

# Atom transfer carbonylation using ionic liquids as reaction media

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## Abstract

Photo-induced ATC reactions of RI, CO, and amines to produce amides, were examined using ionic liquids, such as [bmim]PF<sub>6</sub> and [bmim]NTf<sub>2</sub>, as reaction media in the presence of a catalytic amount of a Pd–carbene complex. When the primary alkyl iodide was used, the yield of the amide was lowered due to competing S<sub>N</sub>2 reactions between RI and amines, whereas the reaction of the tertiary alkyl iodides was dependent on the structure of the substrates. ATC reactions of a wide variety of secondary RI proceeded smoothly when ionic liquids were used as reaction media. The Pd-catalyst and ionic liquid could also be recycled.

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*Keywords:* Atom transfer carbonylation; Ionic liquids; Carbon monoxide; Amide; Palladium

## 1. Introduction

Ionic liquids have recently attracted considerable interest as potent reaction media, replacing volatile organic solvents without sacrificing the function as a solvent [1]. A wide range of reactions using ionic liquids have been examined to date, including transition-metal catalyzed cross-coupling reactions [2,3], enzyme-reactions [4], to mention a few. Although radical polymerization using ionic liquids has been extensively studied [5], an examination of their feasibility for ordinary radical reactions in organic synthesis is yet to be sufficient. Yorimitsu and Oshima previously reported that iodine atom transfer reaction of alkynes can be effectively carried out using [bmim]PF<sub>6</sub> as a reaction medium [6]. We became interested in the use of ionic liquids for atom transfer carbonylation (ATC) reactions [7] for two reasons. Since ATC reactions of alkyl iodides in organic solvents proceeds in the presence of nucleophilic reagents such as amines, the issue of whether such a reaction system containing both alkyl iodides and nucleophiles would proceed in highly polar ionic liquids or not was of our primary concern. Since the recent study, revealing that

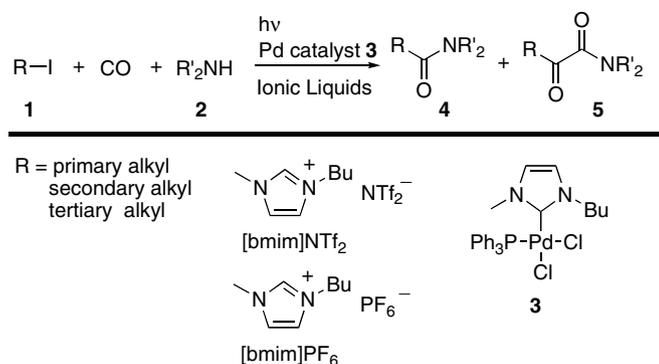
the addition of Pd(0)-complexes accelerates photo-irradiative ATC reactions [8], we were interested as to whether the Pd-catalyst can be immobilized effectively in ionic liquids, allowing for the recycling of both the catalyst and reaction medium. In this paper, we report on a systematic study of some ATC reactions involving a wide range of alkyl iodides leading to amides using ionic liquids and a Pd–carbene complex (Scheme 1).

## 2. Results and discussion

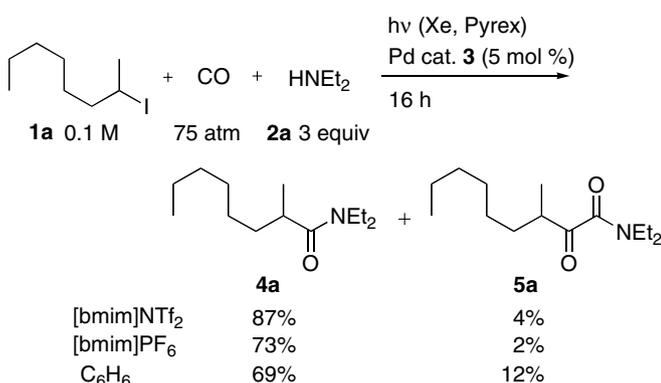
We examined the atom transfer carbonylation of 2-iodooctane (**1a**) with diethylamine (**2a**) under irradiation conditions (Xenon, Pyrex) using the Pd–carbene complex **3** [3b], which is readily soluble in ionic liquids, as a catalyst (Scheme 2). When the reaction of **1a** with **2a** (3 equiv.) was carried out using [bmim]NTf<sub>2</sub> (1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide) as a solvent for 16 h, the mono carbonylation product, **4a** was obtained in 87% yield, along with a small amount of double carbonylation product **5a** (4%) [9]. The direct nucleophilic substitution product, diethyl(1-methylheptyl)amine, was not formed in this case. When [bmim]PF<sub>6</sub> was used, the yield of **4a** was 73%. In these two cases, the amount of ketoamide **5a** that was formed was relatively small, compared with the case of the reaction using benzene as a solvent

