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Supporting Information

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Highly Efficient Asymmetric Michael Addition of Aldehydes to Nitroalkenes Catalyzed by a Simple *Trans*-4-Hydroxyproline

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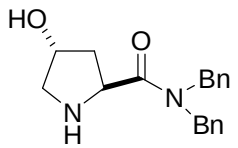
A) General information:

All reactions were carried out under nitrogen atmosphere in flame dried glassware with efficient magnetic stirring. Dichloromethane (CH_2Cl_2) was distilled from CaH_2. Toluene was dried in the presence of sodium metal. Isopropanol, ethyl acetate, DMF and dimethyl sulphoxide (DMSO) were used as reagent grade. S-(-)-α,α-diphenylmethylpyrrolidine is commercially available and can be also prepared from S-(-)-α,α-diphenyl-2-pyrrolidinemethanol via the hydrogenation of the corresponding

oxazolidinone in 65% overall yield.[1] Purification of reaction products was carried out by flash column chromatography using silica gel 60 (0.040-0.063 mm, 230-400 mesh). Analytical thin layer chromatography (TLC) was performed on 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light and a solution obtained by admixing in 470 mL of water ammonium molybdate (21 g), cerium sulphate (1 g) and concentrated sulphuric acid (31 mL), followed by heating. Melting points were measured with a Buchi SMP-20 melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Advance-500 and are reported in ppm from internal tetramethylsilane (TMS). Analytical high performance liquid chromatography (HPLC) was performed on waters-600E and Hewlett Packard series 1050 chromatographs, equipped with diode array UV detector, using Daicel Chiralpak AD, IB and IA columns. Optical rotations were recorded on a Perkin Elmer polarimeter. MS spectra were recorded on an ESI-ion trap Mass spectrometer (Agilent 1100 series LC/MSD, SL model).

B) Preparation of catalysts 16, 18, 19 and 20

B, 1) Preparation of catalysts 16



16

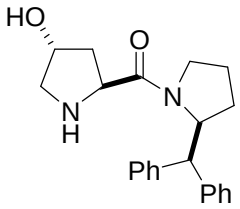
Dibenzylamine (0.75 mL, 4 mmol) was added to a solution of *Z-trans*-4-hydroxy-*L*-Proline (1.05g, 4 mmol) in anhydrous CH_2Cl_2 (32 mL) under a nitrogen atmosphere, and the mixture was cooled to 0ºC. EDC (1.08g, 5.6 mmol), HOBt (0.76g, 5.6 mmol) were then added and stirring was continued for 1h at 0ºC and then at RT overnight. EtOAc (40mL) was added and the mixture was washed with 0.1N HCl (2 x 25 mL), $NaHCO_3$ sat. sol. (1 x 25 mL) and NaCl sat. sol. (1 x 25 mL). The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure to afford 1,3 g (3.3 mmol) of an oil. The resulting residue was dissolved in EtOAc (6 ml) and Pd/C (20% in weight) was added. The mixture was stirred at room temperature under a H_2 atmosphere (P=1 atm) overnight. Then, the mixture was filtered through celite and the solvent evaporated under reduced pressure to afford a crude which was further purified by flash column chromatography on silicagel (CH_2Cl_2 : MeOH 90 : 10). This afforded the title compound as a white solid. 0.7 g (2.25 mmol). M.p. (Et_2O): 130-131ºC. Overall yield: 56%. $[a]_D^{25}$ = -32.6 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 500 MHz), δ: 7.39-7.16 (m, 10H, arom); 4.81 (d, 1H, J=15.0Hz, NHC<u>H</u>Ph); 4.57-4.49 (m, 2H, NHC<u>H</u>Ph, C<u>H</u>OH); 4.44-4.37 (m, 2H, N<u>H</u>CHPh, N<u>H</u>CHPh); 4.27 (t, 1H, NHC<u>H</u>CO); 3.36 (dd, 1H, J_1= 4.6Hz, J_2= 11.6Hz, NH<u>H</u>CHCHOH); 2.93 (d, 1H, NHHC<u>H</u>CHOH); 2.05-1.94 (m, 2H, OHCHC<u>H</u>$_2$CH).^{13}C NMR (125 MHz, $CDCl_3$) d: 174.4, 136.9, 135.9, 129.0, 128.7, 128.2, 127.8, 127.5, 126.7, 73.0, 56.9, 55.6, 49.2, 48.3, 40.7. MS (ESI, m/z): calcd for $C_{19}H_{22}N_2O_2$ ($M + H^+$), 311.39; found, 311.3

[1] To a solution of S-(-)-α,α-diphenyl-2-pyrrolidinemethanol (40 mmol) in CH_2Cl_2 (100 mL) was added NaOH 6N (30mL). The resulting mixture was cooled to 0ºC and a solution of trifosgene (19.2 mmol) in CH_2Cl_2 (30mL) was added dropwise. After stirring the mixture for 2h at room temperature, the organic layer was separated, washed with NH_4Cl, dried over Na_2SO_4 and evaporated to afford the oxazolidinone, which was then hydrogenated following the procedure of O'Hagan to yield the expected S-(-)-α,α-diphenylmethylpyrrolidine: a) D. O'Hagan, M. Tavasli *Tetrahedron Asymmetry* **1999**, 1189-1192. b) D.J. Bailey, D. O'Hagan, M. Tavasli *Tetrahedron Asymetry*. **1997**, *8*, 149-153.

B, 2) General procedure for the preparation of catalysts 18 and 20

To a stirred solution of the corresponding *N*-(benzyloxycarbonyl)-proline (5.2 mmol) and triethylamine (1.8ml, 13.5mmol) in anhydrous dichloromethane (12ml) and under a nitrogen atmosphere, were added bis(2-oxo-3-oxazolidinyl)phosphinic chloride[2] (BOP-Cl, 1.3g, 5.2mmol) at 0ºC. After 30min of stirring, the corresponding amine (4mmol) was added and the mixture was further stirred overnight. It was diluted with 10ml of CH_2Cl_2 and washed once with 1N HCl, water and brine. Then, it was dried over Na_2SO_4 and the solvent was removed in vacuo, affording a residue which was purified over silicagel flash column chromatography. The resulting product was dissolved in EtOAc (10 ml) and Pd/C (20% in weight) was added. The mixture was stirred at room temperature under a H_2 atmosphere (P=1 atm) overnight. Then, the mixture was filtered through celite and the solvent evaporated under reduced pressure to afford the title compounds.

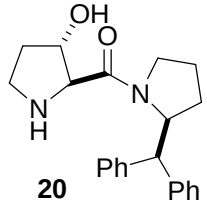
Catalyst 18



18

This title compound was prepared according to the general procedure B, 2 starting from *N*-(benzyloxycarbonyl)-*L*-4-trans- hydroxyproline (6.85g, 26mmol) and (S)-(-)-a,a-diphenylmethylpyrrolidine (4.4mL, 20mmol). The *N*-benzyloxycarbonyl intermediate derivative was purified by flash column chromatography (EtOAc) prior to hydrogenation. The hydrogenated product was also subjected to purification by flash column chromatography on silicagel (CH_2Cl_2 : MeOH, 90 : 10) to yield the title product **18** as a waxy white solid which upon trituration with hexane/diethyl ether (3 : 1) solidifies (5.0g, 14.2 mmol). Overall yield: 70%. M.p.: 58-59ºC. $[a]_D^{25}$ = -53.0 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 500 MHz), δ: 7.31-7.14 (m, 10H, arom); 5.15 (t, 1H, J= 7.4Hz, $CHPh_2$); 4.35-4.31 (m, 2H, C<u>H</u>CHPh_2, NHC<u>H</u>CON); 4.07 (1H, t, J= 8.0Hz, C<u>H</u>OH); 3.54-3.49 (m, 1H, <u>H</u>CHNCO); 3.20-3.16 (m, 1H, HC<u>H</u>NCO); 3.09 (dd, 1H, J_1=4.2Hz, J_2= 11.5Hz, <u>H</u>CHNH); 2.92 (d, 1H, J=11.4Hz, HC<u>H</u>NH); 2.08-1.82 (m, 4H, C<u>H</u>$_2$OH, C<u>H</u>$_2$CH$_2$NCO); 1.65-1.59 (m, 1H, CH_2); 1.45-1.40 (m, 1H, CH_2). ^{13}C-NMR (125 MHz, $CDCl_3$) d: 172.1, 142.0, 141.7, 129.3, 128.9, 128.4, 127.9, 126.8, 126.3, 72.6, 60.1, 57.8, 55.2, 53.2, 45.9, 39.5, 27.7, 23.7. MS (ESI, m/z): calcd for $C_{22}H_{26}N_2O_2$ (M + H^+), 351,46; found, 351,4.

Catalyst 20



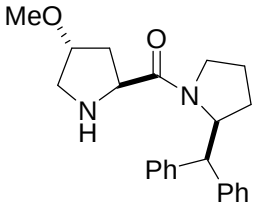
20

This title compound was prepared according to the general procedure B, 2 starting from *N*-(benzyloxycarbonyl)-L-3-trans-hydroxyproline (1.37g, 5.2 mmol) and (S)-(-)-a,a-diphenylmethylpyrrolidine (0.88mL, 4 mmol). The *N*-benzyloxycarbonyl intermediate derivative was purified by flash column chromatography (EtOAc) prior to hydrogenation. The hydrogenated product was crystallized from EtOAc to yield the title product **20** as a solid (0.52g, 1.47 mmol). Overall yield: 37%. $[a]_D^{25}$ = +26.4 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR

[2] a) D. Bhuniya, V.K. Singh *Synthetic Communications* **1994**, *24*, 375-385. b) J. Diago-Meseguer, A.L. Palomo-Coll *Synthesis* **1980**, 547.

($CDCl_3$, 500 MHz), δ: 7.38-7.14 (m, 10H, arom); 5.20 (t, 1H, J=7.6Hz, NCHCHPh$_2$); 4.23 (d, 1H, J= 8.3Hz, CHPh$_2$); 3.90-3.83 (m, 2H, CHOH, NHCHCON); 3.71-3.66 (m, 1H, HCHNCO); 3.50-3.44 (m, 1H, HCHNCO); 3.10-2.98 (m, 2H, CH_2NH); 1.95-1.79 (m, 4H, CH_2CH_2NCO, $CH_2CHCHPh_2$); 1.69-1.62 (m, 1H, HCHNH); 1.50-1.43 (m, 1H, HCHNH). ^{13}C-NMR (125 MHz, $CDCl_3$) d: 169.7, 142.0, 141.6, 129.1, 128.9, 128.5, 127.3, 126.9, 126.4, 76.1, 68.0, 60.4, 53.9, 46.4, 45.0, 34.6, 27.9, 23.7.

B, 3) Preparation of catalyst 19



19

Catalyst **18** (0.484g, 1mmol) and MeI (0.18mL, 3mmol) were added to a suspension of NaH (0.6g, 1.5mmol) in anhydrous DMF (3mL) at 0ºC. The temperature was slowly raised to room temperature and the mixture was stirred overnight. The mixture was then cooled to 0ºC and a saturated NH_4Cl solution (2 mL) was slowly added. The mixture was extracted with EtOAc (3 x 5 mL) and the combined organic layers were washed with brine (5 x 3 mL), dried over Na_2SO_4 and concentrated in vacuo. To a solution of the resulting residue in MeOH (4 mL) was added Pd/C (20% in weight, 40 mg) and the mixture was stirred under hydrogen atmosphere (P= 1 atm) overnight. Then, the mixture was filtered through celite and the solvent evaporated under reduced pressure to afford a residue which was purified by flash column chromatography on silicagel (CH_2Cl_2 : MeOH, 90 : 10). This afforded compound **19** as a yellow oil (0.17g, 0.46mmol). Overall yield: 42%. $[a]_D^{25}$ = -10.0 (*c* 1.0, CH_2Cl_2); ^{1}H-NMR ($CDCl_3$, 500 MHz), δ: 7.31-7.16 (m, 10H, arom); 5.16 (t, 1H, J= 9.7Hz, CHPh$_2$); 4.36 (d, 1H, J= 7.4Hz, CHCHPh$_2$); 3.99 (t, 1H, J= 7.9Hz, NHCHCON); 3.83-3.80 (m, 1H, CHOMe); 3.53 (m, 1H, HCHNCO); 3.23 (s, 3H, OMe); 3.21-3.18 (m, 2H, HCHNCO, HCHNH); 2.97 (dd, 1H, J_1= 3.1Hz, J_2= 11.9Hz, HCHNH); 2.04-1.65 (m, 4H, CH_2); 1.52-1.47 (m, 1H, CH_2); 1.43-1.28 (m, 1H, CH_2). ^{13}C-NMR (125 MHz, $CDCl_3$) d: 171.5, 142.0, 141.7, 129.3, 128.9, 128.4, 127.9, 126.8, 126.3, 81.4, 60.1, 58.1, 56.8, 53.1, 51.6, 46.0, 36.5, 27.7, 23.6.

C) General procedure for the Michael reaction

1 **2-7** **8-13**

2,8 R1: Ph; **3,9** R^1: 4-$MeOC_6H_4$; **4,10** R^1: 4-BrC_6H_4; **5,11** R^1:  **6,12** R^1: CH_2CH_2Ph; **7,13** R^1: c-C_6H_{11}

a R: Et; **b** R: n-Pr; **c** R: n-Pent; **d** R: ^{i}Pr

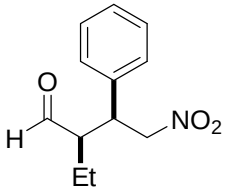
To a solution of the nitroolefin (1mmol) and the carbonyl compound (1.5mmol, 1.5 eq.) in dichoromethane (0.5ml) under a nitrogen atmosphere, was added catalyst **18** (17mg, 0.05mmol) at 0ºC. The resulting solution was stirred at the same temperature for 20 h. Then it was quenched with 1M HCl (3ml), and extracted with CH_2Cl_2 (3 x 4ml).

