Supporting Information

Copper-Catalyzed Intermolecular Hydroamination Reactions of Alkenes.

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Experimental

General Remarks. Column chromatography was performed on silica gel (Kieselgel 60, 63-200 μm). ^1H and ^{13}C NMR spectra were acquired using a Bruker DRX 400MHz instrument (^1H at 400 MHz and ^{13}C at 100 MHz) and a Jeol EX270 instrument (^1H at 270 MHz). The chemical shifts are reported in δ (ppm) reference to residual protons and ^{13}C signals in deuterated chloroform. The coupling constants (J) are expressed in Hertz (Hz). HPLC analysis was performed on a Gilson HPLC system using Daicel Chiralpak OD-H column: detection was effected by UV absorption at 254 nm. Infrared spectra were recorded on a Mattson Instrument Satellite FTIR spectrometer; the samples were prepared as either a liquid film between NaCl plates, or pressed into KBr discs. Melting points (uncorrected) were determined using an Electrothermal Gallenamp apparatus and a calibrated thermometer ($\pm 2^\circ\text{C}$). Boiling points were determined by distillation, heating in a Buchi B-580 glass oven under vacuum and measured with a calibrated thermometer ($\pm 2^\circ\text{C}$). Elemental analysis Service was provided by London Metropolitan University. Mass spectra (MS) were recorded on a Micromass Autospec-Q Mass Spectrometer. All dried solvents were purchased from Sigma-Aldrich and stored under nitrogen atmosphere. All other commercial reagents were used as received.

General Catalytic Procedure.

Catalytic reactions were conducted in parallel using Radley's 12-placed reaction carousel. For a typical catalytic experiment, reaction tubes loaded with the catalyst, ligand and a Teflon coated stirrer bar and fitted with a screw cap. The reaction tubes atmosphere was purged under vacuum for 20 minutes and filled with nitrogen. Copper trifluoromethanesulfonate (18 mg, 0.05 mmol) and *rac*-BINAP (31 mg, 0.05 mmol) was stirred in anhydrous 1, 4-dioxane (1 mL) and heated at 75 $^\circ\text{C}$ for 15 minutes. Norbornene (144 mg, 1.5 mmol) or vinylarene (1.0 mmol) and the requisite sulfonamide (1.0 - 2.0 mmol) was dissolved in anhydrous 1, 4-dioxane (1 mL) and introduced into the reaction tube through the rubber septum using a syringe needle. The reaction was refluxed at 75

°C (18 hours). Upon completion the reaction mixture were concentrated under vacuum, and purified by column chromatography (4:1 hexanes/ethyl acetate).

The reactions were subsequently assembled and performed in air using reagent-grade dioxane, with no noticeable effect on the reaction outcome.

1-Phenyl-*N*-tosylethanamine, 4-Methyl-*N*-(1-phenyl-ethyl)-benzenesulfonamide, **1a**. White crystalline solid. mp. 78-80°C (lit.¹ 77-80 °C); R_f = 0.4 (Hexanes/EtOAc, 4/1); $\nu_{\max}/\text{cm}^{-1}$ (KBr disc): 3243, 3061, 2970, 2929, 2870, 1807, 1757, 1597, 1494, 1449, 1302, 1150, 1120, 1103, 958, 869, 812, 766, 702, 671, 559; δ_H (400 MHz, CDCl_3): 7.63 (2H, d, J 8.0, H_{ortho}), 7.18 (5H, m, H-2, H-3, H-4), 7.10 (2H, d, J 8.0, H_{meta}), 4.84 (1H, d, J 6.8, NH), 4.46 (1H, quintet, J 6.8, CH), 2.39 (3H, s, Ar-CH₃), 1.43 (3H, d, J 6.8, CH₃); δ_C (100 MHz, CDCl_3): 143.2 (C_{ipso}), 142.0 (C-1), 137.7 (C_{para}), 129.5 (C_{meta}), 128.6 (C-2), 127.5 (C-4), 127.1 (C-3), 126.1 (C_{ortho}), 53.6 (CH), 23.6 (Ar-CH₃), 21.5 (CH₃); m/z (EI): 260 (M^+ , 100%), 155 (65%), 120 (65%), 91 (85%), 77 (15%).

