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Supplementary Information

Enantioselective nitro-Michael reactions catalyzed by short peptides on water

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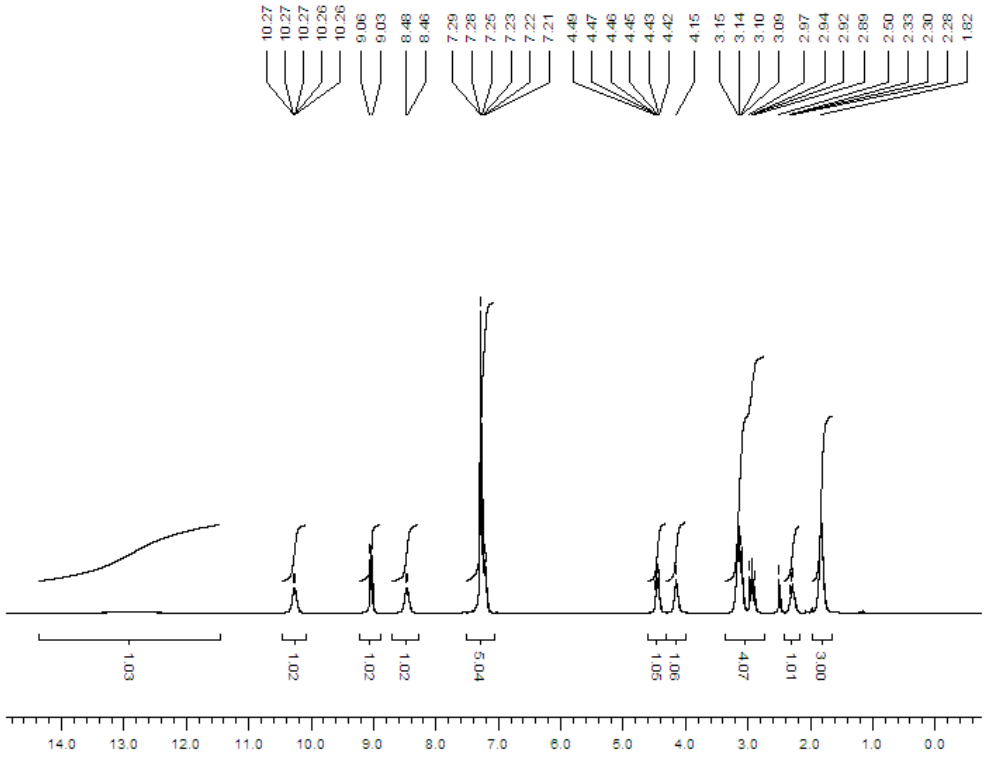
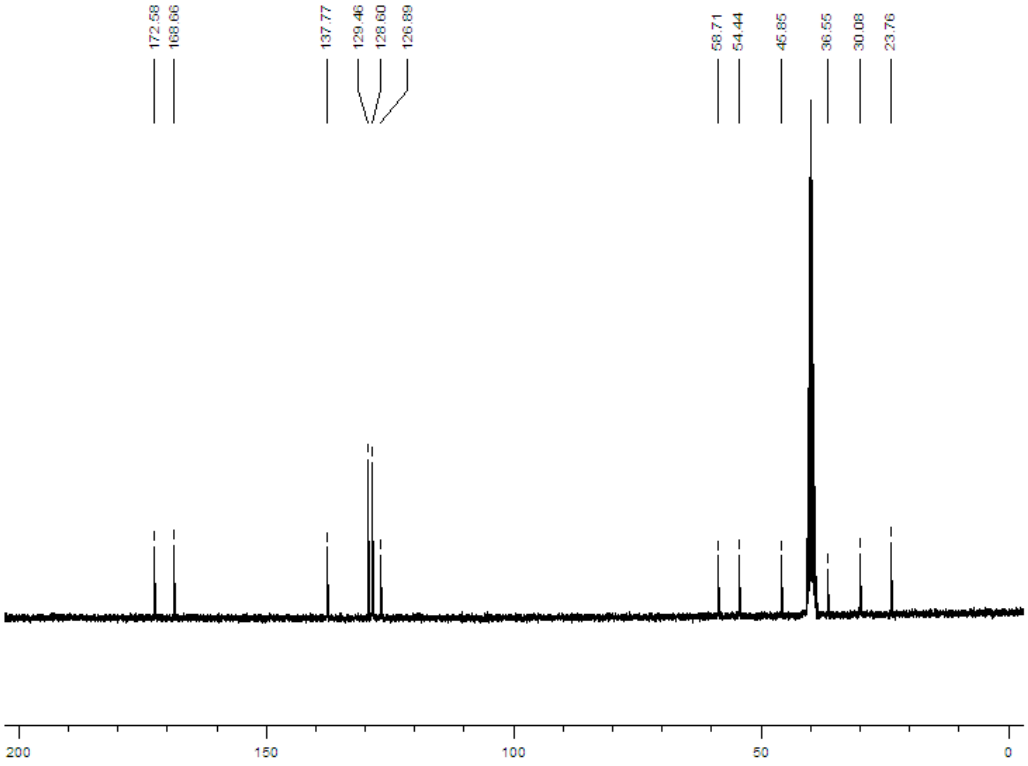
1 NMR-Spectra of Catalysts and Catalytic Products:

1.1 (*S*)-Prolyl-(*S*)-phenylalanine-hydrochloride (H-Pro-Phe-OH•HCl) (1):

^{1}H-NMR (300 MHz; DMSO[d6]):

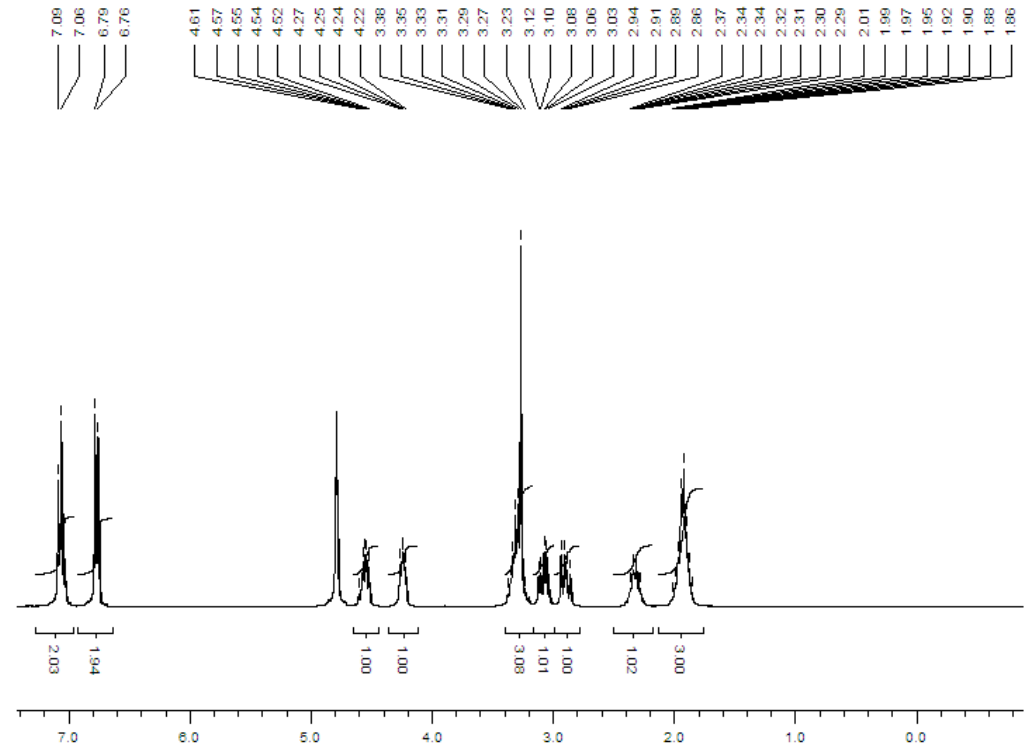


^{13}C-NMR (300 MHz; DMSO[d6]):

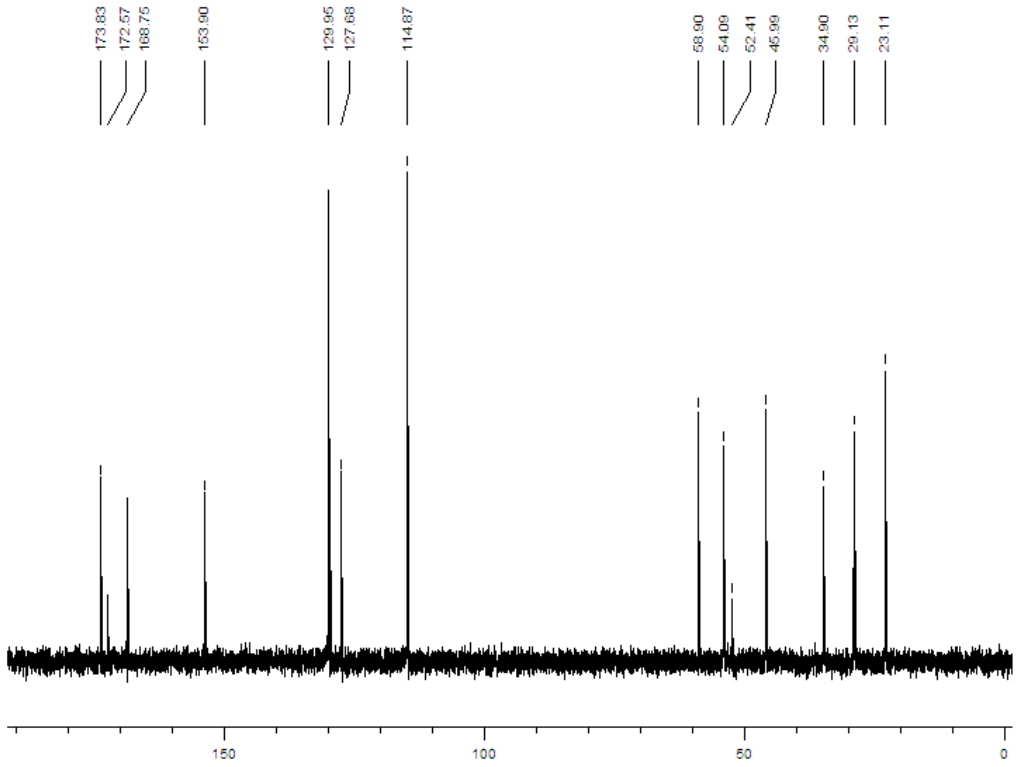


1.2 (*S*)-Prolyl-(*S*)-tyrosine-hydrochloride (H-Pro-Tyr-OH•HCl) (2):

^{1}H-NMR (300 MHz; D_2O):