The combined organic phases were dried over $MgSO_4$, concentrated under reduced pressure and purified over silicagel by flash column chromatography to afford the Michael adducts.[3]

***Recovery of the catalyst*:**

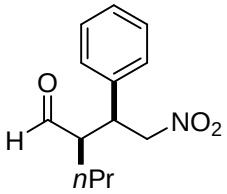
The acidic aqueous phase was mixed with CH_2Cl_2 (10 mL) and the mixture was carefully basified by dropwise addition of a solution of NaOH (40% w/v) at 0ºC until pH>10. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layers were dried over $MgSO_4$ and evaporated to afford the expected catalyst which was later purified by flash column chromatography (CH_2Cl_2 : MeOH 90 : 10). Yields of the optically pure recovered catalyst were regularly within 70-80% range.

(2R, 3S)-2-Ethyl-4-nitro-3-phenylbutanal 8a[4, 5, 6]



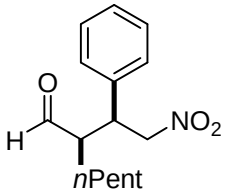
The title compound was prepared from trans-ß-nitrostyrene and butanal according to General Procedure. The enantiomeric excess and diastereomeric ratio were determined by HPLC with Chiralpak IA column at 210nm (hexane/iPrOH in the ratio of 99/1, flow 0.75ml; major syn enantiomer tr=27.3min, minor syn enantiomer tr=33.9min). Spectroscopic data are in agreement with published data.

(2R)-[(S)-2-Nitro-1-phenylethyl]-pentanal 8b[5, 6, 7]



The title compound was prepared from trans-ß-nitrostyrene and pentanal according to General Procedure. The enantiomeric excess and diastereomeric ratio were determined by HPLC with Chiralpak IA column at 210nm (hexane/iPrOH in the ratio of 99/1, flow 0.7ml; major syn enantiomer tr= 20.7min, minor syn enantiomer tr= 25.1min). Spectroscopic data are in agreement with published data.

(2R)-[(S)-2-Nitro-1-phenylethyl]-heptanal 8c[7]



The title compound was prepared from trans-ß-nitrostyrene and hexanal according to General Procedure. The enantiomeric excess and diastereomeric ratio were determined by HPLC with Chiralpak IA column at 210nm (hexane/iPrOH in the ratio of 99/1, flow 0.75ml; major syn enantiomer tr= 19.9min, minor syn enantiomer tr= 21.9min).

(2R, 3S)-2-(methylethyl)-4-nitro-3-phenylbutanal 8d[4, 5, 6]

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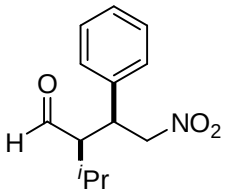
[3] The same procedure was followed on a 20 mmol scale.

[4] J.M. Betancort, C.F: Barbas III *Org. Lett.* **2001**, *3*, 3737.

[5] A. Alexakis, O. Andrey *Org. Lett.* **2002**, *4*, 3611.

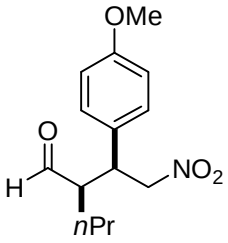
[6] O. Andrey, A. Alexakis, A. Tomassini, G. Bernardinelli *Adv. Synth. Cat.* **2004**, *346*, 1147.

[7] W. Wang, J. Wang, H. Li *Angew. Chem. Int. Ed.* **2005**, *44*, 1369.



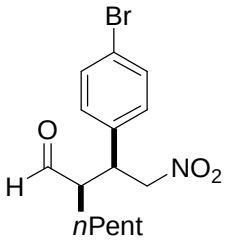
The title compound was prepared from trans-ß-nitrostyrene and hexanal according to General Procedure. The enantiomeric excess and diastereomeric ratio were determined by HPLC with Chiralpak IA column at 210nm (hexane/iPrOH in the ratio of 95/5, flow 0.5ml; major syn enantiomer tr= 20.9min, minor syn enantiomer tr= 24.0min).

(R)-2-[(S)-1-(4-Methoxyphenyl)-2-nitroethyl]pentanal 9b[7]



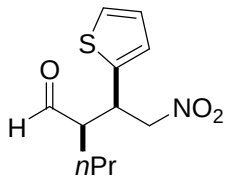
The title compound was prepared from trans-4-methoxy-ß-nitrostyrene and pentanal according to General Procedure. The enantiomeric excess and diastereomeric ratio were determined by HPLC with Chiralpak AD column at 210nm (hexane/iPrOH in the ratio of 95/5, flow 1ml; major syn enantiomer tr= 14.3min, minor syn enantiomer tr= 18.2min).

(R)-2-[(S)-1-(4-Brophenyl-2-nitroethyl]heptanal 10c



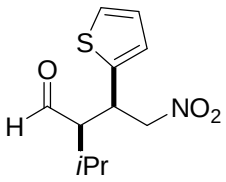
The title compound was prepared from trans-4-bromo-ß-nitrostyrene and pentanal according to General Procedure. $[a]_D^{25}$ = +27.6 (*c* 1.0, CH_2Cl_2, 15% of the anti isomer). ^{1}H-NMR ($CDCl_3$, 500 MHz), δ: 9.71 (s, 1H, CHO); 7.49 (d, 2H, J=8.37Hz, arom); 7.07 (d, 2H, J=8.37Hz, arom); 4.70 (dd, 1H, J_1=4.82Hz, J_2=12.85Hz, $\underline{H}CHNO_2$); 4.60 (dd, 1H, J_1=9.8Hz, J_2=12.82Hz, $HC\underline{H}NO_2$); 3.87-3.74 (m, 1H, $C\underline{H}Ph$); 2.71-2.66 (m, 1H, $C\underline{H}CHO$); 1.58-1.11 (m, 8H, CH_2); 0.82 (t, 3H, J=6.84Hz, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$) d: 203.5, 136.1, 132.6, 130.1, 122.1, 78.3, 53.9, 42.7, 31.6, 27.3, 26.0, 22.3, 14.2. The enantiomeric excess and diastereomeric ratio were determined by HPLC with Chiralpak AD column at 210nm (hexane/iPrOH in the ratio of 98/2, flow 0.75ml; major syn enantiomer tr= 21.6min, minor syn enantiomer tr= 25.5min).

(2R)-[(S)-2-Nitro-1-(thiophen-2-yl)ethyl]-pentanal 11b



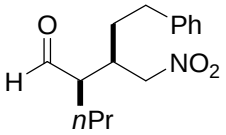
The title compound was prepared from nitrovinylthiophene and pentanal according to General Procedure. $[a]_D^{25}$ = +10.3 (*c* 1.0, CH_2Cl_2, 15% of the anti isomer). ^{1}H-NMR ($CDCl_3$, 500 MHz), δ: 9.74 (s, 1H, CHO); 7.28-6.93 (m, 3H, arom.); 4.74 (dd, 1H, J_1 = 5.4Hz, J_2 = 12.8Hz, $\underline{H}CHNO_2$); 4.69 (dd, 1H, J_1 = 9.0Hz, J_2 = 12.8Hz, $HC\underline{H}NO_2$); 4.21-4.18 (m, 1H, $C\underline{H}CH_2NO_2$); 2.77-2.73 (m, 1H, $C\underline{H}CHO$); 1.67-1.26 (m, 4H, CH_2); 1.09-0.89 (t, 3H, J = 7.2Hz, CH_3). ^{13}C-NMR (75 MHz, $CDCl_3$) d: 202.5, 127.3, 126.7, 125.3, 78.8, 54.5, 38.8, 29.3, 20.0, 14.0. The enantiomeric excess and diastereomeric ratio were determined by HPLC with Chiralpak AD column at 254nm (hexane/iPrOH in the ratio of 98/2, flow 0.5ml; major syn enantiomer tr=41.7min, minor syn enantiomer tr= 49.6min).

(2R, 3S)-2-isopropyl-4-nitro-3-(thiophen-2 yl) butanal 11d[4, 8]



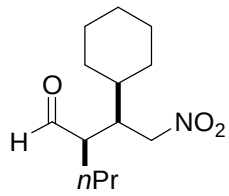
The title compound was prepared from nitrovinylthiophene and isovaleraldehyde according to General Procedure. The enantiomeric excess and diastereomeric ratio were determined by HPLC with Chiralpak AD column at 210nm (hexane/iPrOH in the ratio of 95/5, flow 1ml; major syn enantiomer tr=12.0min, minor syn enantiomer tr=13.1min).

R-2-[(R)-1-Nitro-4-phenylbutan-2-yl]pentanal 12b



The title compound was prepared from nitrostyrene and pentanal according to General Procedure. The enantiomeric excess and diastereomeric ratio were determined by HPLC with Chiralpak AD column at 254nm (hexane/iPrOH in the ratio of 95/5, flow 0.5ml; mino syn enantiomer tr=33.7min, minor syn enantiomer tr=37.7min).

R-2-[(R)-1-Nitro-4-cyclohexylbutan-2-yl]pentanal 13b



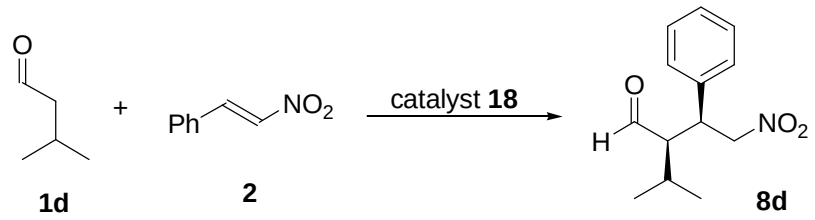
The title compound was prepared from nitrostyrene and pentanal according to General Procedure, as described above in 70% yield after purification by flash column chromatography on silicagel. $[a]_D^{25}$ = +21.9 (*c* 1.0, CH_2Cl_2). ^{1}H-NMR ($CDCl_3$, 500 MHz), δ: 9.70 (s, 1H, CHO); 4.57 (dd, 1H, J_1= 6.68Hz, J_2= 13.62Hz, $\underline{H}CHNO_2$); 4.39 (dd, 1H, J_1= 5.38Hz, J_2= 13.62Hz, $HC\underline{H}NO_2$); 2.52-2.48 (m, 1H, $\underline{H}CHO$); 1.81-1.28 (m, 4H, CH_2); 0.97 (t, 3H, J= 7.1Hz, CH_3).^{13}C NMR (125 MHz, $CDCl_3$) d: 203.6, 75.7, 51.4, 43.3, 39.0, 31.3, 30.2, 29.2, 26.4, 26.3, 26.1, 21.0, 14.0.

The enantiomeric excess and diastereomeric ratio were determined by HPLC with IB column at 254nm (hexane/iPrOH in the ratio of 98/2, flow 0.75ml; major syn enantiomer tr=10.6min, minor syn enantiomer tr=11.2min).

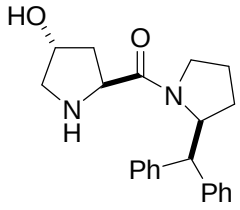
[8] P. Kotrusz, S. Toma, H.-G. Schmalz, A. Adler *Eur. J. Org. Chem.* **2004**, 1577-1583.

D) Effect of the solvent in the Michael addition reaction

To study the solvent effect on the Michael addition, the reaction between isovaleraldehyde **1e** and trans-β-nitrostyrene **2** catalyzed by **18** was checked in different solvents. The corresponding results are sumarized below.



1d **2** **8d**



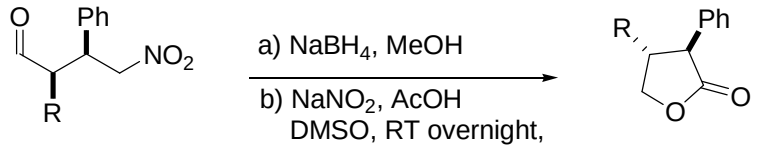
18

Table 1. Effect of solvents on the reaction of isovaleraldehyde **1d** to trans-β-nitrostyrene **2** catalyzed by hydroxyprolylamide **18**.[a]

Solvent	Conv.[%][b]	Syn:anti[c]	ee[%][d]
DMSO	15	75 : 25	60
DMF	nr	--	--
^{i}PrOH	30	92 : 8	86
$CHCl_3$	84	96 : 4	92
CH_2Cl_2	100	95 : 5	91
Toluene	70	96 : 4	94
Hexane	63	94 : 6	94

[a] Reactions conducted on a 0.25 mmol scale using tenfold excess of aldehyde. [b] Determined by ^{1}H-NMR spectroscopy (500 MHz) after 20-24h reaction at room temperature. [c] Determined by HPLC.

E) Preparation of γ-butyrolactones 21 and 22

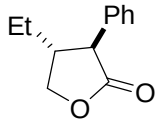


8a R: Et
8c R: n-Pr

21 R: Et, 70%yield,
22 R: n-Pent, 72% yield

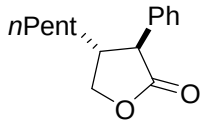
$NaBH_4$ (1 mmol, 37,84 mg) was added to a solution of the nitroadduct (1 mmol) in EtOH (2 mL) cooled to 0ºC. The mixture was stirred for 15 min. at the same temperature and H_2O (2 mL) was added. After evaporation of the ethanol under reduced

pressure HCl 1M (2 mL) was added and the aqueous phase was extracted with Cl_2CH_2 (3 x 3 mL). The combined organic layers were dried over $MgSO_4$ and the solvent evaporated. This afforded the expected nitroalcohol, which was redissolved in DMSO (1.7mL). Sodium nitrite (2.55 mmol) and acetic acid (0.34 mL, 8.5 mmol) were then added, and the solution was stirred at room temperature overnight and at 40ºC for 6h.[9] The mixture was allowed to cool and HCl 1M (20 mL) was added. The aqueous phase was extracted with Cl_2CH_2 (3 x 15 mL). The organic layers were combined, dried over $MgSO_4$ and evaporated under vacuum to afford the γ-butyrolactones which were then purified by flash column chromatography.



