Highly Efficient and Reusable Ionic Liquids for the Catalyzed Hydroamination of Alkenes with Sulfonamides, Carbamates, and Carboxamides

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Abstract: SO_3H-Functionalized ionic liquids were found to be efficient and reusable catalysts in the hydroamination of sulfonamides, carboxamides, *p*-nitroaniline and carbamates with nonactivated alkenes. The hydroamination could be performed on a large scale and the acidic ionic liquid catalyst could be reused successfully.

Key words: hydroamination, ionic liquid, green chemistry, alkene, homogeneous catalysis

New C–N bond-forming processes are highly fundamental and interesting for both organic syntheses and industrial processes due to the importance of nitrogen-containing molecules as fine chemicals, pharmaceuticals and useful building blocks.[1] In the existing methods for the construction of the C–N bond, the direct addition of amines to alkenes and alkynes, hydroamination, is rapidly increasing in interest as a convenient and atom-economical method for the preparation of amines, enamines and imines.[2] Despite significant efforts that have been devoted to the intermolecular hydroamination of alkenes with alkylamines and arylamines, only a few reports of the intermolecular hydroamination of nonactivated alkenes with weakly basic amine nucleophiles such as sulfonamides, carbamates and carboxamides are known.

Recently, efficient hydroaminations of amides and carbamates catalyzed by platinum(II),[3] gold(I),[4] copper(II),[5] iron(III),[6] and other metal salts[7] were reported. Along with the metal catalysts, there were some examples using metal-free catalysts for the hydroamination of alkenes and amides.[8] Although some notable progress has been made on the hydroamination reactions of alkenes with amides in the past two years, there were also some drawbacks on the reported methods, such as, using expensive and toxic metals, high reaction temperature, large excess amounts of alkenes and tedious reaction procedures. Additionally, most of the reported methods must be carried out under an inert atmosphere. Therefore, the development of a general, efficient, green and practical catalyst for addition reactions of nonactivated alkenes with sulfonamides, carboxamides and carbamates is highly desirable.

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In recent years, ionic liquids (ILs) have attracted considerable interest and been successfully used in a variety of catalytic reactions as environmentally benign reaction media and catalysts due to their unique properties such as a wide liquid range, good solvating ability, tuneable polarity, high thermal stability, negligible vapor pressure, and ease of recyclability.[9] Recently, advances in the field of ionic liquids research provides another route to achieving task-specific ionic liquids (TSILs) in which a functional group is covalently tethered to the cation or anion of the ionic liquid.[10] When an alkane sulfonic acid group is covalently tethered to the IL cation, the IL would be a strong Brønsted acid. These functionalized ionic liquids have exhibited great potential in replacement of conventional homogenous and heterogeneous acidic catalysts because they are nonvolatile, noncorrosive and immiscible with many organic solvents.

Although some examples of the addition of amines to alkenes in ionic liquids were reported recently,[11] to the best of our knowledge hydroamination of amides with alkenes catalyzed by functional ionic liquids was unknown. As part of our studies to explore the use of existing ionic liquids in chemical reactions,[12] and in continuation of our work on the construction of the C–N bond,[13] we first report here the hydroamination of alkenes with sulfonamides, carboxamides and carbamates using SO_3H-functionalized acidic ionic liquids catalysts.

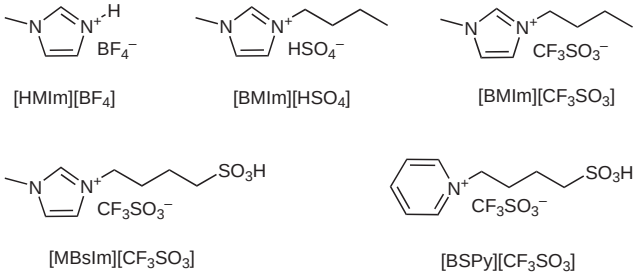


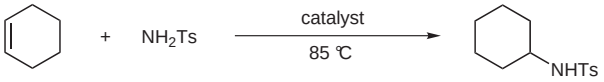
Figure 1 Five existing ionic liquids used in hydroamination

