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Asymmetric 1,3-dipolar cycloadditions of chiral carboxyloyl nitrile oxides to cycloalkenes

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Abstract—Asymmetric 1,3-dipolar cycloadditions of chiral carboxyloyl nitrile oxides derived from (2*R*)-bornane-10,2-sultam, (1*R*)-8-phenylmenthol, *N*,*N*-dicyclohexyl-10-sulfamoyl-(2*R*)-isoborneol, and 7,7-dimethylnorbornane-(1*S*,2*R*)-oxazolidinone to four cycloalkenes, leading to the corresponding 2-isoxazolines in both moderate yields and diastereoselectivities, are presented. All cycloadducts were converted into the corresponding alcohols, which were used for the determination of enantiomeric purity via chiral gas chromatography. In the case of the six-membered ring cycloadduct, the absolute configuration was determined by X-ray analysis.

1. Introduction

The asymmetric 1,3-dipolar cycloaddition of nitrile oxides to alkenes provides a powerful tool for the stereocontrolled synthesis of 4,5-dihydroisoxazoles.[1] With respect to the easy cleavage of the weak N–O bond,[2] their simple hydrolysis,[3] as well as their potential nucleophilic or electrophilic reactive centres, these heterocycles have demonstrated their practical usefulness for the synthesis of several pharmaceuticals[4] and natural products.[5] Much attention has been devoted to intermolecular diastereoselective cycloadditions of achiral nitrile oxides to optically active dipolarophiles.[6] These, using acryloyl derivatives of chiral auxiliaries from menthol,[7] isoborneol,[8] chiral sultams,[9] sugars or steroids,[10] and chiral amines[11] families, are amongst the most versatile types of compounds. More recently, chiral *Lewis* acids were explored under stoichiometric[12] or catalytic[13] conditions. On the other hand, the literature offers only a few examples of diastereoselective 1,3-dipolar cycloadditions of optically active nitrile oxides.[14] The linearity of the dipole, both its *endo*/*exo* and π_z/π_y modes of addition, or the distance between pre-existing and forming stereocentres, account for the reported poor stereoselectivity. Furthermore, very few of them are either directly conjugated to a carboxy moiety or directed by a recoverable chiral auxiliary. Recently, we have published a communication concerning the efficient preparation of the chiral nitrile oxide derived from *N*-glyoxyloyl-(2*R*)-bornane-10,2-sultam **1a**, and its 1,3-dipolar cycloadditions with linear olefins as dipolarophiles.[15] The reaction afforded 2-isoxazolines in both moderate yields (57–84%) and diastereoselectivities (⩽30% de). We then improved the preparation protocol and extended it towards the carboxyloyl nitrile oxides derived from other chiral auxiliaries.[16] These results prompted us to pursue our studies, and we decided to subject chiral nitrile oxides derived from **2a**, **2b**, **2c** and **2d** to 1,3-dipolar cycloadditions with four cycloalkenes **3**–**6** (Scheme 1).

2. Results and discussion

Compounds **2a**–**d** are readily available by oximation of their corresponding precursors **1a**–**d**. The chiral nitrile oxides were generated from aldoximes **2a**–**d** via mild oxidation with MnO_2, and trapped in situ with cycloalkenes **3**–**6** to furnish 2-isoxazolines **7**–**10** in moderate to good yields (Table 1). In all cases, 2-isoxazolines were formed as mixtures of diastereomers; the best selectivity and yield were obtained for cycloadducts **9b** and **10b**, respectively. The major cycloadduct **8a**, after crystallization, was

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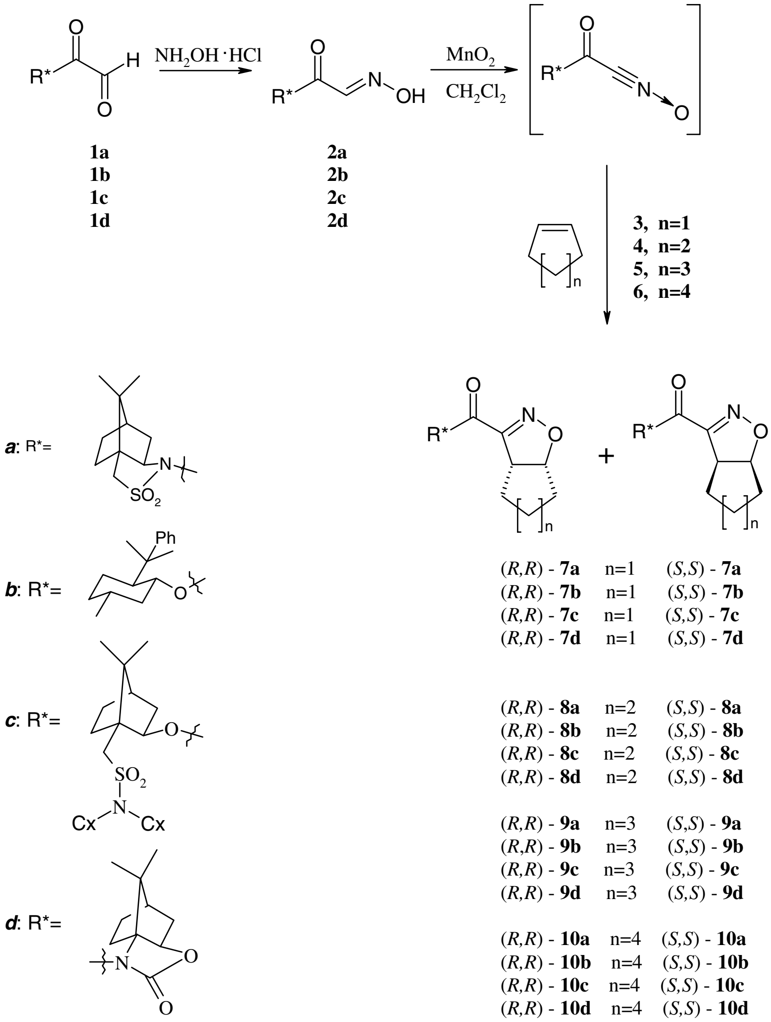


Scheme 1.

Table 1.

