

## Supplementary Information

### **D-Fructose derived $\beta$ -amino alcohol-catalyzed direct asymmetric aldol reaction in the presence of *p*-nitrophenol**

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## Supporting information

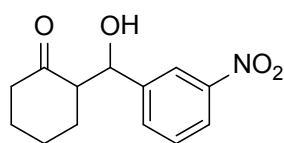
**Table 1: HPLC data for aldol products**

S.No	Aldol Product	<sup>1</sup> H NMR (CDCl <sub>3</sub> -CH <sub>2</sub> OH, δ)		HPLC data							
		syn	anti	Column	λ (nm)	Flow rate	Solvent IPA:Hex	Syn product		Anti product	
								<i>t</i> R (min)	<i>t</i> R (min)	<i>t</i> R (min)	<i>t</i> R (min)
1.	<b>6a</b>	5.49	4.83	Chiralpak AD-3	254	1mL/min	90:10	10.80	11.75	13.14	16.46
2.	<b>6b</b>	5.97	5.45	Chiralpak AD-3	254	1mL/min	95:5	7.78	11.24	13.52	14.56
3.	<b>6c</b>	5.49	4.90	Chiralpak AD-3	254	1mL/min	95:5	21.24	28.21	30.97	41.99
4.	<b>6d</b>	5.85	5.37	Chiralpak AD-3	254	1mL/min	95:5	16.16	17.91	21.23	23.06
5.	<b>6e</b>	5.34	4.77	Chiralpak AD-3	254	1mL/min	95:5	19.77	22.03	24.95	38.02
6.	<b>6f</b>	5.43	4.85	Chiralpak AD-3	254	1mL/min	95:5	17.85	24.50	30.38	31.23
7.	<b>6g</b>	5.30	4.85	Chiralpak AD-3	254	1mL/min	95:5	14.87	17.04	23.21	24.66
8.	<b>6h</b>	5.30	4.68	Chiralpak AD-3	220	1mL/min	90:10	10.36	11.88	15.77	17.37
9.	<b>6i</b>	5.36	4.68	Chiralpak AD-3	220	1mL/min	90:10	11.24	13.10	17.26	19.95
10.	<b>6j</b>	5.35	4.77	Chiralpak AD-3	210	1mL/min	90:10	10.87	12.09	16.80	17.74
11.	<b>6k</b>	5.35	4.74	Chiralpak AD-3	220	1mL/min	90:10	11.76	13.93	18.61	21.75
12.	<b>6l</b>	5.33	4.75	Chiralpak AD-3	210	1mL/min	90:10	10.90	12.49	16.51	18.28
13.	<b>6m</b>	5.41	4.85	Chiralpak IA-3	210	1.5mL/min	90:10 <sup>a</sup>	7.76	11.23	13.52	14.56
14.	<b>6n</b>	5.37	4.76	Chiralpak AD-3	220	1mL/min	90:10	8.08	9.08	13.34	14.56

<sup>a</sup> hextane/EtOH=90:10

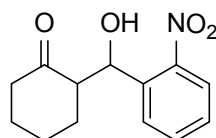
### NMR data for aldol products 6a-n

**2-[Hydroxy-(3-nitro-phenyl)-methyl]-cyclohexanone (6a)**<sup>[1]</sup>: *syn*-diastereomer, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 1.54-2.17 (m, 6H), 2.35-2.53 (m, 2H), 2.61-2.2.70 (m, 1H), 3.2(d, *J* = 4 Hz, 1H), 5.49 (s, 1H), 7.52 (t, *J* = 8 Hz, 1H), 7.65 (d, *J* = 8 Hz, 1H), 8.12 (d, *J* = 8 Hz, 1H), 8.19 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 24.7, 25.9, 27.9, 42.6, 56.7, 69.9, 120.9, 122.1, 129.2, 131.9, 143.7, 148.3, 214.3; *anti*-diastereomer, [α]<sub>D</sub><sup>23</sup> + 23.4 (c 1, CDCl<sub>3</sub>; 87% ee) <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 1.47-2.09 (m, 6H), 2.25-2.36 (m, 1H), 2.38-2.61 (m, 2H), 4.05 (d, *J* = 4 Hz, 1H), 4.84-4.81 (dd, *J* = 4 Hz, 1H), 7.46 (t, *J* = 8 Hz, 1H), 7.60 (d, *J* = 8 Hz, 1H), 8.10 (d, *J* = 8 Hz, 1H), 8.15 (s, 1H); <sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub>) δ (ppm) 24.7, 27.6, 30.7, 42.7, 57.1, 74.1, 122.0, 122.9, 129.3, 133.2, 143.2, 148.3, 214.9.



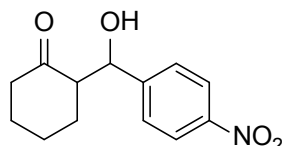
**6a**

**2-[Hydroxy-(2-nitro-phenyl)-methyl]-cyclohexanone (6b)**<sup>[1]</sup>: *syn*-diastereomer, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 1.48-1.88 (m, 5H), 2.07-2.14 (m, 1H), 2.38-2.48(m, 2H), 2.85-2.90 (m, 1H), 3.29 (br, 1H), 5.97 (s, 1H), 7.43 (t, *J* = 8 Hz, 1H), 7.65 (t, *J* = 8 Hz, 1H), 7.84 (d, *J* = 8 Hz, 1H), 8.0 (d, *J* = 8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 24.8, 28.0, 42.5, 54.8, 66.6, 124.7, 127.9, 129.6, 133.2, 137.0, 147.1, 214.1; *anti*-diastereomer, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 1.59-2.49 (m, 8H), 2.68-2.81 (m, 1H), 4.2 (brs, 1H), 5.45 (d, *J* = 8 Hz, 1H), 7.43 (t, *J* = 8 Hz, 1H), 7.64 (t, *J* = 8.4 Hz, 1H), 7.77(d, *J* = 8 Hz, 1H), 7.85 (d, *J* = 8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 25.0, 27.8, 31.1, 42.8, 57.3, 69.8, 124.1, 128.4, 129.0, 133.1, 136.6, 148.7, 215.0.



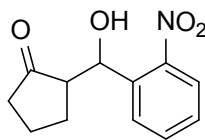
**6b**

**2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclohexanone (6c)** <sup>[1]</sup>: *syn*-diastereomer, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 1.57-1.77 (m, 4H), 1.81-1.90 (m, 1H), 2.08-2.16 (m, 1H), 2.34-2.45 (m, 1H), 2.59-2.67 (m, 1H), 3.18 (d, *J* = 4 Hz, 1H), 5.49 (s, 1H), 7.49 (d, *J* = 8 Hz, 2H), 8.21 (d, *J* = 8 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 24.8, 25.9, 27.9, 42.6, 56.8, 70.1, 123.5, 126.6, 147.0, 149.0, 214.1; *anti*-diastereomer, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 1.52-1.74 (m, 4H), 1.79-1.87 (m, 1H), 2.07-2.17 (m, 1H), 2.31-2.42 (m, 1H), 2.54-2.64 (m, 1H), 4.08 (d, *J* = 4 Hz, 1H), 4.90 (dd, *J* = 8 Hz, 1H), 7.51 (d, *J* = 8 Hz, 2H), 8.21 (d, *J* = 8 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 24.7, 27.6, 30.7, 42.7, 57.2, 74.0, 123.6, 127.9, 147.6, 148.33, 214.8.



**6c**

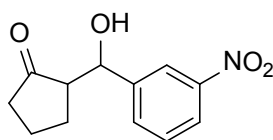
**2-[Hydroxy-(2-nitro-phenyl)-methyl]-cyclopentanone (6d)** <sup>[2]</sup> (**mix**, *syn/anti* = 1:0.36 ): *anti*-diastereomer, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 1.68-1.74 (m, 2H), 1.94-2.15 (m, 4H), 2.36-2.50 (m, 1H), 2.65 (m, 1H), 5.85 (d, *J* = 4 Hz, 1H), 7.37 (t, *J* = 8 Hz, 1H), 7.69 (m, 1H), 7.83 (d, *J* = 8 Hz, 1H), 7.93 (d, *J* = 8 Hz, 1H); *syn*-diastereomer, 4.41 (brs, 0.36H), 5.37 (d, *J* = 8 Hz, 0.36H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 20.2, 20.5, 23.0, 26.6, 38.6, 54.8, 55.5, 66.7, 69.1, 124.0, 124.6, 128.1, 128.6, 129.0, 133.2, 133.4, 136.3, 138.5, 147.0, 148.5, 218.8, 222.1.



**6d**

**2-[Hydroxy-(3-nitro-phenyl)-methyl]-cyclopentanone (6e)** <sup>[3]</sup> (mix, *syn/anti* = 1:0.52 ):

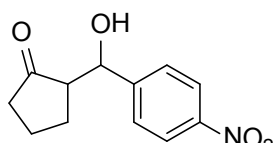
*anti*-diastereomer, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 1.55-1.75 (m, 2H), 1.85-2.00 (m, 2H), 2.02-2.15 (m, 1H), 2.23-2.47 (m, 1H), 4.77 (d, *J* = 8 Hz, 0.41H), 7.52 (m, 2H), 8.02 (m, 2H); *anti*-diastereomer, 3.23 (s, 0.72H), 5.34 (s, 0.78H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 20.3, 22.3, 26.8, 29.6, 38.6, 39.0, 55.0, 56.1, 70.1, 74.3, 120.5, 121.6, 122.2, 123.0, 129.3, 129.5, 131.7, 132.7, 143.6, 145.2, 148.3, 220.0, 222.5.



**6e**

**2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclopentanone (6f)** <sup>[3]</sup> (mix, *syn/anti* = 1:0.15 ):

*anti*-diastereomer, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 1.63-1.83 (m, 2H), 1.88-2.09 (m, 2H), 2.09-2.34 (m, 1H), 2.34-2.55 (m, 2H), 4.78 (s, 0.13H), 4.85 (d, *J* = 8 Hz, 0.15H), 7.54 (d, *J* = 8 Hz, 2H), 8.22 (d, *J* = 8 Hz, 2H); *syn*-diastereomer, 2.79 (s, 0.75H), 5.43 (s, 0.87H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 20.3, 22.3, 26.8, 38.6, 39.0, 55.1, 56.1, 70.4, 74.4, 123.6, 123.7, 126.4, 127.4, 147.1, 148.6, 150.4, 219.8, 222.3.

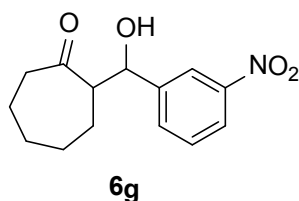


**6f**

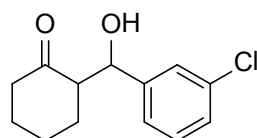
**2-[Hydroxy-(3-nitro-phenyl)-methyl]-cycloheptanone (6g)** <sup>[3]</sup>: *syn*-diastereomer, <sup>1</sup>H NMR

(400 MHz, CDCl<sub>3</sub>) δ (ppm) 1.24-1.32 (m, 2H), 1.41-1.54 (m, 1H), 1.59-1.74 (m, 2H),

1.77-1.95 (m, 3H), 2.42-2.55(m, 1H), 2.58-2.69 (m, 1H), 2.83-2.92 (m, 1H), 3.27 (br, 1H), 5.30 (s, 1H), 7.53( t,  $J = 8$  Hz, 1H), 7.70 (d,  $J = 8$  Hz, 1H), 8.12(d,  $J = 8$  Hz, 1H), 8.22 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 23.5, 23.9, 28.9, 29.1, 43.9, 57.1, 72.2, 121.0, 122.2, 129.2, 132.1, 144.3, 148.3, 217.6; *anti*-diastereomer,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 1.27-1.39 (m, 2H), 1.47-1.57 (m, 1H), 1.59-1.75 (m, 2H), 1.76-1.82 (m, 2H), 2.18-2.59(m, 2H), 2.80-3.01 (m, 1H), 3.63 (brs, 1H), 4.85 (d,  $J = 8$  Hz, 1H), 7.63 (d,  $J = 8$  Hz, 1H), 8.08 (d,  $J = 8$  Hz, 1H), 8.16 (t, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 23.5, 28.2, 28.6, 44.1, 57.9, 74.7, 121.9, 122.8, 129.4, 133.1, 144.1, 148.3, 217.0.



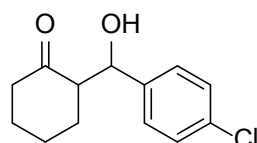
**2-[Hydroxy-(3-chloro-phenyl)-methyl]-cyclohexanone (6h)** <sup>[2]</sup>: *syn*-diastereomer,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 1.48-1.75 (m, 5H), 1.81-1.90 (m, 1H), 2.04-2.14 (m, 1H), 2.30-2.50 (m, 1H), 2.52-2.62 (m, 1H), 3.09 (d,  $J = 4$  Hz, 1H), 5.36 (s, 1H), 7.13-7.35 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 24.8, 25.9, 27.9, 42.6, 57.0, 70.1, 123.8, 126.0, 127.1, 129.4, 134.2, 143.6, 214.5; *anti*-diastereomer,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 1.23-1.73 (m, 5H), 1.74-1.85 (m, 1H), 2.05-2.15 (m, 1H), 2.30-2.40 (m, 1H), 2.44-2.52 (m, 1H), 2.53-2.62 (m, 1H), 3.99 (s, 1H), 4.68 (d,  $J = 8$  Hz, 1H), 7.14-7.30 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 24.7, 27.7, 30.8, 42.7, 57.3, 74.3, 125.3, 127.1, 128.0, 129.6, 134.3, 143.1, 215.2.



**6h**

**2-[Hydroxy-(4-chloro-phenyl)-methyl]-cyclohexanone (6i)** <sup>[2]</sup> (**mix, *syn/anti* = 1:1.27**):

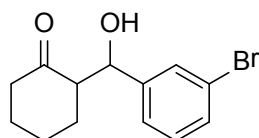
*anti*-diastereomer, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 1.46-1.62 (m, 2H), 1.62-1.74 (m, 2H), 1.75-1.89 (m, 1H), 2.03-2.14(m, 1H), 2.30-2.42 (m, 1H), 2.51-2.61 (m, 1H), 4.0(d, *J* = 4 Hz, 0.54H), 4.77 (dd, *J* = 4 Hz, 0.56H), 7.23-7.33 (m, 4H); *syn*-diastereomer, 3.08 (d, *J* = 4 Hz, 0.4H), 5.35 (s, 0.44H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 24.7, 24.8, 25.9, 27.7, 27.9, 30.7, 42.6, 57.0, 57.3, 70.1, 74.1, 127.2, 128.3, 128.5, 132.7, 133.5, 139.5, 139.9, 214.6, 215.3.



**6i**

**2-[Hydroxy-(3-bromo-phenyl)-methyl]-cyclohexanone (6j)** <sup>[2]</sup>: *syn*-diastereomer, <sup>1</sup>H NMR

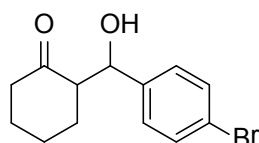
(400 MHz, CDCl<sub>3</sub>) δ (ppm) 1.51-1.75 (m, 4H), 1.80-1.90 (m, 1H), 2.04-2.14 (m, 1H), 2.32-2.49 (m, 1H), 2.52-2.64 (m, 1H), 3.10 (d, *J* = 4 Hz, 1H), 5.35 (s, 1H), 7.21 (m, 2H), 7.37 (m, 1H), 7.48 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 24.8, 25.9, 27.9, 42.6, 57.0, 70.0, 122.5, 124.4, 129.0, 129.8, 130.1, 143.9, 214.5; *anti*-diastereomer, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 1.24-1.36 (m, 1H), 1.52- 1.74 (m, 3H), 1.76-1.84 (m, 1H), 2.01-2.13 (m, 1H), 2.29-2.40 (m, 1H), 2.42-2.51 (m, 1H), 2.52-2.62 (m, 1H), 4.02 (s, 1H), 4.74 (d, *J* = 8 Hz, 1H), 7.22 (m, 2H), 7.42 (m, 1H), 7.49 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 24.8, 27.7, 30.8, 42.7, 57.3, 74.2, 122.6, 125.8, 129.9, 130.0, 143.3, 215.2.



**6j**

**2-[Hydroxy-(4-bromo-phenyl)-methyl]-cyclohexanone (6k)** <sup>[2]</sup> (mix, *syn/anti* = 1.26 :1 ):

*anti*-diastereomer, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 1.47-1.73 (m, 4H), 1.75-1.88 (m, 1H), 2.04-1.13 (m, 1H), 2.30-2.41 (m, 1H), 2.42-2.50 (m, 1H), 2.51-2.90 (m, 1H), 3.99 (s, 0.41H), 4.75 (dd, *J* = 8 Hz, 0.42H), 7.19 (m, 2H), 7.46 (m, 2H); *syn*-diastereomer, 3.08 (s, 0.53H), 5.33 (s, 0.56H); <sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub>) δ (ppm) 24.7, 24.8, 25.9, 27.7, 27.9, 30.7, 42.6, 57.0, 57.3, 70.1, 74.2, 120.8, 121.7, 127.5, 128.7, 131.2, 131.5, 140.0, 140.5, 214.6, 215.3.

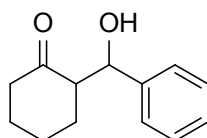


**6k**

**2-[Hydroxy-(4-flouro-phenyl)-methyl]-cyclohexanone (6l)** <sup>[4]</sup> (mix, *syn/anti* = 1.41 :1 ):

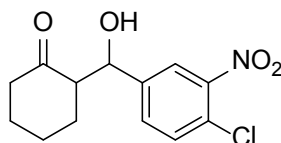
*anti*-diastereomer, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 1.52-1.89 (m, 5H), 2.04-2.14 (m, 1H), 2.29-2.49 (m, 2H), 2.52-2.62 (m, 1H), 4.0 (d, *J* = 4 Hz, 0.42H), 4.77 (d, *J* = 8 Hz, 0.41H), 7.02 (m, 2H), 7.29 (m, 2H); *syn*-diastereomer, 3.06 (d, *J* = 4 Hz, 0.53H), 5.36 (s, 0.59H); <sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub>) δ (ppm) 24.7, 24.8, 26.0, 27.7, 28.0, 30.8, 42.7, 57.2, 57.5, 70.2, 74.1, 115.1, 115.3, 127.4, 128.6, 136.7, 137.1, 160.7, 163.1, 214.8, 215.1.





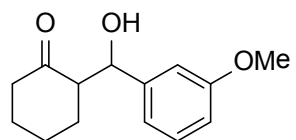
**6l**

**2-[Hydroxy-(4-chloro-3-nitro-phenyl)-methyl]-cyclohexanone (6m)** <sup>[5]</sup> (mix, *syn/anti* = **1.1:1**): *anti*-diastereomer, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 1.48-1.78 (m, 4H), 1.81-1.92 (m, 1H), 2.07-2.17 (m, 1H), 2.31-2.44 (m, 1H), 2.44-2.52 (m, 1H), 2.53-2.66 (m, 1H), 4.10 (d, *J* = 4 Hz, 0.45H), 4.85 (dd, *J* = 4Hz, 0.46H); *syn*-diastereomer, 3.23 (s, 0.48H), 5.41 (s, 0.51H); <sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub>) δ (ppm) 24.6, 24.7, 25.9, 27.5, 27.8, 30.6, 40.5, 40.6, 56.5, 57.0, 69.4, 73.4, 123.0, 124.0, 125.3, 126.1, 130.5, 131.5, 131.6, 131.7, 141.8, 142.4, 147.8, 213.9, 214.6.



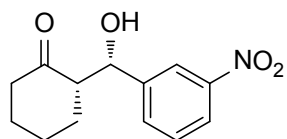
**6m**

**2-[Hydroxy-(3-methoxy-phenyl)-methyl]-cyclohexanone (6n)** <sup>[6]</sup>: *syn*-diastereomer, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 1.61-1.92 (m, 4H), 2.00-2.19 (m, 1H), 2.28- 2.51 (m, 1H), 2.53-2.71 (m, 1H), 3.01 (s, 1H), 3.81 (s, 3H), 5.37 (s, 1H), 6.83 (m, 3H), 7.25 (m, 1H); <sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub>) δ (ppm) 24.9, 26.0, 27.9, 42.7, 55.2, 57.2, 70.1, 111.5, 112.4, 118.0, 129.2, 143.2, 159.6, 214.8; *anti*-diastereomer, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 1.49-1.72 (m, 4H), 1.74- 1.84 (m, 1H), 2.03-2.13 (m, 1H), 2.31-2.40 (m, 1H), 2.44-2.51 (m, 1H), 2.55-2.65 (m, 1H), 3.81 (s, 3H), 3.93 (s, 3H), 4.76 (d, *J* = 8 Hz, 1H), 6.86 (m, 3H), 7.26 (m, 1H); <sup>13</sup>C NMR(100 MHz, CDCl<sub>3</sub>) δ (ppm) 24.7, 27.8, 30.9, 42.7, 55.2, 57.4, 74.7, 112.4, 113.4, 119.5, 129.3, 142.5, 159.7, 215.5.

