

Synthesis of Aliphatic (*E*)- α,β -Unsaturated Amides with High Diastereoselectivity from α,β -Epoxyamides Promoted by SmI_2/HMPA

José M. Concellón^{*[a]} and Eva Bardales^[a]

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Synthesis of aliphatic (*E*)- α,β -unsaturated amides **2**, in which the C=C bond is di- or trisubstituted, is achieved by using samarium diiodide and HMPA. The starting compounds **1** were easily prepared by the reaction of the corresponding

lithium or potassium enolates of α -chloroamides with aldehydes. A mechanism to explain this process is proposed. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

Samarium diiodide has been shown to be a useful reagent in reductive elimination reactions in recent years.^[1] We have described the diastereoselective synthesis of (*Z*)-vinyl halides from *O*-acetylated 1,1-dihaloalkan-2-ols,^[2] the preparation of (*E*)- α,β -unsaturated esters^[3] or amides^[4] from 2-halo-3-hydroxy esters or amides, respectively, and the formation of (*Z*)-vinylsilanes from 1-chloro-1-trialkylsilylalkan-2-ols. In addition, we have described the transformation of α,β -epoxy esters into (*E*)- α,β -unsaturated esters.^[5] In this respect, samarium diiodide has been used to transform epoxides into alkenes, however, this reaction takes place with poor diastereoselectivity,^[6] and to the best of our knowledge no general transformation of aliphatic α,β -epoxyamides into the synthetically interesting aliphatic α,β -unsaturated amides has been reported.

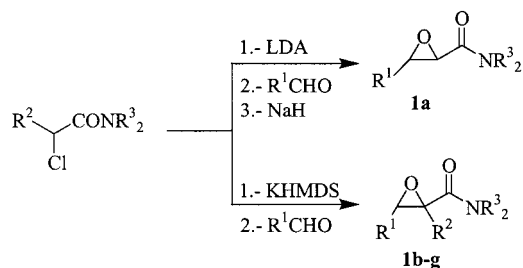
α,β -Unsaturated amides are an important class of compounds not only for their biological^[7] and insecticidal^[8] activities but also because of their presence in the structure of natural products.^[9] However, the preparation of α,β -unsaturated amides has scarcely been reported. For these reasons, an easy and general transformation of aliphatic α,β -epoxyamides into aliphatic α,β -unsaturated amides would be desirable.

Recently, we described the transformation, with total or high diastereoselectivity, of aromatic α,β -epoxyamides, in which the oxirane ring is trisubstituted, into (*Z*)- α,β -unsaturated amides, promoted by SmI_2 in the presence of MeOH, and the synthesis of (*E*)- α,β -unsaturated amides from aromatic di- or tetrasubstituted α,β -epoxyamides by using SmI_2 .^[10]

Here, we report a general synthesis of aliphatic α,β -unsaturated amides **2** from α,β -epoxyamides with high diastereoselectivity by using SmI_2 in the presence of HMPA.

Results and Discussion

The disubstituted epoxyamide **1a** was prepared by reaction of the lithium enolate of chloroacetamide (generated by treatment of α -chloroacetamide with LDA at -78°C) with cyclohexanecarbaldehyde and subsequent treatment with sodium hydride. Trisubstituted epoxyamides **1b–g** were obtained by reaction of the corresponding potassium enolates of α -chloroamides (generated by treatment of α -chloroamides with potassium hexamethyldisilazide at -78°C) with different aldehydes at temperatures ranging from -78 to 25°C (Scheme 1).

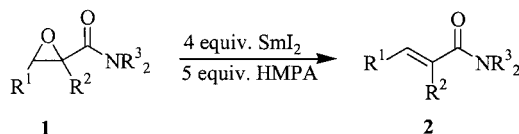


Scheme 1

When the reaction conditions used to obtain aromatic α,β -unsaturated amides from α,β -epoxyamides^[10] were applied to aliphatic α,β -epoxyamides, no elimination reaction was observed. For this reason and because the reduction potential of SmI_2 is higher in a solution of HMPA and THF,^[11] we carried out the β -elimination reaction of aliphatic α,β -epoxyamides by using SmI_2 in the presence of HMPA.