Cyclo-adduct	Yield (%)	Alcohol	Yield (%)	de[a] (%)	Abs. conf.
7a	52	**11**	92	39	(*R*,*R*)
7b	62		81*	35	(*R*,*R*)
7c	50		79*	22	(*R*,*R*)
7d	60		95	27	(*R*,*R*)
8a	45	**12**	90	45	(*R*,*R*)
8b	60		82*	52	(*R*,*R*)
8c	43		79*	11	(*R*,*R*)
8d	52		91	49	(*R*,*R*)
9a	52	**13**	95	48	(*R*,*R*)
9b	48		85*	62	(*R*,*R*)
9c	40		77*	13	(*R*,*R*)
9d	49		93	57	(*R*,*R*)
10a	61	**14**	95	50	(*R*,*R*)
10b	82		83*	57	(*R*,*R*)
10c	65		82*	25	(*R*,*R*)
10d	68		91	32	(*R*,*R*)

[a] Determined by GC using a ID beta-dex 225 column. Yields after two steps (transesterification, reduction).

isolated as a single diastereoisomer (25%); its absolute configuration at both newly formed stereogenic centres was determined as (*R*,*R*) by X-ray analysis (Fig. 1). This structure shows a particularly rare SO_2/C=O *syn*-conformation, already observed in the solid state in cases of peculiar steric crowding or when a heteroatom, possessing an electron lone pair, is located at the β-position.[17]

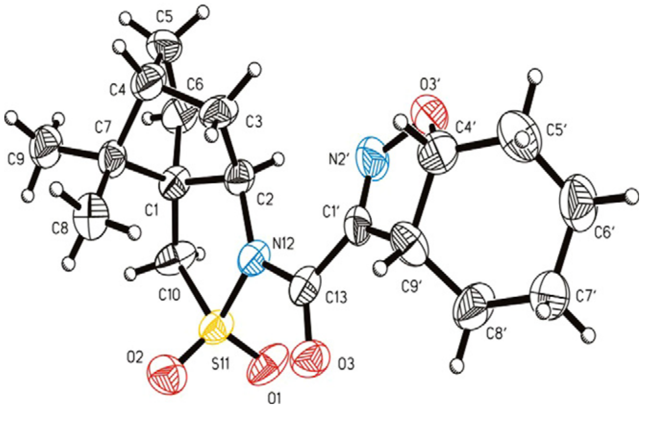


Figure 1. X-ray structure of 3a,4,5,6,7,7a-hexahydro-1,2-benzisoxazole-3-carboxylic acid (2*R*)-*N*-bornane-10,2-sultam imide (**8a**).

A more polar dipolarophile such as 2,5-dihydrofuran, resulted (44–47% yield) in much lower diastereoselectivities

(6–14%) with **2a–d** as precursors. Similarly, for dipolar cycloadditions of bornane-10,2-sultam derived carboxyloyl nitrile oxide (**2a** as precursor), better yields (increased by ca. 12%) but worse diastereoselectivities (decreased by ca.10–18%, for **3**–**6**, respectively) were observed in 1-*N*-butyl-3-methylimidazolium tetrafluoroborate, a more polar ionic solvent.

In order to establish the direction and extent of asymmetric induction, we decided to transform cycloadducts **7a**, **7d**, **8a**, **8d**, **9a**, **9d**, **10a** and **10d**, via simple reduction, into alcohols **11**, **12**, **13** and **14**, respectively. On the other hand, cycloadducts **7b**, **7c**, **8b**, **8c**, **9b**, **9c** and **10b**, **10c** were transformed into the same alcohols via a two-step sequence (high-pressure transesterification[18] and reduction; Scheme 2; Table 1). For cycloadducts **7a**, **8a**, **9a** and **10a**, the major diastereoisomers show systematic downfield shifted ring junction signals in the ^{1}H NMR analyses, as compared to the minor diastereoisomers. A comparison of chiral GC analysis of alcohol **12**, obtained from either a single diastereoisomer or from the reaction mixtures, proved that the configuration of the major cycloadducts **8a–d** were also (*R*,*R*). The configurations of the remaining products, based on comparative ^{1}H NMR analysis, chiral gas chromatographic elution time and mechanistic considerations, were assumed to also be (*R*,*R*) (Table 1).

Based on B3LYP/6-31G** DFT calculations,[19] the nitrile oxide generated from oxime **2a** exists in both reactive conformations **A** (S–N–C=O 160.0°) and **B** (S–N–C=O −16.3°, Fig. 2). The *anti*-SO$_2$/C=O conformer **A** being thermodynamically more stable ($\Delta E = 3.33$ kcal/mol). On the other hand, the LUMO of conformer **B** is slightly lower (0.003588 *hartree*, 2.2% for **4**) and thus possibly more reactive. Moreover, the sultam N lone pair influences the atomic coefficients of the LUMO orbitals and electronically favours the attack of the olefin from the top face, regardless of the conformation. As a consequence, the steric and stereoelectronic effects are mismatched in conformation **B**, whilst matching in conformation **A**, thus contrasting with an earlier rationalization for [4+2] cycloadditions of *N*-alkenoyl or *N*-glyoxyloyl sultams derived from this auxiliary.[20]

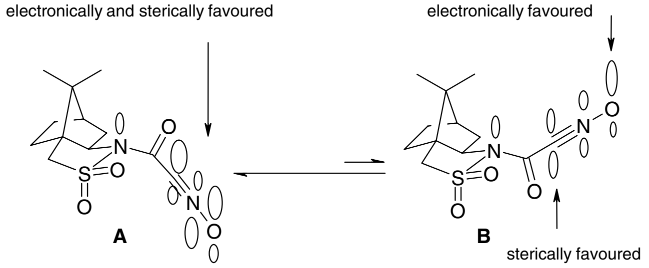


Figure 2. Thermodynamic, steric and stereoelectronic preferences for *anti*/*syn* nitrile oxides derived from **2a**.

