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Amberlyst-15 in Ionic Liquid: An Efficient and Recyclable Reagent for Nucleophilic Substitution of Alcohols and Hydroamination of Alkenes

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The nucleophilic substitution reaction of secondary alcohols and hydroamination of alkenes with amides, sulfonamides, carbamates, and amines using Amberlyst-15 immobilized in [Bmim][BF_4] (1-butyl-3-methylimidazolium tetrafluoroborate) ionic liquid as an efficient recyclable reagent is described. The solvent effect is prominent in the reaction, and the desired substitution products are obtained in good to excellent yield. The protocol is advantageous due to the ease of handling of the reagents, the simple work-up procedure, and the environmentally benign conditions that allow effective recyclability.

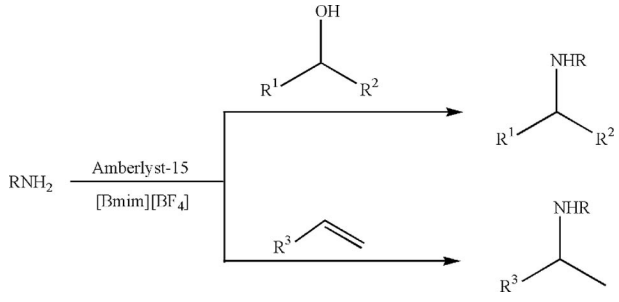
Introduction

Carbon–nitrogen bond-forming reactions are one of the most important types of reactions in organic chemistry.[1] Usually, amines are prepared either by amination of halides or by reduction of compounds such as nitriles, oximes, or amides. Hydroamination of alkenes is one of the most efficient approaches to the synthesis of higher substituted amines and their derivatives. Amination of alcohols results in the formation of very important intermediates that are relevant to the synthesis of various pharmaceuticals and fine chemicals.[2] Substitution of the hydroxyl group in alcohols by a nucleophile generally necessitates preactivation of the hydroxyl group, because of its poor leaving ability. This can be achieved by using high temperature or by adding suitable promoters. Because the latter approach leads to the formation stoichiometric amounts of salt waste, the development of an efficient, more atom-economic and environmentally viable method for the direct substitution of alcohols with a nitrogen nucleophile is highly desirable.

Several transition-metal-complex catalysts based on palladium and ruthenium have been developed for the direct substitution of alcohols with various nitrogen nucleophiles, such as amides, sulfonamides, carboxamides, carbamates, and amines,[3] and, recently, various Lewis and Brønsted acid catalysts ($NaAuCl_4$,[4a] H-Montmorillonite,[4b] $MoCl_5$,[4c] $FeCl_3$,[4d] $Cu(OAc)_2$,[4e] triflate salts,[4f–4i] heteropoly acid,[4j] and Brønsted acid[4k]) have been employed for the amidation of alcohols. In contrast, hydroaminations are generally catalyzed by transition and alkali metals.[5] Recently, we reported a very efficient and economical method for the direct substitution of alcohols and hydroamination of alkenes with various nucleophiles by using Amberlyst-15 immobilized in ionic liquid.[6]

The importance of green reactions in organic synthesis has led us to explore the use of ionic liquids as novel solvents, catalysts, reagents, and also in separation processes.[7] Features that make ionic liquids attractive include their lack of vapor pressure, nonvolatility, nonflammability and their wide liquid-state temperature range. Besides the possibility of recycling the catalytic system, interest in using ionic liquids comes from the unique interactions of these media with the active species and from the possibility of modifying the reaction activity and selectivity.[8] This prompted us to initiate a systematic exploration of the amination reaction of alcohols and alkenes.

In a continuation of our work on the application of ionic liquids in several organic transformations,[6,9] we report herein a simple, facile, and highly efficient protocol for nucleophilic substitution of alcohols, and hydroamination of alkenes by Amberlyst-15 in the ionic liquid [Bmim][BF_4] (= 1-butyl-3-methylimidazolium tetrafluoroborate); see Scheme 1. The reagent, Amberlyst-15, and solvent,



Scheme 1. Nucleophilic substitution of alcohols and hydroamination of alkenes.

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[Bmim][BF_4], are both air-stable and the system is applicable to a wide range of substrates.

