Supplementary Material (ESI) for Chemical Communications

Contra-Friedel-Crafts *tert*-butylation of substituted aromatic rings via directed metallation and sulfinylation

Jonathan Clayden,*[a] Christopher C. Stimson[ab] and Martine Keenan[b]

[a] *School of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK; clayden@man.ac.uk*
[b] *Eli Lilly and Co. Ltd., Erl Wood Manor, Windlesham, Surrey GU20 6PH, UK*

ELECTRONIC SUPPLEMENTARY INFORMATION

Details of spectrometers etc. have been provided before.[1] "Flash Chromatography" refers to chromatography performed on silica by the method of Still *et al.*[2]

Method A *General ortholithiation procedure using s-BuLi*. —*sec*-BuLi (1.3 equiv, 1.3 mmol of a 1.3M solution in hexane) was added dropwise to the amide (1 equiv, 1.0 mmol) stirring in dry THF (20 ml) under nitrogen at –78 °C. After 30 - 60 mins, the electrophile (2 equiv, 2.0 mmol) was added dropwise at –78 °C and the mixture left to warm to room temperature and quenched with saturated ammonium chloride solution. The THF was removed under reduced pressure and the mixture diluted with dichloromethane (50 ml), washed with saturated ammonium chloride solution (3 x 20 ml), dried ($MgSO_4$) and concentrated under reduced pressure.

Method B *General procedure for substitution of tert-butyl sulfoxides*. —*tert*-BuLi (5 equiv, 5.0 mmol of a 1.5M solution in pentane) was added dropwise to the *tert*-butyl sulfoxide (1 equiv, 1.0 mmol) at –78 °C. After 20-90 minutes, saturated ammonium chloride solution was added to quench and the mixture allowed to warm to room temperature. The mixture diluted with diethyl ether (30 ml), washed with saturated ammonium chloride solution (3 x 20 ml), dried ($MgSO_4$) and concentrated under reduced pressure.

tert-Butyl tert-butylthiosulfinate.[3] —By the method of Ellman, *tert*-Butyl disulfide (20 ml, 0.105 mol) was stirred in acetone (46 ml) and the chiral salen ligand[3] (200 mg, 0.55 mmol) and vanadyl acetylacetonate (140 mg, 0.55 mmol) were added. Hydrogen peroxide (14.4 ml of a 27.5% wt. soln in water) was added over eight hours at 0 °C, the mixture turning from green to black. After 18 hours the solution was diluted with ether (30 ml) and washed with saturated ammonium chloride solution (3 x 15 ml), dried ($MgSO_4$) and solvents evaporated under reduced

pressure giving a yellow liquid. Hexane (20 ml) was added and the solution was left to crystallise for three hours at 4 °C. The mother liquor was filtered, concentrated under reduced pressure and rediluted in hexane (15 ml) and left to recrystallise. The process was repeated three time giving the thiosulfinate (12.7 g, 68%) as white prisms, m.p. <21 °C, 94% ee by HPLC ((*R,R*)-Whelk 01), R_f (70:30 Petrol:EtOAc) 0.46; δ_H(400 MHz; $CDCl_3$) 1.38 (9H, s, CH_3), 1.56 (9H, s, CH_3).

Starting materials 1 and **4** were obtained from commercial sources or made by standard methods:

4,5-Dihydro-4,4-dimethyl-2-phenyloxazole **1a**.[4] —2-Methyl-2-amino-1-propanol (14.6 ml, 0.152 mol) was added to benzoyl chloride (8.0 ml, 69.0 mmol) in dichloromethane (125 ml) at 0 °C and the mixture was stirred at room temperature for 18 hours. The mixture was filtered, the cake washed with dichloromethane (30 ml) and cooled to 0 °C. Thionyl chloride (15.1 ml, 0.207 mol) was added and the mixture heated to reflux and then cooled to room temperature and stirred for 3 hours. Water and 40% aq. NaOH were added slowly until the solution reached pH 11 and the organic layer was separated, washed with saturated ammonium chloride solution (2 x 50 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The resulting oil was purified by flash chromatography (SiO_2; Petrol:EtOAc 80:20) to give the oxazoline **1a** as a yellow oil (12.2 g, 100 %); R_f (80:20 Petrol:EtOAc) 0.45; δ_H(500 MHz; $CDCl_3$) 1.21 (6H, s, CH_3), 3.94 (2H, s, CH_2), 7.21 (2H, t, *J* 8, ArH), 7.38 (1H, t, *J* 8, ArH), 7.76 (2H, d, *J* 8, ArH).

N,N-Diethylbenzamide **1b**.[5] —Benzoyl chloride (5 ml, 43 mmol) was added dropwise to a solution of diethylamine (13.2 ml, 128 mmol) in dichloromethane (75 ml) at 0 °C. The mixture was raised to room temperature and left to stir for 18 hours. The mixture was washed with 1M aq. HCl (30 ml) then saturated ammonium chloride solution (2 x 20 ml), dried ($MgSO_4$) and concentrated under reduced pressure giving the amide **1b** as a brown oil (7.0 g, 92%); R_f (70:30 Petrol:EtOAc) 0.39; δ_H(500 MHz; $CDCl_3$) 0.89 (3H, m (broad), CH_3), 1.04 (3H, m (broad), CH_3), 3.04 (2H, s (broad), NCH_2), 3.33 (2H, s (broad), NCH_2), 7.12-7.21 (5H, m, ArH).

N,N-Diisopropylbenzamide **1c**.[6] —Benzoyl chloride (5.0 ml, 43 mmol) was added dropwise to a solution of diisopropylamine (19.0 ml, 128 mmol) in dichloromethane (75 ml) at 0 °C. The

mixture was raised to room temperature and left to stir for 18 hours. The mixture was washed with 1M aq. HCl (30 ml) then saturated ammonium chloride solution (2 x 20 ml), dried ($MgSO_4$) and concentrated under reduced pressure giving the amide **1c** (9.0 g, 100%) as white crystals, m.p. 72-74 °C (Lit,[7] 69-72 °C); R_f (70:30 Petrol:EtOAc) 0.50; δ_H(500 MHz; $CDCl_3$) 1.03 (3H, m (broad), CH_3), 1.20 (3H, m (broad), CH_3), 3.41 (1H, m (broad), NCH), 3.72 (1H, m (broad), NCH), 7.16-7.19 (2H, m, ArH), 7.23-7.26 (3H, m, ArH).

N-tert-Butyl-N-methylbenzamide **1d**.[8] —*N*-Methyl-*tert*-butylamine (5.2 ml, 43.2 mmol) was added dropwise to a stirred solution of benzoyl chloride (5.0 ml, 43.2 mmol) and triethylamine (11.9 ml, 86.4 mmol) in anhydrous dichloromethane (125 ml) under nitrogen at 0 °C. The mixture was stirred at room temperature for 18 hours before washing with 1M aq. HCl (2 x 50 ml) and saturated ammonium chloride (50 ml) and dried ($MgSO_4$). The solvents were evaporated under reduced pressure and the residue was recrystallised (heptane) to give the amide **1d** (6.96 g, 86% yield) as white plates, m.p. 79-80 °C (Lit,[8] 80-81 °C); R_f (70:30 Petrol:EtOAc) 0.77; δ_H(300 MHz; $CDCl_3$) 1.52 (9H, s, ^tBu), 2.88 (3H, s, NMe), 7.35-7.50 (5H, m, ArH).