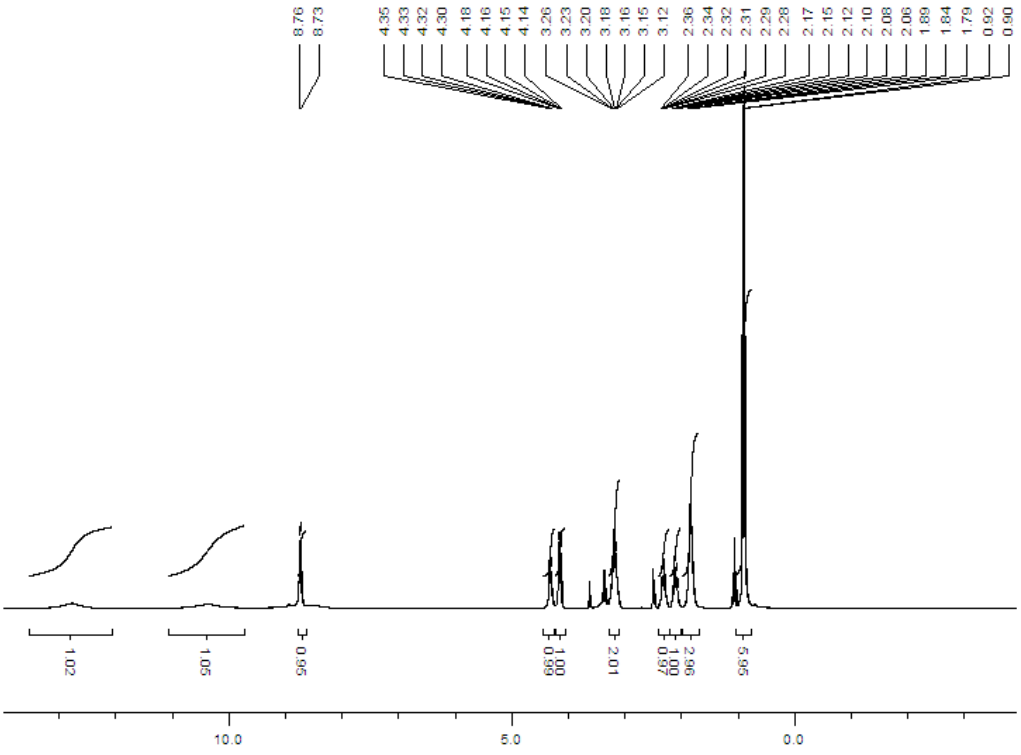


^{13}C-NMR (300 MHz; D_2O):

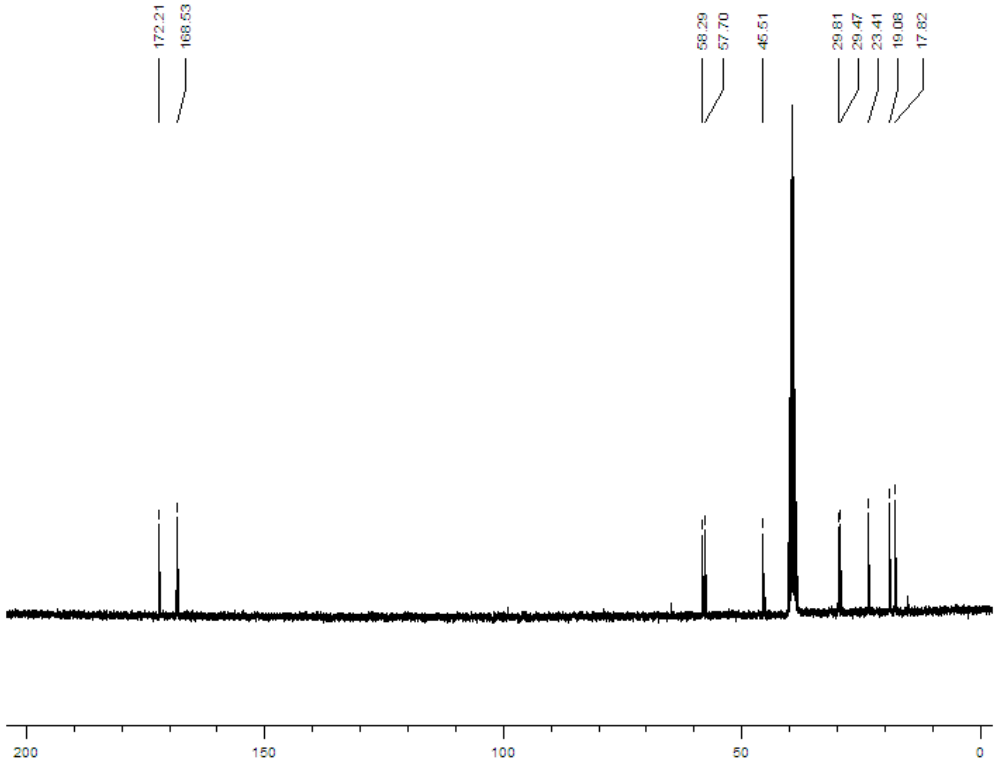


1.3 (*S*)-Prolyl-(*S*)-valine-hydrochloride (H-Pro-Val-OH•HCl) (3):

^{1}H-NMR (300 MHz; DMSO[d6]):

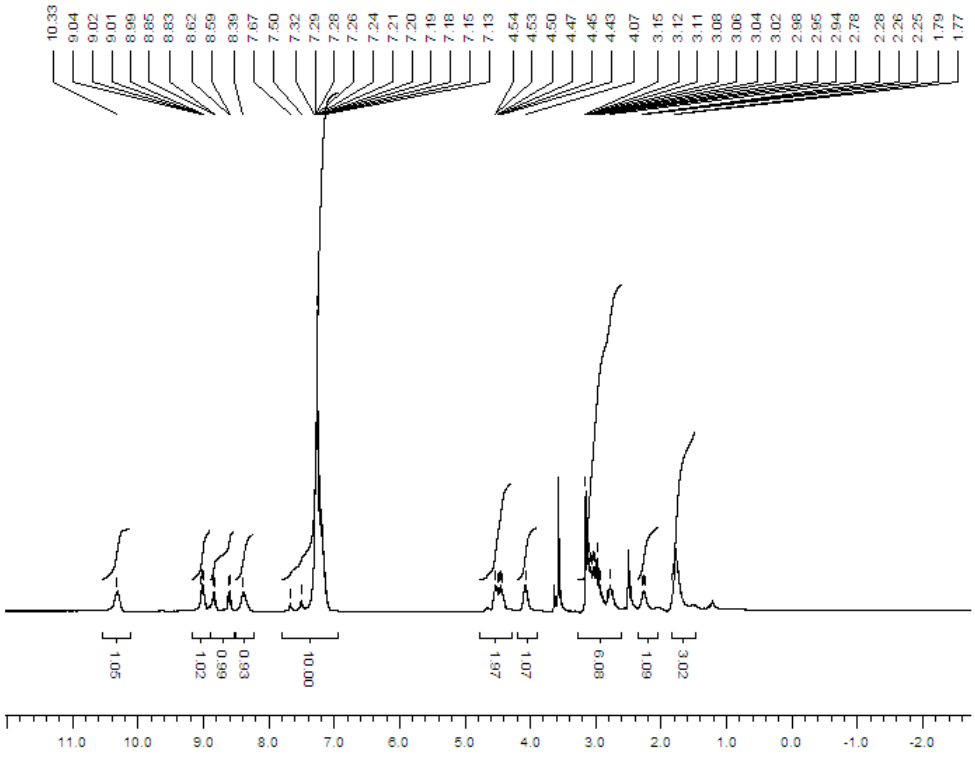


^{13}C-NMR (300 MHz; DMSO[d6]):

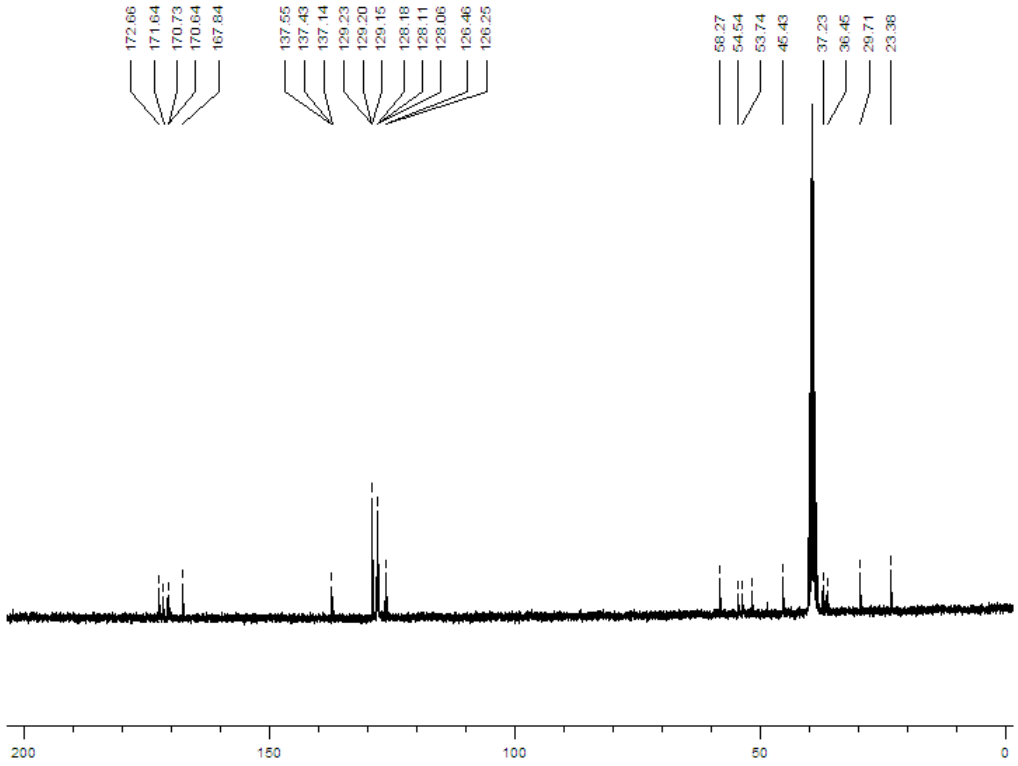


1.4 (*S*)-Prolyl-(*S*)-phenylalanyl-(*S*)-phenylalanine-hydrochloride (H-Pro-Phe-Phe-OH•HCl) (4):

^{1}H-NMR (300 MHz; DMSO[d6]):

