Supporting Information for
Highly Efficient Alkylation to Ketones and Aldimines with Grignard Reagents
Catalyzed by Zinc(II) Chloride

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General Methods. ^1H NMR spectra were measured on a Varian Gemini-2000 spectrometer (300 MHz) at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the TM scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet), coupling constant (Hz), integration, and assignment. ^{13}C NMR spectra were measured on Varian Mercury-300 (75 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuteriochloroform at 77.10 ppm). ^{19}F NMR spectra were measured on Varian Mercury-300 (282 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (BTF at - 63.24 ppm in deuteriochloroform). For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60GF254 0.25 mm) were used. The products were purified by neutral column chromatography on silica gel (Kanto Chemical Co., Inc. 37560). Visualization was accomplished by UV light (254 nm), anisaldehyde, KMnO_4 and phosphomolybdic acid. In experiments that required dry solvents, diethylether (dehydrate) and tetrahydrofuran (dehydrate) were purchased from Kanto Chemical Co., Inc. ZnCl_2 (Wako); LiCl (Wako), EtLi (0.5 M in benzene/cyclohexane, Aldrich); Et_2Zn (1.0 M in hexane, Kanto Chemical Co., Inc.); Me_2Zn (1.0 M in hexane, Kanto Chemical Co., Inc.); MeMgCl (3.0 M in THF, Aldrich); EtMgCl (1.0 M in THF, Kanto Chemical Co., Inc.); EtMgBr (1.0 M in THF, Kanto Chemical Co., Inc.); $n\text{-PrMgCl}$ (2.0 M in Et_2O , Aldrich); $i\text{-PrMgCl}$ (2.0 M in THF, Aldrich); $n\text{-BuMgCl}$ (1.0 M in THF, Kanto Chemical Co., Inc.); $s\text{-BuMgCl}$ (1.0 M in THF, Kanto Chemical Co., Inc.); $c\text{-HexMgCl}$ (2.0 M in Et_2O , Aldrich); $n\text{-OctMgCl}$ (2.0 M in THF, Aldrich); (vinyl) MgCl (1.5 M in THF, Kanto Chemical Co., Inc.); (allyl) MgCl (2.0 M in THF, Aldrich); BnMgCl (1.0 M in THF, Kanto Chemical Co., Inc.) were used.

Representative procedure for alkylation to ketones with stoichiometric Et₃ZnMgCl (Table 1, entry 10):

To a solution of EtMgCl (1.0 *M* in THF, 3.30 mL, 3.30 mmol) was added Et₂Zn (1.0 *M* in hexane, 3.30 mL, 3.30 mmol) at room temperature under nitrogen atmosphere. This solution was stirred at that temperature for 1 h. Then, the solution was cooled to 0 °C, and benzophenone (**5**) (546 mg, 3.00 mmol) was added at 0 °C. The mixture was stirred for 2 h at 0 °C, and the reaction was monitored by TLC. The resulting mixture was quenched by saturated aqueous NH₄Cl (5 mL), extracted with AcOEt (10 mL×3), and washed by brine (5 mL). The combined extracts were dried over MgSO₄. The organic phase was concentrated under reduced pressure and the resultant residue was purified by neutral silica gel column chromatography (eluent: hexane/EtOAc), to give the desired product (**6b**) (541 mg, 85% yield).

Representative procedure for ZnCl₂-catalyzed alkylation to ketones with Grignard reagents (Table 1, entry 11):

To a solution of EtMgCl (1.0 *M* in THF, 3.90 mL, 3.90 mmol) was added ZnCl₂ (40.8 mg, 0.30 mmol) at room temperature under nitrogen atmosphere. This solution was stirred at that temperature for 1 h. Then, the solution was cooled to 0 °C, and benzophenone (**5**) (546 mg, 3.00 mmol) was added at 0 °C. The mixture was stirred for 2 h at 0 °C, and the reaction was monitored by TLC. The resulting mixture was quenched by saturated aqueous NH₄Cl (5 mL), extracted with AcOEt (10 mL×3), and washed by brine (5 mL). The combined extracts were dried over MgSO₄. The organic phase was concentrated under reduced pressure and the resultant residue was purified by neutral silica gel column chromatography (eluent: hexane/EtOAc), to give the desired product (**6b**) (535 mg, 84% yield).