N-Isopropylbenzamide **1f**.[9] —Benzoyl chloride (5 ml, 43 mmol) was slowly added to a solution of isopropylamine (11.0 ml, 130 mmol) in dichloromethane (100 ml) at 0 °C. After stirring for 3 hours the mixture washed with saturated ammonium chloride solution (3 x 30 ml) and solvent removed under reduced pressure. The residue was recrystallised (Heptane/EtOAc) to give the amide **1f** (6.8 g, 95%) as white crystals, m.p. 100-102 °C (Lit,[9] 104-105 °C); R_f (70:30 EtOAc) 0.50; δ_H(500 MHz; $CDCl_3$) 1.13 (6H, d, *J* 7, CH_3), 4.15 (1H, sept, *J* 7, NCH), 5.85 (1H, s (broad), NH), 7.26-7.29 (2H, m, ArH), 7.32 (1H, m, ArH), 7.60-7.62 (2H, m, ArH).

N,N-Diisopropyl-2-methoxybenzamide **4a**.[6] —Diisopropylamine (11.3 ml, 80 mmol) was added dropwise to a stirred solution of 1-anisoyl chloride (3 ml, 20 mmol) in anhydrous dichloromethane (85 ml) under nitrogen at 0 °C. After several hours the colourless mixture was washed with 1% aq. HCl (3 x 50 ml), dried ($MgSO_4$) and solvents evaporated under reduced pressure and the residue was recrystallised (Heptane/EtOAc) to give the amide **4a** (5.59 g, 98%) as white crystals, m.p. 87-89 °C (Lit.,[6] 89-90 °C); R_f (80:20 Petrol:EtOAc) 0.56; δ_H(300 MHz; $CDCl_3$) 1.07 (3H, d, *J* 7, CH_3), 1.18 (3H, d, *J* 7, CH_3), 1.58 (3H, d, *J* 7, CH_3), 1.59 (3H, d, *J* 7,

CH_3), 3.52 (1H, sept, *J* 7, CH), 3.71 (1H, sept, *J* 7, CH), 3.85 (3H, s, OMe), 6.91 (1H, d, *J* 8, ArH), 6.99 (1H, tt, *J* 8 and 1, ArH), 7.18 (1H, m, ArH), 7.33 (1H, m, ArH).

N,N-Diisopropyl-3-methoxybenzamide **4b**.[10] —Diisopropylamine (3.4 ml, 24.2 mmol) was added dropwise to a stirred solution of 3-methoxy benzoylchloride (3.0 ml, 21.9 mmol) and triethylamine (9.2 ml, 69.8 mmol) in anhydrous dichloromethane (50 ml) under nitrogen at 0 °C. The mixture was heated to 50 °C for 18 hours before cooling, washing with 1M aq. HCl (2 x 30 ml) and saturated ammonium chloride (30 ml) and drying ($MgSO_4$). The solvents were evaporated under reduced pressure to give a residue which was recrystallised (heptane) to give the amide **4b** (4.2 g, 81%) as white crystals; R_f (70:30 Petrol:EtOAc) 0.64; δ_H(300 MHz; $CDCl_3$) 1.00-1-40 (6H, m (broad), CH_3), 1.40-1-70 (6H, m (broad), CH_3), 3.60 (1H, m (broad), NCH), 3.79 (1H, m (broad), NCH), 3.82 (3H, s, OMe), 6.82-6.95 (3H, m, ArH), 7.33 (1H, t, *J* 8, ArH).

N,N-Diisopropyl-4-methoxybenzamide **4c**.[6] —Diisopropylamine (3.0 ml, 23.8 mmol) was added dropwise to a stirred solution of 4-methoxy benzoylchloride (3.0 ml, 21.7 mmol) and triethylamine (9.2 ml, 69.8 mmol) in anhydrous dichloromethane (50 ml) under nitrogen at 0 °C. The mixture was heated to 50 °C for 18 hours before cooling, washing with 1M aq. HCl (2 x 30 ml) and saturated ammonium chloride (30 ml). The solvents were evaporated under reduced pressure to give a residue which was purified by flash chromatography (SiO_2; Petrol:EtOAc 80:20) to give the amide **4c** (5.13 g, 100%) as a colourless oil; R_f (70:30 Petrol:EtOAc) 0.55; δ_H(300 MHz; $CDCl_3$) 1.20-1.50 (12H, m (broad), CH_3), 3.60-3.90 (2H, m (broad), NCH), 3.85 (3H, s, OMe), 6.95 (2H, d, *J* 8, ArH), 7.35 (2H, d, *J* 8, ArH).

Naphthalene-1-carboxylic acid diisopropylamide **4d.**[11] —Diisopropylamine (11.2 ml, 80 mmol) was added dropwise to a stirred solution of naphthoyl chloride (3 ml, 20 mmol) in anhydrous dichloromethane (85 ml) under nitrogen at 0 °C. After several hours the mixture was washed with 1% aq. HCl (3 x 50 ml), dried ($MgSO_4$) and concentrated under reduced pressure and the residue was recrystallised (Heptane/EtOAc) to give the amide **4d** (5.65 g, 97%) as white crystals, m.p.=175-178 °C (Lit.,[11] 181-182 °C); R_f (80:20 Petrol:EtOAc) 0.72; δ_H(300 MHz; $CDCl_3$) 1.07 (3H, d, *J* 7, CH_3), 1.12 (3H, d, *J* 7, CH_3), 1.70 (3H, d, *J* 8, CH_3), 1.77 (3H, d, *J* 7, CH_3), 3.61 (1H, sept, *J* 7, CH), 3.66 (1H, sept, *J* 7, CH), 7.36 (1H, dd, *J* 6 and 1, ArH), 7.51 (3H, m, ArH), 7.90 (3H, m, ArH).

N,N-Diisopropyl-2,5-dimethoxybenzamide **4e.** —2,5-Dimethoxybenzoic acid (3.14 g, 17.3 mmol) was dissolved in thionyl chloride (20 ml) and stirred for 60 mins at 90 °C. The mixture was cooled and excess reagent was removed under reduced pressure. The resulting white crystals were dissolved in dichloromethane (25 ml) and was slowly added to a solution of diisopropylamine (7.3 ml, 51.8 mmol) in dichloromethane (50 ml) at 0 °C. After stirring for 3 hours the mixture was diluted with dichloromethane (25 ml), washed with saturated ammonium chloride solution (3 x 30 ml) and solvent removed under reduced pressure. The residue was purified by flash chromoatography (SiO_2; 60:40 Petrol:EtOAc) to give the amide **4e** (3.65 g, 80%) as white crystals, m.p. 92-95 °C; R_f (70:30 EtOAc) 0.33; ν_{max}/cm^{-1} 2962 and 2931 (C-H), 1634 (C=O); δ_H(500 MHz; $CDCl_3$) 0.90 (3H, d, *J* 7, CH_3), 1.01 (3H, d, *J* 7, CH_3), 1.40 (3H, d, *J* 7, CH_3), 1.42 (3H, d, *J* 7, CH_3), 3.32 (1H, sept, *J* 7, NCH), 3.51 (1H, sept, *J* 7, NCH), 3.63 (6H, s, OMe), 6.58 (1H, s, ArH), 6.67 (2H, m, ArH); δ_C(125 MHz; $CDCl_3$) 20.7, 20.8, 21.2, 21.2, 46.1, 51.3, 56.2, 56.5, 112.6, 112.9, 114.8, 129.7, 149.6, 154.2, 168.5; *m/z* (CI) 266 (100%, M+H); Acc. mass found (M+H) 266.1748 ($C_{15}H_{24}NO_3$ requires (*M*) 266.1751).