Results and Discussion

Initial studies were conducted using Amberlyst-15 as the choice of reagent for the nucleophilic substitution reaction of benzamide (**2**) with benzhydrol (**1**) as a prototype reaction. Various reaction conditions for this transformation were investigated, and the results obtained are summarized in Table 1. Initially, screening of different solvents showed that the ionic liquid [Bmim][BF_4] was superior to organic solvents and to other ionic liquids (Table 1, entries 1–7). By varying the reaction temperature from room temperature to 100 °C, a gradual improvement in yield was observed (Table 1, entries 2 and 8–10). However, prolonging the reaction time did not offer any significant advantage (Table 1, entry 11). Several solid acid reagents were also screened (Table 1, entries 2 and 12–15), among which, Amberlyst-15 was found to be the most effective reagent under the present reaction conditions. Amberlyst-15 is a sulfonic acid type styrene/divinylbenzene copolymer, and the probable reason for its higher activity can be explained on the basis of its physical properties, such as H^+ capacity (4.2 meq/g) and high surface area (42 m^2/g). Furthermore, it was observed that lowering the Amberlyst-15 concentration decreased the yield of the substituted product (Table 1, entry 16). Hence, the optimum reaction conditions for the transformation of **1** and **2** into **3** is the use of Amberlyst-15 (0.75 g) as reagent with solvent [Bmim][BF_4] at 80 °C for 2 h.

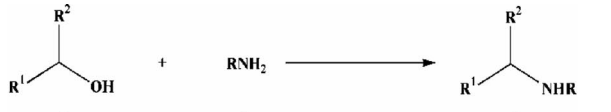
Table 1. Reaction parameters for the addition of benzamide (**2**) to benzhydrol (**1**).[a]

Entry	Reagent	Solvent	Temp. [°C]	Yield [%][b]
1	Amberlyst-15	[Bmim][PF_6]	80	76
2	Amberlyst-15	[Bmim][BF_4]	80	88
3	Amberlyst-15	[Omim][BF_4]	80	55
4	Amberlyst-15	[Bmim][Cl]	80	n.r.
5	Amberlyst-15	1,4-dioxane	80	39
6	Amberlyst-15	toluene	80	59
7	Amberlyst-15	CH_3CN	80	n.r.
8	Amberlyst-15	[Bmim][BF_4]	r.t.	n.r.
9	Amberlyst-15	[Bmim][BF_4]	60	62
10	Amberlyst-15	[Bmim][BF_4]	100	90
11[c]	Amberlyst-15	[Bmim][BF_4]	80	90
12	Amberlite-IR-120	[Bmim][BF_4]	80	n.r.
13	Indion-225H	[Bmim][BF_4]	80	80
14	Montmorillonite K-10	[Bmim][BF_4]	80	trace
15	Lewatit K-2620	[Bmim][BF_4]	80	n.r.
16[d]	Amberlyst-15	[Bmim][BF4]	80	65

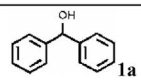
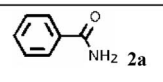
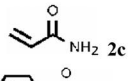
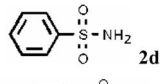
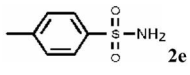
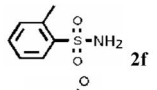
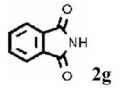
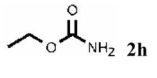
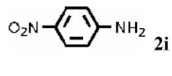
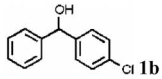
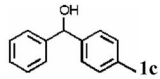
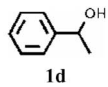
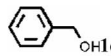
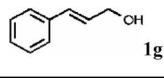
[a] Reagents and conditions: benzhydrol (1 mmol), benzamide (1 mmol), solvent (2 mL), reagent (0.75 g), 2 h. [b] GC yield; n.r.: no reaction. [c] Reaction was carried out for 3 h. [d] Reagent (0.32 g).

To explore the scope of the reaction, we performed a set of experiments with a range of secondary benzylic alcohols and various types of nitrogen nucleophiles, including amide, sulfonamide, carbamates, and amines, using Amberlyst-15 immobilized in ionic liquid [Bmim][BF_4]; the good to excellent yields obtained are summarized in Table 2. After com-

Table 2. Substitution of alcohols with nitrogen-containing nucleophiles.[a]



