Electronic Supplementary Information

For

Role of quaternary ammonium salts as new additives in the enantioselective organocatalytic β-benzylation of enals

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General Methods and Materials

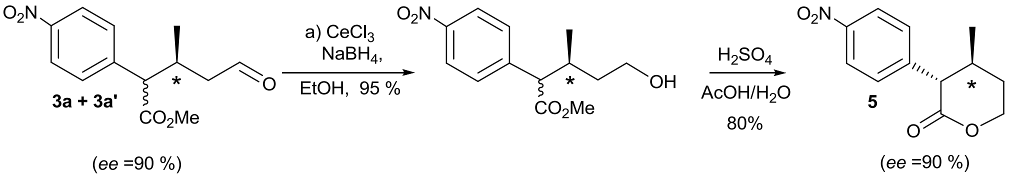
NMR spectra were acquired using $CDCl_3$ as solvent, running at 300 and 75 MHz for ^1H and ^{13}C, respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CHCl_3$, 7.26 ppm for ^1H NMR, $CDCl_3$, and 77.0 ppm for ^{13}C NMR). Melting points were measured using a *Gallenkamp* apparatus in open capillary tubes. Optical rotation was recorded in cells with 10 cm path length on a Perkin- Elmer 241 MC polarimeter. For thin layer chromatography (TLC), silica gel plates 60 (Aldrich) were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of phosphomolybdic acid (12 g), in EtOH (250 mL) followed by heating or treatment with a solution of $KMnO_4$ (1.5 g), K_2CO_3 (10g), and 10% NaOH (1.25 mL) in H_2O (200 mL). Commercial grade reagents and solvents were used without further purification.

Determination of Enantiomeric Purity

Enantiomeric excesses (*ee*) were determined by chiral-phase HPLC using an Agilent-1100 instrument in the column and conditions indicated in each case. HPLC chromatograms were compared to racemic samples by carrying out the reactions in the presence of a racemic mixture of catalysts **(*R*)-II** and **(*S*)-II**.

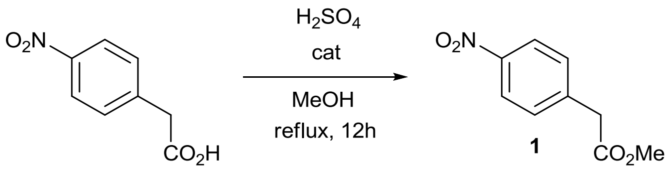
Stereochemical Assignments

The absolute configuration at C-3 was determined after transformation of the Michael adducts **3a** and **3a'** into the known lactone **5** by reduction and cyclization (Scheme S1). The configuration of the rest of the compounds was assigned assuming a stereochemically homogeneous behaviour in the Michael addition.



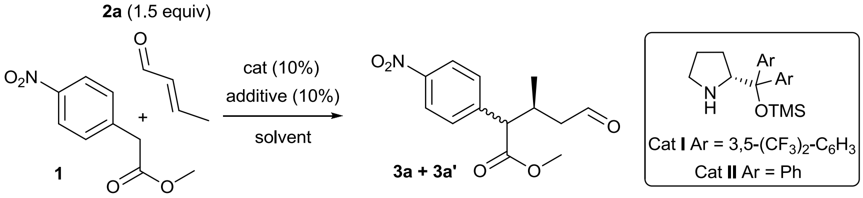
Scheme S1

Synthesis of*p*-nitrophenyl methylacetate1.



To a solution of *p*-nitrophenyl acetic acid (3.5g, 19.3mmol) in MeOH (75 mL) 3.5mLofH_2SO_4 were added. The reaction mixture was heated under refluxfor12 hours. After evaporation of the solvent, 25mLofEtOAc were added and the organic phase was washed with a saturated solution of $NaHCO_3$ (3x15mL), brine (3x15mL) and dried overanhydrous$MgSO_4$. The solvent was evaporated under vacuum to afford 3.5 g of *p*-nitrophenyl methyl acetate **1**(yield95%) as a white crystalline solid. Mp: 46-48ºC.^{1}**H NMR** (300 MHz, $CDCl_3$):δ 8.05 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 3.67 (s, 2H), 3.62 (s, 3H). ^{13}**C NMR** (75 MHz, $CDCl_3$):δ 170.6 (CO), 147.3 (C), 141.2 (C), 130.3 (2 CH), 123.8 (2 CH), 52.4 (CH_3), 40.8 (CH_2).**IR** (film): 3112, 3079, 2961, 2844, 1725 (CO), 1601, 1513, 1340, 1255, 1015, 881, 856, 757 cm^{-1}.**MS** (ESI): m/z 195 (M+1, 28), 106 (100), 89 (57), 78 (41). **HRMS** (ESI) Calcd. for $C_9H_{10}NO_4$ (M+1): 195.0532; found: 195.0536.

Optimization of the Michael addition of *p*-nitrophenyl methyl acetate1 to crotonaldehyde 2a.



To a solution of catalyst ((*R*)-**I** or (*R*)-**II**, 10 mol %, 0.01 mmol) in the corresponding solvent (200 µl), crotonaldehyde **2a** (1.5 equiv, 0.15 mmol) was added. After the resulting mixture was stirred at room temperature for 15 min *p*-nitrophenyl methyl acetate **1** (0.1 mmol, 19.5 mg) and the corresponding additive (10 mol%, 0.01mmol) were sequentially added. After the indicated reaction time in table S1 the reaction mixture was filtered through a short pad of silica gel and the solvent was evaporated under vacuum to give a mixture of **3a/3a’**.

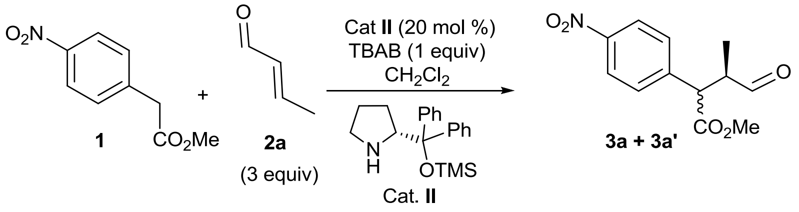
The enantiomeric purity was determined after transformation of the Michael adducts **3a** and **3a’** into the known lactone **5**(see Scheme S1, ESI) by reduction and cyclization by chiral HPLC analysis.

Table S1. Representative results from the screening of different solvents and additives with catalyst **I** and **II**.[a]

Entry	**Cat**	**Additive**	**t(h)**	**Solvent**	**Conv (%)**[b]	***ee***[c] **(%)**
1	**I**	LiOAc	48	EtOH	**67**	**80**
2	**I**	$PhCO_2H$	72	EtOH	**<10**	-
3	**I**	TBAB	24	EtOH	**10**	-
4	**I**	TBAB	24	CH_2Cl_2	**10**	-
5	**II**	$PhCO_2H$	48	CH_2Cl_2	**<10**	-
6	**II**	p-NO_2-C_6H_4-CO_2H	16	EtOH	**15**	-
7	**II**	$PhCO_2H$	16	EtOH	**23**	-
8	**II**	AcOH	16	EtOH	**47**	**88**
9	**II**	-	16	EtOH	**53**	-
10	**II**	LiOAc	16	EtOH	**87**	**89**
11	**II**	TBAB	24	EtOH	**65**	**90**
12	**II**	TBAB [d]	24	EtOH	**70**	**90**
13	**II**	TBAB [e]	24	EtOH	**72**	**87**
14	**II**	TBAB[f]	24	EtOH	**80**	**87**
15	**II**	TBAB[f]	24	CH_2Cl_2	**90**	**90**
16[g]	**II**	TBAB[f]	24	CH_2Cl_2	**100**	**90**
17	**-**	TBAB (1 equiv)	30	CH_2Cl_2	**no reaction**	**-**
18	**-**	Et_3N (1 equiv)	30	CH_2Cl_2	**35**	**-**
19	**-**	DABCO (1 equiv)	30	CH_2Cl_2	**40**	**-**

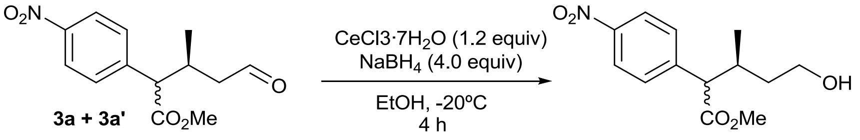
[a] Reactions conditions: **2a** (0.3 mmol), proline derived catalyst (20 mol%), **1** (0.1 mmol, [**1**]$_0$=0.5 M) and additive (10 mol%) at room temperature. [b] Determined by ^{1}H NMR of the crude reaction mixture [c] The *ee* values were determined by HPLC on a chiral stationary phase. [d] 20% TBAB [e] 50% TBAB [f] 100% TBAB. [g] Reaction performed with 20 mol% of catalyst and 3 equiv of aldehyde **2a**.

Optimized procedure for the conjugate addition of *p*-nitrophenyl methyl acetate 1 to crotonaldehyde 2a.



To a solution of (*R*)-α-α-diphenyl-2-pyrrolidinemethanol trimethylsilyl ether (**II**) (20 mol %, 0.02 mmol) inCH_2Cl_2 (150µL) crotonaldehyde **2a** (0.3 mmol, 3.0equiv) was added. After stirring for10 minutes, *p*-nitrophenyl methyl acetate **1** (19.5 mg, 0.1 mmol) and TBAB (32.2mg, 0.1mmol) were sequentially added. The reaction was stirred until completion (TLC) (Hexane /EtOAc = 2:1). The solvent was evaporated under vacuum and the product was filtered through a short pad of silica gel. The solvent was removed under reduced pressure, and the crude was used in the next step without further purification.

Optimized procedure for the reduction reaction.



The mixture of diastereomers **3a** and **3a’** (0.1 mmol) was dissolved in EtOH (1.0 mL), and $CeCl_3{\cdot}7H_2O$ (0.12 mmol) was added[1]. The mixture was introduced in a cooling bath at -20ºC and was stirred for 5 minutes whereupon a suspension of $NaBH_4$ (0.4 mmol) in EtOH (1.0 mL) was added dropwise. The reaction was stirred at -20 ºC for 4 hours whereupon the reaction was quenched with sat. aq. $NaHCO_3$ solution (5 mL), concentrated under reduced pressure and filtered through a short pad of Celite® and washed with EtOAc. The filtrate was washed with water (5 x 10 mL), brine (3 x 10 mL) and dried overanhydrous$MgSO_4$. The solvent was evaporated under vacuum to afford the mixture of the corresponding alcohols, which was used in the next step without further purification.

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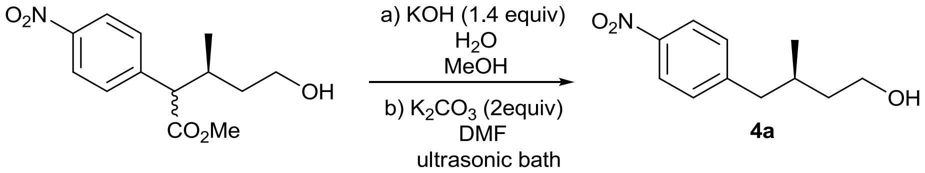
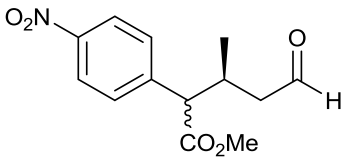
[1] D. Caine, S.D. Venkataramu, A. Kois, *J. Org. Chem.* 1992, **57**, 2960. When this reaction was carried out using only $NaBH_4$ in dry EtOH the partial reduction of the ester was also observed, even controling the amount of the reducing agent and temperature.

Optimized procedure for the decarboxylation reaction.

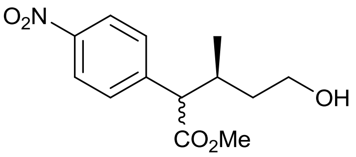


The mixture of diastereomeric alcohols (0.1 mmol) was dissolved in MeOH (1 mL) and a solution of KOH (0.133 mmol) in water (0.5 mL) was added. The mixture was stirred for 2 hours, whereupon MeOH was removed under reduced pressure. The crude was redissolved in DMF (0.5 mL) and K_2CO_3 (2 equiv, 0.2 mmol) was added. The reaction was placed in an ultrasonic bath for 8 hours. The reaction was quenched with sat. NH_4Cl and the organic phase was extracted with diethyl ether (3 x 10 mL). The combined organic layers were washed with water (3 x 10 mL), brine (10 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (hexane/EtOAc = 3:1) to afford the decarboxylated product **4a** in 81% yield (71% overall yield for the 3 steps).



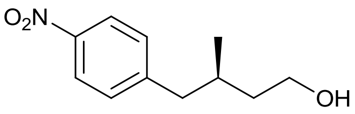
(2*S*, 3*S* and 2*R*, 3*S*)- Methyl 3-methyl-2-(4-nitrophenyl)-5-oxopentanoate (3a and 3a'). **^{1}H NMR** (300 MHz, CDCl$_3$): (mixture of diastereomers1:1) *δ* 9.76 (s, 1H), 9.59 (s, 1H), 8.21 (d, *J* = 8.7 Hz, 2H), 8.20 (d, *J* = 8.7 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 3.70 (s, 3H), 3.68 (s, 3H), 3.61 (d, *J* = 10.2 Hz, 1H), 3.58 (d, *J* = 9.9 Hz, 1H), 2.92 – 2.76 (m, 2H), 2.43 – 1.99 (m, 4H), 1.12 (d, *J* = 6.6 Hz, 3H), 0.81 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (75 MHz, CDCl$_3$): (mixture of diastereomers1:1) *δ* 200.4 (CHO), 200.3 (CHO), 172.1 (CO), 172.0 (CO), 147.1 (2 C), 144.2 (2 C), 129.4 (2 CH), 129.3 (2 CH), 123.5 (2 CH), 123.4 (2 CH), 56.5 (CH), 56.4 (CH), 52.0 (CH$_3$), 51.9 (CH$_3$), 48.3 (CH$_2$), 47.1 (CH$_2$), 31.7 (CH), 31.2 (CH), 18.1 (CH$_3$), 17.2 (CH$_3$). **MS** (ESI): m/z 266 (M+1, 40), 193 (90), 188 (75), 149 (100). **HRMS** (ESI) Calculated for C$_{13}$H$_{16}$NO$_5$ (M+1): 266.1022; found: 266.1034.

(2*S*, 3*S* and 2*R*, 3*S*)-Methyl 5-hydroxy-3-methyl-2-(4-nitrophenyl).



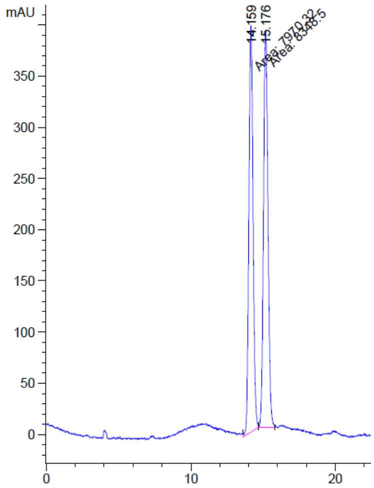
^{1}H NMR (300 MHz, CDCl$_3$): (mixture of diastereomers1:1) *δ* 8.19 (d, *J* = 8.6 Hz, 4H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 3.8-3.5 (m, 4H), 3.68 (s, 6H), 3.48 (d, *J* = 10.3 Hz, 1H), 3.47 (d, *J* = 10.5 Hz, 1H), 2.50-2.35 (m, 2H), 1.54-1.34 (m, 2H), 1.29-1.13 (m, 2H), 1.06 (d, *J* = 6.6 Hz, 3H), 0.73 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (75 MHz, CDCl$_3$): (mixture of diastereomers1:1) *δ* 173.3 (CO), 173.0 (CO), 147.4 (2C), 145.2 (2C), 129.7 (2CH), 129.6 (2CH), 123.8 (2CH), 123.7 (2CH), 60.4 (CH$_2$), 60.2 (CH$_2$), 58.4 (CH), 58.3 (CH), 52.3 (CH), 52.2 (CH), 38.0 (CH$_2$), 36.2 (CH$_2$), 33.8 (CH$_3$), 33.6 (CH$_3$), 17.8 (CH$_3$), 17.0 (CH$_3$). **MS**(ESI): m/z 290 (M+Na, 15), 236 (48), 110 (40). **HRMS** (ESI): Calcd. for C$_{13}$H$_{17}$NO$_5$Na (M+Na): 290.0998; found: 290.1010.

(*R*)-3-Methyl-4-(4-nitrophenyl)butan-1-ol (4a).

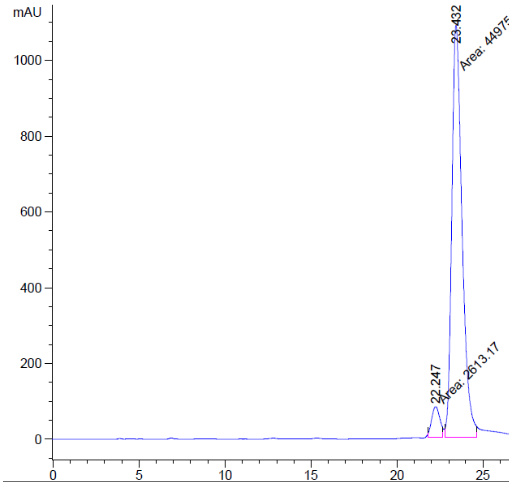


The title compound was obtained following the procedure described above. Yellowish oil. **Yield:** 81% (71% overall yield for the 3 steps). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.12 (d, J = 8.6 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 3.70 (m, 2H), 2.76 (dd, J = 6.4, 13.4 Hz, 1H), 2.52 (dd, J = 8.2, 13.4 Hz, 1H),1.97 (m, 1H), 1.62 (m, 1H), 1.55 (m, 1H), 1.43 (m, 1H), 0.88 (d, J = 6.6 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 149.1 (C), 146.4 (C), 129.9 (2CH), 123.5 (2CH), 60.7 (CH_2), 43.6 (CH_2), 39.3 (CH_2), 31.6 (CH), 19.3 (CH_3). **MS** (ESI): m/z 210 (M+1, 4), 192 (24), 149 (34), 146 (22), 79 (100), 64 (25). **HRMS** (ESI):Calcd. $C_{11}H_{16}NO_3$ (M+1): 210.1124; found: 210.1124.The procedure to obtain this product has been scaled up until 500 mg (2.6 mmol) of ester **1**. Yield = 75% (3 steps).The enantiomeric excess was determined by HPLC using a Chiralpak IA column [hexane/*i*-PrOH = 95:5]; flow rate 1.0 mL/min; ***ee* = 90%**, τ_{minor} = 22.3 min, τ_{major} = 23.4 min. $[\alpha]_D^{20}$ +1,8 (*c* = 2.1, $CHCl_3$).

***rac*-4a**



4a



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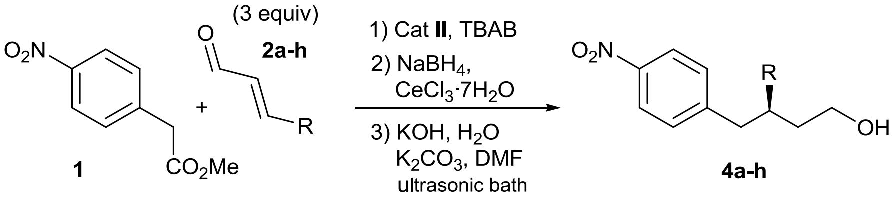
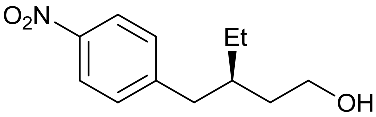
General procedure for the synthesis of alcohols 4a-4f: Sequence Michael/reduction/decarboxylation



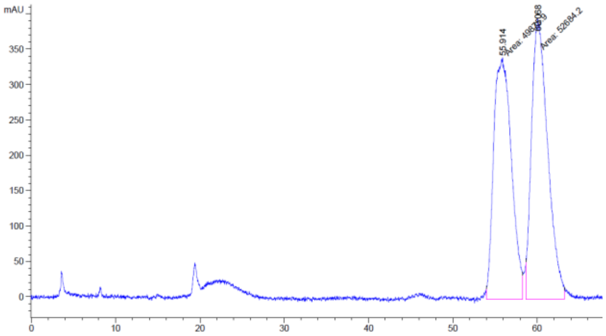
To a solution of (*R*)-α-α-diphenyl-2-pyrrolidinemethanol trimethylsilyl ether (**II**) (20 mol %, 0.04 mmol) inCH_2Cl_2 (400μL) the correspondingaldehyde**2a-h** (0.6 mmol, 3.0equiv) was added. After stirring for 10 minutes, *p*-nitrophenyl methyl acetate **1** (40 mg, 0.2mmol) and TBAB (64mg, 0.2mmol) were sequentially added. The reaction was stirred during the time indicated in each case in table 2 in the manuscript. The solvent was evaporated under vacuum and the product was filtered through a short pad of silica gel. The crude was dissolved in EtOH (2.0 mL), and $CeCl_3{\cdot}7H_2O$ (0.24 mmol) was added. The mixture was introduced in a cooling bath at -20ºC and a suspension of $NaBH_4$ (0.8 mmol) in EtOH (2.0 mL) was added dropwise. The reaction was stirred at -20 ºC for 4 hours whereupon the reaction was quenched with sat. aq. $NaHCO_3$ solution (5 mL), concentrated under reduced pressure and filtrated through a short pad of Celite® and washed with EtOAc. The filtrate was washed with water (5 x 10 mL), brine (3 x 10 mL), dried over anhydrous $MgSO_4$, and concentrated under vacuum. This crude was dissolved in MeOH (1 mL) and a solution of KOH (0.26 mmol) in water (1mL) was added. The mixture was stirred for 2 hours, whereupon the solvent was removed under reduced pressure. The crude was redissolved in DMF (1mL) and was introduced in an ultrasonic bath for 8 hours. The reaction was quenched with NH_4Cl sat and the organic phase was extracted with diethyl ether (3 x 10 mL). The combined organic layers were washed with water (3 x 10 mL), brine (10 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (hexane/EtOAc = 3:1) to afford the corresponding decarboxylated product **4** in the yields indicated in each case.

