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Enantioselective aza-Michael reactions catalyzed by samarium iodobinaphtholate

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Abstract—Samarium iodobinaphtholate is an efficient enantioselective catalyst for the Michael addition of aromatic amines to fumaryl oxazolidinone affording aspartic acid derivatives in good yields. Influence of temperature on the addition of *p*-anisidine revealed an isoinversion effect with the maximum enantiomeric excess of 88% at −40 °C.

1. Introduction

The development of new methods for the enantioselective synthesis of β-amino carbonyl or β-amino acid derivatives has been given considerable attention due to their interesting pharmacologic properties.[1] Amongst the different routes for preparing such compounds, catalytic enantioselective aza-Michael reactions are the most attractive in terms of atom economy and efficiency. These reactions allow the enantioselective formation of carbon–nitrogen bonds by simple addition of amines to double bonds and have been recently the subject of increasing interest and the focus of reviews.[2] Enantioselective intramolecular hydroamination reactions involving addition of an amine to unactivated double bonds (1,2-addition) are catalyzed by chiral lanthanide cyclopentadienyl and non-cyclopentadienyl complexes.[3–5] Jorgensen described the first enantioselective aza-Michael reactions catalyzed by a $TiCl_2$binol complex. These additions of *O*-benzylhydroxylamine to α,β-unsaturated *N*-acyloxazolidinones afforded moderate asymmetric inductions.[6] Sibi reported the use of several Lewis acids in the presence of chiral bisoxazoline ligands for the addition of *O*-benzylhydroxylamine to chelating unsaturated amides in high enantiomeric excesses.[7] Similar catalytic systems furnished moderate asymmetric inductions for conjugate addition of aldoximes.[8] Different lanthanide based catalysts facilitated 1,4-addition of *O*-alkylhydroxylamine to enones, such as yttrium heterobimetallic complex YLB,[9] and scandium triflate coordinated with a chiral phosphate Sc[(*R*)-BNP]$_3$.[10] Carbamates have also been employed as nucleophiles for enantioselective aza-Michael additions to enones catalyzed by Cu(OTf)$_2$bisoxazoline complexes.[11] Highly enantioselective addition of hydrazoic acid, sodium azide or N–H containing heterocycles to α,β-unsaturated chelating imides or on α,β-unsaturated ketones catalyzed by Al–salen complexes have been reported by Jacobsen.[12] Trimethylsilyl azide has been used also as a nucleophile for asymmetric peptide-organocatalyzed aza-Michael reactions.[13] However, conjugate additions of amines to activated olefins involving chiral catalysts are still rare. Togni has reported enantiomeric excesses of up to 69% for the addition of aromatic amines to unsaturated esters or cyanides catalyzed by Ni complexes coordinated by chiral tridentate phosphines.[14] Cationic palladium complexes coordinated to BINAP catalyzed the enantioselective addition of aromatic amines to chelating substrates such as *N*-alkenoyl oxazolidinones or *N*-alkenoyl carbamates.[15] Another cationic BINAP palladium complex involving amines as ligands afforded high enantioselectivities for the same reaction with a wide range of aromatic amines and with benzylamine.[16] Nickel perchlorate coordinated by DBFOx–Ph catalyzed also the enantioselective addition of secondary aromatic amines to α,β-unsaturated *N*-acyloxazolidinones.[17]

In previous investigations, we have studied the use of $SmI_2(THF)_2$ in methylene chloride as an efficient Lewis acid catalyst for carbon–carbon bond forming reactions.[18] Imines have been employed in iminoaldolization or tandem Michael-iminoaldol reactions for the

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preparation of β-amino esters or β-aminoketones.[19] Samarium diiodide catalyzes carbon–nitrogen bond forming reactions such as ring opening of *meso*-epoxides by amines.[20] We recently reported aza-Michael additions of aromatic amines to α,β-unsaturated *N*-acyloxazolidinones.[21] With the aim of developing new enantioselective catalysts, we have prepared lanthanide complexes with binaphthylamine or binaphthol-type ligands. A new family of lanthanide ionic complexes derived from chiral substituted (*R*)-binaphthylamine ligands, $Li(THF)_4Ln[(R)\text{-}C_{20}H_{12}(NR)_2]_2$ proved to be enantioselective for intramolecular hydroamination reactions.[22] Lanthanide iodobinaphtholates are Lewis acid catalysts for Diels–Alder reactions,[23] iminoaldol reactions involving a glyoxylic imine,[24] and for the ring opening of *meso*-epoxides by aromatic amines leading to β-amino alcohols with high enantiomeric excesses.[25] Herein, we present our results concerning enantioselective catalysis of aza-Michael reactions by samarium iodobinaphtholate.

