SUPPORTING INFORMATION

Mimicking Enzymes: Asymmetric Induction Inside a Carbamate-Based Steroidal Cleft

Carmen Concellón,* Judith Martín, Miguel Gallegos, Noé Fanjul–Mosteirín, Aurora Costales, Ángel M. Pendás and Vicente del Amo* (ccf@uniovi.es; vdelamo@uniovi.es)

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SYNTHETIC PROCEDURES

General Considerations

All commercially available reagents and solvents were used without further purification unless otherwise stated. THF was distilled from sodium and bezophenone, DCM was distilled from anhydrous P_2O_5, Hexane and Toluene were distilled from sodium ribbons. Triethyl amine was distilled from CaH_2 and it was stored over molecular sieves and nitrogen atmosphere. Phenyl isocyanate was distilled under reduced pressure before use.

Flash chromatography of reaction products was carried out using Silica 60A, particle size 230-400 micron (Merk). Analytical thin layer chromatography (TLC) was performed on DC-Alufolien Kieselgel $60F_{254}$ 0.2 mm plates (Merk) and compounds were visualised by UV fluorescence or 5% phosphomolybdic acid in methanol.

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker AC-300 or a Bruker AV-400 spectrometer, using deuterated solvents and were referenced internally to the residual solvent peak (δ_H = 7.26 ppm, δ_C = 77.36 ppm) signal.[1] Coupling constants (*J*-values) are given in hertzs (Hz). The DEPT 135 technique was used to assign methylene (CH_2) signals. Chemical shifts are reported as follows: value (number of protons, description of absortion, coupling constant(s) where applicable, assignment). NMR spectra assignation was aided by comparison with literature values for similar compounds. Only clear identifiable peaks have been assigned.

Accurate mass of new compounds was measured in a high-resolution mass spectrometer (IMPACT II, BRUKER) with a quadrupole and a Time-Of-Flight (TOF) tube as analyzers, and a conventional Electrospray Ion Source (ESI). The equipment uses N_2 at the nebulization (2.4 Bar), and as drying gas (250 °C, 6.0 L/min). Mass spectra were acquired in *full scan* mode (4 eV) and positive ion polarity.

High pressure liquid chromatography (HPLC) analysis was performed on a HewlettPackard 1100 Series instrument equipped with a quaternary pump, using a Chiralcel AD-H column (250 x 4.6 mm) or Chiralcel OD–H column (250 x 4.6 mm). UV detection was monitored at 220 nm or at 210 nm.

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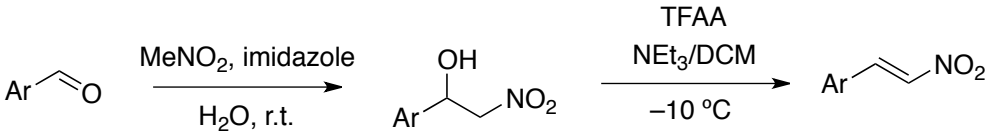
[1] Gottlieb, H. E.; Kotlyar, V.; Nudelman, A. *J. Org. Chem.* **1997**, *62*, 7512.

Nitroalkenes 3a-j.

Nitroalkenes **3a-f** and **3i-j**, were purchased from Aldrich. They were used without further purification. Other nitroalkenes (**3g** and **3h**) were prepared according to the following scheme, reproducing literature procedures:[2], [3]



Standard procedure for the synthesis of enantio-enriched Michael adducts 8a-j (SP1)

Aromatic nitroalkene **3a-j** (0.2 mmol), and steroid **13** (0.03 mmol) were dissolved in dry toluene (1.6 mL), at –78 ºC, before dimethyl malonate **2** (0.6 mmol) and dry triethyl amine (0.2 mmol) were added. The reaction mixtures were stirred for 72 h (unless otherwise stated), and then quenched with 2 mL NH_4Cl (aq. sat.). Organic materials were extracted with DCM (2 x 10 mL), dried (Na_2SO_4) and the volatiles were removed under vacuum. Crude products were filtered through a plug of silica gel (elution with Hex/EtOAC, 3:1) to render the desired adducts **4a-j** in analytically pure form.

Standard procedure for the synthesis of enantio-enriched Michael adduct 8a at 2 mmol scale

Nitrostyrene **3a** (298 mg, 2 mmol), and steroid **13** (234 mg, 0.3 mmol) were dissolved in dry toluene (16 mL), at –78 ºC, inside a Schlenk flask under nitrogen atmosphere, before dimethyl malonate **2** (793 mg, 0.69 mL, 6 mmol) and dry triethyl amine (202 mg, 0.28 mL, 2 mmol) were added. The reaction mixture was stirred for 72 h, and then quenched with 20 mL NH_4Cl (aq. sat.). Organic materials were extracted with DCM (2 x 30 mL), dried (Na_2SO_4) and the volatiles were removed under vacuum. The crude product was filtered through a plug of silica gel (elution with Hex/EtOAC, 3:1) to render the desired adducts **4a** (533 mg, 95% yield) in analytically pure form and 91% *ee* (as determined by HPLC).

Standard procedure for the synthesis of racemic Michael adducts 4a-j.

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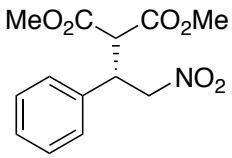
[2] Phukan, M.; Borah, K. J.; Borah, R. *Synth. Commun.* **2008**, *38*, 3068–3073.

[3] Ferraro, A.; Bernardi, L.; Fochi, M. *Adv. Synth. Catal.* **2016**, *358*, 1561–1565.

Racemic products **4a-j**, necessary for HLPC analyses, were prepared according to a published synthetic procedure: Saidi, M. R.; Azizi, N.; Akbari, E.; Ebrahimi, F. *J. Mol. Cat. A* **2008**, *292*, 44–48.

SPECTROSCOPIC CHARACTERIATION AND HPLC CHROMATOGRAMS OF MICHAEL ADDUCTS 4a-j

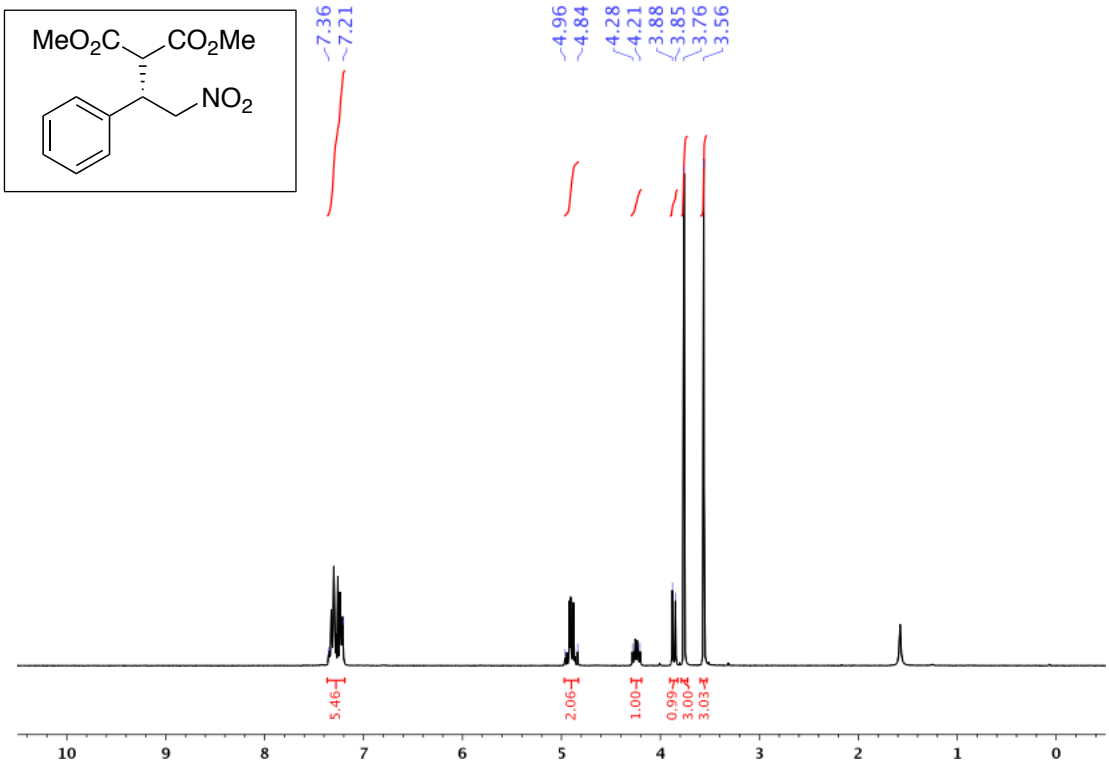
(*S*)-Dimethyl 2-(2-nitro-1-phenylethyl)malonate (4a)[4]



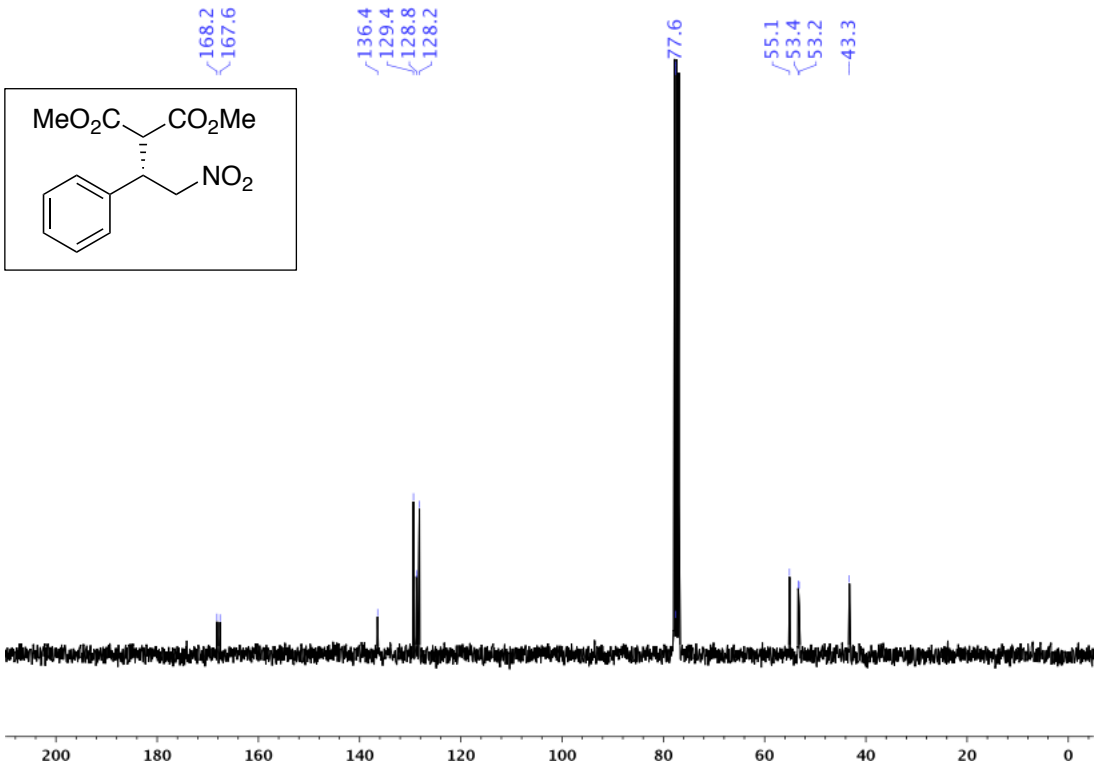
Prepared according to **SP1**. Purified by flash chromatography (Hexane/EtOAc, 3:1). Obtained as a white solid, 94% isolated yield (53 mg), in 91% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.36–7.21 (5H, m, Ar*H*), 4.96–4.84 (2H, m, CH_2), 4.28–4.21 (1H, m, C*H*), 3.86 (1H, d, *J* = 9.1 Hz, C*H*), 3.76 (3H, s, OCH_3), 3.56 (3H, s, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 168.2 (*C*O_2), 167.6 (*C*O_2), 136.4 (Ar*C*), 129.4 (Ar*C*H), 128.8 (Ar*C*H), 128.2 (Ar*C*H), 77.6 (*C*H_2) 55.1 (*C*H), 53.4 (*C*H_3), 53.2 (*C*H_3), 43.3 (*C*H).

[4] H. Li, Y. Wang, L. Tang, L. Deng, *J. Am. Chem. Soc.* **2004**, *126*, 9906–9907.

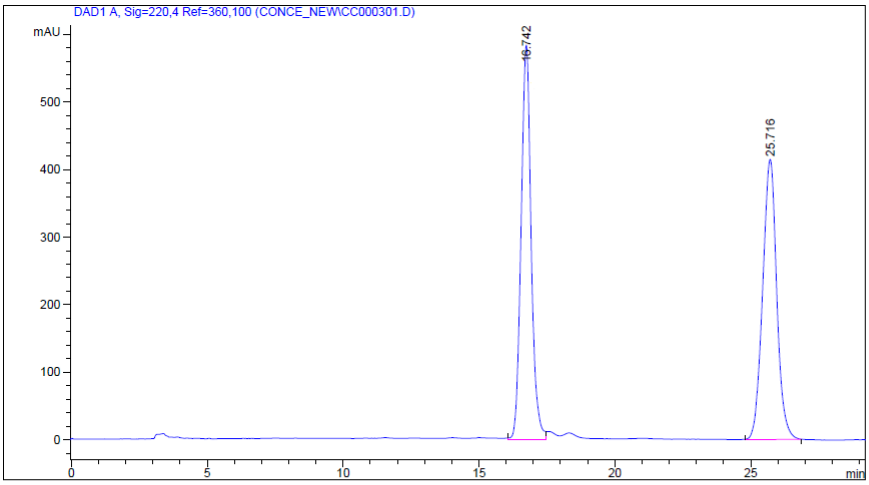
^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C NMR (75 MHz, $CDCl_3$):



Product **4a** was obtained in a maximum of 91% *ee*. The optical purity was determined by HPLC on a chiralcel AD-H column (hexane/2-propanol 90:10), flow rate 1.0 mL/min, λ = 220 nm, 25 ºC.

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   1  16.742 MM    0.4282 1.50004e4   583.83441  50.0406
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Totals :                  2.99764e4   998.48505

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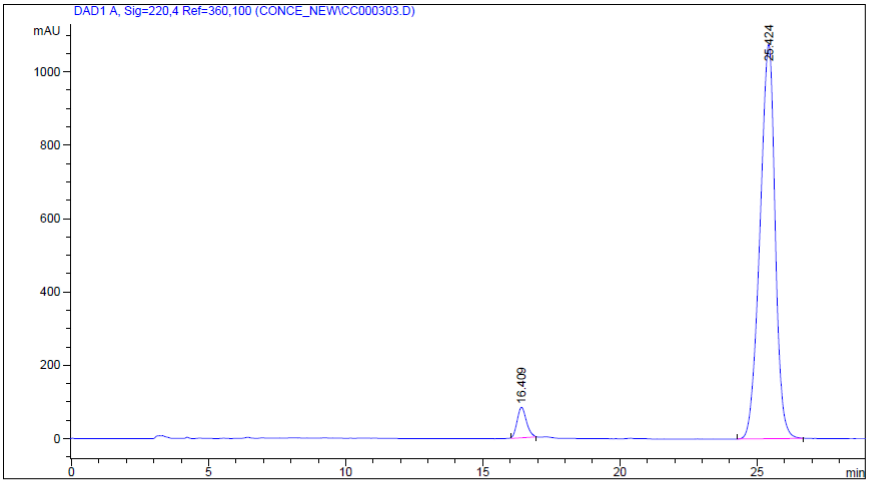


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Signal 1: DAD1 A, Sig=220,4 Ref=360,100

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   1  16.409 MM    0.3938 1964.60168   83.14019   4.5276
   2  25.424 BB    0.5893 4.14272e4  1075.75623  95.4724

Totals :                  4.33918e4  1158.89642

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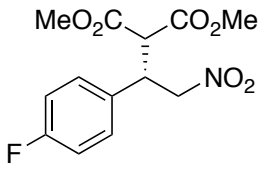
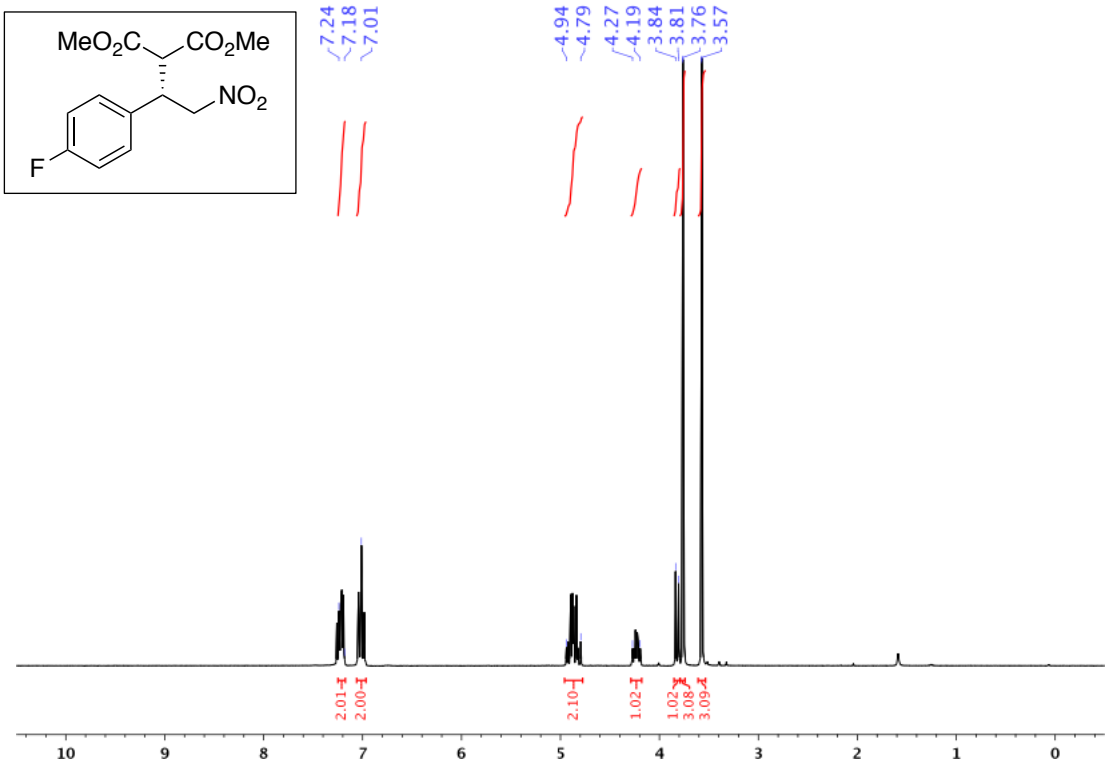
(*S*)-Dimethyl 2-(2-nitro-1-(4-fluorphenyl)-ethyl)malonate (4b)[5]



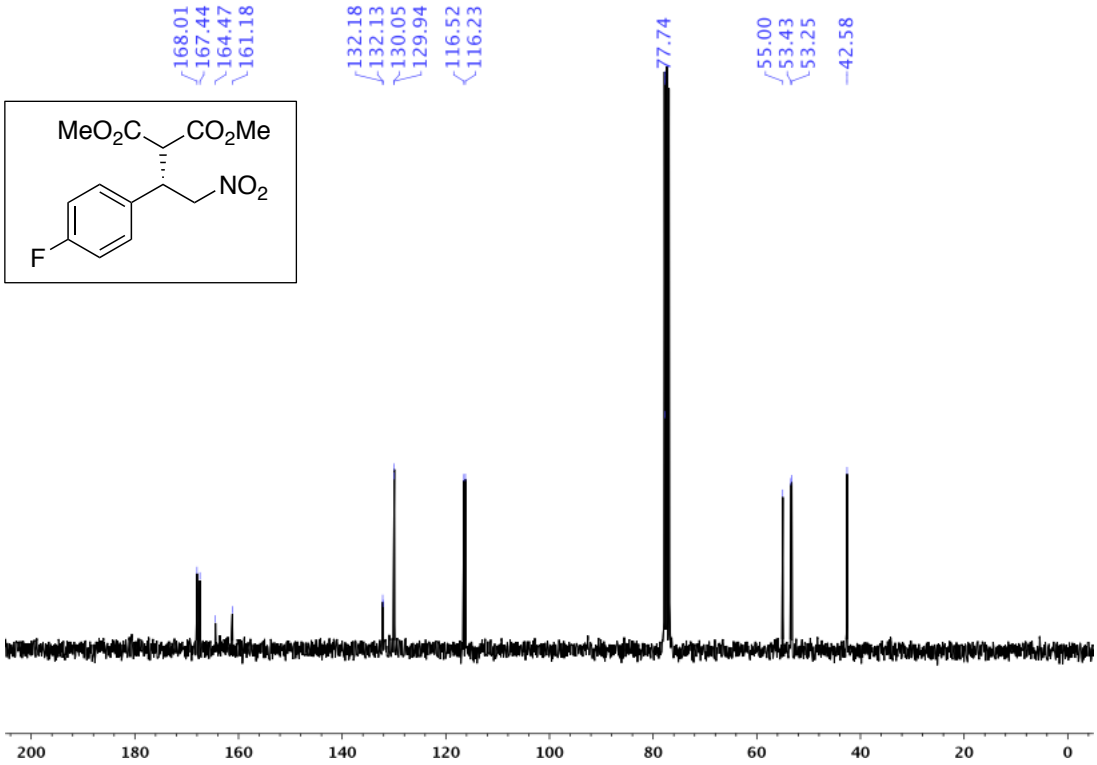
Prepared according to **SP1**. Purified by flash chromatography (Hexane/EtOAc, 3:1). Obtained as a white solid, 84% isolated yield (50 mg), in 90% *ee*.; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.24–7.18 (2H, m, Ar*H*), 7.01 (2H, t, *J* = 8.6 Hz, Ar*H*), 4.94–4.79 (2H, m, CH_2), 4.27–4.19 (1H, m, C*H*), 3.83 (1H, d, *J* = 9.1 Hz, C*H*), 3.76 (3H, s, OCH_3), 3.57 (3H, s, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 168.0 (*C*O_2), 167.4 (*C*O_2), 162.8 (d, *J* = 247.9 Hz, ArC), 132.2 (d, *J* = 3.7 Hz), 130.0 (d, *J* = 8.2 Hz), 116.4 (d, *J* = 21.7 Hz), 77.7 (*C*H_2), 55.0, 53.4, 53.3, 42.6 (*C*H); ^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm) = -113.1 (Ar*F*).

[5] Watanabe, M.; Ikagawa, A.; Wang, H.; Murata, K.; Ikariya, T. *J. Am. Chem. Soc.* **2004**, *126*, 11148–11149.

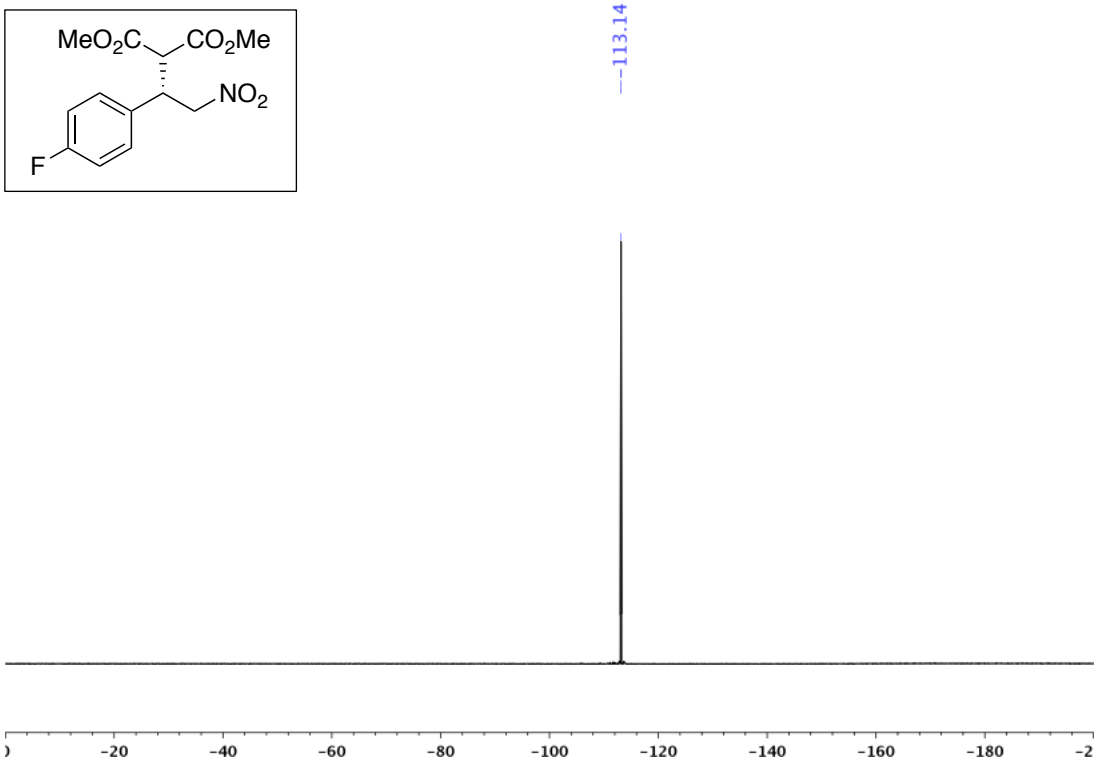
^{1}H NMR (300 MHz, $CDCl_3$):



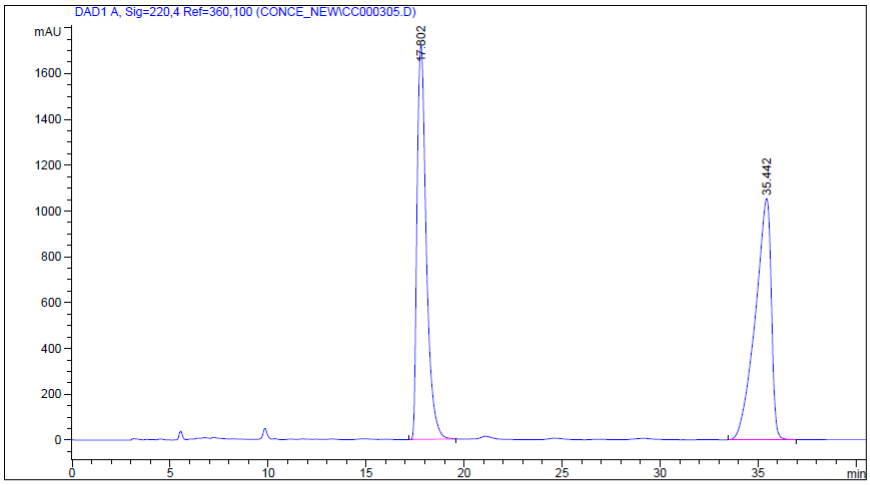
^{13}C NMR (75 MHz, $CDCl_3$):



^{19}F NMR (282 MHz, $CDCl_3$):

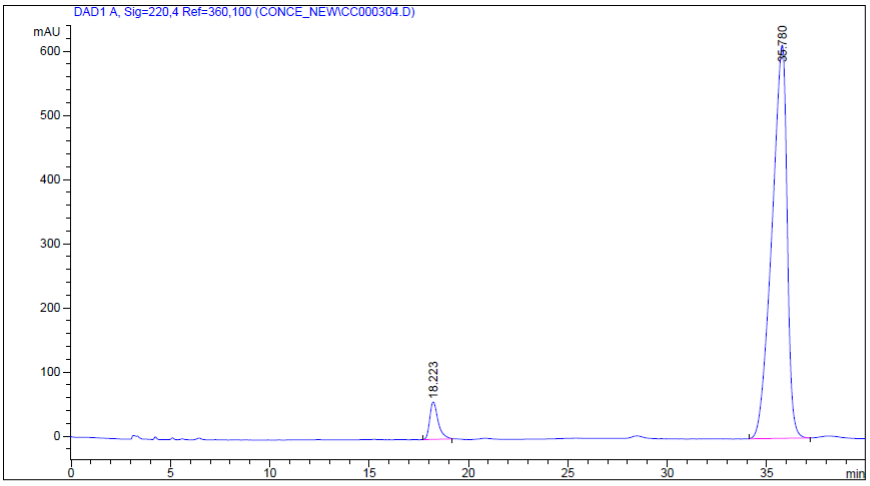


Product **4b** was obtained in a maximum of 90% *ee*. The optical purity was determined by HPLC on a chiralcel AD-H column (hexane/2-propanol 90:10), flow rate 1.0 mL/min, λ = 220 nm, 25 ºC.



Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.802	BB	0.5096	5.65852e4	1720.85254	48.6585
2	35.442	BB	0.8178	5.97052e4	1052.56348	51.3415
Totals :				1.16290e5	2773.41602	

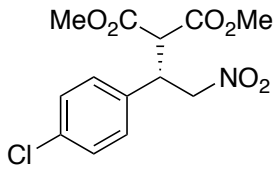


Area Percent Report

Signal 1: DAD1 A, Sig=220,4 Ref=360,100

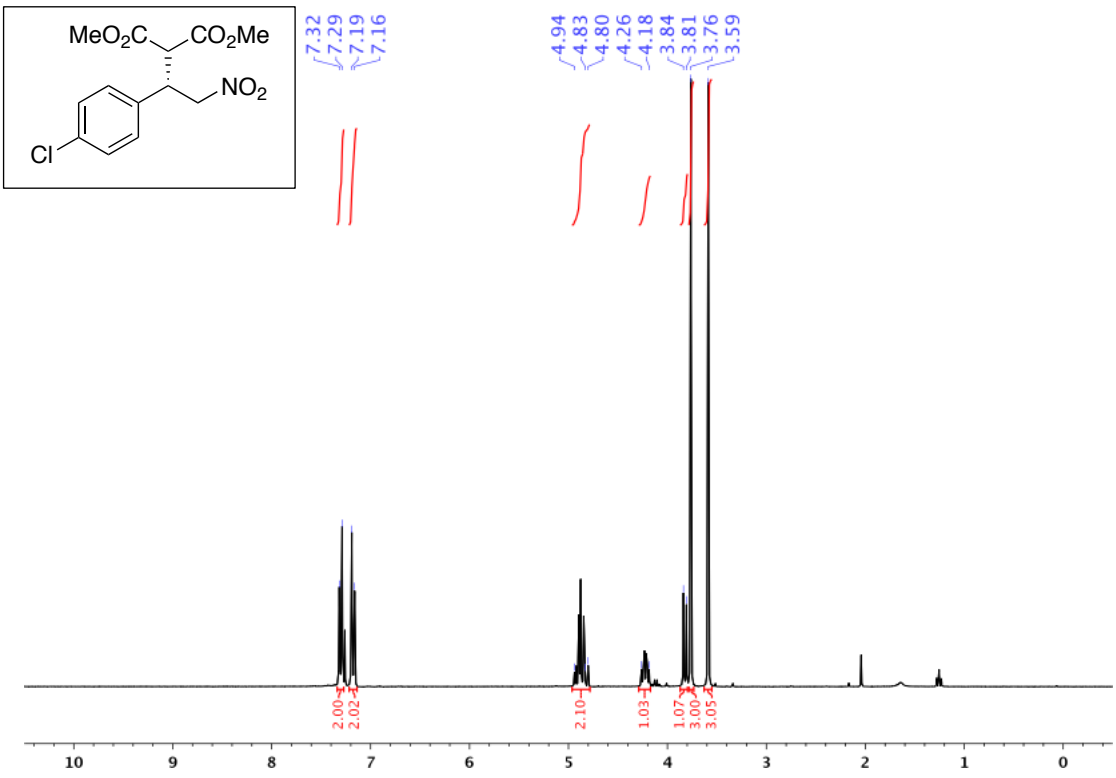
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.223	BB	0.4469	1707.25867	58.42885	4.9859
2	35.780	BB	0.7954	3.25346e4	612.82404	95.0141
Totals :				3.42418e4	671.25288	

(*S*)-Dimethyl 2-(2-nitro-1-(4-chlorophenyl)-ethyl)malonate (4c)[4]

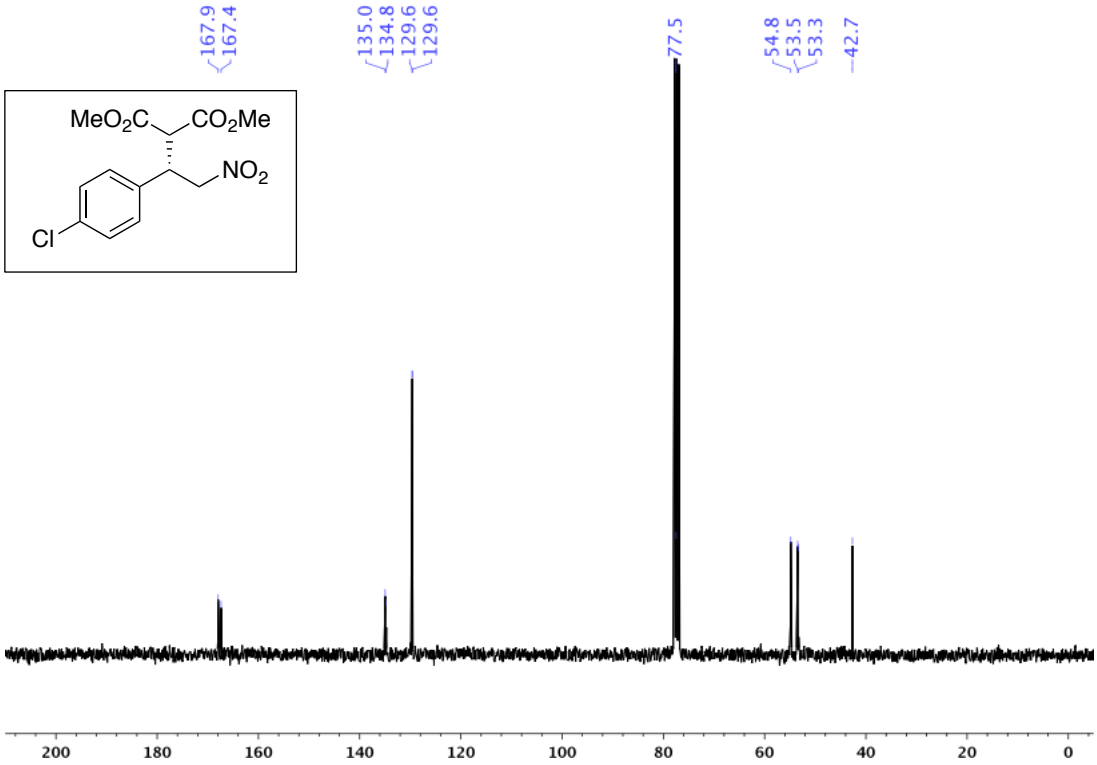


Prepared according to **SP1**. Purified by flash chromatography (Hexane/EtOAc, 3:1). Obtained as a white solid, 99% isolated yield (62 mg), in 89% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.30 (2H, d, *J* = 8.4 Hz, Ar*H*), 7.18 (2H, d, *J* = 8.4 Hz, Ar*H*), 4.94–4.80 (2H, m, CH_2), 4.26–4.18 (1H, m, C*H*), 3.82 (1H, d, *J* = 9.0 Hz, C*H*), 3.76 (3H, s, OCH_3), 3.59 (3H, s, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.9 (*C*O_2), 167.4 (*C*O_2), 135.0 (Ar*C*), 134.8 (Ar*C*), 129.6 (Ar*C*H), 129.6 (Ar*C*H), 77.5 (*C*H_2) 54.8, 53.5, 53.3, 42.7.

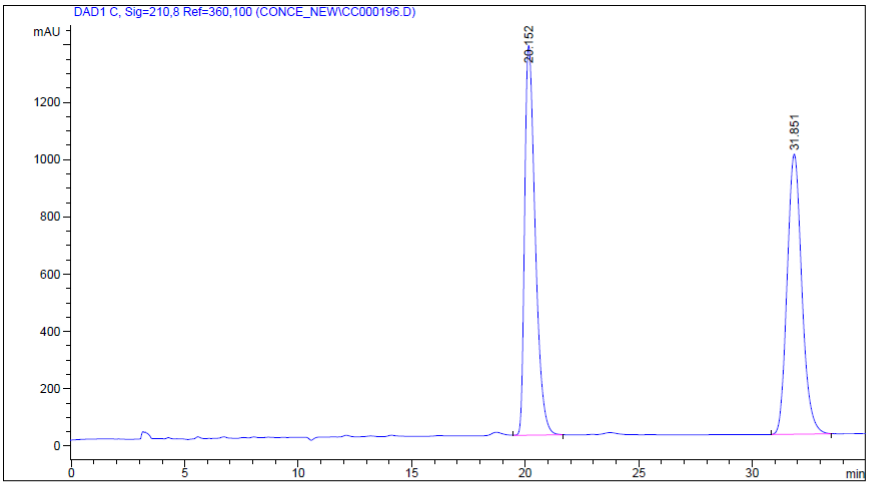
^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C NMR (75 MHz, $CDCl_3$):



Product **4c** was obtained in a maximum of 89% *ee*. The optical purity was determined by HPLC on a chiralcel AD-H column (hexane/2-propanol 90:10), flow rate 1.0 mL/min, λ = 220 nm, 25 ºC.



