

OXIDATION OF UNACTIVATED C–H BONDS
CATALYZED BY MANGANESE COMPLEXES:
CONTROL OVER SITE- SELECTIVITY AND
ENANTIOSELECTIVITY

Michela Milan

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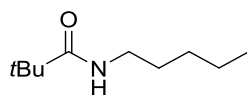
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Digital Experimental Section

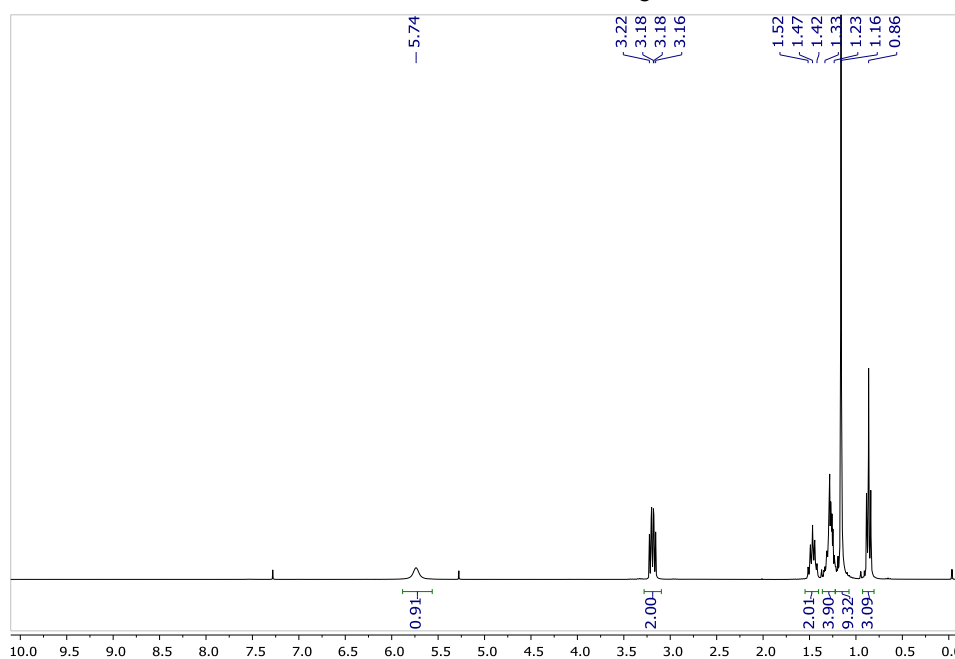
Experimental Section: Chapter VI.1

Tuning Selectivity in Aliphatic C–H Bond Oxidation of *N*-Alkylamides and Phthalimides Catalyzed by Manganese Complexes

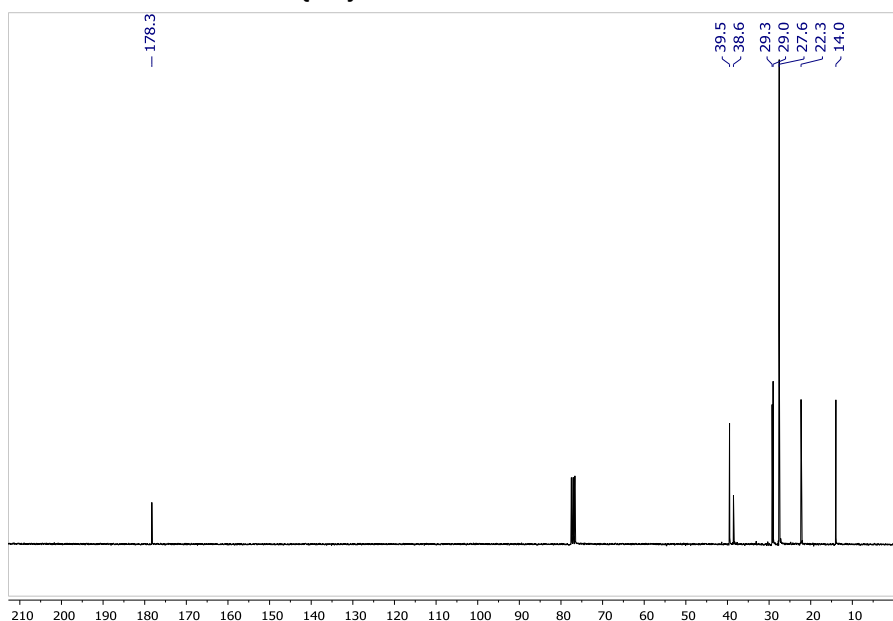
A1 ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of substrates

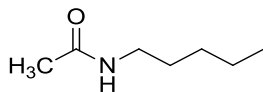


^1H -NMR of **S1** in CDCl_3

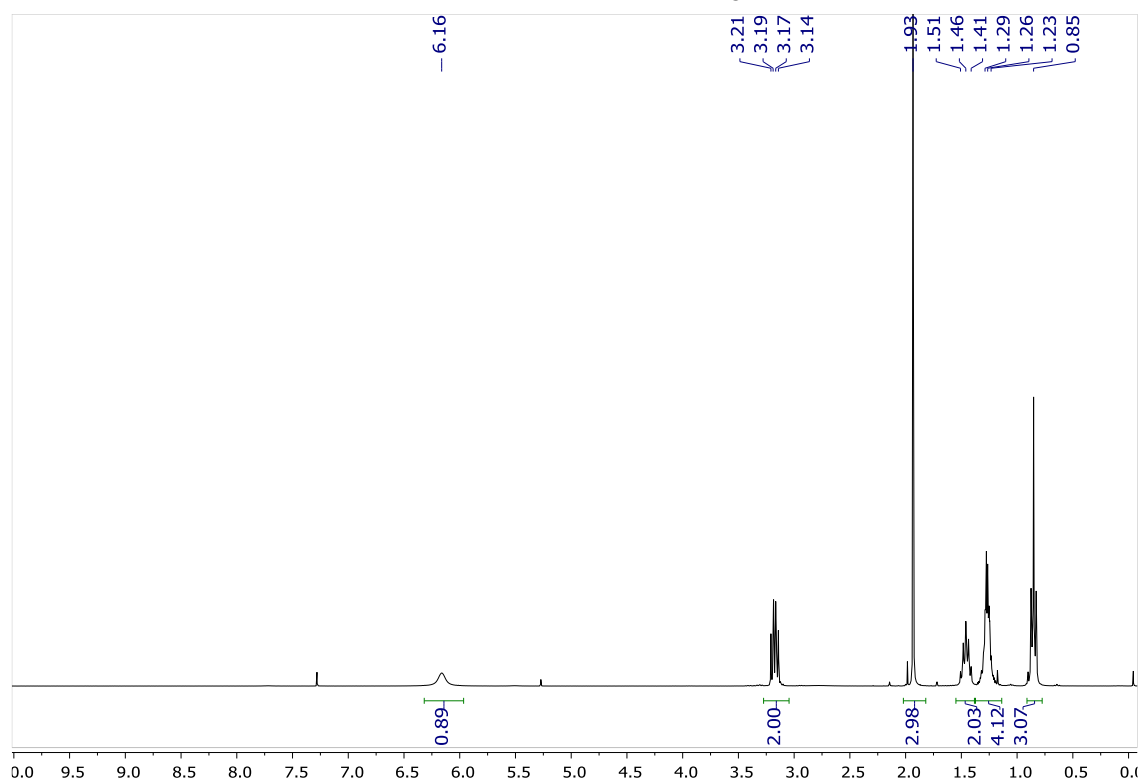


$^{13}\text{C}\{^1\text{H}\}$ -NMR of **S1** in CDCl_3

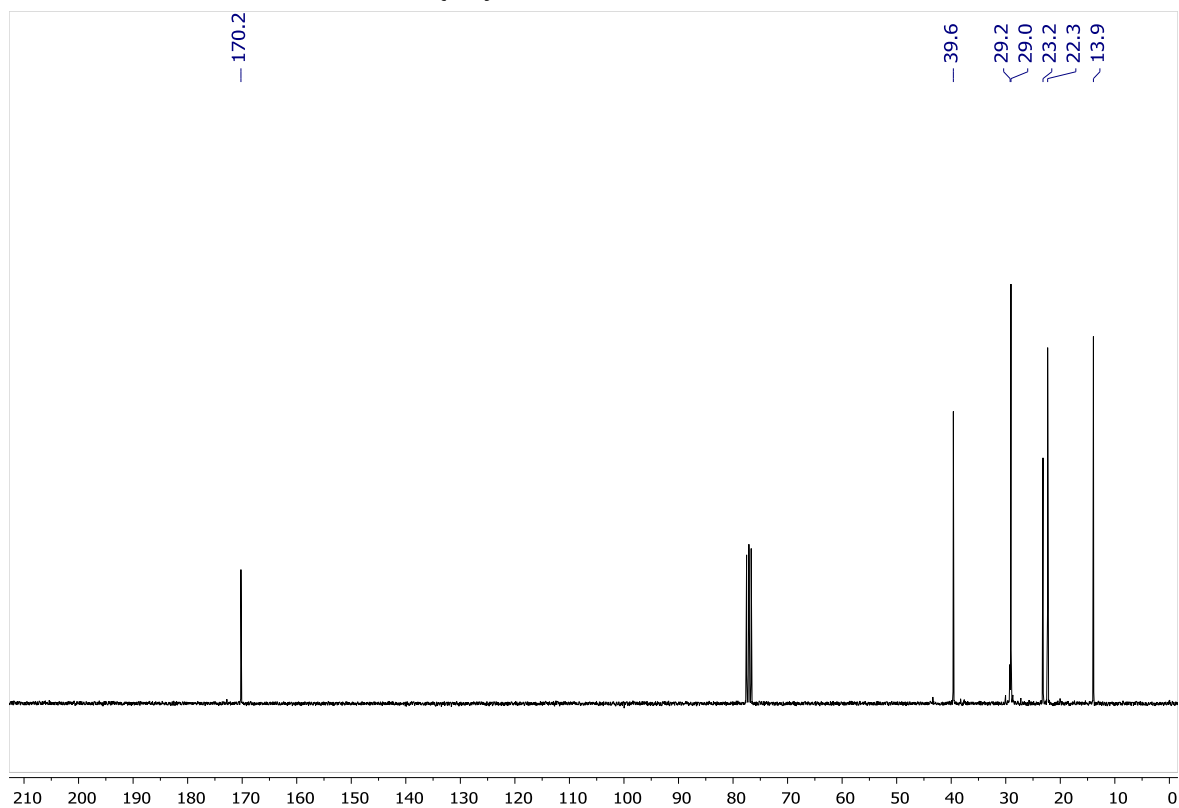


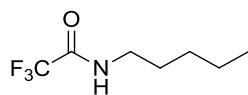
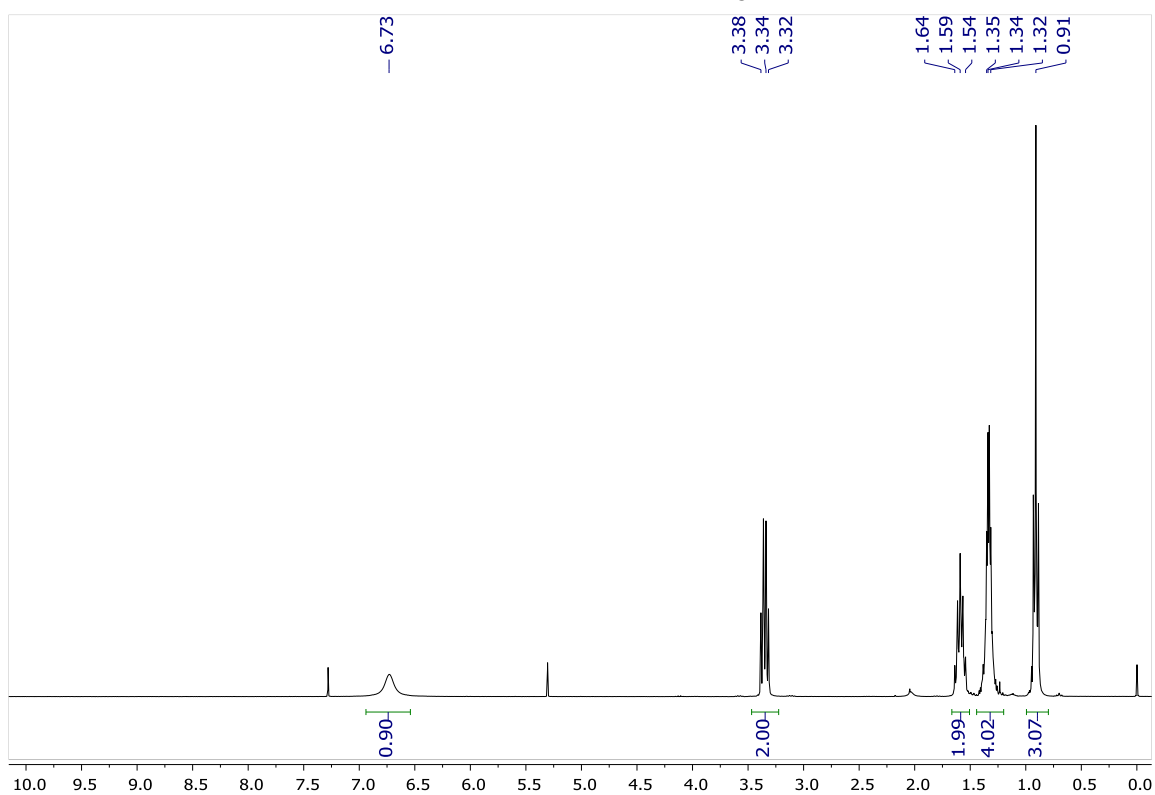
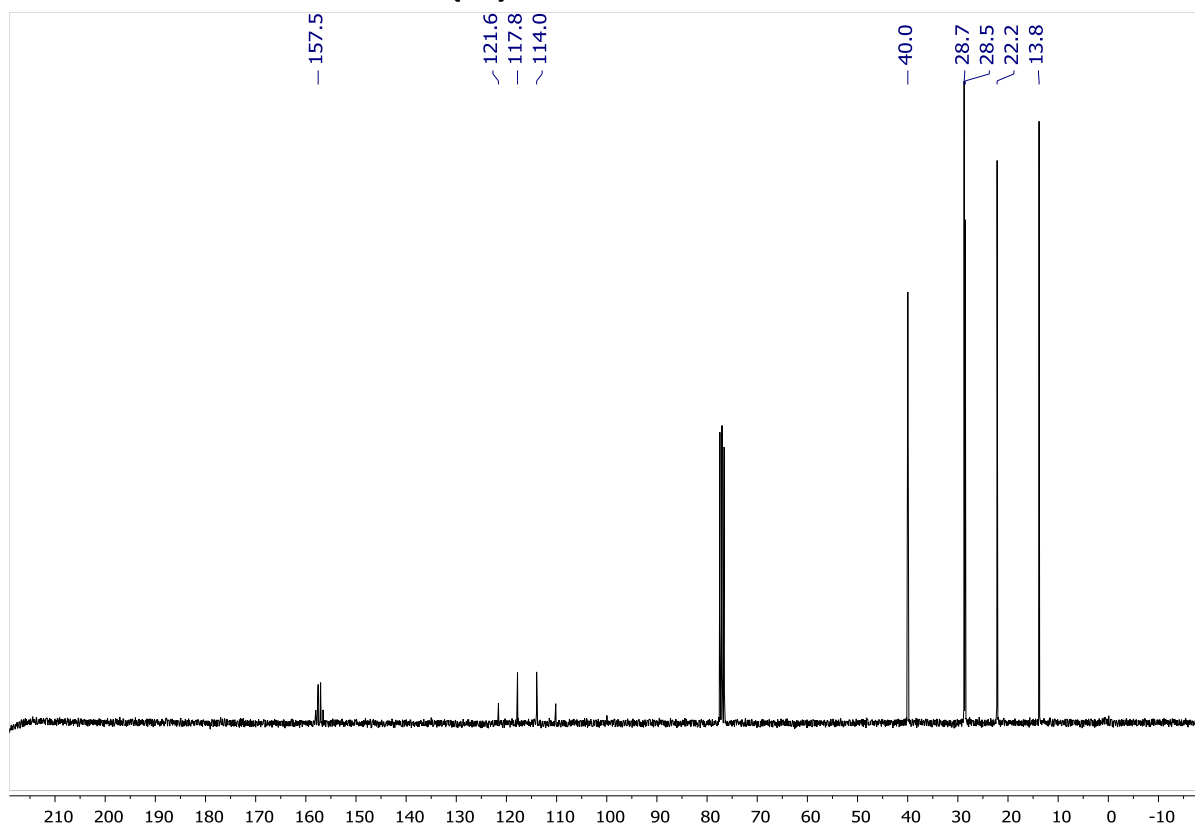


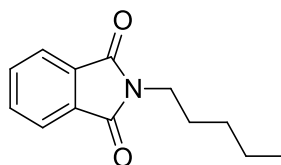
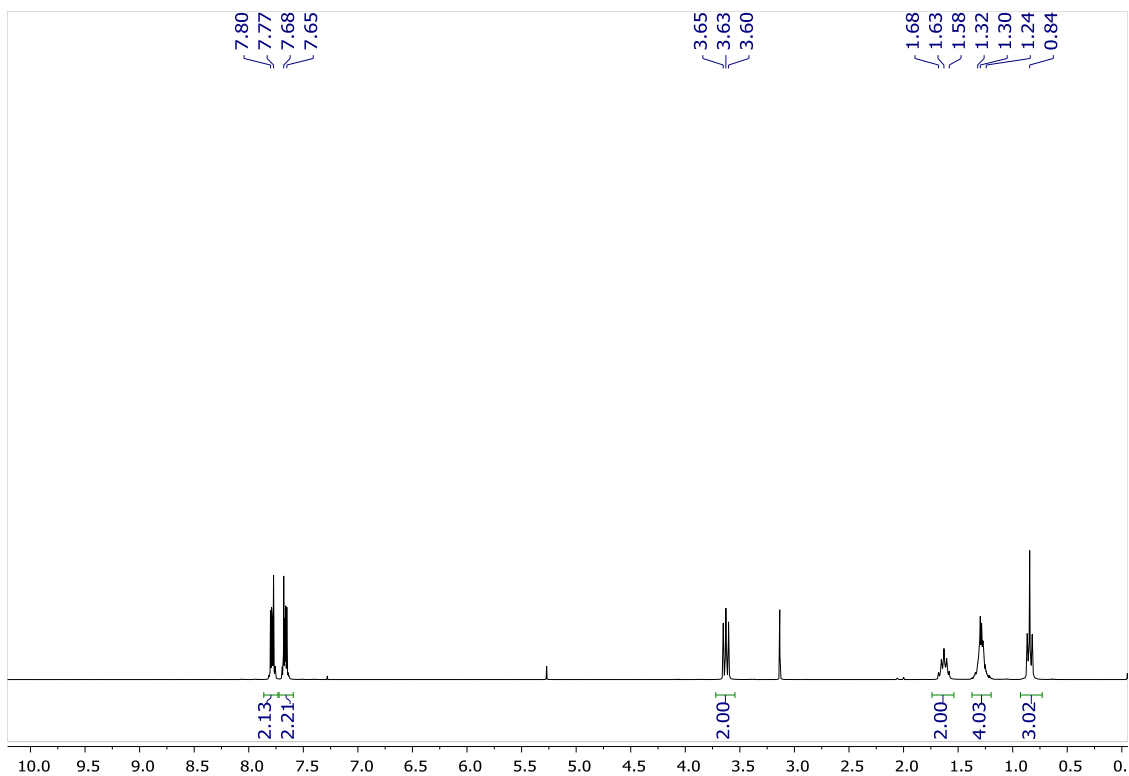
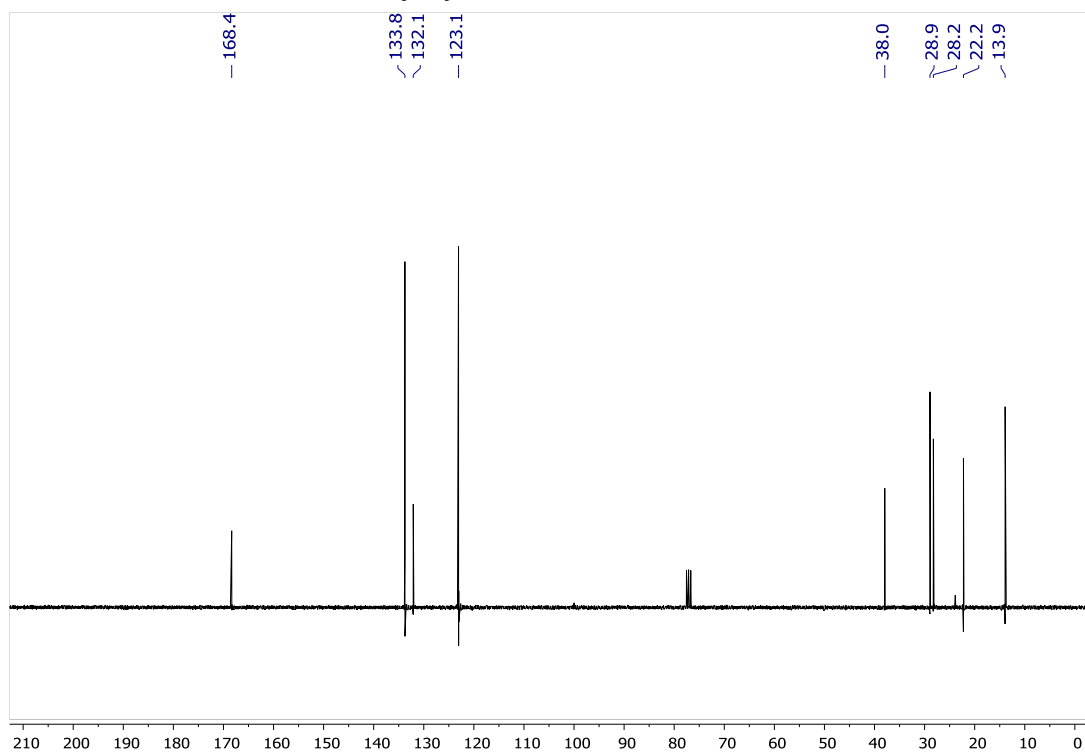
$^1\text{H-NMR}$ of **S2** in CDCl_3

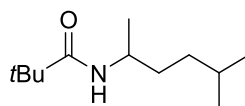
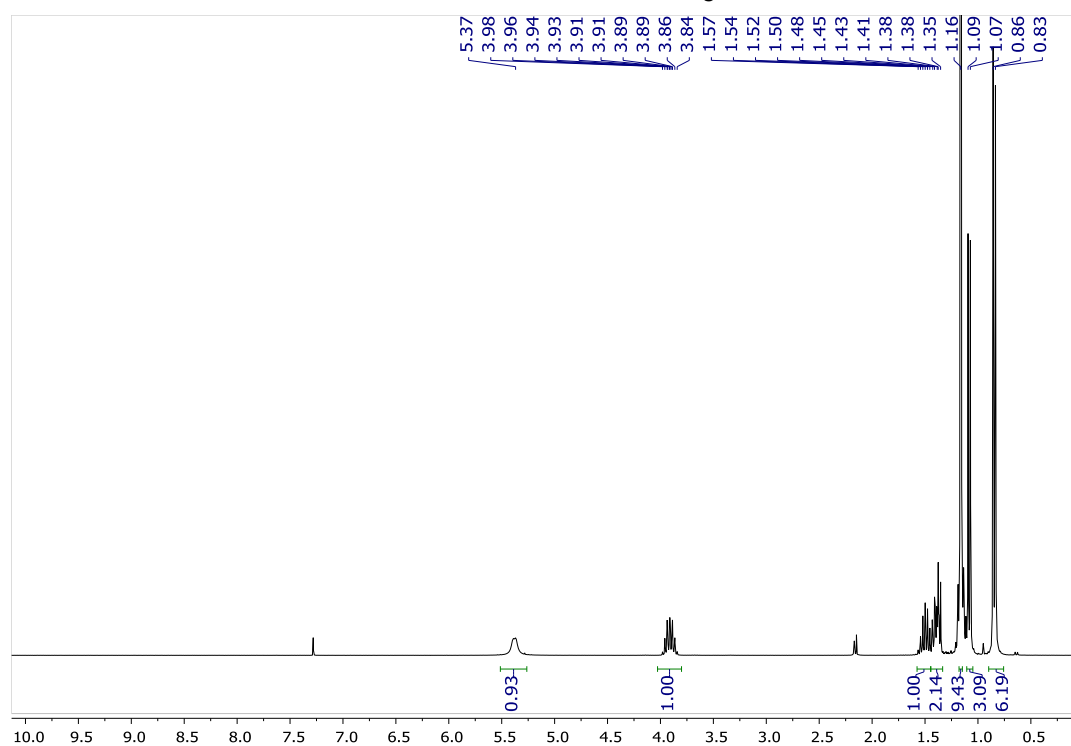
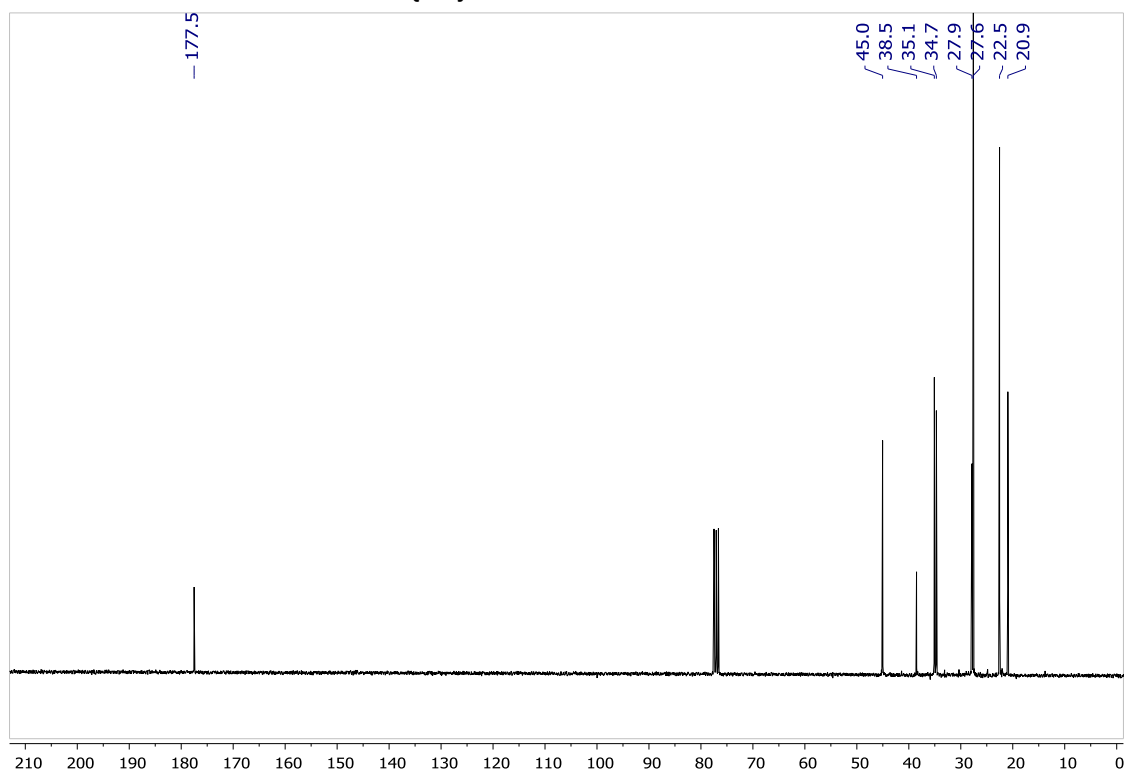


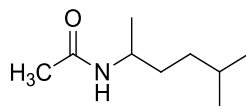
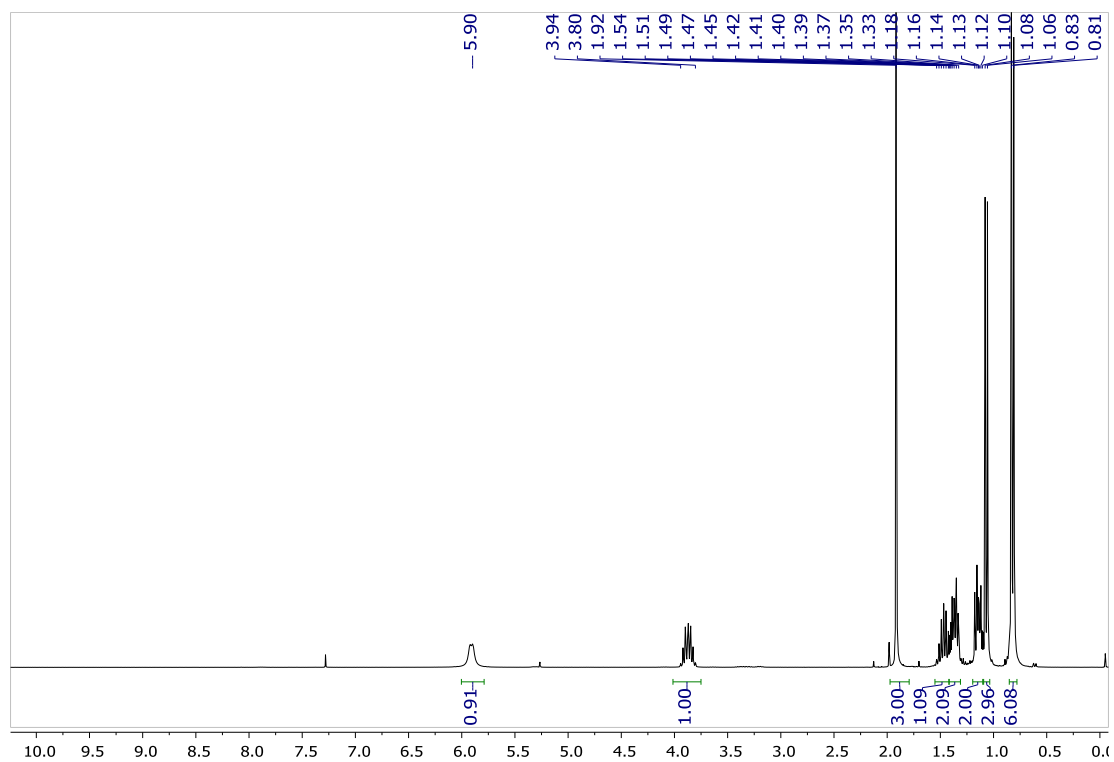
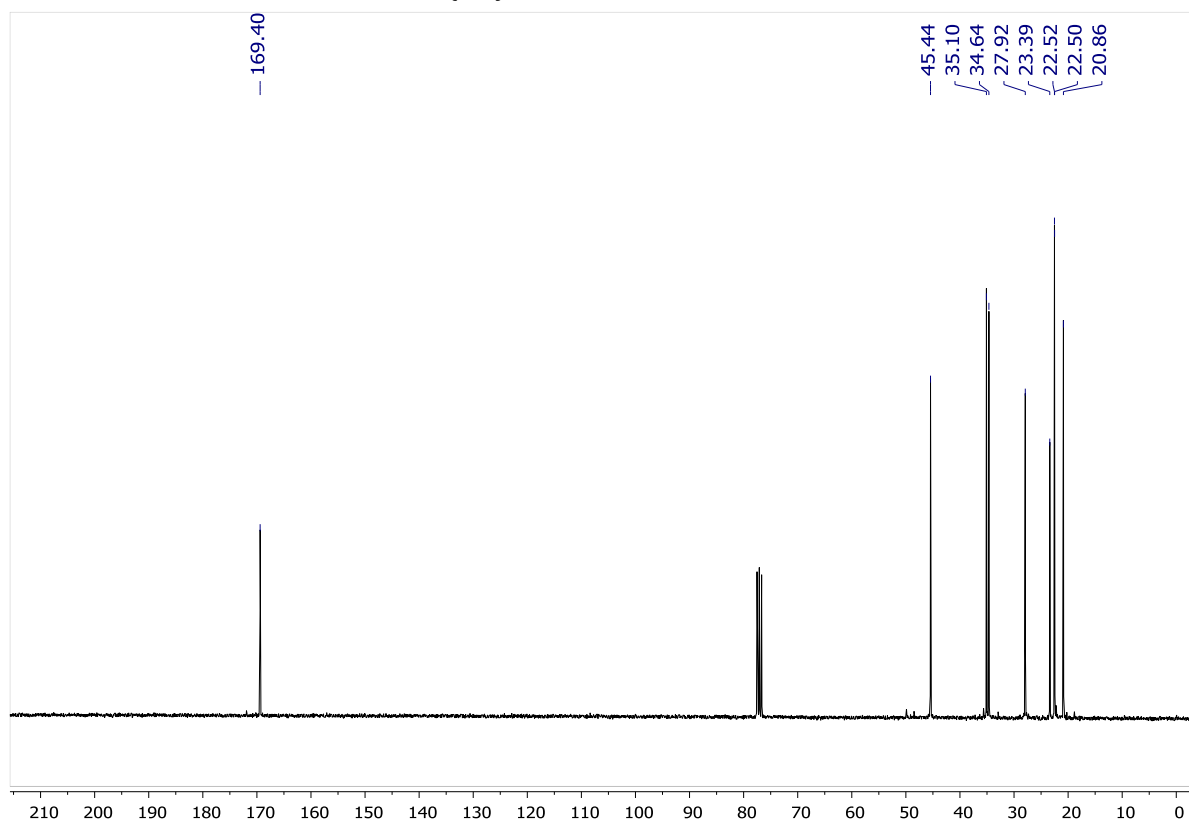
$^{13}\text{C}\{^1\text{H}\}$ -NMR of **S2** in CDCl_3

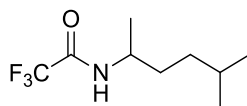
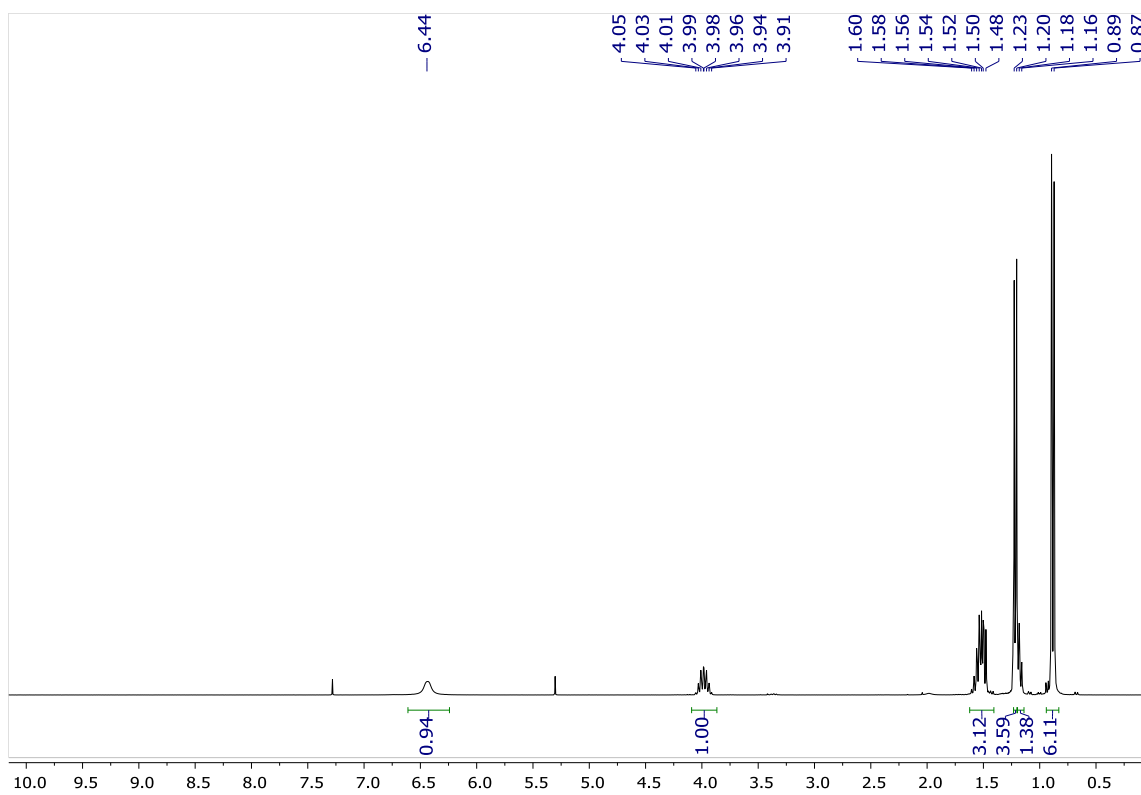
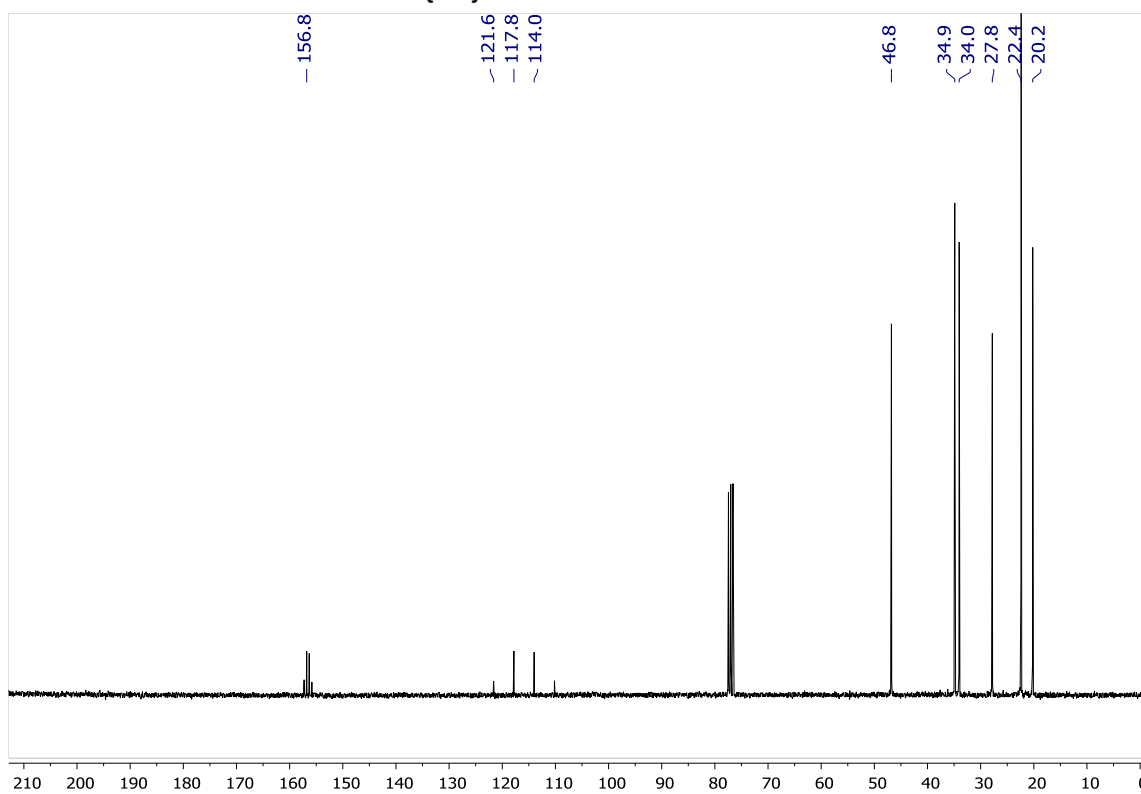


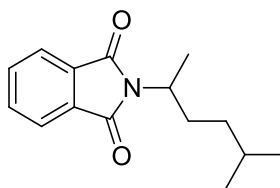
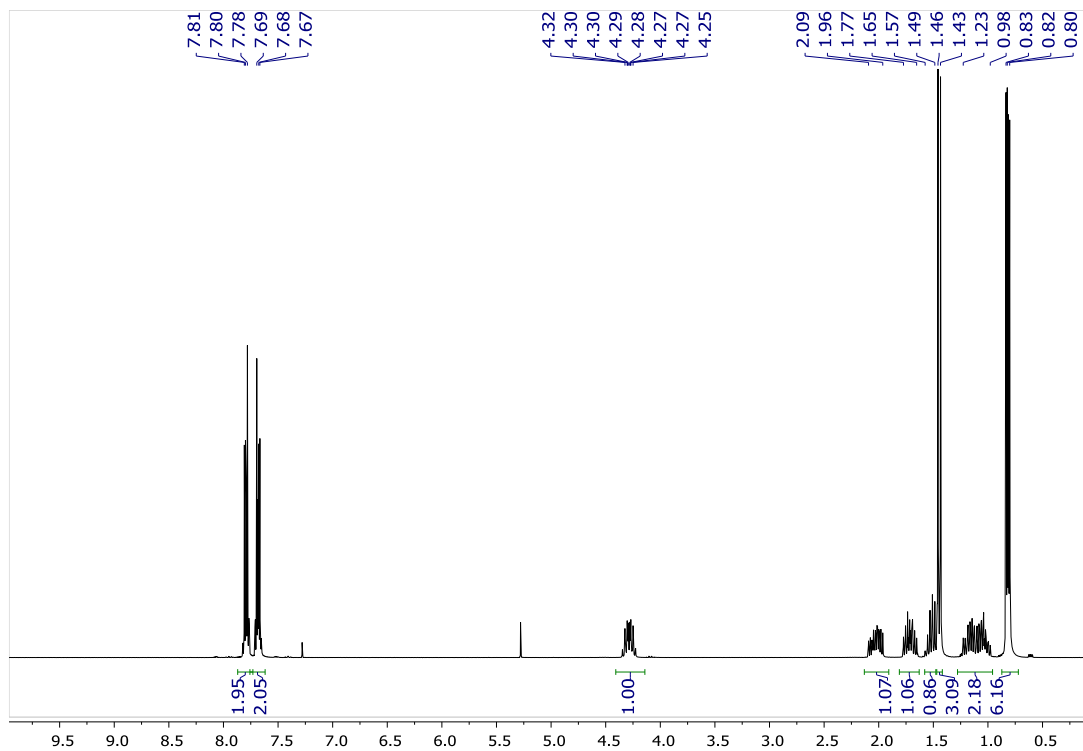
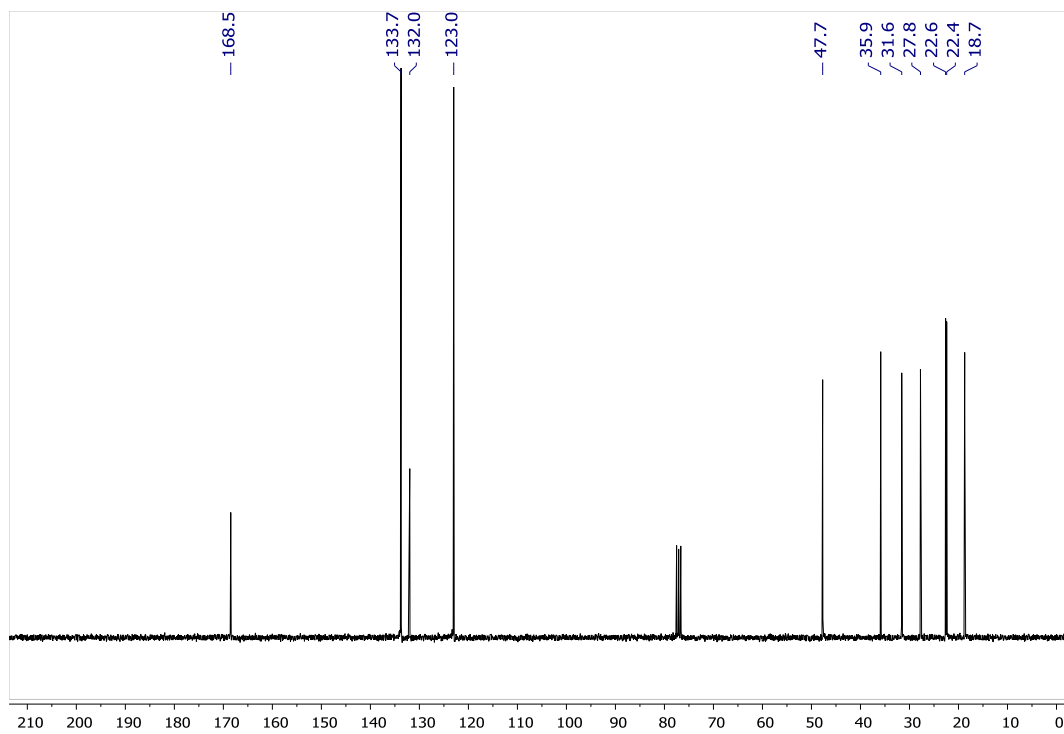
 $^1\text{H-NMR}$ of **S3** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S3** in CDCl_3 

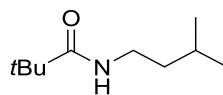
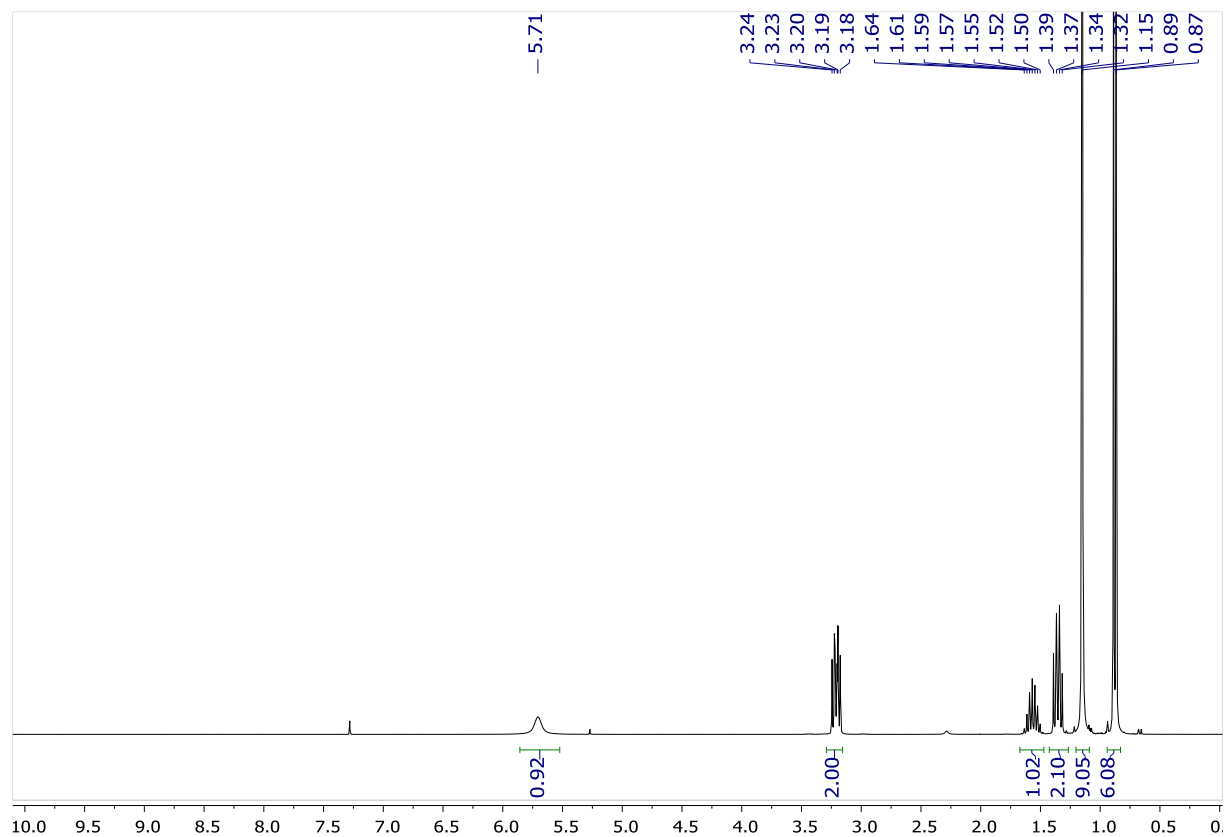
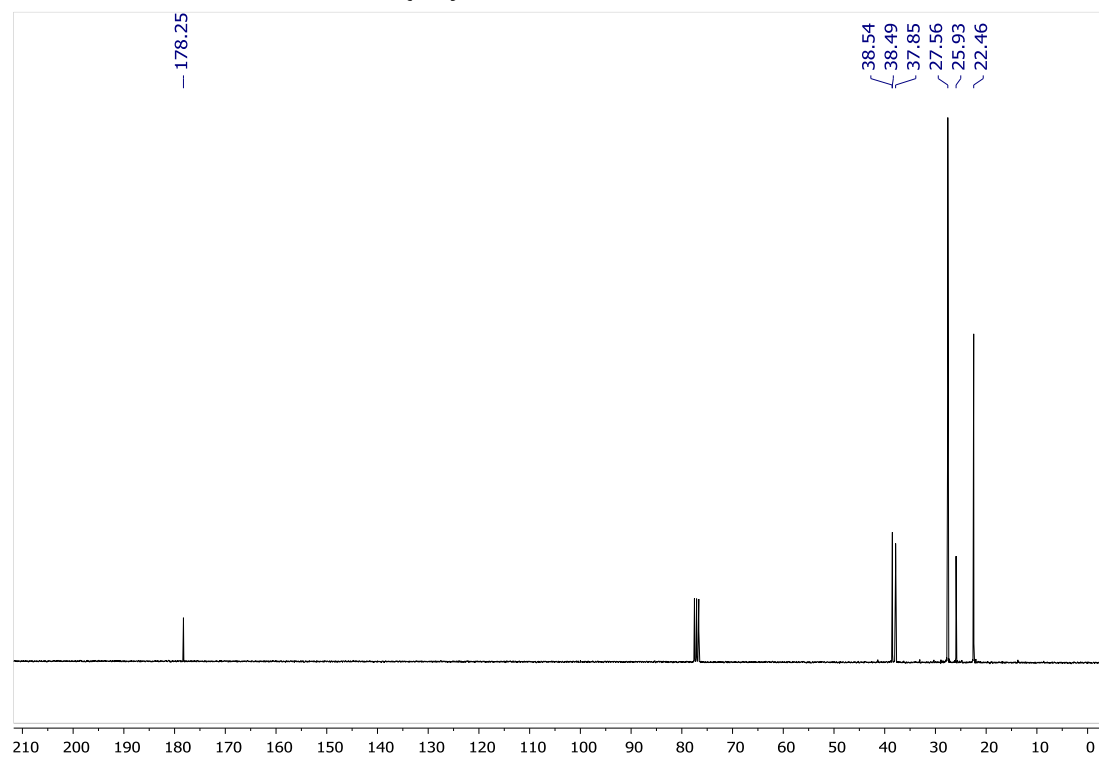
 $^1\text{H-NMR}$ of **S4** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S4** in CDCl_3 

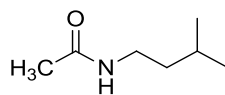
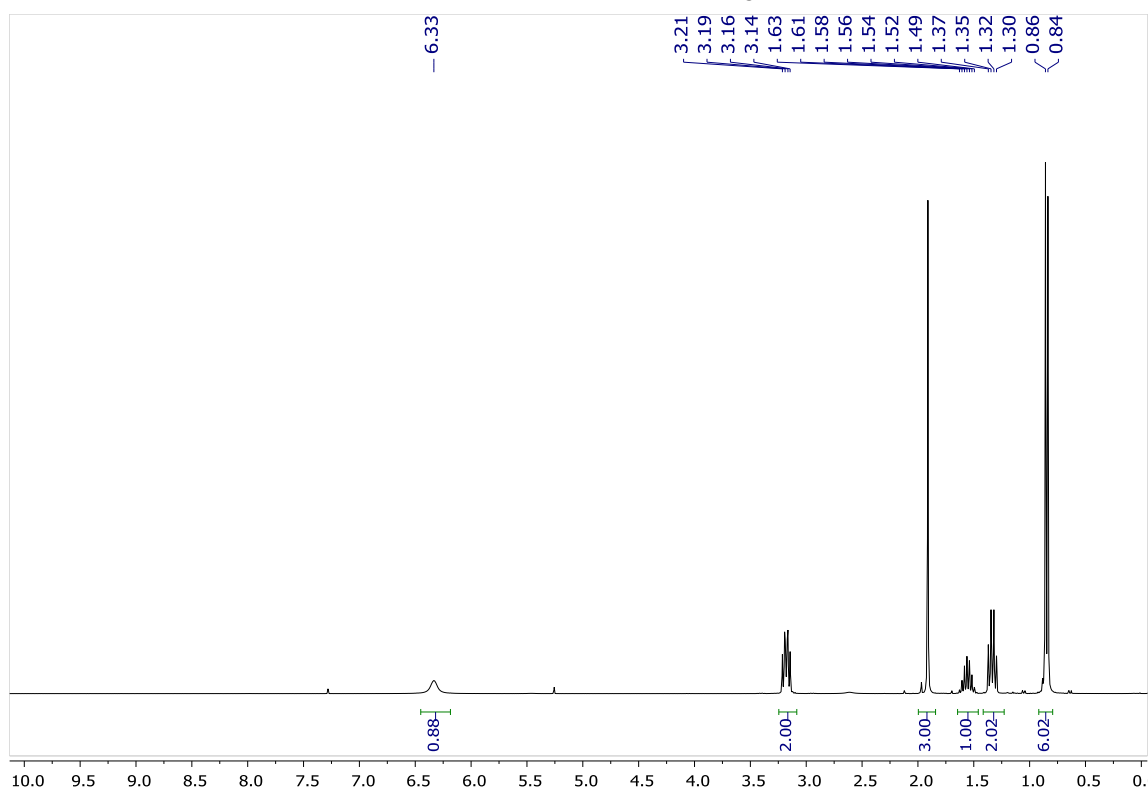
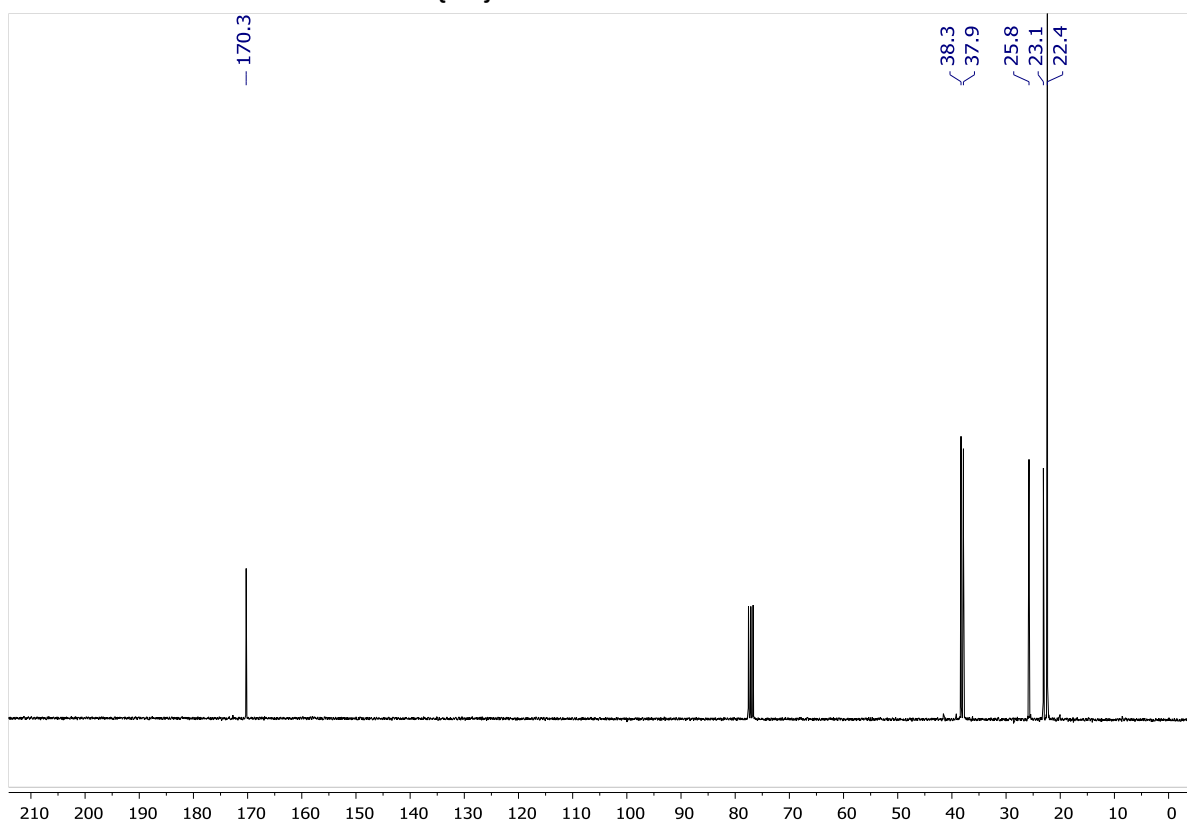
 $^1\text{H-NMR}$ of **S5** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S5** in CDCl_3 

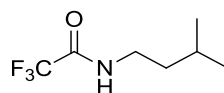
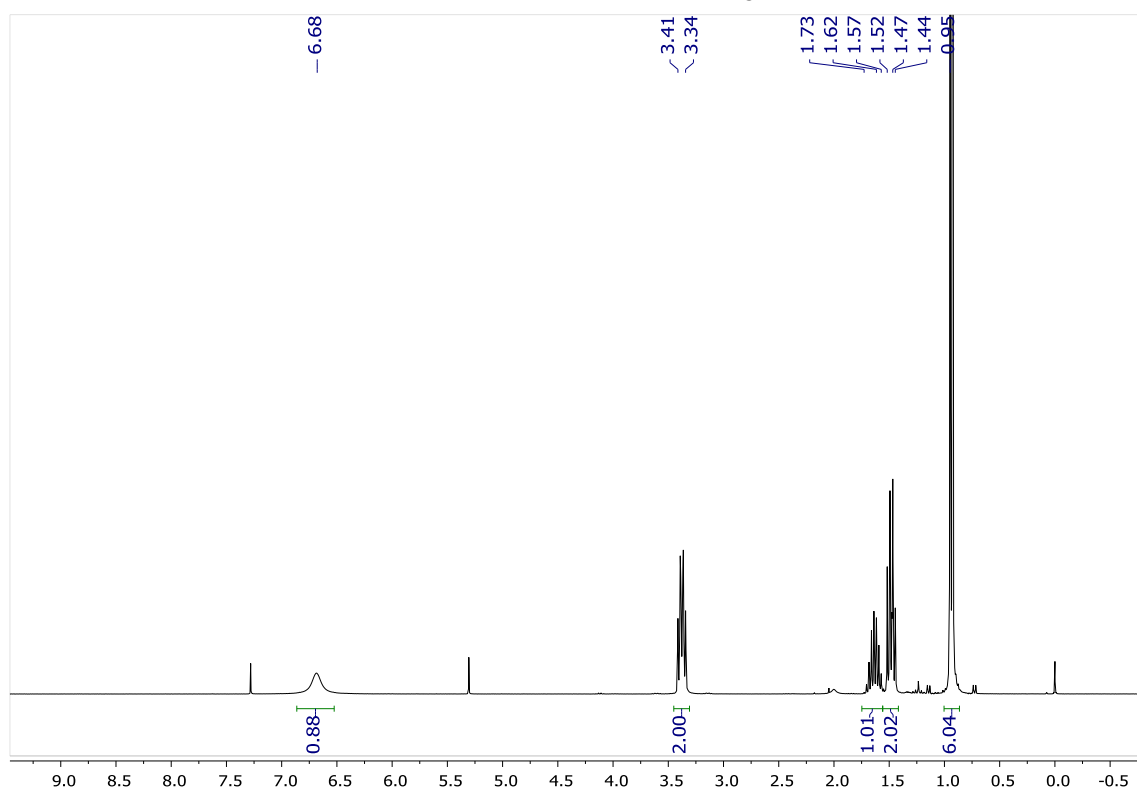
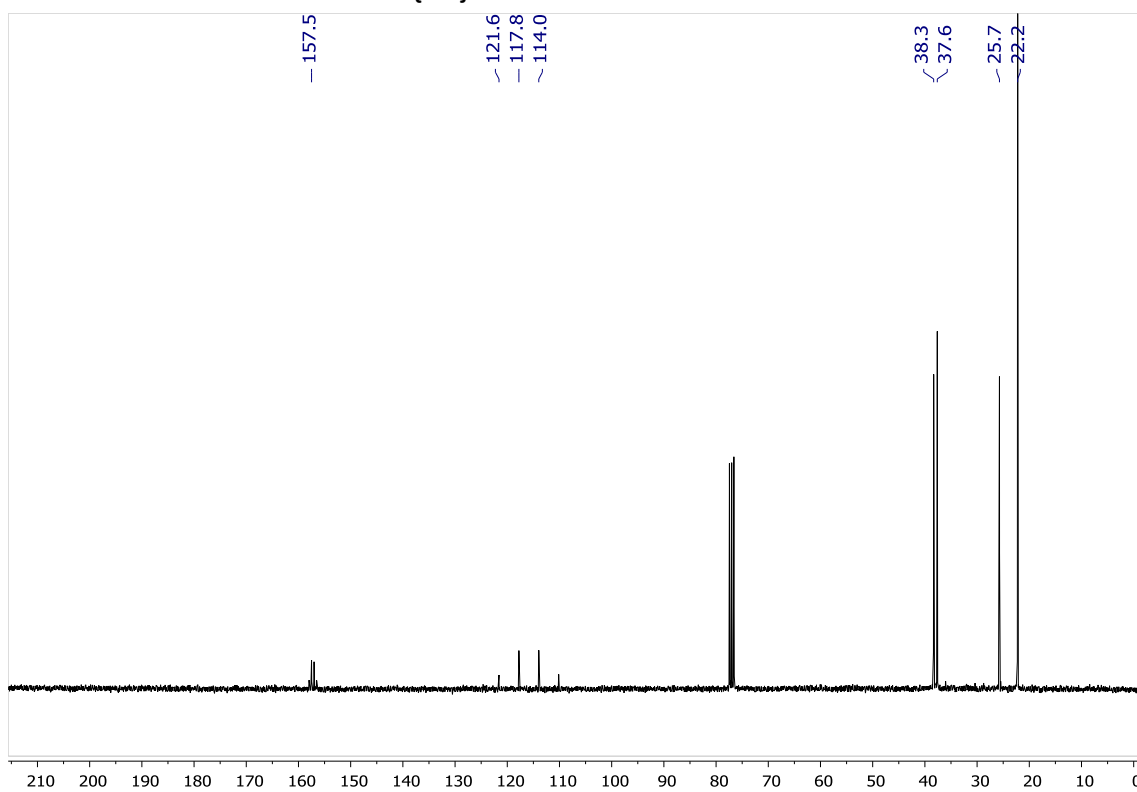
 $^1\text{H-NMR}$ of **S6** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S6** in CDCl_3 

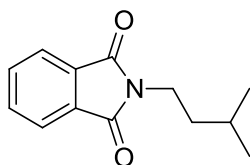
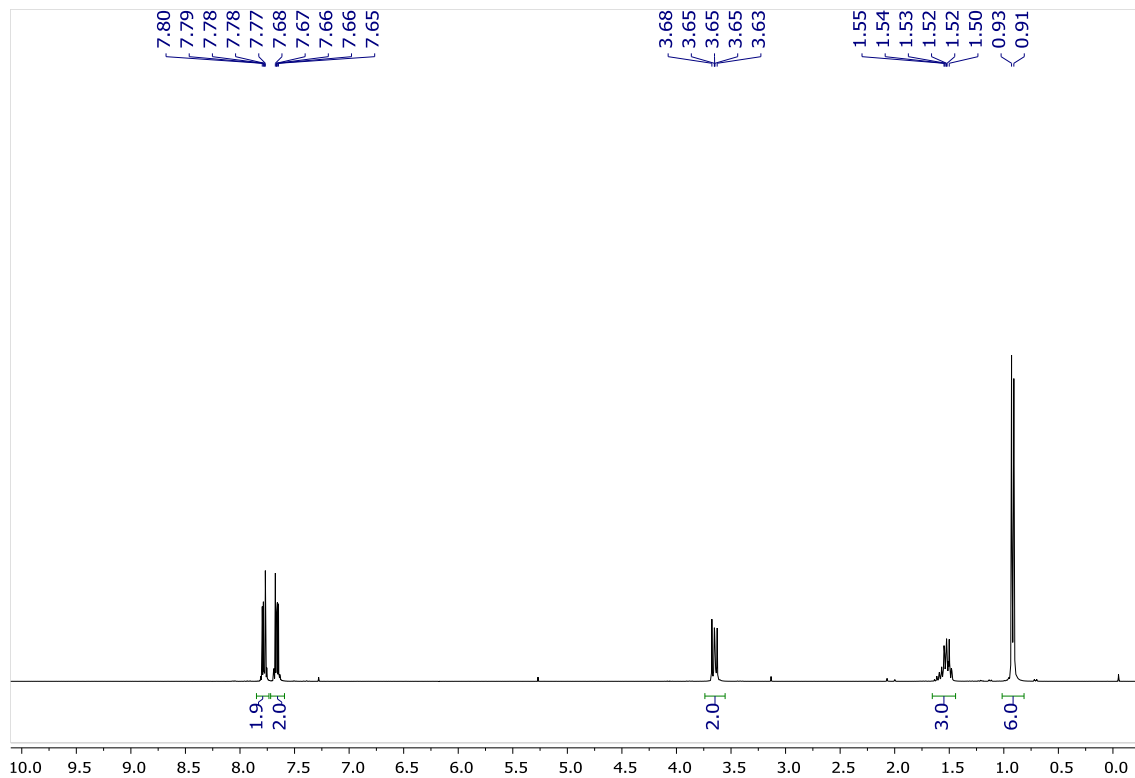
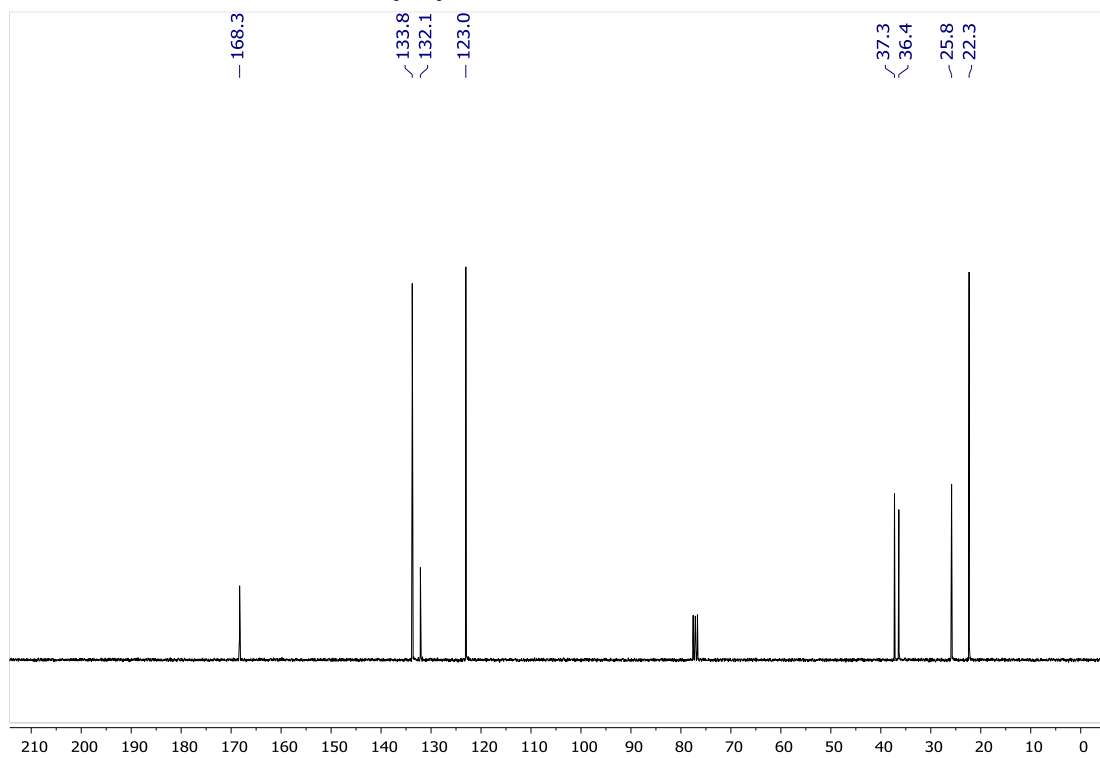
 $^1\text{H-NMR}$ of **S7** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S7** in CDCl_3 

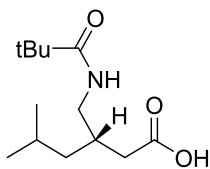
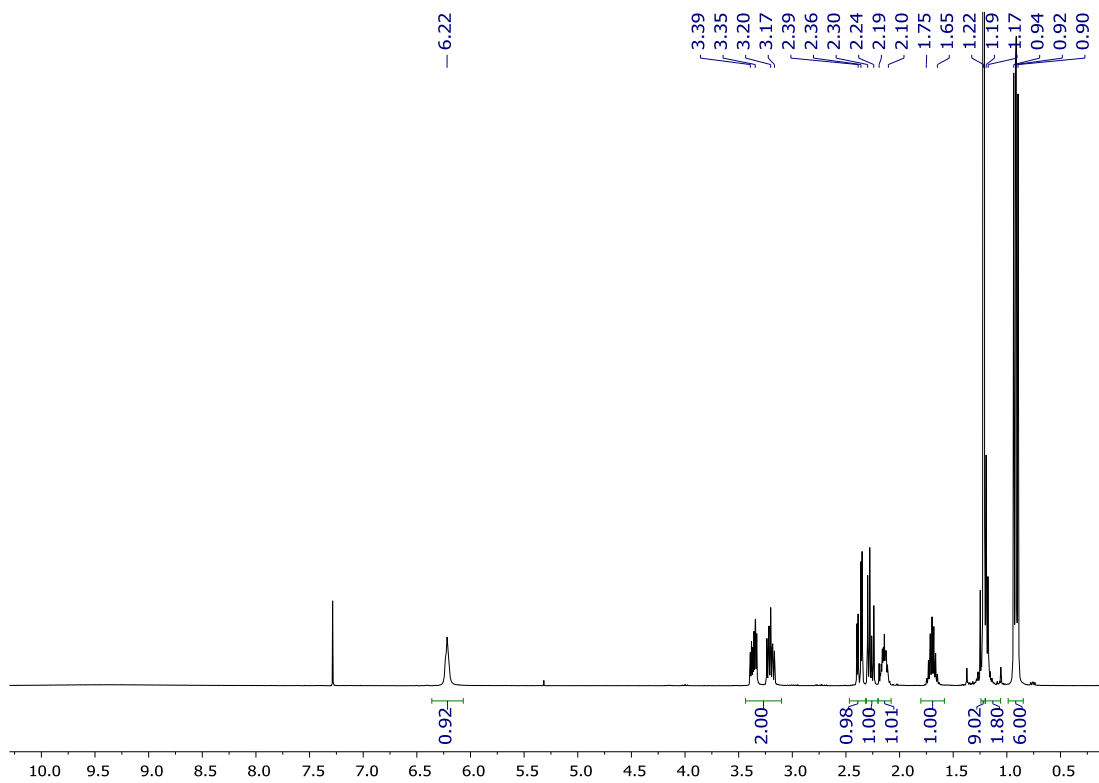
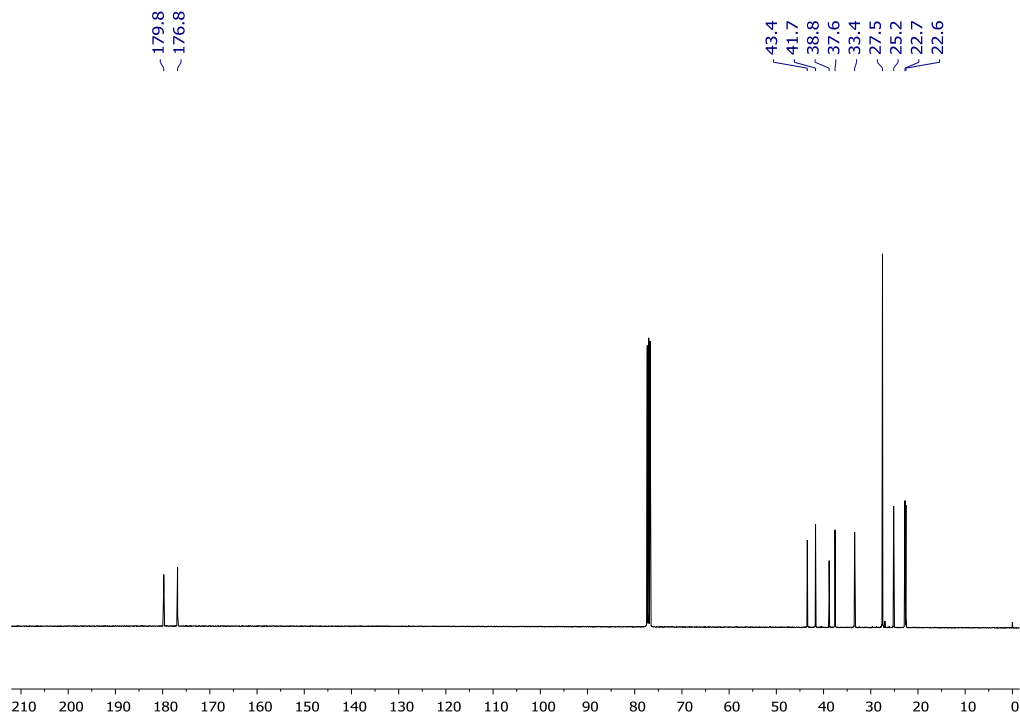
 $^1\text{H-NMR}$ of **S8** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S8** in CDCl_3 

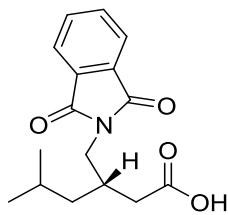
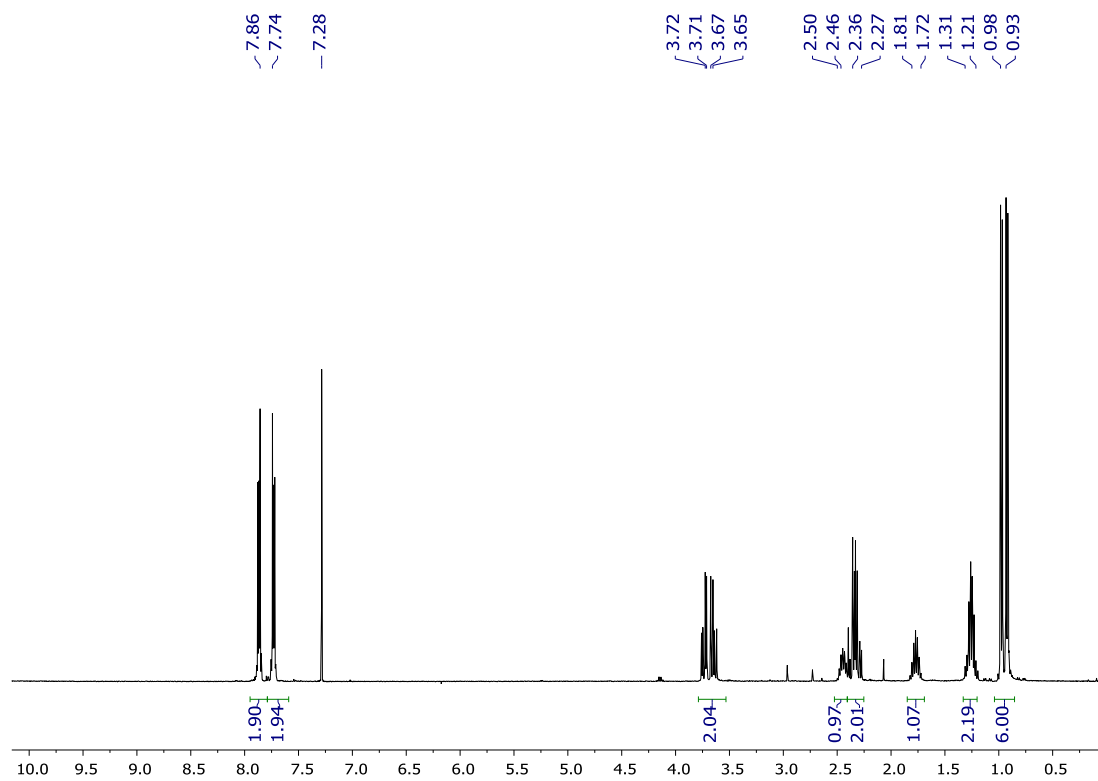
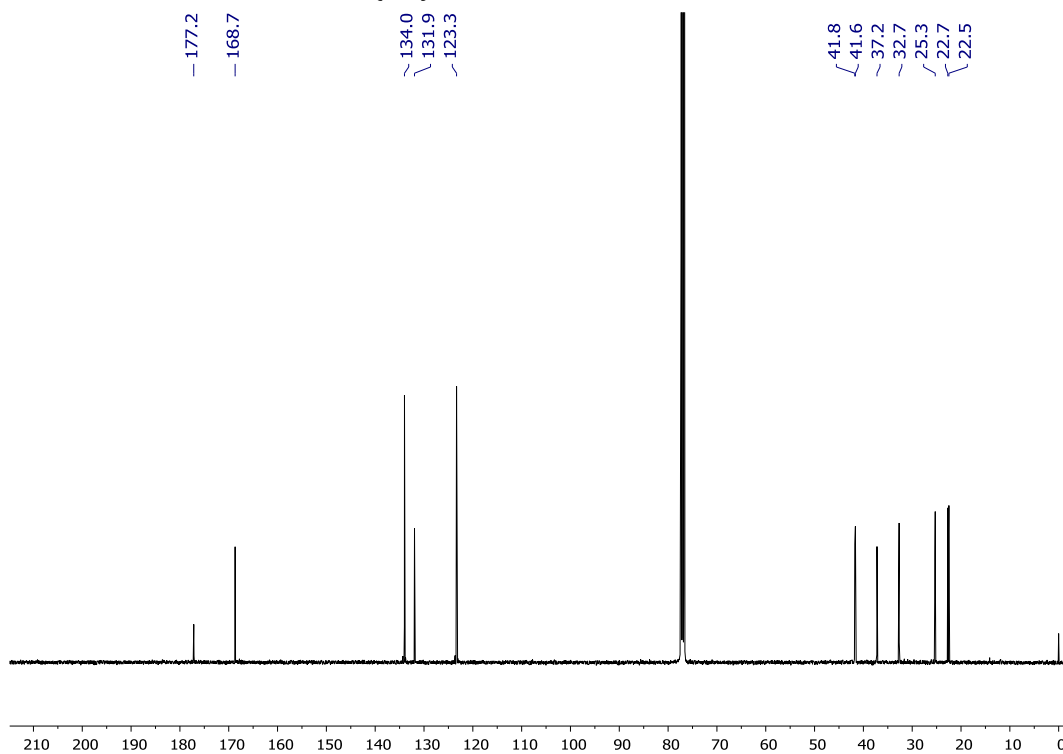
 $^1\text{H-NMR}$ of **S9** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S9** in CDCl_3 

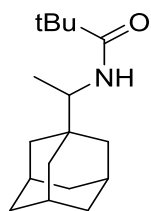
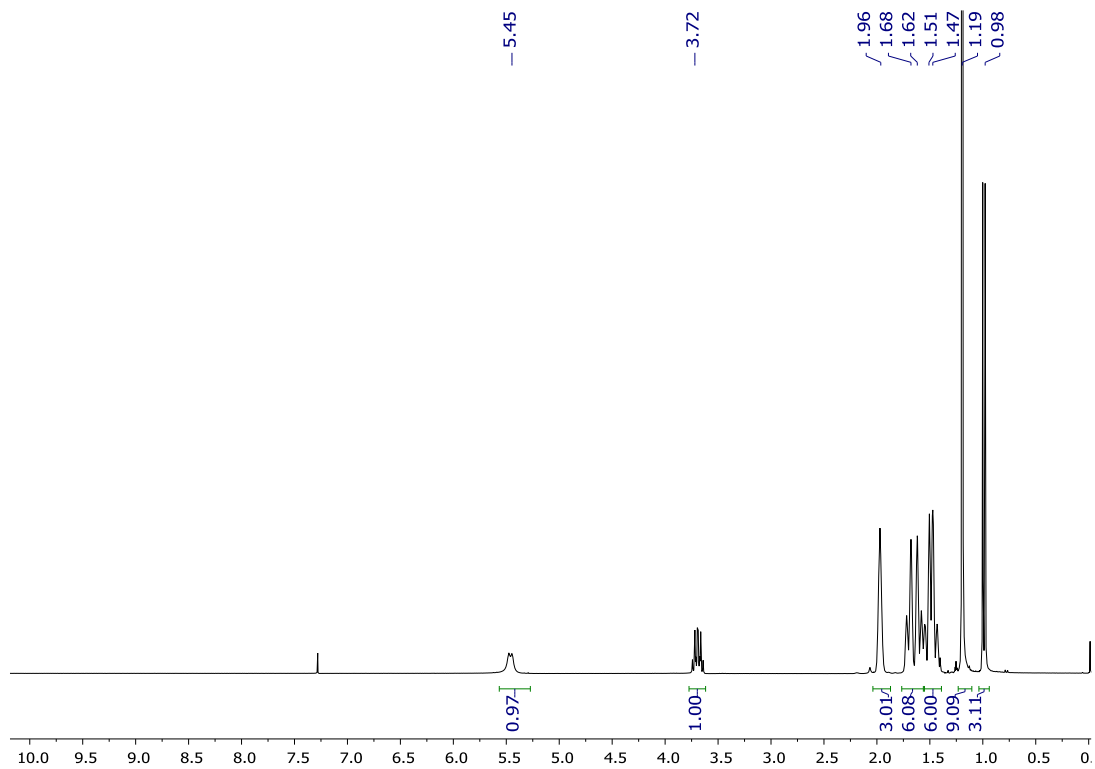
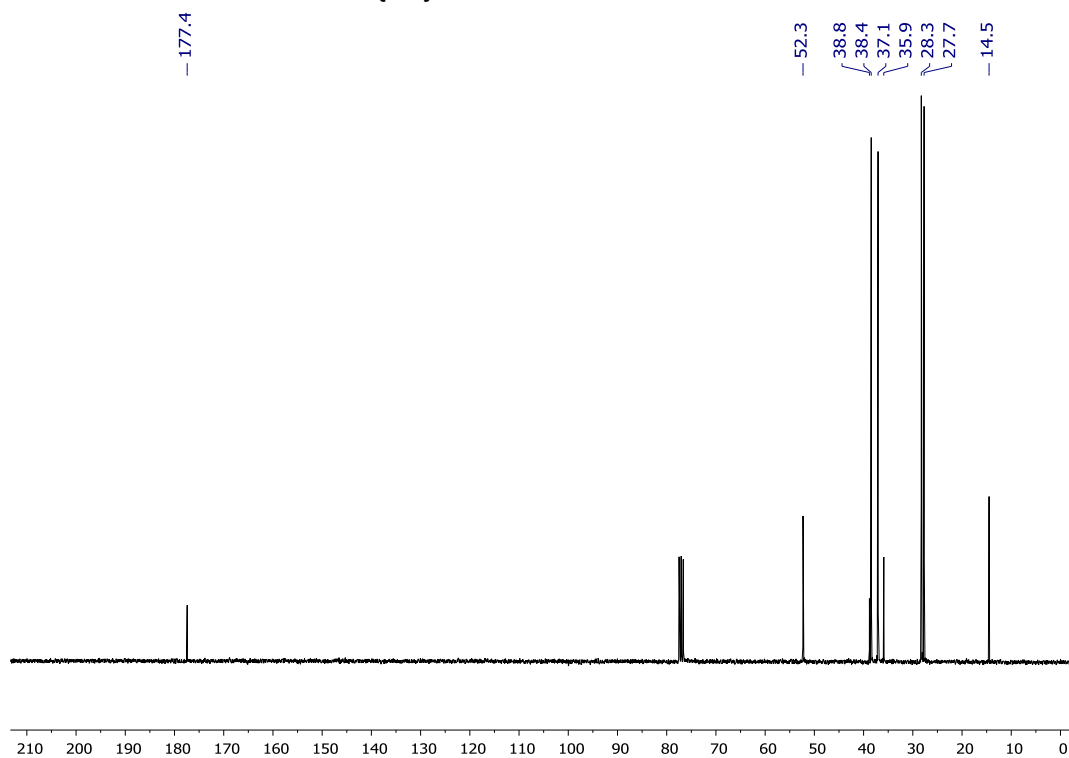
 $^1\text{H-NMR}$ of **S10** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S10** in CDCl_3 

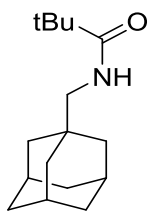
 $^1\text{H-NMR}$ of **S11** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S11** in CDCl_3 

 $^1\text{H-NMR}$ of **S12** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S12** in CDCl_3 

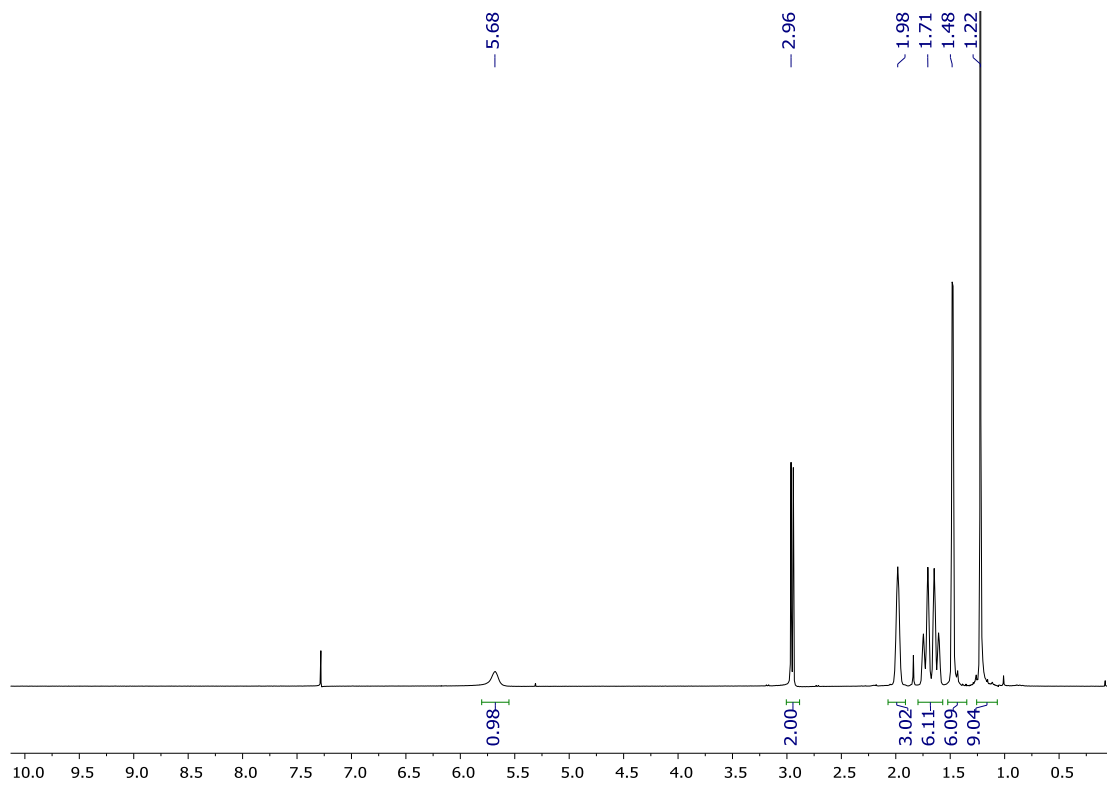
 $^1\text{H-NMR}$ of **S13** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S13** in CDCl_3 

 $^1\text{H-NMR}$ of **S14** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S14** in CDCl_3 

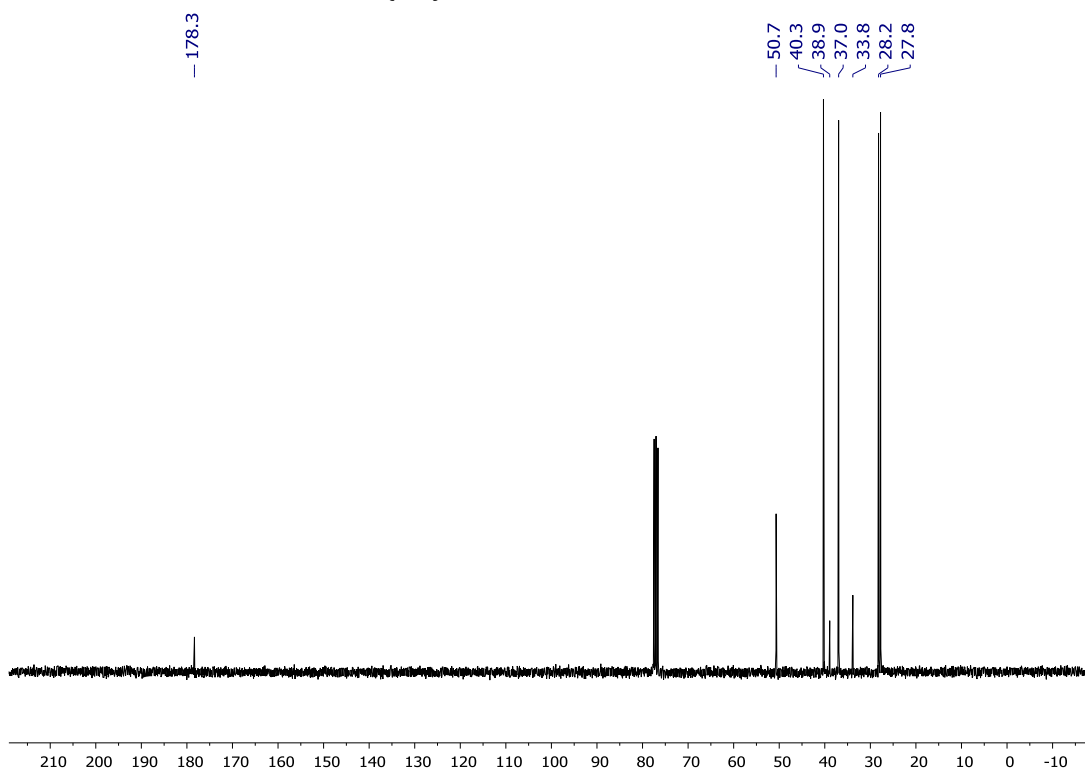
 $^1\text{H-NMR}$ of **S15** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S15** in CDCl_3 

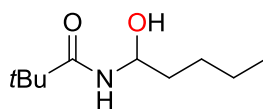
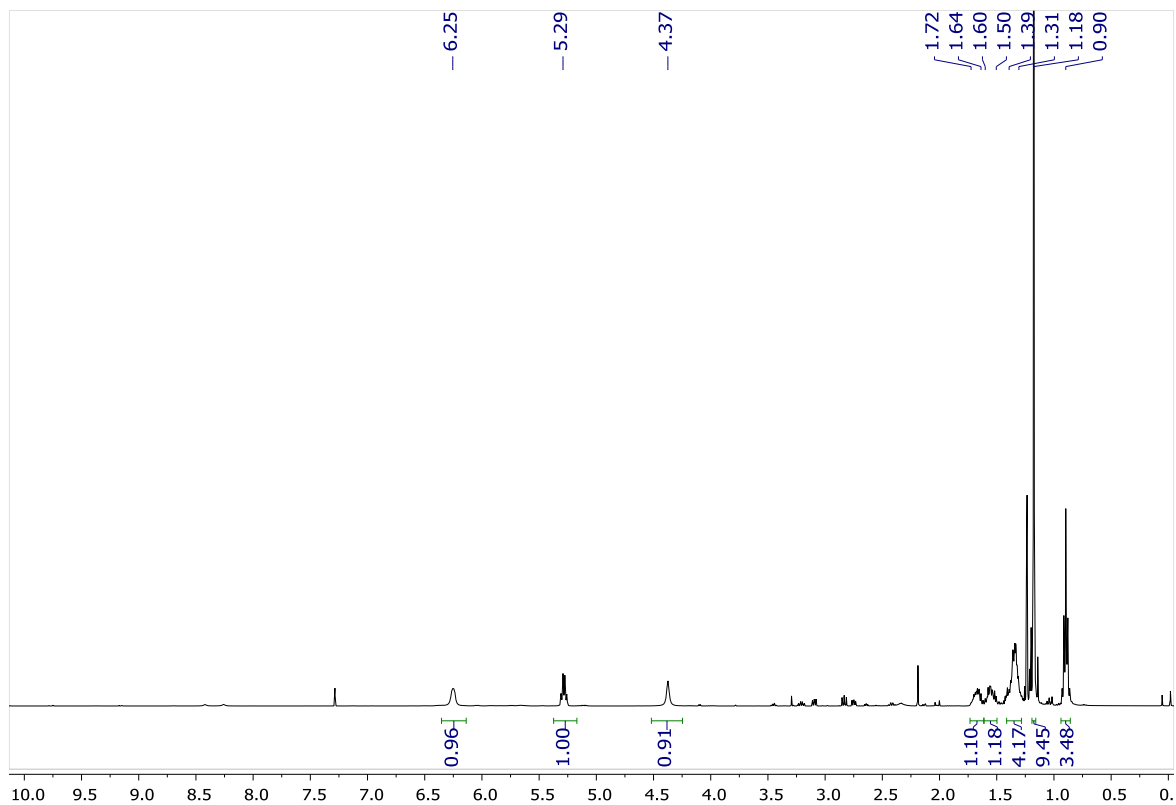
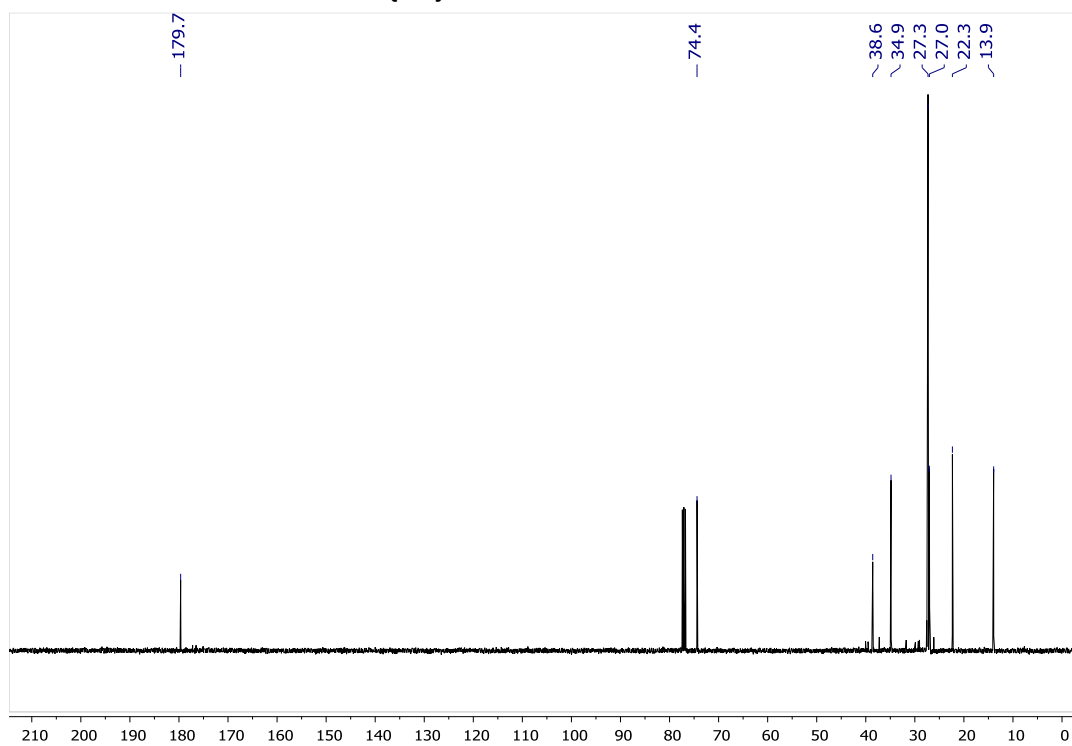


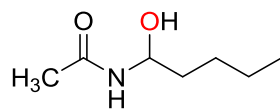
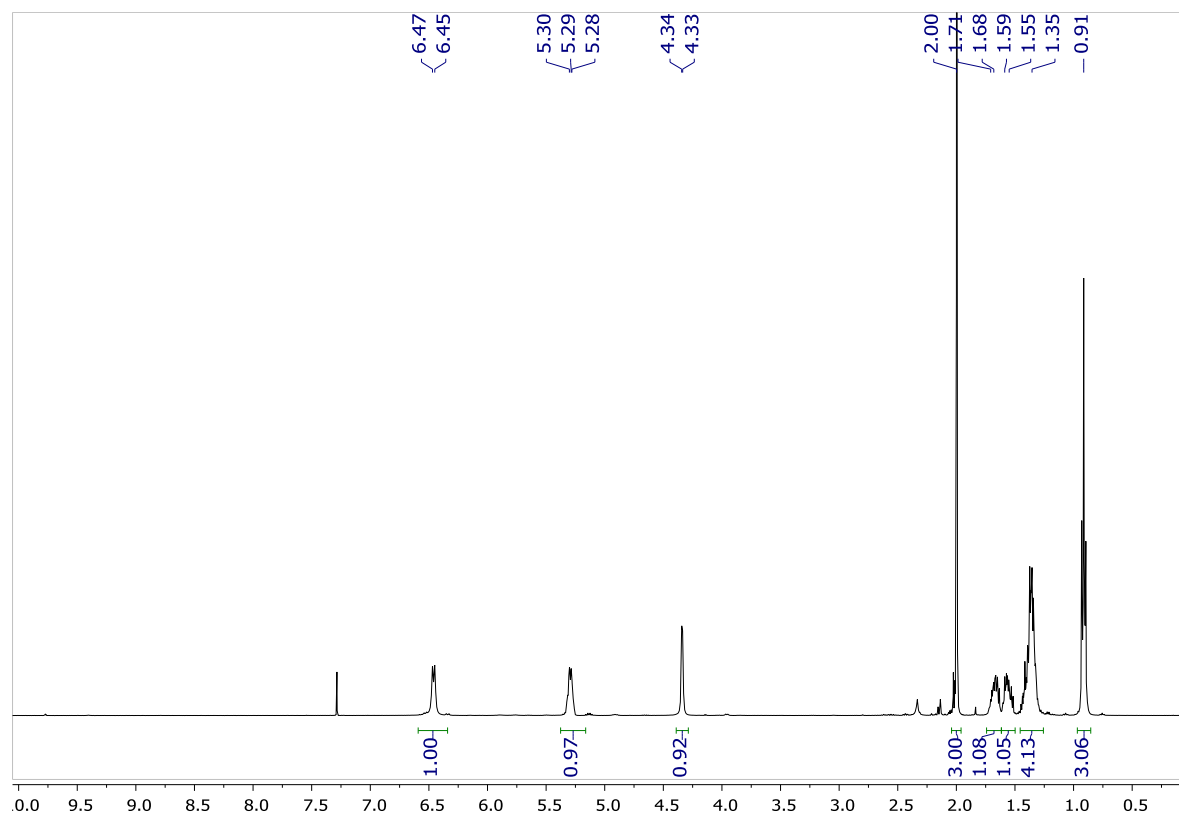
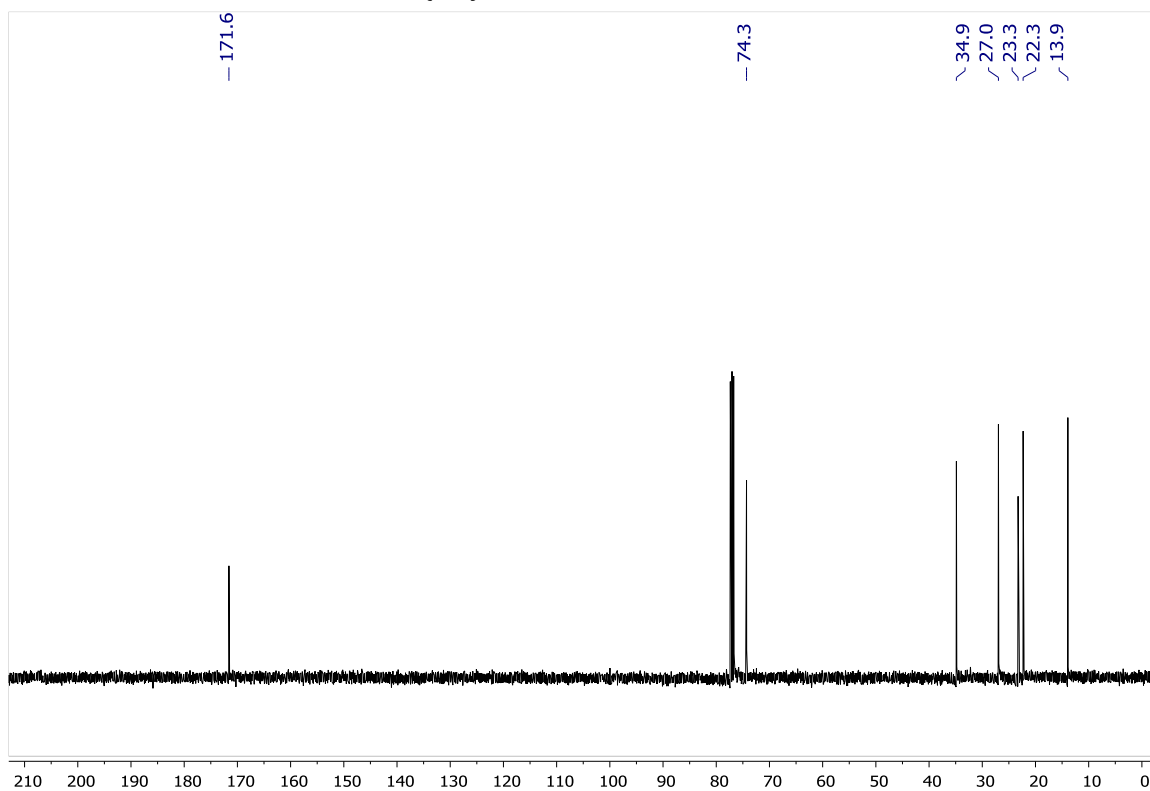
¹H-NMR of **S17** in CDCl₃