21

The title compound was prepared following the general procedure. Yield: 70%. $[a]_D^{25}$ = +33.9 (*c* 1.0, CH_2Cl_2, d.r. 99 : 1, ee > 99%). ^{1}H-NMR ($CDCl_3$, 500 MHz), δ: 7.39-7.21 (m, 5H, arom.); 4.55 (t, 1H, J = 7.7Hz, HCHO); 3.97 (t, 1H, J = 9.2Hz, HCHO); 3.38 (d, 1H, J = 10.7Hz, CHPh); 2.63-2.51 (m, 1H, $CHCH_2CH_3$); 1.75-1.67 (m, 1H, $HCHCH_3$); 1.55-1.46 (m, 1H, $HCHCH_3$); 0.90 (t, 3H, J = 7.5Hz, CH_3).^{13}C NMR (50 MHz, $CDCl_3$) d: 117.6, 136.4, 129.3, 128.1, 127.5, 71.9, 52.9, 46.8, 24.9, 11.7.



22

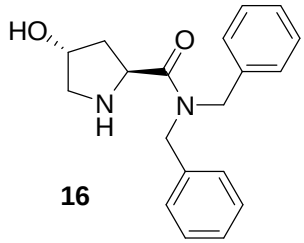
The title compound was prepared following the general procedure. The main diastereoisomer was separated by flash column chromatography (AcOEt:Hex 20:80).Yield: 72%. $[a]_D^{25}$ = +35.6 (*c* 1.0, CH_2Cl_2,, ee > 99%).
Spectroscopic data are in agreement with published values.[10]

F) Preparation of racemic samples

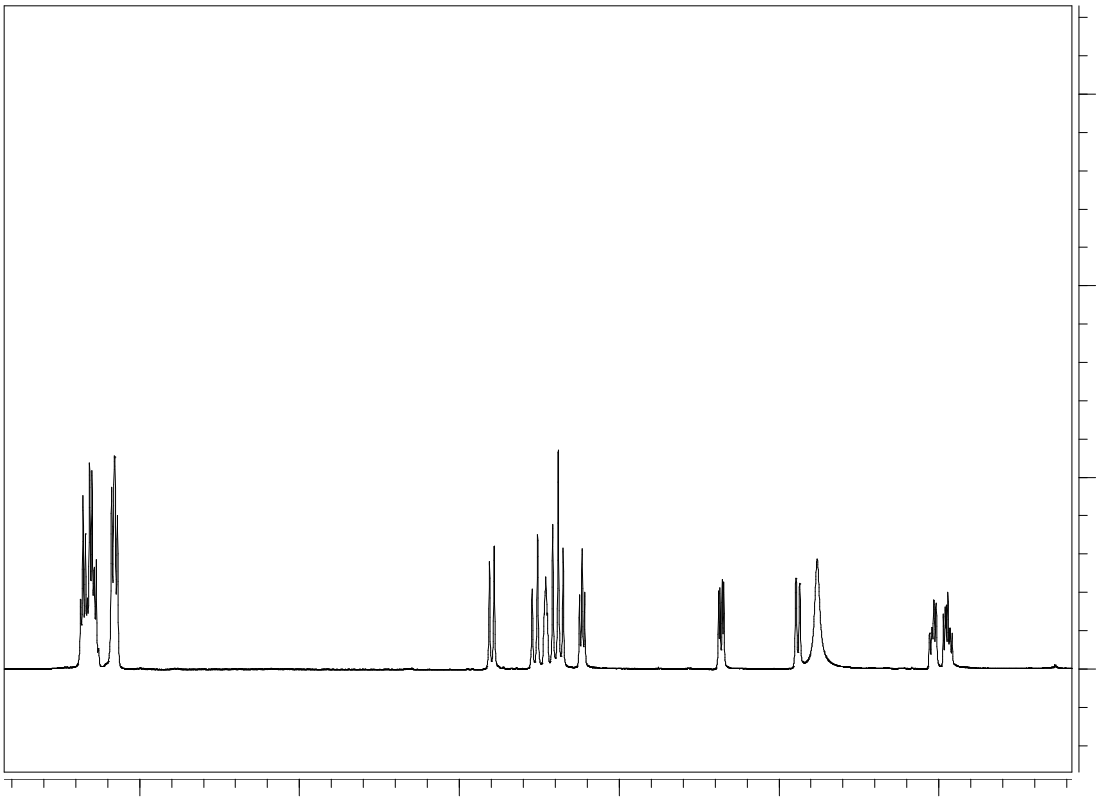
Racemic samples of the nitroadducts were prepared using racemic catalyst **16**, which was synthesized following procedure B,1 starting from racemic *BOC*-L-proline and dibenzylamine.

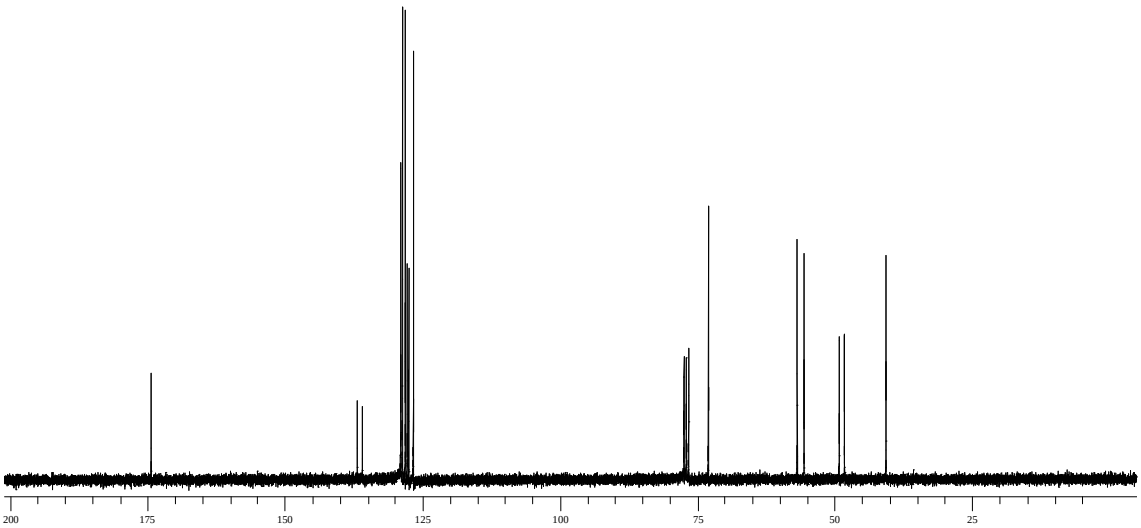
[9] Procedure adapted from: C. Matt, A. Wagner, C. Mioskowski *J. Org. Chem.* **1997**, 62, 234-235.
[10] M. Brunner, H. Alper *J. Org. Chem.* **1997**, *62*, 7565-7568.

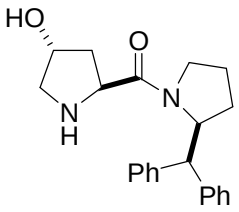
G) ^{1}H and ^{13}C NMR data of representative compounds



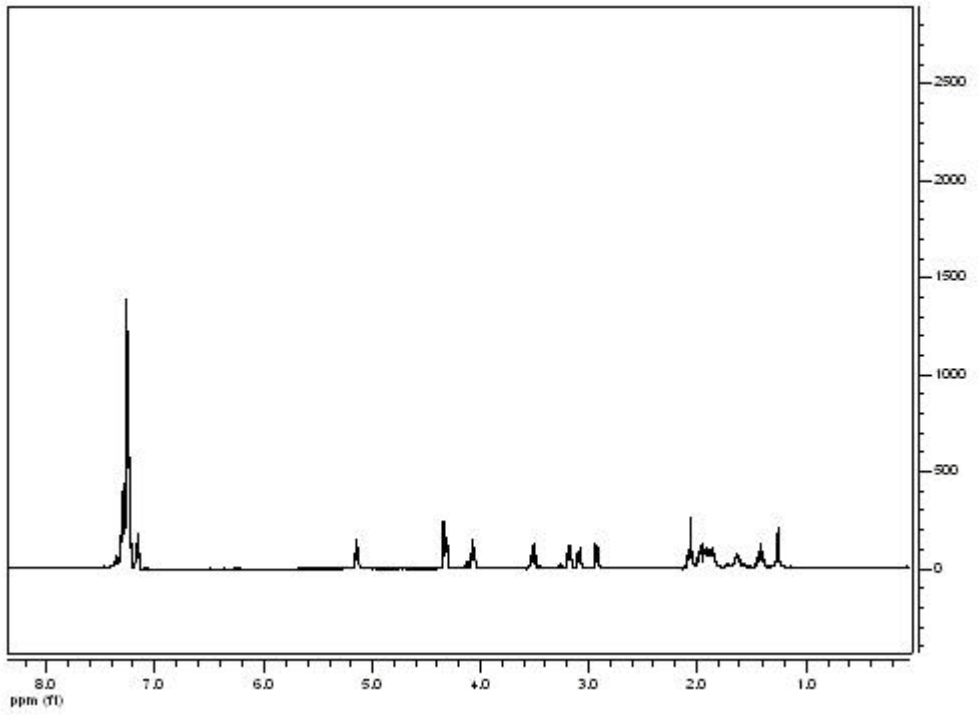
16

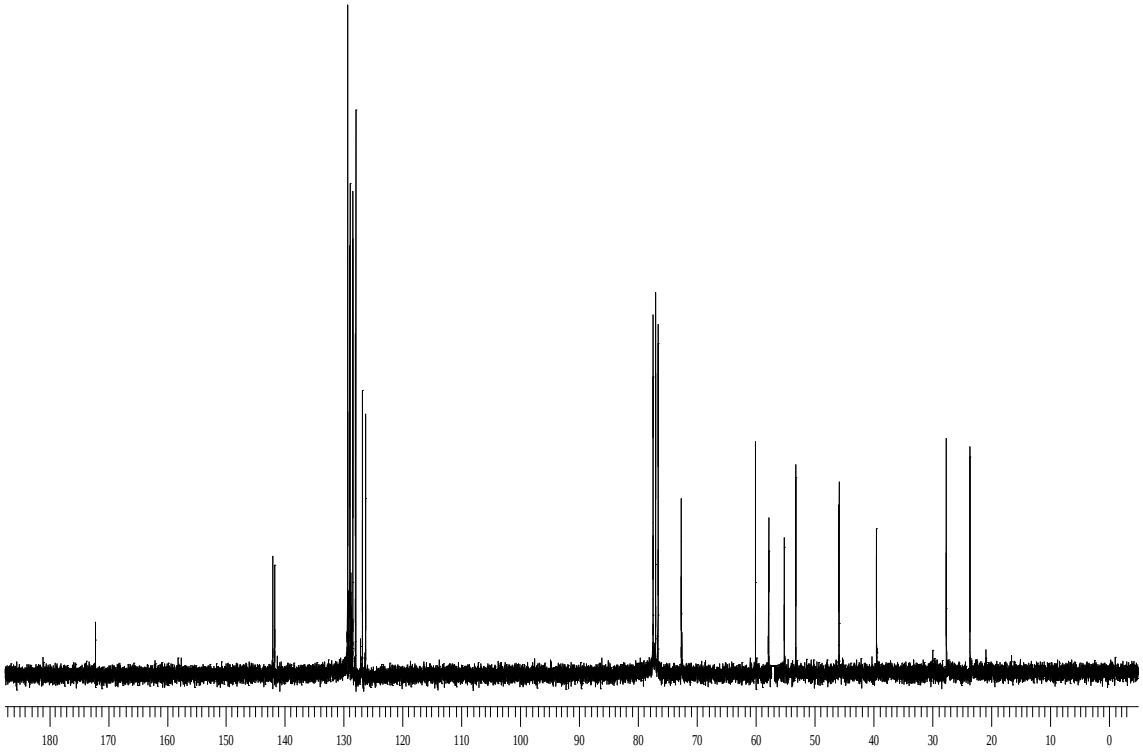





HO
O
N
N
H
Ph
Ph

18


2500
2000
1500
1000
500
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)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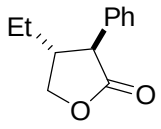
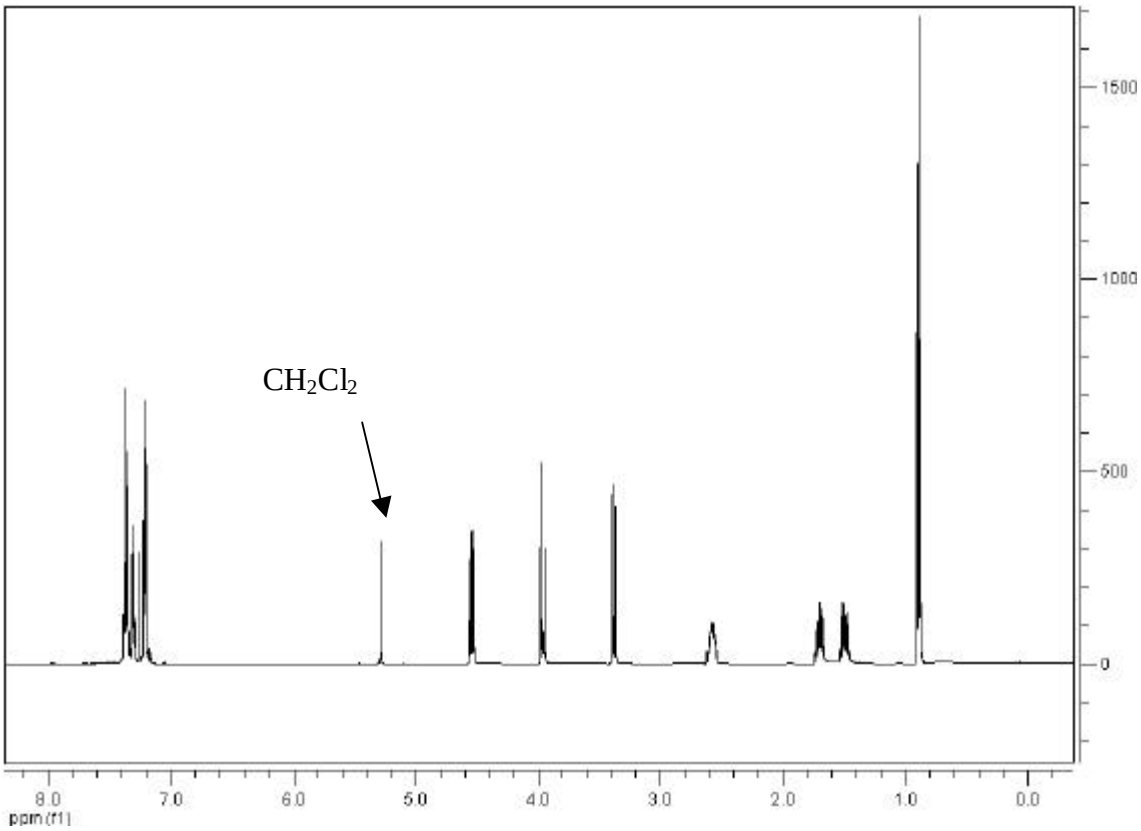
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


