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Stereoselective azide cycloaddition to chiral cyclopentanone enamines

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Abstract: The enamine derived from cyclopentanone and (2*R*,5*R*)-2,5-bis(methoxymethyl)pyrrolidine added ethyl *N*-mesylazidoformimidate [$N_3C(OEt)NMs$] and ethyl azidoformate (N_3CO_2Et) with high asymmetric induction (>95%), while the corresponding cyclohexanone enamine gave ring contraction products. With the same azides the cyclopentanone enamine, prepared from (*S*)-2-(methoxymethyl)pyrrolidine gave *N*-substituted α-amino cyclopentanones in moderate enantiomeric excess. © 1997 Elsevier Science Ltd

Starting from proline-derived cyclohexanone enamines we observed chiral discrimination in reactions with (ethoxycarbonyl)nitrene (NCO_2Et), generated from $NsONHCO_2Et$ in the presence of Et_3N. The best ee (77%) for the *N*-substituted α-amino ketone was observed with enamine bearing (*S*)-2-(methoxymethyl)pyrrolidine as the chiral auxiliary. The configuration of the major enantiomer was *R*. The same product was obtained in a better yield but in a lower ee (35%) using ethyl azidoformate (N_3CO_2Et). The configuration of the major isomer in this case was *S*.[1]

Enamines from pyrrolidines with C_2 symmetry are known to give high asymmetric induction in alkylation reactions.[2] We tested one of these enamines obtained from cyclohexanone and (2*R*,5*R*)-2,5-dimethylpyrrolidine in reactions with different aminating agents[3] without success. Then we turned our attention to ethyl *N*-mesylazidoformimidate [$N_3C(OEt)NMs$]. This versatile azide reacts with alkenes of different nucleophilicity.[4] Recently we used the same azide to successfully aziridinate chiral homoallylic ketals.[5]

In this paper we report on a comparison of the results obtained on reacting $N_3C(OEt)NMs$ or N_3CO_2Et with cyclohexanone and cyclopentanone enamines derived from (*S*)-2-(methoxymethyl)- and (2*R*,5*R*)-2,5-bis(methoxymethyl)pyrrolidine **1**, **6**, **11** and **14**. We started our study testing the cyclohexanone enamines **1** and **6** in reactions with $N_3C(OEt)NMs$. The reactions were performed in CH_2Cl_2 at room temperature. Very fast nitrogen evolution has been observed and the first cycloadduct, quite likely a triazoline, could not be detected. The crude reaction mixtures were chromatographed and the products were characterised by spectral data. The main product has been recognised as the product of ring contraction **2** or **7** and was transformed into cyclopentanecarboxylic acid by hydrolysis.[6]

The compound **9** from a similar fast rearrangement was the main product isolated in the reaction performed with N_3CO_2Et on the enamine **6**. On the contrary, we isolated the *N*-substituted α-aminocyclohexanone **4** in the cycloaddition reaction of the same azide, followed by photolysis.[1] In both cases variable amounts of by-products **3**, **5**, **8** and **10** have been isolated, coming from a nucleophilic attack to the azide C=N or C=O bond by the pyrrolidine nitrogen atom.[7] We like to stress that, although the undesired ring contraction products **7** and **9** were formed, this is the first time an enamine derived from a C_2 symmetric amine reacts with azides.[8]

With the aim to obtain *N*-substituted α-amino ketones, we focused our attention on cyclopentanone enamines **11** and **14**, in the hope of minimising the ring contraction.