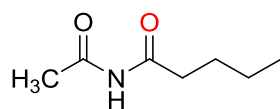
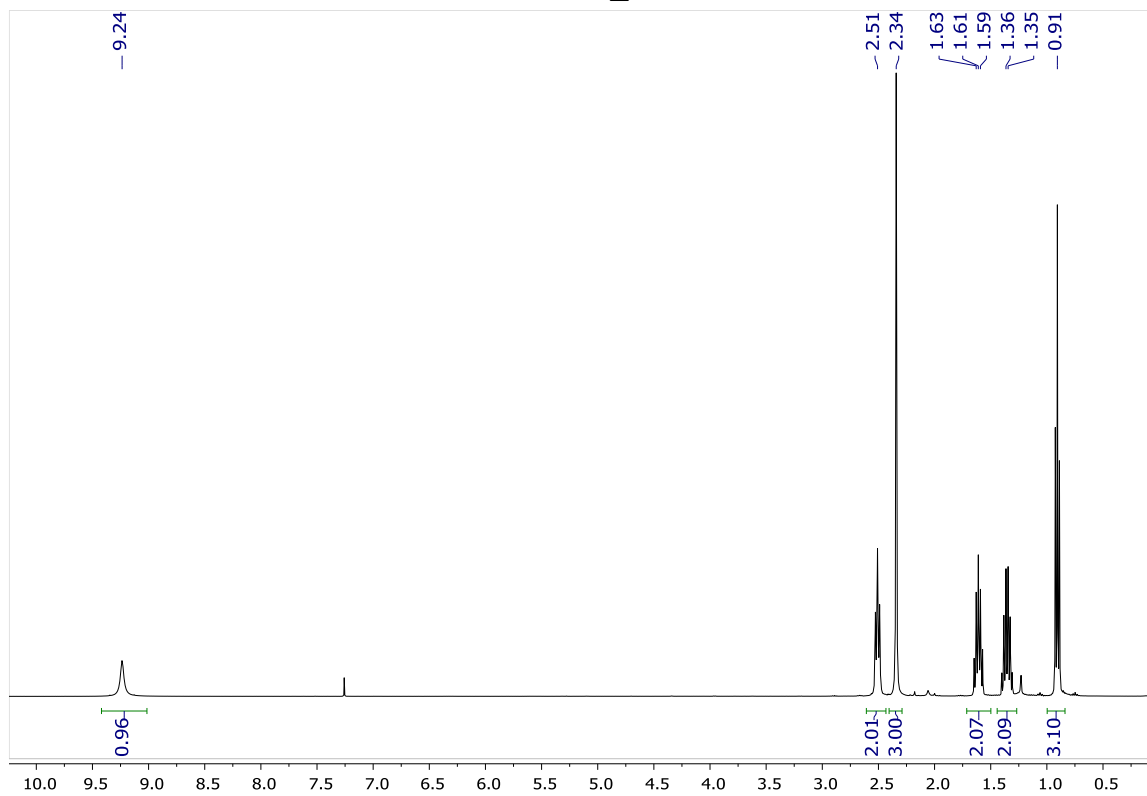
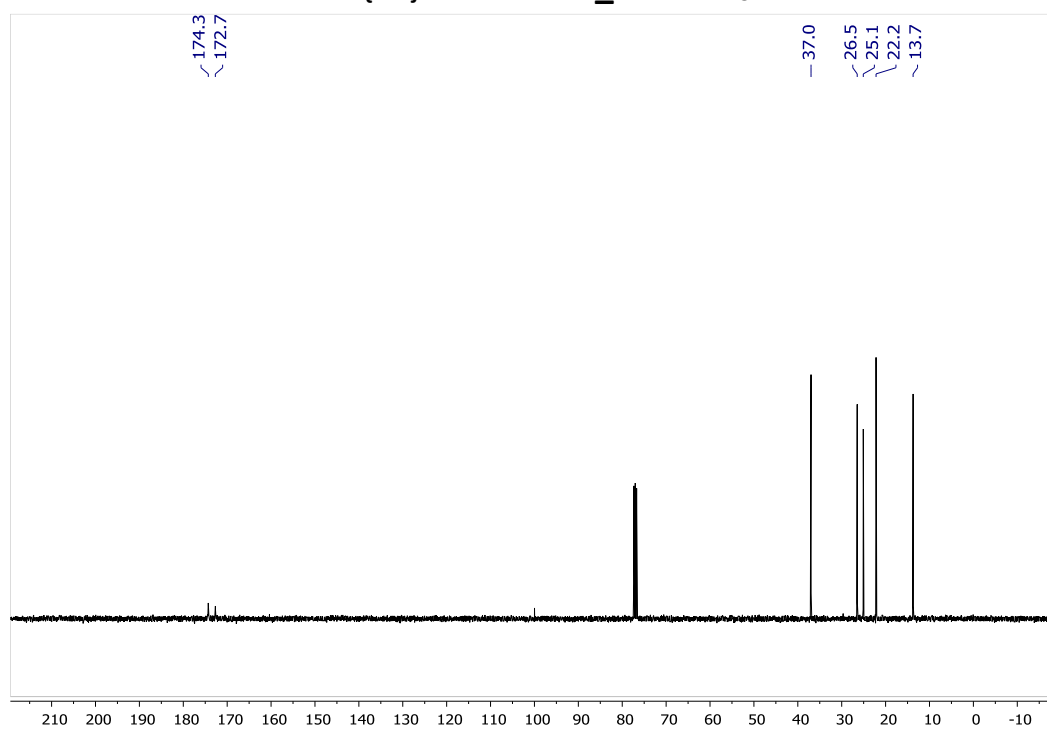


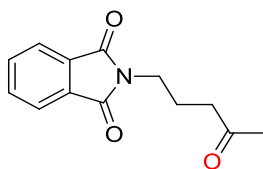
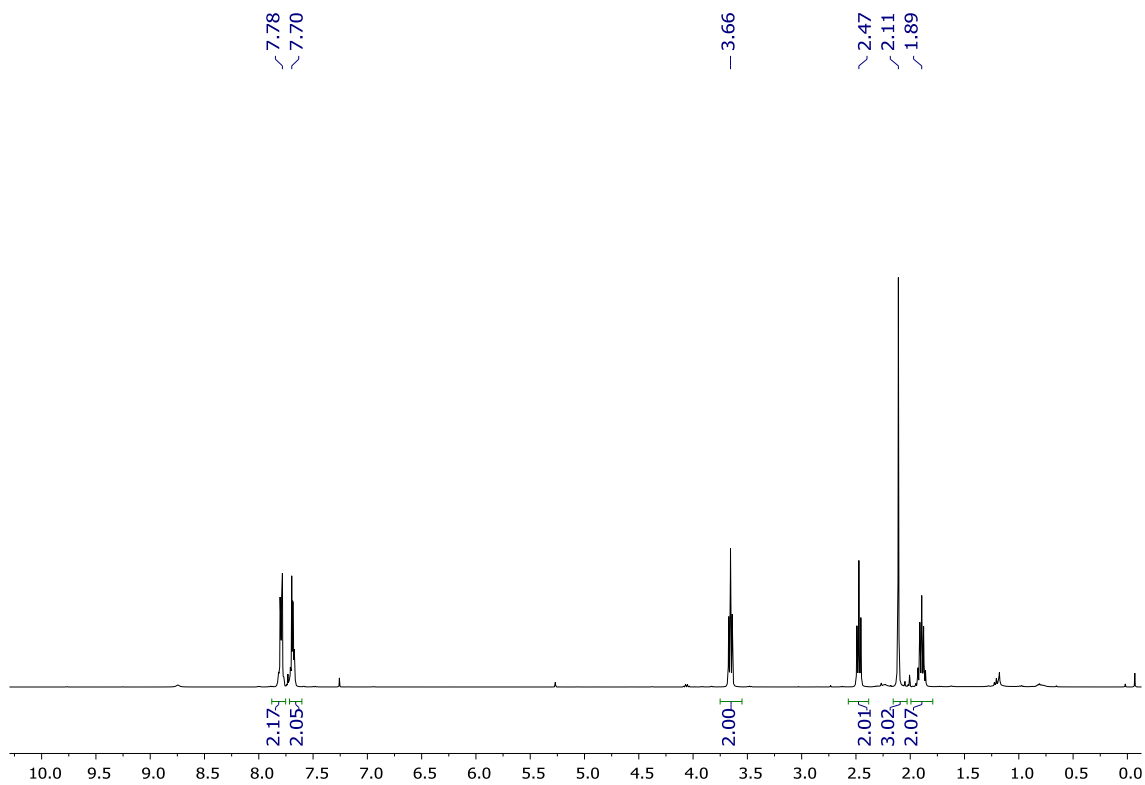
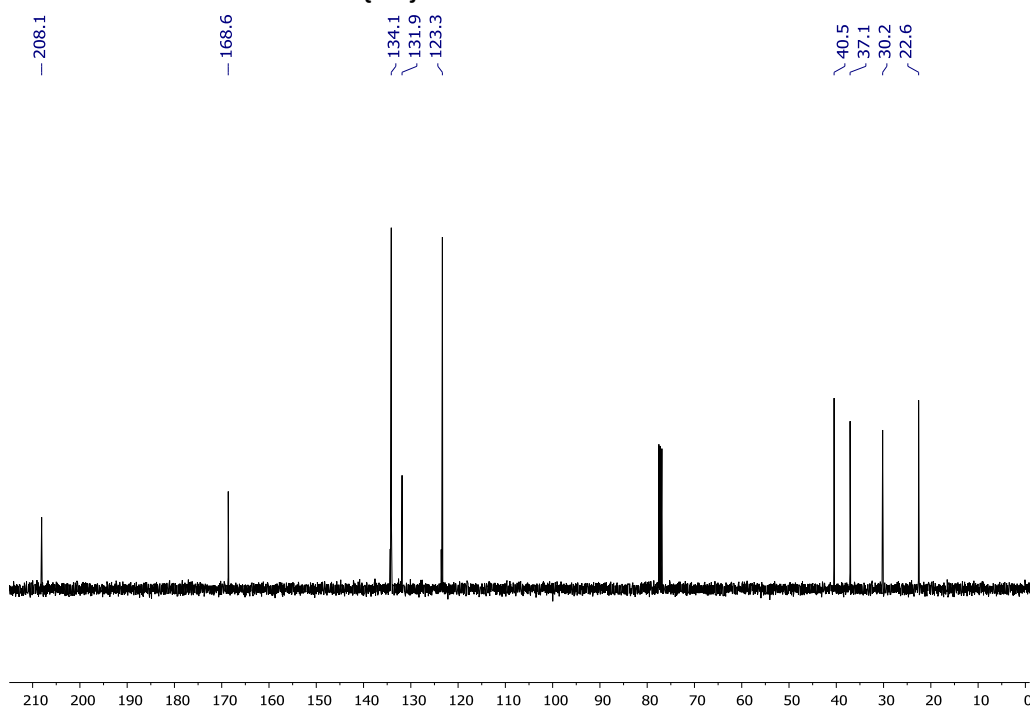
¹³C{¹H}-NMR of **S17** in CDCl₃

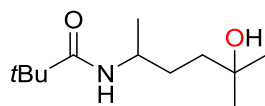
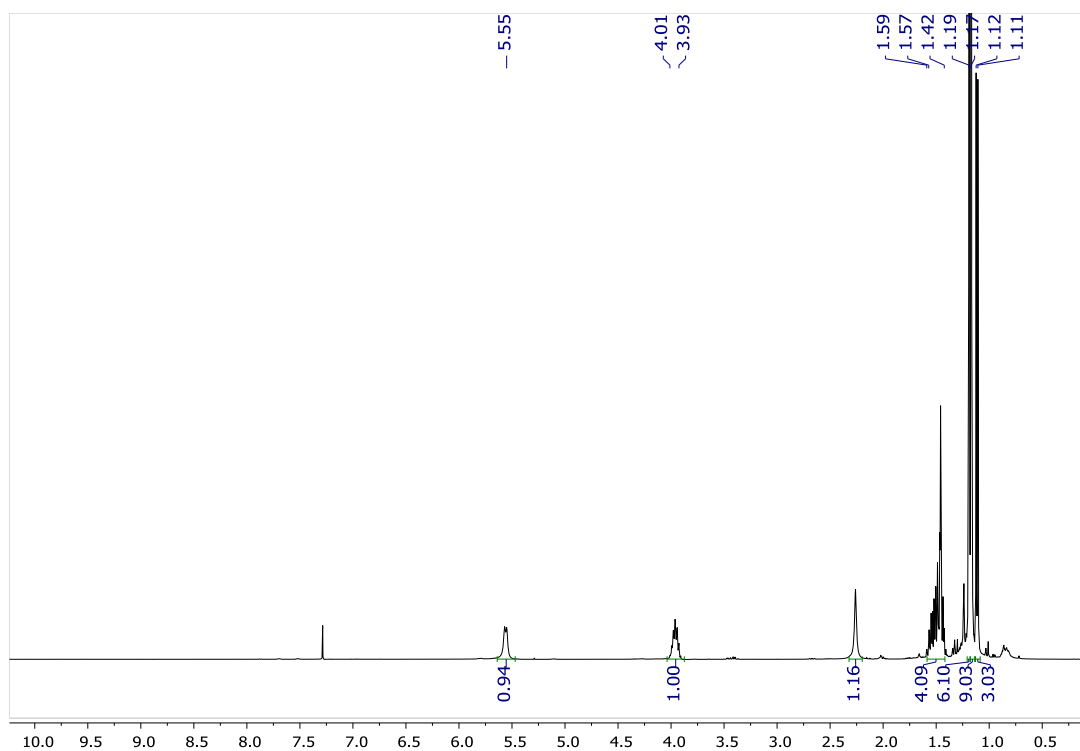
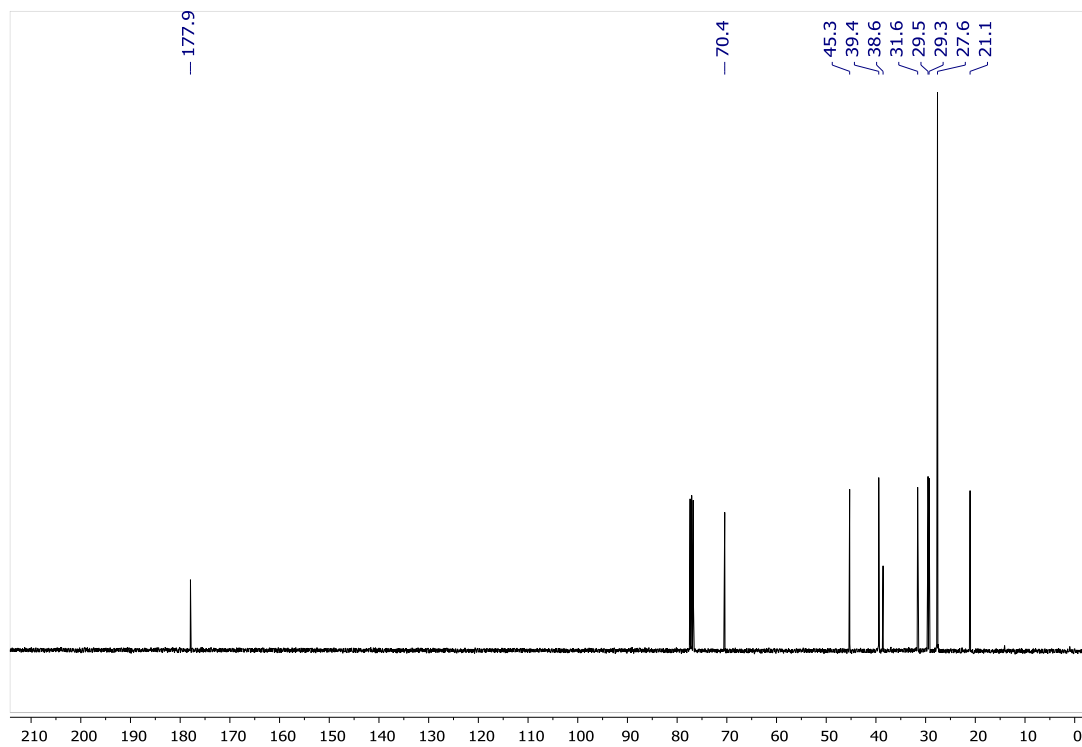


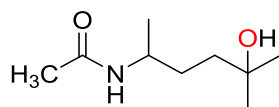
A2 ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of isolated products ^1H -NMR of P1 in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of P1 in CDCl_3 

 $^1\text{H-NMR}$ of **P2** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P2** in CDCl_3 

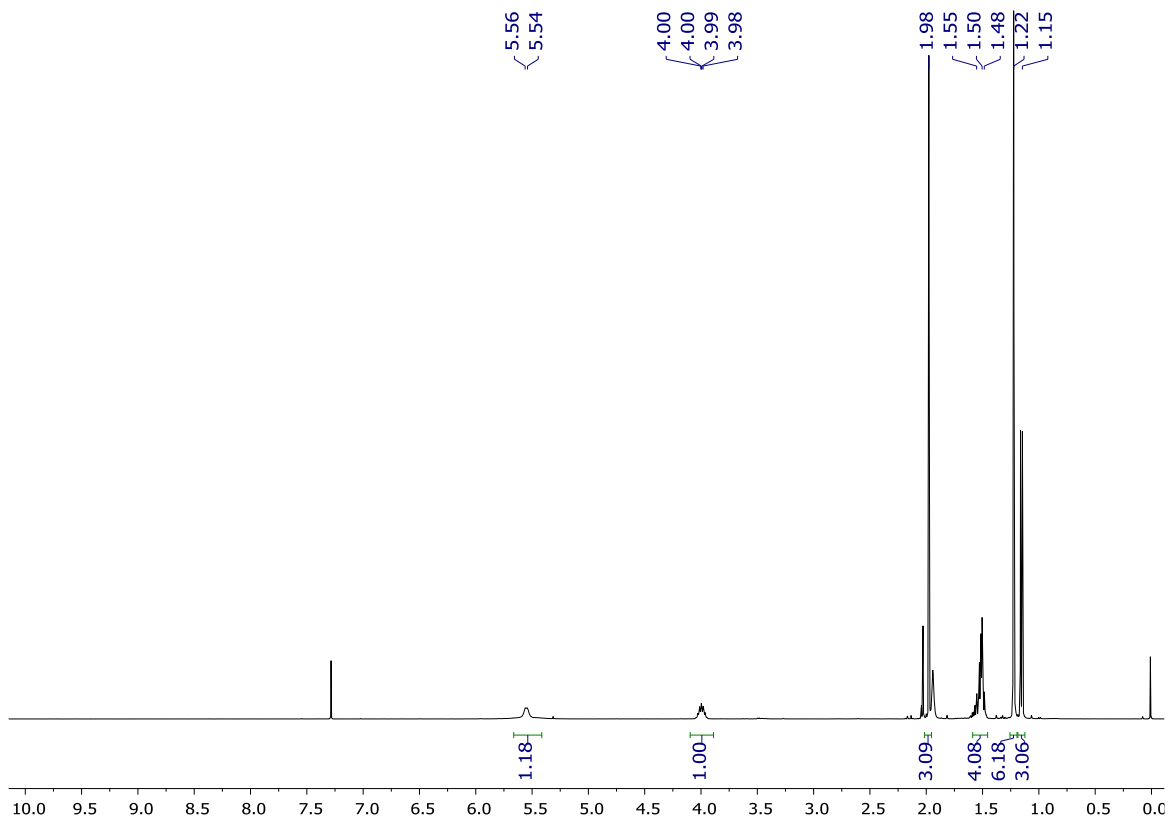
 $^1\text{H-NMR}$ of **P2_i** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P2_i** in CDCl_3 

 $^1\text{H-NMR}$ of **P4** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P4** in CDCl_3 

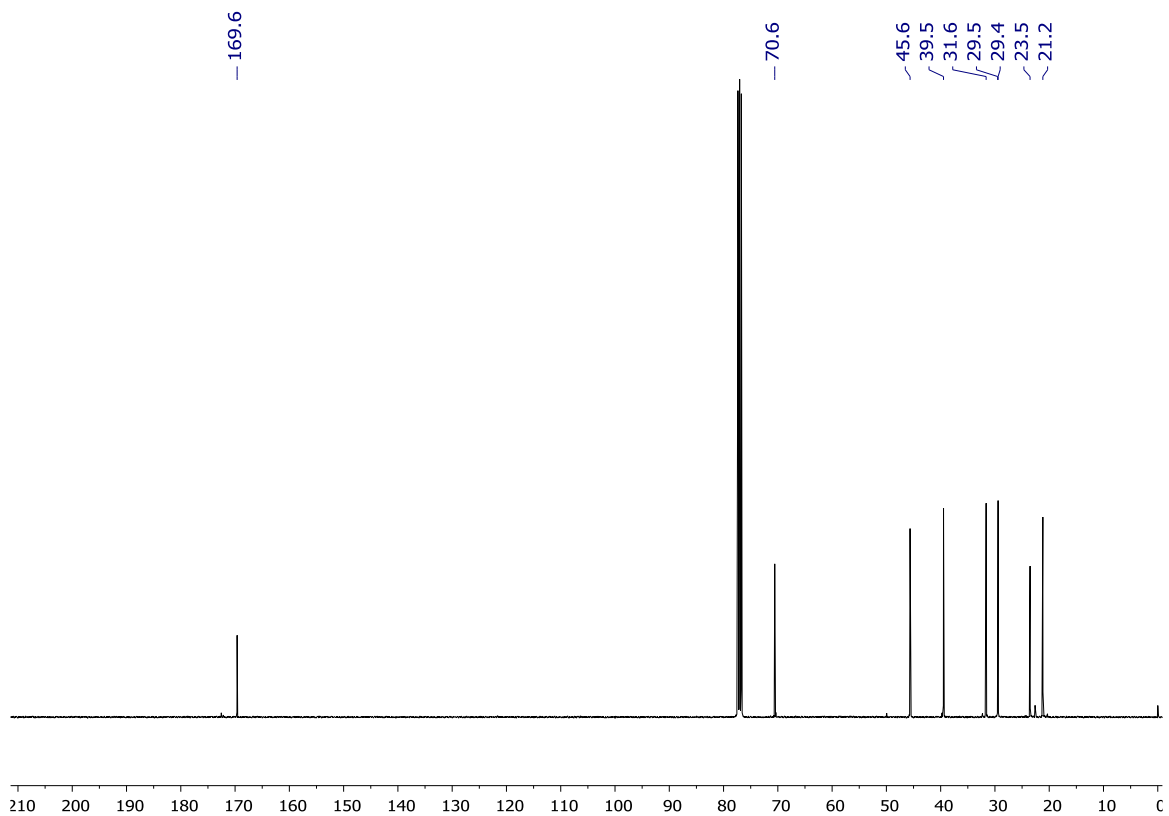
 $^1\text{H-NMR}$ of **P5** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P5** in CDCl_3 

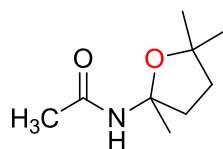
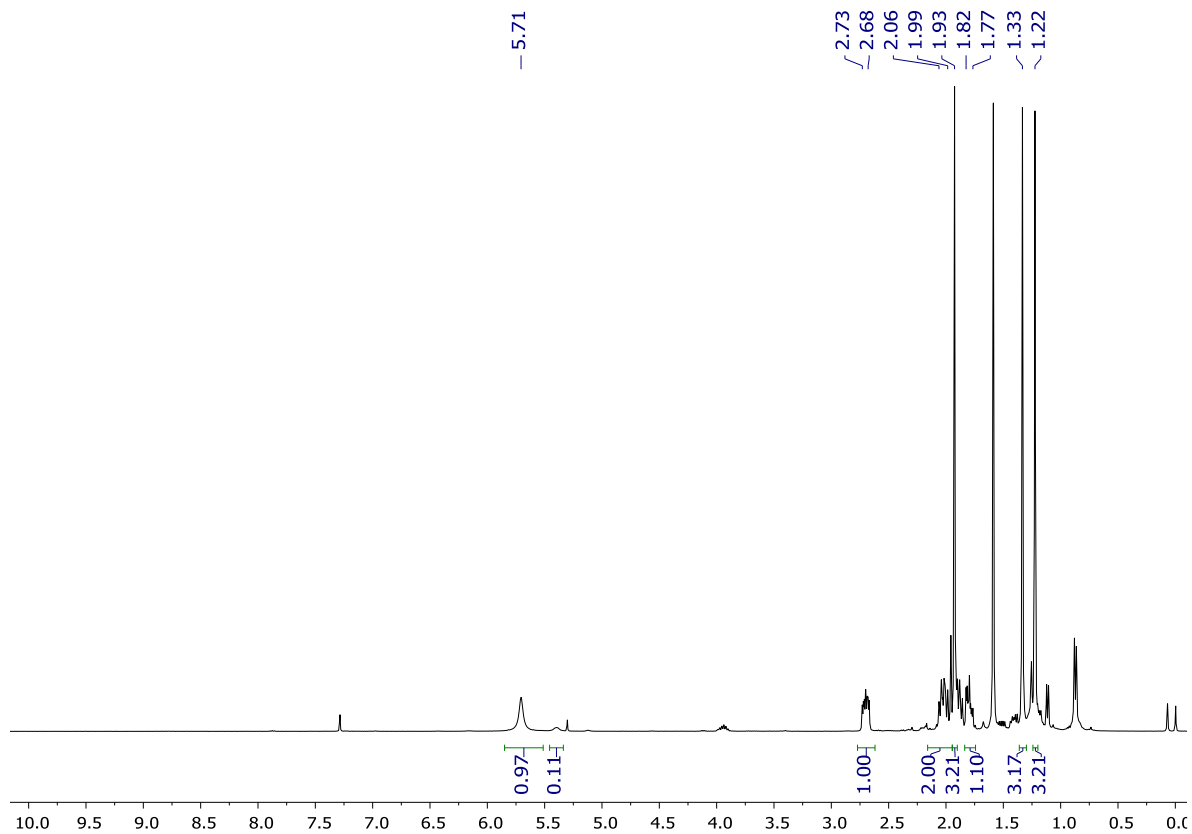
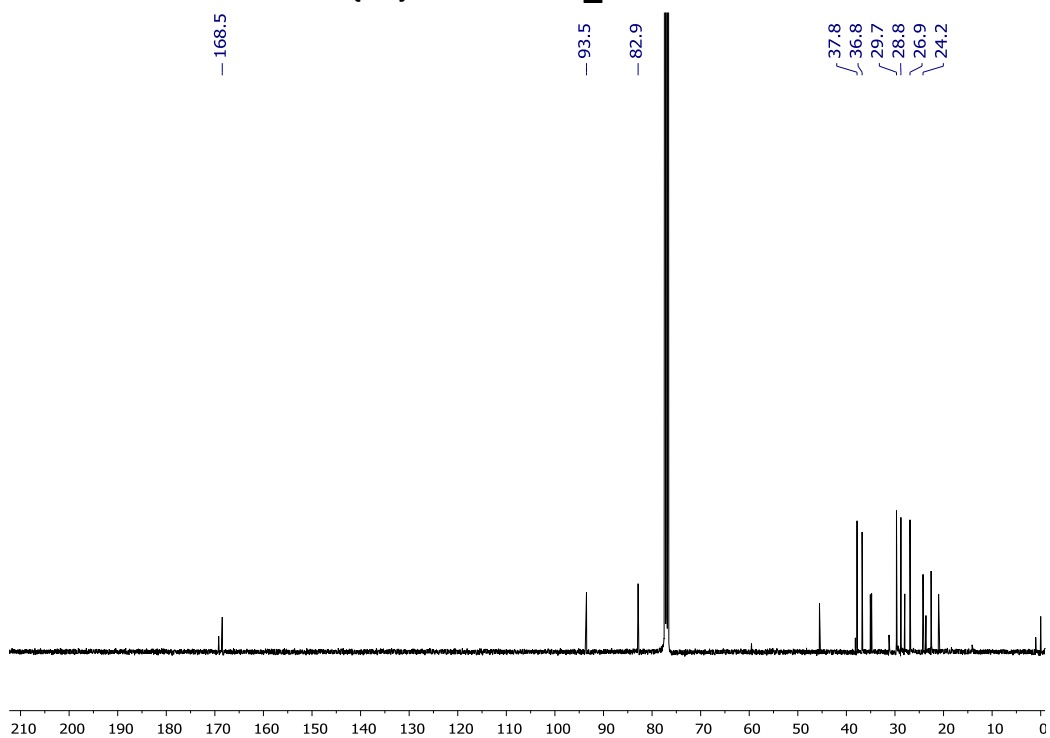


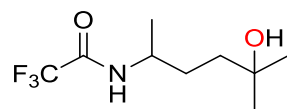
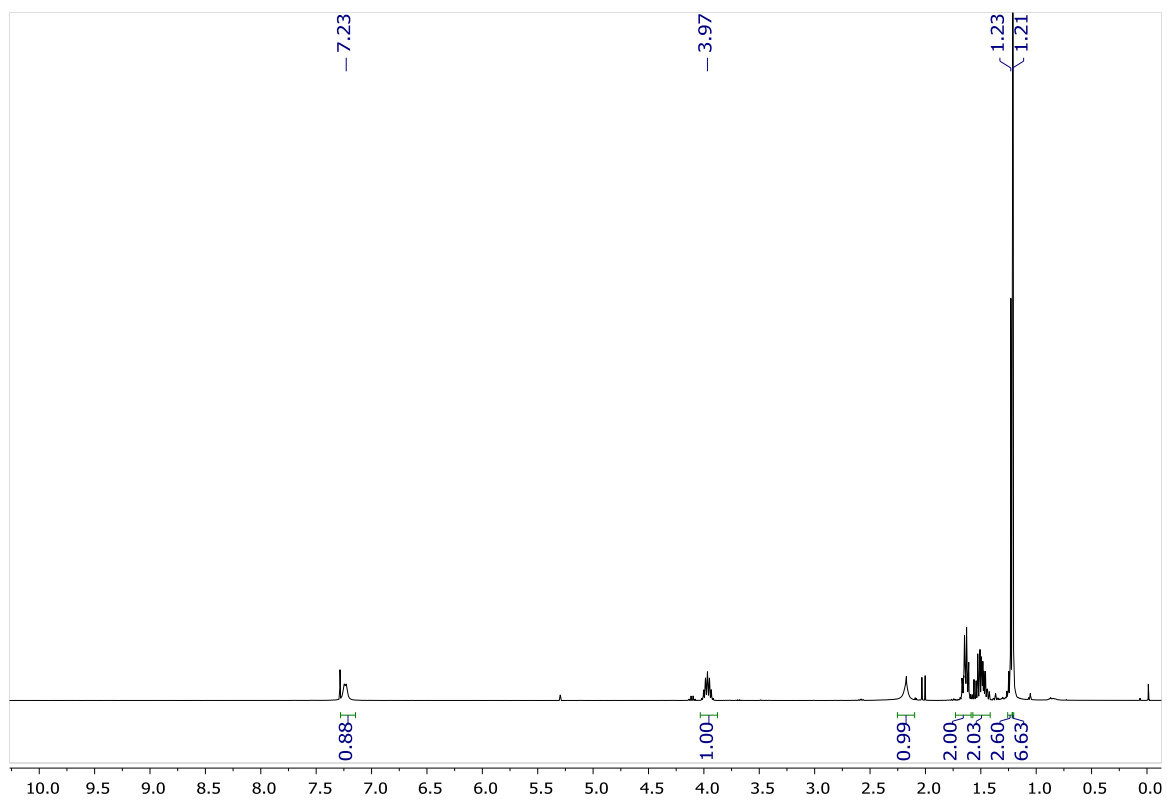
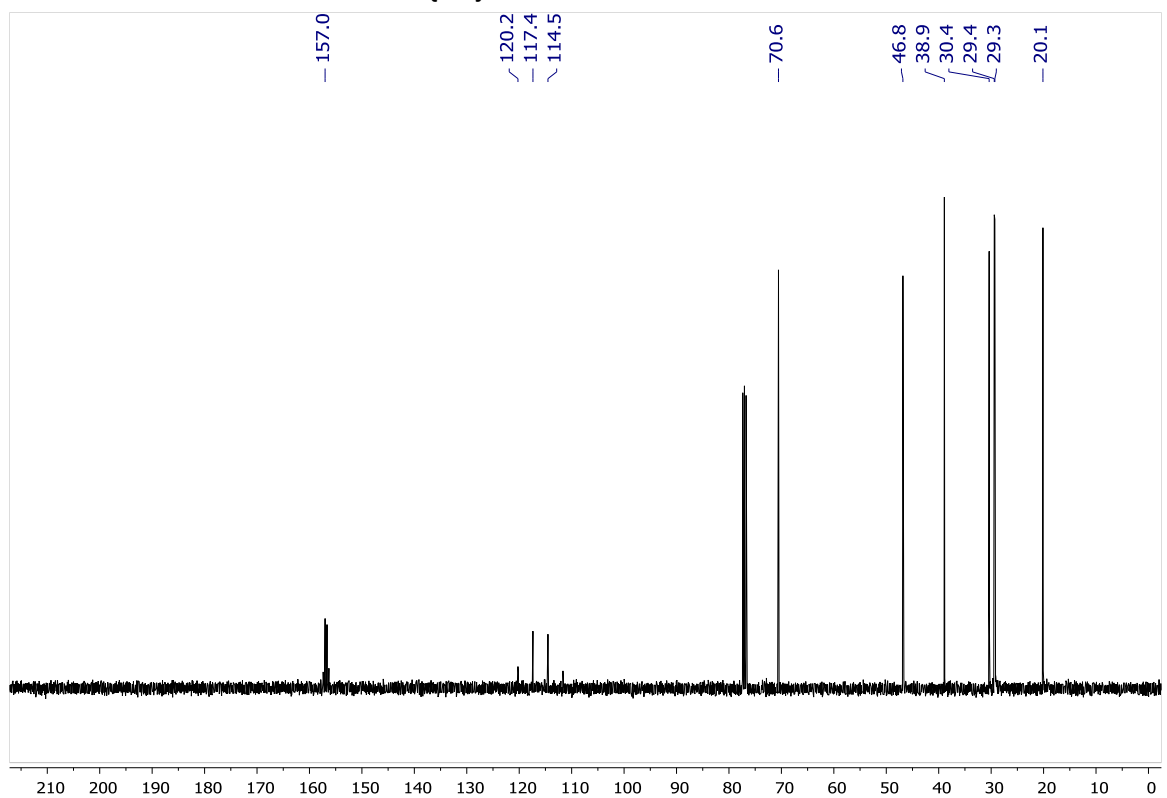
$^1\text{H-NMR}$ of **P6** in CDCl_3

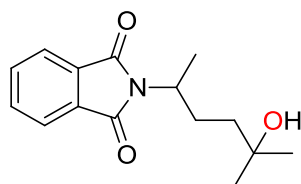
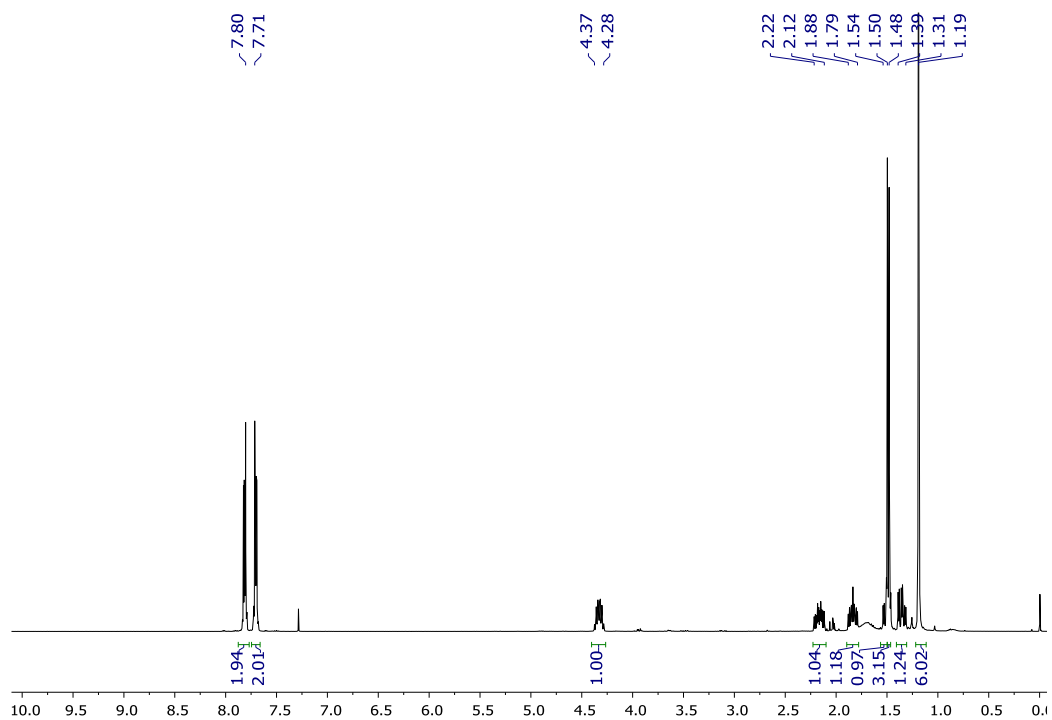
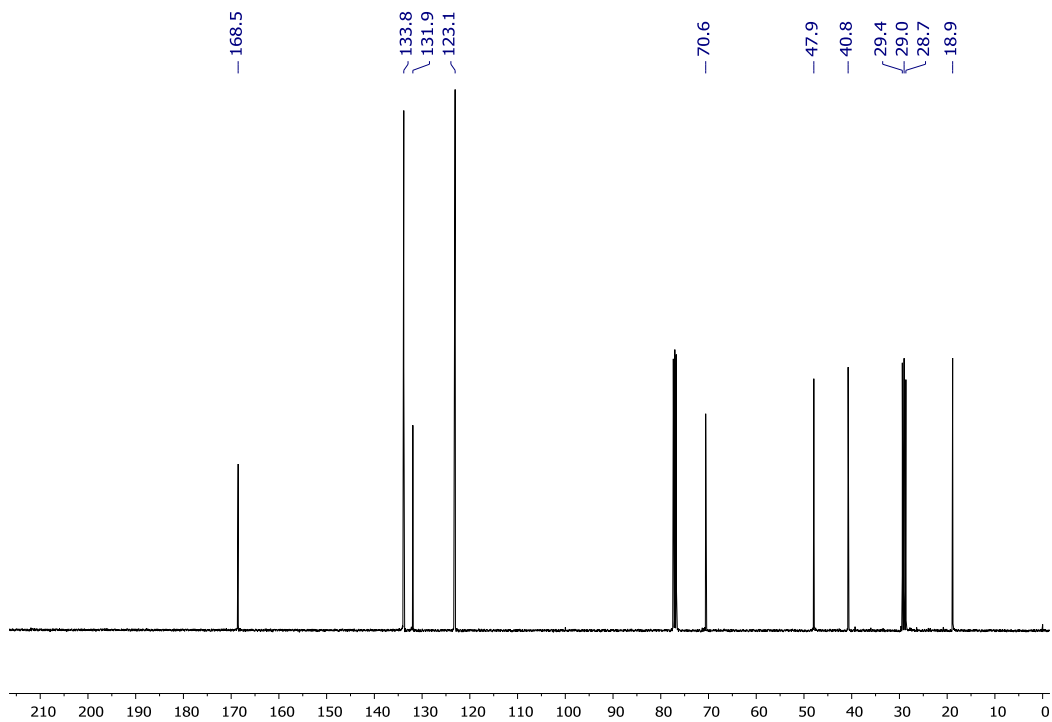


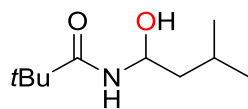
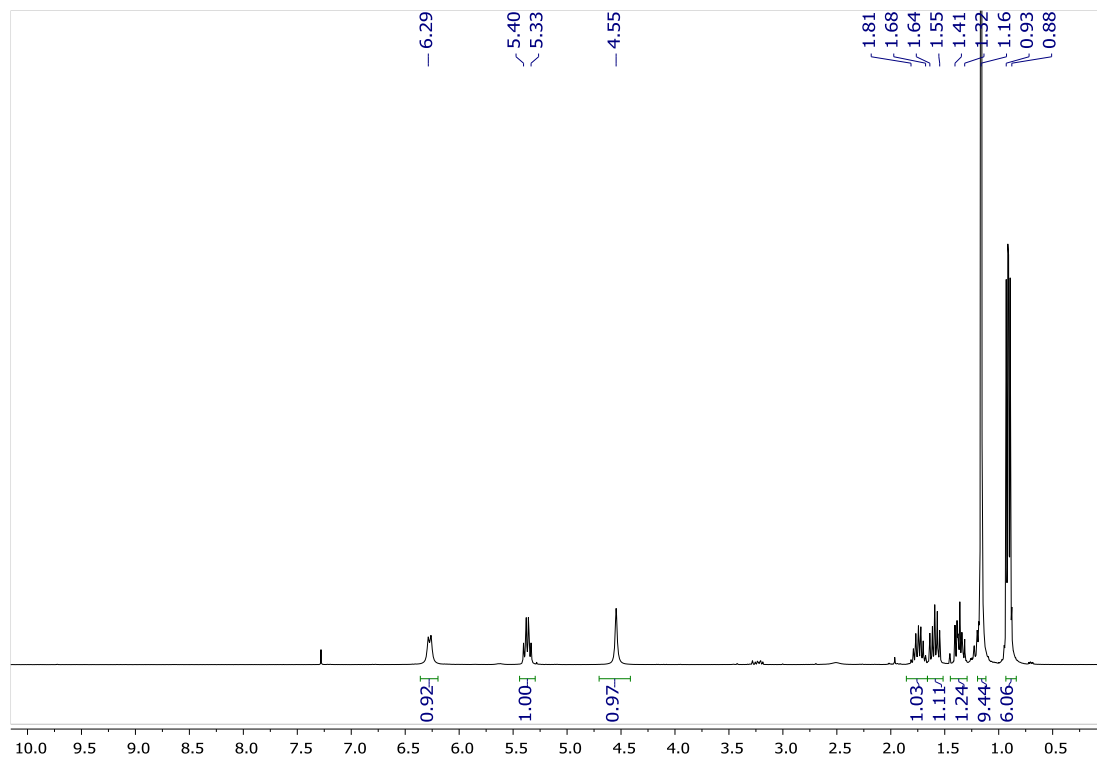
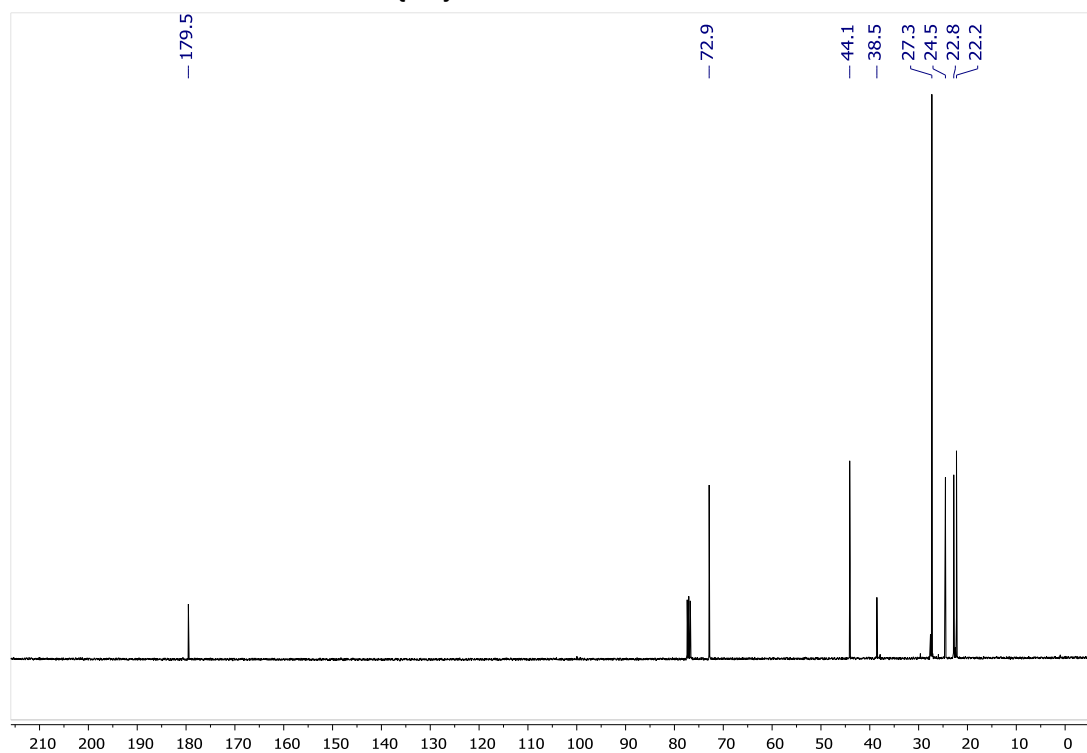
$^{13}\text{C}\{^1\text{H}\}$ -NMR of **P6** in CDCl_3

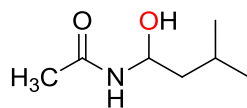
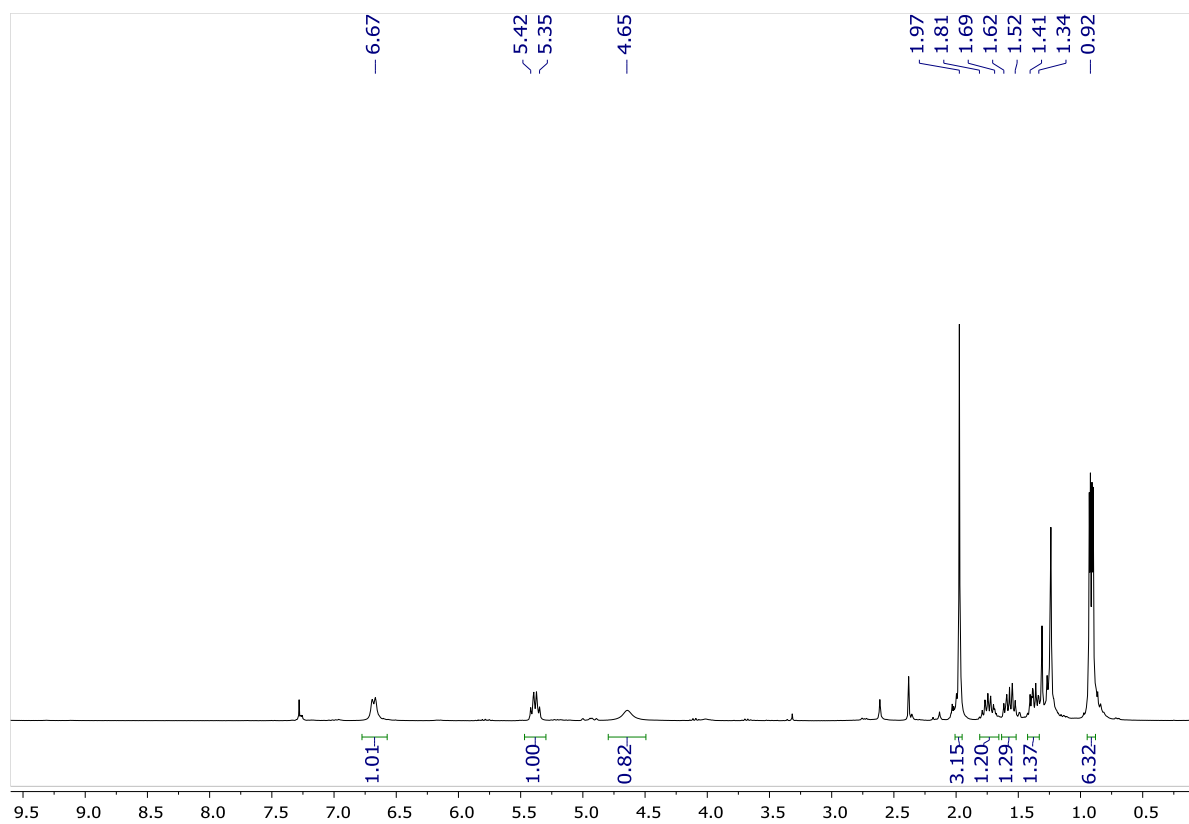
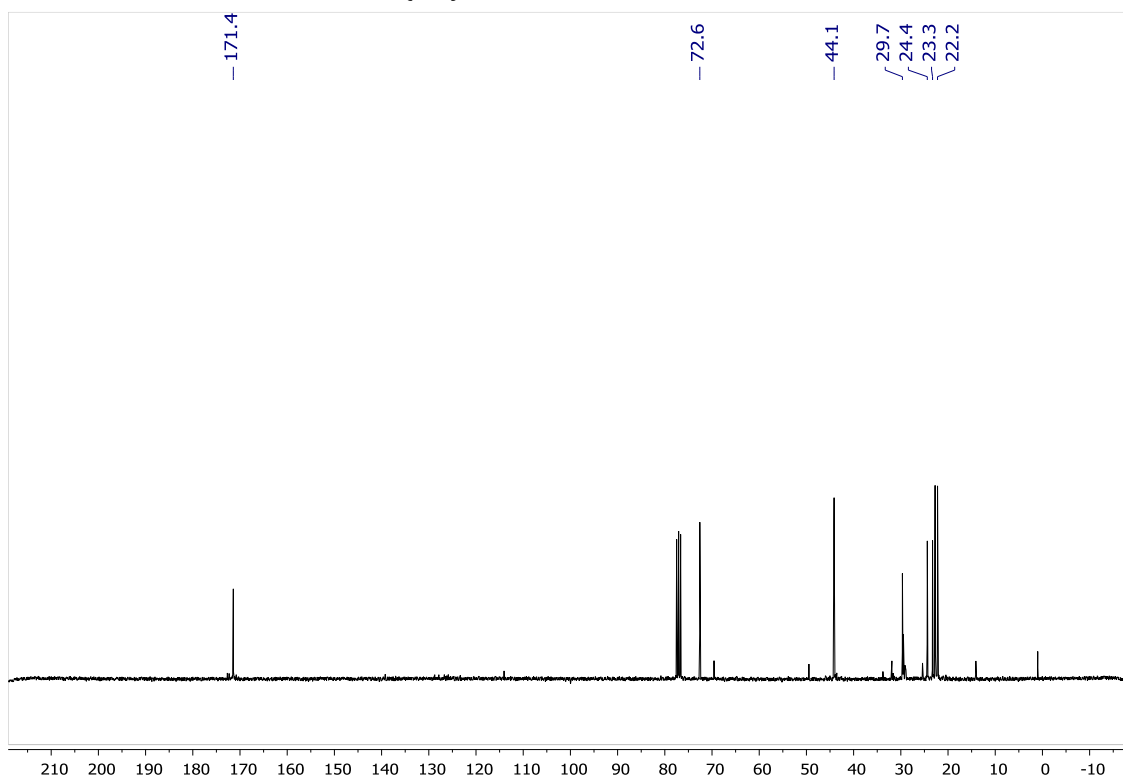


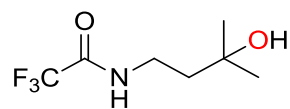
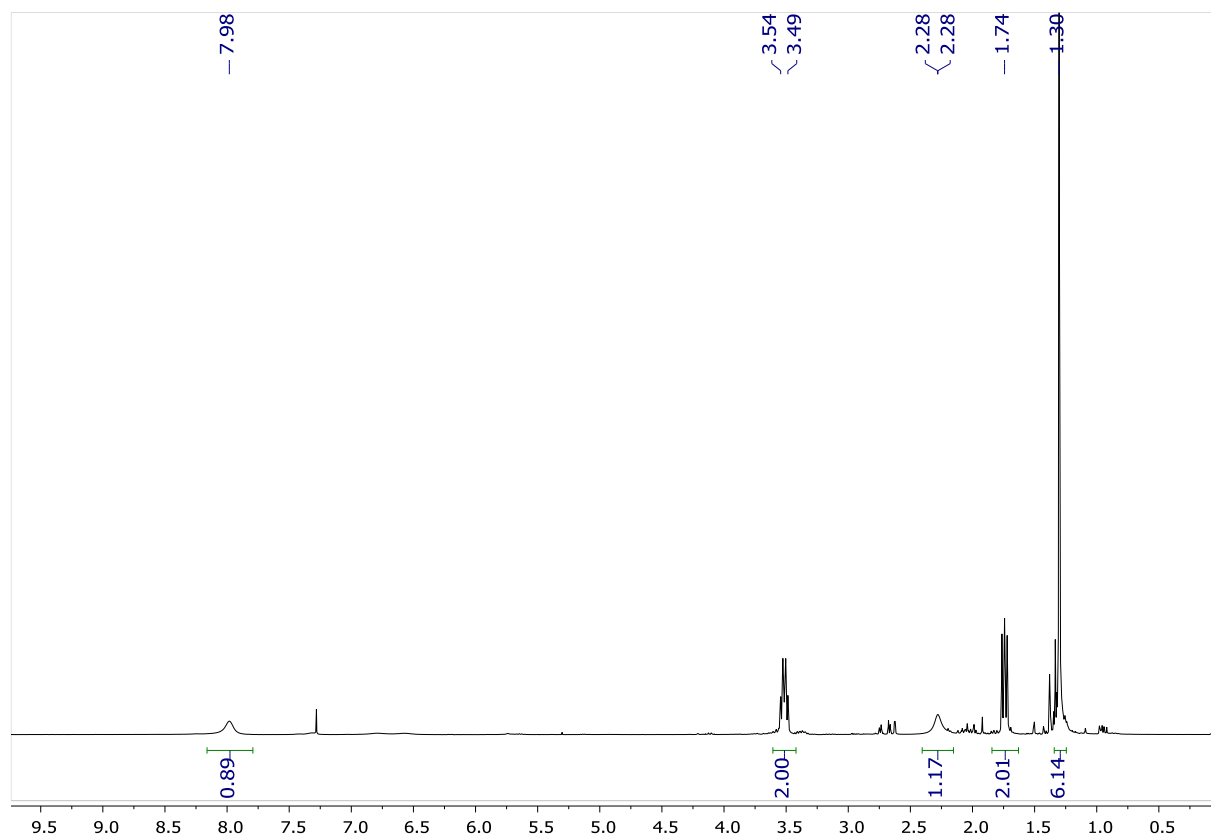
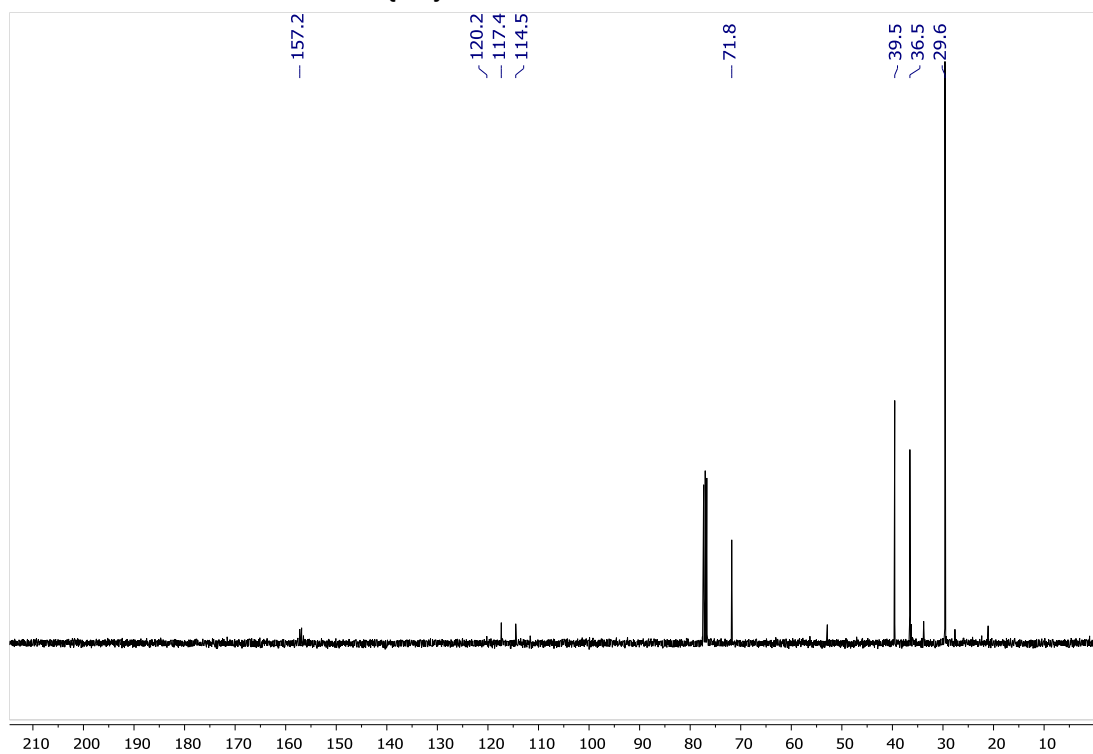
 $^1\text{H-NMR}$ of **P6_a** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P6_a** in CDCl_3 

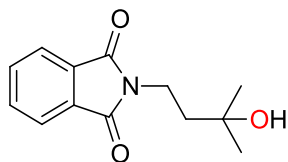
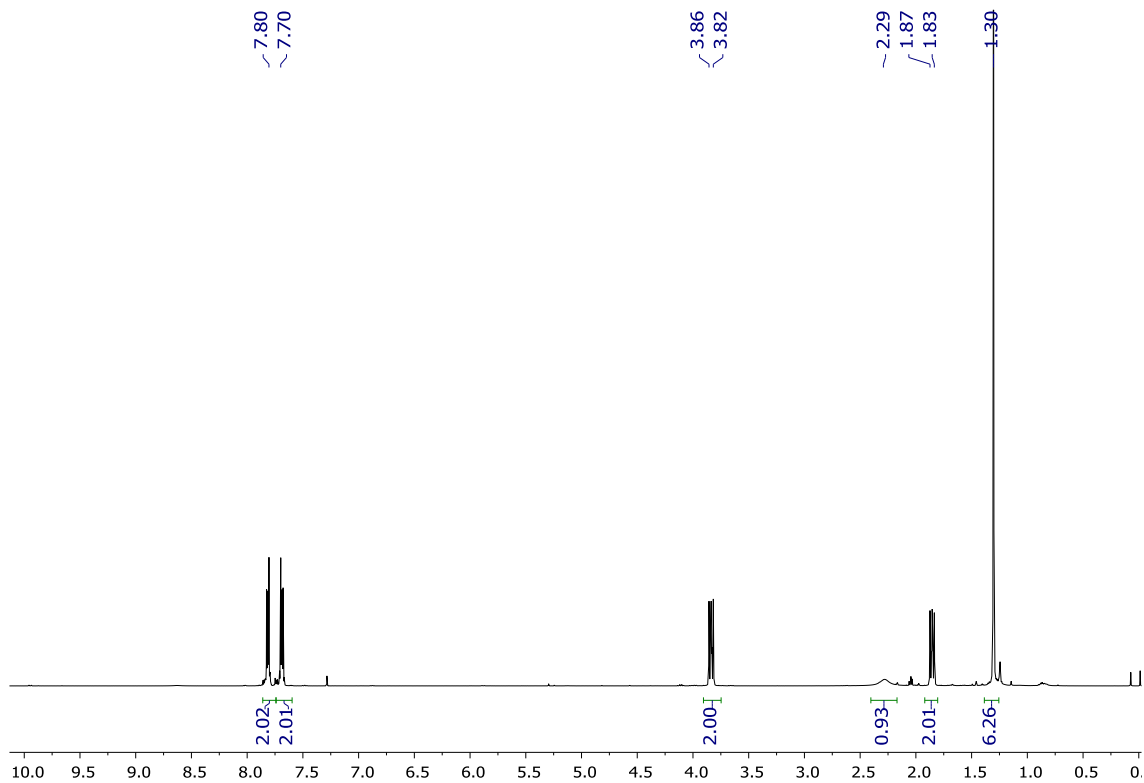
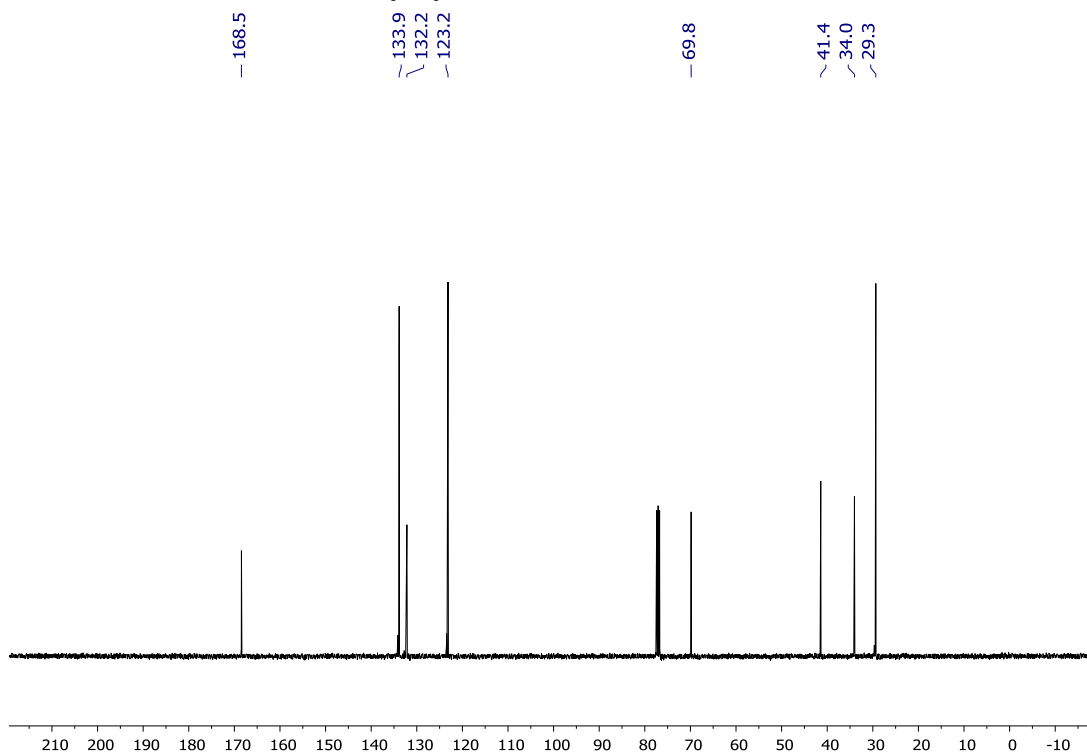
 $^1\text{H-NMR}$ of **P7** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P7** in CDCl_3 

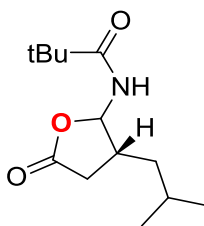
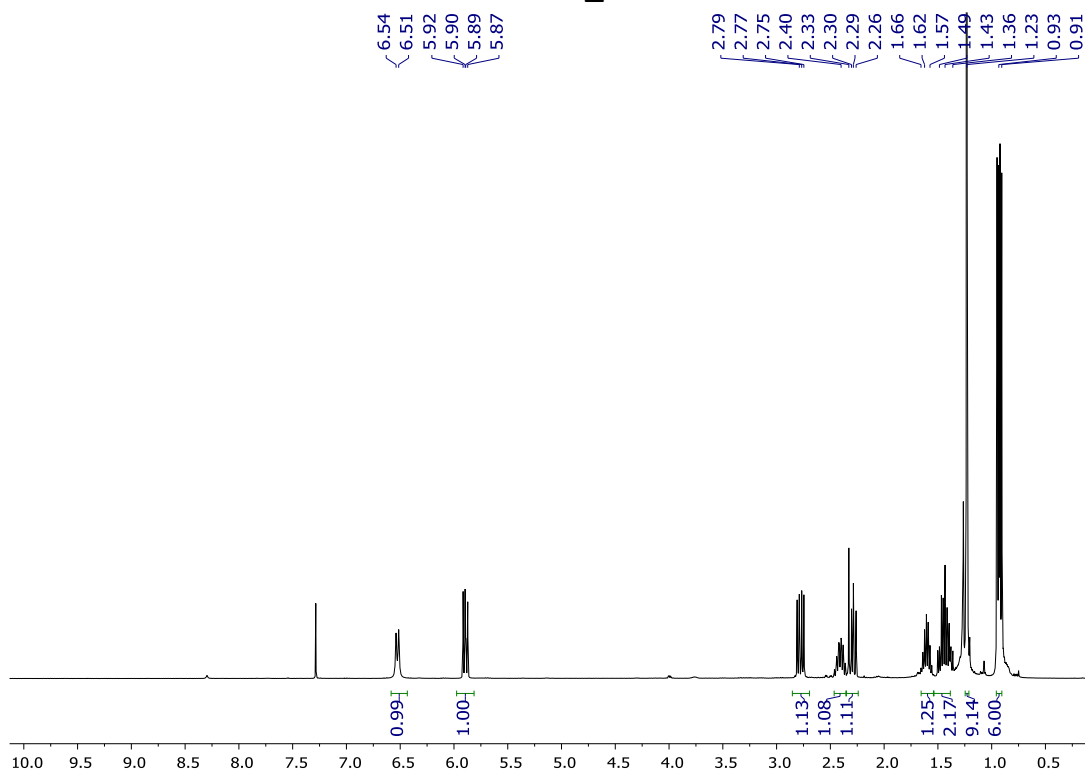
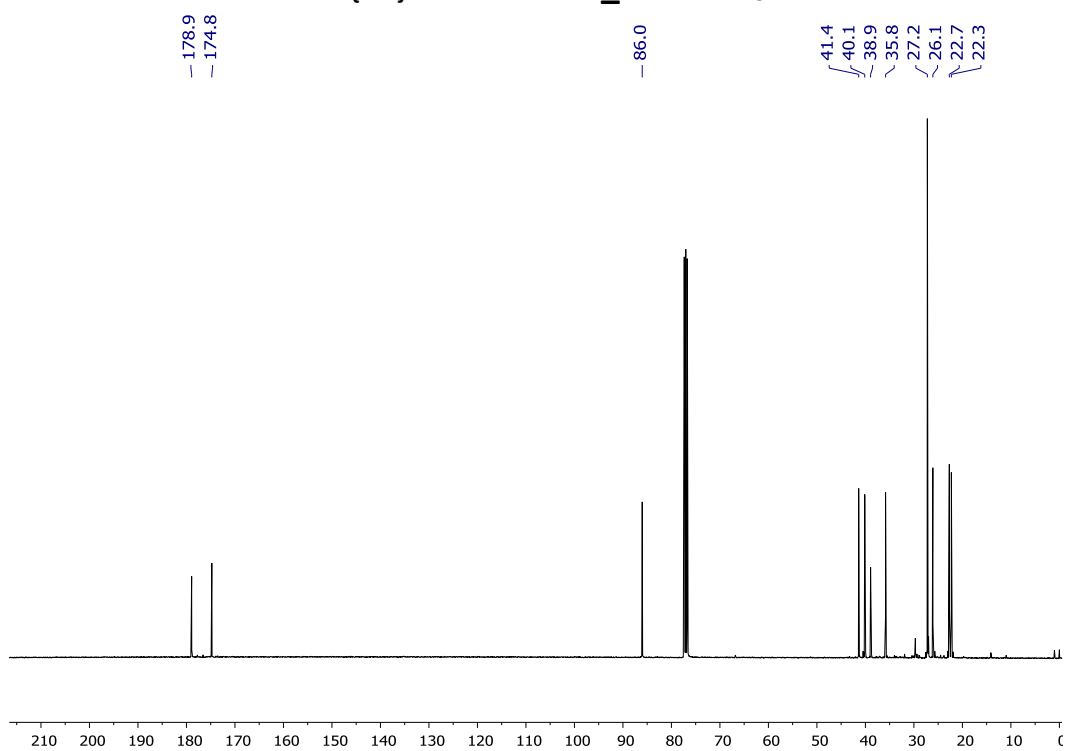
 $^1\text{H-NMR}$ of **P8** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P8** in CDCl_3 

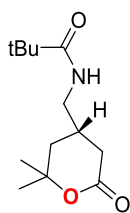
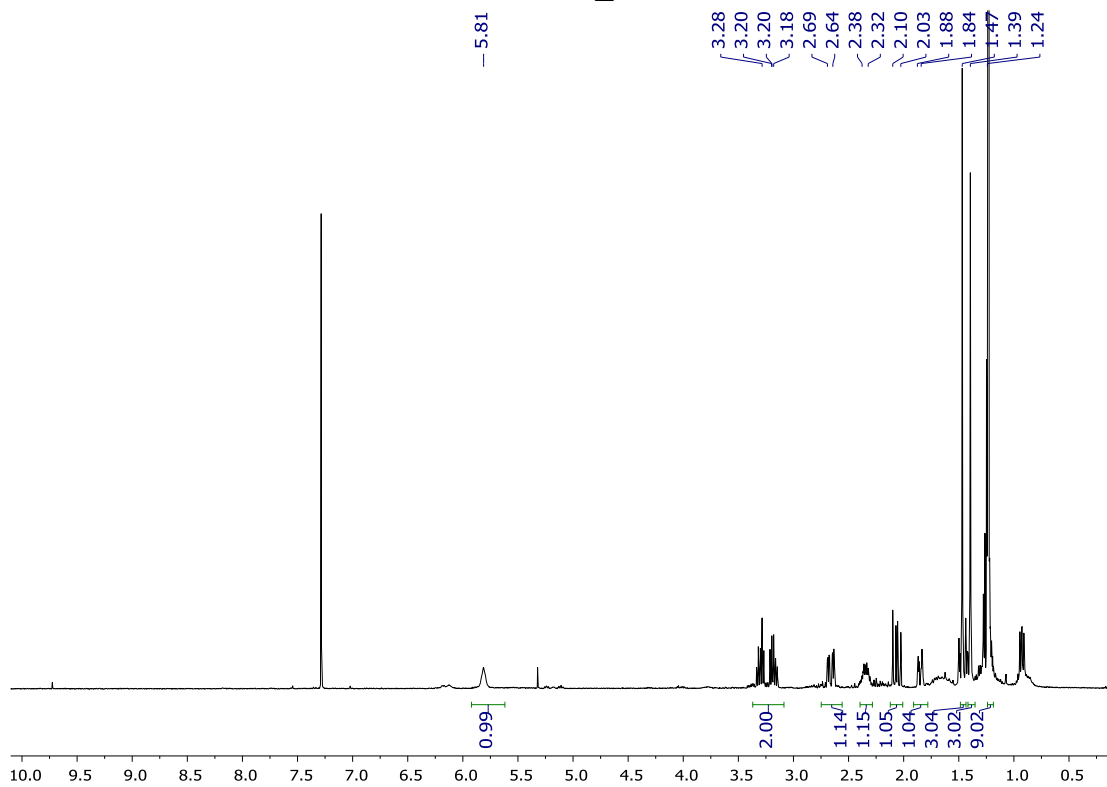
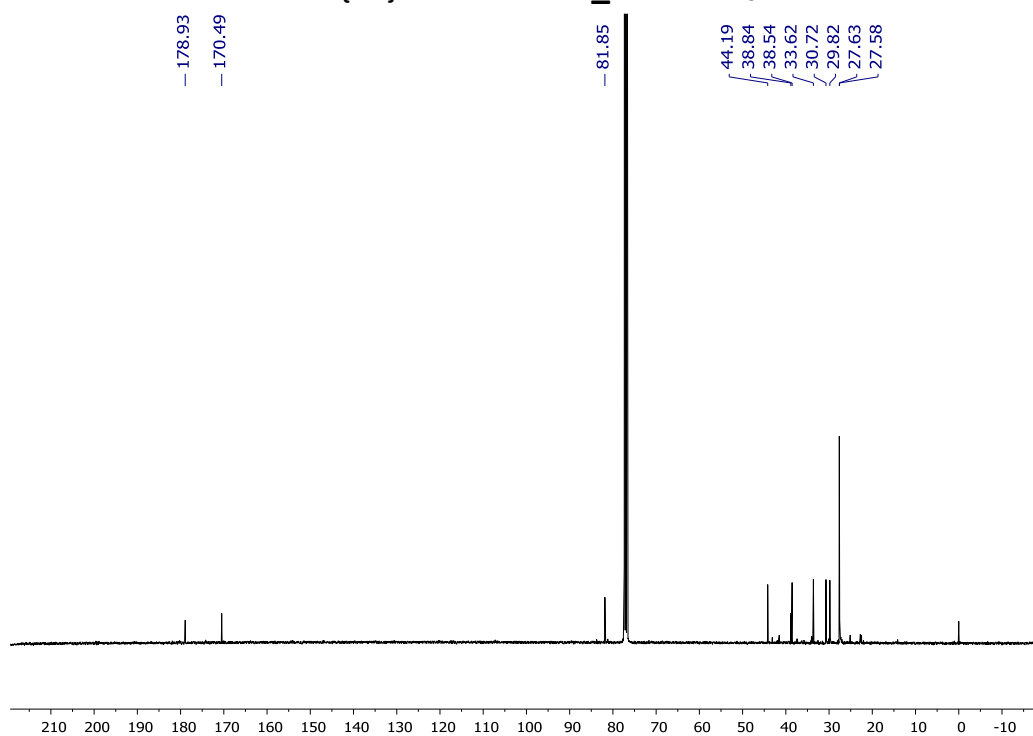
 $^1\text{H-NMR}$ of **P9** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P9** in CDCl_3 

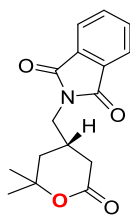
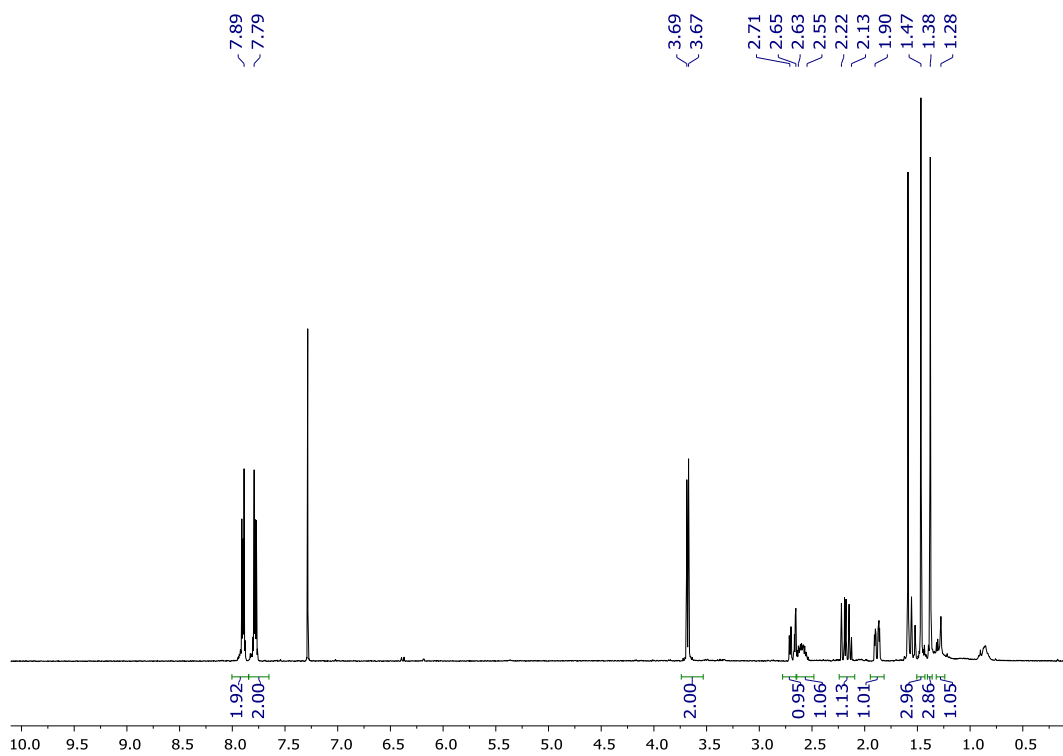
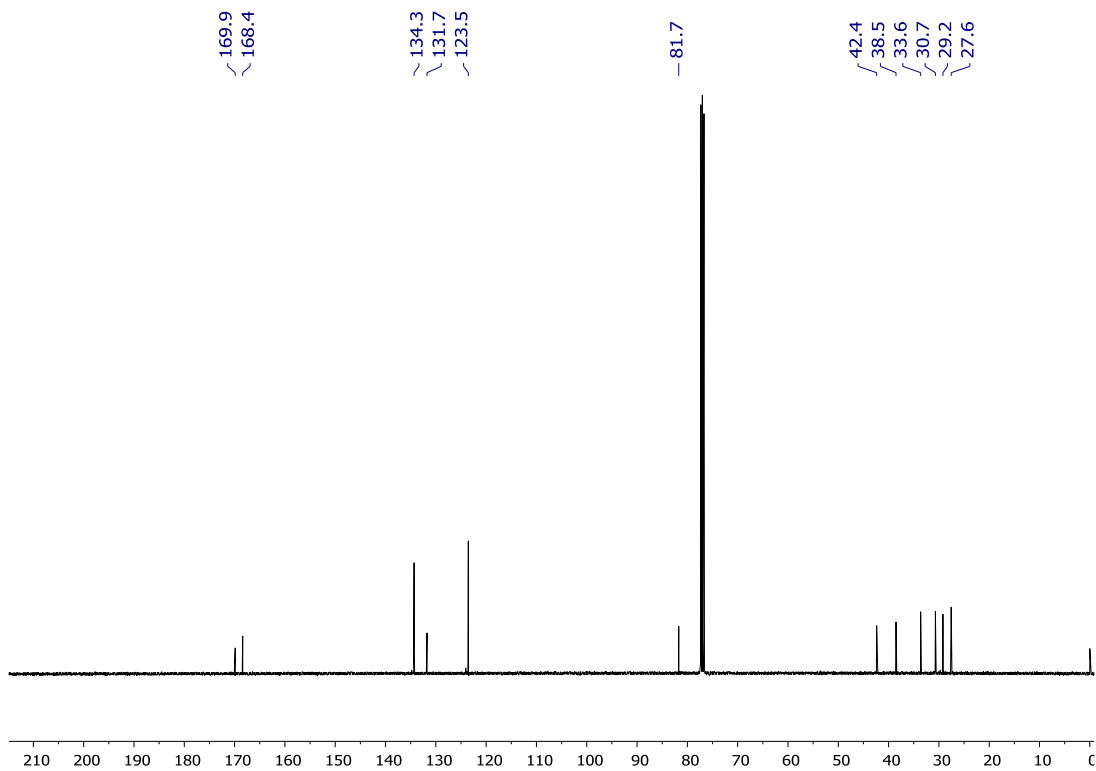
 $^1\text{H-NMR}$ of **P10** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P10** in CDCl_3 

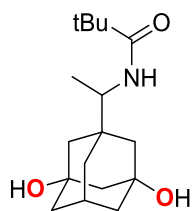
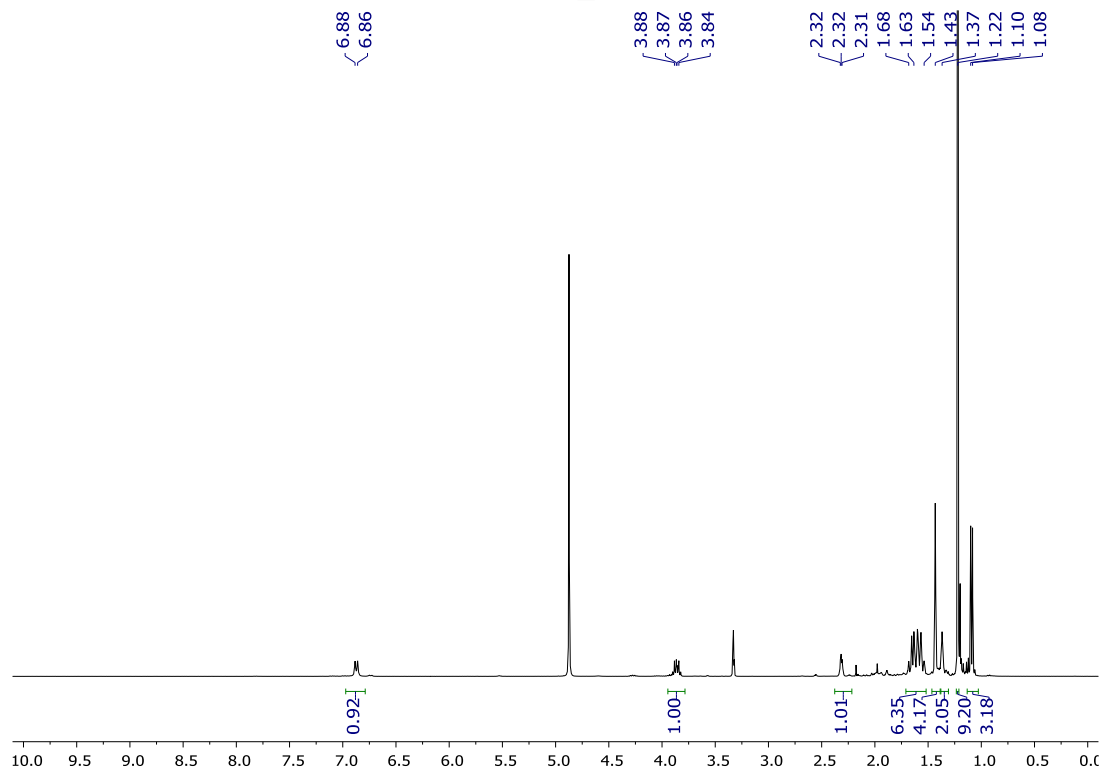
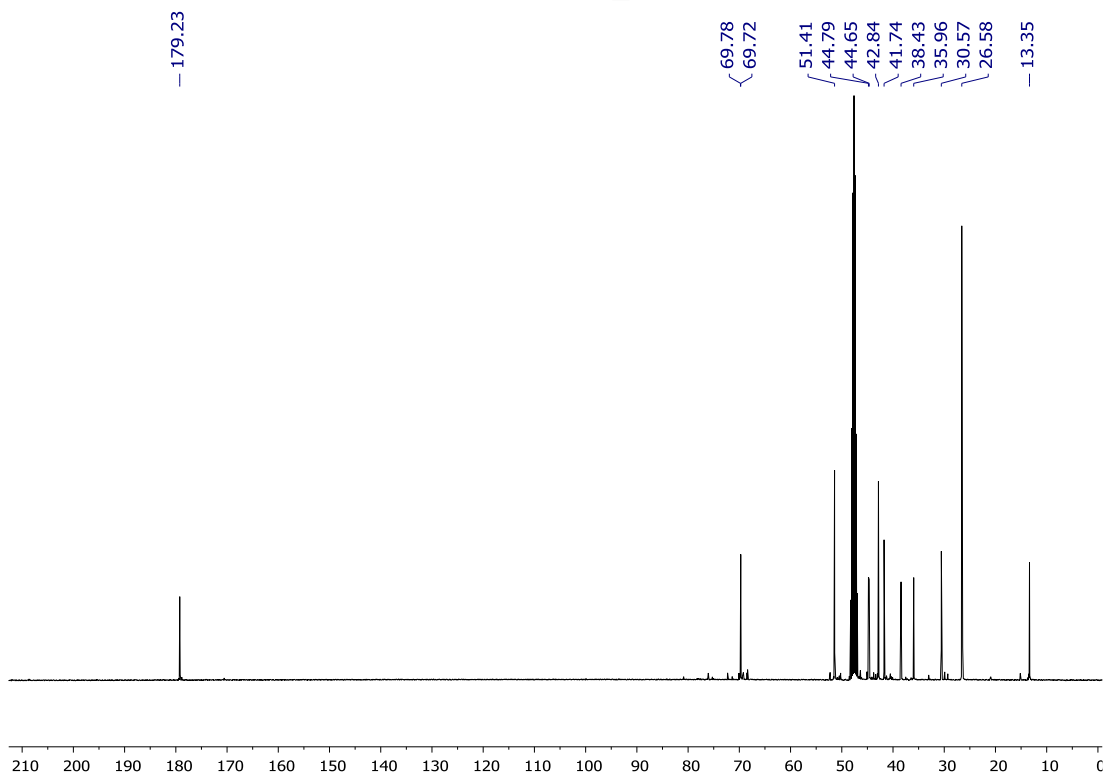
 $^1\text{H-NMR}$ of **P11** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P11** in CDCl_3 

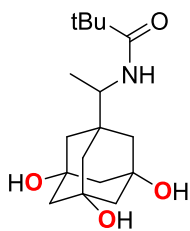
 $^1\text{H-NMR}$ of **P12** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P12** in CDCl_3 

 $^1\text{H-NMR}$ of **P13_a** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P13_a** in CDCl_3 

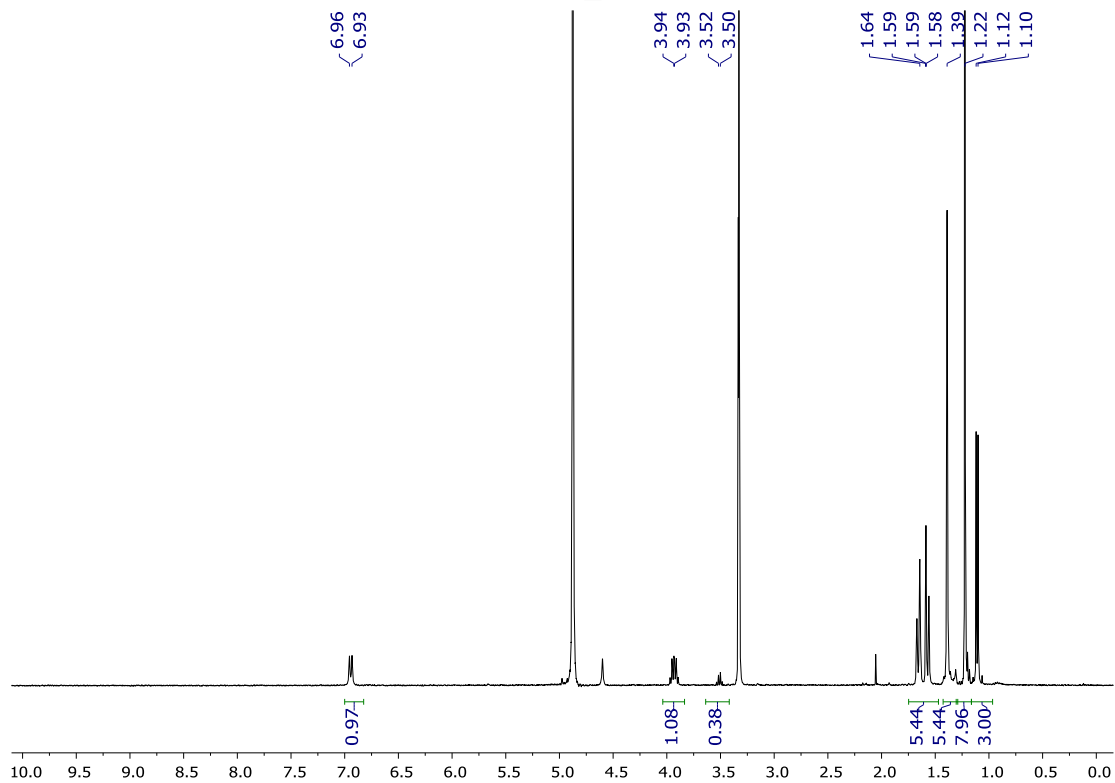
 $^1\text{H-NMR}$ of **P13_b** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P13_b** in CDCl_3 

 $^1\text{H-NMR}$ of **P14** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P14** in CDCl_3 

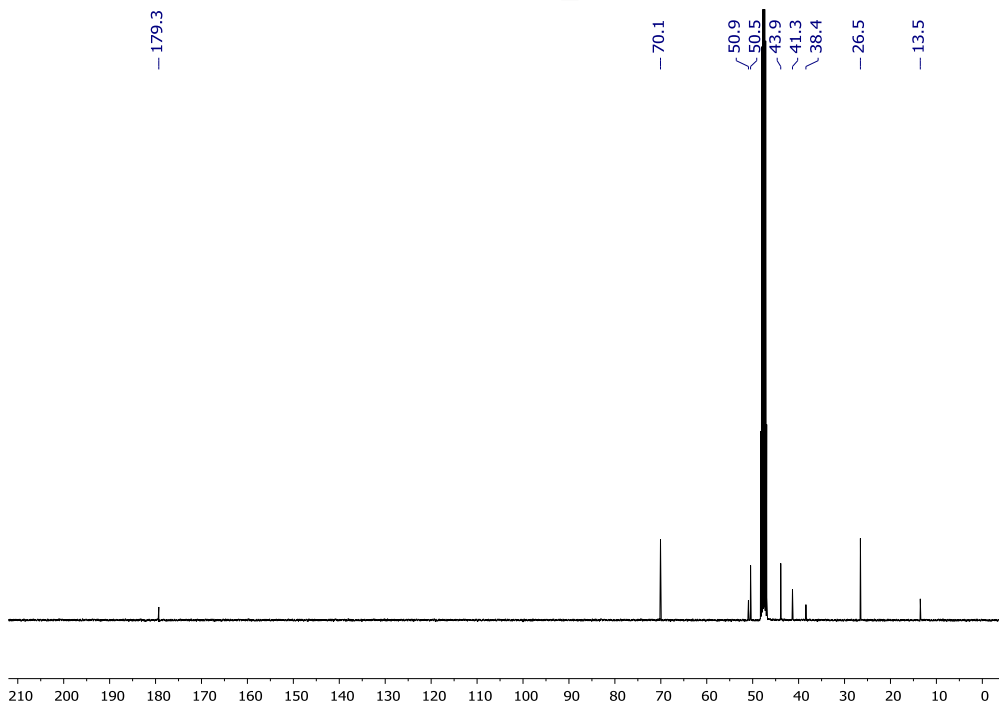
 $^1\text{H-NMR}$ of P15_a in CH_3OD  $^{13}\text{C}\{^1\text{H}\}$ -NMR of P15_a in CH_3OD 

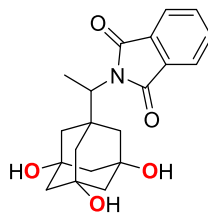
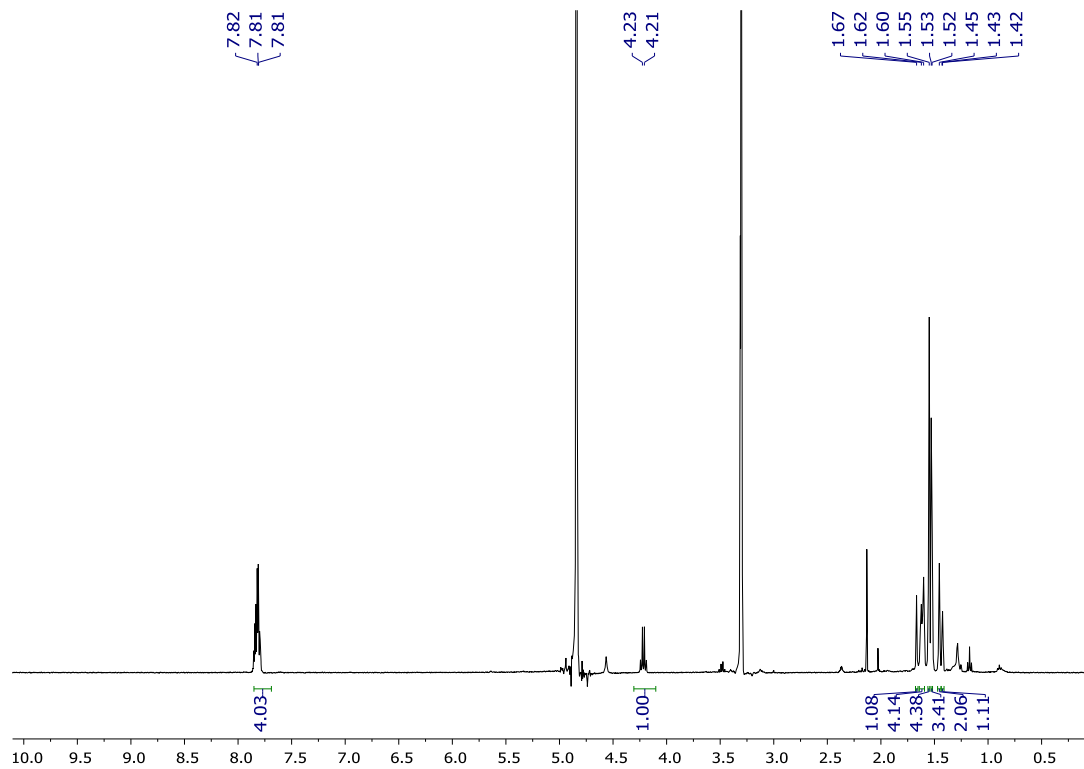
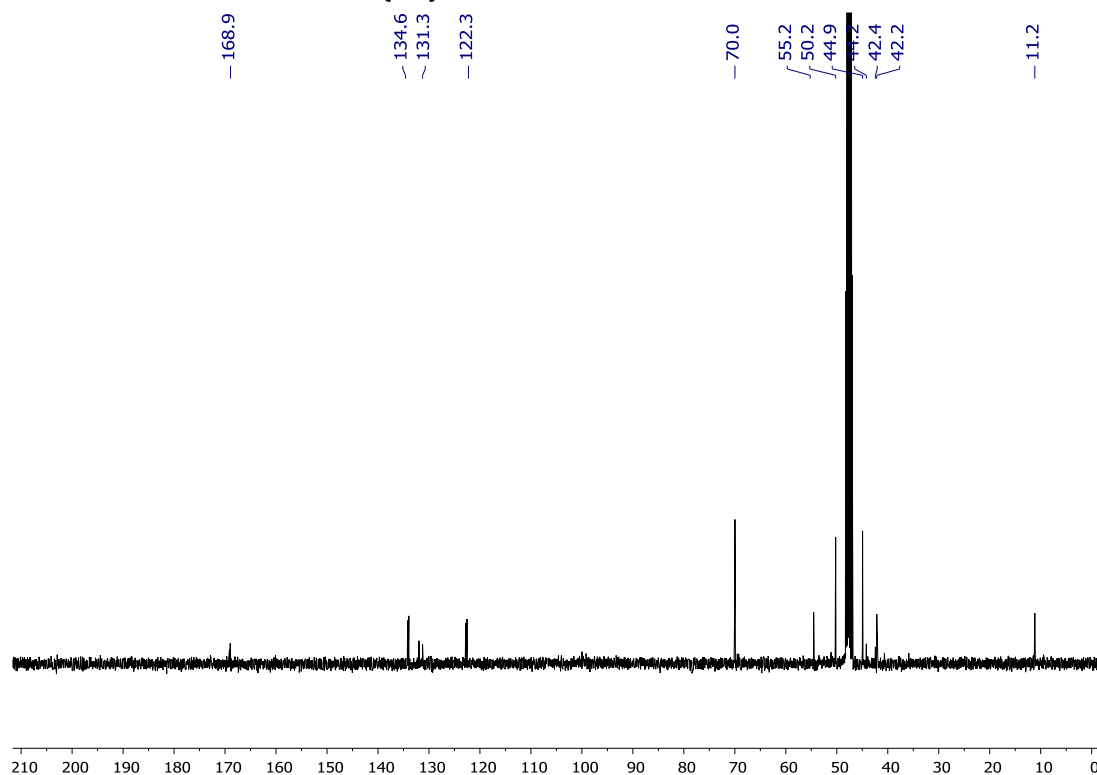


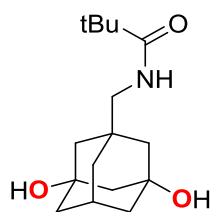
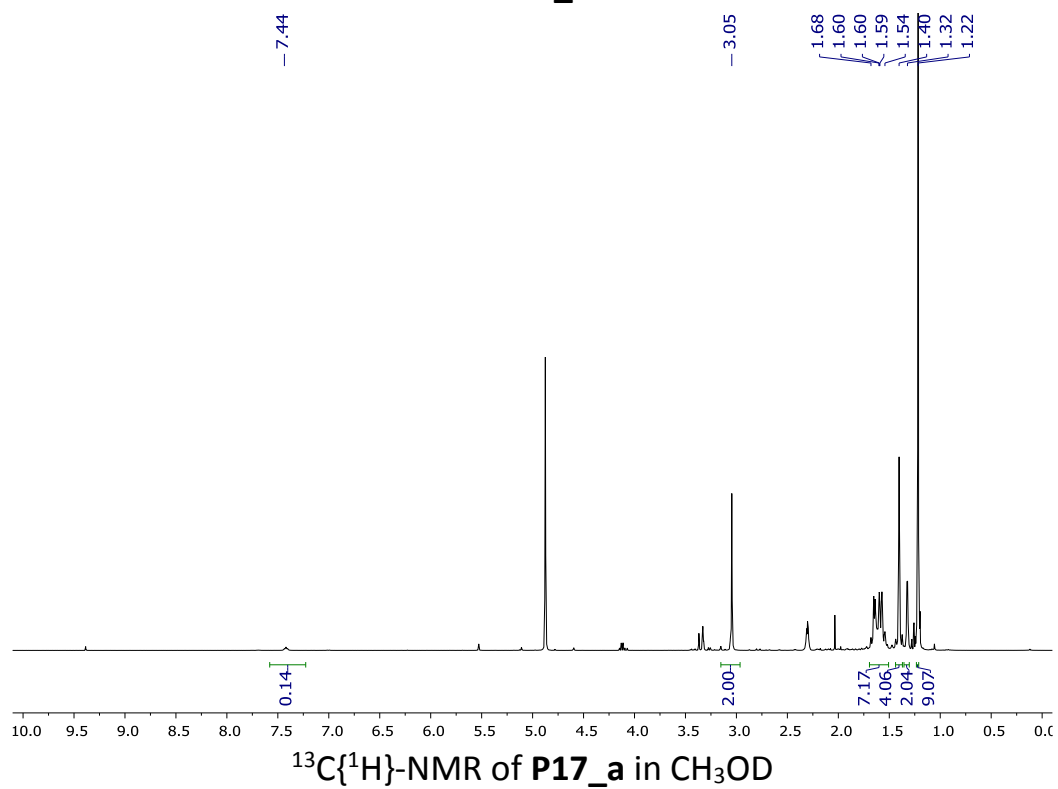
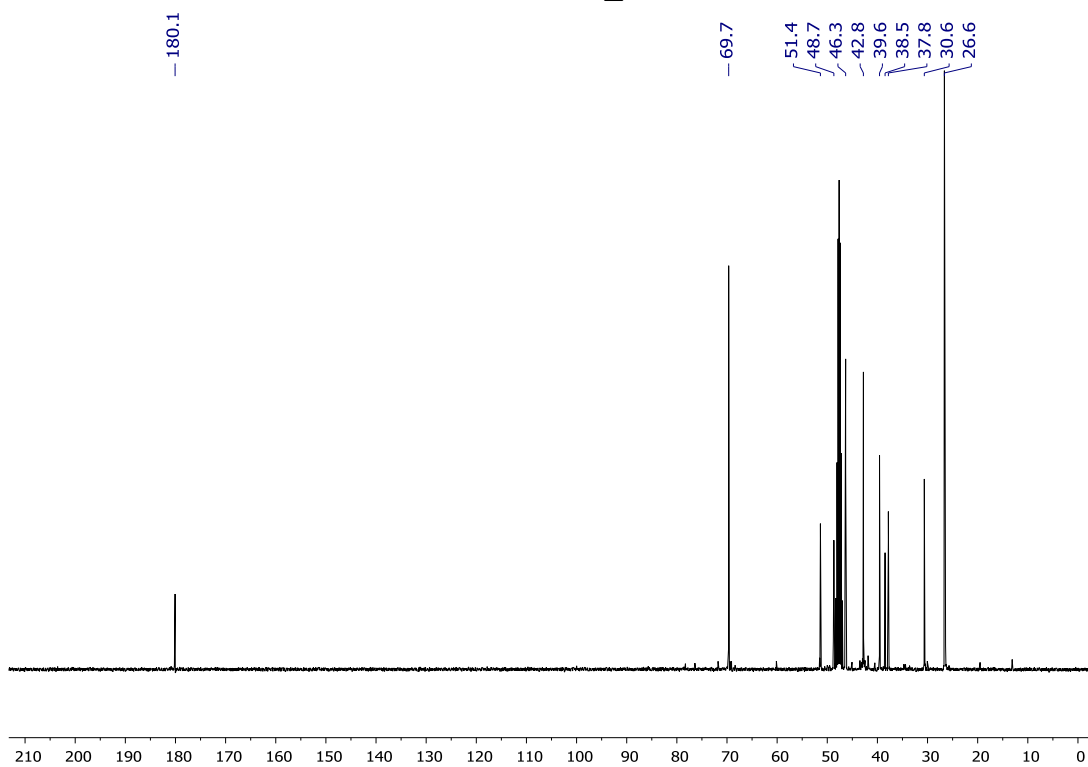
$^1\text{H-NMR}$ of P15_b in CH_3OD