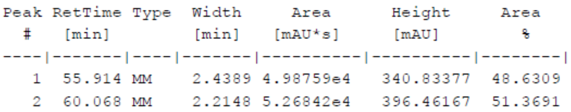
(*R*)-3-(4-Nitrobenzyl)pentan-1-ol (4b)



The title compound was obtained following the general procedure described above. Yellowish oil. **Yield:** 61% (overall yield for the 3 steps). ^{1}**H NMR** (300 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 3.68 (m, 2H), 2.69(m, 2H), 1.82 (sept, 1H), 1.55 (m, 2H), 1.34 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}**C NMR** (75 MHz, $CDCl_3$): δ 149.4 (C), 146.4 (C), 129.9 (2 CH), 123.5 (2 CH), 60.8 (CH_2), 40.1 (CH_2), 37.8 (CH), 35.8 (CH_2), 25.7 (CH_2), 10.6 (CH_3). **MS** (ESI): m/z 224 (M+1, 7), 206 (17), 149 (35), 79 (64), 74 (44), 64 (11). **HRMS** (ESI):Calcd. $C_{12}H_{18}NO_3$ (M+1): 224.1275; found: 224.1281.The enantiomeric excess was determined by HPLC using a Chiralpak OD column [hexane/*i*-PrOH = 98:2]; flow rate 0.9mL/min; ***ee* = 90%**, τ_{minor} = 55.2 min, τ_{major} = 58.9 min.

***rac*-4b**





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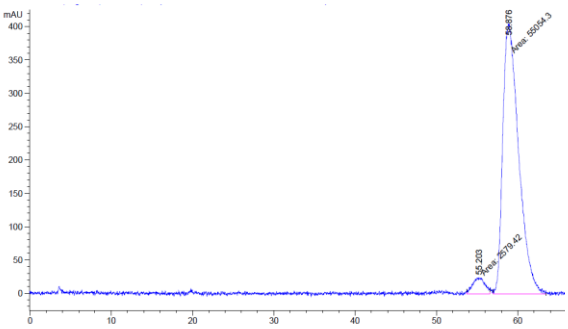
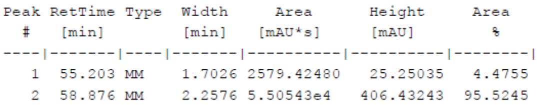
4b





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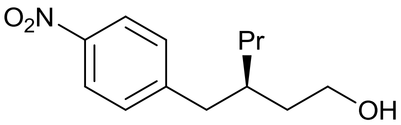
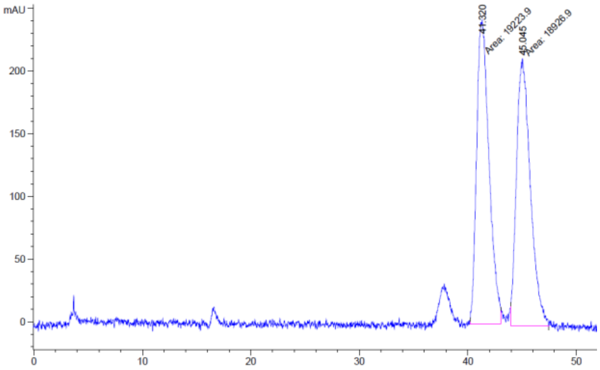
(*R*)-3-(4-Nitrobenzyl) hexan-1-ol (4c)



The title compound was obtained following the general procedure described above. Yellowish oil. **Yield:** 52% (overall yield for the 3 steps). **^{1}H NMR** (300 MHz, $CDCl_3$): *δ* 8.13 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 3.67 (m, 2H), 2.68 (m, 2H), 1.87 (m, 1H), 1.54 (m, 2H), 1.30 (m, 4H), 0.87 (t, *J* = 6.4 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): *δ* 149.4 (C), 146.4 (C), 129.9 (2 CH), 123.5 (2 CH), 60.8 (CH_2), 40.6 (CH_2), 36.3 (CH_2), 36.2 (CH), 35.6 (CH_2), 19.6 (CH_2), 14.3 (CH_3). **MS** (ESI): m/z 238 (M+1, 3), 220 (19), 174 (14), 163 (13), 149 (82), 131 (22), 79 (72), 64 (100). **HRMS** (ESI) calculated $C_{13}H_{20}NO_3$ (M+1): 238.1439; found: 238.1437.The enantiomeric excess was determined by HPLC using a Chiralpak OD column [hexane/*i*-PrOH = 98:2]; flow rate 1.0mL/min; ***ee* = 91%**, **τ** $_{minor}$ = 44.5 min, **τ** $_{major}$ = 48.2 min. $[\alpha]_D^{20}$ +3.7 (*c* = 2.7, $CHCl_3$).

***rac*-4c**



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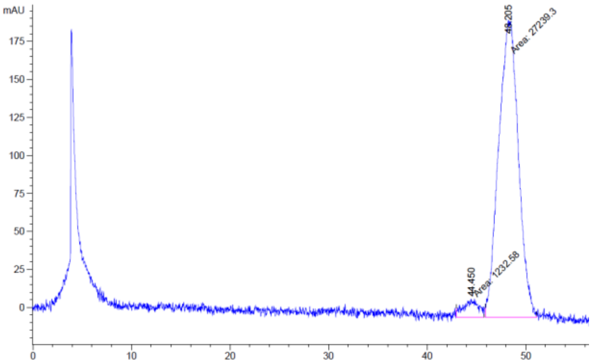
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  41.320 MM    1.3214 1.92239e4  242.46455  50.3893
   2  45.045 MM    1.4786 1.89269e4  213.34441  49.6107
```

4c



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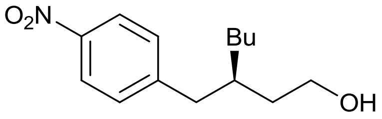
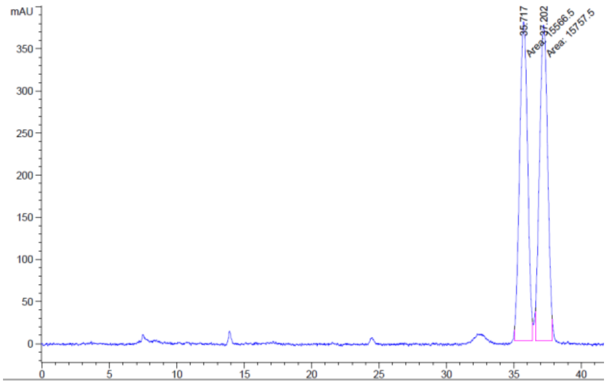
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  44.450 MM    1.7058 1232.57568   12.04289   4.3291
   2  48.205 MM    2.3211 2.72393e4  195.59227  95.6709
```

(*R*)-3-(4-Nitrobenzyl) heptan-1-ol (4d)



The title compound was obtained following the general procedure described above. Yellowish oil. **Yield:** 50% (overall yield for the 3 steps). **^{1}H NMR** (300 MHz, $CDCl_3$): *δ* 8.14 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 3.68 (m, 2H), 2.69(m, 2H), 1.86 (m, 1H), 1.54 (m, 4H), 1.28 (m, 4H), 0.88 (t, *J* = 6.6Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): *δ* 149.4 (C), 146.4 (C), 129.9 (2 CH), 123.5 (2 CH), 60.8 (CH_2), 40.6 (CH_2), 36.4 (CH), 36.3 (CH_2), 33.0 (CH_2), 28.6 (CH_2), 22.9 (CH), 14.0 (CH_3). **MS** (ESI): m/z 252 (M+1, 2), 234 (20), 163 (25), 149 (17), 79 (100), 64 (24). **HRMS** (ESI): Calcd. $C_{14}H_{22}NO_3$ (M+1): 252.1594; found: 252.1594.The enantiomeric excess was determined by HPLC using a Chiralpak IA column [hexane/*i*-PrOH = 95:5]; flow rate 0.9 mL/min; ***ee* = 94%**, τ_{major} = 32.2 min, τ_{minor} = 31.3 min. $[\alpha]_D^{20}$ +10.4 (*c* = 1.0, $CHCl_3$).

***rac*-4d**

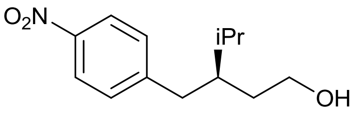


```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  32.235 MM    0.5293 7168.83838  225.74675  49.4639
   2  33.545 MM    0.5509 7324.23193  221.57202  50.5361
```

4d

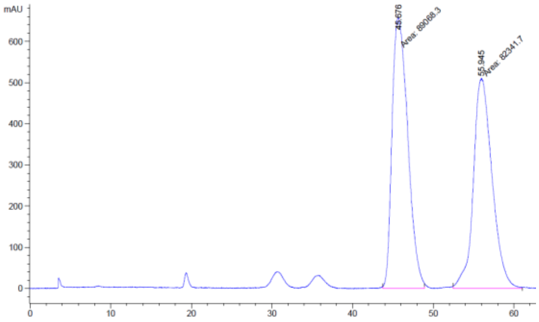
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  31.316 MM    0.4703 1886.60120   66.85144   2.7906
   2  32.223 MM    0.7579 6.57196e4  1445.19202  97.2094
```

(*R*)-4-methyl-3-(4-Nitrobenzyl) pentan-1-ol (4e)



The title compound was obtained following the general procedure described above. Yellowish oil. **Yield:** 59% (overall yield for the 3 steps). **^{1}H NMR** (300 MHz, $CDCl_3$): *δ* 8.14 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 3.60 (m 2H), 2.74 (dd, *J* = 6.3, 13.7 Hz, 1H), 2.57 (dd, *J* = 7.6, 13.6 Hz, 1H), 1.65 (m, 2H), 1.41 (m, 2H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): *δ* 150.0 (C), 146.4 (C), 129.8 (2 CH), 123.6 (2 CH), 61.4 (CH_2), 42.4 (CH), 37.3 (CH_2), 33.0 (CH_2), 29.0 (CH), 18.9 (CH_3), 18.6 (CH_3). **MS** (ESI): m/z 260 (M+23, 20)$^+$, 220 (11), 163 (21), 149 (15), 79 (100), 64 (23). **HRMS** (ESI): Calcd. $C_{13}H_{19}NO_3Na$ (M+23): 260.1261; found: 260.1257. The enantiomeric excess was determined by HPLC using a Chiralpak OD column [hexane/*i*-PrOH = 98:2]; flow rate 0.9 mL/min; ***ee* = 96%**, τ_{minor} = 48.2 min, τ_{major} = 56.6 min. $[\alpha]_D^{20}$ +2.3 (*c* = 1.6, $CHCl_3$).

***rac*-4e**



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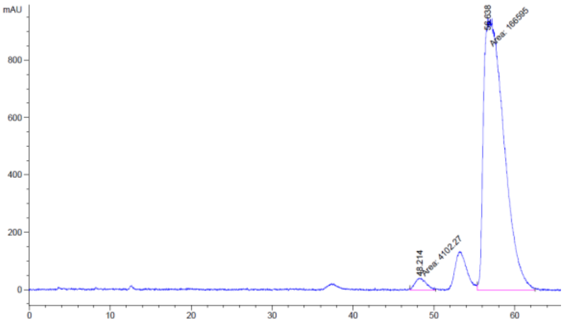
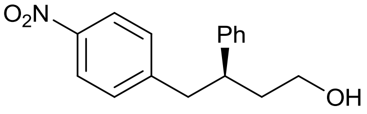
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  45.676 MM    2.2592 8.90683e4  657.07422  51.9621
   2  55.945 MM    2.6878 8.23417e4  510.58923  48.0379
```

4e



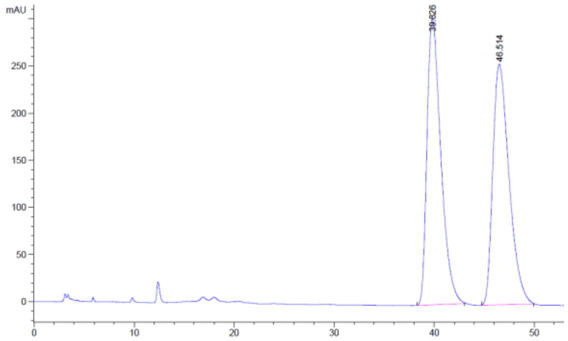
```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  48.214 MM    1.6287 4102.27490   41.97916   2.4032
   2  56.638 MM    2.9266 1.66595e5  948.74677  97.5968
```

(*R*)-4-(4-Nitrophenyl)-3-phenylbutan-1-ol (4f)



The title compound was obtained following the general procedure described above.[2] Colourless oil. **Yield:** 66% (overall yield for the 3 steps). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.7 Hz, 2H), 7.21 (m, 3H), 7.08 (m, 4H), 3.56 (m, 1H), 3.44 (m, 1H), 3.03 (m, 3H), 1.95 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 148.2 (C), 146.4 (C), 142.9 (C), 129.9 (2 CH), 128.6 (2 CH), 127.7 (2 CH), 126.8 (CH), 123.3 (2 CH), 60.7 (CH_2), 44.2 (CH), 43.5 (CH_2), 38.5 (CH_2). **MS** (ESI): m/z 272 (M+1), 149 (21), 79 (100), 64 (22). **HRMS** (ESI): Calcd. $C_{16}H_{18}NO_3$ (M+1): 272.1281; found: 272.1290.The enantiomeric excess was determined by HPLC using a Chiralpak OD column [hexane/*i*-PrOH = 95:5]; flow rate 1.0 mL/min; ***ee* = 86%**, τ_{major} = 38.0 min, τ_{minor} = 44.7 min.$[\alpha]_D^{20}$ +36.1 (*c* = 1.0, $CHCl_3$).

***rac*-4f**



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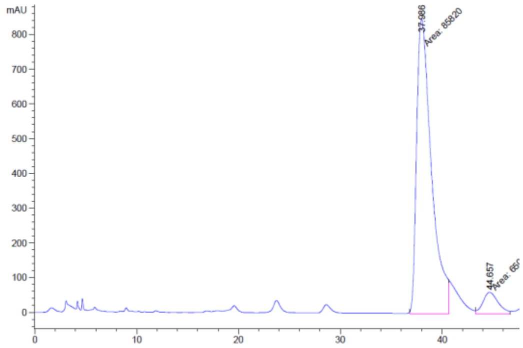
Peak RetTime Type  Width      Area       Height      Area
  #   [min]        [min]    [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  39.826 BB    1.4000 2.93064e4  303.09961  50.4335
   2  46.514 BB    1.5729 2.88027e4  255.55292  49.5665
```

4f



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Peak RetTime Type  Width      Area       Height      Area
  #   [min]        [min]    [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  37.986 MM    1.6878 8.58200e4  847.45361  92.9509
   2  44.657 MM    1.7489 6508.35840  62.02266   7.0491
```

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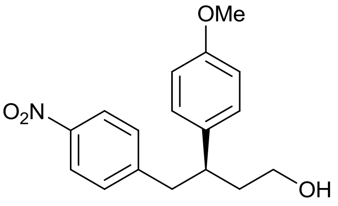
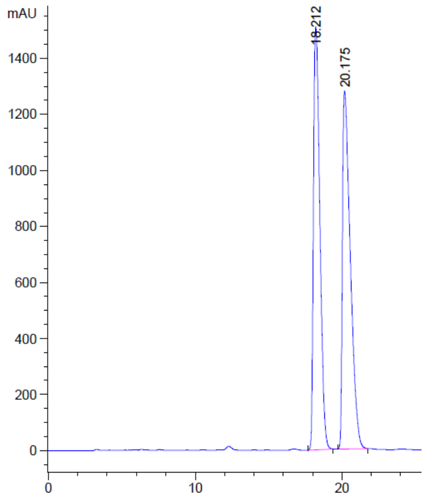
[2] The Michael reaction was isolated after 2 h. It is worth noting that a decrease in the enantiomeric excess was observed when the reaction was stopped at longer reaction times. The racemic product was obtained when the reaction was isolated after 48h.
This variation of the enantioselectivity with time must be a consequence of the reversibility of the Michael addition. The equilibration would avoid an asymmetric (kinetic) control allowing a thermodynamic pathway that affords even in some cases racemic products. This phenomenon has also been observed with other nucleophiles of this series: nitrile and ketone. See: (a) M. B Cid, S. Duce, S. Morales, E. Rodrigo, J. L. García Ruano, *Org. Lett*. 2010, **12**, 3586 (b) S. Duce, M. Jorge, I. Alonso, J. L. García Ruano, M. B. Cid, *Org. Biolmol. Chem.,* 2011, **13**, 3586 and references cited therein.

(*R*)-3-(4-methoxyphenyl)-4-(4-nitrophenyl) butan-1-ol (4g)



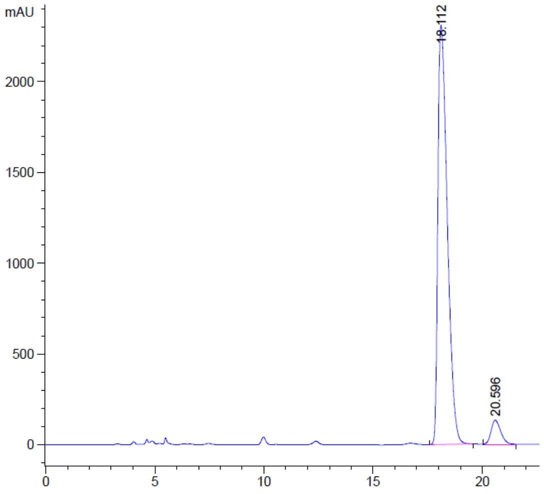
The title compound was obtained following the general procedure described above using (*R*)-α-α-bis[3,5-bis (trifluoromethyl)phenyl]-2-pyrrolidinemethanol trimethylsilyl ether (**I**) as catalyst.[3] Yellow oil. **Yield:** 68% (overall yield for the 3 steps). **^{1}H NMR** (300 MHz, $CDCl_3$): *δ* 8.00 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 3.75 (s, 3H), 3.53 (m, 1H), 3.43 (m, 1H), 3.06-2.86 (m, 3H), 1.99-1.80 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): *δ* 158.4 (C), 148.5 (C), 146.4 (C), 134.9 (C), 130.0 (2 CH), 128.6 (2 CH), 123.3 (2 CH), 114.1 (2 CH), 60.7 (CH_2), 55.2 (CH), 43.6 (CH_2), 43.4 (CH_3), 38.7 (CH_2). The enantiomeric excess was determined by HPLC using a Chiralpak ID column [hexane/*i*-PrOH = 90:10]; flow rate 1.0 mL/min; ***ee* = 90%**, **τ** $_{major}$ = 18.1 min, **τ** $_{minor}$ = 29.5 min. $[\alpha]_D^{20}$ +98.7 (*c* = 1.0, $CHCl_3$).

***rac*-4g**



```
Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  18.212 BB    0.4779 4.58038e4  1509.85071  49.1282
   2  20.175 BB    0.5588 4.74295e4  1278.51160  50.8718
```

4g



```
Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  18.112 BB    0.4684 6.93181e4  2307.73437  94.5164
   2  20.596 BB    0.4689 4021.68726  132.21101   5.4836
```

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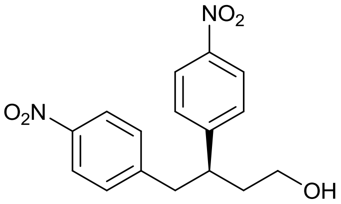
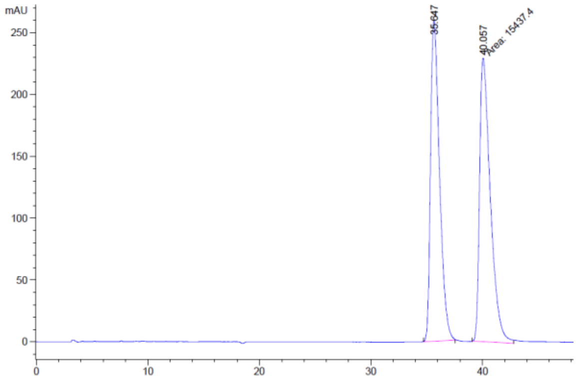
[3] In this cases we have used catalyst **I** instead of catalyst **II** because it usually gives better results in terms of enantioselectivity. Catalyst **I** could not be used in the case of aliphatic aldehydes due to their lower reactivies.

(*R*)-3,4-bis(4-nitrophenyl)butan-1-ol (4h)



The title compound was obtained following the general procedure described above using (*R*)-α-α-bis[3,5-bis (trifluoromethyl)phenyl]-2-pyrrolidinemethanol trimethylsilyl ether (**I**) as catalyst.[3] Yellow solid. **Yield:** 55% (overall yield for the 3 steps). mp = 145-147 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$): *δ* 8.03 (d, *J* = 8.6 Hz, 2H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.6 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 3.54 (m, 1H), 3.35 (m, 1H), 3.23 (m, 1H), 3.09 (dd, *J* = 13.4, 6.1 Hz, 1H), 2.90 (dd, *J* = 13.4, 9.1 Hz, 1H), 1.99 (m, 1H), 1.87 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$): *δ* 151.1 (C), 147.1 (C), 146.8 (C), 146.6 (C), 129.8 (2 CH), 128.6 (2 CH), 123.9 (2 CH), 123.6 (2 CH), 59.9 (CH_2), 43.9 (CH), 42.8 (CH_2), 38.2 (CH_2). The enantiomeric excess was determined by HPLC using a Chiralpak ID column [hexane/*i*-PrOH = 90:10]; flow rate 1.0 mL/min; ***ee* = 64%**, **τ** $_{major}$ = 35.2 min, **τ** $_{minor}$ = 40.2 min. $[\alpha]_D^{20}$ +61.1 (*c* = 1.0, $CHCl_3$).

***rac*-4h**



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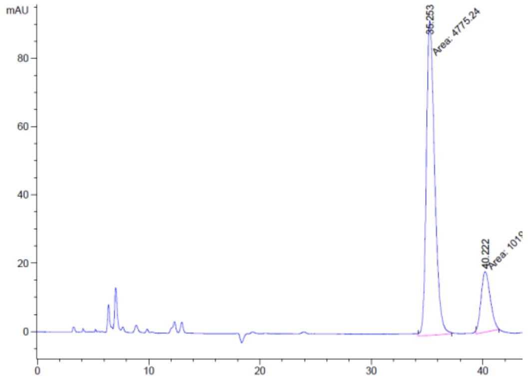
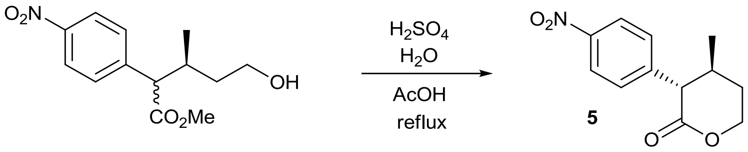
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  35.647 BB    0.8513 1.45584e4  259.18594  48.5348
   2  40.057 MM    1.1218 1.54374e4  229.35425  51.4652
```

4h



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  35.253 MM    0.8638 4775.24316   92.13519  82.4053
   2  40.222 MM    0.9615 1019.58032   17.67259  17.5947
```

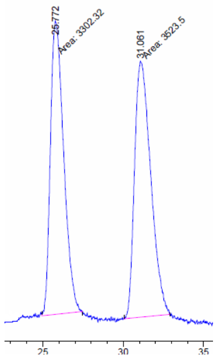
(3*S*,4*S*)-4-Methyl-3-(4-nitrophenyl)tetrahydro-2H-pyran-2-one (5)



This lactone has already been described by us[4] and has been prepared in order to establish the stereochemistry of the new stereogenic centre created in the Michael addition and to determine the *ee* of the Michael adducts during the optimization process (table 1 in the manuscript).