In the case of *anti*-conformer **A**, the *exo* olefin attack (e.g., cyclohexene) at the C$_\alpha$ atom is directed opposite to the axial S=O. This produces the (*R*,*R*)-diastereomer via transition state **C**. Analogously, the *exo* attack on the *syn*-conformer **B** over transition state **D** leads to the same (*R*,*R*)-product (Fig. 3).[21] A combination of both steric and stereoelectronic factors associated with the alternative

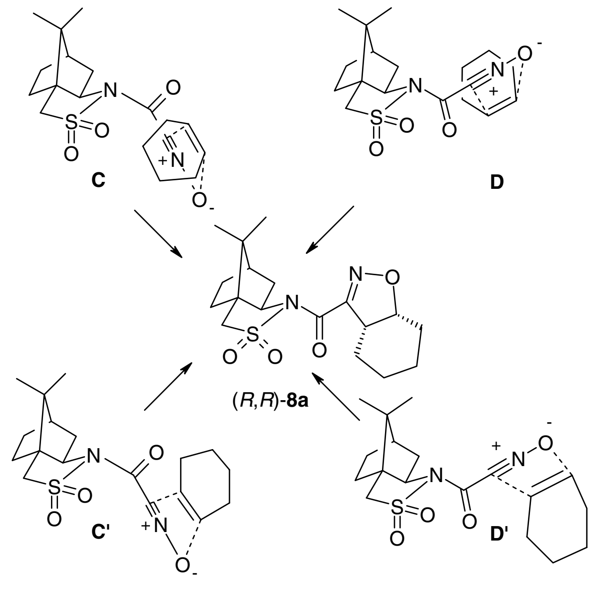
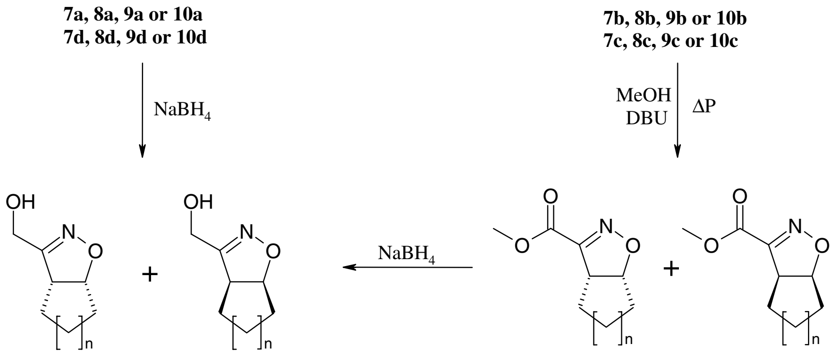


Figure 3.



(*R*,*R*) - 11	**n=1**	**(*S*,*S*) - 11**	**(*R*,*R*) - 15**	**n=1**	**(*S*,*S*) - 15**
(*R*,*R*) - 12	**n=2**	**(*S*,*S*) - 12**	**(*R*,*R*) - 16**	**n=2**	**(*S*,*S*) - 16**
(*R*,*R*) - 13	**n=3**	**(*S*,*S*) - 13**	**(*R*,*R*) - 17**	**n=3**	**(*S*,*S*) - 17**
(*R*,*R*) - 14	**n=4**	**(*S*,*S*) - 14**	**(*R*,*R*) - 18**	**n=4**	**(*S*,*S*) - 18**

Scheme 2.

endo approaches, as well as an additional π_y-orthogonal approach along the C=O bond of type **C**′ and **D**′, may account for the modest diastereoselectivity.

Likewise, both configurations and diastereoselectivities for cycloadducts bearing either 8-phenylmenthol or *N*,*N*-dicyclohexyl-10-sulfamoyl-(2*R*)-isoborneol as auxiliaries, as well as the thermodynamically favoured *anti*-conformer derived from oxime **2d** ($\Delta E_{syn/anti} = 6.5$ kcal/mol) can be interpreted by the π_z *exo*, less hindered face favoured approaches as depicted in TS$^{\#}$ **E**, **F** and **G** (Fig. 4),[22] in addition to their corresponding π_y orthogonal version.

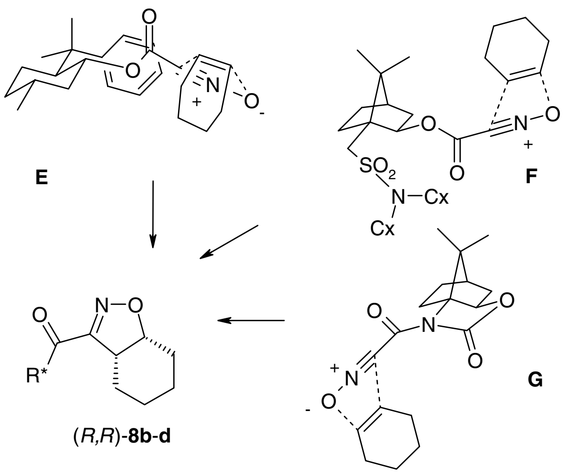


Figure 4.

3. Conclusion

In conclusion, 16 new diastereomeric pairs of isoxazoles bearing four types of recoverable chiral auxiliaries (85–94%) were synthesized and converted into their corresponding methyl esters and alcohols. Enantiomeric pairs of alcohols and esters were easily separated by chiral gas chromatography. Due to the linear geometry of the nitrile oxide, both π_y and π_z-facial approaches, with respect to steric and stereoelectronic factors, depend on both *syn*/*anti* conformations as well as *endo*/*exo* selectivities. As a result, only moderate diastereoselectivities were obtained (11–62% de). Bornane-10,2-sultam and 8-phenyl-menthol are the most promising auxiliaries, due to their crystallinity and efficient chiral transfer. These results open the way for further investigations, including the application of more sterically demanding olefins, more effective chiral auxiliaries, less polar solvents,[23] and detailed TS$^{\#}$ calculations.

4. Experimental

All reactions were carried out under an argon atmosphere with anhydrous solvents dried according to standard laboratory methods. ^{1}H and ^{13}C NMR spectra were measured on Varian Gemini spectrometers using residual TMS as internal reference δ (ppm). Mass spectra were recorded out with AMD-604 Intectra instrument. Optical rotations were measured on a JASCO DIP-360 polarimeter with a thermally jacketed 10 cm cell.[24] Infrared spectra were recorded on a Perkin–Elmer 1640 FT-IR spectrometer (cm^{-1}). Melting points were determined with Köfler hot-stage apparatus and are uncorrected. Flash column chromatography was performed on silica gel (Kieselgel 60, Merck, 200–400 mesh). TLC was performed on Merck aluminium plates (Kieselgel 60 F_{254}) and compounds were visualized with a solution of MoO_3 and $Ce_2(SO_4)_3$ in 15% H_2SO_4.