Area Percent Report

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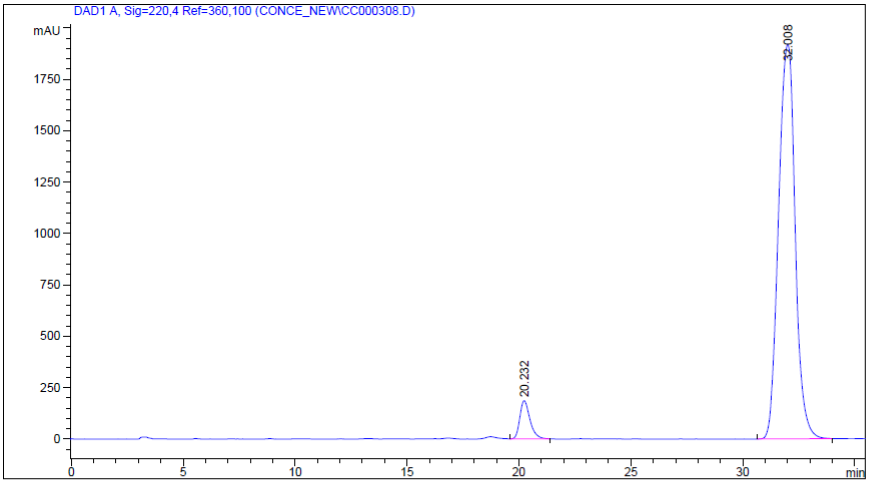
2	31.851	BB	0.6959	4.40748e4	977.79492	49.9856

Totals : 8.81749e4 2338.60144



Area Percent Report

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2	32.008	BB	0.8095	9.90129e4	1920.50403	94.3957

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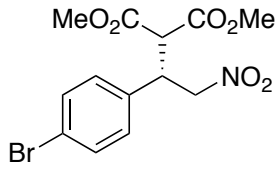
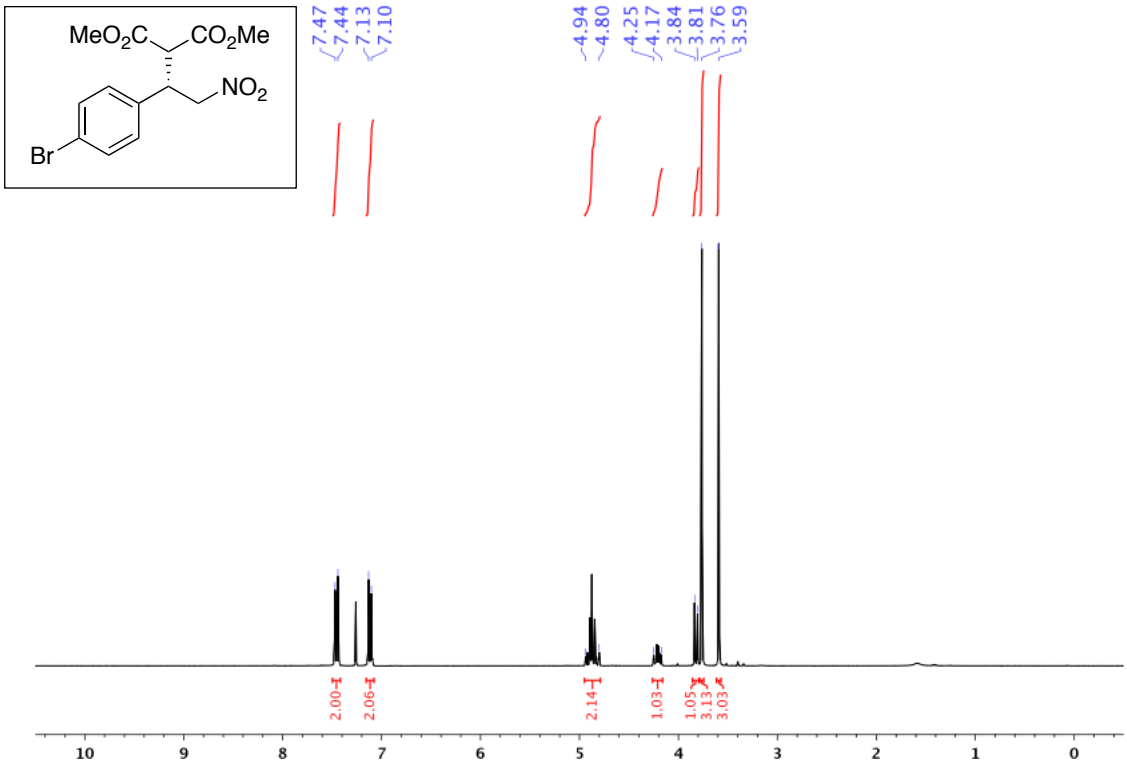
(*S*)-Dimethyl 2-(2-nitro-1-(4-bromophenyl)-ethyl)malonate (4d)[4]

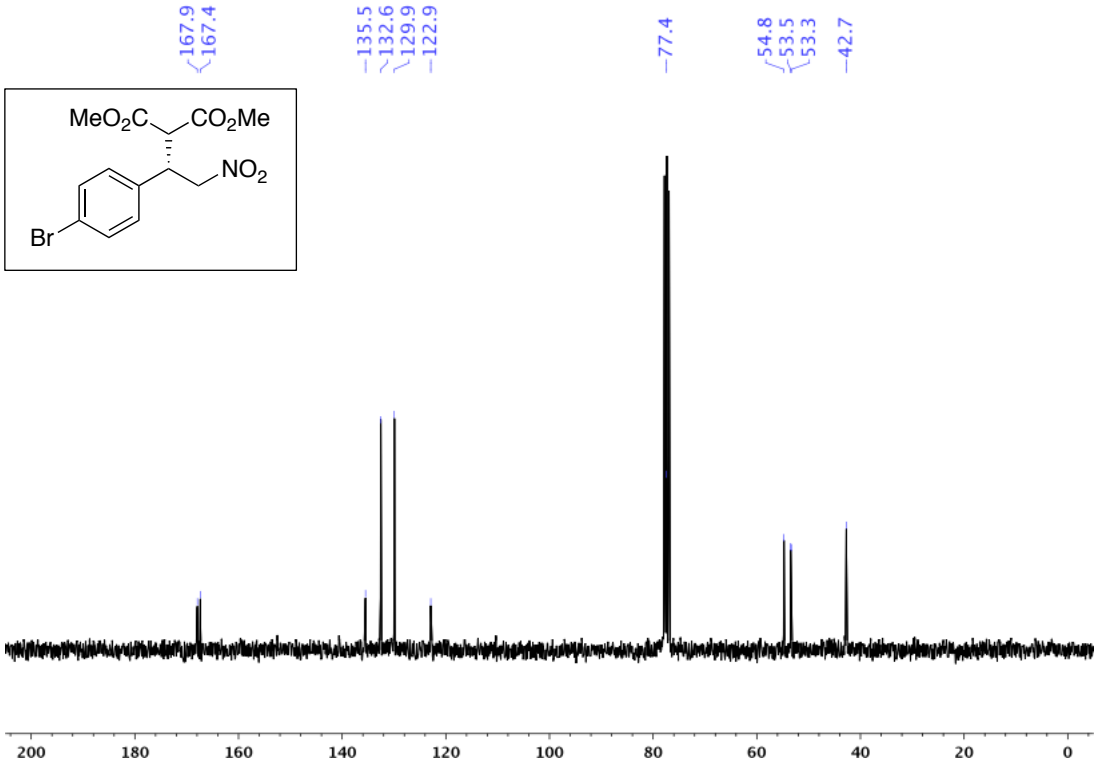


Prepared according to **SP1**. Purified by flash chromatography (Hexane/EtOAc, 3:1). Obtained as a white solid, 80% isolated yield (58 mg), in 90% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.46 (2H, d, J = 8.5 Hz, Ar*H*), 7.12 (2H, d, J = 8.5 Hz, Ar*H*), 4.94–4.80 (2H, m, C*H*$_2$), 4.25–4.17 (1H, m, C*H*), 3.82 (1H, d, *J* = 9.0 Hz, C*H*), 3.76 (3H, s, OC*H*$_3$), 3.59 (3H, s, OC*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.9 (*C*O_2), 167.4 (*C*O_2), 135.5 (Ar*C*), 132.6 (Ar*C*H), 129.9 (Ar*C*H), 122.9 (Ar*C*), 77.4 (*C*H_2), 54.8, 53.5, 53.3, 42.7 (*C*H).

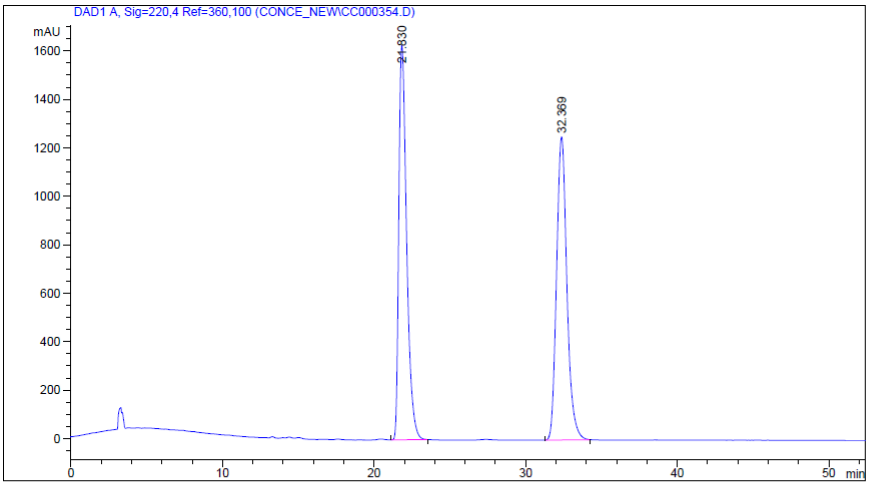
^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C NMR (75 MHz, $CDCl_3$):



Product **4d** was obtained in a maximum of 90% *ee*. The optical purity was determined by HPLC on a chiralcel AD-H column (hexane/2-propanol 90:10), flow rate 1.0 mL/min, λ = 220 nm, 25 ºC.



Area Percent Report

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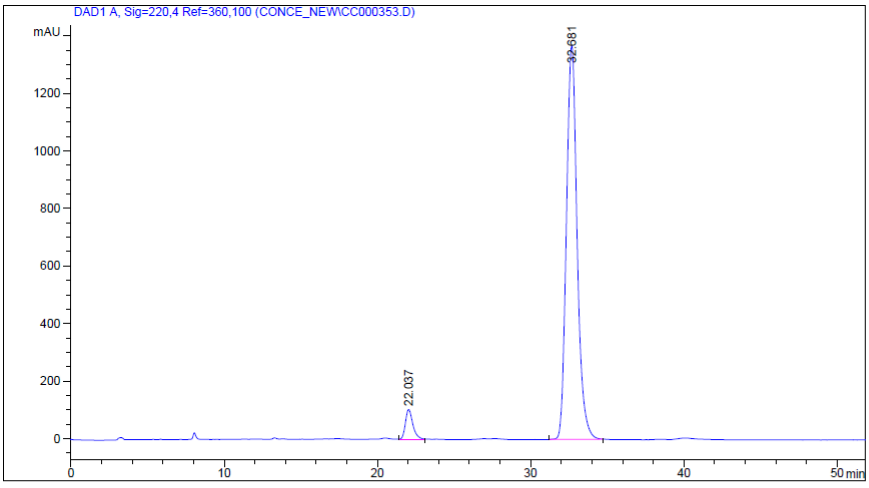
Totals : 1.17716e5 2879.31177



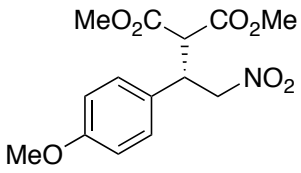
Area Percent Report

Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.037	BB	0.5158	3470.36646	103.34965	4.9556
2	32.681	BB	0.7510	6.65585e4	1369.57458	95.0444

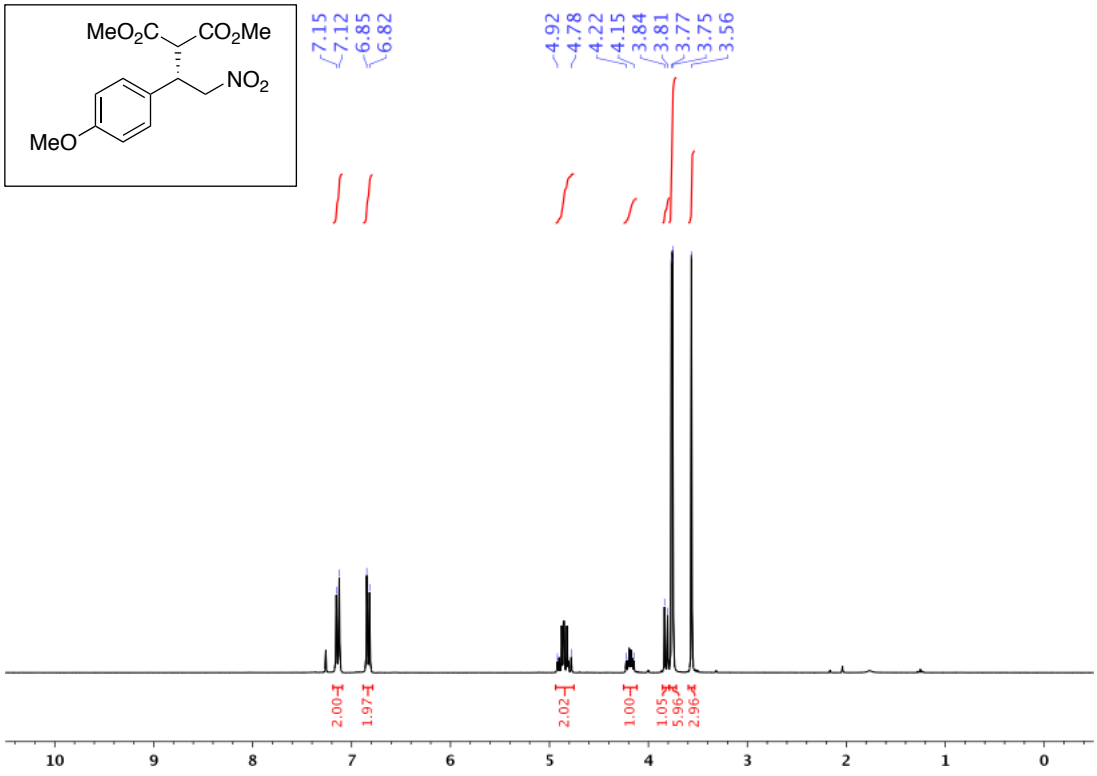
Totals : 7.00289e4 1472.92423

(*S*)-Dimethyl 2-(2-nitro-1-(4-methoxyphenyl)-ethyl)malonate (4e)[4]

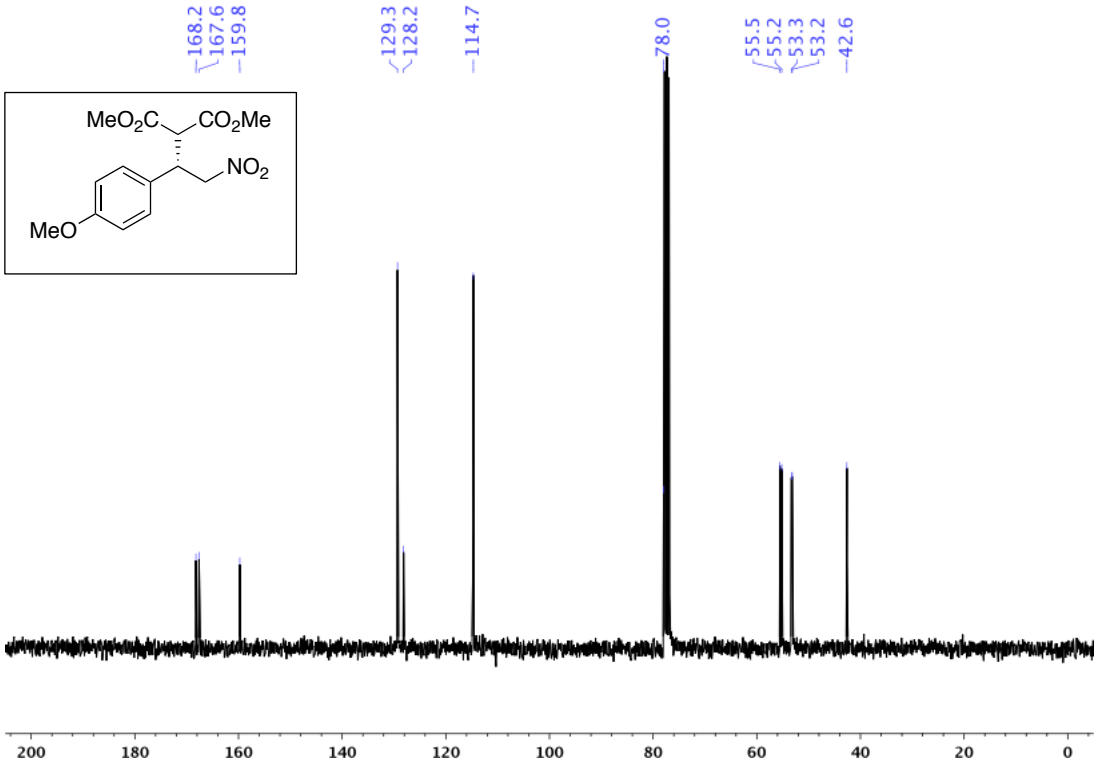


Prepared according to **SP1**. Purified by flash chromatography (Hexane/EtOAc, 3:1). Obtained as a white solid, 76% isolated yield (47 mg), in 80% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.14 (2H, d, J = 8.7 Hz, Ar*H*), 6.83 (2H, d, J = 8.7 Hz, Ar*H*), 4.92–4.78 (2H, m, C*H*$_2$), 4.22–4.15 (1H, m, C*H*), 3.82 (1H, d, *J* = 9.2 Hz, C*H*), 3.77 (3H, s, OC*H*$_3$), 3.75 (3H, s, OC*H*$_3$), 3.56 (3H, s, OC*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 168.2 (*C*O$_2$), 167.6 (*C*O$_2$), 159.8 (Ar*C*), 129.3 (Ar*C*H), 128.2 (Ar*C*), 114.7 (Ar*C*H), 78.0 (*C*H$_2$) 55.5, 55.2, 53.3, 53.2, 42.6 (*C*H).

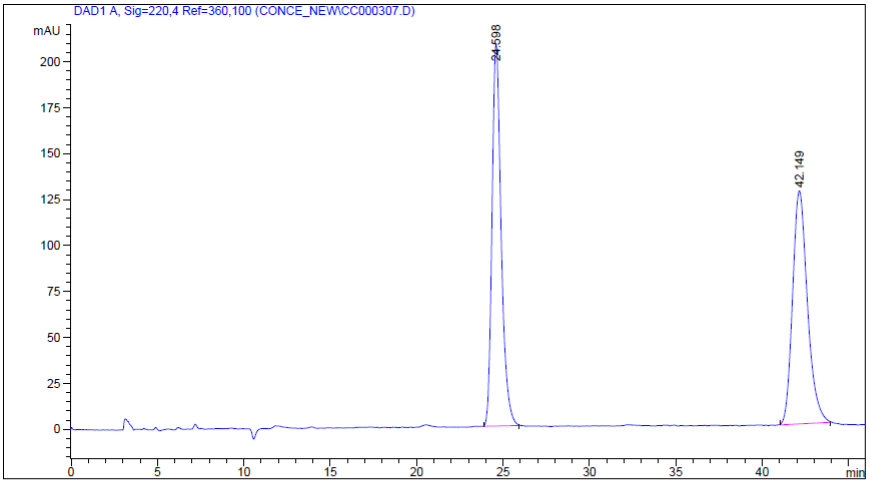
^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C NMR (75 MHz, $CDCl_3$):



Product **4e** was obtained in a maximum of 80% *ee*. The optical purity was determined by HPLC on a chiralcel AD-H column (hexane/2-propanol 90:10), flow rate 1.0 mL/min, λ = 220 nm, 25 ºC.

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==================================================================
                    Area Percent Report
==================================================================
Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  24.598 BB    0.5598 7652.36182  207.73535  50.2225
   2  42.149 BB    0.8801 7584.56494  126.76157  49.7775

Totals :                 1.52369e4   334.49693

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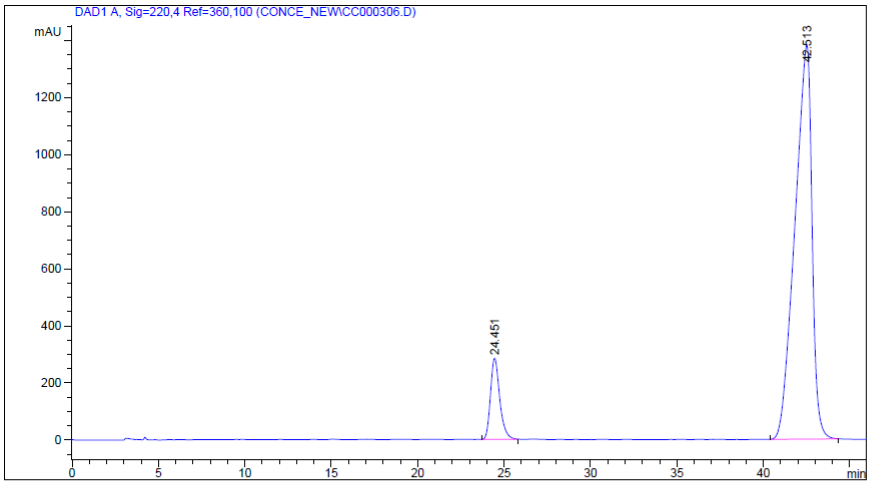


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==================================================================
                    Area Percent Report
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Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  24.451 BB    0.5689 1.06108e4   284.63068  10.0364
   2  42.513 BB    0.9776 9.51120e4  1380.91406  89.9636

Totals :                 1.05723e5  1665.54474

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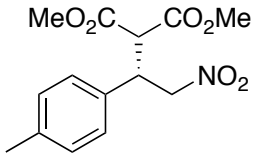
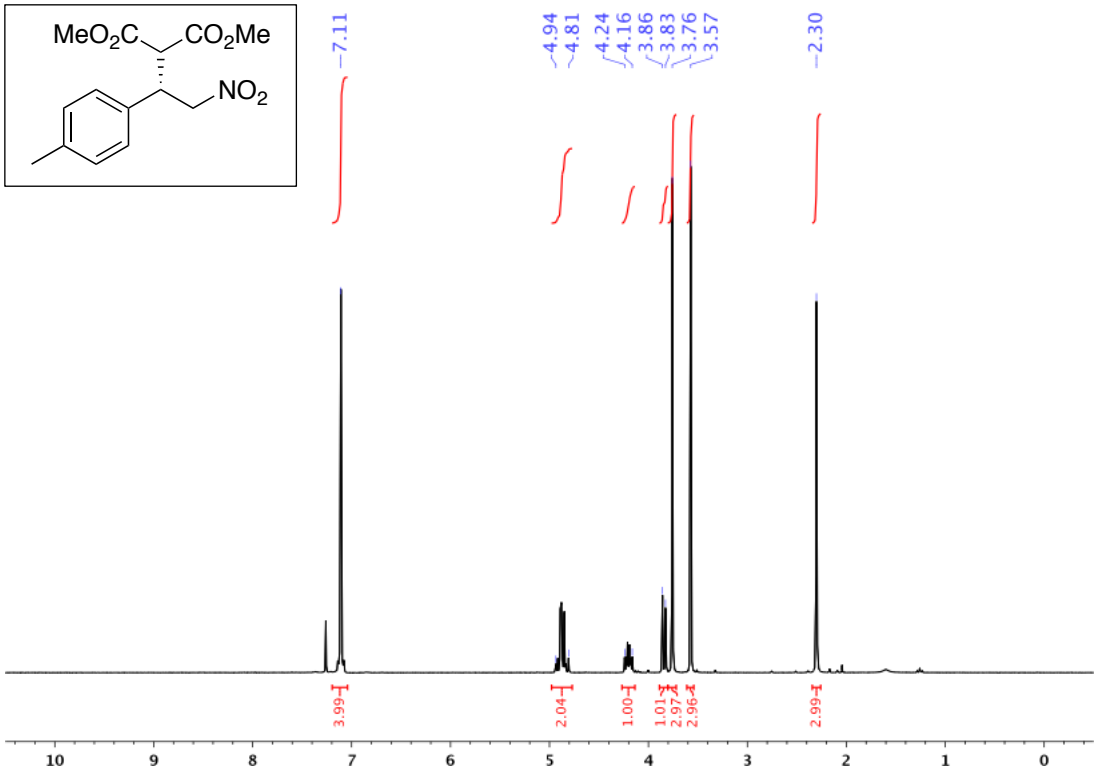
(*S*)-Dimethyl 2-(2-nitro-1-(4-methylphenyl)-ethyl)malonate (4f)[4]

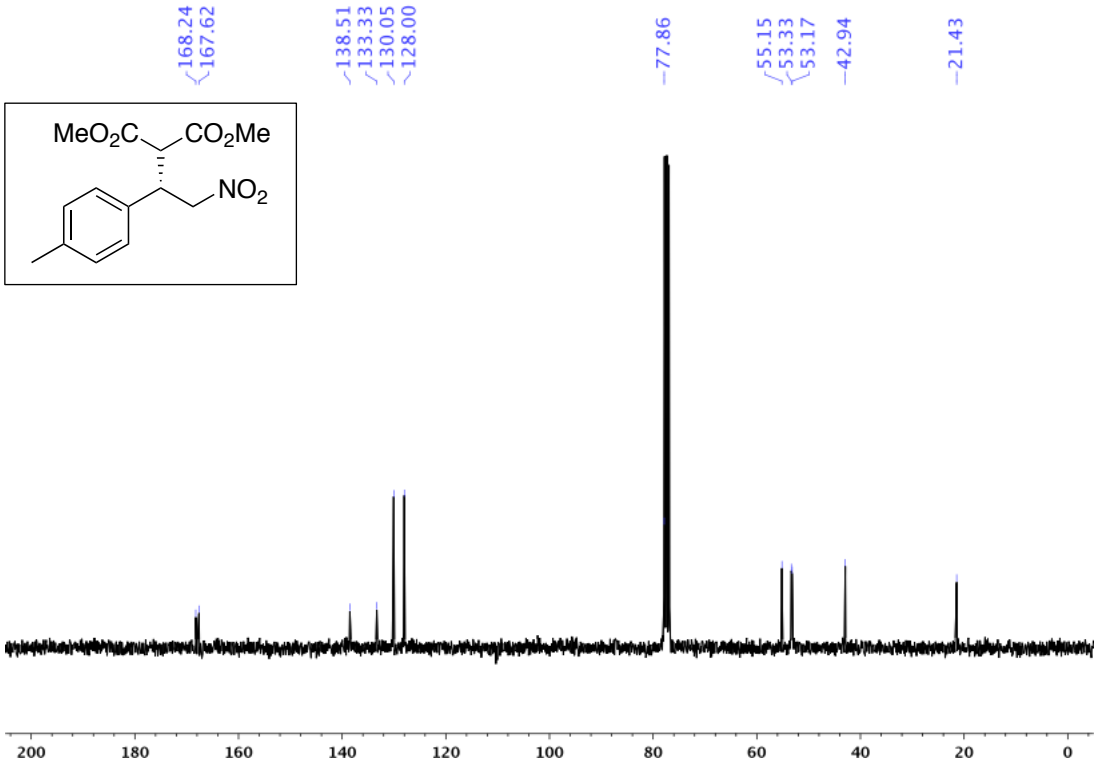


Prepared according to **SP1**. Purified by flash chromatography (Hexane/EtOAc, 3:1). Obtained as a white solid, 65% isolated yield (38 mg), in 85% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.11 (4H, m, Ar*H*), 4.94–4.81 (2H, m, CH_2), 4.24–4.16 (1H, m, C*H*), 3.84 (1H, d, J = 9.1 Hz, C*H*), 3.76 (3H, s, OCH_3), 3.57 (3H, s, OCH_3), 2.30 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 168.2 (*C*O_2), 167.6 (*C*O_2), 138.5 (Ar*C*), 133.3 (Ar*C*), 130.1 (Ar*C*H), 128.0 (Ar*C*H), 77.9 (*C*H_2) 55.2, 53.3, 53.2, 42.9 (*C*H), 21.4 (*C*H_3).

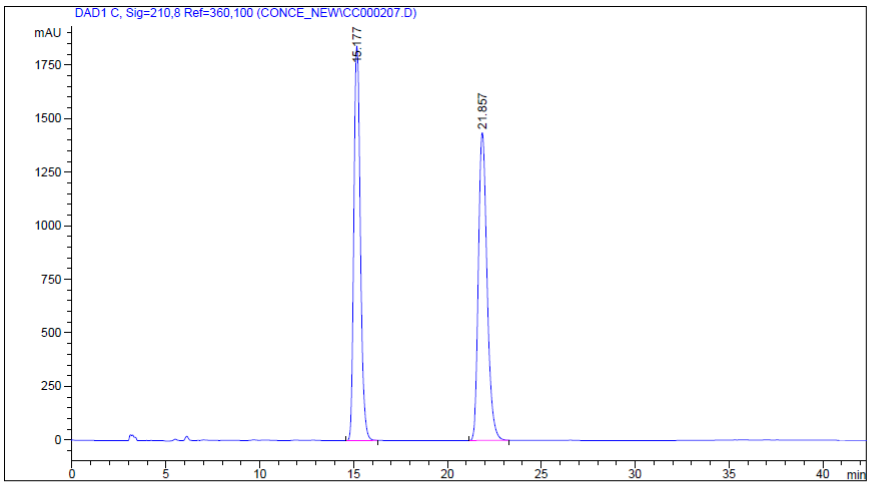
^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C NMR (75 MHz, $CDCl_3$):



Product **4f** was obtained in a maximum of 80% *ee*. The optical purity was determined by HPLC on a chiralcel AD-H column (hexane/2-propanol 90:10), flow rate 1.0 mL/min, λ = 210 nm, 25 ºC.

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================================================================================
                            Area Percent Report
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Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.177 BB    0.3780 4.45002e4  1841.18921  49.0239
   2  21.857 BB    0.4977 4.62722e4  1436.76794  50.9761

Totals :                  9.07724e4  3277.95715

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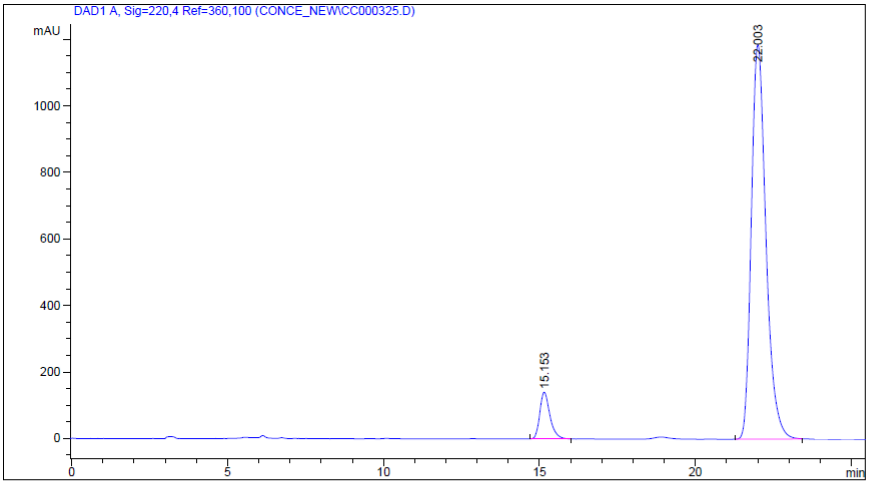


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================================================================================
                            Area Percent Report
================================================================================
Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  15.153 BB    0.3443 3188.12622  140.72917   7.6145
   2  22.003 BB    0.5002 3.86811e4  1186.91919  92.3855

Totals :                  4.18692e4  1327.64836

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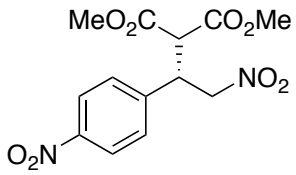
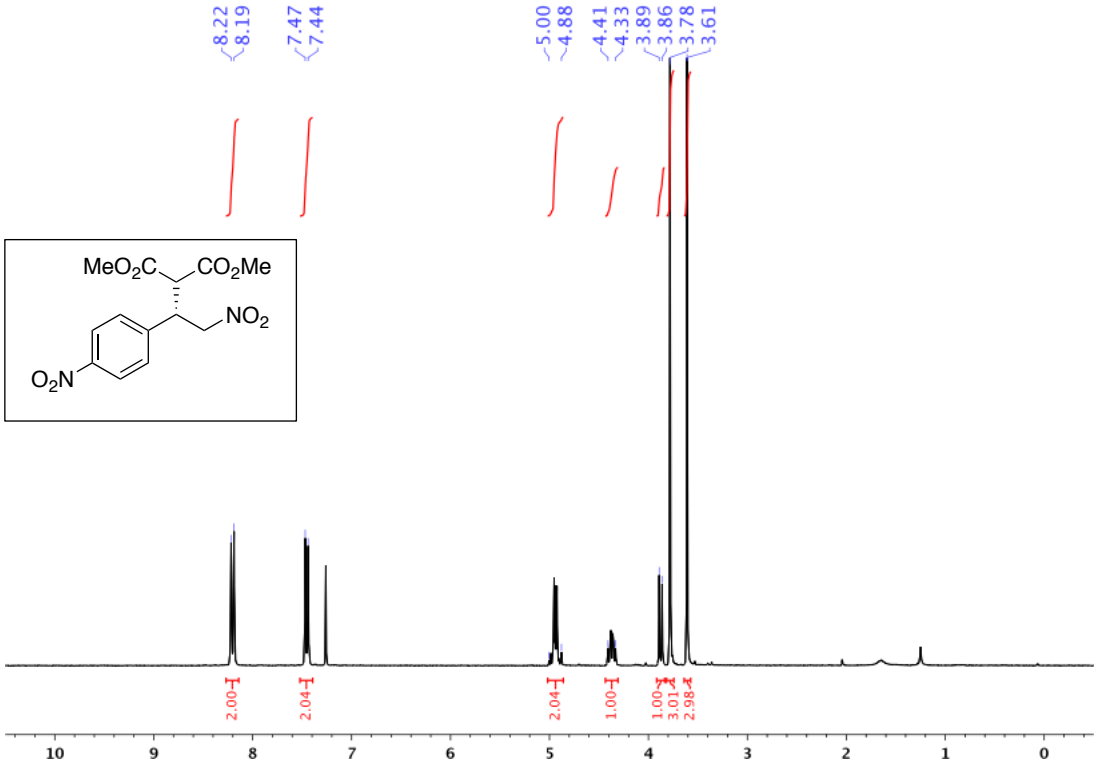
(*S*)-Dimethyl 2-(2-nitro-1-(4-nitrophenyl)-ethyl)malonate (4g)[6]



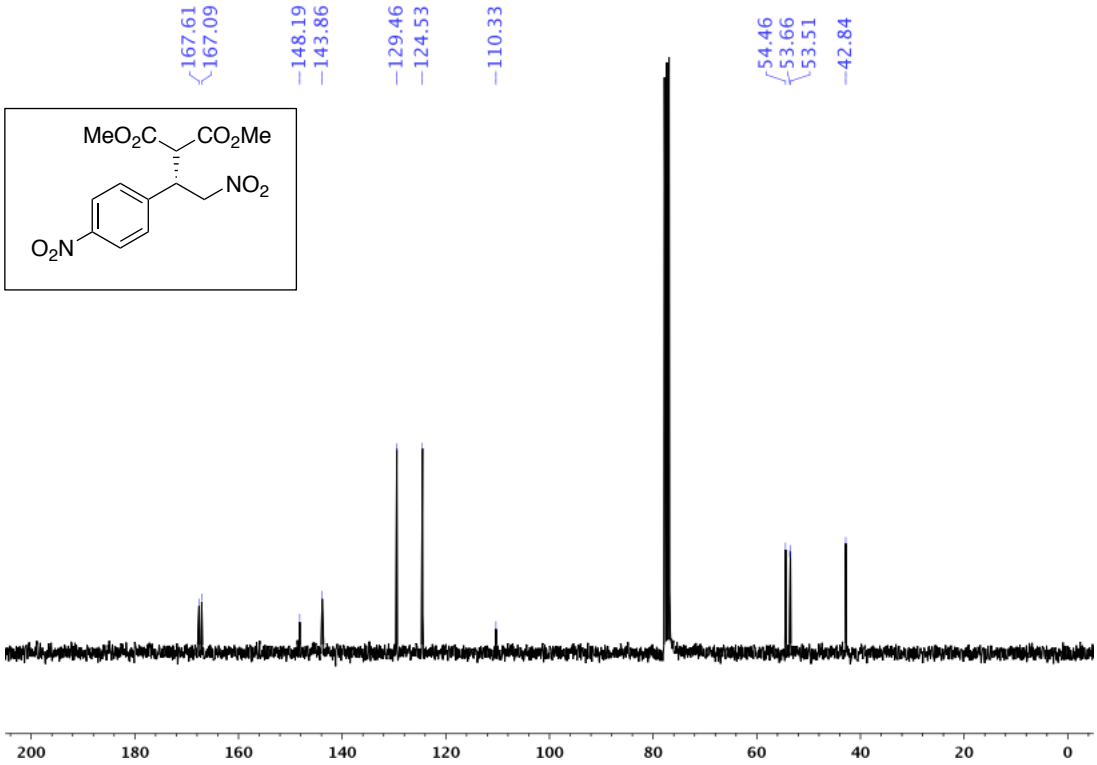
Prepared according to **SP1**. Purified by flash chromatography (Hexane/EtOAc, 3:1). Obtained as a white solid, 98% isolated yield (64 mg), in 82% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.20 (2H, d, J = 8.7 Hz, Ar*H*), 7.45 (2H, d, J = 8.7 Hz, Ar*H*), 5.00–4.88 (2H, m, CH_2), 4.41–4.33 (1H, m, C*H*), 3.88 (1H, d, J = 8.8 Hz, C*H*), 3.78 (3H, s, OCH_3), 3.61 (3H, s, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.6 (*C*O_2), 167.1 (*C*O_2), 148.2 (Ar*C*), 143.9 (Ar*C*), 129.5 (Ar*C*H), 124.5 (Ar*C*H), 110.3 (*C*H_2), 54.5, 53.7, 53.5, 42.8 (*C*H).