Et
Ph
O
O

21


CH2Cl2
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1000
500
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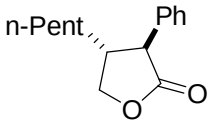
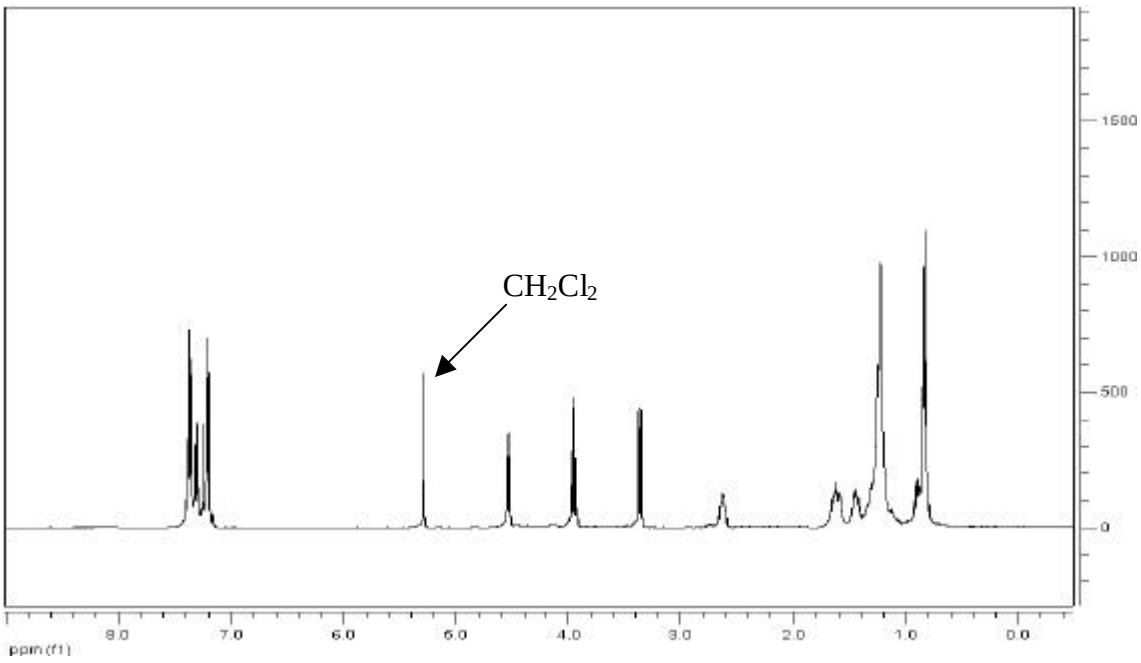
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

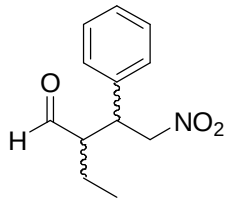

n-Pent
Ph
O
O

22

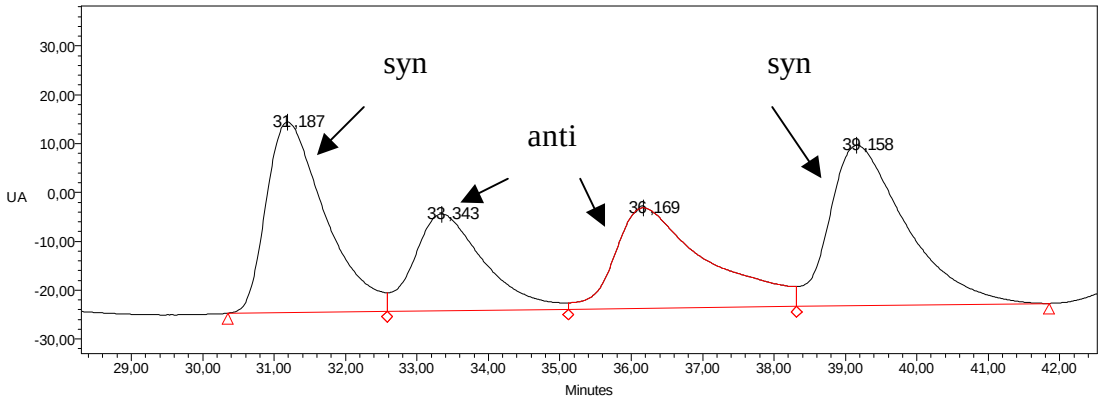

CH2Cl2
1500
1000
500
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

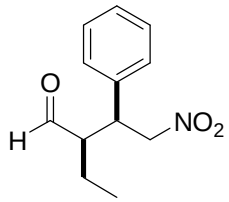
H) HPLC Chromatograms of selected compounds

Chiralpak IA, 99:1 hexane:iPrOH, 0. 75mL/min, λ=254nm



rac-8a





8a

Processed Channel Descr.: 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	254nm	27,257	3247485	98,95	41567
2	254nm	31,457	34460	1,05	721

Processed Channel Descr.: 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
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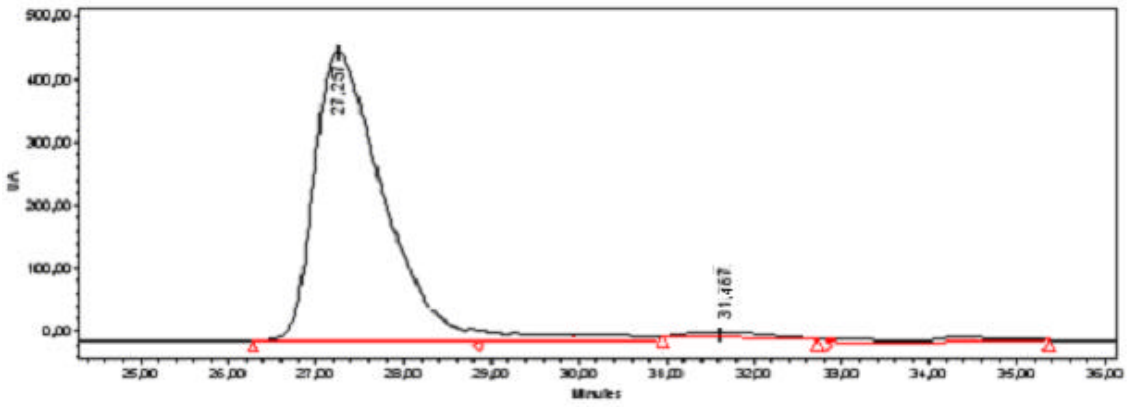
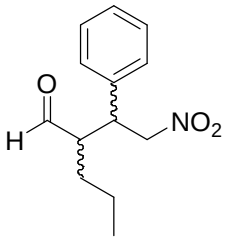
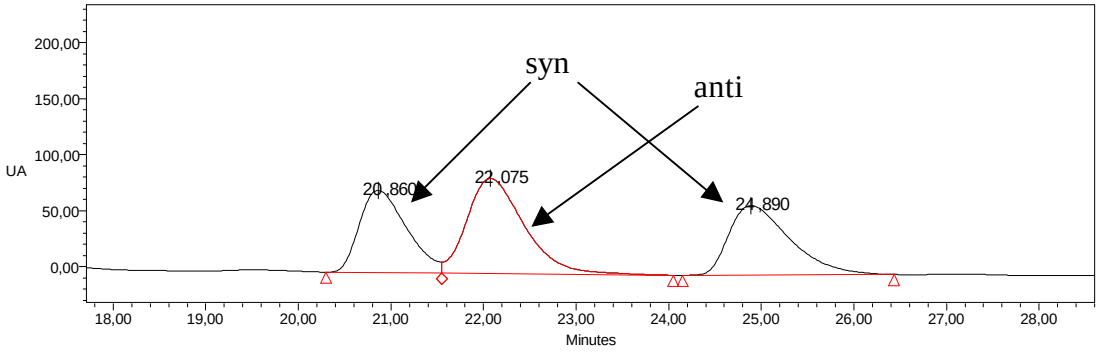


Chiralpak IA, 99:1 hexane:iPrOH, 0.7mL/min, λ=210nm

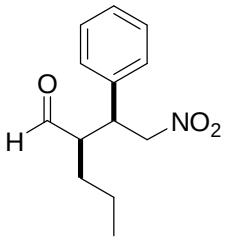


rac-8b



Processed Channel Descr.: 210nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	210nm	20,742	31266014	94,79	795744
2	210nm	22,133	1099062	3,33	39139
3	210nm	25,087	618826	1,88	18494



8b

Processed Channel Descr.: 210nm

	Processed Channel Descr.	RT	Area	% Area	Height
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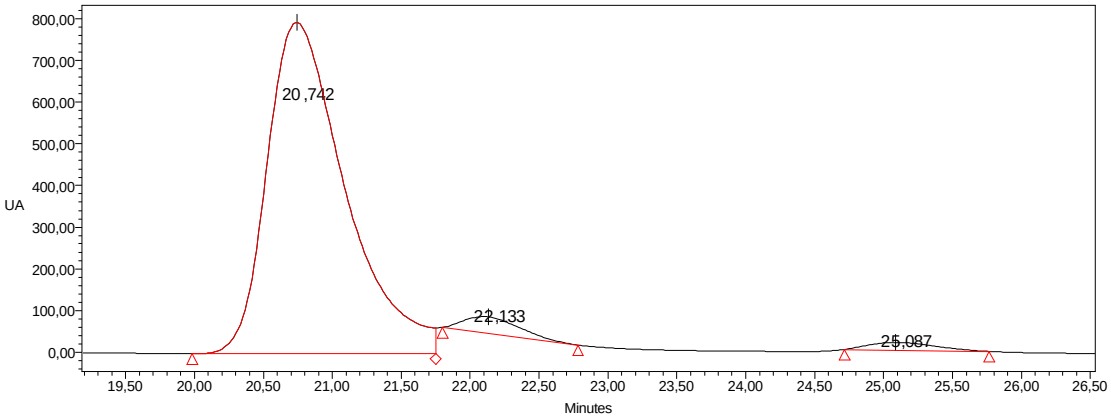
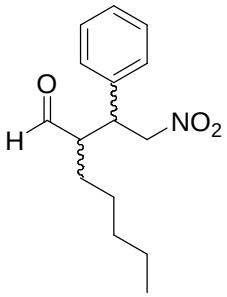
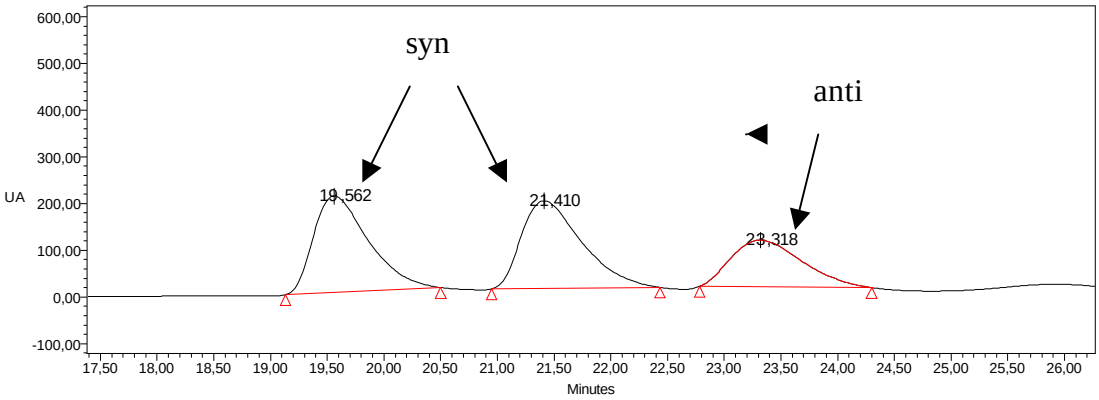
2	210nm	25,087	618826	1,94	18494

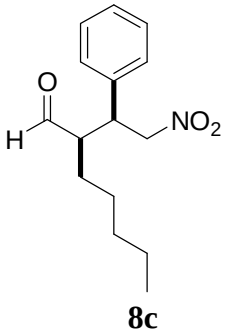


Chiralpak IA, 99:1 hexane:iPrOH, 0.75mL/min, λ=254nm



rac-8c





8c

Processed Channel Descr.: 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	254nm	19,597	1082077738	97,53	1951704
2	254nm	21,847	864417	0,30	29382
3	254nm	24,037	1053040	1,07	40000