X-ray single-crystal diffraction experiments were carried out on a Enraf-Nonius-CAD4 diffractometer using Cu Kα radiation (1.54178 Å). The program used to solve and refine was SHELX-97. The crystallographic data for **8a** have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication No. CCDC 278209. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223336033; e-mail: deposit@ccdc.cam.ac.uk). $C_{18}H_{26}N_2O_4S$ **8a**, $M = 366.47$ g/mol, monoclinic, $a = 9.733(3)$, $b = 8.8190(10)$, $c = 21.258(3)$, $\alpha = 90°$, $\beta = 93°$, $20°$, $\gamma = 90°$, space group I_2, $Z = 4$, $D_{calcd} = 1.336$ Mg/m^3, μ (Mo Kα) = 1793 mm^{-1}. The final $R_1 = 0.0521$ (all data). Residual electron density 0.322 and -0.272 e Å^{-3}.

4.1. General procedure for the oxidation of the oximes

To a solution of oxime **2** (1.0 mmol) in CH_2Cl_2 (5 ml), 3 mmol of MnO_2 and 3 mmol of cycloalkene were added at rt. The progress of the reaction was monitored by TLC and every 3 h, more MnO_2 (3 mmol each time) was added. When the reaction was completed, the solids were filtered off, the solvent evaporated and the residue purified on silica gel (hexane/AcOEt).

4.1.1. 4,5,6,6a-Tetrahydro-3a*H*-cyclopenta[*d*]isoxazole-3-carboxylic acid (2′*R*)-*N*-bornane-10′,2′-sultam imide 7a. Yield: 52%; mp 146–148 °C; HRMS-ESI: calcd for $C_{17}H_{25}O_4N_2S$ $(M+H)^+$ 353.15350; found, 353.15476; EIMS *m/z* 352 (7), 288 (21), 273 (38), 259 (34), 214 (100), 150 (24), 138 (41); LSIMS (+) NBA 8 kV (%) 353 $(M+H)^+$ (100), 138 (70); IR (KBr) 2961, 2880, 1667, 1391, 1344, 1274, 1169, 1139, 1063, 936, 755, 531, 489; ^{1}H NMR (500 MHz) 5.25–5.20 (m, 1H), 4.22–4.13 (m, 1H), 4.13–3.80 (m, 1H), 3.468 (AB, 2H, CH_2SO_2), 2.22–1.86 (m, 6H), 1.80–1.665 (m, 3H), 1.55–1.32 (m, 4H), 1.24 (s, 3H, CH_3), 0.99 (s, 3H, CH_3); ^{13}C NMR (125 MHz) 160.45, 155.08, 89.54, 65.77, 53.18, 51.79, 48.76, 47.87, 45.41, 39.38, 35.45, 33.39, 30.97, 26.25, 23.17, 21.61, 19.94.

4.1.2. 4,5,6,6a-Tetrahydro-3a*H*-cyclopenta[*d*]isoxazole-3-carboxylic acid (1′*R*)-8′-phenylmenthyl ester 7b. Yield: 62%; HRMS-ESI: calcd for $C_{23}H_{32}O_3N$ $(M+H)^+$ 370.23822; found, 370.23786; LSIMS (+) NBA 8 kV (%) 370 $(M+H)^+$ (42), 215 (57), 119 (94), 105 (100), 91 (32); IR (film) 3087, 2958, 2871, 1730, 1711, 1582, 1495, 1455, 1391, 1321, 1259, 1199, 1124, 939, 763, 701; ^{1}H NMR (500 MHz) 7.37–7.09 (m, 5H), 5.18–5.05 (m, 1H), 5.04–4.98 (m, 1H), 3.04–3.294 (m, 1H), 1.93–1.45 (m, 11H), 1.33 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.20–1.04 (m, 3H), 0.89 (s, 3H, CH_3); ^{13}C NMR (125 MHz) 169.09, 154.42, 151.97, 128.58, 126.04, 125.60, 90.74, 76.06, 50.92, 50.75, 42.08, 40.21, 36.03, 34.97, 32.04, 31.85, 29.13, 27.04, 25.12, 23.60, 22.31.

4.1.3. 4,5,6,6a-Tetrahydro-3a*H*-cyclopenta[*d*]isoxazole-3-carboxylic acid *N*,*N*-dicyclohexyl-10-sulfamoyl-(2*R*)-isoborneol ester 7c. Yield: 50%; HRMS-ESI: calcd for $C_{29}H_{47}O_5N_2S$ $(M+H)^+$ 535.32057; found, 535.31898; LSIMS (+) NBA 8 kV (%) 535 $(M+H)^+$ (23), 380 (100), 246 (17), 228 (30), 180 (43), 135 (90), 83 (35); IR (KBr) 3417, 2934, 2853, 1717, 1447, 1323, 1258, 1165, 1143, 1048, 981, 892, 774, 578 (cm^{-1}); ^1H NMR (500 MHz) 5.25–5.04 (m, 2H), 3.91–3.83 (m, 1H), 3.40 (d, $J = 13$, 1H), 3.30–3.16 (m, 2H), 2.64 (d, $J = 13$, 1H), 2.18–1.56 (m, 26H), 1.46–1.06 (m, 7H), 1.03 (s, 3H, CH_3), 0.89 (s, 3H, CH_3); ^{13}C NMR (125 MHz) 159.82, 153.60, 89.94, 79.72, 57.37, 53.48, 51.35, 49.70, 49.18, 44.53, 39.40, 35.75, 32.42, 31.66, 30.29, 26.44, 26.27, 25.24, 23.35, 20.42, 20.10.

4.1.4. *N*-(4,5,6,6a-Tetrahydro-3a*H*-cyclopenta[*d*]isoxazole-3-carbonyl)-7,7-dimethylnorbornane-(1*S*,2*R*)-oxazolidinone 7d. Yield: 60%; HRMS-ESI: calcd for $C_{17}H_{22}O_4N_2$ $(M+Na)^+$ 341.1477; found, 341.1490; IR (film) 2962, 2880, 1790, 1693, 1368, 1305, 1229, 1202, 1174, 1074, 1051, 782, 761, 692; ^1H NMR (500 MHz) 5.28–5.24 (m, 1H), 4.39–4.36 (m, 1H), 4.09–4.06 (t, $J = 8$, 0.6H), 4.01–3.80 (t, $J = 8$, 0.4H), 2.74–2.69 (dt, $J_1 = 5$, $J_2 = 12.5$, 1H), 2.34–2.52 (m, 2H), 2.20–2.13 (m, 1H), 2.10–2.03 (m, 1H), 1.96–1.85 (m, 3H), 1.78–1.68 (m, 3H), 1.38–1.33 (m, 2H), 1.30–1.25 (dt, $J_1 = 3$, $J_2 = 11.5$, 1H), 1.23 (s, 1.8H), 1.20 (s, 1.2H), 1.08 (s, 3H); ^{13}C NMR (125 MHz) 162.48, 154.22, 89.26, 85.64, 72.82, 53.42, 52.33, 48.22, 42.42, 35.36, 34.63, 30.82, 25.88, 24.41, 23.30, 21.52, 19.21.