^[a] Departamento de Química Orgánica e Inorgánica, Universidad de Oviedo, Julián Clavería, 8, 33071 Oviedo, Spain
Fax: (internat.) +34-98-5103446
E-mail: jmcg@saaron.quimica.uniovi.es

Thus, treatment of different α,β -epoxyamides **1** with a solution of SmI_2 (4 equiv.) in THF and HMPA (5 equiv.)^[12] for 30 min at room temperature afforded, after hydrolysis, the corresponding α,β -unsaturated amides **2** with high diastereoselectivity and in good yields (Scheme 2, Table 1).

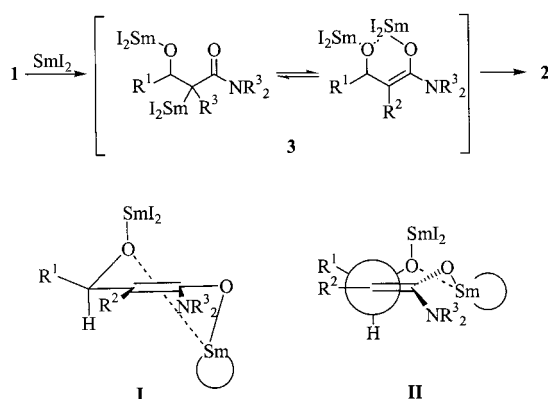


Scheme 2

Table 1. Synthesis of aliphatic (*E*)- α,β -unsaturated amides **2**

2 ^[a]	R^1	R^2	R^3	<i>de</i> (%) ^[b]	Yield (%) ^[c]
2a	Cyclohexyl	H	<i>i</i> Pr	>98	40
2b	Bu	Me	Et	>98	70
2c	Bu	Ph	Et	83	82
2d	C_7H_{15}	Me	Et	95	64
2e	$\text{Me}_2\text{C}=\text{CH}(\text{CH}_2)_2\text{CH}(\text{Me})\text{CH}_2$	Me	Et	94	85
2f	$\text{MeCH}(\text{Ph})$	Me	Et	95	83
2g	Cyclohexyl	Me	Et	93	91

^[a] All products were fully characterized by spectroscopic methods (IR, NMR, and MS). ^[b] Determined on crude reaction products by ^1H NMR spectroscopy and GC-MS. ^[c] Yield of isolated product after column chromatography based on compound **1**.



Scheme 3

This proposed methodology provides a general route to obtain α,β -unsaturated amides **2**, in which R^1 , R^2 and R^3 can be varied widely. Thus linear, branched, cyclic or unsaturated aliphatic aldehydes may be used to introduce different R^1 groups; R^2 may also be varied using different α -chloroamides to prepare the starting compounds **1** (Scheme 1).

The *de* was calculated on the crude reaction products by ^1H NMR spectroscopy and GC-MS.

The (*E*) stereochemistry of the C–C double bond of the α,β -unsaturated amide **2a** was assigned from the value of the coupling constant between the olefinic protons in the

^1H NMR spectrum ($J = 15.1$ Hz). In the case of trisubstituted α,β -unsaturated amides the stereochemistry was established by comparison of the ^1H NMR and ^{13}C NMR spectra with those of authentic samples, as reported in the literature.^[4]

It is noteworthy that although the starting α,β -epoxyamides were mixtures of *cis* and *trans* diastereoisomers, the corresponding α,β -unsaturated amides were obtained with total or very high (*E*)-selectivity.

Different behavior was observed when α,β -epoxyamides **1**, derived from ketones instead of aldehydes, and α -chloroamides were used. Instead of the α,β -unsaturated amides, β,δ -unsaturated α -hydroxyamides were obtained.^[13]

The observed stereochemistry of products **2** may be explained by assuming a chelation-control model (Scheme 3). Thus, reduction of the $\text{C}_\alpha\text{--O}$ bond generates the enolate intermediate **3**, in which the chelation of the Sm^{III} center with the carbonyl oxygen atom of the amide group produces a six-membered ring. Tentatively we propose a transition state model **I** with the R^1 in the equatorial orientation (to avoid 1,3-diaxial interactions). As depicted in **II** ($\text{C}2\text{--C}3$ Newman projection of **I**) R^1 and R^2 show a *cis* relationship. Consequently, elimination from **I** affords (*E*)- α,β -unsaturated amides. This transition state could also explain the total or very high diastereoselectivity observed in the β -elimination reaction from a mixture of diastereoisomers of **1**.

