Supporting Information
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A Facile and Green Protocol for Nucleophilic Substitution Reactions of Sulfonate Esters by Recyclable Ionic Liquids [bmim][X]

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1. General.

All the reagents were purchased from Aldrich or TCI chemicals. Column chromatography was performed on Silica gel 60 (230-400 mesh, Merck®). 1H-NMR and 13C-NMR spectra were recorded on a Varian 500 NMR spectrometer with chemical shifts reported in ppm relative to residual solvent peaks or to TMS as the internal standard. Yields referred to the isolated yields of compounds greater than 95% pure as determined by 1H-NMR and GC analyses. All compounds were characterized by MS, 1H-NMR and 13C-NMR. Gas chromatography analyses were performed on a Hewlett Packard 8906 instrument with HP-1 capillary column and liquid chromatography analyses were performed on HP 5973 MSD with EI as the ionization method. The chiral GC spectra were recorded on an Agilent 6890N instrument with chiral capillary column (Cyclodex-1); 30 m × 0.25 mm) with a programmed temperature method (initial temperature 100 °C for 3 min; ramp up to 215 °C at a rate of 2.5 °C/min; held at 215 °C for 10 min). New compounds were further confirmed by using high resolution mass spectra (HRMS) recorded on a hybrid quadrupole orthogonal time-of-flight (Q-TOF) mass spectrometer (SYNAPT G2, Waters, MS Technologies, Manchester, U. K.) with electrospray ionization (ESI) as ionization method.

2. Preparation of sulfonate esters

General procedure: To a solution of alcohol (10 mmol) in pyridine (5 mL), was added tosyl chloride (15 mmol) or mesyl chloride (15 mmol), then the mixture was stirred for overnight at room temperature. The reaction mixture was acidified with 15% aqueous HCl (pH= ~2), then extracted with ethyl acetate (30 mL x 2). The organic layer was combined and washed with water and brine, then dried over anhydrous MgSO4 and concentrated. The crude product was purified by silica gel column chromatography using ethyl acetate/ hexane as eluent to give sulfonate esters.

3-phenylpropyl methanesulfonate [CAS 69804-99-5]
Colorless liquid (2.05 g, 9.58 mmol, 96% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.32- 7.18 (m, 5H), 4.23 (t, $J = 7.5$ Hz, 2H), 2.98 (s, 3H), 2.76 (t, $J = 7.5$ Hz, 2H), 2.10- 2.06 (m, 2H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 140.8, 128.8, 128.7, 126.6, 69.4, 37.6, 31.8, 30.9; GC-MS (m/z): 214 (M), 117 (100), 91, 65.

3-phenylpropyl 4-methylbenzenesulfonate [CAS 3742-75-4]

Colorless liquid (2.73 g, 9.41 mmol, 94% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.78 (d, $J = 8.0$ Hz, 2H), 7.34- 7.16 (m, 5H), 7.06 (d, $J = 8.0$ Hz, 2H), 4.02 (t, $J = 6.5$ Hz, 2H), 2.64 (t, $J = 7.0$ Hz, 2H), 2.45 (s, 3H), 1.97- 1.93 (m, 2H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 145.0, 140.7, 133.4, 130.1, 128.7, 128.6, 128.2, 126.4, 69.9, 3133.7, 30.7, 21.9; GC-MS (m/z): 290 (M), 155, 118 (100), 91, 65.

1-phenylpropan-2-yl methanesulfonate [CAS 61380-47-0]

Colorless liquid (1.85 g, 8.64 mmol, 86% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.34- 7.22 (m, 5H), 4.90- 4.86 (m, 1H), 2.99- 2.88 (m, 2H), 2.49 (s, 3H), 1.47 (d, $J = 6.5$ Hz, 3H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 137.1, 129.9, 128.9, 127.4, 81.8, 43.2, 37.9, 21.8; GC-MS (m/z): 214(M), 118 (100), 91, 79, 65.

benzyl methanesulfonate [CAS 55791-06-5]

Colorless liquid (1.68 g, 9.03 mmol, 90% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.41- 7.37 (m, 5H), 5.23 (s, 2H), 2.89 (s, 3H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 133.7, 129.7, 129.2, 129.1, 71.9, 38.6; GC-MS (m/z): 186 (M), 142, 122, 91 (100), 77, 65, 51.

phenethyl methanesulfonate [CAS 20020-27-3]
Colorless liquid (1.97 g, 9.86 mmol, 99% yield). $^1$H - NMR (500 MHz, CDCl$_3$): $\delta$ 7.34- 7.30 (m, 2H), 7.27- 7.22 (m, 3H), 4.16 (t, $J = 7.0$ Hz, 2H), 3.05 (t, $J = 7.0$ Hz, 2H), 2.83 (s, 3H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 136.6, 129.3, 129.0, 127.3, 70.6, 37.5, 35.9; GC-MS (m/z): 200 (M), 164 (100), 91, 79, 65, 51.

2-phenoxyethyl methanesulfonate [CAS 141482-06-6]

Colorless liquid (1.92 g, 8.89 mmol, 89% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.35- 7.28 (m, 2H), 7.03- 7.00 (m, 1H), 6.94- 6.90 (m, 2H), 4.58 (t, $J = 9.0$ Hz, 2H), 4.25 (t, $J = 9.0$ Hz, 2H), 3.10 (s, 3H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 158.2, 129.9, 121.9, 114.8, 68.5, 66.0, 38.0; GC-MS (m/z): 216 (M), 123 (100), 107, 94, 79, 65, 51.