1 2 3

Entry	Alcohol	RNH_2	Time (h)	Product	Yield (%)[b]
1	 1a	 2a	1	**3aa**	88
2	**1a**	 2b	1	**3ab**	63
3	**1a**	 2c	1	**3ac**	80
4	**1a**	 2d	3	**3ad**	85
5	**1a**	 2e	1	**3ae**	92
6	**1a**	 2f	2	**3af**	90
7	**1a**	 2g	4	**3ag**	n.r.
8	**1a**	 2h	1	**3ah**	97
9	**1a**	 2i	4	**3ai**	69
10	 1b	**2a**	3	**3ba**	90
11	**1b**	**2e**	3	**3be**	94
12	**1b**	**2h**	1	**3bh**	95
13	 1c	**2a**	3	**3ca**	88
14	**1c**	**2d**	3	**3cd**	87
15	**1c**	**2e**	3	**3ce**	86
16	**1c**	**2h**	1	**3ch**	93
17[c]	 1d	**2a**	2	**3da**	70
18[c]	**1d**	**2c**	2	**3dc**	71
19[c]	**1d**	**2d**	3	**3dd**	83
20[c]	**1d**	**2e**	3	**3de**	86
21[c]	**1d**	**2h**	2	**3dh**	94
22	 1e	**2e**	5	**3ee**	n.r.
23	 1f	**2e**	5	**3fe**	n.r.
24	 1g	**2e**	5	**3ge**	n.r.

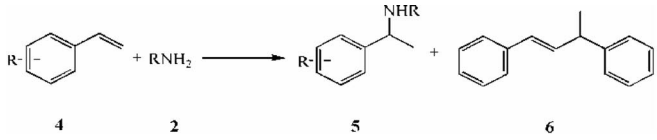
[a] Reagents and conditions: alcohol **1** (1 mmol), nucleophile **2** (1 mmol), Amberlyst-15 (0.75 g), [Bmim][BF_4] (2 mL), 80 °C. [b] GC yield. n.r. (no reaction). [c] Nucleophile **2** (3 mmol).

pletion of the reaction, the ionic liquid phase containing [Bmim][BF_4] and reagent Amberlyst-15 were almost quantitatively recovered by simple extraction of the product with ethyl acetate.

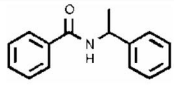
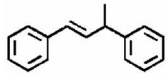
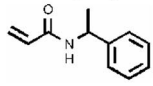
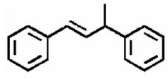
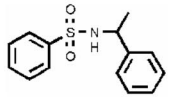
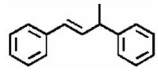
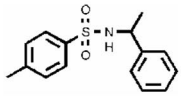
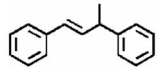
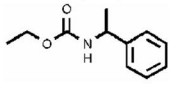
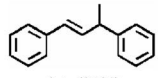
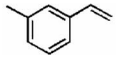
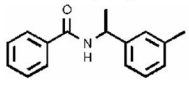
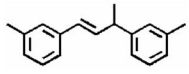
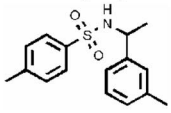
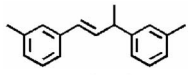
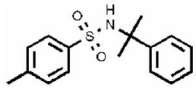
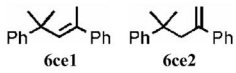
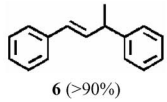
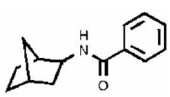
Firstly, when amides (benzamide, acetamide, and acrylamide) were used for the nucleophilic substitution with benzydric alcohol (**1a**), excellent yields of the desired substituted products were obtained (Table 2, entries 1–3). Benzhydric alcohols possessing electron-withdrawing and electron-donating groups reacted effectively with benzamide, providing the corresponding products with excellent 88–90% yields (Table 2, entries 10 and 13). The reaction is highly efficient and proceeds smoothly with primary amides within a short reaction time. The secondary amide phthalamide did not react under these reaction conditions, even after prolonged reaction time (Table 2, entry 7).

The reaction of 1-phenylethanol (**1d**) with **2a** or **2c** afforded the desired benzylated products **3da** and **3dc** in 70–

Table 3. Hydroamination of alkenes with nitrogen-containing nucleophiles.[a]



4 **2** **5** **6**

Entry	Alkenes	RNH_2	Time (h)	Product **5**, yield[b]	Product **6**, yield[b]
1	 **4a**	**2a**	5	 **5aa** (60%)	 **6aa** (33%)
2	**4a**	**2c**	3	 **5ac** (33%)	 **6ac** (52%)
3	**4a**	**2d**	5	 **5ad** (52%)	 **6ad** (45%)
4	**4a**	**2e**	5	 **5ae** (60%)	 **6ae** (32%)
5	**4a**	**2h**	3	 **5ah** (70%)	 **6ah** (21%)
6	 **4b**	**2a**	5	 **5ba** (28%)	 **6ba** (7%)
7	**4b**	**2e**	5	 **5be** (30%)	 **6be** (16%)
8	 **4c**	**2e**	4	 **5ce** (–)	 **6ce1** **6ce2** (55%)
9	**4a**	–	1	–	 **6** (>90%)
10	 **4d**	**2a**	5	 **5da** (51%)	–

[a] Reagents and conditions: alkene **4** (1 mmol), nucleophile **2** (3 mmol), Amberlyst-15 (0.75 g), [Bmim][BF_4] (2 mL), 80 °C. [b] GC yield.

