Highly enantioselective conjugate additions of dialkylzinc reagents to linear nitroalkenes: a catalytic route to β^2 -amino acids, aldehydes and alcohols

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Supporting Information

General. All reactions were carried out under nitrogen atmosphere using dried glassware. Toluene was distilled from sodium. Dimethylzinc (2.0 M in toluene) and diethylzinc (1.1 M in hexanes) were purchased from Aldrich, dibutylzinc (1.0 M in heptane) from Fluka and used without purification. Bis(methyl-6-heptanoate)zinc was prepared following a literature procedure¹ and used as a 1.0 M solution in toluene. Chromatography: Merck silica gel Type 9385 230-400 mesh, TLC: Merck silica gel 60 F₂₅₄. ¹H- and ¹³C-NMR spectra were recorded on a Varian Unity 300 (300 and 75 MHz, respectively) using CDCl₃ as solvent. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CHCl₃: δ 7.25 for ¹H, CDCl₃: δ 77.0 for ¹³C). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. Optical rotations were measured on a Perkin Elmer 241 polarimeter. Mass spectra were recorded on a AEI-MS-902 mass spectrometer. GC measurements were performed on a HP 6890 gas chromatograph using a flame ionisation detector. HPLC analysis was carried out on a Water 600E system controller with a Water 991 photodiode array detector.

General procedure A. Synthesis of nitropropene acetals. To a solution of 2.2 g (15 mmol) of **1a**² in 150 mL of diethylether 5 equiv (75 mmol) of diol and 5.6 mL (45 mmol) of BF₃·Et₂O were added and stirred at room temperature overnight. The reaction mixture was added to 100 mL of pentanes and extracted twice with 100 mL of aqueous 1 M NaOH. The organic layer was washed with brine and dried over Na₂SO₄ and solvents were removed under reduced pressure to yield the corresponding nitropropene acetal.

4,4,5,5-Tetramethyl-2-(2-nitro-vinyl)-[1,3]dioxolane (1b). According to general procedure A, 1.8 g (9.1 mmol, 61% yield) of **1b** was obtained as a colorless oil. ¹H-NMR δ : 7.17 (d, J = 14.1 Hz, 1H), 7.09 (dd, J = 13.8, 3.9 Hz, 1H), 5.57 (d, J = 3 Hz, 1H), 1.20 (d, J = 6.6 Hz, 12H) ppm. ¹³C-NMR δ : 141.1 (d), 138.0 (d), 95.2 (d), 83.3 (s), 23.4 (q), 21.7 (q) ppm. HRMS calcd for C₉H₁₄NO₄ ($[M-H]^+$)³ 200.092 found 200.092. Anal. calcd for C₉H₁₅NO₄ C 53.72; H 7.51; N 6.96 found C 53.59; H 7.60; N 6.80.

5,5-Dimethyl-2-(2-nitro-vinyl)-[1,3]dioxane (1c). According to general procedure A, 2.0 g (10 mmol, 70% yield) of **1c** was obtained as a colorless crystals. M.p. 41-43°C ¹H-NMR δ : 7.23 (dd, J = 13.5, 1.5 Hz, 1H), 7.06 (dd, J = 13.5, 3 Hz, 1H), 5.12 (q, J = 1.5 Hz, 1H), 3.65 (dd, J = 49.8, 11.1 Hz, 4H), 1.18 (s, 3H), 0.75 (s, 3H) ppm. ¹³C-NMR δ : 142.0 (d), 135.6 (d), 95.9 (d), 77.3 (t), 30.2 (s), 22.7 (q), 21.6 (q) ppm. HRMS calcd for C₈H₁₂NO₄ ($[M-H]^+$)³ 186.076 found 186.075 Anal. calcd for C₈H₁₃NO₄ C 51.33; H 7.00; N 7.48 found C 51.37; H 7.08; N 7.42.