1-(4-fluorophenyl)-*N*-tosylethanamine, *N*-[1-(4-fluorophenyl)ethyl]-4-methylbenzenesulfonamide, **1b**. White crystalline solid. mp. 106-108 °C; R_f = 0.4 (Hexanes/EtOAc, 4/1); $\nu_{\max}/\text{cm}^{-1}$ (KBr disc): 3266, 3052, 2966, 2928, 2874, 1917, 1890, 1650, 1605, 1510, 1452, 1306, 1225, 1155, 1090, 1024, 958, 871, 835, 738, 676, 567, 537; δ_H (400 MHz, CDCl_3): 7.61 (2H, d, J 8.4, H_{ortho}), 7.18 (2H, d, J 8.4, H_{meta}), 7.10 (2H, m, H-3), 6.89 (2H, m, H-2), 4.89 (1H, d, J 6.8, NH), 4.48 (1H, quintet, J 6.8, CH), 2.39 (3H, s, Ar-CH₃), 1.40 (3H, d, J 6.8, CH₃); δ_C (100 MHz, CDCl_3): 163.2, 160.9 (d, J_{CF} 245, C-4), 143.3 (C_{ipso}), 137.8 (d, J_{CF} 4, C-1), 137.6 (C_{para}), 129.4 (C_{meta}), 127.8 (d, J_{CF} 8, C-3), 127.1 (C_{ortho}), 115.4 (d, J_{CF} 21, C-2), 52.9 (CH), 23.5 (Ar-CH₃), 21.5 (CH₃); m/z (EI): 293 (M^+ , <1%), 278 (85%), 229 (10%), 155 (67%), 138 (95%), 123 (30%), 91 (100%). Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{FNO}_2\text{S}$: C, 61.41%; H, 5.50%; N, 4.77%. Found: C, 61.47%; H, 5.51%; N, 4.72%.

1-(4-Chlorophenyl)-*N*-tosylethanamine, *N*-[1-(4-chlorophenyl)ethyl]-4-methylbenzenesulfonamide, **1c**. White crystalline solid. mp. 128-130 °C; $R_f = 0.4$ (Hexanes/ EtOAc, 4/1); $\nu_{\max}/\text{cm}^{-1}$ (KBr disc): 3249, 3048, 2975, 2929, 2874, 1912, 1598, 1493, 1450, 1323, 1159, 1088, 1014, 959, 869, 810, 683, 563, 537; δ_H (400 MHz, CDCl_3): 7.59 (2H, d, J 8.4, H_{ortho}), 7.20 (2H, d, J 8.4, H_{meta}), 7.10 (2H, d, J 8.4, H-3), 6.89 (2H, d, J 8.4, H-2), 5.19 (1H, d, J 6.8, NH), 4.44 (1H, quintet, J 6.8, CH), 2.39 (3H, s, Ar- CH_3), 1.39 (3H, d, J 6.8, CH_3); δ_C (100 MHz, CDCl_3): 143.3 (C-4), 140.5 (C_{ipso}), 137.4 (C-1), 133.2 (C_{para}), 129.4 (C-3), 128.5 (C-2), 127.6 (C_{ortho}), 127.0 (C_{meta}), 53.1 (CH), 23.5 (Ar- CH_3), 21.5 (CH_3); m/z (EI): 309 (M^+ , <1%), 294 (55%), 155 (90%), 154 (85%), 139 (27%), 103 (36%), 91 (100%). Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{ClNO}_2\text{S}$: C, 58.15%; H, 5.21%; N, 4.52%. Found: C, 58.19%; H, 5.24%; N, 4.50%.

1-*p*-Tolyl-*N*-tosylethanamine, *N*-[1-(4-methylphenyl)ethyl]-4-methylbenzenesulfonamide, **1d**. White crystalline solid. mp. 116-118 °C; $R_f = 0.4$ (Hexanes/ EtOAc, 4:1); $\nu_{\max}/\text{cm}^{-1}$ (KBr disc): 3338, 3251, 2968, 2925, 2891, 2733, 1902, 1798, 1650, 1597, 1513, 1432, 1324, 1156, 1091, 1021, 960, 868, 810, 730, 664, 576; δ_H (400 MHz, CDCl_3): 7.63 (2H, d, J 8.4, H_{ortho}), 7.20 (2H, d, J 8.4, H_{meta}), 7.00 (4H, m, H-2, H-3), 4.81 (1H, d, J 6.8, NH), 4.41 (1H, quintet, J 6.8, CH), 2.39 (3H, s, Ar- CH_3), 2.28 (3H, s, Ar- CH_3), 1.40 (3H, d, J 6.8, CH_3); δ_C (100 MHz, CDCl_3): 143.0 (C_{ipso}), 139.0 (C-4), 137.7 (C-1), 137.2 (C_{para}), 129.4 (C-3), 129.2 (C-2), 127.1 (C_{ortho}), 126.0 (C_{meta}), 53.4 (CH), 23.4 (Ar- CH_3), 21.5 (CH_3), 21.0 (Ar- CH_3); m/z (EI): 289 (M^+ , <1%), 274 (87%), 155 (55%), 144 (98%), 119 (27%), 91 (100%), 65 (22%). Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_2\text{S}$: C, 66.41%; H, 6.62%; N, 4.84%. Found: C, 66.49%; H, 6.61%; N, 4.87%.