4.1.5. 3a,4,5,6,7,7a-Hexahydro-1,2-benzisoxazole-3-carboxylic acid (2′*R*)-*N*-bornane-10′,2′-sultam imide 8a. Yield: 45%; HRMS-ESI: calcd for $C_{18}H_{26}O_4N_2S$ $(M+H)^+$ 367.16915; found, 367.16937; EIMS *m*/*z* (%) 366 (M^+) (17), 214 (71), 152 (37), 135 (20), 124 (100), 107 (14), 93 (17), 79 (17); LSIMS (+) NBA 8 kV (%) 367 $(M+H)^+$ (100), 152 (40); IR (KBr) 2940, 1662, 1455, 1391, 1338, 1170, 1136, 752, 528 (cm^{-1}); $[\alpha]_D^{23} = -105$ (*c* 0.59, $CHCl_3$); mp 146–148 °C; ^1H NMR (500 MHz) 4.69–4.66 (m, 1H), 4.24–4.21 (m, 1H, CH–N), 3.48 (AB, 2H, CH_2SO_2), 3.51–3.48 (m, 1H), 2.06–1.76 (m, 7H), 1.66–1.35 (m, 8H) 1.24 (s, 3H, CH_3), 1.00 (s, 3H, CH_3); ^{13}C NMR (125 MHz) 160.15, 158.11, 81.94, 65.77, 53.06, 50.35, 48.89, 47.88, 45.37, 44.64, 39.48, 36.08, 33.34, 31.88, 26.25, 23.21, 21.17, 19.94.

4.1.6. 3a,4,5,6,7,7a-Hexahydro-1,2-benzisoxazole-3-carboxylic acid (1′*R*)-8′-phenylmenthyl ester 8b. Yield: 60%; HRMS-ESI: calcd for $C_{24}H_{34}O_3N$ $(M+H)^+$ 384.25387; found, 384.25562; LSIMS (+) NBA 8 kV (%) 384 $(M+H)^+$ (14), 215 (31), 1170 (31), 19 (72), 105 (100), 91 (29); IR (film) 2929, 2866, 1731, 1710, 1569, 1495, 1446, 1390, 1317, 1270, 1220, 1127, 1007, 909, 763, 701; ^1H NMR (500 MHz) 7.33–7.06 (m, 5H), 5.10–4.97 (m, 1H), 4.41–4.30 (m, 1H), 2.26–2.17 (m, 1H), 1.93–1.45 (m, 13H), 1.34 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.20–0.96 (m, 3H), 0.89 (s, 3H, CH_3); ^{13}C NMR (125 MHz) 160.06, 158.86, 152.18, 128.60, 126.02, 125.57, 83.08, 76.12, 50.83, 42.93, 42.06, 40.21, 34.98, 31.84, 29.25, 27.01, 25.83, 25.16, 24.98, 22.30, 21.87, 20.25.

4.1.7. 3a,4,5,6,7,7a-Hexahydro-1,2-benzisoxazole-3-carboxylic acid *N*,*N*-dicyclohexyl-10-sulfamoyl-(2*R*)-isoborneol ester 8c. Yield: 43%; HRMS-ESI: calcd for $C_{30}H_{49}O_5N_2S$ $(M+H)^+$ 549.33622; found, 549.33779; LSIMS (+) NBA 8 kV (%) 549 $(M+H)^+$ (18), 380 (74), 246 (14), 228 (26), 180 (43), 135 (100), 83 (47); IR (film) 3424, 2934, 2854, 1718, 1449, 1394, 1323, 1258, 1222, 1165, 1143, 1079, 1048, 981, 892, 774, 576; ^1H NMR (500 MHz) 5.18–5.06 (m, 1H), 4.54–4.42 (m, 1H), 3.42 (d, $J = 13$, 0.55H), 3.41 (d, $J = 13$, 0.45H), 3.30–3.10 (m, 3H), 2.63 (d, $J = 13$, 0.45H), 2.62 (d, $J = 13$, 0.55H), 2.22–1.54 (m, 28H), 1.42–1.08 (m, 7H), 1.04 (s, 3H, CH_3), 0.89 (s, 3H, CH_3); ^{13}C NMR (125 MHz) 159.80, 158.44, 82.29, 79.61, 57.38, 53.37, 49.35, 49.17, 44.55, 43,67, 39.39, 32.50, 30.25, 27.06, 26.46, 26.26, 25.74, 25.27, 24.82, 21.49, 20.45, 19.72.

4.1.8. *N*-(3a,4,5,6,7,7a-Hexahydro-1,2-benzisoxazole-3-carbonyl)-7,7-dimethylnorbornane-(1*S*,2*R*)-oxazolidinone 8d. Yield: 52%; HRMS-ESI: calcd for $C_{18}H_{24}O_4N_2$ $(M+Na)^+$ 355.1634; found, 355.1640; IR (film) 3459, 3002, 2944, 2880, 1789, 1659, 1575, 1455, 1366, 1303, 1226, 1175, 1078, 1051, 1012, 883, 772, 752, 528; ^1H NMR (500 MHz) 4.74–4.70 (m, 0.62H), 4.67–4.64 (m, 0.38H), 4.40–4.37 (m, 2H), 3.47 (q, $J = 7$, 0.62H), 3.31 (q, $J = 7$, 0.38H), 2.81–2.74 (m, 1H), 2.37–2.28 (m, 2H), 2.12–2.02 (m, 2H), 1.92–1.85 (m, 3H), 1.75–1.72 (m, 1H), 1.62–1.48 (m, 2H), 1.42–1.30 (m, 3H), 1.22 (s, 1.86H), 1.20 (s, 1.14H), 1.08 (s, 3H); ^{13}C NMR (125 MHz) 162.27, 157.87, 174.26, 85.62, 81.42, 72.75, 48.32, 46.33, 45.60, 42.55, 34.67, 25.92, 24.62, 23.37, 21.56, 21.20, 19.99, 19.15.

