Experimental

General

All reagents were obtained from commercial suppliers unless otherwise stated. When necessary, organic solvents were routinely dried and/or distilled prior to use and stored over molecular sieves under nitrogen. THF was distilled from sodium and benzophenone, CH_2Cl_2 and CH_3CN were distilled from calcium hydride. Thin-layer chromatography was performed on silica gel 60 F_{254} on aluminium plates (Merck) and visualized under a UVP Mineralight UVLS-28 lamp (254 nm) and with ninhydrin and phosphomolybdic acid in ethanol. Flash chromatography was conducted on Merck silica gel 60 (40-63 μm) at medium pressure (300 mbar) or on CombiFlash (Serlabo Technologies) using standard procedures. Melting points (**mp**) were measured in capillary tubes on a Büchi B-540 apparatus and are uncorrected. Optical rotations ($[\alpha]_D^{20}$) were determined with a JASCO P-1010 polarimeter. Mass spectra were obtained either with a LCT (Micromass) instrument using electrospray ionization (**ES**), or from a Time of Flight analyzer (ESI-MS) for the high resolution mass spectra (**HRMS**). Elemental analyses (**Anal.**) were performed on a Perkin Elmer CHN 2400 analyzer with a detection by catharometry, at the ICSN, CNRS, Gif-sur-Yvette, France. Infrared spectra (**IR**) were recorded on a Perkin Elmer Spectrum BX FT-IR spectrometer. Proton NMR (^{1}**H**) spectra were recorded with a Bruker 500 MHz or 300 MHz spectrometer. Carbon NMR (^{13}**C**) spectra were recorded at 125 or 75 MHz, using a broadband decoupled mode with the multiplicities obtained using a JMOD or DEPT sequence. Chemical shifts (δ) are reported in parts per million (ppm). NMR experiments were carried out in deuterochloroform ($CDCl_3$). The following abbreviations are used for the ^{1}H spectra multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, quint: quintuplet, m: multiplet, br: broad. Coupling constants (*J*) are reported in Hertz (Hz). Values in italics refer to the minor diastereomer, where applicable.

Experimental procedure

Typical C-H amination procedure. In an oven-dried tube were introduced activated 4 Å molecular sieves (100 mg), $Rh_2\{(S)\text{-nta}\}_4$ (**2**) (7.7 mg, 0.006 mmol) and (-)-*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidamide **(-)-(1)** (78 mg, 0.24 mmol). The tube was capped with a rubber septum and purged with argon. 1,1,2,2-Tetrachloroethane (0.75 mL) and methanol (0.25 mL) were added under argon, and the mixture was stirred for 5 min before addition of the substrate (0.2 mmol). The tube was cooled to –35°C, and bis(*tert*-butylcarbonyloxy)iodobenzene (115 mg, 0.28 mmol) was added. The mixture was stored in the freezer (-35°C) for 3 days. After dilution with dichloromethane (3 mL), the molecular sieves were removed by filtration and the filtrate was evaporated to dryness under reduced pressure. The oily residue was purified by flash chromatography on silica gel, affording the following C-H insertion products.

Spectroscopic data

***(-)-N-(p*-Toluenesulfonyl)-*p*-toluenesulfonimidamide ((*S*)-1).** To an ice cooled suspension of anhydrous sodium *p*-toluenesulfinate (3.75 g, 21 mmol) in toluene (40 mL) under argon was slowly added thionyl chloride (7.5 mL). The reaction mixture was stirred at room temperature for 14 h before being evaporated under vacuum. The resulting yellow oil was dissolved in toluene (60 ml) and anhydrous chloramine-T (4.78 g, 21 mmol) (*Caution !* The trihydrate was dried in a drying pistol at 80°C for 8h. Explosion may occur at higher temperatures) was added at room temperature. The reaction mixture was stirred at 80 °C for 1.5 h. The sodium chloride precipitate was filtered while the reaction mixture was still hot and the filtrate was evaporated. The crude *N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl chloride was dissolved in dichloromethane (80 ml) and a mixture of (*R*)-(-)-α-methylbenzylamine (3.24 mL, 25.2 mmol) and sodium hydrogenocarbonate (2.1 g, 25.2 mmol) in water (50 ml) was added at 0°C. After 30 minutes, the ice bath was removed and the reaction mixture was stirred overnight at room temperature. The organic layer was separated and washed successively with 10% HCl and water, dried with $MgSO_4$ and concentrated under vacuum to afford a pasty yellow solid. The latter was dissolved in ethyl ether (40 ml) and after cooling, filtration afforded 2.1 g of a white solid (d.e.> 95 % as estimated by ^{1}H NMR) of a white solid. A second crop was obtained from the mother liquor (0.8 g) yielding a total of 2.9 g (6.77 mmol, 32%) of pure compound. mp 156-156.5 °C; $[\alpha]_D^{20}$ + 118.8 (c 0.44, $CHCl_3$); IR (neat, cm^{-1}) 3232, 1594, 1301, 1152, 1106, 1070, 1017, 813, 755, 700, 657 ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (d, *J* = 7.0 Hz, 3H, CH_3), 2.41 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 4.52 (q, *J* = 7.0 Hz, 1H, CH-N), 6.18 (d, *J* = 7.0 Hz, 1H, NH), 7.26 (m, 9H, 9 x CH_{Ar}), 7.82 (m, 4H, 4 x CH_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 21.6, 23.0, 54.0, 126.4, 126.9, 127.8, 127.9, 128.7, 129.3, 129.7, 136.2, 140.5, 141.8, 142.9, 144.7; MS (ES) m/z 451 $(M+Na)^+$; Anal. calcd (%) for $C_{22}H_{24}N_2O_3S_2$: C, 61.66; H, 5.64; N, 6.54; S, 14.96; found: C, 61.26; H, 5.53; N, 6.57; S, 14.93.

2.9 g (6.77 mmol) of the pure diastereoisomer was dissolved in trifluoroacetic acid (6 mL). After stirring for 40 h at 35°C, the reaction mixture was evaporated under vacuum, leaving a crude green solid. The latter was purified by flash chromatography (heptane/ethyl acetate 1:1) and then crystallized from ethyl acetate to afford (-)-*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidamide **(*S*)-1** (1.6 g, 72%). mp 152.0-152.5°C ; $[\alpha]_D^{20}$ - 110 (c 0.47, acetone); e.e.>99% (HPLC, Chiracel AD, 4.6*250, 10 μ); IR (KBr, cm^{-1}) 3212, 1284, 1149, 1107, 1087, 810, 748, 660 ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 5.60 (s, 2H, NH_2), 7.25 (d, *J* = 7.5 Hz, 2H, 2 x CH_{Ar}), 7.29 (d, *J* = 7.9 Hz, 2H, 2 x CH_{Ar}), 7.79 (d, *J* = 7.5 Hz, 2H, 2 x CH_{Ar}), 7.84 (d, *J* = 7.6 Hz, 2H, 2 x CH_{Ar}) ; ^{13}C NMR (75 MHz, Acetone) δ 21.3, 21.4, 127.3, 127.8,

129.8, 130.3, 140.3, 142.6, 142.9, 144.8; MS (ES) m/z 347 $(M+Na)^+$; Anal. calcd (%) for $C_{14}H_{16}N_2O_3S_2$: C, 51.83; H, 4.97; N, 8.63; S, 19.77; found: C, 51.58; H, 4.92; N, 8.55; S, 20.04.