2-(2-Nitro-vinyl)-5,5-diphenyl-[1,3]dioxane (1d). According to general procedure A, 0.5 g (1.5 mmol, 10% yield) of **1c** was obtained as a white solid. M.p. 133-135°C ¹H-NMR δ : 7.36 (m, 10H), 5.41 (d, J = 1.8 Hz, 1H), 4.80 (dd, J = 156.3, 12.0 Hz, 4H) ppm. ¹³C-NMR δ : 143.6 (s), 142.7 (s), 142.1 (d), 135.1 (d), 128.7 (d), 128.5 (d), 128.2 (d), 126.4 (d), 126.2 (d), 96.1 (d), 75.0 (t), 44.6 (s) ppm. HRMS calcd for C₁₈H₁₇NO₄ 311.115 found 311.116 Anal. calcd for C₁₈H₁₇NO₄ C 69.44; H 5.50; N 4.50 found C 69.90; H 5.55; N 4.43.

General procedure B. Catalytic asymmetric conjugate addition of dialkylzinc to nitropropene acetals. In a Schlenk tube 3.6 mg (0.01 mmol) of Cu(OTf)₂ was flame-dried, and together with 10.8 mg (0.02 mmol) of phosphoramidite (*S,R,R*) **L1** dissolved in 2 mL of dry toluene. After 30 min of stirring at room temperature 1.0 mmol of nitropropene

¹ Knochel, P.; Singer, R.D.; *Chem. Rev.* **1993**, 93, 2117-2188.

² Duursma, A.; Minnaard, A.J.; Feringa, B.L. *Tetrahedron* **2002**, 58, 5773-5778.

³ Due to the labile nature of the acetal proton the molecular ion could not be detected.

acetal was added to the clear solution. The reaction mixture was cooled to -55 °C and 1.2 mmol of dialkylzinc reagent was added. The reaction mixture was stirred at -55 °C until complete conversion (GC) and then poured into a mixture of 10 mL of saturated aqueous NH₄Cl and 10 mL of ethyl acetate. The aqueous layer was for 5 min rigorously extracted twice with 40 mL of ethyl acetate and the combined organic layers were washed with brine and dried over Na₂SO₄, concentrated and purified with column chromatography.

1,1-Dimethoxy-2-nitromethyl-butane (2a). According to general procedure B, 138 mg (0.8 mmol, 78% yield) of **2a** was obtained as a colorless oil. Spectral data were in accordance with literature.² Enantiomer separation on a Chiraldex G-TA column, 50m x 0.25 mm, 130°C isothermic, 6.3 / 6.8 min. See page S4 for chromatograms.

4,4,5,5-Tetramethyl-2-(1-nitromethyl-propyl)-[1,3]dioxolane (2b). According to general procedure B, 166 mg (0.7 mmol, 72% yield) of **2b** was obtained as a colorless oil. ¹H-NMR δ: 5.00 (d, *J*= 7.8 Hz, 1H), 4.59 (dd, *J*= 19.2, 9.6 Hz, 1H), 4.32 (dd, *J*= 19.2, 10.2 Hz, 1H), 2.39 (m, 1H), 1.64 (m, 1H), 1.42 (m, 2H) 1.16 (s, 12H), 0.97 (t, 7.6 Hz, 3H) ppm. ¹³C-NMR δ: 99.8 (d), 82.1 (s), 75.0 (t), 43.4 (d), 24.3 (q), 24.1 (q), 22.2 (q), 22.1 (q), 20.9 (t) 10.9 (q) ppm. HRMS calcd for C₁₁H₂₀NO₄ ([M-H]⁺)³ 230.139 found 230.139 Anal. calcd for C₁₁H₂₁NO₄ C 57.12; H 9.15; N 6.06 found C 57.13; H 9.12; N 5.93. Enantiomer separation on a Chiraldex G-TA column, 30m x 0.25 mm, 110°C isothermic, 35.7 / 36.5 min. See page S5 for chromatograms.

5,5-Dimethyl-2-(1-nitromethyl-propyl)-[1,3]dioxane (2c). According to general procedure B, 170 mg (0.8 mmol, 78% yield) of **2c** was obtained as a colorless oil. ¹H-NMR δ: 4.74 (dd, *J*= 13.0, 5.8 Hz, 1H), 4.52 (d, *J*= 3.2 Hz, 1H), 4.35 (dd, *J*= 13.2, 7.4 Hz, 1H), 3.61 (d, *J*= 11.0 Hz, 2H), 3.42 (dd, *J*= 11.0, 4.4 Hz, 2H), 2.46 (m, 1H), 1.57 (m, 3H) 1.12 (s, 3H), 0.95 (t, *J*= 7.6 Hz, 3H), 0.70 (s, 3H) ppm. ¹³C-NMR δ: 100.5 (d), 77.1 (t), 75 (t), 43.2 (d), 30.1 (s), 22.8 (q), 21.7 (q) 20.6 (t), 11.2 (q) ppm. HRMS calcd for C₁₀H₁₈NO₄ ([M-H]⁺)³ 216.123 found 216.122 Anal. calcd for C₁₀H₁₉NO₄ C 55.28; H 8.81; N 6.45 found C 55.19; H 8.78; N 6.27. Enantiomer separation on a Chiraldex G-TA column, 30m x 0.25 mm, 130°C isothermic, 17.8 / 18.1 min. See page S6 for chromatograms.