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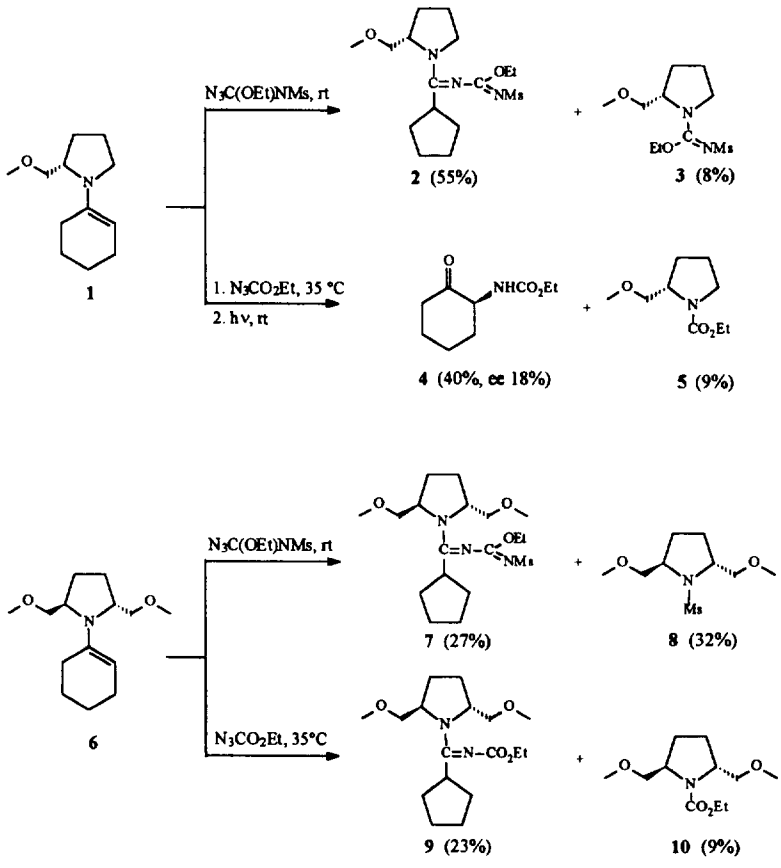
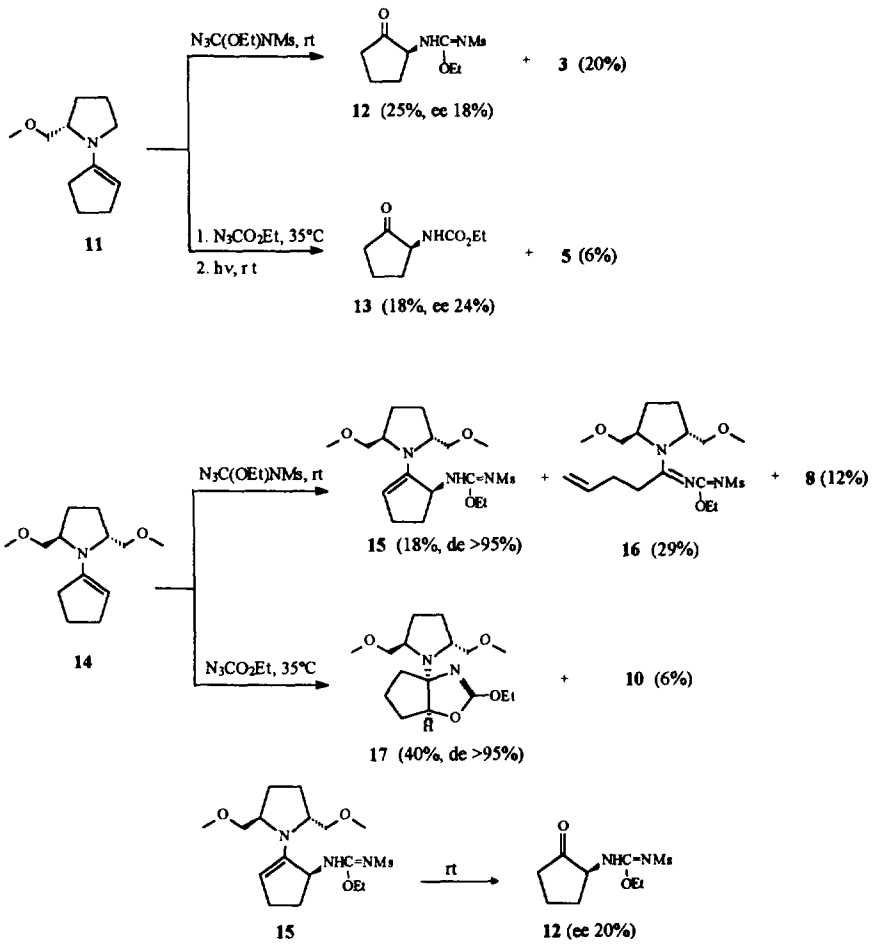


Actually the monosubstituted enamine **11** reacted with both azides giving the *N*-substituted α-aminocyclopentanones **12** and **13** with 18 and 24% ee, respectively. Side products **3** and **5** were also obtained.