[6] Li, X.- J.; Liu, K.; Ma, H.; Nie, J.; Ma, J.- A. *Synlett* **2008**, 3242–3246.

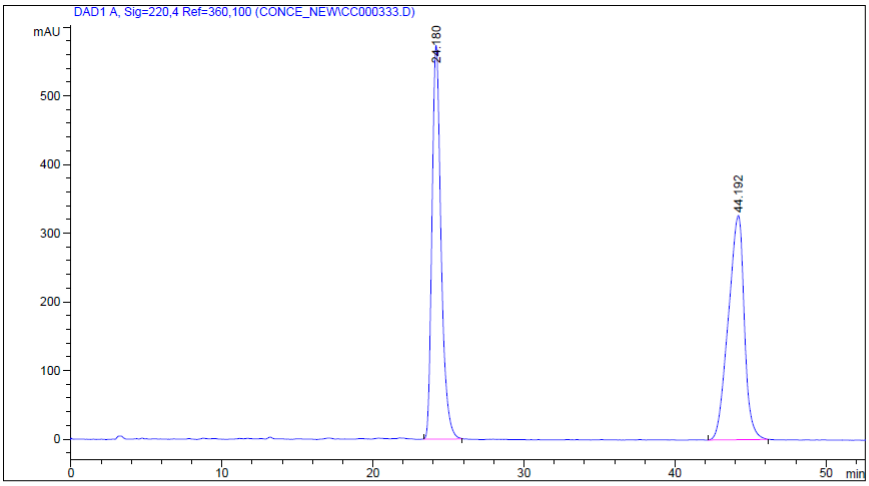
^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C NMR (75 MHz, $CDCl_3$):



Product **4g** was obtained in a maximum of 82% *ee*. The optical purity was determined by HPLC on a chiralcel AD-H column (hexane/2-propanol 80:20), flow rate 1.0 mL/min, λ = 210 nm, 25 ºC.

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==================================================================
                     Area Percent Report
==================================================================
Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  24.180 BB    0.6416 2.39610e4   573.34003  49.9736
   2  44.192 BB    1.0732 2.39863e4   326.46536  50.0264

Totals :                 4.79473e4   899.80539

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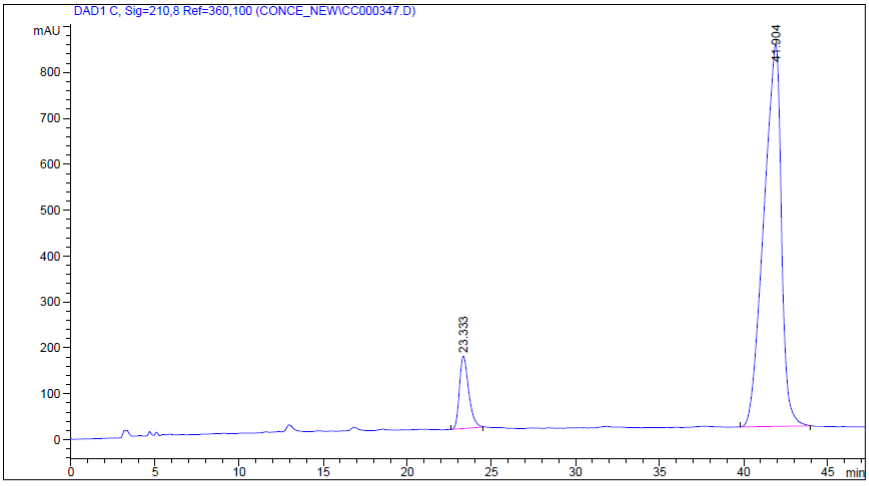


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==================================================================
                     Area Percent Report
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Signal 1: DAD1 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  23.333 BB    0.5781 6024.91553  157.58005   9.0684
   2  41.904 BB    0.9988 6.04135e4   832.32391  90.9316

Totals :                 6.64384e4   989.90396

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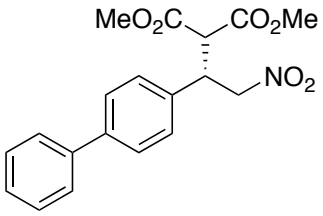
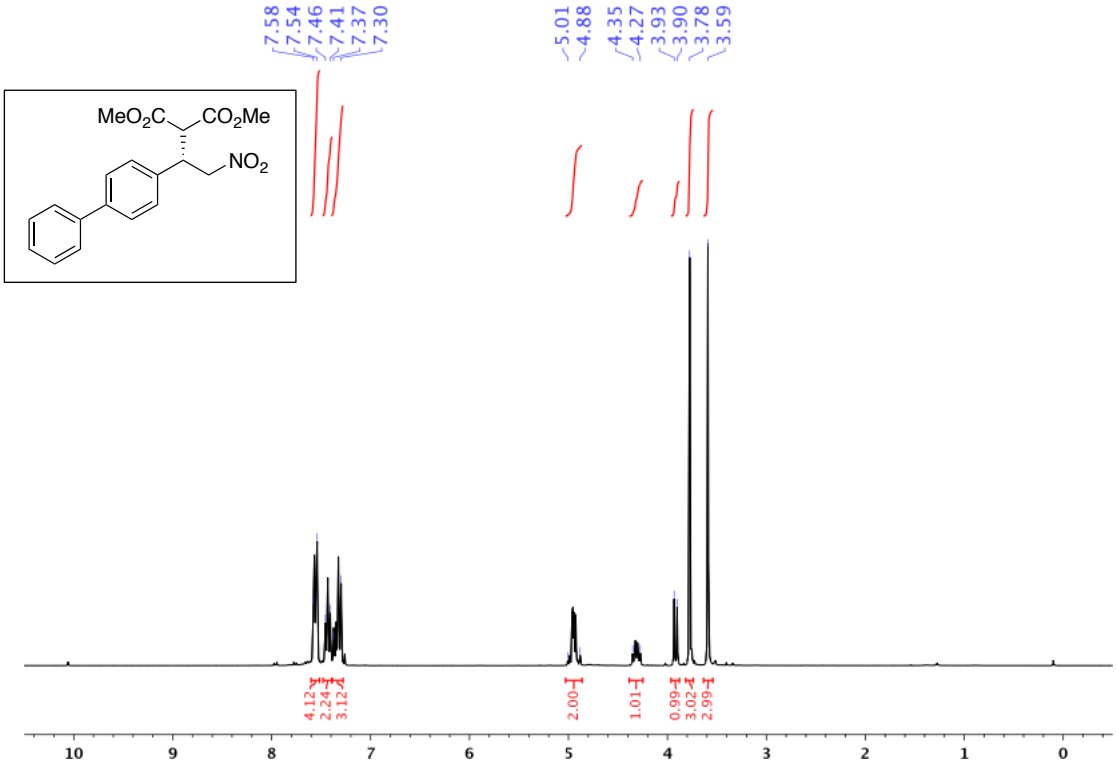
(*S*)-Dimethyl 2-(2-nitro-1-(4-phenylphenyl)-ethyl)malonate (4h)[7]



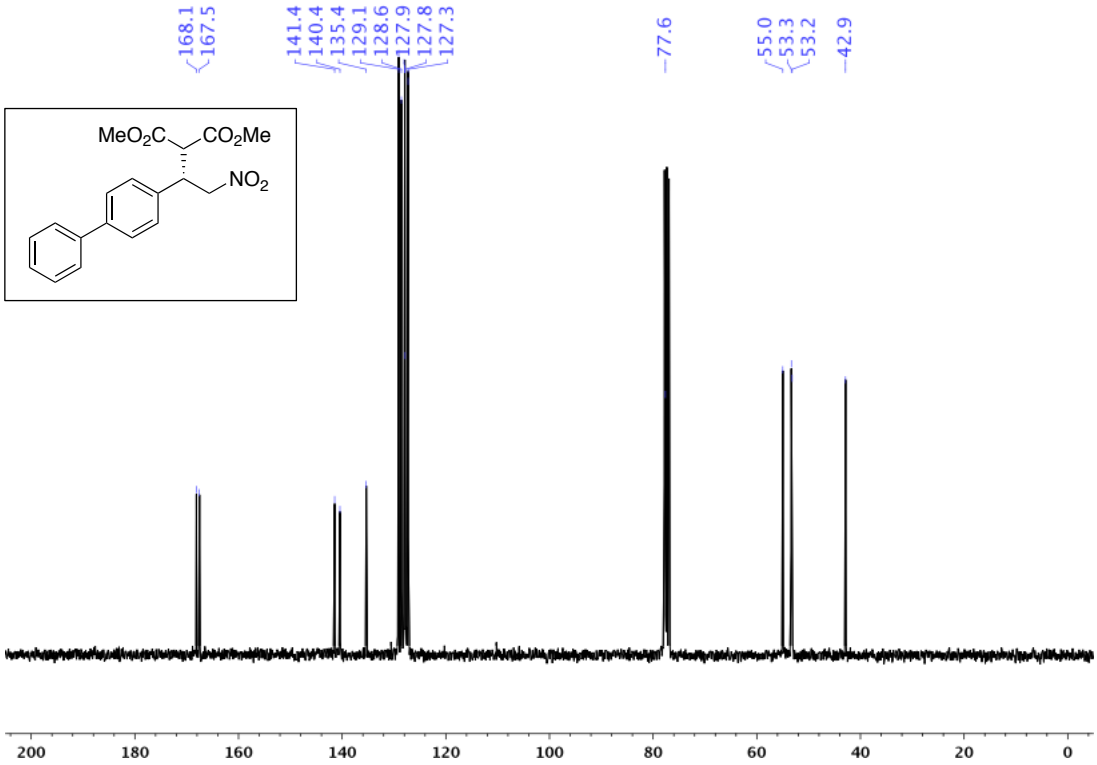
Prepared according to **SP1**. Purified by flash chromatography (Hexane/EtOAc, 3:1). Obtained as a white solid, 99% isolated yield (71 mg), in 85% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.58–7.54 (4H, m, Ar*H*), 7.46–7.41 (2H, m, Ar*H*), 7.37–7.30 (3H, m, Ar*H*), 5.01–4.88 (2H, m, CH_2), 4.35–4.27 (1H, m, C*H*), 3.92 (1H, d, *J* = 9.0 Hz, C*H*), 3.78 (3H, s, OCH_3), 3.59 (3H, s, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 168.1 (*C*O_2), 167.5 (*C*O_2), 141.4 (Ar*C*), 140.4 (Ar*C*), 135.4 (Ar*C*), 129.1 (Ar*C*H), 128.6 (Ar*C*H), 127.9 (Ar*C*H), 127.8 (Ar*C*H), 127.3 (Ar*C*H), 77.6 (*C*H_2), 55.0 (*C*H_3), 53.3 (*C*H_3), 53.2 (*C*H_3), 42.9 (*C*H).

[7] Yang, L.; Zhao, L.; Zhou, Z.; He, C.; Sun, H.; Duan, C. *Dalton Trans.* **2017**, *46*, 4086–4092.

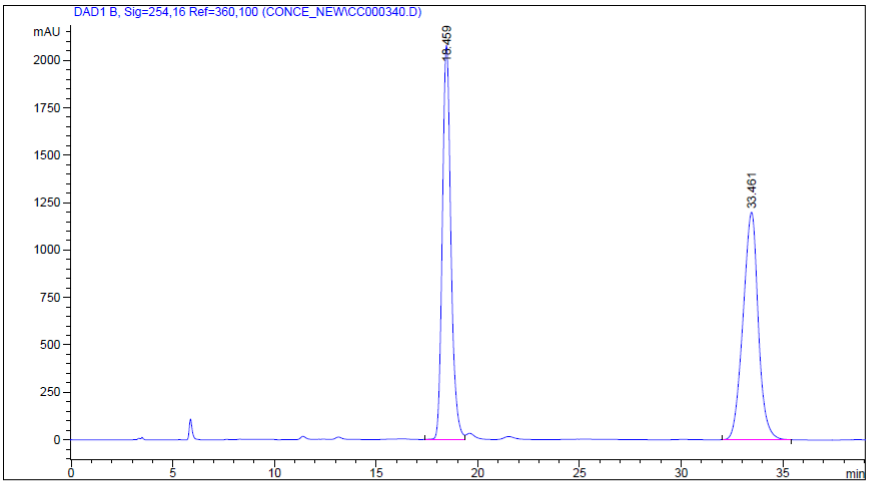
^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C NMR (75 MHz, $CDCl_3$):



Product **4h** was obtained in a maximum of 85% *ee*. The optical purity was determined by HPLC on a chiralcel AD-H column (hexane/2-propanol 85:15), flow rate 1.0 mL/min, λ = 220 nm, 25 ºC.

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==================================================================================
                                Area Percent Report
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Signal 1: DAD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.459 BV    0.4485 6.10543e4  2079.48242  49.3677
   2  33.461 BB    0.7969 6.26182e4  1199.69556  50.6323

Totals :                  1.23672e5  3279.17798

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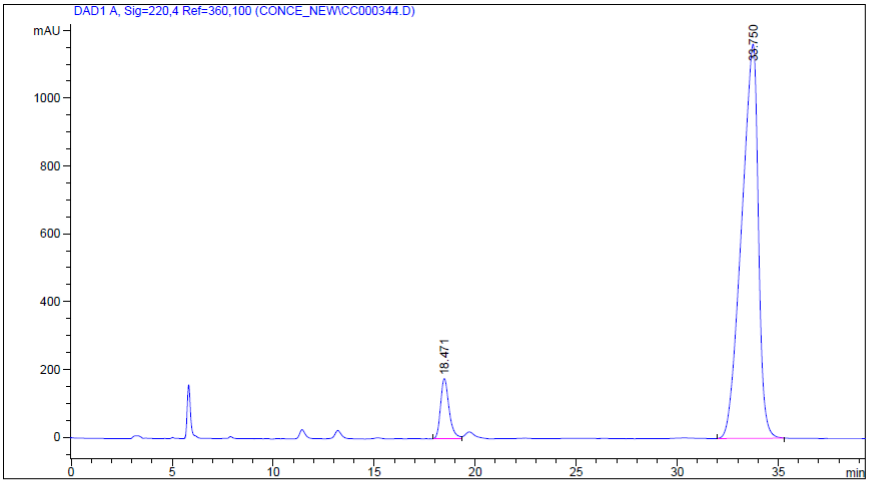


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==================================================================================
                                Area Percent Report
==================================================================================
Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  18.471 BV    0.4493 5226.53662  177.60291   7.2551
   2  33.750 BB    0.8547 6.68131e4  1162.12122  92.7449

Totals :                  7.20397e4  1339.72412

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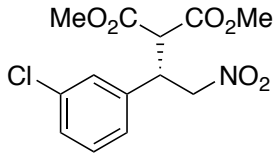
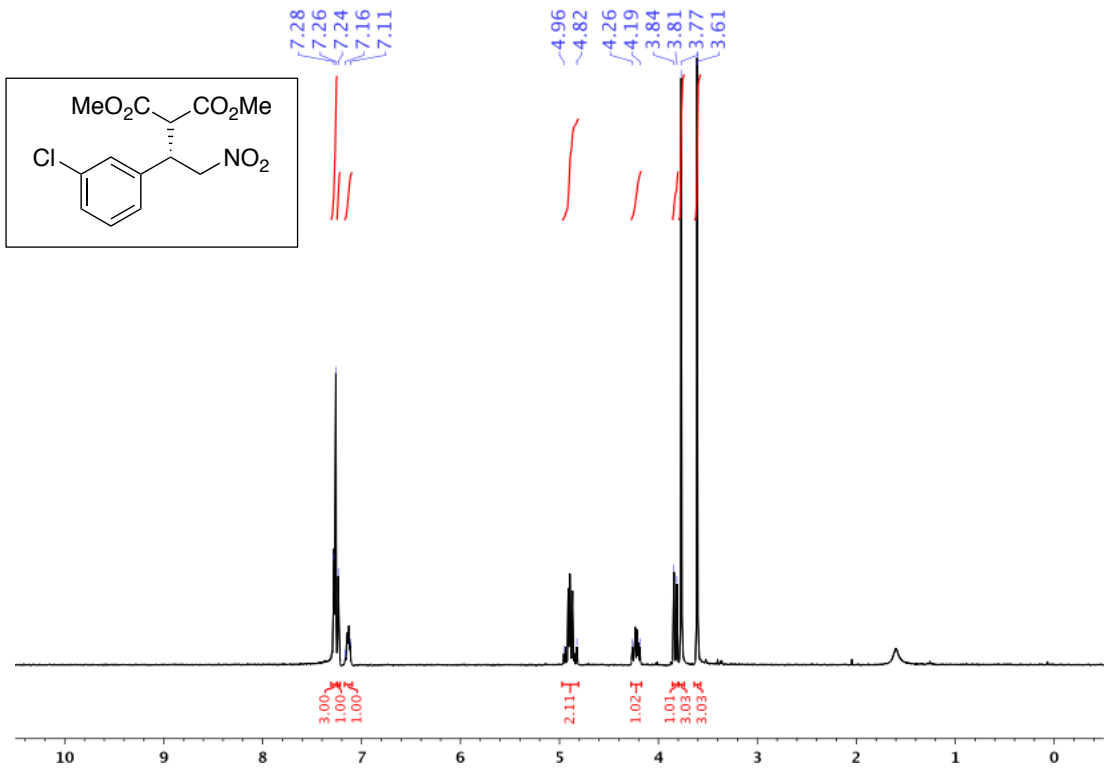
(*S*)-Dimethyl 2-(2-nitro-1-(3-chlorophenyl)-ethyl)malonate (4i)[8]



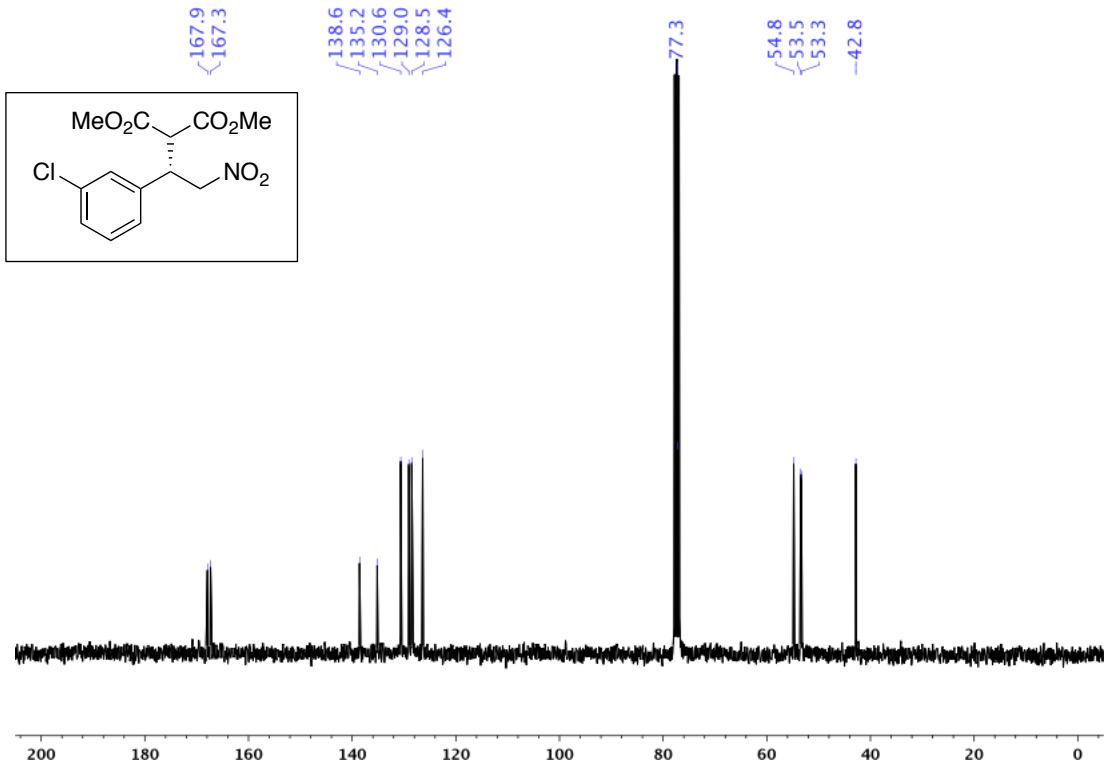
Prepared according to **SP1**. Purified by flash chromatography (Hexane/EtOAc, 3:1). Obtained as a white solid, 96% isolated yield (61 mg), in 86% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.28–7.26 (2H, m, Ar*H*), 7.24 (1H, broad, s, Ar*H*), 7.16–7.11 (1H, m, Ar*H*), 4.96–4.82 (2H, m, CH_2), 4.26–4.19 (1H, m, C*H*), 3.83 (1H, d, *J* = 8.8 Hz, C*H*), 3.77 (3H, s, OCH_3), 3.61 (3H, s, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.9 (*C*O_2), 167.3 (*C*O_2), 138.6 (Ar*C*), 135.2 (Ar*C*), 130.6 (Ar*C*H), 129.0 (Ar*C*H), 128.5 (Ar*C*H), 126.4 (Ar*C*H), 77.3 (*C*H_2) 54.8, 53.5, 53.3, 42.8 (*C*H).

[8] García–García, P.; Zagdoun, A.; Copéret, C.; Lesage, A.; Díaz, U.; Corma, A. *Chem. Sci.* **2013**, *4*, 2006–2012.

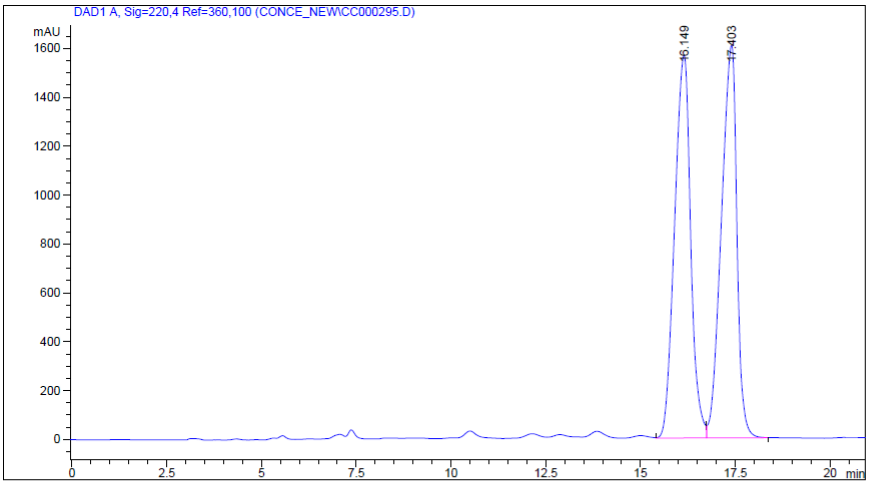
^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C NMR (75 MHz, $CDCl_3$):



Product **4i** was obtained in a maximum of 86% *ee*. The optical purity was determined by HPLC on a chiralcel AD-H column (hexane/2-propanol 90:10), flow rate 1.0 mL/min, λ = 220 nm, 25 ºC.

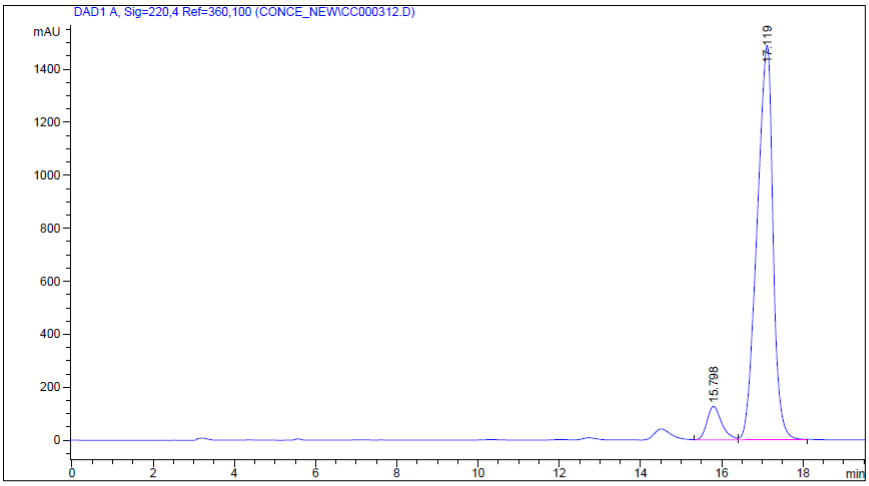


Area Percent Report

Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.149	VV	0.4606	4.62545e4	1565.80969	50.3987
2	17.403	VB	0.4486	4.55226e4	1606.64026	49.6013

Totals : 9.17772e4 3172.44995



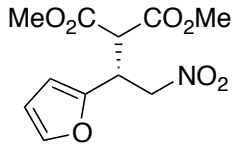
Area Percent Report

Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.798	VV	0.3803	3157.91968	126.05495	7.2243
2	17.119	VB	0.4219	4.05544e4	1488.11365	92.7757

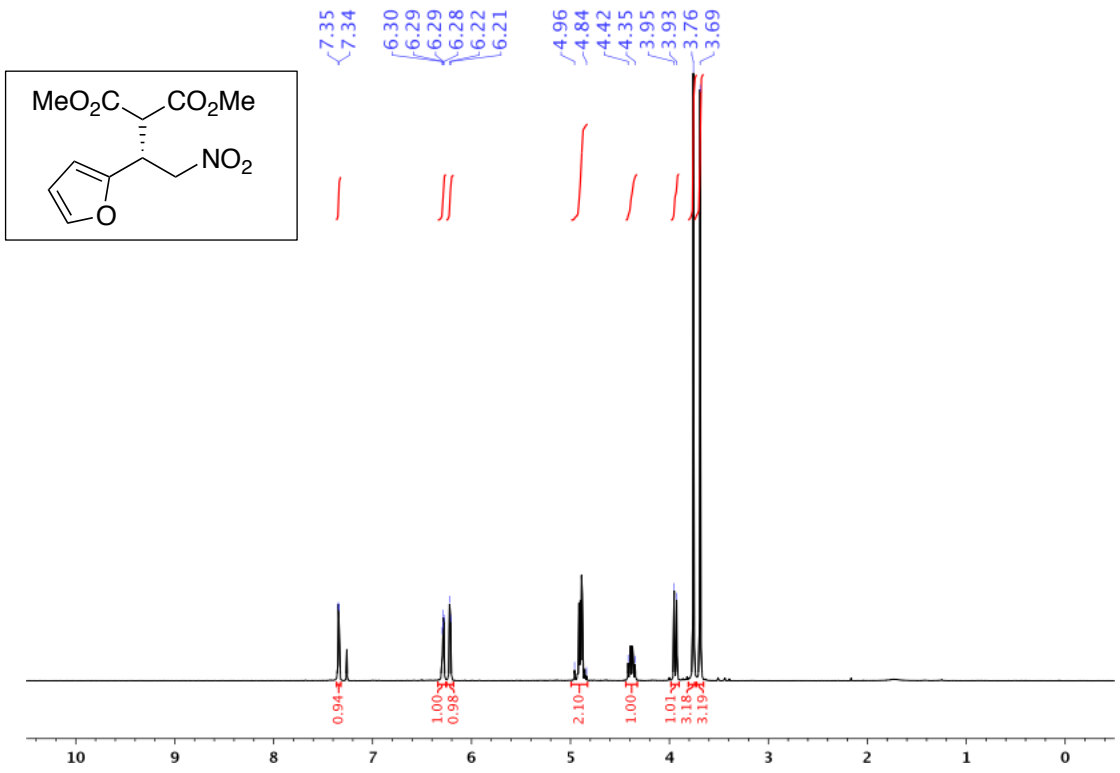
Totals : 4.37123e4 1614.16859

(*R*)-Dimethyl 2-(1-(furan-2-yl)-2-nitroethyl)malonate (4j)[4]

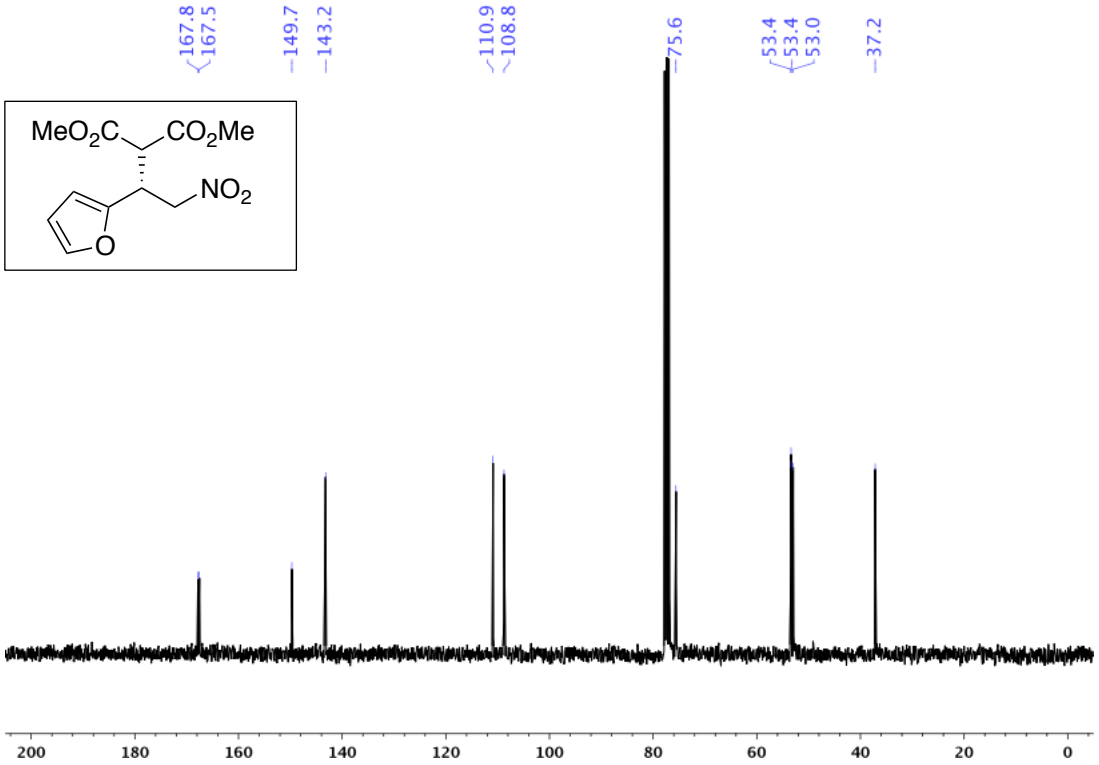


Prepared according to **SP1**. Purified by flash chromatography (Hexane/EtOAc, 3:1). Obtained as a white solid, 71% isolated yield (38 mg), in 73% *ee*; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.35–7.34 (1H, m, Ar*H*), 6.29 (1H, dd, *J* = 3.3, 1.9 Hz, Ar*H*), 6.22 (1H, d, *J* = 3.3 Hz, Ar*H*), 4.96–4.84 (2H, m, CH_2), 4.42–4.35 (1H, m, C*H*), 3.94 (1H, d, *J* = 7.8 Hz, C*H*), 3.76 (3H, s, OCH_3), 3.69 (3H, s, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 167.8 (*C*O_2), 167.5 (*C*O_2), 149.7 (Ar*C*), 143.2 (Ar*C*H), 110.9 (Ar*C*H), 108.8 (Ar*C*H), 75.6 (*C*H_2), 53.4, 53.4, 53.0, 37.2 (*C*H).

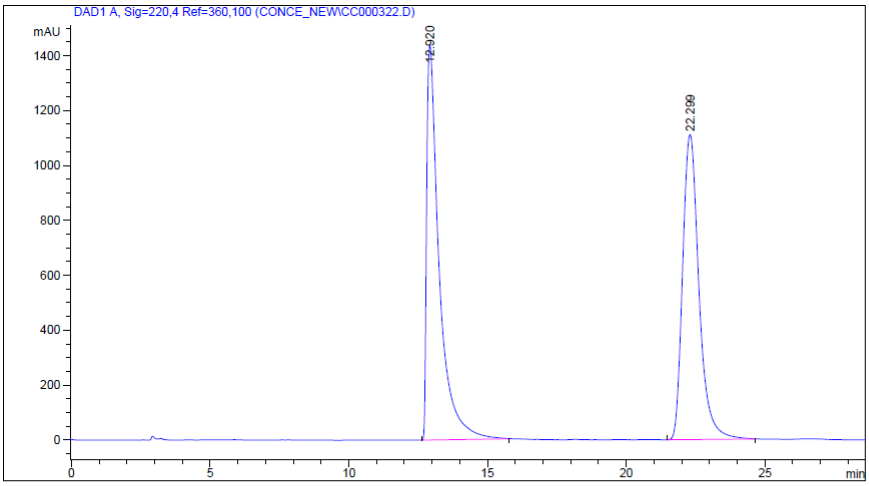
^{1}H NMR (300 MHz, $CDCl_3$):



^{13}C NMR (75 MHz, $CDCl_3$):



Product **4j** was obtained in a maximum of 71% *ee*. The optical purity was determined by HPLC on a chiralcel OD-H column (hexane/2-propanol 90:10), flow rate 1.0 mL/min, λ = 220 nm, 25 ºC.

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==================================================================================
                                Area Percent Report
==================================================================================
Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.920 BB    0.4557 4.50664e4  1437.59412  49.8282
   2  22.299 BB    0.6306 4.53772e4  1110.87109  50.1718

Totals :                 9.04436e4  2548.46521

==================================================================================
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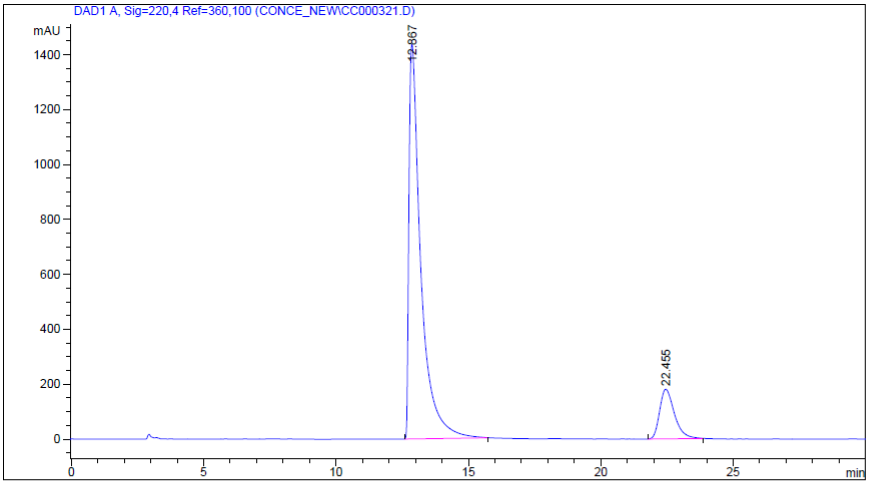


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==================================================================================
                                Area Percent Report
==================================================================================
Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  12.867 BB    0.4566 4.48966e4  1436.61572  86.5001
   2  22.455 BB    0.5902 7006.95508  180.79405  13.4999

Totals :                 5.19036e4  1617.40977

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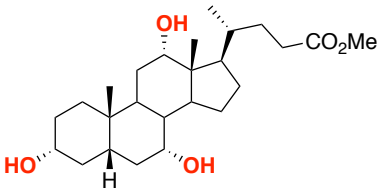
SYNTHETIC PROCEDURES AND SPECTROSCOPIC CHARACTERIZATION OF CATALYSTS 5-17



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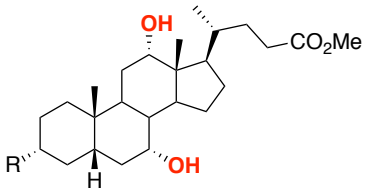
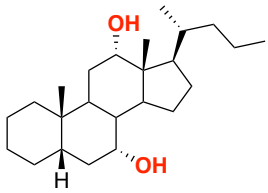


6: OAc
7: OBz
8: OPiv
9: OTBDMS



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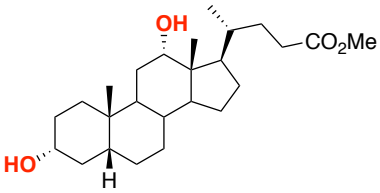

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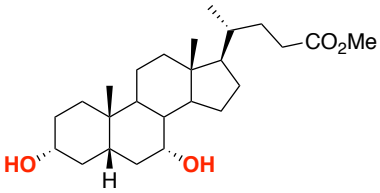

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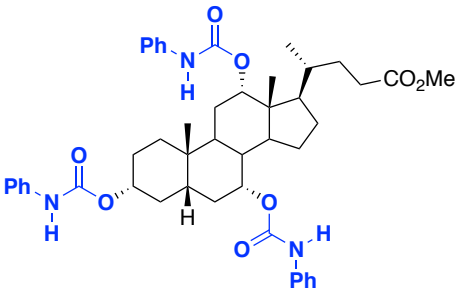

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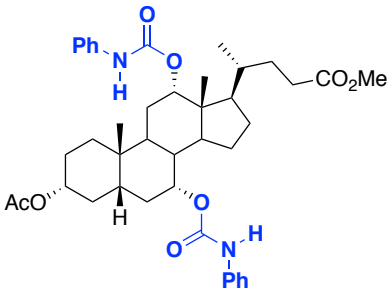

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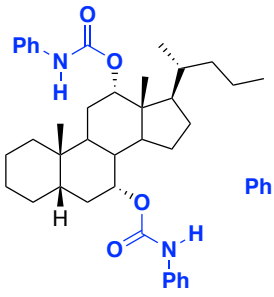

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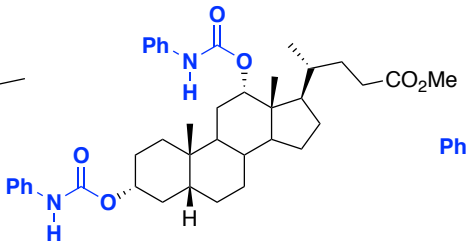

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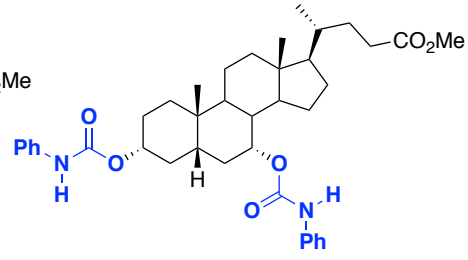
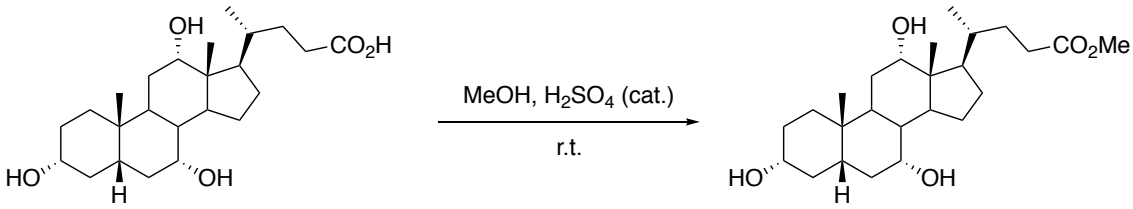


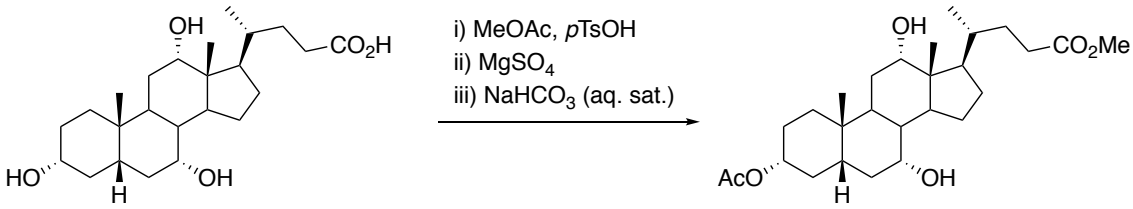
17

Catalyst 9 (methyl cholate).[9]



cholic acid (1) **5**

Catalyst 10.[10]

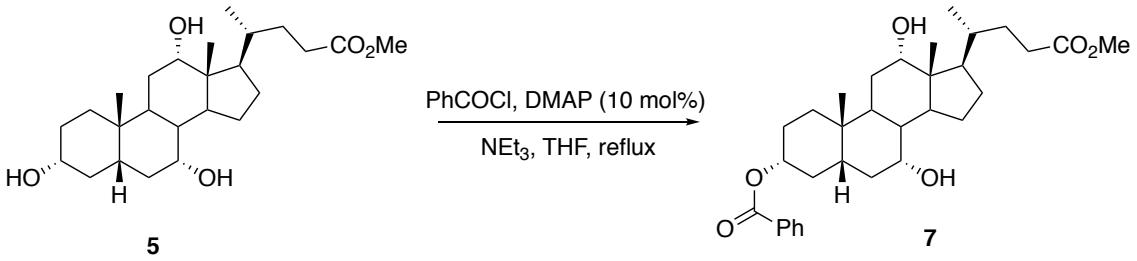


cholic acid (1) **6**

[9] Fieser, L. F.; Rajagopalan, S. *J. Am. Chem. Soc.* **1950**, *72*, 5530–5536.