Processed Channel Descr.: 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
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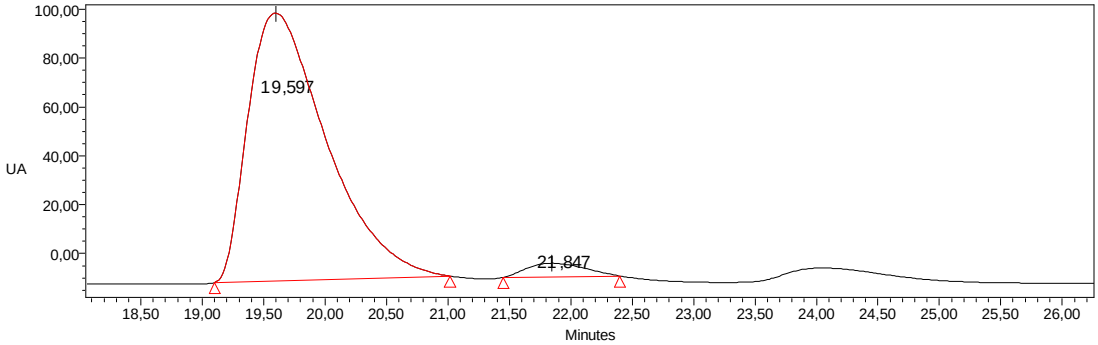
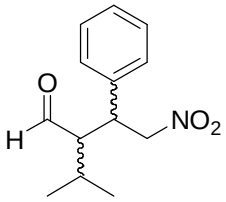
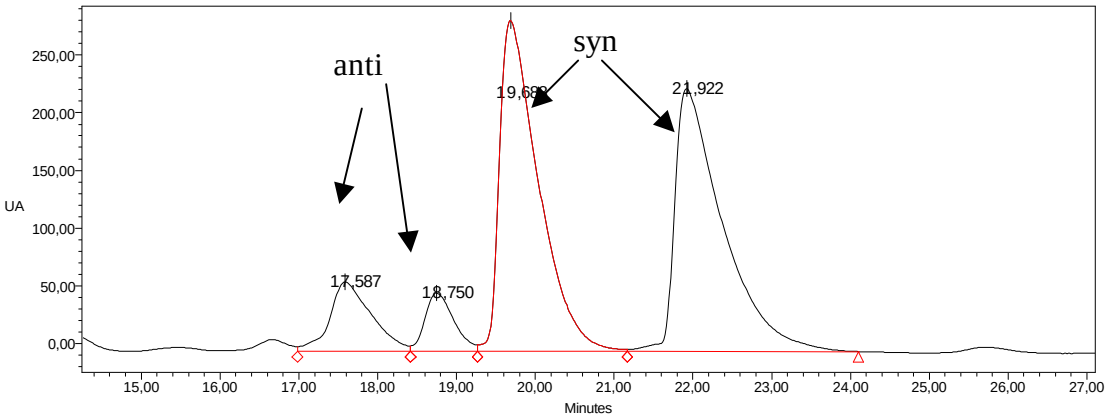
2	254nm	21,847	179778	3,56	5542

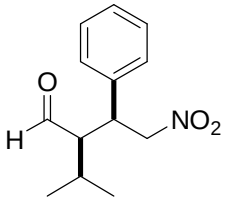


Chiralpak IA, 95:5 hexane:iPrOH, 0. 5mL/min, λ=210nm



rac-8d





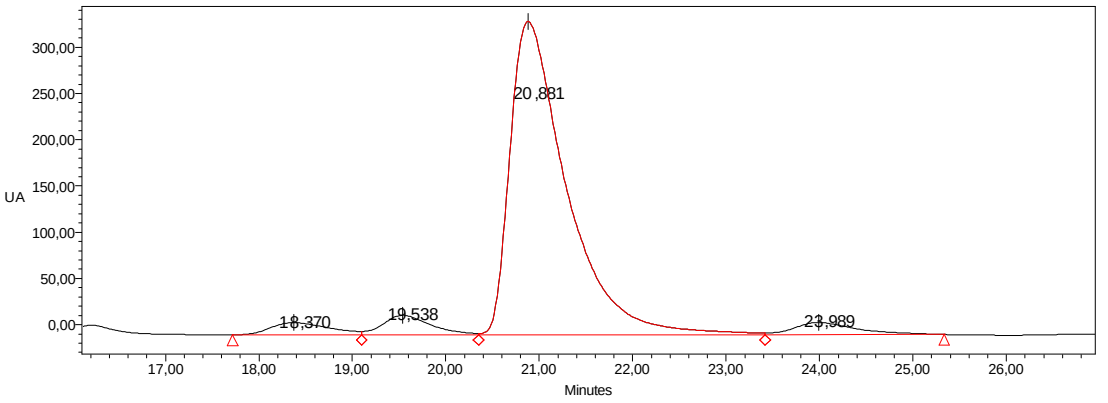
8d

Processed Channel Descr.: 210nm

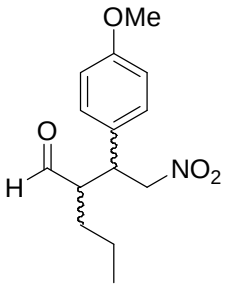
	Processed Channel Descr.	RT	Area	% Area	Height
1	210nm	18,369	349180	2,32	10380
2	210nm	19,538	486164	3,22	17017
3	210nm	20,881	13877524	92,05	337288
4	210nm	23,989	362984	2,41	10457

Processed Channel Descr.: 210nm

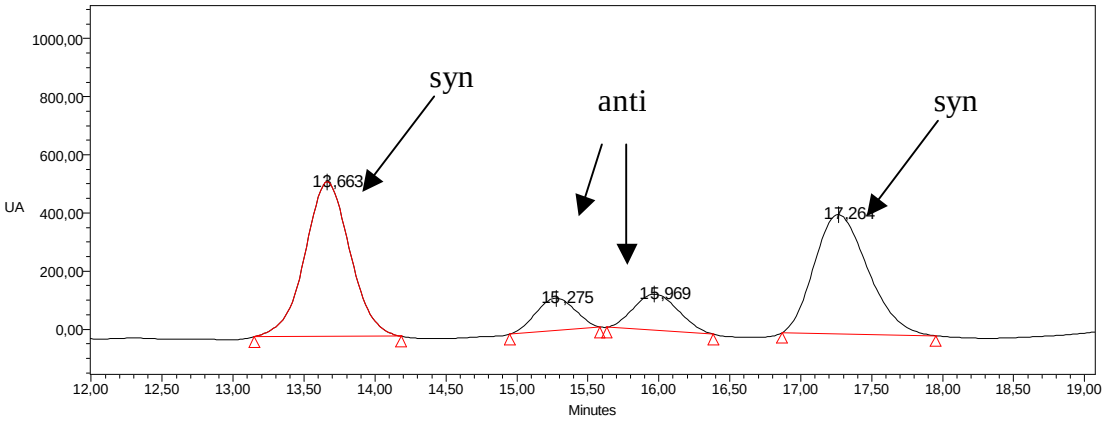
	Processed Channel Descr.	RT	Area	% Area	Height
1	210nm	20,881	14226085	95,91	338856
2	210nm	23,989	606761	4,09	13120

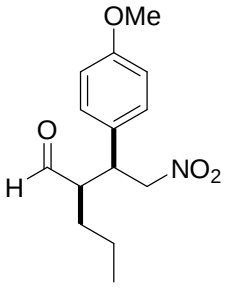


Chiralpak AD, 95:5 hexane:iPrOH, 1mL/min, λ=210nm



rac-9b





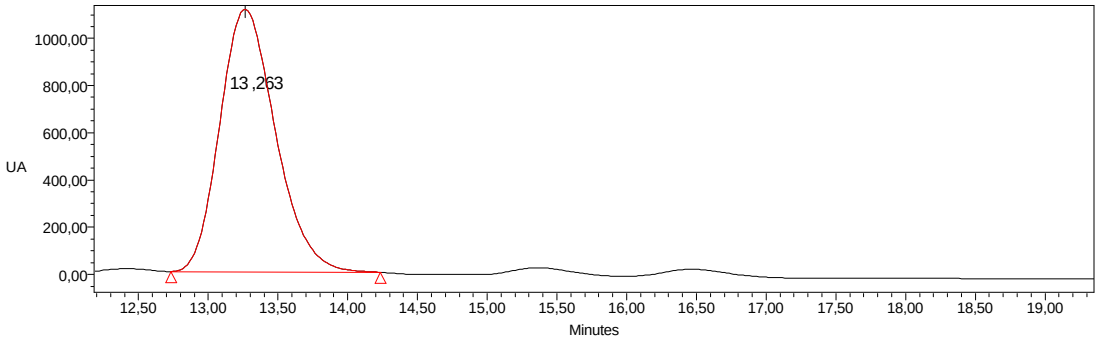
9b

Processed Channel Descr.: 210nm

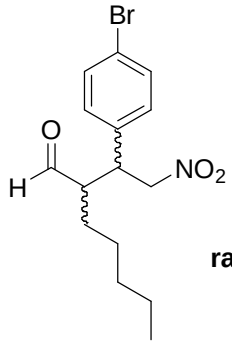
	Processed Channel Descr.	RT	Area	% Area	Height
1	210nm	13,263	30914487	96,30	1113444
2	210nm	15,365	554813	1,73	24851
3	210nm	16,464	632406	1,97	25337

Processed Channel Descr.: 210nm

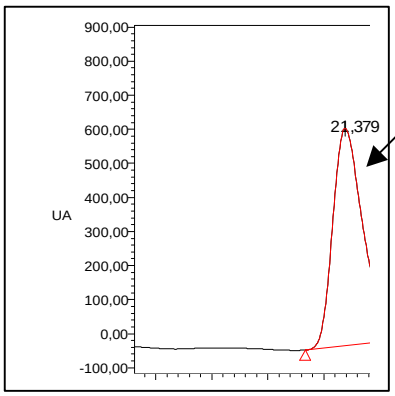
	Processed Channel Descr.	RT	Area	% Area	Height
1	210nm	13,263	30914487	100,00	1113444

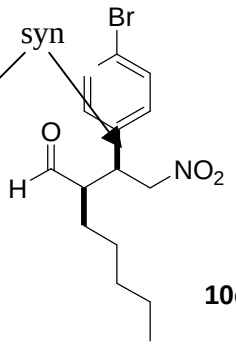


Chiralpak AD, 98:2 hexane:iPrOH, 0.75mL/min, λ=210nm



rac-10c

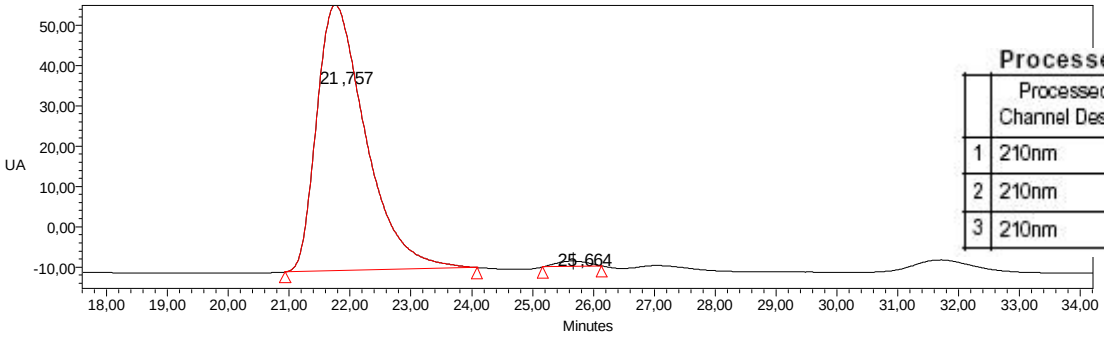




10c

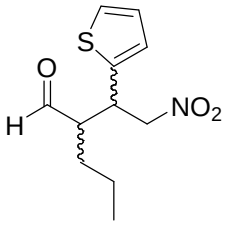
anti

	Processed Channel Descr.	RT	Area
1	210nm	21,757	3692714
2	210nm	25,664	45956

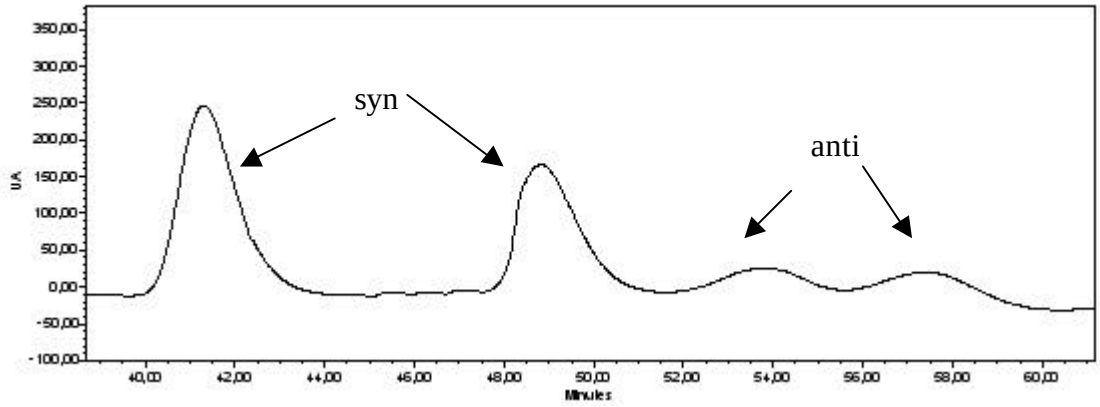


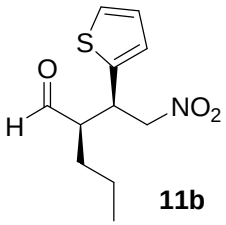
	Processed Channel Descr.	RT	Area
1	210nm	21,757	3592858
2	210nm	25,664	69855
3	210nm	31,703	122716