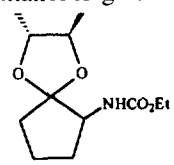
The enamine **14** carrying the C_2 symmetric ring gives two interesting new products. The first one **15**, obtained with a 95% de (as determined by ^{13}C NMR and HPLC), is the product of a formal allylic amination[9] which slowly hydrolyses to the *N*-substituted α-aminocyclopentanone **12**.

Unfortunately during the spontaneous hydrolysis step a dramatic drop of enantiomeric excess was observed and only a 20% ee was obtained. An unprecedented ring opening product[10] **16** was also obtained in addition to **8**.

The cycloaddition of ethyl azidoformate to the same enamine proceeded once again in a high diastereoselective[11] manner (≥95% as desumed by ^{13}C NMR and HPLC) giving the oxazoline **17**, whose regiochemistry has been confirmed by ^{1}H, ^{13}C NMR and HETCOR analyses. Oxazolines have rarely been reported in cycloaddition reactions of N_3CO_2Et but have never been observed in reactions with enamines.[12] However in our experience we observed oxazolines in reactions between silylated compounds and NCO_2Et.[13]



The configuration of the major enantiomer of α-(ethoxycarbonylamino)cyclopentanone ($[\alpha]_D$ +36) has been established by elaboration [ethoxycarbonylation, oxidation and ketalisation by (2*R*,3*R*)-butan-2,3-diol] of (1*S*,2*S*)-*trans*-2-aminocyclopentanol to give the ketals **18**.[14,1]



18

The configuration of the oxazoline **17** has been assumed to be the one derived from the preferential cycloaddition mode previously reported.[11]

Experimental

GC analyses were performed on a HP 5890 Series II gas chromatograph with a capillary column (methyl silicone, 12.5 m x 0.2 mm). GC-MS were done on a HP G1800A GCD System with a capillary column (phenyl methyl silicone, 30 m × 0.25 mm). ^{1}H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$ on a Varian XL-300 spectrometer, with $CHCl_3$ as an internal standard. IR spectra in CCl_4 were done with a Perkin–Elmer 1600 Series FTIR spectrometer. The separations by HPLC were done with a Varian 9001 instrument equipped with a Varian RI-4 differential refractometer. Solvents were HPLC-grade. Optical rotations were recorded at the Sodium D line with a Perkin–Elmer 457 polarimeter

(1-cm cell). N_3CO_2Et,[15] $N_3C(OEt)NMs$[16] (*CAUTION: like all the azides, they might explode and must be manipulated carefully. Their vapours are also toxic, as well as those of* HN_3, *involved in the preparation of the imidoyl azide*) and **1**[17] were prepared according to literature methods. (2*R*,5*R*)-2,5-Bis(methoxymethyl)pyrrolidine is a commercial product (Janssen).

Synthesis of enamines ***6***, ***11*** *and* ***14***

A solution of cyclohexanone or cyclopentanone (5 mmol), (2*R*,5*R*)-2,5-bis(methoxymethyl)pyrrolidine or (*S*)-2-(methoxymethyl)pyrrolidine (5 mmol), benzene and TsOH (5 mg) was refluxed under azeotropic conditions. After 24 h [5 h with (*S*)-2-(methoxymethyl)pyrrolidine], the reaction was completed and the mixture was concentrated *in vacuo*.

6: IR 1637 cm^{-1}; ^1H NMR δ 1.35–2.40 (*m*, 12 H, CH_2), 3.35 (*s*, 6 H, CH_3), 3.20–3.70 (*m*, 6 H, CH_2O, HCN), 4.45 (*m*, 1 H, HC=C).

