

## Supporting Information

# Design and Synthesis of an *s*-Triazene based Asymmetric Organocatalyst and its Application in Enantioselective Alkylation

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### General methods

All the chemicals used in synthesis were of analytical grade and purchased from Sigma-Aldrich, USA. All moisture sensitive reactions were carried out under an anhydrous argon atmosphere in dry and freshly distilled solvents under anhydrous conditions. Commercially available ethyl acetate, DMF, DCM, acetone and ethanol were dried and stored under an argon atmosphere prior to use. All intermediates were purified by silica gel column chromatography. Analytical thin layer chromatography was performed on precoated 250 μm layer thickness silica gel 60 F<sub>254</sub> plates. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on JEOL spectrometer. HPLC purification was done on Shimadzu analytical HPLC system of synthesized amino acids using CHIRALCEL OD-H Chiral Column. The identities of peaks corresponding to minor enantiomers were established with the aid of racemic samples.

For enantiomeric excess, CHIRALCEL OD-H column was used and analysis were done at 90:10 (Hexane: IPA) solvent system with flow rate 1ml/min.

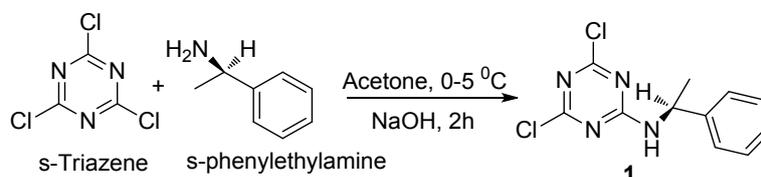
**Table sT1:** Table: Screening of chiral catalyst sT1 with different mol % of base

S. No.	Temp (°C)	% of Base	Solvent	Mol % of Catalyst	Yield (%)	ee (%)
1	-10	5 % KOH	Toluene + CHCl <sub>3</sub>	10 mol % of sT1	NR	-----
2	-10	10	Toluene + CHCl <sub>3</sub>	10 mol % of sT1	NR	-----
3	-10	20	Toluene + CHCl <sub>3</sub>	10 mol % of sT1	24	85
4	-10	30	Toluene + CHCl <sub>3</sub>	10 mol % of sT1	32	84
5	-10	40	Toluene + CHCl <sub>3</sub>	10 mol % of sT1	53	85
6	-10	50	Toluene + CHCl <sub>3</sub>	10 mol % of sT1	90	82
7	-10	60	Toluene + CHCl <sub>3</sub>	10 mol % of sT1	32	86
8	-10	70	Toluene + CHCl <sub>3</sub>	10 mol % of sT1	NR	-----
9	-10	50	Xylene	10 mol % of sT1	65	86
10	-10	50	Xylene + CHCl <sub>3</sub>	10 mol % of sT1	62	78
11	-10	50	MeOH	10 mol % of sT1	32	81
12	-10	50	Ethanol	10 mol % of sT1	43	62
13	-10	50	DMF	10 mol % of sT1	22	58

**Experimental Procedures:****Synthesis of chiral catalysts sT1, sT2 and sT3**

## Step 1.

### (4,6-Dichloro-[1,3,5]triazin-2-yl)-(1-phenyl-ethyl)-amine (1).



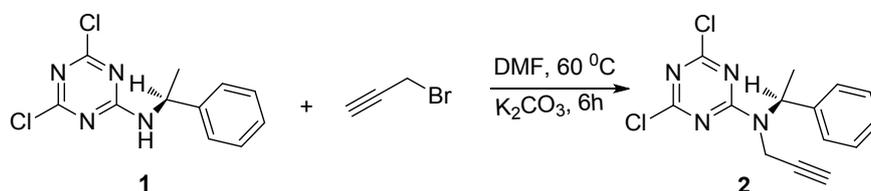
A mixture of cyanuric chloride (1.84gm, 10mmol) in dry acetone (20 ml) was cooled to 0 °C and then s-phenylethyl amine (1.2 ml, 10 mmol) was added. The pH of the reaction mixture was adjusted to 9-10 using 1N NaOH and continued to stir at 0°C until the completion of the reaction, as monitored by TLC. After usual work up, the reaction gave quantitative product. Yield-2.41gm (90%)

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>); δ 7.53-7.31(m, 5H), 6.11-6.09 (d, 1H J=4Hz), 5.25-5.23 (m, 1H), 1.65-1.58 (d, 3H; J=5.5 Hz); <sup>13</sup>C NMR: (400 MHz, CDCl<sub>3</sub>); δ 171.01, 169.94, 164.96, 141.36, 128.91, 127.99, 126.06, 51.05, 21.66. HRMS (ESI-TOF) Calcd: 269.0382 (M+H)<sup>+</sup>; found: 269.0355; [α]<sub>D</sub><sup>25</sup>= -8.6

Reference: R. J. Mattson, *et al*, *Bio Org. & Med. Chem. Lett.* 2004, **14**, 4245-4248.

## Step 2.

### (4,6-Dichloro-[1,3,5]triazin-2-yl)-(1-phenyl-ethyl)-prop-2-ynyl-amine 2

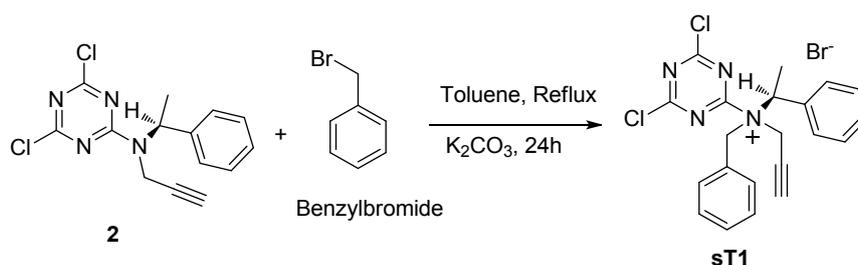


Compound 1 (1.38gm, 5mmol) was added to a suspension of 60% sodium hydride (washed with hexane) (10 mmol) in dry DMF (20 ml). This reaction mixture was stirred until the solids dissolved, then propargyl bromide (0.85 ml, 6mmol) was added and stirring continued for another 12 hr at 60 °C. The completion of the reaction was monitored by TLC. After completion of the reaction, DMF was removed in vacuo and purified by silica gel column chromatography using hexane:EA (7:3) as eluent to get compound 2 as dense oil (1.07gm), yield 70%.

<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>); δ 7.37-7.27 (m, 5H), 6.07 (q, 1H; J=3.7 Hz), 4.80 (d, 2H; J=Hz), 1.90-1.89 (d, 3H; J=6.8 Hz); <sup>13</sup>C NMR: (400 MHz, CDCl<sub>3</sub>); δ 153.87, 149.50, 145.47, 137.96, 128.90, 128.31, 127.48, 126.70, 77.88, 71.21, 52.47, 31.54, 17.80. HRMS (ESI-TOF) Calcd: 307.0439 (M+H)<sup>+</sup>; found: 307.0899 [α]<sub>D</sub><sup>25</sup>= -11.6

## Step 3 (i):

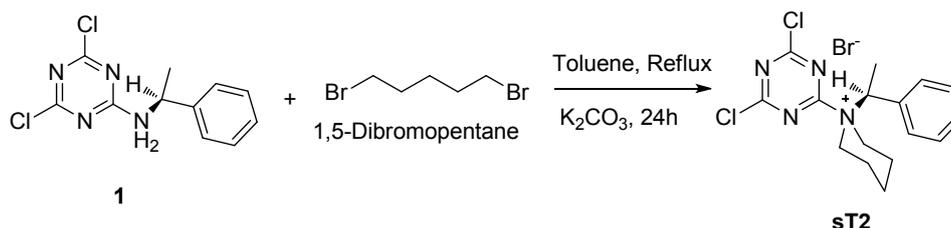
### Quaternary Ammonium Salt (sT1):



Quaternary ammonium salt **sT1** was synthesized by refluxing compound **2** (610 mg, 2mmol), benzyl bromide (0.6 ml, 3 mmol) and  $K_2CO_3$  (100 mg, 2.5 mmol) as base in toluene for 24 h. After this period, solvent was removed under vacuo to get the cationic quaternary salt **sT1**. Yield 0.72 gm, 60%.

$^1H$  NMR: (400MHz,  $CDCl_3$ );  $\delta$  7.34-7.29 (m, 10H);  $\delta$  5.24-5.21 (q, 1H;  $J=4.8$  Hz); 3.47 (s, 2H); 3.47 (d, 2H;  $J=7.8$  Hz); 2.27 (s, 1H); 1.37-1.34 (d, 3H;  $J=2.5$ Hz).  $^{13}C$  NMR: (400MHz,  $CDCl_3$ );  $\delta$  168.5, 164.96, 164.34, 143.7, 143.4, 132.05, 129.78, 128.47, 127.11, 125.89, 81.45, 74.12, 60.29, 50.61, 36.36, 22.55. HRMS (ESI-TOF) Calcd: 398.7654 (M+H-Br); found: 398.0161 (M+H-Br)  $[\alpha]_D^{25} = -7.4$

### Quaternary Ammonium Salt sT2:

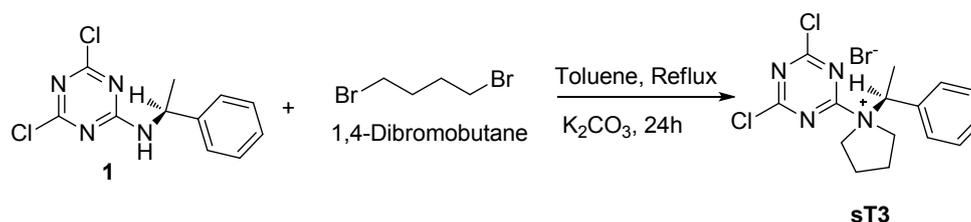


Quaternary ammonium salt **sT2** was prepared by refluxing compound **1** (0.7 gm, 2.5 mmol) and excess of 1,4-dibromopentane (1.8 ml, 7.5 mmol) as substrates and  $K_2CO_3$  (100 mg, 2.5 mmol) as base in toluene for 24h. **sT2** was obtained as dense oil. Yield 0.68 gm, (50%).

$^1H$  NMR: (400MHz,  $CDCl_3$ );  $\delta$  7.34-7.28 (m, 5H); 6.14-6.11 (q, 1H;  $J=7.5$  Hz); 3.39-3.28 (m, 4H); 2.19 (m, 6H); 1.73-1.58 (d, 3H;  $J=13.6$  Hz).  $^{13}C$  NMR (400MHz,  $CDCl_3$ );  $\delta$  170.11, 169.85, 164.34, 138.98, 128.6, 128.13, 127.40, 53.66, 43.79, 33.36, 31.89, 29.66, 26.73, 23.55, 16.52. HRMS (ESI-TOF) calcd: 419.0220 (M+H), found: 419.0210 (M+H).

$[\alpha]_D^{25} = -3.4$

### Quaternary Ammonium Salt sT3:

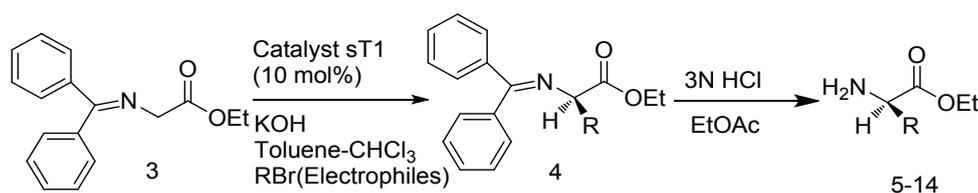


The catalyst **sT3** was synthesized from compound 1( 0.7 gm, 2.5 mmol) in a similar fashion adopted for the synthesis of **sT2**. Compound **sT3** was obtained as dense oil. Yield 0.7 gm, 50%. HRMS (ESI-TOF) calcd for C<sub>13</sub>H<sub>18</sub>Cl<sub>3</sub>N<sub>4</sub>: 359.2552 (M<sup>+</sup>), found: 359.2552 (M<sup>+</sup>).

<sup>1</sup>HNMR: (400MHz, CDCl<sub>3</sub>); δ 7.32-7.24 (m, 5H); 6.15-6.13 (q, 1H; J=4.1 Hz); 3.40-3.28 (t, 4H; J=12.6 Hz); 1.88-1.84 (m, 6H); 1.64 (d, 3H; J=8Hz); 1.57 (m, 2H); <sup>13</sup>C NMR (100MHz, CDCl<sub>3</sub>); δ 168.6, 164.9, 164.3, 143.76, 132.00, 128.8, 125.4, 125.11, 50.66, 36.94, 22.55, 14.13.

[α]<sub>D</sub><sup>25</sup>= -2.32

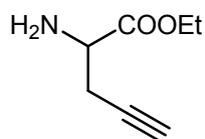
### General procedure for the Enantioselective Catalytic Alkylation of Protected Glycinnate Schiff Base.



Alkyl bromide (12 mmol) was added to a solution of substrate **3** (10 mmol) and quaternary salt **sT1**(10 mol %) in toluene and CHCl<sub>3</sub> Mixture (1:1). 0.5 ml 50% KOH solution ( 5gm in dissolved water and make up 10 ml solution, w/v ) in water was added to the reaction mixture at -10 °C and stirred for 6h. The reaction mixture was diluted with ethyl acetate (20 ml), washed with brine (3 X 5ml), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under vacuum. The residue was purified by column chromatography and deprotect the Schiff base by 3N HCl to afford **5** to **15** respectively. The enantioselectivity was determined by chiral HPLC analysis.

### Characterization of alkylated products:

#### (5) Ethyl 2-aminopent-4-ynoate

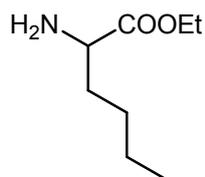


<sup>1</sup>H NMR: (400 MHz, DMSO-d<sub>6</sub>); δ 8.65 (brs, 2H); 4.23-4.21 (q, 2H, J= 5 Hz), 4.21 (m, 1H); 3.12 (s, 1H); 2.88(d, 2H); 1.29 (t, 2H).

<sup>13</sup>C NMR: (100 MHz, DMSO-d<sub>6</sub>): δ 169.18, 77.05, 75.65, 55.6, 50.22, 30.21, 18.92.

[α]<sub>D</sub><sup>25</sup>= -2.67

#### (6) Ethyl 2-aminohexanoate

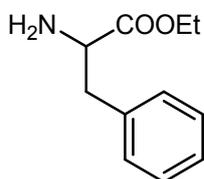


$^1\text{H}$  NMR: (400 MHz, DMSO- $d_6$ );  $\delta$  8.50 (brs, 2H); 4.18-4.14 (t, 1H;  $J=10$  Hz); 3.89-3.88 (q, 2H;  $J=2.5$  Hz); 1.36 (m, 2H); 1.29 (m, 4H); 1.21 (t, 3H;  $J=3.6$  Hz); 0.83-0.81 (t, 3H;  $J=5$  Hz).

$^{13}\text{C}$  NMR: (100 MHz, DMSO- $d_6$ );  $\delta$  168.01, 60.90, 60.17, 39.22, 32.69, 28.23, 22.52, 14.41.

$[\alpha]_D^{25} = -1.33$

### (7) Ethyl 2-amino-3-phenylpropanoate

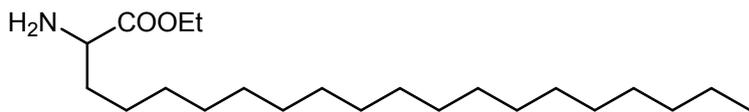


$^1\text{H}$  NMR: (400 MHz, DMSO- $d_6$ );  $\delta$  8.61 (brs, 2H); 7.33-7.24 (m, 5H); 4.31 (m, 1H); 4.24-4.18 (q, 2H;  $J=2$  Hz); 3.21-3.19 (m, 2H); 1.09-1.06 (t, 3H,  $J=3.2$  Hz).

$^{13}\text{C}$  NMR: (100 MHz, DMSO- $d_6$ );  $\delta$  169.01; 134.6; 129.56; 128.52; 127.16; 61.52; 52.71; 38.87; 13.71.

$[\alpha]_D^{25} = -0.87$

### (8) Ethyl 2-aminoicosanoate

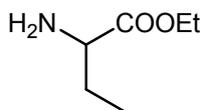


$^1\text{H}$  NMR: (400 MHz, DMSO- $d_6$ );  $\delta$  8.22 (brs, 2H); 4.18-4.13 (m, 1H); 4.18-4.13 (q, 2H;  $J=3.2$  Hz); 3.7-3.4 (m, 2H); 1.22 (s, 32H); 1.20-1.18 (t, 3H;  $J=5$  Hz); 0.93-0.83 (t, 3H;  $J=$  Hz)

$^{13}\text{C}$  NMR: (100 MHz, DMSO- $d_6$ );  $\delta$  168.5; 61.8; 61.5; 29.47; 29.48; 22.67; 14.4; 13.8.

