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Electronic Supplementary Information

2-Arylallyl as a New Protecting Group for Amines, Amides and Alcohols

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General Methods: All reactions were carried out under a nitrogen atmosphere in oven-dried glassware with magnetic stirring. Temperatures are reported as bath temperatures. Tetrahydrofuran was continuously refluxed and freshly distilled from sodium under nitrogen. Solvents used in extraction and purification were distilled prior to use. TLC was performed on aluminium-backed plates coated with silica gel 60 with F_{254} indicator (Merck) and compounds were visualised by UV light (254 nm) or iodine. Flash column chromatography was carried out on silica gel 60, 230-400 mesh (Merck). Melting points were obtained on a Büchi-Tottoli apparatus with open capillary tubes and are uncorrected. ^{1}H (^{13}C) NMR spectra were recorded at 400 (100.6) and 200 (50.3) MHz on Varian spectrometers with $CDCl_3$ (δ=7.26 ppm in ^{1}H NMR spectra and δ=77.0 ppm in ^{13}C NMR spectra) and [D_6]DMSO (δ=2.50 ppm in ^{1}H NMR spectra and δ=39.43 ppm in ^{13}C NMR spectra) as internal standards by use of the DEPT pulse sequence. Low-resolution electron impact mass spectra (EI-LRMS) were obtained at 70 eV on an HP-5987 A instrument. The intensities are reported as percentages relative to the base peak after the corresponding *m/z* value and only the molecular ions and/or base peaks in LRMS are given. Elemental analyses were performed with Perkin Elmer and LECO elemental analysers. All commercially available reagents were used without further purification unless otherwise indicated and were purchased from Aldrich Chemical Co. and Acros Organics. *t*-BuLi was used as 1.5M solution in pentane.

Preparation of 2-*p*-tolylallyl methanesulfonate: To a solution of 4-methylstyrene (100 mmol, 13.15 mL) in CH_2Cl_2 (40 mL) was added dropwise a solution of Br_2 (100 mmol, 5.14 mL) in CH_2Cl_2 (10 mL) at 0 ºC. The resulting mixture was washed with an aq $KHSO_3$ solution (50 mL), dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The residue of 1-(1,2-dibromoethyl)-4-methylbenzene formed in this way, was dissolved in dry Et_2O (85 mL) under N_2. To this solution was added dropwise a solution of NaOMe (500 mmol, 27 g) in MeOH (110 mL). When addition was completed, the reaction was heated to reflux for 6 h. The resulting mixture was poured over cold H_2O (200 mL) and was extracted with Et_2O (4 x 125 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue of α-bromo-4-methylstyrene was purified by distillation (96-99 ºC, 20 mmHg). To a solution of α-bromo-4-methylstyrene (40 mmol, 7.88 g) in Et_2O (130 mL) was slowly added *t*-BuLi (56 mL of a 1.5M sol. in pentane, 84 mmol) at –78 ºC and the reaction mixture was stirred for 1 h at this temperature. After addition of formaldehyde (80 mmol, 2.4 g), the mixture was stirred for an additional hour at –78 ºC. The cooling bath was removed allowing the reaction to reach room temperature and stirring was continued overnight. The mixture

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was quenched with H_2O (50 ml) and extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under vacuum. The residue was purified by flash column chromatography (hexane/EtOAc, 3:1) affording 2-*p*-tolyl-2-propen-1-ol as a white solid (3.64 g, 51%). M.p. 48-50 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.39-7.35 (m, 2H), 7.20-7.16 (m, 2H), 5.47-5.45 (m, 1H), 5.33-5.31 (m, 1H), 4.52 (s, 2H), 2.38 (s, 3H), 2.22 (broad s, 1H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 146.9, 137.6, 135.4, 129.0, 125.8, 111.5, 64.7, 21.0. LRMS (70 eV, EI): m/z, (%): 148 (M^+, 100). Anal. calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.28; H, 8.02. To a solution of 2-*p*-tolyl-2-propen-1-ol (20 mmol, 2.96 g) and NEt_3 (22 mmol, 3.09 mL) in CH_2Cl_2 (40 mL) was added dropwise $MeSO_2Cl$ (22 mmol, 1.70 mL) in CH_2Cl_2 at 0 ºC and under inert atmosphere. When the addition was completed, the reaction mixture was stirred for 1 h at room temperature and quenched with H_2O (40 mL). The organic compound was extracted with CH_2Cl_2 (3 x 30 mL) and the organic layer was washed with H_2O (3 x 40 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure giving rise to 2-*p*-tolylallyl methanesulfonate as a colorless oil (4.39 g, 97%) that was not further purified. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.38-7.34 (m, 2H), 7.21-7.17 (m, 2H), 5.66-5.65 (m, 1H), 5.46-5.45 (m, 1H), 5.11 (s, 2H), 2.38 (s, 3H), 2.94 (s, 3H), 2.36 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 140.5, 138.4, 133.7, 129.3, 125.7, 117.1, 71.2, 38.2, 21.0. LRMS (70 eV, EI): m/z, (%): 226 (M^+, 91), 117 (100).

Preparation of *N*-2-arylallylamines 1a-d, 1f and 1h. General procedure: A mixture of the corresponding secondary amine (*N*-methylaniline, *N*-allylaniline, dibenzylamine, *N*-allyl-2-fluoroaniline, diallylamine and piperidine) (5 mmol), α-bromomethylstyrene or 2-*p*-tolylallyl methanesulfonate (5 mmol) and K_2CO_3 (5 mmol, 0.69 g) in MeCN (10 mL) was stirred overnight under reflux. The mixture was extracted with EtOAc (3 x 10 mL) and the organic layer was dried over Na_2SO_4. The solvents were removed under vacuum and the residue was purified by silica gel flash column chromatography.

***N*-Methyl-*N*-(2-*p*-tolylallyl)aniline (1a)**: Pale yellow oil (0.91 g, 77%). R_f=0.33 (hexane/EtOAc, 25:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.43-7.37 (m, 2H), 7.32-7.19 (m, 4H), 6.80-6.73 (m, 3H), 5.47-5.44 (m, 1H), 5.14-5.10 (m, 1H), 4.31 (s, 2H), 3.06 (s, 3H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 149.3, 142.4, 137.5, 136.6, 129.1, 129.0, 125.7, 116.1, 111.8, 111.5, 59.5, 38.2, 21.1. LRMS (70 eV, EI): m/z, (%): 237 (M^+, 17), 120 (100). Anal. calcd. for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 85.84; H, 8.01; N, 5.98.

***N*-Allyl-*N*-(2-*p*-tolylallyl)aniline (1b)**: Colorless oil (0.94 g, 71%). R_f=0.33 (hexane/EtOAc, 25:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm) 7.46-7.40 (m, 2H), 7.31-7.21 (m, 4H), 6.82-6.73 (m, 3H), 6.02-5.90 (m, 1H), 5.50-5.47 (m, 1H), 5.31-5.22 (m, 2H), 5.18-5.15 (m, 1H), 4.33 (s, 2H), 4.07 (d, *J*=4.5 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 148.6, 141.9, 137.5, 136.5, 133.6, 129.0, 128.9, 125.7, 116.2, 116.0, 112.0, 111.2, 53.9, 52.7, 21.1. LRMS (70 eV, EI): m/z, (%): 263 (M^+, 19), 146 (100). Anal. calcd. for $C_{19}H_{21}N$: C, 86.65; H, 8.04; N, 5.32. Found: C, 86.51; H, 8.13; N, 5.26.