4-phenylbutan-2-yl methanesulfonate [CAS 75803-21-3]

Colorless liquid (2.17 g, 9.52 mmol, 95% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.32- 7.25 (m, 2H), 7.21- 7.18 (m, 3H), 4.86- 4.82 (m, 1H), 2.98 (s, 3H), 2.80- 2.66 (m, 2H), 2.09- 2.01 (m, 1H), 1.95- 1.89 (m, 1H), 1.45 (d, $J = 6.0$ Hz, 3H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 141.0, 128.8, 128.6, 126.4, 79.8, 38.9, 38.5, 31.7, 21.5; GC-MS (m/z): 228 (M), 132, 117 (100), 91, 79, 65, 51.

octan-2-yl 4-methylbenzenesulfonate [CAS 1028-12-2]

Colorless liquid (2.49 g, 8.76 mmol, 88% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.79 (d, $J = 7.5$ Hz, 2H), 7.33 (d, $J = 7.5$ Hz, 2H), 4.63- 4.58 (m, 1H), 2.44 (s, 3H), 1.62- 1.57 (m, 1H), 1.50- 1.45 (m, 1H), 1.27- 1.16 (m, 1H), 0.87- 0.83 (m, 3H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 144.6, 135.0, 129.9, 127.9, 80.9, 36.7, 31.8, 29.0, 25.0, 22.7, 21.8, 14.2; GC-MS (m/z): 284 (M), 199, 173, 155 (100), 112, 91, 70, 55.

cycloheptyl 4-methylbenzenesulfonate [CAS 957-29-9]
Colorless liquid (2.31 g, 8.62 mmol, 86% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.78 (d, $J = 7.5$ Hz, 2H), 7.32 (d, $J = 7.5$ Hz, 2H), 4.68- 4.65 (m, 1H), 2.44 (s, 3H), 1.88- 1.82 (m, 2H), 1.79- 1.72 (m, 2H), 1.65- 1.34 (m, 6H), 1.37- 1.30 (m, 2H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 144.6, 134.9, 130.0, 127.8, 84.7, 34.8, 28.3, 22.4, 21.9; LC-MS (m/z): 286 (M+NH$_4^+$)

octyl 4-methylbenzenesulfonate [CAS 3386-35-4]

Colorless liquid (2.65 g, 9.33 mmol, 93% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.79 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 4.02 (t, $J = 7.0$ Hz, 2H), 2.45 (s, 3H), 1.65- 1.61 (m, 1H), 1.29- 1.19 (m, 11H), 0.87 (t, $J = 7.0$ Hz, 2H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 144.9, 133.5, 130.0, 128.1, 71.0, 31.9, 29.3, 29.1, 29.0, 25.6, 22.8, 21.9, 14.3; GC-MS (m/z): 284 (M), 173 (100), 155, 112, 91, 69, 55.

3-(biphenyl-4-yloxy)propyl methanesulfonate

White solid (2.55 g, 83.3 mmol, 83% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.56- 7.52 (m, 4H), 7.43- 7.40 (m, 2H), 7.33- 7.30 (m, 1H), 6.97 (d, $J = 8.5$ Hz, 2H), 4.47 (t, $J = 6.0$ Hz, 2H), 4.13 (t, $J = 6.0$ Hz, 2H), 3.00 (s, 3H), 2.28- 2.23 (m, 2H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 134.5, 129.0, 128.5, 127.0, 126.9, 115.0, 67.0, 63.5, 37.5, 29.4; HRMS calc. for C$_{16}$H$_{18}$O$_4$S (M+ Na)$^+$ 329.0823 found, 329.0839.

2-adamantyl 4-methybenzenesulfonate [CAS 25139-43-9]

White solid (2.51 g, 82.0 mmol, 82% yield, purified by recrystallization from hexane). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.80 (d, $J = 8.5$ Hz, 2H), 7.32 (d, $J = 8.5$ Hz, 2H), 4.69- 4.67 (m, 1H), 2.44 (s, 3H), 2.06- 2.03 (m, 2H), 1.99- 1.96 (m, 2H), 1.83- 1.79 (m, 4H), 1.72- 1.63 (m, 4H), 1.50- 1.49 (m, 2H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 144.5, 135.2, 129.9, 127.9, 127.7, 86.6, 37.3, 36.8, 36.6, 32.9, 31.4, 27.0, 26.8, 21.9; LC-MS (m/z): 324.0 (M+ NH$_4^+$)

3-(naphthalen-1-yloxy)propyl methanesulfonate [CAS 463934-08-9]

Pale yellow liquid (2.58 g, 9.17 mmol, 92% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 8.24- 8.22 (m, 1H), 7.81- 7.79 (m, 1H), 7.50- 7.27 (m, 4H), 6.83- 6.81 (m, 1H), 4.56 (t, $J = 5.5$ Hz, 2H), 4.28 (t, $J = 5.0$ Hz, 2H), 2.97 (s, 3H), 2.39- 2.36 (m, 2H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$
158.3, 134.7, 128.8, 126.7, 126.1, 125.7, 125.6, 121.9, 121.9, 120.9, 105.0, 67.1, 63.7, 37.5, 29.5; GC-MS (m/z): 280(M), 137 (100), 115, 79, 59.

**octan-3-yl 4-methylbenzenesulfonate [CAS 4883-87-8]**

![Structure](image)

Colorless liquid (2.28 g, 8.03 mmol, 80% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.81- 7.78 (m, 2H), 7.34- 7.31 (m, 2H), 4.52- 4.49 (m, 1H), 2.45 (s, 3H), 1.64- 1.53 (m, 4H), 1.27- 1.15 (m, 6H), 0.89- 0.82 (m, 6H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 144.5, 135.0, 129.9, 127.9, 85.8, 33.7, 31.7, 27.3, 24.6, 22.7, 21.8, 14.1, 9.29; GC-MS (m/z): 284 (M), 255, 213, 173, 155 (100), 112, 91, 70, 55.