2. Results

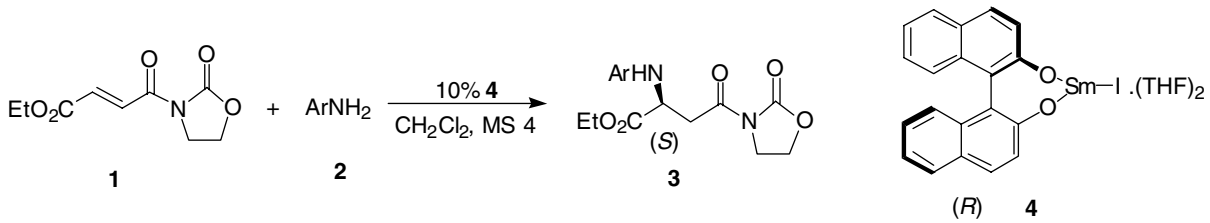
We have previously studied the preparation of lanthanide iodobinaphtholates and found that these complexes could be isolated by the reaction of potassium bisbinaphtholate with lanthanide triiodides in THF. The synthesis of these catalysts was improved by the use of potassium diphenylmethide as the potassium source.[25] A comparison between activity and selectivity of lanthanum and samarium iodobinaphtholates has been realized for Diels–Alder reactions,[23] and for the aminolysis of epoxides. Samarium furnished higher asymmetric inductions for both reactions. We thus decided to study the catalytic activity and enantioselectivity of samarium iodobinaphtholate for aza-Michael additions of aromatic amines to α,β-unsaturated *N*-acyloxazolidinones which are widely employed substrates in asymmetric catalysis due to their chelating properties.[26] When samarium diiodide was used as a catalyst for the latter Michael additions we found that reactions led to β-amino *N*-acyloxazolidinones or β-aminoamides or to both products according to the reaction conditions.[21] We selected the fumaryl oxazolidinone **1** which afforded selectively β-amino *N*-acyloxazolidinone through samarium diiodide-catalyzed reactions. The enantioselectivities provided by lanthanide iodobinaphtholates are dramatically influenced by temperature, since the enantioselectivity increased with temperature for iminoaldolization reactions. Furthermore an isoinversion effect was observed for the aminolysis of *meso*-epoxides.[25] We thus studied the aza-Michael additions of several aromatic amines to α,β-unsaturated *N*-acyloxazolidinone **1** at three different temperatures in order to determine the best temperature range for an optimization of enantioselectivity (Table 1) (see Scheme 1).

We first examined the reaction of α,β-unsaturated *N*-acyloxazolidinone **1** with aniline. This amine was added to 10 mol % samarium iodobinaphtholate **4** in methylene chloride in the presence of molecular sieves, followed by the addition of substrate **1** at room temperature. After 15 h total conversion was observed with formation of a single derivative in the crude product, which could be identified as **3a** after purification. The amine reacted with total regioselectivity on the olefinic carbon in β- to the acyl group bound to the oxazolidinone. The discrimination between the acyl oxazolidinone and the ester groups may be due to the chelation of samarium by the carbonyls of the acyloxazolidinone group. Aza-Michael addition at room temperature led to nearly racemic product (Table 1, entry 1) while at lower temperatures asymmetric inductions were obtained (entries 2 and 3) with a reasonable enantiomeric excess of 65% at −15 °C for β-aminoacyloxazolidinone **3a**. Reaction with *o*-anisidine furnished similarly almost racemic product **3b** at room temperature (entry 4). However a decrease of temperature resulted in only low enantiomeric excesses (entries 5 and 6). The reaction performed with *p*-anisidine gave β-amino *N*-acyloxazolidinone **3c** with a low enantio-

Table 1. Enantioselective aza-Michael catalyzed by samarium complex **4** at different temperatures