The proposed reduction of the $\text{C}_\alpha\text{--O}$ bond, instead of the $\text{C}_\beta\text{--O}$ bond, is supported by the fact that the treatment of aliphatic α,β -epoxyamides with SmI_2 in the presence of water affords β -hydroxyamides.^[14]

Conclusion

In conclusion, we present an easy and general preparation of aliphatic α,β -unsaturated amides **2** with high diastereoselectivity by treating α,β -epoxyamides with samarium diiodide and HMPA. The reaction is general, and the C–C double bond of **2** can be di- or trisubstituted. A mechanism has been proposed to explain this reaction.

Experimental Section

General Remarks: Reactions requiring an inert atmosphere were conducted under dry nitrogen, and the glassware was oven dried (120°C). THF was distilled from sodium/benzophenone ketyl immediately prior to use. All reagents were purchased in the highest quality available and were used without further purification. ^1H NMR spectra were recorded at 200 or 300 MHz. ^{13}C NMR spectra and DEPT experiments were determined at 50 or 75 MHz. GC-MS and HRMS were measured at 70 eV. Chemical shifts are given in δ (ppm) relative to TMS as internal standard in the case of ^1H NMR spectra and relative to CDCl_3 or $[\text{D}_6]\text{DMSO}$ in the case of ^{13}C NMR spectra.

General Procedure for the Synthesis of Compound 1a: A solution of lithium diisopropylamide [prepared from MeLi (3.3 mL of a 1.5 M solution) in diethyl ether (5 mmol) and diisopropylamine (0.8 mL,

5 mmol) in THF (25 mL) at 0 °C] was added dropwise to a stirred solution of the *N,N*-diisopropyl chloroacetamide (0.8 g, 4.5 mmol) in dry THF (4 mL) at –78 °C. After stirring for 10 min, a solution of the cyclohexanecarbaldehyde (0.4 mL, 3.5 mmol) in dry THF (4.5 mL) was added dropwise at –78 °C and the mixture was stirred for 1 h. The reaction mixture was quenched with an aqueous saturated solution of NH_4Cl (20 mL) followed by extraction with diethyl ether which provided the corresponding 2-chloro-3-hydroxyamide, which was treated with sodium hydride (1 g, 45 mmol) at 25 °C. The mixture was stirred for 2.5 h at this temperature, quenched with H_2O (10 mL) and then extracted with diethyl ether (3 $\times$ 10 mL) to afford crude 2,3-epoxyamide **1a**, which was purified by flash column chromatography on silica gel (hexane/EtOAc), yielding pure compound **1a**.

3-Cyclohexyl-2,3-epoxy-*N,N*-diisopropylpropanamide (1a): Yield: 64%, 567 mg. ^1H NMR (200 MHz, CDCl_3): δ = 1.23 (d, J = 6.7 Hz, 3 H), 1.25 (d, J = 6.7 Hz, 3 H), 1.42 (d, J = 6.7 Hz, 6 H), 2.06–1.57 (m, 11 H), 2.93–2.86 (m, 1 H), 3.53–3.37 (m, 1 H), 3.53 (d, J = 4.4 Hz, 1 H) 4.34–4.21 (m, 1 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 18.8 (CH₃), 19.1 (CH₃), 19.4 (CH₃), 19.7 (CH₃), 24.1 (CH₂), 24.2 (CH₂), 25.0 (CH₂), 27.5 (CH₂), 29.1 (CH₂), 35.5 (CH), 44.6 (CH), 46.6 (CH), 53.5 (CH), 60.0 (CH), 164.2 (C) ppm. IR (film): $\tilde{\nu}$ = 2953, 1651, 1454, 1372, 1136 2953, 1651, 1454, 1372, 1136 cm^{-1} ; R_f = 0.2 (hexane/EtOAc, 3:1)

General Procedure for the Synthesis of Compounds 1b–g: A solution of potassium hexamethyldisilazide (6.5 mL of a 0.5 M solution in toluene, 3.25 mmol) was added dropwise to a stirred solution of the appropriate 2-chloroamide (2.5 mmol) in dry THF (4 mL) at –78 °C. After stirring for 10 min, a solution of the corresponding aldehyde (2.5 mmol) in dry THF (4 mL) was added dropwise at –78 °C and the mixture was warmed to room temperature. The resulting solution was quenched with an aqueous saturated solution of NH_4Cl (10 mL) followed by extraction with diethyl ether (3 $\times$ 10 mL) provided crude 2,3-epoxyamides **1b–g**, which were purified by column flash chromatography over silica gel (hexane/EtOAc) affording pure compounds **1b–g**.