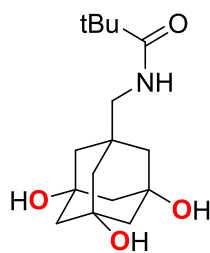
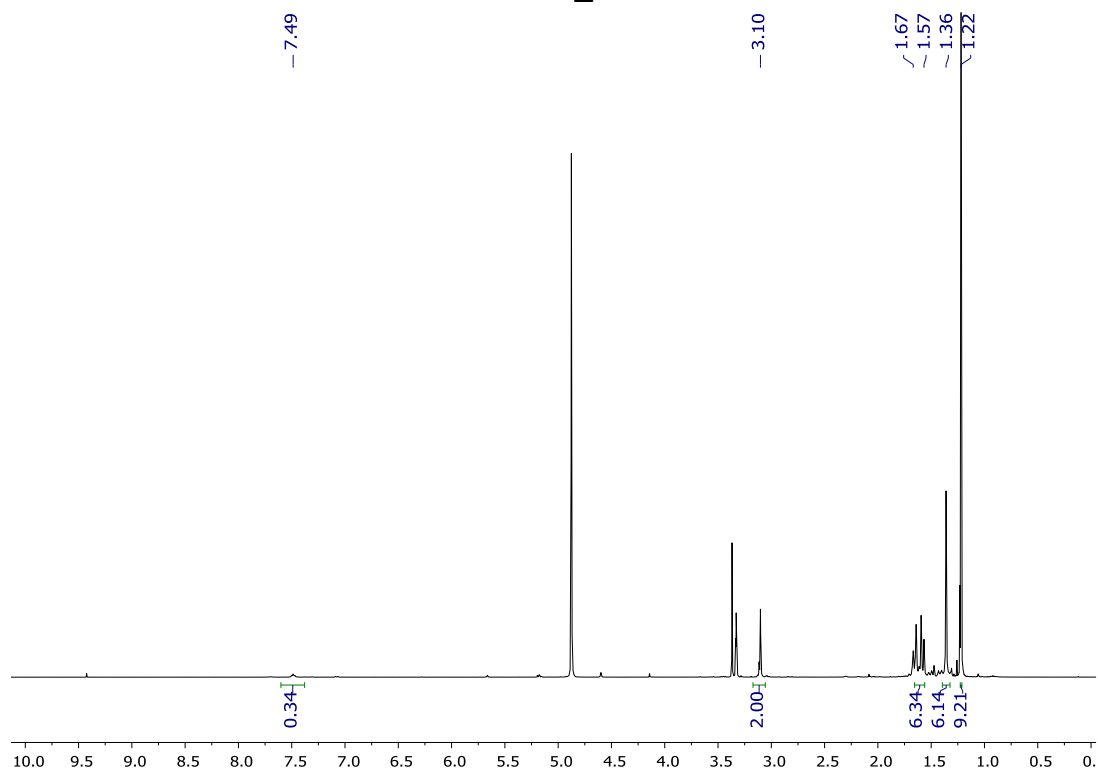
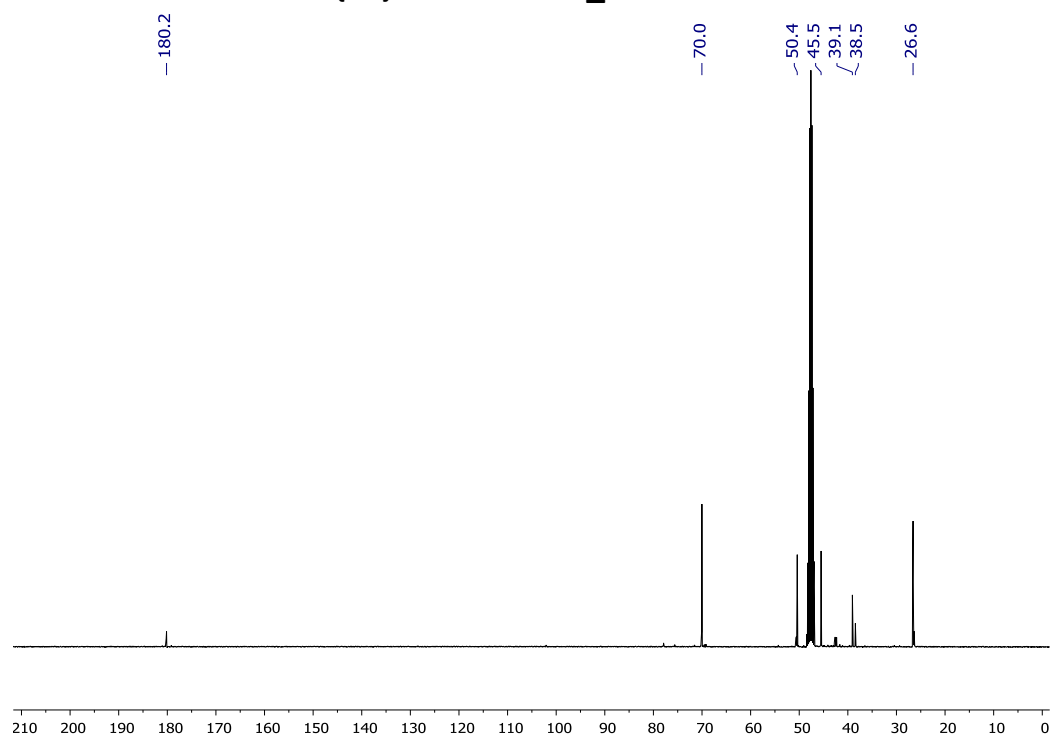


$^{13}\text{C}\{^1\text{H}\}$ -NMR of P15_b in CH_3OD



 $^1\text{H-NMR}$ of P16 in CH_3OD  $^{13}\text{C}\{^1\text{H}\}$ -NMR of P16 in CH_3OD 

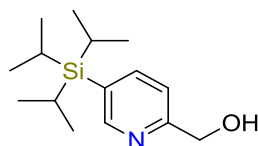
 $^1\text{H-NMR}$ of **P17_a** in CH_3OD  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P17_a** in CH_3OD 

 $^1\text{H-NMR}$ of **P17_b** in CH_3OD  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P17_b** in CH_3OD 

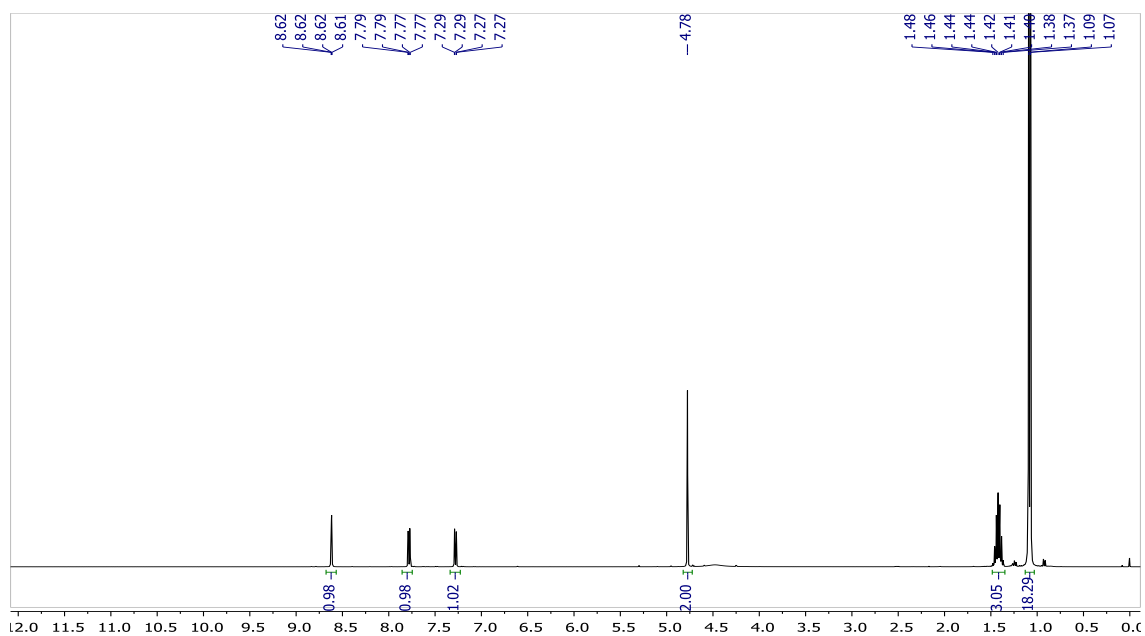
Experimental Section: Chapter VI.2

Highly Enantioselective Oxidation of Nonactivated Aliphatic C–H Bonds with Hydrogen Peroxide Catalyzed by Manganese Complexes

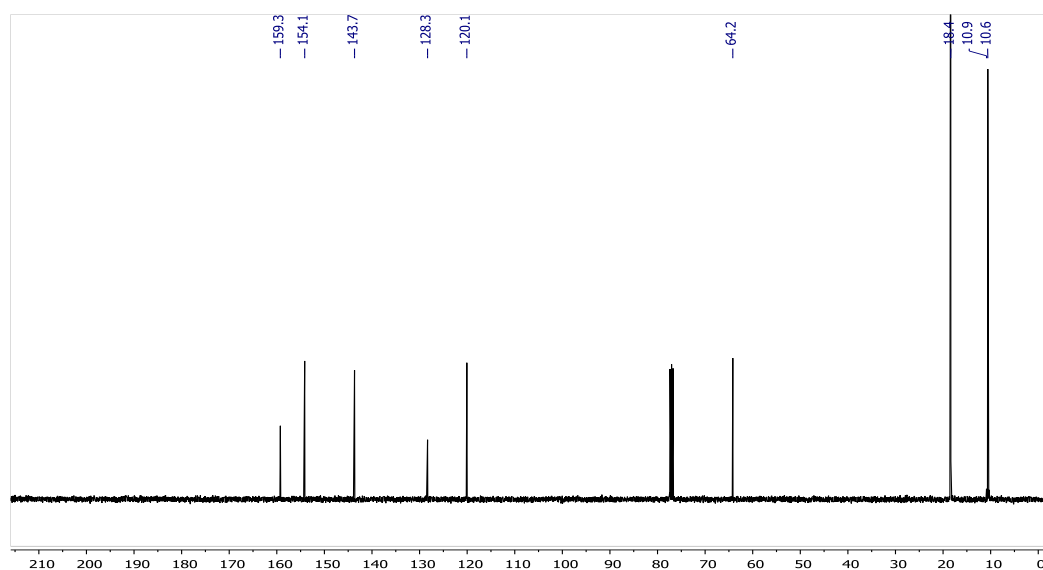
A1 ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of ligands

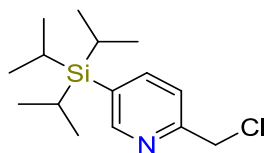


^1H -NMR of TIPSPyOH in CDCl_3



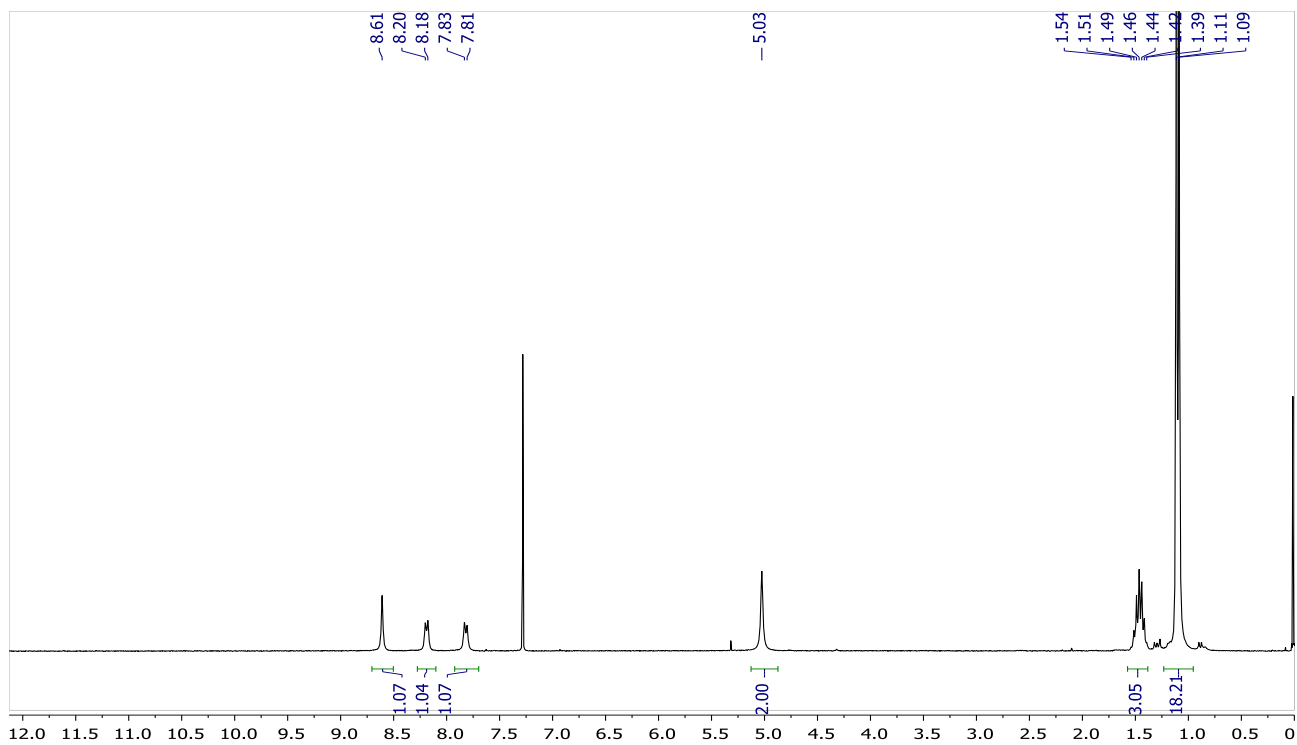
$^{13}\text{C}\{^1\text{H}\}$ -NMR of TIPSPyOH in CDCl_3



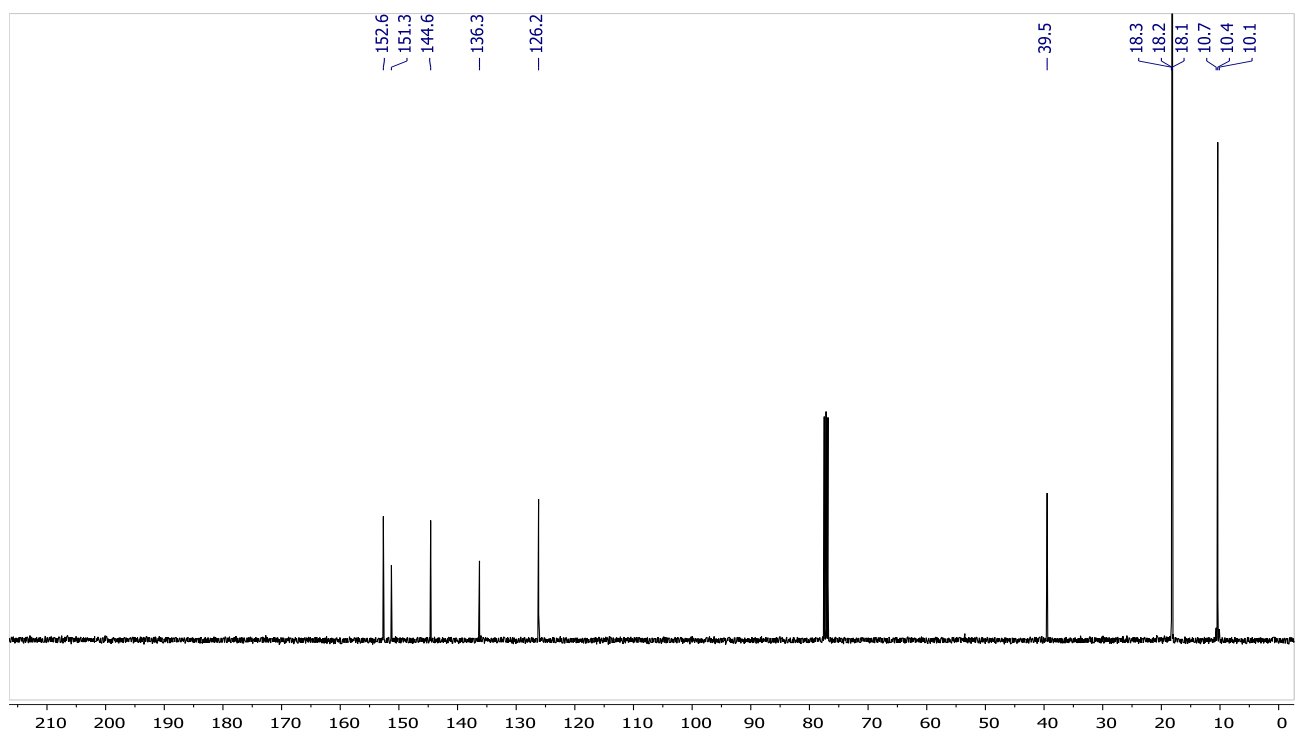


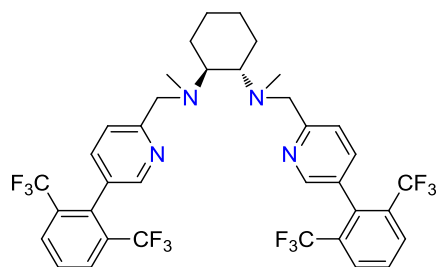
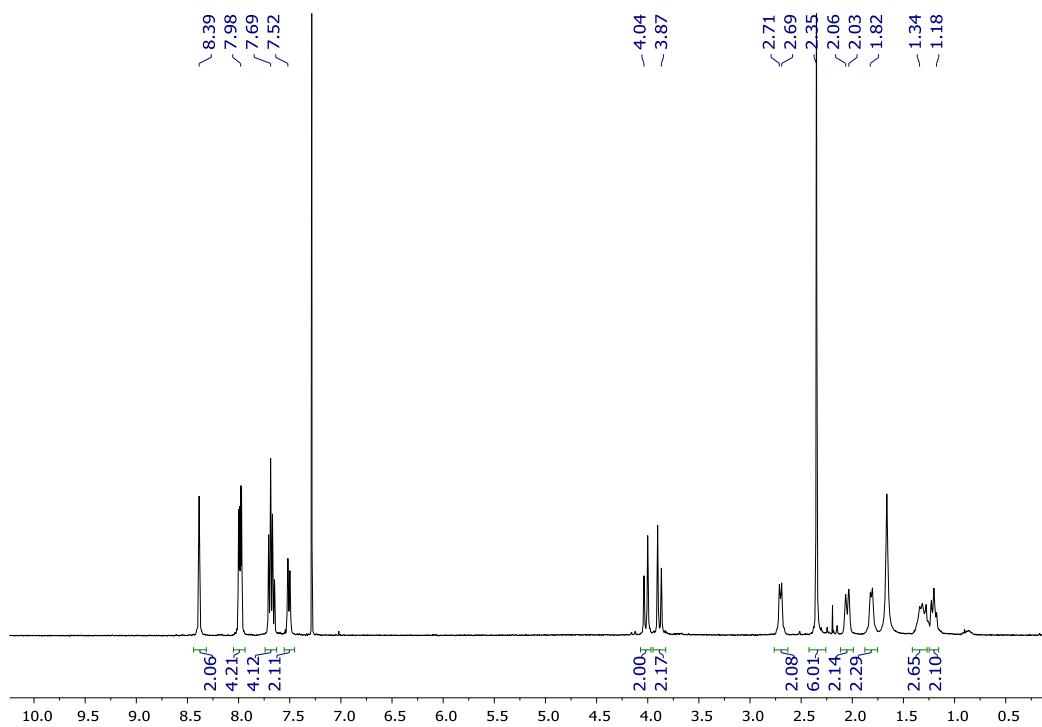
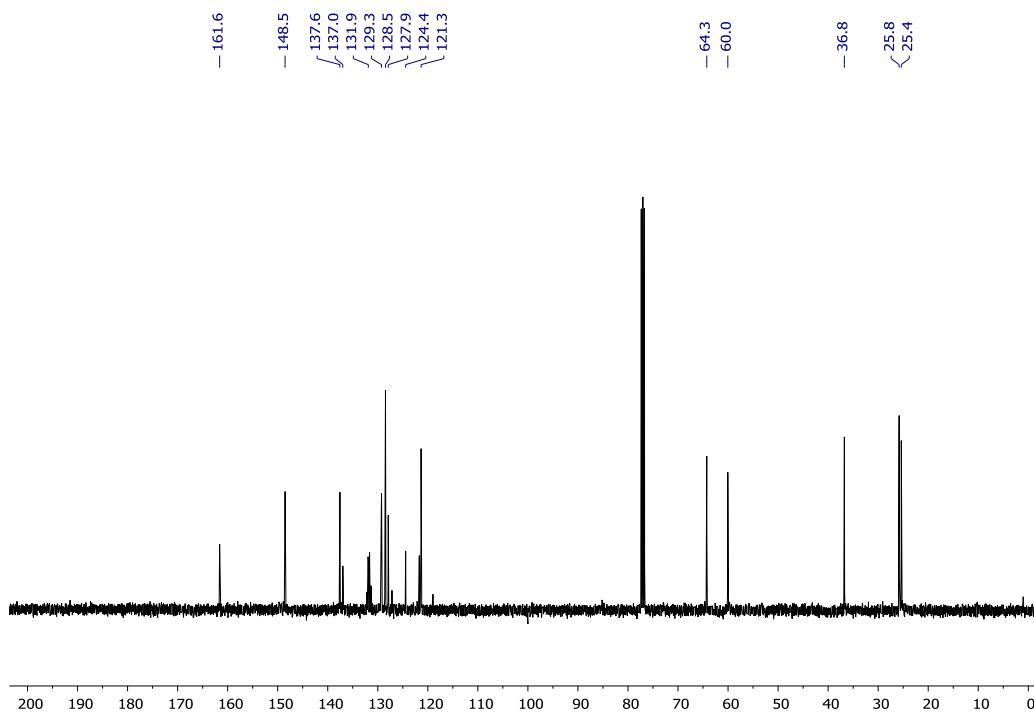
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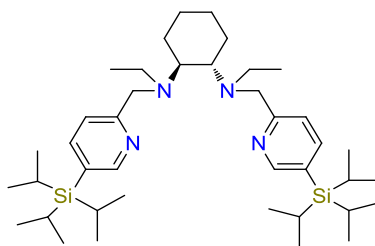
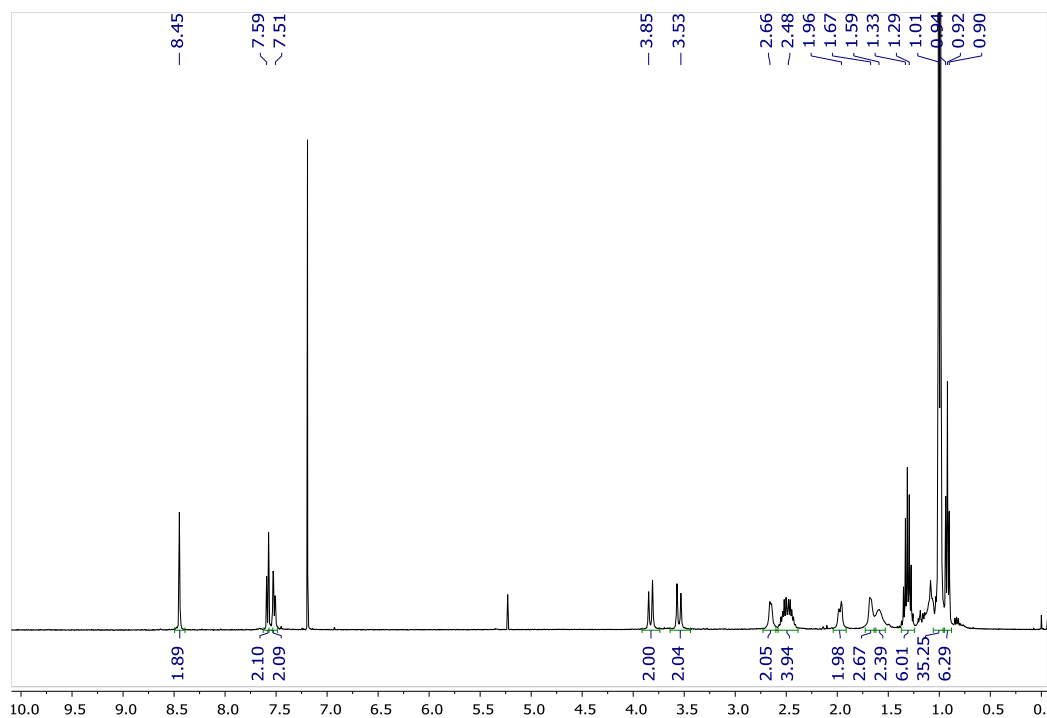
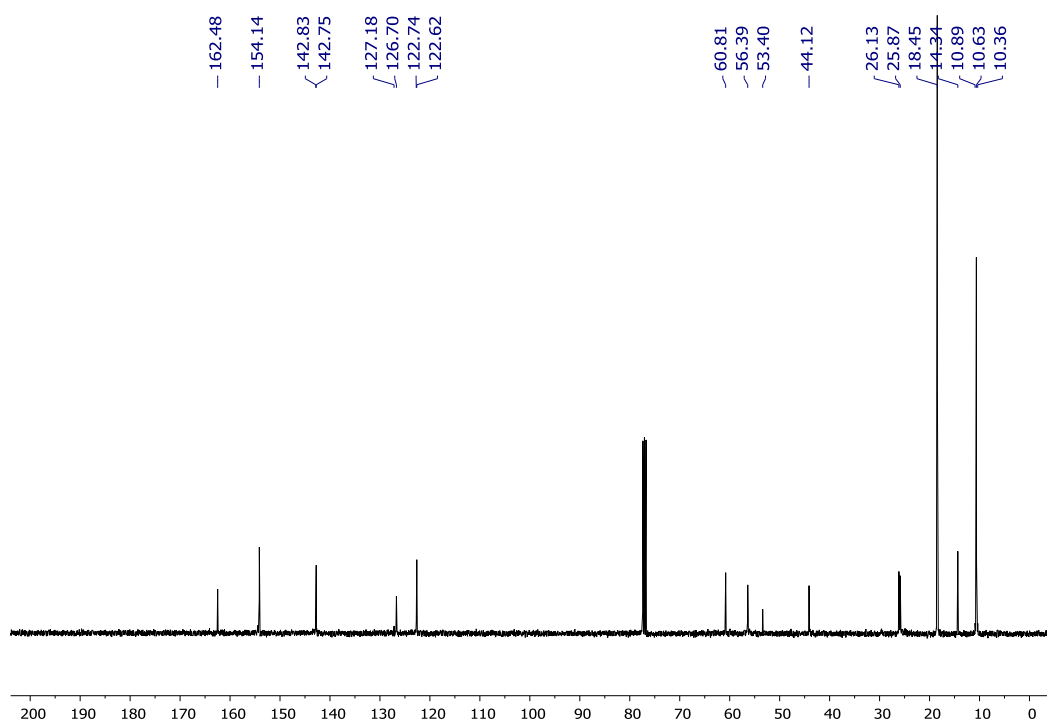
$^1\text{H-NMR}$ of $\text{TIP}^{\text{s}}\text{PyCl}$ in CDCl_3

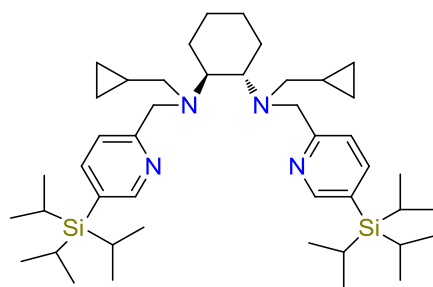
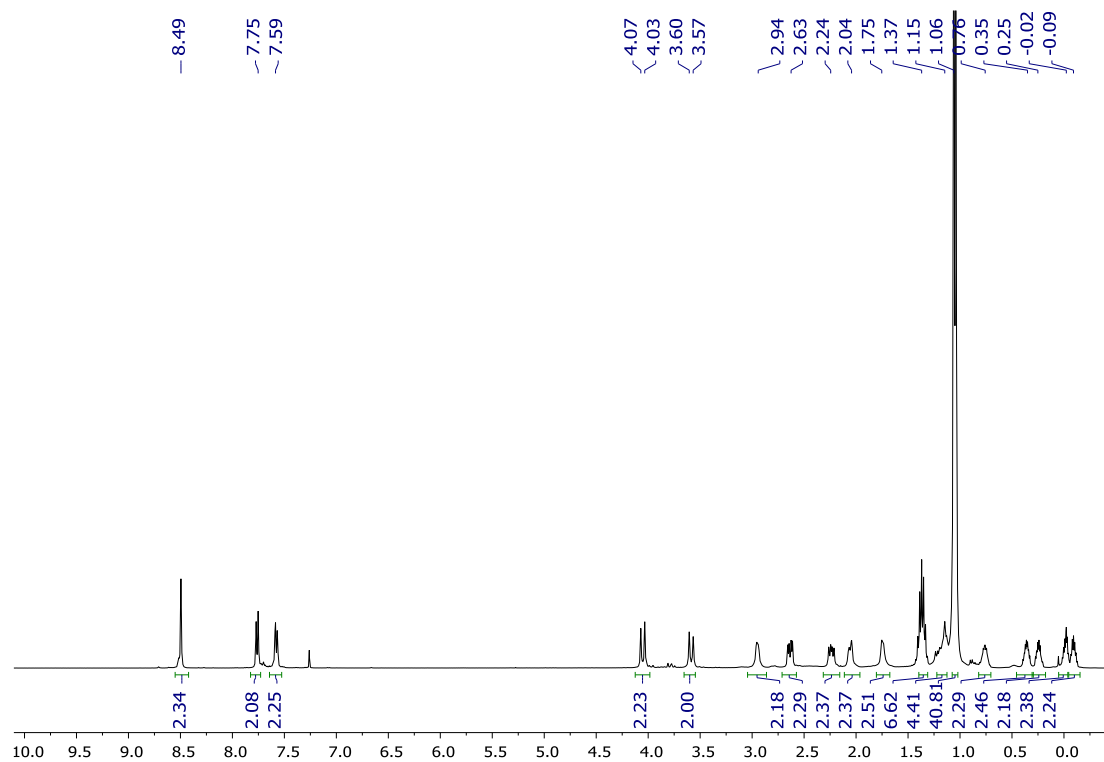
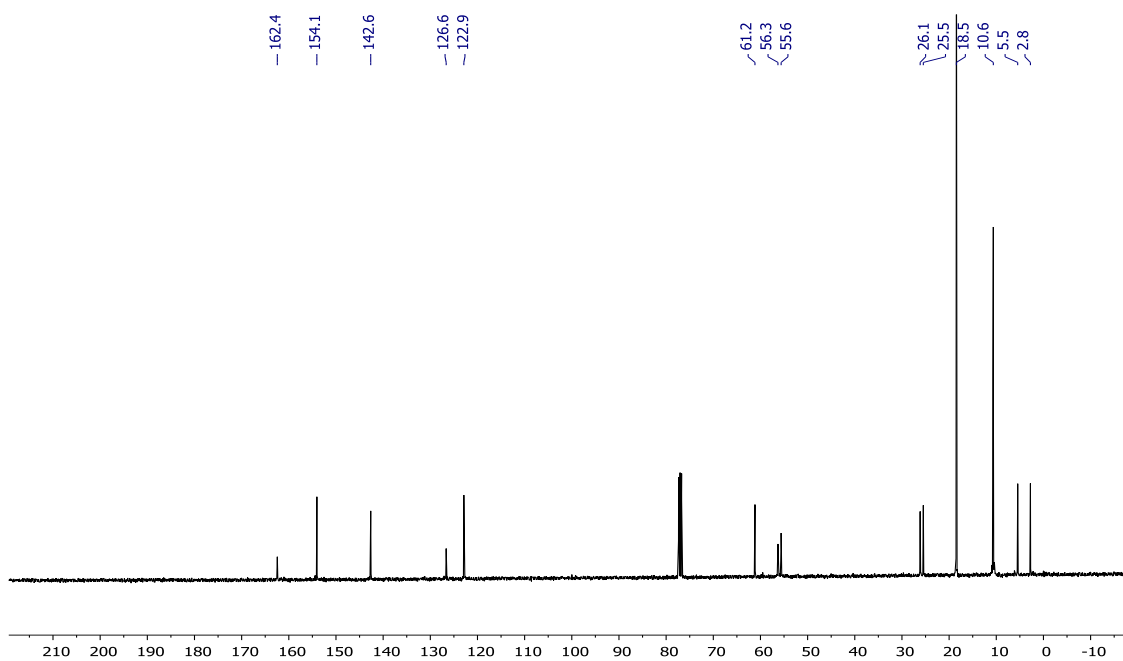


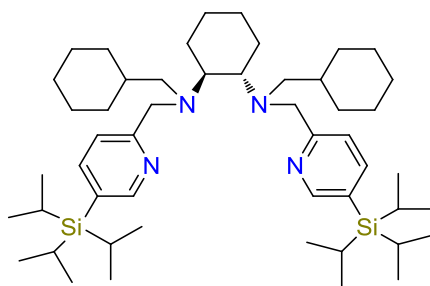
$^{13}\text{C}\{^1\text{H}\}$ -NMR of $\text{TIP}^{\text{s}}\text{PyCl}$ in CDCl_3



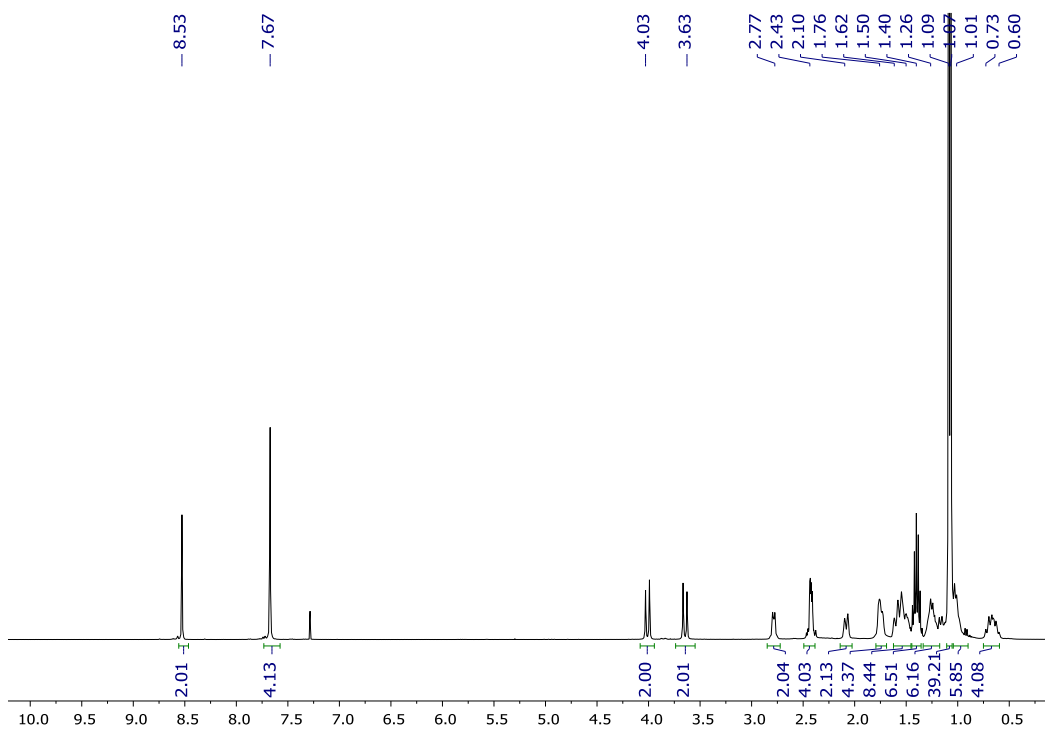
 $^1\text{H-NMR}$ of CF_3mcp in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of CF_3mcp in CDCl_3 

 $^1\text{H-NMR}$ of TIPS^{ecp} in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of TIPS^{ecp} in CDCl_3 

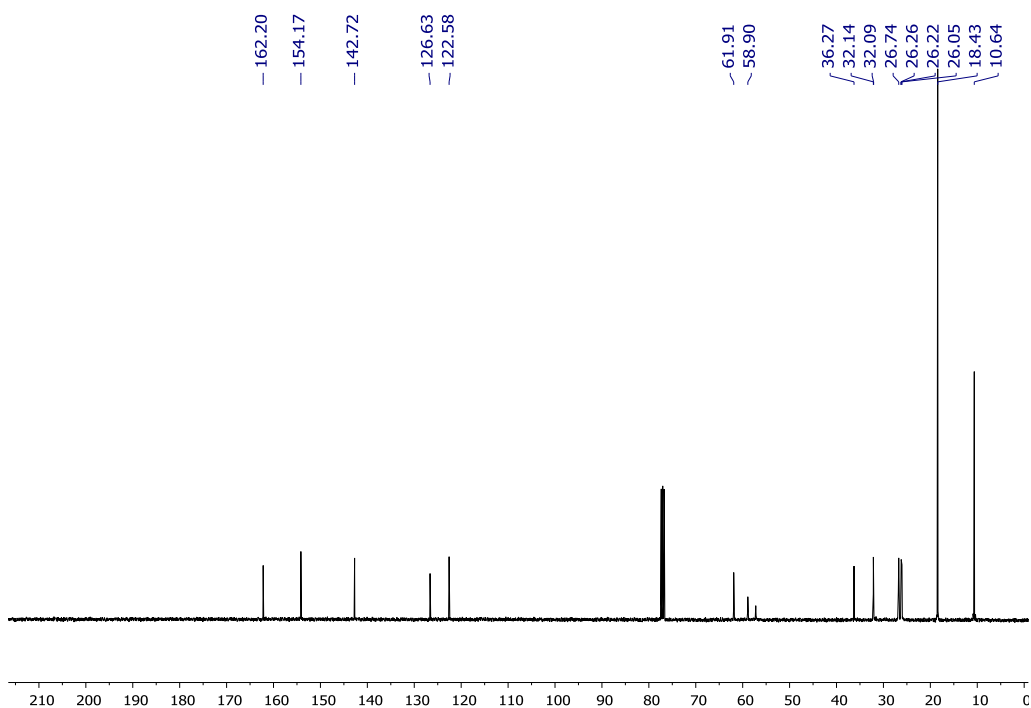
 $^1\text{H-NMR}$ of TIPS-cpcp in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of TIPS-cpcp in CDCl_3 

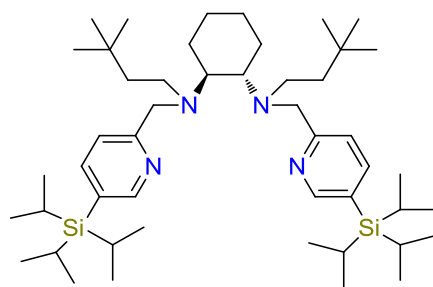
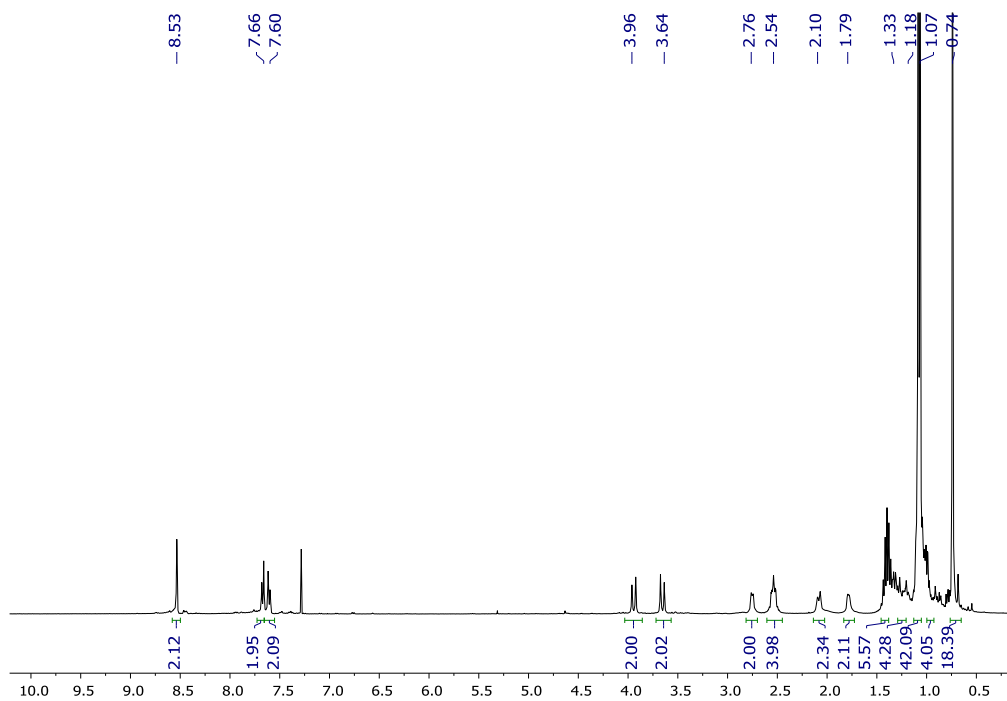
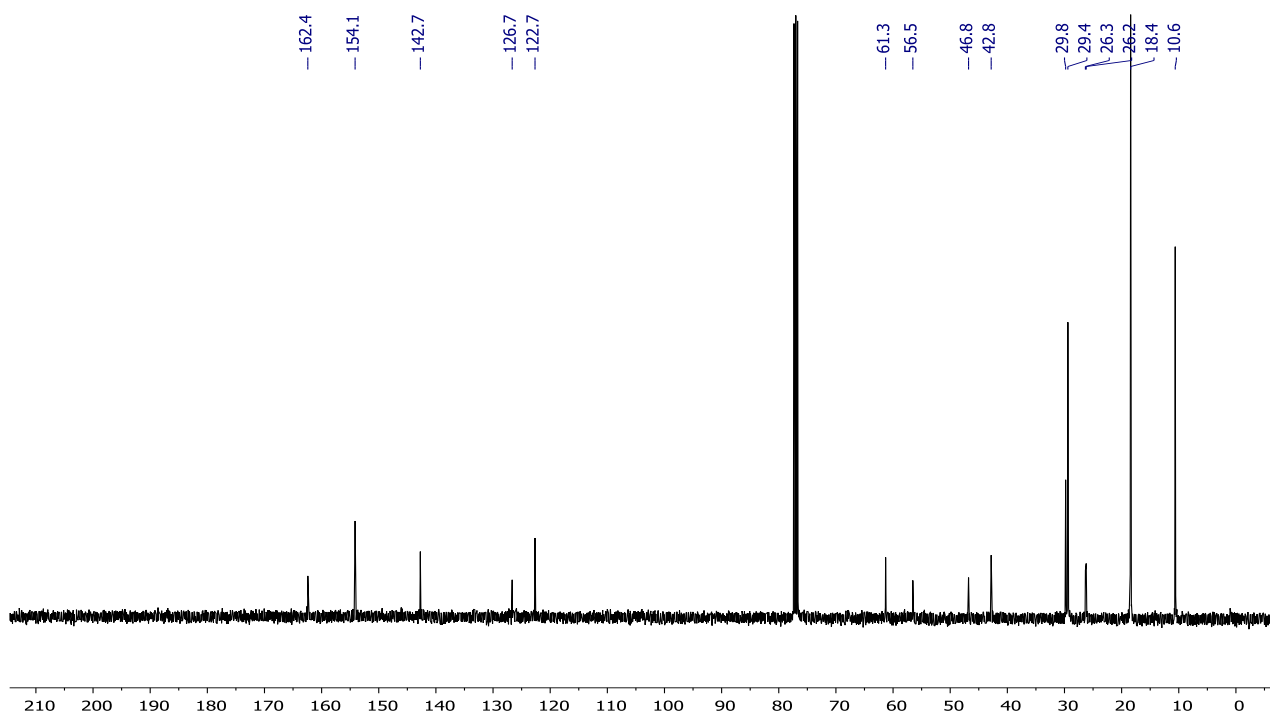


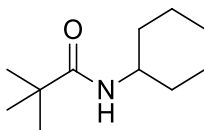
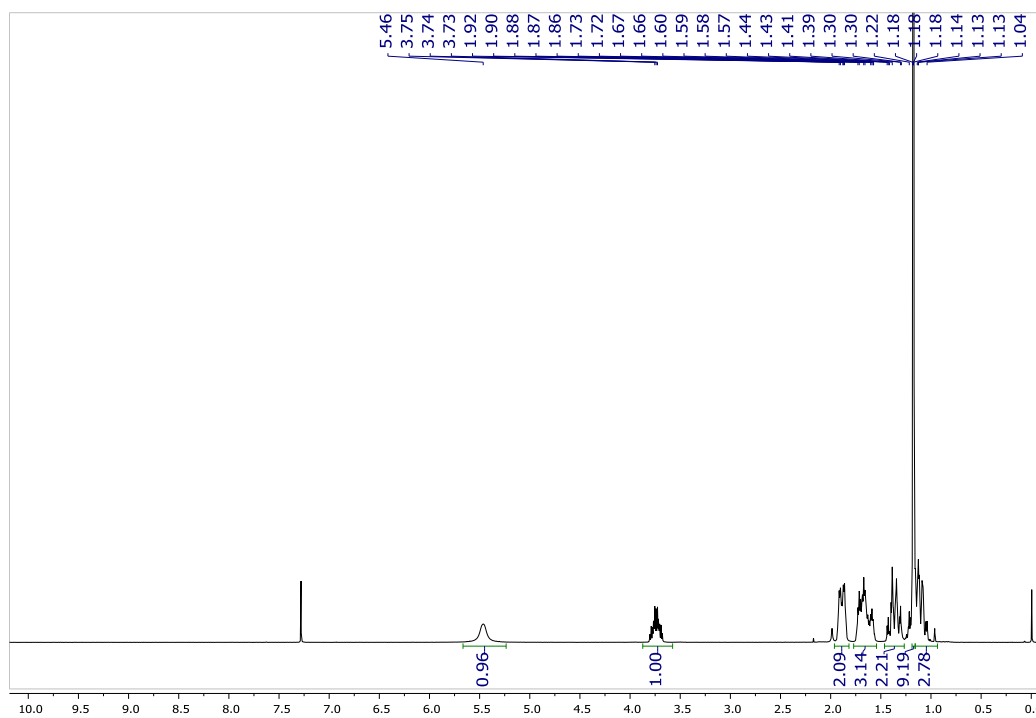
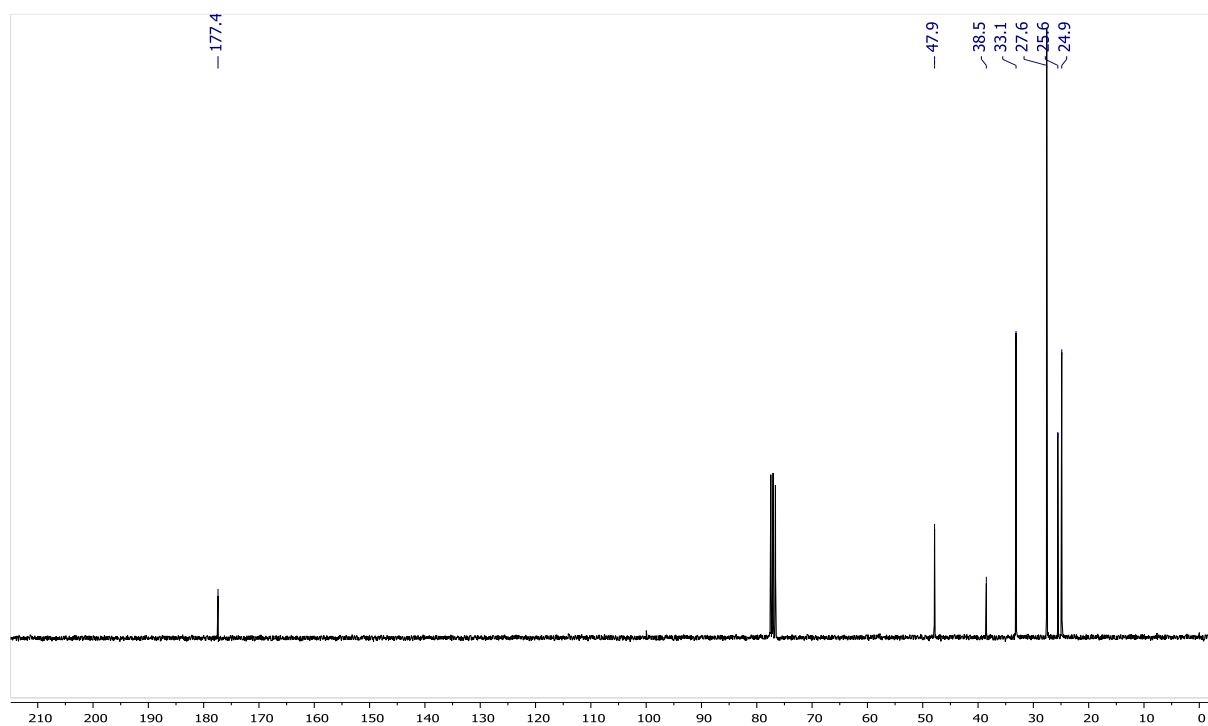
$^1\text{H-NMR}$ of TIPS-chcp in CDCl_3

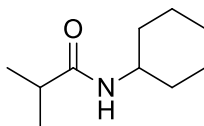
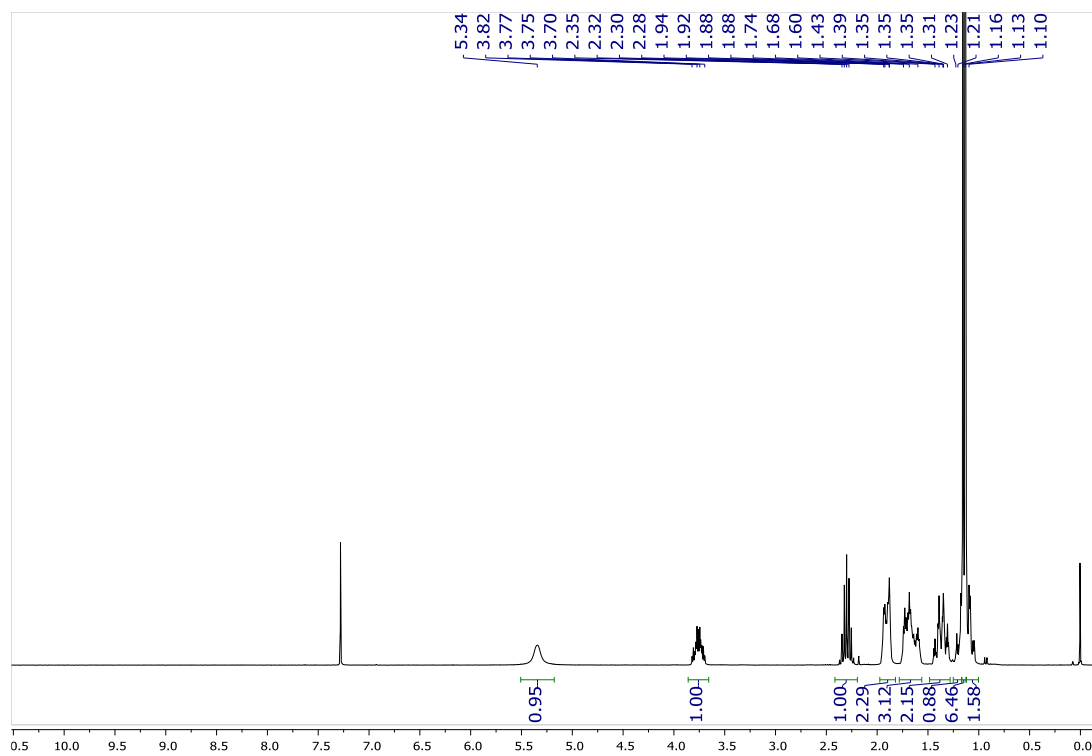
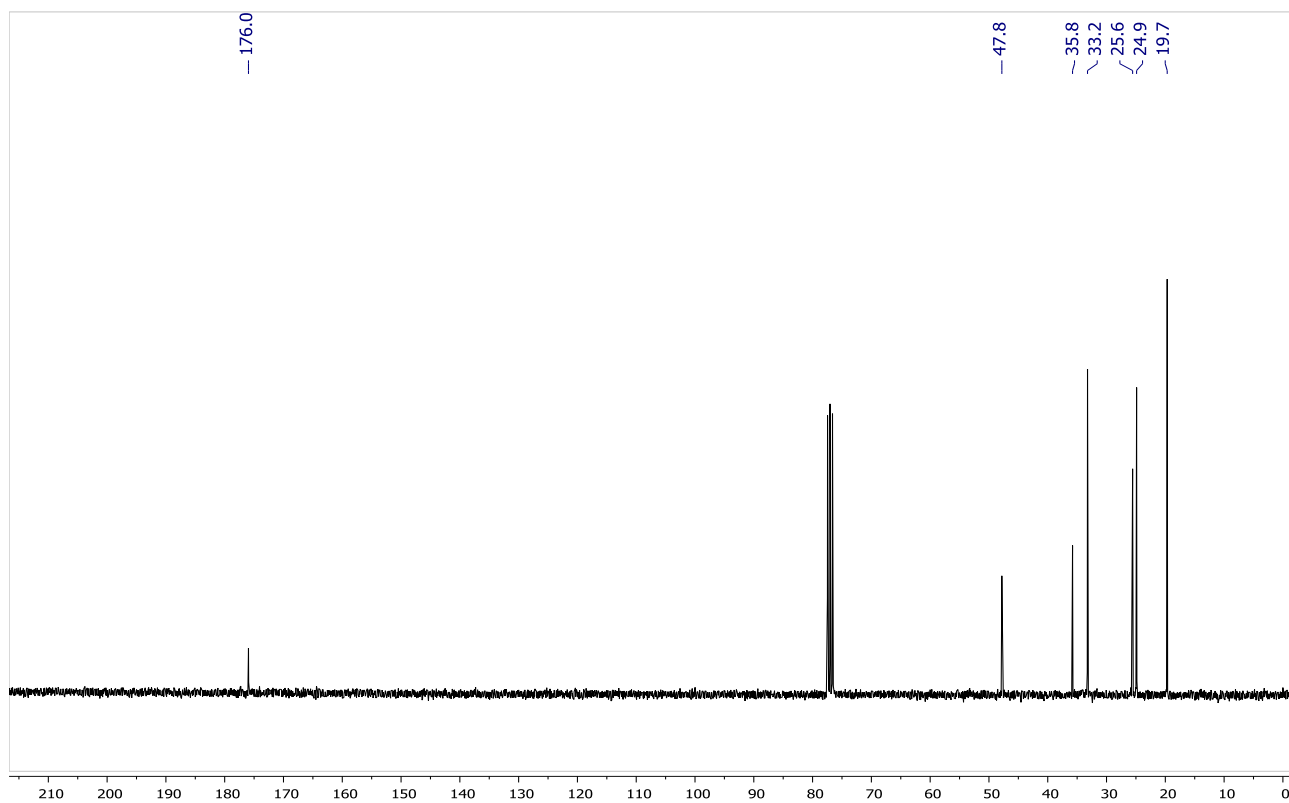


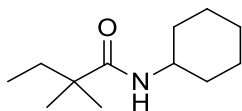
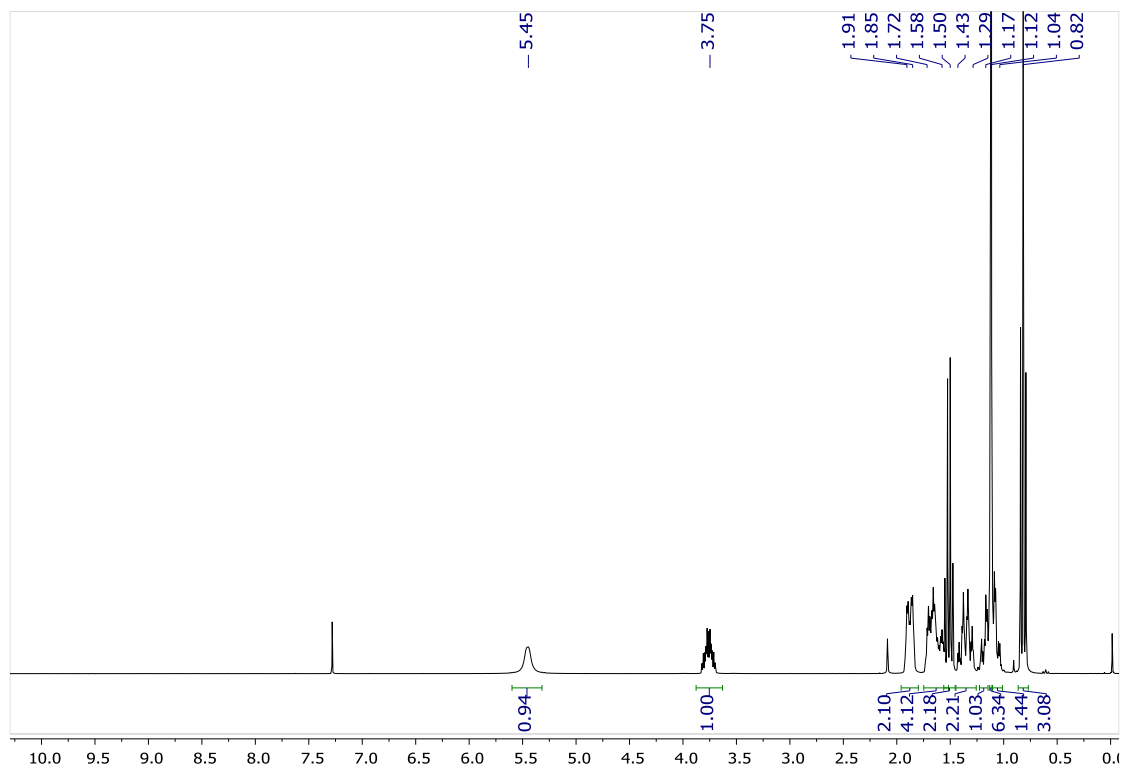
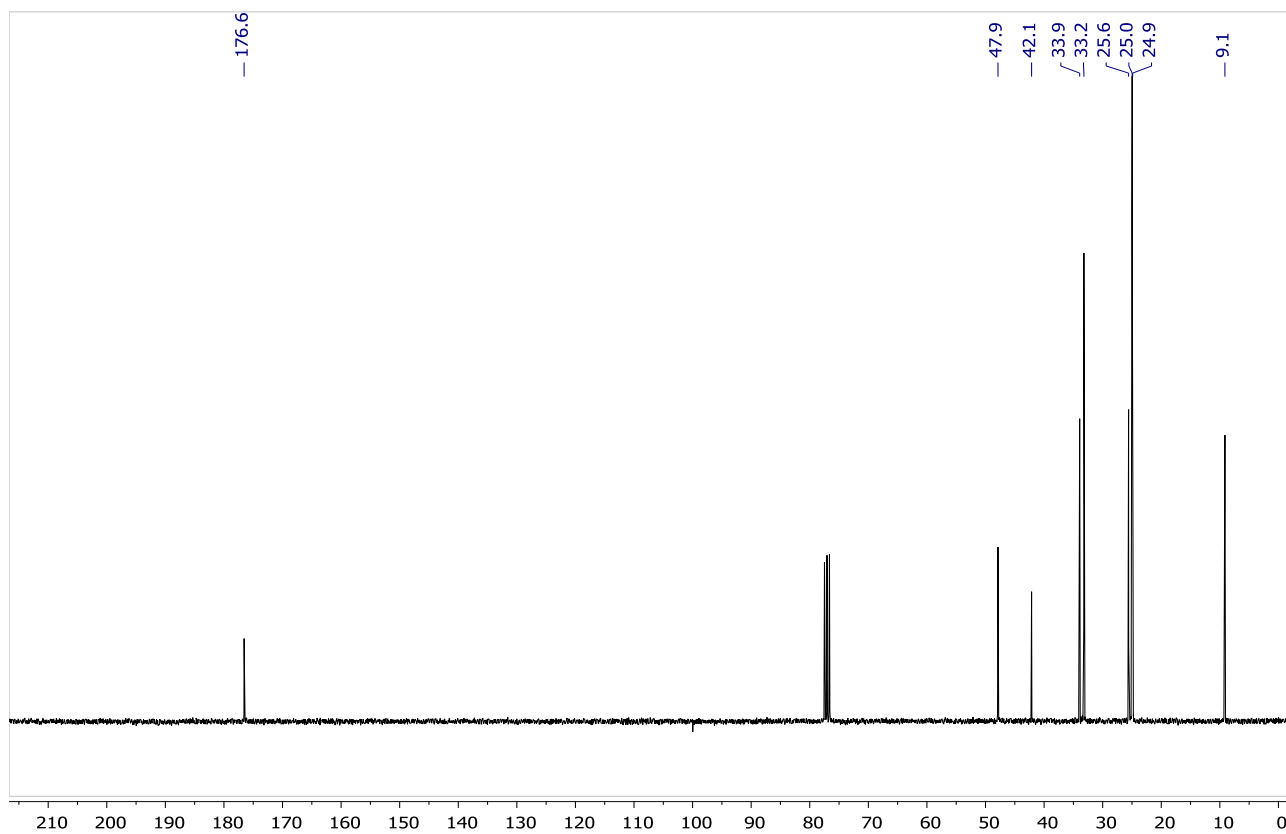
$^{13}\text{C}\{^1\text{H}\}$ -NMR of TIPS-chcp in CDCl_3

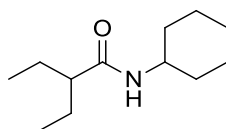
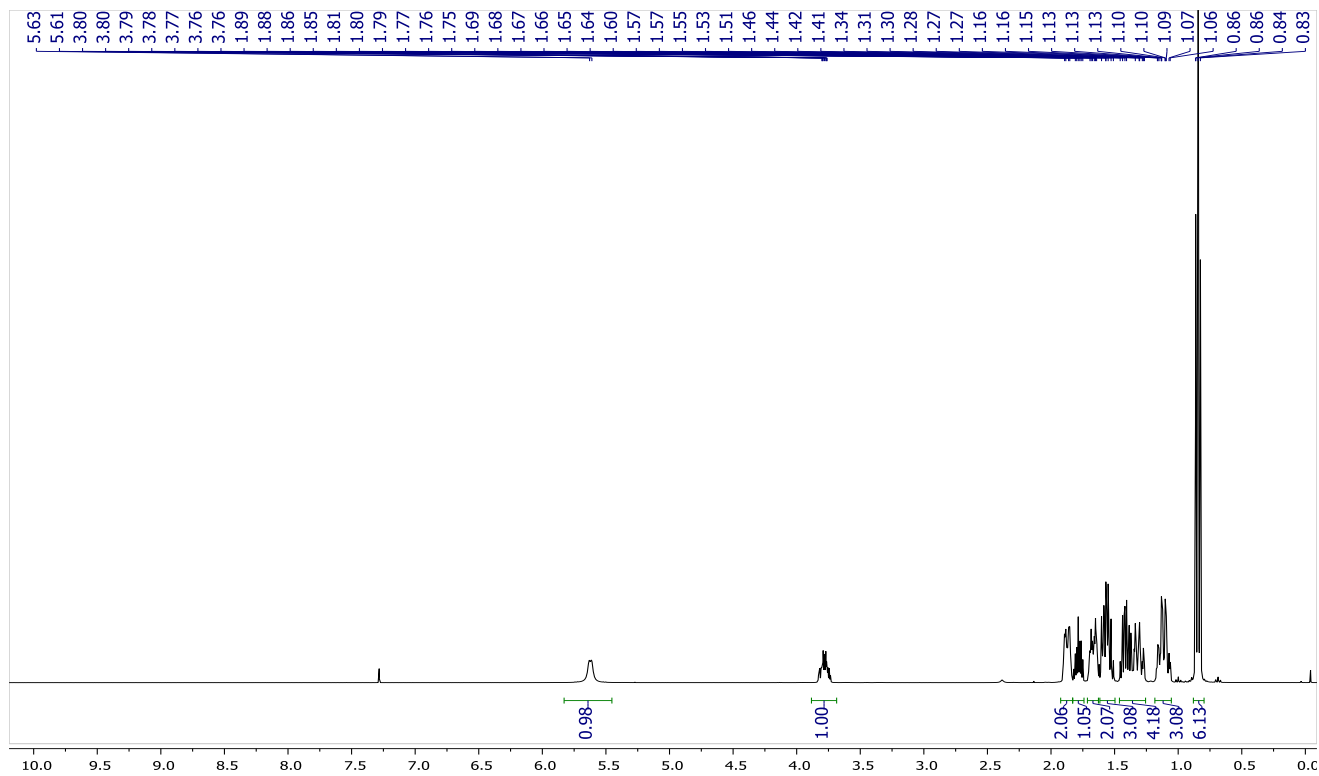
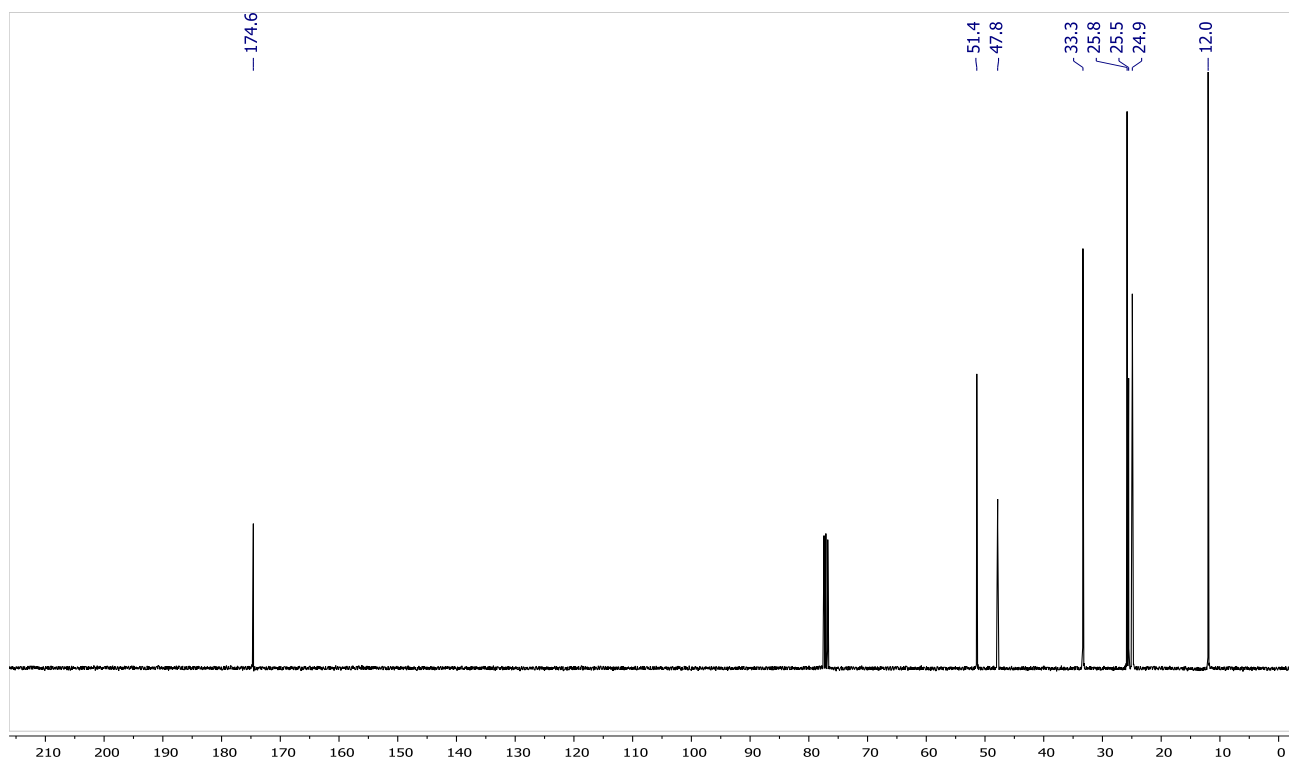


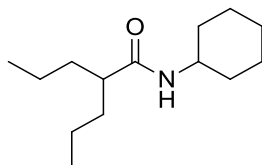
 $^1\text{H-NMR}$ of TIPS-tBucp in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of TIPS-tBucp in CDCl_3 

A2 ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of substrates ^1H -NMR of **S8** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S8** in CDCl_3 

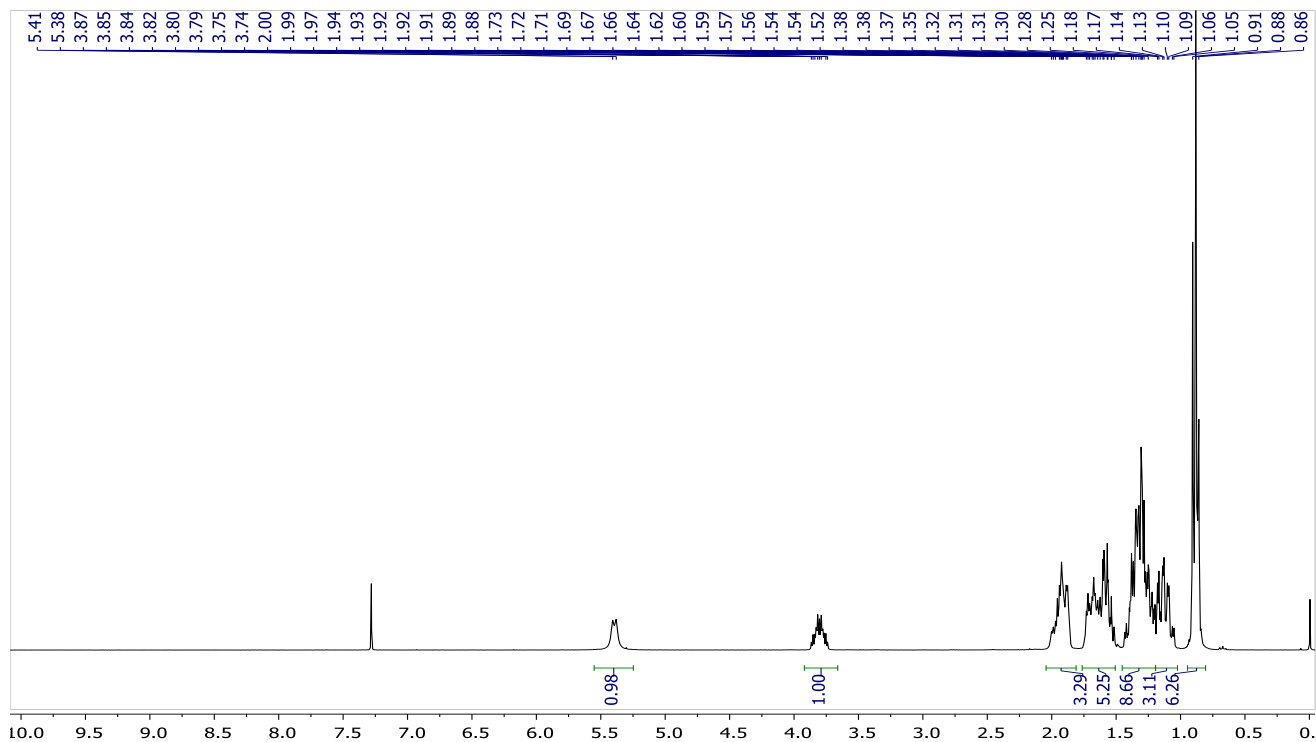
 $^1\text{H-NMR}$ of **S9** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S9** in CDCl_3 

 $^1\text{H-NMR}$ of **S10** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S10** in CDCl_3 

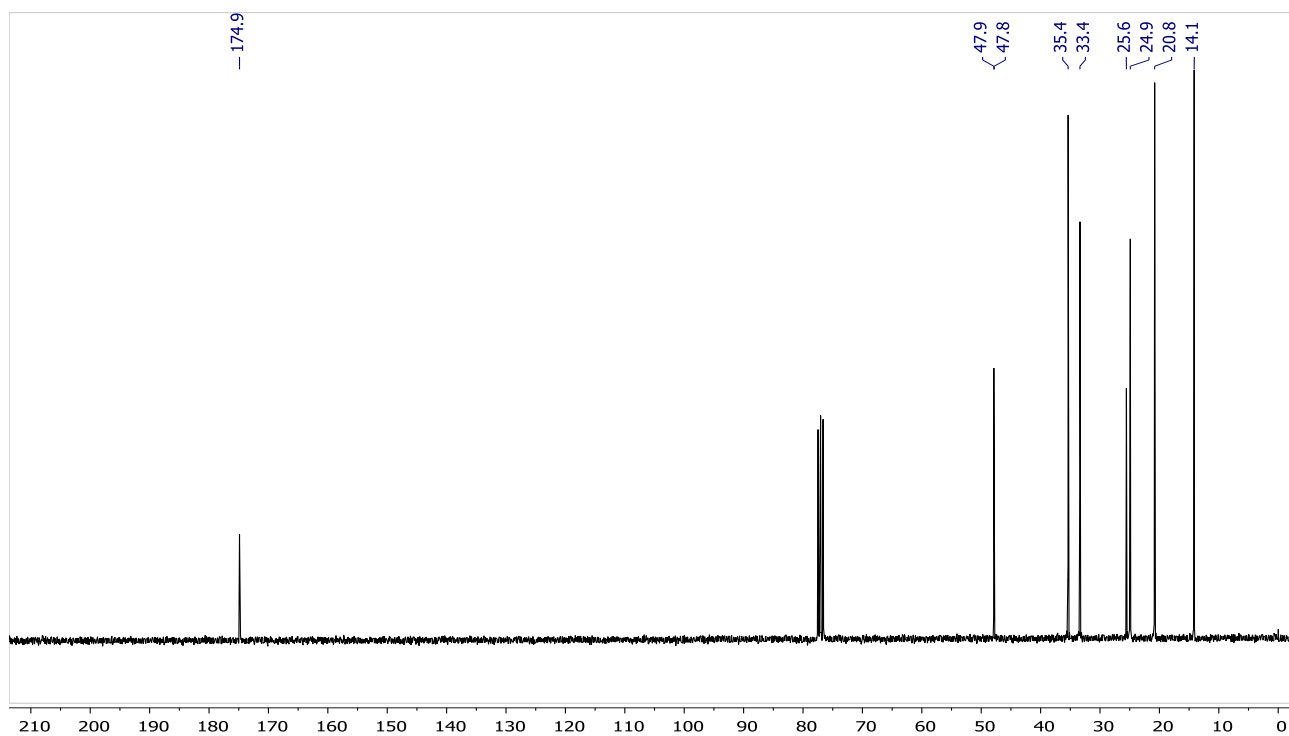
 $^1\text{H-NMR}$ of **S11** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S11** in CDCl_3 

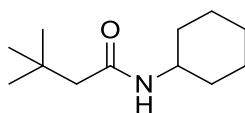
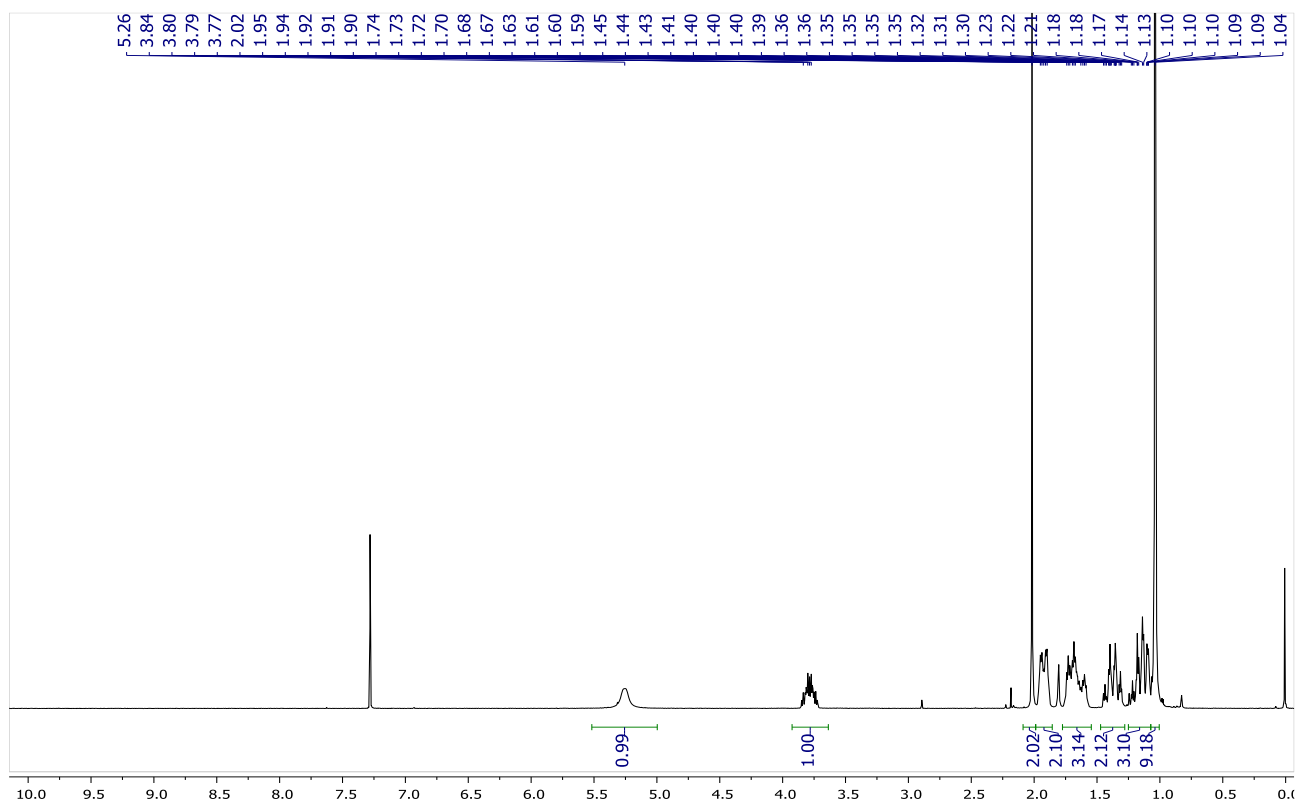
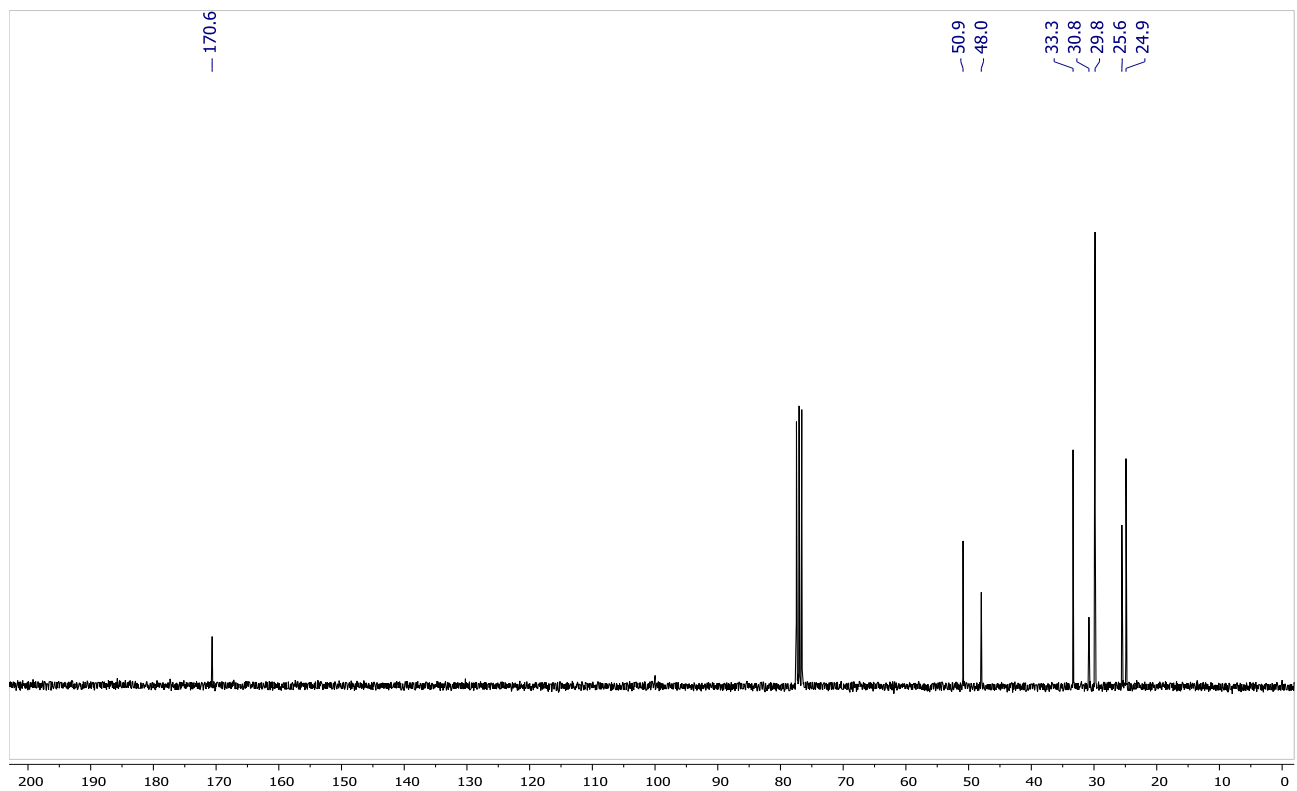


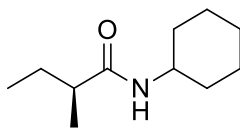
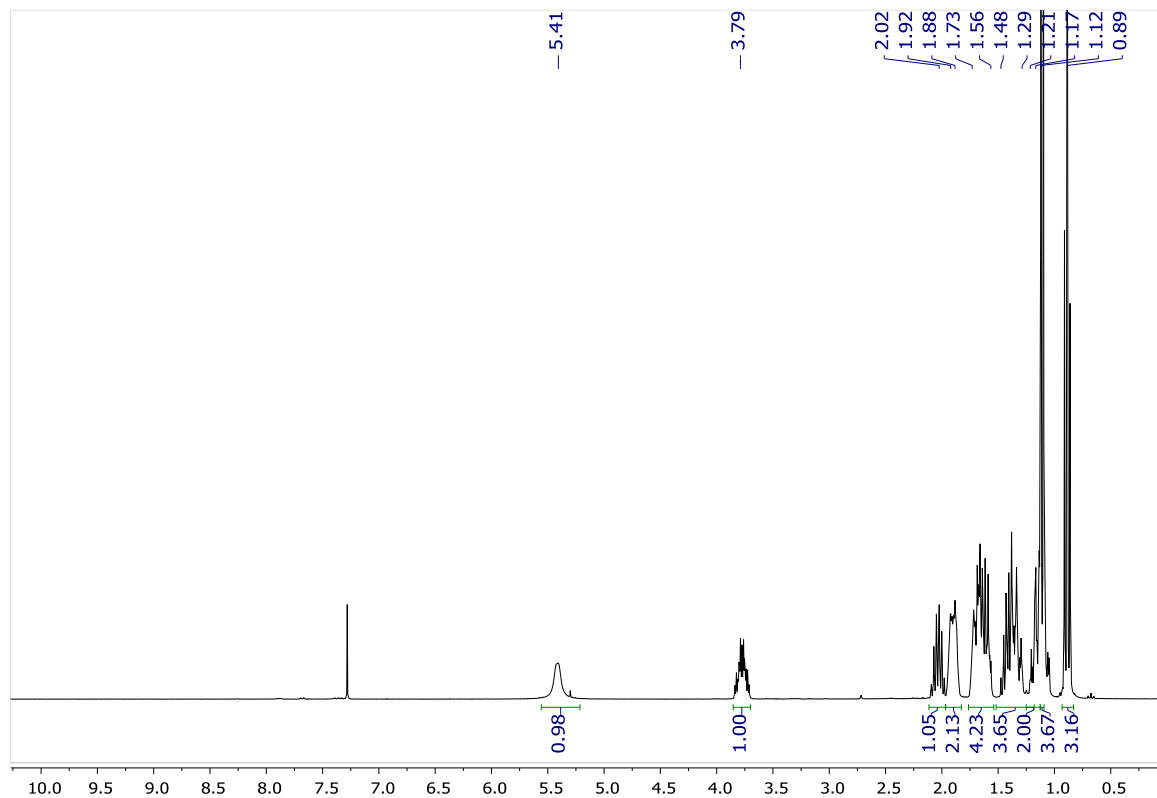
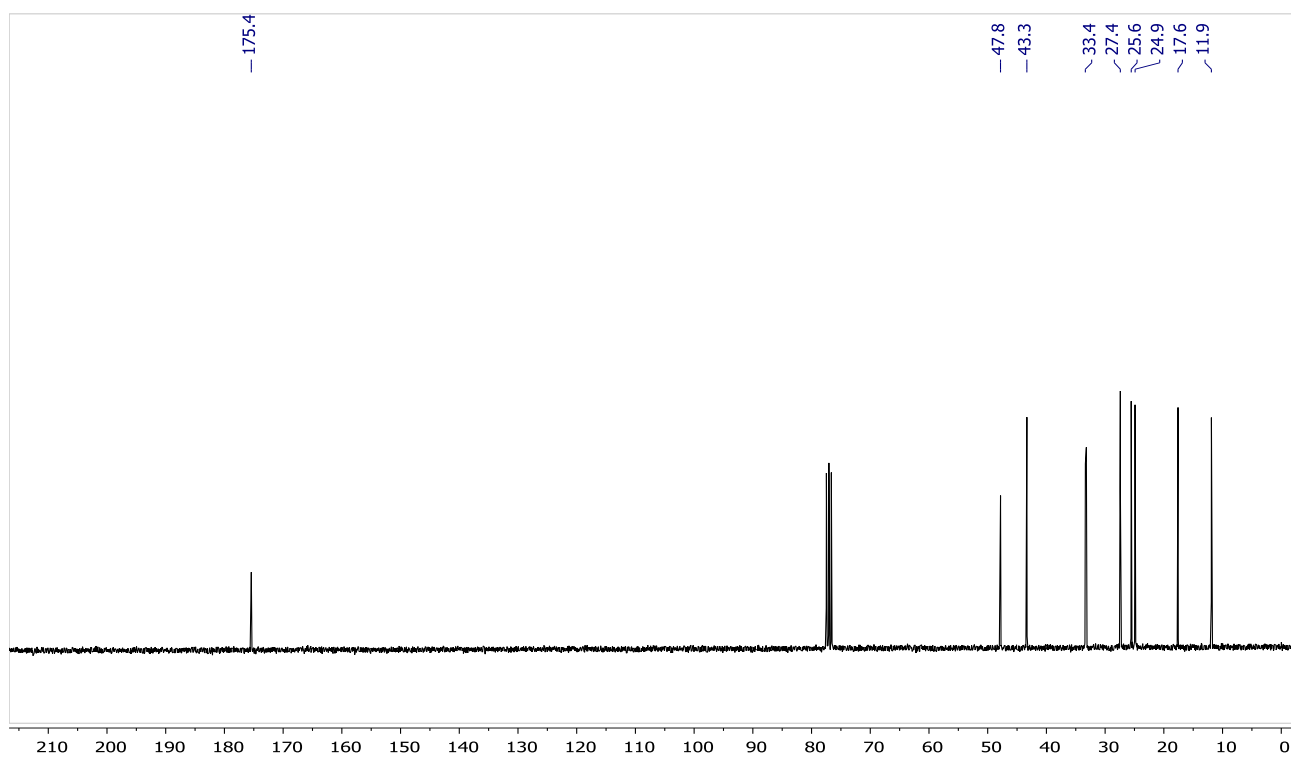
$^1\text{H-NMR}$ of **S12** in CDCl_3

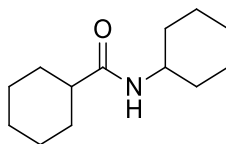
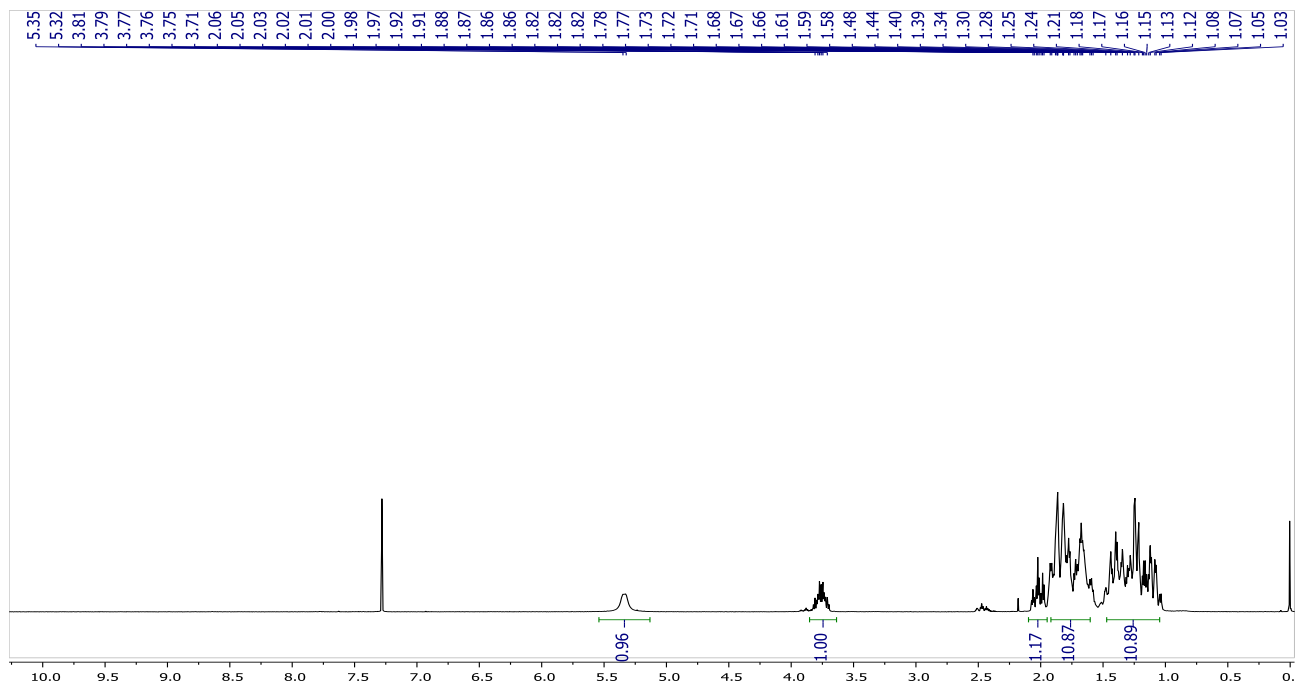
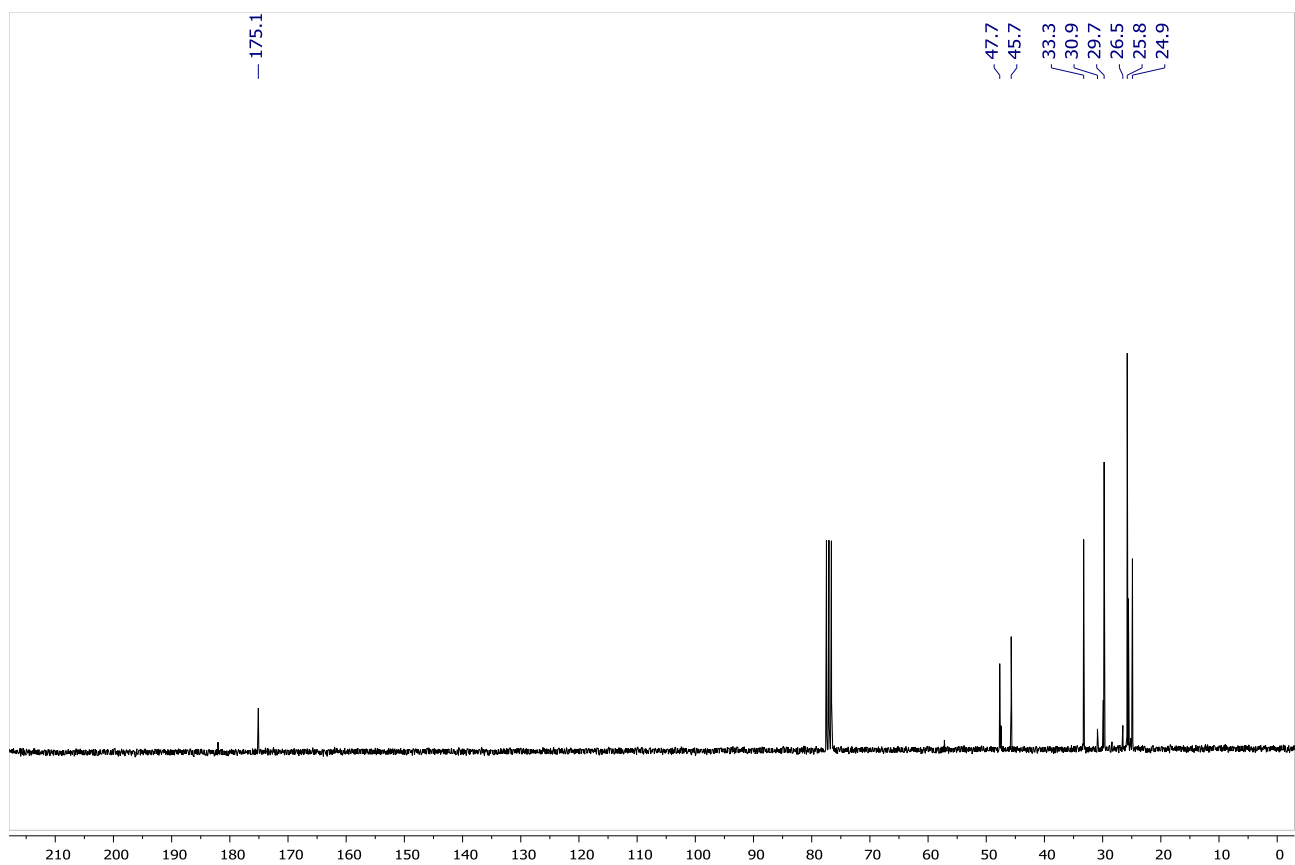


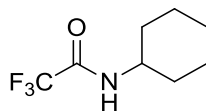
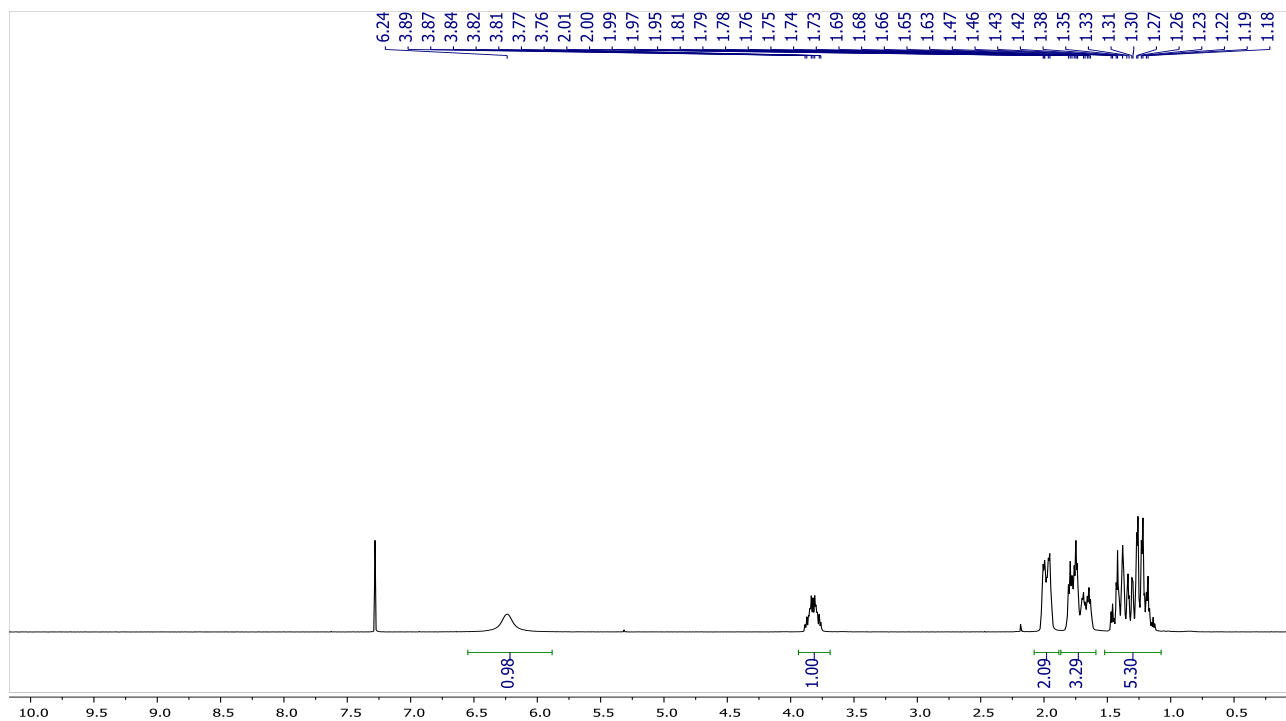
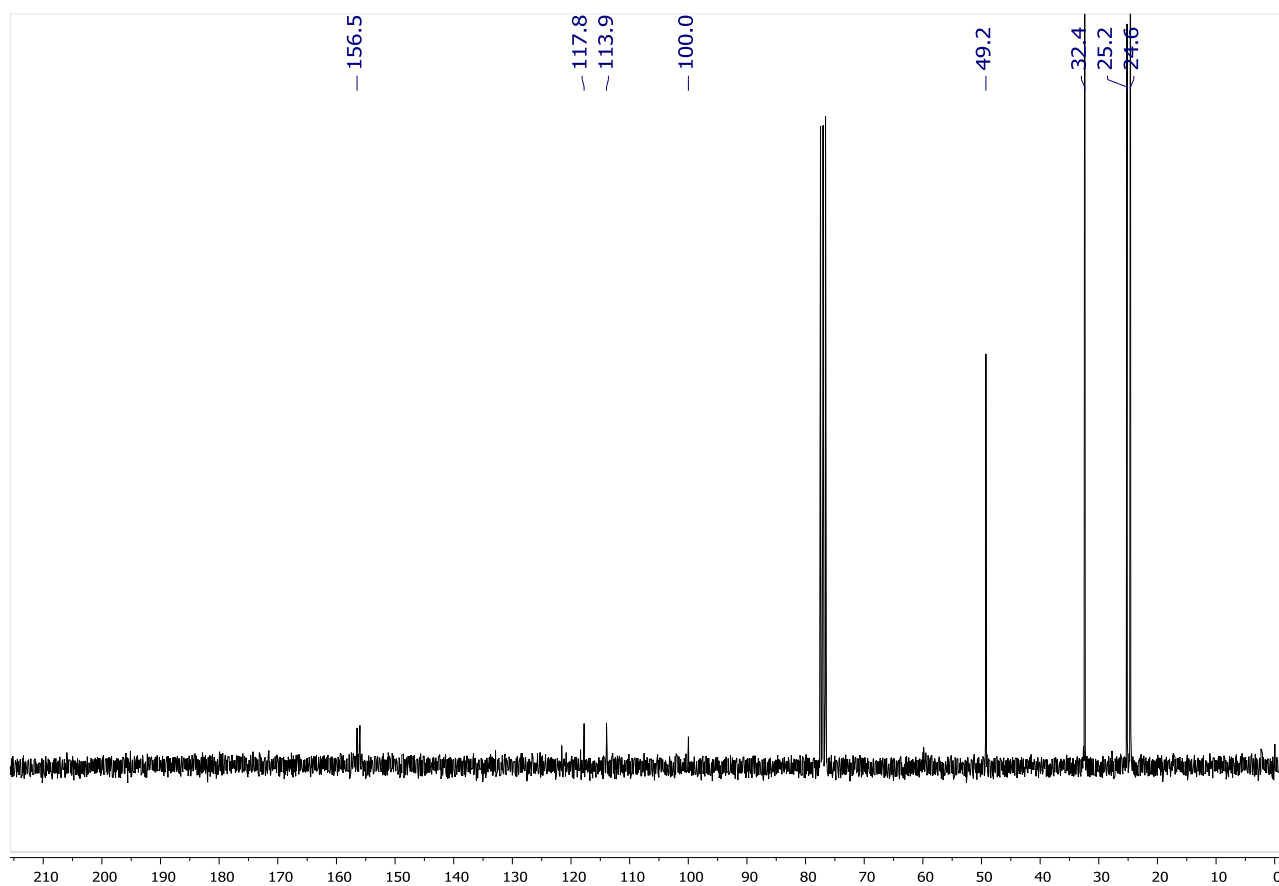
$^{13}\text{C}\{^1\text{H}\}$ -NMR of **S12** in CDCl_3