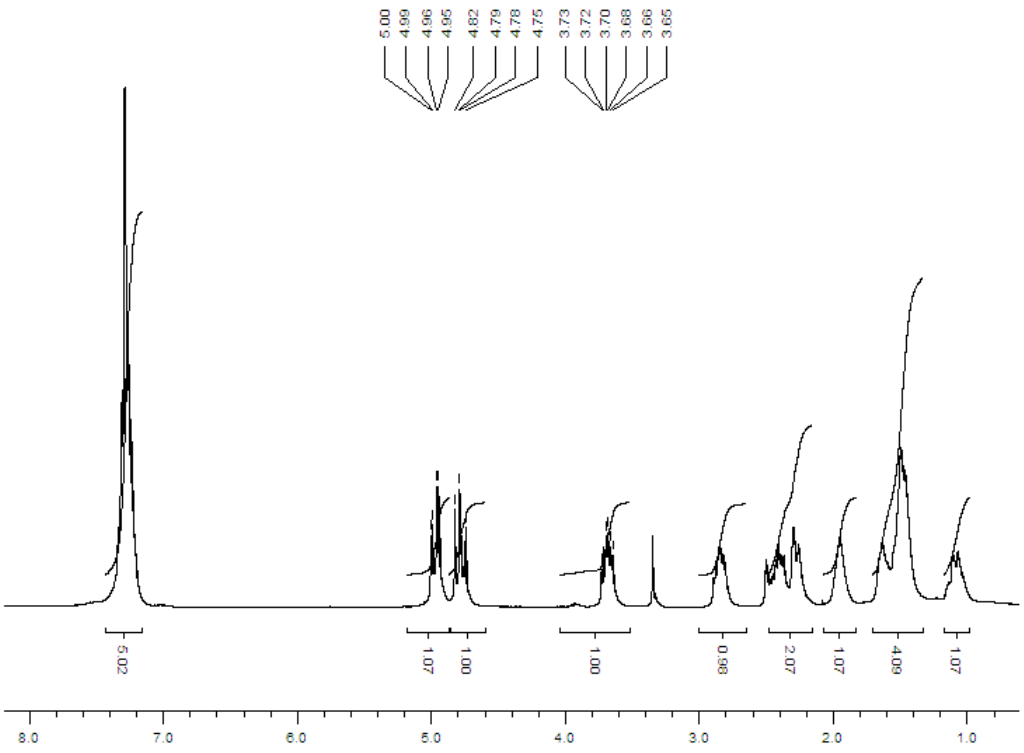


^{13}C-NMR (300 MHz; DMSO[d6]):

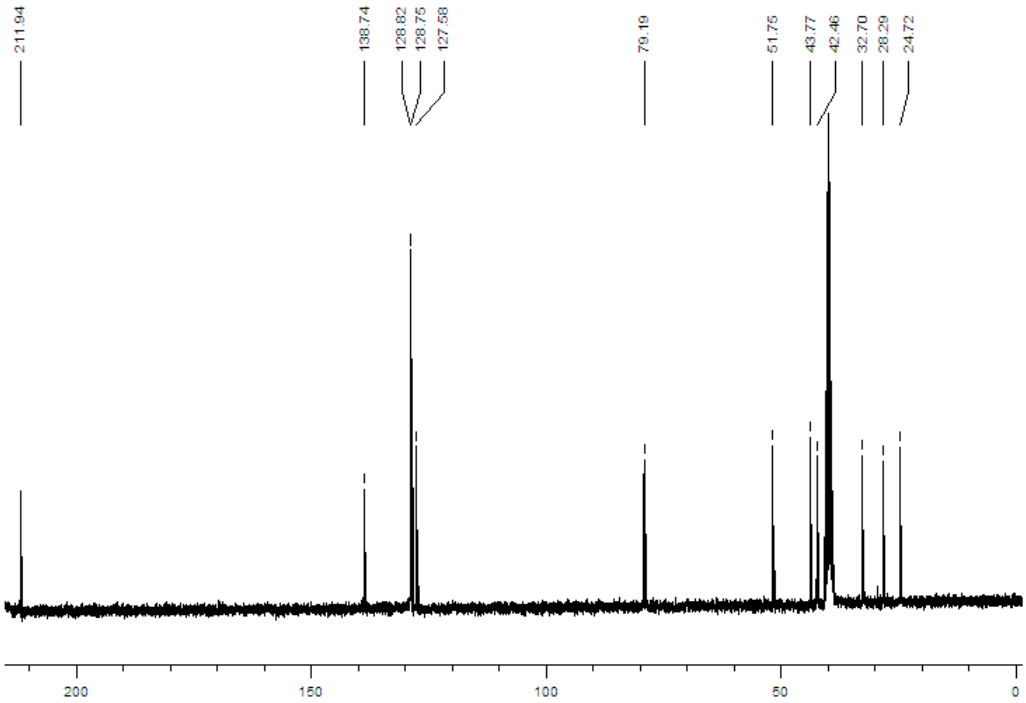


1.5 2-(2-Nitro-1-phenyl-ethyl)-cyclohexanone (7):

^{1}H-NMR (300 MHz; DMSO[d6]):

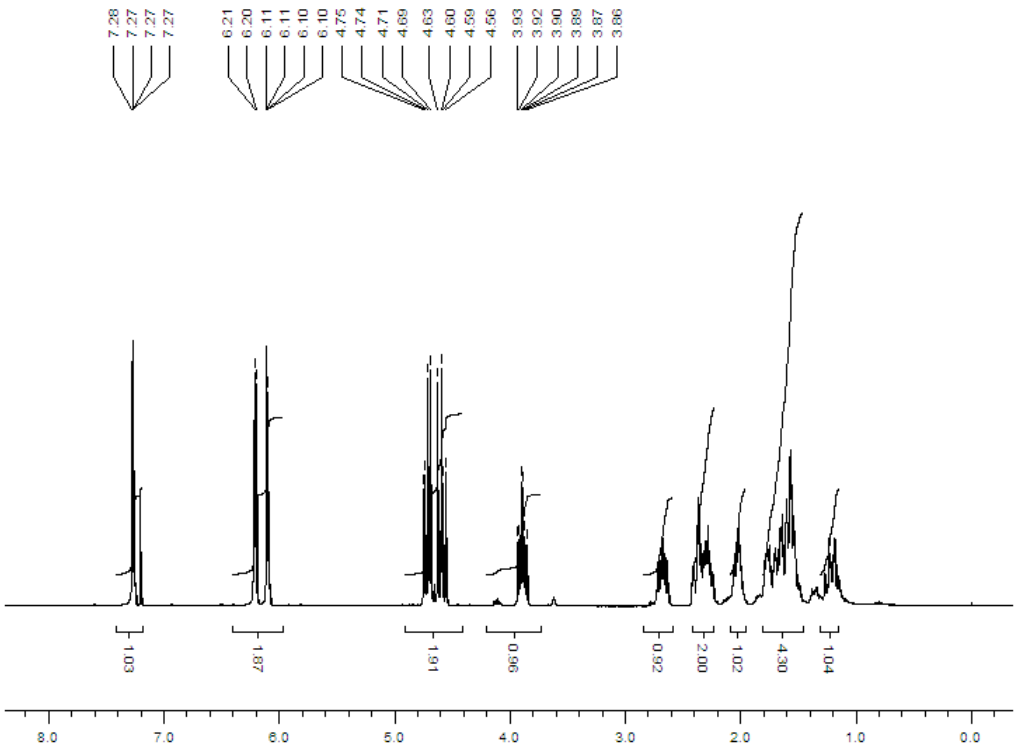


^{13}C-NMR (300 MHz; DMSO[d6]):

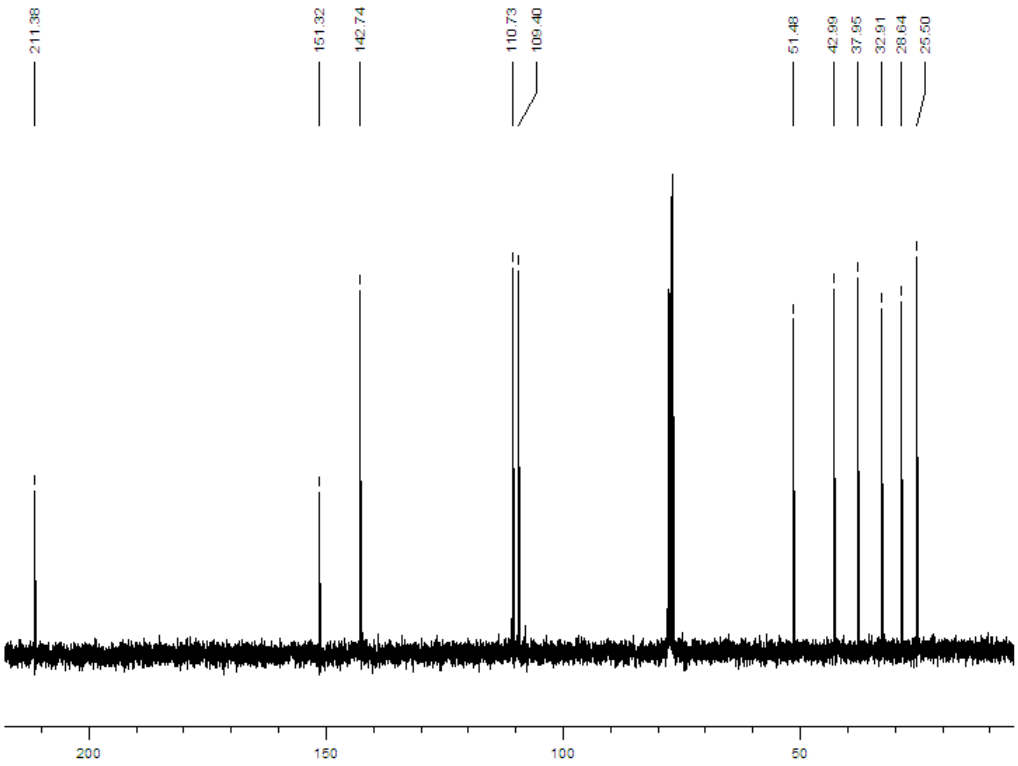


1.6 2-(1-Furan-2-yl-2-nitro-ethyl)-cyclohexanone (8):

^{1}H-NMR (300 MHz; $CDCl_3$):

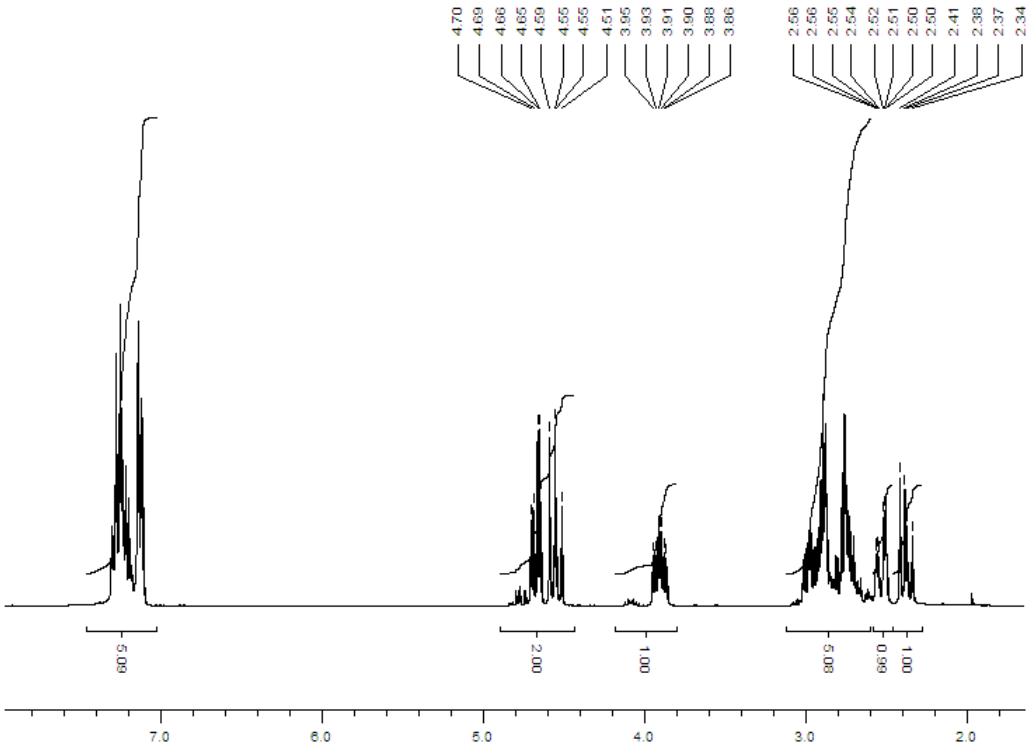


^{13}C-NMR (300 MHz; $CDCl_3$):