(S)-*N*-1,8-Naphthoylalanine. A mixture of L-alanine (0.687 g, 7.72 mmol) and 1,8-naphthalic anhydride (1.71 g, 8.60 mmol) in DMSO (25 mL) was heated under reflux in an atmosphere of argon for 1 h. The solvent was evaporated under reduced pressure and the light-brown residue was purified by flash chromatography (silica, dichloromethane/MeOH: 90/10), to afford (*S*)-nta (1.84 g, 88%) as a brownish solid. mp 266-267°C; $[\alpha]_D^{20}$ -39 (c 0.61, $CHCl_3$/MeOH); IR (KBr, cm^{-1}) 3204, 3013, 1715, 1694, 1652, 1585, 1376, 1335, 1231, 1190, 1092, 1035, 964, 889, 843, 770, 655; ^{1}H NMR (300 MHz, DMSO D6) δ 1.55 (d, *J* = 7.0 Hz, 3H, CH_3), 5.60 (q, *J* = 7.0 Hz, 1H, CH), 7.88 (m, 2H, 2 x CH_{Ar}), 8.50 (m, 4H, 4 x CH_{Ar}); ^{13}C NMR (75 MHz, DMSO D6) δ 15.0, 49.0, 122.2, 127.8, 131.5, 131.8, 135.1, 163.3, 171.8; MS (ES) *m/z* 292 ((M+Na)+) HRMS *m/z* ((M+Na)+) calcd for $C_{15}H_{11}NNaO_4$ 292.0586 found 292.0563.

Rh_2{(S)-nta}$_4$ (2). $[Rh_2(OAc)_4]$ (110 mg, 0.25 mmol) and (S)-*N*-1,8-Naphthoylalanine (645 mg, 2.40 mmol) were heated to reflux under argon in chlorobenzene in a flask fitted with a soxhlet extractor containing a mixture of anhydrous Na_2CO_3 and sand. After 24 h, the solvent was evaporated and the gummy residue was purified by flash chromatography (Alox basic, dichloromethane/methanol: 90/10) to afford the desired catalyst which was precipitated from acetonitrile to give the pure catalyst (288 mg, 90%). $[\alpha]_D^{20}$ -86 (c 0.06, $CHCl_3$/MeOH); IR (KBr, cm^{-1}) 3492, 2939, 1698, 1658, 1585, 1409, 1376, 1357, 1338, 1294, 1237, 1191, 1127, 1096, 1035, 968, 888; ^{1}H NMR (300 MHz, $CDCl_3$/MeOD) δ 1.71 (d, *J* = 6.8 Hz, 3H, CH_3), 5.88 (q, *J* = 7.0 Hz, 1H, CH), 7.67 (t, *J* = 7.7 Hz, 2H, 2 x CH_{Ar}), 8.05 (d, *J* = 8.0 Hz, 2H, 2 x CH_{Ar}), 8.56 (d, *J* = 7.1 Hz, 2H, 2 x CH_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$/MeOD) δ 15.1, 50.6, 122.5, 126.8, 131.2, 131.3, 133.5, 163.3, 188.3; HRMS *m/z* ((M+Na)+) calcd for $C_{60}H_{40}N_4Na0_{16}Rh_2$ 1301.0447 found 1301.0491.

(1*R*)-[*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl]-1-aminoindane (4a). Prepared following the typical amination procedure from indane, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as a white solid in 89% yield and >98% d.e. (HPLC, Hypercarb column, 100*4.6mm, 5µ, MeCN+0.1%HCOOH/H_2O+0.1%HCOOH: 80/20, 1mL/min, t_{maj} = 9.28 min). Spectroscopic data have already been reported in C. Liang, F. Collet, F. Robert-Peillard, P. Müller, R. H. Dodd and P. Dauban, *J. Am. Chem. Soc.*, 2008, **130**, 343.

(1*R*)-[*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl]-1-amino-1,2,3,4-tetrahydronaph-thalene (4b). Prepared following the typical amination procedure from 1,2,3,4-tetrahydronaphthalene, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as a white solid in 86% yield and 98% d.e. (HPLC, Symmetry shield column, 150*4.6mm, 5µ, MeCN+0.1%HCOOH/H_2O+0.1%HCOOH: 46/54, 1mL/min, t_{maj} = 40.25 min). Spectroscopic data have already been reported in C. Liang, F. Collet, F. Robert-Peillard, P. Müller, R. H. Dodd and P. Dauban, *J. Am. Chem. Soc.*, 2008, **130**, 343.

(*R*)-[*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl]-5-amino-6,7,8,9-tetrahydrobenzo [7]annulene (4c). Prepared following the typical amination procedure from 6,7,8,9-tetrahydro-5*H*-benzo[7]annulene (prepared from 1-benzosuberone), the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as an oily solid in 76% yield, >90% d.e (^{1}H NMR evaluation). R_f 0.40 (heptane/ethyl acetate: 60/40); IR (neat, cm^{-1}) 3219, 2925, 1726, 1596, 1453, 1286, 1254, 1149, 1104, 1089, 1015, 811; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.63-1.89 (m, 4H, 2 x CH_2), 2.42 (s, 3H), 2.44 (s, 3H), 2.65-3.10 (m, 4H, 2 x CH_2), 3.50-3.58 (m, 1H, CH-N), 5.53-5.60 (m, 1H, NH), 7.05-7.37 (m, 8H, 8C-H_{Ar}), 7.74-7.86 (m, 4H, 4C-H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.5 (CH_3), 21.6 (CH_3), 35.5 (CH_2), 37.7 (CH_2), 41.2 (CH_2), 42.2 (CH_2), 50.9 (CH-N), 126.6 (CH), 126.7 (2 x CH), 127.5 (CH), 127.8 (2 x CH), 129.0 (CH), 129.1 (2 x CH), 129.2 (CH), 129.7 (CH), 129.8 (CH), 140.5 (C), 142.7 (C), 143.0 (C), 143.1 (C), 144.6 (C), 144.7 (C); MS (ES) *m/z* 469 ((M+H)+), 491 ((M+Na)+), HRMS *m/z* ((M+Na)+) calcd for $C_{25}H_{28}N_2NaO_3S_2$ 491.1439 found 491.1431.

(*R*)-[*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl] amino fluorene (4d). Prepared following the typical amination procedure from fluorene, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as an oily solid in 40% yield. R_f 0.38 (heptane/ethyl acetate: 60/40); IR (neat, cm^{-1}) 3214, 1595, 1451, 1302, 1259, 1151, 1107, 1088, 1041, 1016, 812; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 2.45 (s, 3H), 2.47 (s, 3H), 5.32 (d, *J* = 9.0 Hz, 1H, CH-N), 6.38 (d, *J* = 9.0 Hz, 1H, NH), 7.25-7.48 (m, 6H, 6C-H_{Ar}), 7.56-7.68 (m, 4H, 4C-H_{Ar}), 7.77-7.90 (m, 2H, 2C-H_{Ar}), 7.92 (d, *J* = 8.0 Hz, 2H, 2C-H_{Ar}), 8.03 (d, *J* = 8.5 Hz, 2H, 2C-H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.6 (CH_3), 21.7 (CH_3), 57.9 (CH-N), 119.9 (CH), 122.9 (CH), 123.4 (CH), 125.4 (CH), 126.1 (CH), 126.2 (CH), 126.8 (CH), 126.9 (CH), 127.9 (CH), 128.1 (CH), 128.2 (CH), 129.2 (CH), 129.3 (2 x CH), 129.9 (CH), 130.1 (CH), 136.4 (2 x C), 140.4 (2 x C), 140.5 (2 x C), 144.9 (2 x C); MS (ES) *m/z* 489 ((M+H)+), 511 ((M+Na)+), HRMS *m/z* ((M+Na)+) calcd for $C_{27}H_{24}N_2NaO_3S_2$ 511.1126 found 511.1119.