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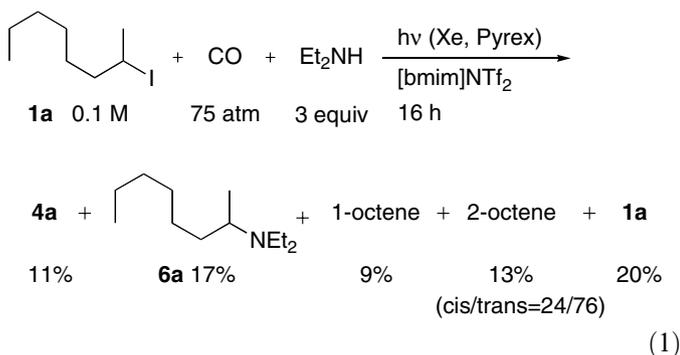


Scheme 1. Atom transfer carbonylation of alkyl iodides in a Pd/hv system using ionic liquids.



Scheme 2. Atom transfer carbonylation of 2-iodooctane.

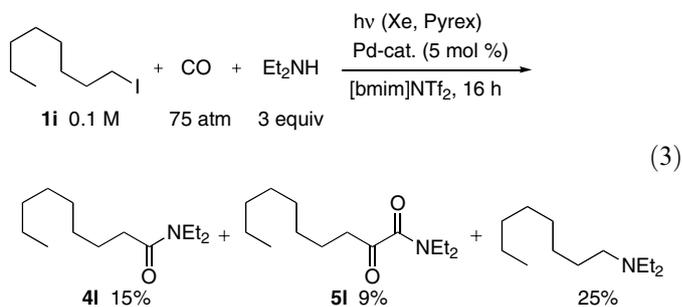
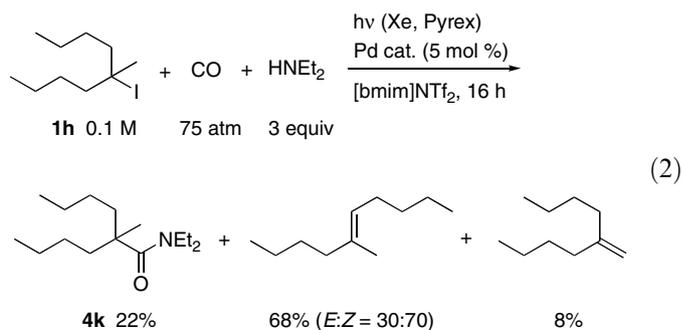
[10]. The reaction in the absence of Pd complex **3** using [bmim]NTf<sub>2</sub> was also examined, which gave a complex mixture. Thus, amide **4a**, S<sub>N</sub>2 product **6a**, elimination products, 1-octene and 2-octene, were obtained in 11%, 17%, 9%, and 13% (*cis/trans* = 24/76) yields, respectively, together with a significant amount of unreacted **1a** (20%) (Eq. (1)). These results clearly demonstrate that the Pd-carbene complex **3** effectively promotes the ATC reaction in ionic liquids.



The reaction of a variety of secondary and tertiary alkyl iodides with amines and CO was conducted using [bmim]NTf<sub>2</sub> as the reaction medium and the results are summarized in Table 1. The ionic liquid containing the Pd catalyst can be reused (entry 2). Primary amines, such

as hexyl amine and benzyl amine, react with **1a** and CO to give the corresponding amides **4b** and **4c** in 58% and 62% yield, respectively (entries 4 and 5). The reaction of secondary alkyl iodides, **1b**, **1c**, and **1d**, also gave the corresponding amides **4e**, **4f**, and **4g** in good yields (entries 7–9). Interestingly, the reaction of iodocyclohexane (**1e**) gave a significant amount of ketoamide **5h**, along with **4h** (entry 10). The efficiency of tertiary alkyl iodides in ATC reactions conducted in [bmim]NTf<sub>2</sub> was dependent on their structures. The reaction of 1-iodoadamantane (**1f**) gave a mixture of single and double carbonylation products **4i** and **5i** in 38% and 33% yield, respectively (entry 11), whereas the carbonylation of *tert*-butyl iodide (**1g**) produced pival amide **4j** in 61% yield as the sole carbonylation product (entry 11).