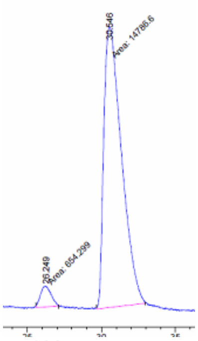
The diastereomeric mixture of alcohols (obtained as described previously) (26 mg, 0.1 mmol) was dissolved in acetic acid (100 µL). Water (50 µL)and concentrated H_2SO_4 (50 µL) were added and the reaction was refluxed overnight. The mixture was diluted with water (10 mL) and extracted with Et_2O (3 x 15 mL). The organic extract was washed with brine, dried over anhydrous $MgSO_4$ and evaporated to give the lactone **5** (80% yield). Yellow solid.**^{1}H NMR** (300 MHz, CDCl3): *δ* 8.22 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.6, 2H), 4.58-4.42 (m, 2H), 3.38 (d, *J* = 11.1 Hz, 1H), 2.33-2.22 (m, 1H), 2.20-2.07 (m, 1H), 1.74-0.98 (m, 1H), 0.96 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (75 MHz, CDCl3): *δ* 171.0 (CO), 147.3 (C), 145.2 (C), 130.0 (2CH), 123.9 (2CH), 68.2 (CH_2), 55.6 (CH), 34.3 (CH), 30.9 (CH_2), 20.3 (CH_3). **MS** (FAB) *m/z* 236 (M+1, 100), 219 (13), 107 (35), 71 (44), 57 (58), 55 (85). **HRMS** (FAB) Calculated for $C_{12}H_{13}NO_4$ [M+1]: 236.0917; found: 236.0923. The *ee* was determined by HPLC using a Chiralpak OD column [hexane/*i*-PrOH = 80:20]; flow rate 1.0 mL/min; ***ee* = 90%**, **τ** $_{\text{major}}$ = 30.5 min, **τ** $_{\text{minor}}$ = 26.2 min. $[\alpha]_D^{20}$ +5.7 (*c* = 0.5, $CHCl_3$) [Lit.[4] + 25 (*c* = 1.0, $CHCl_3$)].

rac-5



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  25.772 MM    0.9559 3302.32153   57.57564  48.3798
   2  31.061 MM    1.1671 3523.50269   50.31555  51.6202
```

5



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Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  26.249 MM    0.8369  654.29877   13.03057   4.2374
   2  30.546 MM    1.3883 1.47866e4   177.50902  95.7626
```

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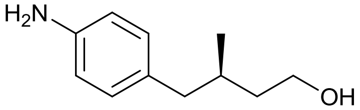
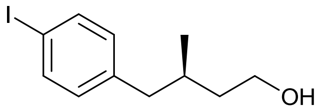
4. M.B. Cid,S. Duce, S. Morales, E. Rodrigo, J.L. García Ruano, *Org. Lett*. 2010, **12**, 3586.

(*R*)-4-(4-Aminophenyl)-3-methylbutan-1-ol (6)



To a solution of (*R*)-3-methyl-4-(4-nitrophenyl) butan-1-ol **4** (0.11 mmol, 23 mg) in CH_2Cl_2 (1130 μL) was added sequentially Zn dust (1.51 mmol, 99 mg) and AcOH (15.82 mmol, 161 μL) at 0ºC. After stirring at room temperature for 20 minutes, the reaction mixture was filtered through Celite® and the filtrate was neutralized with a saturated solution of $NaHCO_3$. The aqueous layer was extracted with ethyl acetate (3 x 5 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated to give the pure product in quantitative yield. Brown oil. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 6.93 (d, *J* = 8.2 Hz, 2H), 6.62 (d, *J* = 8.2, 2H), 3.68 (m, 2H), 3.00 (s, 2H), 2.51 (dd, *J* = 13.6, 6.6 Hz, 1H), 2.33 (dd, *J* = 13.5, 7.7 Hz, 1H), 1.81 (m, 1H), 1.64 (m, 1H), 1.38 (m, 2H), 0.88 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 144.1 (C), 131.2 (C), 130.0 (2CH), 115.2 (2CH), 61.2 (CH_2), 43.0 (CH_2), 39.4 (CH_2), 31.8 (CH), 19.4 (CH_3). **MS** (ESI): *m/z* 180 (M+1, 8), 162 (100). **HRMS**(ESI): Calculated for $C_{11}H_{18}NO$ [M+1]: 180.1390; found: 180.1382. $[\alpha]_D^{20}$ +4.0 (*c* = 0.6, $CHCl_3$).

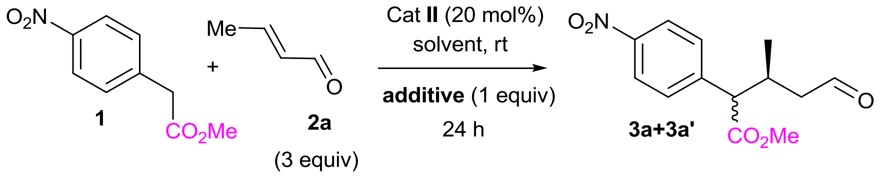
(*R*)-4-(4-Iodophenyl)-3-methylbutan-1-ol (7)



To a suspension of **7** (0.081 mmol, 14.6 mg) in HCl 6N (0.1 mL) at 0 °C, a solution of $NaNO_2$ (1 equiv, 5.5 mg) in water (1 mL) was added dropwise. The resulting mixture was added dropwise to a solution of KI (4 equiv, 53.8 mg) in water (0.6 mL), keeping the bath temperature at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight, then extracted with ethyl acetate. The combined organic layers were washed in sequence with 10% $Na_2S_2O_3$ and brine, then dried over $MgSO_4$ and concentrated under vacuum to give **7a** in 90% yield. Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$): δ7.59 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 8.1, 2H), 3.69 (m, 2H), 2.58 (dd, *J* = 13.4,6.4 Hz, 1H), 2.37 (dd, *J* = 13.6,8.0 Hz, 1H), 1.87 (m, 1H), 1.63 (m, 1H), 1.40 (m, 1H), 0.88 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 140.7 (C), 137.2 (2CH), 131.3 (2CH), 90.9 (C), 61.0 (CH_2), 43.2 (CH_2), 39.4 (CH_2), 31.6 (CH), 19.4 (CH_3). **MS** (ESI): m/z 291 (M+1, 13), 165 (45), 81 (60), 55 (100). **HRMS**(ESI): Calculated for $C_{11}H_{15}OINa$ [M+Na]: 313.0047; found: 313.0049. $[\alpha]_D^{20}$ +3.7 (*c* = 1.0, $CHCl_3$).

Study of the influence of the counteranion in the reactivity and enantioselectivity of the Michael addition

Table S2. Study of the influence of the counteranion in the reactivity and enantioselectivity of the Michael addition.[a]



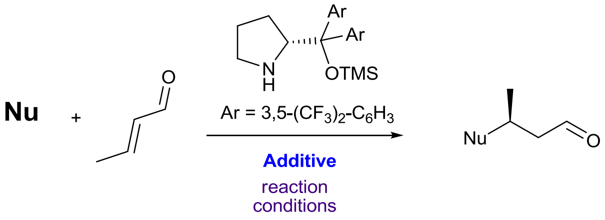
Entry^a	**Additive**	**pKa conjugated acid**	**CH_2Cl_2**		**EtOH**	
			Conv^b(%)	***ee*^{c}(%)**	**Conv^b(%)**	***ee*^{c}(%)**
1	**Et_4NOH**	14	56	10	63	10
2	**Bu_4NOH**	14	51	^{d}	76	^{d}
3	**Bu_4NOAc**	4.76	73	2	85	78
4	**Bu_4NCl**	-6.5	85	86	91	86
5	**Bu_4N Br**	-9	90	90	78	88
6	**Bu_4NI**	-10	75	86	89	86
7	**Me_4NBr**	-9	10	85	77	88
8	**LiOAc**	4.76	25	82	100	86

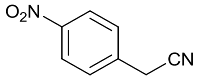
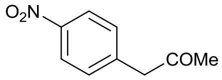
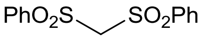
[a] The reactions were carried out on a 0.2 mmol scale with **2a** (3 equiv) and [**1**] = 1 M and isolated after 24 h [b] Determined by ^{1}H NMR of the crude of the Michael addition. [c] Determined by HPLC analysis in lactone **5**. [d] not determined

The use of TBAB as additive in other Michael reactions *via* iminium activation.

We performed the Michael addition of different nucleophiles previously reported in the literature (bis (phenylsulfonyl) methane[5], *p*-nitrophenylacetonitrile[6] and *p*-nitrophenylacetone[7]) under the same reactions conditions optimized for the methyl *p*-nitrophenylacetate **1**. The results are summarized in table S3:

Table S3: Comparison of the results obtained in the organocatalytic Michael additions of the different nucleophiles to crotonaldehyde using the additives reported in the literature and TBAB.



Additive	Nucleophile (Nu)		
	 **ref 4**	 **ref 5**	 **ref 3**
	Reaction conditions		
PhCO$_2$H	Cat 10 mol% THF/H$_2$O, rt Additive 10 mol% **t = 40h** **yield = 90%** ***ee* = 90%**	Cat 10 mol% EtOH, rt Additive 10 mol% **t = 20h** **yield = 95%** ***ee* = 80%**	**no reaction**
LiOAc	Cat 10 mol% THF/H$_2$O, rt Additive 10 mol% **t = 20h** **yield = 95%** ***ee* = 90%**	Cat 10 mol% EtOH, rt Additive 10 mol% **t = 12h** **yield = 95%** ***ee* = 90%**	Cat 20 mol% THF, rt Additive 100 mol% **t = 3-4 days** **yield = 68%** ***ee* = 70%**
TBAB	Cat 20 mol% CH$_2$Cl$_2$, rt Additive 100 mol% **t = 7h** **yield = 90%** ***ee* = 90%**	Cat 20 mol% CH$_2$Cl$_2$, rt Additive 100 mol% **t = 8h** **yield = 90%** ***ee* = 90%**	Cat 20 mol% CH$_2$Cl$_2$, rt Additive 100 mol% **t = 48h** **yield = 80%** ***ee* = 70%**

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[5] J. L. García Ruano, V. Marcos, J. Alemán, *Chem. Commun*.,2009, 4435.
[6] M.B Cid, S.Duce, S. Morales, E. Rodrigo, J. L. García Ruano, *Org. Lett*. 2010, **12**, 3586
[7] S. Duce, M. Jorge, I. Alonso, J.L. García Ruano, M.B. Cid,*Org. Biolmol. Chem.,* 2011, **13**, 3586.

Deuterium exchange experiments and some mechanistic considerations.

1. Deprotonation step. Comparison between TBAB and TBAOH

1.1. Theoretical calculation

The deprotonation of the nuclophile by the resulting Bu_4NOH is supported by theoretical calculations and several experiments explained in the following paragraphs. According to our calculations, the deprotonation step **a₂** (see Scheme 4 in the manuscript) with the hydroxide generated after *iminium* formation seems to be quite favourable under the reaction conditions (Figure 1).

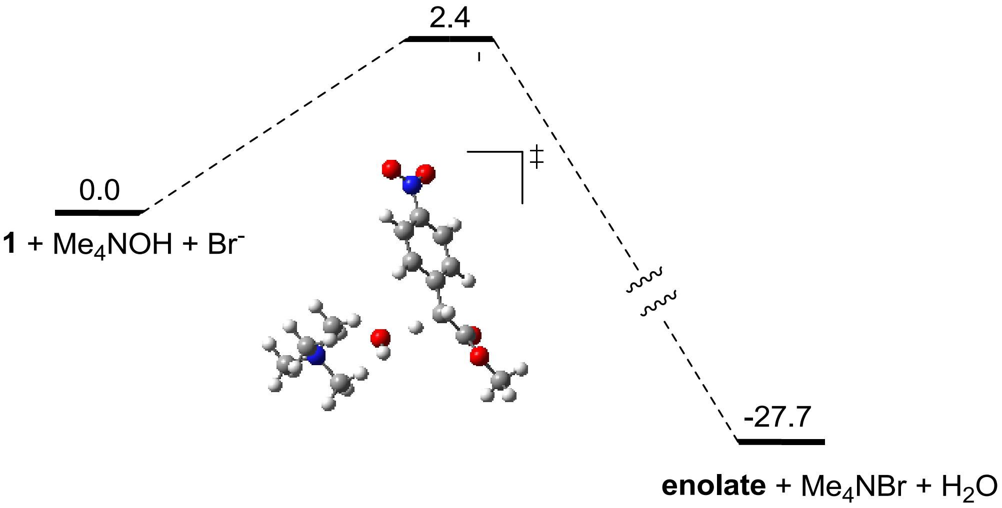


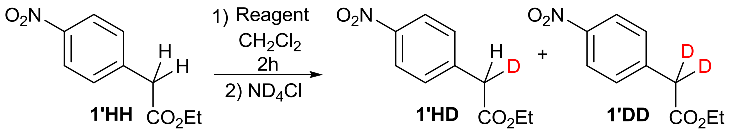
Figure S1. Deprotonation profile using the Gibbs free energies Δ*G* ($kcalmol^{-1}$) computed at the $CPCM_{(DCM)}$/B3LYP/6-311G(d,p)//6-31G(d) level of theory. Me_4N^+ ion has been used as a simplified model for the corresponding tBu_4N^+ one in all the calculations.

1.2. Deuteration studies of *p*-nitrophenyl ethyl acetate 1’ using ND_4Cl using TBAB,LiOAc, TBAOAc and TBAOH.

Deuteration experiments were carried out using commercially available *p*-nitrophenyl ethyl acetate**1’** instead of the corresponding methyl ester **1**for the more clear separation of the ^{1}H NMR signals.

When **1’** (R=Et) was dissolved in CH_2Cl_2 and TBAB (1 equiv) was added to the solution, no deuteration was observed when the reaction was quenched with ND_4Cl after 2 h. The same procedure was performed using LiOAc (1 equiv) in CH_2Cl_2:MeOH-d_4 (due to the low solubility of the LiOAc in CH_2Cl_2) and no deuteration was observed after 2h when the reaction was quenched with ND_4Cl.
Nevertheless, a high level of deuteration was observed when the same protocol was carried out using Bu_4NOH or Bu_4NOAc.

Table S4. Deuteration experiments of nucleophile **1‘**.



	1'HH	1'HD	1'DD
A: **TBAB** (1 equiv)	100	0	0
B: **LiOAc** (1 equiv)	100	0	0
C: **TBAOH** (1 equiv)	10	20	70
D: **TBAOH** (1 equiv)	15	25	60

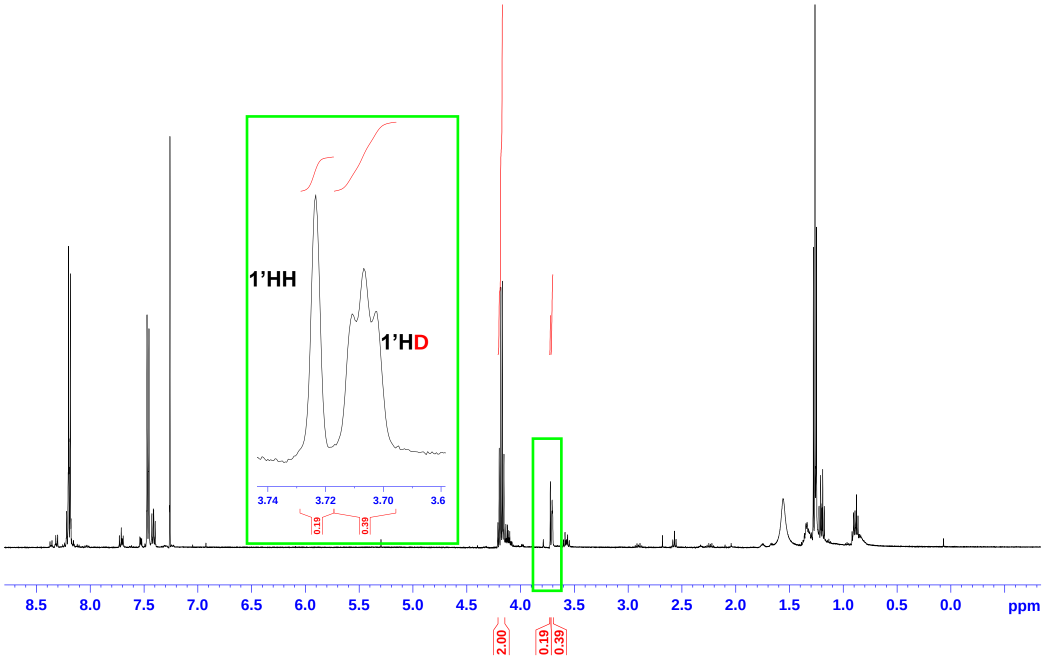


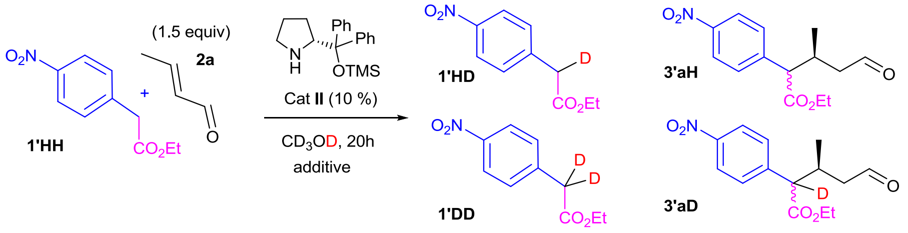
Figure S2: ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of the deuterium exchange reaction of *p*-nitrophenyl ethyl acetate **1’** with TBAOH after 2h.

2. Deuteration experiments of 1' under the Michael reaction conditions with different additives in MeOH-d_4.

Deuteration experiments of the deprotonation reaction (see previous page) have been performed using CH_2Cl_2 as solvent and quenched with ND_4Cl as deuterium source after a period of time. Nevertheless, this procedure cannot be used to detect the amount of anion formed under the reaction conditions after a given time because the ratio is below the detection limit of the NMR. Therefore we carried out the deuteration experiment under the Michael reaction conditions using CD_3OD as a continuous source of deuterium. However, it is worth to note that CD_3OD has a similar pKa value to the nucleophile and therefore it cannot quantitatively deuterate the anion. Therefore, the deuteration values give a qualitative idea of the amount of anion formed in each case.

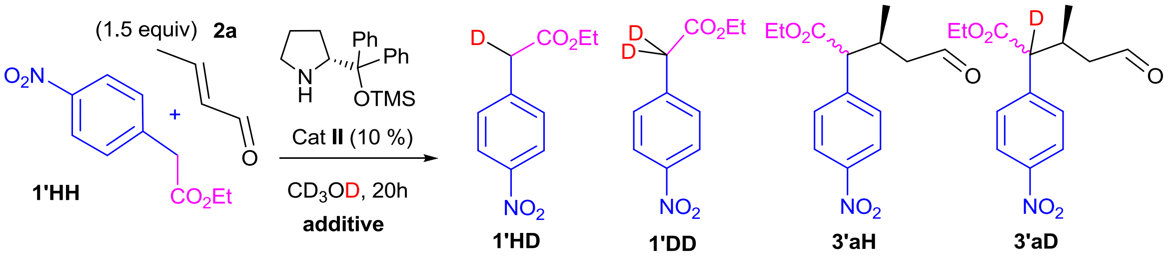
Procedure for the deuteration experiments under the reaction conditions:
To a solution of catalyst (*R*)-**II**, 10 mol %, 0.02 mmol)in CD_3OD (200µL) crotonaldehyde **2a** (1.5 equiv, 0.3 mmol) was added. After the resulting mixture was stirred at room temperature for 15 min *p*-nitrophenyl ethyl acetate **1'** (0.2 mmol, 42 mg) and the corresponding additive (10 mol%, 0.02mmol) were sequentially added. After 20 h the reactions were filtered through a plug of silica gel and the solvent evaporated under vacuum. The fraction of deuterated products and conversion were determined by^{1}H NMR integration of the crude mixture in $CDCl_3$.

Table S5. Deuteration experiments of nucleophile **1'**[a]



Entry	Additive	1'HH (%)	1'HD (%)	1'DD (%)	3'aH (%)	3'aD (%)	Deut (%)	Conv (%)
1	$PhCO_2H$ (10%)	>95	traces	-	<5	-	-	<5
2	-	>95		-	<5	-	-	<5
3	TBAB (1 equiv)	66	14	4	12	4	**22**	**16**
4	LiOAc (10%)	32	24	12	24	8	**44**	**32**

The ethyl ester **1'**turned out to be less reactive than the corresponding methyl ester **1**used in our studies (see manuscript). Therefore the conversions obtained were lower than those obtained for the nucleophile **1**. Only when TBAB and LiOAc were used as additives significant deuteration of nucleophile **1'** as well as conversion were observed.