***N*,*N*-Dibenzyl-2-*p*-tolyl-2-propen-1-amine (1c)**: Colorless oil (1.21 g, 74%). R_f=0.38 (hexane/EtOAc, 20:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.33-7.21 (m, 12H), 7.15-7.10 (m, 2H), 5.46-5.44 (m, 1H), 5.38-5.36 (m, 1H), 3.56 (s, 4H), 3.43 (s, 2H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 145.8, 139.5, 137.2, 137.0, 128.9, 128.5, 128.0, 126.7, 126.5, 114.3, 58.2, 57.9, 21.1. LRMS (70 eV, EI): m/z, (%): 327 (M^+, 2), 91 (100).

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Anal. calcd. for $C_{24}H_{25}N$: C, 88.03; H, 7.70; N, 4.28. Found: C, 87.89, H, 7.58; N, 4.22.

***N*-Allyl-2-fluoro-*N*-(2-*p*-tolylallyl)aniline (1d)**: Colorless oil (0.96 g, 68%). R_f=0.25 (hexane/EtOAc, 40:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.37-7.33 (m, 2H), 7.17-7.14 (m, 2H), 7.05-6.80 (m, 4H), 5.97-5.84 (m, 1H), 5.46-5.44 (m, 1H), 5.26-5.14 (m, 3H), 4.21 (s, 2H), 3.87 (d, *J*=5.8 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 154.8 (d, *J*=241.0 Hz), 143.5, 137.5 (d, *J*=8.4 Hz), 137.3, 136.9, 134.6, 128.9, 126.0, 123.9 (d, *J*=3.7 Hz), 120.5 (d, *J*=7.5 Hz), 120.2 (d, *J*=3.8 Hz), 117.7, 116.2 (d, *J*=21.2 Hz), 113.1, 55.0 (d, *J*=3.4 Hz), 54.4 (d, *J*=4.1 Hz), 21.1. LRMS (70 eV, EI): m/z, (%): 281 (M^+, 11), 164 (100). Anal. calcd. for $C_{19}H_{20}FN$: C, 81.11; H, 7.16; N, 4.98. Found: C 81.22; H, 7.09; N, 5.01.

***N*,*N*-Diallyl-2-phenyl-2-propen-1-amine (1f)**: Colorless oil (0.85 g, 80%). R_f=0.21 (hexane/EtOAc, 30:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.48-7.44 (m, 2H), 7.34-7.23 (m, 3H), 5.89-5.77 (m, 2H), 5.43-5.41 (m, 1H), 5.29-5.27 (m, 1H), 5.19-5.09 (m, 4H), 3.41 (s, 2H), 3.08 (d, *J*=6.4 Hz, 4H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 145.5, 140.4, 135.7, 128.0, 127.3, 126.3, 117.3, 115.0, 57.5, 56.4. LRMS (70 eV, EI): m/z, (%): 213 (M^+, 7), 110 (100). Anal. calcd. for $C_{15}H_{19}N$: C, 84.46; H, 8.98; N, 6.57. Found: C 84.42; H, 8.87; N, 6.52.

1-(2-Phenylallyl)piperidine (1h): Pale yellow oil (0.70 g, 70%). R_f=0.30 (hexane/EtOAc, 2:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.54-7.50 (m, 2H), 7.34-7.23 (m, 3H), 5.46-5.44 (m, 1H), 5.24-5.22 (m, 1H), 3.29 (s, 2H), 2.45-2.35 (m, 4H), 1.58-1.51 (m, 4H), 1.45-1.37 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 144.4, 140.7, 128.0, 127.2, 126.2, 114.8, 63.6, 54.5, 26.0, 24.4. LRMS (70 eV, EI): m/z, (%): 201 (M^+, 10), 98 (100). Anal. calcd. for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96. Found: C 83.39; H, 9.53; N, 6.90.

Preparation of the secondary *N*-2-arylallylamines 1e and 1g, *N*-(2-phenylallyl)aniline, *N*-allyl-2-phenylallylamine and *N*-Allyl-2-fluoroaniline (3d). General procedure: A mixture of the corresponding primary amine (4-methylaniline, benzylamine, aniline or allylamine) (15 mmol), α-bromomethylstyrene, 2-*p*-tolylallyl methanesulfonate or allyl bromide (5 mmol) and K_2CO_3 (5 mmol, 0.69 g) in MeCN (40 mL) was stirred for 24 h under reflux. The mixture was extracted with EtOAc (3 x 20 mL) and the organic layer was dried over Na_2SO_4. The solvents were removed under vacuum and the residue was purified by silica gel flash column chromatography.

4-Methyl-*N*-(2-*p*-tolylallyl)aniline (1e): Pale yellow oil (0.69 g, 58%). R_f=0.28 (hexane/EtOAc, 20:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.43-7.39 (m, 2H), 7.23-7.18 (m, 2H), 7.06-7.01 (m, 2H), 6.72-6.67 (m, 2H), 5.50-5.48 (m, 1H), 5.34-5.32 (m, 1H), 4.16 (s, 2H), 3.79 (broad s, 1H), 2.40 (s, 3H), 2.29 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 145.7, 144.5, 137.6, 136.2, 129.6, 129.1, 126.5, 125.9, 112.9, 112.7, 48.3, 21.1, 20.3. LRMS (70 eV, EI): m/z, (%): 237 (M^+, 38), 120 (100). Anal. calcd. for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C 85.94; H, 8.11; N, 5.84.

***N*-Benzyl-2-phenyl-2-propen-1-amine (1g)**: Pale yellow oil (0.67 g, 60%). R_f=0.23 (hexane/EtOAc, 2:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 77.46-7.42 (m, 2H), 7.37-7.23 (m, 2H), 5.44-5.42 (m, 1H), 5.28-5.26 (m, 1H), 3.80 (s, 2H), 3.69 (s, 2H), 1.59 (broad s, 1H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm), 146.1, 140.1, 139.7, 128.3, 128.2, 128.1, 127.5, 126.8, 126.1, 113.4, 52.8, 52.6. LRMS (70 eV, EI): m/z, (%): 223 (M^+, 4), 91 (100).

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Anal. calcd. for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27. Found: C 86.07; H, 7.55; N, 6.23.

***N*-(2-Phenylallyl)aniline**: Yellow oil (0.59 g, 56%). R_f=0.25 (hexane/EtOAc, 30:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.53-7.49 (m, 2H), 7.43-7.32 (m, 3H), 7.25-7.19 (m, 2H), 6.79-6.74 (m, 1H), 6.69-6.64 (m, 2H), 5.54-5.52 (m, 1H), 5.39-5.37 (m, 1H), 4.20 (s, 2H), 3.92 (broad s, 1H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 147.8, 144.5, 139.1, 129.1, 128.4, 127.8, 126.0, 117.4, 113.6, 112.7, 47.9. LRMS (70 eV, EI): m/z, (%): 209 (M^+, 1), 152 (100). Anal. calcd. for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69. Found: C 87.95; H, 7.15; N, 6.60.