Representative procedure for ZnCl₂-catalyzed alkylation to 2-adamantanone with Grignard reagents:

To a solution of EtMgCl (1.0 *M* in THF, 130 mL, 130 mmol) was added ZnCl₂ (1.33 g, 10.0 mmol) and LiCl (5.49 g, 130 mmol) at room temperature under nitrogen atmosphere. This solution was stirred at that temperature for 1 h. Then, 2-adamantanone (**8I**) (15.0 g, 100 mmol) was added at 0 °C. The mixture was stirred at 0 °C for 5 h, and the reaction was monitored by TLC. The resulting mixture was quenched by saturated aqueous NH₄Cl (100 mL), extracted with AcOEt (100 mL×3), and washed by brine (100 mL). The combined extracts were dried over MgSO₄. The organic phase was concentrated under reduced pressure and the resultant residue was purified by neutral silica gel column chromatography (eluent: hexane/EtOAc), to give the desired product (**11**) (14.8 g, 81% yield).

Representative procedure for ZnCl₂-catalyzed alkylation to aldimine with Grignard reagents (Table 4, entry 1):

To a solution of EtMgCl (1.0 *M* in THF, 3.90 mL, 3.90 mmol) was added ZnCl₂ (40.8 mg, 0.30 mmol) at room temperature under nitrogen atmosphere. This solution was stirred at that temperature for 1 h. Then, *N*-phenylbenzylideneamine (**12**) (547 mg, 3.00 mmol) was added at room temperature. The mixture was stirred for 2 h, and the reaction was monitored by TLC. The resulting mixture was quenched by saturated aqueous NH₄Cl (5 mL), extracted with AcOEt (10 mL×3), and washed by brine (5 mL). The combined extracts were dried over MgSO₄. The organic phase was concentrated under reduced pressure and the resultant residue was purified by neutral silica gel column chromatography (eluent: hexane/EtOAc), to give the desired product (**13b**) (513 mg, 81% yield).

 1,1-diphenyl-1-ethanol (**6a**):^{1,2} ¹H NMR (300 MHz, CDCl₃) δ 1.96 (s, 3H), 2.18 (bs, 1H), 7.20-7.46 (m, 10H). ¹³C NMR (75 MHz, CDCl₃) δ 30.7, 76.1, 125.7, 126.8, 128.0, 147.9.

 1,1-diphenyl-1-propanol (**6b**):^{1,2} ¹H NMR (300 MHz, CDCl₃) δ 0.88 (t, *J* = 7.2, 3H), 2.05 (bs, 1H), 2.32 (q, *J* = 7.2, 2H), 7.18-7.46 (m, 10H). ¹³C NMR (75 MHz, CDCl₃) δ 8.1, 34.4, 78.4, 126.1, 126.7, 128.1, 146.9.

 1,1-diphenyl-1-butanol (**6c**):^{1,3,4} ¹H NMR (300 MHz, CDCl₃) δ 0.93 (t, *J* = 7.2 Hz, 3H), 1.30 (m, 2H), 2.08 (bs, 1H), 2.25 (m, 2H), 7.18-7.44 (m, 10H). ¹³C NMR (75 MHz, CDCl₃) δ 14.4, 17.2, 44.5, 78.5, 126.2, 126.8, 128.1, 147.4.

 2-methyl-1,1-diphenyl-1-propanol (**6d**):^{1,3,5} ¹H NMR (300 MHz, CDCl₃) δ 0.80 (d, *J* = 6.9 Hz, 3H), 0.84 (d, *J* = 6.9 Hz, 3H), 1.53 (bs, 1H), 2.02 (m, 1H), 7.20-7.42 (m, 10H).

 1,1-diphenyl-1-pentanol (**6e**):^{1,6,7} ¹H NMR (300 MHz, CDCl₃) δ 0.87 (t, *J* = 7.2 Hz, 3H), 1.20-1.42 (m, 4H), 2.09 (bs, 1H), 2.27 (m, 2H), 7.15-7.46 (m, 10H). ¹³C NMR (75 MHz, CDCl₃) δ 14.0, 23.1, 26.1, 41.9, 78.4, 126.2, 126.8, 128.2, 147.4.