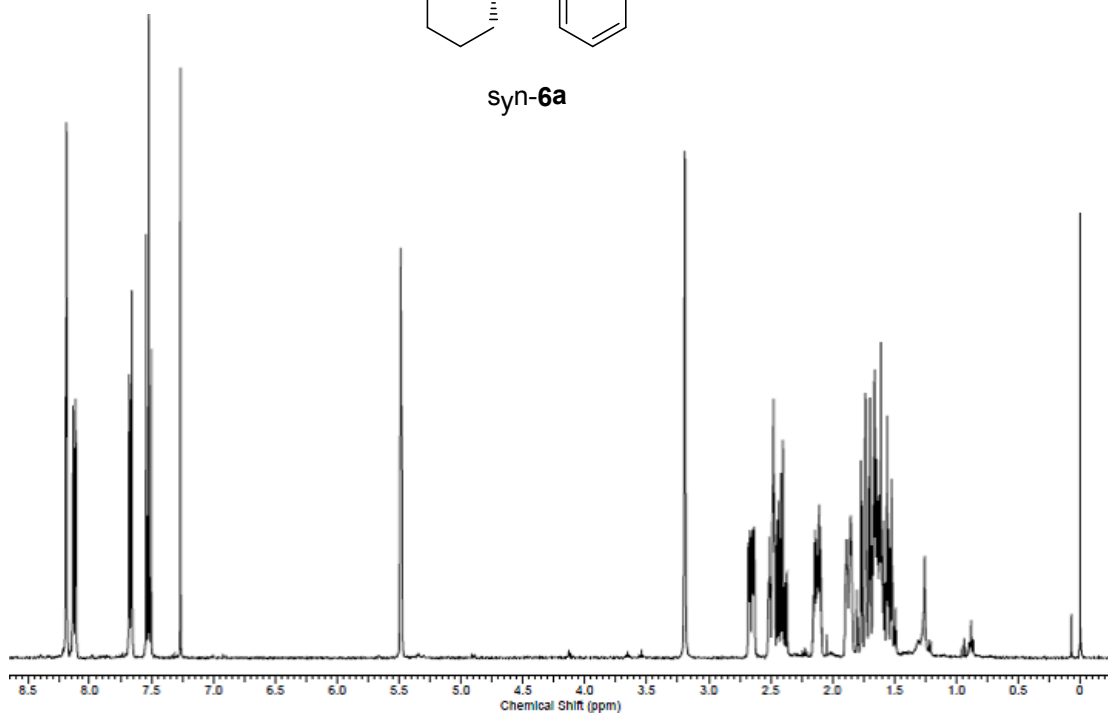


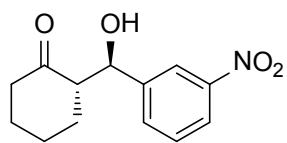
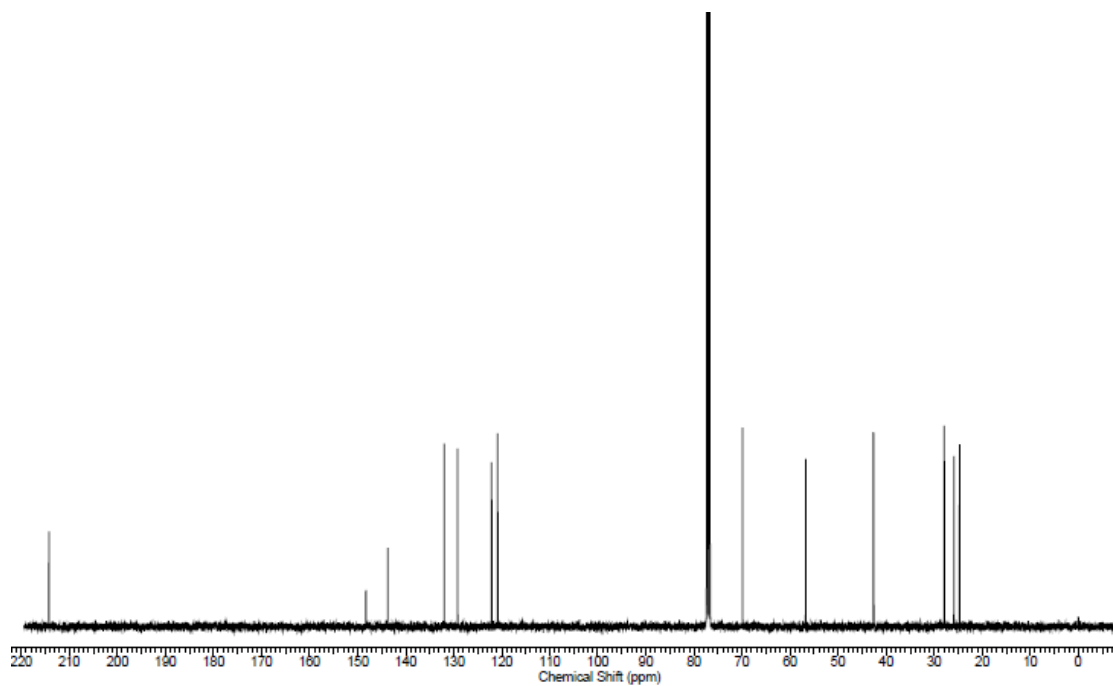
**6n**

### NMR spectra for aldol products 3a-n

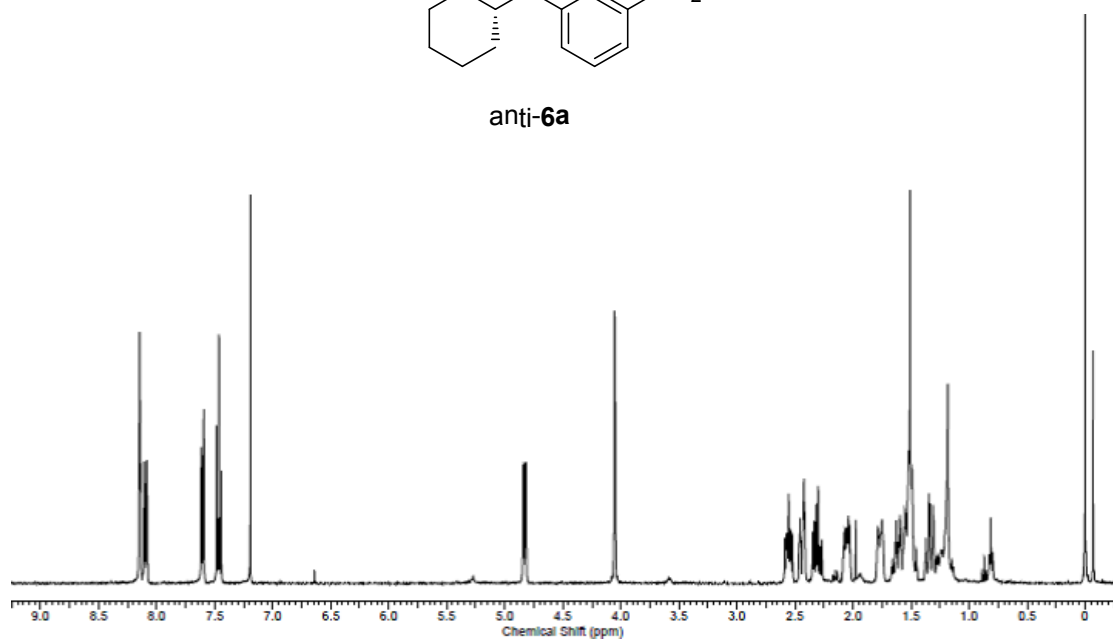


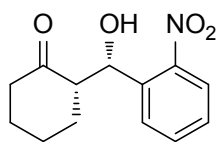
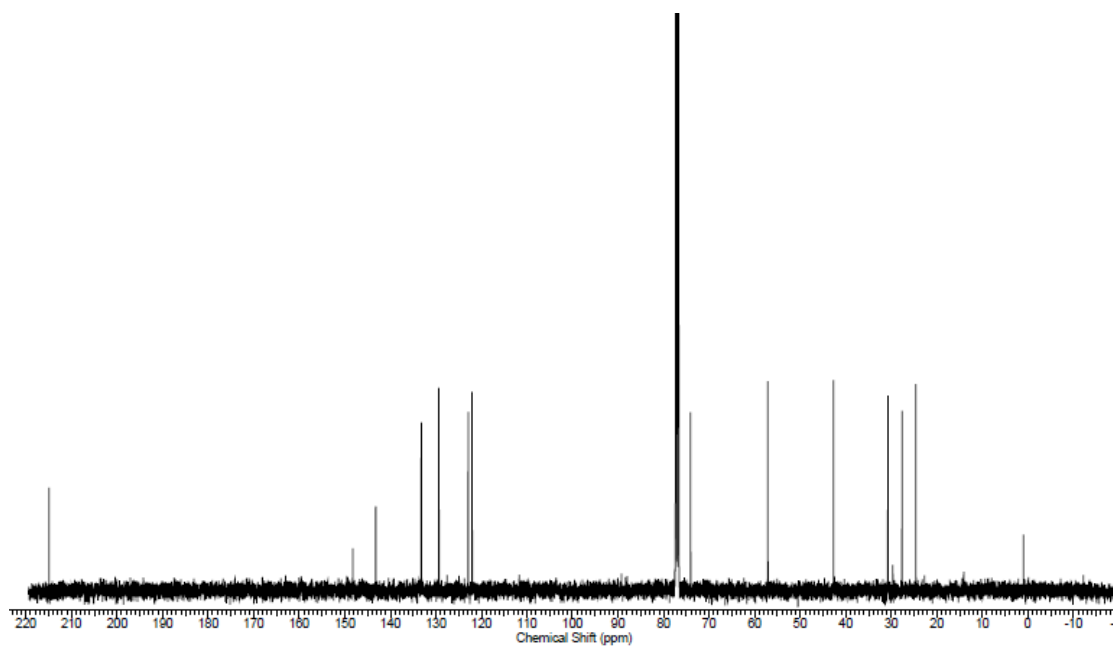
**syn-6a**



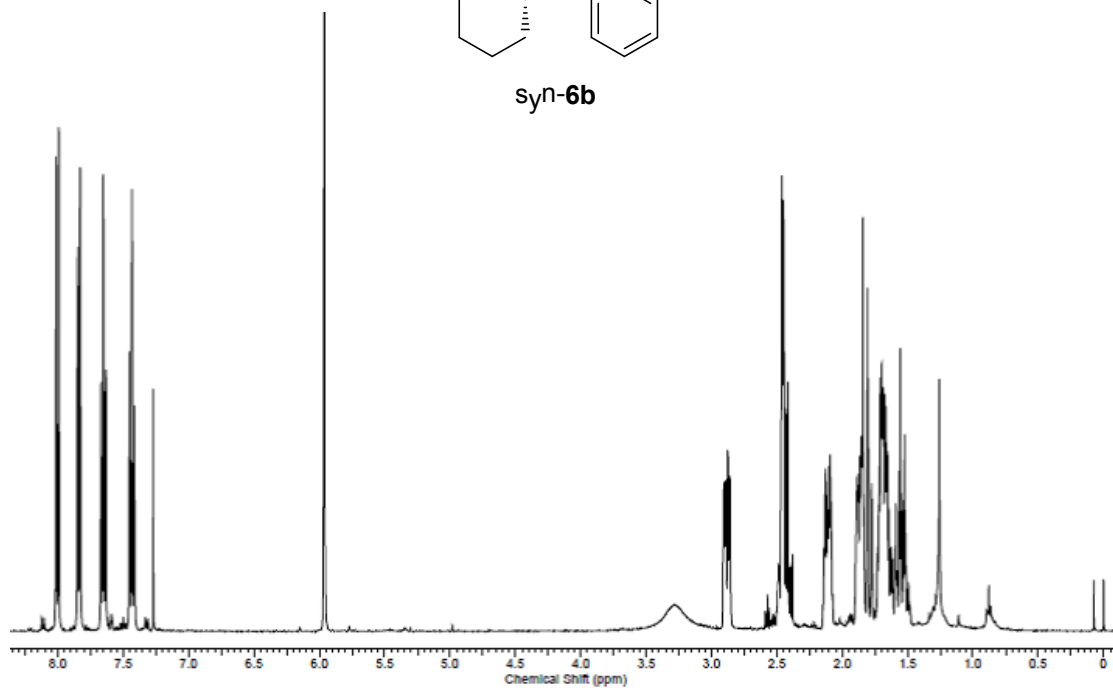


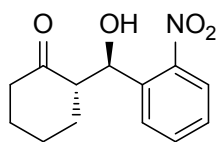
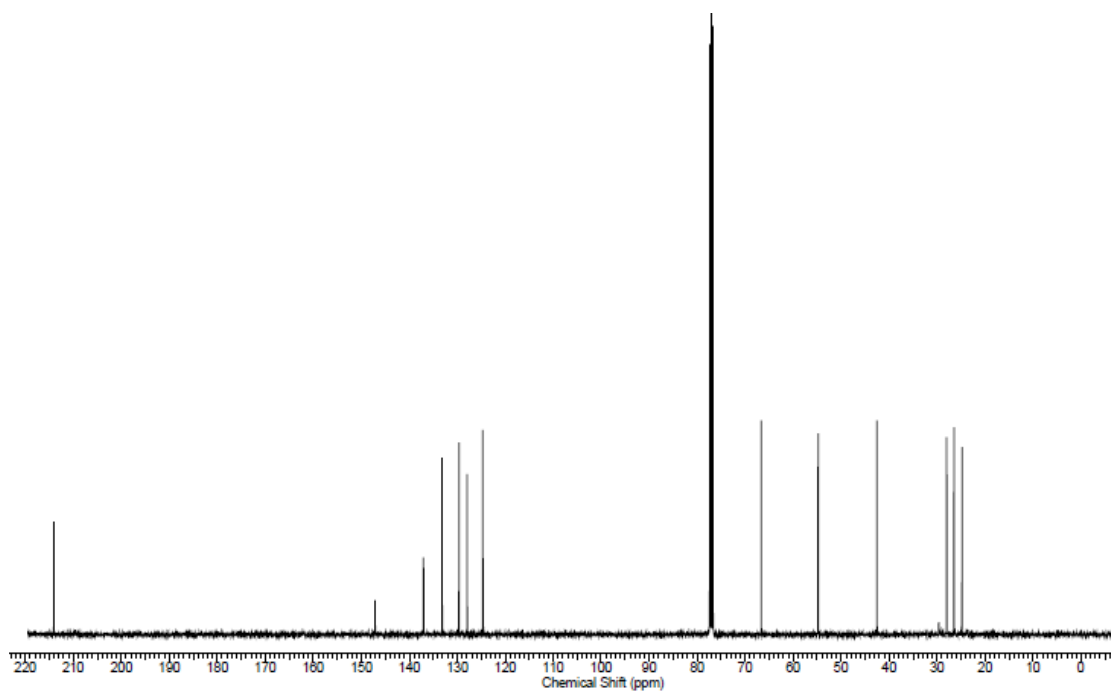
anti-6a



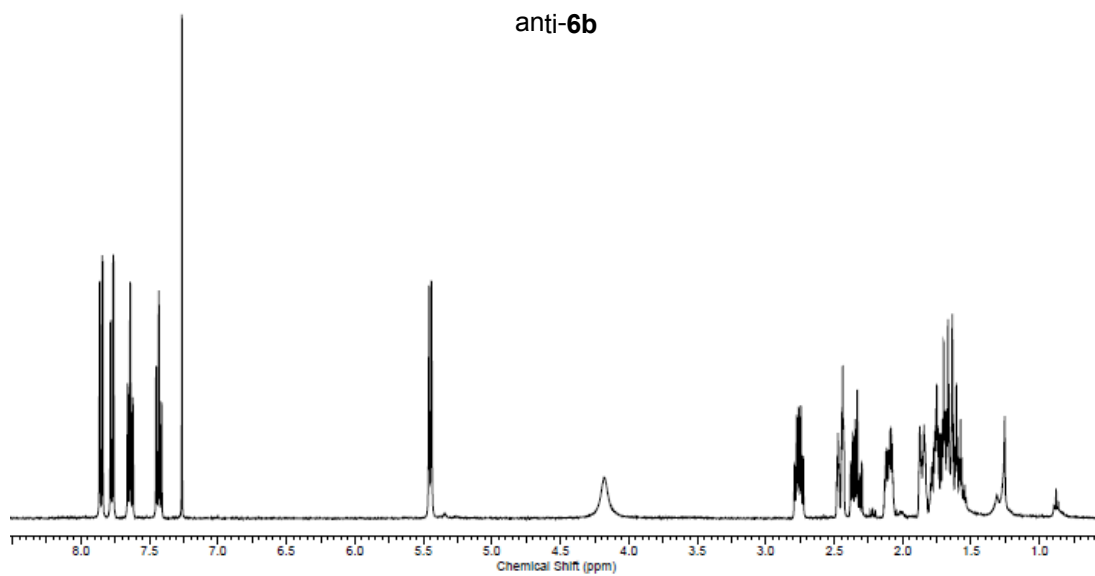


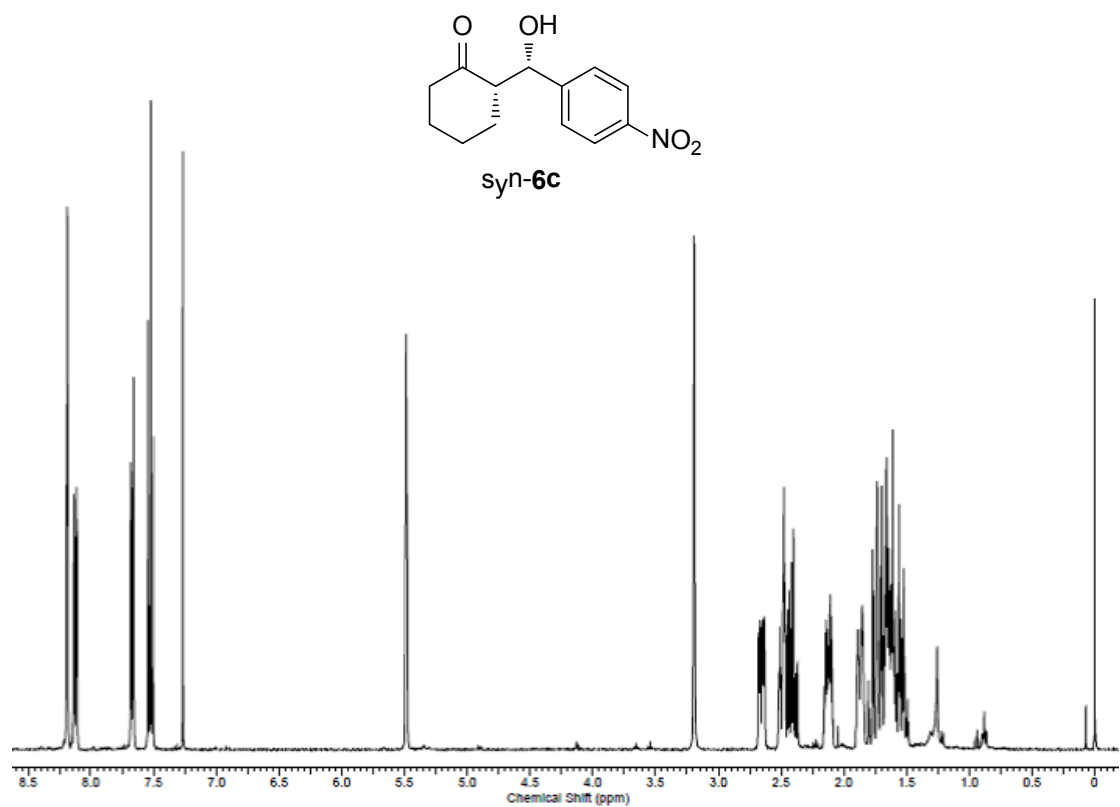
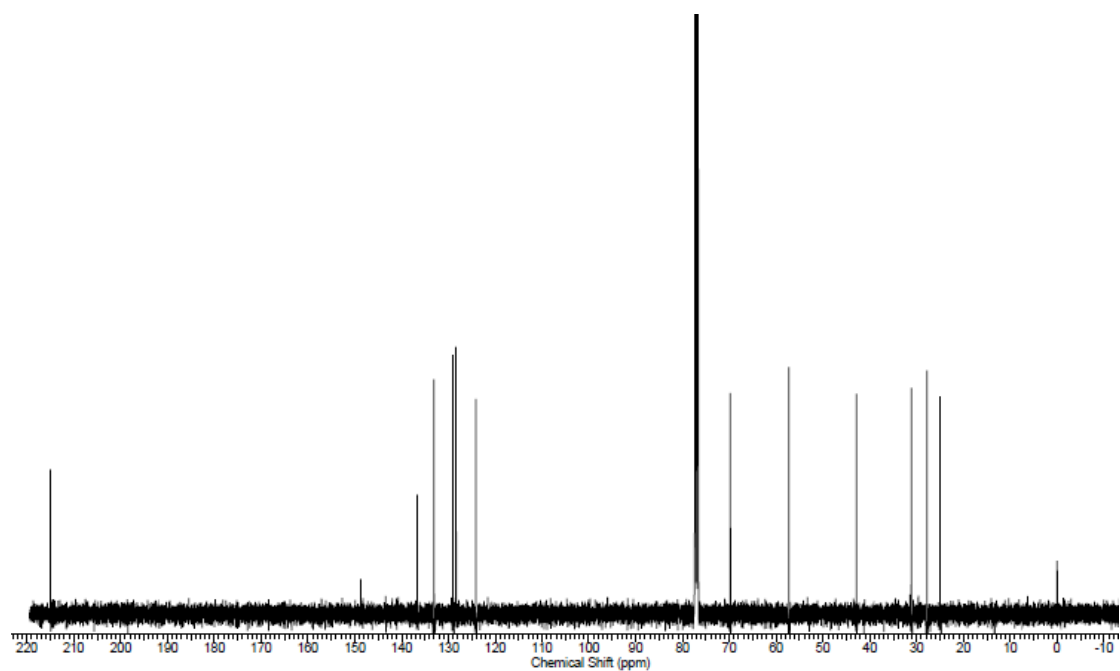
**syn-6b**

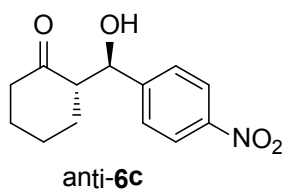
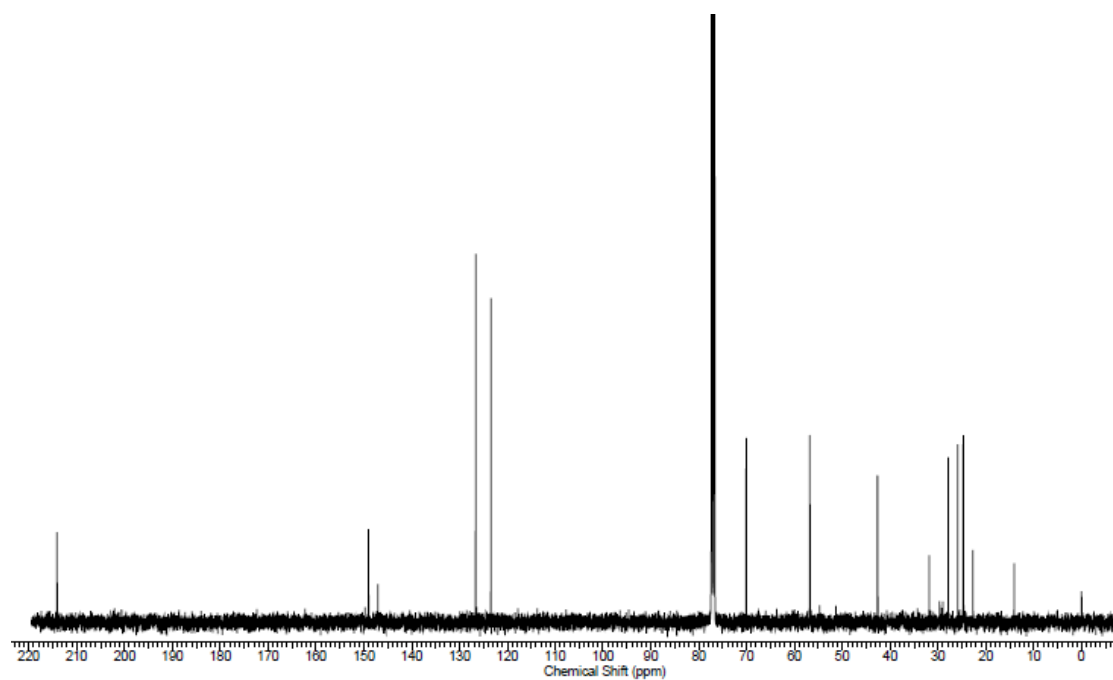