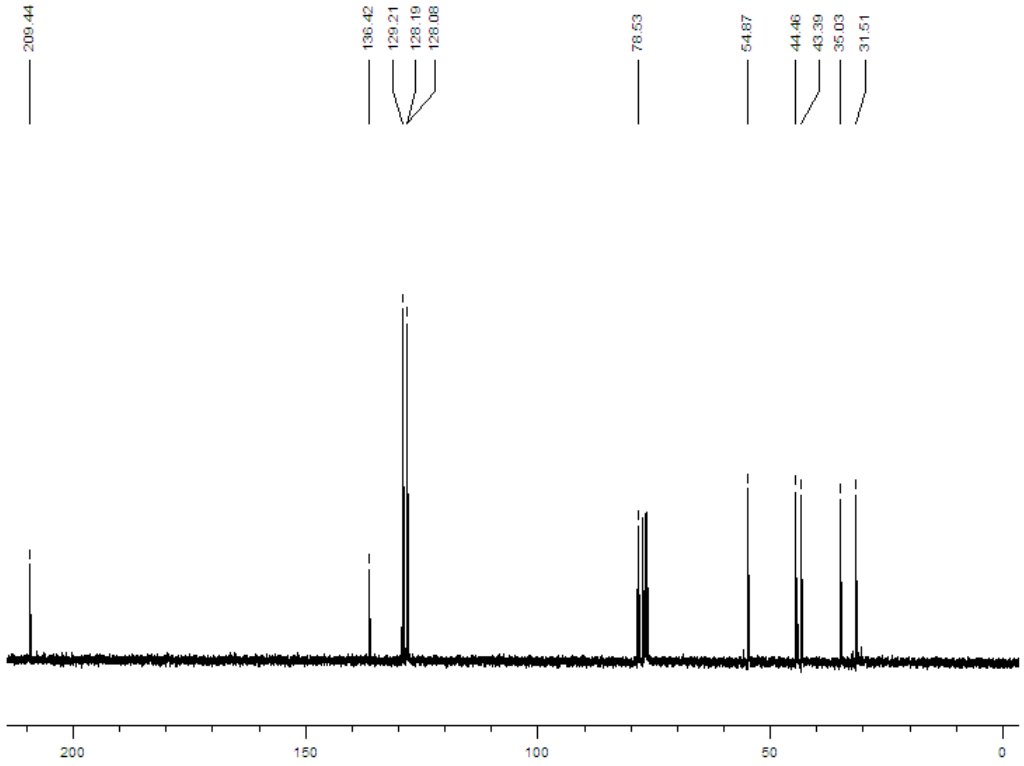


1.7 3-(2-Nitro-1-phenylethyl)-tetrahydro-thiopyran-4-one (9):

^{1}H-NMR (300 MHz; $CDCl_3$):

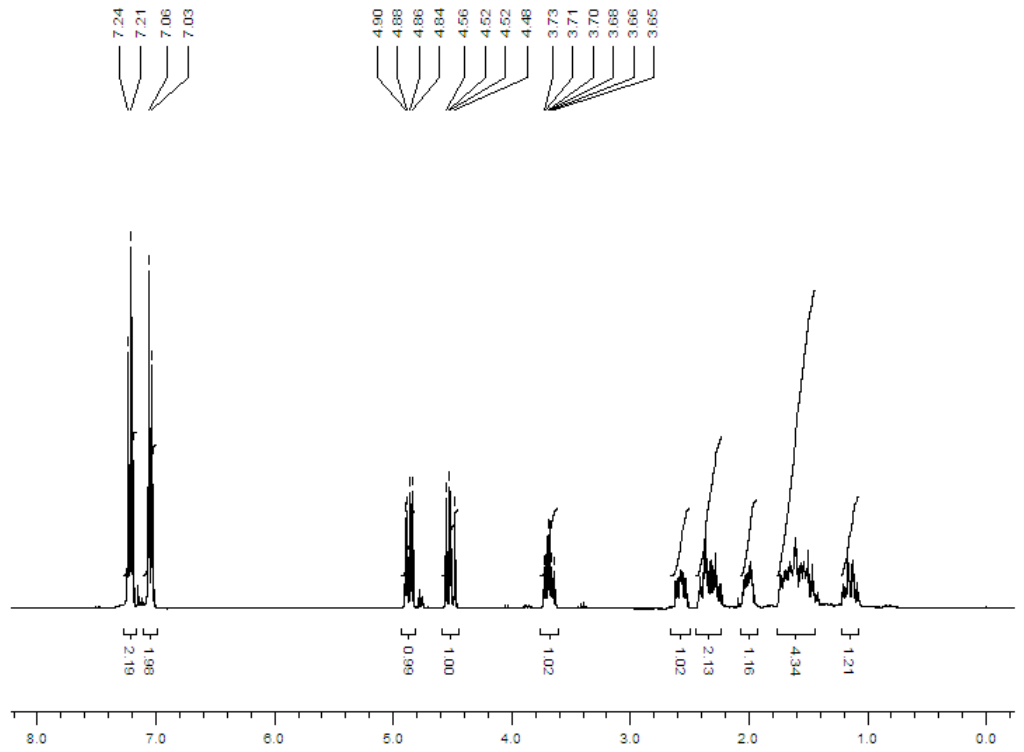


^{13}C-NMR (300 MHz; $CDCl_3$):

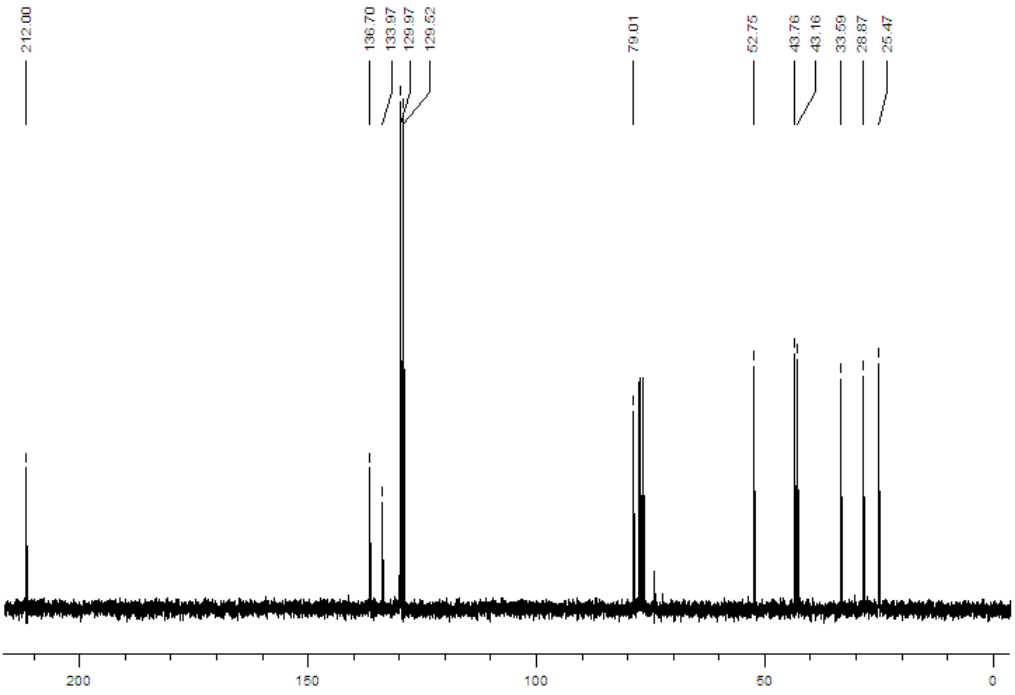


1.8 2-[1-(4-Chloro-phenyl)-2-nitro-ethyl]-cyclohexanone (10):

^{1}H-NMR (300 MHz; $CDCl_3$):

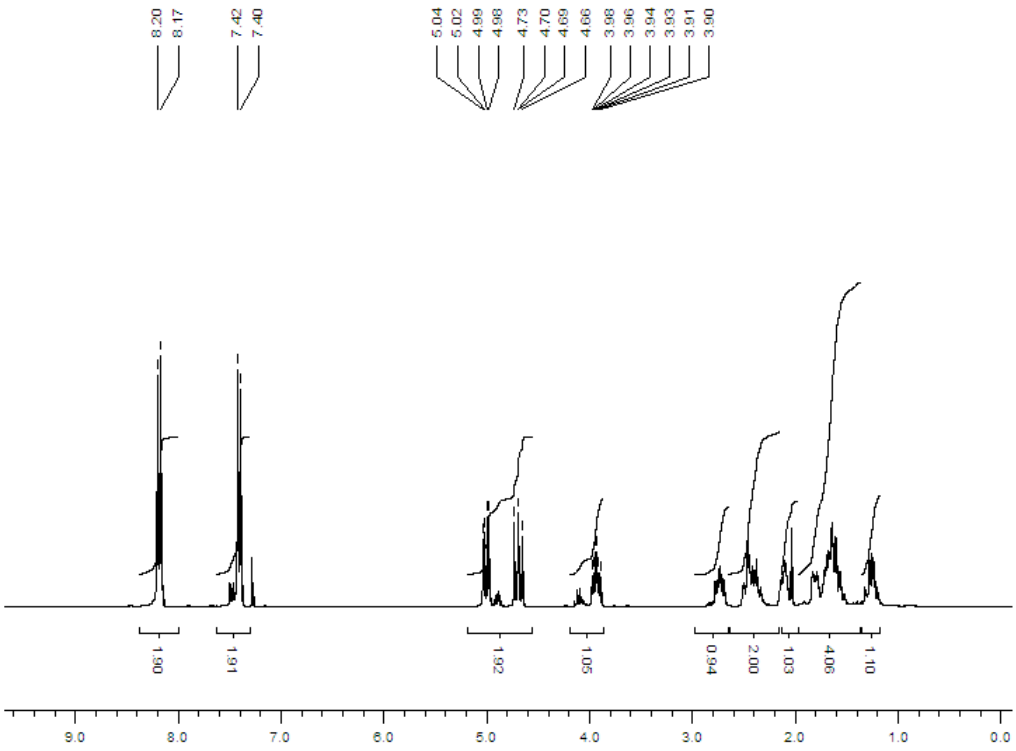


^{13}C-NMR (300 MHz; $CDCl_3$):