**cholesterol tosylate [CAS 1182-65-6]**

![Structure](image)

White solid (4.61 g, 85.2 mmol, 85% yield, purified by recrystalization from hexane/ethyl acetate). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.81- 7.80 (m, 2H), 7.34- 7.32 (m, 2H), 5.30 (s, 1H), 4.34- 4.30 (m, 1H), 2.45- 2.41 (m, 4H), 2.28- 2.25 (m, 1H), 2.01- 1.93 (m, 2H), 1.83- 1.80 (m, 3H), 1.74- 1.68 (m, 1H), 1.60- 1.22 (m, 10H), 1.13- 0.85 (m, 22H), 0.65 (s, 3H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 144.6, 139.1, 134.9, 130.0, 127.9, 123.8, 82.6, 56.9, 56.3, 50.1, 42.5, 39.9, 39.7, 39.1, 37.1, 36.6, 32.1, 32.0, 28.9, 28.4, 28.2, 24.5, 24.0, 23.1, 22.8, 21.9, 21.2, 19.4, 18.9, 12.1.

### 3. Nucleophilic substitution of sulfonate esters by ionic liquid [bmim][X]

General procedure: To a 20 mL closed tube was added sulfonate esters (1.0 mmol) and ionic liquid (1.0 mmol), then the mixture was stirred under Argon in the preheated oil bath. After reaction was completed, the mixture was distributed in water (10 mL) and diethyl ether (10 mL). The organic layer was separated and washed with brine (10 mL), dried over anhydrous MgSO$_4$ and concentrated to give the desired product.

**3-chloropropylbenzene (table 3, entry 2) [CAS 104-52-9]**

![Structure](image)

Colorless liquid (152 mg, 0.99 mmol, 99% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.31- 7.18 (m, 5H), 3.52 (t, $J$ = 6.5 Hz, 2H), 2.78 (t, $J$ = 7.5 Hz, 2H), 2.17- 2.05 (m, 2H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 141.0, 128.8, 128.7, 126.4, 44.5, 34.3, 33.0; GC-MS (m/z): 156 (M), 154 (M), 91 (100), 65.
(3-bromopropyl)benzene (table 3, entry 2) [CAS 637-59-2]

![3-bromopropyl]benzene

Colorless liquid (188 mg, 0.95 mmol, 95% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.30- 7.27 (m, 2H), 7.21- 7.18 (m, 3H), 3.38 (t, $J = 7.0$ Hz, 2H), 2.78- 2.75 (m, 2H), 2.18- 2.14 (m, 2H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 140.8, 128.9, 128.8, 126.5, 34.5, 34.3, 33.4; GC-MS (m/z): 200 (M), 198 (M), 91 (100), 65.

(3-iodopropyl)benzene (table 3, entry 2) [CAS 4119-41-9]

![3-iodopropyl]benzene

Colorless liquid (231 mg, 0.94 mmol, 94% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.30- 7.18 (m, 5H), 3.17 (t, $J = 7.0$ Hz, 2H), 2.77- 2.70 (m, 2H), 2.13 (t, $J = 7.0$ Hz, 2H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 140.7, 128.9, 128.8, 126.4, 36.5, 35.2, 6.7; GC-MS (m/z): 246 (M), 119, 91 (100), 65, 51.

(2-chloroethyl)benzene (table 3, entry 3 ) [CAS 622-24-2]

![2-chloroethyl]benzene

Colorless liquid (138 mg, 0.98 mmol, 98% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.33- 7.20 (m, 5H), 3.70 (t, $J = 7.5$ Hz, 2H), 3.06 (t, $J = 7.5$ Hz, 2H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 138.3, 128.9, 128.7, 126.3, 45.1, 39.4; GC-MS (m/z):142 (M), 140 (M), 91 (100), 77, 65, 51.

(2-bromoethyl)benzene (table 3, entry 3 ) [CAS 103-63-9]

![2-bromoethyl]benzene

Colorless liquid (179 mg, 0.97 mmol, 97% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.33- 7.20 (m, 5H), 3.60- 3.54 (m, 2H), 3.18- 3.14 (m, 2H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 139.1, 128.9, 128.8, 127.2, 39.7, 33.2; GC-MS (m/z):186 (M), 184 (M), 105, 91 (100), 77, 65, 51.

(2-iodoethyl)benzene (table 3, entry 3 ) [CAS 17376-04-4]

![2-iodoethyl]benzene

Colorless liquid (213 mg, 0.92 mmol, 92% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 7.33- 7.18 (m, 5H), 3.35 (t, $J = 7.5$ Hz, 2H), 3.18 (t, $J = 7.5$ Hz, 2H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 140.9, 128.9, 128.6, 127.1, 40.6, 6.0; GC-MS (m/z): 232 (M), 127, 105 (100), 77, 51.
benzyl chloride (table 3, entry 4) [CAS 100-44-7]

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\text{\includegraphics[width=0.2\textwidth]{benzyl chloride.png}}
\]

Colorless liquid (116 mg, 0.92 mmol, 92% yield). \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.38-7.31 (m, 5H), 4.57 (s, 2H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \(\delta\) 137.7, 129.0, 128.9, 128.7, 46.5; GC-MS (m/z): 128 (M), 126 (M), 91 (100), 65, 51.

benzyl bromide (table 3, entry 4) [CAS 100-39-0]

\[
\text{\includegraphics[width=0.2\textwidth]{benzyl bromide.png}}
\]

Colorless liquid (163 mg, mmol, 95% yield). \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.47-7.37 (m, 5H), 4.56 (s, 2H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \(\delta\) 138.1, 129.4, 129.2, 129.1, 128.8, 34.0; GC-MS (m/z): 172 (M), 170 (M), 91 (100), 65, 51.