2-(1-Nitromethyl-propyl)-5,5-diphenyl-[1,3]dioxane (2d). According to general procedure B, 246 mg (0.7 mmol, 72% yield) of **2d** was obtained as a white solid. M.p. 114-117°C ¹H-NMR δ: 7.37 (m, 8H), 7.18 (m, 2H), 4.81 (d, *J*= 3.0 Hz, 1H), 4.76 (m, 2H), 4.51 (dd, *J*= 13.2, 5.0 Hz, 1H), 4.20 (m, 3H), 2.51 (m, 1H), 1.55 (m, 3H), 0.94 (t, *J*= 7.6 Hz, 3H) ppm. ¹³C-NMR δ: 143.8 (s), 143.0 (s), 128.6 (d), 128.2 (d), 127.0 (d), 126.3 (d), 126.2 (d), 100.6 (d), 75.0 (t), 74.8 (t), 74.6 (t), 43.1 (d), 20.6 (t), 11.2 (q) ppm. HRMS calcd for C₂₀H₂₃NO₄ 341.162 found 341.161 Anal. calcd for C₂₀H₂₃NO₄ C 70.36; H 6.79; N 4.10 found C 70.26; H 6.76; N 4.08. Enantiomer separation on a Chiralcel OD column, heptanes/isopropanol 9/1, 254 nm, 8.3 / 9.4 min. See page S7 for chromatograms.

1,1-Dimethoxy-2-methyl-3-nitro-propane (2e). According to general procedure B, 140 mg (0.9 mmol, 86% yield) of **2e** was obtained as a colorless oil. ¹H-NMR δ: 4.56 (dd, *J*= 12.4, 5.4 Hz, 1H), 4.25 (m, 2H), 3.38 (s, 3H), 3.34 (s, 3H), 2.66 (m, 1H), 1.03 (d, *J*= 10.5 Hz, 3H) ppm. ¹³C-NMR δ: 106.2 (d), 77.4 (t), 55.7 (q), 54.4 (q), 35.7 (t), 12.7 (q) ppm. HRMS calcd for C₆H₁₂NO₄ ([M-H]⁺)³ 162.076 found 162.077 Anal. calcd for C₆H₁₃NO₄ C 44.16; H 8.03; N 8.58 found C 43.85; H 7.98; N 8.28. Enantiomer separation on a Chiraldex G-TA column, 30m x 0.25 mm, 120°C isothermic, 6.9 / 7.1 min. See page S8 for chromatograms. Absolute configuration (*R*) was determined by converting **2e** to **5** and comparison of optical rotatory values (vide infra).⁴

5,5-Dimethyl-2-(1-methyl-2-nitro-ethyl)-[1,3]dioxane (2f). According to general procedure B, 118 mg (0.6 mmol, 58% yield) of **2f** was obtained as a colorless oil. ¹H-NMR δ: 4.70 (dd, *J*= 12.8, 5.4 Hz, 1H), 4.40 (d, *J*= 3.8 Hz, 1H), 4.30 (dd, *J*= 12.4, 8.4 Hz, 1H), 3.62 (m, 2H), 3.42 (m, 2H), 2.66 (m, 1H) 1.56 (s, 3H), 1.07 (d, *J*= 7.0 Hz, 3H), 0.70 (s, 3H) ppm. ¹³C-NMR δ: 101.9 (d), 77.6 (t), 77.2 (t), 37.1 (d), 30.3 (s), 23.0 (q), 21.8 (q), 12.8 (q) ppm. HRMS calcd for C₉H₁₆NO₄ ([M-H]⁺)³ 202.107 found 202.107 Anal. calcd for C₉H₁₇NO₄ C 53.19; H 8.43; N 6.89 found C 53.29; H 8.49; N 6.95. Enantiomer separation on a Chiraldex G-TA column, 30m x 0.25 mm, 105°C isothermic, 41.9 / 42.5 min. See page S9 for chromatograms.