71% yield (Table 2, entries 17 and 18) as the coupling products, indicating the influence of the phenyl ring on the benzhydric alcohol. It was noticed that the yield remained relatively constant with sulfonamide nucleophiles of varying electronic and steric properties, because electron-rich 4-methyl- and 2-methylbenzenesulfonamide yielded the corresponding amidation products in 92–90% yield (Table 2, entries 5 and 6). The sulfonamide nucleophile also smoothly underwent substitution with a range of alcohols, giving overall good to excellent yields of the expected products (Table 2, entries 4, 11, 14, 15, 19, and 20). Ethyl carbamate was found to react excellently with benzylic alcohols possessing either electron-withdrawing or electron-donating substituents, and the reaction reached completion within 1–2 h; the corresponding substituted carbamates were obtained with 90–97% yield (Table 2, entries 8, 12, 16, and 21). We then conducted the reaction of benzhydrol **1a** with amines such as *p*-nitroaniline (**2i**), which gave a moderate yield of the product **3ai** (Table 2, entry 9). Unfortunately, other benzylic, cyclic, and allylic alcohols were not compatible with this nucleophilic substitution protocol (Table 2, entries 22–24).

To explore the generality of the protocol, we then extended this methodology to the hydroamination of alkenes, whereby initial reaction of styrene (**4a**) with benzamide (**2a**) using Amberlyst-15 in ionic liquid [Bmim][BF_4] afforded a mixture of the desired intermolecular hydroaminated product **5aa** and 1,3-diphenylbut-1-ene (**6**). Formation of the latter might be due to reaction of styrene with the intermediate phenylethyl cation, which, on subsequent elimination of a proton, gives alkene **6**. Therefore, to increase the yield of the desired hydroaminated product, an excess of nucleophile (amide) was added (3 equiv.); under these conditions, a 60% yield of product was obtained. Further increases in the amount of nucleophile had no profound effect on the product yield.

With the optimized conditions in hand, we further investigated a range of nitrogen nucleophile substrates **2** in the hydroamination reaction of alkenes **4**. The results are summarized in Table 3. The reaction of styrene with nitrogen-containing nucleophiles, namely benzamide, acrylamide, sulfonamide, *p*-toluenesulfonamide, and ethyl carbamates, gave the corresponding hydroaminated derivatives in moderate to good yields (Table 3, entries 1–5). Similarly, 3-methylstyrene (**4b**) also underwent hydroamination with both benzamide (**2a**) and *p*-toluenesulfonamide (**2e**) (Table 3, entries 6 and 7). When α-methyl styrene (**4c**) was treated with *p*-toluenesulfonamide (**2e**) it was observed that, instead of expected product **5ce**, under the acidic conditions α-methylstyrene itself underwent dimerization to form 4-methyl-2,4-diphenyl-2-pentene and 4-methyl-2,4-diphenyl-1-pentene in 55% combined yield (1:1) (Table 3 entry 8). Previously, Shirakawa and co-workers demonstrated the palladium-catalyzed dimerization of vinylarenes using indium triflates as a cocatalyst.[10] Herewith, under the same reaction conditions, we carried out the self-dimerization of styrene to generate the dimerized alkene **6** in more than 90% yield (Table 3, entry 9). Furthermore, it was observed that norbornene also underwent nucleophilic substitution with benzamide to provide the hydroaminated product **5da** (Table 3, entry 10).

Conclusions

Amberlyst-15 in the ionic liquid [Bmim][BF_4] was found to be an efficient, recyclable system for nucleophilic substitution reactions of alcohols and for hydroamination reactions of alkenes with several amides, sulfonamides, carbamates, and amines as nitrogen nucleophiles. Substitution of alcohols with nucleophiles generally provides higher yields of benzylated amides than the corresponding hydroamination of alkenes due to the formation of dimeric by-products. Notable advantages offered by this metal-free reaction system are the use of an ionic liquid as a greener solvent, higher yields of desired products, greater substrate compatibility, and simple workup procedures, making this approach an important supplement to existing methods.