We initially tested the hydroamination of cyclohexene with *p*-toluenesulfonamide at 85 °C in the presence of several ionic liquids under different reaction conditions in air. Five existing ionic liquids, that is, $[HMIm][BF_4]$, $[BMIm][HSO_4]$, $[BMIm][CF_3SO_3]$, $[MBsIm][CF_3SO_3]$ and $[BSPy][CF_3SO_3]$, have been used (Figure 1). As

shown in Table 1, the ionic liquid catalyst has a significant effect on the yield of the reaction, only a trace of hydroamination adduct was obtained in the presence of [HMIm][BF_4] and [BMIm][HSO_4] (entries 1 and 2). Under these conditions, [BSPy][CF_3SO_3] proved to be very active, leading to 72% yield of *N*-cyclohexyl *p*-toluenesulfonamide within 24 hours (entry 5). [BMIm][CF_3SO_3] and [MBsIm][CF_3SO_3] could also be used as catalysts to promote the hydroamination, but their activity seems to be inferior compared with that of [BSPy][CF_3SO_3] (entries 3 and 4). These results indicated that both the anion and the acidity of the ionic liquid were very important for achieving high yield of the product.[10d] In view of this, [BSPy][CF_3SO_3] should be a suitable catalyst for the hydroamination reaction. On the basis of above results, a series of solvents were also screened (entries 6–10). We found that polar solvents such as 1,4-dioxane and acetonitrile tended to shut down the reacting system, whereas nonpolar solvents such as 1,2-dichloroethane (DCE) and toluene seemed to be ideal. Moderate yield of the hydroamination product was obtained when the catalyst loading was decreased to 10% (entry 11). Increasing catalyst loading resulted in no favourable improvement of the yield (entries 12 and 13).

To study the scope of the procedure, other alkenes with amides were then studied, and the results are listed in Table 2. Benzenesulfonamide ($PhSO_2NH_2$), electron-deficient 4-nitrobenzenesulfonamide and hindered *N*-methyl-4-toluenesulfonamide underwent ionic liquid [BSPy][CF_3SO_3]-catalyzed hydroamination of cycloheptene or cyclohexene to form the corresponding products in moderate to good yield (entries 1–4). The hydroamination reactions of *p*-toluenesulfonamide (NH_2Ts) with various vinyl arenes gave fast and high-yielding reactions under mild reaction conditions (entries 5, 7 and 8). Interestingly, in the presence of electron-donating groups such as *p*-Me, the reactions could be carried out at room temperature (entry 6). We also extended this reaction to other nitrogen-containing molecules, such as 2-oxazolidinone. The reaction gave good yield of the desired product under optimized reaction conditions (entry 9). The addition of various amides to the more strained norbornene furnished the hydroamination products in excellent yields (entries 10–13), except benzamide, only affording the product in 28% yield when using dioxane as solvent [benzamide and $NsNH_2$ were not very soluble in toluene or 1,2-dichloroethane (entry 12)]. We further extended the scope of this methodology to 1,3-diene, both benzyl carbamate ($CbzNH_2$) and sulfonamides could be added to 1,3-cyclohexadiene after 24 hours at 50 °C to form allylamines in good yields (entries 14 and 15).

Table 1 Hydroamination of *p*-Toluenesulfonamide and Cyclohexene under Different Conditions[a]