***N*-Allyl-2-phenyl-2-propen-1-amine**: Yellow oil (0.57 g, 54%). R_f=0.18 (hexane/EtOAc, 1:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.52-7.48 (m, 2H), 7.43-7.30 (m, 3H), 6.01-5.90 (m, 1H), 5.47-5.45 (m, 1H), 5.31-5.29 (m, 1H), 5.26-5.20 (m, 1H), 5.17-5.13 (m, 1H), 3.72 (s, 2H), 3.33 (d, *J*=6.1 Hz, 2H), 1.42 (broad s, 1H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 146.1, 139.7, 136.6, 128.3, 127.6, 126.0, 116.0, 113.3, 52.5, 51.5, 47.9. LRMS (70 eV, EI): m/z, (%): 173 (M^+, 4), 70 (100). Anal. calcd. for $C_{12}H_{15}N$: C, 83.19; H, 8.73; N, 8.08. Found: C 83.09; H, 8.80; N, 8.05.

***N*-Allyl-2-fluoroaniline (3d)**: Pale orange oil (0.42 g, 55%). R_f=0.35 (hexane/EtOAc, 30:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.06-6.98 (m, 2H), 6.76-6.63 (m, 2H), 6.04-5.93 (m, 1H), 5.37-5.29 (m, 1H), 5.25-5.20 (m, 1H), 4.10 (s broad, 1H), 3.85 (d, *J*=4.9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 151.6 (d, *J*=238.2 Hz), 136.4 (d, *J*=11.5 Hz), 134.9, 124.4 (d, *J*=3.0 Hz), 116.6 (d, *J*=6.8 Hz), 116.2, 114.2 (d, *J*=18.3 Hz), 112.2 (d, *J*=3.1 Hz), 45.9. LRMS (70 eV, EI): m/z, (%): 151 (M^+, 99), 124 (100). Anal. calcd. for $C_9H_{10}FN$: C, 71.50; H, 6.67; N, 9.26. Found: C 71.64; H, 6.58; N, 9.35.

Preparation of *N*-2-arylallyl aromatic heterocycles 1i, j: To a suspension of α-bromomethylstyrene or 2-*p*-tolylallyl methanesulfonate (7.5 mmol), Bu_4NBr (0.25 mmol, 81 mg) and 50% NaOH aq solution (2.5 mL) in toluene (5 mL), indole or imidazole (5 mmol) was added and the resulting mixture was heated at 50 ºC for 2 h. H_2O (15 mL) was added and the organic compound was extracted with Et_2O (3 x 15 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvents were removed under reduced pressure. The residue was purified by flash column chromatography (hexane/EtOAc) giving rise to compounds **1i,j**.

1-(2-Phenylallyl)imidazole (1i): Pale yellow oil (0.69 g, 75%). R_f=0.13 (EtOAc). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.45 (s, 1H), 7.32-7.23 (m, 5H), 7.01-6.99 (m, 1H), 6.88-6.86 (m, 1H), 5.49-5.47 (m, 1H), 4.99-4.97 (m, 1H), 4.87 (s, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 143.2, 137.6, 137.2, 129.1, 128.4, 128.1, 125.6, 119.1, 115.2, 50.4. LRMS (70 eV, EI): m/z, (%): 184 (M^+, 73), 183 (100). Anal. calcd. for $C_{12}H_{12}N_2$: C, 78.23; H, 6.57; N, 15.21. Found: C 78.09; H, 6.59; N, 15.17.

1-(2-*p*-Tolylallyl)-1*H*-indole (1j): White solid (0.93 g, 78%). M.p. 69-71ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.75-7.71 (m, 1H), 7.44-7.38 (m, 3H), 7.32-7.27 (m, 1H), 7.25-7.19 (m, 3H), 7.18 (d, *J*=3.1 Hz, 1H), 6.60 (d, *J*=3.1 Hz, 1H), 5.52-5.50 (m, 1H), 5.14 (s, 2H), 4.80-4.78 (m, 1H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 142.9, 137.9, 136.2, 135.6, 129.2, 128.5, 128.2, 125.6, 121.5, 120.8, 119.4, 113.2, 109.5, 101.4, 49.8, 21.0. LRMS (70 eV, EI): m/z, (%): 247 (M^+, 100). Anal. calcd. for $C_{18}H_{17}N$: C, 87.41; H, 6.93; N, 5.66. Found: C 87.29; H, 6.90; N, 5.60.

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Preparation of *N*-2-arylallylamides 1k-s. General procedure: To a solution of *N*-benzyl-2-phenyl-2-propen-1-amine **1g**, *N*-2-phenylallylaniline or *N*-allyl-*N*-2-phenylallylamine (2.5 mmol) and NEt_3 (3 mmol, 0.42 mL) in CH_2Cl_2 (5 mL), the corresponding acid chloride (benzoyl chloride, pivaloyl chloride or *p*-toluenesulfonyl chloride) (3 mmol) was added dropwise at 0 ºC. After stirring for 2 h at room temperature, the mixture was quenched with H_2O (5 ml) and extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were washed with a 2M HCl aq solution (2 x 10 mL) and with a saturated $NaHCO_3$ aq solution (2 x 10 mL) and were dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the resulting residues were purified by silica gel column chromatography (hexane/EtOAc).

***N*-Phenyl-*N*-(2-phenylallyl)benzamide (1k)**: White solid (0.68 g, 87%). M.p. 59-61 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.49-7.44 (m, 2H), 7.37-7.27 (m, 3H), 7.24-7.16 (m, 3H), 7.15-7.05 (m, 5H), 6.88-6.83 (m, 2H), 5.44-5.42 (m, 1H), 5.24-5.22 (m, 1H), 5.06 (s, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 170.3, 144.0, 142.8, 138.7, 136.0, 129.4, 128.6, 128.3, 128.2, 127.8, 127.6, 127.5, 126.5, 126.4, 114.9, 52.8. LRMS (70 eV, EI): m/z, (%): 313 (M^+, 71), 105 (100). Anal. calcd. for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C 84.37; H, 6.10; N, 4.52.

***N*-Allyl-*N*-(2-phenylallyl)benzamide (1l)**: White solid (0.60 g, 86%). M.p. 55-57 ºC. ^{1}H NMR (DMSO-d_6, 120 ºC, 400 MHz): δ (ppm) 7.42-7.25 (m, 10H), 5.85-5.74 (m, 1H), 5.47-5.45 (m, 1H), 5.23-5.21 (m, 1H), 5.16-5.08 (m, 2H), 4.40 (s, 2H), 3.88 (d, *J*=5.5 Hz, 2H). ^{13}C NMR (DMSO-d_6, 120 ºC, 100.6 MHz): δ (ppm) 170.1, 143.0, 138.2, 136.0, 132.8, 129.0-124.6 (several peaks), 116.4**,** 113.4-112.9 (several peaks), 48.9-47.7 (several peaks). LRMS (70 eV, EI): m/z, (%): 277 (M^+, 90), 276 (100). Anal. calcd. for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C 82.34; H, 6.89; N, 5.01.