Experimental Section

General: All chemicals and reagents were purchased from commercial suppliers and were used without further purification. Products were characterized by their respective melting points and by using IR (Perkin–Elmer FTIR), ^1H and ^{13}C NMR (Varian Mercury 300 NMR Spectrometer) spectroscopic analyses. The reactions were monitored by GC analysis (Perkin–Elmer/Chemito, 30 m × 0.32 mm, 1D-0.25 μm BP10) and by TLC analysis. The identities of the products were further confirmed by GC–MS analysis (Shimadzu GC–MS QP 2010). The various ionic liquids used were prepared as previously reported.[11]

Typical Procedure for Nucleophilic Substitution of Benzylic Alcohols with Nitrogen Nucleophiles: To a well-stirred mixture of Amberlyst-15 (opaque beads, 0.75 g) in [Bmim][BF_4] (2 mL), nucleophile **2a**–**i** (1 mmol) and alcohol **1a**–**g** (1 mmol) were added. The resulting reaction mass (homogeneous substrate) was further stirred at 80 °C and the progress of the reaction was monitored by GC/TLC. After completion of the reaction, the mixture was cooled to r.t., which led to the precipitation of a solid product. To this was added water (15 mL), which resulted in the separation of the ionic liquid phase as [Bmim][BF_4] is soluble in water. Ethyl acetate (2 × 5 mL) was then added, which separated the Amberlyst-15 resin beads from the reaction mass. This was then filtered off. The aqueous phase was further extracted with ethyl acetate (2 × 5 mL) to leave behind the residual product with the organic extract. This was dried with Na_2SO_4, and the solvent was evaporated in vacuo to yield the product. The crude product was subjected to further purification by column chromatography (silica gel; mesh size 60–120; petroleum ether/ethyl acetate, 90:10).

Typical Procedure for Hydroamination of Alkenes with Nitrogen Nucleophiles: To a well-stirred mixture of Amberlyst-15 (opaque beads, 0.75 g) in [Bmim][BF_4] (2 mL), nucleophile **2a**–**h** (3 mmol) and alkenes **4a**–**d** (1 mmol) were added. The resulting reaction mass (homogeneous substrate) was then stirred at 80 °C in a sealed tube and the reaction was monitored by GC/TLC until completion. After completion of the reaction, the mixture was cooled to r.t., which led to the precipitation of a solid product. To this was added water (15 mL), which resulted in the separation of the ionic liquid phase as [Bmim][BF_4] is soluble in water. Ethyl acetate (2 × 5 mL) was

then added, which separated the Amberlyst-15 resin beads from the reaction mass. This was then filtered off. The aqueous phase was further extracted with ethyl acetate (2× 5 mL) to leave behind the residual product with the organic extract. This was dried with Na_2SO_4, and the solvent was evaporated in vacuo to yield the product. The crude product was subjected to further purification by column chromatography (silica gel; mesh size 60–120; petroleum ether/ethyl acetate, 90:10).

Typical Procedure for Recycling the Ionic Liquid and Reagent for the Nucleophilic Substitution of Benzhydrol with Benzamide: After completion of reaction, the reaction mixture was cooled to r.t. and diluted with water (15 mL). The aqueous solution was then extracted with ethyl acetate (2×5 mL). The aqueous layer consisting of the ionic liquid was distilled for 2 h to remove water, leaving behind the ionic liquid [Bmim][BF_4] (recovery 96%). Filtered Amberlyst-15 and recovered ionic liquid were dried under vacuum for 1 h and then charged with benzhydrol and benzamide again for the recyclability study. It was observed that recovered ionic liquid and reagent could be reused for three consecutive cycles for the amidation of benzhydrol with only a slight decrease in yield (88, 86, then 84%).

***N*-Benzhydrylbenzamide (3aa):** Yield 88% (252 mg), white solid, m.p. 168 °C. IR (KBr): $\tilde{\nu}$ = 3313, 3056, 3027, 1638, 1520, 1495, 1359, 1314, 1262, 1245, 1088, 1028, 940, 853, 799, 754, 738, 706, 692, 600, 577, 464 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.83–7.80 (d, J = 7.6 Hz, 2 H), 7.53–7.25 (m, 13 H), 6.68 (br., 1 H), 6.45 (d, J = 7.6 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.48 (C=O), 141.47 (C), 134.26 (C), 131.70 (C), 128.76 (4×CH), 128.64 (2×CH), 127.6 (3×CH), 127.51 (4×CH), 127.1 (2×CH), 57.46 (CH) ppm. MS (EI): m/z (%) = 287 (62), 210 (11), 182 (25), 165 (24), 105 (100), 77 (58), 45 (31).

