

Supporting Information

Prolinethiol Ether Catalysis in an Asymmetric Michael Reaction: Solvent-free Synthesis of Functionalized Monohaloalkenes

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Republic of China*

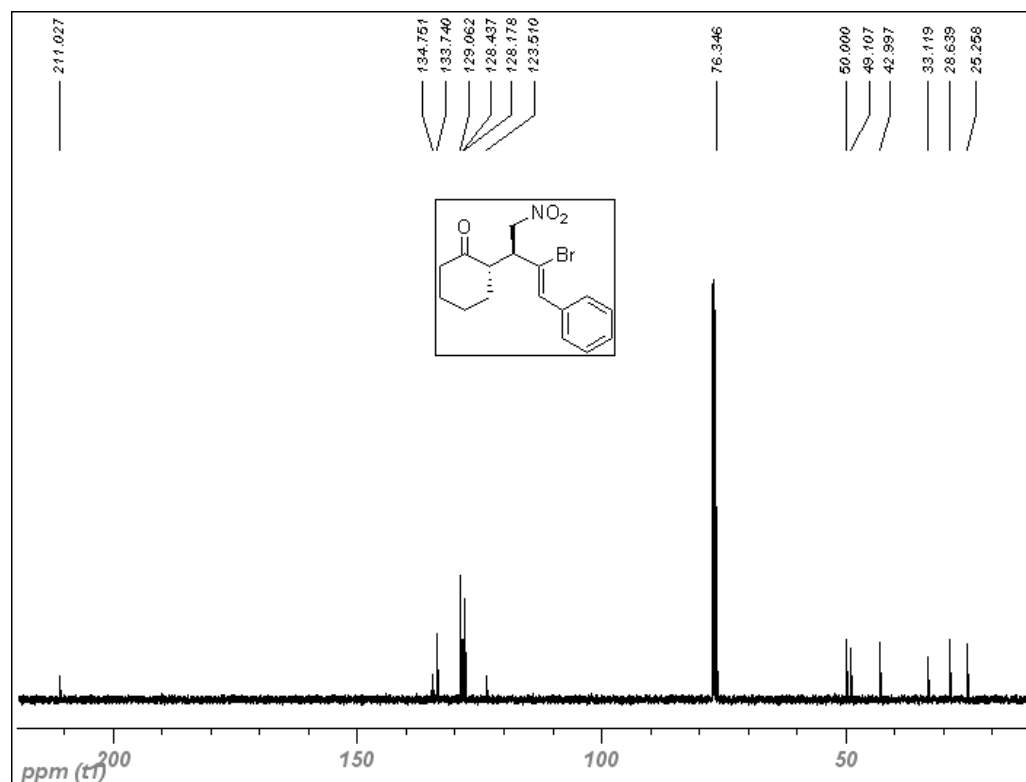
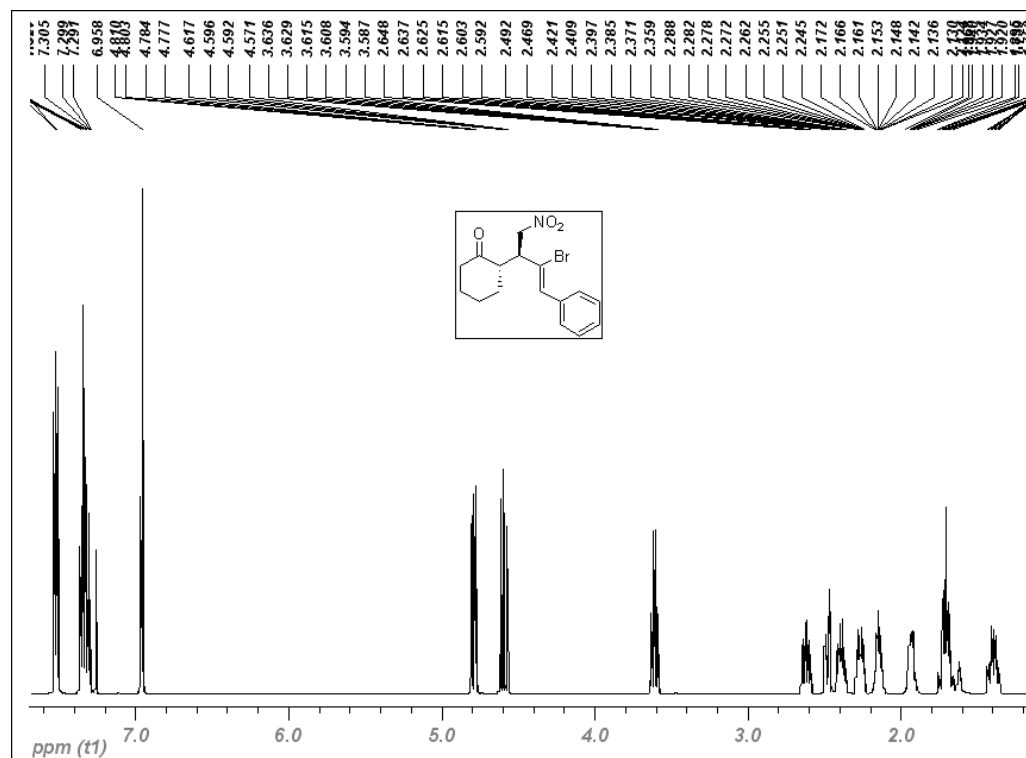
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1. General information

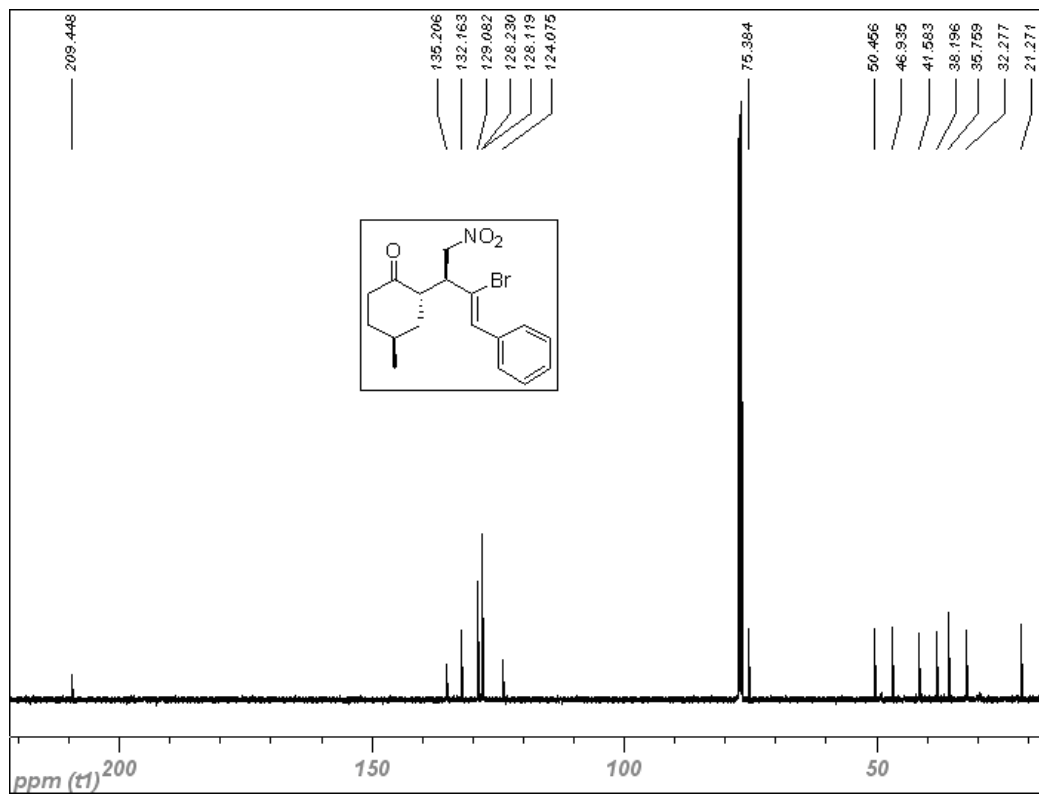
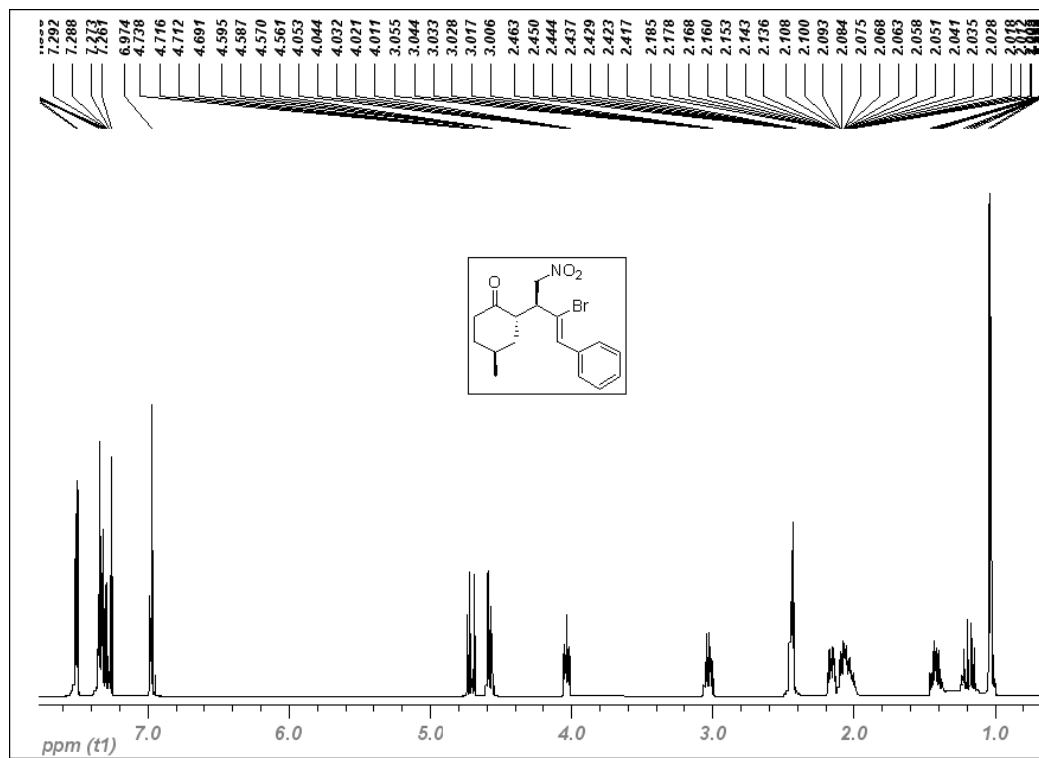
The ^1H NMR and ^{13}C NMR spectra were recorded in CDCl_3 at 500 MHz and 125 MHz, respectively, with TMS as the internal standard. GC-MS experiments were performed on a GC system with a mass selective detector. HRMS data were measured on a LC/TOF-MS with ESI source or GC/ TOF-MS with EI source. Column chromatography and flash chromatography experiments were performed on silica gel (200-300 mesh) eluting with ethyl ether and petroleum ether. TLC experiments were carried out on glass-backed silica plates. In each case, enantiomeric ratio was determined on a chiral column in comparison with authentic racemates by chiral HPLC. Chemicals were used without purification as commercially available.

2. NMR spectra of Michael products

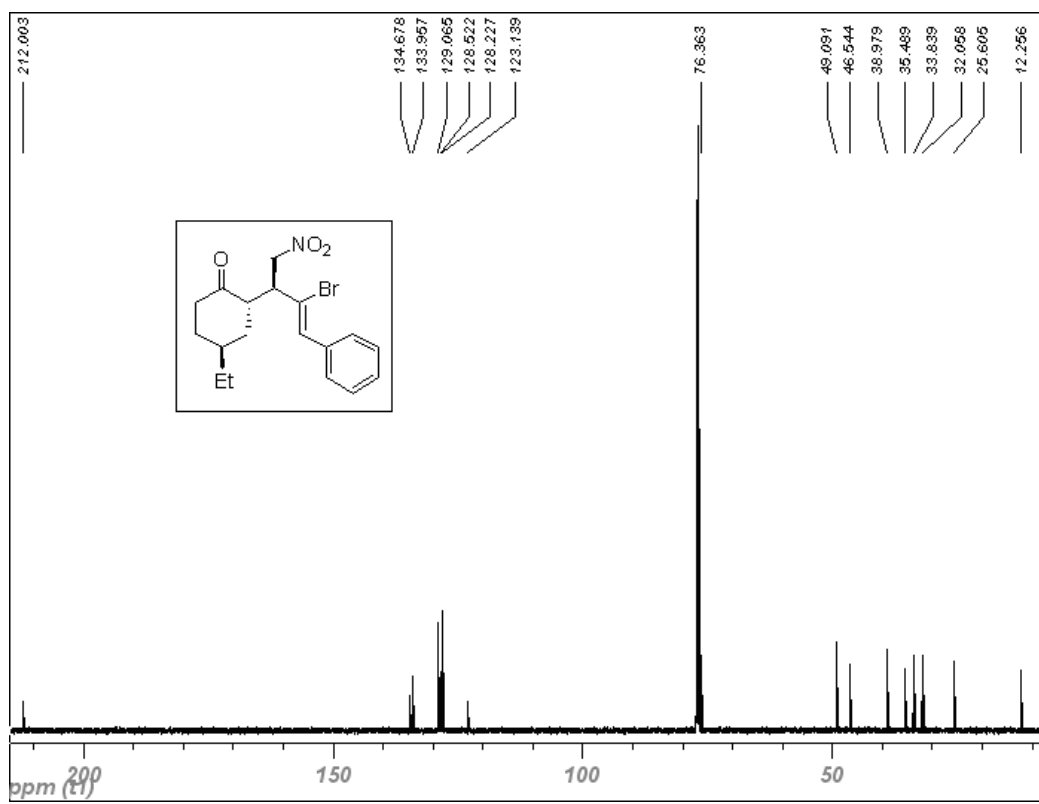
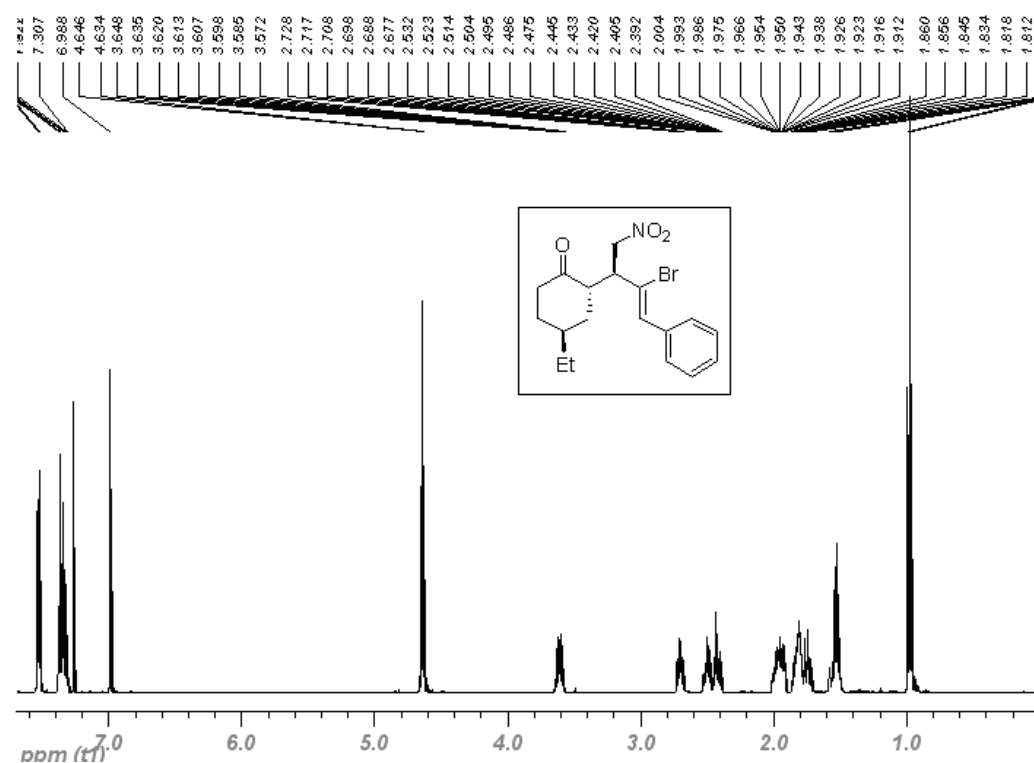
5a