1,1-Dimethoxy-2-nitromethyl-hexane (2g). According to general procedure B, 153 mg (0.8 mmol, 75% yield) of **2g** was obtained as a colorless oil. ¹H-NMR δ: 4.57 (dd, *J*= 13.0, 6.2 Hz, 1H), 4.27 (m, 2H), 3.39 (s, 3H), 3.36 (s, 3H), 2.52 (m, 1H), 1.29 (m, 6H), 0.88 (t, *J*= 4.8 Hz, 3H) ppm. ¹³C-NMR δ: 105.6 (d), 75.4 (t), 56.0 (q), 54.8 (q),

⁴ White, J.D.; Hong, J.; Robarge, L.A. *J. Org. Chem.* **1999**, *64*, 6206-6216.

40.6 (d), 28.7 (t), 27.2 (t), 22.6 (t), 13.8 (q) ppm. HRMS calcd for $C_9H_{18}NO_4$ ($[M-H]^+$)³ 204.123 found 204.122. Enantiomer separation on a Chiraldex G-TA column, 30m x 0.25 mm, initial temp 140°C, initial time 4 min, rate 10°C/min, final temp 150°C, 6.3 / 6.6 min. see page S10 for chromatograms.

9,9-Dimethoxy-8-nitromethyl-nonanoic acid methyl ester (2h). According to general procedure B, 216 mg (0.7 mmol, 74% yield) of **2h** was obtained as a colorless oil. ¹H-NMR δ: 4.56 (dd, *J* = 12.9, 6.3 Hz, 1H), 4.29 (m, 2H), 3.64 (s, 3H), 3.36 (s, 3H), 3.33 (s, 3H), 2.50 (m, 1H), 2.28 (t, *J* = 7.0 Hz, 2H), 1.59 (m, 3H), 1.29 (m, 7H) ppm. ¹³C-NMR δ: 174.1 (s), 105.6 (d), 75.5 (t), 56.0 (q), 54.9 (q), 51.4 (q), 40.7 (d), 33.9 (t), 29.2 (t), 28.8 (t), 27.5 (t), 26.4 (t), 24.7 (t) ppm. MS (CI⁺) 309 $[M+NH_4]^+$. Enantiomer separation on a Chiraldex G-TA column, 30m x 0.25 mm, 160°C isothermic, 53.0 / 54.9 min. See page S11 for chromatograms.

(3,3-Dimethoxy-2-methyl-propyl)-carbamic acid tert-butyl ester (3). A 1 mL Raney[®] 2800 nickel suspension was washed 3 times with 3 mL of abs. EtOH and then a solution of 326 mg (2.0 mmol) of **2e** in 3 mL of abs. EtOH was added. The mixture was hydrogenated with 20 bar of H₂ pressure for 30 min, and then filtered over Celite with 10 mL of abs. EtOH. 235 μL (1.7 mmol) of Et₃N and 370 mg (1.7 mmol) of Boc₂O were added and the reaction mixture was stirred for 5 min at room temperature. The solvent was removed under reduced pressure and the product was purified with column chromatography (pentanes/diethyl ether 3/2, *R_f* 0.6) to give 297 mg (1.2 mmol, 64% yield) of **3** as a colorless oil. ¹H-NMR δ: 4.97 (br s, 1H), 4.10 (d, *J* = 6.2 Hz, 1H), 3.37 (d, *J* = 8.0 Hz, 6H), 3.11 (t, *J* = 5.6 Hz, 2H), 1.93 (m, 1H), 1.42 (s, 9H), 0.92 (d, *J* = 6.8 Hz, 3H) ppm. ¹³C-NMR δ: 156.0 (s), 108.3 (d), 55.0 (q), 53.6 (q), 42.6 (t) 36.1 (d), 28.4 (q), 13.2 (q) ppm. MS (CI⁺) 234 $[M+H]^+$. Enantiomeric excess was determined by oxidizing **3** to **6** (vide infra).