4.1.9. 4,5,6,7,8,8a-Hexahydro-3a*H*-cyclohepta[*d*]isoxazole-3-carboxylic acid (2′*R*)-*N*-bornane-10′,2′-sultam imide 9a. Yield: 52%; HRMS-ESI: calcd for $C_{19}H_{29}O_4N_2S$ $(M+H^+)$ 381.18480; found, 381.18345; LSIMS (+) NBA 8 kV (%) 381 $(M+H)^+$ (70), 166 (100), 149 (35), 135 (44), 107 (24), 93 (31); IR (KBr) 2933, 1668, 1455, 1391, 1344, 1279, 1169, 1138, 1062, 938, 544; ^1H NMR (500 MHz) 4.92–4.85 (m, 1H), 4.23–4.10 (m, 1H), 3.86–3.75 (m, 1H), 3.47 (AB, 2H, CH_2SO_2), 2.08–1.88 (m, 8H), 1.84–1.28 (m, 9H), 1.230 (s, 3H, CH_3), 0.99 (s, 3H, CH_3); ^{13}C NMR (125 MHz) 161.34, 155.66, 87.11, 65.72, 53.00, 50.56, 48.90, 47.88, 45.41, 39.598, 33.33, 30.97, 28.13, 27.36, 26.36, 26.22, 23.81, 21.54, 19.94.

4.1.10. 4,5,6,7,8,8a-Hexahydro-3a*H*-cyclohepta[*d*]isoxazole-3-carboxylic acid (1′*R*)-8′-phenylmenthyl ester 9b. Yield: 48%; HRMS-ESI: calcd for $C_{25}H_{35}O_3N$ $(M+Na)^+$ 420.25146; found, 420.25102; LSIMS (+) NBA 8 kV (%) 420 $(M+Na)^+$ (100), 398 $(M+H)^+$ (7), 215 (20), 170 (31), 119 (18), 105 (40); IR (film) 2926, 2855, 1730, 1710, 1582, 1495, 1455, 1390, 1333, 1266, 1232, 1127, 984, 939, 764, 701; ^1H NMR (500 MHz) 7.31–7.10 (m, 5H), 5.06–4.96 (m, 1H), 4.76–4.66 (m, 1H), 2.68–2.57 (m, 1H), 2.00–1.35 (m, 13H), 1.32 (s, 3H, CH_3), 1.30–1.24 (m, 2H), 1.22 (s, 3H, CH_3), 1.20–1.01 (m, 3H), 0.89 (s, 3H, CH_3); ^{13}C NMR (125 MHz) 159.54, 154.56, 151.70, 128.07, 125.46, 124.96, 87.44, 75.53, 50.28, 49.12, 41.37, 39.63, 34.42, 31.30, 30.97, 30.31, 28.68, 28.08, 26.68, 26.44, 24.31, 23.72, 21.75.

4.1.11. 4,5,6,7,8,8a-Hexahydro-3a*H*-cyclohepta[*d*]isoxazole-3-carboxylic acid *N*,*N*-dicyclohexyl-10-sulfamoyl-(2*R*)-isoborneol ester 9c. Yield: 40%; HRMS-ESI: calcd for $C_{31}H_{51}O_5N_2S$ $(M+H)^+$ 563.35187; found, 563.35018; LSIMS (+) NBA 8 kV (%) 549 $(M+H)^+$ (18), 380 (77), 246 (16), 228 (28), 180 (53), 135 (100), 83 (46); IR (KBr) 3419, 2932, 2854, 1717, 1454, 1392, 1323, 1260, 1222, 1165, 1143, 1100, 1048, 981, 884, 774, 643, 576, 524; ^{1}H NMR (500 MHz) 5.16–5.06 (m, 1H), 4.90–4.79 (m, 1H), 3.66–3.49 (m, 1H), 3.42 (d, $J = 13$, 0.43H), 3.40 (d, $J = 13$, 0.57H), 3.30–3.16 (m, 2H), 2.63 (d, $J = 13$, 0.57H), 2.61 (d, $J = 13$, 0.43H), 2.10–1.56 (m, 30H), 1.42–1.06 (m, 7H), 1.04 (s, 3H, CH_3), 0.89 (s, 3H, CH_3); ^{13}C NMR (125 MHz) 159.76, 154.47, 87.32, 79.59, 57.44, 53.41, 50.61, 49.67, 49.56, 49.16, 44.55, 39.38, 32.56, 31.19, 30.37, 28.37, 26.95, 26.43, 26.31, 25.26, 23.94, 20.43, 20.04.

4.1.12. *N*-(4,5,6,7,8,8a-Hexahydro-3a*H*-cyclohepta[*d*]isoxazole-3-carbonyl)-7,7-dimethylnorbornane-(1*S*,2*R*)-oxazolidinone 9d. Yield: 49%; HRMS-ESI: calcd for $C_{19}H_{26}O_4N_2$ $(M+H)^+$ 369.1790; found, 369.1800; IR (KBr) 3436, 3001, 2927, 2855, 1790, 1692, 1455, 1366, 1322, 1302, 1230, 1202, 1977, 1951, 1007, 939, 782, 761; ^{1}H NMR (500 MHz) 4.96–4.89 (m, 1H), 4.39–4.36 (m, 1H), 3.83–3.72 (m, 1H), 2.74 (dt, $J_1 = 5$, $J_2 = 12.5$, 1H), 2.35 (dq, $J_1 = 4$, $J_2 = 14$, 1H), 2.10–2.02 (m, 1H), 2.00–1.87 (m, 3H), 1.86–1.76 (m, 4H), 1.75–1.60 (m, 2H), 1.52–1.45 (m, 1H), 1.38–1.27 (m, 4H), 1.22 (s, 2.25H), 1.19 (s, 0.75H), 1.07 (s, 3H); ^{13}C NMR (125 MHz) 162.33, 155.01, 154.18, 86.75, 85.55, 72.76, 51.39, 48.28, 42.54, 34.65, 31.02, 30.77, 28.05, 26.47, 25.91, 24.44, 24.26, 21.62, 19.20.