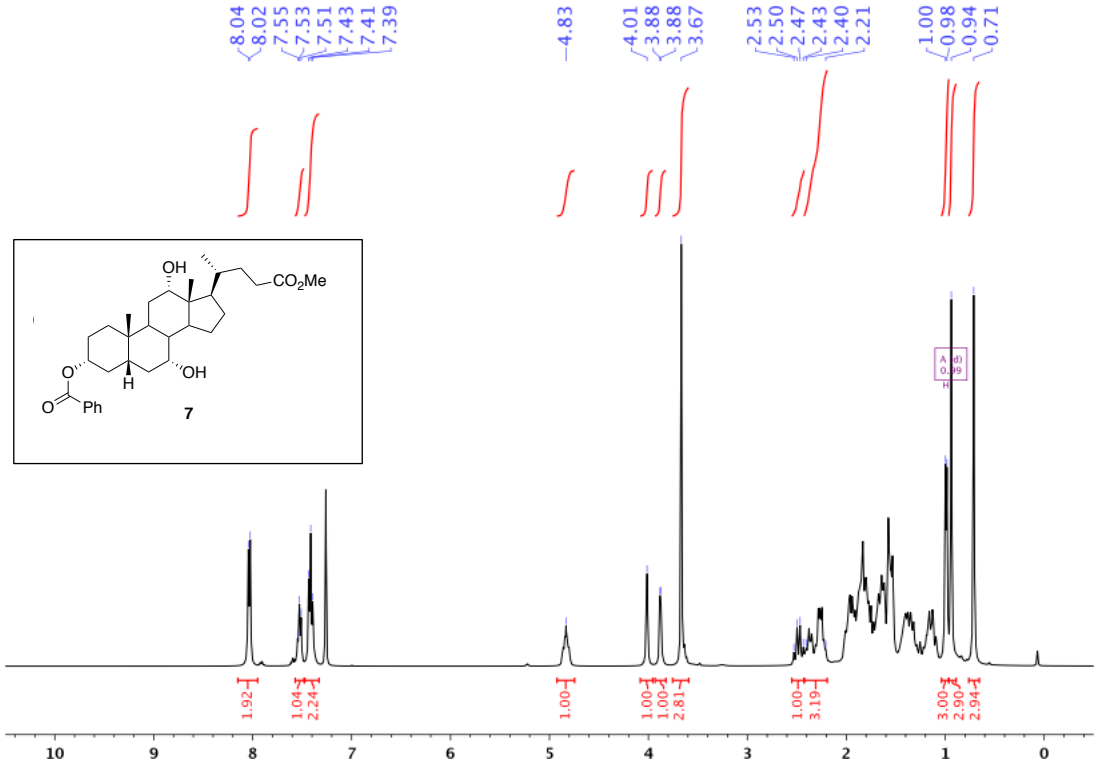
[10] del Amo, V.; Siracusa, L.; Markidis, T.; Baragaña, B.; Bhattarai, K.- M.; Galobardes, M.; Naredo, G.; Pérez-Payán, M. N.; Davis, A. P. *Org. Biomol. Chem.* **2004**, *2*, 3320–3328.

Catalyst 7.

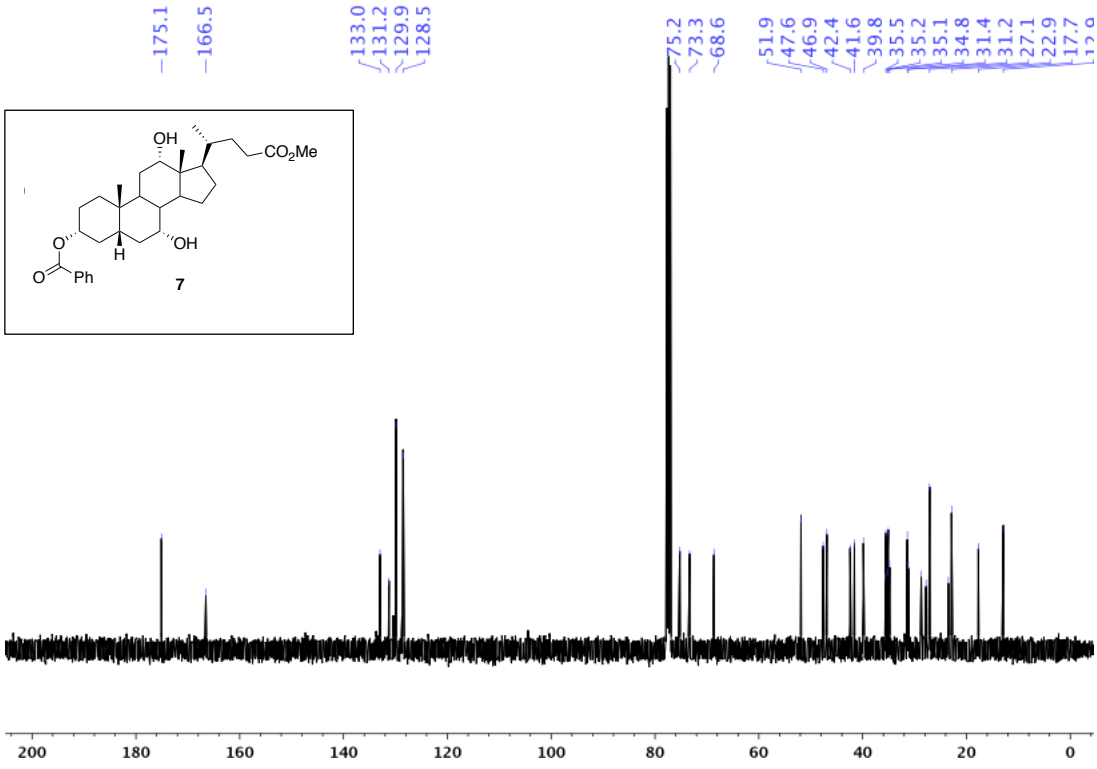


Methyl cholate, **5** (300 mg, 0.71 mmol) and DMAP (8.6 mg, 0.07 mmol) were dissolved in dry THF (5 mL) and dry NEt_3 (0.15 mL, 109 mg, 1.07 mmol). To the former solution was added benzoyl chloride (0.11 mL, 130 mg, 0.92 mmol), dissolved in 2 mL of dry THF. The resulting mixture was refluxed for 24 h before the solvent and volatiles were evacuated and the resulting crude material was extracted from EtOAc (15 mL), washed with 0.1 M HCl (aq., sat., 10 mL) and dried ($MgSO_4$). Flash chromatography (Hex/EtOAc, 3:1) afforded diol **7** (204 mg, 55% yield) as a white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.03 (2H, d, J = 7.4 Hz, ArC*H*), 7.53 (1H, t, J = 7.1 Hz, ArC*H*), 7.41 (2H, t, J = 7.5 Hz, ArC*H*), 4.83 (1H, m, C*H*OR), 4.01 (1H, s, C*H*OH), 3.88 (1H, m, C*H*OH), 2.48 (1H, q, J = 12.6 Hz, C*H*), 2.40–2.21 (3H, m, C*H* + CH_2), 0.99 (3H, d, J = 5.7 Hz, CH_3), 0.94 (3H, s, CH_3), 0.71 (3H, s, CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 175.5 (CO_2CH_3), 116.5 (PhCO_2), 133.0 (Ar*C*H), 131.2 (Ar*C*), 129.9 (Ar*C*H), 128.5 (Ar*C*H), 75.2 (*C*HOR), 73.3 (*C*HOH), 68.6 (*C*HOH), 51.9 (CO_2CH_3), 47.6 (*C*H), 46.9 (*C*), 42.4 (*C*H), 41.6 (*C*H), 39.8 (*C*H), 35.6 (CH_2), 35.5 (*C*H), 35.2 (CH_2), 35.1 (*C*), 34.8 (CH_2), 31.4 (CH_2), 31.2 (CH_2), 28.7 (CH_2), 27.8 (CH_2), 27.1 (*C*H), 23.5 (CH_2), 22.8 (CH_3), 17.7 (CH_3), 12.9 (CH_3); MS (ESI+): *m/z* (%) = 1075 (40) $[M+M+Na]^+$, 549 (100) $[M+Na]^+$; HRMS (ESI+): *m/z* calcd. for $[C_{32}H_{46}O_6Na]^+$ 549.3192, found 549.3187.

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



^{13}C NMR (75 MHz, $CDCl_3$):



Mass Spectrum SmartFormula Report

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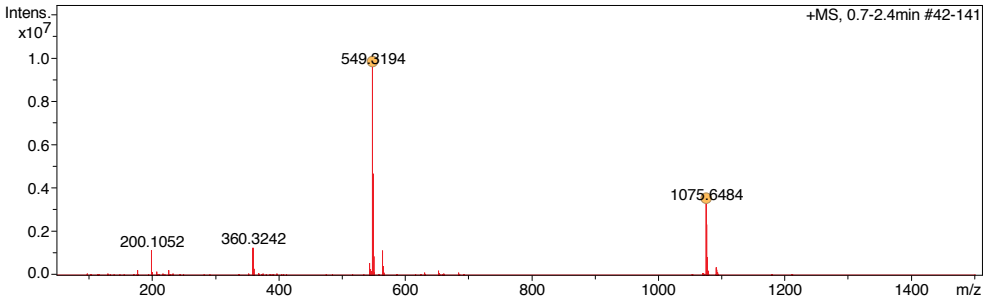
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	250 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
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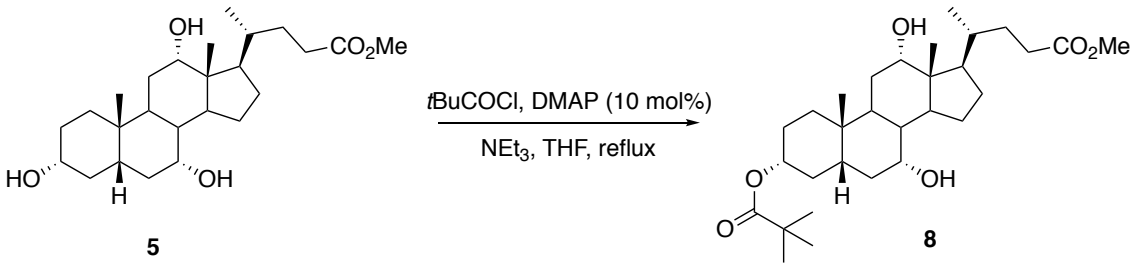
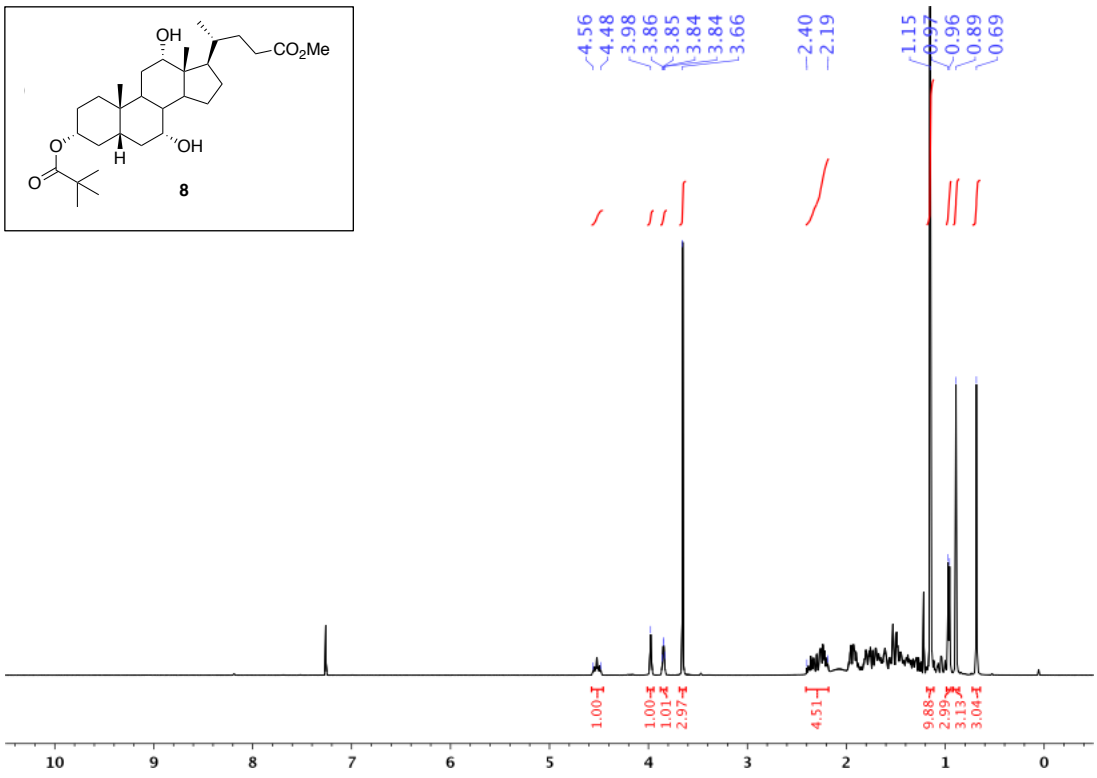
1075.6484	1	C64H92NaO12	1075.6481	-0.3	9.4	2	100.00	19.0	even	ok	2M+Na

Catalyst 8.

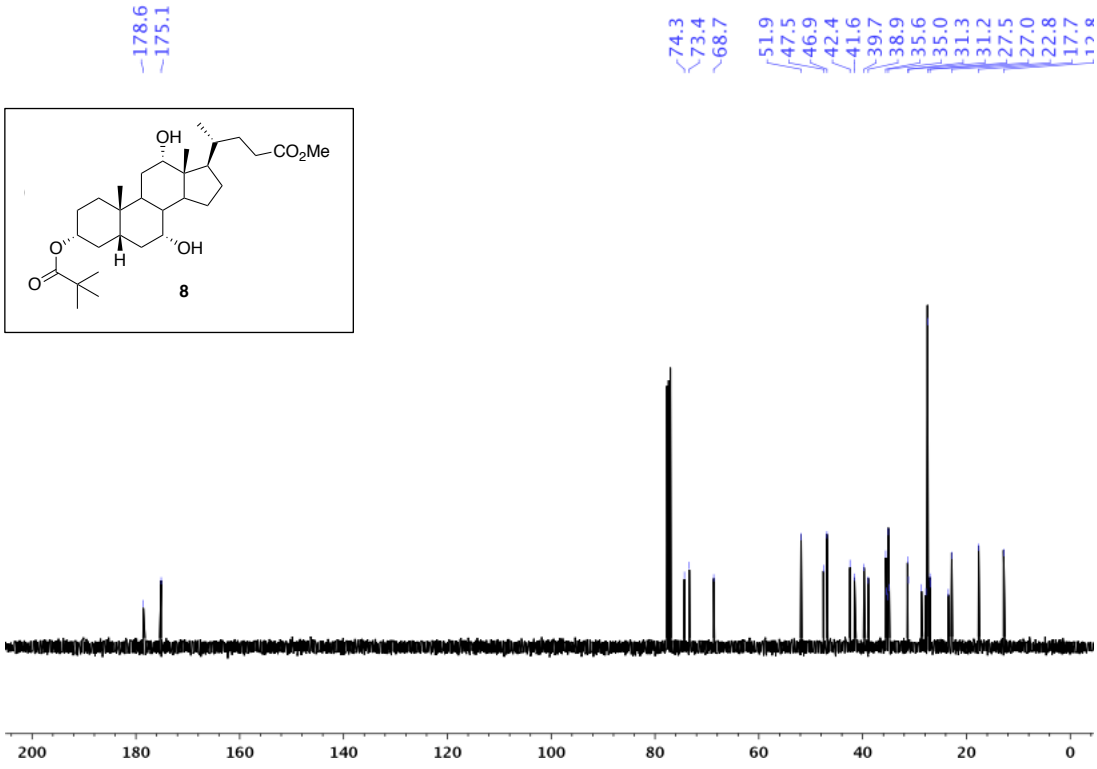


Methyl cholate, **5** (300 mg, 0.71 mmol) and DMAP (8.6 mg, 0.07 mmol) were dissolved in dry THF (5 mL) and dry NEt_3 (0.15 mL, 109 mg, 1.07 mmol). To the former solution was added pivaloyl chloride (0.11 mL, 111 mg, 0.92 mmol), dissolved in 2 mL of dry THF. The resulting mixture was refluxed for 24 h before the solvent and volatiles were evacuated and the resulting crude material was extracted from EtOAc (15 mL), washed with 0.1 M HCl (aq., sat., 10 mL) and dried (MgSO4). Flash chromatography (Hex/EtOAc, 3:1) afforded diol **8** (220 mg, 61% yield) as a white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.56–4.48 (1H, m, C*H*OR), 3.98 (1H, m, C*H*OH), 3.84 (1H, m, CHOH), 3.66 (3H, s, CO_2CH_3), 2.40–2.19 (4H, m, C*H* + CH_2), 1.15 (9H, s, $C(CH_3)_3$), 0.96 (3H, d, J = 6.2 Hz, CH_3), 0.89 (3H, s, CH_3), 0.69 (3H, s, CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 178.6 (*t*Bu*C*O_2), 175.1 (*C*O_2CH_3), 74.3 (*C*HOR), 73.4 (*C*HOH), 68.7 (*C*HOH), 51.9 (CO_2CH_3), 47.5 (*C*H), 46.9 (*C*), 42.4 (*C*H), 41.6 (*C*H), 39.7 (*C*H), 38.9 (*C*), 35.6 (*C*H), 35.4 (CH_2), 35.2 (CH_2), 35.0 (*C*), 34.9 (CH_2), 31.3 (CH_2), 31.2 (CH_2), 28.7 (CH_2), 27.8 (CH_2), 27.5 ($C(CH_3)_3$), 27.0 (*C*H), 27.0 (CH_2), 23.5 (CH_2), 22.8 (CH_3), 17.7 (CH_3), 12.8 (CH_3); MS (ESI+): *m/z* (%) = 545 (58) $[M+K]^+$, 529 (48) $[M+Na]^+$; HRMS (ESI+): *m/z* calcd. for $[C_{30}H_{50}O_6Na]^+$ 529.3505, found 529.3500.

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



Mass Spectrum SmartFormula Report

Analysis Info

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Method	MS 50-1000 orgánica.m	Operator	Demo User
Sample Name	30042018_MNF123	Instrument	impact II 1825265.10101
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.4 Bar
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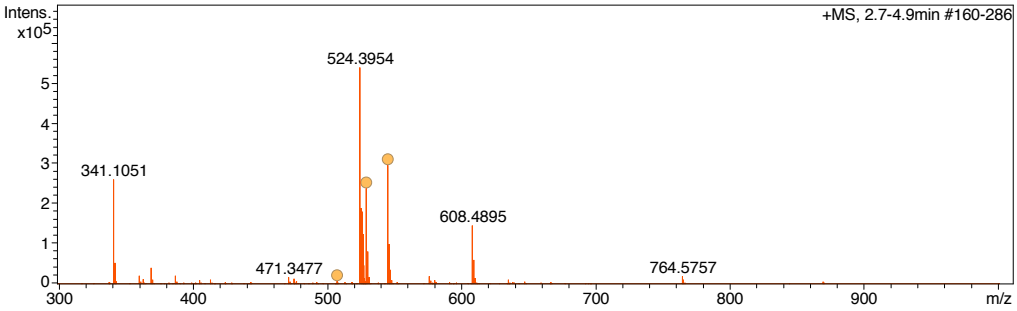
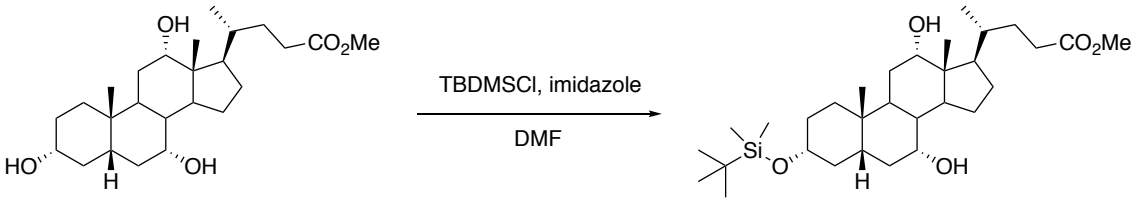
Scan Begin	300 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



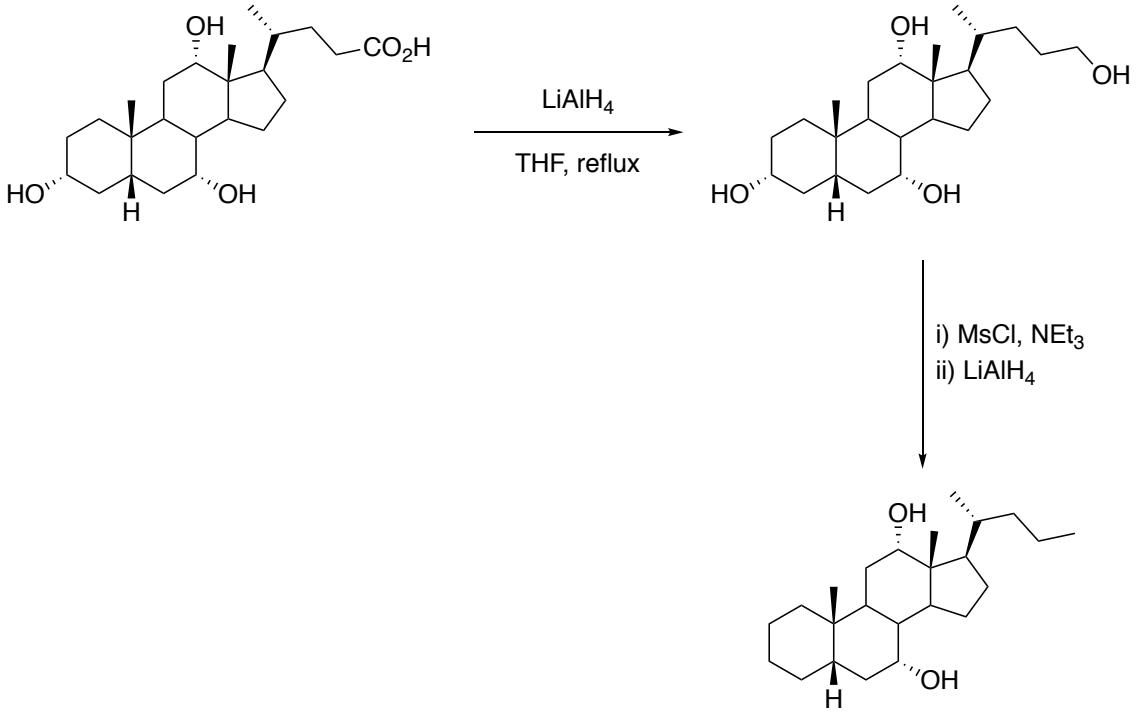
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
507.3689	1	C30H51O6	507.3680	-1.8	24.9	1	100.00	6.0	even	ok	M+H
529.3508	1	C30H50NaO6	529.3500	-1.6	3.0	1	100.00	6.0	even	ok	M+Na
545.3247	1	C30H50KO6	545.3239	-1.5	10.1	1	100.00	6.0	even	ok	M+K

Catalyst 9.[11]



5 **9**

Catalyst 10.[12]

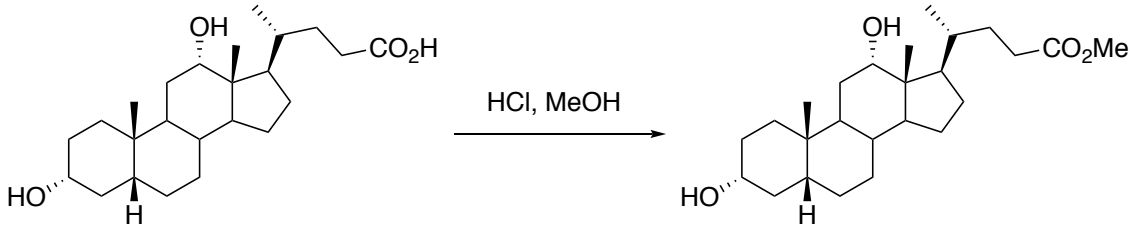


10

[11] Wilson, C. P.; Webb, S. J. *Chem. Commun.* **2008**, 4007–4009.

[12] Zhang, Q.; Ma, X.; Ward, A.; Hong, W.- X.; Jaakola, V.- P.; Stevens, R. C.; Finn, M. G.; Chang, G. *Angew. Chem. Int. Ed.* **2007**, *46*, 7023–7025.

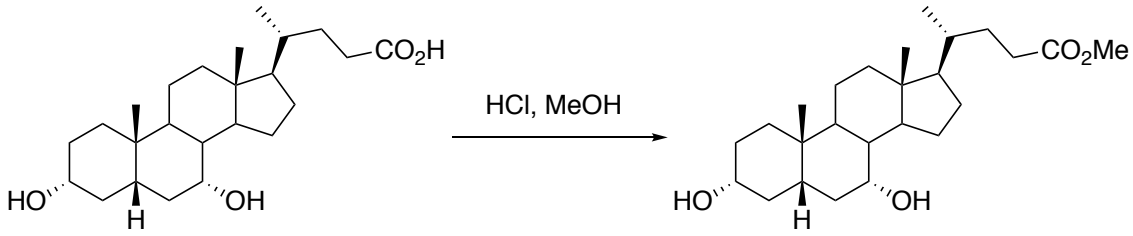
Catalyst 11.[13]



deoxycholic acid

11

Catalyst 12.[13]

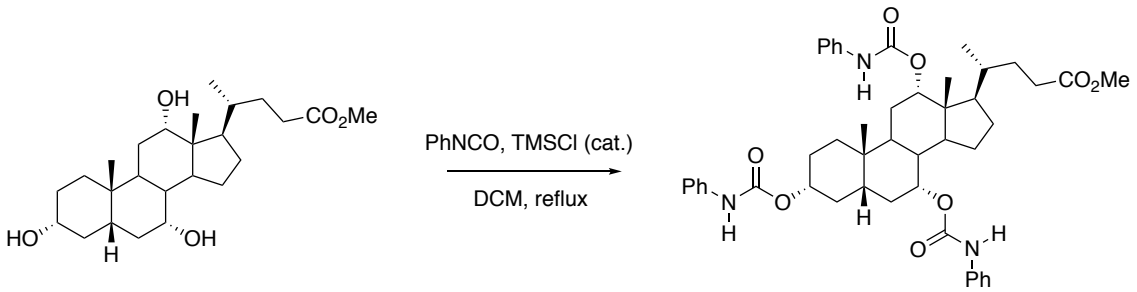


chenodeoxycholic acid

12

[13] Májer, F.; Sharma, R.; Mullins, C.; Keogh, L.; Phipps, S.; Duggan, S.; Kelleher, D.; Keely, S.; Long, A.; Radics, G.; Wang, J.; Gilmer, J. F. *Bioorg. Med. Chem.* **2014**, *22*, 256–268.

Catalyst 13.

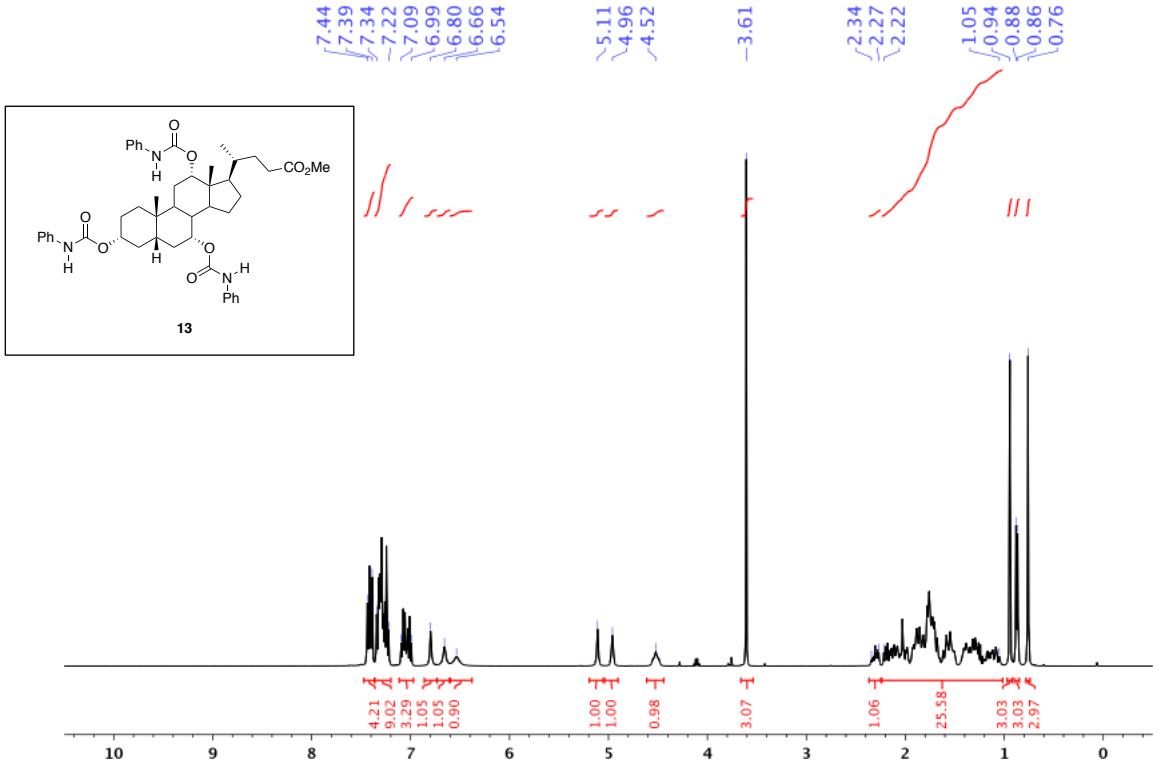


5 **13**

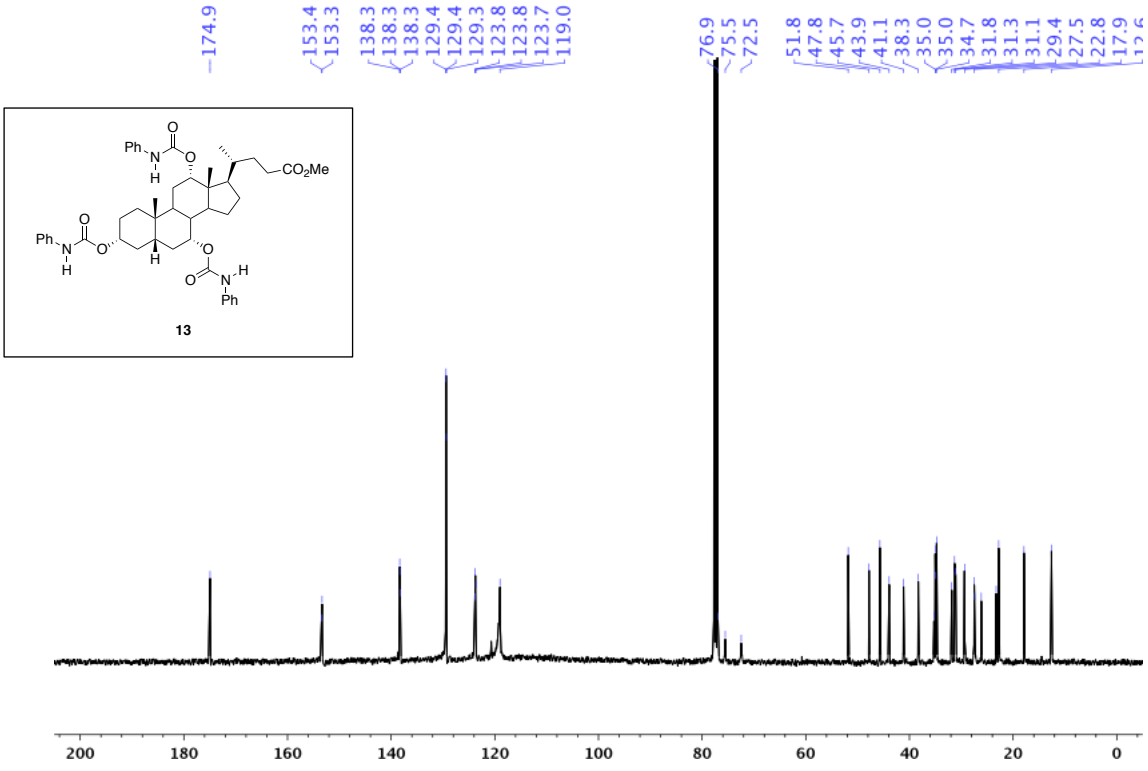
Methyl cholate, **5** (800 mg, 1.90 mmol) was dissolved in dry DCM (8 mL) inside a Slenck flask, under nitrogen atmosphere. Two drops of freshly distilled TMSCl were added, followed by phenyl isocyanate (1.02 g, 0.93 mL, 8.55 mmol). The resulting mixture was refluxed for 24 h. before the solvent and volatiles were removed under vacuum, with the aid of a vacuum trap. To the resulting crude material 20 mL of DCM were added. Insoluble stuff was removed by filtration. The liquors were concentrated to dryness and the resulting white foam was purified by flash chromatography (DCM/1% EtOAc to DCM/2% EtOAc) to afford triscarbamate **13** (1.06 g, 72% yield) as a white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.44–7.39 (4H, m, Ar*H*), 7.34–7.22 (8H, m, Ar*H*), 7.09–6.99 (3H, m, Ar*H*), 6.80 (1H, broad s, N*H*), 6.66 (1H, broad s, N*H*), 6.54 (1H, broad s, N*H*), 5.11 (1H, s, C*H*OR), 4.96 (1H, s, C*H*OR), 4.52 (1H, m, C*H*OR), 3.61 (3H, s, CO_2CH_3), 2.34–2.27 (1H, m, C*H*), 2.22–1.05 (23H, m, CH_2s + C*H*s), 0.94 (3H, s, CH_3), 0.87 (3H, d, J = 6.5 Hz, CH_3), 0.76 (3H, s, CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 174.9 (CO_2CH_3), 153.4 (O*C*(O)NH), 153.3 (2 x O*C*(O)NH), 138.4 (Ar*C*), 138.3 (Ar*C*), 138.3 (Ar*C*), 129.4 (Ar*C*H), 129.4 (Ar*C*H), 129.3 (Ar*C*H), 123.8 (Ar*C*H), 123.8 (Ar*C*H), 123.7 (Ar*C*H), 119.3 (broad C, 2 x Ar*C*H), 119.0 (Ar*C*H), 76.9 (*C*HOR), 75.5 (*C*HOR), 72.5 (*C*HOR), 51.8 (CO_2CH_3), 47.8 (*C*H), 45.7 (*C*), 43.9 (*C*H), 41.1 (*C*H), 38.3 (*C*H), 35.3 (CH_2), 35.0 (*C*H), 35.0 (CH_2), 34.7 (*C*), 31.8 (CH_2), 31.3 (CH_2), 31.1 (CH_2), 29.4 (*C*H), 27.5 (CH_2), 27.4 (CH_2), 26.1 (CH_2), 23.3 (CH_2), 21.8 (CH_3), 17.9 (CH_3), 12.6 (CH_3); MS (ESI+): *m/z* (%) = 818 (24) $[M+K]^+$, 802 (100) $[M+Na]^+$, 780 (4) $[M+H]^+$; HRMS (ESI+): *m/z* calcd. for $[C_{46}H_{57}N_3O_8Na]^+$ 802.4043, found 802.4038.