 2-methyl-1,1-diphenyl-1-butanol (**6f**):^{8,9} ¹H NMR (300 MHz, CDCl₃) δ 0.87 (d, *J* = 6.6 Hz, 3H), 0.94 (d, *J* = 7.2 Hz, 3H), 1.40-1.70 (m, 2H), 2.01 (bs, 1H), 2.53 (m, 1H), 7.10-7.54 (m, 10H).

 cyclohexyldiphenylmethanol (**6g**):¹⁰ ¹H NMR (300 MHz, CDCl₃) δ 1.00-1.80 (m, 10H), 2.06 (s, 1H), 2.43 (m, 1H), 7.13-7.34 (m, 6H), 7.48 (d, *J* = 7.8 Hz, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 26.7, 26.9, 27.5, 46.1, 80.5, 126.0, 127.3, 128.1, 146.7.

 1,1-diphenyl-2-propen-1-ol (**6h**):^{11,12} ¹H NMR (300 MHz, CDCl₃) δ 2.27 (bs, 1H), 5.32 (d, *J* = 11.4 Hz, 1H), 5.33 (d, *J* = 16.2 Hz, 1H), 6.51 (dd, *J* = 15.9, 11.7 Hz, 1H), 7.20-7.44 (m, 10H). ¹³C NMR (75 MHz, CDCl₃) δ 79.4, 114.0, 126.9, 127.3, 128.2, 143.6, 145.8.

 1,1-diphenyl-3-buten-1-ol (**6i**):^{13,14} ¹H NMR (300 MHz, CDCl₃) δ 2.56 (bs, 1H), 3.08 (d, *J* = 7.5 Hz, 2H), 5.18 (d, *J* = 10.2 Hz, 1H), 5.25 (d, *J* = 17.4 Hz, 1H), 5.66 (ddt, *J* = 17.1, 10.2,

7.2 Hz, 1H), 7.22 (t, $J = 7.8$ Hz, 2H), 7.31 (t, $J = 7.8$ Hz, 4H), 7.45 (d, $J = 7.8$ Hz, 4H).

1,1,2-triphenyl-1-ethanol (**6j**):¹⁵ ^1H NMR (300 MHz, CDCl_3) δ 2.29 (s, 1H), 3.64 (bs, 2H), 6.86-6.92 (m, 2H), 7.10-7.34 (m, 9H), 7.40-7.46 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3) δ 47.8, 77.9, 126.1, 126.7, 126.8, 127.9, 128.0, 130.8, 135.7, 146.5.

diphenylmethanol (**7**):¹⁶ ^1H NMR (300 MHz, CDCl_3) δ 2.35 (bs, 1H), 5.80 (bs, 1H), 7.20-7.43 (m, 10H). ^{13}C NMR (75 MHz, CDCl_3) δ 76.3, 126.6, 127.6, 128.5, 143.8.

3-methyl-2-phenyl-2-butanol (**9a**):¹⁷ ^1H NMR (300 MHz, CDCl_3) δ 0.80 (d, $J = 6.9$ Hz, 3H), 0.89 (d, $J = 6.9$ Hz, 3H), 1.53 (s, 3H), 1.63 (s, 1H), 2.02 (m, 1H), 7.20-7.45 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3) δ 17.2, 17.4, 26.7, 38.6, 77.8, 125.2, 126.4, 127.8, 147.8.

2-methyl-3-phenyl-3-pentanol (**9b**):¹⁸ ^1H NMR (300 MHz, CDCl_3) δ 0.68 (t, $J = 7.2$ Hz, 3H), 0.72 (d, $J = 6.9$ Hz, 3H), 0.94 (d, $J = 6.9$ Hz, 3H), 1.58 (s, 1H), 1.89 (q, $J = 6.9$ Hz, 2H), 2.05 (m, 1H), 7.18-7.40 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3) δ 7.9, 16.6, 17.5, 32.0, 37.5, 79.3, 125.9, 126.1, 127.7, 145.0.