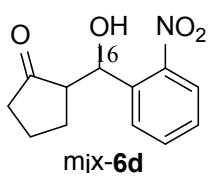
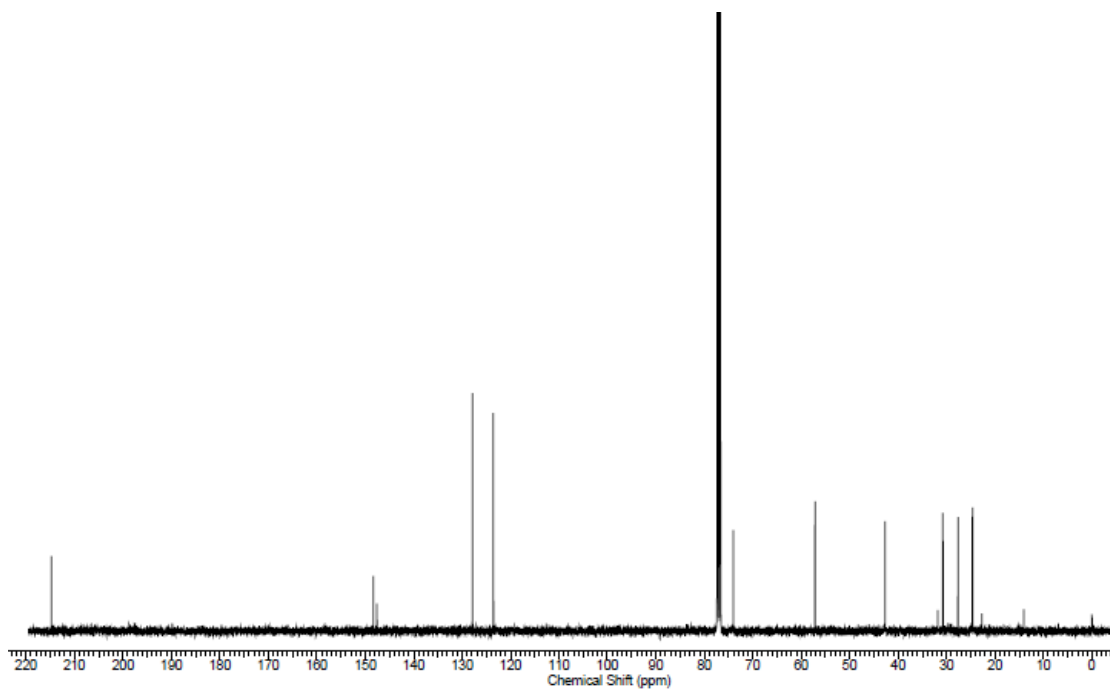
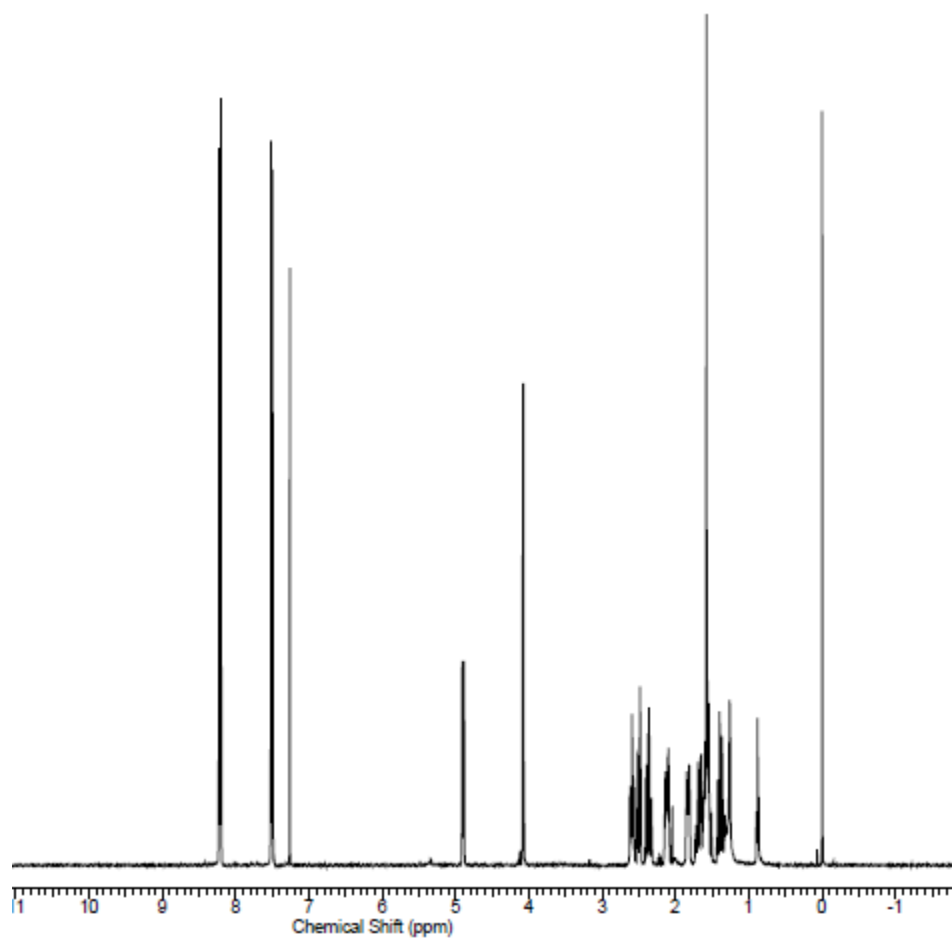


**anti-6b**

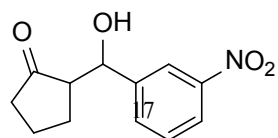
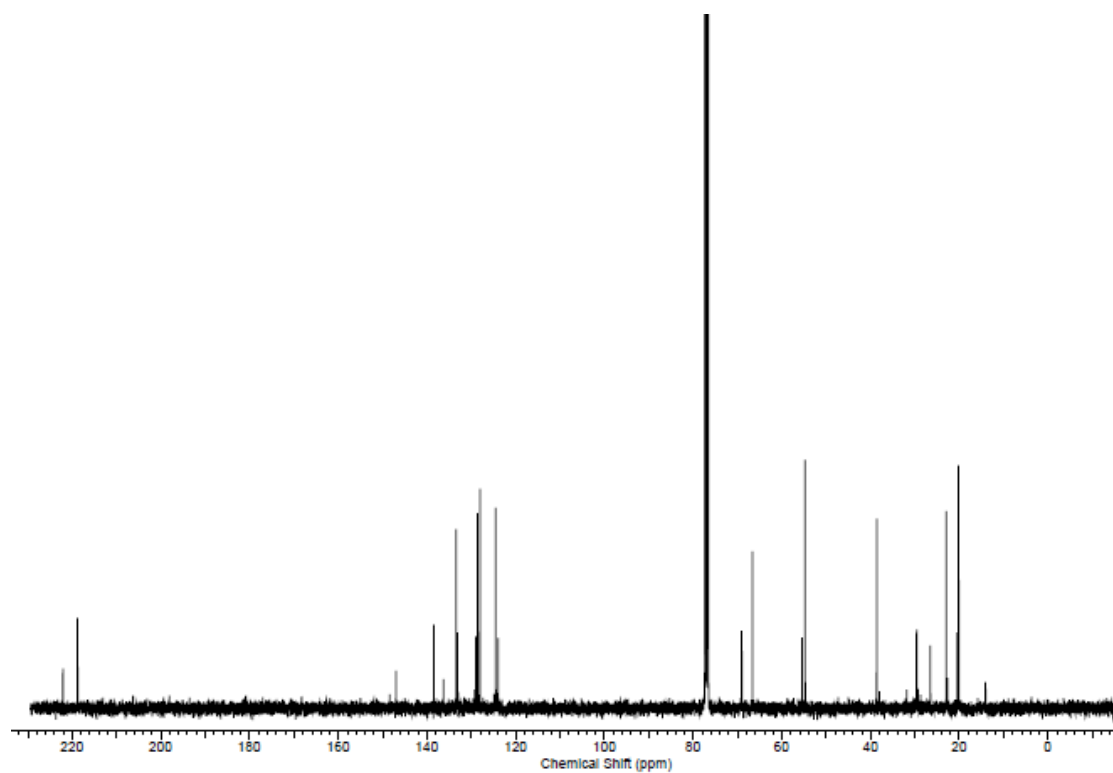
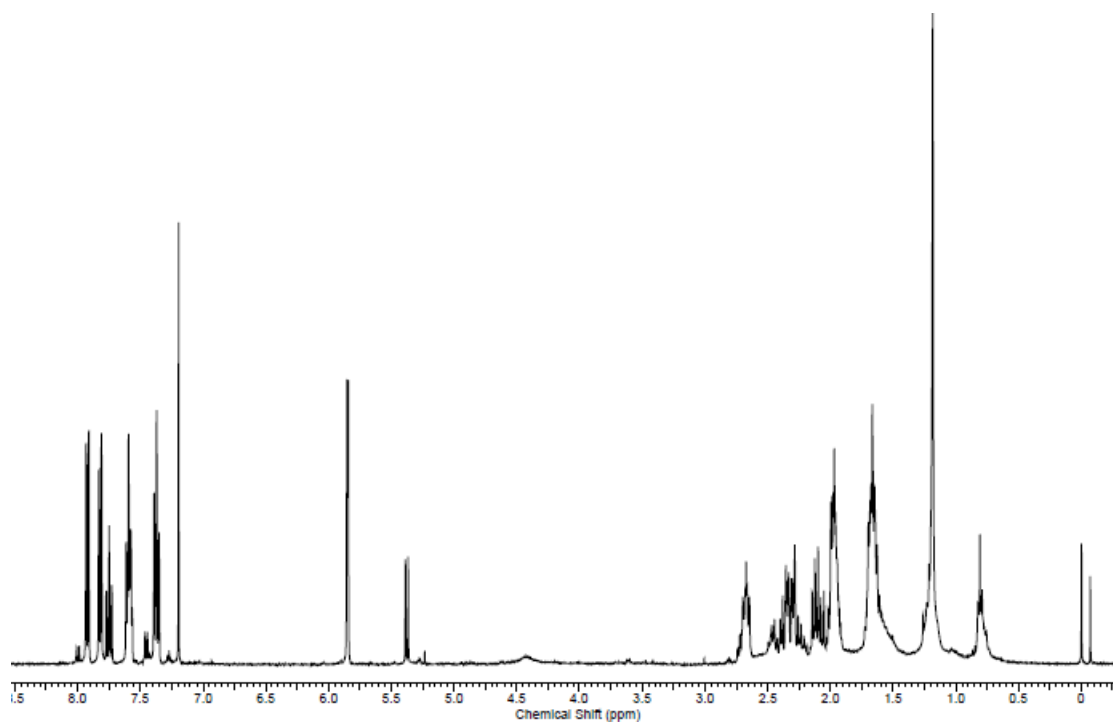




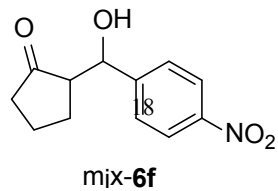
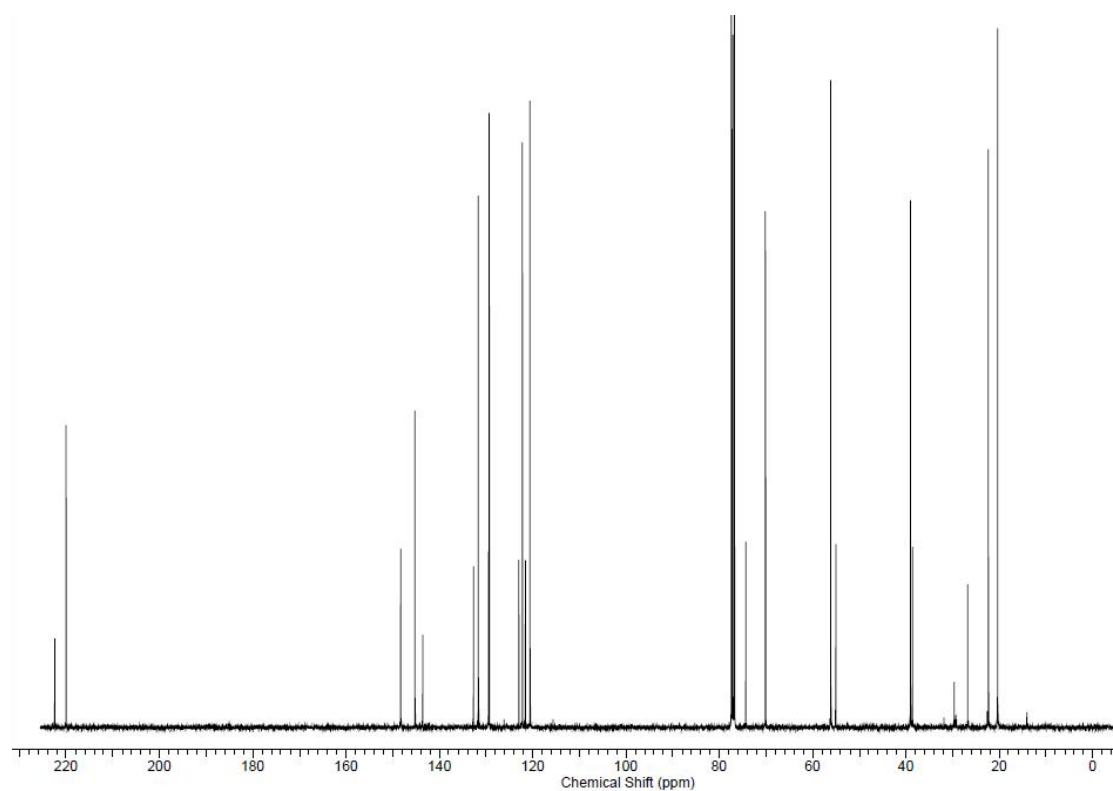
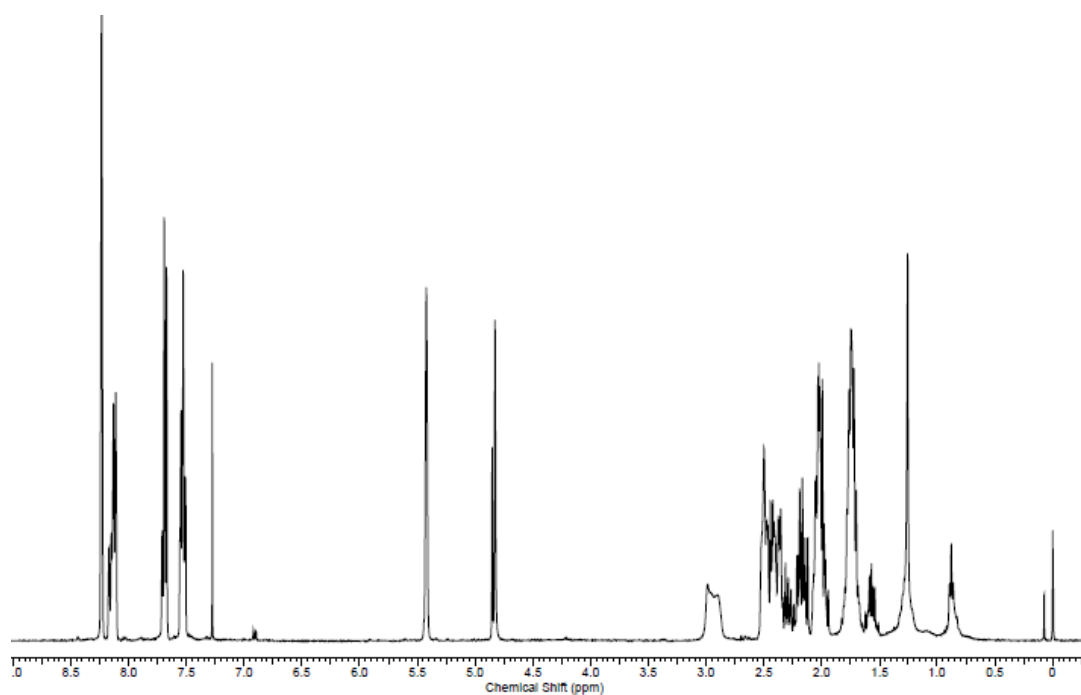


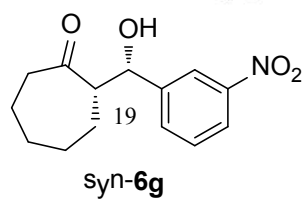
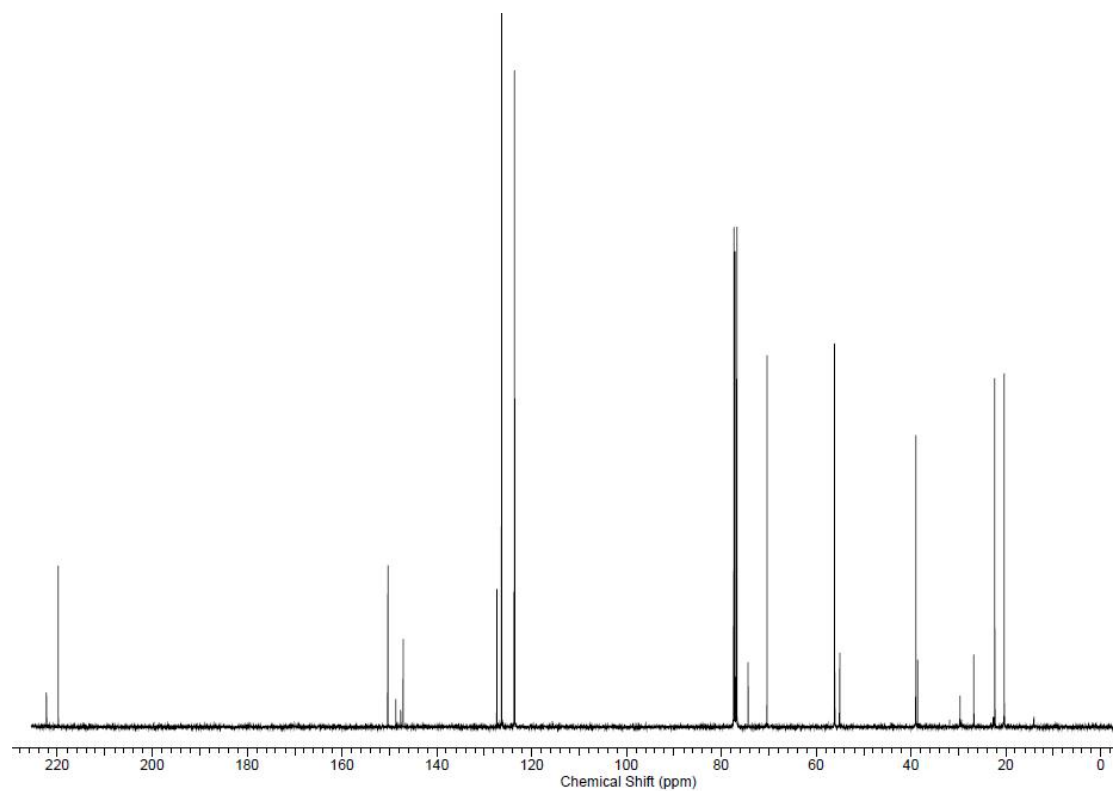
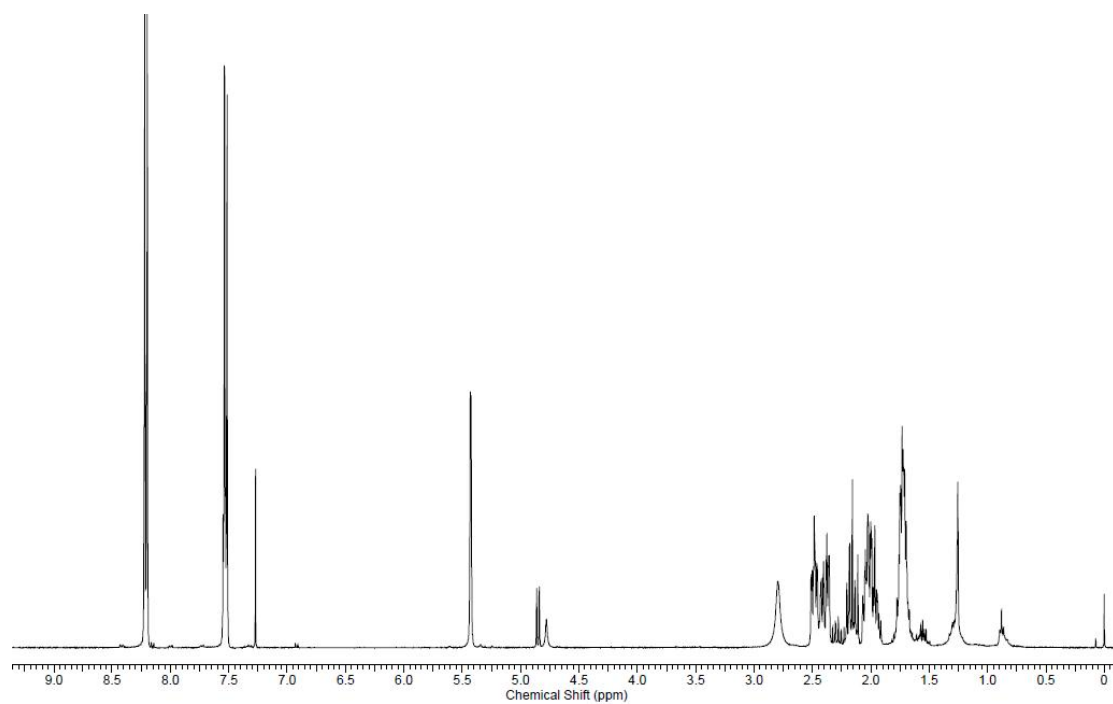


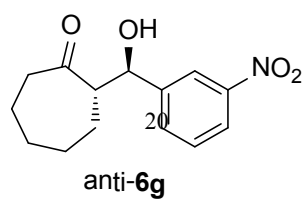
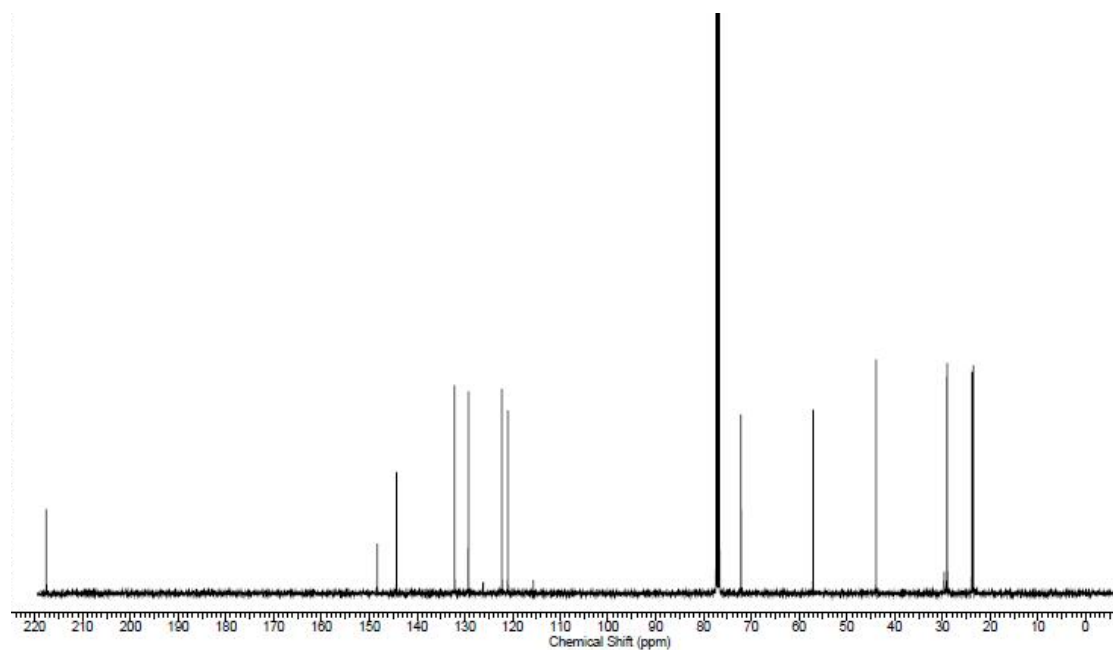
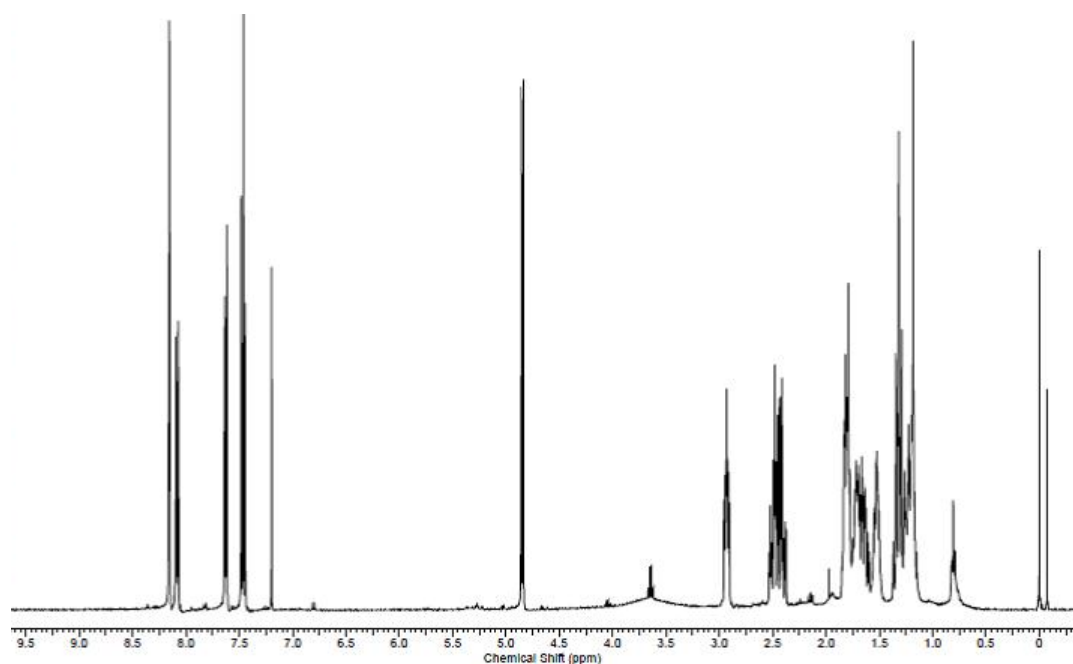