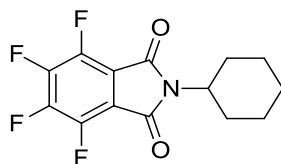
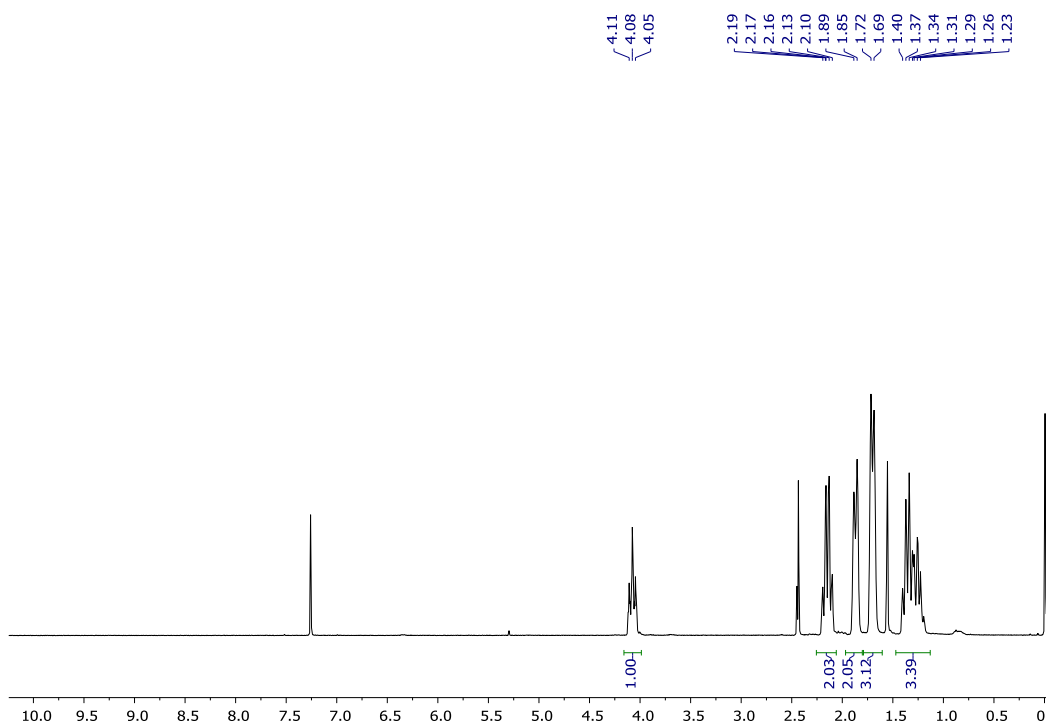
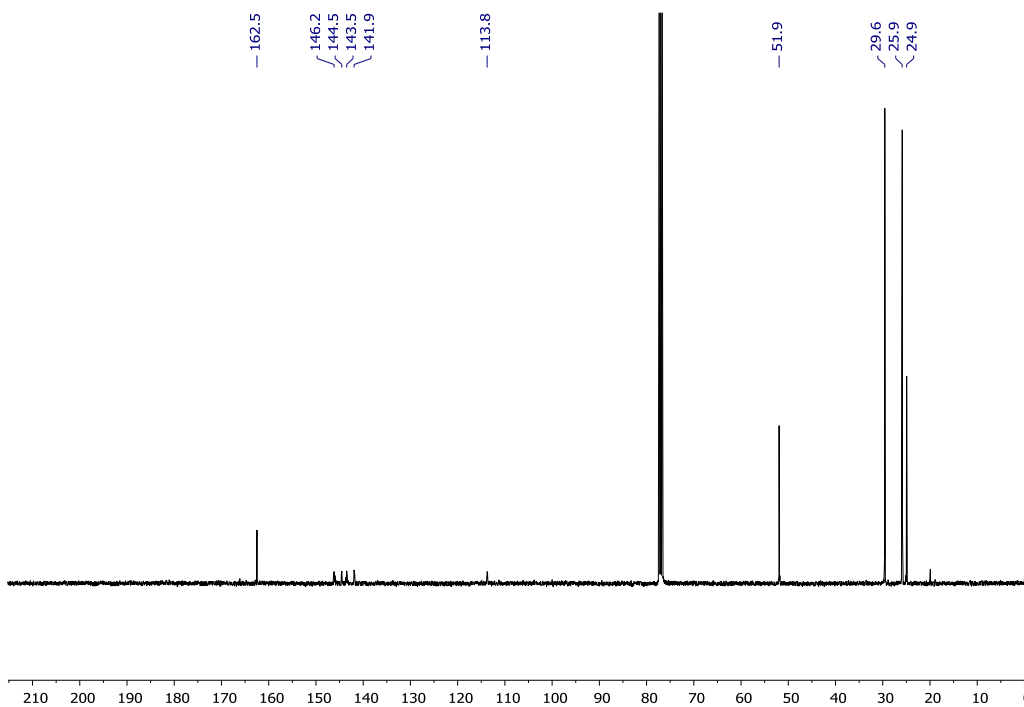


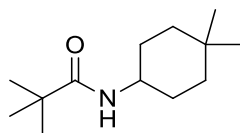
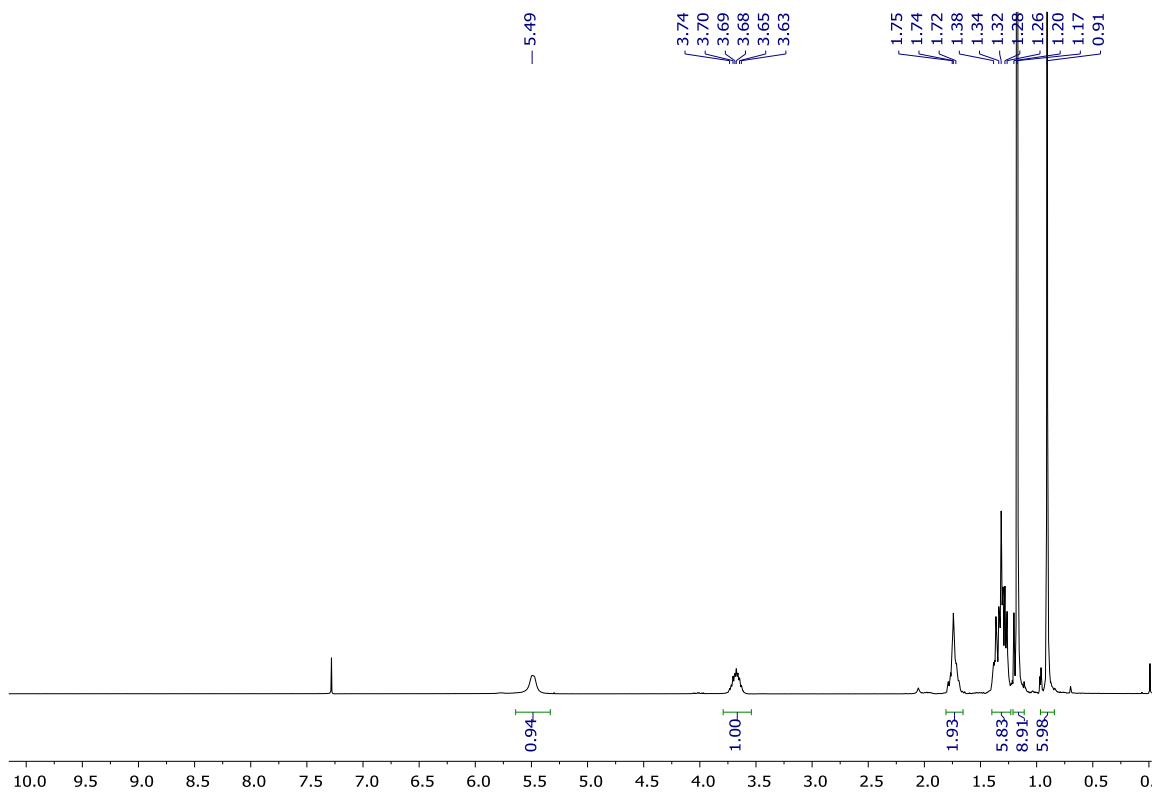
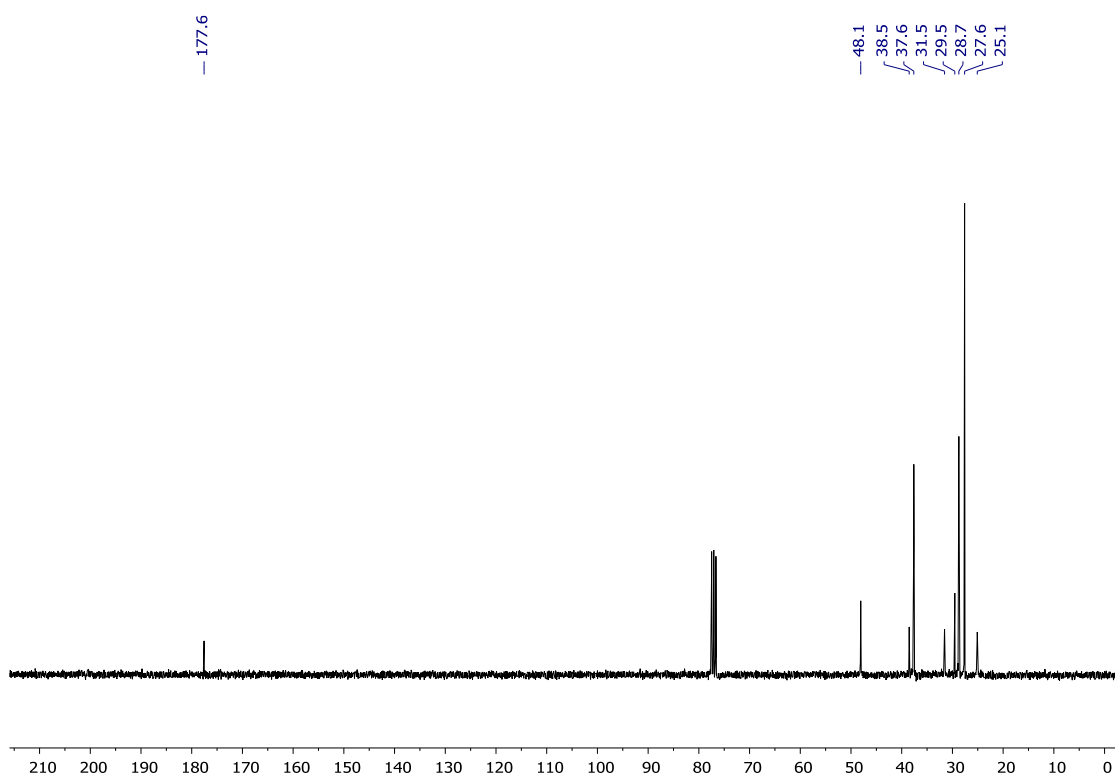
 $^1\text{H-NMR}$ of **S13** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S13** in CDCl_3 

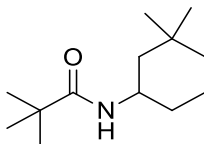
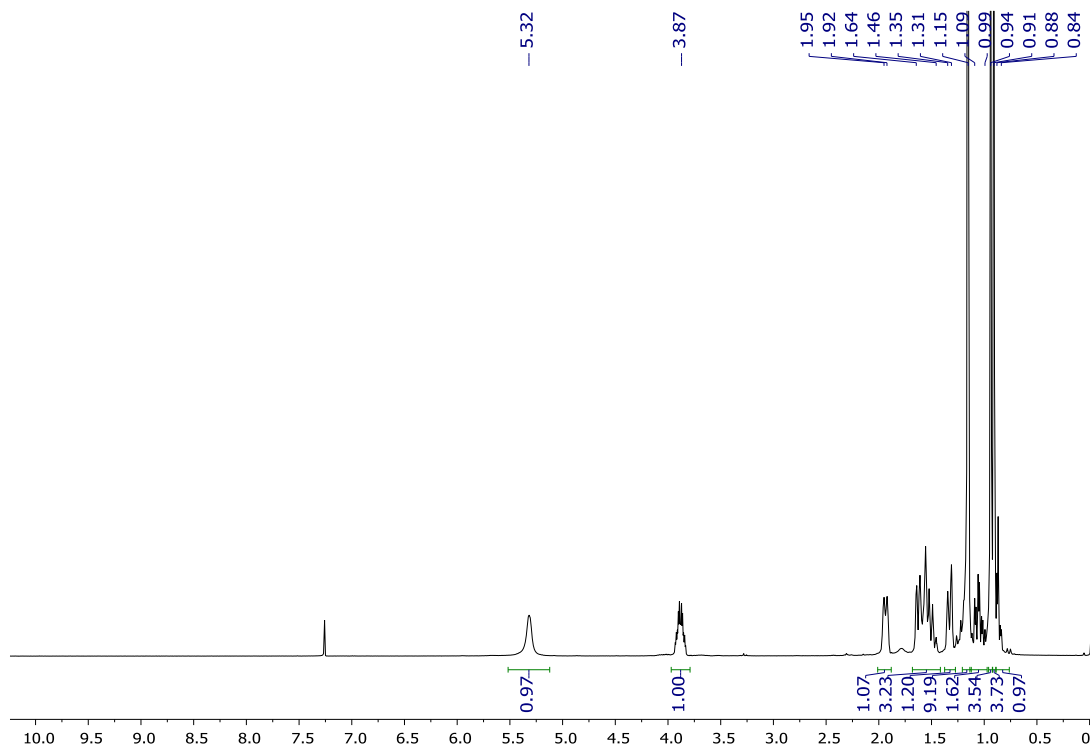
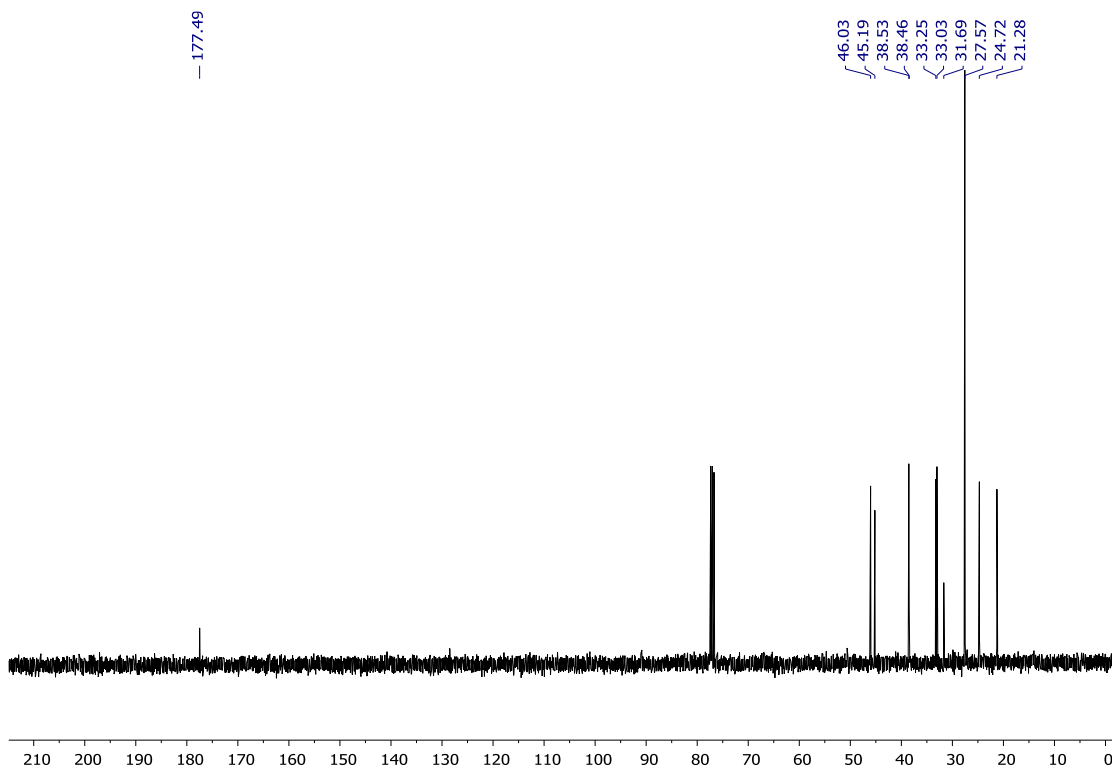
 $^1\text{H-NMR}$ of **S14** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S14** in CDCl_3 

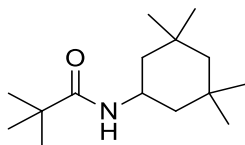
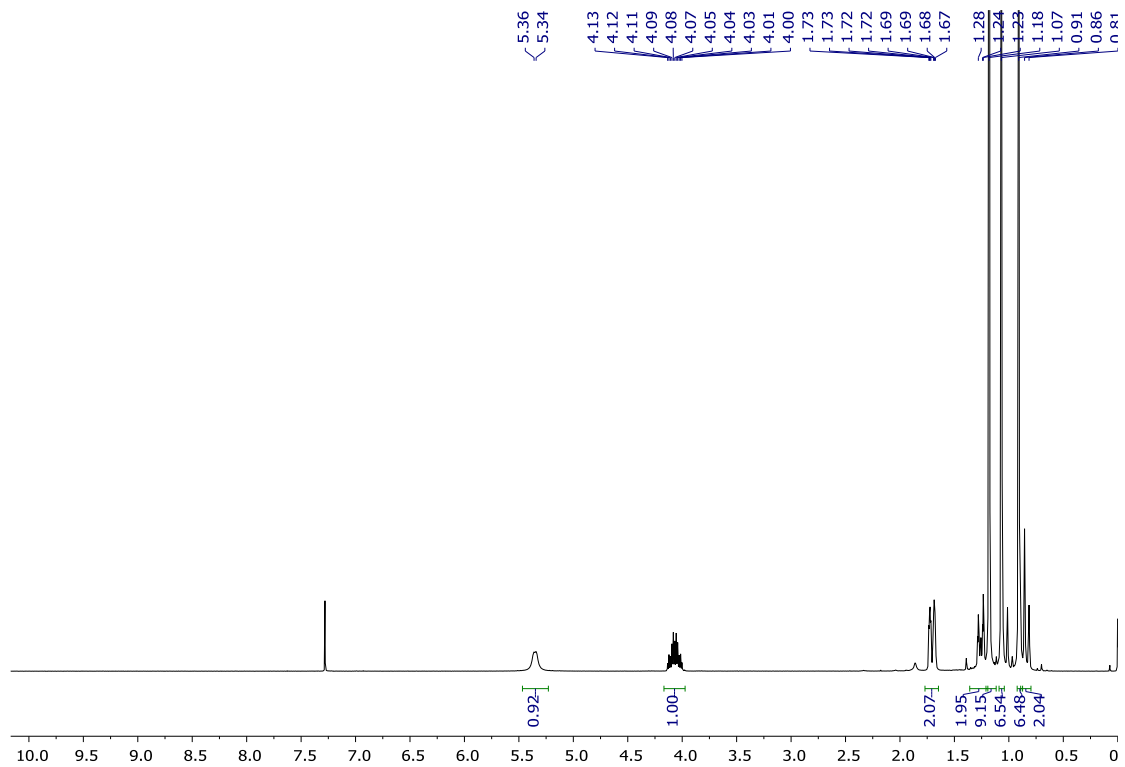
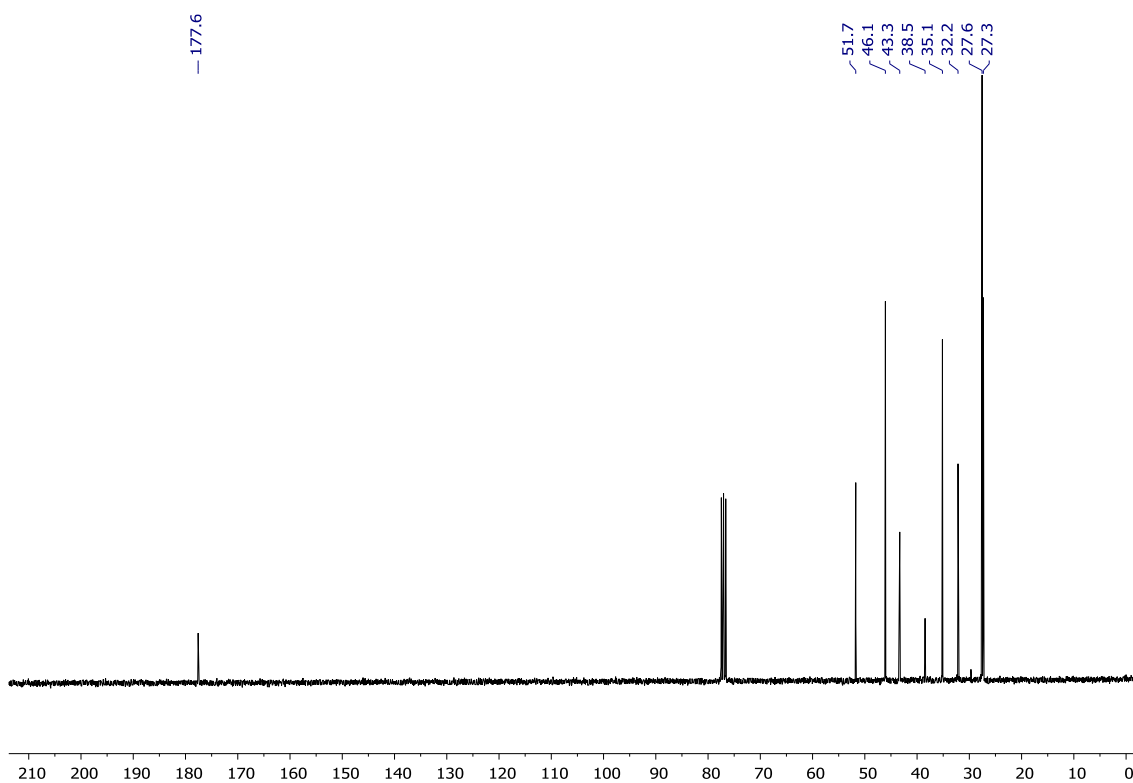
 $^1\text{H-NMR}$ of **S15** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S15** in CDCl_3 

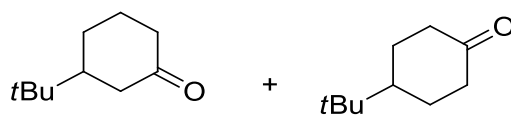
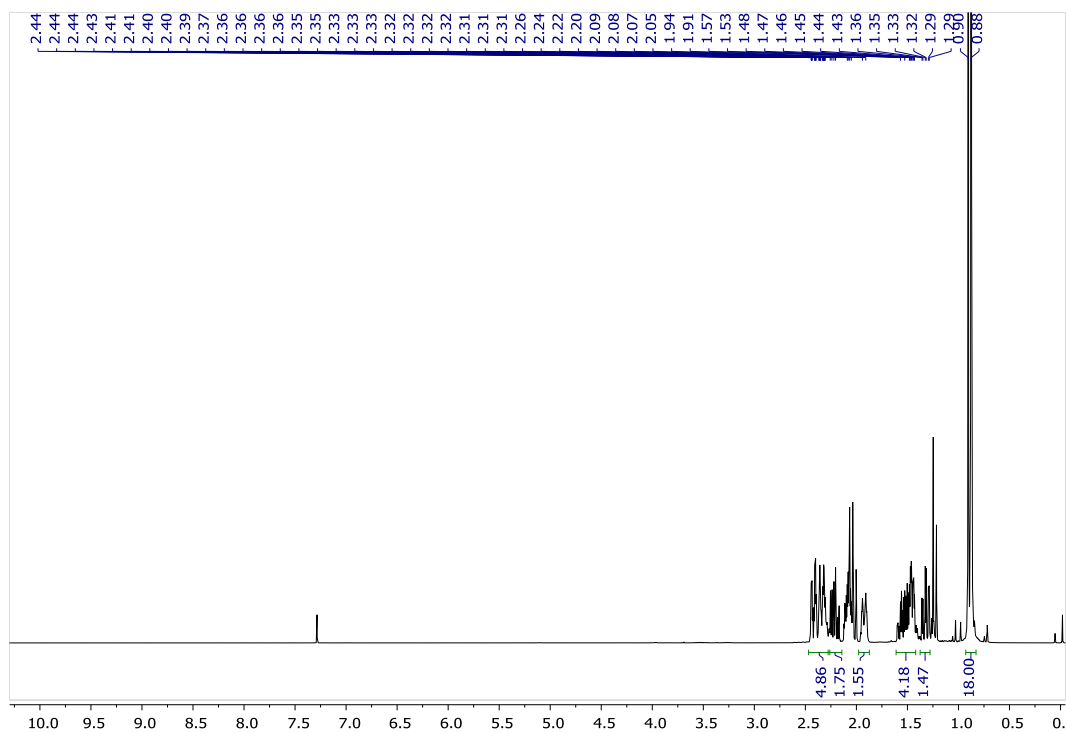
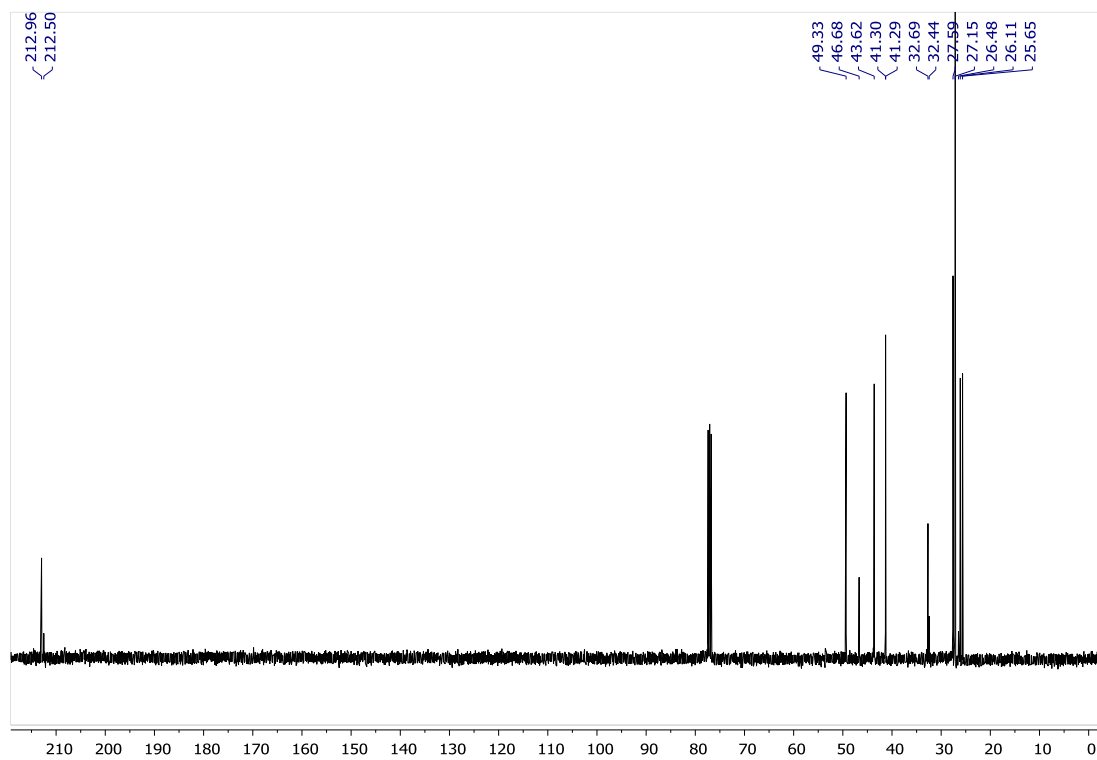
 $^1\text{H-NMR}$ of **S17** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S17** in CDCl_3 

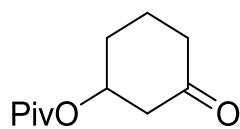
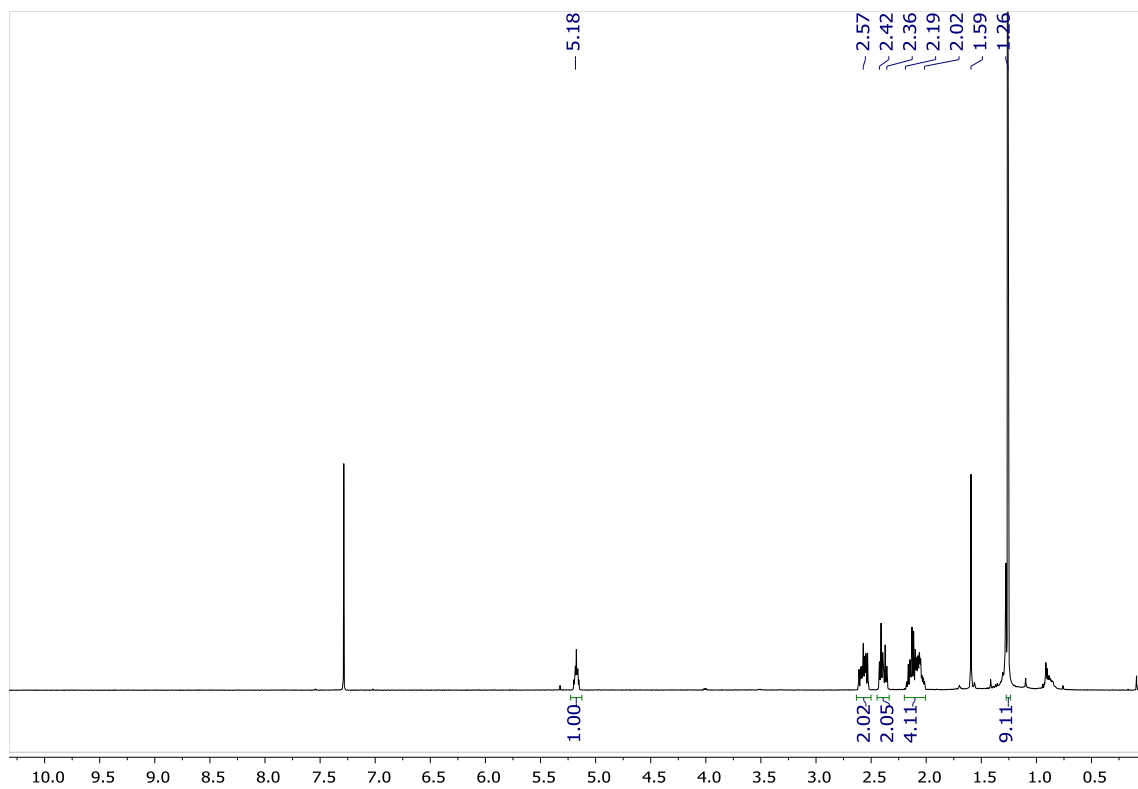
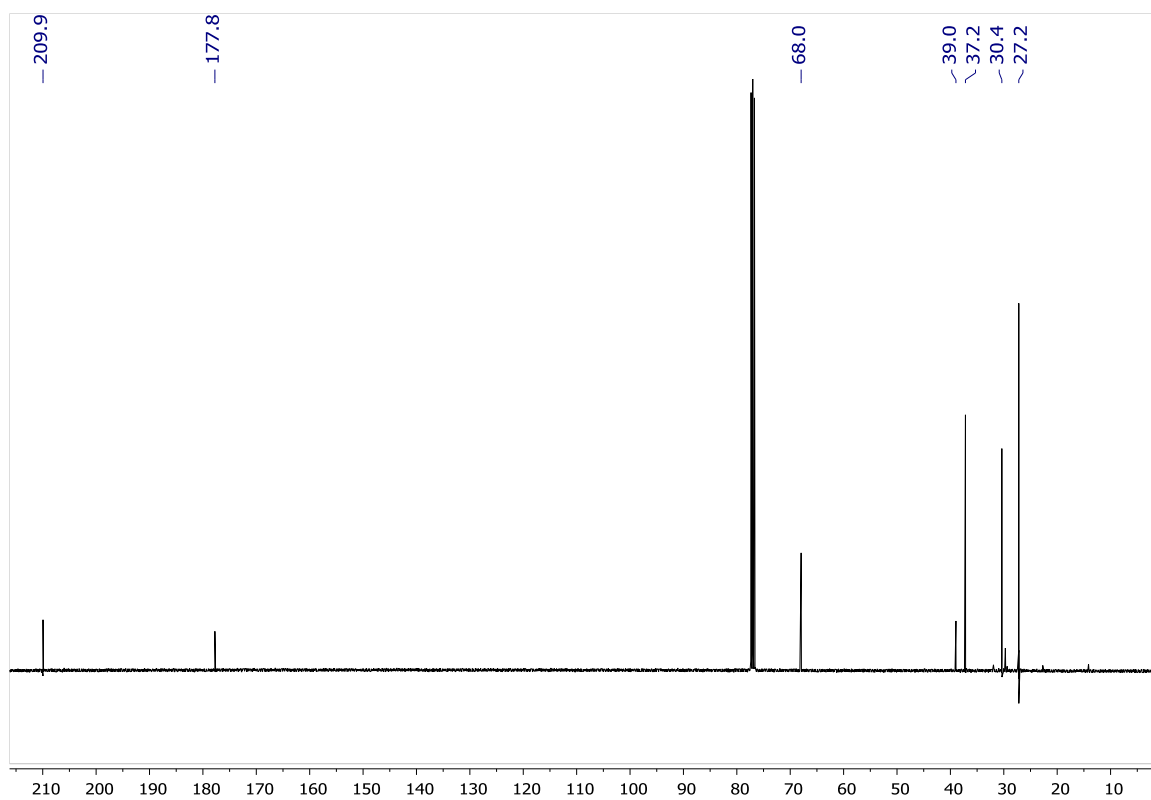
 $^1\text{H-NMR}$ of **S19** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S19** in CDCl_3 

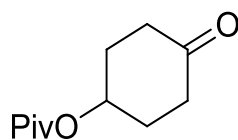
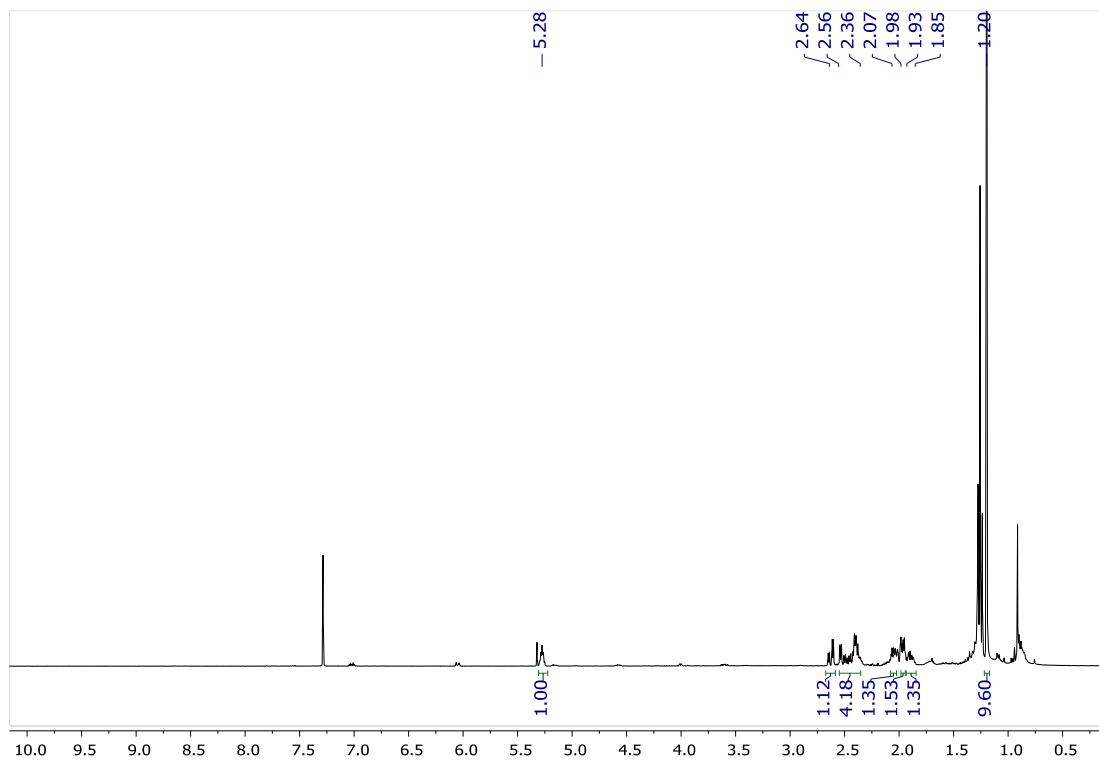
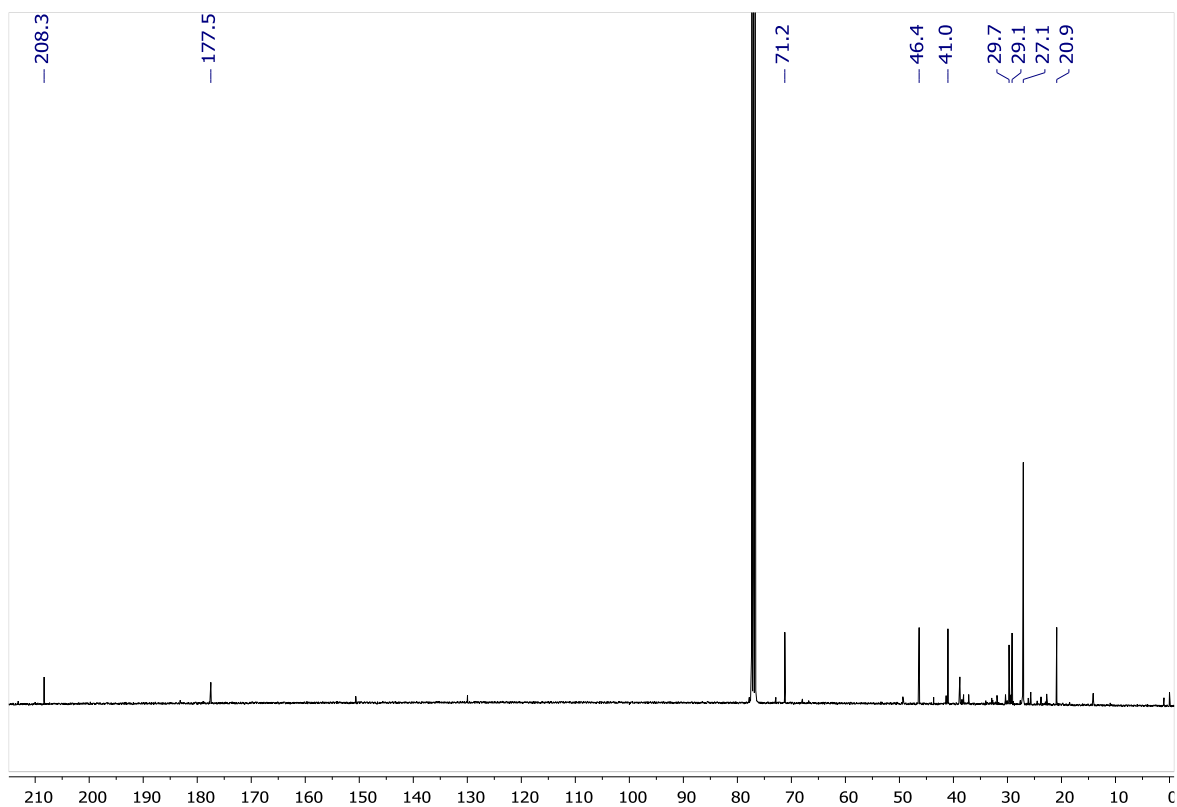
 $^1\text{H-NMR}$ of **S20** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S20** in CDCl_3 

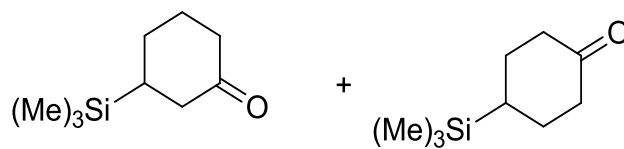
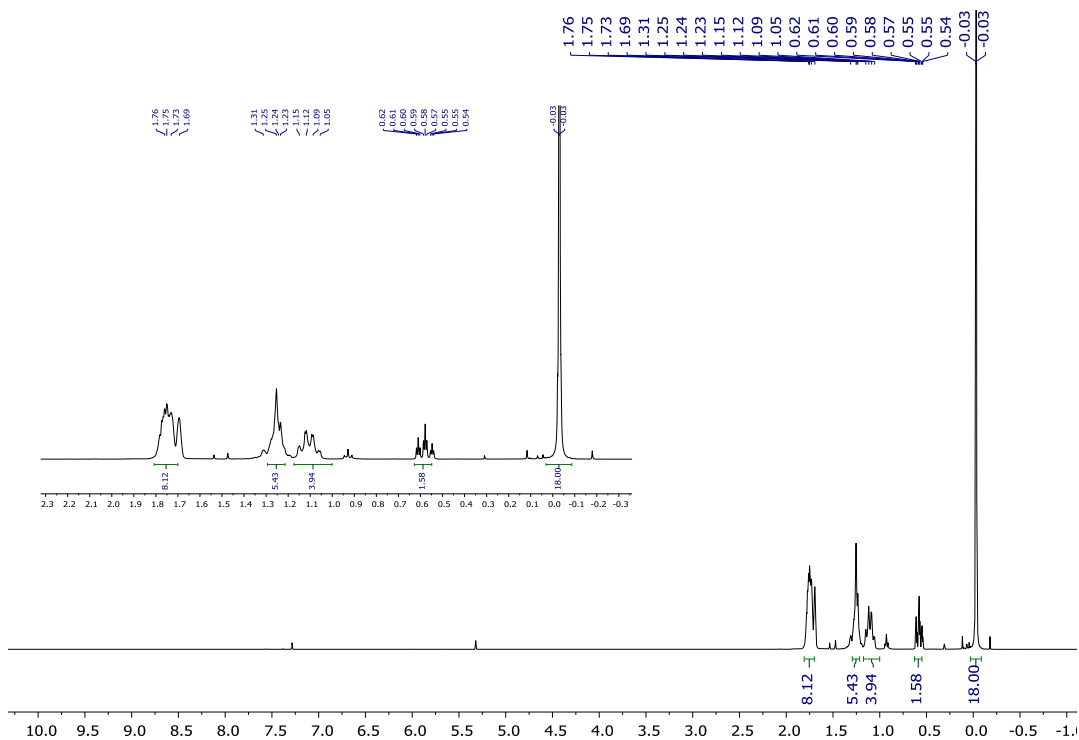
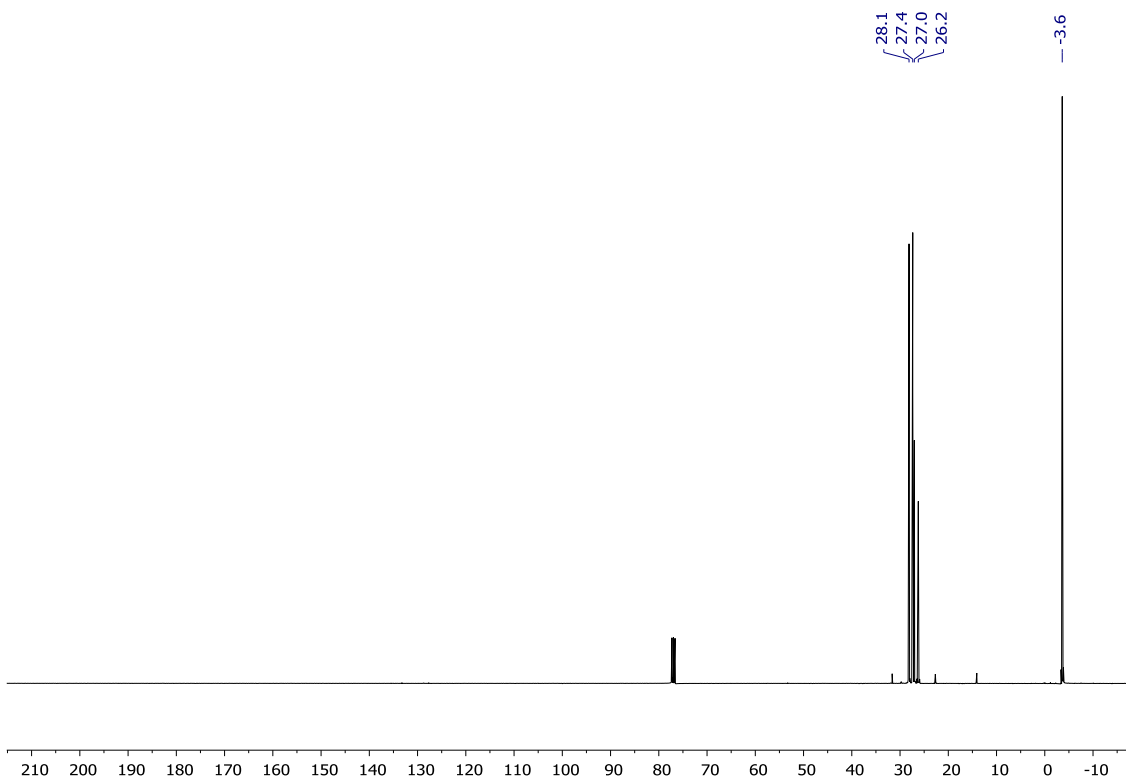
 $^1\text{H-NMR}$ of **S21** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S21** in CDCl_3 

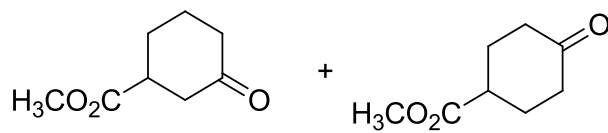
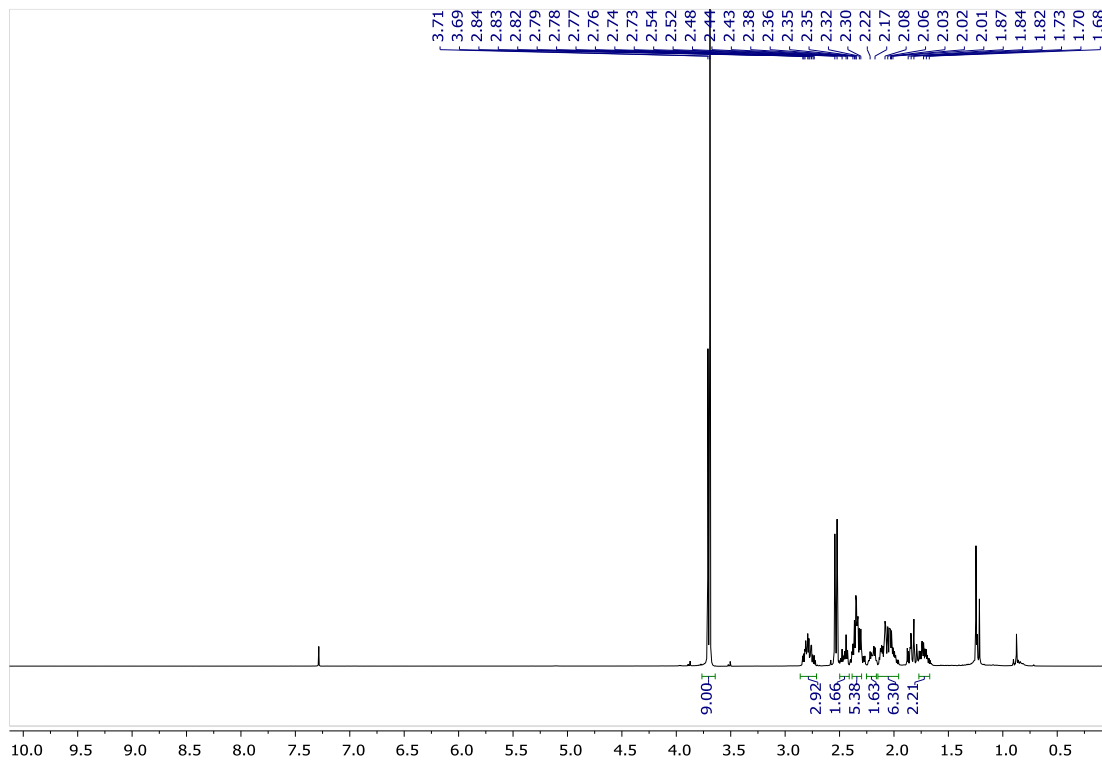
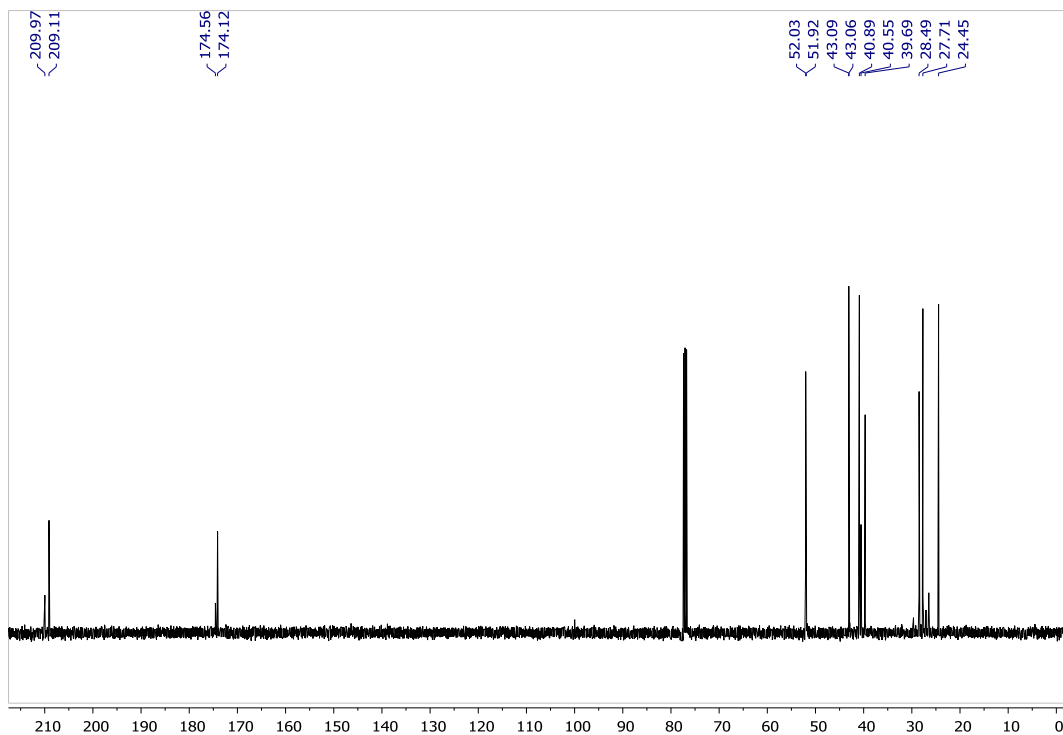
 $^1\text{H-NMR}$ of **S22** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **S22** in CDCl_3 

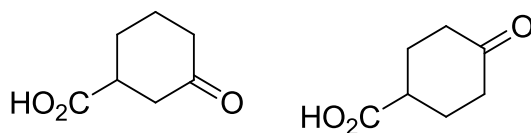
A3 ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of isolated products ^1H -NMR of P1 (K₃+K₄) in CDCl₃ $^{13}\text{C}\{^1\text{H}\}$ -NMR of P1 (K₃+K₄) in CDCl₃

 $^1\text{H-NMR}$ of **P2 (K₃)** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P2 (K₃)** in CDCl_3 

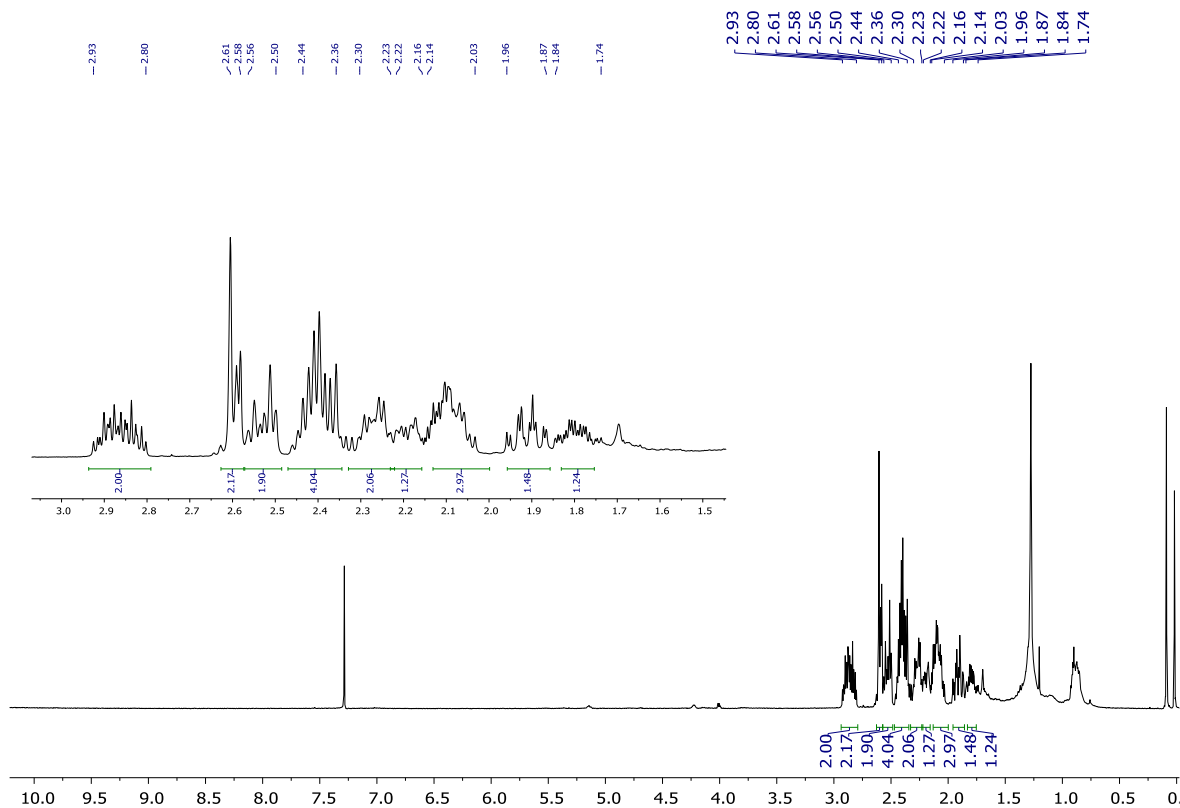
 $^1\text{H-NMR}$ of **P2 (K₄)** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P2 (K₄)** in CDCl_3 

 $^1\text{H-NMR}$ of **P3** (K_3+K_4) in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P3** (K_3+K_4) in CDCl_3 

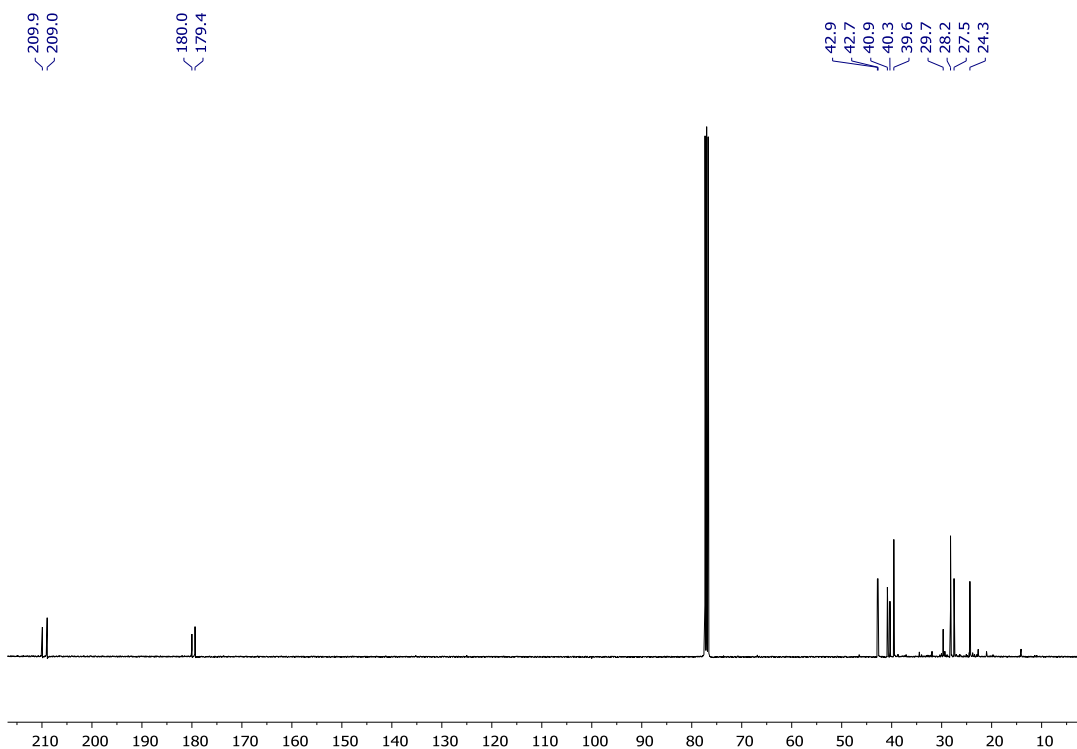
 $^1\text{H-NMR}$ of P4 (K_3+K_4) in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of P4 (K_3+K_4) in CDCl_3 

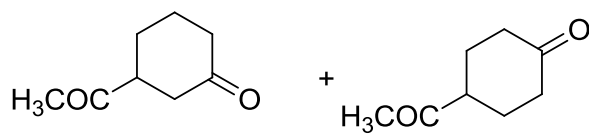
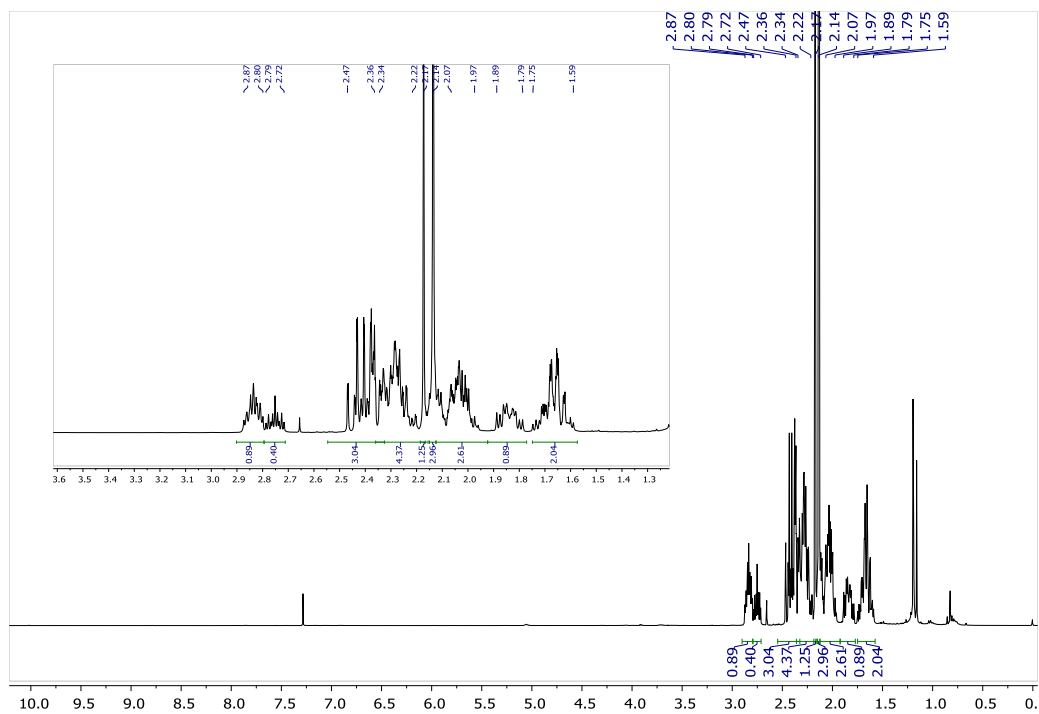
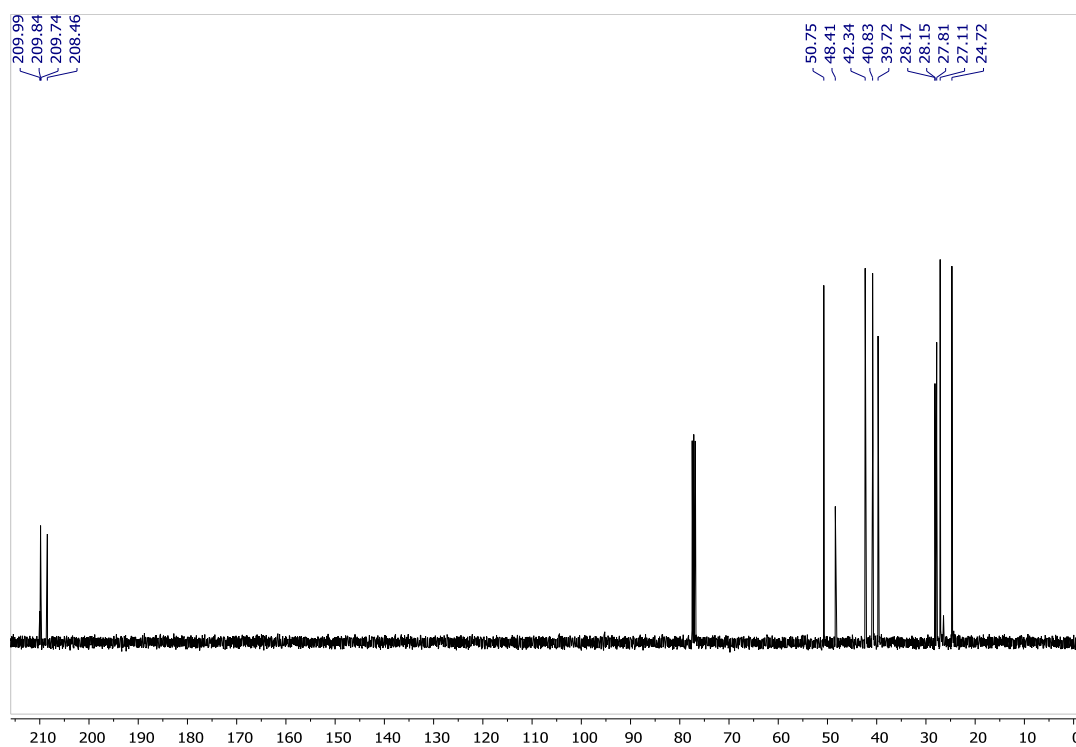


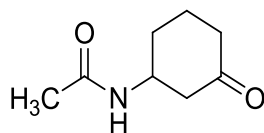
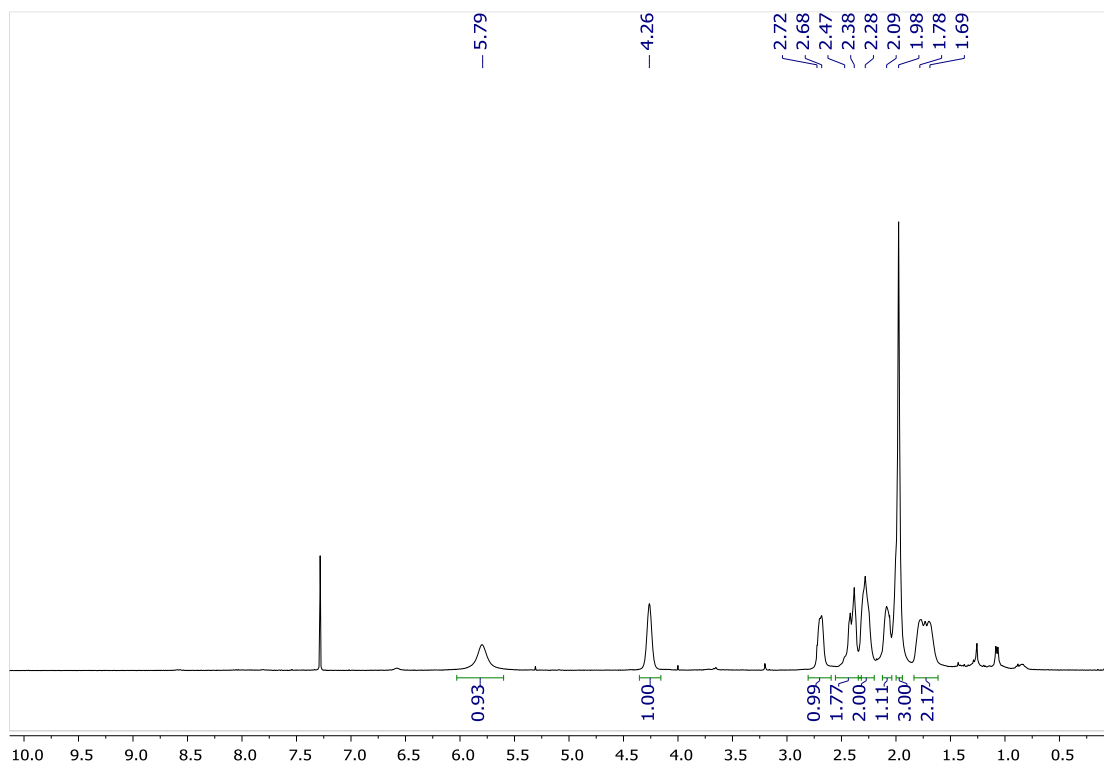
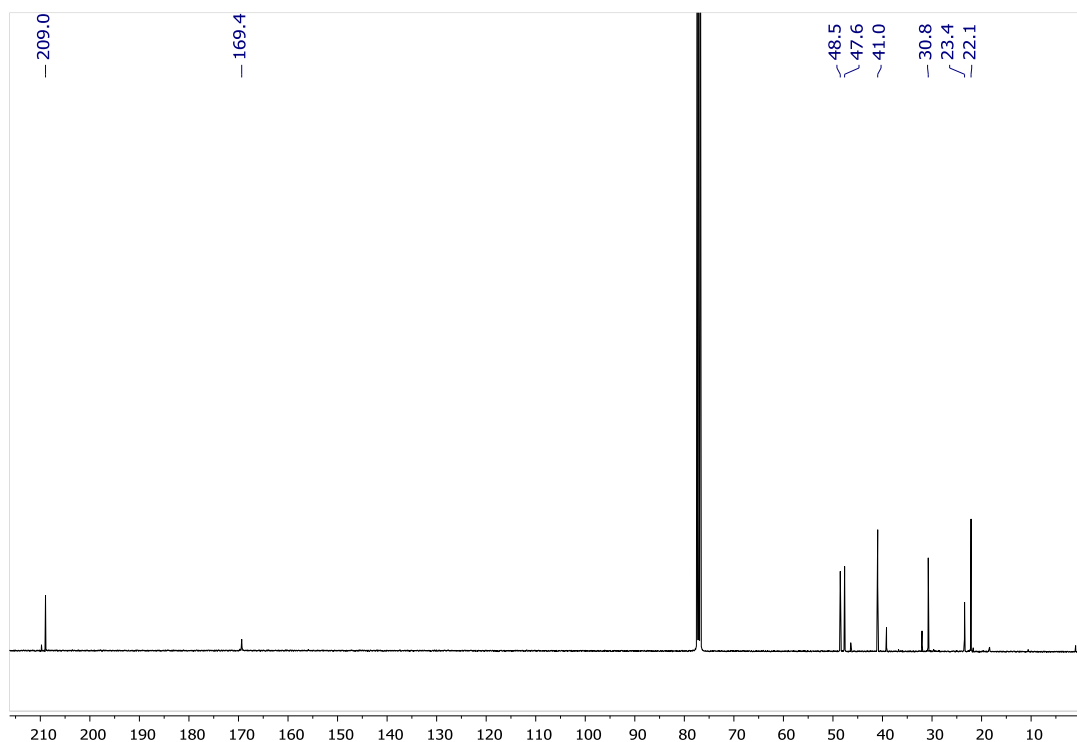
$^1\text{H-NMR}$ of **P5** (K_3+K_4) in CDCl_3

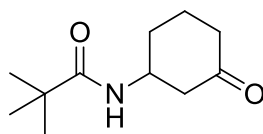
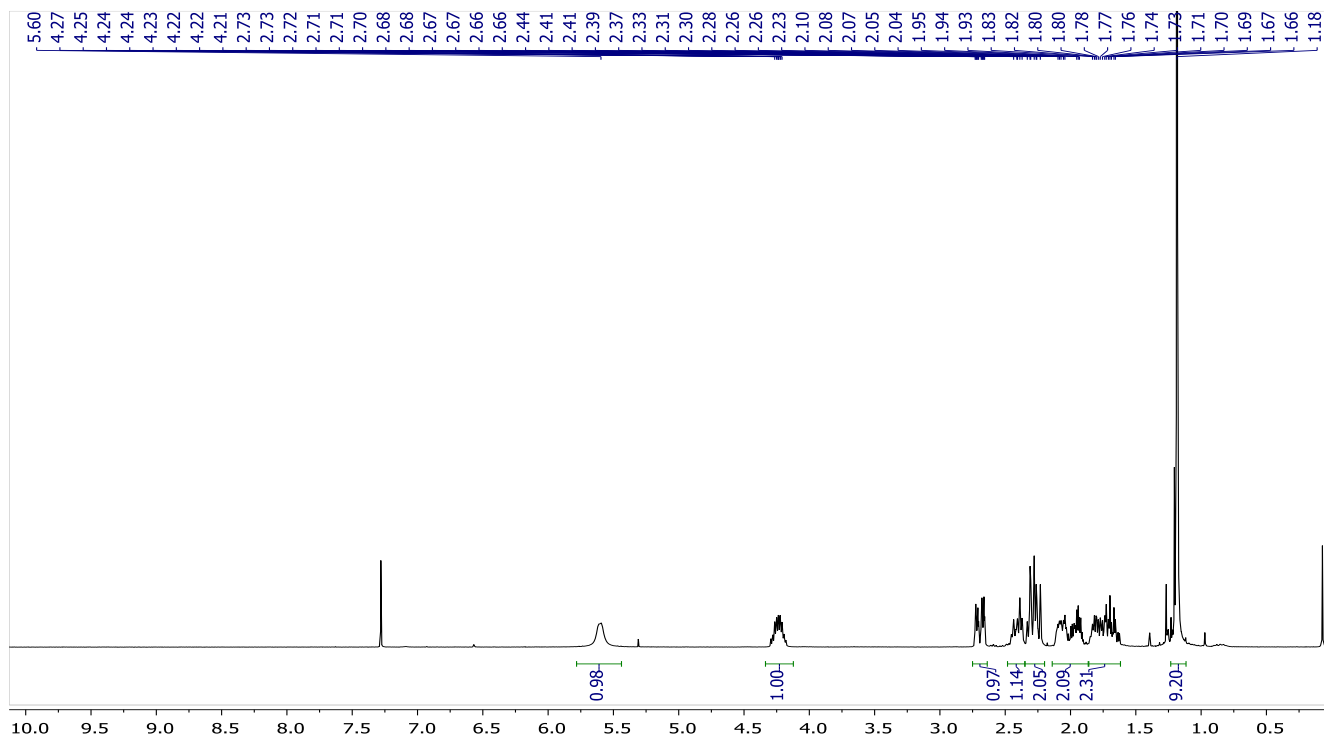
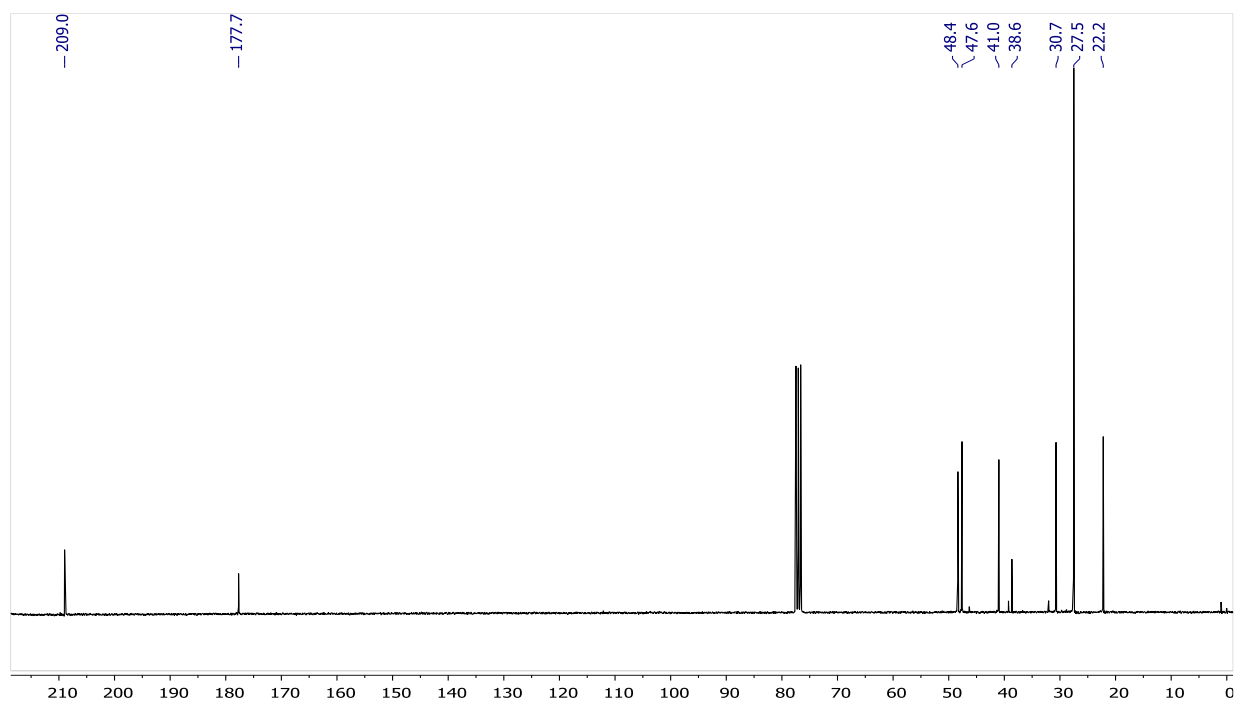


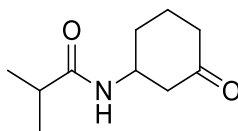
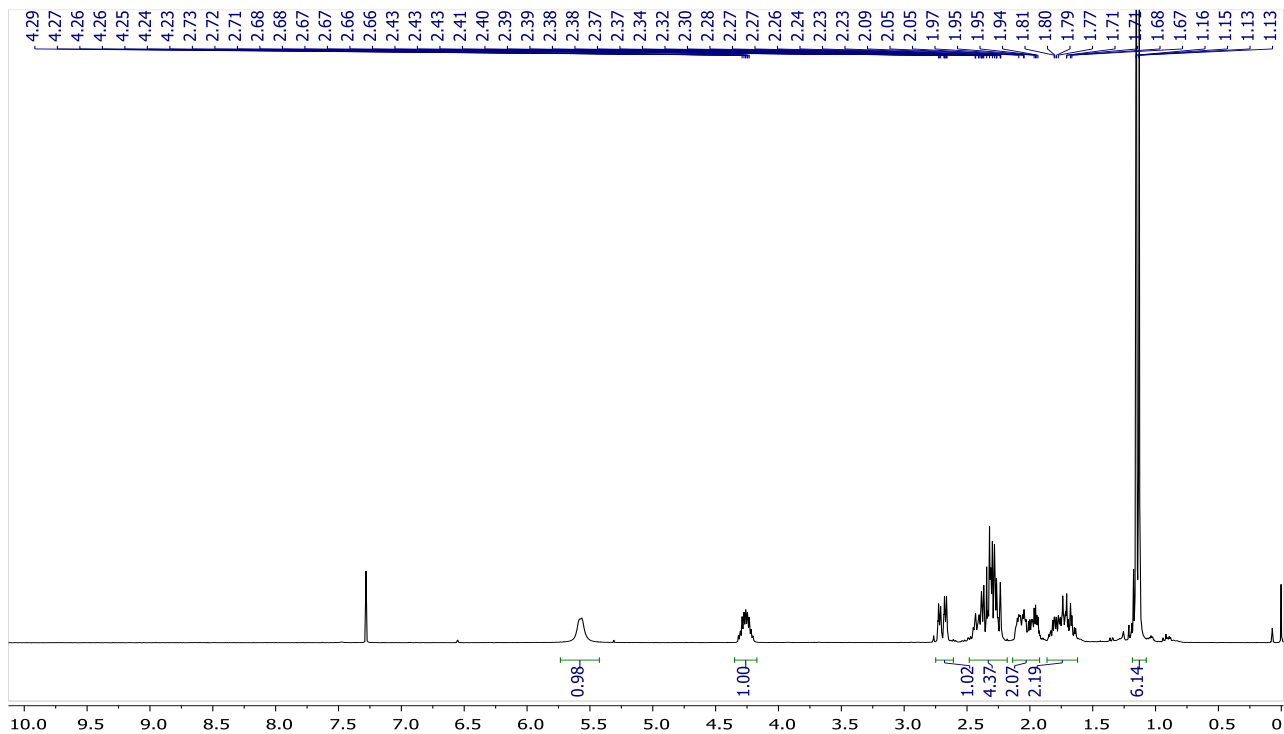
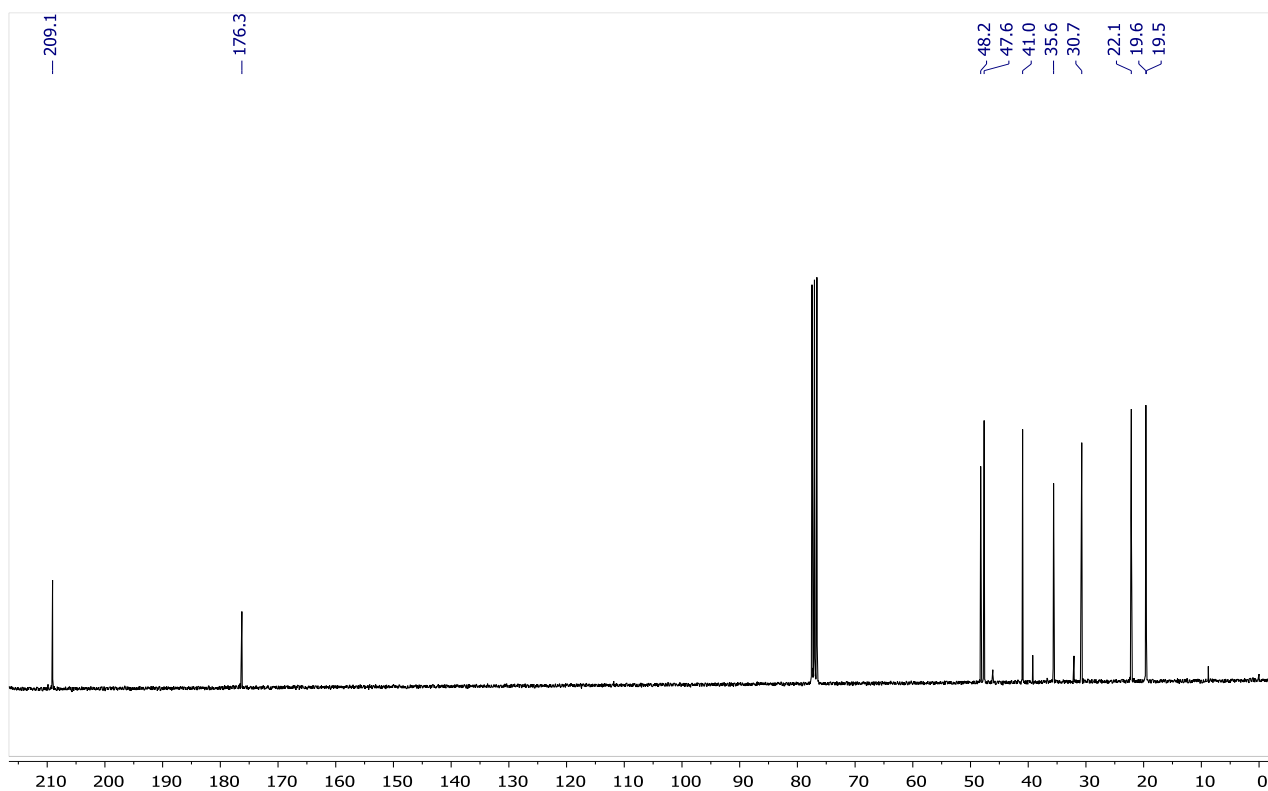
$^{13}\text{C}\{^1\text{H}\}$ -NMR of **P5** (K_3+K_4) in CDCl_3

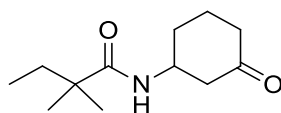
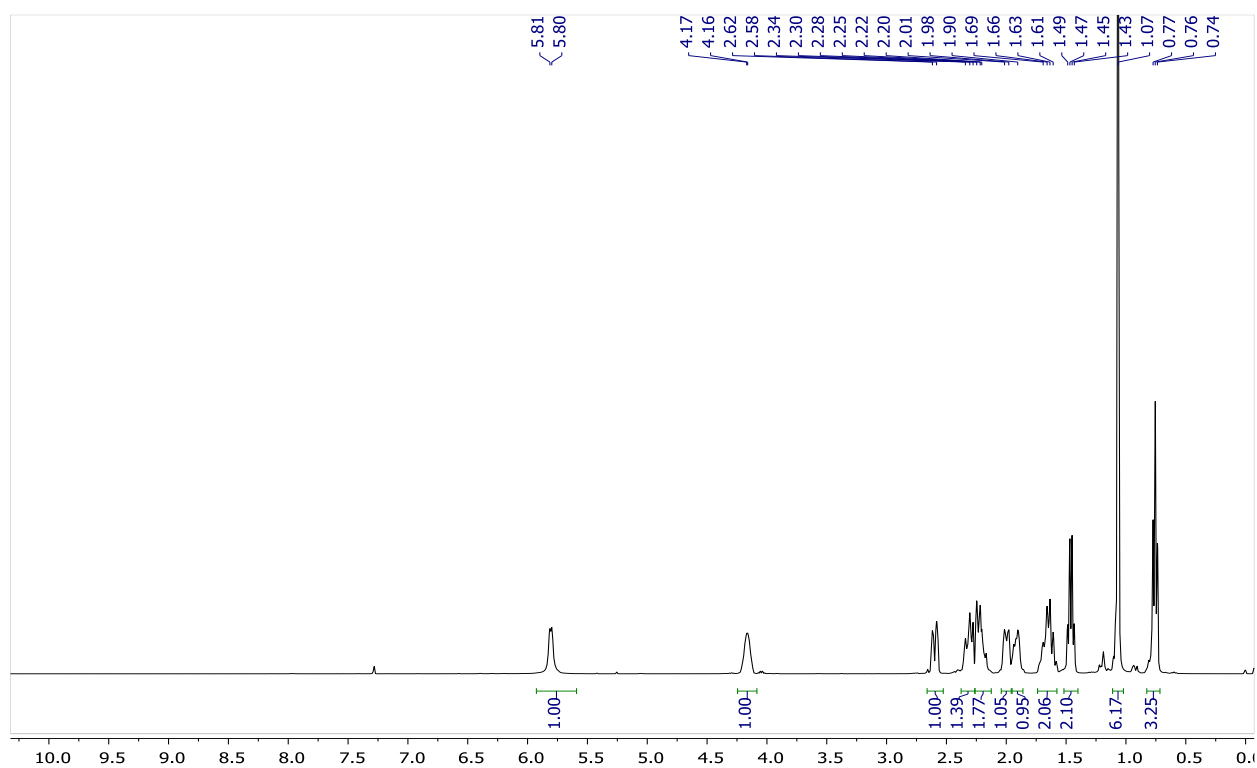
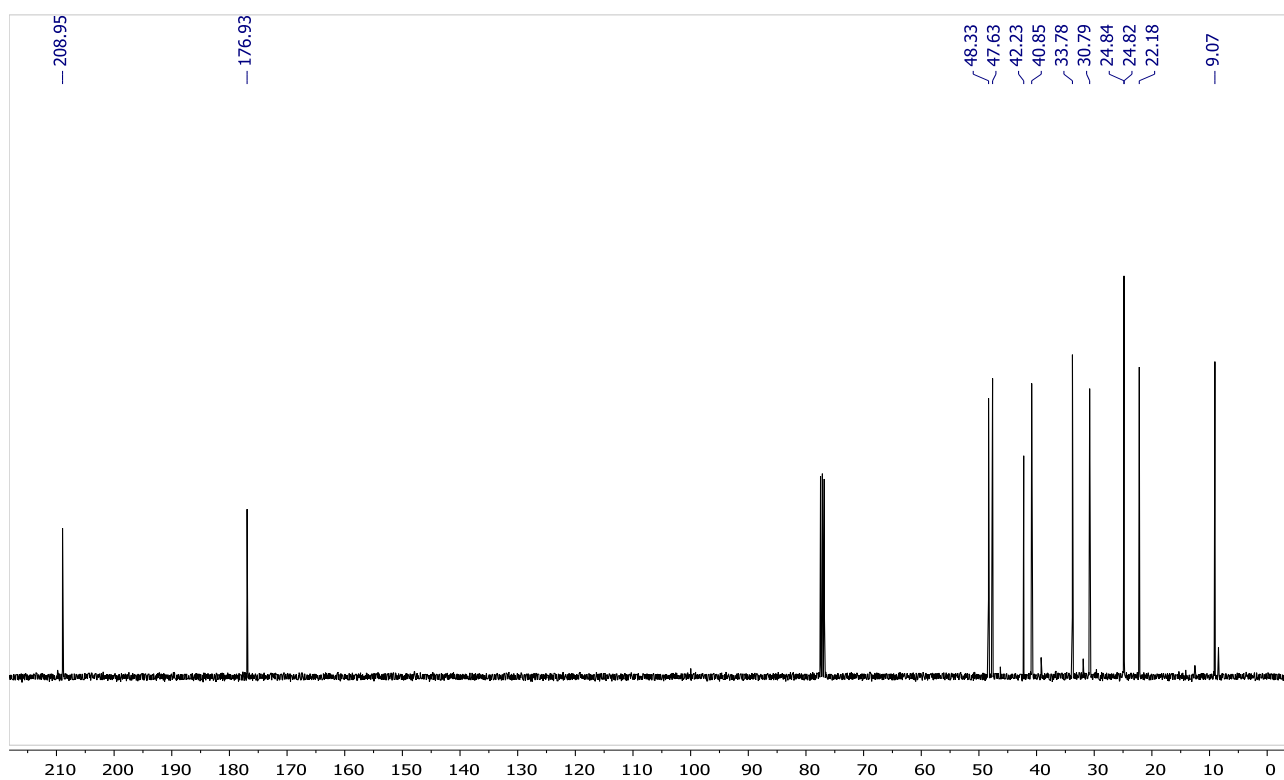


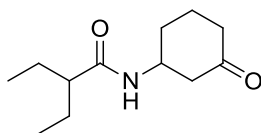
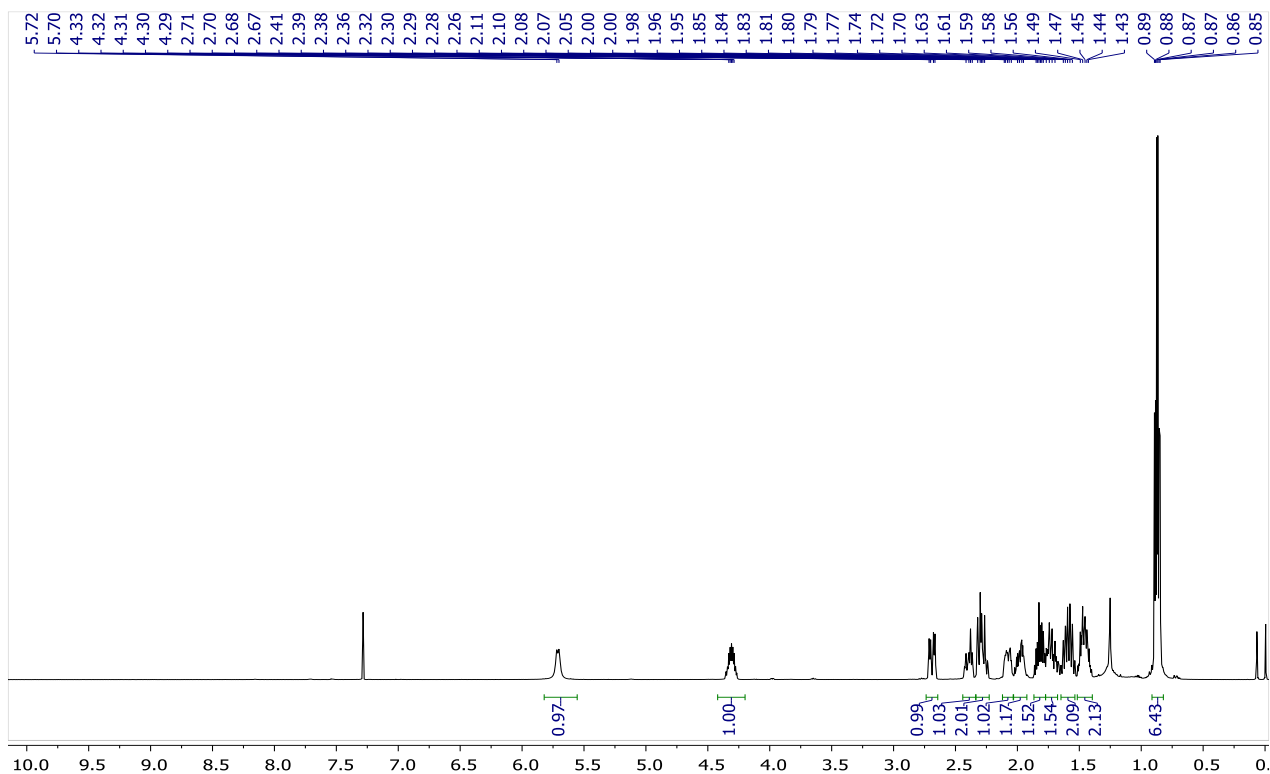
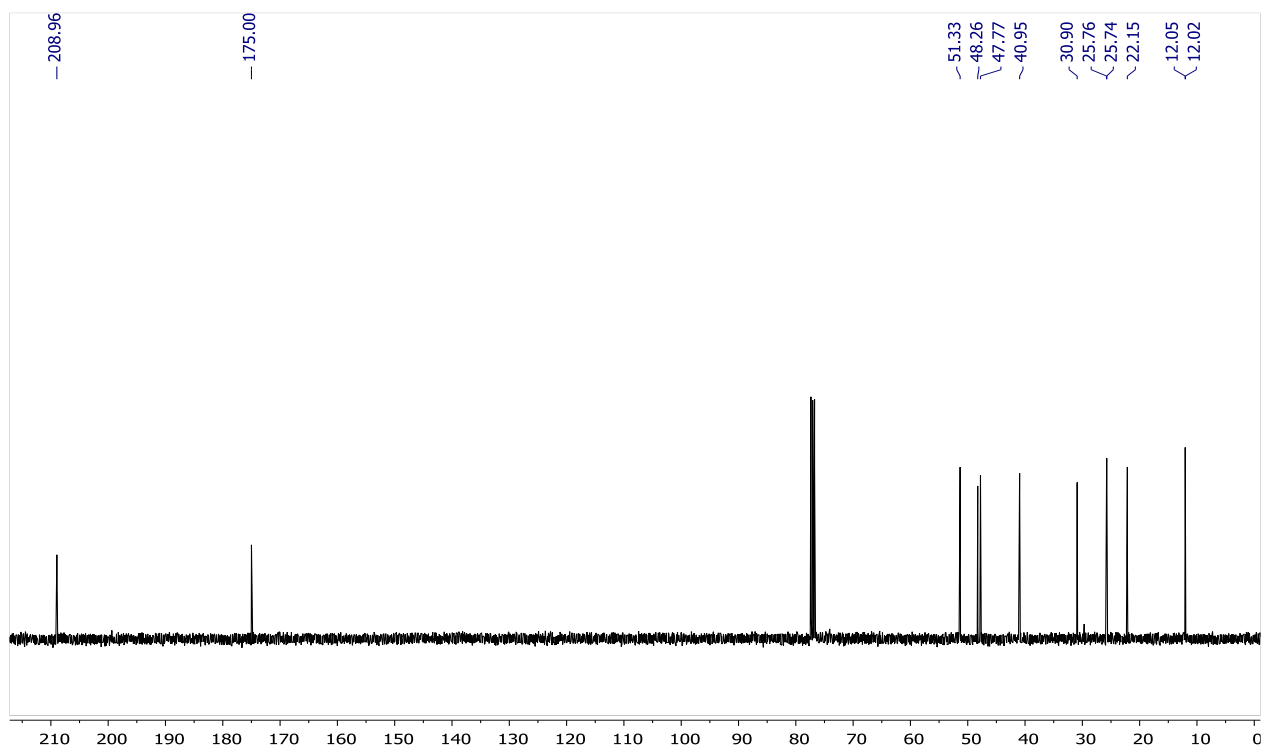
 $^1\text{H-NMR}$ of **P6** (K_3+K_4) in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P6** (K_3+K_4) in CDCl_3 

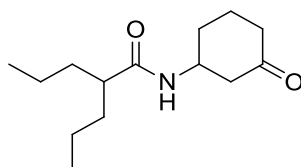
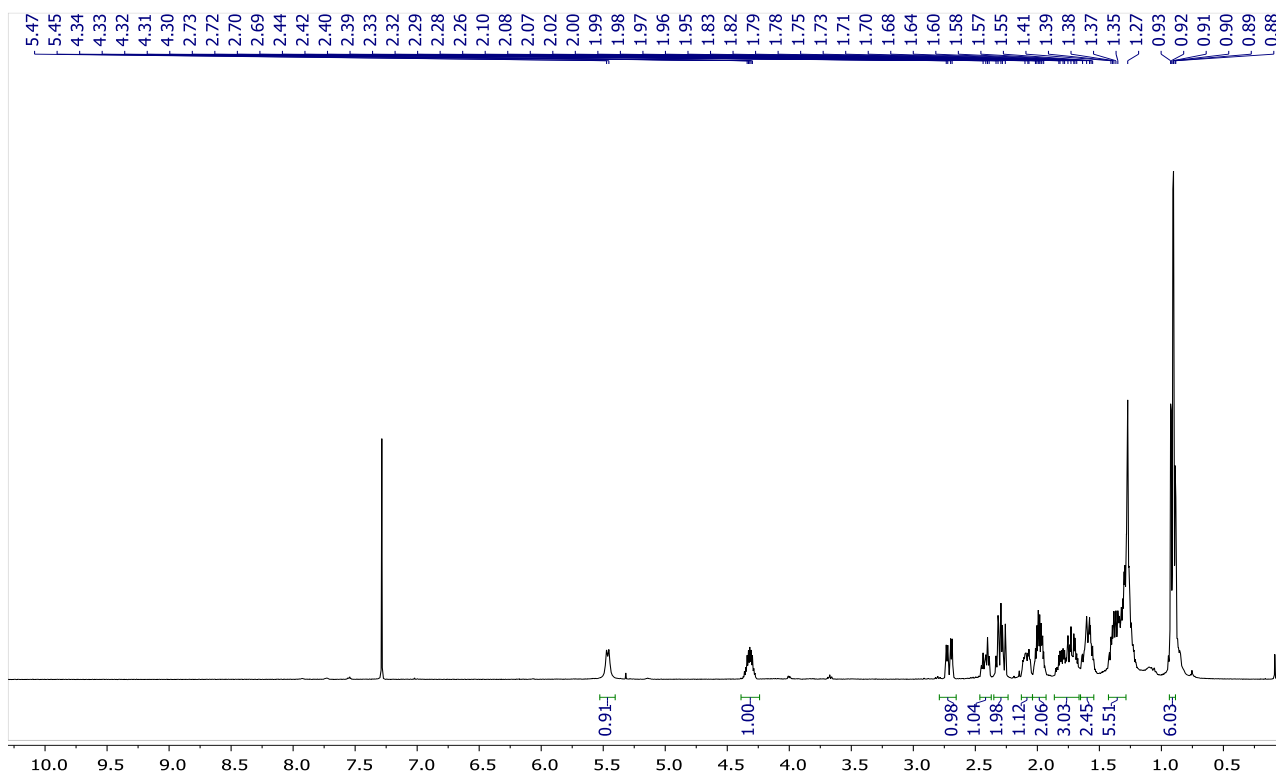
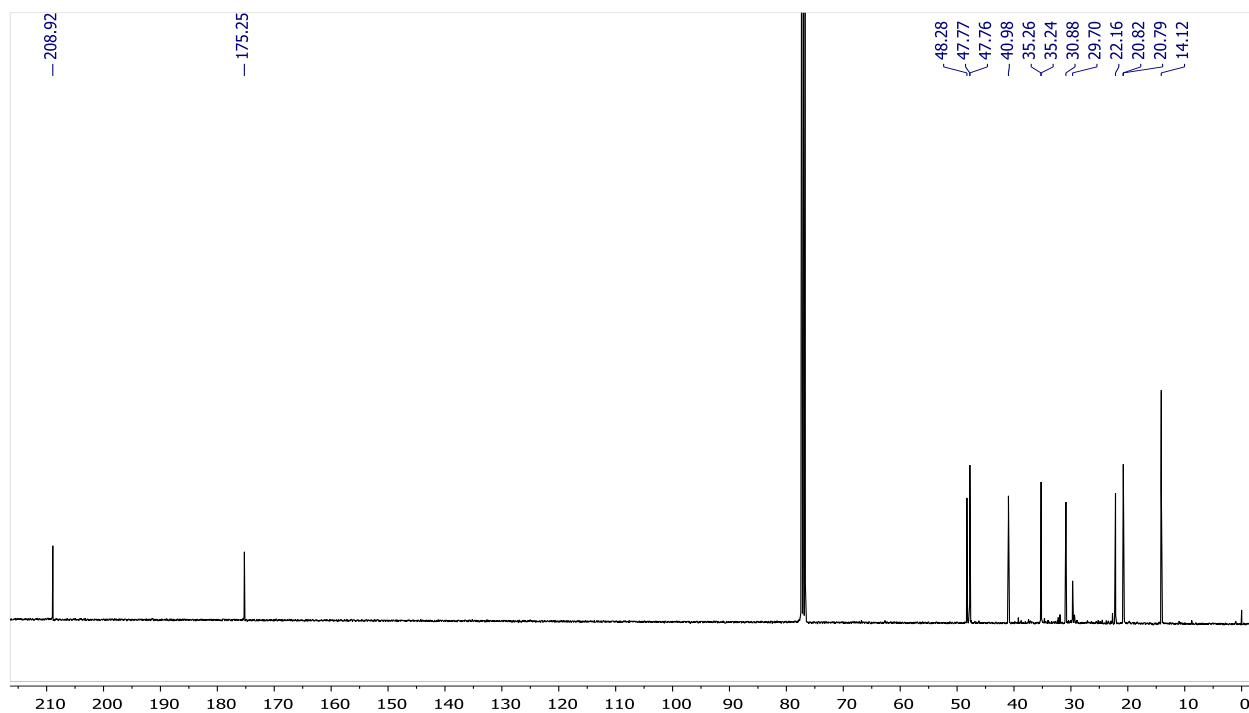
 $^1\text{H-NMR}$ of **P7** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P7** in CDCl_3 

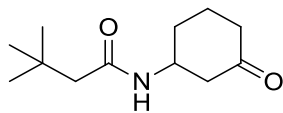
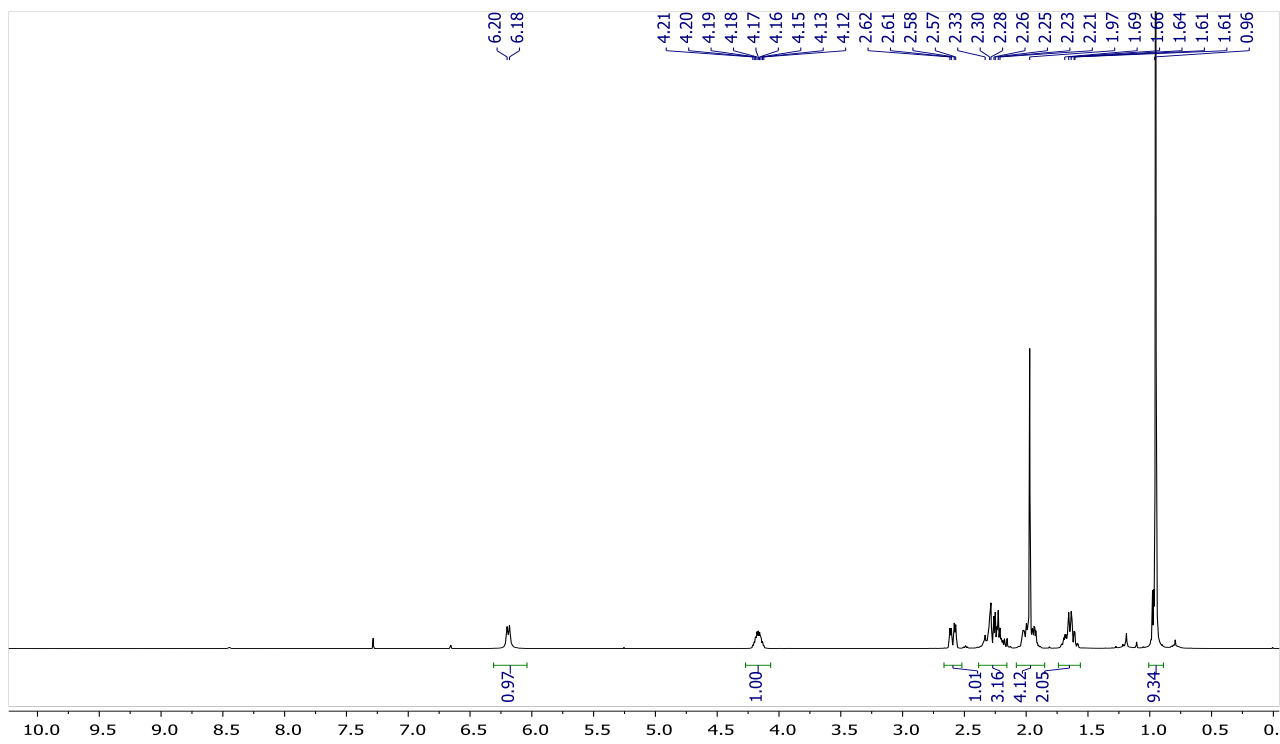
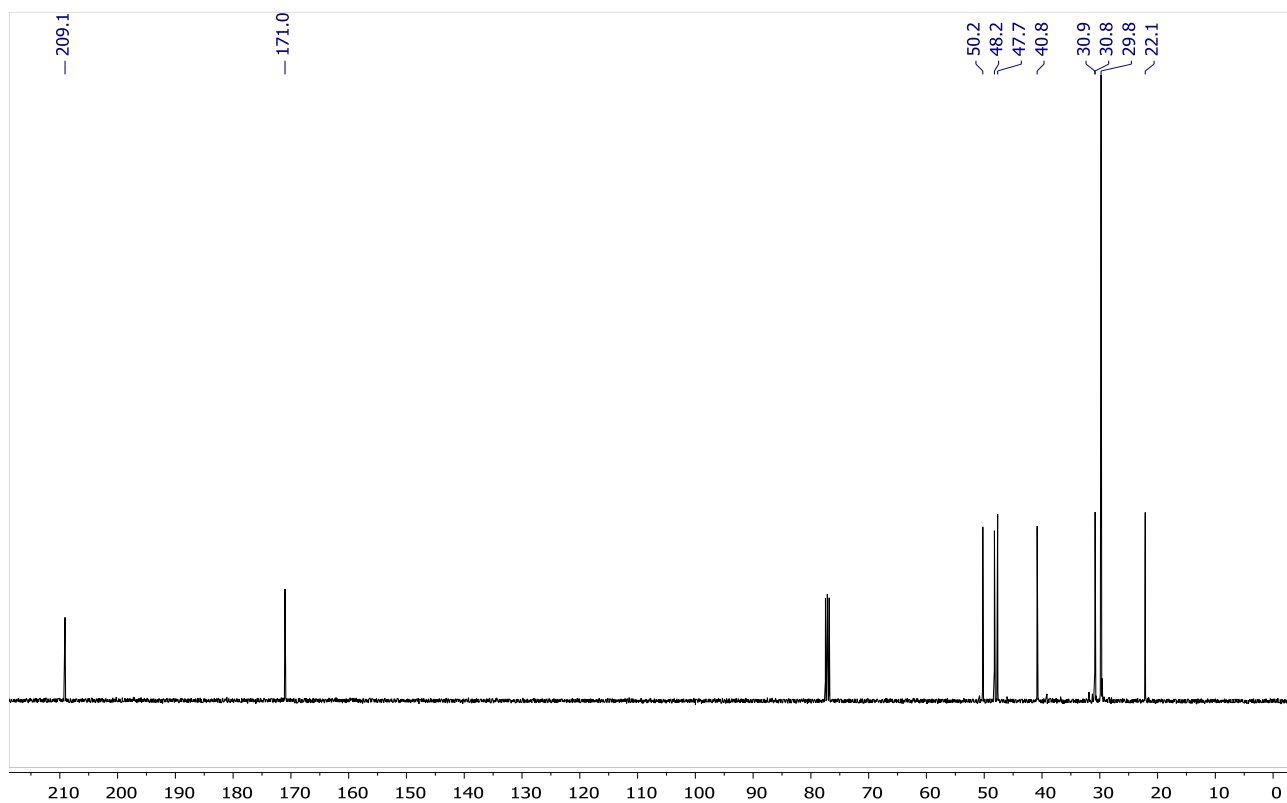
 $^1\text{H-NMR}$ of **P8** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P8** in CDCl_3 

