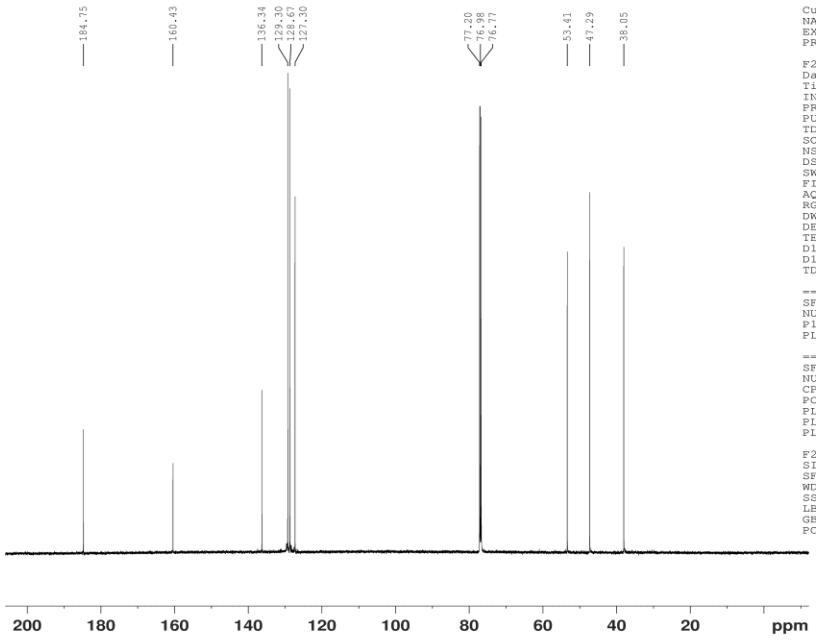
Recrystallized:



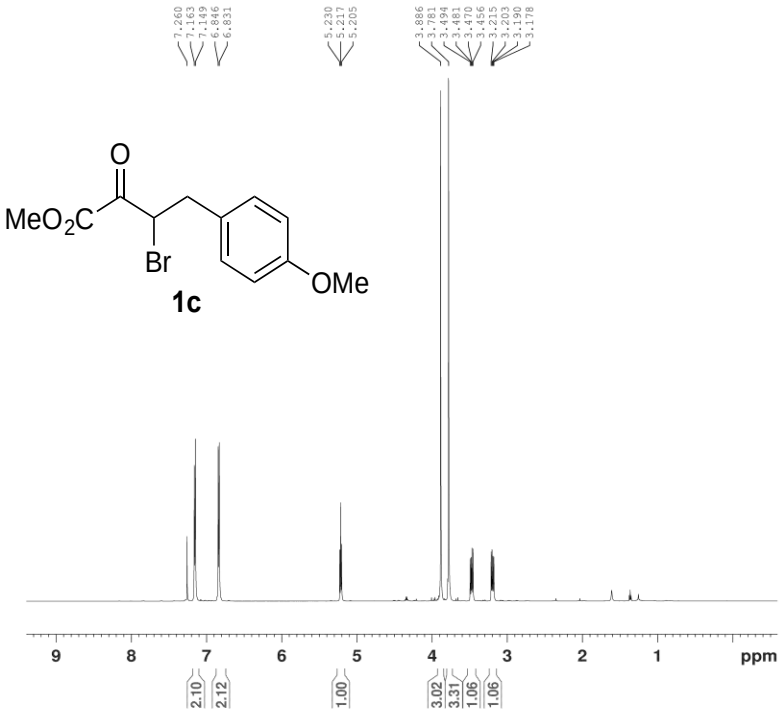
^{1}H, ^{13}C ^{19}F, NMR Spectra



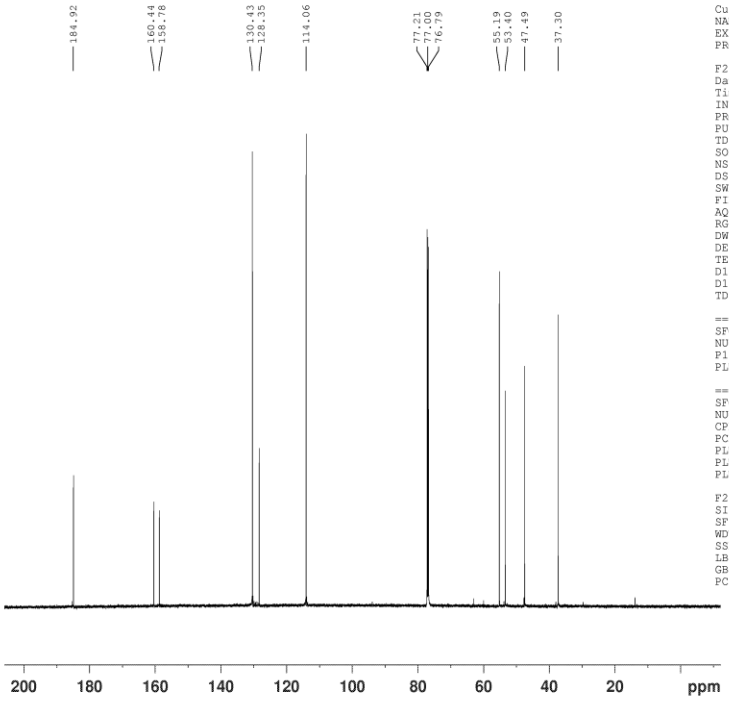

```
Current Data Parameters
NAME              GG-7-159
EXPNO                    1
PROCNO                   1

F2 - Acquisition Paramet
Date_              20140613
Time                   8.06
INSTRUM               spect
PROBHD   5 mm CPQCI 1H/
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       9
DS                       0
SWH              12019.230 H
FIDRES           0.183399 H
AQ               2.7262976 s
RG                    12.7
DW                   41.600 u
DE                   10.00 u
TE                   298.2 K
D1              1.00000000 s
TD0                      1

======== CHANNEL f1 =====
SFO1          600.1337060 M
NUC1                   1H
P1                  11.00 u
PLW1          13.00000000 W

F2 - Processing paramete
SI                   65536
SF            600.1300000 M
WDW                    EM
SSB       0
LB                  0.30 H
GB        0
PC                  1.00
```



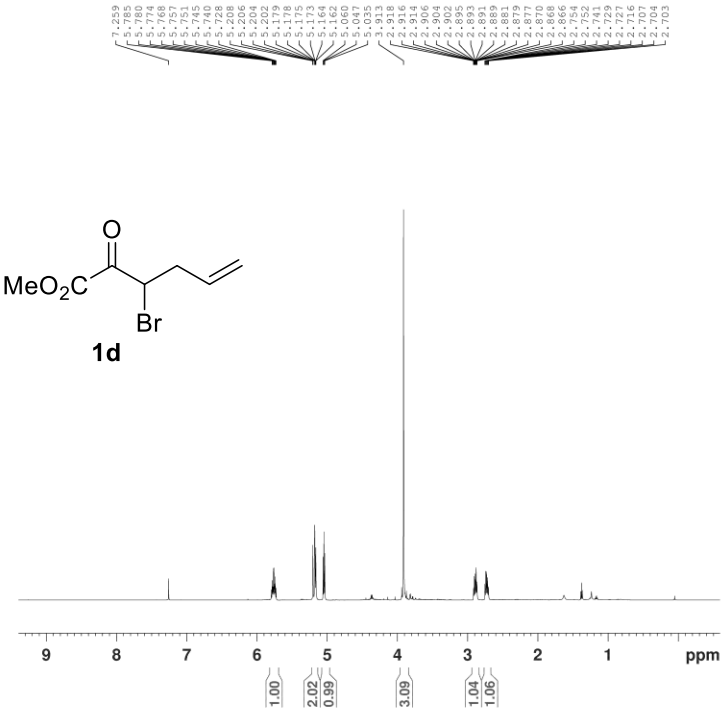

```
Current Data Parameters
NAME          GG-7-159-C13
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_              20140613
Time                   1.08
INSTRUM               spect
PROBHD   5 mm CPQCI 1H/
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     128
DS                       4
SWH            36057.691 Hz
FIDRES          0.550197 Hz
AQ              0.9087659 sec
RG                     203
DW                13.867 usec
DE                 18.00 usec
TE                 298.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1          150.9178981 MHz
NUC1                    13C
P1                  11.35 usec
PLW1        230.00000000 W

======== CHANNEL f2 ========
SFO2          600.1324005 MHz
NUC2                    1H
CPDPRG[2          waltz16
PCPD2               90.00 usec
PLW2          13.00000000 W
PLW12          0.19774000 W
PLW13          0.16017000 W

F2 - Processing parameters
SI                   32768
SF            150.9028217 MHz
WDW                    EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```



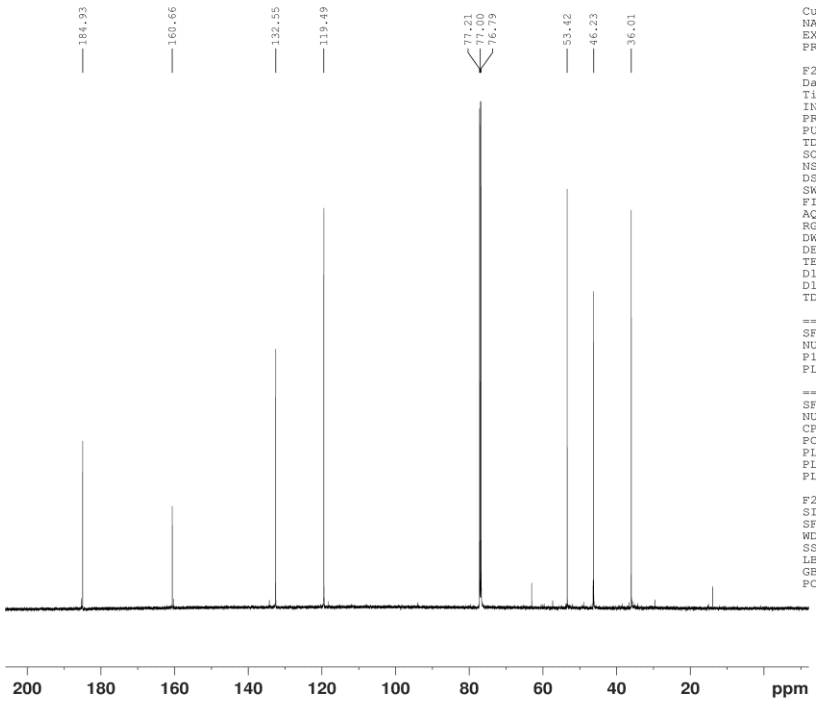

```
Current Data Parameters
NAME            GG-7-115
EXPNO                  1
PROCNO                 1

F2 - Acquisition Paramete
Date_           20140613
Time                8.04
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH            12019.230 H
FIDRES          0.183399 H
AQ             2.7262976 s
RG                  12.7
DW                41.600 u
DE                10.00 u
TE                298.2 K
D1            1.00000000 s
TD0                    1

======== CHANNEL f1 =====
SFO1          600.1337060 M
NUC1                   1H
P1                  11.00 u
PLW1          13.00000000 W

F2 - Processing paramete
SI                 65536
SF            600.1300145 M
WDW                   EM
SSB       0
LB                 0.30 H
GB        0
PC                 1.00
```



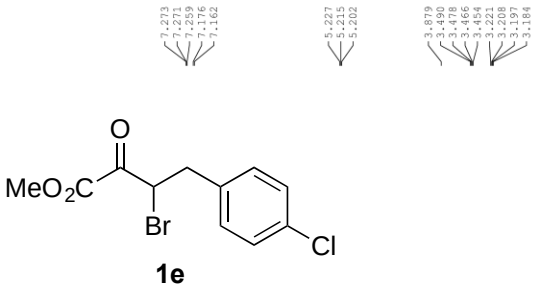

```
Current Data Parameters
NAME        GG-7-115-C13
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_           20140613
Time                0.58
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     4
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ            0.9087659 sec
RG                   203
DW               13.867 usec
DE                18.00 usec
TE                298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         150.9178981 MHz
NUC1                   13C
P1                 11.35 usec
PLW1        230.00000000 W

======== CHANNEL f2 ========
SFO2         600.1324005 MHz
NUC2                   1H
CPDPRG[2           waltz16
PCPD2             90.00 usec
PLW2         13.00000000 W
PLW12         0.19774000 W
PLW13         0.16017000 W

F2 - Processing parameters
SI                 32768
SF           150.9028182 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```



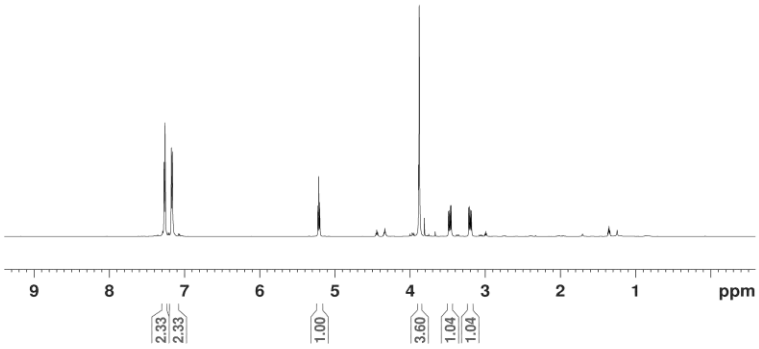

```
Current Data Parameters
NAME              GG-7-108
EXPNO                    1
PROCNO                   1

F2 - Acquisition Paramete
Date_              20140613
Time                   8.02
INSTRUM               spect
PROBHD    5 mm CPQCI 1H/
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                        6
DS                        0
SWH               12019.230 H
FIDRES                0.183399 H
AQ                2.7262976 s
RG                     12.7
DW                    41.600 u
DE                    10.00 u
TE                    298.2 K
D1                1.00000000 s
TD0                       1

======== CHANNEL f1 =====
SFO1            600.1337060 M
NUC1                     1H
P1                    11.00 u
PLW1           13.00000000 W

F2 - Processing paramete
SI                    65536
SF              600.1300151 M
WDW                      EM
SSB       0
LB                     0.30 H
GB        0
PC                     1.00
```



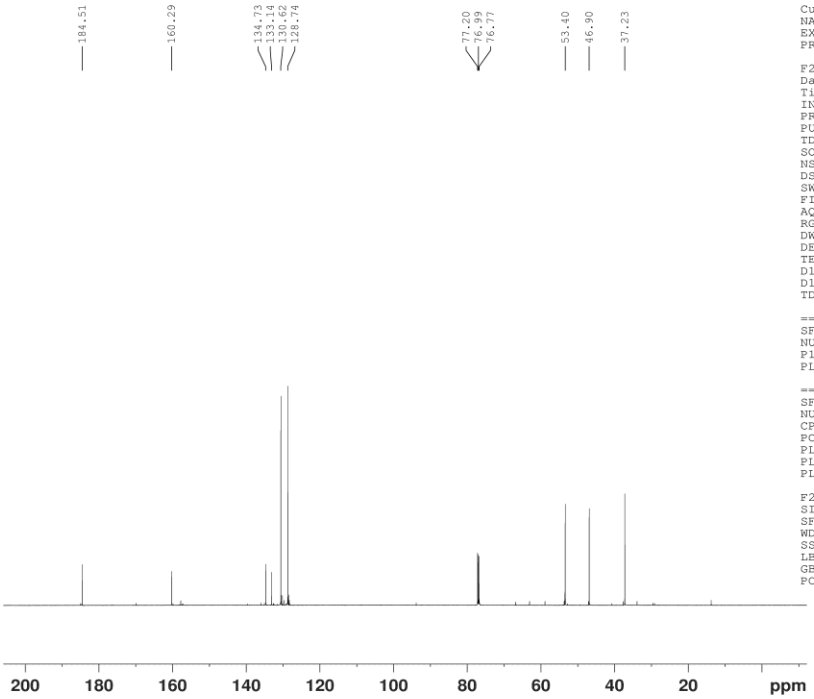

```
Current Data Parameters
NAME          GG-7-108-C13
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_              20140613
Time                   0.49
INSTRUM               spect
PROBHD    5 mm CPQCI 1H/
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      128
DS                        4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ                0.9087659 sec
RG                      203
DW                  13.867 usec
DE                  18.00 usec
TE                  298.1 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            150.9178981 MHz
NUC1                     13C
P1                  11.35 usec
PLW1           230.00000000 W

======== CHANNEL f2 ========
SFO2            600.1324005 MHz
NUC2                     1H
CPDPRG[2              waltz16
PCPD2                90.00 usec
PLW2           13.00000000 W
PLW12           0.19774000 W
PLW13           0.16017000 W

F2 - Processing parameters
SI                    32768
SF              150.9028166 MHz
WDW                      EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.40
```