4.1.13. 3a,4,5,6,7,8,9,9a-Octahydrocycloocta[*d*]isoxazole-3-carboxylic acid (2′*R*)-*N*-bornane-10′,2′-sultam imide 10a. Yield: 61%; HRMS-ESI: calcd for $C_{20}H_{31}O_4N_2S$ $(M+H^+)$ 395.20045; found, 395.20057; LSIMS (+) NBA 8 kV (%) 417 $(M+H)^+$ (16), 395 (M^+) (100), 180 (50), 136 (76), 107 (29), 91 (31); IR (KBr) 3444, 2933, 2856, 1663, 1592, 1467, 1392, 1342, 1236, 1170, 1138, 1063, 936, 886, 760, 617, 544, 480; ^{1}H NMR (500 MHz) 4.68–4.49 (m, 1H), 4.22–4.00 (m. 1H), 3.46 (AB, 2H, CH_2SO_2), 3.56–3.25 (m, 1H), 2.16–1.86 (m, 7H), 1.78–1.24 (m, 12H), 1.23 (s, 3H, CH_3), 0.99 (s, 3H, CH_3); ^{13}C NMR (125 MHz) 161.45, 157.29, 87.47, 65.65, 53.08, 51.34, 49.22, 47.90, 45.39, 39.60, 33.31, 29.28, 26.53, 26.26, 25.34, 25.08, 24.73, 23.89, 21.54, 19.93.

4.1.14. 3a,4,5,6,7,8,9,9a-Octahydrocycloocta[*d*]isoxazole-3-carboxylic acid (1′*R*)-8′-phenylmenthyl ester 10b. Yield: 82%; HRMS-ESI: calcd for $C_{26}H_{38}O_3N$ $(M+H)^+$ 412.28515; found, 412.28553; LSIMS (+) NBA 8 kV (%) 412 $(M+H)^+$ (28), 198 (47), 119 (65), 105 (100), 91 (17); IR (film) 2953, 2924, 2856, 1730, 1711, 1585, 1495, 1445, 1388, 1309, 1268, 1224, 1130, 1108, 1033, 963, 933, 764, 701; ^{1}H NMR (500 MHz) 7.31–7.08 (m, 5H), 5.06–4.98 (m, 1H), 4.36–4.28 (m, 1H), 2.21–2.14 (m, 1H), 2.13–1.39 (m, 14H), 1.33 (s, 3H, CH_3), 1.30–1.22 (m, 1H), 1.21 (s, 3H, CH_3), 1.20–0.92 (m, 5H), 0.90 (s, 3H, CH_3); ^{13}C NMR (125 MHz) 159.35, 156.74, 152.07, 128.12, 125.42, 124.95, 87.97, 75.34, 50.37, 47.52, 41.44, 39.50, 34.42, 31.28, 29.50, 29.48, 26.30, 25.53, 25.41, 24.95, 24.89, 24.53, 23.29, 21.75.

4.1.15. 3a,4,5,6,7,8,9,9a-Octahydrocycloocta[*d*]isoxazole-3-carboxylic acid *N*,*N*-dicyclohexyl-10-sulfamoyl-(2*R*)-isoborneol ester 10c. Yield: 65%; HRMS-ESI: calcd for $C_{32}H_{53}O_5N_2S$ $(M+H)^+$ 577.36752; found, 577.36676; LSIMS (+) NBA 8 kV (%) 577 $(M+H)^+$ (25), 380 (88), 246 (16), 228 (32), 180 (65), 135 (100), 83 (40); IR (KBr) 3424, 2932, 2855, 1719, 1454, 1393, 1326, 1225, 1165, 1144, 1109, 1048, 982, 892, 854, 776, 643, 575, 525; ^{1}H NMR (500 MHz) 5.16–5.09 (m, 1H), 4.58–4.43 (m, 1H), 3.44–3.14 (m, 3H), 3.41 (d, $J = 13$, 0.45H), 3.39 (d, $J = 13$, 0.55H), 2.63 (d, $J = 13$, 0.55H), 2.61 (d, $J = 13$, 0.45H), 2.18–1.44 (m, 32H), 1.40–1.06 (m, 7H), 1.04 (s, 3H, CH_3), 0.89 (s, 3H, CH_3); ^{13}C NMR (125 MHz) 159.81, 156.67, 87.75, 79.56, 57.42, 53.40, 49.66, 49.18, 49.07, 44.57, 39.41, 32.61, 30.19, 29.78, 27.07, 26.44, 26.27, 25.55, 25.27, 25.18, 25.07, 24.49, 20.42, 20.03.

4.1.16. *N*-(3a,4,5,6,7,8,9,9a-Octahydrocycloocta[*d*]isoxazole-3-carbonyl)-7,7-dimethylnorbornane-(1*S*,2*R*)-oxazolidinone 10d. Yield: 66%; HRMS-ESI: calcd for $C_{20}H_{28}O_4N_2$ $(M+Na)^+$ 383.1947; found, 383.1957; IR (KBr) 3430, 2965, 2927, 2856, 1789, 1690, 1594, 1467, 1378, 1319, 1301, 1274, 1252, 1172, 1078, 1071, 1050, 1003, 939, 882, 784, 760 690; ^{1}H NMR (500 MHz) 4.74–4.62 (m, 1H), 4.39–4.37 (m, 1H), 3.50 (t, $J = 10$, 0.7H), 3.44 (t, $J = 10$, 0.3H), 2.90–2.70 (m, 1H), 2.33–2.29 (m, 1H), 2.12–2.00 (m, 2H), 1.95–1.85 (m, 4H), 1.83–1.74 (m, 1H), 1.72–1.48 (m, 3H), 1.47–1.24 (m, 7H), 1.23–1.19 (m,3H), 1.07 (s, 3H); ^{13}C NMR (125 MHz) 162.62, 156.47, 154.30, 86.95, 85.65, 72.70, 51.76, 50.28, 48.27, 42.53, 34.63, 29.21, 27.30, 26.63, 25.89, 25.30, 24.46, 23.62, 21.57, 19.22.

4.2. General procedure for preparation of alcohols

To the pre-cooled solution of cycloadducts **7a**, **7d**, **8a**, **8d**, **9a**, **9d**, **10a**, **10d** or methyl esters **15**, **16**, **17**, **19** (1.0 mmol) in CH_3OH (5 ml), 1.1 mmol of $NaBH_4$ was added. The progress of the reaction was monitored by TLC. When the reaction was completed, the solvent was evaporated and the residue purified on silica gel (hexane/AcOEt).

4.2.1. 4,5,6,6a-Tetrahydro-3a*H*-cyclopenta[*d*]isoxazol-3-ylmethanol 11. HRMS-ESI: calcd for $C_7H_{12}O_2N$ $(M+H)^+$ 142.08680; found, 142.0856; ^{1}H NMR (500 MHz) 5.15–5.07 (m, 1H), 4.48–4.30 (m, 2H), 3.18 (t, $J = 8$, 1H), 2.42 (m, 1H), 2.04–1.40 (m, 6H); ^{13}C NMR (125 MHz) 159.48, 87.23, 57.61, 52.44, 35.68, 30.44, 23.37.