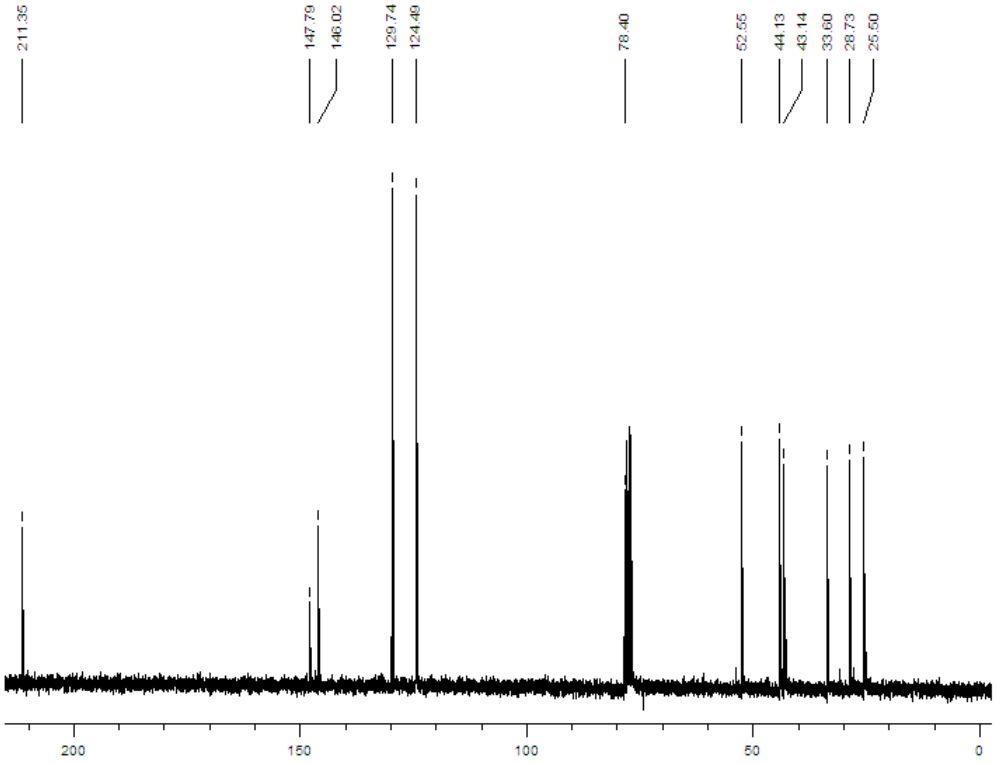


1.9 2-[2-Nitro-1-(4-nitro-phenyl)-ethyl]-cyclohexanone (11):

^{1}H-NMR (300 MHz; $CDCl_3$):

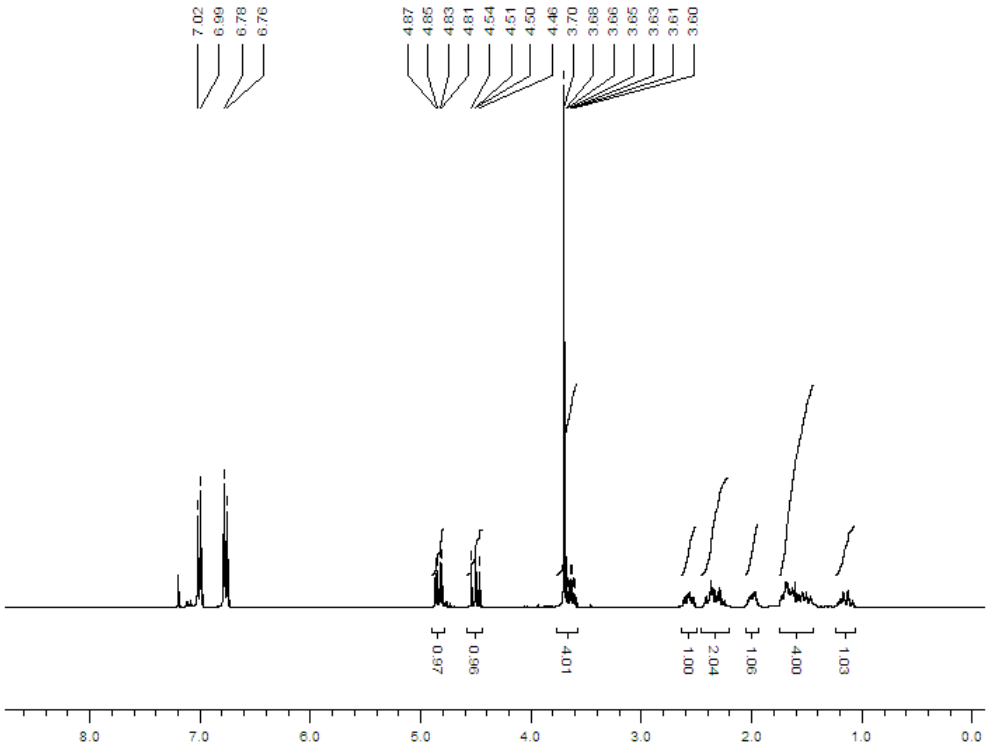


^{13}C-NMR (300 MHz; $CDCl_3$):

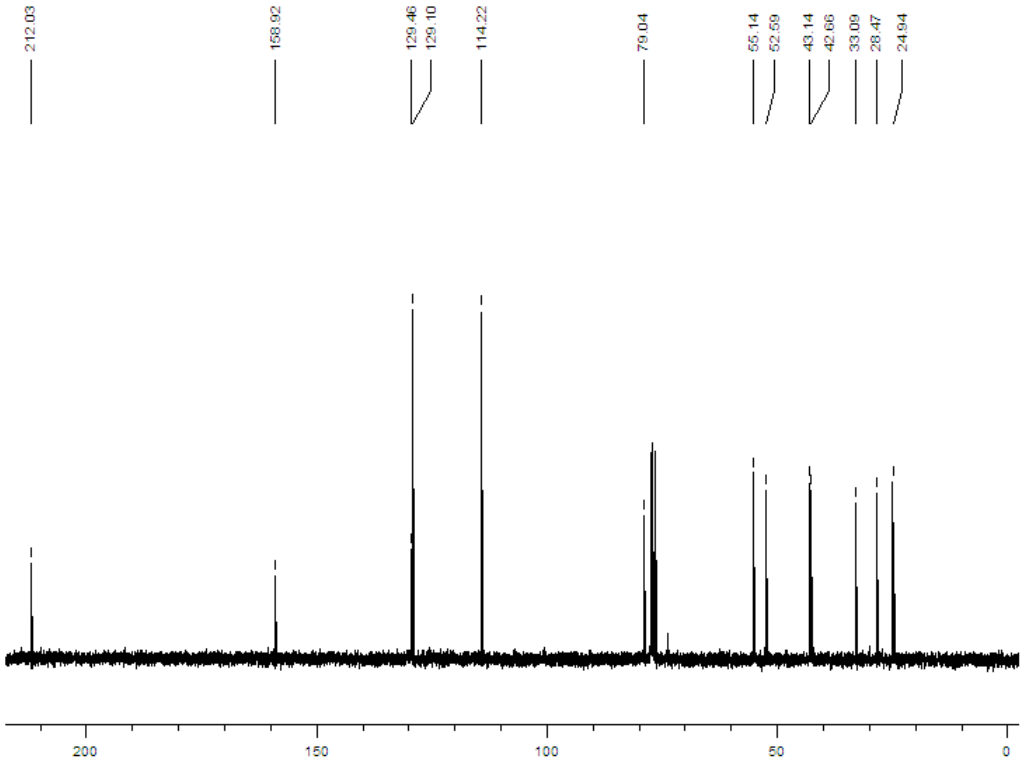


1.10 2-[1-(4-Methoxy-phenyl)-2-nitro-ethyl]-cyclohexanone (12):

^{1}H-NMR (300 MHz; $CDCl_3$):

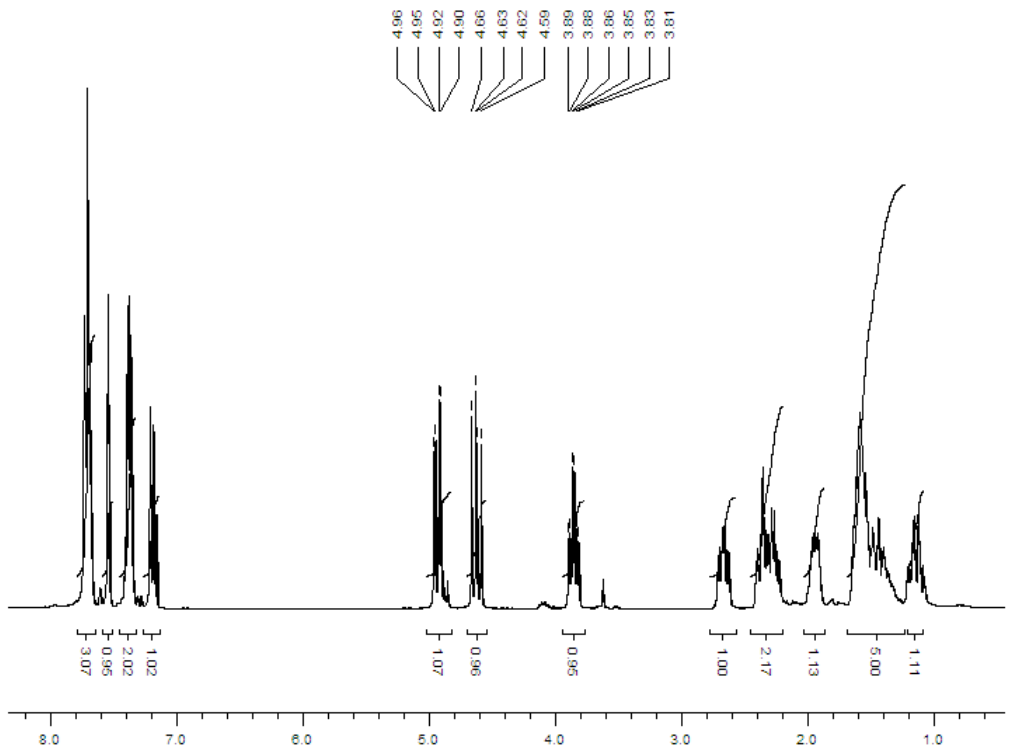


^{13}C-NMR (300 MHz; $CDCl_3$):