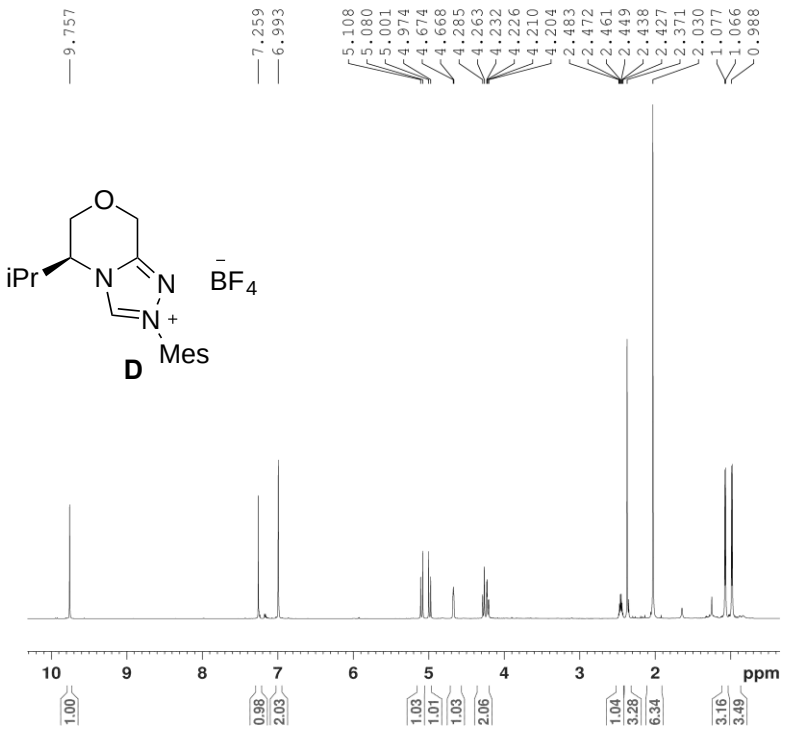
1e



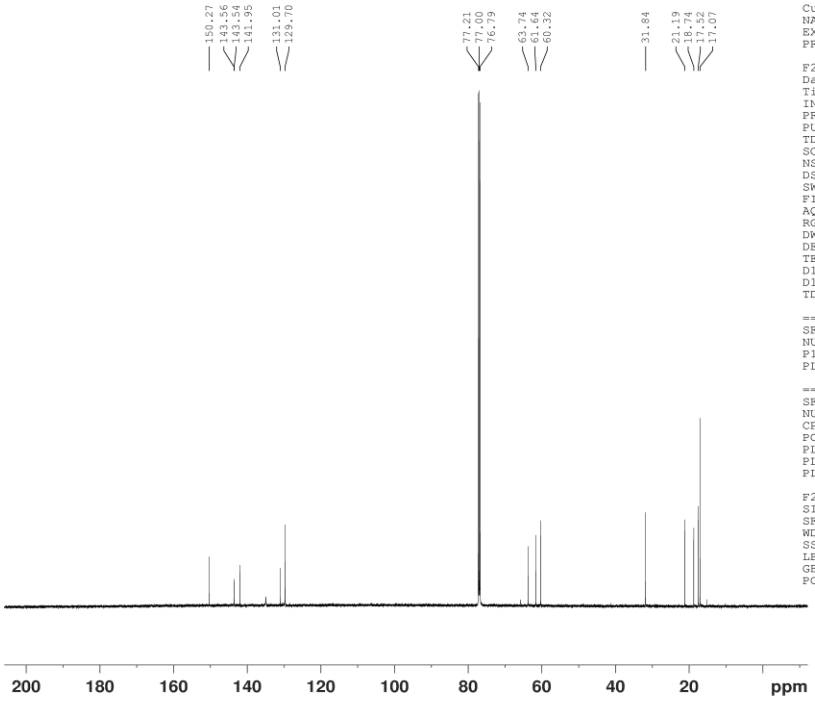

```
Current Data Parameters
NAME                  GG-7-118
EXPNO                        1
PROCNO                       1

F2 - Acquisition Paramete
Date_               20140613
Time                    8.07
INSTRUM                spect
PROBHD    5 mm CPQCI 1H/
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        10
DS                         0
SWH                12019.230 H
FIDRES              0.183399 H
AQ                  2.7262976 s
RG                        10
DW                     41.600 u
DE                     10.00 u
TE                     298.1 K
D1                 1.00000000 s
TD0                        1

======== CHANNEL f1 =====
SFO1             600.1337060 M
NUC1                      1H
P1                     11.00 u
PLW1            13.00000000 W

F2 - Processing paramete
SI                     65536
SF               600.1300140 M
WDW                       EM
SSB          0
LB                      0.30 H
GB           0
PC                     1.00
```



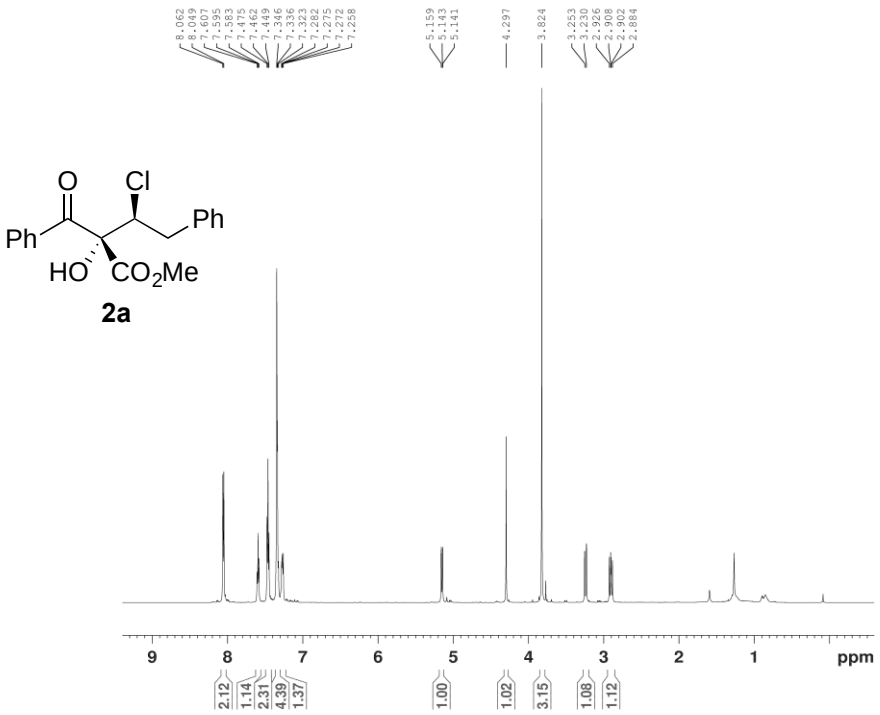

```
Current Data Parameters
NAME          GG-7-118-C13
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_               20140613
Time                    8.17
INSTRUM                spect
PROBHD    5 mm CPQCI 1H/
PULPROG             zgpg30
TD                     65536
SOLVENT                CDCl3
NS                       273
DS                         0
SWH                36057.691 Hz
FIDRES              0.550197 Hz
AQ                  0.9087659 sec
RG                       203
DW                    13.867 usec
DE                    18.00 usec
TE                    298.2 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             150.9178981 MHz
NUC1                      13C
P1                    11.35 usec
PLW1            230.00000000 W

======== CHANNEL f2 ========
SFO2             600.1324005 MHz
NUC2                      1H
CPDPRG[2              waltz16
PCPD2                 90.00 usec
PLW2            13.00000000 W
PLW12            0.19774000 W
PLW13            0.16017000 W

F2 - Processing parameters
SI                     32768
SF               150.9028309 MHz
WDW                       EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```



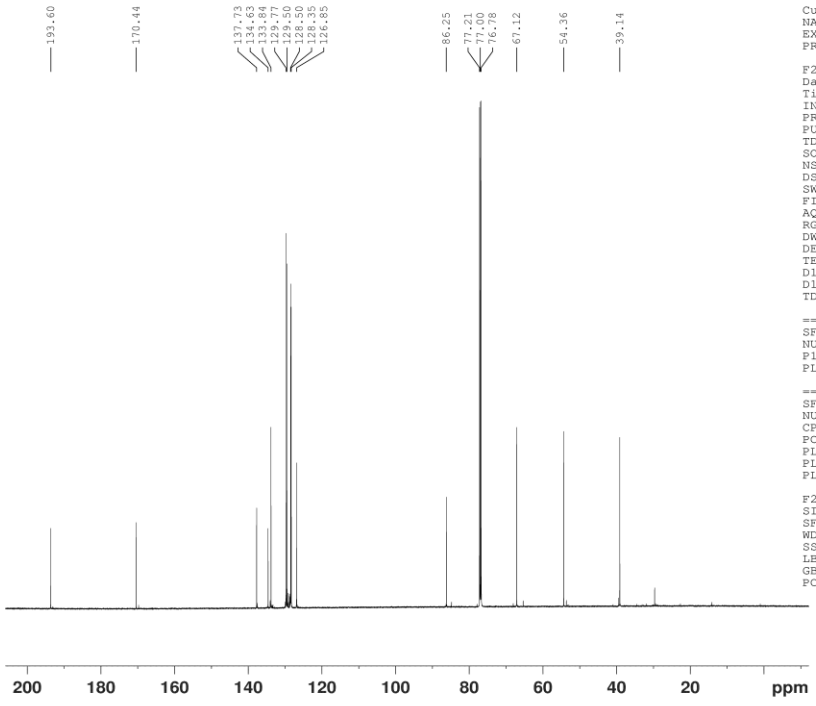

```
Current Data Parameters
NAME                  GG-6-269
EXPNO                        1
PROCNO                       1

F2 - Acquisition Paramet
Date_                 20140613
Time                      8.28
INSTRUM                  spect
PROBHD    5 mm CPQCI 1H/
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          0
SWH                 12019.230
FIDRES                0.183399
AQ                    2.7262976
RG                         32
DW                       41.600
DE                       10.00
TE                       298.2
D1                   1.00000000
TD0                          1

======== CHANNEL f1 ====
SFO1                600.1337060
NUC1                         1H
P1                       11.00
PLW1                13.00000000

F2 - Processing paramete
SI                       65536
SF                  600.1300148
WDW                         EM
SSB          0
LB                        0.30
GB           0
PC                        1.00
```



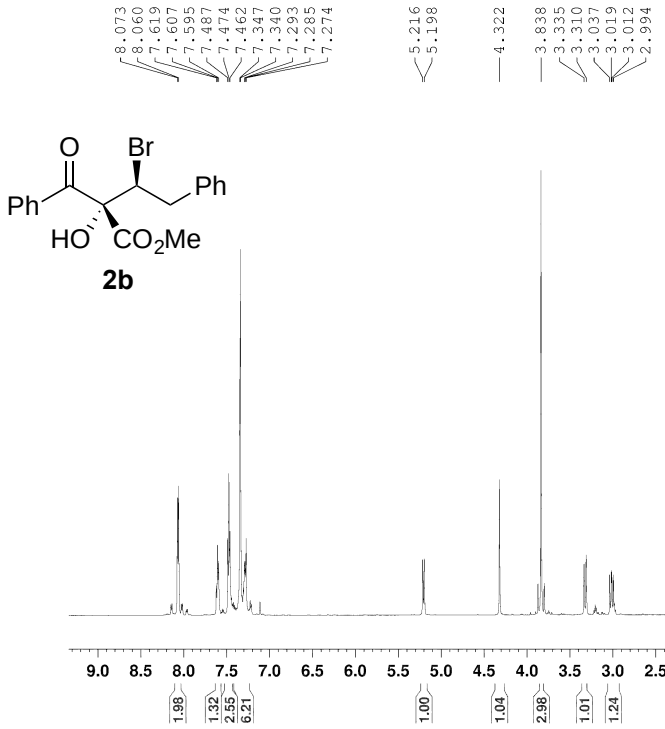

```
Current Data Parameters
NAME              GG-6-269-C13
EXPNO                       2
PROCNO                      1

F2 - Acquisition Parameters
Date_                20140613
Time                     0.39
INSTRUM                 spect
PROBHD    5 mm CPQCI 1H/
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDC13
NS                        128
DS                          4
SWH                36057.691 Hz
FIDRES                0.550197 Hz
AQ                    0.9087659 sec
RG                        203
DW                     13.867 usec
DE                      18.00 usec
TE                      298.1 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1               150.9178981 MHz
NUC1                       13C
P1                      11.35 usec
PLW1           230.00000000 W

======== CHANNEL f2 ========
SFO2               600.1324005 MHz
NUC2                       1H
CPDPRG[2                waltz16
PCPD2                   90.00 usec
PLW2           13.00000000 W
PLW12           0.19774000 W
PLW13           0.16017000 W

F2 - Processing parameters
SI                        32768
SF                 150.9028150 MHz
WDW                         EM
SSB          0
LB                      1.00 Hz
GB           0
PC                        1.40
```



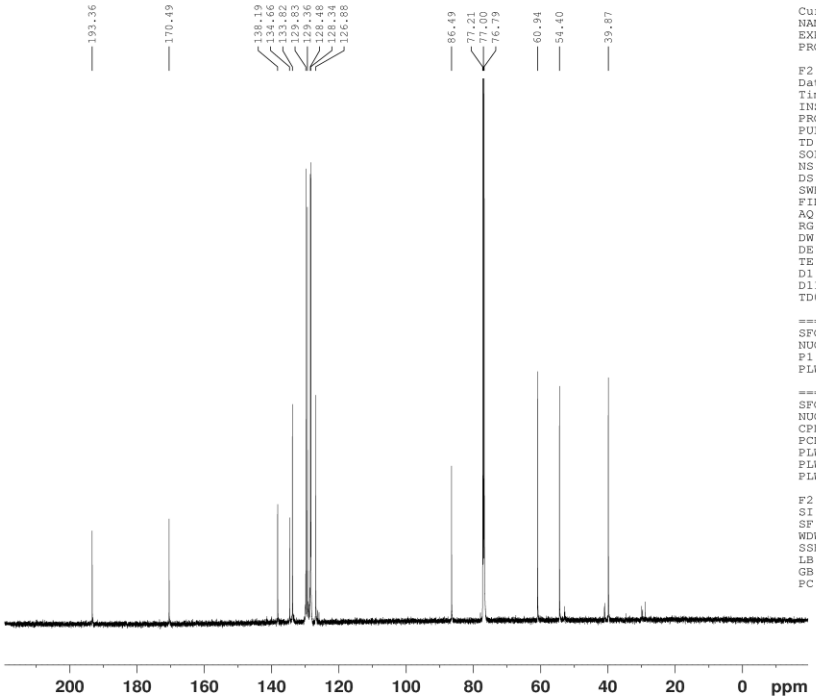