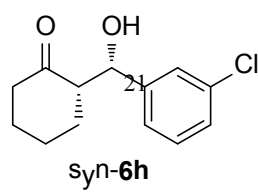
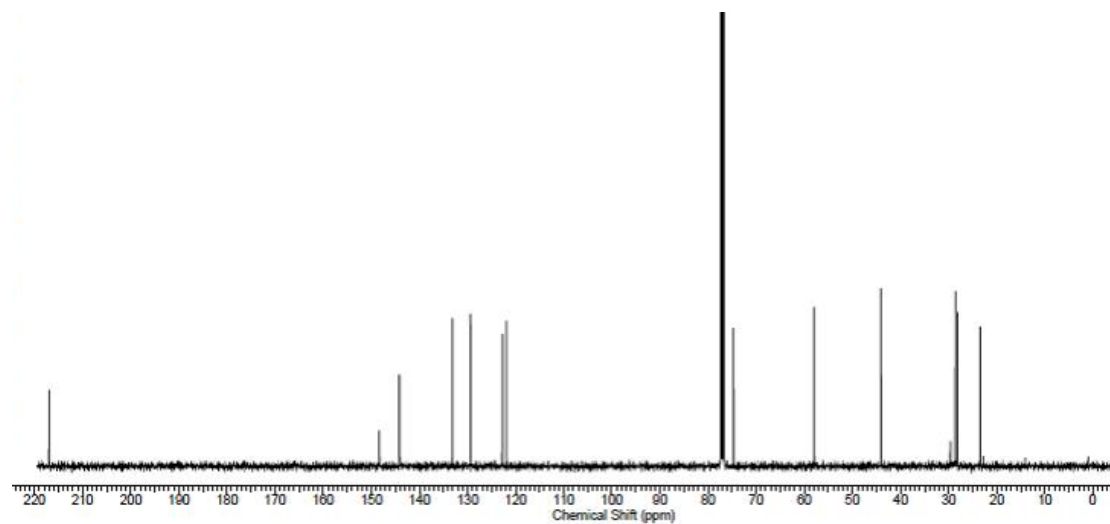
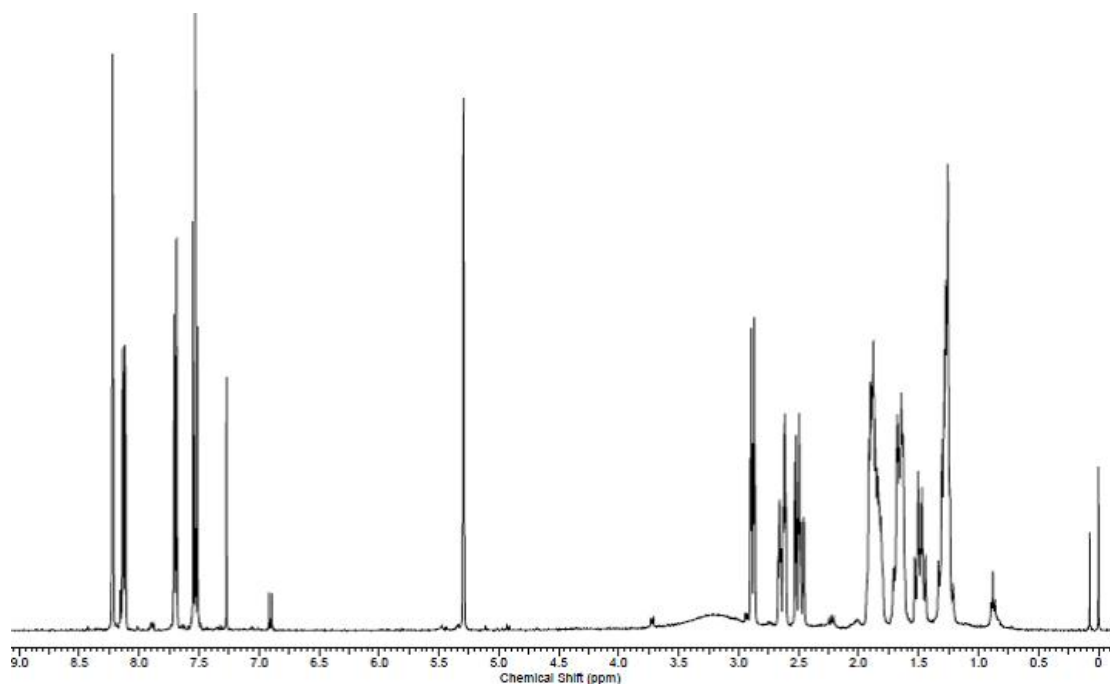


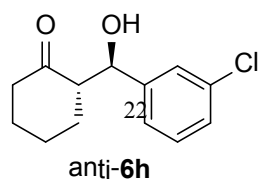
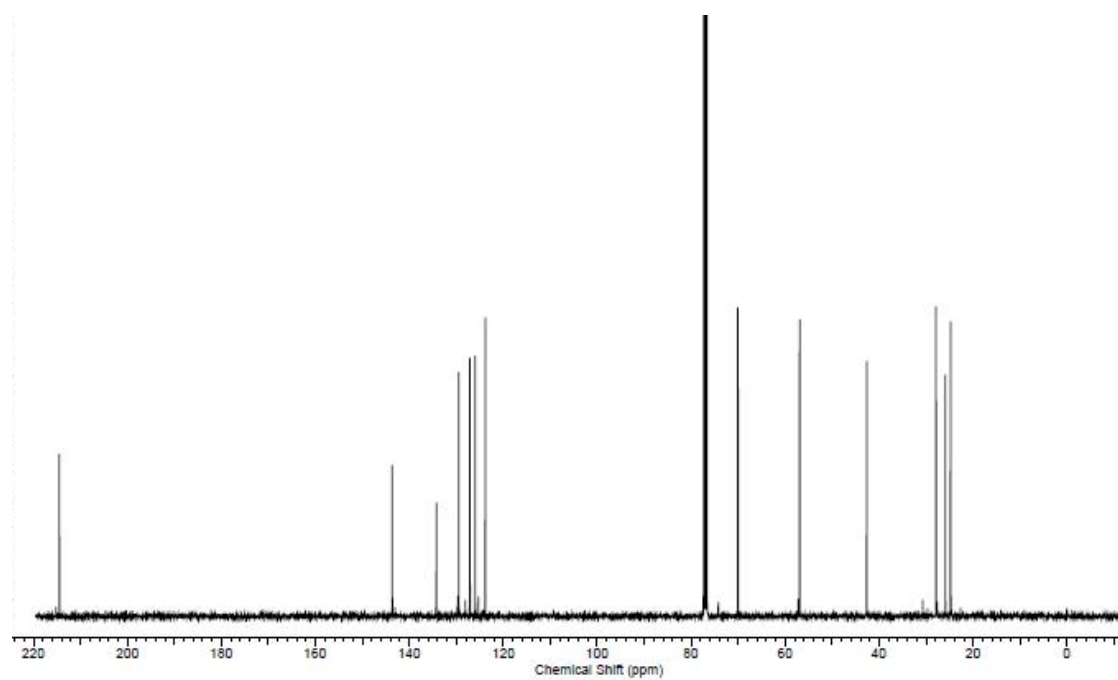
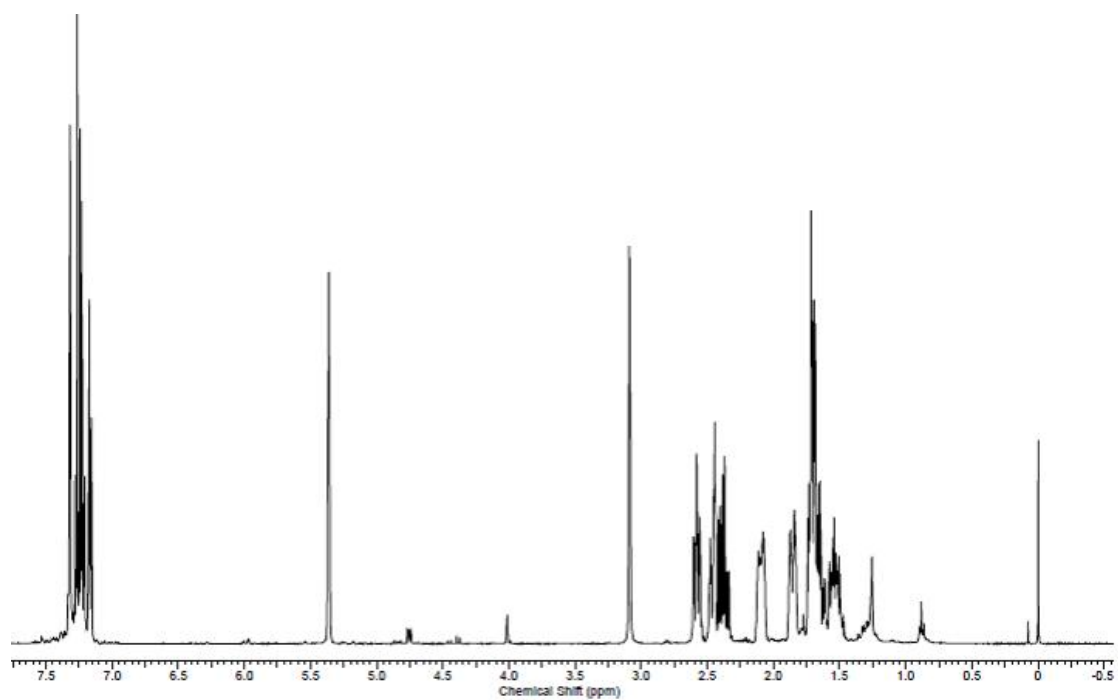
m1x-6e

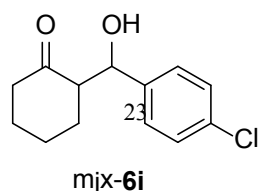
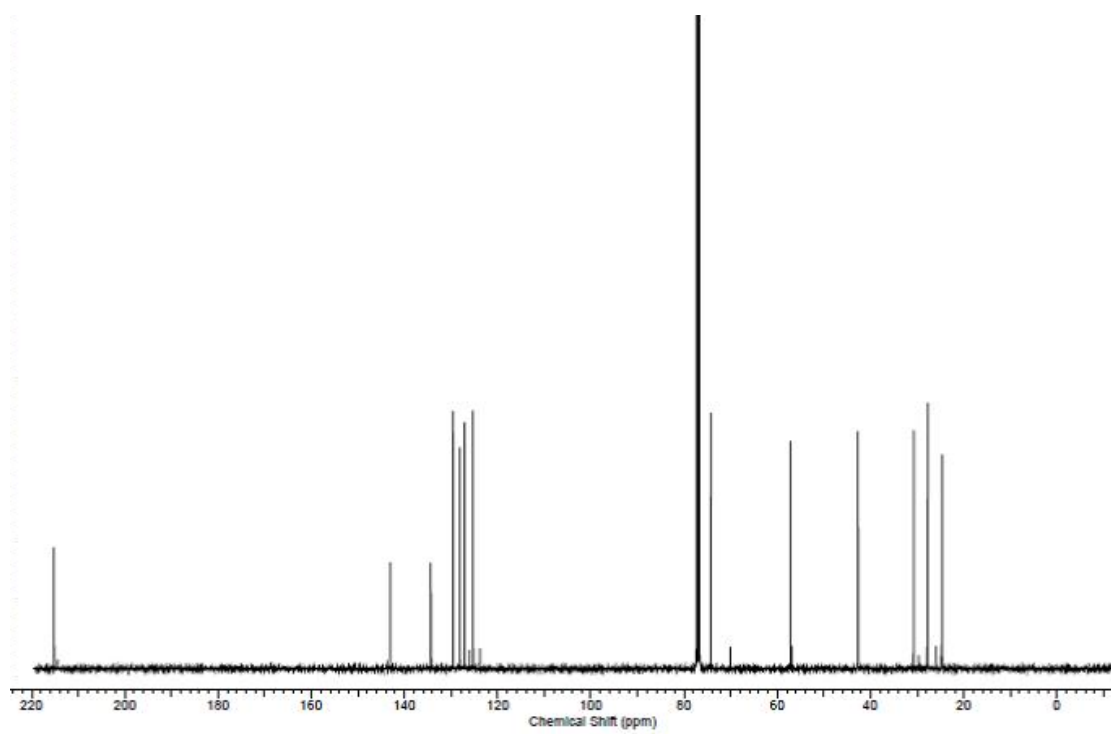
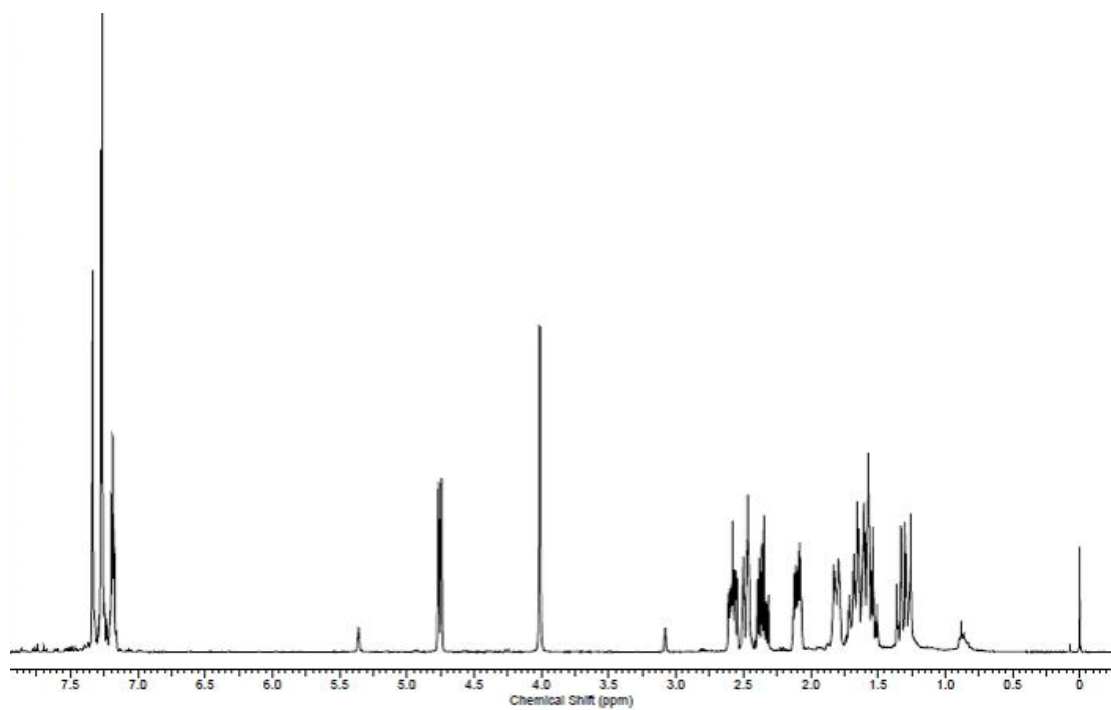


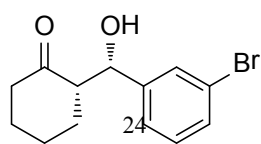
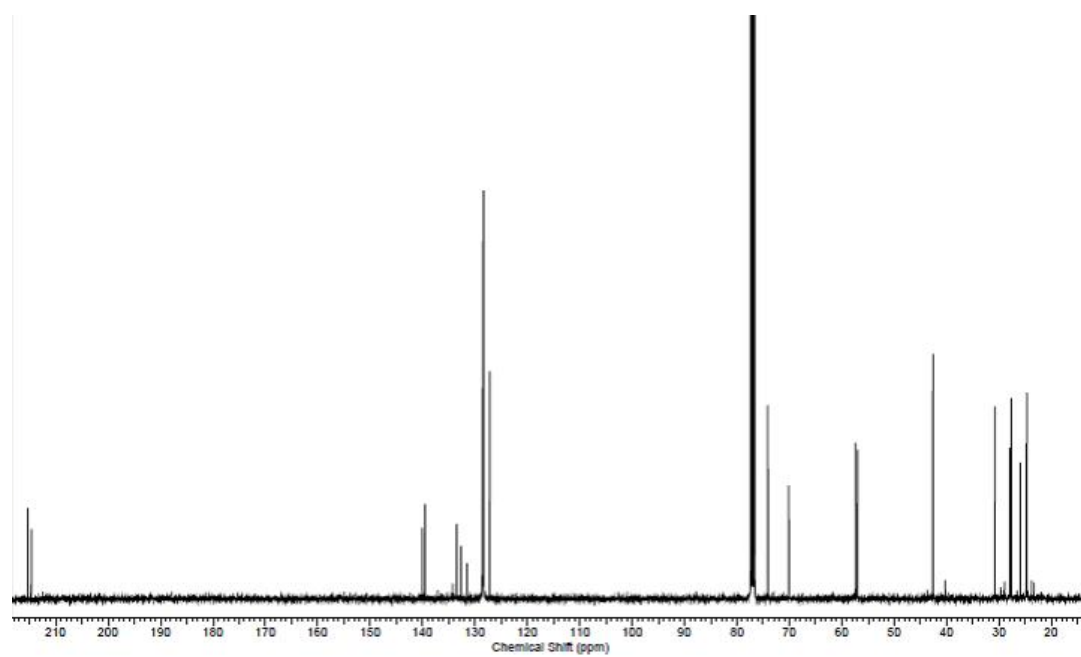
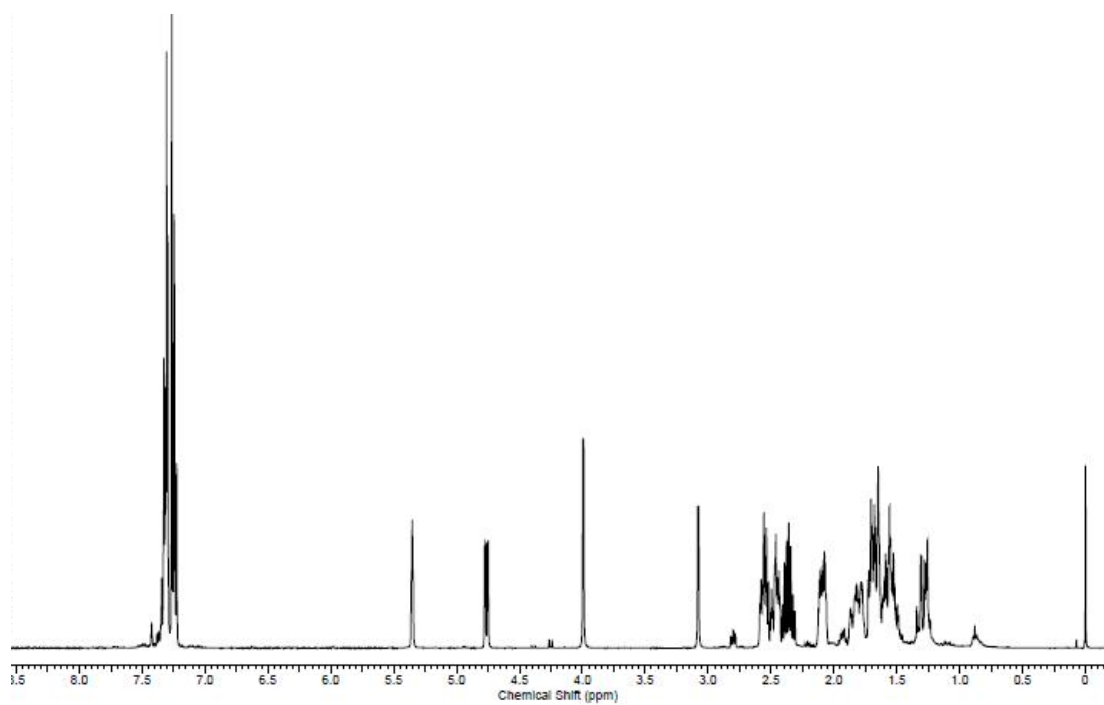






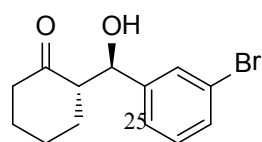
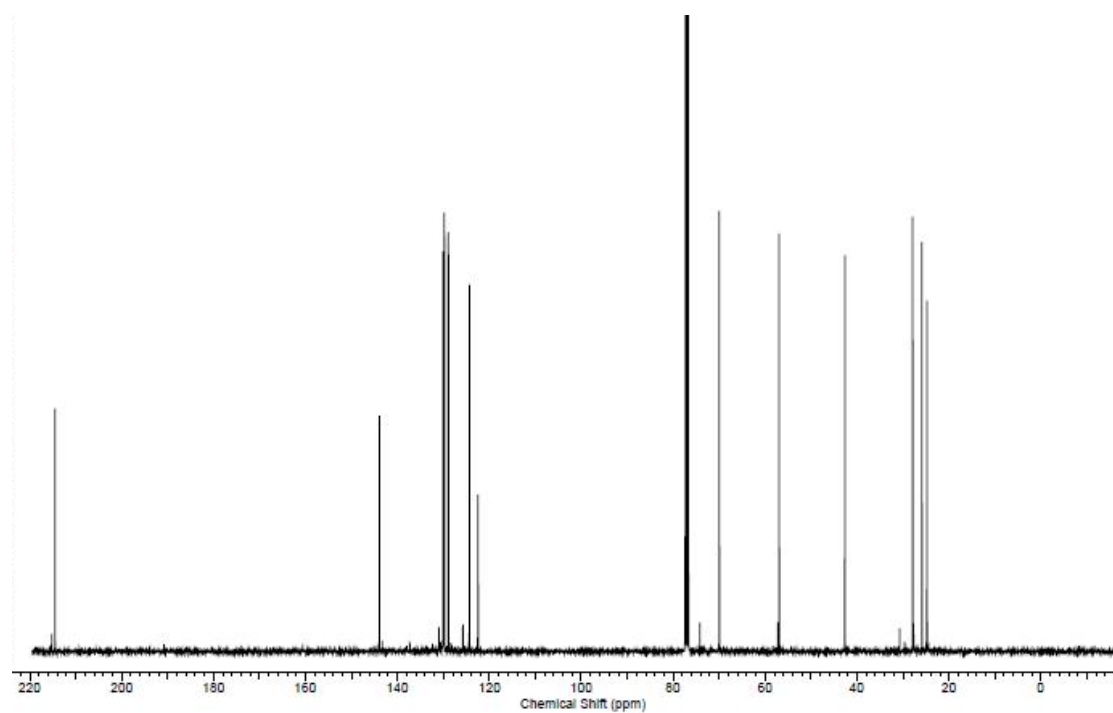
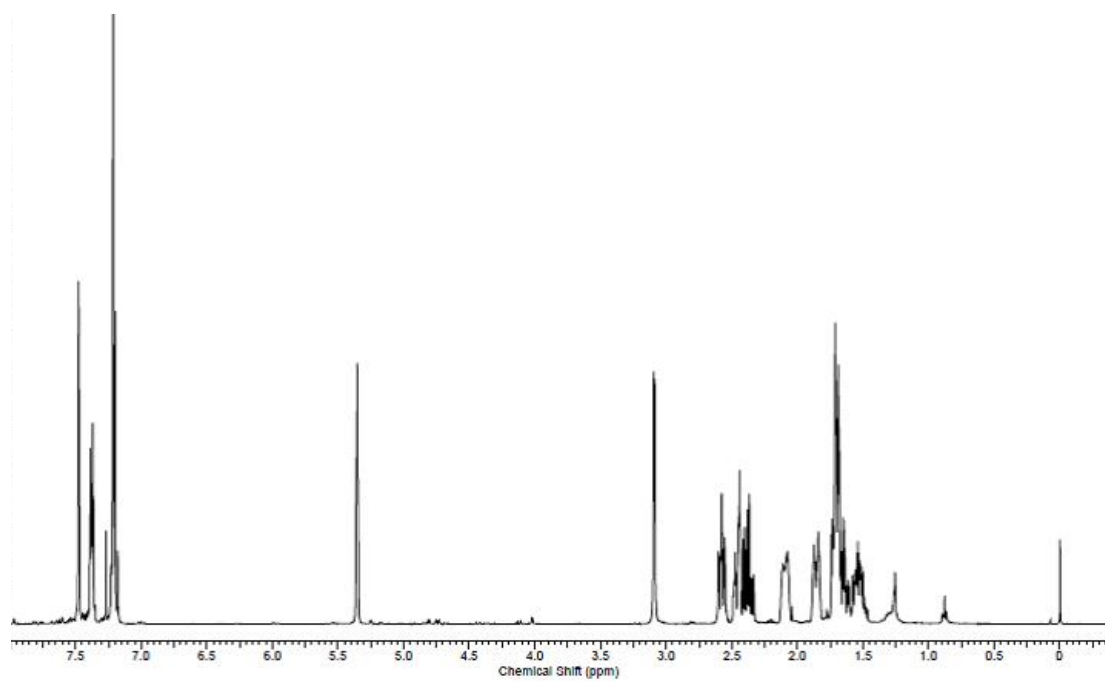