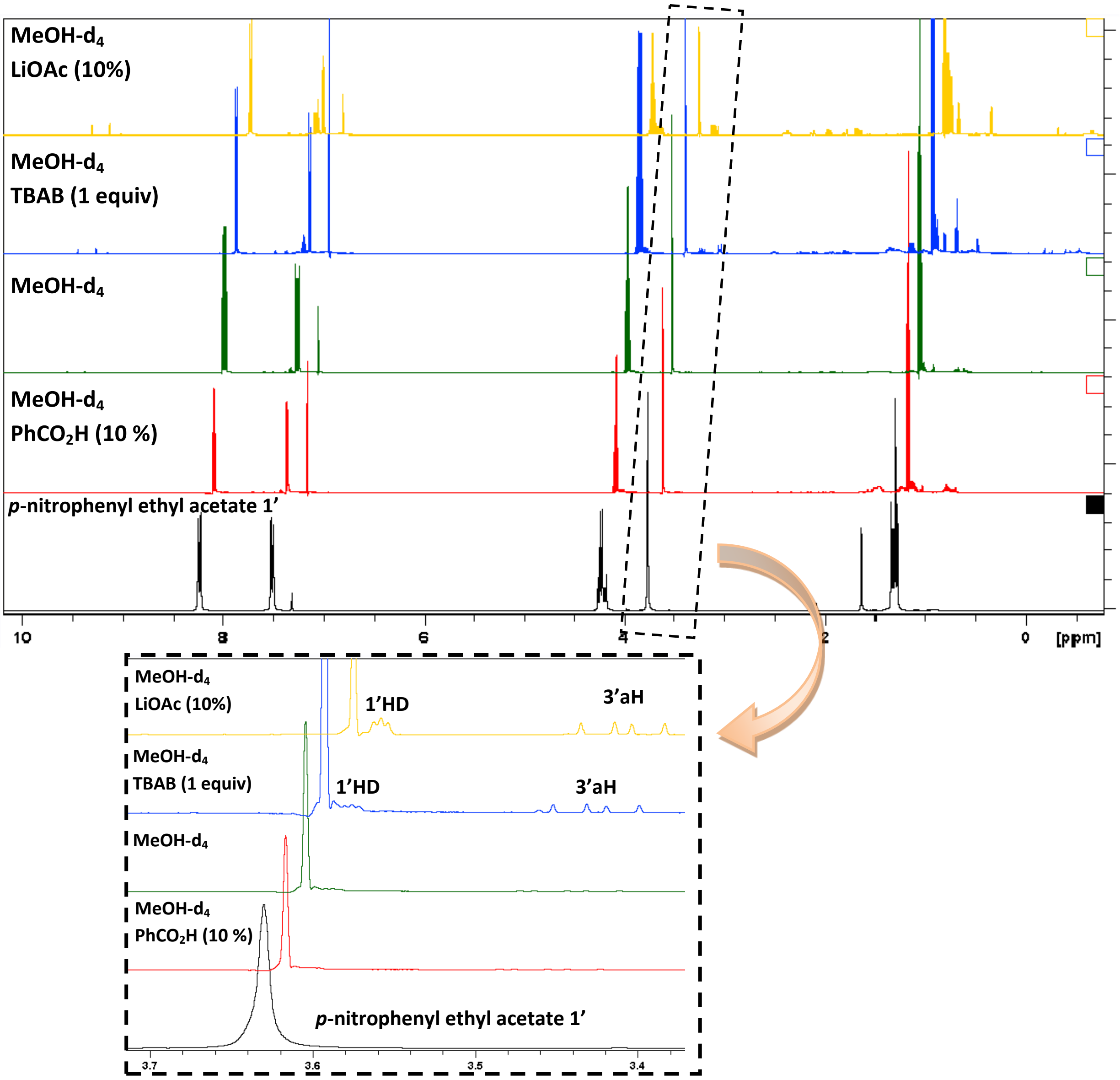
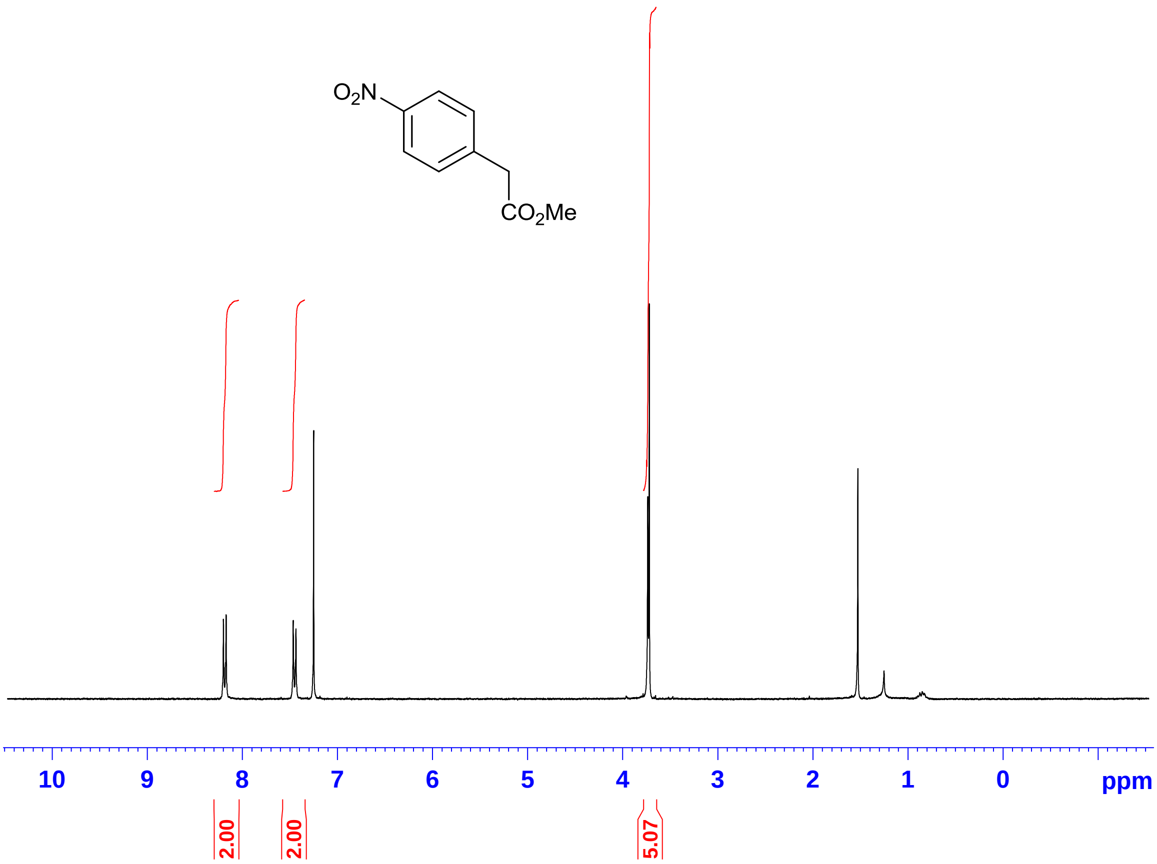
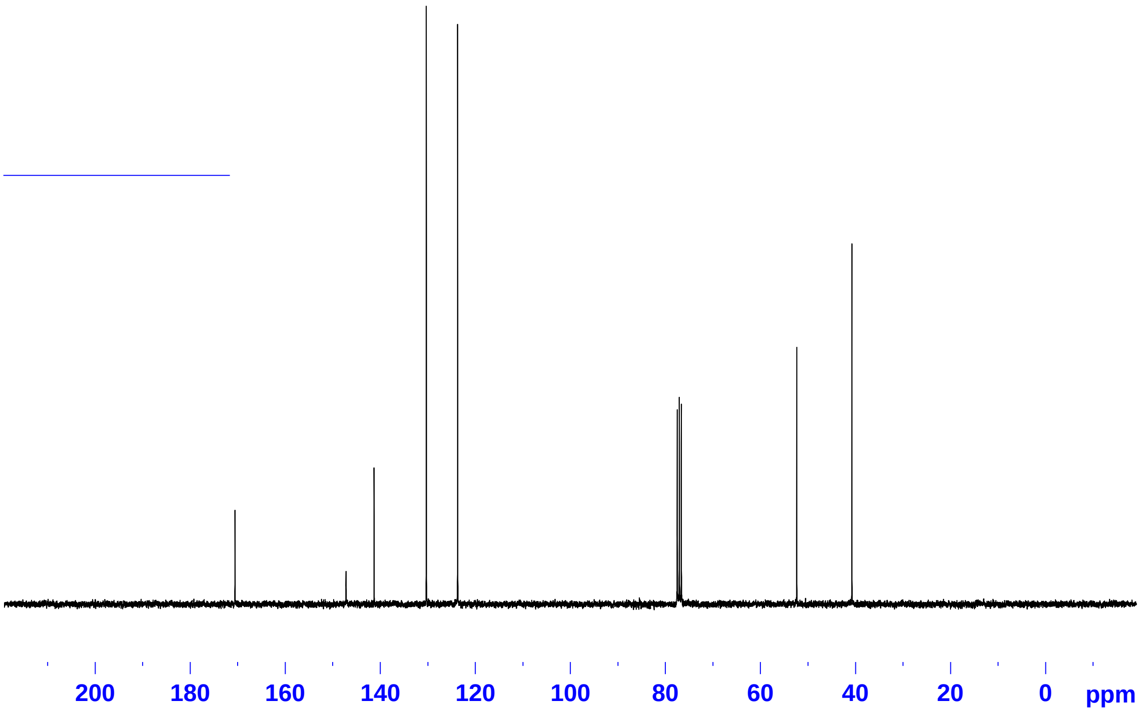
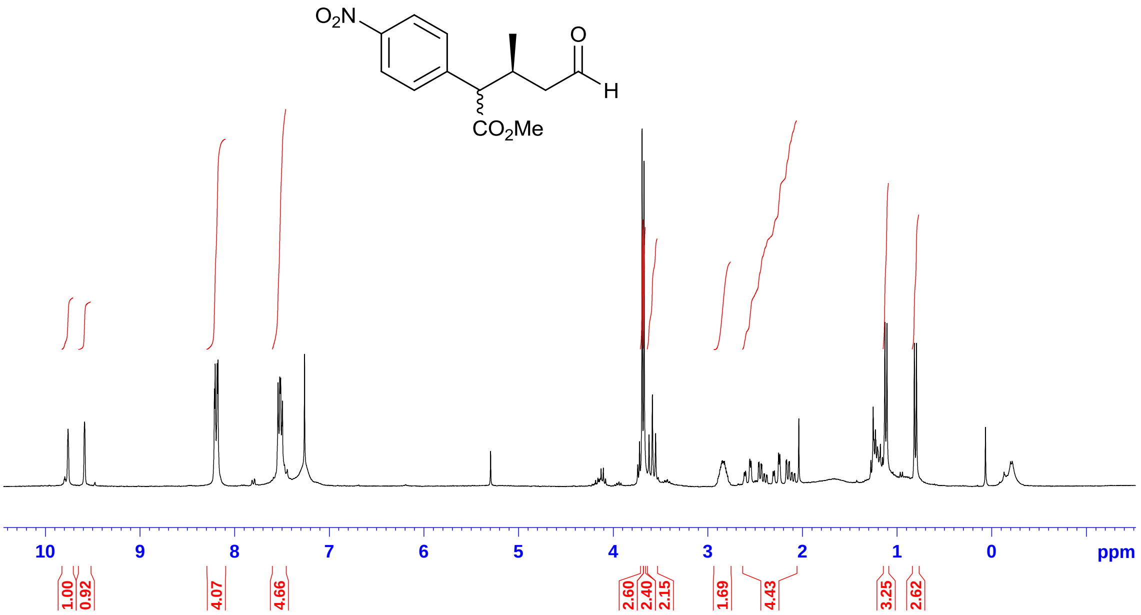


Figure S3: ^{1}H NMR spectra (CDCl$_3$, 500 MHz) of the deuterium exchange of *p*-nitrophenyl ethyl acetate **1’** with different additives after 20h under the Michael reaction conditions.