2,3-Epoxy-*N,N*-diethyl-2-methylheptanamide (1b): Yield: 55%, 294 mg. ^1H NMR (200 MHz, CDCl_3): δ = 0.96–0.76 (m, 6 H), 1.07 (t, J = 7.1 Hz, 6 H), 1.15 (t, J = 7.1 Hz, 6 H), 1.43 (s, 6 H), 1.87–1.24 (m, 8 H), 3.02–2.96 (m, 4 H), 3.59–3.12 (m, 8 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 12.8 (CH₃), 13.4 (CH₃), 14.2 (CH₃), 14.4 (CH₃), 14.6 (CH₃), 15.8 (CH₃), 15.6 (CH₃), 15.9 (CH₃), 25.1 (CH₂), 27.9 (CH₂), 28.6 (CH₂), 39.5 (CH₂), 41.5 (CH₂), 60.6 (C), 61.0 (CH), 62.7 (C), 169.9 (C), 170.0 (C) ppm. IR (film): $\tilde{\nu}$ = 2959, 1639, 1467, 1382, 1073 cm^{-1} ; R_f = 0.2 (hexane/EtOAc, 3:1)

2,3-Epoxy-*N,N*-diethyl-2-phenylheptanamide (1c): Yield: 74%, 509 mg. ^1H NMR (300 MHz, CDCl_3): δ = 0.72 (t, J = 7.1 Hz, 3 H), 0.80 (t, J = 7.1 Hz, 3 H), 0.86 (t, J = 7.1 Hz, 3 H), 0.97 (t, J = 7.1 Hz, 3 H), 1.03 (t, J = 7.1 Hz, 3 H), 1.10 (t, J = 7.1 Hz, 3 H), 1.55–1.15 (m, 12 H), 3.46–2.88 (m, 10 H), 7.45–7.23 (m, 10 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 12.2 (CH₃), 12.4 (CH₃), 13.2 (CH₃), 13.6 (CH₃), 13.7 (CH₃), 13.9 (CH₃), 21.9 (CH₂), 22.3 (CH₂), 26.5 (CH₂), 27.8 (CH₂), 28.3 (CH₂), 30.7 (CH₂), 39.2 (CH₂), 39.3 (CH₂), 40.8 (CH₂), 41.4 (CH₂), 64.0 (C), 64.9 (CH), 65.9 (C), 68.2 (CH), 124.7 (CH), 126.0 (CH), 127.7 (CH), 127.8 (CH), 127.9 (CH) ppm. IR (film): $\tilde{\nu}$ = 2940, 1644, 1463, 1380, 1032 cm^{-1} ; R_f = 0.4, 0.3 (hexane/EtOAc, 5:1)

2,3-Epoxy-*N,N*-diethyl-2-methyldecanamide (1d): Yield: 92%, 587 mg. ^1H NMR (200 MHz, CDCl_3): δ = 0.89–0.79 (m, 6 H), 1.08 (t, J = 7.1 Hz, 6 H), 1.15 (t, J = 7.1 Hz, 6 H), 1.42–1.20 (m, 24 H), 1.45 (s, 3 H), 1.50 (s, 3 H), 3.56–2.96 (m, 10 H) ppm. ^{13}C

NMR (75 MHz, CDCl_3): δ = 12.3 (CH₃), 12.4 (CH₃), 13.9 (CH₃), 14.0 (CH₃), 14.1 (CH₃), 15.4 (CH₃), 20.5 (CH₂), 22.4 (CH₂), 26.1 (CH₂), 27.8 (CH₂), 29.0 (CH₂), 29.1 (CH₂), 30.0 (CH₂), 31.5 (CH₂), 39.1 (CH₂), 39.2 (CH₂), 41.0 (CH₂), 41.3 (CH₂), 60.8 (CH), 61.2 (CH), 61.9 (C), 63.9 (C), 168.5 (C), 169.9 (C) ppm. IR (film): $\tilde{\nu}$ = 2927, 1644, 1464, 1380, 1079 cm^{-1} ; R_f = 0.1 (hexane/EtOAc, 5:1).