2-(Di-tert-butylphosphino)-N,N-diethylbenzamide **4f**.[12] —By method A, amide **1b** (1.07 g, 6.0 mmol) and di(*tert*-butyl)phosphine chloride (1.26 ml, 6.6 mmol) gave a residue which was purified by flash chromatography (SiO_2; Petrol:EtOAc 70:30) to give the phosphine (1.15 g, 60%) as yellow crystals, m.p. 58-60 °C; R_f (70:30 EtOAc) 0.50; ν_{max}/cm^{-1} 2970 & 2864 (C-H), 1634 (C=O); δ_H(500 MHz; $CDCl_3$) 1.08 (3H, t, *J* 7, CH_3), 1.19 (9H, d, *J* 12, ^{t}Bu), 1.23 (9H, d, *J* 12, ^{t}Bu), 1.29 (3H, t, *J* 7, CH_3), 3.02 (1H, m, NCH_2), 3.17 (1H, m, NCH_2), 3.36 (1H, m, NCH_2), 3.82 (1H, m, NCH_2), 7.23 (1H, m, ArH), 7.33-7.38 (2H, m, ArH), 7.82 (1H, d, *J* 8, ArH); δ_C(125 MHz; $CDCl_3$) 12.9, 14.4, 30.7 (3C, d, *J* 18, PC<u>C</u>H_3), 31.7 (3C, d, *J* 18, PCH<u>C</u>H_3), 32.7 (1C, d, *J* 24, P<u>C</u>), 33.3 (1C, d, *J* 24, P<u>C</u>), 38.7, 43.4, 126.4, 126.4, 127.3, 129.3, 135.6, 146.9, 147.2; *m/z* (CI) 322 (100%, M+H); Acc. mass found (M+H) 322.2291 ($C_{19}H_{32}NOP$ requires (*M*) 322.2294).

2-(Dimethylamino)-N,N-diethylbenzamide **4g**.[13] —2-(Diimethylamino)benzoic acid (3.89 g, 23.0 mmol) was dissolved in thionyl chloride (20 ml) and stirred for 30 mins. Excess reagent was removed under reduced pressure. The resulting yellow oil was dissolved in dichloromethane (25 ml) and was slowly added to a solution of diethylamine (7.1 ml, 69 mmol) in dichloromethane (100 ml) at 0 °C. After stirring for 3 hours the mixture was diluted with dichloromethane (25

ml), washed with saturated ammonium chloride solution (3 x 30 ml) and solvent removed under reduced pressure. The residue was purified by flash chromatography (SiO_2; 80:20 Petrol:EtOAc) to give the amide (3.33 g, 65%) as an orange oil, R_f (70:30 Petrol:EtOAc) 0.52; δ_H(300 MHz; $CDCl_3$) 1.04 (3H, t, *J* 7, CH_3), 1.22 (3H, t, *J* 7, CH_3), 2.82 (6H, s, CH_3), 3.09 (1H, m, NCH_2), 3.23 (1H, m, NCH_2), 3.36 (1H, m, NCH_2), 3.84 (1H, m, NCH_2), 6.93 (1H, d, *J* 8, ArH), 6.95 (1H, t, *J* 8, ArH), 7.20 (1H, d, *J* 8, ArH), 7.30 (1H, t, *J* 8, ArH).

2-(2-(tert-Butylsulfinyl)phenyl)-4,5-dihydro-4,4-dimethyloxazole **2a**. —By method A, oxazole **1a** (270 mg, 1.54 mmol) and *t*-butyl *t*-butylthiosulfinate[3] (270 mg, 1.85 mmol) gave a residue which was purified by flash chromatography (SiO_2; Petrol:EtOAc 20:80) to give the *sulfoxide* **2a** (238 g, 56%) as white crystals, R_f (EtOAc) 0.46; ν_{max}/cm^{-1} 2975 (C-H), 1633 (C=O); δ_H(500 MHz; $CDCl_3$) 1.12 (9H, s, ^tBu), 1.31 (3H, s, CH_3), 1.34 (3H, s, CH_3), 4.05 (2H, m, CH_2O), 7.44 (1H, t, *J* 8, ArH), 7.59 (1H, t, *J* 8, ArH), 7.91 (1H, d, *J* 8, ArH), 8.02 (1H, d, *J* 8, ArH); δ_C(125 MHz; $CDCl_3$) 23.9, 28.6, 28.8, 58.9, 68.3, 79.5, 126.8, 128.0, 130.4, 130.7, 131.1, 142.3, 161.0; *m/z* (CI) 280 (100%, M+H); Acc. mass found (M+H) 280.1364 ($C_{15}H_{21}NSO_2$ requires (*M*) 280.1371).

2-(tert-Butylsulfinyl)-N,N-diisopropylbenzamide **2b**. —By method A, amide **1b** (1.0 g, 5.62 mmol) and *t*-butyl *t*-butylthiosulfinate[3] (984 mg, 6.74 mmol,) gave a residue which was purified by flash chromatography (SiO_2; Petrol:EtOAc 30:70) to give the *sulfoxide* **2b** (1.0 g, 63%) as a pale yellow oil, R_f (70:30 EtOAc) 0.10; ν_{max}/cm^{-1} 2976, 2934 (C-H), 1632 (C=O); δ_H(500 MHz; $CDCl_3$) 1.03 (3H, t, *J* 7, CH_3), 1.23 (9H, s, ^tBu), 1.26 (3H, t, *J* 7, CH_3), 3.17-3.20 (2H, m, NCH_2), 3.28 (1H, m, NCH_2), 3.86 (1H, m, NCH_2), 7.34 (1H, d, *J* 8, ArH), 7.54-7.59 (2H, m, ArH), 7.93 (1H, d, *J* 8, ArH); δ_C(125 MHz; $CDCl_3$) 12.9, 14.3, 23.7, 39.5, 43.5, 48.1, 126.9, 127.3, 129.5, 132.1, 137.8, 139.0, 168.0; *m/z* (CI) 282 (80%, M+H), 209 (100%); Acc. mass found (M+H) 282.1518 ($C_{15}H_{23}NSO_2$ requires (*M*) 282.1522).