Chiralpak AD, 98:2 hexane:iPrOH, 0.5mL/min, λ=254nm



rac-11b

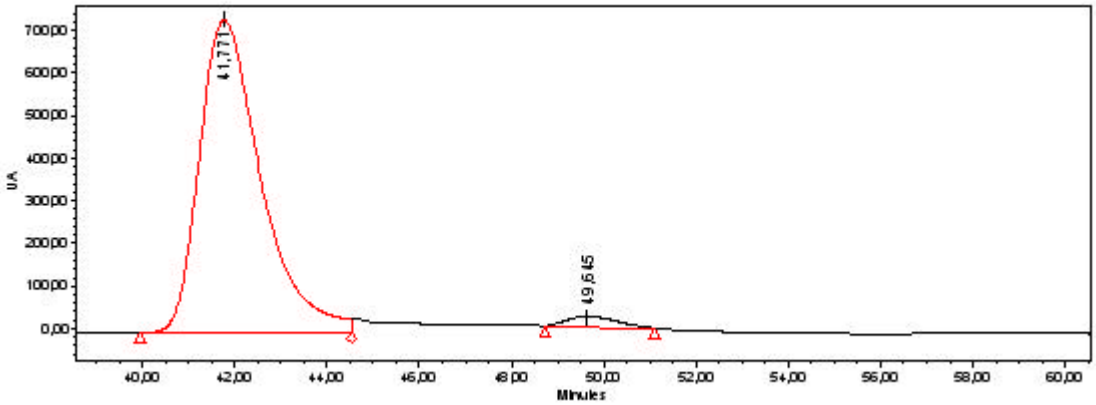




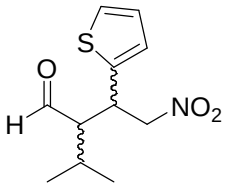
11b

Processed Channel Descr.: 254nm

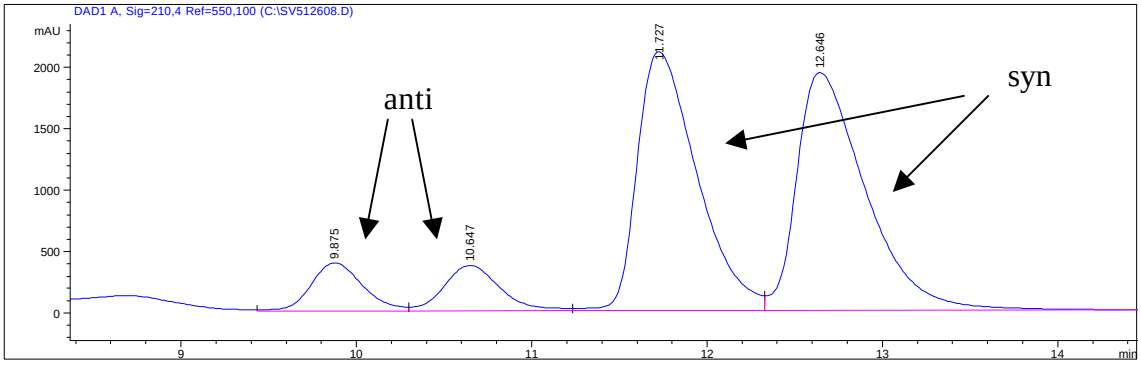
	Processed Channel Descr.	RT	Area	% Area	Height
1	254nm	41,771	67750355	97,20	733272
2	254nm	49,645	1954713	2,80	25356

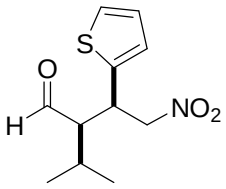


Chiralpak AD, 95:5 hexane:iPrOH, 1mL/min, λ=210nm



rac-11d





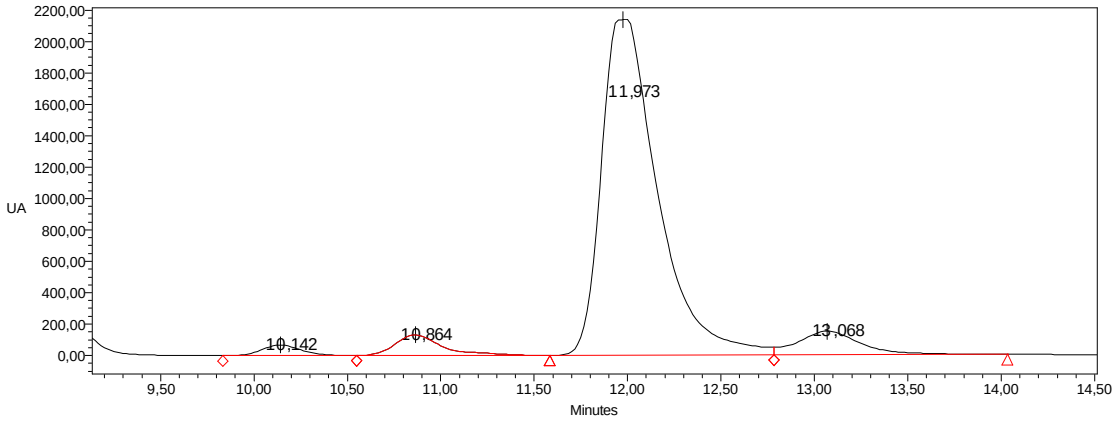
11d

Processed Channel Descr.: 210nm

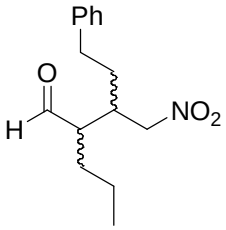
	Processed Channel Descr.	RT	Area	% Area	Height
1	210nm	10,142	859637	1,75	63252
2	210nm	10,864	1646117	3,35	117229
3	210nm	11,973	44805782	91,17	2141254
4	210nm	13,068	1835381	3,73	108254

Processed Channel Descr.: 210nm

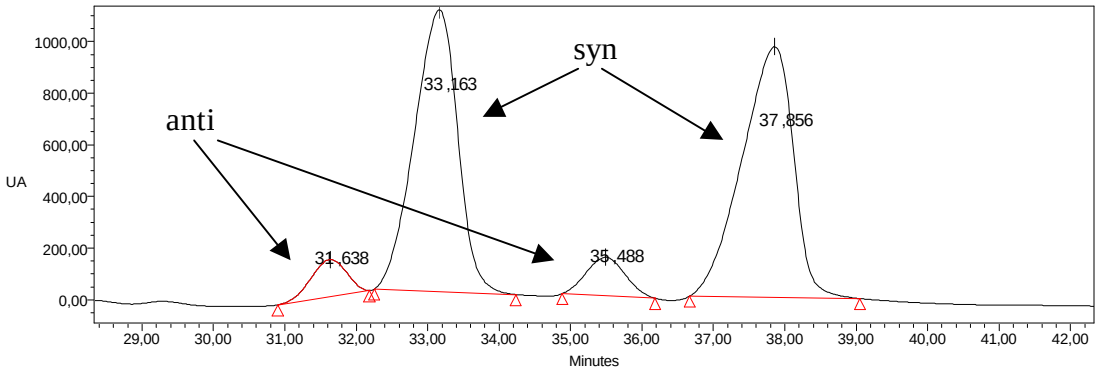
	Processed Channel Descr.	RT	Area	% Area	Height
1	210nm	11,973	44805782	96,06	2141254
2	210nm	13,068	1835381	3,94	108254

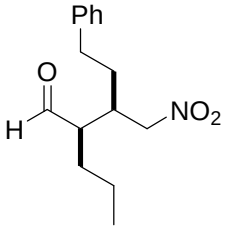


Chiralpak IB, 95:5 hexane:iPrOH, 0. 5mL/min, λ=254nm



rac-12b

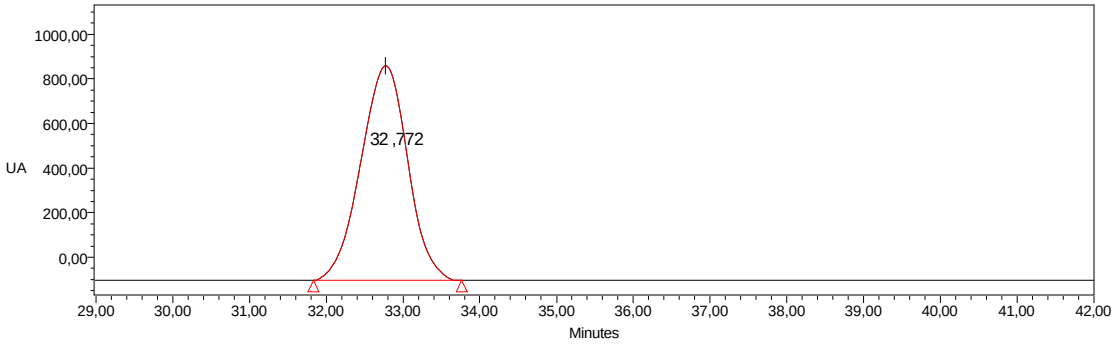




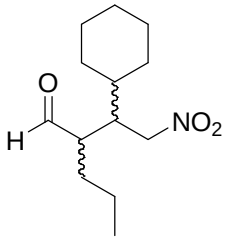
12b

Processed Channel Descr.: 254nm

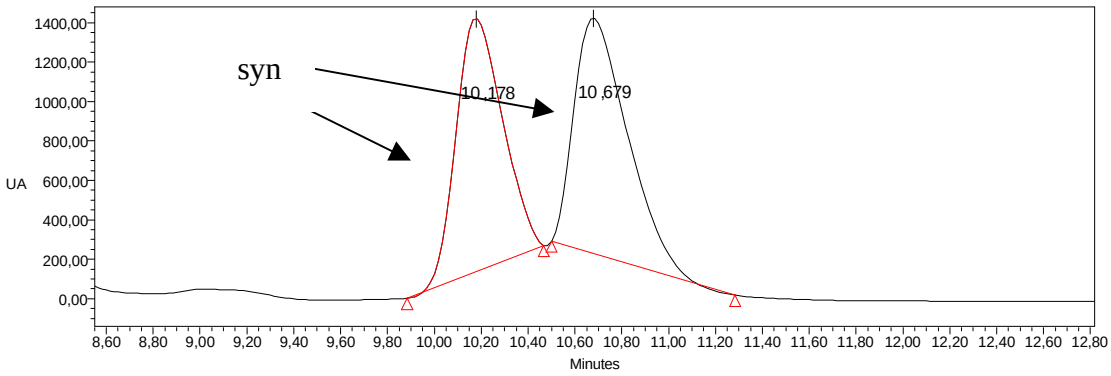
	Processed Channel Descr.	RT	Area	% Area	Height
1	254nm	32,772	40877688	100,00	963470

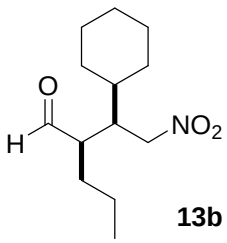


Chiralpak IB, 98:2 hexane:iPrOH, 0. 75mL/min, λ=254nm



rac-13b

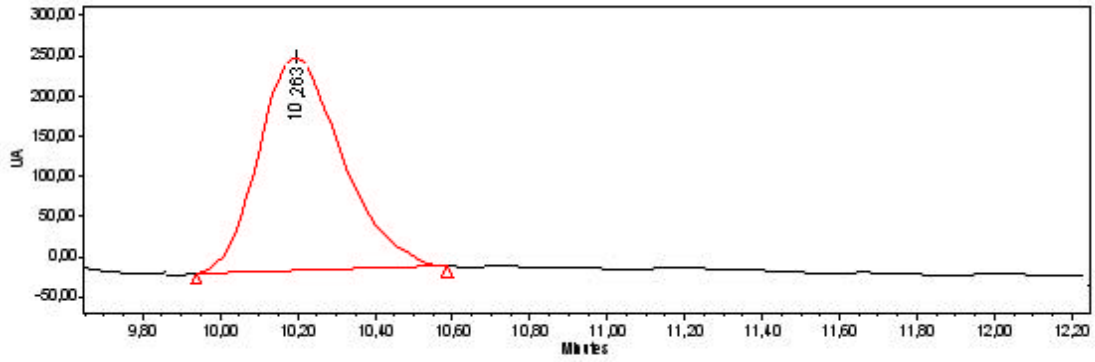




13b

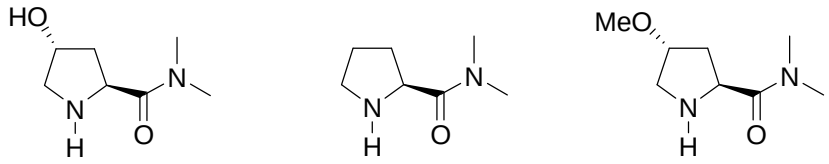
Processed Channel Descr.: 254nm

	Processed Channel Descr.	RT	Area	% Area	Height
1	254nm	10,263	1082077,38	100,00	1951704



I) Mechanistic study by computational methods

All structures were computed using the functional B3LYP[11] and the 6-31G* basis sets as implemented in Gaussian 03.[12] All energy minima and transition structures were characterized by frequency analysis.
The energies reported in this work include the zero-point vibrational energy corrections (ZPVE).
The stationary points were characterized by frequency calculations in order to verify that they have the right number of negative eigenvalues.
The intrinsic reaction coordinates (IRC)[13] were followed in order to verify the energy profiles connecting each TS to the correct associated local minima.
As a model reaction, we chose the addition of propionaldehyde to *trans*-nitropropene catalyzed by different prolylamides. To check the influence of the H-bonding, we studied three different catalysts, *N*,*N*-dimethyl-*trans*-4-hydroxyprolylamide **23,** *N*,*N*-dimethyl-prolylamide **24** and *N*,*N*-dimethyl-*trans*-4-methoxyprolylamide **25**.



23 **24** **25**

We assume that the Michael reaction occurs through a similar mechanism to that of the proline catalyzed aldol reactions, involving initial formation of the enamine between the aldehyde and the proline with concomitant loosing of a molecule of water.[14] This step should be independent of the proline derivative used, and should not interfere in neither the reactivity nor the stereoselectivity of the final process. We did not study the

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[11] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.

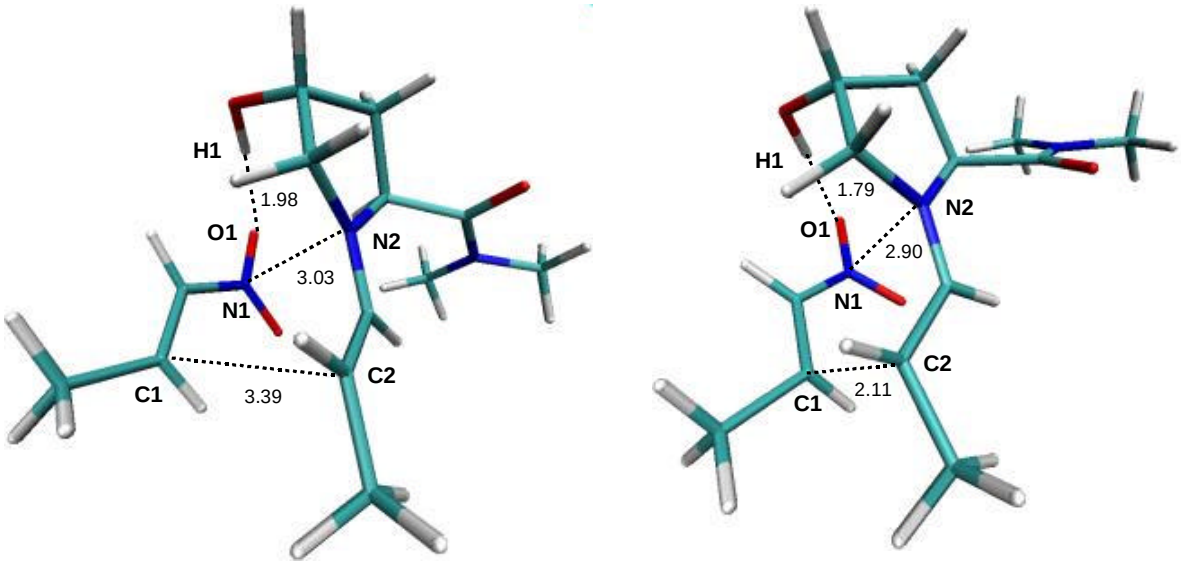
[12] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A. Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, **2004**.