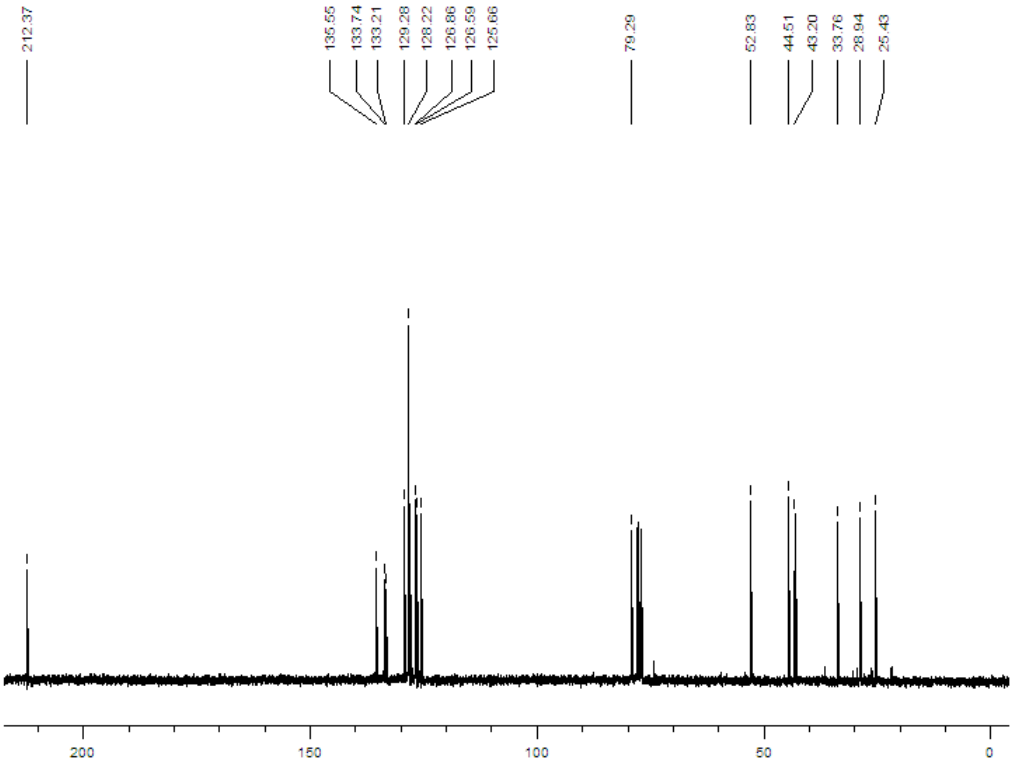


1.11 2-(1-Napht-2-yl-2-nitro-ethyl)-cyclohexanone (13):

^{1}H-NMR (300 MHz; $CDCl_3$):

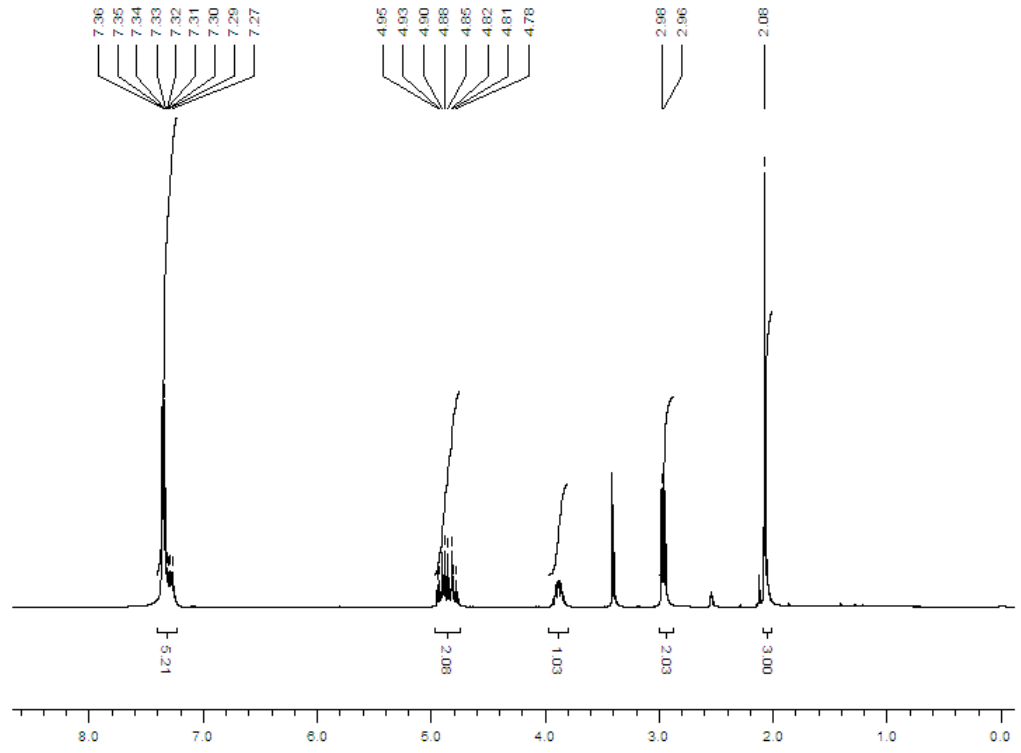


^{13}C-NMR (300 MHz; $CDCl_3$):

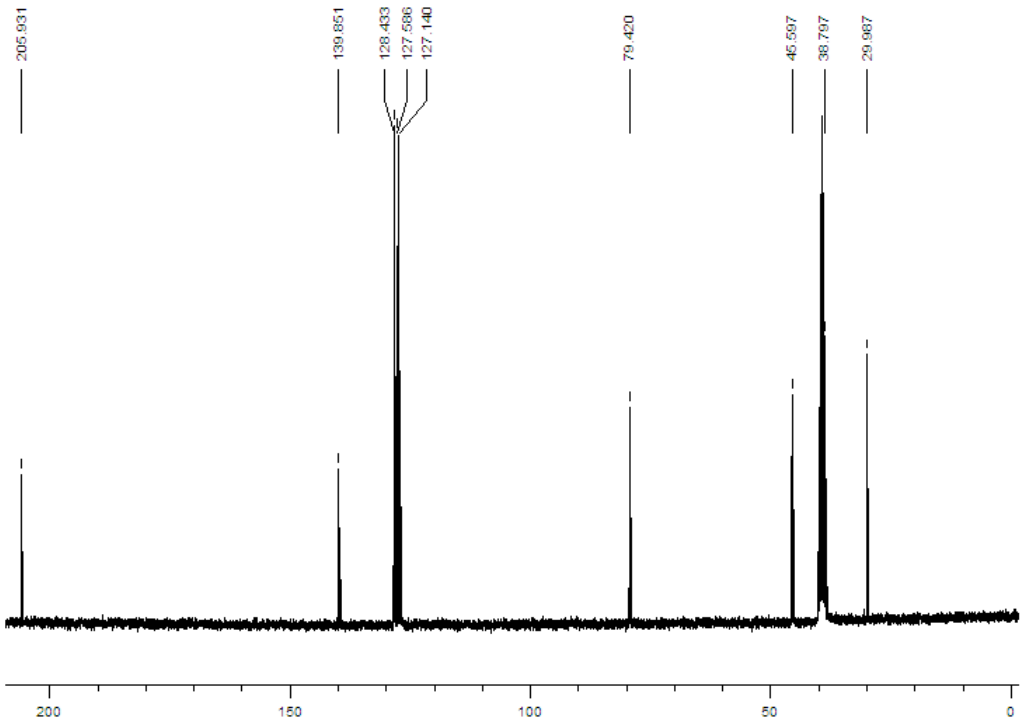


1.12 5-Nitro-4-phenyl-pentan-2-one (14):

^{1}H-NMR (300 MHz; DMSO[d6]):



^{13}C-NMR (300 MHz; DMSO[d6])

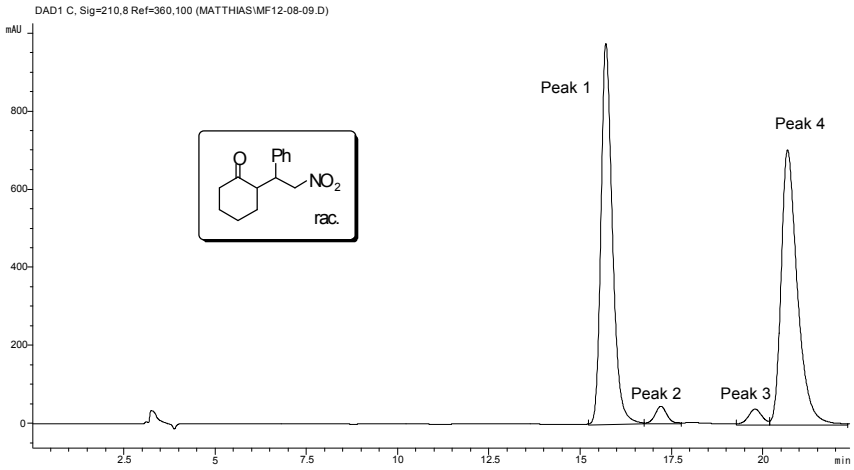


2 HPLC Chromatograms of the Catalytic Products (7-14) in Comparison with Authentic Racemic Compounds

Using DL-proline as a catalyst, we prepared all racemic Michael products with prevailing *syn* configuration, which was also observed in the catalytic products.

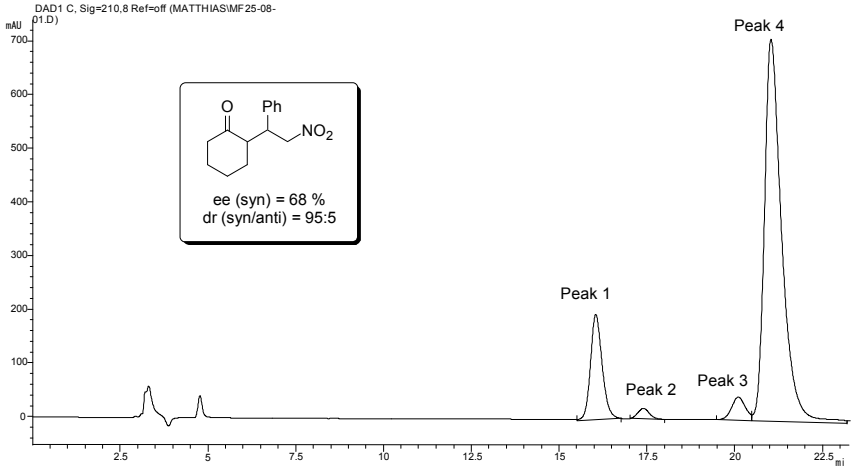
2.1 2-(2-Nitro-1-phenyl-ethyl)-cyclohexanone (7):

Racemic Product (Daicel Chiralpak IA, 2-PrOH/*n*-Hexane 3:97, 1.00 ml/min, 25 °C):



Peak	t_R [min]	Area	Area [%]
1 (*syn*)	15.7	21397	47.00
2 (*anti*)	17.2	1068	2.35
3 (*anti*)	19.8	1126	2.47
4 (*syn*)	20.7	21932	48.18