2-(tert-Butylsulfinyl)-N,N-diisopropylbenzamide **2c**. —By method A, amide **1c** (527 mg, 2.56 mmol) and *t*-butyl *t*-butylthiosulfinate[3] (411 mg, 2.82 mmol) gave a residue which was purified by flash chromatography (SiO_2; Petrol:EtOAc 30:70) to give the *sulfoxide* **2c** (341 mg, 43%) as white crystals, m.p. 80-81 °C; R_f (70:30 EtOAc) 0.16; ν_{max}/cm^{-1} 2969 (C-H), 1635 (C=O); δ_H(500 MHz; $CDCl_3$) 0.91 (3H, d, *J* 7, CH_3), 1.26-1.27 (12H, m, CH_3), 1.55 (3H, d, *J* 7, CH_3),

1.57 (3H, d, *J* 7, CH_3), 3.52-3.61 (2H, m, NCH), 7.25 (1H, m, ArH), 7.52-7.62 (2H, m, ArH), 7.95 (1H, m, ArH); δ_C(125 MHz; $CDCl_3$) 20.3, 20.8, 21.0, 21.2, 23.8, 46.4, 51.5, 58.1, 126.3, 127.0, 129.0, 132.3, 138.2, 139.5, 167.8; *m/z* (CI) 310 (20%, M+H), 238 (40%), 206 (100%); Acc. mass found (M+H) 310.1838 ($C_{17}H_{27}NSO_2$ requires (*M*) 310.1835).

N-tert-Butyl-2-(tert-butylsulfinyl)-N-methylbenzamide **2d**. —By method A, **1d** (1.09 g, 5.7 mmol) and *t*-butyl *t*-butylthiosulfinate[3] (1.44 g, 7.4 mmol) gave a residue which was purified by flash chromatography (SiO_2; Petrol:EtOAc 20:80) to give the *sulfoxide* **2d** (1.49 g, 89%) as a colourless oil, R_f (EtOAc) 0.45; ν_{max}/cm^{-1} 2963, 2926 (C-H), 1634 (C=O); δ_H(300 MHz; $CDCl_3$) 1.22 (9H, s, ^tBu), 1.55 (9H, s, ^tBu), 2.82 (3H, s, NMe), 7.35 (1H, m, ArH), 7.56-7.60 (2H, m, ArH), 7.95 (1H, m, ArH); δ_C(75 MHz; $CDCl_3$) 23.5, 28.2, 34.6, 57.6, 58.1, 126.6, 127.3, 129.1, 132.2, 137.3, 140.0, 169.3; *m/z* (CI) 296 (30%, M+H), 222 (40%), 209 (100%); Acc. mass found (M+H) 296.1685 ($C_{16}H_{25}NO_2S$ requires (*M*) 296.1679).

2-(tert-Butylsulfinyl)-N-isopropylbenzamide **2f**. —By method A, amide **1f** (287 mg, 1.76 mmol) and *t*-butyl *t*-butylthiosulfinate[3] (309 mg, 2.12 mmol) gave a residue which was purified by flash chromatography (SiO_2; EtOAc) to give the *sulfoxide* **2f** (326 mg, 69%) as a colourless oil, R_f (EtOAc) 0.41; ν_{max}/cm^{-1} 2973 (C-H), 1643 (C=O); δ_H(500 MHz; $CDCl_3$) 1.01 (9H, s, ^tBu), 1.16 (3H, d, *J* 7, CH_3), 1.19 (3H, d, *J* 7, CH_3), 4.11 (1H, sept, *J* 7, NCH), 7.25 (1H, t, *J* 8, ArH), 7.33 (1H, t, *J* 8, ArH), 7.41 (1H, d, *J* 8, ArH), 7.51 (1H, d, *J* 8, ArH), 7.66 (1H, d, *J* 8, NH); δ_C(125 MHz; $CDCl_3$) 22.7, 22.9, 23.4, 42.4, 57.8, 126.0, 128.7, 130.0, 131.0, 137.4, 138.4, 166.4; *m/z* (CI) 268 (80%, M+H), 211 (50%), 194 (100%); Acc. mass found (M+H) 268.1364 ($C_{14}H_{21}NSO_2$ requires (*M*) 268.1366).

1-(tert-Butylsulfinyl)-2-methoxybenzene **2g**. —By method A, freshly distilled anisole (0.15 ml, 1.37 mmol) and *t*-butyl *t*-butylthiosulfinate[3] (240 mg, 1.64 mmol) gave a residue which was purified by flash chromatography (SiO_2; Petrol:EtOAc 60:40) to give the sulfoxide (116 mg, 40%) as a colourless liquid, R_f (EtOAc) 0.66; ν_{max}/cm^{-1} 2976, 2900 (C-H), 1586 (C=O); δ_H(500 MHz; $CDCl_3$) 1.17 (9H, s, ^tBu), 3.81 (3H, s, OMe), 6.87 (1H, d, *J* 8, ArH), 7.11 (1H, t, *J* 8, ArH), 7.40 (1H, t, *J* 8, ArH), 7.72 (1H, d, *J* 8, ArH); δ_C(125 MHz; $CDCl_3$) 21.5, 55.8, 57.8, 111.1, 121.3, 127.7, 128.9, 132.6, 132.6, 157.5; *m/z* (CI) 213 (100%, M+H); Acc. mass found (M+H) 212.0867 ($C_{11}H_{16}SO_2$ requires (*M*) 212.0866).

2-(tert-Butylsulfinyl)-N,N-dimethylbenzenamine **2h**. —*n*-BuLi (2.06 ml of a 2.5M solution in hexane) and TMEDA (0.42 ml, 2.9 mmol) were stirred in dry hexane (15 ml) under nitrogen at room temperature before freshly distilled N,N,dimethylaniline (0.15 ml, 1.37 mmol) was added dropwise. The mixture was heated at reflux for 4 hours before being cooled to –78 °C and *t*-butyl *t*-butylthiosulfinate[3] (240 mg in 2 ml dry THF, 1.64 mmol) was added dropwise at –78 °C. The mixture left to warm to room temperature and quenched with saturated ammonium chloride solution. The THF was removed under reduced pressure and the mixture diluted with dichloromethane (50 ml), washed with saturated ammonium chloride solution (3 x 20 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_2; Petrol:EtOAc 20:80) to give the *sulfoxide* **2g** (179 mg, 32%) as yellow prisms, R_f (EtOAc) 0.65; ν_{max}/cm^{-1} 2977, 2790 (C-H), 1054 (S=O); δ_H(500 MHz; $CDCl_3$) 0.99 (9H, s, ^tBu), 2.55 (6H, s, NMe_2), 6.93 (1H, dd, *J* 1,8, ArH), 7.04 (1H, td, *J* 1,8, ArH), 7.23 (1H, td, *J* 1,8, ArH), 7.60 (1H, dd, *J* 1,8, ArH); δ_C(125 MHz; $CDCl_3$) 23.4, 44.9, 57.9, 119.9, 123.9, 127.3, 132.2, 134.9, 153.6; *m/z* (CI) 226 (100%, M+H); Acc. mass found (M+H) 226.1261 ($C_{12}H_{19}NSO$ requires (*M*) 226.1260).