***N*-Benzhydryl-4-methylbenzenesulfonamide (3ae):** Yield 92% (310 mg), white solid, m.p. 156 °C. IR (KBr): $\tilde{\nu}$ = 3249, 2656, 2358, 1599, 1495, 1451, 1315, 1161, 1096, 1059, 1029, 941, 811, 751, 700, 677, 572, 488 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.5–7.54 (d, J = 8.2 Hz, 2 H), 7.25–7.09 (m, 12 H), 5.57–5.55 (d, J = 7.1 Hz, 1 H), 5.4–5.37 (d, J = 7.0 Hz, 1 H), 2.35 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.22 (C), 140.53 (C), 137.38 (2×C), 129.37 (2×CH), 128.57 (4×CH), 127.61 (2×CH), 127.38 (4×CH), 127.22 (2×CH), 61.35 (CH), 21.50 (CH_3) ppm. MS (EI): m/z (%) = 337 (1), 322 (1), 260 (2), 183 (15), 167 (17), 155 (16), 104 (27), 91 (40), 77 (23), 45 (53).

***N*-Benzhydryl-2-methylbenzenesulfonamide (3af):** Yield 90% (303 mg), white solid, m.p. 159–161 °C. IR (KBr): $\tilde{\nu}$ = 3423, 3297, 3080, 2961, 2879, 1571, 1455, 1314, 1163, 1042, 832, 763, 703, 612, 562 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.83–7.81 (d, J = 7.6 Hz, 2 H), 7.38–7.07 (m, 12 H), 5.51–5.49 (d, J = 7.1 Hz, 1 H), 5.09–5.07 (d, J = 6.3 Hz, 1 H), 2.43 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.41 (C), 138.04 (C), 136.91 (C), 136.43 (C), 132.69 (CH), 132.27 (CH), 129.68 (CH), 128.53 (4×CH), 127.65 (4×CH), 127.23 (CH), 125.99 (2×CH), 61.34 (CH), 20.09 (CH_3) ppm. MS–MS (ESI–): m/z calcd. for [M – 1] 336.44; found 336.20.

Ethyl Benzhydrylcarbamate (3ah): Yield 97% (247 mg), white solid, m.p. 127–130 °C. IR (KBr): 3286, 3027, 2989, 1712, 1686, 1530, 1492, 1443, 1366, 1273, 1239, 1179, 1130, 1078, 1041, 1026, 890, 825, 760, 742, 698, 609, 582, 469, 496 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.24 (m, 10 H), 5.99–5.96 (d, J = 7.6 Hz, 1 H), 5.37 (br., 1 H), 4.16–4.09 (q, J = 7 Hz, 2 H), 1.26–1.21 (t, J = 6.75 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.83 (C=O), 141.84 (2×C), 128.64 (2×CH), 127.45 (2×CH), 127.26 (2×CH), 61.14 (CH_2), 58.71 (CH), 14.56 (CH_3) ppm. MS (EI): m/z (%) = 255 (42), 226 (16), 225 (99), 182 (100), 152 (17), 134 (6), 104 (96), 77 (43), 51 (14). MS–MS (ESI–): m/z calcd. for [M – 1] 254.31; found 253.93.

***N*-[(4-Chlorophenyl)phenylmethyl]-4-methylbenzenesulfonamide (3be):** Yield 94% (349 mg), white solid, m.p. 115 °C. IR (KBr): 3240, 3057, 3032, 2866, 1914, 1598, 1489, 1433, 1321, 1161, 1092, 1049, 935, 904, 871, 836, 804, 745, 701, 670, 629, 573, 539, 483 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.52 (d, J = 8.2 Hz, 2 H), 7.25–7.03 (m, 11 H), 5.54–5.51 (d, J = 7.6 Hz, 1 H), 5.47–5.45 (d, J = 7 Hz, 1 H), 2.38 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.46 (C), 140.06 (C), 138.99 (C), 137.17 (C), 133.46 (C), 129.42 (2×CH), 128.78 (2×CH), 128.73 (2×CH), 128.62 (2×CH), 127.86 (2×CH), 127.27 (CH), 127.18 (2×CH), 60.75 (CH), 21.50 (CH_3) ppm. MS–MS (ESI–): m/z calcd. for [M – 1] 370.88; found 370.20.