```
Current Data Parameters
NAME          GG-7-22-2a
EXPNO                  1
PROCNO                 1

F2 - Acquisition Paramete
Date_           20140404
Time               15.08
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   12
DS                    2
SWH           12019.230 H
FIDRES         0.183399 H
AQ             2.7262976 s
RG                   32
DW                41.600 u
DE                10.00 u
TE                298.0 K
D1             1.00000000 s
TD0                    1

======== CHANNEL f1 =====
SFO1          600.1337060 M
NUC1                   1H
P1                  13.75 u
PLW1           9.00000000 W

F2 - Processing paramete
SI                 65536
SF            600.1300153 M
WDW                   EM
SSB       0
LB                 0.30 H
GB        0
PC                 1.00
```



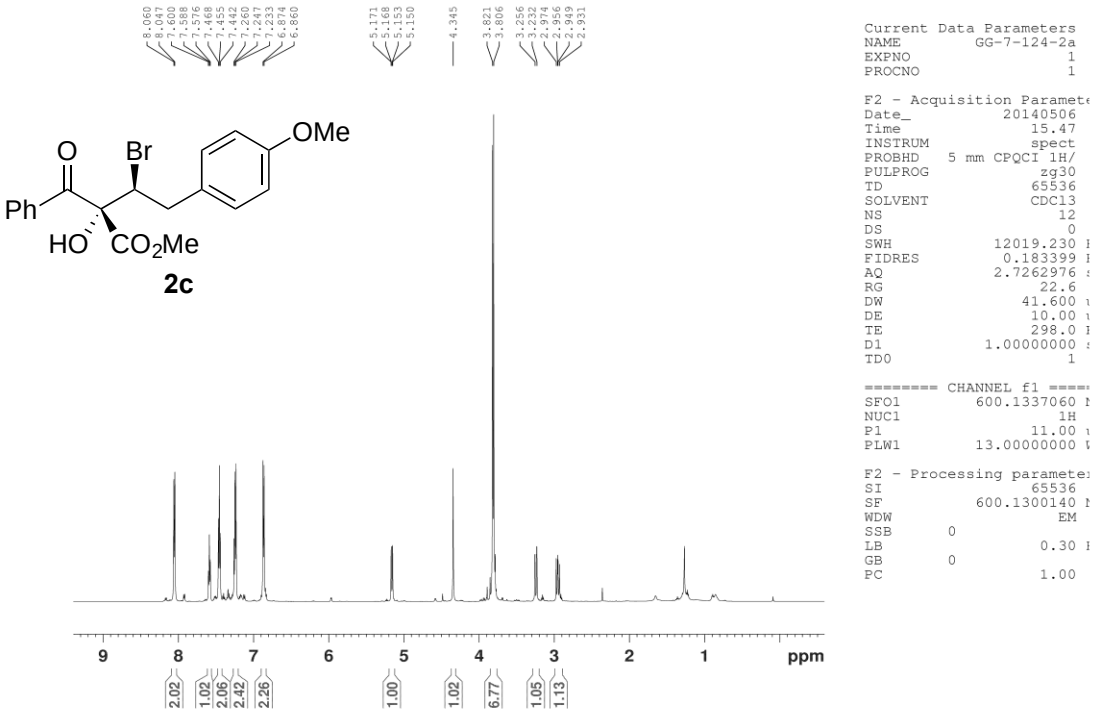

```
Current Data Parameters
NAME      GG-7-22-1a-C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140404
Time               15.10
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  171
DS                    0
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ             0.9087659 sec
RG                  203
DW               13.867 usec
DE               18.00 usec
TE                298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         150.9178981 MHz
NUC1                   13C
P1                 11.25 usec
PLW1        30.00000000 W

======== CHANNEL f2 ========
SFO2         600.1324005 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2           9.00000000 W
PLW12          0.26587000 W
PLW13          0.17016000 W

F2 - Processing parameters
SI                 32768
SF           150.9028171 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```



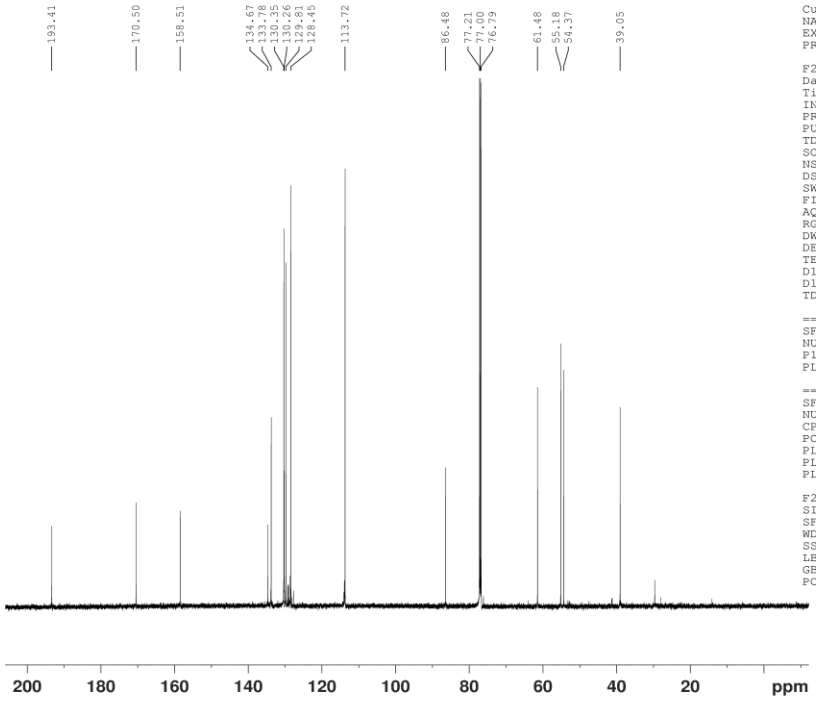

```
Current Data Parameters
NAME            GG-8-92-1
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140923
Time                14.20
INSTRUM             spect
PROBHD   5 mm CPQCI 1H/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            12019.230 Hz
FIDRES             0.183399 Hz
AQ              2.7262976 sec
RG                  14.2
DW                 41.600 usec
DE                 10.00 usec
TE                 298.0 K
D1              1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          600.1337060 MHz
NUC1                  1H
P1                 10.35 usec
PLW1          13.00000000 W

F2 - Processing parameters
SI                 65536
SF            600.1300076 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```



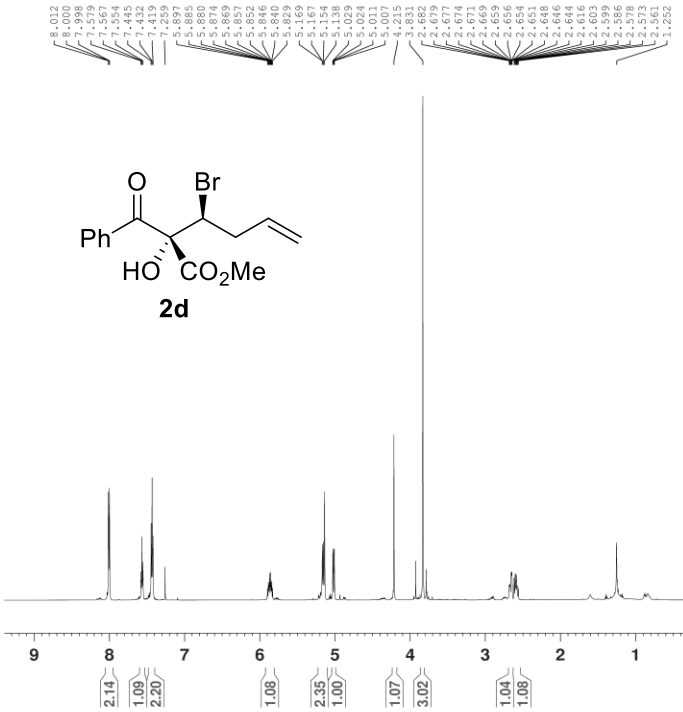

```
Current Data Parameters
NAME      GG-6-302-2a-C13
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140402
Time                12.52
INSTRUM             spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                 65536
SOLVENT             CDCl3
NS                    33
DS                     0
SWH            36057.691 Hz
FIDRES             0.550197 Hz
AQ              0.9087659 sec
RG                   203
DW                 13.867 usec
DE                 18.00 usec
TE                 298.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          150.9178981 MHz
NUC1                  13C
P1                 11.25 usec
PLW1          30.00000000 W

======== CHANNEL f2 ========
SFO2          600.1324005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2           9.00000000 W
PLW12          0.26587000 W
PLW13          0.17016000 W

F2 - Processing parameters
SI                 32768
SF            150.9028195 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```



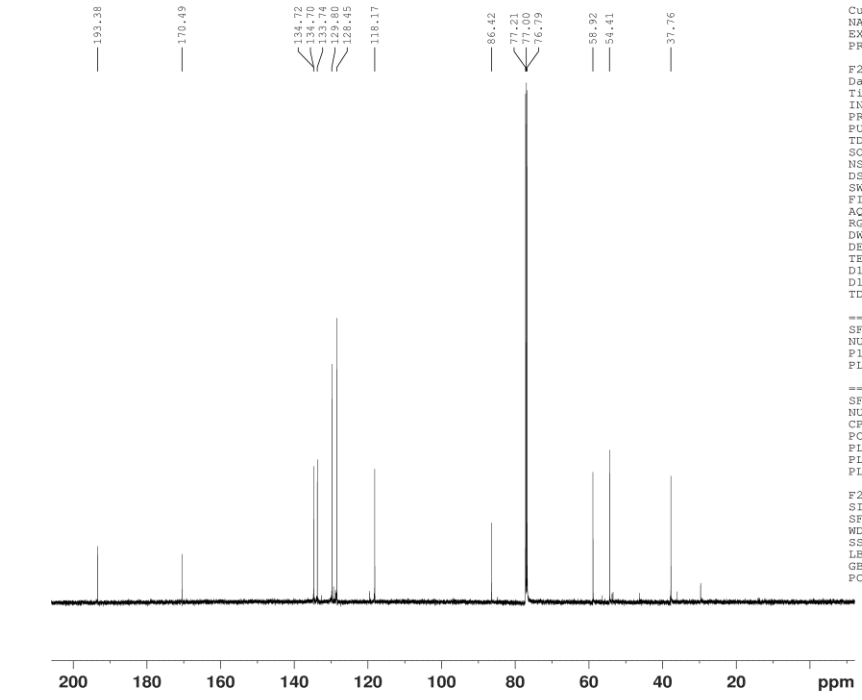

```
Current Data Parameters
NAME         GG-7-124-2a
EXPNO                  1
PROCNO                 1

F2 - Acquisition Paramete
Date_           20140506
Time               15.47
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG            zg30
TD                65536
SOLVENT           CDC13
NS                   12
DS                    0
SWH           12019.230 H
FIDRES         0.183399 H
AQ            2.7262976 s
RG                 22.6
DW                41.600 u
DE                10.00 u
TE                298.0 K
D1           1.00000000 s
TD0                    1

======== CHANNEL f1 =====
SFO1         600.1337060 M
NUC1                1H
P1                 11.00 u
PLW1         13.00000000 W

F2 - Processing paramete
SI                 65536
SF           600.1300140 M
WDW                   EM
SSB       0
LB                 0.30 H
GB        0
PC                 1.00
```