***N*-Benzyl-*N*-(2-phenylallyl)benzamide (1m)**: Pale yellow solid (0.63 g, 77%). M.p. 116-118 ºC. ^{1}H NMR (DMSO-d_6, 120 ºC, 400 MHz): δ (ppm) 7.42-7.20 (m, 15H), 5.46-5.44 (m, 1H), 5.17-5.15 (m, 1H), 4.53 (s, 2H), 4.34 (s, 2H). ^{13}C NMR (DMSO-d_6, 120 ºC, 100.6 MHz): δ (ppm) 170.4, 142.9, 138.1, 136.5, 135.8, 129.0-125.0 (several peaks), 113.7-113.3 (several peaks), 49.4-48.5 (several peaks). LRMS (70 eV, EI): m/z, (%): 327 (M^+, 67), 105 (100). Anal. calcd. for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.28. Found: C 84.48; H, 6.39; N, 4.26.

4-Methyl-*N*-phenyl-*N*-(2-phenylallyl)benzenesulfonamide (1n): Pale yellow solid (0.68 g, 75%). M.p. 102-104 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.49, 7.45 (m, 2H), 7.40-7.16 (m, 10H), 6.82-6.78 (m, 2H), 5.28-5.26 (m, 1H), 5.05-5.03 (m, 1H), 4.62 (m, 2H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 143.4, 142.2, 138.2, 138.0, 134.8, 129.3, 128.9, 128.5, 128.1, 127.8, 127.7, 127.6, 126.4, 116.9, 54.1, 21.5. LRMS (70 eV, EI): m/z, (%): 363 (M^+, 79), 91 (100). Anal. calcd. for $C_{22}H_{21}NO_2S$: C, 72.70; H, 5.82; N, 3.85. Found: C 72.53; H, 5.90; N, 3.79.

***N*-Allyl-4-methyl-*N*-(2-phenylallyl)benzenesulfonamide (1o)**: White solid (0.70 g, 86%). M.p. 38-40 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.66-7.62 (m, 2H), 7.41-7.23 (m, 7H), 5.56-5.45 (m, 1H), 5.45-5.43 (m, 1H), 5.23-5.21 (m, 1H), 5.10-5.03 (m, 2H), 4.22 (s, 2H), 3.73 (d, *J*=6.6 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 143.1, 142.5, 138.5, 136.9, 132.2, 129.5, 128.3, 127.9, 127.2, 126.4, 119.2, 116.1, 50.2, 49.3, 21.4. LRMS (70 eV, EI): m/z, (%): 327 (M^+, 70), 155 (100). Anal. calcd. for $C_{19}H_{21}NO_2S$: C, 66.69; H,

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6.46; N, 4.28. Found: C 66.71; H, 6.39; N, 4.31.

***N*-Benzyl-4-methyl-*N*-(2-phenylallyl)benzenesulfonamide (1p)**: White solid (0.66 g, 70%). M.p. 85-87 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.65-7.61 (m, 2H), 7.27-7.09 (m, 12H), 5.30-5.28 (m, 1H), 5.07-5.05 (m, 1H), 4.30 (s, 2H), 4.22 (s, 2H), 2.43 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 143.1, 142.5, 138.5, 136.9, 135.8, 129.5, 128.4, 128.2, 128.1, 127.7, 127.4, 127.2, 126.3, 116.5, 51.1, 50.8, 21.4. LRMS (70 eV, EI): m/z, (%): 377 (M^+, 1), 91 (100). Anal. calcd. for $C_{23}H_{23}NO_2S$: C, 73.18; H, 6.14; N, 3.71. Found: C 72.97; H, 6.17; N, 3.64.

***N*-Phenyl-*N*-(2-phenylallyl)pivalamide (1q)**: White solid (0.62 g, 84%). M.p. 62-64 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.42-7.39 (m, 2H), 7.34-7.24 (m, 6H), 7.00-6.96 (m, 2H), 5.33-5.31 (m, 1H), 4.97-4.95 (m, 1H), 4.79 (s, 2H), 0.93 (s, 9H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 177.5, 144.0, 142.8, 138.7, 129.7, 128.6, 128.2, 127.8, 127.7, 124.4, 115.1, 55.3, 41.0, 29.3. LRMS (70 eV, EI): m/z, (%): 293 (M^+, 63), 57 (100). Anal. calcd. for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C 82.01; H, 7.79; N, 4.71.

***N*-Allyl-*N*-(2-phenylallyl)pivalamide (1r)**: Colorless oil (0.51 g, 80%). R_f=0.40 (hexane/EtOAc, 3:1). ^{1}H NMR (DMSO-d_6, 80 ºC, 400 MHz): δ (ppm) 7.43-7.28 (m, 5H), 5.86-5.75 (m, 1H), 5.45-5.43 (m, 1H), 5.21-5.11 (m, 2H), 5.02-5.00 (m, 1H), 4.36 (s, 2H), 3.99 (d, *J*=5.1 Hz, 2H), 1.19 (s, 9H). ^{13}C NMR (DMSO-d_6, 80 ºC, 100.6 MHz): δ (ppm) 175.9, 143.1, 138.5, 133.6, 127.8, 127.3, 125.4, 116.2, 112.1-111.7 (several peaks), 48.9, 48.6, 38.1, 27.8. LRMS (70 eV, EI): m/z, (%): 257 (M^+, 82), 57 (100). Anal. calcd. for $C_{17}H_{23}NO$: C, 79.33; H, 9.01; N, 5.44. Found: C 79.27; H, 8.91; N, 5.50.

***N*-Benzyl-*N*-(2-phenylallyl)pivalamide (1s)**: White solid (0.58 g, 75%). M.p. 45-47 ºC. ^{1}H NMR (DMSO-d_6, 80 ºC, 400 MHz): δ (ppm) 7.40-7.19 (m, 10H), 5.49-5.47 (m, 1H), 5.01-4.99 (m, 1H), 4.62 (s, 2H), 4.35 (s, 2H), 1.22 (s, 9H). ^{13}C NMR (DMSO-d_6, 80 ºC, 100.6 MHz): δ (ppm) 176.4, 142.9, 138.4, 137.3, 127.9, 127.8, 127.3, 126.4, 125.4, 112.4-112.0 (several peaks), 49.6, 49.2, 38.3, 27.8. LRMS (70 eV, EI): m/z, (%): 307 (M^+, 98), 57 (100). Anal. calcd. for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56. Found: C 81.98; H, 8.22; N, 4.51.

Preparation of *N*,*N*-bis-2-(*p*-tolyl)allylamines 1t,u. General procedure: A mixture of the corresponding primary amine (4-methylaniline or benzylamine) (3 mmol), 2-*p*-tolylallyl methanesulfonate (6 mmol, 1.36 g) and K_2CO_3 (6 mmol, 0.83 g) in MeCN (15 mL) was heated to reflux overnight. The mixture was extracted with EtOAc (3 x 20 mL) and the organic layer was dried over Na_2SO_4. The solvents were removed under vacuum and the residue was purified by silica gel flash column chromatography.