(*R*)-[*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl] amino dihydrophenanthrene (4e). Prepared following the typical amination procedure from 9,10-dihydrophenanthrene, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as an oily solid in 20% yield, >90% d.e (^{1}H NMR evaluation). R_f 0.40 (heptane/ethyl acetate: 60/40); IR (neat, cm^{-1}) 3214, 1596, 1434, 1300, 1255, 1149, 1105, 1088, 1044, 1016, 811; ^{1}H NMR (500 MHz,

$CDCl_3$) δ (ppm) 2.44 (s, 3H), 2.47 (s, 3H), 2.76-2.80 (m, 2H, CH_2), 4.57-4.60 (m, 1H, CH-N), 5.98 (d, *J* = 7.0 Hz, 1H, NH), 7.12-7.28 (m, 10H, 10C-H_{Ar}), 7.64-7.70 (m, 2H, 2C-H_{Ar}), 7.74 (d, *J* = 8.5 Hz, 2H, 2C-H_{Ar}), 7.82 (d, *J* = 8.5 Hz, 2H, 2C-H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.5 (CH_3), 21.6 (CH_3), 29.0 (CH_2), 51.9 (CH-N), 123.2 (CH), 123.7 (CH), 126.7 (CH), 126.8 (2 x CH), 126.9 (2 x CH), 127.0 (CH), 127.4 (CH), 127.8 (2 x CH), 128.1 (2 x CH), 129.2 (2 x CH), 129.9 (CH), 136.6 (2 x C), 140.5 (2 x C), 140.6 (2 x C), 145.6 (2 x C); MS (ES) *m/z* 501 ((M-H)-), HRMS *m/z* ((M-H)-) calcd for $C_{28}H_{25}N_2O_3S_2$ 501.1307 found 501.1298.

(*R*)-[*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl] amino dibenzosuberane (4g). Prepared following the typical amination procedure from dibenzosuberane, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as a white solid in 85% yield, 99% d.e (UPLC, BEH shield RP18 column, 50*2.1mm, 1.8µm, MeCN+0.1%HCOOH/H_2O+0.1%HCOOH: 50/50, 0.6 mL/min, t_{maj} = 2.51 min). R_f 0.40 (heptane/ethyl acetate: 60/40); mp 70-72°C; $[\alpha]_D^{20}$ + 38.1 (c 1.00, $CHCl_3$); IR (neat, cm^{-1}) 3233, 1596, 1492, 1400, 1315, 1249, 1150, 1112, 1091, 1014, 808, 750; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.40 (s, 3H), 2.50 (s, 3H), 2.70-2.77 (m, 1H, CH_{2b}), 3.15-3.20 (m, 1H, CH_{2b}), 3.87 (d, *J* = 15.0 Hz, 1H, CH_{2a}), 4.17 (d, *J* = 15.0 Hz, 1H, CH_{2a}), 4.99-5.04 (m, 1H, CH-N), 5.59 (d, *J* = 7.0 Hz, 1H, NH), 6.72 (d, *J* = 8.0 Hz, 1H, CH_{Ar}), 7.11-7.25 (m, 8H, 8C-H_{Ar}), 7.39-7.46 (m, 3H, 3C-H_{Ar}), 7.76 (d, *J* = 8.0 Hz, 2H, 2C-H_{Ar}), 7.93 (d, *J* = 8.5 Hz, 2H, 2C-H_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.6 (CH_3), 21.7 (CH_3), 37.5 (CH_{2b}), 41.0 (CH_{2a}), 54.2 (CH-N), 126.7 (2 x CH), 126.9 (CH), 127.3 (CH), 127.4 (CH), 127.8 (2 x CH), 128.0 (CH), 128.5 (CH), 129.2 (2 x CH), 129.8 (CH), 129.9 (2 x CH), 130.0 (CH), 132.2 (CH), 134.4 (C), 136.2 (C), 137.1 (C), 137.5 (C), 140.4 (C), 140.5 (C), 142.8 (C), 144.9 (C); MS (ES) *m/z* 517 ((M+H)+), 539 ((M+Na)+), HRMS *m/z* ((M+Na)+) calcd for $C_{29}H_{28}N_2NaO_3S_2$ 539.1439 found 539.1445.

(*R*)-1,2-Diphenyl-1-[*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl]amino ethane (6b). Prepared following the typical amination procedure from 1,2-diphenylethane, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as a white solid in 73% yield, 99% d.e (UPLC, BEH shield RP18 column, 50*2.1mm, 1.8µm, MeCN+0.1%HCOOH/H_2O+0.1%HCOOH: 55/45, 0.6 mL/min, t_{maj} = 1.26 min). R_f 0.52 (heptane/ethyl acetate: 50/50); mp 139-141°C; $[\alpha]_D^{20}$ + 106.9 (c 1.00, $CHCl_3$); IR (neat, cm^{-1}) 3229, 1695, 1597, 1454, 1287, 1148, 1067, 1041, 1014, 809, 696; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 2.38 (s, 3H), 2.39 (s, 3H), 2.91-3.00 (m, 2H, CH_2), 4.42-4.46 (m, 1H, CH-N), 6.44 (d, *J* = 7.0 Hz, 1H, NH), 6.91 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.14-7.30 (m, 10H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.5 (CH_3), 21.6 (CH_3), 43.9 (CH_2), 59.9 (CH-N), 126.7 (CH), 126.8 (2 x CH), 126.9 (2 x CH), 127.6 (2 x CH), 127.7 (CH), 128.4 (2 x CH), 128.5 (2 x CH), 129.1 (2 x CH), 129.3 (2 x CH), 129.5 (2 x CH), 135.3 (C), 136.4 (C), 140.2 (C), 140.6 (C), 142.8 (C), 144.2 (C); MS (ES) *m/z* 527 ((M+Na)+), HRMS *m/z* ((M+Na)+) calcd for $C_{28}H_{28}N_2NaO_3S_2$ 527.1439 found 527.1436.

(*R*)-1,3-Diphenyl-1-[*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl]aminopropane (6c). Prepared following the typical amination procedure from 1,3-diphenylpropane, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as an oily solid in 32% yield, 75% d.e (^{1}H NMR evaluation). R_f 0.33 (heptane/ethyl acetate: 60/40); IR (neat, cm^{-1}) 3242, 2922, 1724, 1597, 1455, 1264, 1151, 1109, 1016, 812, 738; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 1.98-2.05 (m, 2H, CH_{2m}), 2.30-2.34 (m, 2H, CH_2), 2.38 (s, 3H), 2.44 (s, 3H), 4.26 (q, *J* = 7.5 Hz, 1H, CH-N), 6.40 (d, *J* = 7.5 Hz, 1H, NH), *6.46 (d, J = 7.5 Hz, 1H, NH)*, 6.90 (d, *J* = 7.5 Hz, 2H), 7.16-7.34 (m, 12H), 7.68 (d, *J* = 7.5 Hz, 2H), 7.76 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.5 (CH_3), 21.6 (CH_3), 31.8 (CH_2), 38.4 (CH_{2m}), 58.0 (CH-N), 126.1 (CH), 126.7 (2 x CH), 126.8 (2 x CH), 127.6 (CH), 127.8 (2 x CH), 128.2 (2 x CH), 128.4 (2 x CH), 128.7 (2 x CH), 129.2 (2 x CH), 129.7 (2 x CH), 135.9 (C), 140.2 (C), 140.4 (2 x C), 142.8 (C), 144.6 (C); MS (ES) *m/z* 541 ((M+Na)+), HRMS *m/z* ((M+Na)+) calcd for $C_{29}H_{30}N_2NaO_3S_2$ 541.1596 found 541.1589.