^{1}H and ^{13}C NMR spectra



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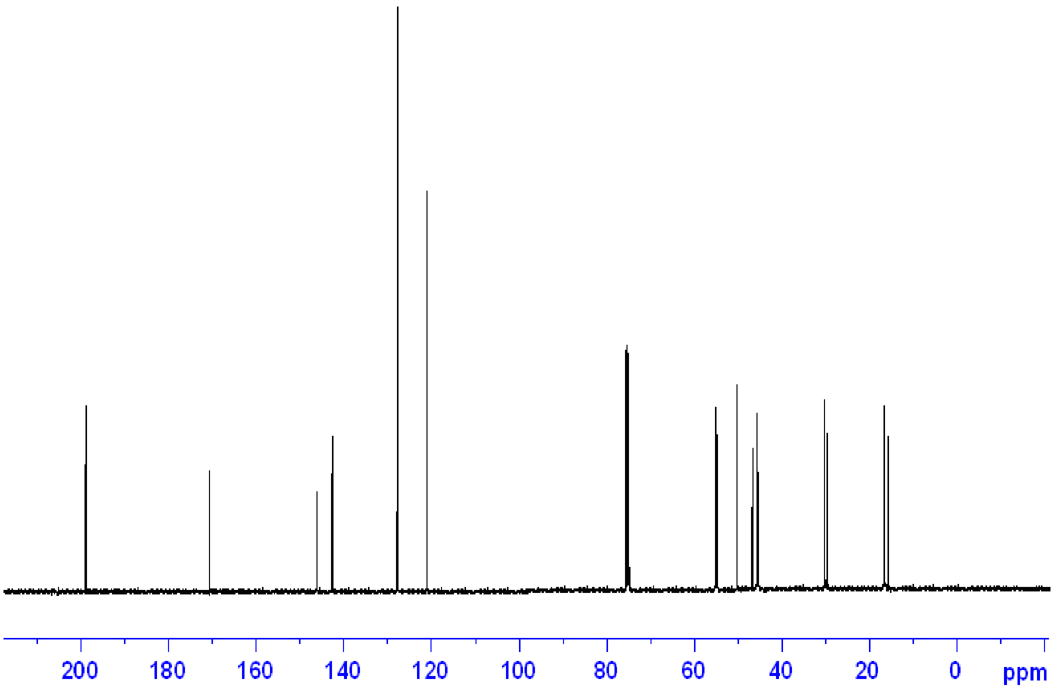
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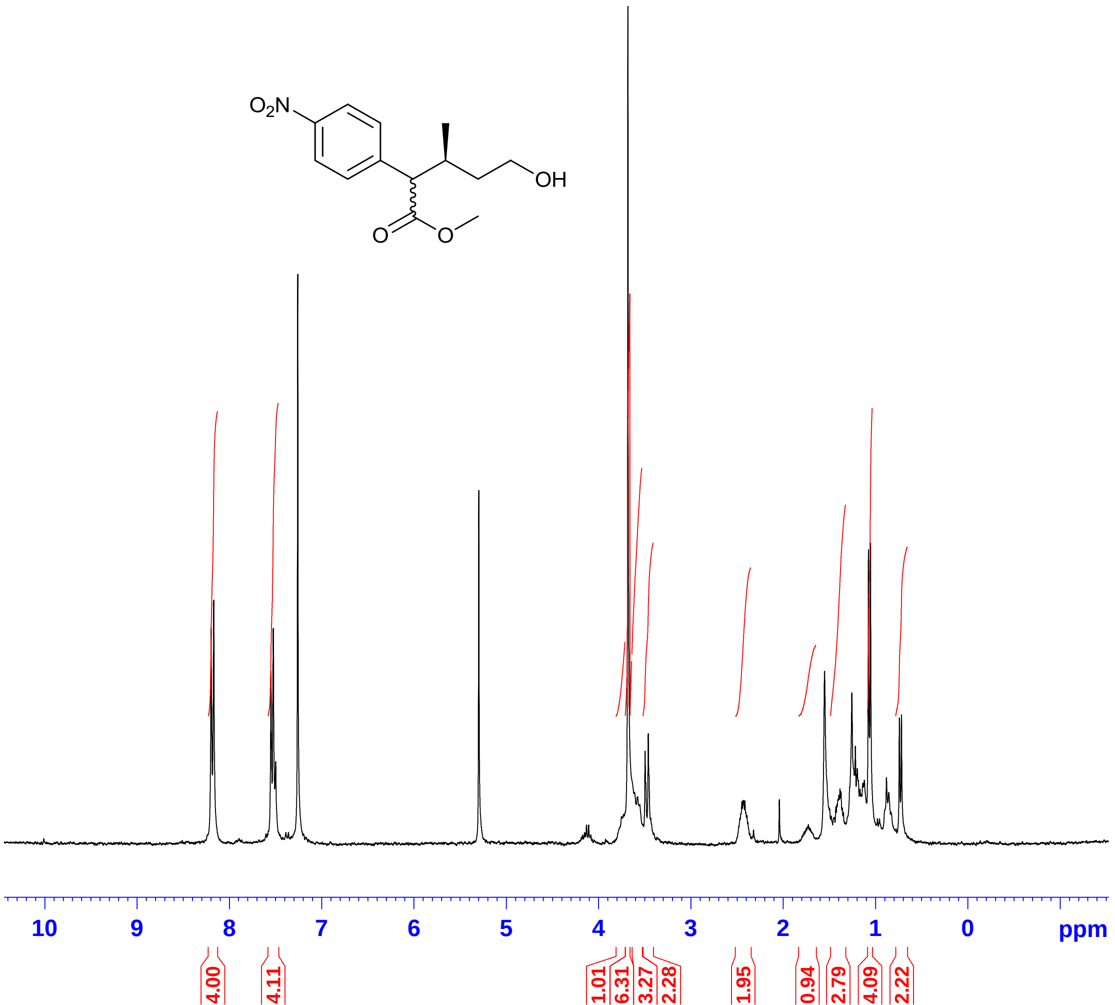
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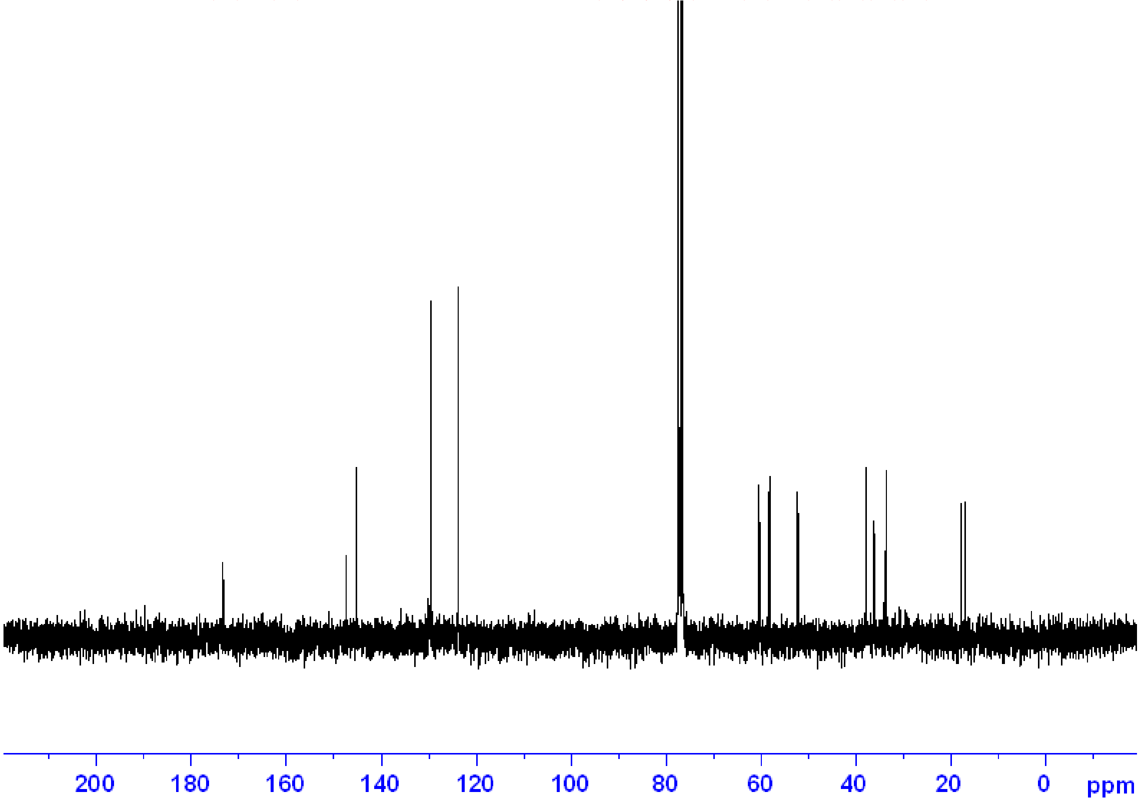
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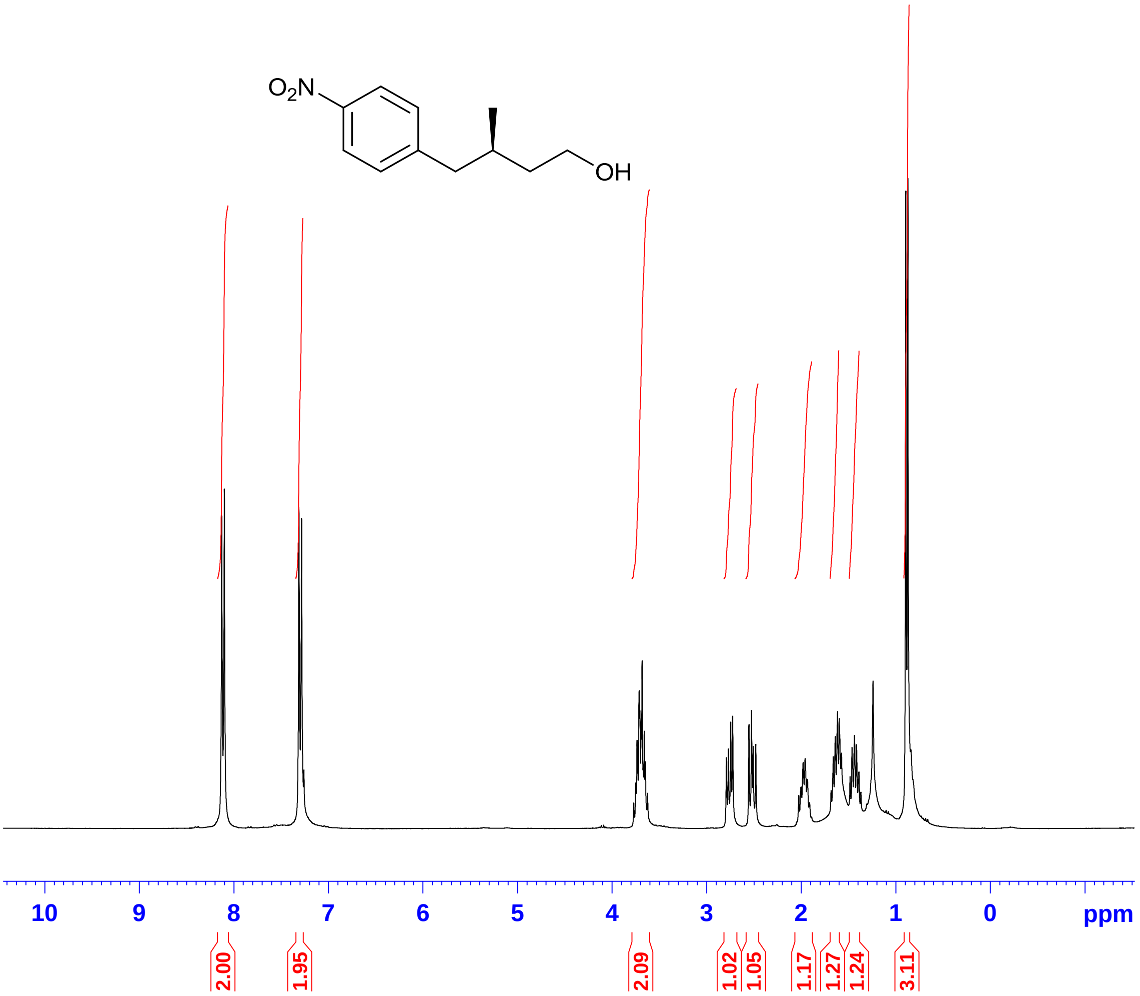
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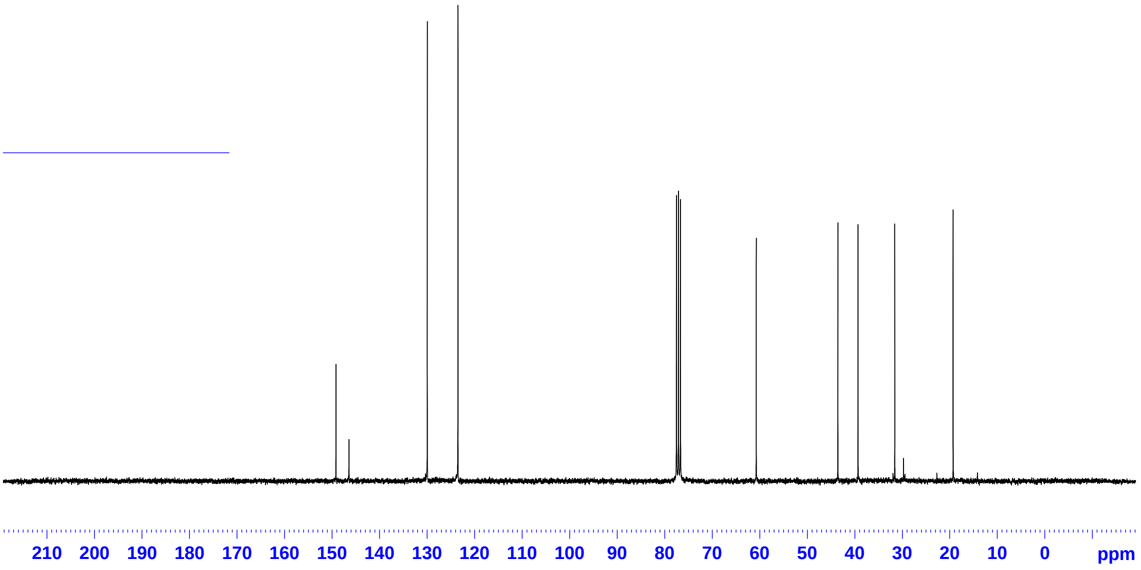
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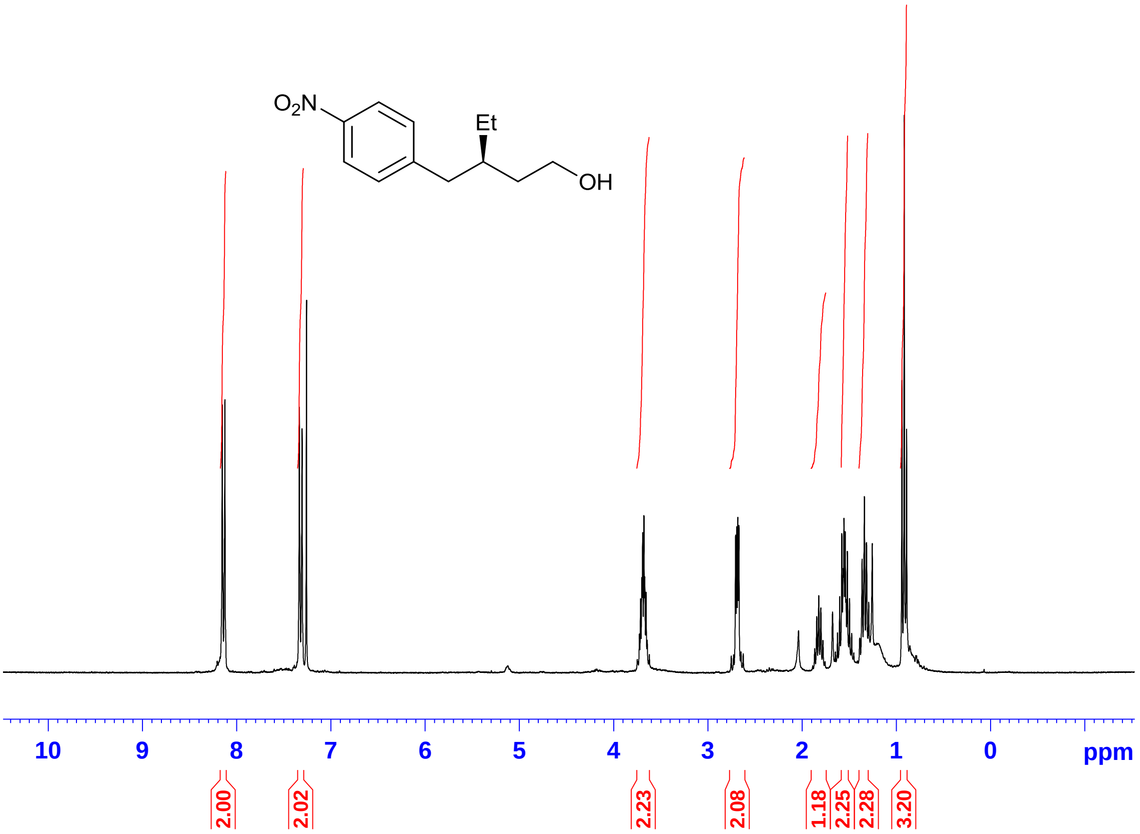
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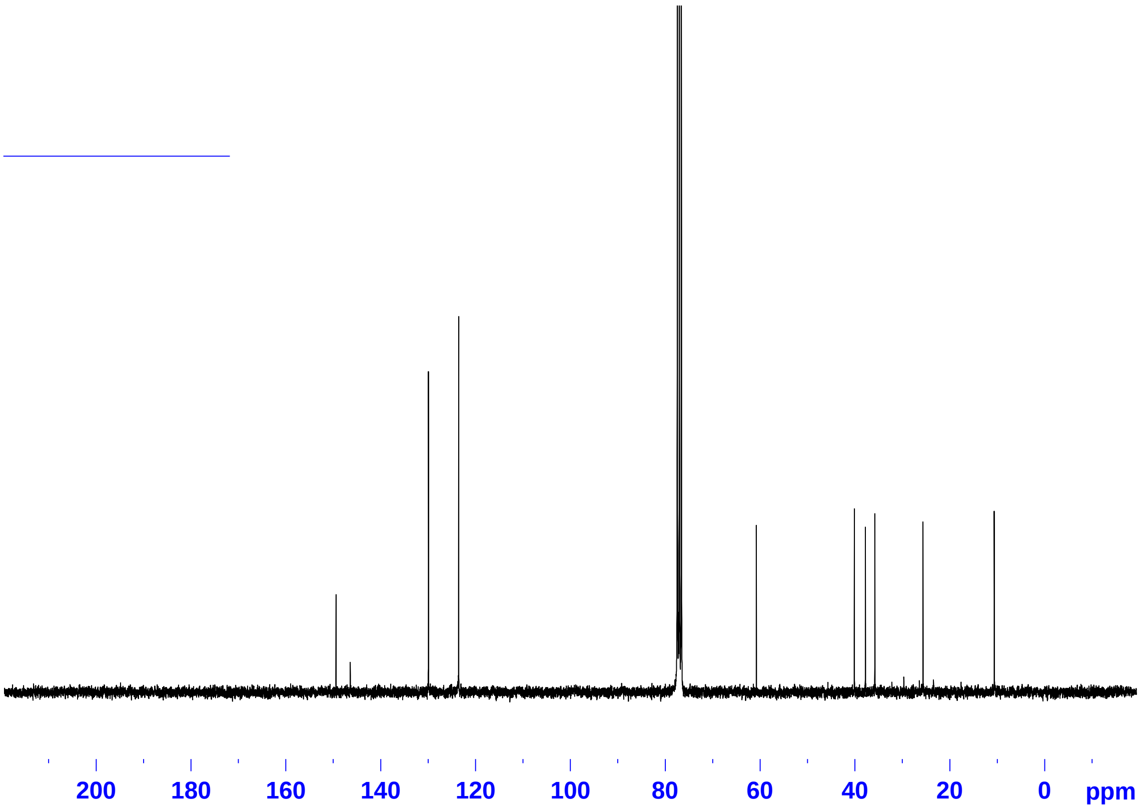
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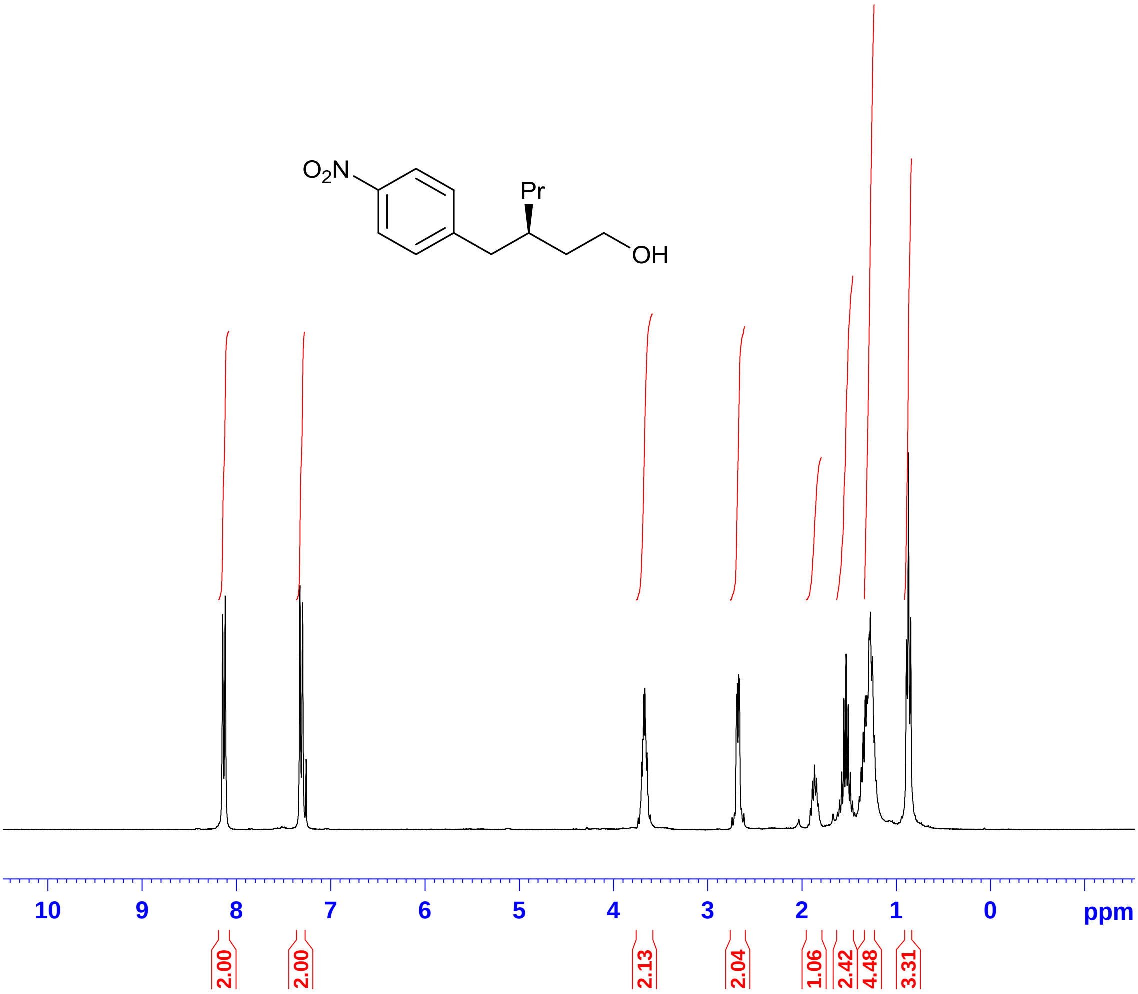
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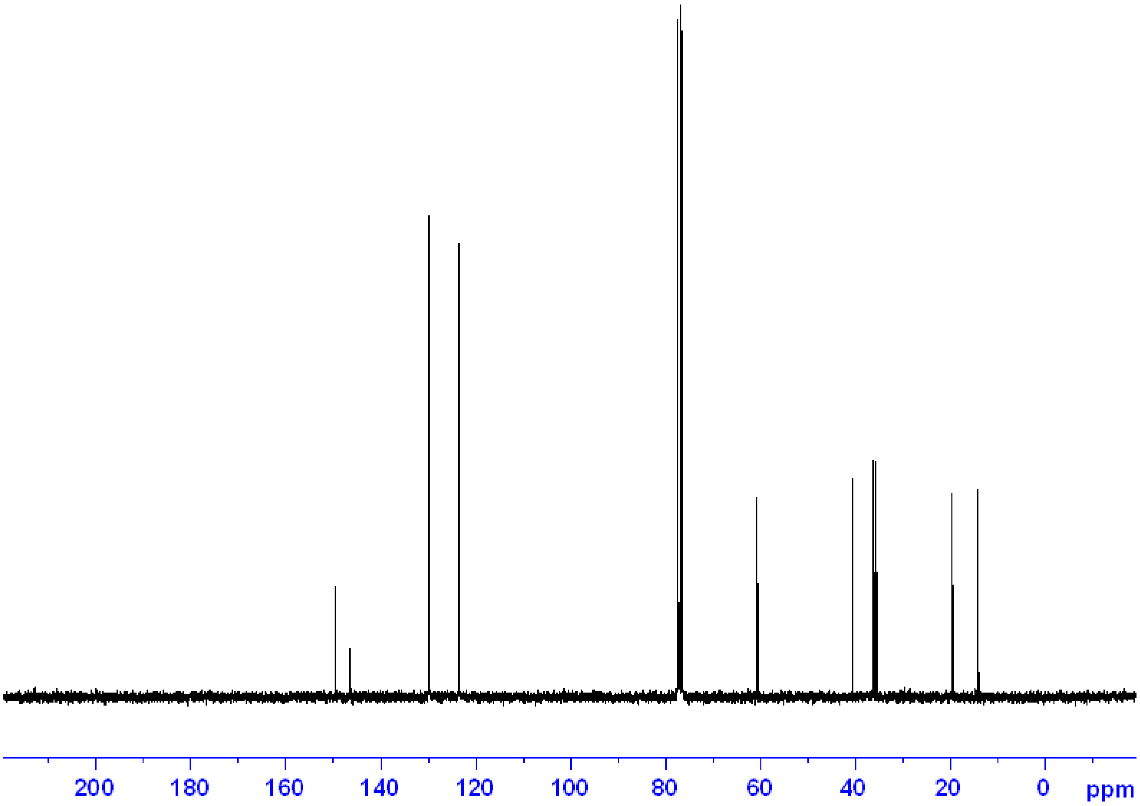
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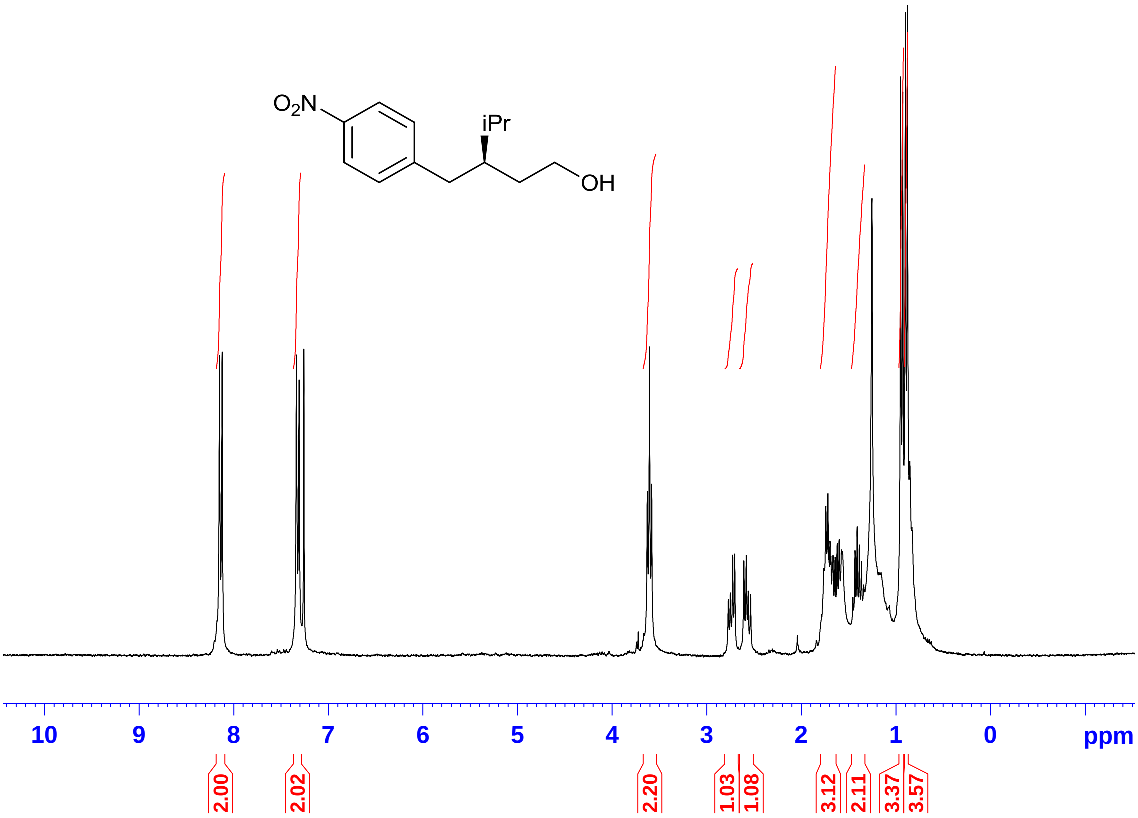
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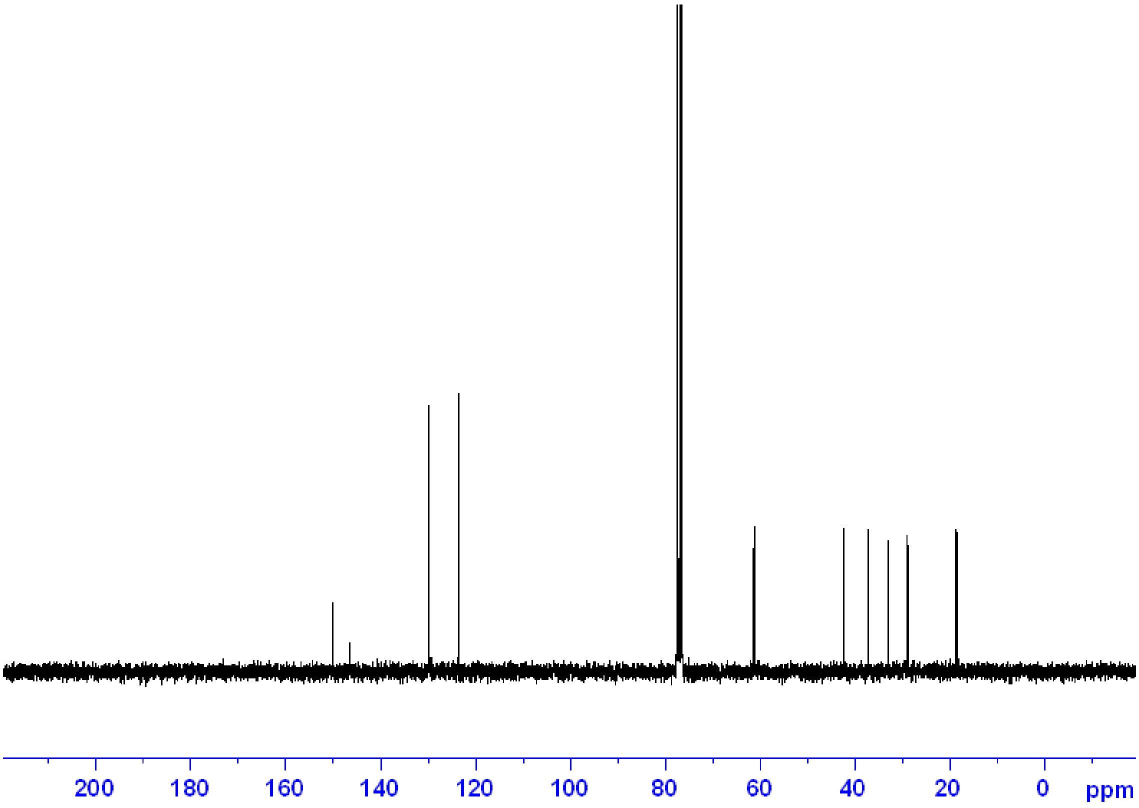
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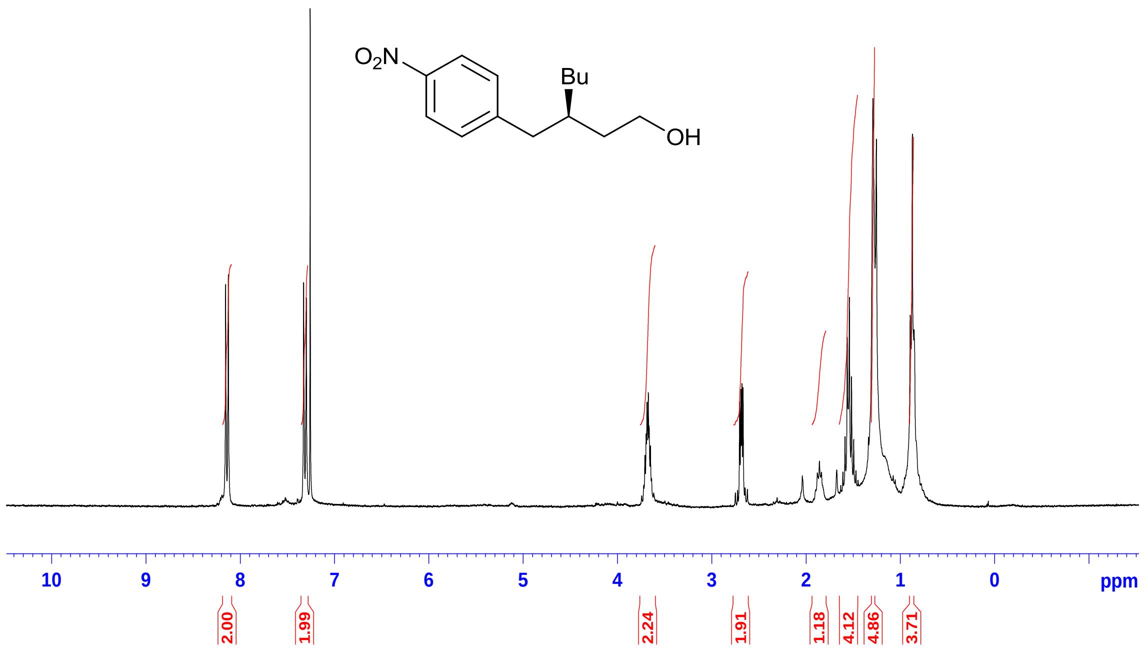
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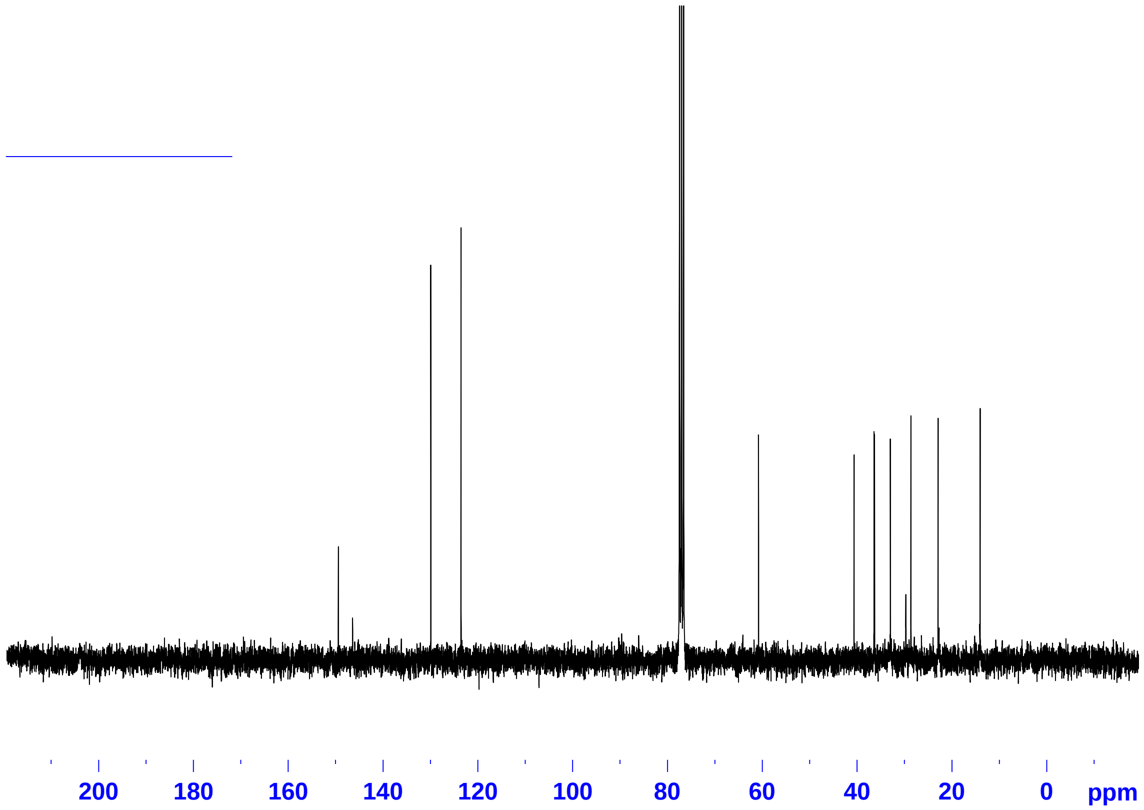