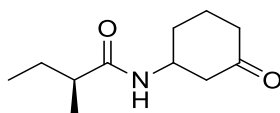
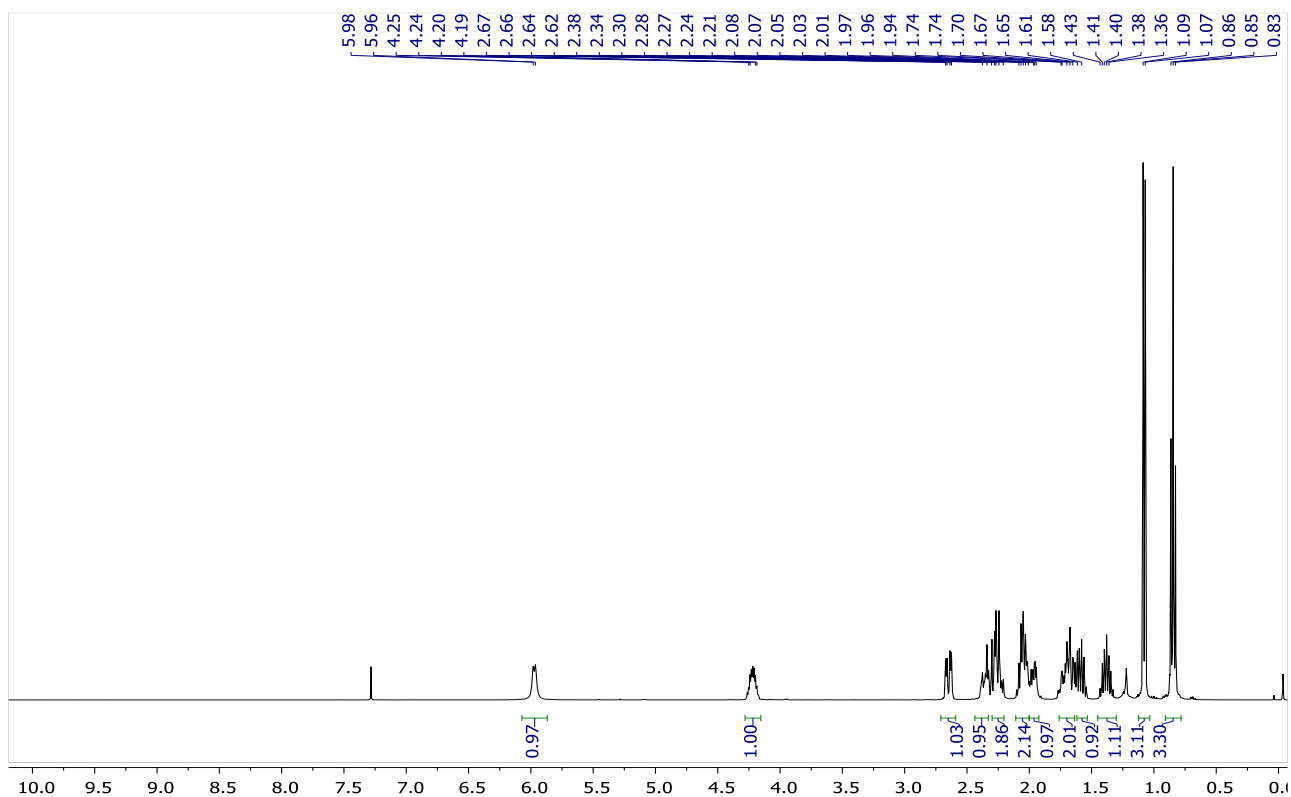
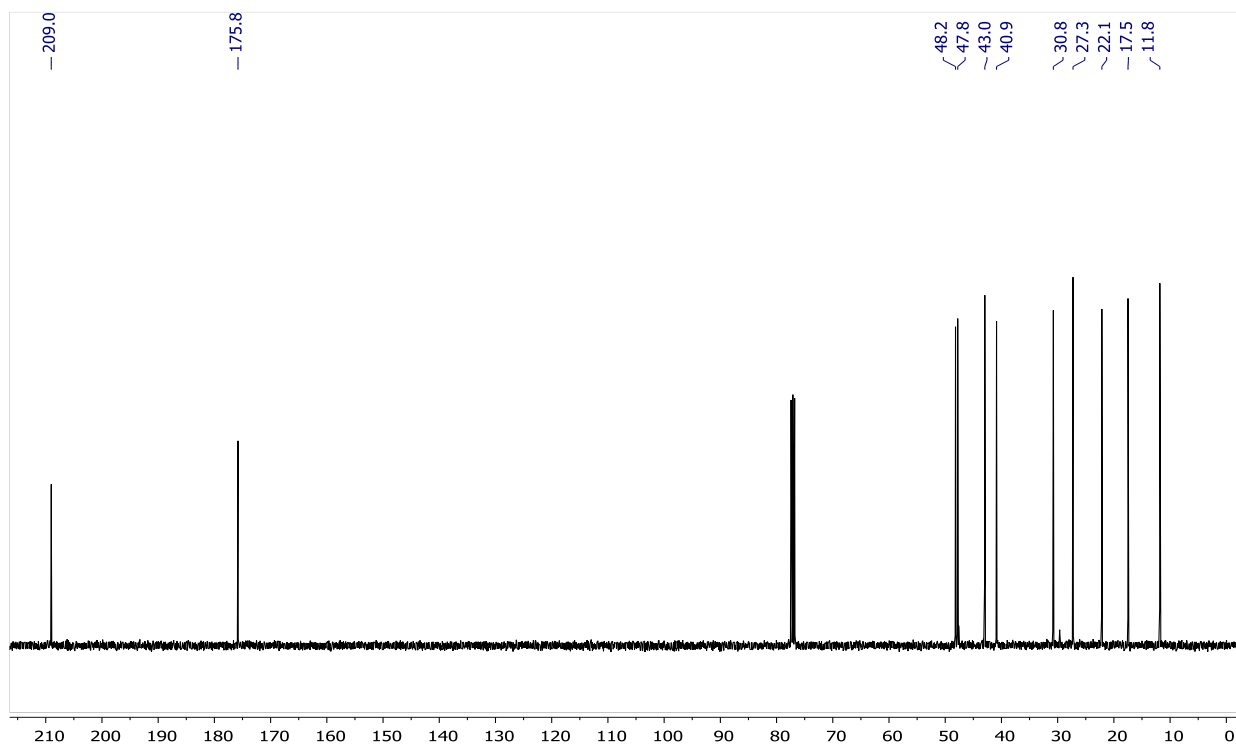
 $^1\text{H-NMR}$ of **P9** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P9** in CDCl_3 

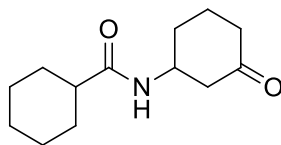
 $^1\text{H-NMR}$ of **P10** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P10** in CDCl_3 

 $^1\text{H-NMR}$ of **P11** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P11** in CDCl_3 

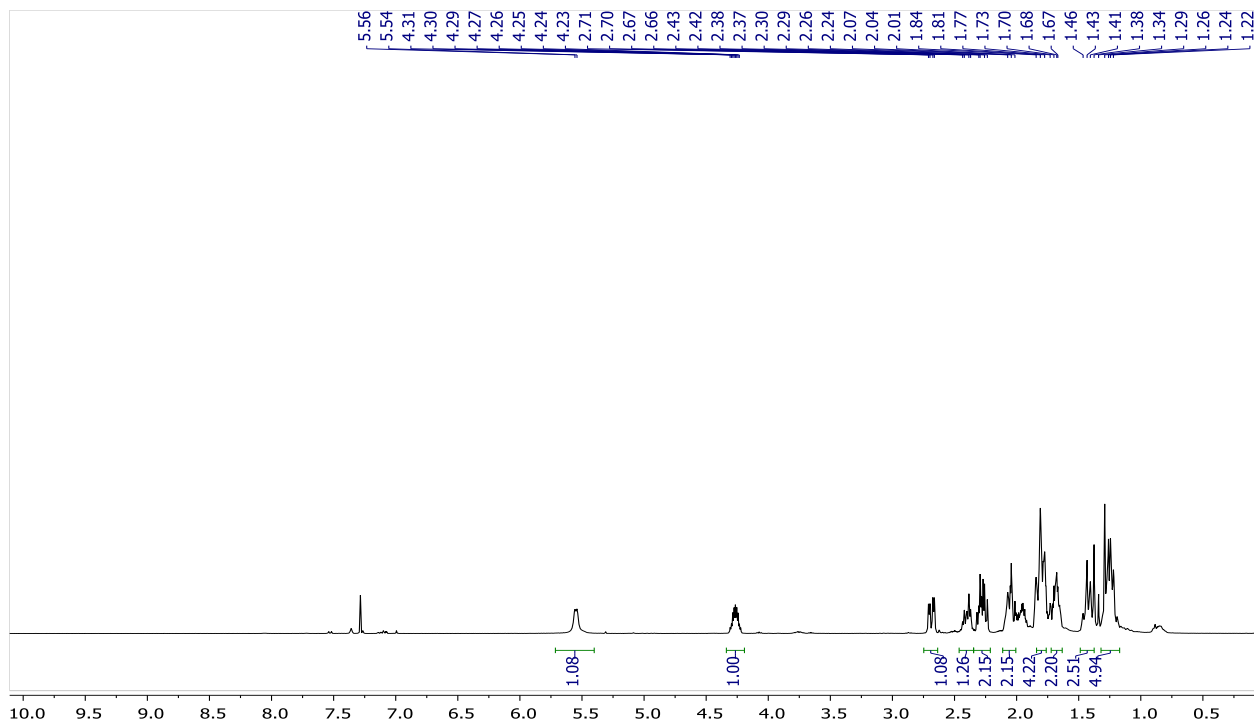
 $^1\text{H-NMR}$ of **P12** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P12** in CDCl_3 

 $^1\text{H-NMR}$ of **P13** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P13** in CDCl_3 

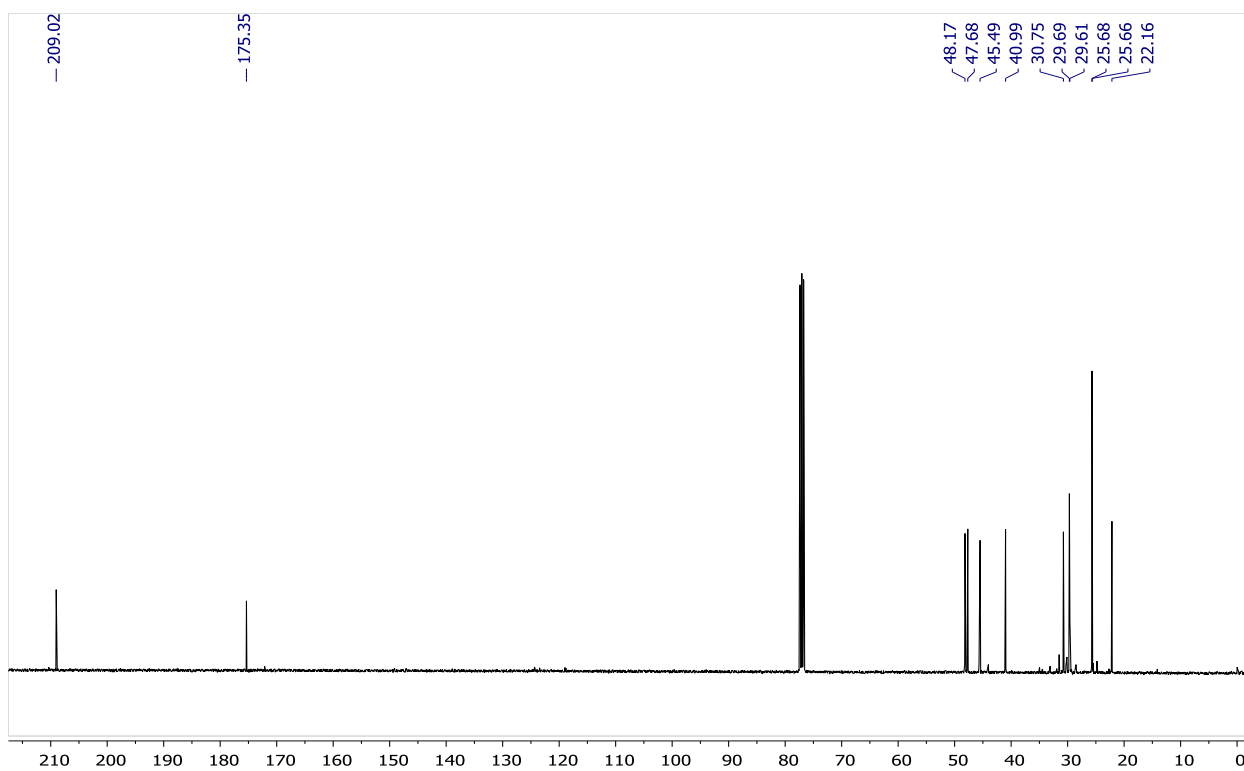
 $^1\text{H-NMR}$ of **P14** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P14** in CDCl_3 

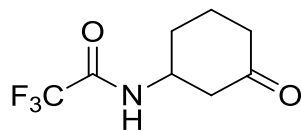
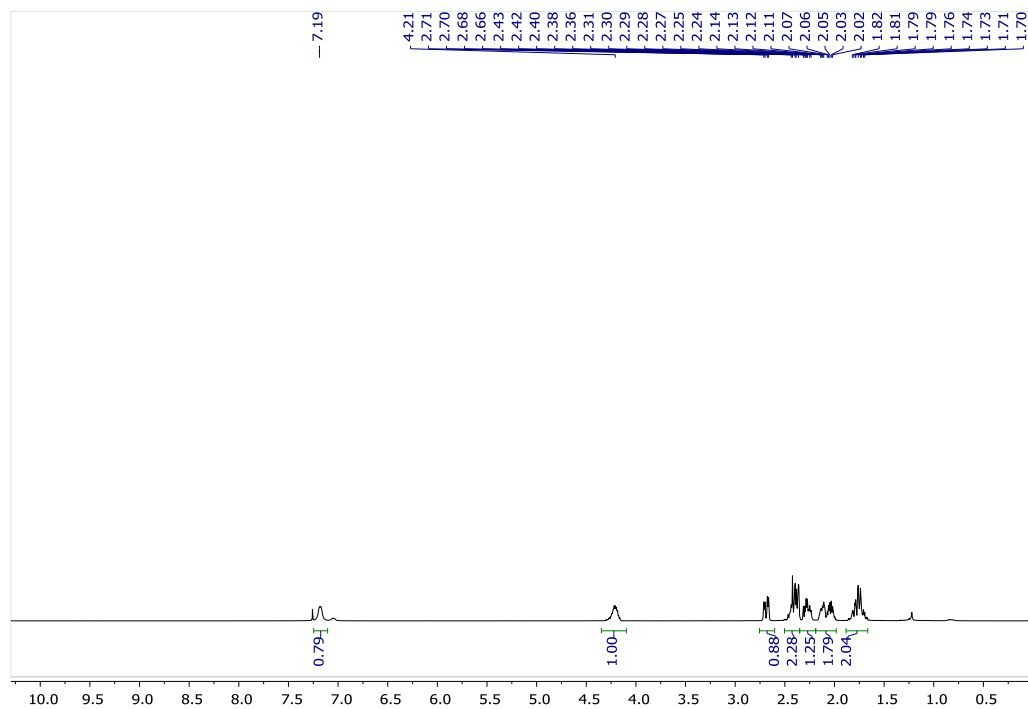
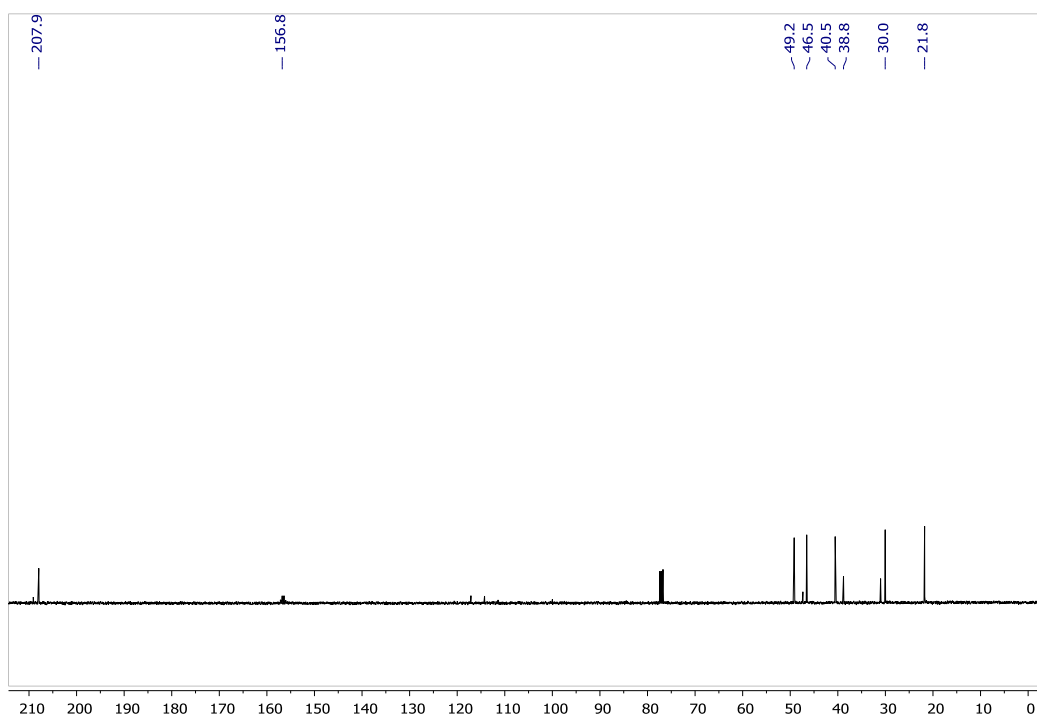


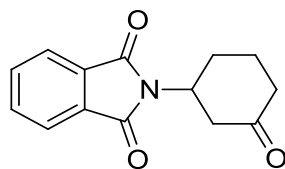
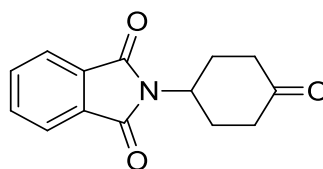
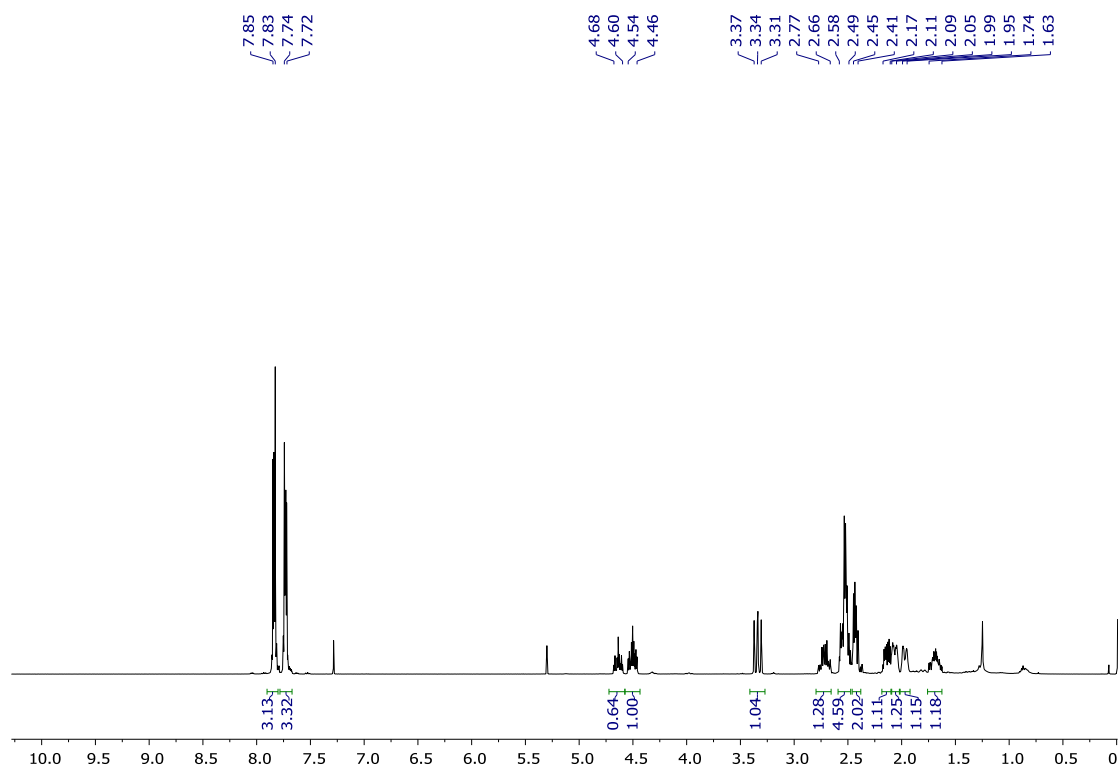
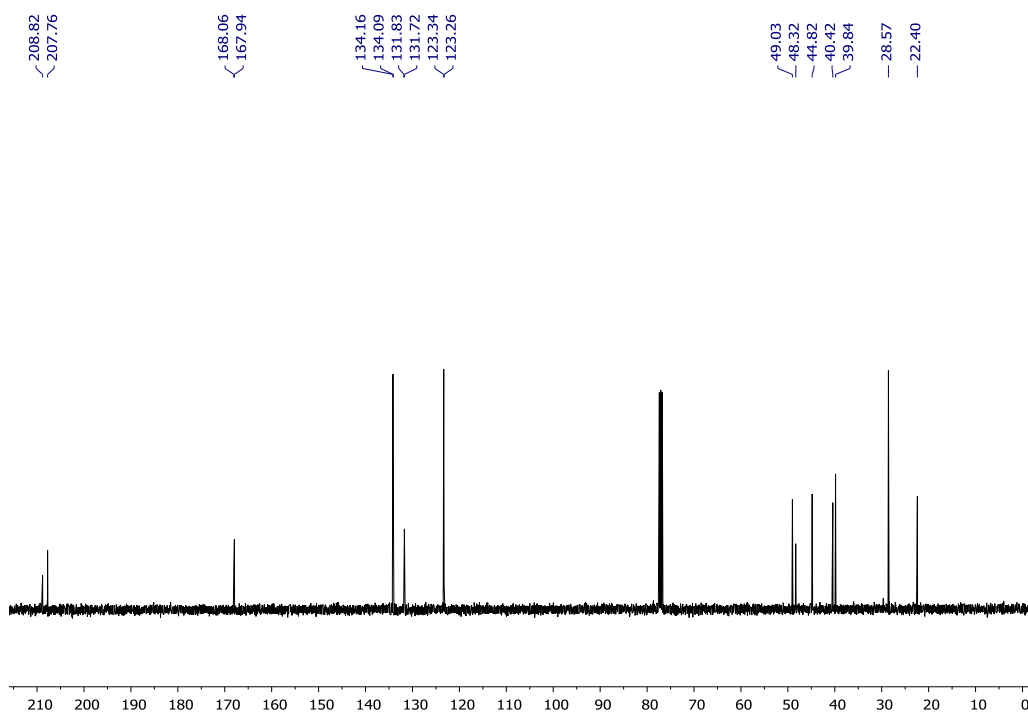
$^1\text{H-NMR}$ of **P15** in CDCl_3

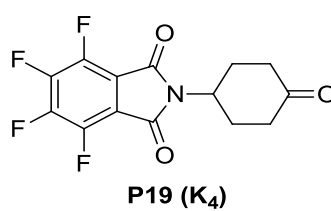
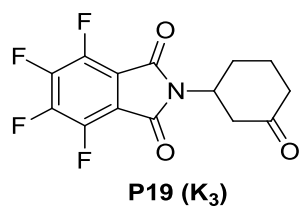


$^{13}\text{C}\{^1\text{H}\}$ -NMR of **P15** in CDCl_3



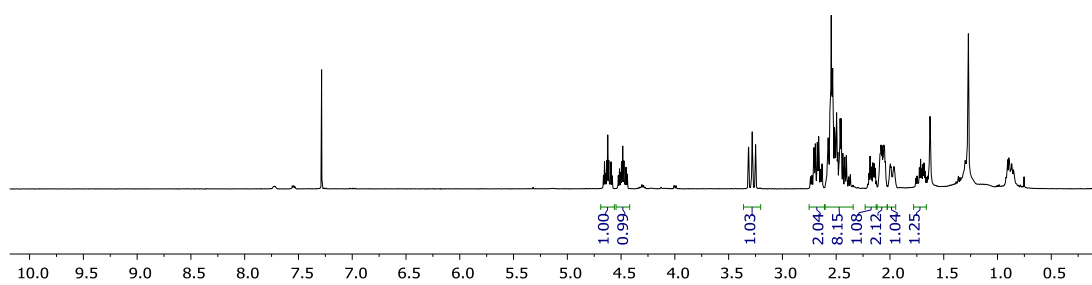
 $^1\text{H-NMR}$ of **P17** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P17** in CDCl_3 

P18 (K₃)P18 (K₄)¹H-NMR of P18 (K₃+K₄) in CDCl₃¹³C{¹H}-NMR of P18 (K₃+K₄) in CDCl₃

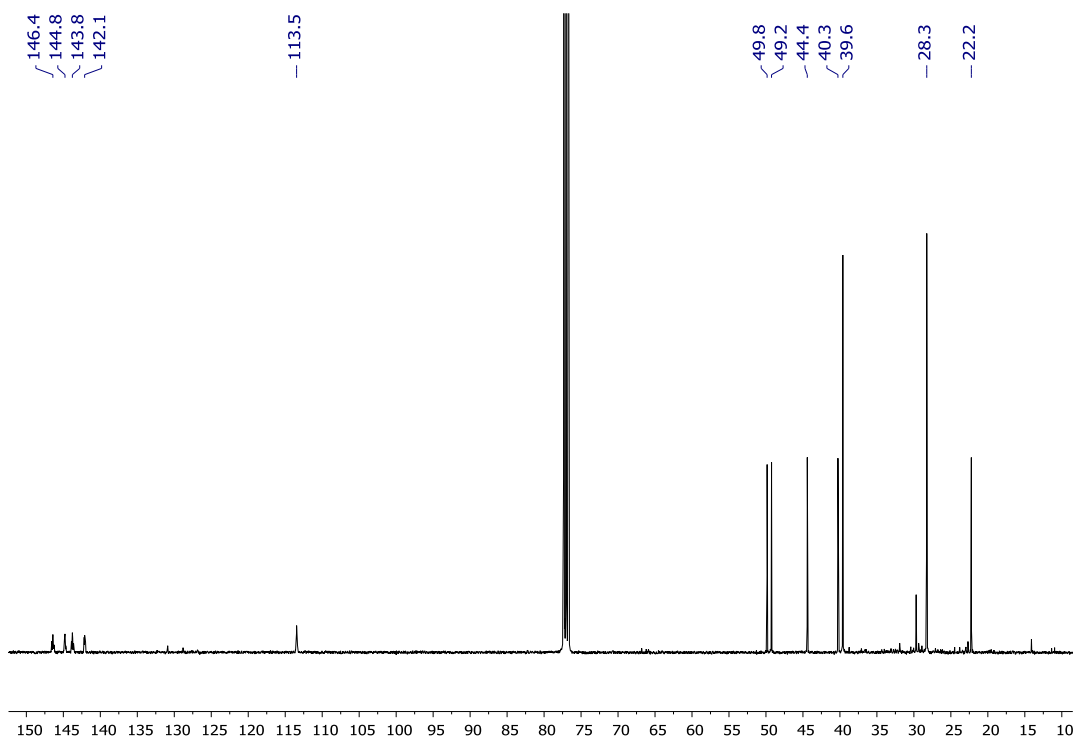


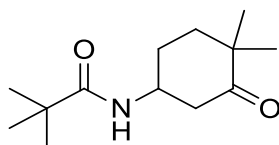
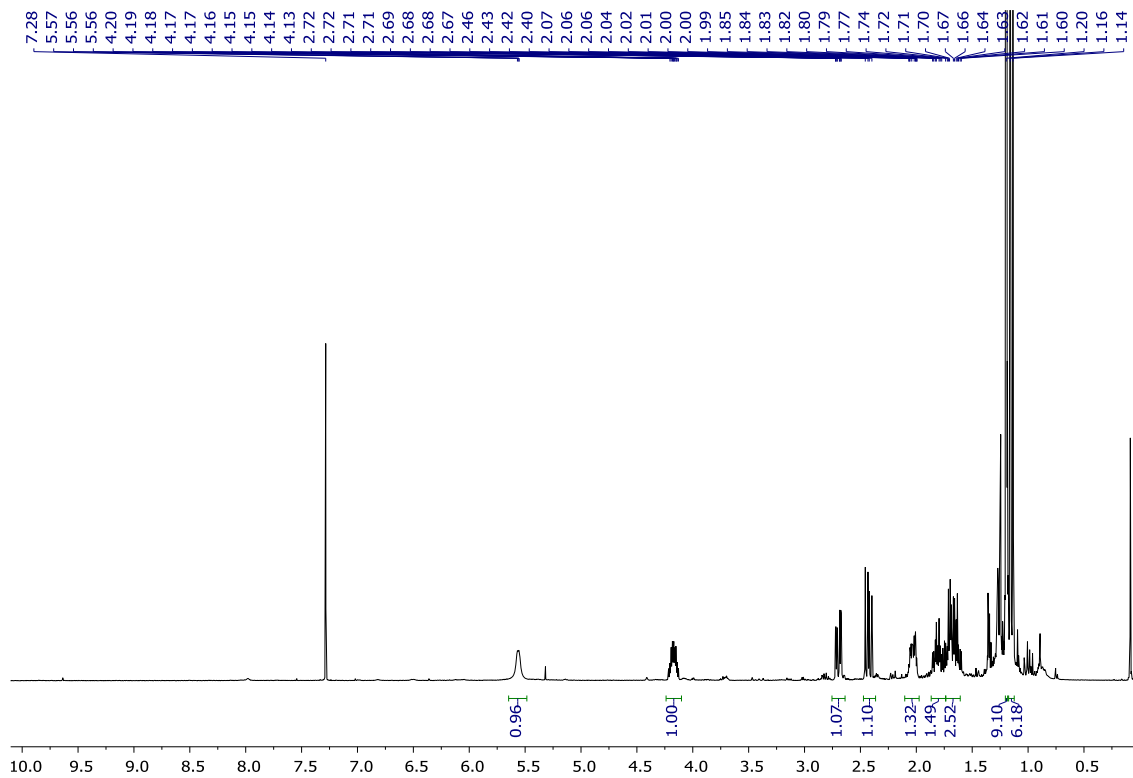
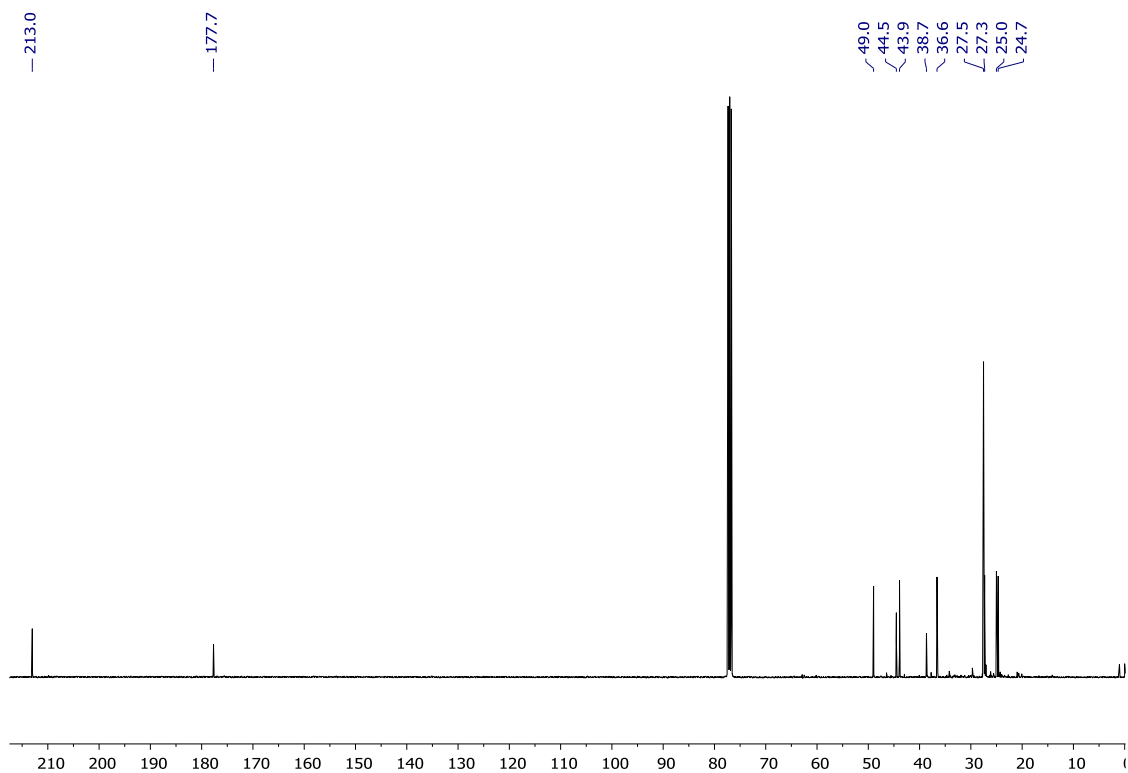
¹H-NMR of P19 (K₃+K₄) in CDCl₃

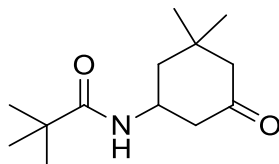
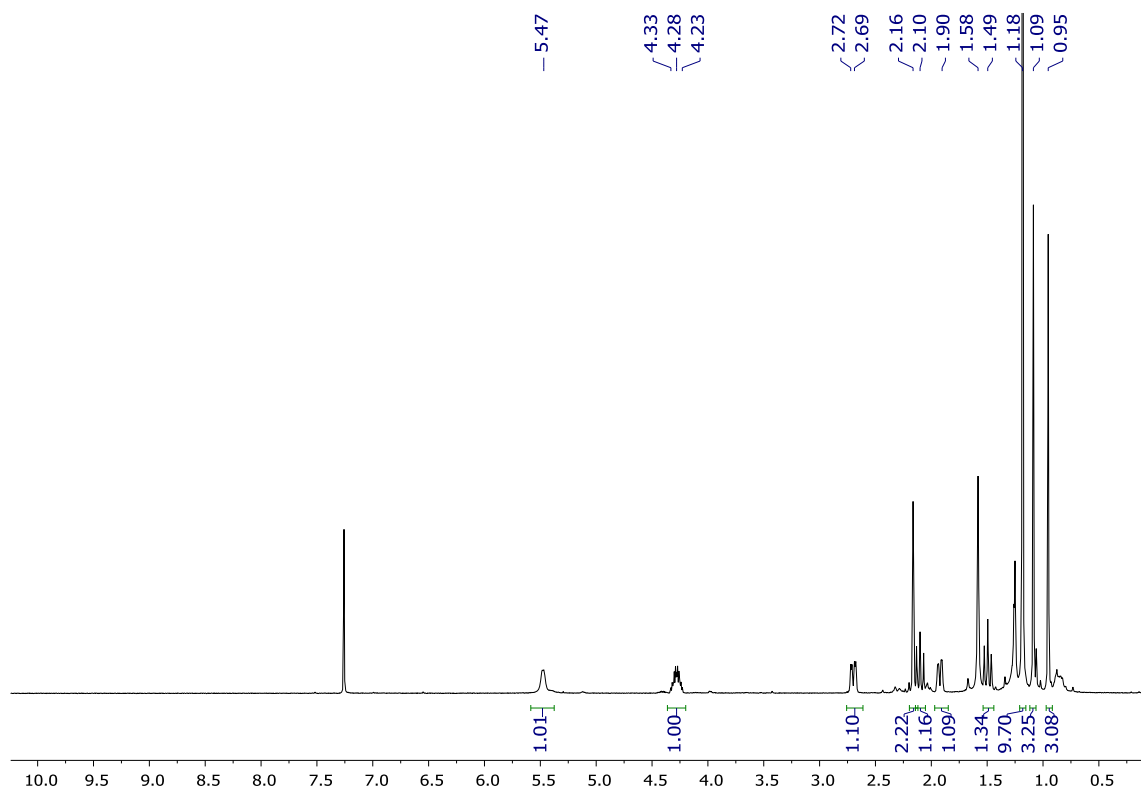
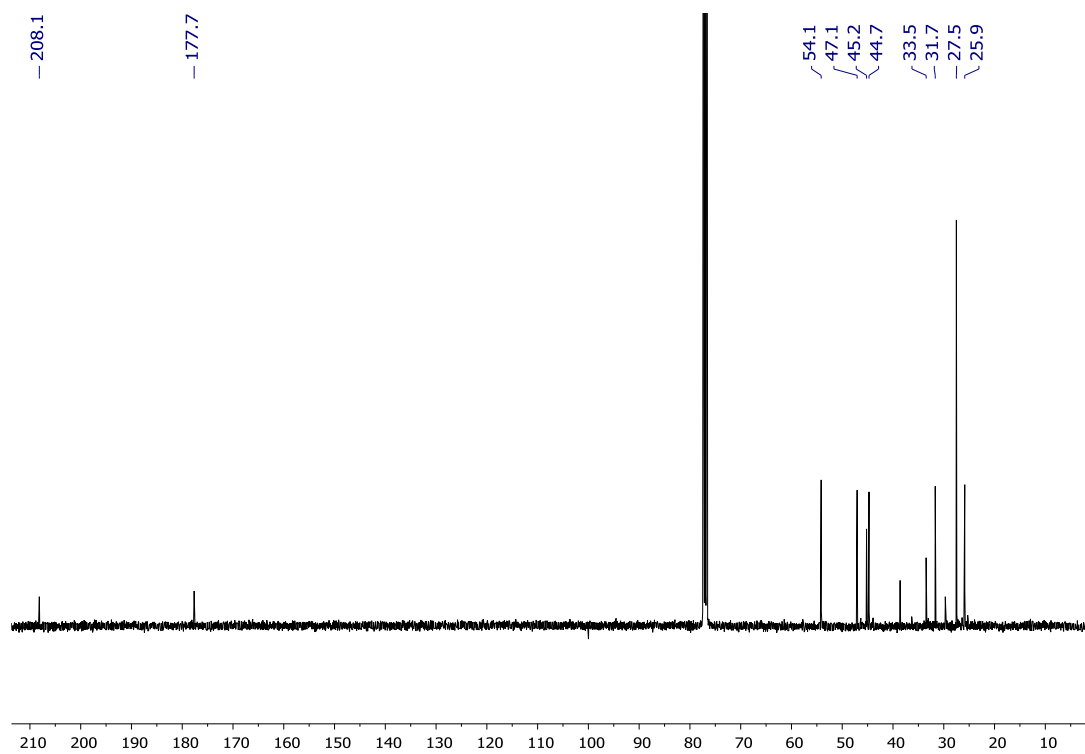
4.62
4.53
4.44
3.28
2.68
2.57
2.37
2.20
2.13
2.10
2.04
2.00
1.96
1.76
1.65

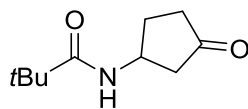
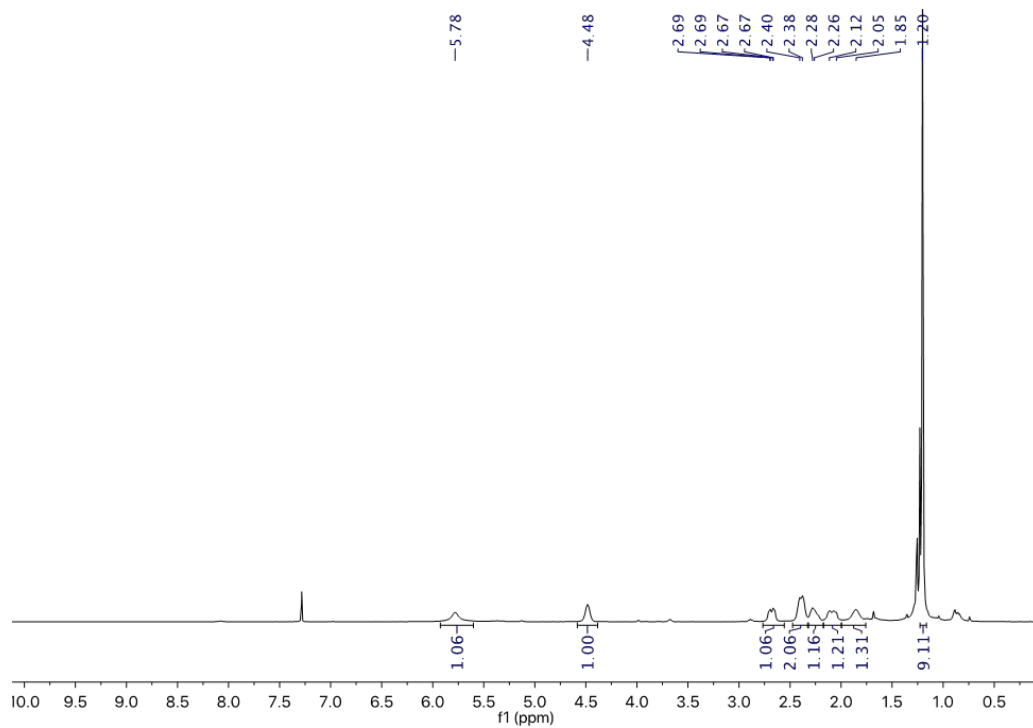
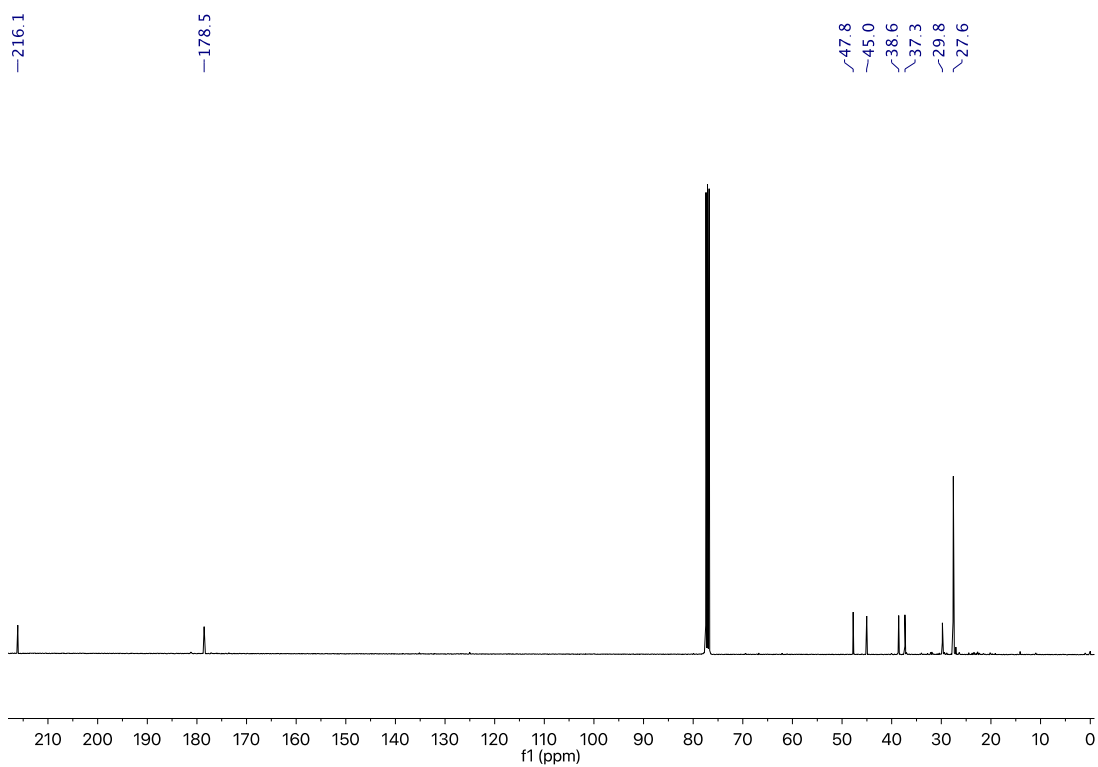


¹³C{¹H}-NMR of P19 (K₃+K₄) in CDCl₃



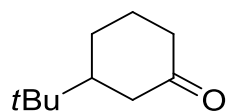
 $^1\text{H-NMR}$ of **P20** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P20** in CDCl_3 

 $^1\text{H-NMR}$ of **P21** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P21** in CDCl_3 

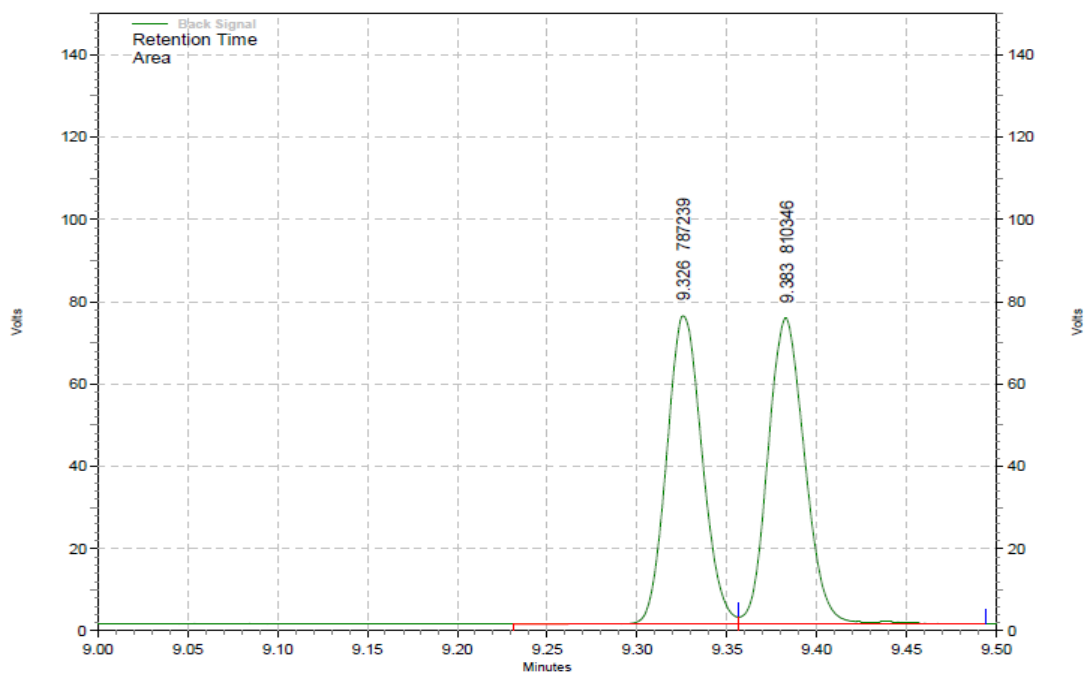
 $^1\text{H-NMR}$ of **P22** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **P22** in CDCl_3 

A4 HPLC and GC spectra of products

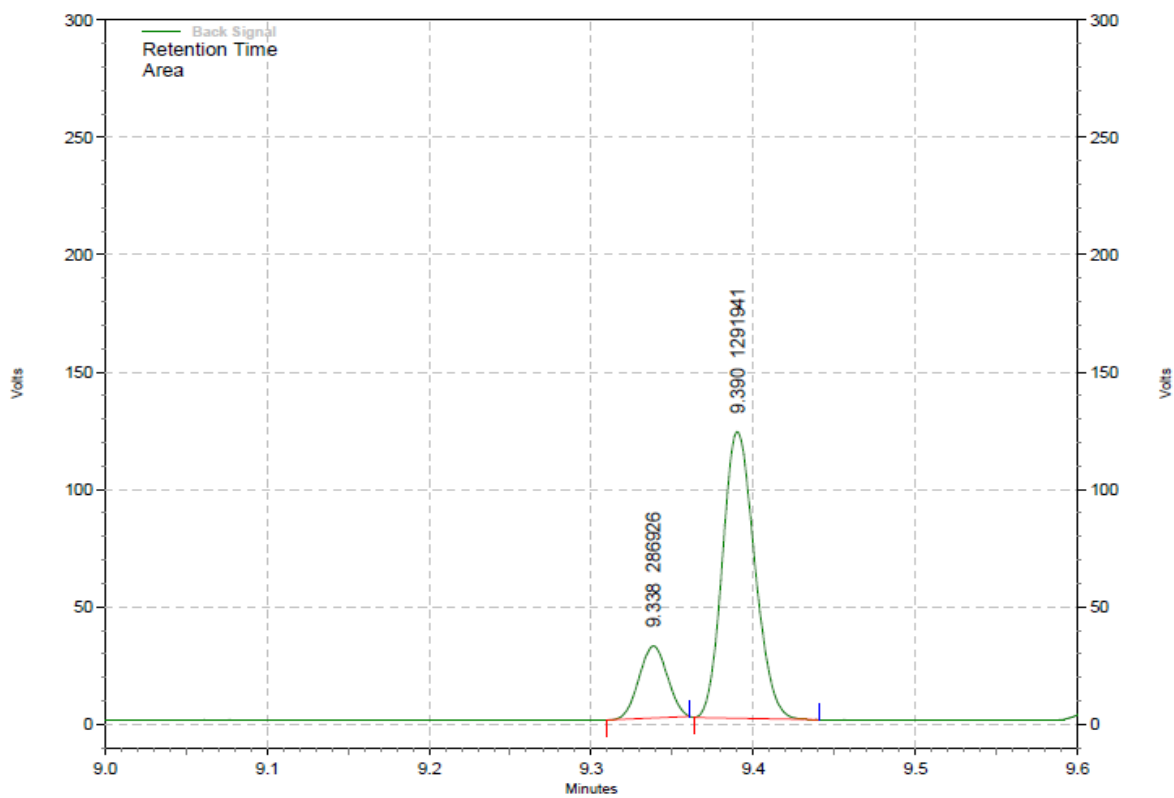
The racemic products were obtained by using the racemic $[\text{Mn}(\text{CF}_3\text{SO}_3)_2(\text{TIPS}^m\text{mcp})]$ complex.

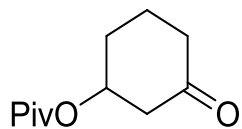


Rac

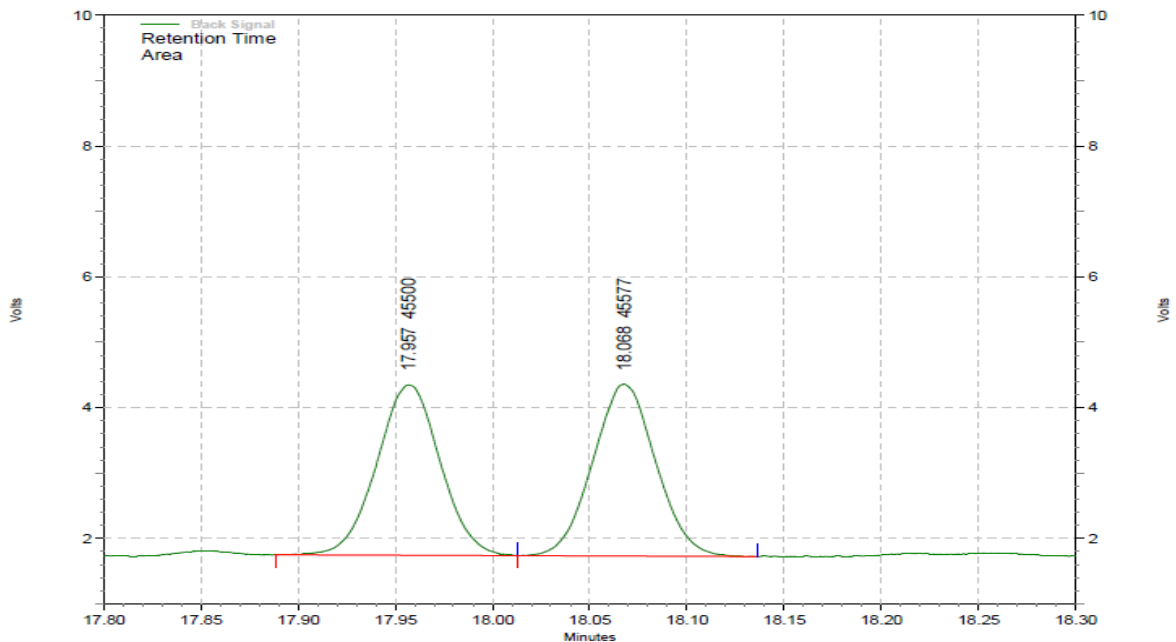


P1 (K₃)

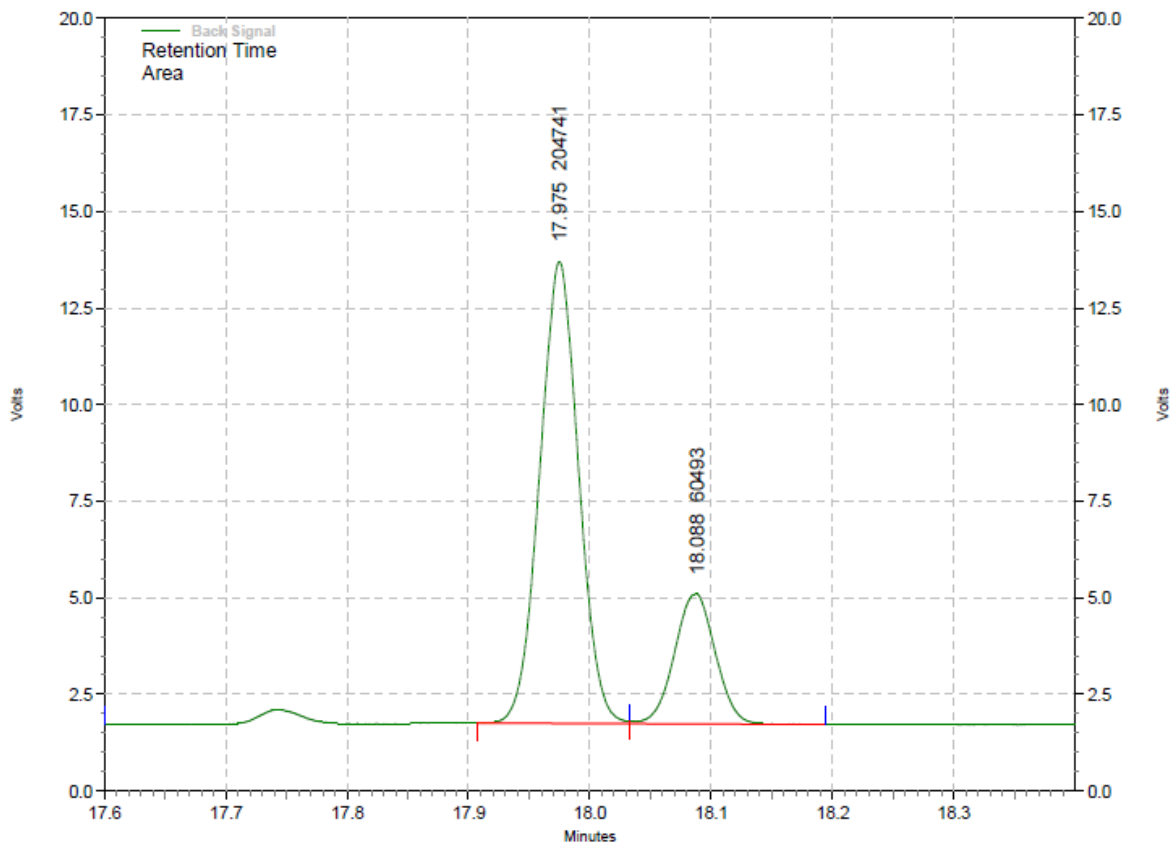


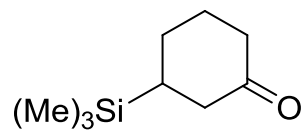
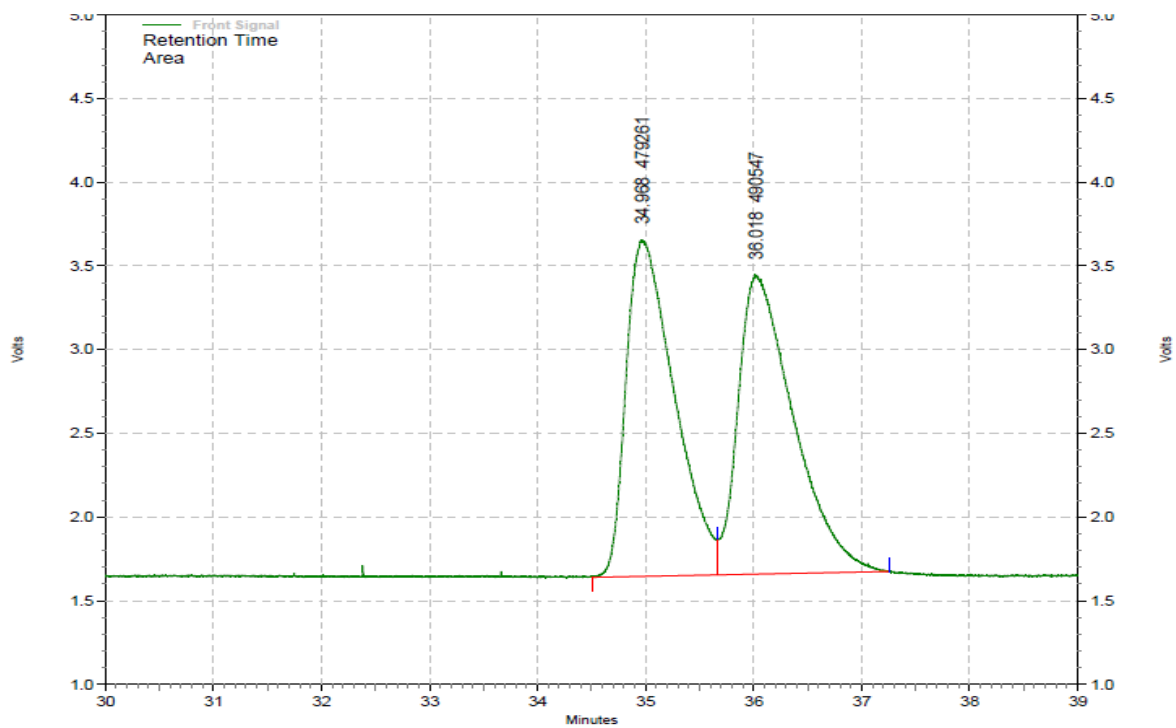
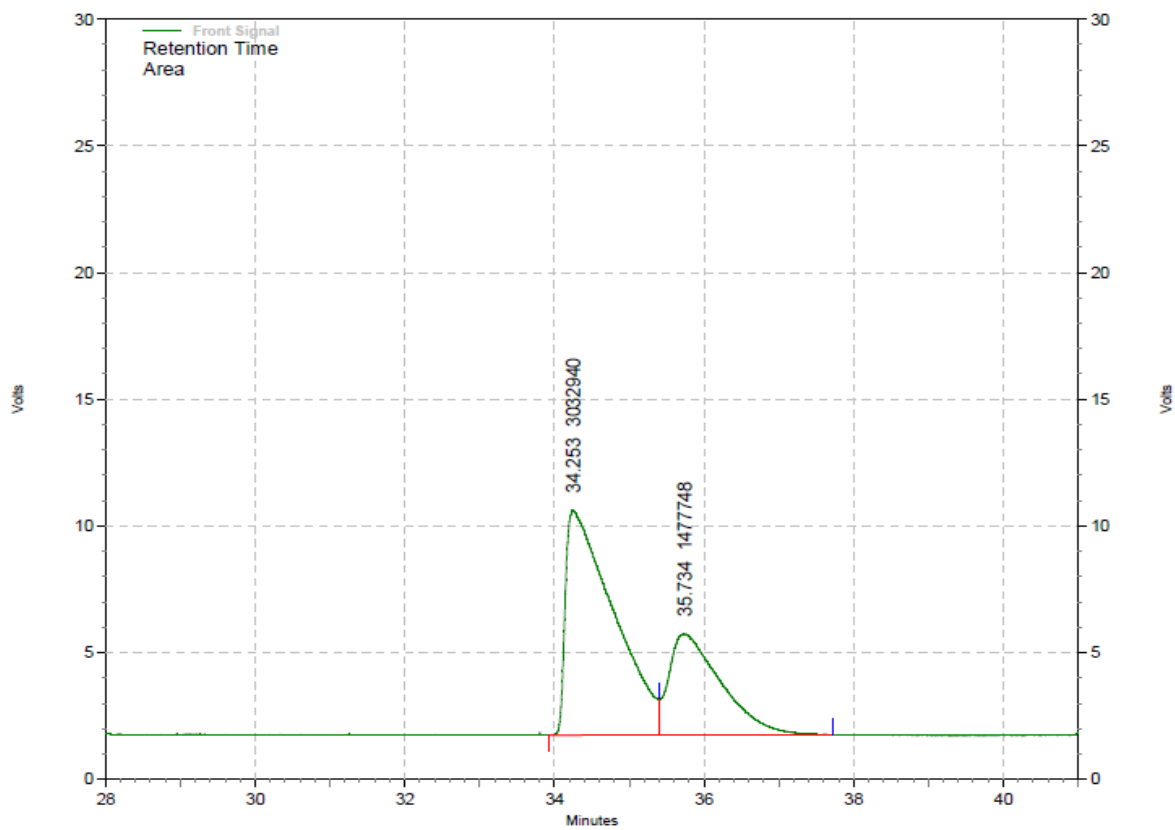


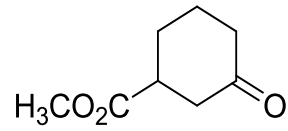
Rac



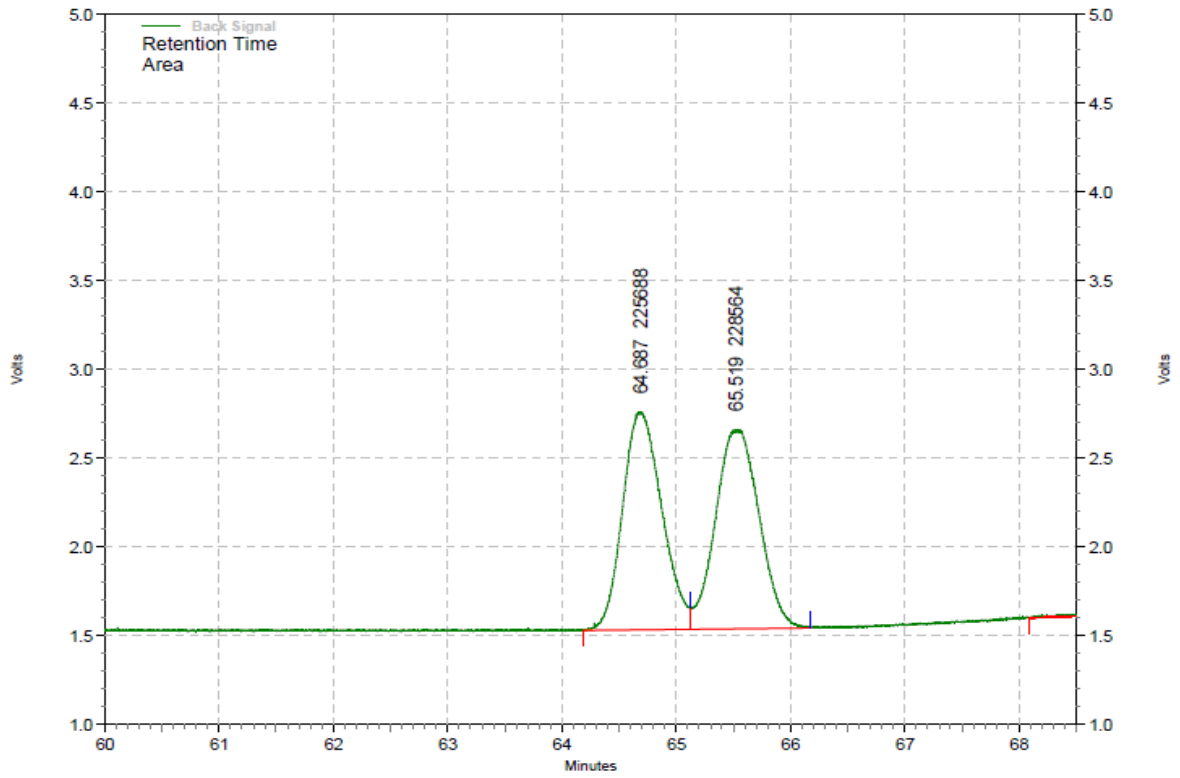
P2 (K₃)



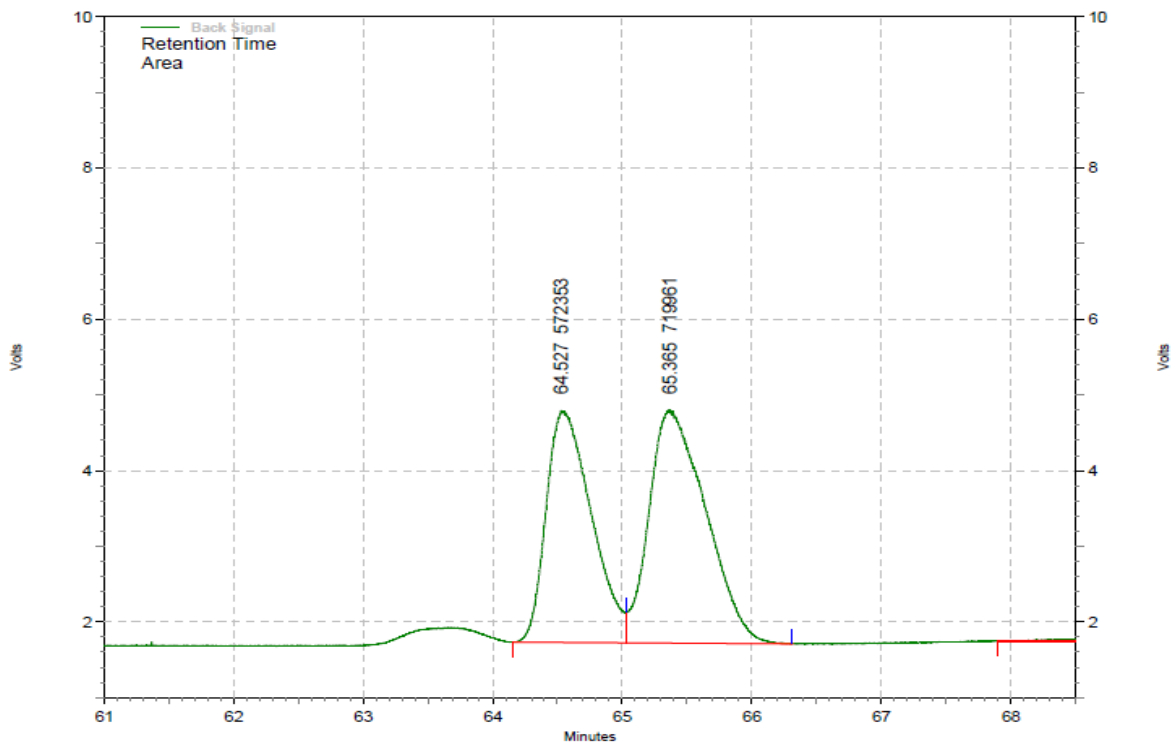
**Rac****P3 (K₃)**

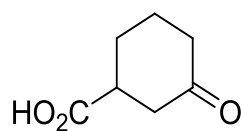


Rac

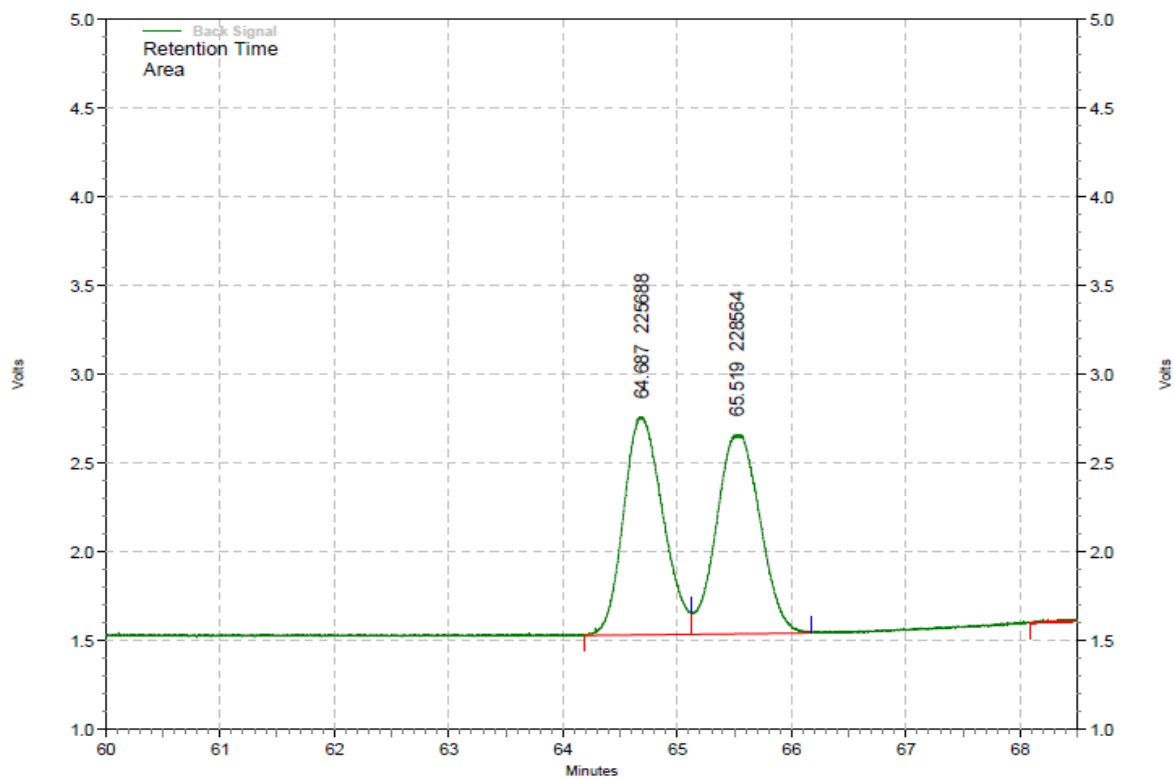
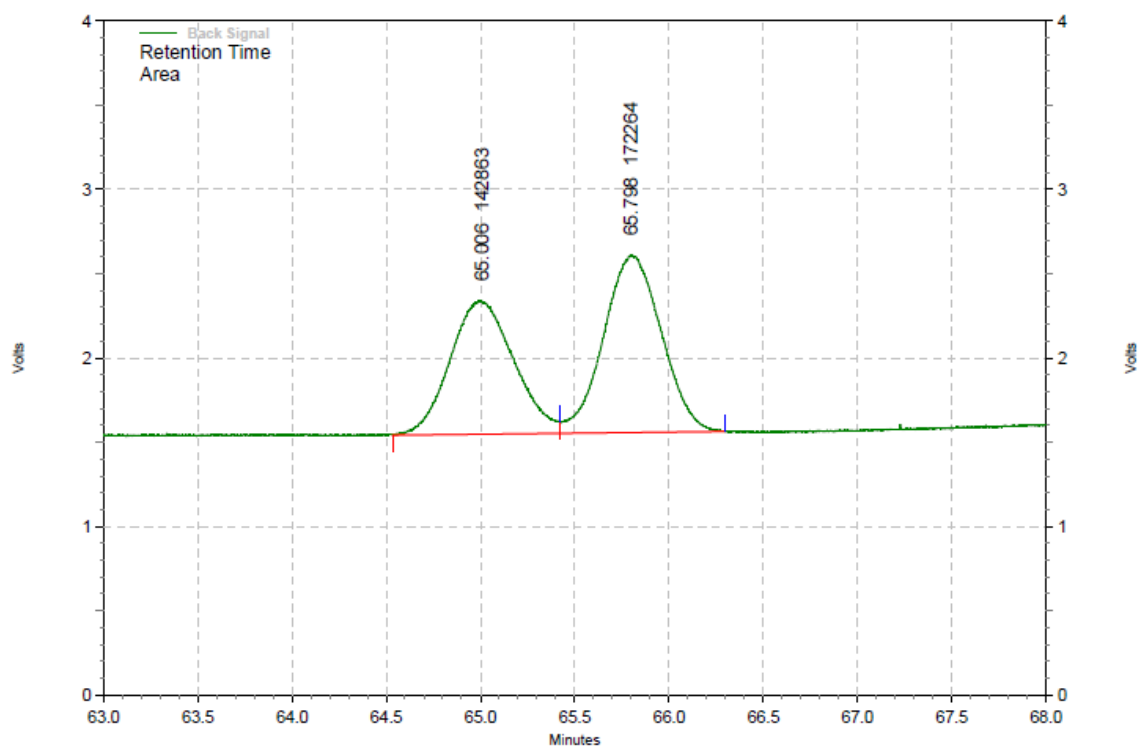


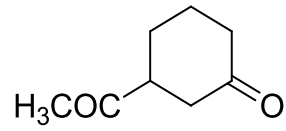
P4 (K₃)



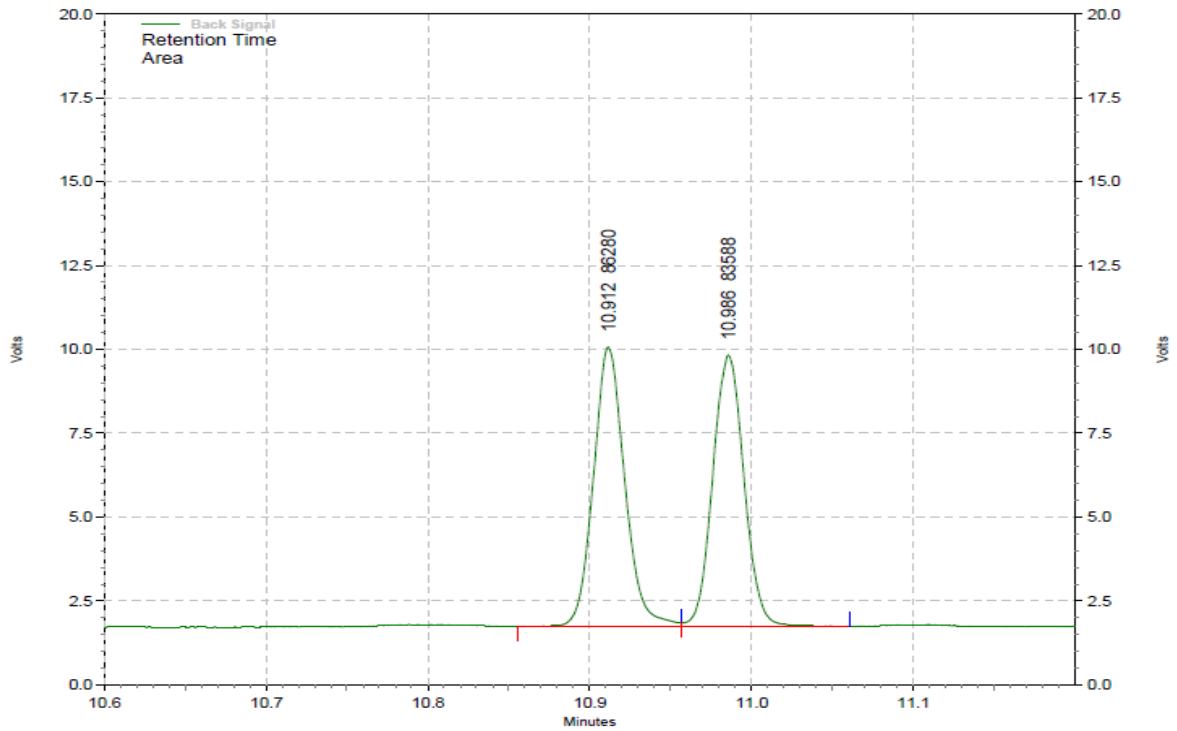


Rac

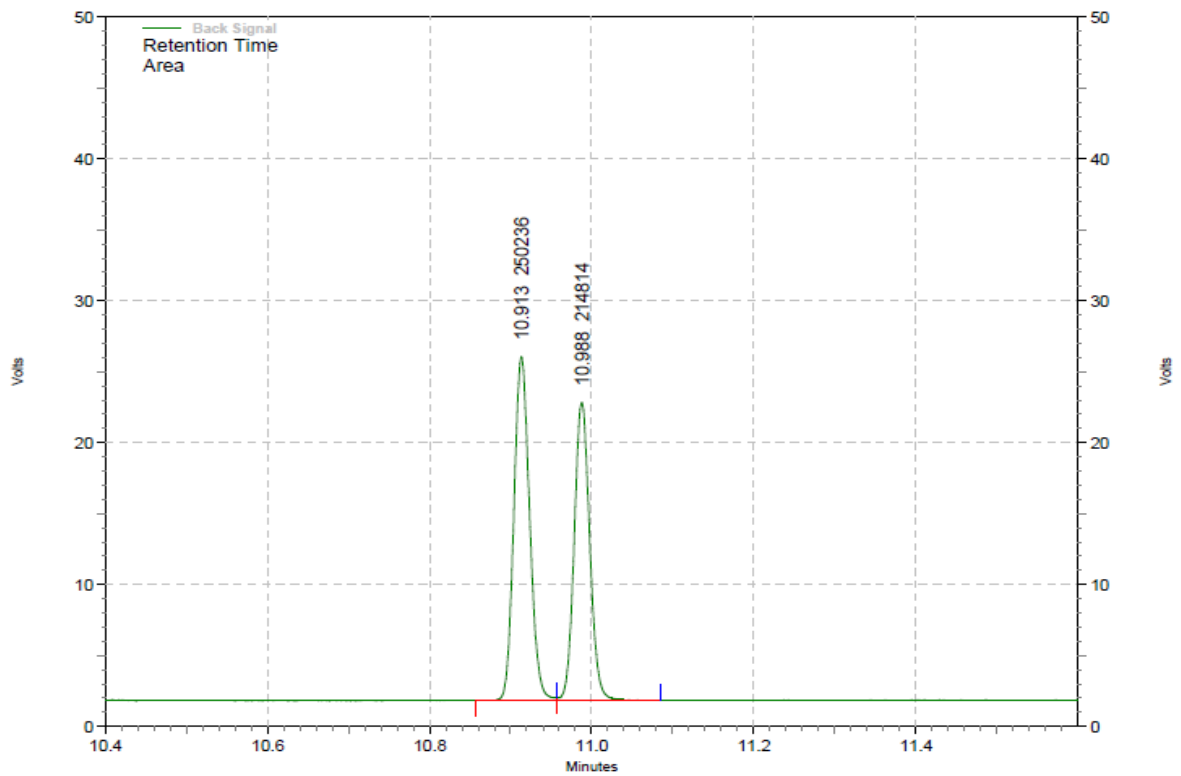
P5 (K₃) after esterification

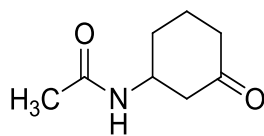
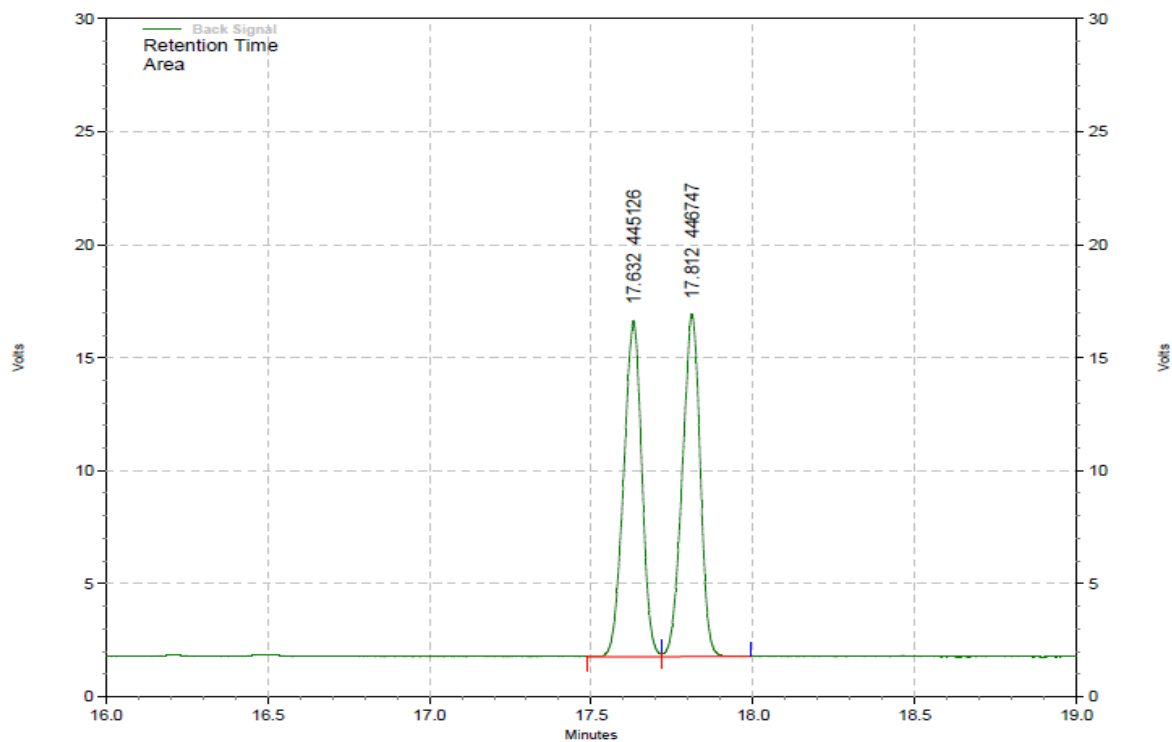
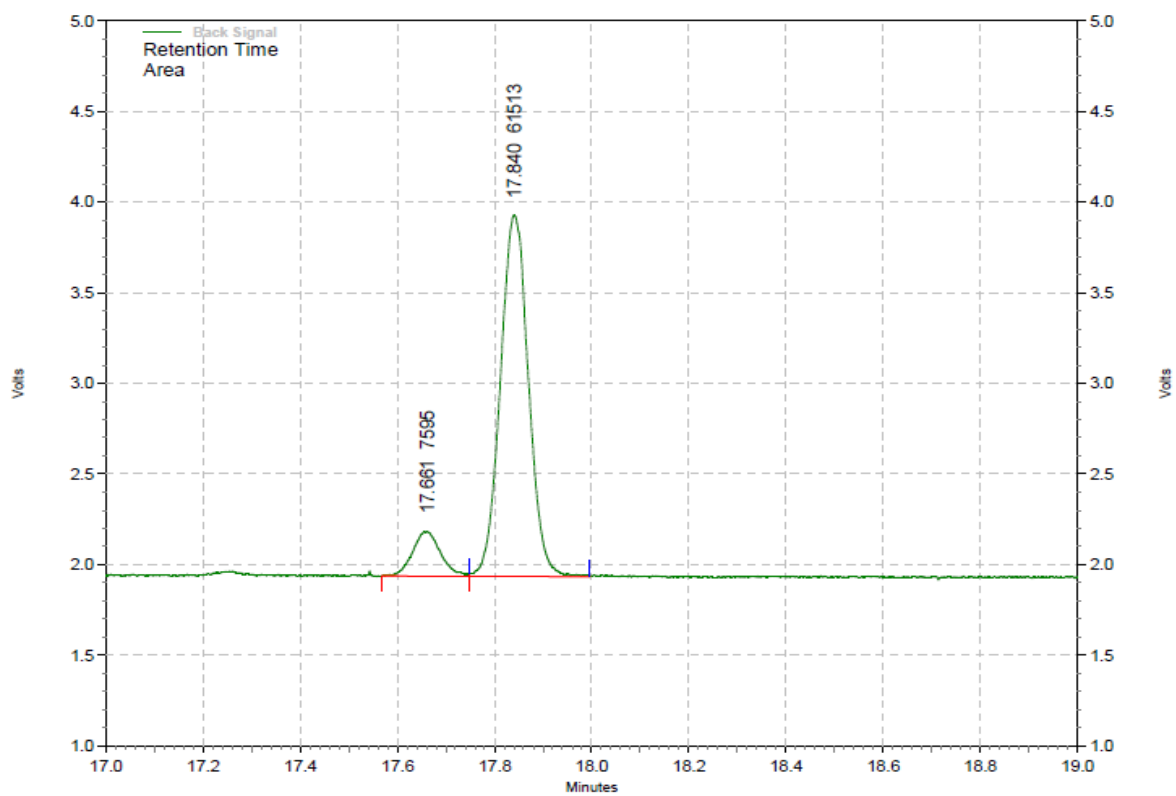


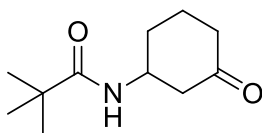
Rac



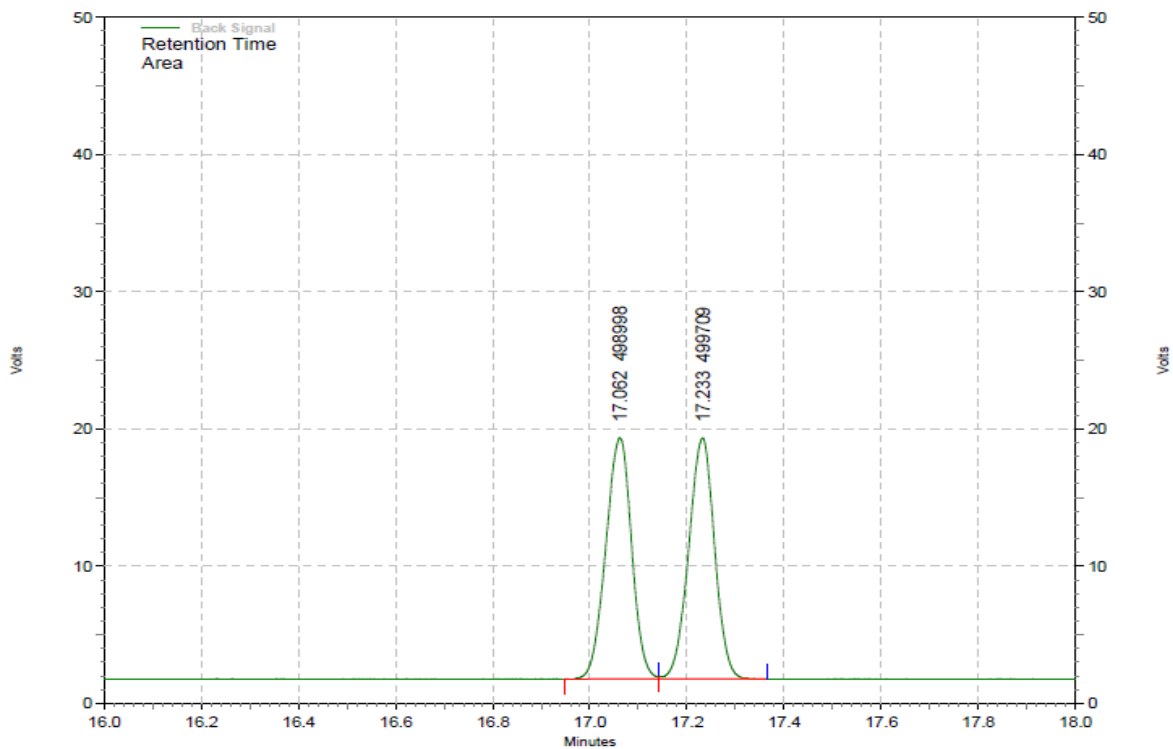
P6 (K₃)



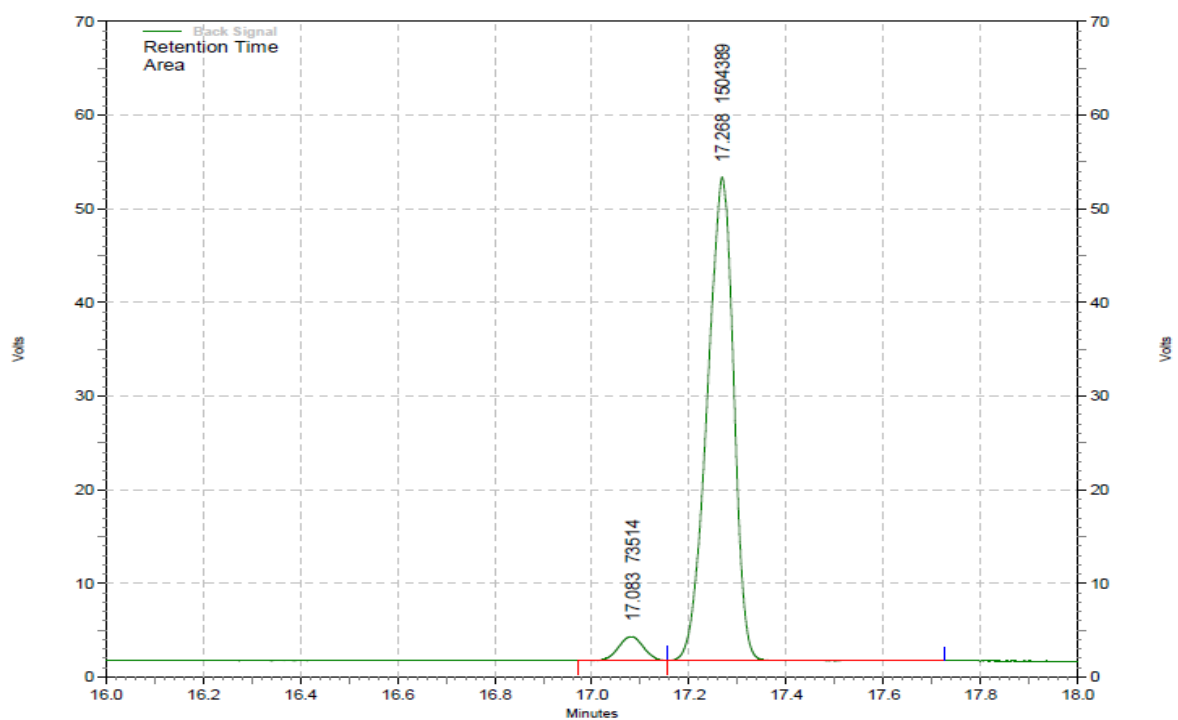
**Rac****P7**

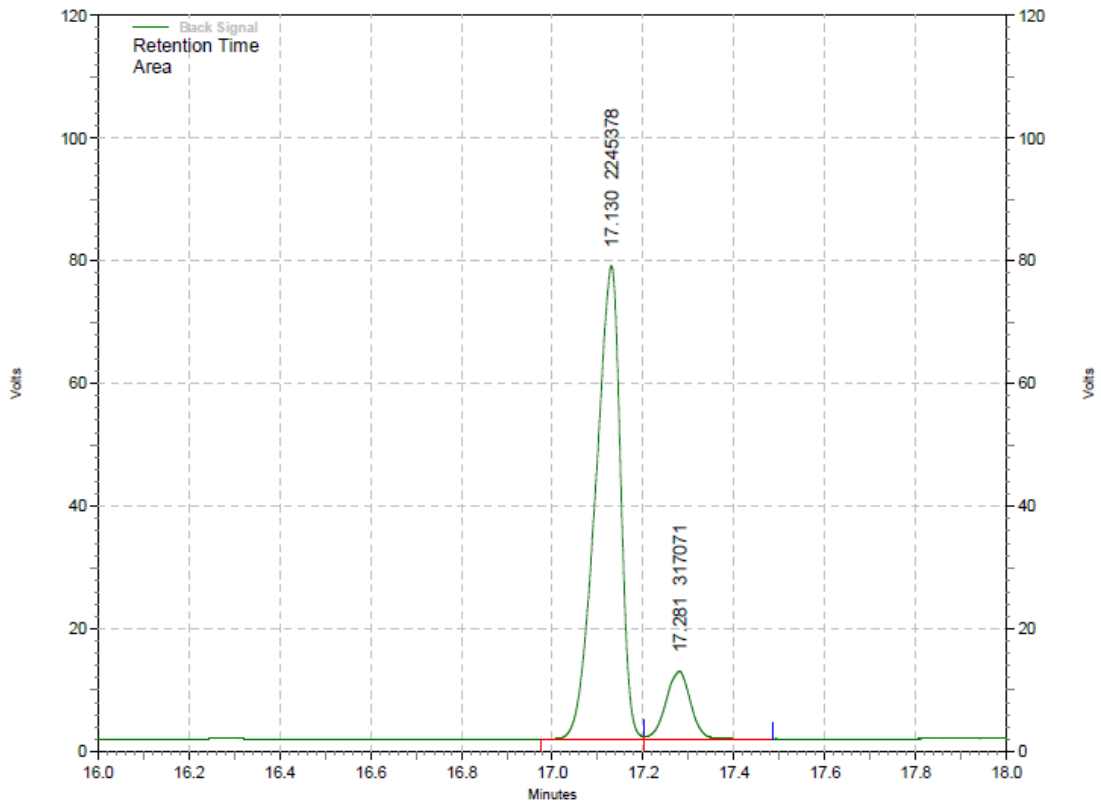
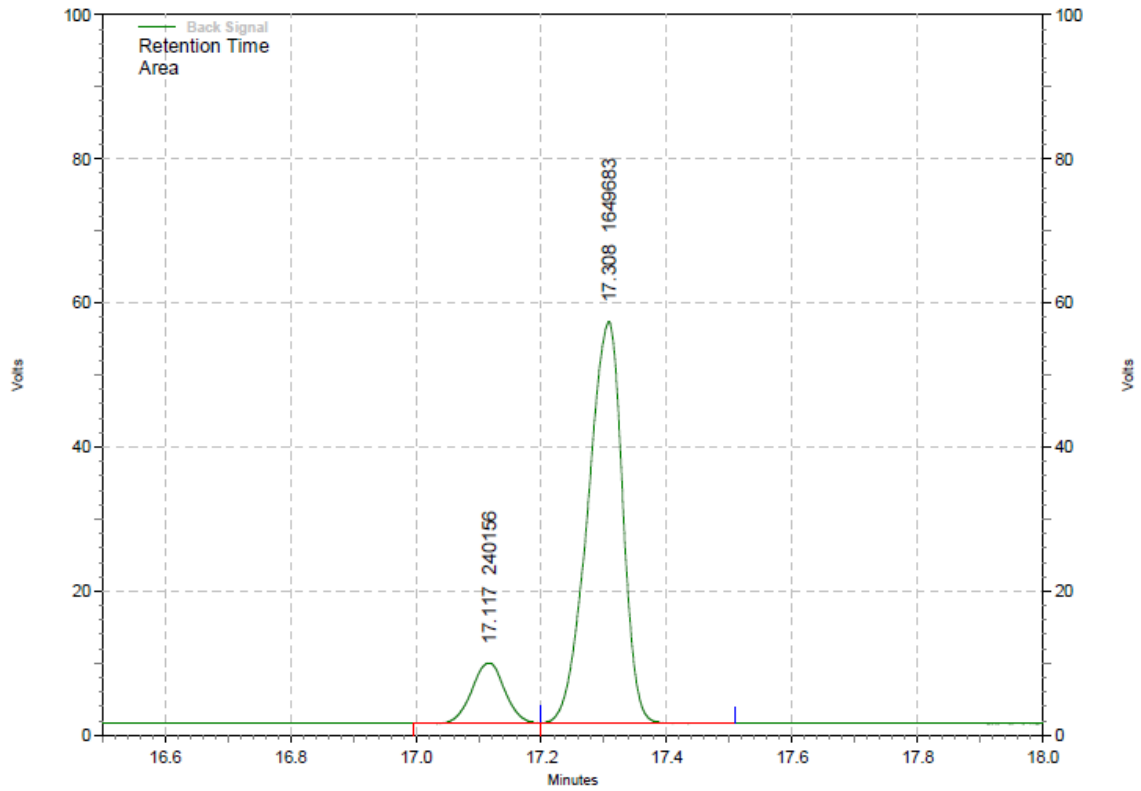


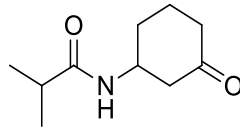
Rac



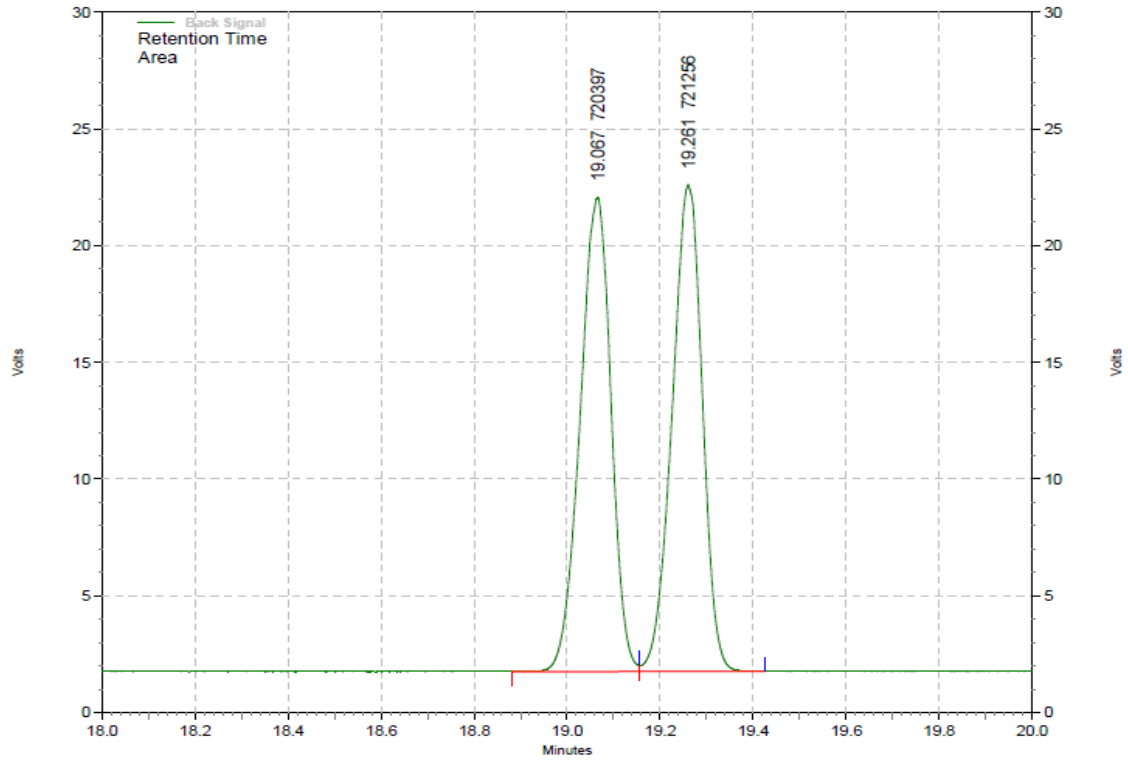
P8 (S,S)-(TIPSe₂cp)



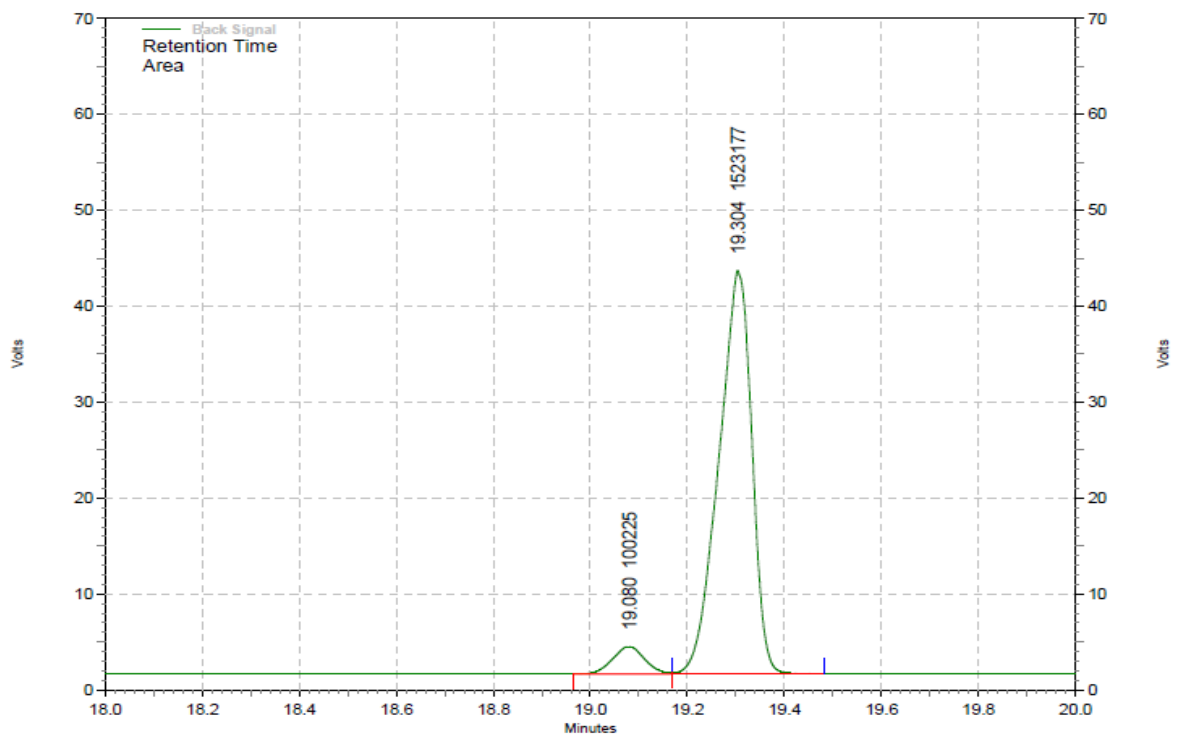
P8 (R_LR)-(TIPS^{mcp})P8 (S_LS)-(TIPS^{mcp})