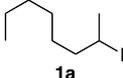
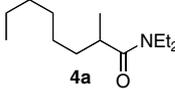
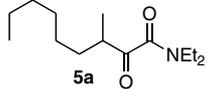
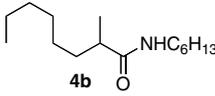
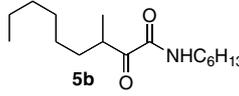
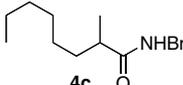
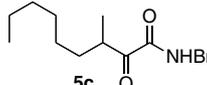
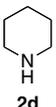
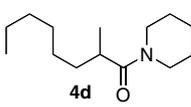
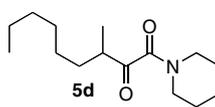
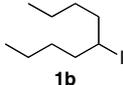
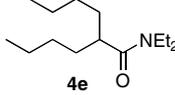
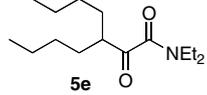
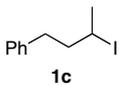
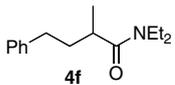
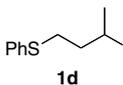
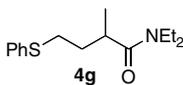
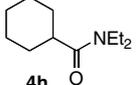
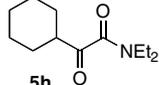
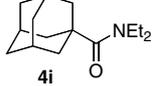
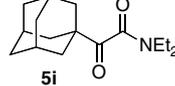
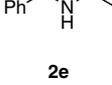
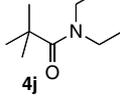
In contrast, 5-methyl-5-iodononane (**1h**), gave the anticipated amide **4k** in only 22% yield (Eq. (2)). In this case, a mixture of olefins arising from **1h** via the elimination of HI was formed as the major products. We also examined the reaction of a primary alkyl iodide **1i**, which gave low yields of carbonylated products (Eq. (3)). The reaction suffered a competing S<sub>N</sub>2 reaction with diethylamines to give diethyloctylamine. This is consistent with previously reported observations that ionic liquids accelerate the nucleophilic substitution of alkyl halides and sulfonates in terms of their highly polar characteristics [11].



In all of the reactions described above, the products can be separated from the catalyst solution of the ionic liquid by biphasic workup using organic solvents. Therefore, we checked the solubility of [bmim]NTf<sub>2</sub> and [bmim]PF<sub>6</sub> with several common organic solvents, including ether, benzene, toluene, diisopropyl ether (IPE), and cyclohexane and the results are summarized in Fig. 1. When [bmim]NTf<sub>2</sub> (895.4 mg) was treated with 5 mL of ether three times, 6.3% (56.6 mg) of [bmim]NTf<sub>2</sub> was isolated from the ether layer after evaporation, whereas [bmim]NTf<sub>2</sub> had a low

Table 1

Atom transfer carbonylation of alkyl iodides with amines in the Pd/hv system<sup>a</sup>

Entry	Reaction			Products		
	R-I <b>1</b>	+ CO 75 atm	+ HNR'R" <b>2</b>	R-C(=O)NR'R" <b>4</b>	R-C(=O)C(=O)NR'R" <b>5</b>	
	R-I <b>1</b>	Amine <b>2</b>	Amide <b>4</b>	Yield (%) <sup>b</sup>	Ketoamide <b>5</b>	Yield (%) <sup>b</sup>
1		HNEt <sub>2</sub> <b>2a</b>		87		4
2 <sup>c</sup>				76		5
3 <sup>d</sup>				73		2
4	<b>1a</b>	H <sub>2</sub> NC <sub>6</sub> H <sub>13</sub> <b>2c</b>		58		14
5	<b>1a</b>	H <sub>2</sub> NBn <b>2c</b>		62		9
6	<b>1a</b>			44		4
7		<b>2a</b>		80		Trace
8		<b>2a</b>		74		
9		<b>2a</b>		63		
10		<b>2a</b>		53		32
11		<b>2a</b>		38		33
12				61		