(*R*)-1-Bromo-2-phenyl-2-[*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl]aminoethane (6d). Prepared following the typical amination procedure from (2-bromoethyl)benzene, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as a white solid in 85% yield, >90% d.e (^{1}H NMR evaluation). R_f 0.32 (heptane/ethyl acetate: 60/40); mp 130-131°C; $[\alpha]_D^{20}$ + 89.0 (c 0.55, $CHCl_3$); IR (neat, cm^{-1}) 3218, 1595, 1494, 1441, 1300, 1260, 1147, 1102, 1088, 1072, 1033, 810, 752, 658; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 2.40 (s, 3H), 2.43 (s, 3H), 3.48-3.56 (m, 2H, CH_2-Br), 4.62 (q, *J* = 7.0 Hz, 1H, CH-N), 6.49 (d, *J* = 7.0 Hz, 1H, NH), 7.21 (d, *J* = 8.0 Hz, 2H), 7.26-7.35 (m, 7H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.5 (CH_3), 21.6 (CH_3), 36.0 (CH_2-Br), 58.2 (CH-N), 126.7 (2 x CH), 126.9 (2 x CH), 127.8 (2 x CH), 128.5 (CH), 128.7 (2 x CH), 129.2 (2 x CH), 129.7 (2 x CH), 135.4 (C), 137.5 (C), 140.1 (C), 142.9 (C), 145.0 (C); MS (ES) *m/z* ^{79}Br: 529 ((M+Na)+), ^{81}Br: 531 ((M+Na)+), HRMS *m/z* ((M+Na)+) calcd for $C_{22}H_{23}N_2O_3S_2{}^{79}Br$ 529.0231 found 529.0231, *m/z* ((M+Na)+) calcd for $C_{22}H_{23}N_2O_3S_2{}^{81}Br$ 531.0211 found 531.0201.

(*R*)-1-Bromo-3-phenyl-3-[*N*-(*p*-toluenesulfonyl)-*p*toluenesulfonimidoyl]aminopropane (6e). Prepared following the typical amination procedure from 1-bromo-3-phenylpropane, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as a white solid in 42% yield, 99% d.e (HPLC, Hypercarb column, 100*4.6mm, 5µ, MeCN+0.2%TFA/H_2O+0.2%TFA: 100/0, 1mL/min, t_{maj} = 10.18 min). R_f 0.36 (heptane/ethyl acetate: 60/40); mp 147-148°C;

$[\alpha]_D^{20}$ + 103.6 (c 0.62, $CHCl_3$); IR (neat, cm^{-1}) 3235, 1596, 1494, 1433, 1304, 1261, 1147, 1102, 1074, 1030, 1016, 811, 659; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 2.16-2.31 (m, 2H, CH_2), 2.39 (s, 3H), 2.44 (s, 3H), 3.05-3.16 (m, 2H, CH_2-Br), 4.56 (q, *J* = 7.5 Hz, 1H, CH-N), 6.55 (d, *J* = 7.5 Hz, 1H, NH), 7.18 (d, *J* = 8.0 Hz, 2H), 7.27-7.34 (m, 7H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.5 (CH_3), 21.6 (CH_3), 29.1 (CH_2-Br), 39.6 (CH_2), 56.6 (CH-N), 126.7 (2 x CH), 126.8 (2 x CH), 127.8 (2 x CH), 128.2 (CH), 128.9 (2 x CH), 129.2 (2 x CH), 129.8 (2 x CH), 135.7 (C), 139.5 (C), 140.0 (C), 142.9 (C), 144.9 (C); MS (ES) *m/z* ^{79}Br: 519 ((M-H)-), ^{81}Br: 521 ((M-H)-), ^{79}Br: 543 ((M+Na)+), ^{81}Br: 545 ((M+Na)+), HRMS *m/z* ((M-H)-) calcd for $C_{23}H_{24}N_2O_3S_2{}^{79}Br$ 519.0412 found 519.0434, *m/z* ((M-H)-) calcd for $C_{23}H_{24}N_2O_3S_2{}^{81}Br$ 521.0391 found 521.0417.

(*R*)-2-(*o*-Bromophenyl)-1-phenyl-1-[*N*-(*p*-toluenesulfonyl)-*p*toluenesulfonimidoyl] aminoethane (6g). Prepared following the typical amination procedure from 1-bromo-2-phenethylbenzene, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as a clear oil in 42% yield, 70% d.e (^1H NMR evaluation). R_f 0.51 (heptane/ethyl acetate: 50/50); IR (neat, cm^{-1}) 3222, 1596, 1454, 1287, 1148, 1089, 1041, 1014, 810, 697; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 2.38 (s, 3H), 2.39 (s, 3H), 2.91-3.01 (m, 2H, CH_2), 4.42-4.47 (m, 1H, CH-N), *4.56-4.62 (m, 1H, CH-N)*, 6.41 (d, *J* = 7.0 Hz, 1H, NH), *6.50 (d, J = 7.0 Hz, 1H, NH)*, 6.87-6.91 (m, 2H), 6.98-7.10 (m, 2H), 7.12-7.28 (m, 6H), 7.31-7.37 (m, 2H), 7.43-7.48 (m, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.82-7.86 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.5 (CH_3), 21.6 (CH_3), 44.0 (CH_2), 59.8 (CH-N), 126.4 (CH), 126.7 (4 x CH), 127.6 (2 x CH), 127.7 (CH), 128.5 (2 x CH), 128.6 (CH), 129.1 (2 x CH), 129.3 (CH), 129.5 (2 x CH), 129.8 (CH), 132.8 (C), 132.9 (C), 135.2 (C), 136.3 (C), 140.2 (C), 142.8 (C), 144.3 (C); MS (ES) *m/z* ^{79}Br: 605 ((M+Na)+), ^{81}Br: 607 ((M+Na)+), HRMS *m/z* ((M+Na)+) calcd for $C_{28}H_{27}N_2NaO_3S_2{}^{79}Br$ 605.0544 found 605.0532, *m/z* ((M+Na)+) calcd for $C_{28}H_{27}N_2NaO_3S_2{}^{81}Br$ 607.0524 found 607.0511.

(*R*)-3-(*o*-Bromophenyl)-1-phenyl-1-[*N*-(*p*-toluenesulfonyl)-*p*toluenesulfonimidoyl] aminopropane (6h). Prepared following the typical amination procedure from 1-bromo-2-(3-phenylpropyl)benzene, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as a yellow oil in 18% yield, 70% d.e (^1H NMR evaluation). R_f 0.49 (heptane/ethyl acetate: 50/50); IR (neat, cm^{-1}) 3221, 1596, 1454, 1301, 1150, 1107, 1090, 1016, 906, 812; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 1.96-2.01 (m, 2H, CH_2), 2.38 (s, 3H), 2.42 (s, 3H), 2.69-2.81 (m, 2H, CH_2), 4.30-4.34 (m, 1H, CH-N), 6.45 (d, *J* = 8.0 Hz, 1H, NH), 7.14-7.17 (m, 2H), 7.21-7.33 (m, 10H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.82-7.85 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.5 (CH_3), 21.6 (CH_3), 35.6 (CH_2), 36.7 (CH_2), 58.2 (CH-N), 125.8 (C-Br), 126.7 (4 x CH), 126.9 (2 x CH), 127.8 (2 x CH), 128.3 (CH), 128.4 (CH), 128.7 (CH), 129.2 (2 x CH), 129.3 (CH), 129.7 (2 x CH), 132.8 (CH), 135.9 (C), 140.0 (C), 140.2 (C), 140.3 (C), 142.8 (C), 144.7 (C); MS (ES) *m/z* ^{79}Br: 597 ((M+H)+), ^{81}Br: 599 ((M+H)+), ^{79}Br: 619 ((M+Na)+), ^{81}Br: 621 ((M+Na)+), HRMS *m/z* ((M+Na)+) calcd for $C_{29}H_{29}N_2NaO_3S_2{}^{79}Br$ 619.0701 found 619.0698, *m/z* ((M+Na)+) calcd for $C_{29}H_{29}N_2NaO_3S_2{}^{81}Br$ 621.0680 found 621.0695.