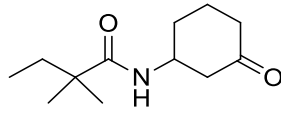
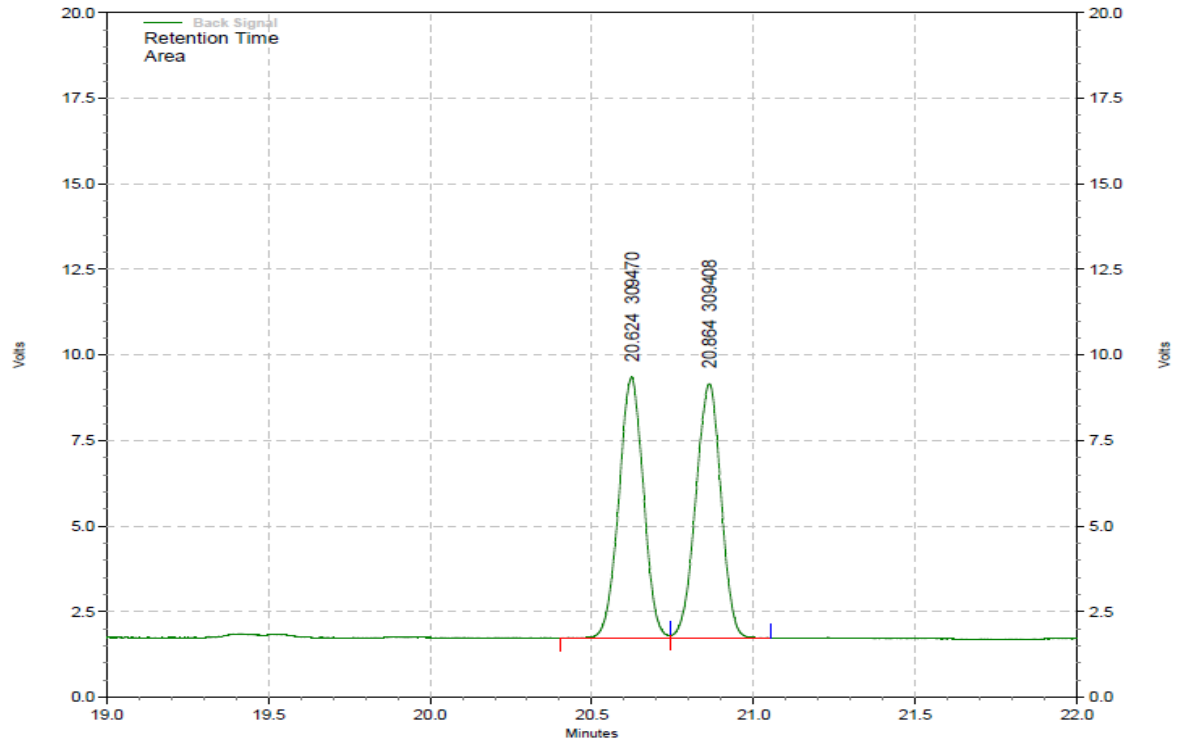
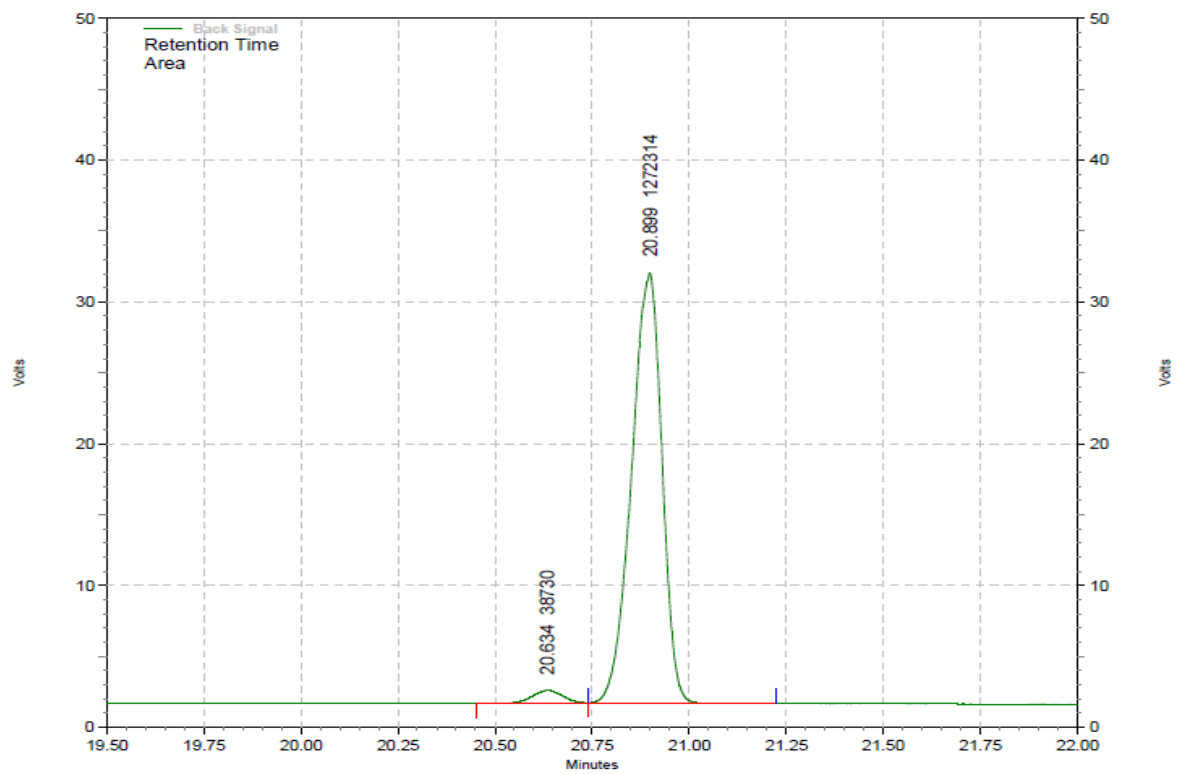


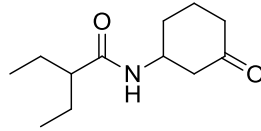
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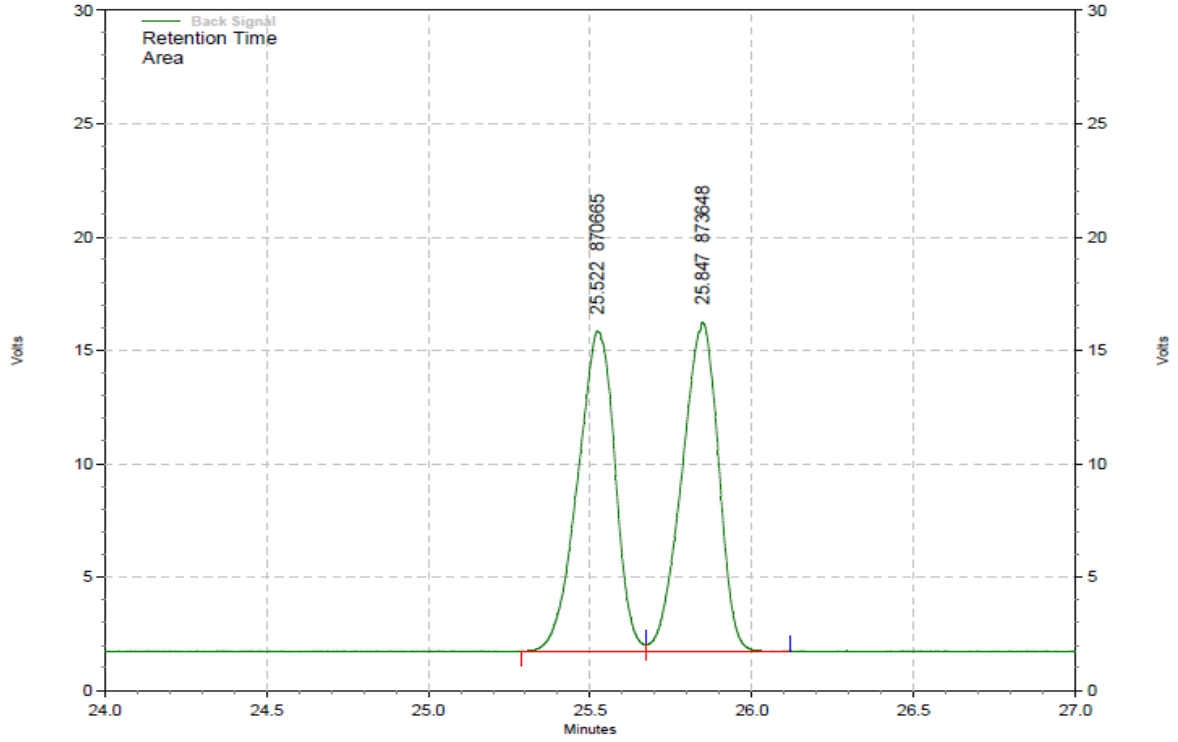
P9



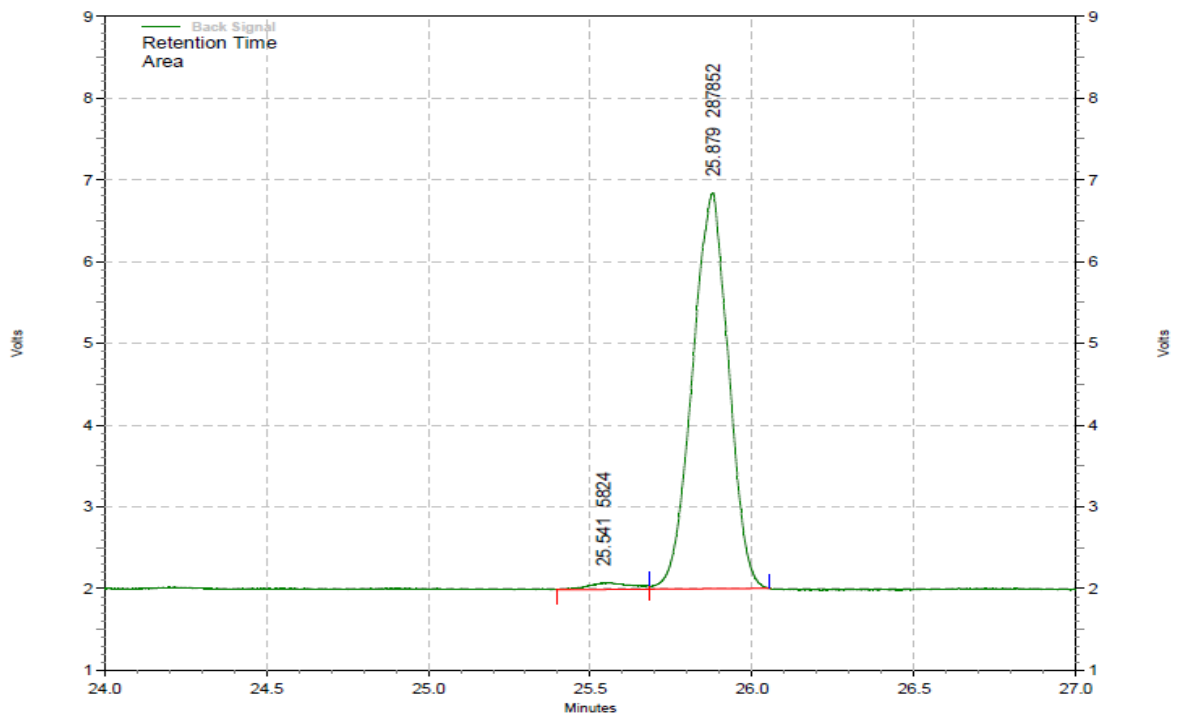
**Rac****P10**

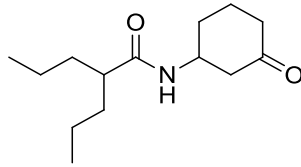
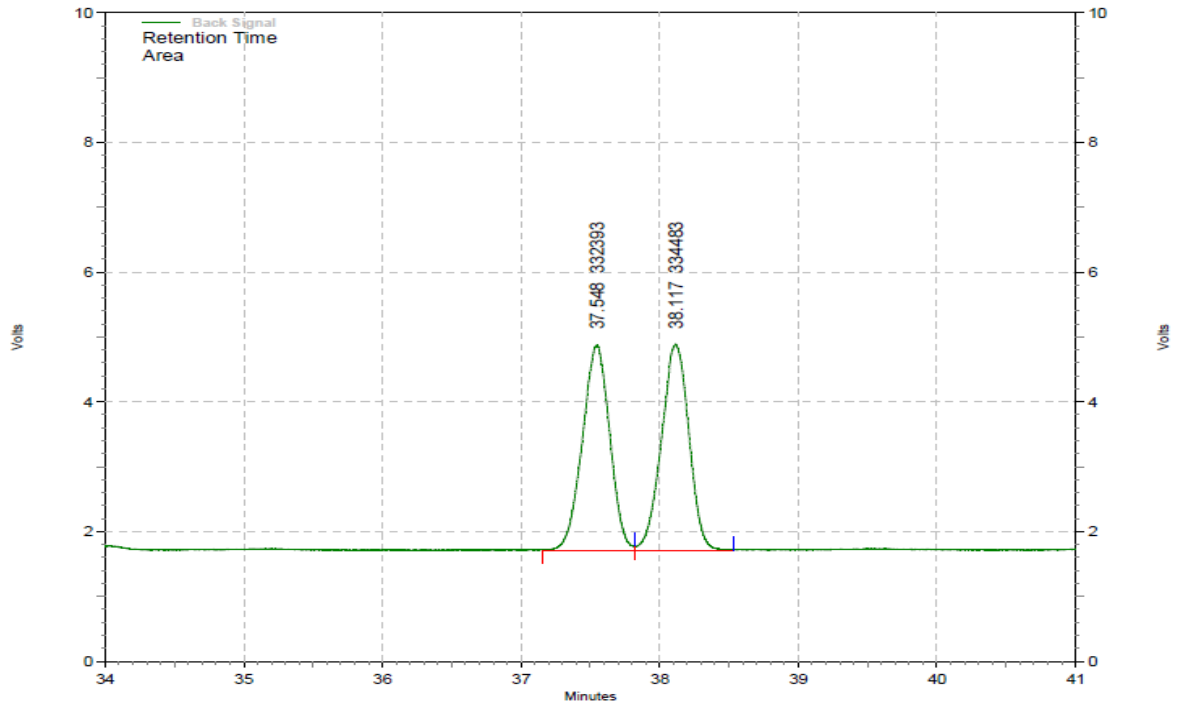
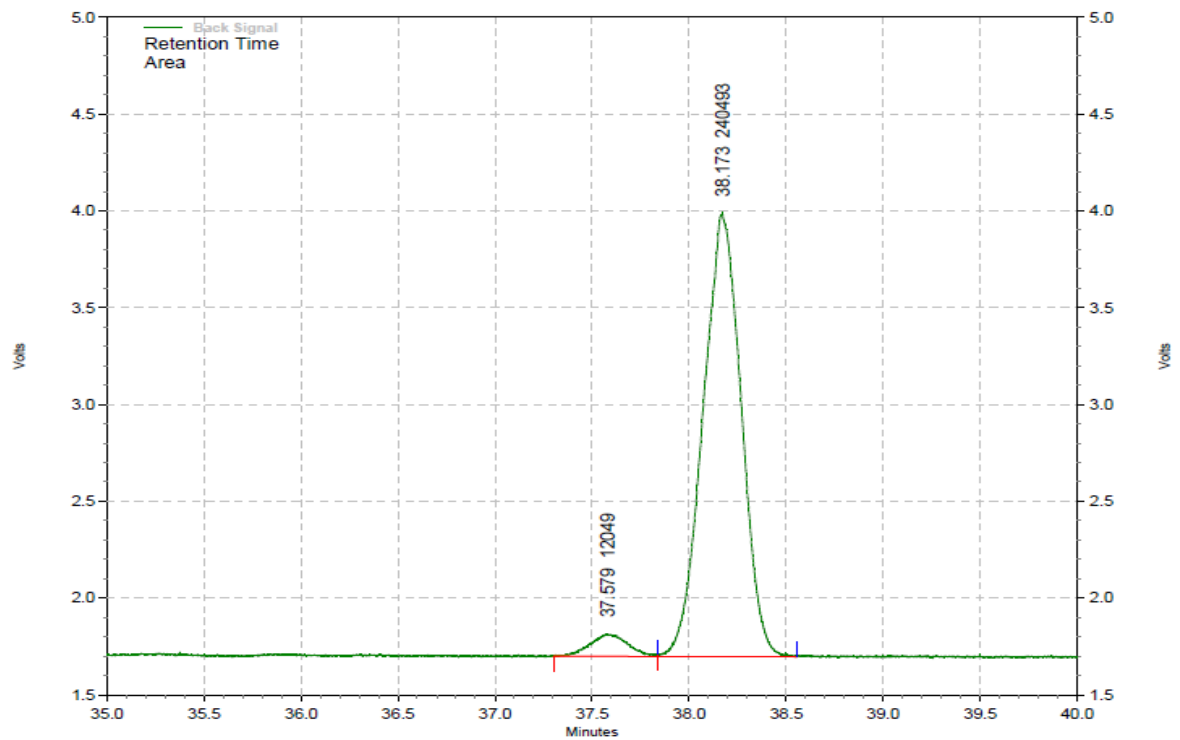


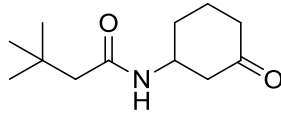
Rac



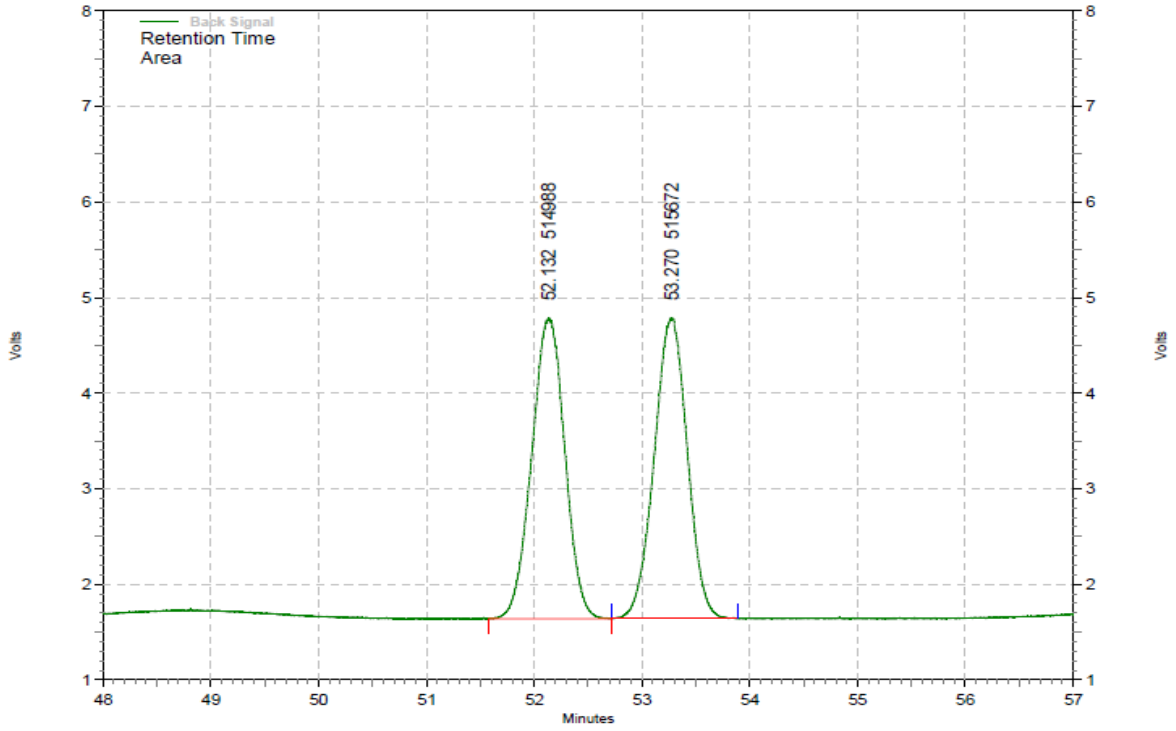
P11



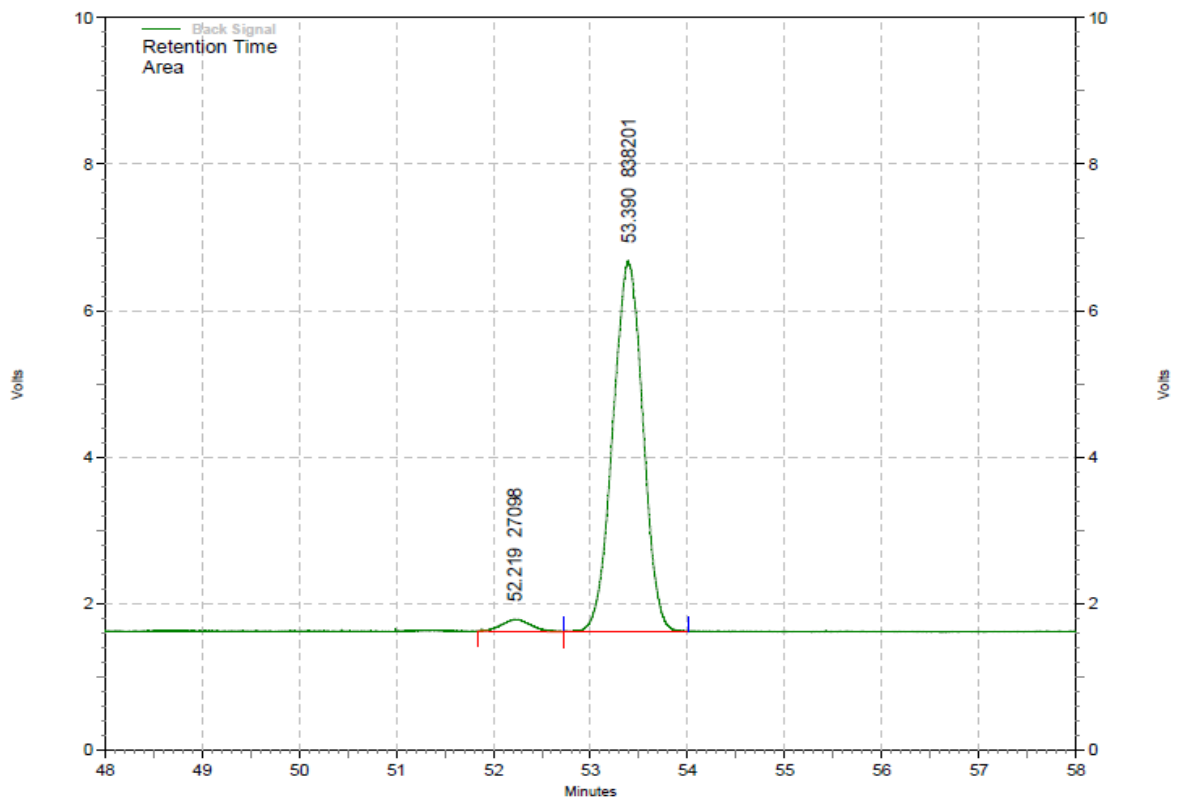
**Rac****P12**

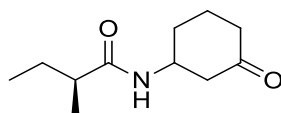
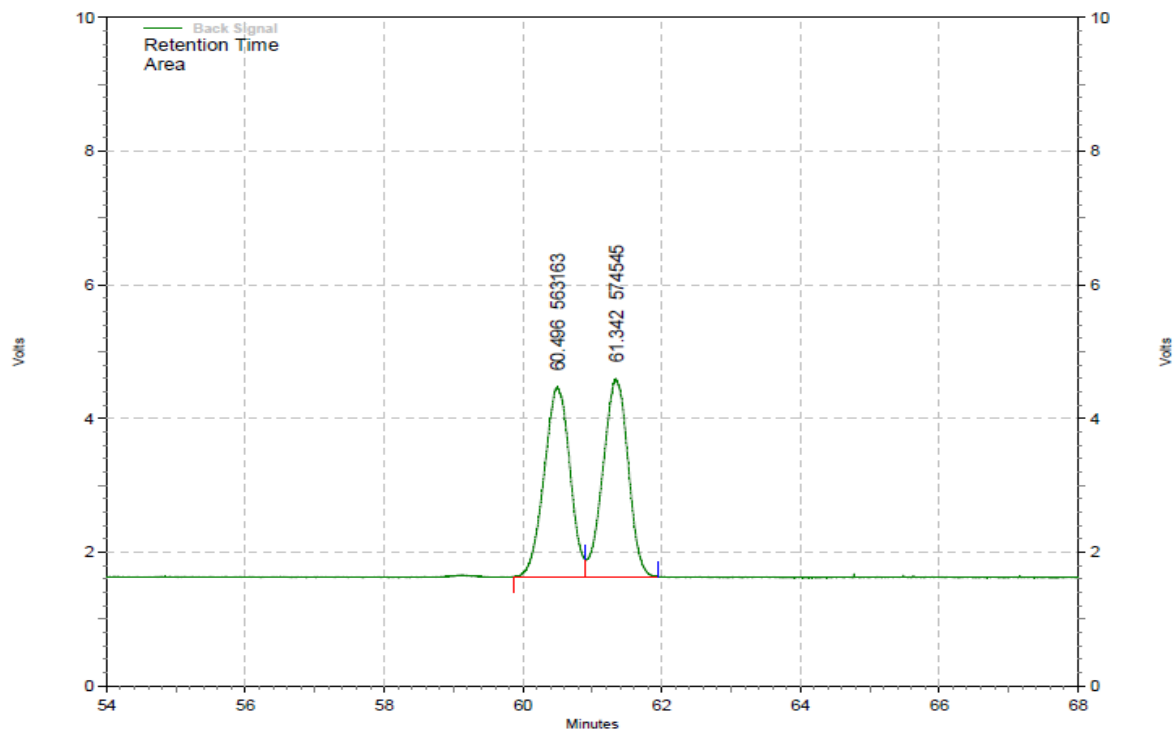
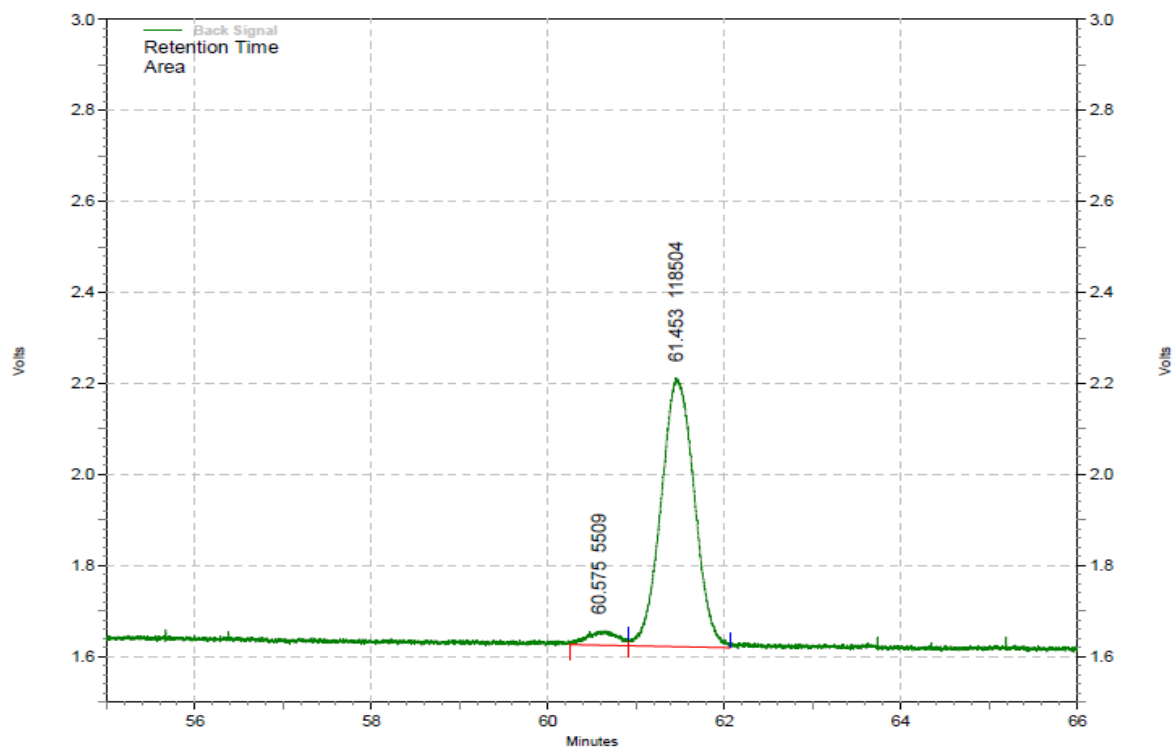


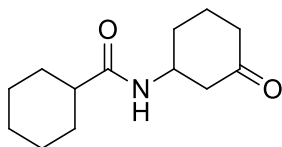
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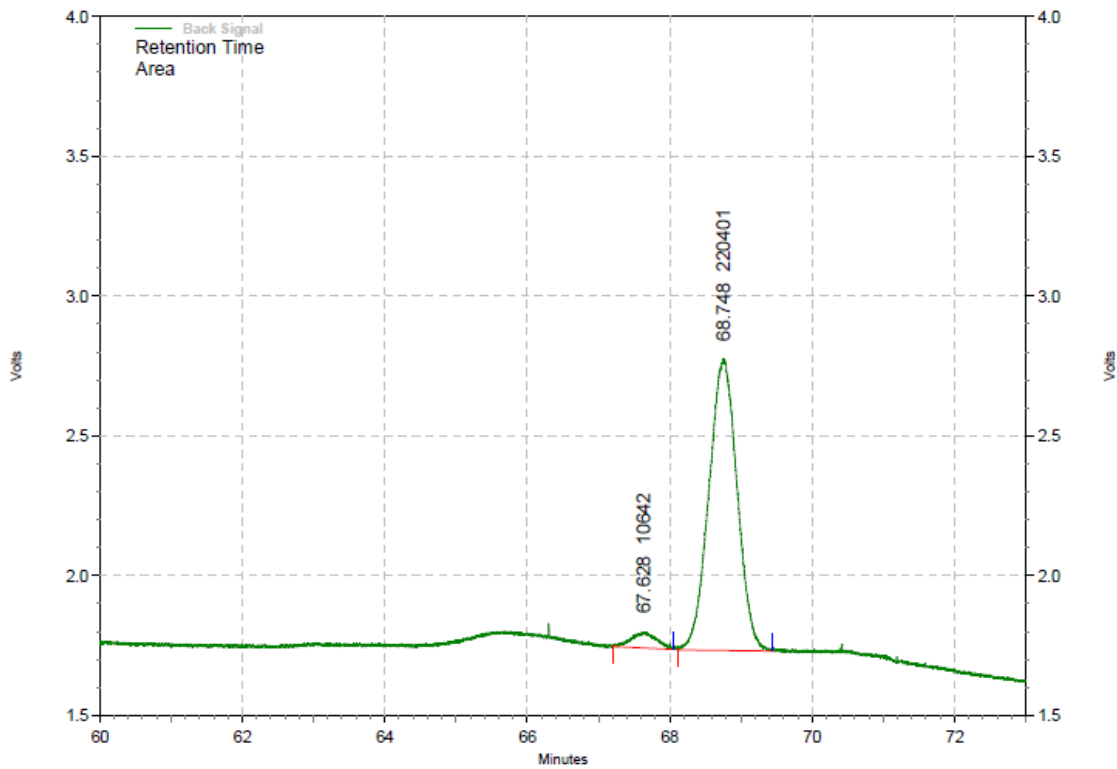
P13



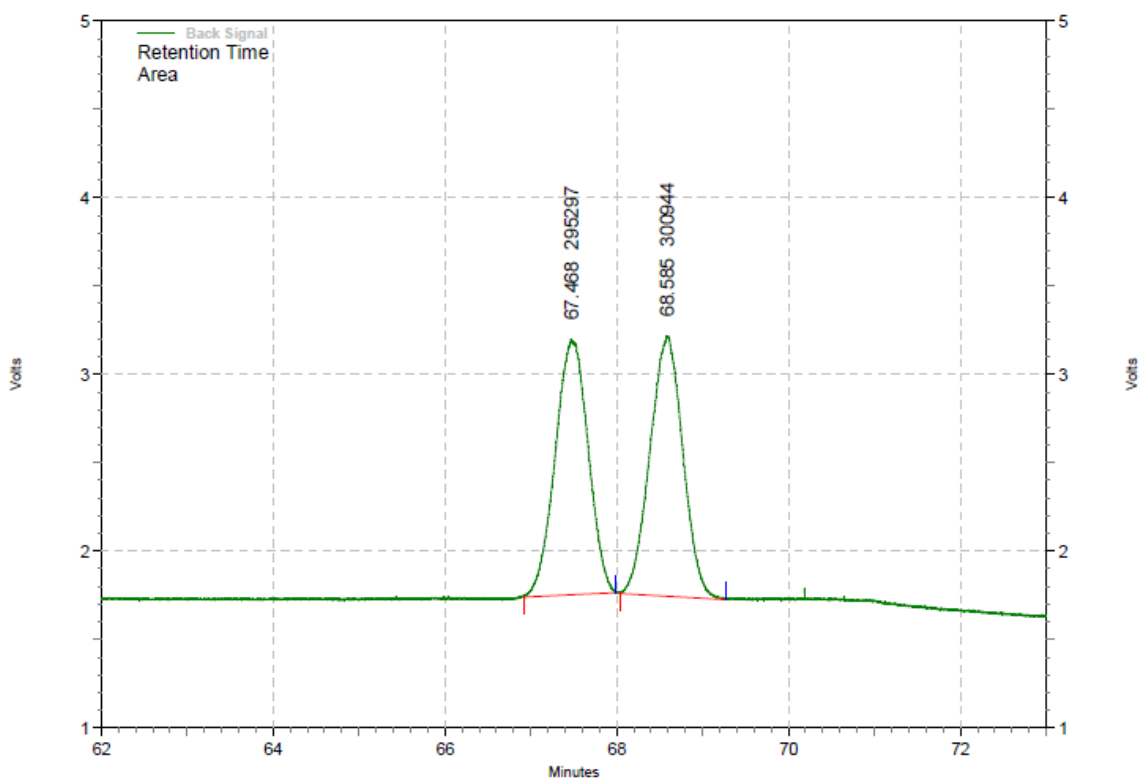
**Rac****P14**

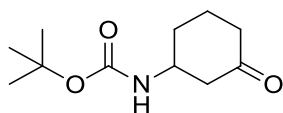


Rac

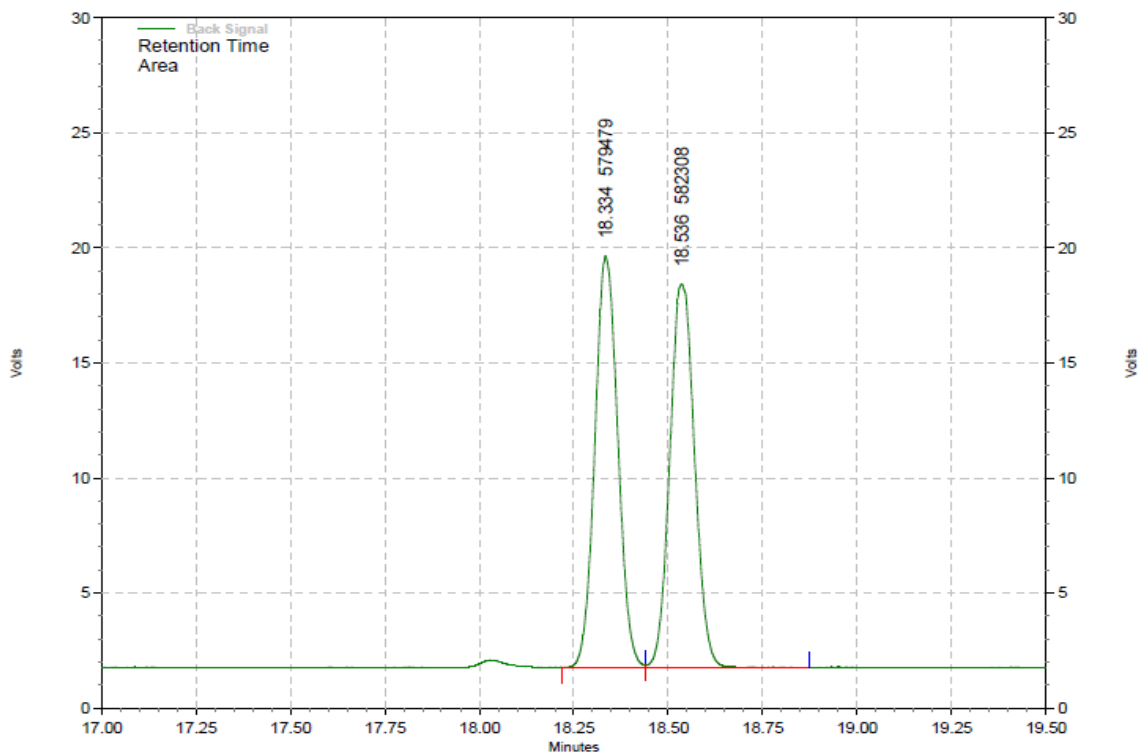


P15

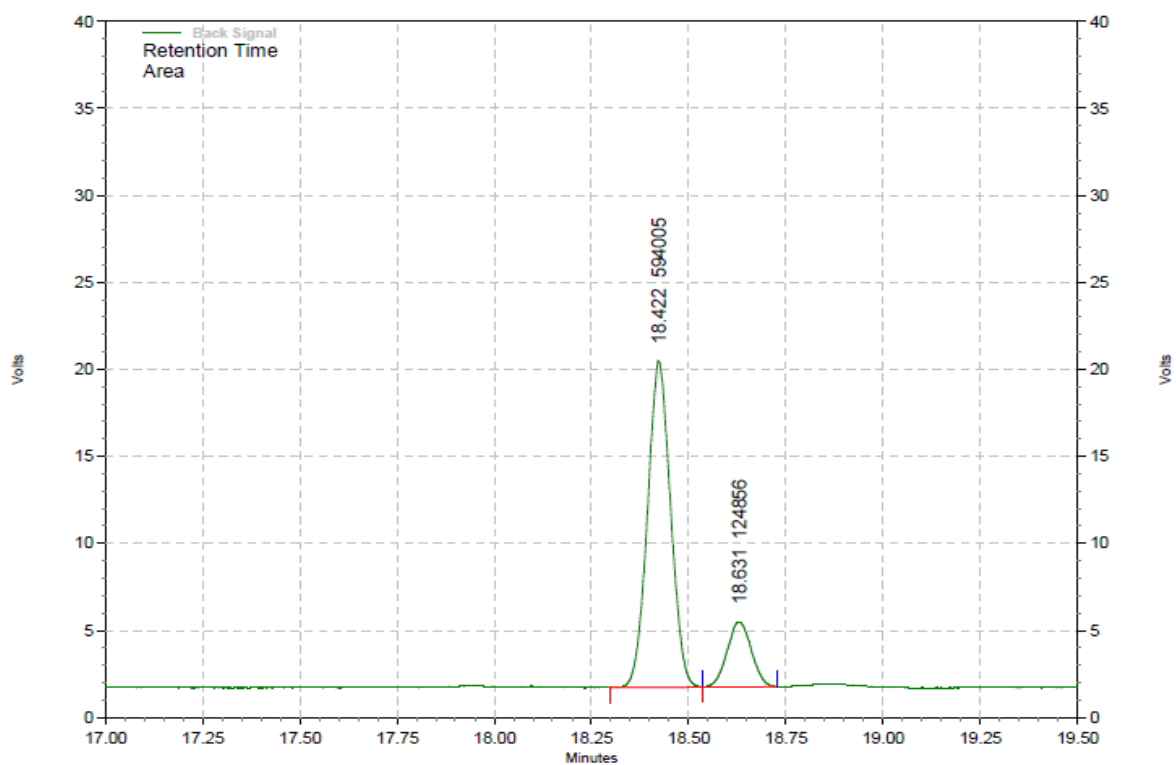


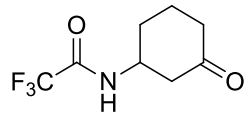


Rac

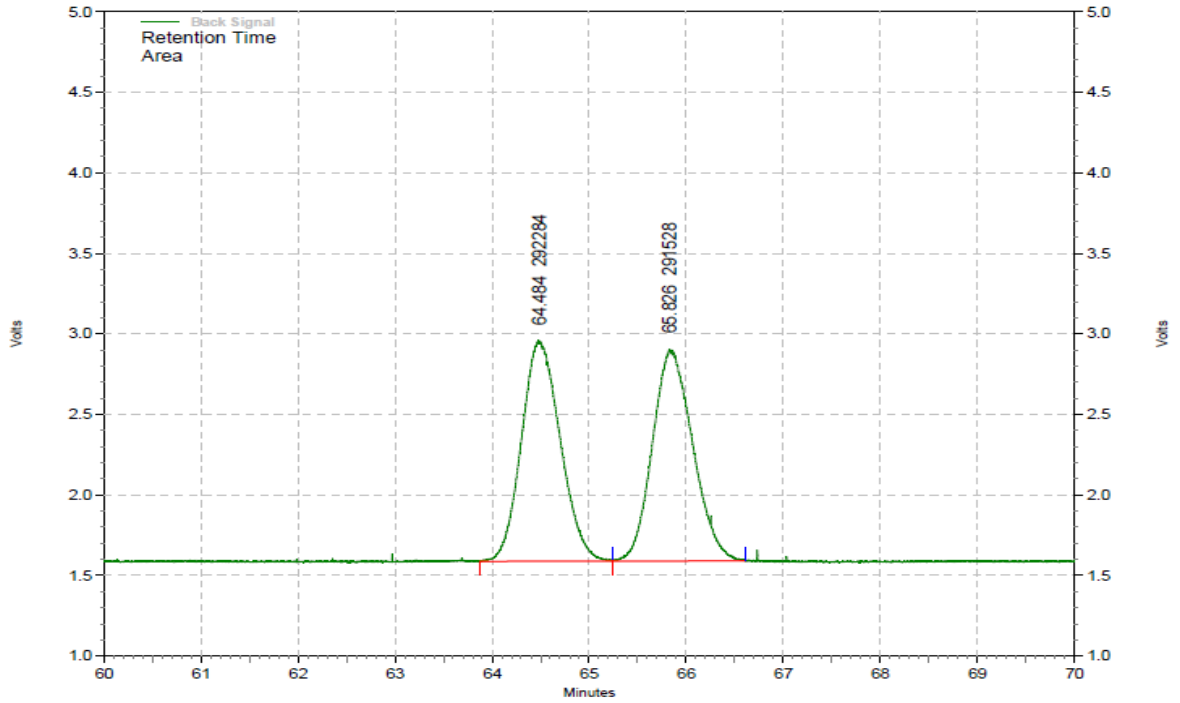


P16

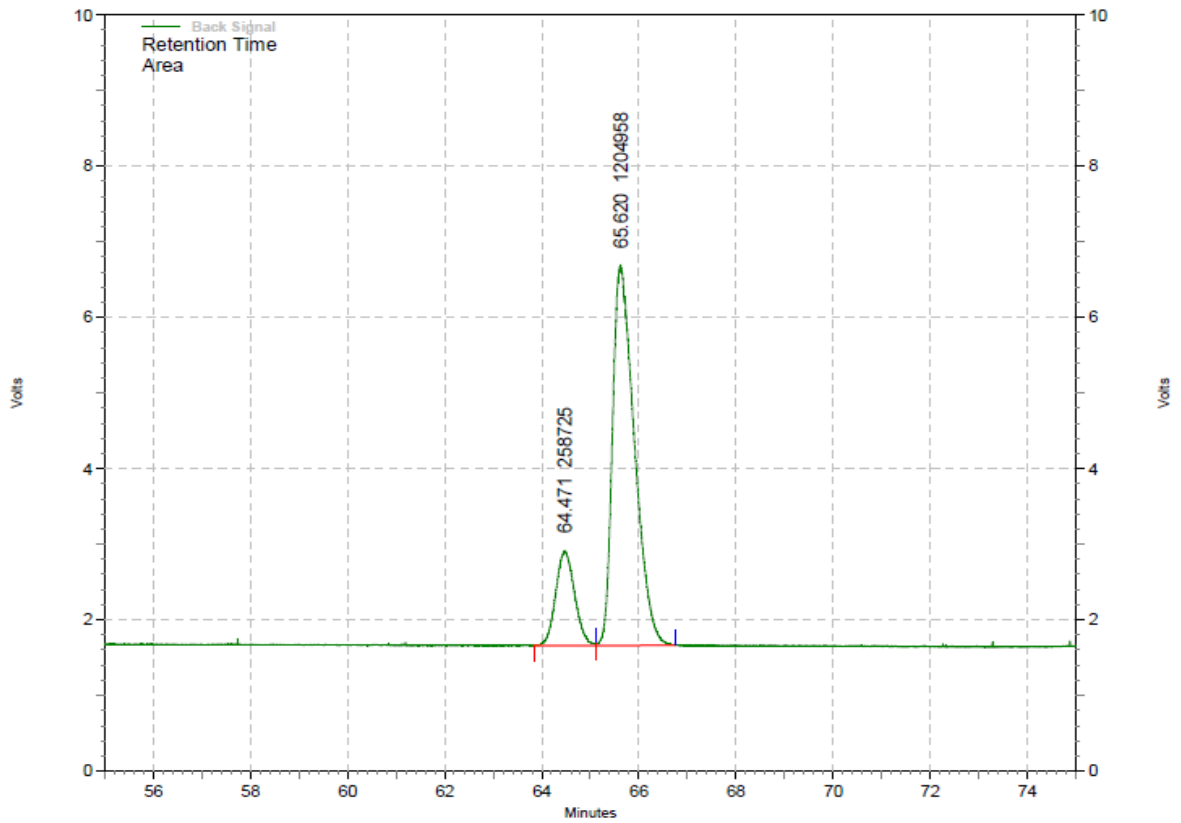




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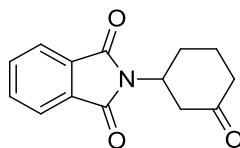


P17

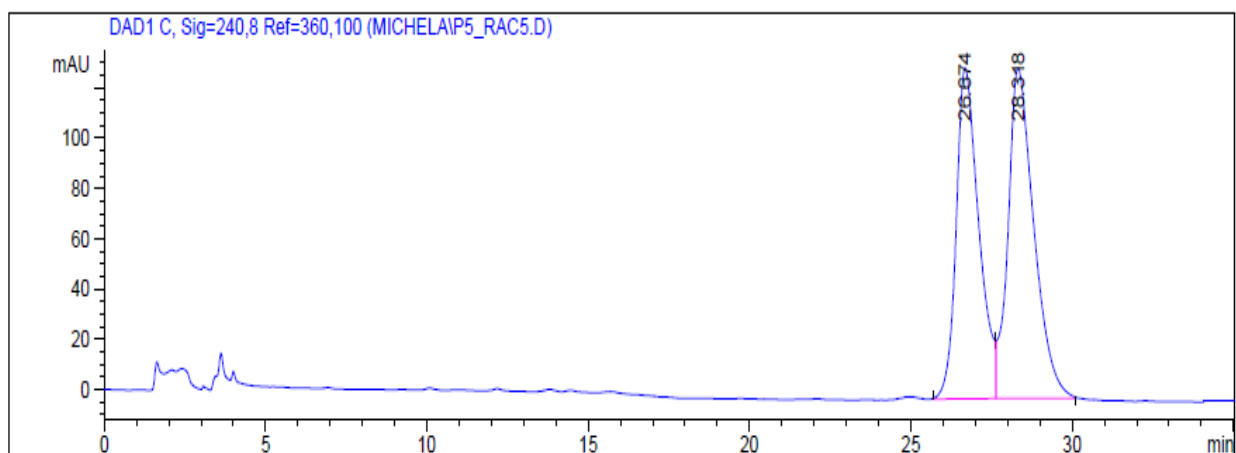


HPLC-separation conditions: Chiralpack IA 25°C, 240.8 nm, 88/12 hexane/*i*-PrOH, 1.0 mL/min;

r.t.(*minor*) = 26.166 min, r.t.(*major*) = 27.910 min.

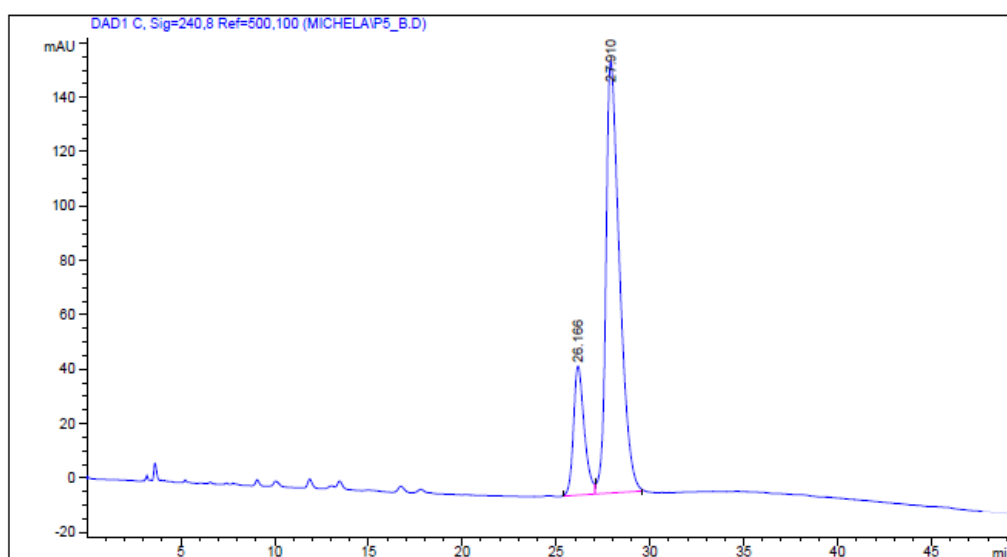


Rac

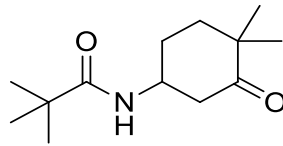


Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	26.674	1	BV	6397.72949	131.63432	46.6248
2	28.318	1	VB	7323.99268	131.42468	53.3752

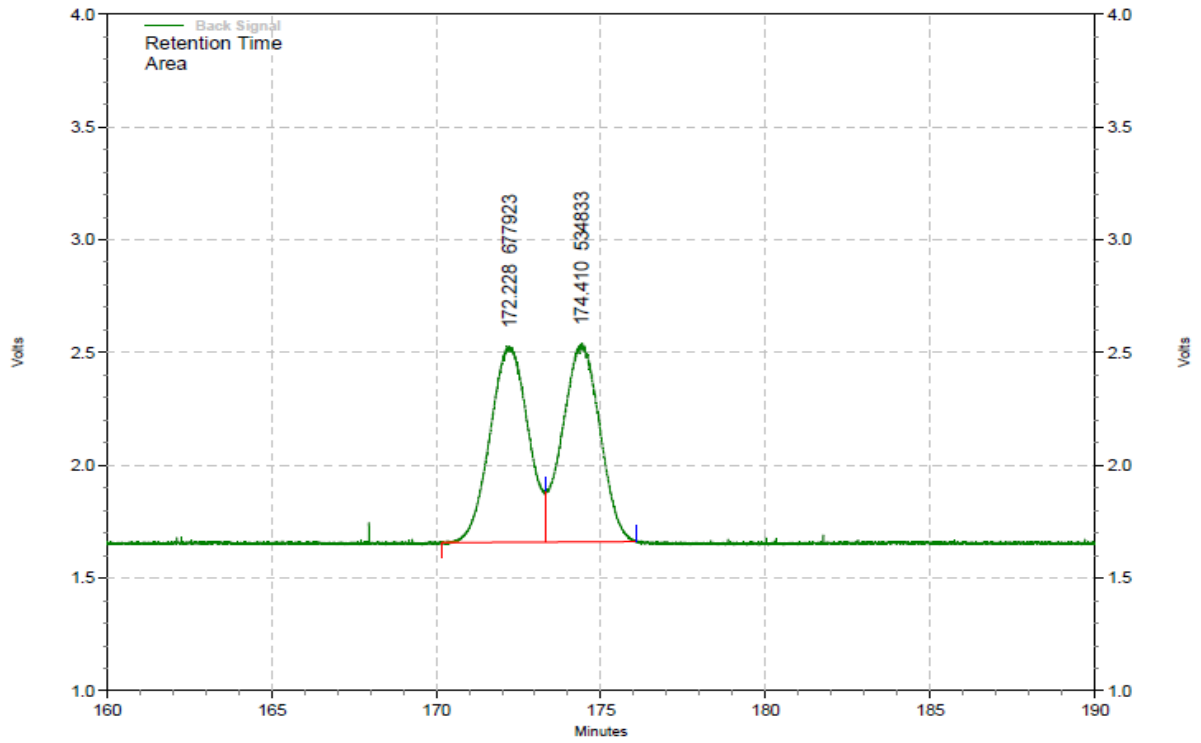
P18 (K₃)



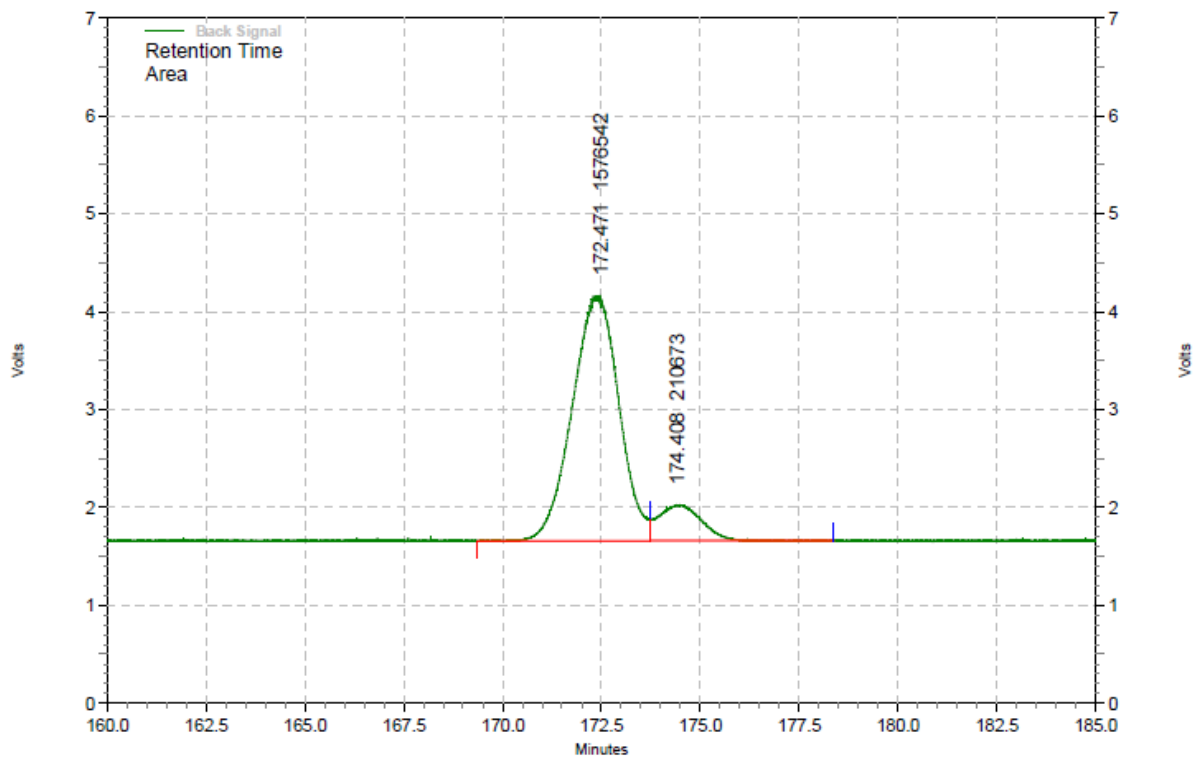
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.166	BV	0.5937	1895.62903	47.48789	19.1476
2	27.910	VB	0.7504	8004.47949	158.72383	80.8524

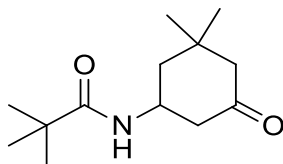
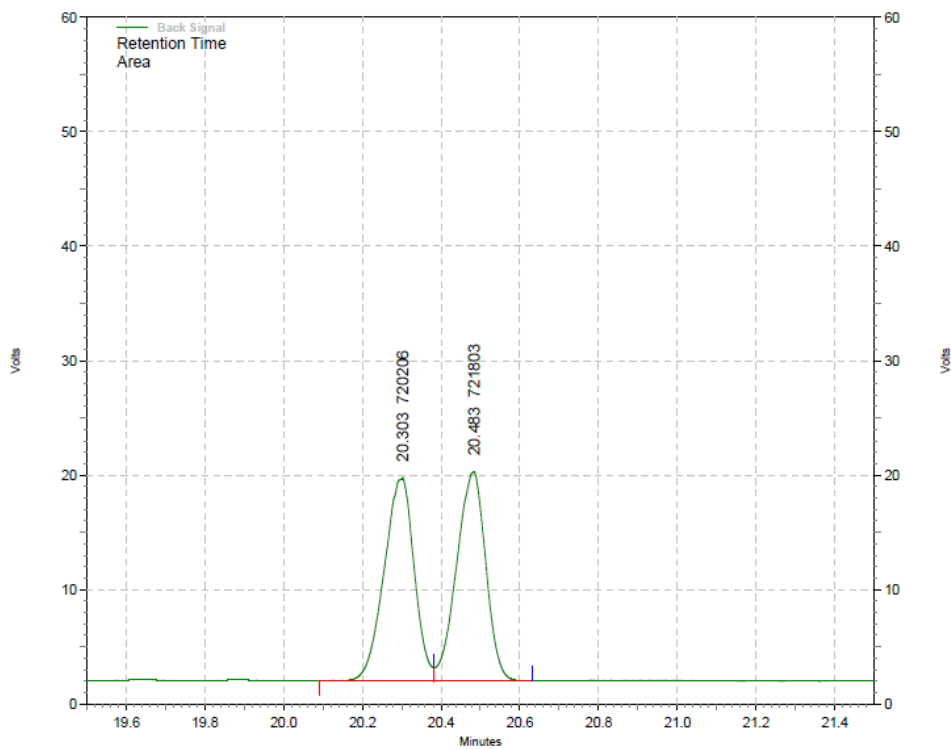
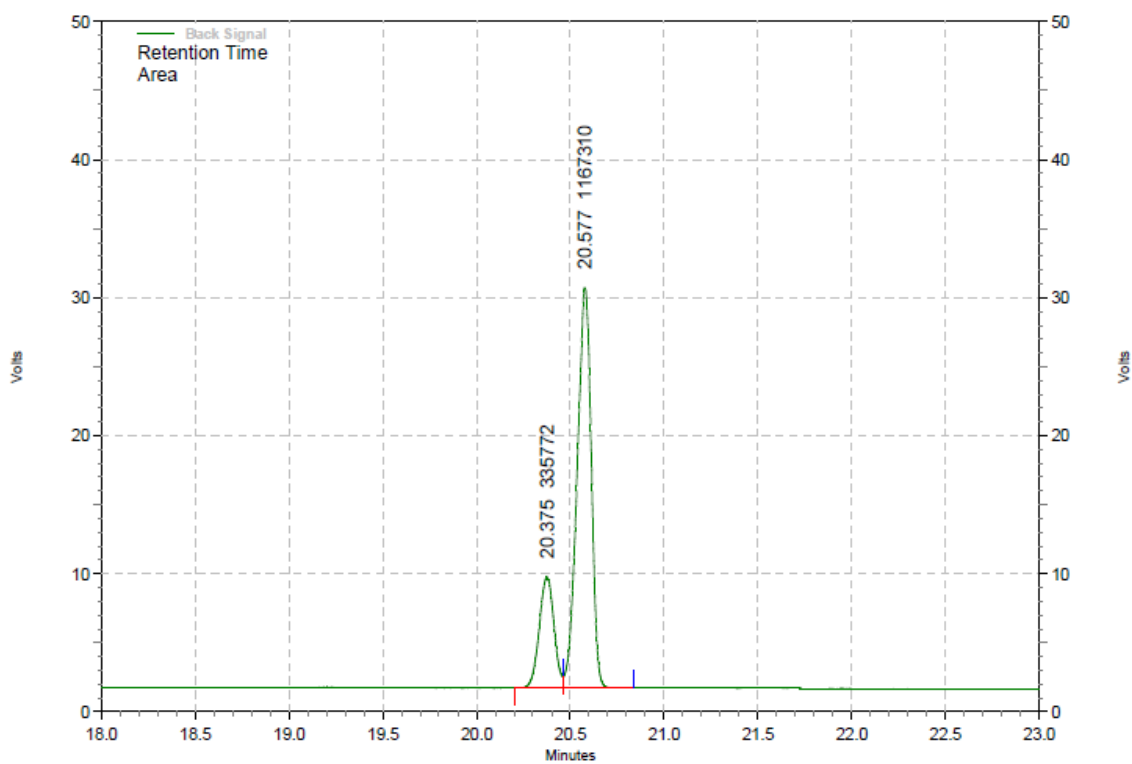


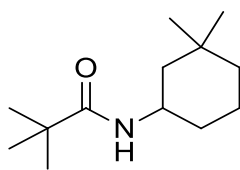
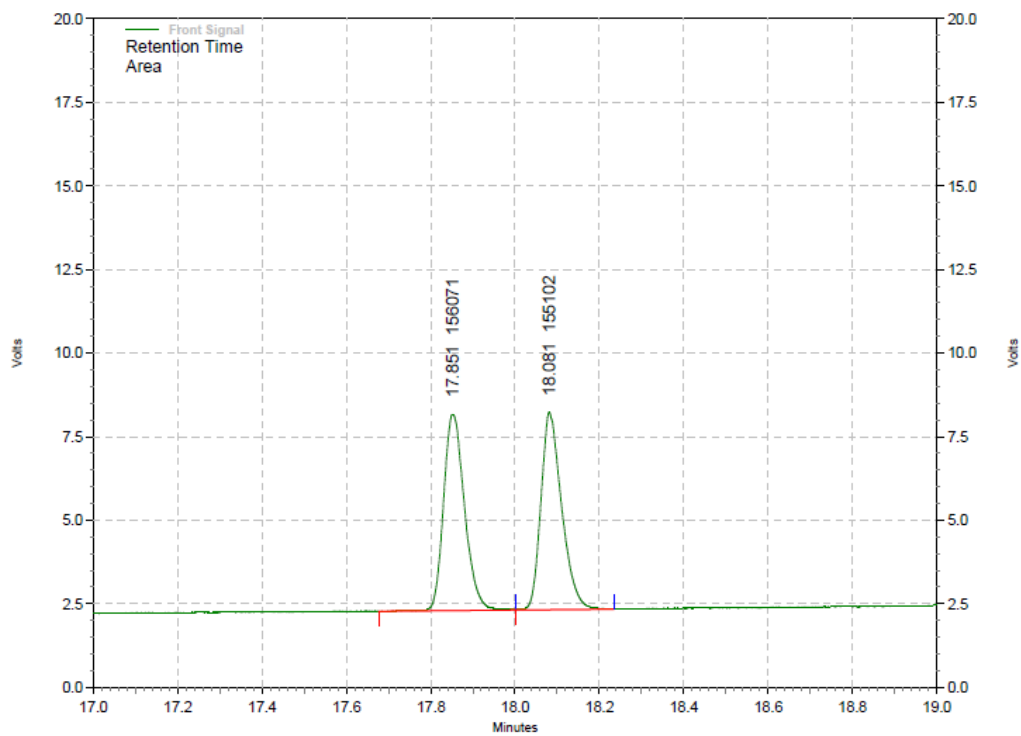
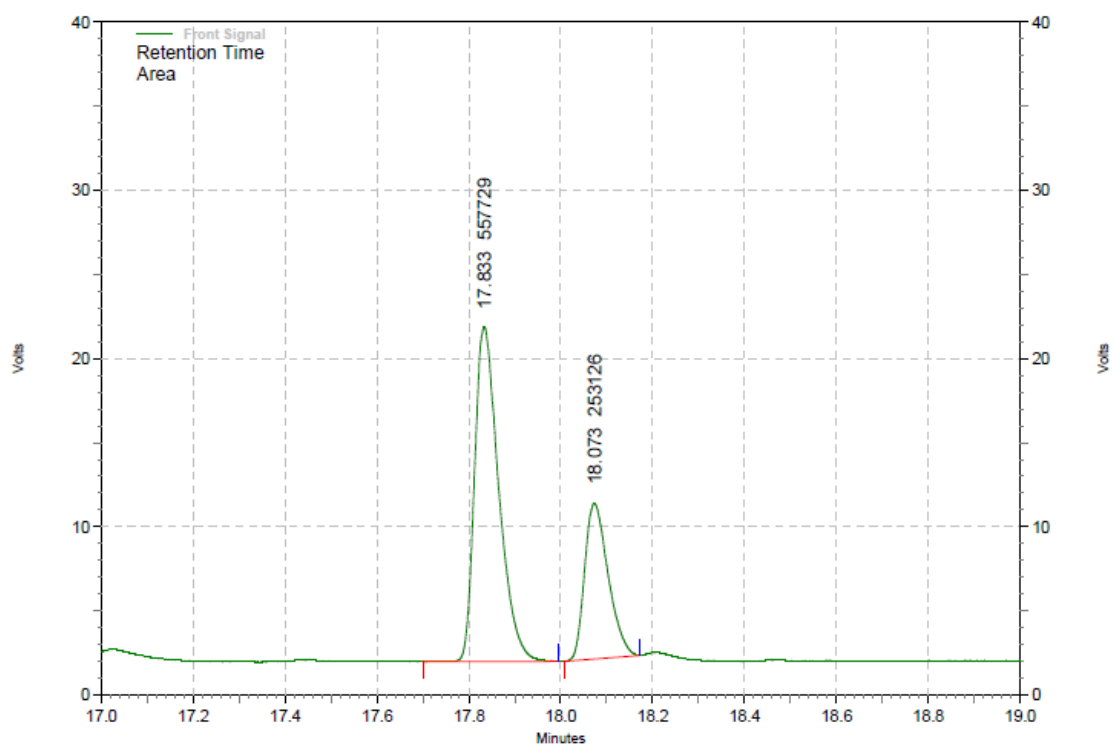
Rac

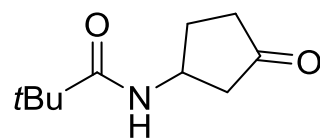
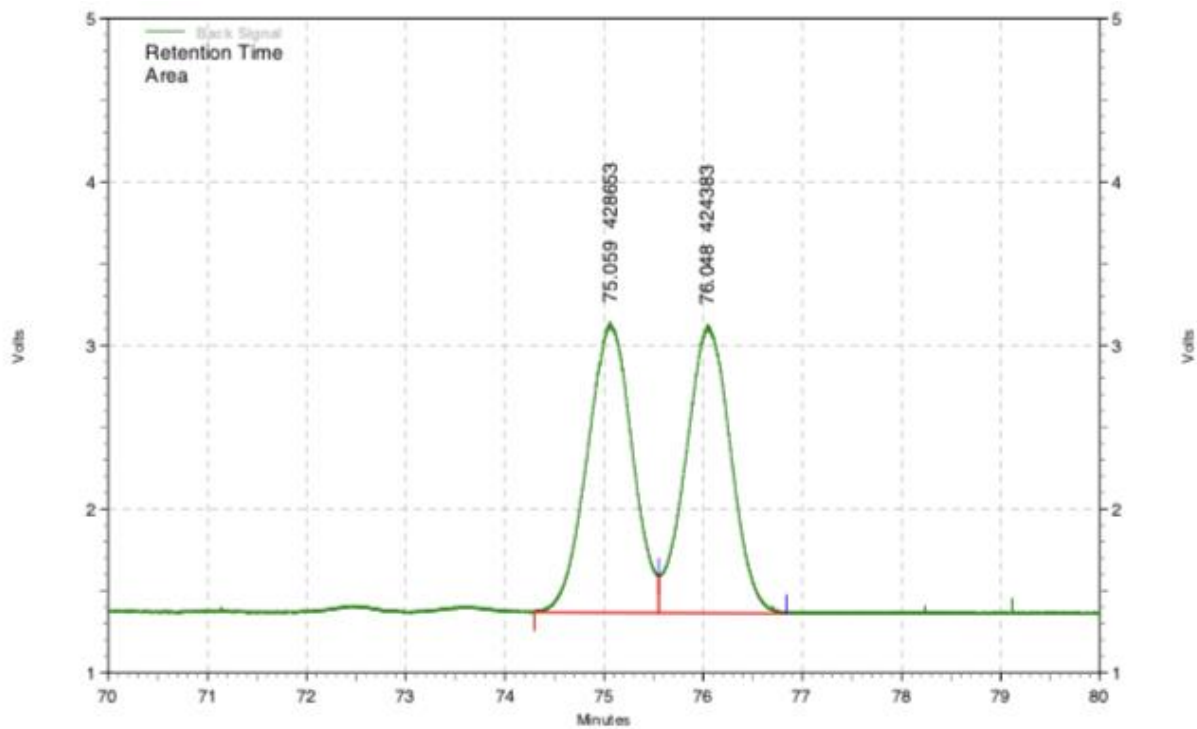
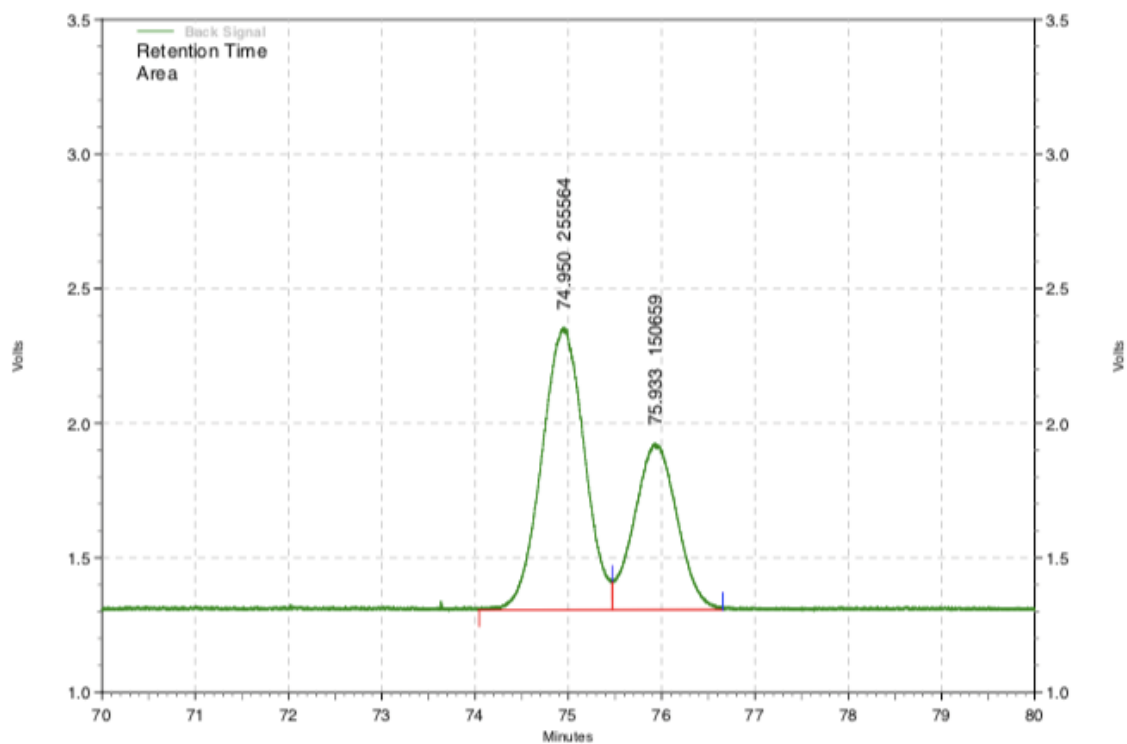


P20



**Rac****P21**

Chiral resolution of **S21**:**Rac****S21**

**Rac****P22**

DIGITAL EXPERIMENTAL SECTION

The following GC methods were used to separate the enantiomers:

For **P1, P3, P6:**

	Rate °C/min	Value °C	Hold Time min	Run Time min
▶ (Initial)		75	0.5	0.5
Ramp 1	10	180	1	12
Ramp 2	13	75	0	20.077
*				

For **P2:**

	Rate °C/min	Value °C	Hold Time min	Run Time min
▶ (Initial)		75	0.5	0.5
Ramp 1	5	180	10	31.5
Ramp 2	13	75	0	39.577
*				

For **P4, P5:**

	Rate °C/min	Value °C	Hold Time min	Run Time min
▶ (Initial)		75	0.5	0.5
Ramp 1	1	100	40	65.5
Ramp 2	10	180	3	76.5
Ramp 3	13	75	0	84.577
*				

For **P7, P8, P9, P10, P12, P16, P21:**

	Rate °C/min	Value °C	Hold Time min	Run Time min
▶ (Initial)		75	0.5	0.5
Ramp 1	10	180	10	21
Ramp 2	13	75	0	29.077
*				

For **P11, P17, P22:**

	Rate °C/min	Value °C	Hold Time min	Run Time min
▶ (Initial)		75	0.5	0.5
Ramp 1	10	130	80	86
*				

For **P13:**

	Rate °C/min	Value °C	Hold Time min	Run Time min
▶ (Initial)		75	0	0
Ramp 1	10	160	60	68.5
Ramp 2	13	75	0	75.038
*				

For **P14**:

	Rate °C/min	Value °C	Hold Time min	Run Time min
▶ (Initial)		75	0	0
Ramp 1	10	150	60	67.5
Ramp 2	13	75	0	73.269
*				

For **P15**:

	Rate °C/min	Value °C	Hold Time min	Run Time min
▶ (Initial)		75	0	0
Ramp 1	10	180	60	70.5
Ramp 2	13	75	0	78.577
*				

For **P20**:

	Rate °C/min	Value °C	Hold Time min	Run Time min
▶ (Initial)		75	0.5	0.5
Ramp 1	10	120	200	205
Ramp 2	13	75	0	208.46
*				

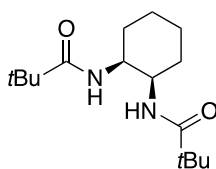
For **S21**:

	Rate °C/min	Value °C	Hold Time min	Run Time min
▶ (Initial)		75	0	0
Ramp 1	5	170	10	29
Ramp 2	5	75	0	48
*				

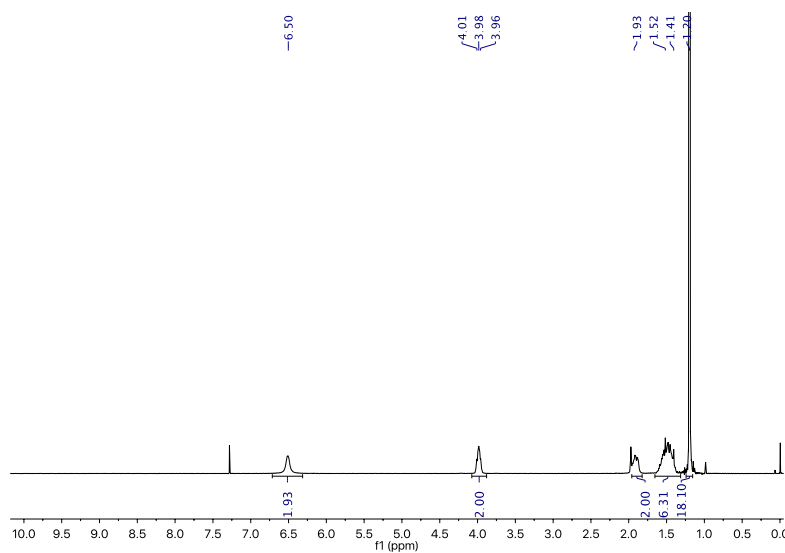
Experimental Section: Chapter VI.3

Aliphatic C–H Bonds Oxidations with Hydrogen Peroxide Catalyzed by Manganese Complexes: Directing Selectivity through Torsional Effects

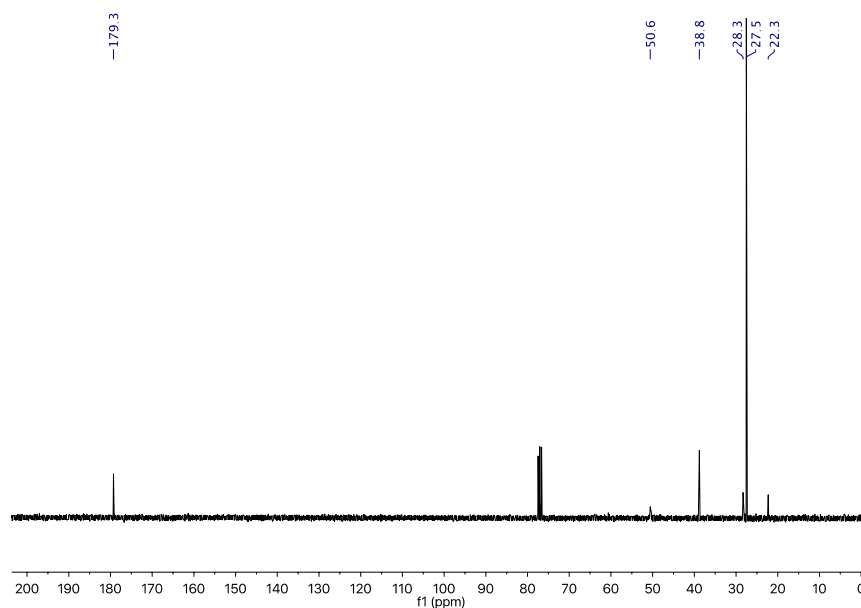
A1 ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of substrates

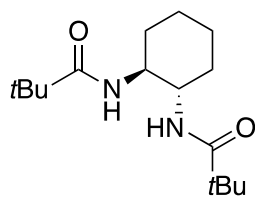
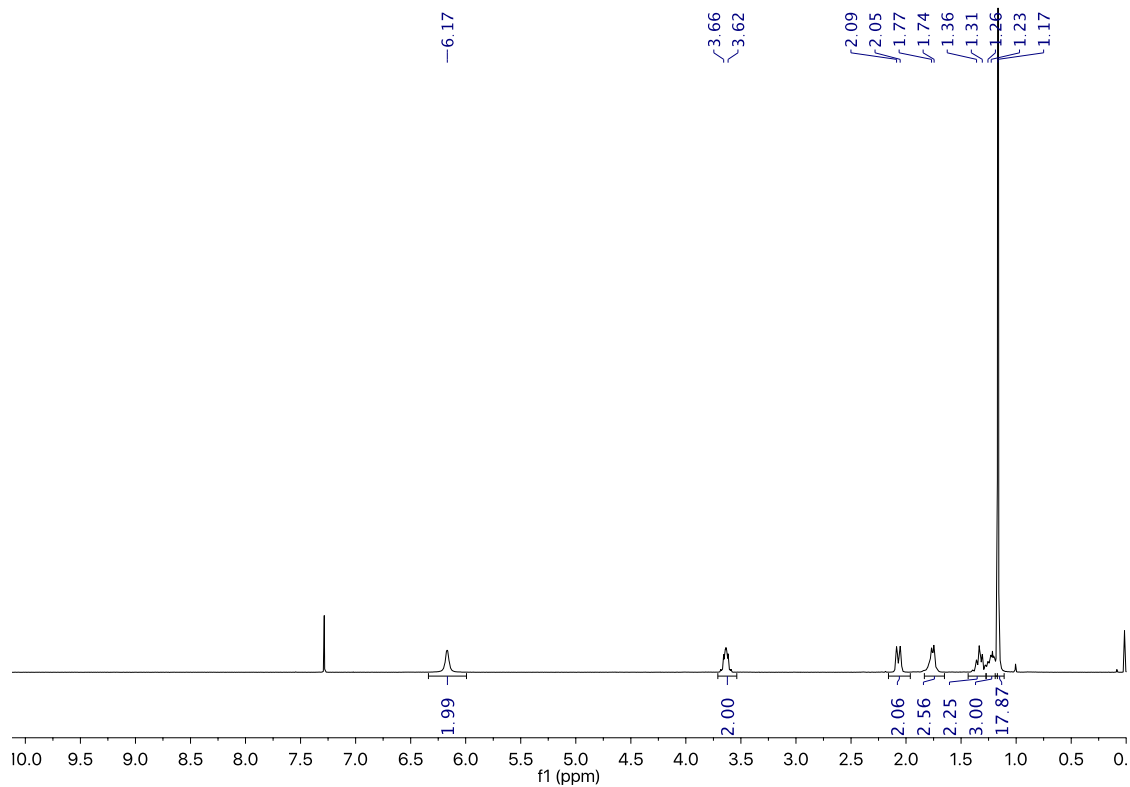
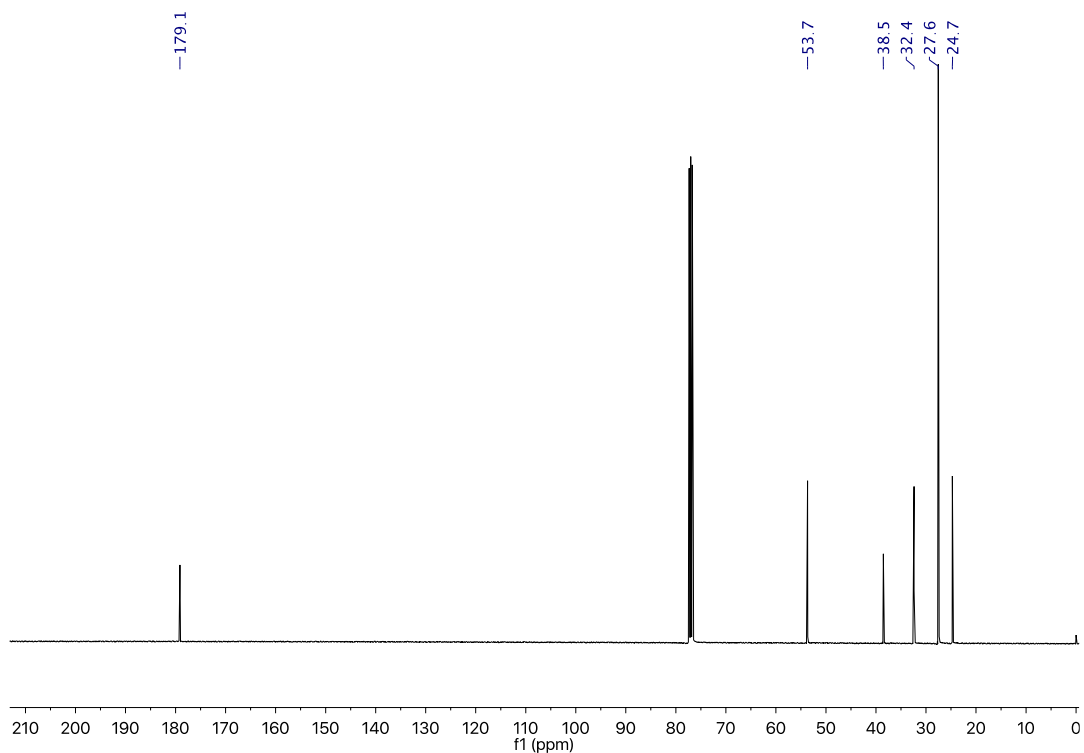


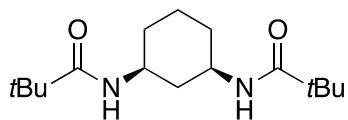
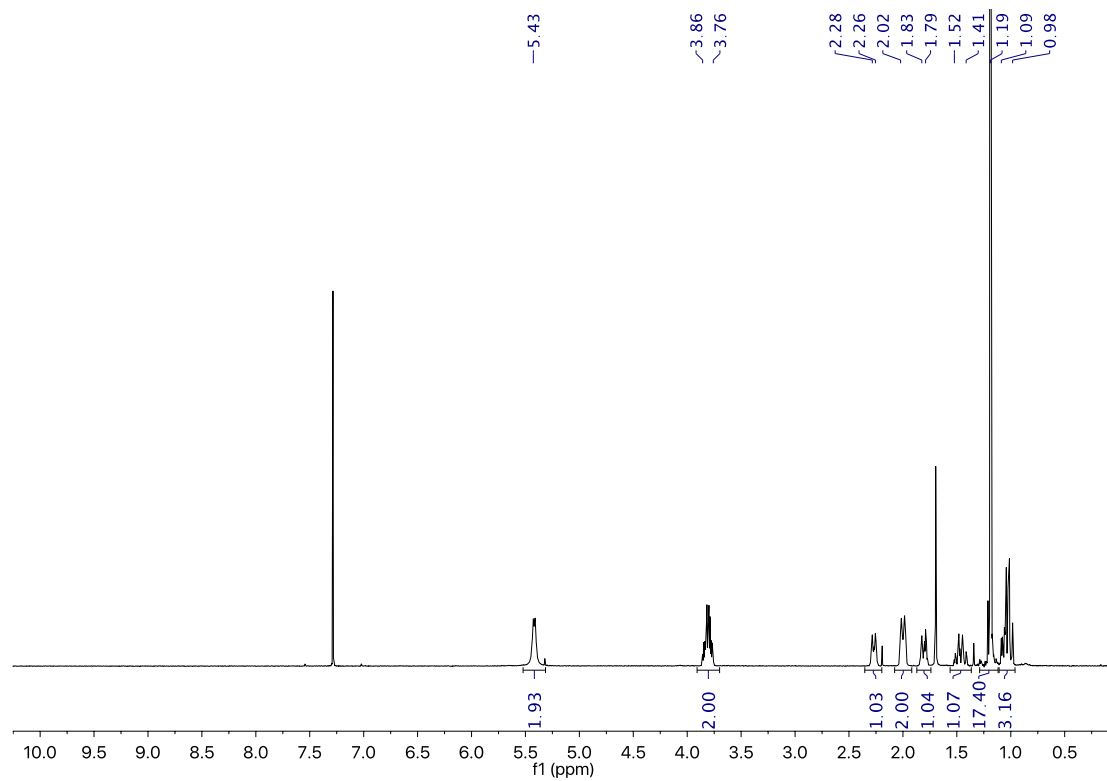
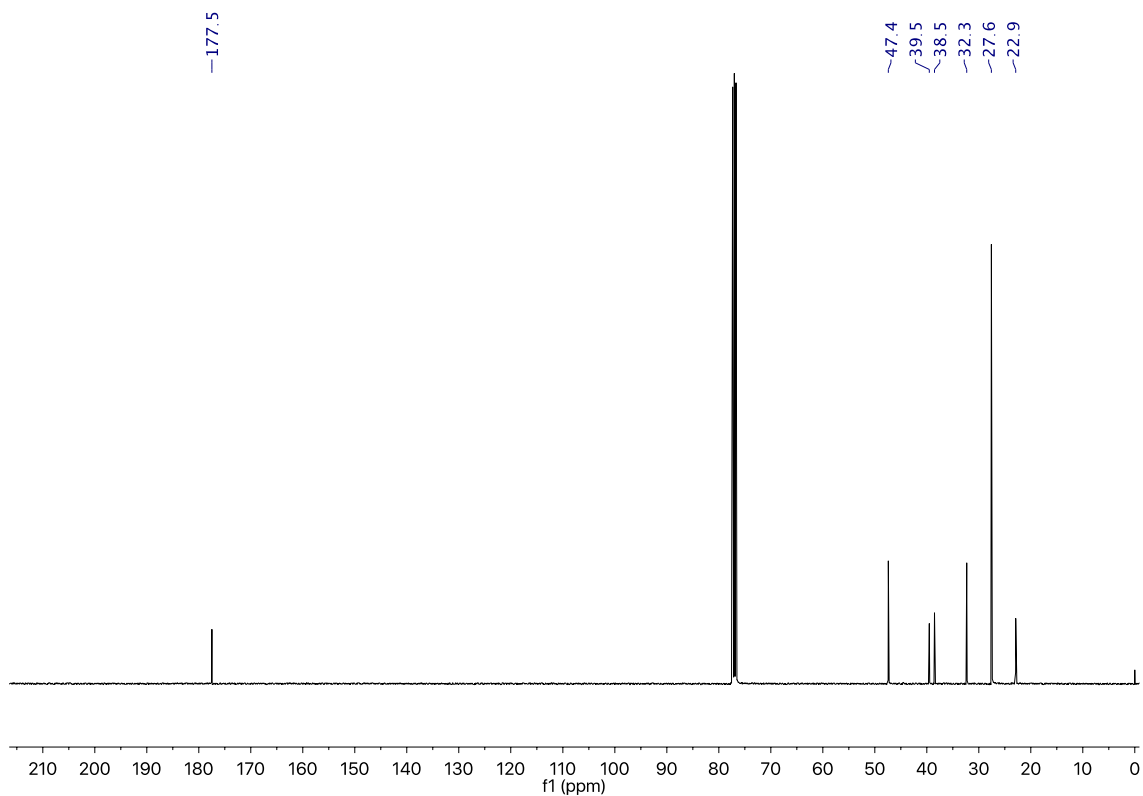
^1H -NMR of *cis*-1 in CDCl_3

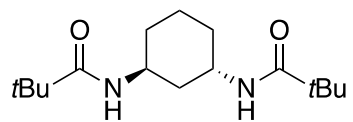
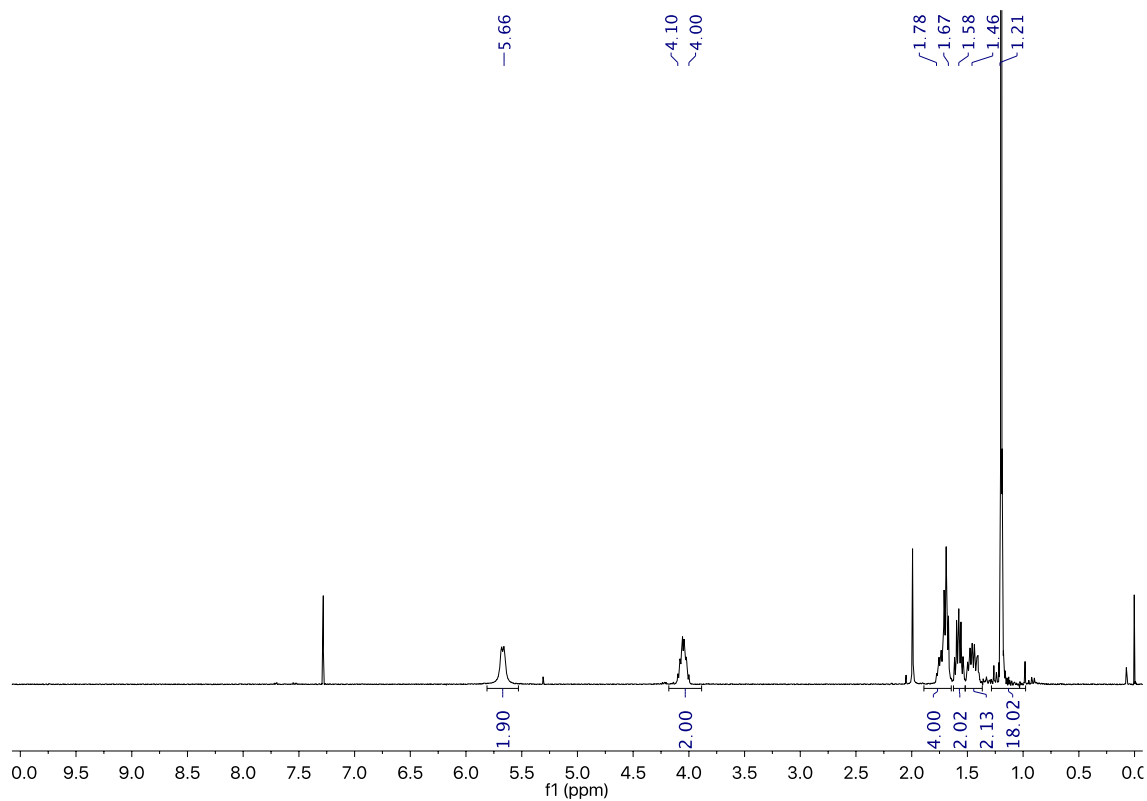
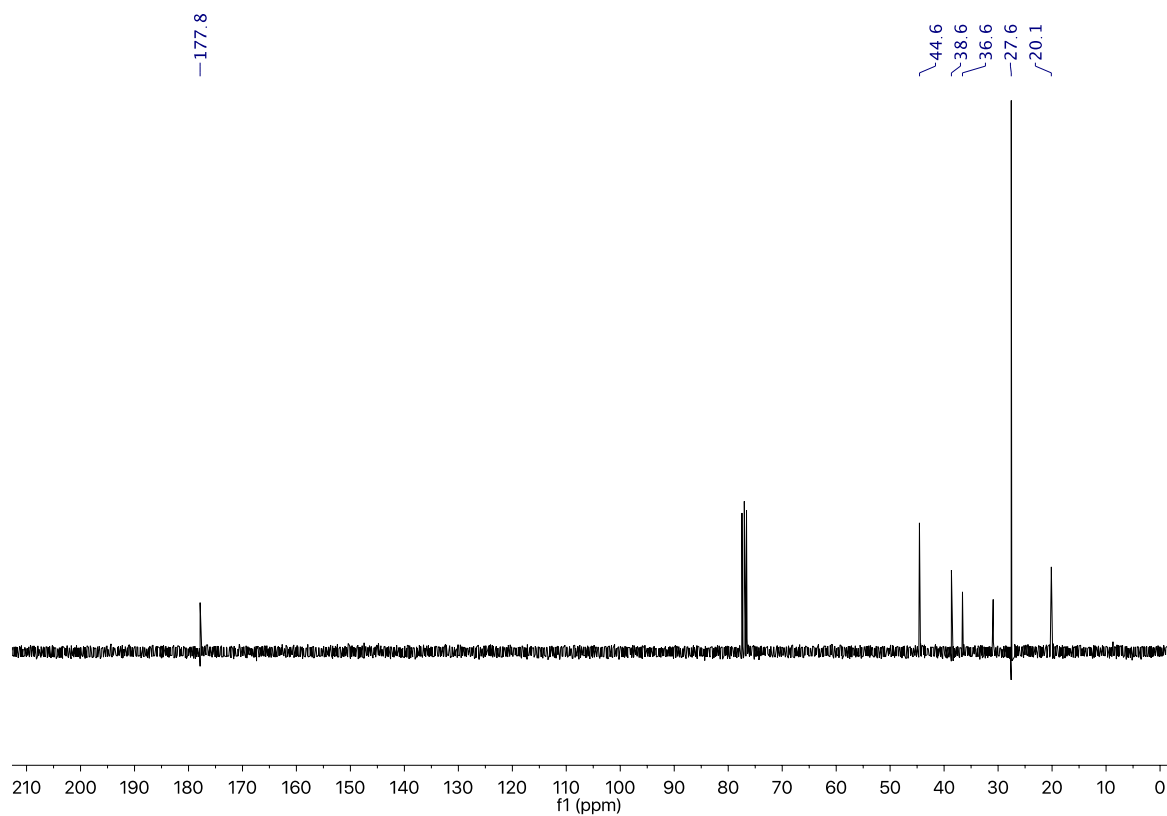


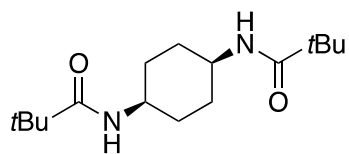
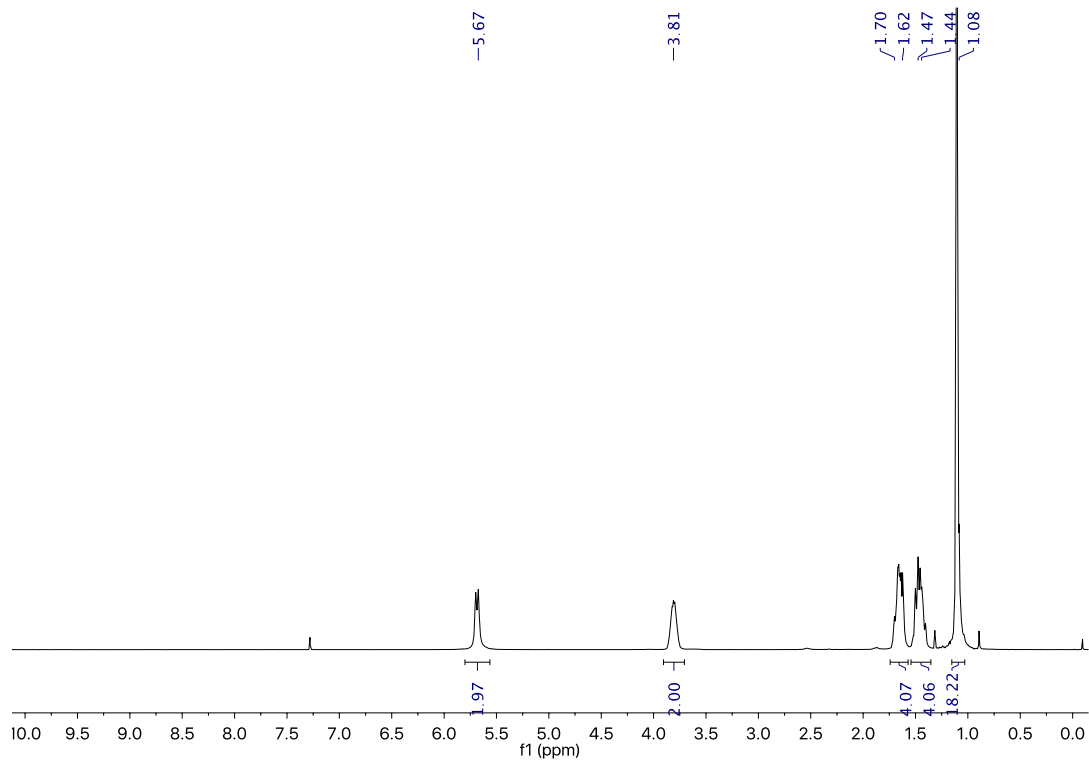
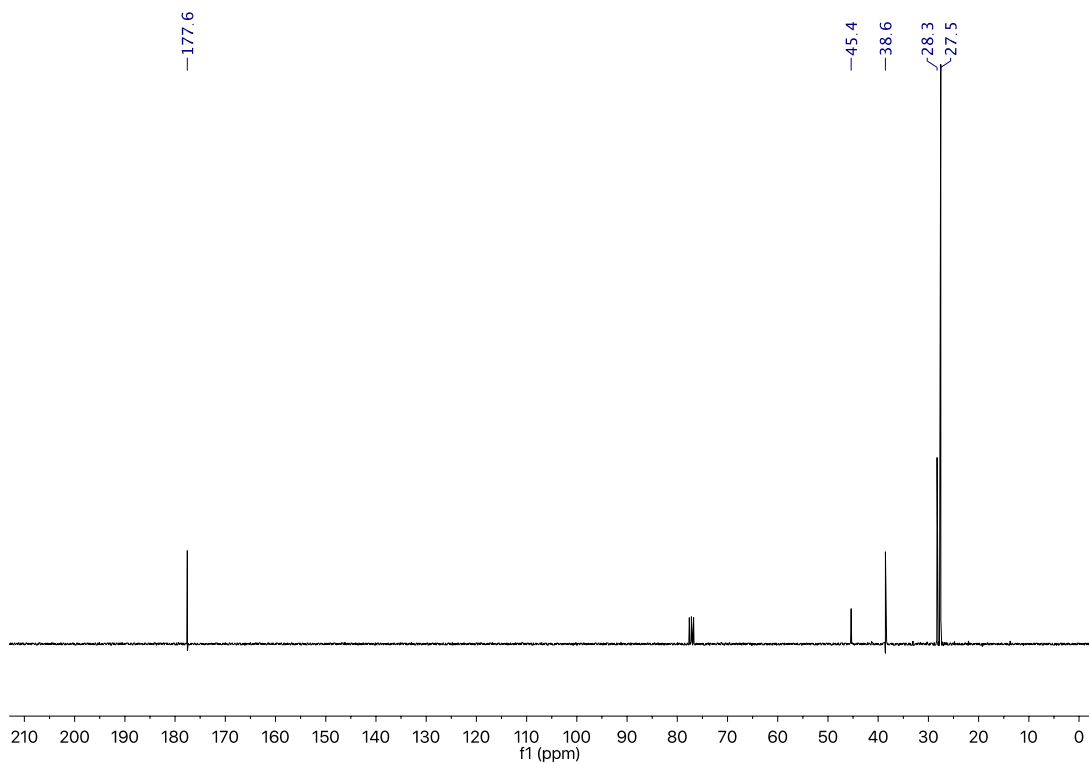
$^{13}\text{C}\{^1\text{H}\}$ -NMR of *cis*-1 in CDCl_3