Catalyst **13** was lyophilized twice prior to use, as it includes water and EtOAc inside its cavity.

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



Mass Spectrum SmartFormula Report

Analysis Info

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Comment			

Acquisition Parameter

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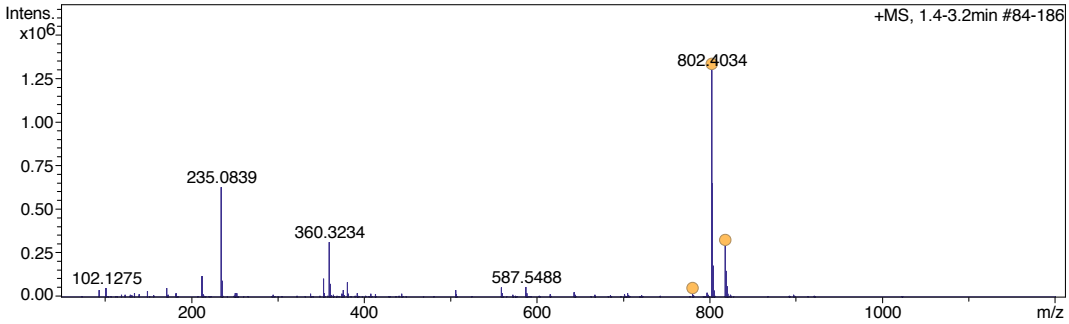
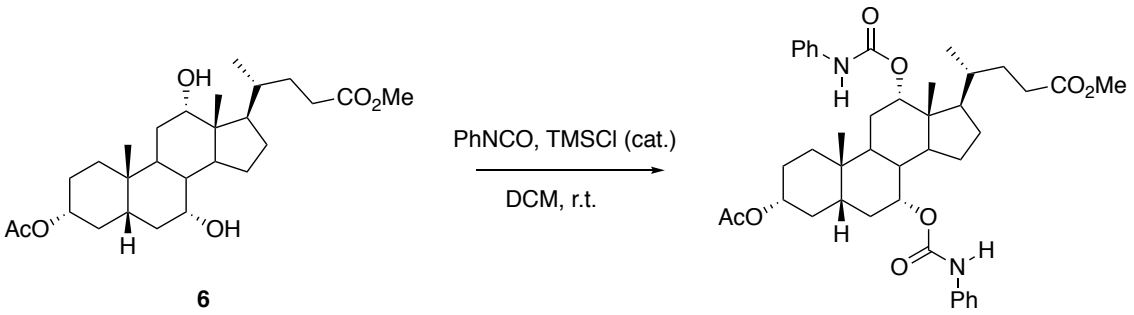
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1200 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
780.4219	1	C46H58N3O8	780.4218	-0.0	8.3	2	100.00	20.0	even	ok	M+H
802.4034	1	C46H57N3NaO8	802.4038	0.5	9.6	2	100.00	20.0	even	ok	M+Na
818.3776	1	C46H57KN3O8	818.3777	0.1	7.2	2	100.00	20.0	even	ok	M+K

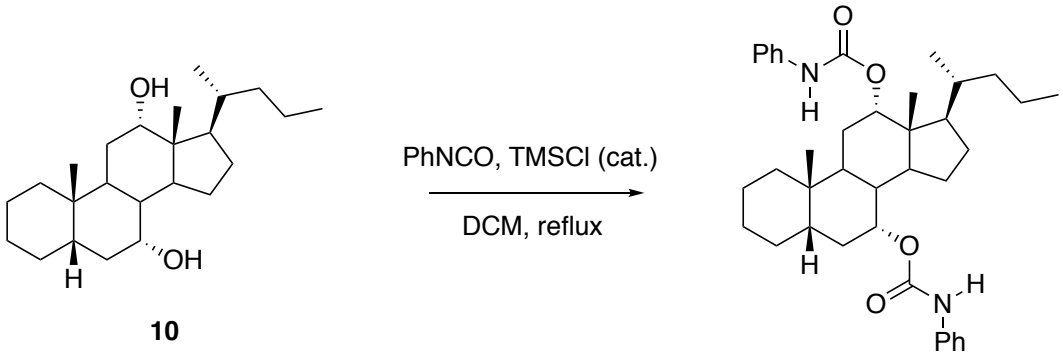
Catalyst 14.[14]



6 **14**

[14] Fang, L.; Chan, W.- H.; He, Y.- B.; Kwong, D. W. J.; Lee, A. W. M. *J. Org. Chem.* **2005**, *70*, 7640–7646.

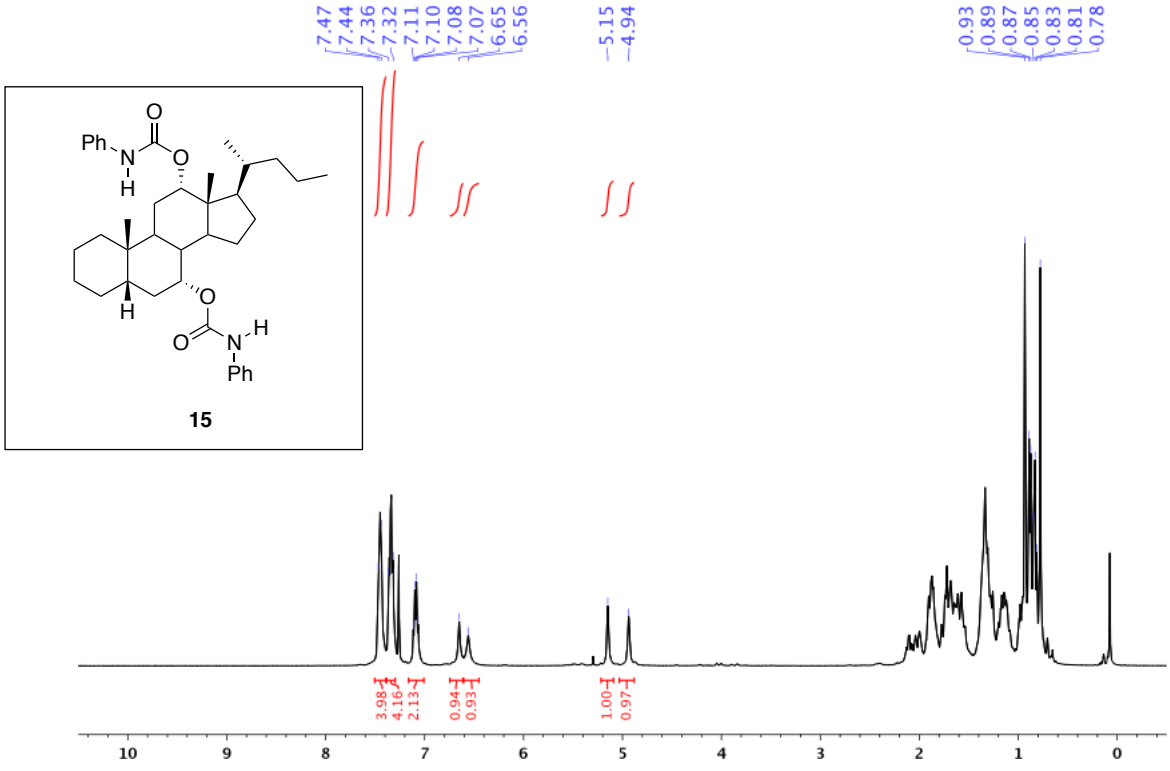
Catalyst 15.



10 **15**

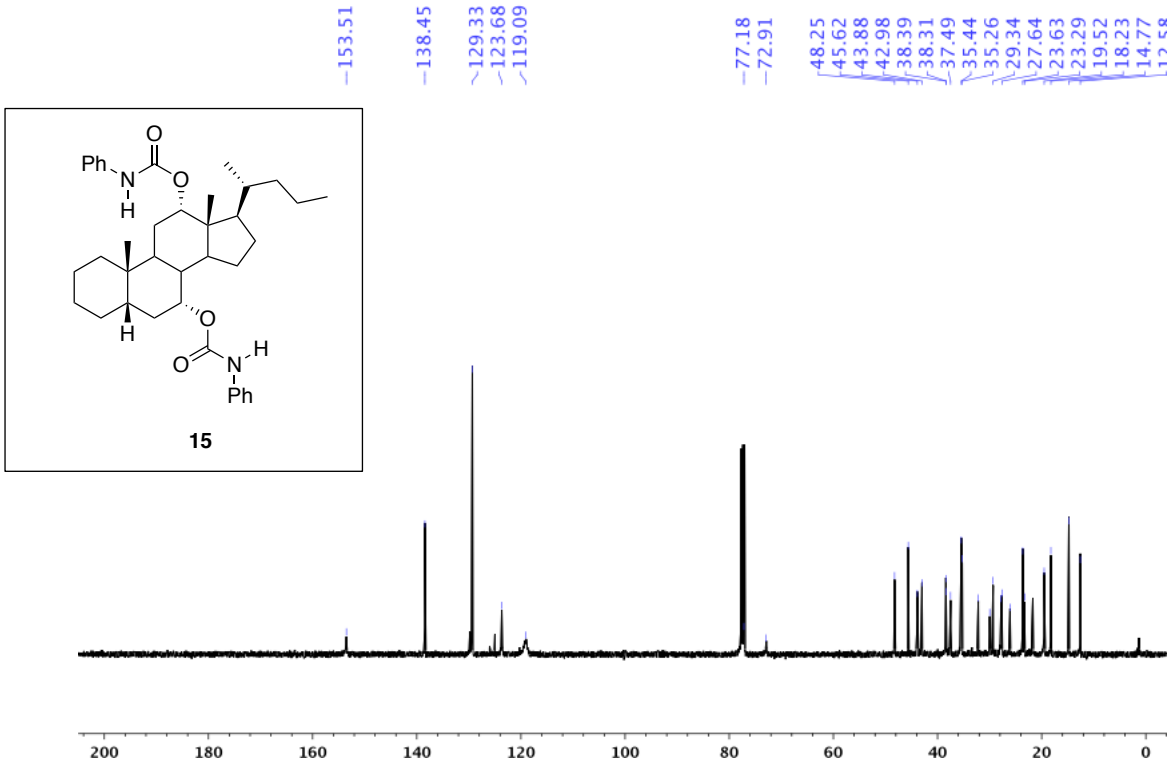
Diol **10** (66 mg, 0.182 mmol) was dissolved in dry DCM (1 mL) inside a Slenck flask, under nitrogen atmosphere. One drop of freshly distilled TMSCl was added, followed by phenyl isocyanate (48 mg, 44 μL, 0.40 mmol). The resulting mixture was refluxed for 24 h. before the solvent and volatiles were removed under vacuum, with the aid of a vacuum trap. The resulting white foam was purified by flash chromatography (Hexane/DCM, 1:1) to afford biscarbamate **15** (63 mg, 58% yield) as a white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.47–7.44 (4H, m, Ar*H*), 7.36–7.32 (4H, m, Ar*H*), 7.09 (2H, q, *J* = 6.5 Hz, Ar*H*), 6.65 (1H, s, N*H*), 6.56 (1H, s, N*H*), 5.15 (1H, s, C*H*OR), 4.94 (1H, s, C*H*OR), 0.93 (3H, s, CH_3), 0.88 (3H, d, *J* = 6.5 Hz, CH_3), 0.83 (3H, t, *J* = 6.9 Hz, CH_3), 0.78 (3H, s, CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 153.5 (2 x O*C*(O)NH), 138.5 (2 x Ar*C*), 129.3 (Ar*C*H), 123.7 (Ar*C*H), 119.1 (broad C, 2 x Ar*C*H), 77.2 (*C*HOR), 72.9 (*C*HOR), 48.3 (*C*H), 45.6 (*C*), 43.9 (*C*H), 43.0 (*C*H), 38.4 (*C*H_2), 38.3 (*C*H), 37.5 (*C*H_2), 35.4 (*C*), 35.3 (*C*H), 32.2 (*C*H_2), 30.0 (*C*H_2), 29.3 (*C*H), 27.8 (*C*H_2), 27.6 (*C*H_2), 26.1 (*C*H_2), 23.6 (*C*H_3), 23.3 (*C*H_2), 21.7 (*C*H_2), 19.5 (*C*H_2), 18.2 (*C*H_3), 14.8 (*C*H_3), 12.6 (*C*H_3); MS (ESI+): *m/z* (%) = 639 (11) $[M+K]^+$, 623 (100) $[M+Na]^+$; HRMS (ESI+): *m/z* calcd. for $[C_{38}H_{52}N_2O_4Na]^+$ 623.3825, found 623.3811.

^{1}H NMR (400 MHz, $CDCl_3$):



15

^{13}C NMR (100 MHz, $CDCl_3$):



15

Mass Spectrum SmartFormula Report

Analysis Info

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Comment			

Acquisition Parameter

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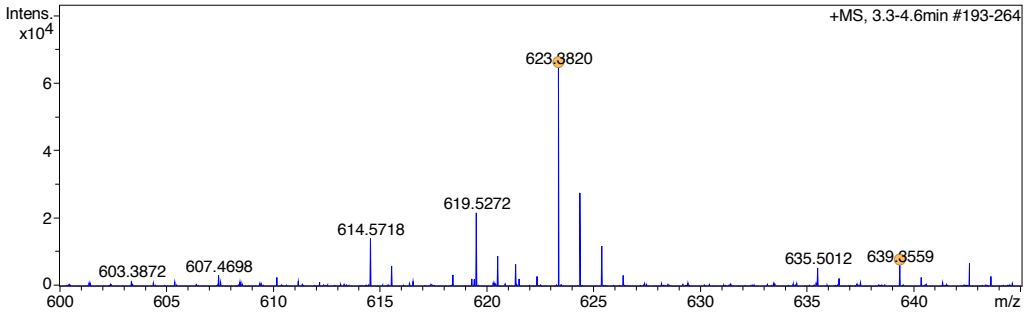
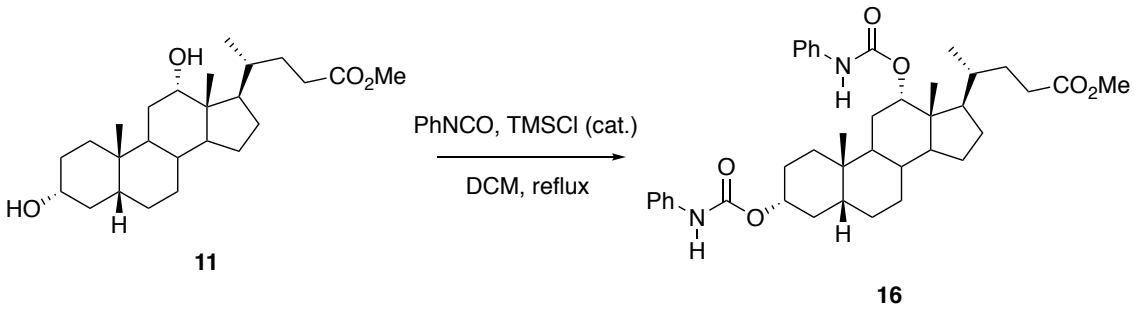
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
601.3992	1	C38H53N2O4	601.4000	1.3	502.5	1	100.00	14.0	even	ok	M+H
623.3820	1	C38H52N2NaO4	623.3819	-0.1	47.0	1	100.00	14.0	even	ok	M+Na
639.3559	1	C38H52KN2O4	639.3559	-0.1	10.8	1	100.00	14.0	even	ok	M+K

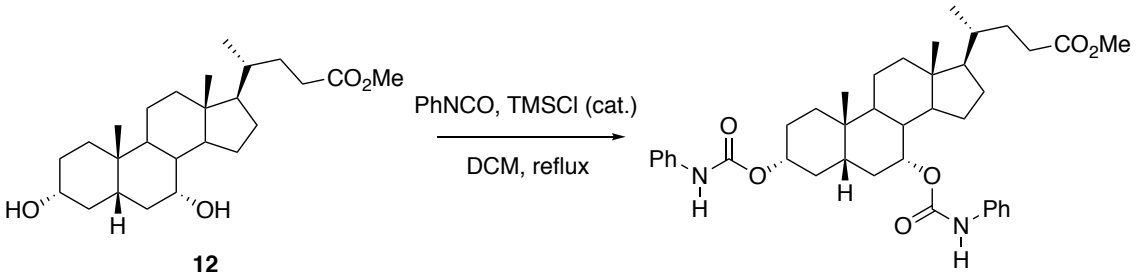
Catalyst 16.[15]



11 **16**

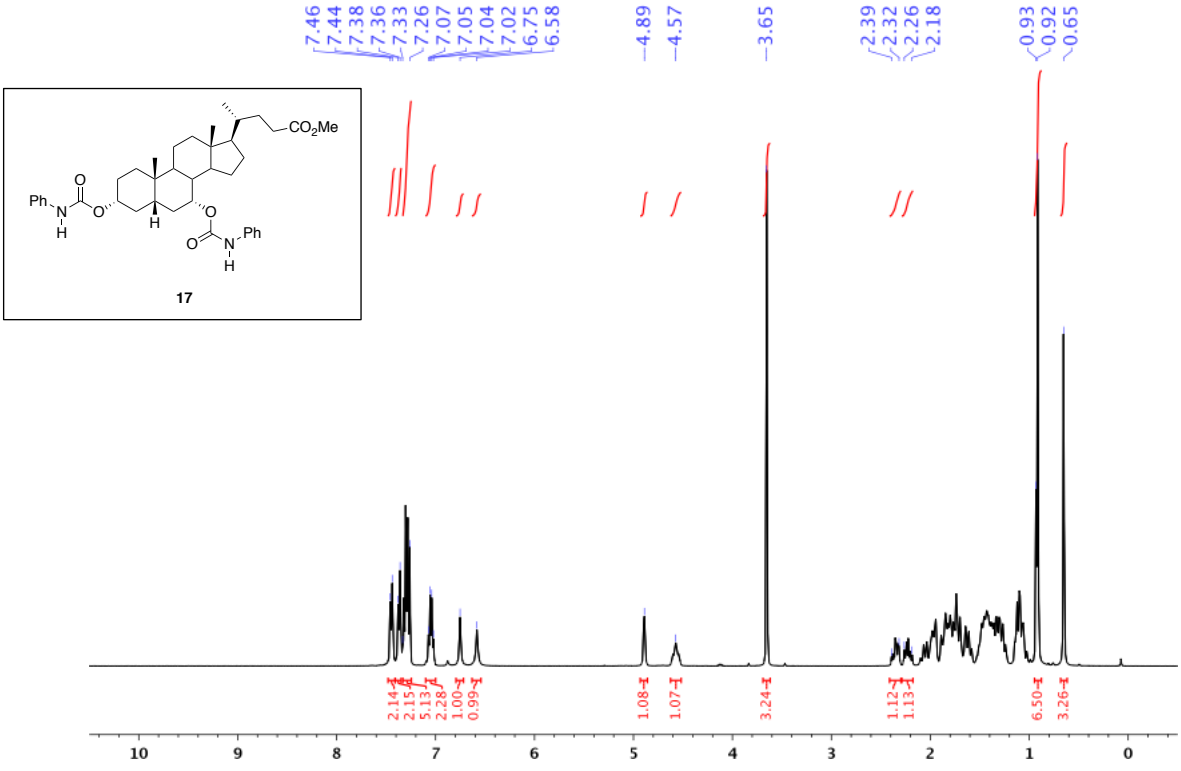
[15] Zhao, Z.- G.; Liu, X.- L.; Chen, Y.; Shi, Z.- C. *J. Chem. Res.* **2010**, *34*, 481–484.

Catalyst 17.

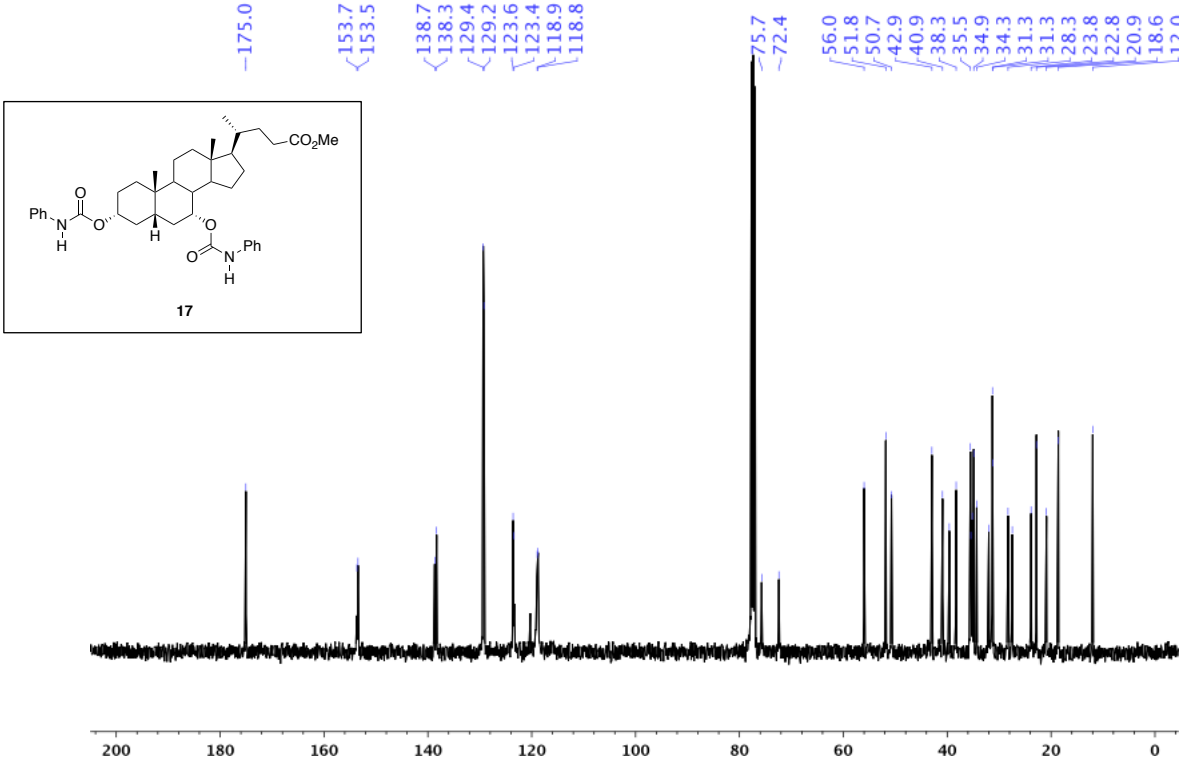


Methyl chenodeoxycholate, **12** (240 mg, 0.59 mmol) was dissolved in dry DCM (2.5 mL) inside a Slenck flask, under nitrogen atmosphere. One drop of freshly distilled TMSCl was added, followed by phenyl isocyanate (155 mg, 0.14 mL, 1.30 mmol). The resulting mixture was refluxed for 24 h. before the solvent and volatiles were removed under vacuum, with the aid of a vacuum trap. The resulting white foam was purified by flash chromatography (DCM/1% EtOAc) to afford biscarbamate **17** (215 mg, 56% yield) as a white solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.45 (2H, d, J = 7.9 Hz, Ar*H*), 7.37 (2H, d, J = 8.0 Hz, Ar*H*), 7.33–7.26 (4H, m, Ar*H*), 7.05 (2H, q, J = 7.1 Hz, Ar*H*), 6.75 (1H, broad s, N*H*), 6.58 (1H, broad s, N*H*), 4.89 (1H, s, C*H*OR), 4.57 (1H, m, C*H*OR), 3.65 (3H, s, CO_2CH_3), 2.39–2.32 (1H, m, C*H*), 2.26–2.18 (1H, m, C*H*), 0.93 (3H, s, CH_3), 0.92 (3H, d, J = 6.5 Hz, CH_3), 0.65 (3H, s, CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 175.0 (CO_2CH_3), 153.7 (O*C*(O)NH), 153.5 (O*C*(O)NH), 138.7 (Ar*C*), 138.3 (Ar*C*), 129.4 (Ar*C*H), 129.2 (Ar*C*H), 123.6 (Ar*C*H), 123.4 (Ar*C*H), 118.9 (Ar*C*H), 118.8 (Ar*C*H), 75.7 (*C*HOR), 72.4 (*C*HOR), 56.0 (CO_2CH_3), 51.8 (*C*H), 50.7 (*C*H), 42.9 (*C*), 40.9 (*C*H), 39.6 (CH_2), 38.3 (*C*H), 35.5 (*C*H), 35.4 (CH_2), 35.2 (CH_2), 34.9 (*C*), 34.3 (*C*H), 32.0 (CH_2), 31.3 (CH_2), 31.3 (CH_2), 28.3 (CH_2), 27.5 (CH_2), 23.8 (CH_2), 22.8 (CH_3), 20.9 (CH_2), 18.6 (CH_3), 12.0 (CH_3); MS (ESI+): *m/z* (%) = 683 (12) $[M+K]^+$, 667 (100) $[M+Na]^+$, 645 (4) $[M+H]^+$; HRMS (ESI+): *m/z* calcd. for $[C_{39}H_{52}N_2O_6Na]^+$ 667.3723, found 667.3718.

^{1}H NMR (400 MHz, $CDCl_3$):



^{13}C NMR (100 MHz, $CDCl_3$):



Mass Spectrum SmartFormula Report

Analysis Info

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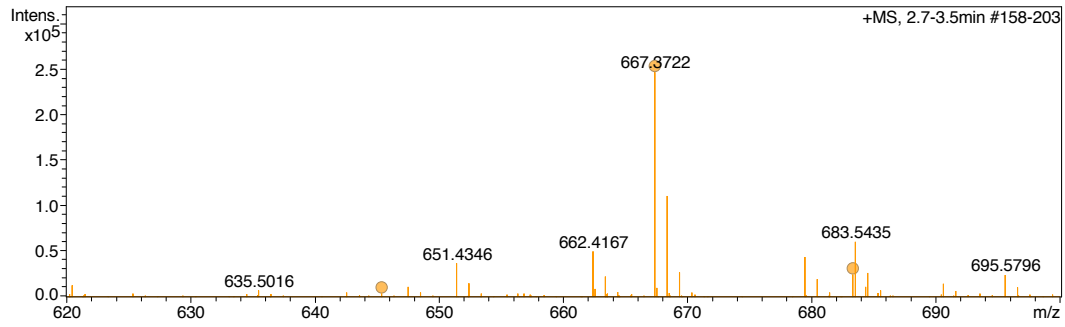
Sample Name	03102018_VAS_1048_P	Instrument	impact II 1825265.10101
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	250 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	6.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Waste
		Set Corona	0 nA	Set APCI Heater	0 °C



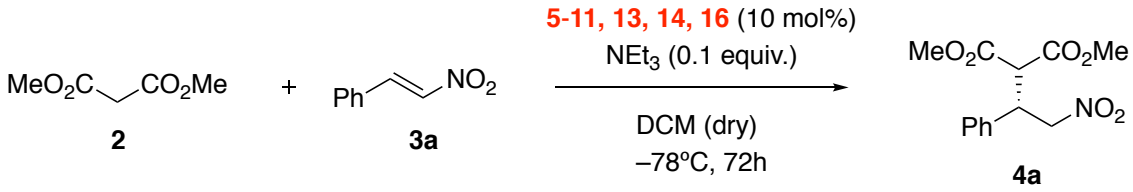
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule	Adduct
645.3894	1	C39H53N2O6	645.3898	0.6	31.8	1	100.00	15.0	even	ok	M+H
667.3722	1	C39H52N2NaO6	667.3718	-0.6	5.7	1	100.00	15.0	even	ok	M+Na
683.3458	1	C39H52KN2O6	683.3457	-0.2	7.1	1	100.00	15.0	even	ok	M+K

OPTIMIZATION OF THE REACTION CONDITIONS

Initial screening:

From the very first attempts, under any experimental conditions, triscarbamate **13** proved to be superior respect to structures **5-12**, **14-17**. Initially the Michael-type addition reaction was attempted employing DCM as the solvent.

Table SI_1. Initial screening of potential steroid-based catalysts **5-11**, **13**, **14**, **16**, in the Michael-type addition of dimethyl malonate, **2**, to nitrostyrene, **3a**.[a]



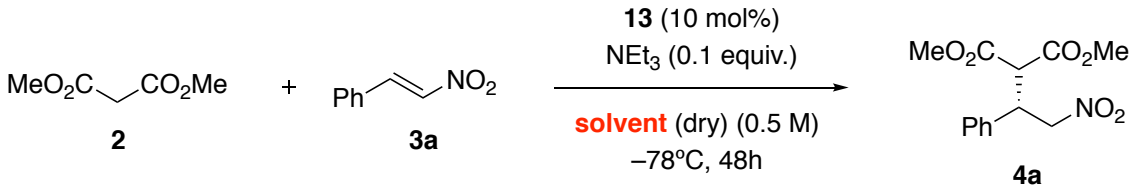
steroid	conversion (%)[b]	*ee* (%)[c]
5	25	rac
6	14	rac
7	17	rac
8	21	rac
9	23	rac
10	14	rac
11	23	rac
13	78	54
14	77	10
16	56	3

[a] General reaction conditions: nitrostyrene **3a** (0.2 mmol), and steroid (0.02 mmol) were dissolved in dry DCM (0.4 mL), at –78 °C, before dimethyl malonate **2** (0.6 mmol) and dry NEt_3 (0.02 mmol) were added. The reaction mixtures were stirred for 72 h before quenching with NH_4Cl (aq., sat.).

[b] Conversion of limiting reagent **3a** into product **4a**, as determined by ^1H NMR spectroscopy on crude reaction mixtures. Resonances of **4a** were integrated and quantified against a signal of the corresponding steroid.

[c] Enantiomeric excess of product **4a** as determined by chiral HPLC from crude reaction mixtures.

Table SI_2. Screening of solvents in the Michael-type addition of dimethyl malonate, **2**, to nitrostyrene, **3a** catalyzed by steroidal triscarbamate **13**.[a]



solvent	conversion (%)[b]	*ee* (%)[c]
toluene	40	70
hexane	10	14
$CHCl_3$	10	30
THF	4	rac
Et_2O	52	12
p-xilene[d]	>99	25
Benzene[d]	>99	32
Chlorobenzene[e]	>99	36

[a] General reaction conditions: nitrostyrene **3a** (0.2 mmol), and steroid **13** (0.02 mmol) were dissolved in dry solvent (0.4 mL), at –78 °C, before dimethyl malonate **2** (0.6 mmol) and dry NEt_3 (0.02 mmol) were added. The reaction mixtures were stirred for 48 h before quenching with NH_4Cl (aq., sat.).

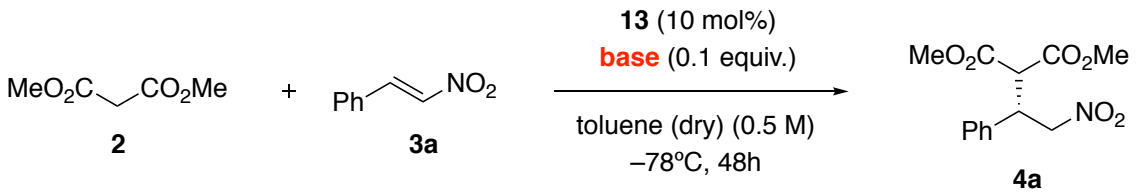
[b] Conversion of limiting reagent **3a** into product **4a**, as determined by ^1H NMR spectroscopy on crude reaction mixtures. Resonances of **4a** were integrated and quantified against a signal of the steroid.

[c] Enantiomeric excess of product **4a** as determined by chiral HPLC from crude reaction mixtures.

[d] Reaction carried out at 0 ºC.

[e] Reaction carried out at –20 ºC.

Table SI_3. Screening of different bases in the Michael-type addition of dimethyl malonate, **2**, to nitrostyrene, **3a** catalyzed by steroidal triscarbamate **13**.[a]



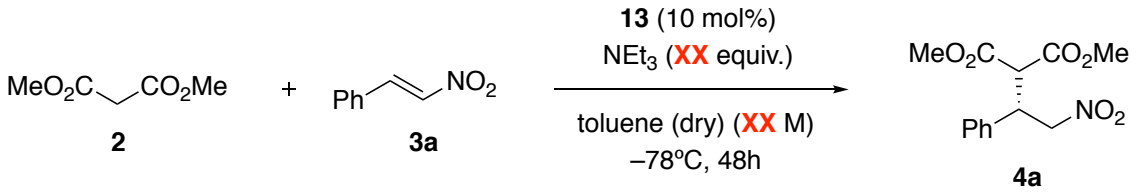
base	conversion (%)[b]	*ee* (%)[c]
DIPEA	21	43
2,6-lutidine	0	-
K_2CO_3	55	rac
DBU	91	27
Pyridine	0	-
NEt_3	40	70

[a] General reaction conditions: nitrostyrene **3a** (0.2 mmol), and steroid **13** (0.02 mmol) were dissolved in dry toluene (0.4 mL), at –78 °C, before dimethyl malonate **2** (0.6 mmol) and dry base (0.02 mmol) were added. The reaction mixtures were stirred for 48 h before quenching with NH_4Cl (aq., sat.).

[b] Conversion of limiting reagent **3a** into product **4a**, as determined by ^1H NMR spectroscopy on crude reaction mixtures. Resonances of **4a** were integrated and quantified against a signal of the steroid.

[c] Enantiomeric excess of product **4a** as determined by chiral HPLC from crude reaction mixtures.

Table SI_4. Screening of reaction concentration and amount of base employed in the Michael-type addition of dimethyl malonate, **2**, to nitrostyrene, **3a** catalyzed by steroidal triscarbamate **13**.[a]



[ ] (M)[b]	NEt_3 (mol%)[c]	conversion (%)[d]	*ee* (%)[e]
0.5	20	71	75
0.25	10	45	79
0.25[f]	20	92	80
0.25[f]	30	>99	78
0.125[f]	100	99	83

[a] General reaction conditions: nitrostyrene **3a** (0.2 mmol), and steroid **13** (0.02 mmol) were dissolved in dry toluene (stated amount), at –78 °C, before dimethyl malonate **2** (0.6 mmol) and dry NEt_3 (stated amount) were added. The reaction mixtures were stirred for 48 h before quenching with NH_4Cl (aq., sat.).

[b] Concentration of nitrostyrene **3a** (limiting reagent) in dry toluene.

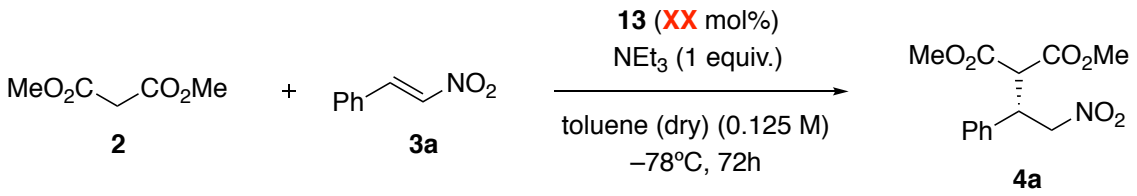
[c] Amount of NEt_3 used in the reaction, referred as %mol respect to nitrostyrene **3a**.

[d] Conversion of limiting reagent **3a** into product **4a**, as determined by ^1H NMR spectroscopy on crude reaction mixtures. Resonances of **4a** were integrated and quantified against a signal of the steroid.

[e] Enantiomeric excess of product **4a** as determined by chiral HPLC from crude reaction mixtures.

[f] The reactions mixtures were stirred for 72 h.

Table SI_5. Study on the amount of steroid **13** employed in the Michael-type addition of dimethyl malonate, **2**, to nitrostyrene, **3a**.[a]



Catalyst **17** (mol%)[b]	conversion (%)[c]	*ee* (%)[d]
10	97	83
15	99	91
20	99	90

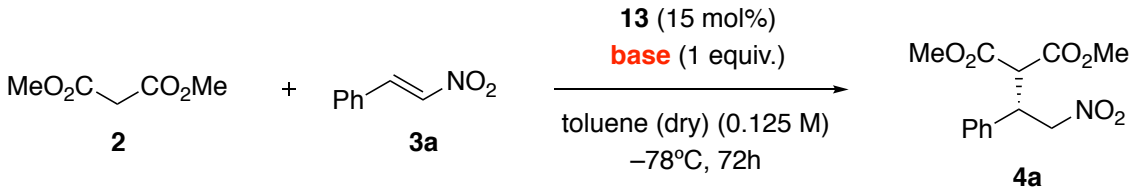
[a] General reaction conditions: nitrostyrene **3a** (0.2 mmol), and steroid **13** (stated amount) were dissolved in dry toluene (1.6 mL), at –78 °C, before dimethyl malonate **2** (0.6 mmol) and dry NEt_3 (0.2 mmol) were added. The reaction mixtures were stirred for 72 h before quenching with NH_4Cl (aq., sat.).

[b] Amount of steroid **13** used in the reaction, referred as %mol respect to nitrostyrene **3a**.

[c] Conversion of limiting reagent **3a** into product **4a**, as determined by ^1H NMR spectroscopy on crude reaction mixtures. Resonances of **4a** were integrated and quantified against a signal of the steroid.

[d] Enantiomeric excess of product **4a** as determined by chiral HPLC from crude reaction mixtures.