<sup>a</sup> Reaction conditions; **1** (0.5 mmol), **2** (1.5 mmol), Pd-cat. **3** (5 mol %), CO (75 atm), [bmim]NTf<sub>2</sub> (5 mL), hv (Xe, Pyrex), 16 h.<sup>b</sup> Isolated yield.<sup>c</sup> The ionic liquid solution recovered from entry 1 was used.<sup>d</sup> [bmim]PF<sub>6</sub> was used as a solvent.

solubility in cyclohexane. It was found that amide **3a** can be extracted nearly quantitatively with six portions of cyclohexane (5 mL) from the [bmim]NTf<sub>2</sub> (5 mL). Compared to [bmim]NTf<sub>2</sub>, [bmim]PF<sub>6</sub> showed a low solubility in all solvents examined.

### 3. Conclusion

The ATC reaction of alkyl iodides leading to amides was examined using ionic liquids, [bmim]NTf<sub>2</sub>, as a solvent and a Pd-carbene complex **3** as a catalyst. The

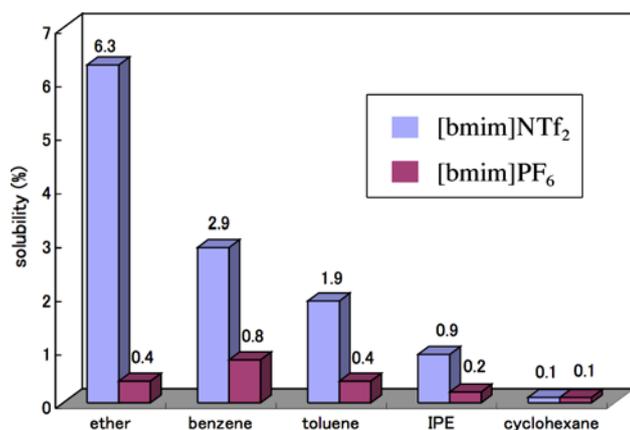


Fig. 1. Solubility of [bmim]NTf<sub>2</sub> and [bmim]PF<sub>6</sub> in several common organic solvents.

reaction of secondary alkyl iodides proceeded well, whereas primary alkyl iodides were not suitable for the present system because of competing S<sub>N</sub>2 reactions. Concerning tertiary alkyl iodides, the course of the reaction was dependent on the structures of substrates. The ionic liquid, containing the Pd catalyst could be recycled. Cyclohexane was found to be an excellent solvent for extracting the products from the ionic liquids without being contaminated by the ionic liquid.

## 4. Experimental

### 4.1. General

<sup>1</sup>H NMR spectra were recorded with a JEOL JMN ECP-500 (500 MHz) spectrometer in CDCl<sub>3</sub>. Chemical shifts are reported in parts per million (δ) downfield from internal TMS at 0.00. <sup>13</sup>C NMR spectra were recorded with a JEOL JMN ECP-500 (125 MHz) spectrometer and referenced to the solvent peak at 77.00 ppm. Infrared spectra were obtained on a JASCO FT/IR 4100 spectrometer; absorption data are reported in reciprocal centimeters. Conventional mass spectra were obtained on a JEOL MS700 spectrometer or SHIMADZU GCMS-QP 5050A instrument. High-resolution mass spectra were obtained on a JEOL MS700 spectrometer. Analytical GC was SHIMADZU GC-17A using J&W DB-1 column (30 m/0.32 mm i.d.). Benzene was distilled from benzophenone/Na prior to use. The products were purified by flash chromatography on silica gel (NACALAI TESQUE Inc., Silica Gel 60, 70–230 mesh) and, if necessary, were further purified by recycling preparative HPLC (Japan Analytical Industry Co. Ltd., LC-908) on GPC columns using CHCl<sub>3</sub> as the eluent. Photolysis experiments were conducted using a stainless steel autoclave with quartz glass windows lined with a Pyrex glass liner and using a 500 W xenon short arc lamp (Ushio Co. Ltd., lamp house: SX-UI500XQ, xenon short arc lamp: UXL-500SX, power supply: BA-X500). Alkyl iodides were pre-

pared from the corresponding alcohols. Ionic liquids [bmim]NTf<sub>2</sub>, [bmim]PF<sub>6</sub> was prepared according to a previously reported procedure [12]. The Pd–carbene complex **3** was prepared using a previous reported procedure [3b]. Amides **4a** and **4h** are commercially available. Amides **4b**, **4c**, and ketoamide **5h** are known product. Amides **4i** and **4l**, ketoamides **5a**, **5i**, and **5k** are previously reported [8b]. These compounds were identified by comparison with literature data.