$[\alpha]_D^{25} = -4.11$

### (9) Ethyl 2-aminobutanoate

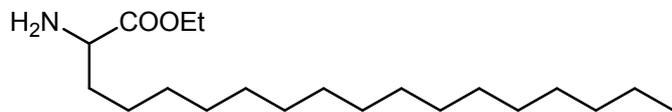


$^1\text{H}$  NMR: (400 MHz, DMSO- $d_6$ );  $\delta$  8.56 (brs, 2H); 4.23-4.20 (t, 1H;  $J=7.4$  Hz); 3.98-3.93 (q, 2H;  $J=2.5$  Hz); 1.92-1.91 (m, 2H); 1.18-1.20 (t, 3H;  $J=2.5$  Hz), 1.09-.0.98 (t, 3H;  $J=4$  Hz).

$^{13}\text{C}$  NMR: (100 MHz, DMSO-d<sub>6</sub>);  $\delta$  170.82; 61.93; 60.26; 21.12; 14.50; 14.29.

$[\alpha]_{\text{D}}^{25} = -1.11$

**(10) Ethyl 2-aminooctadecanoate**

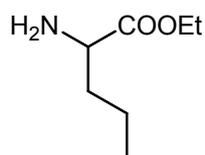


$^1\text{H}$  NMR: (400 MHz, DMSO-d<sub>6</sub>);  $\delta$  7.93 (brs, 2H); 4.16-4.10 (m, 3H); 2.73-2.48 (m, 2H); 1.22 (s, 28H); 1.05-1.01 (t, 3H; J=2.5 Hz); 0.85-0.81 (t, 3H; J=4 Hz).

$^{13}\text{C}$  NMR: (100 MHz, DMSO-d<sub>6</sub>);  $\delta$  166.11, 60.90; 55.71; 40.12; 31.30; 29.06; 28.89; 28.62; 28.57; 22.10; 14.13; 13.61.

$[\alpha]_{\text{D}}^{25} = -0.46$

**(11) Ethyl 2-aminopentanoate**

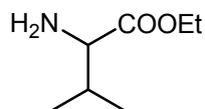


$^1\text{H}$  NMR: (400 MHz, DMSO-d<sub>6</sub>);  $\delta$  8.60 (brs, 2H); 4.19-4.14 (t, 1H; J=2 Hz); 3.75 (q, 2H; J=2.5 Hz); 2.48-2.26 (m, 2H); 1.21 (m, 2H); 1.20-1.19 (t, 3H; J= 2 Hz); 0.83-0.81 (t, 3H; J= 2.4 Hz).

$^{13}\text{C}$  NMR: (100 MHz, DMSO-d<sub>6</sub>);  $\delta$  167.52; 61.52; 51.78; 30.10; 13.89; 22.32; 13.91; 13.65.

$[\alpha]_{\text{D}}^{25} = -2.21$

**(12) Ethyl 2-amino-3-methylbutanoate**

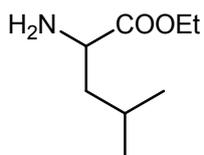


$^1\text{H}$  NMR: (400 MHz, DMSO-d<sub>6</sub>);  $\delta$  8.56 (brs, 2H); 4.14-4.12 (q, 2H; J= 2.5 Hz); 3.72-3.69 (m, 2H); 1.17-1.15 (t, 3H; J= 2 Hz); 0.98-0.96 (d, 6H; J=10 Hz).

$^{13}\text{C}$  NMR: (100 MHz, DMSO-d<sub>6</sub>);  $\delta$  167.98; 62.46; 61.98; 40.14; 25.92; 14.44.

$[\alpha]_{\text{D}}^{25} = -1.33$

**(13) Ethyl 2-amino-4-methylpentanoate**

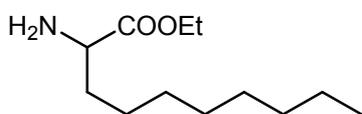


<sup>1</sup>H NMR: (400 MHz, DMSO-d<sub>6</sub>); δ 8.46 (brs, 2H); 4.14-4.12 (q, 2H; J=2.5 Hz); 3.72- 3.67 (m, 1H); 2.83 (m, 1H); 2.28-1.96 (m, 2H); 1.17-1.15 (t, 3H; J=2.5 Hz); 0.98-0.93 (d, 6H; J=8 Hz)

<sup>13</sup>C NMR: (100 MHz, DMSO-d<sub>6</sub>): δ 167.84; 61.89; 51.52; 30.38; 23.71; 22.29; 13.52.

[α]<sub>D</sub><sup>25</sup> = -1.37

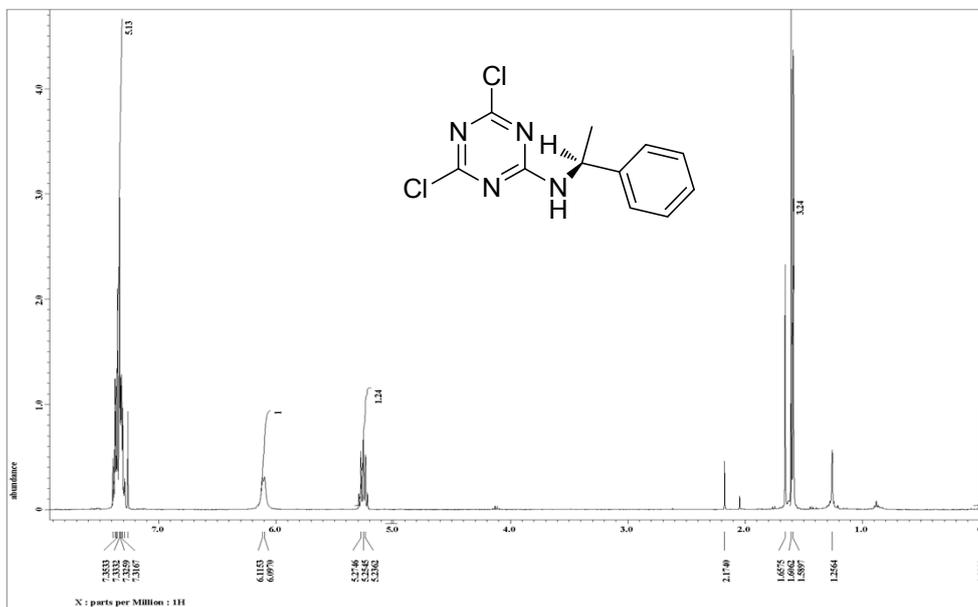
#### (14) Ethyl 2-aminodecanoate



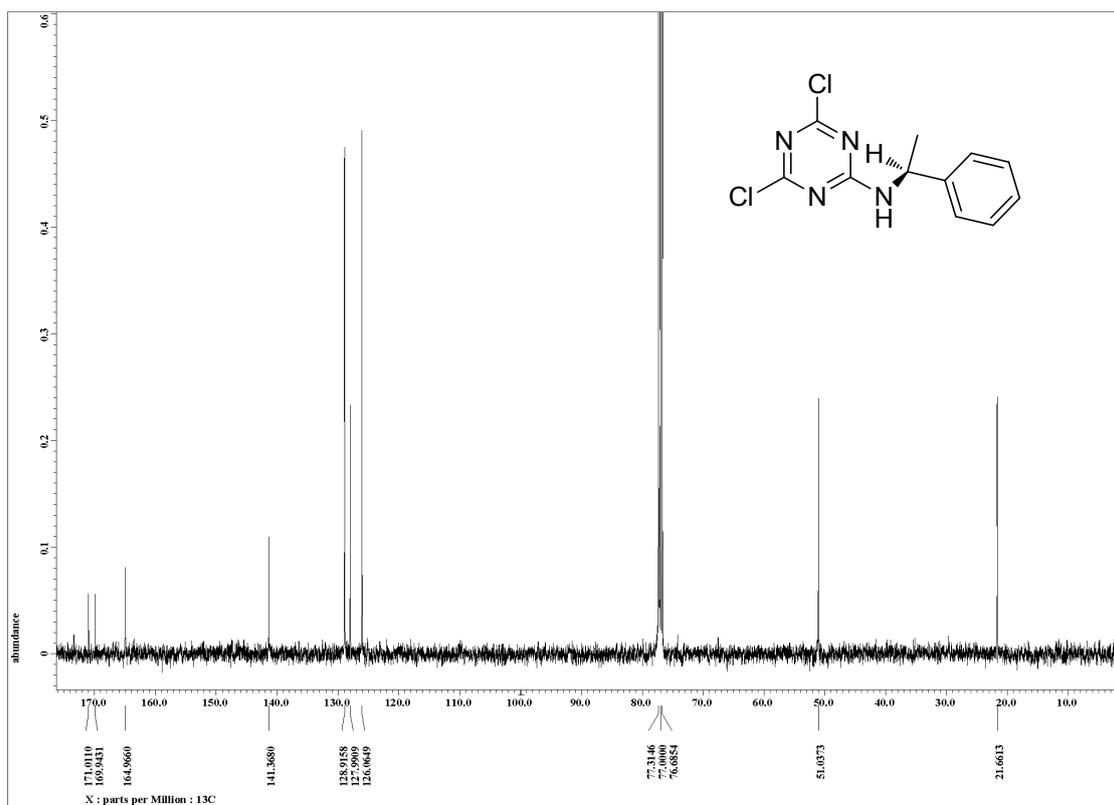
<sup>1</sup>H NMR: (400 MHz, DMSO-d<sub>6</sub>); δ 8.00 (brs, 2H); 4.00-3.94 (m, 1H); 4.00-3.94 (q, 2H; J=3 Hz); 3.12 (m, 2H); 1.68 (s, 10H); 1.12-1.06 (t, 3H; J=4.5 Hz); 0.75- 0.71 (t, 3H; J=3.5 Hz).

<sup>13</sup>C NMR: (100 MHz, DMSO-d<sub>6</sub>); δ 174.18; 59.86; 55.97; 40.36; 30.64; 31.26; 30.62; 28.84; 28.71; 26.28; 22.13; 13.91; 12.59. [α]<sub>D</sub><sup>25</sup> = -1.89

### <sup>1</sup>H NMR spectra of compound 1.



### <sup>13</sup>C NMR spectra of compound 1



# Mass spectra of Compound 1

## Qualitative Compound Report

Data File	ST 01.d	Sample Name	ST 01
Sample Type	Sample	Position	P2-C9
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IRM Calibration Status	Success	DA Method	Default.m
Comment			

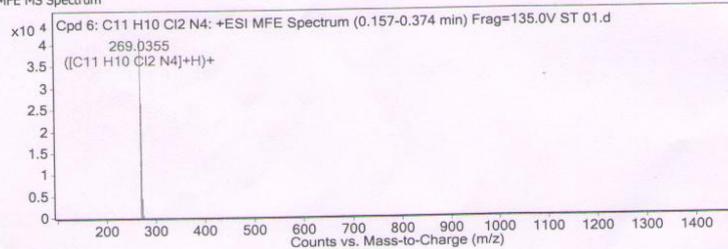
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Acquisition SW	6200 series TOF/6500 series	
Version	Q-TOF B.05.01 (B5125)	

### Compound Table

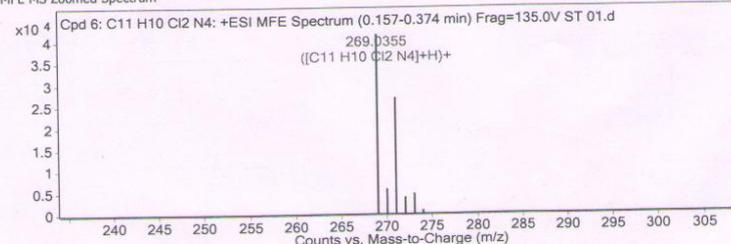
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
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Compound Label	m/z	RT	Algorithm	Mass
Cpd 6: C11 H10 Cl2 N4	269.0355	0.209	Find by Molecular Feature	268.0285

### MFE MS Spectrum



### MFE MS Zoomed Spectrum

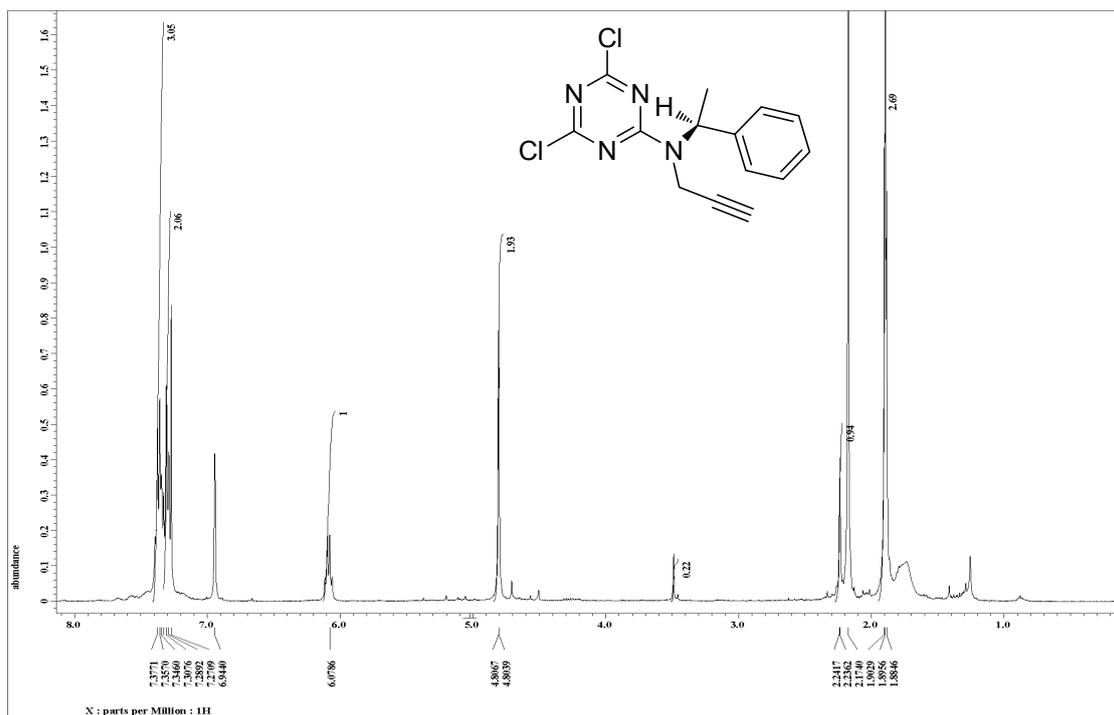


### MS Spectrum Peak List

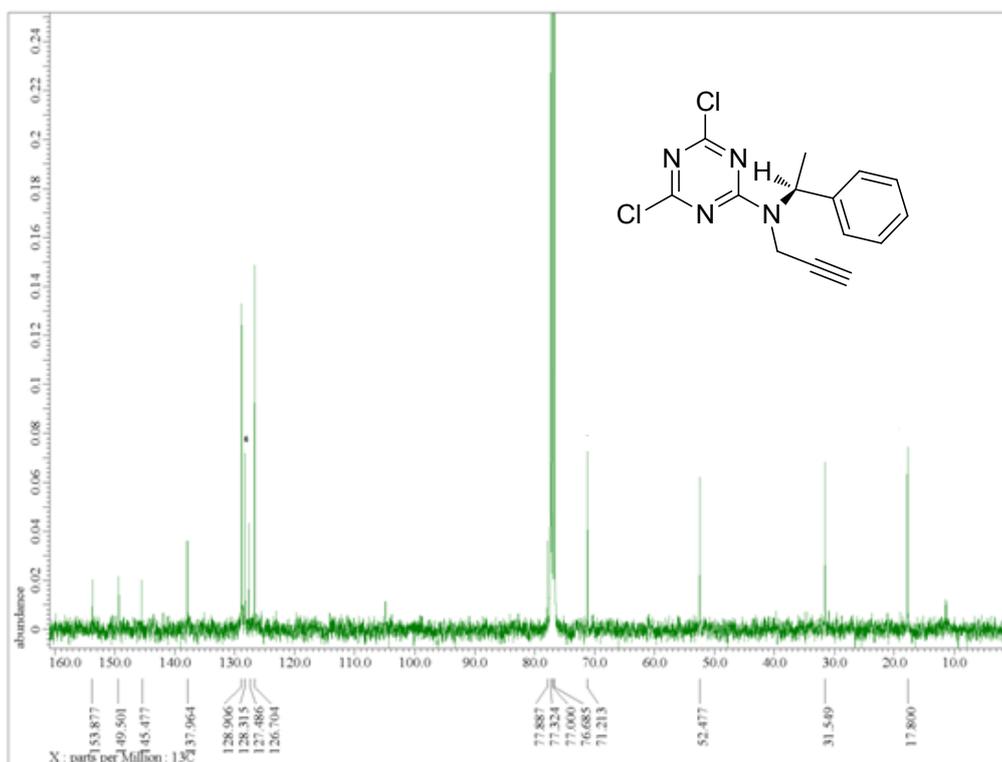
m/z	z	Abund	Formula	Ion
269.0355	1	41527.85	C11 H10 Cl2 N4	(M+H)+
270.0381	1	5702.59	C11 H10 Cl2 N4	(M+H)+
271.0334	1	26608.13	C11 H10 Cl2 N4	(M+H)+
272.0361	1	3594.1	C11 H10 Cl2 N4	(M+H)+
273.0298	1	4517.17	C11 H10 Cl2 N4	(M+H)+
274.0337	1	561.22	C11 H10 Cl2 N4	(M+H)+