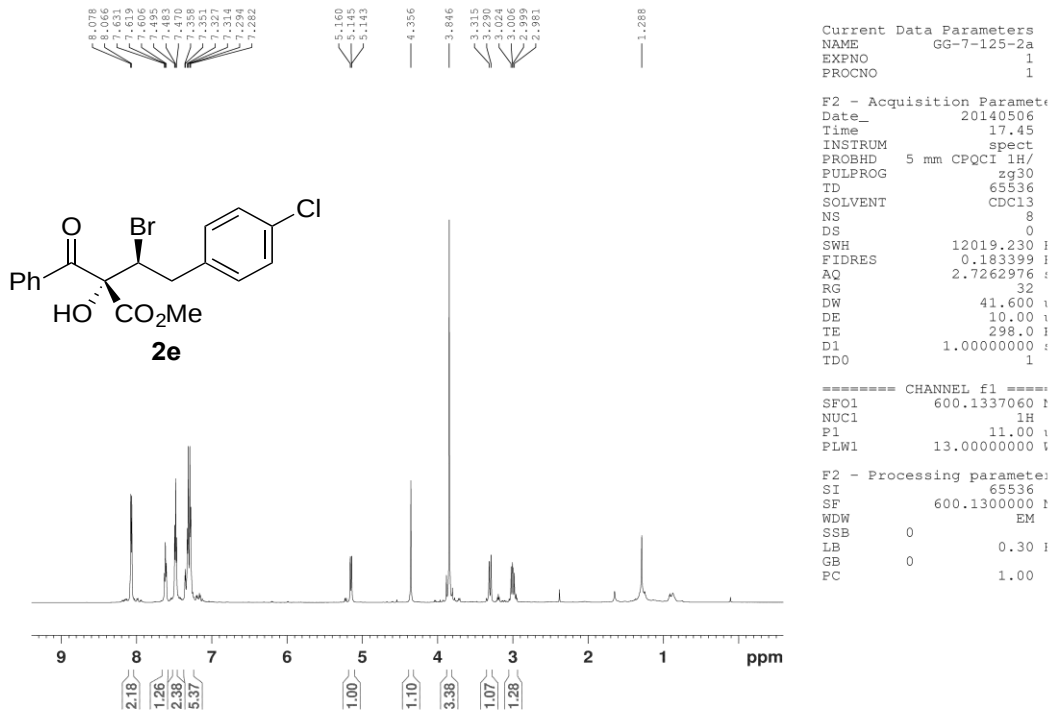

```
Current Data Parameters
NAME      GG-7-124-2-C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140506
Time               15.50
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDC13
NS                   53
DS                    0
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ            0.9087659 sec
RG                  203
DW               13.867 usec
DE               18.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        150.9178981 MHz
NUC1                  13C
P1                11.35 usec
PLW1       230.00000000 W

======== CHANNEL f2 ========
SFO2        600.1324005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2            90.00 usec
PLW2        13.00000000 W
PLW12        0.19774000 W
PLW13        0.16017000 W

F2 - Processing parameters
SI                 32768
SF          150.9028195 MHz
WDW                   EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

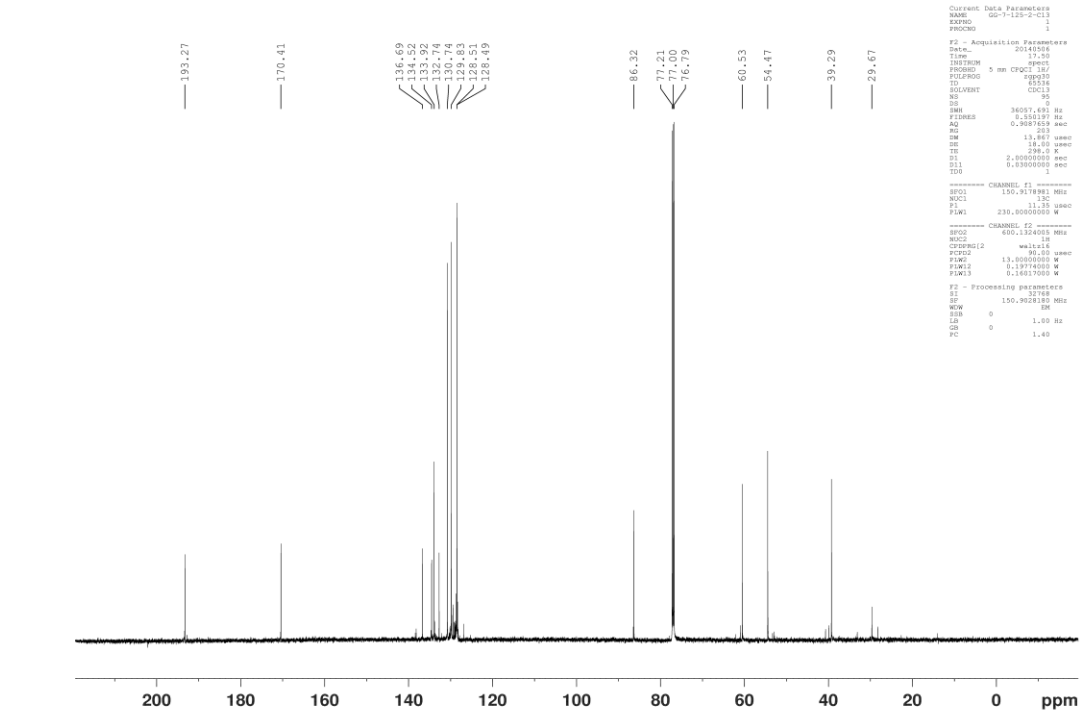


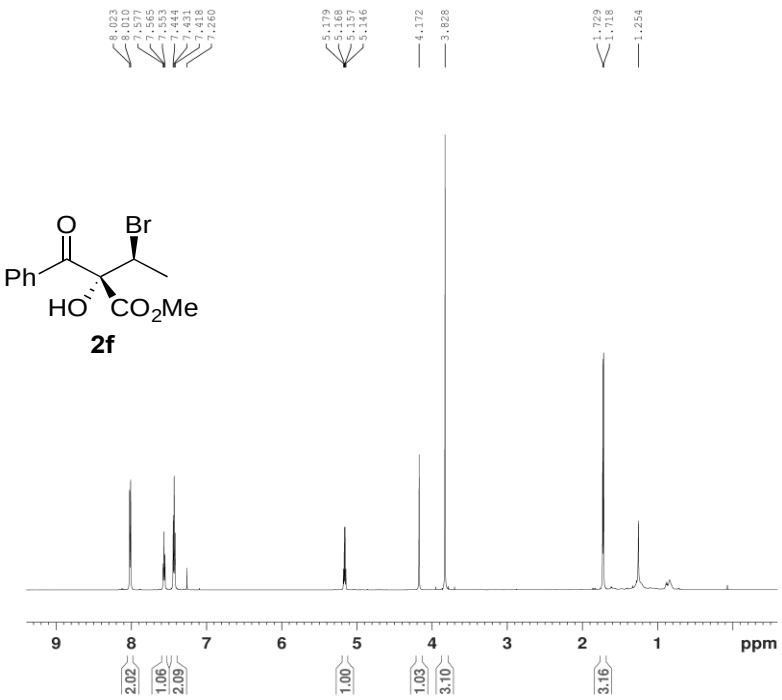

```
Current Data Parameters
NAME         GG-7-123-2a
EXPNO                  1
PROCNO                 1

F2 - Acquisition Paramete
Date_           20140506
Time               15.42
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    9
DS                    0
SWH           12019.230 H
FIDRES         0.183399 H
AQ            2.7262976 s
RG                 14.2
DW                41.600 u
DE                10.00 u
TE                298.0 K
D1            1.00000000 s
TD0                    1

======== CHANNEL f1 =====
SFO1         600.1337060 M
NUC1                1H
P1                 11.00 u
PLW1         13.00000000 W

F2 - Processing paramete
SI                65536
SF           600.1300147 M
WDW                  EM
SSB       0
LB                 0.30 H
GB        0
PC                 1.00
```



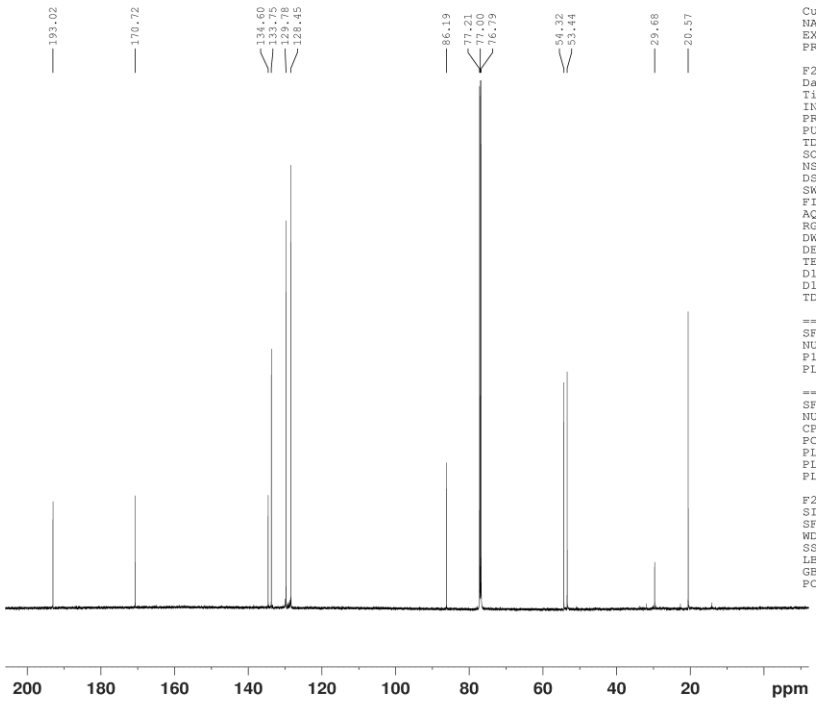

```
Current Data Parameters
NAME      GG-7-123-2-C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140506
Time               15.45
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   49
DS                    0
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ            0.9087659 sec
RG                  203
DW               13.867 usec
DE                18.00 usec
TE                298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         150.9178981 MHz
NUC1                13C
P1                 11.35 usec
PLW1        230.00000000 W

======== CHANNEL f2 ========
SFO2         600.1324005 MHz
NUC2                1H
CPDPRG[2          waltz16
PCPD2              90.00 usec
PLW2         13.00000000 W
PLW12         0.19774000 W
PLW13         0.16017000 W

F2 - Processing parameters
SI                32768
SF           150.9028150 MHz
WDW                  EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```


8.078
8.066
7.631
7.619
7.495
7.490
7.483
7.470
7.358
7.351
7.327
7.314
7.294
7.282
5.160
5.145
5.143
4.356
3.846
3.315
3.290
3.024
3.006
2.999
2.981
1.288
Cl
O
Br
Ph
HO
CO2Me
2e
Current Data Parameters
NAME GG-7-125-2a
EXPNO 1
PROCNO 1
F2 - Acquisition Paramete
Date_ 20140506
Time 17.45
INSTRUM spect
PROBHD 5 mm CPQCI 1H/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 8
DS 0
SWH 12019.230
FIDRES 0.183399
AQ 2.7262976
RG 32
DW 41.600
DE 10.00
TE 298.0
D1 1.00000000
TD0 1
======== CHANNEL f1 ====
SFO1 600.1337060
NUC1 1H
P1 11.00
PLW1 13.00000000
F2 - Processing paramete
SI 65536
SF 600.1300000
WDW EM
SSB 0
LB 0.30
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
ppm
2.18
1.26
2.38
5.37
1.00
1.10
3.38
1.07
1.28

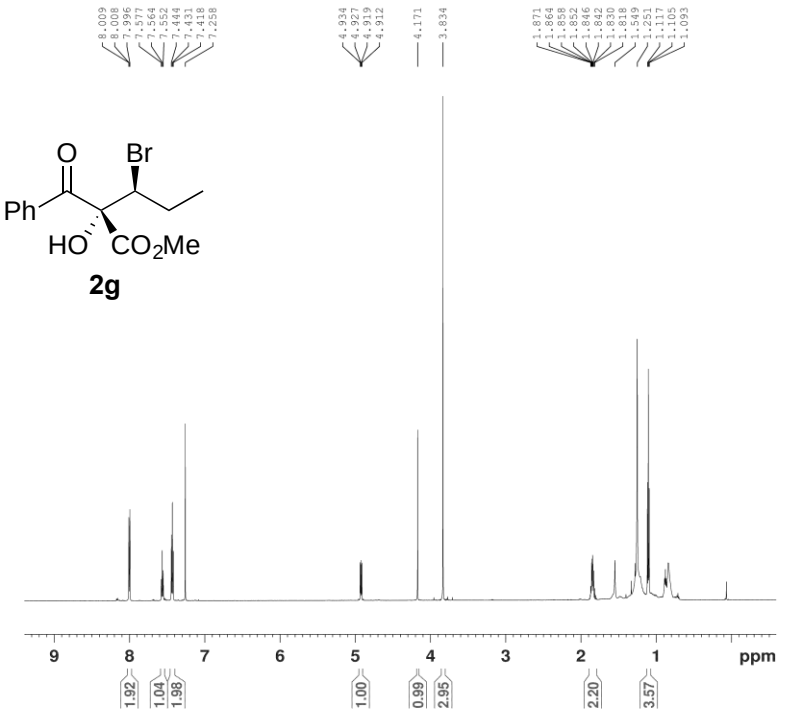

193.27
170.41
136.69
134.52
133.92
132.74
130.74
129.83
128.51
128.49
86.32
77.21
77.00
76.79
60.53
54.47
39.29
29.67
200
180
160
140
120
100
80
60
40
20
0
ppm



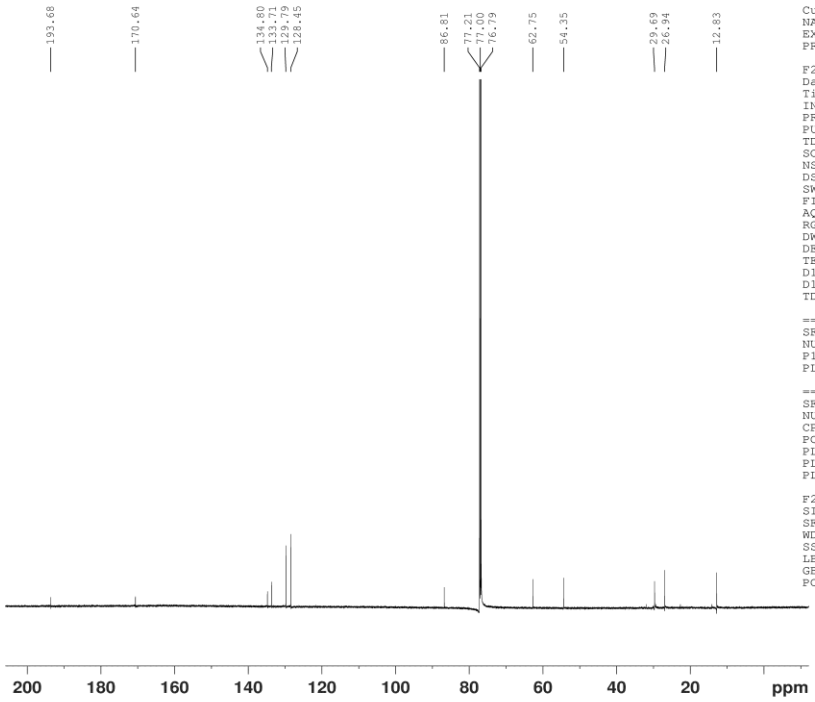

```
Current Data Parameters
NAME          GG-7-69-1a
EXPNO                  1
PROCNO                 1

F2 - Acquisition Paramete
Date_           20140421
Time                7.25
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG             zg30
TD                 65536
SOLVENT            CDC13
NS                     6
DS                     0
SWH            12019.230 H
FIDRES             0.183399 H
AQ             2.7262976 s
RG                  12.7
DW                 41.600 u
DE                 10.00 u
TE                 298.0 K
D1              1.00000000 s
TD0                    1

======== CHANNEL f1 =====
SFO1          600.1337060 M
NUC1                  1H
P1                 11.00 u
PLW1          13.00000000 W

F2 - Processing paramete
SI                 65536
SF            600.1300137 M
WDW                   EM
SSB       0
LB                 0.30 H
GB        0
PC                 1.00
```



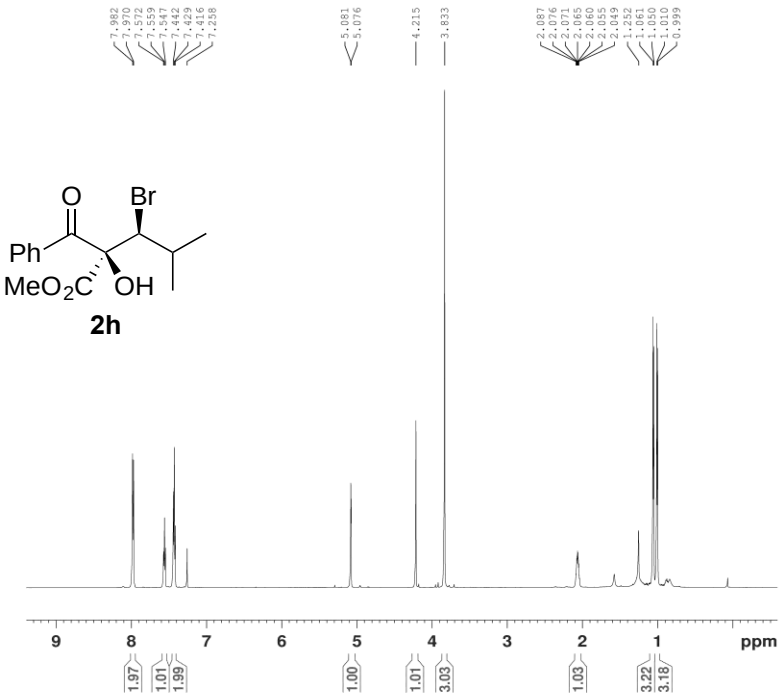

```
Current Data Parameters
NAME          GG-7-69-C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140421
Time                7.48
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDC13
NS                   230
DS                     0
SWH            36057.691 Hz
FIDRES             0.550197 Hz
AQ             0.9087659 sec
RG                   203
DW                13.867 usec
DE                 18.00 usec
TE                 298.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          150.9178981 MHz
NUC1                  13C
P1                 11.35 usec
PLW1       230.00000000 W

======== CHANNEL f2 ========
SFO2          600.1324005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              90.00 usec
PLW2          13.00000000 W
PLW12          0.19774000 W
PLW13          0.16017000 W

F2 - Processing parameters
SI                 32768
SF            150.9028151 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```



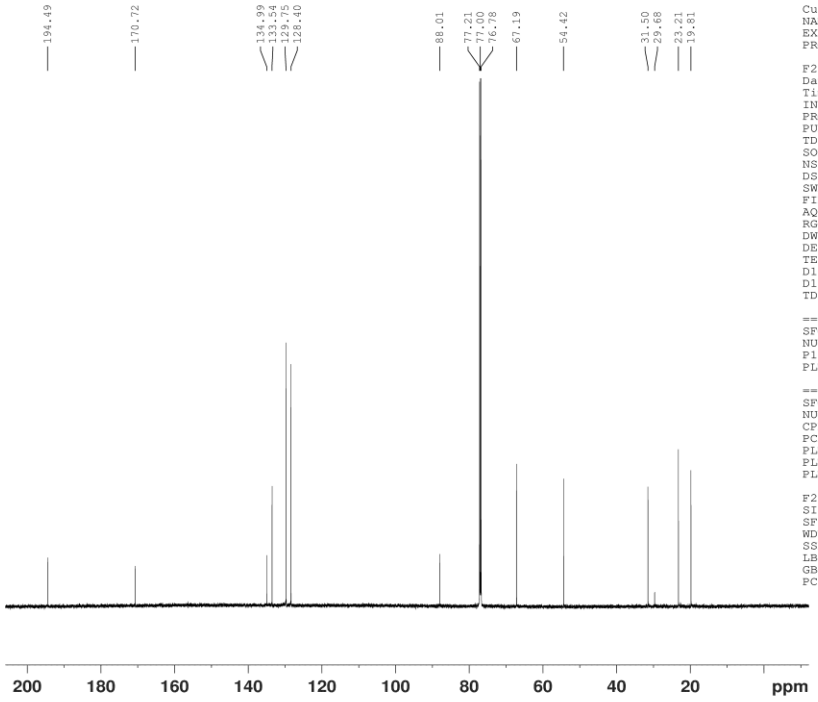