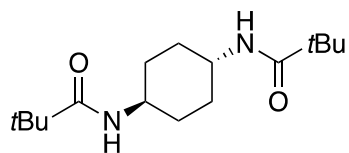
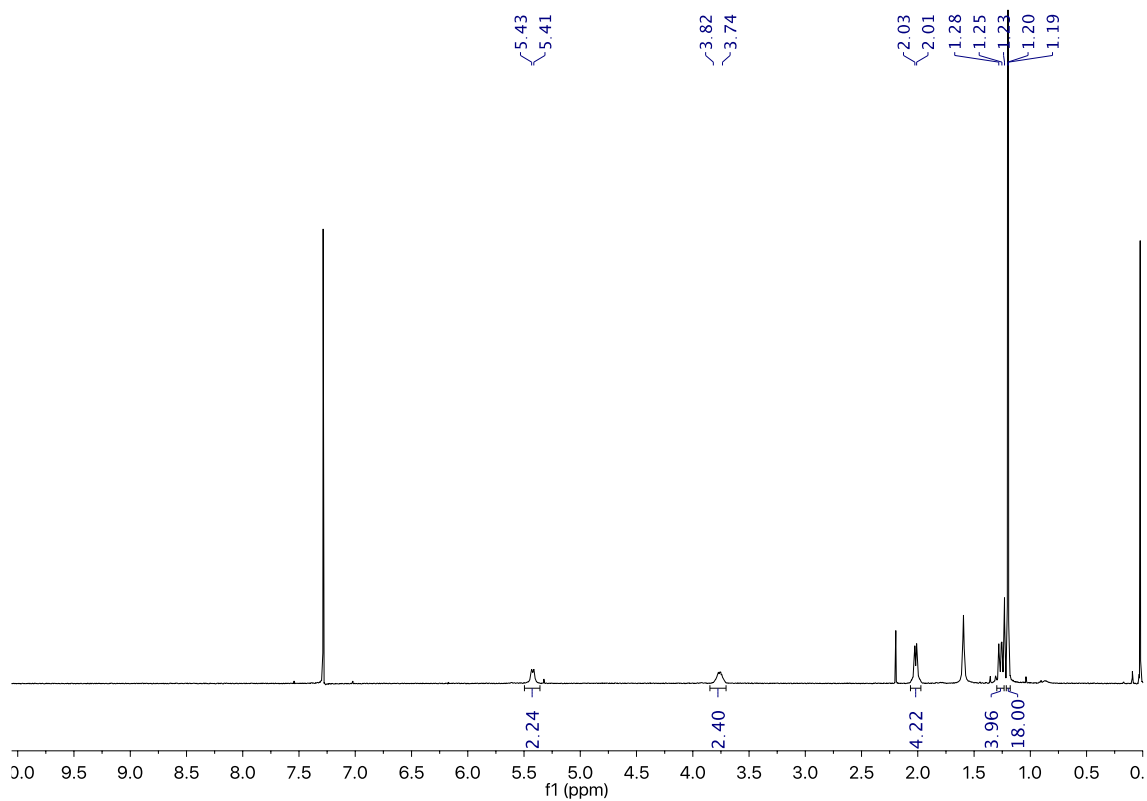
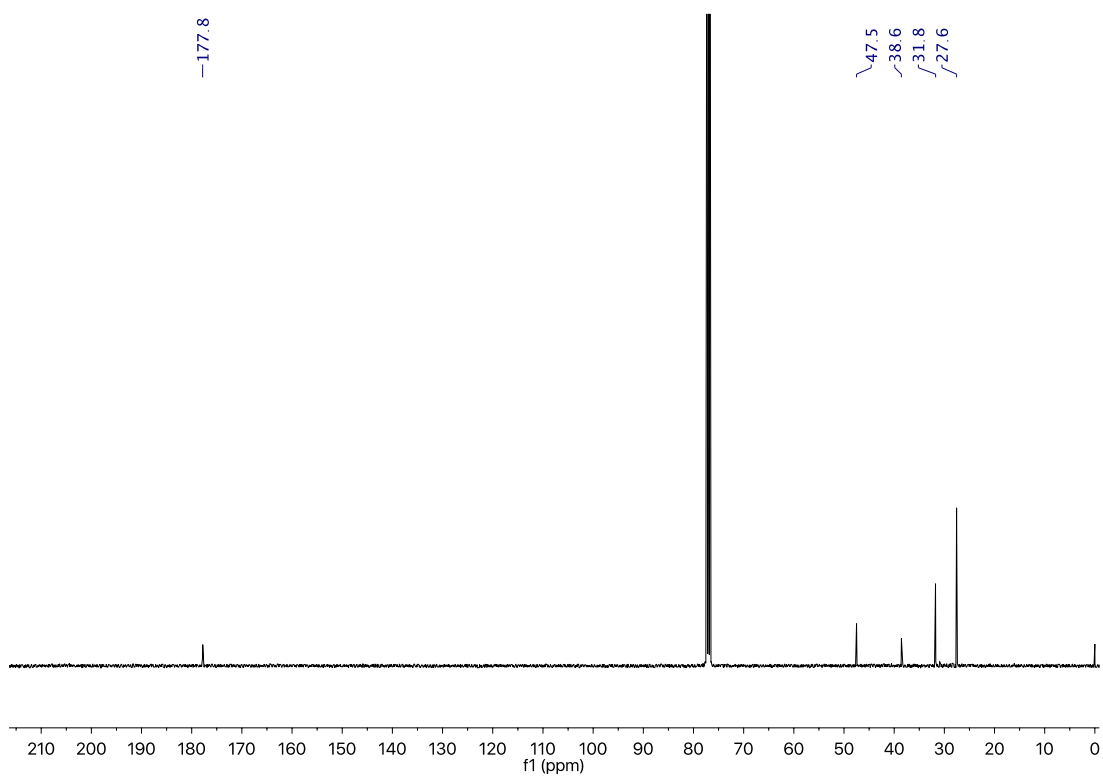


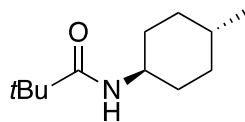
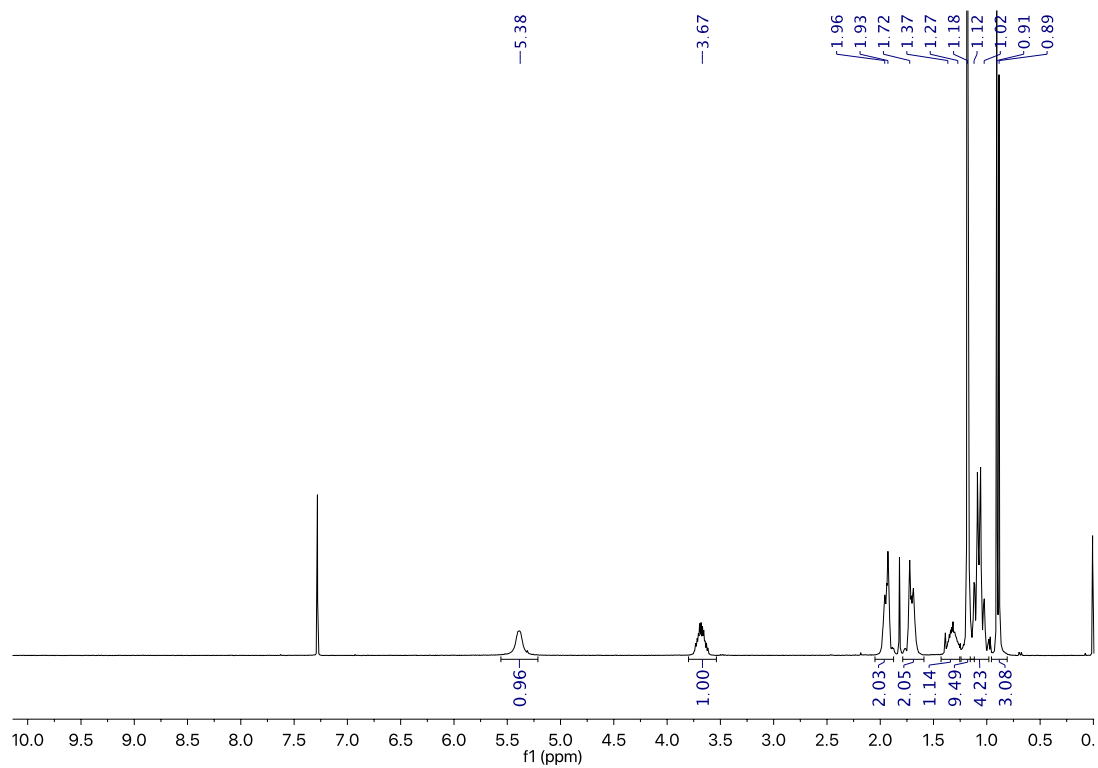
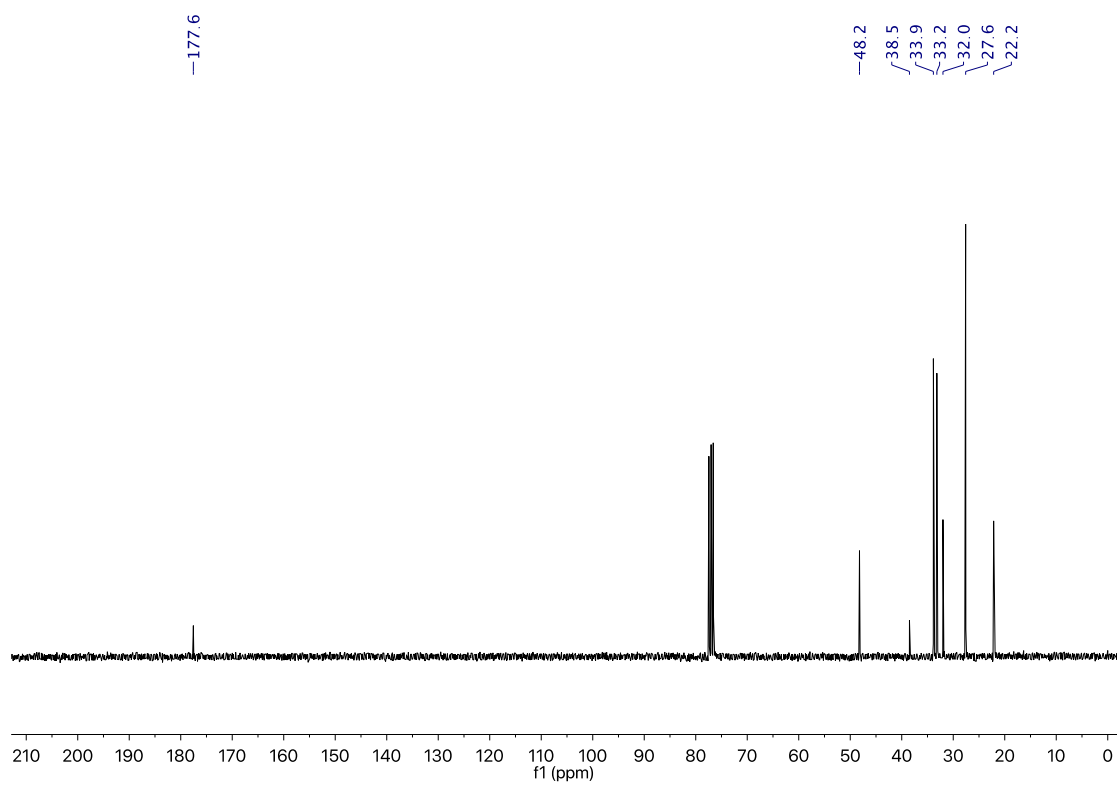
 $^1\text{H-NMR}$ of *trans*-1 in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of *trans*-1 in CDCl_3 

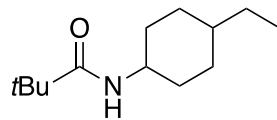
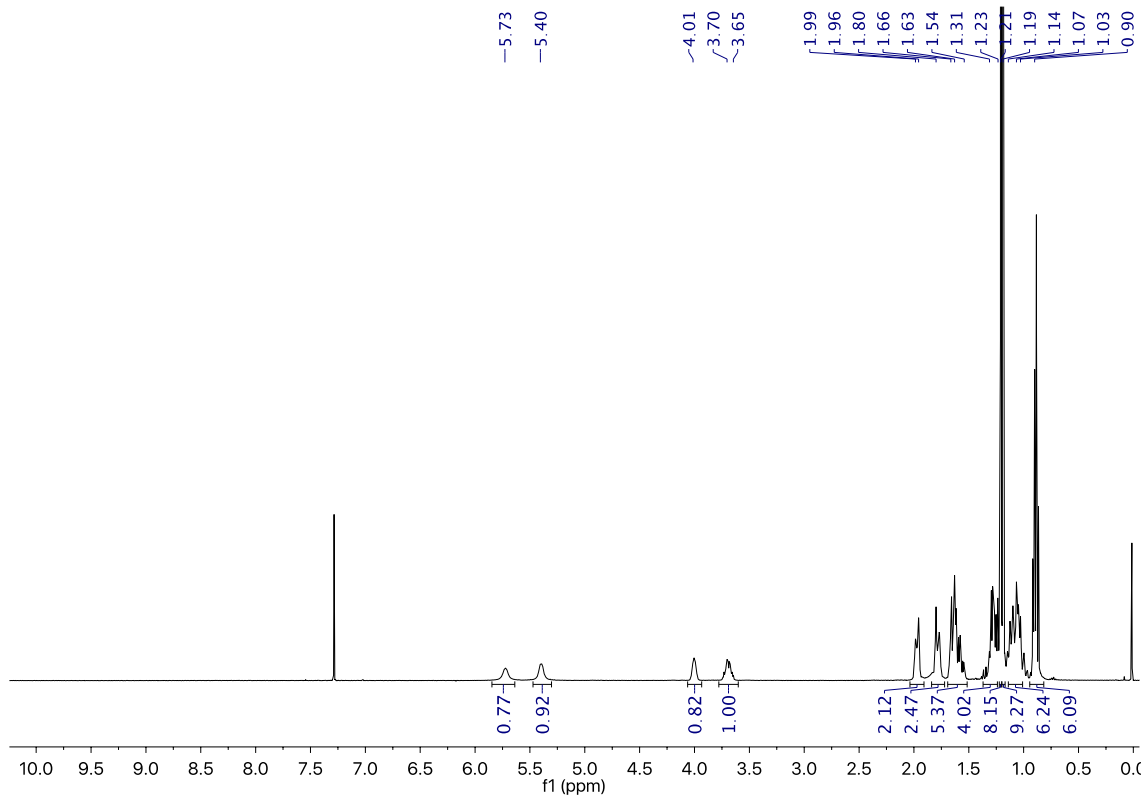
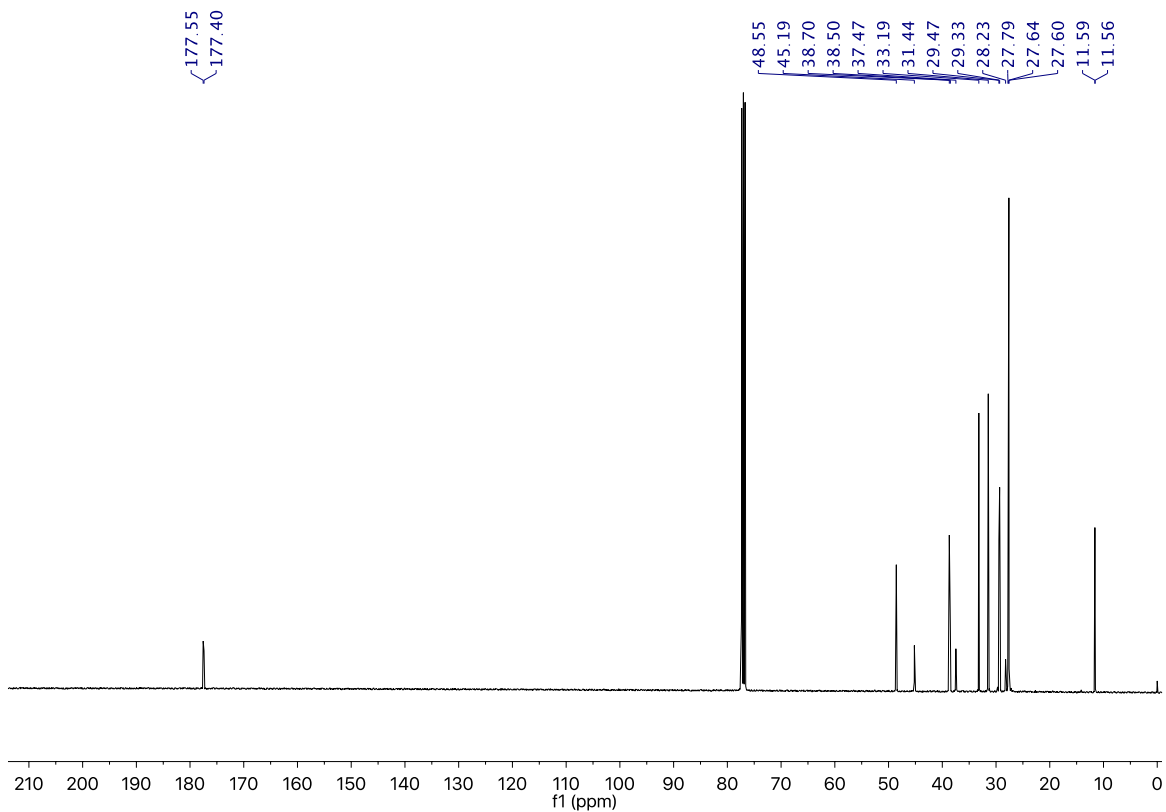
 $^1\text{H-NMR}$ of *cis*-**2** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of *cis*-**2** in CDCl_3 

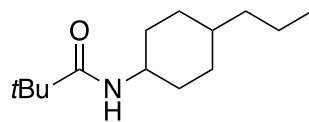
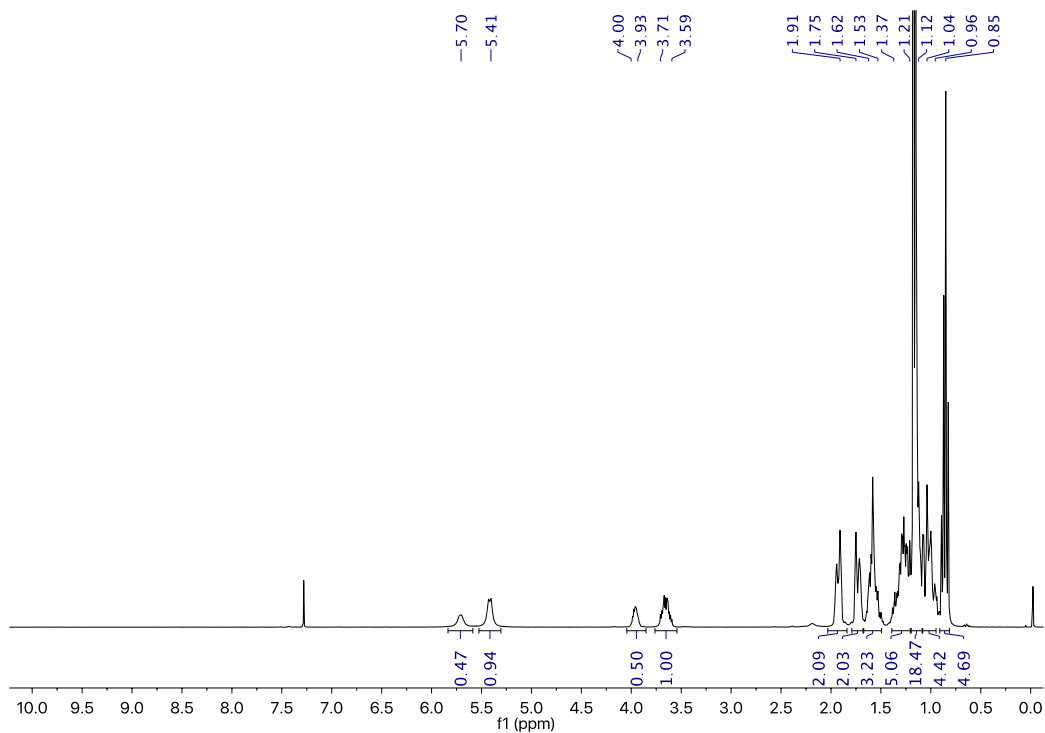
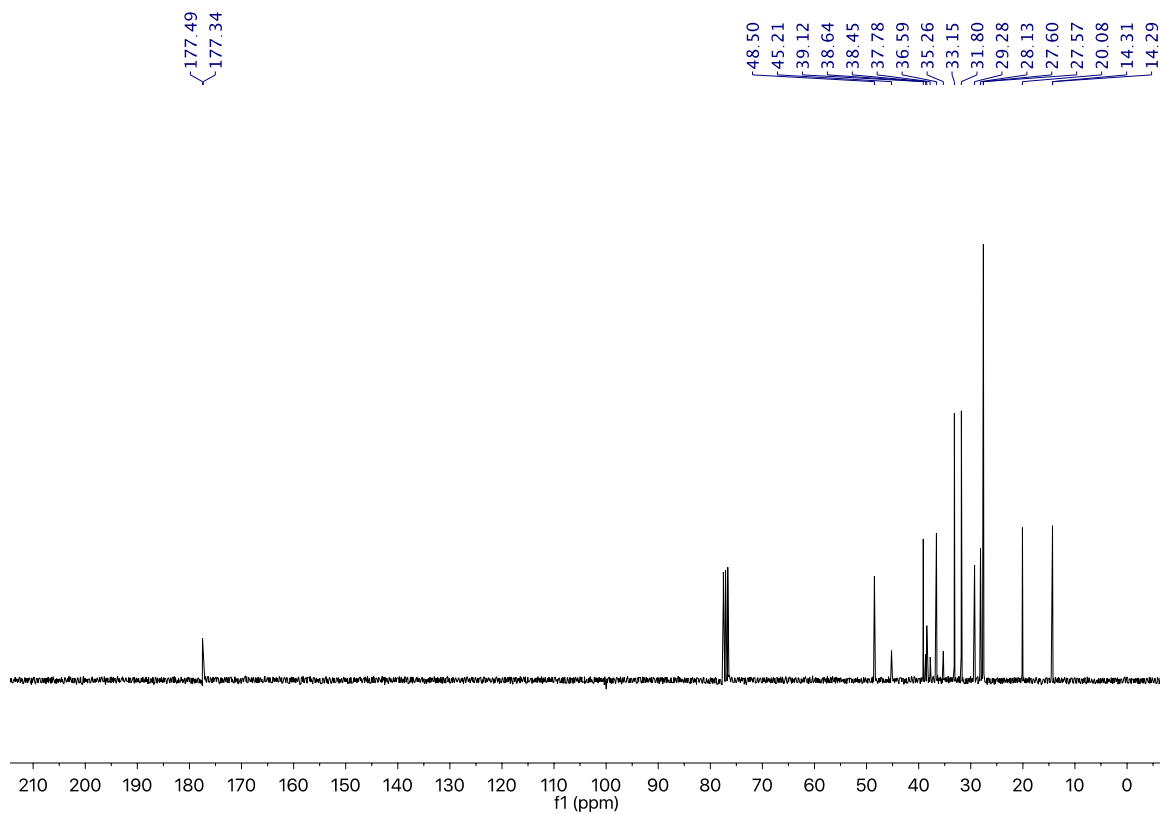
 $^1\text{H-NMR}$ of *trans*-**2** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of *trans*-**2** in CDCl_3 

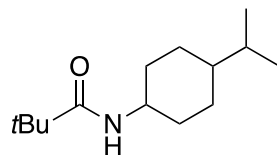
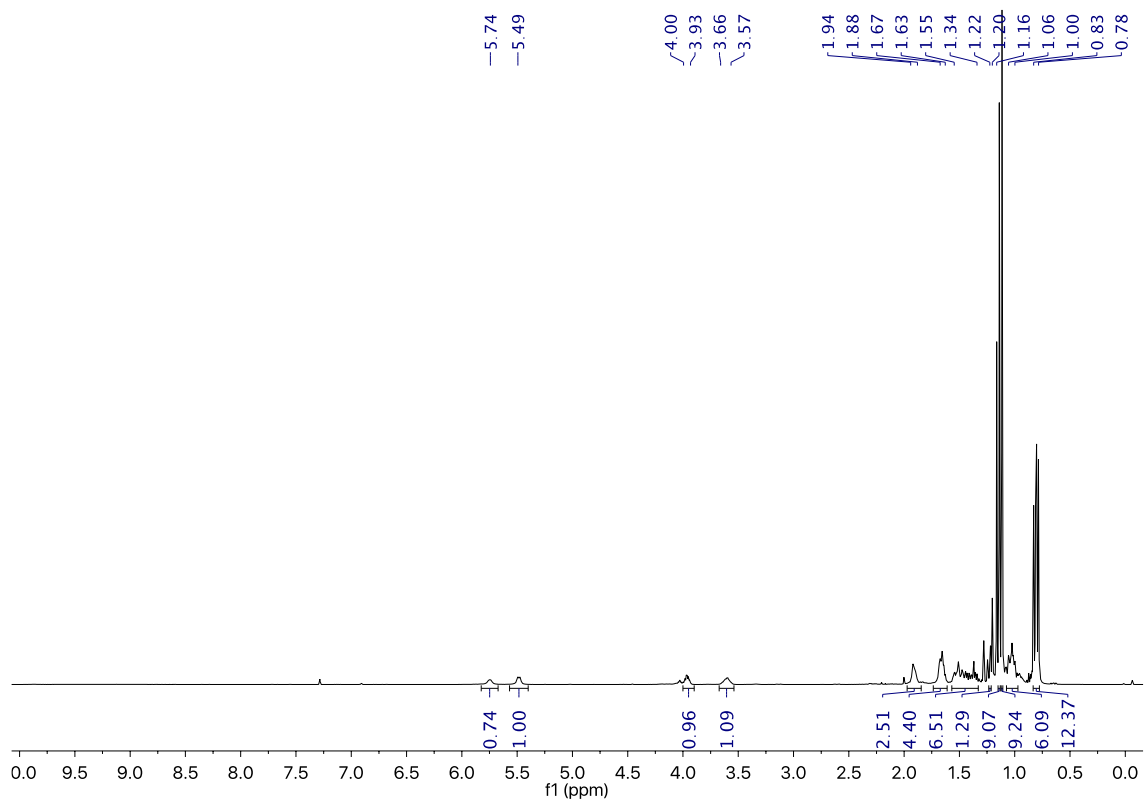
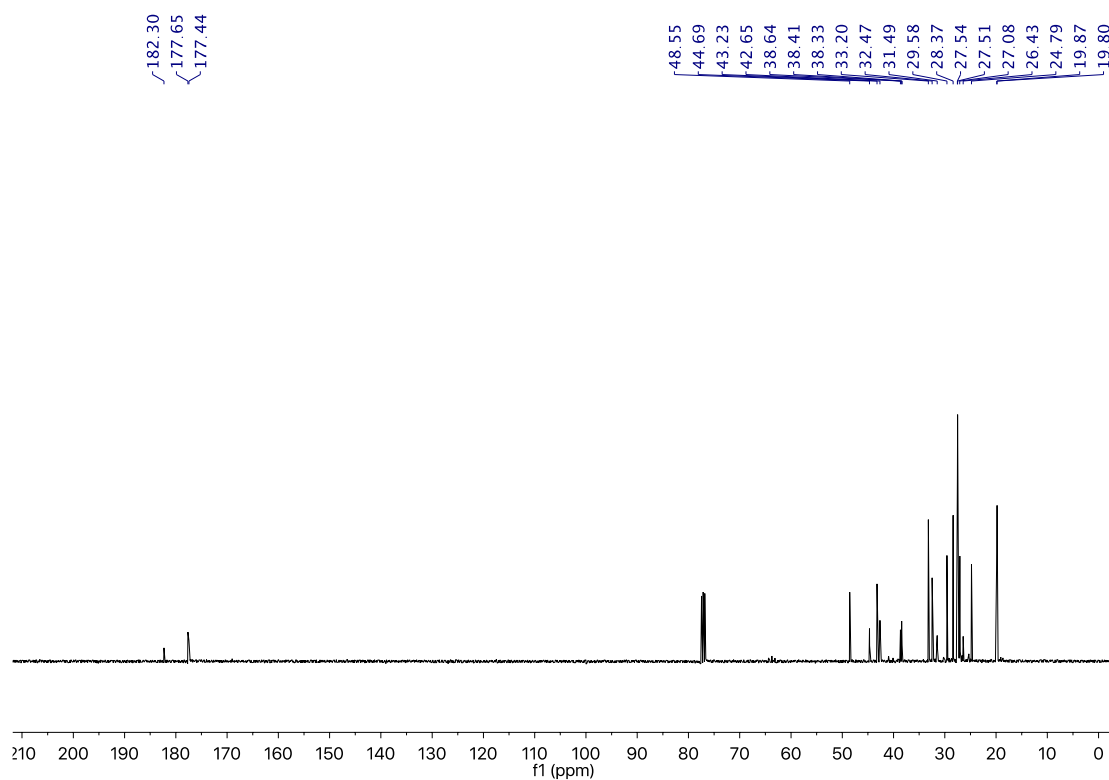
 $^1\text{H-NMR}$ of *cis*-**3** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of *cis*-**3** in CDCl_3 

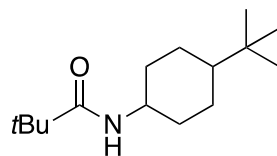
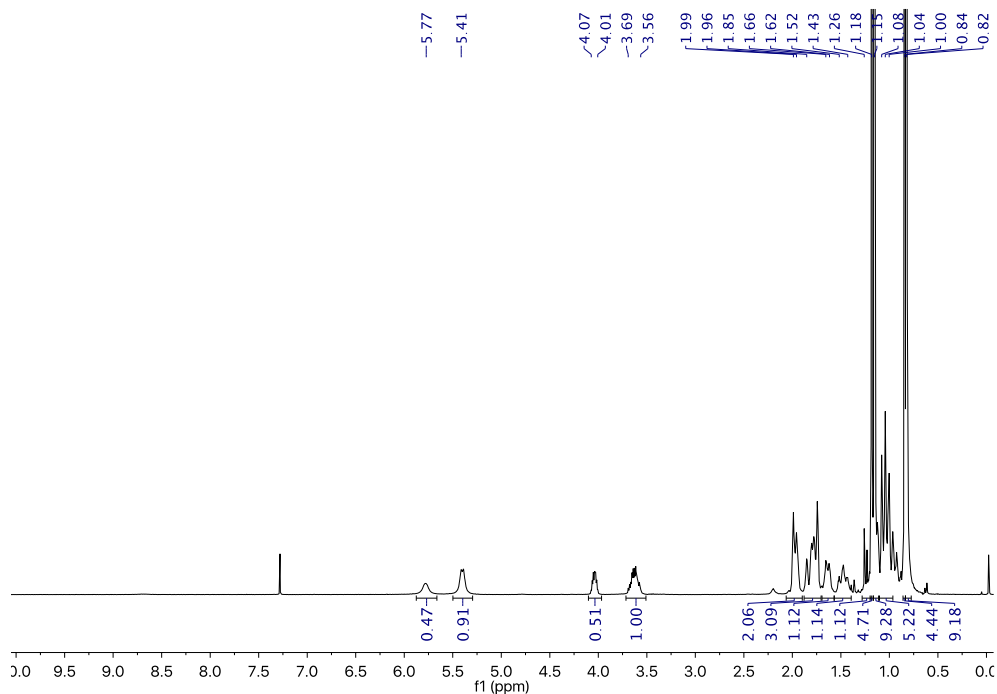
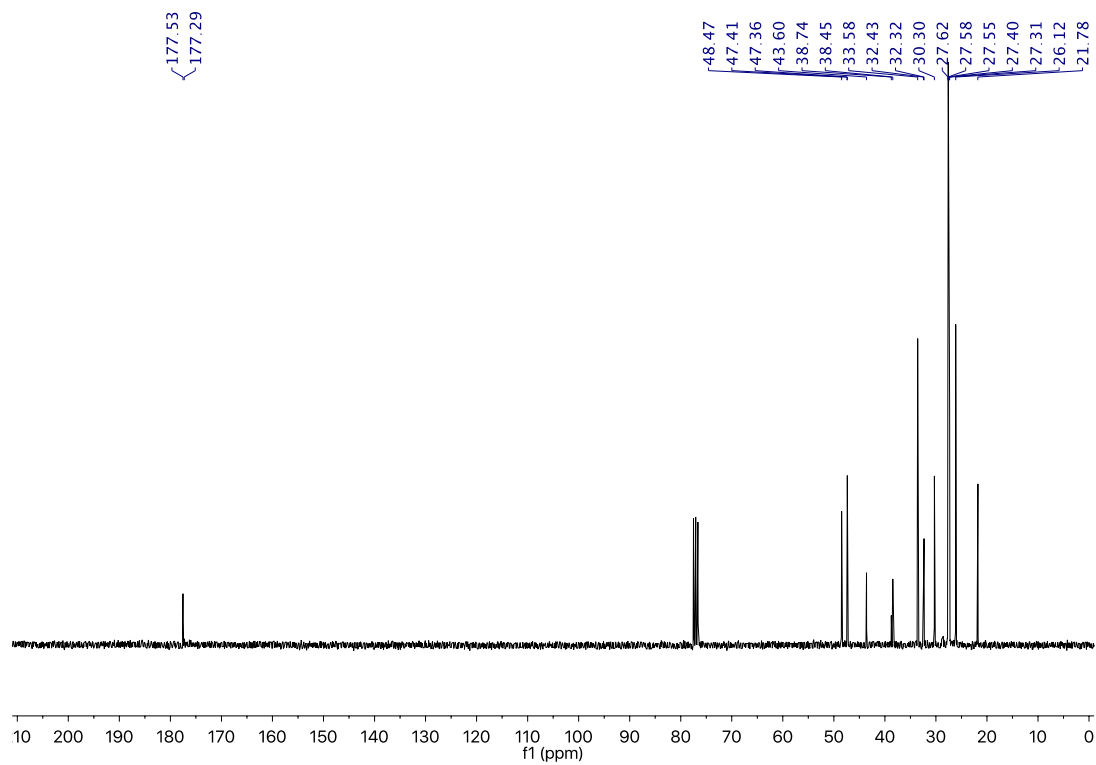
 $^1\text{H-NMR}$ of *trans*-3 in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of *trans*-3 in CDCl_3 

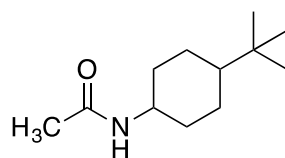
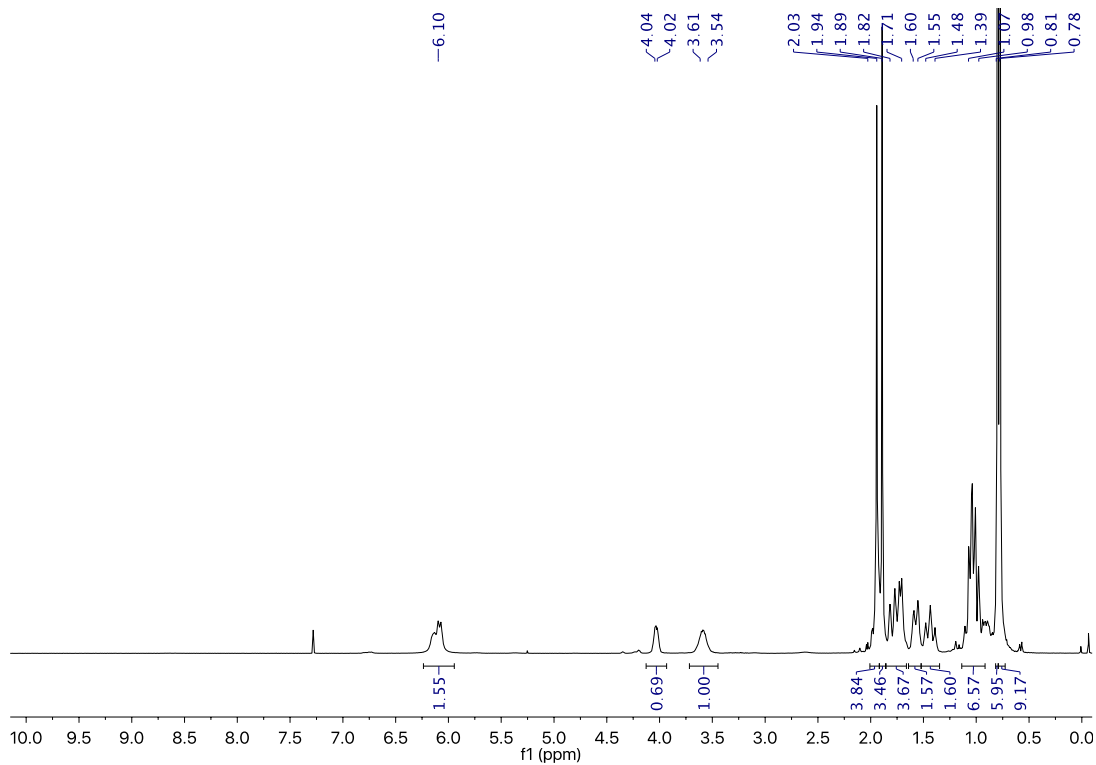
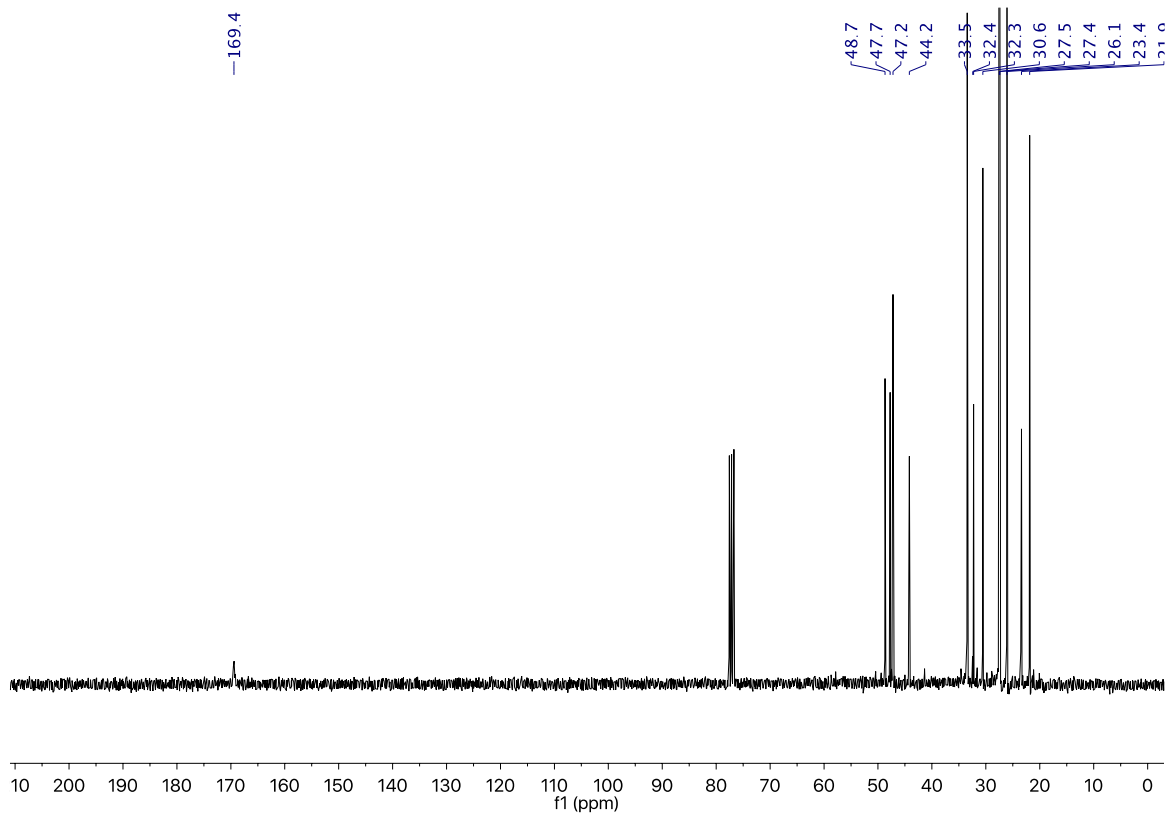
 $^1\text{H-NMR}$ of *trans*-4 in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of *trans*-4 in CDCl_3 

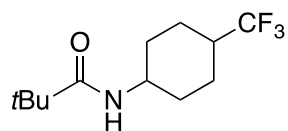
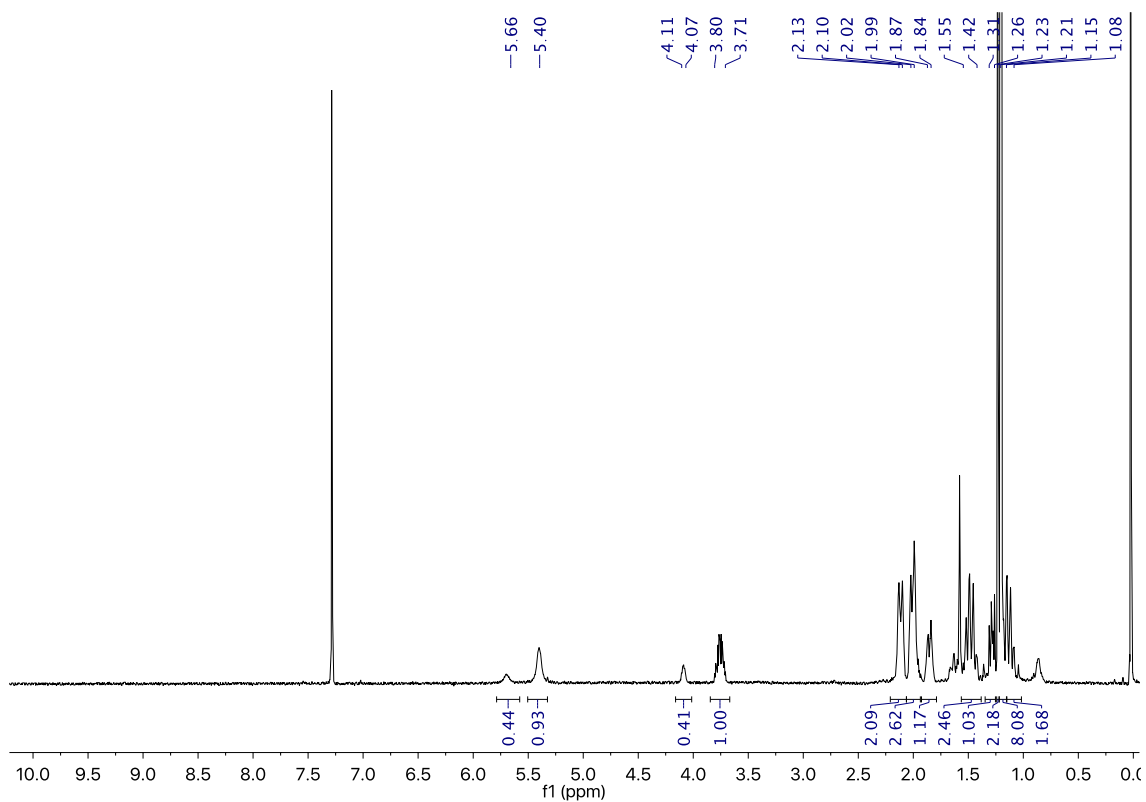
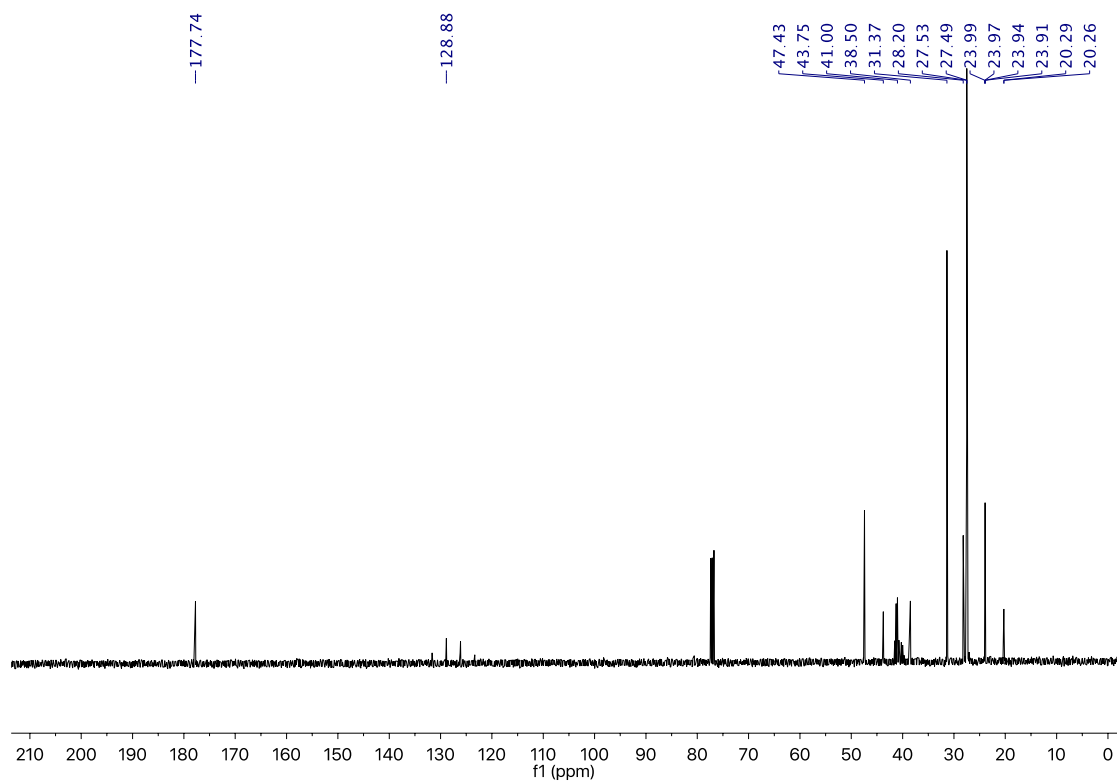
 $^1\text{H-NMR}$ of **5** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **5** in CDCl_3 

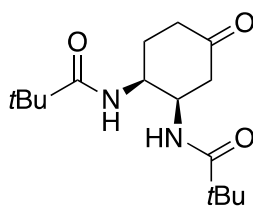
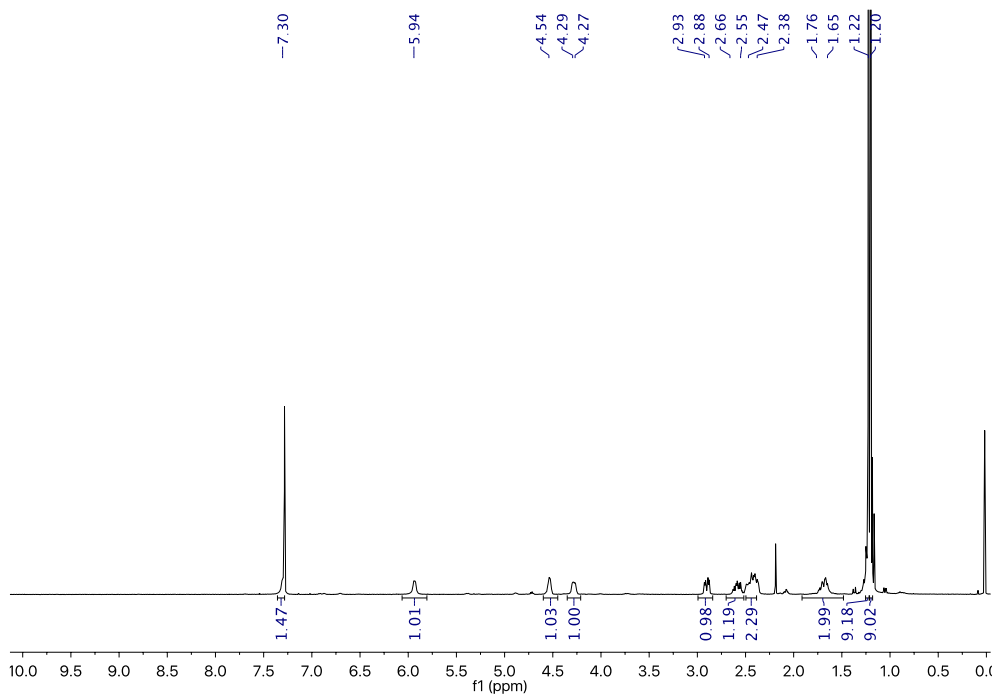
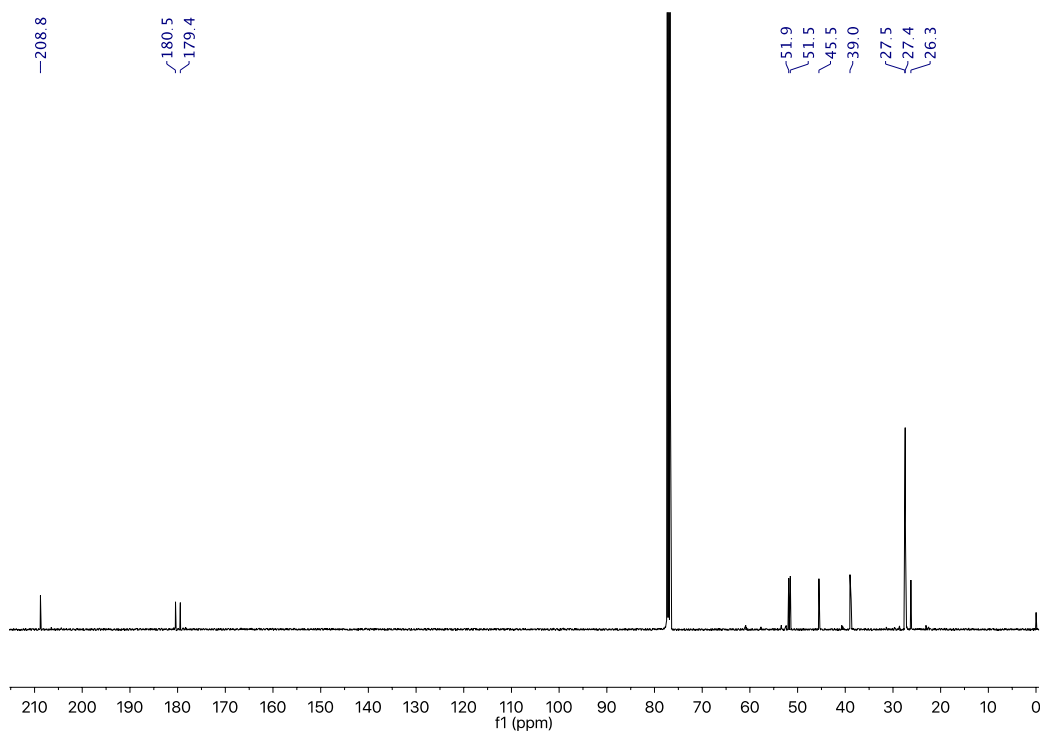
 $^1\text{H-NMR}$ of **6** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **6** in CDCl_3 

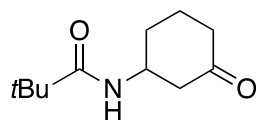
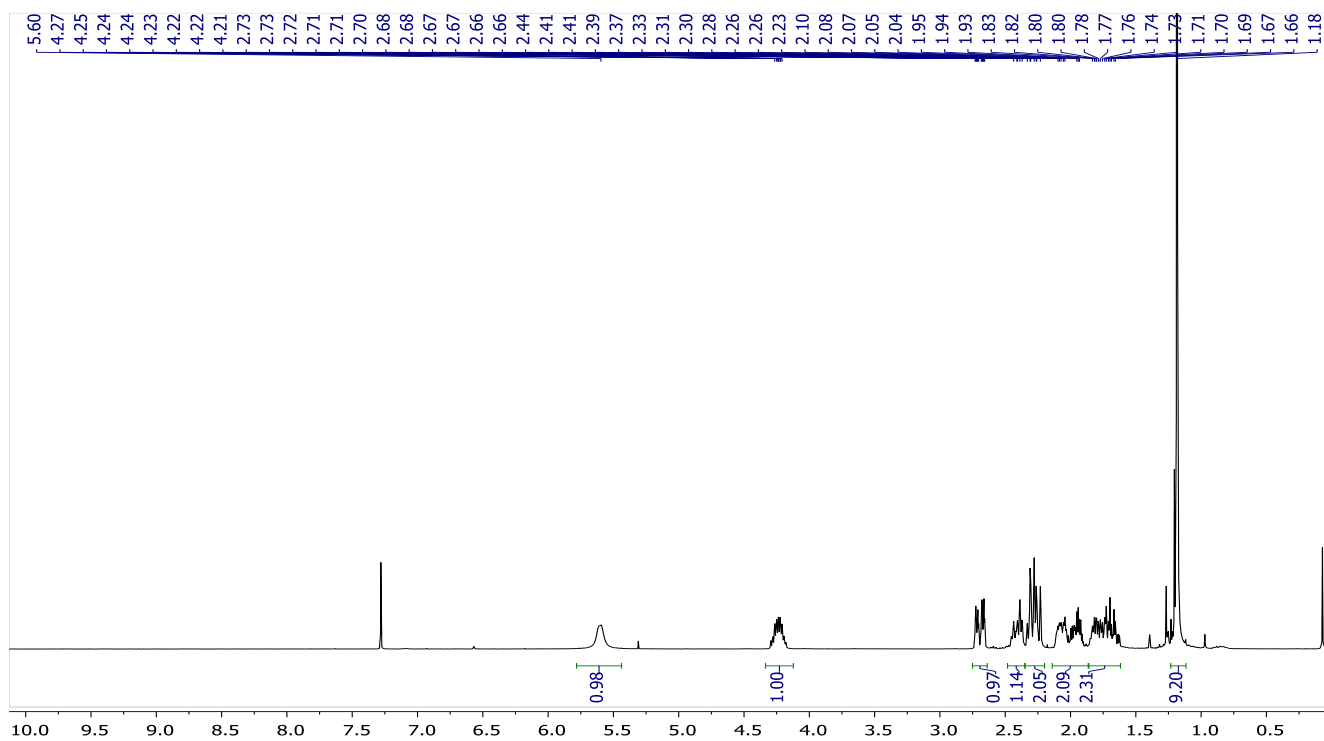
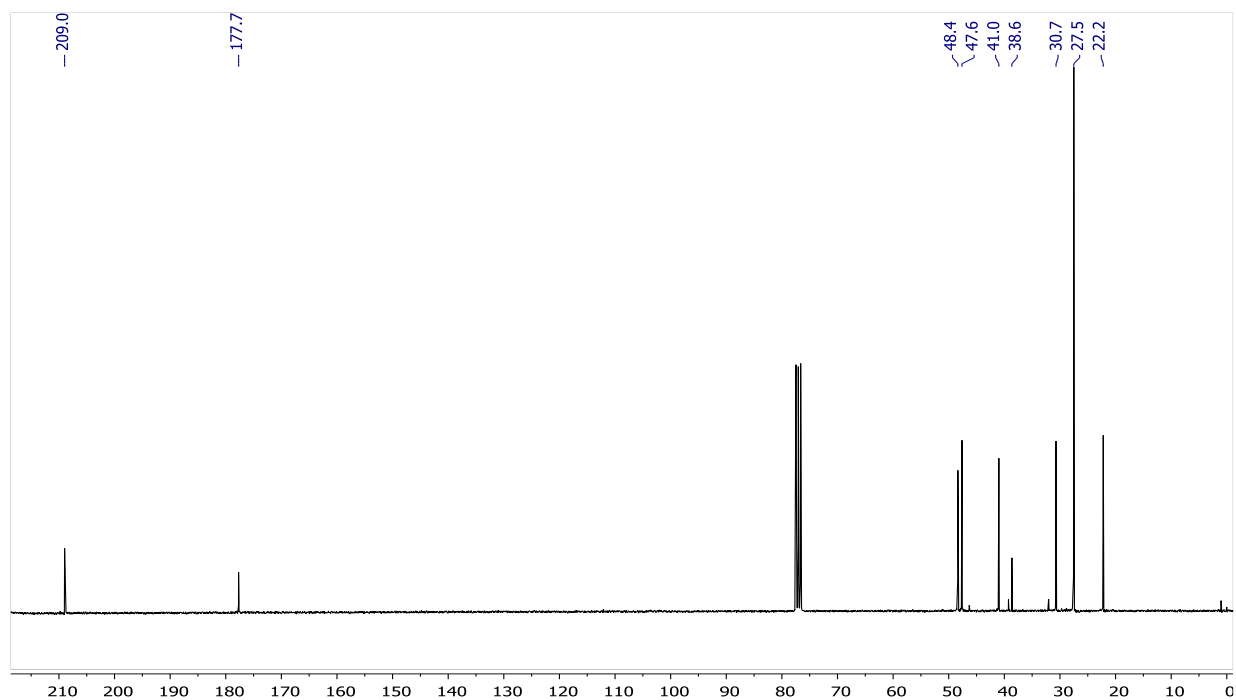
 $^1\text{H-NMR}$ of **7** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **7** in CDCl_3 

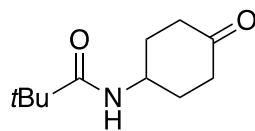
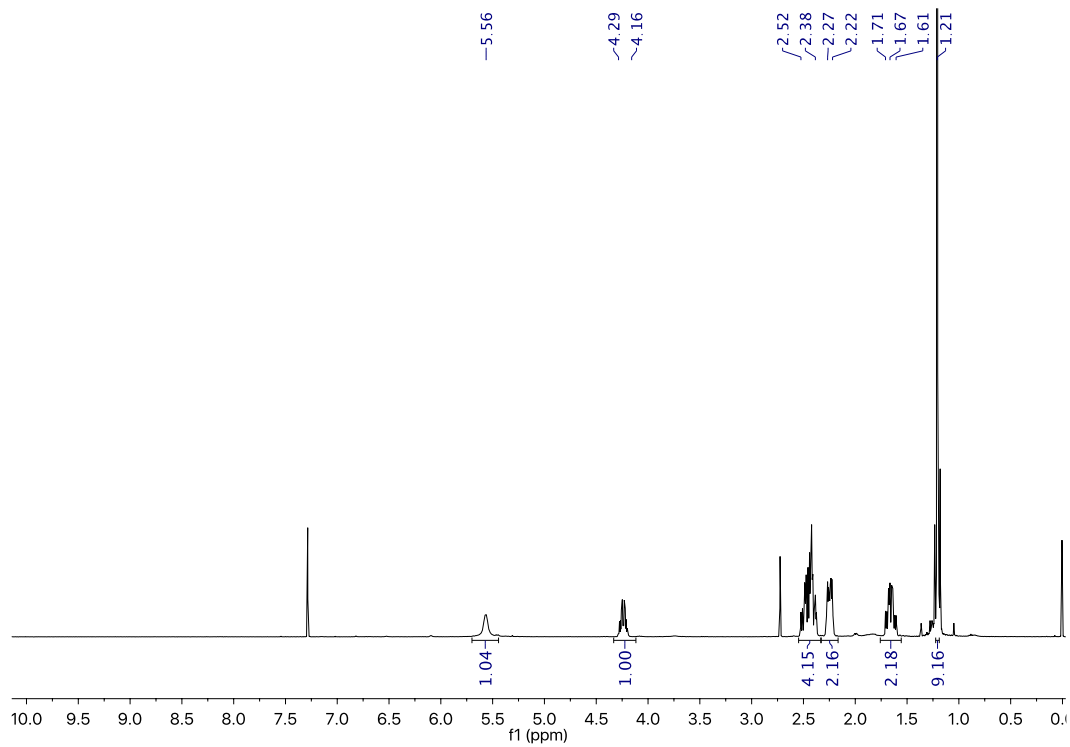
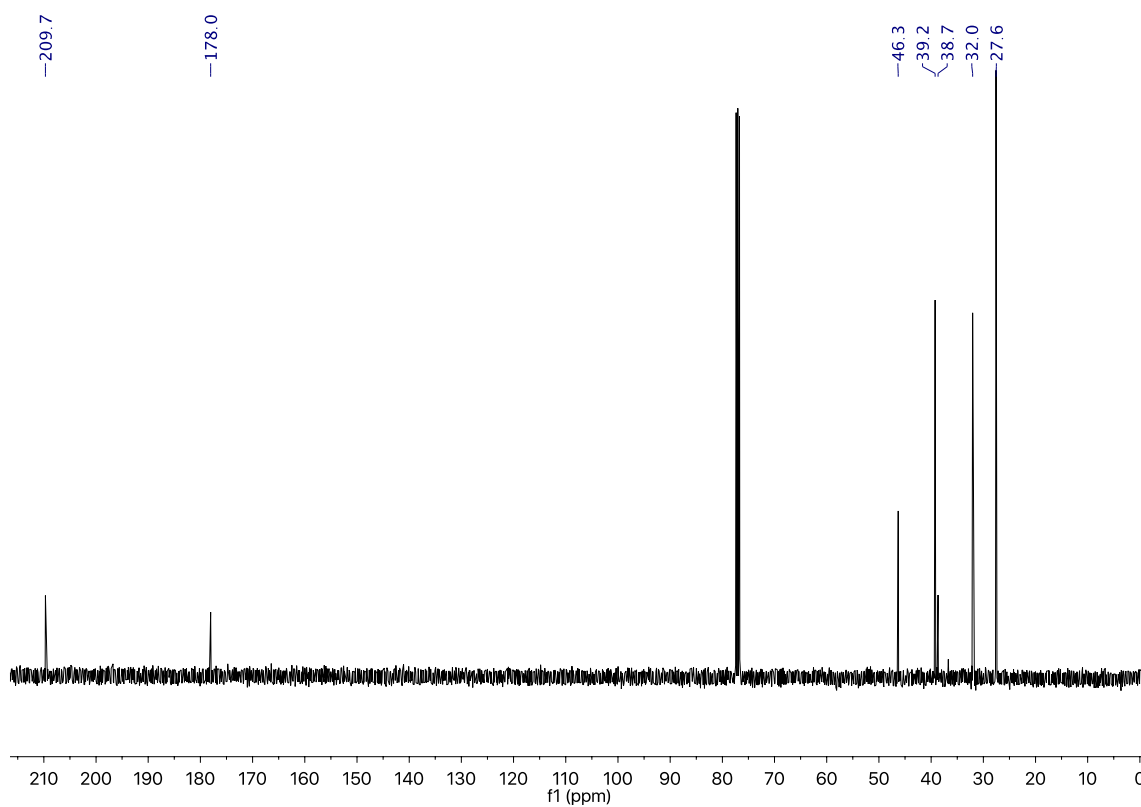
 $^1\text{H-NMR}$ of **8** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **8** in CDCl_3 

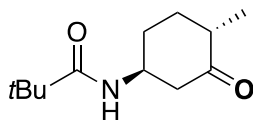
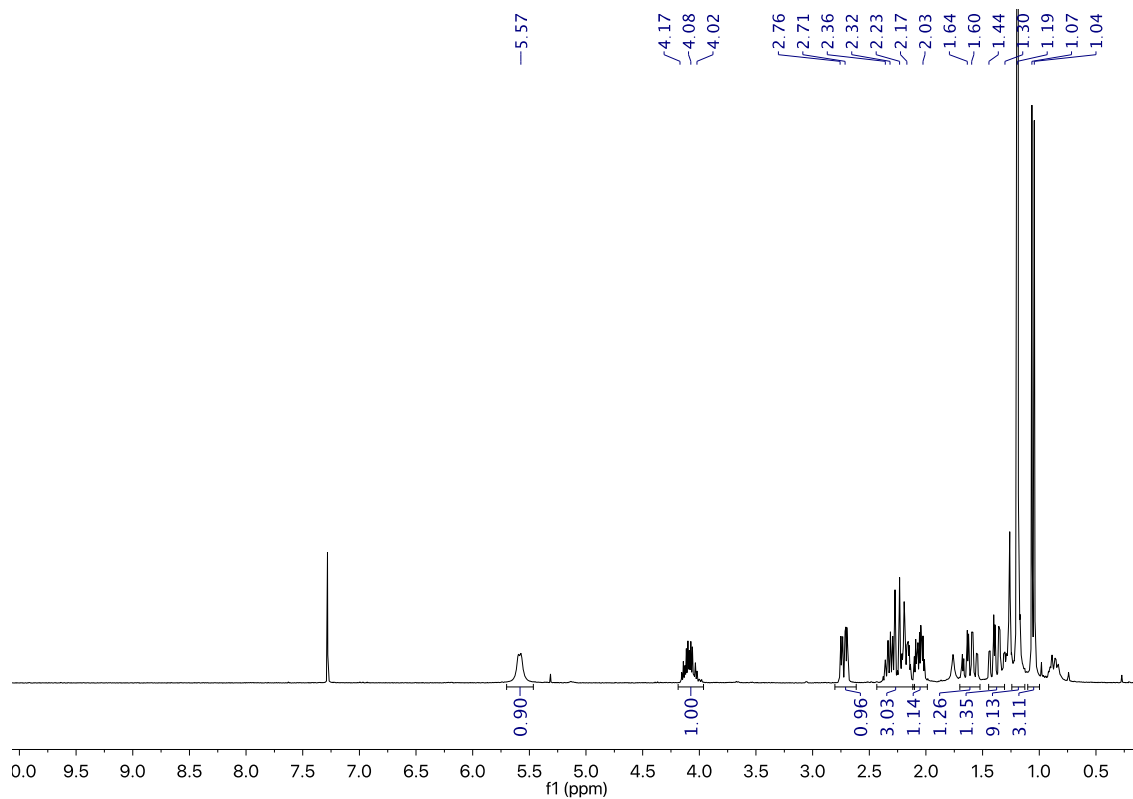
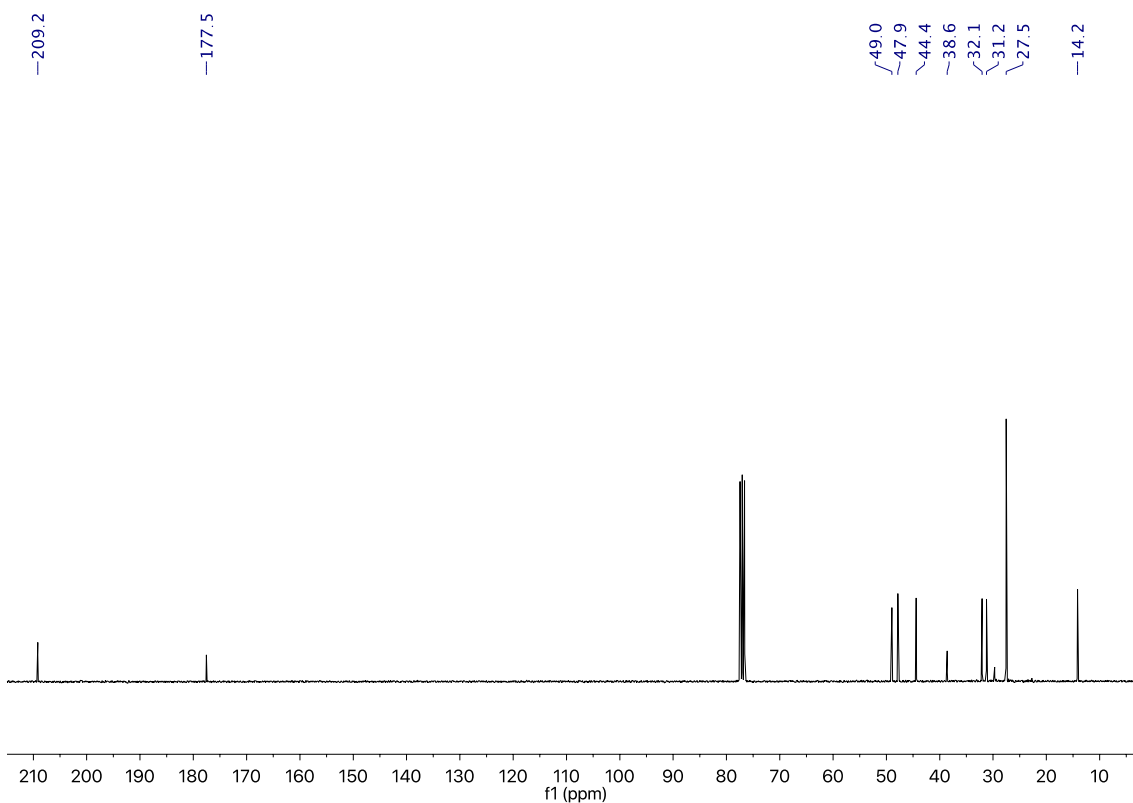
 $^1\text{H-NMR}$ of **9** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **9** in CDCl_3 

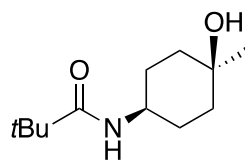
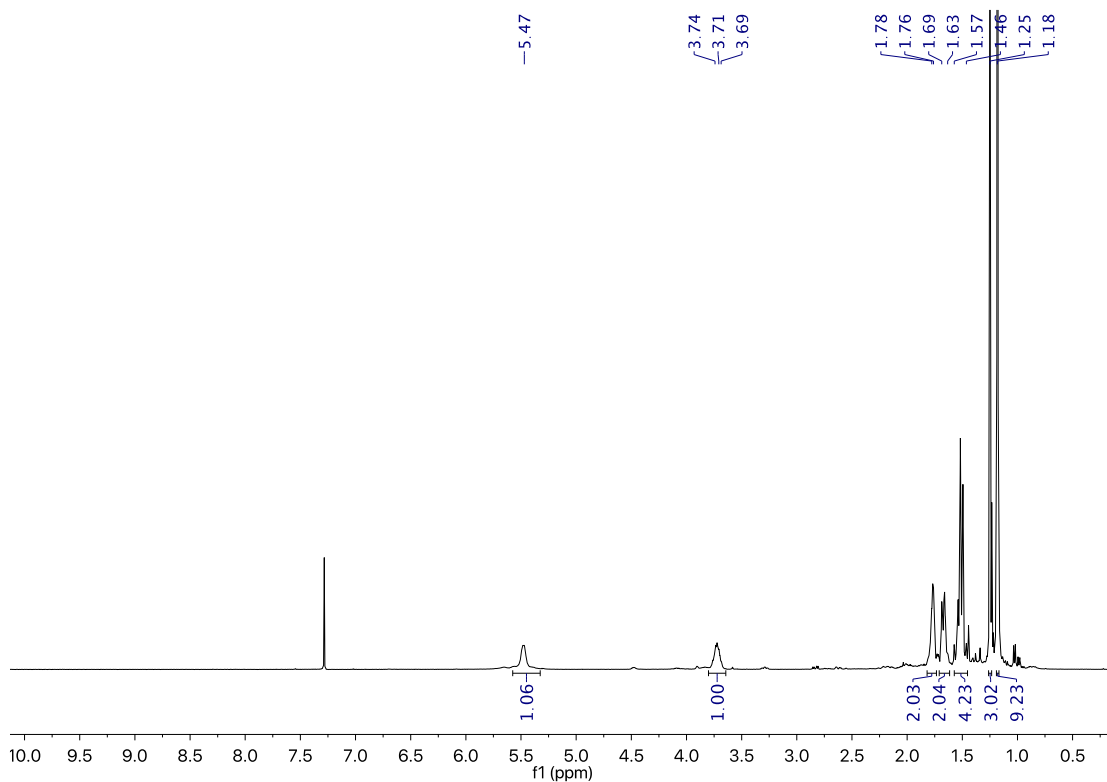
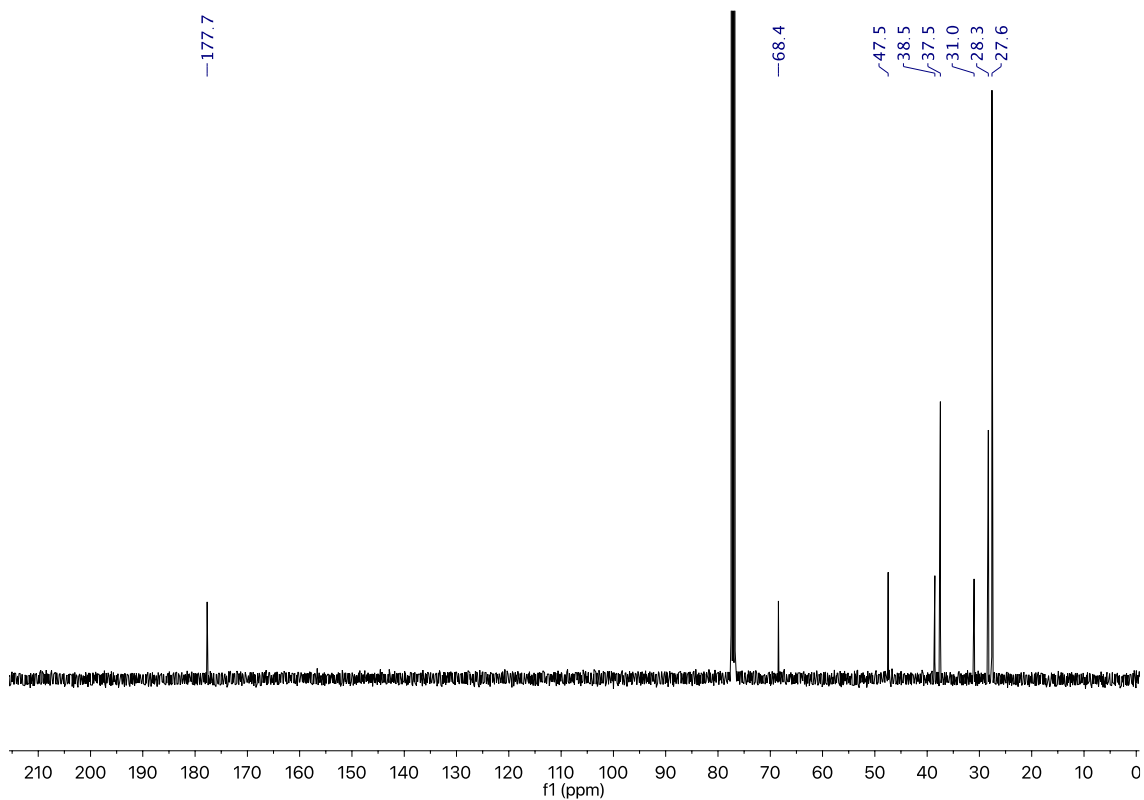
 $^1\text{H-NMR}$ of **10** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **10** in CDCl_3 

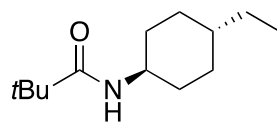
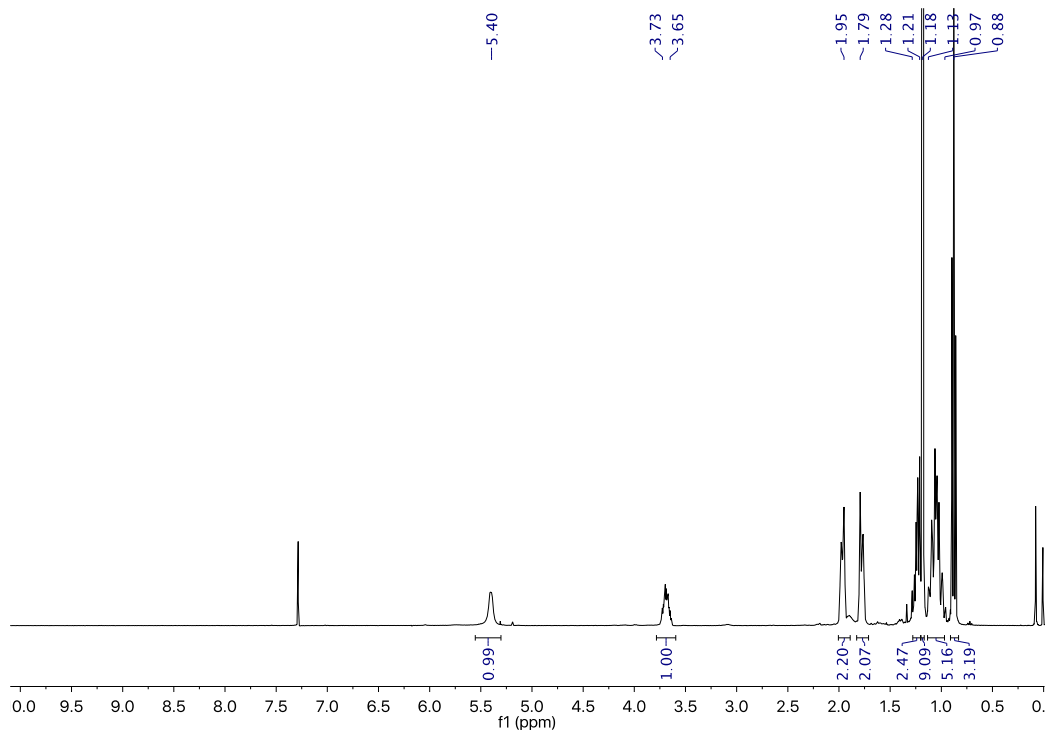
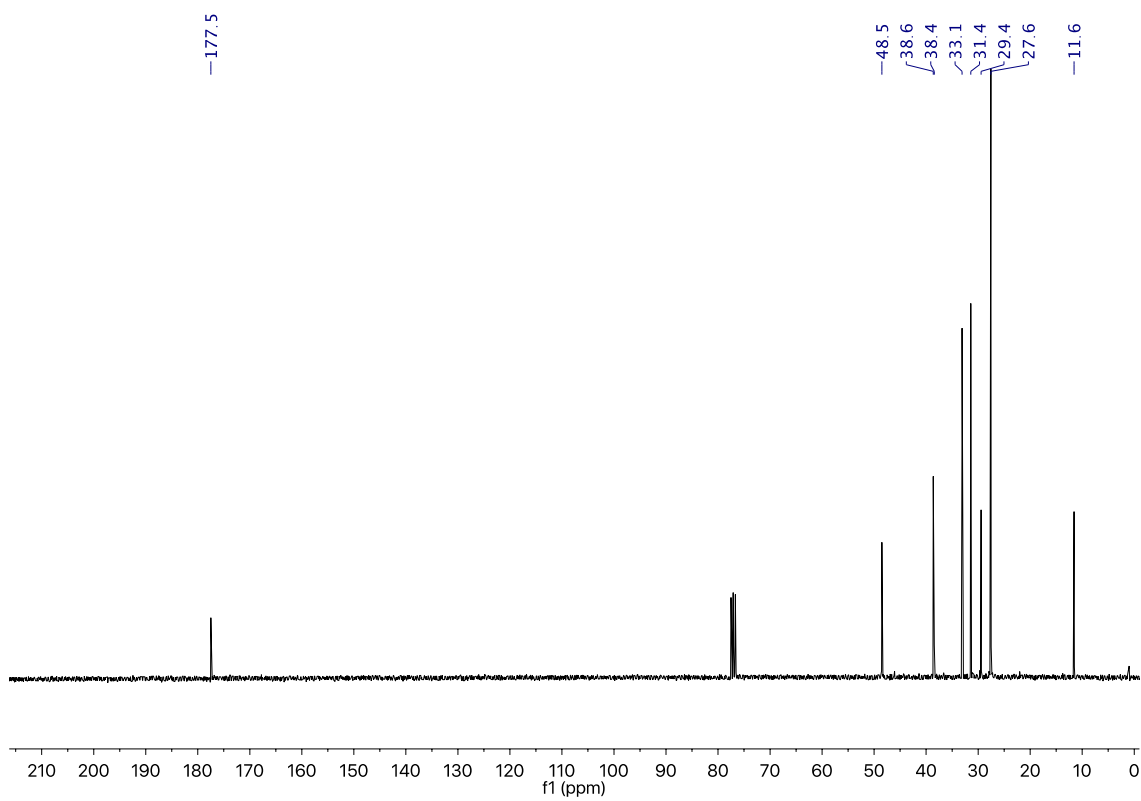
A1 ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of products ^1H -NMR of **1a** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **1a** in CDCl_3 

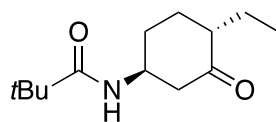
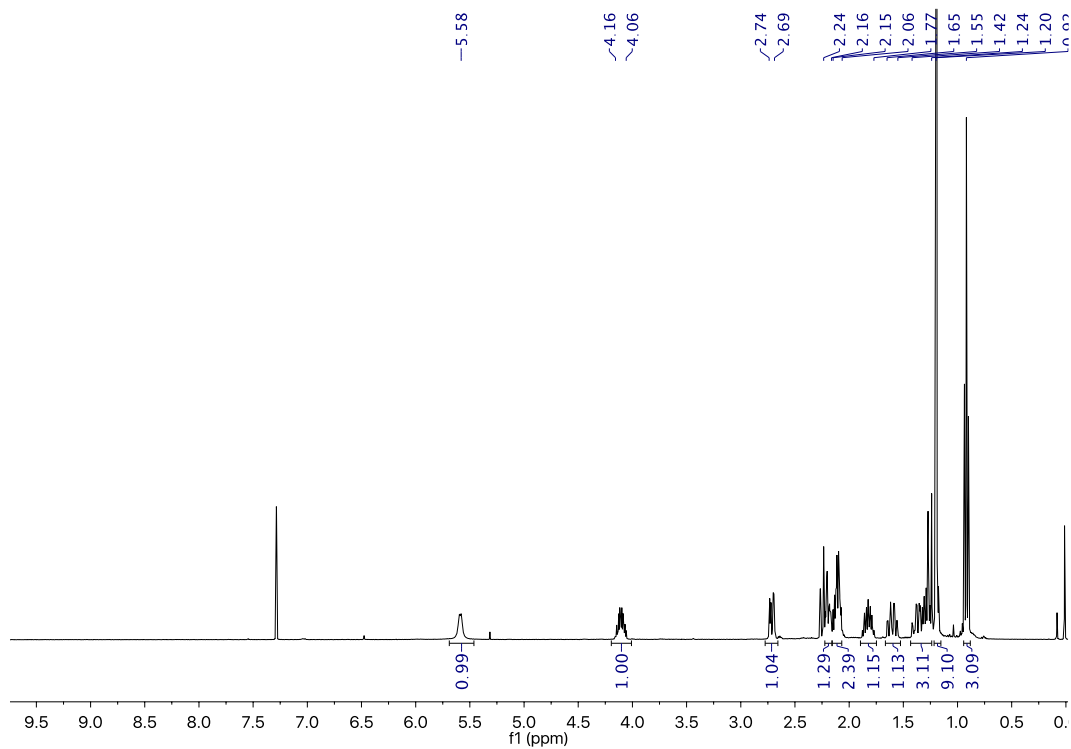
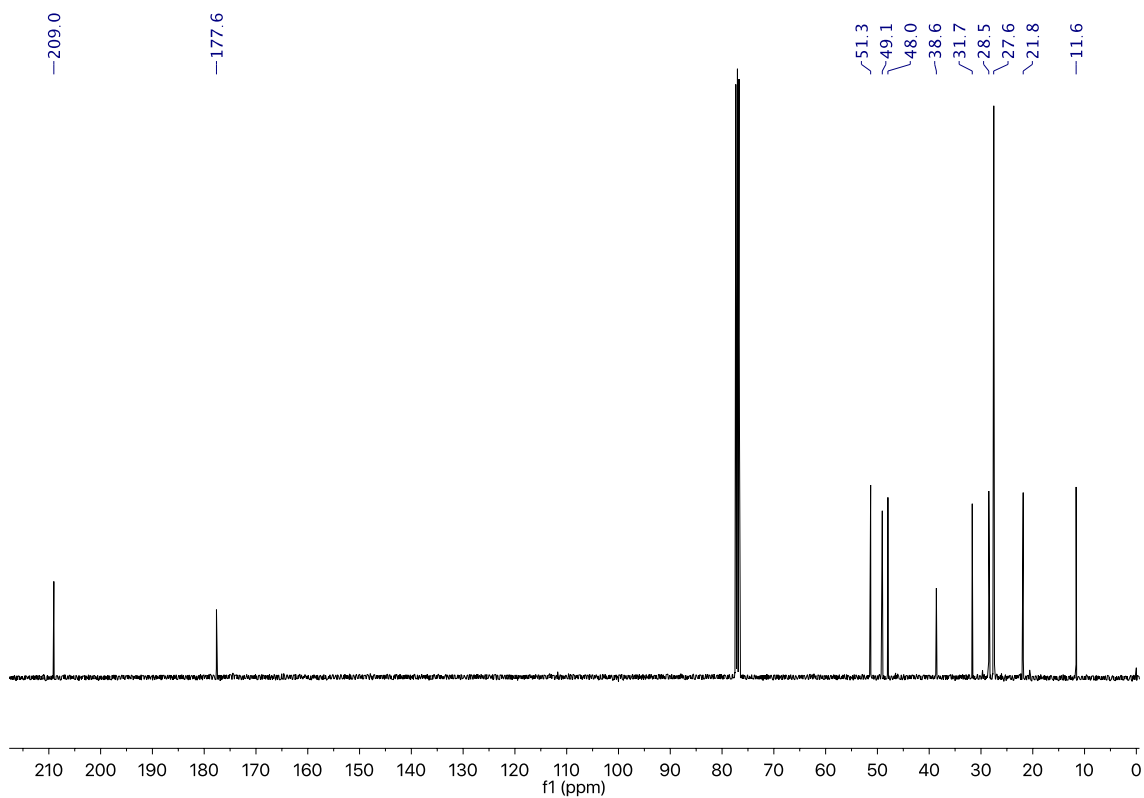
 $^1\text{H-NMR}$ of **2a** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **2a** in CDCl_3 

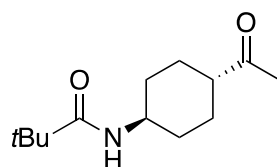
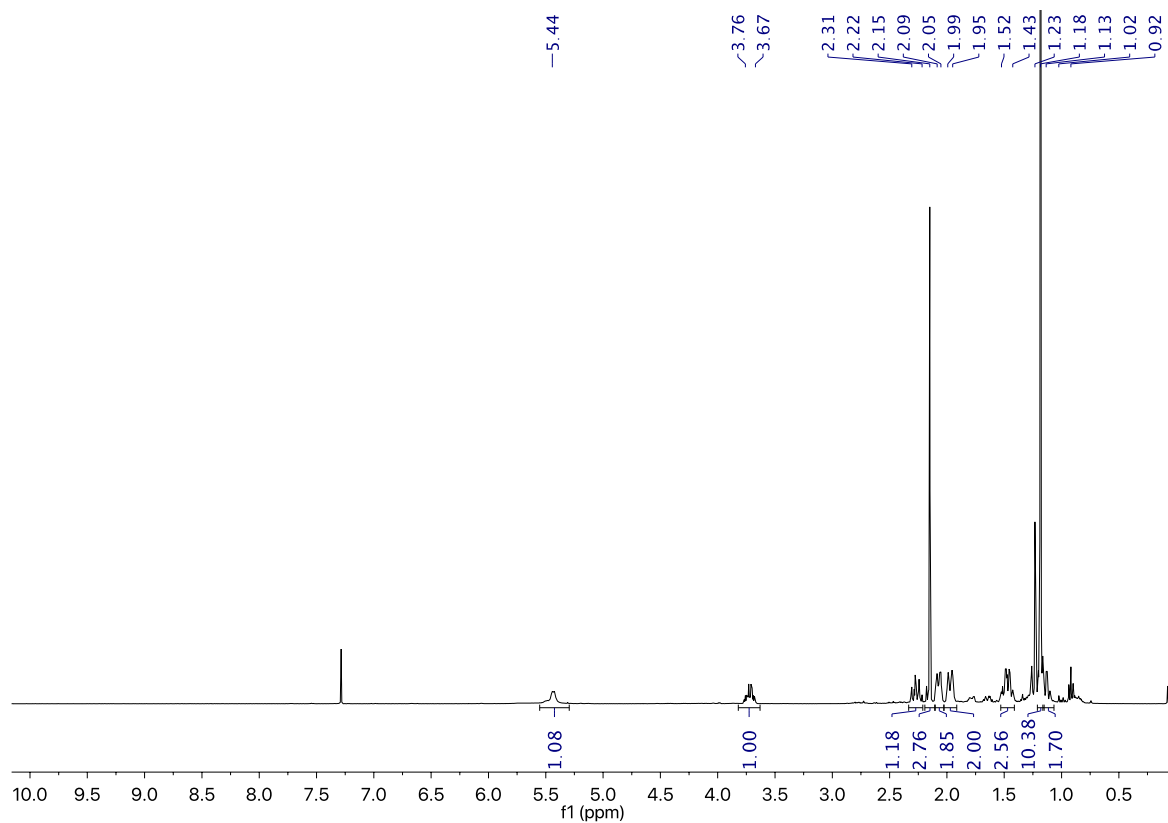
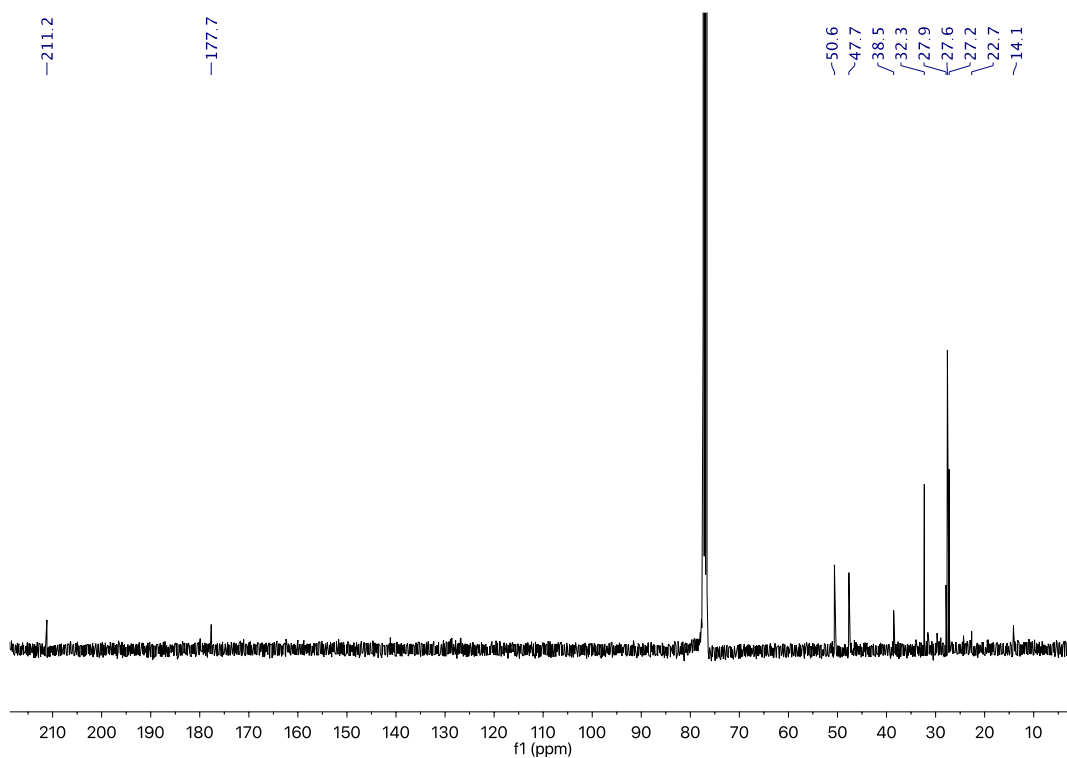
 $^1\text{H-NMR}$ of **3a** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **3a** in CDCl_3 

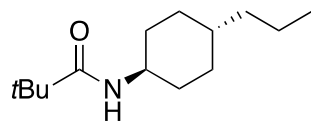
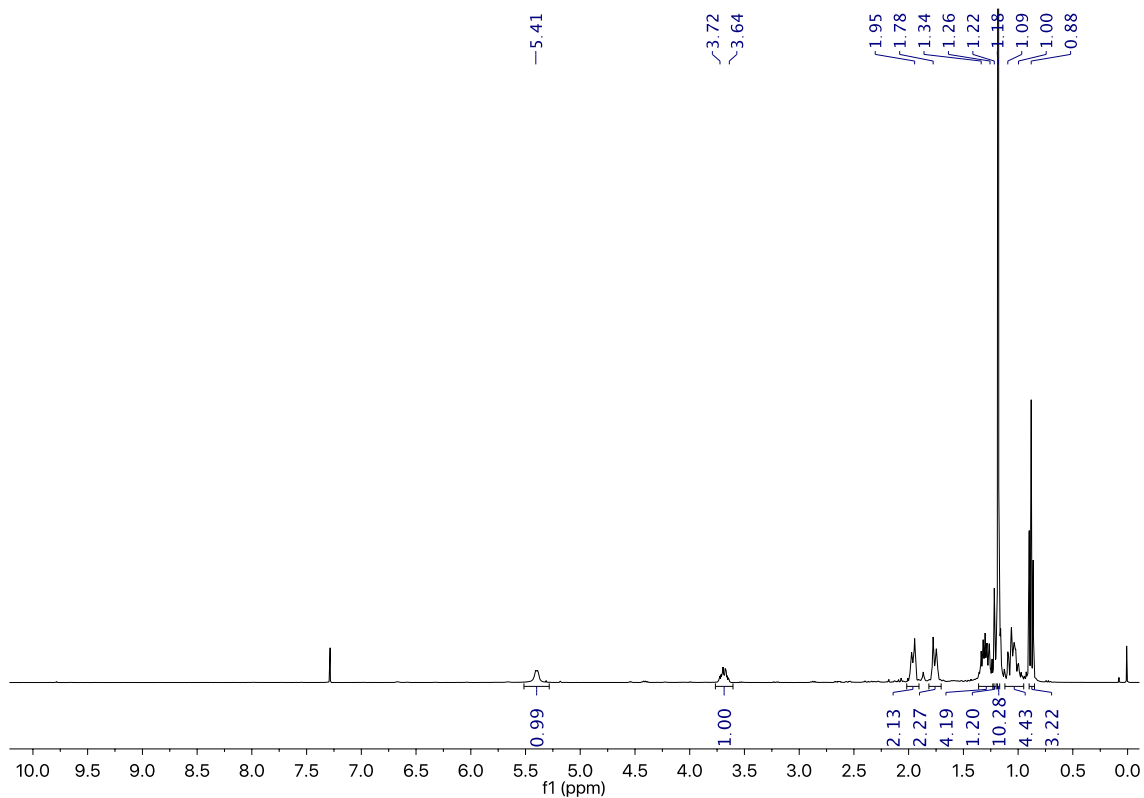
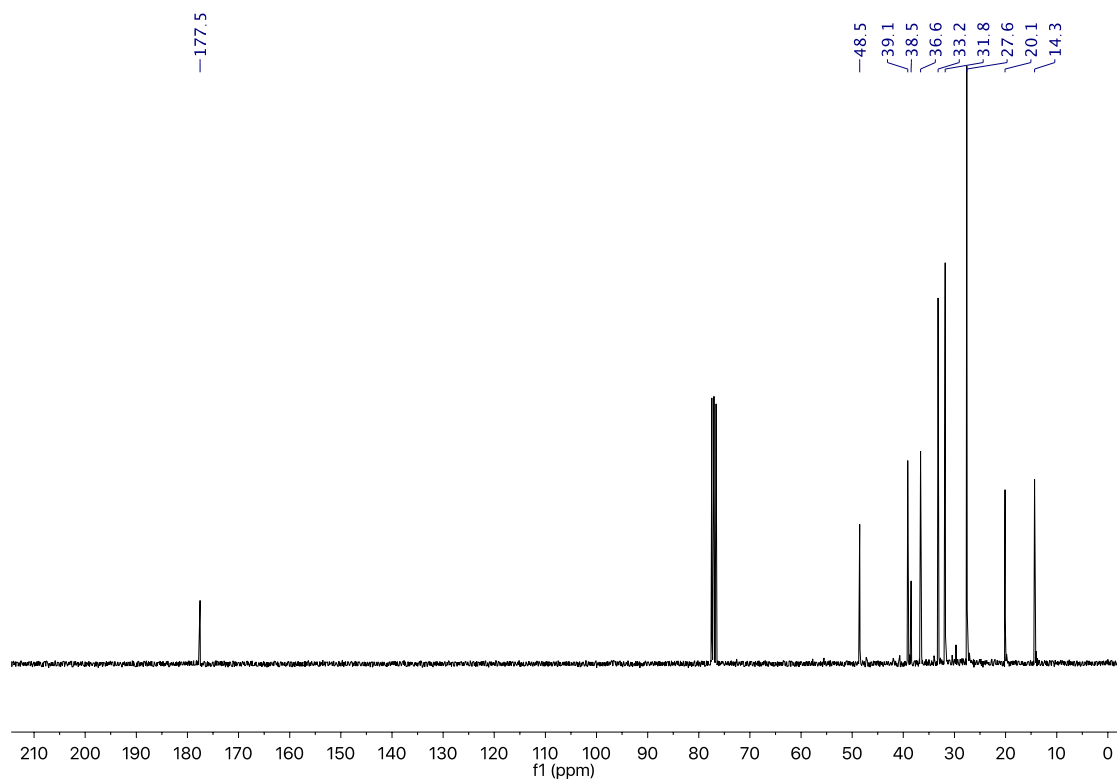
 $^1\text{H-NMR}$ of **4a** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **4a** in CDCl_3 

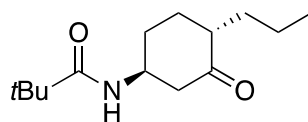
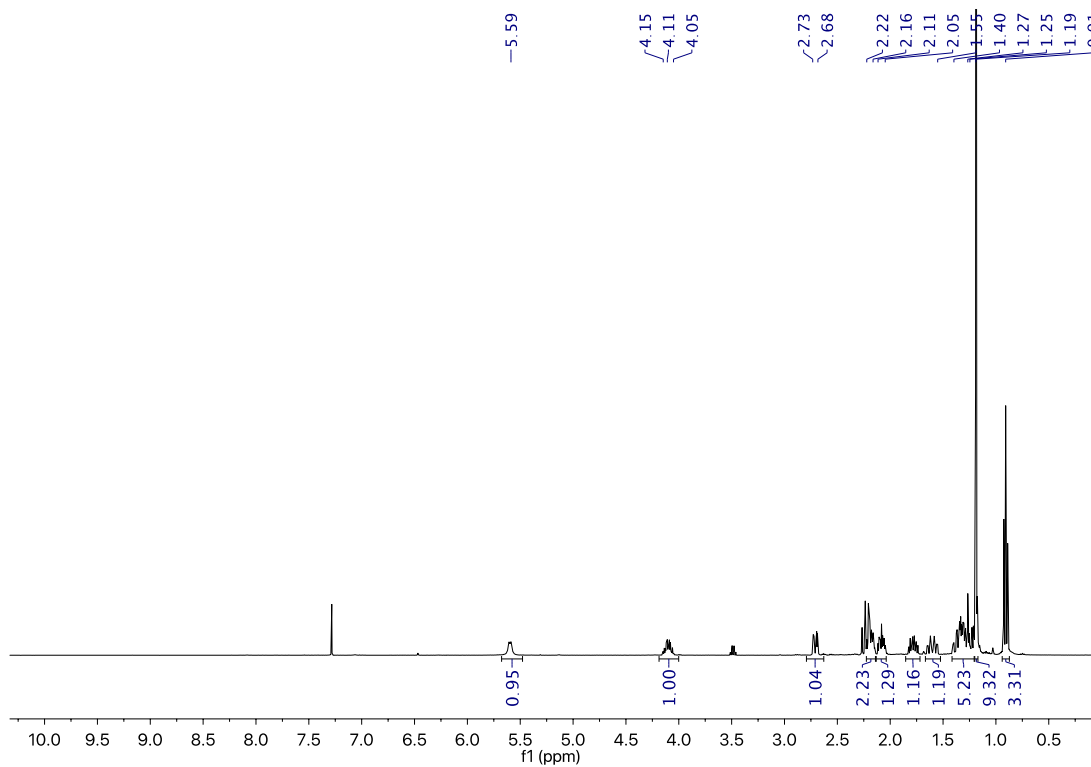
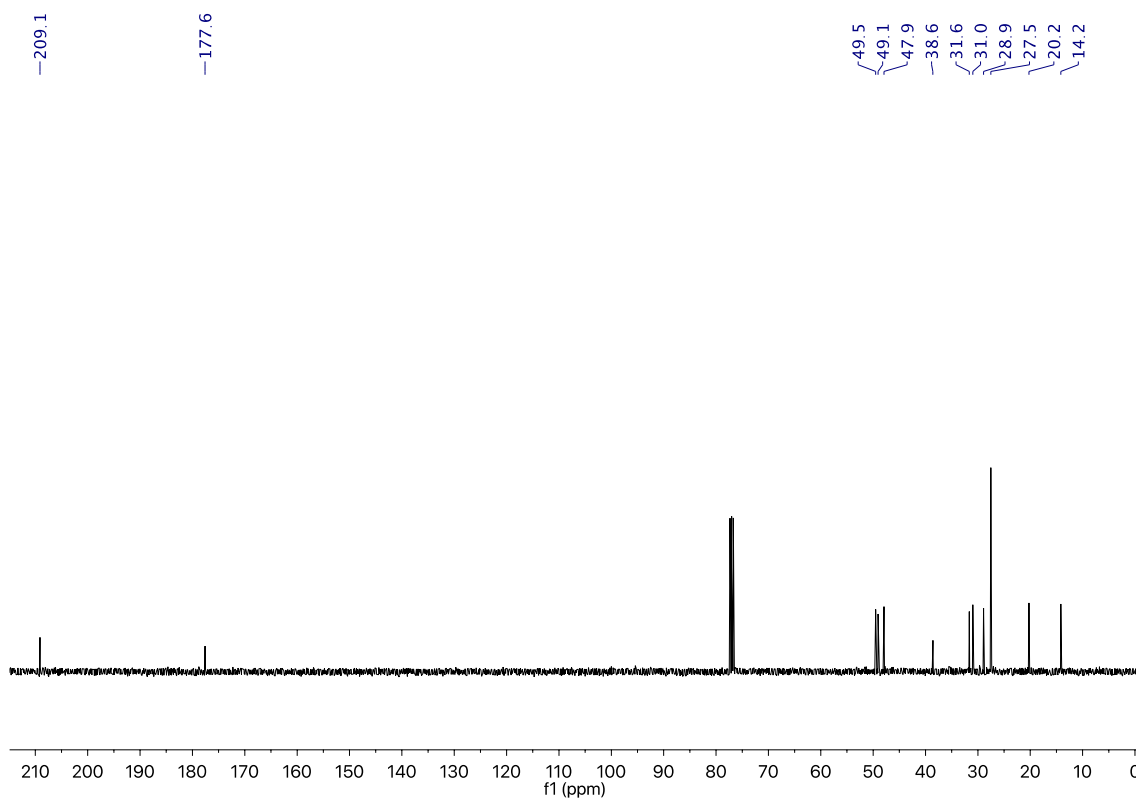
 $^1\text{H-NMR}$ of **4b** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **4b** in CDCl_3 