Entry	RNH_2	Product	*T* (°C)	*t* (h)	Yield[a,b] (%)	ee (%)
1	**2a** $PhNH_2$	**3a**	25	18	40	2
2	**2a** $PhNH_2$	**3a**	−15	48	70	65
3	**2a** $PhNH_2$	**3a**	−40	48	73	42
4	**2b** *o*-MeO–C_6H_4–NH_2	**3b**	25	48		5
5	**2b** *o*-MeO–C_6H_4–NH_2	**3b**	−15	48	74	19
6	**2b** *o*-MeO–C_6H_4–NH_2	**3b**	−40	48		21
7	**2c** *p*-MeO–C_6H_4–NH_2	**3c**	25	18	21	25
8	**2c** *p*-MeO–C_6H_4–NH_2	**3c**	−15	48	47	78
9	**2c** *p*-MeO–C_6H_4–NH_2	**3c**	−40	48	65	88
10	**2c** *p*-MeO–C_6H_4–NH_2	**3c**	−40	48	72	85[c]
11	**2d** *p*-Br–C_6H_4–NH_2	**3d**	25	18	55	35
12	**2d** *p*-Br–C_6H_4–NH_2	**3d**	−15	48	68	46
13	**2d** *p*-Br–C_6H_4–NH_2	**3d**	−40	48	53	39
14	**2e** *p*-Cl–C_6H_4–NH_2	**3e**	25	18	56	22
15	**2e** *p*-Cl–C_6H_4–NH_2	**3e**	−15	48	51	26
16	**2e** *p*-Cl–C_6H_4–NH_2	**3e**	−40	72	64	25

[a] Isolated yield, 100% conversion, reaction time 18 h.
[b] 10% Catalyst **4**.
[c] 5% Catalyst **4**.



Scheme 1.

meric excess (25%) at room temperature (entry 7). A decrease in temperature resulted in an impressive increase in enantiomeric excess (entries 8 and 9) with a maximum value of 88% ee at −40 °C. Conversely, Michael additions of *p*-bromoaniline (entries 11–13) or *p*-chloroaniline (entries 14–16) afforded products **3d** and **3e**, respectively, with moderate enantiomeric excesses. For these two amines only very small variations of enantiomeric excess with temperature could be detected. Compound **3c** has been transformed in aspartic acid by successive reactions with CAN and with lithium hydroxide following described procedures.[17,27] The positive sign of the aspartic acid specific rotation allowed the (*S*)-absolute configuration to be assigned to the major enantiomer of **3c** and by analogy for the major enantiomer of the other compounds. For all aza-Michael reactions, a total conversion was observed after 15 h, even at −40 °C and the new β-aminoester *N*-acyloxazolidinones **3** were isolated in moderate to good yields. We checked also that reactions can be carried out with small amount of catalyst without loss of asymmetric induction. Using 5% samarium complex **4**, a total conversion in **3c** was observed after 15 h at −40 °C and the isolated product showed a 85% enantiomeric excess (entries 9 and 10). No trace of amidation reaction (replacement of oxazolidinone by amine **2**) was detected in the samarium iodo catalyzed reactions, as was observed in some samarium diiodide-catalyzed aza-Michael reactions and in the literature.[21,28]

The aza-Michael addition of *p*-anisidine **2c** to α,β-unsaturated *N*-acyloxazolidinone **1** is of synthetic interest since adduct **3c** was isolated with high asymmetric induction and deprotection of nitrogen substituted by *p*-methoxy phenyl groups has been described in the literature.[29] We examined the influence of temperature on aza-Michael reaction affording **3c** catalyzed by samarium iodo to try to optimize the enantiomeric excess (Table 2). We found that variation of enantiomeric excesses was not continuous with the temperature. The enantiomeric excess increased first upon decrease of the temperature to reach a maximum value of 88% at −40 °C. Reactions performed at lower temperatures gave lower asymmetric inductions. Such variations of enantioselectivity, with an isoinversion effect have been already reported.[30] We have previously described a similar behaviour for the ring opening of cyclohexene oxide by *o*-anisidine catalyzed by samarium iodobinaphtholate with an inversion temperature of −39 °C.[25] For aza-Michael addition leading to **3c**, the Eyring plot (Fig. 1) shows a nonlinear behaviour, consisting of two linear regions intersecting at the inversion temperature (T_{inv}). This intersection corresponds to a value of −39 °C in Figure 1.