Table SI_6. Re-screening of different bases, under the finest reaction conditions, in the Michael-type addition of dimethyl malonate, **2**, to nitrostyrene, **3a** catalyzed by steroidal triscarbamate **13**.[a]



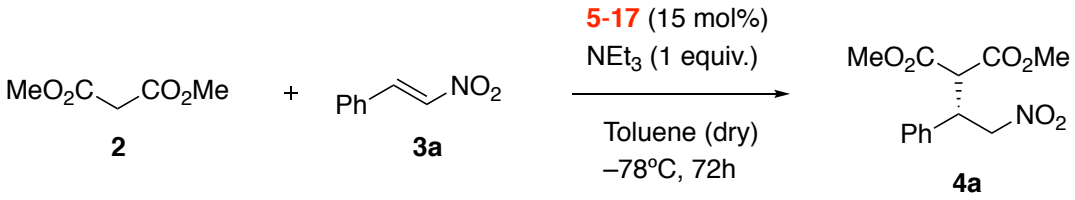
base	conversion (%)[b]	*ee* (%)[c]
DIPEA	24	70
Pyridine	0	-
NEt_3	99	91

[a] General reaction conditions: nitrostyrene **3a** (0.2 mmol), and steroid **13** (0.03 mmol) were dissolved in dry toluene (1.6 mL), at –78 °C, before dimethyl malonate **2** (0.6 mmol) and dry base (0.2 mmol) were added. The reaction mixtures were stirred for 72 h before quenching with NH_4Cl (aq., sat.).

[b] Conversion of limiting reagent **3a** into product **4a**, as determined by ^1H NMR spectroscopy on crude reaction mixtures. Resonances of **4a** were integrated and quantified against a signal of the steoid **13**.

[c] Enantiomeric excess of product **4a** as determined by chiral HPLC from crude reaction mixtures.

Table SI_7. Re-screening of the steroid-based catalysts **5-17**, under our finest reaction conditions, in the Michael-type addition of dimethyl malonate, **2**, to nitrostyrene, **3a**.[a]



steroid	conversion (%)[b]	*ee* (%)[c]
5	5	-
6	7	-
7	6	-
8	6	-
9	5	-
10	4	-
11	8	-
12	0	-
13	99 (94)	91
14	5	-
15	11	-
16	4	-
17	14	-

[a] General reaction conditions: nitrostyrene **3a** (0.2 mmol), and steroid **5-17** (0.03 mmol) were dissolved in dry toluene (1.6 mL), at –78 °C, before dimethyl malonate **2** (0.6 mmol) and dry triethyl amine (0.2 mmol) were added. The reaction mixtures were stirred for 72 h before quenching with NH_4Cl (aq., sat.).

[b] Conversion of limiting reagent **3a** into product **4a**, as determined by ^1H NMR spectroscopy on crude reaction mixtures. Resonances of **4a** were integrated and quantified against a signal of the steroid. In brackets is given the yield of isolated product **4a** in analytically pure form.

[c] Enantiomeric excess of analytically pure product **4a** as determined by chiral HPLC.

NMR STUDY AND DETERMINATION OF ASSOCIATION CONSTANTS

General considerations

Association constants for the complexes were determined by means of the ^{1}H NMR titration method, using 400 MHz ^{1}H NMR spectroscopy at a temperature of 298 K. All solutions were made up in toluene-d_8 using volumetric flasks with an accuracy of ± 0.02 mL. Samples were equilibrated at 298 K prior to use. The corresponding variation in chemical shift, with respect to guest concentration, was monitored and the association constant was determined by fitting this experimental data to the following equation, using the "Solver" tool implemented on Microsoft Excel, using non-linear curve-fittings:

$$\delta_{obs} = \delta_G + \frac{\Delta\delta}{2G_0}\left[K_d + H_0 + G_0 - \sqrt{\left(K_d + H_0 + S_0\right)^2 - 4H_0G_0} \right]$$

This allows the calculation of the dissociation constant, K_d, where δ_{obs} is the chemical shift at concentration G_0 of the guest molecule, H_0 is the concentration of the host molecule, and $\Delta\delta$ is the maximum change in the chemical shift of the bound species. The value of the association constant, K_a is obtained from the best-fit value of K_d:

$$K_d = \frac{1}{K_a}$$

Determination of binding constant for the complex [13·3a]

The association constant, between steroid **13** and nitrostyrene, **3a**, was determined by titration as 2-3 M^{-1}, using 400 MHZ ^{1}H NMR spectroscopy, at 298 K in toluene-d_8. Since **13** and **3a** are inert when mixed together we were able to assign any chemical shift changes as a consequence of the association between complementary recognition sites on **13** and **3a**. Considering the chemical shift manifested by the N-H motifs of the C3, C7 and C12 carbamates upon formation of the complex (Figure SI_1), it is assumed that nitrostyrene incorporates within the cavity of the steroid according to the general model represented in Figure SI_2 (see below).

Figure SI_1. Stacked representation of NMR spectra (toluene-d_8, 298 K) for steroid **13** (50 mM) with increasing amounts of nitrostyrene **3a**, as stated.

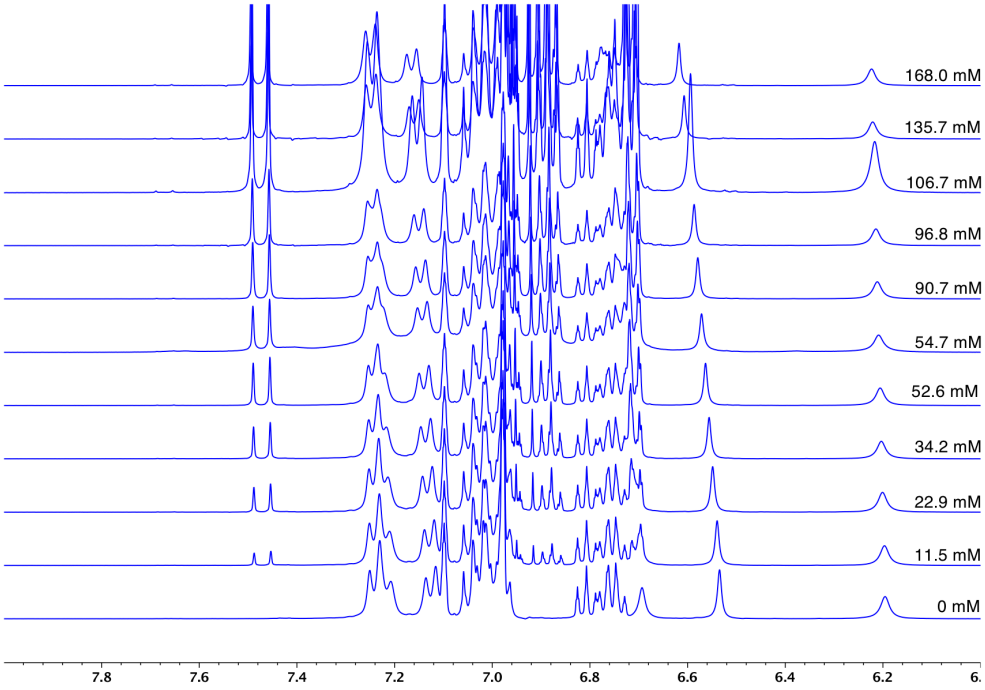
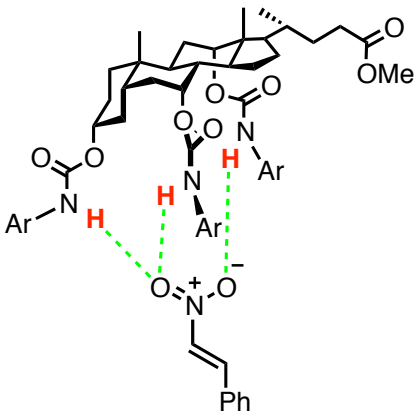


Figure SI_2. Binding model for the formation of complex [**13**•**3a**].



For the binding study, the concentration of **3a** (guest) was varied between zero and 168 mM. Host **13** was maintained at 50 mM throughout the study. The observed change in chemical shift of the singlet at δ = 6.53 ppm, or δ = 6.19 ppm, from compound **13** was monitored as the concentration of guest varied (Figure SI_1). From the data presented in Figures SI_3 and SI_4, and making use of the equations presented above, the association constant K_a was calculated as 2–3 M^{-1}.

Figure SI_3. Saturation plot showing the change in chemical shift of the signal at δ = 6.535 ppm arising from compound **13** as the concentration of **3a** increases. The closed circles represent the experimentally determined points and the solid line represents the best-fit value.

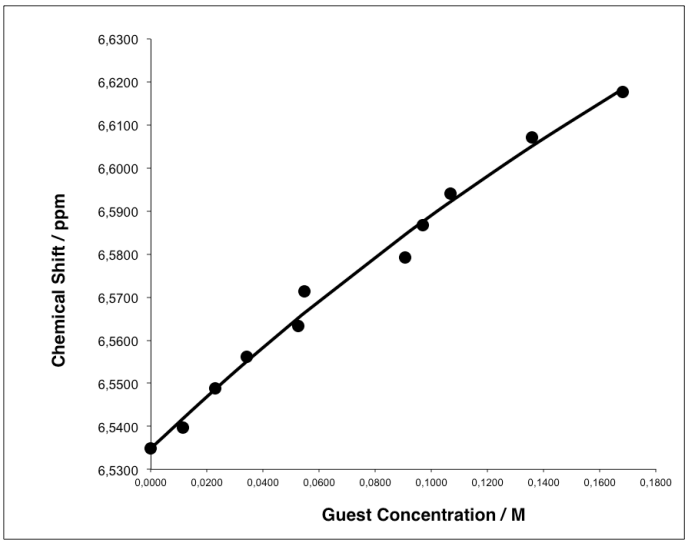
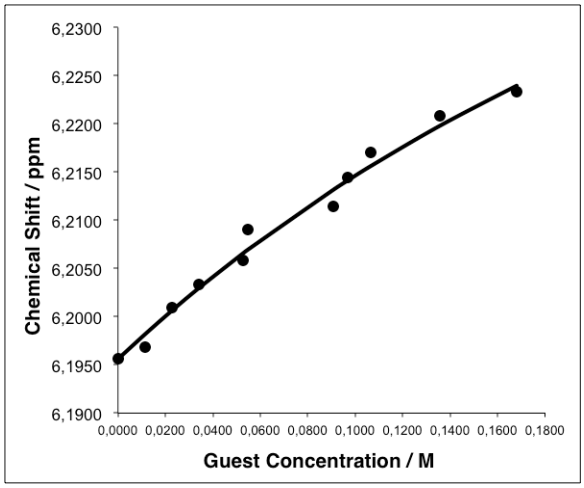


Figure SI_4. Saturation plot showing the change in chemical shift of the signal at δ = 6.196 ppm arising from compound **13** as the concentration of **3a** increases. The closed circles represent the experimentally determined points and the solid line represents the best-fit value.

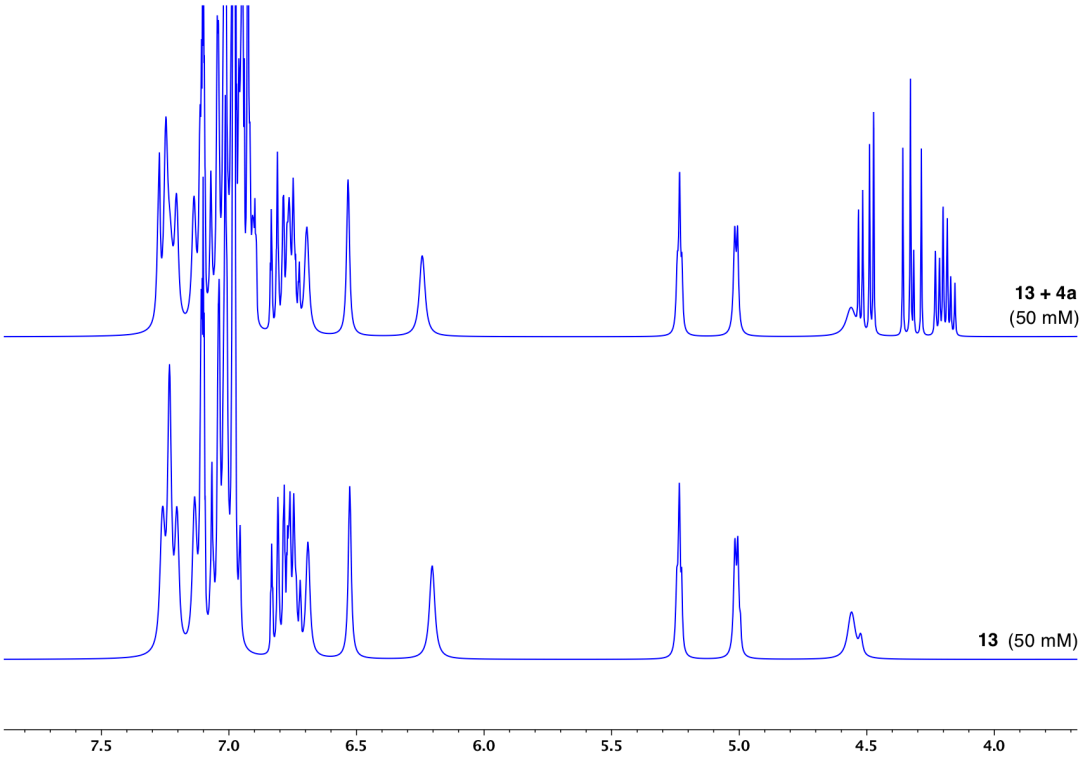


Study of the lack of association between steroid 13 and reaction product 4a

The absence of association between steroid **13** and reaction product **4a** was determined by 400 MHZ ^{1}H NMR spectroscopy, at 298 K in toluene-d_8. Since **13** and **4a** are inert when mixed together any chemical shift changes would be a consequence of the association between these two compounds. A 50 mM stock solution of steroid **13** in toluene-d_8 was prepared and a ^{1}H NMR spectrum registered. Subsequently, an equimolar amount of enantioenriched product **4a** (91% *ee*, prepared according to **SP1**)

was added to the previous sample and it was then analysed by ^{1}H NMR. No appreciable changes in chemical shift of the singlets at δ = 6.69 ppm and δ = 6.53 ppm from compound **13** (assignable to the NHs of the carbamate units borne on C7 and C12) was monitored (Figure SI_5). A negligible change was appreciated for the singlet at δ = 6.20 ppm (NH of carbamate at C3).

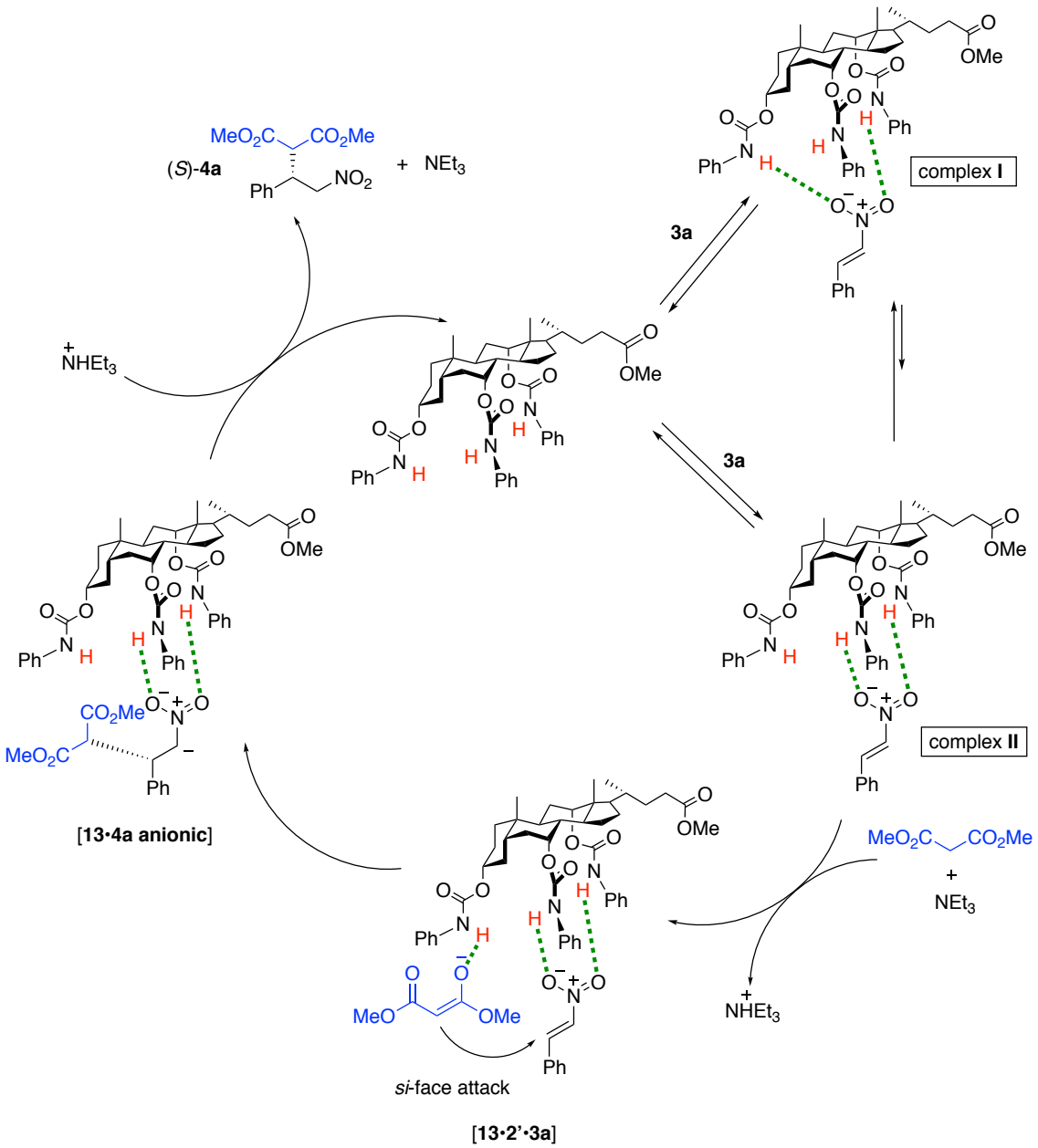
Figure SI_5. Stacked representation of NMR spectra (toluene-d_8, 298 K) for steroid **13** (50 mM) and for a sample containing equimolar amounts of **13** and reaction product **4a**.



PROPOSED REACTION MECHANISM

Based on the experimental and theoretical findings, discussed later on, the following mechanism is put forward for asymmetric reaction between dimethyl malonate, **2**, and nitrostyrene, **3a**, catalyzed by the cavity steroidal triscarbamate **13**.

Figure SI_6. Proposed mechanism for the addition reaction between dimethyl malonate, **2**, and nitrostyrene, **3a**, catalyzed by the cavity of steroid **13**. H-bonds are represented by green dashed lines.



QUANTUM CHEMICAL STUDY

Computational Details

All the chemical structures were optimized in the gas phase using the Minnesota functional M06-2X in combination with the cc-pvdz basis set as implemented in the Gaussian 09 program. Considering the low dielectric constant of the solvent employed (toluene) the effect of the solvent in the studied species was considered to be reasonably small. Hence, all the calculations were performed in the gas phase. All stationary states were characterized through their vibrational spectra. All critical points, except for the transition states, exhibit positive vibration armonic frequencies. Transition states were characterized as a first order saddle points showing only one negative frequency. The reaction energy profiles of the C–C bond-forming step within the studied reactions were computed using the Gaussian 09 program, after the optimization of the involved critical points using the calculation setup previously described. The binding energies have been properly corrected for Basis Set Superposition Errors (BSSE). All the thermodynamic properties were computed at both 195 and 298 K employing the geometry computed at room temperature.

General notes regarding the computational study

Considering the experimental procedure, the Michael-type addition reaction was considered to proceed *via* the initial formation of nitrostyrene-triscarbamate supramolecular species [**3a•13**], which then leads to a pre-reactive complex with the methyl malonate anion, [**2'•3a•13**]. This pre-reactive complex affords the corresponding addition product **4a** by the reaction of the styrene derivative and the nucleophile.

Selection of the functional and basis set

With the aim of validating the proposed calculation setup, a preliminary analysis was performed to test the validity and applicability of a set of functionals and basis sets on the studied systems. For that purpose, the structures of the cyclopentane perhydrophenanthrene starting material (cholic acid, **1**) obtained with a combination of different basis set (cc-pVDZ and 6-31G*) and functionals (B3LYP and M06-2X) employing the Gaussian 09 program, were compared with the experimental X-ray

structure (Figure SI_7).[16] For all four possible combinations the total discrepancy between the experimental and the theoretical findings was found to be below 2.0% (Table SI_8). The minimum deviation in bond lengths was obtained using the M06-2X/cc-pVDZ combination (Table SI_8, entry 1). Therefore, this setup was considered to be optimal for our study.

Table SI_8. Error percentage in bond angles and bond lengths, as calculated employing different basis set and functionals with respect to the experimental values obtained from the X-ray structure of cholic acid, **1**.

entry	basis set	functional	angle (%)	length (%)
1	cc-pVDZ	M06-2x	1.64%	0.88%
2	6-31G*	M06-2x	1.29%	0.89%
3	cc-pVDZ	B3LYP	1.16%	1.15%
4	6-31G*	B3LYP	1.80%	1.21%

X-ray structure of cholic acid.[16]

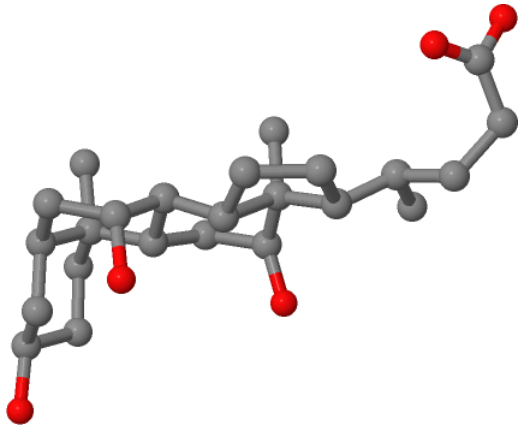
XYZ coordinates (in Ångströms):

O	25.31227	3.04519	8.57345
O	23.43473	-0.96611	9.53248
O	19.28024	1.22889	8.77338
O	32.56856	2.33413	11.62547
O	31.22962	0.63377	11.22718
C	21.29945	2.73758	11.60517
C	20.69312	2.65333	10.19474
C	20.97109	0.16926	10.22754
C	21.61805	0.25814	11.60829
C	22.56754	-0.90428	11.83634
C	23.78728	-0.77057	10.91167
C	24.51022	0.56112	11.20375
C	23.52568	1.71581	10.85700
C	22.30978	1.59679	11.80041
C	24.30413	3.03591	10.85700
C	25.53190	2.98490	9.93546
C	26.47827	1.95309	10.46027
C	25.57400	0.50315	10.15101
C	26.68438	-0.50547	10.42122
C	27.99704	0.13294	9.86518
C	27.67772	1.64007	9.54654
C	28.95829	2.47788	9.74178
C	28.68784	3.94947	9.37785

[16] Nonappa; Lathinen, M.; Ikonen, S.; Kolehmainen, E.; Kauppinen, R. *Cryst. Growth Des.* **2009**, *9*, 4710–4719. Structure deposited in the Cambridge Crystallographic Data Centre (number: 989890).

C	30.16471	1.97860	8.93270
C	31.54155	2.31867	9.56216
C	31.77841	1.66171	10.81952
C	22.77020	1.70036	13.27800
C	26.95936	2.19037	11.88944
C	19.96464	1.30618	10.04636

Figure SI_7. Balls and sticks representation of the x-ray structure of cholic acid, rendered with Jmol.[17] C atoms are colored grey. O atoms are colored red. H atoms have omitted for clarity.

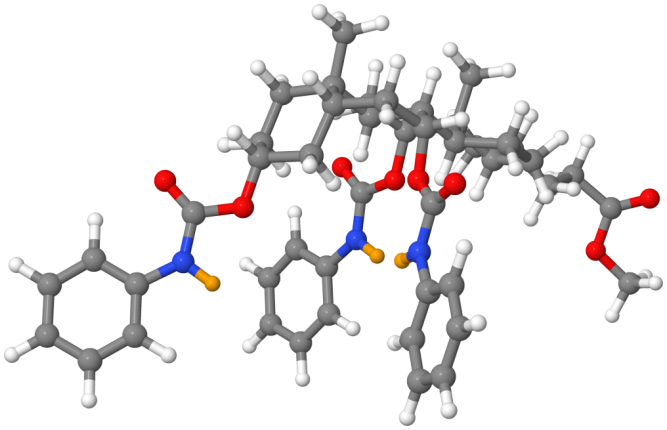


[17] Jmol: an open-source Java viewer for chemical structures in 3D. http://www.jmol.org/

Optimized structure of catalyst 13.

Considering the rigidity of the steroidal core, the x-ray resolved crystalline structure of cholic acid was employed as a starting point for the initial guess of the energetically minimized structure of the tripodal catalyst **13**, utilizing the M06-2X/cc-pVDZ set. The resulting minimized structure is represented in Figure SI_8.

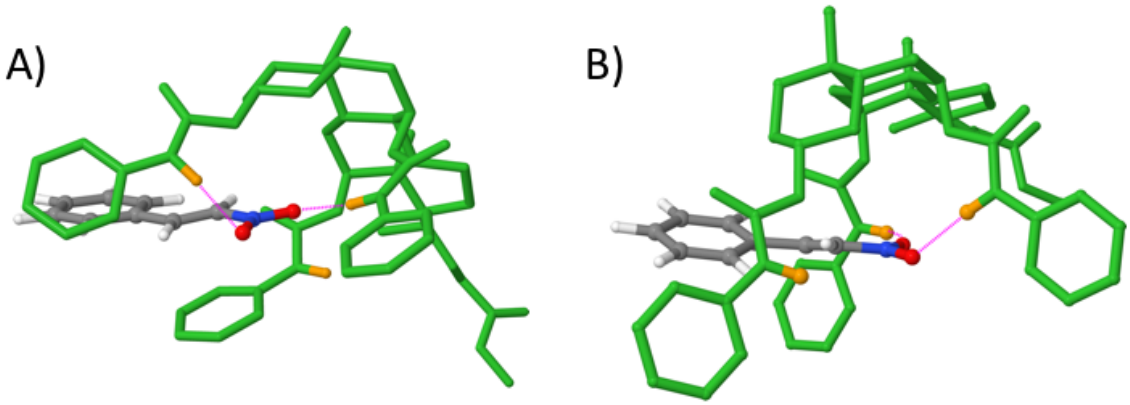
Figure SI_8. Ball and stick representation of the optimized structure (M06-2X/cc-pVDZ) of triscarbamate **13** in the gas phase. C atoms are represented in grey, O in red, N in blue, H in white. H atoms borne on the carbamate units are represented in orange. The optimization of the structure was done with Gaussian09 code and rendered with Jmol.[17]



Computational study for the formation of the supramolecular complex [13•3a]

In agreement with the NMR experiments presented above (Figures SI_1 to SI_4), DFT calculations (M06-2X/cc-pVDZ, run with the code of Gausian09) revealed that nitrostyrene **3a** docks inside the cavity of steroid **13** adopting two minimum energy conformations, differing on the orientation adopted by **3a**. Both supramolecular complexes [**13•3a**] were named after complex **I** and complex **II** (Figure SI_9). They are held together by H-bond contacts (between the nitro group of **3a**, and the N-Hs of the C3 and C7 cabamate units in complex **I**, and the C7 and C12 appendages in the case of complex **II**) and π-π stacking interactions. The net binding energies (ΔG) of the steroid **17** with nitrostyrene **3a** account for –6.75 *kcal mol*$^{-1}$ and –3.90 *kcal mol*$^{-1}$, for complex **I** and **II** respectively (at a temperature of 195 K).

Figure SI_9. Representations of the optimized structures of supramolecular complexes [**3a•13**] **I** and **II** (M06-2X/cc-pVDZ), rendered with Jmol. A) complex **I**. B) complex **II**. The steroidal backbone is coloured green (H atoms are omitted for clarity). C atoms are colored grey, O atoms are coloured red, N atoms are coloured blue, H atoms are coloured white. Carbamate H atoms are coloured orange. H-bonds are represented by pink dashed lines.

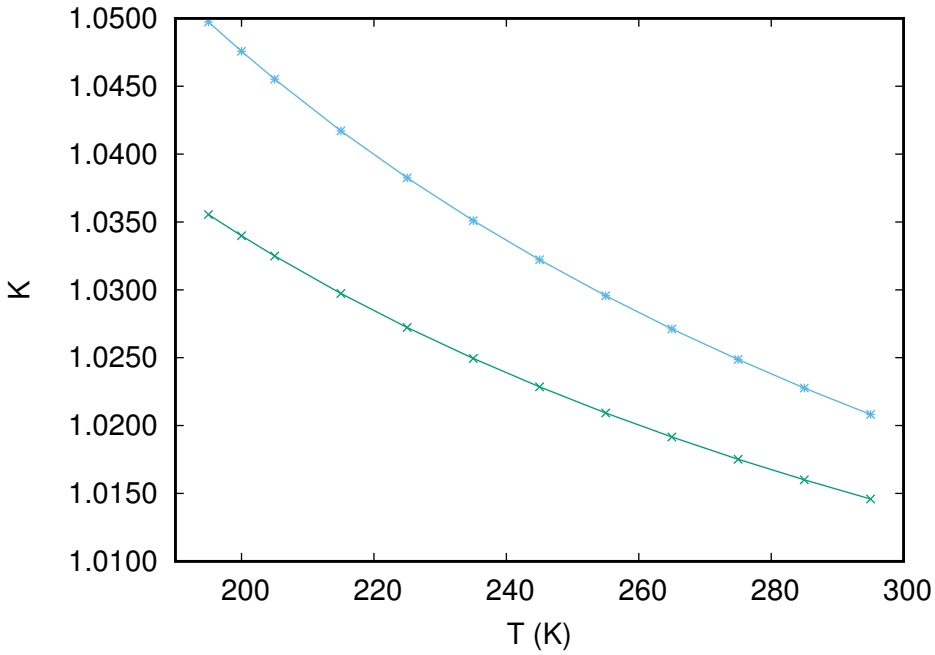


ΔG values for the formation of complexes **I** and **II** [**13•3a**] were computed at different temperatures. From these figures equilibrium constants (K) for the process **13** + **3a** ←==→ [**13•3a**] were inferred

$$K = e^{\frac{-\Delta G}{RT}}$$

and represented against T (Figure SI_10).

Figure SI_10. Computed equilibrium constants (K) at different temperatures, ranging from 195 K to 298 K, for the binding process between nitrostyrene **3a** and steroidal triscarbamate **13**. Points represent real computed values. Solid lines represent the best-fit values (blue for complex **I** [**3a**•**13**]; green for complex **II** [**3a**•**13**]).



Reaction energy profiles for the C–C bond-forming step

With the aim of studying the effect of the triscarbamate **13** in the Michael-type addition reaction, and rationalizing the stereopreference observed in the formation of product (*S*)-**4a**, the C–C bond-forming step was characterized and studied through computational calculations (Figures SI_11 and SI_12).

Figure SI_11. Representation of the reaction energy profile (PES along the C–C bond formation) of the non-catalyzed reaction. Activation energies are given at the DFT (M06-2X/cc-pVDZ) and HF/cc-pvdz level of theory.

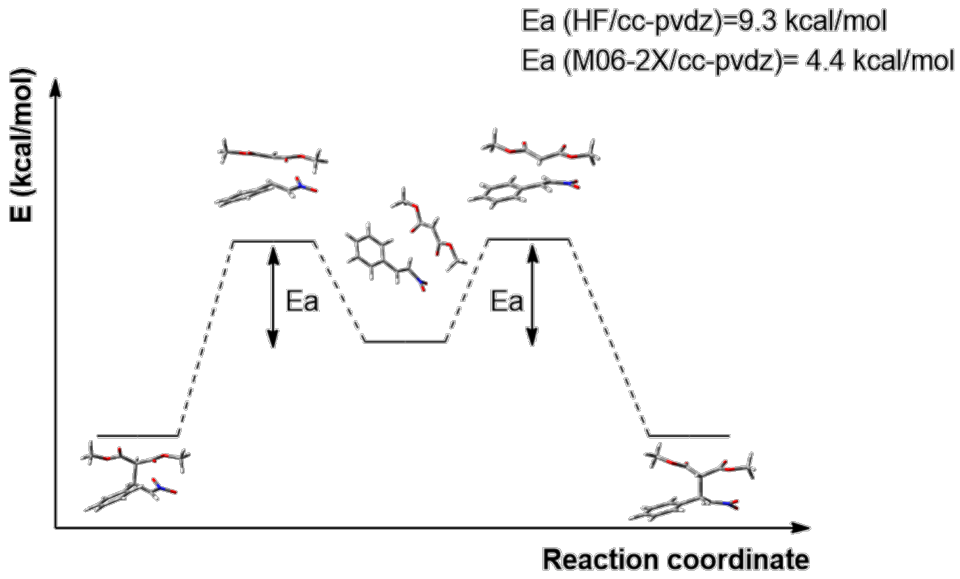
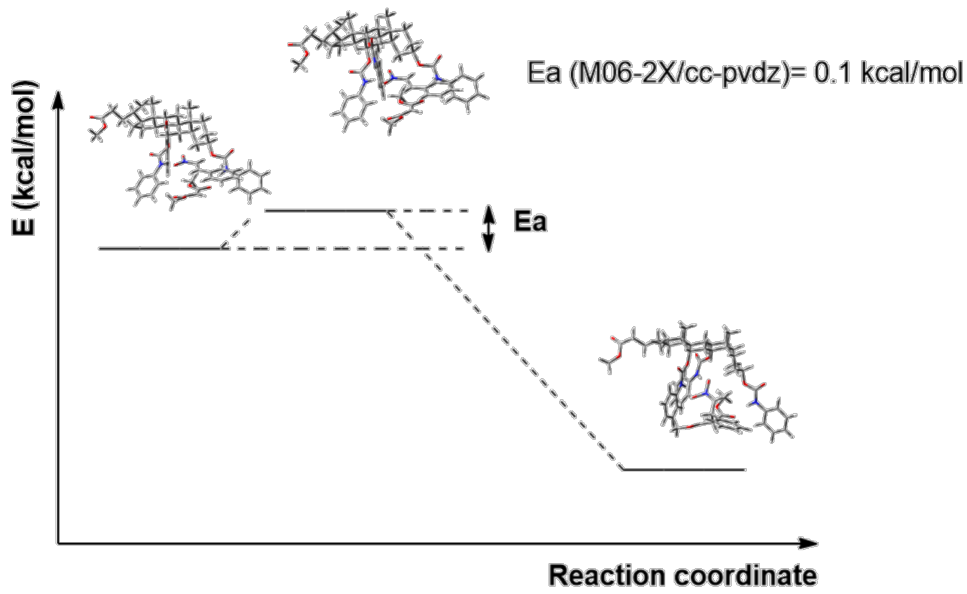


Figure SI_12. Representation of the reaction energy profile (PES along the C–C bond formation) of the catalyzed reaction. The activation energies are given at the DFT (M06-2X/cc-pVDZ) level of theory.



The calculations of the transition states are referred to the reaction between the anionic nucleophile **2'** and the electrophile **3a** leading to the formation of the corresponding addition product. The protonation of the final product, resulting in the formation of neutral species, is not accounted computationally. As it can be observed from the diagrams, a significant decrease in the activation energy of the catalyzed reaction was computed, proving the catalytic nature of the steroidal triscarbamate **13**. The corresponding activation energies are computed with respect to a reference pre-reactive complex.

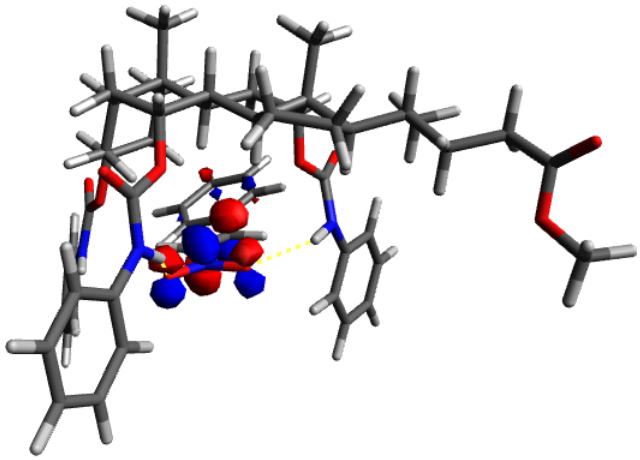
Evaluation of the effect of catalyst 13 in the electrophilicity of nitrostyrene 3a

To assess the effect of the H-bond interactions existing in the supramolecular complex **II** [**3a•13]** in the electrophilic character of nitrostyrene **3a**, a frontier molecular orbital analysis was performed. This analysis revealed that, upon complexation, a significant increase in the reactivity of nitrostyrene (represented by the electrophillicity index, Figure SI_13) towards a nucleophilic attack is produced, which supports the catalytic activity of the catalyst. Hence, the catalytic effect of the triscarbamate **13** can be attributed to both, the increase in the reactivity of the electrophile and the preorganization phenomenon experienced inside its cavity.

Table SI_9. HOMO and LUMO orbital energies, electronic chemical potencial (μ), chemical hardness (η), and electrophiliicity index (ω),[18] calculated for nitrostyrene **3a**, and for nitrostyrene **3a** within the supramolecular complex **II** [**3a•13**]. All values are given in eV.

	HOMO	LUMO	μ	η	ω
3a	-8.360	-1.638	-5.000	3.36	3.717
3a, in complex **II** [**3a•13**]	-7.067	-2.167	-4.617	2.45	4.350

Figure SI_13. Representation of the LUMO orbital for the nitrostyrene-triscarbamate supramolecular complex **II** [**3a•13**]. Isosurface value: 0.07 au. Rendered with the Avogadro program.[19]



[18] Chattaraj, P. K.; Sarkar, U.; Roy, D. R. *Chem. Rev.* **2006**, *106*, 2065–2091.