--- End Of Report ---

## <sup>1</sup>H NMR spectra of compound 2



## <sup>13</sup>C NMR spectra of compound 2



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## Mass spectra of compound 2

### Qualitative Compound Report

Data File	.ST 11.d	Sample Name	ST 11
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IRM Calibration Status	Success	DA Method	Default.m
Comment			

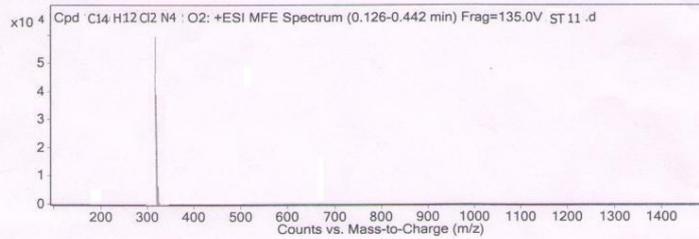
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#### Compound Table

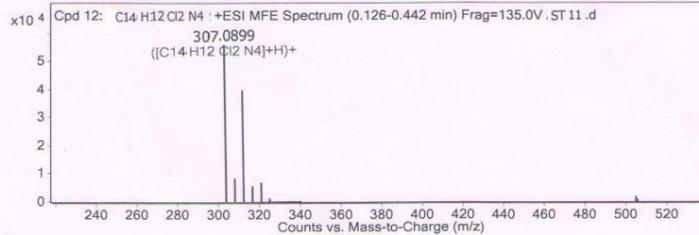
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
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Compound Label	m/z	RT	Algorithm	Mass
Cpd 12: C14 H12 Cl2 N4	253.0971	0.206	Find by Molecular Feature	307.0899

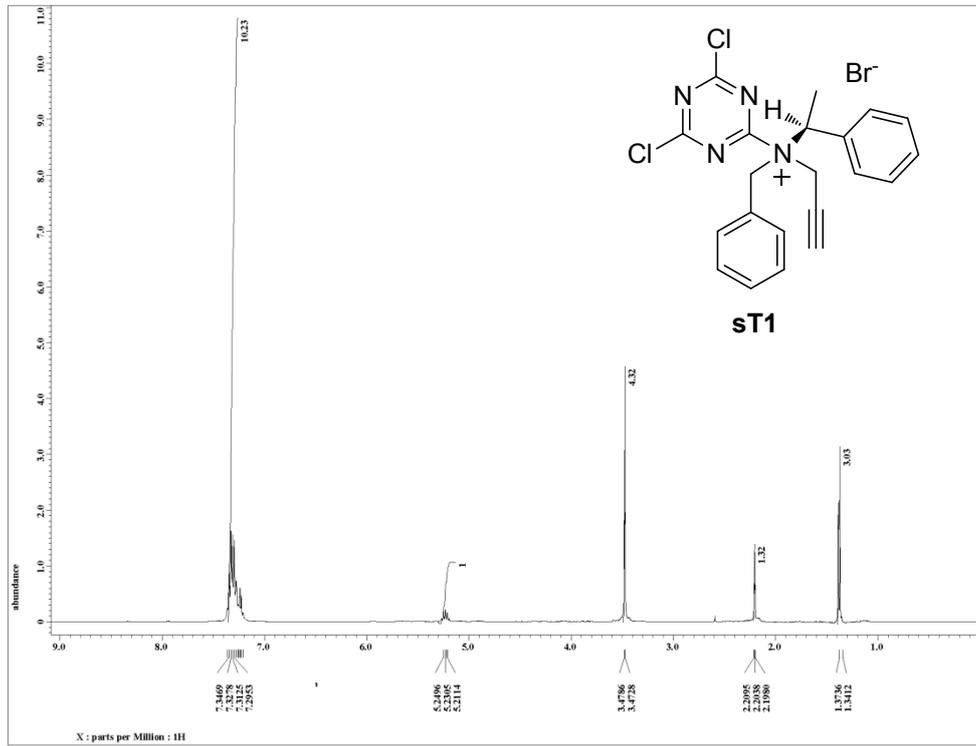
#### MFE MS Spectrum



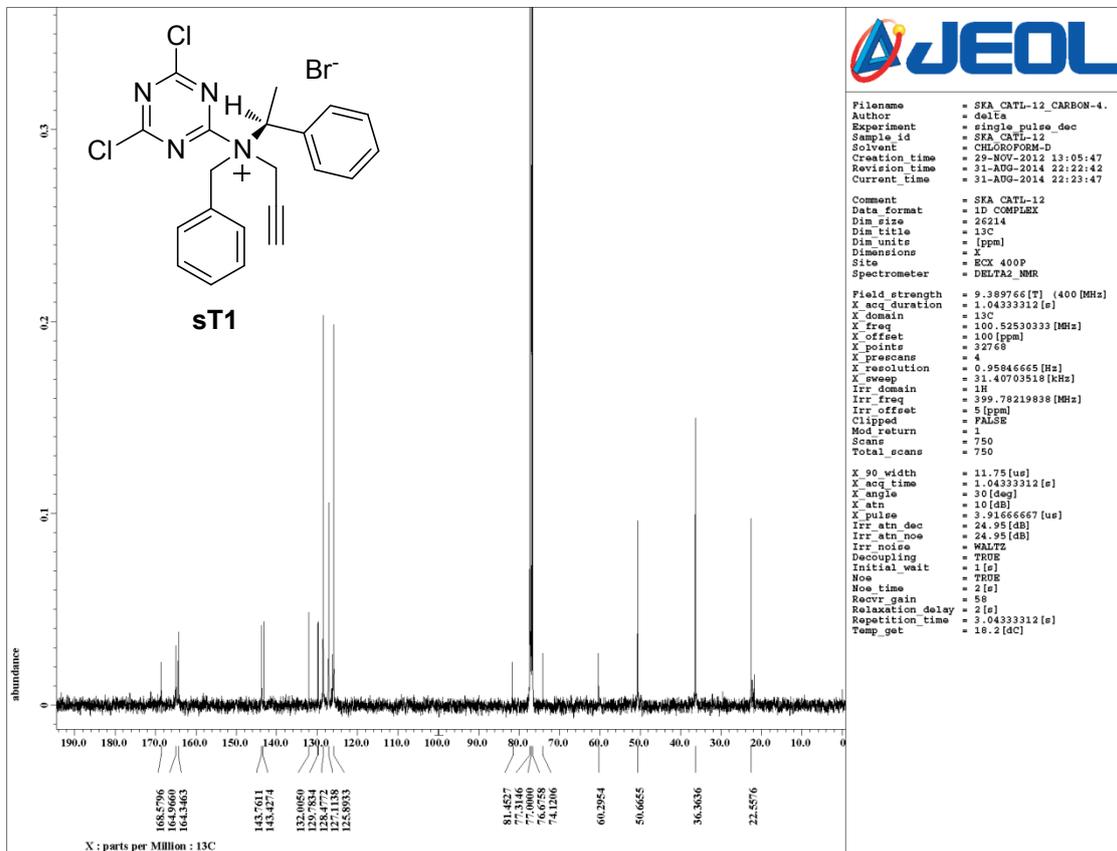
#### MFE MS Zoomed Spectrum



### <sup>1</sup>H NMR spectra of compound sT1



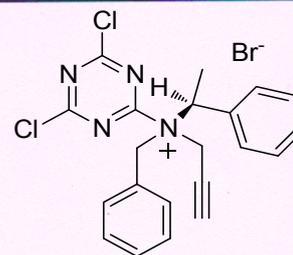
### <sup>13</sup>C NMR spectra of compound sT1



# Mass Spectra of compound sT1

## Qualitative Compound Report

<b>Data File</b>	ST-6C.d	<b>Sample Name</b>	ST-6C
<b>Sample Type</b>	Sample	<b>Position</b>	P1A4
<b>Instrument Name</b>	6530 QTOF LCMS	<b>User Name</b>	lcmdu-PC\admin
<b>Acq Method</b>	Union.m	<b>Acquired Time</b>	11-05-2015 15:03:23
<b>IRM Calibration Status</b>	Success	<b>DA Method</b>	Default.m
<b>Comment</b>			



**sT1**

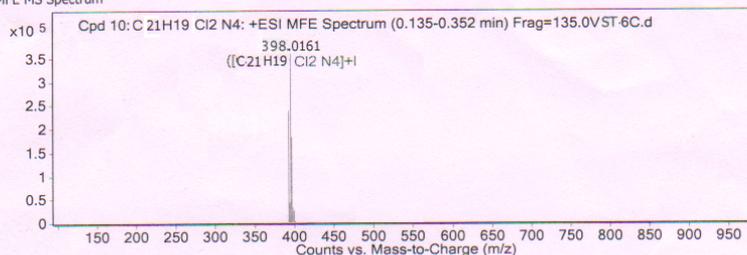
<b>Sample Group</b>		<b>Info.</b>
<b>Acquisition SW</b>	6200 series TOF/6500 series	
<b>Version</b>	Q-TOF B.05.01 (B5125)	

### Compound Table

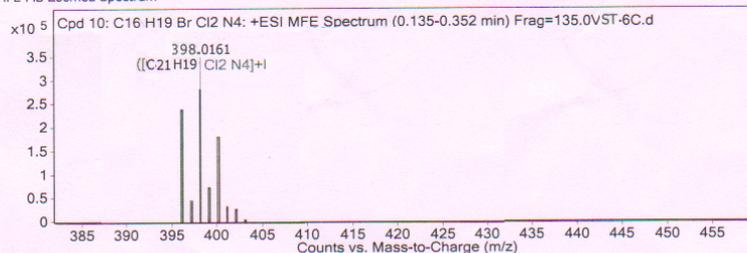
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 10: C <sub>21</sub> H <sub>19</sub> Cl <sub>2</sub> N <sub>4</sub>	0.192	398.0161	C <sub>21</sub> H <sub>19</sub> Cl <sub>2</sub> N <sub>4</sub>	C <sub>21</sub> H <sub>19</sub> Cl <sub>2</sub> N <sub>4</sub>	2.29	C <sub>21</sub> H <sub>19</sub> Cl <sub>2</sub> N <sub>4</sub>

Compound Label	m/z	RT	Algorithm	Mass
Cpd 10: C <sub>21</sub> H <sub>19</sub> Cl <sub>2</sub> N <sub>4</sub>	399.0233	0.192	Find by Molecular Feature	398.0161

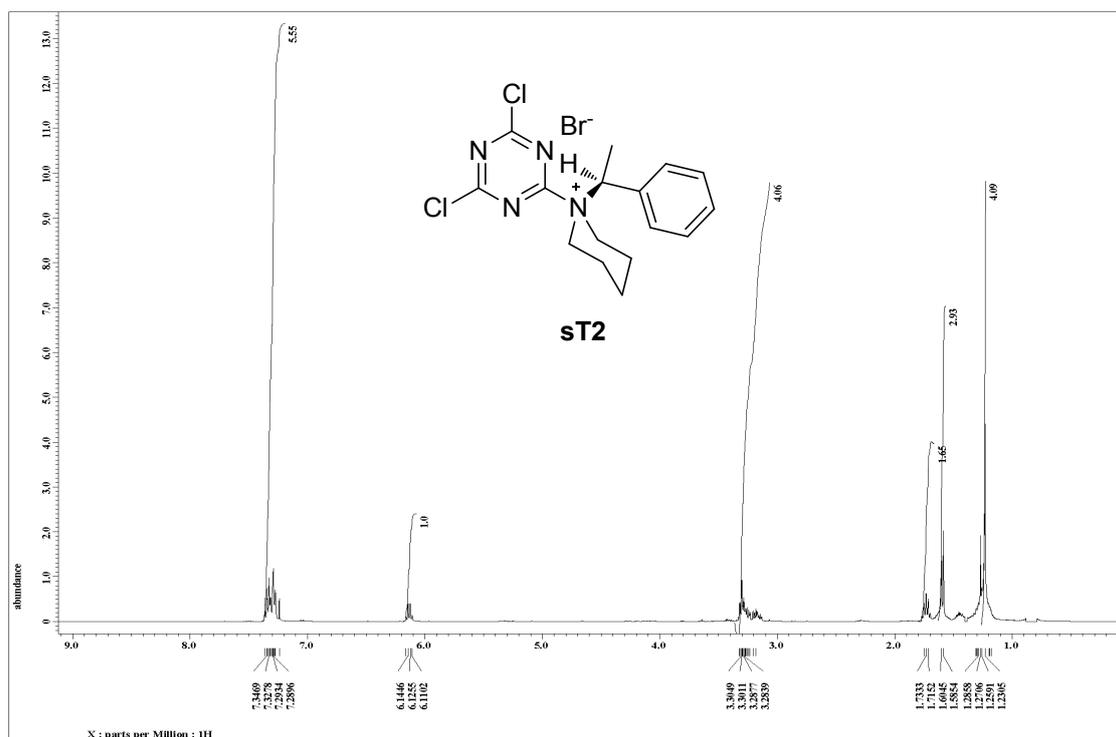
### MFE MS Spectrum



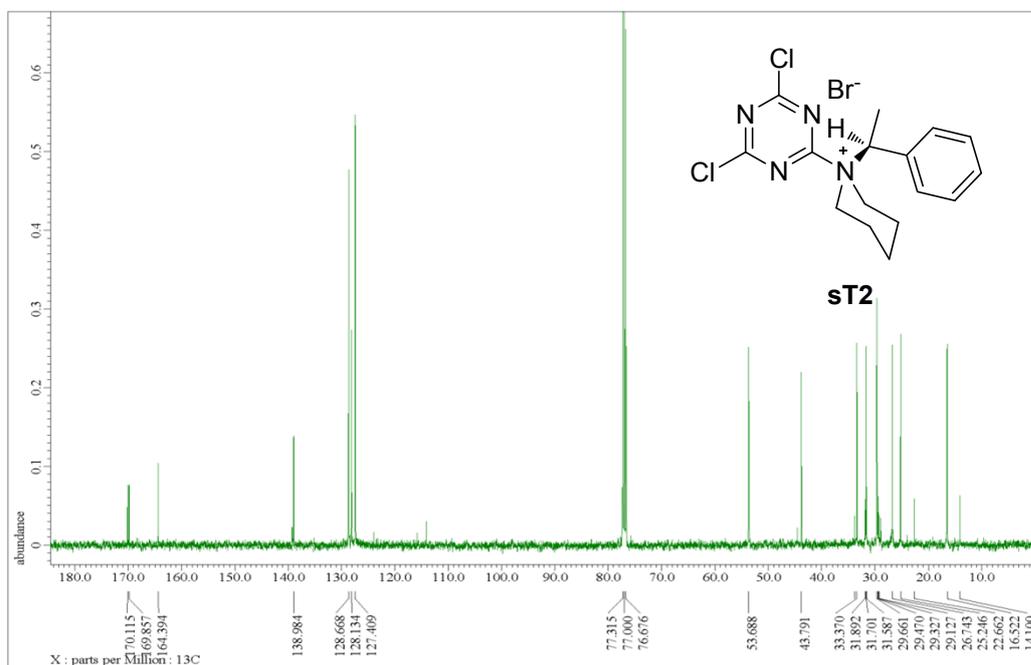
### MFE MS Zoomed Spectrum



## <sup>1</sup>H NMR Spectra of compound sT2



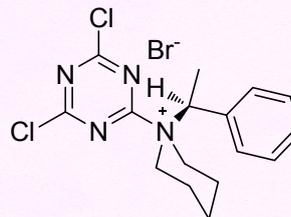
## <sup>13</sup>C NMR Spectra of sT2



# Mass Spectra of sT2

## Qualitative Compound Report

<b>Data File</b>	Q-6C.d	<b>Sample Name</b>	Q-6C
<b>Sample Type</b>	Sample	<b>Position</b>	P1A4
<b>Instrument Name</b>	6530 QTOF LCMS	<b>User Name</b>	lcmsdu-PC\admin
<b>Acq Method</b>	Union.m	<b>Acquired Time</b>	09-09-2014 15:03:23
<b>IRM Calibration Status</b>	Success	<b>DA Method</b>	Default.m
<b>Comment</b>			