11: IR 1621 cm^{-1}; ^1H NMR δ 1.30–2.15 (*m*, 10 H, CH_2), 3.15–3.30 (*m*, 1 H, CHN), 3.35 (*s*, 3 H, CH_3), 3.45–3.80 (*m*, 4 H, OCH_2, NCH_2), 4.18 (*m*, 1 H, HC=C).

14: IR 1621 cm^{-1}; ^1H NMR δ 1.45–2.30 (*m*, 10 H, CH_2), 3.38 (*s*, 6 H, CH_3), 3.15–3.70 (*m*, 6 H, CH_2O, HCN), 4.35 (*m*, 1 H, HC=C).

Reaction of ***1***, ***6***, ***11*** *and* ***14*** *with* $N_3C(OEt)NMs$

To a stirred solution of the enamine (3 mmol) in 6 ml of anhydrous CH_2Cl_2 at room temperature, $N_3C(OEt)NMs$ (3 mmol) was added slowly. After 30 min of stirring, the azide band is disappeared in the IR spectrum and the crude mixture was concentrated *in vacuo*. The products coming from **1** and **6** were separated by flash chromatography on silica gel (ethyl acetate), while the products from **11** and **14** were separated by HPLC (hexane/ethyl acetate, 4:6 and 2.5:7.5, respectively).

2 (*E*,*Z* mixture): IR 1620, 1605 cm^{-1}; ^1H NMR δ 1.25 (*t*, 3 H, CH_3), 1.40–2.10 (*m*, 12 H, CH_2), 2.80–2.90 (*m*, 1 H, HC–C=N), 2.95 (*s*, 3 H, CH_3SO_2), 3.20–3.60 (*m*, 8 H, CH_2OCH_3, CH_2N, CHN), 4.15 (*q*, 2 H, OCH_2CH_3); ^{13}C NMR δ 13.99 (CH_3), 21.81, 23.56, 25.35, 25.41, 25.79, 27.07, 27.70, 29.02, 29.87, 30.85, 31.72 (CH_2), 40.22, 40.38 (CH_3SO_2), 43.42, 45.18 (HC–C=N), 48.37, 48.50 (CH_2N), 58.94, 59.17, 59.28, 59.49 (OCH_3, CHN), 64.12 (OCH_2CH_3), 71.52, 73.49 (CH_2O), 160.06 ($CNSO_2$), 167.89, 168.50 (NC); MS *m/z* 359 (M^+, 0.6), 314 (19), 280 (13), 236 (23), 124 (81), 122 (38), 114 (51), 98 (16), 97 (19), 96 (100), 82 (11), 79 (28), 71 (15), 70 (71), 69 (52), 68 (17), 67 (21), 56 (11), 55 (12), 45 (34), 42 (13), 41 (44). HRMS Calcd for $C_{16}H_{29}N_3O_4S$: 359.1879. Found: 359.1871.

3: IR 1592 cm^{-1}; ^1H NMR δ 1.25 (*t*, 3 H, CH_3), 1.75–1.95 (*m*, 4 H, CH_2), 2.98 (*s*, 3 H, CH_3SO_2), 3.20–3.80 (*m*, 8 H, CH_2OCH_3, CHN, CH_2N), 4.15 (*q*, 2 H, OCH_2CH_3); ^{13}C NMR δ 14.37 (CH_3), 23.52, 27.85 (CH_2), 44.31 (CH_3SO_2), 49.78 (CH_2N), 58.89, 59.09 (CHN, OCH_3), 65.55 (OCH_2CH_3), 72.70 (CH_2O), 154.28 (CN); MS *m/z* 264 (M^+, 1.4), 219 (38), 148 (10), 122 (35), 98 (31), 79 (16), 70 (100), 69 (10), 68 (12), 45 (19), 42 (10), 41 (19). HRMS Calcd for $C_{10}H_{20}N_2O_4S$: 264.1144. Found: 264.1136.