(2-chloroethoxy)benzene (table 3, entry 5) [CAS 622-86-6]

\[
\text{\includegraphics[width=0.2\textwidth]{2-chloroethoxybenzene.png}}
\]

Colorless liquid (151 mg, 0.97 mmol, 97% yield). \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.30-7.26 (m, 2H), 6.99-6.89 (m, 3H), 4.20 (t, \(J = 6.0\) Hz, 2H), 3.79(t, \(J = 6.0\) Hz, 2H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \(\delta\) 158.4, 129.9, 129.8, 121.7, 115.0, 68.2, 42.2; GC-MS (m/z): 158 (M), 156 (M), 107, 94, 77, 65, 51.

(2-bromoethoxy)benzene (table 3, entry 5) [CAS 589-10-6]

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\text{\includegraphics[width=0.2\textwidth]{2-bromoethoxybenzene.png}}
\]

Colorless liquid (191 mg, 0.95 mmol, 95% yield). \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.31-7.26(m, 2H), 6.99-6.87(m, 3H), 4.28(t, \(J = 6.0\) Hz, 2H), 3.63(t, \(J = 6.0\) Hz, 2H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \(\delta\) 129.9, 121.7, 115.0, 68.0, 29.4; GC-MS (m/z): 202 (M), 200 (M), 121, 107 (100), 94, 77, 65, 51.

1-(4-chloropropoxy)naphthalene (table 3, entry 6) [CAS 56231-42-6]

\[
\text{\includegraphics[width=0.2\textwidth]{1-(4-chloropropoxy)naphthalene.png}}
\]

Colorless liquid (216 mg, 0.98 mmol, 98% yield). \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.24 (d, \(J = 7.5\) Hz, 1H), 7.81-7.79 (m, 1H), 7.49-7.34 (m, 4H), 6.81 (d, \(J = 7.5\) Hz, 1H), 4.29-4.26 (m,
2H), 3.86-3.82 (m, 2H), 2.39-2.35 (m, 2H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \(\delta\) 154.6, 134.8, 127.8, 126.7, 126.1, 125.8, 125.5, 122.1, 120.7, 105.0, 64.7, 42.0, 32.7; GC-MS (m/z): 222 (M), 220 (M), 144 (100), 115, 89, 63.

1-(4-bromopropoxy)naphthalene (table 3, entry 6) [CAS 3245-62-3]

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\begin{array}{c}
\text{O} \\
\text{Br} \\
\end{array}
\]

Colorless liquid (262 mg, 0.99 mmol, 99% yield). \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.24 (d, \(J = 7.0\) Hz, 1H), 7.81-7.79 (m, 1H), 7.50-7.41 (m, 4H), 6.81 (d, \(J = 7.5\) Hz, 1H), 4.27-4.25 (m, 2H), 3.71-3.68 (m, 2H), 2.45-2.41 (m, 2H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \(\delta\) 154.6, 134.8, 127.8, 126.7, 126.1, 125.8, 125.5, 122.1, 120.7, 105.0, 65.7, 32.8, 30.5; GC-MS (m/z): 266 (M), 264 (M), 144 (100), 115, 89, 63.

1-chlorooctane (table 3, entry 7) [CAS 111-85-3]

\[
\begin{array}{c}
\text{Cl} \\
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\]

Colorless liquid (145 mg, 0.98 mmol, 98% yield). \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 3.55-3.11 (m, 2H), 1.79-1.74 (m, 2H), 1.43-1.27 (m, 10H), 0.90-0.87 (m, 3H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \(\delta\) 45.4, 32.0, 31.1, 29.4, 29.1, 27.1, 22.9, 14.3; GC-MS (m/z): 150 (M), 148 (M), 105, 91 (100), 83, 69, 55.

1-bromooctane (table 3, entry 7) [CAS 111-83-1]

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\begin{array}{c}
\text{Br} \\
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\]

Colorless liquid (179 mg, 0.93 mmol, 93% yield). \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 3.40 (t, \(J = 7\) Hz, 2H), 1.88-1.82 (m, 2H), 1.44-1.40 (m, 2H), 1.30-1.20 (m, 8H), 0.89 (t, \(J = 7.5\) Hz, 3H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \(\delta\) 34.3, 33.1, 32.0, 29.4, 29.0, 28.4, 22.9, 14.3; GC-MS (m/z): 194 (M), 192 (M), 151, 149, 137 (100), 135 (100), 71, 55.

1-iodooctane (table 3, entry 7) [CAS 629-27-6]

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\begin{array}{c}
\text{I} \\
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\]

Colorless liquid (225 mg, 0.94 mmol, 94% yield). \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 3.19 (t, \(J = 7.0\) Hz, 2H), 1.84-1.78 (m, 2H), 1.40-1.27 (m, 10H), 0.89 (t, \(J = 7.0\) Hz, 3H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \(\delta\) 33.8, 32.0, 30.8, 29.3, 28.8, 22.9, 14.3, 7.6; GC-MS (m/z): 240 (M), 155, 113, 71, 57 (100).

(2-chloropropyl)benzene (table 3, entry 8) [CAS 10304-81-1]
Colorless liquid (147 mg, 0.94 mmol, 94% yield). $^1$H-NMR (500 MHz, CDCl$_3$): δ 7.33- 7.19 (m, 5H), 4.25- 4.20 (m, $J = 7.0$ Hz, 1H), 3.11- 3.06 (m, 1H), 2.98- 2.94 (m, 1H), 1.51 (d, $J = 7.0$ Hz, 3H); $^{13}$C-NMR (125 MHz, CDCl$_3$): δ 138.2, 129.6, 128.7, 127.1, 58.8, 46.9, 24.9; GC-MS (m/z): 156 (M), 154 (M), 91 (100), 77, 65, 51.