(2-Methyl-3-oxo-propyl)-carbamic acid tert-butyl ester (4). To a solution of 291 mg (1.2 mmol) of **3** in 50 mL acetone was added 50 μL (2.7 mmol) of H₂O and 50 mg of Amberlyst-15. The reaction mixture was stirred at room temperature overnight, filtered and the solvents were removed under reduced pressure to yield 208 mg (1.1 mmol, 89% yield) of **4** as a colorless oil. ¹H-NMR δ: 9.64 (s, 1H), 4.88 (br s, 1H), 3.34 (t, *J* = 5.6 Hz, 2H), 2.64 (m, 1H), 1.39 (s, 9H), 1.11 (d, *J* = 7.2 Hz, 3H) ppm. ¹³C-NMR δ: 203.9 (s), 155.9 (s), 79.4 (s), 47.1 (d), 40.5 (t), 28.2 (q), 11.2 (q) ppm. Aldehyde **4** decomposes slowly upon standing and is therefore converted to **5**, also to enable determination of enantiomeric excess (vide infra).

(3-Hydroxy-2-methyl-propyl)-carbamic acid tert-butyl ester (5). To a cooled solution of 200 mg (1.1 mmol) of **4** in 20 mL of abs. EtOH was added 40 mg (1.1 mmol) of NaBH₄ at 0°C. After 1h the reaction mixture was added to 10 mL of saturated aqueous NH₄Cl and extracted 3 times with 50 mL of ethyl acetate. The combined organic layers were dried with brine and over Na₂SO₄, the solvents were removed under reduced pressure to yield 208 mg (1.1 mmol, 91% yield) of **5** as a colorless oil. Spectral data were in accordance with literature.⁴ $[\alpha]^{21}_D$ -12.5 (*c* 2.00, CHCl₃), lit.⁴ $[\alpha]^{21}_D$ -12.9 (*c* 1.93, CHCl₃). Enantiomeric excess was determined by derivatizing **5** to **6** using the same method described for the oxidation of **3** to **6** (vide infra).

3-tert-Butoxycarbonylamino-2-methyl-propionic acid (6). To a cooled solution of 257 mg (1.1 mmol) of **3** in 10 mL acetonitrile and 75 μL (4.1 mmol) of H₂O, 4 mL of a freshly prepared 0.5 M solution of H₅IO₆ and 1% CrO₃ in acetonitrile was added at 0°C. After 30 min 25 mL of cooled 1M aqueous HCl was added and the reaction mixture was extracted 3 times with 50 mL of ethyl acetate. The combined organic layers were dried with brine and over Na₂SO₄, the solvents were removed under reduced pressure to give 223 mg of **6** as a colorless oil. The oil was dissolved in 1 mL of diethyl ether and 20 mL of pentanes were added which gave 185 mg (0.9 mmol, 82% yield) of **6** as white crystals after standing in the freezer overnight. M.p. 87-90°C Lit⁵ 81-83°C. Spectral data were in accordance with literature.⁵ Enantiomeric excess was determined by derivatizing **6** to the methyl ester (**7**) using TMSCHN₂, enantiomer separation on a CP-Chirasil-Dex CB column, 25m x 0.25 mm, 140°C isothermic, 10.8 / 11.4 min. See page S12 for the structure of **7** and chromatograms.

⁵ Sibi, M.P.; Deshpande, P.K. *J. Chem. Soc., Perkin I*, **2000**, 1461-1466.

racemic sample

Signal 1: FID2 B,

Peak #	RT [min]	Type	Name	Width [min]	Area	Area %	Response	Amount
1	6.356	BB	d-acetal	0.042	117.900	49.890	0.000	0.000
2	6.816	BB	l-acetal	0.047	118.418	50.110	0.000	0.000

catalytic asymmetric conjugate addition sample

Signal 1: FID2 B,

Peak #	RT [min]	Type	Name	Width [min]	Area	Area %	Response	Amount
1	6.268	BB	d-acetal	0.045	151.018	98.059	0.000	0.000
2	6.738	BB	l-acetal	0.041	2.989	1.941	0.000	0.000

racemic sample

Signal 1: FID2 B,

Peak #	RT [min]	Type	Name	Width [min]	Area	Area %	Response	Amount
1	35.721	BB	d-pinacetal	0.182	544.902	50.259	0.000	0.000
2	36.515	BB	l-pinacetal	0.188	539.281	49.741	0.000	0.000