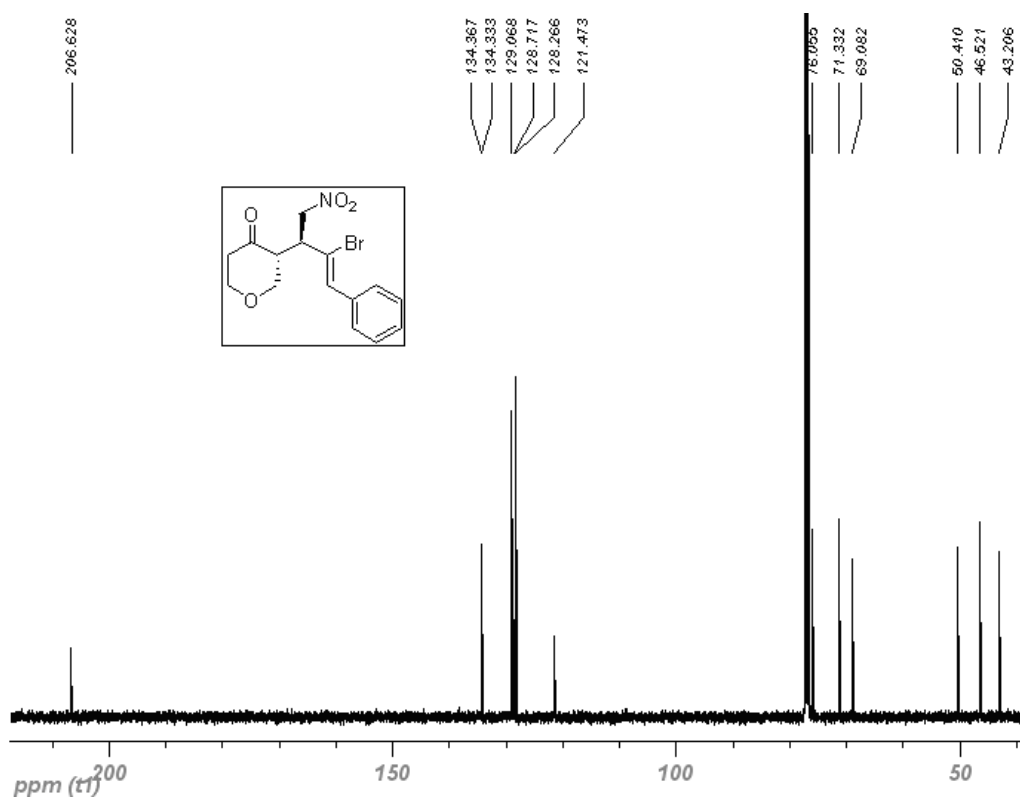
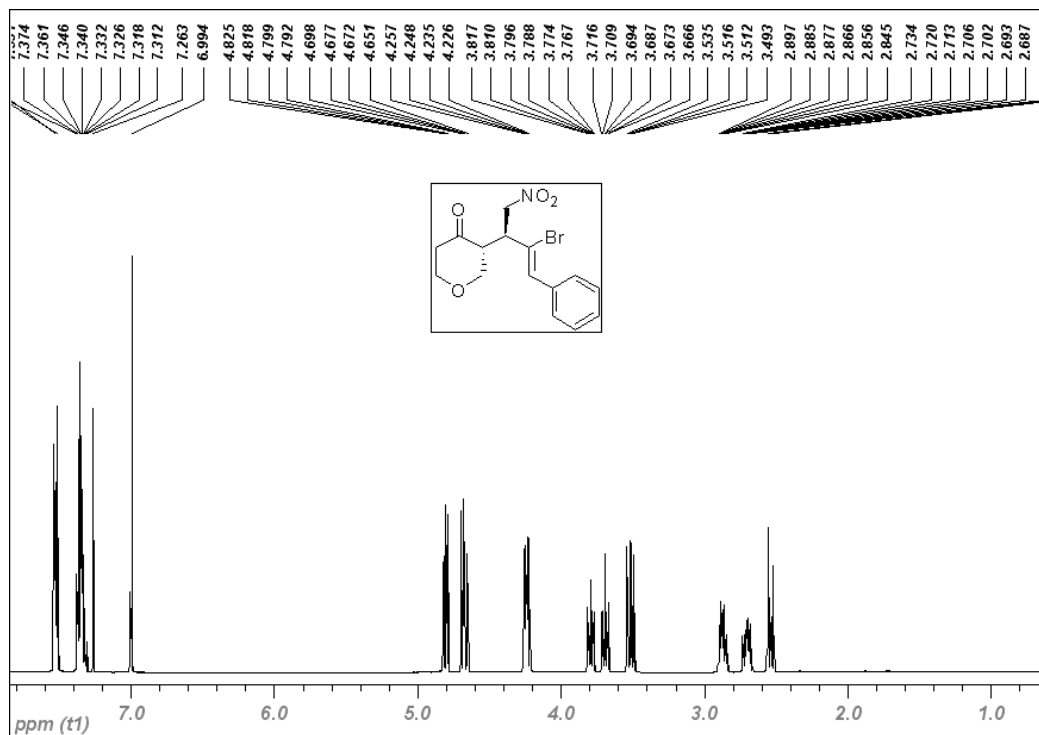
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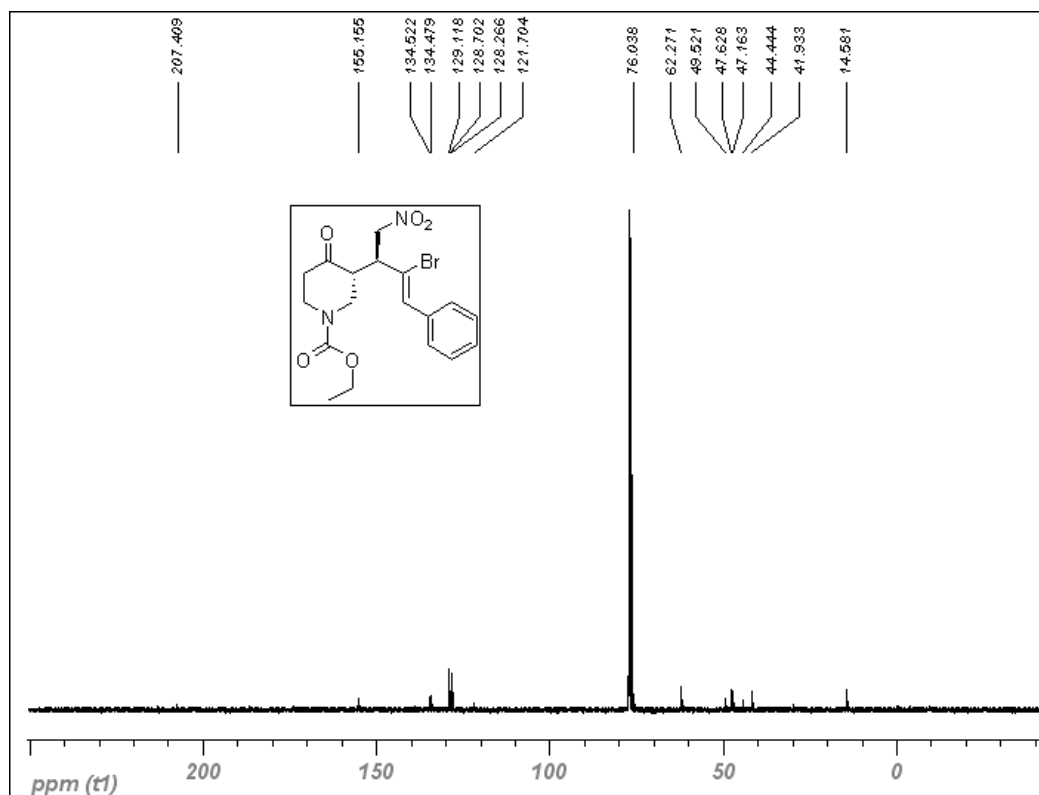
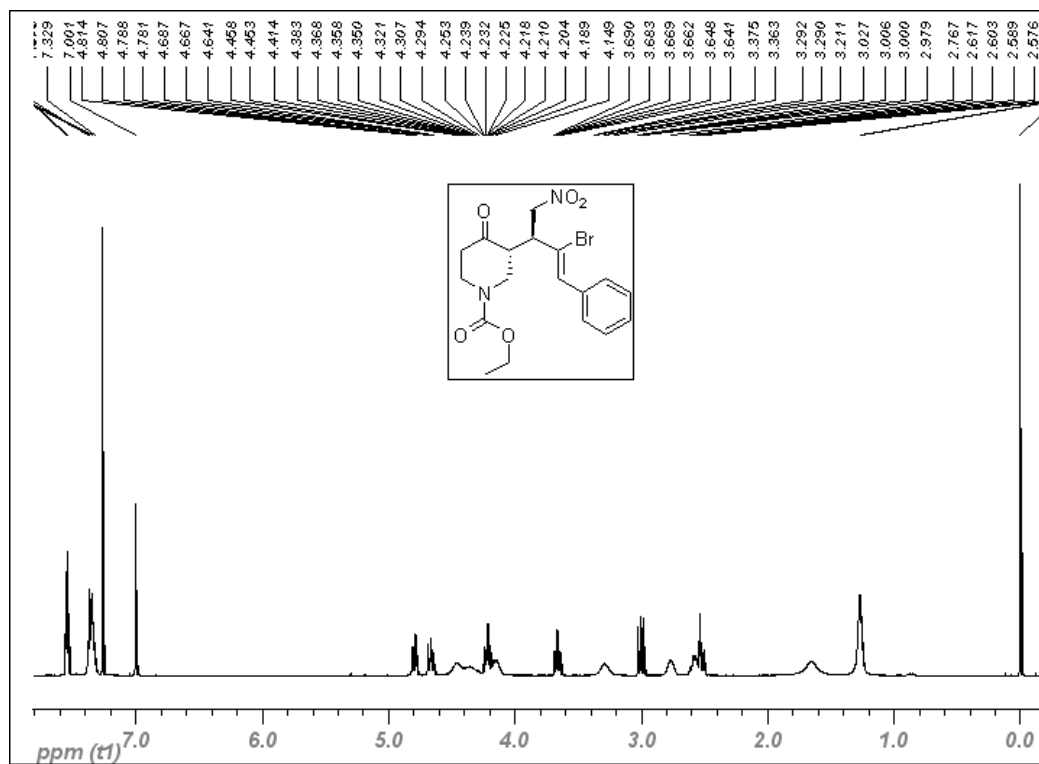
5c



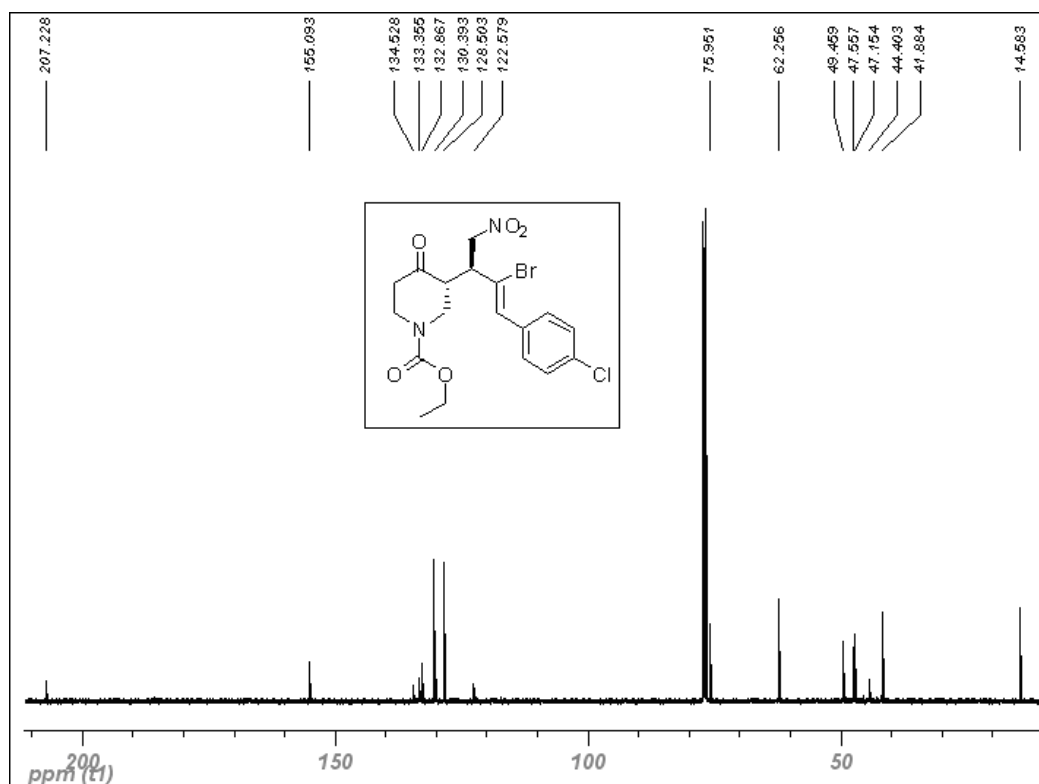
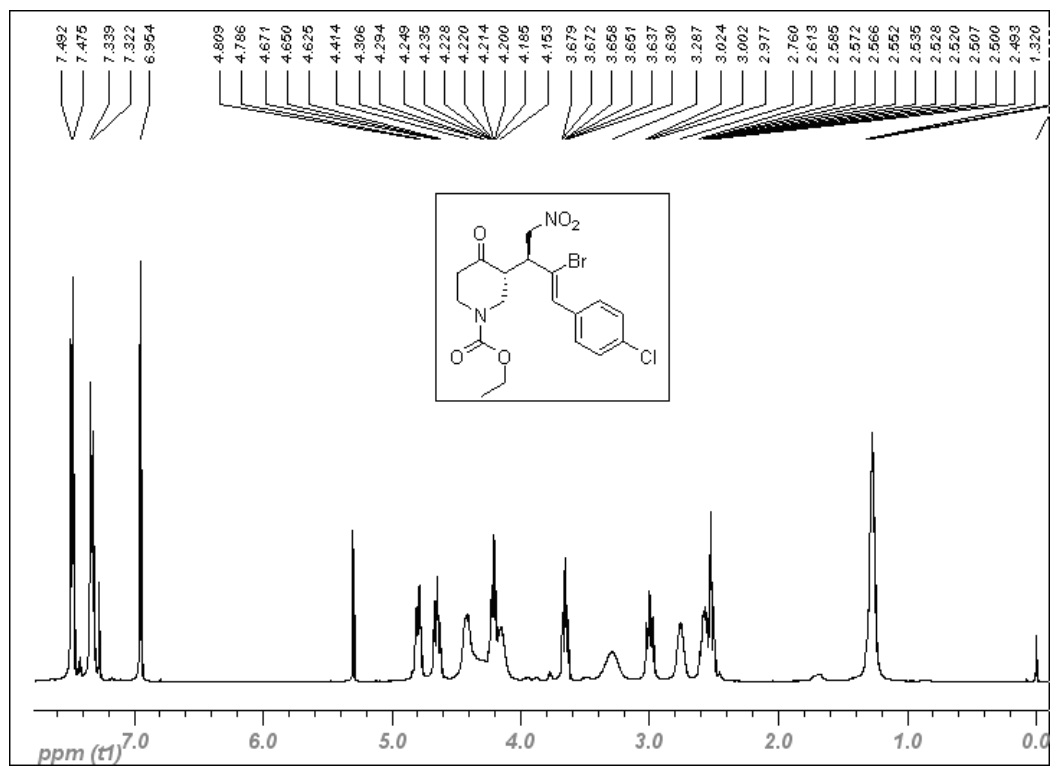
5d



5e



5f

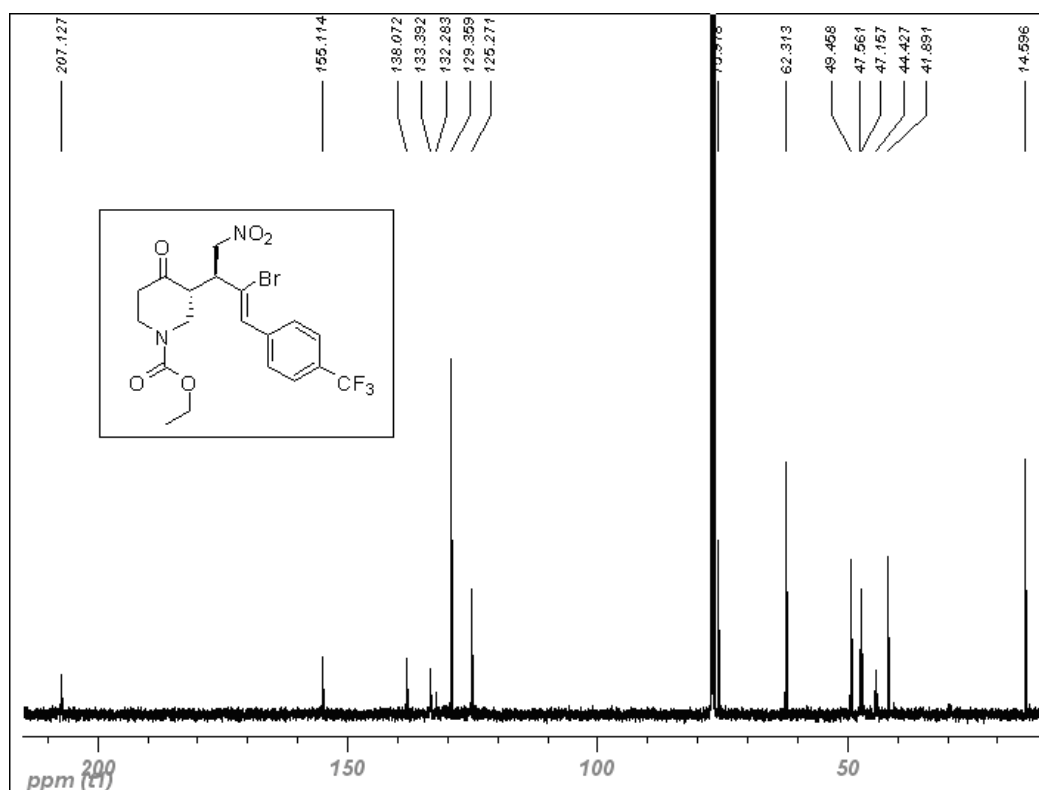


Chemical structure of compound 10 is shown in the inset:

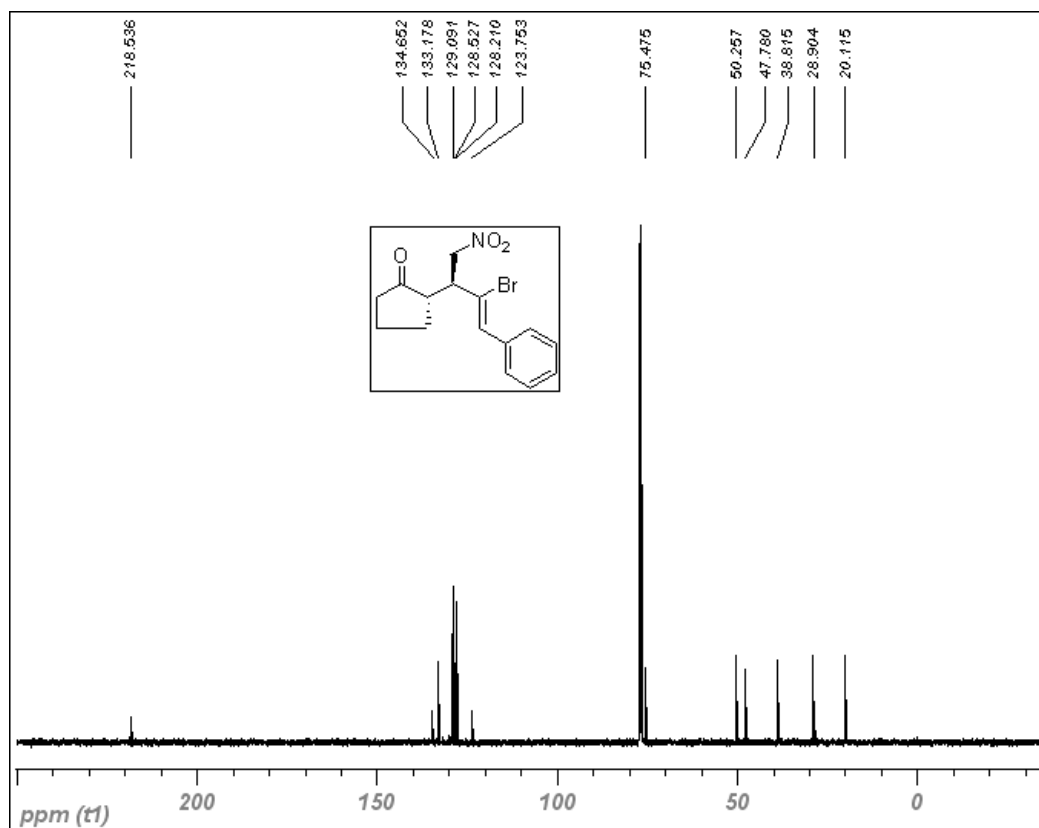
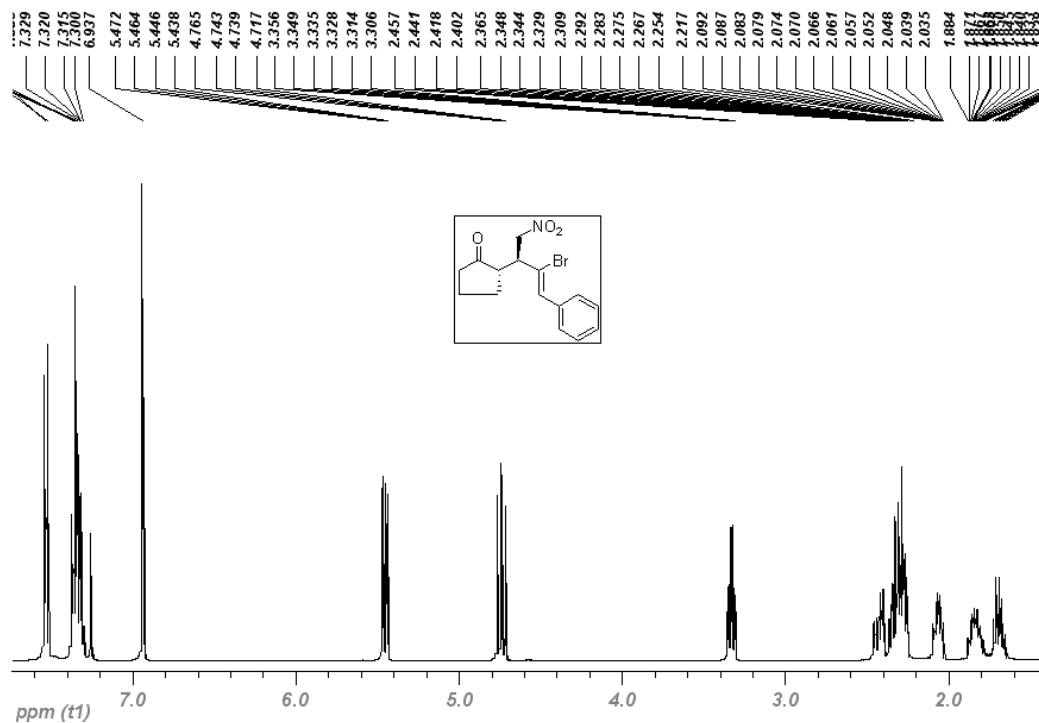
CCOC(=O)N1CC(=O)C(C1)C(C#Cc2ccc(C(F)(F)F)cc2)C(C)C([N+](=O)[O-])

Peak list (ppm):

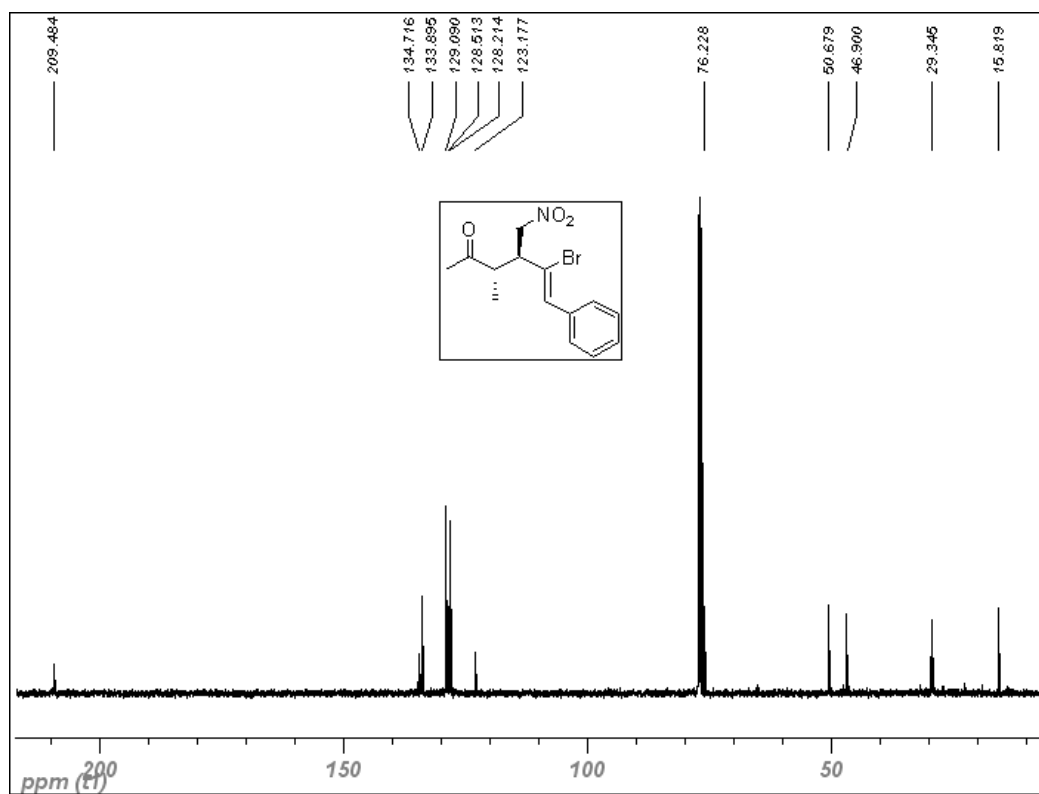
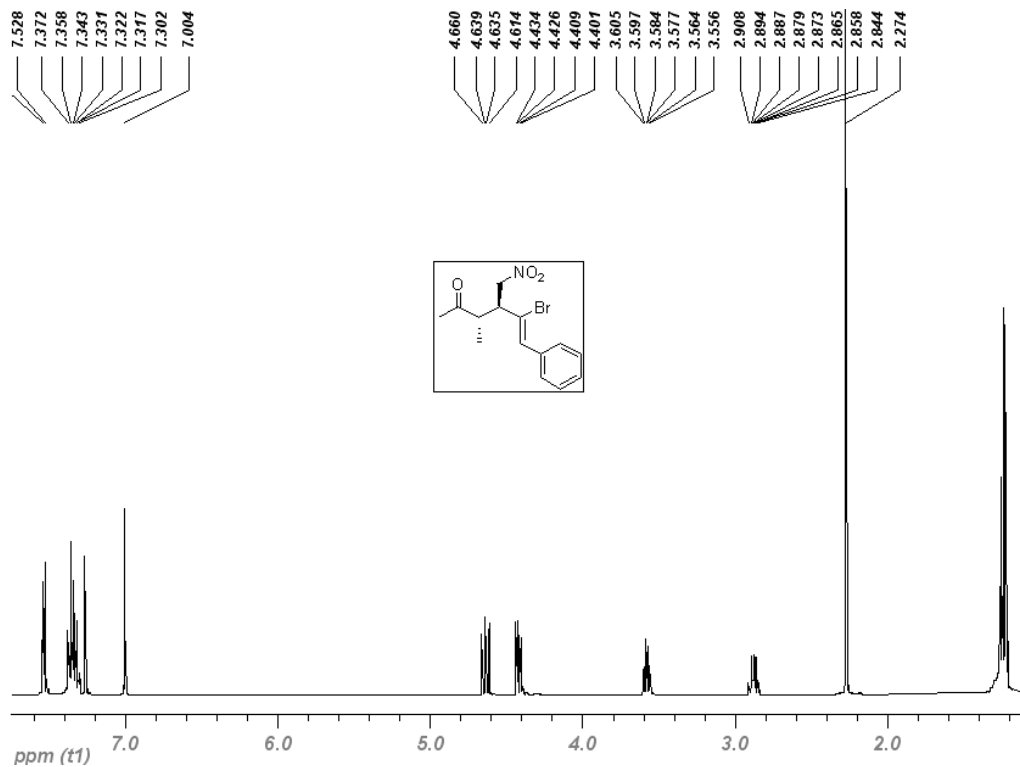
- 4.661
- 4.646
- 4.637
- 4.634
- 4.554
- 4.447
- 4.428
- 4.420
- 4.258
- 4.253
- 4.243
- 4.237
- 4.229
- 4.222
- 4.215
- 4.208
- 4.194
- 4.175
- 4.164
- 4.143
- 4.129
- 4.115
- 4.100
- 3.712
- 3.704
- 3.691
- 3.683
- 3.670
- 3.663
- 3.497
- 3.488
- 3.482
- 3.474
- 3.455
- 3.430
- 3.390
- 3.346
- 3.341
- 3.316
- 3.312
- 3.306
- 3.299
- 3.294
- 3.285
- 3.282
- 3.272
- 3.216
- 3.026
- 2.989
- 2.874
- 2.854



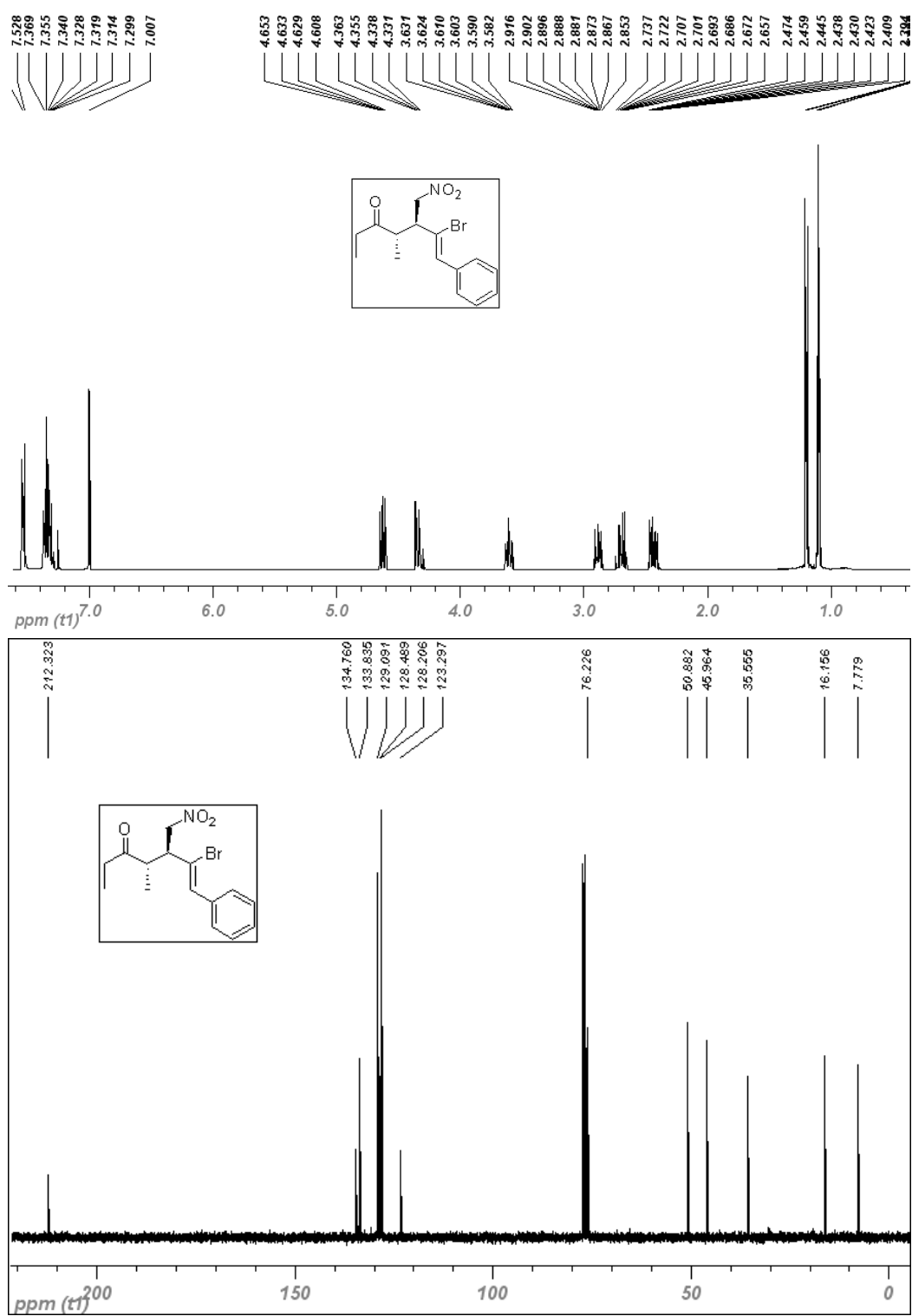
5h



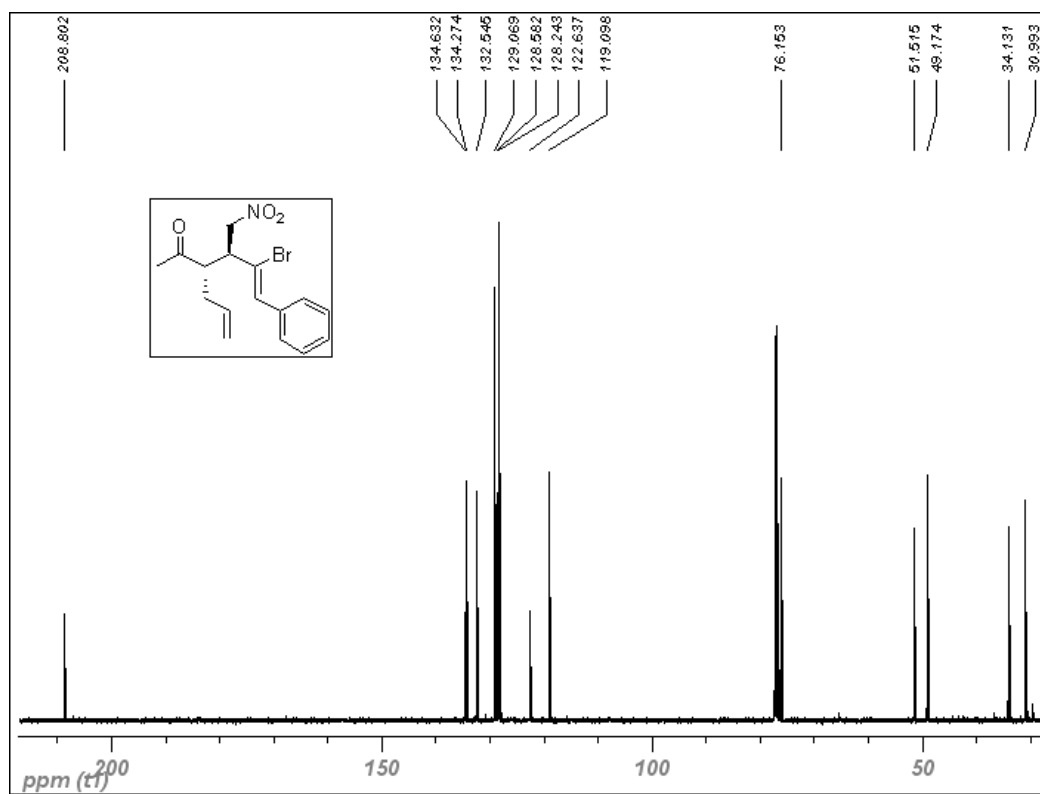
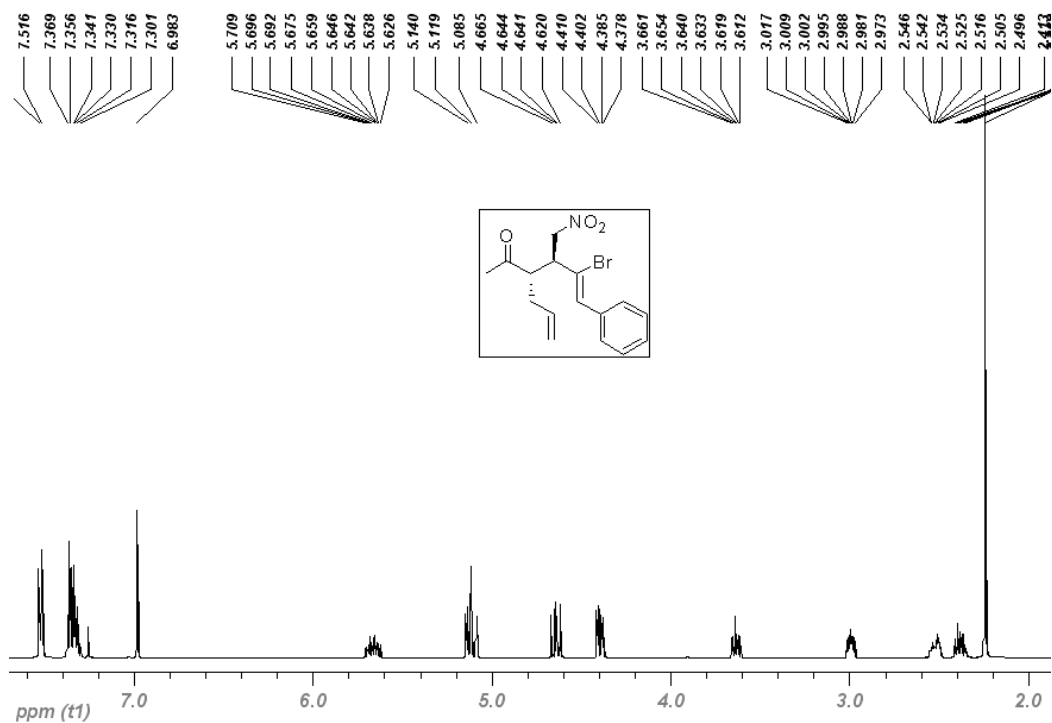
5i