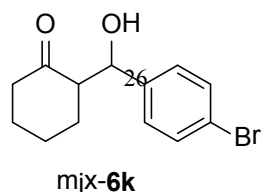
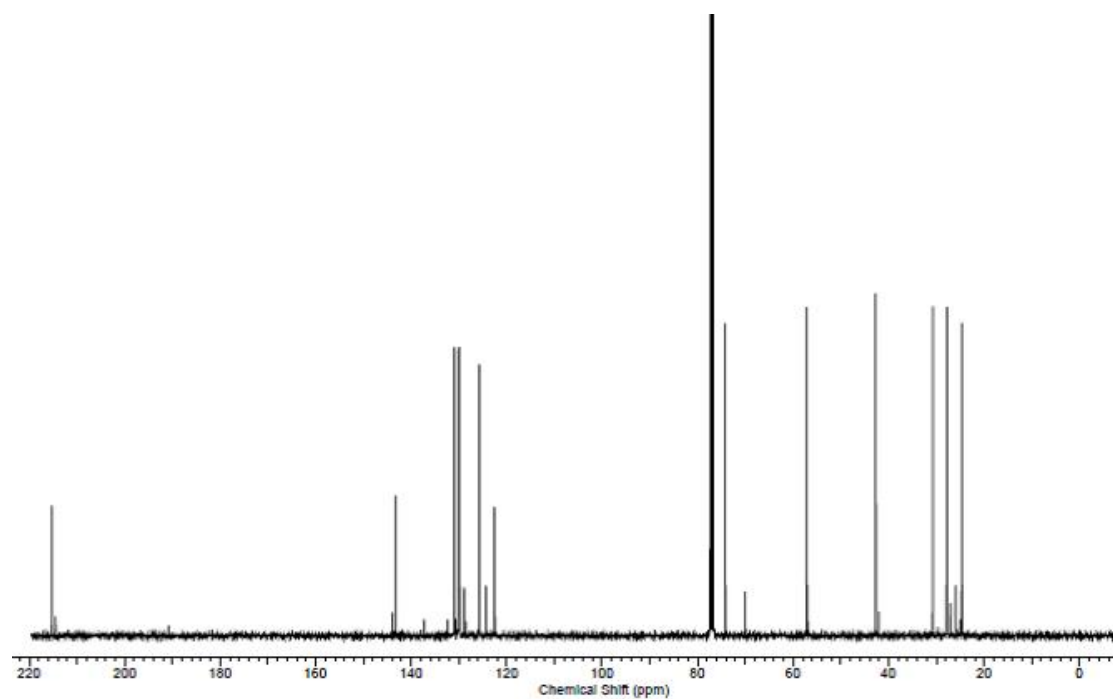
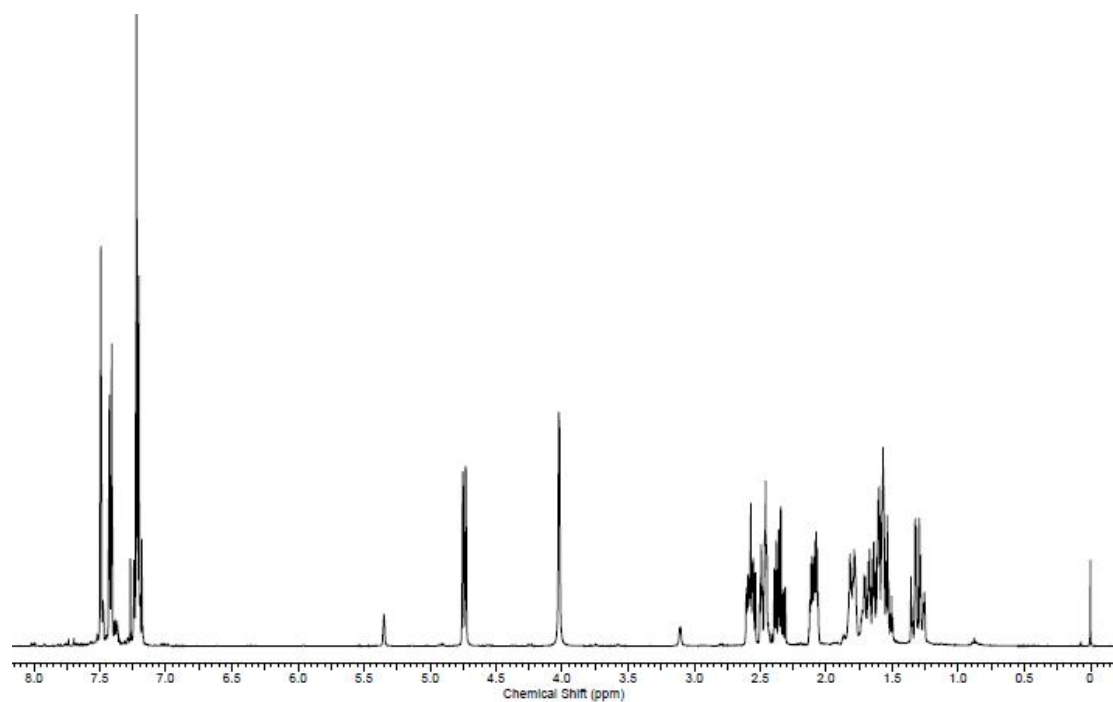


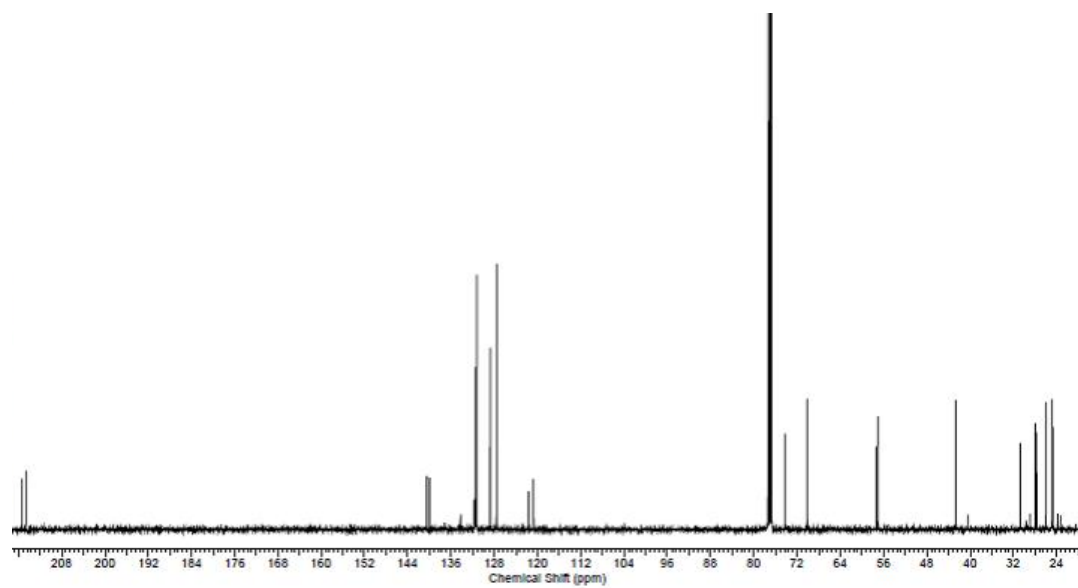
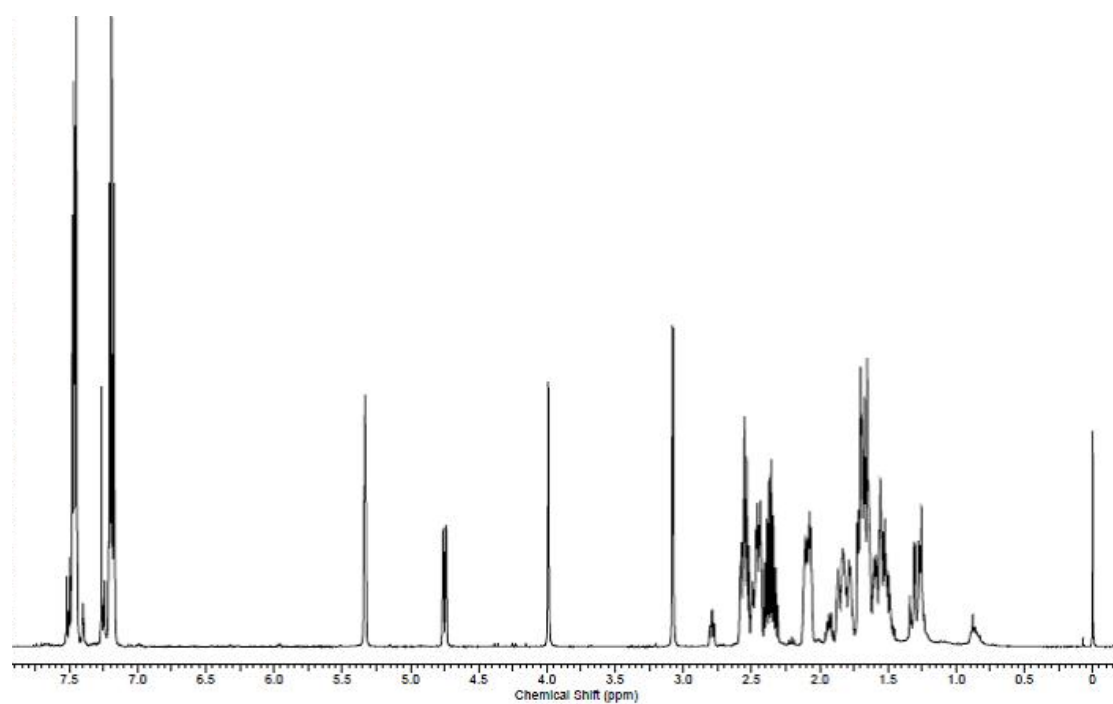
**syn-6j**

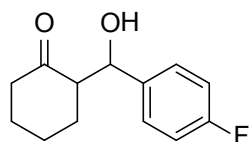




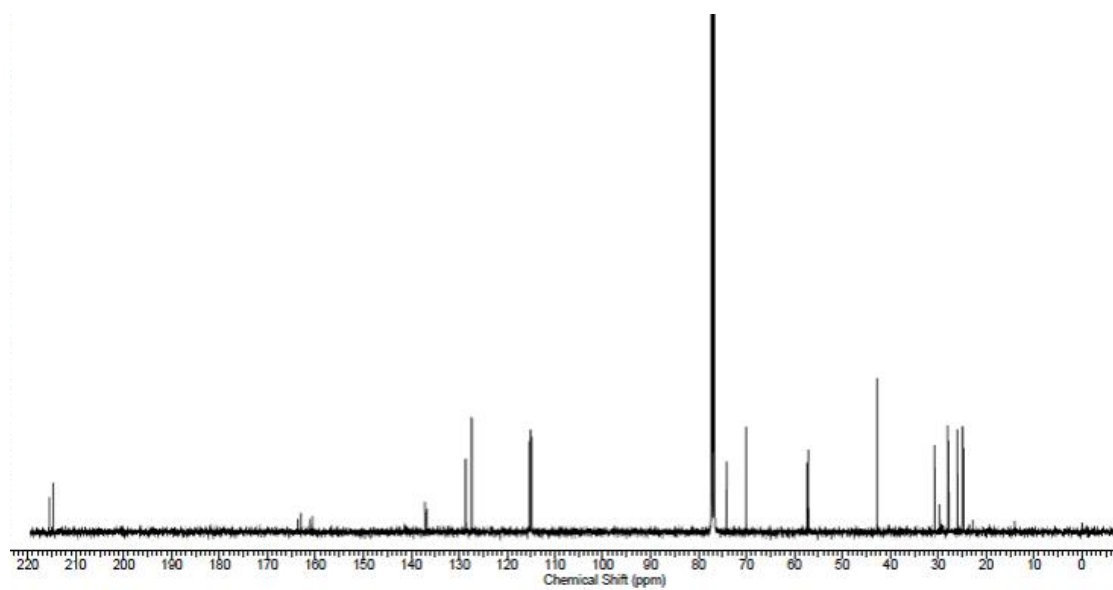
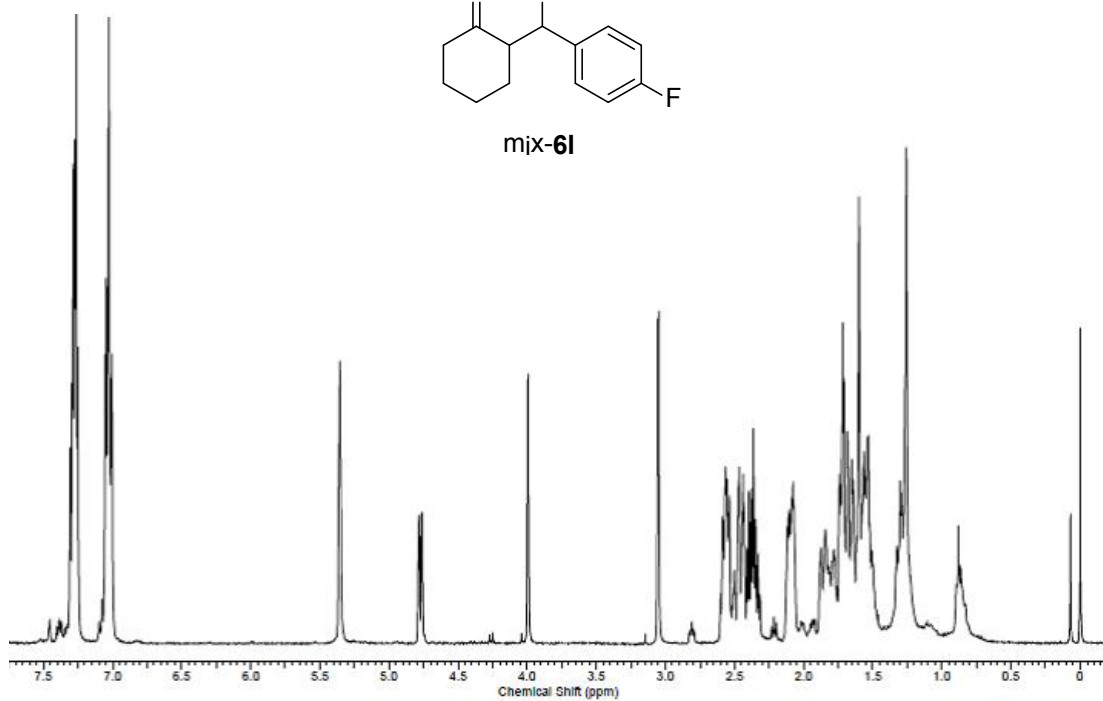
anti-6j

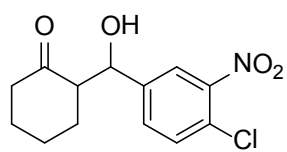




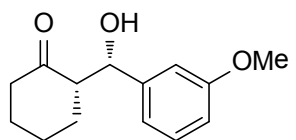
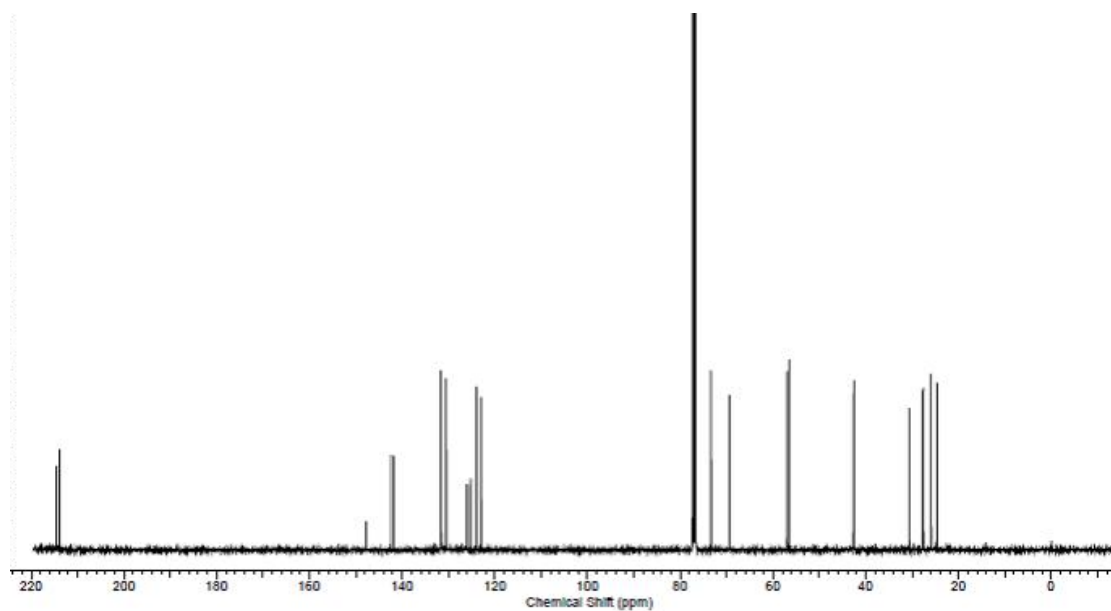
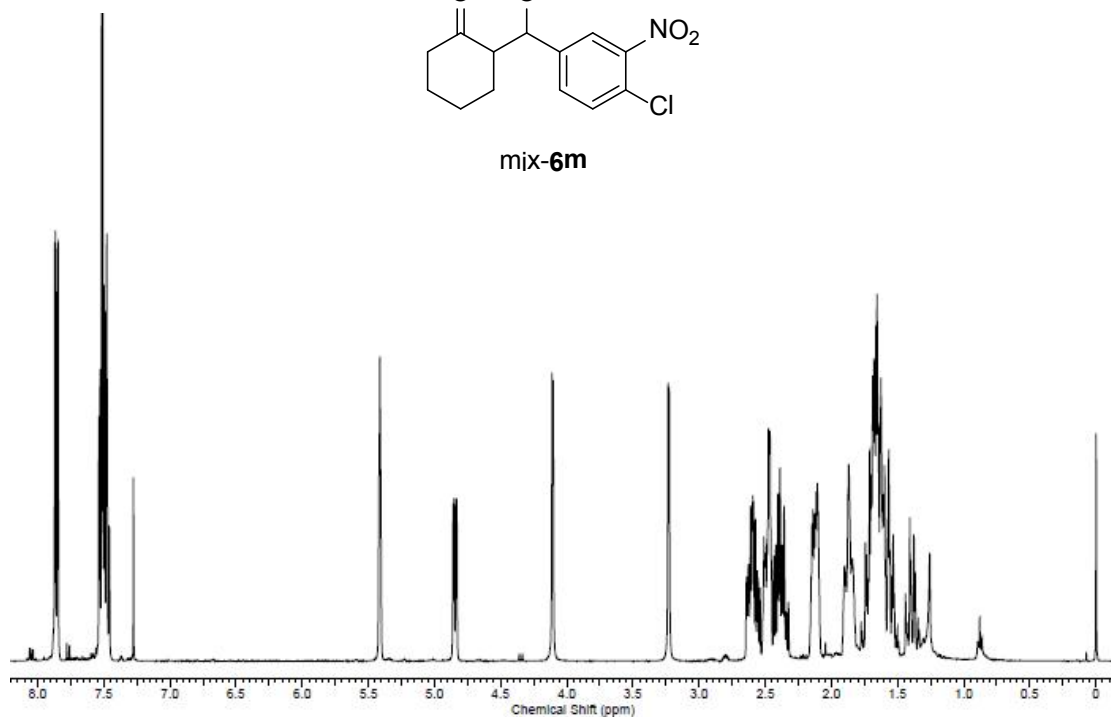


mix-6I

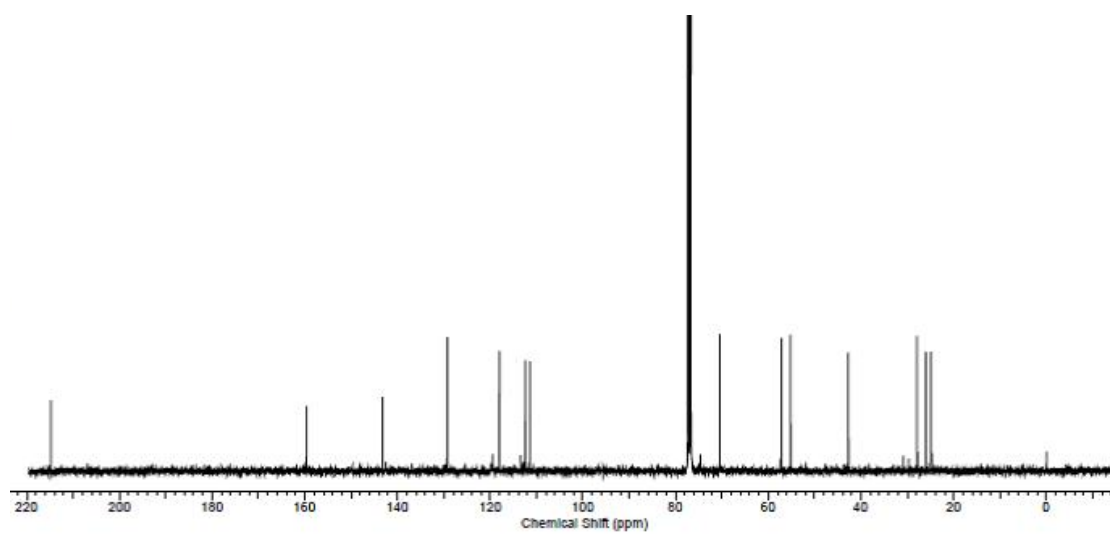
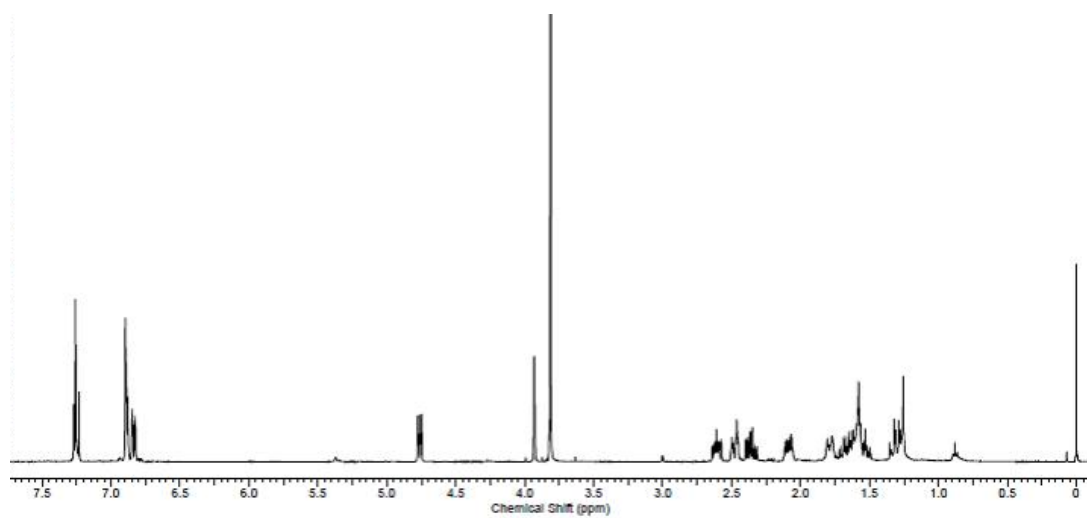