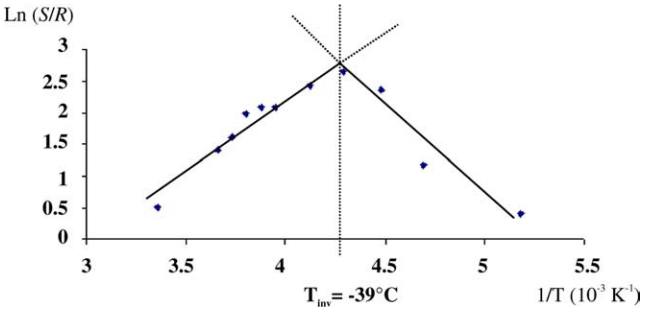


Figure 1. Eyring plot for aza-Michael addition of *p*-anisidine on **1** catalyzed by samarium complex **4**.

Inversion temperatures can be explained by a reaction pathway with at least two enantioselective steps weighted differentially according to the temperature. Cainelli proposed T_{inv} as the temperature value for the interconversion between two different solvation clusters behaving as two different molecules.[30e,f] For aza-Michael reactions as well as for the aminolysis of *meso*-epoxides catalyzed by samarium iodobinaphtholate the inversion temperature could be explained similarly. Several catalytic species with variable numbers of THF molecules and/or amines coordinated can be envisaged. The similarity of the coordinating reagents (*o*-anisidine and *p*-anisidine) and of the inversion temperatures for both reactions is in favour of such explanation. Further studies, especially those concerning the structure of active species involved in enantioselective catalysis, are needed to understand the inversion phenomenon.

Table 2. Influence of temperature on enantiomeric excess of product **3c**

T (°C)	−80	−60	−50	−40	−30	−20	−15	−10	−5	0	25
ee (%)	20	53	83	88	84	78	78	76	67	61	25

3. Conclusion

We have found that samarium iodobinaphtholate catalyzes the aza-Michael addition of aromatic amines to an α,β-unsaturated *N*-acyloxazolidinone **1** leading to new enantiomerically enriched derivatives of aspartic acid. For the reaction involving *p*-anisidine an inversion temperature of −39 °C has been determined and the aza-Michael adduct was isolated with a maximum enantiomeric excess 88%. We are currently extending the scope of enantioselective aza-Michael reactions catalyzed by lanthanide binaphtholates and studying their synthetic applications.

4. Experimental

4.1. General

All manipulations were carried out under an argon atmosphere using standard Schlenk or glove box techniques. CH_2Cl_2 was distilled from CaH_2 and degassed immediately prior to use. The method for preparing samarium iodobinaphtholate has been previously described.[25] All catalysts have been prepared from enantiopure (*R*)-1,1′-binaphthol. α,β-Unsaturated *N*-acyloxazolidinone **1** has been prepared according to literature procedure.[31] Bruker AM 250 and AM 360 spectrometers, operating at 250 and 360 MHz for ^1H, and at 62.5 and 90.6 MHz for ^{13}C, were used for the NMR spectra; chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane for spectra in $CDCl_3$. Infrared spectra were recorded in $CHCl_3$ solution using CaF_2 cells on a Perkin–Elmer 1000 FT-IR spectrometer and are reported in cm^{-1}. HRMS were measured with a Perkin–Elmer Finnigan-Mat 955 spectrometer. Optical rotations were determined using a Perkin–Elmer 241 Polarimeter at room temperature using a cell of 1 dm length and $\lambda = 589$ nm. Data are reported as follows: $[\alpha]_D^{20}$ (concentration in g/100 mL, solvent). The enantiomeric excesses were measured by chiral stationary phase HPLC on WHELK O1, or Chiralpak AD columns. Thin layer chromatographic plates were prepared from silica gel 60 PF_{254} for preparative layer chromatography.

4.2. Typical procedure for aza-Michael reactions

Samarium iodobinaphtholate **4** (35 mg, 0.05 mmol) was weighed in a glove-box and molecular sieves 4 Å (100 mg) and dichloromethane (2 mL) were added. Amine **2** (74 mg, 1.2 mmol) was then added to the reaction mixture which was stirred for 10 min at room temperature. Outside the glove-box, the reaction mixture was cooled at −40 °C and a solution of α,β-unsaturated *N*-acyloxazolidinone **1** (106 mg, 0.5 mmol) in 1 mL CH_2Cl_2 was introduced by syringe. The reaction mixture was stirred for 18 h and quenched by addition of 10 mL HCl 0.1 N aqueous solution and extracted by CH_2Cl_2. The crude product was purified by preparative silica gel TLC (heptane/AcOEt: 75/25) to afford 109 mg of the desired product **3c**. The enantiomeric excess of **3c** was determined by chiral HPLC as described below.