### 4.2. Typical procedure for the atom transfer carbonylation of alkyl iodides with an amine using an ionic liquid

In the photoreactions, a magnetic stirring bar, 2-iodooctane (**1a**, 124 mg, 0.52 mmol), diethylamine (**2a**, 122 mg, 1.5 mmol), Pd-complex (**3**, 15 mg, 0.025 mmol) and [bmim]NTf<sub>2</sub> (5.2 mL) were placed in a stainless steel autoclave in which a Pyrex glass liner was inserted. The autoclave was purged four times with carbon monoxide, pressurized with 75 atm of CO and then irradiated with a xenon arc lamp (500 W) with stirring. After 16 h, excess CO was discharged at room temperature. The product was extracted from the reaction mixture with cyclohexane. The residue was subjected to silica gel column chromatography using hexane/EtOAc = 2/1 as the eluent, to afford *N,N*-diethyl-2-methyloctanamide (**4a**, 97 mg, 87%) and *N,N*-diethyl-3-methyl-2-oxononanamide (**5a**, 5 mg, 4%).

### 4.3. Recycling of Pd catalyst and [bmim]NTf<sub>2</sub>

After the reaction, the product was extracted from the reaction mixture with cyclohexane, and the ammonium salts were removed by washing with water, in which both the cyclohexane and water were degassed by N<sub>2</sub> bubbling prior to use. Excess cyclohexane and water were removed under reduced pressure, and the remaining ionic liquid layer, containing the Pd catalyst, was used in the next reaction.

### 4.4. Reaction of the atom transfer carbonylation without Pd catalyst using an ionic liquid

A magnetic stirring bar, 2-iodooctane (**1b**) (0.119 g, 0.50 mmol), diethylamine (0.109 g, 1.5 mmol) and [bmim]NTf<sub>2</sub> (5.0 mL) were placed in a stainless steel autoclave in which a Pyrex glass liner was inserted. The autoclave was purged four times with carbon monoxide, pressurized with 75 atm of CO and then irradiated with a xenon arc lamp (500 W) with stirring. After 16 h, excess CO was discharged at room temperature. The product was extracted from the reaction mixture with cyclohexane. The products were identified from GC, GC–MS, and NMR data. The yields were determined by GC (internal standard: nonane) and <sup>1</sup>H NMR (internal standard: 1,1,2,2-tetrachloroethene): **4a** (11%; NMR), olefins (21%; GC), diethyl-(1-methyl-heptyl)amine (17%; GC), **1a** (20%; GC).

#### 4.5. Determination of solubility of ionic liquids to organic solvents

A mixture of [bmim]NTf<sub>2</sub> (895.4 mg) and ether (5 mL) was vigorously stirred at room temperature for 5 min. After standing for 5 min, the ether layer was decanted. This was repeated an additional two times. The combined ether layer was evaporated and the residue weighed to give 56.6 mg (6.3 wt%) of [bmim]NTf<sub>2</sub>.

#### 4.6. *N*-hexyl-3-methyl-2-oxononanamide (5b)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 6.94 (s, 1H), 3.98–3.53 (m, 1H), 3.29 (q, *J* = 6.7 Hz, 2H), 1.67 (m, 1H), 1.56–1.51 (m, 3H), 1.34–1.25 (m, 16H), 1.10 (d, *J* = 6.9 Hz, 3H), 0.90–0.86 (m, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 14.05, 14.13, 15.68, 15.71, 22.58, 22.64, 26.59, 27.18, 29.30, 31.45, 31.72, 32.56, 38.91, 39.44, 160.03, 202.71; IR (neat) 1461 cm<sup>-1</sup>, 1677 cm<sup>-1</sup>, 1716 cm<sup>-1</sup>, 3330 cm<sup>-1</sup>; MS (relative intensity) *m/z* 269 (M<sup>+</sup>, 7), 85 (26), 81 (22), 71 (71), 57 (100), 55 (44); HRMS (EI) calc. for C<sub>16</sub>H<sub>31</sub>NO<sub>2</sub> *m/z* 269.2355, found: 269.2357.