**sT2**

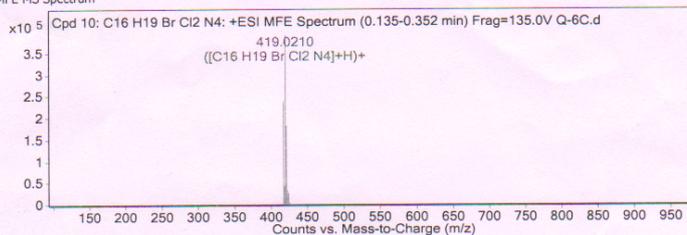
**Sample Group** Info.  
**Acquisition SW** 6200 series TOF/6500 series  
**Version** Q-TOF B.05.01 (B5125)

### Compound Table

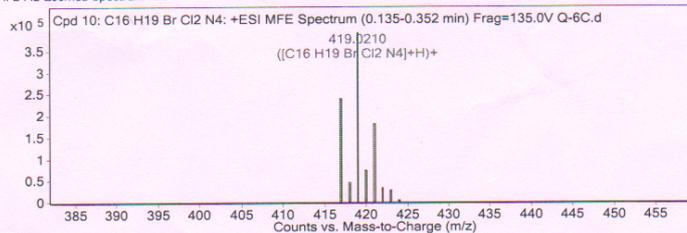
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 10: C16 H19 Br Cl2 N4	0.192	416.0161	C16 H19 Br Cl2 N4	C16 H19 Br Cl2 N4	2.29	C16 H19 Br Cl2 N4

Compound Label	m/z	RT	Algorithm	Mass
Cpd 10: C16 H19 Br Cl2 N4	417.0233	0.192	Find by Molecular Feature	416.0161

### MFE MS Spectrum



### MFE MS Zoomed Spectrum

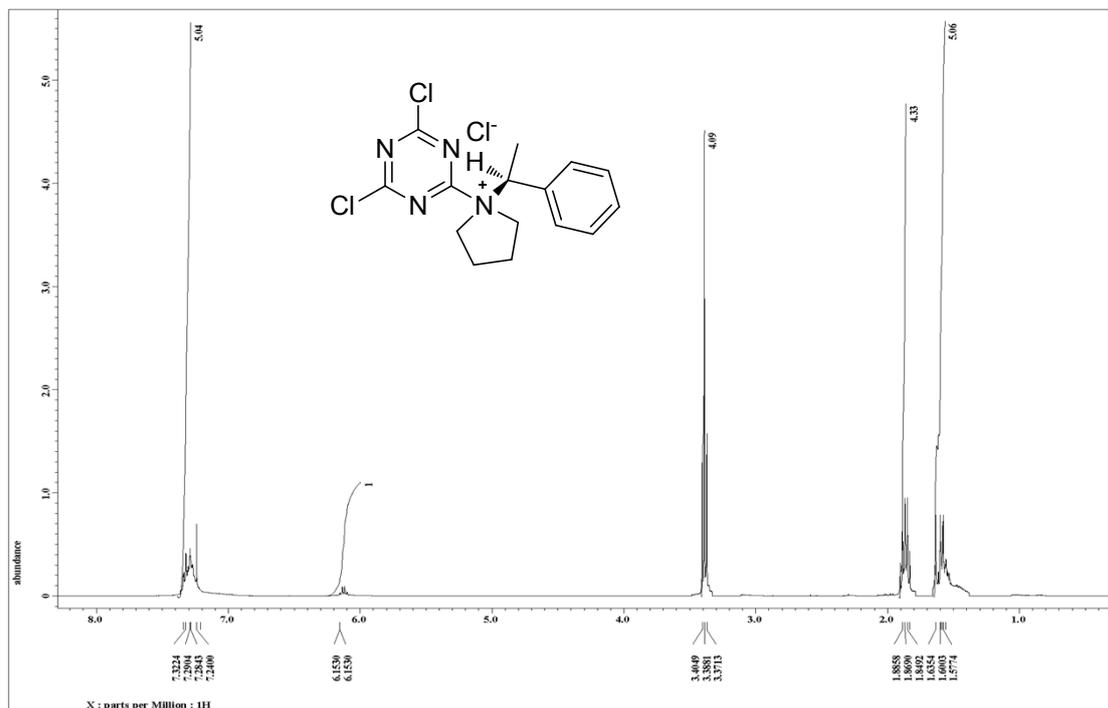


### MS Spectrum Peak List

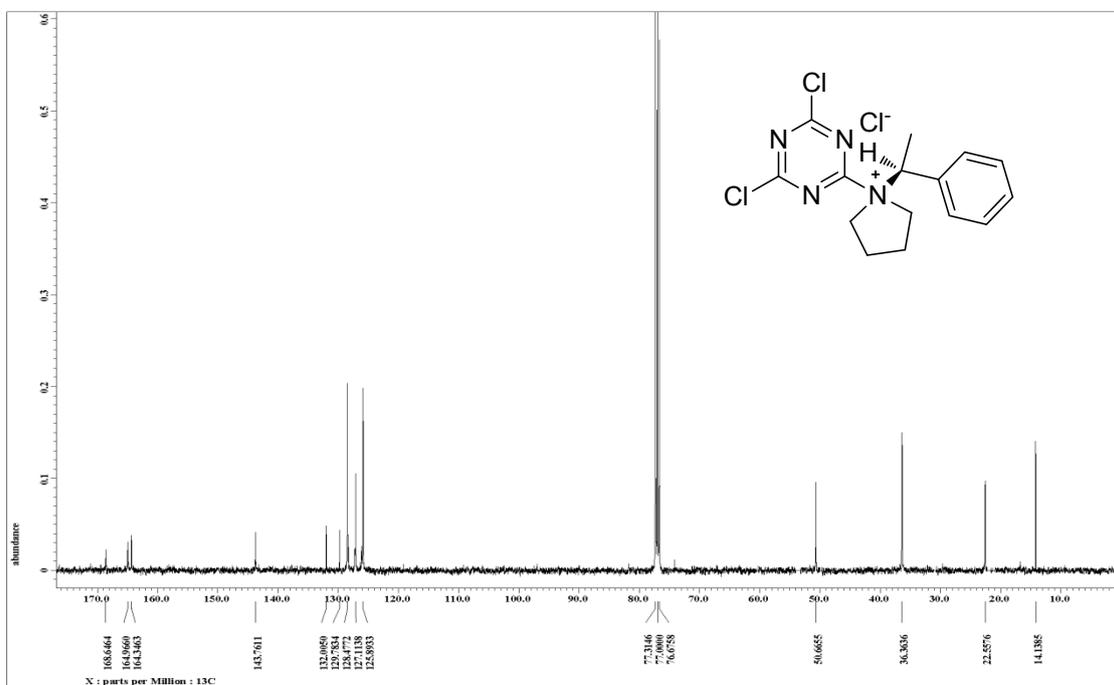
m/z	z	Abund	Formula	Ion
417.0233	1	239485.94	C16 H19 Br Cl2 N4	(M+H)+
418.0262	1	43137.15	C16 H19 Br Cl2 N4	(M+H)+
419.021	1	392155.13	C16 H19 Br Cl2 N4	(M+H)+
420.0239	1	72592.36	C16 H19 Br Cl2 N4	(M+H)+
421.0185	1	181707.64	C16 H19 Br Cl2 N4	(M+H)+
422.0212	1	32557.84	C16 H19 Br Cl2 N4	(M+H)+
423.0173	1	25940.88	C16 H19 Br Cl2 N4	(M+H)+
424.0193	1	4585.62	C16 H19 Br Cl2 N4	(M+H)+
425.028	1	292.23	C16 H19 Br Cl2 N4	(M+H)+

--- End Of Report ---

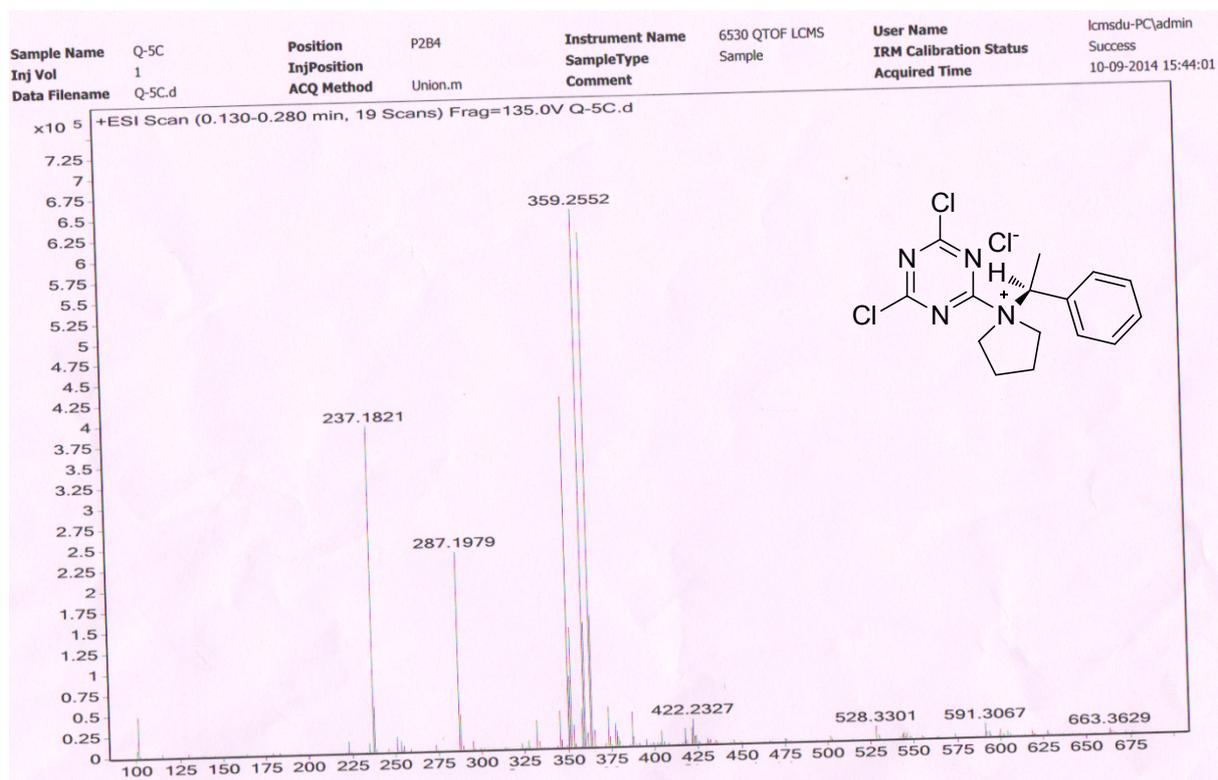
### <sup>1</sup>H NMR spectra of compound sT3