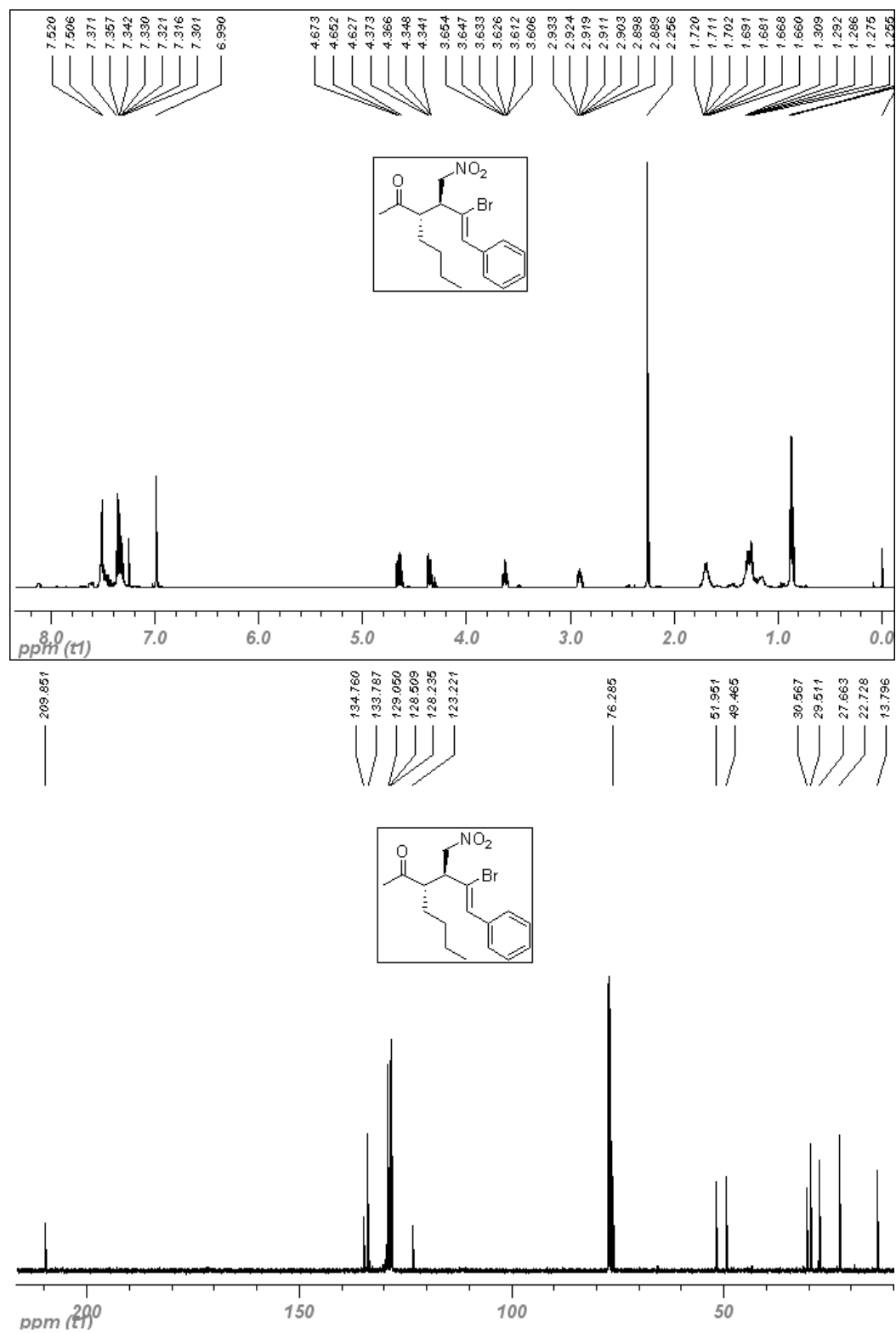


5j

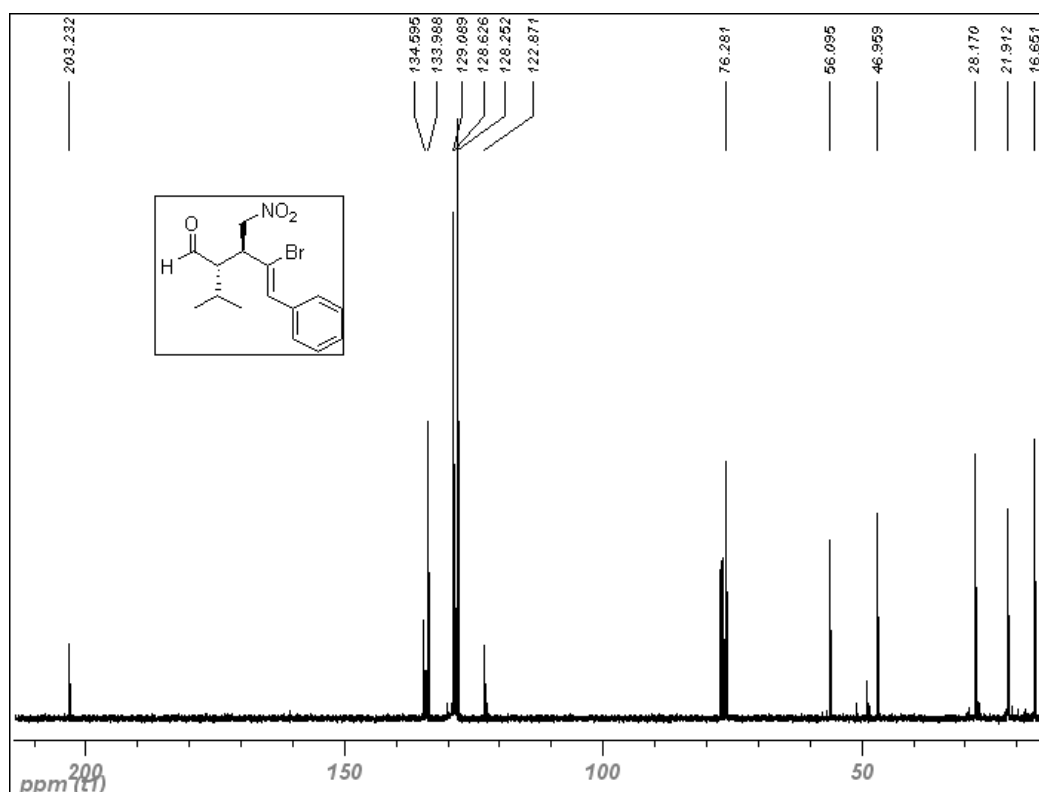
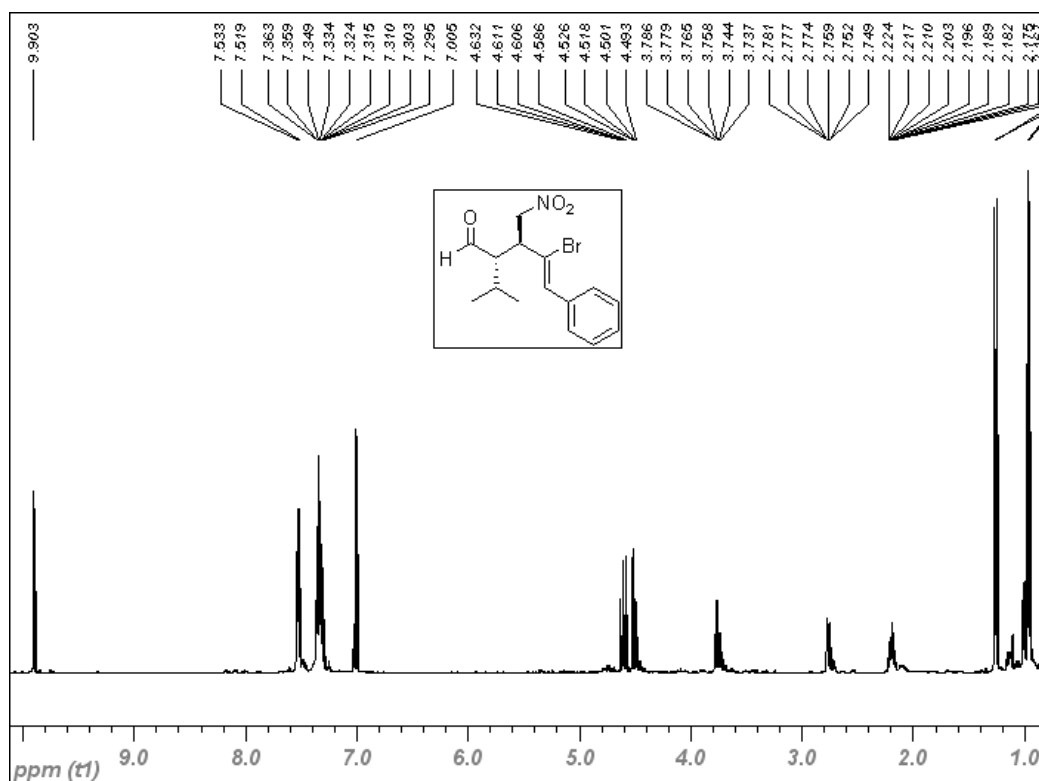