2-(2-tert-Butylphenyl)-4,5-dihydro-4,4-dimethyloxazole **3a**. —Method B was used with amide **2a** (169 mg, 0.60 mmol) to give a residue that was purified by flash chromatography (SiO_2; Petrol:EtOAc 80:20) to give the *2-tert-butyl oxazoline* **3a** (111 mg, 73%) as white crystals, R_f (EtOAc) 0.46; ν_{max}/cm^{-1} 2975 (C-H), 1633 (C=O); δ_H(500 MHz; $CDCl_3$) 1.12 (9H, s, ^tBu), 1.31 (3H, s, CH_3), 1.34 (3H, s, CH_3), 4.05 (2H, m, CH_2O), 7.44 (1H, t, *J* 8, ArH), 7.59 (1H, t, *J* 8, ArH), 7.91 (1H, d, *J* 8, ArH), 8.02 (1H, d, *J* 8, ArH); δ_C(125 MHz; $CDCl_3$) 23.9, 28.6, 28.8, 58.9, 68.3, 79.5, 126.8, 128.0, 130.4, 130.7, 131.1, 142.3, 161.0; *m/z* (CI) 280 (100%, M+H); Acc. mass found (M+H) 280.1364 ($C_{15}H_{21}NSO_2$ requires (*M*) 280.1371).

2-tert-Butyl-N,N-diethylbenzamide **3b**. —Method B was used with sulfoxide **2b** (107 mg, 0.32 mmol) to give a residue that was purified by flash chromatography (SiO_2; Petrol:EtOAc 80:20) to give the *ortho-tert-butyl amide* **3b** (128 mg, 100%) as a colourless oil; R_f (70:30 EtOAc) 0.33; ν_{max}/cm^{-1} 2967 (C-H), 1632 (C=O); δ_H(500 MHz; $CDCl_3$) 0.99 (3H, t, *J* 7, CH_3), 1.17 (3H, t, *J* 7, CH_3), 1.31 (9H, s, ^tBu), 2.96 (1H, m, NCH_2), 3.08 (1H, m, NCH_2), 3.25 (1H, m, NCH_2), 3.71 (1H, m, NCH_2), 6.97 (1H, dd, *J* 8 and 2, ArH), 7.09 (1H, td, *J* 8 and 1, ArH), 7.22 (1H, td, *J* 8

and 2, ArH), 7.40 (1H, dd, *J* 8 and 1, ArH); δ_C(125 MHz; $CDCl_3$) 12.3, 13.6, 31.9, 36.8, 38.8, 43.6, 126.0, 127.7, 127.9, 128.9, 136.1, 146.8, 173.4; *m/z* (CI) 233 (100%, M+H); Acc. mass found (M+H) 234.1847 ($C_{15}H_{23}NO$ requires (*M*) 234.1852).

2-tert-Butyl-N,N-diisopropylbenzamide **3c**. —Method B was used with sulfoxide **2c** (100 mg, 0.32 mmol) to give a residue that was purified by flash chromatography (SiO_2; Petrol:EtOAc 80:20) to give the *ortho-ter*t-butyl amide **3c** (35 mg, 73%) as white crystals, m.p. 86-87 °C; R_f (70:30 EtOAc) 0.68; ν_{max}/cm^{-1} 2966 (C-H), 1633 (C=O); δ_H(500 MHz; $CDCl_3$) 1.02 (3H, d, *J* 7, CH_3), 1.07 (3H, d, *J* 7, CH_3), 1.35 (9H, s, ^{t}Bu), 1.45-1.50 (6H, m, CH_3), 3.39 (1H, m, NCH), 3.57 (1H, m, NCH), 6.93 (1H, d, *J* 8, ArH), 7.09 (1H, t, *J* 8, ArH), 7.19 (1H, t, *J* 8, ArH), 7.40 (1H, d, *J* 8, ArH); δ_C(125 MHz; $CDCl_3$) 20.1, 20.1, 20.7, 20.7, 32.1, 36.8, 45.9, 51.1, 125.8, 127.4, 128.1, 128.6, 137.3, 146.9, 173.0; *m/z* (CI) 262 (100%, M+H); Acc. mass found (M+H) 262.2167 ($C_{17}H_{27}NO$ requires (*M*) 262.2165).

N,2-Di-tert-butyl-N-methylbenzamide **3d**. —Method B was used with amide **2d** (383 mg, 1.55 mmol) to give a residue that was purified by flash chromatography (SiO_2; Petrol:EtOAc 80:20) to give the *ortho-tert-butyl amide* **3d** (251 mg, 82% yield) as a colourless oil; R_f (70:30 Petrol:EtOAc) 0.79; ν_{max}/cm^{-1} 2959, 2869 (C-H), 1651 (C=O); δ_H(300 MHz; $CDCl_3$) 1.42 (9H, s, ^{t}Bu), 1.57 (9H, s, ^{t}Bu), 2.75 (3H, s, NMe), 7.00 (1H, d, *J* 8, ArH), 7.17 (1H, t, *J* 8, ArH), 7.27 (1H, t, *J* 8, ArH), 7.45 (1H, t, *J* 8, ArH); δ_C(75 MHz; $CDCl_3$) 27.4, 27.9, 31.7, 35.5, 36.5, 126.1, 127.4, 127.8, 128.4, 138.4, 146.2, 174.6; *m/z*(CI) 265 (30%, $M+NH_4^+$), 248 (100%, M+H); Acc. mass found (M+H) 248.2012 ($C_{16}H_{25}NO$ requires (*M*) 248.2009).

2-tert-Butyl-N-methylbenzamide **3e**. —The amide **3d** (178 mg, 0.89 mmol) was dissolved in 3M HCl in dioxane (10 ml) and stirred at reflux for 18 hours. The mixture was then diluted with diethylether (30 ml) and washed with saturated ammonium chloride solution (3 x 20 ml). The residue was then purified via flash chromatography (70:30 Petrol:EtOAC) to give the *amide* **3e** (121 mg, 95% yield) as white crystals, m.p. 136-138 °C; ν_{max}/cm^{-1} 3282 (N-H), 2959 (C-H), 1634 (C=O); δ_H(500 MHz; $CDCl_3$) 1.42 (9H, s, ^{t}Bu), 3.00 (3H, d, *J* 5, NMe), 5.70 (1H, s (broad), NH), 7.20-7.23 (2H, m, ArH), 7.49 (1H, d, *J* 8, ArH), 7.50 (1H, d, *J* 8, ArH); δ_C(75 MHz; $CDCl_3$) 26.9, 31.7, 36.4, 125.8, 127.3, 128.5, 129.4, 137.0, 147.6, 173.9; *m/z*(CI) 209

(100%, M+NH_4^+), 192 (50%); Acc. mass found (M+H) 192.1384 ($C_{12}H_{18}NO$ requires (*M*) 192.1383).

2-tert-Butylanisole **3g**.[14] —Method B was used with amide **2g** (98 mg, 0.46 mmol) to give a residue that was purified by flash chromatography (SiO_2; Petrol:EtOAc 80:20) to give *ortho-tert-butylanisole* **3g** (54 mg, 75%) as a clear liquid, R_f (70:30 Petrol:EtOAc) 0.92; ν_{max}/cm^{-1} 2997, 2955 (C-H); δ_H(500 MHz; $CDCl_3$) 1.30 (9H, s, ^tBu), 3.74 (3H, s, OMe), 6.78 (1H, dd, *J* 8 and 2, ArH), 6.81 (1H, td, *J* 8 and 2, ArH), 7.10 (1H, td, *J* 8 and 2, ArH), 7.21 (1H, dd, *J* 8 and 2, ArH); δ_C(125 MHz; $CDCl_3$) 29.3, 35.2, 55.4, 111.9, 120.7, 126.9, 127.4, 138.6, 158.9; *m/z* (CI) 165 (100%, M+H); Acc. mass found (M^+) 164.1192 ($C_{11}H_{16}O$ requires (*M*) 164.1198).