4-Methyl-*N*,*N*-bis-(2-(*p*-tolyl)allyl)aniline (1t): Pale yellow oil (0.77 g, 70%). R_f=0.38 (hexane/EtOAc, 20:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.39-7.35 (m, 4H), 7.20-7.16 (m, 4H, 7.04-7.00 (m, 2H), 6.66-6.62 (m, 2H), 5.44-5.42 (m, 2H), 5.11-5.09 (m, 2H), 4.35 (s, 4H), 2.38 (s, 6H), 2.26 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 146.2, 141.7, 137.5, 136.6, 129.5, 129.0, 125.7, 125.2, 111.8, 111.2, 54.1, 21.1, 20.2. LRMS (70 eV, EI): m/z, (%): 367 (M^+, 9), 265 (100). Anal. calcd. for $C_{27}H_{29}N$: C, 88.24; H, 7.95; N, 3.81. Found: C 88.33; H, 7.86; N, 3.80.

***N*-Benzyl-*N*,*N*-bis-(2-(*p*-tolyl)allyl)amine (1u)**: Colorless oil (0.84 g, 76%). R_f=0.35 (hexane/EtOAc, 20:1). ^{1}H

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NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.29-7.21 (m, 3H), 7.15-7.05 (m, 6H), 7.01-6.95 (m, 4H), 5.45-5.42 (m, 2H), 5.27-5.24 (m, 2H), 3.49 (s, 2H), 3.40 (s, 4H), 2.37 (s, 6H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 145.5, 139.4, 136.8, 136.7, 129.3, 128.4, 127.8, 126.7, 126.6, 114.4, 58.7, 57.9, 21.1. LRMS (70 eV, EI): m/z, (%): 367 (M^+, 3), 91 (100). Anal. calcd. for $C_{27}H_{29}N$: C, 88.24; H, 7.95; N, 3.81. Found: C 88.11; H, 7.94; N, 3.79.

Preparation of *N*,*N*-bis-(2-phenylallyl)amides 1v,w. General procedure: To a mixture of benzamide or benzenesulfonamide (5 mmol), finely powdered NaOH (25 mmol, 1 g), K_2CO_3 (7 mmol, 0.97 g), Bu_4NHSO_4 (0.5 mmol, 170 mg) and toluene (6 mL), a solution of α-bromomethylstyrene (12 mmol, 2.35 g) in toluene (2 ml) was added dropwise. When addition was completed, stirring was continued for 2.5 h at reflux temperature. H_2O (10 mL) was added and the mixture was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with H_2O(3 x 10 mL) and dried over anhydrous Na_2SO_4. The solvents were evaporated under reduced pressure and the resulting residues were purified by flash column chromatography.

***N*,*N*-Bis-(2-phenylallyl)benzamide (1v)**: Orange oil (0.92 g, 52%). R_f=0.15 (hexane/EtOAc, 5:1). ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.58-7.07 (m, 15H), 5.58-5.44 (m, 2H), 5.27-5.23 (m, 2H), 4.70 (s, 2H), 4.10 (s, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 172.1, 143.5, 135.9, 129.5, 128.3, 128.2, 128.0, 126.4, 126.2, 126.1, 114.9, 114.1, 51.3, 46.8. LRMS (70 eV, EI): m/z, (%): 353 (M^+, 37), 77 (100). Anal. calcd. for $C_{25}H_{23}NO$: C, 84.95; H, 6.56; N, 3.96. Found: C 85.17; H, 6.45; N, 3.88.

***N*,*N*-Bis-(2-phenylallyl)benzenesulfonamide (1w)**: Orange oil (1.07 g, 55%). R_f=0.37 (hexane/EtOAc, 3:1). ^1H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.76-7.72 (m, 2H), 7.58-7.53 (m, 1H), 7.47-7.41 (m, 2H), 7.27-7.24 (m, 10H), 5.34-5.32 (m, 2H), 5.11-5.09 (m, 2H), 4.24 (s, 4H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 142.1, 139.7, 138.8, 132.3, 128.8, 128.2, 127.8, 127.2, 126.2, 116.2, 50.9. LRMS (70 eV, EI): m/z, (%): 389 (M^+, 47), 77 (100). Anal. calcd. for $C_{24}H_{23}NO_2S$: C, 74.00; H, 5.95; N, 3.60. Found: C 73.87; H, 6.02; N, 3.63.

Deprotection of *N*-2-aryl-2-propenylamines and *N*-2-aryl-2-propenylamides 1. General procedure: A solution of the corresponding amine or amide **1** (1 mmol) in THF (1 mL) was treated with *t*-BuLi (0.67 mL of a 1.5M sol. in pentane, 1 mmol) at –78 ºC (in the case of amide **1k**, 2 equiv of *t*-BuLi were necessary). After stirring for 5 min at this temperature, the reaction mixture was warmed to 0 ºC and it was stirred for 15 min at this temperature. The reaction was quenched with MeOH. H_2O (10 mL) was added and the organic compound was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvents were removed under vacuum affording the corresponding secondary amines and amides **3**, together with the α-neopentylstyrene derivatives **5**, which were separated and purified by silica gel column chromatography (hexane/EtOAc).

***N*-Methylaniline (3a), *N*-Allylaniline (3b), Dibenzylamine (3c), Diallylamine (3f), Piperidine (3h), Imidazole (3i), Indole (3j), *N*-Phenylbenzamide (3k), *N*-Benzylbenzamide (3m)**: Data are in good agreement with the corresponding commercial products.

***N*-Allyl-2-fluoroaniline (3d)**: Data are showed above.

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***N*-Allylbenzamide (3l)**: White solid (147 mg, 91%). M.p 122-124 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.81-7.76 (m, 2H), 7.53-7.41 (m, 3H), 6.22 (broad s, 1H), 6.00-5.89 (m, 1H), 5.27 (ddd, *J*=17.2, 3.0 and 1.5 Hz, 1H), 5.19 (ddd, *J*=10.3, 3.0 and 1.5 Hz, 1H), 4.10 (tt, *J*=5.7 and 1.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 167.3, 134.2, 134.0, 131.3, 128.4, 126.8, 116.3, 42.3. LRMS (70 eV, EI): m/z, (%): 151 (M^+, 54), 77 (100). Anal. calcd. for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C 74.44; H, 6.85; N, 8.68.

4-Methyl-*N*-phenylbenzenesulfonamide (3n): White solid (198 mg, 80%). M.p 102-104 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.71-7.67 (m, 2H), 7.27-7.19 (m, 5H), 7.12-7.06 (m, 3H), 2.36 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 143.8, 136.5, 135.8, 129.5, 129.2, 127.2, 125.1, 121.3, 22.4. LRMS (70 eV, EI): m/z, (%): 247 (M^+, 95), 91 (100). Anal. calcd. for $C_{13}H_{13}NO_2S$: C, 63.13; H, 5.30; N, 5.66. Found: C 62.97; H, 5.31; N, 5.64.