5k

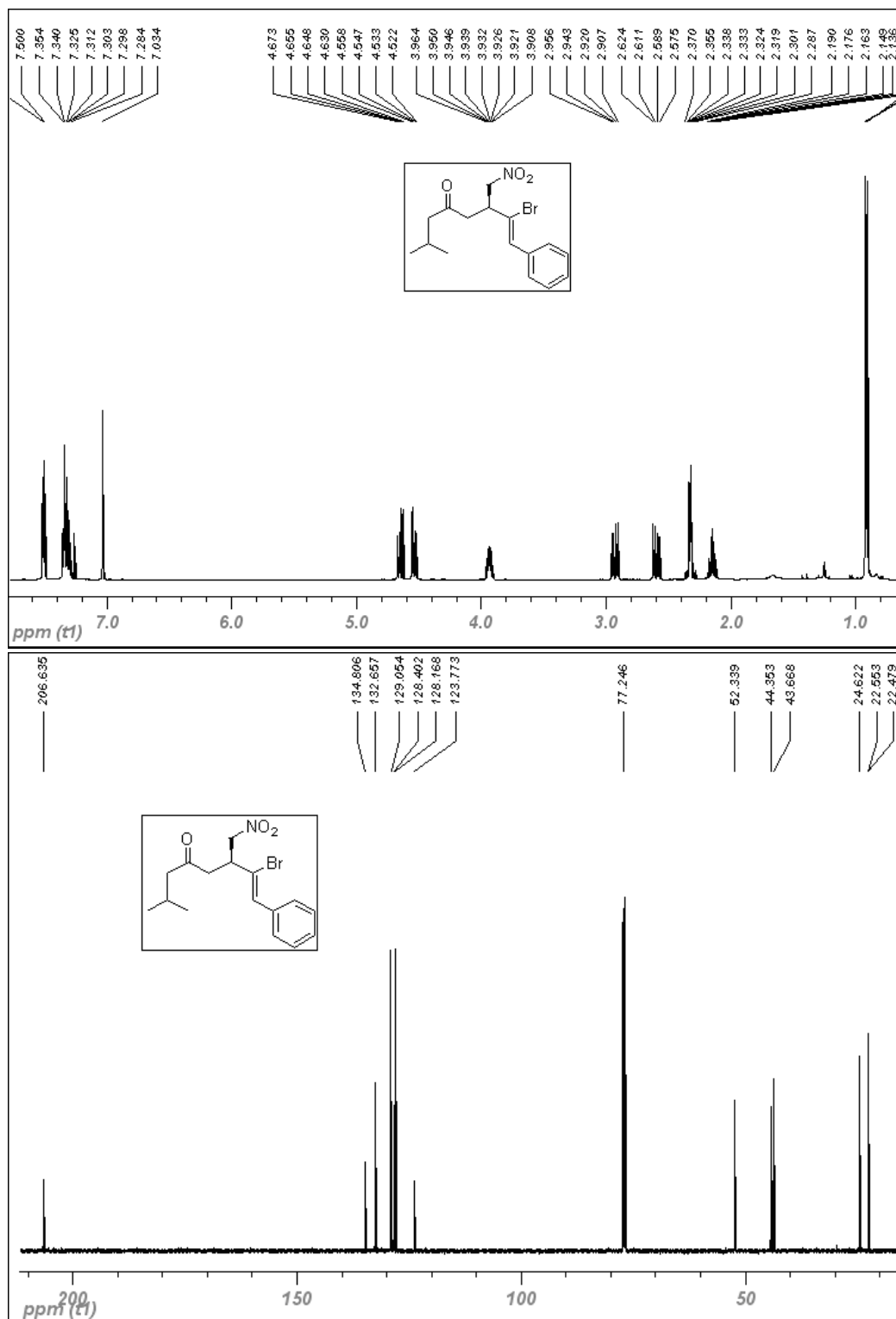




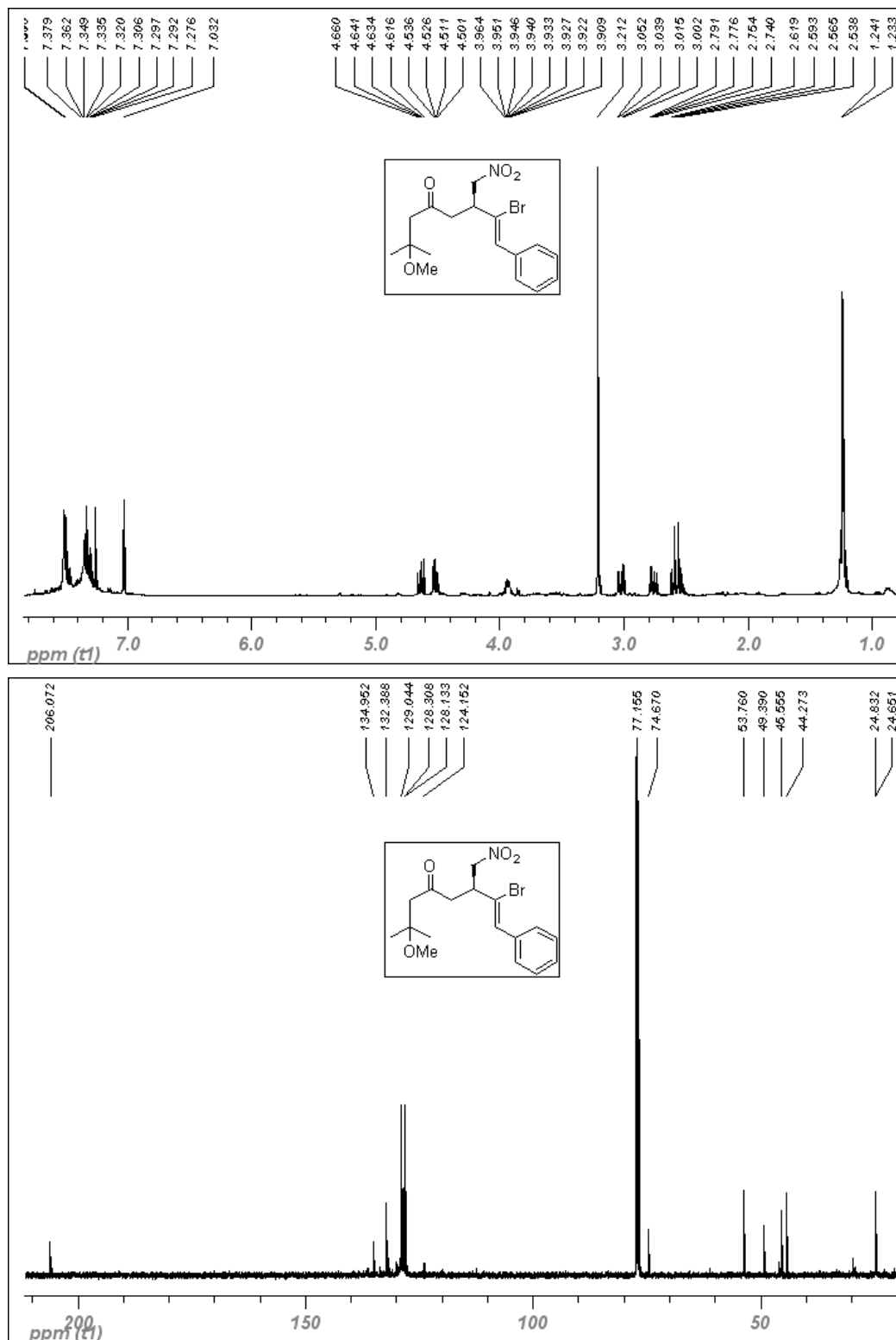
5m



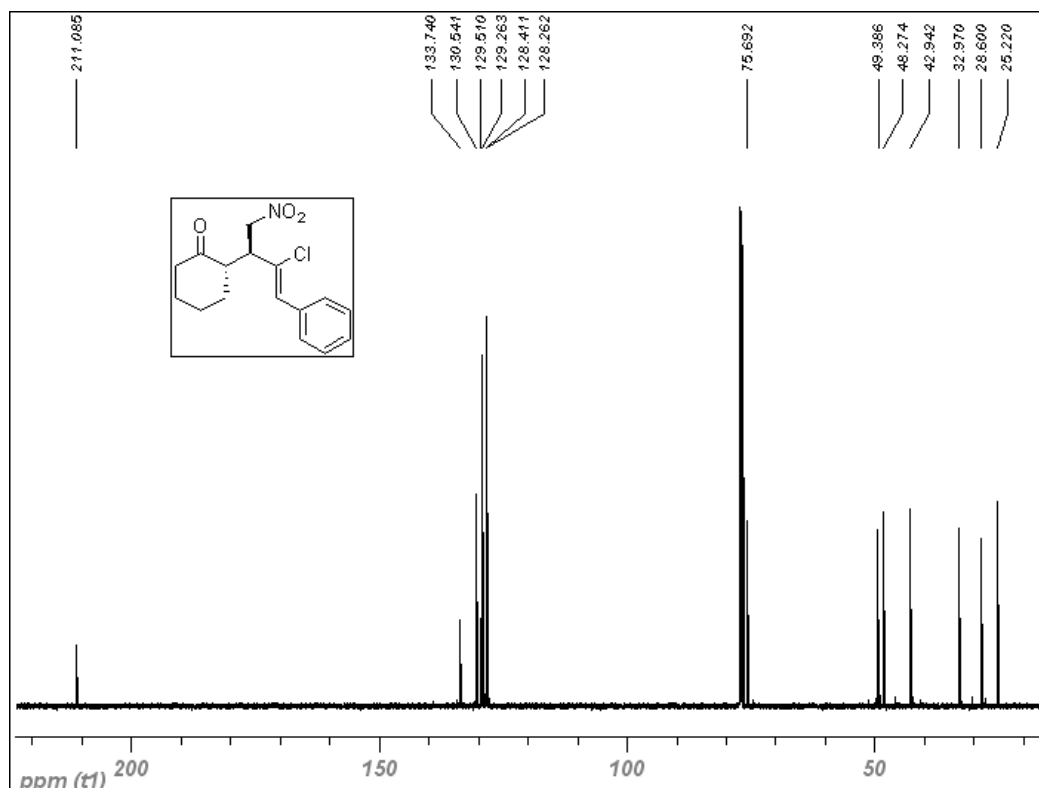
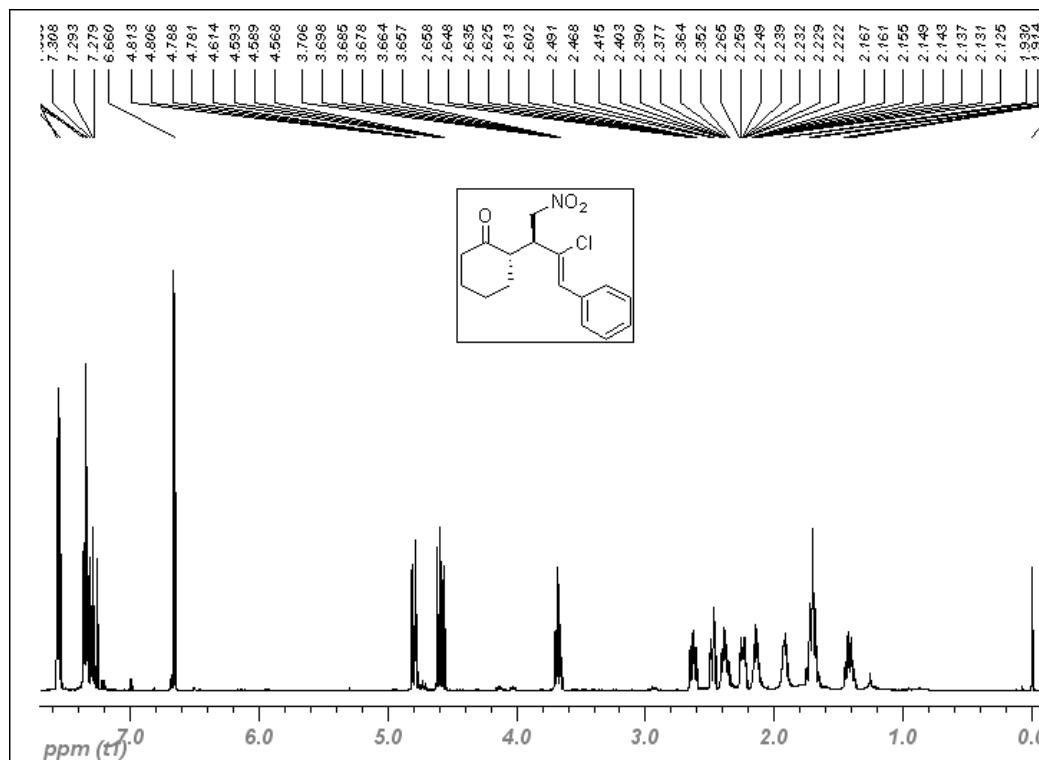
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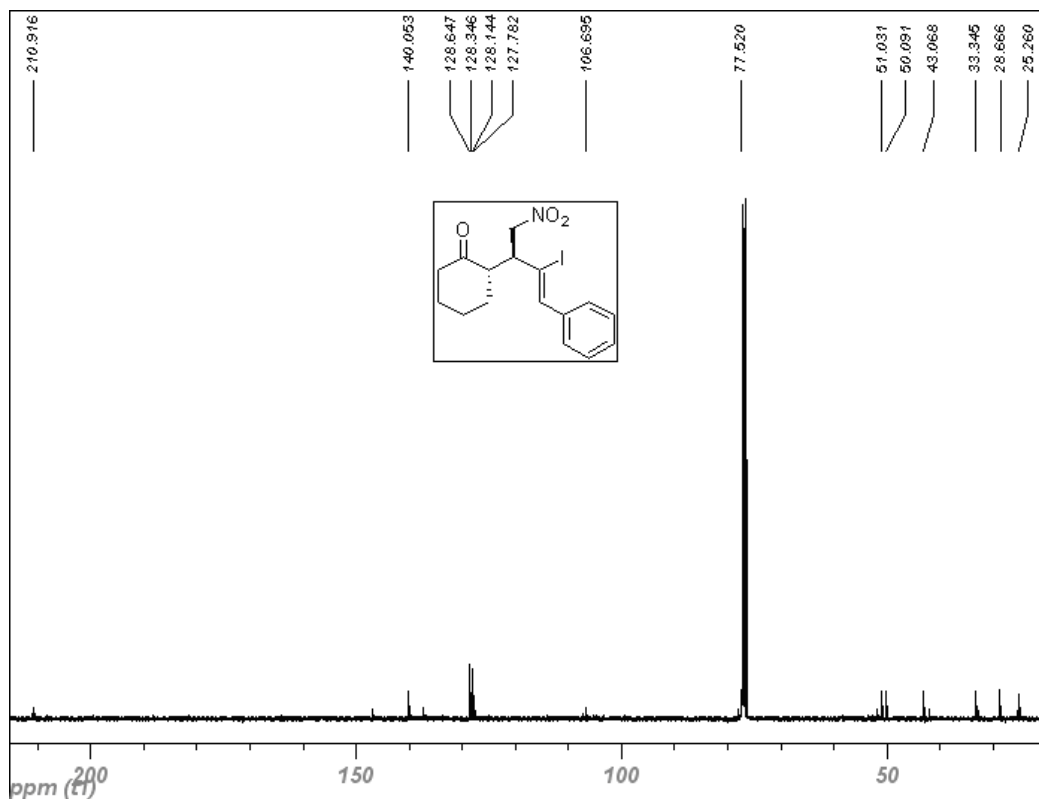
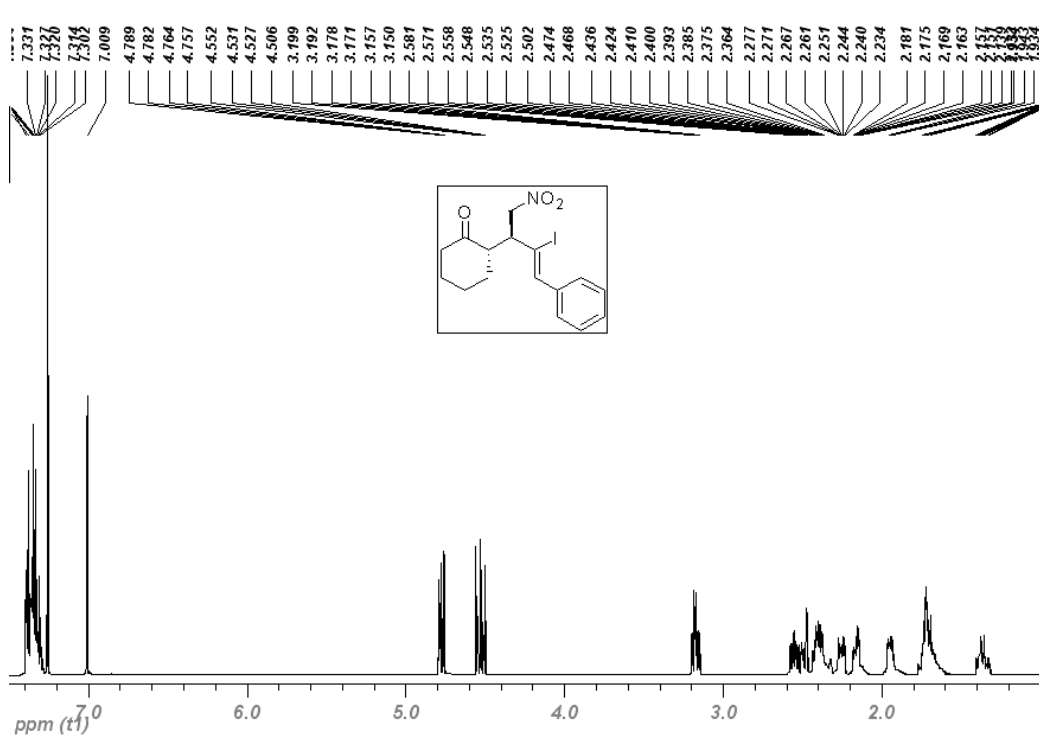
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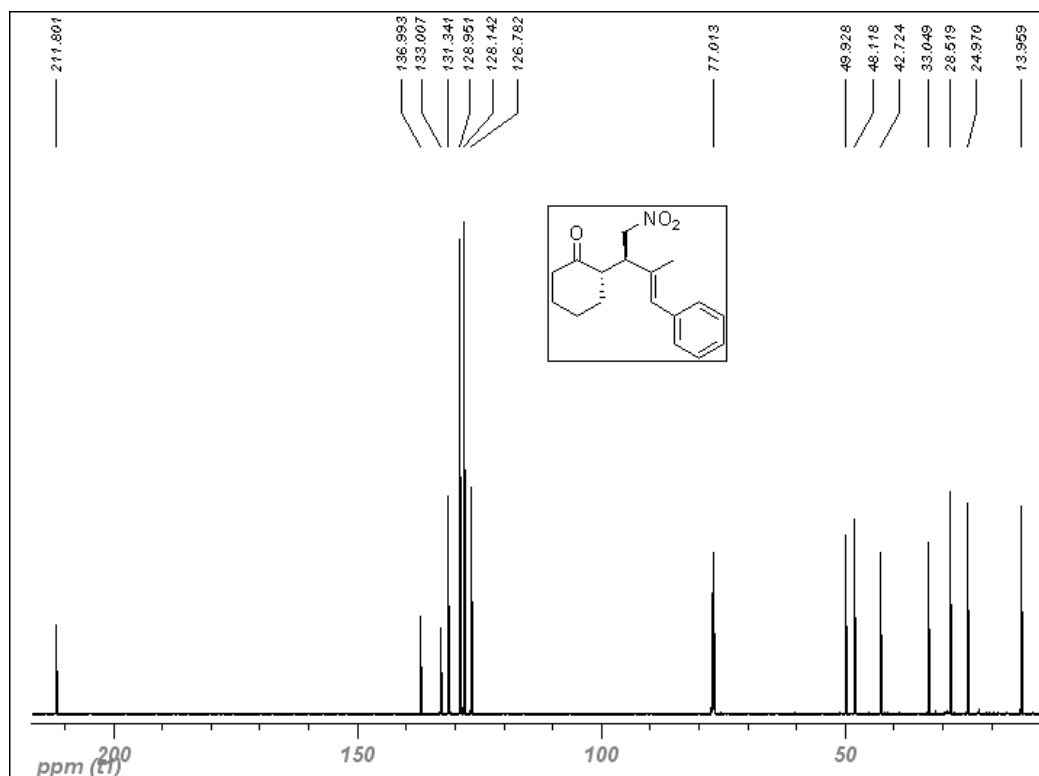
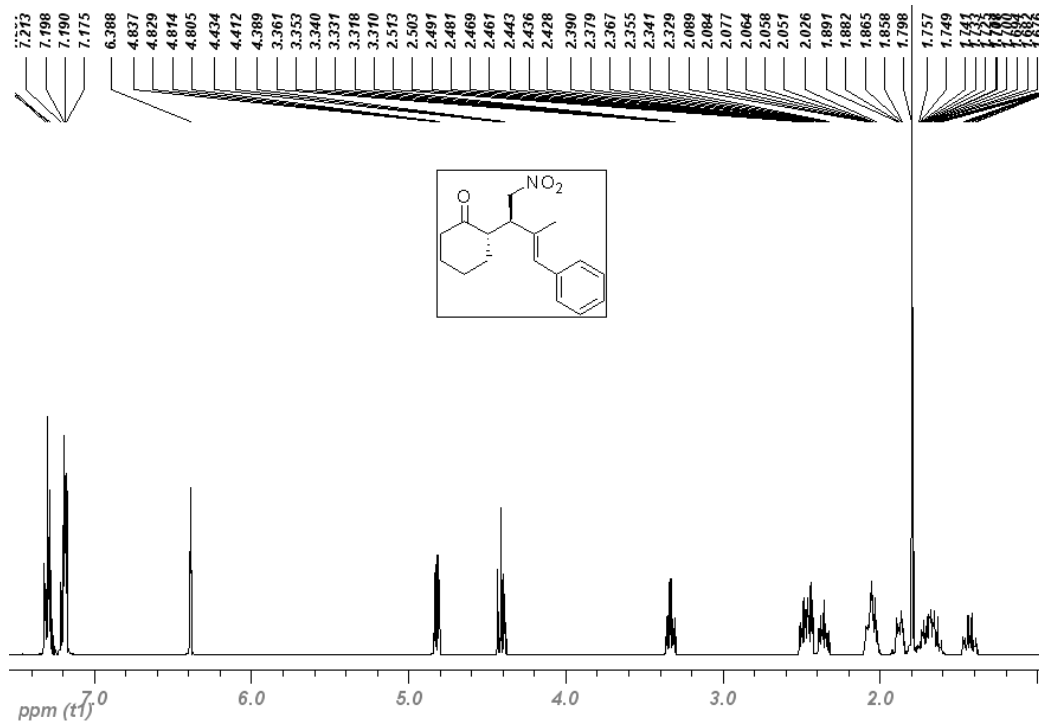
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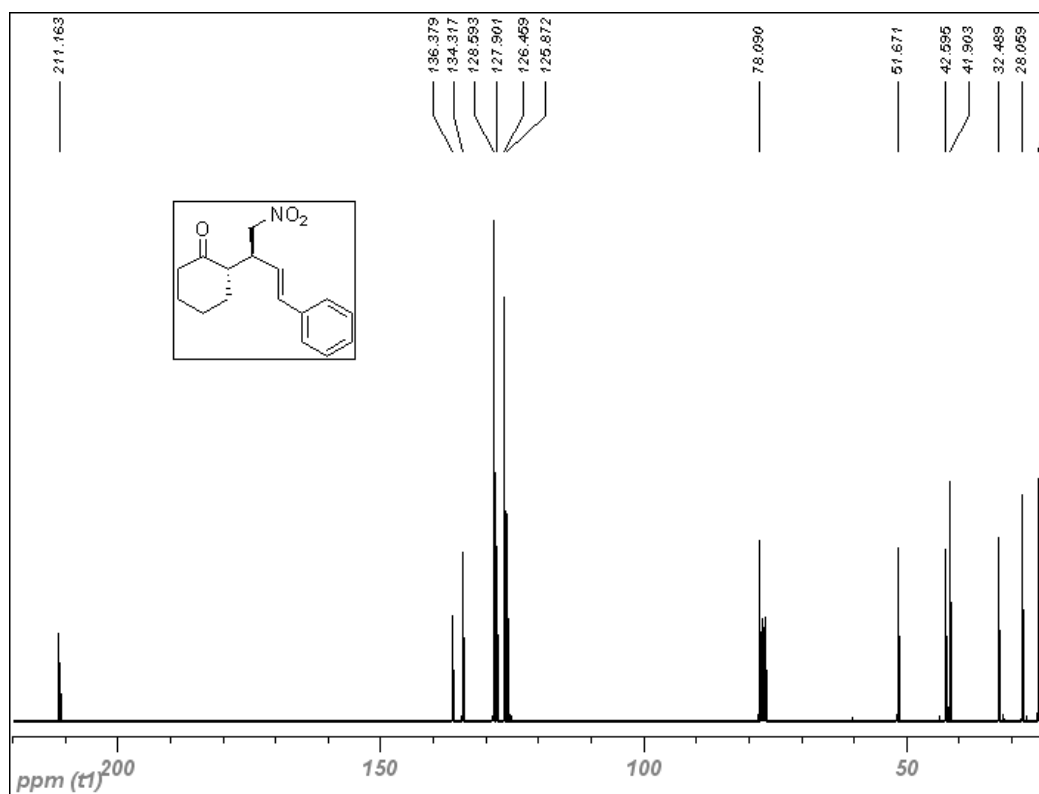
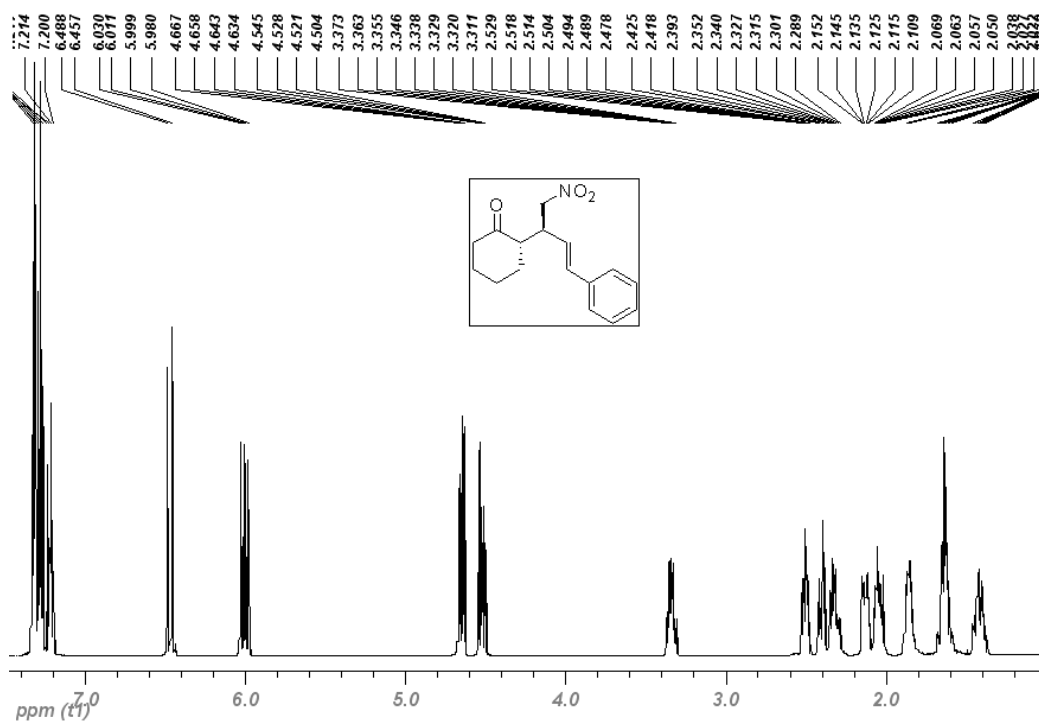
5q