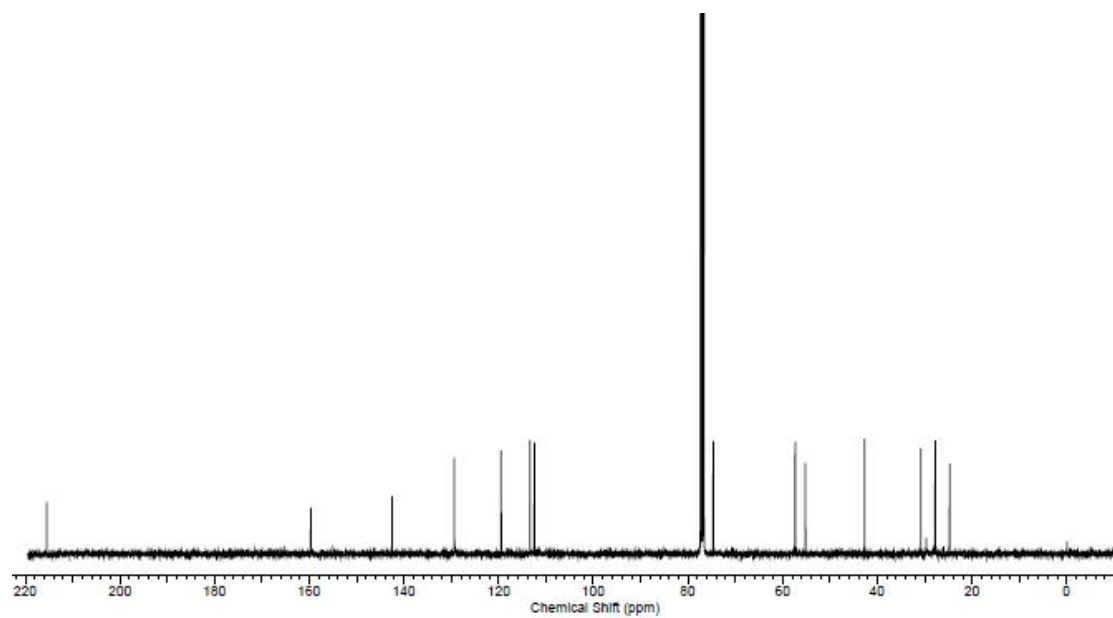
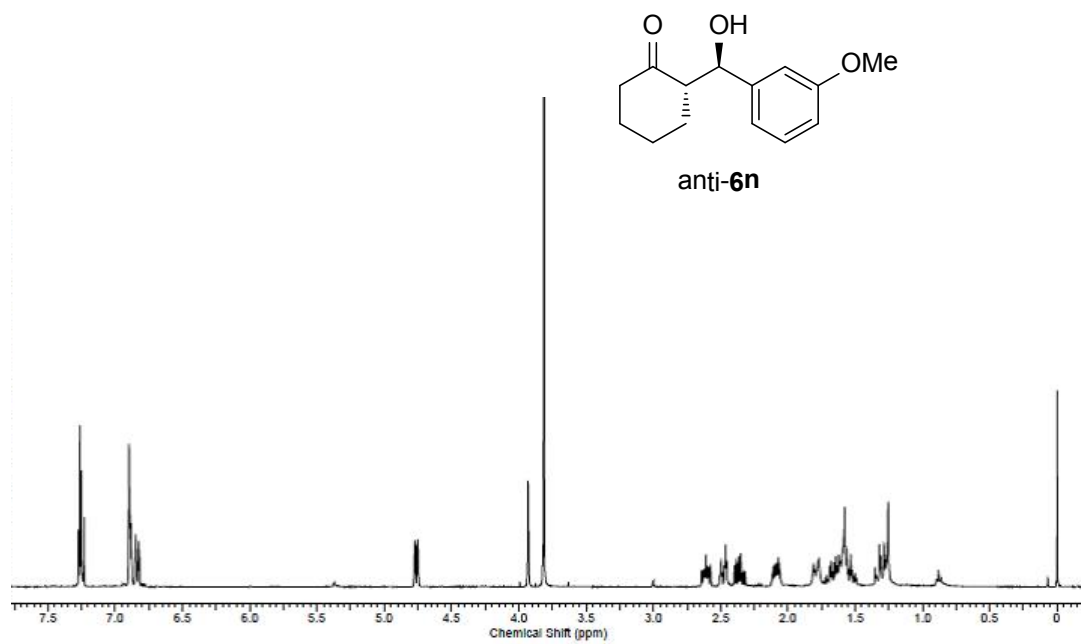


**mix-6m**

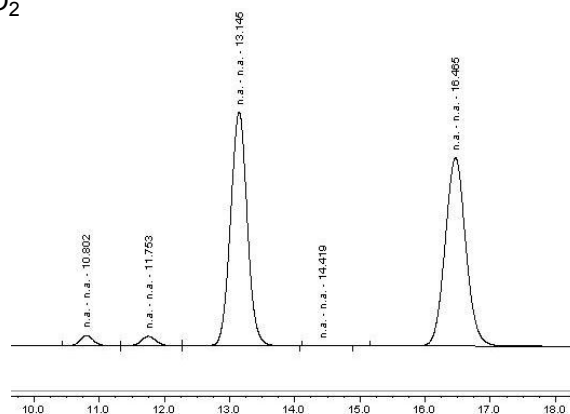
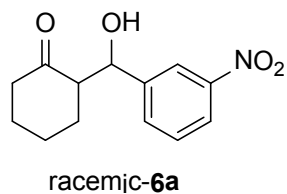


**syn-6n**

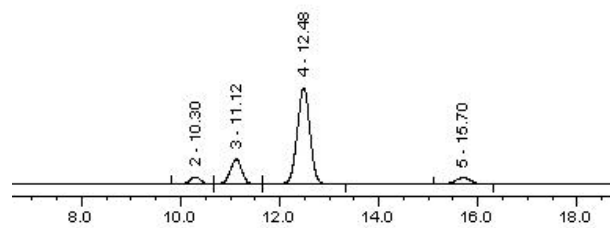
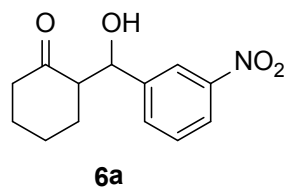




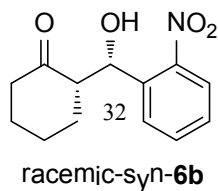
### HPLC Chromatograms for aldol products 6a-n



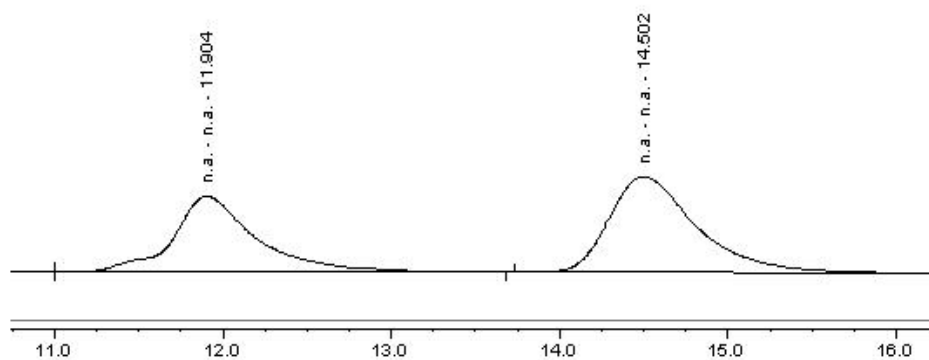
No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	10.802	11.1905	46.705	1.73
2	n.a.	11.753	11.1699	42.602	1.73
3	n.a.	13.145	311.2310	1051.665	48.13
4	n.a.	14.419	0.2870	0.794	0.04
5	n.a.	16.465	312.8126	847.353	48.37
<b>Total:</b>			<b>646.6909</b>		<b>100.000000</b>



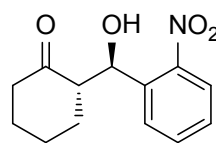
No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	10.301	1.4050	5.610	4.51
2	n.a.	11.119	5.3011	19.439	17.02
3	n.a.	12.482	22.5365	75.465	72.36
4	n.a.	15.698	1.9006	5.190	6.10
<b>Total:</b>			<b>31.1432</b>		<b>100.000000</b>



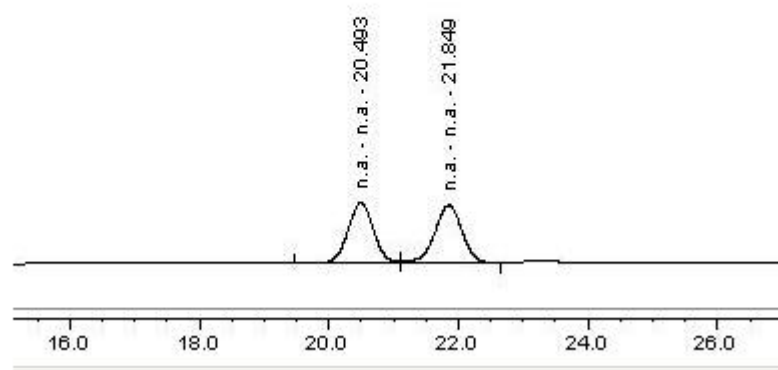




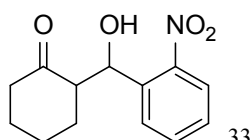
No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	11.904	8.1351	14.261	42.67
2	n.a.	14.502	10.9281	18.073	57.33
<b>Total:</b>			<b>19.0632</b>		<b>100.000000</b>



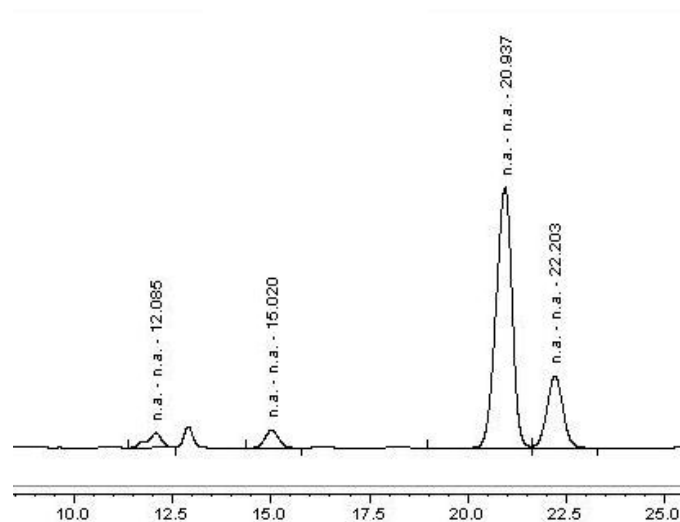
racemic-anti-**6b**



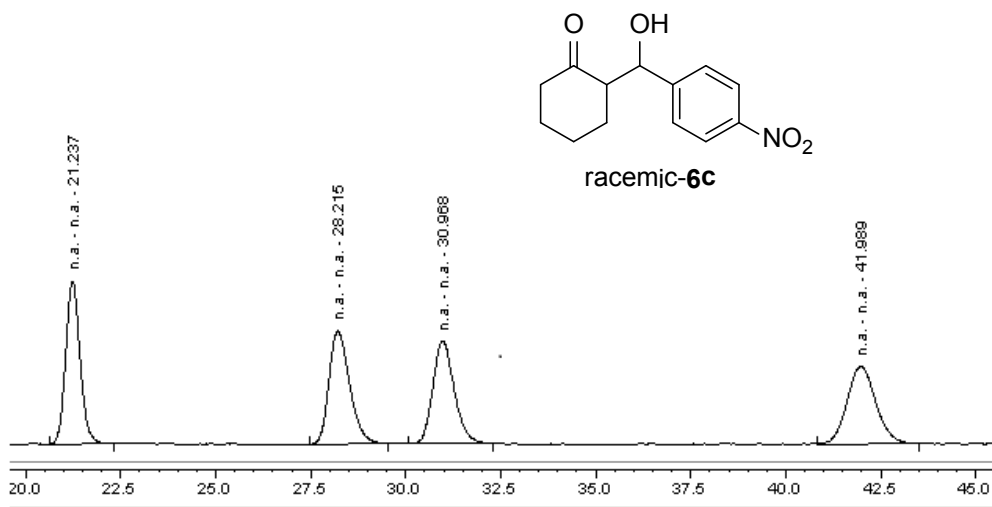
No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	20.493	50.5397	109.201	49.38
2	n.a.	21.849	51.8028	104.661	50.62
<b>Total:</b>			<b>102.3424</b>		<b>100.000000</b>



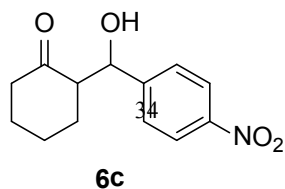
**6b**

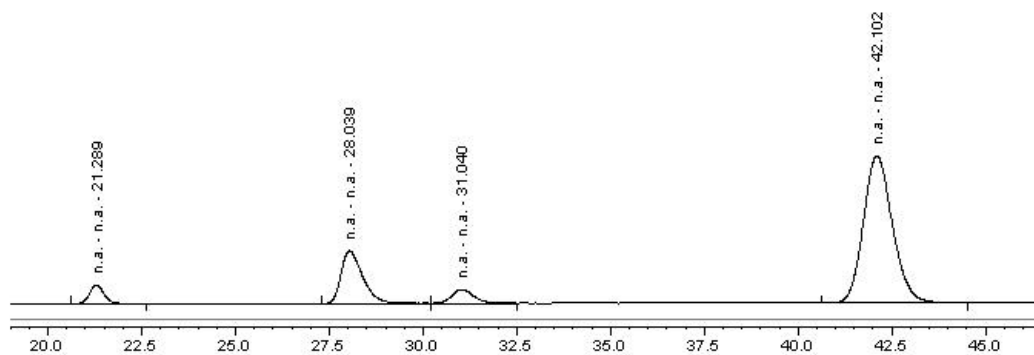


No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
2	n.a.	12.085	16.8650	39.862	3.68
3	n.a.	15.020	18.9581	47.798	4.14
4	n.a.	20.937	331.1363	703.652	72.24
5	n.a.	22.203	91.4022	193.926	19.94
<b>Total:</b>			<b>458.3620</b>		<b>100.000000</b>

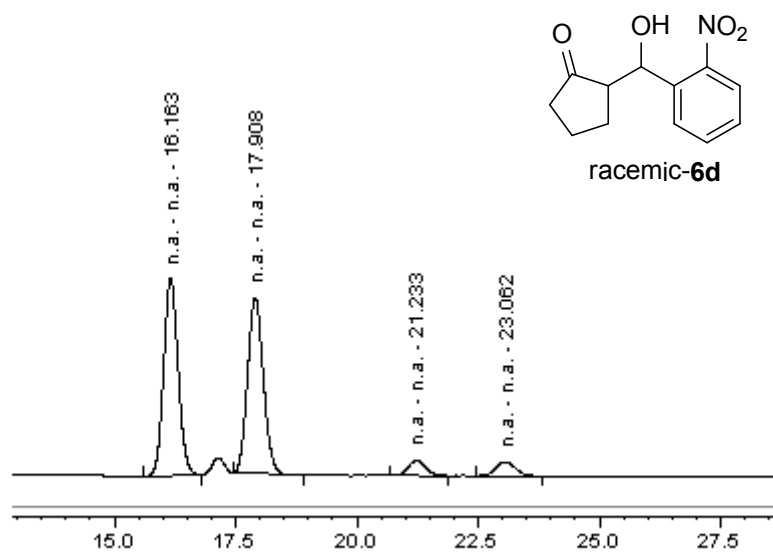


No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	21.237	4.0221	9.146	25.71
2	n.a.	28.215	3.9978	6.341	25.56
3	n.a.	30.968	3.7849	5.744	24.20
4	n.a.	41.989	3.8376	4.337	24.53
<b>Total:</b>			<b>15.6423</b>		<b>100.000000</b>

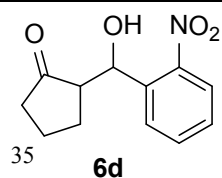


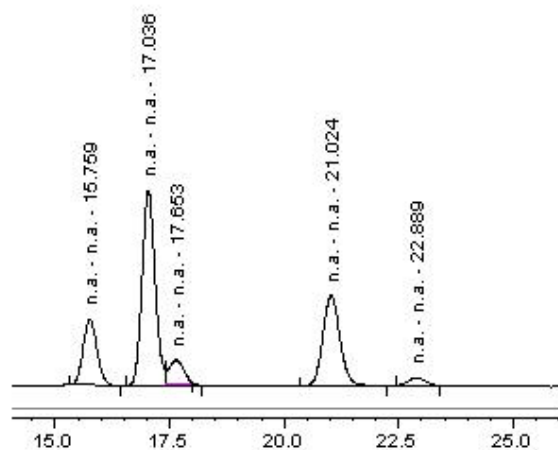


No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	21.289	2.7022	5.938	4.61
2	n.a.	28.039	11.1358	16.622	19.01
3	n.a.	31.040	2.9564	4.358	5.05
4	n.a.	42.102	41.7759	46.437	71.33
<b>Total:</b>			<b>58.5703</b>		<b>100.000000</b>

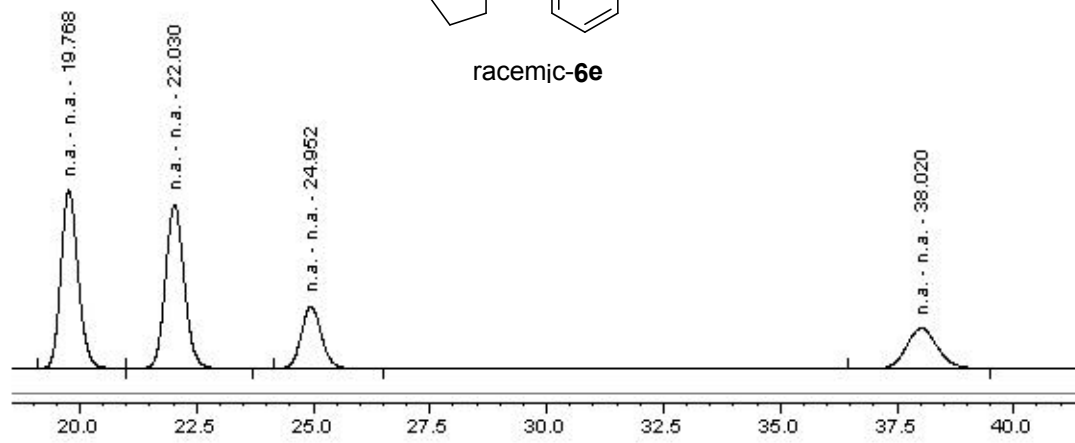
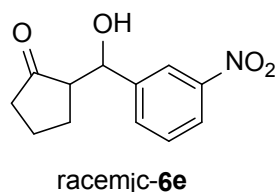


No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	16.163	14.1074	40.910	46.03
2	n.a.	17.908	13.8398	36.561	45.15
3	n.a.	21.233	1.3260	3.149	4.33
4	n.a.	23.062	1.3782	2.966	4.50
<b>Total:</b>			<b>30.6514</b>		<b>100.000000</b>

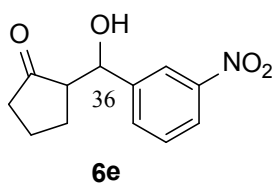


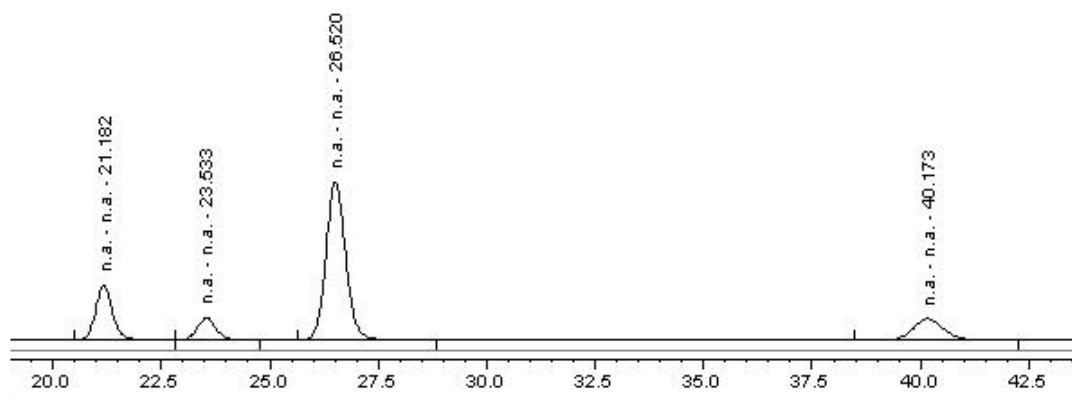


No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	15.759	1.3658	3.875	16.49
2	n.a.	17.036	3.9090	11.490	47.20
3	n.a.	17.653	0.4838	1.361	5.84
4	n.a.	21.024	2.3218	5.309	28.03
5	n.a.	22.889	0.2022	0.466	2.44
<b>Total:</b>			<b>8.2826</b>		<b>100.00000</b>

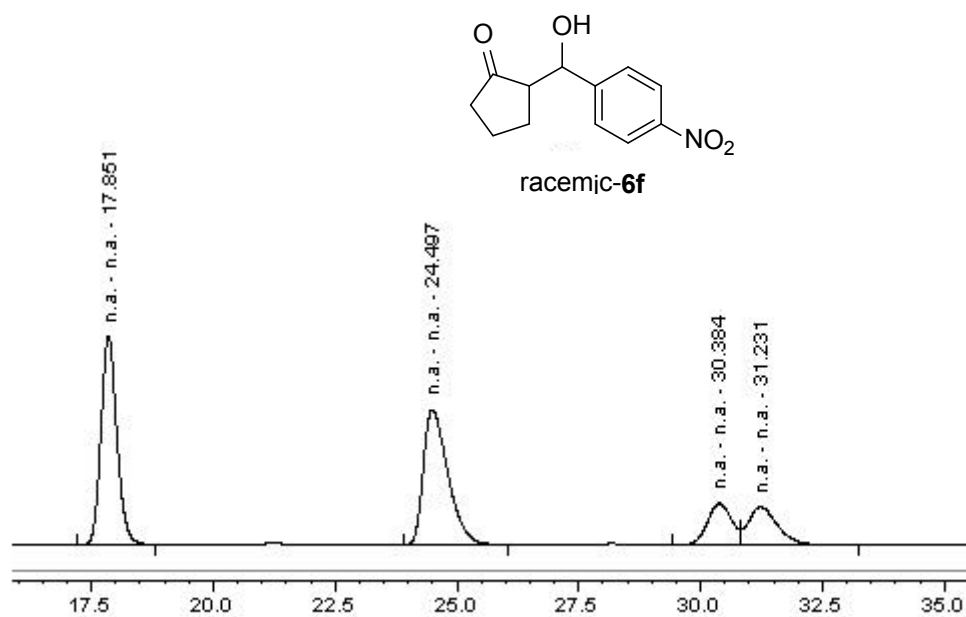


No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	19.768	31.2147	72.985	35.47
2	n.a.	22.030	31.3909	67.099	35.67
3	n.a.	24.952	12.6794	25.365	14.41
4	n.a.	38.020	12.7086	16.507	14.44
<b>Total:</b>			<b>87.9935</b>		<b>100.00000</b>