```
Current Data Parameters
NAME          GG-7-70-1a
EXPNO                  1
PROCNO                 1

F2 - Acquisition Paramete
Date_           20140421
Time                7.27
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    5
DS                    0
SWH           12019.230 H
FIDRES         0.183399 H
AQ            2.7262976 s
RG                 14.2
DW                41.600 u
DE                10.00 u
TE                298.0 K
D1            1.00000000 s
TD0                   1

======== CHANNEL f1 =====
SFO1         600.1337060 M
NUC1                1H
P1                11.00 u
PLW1         13.00000000 W

F2 - Processing paramete
SI                65536
SF           600.1300150 M
WDW                  EM
SSB       0
LB                0.30 H
GB        0
PC                1.00
```



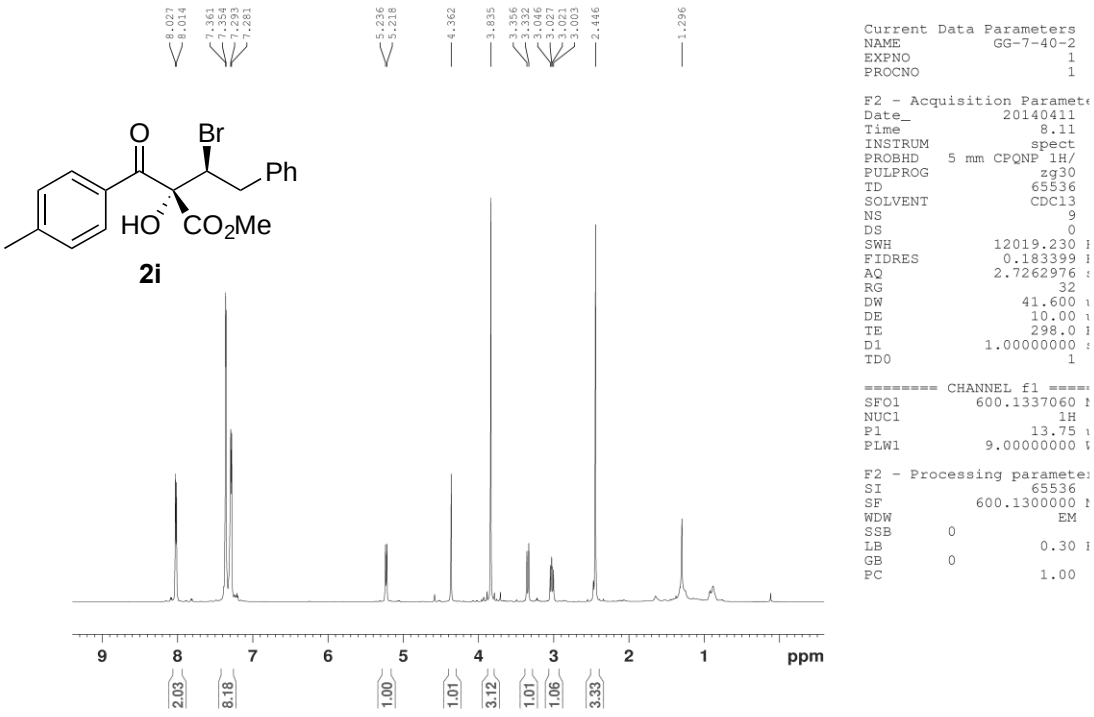

```
Current Data Parameters
NAME         GG-7-70-C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140421
Time                8.00
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  528
DS                    0
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ            0.9087659 sec
RG                  203
DW               13.867 usec
DE                18.00 usec
TE                298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9178981 MHz
NUC1                13C
P1                11.35 usec
PLW1       230.00000000 W

======== CHANNEL f2 ========
SFO2        600.1324005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2        13.00000000 W
PLW12        0.19774000 W
PLW13        0.16017000 W

F2 - Processing parameters
SI                32768
SF          150.9028119 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```



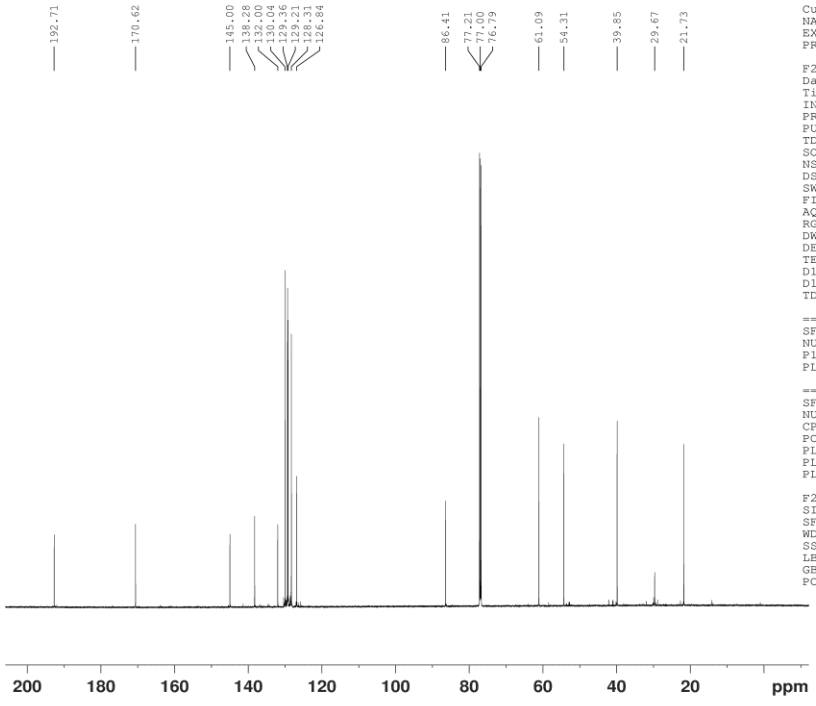

```
Current Data Parameters
NAME           GG-7-71-1a
EXPNO                   1
PROCNO                  1

F2 - Acquisition Paramete
Date_            20140425
Time                9.03
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH            12019.230 H
FIDRES          0.183399 H
AQ             2.7262976 s
RG                  12.7
DW                41.600 u
DE                10.00 u
TE                298.0 K
D1             1.00000000 s
TD0                    1

======== CHANNEL f1 =====
SFO1          600.1337060 M
NUC1                   1H
P1                 11.00 u
PLW1          13.00000000 W

F2 - Processing paramete
SI                 65536
SF            600.1300147 M
WDW                   EM
SSB       0
LB                0.30 H
GB        0
PC                1.00
```



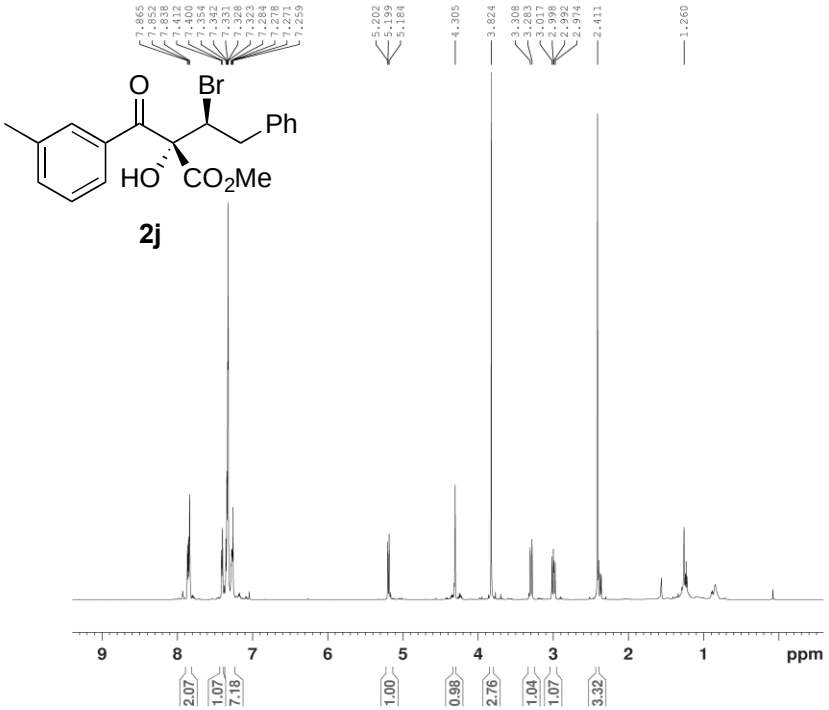

```
Current Data Parameters
NAME          GG-7-71-C13
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140425
Time                5.38
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     4
SWH            36057.691 Hz
FIDRES          0.550197 Hz
AQ             0.9087659 sec
RG                   203
DW                13.867 usec
DE                18.00 usec
TE                298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          150.9178981 MHz
NUC1                  13C
P1                 11.35 usec
PLW1          230.00000000 W

======== CHANNEL f2 ========
SFO2          600.1324005 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2              90.00 usec
PLW2          13.00000000 W
PLW12          0.19774000 W
PLW13          0.16017000 W

F2 - Processing parameters
SI                 32768
SF            150.9028140 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```



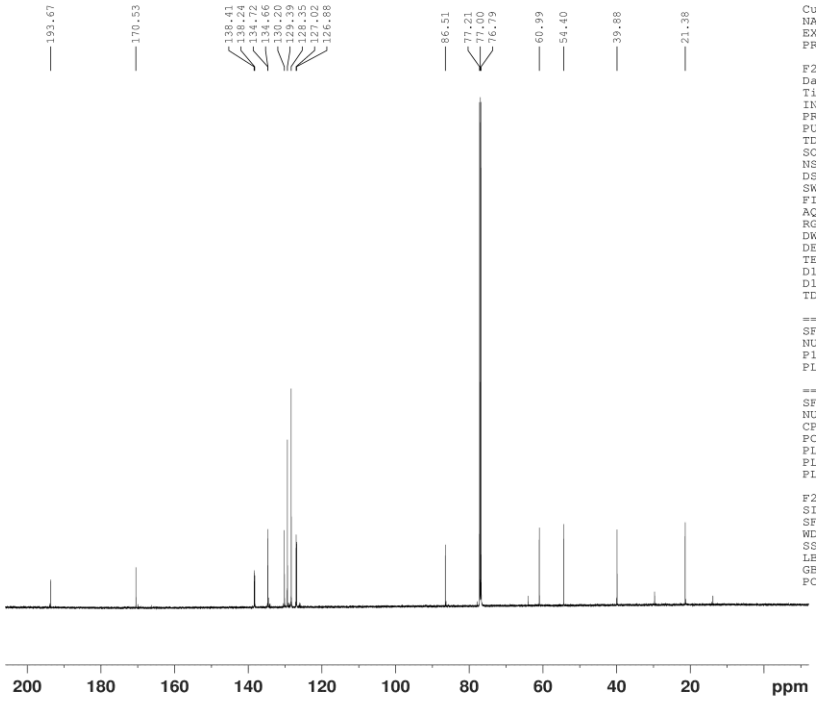

```
Current Data Parameters
NAME                  GG-7-40-2
EXPNO                         1
PROCNO                        1

F2 - Acquisition Paramete
Date_                  20140411
Time                       8.11
INSTRUM                   spect
PROBHD    5 mm CPQNP 1H/
PULPROG                   zg30
TD                       65536
SOLVENT                  CDC13
NS                           9
DS                           0
SWH                  12019.230 H
FIDRES                0.183399 H
AQ                   2.7262976 s
RG                          32
DW                       41.600 u
DE                       10.00 u
TE                       298.0 K
D1                  1.00000000 s
TD0                           1

======== CHANNEL f1 =====
SFO1                600.1337060 M
NUC1                        1H
P1                       13.75 u
PLW1                9.00000000 W

F2 - Processing paramete
SI                       65536
SF                  600.1300000 M
WDW                         EM
SSB          0
LB                        0.30 H
GB           0
PC                        1.00
```




```
Current Data Parameters
NAME          GG-7-40-2-C13
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20140411
Time                   8.16
INSTRUM               spect
PROBHD   5 mm CPQNP 1H/
PULPROG              zgpg30
TD                    65536
SOLVENT              CDC13
NS                       76
DS                        0
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ                0.9087659 sec
RG                      203
DW                   13.867 usec
DE                   18.00 usec
TE                   298.0 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1            150.9178981 MHz
NUC1                    13C
P1                   11.25 usec
PLW1            30.00000000 W

======== CHANNEL f2 ========
SFO2            600.1324005 MHz
NUC2                    1H
CPDPRG[2             waltz16
PCPD2                80.00 usec
PLW2             9.00000000 W
PLW12            0.26587000 W
PLW13            0.17016000 W

F2 - Processing parameters
SI                      32768
SF              150.9028194 MHz
WDW                        EM
SSB          0
LB                    1.00 Hz
GB           0
PC                    1.40
```

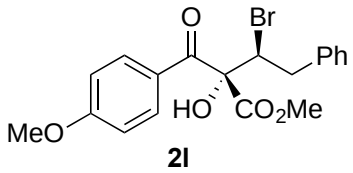



```
Current Data Parameters
NAME                  GG-7-47-1
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameter
Date_                20140411
Time                     8.18
INSTRUM                 spect
PROBHD    5 mm CPQNP 1H/
PULPROG                 zg30
TD                     65536
SOLVENT                CDCl3
NS                        16
DS                         0
SWH                12019.230
FIDRES              0.183399
AQ                 2.7262976
RG                        64
DW                     41.600
DE                     10.00
TE                     298.0
D1                1.00000000
TD0                        1

======== CHANNEL f1 =====
SFO1              600.1337060
NUC1                      1H
P1                     13.75
PLW1              9.00000000