2,4-dimethyl-3-phenyl-3-pentanol (**9c**):¹⁹ ^1H NMR (300 MHz, CDCl_3) δ 0.76 (d, $J = 6.6$ Hz, 6H), 0.84 (d, $J = 6.6$ Hz, 6H), 1.50 (s, 1H), 2.31 (m, 2H), 7.22-7.45 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3) δ 16.5, 17.4, 33.7, 80.9, 126.1, 126.6, 127.2, 142.8.

1,1,1-trifluoro-3-methyl-2-phenylbutan-2-ol (**9d**):²⁰ ^1H NMR (300 MHz, CDCl_3) δ 0.71 (d, $J = 6.9$ Hz, 3H), 1.11 (d, $J = 6.9$ Hz, 3H), 2.39 (bs, 1H), 2.51 (m, 1H), 7.30-7.45 (m, 3H), 7.54 (d, $J = 7.2$ Hz, 2H). ^{19}F NMR (282 MHz, CDCl_3) δ - 74.2.

3-methyl-2-(1-naphthalenyl)-2-butanol (**9e**):²¹ ^1H NMR (300 MHz, CDCl_3) δ 0.78 (d, $J = 6.9$ Hz, 3H), 0.99 (d, $J = 6.9$ Hz, 3H), 1.74 (s, 3H), 1.93 (bs, 1H), 2.81 (m, 1H), 7.00-8.05 (m, 6H), 8.76 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 17.0, 18.2, 25.1, 36.1, 78.9, 124.2, 124.5, 124.9, 127.1, 128.3, 129.1, 130.8, 135.0, 143.2.

3-methyl-2-(2-naphthalenyl)-2-butanol (**9f**).²² ^1H NMR (300 MHz, CDCl_3) δ 0.82 (d, $J = 6.9$ Hz, 3H), 0.94 (d, $J = 6.9$ Hz, 3H), 1.62 (bs, 3H), 1.73 (bs, 1H), 2.15 (m, 1H), 7.40-7.95 (m, 7H). ^{13}C NMR (75 MHz, CDCl_3) δ 17.3, 17.6, 26.9, 38.5, 76.9, 123.7, 124.1, 125.6, 125.9, 127.4, 127.5, 128.2, 132.3, 133.2, 145.5.

1-isopropyl-1,2,3,4-tetrahydro-1-naphthol (**9g**).²³ ^1H NMR (300 MHz, CDCl_3) δ 0.65 (d, $J = 6.9$ Hz, 3H), 1.09 (d, $J = 6.9$ Hz, 3H), 1.68-1.94 (m, 4H), 2.40 (m, 1H), 2.60-2.84 (m, 2H), 7.09 (d, $J = 6.9$ Hz, 1H), 7.12-7.26 (m, 2H), 7.52 (d, $J = 7.5$ Hz, 1H).

3-methyl-2-(2-thienyl)-2-butanol (**9h**).²⁴ ^1H NMR (300 MHz, CDCl_3) δ 0.86 (d, $J = 6.9$ Hz, 3H), 0.87 (d, $J = 6.9$ Hz, 3H), 1.53 (s, 3H), 1.92 (s, 1H), 2.05 (m, 1H), 6.90 (dd, $J = 3.6, 1.2$ Hz, 1H), 6.95 (dd, $J = 4.8, 3.6$ Hz, 1H), 7.20 (dd, $J = 4.8, 1.2$ Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 17.4, 17.6, 26.8, 39.7, 76.4, 122.7, 123.6, 126.5, 153.1.

3-methyl-2-(3-thienyl)-2-butanol (**9i**).²⁴ ^1H NMR (300 MHz, CDCl_3) δ 0.86 (d, $J = 6.9$ Hz, 3H), 0.87 (d, $J = 6.9$ Hz, 3H), 1.51 (s, 3H), 1.71 (s, 1H), 2.00 (m, 1H), 7.04 (dd, $J = 4.8, 1.5$ Hz, 1H), 7.13 (d, $J = 3.3, 1.5$ Hz, 1H), 7.26 (d, $J = 5.1, 3.3$ Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 17.3, 17.5, 26.3, 38.6, 76.1, 119.8, 125.2, 126.1, 149.6.