(2-bromopropyl)benzene (table 3, entry 8) [CAS 2114-39-8]

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{Br}
\end{array}
\]

Colorless liquid (189 mg, 0.95 mmol, 95% yield). $^1$H-NMR (500 MHz, CDCl$_3$): δ 7.32- 7.17 (m, 5H), 4.31- 4.26 (m, 1H), 3.23- 3.18 (m, 1H), 3.07- 3.02 (m, 1H), 1.67 (d, $J = 6.5$ Hz, 3H); $^{13}$C-NMR (125 MHz, CDCl$_3$): δ 138.8, 129.5, 128.8, 127.2, 50.8, 47.8, 26.0; GC-MS (m/z): 200 (M), 198 (M), 119, 91 (100), 77, 65, 51.

(3-chlorobutyl)benzene (table 3, entry 9) [CAS 4830-94-8]

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{Cl}
\end{array}
\]

Colorless liquid (156 mg, 0.93 mmol, 93% yield). $^1$H-NMR (500 MHz, CDCl$_3$): δ 7.31- 7.27 (m, 2H), 7.22- 7.17 (m, 3H), 4.01- 3.96 (m, 1H), 2.88- 2.82 (m, 1H), 2.77- 2.71 (m, 1H), 2.03- 1.96 (m, 2H), 1.53 (d, $J = 6.5$ Hz, 3H); $^{13}$C-NMR (125 MHz, CDCl$_3$): δ 141.32, 128.8, 128.7, 126.3, 58.1, 42.2, 33.1, 25.7; GC-MS (m/z): 170 (M), 168 (M), 117, 91 (100), 77, 65, 51.

(3-bromobutyl)benzene (table 3, entry 9) [CAS 21953-83-3]

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{Br}
\end{array}
\]

Colorless liquid (196 mg, 0.92 mmol, 92% yield). $^1$H-NMR (500 MHz, CDCl$_3$): δ 7.31- 7.17 (m, 5H), 4.13- 4.04 (m, 1H), 2.89- 2.82 (m, 1H), 2.78- 2.71 (m, 1H), 2.17- 2.09 (m, 1H), 2.08- 2.01 (m, 1H), 1.69 (d, $J = 6.5$ Hz, 3H); $^{13}$C-NMR (125 MHz, CDCl$_3$): δ 141.2, 128.8, 128.7, 126.3, 51.1, 42.9, 34.2, 26.8; GC-MS (m/z): 214 (M), 212 (M), 132, 117, 91 (100), 65.

(3-iodobutyl)benzene (table 3, entry 9) [CAS 59456-20-1]

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{I}
\end{array}
\]

Colorless liquid (229 mg, 0.88 mmol, 88% yield). $^1$H-NMR (500 MHz, CDCl$_3$): δ 7.33- 7.20 (m, 5H), 4.14- 4.09 (m, 1H), 2.88- 2.82 (m, 1H), 2.73- 2.66 (m, 1H), 2.18- 2.12 (m, 1H), 1.95 (d, $J = 7.0$ Hz, 3H), 1.92- 1.85 (m, 1H); $^{13}$C-NMR (125 MHz, CDCl$_3$): δ 141.0, 128.8, 128.7, 126.4, 44.7, 36.1, 29.9, 29.3; GC-MS (m/z): 260 (M), 133, 91 (100), 65.
3-chlorooctane (table 3, entry 10) [CAS 1117-79-9]

\[\text{Cl}\]

Colorless liquid (137 mg, 0.93 mmol, 93% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 3.87-3.82 (m, 1H), 1.84-1.76 (m, 1H), 1.75-1.67 (m, 3H), 1.57-1.49 (m, 1H), 1.45-1.19 (m, 5H), 1.08-0.91 (m, 3H), 0.93-0.89 (m, 3H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 66.2, 38.3, 31.7, 31.6, 26.4, 22.8, 14.2, 11.2; GC-MS (m/z): 112 (M-HCl), 97, 83, 70 (100), 55.

3-bromooctane (table 3, entry 10) [CAS 999-64-4]

\[\text{Br}\]

Colorless liquid (183 mg, 0.95 mmol, 95% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 4.00-3.95 (m, 1H), 1.89-1.76 (m, 5H), 1.55-1.51 (m, 1H), 1.44-1.21 (m, 7H), 0.91-0.88 (m, 3H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 60.9, 39.0, 32.4, 31.5, 27.5, 22.8, 14.3, 12.3; GC-MS (m/z): 194 (M), 192 (M), 113, 71 (100), 57.

2-chlorooctane (table 3, entry 11) [CAS 628-61-5]

\[\text{Cl}\]

Colorless liquid (134 mg, 0.90 mmol, 90% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 4.06-4.00 (m, 1H), 1.73-1.67 (m, 2H), 1.51-1.46 (m, 4H), 1.42-1.28 (m, 7H), 0.91-0.87 (m, 3H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 59.2, 40.6, 31.9, 29.0, 26.9, 25.6, 22.8, 14.3; GC-MS (m/z): 150 (M), 148 (M), 112, 83, 70 (100), 55.

2-bromooctane (table 3, entry 11) [CAS 557-36-8]

\[\text{Br}\]

Colorless liquid (179 mg, 0.93 mmol, 93% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 4.11-4.06 (m, 1H), 1.86-1.51 (m, 5H), 1.50-1.31 (m, 8H), 0.89 (t, $J = 7.5$ Hz, 3H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 52.2, 41.4, 31.9, 28.9, 28.0, 26.7, 22.8, 14.3; GC-MS (m/z): 113 (M-HBr), 71 (100), 57.