1-(2,4-Dimethylphenyl)-*N*-tosylethanamine, *N*-[1-(2,4-dimethylphenyl)ethyl]-4-methylbenzenesulfonamide, **1e**. White crystalline solid. mp. 124-125 °C; $R_f = 0.4$ (Hexanes/ EtOAc, 4/1); $\nu_{\max}/\text{cm}^{-1}$ (KBr disc): 3258, 2973, 2925, 2309, 1919, 1597, 1497, 1419, 1359, 1304, 1139, 1078,

1019, 952, 873, 825, 671, 550, 810; δ_{H} (400 MHz, CDCl_3): 7.61 (2H, d, J 8.4, H_{ortho}), 7.17 (2H, d, J 8.4, H_{meta}), 7.03 (1H, s, H-3), 6.85 (2H, m, H-5, H-6), 5.05 (1H, d, J 6.8, NH), 4.67 (1H, quintet, J 6.8, CH), 2.37 (3H, s, Ar- CH_3), 2.23 (3H, s, Ar- CH_3), 2.14 (3H, s, Ar- CH_3) 1.36 (3H, d, J 6.8, CH_3); δ_{C} (100 MHz, CDCl_3): 143.0 (C_{ipso}), 137.8 (C-2), 137.3 (C_{para}), 136.9 (C-1), 134.3 (C-4), 131.3 (C-3), 129.4 (C-6), 127.1 (C-5), 127.0 (C_{ortho}), 125.4 (C_{meta}), 49.6 (CH), 23.1 (Ar- CH_3), 21.5 (CH_3), 20.9 (Ar- CH_3), 18.9 (Ar- CH_3); m/z (EI): 303 (M^+ , 5%), 289 (12%), 288 (100%), 198 (5%), 155 (35%), 133 (25%), 132 (72%), 91 (65%). Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_2\text{S}$: C, 67.29%; H, 6.98%; N, 4.62%. Found: C, 67.24%; H, 6.97%; N, 4.55%.

1-(Naphthalen-6-yl)-N-tosylethanamine, 4-methyl-N-(1-naphthalene-2-yl-ethyl)-benzenesulfonamide, **1g**. White crystalline solid. mp. 146-148°C (lit.² 148-149 °C); R_f = 0.4 (Hexanes/EtOAc, 4/1); $\nu_{\text{max}}/\text{cm}^{-1}$ (KBr disc): 3277, 3047, 2971, 2933, 2862, 1915, 1802, 1598, 1504, 1452, 1301, 1155, 1085, 1037, 974, 944, 865, 815, 750, 699, 571; δ_{H} (400 MHz, CDCl_3): 7.63 (2H, d, J 8.0, H_{ortho}), 7.56 – 7.43 (7H, m, Np), 7.01 (2H, d, J 8.0, H_{meta}), 5.35 (1H, d, J 6.8, NH), 4.63 (1H, quintet, J 6.8, CH), 2.18 (3H, s, Ar- CH_3), 1.32 (3H, d, J 6.8, CH_3); δ_{C} (100 MHz, CDCl_3): 143.1 (C_{ipso}), 139.1 (C-1), 137.6 (C_{para}), 133.1 (C-9), 132.7 (C-4), 129.3 (C_{meta}), 128.4 (C-2), 127.9 (C-10), 127.5 (C-3), 127.0 (C_{ortho}), 126.1 (C-8), 125.9 (C-5), 125.1 (C-7), 124.1 (C-6), 53.9 (CH), 23.5 (Ar- CH_3), 21.3 (CH_3); m/z (EI): 325 (M^+ , 35%), 310 (75%), 170 (88%), 169 (100%), 155 (52%), 154 (70%), 127 (28%), 91 (82%).