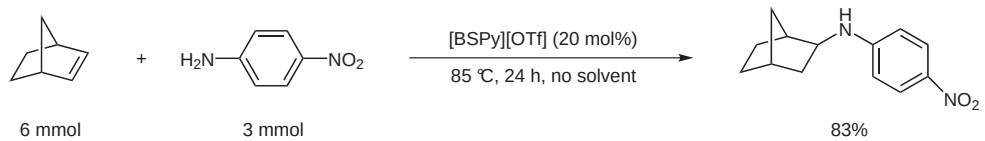


Entry	Ionic liquid	Solvent	Yield (%)[b]
1	[HMIm][BF_4]	MePh	trace
2	[BMIm][HSO_4]	MePh	trace
3	[BMIm][CF_3SO_3]	MePh	23
4	[MBsIm][CF_3SO_3]	MePh	65
5	[BSPy][CF_3SO_3]	MePh	72
6	[BSPy][CF_3SO_3]	DCE	62
7	[BSPy][CF_3SO_3]	dioxane	trace
8	[BSPy][CF_3SO_3]	CH_2Cl_2	25
9	[BSPy][CF_3SO_3]	MeCN	trace
10	[BSPy][CF_3SO_3]	*n*-heptane	34
11[c]	[BSPy][CF_3SO_3]	MePh	42
12[d]	[BSPy][CF_3SO_3]	MePh	75
13[e]	[BSPy][CF_3SO_3]	MePh	80

[a] Reaction conditions: cyclohexene (2 mmol), NH_2Ts (1 mmol), ionic liquid (0.2 mmol), solvent (2 mL), 85 °C, 24 h, sealed tube.
[b] Isolated yield.
[c] Using 0.1 mmol of ionic liquid.
[d] Using 0.3 mmol of ionic liquid.
[e] Using 1 mmol of ionic liquid.

Further studies also showed that the addition of *p*-nitroaniline to norbornene furnished the hydroamination product in high yield under solvent-free conditions (Scheme 1).

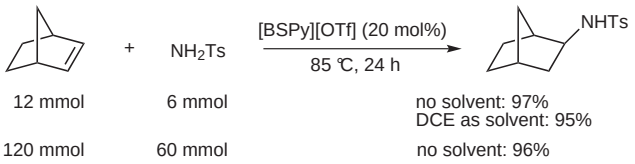
In order to broaden the scope of the reaction, we also wanted to show that the reaction could be performed at larger scales, demonstrating that acidic ionic liquid could be suitable for a scaleup experiment. In a typical procedure, into a test tube were placed [BSPy][CF_3SO_3] (20 mol%), NH_2Ts (6 mmol), norbornene (12 mmol) and 1,2-dichloroethane (5 mL). After sealing, the reaction mixture was heated at 85 °C and stirred vigorously for 24 hours. When the reaction was complete, the mixture was concentrated in vacuo to remove the 1,2-dichloroethane. The crude product was then separated by simple extraction (EtOAc–Et_2O, 1:1) and purified by column chromatography to give the pure product. We were also pleased to find that the same addition reaction could be performed under



Scheme 1 Hydroamination of *p*-nitroaniline with norbornene

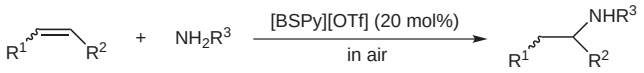
solvent-free conditions, yielding the hydroamination product in a gram scale. In addition, we obtained the product in 96% yield even using 60 mmol of the NH_2Ts (Scheme 2).

Finally, we investigated the reusability and the recycling of the acidic ionic liquid [BSPy][CF_3SO_3], and found that the catalyst could be easily recovered after completion of the reaction and reused in subsequent recycles (Table 3). The activity of the catalyst only showed a slight decrease after three runs.



Scheme 2 Hydroamination of NH_2Ts with norbornene on a large scale

Table 2 Hydroamination of Nonactivated Alkenes with Nitrogen Nucleophiles[a]