C-H insertion product of (*S*)-limonene (8a). Prepared following the typical amination procedure from (*S*)-limonene, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as a white solid in 73% yield, 96% d.e (HPLC, Hypercarb column, 100*4.6mm, 5µ, MeCN+0.1%HCOOH/H_2O+0.1%HCOOH: 80/20, 1mL/min, t_{maj} = 46.38 min, or UPLC, BEH shield RP18 column, 50*2.1mm, 1.8µm, MeCN+0.1%HCOOH/H_2O+0.1%HCOOH: 55/45, 0.6 mL/min, t_{maj} = 1.40 min). R_f 0.54 (heptane/ethyl acetate: 50/50); mp 83-85°C; $[\alpha]_D^{20}$ + 105.5 (c 1.00, $CHCl_3$); IR (neat, cm^{-1}) 3190, 1597, 1424, 1299, 1283, 1146, 1109, 1030, 1014, 806; ^1H NMR (300 MHz, $CDCl_3$) δ 1.03 (s, 3H, CH_3), 1.39-1.56 (m, 2H, CH_2), 1.60 (s, 3H, CH_3), 1.79-1.81 (m, 1H, $1CH_2$), 1.81-1.98 (m, 2H, CH + $1CH_2$), 2.33 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 3.49-3.54 (m, 1H, CH-N), 4.49 (br s, 1H, $1CH_{2\text{-isopren}}$), 4.54 (br s, 1H, $1CH_{2\text{-isopren}}$), 5.41 (br s, 1H, CH_{vinyl}), 5.67 (d, *J* = 8.0 Hz, 1H, NH), 7.16-7.19 (m, 4H, 4 x CH_{Ar}), 7.69 (d, *J* = 8.5 Hz, 2H, 2 x CH_{Ar}), 7.76 (d, *J* = 8.5 Hz, 2H, 2 x CH_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.4 (CH_3), 21.5 (CH_3), 21.6 (CH_3), 23.2 (CH_3), 26.9 (CH_2), 29.4 (CH_2), 48.2 (CH), 52.9 (CH-N), 113.5 ($CH_{2\text{-isopren}}$), 122.7 (CH_{vinyl}), 126.8 (2 x CH_{Ar}), 128.4 (2 x CH_{Ar}), 129.2 (2 x CH_{Ar}), 129.4 (2 x CH_{Ar}), 135.4 (C), 138.0 (C), 140.5 (C), 142.8 (C), 144.6 (C), 144.9 (C). MS (ES) *m/z* 481 ((M+Na)+), HRMS *m/z* ((M+Na)+) calcd for $C_{24}H_{30}N_2NaO_3S_2$ 481.1596 found 481.1608.

C-H insertion product of (*R*)-limonene (8b). Prepared following the typical amination procedure from (*R*)-limonene, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as an oily solid in 68% yield, 94% d.e (HPLC, Hypercarb column, 100*4.6mm, 5µ, MeCN+0.1%HCOOH/H_2O+0.1%HCOOH: 80/20, 1mL/min, t_{maj} = 26.34 min). R_f 0.54 (heptane/ethyl acetate: 50/50); $[\alpha]_D^{20}$ - 1.6 (c 1.00, $CHCl_3$); IR (neat, cm^{-1}) 3236, 2924, 1596, 1436, 1300, 1257, 1149, 1104, 1088, 1015, 812; ^1H NMR (300 MHz, $CDCl_3$) δ 1.52 (s, 3H, CH_3), 1.66 (s, 3H, CH_3), 1.69-1.78 (m, 2H, CH_2), 1.84-1.91 (m, 2H, CH_2), 2.17-2.24 (m, 1H, CH), 2.40 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.80-3.85 (m, 1H, CH-N), 4.72 (br s, 1H, $1CH_{2\text{-isopren}}$), 4.82 (br s, 1H, $1CH_{2\text{-isopren}}$), 4.88 (br s, 1H, CH_{vinyl}), 5.77 (d, *J* = 7.5 Hz, 1H, NH), 7.22-7.31 (m, 4H, 4 x CH_{Ar}), 7.79-7.86 (m, 4H, 4 x CH_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.8 (CH_3), 21.5 (CH_3), 21.6 (CH_3), 23.3 (CH_3), 25.3 (CH_2), 28.5 (CH_2), 47.6 (CH), 52.5 (CH-N), 112.8 ($CH_{2\text{-isopren}}$), 120.0 (CH_{vinyl}), 126.8 (2 x CH_{Ar}), 127.8 (2 x CH_{Ar}), 129.1 (2 x CH_{Ar}), 129.7 (2 x CH_{Ar}), 136.8 (C), 139.1 (C), 140.5 (C), 142.7 (C), 144.6 (C), 144.7 (C). MS (ES) *m/z* 459 ((M+H)+), 481 ((M+Na)+), HRMS *m/z* ((M+H)+) calcd for $C_{24}H_{31}N_2O_3S_2$ 459.1776 found 459.1796.

C-H insertion product of (*S*)-pinene (8c). Prepared following the typical amination procedure from (*S*)-pinene, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as a white solid in 91% yield, 95% d.e (HPLC, Hypercarb column, 100*4.6mm, 5µ, MeCN+0.1%HCOOH/H_2O+0.1%HCOOH: 80/20, 1mL/min, t_{maj} = 17.25 min, or UPLC, BEH shield RP18 column, 50*2.1mm, 1.8µm, MeCN+0.1%HCOOH/H_2O+0.1%HCOOH: 55/45, 0.6 mL/min, t_{maj} = 1.40 min). R_f 0.60 (heptane/ethyl acetate: 50/50); mp 55-57°C; $[\alpha]_D^{20}$ - 10.6 (c 1.00, $CHCl_3$); IR (neat, cm^{-1}) 3218, 2925, 1596, 1403, 1301, 1258, 1150, 1105, 1089, 1074, 1016, 1002, 810; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.69 (s, 3H, CH_3), 1.17-1.20 (m, 1H, $1CH_2$), 1.21 (s, 3H, CH_3), 1.55-1.57 (m, 3H, CH_3), 1.91-1.95 (m, 1H, CH), 2.12-2.17 (m, 1H, CH), 2.24-2.31 (m, 1H, $1CH_2$), 2.33 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 3.70-3.73 (m, 1H, CH-N), 4.74-4.76 (m, 1H, CH_{vinyl}), 5.83 (d, *J* = 9.0 Hz, 1H, NH), 7.15-7.25 (m, 4H, 4 x CH_{Ar}), 7.71-7.75 (m, 4H, 4 x CH_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.3 (CH_3), 21.5 (CH_3), 21.6 (CH_3), 22.7 (CH_3), 26.2 (CH_3), 28.6 (CH_2), 44.4 (C), 46.5 (CH), 47.0 (CH), 54.1 (CH-N), 114.8 (CH_{vinyl}), 126.8 (2 x CH_{Ar}), 127.7 (2 x CH_{Ar}), 129.1 (2 x CH_{Ar}), 129.8 (2 x CH_{Ar}), 136.4 (C), 140.4 (C), 142.8 (C), 144.6 (C), 150.5 (C); MS (ES) *m/z* 459 ((M+H)+), 481 ((M+Na)+), HRMS *m/z* ((M+Na)+) calcd for $C_{24}H_{30}N_2NaO_3S_2$ 481.1596 found 481.1588.