3-methyl-2-(4-pyridinyl)-2-butanol (**9j**).²⁵ ^1H NMR (300 MHz, CDCl_3) δ 0.77 (d, $J = 6.9$ Hz, 3H), 0.94 (d, $J = 6.9$ Hz, 3H), 1.51 (s, 3H), 1.72 (bs, 1H), 1.99 (m, 1H), 7.33 (d, $J = 6.3$ Hz, 2H), 8.53 (d, $J = 6.3$ Hz, 2H).

1-isopropyl-1-cyclohexanol (**9k**).^{26,27} ^1H NMR (300 MHz, CDCl_3) δ 0.90 (d, $J = 6.9$ Hz, 6H), 1.07 (s, 1H), 1.20-1.65 (m, 11H). ^{13}C NMR (75 MHz, CDCl_3) δ 16.7, 22.0, 26.0, 34.2, 37.6, 73.1.

2-isopropyl-2-adamantanol (**9l**).^{28,29} ^1H NMR (300 MHz, CDCl_3) δ 0.86 (d, $J = 6.9$ Hz, 6H), 1.17 (s, 1H), 1.40-2.20 (14H), 2.30 (m, 1H).

 1-phenylethanol (**10a**):¹⁶ ¹H NMR (300 MHz, CDCl₃) δ 1.40 (d, *J* = 6.6 Hz, 3H), 4.40 (bs, 1H), 4.76 (q, *J* = 6.6 Hz, 1H), 7.18 (m, 1H), 7.24-7.32 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 25.1, 70.3, 125.3, 127.3, 128.3, 145.8.

 1-phenyl-1-propanol (**10b**):¹⁶ ¹H NMR (300 MHz, CDCl₃) δ 0.81 (t, *J* = 7.5 Hz, 3H), 1.67 (m, 2H), 2.94 (bs, 1H), 4.41 (t, *J* = 6.3 Hz, 1H), 7.16-7.25 (m, 5H). ¹³C NMR (75 MHz, CDCl₃) δ 10.1, 31.9, 75.9, 125.9, 127.4, 128.3, 144.6.

 2-methyl-1-phenyl-1-propanol (**10c**):¹⁶ ¹H NMR (300 MHz, CDCl₃) δ 0.78 (d, *J* = 6.9 Hz, 3H), 0.98 (d, *J* = 6.6 Hz, 3H), 1.92 (m, 1H), 2.26 (bs, 1H), 4.31 (d, *J* = 6.9 Hz, 1H), 7.22-7.26 (m, 5H). ¹³C NMR (75 MHz, CDCl₃) δ 18.2, 19.0, 35.2, 80.0, 126.5, 127.3, 128.1, 143.6.

 2,2,2-trifluoro-1-phenylethanol (**10d**):¹⁶ ¹H NMR (300 MHz, CDCl₃) δ 2.91 (bs, 1H), 4.93 (q, *J* = 6.9 Hz, 1H), 7.25-7.50 (m, 5H). ¹³C NMR (75 MHz, CDCl₃) δ 72.8 (q, *J* = 31.5 Hz), 124.2 (q, *J* = 285 Hz), 127.4, 128.6, 129.5, 133.8.

 1-(1-naphthyl)-1-ethanol (**10e**):¹⁶ ¹H NMR (300 MHz, CDCl₃) δ 1.43 (d, *J* = 6.6 Hz, 3H), 3.32 (bs, 1H), 5.35 (q, *J* = 6.6 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 1H), 7.33-7.36 (m, 2H), 7.48 (d, *J* = 6.9 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.72 (m, 1H), 7.85 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 36.1, 62.8, 123.6, 125.4, 125.5, 125.9, 127.0, 127.2, 128.8, 132.0, 133.9, 134.4.

 1-(2-naphthyl)-1-ethanol (**10f**):¹⁶ ¹H NMR (300 MHz, CDCl₃) δ 1.57 (d, *J* = 6.3 Hz, 3H), 2.33 (bs, 1H), 5.54 (m, 1H), 7.25-7.50 (m, 3H), 7.59 (d, *J* = 6.9 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.78-7.84 (m, 1H), 7.98-8.04 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 39.2, 63.4, 125.3, 126.0, 127.3, 127.4, 127.4, 127.5, 128.1, 132.1, 133.4, 135.9.