4.3. (*S*)-Ethyl 4-oxo-4-(2-oxooxazolidin-3-yl)-2-phenylaminobutanoate 3a

Mp 101–102 °C. $[\alpha]_D^{25} = +1.5$ (*c* 1.08, $CHCl_3$) for 65% ee. ^1H NMR (360 MHz, $CDCl_3$): δ 7.10 (t, 2H, $J = 7.9$ Hz), 6.67 (t, 1H, $J = 7.3$ Hz), 6.60 (d, 2H, $J = 7.9$ Hz), 4.45 (m, 1H), 4.29 (t, 2H, $J = 7{,}9$ Hz), 4,12 (q, 2H, $J = 6.7$ Hz), 3.90 (t, 2H, $J = 7.9$ Hz), 3.50 (dd, 1H, $J_1 = 17.1$ Hz, $J_2 = 4.9$ Hz), 3.39 (dd, 1H, $J_1 = 17.1$ Hz, $J_2 = 4.3$ Hz), 1.17 (t, 3H, $J = 6.7$ Hz); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ 172.27, 170.41, 153.47, 146.34, 129.29, 118.64, 113.73, 62.17, 61.58, 53.13, 42.30, 37.87, 14.06; IR (CaF_2, $CHCl_3$) (cm^{-1}): *v* 3419, 1784, 1736, 1700, 1603, 1297; MS (ESI): 329.3 (M+Na), 307.3 (M+1), 178.2 (M−128); HRMS: calcd for $C_{15}H_{18}N_2O_5Na$ 329.1108, found 329.1118; HPLC (WHELK O1, hexane/*iso*-propanol: 90/10, 0.8 mL/min, $\lambda = 254$ nm, $t_R = 42.6$ and 55.6 min).

4.4. (*S*)-Ethyl 2-(2-methoxyphenylamino)-4-oxo-4-(2-oxooxazolidin-3-yl)-butanoate 3b

Oil. $[\alpha]_D^{25} = +3.5$ (*c* 4.53, $CHCl_3$) for 21% ee. ^1H NMR (250 MHz, $CDCl_3$): δ 6.82–6.60 (m, 4H), 4.51 (t, 1H, $J = 7.4$ Hz), 4.32 (t, 2H, $J = 7.4$ Hz), 4.16 (q, 2H, $J = 7.4$ Hz), 3.96 (t, 2H, $J = 7.4$ Hz), 3.80 (s, 3H), 3.49 (dd, 2H, $J_1 = 7.4$ Hz, $J_2 = 0.5$ Hz), 1.22 (t, 3H, $J = 7.4$ Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 172.26, 170.33, 153.43, 147.21, 136.08, 121.04, 117.83, 110.63, 109.83, 62.20, 61.47, 55.45, 52.61, 42.30, 38.00, 14.03. IR (CaF_2, $CHCl_3$) (cm^{-1}): *v* 3420, 1784, 1737, 1702, 1603, 1389. MS (ESI): 359.2 (M+Na), 337.2 (M+1), 208.1 (M−128). HRMS: calcd for $C_{16}H_{20}N_2O_6Na$ 359.1214, found 359.1227. HPLC (WHELK O1, hexane/*iso*-propanol: 85/15, 0.7 mL/min, $\lambda = 254$ nm, $t_R = 47.3$ and 55.4 min).

4.5. (*S*)-Ethyl 2-(4-methoxyphenylamino)-4-oxo-4-(2-oxooxazolidin-3-yl)-butanoate 3c