F2 - Processing parameter
SI                     65536
SF                600.1300144
WDW                       EM
SSB          0
LB                      0.30
GB           0
PC                      1.00
```



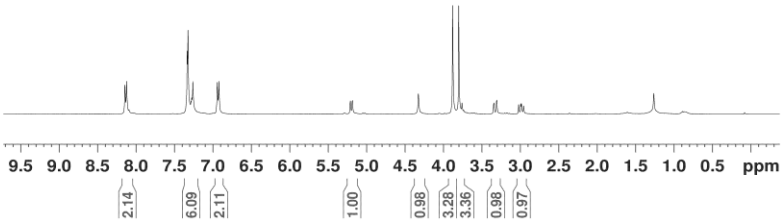

```
Current Data Parameters
NAME          GG-7-47-1-C13
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_            20140411
Time                 8.26
INSTRUM             spect
PROBHD   5 mm CPQNP 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   78
DS                    0
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ            0.9087659 sec
RG                  203
DW             13.867 usec
DE                 18.00 usec
TE                298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1         150.9178981 MHz
NUC1                  13C
P1                 11.25 usec
PLW1         30.00000000 W

======== CHANNEL f2 ========
SFO2         600.1324005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2          9.00000000 W
PLW12         0.26587000 W
PLW13         0.17016000 W

F2 - Processing parameters
SI                   32768
SF           150.9028141 MHz
WDW                     EM
SSB          0
LB                 1.00 Hz
GB           0
PC                 1.40
```

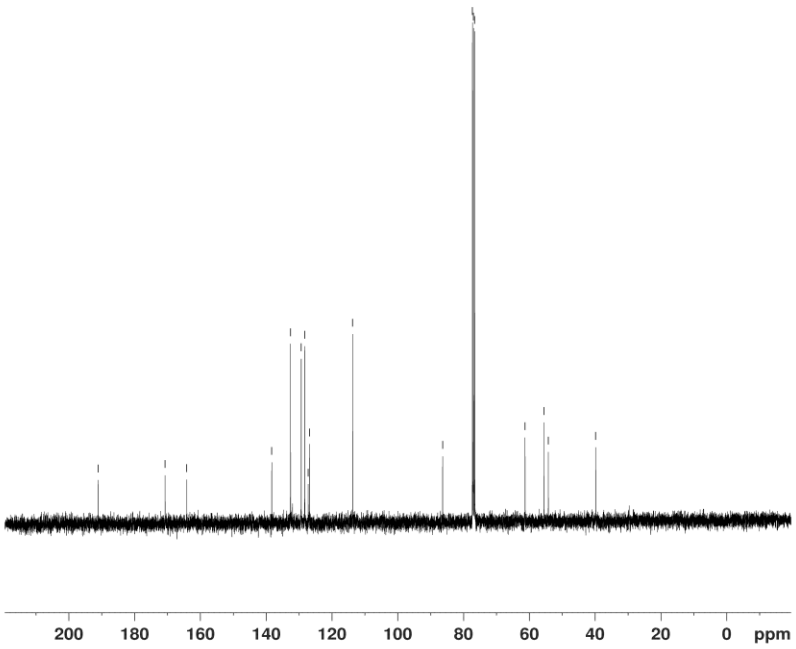
GG-7-58-1a



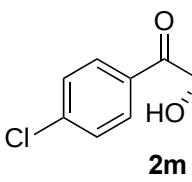
2l

```
Current Data Parameters
NAME          GG-7-58-1a
EXPNO                  1
PROCNO                 1

F2 - Acquisition Paramete
Date_           20140531
Time              11.43
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG           zg30
TD               65536
SOLVENT          CDCl3
NS                   5
DS                   0
SWH           8012.820 H
FIDRES        0.122266 H
AQ            4.0894465 s
RG                97.5
DW               62.400 u
DE                6.50 u
TE               296.4 K
D1           1.00000000 s
TD0                  1

======== CHANNEL f1 =====
SFO1        399.9824700 M
NUC1               1H
P1               12.38 u
PLW1        11.19999981 W

F2 - Processing parameter
SI                65536
SF          399.9800098 M
WDW                EM
SSB       0
LB                0.30 H
GB        0
PC                1.00
```

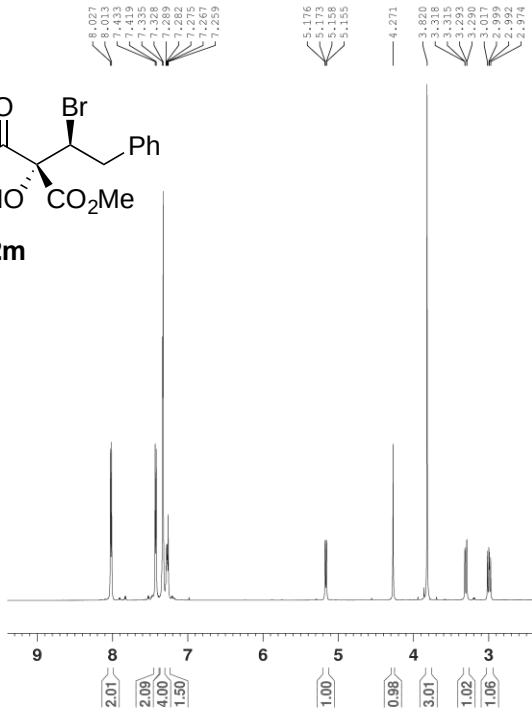




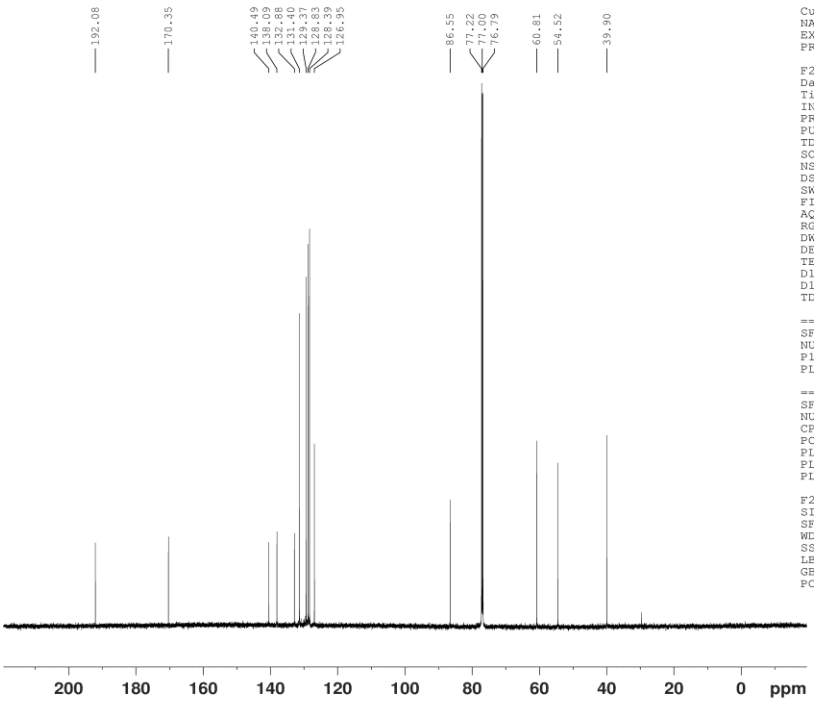

```
Current Data Parameters
NAME         GG-7-58-C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameter
Date_           20140531
Time              11.51
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                  70
DS                   0
SWH          24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631488 se
RG                200.09
DW               20.800 us
DE                6.50 us
TE               297.1 K
D1           2.00000000 se
D11          0.03000000 se
TD0                  1

======== CHANNEL f1 ======
SFO1        100.5851080 MH
NUC1               13C
P1                7.50 us
PLW1        61.20000076 W

======== CHANNEL f2 ======
SFO2        399.9815999 MH
NUC2               1H
CPDPRG[2         waltz16
PCPD2             80.00 us
PLW2        11.19999981 W
PLW12        0.26820999 W
PLW13        0.17166001 W

F2 - Processing parameters
SI                32768
SF          100.5750555 MH
WDW                EM
SSB       0
LB             1.00 Hz
GB        0
PC                1.40
```



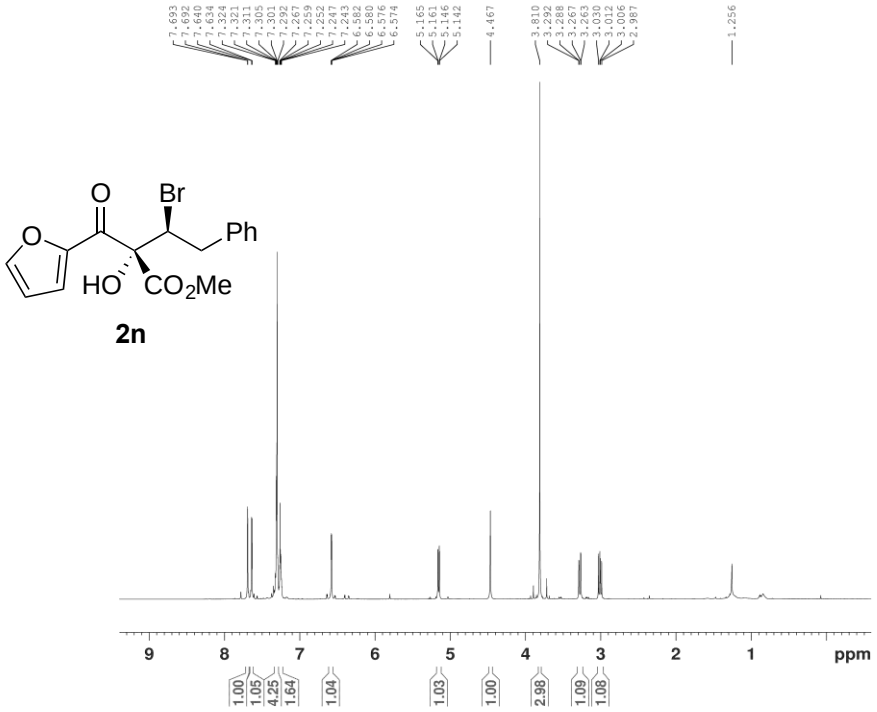
2m



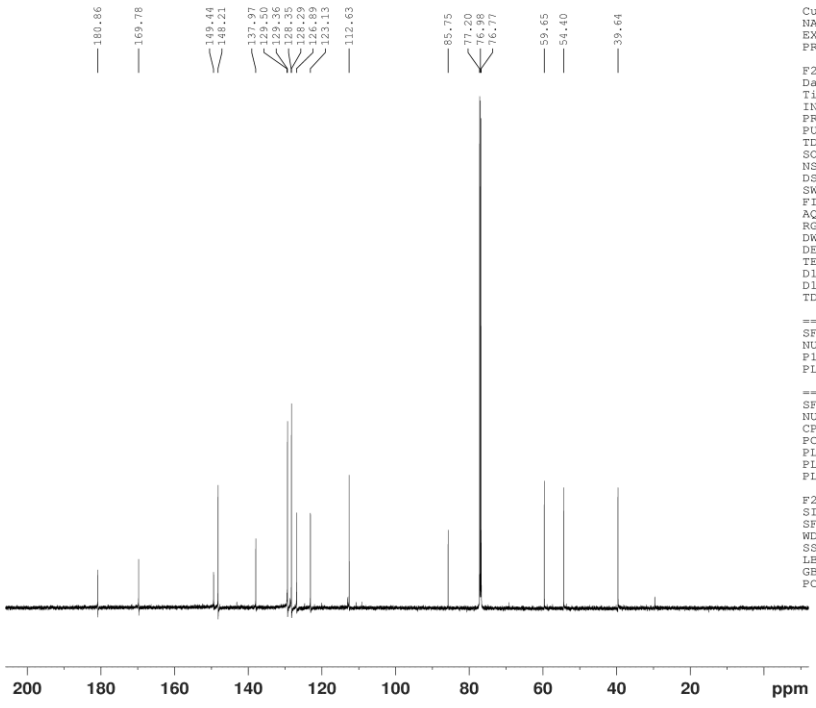

```
Current Data Parameters
NAME          GG-7-75-1b
EXPNO                  1
PROCNO                 1

F2 - Acquisition Paramete
Date_           20140423
Time               10.48
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   11
DS                    0
SWH           12019.230 H
FIDRES         0.183399 H
AQ            2.7262976 s
RG                 14.2
DW                41.600 u
DE                10.00 u
TE                298.0 K
D1           1.00000000 s
TD0                    1

======== CHANNEL f1 =====
SFO1         600.1337060 M
NUC1                1H
P1                 11.00 u
PLW1         13.00000000 W

F2 - Processing paramete
SI                 65536
SF           600.1300146 M
WDW                   EM
SSB       0
LB                  0.30 H
GB        0
PC                  1.00
```



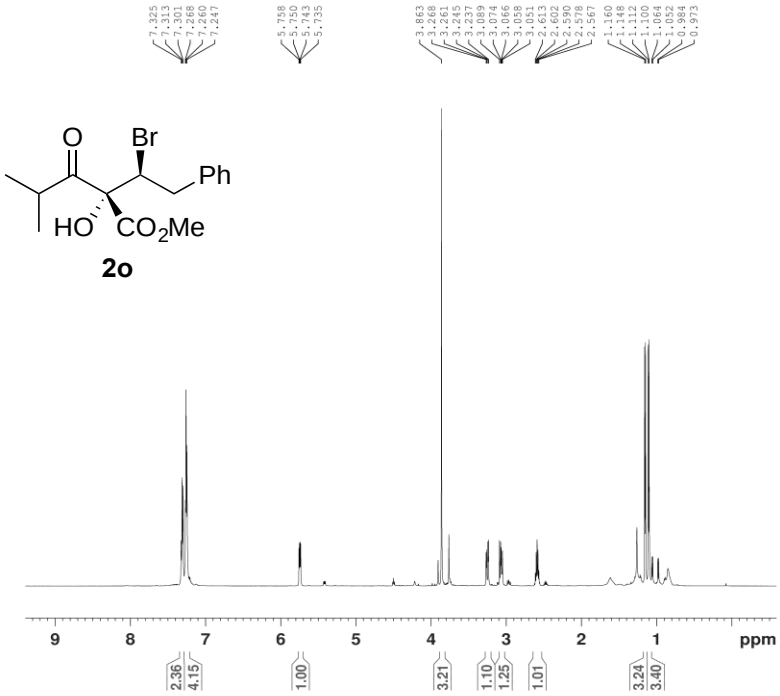

```
Current Data Parameters
NAME        GG-7-75-C13
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_           20140423
Time               10.55
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                   86
DS                    0
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ            0.9087659 sec
RG                  203
DW               13.867 usec
DE                18.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9178981 MHz
NUC1                13C
P1                11.35 usec
PLW1       230.00000000 W

======== CHANNEL f2 ========
SFO2        600.1324005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2        13.00000000 W
PLW12        0.19774000 W
PLW13        0.16017000 W

F2 - Processing parameters
SI                 32768
SF          150.9028150 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```