#### 4.7. *N*-benzyl-3-methyl-2-oxononanamide (5c)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.42–7.24 (m, 5H), 4.49 (s, 2H), 1.73–1.68 (m, 1H), 1.56 (s, 1H), 1.35–1.26 (m, 9H), 1.12 (d, *J* = 5.9 Hz, 3H), 0.88 (t, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 14.15, 15.71, 22.66, 27.20, 29.34, 31.74, 32.57, 39.12, 43.52, 127.93, 128.91, 159.94, 202.36; IR (neat) 1455 cm<sup>-1</sup>, 1679 cm<sup>-1</sup>, 1716 cm<sup>-1</sup>, 3340 cm<sup>-1</sup>; MS (relative intensity) *m/z* 275 (M<sup>+</sup>, 2), 141 (27), 91 (100), 71 (74), 57 (79); HRMS (EI) calc. for C<sub>17</sub>H<sub>25</sub>NO<sub>2</sub> *m/z* 275.1885, found: 275.1879.

#### 4.8. 1-(2-Methyl-1-oxooctyl)piperidine (4d)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 3.63–3.41 (m, 4H), 2.68 (sext, *J* = 6.8 Hz, 1H), 1.69–1.64 (m, 3H), 1.57–1.52 (m, 4H), 1.37–1.26 (m, 9H), 1.09 (d, *J* = 6.9 Hz, 3H), 0.87 (t, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 14.12, 17.71, 22.68, 24.79, 25.82, 26.89, 27.53, 29.46, 31.83, 34.22, 35.26, 42.88, 46.62, 175.00; IR (neat) 1434 cm<sup>-1</sup>, 1643 cm<sup>-1</sup>; MS (relative intensity) *m/z* 225 (M<sup>+</sup>, 8), 154 (62), 142 (31), 141 (100), 140 (36), 112 (66), 86 (35), 85 (71), 84 (77), 71 (32), 70 (33), 69 (70), 57 (26), 56 (45), 55 (30), 44 (40), 43 (70), 42 (55), 41 (82); HRMS (EI) calc. for C<sub>14</sub>H<sub>27</sub>NO *m/z* 225.2093, found: 225.2081.

#### 4.9. 1-(3-Methyl-1,2-dioxononyl)piperidine (5d)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 3.58 (t, *J* = 5.5 Hz, 2H), 3.31 (t, *J* = 5.5 Hz, 2H), 3.08 (sext, *J* = 6.7 Hz, 1H), 1.77–1.66 (m, 2H), 1.64–1.57 (m, 5H), 1.36–1.28 (m, 9H), 1.12 (d, *J* = 6.9 Hz, 3H), 0.88 (t, *J* = 6.9 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 14.13, 14.57, 22.66,

24.49, 25.48, 26.42, 27.08, 29.33, 31.40, 31.75, 42.45, 42.88, 46.84, 166.20, 204.60; IR (neat) 1447 cm<sup>-1</sup>, 1641 cm<sup>-1</sup>, 1709 cm<sup>-1</sup>; MS (relative intensity) *m/z* 253 (M<sup>+</sup>, 15), 113 (29), 112 (100), 71 (66), 69 (89), 57 (73); HRMS (EI) calc. for C<sub>15</sub>H<sub>27</sub>NO<sub>2</sub> *m/z* 253.2042, found: 253.2034.

#### 4.10. *N,N*-diethyl-2-butylhexanamide (4e)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 3.41–3.32 (m, 4H), 2.53–2.48 (m, 1H), 1.65–1.58 (m, 3H), 1.46–1.39 (m, 2H), 1.32–1.20 (m, 10H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.88 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 13.09, 13.97, 14.00, 14.91, 22.99, 29.94, 33.07, 40.37, 41.32, 41.83, 175.60; IR (neat) 1460 cm<sup>-1</sup>, 1638 cm<sup>-1</sup>; MS (relative intensity) *m/z* 227 (M<sup>+</sup>, 2), 184 (23), 171 (50), 128 (30), 128 (100), 115 (49), 100 (53), 73 (34), 71 (45), 58 (66), 57 (37), 44 (48), 43 (64), 41 (49); HRMS (EI) calc. for C<sub>14</sub>H<sub>29</sub>NO *m/z* 227.2249, found: 227.2235.