2-(tert-Butylsulfinyl)-N,N-diisopropyl-6-methoxybenzamide **5a**. —By method A, amide **4a** (860 mg, 4.15 mmol) and *t*-butyl *t*-butylthiosulfinate[3] (789 mg, 5.40 mmol) gave a residue which was purified by flash chromatography (SiO_2; Petrol:EtOAc 30:70) to give the *sulfoxide* **5a** (932 mg, 72%). m.p. 72-74 °C; R_f (70:30 EtOAc) 0.40; ν_{max}/cm^{-1} 2970, 2934 (C-H), 1634 (C=O); δ_H(500 MHz; $CDCl_3$) 1.08 (3H, d, *J* 7, CH_3), 1.21 (3H, d, *J* 7, CH_3), 1.28 (9H, s, ^tBu), 1.55 (3H, d, *J* 7, CH_3), 1.56 (3H, d, *J* 7, CH_3), 3.52 (1H, sept, *J* 7, NCH), 3.57 (1H, sept, *J* 7, NCH), 3.84 (3H, s, OMe), 7.01 (1H, d, *J* 8, ArH), 7.47-7.49 (2H, m, ArH); δ_C(125 MHz; $CDCl_3$) 20.5, 20.7, 21.0, 21.1, 24.0, 46.4, 51.5, 56.3, 58.2, 113.8, 118.7, 129.1, 129.7, 139.5, 155.6, 164.9; *m/z* (CI) 340 (90%, M+H), 284 (90%), 268 (100%); Acc. mass found (M+H) 340.1938 ($C_{18}H_{29}NSO_3$ requires (*M*) 340.1941).

2-(tert-Butylsulfinyl)-N,N-diisopropyl-3-methoxybenzamide **5b**. —By method A, **4b** (270 mg, 1.15 mmol) and *t*-butyl *t*-butylthiosulfinate[3] (290 mg, 1.49 mmol) gave a residue which was purified by flash chromatography (SiO_2; Petrol:EtOAc 40:60) to give the *sulfoxide* **5b** (330 mg, 85%) as white crystals, m.p. 98-100 °C; R_f (70:30 Petrol:EtOAc) 0.16; ν_{max}/cm^{-1} 2969 (C-H), 1631 (C=O); δ_H(300 MHz; $CDCl_3$) 1:1 mixture of diastereoisomeric signals 0.86 (3H, d, *J* 7, CH_3), 0.94 (3H, d, *J* 7, CH_3), 1.08 (3H, d, *J* 7, CH_3), 1.17 (3H, d, *J* 7, CH_3), 1.21 (9H, s, ^tBu), 1.26 (9H, s, ^tBu), 1.40-1.47 (12H, m, CH_3), 3.23 (1H, sept, *J* 7, NCH), 3.28 (1H, sept, *J* 7, NCH), 3.39 (1H, sept, *J* 7, NCH), 3.61 (1H, sept, *J* 7, NCH), 3.73 (3H, s, OMe), 3.80 (3H, s, OMe), 6.67 (2H, t, *J* 8, ArH), 6.72 (1H, d, *J* 8, ArH), 6.86 (1H, d, *J* 8, ArH), 7.26 (1H, t, *J* 8, ArH), 7.35 (1H, t, *J* 8, ArH); δ_C(75 MHz; $CDCl_3$) 19.3, 19.7, 20.6, 20.7, 20.7, 20.8, 20.9, 20.9,

25.2, 25.9, 45.4, 46.0, 50.8, 51.2, 55.7, 55.8, 58.8, 60.1, 110.2, 112.1, 117.7, 121.1, 123.9, 126.4, 131.9, 133.7, 140.1, 142.9, 157.2, 159.6, 167.7, 168.3; *m/z* (CI) 340 (100%, M+H) 266 (40%); Acc. mass found (M+H) 340.1950 ($C_{18}H_{30}NO_3S$ requires (*M*) 340.1941).

2-(tert-Butylsulfinyl)-N,N-diisopropyl-4-methoxybenzamide **5c**. —By method A, **4c** (295 mg, 1.26 mmol) and *t*-butyl *t*-butylthiosulfinate[3] (317 mg, 1.63 mmol) gave a residue which was purified by flash chromatography (SiO_2; Petrol:EtOAc 40:60) to give the *sulfoxide* **5c** (374 mg, 88%) as a colourless oil, R_f (70:30 Petrol:EtOAc) 0.15; ν_{max}/cm^{-1} 2965, 2933 (C-H), 1651 (C=O); δ_H(300 MHz; $CDCl_3$) 0.85 (6H, m (broad), CH_3), 1.13 (9H, s, ^tBu), 1.20 (6H, m (broad), CH_3), 3.30-3.50 (2H, m, NCH), 3.73 (3H, s, OMe), 6.92 (1H, dd, *J* 8 and 1, ArH), 7.05 (1H, d, *J* 8, ArH), 7.28 (1H, d, *J* 1, ArH); δ_C(75 MHz; $CDCl_3$) 20.1, 20.5, 20.8, 21.0, 23.6., 46.1, 51.2, 55.7, 57.9, 110.3, 118.9, 127.5, 131.7, 138.9, 159.7, 167.6; *m/z* (CI) 340 (100%, M+H) 266 (80%); Acc. mass found (M+H) 340.1946 ($C_{18}H_{29}NO_3S$ requires (*M*) 340.1941).

2-(tert-Butylsulfinyl)-N,N-diisopropylnaphthalene-1-carboxamide **5d**. —By method A, **4d** (811 mg, 3.18 mmol) and *t*-butyl *t*-butylthiosulfinate[3] (603 mg, 4.13 mmol, 94% ee) gave a residue which was purified by flash chromatography (SiO_2; Petrol:EtOAc 50:50) to give the sulfoxide (730 mg, 64%) as yellow crystals, m.p. 35-36 °C; R_f (70:30 Petrol:EtOAc) 0.20; ν_{max}/cm^{-1} 2973, 2934 (C-H), 1633 (C=O); δ_H(500 MHz; $CDCl_3$) 0.72 (3H, d, *J* 7, CH_3), 1.04 (3H, d, *J* 7, CH_3), 1.10 (9H, s, ^tBu), 1.45 (3H, d, *J* 7, CH_3), 1.54 (3H, d, *J* 7, CH_3), 3.21 (1H, sept, *J* 7, NCH), 3.44 (1H, sept, *J* 7, NCH), 7.37-7.43 (2H, m, ArH), 7.68-7.78 (4H, m, ArH); δ_C(125 MHz; $CDCl_3$) 20.4, 20.9, 21.0, 21.6, 24.1, 46.8, 51.8, 58.5, 121.9, 126.2, 128.1, 128.7, 128.8, 129.0, 129.5, 134.3, 135.2, 137.9, 166.7; *m/z* (CI) 360 (70%, M+H), 304 (100%); Acc. mass found (M+H) 360.1985 ($C_{21}H_{29}NSO_2$ requires (*M*) 360.1992).