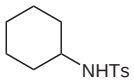
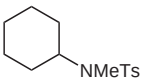
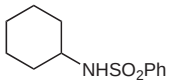
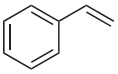
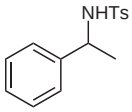
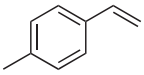
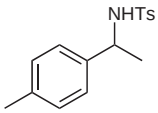
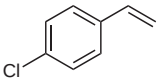
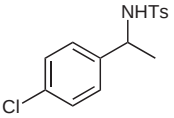
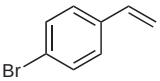
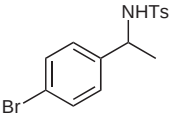
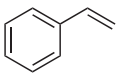
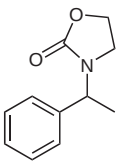
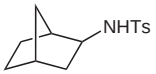
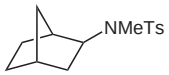
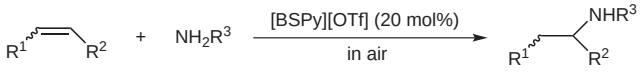
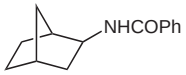
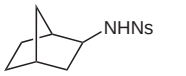
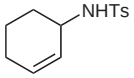
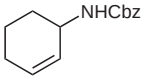
Entry	Alkene	Nucleophile	Time (h)/ Temp (°C)	Solvent	Product	Yield (%)[b]
1		NH_2Ts	24/85	MePh		66
2		NH_2Ns	36/85	MePh		52
3		NHMeTs	34/85	MePh		42
4		$PhSO_2NH_2$	28/85	MePh		54
5		NH_2Ts	22/45	DCE		72
6		NH_2Ts	24/r.t.	DCE		70
7		NH_2Ts	24/45	DCE		91
8		NH_2Ts	24/45	DCE		89
9		2-Oxa[c]	24/85	MePh		79
10		NH_2Ts	24/85	DCE		96
11		NHMeTs	24/85	DCE		86

Table 2 Hydroamination of Nonactivated Alkenes with Nitrogen Nucleophiles[a] (continued)



Entry	Alkene	Nucleophile	Time (h)/ Temp (°C)	Solvent	Product	Yield (%)[b]
12		$PhCONH_2$	24/85	dioxane		28
13		NH_2Ns	24/85	dioxane		92
14		NH_2Ts	24/50	DCE		54
15		NH_2Cbz	24/50	DCE		62

[a] Reaction conditions: alkene (2 mmol), NH_2Ts (1 mmol), [BSPy][CF_3SO_3] (0.2 mmol), solvent (2 mL), sealed tube, in air.
[b] Isolated yield.
[c] 2-Oxa = 2-oxazolidinine.

Table 3 Reuse of the [BSPy][CF_3SO_3] Ionic Liquid for the Hydroamination of NH_2Ts with Norbornene[a]

Recycle number	1st	2nd	3rd	4th
Product yield (%)[b]	97	95	94	90

[a] Reaction conditions: norbornene (6 mmol), NH_2Ts (3 mmol), [BSPy][CF_3SO_3] (0.6 mmol), 85 °C, no solvent, 24 h.
[b] Isolated yield.

In summary, the use of acidic ionic liquids as catalysts for the hydroamination of sulfonamides, carboxamides, carbamates and anilines to various alkenes in good to excellent yields avoids the use of expensive and air-sensitive metal reagents or high temperature reaction conditions to promote the reaction. The acidic ionic liquid [BSPy][CF_3SO_3] can be recovered conveniently and reused up to four times under solvent-free conditions, although with some loss of activity. Moreover, this methodology offers significant improvements with regard to the scope of this transformation, simplicity in operation, and green aspects by avoiding expensive and toxic metals catalysts or corrosive catalysts. These advantages of this novel catalytic system are expected to contribute to the development of further benign hydroaminations of amides with alkenes.

All reactions were performed in sealed oven-dried glass tubes in air. Ionic liquids used were prepared according to previous methods.[14] All common reagents were obtained from commercial suppliers and used without further purification. Thin-layer chromatography (TLC) was performed on silica gel GF254 eluting with PE–EtOAc, 5:1 unless noted otherwise. Column chromatography was carried out using silica gel (200–300 mesh) eluting with PE–EtOAc. NMR spectra were obtained on a Varian spectrometer operating at 400 MHz for ^1H and 100 MHz for ^{13}C in $CDCl_3$ unless noted otherwise. All coupling constants are reported in hertz (Hz). GC-MS data was obtained on an Agilent 6890-N GC system with an Alltech EC-1 capillary column (30 m × 0.25 mm × 0.25 μm) and an Agilent 5973 mass selective detector.