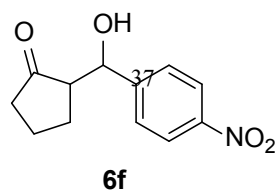


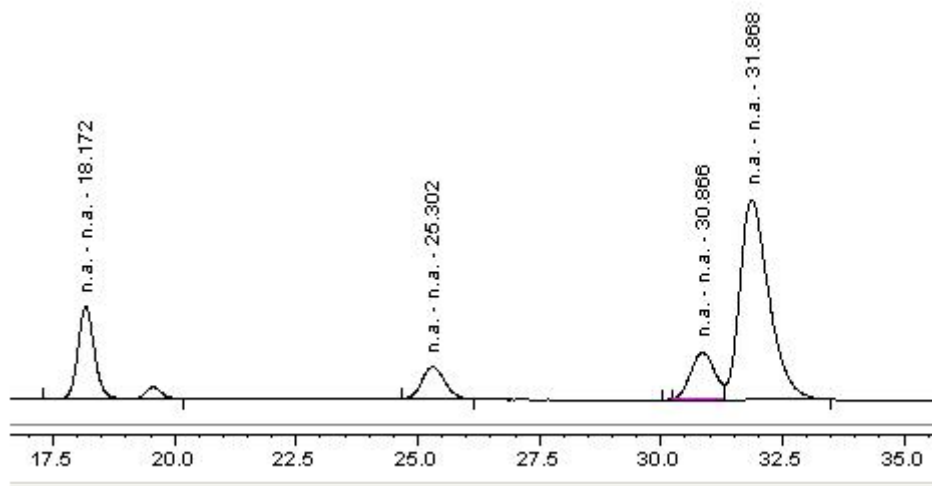


No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	21.182	9.3865	21.029	18.02
2	n.a.	23.533	4.0830	8.377	7.84
3	n.a.	26.520	32.0632	60.584	61.56
4	n.a.	40.173	6.5540	8.099	12.58
<b>Total:</b>			<b>52.0866</b>		<b>100.00000</b>

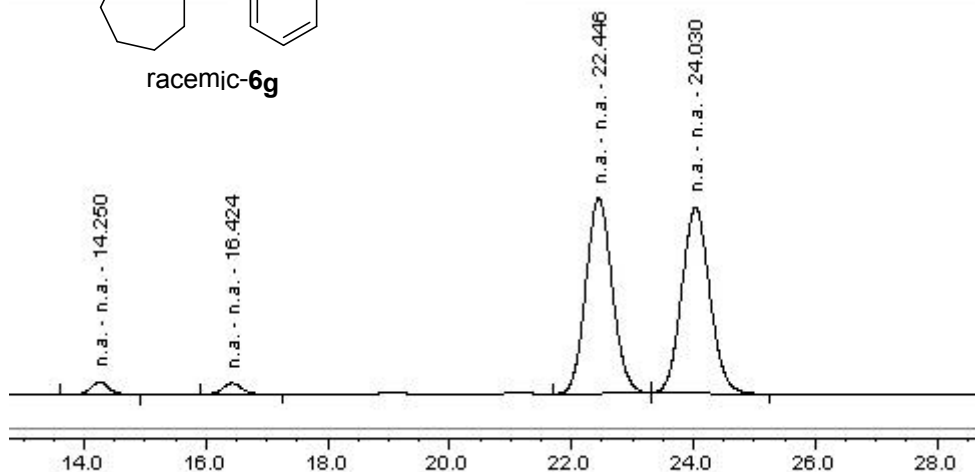
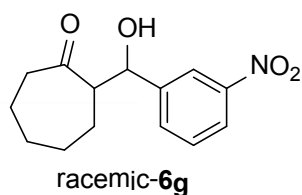


No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	17.851	30.9818	81.696	37.82
2	n.a.	24.497	30.9947	53.138	37.84
3	n.a.	30.384	9.4381	16.239	11.52
4	n.a.	31.231	10.5050	14.987	12.82
<b>Total:</b>			<b>81.9196</b>		<b>100.00000</b>

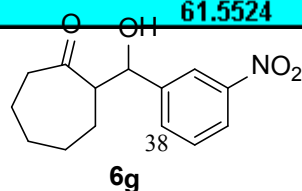


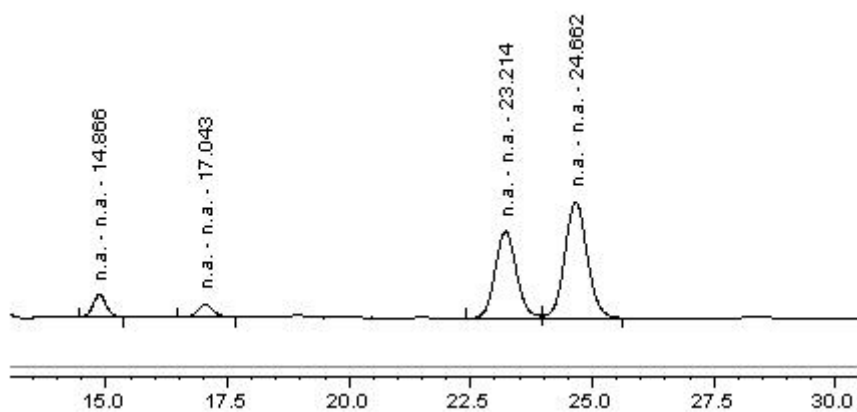


No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	18.172	2.9557	6.781	17.73
2	n.a.	25.302	1.2834	2.354	7.70
3	n.a.	30.866	1.9973	3.473	11.98
4	n.a.	31.868	10.4308	14.813	62.58
<b>Total:</b>			<b>16.6672</b>		<b>100.00000</b>

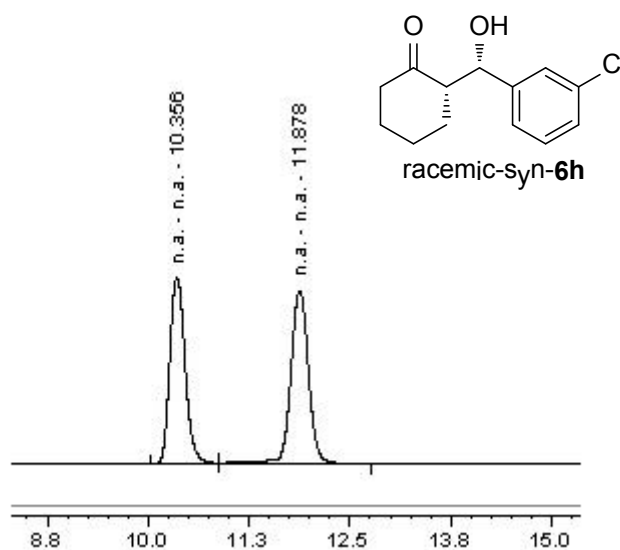


No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	14.250	1.2187	3.746	1.98
2	n.a.	16.424	1.2045	3.250	1.96
3	n.a.	22.446	29.3570	58.511	47.69
4	n.a.	24.030	29.7721	55.627	48.37
<b>Total:</b>			<b>61.5524</b>		<b>100.00000</b>

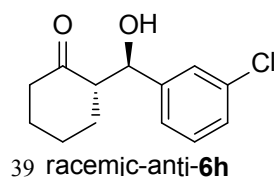


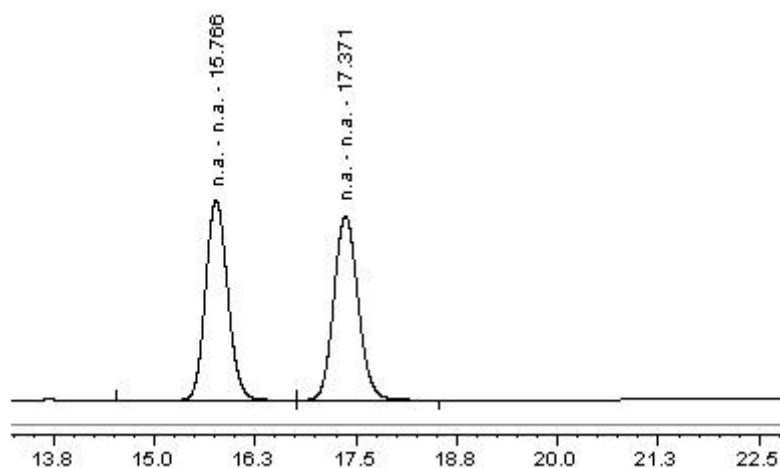


No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	14.866	0.7414	2.299	6.05
2	n.a.	17.043	0.5004	1.338	4.08
3	n.a.	23.214	4.5774	9.001	37.33
4	n.a.	24.662	6.4422	12.034	52.54
<b>Total:</b>			<b>12.2614</b>		<b>100.000000</b>

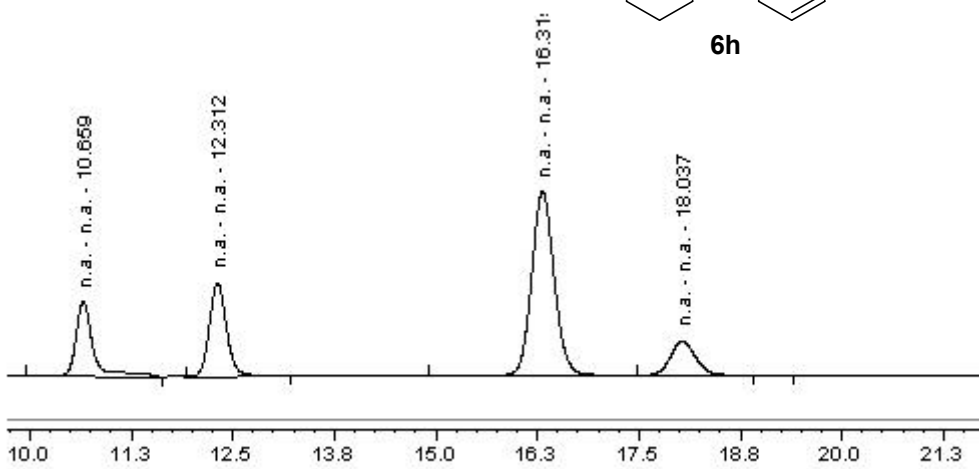
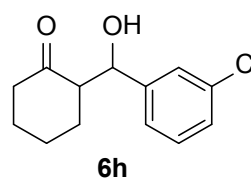


No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	10.356	480.7298	2155.678	47.87
2	n.a.	11.878	523.5057	2003.445	52.13
<b>Total:</b>			<b>1004.2354</b>		<b>100.000000</b>

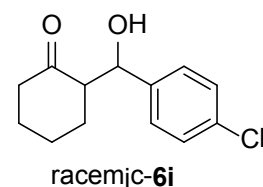




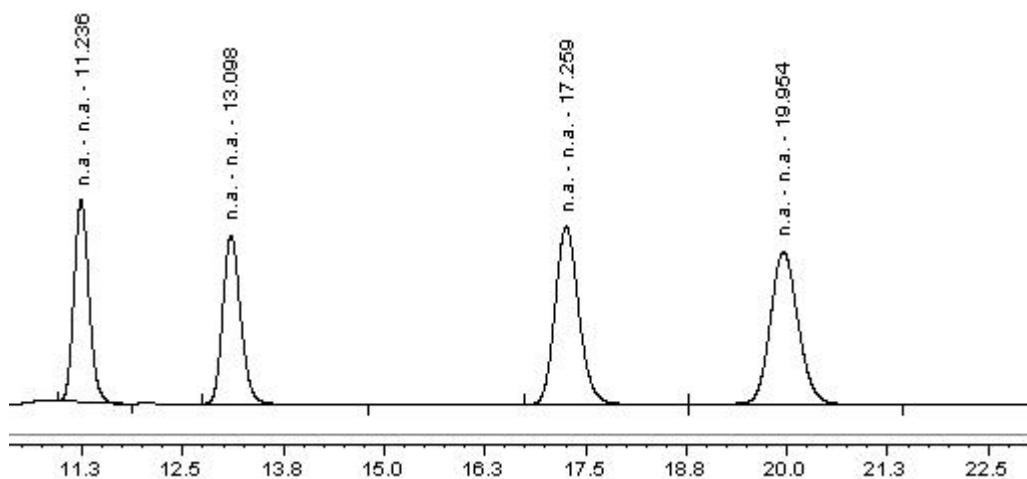
No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	15.766	543.9930	1707.031	49.76
2	n.a.	17.371	549.3037	1577.142	50.24
<b>Total:</b>			<b>1093.2967</b>		<b>100.000000</b>



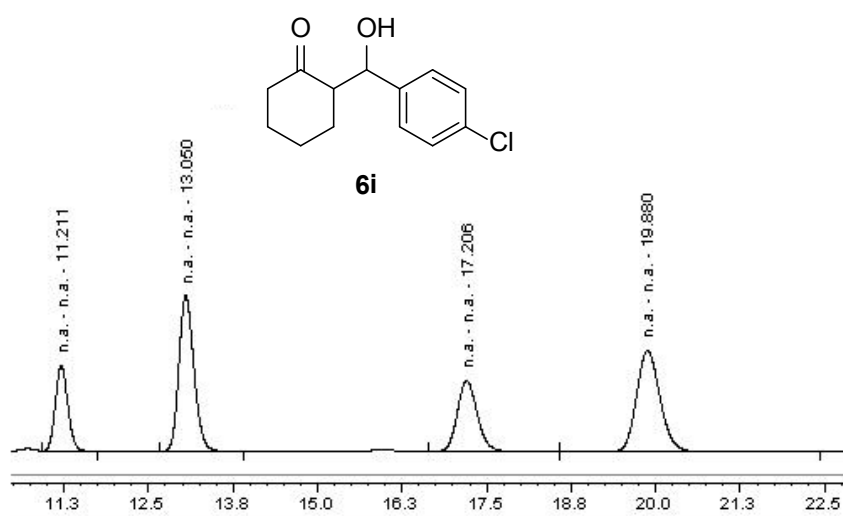
No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	10.659	20.5346	85.566	15.96
2	n.a.	12.312	26.2114	107.829	20.37
3	n.a.	16.315	68.1544	212.127	52.97
4	n.a.	18.037	13.7727	39.098	10.70
<b>Total:</b>			<b>128.6731</b>		<b>100.000000</b>



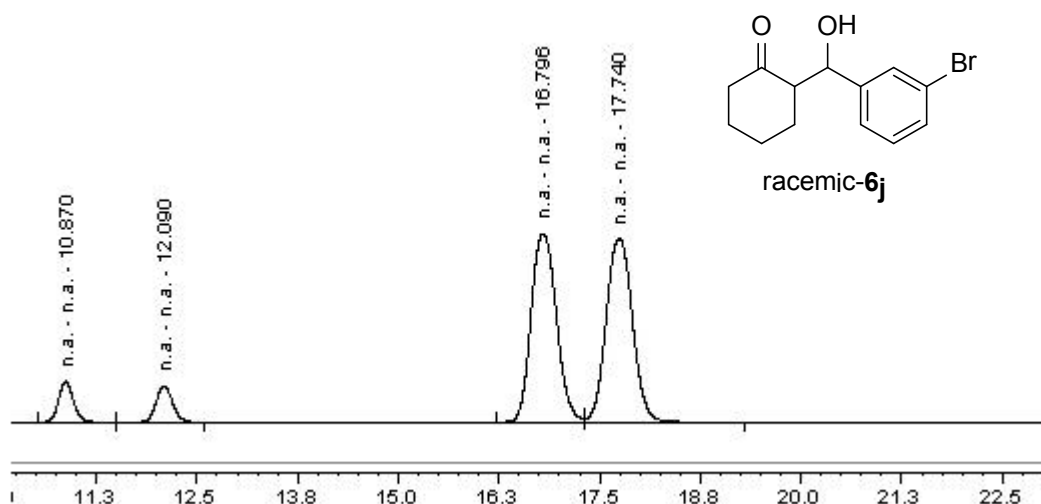




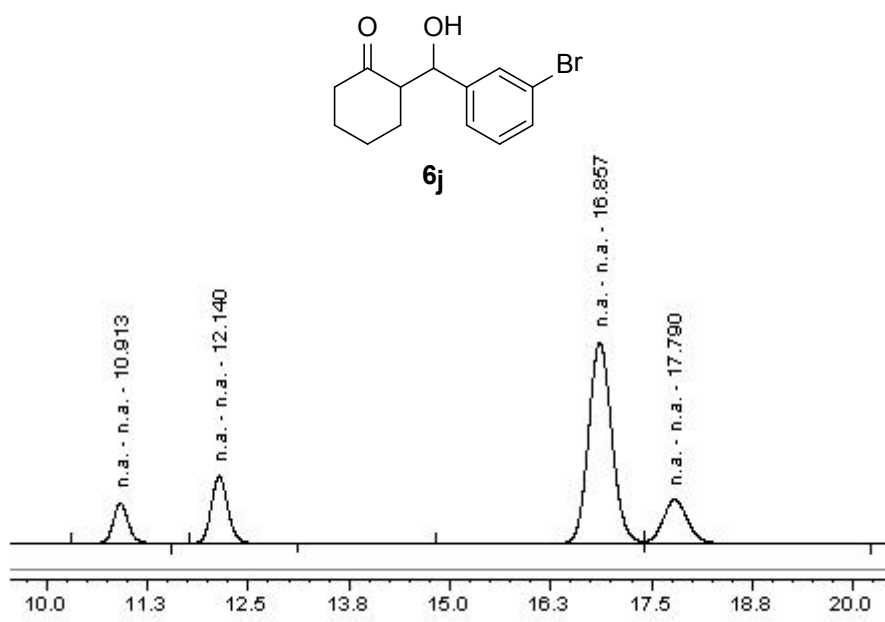
No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	11.236	150.3882	698.903	20.75
2	n.a.	13.098	150.0434	583.817	20.71
3	n.a.	17.259	211.1609	615.929	29.14
4	n.a.	19.954	212.9961	528.005	29.40
<b>Total:</b>			<b>724.5887</b>		<b>100.00000</b>



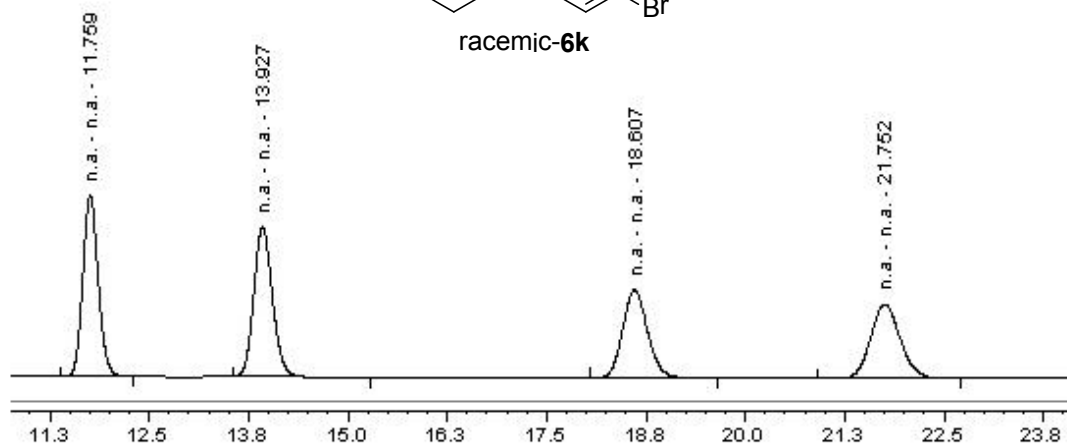
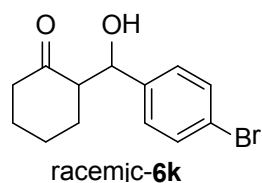
No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	11.211	161.0607	754.458	14.86
2	n.a.	13.050	354.4753	1372.281	32.71
3	n.a.	17.206	212.0110	623.679	19.56
4	n.a.	19.880	356.1520	890.713	32.86
<b>Total:</b>			<b>1083.6990</b>		<b>100.00000</b>



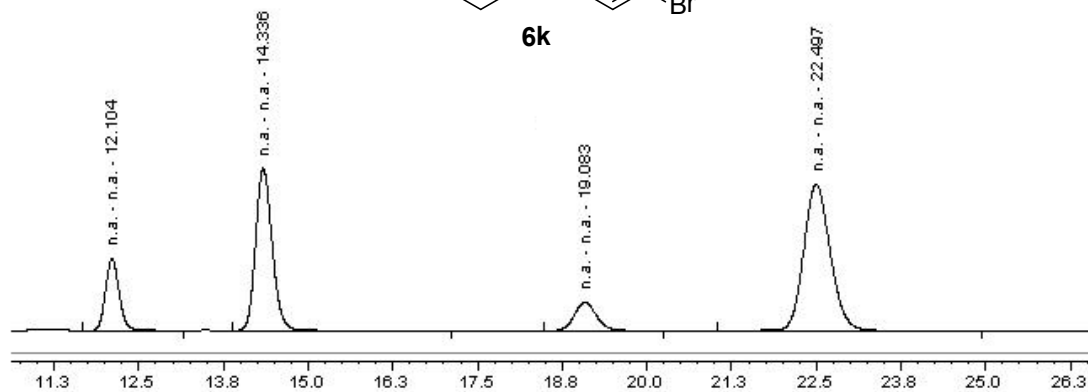
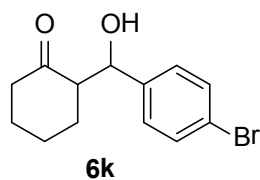
No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	10.870	108.9754	514.621	5.52
2	n.a.	12.090	108.0979	459.314	5.48
3	n.a.	16.796	870.5441	2386.878	44.12
4	n.a.	17.740	885.3910	2333.450	44.88
<b>Total:</b>			<b>1973.0084</b>		<b>100.000000</b>



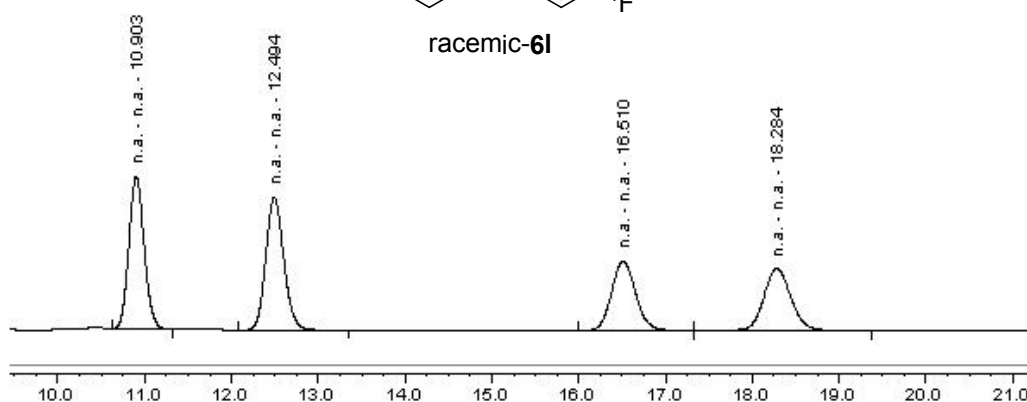
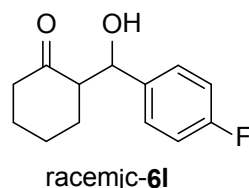
No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	10.913	33.7491	158.881	8.07
2	n.a.	12.140	61.9554	262.637	14.81
3	n.a.	16.857	262.4087	787.627	62.72
4	n.a.	17.790	60.2767	171.333	14.41
<b>Total:</b>			<b>418.3898</b>		<b>100.000000</b>