2-iodooctane (table 3, entry 11) [CAS 557-35-7]

\[\text{I}\]

Colorless liquid (238 mg, 0.99 mmol, 99% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 4.21-4.15 (m, 1H), 1.92 (d, $J = 6.5$ Hz, 3H), 1.88-1.79 (m, 1H), 1.64-1.49 (m, 1H), 1.48-1.39 (m, 1H), 1.38-1.15 (m, 7H), 0.91-0.87 (t, $J = 6.5$ Hz, 3H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 43.2, 31.9, 31.1, 29.9, 29.2, 28.7, 22.8, 14.3; GC-MS (m/z): 240 (M), 113, 71 (100), 57.
Chlorocycloheptane (table 3, entry 12) [CAS 2453-46-5]

![Image of Chlorocycloheptane]

Colorless liquid (102 mg, 0.77 mmol, 77% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 4.20-4.15 (m, 1H), 2.18-2.12 (m, 2H), 1.94-1.86 (m, 2H), 1.76-1.70 (m, 2H), 1.60-1.54 (m, 4H), 1.48-1.41 (m, 2H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 63.3, 39.1, 27.9, 24.0; GC-MS (m/z): 134 (M), 132 (M), 96, 81 (100), 67, 55.

Bromocycloheptane (table 3, entry 12) [CAS 2404-35-5]

![Image of Bromocycloheptane]

Colorless liquid (138 mg, 0.78 mmol, 78% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 4.37-4.30 (m, 1H), 2.30-2.24 (m, 2H), 2.10-2.03 (m, 2H), 2.03-1.42 (m, 8H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 56.8, 40.1, 27.8, 25.2; GC-MS (m/z): 178 (M), 176 (M), 97 (100), 67, 55.

2-chloroadamantane (table 3, entry 13) [CAS 7346-41-0]

![Image of 2-chloroadamantane]

White solid (157 mg, 0.92 mmol, 92% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 4.40 (s, 1H), 2.29-2.26 (m, 2H), 2.08 (br, 2H), 1.96-1.93 (m, 2H), 1.87-1.76 (m, 6H), 1.59-1.56 (m, 2H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 68.5, 38.3, 37.9, 36.0, 31.2, 27.6, 27.0; GC-MS (m/z): 172 (M), 170 (M), 134 (100), 119, 92, 79, 67.

2-bromoadamantane (table 3, entry 13) [CAS 7314-85-4]

![Image of 2-bromoadamantane]

White solid (198 mg, 0.92 mmol, 92% yield). $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 4.68 (s, 1H), 2.36-2.33 (m, 2H), 2.15 (br, 2H), 1.99-1.96 (m, 2H), 1.88-1.85 (m, 4H), 1.77 (br, 2H), 1.64-1.61 (m, 2H); $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ 64.2, 38.9, 38.1, 36.6, 31.9, 27.7, 27.1; GC-MS (m/z): 216 (M), 214 (M), 135 (100), 93, 79, 67.

2-iodoadamantane (table 3, entry 13) [CAS 18971-91-0]

![Image of 2-iodoadamantane]
White solid (259 mg, 0.99 mmol, 99% yield). $^1$H-NMR (500 MHz, CDCl$_3$): δ 4.97 (s, 1H), 2.39- 2.36 (m, 2H), 2.16 (br, 2H), 1.99- 1.92 (m, 5H), 1.88 (br, 1H), 1.79 (br, 2H), 1.72-1.69 (m, 2H); $^{13}$C-NMR (125 MHz, CDCl$_3$): δ 47.1, 39.1, 38.4, 37.9, 33.3, 28.0, 27.4; GC-MS (m/z): 262 (M), 135 (100), 119, 92, 79, 67.

3-bromo-5-cholestene (table 3, entry 14) [CAS 2871-53-6]

Purification of the concentrated crude product by column chromatography (EtOAc : n-hexane = 1 : 50) afforded the desired product as white solid (268 mg, 0.60 mmol, 60% yield). $^1$H-NMR (500 MHz, CDCl$_3$): δ 5.38 (s, 1H), 3.80- 3.74 (m, 1H), 2.50- 2.47 (m, 2H), 2.08- 1.96 (m, 3H), 1.90- 1.79 (m, 3H), 1.60- 1.22 (m, 10H), 1.16- 0.86 (m, 22H), 0.68 (s, 3H); $^{13}$C-NMR (125 MHz, CDCl$_3$): δ 141.0, 122.7, 60.6, 56.9, 56.4, 50.3, 43.6, 42.5, 39.9, 39.8, 39.3, 36.6, 36.4, 36.0, 33.6, 32.1, 32.0, 28.5, 28.3, 24.5, 24.1, 23.1, 22.8, 21.2, 19.5, 19.0, 12.1.

3-chloro-5-cholestene (table 3, entry 14) [CAS 2863-79-8]

Purification of the concentrated crude product by column chromatography (EtOAc : n-hexane = 1 : 50) afforded the desired product as white solid (206 mg, 0.51 mmol, 51% yield). $^1$H-NMR (500 MHz, CDCl$_3$): δ 5.36 (s, 1H), 3.95- 3.90 (m, 1H), 2.77- 2.72 (m, 1H), 2.60- 2.56 (m, 1H), 2.19- 2.16(m, 2H), 2.07- 1.95(m, 4H), 1.88-1.76(m, 3H), 1.60-1.39(m, 13H), 1.32-0.85 (m, 16H), 0.67 (s, 3H); $^{13}$C-NMR (125 MHz, CDCl$_3$): δ 141.8, 122.6, 56.9, 56.4, 52.9, 50.4, 44.5, 42.6, 40.6, 39.9, 39.8, 36.6, 36.4, 36.0, 34.6, 32.0, 32.0, 28.5, 28.3, 24.5, 24.1, 23.1, 22.8, 21.1, 19.5, 19.0, 12.1.