(E)-1,3-diphenylbut-1-ene, **2**. Pale yellow oil. bp. 120-125 °C, 1.0 mmHg (lit.³ 113-116 °C, 1.0 mmHg); R_f = 0.8 (Hexanes/Acetone, 19/1); $\nu_{\text{max}}/\text{cm}^{-1}$ (thin film): 3059, 3025, 2965, 2928, 2871, 1946, 1804, 1600, 1493, 1450, 1265, 1073, 1017, 966, 909, 841, 743; δ_{H} (400 MHz, CDCl_3): 7.10 – 7.35 (10H, m, Ar-H), 6.36 (2H, m, $\text{CH}=\text{CH}$), 3.56 (1H, m, CH), 1.39 (3H, d, J 6.8, CH_3); δ_{C} (100 MHz, CDCl_3): 145.7 (C_{ipso}), 137.6 (C-1), 128.6 (C-2), 128.5 (C_{ortho}), 127.8 (C-3), 127.5 (C_{meta}), 127.3 (C-4), 126.3 (C_{para}), 42.6 (CH), 21.3 (CH_3); m/z (EI): 208 (M^+ , 100%), 193 (95%), 115 (95%), 91 (35%), 77 (15%).

4-Nitro-*N*-(1-phenylethyl)benzenesulfonamide, 3a. White crystalline solid. 124-125 °C (lit.⁴ 124-126 °C); R_f = 0.4 (Hexanes/ EtOAc, 4/1); $\nu_{\max}/\text{cm}^{-1}$ (KBr disc): 3264, 3117, 2997, 2868, 1934, 1814, 1682, 1607, 1529, 1433, 1330, 1166, 1088, 1011, 965, 852, 770, 736, 703, 632, 543, 464; δ_{H} (400 MHz, CDCl_3): 8.13 (2H, d, J 8.8, H_{meta}), 7.79 (2H, d, J 8.8, H_{ortho}), 7.13 (3H, m, H-3, H-4), 7.05 (2H, m, H-2), 5.28 (1H, d, J 6.8, NH), 4.60 (1H, quintet, J 6.8, CH), 1.49 (3H, d, J 6.8, CH_3); δ_{C} (100 MHz, CDCl_3): 149.7 (C_{para}), 146.6 (C_{ipso}), 141.0 (C-1), 128.6 (C-3), 128.2 (C-2), 127.9 (C-4), 126.2 (C_{ortho}), 123.8 (C_{meta}), 54.2 (CH), 23.6 (CH_3); m/z (EI): 306 (M^+ , <1%), 291 (100%), 186 (20%), 122 (32%), 120 (36%), 105 (24%), 77 (16%).

4-Nitro-*N*-(1-(4-fluorophenyl)ethyl)benzenesulfonamide, 3b. White crystalline solid. 100-102 °C; R_f = 0.4 (Hexanes/ EtOAc, 4/1); $\nu_{\max}/\text{cm}^{-1}$ (KBr disc): 3304, 3235, 3118, 2974, 2929, 2866, 2453, 1896, 1604, 1511, 1431, 1312, 1226, 1154, 1089, 1015, 963, 855, 734, 620, 556; δ_{H} (400 MHz, CDCl_3): 8.20 (2H, d, J 8.8, H_{meta}), 7.84 (2H, d, J 8.8, H_{ortho}), 7.03 (2H, m, H-3), 6.84 (2H, m, H-2), 5.47 (1H, d, J 6.8, NH), 4.58 (1H, quintet, J 6.8, CH), 1.43 (3H, d, J 6.8, CH_3); δ_{C} (100 MHz, CDCl_3): 163.4 (d, J_{CF} 247, C-4), 149.7 (C_{para}), 146.5 (C_{ipso}), 136.9 (d, J_{CF} 3, C-1), 128.2 (C_{ortho}), 127.9 (d, J_{CF} 8, C-3), 127.8 (C_{meta}), 115.4 (d, J_{CF} 21, C-2), 53.5 (CH), 23.5 (CH_3); m/z (EI): 324 (M^+ , <1%), 309 (100%), 186 (32%), 138 (56%), 137 (25%), 123 (28%), 122 (80%), 103 (10%), 75 (10%). Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{FN}_2\text{O}_4\text{S}$: C, 51.85%; H, 4.04%; N, 8.64%. Found: C, 51.92%; H, 4.10%; N, 8.61%.