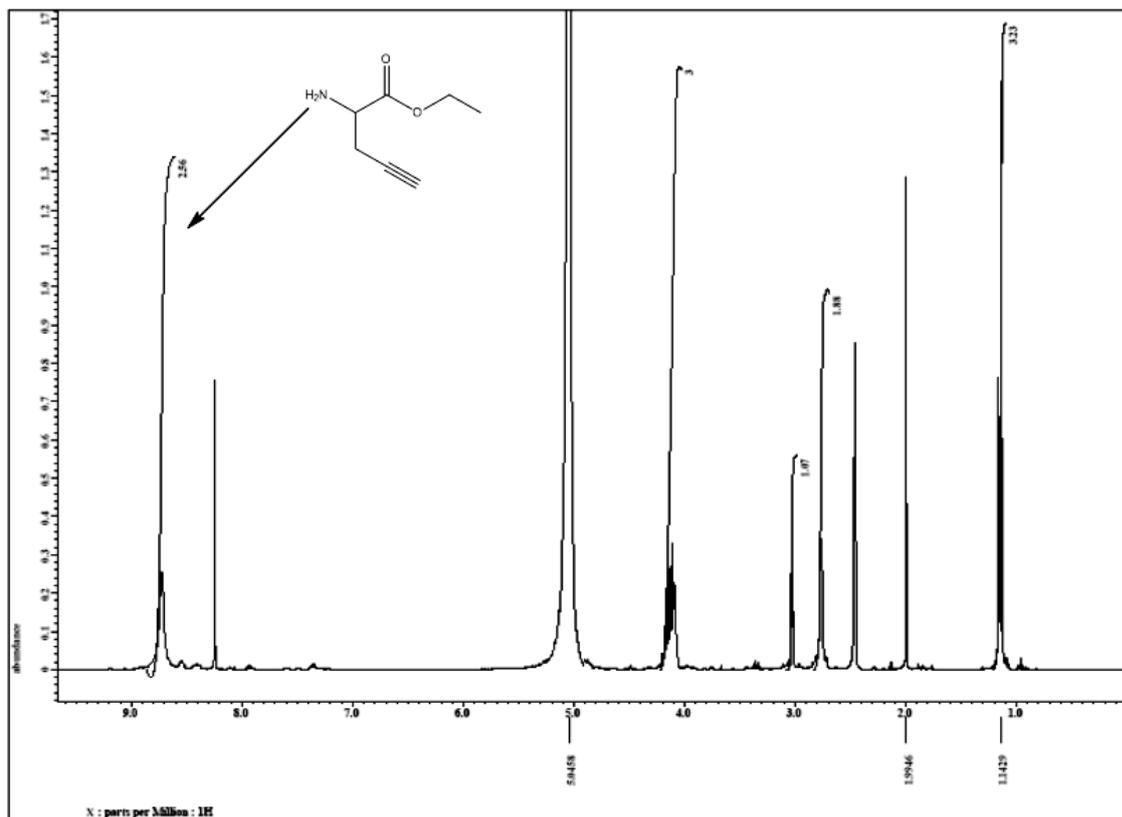
### <sup>13</sup>C NMR of compound sT3



## Mass spectra of sT3

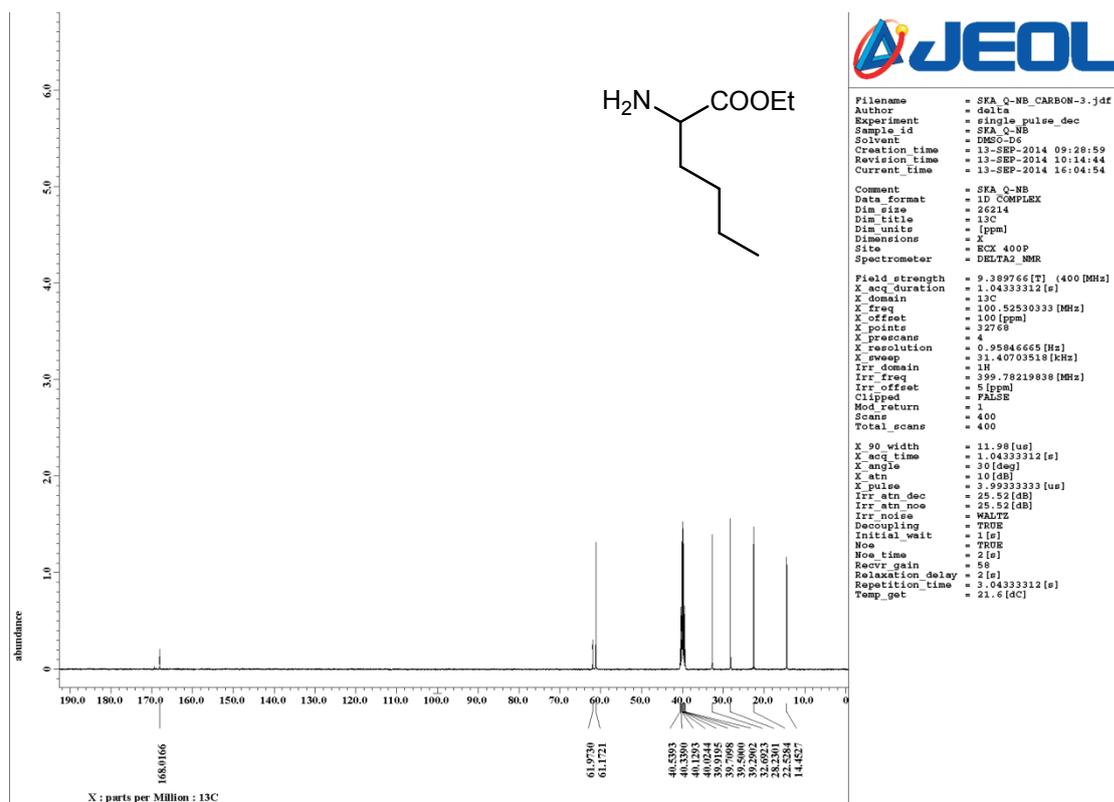


## <sup>1</sup>H NMR spectra of product 5

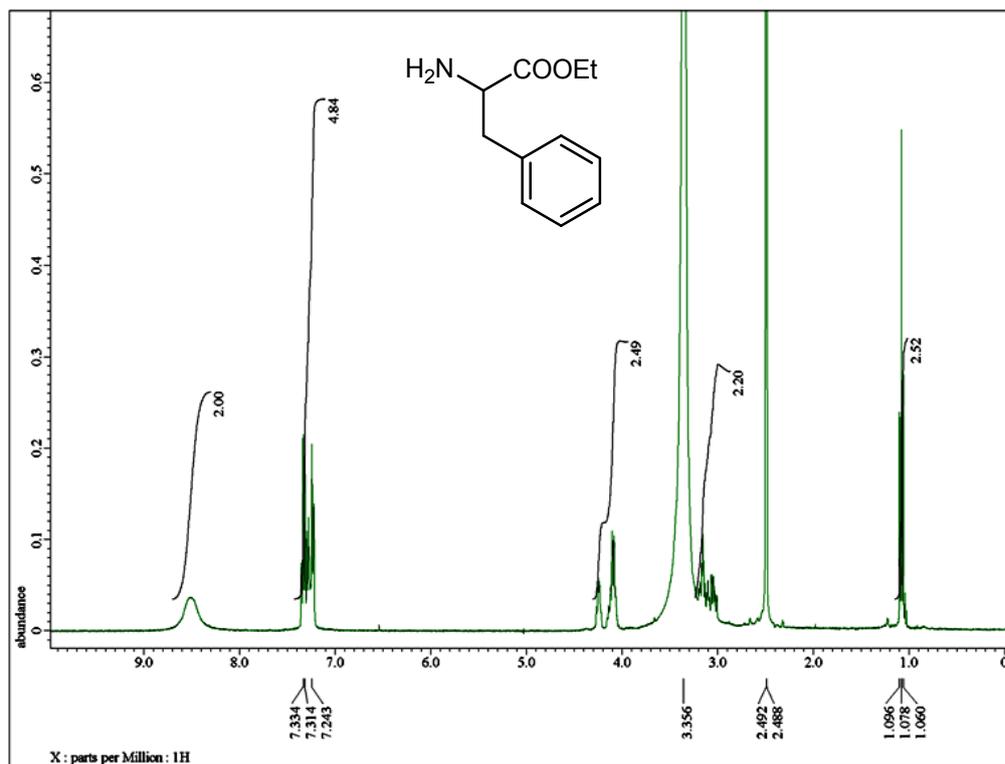




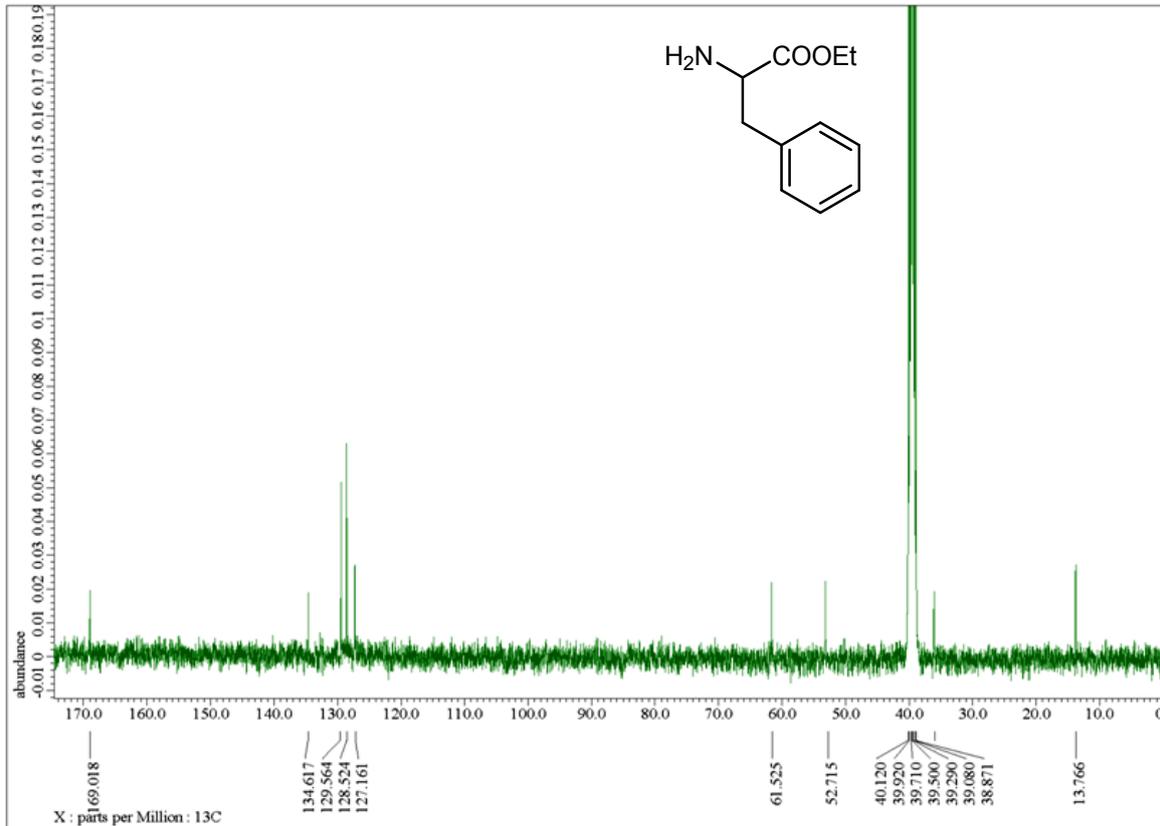
### <sup>13</sup>C NMR spectra of product 6



### <sup>1</sup>H NMR spectra of product 7

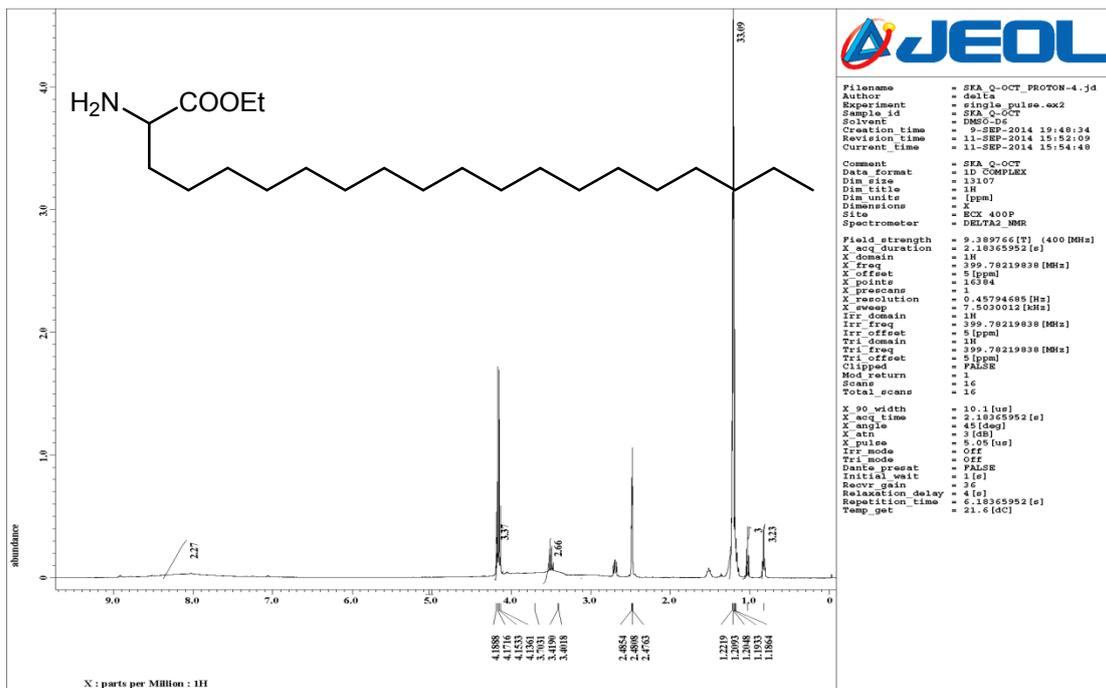


### <sup>13</sup>C NMR spectra of product 7

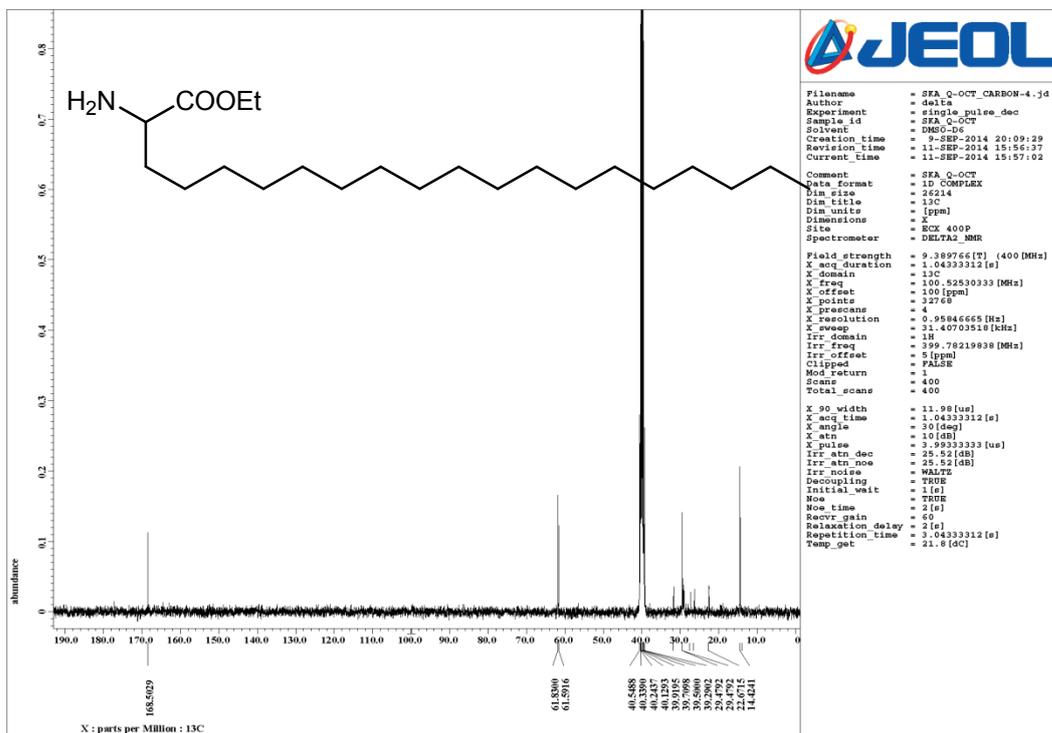


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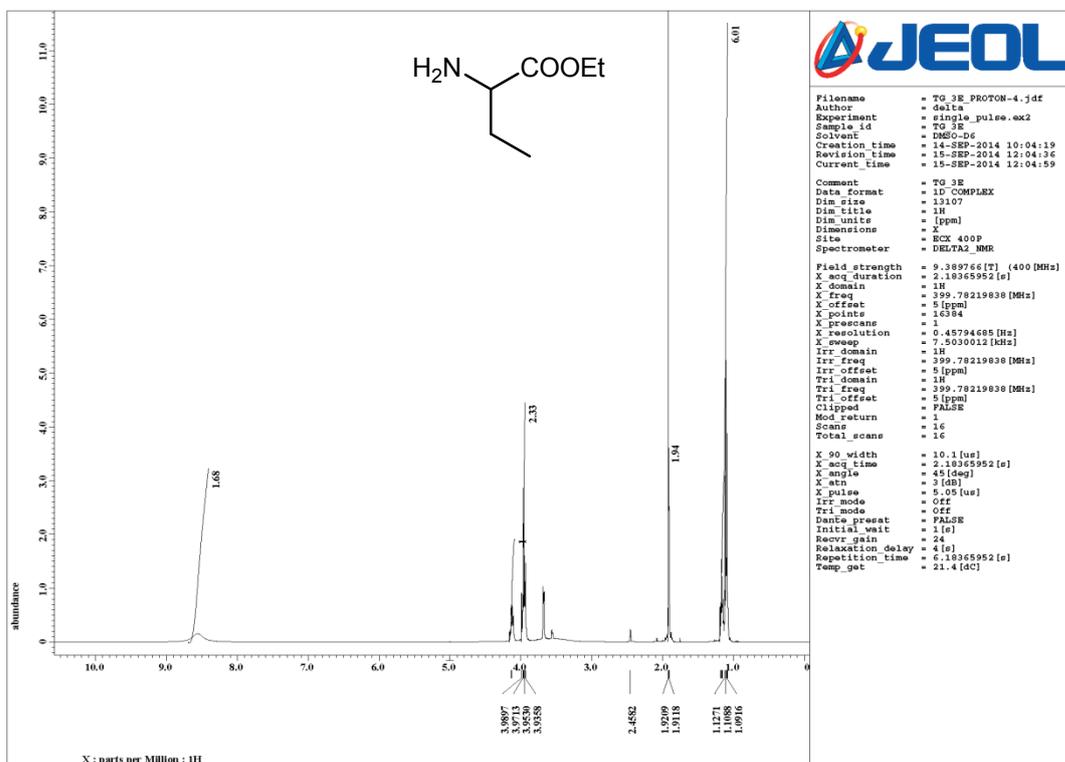
### <sup>1</sup>H NMR spectra of product 8



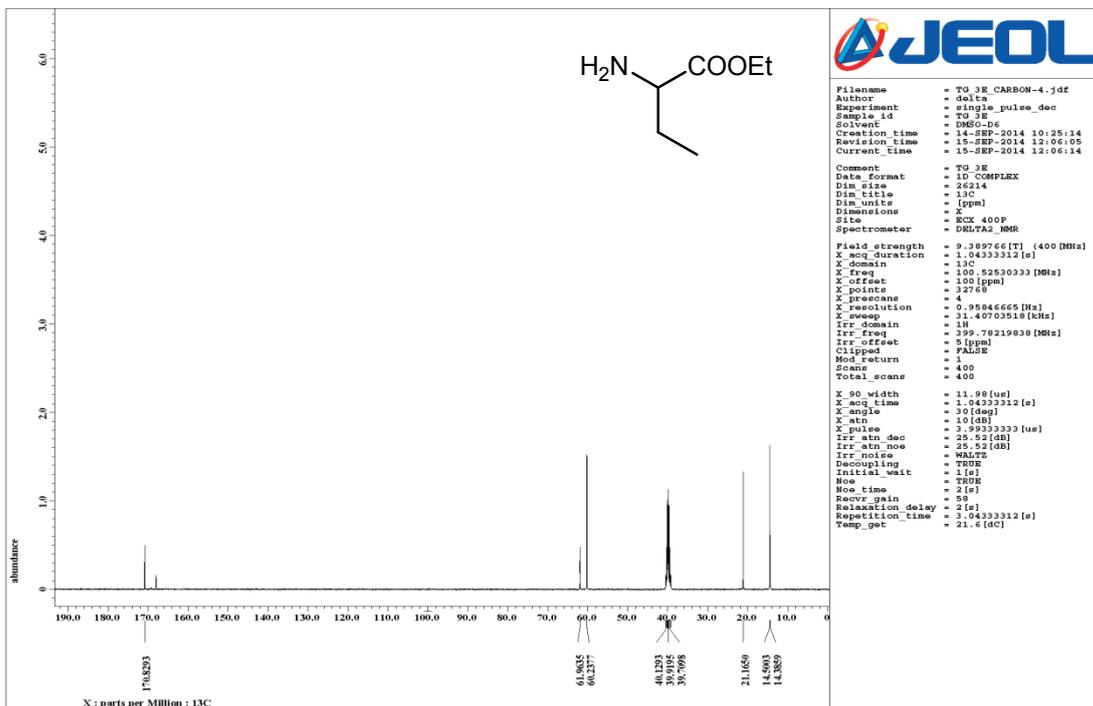
### <sup>13</sup>C NMR spectra of product 8