[13] Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523

[14] a) Bahmanyar, S.; Houk, K. N. *J. Am. Chem. Soc.* **2001**, *123*, 11273-11283. b) List, B.; Huang, L.; Martin, H. J. *Proc. Nat. Acad. Science* **2004**, *101*, 5839-5842.

influence of the water molecule liberated during enamine formation since it must be similar in all cases and would interfere in the study of the pure H-bonding effect. The initial enamine complex can adopt two different conformations, *syn* or *anti*, depending on the proximity of the double bond of the enamine to the amide in the pyrrolidine ring. To understand the origin of the stereoselectivity of the reaction in more detail, we computed and compared the activation energies for the approaches of the **A-syn** and **A-anti** enamines derived from catalyst **23**, as well as the approaches of the **B-anti** and **C-anti** enamines derived from catalysts **24** and **25** respectively. In all cases, we characterized the initial complexes with *trans*-nitropropene and the transition states of the rate limiting step.

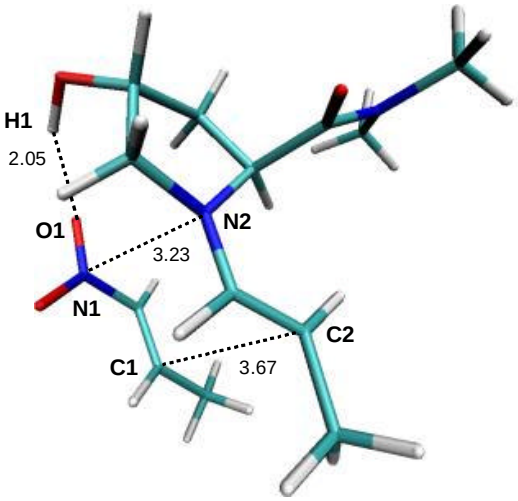
According to Seebach´s model,[15] we found an acyclic synclinal transition state, in which there are positive electrostatic interactions between the nitrogens in the enamine and in the nitro group. In our case, there is also a stabilizing interaction between the nitro group and the OH, in the transition state promoted by the **A-anti** and **A-syn** enamines derived from catalyst **23**. We found a lower activation barrier for Si-*anti* approach, in full accordance with experimental data, a preference that correlates well with the shorter hydrogen bond distance in **A-anti** (1.79 Å) than in **A-syn** (1.89 Å).

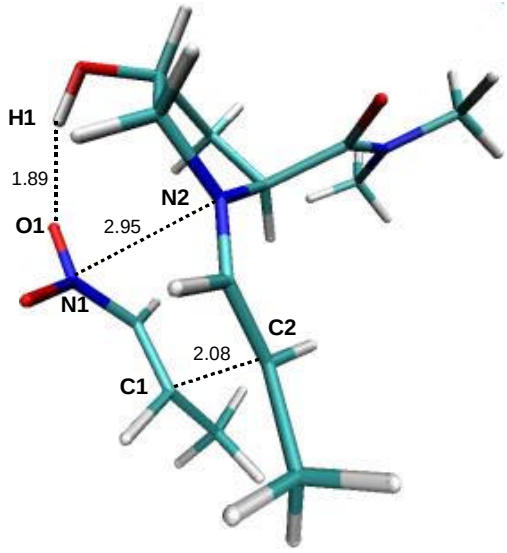


Complex of A-anti+nitropropene **A-anti+nitropropene (Transition State)**

Figure 1. Geometries of the initial complex of **A-anti** with *trans*-nitropropene and the transition state of the C-C bond-formation step of the Michael addition obtained at the B3LYP/6-31G* level of theory.

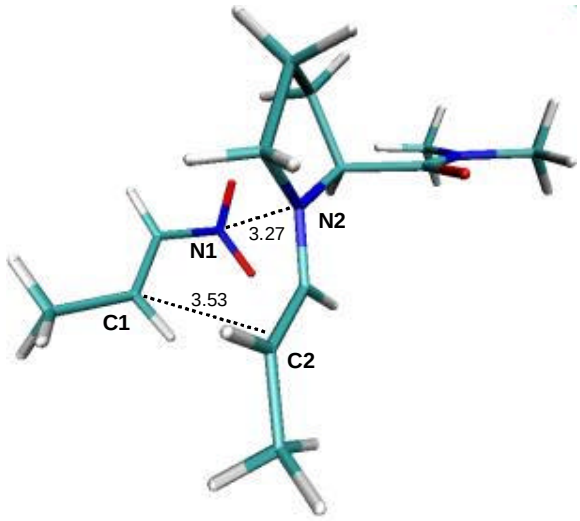
[15] a) Seebach, D.; Golinski, J. *Helv. Chim. Acta* **1981**, *64*, 1413-1423. b) Seebach, D.; Beck, A. K.; Golinski, J.; Hay, J. N.; Laube, T. *Helv. Chim. Acta* **1985**, *68*, 162-172.

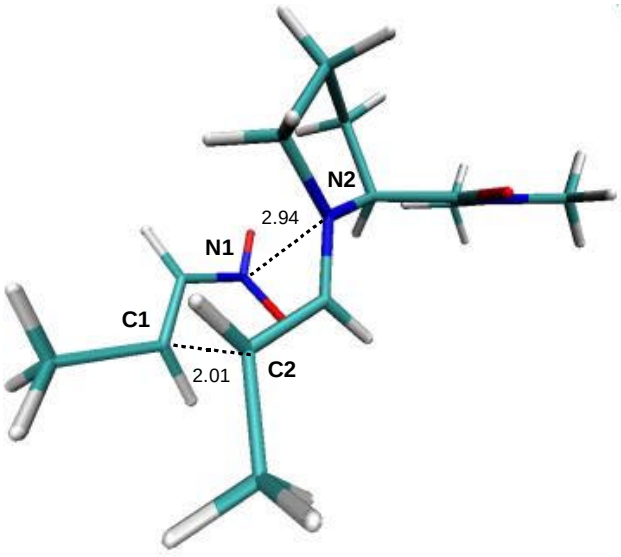




Complex of A-syn+ nitropropene **A-syn+nitropropene (Transition State)**

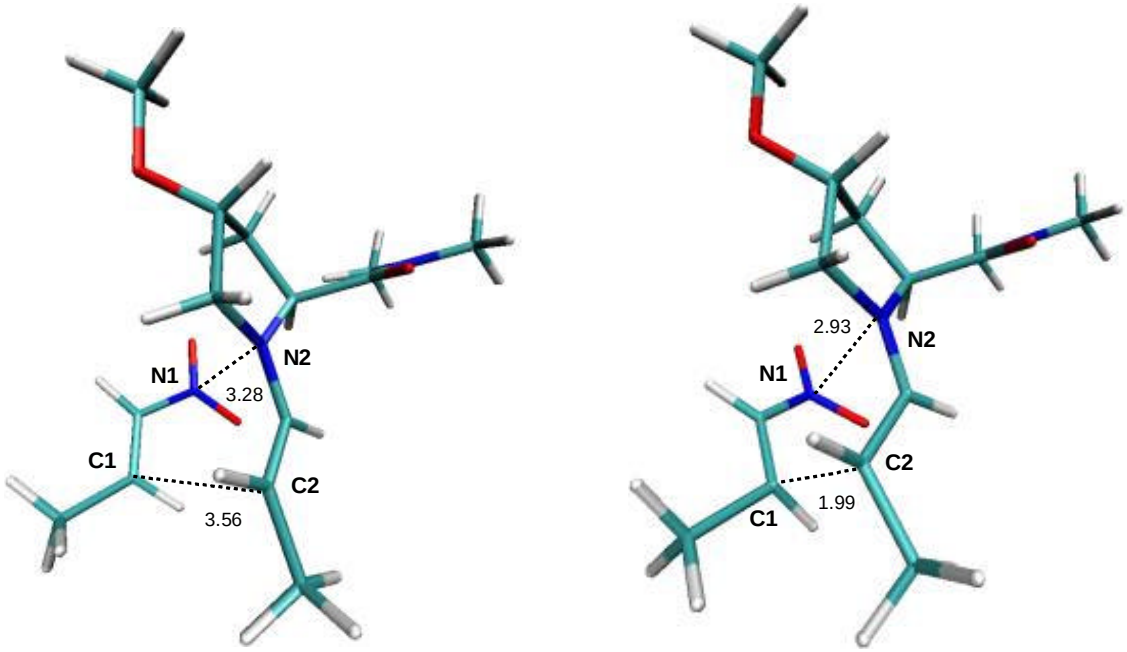
Figure 2. Geometries of the initial complex of **A-syn** with *trans*-nitropropene and the transition state of the C-C bond-formation step of the Michael addition obtained at the B3LYP/6-31G* level of theory.





Complex of B-anti+nitropropene **B-anti+nitropropene (Transition State)**

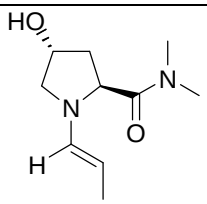
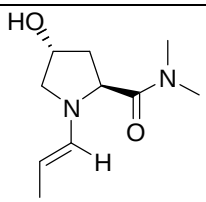
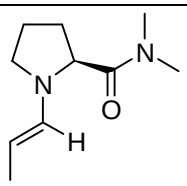
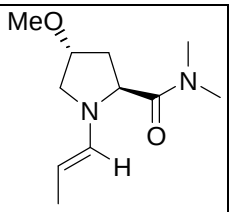
Figure 3. Geometries of the initial complex of **B-anti** with *trans*-nitropropene and the transition state of the C-C bond-formation step of the Michael addition obtained at the B3LYP/6-31G* level of theory.



Complex of C-anti+nitropropene **C-anti+nitropropene (Transition State)**

Figure 4. Geometries of the initial complex of **C-anti** with *trans*-nitropropene and the transition state of the C-C bond-formation step of the Michael addition obtained at the B3LYP/6-31G* level of theory.

Table 2. DFT results for initial complexes and transition states in the C-C bond forming rate limiting step of the Michael reaction between the enamines **A-syn, A-anti, B-anti** and **C-anti** and *trans*-nitropropene.

				
	A-syn (2S,3R)	**A-anti** (2R,3S)	**B-anti**	**C-anti**
Initial complex				
Energy (hartrees)	-973.878266	-973.882542	-898.673149	-1013.157020
Complex stabilization*	-4.99	-7.68	-4.48	-4.89
H1---O1 (Å)	2.050	1.985		
N1---N2 (Å)	3.229	3.033	3.267	3.283
C1---C2(Å)	3.666	3.386	3.531	3.563
Transition states				
Energy (hartrees)	-973.859836	-973.867448	-898.652547	-1013.135040
Activation energy*	11.56	9.47	12.93	13.80
H1---O1 (Å)	1.890	1.794		
N1---N2 (Å)	2.950	2.897	2.938	2.931
C1---C2 (Å)	2.079	2.107	2.010	1.997

*Energy in Kcal/mol. Difference between the starting reactants and the reactive complex.
**Difference between the reactive complex and the transition states.

Cartesian coordinates of the Initial complexes and Stationary points of the Michael addition of model enamines and *trans*-ß-nitropropene.