octyl acetate (table 4, entry 1) [CAS 112-14-1]

Colorless liquid (170 mg, 0.99 mmol, 99% yield). $^1$H-NMR (500 MHz, CDCl$_3$): δ 4.08- 4.03 (m, 2H), 2.05 (s, 3H), 1.63- 1.60 (m, 2H), 1.28 (br, 10H), 0.90- 0.87(m, 3H); $^{13}$C-NMR (125 MHz, CDCl$_3$): δ 171.5, 64.9, 32.0, 29.4, 28.8, 26.1, 22.9, 21.2, 14.3; GC-MS (m/z): 112 (M-HOAc), 84, 70 (100), 61, 55.
1-thiocyanatoctane (table 4, entry 1) [CAS 19942-78-0]

\[
\text{SCN}
\]

Colorless liquid (169 mg, 0.99 mmol, 99% yield). \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 3.02 (t, \(J = 7.0\) Hz, 2H), 1.93- 1.88 (m, 2H), 1.53- 1.37 (m, 10H), 0.97 (t, \(J = 7.0\) Hz, 3H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \(\delta\) 112.7, 34.4, 32.0, 30.2, 29.4, 29.2, 28.3, 22.9, 14.4; GC-MS (m/z): 170 (M), 144, 101, 87, 83, 69, 55 (100).

3-phenylpropyl acetate (table 4, entry 2) [CAS 122-72-5]

\[
\text{CH}_3\text{CH}_2\text{C}(-\text{OCOC}_2\text{H}_5)
\]

Colorless liquid (171 mg, 0.96 mmol, 96% yield). \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.31- 7.26 (m, 2H), 7.21- 7.17 (m, 3H), 4.09 (t, \(J = 6.5\) Hz, 2H), 2.71- 2.67 (m, 2H), 2.06 (s, 3H), 1.99- 1.93 (m, 2H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \(\delta\) 171.4, 141.5, 128.7, 128.6, 126.3, 64.1, 32.4, 30.4, 21.2; GC-MS (m/z): 178 (M), 117 (100), 105, 91, 77, 65.

(3-thiocyanatopropyl)benzene (table 4, entry 2) [CAS 79528-83-9]

\[
\text{C}_6\text{H}_5\text{CH}_2\text{C}(-\text{SCN})
\]

Colorless liquid (168 mg, 0.95 mmol, 95% yield). \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.32- 7.16 (m, 5H), 2.91 (t, \(J = 7.0\) Hz, 2H), 2.78 (t, \(J = 7.5\) Hz, 2H), 2.18- 2.13 (m, 2H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \(\delta\) 140.7, 128.9, 128.7, 126.7, 112.4, 65.0, 31.1, 29.8; GC-MS (m/z): 177 (M), 117, 91 (100), 65, 51.

4-(3-thiocyanatopropyloxy)biphenyl (table 4, entry 3) [CAS 854664-86-1]

\[
\text{O} - \text{C}_6\text{H}_4\text{CH}_2\text{C}(-\text{SCN})
\]

White solid (266 mg, 0.99 mmol, 99% yield). \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.57- 7.30 (m, 7H), 6.99- 6.95 (m, 2H), 4.15 (t, \(J = 5.5\) Hz, 2H), 3.22- 3.18 (m, 2H), 2.35- 2.32 (m, 2H); \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \(\delta\) 158.2, 140.9, 134.6, 129.0, 128.5, 127.1, 127.0, 115.0, 112.3, 65.0, 31.1, 29.8; GC-MS (m/z): 269 (M, 100), 170, 141, 115, 76, 51.

3-(biphenyl-4-yloxy)propyl acetate (table 4, entry 3)

\[
\text{O} - \text{C}_6\text{H}_4\text{CH}_2\text{C}(-\text{OAc})
\]

White solid (266 mg, 0.99 mmol, 99% yield). \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.57- 7.50 (m, 4H), 7.44- 7.40 (m, 2H), 7.33- 7.29 (m, 1H), 6.99- 6.95 (m, 2H), 4.29 (t, \(J = 6.0\) Hz, 2H), 4.09
octan-2-yl acetate (table 4, entry 4) [CAS 2051-50-5]

\[
\text{\textsuperscript{1}H-NMR (500 MHz, CDCl}_3\text{): } \delta 4.91-4.85 \text{ (m, 1H), 2.03 (s, 3H), 1.60-1.40 \text{ (m, 2H), 1.28-1.13 \text{ (m, 11H), 0.90-0.86 \text{ (m, 3H); }}}
\]

\[
\text{\textsuperscript{13}C-NMR (125 MHz, CDCl}_3\text{): } \delta 171.0, 71.3, 36.1, 32.0, 29.3, 25.6, 22.8, 21.6, 20.2, 14.3; \text{ GC-MS (m/z): 172 (M), 143, 112, 101 (100), 83, 70, 55.}
\]

2-thiocyanatoctane (table 4, entry 4) [CAS 69891-64-1]

\[
\text{\textsuperscript{1}H-NMR (500 MHz, CDCl}_3\text{): } \delta 3.29-3.19 \text{ (m, 1H), 1.75-1.67 \text{ (m, 2H), 1.52 (d, } J = 6.5 \text{ Hz, 3H), 1.50-1.19 \text{ (m, 8H), 0.91-0.87 \text{ (m, 3H); }}}
\]

\[
\text{\textsuperscript{13}C-NMR (125 MHz, CDCl}_3\text{): } \delta 101.9, 46.0, 37.2, 31.8, 29.0, 27.2, 22.8, 22.2, 14.3; \text{ GC-MS (m/z): 171 (M), 144, 138, 129, 86, 71, 57 (100).}
\]