 1,2,3,4-tetrahydro-1-naphthol (**10g**):¹⁶ ¹H NMR (300 MHz, CDCl₃) δ 1.60-2.00 (m, 4H), 2.17 (d, *J* = 6.0 Hz, 1H), 2.61-2.75 (m, 2H), 4.71 (m, 1H), 7.07 (m, 1H), 7.12-7.23 (m, 2H), 7.38 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 18.8, 29.2, 32.2, 68.0, 126.0, 127.4, 128.6, 128.9, 137.0, 138.7.

1-(2-thienyl)-1-ethanol (**10h**):¹⁶ ^1H NMR (300 MHz, CDCl_3) δ 1.60 (d, $J = 6.3$ Hz, 3H), 2.09 (d, $J = 4.2$ Hz, 1H), 5.12 (dd, $J = 6.3, 4.2$ Hz, 1H), 6.98-6.93 (m, 2H), 7.23 (dd, $J = 4.5, 1.5$ Hz, 1H).

1-(3-thienyl)-1-ethanol (**10i**):¹⁶ ^1H NMR (300 MHz, CDCl_3) δ 1.45 (d, $J = 6.6$ Hz, 3H), 3.19 (d, $J = 3.9$ Hz, 1H), 4.87 (m, 1H), 7.05 (dd, $J = 5.1, 1.2$ Hz, 1H), 7.12 (m, 1H), 7.25 (dd, $J = 5.1, 3.0$ Hz, 1H).

1-(4-pyridinyl)-1-ethanol (**10j**):¹⁶ ^1H NMR (300 MHz, CDCl_3) δ 1.48 (d, $J = 6.6$ Hz, 3H), 4.10 (bs, 1H), 4.88 (q, $J = 6.6$ Hz, 1H), 7.30 (dd, $J = 4.8, 1.5$ Hz, 2H), 8.44 (dd, $J = 4.5, 1.5$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 25.1, 68.1, 120.7, 149.0, 156.1.

cyclohexanol (**10k**):¹⁶ ^1H NMR (300 MHz, CDCl_3) δ 1.10-1.37 (m, 5H), 1.55 (m, 1H), 1.65-1.80 (m, 2H), 1.82-1.96 (m, 2H), 2.21 (bs, 1H), 3.59 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 24.2, 25.5, 35.5, 70.2.

2-adamanthanol (**10l**):¹⁶ ^1H NMR (300 MHz, CDCl_3) δ 1.52 (d, $J = 12.6$ Hz, 2H), 1.60-1.95 (m, 11H), 2.07 (d, $J = 12.9$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 27.1, 27.5, 31.0, 34.6, 36.5, 37.6, 74.5.

2-ethyl-2-adamantanol (**11**):³¹ ^1H NMR (300 MHz, CDCl_3) δ 0.89 (d, $J = 7.8$ Hz, 3H), 1.69 (d, $J = 7.5$ Hz, 2H), 1.32 (s, 1H), 1.50-2.25 (14H). ^{13}C NMR (75 MHz, CDCl_3) δ 6.3, 27.5, 30.6, 33.2, 34.7, 36.8, 38.5, 39.4, 74.9.

N-phenyl-(1-phenylpropyl)amine (**13a**):^{31,32,33,34} ^1H NMR (300 MHz, CDCl_3) δ 0.97 (t, $J = 6.9$ Hz, 3H), 1.85 (m, 2H), 4.07 (bs, 1H), 4.24 (t, $J = 6.9$ Hz, 1H), 6.51 (d, $J = 7.5$ Hz, 2H), 6.63 (t, $J = 7.5$ Hz, 1H), 7.04-7.11 (m, 2H), 7.18-7.36 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3) δ 11.0, 31.8, 59.9, 113.4, 117.3, 126.7, 127.0, 128.7, 129.2, 144.4, 147.7.