5r



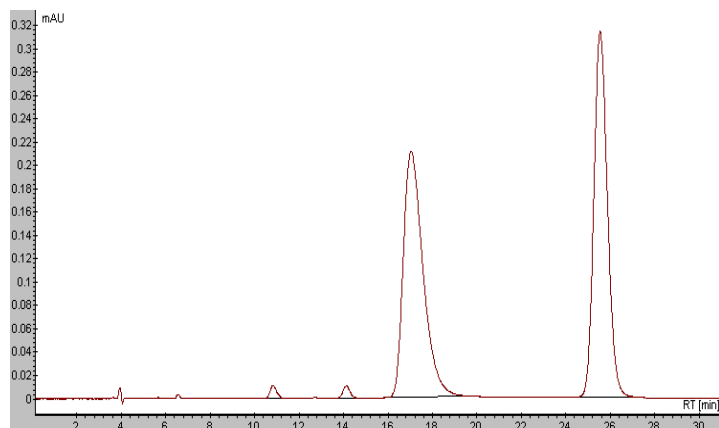
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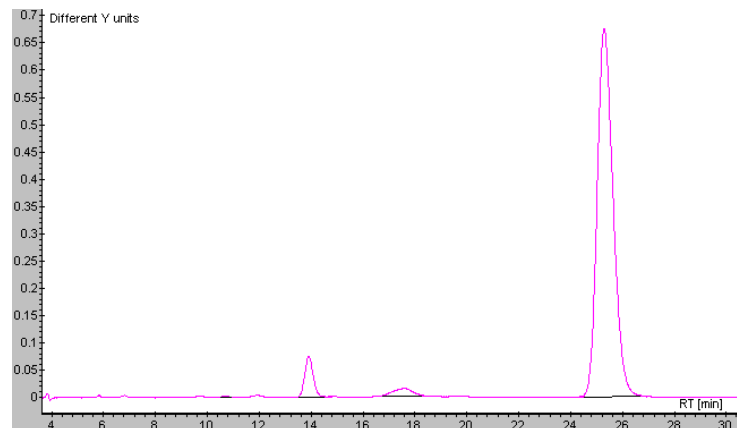
3. HPLC spectra of Michael adducts

5a

Racimic adduct



Asymmetric adduct

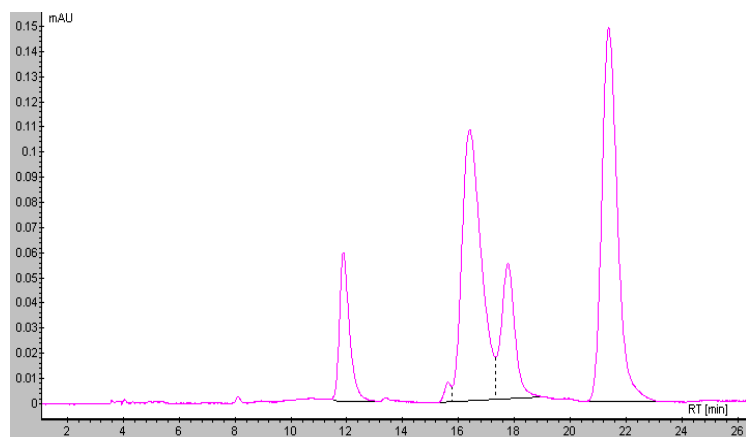


#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	10.43	10.83	11.43	0.85
2	13.69	14.12	14.69	0.85
3	15.81	17.04	19.41	48.58
4	24.50	25.55	27.14	49.73

#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	10.37	10.67	11.03	0.15
2	13.39	13.91	14.55	5.33
3	16.52	17.57	18.50	2.52
4	24.30	25.28	26.92	92.00

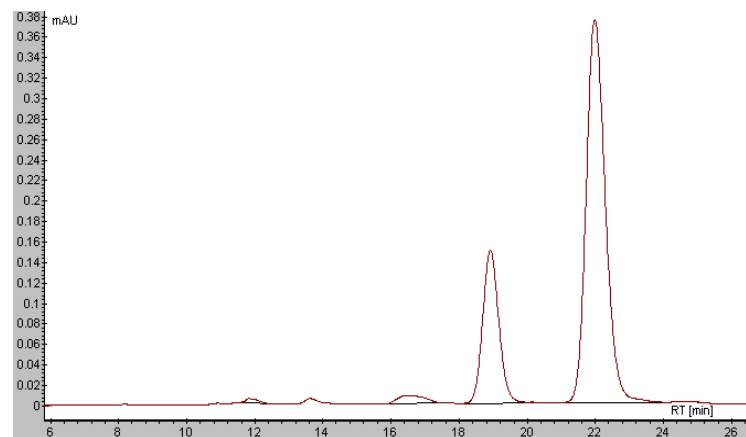
5b

Racimic adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	11.49	11.88	13.16	10.26
2	15.76	16.40	17.33	36.41
3	17.33	17.77	19.02	12.86
4	20.55	21.37	23.18	40.47

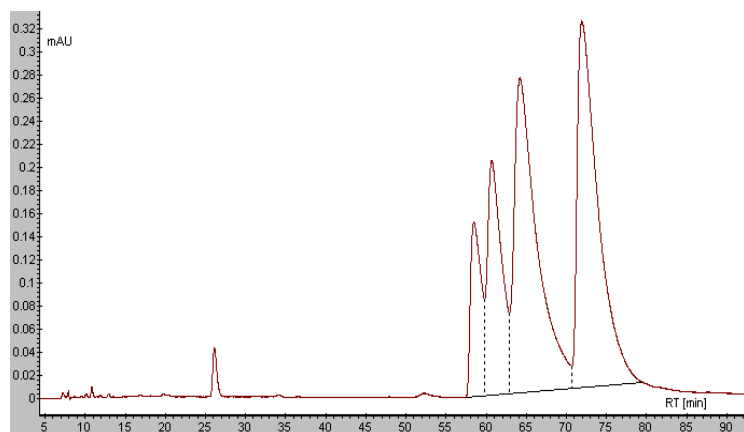
Asymmetric adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	11.62	11.83	12.66	0.49
2	15.79	16.49	17.70	2.25
3	18.06	18.92	20.49	24.43
4	20.89	21.98	24.13	72.82

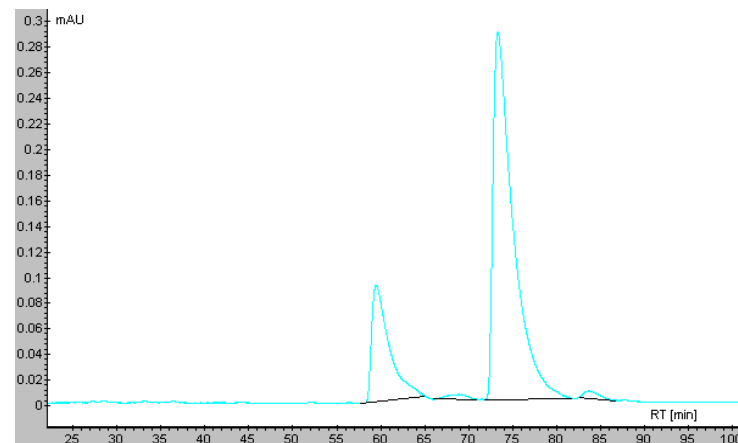
5c

Racimic adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	57.38	58.46	59.80	9.17
2	59.80	60.68	62.90	16.68
3	62.90	64.22	70.67	36.08
4	70.67	71.92	79.59	38.07

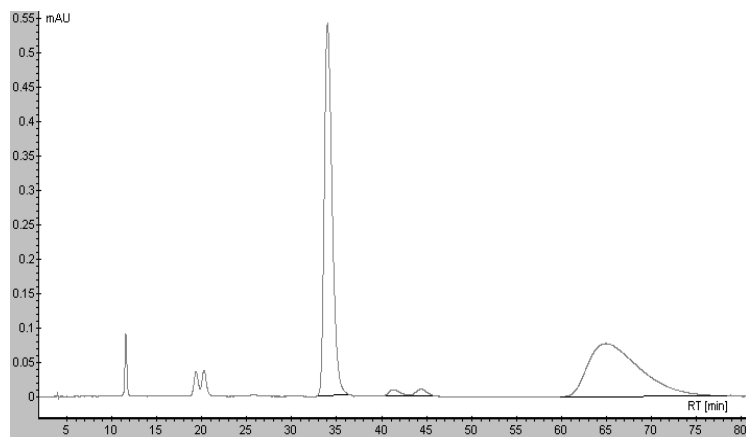
Asymmetric adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	57.44	59.22	64.80	21.27
2	65.63	68.57	70.90	1.13
3	71.59	73.08	81.58	76.37
4	82.13	83.49	96.57	1.23

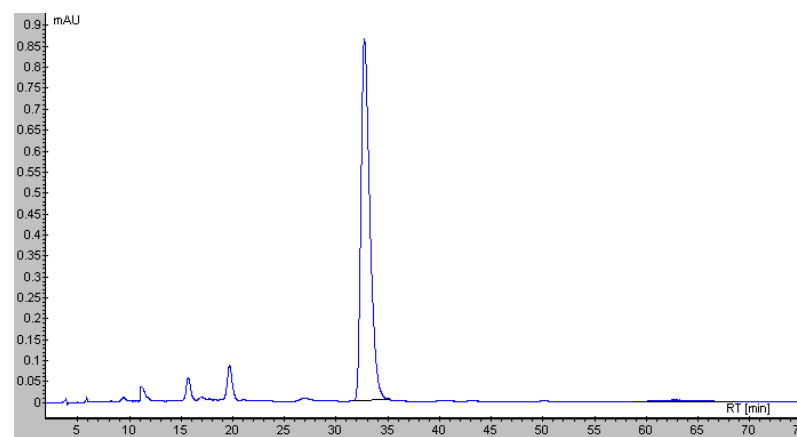
5d

Racimic adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	32.76	33.99	36.60	50.33
2	40.21	41.32	43.05	1.19
3	43.05	44.37	45.72	1.13
4	59.92	64.96	78.46	47.36

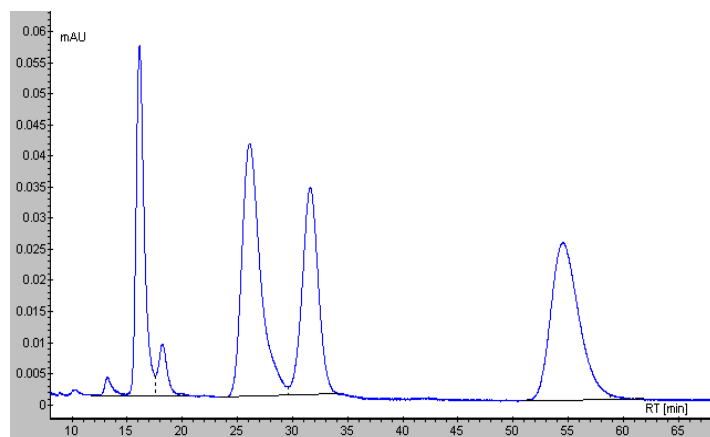
Asymmetric adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	31.58	32.72	35.21	97.76
2	58.67	62.78	68.73	2.24

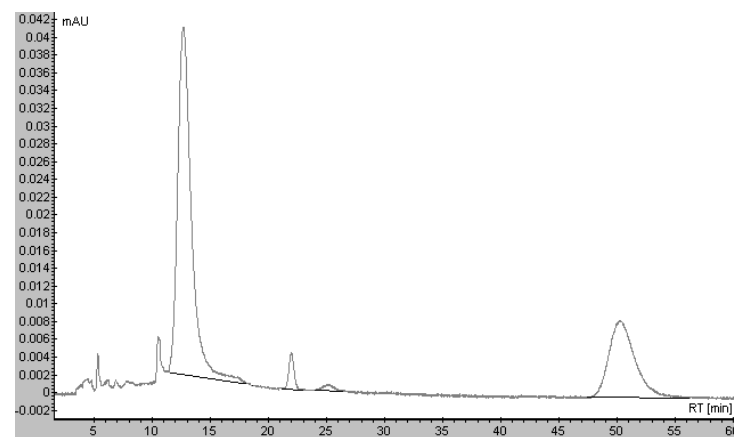
5e

Racimic adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	14.86	16.11	17.54	18.74
2	23.39	26.10	29.60	30.89
3	29.60	31.60	34.20	21.58
4	51.46	54.51	58.79	28.79

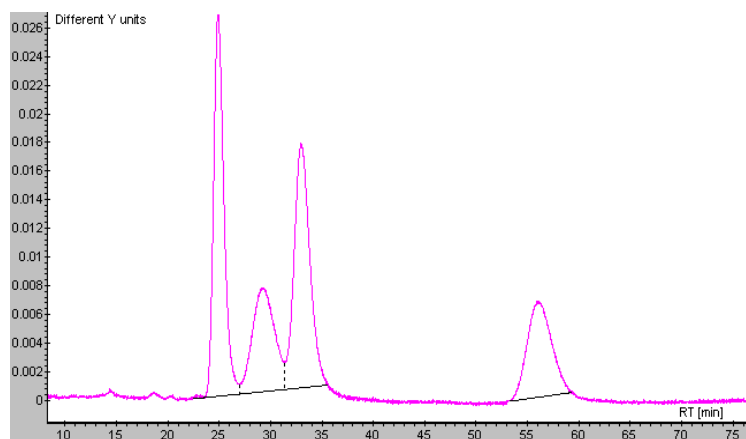
Asymmetric adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	11.17	12.68	18.33	67.87
2	21.17	21.96	23.033	2.69
3	24.01	25.08	26.46	1.03
4	47.44	50.18	56.26	28.41

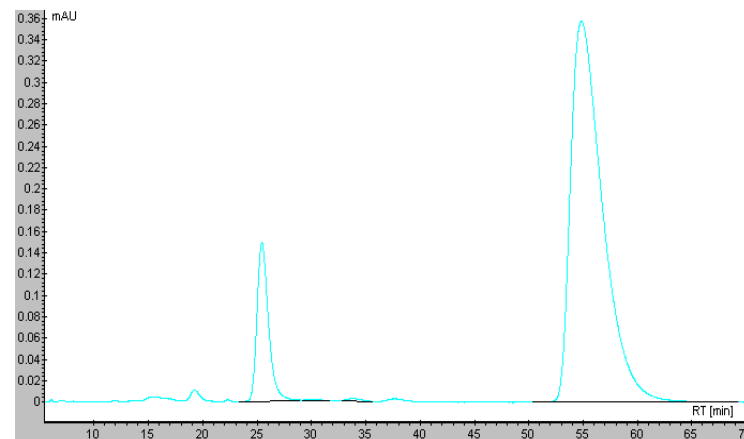
5f

Racimic adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	23.52	24.90	27.03	31.46
2	27.03	29.24	31.39	18.44
3	31.39	33.00	35.57	30.55
4	52.97	56.05	59.36	28.58

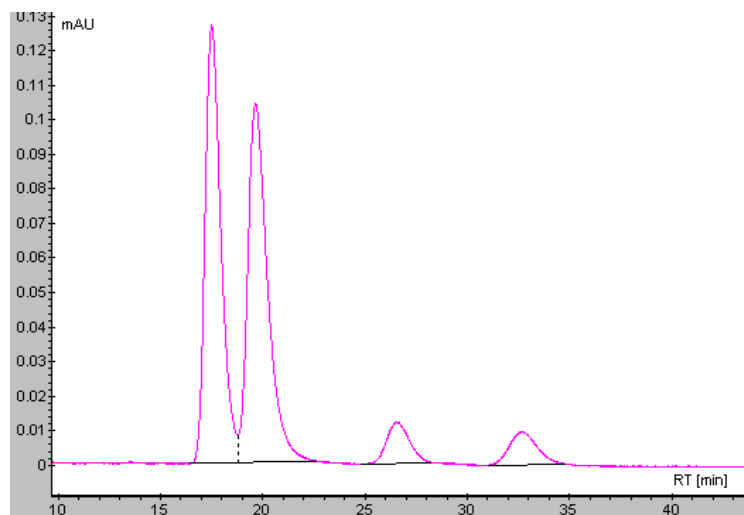
Asymmetric adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	23.38	25.44	29.10	12.87
2	29.22	30.46	32.21	0.05
3	32.55	33.74	35.75	0.24
4	50.41	54.83	69.31	86.84

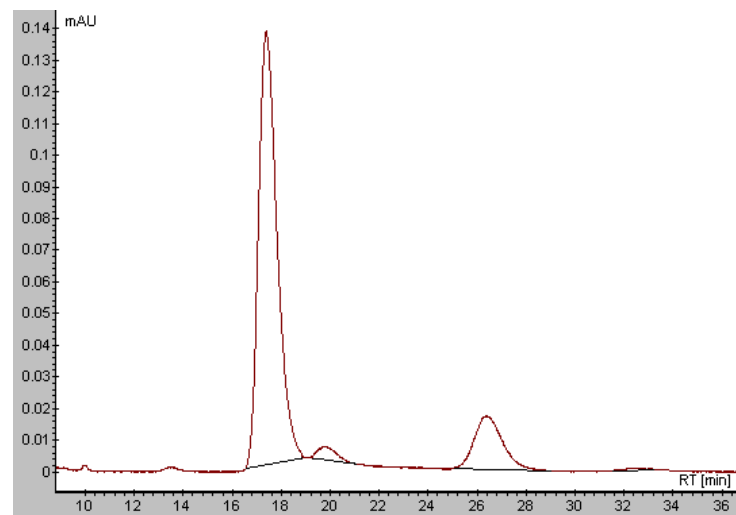
5g

Racimic adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	16.41	17.49	18.77	43.63
2	18.77	19.64	22.70	44.84
3	24.84	26.56	28.29	5.81
4	31.06	32.66	34.86	5.72