Intermolecular Addition Reactions of Amides or Carbamates to Alkenes; Typical Procedure

Into a test tube were placed [BSPy][CF_3SO_3] (20% mol), NH_2Ts (1 mmol), toluene (2 mL) and cyclohexene (2 mmol) together in air. After sealing, the mixture was heated at 80 °C and stirred vigorously for 24 h. After the reaction was completed, the mixture was concentrated in vacuo to remove the toluene. The product was then separated by simple extraction (EtOAc–Et_2O, 1:1), and purified by column chromatography (EtOAc–PE, 1:10 to 1:5) to give the analytically pure product (72% yield). The insoluble ionic liquid left in the reaction vessel could be directly recycled for subsequent runs. All the known compounds were determined by GC-MS or NMR.

Intermolecular Addition Reactions of Amides or Anilines to Alkenes under Solvent-Free Conditions: General Procedure

Into a test tube were placed [BSPy][CF_3SO_3] (20% mol), NH_2Ts (6 mmol, 1.03 g) and norbornene (12 mmol) together in air. After sealing, the mixture was heated at 85 °C and stirred vigorously for 24 h. After the reaction was completed, the crude product was then separated by simple extraction (EtOAc–Et_2O, 1:1) and further purified by column chromatography to give the pure product (97% yield). The insoluble ionic liquid left in the reaction vessel could be directly recycled for subsequent runs.

All the compounds are known and NMR or GC-MS data for some representative products are given below.

***N*-Cyclohexyl-*p*-toluenesulfonamide**

White solid; mp 83–85 °C.

^1H NMR (400 MHz): δ = 7.77 (d, *J* = 8.0 Hz, 2 H), 7.28–7.26 (t, *J* = 8.0 Hz, 2 H), 4.55 (d, *J* = 6.4 Hz, 1 H), 3.10–3.07 (m, 1 H), 2.40 (s, 3 H), 1.73–1.70 (m, 2 H), 1.62–1.58 (m, 2 H), 1.50–1.46 (m, 1 H), 1.29–1.06 (m, 5 H).

^{13}C NMR (100 MHz): δ = 143.09, 138.40, 129.60, 126.90, 52.53, 33.89, 25.10, 24.60, 21.51.

GC-MS: *m*/*z* = 253.

***N*-Cyclopentyl-*p*-toluenesulfonamide**

White solid; mp 81–83 °C.

^{1}H NMR (400 MHz): δ = 7.75 (d, *J* = 8.0 Hz, 2 H), 7.26 (d, *J* = 8.0 Hz, 2 H), 4.96 (s, 1 H), 3.56–3.51 (m, 1 H), 2.44 (s, 3 H), 1.73–1.70 (m, 2 H), 1.64–1.59 (m, 2 H), 1.52–1.46 (m, 1 H), 1.25–1.08 (m, 5 H).

^{13}C NMR (100 MHz): δ = 143.15, 137.77, 129.59, 127.06, 55.06, 33.30, 23.05, 21.47.

GC-MS: *m*/*z* = 239.

***N*-Cyclohexyl-*p*-nitrobenzenesulfonamide**
White solid; mp 135–137 °C.

^{1}H NMR (400 MHz): δ = 8.36–8.32 (m, 2 H), 8.07–8.04 (m, 2 H), 4.77 (d, *J* = 8.0 Hz, 1 H), 3.23–3.16 (m, 1 H), 1.75–1.72 (m, 2 H), 1.65–1.53 (m, 2 H), 1.53–1.48 (m, 1 H), 1.28–1.07 (m, 5 H).

^{13}C NMR (100 MHz): δ = 149.89, 147.41, 128.09, 124.37, 53.09, 33.95, 24.93, 24.55.

GC-MS: *m*/*z* = 284.

***N*-Cyclohexylbenzenesulfonamide**
White solid; mp 88–90 °C.

^{1}H NMR (400 MHz): δ = 7.89–7.86 (m, 2 H), 7.56–7.46 (m, 3 H), 4.85 (br s, 1 H), 3.15–3.08 (m, 1 H), 1.72–1.69 (m, 2 H), 1.62–1.57 (m, 2 H), 1.49–1.44 (m, 1 H), 1.24–1.02 (m, 5 H).

^{13}C NMR (100 MHz): δ = 141.37, 132.36, 128.98, 126.81, 52.58, 33.81, 25.05, 24.55.

GC-MS: *m*/*z* = 239.