 PhHN $n\text{-Pr}$
 Ph H *N*-phenyl-(1-phenylbutyl)amine (**13b**):^{33,34,35} ^1H NMR (300 MHz, CDCl_3) δ 0.93 (t, $J = 7.2$ Hz, 3H), 1.26-1.50 (m, 2H), 1.66-1.82 (m, 2H), 4.06 (bs, 1H), 4.30 (t, $J = 6.9$ Hz, 1H), 6.50 (d, $J = 7.2$ Hz, 2H), 6.61 (t, $J = 7.5$ Hz, 1H), 7.06 (m, 2H), 7.18-7.40 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3) δ 14.0, 19.6, 41.2, 58.1, 113.3, 117.2, 126.4, 126.9, 128.5, 129.1, 144.4, 147.6.

 PhHN $i\text{-Pr}$
 Ph H *N*-phenyl-(2-methyl-1-phenylpropyl)amine (**13c**):^{33,34} ^1H NMR (300 MHz, CDCl_3) δ 0.92 (d, $J = 6.9$ Hz, 3H), 0.98 (d, $J = 6.9$ Hz, 3H), 2.03 (m, 1H), 4.11 (bs, 1H), 4.80 (bs, 1H), 6.50 (d, $J = 7.5$ Hz, 2H), 6.60 (t, $J = 7.5$ Hz, 1H), 7.02-7.10 (m, 2H), 7.18-7.36 (m, 5H).

 PhHN $n\text{-Bu}$
 Ph H *N*-phenyl-(1-phenylpentyl)amine (**13d**):^{32,33,35} ^1H NMR (300 MHz, CDCl_3) δ 0.89 (m, 3H), 1.20-1.46 (m, 4H), 1.79 (m, 2H), 4.05 (bs, 1H), 4.28 (t, $J = 6.6$ Hz, 1H), 6.51 (d, $J = 8.4$ Hz, 2H), 6.61 (t, $J = 7.5$ Hz, 1H), 7.02-7.12 (m, 2H), 7.16-7.40 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3) δ 13.9, 22.6, 28.5, 38.7, 58.2, 113.2, 117.1, 126.4, 126.8, 128.5, 129.1, 144.1, 147.5.

 PhHN $s\text{-Bu}$
 Ph H *N*-phenyl-(1-phenyl-2-methylbutyl)amine (**13e**, ca. 3:2 diastereo mixture): ^1H NMR (300 MHz, CDCl_3) δ 0.87 (d, $J = 6.9$ Hz, 3H-a), 0.90 (d, $J = 6.9$ Hz, 3H-b), 0.91 (t, $J = 7.5$ Hz, 3H-a), 0.94 (t, $J = 7.2$ Hz, 3H-b), 1.06-1.88 (m, 3H), 4.10 (bs, 1H), 4.19 (m, 1H-a), 4.29 (m, 1H-b), 6.49 (d, $J = 7.5$ Hz, 2H), 6.60 (t, $J = 6.9$ Hz, 1H), 7.05 (m, 2H), 7.16-7.26 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3) a: δ 11.8, 16.1, 25.4, 41.4, 62.7, 113.3, 117.0, 126.8, 127.4, 128.2, 129.1, 142.4, 147.8; b: δ 12.0, 14.5, 25.7, 41.9, 61.6, 113.2, 117.0, 126.7, 127.0, 128.2, 128.3, 143.1, 147.8.

 PhHN $c\text{-Hex}$
 Ph H *N*-phenyl-(1-phenyl-1-cyclohexylmethyl)amine (**13f**): ^1H NMR (300 MHz, CDCl_3) δ 0.90-1.94 (m, 11H), 4.09 (d, $J = 6.3$ Hz, 1H), 4.11 (bs, 1H), 6.47 (d, $J = 7.8$ Hz, 2H), 6.59 (t, $J = 7.5$ Hz, 1H), 7.05 (m, 2H), 7.18-7.31 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3) δ 26.4, 29.5, 30.3, 45.0, 63.5, 113.2, 117.0, 126.7, 127.2, 128.2, 129.0, 142.7, 147.8.