A-anti + *trans*-nitropropene (Initial Complex):

C	-0.033325	-2.843948	-1.340790
C	1.380554	-2.613373	-0.782500
C	1.301376	-1.249969	-0.058624
N	0.143127	-0.589539	-0.695557
C	-0.450562	-1.421204	-1.738144
C	-0.050323	0.773895	-0.651520
C	-0.911102	1.495255	-1.400757
C	-1.069366	2.983978	-1.263962
O	-0.925552	-3.443314	-0.409668
C	2.600677	-0.443970	-0.270294
O	3.072525	-0.355026	-1.401566
N	3.177521	0.166748	0.815308
C	2.726715	0.076218	2.203200
C	4.456039	0.844300	0.624268
H	-0.025375	-3.510025	-2.208328
H	2.094193	-2.527740	-1.607010
H	1.695084	-3.424637	-0.119781
H	1.087952	-1.407440	1.002060
H	-0.062515	-1.148819	-2.733276
H	-1.540314	-1.313965	-1.751205
H	0.548782	1.277939	0.103531
H	-1.489120	1.007600	-2.183029
H	-2.108292	3.275543	-1.049881
H	-0.785217	3.510040	-2.186630
H	-0.444702	3.378845	-0.454407
H	-0.788803	-3.045715	0.470810
H	3.008453	1.002090	2.715591
H	3.204712	-0.759857	2.733261
H	1.644821	-0.024033	2.286179
H	4.700150	0.830215	-0.436417
H	5.249207	0.337662	1.190613
H	4.390411	1.881546	0.974900
C	-3.180771	0.266846	0.791336
C	-4.414307	0.334457	-0.049438
C	-2.548065	-0.872986	1.092880
N	-1.369507	-0.866165	1.918503
O	-0.944855	0.195572	2.382462
O	-0.830109	-1.970139	2.139023
H	-2.788376	1.191100	1.204483
H	-4.710220	-0.646164	-0.432892
H	-4.258484	1.011124	-0.898117
H	-5.249222	0.746536	0.532837
H	-2.802170	-1.862061	0.736938

A-anti + *trans*-nitropropene (TS):

C	-0.814056	2.874802	1.633545
C	0.350600	2.958694	0.623505
C	0.524094	1.514587	0.097336
N	-0.021805	0.679047	1.183000
C	-0.583527	1.493240	2.274796
C	0.046631	-0.648500	1.163651
C	-0.676437	-1.508392	2.004227
C	-0.281662	-2.970276	2.028610
O	-2.089142	3.023712	1.059586
C	1.999069	1.181534	-0.194519
O	2.682220	0.606018	0.648712
N	2.500671	1.591949	-1.399811
C	1.764328	2.266251	-2.461060
C	3.913010	1.365143	-1.681976
H	-0.732742	3.658951	2.392900
H	1.264679	3.279495	1.136917
H	0.131744	3.672150	-0.174164
H	-0.106308	1.339279	-0.780823
H	0.147232	1.546021	3.094376
H	-1.515656	1.072311	2.650345
H	0.611465	-1.067886	0.340317
H	-0.999619	-1.102463	2.960938
H	-1.120453	-3.611542	2.322342
H	0.531250	-3.158173	2.741700
H	0.058960	-3.302017	1.041367
H	-2.180023	2.457932	0.254578
H	1.877533	1.710312	-3.400085
H	2.156754	3.280457	-2.616623
H	0.701233	2.335953	-2.241272
H	4.362564	0.863617	-0.826660
H	4.424561	2.319778	-1.861404
H	4.024963	0.739807	-2.576981
C	-2.579697	-1.478195	1.101288
C	-3.482162	-1.904678	2.239578
C	-2.842285	-0.237427	0.501373
N	-2.193359	0.120056	-0.650482
O	-1.413284	-0.694962	-1.210876
O	-2.338486	1.303100	-1.115997
H	-2.273575	-2.264664	0.417664
H	-3.722412	-1.065277	2.901230
H	-3.040909	-2.702515	2.843689
H	-4.427917	-2.288254	1.835464
H	-3.425476	0.551254	0.956253

A-syn + *trans*-nitropropene (Initial Complex):

C	0.256851	-1.791672	1.098083
C	0.492279	-2.822723	-0.040680
C	0.216721	-2.037109	-1.351685
N	-0.132980	-0.682587	-0.914749
C	0.376328	-0.411331	0.416200
O	-0.273392	-4.001556	0.103745
C	1.852234	0.066345	0.382919
C	-0.383881	0.317490	-1.831635
C	-0.370377	1.651093	-1.631927
C	-0.716904	2.647690	-2.702835
N	2.328918	0.783539	1.456039
O	2.567383	-0.231720	-0.568344
C	3.712143	1.240738	1.436310
C	1.585983	1.122009	2.658707
H	0.953613	-1.926788	1.930725
H	-0.759888	-1.923141	1.481705
H	1.532715	-3.157135	-0.030991
H	-0.619568	-2.486282	-1.900635
H	1.101456	-2.030945	-1.999283
H	-0.265396	0.339081	0.889053
H	-1.213837	-3.749313	0.038620
H	-0.662888	-0.071503	-2.810150
H	-0.052139	2.055389	-0.672546
H	-1.548141	3.308411	-2.410919
H	0.130768	3.307632	-2.936569
H	-1.008255	2.147064	-3.633789
H	3.754715	2.331879	1.552017
H	4.154984	0.955246	0.483429
H	4.282516	0.784668	2.256683
H	1.413071	2.205750	2.727676
H	2.157211	0.817093	3.545547
H	0.624725	0.612793	2.695770
C	-3.811203	0.523438	-1.059265
C	-4.273376	1.879822	-0.639221
C	-3.624786	-0.496765	-0.218094
N	-3.161240	-1.782028	-0.691620
O	-3.036850	-1.985809	-1.898285
O	-2.923004	-2.627472	0.188934
H	-3.617400	0.351578	-2.114227
H	-4.441238	1.947464	0.439560
H	-3.529922	2.632904	-0.927704
H	-5.206192	2.141891	-1.155167
H	-3.760468	-0.480743	0.854782

A-syn + *trans*-nitropropene (TS):

C	-0.321762	1.344360	-1.186768
C	-1.867279	1.301178	-1.379623
C	-2.284988	-0.121674	-0.919357
N	-1.038376	-0.790833	-0.514664
C	0.018997	0.184219	-0.226547
O	-2.270462	1.609909	-2.688690
C	-0.068085	0.597504	1.265427
C	-0.968765	-2.105774	-0.359619
C	0.194260	-2.874939	-0.190918
C	0.013275	-4.310760	0.262009
N	1.004150	1.262039	1.802155
O	-1.081711	0.349197	1.910568
C	0.944138	1.679214	3.198303
C	2.238312	1.602234	1.110931
H	0.020844	2.314865	-0.818497
H	0.138443	1.157318	-2.160675
H	-2.346985	2.046219	-0.738571
H	-2.728226	-0.682053	-1.747757
H	-2.975281	-0.093292	-0.071091
H	0.986938	-0.260788	-0.453476
H	-1.883133	0.925339	-3.279633
H	-1.908737	-2.621582	-0.529816
H	1.062744	-2.369965	0.228714
H	0.851303	-4.944931	-0.046860
H	-0.059906	-4.384644	1.354553
H	-0.900345	-4.743271	-0.161697
H	1.769409	1.229126	3.765121
H	-0.007065	1.353836	3.616119
H	1.026138	2.770966	3.275681
H	3.092300	1.075867	1.559448
H	2.427490	2.680496	1.190811
H	2.193268	1.351807	0.052704
C	0.893829	-2.996948	-2.145142
C	2.341354	-3.397949	-1.938278
C	0.672668	-1.815659	-2.870500
N	-0.578079	-1.493500	-3.342712
O	-1.543991	-2.274033	-3.125961
O	-0.727051	-0.399750	-3.972260
H	0.205978	-3.808472	-2.367432
H	2.970871	-2.529100	-1.715042
H	2.467270	-4.125839	-1.132324
H	2.728790	-3.858322	-2.856018
H	1.425995	-1.060486	-3.048416

B-anti + *trans*-nitropropene (Initial Complex):

C	-0.647842	2.286514	-0.056168
C	0.806473	2.185089	-0.555130
C	1.287552	0.847733	0.053787
N	0.089020	0.029785	-0.033615
C	-1.135193	0.824585	0.001175
C	0.095169	-1.311890	0.276672
C	-0.979126	-2.112091	0.440277
C	-0.869156	-3.577621	0.759277
C	1.746841	1.048340	1.519089
O	0.944016	0.902924	2.437180
N	3.051041	1.422836	1.741562
C	4.063232	1.657500	0.723236
C	3.498581	1.628998	3.112000
H	-1.269836	2.910080	-0.705704
H	-0.669281	2.719360	0.948013
H	1.419571	3.038528	-0.249512
H	0.849258	2.106552	-1.645889
H	2.075745	0.386551	-0.548050
H	-1.705063	0.620743	0.917679
H	-1.775436	0.561035	-0.854263
H	1.094254	-1.737488	0.344009
H	-1.981705	-1.690933	0.394485
H	-1.389800	-4.208176	0.022827
H	-1.311188	-3.817764	1.737213
H	0.177994	-3.901443	0.785690
H	4.892532	0.944229	0.828949
H	4.475769	2.670181	0.830185
H	3.658890	1.565247	-0.282730
H	2.671463	1.400665	3.782455
H	3.817276	2.669418	3.262527
H	4.349747	0.972977	3.337952
C	-0.627304	-2.095367	-3.073074
C	-2.038071	-2.334854	-3.504364
C	0.060333	-0.987595	-3.362167
N	1.418945	-0.804000	-2.899307
O	1.986755	-1.716385	-2.293076
O	1.938354	0.293533	-3.146347
H	-0.130646	-2.862915	-2.487549
H	-2.444595	-1.498703	-4.081085
H	-2.674988	-2.496902	-2.626358
H	-2.104126	-3.244507	-4.115234
H	-0.299881	-0.132996	-3.918976

B-anti + *trans*-nitropropene (TS):

C	0.778137	0.549149	1.967941
C	1.291733	1.491730	0.867615
C	1.051239	0.683319	-0.427780
N	-0.171982	-0.068207	-0.110718
C	-0.466293	-0.090607	1.337326
C	-0.864517	-0.713242	-1.039230
C	-2.192764	-1.157379	-0.872482
C	-2.721588	-2.155075	-1.886261
C	2.213043	-0.282028	-0.741333
O	2.146591	-1.461792	-0.403488
N	3.308792	0.247162	-1.370407
C	3.461807	1.625275	-1.817276
C	4.448044	-0.619629	-1.643188
H	0.543518	1.070892	2.900040
H	1.522476	-0.223969	2.183258
H	2.340851	1.768967	1.002213
H	0.691025	2.405060	0.812134
H	0.817459	1.333252	-1.275421
H	-0.627686	-1.124405	1.660675
H	-1.370361	0.487700	1.545792
H	-0.407791	-0.749924	-2.020920
H	-2.499786	-1.349319	0.155426
H	-3.816223	-2.144547	-1.928802
H	-2.416321	-3.180908	-1.645142
H	-2.349731	-1.923920	-2.891006
H	3.640808	1.652618	-2.900024
H	4.322525	2.092285	-1.319595
H	2.578674	2.224655	-1.606094
H	4.219131	-1.618652	-1.275696
H	5.347641	-0.238632	-1.142090
H	4.645600	-0.659790	-2.722275
C	-3.252823	0.526474	-1.156570
C	-4.564651	0.228592	-0.451248
C	-2.577225	1.693054	-0.737213
N	-1.511993	2.175735	-1.453552
O	-1.159348	1.554337	-2.505615
O	-0.871674	3.180893	-1.040009
H	-3.267456	0.384781	-2.235062
H	-4.483475	0.388611	0.629837
H	-4.905853	-0.797333	-0.617706
H	-5.347641	0.898712	-0.827179
H	-2.767029	2.209747	0.193985

C-anti + *trans*-nitropropene (Initial Complex):

C	0.951477	1.372162	0.483704
C	0.443634	1.559113	-0.964722
C	0.795944	0.216568	-1.638184
N	0.583878	-0.732483	-0.555328
C	0.782776	-0.132813	0.756973
C	0.672989	-2.093872	-0.752106
C	0.713959	-3.047119	0.201157
C	0.790070	-4.516785	-0.107513
O	0.221375	2.098541	1.458115
C	0.502441	3.483444	1.463409
C	2.265915	0.223770	-2.126175
O	3.162689	-0.122589	-1.360886
N	2.522034	0.657364	-3.404541
C	1.536530	1.120926	-4.370361
C	3.898697	0.663071	-3.881241
H	2.015060	1.643646	0.543472
H	0.888916	2.419815	-1.472809
H	-0.643921	1.681274	-0.949677
H	0.108841	-0.021423	-2.453888
H	1.664902	-0.556549	1.254578
H	-0.090485	-0.297791	1.403107
H	0.663406	-2.382172	-1.801407
H	0.735703	-2.761002	1.250916
H	-0.037079	-5.083618	0.345900
H	1.717484	-4.967773	0.274292
H	0.759171	-4.699127	-1.188232
H	-0.050995	3.917618	2.300385
H	0.181427	3.979324	0.534698
H	1.577576	3.677826	1.606796
H	1.470764	0.432404	-5.224396
H	1.830688	2.106522	-4.755035
H	0.546219	1.216965	-3.929871
H	4.538895	0.273422	-3.091248
H	4.213104	1.683060	-4.140213
H	3.994095	0.035843	-4.777496
C	-2.784485	-2.532425	-0.238297
C	-3.271164	-3.017151	1.088593
C	-2.898788	-1.270004	-0.658432
N	-2.386444	-0.861053	-1.948608
O	-1.893875	-1.702698	-2.705933
O	-2.472534	0.344696	-2.216690
H	-2.307602	-3.246780	-0.902527
H	-3.724777	-2.218674	1.682938
H	-2.437271	-3.446198	1.657410
H	-4.010086	-3.818268	0.956970
H	-3.331924	-0.444321	-0.109985

C-anti + *trans*-nitropropene (TS):

C	-0.197861	1.193726	1.208679
C	1.061844	1.389984	0.340927
C	1.633072	-0.037140	0.216705
N	0.418991	-0.869980	0.220078
C	-0.759659	-0.150452	0.725555
C	0.442276	-2.152802	-0.114990
C	-0.705475	-2.896362	-0.463593
C	-0.565186	-4.407425	-0.499588
O	-1.201752	2.172760	1.044724
C	-0.901932	3.412277	1.658676
C	2.546570	-0.407074	1.403503
O	2.085022	-1.004410	2.373718
N	3.854263	-0.007797	1.332047
C	4.482483	0.690400	0.217484
C	4.737869	-0.296494	2.454636
H	0.086670	1.118881	2.269196
H	1.779877	2.092209	0.772644
H	0.771118	1.737381	-0.655869
H	2.123917	-0.193130	-0.747162
H	-1.231903	-0.726105	1.527740
H	-1.489746	0.030121	-0.066895
H	1.426514	-2.577850	-0.269989
H	-1.642242	-2.538971	-0.035889
H	-1.333557	-4.867798	-1.130066
H	-0.658585	-4.848465	0.500519
H	0.411362	-4.698410	-0.903259
H	-1.781250	4.048187	1.530457
H	-0.037354	3.907745	1.193329
H	-0.700272	3.291702	2.734772
H	5.312393	0.093521	-0.182373
H	4.889435	1.652420	0.556702
H	3.782822	0.882935	-0.593231
H	4.165298	-0.814453	3.222305
H	5.150146	0.634415	2.865326
H	5.573563	-0.928970	2.128342
C	-1.039261	-2.332657	-2.349655
C	-2.514923	-2.635071	-2.548615
C	-0.641846	-1.003708	-2.620331
N	0.687836	-0.679398	-2.692215
O	1.545364	-1.603668	-2.517609
O	1.044113	0.517900	-2.869766
H	-0.359833	-3.086090	-2.742798
H	-3.146393	-1.842133	-2.132339
H	-2.813950	-3.582443	-2.090256
H	-2.736511	-2.706375	-3.620605
H	-1.317276	-0.160767	-2.677444