4-Nitro-*N*-(1-(4-chlorophenyl)ethyl)benzenesulfonamide, 3c. White crystalline solid. 122-124 °C; R_f = 0.4 (Hexanes/ EtOAc, 4/1); $\nu_{\max}/\text{cm}^{-1}$ (KBr disc): 3252, 3110, 2981, 2870, 1607, 1530, 1491, 1431, 1338, 1311, 1164, 1089, 1021, 964, 851, 826, 737, 684, 614, 544, 465; δ_{H} (400 MHz, CDCl_3): 8.22 (2H, d, J 8.8, H_{meta}), 7.83 (2H, d, J 8.8, H_{ortho}), 7.16 (2H, d, J 8.4, H-3), 7.03 (2H, d, J

8.4, H-2), 5.21 (1H, d, J 6.8, NH), 4.57 (1H, quintet, J 6.8, CH), 1.46 (3H, d, J 6.8, CH₃); δ_C (100 MHz, CDCl₃): 149.8 (C_{para}), 146.4 (C_{ipso}), 139.6 (C-1), 133.8 (C-4), 128.8 (C_{ortho}), 128.2 (C-3), 127.6 (C_{meta}), 127.4 (C-2), 53.5 (CH), 23.4 (CH₃); m/z (EI): 340 (M⁺, 2%), 327 (45%), 325 (100%), 186 (55%), 154 (73%), 153 (56%), 139 (36%), 138 (56%), 122 (68%), 103 (40%), 77 (25%). Anal. Calcd for C₁₄H₁₃ClN₂O₄S: C, 49.34%; H, 3.85%; N, 8.22%. Found: C, 49.40%, H, 3.79%, N, 8.18%.

4-Nitro-*N*-(1-(*p*-tolyl-ethyl)benzenesulfonamide, 3d. White crystalline solid. 94-96 °C; R_f = 0.4 (Hexanes/ EtOAc, 4/1); $\nu_{\max}/\text{cm}^{-1}$ (KBr disc): 3258, 3118, 2976, 2863, 1932, 1903, 1797, 1609, 1529, 1426, 1344, 1310, 1166, 1089, 1020, 963, 852, 815, 737, 640, 616, 539, 463; δ_H (400 MHz, CDCl₃): 8.13 (2H, d, J 8.8, H_{meta}), 7.78 (2H, d, J 8.8, H_{ortho}), 6.92 (4H, m, H-3, H-2), 5.32 (1H, d, J 6.8, NH), 4.55 (1H, quintet, J 6.8, CH), 2.21 (3H, s, Ar-CH₃), 1.44 (3H, d, J 6.8, CH₃); δ_C (100 MHz, CDCl₃): 149.6 (C_{para}), 146.5 (C_{ipso}), 138.0 (C-4), 137.8 (C-1), 129.2 (C_{ortho}), 128.3 (C-3), 126.1 (C_{meta}), 123.8 (C-2), 54.0 (CH), 23.5 (CH₃), 20.9 (Ar-CH₃); m/z (EI): 320 (M⁺, 3%), 305 (100%), 186 (12%), 133 (42%), 119 (28%), 118 (40%), 91 (16%). Anal. Calcd for C₁₅H₁₆N₂O₄S: C, 56.24%; H, 5.03%; N, 8.74%. Found: C, 56.14%; H, 4.98%; N, 8.65%.

4-Nitro-*N*-(1-(2,4-dimethylphenyl)ethyl)benzenesulfonamide, 3e. White crystalline solid. 124-126 °C; R_f = 0.4 (Hexanes/ EtOAc, 4/1); $\nu_{\max}/\text{cm}^{-1}$ (KBr disc): 3271, 3112, 2976, 2925, 2866, 1606, 1526, 1427, 1311, 1162, 1080, 1012, 958, 851, 736, 624, 555; δ_H (400 MHz, CDCl₃): 8.10 (2H, d, J 8.8, H_{meta}), 7.73 (2H, d, J 8.8, H_{ortho}), 6.80-6.71 (3H, m, H-3, H-5, H-6), 5.22 (1H, d, J 6.8, NH), 4.82 (1H, quintet, J 6.8, CH), 2.22 (3H, s, Ar-CH₃), 2.18 (3H, s, Ar-CH₃), 1.44 (3H, d, J 6.8, CH₃); δ_C (100 MHz, CDCl₃): 149.6 (C_{para}), 146.5 (C_{ipso}), 138.0 (C-4), 136.1 (C-2), 129.2 (C_{ortho}), 128.3 (C-3), 128.1 (C-5), 125.3 (C_{meta}), 123.7 (C-6), 50.0 (CH), 23.1 (CH₃), 20.8 (Ar-CH₃), 18.9 (Ar-CH₃); m/z (EI): 334 (M⁺, 6%), 322 (15%), 320 (16%), 319 (100%), 186 (16%), 133 (40%), 132 (84%), 117 (15%). Anal. Calcd for C₁₆H₁₈N₂O₄S: C, 57.47%; H, 5.43%; N, 8.38%. Found: C, 57.54%; H, 5.35%; N, 8.37%.