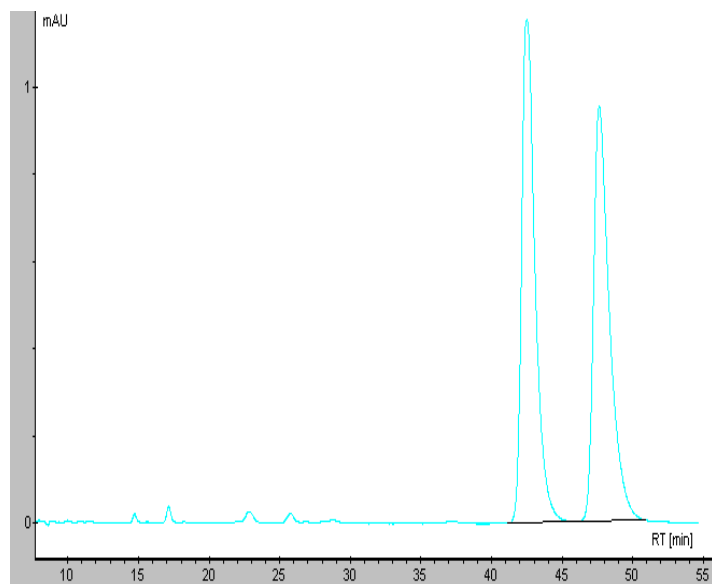
Asymmetric adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	15.98	17.38	19.01	81.58
2	19.12	19.81	21.18	2.63
3	24.77	26.38	29.11	15.24
4	31.56	32.42	33.63	0.55

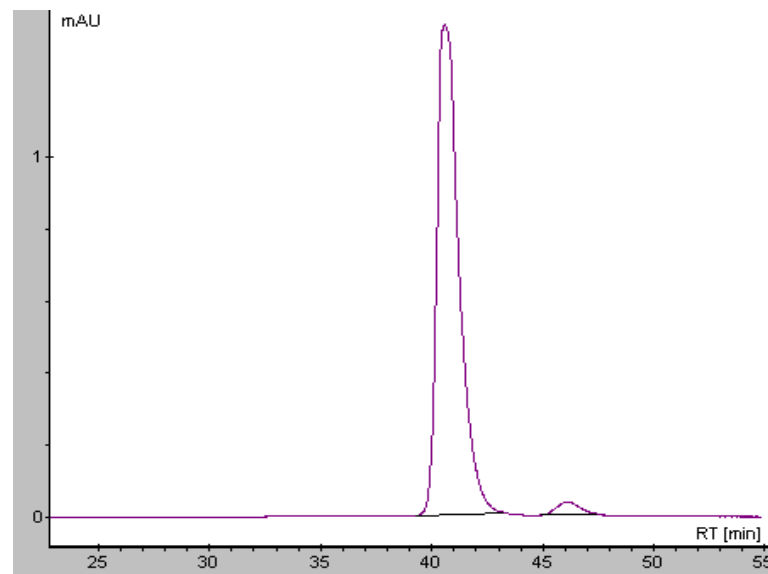
5h

Racimic adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	41.16	42.48	45.89	50.61
2	45.89	47.62	50.97	49.39

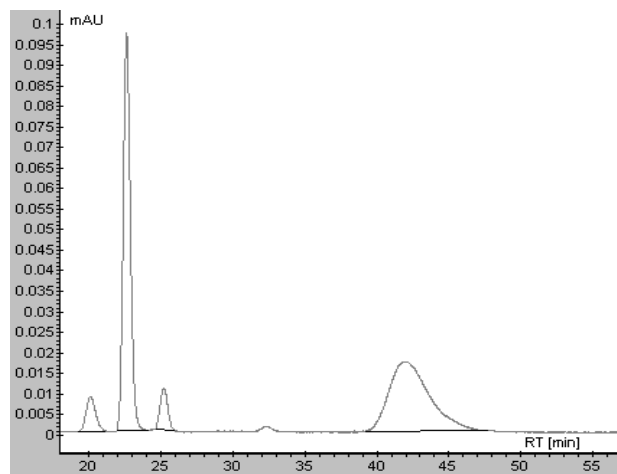
Asymmetric adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	39.29	40.58	43.40	97.30
2	44.93	46.09	47.56	2.70

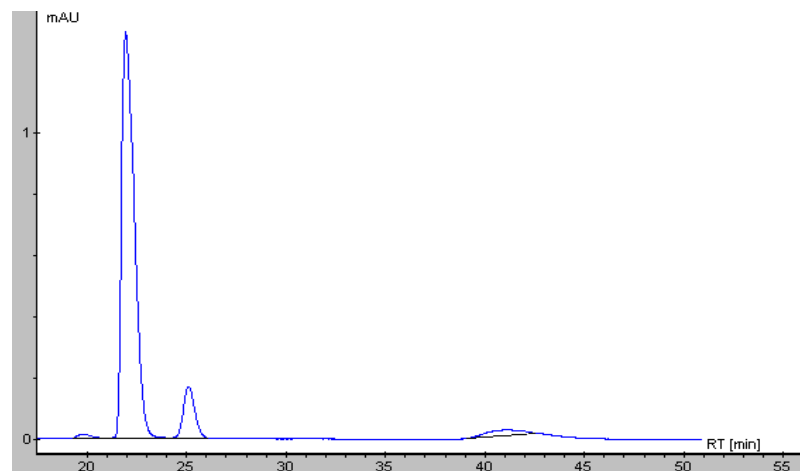
5i

Racimic adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	19.12	20.09	21.18	5.32
2	21.57	22.59	24.03	45.14
3	24.42	25.18	26.03	5.14
4	38.38	41.96	47.81	44.40

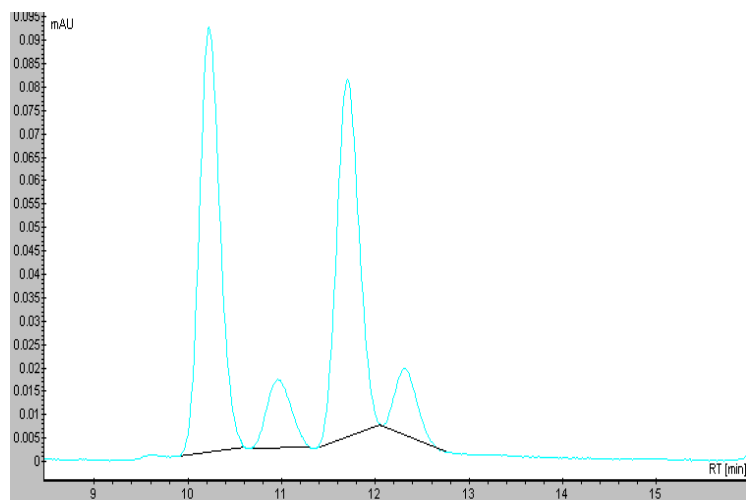
Asymmetric adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	19.13	19.80	21.00	1.09
2	21.00	21.93	24.17	85.62
3	24.17	25.09	26.17	9.83
4	39.06	40.81	42.68	3.46

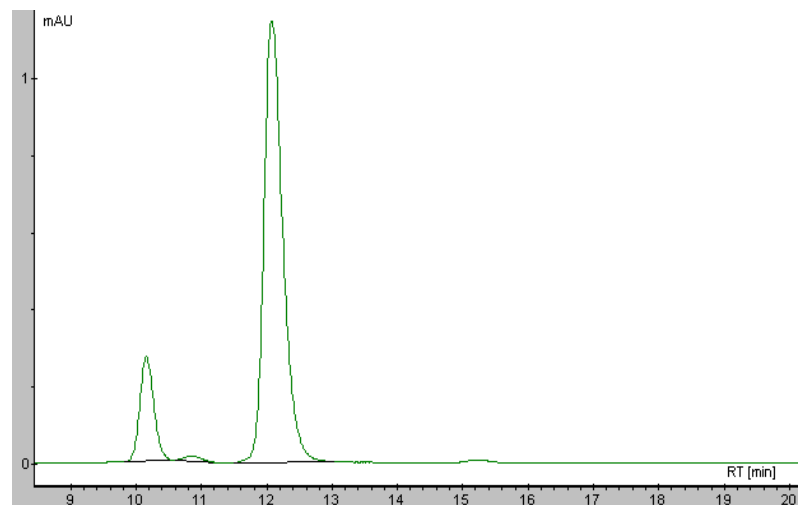
5j

Racemic adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	9.90	10.23	10.62	44.06
2	10.67	10.96	11.30	8.38
3	11.37	11.71	12.05	40.17
4	12.08	12.32	12.78	7.39

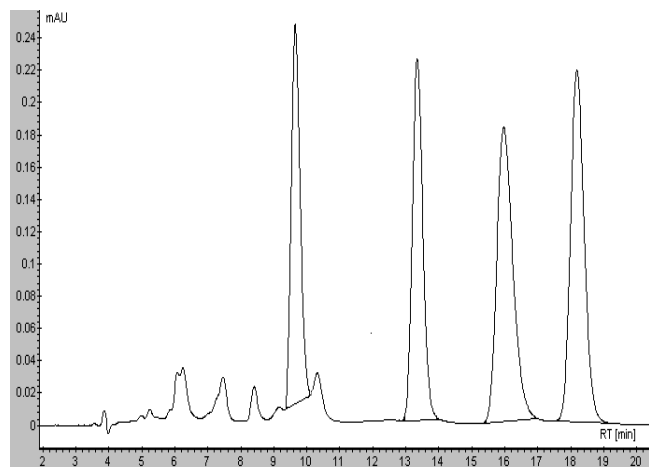
Asymmetric adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	9.78	10.16	10.54	14.62
2	10.60	10.85	11.27	0.88
3	11.48	12.08	13.17	84.50

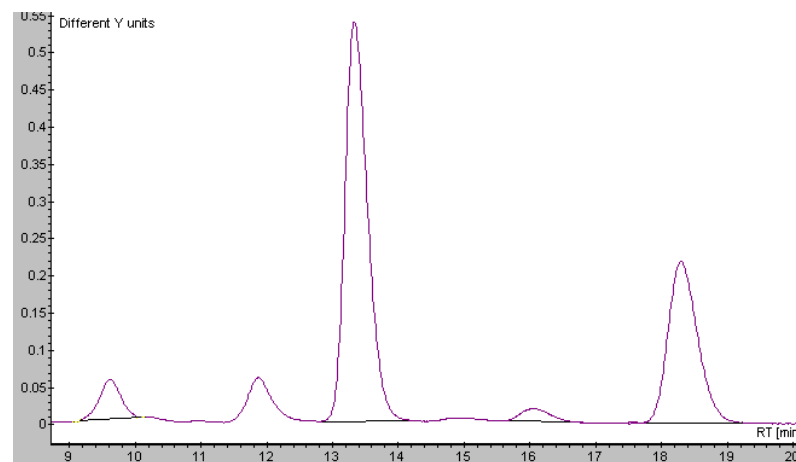
5k

Racimic adduct



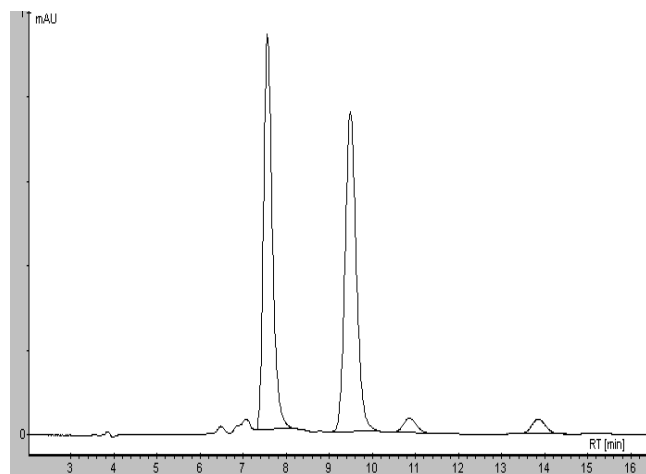
#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	9.32	9.65	10.15	20.22
2	12.89	13.35	14.03	22.67
3	15.36	18.97	17.00	28.22
4	17.50	18.18	19.38	28.90

Asymmetric adduct

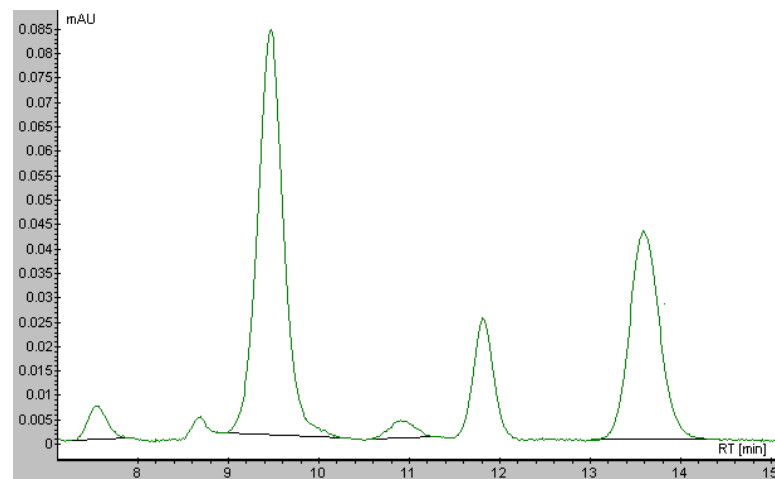


#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	9.12	9.61	10.10	5.56
2	12.81	13.33	14.21	59.92
3	15.56	16.05	16.75	2.60
4	17.65	18.29	19.36	31.81

51

Racimic adduct

#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	7.28	7.56	8.15	46.72
2	9.01	9.48	10.12	48.14
3	10.54	10.85	11.44	2.49
4	13.42	13.85	14.35	2.66

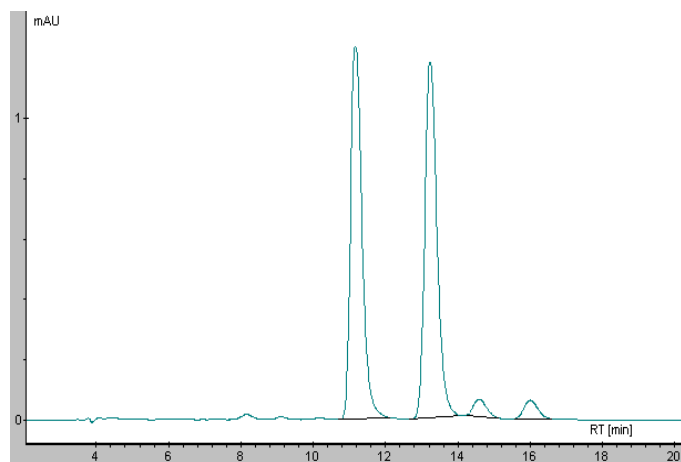
Asymmetric adduct

#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	7.28	7.53	7.91	3.74
2	8.95	9.47	10.29	59.04
3	10.58	10.92	11.30	2.49
4	13.05	13.59	14.32	34.73

S33

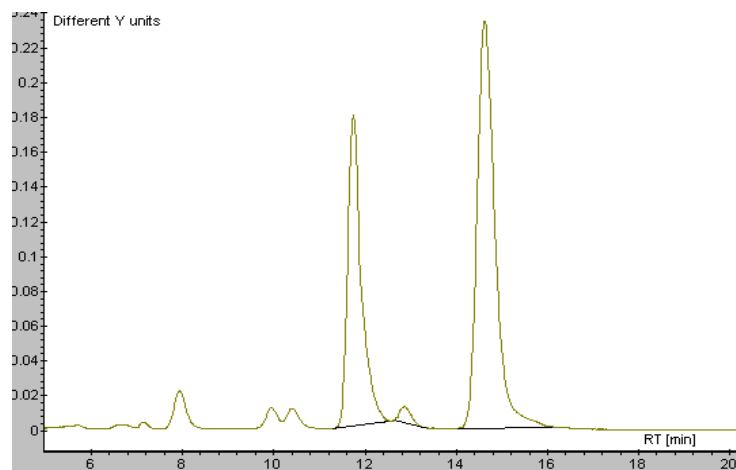
5m

Racimic adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	10.71	11.17	12.26	47.13
2	12.67	13.23	14.10	47.13
3	14.22	14.60	15.34	2.53
4	15.46	16.00	16.69	2.91

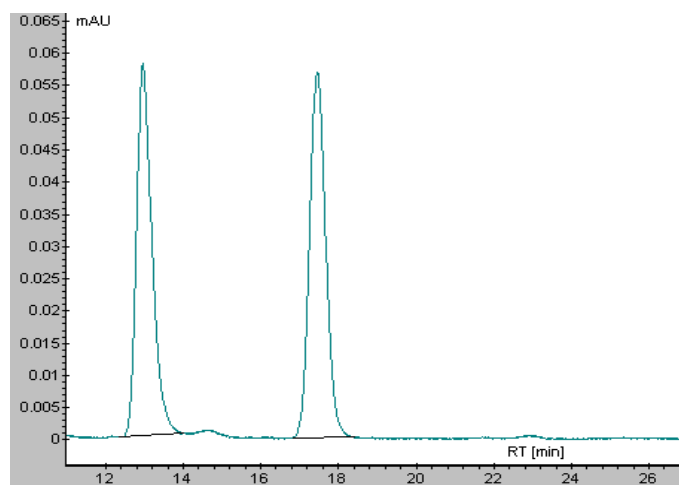
Asymmetric adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	11.27	11.75	12.51	36.24
2	12.64	12.87	13.40	1.48
3	14.05	14.63	16.12	62.27