***N*-Allyl-4-methylbenzenesulfonamide (3o)**: White solid (182 mg, 86%). M.p 60-62 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.78-7.73 (m, 2H), 7.33-7.28 (m, 2H), 5.76-5.66 (m, 1H), 5.18-5.06 (m, 2H), 4.72 (t, *J*=6.1 Hz, 1H), 3.57 (tt, *J*=6.1 and 1.5 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 143.2, 136.8, 132.8, 129.5, 127.0, 117.3, 45.5, 21.3. LRMS (70 eV, EI): m/z, (%): 211 (M^+, 13), 91 (100). Anal. calcd. for $C_{10}H_{13}NO_2S$: C, 56.95; H, 6.20; N, 6.63. Found: C 57.01; H, 6.14; N, 6.60.

***N*-Benzyl-4-methylbenzenesulfonamide (3p)**: White solid (248 mg, 95%). M.p 115-117 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.75-7.71 (m, 2H), 7.30-7.15 (m, 7H), 5.04 (t, *J*=6.2 Hz, 1H), 4.08 (d, *J*=6.2 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 144.3, 136.6, 136.2, 129.6, 128.5, 127.7, 127.6, 127.0, 47.1, 21.4. LRMS (70 eV, EI): m/z, (%): 261 (M^+, 2), 91 (100). Anal. calcd. for $C_{14}H_{15}NO_2S$: C, 64.34; H, 5.79; N, 5.36. Found: C 64.47; H, 5.90; N, 5.28.

***N*-Phenylpivalamide (3q)**: White solid (138 mg, 78%). M.p. 132-134 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.55-7.51, (m, 2H), 7.43 (broad s, 1H), 7.33-7.27 (m, 2H), 7.11-7.06 (m, 1H), 1.31 (s, 9H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 176.5, 137.9, 128.8, 124.0, 119.9, 39.4, 27.5. LRMS (70 eV, EI): m/z, (%): 177 (M^+, 90), 93 (100). Anal. calcd. for $C_{11}H_{15}NO$: C, 74.54; H, 8.53; N, 7.90. Found: C 74.35; H, 8.61; N, 7.81.

***N*-Allylpivalamide (3r)**: White solid (119 mg, 84%). M.p 25-27 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 5.86-5.74 (m, 2H), 5.15-5.06 (m, 2H), 3.83 (tt, *J*=5.7 and 1.6 Hz, 2H), 1.17 (s, 9H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 178.2, 134.4, 115.9, 41.7, 38.5, 27.4. LRMS (70 eV, EI): m/z, (%): 141 (M^+, 79), 57 (100). Anal. calcd. for $C_8H_{15}NO$: C, 68.04; H, 10.71; N, 9.92. Found: C 67.99; H, 10.76; N, 9.85.

***N*-Benzylpivalamide (3s)**: White solid (164 mg, 86%). M.p 79-81 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.35-7.22 (m, 5H), 5.98 (broad s, 1H), 4.41 (d, *J*=5.6 Hz, 2H), 1.21 (s, 9H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 178.2, 138.5, 128.6, 127.5, 127.3, 43.4, 38.6, 27.5. LRMS (70 eV, EI): m/z, (%): 191 (M^+, 97), 91 (100). Anal. calcd. for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C 75.43; H, 9.04; N, 7.25.

4,4-Dimethyl-2-phenyl-1-pentene (5a): Colorless oil. R_f=0.37 (hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.42-7.37 (m, 2H), 7.34-7.28 (m, 2H), 7.27-7.22 (m, 1H), 5.27-5.25 (m, 1H), 5.04-5.02 (m, 1H), 2.50-2.47 (m,

2H), 0.81 (s, 9H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 147.5, 143.6, 128.0, 126.8, 126.4, 116.3, 48.8, 31.7, 30.0. LRMS (70 eV, EI): m/z, (%): 174 (M^+, 7), 57 (100). Anal. calcd. for $C_{13}H_{18}$: C, 89.59; H 10.41. Found: C, 89.53; H, 10.37.

4,4-Dimethyl-2-*p*-tolyl-1-pentene (5b): Colorless oil. R_f=0.55 (hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.29-7.25, (m, 2H), 7.12-7.08 (m, 2H), 5.22 (d, *J*=2.2 Hz, 1H), 4.98-4.96 (m, 1H), 2.45 (s, 2H), 2.33 (s, 3H), 0.80 (s, 9H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 147.3, 140.7, 136.5, 128.7, 126.3, 115.5, 48.8, 31.7, 30.0, 21.0. LRMS (70 eV, EI): m/z, (%): 188 (M^+, 9), 132 (100). Anal. calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C 89.14; H, 10.68.

Deprotection of *N*-2-arylallylamines 1e and 1g and deprotection of *N*,*N*-bis(2-arylallyl)amines and *N*,*N*-bis(2-arylallyl)amides 1t-w. General procedure: A solution of the corresponding *N*-2-arylallylamine **1e**,**g** or a solution of the corresponding *N*,*N*-bis-(2-arylallyl)amine or amide **1t,w** (1 mmol) in THF (1 mL) was treated with 2 equiv of *t*-BuLi (1.33 mL of a 1.5M sol. in pentane, 2 mmol) at –78 ºC. After stirring for 5 min at this temperature, the reaction mixture was warmed to 0 ºC and it was stirred for 15 min at this temperature. The reaction was quenched with MeOH. H_2O (10 mL) was added and the organic compound was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvents were removed under vacuum affording the corresponding primary amines or amides, together with the α-neopentylstyrene derivatives **5**, which were separated and purified by silica gel column chromatography (hexane/EtOAc).

***p*-Toluidine (3e) , Benzylamine (3g), Benzamide, Benzenesulfonamide**: Data are in good agreement with the corresponding commercial products.

Representative procedure for the synthesis of the starting ethers 2a-d and 2f,l: The corresponding phenol or naphtol (10 mmol) and α-bromomethylstyrene (10 mmol) were dissolved in acetone (50 mL). K_2CO_3 (1.38 g, 10 mmol) was added to the solution and the resulting mixture was heated at reflux for 10 h. Then, the mixture was cooled to room temperature, filtered through Celite and concentrated under reduced pressure. The residue was purified by flash chromatography (hexane/EtOAc) to afford the corresponding ethers.

2-*tert*-Butyl-4-methyl-1-(2-phenylallyloxy)benzene (2a): Colorless oil (1.71 g, 61%). R_f=0.55 (hexane/EtOAc, 7:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.59-7.54 (m, 2H), 7.46-7.35 (m, 3H), 7.20 (d, *J*=2.1 Hz, 1H), 7.07 (dd, *J*=8.2 and 2.1 Hz, 1H), 6.93 (d, *J*=8.2 Hz, 1H), 5.68-5.66 (m, 1H), 5.62-5.59 (m, 1H), 5.00-4.97 (m, 2H), 2.39 (s, 3H), 1.43 (s, 9H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 155.2, 143.6, 138.6, 138.0, 129.4, 128.3, 127.8, 127.5, 127.0, 126.0, 114.1, 112.2, 69.9, 34.9, 29.7, 20.8. LRMS (70 eV, EI): m/z, (%): 280 (M^+, 100). Anal. calcd. for $C_{20}H_{24}O$: C, 85.67; H 8.63. Found: C, 85.56; H, 8.58.