[19] (a) Avogadro: an open-source molecular builder and visualization tool. http://avogadro.cc. (b) Hanwell, M. D.; Curtis, D. E.; Lonie, D. C.; Vandermeersch, T.; Zurek, E.; Hutchison, G. R. *J. Cheminform.* **2012**, 4–17.

Insertion of MeOH inside the cavity of steroid 13

According to calculations, MeOH (one, two, or three units) can be incorporated to the cavity of triscarbamate **13**, as represented in Figures SI_14 to 16. It docks within the steroid by means of multiple H-bond contacts.

Figure SI_14. Representation of the supramolecular complex [**MeOH•13**], optimized with Gausian09 at the DFT (M06-2X/cc-pVDZ) level of theory. Rendered with the Jmol program.

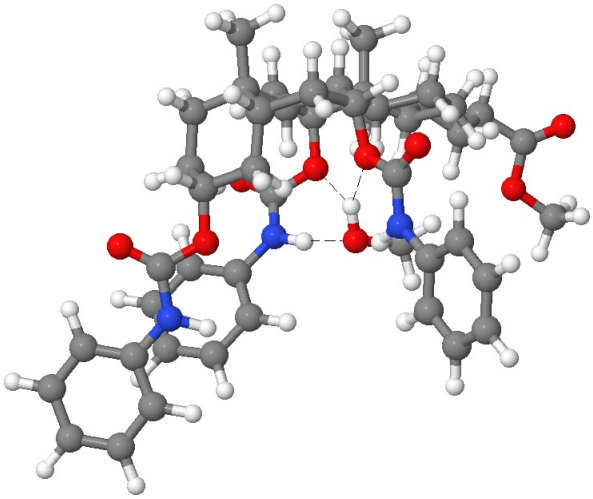


Figure SI_15. Representation of the supramolecular complex [**2 MeOH•13**], optimized with Gausian09 at the DFT (M06-2X/cc-pVDZ) level of theory. Rendered with the Jmol program.

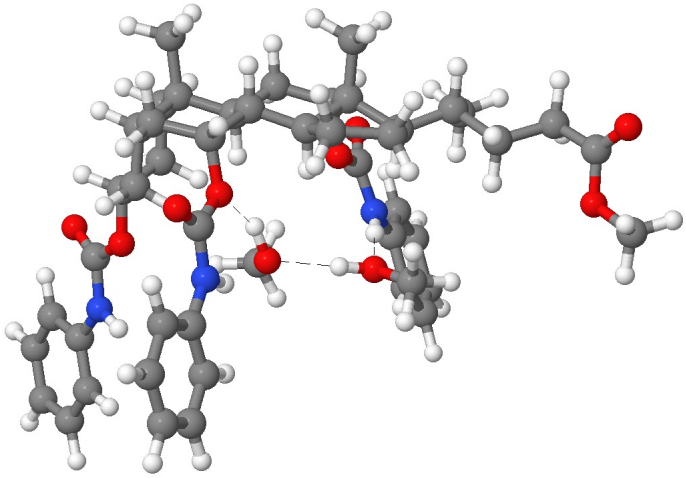
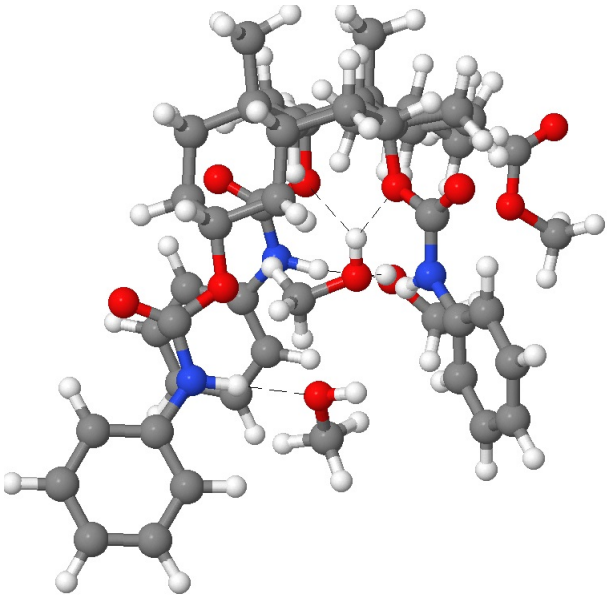


Figure SI_16. Representation of the supramolecular complex [**3 MeOH·13**], optimized with Gausian09 at the DFT (M06-2X/cc-pVDZ) level of theory. Rendered with the Jmol program.



Calculation of energies and thermodynamic parameters

Table SI_10. Electronic energies (E_0), enthalpies (H), entropy (S) and Gibbs free energies (G) at 298 K and 195 K (–78 ºC) for the systems involved in our study. All values are given in *au*.

system	E_0	H (195 K)	S (195 K)	G (298 K)	G (195 K)
13	-2552.620429	-2551.718164	0.000413752	-2551.737243	-2551.798908
[**3a•13**] complex **I**	-3066.662374	-3066.662374	0.000441950	-3065.641421	-3066.662374
[**3a•13**] complex **II**	-3066.647996	-3065.615406	0.000468512	-3065.635836	-3065.706837
TS	-3562.240524	-3561.099979	0.000499962	-3561.117489	-3561.197546
[**3a•13**] complex **II** + **2'**	-3562.267809	-3561.118617	0.000484270	-3561.130376	-3561.213122
3a	-513.9884249	-513.8596769	0.000206739	-513.885917	-513.8862829
4a (neutral)	-1010.132619	-1009.873548	0.000206739	-1009.905789	-1009.913893
4a (anionic)	-1009.557171	-1009,311916	0.000200502	-1009.343958	-1009.351044
2 (neutral)	-496.0506259	-495.9227629	0.000142463	-495.950963	-495.9505649
2' (anionic)	-495.5290465	-495.4153625	0.000137117	-495.44366	-495.4421195
[**3a•13**] complex **II** + **4a** (anionic)	-3562.28973	-3561,138603	0.000490910	-3561.15207	-3561.234404
[**3a•13**] complex **II** + **4a** (neutral)	-3562.804353	-3561.64107	0.000494156	-3561.654054	-3561.737505

Table SI_11. Interaction energies (E_{int}), BSSE, interaction enthalpies (ΔH_{int}), interaction entropies (ΔS_{int}), free Gibbs interaction energies (ΔG_{int}), calculated for different systems. All the interaction quantities are calculated at 195 K. All values are given in *kcal/mol*, except for ΔS_{int}, which are expressed in *cal/mol K*. The interaction magnitudes are computed as the difference between those of given systems.

system A	system B	System B	E_{int}	BSSE	ΔH_{int}	ΔS_{int}	ΔG_{int}
3a	**13**	[**3a•13**] complex **II**	-24.56	-9.68	-23.57	-51.19	-13.58
3a	**13**	[**3a•13**] complex **I**	-33.58	-12.13	-32.11	-67.86	-18.87
4a anionic	**13**	[**3a•13**] complex **II** + **4a** (anionic)	-69.93	-21.38	-68.10	-77.40	-52,99
4a neutral	**13**	[**3a•13**] complex **II** + **4a** (neutral)	-33.46	-12.58	-32.24	-79.28	-16.77
2'	[**3a•13**] complex **II**	[**3a•13**] complex **II** + **2'**	-56.96	-14.21	-55.12	-76.15	-40.26
4a neutral	17	[**3a•13**] complex **I** + **2'**	-81.52	-16.72	-78.70	-127.34	-53.85

XYZ coordinate (in Ångströms) for the optimized structures

Dimethyl malonate (2)

C	-2.96022	-1.04449	-0.17135
O	-1.71326	-0.52561	-0.63331
C	-1.30612	0.58767	-0.01090
O	-1.94641	1.17010	0.82463
C	0.06294	1.00103	-0.49921
C	1.11790	0.07142	0.06741
O	2.31823	0.34117	-0.46355
O	0.92107	-0.78286	0.89213
C	3.38687	-0.46527	0.03596
H	-3.15054	-1.93544	-0.76743
H	-3.75378	-0.30746	-0.31202
H	-2.89078	-1.29687	0.88882
H	0.26966	2.02072	-0.16656
H	0.11330	0.97019	-1.59091
H	4.28266	-0.12008	-0.47752
H	3.19861	-1.51880	-0.18098
H	3.48566	-0.33692	1.11595

Dimethyl malonate anion (2')

C	-3.57138	0.24237	0.00002
O	-2.30032	0.83503	-0.00002
C	-1.24358	-0.10231	-0.00009
O	-1.53066	-1.29176	-0.00003
C	0.00000	0.57049	-0.00002
C	1.24358	-0.10231	0.00006
O	2.30032	0.83503	0.00002
O	1.53066	-1.29176	0.00003
C	3.57138	0.24237	0.00001
H	-4.30156	1.06583	0.00007
H	-3.73104	-0.39610	0.88537
H	-3.73112	-0.39604	-0.88537
H	0.00000	1.65669	-0.00002
H	4.30156	1.06583	-0.00003
H	3.73107	-0.39610	-0.88534
H	3.73110	-0.39604	0.88540

Nitrostyrene (3a)

C	0.62027	0.44777	-0.00010
C	1.59580	-0.46257	-0.00009
N	2.99059	-0.03032	-0.00013
O	3.23955	1.15774	0.00016
O	3.81463	-0.92300	0.00022
C	-0.81943	0.17630	-0.00006
H	1.51190	-1.54562	-0.00004
C	-1.34898	-1.12382	-0.00007
C	-1.70105	1.26524	-0.00002
C	-3.07901	1.06540	0.00003
C	-3.59278	-0.22917	0.00002
C	-2.72346	-1.32290	-0.00003

H	0.93561	1.49450	-0.00014
H	-0.68187	-1.98652	-0.00011
H	-3.12264	-2.33747	-0.00003
H	-4.67126	-0.39004	0.00005
H	-3.75177	1.92315	0.00006
H	-1.29572	2.27881	-0.00001

Triscarbamate 13

C	-1.87781	-0.27536	-3.64864
C	-2.66634	-0.68404	-2.40733
C	-3.50053	0.49996	-1.94473
O	-4.21350	0.19756	-0.73125
C	-2.61816	1.69541	-1.64068
C	-1.77861	2.10719	-2.86212
C	-0.90679	3.33540	-2.56871
C	0.30689	3.04112	-1.69145
O	-0.09702	2.72445	-0.33941
C	1.11548	1.84857	-2.19793
C	0.22224	0.61555	-2.46406
C	-0.94225	0.93452	-3.44435
C	-0.41615	1.31836	-4.83623
C	1.06124	-0.59512	-2.89548
C	2.23910	-0.90506	-1.96621
O	1.73676	-1.31387	-0.67518
C	3.13416	0.32146	-1.74180
C	3.84769	0.66227	-3.05769
C	2.23354	1.46887	-1.23507
C	3.21774	2.55206	-0.80165
C	4.41665	1.75097	-0.24205
C	4.16717	0.25296	-0.58222
C	5.46989	-0.53279	-0.79947
C	5.21333	-1.98964	-1.18979
C	6.33065	-0.45077	0.47078
C	7.73210	-1.05085	0.31427
C	8.59987	-0.77065	1.51497
O	9.65516	-0.19130	1.50509
O	8.03900	-1.25124	2.64294
C	8.79757	-1.02068	3.82793
H	-2.59900	-0.00445	-4.44007
H	-1.31130	-1.13183	-4.04234
H	-3.32519	-1.53223	-2.63640
H	-1.99432	-0.99046	-1.58755
H	-4.24141	0.74406	-2.72292
C	-5.33207	-0.54770	-0.88336
H	-1.97763	1.43415	-0.78691
H	-3.24253	2.54595	-1.32362
H	-2.49692	2.40021	-3.64958
H	-1.50096	4.13246	-2.09844
H	-0.52462	3.74965	-3.51471
H	0.94216	3.93691	-1.63764
C	-0.49539	3.77177	0.41788
H	1.56963	2.18660	-3.14494
H	-0.22467	0.35629	-1.48864
H	0.32348	2.13038	-4.81669
H	-1.25246	1.64933	-5.47129

H	0.04711	0.45454	-5.33590
H	1.46299	-0.44615	-3.90963
H	0.44288	-1.50256	-2.93740
H	2.79574	-1.75179	-2.38394
H	4.55620	1.49223	-2.92146
H	3.15236	0.95015	-3.85753
H	4.42371	-0.20353	-3.41852
H	1.75050	1.08266	-0.32210
H	2.78388	3.23526	-0.05875
H	3.51884	3.16582	-1.66583
H	4.52231	1.89396	0.84177
H	5.36288	2.09029	-0.69350
H	3.64621	-0.21558	0.26954
H	6.03800	-0.04325	-1.61259
H	6.14090	-2.57855	-1.19656
H	4.78069	-2.07664	-2.19464
H	4.51701	-2.46511	-0.47875
H	6.44316	0.60398	0.76596
H	5.81049	-0.95722	1.30083
H	7.67787	-2.14320	0.19698
H	8.24816	-0.63089	-0.55934
H	8.22506	-1.47217	4.64433
H	8.93043	0.05667	3.99626
H	9.78920	-1.48580	3.74616
C	1.36342	-2.61062	-0.57182
O	1.40361	-3.41179	-1.47647
N	0.94590	-2.84151	0.71045
C	0.47469	-4.04473	1.26391
H	1.01455	-2.04522	1.33158
C	0.16226	-4.03772	2.62998
C	0.30467	-5.21941	0.52116
C	-0.17720	-6.36137	1.15848
C	-0.49090	-6.35870	2.51582
C	-0.31715	-5.18608	3.24902
H	-0.55490	-5.16131	4.31321
H	0.29926	-3.12054	3.20802
H	0.54945	-5.22886	-0.53697
H	-0.30795	-7.27240	0.57264
H	-0.86741	-7.26076	2.99803
O	-5.73846	-0.96785	-1.94216
N	-5.90655	-0.73023	0.34529
C	-7.07802	-1.44233	0.65163
H	-5.43060	-0.27014	1.11127
C	-7.50532	-1.42840	1.98632
C	-7.81559	-2.15560	-0.30206
C	-8.96172	-2.84007	0.09769
C	-9.38965	-2.82978	1.42336
C	-8.65132	-2.11698	2.36685
H	-8.96687	-2.09400	3.41077
H	-6.93065	-0.87011	2.72914
H	-7.48978	-2.16588	-1.33802
H	-9.52868	-3.39312	-0.65263
H	-10.28783	-3.37200	1.71886
O	-0.43006	4.92995	0.07731
N	-0.97577	3.29164	1.60619
C	-1.46919	4.02628	2.69821

H	-0.93623	2.28523	1.70796
C	-1.60657	5.42009	2.68941
C	-2.11452	6.05922	3.81900
C	-2.48787	5.34272	4.95392
C	-2.34784	3.95570	4.95549
C	-1.84276	3.30145	3.83804
H	-1.31736	5.98598	1.80867
H	-2.21874	7.14501	3.80339
H	-2.88408	5.85862	5.82853
H	-2.63223	3.37376	5.83300
H	-1.73379	2.21427	3.84305

Supramolecular complex I [3a•13]

C	-0.92025	0.74156	-3.89590
C	-1.85259	0.45687	-2.72710
C	-2.47484	1.76529	-2.26479
O	-3.27755	1.56018	-1.08387
C	-1.40606	2.76722	-1.86682
C	-0.35945	3.00840	-2.96969
C	0.73638	3.97517	-2.48576
C	1.77371	3.34109	-1.55725
O	1.17770	2.96525	-0.30162
C	2.34410	2.04395	-2.13464
C	1.17428	1.08162	-2.44808
C	0.23857	1.68925	-3.53329
C	0.99057	1.97418	-4.84245
C	1.61740	-0.35479	-2.74763
C	2.64051	-0.90330	-1.74965
O	2.10115	-0.95922	-0.40702
C	3.86525	0.02264	-1.65483
C	4.56887	0.08703	-3.01776
C	3.34511	1.40019	-1.18529
C	4.61134	2.18329	-0.84437
C	5.57619	1.10475	-0.29798
C	4.90344	-0.27747	-0.53692
C	5.92584	-1.40190	-0.76727
C	5.26021	-2.74716	-1.06018
C	6.85506	-1.50374	0.45199
C	8.01045	-2.49570	0.27829
C	9.01163	-2.39200	1.40096
O	10.18604	-2.15554	1.28119
O	8.42320	-2.59314	2.59687
C	9.30092	-2.49173	3.71597
H	-1.50288	1.21558	-4.70530
H	-0.52652	-0.19577	-4.31593
H	-2.64109	-0.25483	-3.00926
H	-1.28247	0.02923	-1.88713
H	-3.12994	2.15855	-3.05862
C	-4.48613	0.98956	-1.28061
H	-0.93312	2.38005	-0.95475
H	-1.87979	3.72478	-1.59849
H	-0.88333	3.50225	-3.80847
H	0.28669	4.84014	-1.97473
H	1.28599	4.37941	-3.35005
H	2.57250	4.06844	-1.35070

C	0.86026	3.96372	0.55747
H	2.87234	2.32079	-3.06142
H	0.59951	1.02055	-1.50897
H	1.77394	2.73645	-4.74365
H	0.28182	2.33217	-5.60482
H	1.45884	1.05899	-5.23760
H	2.06215	-0.44253	-3.75107
H	0.74968	-1.02652	-2.73535
H	2.90112	-1.93072	-2.03578
H	5.51960	0.63534	-2.94310
H	3.96416	0.58418	-3.78790
H	4.80525	-0.92438	-3.38440
H	2.81273	1.21060	-0.24128
H	4.42050	2.98147	-0.11424
H	5.02423	2.66279	-1.74686
H	5.78746	1.25830	0.76862
H	6.54733	1.14678	-0.81731
H	4.32514	-0.54283	0.36385
H	6.55319	-1.12532	-1.63489
H	5.99381	-3.56492	-1.08852
H	4.75312	-2.74750	-2.03373
H	4.51321	-2.98745	-0.28483
H	7.28630	-0.51251	0.66075
H	6.26680	-1.78473	1.34135
H	7.63882	-3.53113	0.26532
H	8.55699	-2.31027	-0.65612
H	8.68375	-2.68108	4.59997
H	9.75008	-1.49035	3.76348
H	10.10781	-3.23304	3.64038
C	1.17137	-1.87763	-0.11546
O	0.61608	-2.59757	-0.92158
N	0.96554	-1.87624	1.24319
C	-0.10593	-2.51711	1.89230
H	1.36847	-1.07439	1.71546
C	-0.68174	-1.89275	3.00607
C	-0.60602	-3.74666	1.44574
C	-1.71357	-4.30400	2.07788
C	-2.31930	-3.66429	3.15886
C	-1.78580	-2.46418	3.63047
H	-2.23949	-1.95760	4.48312
H	-0.28647	-0.93488	3.35326
H	-0.13967	-4.24070	0.59670
H	-2.11510	-5.24882	1.70806
H	-3.19331	-4.10509	3.63887
O	-4.93201	0.67261	-2.35847
N	-5.10020	0.84537	-0.06163
C	-6.22060	0.05276	0.22348
H	-4.52433	1.12118	0.72986
C	-6.49866	-0.19131	1.57793
C	-7.04089	-0.51309	-0.76186
C	-8.11041	-1.31997	-0.37637
C	-8.38483	-1.57291	0.96703
C	-7.57188	-0.99731	1.94399
H	-7.77135	-1.17453	3.00168
H	-5.85839	0.25632	2.34265
H	-6.82881	-0.32609	-1.81061

H	-8.74124	-1.75857	-1.15114
H	-9.22834	-2.20225	1.25100
O	1.26205	5.10084	0.45593
N	0.03419	3.45201	1.51582
C	-0.52366	4.12985	2.61237
H	-0.25458	2.48545	1.37175
C	-0.13851	5.41895	3.00036
C	-0.73953	6.00015	4.11587
C	-1.71250	5.32458	4.84916
C	-2.09185	4.04222	4.45259
C	-1.50554	3.44550	3.34246
H	0.61647	5.95207	2.42913
H	-0.43500	7.00496	4.41271
H	-2.17414	5.79341	5.71837
H	-2.85757	3.49919	5.00856
H	-1.81372	2.44930	3.01633
C	-3.42255	-1.75645	0.50057
C	-2.26090	-1.12826	0.27616
N	-1.93012	0.06690	1.00318
O	-0.82078	0.54459	0.78997
O	-2.72871	0.54724	1.79004
C	-3.85925	-2.96340	-0.19319
H	-1.46873	-1.43821	-0.39917
C	-5.17117	-3.40874	0.02103
C	-3.01410	-3.68320	-1.05642
C	-3.48511	-4.82629	-1.68902
C	-4.79717	-5.26092	-1.47605
C	-5.63942	-4.55098	-0.62278
H	-4.10083	-1.33955	1.24761
H	-5.82830	-2.84304	0.68680
H	-6.66473	-4.88371	-0.45722
H	-5.16012	-6.15837	-1.97922
H	-2.82657	-5.38723	-2.35295
H	-1.98061	-3.36351	-1.21301

Supramolecular complex II [3a·13]

C	-1.94689	0.02786	-3.74375
C	-2.72410	-0.21326	-2.45849
C	-3.38556	1.08543	-2.02616
O	-4.08052	0.95236	-0.75434
C	-2.33741	2.18289	-1.81865
C	-1.50693	2.41635	-3.08618
C	-0.48049	3.54547	-2.90128
C	0.74057	3.13618	-2.06601
O	0.37777	3.02914	-0.68586
C	1.34030	1.81915	-2.50176
C	0.27944	0.70133	-2.62148
C	-0.84290	1.11664	-3.61335
C	-0.31117	1.35105	-5.02522
C	0.93329	-0.64753	-2.95464
C	2.13869	-1.01761	-2.08505
O	1.69482	-1.26977	-0.73842
C	3.18643	0.08810	-2.02351
C	3.85983	0.22242	-3.39810
C	2.46673	1.36538	-1.58592

C	3.58354	2.35996	-1.28906
C	4.72557	1.47863	-0.74960
C	4.27540	0.00035	-0.91313
C	5.45569	-0.97207	-1.08580
C	4.97633	-2.42269	-1.13805
C	6.44689	-0.77430	0.05715
C	7.67165	-1.69125	-0.02146
C	8.74360	-1.27175	0.95611
O	9.88557	-0.97839	0.68481
O	8.26214	-1.22367	2.21765
C	9.21522	-0.81201	3.20152
H	-2.64752	0.36375	-4.52572
H	-1.50549	-0.90668	-4.12803
H	-3.50340	-0.99235	-2.61145
H	-2.05774	-0.57918	-1.65701
H	-4.11834	1.37877	-2.78554
C	-5.29166	0.34322	-0.79525
H	-1.70990	1.89453	-0.96739
H	-2.84654	3.11045	-1.51788
H	-2.22360	2.74684	-3.86610
H	-0.94812	4.41920	-2.42051
H	-0.11233	3.87181	-3.87514
H	1.50592	3.93542	-2.15290
C	0.46824	4.20044	0.02213
H	1.78693	2.01222	-3.50223
H	-0.15848	0.59363	-1.62607
H	0.50050	2.08769	-5.08162
H	-1.11672	1.71167	-5.68046
H	0.05917	0.40873	-5.47491
H	1.27710	-0.65009	-4.01067
H	0.20057	-1.47337	-2.87361
H	2.53250	-1.95667	-2.47094
H	4.66298	0.95768	-3.38822
H	3.14834	0.51921	-4.18364
H	4.29292	-0.73666	-3.70713
H	1.99149	1.11903	-0.60886
H	3.28139	3.14624	-0.57652
H	3.89732	2.88180	-2.21137
H	4.97189	1.71111	0.28688
H	5.65394	1.65033	-1.33294
H	3.74586	-0.28544	0.00969
H	5.97945	-0.71990	-2.03144
H	5.81708	-3.12547	-1.25743
H	4.28833	-2.61454	-1.98026
H	4.45191	-2.69533	-0.20393
H	6.79863	0.26871	0.07253
H	5.94094	-0.93297	1.02429
H	7.38735	-2.73551	0.22645
H	8.12949	-1.67794	-1.01065
H	8.66825	-0.77665	4.15615
H	9.61467	0.17820	2.95729
H	10.03026	-1.53043	3.27381
C	1.69013	-2.53822	-0.31159
O	1.58853	-3.50853	-1.02379
N	1.76346	-2.55610	1.07516
C	1.33293	-3.63514	1.88395

H	1.72861	-1.63850	1.49164
C	0.80123	-3.29977	3.13850
C	1.42018	-4.96295	1.47085
C	0.88282	-5.96881	2.32013
C	0.32189	-5.64211	3.55245
C	0.29484	-4.31706	3.95850
H	-0.17042	-4.03196	4.91247
H	0.71589	-2.25823	3.44115
H	1.82178	-5.21419	0.50174
H	0.88044	-7.00216	1.96340
H	-0.11660	-6.43643	4.18936
O	-5.74360	-0.22236	-1.76423
N	-5.87223	0.47637	0.44482
C	-7.00718	-0.22047	0.90709
H	-5.32861	0.99616	1.12482
C	-7.11605	-0.37957	2.34264
C	-7.99657	-0.74069	0.02426
C	-9.09090	-1.42654	0.57893
C	-9.20080	-1.58973	2.00555
C	-8.21377	-1.04924	2.87632
H	-8.29224	-1.18591	3.99396
H	-6.32781	-0.00623	3.03969
H	-7.89883	-0.61185	-1.07357
H	-9.84043	-1.84417	-0.10897
H	-10.05788	-2.12353	2.42319
O	0.94267	5.23951	-0.44502
N	-0.02995	3.98366	1.29332
C	-0.08436	4.93763	2.32953
H	-0.35194	3.05434	1.51785
C	0.33565	6.27079	2.20014
C	0.18900	7.13376	3.29562
C	-0.35124	6.68197	4.49716
C	-0.75027	5.35312	4.61800
C	-0.61150	4.47687	3.53729
H	0.76795	6.63841	1.27360
H	0.55185	8.18028	3.18972
H	-0.42181	7.37435	5.34395
H	-1.16760	4.98589	5.55939
H	-0.92417	3.42722	3.63745
C	-1.57285	-1.76650	0.72860
C	-1.88069	-0.48283	0.99859
N	-0.92756	0.35279	1.68092
O	0.23379	-0.01142	1.83872
O	-1.35695	1.45728	2.07013
C	-2.48861	-2.68883	0.05977
H	-2.80171	0.03091	0.78887
C	-3.87777	-2.47172	0.09755
C	-1.97806	-3.78308	-0.64151
C	-2.84711	-4.63839	-1.34319
C	-4.22353	-4.40168	-1.31893
C	-4.74078	-3.31307	-0.59967
H	-0.56365	-2.11491	0.96432
H	-4.29333	-1.64883	0.69750
H	-5.81739	-3.10810	-0.58656
H	-4.89470	-5.05957	-1.87681
H	-2.43901	-5.46671	-1.91476

H	-0.89661	-3.96109	-0.68596

TS for the reaction between 2' and 3a without catalyst 13

C	-0.57957	1.62667	-0.41614
O	-1.78811	2.07262	0.13342
C	-2.81660	2.30703	-0.79583
H	-2.83528	1.53881	-1.58128
H	-2.69619	3.29312	-1.28345
H	-3.76386	2.29548	-0.23540
O	-0.55135	1.26085	-1.58563
C	0.44234	1.65828	0.56431
C	1.78805	1.33228	0.25950
O	2.26987	0.89620	-0.78262
O	2.61843	1.53736	1.35498
C	3.95898	1.15501	1.13024
H	4.49138	1.34699	2.07303
H	4.41658	1.74134	0.31658
H	4.03236	0.08939	0.86401
C	0.10680	-1.37807	0.36178
H	0.20680	2.05461	1.54788
C	-1.34623	-1.18423	0.36854
C	-1.99938	-1.01611	1.59646
C	-2.11501	-1.18301	-0.80469
C	-3.49697	-1.03722	-0.74111
C	-4.13656	-0.87460	0.48830
C	-3.37980	-0.85809	1.65954
H	-3.86625	-0.71569	2.62607
H	-1.40033	-0.99027	2.50876
H	-4.08112	-1.03622	-1.66319
H	-5.22052	-0.75172	0.53164
H	-1.62206	-1.28930	-1.77039
C	0.88498	-1.42931	-0.72243
H	0.59425	-1.53851	1.32528
N	2.28751	-1.76682	-0.57257
O	2.90962	-1.97155	-1.59491
O	2.75742	-1.88181	0.54849
H	0.62289	-1.18297	-1.74994

TS for the reaction between 2' and 3a inside steroidal triscarbamate 13

C	0.96673	-3.88964	-2.51018
C	1.96835	-2.82774	-2.04175
C	2.72074	-3.36130	-0.82676
O	3.67384	-2.36597	-0.33931
C	1.75503	-3.68247	0.30477
C	0.69375	-4.72516	-0.12826
C	-0.27085	-5.06225	1.03153
C	-1.36795	-4.02360	1.27966
O	-0.76262	-2.80576	1.77552
C	-2.13022	-3.67935	-0.01527
C	-1.13448	-3.22206	-1.12629
C	-0.07394	-4.34230	-1.44542
C	-0.74900	-5.61146	-2.02325
C	-1.86641	-2.68797	-2.38172
C	-3.00496	-1.69154	-2.10231

O	-2.42042	-0.46613	-1.56472
C	-4.01721	-2.25570	-1.07682
C	-4.73174	-3.48378	-1.69208
C	-3.21483	-2.61760	0.20827
C	-4.30153	-2.88402	1.25900
C	-5.39585	-1.83785	0.92579
C	-5.07360	-1.24971	-0.49354
C	-6.36305	-0.93863	-1.30146
C	-6.11616	-0.47794	-2.74800
C	-7.19797	0.11787	-0.53828
C	-8.63435	0.29908	-1.06981
C	-9.43978	1.27225	-0.24025
O	-10.43577	1.01184	0.40476
O	-8.89913	2.51990	-0.29285
C	-9.56997	3.51658	0.49553
H	1.53710	-4.78582	-2.81987
H	0.44994	-3.54486	-3.41988
H	2.67796	-2.60077	-2.85521
H	1.45989	-1.89065	-1.77019
H	3.30636	-4.24657	-1.11789
C	4.97165	-2.52448	-0.73868
H	1.28411	-2.75271	0.64046
H	2.31657	-4.09034	1.16381
H	1.24916	-5.65538	-0.35819
H	0.30052	-5.21145	1.96337
H	-0.77638	-6.02170	0.82507
H	-2.05263	-4.39088	2.05651
C	-1.19861	-2.27511	2.95846
H	-2.62429	-4.61699	-0.32303
H	-0.59446	-2.36274	-0.70644
H	-1.53199	-6.02829	-1.37310
H	0.00158	-6.40523	-2.17854
H	-1.21102	-5.41248	-3.00430
H	-2.29341	-3.51579	-2.97120
H	-1.15079	-2.18353	-3.04822
H	-3.48439	-1.42179	-3.04942
H	-5.52905	-3.85848	-1.03347
H	-4.05099	-4.32535	-1.87797
H	-5.20076	-3.23304	-2.65590
H	-2.69910	-1.69039	0.50080
H	-3.93206	-2.78908	2.28829
H	-4.69615	-3.91114	1.15860
H	-5.41180	-1.03809	1.68244
H	-6.39838	-2.29834	0.94221
H	-4.54075	-0.29619	-0.34971
H	-6.96880	-1.86546	-1.33728
H	-7.06348	-0.21815	-3.24984
H	-5.64758	-1.26088	-3.36071
H	-5.45687	0.40163	-2.79808
H	-7.26672	-0.16142	0.52468
H	-6.67586	1.08968	-0.57178
H	-8.61544	0.67382	-2.10709
H	-9.17889	-0.65792	-1.06152
H	-9.00021	4.44421	0.34767
H	-9.57760	3.23644	1.56159
H	-10.61290	3.64693	0.16265

C	-2.51137	0.66178	-2.32970
O	-3.04458	0.70225	-3.43244
N	-1.94145	1.70930	-1.66021
C	-1.91270	3.05689	-2.07049
H	-1.45926	1.49652	-0.77803
C	-1.31913	3.98498	-1.18914
C	-2.45030	3.51642	-3.28945
C	-2.39072	4.87836	-3.60252
C	-1.80539	5.80063	-2.72902
C	-1.26933	5.33931	-1.52031
H	-0.80383	6.03991	-0.82058
H	-0.89061	3.62680	-0.25293
H	-2.90218	2.80229	-3.97286
H	-2.81262	5.21854	-4.55350
H	-1.76511	6.86295	-2.98602
O	5.36384	-3.44174	-1.44688
N	5.73191	-1.50555	-0.22402
C	7.11856	-1.31804	-0.39381
H	5.25523	-0.81500	0.36606
C	7.68631	-0.16468	0.18820
C	7.94732	-2.21016	-1.10336
C	9.31563	-1.94214	-1.21441
C	9.88268	-0.80245	-0.63452
C	9.05380	0.08268	0.06643
H	9.47341	0.98333	0.52500
H	7.03960	0.52960	0.72588
H	7.50842	-3.09507	-1.55731
H	9.94676	-2.64495	-1.76761
H	10.95441	-0.60480	-0.72815
O	-1.87504	-2.88623	3.77764
N	-0.74196	-0.99139	3.03176
C	-0.85875	-0.09443	4.11249
H	-0.28581	-0.65701	2.17038
C	-1.54911	-0.39915	5.30242
C	-1.59769	0.54795	6.33107
C	-0.97032	1.79238	6.20114
C	-0.28709	2.08999	5.01523
C	-0.23364	1.16080	3.97619
H	-2.03300	-1.36806	5.40403
H	-2.13738	0.30078	7.25126
H	-1.01159	2.52135	7.01617
H	0.22457	3.04489	4.87728
H	0.29312	1.41964	3.05890
C	2.51664	2.31622	-0.55421
C	2.04641	0.99533	-0.44217
N	0.86751	0.71754	0.18880
O	0.05107	1.63868	0.51677
O	0.57743	-0.49784	0.44303
C	3.56311	2.67923	-1.53094
C	4.53548	1.76528	-1.98601
C	3.59499	3.99464	-2.03759
C	4.55540	4.38056	-2.97465
C	5.51416	3.46198	-3.41908
C	5.50076	2.15491	-2.91621
H	4.55460	0.74954	-1.59669
H	6.25104	1.43152	-3.24605

H	6.27003	3.76304	-4.15018
H	4.55639	5.40502	-3.35901
H	2.85913	4.71786	-1.67988
C	1.98881	6.01947	1.98101
O	2.83345	5.01744	1.40912
C	2.73421	3.76873	2.00607
O	1.98060	3.58247	2.94791
C	3.61326	2.83668	1.30408
C	3.88994	1.48613	1.75364
O	2.94213	0.95185	2.55132
O	4.85385	0.81589	1.35360
C	3.12506	-0.42468	2.92473
H	2.17359	6.93457	1.39864
H	2.23024	6.19216	3.04414
H	0.92442	5.73605	1.91746
H	3.04110	-1.08280	2.04871
H	2.31704	-0.64016	3.63435
H	4.10778	-0.57401	3.40026
H	4.45244	3.30091	0.79083
H	1.77039	3.08598	-0.36954
H	2.63435	0.11295	-0.66856

Preorganized reagents within the catalyst: [2'•3a•13]

C	0.65882	-0.61566	-4.54057
C	1.46585	0.19920	-3.53493
C	2.58000	-0.64573	-2.93167
O	3.15946	0.13032	-1.86885
C	2.03681	-1.94583	-2.35802
C	1.21152	-2.74970	-3.37366
C	0.70875	-4.06984	-2.77781
C	-0.37517	-3.88213	-1.71691
O	0.16247	-3.26730	-0.53747
C	-1.50322	-2.96493	-2.19783
C	-0.98672	-1.65331	-2.83994
C	0.04977	-1.91358	-3.96907
C	-0.58279	-2.65456	-5.15672
C	-2.17095	-0.78811	-3.28895
C	-3.22072	-0.51388	-2.20712
O	-2.69551	0.39004	-1.21545
C	-3.68675	-1.79029	-1.49273
C	-4.59522	-2.56022	-2.46185
C	-2.44325	-2.59312	-1.05742
C	-3.00934	-3.71000	-0.18241
C	-4.23260	-3.05418	0.50337
C	-4.38075	-1.63423	-0.10838
C	-5.81633	-1.09070	-0.04830
C	-5.90542	0.35427	-0.54369
C	-6.34995	-1.19647	1.38952
C	-7.77862	-0.66910	1.56131
C	-8.34340	-0.98924	2.92049
O	-9.36351	-1.59148	3.14391
O	-7.55241	-0.50973	3.90136
C	-8.00986	-0.78128	5.22171
H	1.32052	-0.90987	-5.37575
H	-0.12851	0.01206	-4.98520