C-H insertion product of (*R*)-pinene (8d). Prepared following the typical amination procedure from (*R*)-pinene, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as a white solid in 71% yield, 96% d.e (HPLC, Hypercarb column, 100*4.6mm, 5µ, MeCN+0.1%HCOOH/H_2O+0.1%HCOOH: 90/10, 1mL/min, t_{maj} = 13.08 min). R_f 0.60 (heptane/ethyl acetate: 50/50); mp 123-125°C; $[\alpha]_D^{20}$ + 142.0 (c 1.00, $CHCl_3$); IR (neat, cm^{-1}) 3236, 2920, 1596, 1420, 1300, 1245, 1150, 1104, 1088, 1016, 1000, 811; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.69 (s, 3H, CH_3), 1.11-1.14 (m, 1H, $1CH_2$), 1.12 (s, 3H, CH_3), 1.62-1.64 (m, 3H, CH_3), 1.69-1.75 (m, 1H, CH), 1.89-1.93 (m, 1H, CH), 2.10-2.17 (m, 1H, $1CH_2$), 2.34 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 3.78-3.83 (m, 1H, CH-N), 5.12-5.15 (m, 1H, CH_{vinyl}), 5.77 (d, *J* = 8.7 Hz, 1H, NH), 7.17-7.22 (m, 4H, 4 x CH_{Ar}), 7.69-7.77 (m, 4H, 4 x CH_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.3 (CH_3), 21.5 (CH_3), 21.6 (CH_3), 22.7 (CH_3), 26.2 (CH_3), 28.6 (CH_2), 44.3 (C), 46.3 (CH), 46.9 (CH), 54.1 (CH-N), 116.2 (CH_{vinyl}), 126.8 (2 x CH_{Ar}), 127.7 (2 x CH_{Ar}), 129.2 (2 x CH_{Ar}), 129.7 (2 x CH_{Ar}), 136.6 (C), 140.4 (C), 142.8 (C), 144.6 (C), 149.8 (C); MS (ES) *m/z* 459 ((M+H)+), 481 ((M+Na)+), HRMS *m/z* ((M+Na)+) calcd for $C_{24}H_{30}N_2NaO_3S_2$ 481.1596 found 481.1575.

(*R*)-3,7-dimethyl-5-[*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl]-aminoocta-2,6-dien-1-yl acetate (8e). Prepared following the typical amination procedure from (*E*)-3,7-dimethylocta-2,6-dienylacetate, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as a clear oil in 90% yield, 90% d.e (HPLC, Hypercarb column, 100*4.6mm, 5µ, MeCN+0.1%HCOOH/H_2O+0.1%HCOOH: 80/20, 1mL/min, t_{maj} = 29.28 min, or UPLC, BEH shield RP18 column, 50*2.1mm, 1.8µm, MeCN+0.1%HCOOH/H_2O+0.1%HCOOH: 55/45, 0.6 mL/min, t_{maj} = 1.04 min). R_f 0.36 (heptane/ethyl acetate: 60/40); $[\alpha]_D^{20}$ + 25.4 (c 1.00, $CHCl_3$); IR (neat, cm^{-1}) 3229, 1732 (C=O (Ac)), 1596, 1443, 1232, 1151, 1105, 1089, 1016, 812; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 1.51 (s, 3H), 1.55 (s, 3H), 1.60 (s, 3H), 2.03-2.14 (m, 2H, CH_2), 2.08 (s, 3H, Ac), 2.41 (s, 3H), 2.44 (s, 3H), 4.11-4.14 (m, 1H, CH-N), 4.51 (d, *J* = 7.0 Hz, 2H, $CH_{2\text{-}OAc}$), 4.90 (d, *J* = 9.0 Hz, 1H, $CH_{vinyl\text{-}CHN}$), 5.32-5.34 (m, 1H, CH_{vinyl}), 5.59 (d, *J* = 5.0 Hz, 1H, NH), 7.25-7.30 (m, 4H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 16.2 (CH_3), 18.1 (CH_3), 21.0 (CH_3, Ac), 21.5 (CH_3), 21.6 (CH_3), 25.5 (CH_3), 45.9 (CH_2), 50.8 (CH-N), 60.9 ($CH_{2\text{-}OAc}$), 123.1 (CH_{vinyl}), 124.1 ($CH_{vinyl\text{-}CHN}$), 126.7 (2 x CH_{Ar}), 127.9 (2 x CH_{Ar}), 129.2 (2 x CH_{Ar}), 129.5 (2 x CH_{Ar}), 135.8 (C), 136.4 (C), 136.9 (C), 140.5 (C), 142.7 (C), 144.6 (C), 171.0 (C=O, Ac); MS (ES) *m/z* 541 ((M+Na)+), HRMS *m/z* ((M+Na)+) calcd for $C_{26}H_{34}N_2NaO_5S_2$ 541.1807 found 541.1779.

Typical procedure for the removal of the sulfonimidoyl moiety. To a solution of the (*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl)amino product in dichloromethane were added 3 equiv. of di-tert-butyl dicarbonate $(Boc)_2O$ and 0.5 equiv. of DMAP. The mixture was stirred at room temperature for 12 h under argon. The solvent was evaporated and the residue was purified by flash chromatography (dichloromethane/ethyl acetate: 90/10) to afford the Boc-protected products.
To a solution of the *N*-Boc sulfonimidamide in methanol were added 10 equiv. of magnesium (powder, 50 Mesh). The mixture was sonicated at room temperature for 25 minutes in a Bransonic® DTH-2510 apparatus (Digital control, plus Heat and Timer, 2.8 L, 130 W). The solvent was evaporated and the residue was diluted with ether. The organic layer was washed with a solution of saturated NH_4Cl, dried over $MgSO_4$ and concentrated under vacuum to afford a clear oil which was purified by flash chromatography (dichloromethane/ethyl acetate: 90/10) to afford the deprotected amines.