***N*-Cyclohexyl-*N*-methyl-*p*-toluenesulfonamide**
White solid; mp 74–76 °C.

^{1}H NMR (400 MHz): δ = 7.66 (d, *J* = 8.2 Hz, 2 H), 7.25 (d, *J* = 8.2 Hz, 2 H), 3.74–3.70 (m, 1 H), 2.69 (s, 3 H), 2.39 (s, 3 H), 1.70–1.68 (m, 2 H), 1.59–1.55 (m, 1 H), 1.46–1.44 (m, 2 H), 1.30–1.22 (m, 4 H), 0.98–0.94 (m, 1 H).

^{13}C NMR (100 MHz): δ = 142.80, 137.33, 129.57, 126.86, 56.71, 30.21, 28.56, 25.71, 25.31, 21.47.

GC-MS: *m*/*z* = 267.

***N*-[1-(4-Bromophenyl)ethyl]-*p*-methylbenzenesulfonamide**
White solid; mp 120–122 °C.

^{1}H NMR (400 MHz): δ = 7.57 (d, *J* = 8.4 Hz, 2 H), 7.27 (d, *J* = 8.4 Hz, 2 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 6.97 (d, *J* = 8.0 Hz, 2 H), 5.42 (d, *J* = 7.2 Hz, 1 H), 4.41 (quintet, *J* = 6.8 Hz, 1 H), 2.39 (s, 3 H), 1.37 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz): δ = 143.32, 140.00, 137.33, 131.43, 129.42, 127.92, 127.00, 121.16, 53.06, 23.35, 21.47.

GC-MS: *m*/*z* = 354.

***N*-[1-(4-Chlorophenyl)ethyl]-*p*-methylbenzenesulfonamide**
White solid; mp 129–131 °C.

^{1}H NMR (400 MHz): δ = 7.58 (d, *J* = 8.4 Hz, 2 H), 7.16 (d, *J* = 8.4 Hz, 2 H), 7.14 (d, *J* = 8.4 Hz, 2 H), 7.01 (d, *J* = 8.4 Hz, 2 H), 4.76 (d, *J* = 6.8 Hz, 1 H), 4.45 (quintet, *J* = 6.8 Hz, 1 H), 2.40 (s, 3 H), 1.38 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz): δ = 143.31, 140.50, 137.36, 133.09, 129.42, 128.49, 127.57, 127.01, 52.59, 23.42, 21.44.

GC-MS: *m*/*z* = 310.

***N*-[1-(4-Methylphenyl)ethyl]-*p*-methylbenzenesulfonamide**
White solid; mp 118–120 °C.

^{1}H NMR (400 MHz): δ = 7.62 (d, *J* = 8.4 Hz, 2 H), 7.13 (d, *J* = 8.4 Hz, 2 H), 7.00 (m, 4 H), 4.80 (d, *J* = 6.8 Hz, 1 H), 4.41 (quintet, *J* = 6.8 Hz, 1 H), 2.38 (s, 3 H), 2.27 (s, 3 H), 1.37 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz): δ = 143.03, 140.00, 137.65, 137.18, 129.42, 129.04, 127.02, 125.86, 53.20, 23.36, 21.41, 21.0.

GC-MS: *m*/*z* = 289.

***N*-Phenylethyl-oxazolidinone**
Light yellow oil.

^{1}H NMR (400 MHz): δ = 7.36–7.24 (m, 5 H), 7.27 (q, *J* = 6.8, 7.2 Hz, 1 H), 4.30–4.17 (m, 2 H), 3.51–3.44 (m, 1 H), 3.16–3.09 (m, 1 H), 1.55 (d, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz): δ = 157.91, 139.39, 128.62, 127.80, 126.96, 61.85, 51.35, 39.94, 16.25.

GC-MS: *m*/*z* = 191.