Ethyl [(4-Chlorophenyl)phenylmethyl]carbamate (3bh): Yield 95% (274 mg), white solid, m.p. 117 °C; (KBr): 3283, 3027, 2983, 2763, 1909, 1711, 1684, 1531, 1491, 1367, 1278, 1238, 1171, 1089, 1041, 894, 848, 755, 700, 609, 504, 482 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.16 (m, 9 H), 5.94–5.91 (d, J = 7.6 Hz, 1 H), 5.33 (br., 1 H), 4.16–4.08 (q, J = 7 Hz, 2 H), 1.25–121 (t, J = 6.45 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.74 (C=O), 141.20 (C), 140.34 (C), 133.16 (C), 128.76 (2×CH), 128.71 (2×CH), 128.53 (2×CH), 127.69 (2×CH), 127.23 (CH), 61.19 (CH_2), 58.14 (CH), 14.51 (CH_3) ppm. MS (EI): m/z (%) = 289 (34), 260 (97), 216 (100), 201 (23), 180 (14), 165 (50), 152 (5), 165 (50), 138 (46), 127 (2), 104 (75), 79 (12), 77 (35), 51 (12). MS–MS (ESI–): m/z calcd. for [M – 1] 288.76; found 288.07.

***N*-[Phenyl(*p*-tolyl)methyl]benzamide (3ca):** Yield 88% (264 mg), white solid, m.p. 162 °C. IR (KBr): 3313, 3060, 3032, 2917, 1908, 1638, 1579, 1523, 1489, 1353, 1321, 1246, 1178, 1084, 1053, 929, 856, 796, 775, 741, 703, 577, 478 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.81–7.79 (d, J = 7 Hz, 2 H), 7.52–7.42 (t, J = 7.05 Hz, 1 H), 7.44–7.41 (t, J = 7.35 Hz, 2 H), 7.36–7.27 (m, 5 H), 7.19–7.17 (d, J = 8.2 Hz, 2 H), 7.13–7.15 (d, J = 7.6 Hz, 2 H), 6.70–6.68 (d, J = 7 Hz, 1 H), 6.42–6.39 (d, J = 7.6 Hz, 1 H), 2.33 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.44 (C=O), 141.62 (C), 138.55 (C), 137.30 (C), 134.31 (C), 131.65 (CH), 129.44 (2×CH), 128.70 (2×CH), 128.62 (2×CH), 127.46 (3×CH), 127.41 (2×CH), 127.04 (2×CH), 57.2 (CH), 21.1 (CH_3) ppm. MS–MS (ESI–): m/z calcd. for [M – 1] 300.38; found 300.20.

***N*-[Phenyl(*p*-tolyl)methyl]benzenesulfonamide (3cd):** Yield 87% (293 mg), white solid, m.p. 148 °C. IR (KBr): 3248, 3054, 2873, 1508, 1435, 1317, 1159, 1092, 1052, 929, 845, 757, 723, 699, 593, 555, 480 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.68–7.65 (d, J = 7.9 Hz, 2 H), 7.48–7.43 (t, J = 7.5 Hz, 1 H), 7.35–7.30 (t, J = 7.7 Hz, 2 H), 7.20–7.14 (m, 3 H), 7.11–7.07 (m, 2 H), 7.01–6.98 (d, J = 8.5 Hz, 2 H), 6.97–6.94 (d, J = 8.5 Hz, 2 H), 5.56–5.54 (d, J = 7.1 Hz, 1 H), 5.33–5.30 (d, J = 7.3 Hz, 1 H), 2.26 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.48 (C), 140.37 (C), 137.5 (C), 137.46 (C), 132.35 (CH), 129.27 (2×CH), 128.75 (2×CH), 128.54 (2×CH), 127.57 (1×CH), 127.29 (2×CH), 127.27 (2×CH), 127.16 (2×CH), 61.17 (CH), 21.02 (CH_3) ppm. MS–MS (ESI–): m/z calcd. for [M – 1] 336.44; found 336.20.