***N*-Boc-aminolimonene (9a/9b).** Prepared following the typical deprotection procedure from aminolimonene **8a** and **8b**, the corresponding Boc-protected products were obtained (heptane/ethyl acetate: 90/10) as oily solids in 46% and 48% yield respectively over 2 steps. R_f 0.42 (heptane/ethyl acetate: 90/10); IR (neat, cm^{-1}) 3356, 2924, 1683, 1515, 1364, 1324, 1245, 1159, 1128, 1004, 864; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.44 (s, 9H, 3 x CH_3), 1.67 (s, 3H, CH_3), 1.68-1.72 (m, 2H, CH_2), 1.73 (s, 3H, CH_3), 1.91-2.06 (m, 3H, CH_2 + CH), 4.14-4.17 (m, 1H, CH-N), 4.34 (br s, 1H, NH), 4.76 (br s, 1H, $1CH_{2\text{-}isopren}$), 4.79 (br s, 1H, $1CH_{2\text{-}isopren}$), 5.35 (br s, 1H, CH_{vinyl}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2 (CH_3), 23.2 (CH_3), 27.1 (CH_2), 28.5 (3 x CH_3), 29.8 (CH_2), 49.2 (CH), 49.7 (CH-N), 112.0 ($CH_{2\text{-}isopren}$), 120.6 (C), 121.1 (C), 123.8 (CH_{vinyl}), 136.4 (C), 155.7 (C=O). MS (ES) *m/z* 252 ((M+H)+), 274 ((M+Na)+), HRMS *m/z* ((M+Na)+) calcd for $C_{15}H_{25}NNaO_2$ 274.1783 found 274.1781.
N-Boc-aminolimonene **9a** (from (*S*)-limonene): $[\alpha]_D^{20}$ + 66.8 (c 0.43, $CHCl_3$),
N-Boc-aminolimonene **9b** (from (*R*)-limonene): $[\alpha]_D^{20}$ - 58.0 (c 0.43, $CHCl_3$).

3,7-dimethyl-7-[*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl]-aminoocta-1-yl acetate (11). Prepared following the typical amination procedure from **5 equivalents** of 3,7-dimethyloctylacetate, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as a clear oil in 30% yield. R_f 0.48 (heptane/ethyl acetate: 50/50); IR (neat, cm^{-1}) 3239, 2926, 1732 (C=O (Ac)), 1596, 1367, 1245, 1149, 1103, 1090, 1068, 1017, 812; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 0.88-0.91 (m, 3H), 1.01-1.06 (m, 1H, $CH_{(2)}$), 1.11 (s, 3H), 1.17-1.20 (m, 1H, $CH_{(2)}$), 1.23 (s, 3H), 1.39-1.45 (m, 2H, CH_2), 1.50-1.54 (m, 2H, CH_2), 1.61-1.66 (m, 2H, CH_2), 2.06 (s, 3H, Ac), 2.42 (s, 3H), 2.43 (s, 3H), 4.06-4.14 (m, 2H, $CH_{2\text{-}OAc}$), 6.21 (br s, 1H, NH), 7.26-7.29 (m, 4H), 7.30-7.32 (m, 1H, CH), 7.79-7.84 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 19.4 (CH_3), 21.0 (CH_3, Ac), 21.1 (CH_2), 21.5 (CH_3), 21.6 (CH_3), 27.0 (CH_3), 28.0 (CH_3), 35.5 (CH_2), 37.0 (CH_2), 43.5 (CH_2), 59.5 (C-N), 62.9 ($CH_{2\text{-}OAc}$), 77.2 (CH), 126.7 (2 x CH), 127.7 (2 x CH), 129.2 (2 x CH), 129.6 (2 x CH), 138.7 (C), 140.4 (C), 142.8 (C), 144.3 (C), 171.2 (C=O, Ac); MS (ES) *m/z* 545 ((M+Na)+), HRMS *m/z* ((M+Na)+) calcd for $C_{26}H_{38}N_2NaO_5S_2$ 545.2120 found 545.2114.

C-H insertion product of *cis*-decalin (15). Prepared following the typical amination procedure from *cis*-decalin, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as an oily solid in 89% yield. R_f 0.51 (heptane/ethyl acetate: 50/50); IR (neat, cm^{-1}) 3231, 2921, 2856, 1699, 1596, 1444, 1314, 1244, 1151, 1104, 1083, 1048, 1015, 971, 903, 809; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 1.18-1.63 (m, 16H, 8 x CH_2), 2.32 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), *2.97-3.04 (m, 1H, CH),* 3.19-3.29 (m, 1H, CH), 5.66-5.88 (m, 2H, NH +*NH*), 7.15-7.21 (m, 4H, 4 x CH_{Ar}), 7.73 (td, *J* = 1.7 Hz and 8.3 Hz, 4H, 4 x CH_{Ar}); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.7 (CH_2), 21.6 (2 x CH_3), 25.0 (CH_2), 25.4 (CH_2), 26.6 (CH_2), 28.0 (CH_2), 30.7 (CH_2), 31.5 (CH_2), 33.9 (CH_2), 49.4 and 54.0 (CH + *CH*), 126.7 (2 x CH_{Ar}), 127.7 (2 x CH_{Ar}), 129.2 (2 x CH_{Ar}), 129.7 (2 x CH_{Ar}), 136.4 (C), 140.5 (C), 142.7 (C), 144.5 (2 x C); MS (ES) *m/z* 461 ((M+H)+), 483 ((M+Na)+), HRMS *m/z* ((M+Na)+) calcd for $C_{24}H_{32}N_2NaO_3S_2$ 483.1752 found 483.1735.

Typical procedure for cross experiments with quasi-enantiomeric sulfonimidamides. (Based on the typical procedure for kinetic resolution of sulfonimidamides described in C. Liang, F. Collet, F. Robert-Peillard, P. Müller, R. H. Dodd and P. Dauban, *J. Am. Chem. Soc.*, 2008, **130**, 343). In an oven-dried tube were introduced 4 Å molecular sieves (100 mg), chiral rhodium catalyst $Rh_2\{(S)\text{-nta}\}_4$ **(2)** (3 mol%), 1.1 equiv. of (*S or R*)-*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidamide **(1)** and 1.1 equiv. of (*S or R*)-*N*-(*p*-toluenesulfonyl)-*p*-nitrobenzenesulfonimidamide **(17)**, 1 mL of $Cl_2CHCHCl_2$/MeOH (v/v: 3/1) and substrate (0.2 mmol). After stirring at room temperature for 5 min, the mixture was cooled to -35°C, and $PhI(OCOt\text{-}Bu)_2$ (1.1 equiv.) was added. The mixture was stored in freezer (-35°C) for 3 days. After reaction, the molecular sieves were removed by filtration and the filtrate was evaporated to dryness under reduced pressure. The oily residue was purified by flash chromatography on silica gel, affording the C-H insertion products (CH_2Cl_2/EtOAc: 20/1) and the sulfonimidamide (CH_2Cl_2/EtOAc: 5/2).

(1*R*)-[*N*-(*p*-toluenesulfonyl)-*p*-nitrobenzenesulfonimidoyl]-1-amino indane (18). Prepared following the cross experiments procedure from indane using 1.1 equiv. of (+)-(*R*)-*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidamide **(1)** and 1.1 equiv. of (-)-(*S*)-*N*-(*p*-toluenesulfonyl)-*p*-nitrobenzenesulfonimidamide **(17)**, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as a white solid in 72% yield and >98% d.e. (HPLC, Hypercarb column, 100*4.6mm, 5µ, MeCN+0.2%TFA/H_2O+0.2%TFA: 100/0, 1mL/min, t_{maj} = 29.16 min). R_f 0.42 (heptane/ethyl acetate: 60/40); mp 159-161°C; $[\alpha]_D^{20}$ + 82.8 (c 1.00, $CHCl_3$); IR (neat, cm^{-1}) 3161, 1524, 1300, 1288, 1146, 1108, 1078, 1062, 986; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.61-1.72 (m, 1H, CH_2-H_a), 2.00-2.11 (m, 1H, CH_2-H_a), 2.35 (s, 3H), 2.58-2.69 (m, 1H, CH_2'-H_b), 2.78-2.88 (m, 1H, CH_2'-H_b), 4.80 (q, *J* = 7.8 Hz, 1H, CH-N), 6.49 (d, *J* = 8.5 Hz, 1H, NH), 7.11-7.29 (m, 6H), 7.68-7.80 (m, 2H), 8.11 (d, *J* = 8.5 Hz, 2H), 8.24 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (75MHz, $CDCl_3$) δ 21.6 (CH_3), 30.0 (CH_{2b}), 33.3 (CH_{2a}), 58.7 (CH-N), 124.4 (2 x CH_{Ar}), 124.7 (CH_{Ar}), 124.9 (CH_{Ar}), 126.7 (2 x CH_{Ar}), 127.1 (CH_{Ar}), 127.9 (CH_{Ar}), 129.0 (2 x CH_{Ar}), 129.4 (2 x CH_{Ar}), 139.8 (C), 140.4 (C), 142.7 (C), 143.5 (C), 145.8 (C), 150.4 (C); MS (ES) *m/z* 494 ((M+Na)+), HRMS *m/z* ((M+Na)+) calcd for $C_{22}H_{21}N_3NaO_5S_2$ 494.0820 found 494.0819.