Mp 109 °C. $[\alpha]_D^{25} = -3.9$ (*c* 3.00, $CHCl_3$) for 88% ee. ^1H NMR (250 MHz, $CDCl_3$): δ 6.74 (d, 2H, $J = 8.8$ Hz), 6.64 (d, 2H, $J = 8.8$ Hz), 4.45–4.30 (m, 3H), 4.15 (q, 2H, $J = 7.3$ Hz), 3.97 (t, 2H, $J = 7.8$ Hz), 3.72 (s, 3H), 3.55 (dd, 1H, $J_1 = 16.6$ Hz, $J_2 = 5.8$ Hz), 3.38 (dd, 1H, $J_1 = 16.6$ Hz, $J_2 = 5.4$ Hz), 1.15 (t, 3H, $J = 7.3$ Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 172.62, 170.47, 153.99, 152.99, 140.46, 115.69, 114.76, 62.17, 61.49, 55.62, 54.54, 42.32, 38.03, 14.05. IR (CaF_2, $CHCl_3$) (cm^{-1}): *v* 3394, 1784, 1735, 1602, 1389, 1336. MS (ESI): 359.3 (M+Na), 337.3 (M+1), 208.3 (M−128). HRMS: calcd for $C_{16}H_{20}N_2O_6Na$ 359.1214, found 359.1231. HPLC (Chiralpak AD, hexane/*iso*-propanol: 75/25, 1.0 mL/min, $\lambda = 254$ nm, $t_R = 36.2$ and 48.9 min).

4.6. (*S*)-Ethyl 2-(4-bromophenylamino)-4-oxo-4-(2-oxooxazolidin-3-yl)-butanoate 3d

Mp 93–94 °C. $[\alpha]_D^{25} = +6.2$ (*c* 1.12, $CHCl_3$) for 46% ee. ^1H NMR (250 MHz, $CDCl_3$): δ 7.15 (d, 2H, $J = 8.8$ Hz), 6.48 (d, 2H, $J = 8.8$ Hz), 4.35–4.42 (m, 1H), 4.27 (t, 2H, $J = 8.3$ Hz), 4.09 (q, 2H, $J = 7.3$ Hz),

3.86 (t, 2H, $J = 8.3$ Hz), 3.45 (dd, 1H, $J_1 = 17.6$ Hz, $J_2 = 7.8$ Hz), 3.35 (dd, 1H, $J_1 = 17.6$ Hz, $J_2 = 5.4$ Hz), 1.14 (t, 3H, $J = 7.3$ Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 171.83, 170.09, 153.35, 145.38, 131.73, 115.07, 109.83, 62.11, 61.45, 52.64, 42.11, 37.54, 13.87. IR (CaF_2, $CHCl_3$) (cm^{-1}): ν 3409, 1785, 1735, 1697, 1389. MS (ESI): 409.2 and 407.2 (M+Na), 387.2 and 385.2 (M+1), 258.2 and 256.2 (M−128). HRMS: calcd for $C_{15}H_{17}N_2O_5BrNa$ 407.0213, found 407.0221. HPLC (Chiralpak AD, hexane/*iso*-propanol: 75/25, 1.0 mL/min, $\lambda = 254$ nm, $t_R = 33.3$ and 42.9 min).

4.7. (*S*)-Ethyl 2-(4-chlorophenylamino)-4-oxo-4-(2-oxooxazolidin-3-yl)-butanoate 3e

Mp 102 °C; $[\alpha]_D^{25} = +3.0$ (*c* 1.04, $CHCl_3$) for 22% ee. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.06 (d, 2H, $J = 8.8$ Hz), 6.56 (d, 2H, $J = 8.8$ Hz), 4.40 (m, 1H), 4.32 (t, 2H, $J = 8.3$ Hz), 4.12 (q, 2H, $J = 6.8$ Hz), 3.91 (t, 2H, $J = 8.3$ Hz), 3.50 (dd, 1H, $J_1 = 17.1$ Hz, $J_2 = 5.3$ Hz), 3.38 (dd, 1H, $J_1 = 17.1$ Hz, $J_2 = 4.9$ Hz), 1.18 (t, 3H, $J = 6.8$ Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 171.93, 170.15, 153.39, 144.97, 128.91, 122.85, 114.69, 62.14, 61.51, 52.87, 42.15, 37.63, 13.91; IR (CaF_2, $CHCl_3$) (cm^{-1}): ν 3413, 1784, 1738, 1700, 1389, 1296. MS (ESI): [365.2 (26%) and 363.2 (74%)] (M+Na), [343.3 (26%) and 341.3 (74%)] (M+1), [214.2 (26%) and 212.2 (74%)] (M−128). HRMS: calcd for $C_{15}H_{17}N_2O_5ClNa$ 363.0718, found 363.0721. HPLC (Chiralpak AD, hexane/*iso*-propanol: 75/25, 1.0 mL/min, $\lambda = 254$ nm, $t_R = 34.8$ and 46.1 min).

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