H	1.89118	1.09353	-4.01543
H	0.80296	0.55628	-2.73075
H	3.35931	-0.84963	-3.68370
C	4.31850	-0.36994	-1.33104
H	1.42975	-1.67699	-1.48260
H	2.87698	-2.56082	-2.00047
H	1.88452	-3.00316	-4.21454
H	1.54034	-4.63846	-2.33738
H	0.28426	-4.70201	-3.57434
H	-0.78248	-4.86400	-1.42979
C	1.04876	-4.00143	0.17639
H	-2.06160	-3.54757	-2.95271
H	-0.47901	-1.10704	-2.02721
H	-1.15231	-3.54659	-4.86197
H	0.20520	-2.97907	-5.85502
H	-1.26237	-1.99299	-5.71565
H	-2.68775	-1.27256	-4.13390
H	-1.83101	0.19347	-3.65206
H	-4.05867	-0.00718	-2.69955
H	-4.98559	-3.48264	-2.00730
H	-4.07090	-2.84318	-3.38560
H	-5.45875	-1.94107	-2.75238
H	-1.87158	-1.92134	-0.39591
H	-2.26611	-4.07414	0.53878
H	-3.31655	-4.57214	-0.79717
H	-4.10772	-2.99972	1.59308
H	-5.14851	-3.64055	0.32004
H	-3.74606	-0.94669	0.47559
H	-6.45957	-1.72793	-0.68427
H	-6.93649	0.73529	-0.51102
H	-5.56594	0.46631	-1.58051
H	-5.28032	1.01167	0.08418
H	-6.33058	-2.24914	1.71038
H	-5.67949	-0.64622	2.07073
H	-7.79994	0.42533	1.45097
H	-8.45975	-1.10594	0.81839
H	-7.26659	-0.34213	5.89463
H	-8.08966	-1.86448	5.38691
H	-8.99808	-0.33050	5.38735
C	-2.99476	1.69814	-1.39889
O	-3.43518	2.16130	-2.42848
N	-2.74915	2.37160	-0.23615
C	-2.76975	3.75840	-0.03535
H	-2.34932	1.80647	0.51490
C	-2.47702	4.20986	1.26169
C	-3.03449	4.69016	-1.04741
C	-2.99077	6.05119	-0.74796
C	-2.69358	6.50458	0.53605
C	-2.43755	5.57094	1.54141
H	-2.19415	5.89974	2.55253
H	-2.26039	3.47762	2.04377
H	-3.25923	4.34275	-2.05177
H	-3.18791	6.76980	-1.54537
H	-2.65903	7.57273	0.75218
O	4.99228	-1.20183	-1.90409
N	4.54598	0.21069	-0.13100

C	5.63614	-0.02287	0.71781
H	3.85539	0.89382	0.21830
C	5.61453	0.63935	1.95763
C	6.71038	-0.86892	0.40673
C	7.74936	-1.02337	1.32462
C	7.74392	-0.35307	2.54581
C	6.66416	0.47795	2.85380
H	6.62933	1.00529	3.80884
H	4.76206	1.27669	2.19437
H	6.71655	-1.40289	-0.53903
H	8.57781	-1.68808	1.07215
H	8.56424	-0.48145	3.25345
O	1.17064	-5.20337	0.05552
N	1.75044	-3.18159	1.01003
C	2.89495	-3.55277	1.74648
H	1.55413	-2.18129	0.93354
C	3.20198	-4.88141	2.06848
C	4.36600	-5.15574	2.78574
C	5.22524	-4.13489	3.18565
C	4.90710	-2.81413	2.86749
C	3.74842	-2.51946	2.15661
H	2.54257	-5.68238	1.74784
H	4.60024	-6.19418	3.02908
H	6.13789	-4.36438	3.73741
H	5.56930	-1.99609	3.15645
H	3.49120	-1.48444	1.91513
C	0.44790	2.65919	-0.02634
C	0.64504	1.33835	-0.14471
N	-0.14892	0.43217	0.63516
O	-0.94264	0.86344	1.46712
O	-0.01781	-0.75965	0.40826
C	1.08049	3.67844	-0.86197
H	1.38272	0.82458	-0.75277
C	2.11202	3.37763	-1.76728
C	0.60095	4.99252	-0.77956
C	1.11527	5.98658	-1.60967
C	2.11712	5.67514	-2.52678
C	2.61680	4.37104	-2.59747
H	-0.27208	3.00789	0.71273
H	2.53559	2.37284	-1.79571
H	3.42006	4.13100	-3.29569
H	2.52022	6.44928	-3.18227
H	0.72670	7.00363	-1.53891
H	-0.19126	5.22776	-0.06512
C	0.87530	-0.63457	3.74944
O	1.21110	0.74107	3.74432
C	1.93780	1.16084	2.66099
O	2.28985	0.33158	1.80425
C	2.16271	2.55445	2.66652
C	2.93876	3.18767	1.66646
O	2.99082	4.55018	1.84312
O	3.54298	2.68638	0.70967
C	3.82689	5.23237	0.92851
H	0.32350	-0.80263	4.68294
H	1.77248	-1.27163	3.72864
H	0.23404	-0.89491	2.89266

H	1.75472	3.15286	3.47547
H	3.80927	6.28682	1.23351
H	3.46116	5.13520	-0.10371
H	4.85615	4.84391	0.96420

Reaction product 4a (neutral)

C	-0.15418	-1.57482	0.81468
O	-0.85090	-1.35775	1.93867
C	-1.86070	-2.33217	2.21054
H	-2.59207	-2.35019	1.39069
H	-2.33362	-2.01783	3.14599
H	-1.41253	-3.32855	2.31576
O	-0.27784	-2.54373	0.11589
C	0.78113	-0.40828	0.54332
C	1.63327	-0.74874	-0.66765
O	1.47490	-0.34007	-1.79187
O	2.60316	-1.58800	-0.31463
C	3.46213	-1.99351	-1.38119
H	2.88306	-2.50900	-2.15839
H	4.19592	-2.66849	-0.93127
H	3.95514	-1.11589	-1.81966
C	-0.03956	0.90660	0.46543
H	1.47049	-0.34586	1.39833
C	-1.39334	0.77211	-0.21379
C	-1.52516	0.42229	-1.56291
C	-2.54838	1.00002	0.54228
C	-3.81244	0.89169	-0.03359
C	-3.93631	0.54779	-1.37860
C	-2.79108	0.31296	-2.13703
H	-2.87954	0.03630	-3.18842
H	-0.63464	0.21834	-2.15757
H	-4.70159	1.07646	0.57094
H	-4.92372	0.45871	-1.83346
H	-2.45286	1.26013	1.59892
C	0.74879	2.06609	-0.15591
H	-0.24138	1.18663	1.50939
N	2.00482	2.25955	0.63452
O	2.95903	1.56833	0.33427
O	1.96840	3.04373	1.55509
H	0.18422	2.99919	-0.07053
H	1.05049	1.85095	-1.18503

Reaction product 4a (anionic form)

C	-0.09887	-1.72940	0.65579
O	-0.62467	-1.65434	1.89978
C	-1.57256	-2.66772	2.19672
H	-2.42937	-2.60415	1.50962
H	-1.89308	-2.48765	3.22912
H	-1.12223	-3.66567	2.10048
O	-0.36318	-2.63436	-0.09925
C	0.78631	-0.54927	0.36760
C	1.38942	-0.74374	-1.00395
O	1.05882	-0.22826	-2.04022
O	2.39931	-1.63973	-0.94035

C	2.98682	-1.94579	-2.19422
H	2.23889	-2.37265	-2.87783
H	3.77918	-2.67432	-1.98867
H	3.40597	-1.04152	-2.65761
C	0.06469	0.82495	0.59828
H	1.60940	-0.51720	1.10209
C	-1.29309	0.90326	-0.07157
C	-1.45618	1.25552	-1.41803
C	-2.44353	0.61413	0.67457
C	-3.71420	0.66246	0.10126
C	-3.86037	1.01037	-1.23974
C	-2.72452	1.30896	-1.99265
H	-2.82589	1.58472	-3.04445
H	-0.57132	1.46614	-2.01635
H	-4.59286	0.43303	0.70817
H	-4.85199	1.05305	-1.69489
H	-2.32918	0.35223	1.72884
C	0.97027	1.96388	0.27593
H	-0.09889	0.81983	1.68822
N	2.04020	2.15784	1.06139
O	2.24770	1.34784	2.02622
O	2.82715	3.11427	0.85713
H	0.83374	2.66034	-0.54284

Supramolecular complex II [3a·13] + product 4a (neutral)

C	1.03989	-3.49042	-3.20309
C	1.97747	-2.53830	-2.47167
C	2.59271	-3.27976	-1.29529
O	3.48116	-2.41734	-0.55460
C	1.52669	-3.78133	-0.33796
C	0.51650	-4.69411	-1.05955
C	-0.57399	-5.21457	-0.11058
C	-1.65399	-4.19444	0.24642
O	-1.09836	-3.22345	1.15604
C	-2.20549	-3.45715	-0.97989
C	-1.06333	-2.90318	-1.85913
C	-0.10126	-4.03302	-2.32240
C	-0.82742	-5.09361	-3.16429
C	-1.57871	-2.03304	-3.01501
C	-2.58048	-0.96287	-2.58344
O	-1.88959	-0.02125	-1.72896
C	-3.74795	-1.56547	-1.79249
C	-4.56479	-2.47093	-2.72684
C	-3.15644	-2.33198	-0.58779
C	-4.38551	-2.67799	0.25180
C	-5.29044	-1.43545	0.08971
C	-4.69097	-0.57218	-1.05959
C	-5.77352	0.15857	-1.87286
C	-5.20802	0.93612	-3.06178
C	-6.56175	1.09030	-0.93916
C	-7.78982	1.73251	-1.59262
C	-8.63063	2.48916	-0.59636
O	-9.79651	2.29742	-0.36391
O	-7.90647	3.43818	0.03075
C	-8.63212	4.19710	0.99486

H	1.63267	-4.35335	-3.55432
H	0.63075	-3.01952	-4.10846
H	2.77114	-2.18494	-3.14303
H	1.42947	-1.65683	-2.09484
H	3.19001	-4.12033	-1.68297
C	4.68220	-2.20339	-1.14270
H	1.02668	-2.92146	0.12850
H	2.00339	-4.34181	0.48121
H	1.08525	-5.57388	-1.41318
H	-0.12268	-5.58599	0.82238
H	-1.07868	-6.07445	-0.57727
H	-2.47474	-4.69814	0.77270
C	-1.63700	-3.16471	2.40483
H	-2.77597	-4.21188	-1.54661
H	-0.49079	-2.22750	-1.19976
H	-1.68020	-5.55830	-2.65255
H	-0.12443	-5.89918	-3.42753
H	-1.19604	-4.66533	-4.10887
H	-2.05245	-2.65265	-3.79195
H	-0.74066	-1.51241	-3.50217
H	-2.92125	-0.41316	-3.46629
H	-5.47802	-2.82985	-2.23094
H	-4.00266	-3.35296	-3.06282
H	-4.87770	-1.91715	-3.62496
H	-2.56420	-1.58940	-0.02474
H	-4.14088	-2.89642	1.29833
H	-4.87472	-3.57796	-0.15547
H	-5.34146	-0.85941	1.02352
H	-6.32470	-1.72762	-0.15347
H	-4.04193	0.20103	-0.61210
H	-6.48377	-0.59860	-2.25504
H	-5.98526	1.53647	-3.55538
H	-4.79432	0.27104	-3.83076
H	-4.40297	1.62030	-2.74763
H	-6.89913	0.52210	-0.05865
H	-5.89441	1.88474	-0.56521
H	-7.48494	2.44756	-2.37143
H	-8.43965	0.97512	-2.05085
H	-7.91772	4.91225	1.41443
H	-9.03158	3.54072	1.77984
H	-9.47148	4.72171	0.51863
C	-1.60873	1.18911	-2.25828
O	-1.80990	1.51416	-3.40480
N	-1.05492	1.97486	-1.27766
C	-0.80470	3.35590	-1.36767
H	-1.04028	1.56128	-0.34770
C	-0.69632	4.06394	-0.16232
C	-0.62326	4.02804	-2.58288
C	-0.33531	5.39242	-2.56903
C	-0.21387	6.09774	-1.37222
C	-0.39599	5.42201	-0.16523
H	-0.30569	5.95085	0.78474
H	-0.83529	3.53206	0.78107
H	-0.70958	3.48371	-3.51920
H	-0.19770	5.90830	-3.52045
H	0.01616	7.16326	-1.37931

O	5.02524	-2.70153	-2.19062
N	5.41872	-1.34617	-0.37070
C	6.61886	-0.71161	-0.73924
H	4.98413	-1.04272	0.49855
C	7.14611	0.22043	0.16706
C	7.27433	-0.93114	-1.95852
C	8.43077	-0.20804	-2.25073
C	8.94924	0.72803	-1.35818
C	8.29786	0.93408	-0.14219
H	8.68659	1.66007	0.57335
H	6.62358	0.38460	1.11023
H	6.87818	-1.65573	-2.66312
H	8.93163	-0.38609	-3.20351
H	9.85177	1.28743	-1.60418
O	-2.52777	-3.88122	2.80674
N	-1.01142	-2.17497	3.09494
C	-1.27203	-1.73941	4.40277
H	-0.25776	-1.70363	2.60170
C	-2.32222	-2.21649	5.19647
C	-2.49701	-1.68932	6.47618
C	-1.65091	-0.70248	6.97835
C	-0.60391	-0.23851	6.18145
C	-0.41250	-0.75196	4.90452
H	-2.98262	-2.98911	4.81266
H	-3.31722	-2.06425	7.09054
H	-1.80194	-0.30299	7.98151
H	0.08166	0.52544	6.55270
H	0.41140	-0.39100	4.28653
C	2.22410	2.04406	0.31937
C	1.88697	0.58142	-0.00008
N	0.97752	-0.00453	1.03711
O	-0.08884	0.55502	1.24182
O	1.35077	-0.98917	1.62994
C	3.16464	2.58286	-0.74515
C	4.36162	1.92776	-1.05241
C	2.84490	3.76725	-1.41588
C	3.71402	4.28376	-2.37645
C	4.90979	3.62895	-2.67082
C	5.23532	2.44794	-2.00497
H	4.62135	1.00171	-0.54424
H	6.16859	1.92051	-2.21675
H	5.58791	4.03843	-3.42054
H	3.44893	5.20413	-2.89889
H	1.90965	4.28573	-1.19193
C	-0.40955	2.79227	3.57433
O	0.69401	3.00995	2.68119
C	1.69689	2.14596	2.82540
O	1.76185	1.31590	3.69713
C	2.76135	2.32363	1.74466
C	3.94556	1.49144	2.19945
O	4.58031	2.10229	3.19285
O	4.25370	0.40316	1.77056
C	5.57352	1.32282	3.86643
H	-1.14251	3.56875	3.33331
H	-0.07693	2.88029	4.61647
H	-0.82431	1.78871	3.40759

H	5.14210	0.36498	4.18406
H	5.87978	1.91959	4.73005
H	6.43159	1.13969	3.20625
H	3.05875	3.38223	1.77112
H	1.29081	2.61732	0.25164
H	1.30607	0.55136	-0.93270
H	2.74689	-0.09105	-0.04489

Supramolecular complex II [3a·13] + product 4a (anionic form)

C	1.05688	-2.48029	-3.72103
C	1.92630	-1.56560	-2.85931
C	2.79013	-2.44402	-1.97466
O	3.63844	-1.58095	-1.18407
C	1.91936	-3.29571	-1.06660
C	0.96999	-4.19047	-1.88361
C	0.09055	-5.06648	-0.97578
C	-1.03510	-4.30213	-0.28390
O	-0.44941	-3.37749	0.63474
C	-1.87616	-3.49201	-1.28186
C	-0.97922	-2.59284	-2.16662
C	0.11714	-3.40202	-2.91488
C	-0.49914	-4.38649	-3.92363
C	-1.83822	-1.74977	-3.11833
C	-2.93313	-0.93125	-2.43143
O	-2.33657	0.11407	-1.65453
C	-3.80126	-1.78458	-1.50270
C	-4.69455	-2.66774	-2.38725
C	-2.88681	-2.60239	-0.56278
C	-3.87772	-3.24793	0.41121
C	-4.99430	-2.18556	0.56188
C	-4.66010	-1.04582	-0.43762
C	-5.88377	-0.23556	-0.89363
C	-5.48019	1.00399	-1.69664
C	-6.72176	0.17581	0.32791
C	-7.96858	0.99578	-0.02647
C	-8.88273	1.16828	1.15696
O	-10.03284	0.81302	1.22873
O	-8.24846	1.78334	2.17618
C	-9.03726	1.96224	3.34651
H	1.72029	-3.12757	-4.32404
H	0.47663	-1.88881	-4.44383
H	2.55853	-0.92203	-3.48959
H	1.30628	-0.91256	-2.22185
H	3.44822	-3.07580	-2.59206
C	4.77852	-2.13393	-0.72423
H	1.36811	-2.61128	-0.40694
H	2.55950	-3.93757	-0.44092
H	1.61077	-4.87469	-2.47241
H	0.71179	-5.55004	-0.20614
H	-0.37005	-5.87175	-1.57088
H	-1.66987	-4.99660	0.28685
C	-0.90775	-3.31178	1.91276
H	-2.41864	-4.22439	-1.90772
H	-0.47798	-1.89911	-1.46814
H	-1.27576	-5.02674	-3.48193

H	0.28444	-5.04529	-4.33094
H	-0.95056	-3.85198	-4.77332
H	-2.32252	-2.39634	-3.86851
H	-1.22241	-1.03068	-3.67855
H	-3.53802	-0.46628	-3.21922
H	-5.39574	-3.26712	-1.78898
H	-4.10992	-3.36305	-3.00640
H	-5.29084	-2.04182	-3.06977
H	-2.29347	-1.85223	-0.00914
H	-3.42233	-3.51680	1.37149
H	-4.27843	-4.17953	-0.02316
H	-5.05206	-1.80201	1.58956
H	-5.98248	-2.61786	0.33096
H	-3.97628	-0.34246	0.06631
H	-6.52136	-0.88355	-1.52456
H	-6.35766	1.56939	-2.04390
H	-4.88851	0.76433	-2.58770
H	-4.86836	1.67541	-1.07025
H	-7.04534	-0.72419	0.87234
H	-6.09370	0.75718	1.02351
H	-7.68208	2.00034	-0.37104
H	-8.55292	0.50757	-0.81828
H	-8.38392	2.44814	4.07839
H	-9.39059	0.99392	3.72643
H	-9.91241	2.59069	3.12992
C	-2.14323	1.29292	-2.28997
O	-2.45696	1.50128	-3.44643
N	-1.58119	2.17630	-1.42002
C	-1.28948	3.51845	-1.68158
H	-1.27638	1.80073	-0.49590
C	-0.94636	4.30920	-0.57139
C	-1.29632	4.10211	-2.95736
C	-0.96228	5.44948	-3.09628
C	-0.61563	6.23294	-1.99609
C	-0.60764	5.64728	-0.72821
H	-0.32893	6.22939	0.15231
H	-0.91965	3.83762	0.41119
H	-1.55953	3.49774	-3.82065
H	-0.96996	5.88979	-4.09544
H	-0.35429	7.28411	-2.12463
O	5.17028	-3.24216	-1.01907
N	5.41460	-1.23940	0.09631
C	6.64681	-1.42291	0.73829
H	4.90714	-0.38117	0.30938
C	7.10632	-0.36436	1.53722
C	7.42955	-2.58073	0.62013
C	8.64480	-2.65561	1.29980
C	9.10272	-1.60772	2.09496
C	8.31923	-0.45891	2.20751
H	8.65342	0.37750	2.82493
H	6.48560	0.52792	1.61257
H	7.07973	-3.40544	0.00691
H	9.24251	-3.56396	1.20244
H	10.05488	-1.68499	2.62097
O	-1.45555	-4.23275	2.48970
N	-0.63023	-2.06943	2.37785

C	-0.76028	-1.59144	3.68144
H	-0.24441	-1.41915	1.65377
C	-1.34327	-2.31061	4.73419
C	-1.40600	-1.73183	6.00221
C	-0.89893	-0.45669	6.24402
C	-0.31960	0.25275	5.18894
C	-0.25486	-0.30177	3.91800
H	-1.73322	-3.30853	4.54888
H	-1.86262	-2.29811	6.81683
H	-0.95120	-0.02198	7.24340
H	0.10483	1.24624	5.34579
H	0.19753	0.25610	3.09418
C	2.03230	2.45416	-0.29356
C	1.77096	0.98959	-0.17308
N	0.63141	0.56598	0.31440
O	-0.22805	1.38607	0.83232
O	0.33681	-0.68360	0.28279
C	2.84324	2.80541	-1.52932
C	3.90021	2.01127	-1.99028
C	2.50596	3.95881	-2.24776
C	3.21780	4.32164	-3.39022
C	4.27767	3.53256	-3.83425
C	4.61160	2.37483	-3.13264
H	4.16551	1.09409	-1.46445
H	5.43036	1.74135	-3.47795
H	4.83440	3.81099	-4.73061
H	2.92928	5.21806	-3.94205
H	1.65709	4.56547	-1.91956
C	-0.34566	3.50897	3.07976
O	0.70518	3.80203	2.15527
C	1.70374	2.91250	2.17053
O	1.85850	2.07599	3.02415
C	2.63562	3.10455	0.98312
C	3.98399	2.55455	1.38906
O	4.56145	3.36248	2.28739
O	4.50039	1.53531	0.99613
C	5.78535	2.88850	2.84062
H	-1.11482	4.26975	2.90577
H	0.02606	3.56886	4.11207
H	-0.73191	2.50093	2.87241
H	5.63340	1.91105	3.31917
H	6.08722	3.63556	3.58152
H	6.55181	2.79389	2.05792
H	2.74436	4.18690	0.81779
H	1.05597	2.94234	-0.39887
H	2.44112	0.21314	-0.52425

Supramolecular complex [MeOH•13]

C	1.71981	0.92921	-3.69861
C	2.48284	1.04715	-2.38422
C	3.16542	-0.27873	-2.08375
O	3.78255	-0.25473	-0.78540
C	2.16912	-1.42684	-2.05199
C	1.33177	-1.51973	-3.34149
C	0.31428	-2.66896	-3.29318

C	-0.88490	-2.41253	-2.38195
O	-0.48197	-2.50447	-0.98909
C	-1.51619	-1.03292	-2.59128
C	-0.46052	0.09353	-2.64908
C	0.64491	-0.17581	-3.70154
C	0.07061	-0.23268	-5.12383
C	-1.12403	1.46837	-2.78594
C	-2.12835	1.73218	-1.65863
O	-1.44797	1.62196	-0.38794
C	-3.23613	0.66612	-1.66241
C	-4.05783	0.77857	-2.95486
C	-2.54899	-0.71072	-1.51499
C	-3.70113	-1.67968	-1.27627
C	-4.68333	-0.85223	-0.41261
C	-4.18882	0.62564	-0.43551
C	-5.33913	1.64229	-0.36451
C	-4.84674	3.08713	-0.46549
C	-6.12139	1.42871	0.94056
C	-7.44835	2.19361	1.01065
C	-8.20043	1.85566	2.27276
O	-9.25811	1.28400	2.33620
O	-7.51939	2.26062	3.36340
C	-8.14422	1.94703	4.60605
H	2.43996	0.69197	-4.50188
H	1.27495	1.89670	-3.97344
H	3.23916	1.84012	-2.44837
H	1.81262	1.29706	-1.54386
H	3.95085	-0.45885	-2.83581
C	4.92297	0.46644	-0.69067
H	1.53084	-1.28231	-1.16823
H	2.70534	-2.37623	-1.89434
H	2.03715	-1.74562	-4.16189
H	0.79607	-3.60831	-2.98362
H	-0.08172	-2.84784	-4.30469
H	-1.63753	-3.19677	-2.53960
C	-0.30098	-3.77361	-0.51154
H	-2.03120	-1.09586	-3.56527
H	0.03315	0.09849	-1.66180
H	-0.74464	-0.95919	-5.24238
H	0.86423	-0.50777	-5.83606
H	-0.31234	0.75297	-5.42867
H	-1.64186	1.56641	-3.75169
H	-0.36913	2.26357	-2.75257
H	-2.52409	2.75140	-1.74763
H	-4.95494	0.14441	-2.90767
H	-3.49336	0.48012	-3.84822
H	-4.39984	1.81336	-3.11046
H	-2.00432	-0.63330	-0.56244
H	-3.37363	-2.60286	-0.77664
H	-4.16135	-1.97688	-2.23222
H	-4.72318	-1.23446	0.61684
H	-5.70970	-0.91849	-0.80724
H	-3.55848	0.80009	0.45252
H	-6.03235	1.44233	-1.20285
H	-5.64687	3.80364	-0.23253
H	-4.48996	3.33049	-1.47468

H	-4.01756	3.26377	0.23908
H	-6.34453	0.35761	1.06497
H	-5.49037	1.72347	1.79586
H	-7.27464	3.27924	1.00425
H	-8.09791	1.93225	0.16521
H	-7.47727	2.33332	5.38323
H	-8.27192	0.86077	4.70880
H	-9.13238	2.42222	4.67152
C	-0.42318	2.50044	-0.18834
O	-0.34042	3.57482	-0.73871
N	0.45282	1.95205	0.69886
C	1.67375	2.49053	1.14285
H	0.24209	0.99751	0.99635
C	2.31881	1.80867	2.18534
C	2.27161	3.62417	0.58146
C	3.50781	4.05325	1.06670
C	4.15201	3.38357	2.10400
C	3.54334	2.25963	2.66452
H	4.03423	1.72728	3.48152
H	1.84345	0.92190	2.61105
H	1.77054	4.15604	-0.22292
H	3.97362	4.93032	0.61540
H	5.12547	3.71928	2.46478
O	5.45829	1.03100	-1.61684
N	5.36290	0.41898	0.60414
C	6.42297	1.13952	1.17396
H	4.74447	-0.06746	1.24208
C	6.70731	0.89526	2.52472
C	7.16965	2.09571	0.47440
C	8.16831	2.80170	1.14330
C	8.44064	2.57609	2.49128
C	7.70329	1.61185	3.17808
H	7.90587	1.40980	4.23073
H	6.13555	0.13565	3.06324
H	6.95736	2.28196	-0.57442
H	8.74106	3.54853	0.59130
H	9.22372	3.13814	3.00021
O	-0.59961	-4.76622	-1.13157
N	0.24803	-3.70677	0.73377
C	0.52073	-4.77884	1.60402
H	0.44038	-2.77090	1.08745
C	0.34199	-6.12414	1.26169
C	0.64291	-7.10871	2.20177
C	1.11780	-6.78133	3.46950
C	1.29553	-5.43886	3.80189
C	0.99851	-4.44396	2.87824
H	-0.02617	-6.38785	0.27442
H	0.50042	-8.15526	1.92873
H	1.34716	-7.56403	4.19264
H	1.66645	-5.15974	4.78892
H	1.13722	-3.39130	3.13723
C	-1.35764	-0.93978	1.95291
O	-0.12040	-0.84632	1.25178
H	-1.12877	-0.93732	3.02604
H	-1.88531	-1.87537	1.70183
H	-2.00523	-0.07919	1.71972

H	-0.29946	-1.06584	0.31834

Supramolecular complex [2 MeOH·13]

C	2.22284	0.23063	-3.81473
C	2.91056	0.73469	-2.54956
C	3.77119	-0.37731	-1.96973
O	4.35000	0.01366	-0.70962
C	2.95323	-1.62439	-1.68938
C	2.21381	-2.12059	-2.94359
C	1.40091	-3.39120	-2.66757
C	0.13240	-3.15183	-1.85345
O	0.45841	-2.81863	-0.48063
C	-0.71284	-2.00151	-2.40086
C	0.11888	-0.73137	-2.69306
C	1.34341	-1.01904	-3.60671
C	0.90169	-1.48089	-5.00418
C	-0.78583	0.38890	-3.22087
C	-2.00892	0.68420	-2.34723
O	-1.58602	1.24612	-1.09592
C	-2.82881	-0.57417	-2.02908
C	-3.54909	-1.01947	-3.30779
C	-1.86250	-1.63958	-1.46859
C	-2.77918	-2.75624	-0.97199
C	-4.04350	-2.00274	-0.49353
C	-3.82600	-0.50349	-0.83490
C	-5.13043	0.29145	-0.98985
C	-4.86397	1.79022	-1.14176
C	-6.03862	0.03038	0.22264
C	-7.36977	0.78892	0.18262
C	-8.30234	0.31907	1.26927
O	-9.38548	-0.18163	1.10737
O	-7.76224	0.51575	2.48929
C	-8.57256	0.07326	3.57579
H	3.00151	-0.03406	-4.55211
H	1.63598	1.03772	-4.27664
H	3.54218	1.60375	-2.77731
H	2.16976	1.04827	-1.79560
H	4.59443	-0.59728	-2.66818
C	5.42903	0.83085	-0.78532
H	2.25298	-1.39586	-0.87347
H	3.61397	-2.42184	-1.31363
H	2.99421	-2.38724	-3.67964
H	2.01395	-4.14777	-2.15675
H	1.08818	-3.84002	-3.62329
H	-0.46163	-4.07580	-1.82104
C	0.88073	-3.85720	0.30197
H	-1.13770	-2.37867	-3.34686
H	0.50799	-0.38329	-1.71822
H	0.18530	-2.31325	-4.98420
H	1.77899	-1.81265	-5.58074
H	0.43958	-0.65426	-5.56347
H	-1.14396	0.13790	-4.23169
H	-0.23092	1.33415	-3.30968
H	-2.60916	1.43643	-2.87215
H	-4.19473	-1.89087	-3.12741

H	-2.85129	-1.28601	-4.11405
H	-4.18891	-0.20665	-3.68502
H	-1.42204	-1.16093	-0.57588
H	-2.31066	-3.34793	-0.17354
H	-3.01851	-3.45308	-1.79141
H	-4.22098	-2.14529	0.58135
H	-4.94209	-2.38097	-1.00687
H	-3.26675	-0.03829	-0.00468
H	-5.66633	-0.07289	-1.88644
H	-5.79760	2.35995	-1.24822
H	-4.25404	2.02443	-2.02259
H	-4.33174	2.17413	-0.25382
H	-6.26168	-1.04561	0.28721
H	-5.49928	0.29836	1.14741
H	-7.20641	1.86685	0.32643
H	-7.88466	0.63575	-0.77536
H	-8.01317	0.31364	4.48537
H	-8.75307	-1.00814	3.50594
H	-9.54185	0.58989	3.56906
C	-1.59303	2.60669	-1.01603
O	-1.65516	3.33602	-1.98092
N	-1.50932	2.95257	0.29625
C	-1.40148	4.24450	0.83458
H	-1.59817	2.17279	0.95698
C	-1.29720	4.33322	2.23046
C	-1.38937	5.41166	0.06086
C	-1.27256	6.64661	0.69695
C	-1.17084	6.74156	2.08304
C	-1.18501	5.57397	2.84664
H	-1.10607	5.62707	3.93347
H	-1.30392	3.41249	2.81857
H	-1.47429	5.34253	-1.02017
H	-1.26387	7.55186	0.08813
H	-1.08029	7.71523	2.56493
O	5.90811	1.23489	-1.81878
N	5.85977	1.10275	0.48349
C	6.93847	1.91581	0.87328
H	5.34391	0.63830	1.22059
C	7.18274	2.03392	2.24799
C	7.75519	2.59909	-0.03606
C	8.79763	3.38728	0.44807
C	9.04378	3.50861	1.81375
C	8.22725	2.82430	2.71271
H	8.40096	2.90400	3.78652
H	6.54443	1.49923	2.95542
H	7.57049	2.50779	-1.10241
H	9.42896	3.91695	-0.26679
H	9.86306	4.13045	2.17445
O	0.87439	-5.00861	-0.06423
N	1.29124	-3.36728	1.50454
C	1.76235	-4.10410	2.60650
H	1.19543	-2.36069	1.63258
C	1.95155	-5.49140	2.59080
C	2.43462	-6.12383	3.73534
C	2.73256	-5.40549	4.89091
C	2.54032	-4.02434	4.89933

C	2.05863	-3.37705	3.76777
H	1.72016	-6.05905	1.69437
H	2.57927	-7.20490	3.71513
H	3.11062	-5.91553	5.77698
H	2.76714	-3.44254	5.79359
H	1.90586	-2.29520	3.77419
C	1.19353	0.69529	0.87436
H	2.23850	0.53077	0.56504
O	0.52735	-0.54284	1.12763
H	0.65991	1.27200	0.10298
H	1.17431	1.26704	1.81135
H	0.42125	-1.03296	0.29252
C	-2.75885	0.14262	2.82483
O	-1.71834	0.73769	2.07769
H	-2.39340	-0.26506	3.78180
H	-3.26300	-0.66317	2.26390
H	-3.50050	0.92346	3.04171
H	-1.05801	0.06606	1.81827

Supramolecular complex [3 MeOH•13]

C	1.62005	-0.54992	-4.13225
C	2.39268	0.19534	-3.04661
C	3.33881	-0.76301	-2.33758
O	3.91095	-0.17099	-1.16352
C	2.59885	-1.97749	-1.80787
C	1.76041	-2.70332	-2.86763
C	1.02277	-3.90490	-2.26581
C	-0.15181	-3.52443	-1.36746
O	0.29002	-2.88296	-0.14252
C	-1.09725	-2.53157	-2.04715
C	-0.34660	-1.32580	-2.66323
C	0.79652	-1.75341	-3.62565
C	0.24167	-2.46299	-4.87017
C	-1.33711	-0.34264	-3.29845
C	-2.47075	0.09946	-2.36996
O	-1.94394	0.88037	-1.28116
C	-3.22062	-1.09176	-1.75566
C	-4.03338	-1.78827	-2.85431
C	-2.17370	-2.01758	-1.09783
C	-3.00675	-3.02904	-0.31473
C	-4.22300	-2.20001	0.16490
C	-4.11737	-0.80696	-0.51717
C	-5.47843	-0.12736	-0.72366
C	-5.33971	1.23087	-1.41424
C	-6.17391	0.02349	0.63855
C	-7.59128	0.60091	0.55802
C	-8.29322	0.54541	1.89043
O	-9.31781	-0.04044	2.12881
O	-7.61760	1.24523	2.82502
C	-8.21882	1.24075	4.11723
H	2.34283	-0.93845	-4.87183
H	0.97486	0.14802	-4.68527
H	2.96891	1.02360	-3.48055
H	1.70430	0.62732	-2.30195
H	4.15477	-1.04806	-3.02194
C	4.92948	0.70625	-1.33399

H	1.97406	-1.61786	-0.97861
H	3.32052	-2.68128	-1.36296
H	2.46791	-3.09794	-3.61938
H	1.71472	-4.54718	-1.70386
H	0.60684	-4.52598	-3.07464
H	-0.69779	-4.43187	-1.07009
C	0.96955	-3.65249	0.75162
H	-1.58442	-3.10207	-2.85636
H	0.12248	-0.78538	-1.82024
H	-0.45024	-3.28398	-4.63532
H	1.07122	-2.88745	-5.45685
H	-0.28932	-1.75510	-5.52348
H	-1.79293	-0.79258	-4.19461
H	-0.82492	0.57153	-3.62993
H	-3.13858	0.74744	-2.94945
H	-4.62684	-2.61828	-2.44428
H	-3.40393	-2.19673	-3.65722
H	-4.73700	-1.07912	-3.31707
H	-1.67441	-1.37377	-0.35317
H	-2.44351	-3.47148	0.51851
H	-3.32261	-3.85871	-0.96780
H	-4.23125	-2.09834	1.25865
H	-5.16953	-2.69301	-0.11069
H	-3.52879	-0.15015	0.14294
H	-6.11408	-0.78263	-1.34876
H	-6.29092	1.78078	-1.43335
H	-5.02080	1.13073	-2.45948
H	-4.59746	1.85474	-0.88775
H	-6.23566	-0.96234	1.12524
H	-5.55706	0.66236	1.29285
H	-7.56445	1.65512	0.24639
H	-8.20907	0.03904	-0.15520
H	-7.57267	1.85485	4.75235
H	-8.28679	0.21619	4.50775
H	-9.23155	1.66363	4.07129
C	-1.83602	2.21728	-1.51073
O	-1.86595	2.71643	-2.61374
N	-1.68743	2.84746	-0.31271
C	-1.36988	4.19578	-0.09120
H	-1.81557	2.25262	0.51231
C	-1.18566	4.58358	1.24416
C	-1.22169	5.14249	-1.11291
C	-0.88652	6.45416	-0.78021
C	-0.70162	6.84337	0.54458
C	-0.85591	5.89675	1.55726
H	-0.71749	6.18039	2.60156
H	-1.30731	3.83698	2.03250
H	-1.37175	4.84740	-2.14779
H	-0.77070	7.18585	-1.58111
H	-0.44226	7.87411	0.78680
O	5.35170	1.05868	-2.41161
N	5.35546	1.08916	-0.09505
C	6.41874	1.94887	0.21199
H	4.89759	0.60731	0.68148
C	6.79576	2.03336	1.56025
C	7.09450	2.71859	-0.74355

C	8.12818	3.55853	-0.33325
C	8.50201	3.65016	1.00588
C	7.82729	2.87873	1.95157
H	8.10799	2.92936	3.00466
H	6.27366	1.41526	2.29454
H	6.80999	2.64908	-1.78997
H	8.64968	4.15335	-1.08473
H	9.31308	4.31184	1.31002
O	1.11515	-4.84633	0.64151
N	1.43662	-2.84803	1.75237
C	2.20775	-3.23347	2.85717
H	1.18412	-1.86098	1.69073
C	2.84013	-4.47801	2.97072
C	3.62739	-4.74071	4.09019
C	3.80185	-3.79301	5.09760
C	3.15875	-2.56086	4.98799
C	2.36126	-2.28434	3.88077
H	2.70793	-5.22315	2.19121
H	4.11771	-5.71197	4.17020
H	4.42424	-4.01648	5.96384
H	3.26508	-1.81124	5.77361
H	1.82374	-1.33497	3.80772
C	1.02076	0.86934	0.44043
H	2.07958	0.64136	0.24322
O	0.33354	-0.28479	0.93513
H	0.52839	1.24851	-0.46814
H	0.94554	1.64213	1.21782
C	3.40754	0.96379	3.04432
H	2.34755	0.86757	3.33838
H	4.03398	0.94839	3.95174
H	3.53940	1.93579	2.54865
O	3.78931	-0.03058	2.11237
H	0.22663	-0.93153	0.21465
H	3.78975	-0.89249	2.55581
C	-2.15202	0.78271	3.16667
O	-1.99454	0.90633	1.76970
H	-1.24105	1.07840	3.71674
H	-2.41898	-0.24697	3.45754
H	-2.97058	1.44805	3.47247
H	-1.25416	0.33301	1.48350