1-Chloro-3-(2-phenylallyloxy)benzene (2b): Colorless oil (1.59 g, 65%). R_f=0.38 (hexane/EtOAc, 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.54-7.49 (m, 2H), 7.44-7.34 (m, 3H), 7.24 (t, *J*=8.1 Hz, 1H), 7.04-6.98 (m, 2H), 6.91-6.87 (m, 1H), 5.68-5.66 (m, 1H), 5.52-5.50 (m, 1H), 4.92-4.90 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 159.2, 142.4, 137.9, 134.7, 130.1, 128.4, 128.0, 125.9, 121.1, 115.2, 115.0, 113.3, 69.8. LRMS

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(70 eV, EI): m/z, (%): 246 (M^++2, 11), 244 (M^+, 31), 115 (100). Anal. calcd. for $C_{15}H_{13}ClO$: C, 73.62; H 5.35. Found: C, 73.70; H, 5.32.

2-Chloro-4-methoxy-1-(2-phenylallyloxy)benzene (2c): Colorless oil (1.84 g, 67%). R_f=0.31 (hexane/EtOAc, 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.55-7.55 (m, 2H), 7.42-7.31 (m, 3H), 6.99 (d, *J*=3.0 Hz, 1H), 6.92 (d, *J*=9.0 Hz, 1H), 6.76 (dd, *J*=9.0 and 3.0 Hz, 1H), 5.64-5.62 (m, 1H), 5.56-5.53 (m, 1H), 4.93-4.90 (m, 2H), 3.76 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 154.1, 148.1, 142.6, 138.2, 128.3, 127.9, 125.9, 123.9, 115.8, 115.7, 114.6, 112.7, 71.4, 55.6. LRMS (70 eV, EI): m/z, (%): 276 (M^++2, 17), 274 (M^+, 51), 157 (100). Anal. calcd. for $C_{16}H_{15}ClO_2$: C, 69.95; H 5.50. Found: C, 69.87; H, 5.52.

1-(2-Phenylallyloxy)naphthalene (2d): Colorless oil (1.33 g, 51%). R_f=0.33 (hexane/EtOAc, 30:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 8.42-8.37 (m, 1H), 7.94-7.89 (m, 1H), 7.68-7.39 (m, 9H), 6.98 (d, *J*=7.8 Hz, 1H), 5.81-5.77 (m, 1H), 5.73-5.69 (m, 1H), 5.17-5.13 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 154.2, 142.6, 138.3, 134.4, 128.4, 127.9, 127.3, 126.3, 125.9, 125.7, 125.6, 125.1, 122.0, 120.4, 114.6, 105.0, 69.8. LRMS (70 eV, EI): m/z, (%): 260 (M^+, 100). Anal. calcd. for $C_{19}H_{16}O$: C, 87.66; H 6.19. Found: C, 87.70; H, 6.10.

1-[(*tert*-Butyldimethylsiloxy)methyl]-4-(2-phenylallyloxy)benzene (2f): Pale yellow oil (2.23 g, 63%). R_f=0.38 (hexane/EtOAc, 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.55-7.50 (m, 2H), 7.42-7.34 (m, 3H), 7.31-7.28 (m, 2H), 7.00-7.96 (m, 2H), 5.67-5.64 (m, 1H), 5.52-5.50 (m, 1H), 4.94-4.92 (m, 2H), 4.73 (s, 2H), 0.99 (s, 9H), 0.15 (s, 6H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 157.6, 142.9, 138.2, 133.8, 128.4, 127.9, 127.4, 125.9, 114.7, 114.6, 69.8, 64.6, 25.9, 18.4, -5.3. HRMS calcd. for $C_{22}H_{30}O_2Si$: 354.2015, found: 354.2021.

1-(Allyloxy)-4-(2-phenylallyloxy)benzene (2l): Yellow solid (1.65 g, 62%). M.p. 38-40 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.64-7.60 (m, 2H), 7.51-7.40 (m, 3H), 7.06-6.97 (m, 4H), 6.23-6.12 (m, 1H), 5.76-5.73 (m, 1H), 5.62-5.59 (m, 1H), 5.53 (dq, *J*=17.3 and 1.6 Hz, 1H), 5.40 (dq, *J*=10.5 and 1.6 Hz, 1H), 4.97-4.94 (m, 2H), 4.58 (dt, *J*=5.3 and 1.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 152.7, 152.6, 142.9, 138.1, 133.3, 128.2, 127.7, 125.7, 117.1, 115.6, 115.3, 114.4, 70.2, 69.0. LRMS (70 eV, EI): m/z, (%): 266 (M^+, 24), 117 (100). Anal. calcd. for $C_{18}H_{18}O_2$: C, 81.17; H 6.81. Found: C, 81.05; H, 6.75.

Representative procedure for the synthesis of the starting ethers 2e-k: The corresponding alcohol (10 mmol) dissolved in THF (10mL) was added to a stirred suspension of NaH (10 mmol, 0.24 g) in THF (20 mL) at 0 ºC. After additional 30 min at room temperature, α-bromomethylstyrene (1.97 g, 10 mmol) in THF (10 mL) was added to the solution and the resulting mixture was heated at reflux for 10 h. Then, the mixture was cooled to room temperature, filtered through Celite and concentrated under reduced pressure. The residue was purified by flash chromatography (hexane/EtOAc) to afford the corresponding ethers.

(2-Phenylallyloxy)methylbenzene (2e): Pale yellow oil (1.30 g, 58%). R_f=0.19 (hexane/EtOAc, 30:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.55-7.51 (m, 2H), 7.42-7.30 (m, 8H), 5.62-5.60 (m, 1H), 5.44-5.42 (m, 1H), 4.62 (s, 2H), 4.48-4.46 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 144.1, 138.6, 138.1, 128.3, 128.2, 127.7, 127.6, 127.5, 126.0, 114.4, 71.9, 71.8. LRMS (70 eV, EI): m/z, (%): 224 (M^+, 1), 118 (100). Anal. calcd.

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for $C_{16}H_{16}O$: C, 85.68; H 7.19. Found: C, 85.53; H, 7.13.

5-[(2-Phenylallyloxy)methyl]benzo[*d*][1,3]dioxole (2g): Pale yellow oil (1.55 g, 58%). R_f=0.27 (hexane/EtOAc, 10:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.54-7.50 (m, 2H), 7.41-7.30 (m, 3H), 6.86 (s, 1H), 6.84-6.78 (m, 2H), 5.95 (s, 2H), 5.61-5.59 (m, 1H), 5.42-5.40 (m, 1H), 4.49 (s, 2H), 4.44-4.42 (m, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 147.5, 146.9, 144.0, 138.5, 131.9, 128.2, 127.6, 125.9, 121.2, 114.3, 108.4, 107.8, 100.8, 71.6, 71.5. LRMS (70 eV, EI): m/z, (%): 268 (M^+, 2), 150 (100). Anal. calcd. for $C_{17}H_{16}O_3$: C, 76.10; H 6.01. Found: C, 76.19; H, 6.03.