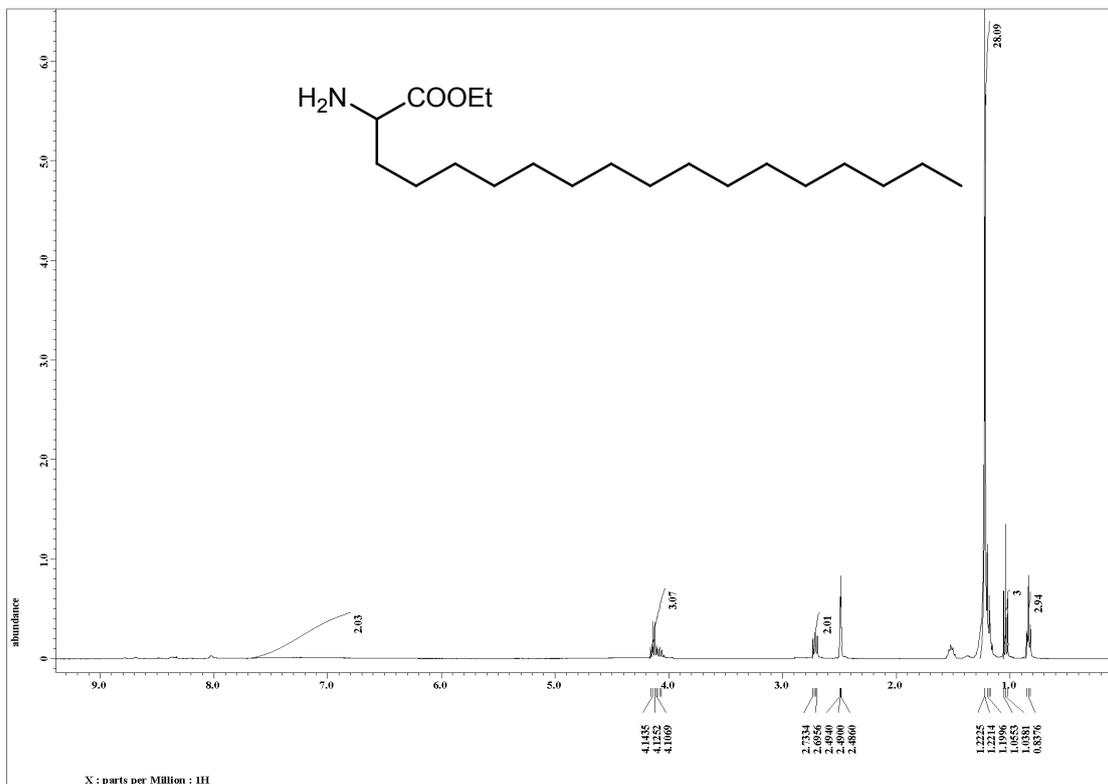
### <sup>1</sup>H NMR spectra of product 9



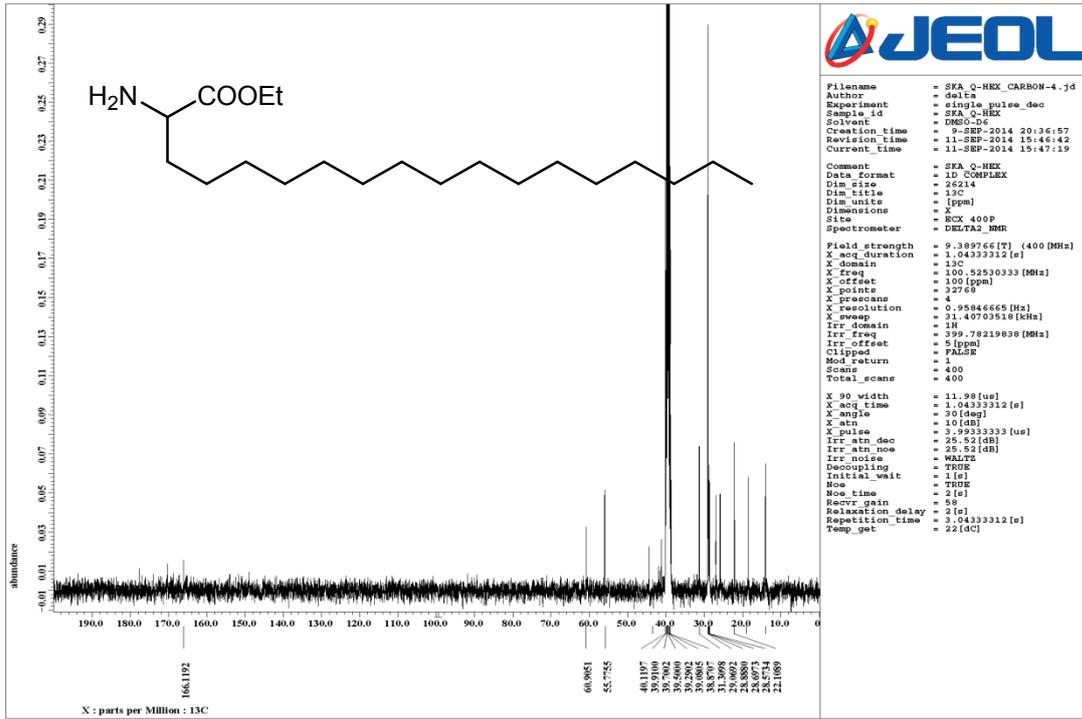
### <sup>13</sup>C NMR spectra of product 9



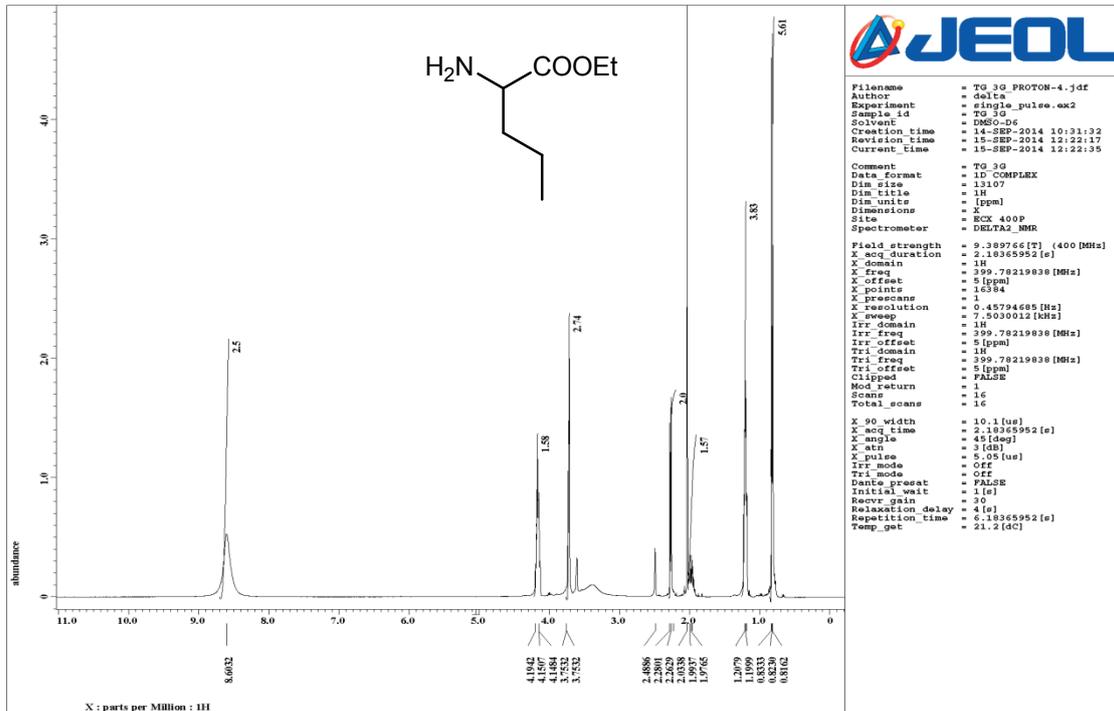
### <sup>1</sup>H NMR spectra of product 10



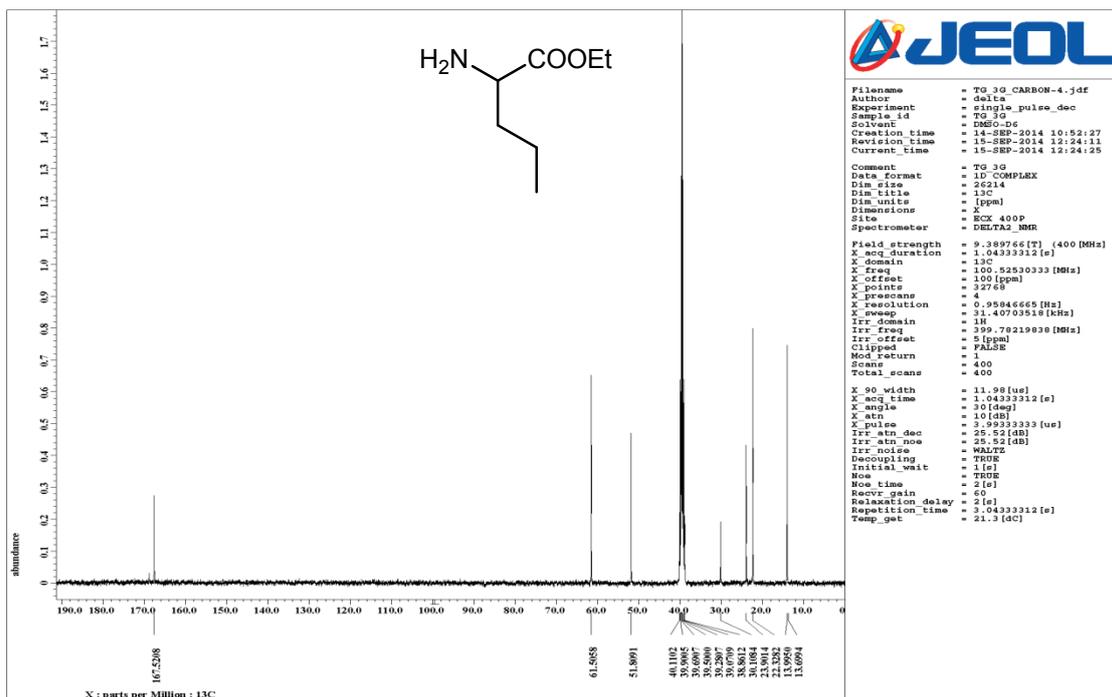
### <sup>13</sup>C NMR spectra of product 10



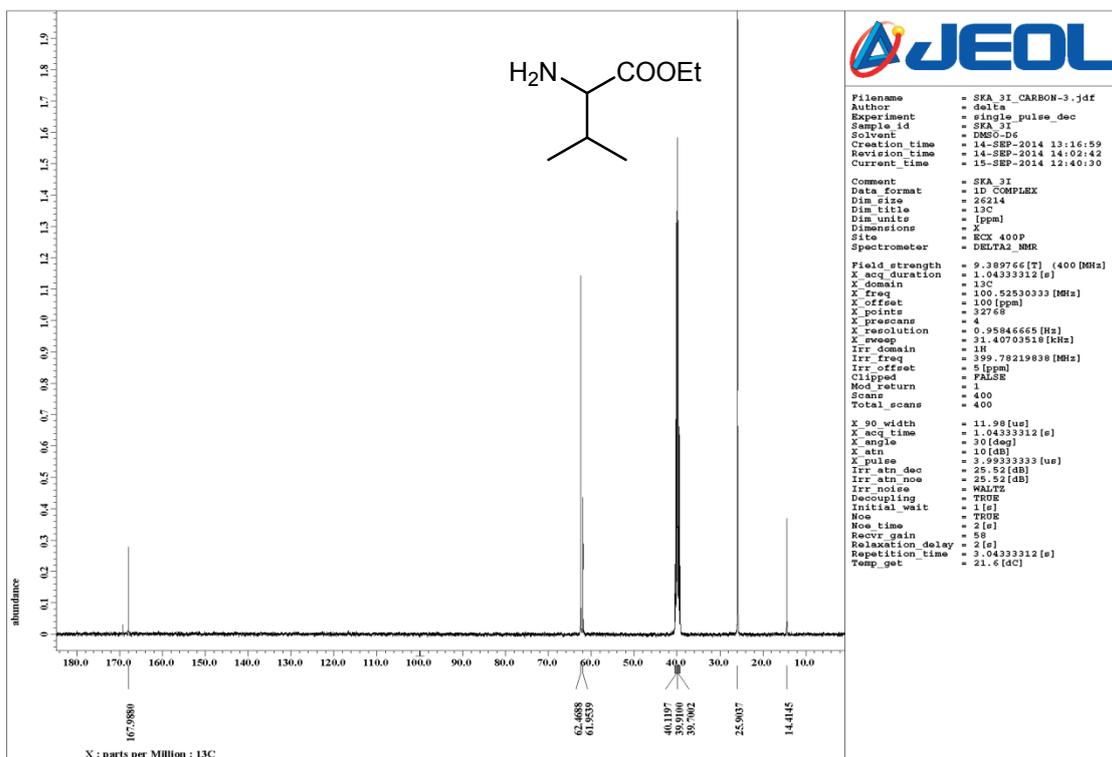
### <sup>1</sup>H NMR spectra of product 11



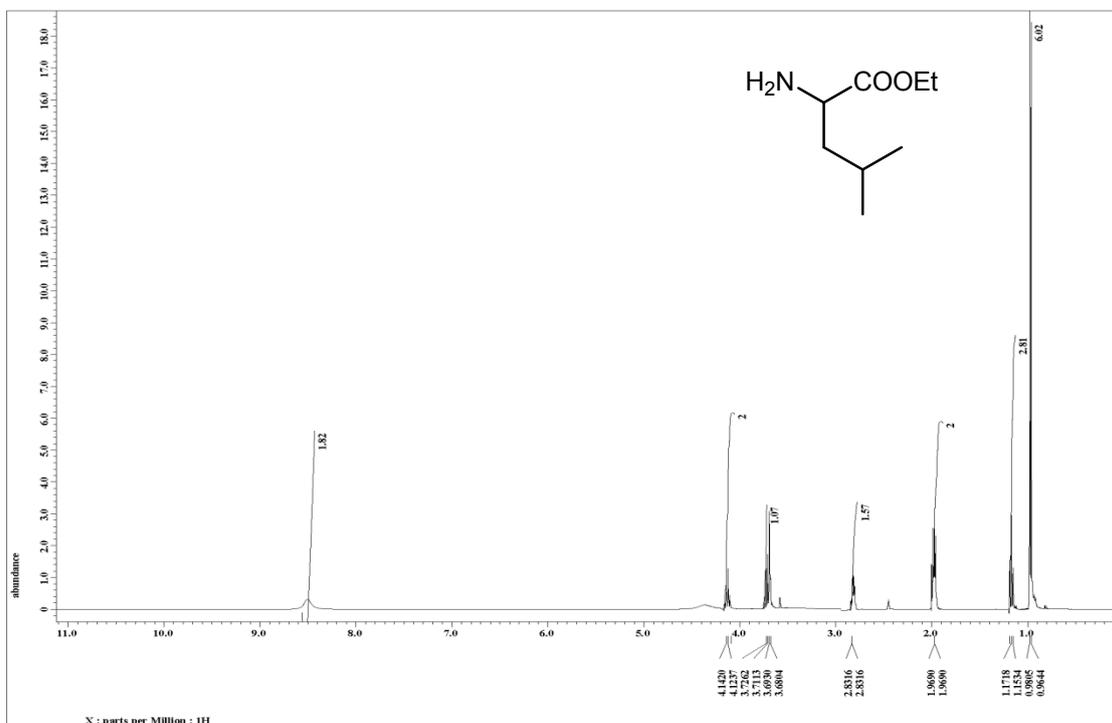
### <sup>13</sup>C NMR spectra of product 11