***N*-Tosylbicyclo[2.2.1]heptan-2-amine**, *exo-N*-Bicyclo[2.2.1]hept-2-yl-4-methylbenzenesulfonamide, **6a**. Crystalline white solid. mp. 126-128 °C (lit.⁵ 129-130 °C); R_f = 0.4 (Hexanes/EtOAc, 4/1); $\nu_{\max}/\text{cm}^{-1}$ (KBr disc): 3262, 2945, 2868, 1917, 1805, 1597, 1494, 1427, 1321, 1150, 1023, 950, 896, 811, 686; δ_H (400 MHz, CDCl_3): 7.77 (2H, d, J 9.0, H_{ortho}), 7.31 (2H, d, J 9.0, H_{meta}), 4.67 (1H, d, J 7.4, NH), 3.11 (1H, m, H-1), 2.43 (3H, s, Ar-CH₃) 2.18 (1H, br s, H-4), 2.09 (1H, br s, H-7), 1.77 (1H, ddd, J 2.0, 7.0, 13, H-2), 1.10-1.60 (7H, m, H-2, H-3, H-5 and H-6 and H-7); δ_C (100 MHz, CDCl_3): 143.1 (C_{ipso}), 137.9 (C_{para}), 129.6 (C_{ortho}), 127.1 (C_{meta}), 55.6 (C-1), 42.4 (C-4), 40.7 (C-2), 35.5 (C-3), 35.1 (C-7), 28.0 (C-5), 26.3 (C-6), 21.5 (CH₃); m/z (EI): 265 (M^+ , 5%), 155 (25%), 139 (42%), 110 (100%), 91 (88%), 81 (32 %), 65 (35%).

***exo-N*-Nosylbicyclo[2.2.1]heptan-2-amine**, *exo-N*-Bicyclo[2.2.1]hept-2-yl-4-nitrobenzenesulfonamide, **6b**. Crystalline pale yellow solid. mp. 130-132 °C (lit.⁴ 125-127 °C); R_f = 0.4 (Hexanes/EtOAc, 4/1); $\nu_{\max}/\text{cm}^{-1}$ (KBr disc): 3303, 3106, 2961, 2870, 1606, 1535, 1421, 1348, 1164, 1090, 1025, 961, 900, 852, 736, 684, 612, 536, 462; δ_H (400 MHz, CDCl_3): 8.37 (2H, d, J 12.0, H_{meta}), 8.07 (2H, d, J 12.0, H_{ortho}), 4.76 (1H, d, J 6.8, NH), 3.22 (1H, m, H-1), 2.23 (1H, br s, H-4), 2.21 (1H, br s, H-7), 1.68 (1H, ddd, J 2.0, 7.0, 13, H-2), 1.1-1.6 (7H, m, H-2, H-3, H-5 and H-6 and H-7); δ_C (100 MHz, CDCl_3): 150.1 (C_{para}), 146.9 (C_{ipso}), 129.6 (C_{meta}), 127.1 (C_{ortho}), 56.9 (C-1), 42.6 (C-4), 40.8 (C-2), 35.6 (C-3), 35.1 (C-7), 27.8 (C-5), 26.2 (C-6); m/z (EI): 296 (M^+ , 10%), 215 (43%), 186 (42%), 122 (56%), 110 (100%), 94 (59%), 81 (70 %), 67 (55%).