2,3-Epoxy-*N,N*-diethyl-2,5,9-trimethyldecan-8-enamide (1e): Yield: 90%, 632 mg. ^1H NMR (200 MHz, CDCl_3): δ = 1.01 (d, J = 6.4 Hz, 6 H), 1.15 (t, J = 7.2 Hz, 6 H), 1.20 (t, J = 7.1 Hz, 6 H), 1.49 (s, 6 H), 1.60 (s, 6 H), 1.68 (s, 6 H), 2.10–1.31 (m, 14 H), 3.68–3.03 (m, 10 H), 5.13–5.05 (m, 2 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 12.0 (CH₃), 13.7 (CH₃), 15.2 (CH₃), 15.3 (CH₃), 17.1 (CH₃), 18.8 (CH₃), 19.2 (CH₃), 20.1 (CH₃), 24.9 (CH₃), 25.2 (CH₂), 30.2 (CH), 30.6 (CH), 34.4 (CH₂), 34.5 (CH₂), 36.4 (CH₂), 36.6 (CH₂), 38.8 (CH₂), 39.1 (CH₂), 40.7 (CH₂), 41.1 (CH₂), 59.9 (C), 60.6 (CH), 60.7 (CH), 124.0 (CH), 124.1 (CH) ppm. IR (film): $\tilde{\nu}$ = 2968, 1635, 1434, 1380, 1076 cm^{-1} ; R_f = 0.3 (hexane/EtOAc, 5:1).

2,3-Epoxy-*N,N*-diethyl-2-methyl-4-phenylpentanamide (1f): Yield: 62%, 404 mg. ^1H NMR (200 MHz, CDCl_3): δ = 0.95 (t, J = 7.2 Hz, 6 H), 1.08 (t, J = 7.2 Hz, 6 H), 1.40 (d, J = 6.9 Hz, 3 H), 1.50 (d, J = 6.9 Hz, 3 H), 1.54 (s, 3 H), 1.52 (s, 3 H), 3.57–2.48 (m, 12 H), 7.37–7.24 (m, 10 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 12.1 (CH₃), 12.3 (CH₃), 13.5 (CH₃), 13.9 (CH₃), 15.5 (CH₃), 17.4 (CH₃), 18.6 (CH₃), 20.6 (CH₃), 39.4 (CH), 40.5 (CH₂), 41.2 (CH₂), 41.5 (CH₂), 61.3 (C), 62.5 (C), 65.9 (CH), 67.7 (CH), 126.3 (CH), 126.5 (CH), 127.2 (CH), 127.9 (CH), 128.0 (CH), 128.1 (CH), 141.3 (C), 141.9 (C) ppm. IR (film): $\tilde{\nu}$ = 2972, 1637, 1452, 1381, 1086 cm^{-1} ; R_f = 0.3, 0.2 (hexane/EtOAc, 3:1).

3-Cyclohexyl-2,3-epoxy-*N,N*-diethyl-2-methylpropanamide (1g): Yield: 85%, 508 mg. ^1H NMR (200 MHz, CDCl_3): δ = 1.11 (t, J = 6.9 Hz, 6 H), 1.19 (t, J = 6.9 Hz, 6 H), 1.51 (s, 3 H), 1.53 (s, 3 H), 2.01–1.39 (m, 22 H), 2.57 (d, J = 8.2 Hz, 1 H), 2.75 (d, J = 7.4 Hz, 1 H), 3.69–3.20 (m, 8 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ = 12.3 (CH₃), 12.4 (CH₃), 14.0 (CH₃), 14.2 (CH₃), 15.5 (CH₃), 25.1 (CH₂), 25.2 (CH₂), 25.9 (CH₂), 26.0 (CH₂), 28.2 (CH₂), 28.3 (CH₂), 29.8 (CH₂), 30.0 (CH₂), 36.8 (CH), 38.6 (CH₂), 39.0 (CH₂), 40.9 (CH₂), 41.6 (CH₂), 60.9 (CH), 61.8 (CH), 65.8 (C), 67.6 (C), 169.8 (C) ppm. IR (film): $\tilde{\nu}$ = 2930, 1636, 1450, 1381, 1074 cm^{-1} . R_f = 0.3, 0.2 (hexane/EtOAc, 3:1).

General Procedure for the Synthesis of Compounds 2: A solution of SmI_2 (1.6 mmol) in THF (19 mL) and HMPA (2 mmol) was added, under nitrogen, to a stirred solution of the appropriate epoxyamide **1** (0.4 mmol) in THF (4 mL) at room temperature. After stirring for 30 min the reaction was quenched with aqueous HCl (20 mL of a 0.1 M solution) followed by extraction with diethyl ether (3 $\times$ 10 mL) affording crude α,β -unsaturated amide **2**, which was purified by column flash chromatography over silica gel (hexane/EtOAc, 10:1).