### <sup>13</sup>C NMR spectra of product 12

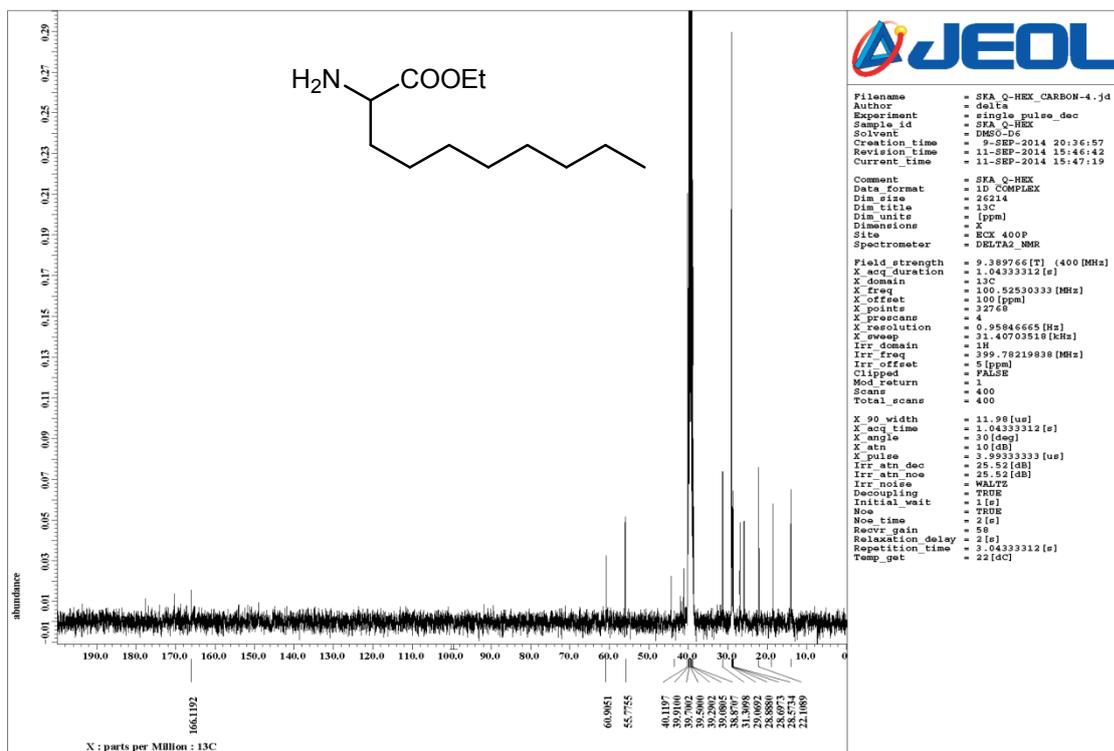


### <sup>1</sup>H NMR spectra of product 13





# <sup>13</sup>C NMR spectra of product 14



HPLC traces:

HPLC chromatogram of racemic product of table 1.

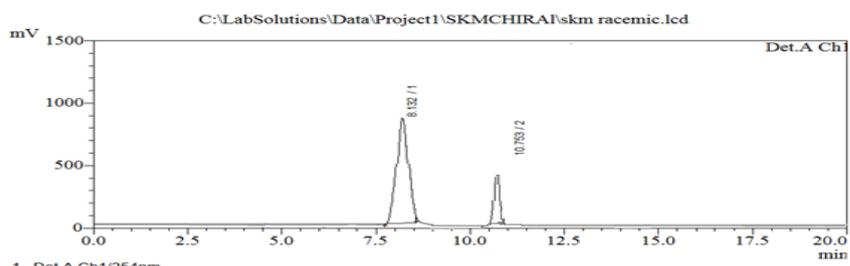
Table 1, Entry 3

1/1/2007 04

==== Shimadzu LCsolution Analysis Report ====

Acquired by : C:\LabSolutions\Data\Project1\SKMCHIRAL\skm racemic.lcd  
 Sample Name : SKMCHIRAL  
 Sample ID : P  
 Injection Volume : 50 uL  
 Data File Name : skm racemic.lcd  
 Method File Name : 20-8.lcm  
 Report File Name : Default.lcr  
 Data Acquired : 1/1/2007 5:34:28 AM  
 Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Acquisition Time\$Report Name\$

<Chromatogram>



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	8.132	33059985	1435072	73.532	64.330	1
2	10.753	11900025	794838	26.468	35.670	2
Total		44960010	2229910	100.000	100.000	

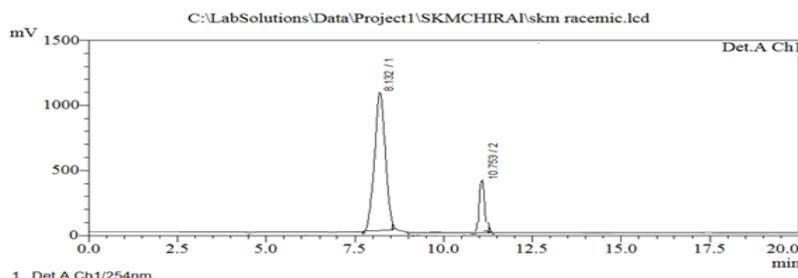
Table 1, Entry 6:

1/1/2007 04:49:24 1 / 1

==== Shimadzu LCsolution Analysis Report ====

Acquired by : C:\LabSolutions\Data\Project1\SKMCHIRAL\skm racemic.lcd  
 Sample Name : SKMCHIRAL  
 Sample ID : P0  
 Injection Volume : 50 uL  
 Data File Name : skm racemic.lcd  
 Method File Name : 20-8.lcm  
 Report File Name : Default.lcr  
 Data Acquired : 1/1/2007 6:20:00 AM  
 Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Acquisition Time\$Report Name\$

<Chromatogram>



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	8.132	35972494	1663877	80.010	70.549	1
2	10.753	9008227	477586	19.990	30.451	2
Total		44980721	2141463	100.000	100.000	

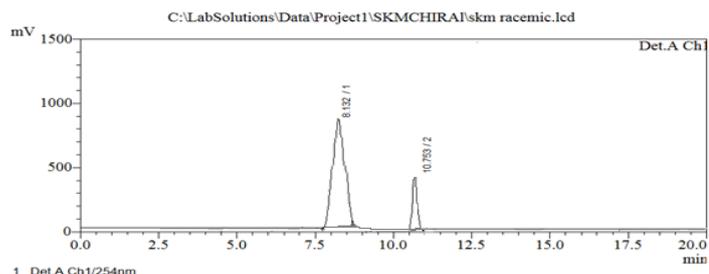
### Table 1, Entry 9:

1/1/2007 04

#### ==== Shimadzu LCsolution Analysis Report ====

Acquired by : C:\LabSolutions\Data\Project1\SKMCHIRAI\skm racemic.lcd  
 Sample Name : SKMCHIRAL  
 Sample ID : P1  
 Injection Volume : 50 uL  
 Data File Name : skm racemic.lcd 83  
 Method File Name : 20-8.lcm  
 Report File Name : Default.lcr  
 Data Acquired : 1/1/2007 5:54:20 AM  
 Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Acquisition Time\$Report Name\$

#### <Chromatogram>



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	8.132	38223641	1466955	85.330	65.000	1
2	10.753	3400007	604040	14.670	35.000	2
Total		41623648	2070995	100.000	100.000	

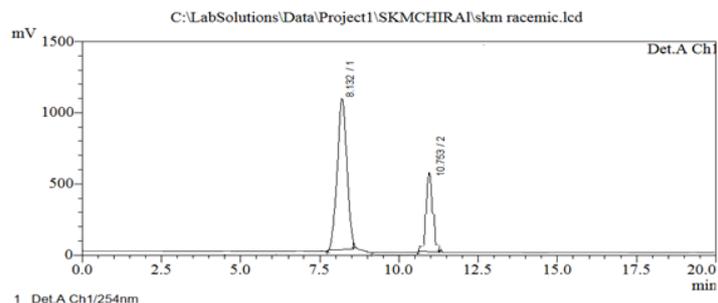
### Table 1, Entry 13:

1/1/2007 04:49:24 1 / 1

#### ==== Shimadzu LCsolution Analysis Report ====

Acquired by : C:\LabSolutions\Data\Project1\SKMCHIRAI\skm racemic.lcd  
 Sample Name : SKMCHIRAL  
 Sample ID : P  
 Injection Volume : 50 uL  
 Data File Name : skm racemic.lcd  
 Method File Name : 20-8.lcm  
 Report File Name : Default.lcr  
 Data Acquired : 1/1/2007 5:34:28 AM  
 Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Acquisition Time\$Report Name\$

#### <Chromatogram>



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	8.132	22495495	1260722	75.070	66.999	1
2	10.753	12475529	1170086	24.930	33.001	2
Total		34971024	2330808	100.000	100.000	

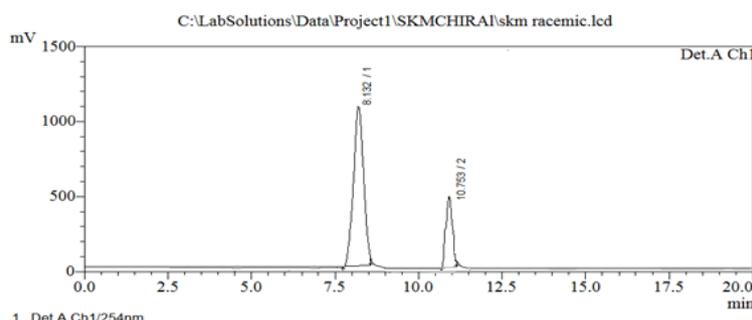
### Table 1, Entry 15:

1/1/2007 04:49:24 1 / 1

#### ==== Shimadzu LCsolution Analysis Report ====

Acquired by : C:\LabSolutions\Data\Project1\SKMCHIRAL\skm racemic.lcd  
 Sample Name : SKMCHIRAL  
 Sample ID : P5  
 Injection Volume : 50 uL  
 Data File Name : skm racemic.lcd  
 Method File Name : 20-8.lcm  
 Report File Name : Default.lcr  
 Data Acquired : 1/1/2007 7:04:18 AM  
 Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Acquisition Time\$Report Name\$

#### <Chromatogram>



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	8.132	39328603	1459284	69.800	66.200	1
2	10.753	13760527	693731	30.200	33.800	2
Total		43089130	2153015	100.000	100.000	

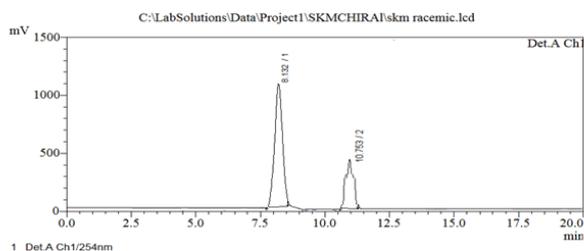
### Table 1, Entry 18:

1/1/2007 04:49:24 1 / 1

#### ==== Shimadzu LCsolution Analysis Report ====

Acquired by : C:\LabSolutions\Data\Project1\SKMCHIRAL\skm racemic.lcd  
 Sample Name : SKMCHIRAL  
 Sample ID : P4  
 Injection Volume : 50 uL  
 Data File Name : skm racemic.lcd  
 Method File Name : 20-8.lcm  
 Report File Name : Default.lcr  
 Data Acquired : 1/1/2007 8:34:25 AM  
 Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Acquisition Time\$Report Name\$

#### <Chromatogram>



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	8.132	22484496	1260272	75.720	75.559	1
2	10.753	12475528	570047	24.280	24.441	2
Total		4960024	2830319	100.000	100.000	

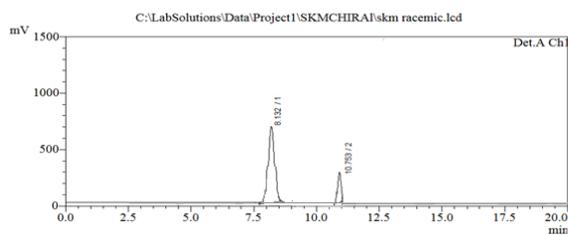
# Table 1, Entry 19:

1/1/2007 04:49:24 1 / 1

## ==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\SKMCHIRAL\skm racemic.lcd  
 Acquired by :  
 Sample Name : SKMCHIRAL  
 Sample ID : PS  
 Injection Volume : 50 uL  
 Data File Name : skm racemic.lcd  
 Method File Name : 20-8.lcm  
 Report File Name : Default.lcr  
 Data Acquired : 1/1/2007 16:34:18 AM  
 Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Acquisition Time\$Report Name\$

### <Chromatogram>



PeakTable						
Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	8.132	31028000	1437492	69.000	66.100	1
2	10.753	13760130	638533	31.000	33.900	2
Total		44788130	2076025	100.000	100.000	

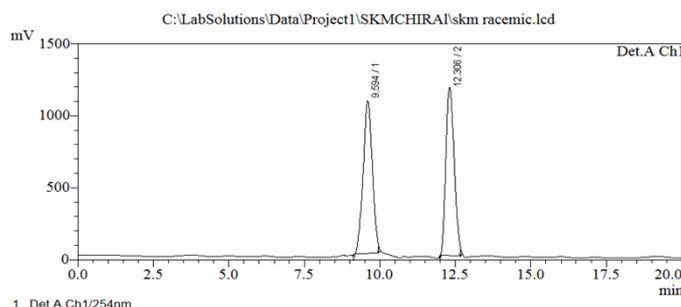
# HPLC chromatogram of product 5 (Racemic) without catalyst

1/1/2007 04:49:24 1 / 1

## ==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\SKMCHIRAL\skm racemic.lcd  
 Acquired by :  
 Sample Name : SKMCHIRAL  
 Sample ID : P  
 Injection Volume : 50 uL  
 Data File Name : skm racemic.lcd  
 Method File Name : 20-8.lcm  
 Report File Name : Default.lcr  
 Data Acquired : 1/1/2007 5:34:28 AM  
 Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Acquisition Time\$Report Name\$

### <Chromatogram>



PeakTable						
Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	9.594	22484495	1060722	50.010	47.349	1
2	12.306	22475528	1170086	49.990	52.451	2
Total		44960024	2230808	100.000	100.000	

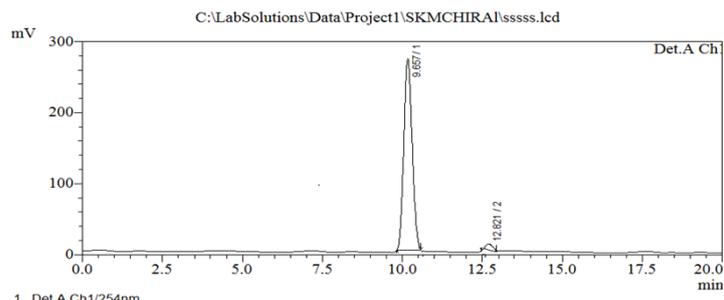
# HPLC chromatogram of product 5 using catalyst sT1

1/1/2007 04:39:20 1 / 1

## ==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\SKMCHIRAI\sssss.lcd  
 Acquired by :  
 Sample Name : SKMCHIRAL  
 Sample ID : P  
 Injection Volume : 50 uL  
 Data File Name : ssss.lcd  
 Method File Name : 20-8.lcm  
 Report File Name : Default.lcr  
 Data Acquired : 1/1/2007 3:49:44 AM  
 Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Acquisition Time\$Report Name\$

### <Chromatogram>



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	9.657	4872667	269331	97.636	97.002	1
2	12.821	117980	8325	2.364	2.998	2
Total		4990647	277656	100.000	100.000	

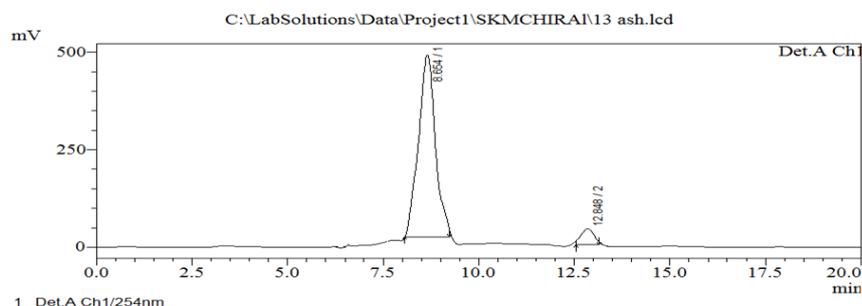
# HPLC chromatogram of product 6 using catalyst sT1

1/1/2007 05:01:39 1 / 1

## ==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\SKMCHIRAI\13 ash.lcd  
 Acquired by :  
 Sample Name : SKMCHIRAL  
 Sample ID : P  
 Injection Volume : 50 uL  
 Data File Name : 13 ash.lcd  
 Method File Name : 20-8.lcm  
 Report File Name : Default.lcr  
 Data Acquired : 1/1/2007 7:35:13 AM  
 Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Acquisition Time\$Report Name\$