catalytic asymmetric conjugate addition sample

Signal 1: FID2 B,

Peak #	RT [min]	Type	Name	Width [min]	Area	Area %	Response	Amount
1	35.715	MM	d-pinacetal	0.250	185.749	95.575	0.000	0.000
2	36.590	MM	l-pinacetal	0.234	8.600	4.425	0.000	0.000

racemic sample

Signal 1: FID2 B,

RT [min]	Type	Name	Width [min]	Area	Area %	Response	Amount
17.801	BP	d-acetal	0.090	820.361	50.139	0.000	0.000
18.195	BB	l-acetal	0.097	815.811	49.861	0.000	0.000

catalytic asymmetric conjugate addition sample

Signal 1: FID2 B,

Peak #	RT [min]	Type	Name	Width [min]	Area	Area %	Response	Amount
1	17.820	BP	d-acetal	0.087	25.550	4.106	0.000	0.000
2	18.195	BB	l-acetal	0.095	596.716	95.894	0.000	0.000

racemic sample

1: 254 nm, 8 nm

Pk #	Name	Retention Time	Area	Area Percent
1	Peak1	8.064	1879715	50.74
2	Peak2	9.067	1824547	49.26

catalytic asymmetric conjugate addition sample

1: 220 nm, 8 nm

Pk #	Name	Retention Time	Area	Area Percent
1	Peak1	8.309	2257091	7.94
2	Peak2	9.419	26154922	92.06

Totals			28412013	100.00
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racemic sample

Signal 1: FID2 B,

Peak #	RT [min]	Type	Name	Width [min]	Area	Area %	Response	Amount
1	6.902	BB	d-acetal	0.046	166.343	49.947	0.000	0.000
2	7.118	BB	l-acetal	0.054	166.694	50.053	0.000	0.000

catalytic asymmetric conjugate addition sample

Signal 1: FID2 B,

Peak #	RT [min]	Type	Name	Width [min]	Area	Area %	Response	Amount
1	6.836	PB	d-acetal	0.062	449.333	98.973	0.000	0.000
2	7.149	PP	l-acetal	0.054	4.662	1.027	0.000	0.000

racemic sample

Signal 1: FID2 B,

Peak #	RT [min]	Type	Name	Width [min]	Area	Area %	Response	Amount
1	44.038	MM	d-acetal	0.408	519.148	49.876	0.000	0.000
2	45.197	MM	l-acetal	0.499	521.731	50.124	0.000	0.000

catalytic asymmetric conjugate addition sample

Signal 1: FID2 B,

Peak #	RT [min]	Type	Name	Width [min]	Area	Area %	Response	Amount
1	41.963	BP	d-acetal	0.145	1160.877	98.199	0.000	0.000
2	42.517	BP	l-acetal	0.087	21.294	1.801	0.000	0.000

racemic sample

Signal 1: FID2 B,

Peak #	RT [min]	Type	Name	Width [min]	Area	Area %	Response	Amount
1	6.345	BB	d-acetal	0.033	115.326	49.998	0.000	0.000
2	6.626	BP	l-acetal	0.034	115.336	50.002	0.000	0.000

catalytic asymmetric conjugate addition sample

Signal 1: FID2 B,

Peak #	RT [min]	Type	Name	Width [min]	Area	Area %	Response	Amount
1	6.340	BB	d-acetal	0.034	164.388	97.410	0.000	0.000
2	6.623	PP	l-acetal	0.033	4.371	2.590	0.000	0.000

racemic sample

catalytic asymmetric conjugate addition sample

racemic sample

Signal 1: FID1 A,

Peak #	RT [min]	Type	Name	Width [min]	Area	Area %	Response	Amount
1	10.867	BB	d-ester	0.074	164.030	50.017	0.000	0.000
2	11.477	BB	l-ester	0.086	163.916	49.983	0.000	0.000

catalytic asymmetric conjugate addition sample

Signal 1: FID1 A,

Peak #	RT [min]	Type	Name	Width [min]	Area	Area %	Response	Amount
1	10.661	BB	d-ester	0.130	1335.976	99.071	0.000	0.000
2	11.532	BP	l-ester	0.080	12.533	0.929	0.000	0.000