(*E*)-3-Cyclohexyl-*N,N*-diisopropylpropanamide (2a): Yield: 40%, 38 mg. ^1H NMR (200 MHz, CDCl_3): δ = 2.22–1.08 (m, 23 H), 4.12–3.58 (m, 2 H), 6.14 (d, J = 15.1 Hz, 1 H), 6.74 (dd, J = 15.1, 7.4 Hz, 1 H) ppm. ^{13}C NMR (50 MHz, CDCl_3): δ = 20.3 (CH₃), 21.2 (CH₃), 25.8 (CH₂), 25.9 (CH₂), 32.1 (CH₂), 40.6 (CH), 45.5 (CH), 48.1 (CH), 120.5 (CH), 149.5 (CH), 166.7 (C) ppm. MS (70 eV): m/z (%) = 237 [$\text{M}]^+$ (2), 222 (5), 194 (26), 124 (62), 55 (100). IR (film): $\tilde{\nu}$ = 2926, 1654, 1438, 1337 cm^{-1} . R_f = 0.2 (hexane/EtOAc, 3:1).

(*E*)-*N,N*-Diethyl-2-methylhep-2-enamide (2b): Yield: 70%, 55 mg. ^1H NMR (200 MHz, CDCl_3): δ = 0.91 (t, J = 6.9 Hz, 3 H), 1.14

(t, $J = 7.2$ Hz, 6 H), 1.58–1.12 (m, 4 H), 1.83 (s, 3 H), 2.14–2.03 (m, 2 H), 3.33 (q, $J = 7.2$ Hz, 4 H), 5.48 (t, $J = 7.2$ Hz, 1 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): $\delta = 13.8$ (CH_3), 14.0 (CH_3), 14.3 (CH_3), 22.3 (CH_2), 22.6 (CH_3), 27.1 (CH_2), 31.1 (CH_2), 31.5 (CH_2), 129.6 (CH), 131.7 (C), 173.5 (C). MS (70 eV): m/z (%) = 197 (4) $[\text{M}]^+$, 168 (6), 140 (72), 125 (49) ppm. IR (film): $\tilde{\nu} = 2938$, 1624, 1458, 1431, 1380 cm^{-1} . $R_f = 0.3$ (hexane/EtOAc, 3:1)

(E)-N,N-Diethyl-2-phenylhep-2-enamide (2c): Yield: 82%, 85 mg. ^1H NMR (300 MHz, CDCl_3): $\delta = 0.96$ – 0.89 (m, 6 H), 1.23 (t, $J = 7.1$ Hz, 3 H), 1.54–1.33 (m, 4 H), 2.25–2.18 (m, 2 H), 3.24 (q, $J = 7.1$ Hz, 2 H), 3.54 (q, $J = 7.1$ Hz, 2 H), 6.04 (t, $J = 7.6$ Hz, 1 H), 7.39–7.21 (m, 5 H) ppm. ^{13}C NMR (75 MHz, CDCl_3): $\delta = 12.5$ (CH_3), 13.6 (CH_3), 13.7 (CH_3), 22.3 (CH_2), 29.5 (CH_2), 31.2 (CH_2), 38.2 (CH_2), 42.3 (CH_2), 125.1 (CH), 127.3 (CH), 128.4 (CH), 129.3 (CH), 136.4 (C), 137.5 (C), 169.1 (C) ppm. MS (70 eV): m/z (%) = 259 (86) $[\text{M}]^+$, 230 (71), 202 (100), 159 (4), 77 (9). IR (film): $\tilde{\nu} = 2960$, 1627, 1430, 1435, 1387 cm^{-1} . $R_f = 0.5$ (hexane/EtOAc, 1:1)

(E)-N,N-Diethyl-2-methyldec-2-enamide (2d): Yield: 64%, 70 mg. ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$, 373 K): $\delta = 0.84$ (t, $J = 6.7$ Hz, 3 H), 1.11 (t, $J = 7.2$ Hz, 6 H), 1.50–1.22 (m, 10 H), 1.78 (s, 3 H), 2.04 (q, $J = 6.9$ Hz, 2 H), 3.34 (q, $J = 7.2$ Hz, 4 H), 5.46 (dt, $J = 7.4$, 1.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $[\text{D}_6]\text{DMSO}$, 373 K): $\delta = 12.8$ (CH_3), 13.9 (CH_3), 14.2 (CH_3), 22.4 (CH_2), 27.3 (CH_2), 28.8 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 31.6 (CH_2), 41.5 (CH_2), 130.3 (CH), 130.8 (C), 173.7 (C) ppm. MS (70 eV): m/z (%) = 239 $[\text{M}]^+$ (2), 167 (27), 140 (100), 55 (40), 41 (40). IR (film): $\tilde{\nu} = 2928$, 2856, 1624, 1460, 1379 cm^{-1} ; $R_f = 0.5$ (hexane/EtOAc, 1:1)