2,2-Dimethyl-4-[(2-phenylallyloxy)methyl]-1,3-dioxolane (2h): Yellow oil (1.34 g, 54%). R_f=0.34 (hexane/EtOAc, 5:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.49-7.44 (m, 2H), 7.36-7.24 (m, 3H), 5.55-5.53 (m, 1H), 5.34-5.31 (m, 1H), 4.47 (d, *J*=13.0 Hz, 1H), 4.39 (d, *J*=13.0 Hz, 1H), 4.25 (quint, *J*=6.0 Hz, 1H), 3.99 (dd, *J*=8.3 and 6.0 Hz, 1H), 3.67 (dd, *J*=8.3 and 6.0 Hz, 1H), 3.55 (dd, *J*=9.8 and 6.0 Hz, 1H), 3.48 (dd, *J*=9.8 and 6.0 Hz, 1H), 1.40 (s, 3H), 1.35 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 143.7, 138.4, 128.2, 127.7, 125.9, 114.5, 109.2, 74.5, 73.2, 70.5, 66.7, 26.6, 25.2. LRMS (70 eV, EI): m/z, (%): 248 (M^+, 15), 117 (100). Anal. calcd. for $C_{15}H_{20}O_3$: C, 72.55; H 8.12. Found: C, 72.60; H, 8.09.

(*E*)-3,7-Dimethyl-1-(2-phenylallyloxy)-2,6-octadiene (2i): Pale yellow oil (1.67 g, 62%). R_f=0.09 (hexane/EtOAc, 30:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.49-7.45 (m, 2H), 7.36-7.24 (m, 3H), 5.53-5.51 (m, 1H), 5.39-5.32 (m, 2H), 5.11-5.05 (m, 1H), 4.37-4.34 (m, 2H), 4.03 (d, *J*=6.9 Hz, 2H), 2.12-1.99 (m, 4H), 1.66 (s, 3H), 1.63 (s, 3H), 1.59 (s, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 144.4, 140.4, 138.8, 131.6, 128.2, 127.6, 126.0, 123.9, 120.6, 114.3, 71.6, 66.3, 39.5, 26.3, 25.6, 17.6, 16.4. LRMS (70 eV, EI): m/z, (%): 270 (M^+, 2), 69 (100). Anal. calcd. for $C_{19}H_{26}O$: C, 84.39; H 9.69. Found: C, 84.49; H, 9.65.

(*E*)-1-(2-Phenylallyloxy)-3-phenyl-2-propene (2j): Pale yellow solid (1.43 g, 57%). M.p. 34-36 ºC. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.70-7.65 (m, 2H), 7.57-7.35 (m, 8H), 6.78 (dt, *J*=16.0 and 1.3 Hz, 1H), 6.49 (dt, *J*=16.0 and 6.0 Hz, 1H), 5.75-5.73 (m, 1H), 5.59-5.56 (m, 1H), 4.61-4.57 (m, 2H), 4.35 (dd, *J*=6.0 and 1.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 144.0, 138.6, 136.4, 132.1, 128.3, 128.1, 127.5, 127.4, 126.2, 125.8, 125.7, 114.1, 71.7, 70.3. LRMS (70 eV, EI): m/z, (%): 250 (M^+, 39), 105 (100). Anal. calcd. for $C_{18}H_{18}O$: C, 86.36; H 7.25. Found: C, 86.29; H, 7.23.

1-(2-Phenylallyloxy)-3-phenyl-2-propyne (2k): Yellow oil (1.66 g, 67%). R_f=0.20 (hexane/EtOAc, 30:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.60-7.56 (m, 2H), 7.54-7.49 (m, 2H), 7.42-7.31 (m, 6H), 5.66-5.64 (m, 1H), 5.48-5.46 (m, 1H), 4.62-4.59 (m, 2H), 4.47 (s, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 143.4, 138.4, 131.6, 128.3, 128.3, 128.2, 127.7, 125.9, 122.5, 115.2, 86.4, 84.9, 71.3, 57.6. LRMS (70 eV, EI): m/z, (%): 248 (M^+, 5), 115 (100). Anal. calcd. for $C_{18}H_{16}O$: C, 87.06; H 6.49. Found: C, 87.19; H, 6.47.

Representative procedure for the deprotection of 2-phenylallyl ethers 2a-l. General procedure: A solution of the corresponding starting ether (2.0 mmol) in THF (2 mL) was treated with *t*-BuLi (2.1 mmol, 1.4 mL of a

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1.5 M sol. in pentane) at –78 ºC. After additional 30 min at this temperature, the resulting solution was quenched with MeOH, allowed to reach room temperature and H_2O was added. The extraction was carried out with EtOAc (3 x 10 mL) and the combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude was purified by column chromatography (hexane/EtOAc) to afford the corresponding alcohol **4** and compound **5a**.

4a-e and **4g-j**: Spectral data were in agreement with those of the starting alcohol or phenol.

4-[(*tert*-Butyldimethylsiloxy)methyl]phenol (4f): Pale yellow oil (0.415 g, 87%). R_f=0.16 (hexane/EtOAc, 5:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.22-7.16 (m, 2H), 6.81-6.75 (m, 2H), 5.66 (s, 1H), 4.68 (s, 2H), 0.95 (s, 9H), 0.11 (s, 6H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) 154.6, 133.2, 127.8, 115.1, 64.8, 25.9, 18.4, -5.2. HRMS calcd. for $C_{13}H_{22}O_2Si$: 238.1389, found: 238.1393.

3-Phenyl-2-propyn-1-ol (4k): Pale yellow oil (0.219 g, 83%). R_f=0.14 (hexane/EtOAc, 5:1). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.47-7.41 (m, 2H), 7.33-7.25 (m, 3H), 4.49 (s, 2H), 2.82 (s, 1H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) 131.5, 128.3, 128.1, 122.4, 87.2, 85.4, 51.2. LRMS (70 eV, EI): m/z, (%): 132 (M^+, 62), 131 (100). HRMS calcd. for C_9H_8O: 132.0575, found: 132.0573.

4-Allyloxyphenol (4l): Colorless oil (0.258 g, 86%). R_f=0.21 (hexane/EtOAc, 3:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 6.84-6.76 (m, 5H), 6.22 (s, 1H), 6.11-6.00 (m, 1H), 5.41 (dq, *J*=17.2 and 1.6 Hz, 1H), 5.28 (dq, *J*=10.5 and 1.6 Hz, 1H), 4.49 (dt, *J*=5.4 and 1.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ (ppm) 152.3, 150.0, 133.3, 117.6, 116.0, 115.8, 69.6. LRMS (70 eV, EI): m/z, (%): 150 (M^+, 34), 109 (100). HRMS calcd. for $C_9H_{10}O_2$: 150.0681, found: 150.0679.