***N*-*exo*-Bicyclo[2.2.1]hept-2-yl-*p*-toluenesulfonamide**
White solid; mp 127–129 °C.

^{1}H NMR (400 MHz): δ = 7.73 (d, *J* = 7.2 Hz, 2 H), 7.28 (d, *J* = 7.6 Hz, 2 H), 4.61 (d, *J* = 6.4 Hz, 1 H), 3.10 (s, 1 H), 2.41 (s, 3 H), 2.16 (s, 1 H), 2.07 (s, 1 H), 1.59–1.54 (m, 1 H), 1.43–1.38 (m, 2 H), 1.31–1.29 (m, 2 H), 1.15–1.03 (m, 2 H), 0.99–0.87 (m, 2 H).

^{13}C NMR (100MHz): δ = 143.19, 137.84, 129.63, 127.06, 56.61, 42.44, 40.74, 35.54, 35.14, 27.96, 26.27, 21.51.

GC-MS: *m*/*z* = 265.

***N*-Methyl-*N*-*exo*-bicyclo[2.2.1]hept-2-yl-*p*-methylbenzenesulfonamide**
White solid; mp 76–78 °C.

^{1}H NMR (400 MHz): δ = 7.63 (d, *J* = 6.4 Hz, 2 H), 7.25 (d, *J* = 8.0 Hz, 2 H), 3.82–3.78 (m, 1 H), 2.68 (s, 3 H), 2.38 (s, 3 H), 2.17 (br s, 1 H), 1.83 (br s, 1 H), 1.55–1.48 (m, 1 H), 1.41–1.30 (m, 4 H), 1.16–1.10 (m, 1 H), 1.06–1.00 (m, 2 H).

^{13}C NMR (100 MHz): δ = 142.95, 136.16, 129.50, 127.16, 59.81, 39.02, 36.71, 36.55, 35.67, 29.78, 29.10, 27.24, 21.44.

GC-MS: *m*/*z* = 279.

Cyclohex-2-enyl-*p*-toluenesulfonamide
White solid; mp 102–104 °C.

^{1}H NMR (400 MHz): δ = 7.75 (d, *J* = 7.6 Hz, 2 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 5.71 (d, *J* = 10 Hz, 1 H), 5.31 (d, *J* = 10.4 Hz, 1 H), 4.84 (d, *J* = 8.4 Hz, 1 H), 3.77 (s, 1 H), 2.39 (s, 3 H), 1.94–1.77 (m, 2 H), 1.74–1.61 (m, 1 H), 1.57–1.50 (m, 3 H).

^{13}C NMR (100 MHz): δ = 143.14, 138.24, 131.39, 129.60, 126.95, 126.91, 48.89, 30.12, 24.38, 21.45, 19.22.

GC-MS: *m*/*z* = 251.

Benzyl Cyclohex-2-enylcarbamate
White solid; mp 51–53 °C.

^{1}H NMR (400 MHz): δ = 7.34–7.24 (m, 5 H), 5.81 (d, *J* = 8.8 Hz, 1 H), 5.59 (d, *J* = 10 Hz, 1 H), 5.08 (m, 2 H), 4.71 (br s, 1 H), 4.19 (br s, 1 H), 1.96 (s, 2 H), 1.90–1.88 (m, 1 H), 1.62–1.60 (m, 2 H), 1.57–1.51 (m, 1 H).

^{13}C NMR (100 MHz): δ = 155.60, 136.56, 130.87, 128.51, 128.14, 128.09, 127.65, 66.57, 46.30, 29.70, 24.73, 19.54.

GC-MS: *m*/*z* = 231.

***N*-(4-Nitrophenyl)bicyclo[2.2.1]heptan-2-amine**
Yellow solid; mp 115–117 °C.

^{1}H NMR (400 MHz): δ = 8.09–8.05 (m, 2 H), 6.50–6.46 (m, 2 H), 4.49 (s, 1 H), 3.31 (m, 1 H), 2.35 (s, 1 H), 2.29 (s, 1 H), 1.92–1.86

(m, 1 H), 1.56–1.50 (m, 2 H), 1.46–1.43 (dd, *J* = 8.4, 1.6 Hz 1 H), 1.43–1.16 (m, 4 H).

^{13}C NMR (100 MHz): δ = 152.51, 137.57, 126.38, 111.36, 56.32, 41.40, 40.89, 35.62, 35.48, 28.22, 26.22.

GC-MS: *m*/*z* = 232.

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