2-(tert-Butylsulfinyl)-N,N-diisopropyl-3,6-dimethoxybenzamide **5e**. —By method A, **4e** (295 mg, 1.11 mmol) and *t*-butyl *t*-butylthiosulfinate[3] (281 mg, 1.45 mmol,) gave a residue which was purified by flash chromatography (SiO_2; EtOAc) to give the *sulfoxide* **5e** (61 mg, 15%) as white crystals, m.p. 116-118 °C; R_f (EtOAc) 0.22; ν_{max}/cm^{-1} 2969, 2838 (C-H), 1633 (C=O); δ_H(500 MHz; $CDCl_3$) 1.08 (3H, d, *J* 7, CH_3), 1.22 (3H, d, *J* 7, CH_3), 1.35 (9H, s, ^tBu), 1.51-1.53 (6H, d, *J* 7, CH_3), 3.47 (1H, sept, *J* 7, NCH), 3.67 (1H, sept, *J* 7, NCH), 3.76 (3H, s, OMe), 3.84 (3H, s, OMe), 6.85 (1H, d, *J* 8, ArH), 6.93 (1H, d, *J* 8, ArH); δ_C(75 MHz; $CDCl_3$) 20.1, 20.8, 20.9,

21.2, 26.3, 46.4, 51.6, 56.1, 56.6, 59.1, 112.3, 115.4, 125.8, 132.1, 149.2, 153.5, 164.9; *m/z* (CI) 370 (10%, M+H), 314 (50%), 298 (100%); Acc. mass found (M+H) 370.2051 ($C_{19}H_{32}NO_4S$ requires (*M*) 370.2047).

2-(Di-tert-butylphosphino)-6-(tert-butylsulfinyl)-N,N-diethylbenzamide **5f**. —By method A, amide **4f** (323 mg, 1.0 mmol) and *t*-butyl *t*-butylthiosulfinate[3] (160 mg, 1.4 mmol) gave a residue which was purified by flash chromatography (SiO_2; Petrol:EtOAc 70:30) to give the *sulfoxide* **5f** (207 mg, 49%) as an opaque oil, m.p. 50-52 °C; R_f (70:30 EtOAc) 0.23; ν_{max}/cm^{-1} 2934, 2568 (C-H), 1632 (C=O); δ_H(500 MHz; $CDCl_3$) 1.16 (9H, d, *J* 12, P^{t}Bu), 1.19 (3H, t, *J* 7, CH_3), 1.25 (9H, d, *J* 12, P^{t}Bu), 1.26 (9H, s, S(O)^{t}Bu), 1.31 (3H, t, *J* 7, CH_3), 3.03 (1H, m, NCH_2), 3.08 (1H, m, NCH_2), 3.58-3.63 (2H, m, NCH_2), 7.54 (1H, t, *J* 8, ArH), 7.97 (2H, d, *J* 8, ArH); δ_C(125 MHz; $CDCl_3$) 12.5, 14.4, 23.9, 30.5 (3C, d, *J* 15, PC<u>C</u>H$_3$), 31.7 (3C, d, *J* 15, PC<u>C</u>H$_3$), 32.7 (1C, d, *J* 25, P<u>C</u>), 33.4 (1C, d, *J* 25, P<u>C</u>), 39.0, 43.5, 58.4, 127.4, 127.6, 138.6, 139.1, 145.8, 146.1, 166.8; *m/z* (CI) 426 (30%, M+H), 354 (100%); Acc. mass found (M+H) 426.2586 ($C_{23}H_{40}NSO_2P$ requires (*M*) 426.2590).

2-(tert-Butylsulfinyl)-6-(dimethylamino)-N,N-diethylbenzamide **5g**. —By method A, amide **4g** (385 mg, 1.75 mmol) and *t*-butyl *t*-butylthiosulfinate[3] (383 mg, 2.63 mmol) gave a residue which was purified by flash chromatography (SiO_2; Petrol:EtOAc 50:50) to give the *sulfoxide* **5g** (473 mg, 83%) as an orange oil; R_f (70:30 Petrol:EtOAc) 0.08; ν_{max}/cm^{-1} 2974, 2790 (C-H), 1635 (C=O); δ_H(500 MHz; $CDCl_3$) 0.95 (3H, t, *J* 7, CH_3), 1.18 (3H, t, *J* 7, CH_3), 1.20 (9H, s, ^{t}Bu), 2.74 (6H, s, NMe_2), 2.91 (2H, m, NCH_2), 3.47 (2H, m, NCH_2), 7.03 (1H, dd, *J* 8 and 1, ArH), 7.38 (1H, t, *J* 8, ArH), 7.43 (1H, dd, *J* 8 and 1, ArH); δ_C(125 MHz; $CDCl_3$) 12.8, 14.2, 24.1, 39.8, 43.3, 44.9, 58.3, 119.7, 121.2, 129.8, 132.2, 140.4, 150.7, 167.3; *m/z* (CI) 325 (50%, M+H), 269 (40%), 252 (100%); Acc. mass found (M+H) 325.1949 ($C_{19}H_{32}N_2SO_2$ requires (*M*) 325.1944).

2-tert-Butyl-N,N-diisopropyl-6-methoxybenzamide **6a**. —Method B was used with sulfoxide **5a** (114 mg, 0.37 mmol, 98% ee) to give a residue that was purified by flash chromatography (SiO_2; Petrol:EtOAc 70:30) to give the *amide* **6a** (36 mg, 38%) as white crystals, m.p. 74-76 °C; R_f (70:30 EtOAc) 0.65; ν_{max}/cm^{-1} 2926 (C-H), 1614 (C=O); δ_H(500 MHz; $CDCl_3$) 1.00 (3H, d, *J* 7, CH_3), 1.04 (3H, d, *J* 7, CH_3), 1.33 (9H, s, ^{t}Bu), 1.36 (3H, d, *J* 7, CH_3), 1.48 (3H, d, *J* 7, CH_3),

3.38 (1H, sept, *J* 7, NCH), 3.54 (1H, sept, *J* 7, NCH), 3.67 (3H, s, OMe), 6.63 (1H, d, *J* 8, ArH), 6.99 (1H, d, *J* 8, ArH), 7.13 (1H, t, *J* 8, ArH); δ_C(125 MHz; $CDCl_3$); 20.2, 20.3, 20.4, 20.5, 32.5, 33.1, 46.2, 50.9, 55.7, 108.5, 120.6, 126.8, 126.8, 128.7, 148.3, 156.5, 169.8; *m/z* (CI) 292 (100%, M+H); Acc. mass found (M+H) 292.2268 ($C_{18}H_{29}NO_2$ requires (*M*) 292.2271).