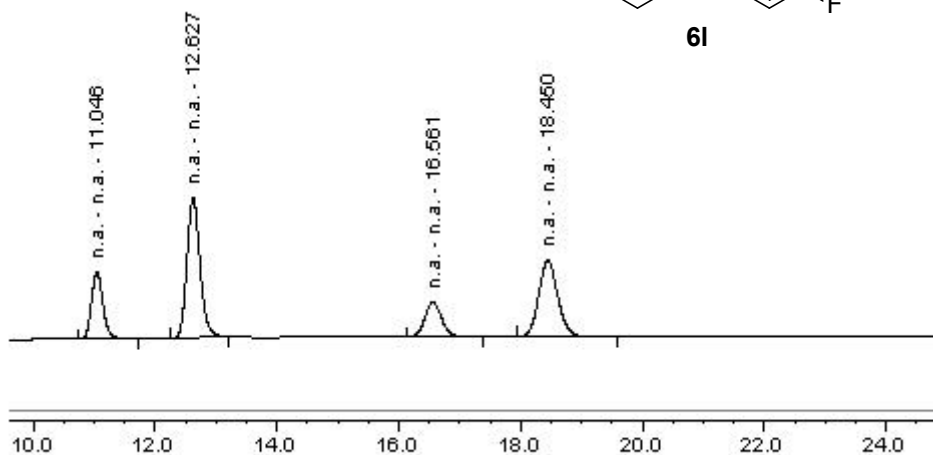
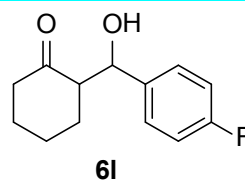
No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	11.759	81.9121	362.974	28.12
2	n.a.	13.927	81.0752	300.180	27.83
3	n.a.	18.607	64.2414	175.867	22.05
4	n.a.	21.752	64.0890	148.233	22.00
<b>Total:</b>			<b>291.3177</b>		<b>100.000000</b>



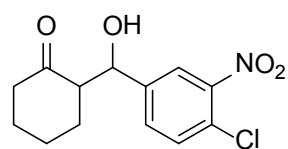
No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	12.104	80.7843	338.209	12.32
2	n.a.	14.336	215.4357	757.735	32.84
3	n.a.	19.083	49.7389	132.100	7.58
4	n.a.	22.497	309.9908	683.065	47.26
<b>Total:</b>			<b>655.9497</b>		<b>100.000000</b>



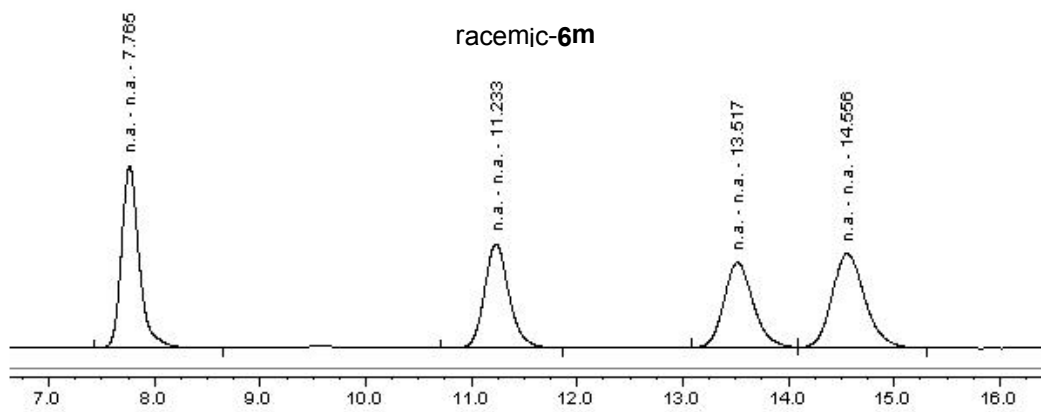
No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	10.903	46.4014	225.386	29.20
2	n.a.	12.494	47.2134	195.790	29.71
3	n.a.	16.510	32.4676	102.329	20.43
4	n.a.	18.284	32.8202	91.203	20.65
<b>Total:</b>			<b>158.9026</b>		<b>100.00000</b>



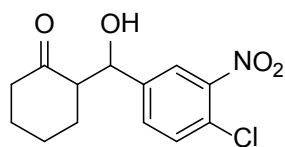
No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	11.046	10.2121	46.201	16.78
2	n.a.	12.627	24.1198	96.512	39.64
3	n.a.	16.561	7.6209	23.665	12.52
4	n.a.	18.450	18.8975	52.302	31.06
<b>Total:</b>			<b>60.8503</b>		<b>100.00000</b>



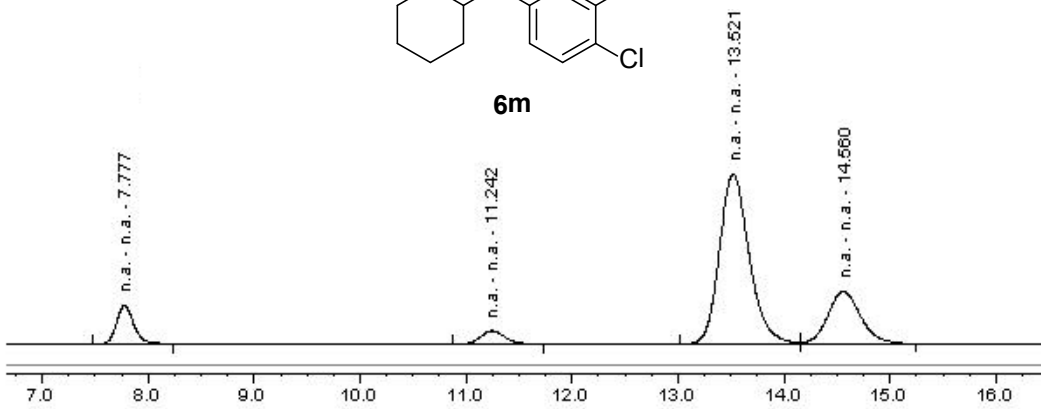
racemic-6m



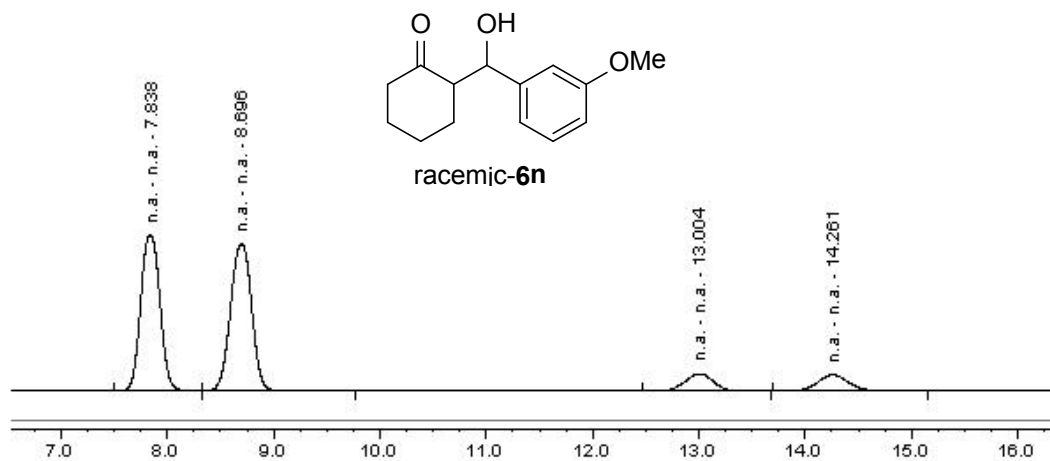
No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	7.765	8.9400	45.965	28.42
2	n.a.	11.233	7.0660	26.255	22.46
3	n.a.	13.517	6.8875	21.437	21.90
4	n.a.	14.556	8.5608	23.748	27.22
<b>Total:</b>			<b>31.4544</b>		<b>100.000000</b>



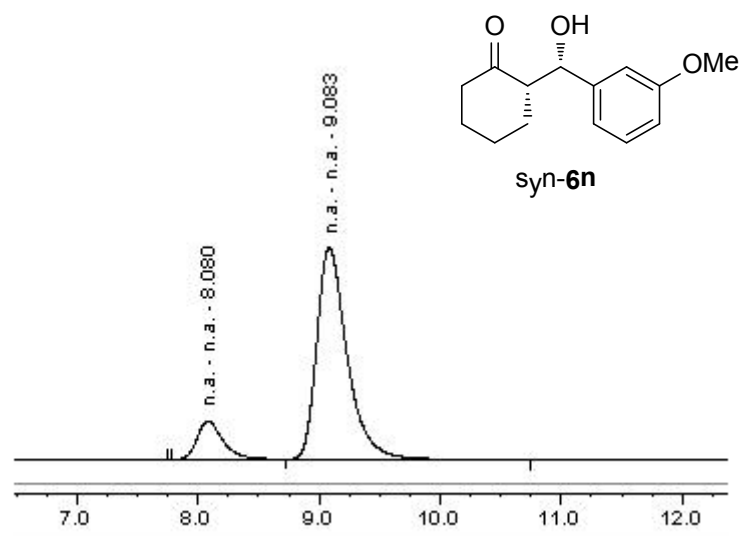
6m



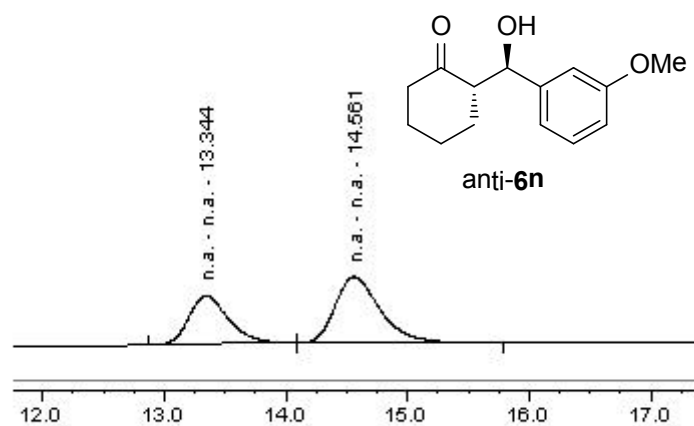
No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	7.777	1.8344	9.654	8.58
2	n.a.	11.242	0.8885	3.321	4.16
3	n.a.	13.521	13.9110	42.686	65.09
4	n.a.	14.560	4.7381	13.162	22.17
<b>Total:</b>			<b>21.3720</b>		<b>100.000000</b>



No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	7.838	555.6554	2645.655	42.11
2	n.a.	8.696	578.7786	2501.814	43.87
3	n.a.	13.004	92.3822	296.052	7.00
4	n.a.	14.261	92.5605	275.314	7.02
<b>Total:</b>			<b>1319.3767</b>		<b>100.000000</b>

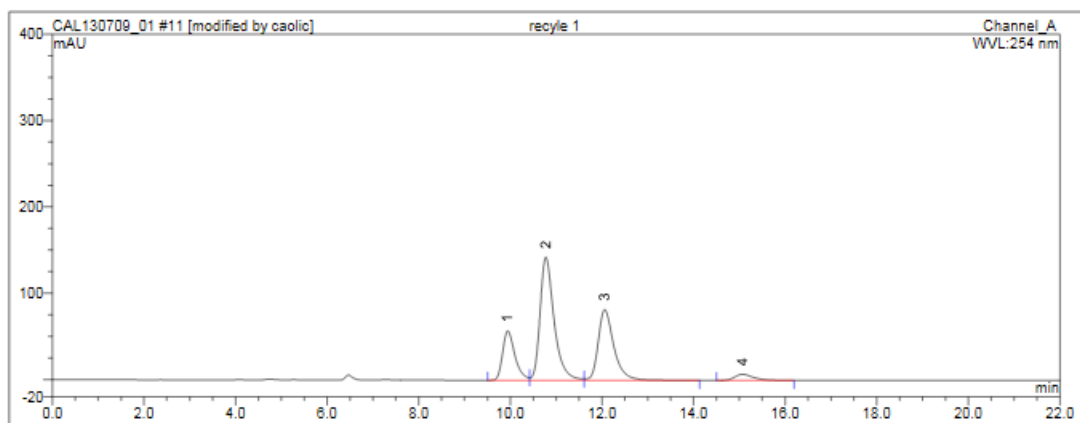


No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	8.080	81.0885	328.821	13.27
2	n.a.	9.083	530.1940	1812.032	86.73
<b>Total:</b>			<b>611.2825</b>		<b>100.000000</b>

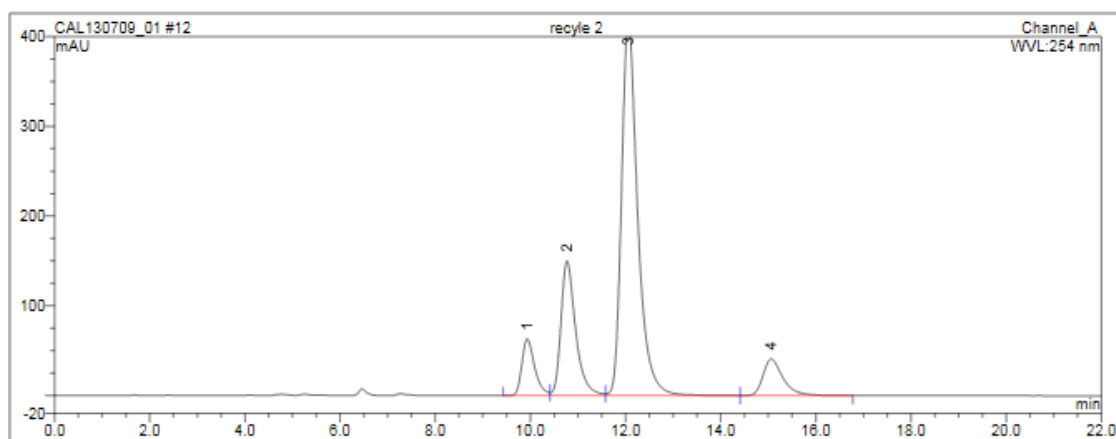


No.	Peakname	Ret.Time min	Area mAU*min	Height mAU	Rel.Area %
1	n.a.	13.344	38.3848	100.523	39.32
2	n.a.	14.561	59.2303	137.243	60.68
<b>Total:</b>			<b>97.6152</b>		<b>100.00000</b>

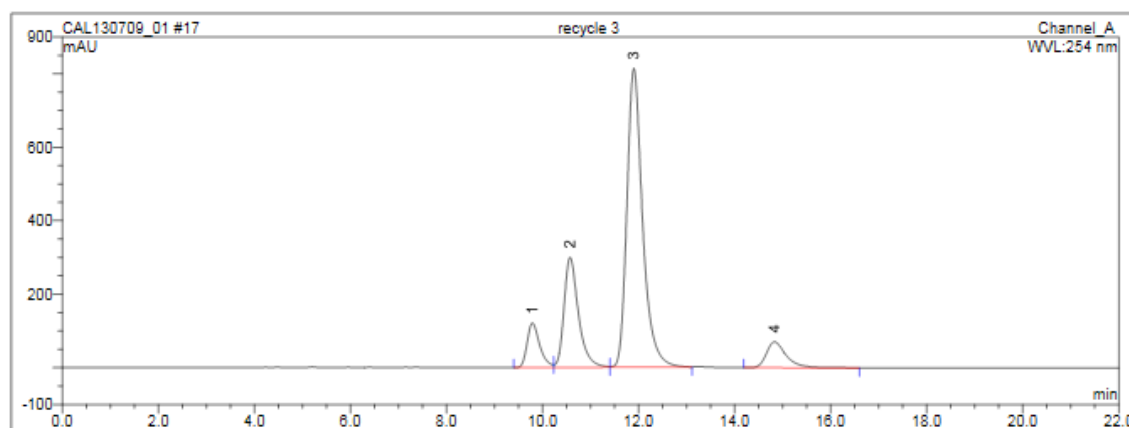
### HPLC Chromatograms data for recycle experiments



Peak	Ret.Time [min]	Peak Name	Rel.Ret.Time (to Main)	Peak Type	Area [mAU*min]	Rel.Area %	Area >=LOQ	Rel.Area >=LOQ
1	9.94	n.a.	n.a.	BM	17.861	17.0902	<LOQ	<LOQ
2	10.77	n.a.	n.a.	M	50.739	48.5484	<LOQ	<LOQ
3	12.06	n.a.	n.a.	MB	32.475	31.0733	<LOQ	<LOQ
4	15.07	n.a.	n.a.	BMB	3.436	3.2880	<LOQ	<LOQ
<b>Total:</b>							<b>0.00</b>	<b>0.00</b>

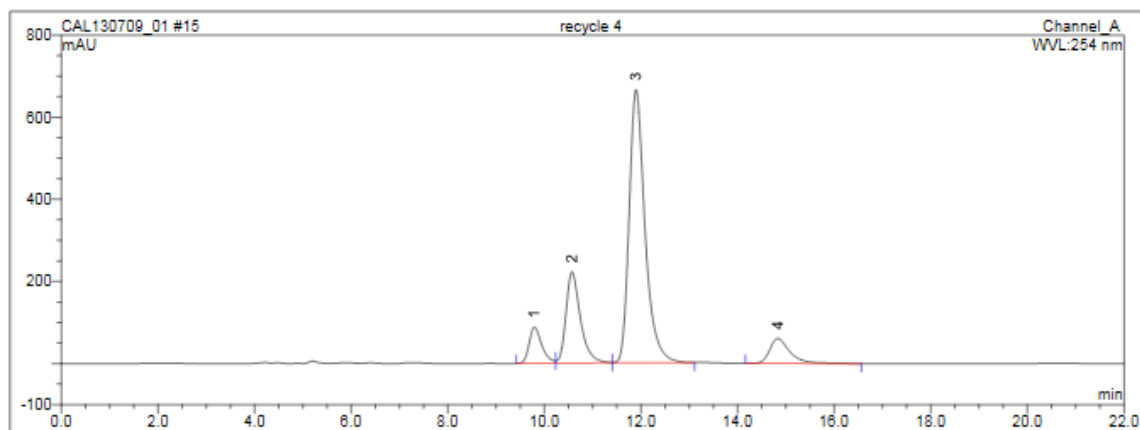


Peak	Ret.Time [min]	Peak Name	Rel.Ret.Time (to Main)	Peak Type	Area [mAU*min]	Rel.Area %	Area >=LOQ	Rel.Area >=LOQ
1	9.93	n.a.	n.a.	BM	19.730	7.6563	<LOQ	<LOQ
2	10.77	n.a.	n.a.	M	53.723	20.8475	<LOQ	<LOQ
3	12.06	n.a.	n.a.	M	164.386	63.7909	<LOQ	<LOQ
4	15.06	n.a.	n.a.	MB	19.856	7.7053	<LOQ	<LOQ
<b>Total:</b>							0.00	0.00

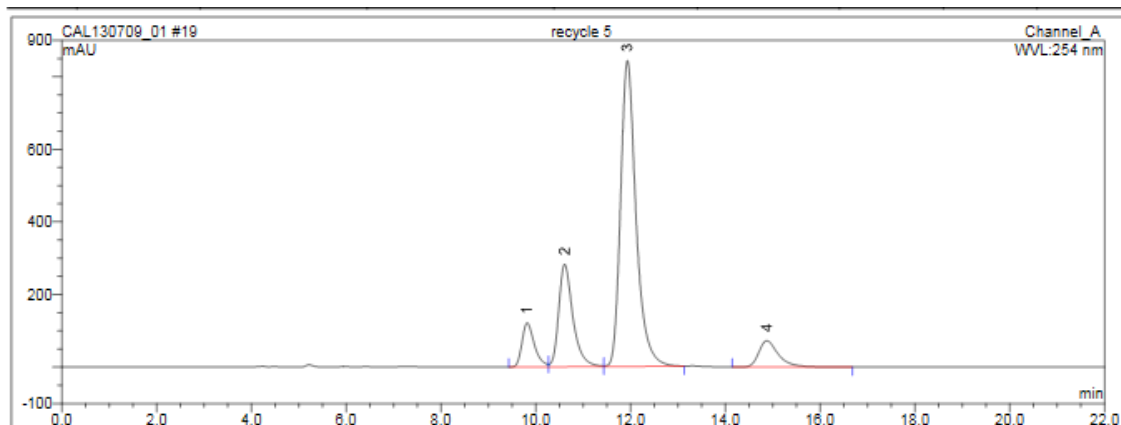


Peak	Ret.Time [min]	Peak Name	Rel.Ret.Time (to Main)	Peak Type	Area [mAU*min]	Rel.Area %	Area >=LOQ	Rel.Area >=LOQ
1	9.79	n.a.	n.a.	BM	36.858	7.6683	<LOQ	<LOQ
2	10.57	n.a.	n.a.	M	104.017	21.6407	<LOQ	<LOQ
3	11.90	n.a.	n.a.	MB	306.221	63.7089	<LOQ	<LOQ
4	14.83	n.a.	n.a.	BMB	33.560	6.9821	<LOQ	<LOQ
<b>Total:</b>							0.00	0.00

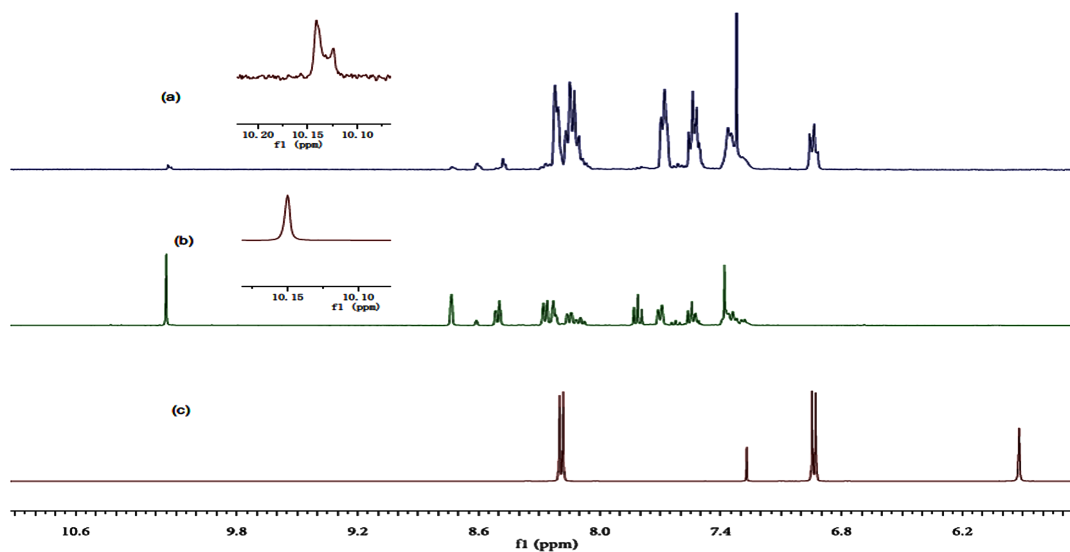




Peak	Ret.Time [min]	Peak Name	Rel.Ret.Time (to Main)	Peak Type	Area [mAU*min]	Rel.Area %	Area >=LOQ	Rel.Area >=LOQ
1	9.79	n.a.	n.a.	BM	26.596	6.9174	<LOQ	<LOQ
2	10.57	n.a.	n.a.	M	77.038	20.0367	<LOQ	<LOQ
3	11.90	n.a.	n.a.	MB	252.021	65.5474	<LOQ	<LOQ
4	14.84	n.a.	n.a.	BMB	28.831	7.4986	<LOQ	<LOQ
<b>Total:</b>							0.00	0.00



Peak	Ret.Time [min]	Peak Name	Rel.Ret.Time (to Main)	Peak Type	Area [mAU*min]	Rel.Area %	Area >=LOQ	Rel.Area >=LOQ
1	9.82	n.a.	n.a.	BM	36.872	7.5596	<LOQ	<LOQ
2	10.61	n.a.	n.a.	M	97.922	20.0763	<LOQ	<LOQ
3	11.93	n.a.	n.a.	MB	318.279	65.2545	<LOQ	<LOQ
4	14.88	n.a.	n.a.	BMB	34.677	7.1096	<LOQ	<LOQ
<b>Total:</b>							0.00	0.00



**Fig. 2.**  $^1\text{H}$  NMR spectra for different reaction systems and *p*-nitrophenol. (a) The reaction mixture of 3-nitrobenzaldehyde, cyclohexanone and organocatalyst 2 with *p*-nitrophenol as cocatalyst; (b) The same reaction conditions with (a) without *p*-nitrophenol; (c)  $^1\text{H}$  NMR spectrum of *p*-nitrophenol.

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