(E)-N,N-Diethyl-2,5,9-trimethyldec-2,8-dienamide (2e): Yield: 85%, 90 mg. ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$, 373 K): $\delta = 0.99$ (d, $J = 6.7$ Hz, 3 H), 1.17 (t, $J = 7.3$ Hz, 6 H), 1.68 (s, 3 H), 1.75 (s, 3 H), 1.83 (s, 3 H), 2.21–0.93 (m, 7 H), 3.41 (q, $J = 7.3$ Hz, 4 H), 5.21–5.17 (m, 1 H), 5.53–5.48 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $[\text{D}_6]\text{DMSO}$, 373 K): $\delta = 13.4$ (CH_3), 14.2 (CH_3), 17.3 (CH_3), 19.3 (CH_3), 25.2 (CH_2), 32.5 (CH), 34.2 (CH_2), 36.4 (CH_2), 40.4 (CH_2), 124.6 (CH), 127.3 (CH), 130.5 (C), 132.9 (C), 172.4 (C) ppm. MS (70 eV): m/z (%) = 265 (6) $[\text{M}]^+$, 250 (10), 182 (67), 154 (12). IR (film): $\tilde{\nu} = 2966$, 1624, 1459, 1379 cm^{-1} ; $R_f = 0.2$ (hexane/EtOAc, 3:1).

(E)-N,N-Diethyl-2-methyl-4-phenylpent-2-enamide (2f): Yield: 83%, 81 mg. ^1H NMR (200 MHz, CDCl_3): $\delta = 1.27$ – 1.01 (m, 6 H), 1.39 (d, $J = 6.9$ Hz, 3 H), 1.91 (s, 3 H), 3.48–3.21 (m, 4 H), 3.80–3.70 (m, 1 H), 5.63 (d, $J = 9.4$ Hz, 1 H), 7.42–7.11 (m, 5 H) ppm. ^{13}C NMR (50 MHz, CDCl_3): $\delta = 14.2$ (CH_3), 14.5 (CH_3), 21.4 (CH_3), 36.6 (CH_2), 36.7 (CH_2), 37.6 (CH), 126.0 (CH), 126.6 (CH), 128.4 (CH), 130.8 (C), 133.7 (CH), 145.3 (C), 172.9 (C) ppm. MS (70 eV): m/z (%) = 245 (33) $[\text{M}]^+$, 173 (37), 140 (100), 126 (100), 77 (19). IR (film): $\tilde{\nu} = 3008$, 2945, 1647 cm^{-1} . $R_f = 0.5$ (hexane/EtOAc, 1:1)

(E)-3-Cyclohexyl-N,N-diethyl-2-methylpropenamide (2g): Yield: 91%, 81 mg. ^1H NMR (300 MHz, $[\text{D}_6]\text{DMSO}$, 373 K): $\delta = 1.17$ (t, $J = 7.0$ Hz, 6 H), 1.50–1.21 (m, 5 H), 1.81–1.68 (m, 5 H), 1.84 (d, $J = 1.7$ Hz, 3 H), 2.43–2.30 (m, 1 H), 3.39 (q, $J = 7.0$ Hz, 4 H), 5.33 (dq, $J = 8.9$, 1.7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $[\text{D}_6]\text{DMSO}$, 373 K): $\delta = 13.4$ (CH_3), 14.0 (CH_3), 25.1 (CH_2), 25.6 (CH_2), 32.0 (CH_2), 36.0 (CH), 40.4 (CH_2), 130.4 (C), 134.0 (CH), 172.5 (C) ppm. MS (70 eV): m/z (%) = 223 $[\text{M}]^+$ (9), 208 (2), 151

(57), 140 (100). IR (film): $\tilde{\nu} = 2974$, 1623, 1457, 1380 cm^{-1} . $R_f = 0.2$ (hexane/EtOAc, 3:1)

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