(1*R*)-[*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl]-1-amino ethyl benzene (XX). Prepared following the typical amination procedure from ethylbenzene, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as a white solid in 80% yield, 98% d.e. (HPLC, Hypercarb column, 100*4.6mm, 5µ, MeCN+0.1%HCOOH/H_2O+0.1%HCOOH: 70/30, 1mL/min, t_{maj} = 12.03 min). R_f 0.40 (heptane/ethyl acetate: 50/50); mp 157-158°C; $[\alpha]_D^{20}$ + 103.0 (c 0.52, $CHCl_3$); IR (neat, cm^{-1}) 3289, 1597, 1493, 1317, 1244, 1153, 1113, 1087, 1068, 1033; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) 1.35 (d, *J* = 7.0 Hz, 3H, CH_3), 2.40 (s, 3H), 2.42 (s, 3H), 4.51 (q, *J* = 7.0 Hz, 1H, CH-N), 6.18 (d, *J* = 7.0 Hz, 1H, NH), 7.20-7.31 (m, 9H), 7.77-7.80 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.5 (CH_3), 21.6 (CH_3), 23.4 (CH_3), 54.3 (CH-N), 126.8 (2 x CH_{Ar}), 127.2 (2 x CH_{Ar}), 128.1 (CH_{Ar}), 128.2 (2 x CH_{Ar}), 129.0 (2 x CH_{Ar}), 129.6 (2 x CH_{Ar}), 130.0 (2 x CH_{Ar}), 136.4 (C), 140.8 (C), 142.1 (C), 143.2 (C), 145.0 (C); MS (ES) *m/z* 428 (M+), HRMS *m/z* ((M+Na)+) calcd for $C_{22}H_{24}N_2NaO_3S_2$ 451.1126 found 451.1103.

(1*R*)-[*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl]-1-amino-1-deuterio-ethylbenzene (XX). Prepared following the typical amination procedure from ethyl-α,α-d_2- benzene, the corresponding C-H insertion product was obtained (dichloromethane/ethyl acetate: 20/1) as a pale yellow solid in 25% yield. R_f 0.48 (heptane/ethyl acetate: 50/50); mp 150-

152°C; IR (neat, cm^{-1}) 3259, 2927, 1594, 1450, 1388, 1312, 1260, 1148, 1100, 1060, 1015, 972; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) 1.35 (s, 3H, CH_3), 2.40 (s, 3H), 2.42 (s, 3H), 6.14 (br s, 1H, NH), 7.20-7.31 (m, 9H), 7.76-7.79 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 21.6 (2 x CH_3), 22.8 (CH_3), 53.5 (t, J = 21.3 Hz, C-D), 126.3 (2 x CH_{Ar}), 126.8 (2 x CH_{Ar}), 127.7 (CH_{Ar}), 127.8 (2 x CH_{Ar}), 128.6 (2 x CH_{Ar}), 129.2 (2 x CH_{Ar}), 129.7 (2 x CH_{Ar}), 136.0 (C), 140.3 (C), 141.5 (C), 142.8 (C), 144.6 (C); MS (ES) *m/z* 428 (M+), HRMS *m/z* ((M+Na)+) calcd for $C_{22}H_{24}N_2NaO_3S_2$ 451.1126 found 451.1103.

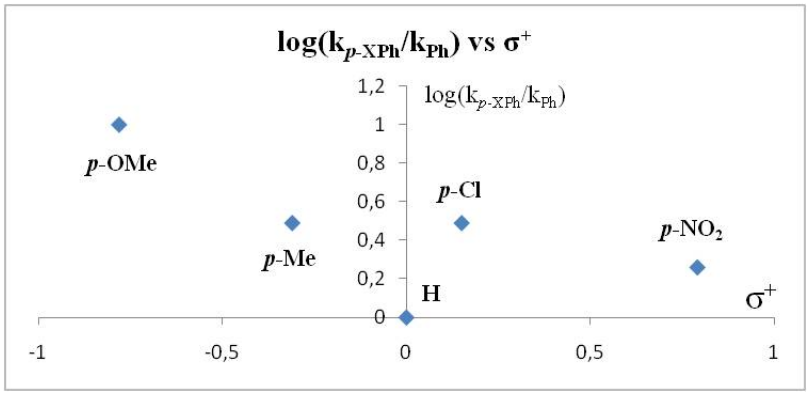
Typical procedure for Hammett experiments. In an oven-dried tube were introduced activated 4 Å molecular sieves (100 mg), Rh_2{(S)-nta}$_4$ (**2**) (7.7 mg, 0.006 mmol) and (-)-*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidamide **(-)-(1)** (65 mg, 0.2 mmol). The tube was capped with a rubber septum and purged with argon. 1,1,2,2-Tetrachloroethane (0.75 mL) and methanol (0.25 mL) were added under argon, and the mixture was stirred for 5 min before addition of the substrates (10 equiv. of ethylbenzene, 1 mmol and 10 equiv. of *para*-substituted ethylbenzene, 1 mmol). The tube was cooled to –35°C, and bis(*tert*-butylcarbonyloxy)iodobenzene (98 mg, 0.24 mmol) was added. The mixture was stored in the freezer (-35°C) for 3 days. After dilution with dichloromethane (3 mL), the molecular sieves were removed by filtration and the filtrate was evaporated to dryness under reduced pressure. The oily residue was purified by flash chromatography on silica gel, affording a mixture of (1*R*)-[*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl]-1-amino ethyl benzene **(XX)** and the corresponding *para*-substituted C-H insertion products (already fully described in C. Liang, F. Collet, F. Robert-Peillard, P. Müller, R. H. Dodd and P. Dauban, *J. Am. Chem. Soc.*, 2008, **130**, 343).

(1*R*)-[*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl]-4-(1-aminoethyl) anisole (XX).
(1*R*)-[*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl]-1-(1-aminoethyl)-toluene(XX).
(1*R*)-[*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl]-1-(1-aminoethyl)-4-bromobenzene (XX).
(1*R*)-[*N*-(*p*-toluenesulfonyl)-*p*-toluenesulfonimidoyl]-1-(1-aminoethyl)-4-nitrobenzene (XX).

N.B The C-H insertion products obtained during BHT studies (from indane, phenylcyclohexene, adamantane, cycloheptane and 2-methylbutane) have already been described in C. Liang, F. Collet, F. Robert-Peillard, P. Müller, R. H. Dodd and P. Dauban, *J. Am. Chem. Soc.*, 2008, **130**, 343.

Hammett Analysis

Plot of $\log(k_{p\text{-XPh}}/k_{Ph})$ *vs* σ^+



Plot of $\log(k_{p\text{-XPh}}/k_{Ph})$ *vs* TE