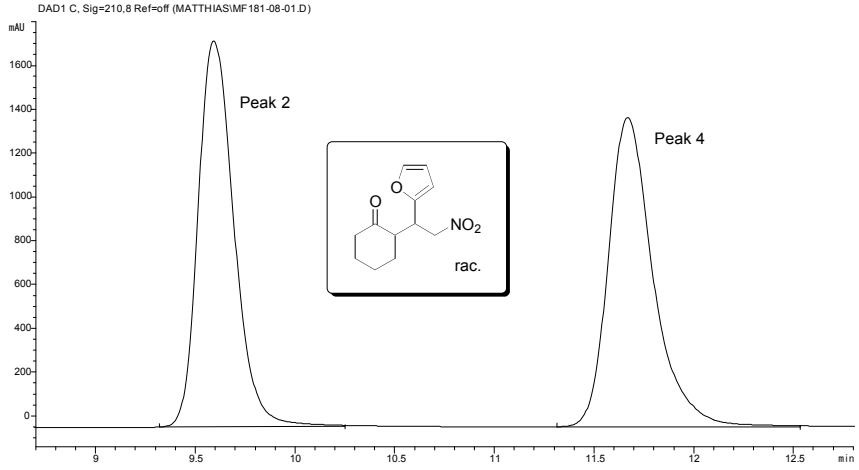
Catalytic Product (Daicel Chiralpak IA, 2-PrOH/*n*-Hexane 3:97, 1.00 ml/min, 25 °C):



Peak	t_R [min]	Area	Area [%]
1 (*syn*)	16.0	4560	14.91
2 (*anti*)	17.4	467	1.53
3 (*anti*)	20.1	1191	3.90
4 (*syn*)	20.7	24356	79.66

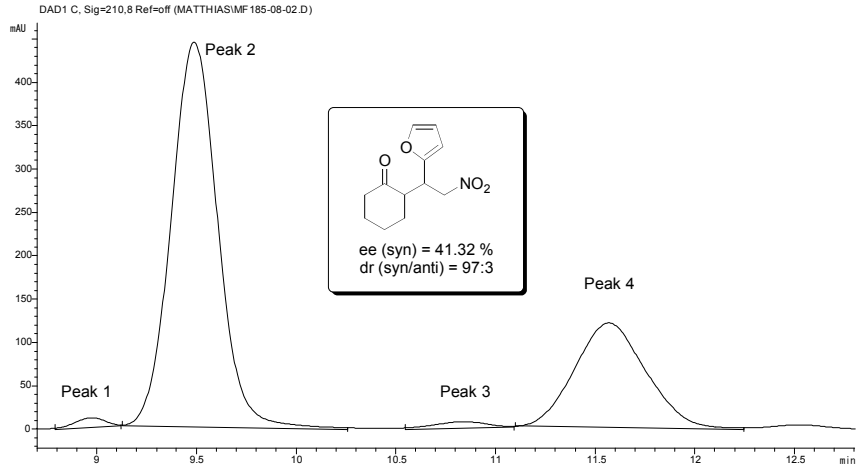
2.2 2-(1-Furan-2-yl-2-nitro-ethyl)-cyclohexanone (8):

Racemic Product (Daicel Chiralpak IA, 2-PrOH/*n*-Hexane 10:90, 1.0 ml/min, 25 °C):



Peak	t_R [min]	Area	Area [%]
1 (*anti*)	-	-	-
2 (*syn*)	9.5	21985	49.76
3 (*anti*)	-	-	-
4 (*syn*)	11.7	22196	50.24

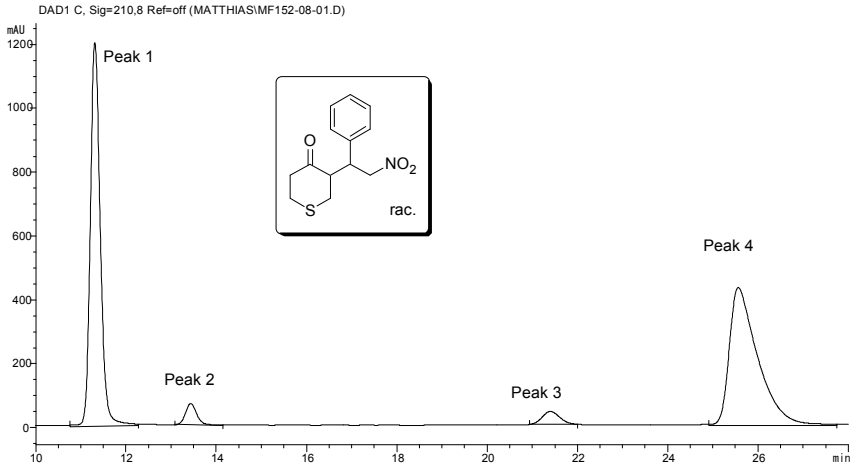
Catalytic Product (Daicel Chiralpak IA, 2-PrOH/*n*-Hexane 10:90, 1.0 ml/min, 25 °C):



Peak	t_R [min]	Area	Area [%]
1 (*anti*)	9.0	123	1.17
2 (*syn*)	9.5	7217	68.86
3 (*anti*)	10.8	144	1.37
4 (*syn*)	11.6	2997	28.59

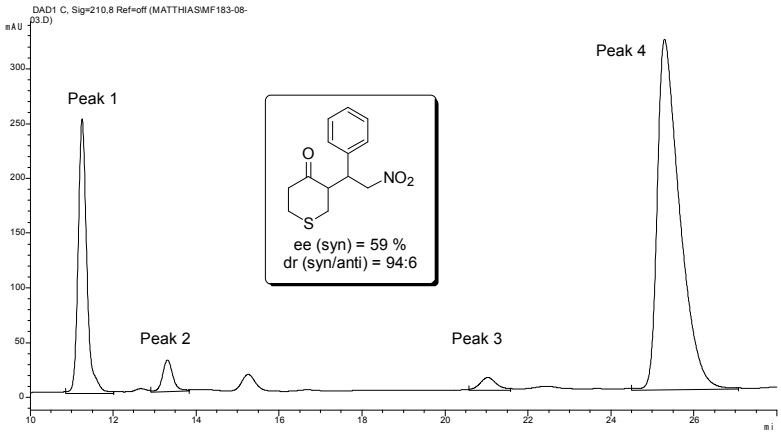
2.3 3-(2-Nitro-1-phenylethyl)-tetrahydro-thiopyran-4-one (9):

Racemic Product (Daicel Chiralpak IA, 2-PrOH/*n*-Hexane 15:85, 0.95 ml/min, 25 °C):



Peak	t_R [min]	Area	Area [%]
1 (*syn*)	11.3	18462	46.45
2 (*anti*)	13.4	1171	2.95
3 (*anti*)	21.4	1085	2.73
4 (*syn*)	25.6	19031	47.88

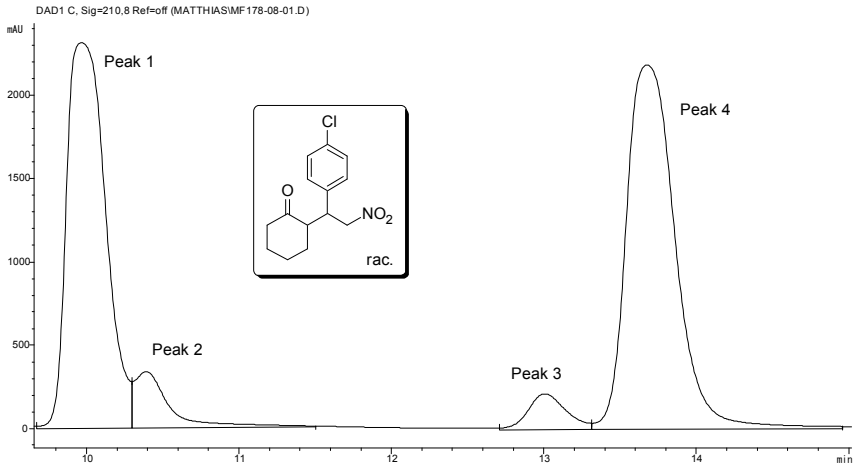
Catalytic Product (Daicel Chiralpak IA, 2-PrOH/*n*-Hexane 15:85, 0.95 ml/min, 25 °C):



Peak	t_R [min]	Area	Area [%]
1 (*syn*)	11.3	3115	19.19
2 (*anti*)	13.4	721	4.44
3 (*anti*)	21.3	414	2.55
4 (*syn*)	25.6	11984	73.82

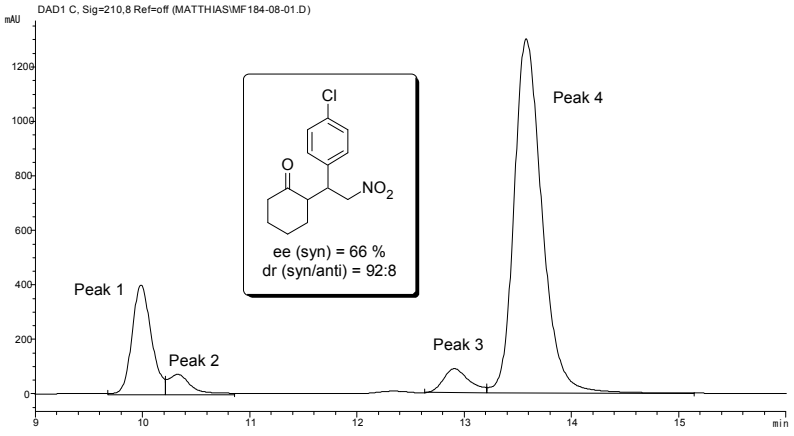
2.4 2-[1-(4-Chloro-phenyl)-2-nitro-ethyl]-cyclohexanone (10):

Racemic Product (Daicel Chiralpak IA, 2-PrOH/*n*-Hexane 15:85, 0.95 ml/min, 25 °C):



Peak	t_R [min]	Area	Area [%]
1 (*syn*)	10.0	41145	41.50
2 (*anti*)	10.4	5425	5.47
3 (*anti*)	13.0	3793	3.83
4 (*syn*)	13.7	48774	49.20

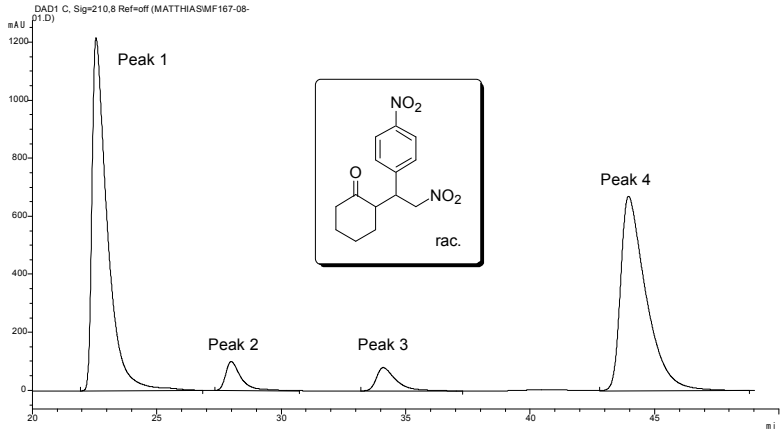
Catalytic Produkt (Daicel Chiralpak IA, 2-PrOH/*n*-Hexane 15:85, 1.00 ml/min, 25 °C):



Peak	t_R [min]	Area	Area [%]
1 (*syn*)	10.0	4920	15.64
2 (*anti*)	10.3	888	2.82
3 (*anti*)	12.9	1617	5.14
4 (*syn*)	13.6	24039	76.40