7: IR 1634, 1619 cm^{-1}; ^1H NMR δ 1.23 (*t*, 3 H, OCH_2CH_3), 1.40–2.22 (*m*, 12 H, CH_2), 2.96 (*s*, 3 H, CH_3SO_2), 3.15 (*quintuplet*, 1 H, HC–C=N), 3.20–3.50 (*m*, 10 H, CH_2OCH_3), 4.00–4.10 (*m*, 2 H, CHN), 4.20 (*q*, 2 H, OCH_2CH_3); ^{13}C NMR δ 14.15 (CH_3), 25.55, 25.75, 25.88, 26.94, 29.06, 30.03 (CH_2), 40.70 (CH_3SO_2), 44.68 (HC–C=N), 58.99, 59.04, 59.27 (CHN, OCH_3), 64.29 (OCH_2CH_3), 71.32, 74.19 (CH_2O), 159.73 ($CNSO_2$), 167.22 (CN); MS *m/z* 403 (M^+, 0.3), 358 (37), 280 (19), 158 (14), 124 (88), 122 (37), 114 (41), 97 (13), 96 (100), 82 (19), 79 (27), 71 (40), 69 (48), 68 (13), 67 (17), 56 (12), 55 (21), 54 (10), 45 (75), 41 (40). HRMS Calcd for $C_{18}H_{33}N_3O_5S$: 403.2141. Found: 403.2150.

8: IR 1342, 1216 cm^{-1}; ^1H NMR δ 1.85–2.20 (*m*, 4 H, CH_2), 2.91 (*s*, 3 H, CH_3SO_2), 3.50–3.60 (*m*, 10 H, CH_2OCH_3), 3.80–3.85 (*m*, 2 H, CHN); ^{13}C NMR δ 27.73 (CH_2), 39.40 (CH_3SO_2), 58.83, 58.97 (CHN, OCH_3), 73.74 (CH_2O); MS *m/z* 237 (M^+, 0.05), 192 (100), 114 (11), 113 (65), 82 (12), 71 (28), 68 (34), 67 (10), 45 (23), 41 (10).

12: IR 3306, 1740, 1620 cm^{-1}; ^1H NMR δ 1.25 (*t*, 3 H, OCH_2CH_3), 1.65–2.50 (*m*, 6 H, CH_2),

2.96 (*s*, 3 H, CH_3SO_2), 3.80–4.05 (*m*, 1 H, CH), 4.25 (*q*, 2 H, OCH_2CH_3), 7.52 (*br*, 1 H, NH); ^{13}C NMR δ 13.87 (OCH_2CH_3), 17.72, 29.67 (CH_2), 34.48 (CH_2CO), 41.99 (CH_3SO_2), 58.99 (CNH), 64.80 (OCH_2), 158.12 (CN), 212.65 (CO); MS *m/z* 248 (M^+, 3), 192 (15), 169 (27), 122 (19), 113 (56), 98 (15), 85 (100), 79 (20), 56 (11), 55 (16), 43 (20), 42 (10). HRMS Calcd for $C_9H_{16}N_2O_4S$: 248.0831. Found: 248.0833.

15: $[\alpha]_D$ −32.6 (CH_2Cl_2); IR 3243, 1617 cm^{-1}; ^1H NMR δ 1.35 (*t*, 3 H, OCH_2CH_3), 1.60–2.50 (*m*, 8 H, CH_2), 2.98 (*s*, 3 H, CH_3SO_2), 3.10–3.55 (*m*, 11 H, CH_2OCH_3, HC–NH), 4.05–4.20 (*m*, 2 H, CHN), 4.32 (*q*, 2 H, OCH_2CH_3), 5.36 (*m*, 1 H, HC=C), 9.15 (*br*, 1 H, NH); ^{13}C NMR δ 13.95 (CH_3), 23.32 (CH_2), 27.12 (pyrrolidine ring CH_2), 28.77 (H_2C–C=C), 42.30 (CH_3SO_2), 58.88, 58.99 (CHN, OCH_3), 62.99 (HC–NH), 64.95 (OCH_2CH_3), 74.91 (CH_2O), 109.70 (HC=CN), 137.05 (HC=CN), 156.29 (CN); MS *m/z* 389 (M^+, 9), 345 (19), 344 (100), 298 (25), 219 (12), 179 (11), 178 (83), 146 (21), 122 (12), 80 (13), 79 (16), 71 (31), 45 (23), 41 (14). HRMS Calcd for $C_{17}H_{31}N_3O_5S$: 389.1984. Found: 389.1991.