### <Chromatogram>



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	8.654	14367132	466976	93.706	91.908	1
2	12.848	965083	41114	6.294	8.092	2
Total		15332215	508090	100.000	100.000	

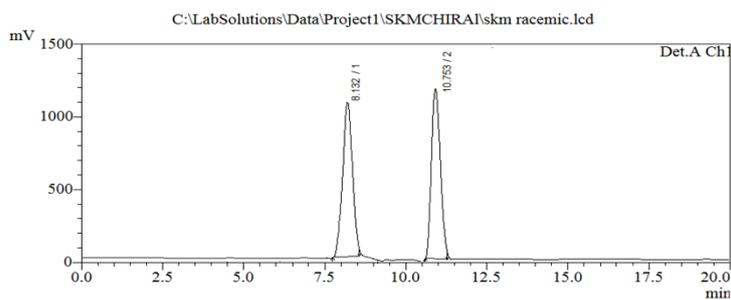
# HPLC chromatogram of Compound 7 racemic mixture without catalyst

1/1/2007 04:49:24 1 / 1

## ==== Shimadzu LCsolution Analysis Report ====

Acquired by : C:\LabSolutions\Data\Project1\SKMCHIRAL\skm racemic.lcd  
Sample Name : SKMCHIRAL  
Sample ID : P  
Injection Volume : 50 uL  
Data File Name : skm racemic.lcd  
Method File Name : 20-8.lcm  
Report File Name : Default.lcr  
Data Acquired : 1/1/2007 5:34:28 AM  
Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Acquisition Time\$Report Name\$

### <Chromatogram>



PeakTable

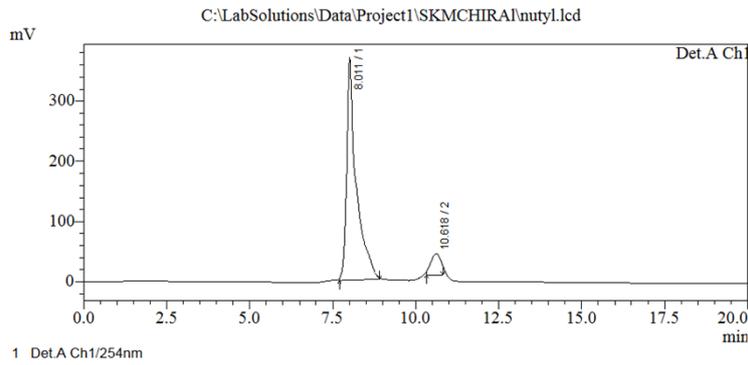
Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	8.132	22484495	1060722	50.010	47.549	1
2	10.753	22475528	1170086	49.990	52.451	2
Total		44960024	2230808	100.000	100.000	

# HPLC chromatogram of compound 7 using catalyst sT1

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\SKMCHIRAL\nutyl.lcd  
 Acquired by :  
 Sample Name : SKMCHIRAL  
 Sample ID : P  
 Injection Volume : 50 uL  
 Data File Name : nutyl.lcd  
 Method File Name : 1.lcm  
 Report File Name : Default.lcr  
 Data Acquired : 1/4/2007 4:20:48 PM  
 Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Acquisition Time\$Report Name\$

<Chromatogram>



PeakTable

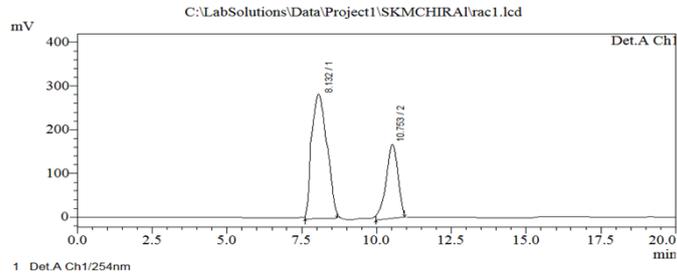
Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	8.011	7399281	369679	90.861	91.206	1
2	10.618	744269	35642	9.139	8.794	2
Total		8143551	405321	100.000	100.000	

HPLC chromatogram of Compound 7 using catalyst sT2

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\SKMCHIRAL\rac1.lcd  
 Acquired by :  
 Sample Name : SKMCHIRAL  
 Sample ID : P  
 Injection Volume : 50 uL  
 Data File Name : rac1.lcd  
 Method File Name : 1.lcm  
 Report File Name : Default.lcr  
 Data Acquired : 1/2/2007 3:11:43 AM  
 Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Acquisition Time\$Report Name\$

<Chromatogram>



PeakTable

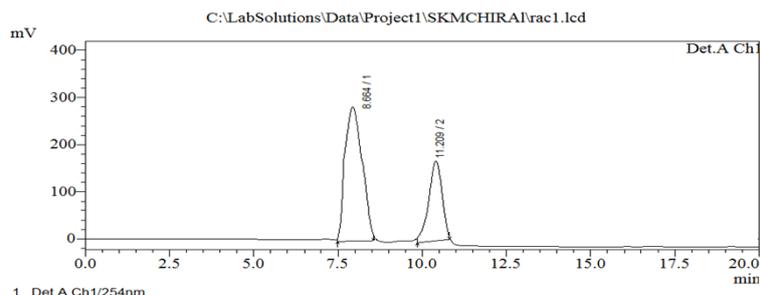
Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	8.132	10401109	381775	69.073	69.291	1
2	10.753	4656979	169201	30.927	30.709	2
Total		15058088	550977	100.000	100.000	

HPLC chromatogram of compound 7 using catalyst sT3

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\SKMCHIRAL\rac1.lcd  
 Acquired by :  
 Sample Name : SKMCHIRAL  
 Sample ID : P  
 Injection Volume : 50 uL  
 Data File Name : rac1.lcd  
 Method File Name : 1.lcm  
 Report File Name : Default.lcr  
 Data Acquired : 1/2/2007 3:11:43 AM  
 Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Report Name\$

<Chromatogram>



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	8.664	10401109	381775	69.073	69.291	1
2	11.209	4656979	169201	30.927	30.709	2
Total		15058088	550977	100.000	100.000	

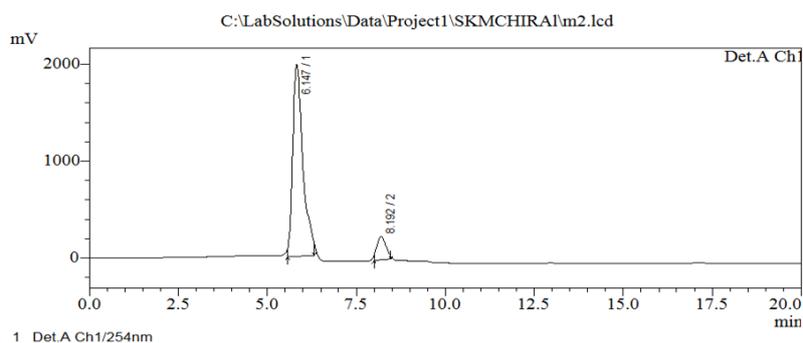
HPLC chromatogram of compound 8 using catalyst sT1

1/1/2007 01:04:33 1 / 1

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\SKMCHIRAL\m2.lcd  
 Acquired by :  
 Sample Name : SKMCHIRAL  
 Sample ID : P  
 Injection Volume : 50 uL  
 Data File Name : m2.lcd  
 Method File Name : 20-8.lcm  
 Report File Name : Default.lcr  
 Data Acquired : 1/1/2007 12:34:31 AM  
 Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Acquisition Time\$Report Name\$

<Chromatogram>



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	6.147	39363408	1981418	90.363	89.241	1
2	8.192	4198039	238882	9.637	10.759	2
Total		43561447	2220300	100.000	100.000	

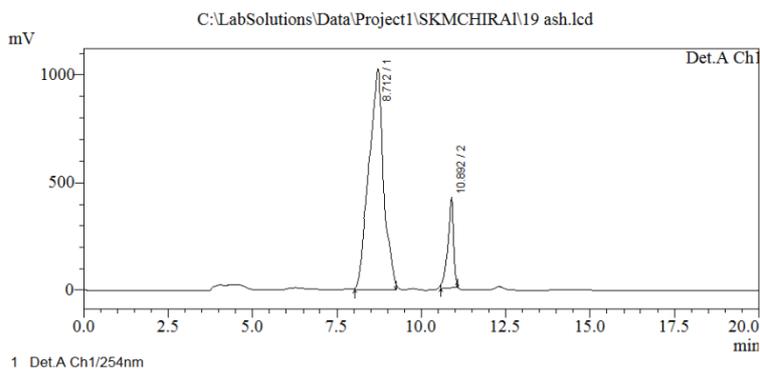
## HPLC chromatogram of compound 9 using catalyst sT1

1/1/2007 07:40:29 1 / 1

### ==== Shimadzu LCsolution Analysis Report ====

Acquired by :  
 Sample Name : SKMCHIRAL  
 Sample ID : P  
 Injection Volume : 50 uL  
 Data File Name : 19 ash.lcd  
 Method File Name : 20-8.lcm  
 Report File Name : Default.lcr  
 Data Acquired : 1/1/2007 7:15:24 AM  
 Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Acquisition Time\$Report Name\$

#### <Chromatogram>



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	8.712	32618967	1058107	87.033	71.634	1
2	10.892	4859892	418985	12.967	28.366	2
Total		37478858	1477091	100.000	100.000	

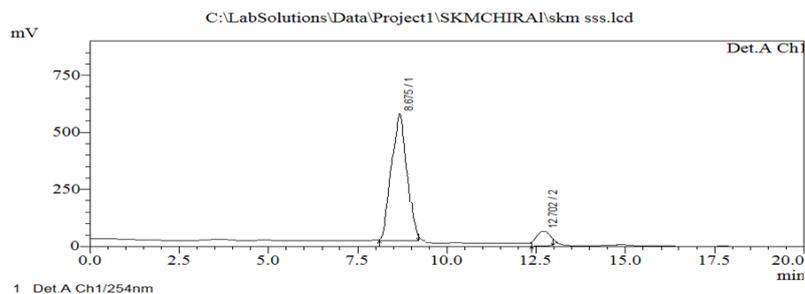
## HPLC chromatogram of compound 10 using catalyst sT1

1/1/2007 05:43:23 1 / 1

### ==== Shimadzu LCsolution Analysis Report ====

Acquired by :  
 Sample Name : SKMCHIRAL  
 Sample ID : P  
 Injection Volume : 50 uL  
 Data File Name : skm sss.lcd  
 Method File Name : 20-8.lcm  
 Report File Name : Default.lcr  
 Data Acquired : 1/1/2007 5:13:10 AM  
 Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Acquisition Time\$Report Name\$

#### <Chromatogram>



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	8.675	20466191	578126	92.316	89.926	1
2	12.702	1703560	64763	7.684	10.074	2
Total		22169751	642888	100.000	100.000	

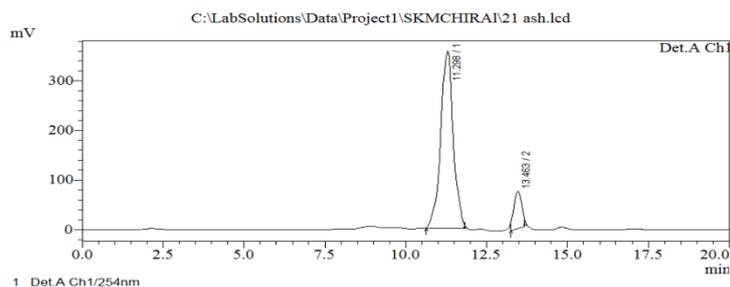
## HPLC chromatogram of compound 11 using catalyst sT1

1/1/2007 07:58:42 1 / 1

### ==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\SKMCHIRAL\21 ash.lcd  
 Acquired by :  
 Sample Name : SKMCHIRAL  
 Sample ID : P  
 Injection Volume : 50 uL  
 Data File Name : 21 ash.lcd  
 Method File Name : 20-8.lcm  
 Report File Name : Default.lcr  
 Data Acquired : 1/1/2007 7:35:47 AM  
 Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Acquisition Time\$Report Name\$

#### <Chromatogram>



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	11.298	9735696	357902	88.429	82.649	1
2	13.463	1273914	75135	11.571	17.351	2
Total		11009610	433037	100.000	100.000	

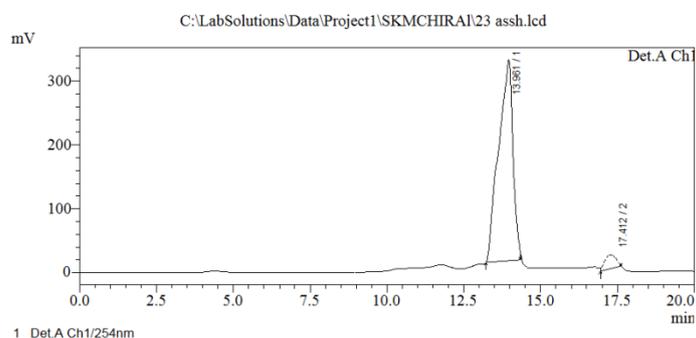
## HPLC chromatogram of compound 12 using catalyst sT1

1/1/2007 08:22:07 1 / 1

### ==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\SKMCHIRAL\23 assh.lcd  
 Acquired by :  
 Sample Name : SKMCHIRAL  
 Sample ID : P  
 Injection Volume : 50 uL  
 Data File Name : 23 assh.lcd  
 Method File Name : 20-8.lcm  
 Report File Name : Default.lcr  
 Data Acquired : 1/1/2007 7:56:18 AM  
 Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Acquisition Time\$Report Name\$

#### <Chromatogram>



PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	13.961	10197610	315112	93.797	92.467	1
2	17.412	674388	25672	6.203	7.533	2
Total		10871998	340784	100.000	100.000	

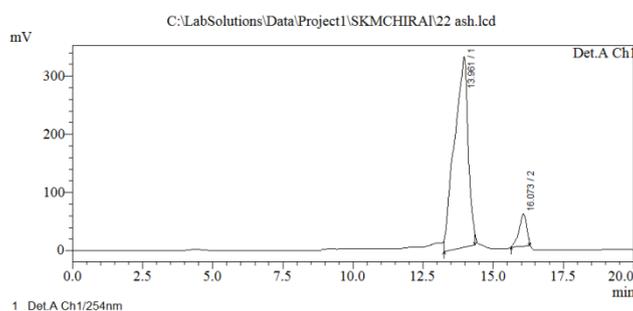
## HPLC chromatogram of compound 13 using catalyst sT1

1/1/2007 08:18:31 1 / 1

### ==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\SKMCHIRAI\22 ash.lcd  
 Acquired by :  
 Sample Name : SKMCHIRAL  
 Sample ID : P  
 Injection Volume : 50 uL  
 Data File Name : 22 ash.lcd  
 Method File Name : 20-8.lcm  
 Report File Name : Default.lcr  
 Data Acquired : 1/1/2007 7:56:18 AM  
 Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Acquisition Time\$Report Name\$

#### <Chromatogram>



1 Det.A Ch1/254nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	13.961	11099713	327621	91.434	85.552	1
2	16.073	1039929	55327	8.566	14.448	2
Total		12139642	382949	100.000	100.000	

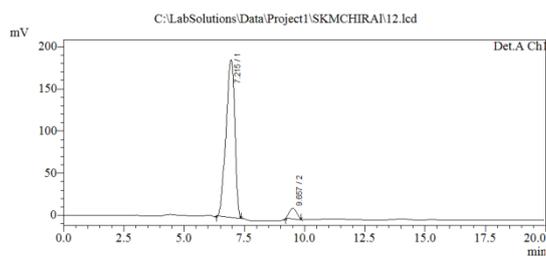
## HPLC chromatogram of compound 14 using catalyst sT1

1/1/2007 00:03:50 1 / 1

### ==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\Project1\SKMCHIRAI\12.lcd  
 Acquired by :  
 Sample Name : SKMCHIRAL  
 Sample ID : P  
 Injection Volume : 50 uL  
 Data File Name : 12.lcd  
 Method File Name : pk1.lcm  
 Report File Name : Default.lcr  
 Data Acquired : 1/4/2007 11:16:42 AM  
 Data Processed : Report Name\$Acquisition Time\$Acquisition Time\$Acquisition Time\$Report Name\$

#### <Chromatogram>



1 Det.A Ch1/254nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %	Name
1	7.215	4753648	186770	94.727	93.823	1
2	9.657	264615	12296	5.273	6.177	2
Total		5018263	199066	100.000	100.000	