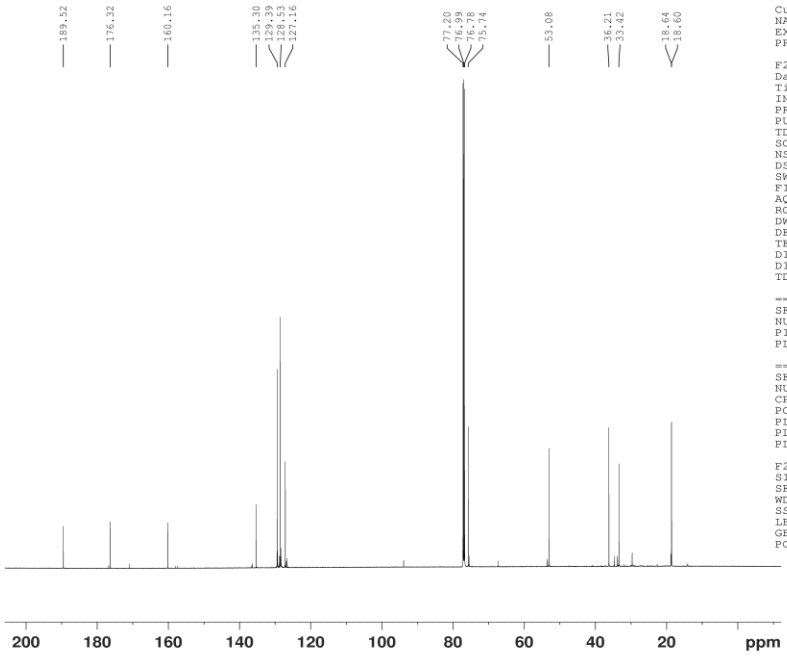

```
Current Data Parameters
NAME          GG-7-88-2a
EXPNO                  1
PROCNO                 1

F2 - Acquisition Paramete
Date_           20140502
Time               16.33
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG             zg30
TD                 65536
SOLVENT            CDC13
NS                     5
DS                     0
SWH            12019.230 H
FIDRES          0.183399 H
AQ             2.7262976 s
RG                  12.7
DW                41.600 u
DE                10.00 u
TE                298.0 K
D1             1.00000000 s
TD0                    1

======== CHANNEL f1 =====
SFO1         600.1337060 M
NUC1                1H
P1                 11.00 u
PLW1         13.00000000 W

F2 - Processing paramete
SI                 65536
SF           600.1300140 M
WDW                  EM
SSB       0
LB                0.30 H
GB        0
PC                 1.00
```



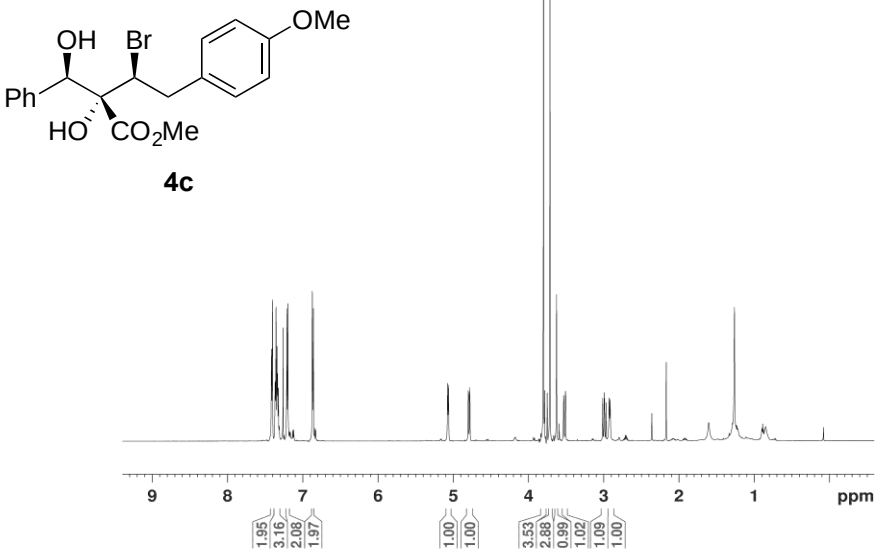

```
Current Data Parameters
NAME         GG-7-88-C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140502
Time               16.37
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDC13
NS                    56
DS                     0
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ             0.9087659 sec
RG                   203
DW                13.867 usec
DE                18.00 usec
TE                298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        150.9178981 MHz
NUC1                13C
P1                 11.35 usec
PLW1        230.00000000 W

======== CHANNEL f2 ========
SFO2        600.1324005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         13.00000000 W
PLW12         0.19774000 W
PLW13         0.16017000 W

F2 - Processing parameters
SI                 32768
SF          150.9028194 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                 1.40
```




```
Current Data Parameters
NAME          GG-7-24-2a
EXPNO                  1
PROCNO                 1

F2 - Acquisition Paramet
Date_           20140408
Time                7.27
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     7
DS                     0
SWH            12019.230
FIDRES             0.183399
AQ             2.7262976
RG                    32
DW                 41.600
DE                 10.00
TE                 298.0
D1             1.00000000
TD0                    1

========= CHANNEL f1 ====
SFO1          600.1337060
NUC1                1H
P1                 13.75
PLW1           9.00000000

F2 - Processing paramete
SI                 65536
SF            600.1300098
WDW                  EM
SSB       0
LB                  0.30
GB        0
PC                  1.00
```

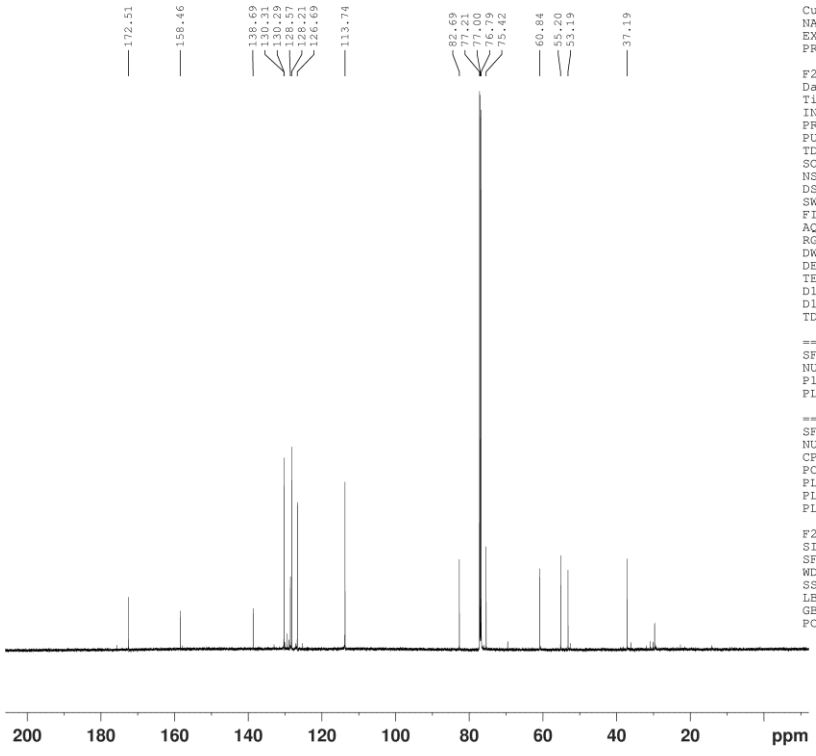



```
Current Data Parameters
NAME      GG-7-24-2a-C13
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_           20140408
Time                7.36
INSTRUM            spect
PROBHD   5 mm CPQNP 1H/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   953
DS                     0
SWH            36057.691 Hz
FIDRES             0.550197 Hz
AQ             0.9087659 sec
RG                   203
DW                 13.867 usec
DE                 18.00 usec
TE                 298.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

========= CHANNEL f1 ========
SFO1          150.9178981 MHz
NUC1                  13C
P1                 11.25 usec
PLW1          30.00000000 W

========= CHANNEL f2 ========
SFO2          600.1324005 MHz
NUC2                  1H
CPDPRG[2           waltz16
PCPD2              80.00 usec
PLW2           9.00000000 W
PLW12          0.26587000 W
PLW13          0.17016000 W

F2 - Processing parameters
SI                 32768
SF            150.9028162 MHz
WDW                  EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

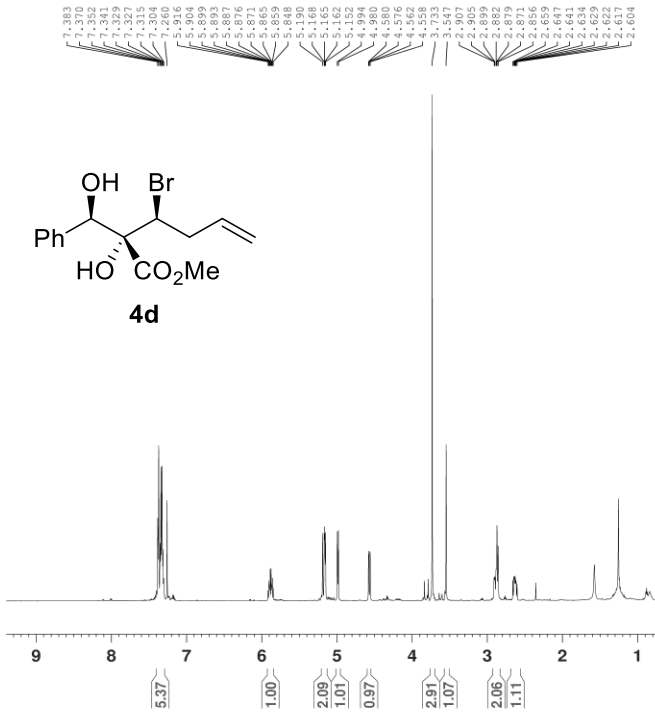


4c

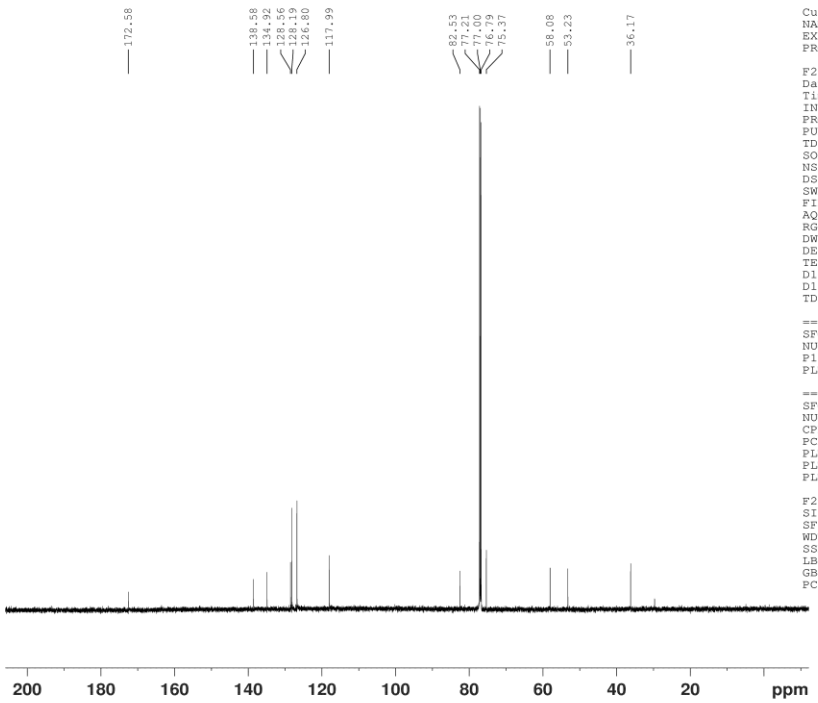

```
Current Data Parameters
NAME         GG-7-131-1a
EXPNO                  1
PROCNO                 1

F2 - Acquisition Paramete
Date_           20140519
Time               10.18
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    10
DS                     0
SWH            12019.230 H
FIDRES          0.183399 H
AQ             2.7262976 s
RG                    18
DW                41.600 u
DE                10.00 u
TE                298.0 K
D1           1.00000000 s
TD0                    1

======== CHANNEL f1 =====
SFO1         600.1337060 M
NUC1                1H
P1                 11.00 u
PLW1        13.00000000 W

F2 - Processing paramete
SI                 65536
SF           600.1300129 M
WDW                   EM
SSB       0
LB                 0.30 H
GB        0
PC                 1.00
```



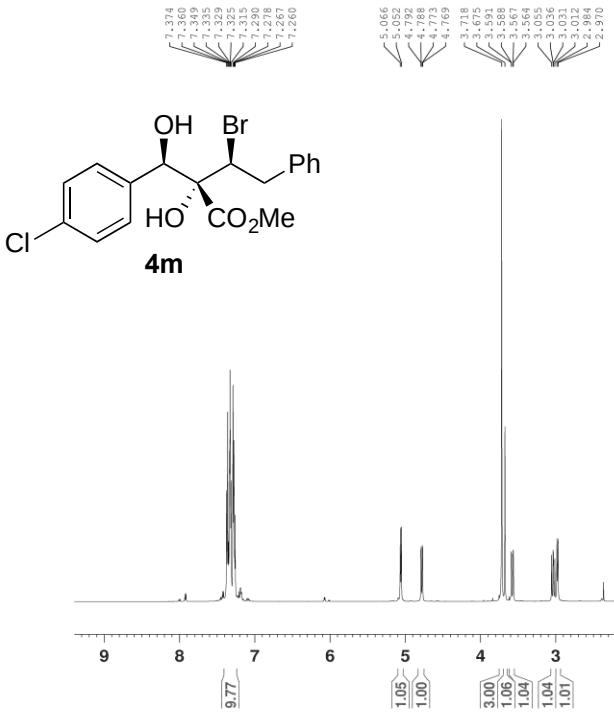

```
Current Data Parameters
NAME       GG-7-131-C13
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_           20140519
Time               13.19
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   173
DS                     0
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ             0.9087659 sec
RG                   203
DW                13.867 usec
DE                18.00 usec
TE                298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        150.9178981 MHz
NUC1                  13C
P1                 11.35 usec
PLW1       230.00000000 W

======== CHANNEL f2 ========
SFO2        600.1324005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              90.00 usec
PLW2        13.00000000 W
PLW12        0.19774000 W
PLW13        0.16017000 W

F2 - Processing parameters
SI                 32768
SF          150.9028159 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```



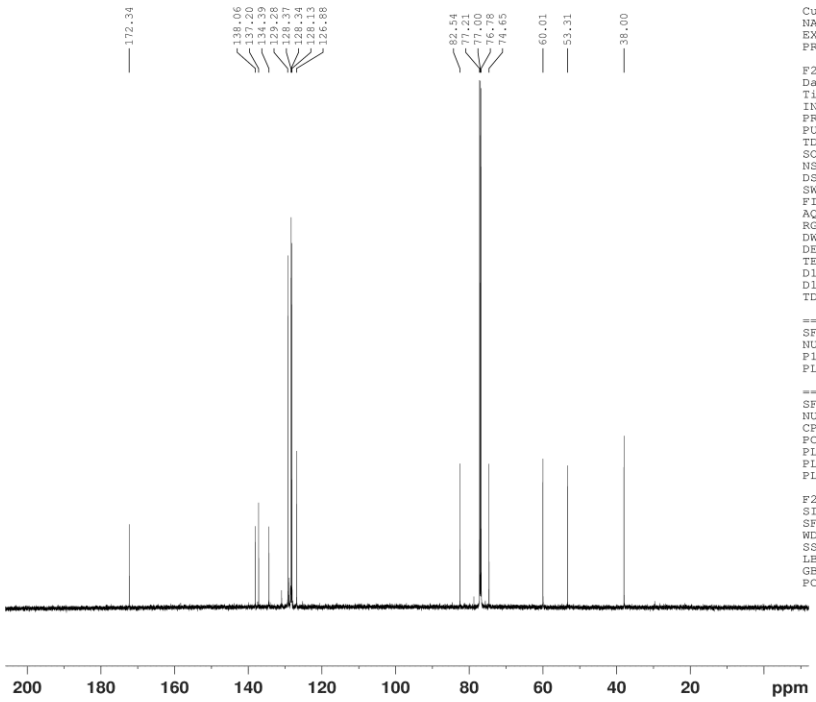

```
Current Data Parameters
NAME         GG-7-130-1a
EXPNO                  1
PROCNO                 1

F2 - Acquisition Paramet
Date_           20140519
Time               10.16
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG            zg30
TD                65536
SOLVENT           CDC13
NS                    7
DS                    0
SWH           12019.230 H
FIDRES         0.183399 H
AQ            2.7262976 s
RG                 20.2
DW                41.600 u
DE                10.00 u
TE                298.0 K
D1           1.00000000 s
TD0                   1

======== CHANNEL f1 ====
SFO1         600.1337060 M
NUC1                1H
P1                 11.00 u
PLW1         13.00000000 W

F2 - Processing paramete
SI                65536
SF           600.1300145 M
WDW                  EM
SSB       0
LB                0.30 H
GB        0
PC                1.00
```