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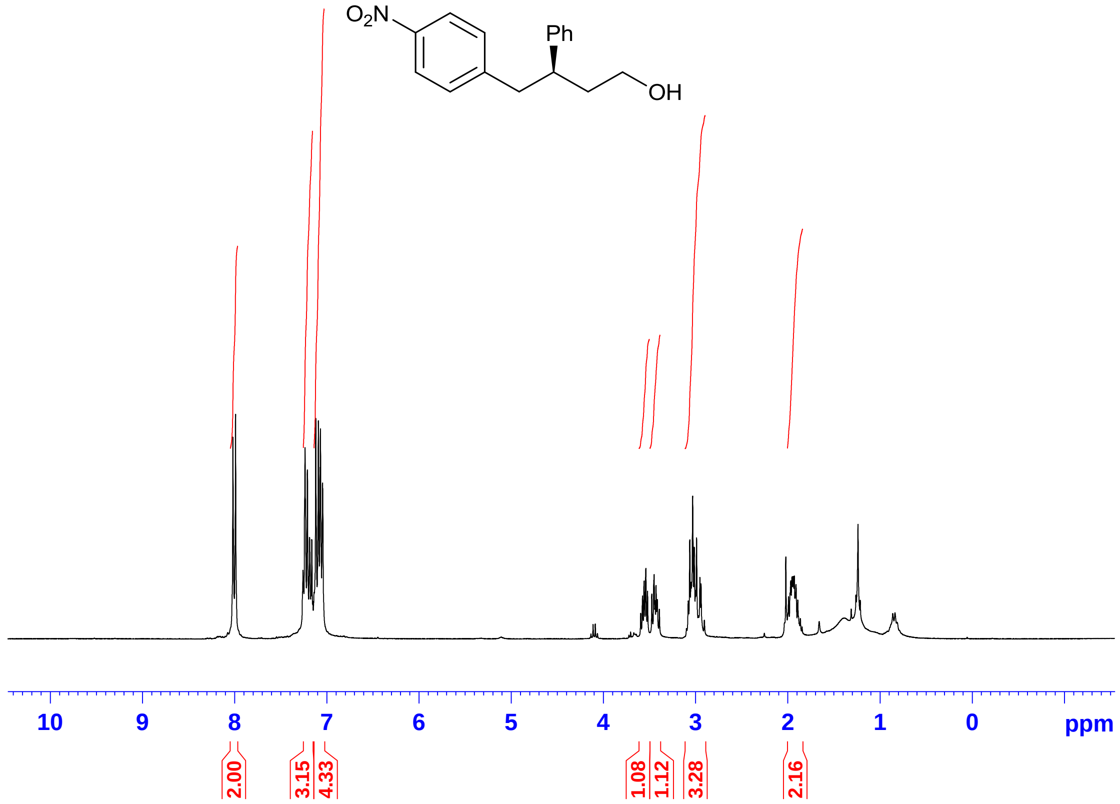
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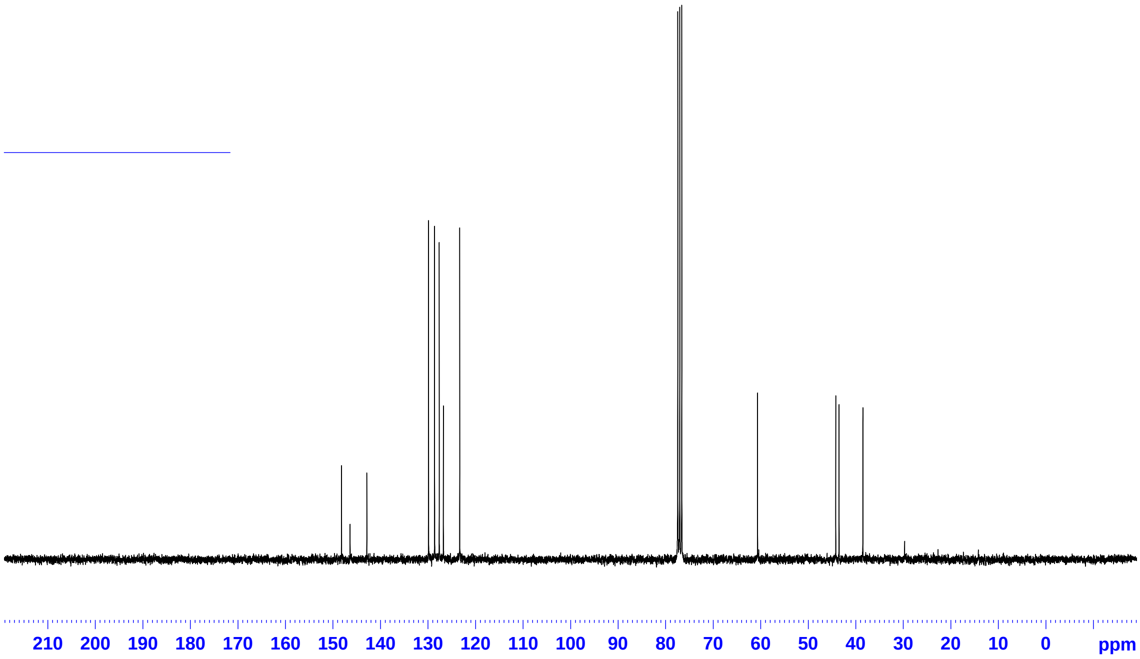
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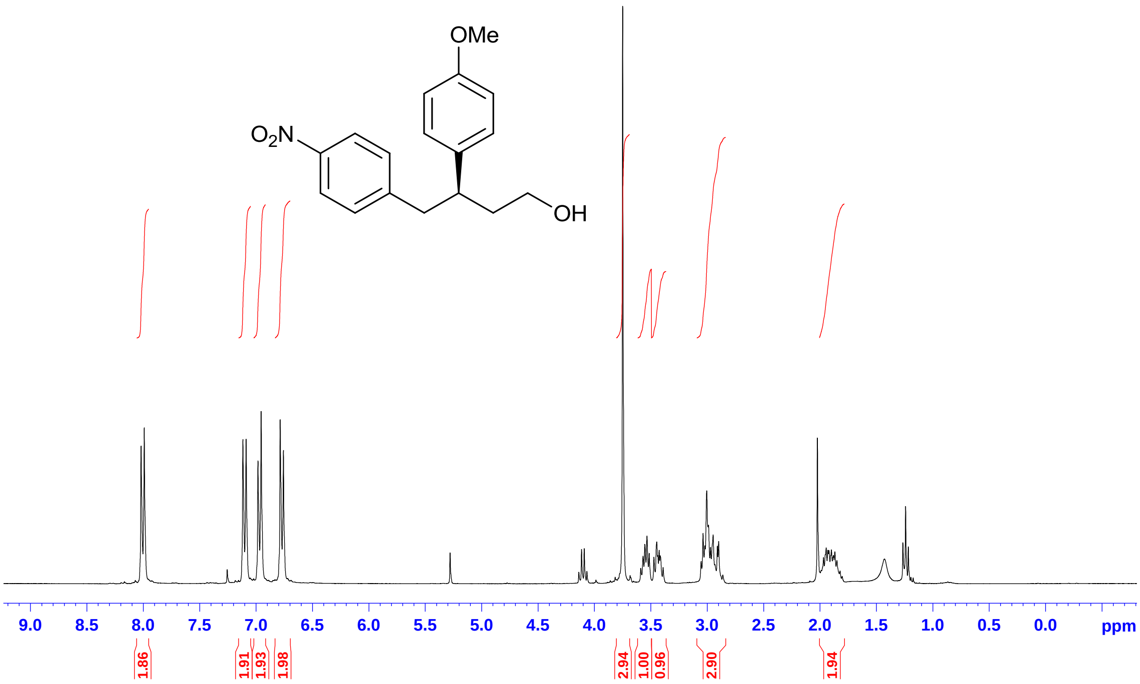
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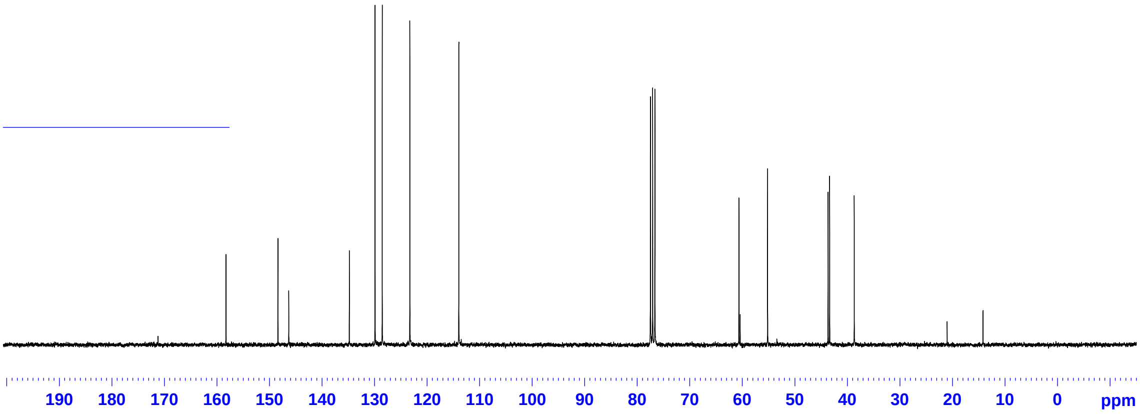
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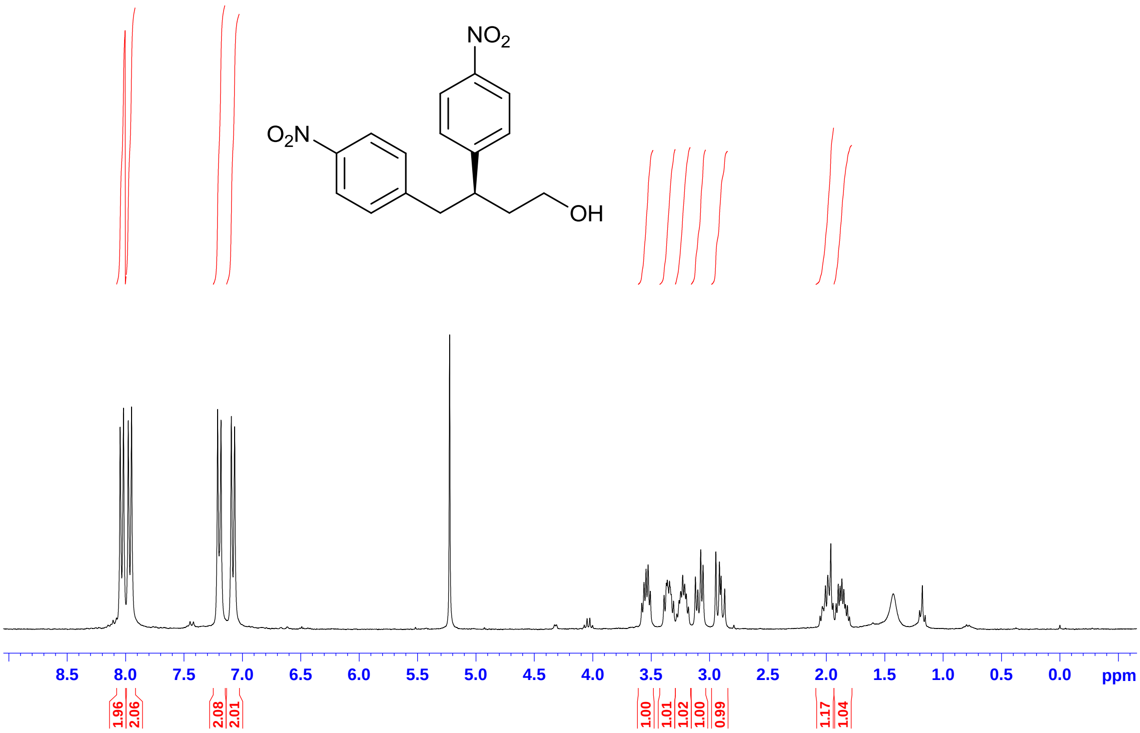
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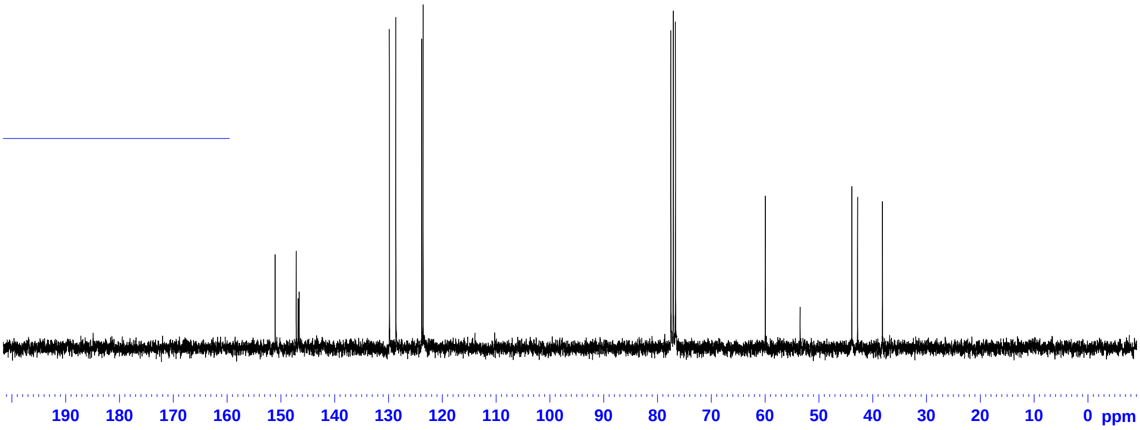
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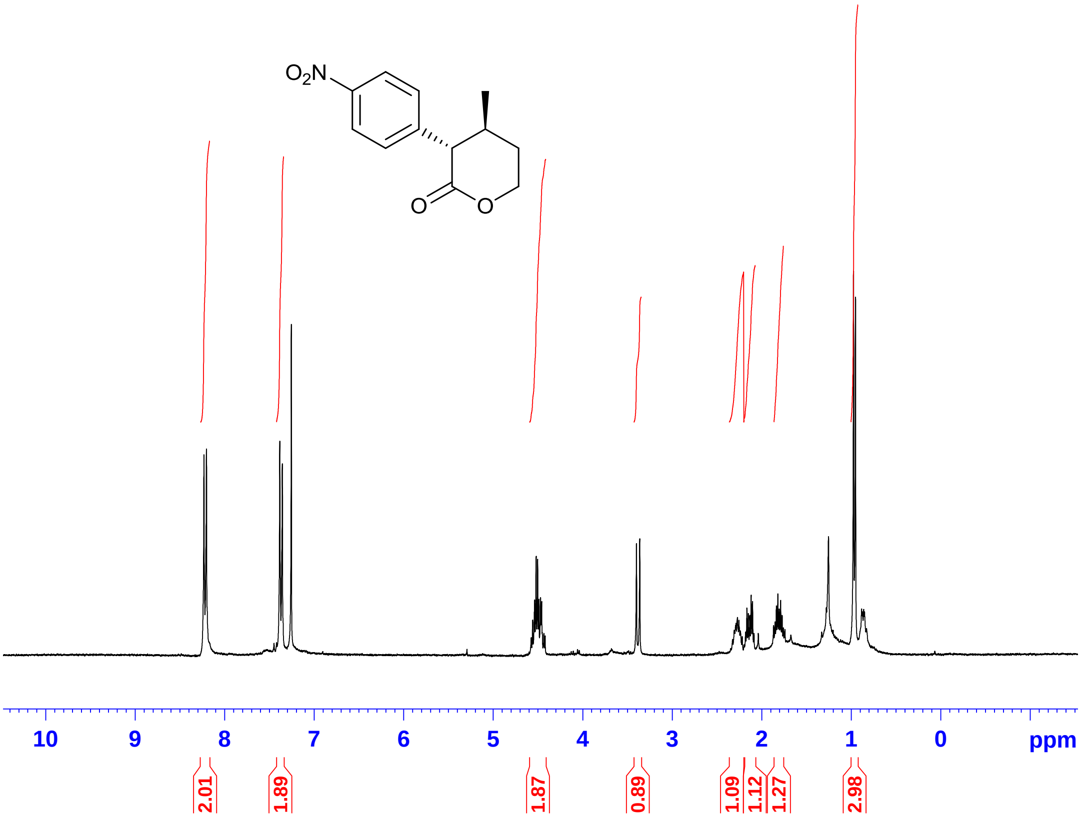
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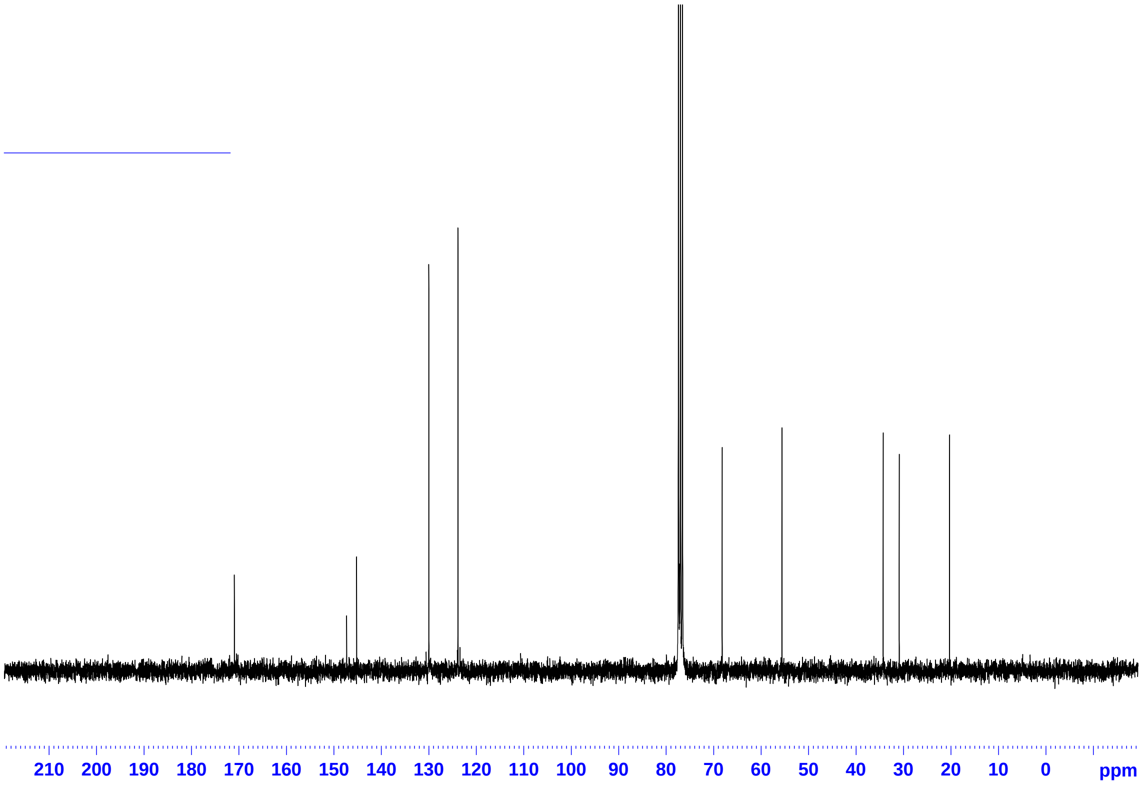
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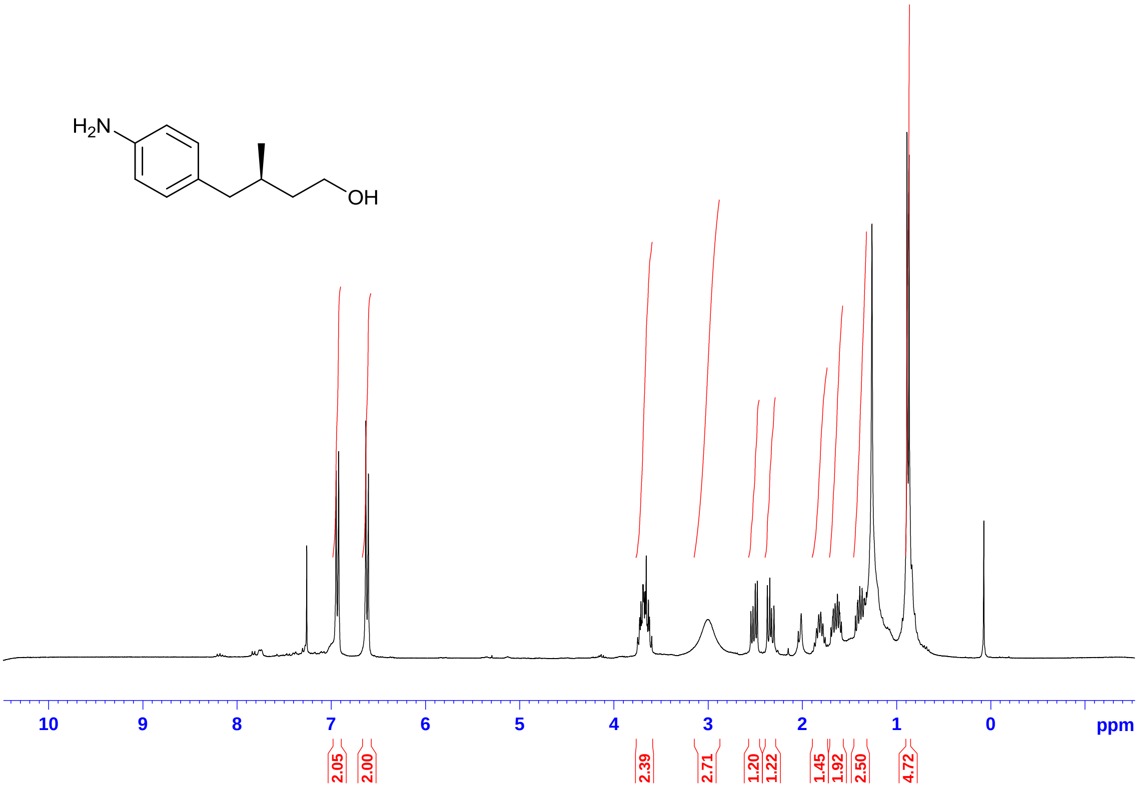
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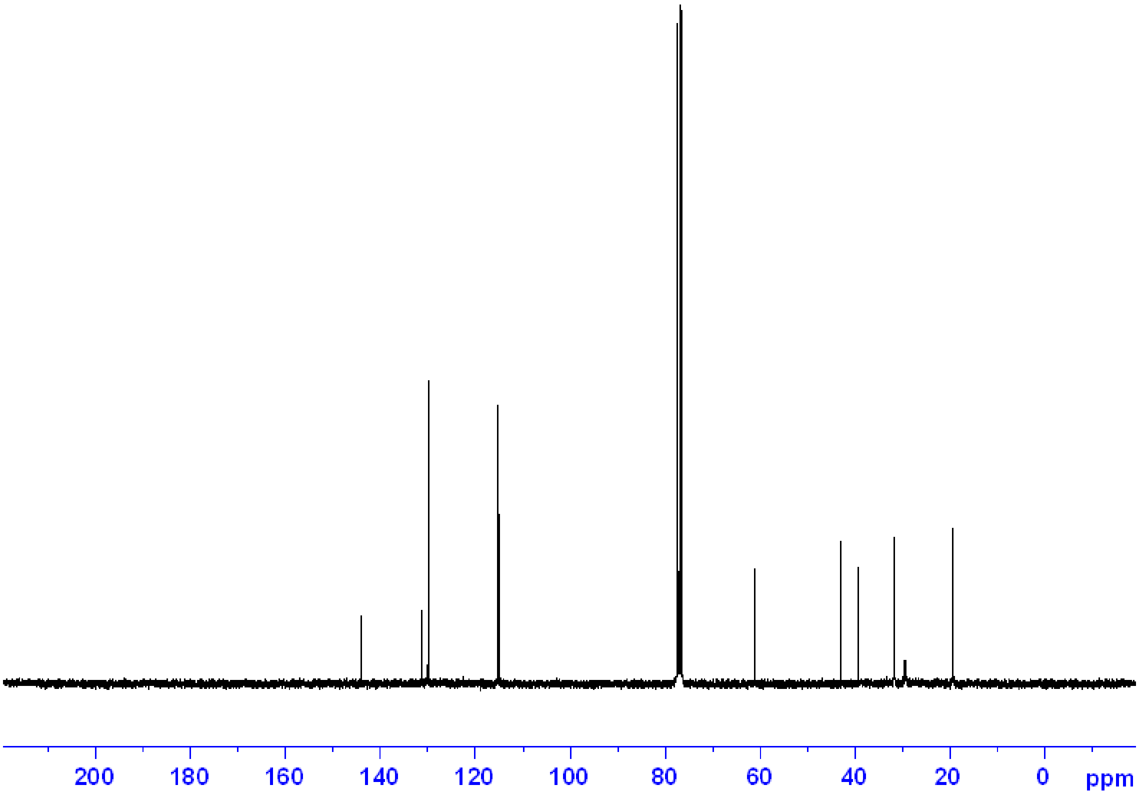
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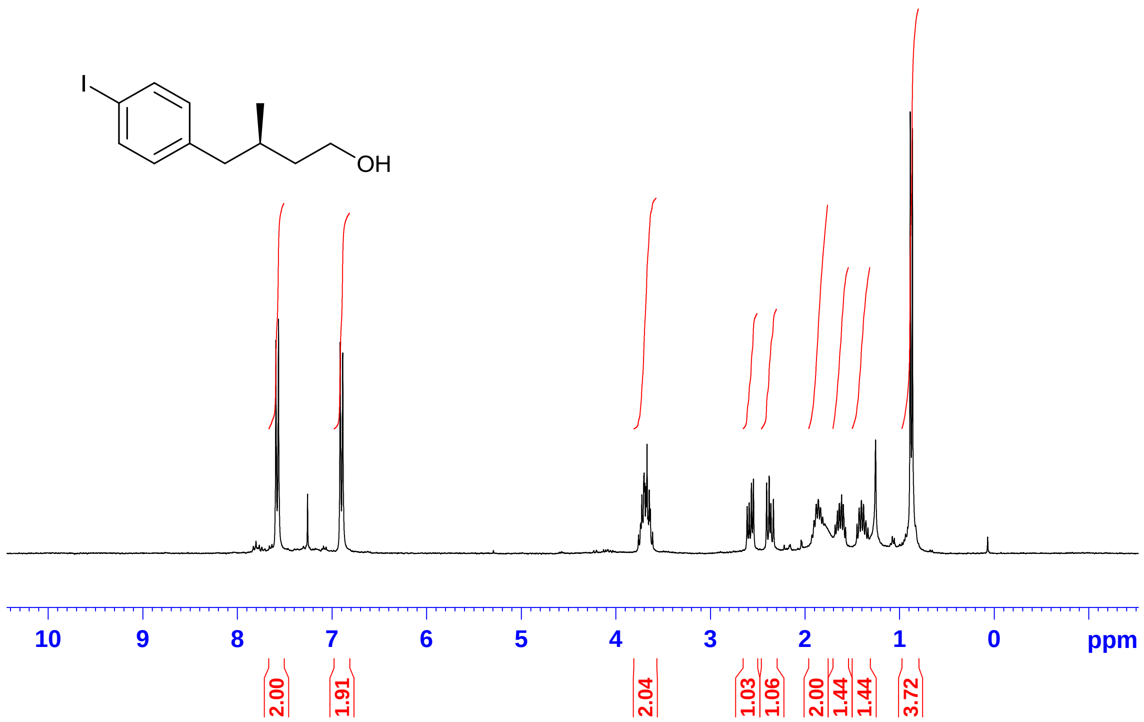
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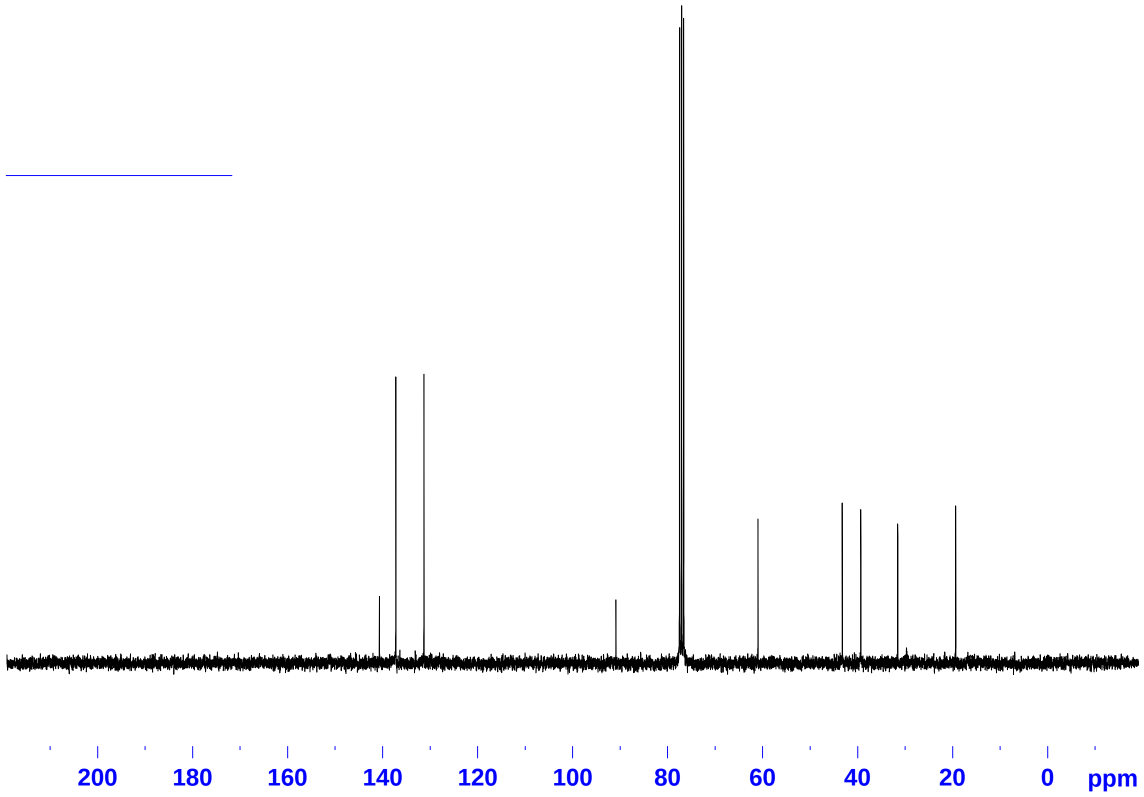
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Theoretical calculations.