4.2.2. 3a,4,5,6,7,7a-Hexahydro-1,2-benzisoxazol-3-ylmethanol 12. HRMS-ESI: calcd for $C_8H_{13}O_2N$ $(M+H)^+$ 156.1024; found, 156.1017; ^{1}H NMR (200 MHz) 4.44–5.07 (m, 2H), 3.16 (s, 1H), 3.01 (q, 1H), 1.98–1.60 (m, 3H), 1.58–1.00 (m, 6H); ^{13}C NMR (50 MHz) 165.08, 79.91, 57.54, 44.90, 25.64, 24.88, 22.09, 20.32.

4.2.3. 4,5,6,7,8,8a-Hexahydro-3a*H*-cyclohepta[*d*]isoxazol-3-ylmethanol 13. HRMS-ESI: calcd for $C_9H_{15}O_2N$

$(M+H)^+$ 170.1181; found, 170.1188; ^{1}H NMR (200 MHz) 4.77–4.64 (m, 1H), 4.40–4.17 (m, 2H), 3.15–3.40 (m, 2H), 1.88–1.18 (m, 10H); ^{13}C NMR (50 MHz) 161.26, 84.69, 56.92, 51.33, 31.27, 30.68, 28.18, 26.80, 24.21.

4.2.4. 3a,4,5,6,7,8,9,9a-Octahydrocycloocta[*d*]isoxazol-3-yl-methanol 14. HRMS-ESI: calcd for $C_{10}H_{17}O_2N$ $(M+H)^+$ 184.1338; found, 170.1341; ^{1}H NMR (200 MHz) 4.25–4.35 (m, 2H), 3.19–3.08 (m, 1H), 2.75 (t, $J = 5.7$, 1H), 1.98–1.87 (m, 2H), 1.78–1.28 (m, 11H); ^{13}C NMR (50 MHz) 162.81, 85.35, 57.25, 50.07, 29.77, 26.01, 25.98, 25.37, 25.07, 23.36.

4.3. General procedure for transesterification of the cycloadducts

In a 2 ml Teflon ampoule were placed the cycloadduct (**7**–**10**) and 2 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene. The ampoule was filled with methanol, closed and placed in a high-pressure vessel, and the pressure was slowly increased to 10 kbar at 20 °C. After stabilization of pressure, the reaction mixture was kept under these conditions for 20 h. After decompression, the solvent was evaporated and the residue was chromatographed on a silica gel column using hexane/EtOAc.

4.3.1. Methyl 4,5,6,6a-tetrahydro-3a*H*-cyclopenta[*d*]isoxazole-3-carboxylate 15. HRMS-ESI: calcd for $C_8H_{11}O_3N$ $(M+Na)^+$ 192.0637; found, 192.0640; IR (film) 2959, 2873, 1741, 1719, 1582, 1442, 1372, 1262, 1202, 1122, 1079, 952, 939, 803, 771, 760; ^{1}H NMR (500 MHz) 5.29–5.26 (m, 1H), 3.88 (s, 3H), 2.20–2.16 (m, 1H), 2.02–2.00 (m, 1H), 1.84–1.70 (m, 4H), 1.47–1.37 (m, 1H); ^{13}C NMR (125 MHz) 161.32, 153.22, 90.43, 52.63, 50.88, 35.60, 31.58, 23.13.

4.3.2. Methyl 3a,4,5,6,7,7a-hexahydro-1,2-benzisoxazole-3-carboxylate 16. HRMS-ESI: calcd for $C_9H_{13}O_3N$ $(M+Na)^+$ 206.0793; found, 206.0787; IR (film) 2940, 2863, 1727, 1570, 1443, 1370, 1272, 1227, 1125, 1010, 929, 908, 790, 775; ^{1}H NMR (500 MHz) 4.60–4.56 (m, 1H), 3.89 (s, 3H), 3.19 (q, $J = 8$, 1H), 2.20–2.12 (m, 1H), 2.24–1.94 (m, 1H), 1.82–1.70 (m, 1H), 1.66–1.57 (m, 2H), 1.54–1.42 (m, 1H), 1.34–1.18 (m, 2H); ^{13}C NMR (125 MHz) 161.35, 157.62, 82.72, 52.63, 43.40, 25.33, 24.67, 21.30, 19.68.

4.3.3. Methyl 4,5,6,7,8,8a-hexahydro-3a*H*-cyclohepta[*d*]-isoxazole-3-carboxylate 17. HRMS-ESI: calcd for $C_{10}H_{15}O_3N$ $(M+Na)^+$ 220.0950; found, 220.0949; IR (KBr) 3418, 2944, 2852, 1723, 1578, 1443, 1357, 1278, 1238, 1196, 1123, 975, 961, 937, 861, 801, 770, 722; ^{1}H NMR (500 MHz) 4.96–4.90 (m, 1H), 3.87 (s, 3H), 3.60–3.55 (m, 1H), 2.02–1.68 (m, 5H), 1.64–1.35 (m, 5H); ^{13}C NMR (125 MHz) 161.30, 153.85, 87.60, 52.56, 50.02, 30.99, 30.26, 28.11, 26.89, 23.80.

4.3.4. Methyl 3a,4,5,6,7,8,9,9a-octahydrocycloocta[*d*]-isoxazole-3-carboxylate 18. HRMS-ESI: calcd for $C_{11}H_{17}O_3N$ $(M+Na)^+$ 234.1106; found, 234.1100; IR (film) 3409, 2940, 2861, 2849, 1717, 1580, 1465, 1446, 1441, 1369, 1310, 1269, 1222, 1210, 1197, 1130, 1107, 1035, 958, 942, 933, 895, 832, 793, 779; ^{1}H NMR (500 MHz) 4.59–4.56 (m, 1H), 3.87 (s, 3H), 3.30 (t, $J = 10$, 1H), 2.08–1.94 (m, 2H), 1.79–1.60 (m, 6H), 1.51–1.45 (m, 1H), 1.39–1.20 (m, 3H); ^{13}C NMR (125 MHz) 161.30, 156.09, 88.12, 52.59, 48.89, 29.75, 25.51, 25.41, 25.08, 25.06, 24.56.

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