exo-N-Benzyl-N-tosylbicyclo[2.2.1]heptan-2-amine, *N*-Benzyl-*N*-bicyclo[2.2.1]hept-2-yl-4-methylbenzenesulfonamide, **6c**. Crystalline white solid. mp. 84-86 °C; R_f = 0.4 (Hexanes/EtOAc, 4/1); $\nu_{\max}/\text{cm}^{-1}$ (KBr disc): 3269, 3032, 2950, 2871, 1598, 1494, 1453, 1332, 1153, 1091, 1059, 961, 875, 811, 809, 742, 659, 593, 552; δ_{H} (400 MHz, CDCl_3): 7.73 (2H, d, J 6.8, H_{ortho}), 7.40 (2H, d, J 6.8, H_{meta}), 7.20 – 7.35 (5H, m, Ar-H), 4.58 (1H, closeAB, CH_2), 4.38 (1H, closeAB, CH_2) 3.91 (1H, m, H-1), 2.44 (3H, s, Ar- CH_3) 2.10 (1H, br s, H-4), 1.94 (1H, br s, H-7), 1.77 (1H, ddd, J 2.0, 7.0, 13, H-2), 1.1-1.6 (7H, m, H-2, H-3, H-5 and H-6 and H-7); δ_{C} (100 MHz, CDCl_3): 143.4 (C_{ipso}), 137.9 (C_{para}), 129.6 (C_{ortho}), 128.6 – 127.1 (phenyl), 127.0 (C_{meta}), 61.2 (C-1), 47.6 (CH_2), 47.3 (C-4), 40.5 (C-2), 37.8 (C-3), 35.8 (C-7), 29.5 (C-5), 27.5 (C-6), 21.5 (CH_3); m/z (EI): 355 (M^+ , 65%), 264 (65%), 223 (55%), 106 (65%), 91 (100%), 65 (15%). Anal. Calcd for $\text{C}_{21}\text{H}_{25}\text{NO}_2\text{S}$: C, 70.95%; H, 7.09%; N, 3.94%. Found: C, 70.85%; H, 7.16%; N, 4.02%.

N-Cyclohex-2-enyltoluene-*p*-sulfonamide, *N*-cyclohex-2-enyl-4-methyl-benzenesulfonamide, **7**. White crystalline solid. mp. 99-101°C (lit.^[6] 101-102 °C.); R_f = 0.4 (Hexanes/EtOAc, 4/1); $\nu_{\max}$ (KBr disc, cm^{-1}): 3272, 3028, 2943, 2860, 1918, 1803, 1650, 1596, 1421, 1321, 1158, 1090, 1067, 980, 940, 898, 810, 673, 580, 551, 516; δ_{H} (400 MHz, CDCl_3): 7.81 (2H, d, J 8.0, H_{ortho}), 7.33 (2H, d, J 8.0, H_{meta}), 5.78 (1H, m, H-2), 5.37 (1H, m, H-3), 4.76 (1H, d, J 8.4, NH), 3.82 (1H, m, H-1), 2.45 (3H, s, Ar- CH_3), 1.94-1.53 (6H, m, H-4, H-5, H-6); δ_{C} (100 MHz, CDCl_3): 143.3 (C_{ipso}), 138.4 (C_{para}), 131.5 (C-2), 129.7 (C_{meta}), 127.1 (C-3) 127.0 (C_{ortho}), 50.0 (C-1), 30.3 (C-6), 24.5 (Ar- CH_3), 21.6 (C-4), 19.3 (C-5); m/z (EI): 251 (M^+ , 10%), 223 (40%), 187 (50%), 155 (45%), 96(85%), 91 (100%), 68 (35%).

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Styrene-tosylamine

Av-400B

Fig. S1. ¹H NMR spectrum of compound **1a**.

Fig. S2. ¹³C NMR spectrum of compound **1a**.

Fig. S3. ^1H NMR spectrum of compound **2**.

Fig. S4. ^{13}C NMR spectrum of compound 2.

Fig. S5. ¹H NMR spectrum of compound **3a**.

Fig. S6. ^{13}C NMR spectrum of compound **3a**.

J Taylor jgt21.1 in CDCl₃ ; ¹H spectrum using DRX400 ; Aug11/5

Fig. S7. ¹H NMR spectrum of compound **6a**.

J Taylor jgt21.1 in CDC13 ; $^{13}\text{C}\{^1\text{H}\}$ spectrum using DRX400 ; Aug11/7

Fig. S8. ^{13}C NMR spectrum of compound **6a**.

J Taylor jgt21.1 in CDC13 ; cosy spectrum using DRX400 ; Aug11/6

Fig. S9. COSY spectrum of compound **6a**.

Fig. S10. ¹H NMR spectrum of compound **6c**.

Fig. S11. ^{13}C NMR spectrum of compound **4c**.