Geometries have been fully optimized at the DFT (B3LYP)[8] level, in the solvent-phase (CH_2CL_2) with the CPCM model,[9] by using the Gaussian09 program.[10] The standard 6-31G(d)[11] basis set was used for all the atoms. Frequencies and zero-point energy (ZPE) were also computed at the same level of theory. Final energies were obtained using the more extended 6-311G(d,p)[12] basis set for all atoms. Relative free energies (in kcal/mol) were evaluated at the B3LYP/6-311G(d,p) level with ZPE and entropy corrections evaluated at 298 K using the frequencies previously calculated at B3LYP/6-31G(d) level. For the study of the deprotonation step, Me_4N^+ ion has been used as a simplified model for the corresponding $t\mathrm{Bu}_4N^+$ one.

Several conformations and orientations of the nucleophilic enol were studied being the approach through *Re*-faces of both iminium ion (the less hindered face of iminium) and enol the less energy demanding. From this approach the corresponding TSs with enolate were studied as well as the corresponding TSs through *si*-faces of both enol and enolate. In the case of the study of the Michael addition, the enantiomer of the catalyst, (*S*)-**II**, was used in all the calculations.

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[8] (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B***1988**, *37*, 785. (b) Becke, A. D. *J. Chem. Phys.***1993**, *98*, 5648.

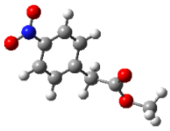
[9] (a) Barone, V.; Cossi, M. *J. Phys. Chem*. A **1998**, *102*, 1995. (b) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. J. *Comput. Chem.***2003**, *24*, 669.

[10] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

[11] (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Francl, M. M.; Petro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

[12] Krishnan, R.; Binkley, J.S.; Seeger, R.; Pople, J.A. *J. Chem. Phys.***1980**, *72*, 650. The inclusion of diffuse functions in the basis sets are avoided in the PCM single-point energy calculations, as this could lead to electron density tails going beyond the solute cavities generated by the molecularly shaped interlocking spheres. It has also been reported that the use of more extended basis sets often worsen the results obtained using the continuum models. See: (a) Patil, M. P.; Sunoj, R. B. *Chem. Asian J*. **2009**, *4*, 714. (b) Sadlej-Sosnowska, N. *Theor. Chem. Acc*. **2007**, *118*, 281.

Cartesian coordinates (Å) and energies (hartrees) of all the optimized structures.



1

E(B3LYP 6-31G*) = -703.949193189

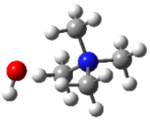
Zero-point correction= 0.174659

Thermal correction to Gibbs Free Energy= 0.132691

E(B3LYP 6-311G**) = -704.136649816

Number of imaginary frequencies: 0

6	0	0.41869	0.38284	0.61906
6	0	-2.27386	0.02779	0.02188
6	0	-0.19056	-0.86994	0.79377
6	0	-0.35117	1.45087	0.13805
6	0	-1.69997	1.28443	-0.16358
6	0	-1.53591	-1.05699	0.49838
1	0	0.39364	-1.70552	1.16531
1	0	0.10712	2.42563	-0.00074
1	0	-2.30076	2.10552	-0.53362
1	0	-2.01431	-2.0188	0.63313
7	0	-3.6925	-0.15856	-0.28802
8	0	-4.18395	-1.2768	-0.11604
8	0	-4.32952	0.81134	-0.70664
6	0	1.87853	0.58193	0.94717
1	0	2.1013	0.19093	1.94947
1	0	2.1395	1.6434	0.96676
6	0	2.825	-0.13379	-0.01184
8	0	2.5371	-1.07347	-0.72368
8	0	4.05518	0.40245	0.06326
6	0	5.06666	-0.2239	-0.75301
1	0	4.79526	-0.16041	-1.80929
1	0	5.98225	0.33376	-0.55907
1	0	5.18835	-1.27222	-0.47035



Me_4NOH

E(B3LYP 6-31G*) = -290.141006113

Zero-point correction= 0.17487711

Thermal correction to Gibbs Free Energy= 0.14241111

E(B3LYP 6-311G**) = -290.244499533

Number of imaginary frequencies: 0

7	0	0.57889	-0.00692	-0.00003
6	0	-0.02707	-0.65923	-1.22124
1	0	0.37943	-0.16801	-2.10817
1	0	0.25337	-1.71483	-1.21712
1	0	-1.12235	-0.50009	-1.09035
6	0	0.1674	1.44233	-0.00032
1	0	0.57417	1.9195	0.89328
1	0	-0.92582	1.43863	0.00086
1	0	0.57223	1.91863	-0.89527
6	0	-0.02677	-0.65836	1.22175
1	0	-1.12195	-0.49906	1.09086
1	0	0.2535	-1.71399	1.21829
1	0	0.37993	-0.16656	2.10827
6	0	2.06797	-0.13339	-0.00014
1	0	2.33144	-1.19215	0.00012
1	0	2.46587	0.3493	-0.89463
1	0	2.46598	0.34974	0.89408
8	0	-2.587	0.10902	-0.00044
1	0	-2.95125	-0.79299	0.00312

Br^-

E(B3LYP 6-31G*) = -13.3363474535

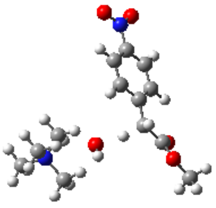
Zero-point correction= 0.000000

Thermal correction to Gibbs Free Energy= -0.016176

E(B3LYP 6-311G**) = -13.5525490616

Number of imaginary frequencies: 0

35	0	-1.99367	3.10365	-0.82681



$TS_{deprotonation}$

E(B3LYP 6-31G*) = -994.107756861

Zero-point correction= 0.34901486

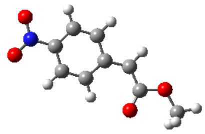
Thermal correction to Gibbs Free Energy= -0.29296786

E(B3LYP 6-311G**) = -994.395176

Number of imaginary frequencies: 1 (-112.6552)

6	0	-1.23725	0.95144	0.46948
6	0	-3.24982	-0.94998	0.0352
6	0	-1.42955	-0.12767	1.36123
6	0	-2.0747	1.03053	-0.66007
6	0	-3.07827	0.09346	-0.87754
6	0	-2.42432	-1.07085	1.15891
1	0	-0.75654	-0.22776	2.20717
1	0	-1.93169	1.83524	-1.37007
1	0	-3.72929	0.16355	-1.74043
1	0	-2.56751	-1.89599	1.84568
7	0	-4.2967	-1.93006	-0.18912
8	0	-4.43827	-2.84134	0.63678
8	0	-5.00624	-1.81635	-1.19689
6	0	-0.13434	1.90608	0.79242
1	0	0.86287	1.22798	0.88416
1	0	-0.23922	2.2826	1.81555
6	0	0.15006	3.03106	-0.13046
8	0	0.01399	3.05111	-1.34634
8	0	0.7022	4.0773	0.54363
6	0	1.134	5.18229	-0.2645
1	0	0.29244	5.61632	-0.81134
1	0	1.54762	5.91216	0.43229
1	0	1.89857	4.86646	-0.97987
7	0	3.74349	-2.07539	-0.30535
6	0	3.66689	-2.32274	1.18147
1	0	3.25956	-3.32231	1.3439
1	0	4.67574	-2.25932	1.59322
1	0	3.00992	-1.5371	1.58013
6	0	2.34761	-2.14238	-0.86953
1	0	2.39615	-1.93822	-1.94021
1	0	1.76216	-1.38555	-0.34541
1	0	1.95057	-3.14396	-0.69747
6	0	4.28161	-0.68266	-0.53269
1	0	3.5777	-0.00789	-0.02001
1	0	5.28554	-0.62986	-0.10758
1	0	4.32153	-0.50172	-1.60831

6	0	4.62114	-3.09534	-0.96392
1	0	5.62263	-3.02572	-0.53735
1	0	4.20661	-4.08827	-0.78358
1	0	4.65613	-2.89246	-2.03519
8	0	1.96177	0.21039	1.198
1	0	2.465	0.7215	1.85448



Enolate

E(B3LYP 6-31G*) = -703.4555885

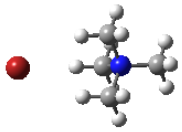
Zero-point correction= 0.16123648

Thermal correction to Gibbs Free Energy= -0.12158348

E(B3LYP 6-311G**) = -703.64982

Number of imaginary frequencies: 0

6	0	-0.44959	0.51487	-0.00003
6	0	2.35953	0.00407	-0.00002
6	0	0.08182	-0.82454	-0.00004
6	0	0.52614	1.57504	-0.00001
6	0	1.87692	1.33451	0.
6	0	1.4342	-1.06621	-0.00004
1	0	-0.61951	-1.64953	-0.00005
1	0	0.16875	2.60249	0.
1	0	2.58971	2.151	0.00003
1	0	1.81371	-2.08177	-0.00005
7	0	3.7448	-0.24962	0.00001
8	0	4.15386	-1.43726	0.00003
8	0	4.54709	0.71724	0.00005
6	0	-1.81618	0.83334	-0.00003
1	0	-2.09126	1.88411	-0.00001
6	0	-2.90123	-0.09389	-0.00002
8	0	-2.87755	-1.33171	-0.00001
8	0	-4.11943	0.57296	-0.00002
6	0	-5.27282	-0.26507	0.00008
1	0	-5.30371	-0.90533	0.88822
1	0	-6.13207	0.40923	0.00005
1	0	-5.30376	-0.90546	-0.88797



Me$_4$NBr

E(B3LYP 6-31G*) = -227.5922744

Zero-point correction= 0.1652184

Thermal correction to Gibbs Free Energy= 0.1301644

E(B3LYP 6-311G**) = -227.870466

Number of imaginary frequencies: 0

7	0	1.83393	-0.00061	-0.00009
6	0	1.32266	-0.68572	1.24251
1	0	1.69323	-1.71158	1.24955
1	0	1.69551	-0.14588	2.11387
1	0	0.2303	-0.66648	1.21106
6	0	1.31952	-0.73372	-1.21372
1	0	1.6893	-0.22784	-2.10649
1	0	0.22723	-0.71372	-1.17929
1	0	1.691	-1.75878	-1.18182
6	0	1.322	1.41784	-0.02712
1	0	0.2297	1.37981	-0.02623
1	0	1.69432	1.93669	0.8572
1	0	1.69408	1.90273	-0.93062
6	0	3.33636	0.00072	-0.00172
1	0	3.68784	0.53538	0.88147
1	0	3.69002	-1.03071	0.01742
1	0	3.68611	0.50073	-0.90564
35	0	-2.24427	0.00026	0.00001