16: IR 1604, 1589 cm^{-1}; ^1H NMR δ 1.25 (*t*, 3 H, OCH_2CH_3), 1.85–2.40 (*m*, 6 H, CH_2), 2.65–2.80 (*m*, 2 H, H_2C–CN), 2.95 (*s*, 3 H, CH_3SO_2), 3.20–3.70 (*m*, 10 H, CH_2OCH_3), 3.95–4.10 (*m*, 2 H, CHN), 4.25 (*q*, 2 H, OCH_2CH_3), 4.95–5.12 (*m*, 2 H, HC=CH_2), 5.65–5.85 (*m*, 1 H, HC=CH_2); ^{13}C NMR δ 13.98 (CH_3), 25.65, 27.08 (ring CH_2), 31.25, 31.73 (CH_2), 40.64 (CH_3SO_2), 58.87, 58.93, 59.03, 59.18 (CHN, OCH_3), 64.75 (OCH_2CH_3), 71.14, 74.24 (CH_2O), 116.26 (HC=CH_2), 136.14 (HC=CH_2), 162.96 (C=NSO_2), 165.02 (N=C); MS *m/z* 389 (M^+, 0.3), 344 (50), 266 (28), 236 (10), 122 (52), 114 (62), 110 (64), 82 (100), 80 (11), 79 (28), 71 (38), 55 (34), 54 (10), 45 (46), 41 (23). HRMS Calcd for $C_{17}H_{31}N_3O_5S$: 389.1984. Found: 389.1970.

*Reaction of **6**, **11** and **14** with N_3CO_2Et*

A solution of the substrate (3 mmol) and N_3CO_2Et (3 mmol), in 6 ml of anhydrous CH_2Cl_2, was refluxed in an atmosphere of nitrogen. When the azide band is disappeared in the IR spectrum (1.5 h), the reaction performed on the enamine **11** was photholysed in a quarz vessel under an atmosphere of nitrogen at room temperature (4 h), using a medium pressure Hanovia PCR lamp (100 W). The products **13** and **5** were purified by flash chromatography on silica gel (hexane/ethyl acetate, 6:4). The crude mixtures obtained from the enamines **6** and **14** were directly concentrated *in vacuo* and separated by HPLC (hexane/ethyl acetate, 1:1) or by flash chromatography on silica gel (hexane/ethyl acetate, 6:4) respectively.

9: IR 1681, 1604 cm^{-1}; ^1H NMR δ 1.25 (*t*, 3 H, OCH_2CH_3), 1.45–2.20 (*m*, 12 H, CH_2), 3.00 (*quintuplet*, 1 H, CH), 3.28, 3.30 (2 *s*, 6 H, OCH_3), 3.10–3.55 (*m*, 4 H, CH_2O), 4.00–4.15 (*m*, 2 H, CHN), 4.22 (*q*, 2 H, OCH_2CH_3); ^{13}C NMR δ 14.54 (CH_3), 25.50, 26.16, 26.22, 27.00, 28.79, 31.77 (CH_2), 43.96 (CH), 57.88, 58.36, 59.10, 59.20 (CHN, OCH_3), 61.11 (OCH_2CH_3), 71.55, 74.61 (CH_2O), 160.62 (CN), 165.31 (CO); MS *m/z* 326 (M^+, 5), 282 (18), 281 (100), 192 (10), 160 (10), 71 (26), 45 (23), 41 (17). HRMS Calcd for $C_{17}H_{30}N_2O_4$: 329.2205. Found: 329.2205.