#### 4.11. *N,N*-diethyl-2-methyl-4-phenylbutylamide (4f)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.27–7.26 (m, 3H), 7.18 (d, *J* = 7.8 Hz, 2H), 3.47–3.40 (m, 2H), 3.35–3.24 (m, 2H), 3.28–3.14 (m, 2H), 2.60–2.55 (m, 1H), 2.07–2.00 (m, 1H), 1.74–1.07 (m, 1H), 1.14 (d, *J* = 6.4 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.3 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 13.21, 14.89, 33.62, 34.79, 35.98, 40.43, 128.37, 128.41, 128.45, 142.07, 175.57; IR (neat) 1454 cm<sup>-1</sup>, 1939 cm<sup>-1</sup>; MS (relative intensity) *m/z* 233 (M<sup>+</sup>, 1), 129 (100), 114 (25), 91 (55), 72 (24), 58 (34), 44 (28); HRMS (EI) calc. for C<sub>15</sub>H<sub>23</sub>NO *m/z* 233.1780, found: 233.1779.

#### 4.12. *N,N*-diethyl-2-methyl-4-phenylsulfanylbutylamide (4g)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.31 (t, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 6.4 Hz, 1H), 7.10 (t, *J* = 7.3 Hz, 2H), 3.41–3.25 (m, 4H), 3.02–2.97 (m, 1H), 2.92–2.81 (m, 2H), 2.11 (sext, *J* = 7.0 Hz, 1H), 1.69 (sext, *J* = 6.8 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.13–1.08 (m, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 13.21, 15.02, 18.05, 31.40, 33.32, 34.20, 40.47, 41.97, 125.84, 128.95, 128.97, 136.47, 175.00; IR (neat) 1439 cm<sup>-1</sup>, 1635 cm<sup>-1</sup>; MS (relative intensity) *m/z* 265 (M<sup>+</sup>, 43), 156 (74), 129 (100), 123 (28), 100 (35); HRMS (EI) calc. for C<sub>15</sub>H<sub>23</sub>NOS *m/z* 265.1500, found: 265.1506.

#### 4.13. *N*-benzyl-*N*-ethyl-2,2-dimethylpropionamide (4j)

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) δ 7.32 (t, *J* = 7.6 Hz, 2H), 7.26–7.24 (m, 1H), 7.19 (d, *J* = 6.9 Hz, 2H), 4.66 (s, 2H), 3.38 (s, 2H), 1.38 (s, 9H), 1.13–1.11 (m, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz) δ 28.71, 28.74, 39.16, 41.69, 127.15,

128.65, 177.55; IR (neat) 1453  $\text{cm}^{-1}$ , 1628  $\text{cm}^{-1}$ ; MS (relative intensity)  $m/z$  219 ( $\text{M}^+$ , 41), 92 (22), 91 (100), 57 (86); HRMS (EI) calc. for  $\text{C}_{14}\text{H}_{21}\text{NO}$   $m/z$  219.1623, found: 219.1627.

#### 4.14. *N,N*-diethyl-2-butyl-2-methylhexanamide (**4k**)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  3.40 (br.s, 4H), 1.71–1.65 (m, 2H), 1.43–1.37 (m, 2H), 1.35–1.25 (m, 8H), 1.21 (s, 3H), 1.15–1.12 (m, 6H), 0.89 (t,  $J = 7.1$  Hz, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz)  $\delta$  14.10, 23.43, 25.14, 26.93, 40.11, 41.37, 46.75, 175.05; IR (neat) 1466  $\text{cm}^{-1}$ , 1626  $\text{cm}^{-1}$ ; MS (relative intensity)  $m/z$  241 ( $\text{M}^+$ , 2), 185 (100), 184 (22); HRMS (EI) calc. for  $\text{C}_{15}\text{H}_{31}\text{NO}$   $m/z$  241.2406, found: 241.2393.

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