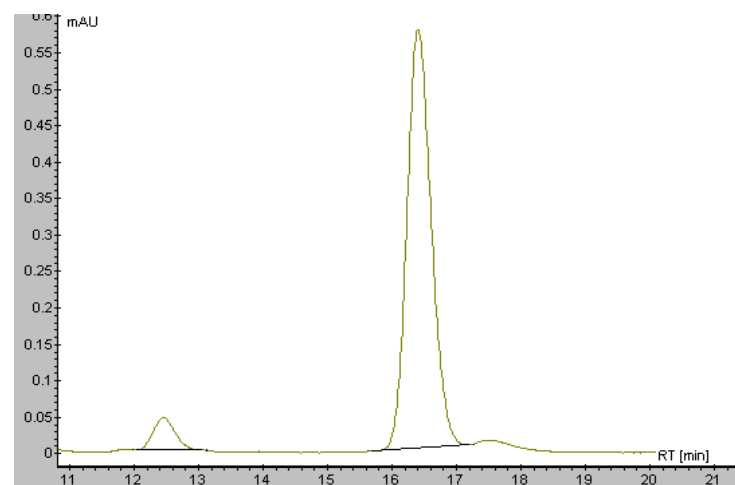
5n

Racimic adduct



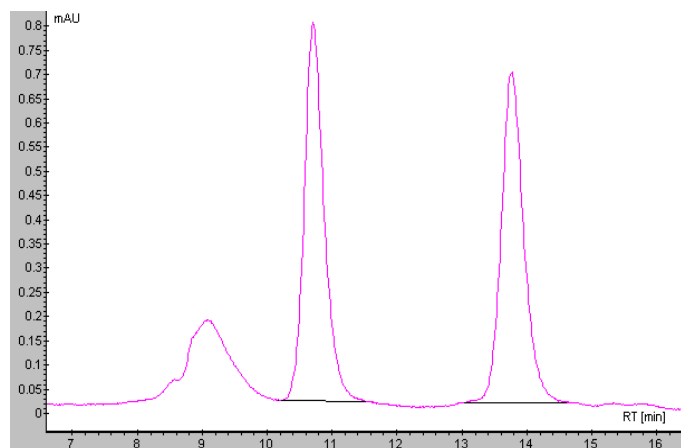
#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	12.33	12.93	14.02	49.02
2	16.75	17.44	18.52	50.98

Asymmetric adduct

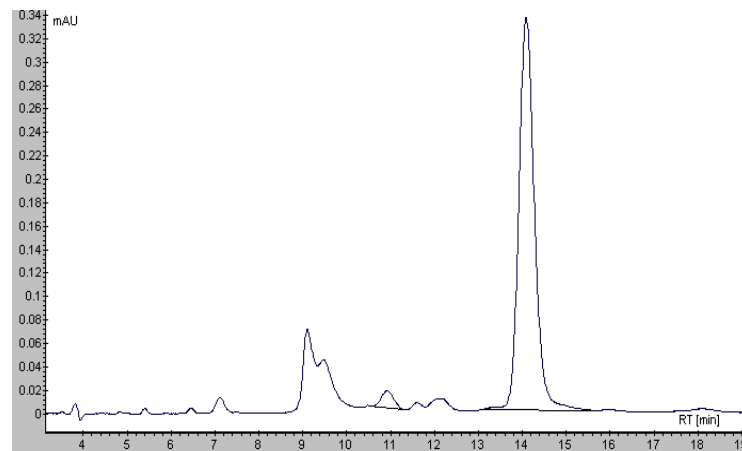


#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	12.04	12.45	13.06	6.34
2	15.69	16.41	17.21	93.66

50

Racimic adduct

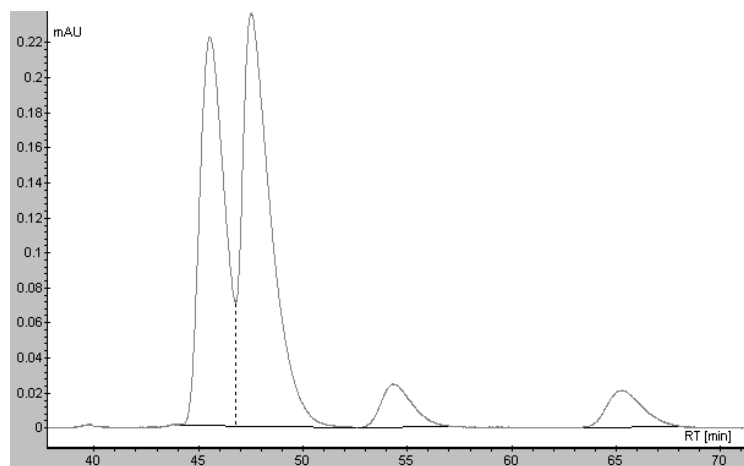
#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	10.22	10.71	11.56	50.30
2	13.01	13.77	14.74	49.70

Asymmetric adduct

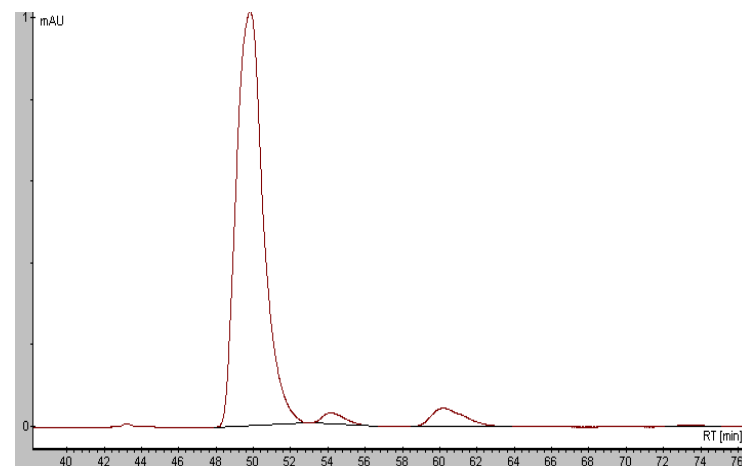
#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	10.48	10.92	11.30	3.30
2	13.05	14.09	15.66	96.70

5p

Racimic adduct



Asymmetric adduct

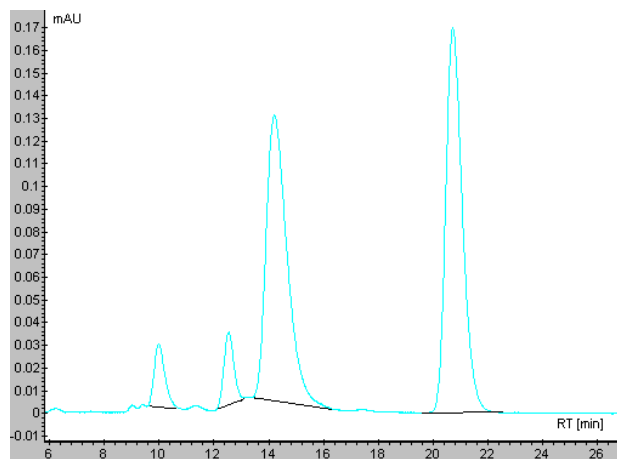


#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	44.17	44.54	46.78	40.65
2	46.78	47.53	52.61	48.64
3	52.66	54.34	56.99	5.45
4	63.48	65.24	68.02	5.26

#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	47.87	49.84	52.93	92.42
2	53.13	54.19	56.74	2.15
3	58.45	60.18	63.97	5.08
4	72.12	73.45	75.20	0.35

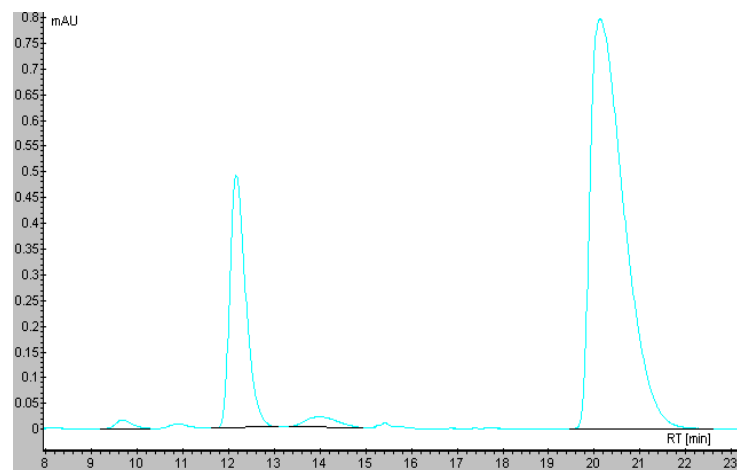
5q

Racimic adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	9.49	9.99	10.83	4.91
2	11.98	12.53	13.13	5.19
3	13.35	14.21	16.33	43.31
4	19.61	20.72	22.58	46.59

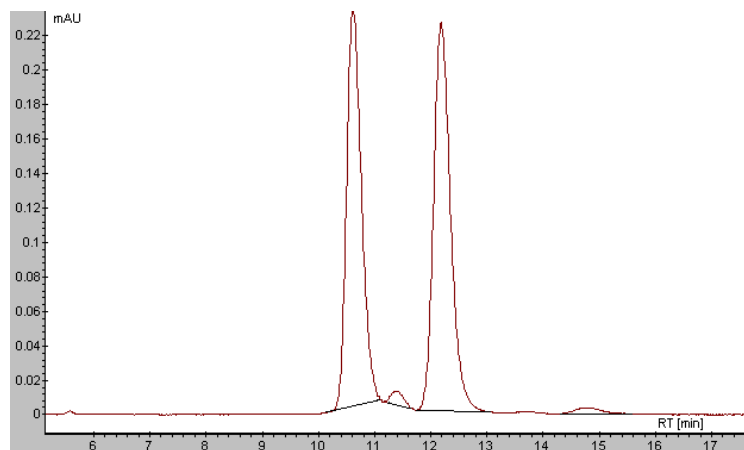
Asymmetric adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	9.20	9.67	10.31	0.75
2	11.62	12.16	13.12	22.00
3	13.31	13.97	14.96	1.84
4	19.46	20.12	22.65	75.41

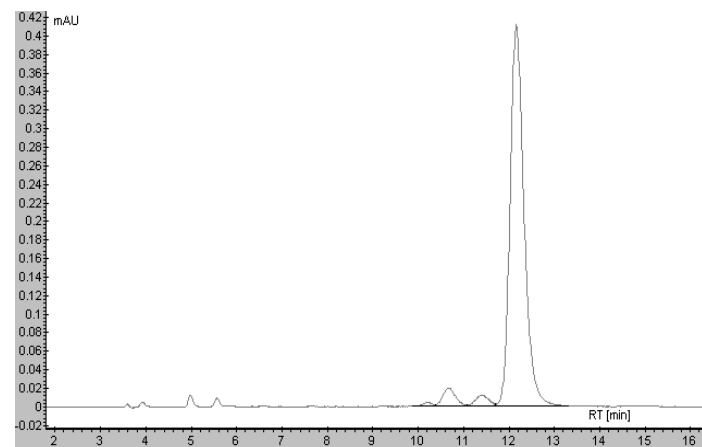
5r

Racimic adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	10.08	10.61	11.10	46.11
2	11.19	11.40	11.69	1.36
3	11.75	12.19	13.08	51.25
4	14.31	14.79	15.65	1.27

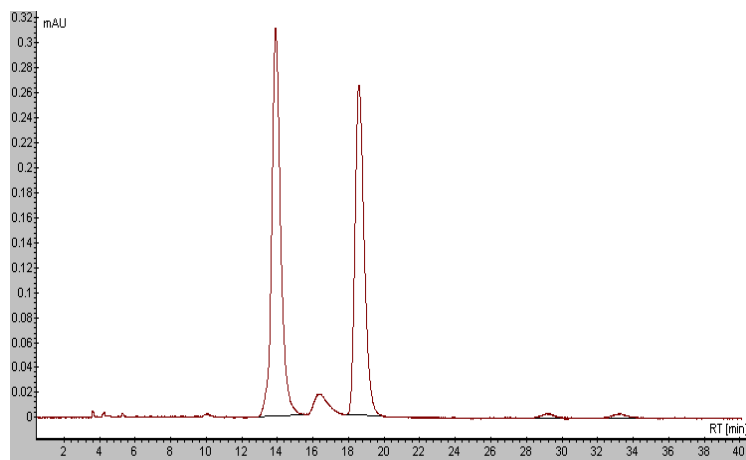
Asymmetric adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	10.37	10.67	11.07	4.15
2	11.07	11.40	11.71	2.71
3	11.71	12.16	13.33	93.14

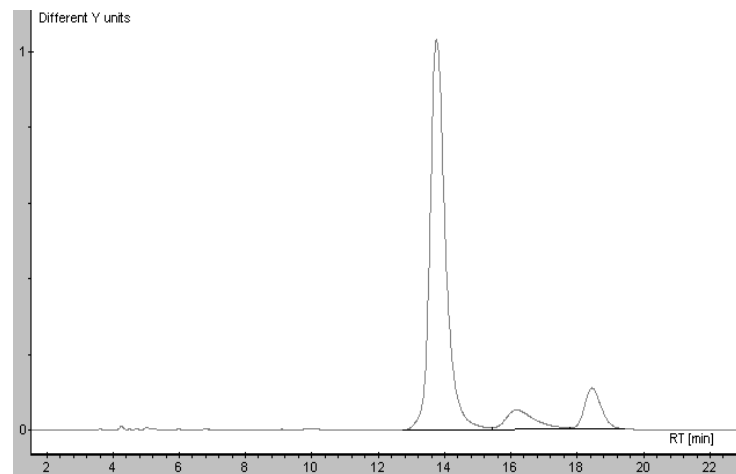
5s

Racimic adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	12.61	13.91	15.50	52.28
2	17.89	18.58	20.10	46.21
3	28.37	29.21	30.03	0.74
4	32.42	33.24	34.29	0.77

Asymmetric adduct



#	Start [Min]	Time [Min]	End [Min]	Area% [%]
1	12.75	13.76	15.44	89.64
2	17.77	18.44	19.50	10.36

4. Crystal structure of the Michael adduct **5a**¹ and **5b**².

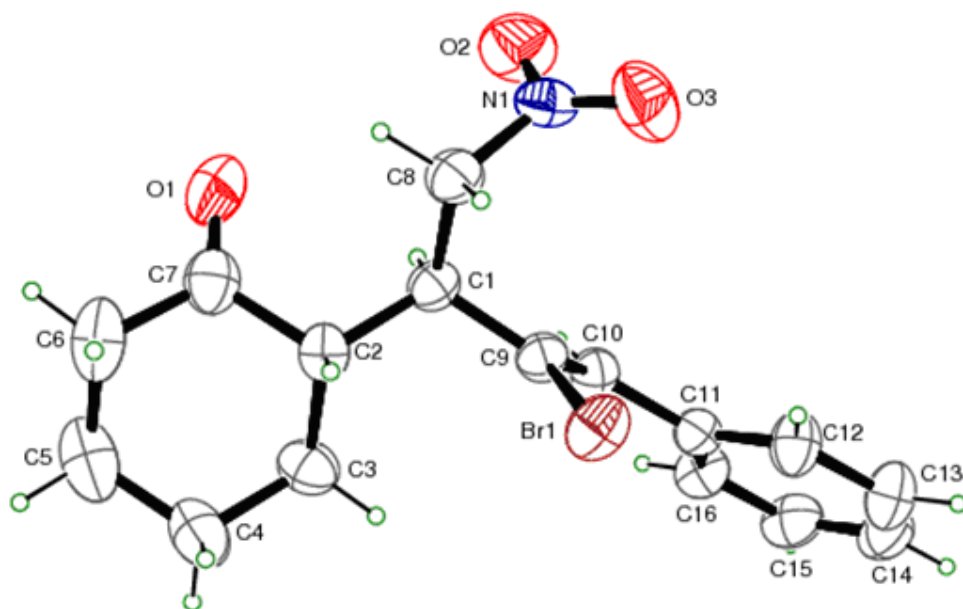


Figure 1S X-ray crystal structure of the Michael adduct **5a**

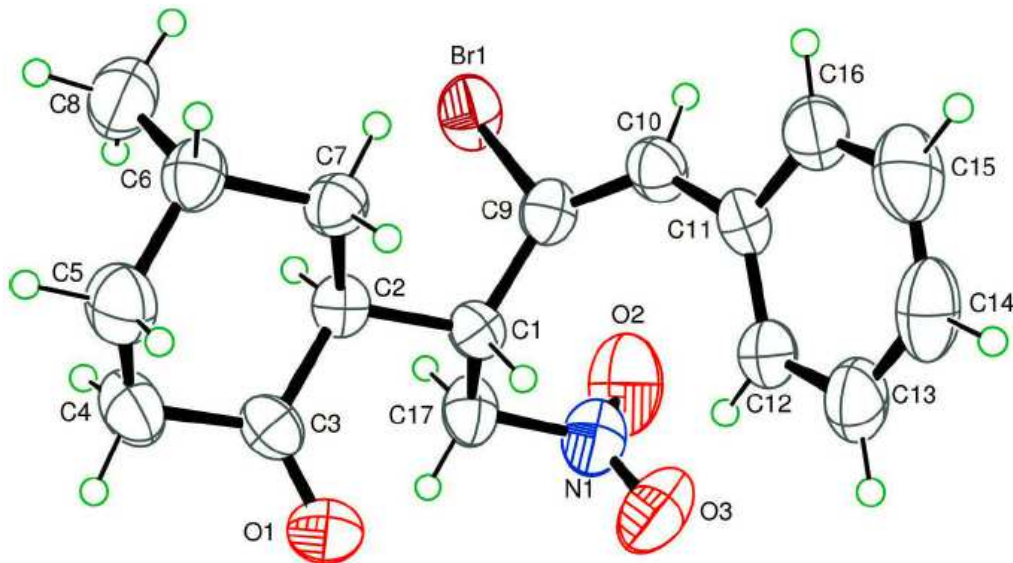


Figure 2S X-ray crystal structure of the Michael adduct **5b**

6. References.

- (1) C. Wu, L. Zhao and A. -B. Xia, *Acta Cryst.* 2011, **E67**, o1939.
- (2) L. Zhao, C. Wu, W. -Z. Weng, C. -X. Yan and A. -B. Xia, *Acta Cryst.* 2012, **E68**, o1253.