10: IR 1698 cm^{-1}; ^1H NMR δ 1.20 (*t*, 3 H, OCH_2CH_3), 1.85–2.10 (*m*, 4 H, CH_2), 3.29 (*s*, 6 H, OCH_3), 3.10–3.60 (*m*, 4 H, CH_2O), 3.80–4.05 (*m*, 2 H, CHN), 4.11 (*q*, 2 H, OCH_2CH_3); ^{13}C NMR δ 14.65 (CH_3), 25.56, 26.56 (CH_2), 56.72, 57.13, 58.90, 58.99 (OCH_3, CHN), 60.78 (OCH_2CH_3), 71.87, 72.83 (CH_2O), 154.47 (CO); MS *m/z* 231 (M^+, 0.3), 187 (11), 186 (100), 140 (21), 114 (26), 82 (31), 71 (30), 55 (18), 45 (22), 41 (11). HRMS Calcd for $C_{11}H_{21}NO_4$: 231.1470. Found: 231.1478.

13: IR 3423, 1752, 1728 cm^{-1}; ^1H NMR δ 1.23 (*t*, 3 H, OCH_2CH_3), 1.45–2.40 (*m*, 6 H, CH_2), 3.95 (*m*, 1 H, CH), 4.12 (*q*, 2 H, OCH_2CH_3), 5.12 (*br*, 1 H, NH); ^{13}C NMR δ 14.51 (CH_3), 17.82, 30.26, 34.83 (CH_2), 59.12 (CH), 61.16 (OCH_2CH_3), 156.44 (COO), 214.82 (CO); MS *m/z* 171 (M^+, 15), 115 (100), 56 (26), 55 (13), 43 (48), 42 (13). HRMS Calcd for $C_8H_{13}NO_3$: 171.0895. Found: 171.0892.

17: $[\alpha]_D$ −66.5 (CH_2Cl_2); IR 1721 cm^{-1}; ^1H NMR δ 1.35 (*t*, 3 H, OCH_2CH_3), 1.60–2.27 (*m*, 10 H, CH_2), 2.70–3.40 (*m*, 6 H, CHN, CH_2O), 3.28 (*s*, 6 H, OCH_3), 4.32 (*q*, 2 H, OCH_2CH_3), 4.58 (*dd*, 1 H, HCO); ^{13}C NMR δ 14.22 (CH_3), 22.54, 27.69, 31.79, 36.71 (CH_2), 58.13, 58.80 (CHN, OCH_3), 62.45 (OCH_2CH_3), 73.94 (CH_2O), 85.89 (NCN), 89.49 (HCO), 151.48 (C=N); MS *m/z* 312 (M^+, 9),

268 (17), 267 (100), 178 (32), 146 (20), 71 (23), 45 (17), 41 (11). HRMS Calcd for $C_{16}H_{28}N_2O_4$: 312.2049. Found: 312.2057.

*2-(Ethoxycarbonylamino)cyclopentanone 1,2-dimethylethylene ketals (**18**)*[18]

IR 3447, 1733, 1709 cm^{-1}; ^1H NMR δ 1.05–2.15 (*m*, 15 H, OCH_2CH_3), 3.52–3.63 (*m*, 2 H, OCH), 3.87 (*m*, 1 H, CHN), 4.10 (*q*, 2 H, OCH_2CH_3), 4.91 (*br*, 1 H, NH); ^{13}C NMR δ 14.62, 14.65, 16.25, 16.40, 16.80, 17.04, 18.76, 19.13, 29.67, 30.45, 35.20, 36.22 (CH_3, CH_2), 56.78, 57.03 (CHN), 60.67 (OCH_2CH_3), 78.30, 78.58, 78.92, 79.38 (OCH), 114.43, 114.59 (COO), 156.03, 156.15 (CO); MS *m/z* 243 (M^+, 16), 214 (30), 128 (38), 127 (100), 116 (11), 98 (21), 73 (12), 56 (37), 55 (53), 43 (16). HRMS Calcd for $C_{12}H_{21}NO_3$: 227.1521. Found: 227.1530.

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8. For comparative purpose we tested also the α-elimination reaction between the enamines **6** or **14** and $NsONHCO_2Et$ in the presence of CaO or Et_3N.[3] Both attempts gave very complex reaction mixtures mainly constituted of isomeric functionalisation products.
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