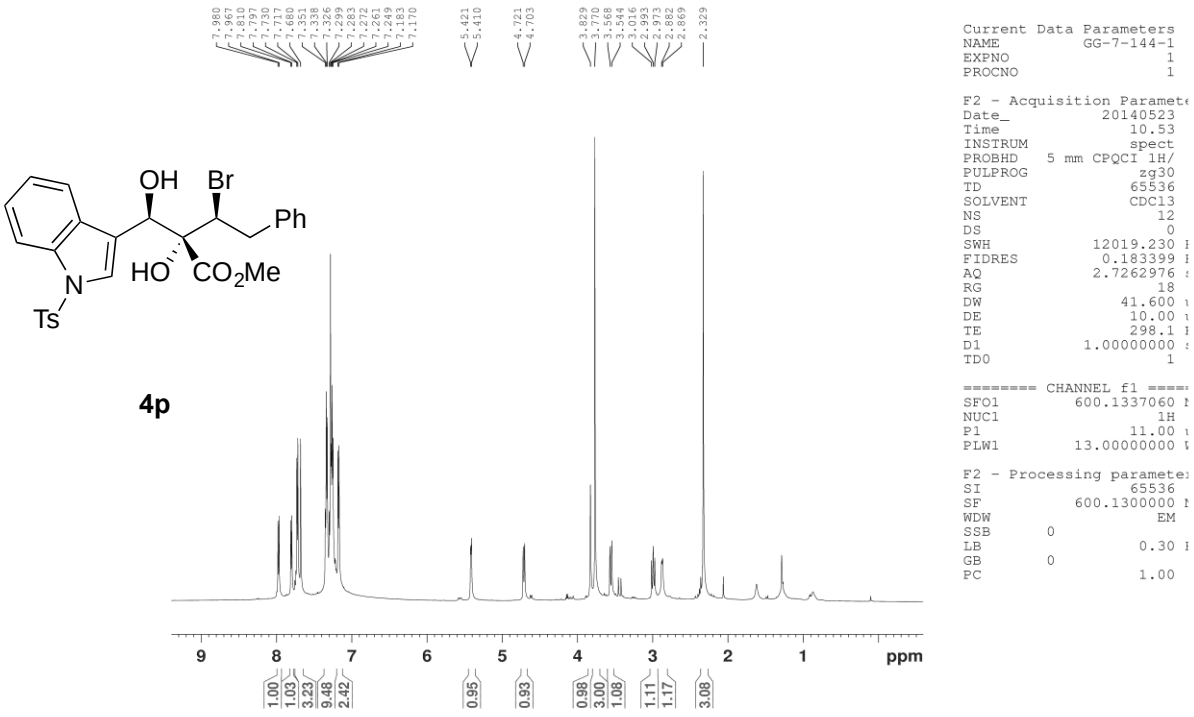

```
Current Data Parameters
NAME       GG-7-130-C13
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_           20140519
Time               13.10
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDC13
NS                   35
DS                    0
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ             0.9087659 sec
RG                  203
DW               13.867 usec
DE                18.00 usec
TE                298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9178981 MHz
NUC1                  13C
P1                11.35 usec
PLW1       230.00000000 W

======== CHANNEL f2 ========
SFO2        600.1324005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2             90.00 usec
PLW2        13.00000000 W
PLW12        0.19774000 W
PLW13        0.16017000 W

F2 - Processing parameters
SI                32768
SF          150.9028140 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```



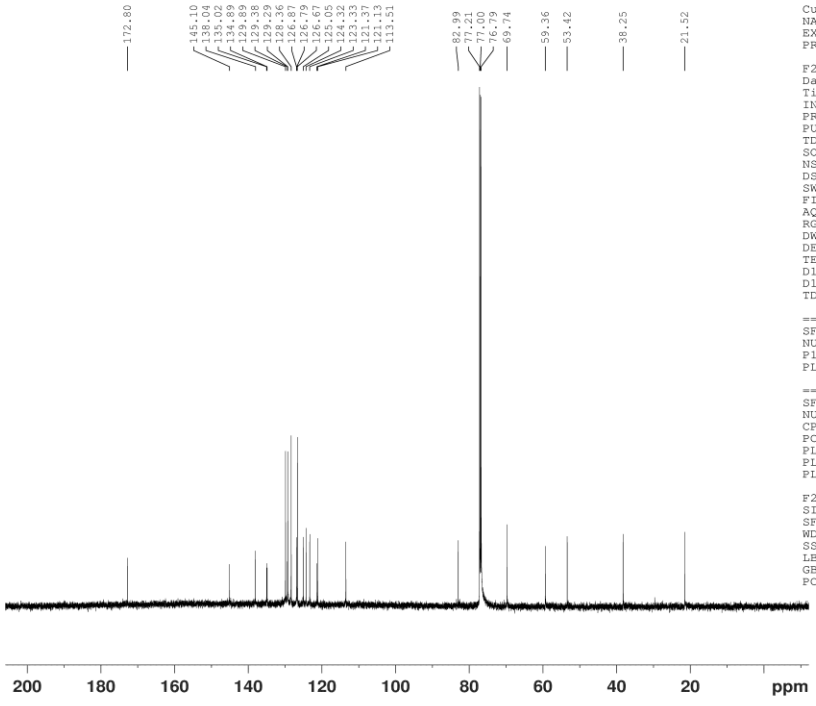

```
Current Data Parameters
NAME         GG-7-132-rec
EXPNO                   1
PROCNO                  1

F2 - Acquisition Paramete
Date_           20140614
Time               14.49
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    7
DS                    0
SWH           12019.230 H
FIDRES         0.183399 H
AQ            2.7262976 s
RG                 12.7
DW                41.600 u
DE                10.00 u
TE                298.2 K
D1            1.00000000 s
TD0                   1

======== CHANNEL f1 =====
SFO1         600.1337060 M
NUC1                1H
P1                11.00 u
PLW1         13.00000000 W

F2 - Processing paramete
SI                65536
SF           600.1300140 M
WDW                 EM
SSB       0
LB             0.30 H
GB        0
PC                1.00
```



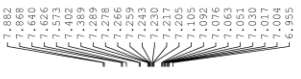

```
Current Data Parameters
NAME         GG-7-132-C13
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20140614
Time               14.51
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   32
DS                    0
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ            0.9087659 sec
RG                  203
DW               13.867 usec
DE               18.00 usec
TE                298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9178981 MHz
NUC1                13C
P1               11.35 usec
PLW1        230.00000000 W

======== CHANNEL f2 ========
SFO2        600.1324005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         13.00000000 W
PLW12         0.19774000 W
PLW13         0.16017000 W

F2 - Processing parameters
SI                32768
SF          150.9028206 MHz
WDW                 EM
SSB       0
LB             1.00 Hz
GB        0
PC                1.40
```

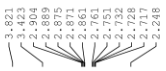


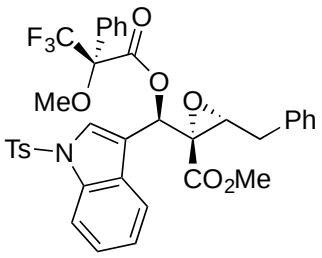

```
Current Data Parameters
NAME          GG-7-144-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameter
Date_           20140523
Time               10.53
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    12
DS                     0
SWH           12019.230 H
FIDRES         0.183399 H
AQ            2.7262976 s
RG                    18
DW               41.600 u
DE               10.00 u
TE                298.1 K
D1            1.00000000 s
TD0                    1

======== CHANNEL f1 =====
SFO1         600.1337060 M
NUC1                1H
P1                11.00 u
PLW1         13.00000000 W

F2 - Processing parameter
SI                 65536
SF           600.1300000 M
WDW                  EM
SSB       0
LB                0.30 H
GB        0
PC                1.00
```



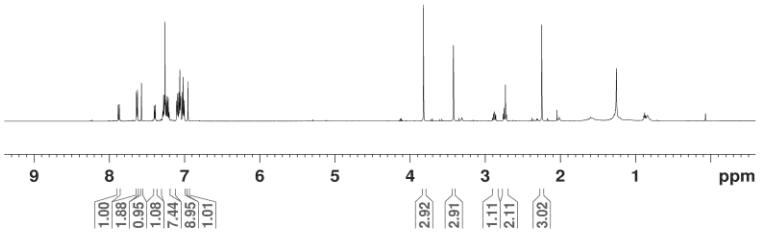

```
Current Data Parameters
NAME       GG-7-144-C13
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_           20140523
Time               10.58
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   70
DS                    0
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ            0.9087659 sec
RG                  203
DW               13.867 usec
DE                18.00 usec
TE                298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        150.9178981 MHz
NUC1                13C
P1                11.35 usec
PLW1        230.00000000 W

======== CHANNEL f2 ========
SFO2        600.1324005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         13.00000000 W
PLW12         0.19774000 W
PLW13         0.16017000 W

F2 - Processing parameters
SI                 32768
SF          150.9028161 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```



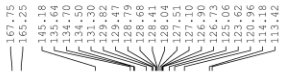


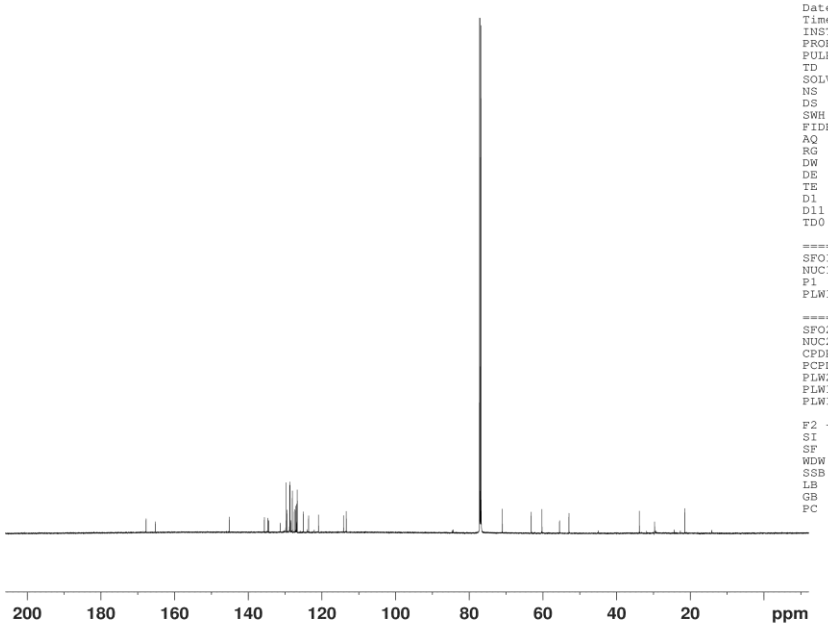


5

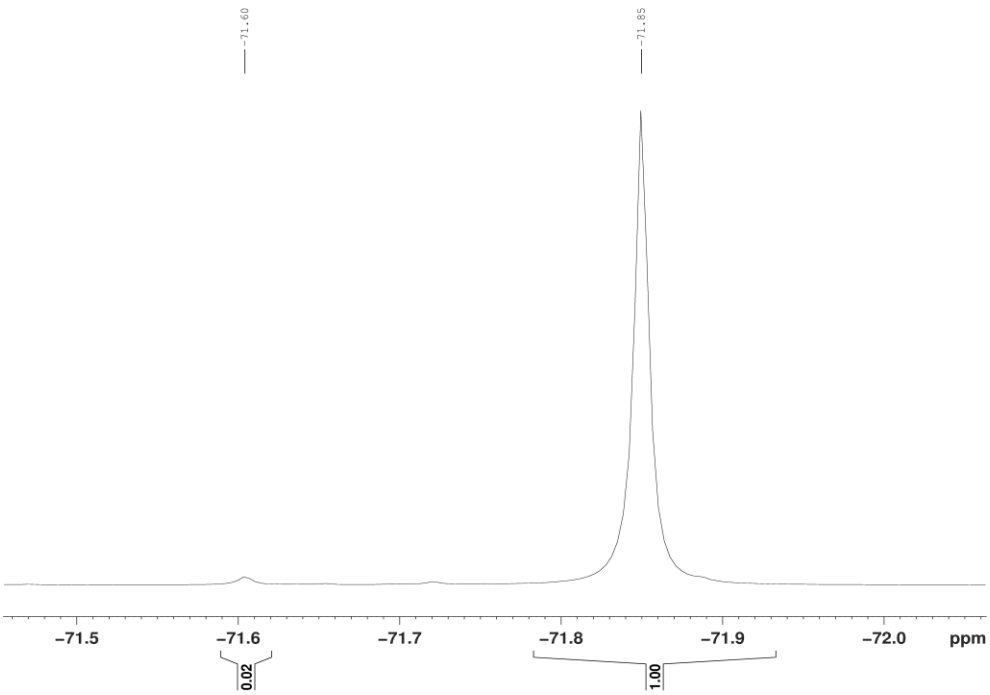



```
Current Data Parameters
NAME          GG-7-149-1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Paramete
Date_           20140525
Time               17.05
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     7
DS                     0
SWH            12019.230 H
FIDRES          0.183399 H
AQ             2.7262976 s
RG                  22.6
DW                41.600 u
DE                10.00 u
TE                298.2 K
D1            1.00000000 s
TD0                    1

======== CHANNEL f1 =====
SFO1          600.1337060 M
NUC1                   1H
P1                 11.00 u
PLW1          13.00000000 W

F2 - Processing paramete
SI                 65536
SF            600.1300147 M
WDW                   EM
SSB       0
LB                 0.30 H
GB        0
PC                 1.00
```






```
Current Data Parameters
NAME        GG-7-149-C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140525
Time               17.12
INSTRUM            spect
PROBHD   5 mm CPQCI 1H/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   794
DS                     0
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ             0.9087659 sec
RG                   203
DW               13.867 usec
DE                18.00 usec
TE                298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1        150.9178981 MHz
NUC1                  13C
P1                11.35 usec
PLW1        230.00000000 W

======== CHANNEL f2 ========
SFO2        600.1324005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2             90.00 usec
PLW2         13.00000000 W
PLW12         0.19774000 W
PLW13         0.16017000 W

F2 - Processing parameters
SI                 32768
SF          150.9028126 MHz
WDW                   EM
SSB       0
LB                1.00 Hz
GB        0
PC                 1.40
```


-71.60
-71.85
−71.5
−71.6
−71.7
−71.8
−71.9
−72.0
ppm
0.02
1.00