 PhHN $n\text{-Oct}$
 Ph H *N*-phenyl-(1-phenylnonyl)amine (**13g**): ^1H NMR (300 MHz, CDCl_3) δ 0.80-1.90 (m, 17H), 4.05 (bs, 1H), 4.28 (bs, 1H), 6.50 (d, $J = 7.2$ Hz, 2H), 6.18 (t, $J = 7.2$ Hz, 1H), 7.07 (t, $J = 7.5$ Hz, 2H), 7.20-7.40 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3) δ 14.0, 22.7, 26.4, 29.2, 29.5, 29.6, 31.9, 39.0, 58.6, 113.5, 117.3, 126.5, 126.9, 128.6, 129.1, 144.5, 147.8.

 PhHN
 Ph H *N*-phenyl-(1-phenylallyl)amine (**13h**):³⁶ ^1H NMR (300 MHz, CDCl_3) δ 4.04 (bs, 1H), 4.93 (bs, 1H), 5.22 (d, $J = 10.2$ Hz, 1H), 5.27 (d, $J = 17.4$ Hz, 1H), 6.04 (ddd, $J = 17.1, 10.2, 6.3$ Hz, 1H), 6.60 (d, $J = 7.8$ Hz, 2H), 6.69 (t, $J = 7.2$ Hz, 1H), 7.13 (t, $J = 7.2$ Hz, 2H), 7.20-7.40 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3) δ 60.9, 113.6, 116.1, 117.7, 127.2, 127.5, 128.8, 129.1, 139.1, 141.9, 147.3.

N-phenyl-(1-phenyl-3-butenyl)amine (**13i**):^{37,38,39} ^1H NMR (300 MHz, CDCl_3) δ 2.42-2.68 (m, 2H), 4.15 (bs, 1H), 4.37 (m, 1H), 5.14 (d, $J = 8.4$ Hz, 1H), 5.18 (d, $J = 16.8$ Hz, 1H), 5.75 (m, 1H), 6.48 (d, $J = 7.8$ Hz, 2H), 6.39 (d, $J = 7.5$ Hz, 1H), 7.07 (m, 2H), 7.20-7.39 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3) δ 43.3, 57.1, 113.4, 117.3, 118.3, 126.2, 126.9, 128.6, 129.0, 134.6, 143.5, 147.3.

N-phenyl-(1,2-diphenylethyl)amine (**13j**):⁴⁰ ^1H NMR (300 MHz, CDCl_3) δ 3.00 (dd, $J = 13.8, 8.4$ Hz, 1H), 3.14 (dd, $J = 14.1, 5.7$ Hz, 1H), 4.12 (bs, 1H), 4.57 (m, 1H), 6.45 (d, $J = 7.8$ Hz, 2H), 6.62 (t, $J = 6.9$ Hz, 1H), 7.04 (t, $J = 7.5$ Hz, 2H), 7.11 (d, $J = 6.3$ Hz, 2H), 7.15-7.35 (m, 8H). ^{13}C NMR (75 MHz, CDCl_3) δ 45.0, 59.5, 113.9, 117.8, 126.5, 126.7, 127.1, 128.5, 128.5, 129.0, 129.2, 137.6, 143.1, 146.9.

4-methyl-*N*-(1-phenylpropyl)benzenesulfonamide (**14**):⁴¹ ^1H NMR (300 MHz, CDCl_3) δ 0.80 (t, $J = 7.5$ Hz, 3H), 1.79 (m, 2H), 2.38 (s, 3H), 4.20 (m, 1H), 5.49 (bs, 1H), 7.01 (m, 2H), 7.16 (m, 5H), 7.55 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 10.4, 21.3, 30.5, 59.7, 126.5, 126.9, 127.0, 128.2, 129.1, 137.6, 140.6, 142.7.

4-methyl-*N*-(2-methyl-1-phenylpropyl)benzenesulfonamide (**15**):⁴² ^1H NMR (300 MHz, CDCl_3) δ 0.72 (d, $J = 6.6$ Hz, 1H), 0.95 (d, $J = 6.6$ Hz, 1H), 1.92 (m, 1H), 2.31 (s, 3H), 4.02 (m, 1H), 5.66 (bs, 1H), 6.95-7.52 (m, 7H), 7.49 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) δ 18.7, 19.2, 21.2, 34.2, 64.1, 126.7, 126.8, 126.9, 127.8, 128.9, 137.5, 139.8, 142.5.

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