4-phenylbutan-2-yl acetate (table 4, entry 5) [CAS 10415-88-0]

\[
\text{\textsuperscript{1}H-NMR (500 MHz, CDCl}_3\text{): } \delta 7.29-7.24 \text{ (m, 2H), 7.20-7.16 \text{ (m, 3H), 4.95-4.90 \text{ (m, 1H), 2.70-2.58 \text{ (m, 2H), 2.03 \text{ (s, 3H), 1.95-1.89 \text{ (m, 1H), 1.82-1.77 \text{ (m, 1H), 0.89 (d, } J = 6.0 \text{ Hz, 3H); }}}
\]

\[
\text{\textsuperscript{13}C-NMR (125 MHz, CDCl}_3\text{): } \delta 171.0, 141.8, 128.7, 128.6, 126.2, 70.8, 37.8, 32.1, 21.6, 20.3; \text{ GC-MS (m/z): 192 (M), 132, 117 (100), 91, 77, 65, 51.}
\]

(3-thiocyanatobutyl)benzene (table 4, entry 5)

\[
\text{\textsuperscript{1}H-NMR (500 MHz, CDCl}_3\text{): } \delta 7.31-7.17 \text{ (m, 5H), 3.19-3.14 \text{ (m, 1H), 2.81-2.68 \text{ (m, 2H), 2.08-1.97 \text{ (m, 2H), 1.53 (d, } J = 8.5 \text{ Hz, 3H); }}}
\]

\[
\text{\textsuperscript{13}C-NMR (125 MHz, CDCl}_3\text{): } \delta 140.34, 128.9, 128.7, 126.7, 111.3, 44.9, 38.7, 33.3, 22.4; \text{ HRMS calc. for C11H13NS (M+ Na)}^+ \text{ 214.0666; found, 214.0682.}
\]
2-adamantyl acetate (table 4, entry 6) [CAS 19066-22-9]

\[\text{White solid (189 mg, 0.98 mmol, 98\% yield). } \^1H-\text{NMR (500 MHz, CDCl}_3\text{): } \delta 4.91 (s, 1H), 2.08 (s, 3H), 2.03- 1.99 (m, 4H), 1.86- 1.73 (m, 8H), 1.57- 1.54 (m, 2H); } ^{13}\text{C-NMR (125 MHz, CDCl}_3\text{): } \delta 170.9, 37.6, 36.6, 32.1, 32.0, 27.5, 27.2, 21.8; \text{ GC-MS (m/z): 194 (M), 134 (100), 119, 92, 79, 67, 56.}]

2-thiocyanatoadamantane (table 4, entry 6) [CAS 153757-17-6]

\[\text{White solid (191 mg, 0.99 mmol, 99\% yield). } \^1H-\text{NMR (500 MHz, CDCl}_3\text{): } \delta 4.40 (br, 1H), 2.28- 2.25 (m, 2H), 2.11- 2.07 (m, 2H), 1.96- 1.92 (m, 2H), 1.86- 1.75 (m, 6H), 1.58- 1.55 (m, 2H); } ^{13}\text{C-NMR (125 MHz, CDCl}_3\text{): } \delta 68.5, 38.3, 37.9, 36.0, 31.2, 27.6, 27.0; \text{ GC-MS (m/z): 193 (M), 135 (100), 107, 93, 79, 67.}]}
4. Procedure for recycling ionic liquid [bmIm][X]

**General procedure for recylization of ionic liquid [bmim][Br]:** To a 20 mL closed tube was added 2-octanyl 4-methylbenzenesulfonate (276 mg, 1.0 mmol) and ionic liquid [bmim][Br] (219 mg, 1.0 mmol), then the mixture was stirred under argon at 60 °C for 8 hr. After extracting the reaction mixture with ether and water, the water layer was collected and evaporated to dryness to give [bmim][OTs] (310 mg, 0.99 mmol, 99% yield). The residue was dissolved in 1.0 mL of acetonitrile and lithium bromide (87 mg, 1.0 mmol) was added. The mixture was stirred at 80 °C for overnight. The insoluble salt was filtered and washed with a small amount of acetonitrile. The filtrate was collected and evaporated to give recovered [bmim][Br] which could be reused without further purification (216 mg, 99%).

**[bmim][Cl]:** Lithium chloride was used as chloride source. 222 mg (88% [bmim][Cl] + 12% [bmim][OTs] by $^1$H-NMR)

**[bmim][I]:** Sodium iodide was used as iodide source. 263 mg (99%).

**[bmim][SCN]:** Sodium thiocyanate was used as thiocyanate source. 197 mg (99%).

**1-butyl-3-methylimidazolium 4-methylbenzenesulfonate ([bmim][OTs]) [CAS 410522-18-8].** White crystal (310 mg, 0.99 mmol, 99% yield). $^1$H-NMR (500 MHz, D$_2$O): δ 8.48 (s, 1H), 7.53 (d, $J$ = 8.0 Hz, 2H), 7.26 (s, 1H), 7.22 (s, 1H), 7.20 (d, $J$ = 8.0 Hz, 2H), 3.98 (t, $J$ = 7.5 Hz, 2H), 3.70 (s, 3H), 2.23 (s, 3H), 1.67- 1.63 (m, 2H), 1.16- 1.11 (m, 2H), 0.76 (t, $J$ = 7.5 Hz, 3H); $^{13}$C-NMR (125 MHz, D$_2$O): δ 142.5, 139.8, 135.8, 129.6, 125.5, 123.6, 122.3, 49.4, 35.7, 31.4, 20.6, 18.9, 12.8.
5. The spectra for new compounds: HRMS, $^1$H-NMR and $^{13}$C-NMR
6. The chiral GC spectra for stereochemistry study
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Totals : 1891.85669 300.86298

*** End of Report ***

Instrument 1 4/10/2012 1:17:51 PM SJ