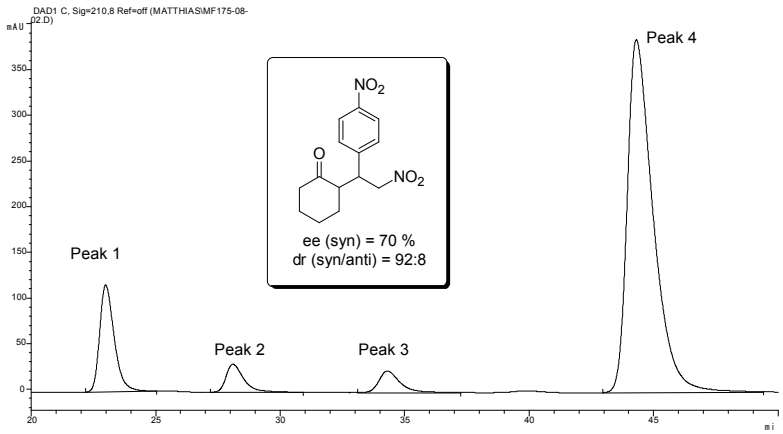
2.5 2-[2-Nitro-1-(4-nitro-phenyl)-ethyl]-cyclohexanone (11):

Racemic Product (Daicel Chiralpak IA, 2-PrOH/*n*-Hexane 15:85, 0.95 ml/min, 25 °C):



Peak	t_R [min]	Area	Area [%]
1 (*syn*)	22.6	52141	47.96
2 (*anti*)	28.0	4367	4.02
3 (*anti*)	34.1	4617	4.25
4 (*syn*)	44.0	47596	43.78

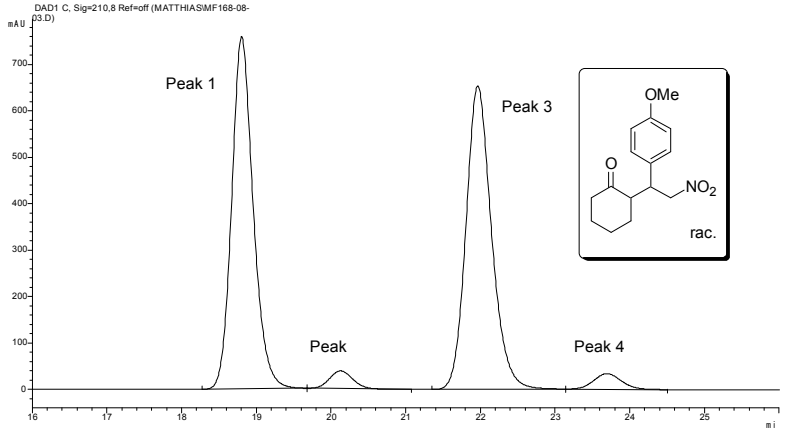
Catalytic Product (Daicel Chiralpak IA, 2-PrOH/*n*-Hexane 15:85, 0.95 ml/min, 25 °C):



Peak	t_R [min]	Area	Area [%]
1 (*syn*)	23.0	4908	13.59
2 (*anti*)	28.1	1586	4.39
3 (*anti*)	34.3	1283	3.55
4 (*syn*)	44.3	28336	78.47

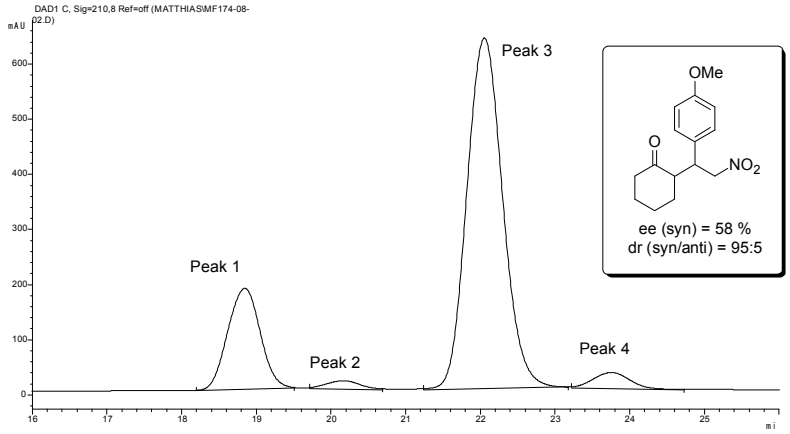
2.6 2-[1-(4-Methoxy-phenyl)-2-nitro-ethyl]-cyclohexanone (12):

Racemic Product (Daicel Chiralpak IA, 2-PrOH/*n*-Hexane 10:90, 0.50 ml/min, 25 °C):



Peak	t_R [min]	Area	Area [%]
1 (*syn*)	18.8	15230	46.78
2 (*anti*)	20.1	851	2.61
3 (*syn*)	22.0	15572	47.83
4 (*anti*)	23.7	902	2.77

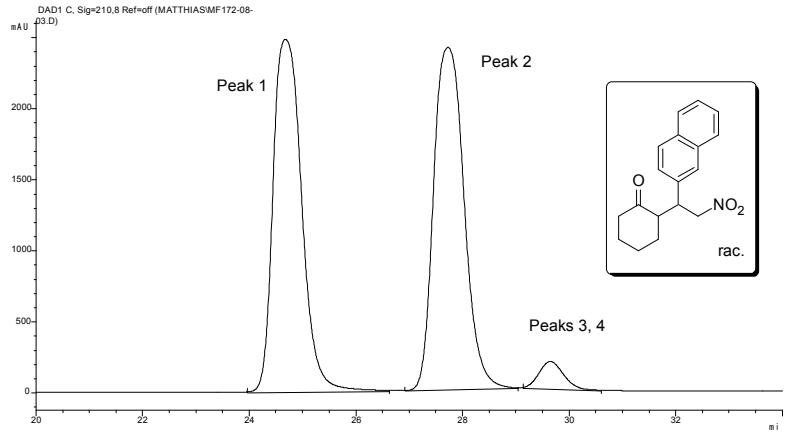
Catalytic Product (Daicel Chiralpak IA, 2-PrOH/*n*-Hexane 10:90, 0.50 ml/min, 25 °C):



Peak	t_R [min]	Area	Area [%]
1 (*syn*)	18.8	5554	19.67
2 (*anti*)	20.1	503	1.78
3 (*syn*)	22.1	21178	74.99
4 (*anti*)	23.8	1006	3.56

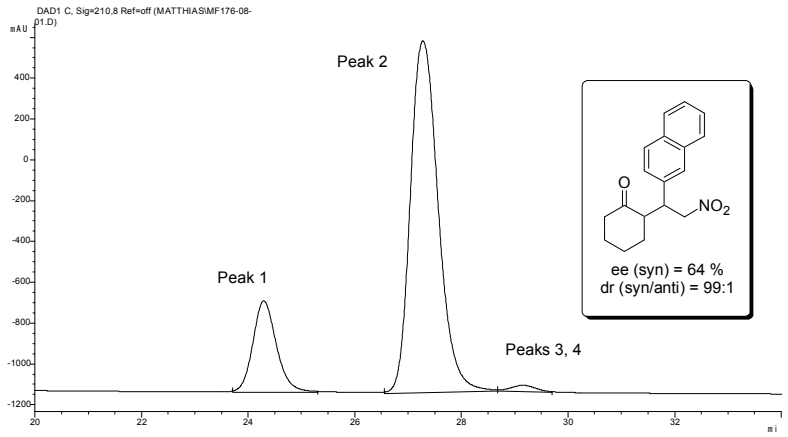
2.7 2-(1-Napht-2-yl-2-nitro-ethyl)-cyclohexanone (13):

Racemic Product (Daicel Chiralpak IA, 2-PrOH/*n*-Hexane 10:90, 0.50 ml/min, 25 °C):



Peak	t_R [min]	Area	Area [%]
1 (*syn*)	24.7	93174	47.69
2 (*syn*)	27.7	95761	49.00
3 and **4** (*anti*)	29.7	6456	3.3

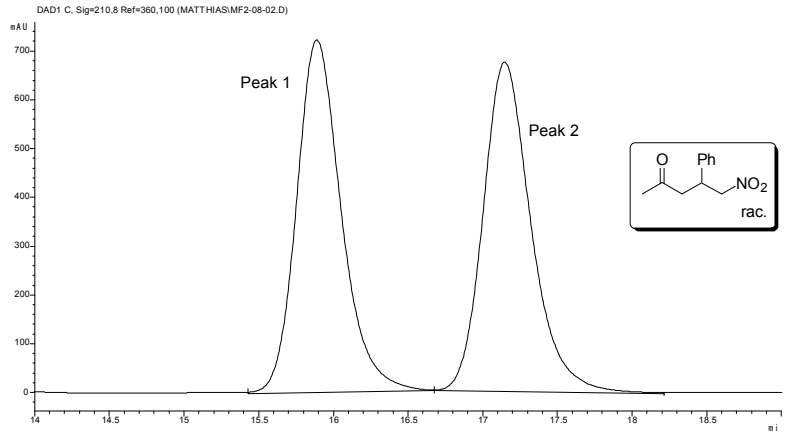
Catalytic Product (Daicel Chiralpak IA, 2-PrOH/*n*-Hexane 10:90, 0.50 ml/min, 25 °C):



Peak	t_R [min]	Area	Area [%]
1 (*syn*)	24.3	13800	17.80
2 (*syn*)	27.3	62639	80.80
3 and **4** (*anti*)	29.2	1081	1.39

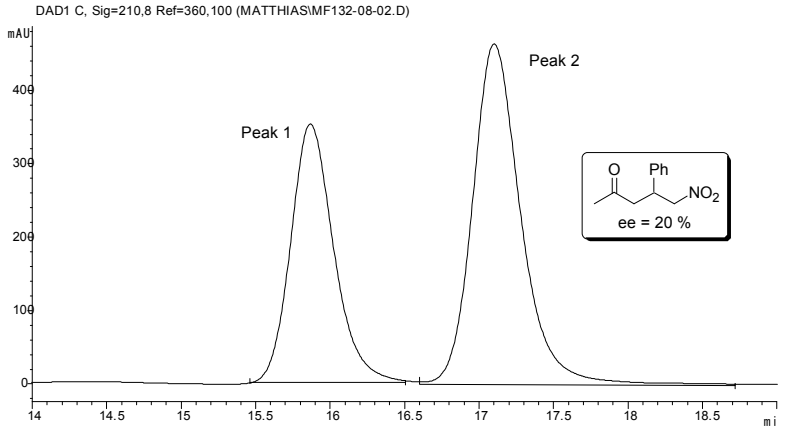
2.8 5-Nitro-4-phenyl-pentan-2-one (14):

Racemic Product (Daicel Chiralpak IA, 2-PrOH/*n*-Hexane 35:65, 0.85 ml/min, 25 °C):



Peak	t_R [min]	Area	Area [%]
1	15.9	15070	49.92
2	17.1	15120	50.08

Catalytic Product (Daicel Chiralpak IA, 2-PrOH/*n*-Hexane 35:65, 0.85 ml/min, 25 °C):



Peak	t_R [min]	Area	Area [%]
1	15.9	7083	40.24
2	17.1	10519	59.76