Ethyl (Phenyl-*p*-tolylmethyl)carbamate (3ch): Yield 93% (250 mg), white solid, m.p. 104 °C. IR (KBr): 3323, 3029, 2967, 2862, 2774, 1912, 1805, 1706, 1688, 1539, 1495, 1459, 1368, 1338, 1297, 1251, 1169, 1080, 1038, 919, 886, 814, 738, 701, 677, 617, 591, 507, 463 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.05–7.31 (m, 9 H), 5.90–5.88 (d, J = 6.5 Hz, 1 H), 5.24 (br., 1 H), 4.12–4.05 (q, J = 7.2 Hz, 2 H), 2.29 (s, 3 H), 1.22–4.17 (t, J = 7 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.80 (C=O), 141.97 (C), 138.87

(C), 137.10 (C), 129.29 (2×CH), 128.56 (2×CH), 127.31 (2×CH), 127.14 (2×CH), 121.95 (CH), 61.02 (CH_2), 58.43 (CH), 21.02 (CH_3) ppm. MS (EI): *m/z* (%) = 269 (44), 254 (2), 240 (11), 223 (5), 208 (6), 196 (87), 192 (7), 181 (28), 165 (30), 152 (5), 141 (2), 134 (1), 120 (10), 118 (32), 104 (79), 91 (20), 77 (23), 65 (8), 51 (5), 45 (3). MS–MS (ESI–): *m/z* calcd. for [M – 1] 268.34; found 268.15.

***N*-(1-Phenylethyl)-*p*-toluenesulfonamide (3de):** Yield 86% (236 mg), white solid, m.p. 82 °C. IR (KBr): 3253, 3068, 2970, 1597, 1494, 1451, 1430, 1323, 1303, 1209, 1156, 1121, 1083, 1018, 957, 869, 812, 766, 703, 673, 559, 539 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.64–7.6 (d, *J* = 8.2 Hz, 2 H), 7.25–7.01 (m, 7 H), 5.34–5.32 (d, *J* = 7.1 Hz, 1 H), 4.47–4.42 (qd, *J* = 7 Hz, 1 H), 2.37 (s, 3 H), 1.14–1.39 (d, *J* = 7 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.02 (C), 142.15 (C), 137.65 (C), 129.4 (2×CH), 128.44 (2×CH), 127.30 (2×CH), 127.07 (CH), 126.13 (2×CH), 53.65 (CH), 23.57 (CH_3), 21.46 (CH_3) ppm. MS (EI): *m/z* (%) = 275 (1), 211 (2), 196 (12), 155 (63), 120 (66), 91 (100), 77 (22), 65 (26).

Ethyl (1-Phenylethyl)carbamate (3dh): Yield 94% (181 mg), pale yellow oil. IR (KBr): 3325, 2979, 2928, 2361, 1704, 1534, 1450, 1383, 1331, 1248, 1098, 1070, 781, 763, 700, 618, 559 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.24 (m, 5 H), 5.10–5.08 (d, *J* = 5.9 Hz, 1 H), 4.83 (br., 1 H), 4.14–4.05 (q, *J* = 6 Hz, 2 H), 1.47–1.45 (d, *J* = 6.5 Hz, 3 H), 1.33–1.18 (t, *J* = 8 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.93 (C=O), 143.82 (C), 128.59 (2×CH), 127.22 (2×CH), 125.94 (1×CH), 60.78 (CH_2), 50.54 (CH), 22.53 (CH_3), 14.60 (CH_3) ppm. MS (EI): *m/z* (%) = 193 (36), 178 (100), 164 (85), 150 (71), 134 (24), 120 (60), 106 (11), 103 (19), 91 (8), 79 (78), 51 (19), 42 (51). MS–MS (ESI–): *m/z* calcd. for [M – 1] 192.11; found 191.93.

1,3-Diphenylbut-1-ene (6): Yield 90% (187 mg), pale yellow oil. IR (KBr): 3026, 2963, 2854, 1687, 1600, 1493, 1451, 1384, 1264, 1113, 1017, 965, 909, 743, 698, 617, 539, 487 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.15 (m, 10 H), 6.39–6.38 (m, 2 H), 3.67–3.59 (m, 1 H), 1.47–1.44 (d, *J* = 7 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.60 (C_{ipso}), 137.6 (C-1), 128.5 (C-2), 128.4 (C_{ortho}), 128.29 (C-3), 127.03 (C_{meta}), 126.20 (C-4), 126.14 (C_{para}), 42.60 (CH), 21.21 (CH_3) ppm. MS (EI): *m/z* (%) = 208 (60), 193 (57), 178 (26), 179 (19), 152 (4), 115 (100), 91 (39), 77 (16), 44 (12).

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