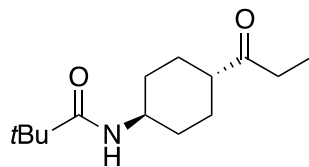
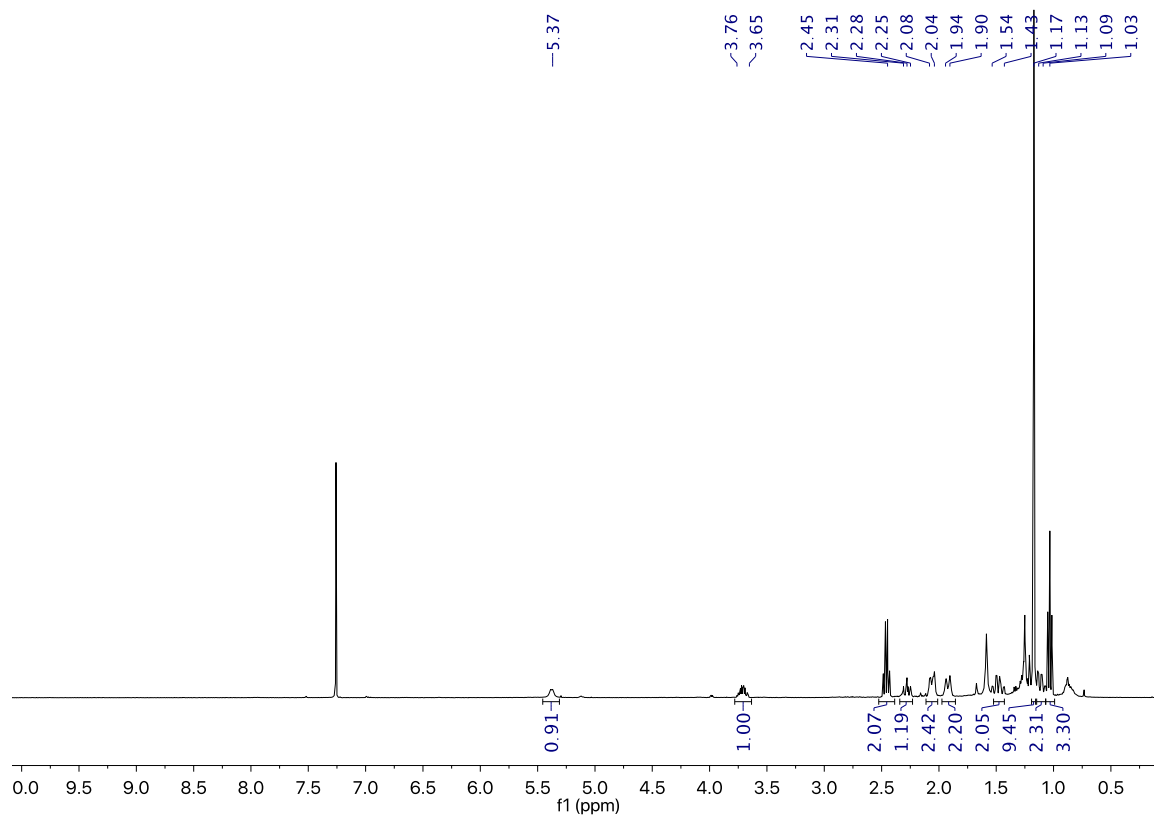
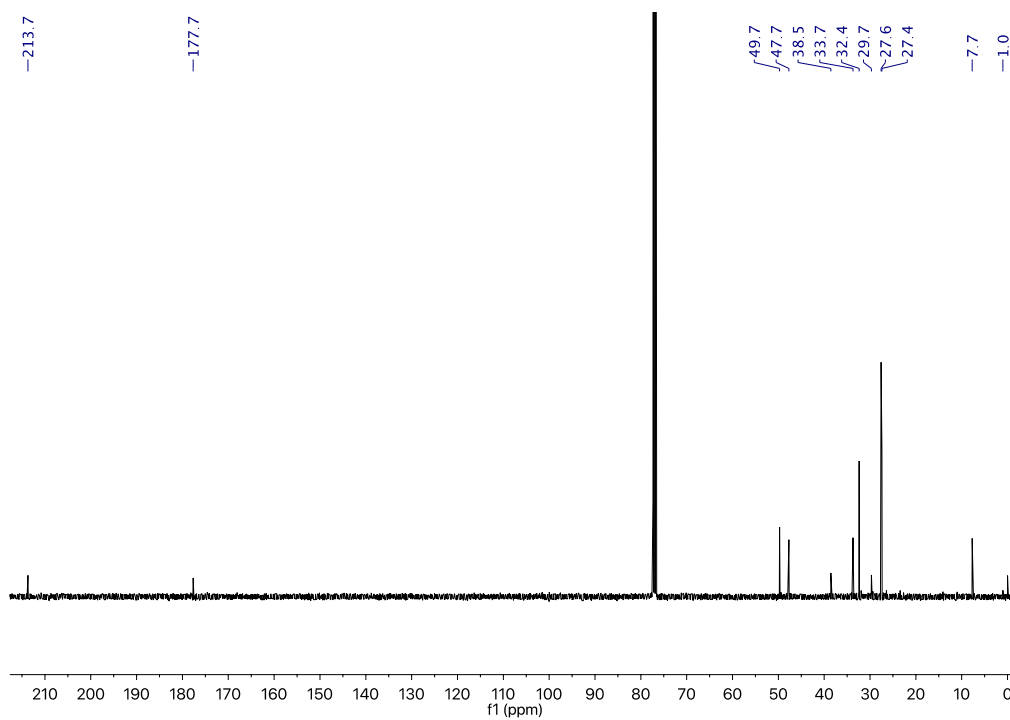
 $^1\text{H-NMR}$ of *trans*-5 in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of *trans*-5 in CDCl_3 

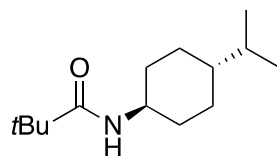
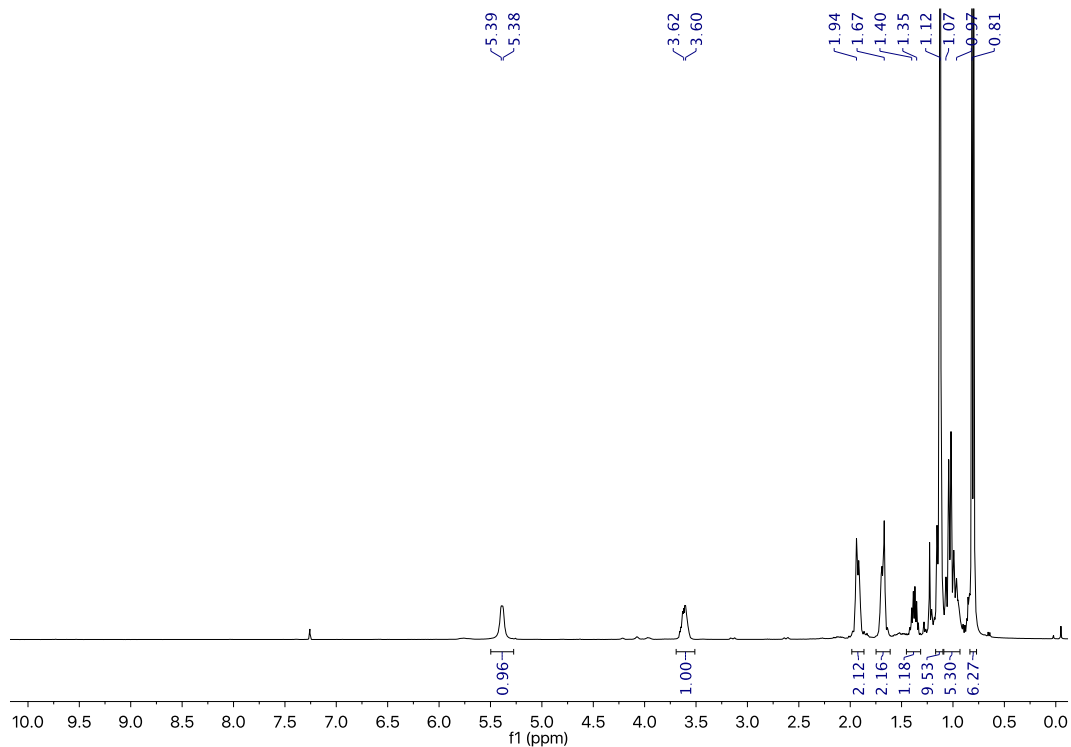
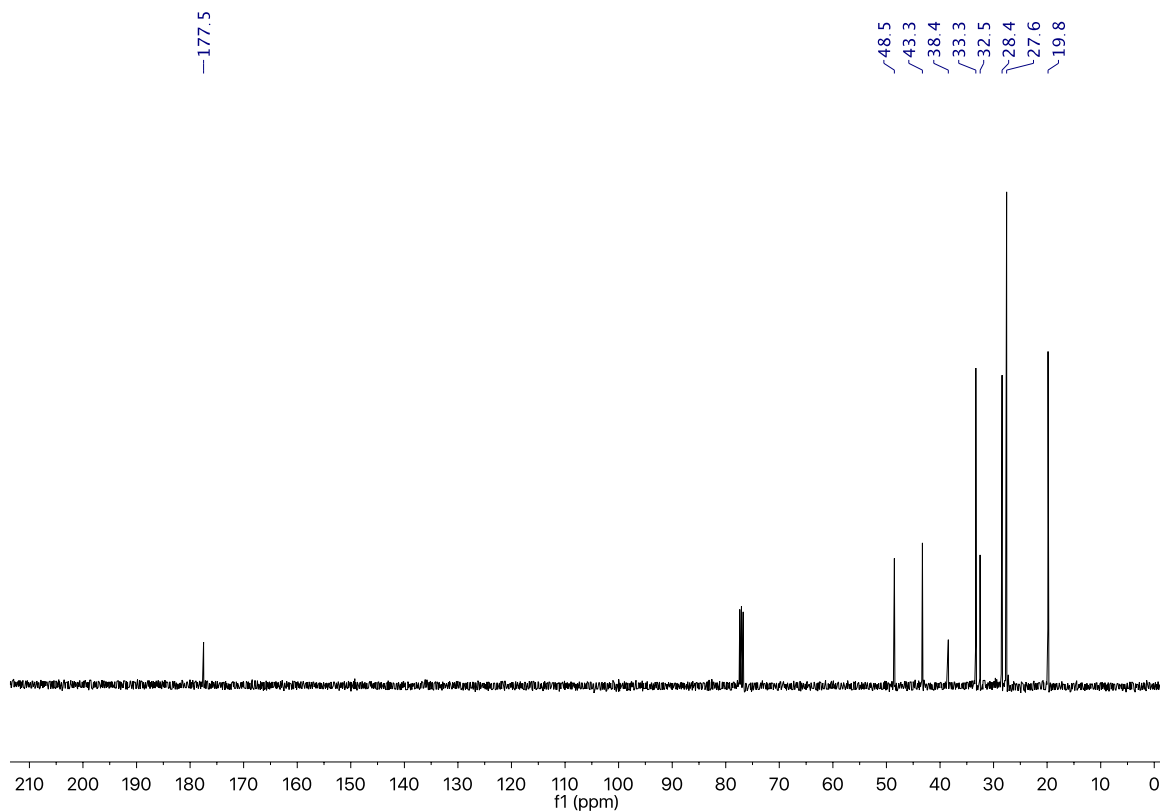
 $^1\text{H-NMR}$ of **5a** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **5a** in CDCl_3 

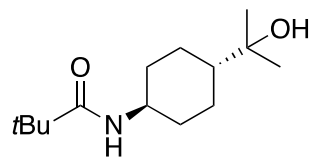
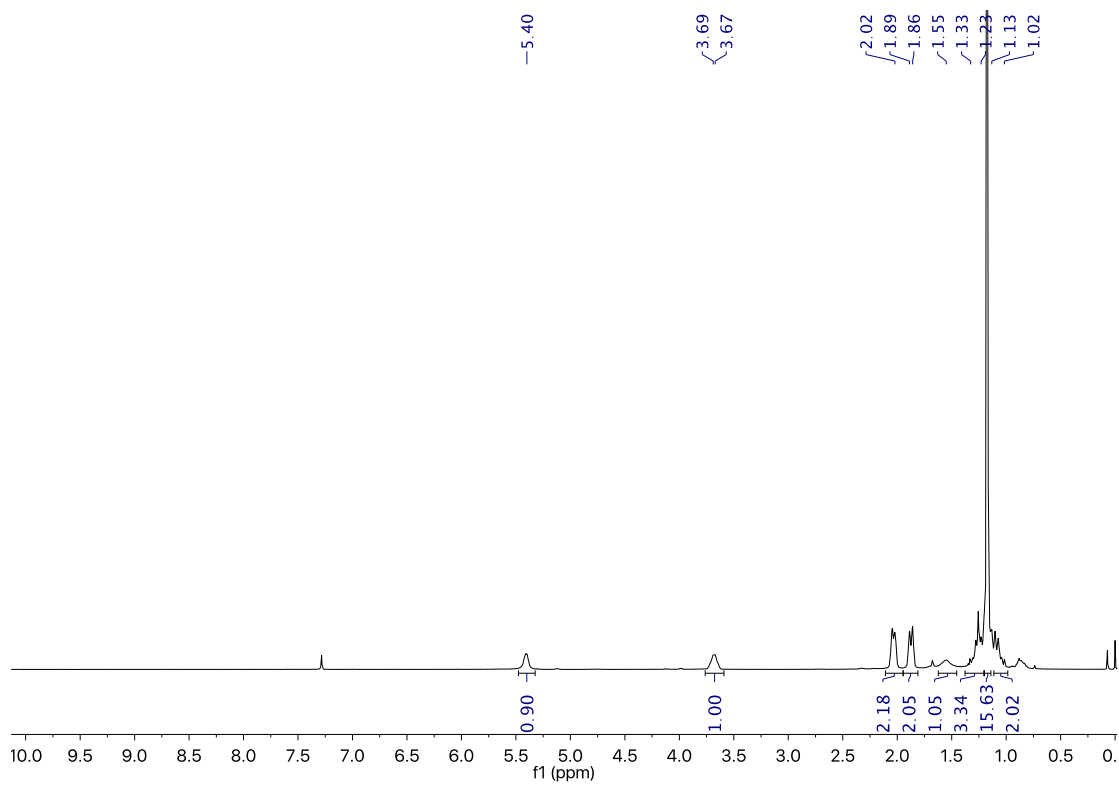
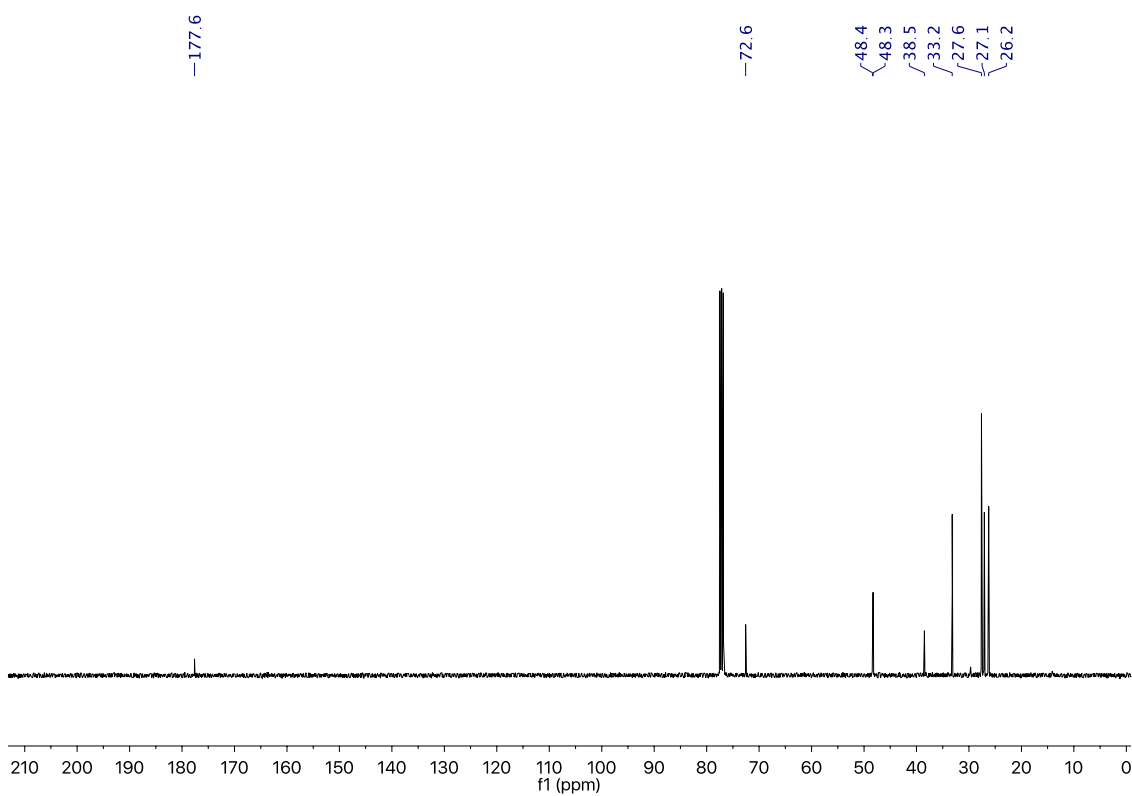
 $^1\text{H-NMR}$ of **5b** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **5b** in CDCl_3 

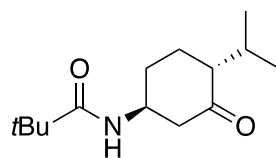
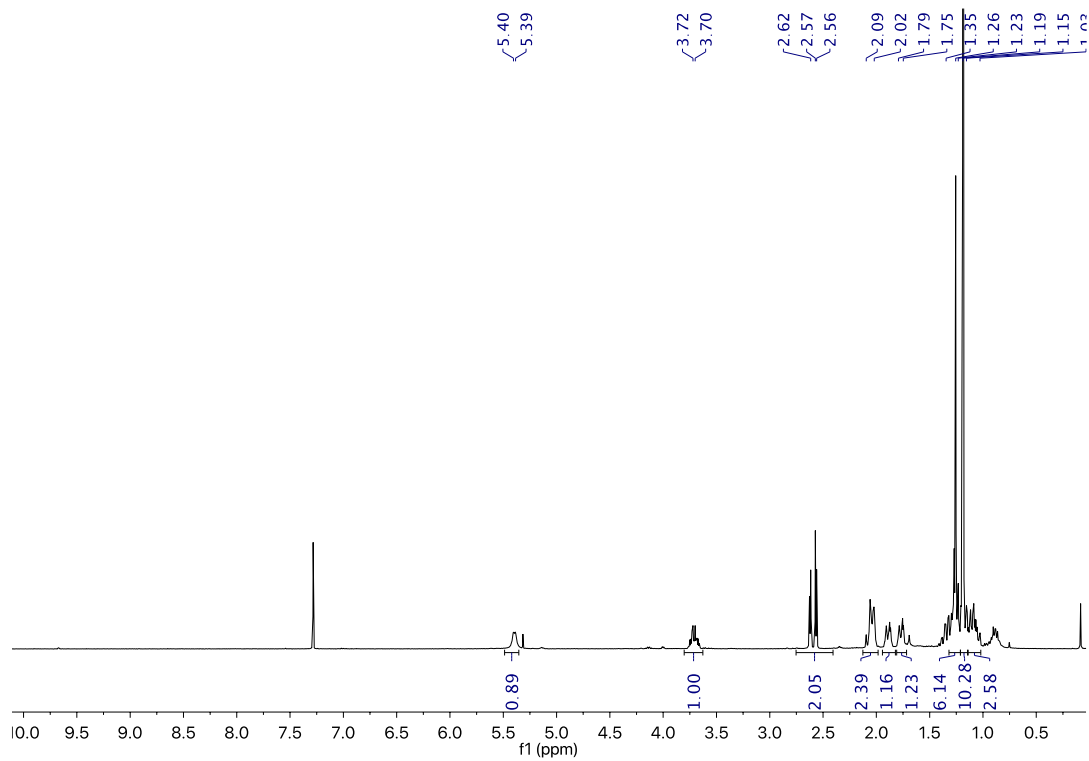
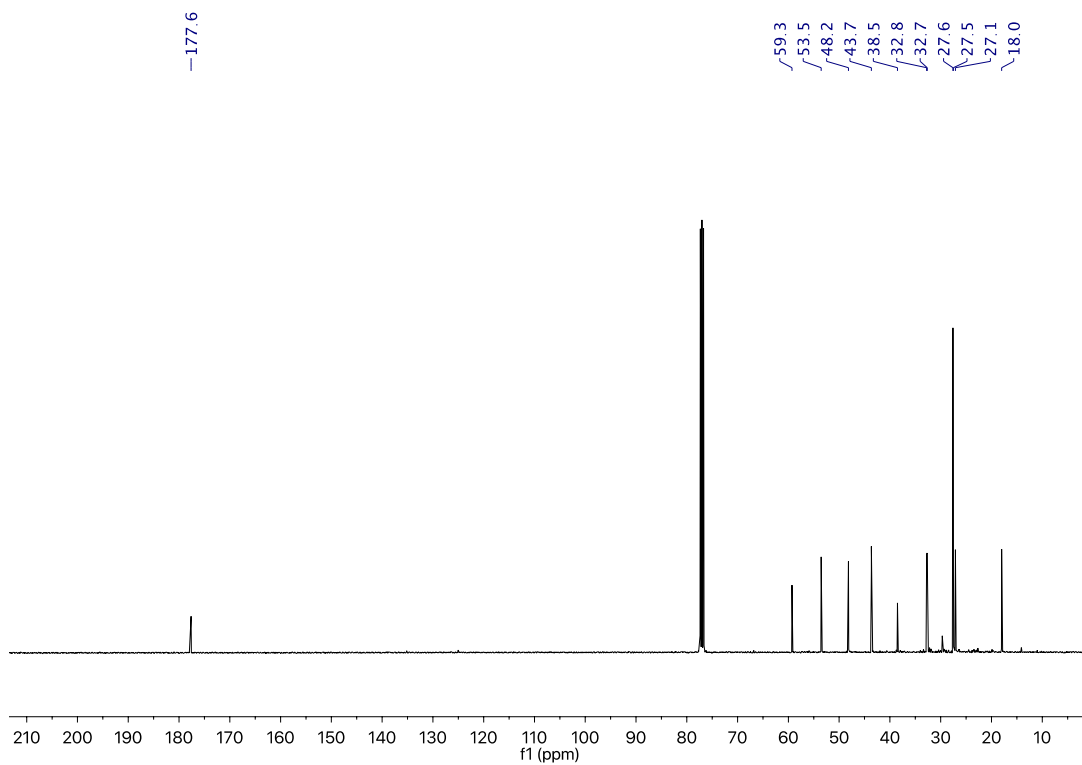
 $^1\text{H-NMR}$ of *trans*-6 in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of *trans*-6 in CDCl_3 

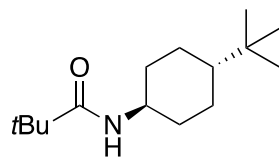
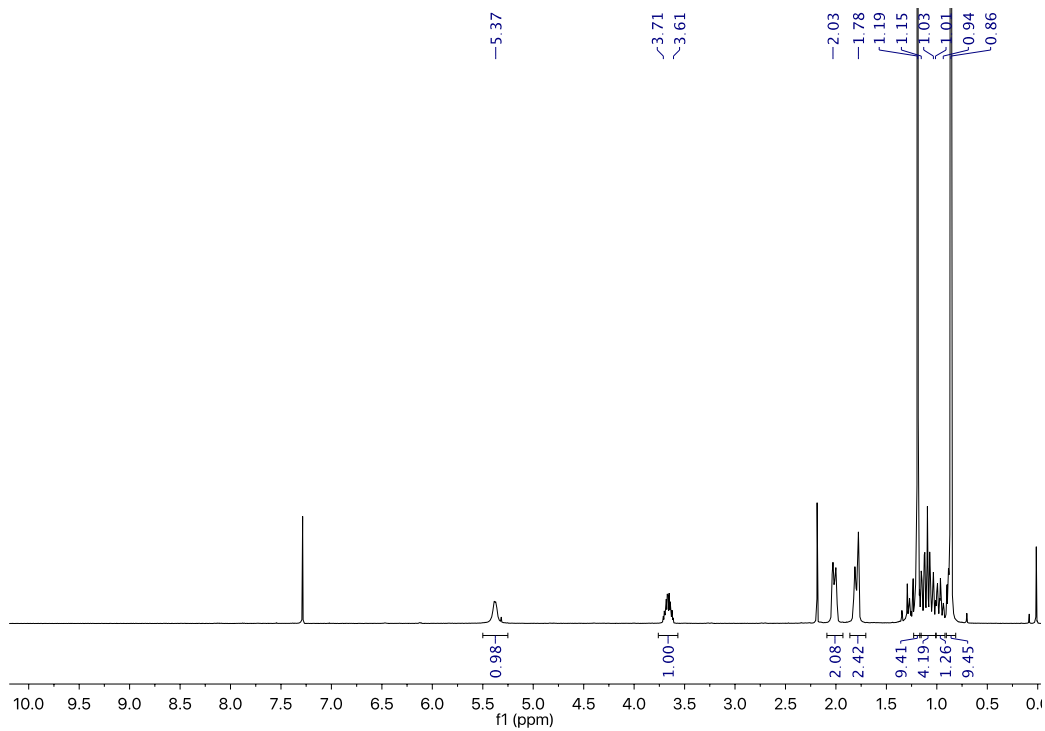
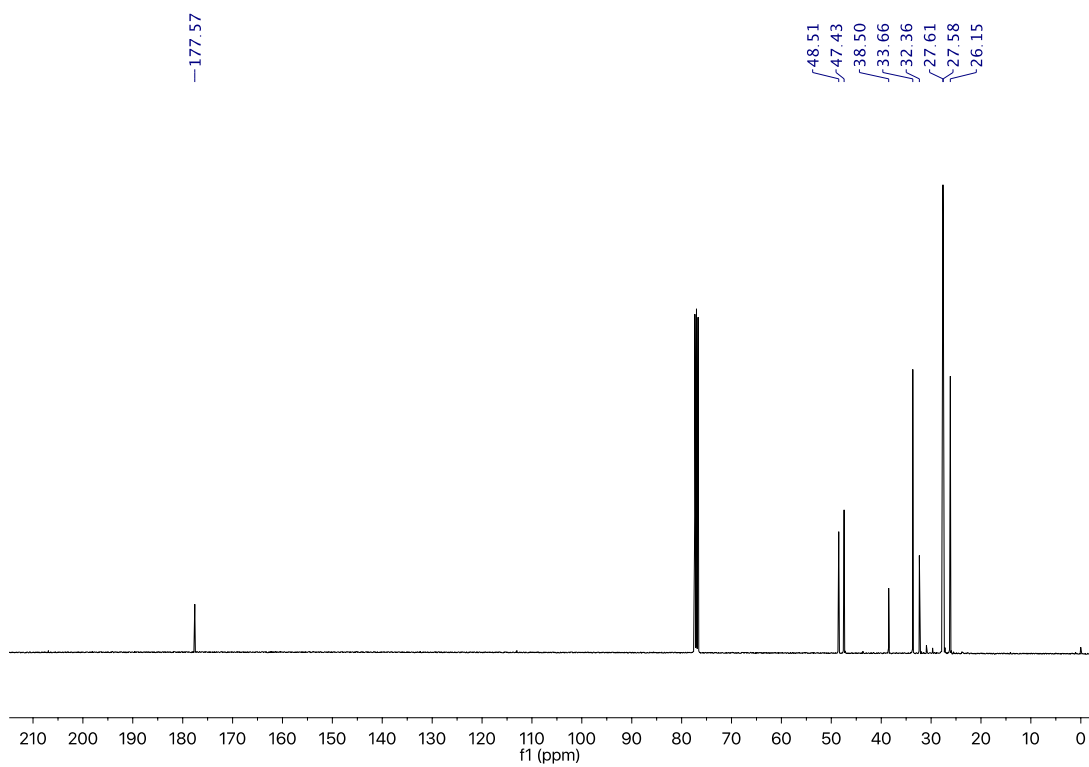
 $^1\text{H-NMR}$ of **6a** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **6a** in CDCl_3 

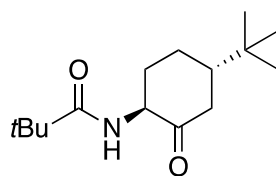
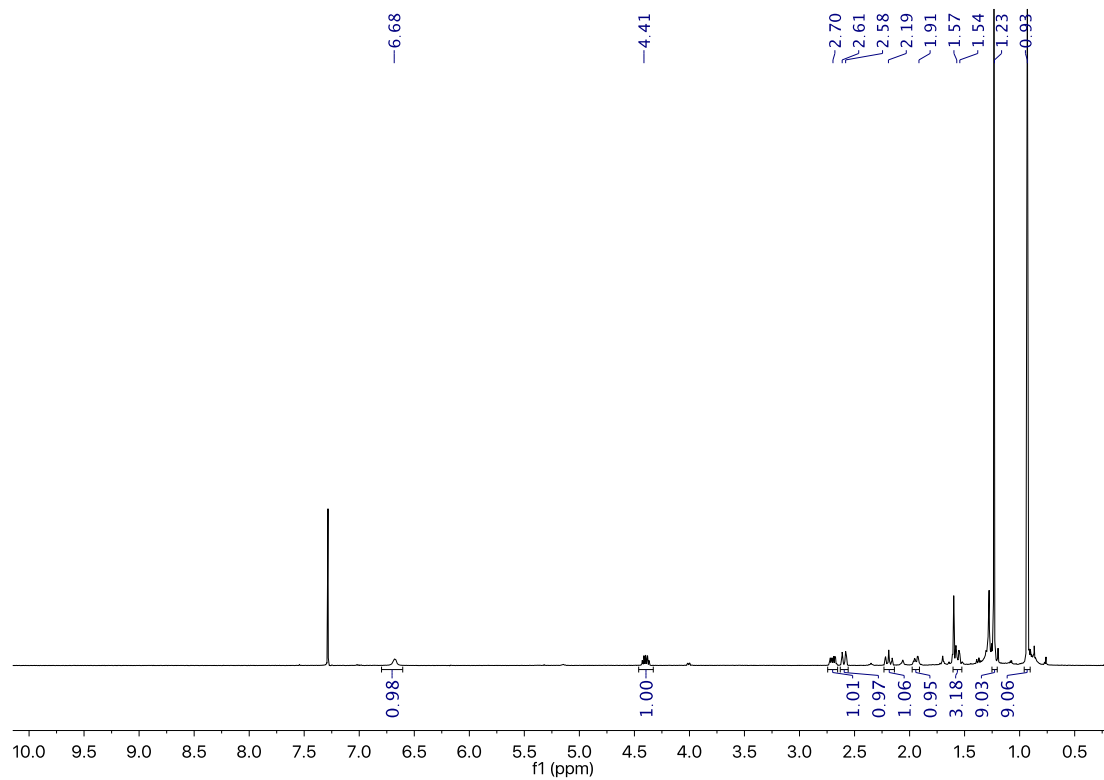
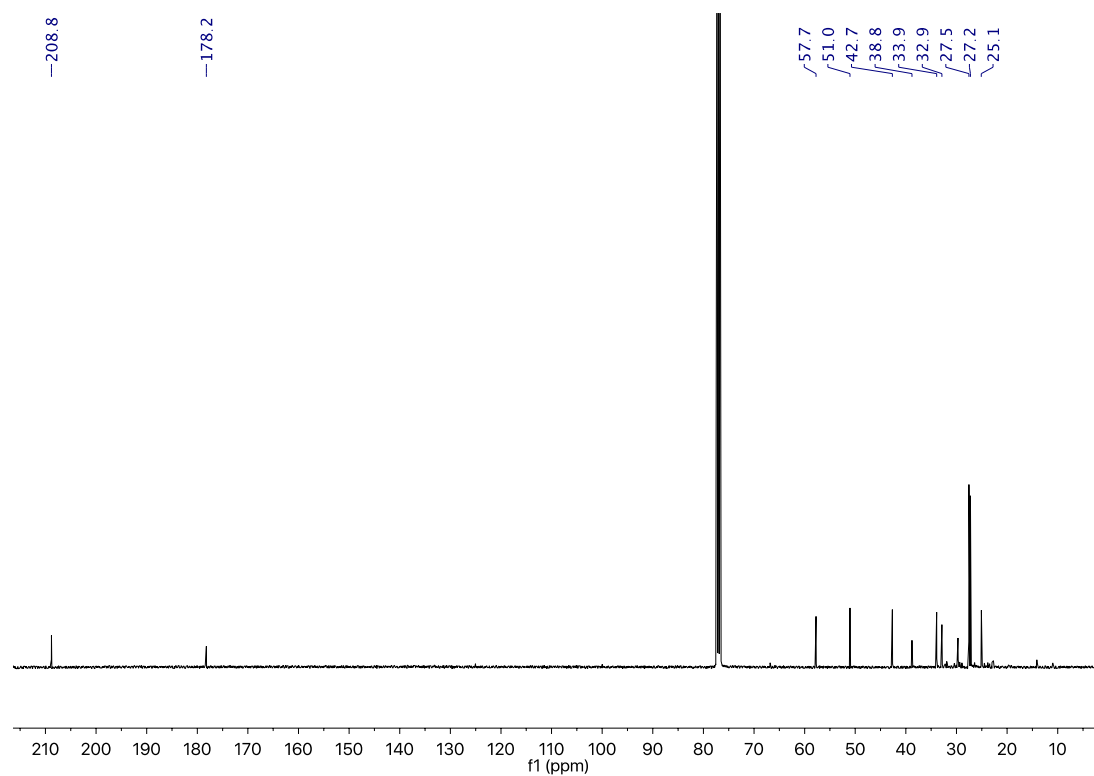
 $^1\text{H-NMR}$ of **6b** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **6b** in CDCl_3 

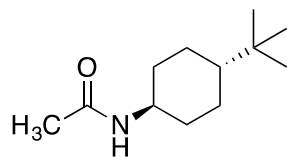
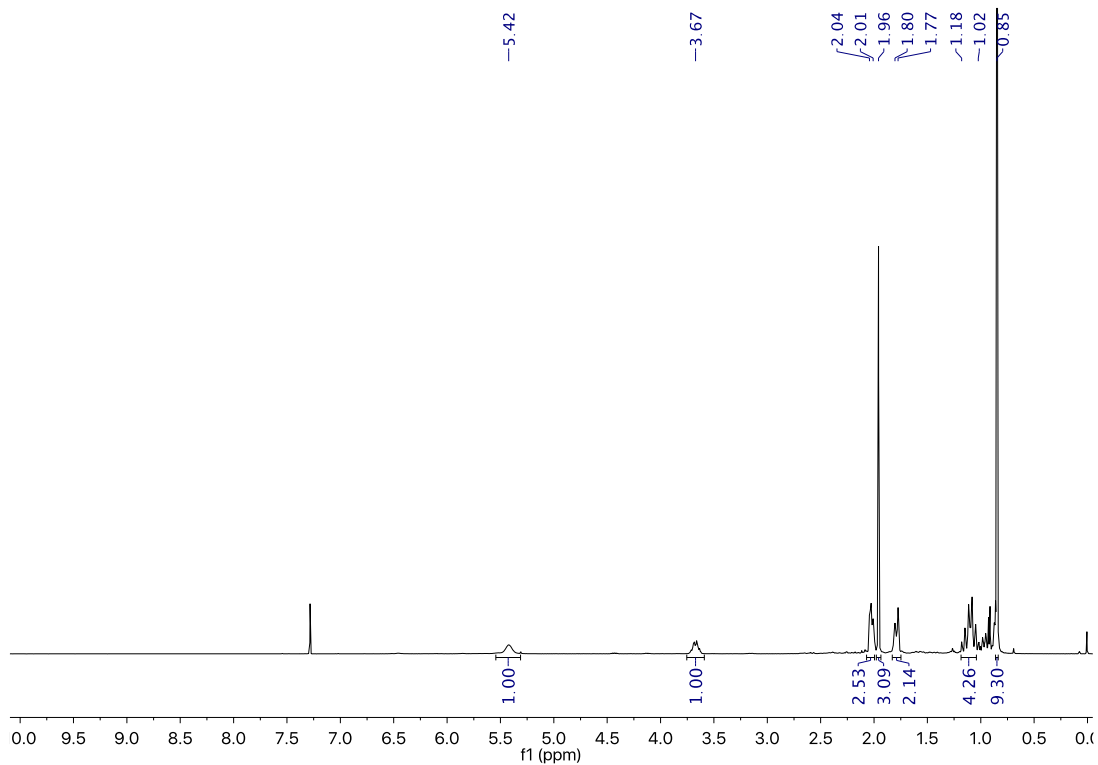
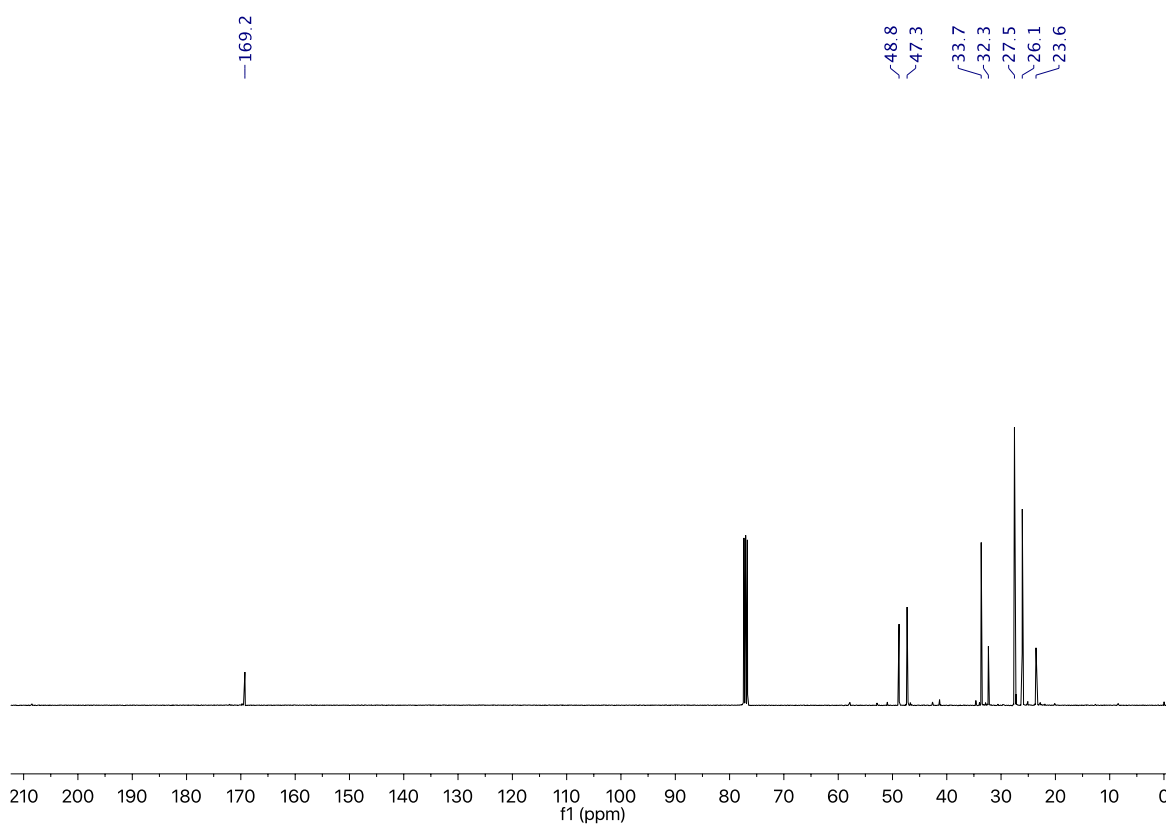
 $^1\text{H-NMR}$ of *trans*-7 in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of *trans*-7 in CDCl_3 

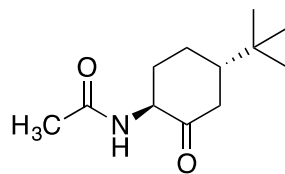
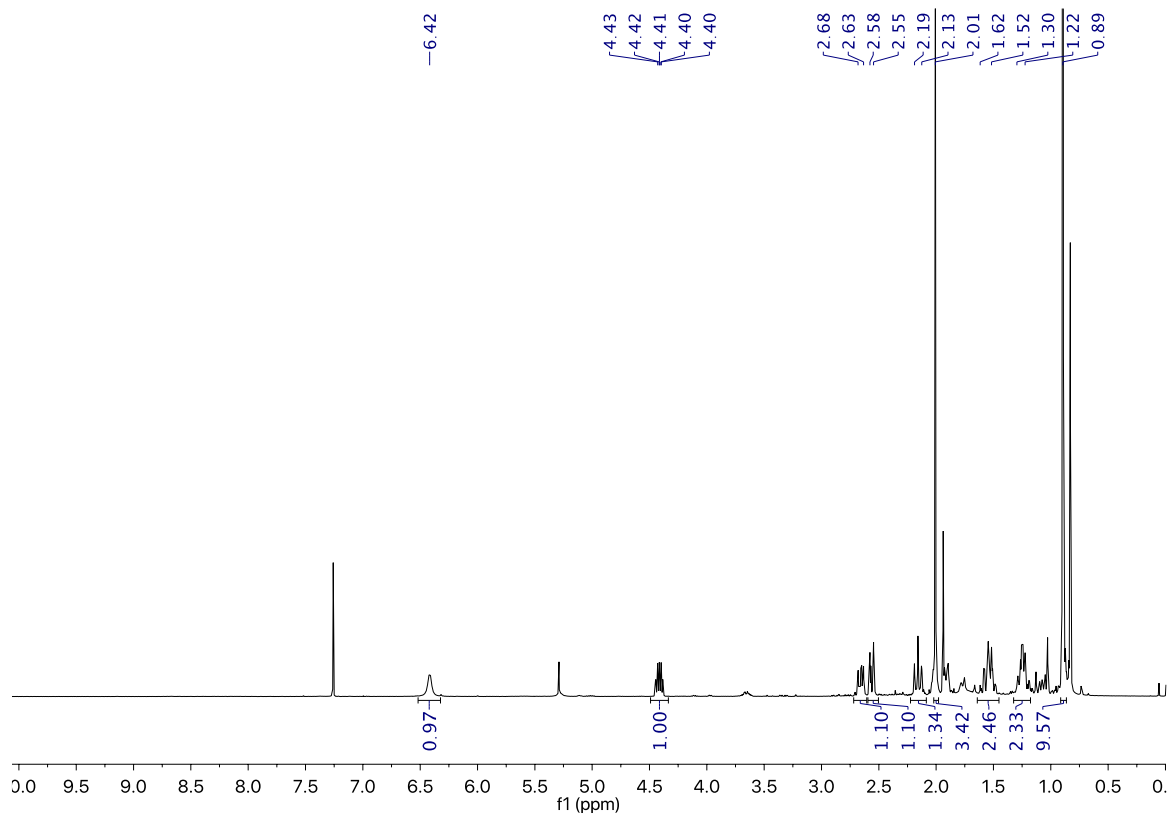
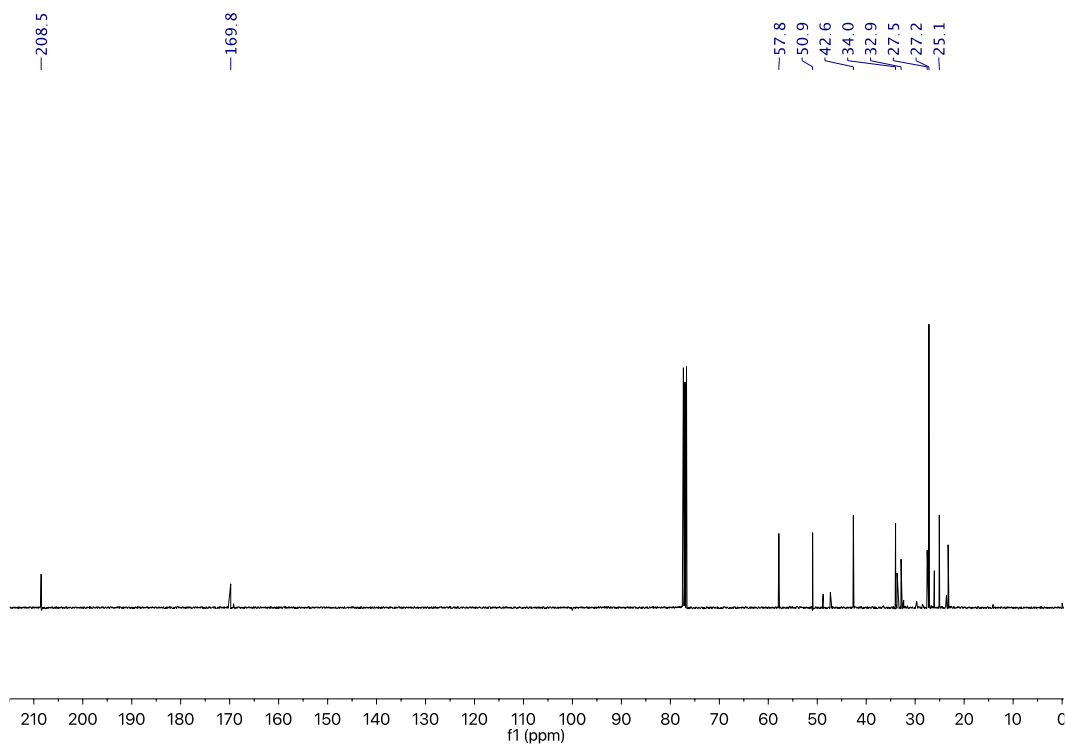
 $^1\text{H-NMR}$ of **7a** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **7a** in CDCl_3 

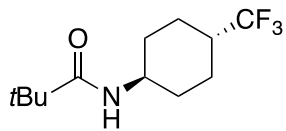
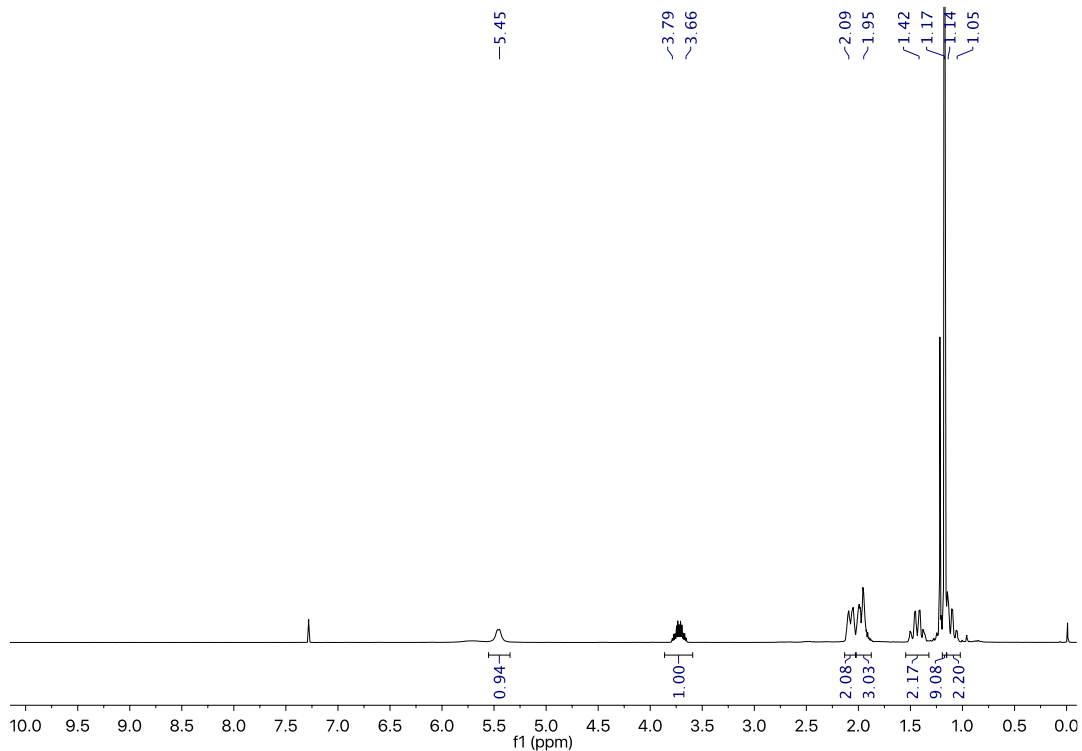
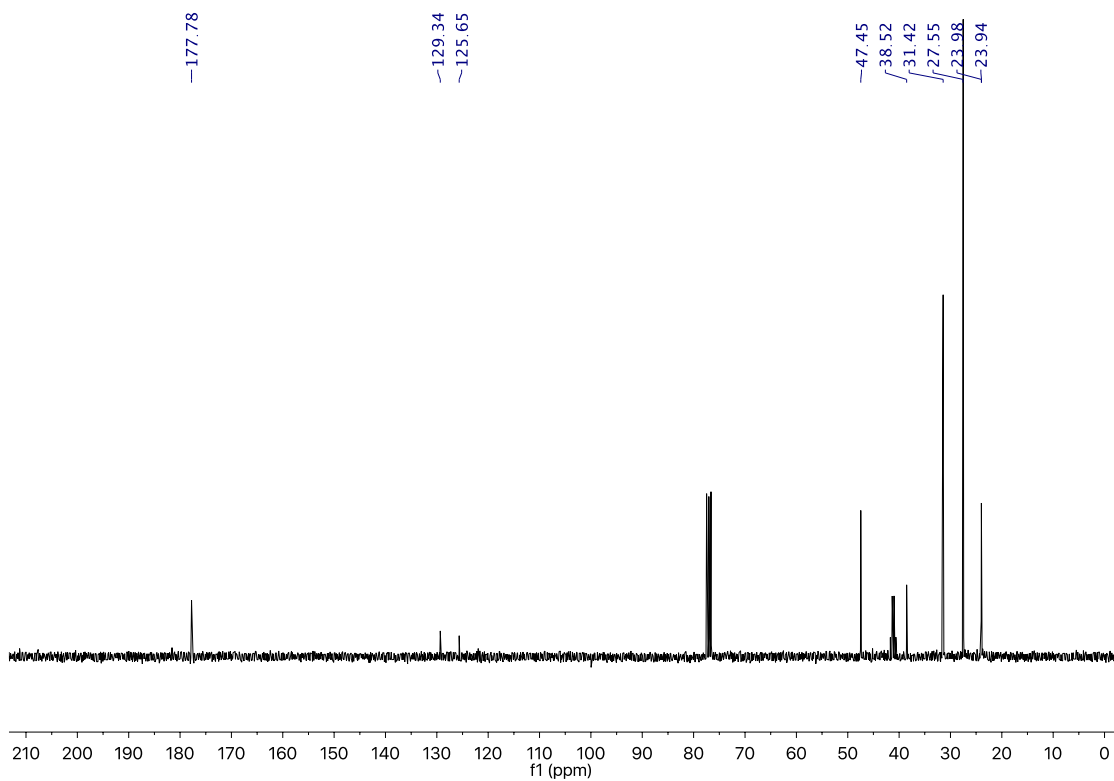
 $^1\text{H-NMR}$ of **7b** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **7b** in CDCl_3 

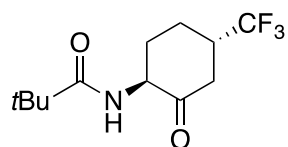
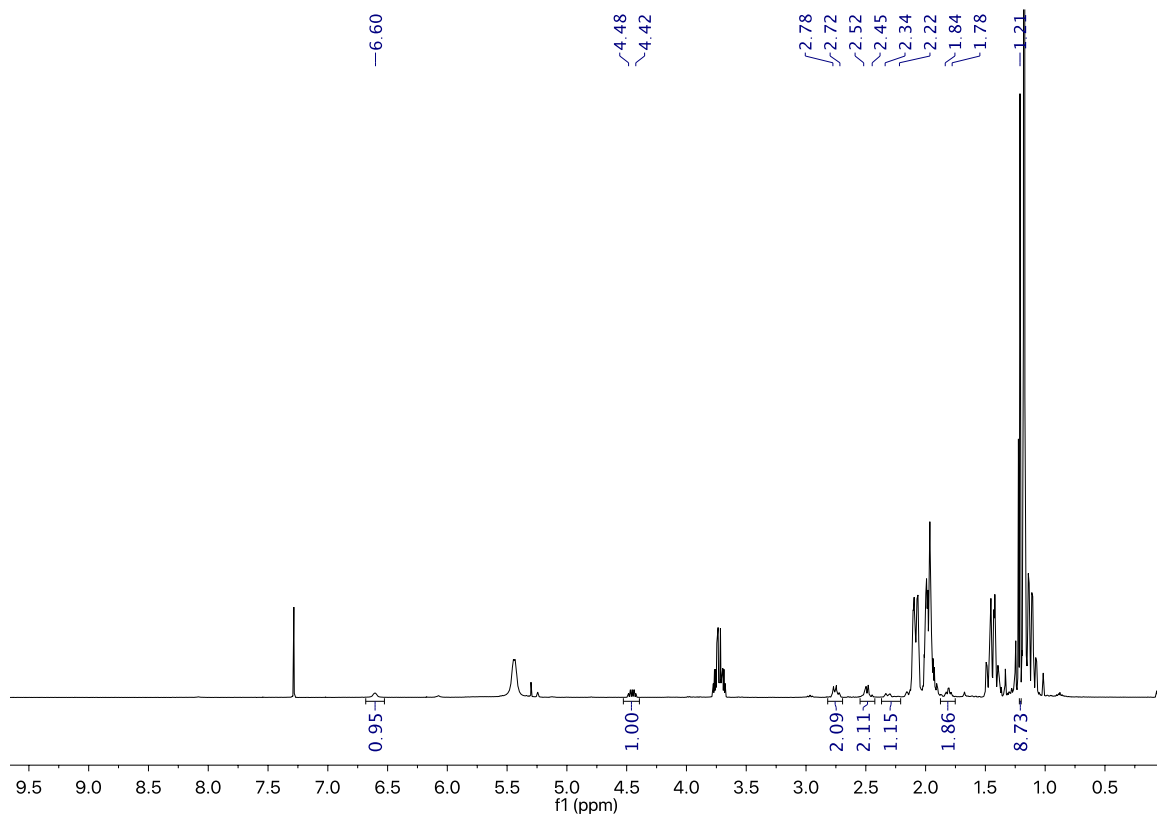
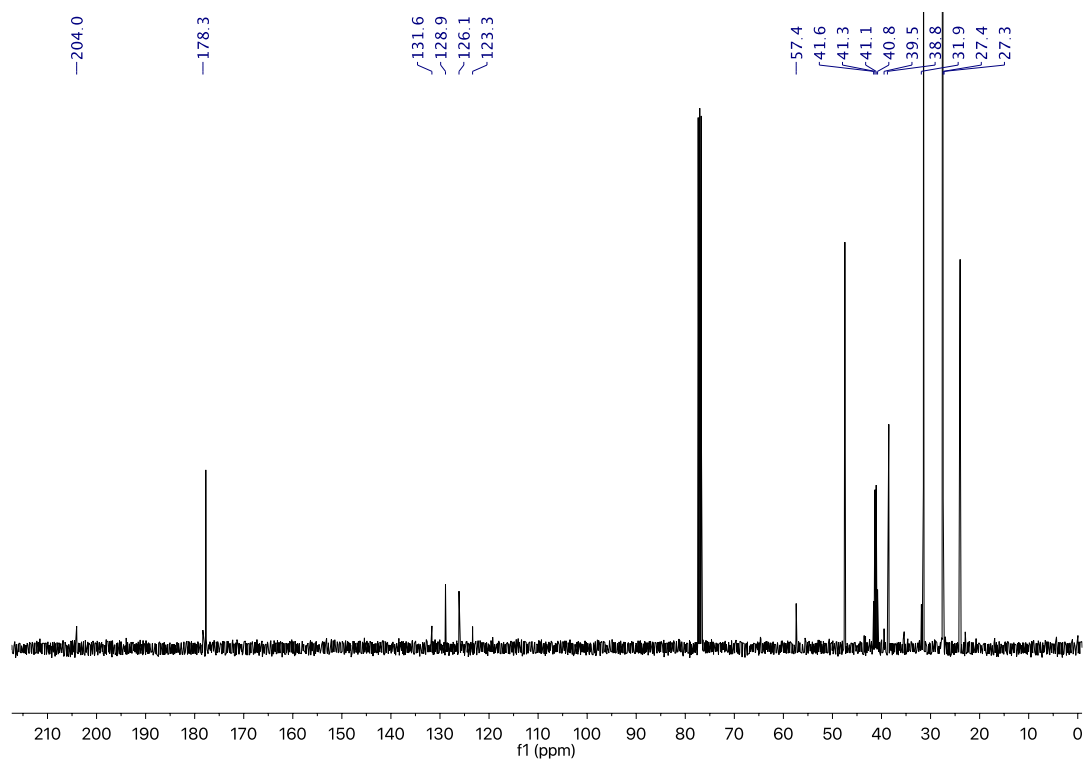
 $^1\text{H-NMR}$ of *trans*-**8** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of *trans*-**8** in CDCl_3 

 $^1\text{H-NMR}$ of **8a** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **8a** in CDCl_3 

 $^1\text{H-NMR}$ of *trans*-9 in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of *trans*-9 in CDCl_3 

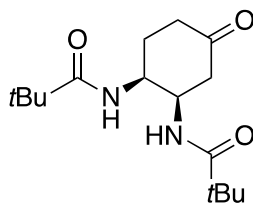
 $^1\text{H-NMR}$ of **9a** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **9a** in CDCl_3 

 $^1\text{H-NMR}$ of *trans*-**10** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of *trans*-**10** in CDCl_3 

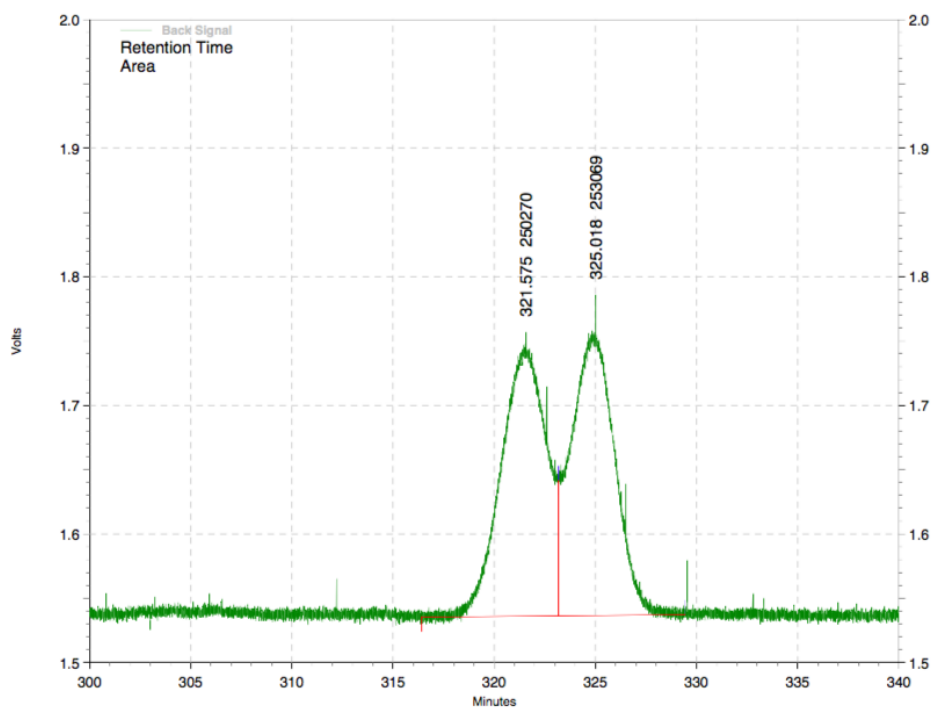
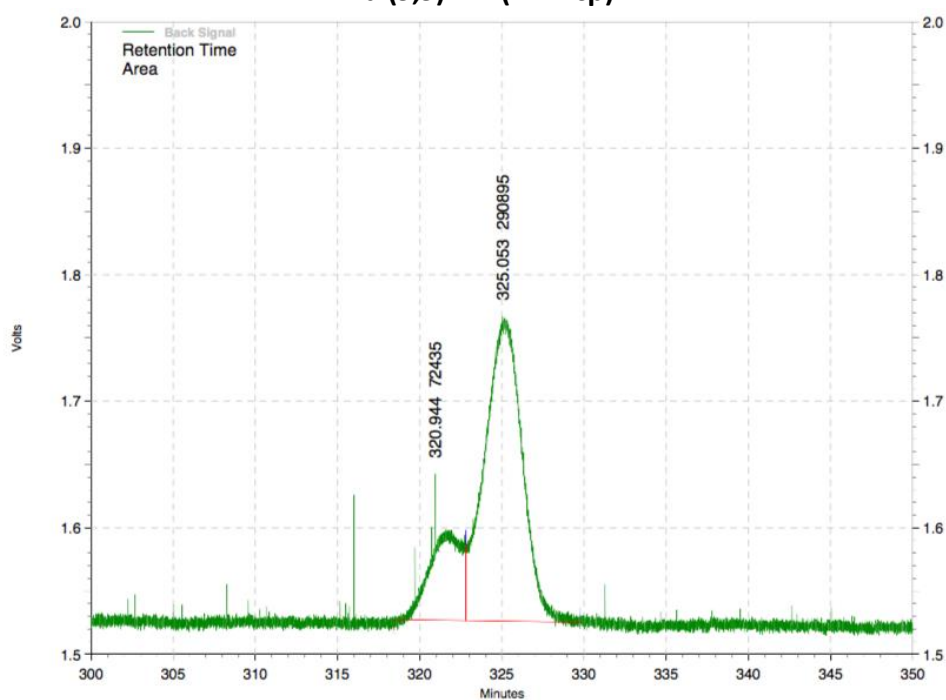
 $^1\text{H-NMR}$ of **10a** in CDCl_3  $^{13}\text{C}\{^1\text{H}\}$ -NMR of **10a** in CDCl_3 

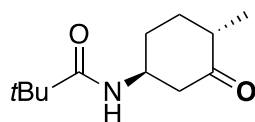
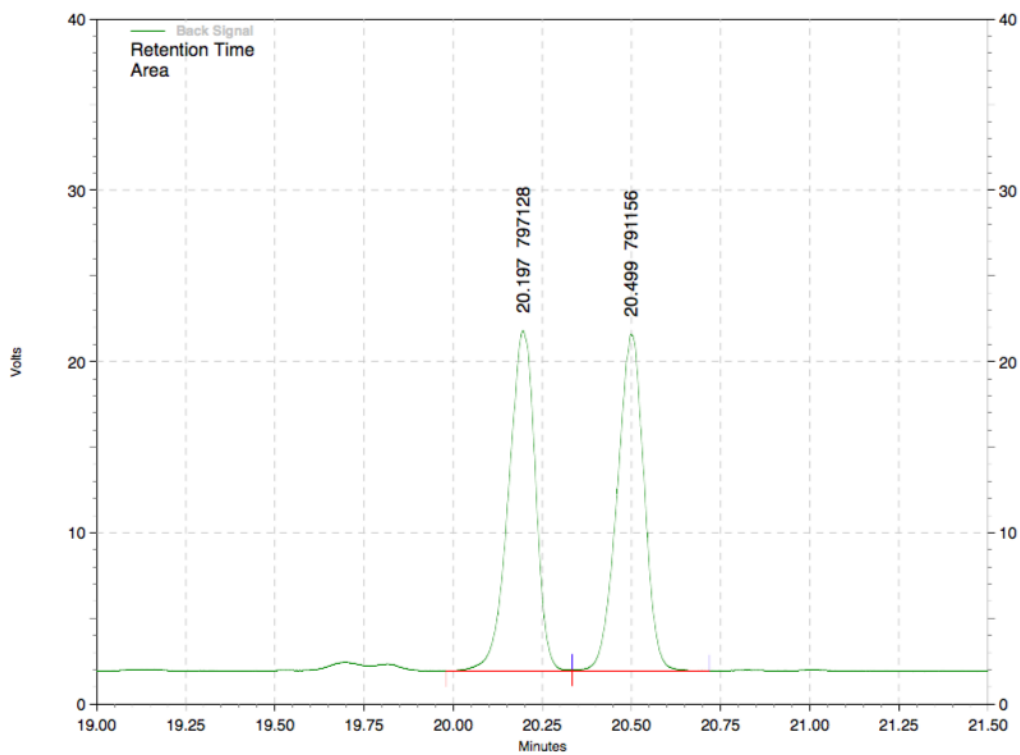
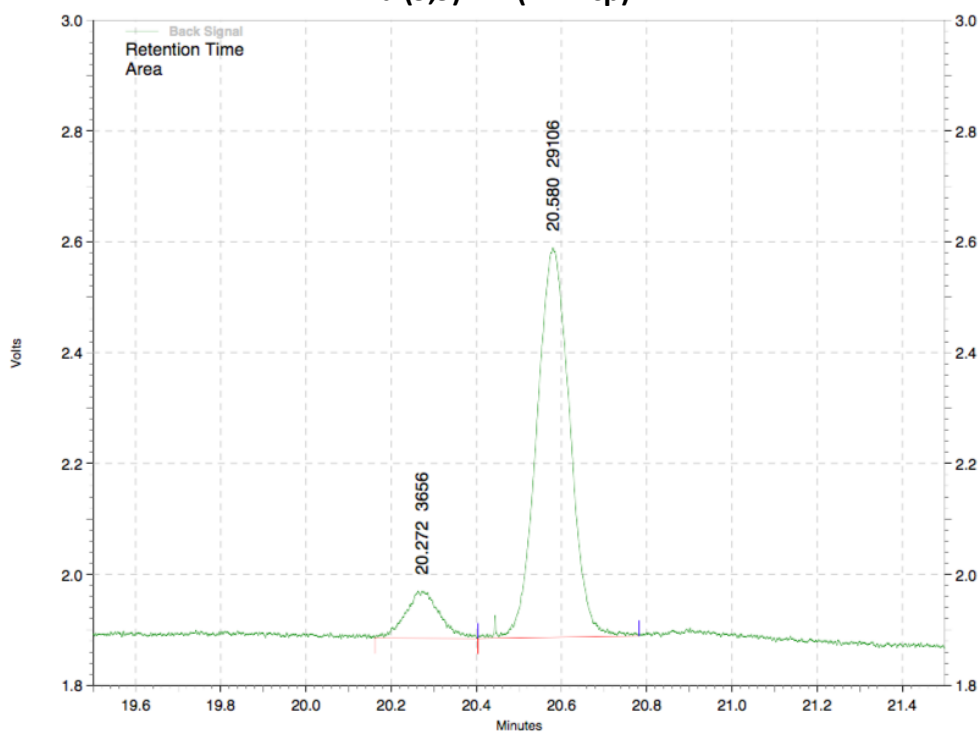
GC Spectra of Products

The racemic products were obtained by using the racemic $[\text{Mn}(\text{CF}_3\text{SO}_3)_2(\text{TIPS}^s\text{mcp})]$ complex.

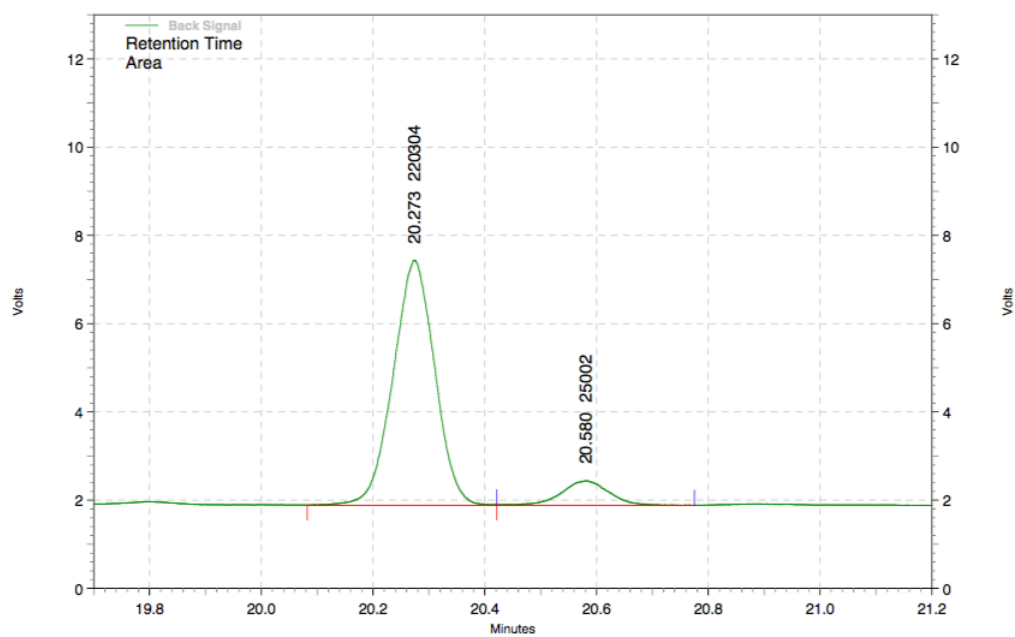


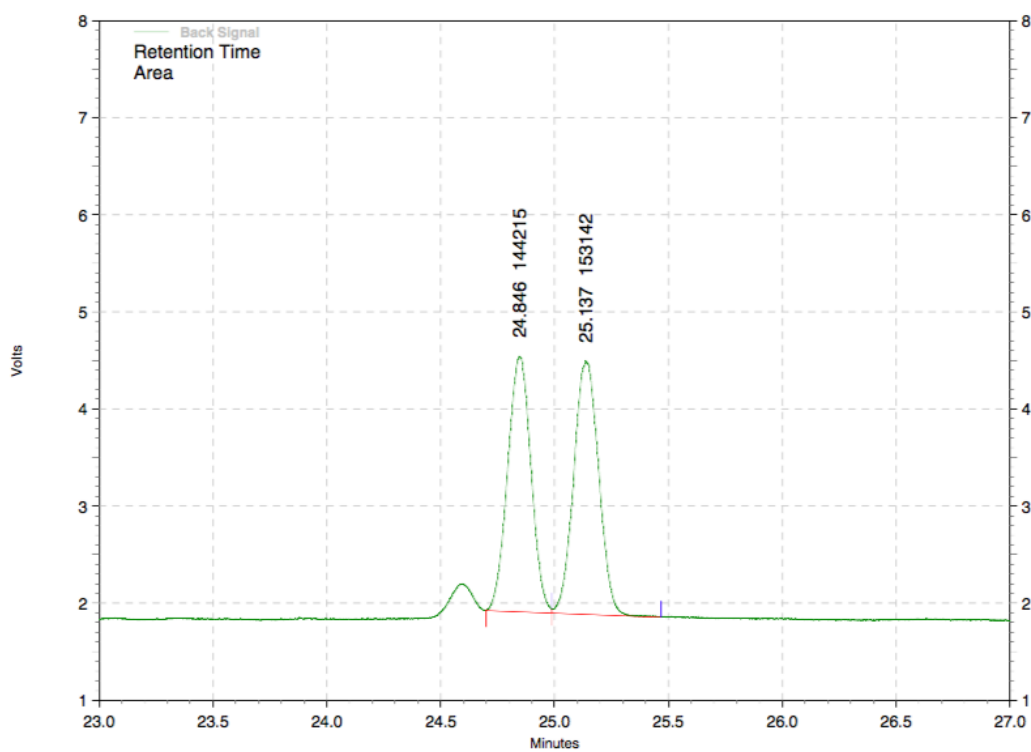
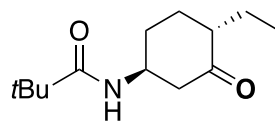
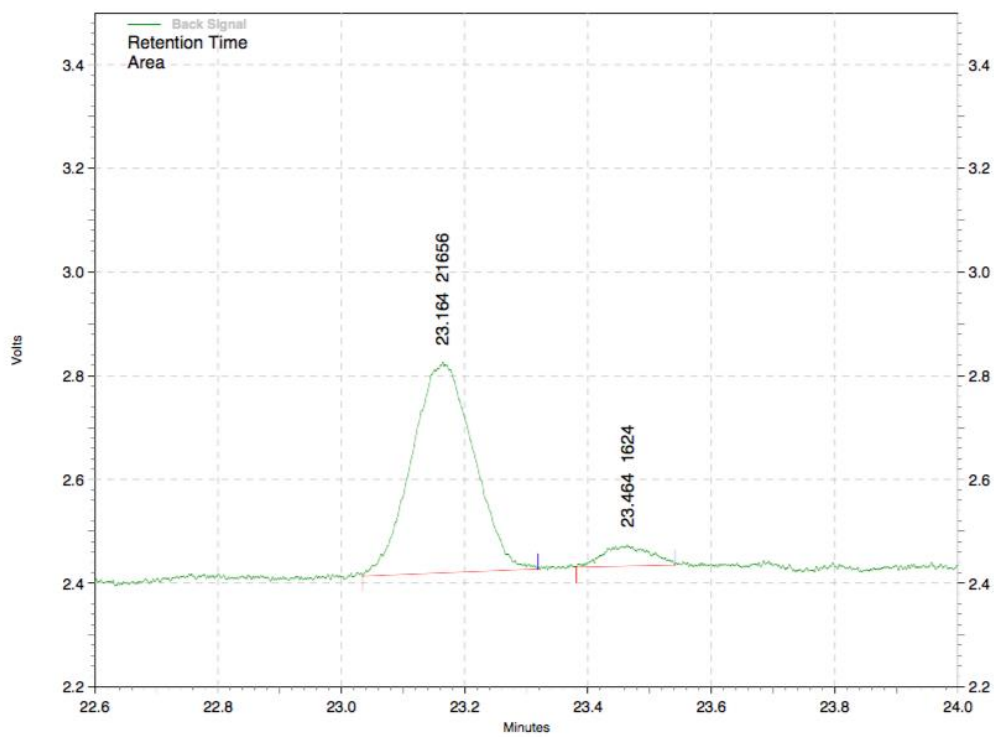
Rac

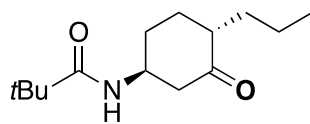
1a (*S,S*)-Mn(TIPS^smcp)

**Rac****4a (S,S)-Mn(TIPS^{mcp})**

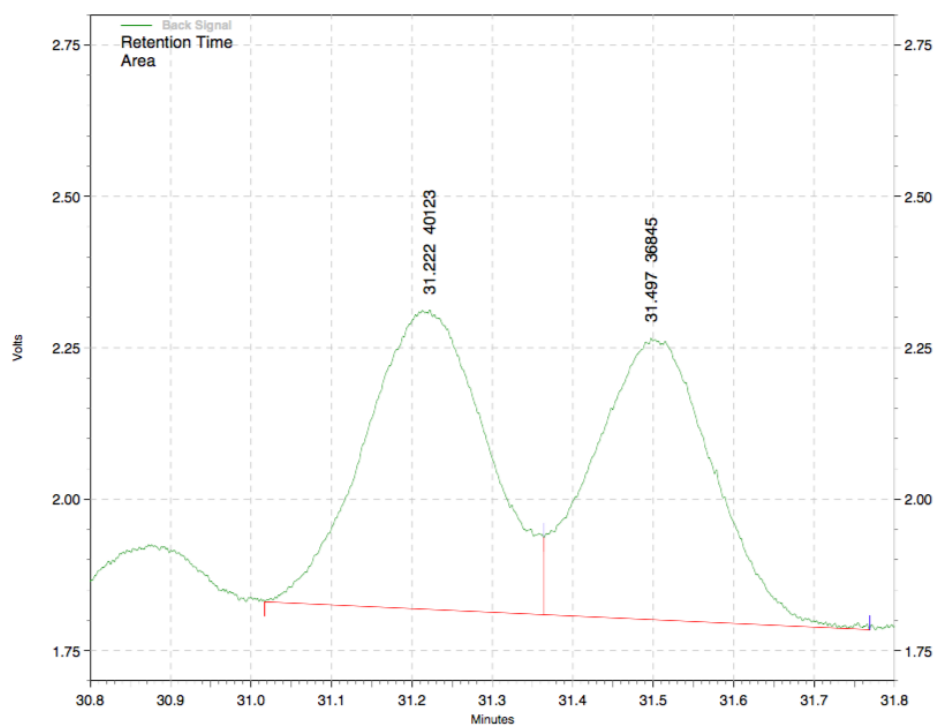
4a (R,R)-Mn(TIPStmcp)



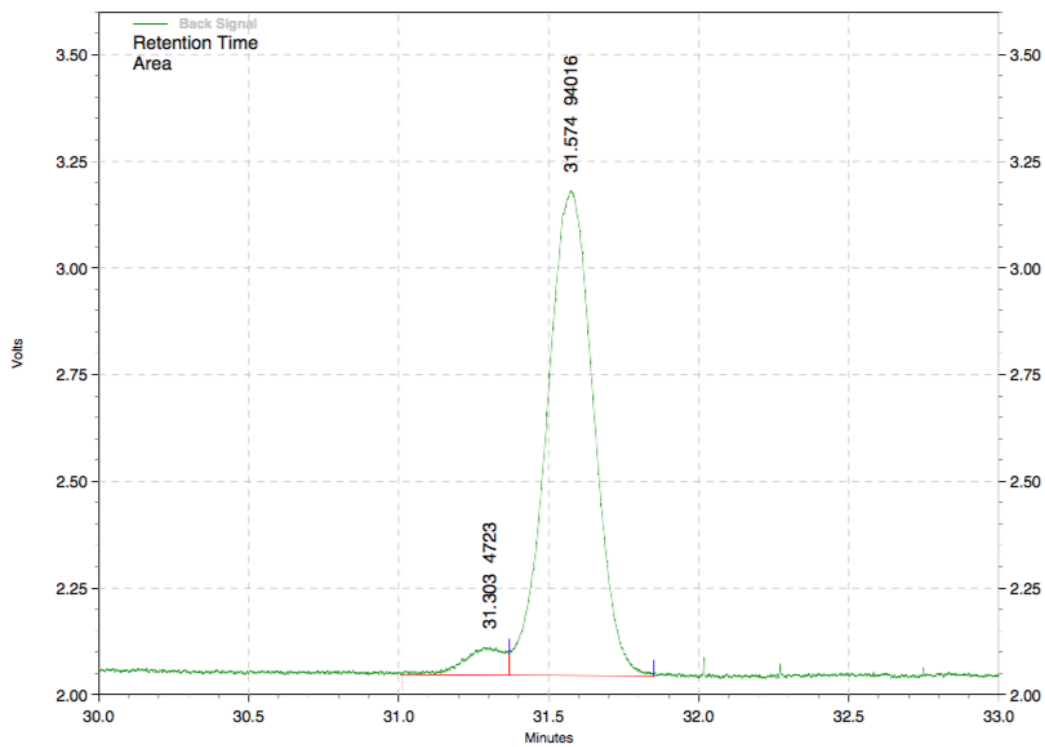
**5a (R,R)-Mn(TIPSMcp)**

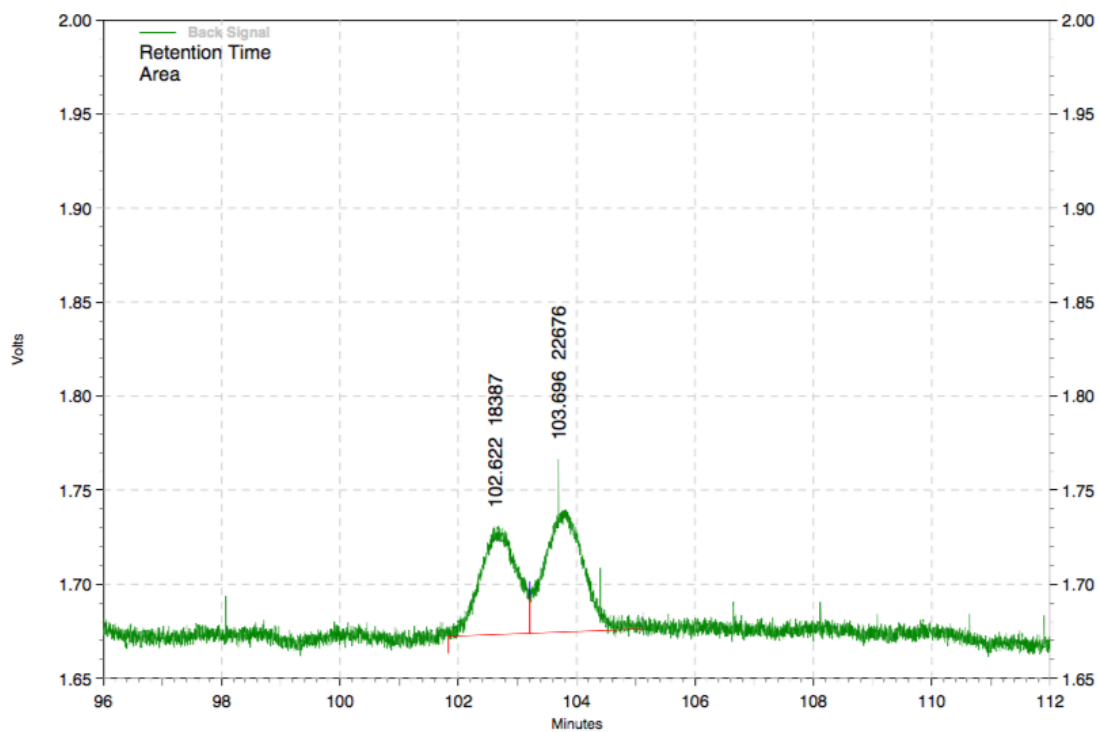
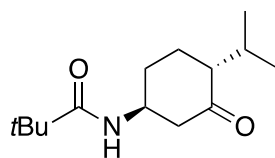
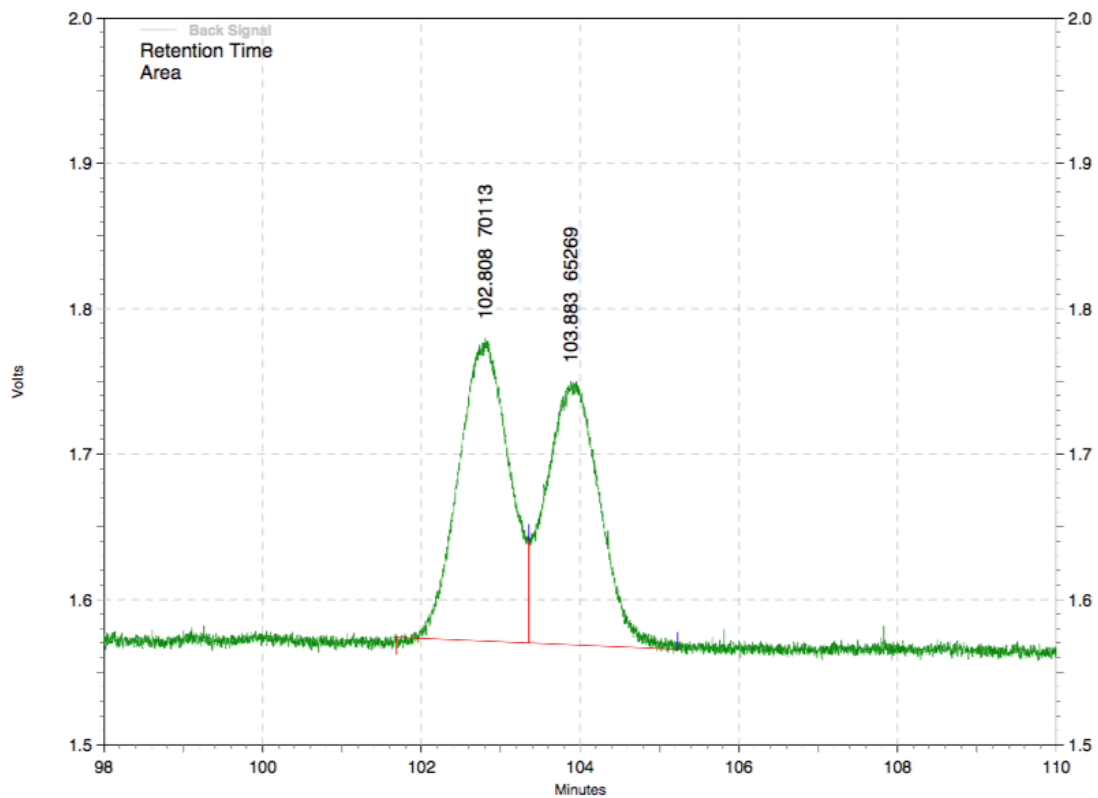


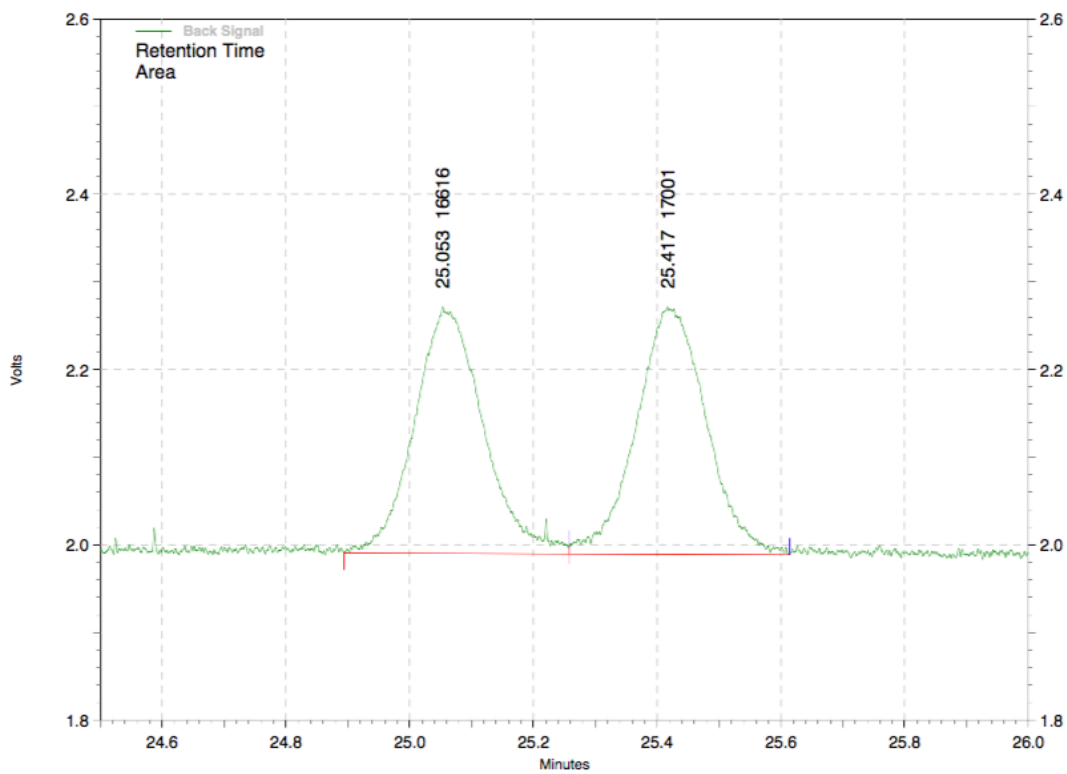
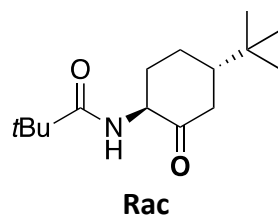
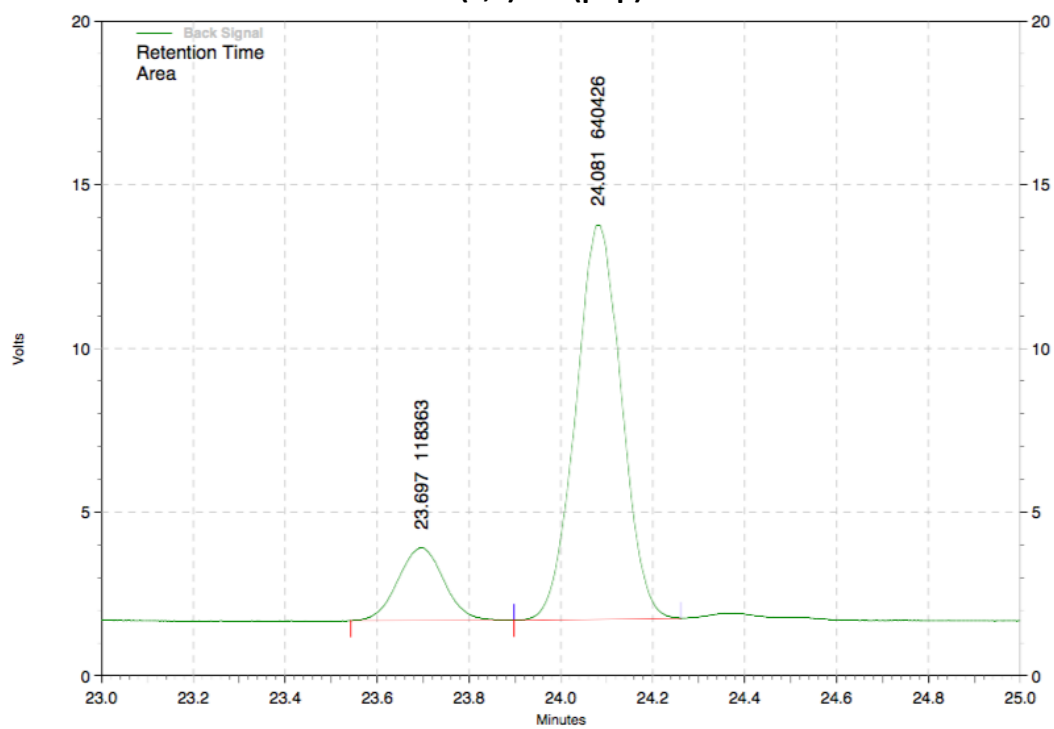
Rac

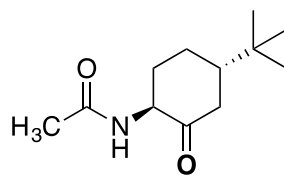
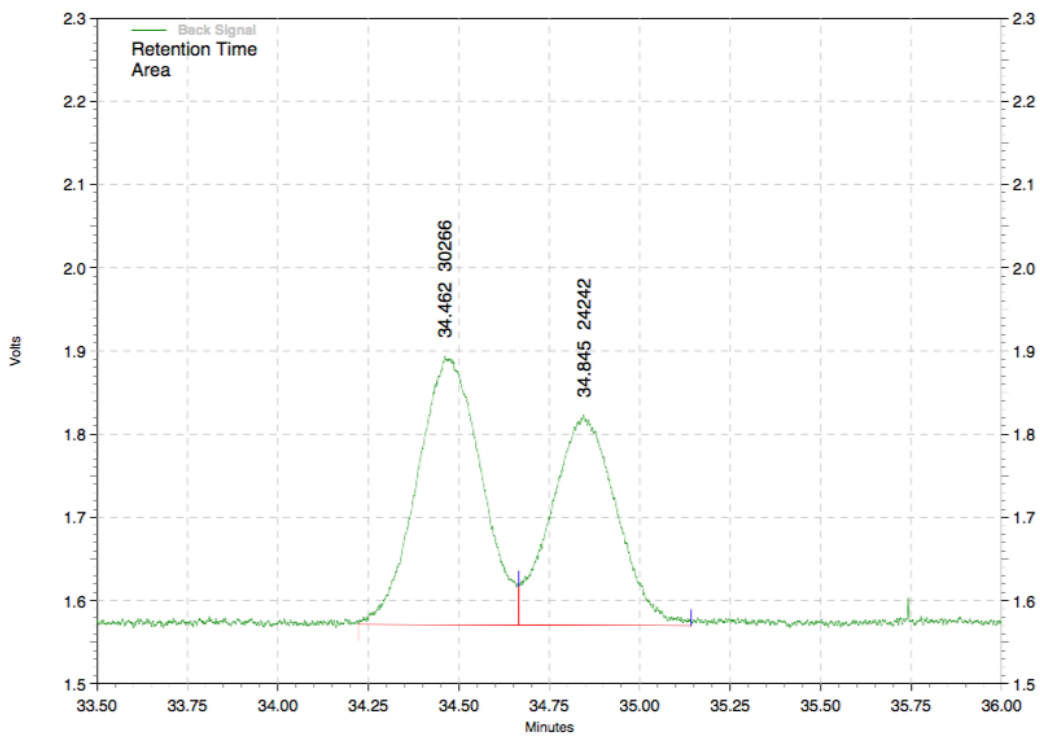
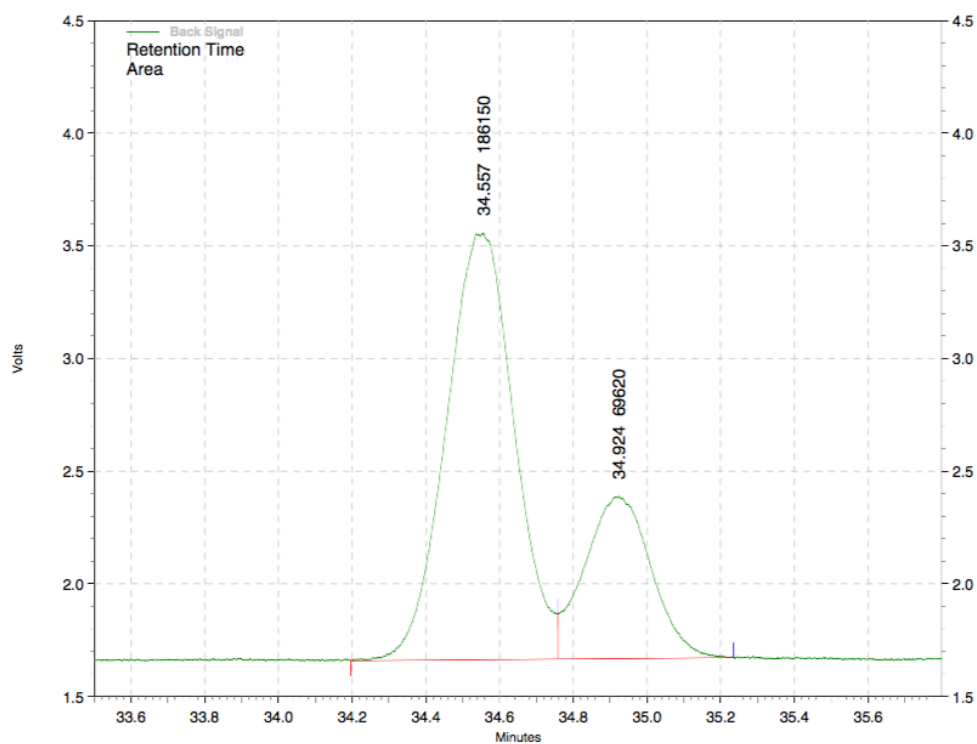


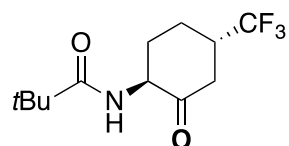
6a (*S,S*)-Mn(TIPSMcp)



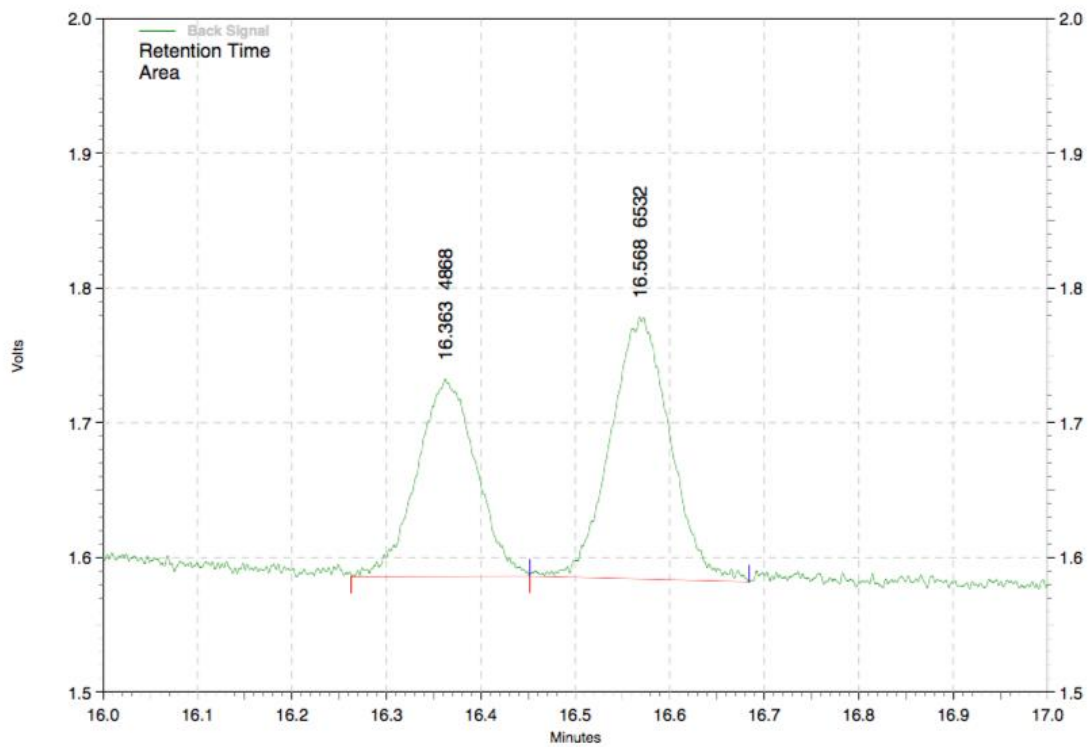
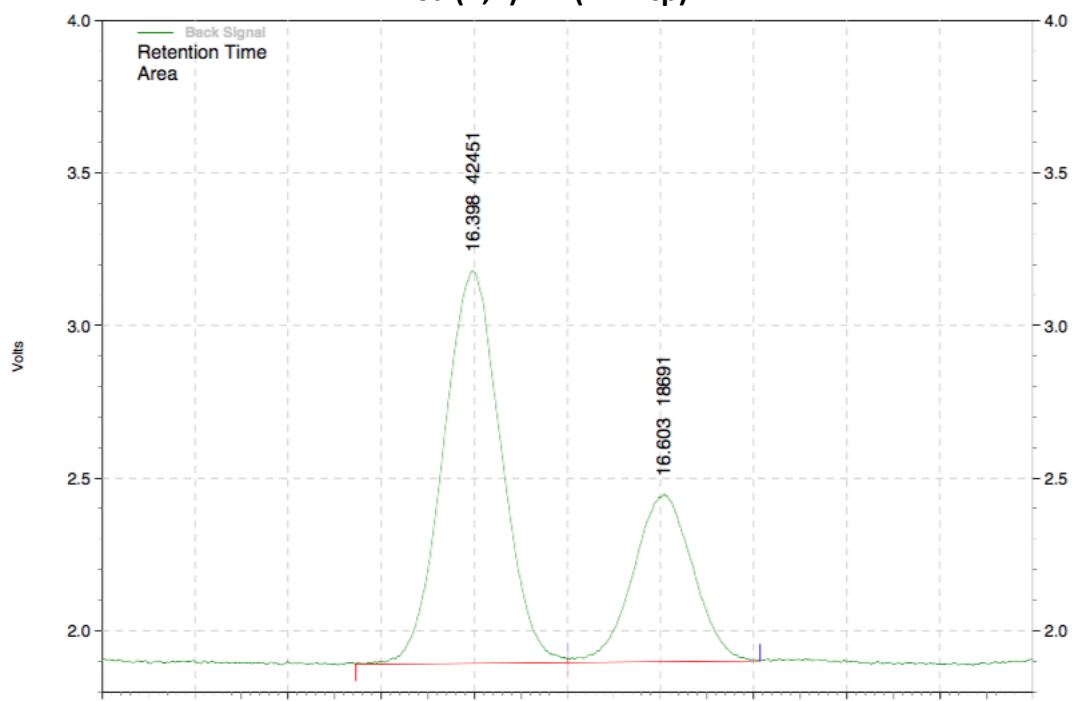
**7a (R,R)-Mn(TIPSMcp)**

**8a (S,S)-Mn(pdp)**

**Rac****9a (*R,R*)-Mn(^{TIPS}mcp)**



Rac

10a (*R,R*)-Mn(TIPSMcp)

The following GC methods were used to separate the enantiomers:

For **1a**:

	Rate °C/min	Value °C	Hold Time min	Run Time min
▶ (Initial)		75	0	0
Ramp 1	10	150	360	367.5
Ramp 2	13	75	0	373.27
*				

For **4a**:

	Rate °C/min	Value °C	Hold Time min	Run Time min
▶ (Initial)		75	0.5	0.5
Ramp 1	10	180	10	21
Ramp 2	13	75	0	29.077
*				

For **5a, 6a**:

	Rate °C/min	Value °C	Hold Time min	Run Time min
▶ (Initial)		75	0	0
Ramp 1	10	180	60	70.5
Ramp 2	13	75	0	78.577
*				

For **7a**:

	Rate °C/min	Value °C	Hold Time min	Run Time min
▶ (Initial)		75	0	0
Ramp 1	10	150	120	127.5
*				

For **8a, 10a**:

	Rate °C/min	Value °C	Hold Time min	Run Time min
▶ (Initial)		75	0.5	0.5
Ramp 1	10	180	30	41
*				

For **9a**:

	Rate °C/min	Value °C	Hold Time min	Run Time min
▶ (Initial)		75	0.5	0.5
Ramp 1	10	160	30	39
*				