H$_2$O

E(B3LYP 6-31G*) = -76.41554103

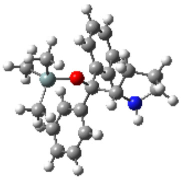
Zero-point correction= 0.02113403

Thermal correction to Gibbs Free Energy= 0.00346303

E(B3LYP 6-311G**) = -76.4538219

Number of imaginary frequencies: 0

8	0	0.	0.	0.12062
1	0	0.	0.75912	-0.48249
1	0	0.	-0.75912	-0.48249



(*S*)-II

E(B3LYP 6-31G*) = -1197.920984

Zero-point correction= 0.42692963

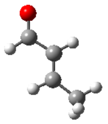
Thermal correction to Gibbs Free Energy= 0.37231063

E(B3LYP 6-311G**) = -1198.1832

Number of imaginary frequencies: 0

14	0	-2.10449	-1.6684	-0.54433
8	0	-0.57236	-1.01041	-0.77061
7	0	1.85316	1.75185	-1.29324
6	0	1.91834	-0.50902	-2.16896
1	0	2.3123	-1.17262	-1.39247
1	0	1.38752	-1.12973	-2.89515
6	0	0.99305	0.57115	-1.55283
1	0	0.23098	0.81687	-2.30083
6	0	3.2218	1.4413	-1.76158
1	0	3.69866	2.34131	-2.16277
1	0	3.82713	1.09719	-0.9118
6	0	3.06454	0.30786	-2.78524
1	0	2.76731	0.71727	-3.75948
1	0	3.97931	-0.27764	-2.92957
6	0	0.19696	0.10056	-0.28507
6	0	-0.74051	1.20877	0.24688
6	0	-1.24717	2.2237	-0.57992
1	0	-0.95054	2.28897	-1.62069
6	0	-2.15059	3.17168	-0.09442
6	0	-2.5782	3.12509	1.23312
1	0	-3.28055	3.86308	1.61103
6	0	-2.08835	2.12095	2.06993
6	0	-1.17907	1.18133	1.58117
1	0	-0.79896	0.41849	2.25211
6	0	1.16877	-0.37886	0.80746
6	0	1.35246	-1.74231	1.06989
1	0	0.7794	-2.47057	0.50829
6	0	2.26666	-2.17421	2.03604
6	0	3.02181	-1.24719	2.75407
1	0	3.73228	-1.58048	3.50599
6	0	2.85303	0.11619	2.49691

6	0	1.9356	0.54564	1.53716
1	0	1.8153	1.60435	1.34108
6	0	-3.48123	-0.52666	-1.1468
1	0	-4.43702	-1.06679	-1.13424
1	0	-3.30129	-0.19667	-2.17693
1	0	-3.59116	0.36536	-0.52232
6	0	-2.4378	-2.18501	1.24232
1	0	-3.37262	-2.75901	1.28691
1	0	-2.54423	-1.32601	1.91267
1	0	-1.63723	-2.82275	1.63442
6	0	-2.05496	-3.20513	-1.63639
1	0	-3.01782	-3.73028	-1.61076
1	0	-1.28233	-3.90925	-1.30555
1	0	-1.84452	-2.94381	-2.68023
1	0	3.43371	0.85073	3.04935
1	0	2.38622	-3.2385	2.22268
1	0	-2.40692	2.06965	3.10778
1	0	-2.51948	3.94781	-0.75984
1	0	1.49328	2.54604	-1.81387



2a

E(B3LYP 6-31G*) = -231.2399495

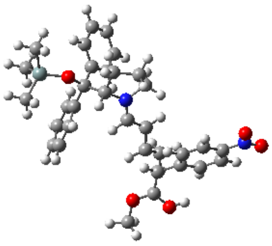
Zero-point correction= 0.09003648

Thermal correction to Gibbs Free Energy= 0.06140948

E(B3LYP 6-311G**) = -231.306412

Number of imaginary frequencies: 0

6	0	1.39859	0.33278	-0.0002
1	0	1.35794	1.44385	-0.00057
6	0	0.0936	-0.32853	-0.00056
1	0	0.08606	-1.41696	-0.00095
6	0	-1.04278	0.39052	-0.00011
1	0	-0.96135	1.47913	0.00025
6	0	-2.42887	-0.16598	0.00024
1	0	-2.43285	-1.25967	-0.00173
1	0	-2.98294	0.18693	0.88013
1	0	-2.98492	0.19027	-0.87702
8	0	2.47435	-0.24953	0.00046



TSiminium-*re*-enol

E(B3LYP 6-31G*) = -2057.08267

Zero-point correction= 0.68327587

Thermal correction to Gibbs Free Energy= 0.60399287

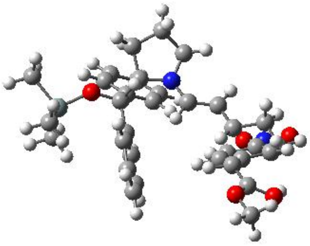
E(B3LYP 6-311G**) = -2057.564

Number of imaginary frequencies: 1 (-351.2546)

14	0	-5.49686	-0.01298	-1.47741
8	0	-3.97533	-0.66875	-1.11882
7	0	-0.40818	-1.04247	-0.14938
6	0	-1.86435	-2.49595	-1.35127
1	0	-2.60504	-2.9779	-0.70876
1	0	-2.22483	-2.56392	-2.37907
6	0	-1.67068	-1.02068	-0.92629
1	0	-1.51388	-0.40005	-1.81189
6	0	0.09755	-2.41193	0.04253
1	0	1.19009	-2.40259	0.05189
1	0	-0.25776	-2.81841	0.99739
6	0	-0.49075	-3.15815	-1.15766
1	0	0.14555	-2.99827	-2.03515
1	0	-0.56236	-4.23491	-0.98185
6	0	-2.93716	-0.42545	-0.17067
6	0	-2.80131	1.09977	0.06083
6	0	-2.40605	1.92978	-1.00499
1	0	-2.17559	1.501	-1.97498
6	0	-2.3195	3.31406	-0.85559
6	0	-2.64171	3.91092	0.36559
1	0	-2.57529	4.98864	0.4849
6	0	-3.06044	3.10705	1.42457
6	0	-3.14093	1.71963	1.27233
1	0	-3.47981	1.12336	2.11062
6	0	-3.18639	-1.2237	1.12318
6	0	-4.23403	-2.15094	1.20194
1	0	-4.89168	-2.28399	0.35198

6	0	-4.43526	-2.92146	2.35066
6	0	-3.5836	-2.78769	3.44629
1	0	-3.73755	-3.38595	4.34
6	0	-2.52876	-1.87455	3.38095
6	0	-2.33262	-1.10275	2.23466
1	0	-1.51229	-0.39366	2.21928
6	0	-5.34308	1.33367	-2.78854
1	0	-6.34133	1.62385	-3.14076
1	0	-4.77631	0.9773	-3.65712
1	0	-4.84692	2.2314	-2.4066
6	0	-6.40047	0.65517	0.0377
1	0	-7.4193	0.94317	-0.25204
1	0	-5.90972	1.54038	0.45458
1	0	-6.47942	-0.09444	0.83257
6	0	-6.43402	-1.47256	-2.21381
1	0	-7.4239	-1.15454	-2.56373
1	0	-6.58218	-2.27778	-1.48496
1	0	-5.89724	-1.89269	-3.07255
6	0	0.28997	0.05365	0.17096
1	0	-0.12615	0.98116	-0.21344
6	0	1.43052	0.11672	0.94836
1	0	1.84814	-0.78121	1.39363
6	0	2.08969	1.36017	1.183
1	0	1.5189	2.24643	0.90626
6	0	2.87205	1.50711	2.46737
1	0	3.53303	0.65223	2.63958
1	0	3.46099	2.42787	2.5073
1	0	2.15888	1.53776	3.30088
1	0	-1.85599	-1.75567	4.22603
1	0	-5.25859	-3.63	2.3811
1	0	-3.33026	3.55464	2.37717
1	0	-2.00599	3.92487	-1.69773
6	0	3.42874	1.62025	-0.32283
1	0	2.66248	1.60623	-1.0906
6	0	3.91506	2.94337	-0.14079
8	0	5.10737	3.28719	0.29957
1	0	5.72169	2.52624	0.28141
6	0	4.35749	0.47006	-0.38118
6	0	6.02019	-1.76881	-0.57034
6	0	4.15887	-0.49789	-1.38633

6	0	5.39968	0.25949	0.54788
6	0	6.2378	-0.84717	0.45092
6	0	4.97999	-1.61297	-1.48744
1	0	3.35725	-0.36247	-2.10537
1	0	5.54033	0.92205	1.39734
1	0	7.03792	-1.0057	1.16268
1	0	4.83083	-2.35054	-2.26593
7	0	6.8976	-2.93516	-0.67639
8	0	7.8181	-3.04371	0.13679
8	0	6.6716	-3.74988	-1.57375
8	0	3.08271	3.92731	-0.34229
6	0	3.51462	5.30295	-0.12944
1	0	2.64999	5.90323	-0.40266
1	0	4.36555	5.52534	-0.77405
1	0	3.77552	5.44834	0.9195



TSiminium-*si*-enol

E(B3LYP 6-31G*) = -2057.082768

Zero-point correction= 0.6832711

Thermal correction to Gibbs Free Energy= 0.6043321

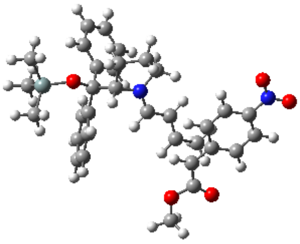
E(B3LYP 6-311G**) = -2057.56332

Number of imaginary frequencies: 1 (-348.2244)

14	0	-5.24728	-0.59769	-0.76446
8	0	-4.03614	-0.19004	0.34942
7	0	-0.80572	-0.08873	2.17515
6	0	-2.9968	0.56792	2.85903
1	0	-3.3513	1.48834	2.38881
1	0	-3.86999	0.03746	3.24284
6	0	-2.23132	-0.29787	1.82869
1	0	-2.46763	-1.35349	1.98286
6	0	-0.64184	0.95803	3.19991
1	0	0.2228	0.729	3.82616
1	0	-0.48376	1.93307	2.72463
6	0	-1.97138	0.89551	3.95742

1	0	-1.92919	0.09256	4.70153
1	0	-2.19504	1.83028	4.47878
6	0	-2.62853	0.03598	0.32613
6	0	-1.96111	-0.9496	-0.66323
6	0	-2.07477	-2.3332	-0.43313
1	0	-2.61813	-2.69781	0.43279
6	0	-1.51675	-3.26476	-1.30877
6	0	-0.83849	-2.83624	-2.45252
1	0	-0.40389	-3.55928	-3.13688
6	0	-0.74169	-1.46949	-2.7124
6	0	-1.29887	-0.53865	-1.82899
1	0	-1.22085	0.51528	-2.06639
6	0	-2.32217	1.5152	0.02045
6	0	-3.35806	2.4478	-0.11906
1	0	-4.38532	2.1184	-0.03076
6	0	-3.0909	3.80061	-0.34796
6	0	-1.7755	4.25434	-0.43243
1	0	-1.56504	5.30539	-0.60904
6	0	-0.73015	3.33992	-0.28444
6	0	-1.00007	1.98873	-0.06168
1	0	-0.16751	1.30198	0.04187
6	0	-5.56242	-2.45727	-0.73788
1	0	-6.47205	-2.68585	-1.30794
1	0	-5.71567	-2.8175	0.28655
1	0	-4.73917	-3.0287	-1.17827
6	0	-4.87086	-0.02178	-2.52032
1	0	-5.74686	-0.21001	-3.15428
1	0	-4.02064	-0.55415	-2.95853
1	0	-4.65546	1.05161	-2.56039
6	0	-6.77709	0.27778	-0.09662
1	0	-7.65807	0.01647	-0.69594
1	0	-6.674	1.36885	-0.11747
1	0	-6.98043	-0.01936	0.93899
6	0	0.16869	-0.93834	1.82245
1	0	-0.17248	-1.79657	1.24918
6	0	1.51374	-0.83746	2.1192
1	0	1.90632	0.04841	2.60915
6	0	2.42562	-1.88438	1.78873
1	0	1.97074	-2.84118	1.53597
6	0	3.66947	-2.00355	2.64025

1	0	3.36871	-2.33864	3.64103
1	0	4.38806	-2.73192	2.25482
1	0	4.1707	-1.03829	2.76264
1	0	0.30163	3.67597	-0.34394
1	0	-3.91782	4.49758	-0.45386
1	0	-0.23898	-1.11774	-3.60923
1	0	-1.6183	-4.32576	-1.09801
6	0	3.05841	-1.59981	-0.12609
1	0	2.08334	-1.81627	-0.55151
6	0	3.94892	-2.68111	-0.35974
8	0	5.26078	-2.60834	-0.45127
1	0	5.55519	-1.68051	-0.54901
6	0	3.50712	-0.20445	-0.33537
6	0	4.23173	2.45974	-0.7635
6	0	2.69323	0.65312	-1.10185
6	0	4.68669	0.32507	0.22965
6	0	5.05741	1.64901	0.01132
6	0	3.04616	1.97824	-1.3202
1	0	1.78079	0.26658	-1.54487
1	0	5.30724	-0.27062	0.89272
1	0	5.96185	2.05459	0.44668
1	0	2.42496	2.63239	-1.91893
7	0	4.61045	3.85554	-0.98873
8	0	5.67835	4.2498	-0.51554
8	0	3.84077	4.5659	-1.63921
8	0	3.44563	-3.884	-0.40586
6	0	4.31889	-5.03258	-0.61072
1	0	3.64346	-5.88441	-0.6387
1	0	5.0195	-5.11689	0.22079
1	0	4.85229	-4.92458	-1.55572



TSiminium-*re*-enolate

E(B3LYP 6-31G*) = -2056.662218

Zero-point correction= 0.6690149

Thermal correction to Gibbs Free Energy= 0.5884069

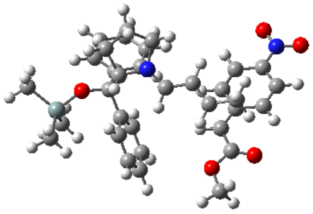
E(B3LYP 6-311G**) = -2057.14554

Number of imaginary frequencies: 1 (-83.1914)

14	0	-5.36685	0.06144	-1.54615
8	0	-3.86464	-0.61452	-1.14356
7	0	-0.32894	-1.01168	-0.07142
6	0	-1.73954	-2.4167	-1.38878
1	0	-2.49123	-2.93472	-0.78852
1	0	-2.07283	-2.43777	-2.42746
6	0	-1.57132	-0.96234	-0.89223
1	0	-1.38006	-0.3035	-1.74131
6	0	0.18072	-2.39214	0.06357
1	0	1.27123	-2.37844	0.11085
1	0	-0.21156	-2.84112	0.98321
6	0	-0.36452	-3.07377	-1.19265
1	0	0.29531	-2.86013	-2.04053
1	0	-0.42768	-4.15871	-1.07572
6	0	-2.8621	-0.40256	-0.1521
6	0	-2.74076	1.11202	0.14535
6	0	-2.304	1.98569	-0.86824
1	0	-2.02887	1.59911	-1.84436
6	0	-2.2287	3.36268	-0.65849
6	0	-2.60488	3.90795	0.57129
1	0	-2.54566	4.9797	0.73793
6	0	-3.06571	3.0606	1.57757
6	0	-3.13428	1.68055	1.36579
1	0	-3.50548	1.04988	2.16423
6	0	-3.15098	-1.2561	1.09854
6	0	-4.19071	-2.19574	1.09554
1	0	-4.81236	-2.29803	0.21485
6	0	-4.42954	-3.01578	2.20184
6	0	-3.62467	-2.92032	3.33614
1	0	-3.80784	-3.55732	4.1969
6	0	-2.57895	-1.99477	3.35272
6	0	-2.34577	-1.17299	2.24886
1	0	-1.53666	-0.4529	2.30109
6	0	-5.15172	1.44872	-2.80451
1	0	-6.13152	1.7456	-3.20016
1	0	-4.53717	1.1222	-3.65199

1	0	-4.68206	2.33595	-2.36857
6	0	-6.32866	0.68068	-0.04651
1	0	-7.33772	0.97413	-0.36361
1	0	-5.85721	1.55359	0.41606
1	0	-6.43257	-0.09463	0.72053
6	0	-6.2764	-1.37091	-2.36481
1	0	-7.24907	-1.03772	-2.74738
1	0	-6.45944	-2.19518	-1.66575
1	0	-5.70523	-1.76998	-3.2113
6	0	0.33215	0.06089	0.33613
1	0	-0.08544	1.01112	0.01625
6	0	1.47732	0.07864	1.14528
1	0	1.88553	-0.84942	1.5326
6	0	2.10068	1.27206	1.46035
1	0	1.64148	2.2012	1.13242
6	0	3.15931	1.36822	2.50949
1	0	3.67827	0.41483	2.64768
1	0	3.89389	2.14584	2.28251
1	0	2.68729	1.63581	3.46717
1	0	-1.94283	-1.90396	4.22894
1	0	-5.24551	-3.73265	2.16879
1	0	-3.37642	3.46813	2.53561
1	0	-1.87987	4.00774	-1.46
6	0	3.60555	1.77573	-0.62409
1	0	2.69928	1.75344	-1.21924
6	0	4.00548	3.07351	-0.16252
8	0	5.01106	3.38391	0.48554
6	0	4.40826	0.60412	-0.62292
6	0	5.85797	-1.82938	-0.61658
6	0	3.90914	-0.57412	-1.26307
6	0	5.68478	0.49618	0.01348
6	0	6.39016	-0.6891	0.01478
6	0	4.60912	-1.76232	-1.2601
1	0	2.95238	-0.5225	-1.77578
1	0	6.09518	1.3743	0.49521
1	0	7.35746	-0.75812	0.49826
1	0	4.21743	-2.64466	-1.75188
7	0	6.58792	-3.05679	-0.60834
8	0	7.69159	-3.09768	-0.03058
8	0	6.09854	-4.05251	-1.17746

8	0	3.05818	4.02325	-0.48317
6	0	3.34371	5.35296	-0.03885
1	0	2.49705	5.96078	-0.36244
1	0	4.26758	5.72953	-0.48869
1	0	3.44145	5.39514	1.05015



TSiminium-*si*-enolate

E(B3LYP 6-31G*) = -2056.661692

Zero-point correction= 0.66952145

Thermal correction to Gibbs Free Energy= 0.59155645

E(B3LYP 6-311G**) = -2057.14477

Number of imaginary frequencies: 1 (-99.1676)

14	0	5.41324	0.32044	-0.60155
8	0	4.14469	-0.22592	0.38328
7	0	0.86001	-0.46508	2.10473
6	0	2.97918	-1.4314	2.64556
1	0	3.26793	-2.25582	1.9896
1	0	3.88253	-1.07082	3.14023
6	0	2.31386	-0.30333	1.82152
1	0	2.61751	0.66964	2.21229
6	0	0.59637	-1.69973	2.87285
1	0	-0.27062	-1.55876	3.51926
1	0	0.39371	-2.52461	2.18108
6	0	1.9046	-1.89918	3.64063
1	0	1.90211	-1.27033	4.5375
1	0	2.04221	-2.93759	3.95329
6	0	2.72556	-0.32513	0.28743
6	0	2.16722	0.90783	-0.46274
6	0	2.37603	2.19047	0.07825
1	0	2.91044	2.30722	1.0156
6	0	1.92332	3.3371	-0.57388
6	0	1.2571	3.233	-1.79731
1	0	0.89958	4.1237	-2.3057
6	0	1.0653	1.97253	-2.36113
6	0	1.51749	0.82455	-1.7023

1	0	1.36376	-0.13886	-2.17239
6	0	2.32052	-1.67095	-0.3455
6	0	3.28788	-2.63548	-0.65732
1	0	4.33232	-2.42257	-0.46836
6	0	2.92817	-3.87771	-1.1877
6	0	1.58718	-4.18809	-1.40852
1	0	1.30514	-5.15304	-1.82019
6	0	0.60904	-3.24351	-1.09027
6	0	0.97147	-2.00181	-0.56611
1	0	0.18938	-1.28632	-0.33805
6	0	5.84799	2.1059	-0.17848
1	0	6.78473	2.38678	-0.67681
1	0	5.9971	2.23111	0.90075
1	0	5.07404	2.81112	-0.49726
6	0	5.05646	0.14944	-2.44538
1	0	5.96251	0.4075	-3.00879
1	0	4.255	0.8164	-2.77857
1	0	4.77829	-0.87554	-2.71443
6	0	6.8582	-0.78488	-0.10847
1	0	7.77649	-0.4588	-0.61242
1	0	6.68788	-1.83391	-0.37719
1	0	7.03869	-0.74042	0.97201
6	0	-0.03417	0.49411	1.9083
1	0	0.36382	1.41094	1.48265
6	0	-1.40386	0.44561	2.20049
1	0	-1.85811	-0.47451	2.55462
6	0	-2.192	1.5756	2.05653
1	0	-1.70992	2.50682	1.7715
6	0	-3.56469	1.66728	2.6388
1	0	-3.48641	2.02798	3.67589
1	0	-4.19517	2.37408	2.09365
1	0	-4.05739	0.69034	2.6643
1	0	-0.44147	-3.46789	-1.25377
1	0	3.70306	-4.60279	-1.42133
1	0	0.56396	1.87297	-3.31978
1	0	2.09517	4.31146	-0.12511
6	0	-2.91656	1.69165	-0.44102
1	0	-1.87438	1.57215	-0.71555
6	0	-3.37223	3.04817	-0.3309
8	0	-4.51381	3.46	-0.09815

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6          0   -3.74967   0.54361  -0.54098
6          0   -5.27646  -1.83754  -0.69145
6          0   -3.15135  -0.71987  -0.84176
6          0   -5.16445   0.5482   -0.33208
6          0   -5.90688  -0.61257  -0.40607
6          0   -3.88786  -1.88267  -0.91263
1          0   -2.08254  -0.75537  -1.03393
1          0   -5.65059   1.4918   -0.12112
1          0   -6.97875  -0.5961   -0.24806
1          0   -3.41792  -2.83153  -1.14238
7          0   -6.04722  -3.03805  -0.76362
8          0   -7.2761   -2.97799  -0.56497
8          0   -5.4672   -4.11104  -1.02169
8          0   -2.32279   3.9337   -0.46369
6          0   -2.66465   5.31768  -0.33921
1          0   -1.7282    5.86485  -0.45978
1          0   -3.10105   5.53186   0.641
1          0   -3.3766    5.6193   -1.11364
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