2-tert-Butyl-N,N-diisopropyl-3-methoxybenzamide **6b**. —Method B was used with amide **5b** (230 mg, 0.68 mmol) to give a residue that was purified by flash chromatography (SiO_2; Petrol:EtOAc 80:20) to give the *amide* **6b** (30 mg, 15% yield) as a colourless oil (mixture of product and starting material); R_f (70:30 Petrol:EtOAc) 0.75; ν_{max}/cm^{-1} 2966 (C-H), 1632 (C=O); δ_H(500 MHz; $CDCl_3$) 1.08-1.12 (6H, m, CH_3), 1.39 (9H, s, ^{t}Bu), 1.42-1.50 (6H, m, CH_3), 3.43-3.47 (2H, m, NCH), 3.61 (3H, s, OMe), 6.50 (1H, d, *J* 7, ArH), 6.77 (1H, t, *J* 8, ArH), 7.05 (1H, t, *J* 8, ArH); δ_C(75 MHz; $CDCl_3$) Mixture of compounds; *m/z*(CI) 292 (100%, M+H); Acc. mass found (M+H) 292.2275 ($C_{18}H_{30}NO_2$ requires (*M*) 292.2271).

2-tert-Butyl-N,N-diisopropyl-4-methoxybenzamide **6c**. —Method B was used with amide **5c** (176 mg, 0.52 mmol) to give a residue that was purified by flash chromatography (SiO_2; Petrol:EtOAc 80:20) to give the *amide* **6c** (119 mg, 79% yield) as a colourless oil; R_f (70:30 Petrol:EtOAc) 0.85; ν_{max}/cm^{-1} 2965 (C-H), 1634 (C=O); δ_H(300 MHz; $CDCl_3$) 1.10 (3H, d, *J* 7, CH_3), 1.13 (3H, d, *J* 7, CH_3), 1.43 (9H, s, ^{t}Bu), 1.55 (3H, d, *J* 7, CH_3), 1.56 (3H, d, *J* 7, CH_3), 3.46 (1H, sept, *J* 7, NCH), 3.71 (1H, sept, *J* 7, NCH), 3.82 (3H, s, OMe), 6.70 (1H, dd, *J* 3,8, ArH), 6.96 (1H, d, *J* 8, ArH), 7.03 (1H, d, *J* 3,8, ArH); δ_C(75 MHz; $CDCl_3$) 20.0, 20.1, 20.5, 20.6, 31.9, 36.7, 45.7, 50.9, 55.4, 110.0, 114.4, 128.5, 130.1, 148.9, 159.4, 172.9; *m/z*(CI) 292 (100%, M+H); Acc. mass found (M+H) 292.2277 ($C_{18}H_{30}NO_2$ requires (*M*) 292.2271).

N,N,2-Triisopropyl-4-methoxybenzamide **6c'**. —Method B was used with amide **5c** (140 mg, 0.41 mmol) to give a residue that was purified by flash chromatography (SiO_2; Petrol:EtOAc 80:20) to give the *ortho-isopropyl amide* **6c'** (57 mg, 50% yield) as a colourless oil; R_f (70:30 Petrol:EtOAc) 0.71; ν_{max}/cm^{-1} 2964 (C-H), 1633 (C=O); δ_H(300 MHz; $CDCl_3$) 1.10 (3H, d, *J* 7, CH_3), 1.12 (3H, d, *J* 7, CH_3), 1.25 (3H, d, *J* 7, CH_3), 1.29 (3H, d, *J* 7, CH_3), 1.57-1.59 (6H, m, CH_3), 3.00 (1H, sept, *J* 7, ArCH), 3.48 (1H, sept, *J* 7, NCH), 3.76 (1H, sept, *J* 7, NCH), 3.84 (3H, s, OMe), 6.71 (1H, dd, *J* 3, 8, ArH), 6.86 (1H, d, *J* 3, ArH), 7.02 (1H, d, *J* 8, ArH); δ_C(75 MHz; $CDCl_3$) 20.8, 20.8, 20.9, 20.9, 23.6, 24.9, 30.9, 45.9, 50.9, 55.4, 111.0, 111.9, 126.2,

130.7, 147.0, 160.0, 171.1; *m/z*(CI) 278 (100%, M+H); Acc. mass found (M+H) 278.2116 ($C_{17}H_{28}NO_2$ requires (*M*) 278.2115).

2-tert-Butyl-N,N-diisopropylnaphthalene-1-carboxamide **6d**. —Method B was used with amide **5d** (125 mg, 0.35 mmol, 52% ee) to give a residue that was purified by flash chromatography (SiO_2; Petrol:EtOAc 80:20) to give the *amide* **6d** (62 mg, 58%) as white crystals, m.p. 94-97 °C; R_f (70:30 EtOAc) 0.57; ν_{max}/cm^{-1} 2966 (C-H), 1603 (C=O); δ_H(500 MHz; $CDCl_3$) 0.73 (3H, d, *J* 7, CH_3), 1.04 (3H, d, *J* 7, CH_3), 1.43 (9H, s, ^tBu), 1.56 (3H, d, *J* 7, CH_3), 1.71 (3H, d, *J* 7, CH_3), 3.41 (1H, sept, *J* 7, NCH), 3.51 (1H, sept, *J* 7, NCH), 7.30-7.37 (2H, m, ArH), 7.52 (1H, d, *J* 8, ArH), 7.63-7.67 (2H, m, ArH), 7.81 (1H, d, *J* 8, ArH); δ_C(125 MHz; $CDCl_3$) 19.9, 19.9, 20.8, 21.1, 32.5, 37.7, 46.7, 51.4, 126.0, 126.1, 126.2, 126.4, 127.1 127.9, 128.1, 131.0, 132.2, 142.8, 171.6; *m/z* (CI) 312 (100%, M+H); Acc. mass found (M+H) 312.2325 ($C_{21}H_{29}NO$ requires (*M*) 312.2322).

2-tert-Butyl-N,N-diisopropyl-3-methoxybenzamide **6e**. —Method B was used with sulfoxide **5e** (45 mg, 0.12 mmol) to give a residue that was purified by flash chromatography (SiO_2; Petrol:EtOAc 80:20) to give the *amide* **6e** (30 mg, 76% yield) as white needles, m.p. 119-122 °C ; R_f (70:30 Petrol:EtOAc) 0.63; ν_{max}/cm^{-1} 2967 (C-H), 1621 (C=O); δ_H(500 MHz; $CDCl_3$) 0.95 (3H, d, *J* 7, CH_3), 1.07 (3H, d, *J* 7, CH_3), 1.39 (9H, s, ^tBu), 1.43 (3H, d, *J* 7, CH_3), 1.47 (3H, d, *J* 7, CH_3), 3.36 (1H, sept, *J* 7, NCH), 3.58 (1H, sept, *J* 7, NCH), 3.62 (3H, s, OMe), 3.72 (3H, s, OMe), 6.62 (1H, d, *J* 8, ArH), 6.72 (1H, d, *J* 8, ArH); δ_C(125 MHz; $CDCl_3$) 19.9, 20.0, 20.4, 20.5, 30.8, 37.6, 46.1, 50.9, 56.0, 56.6, 109.9, 112.3, 128.8, 135.9, 150.6, 154.1, 169.5; *m/z*(CI) 322 (100%, M+H); Acc. mass found (M+H) 322.2376 ($C_{19}H_{31}NO_3$ requires (*M*) 322.2377).

2-tert-Butyl-6-(dimethylamino)-N,N-diethylbenzamide **6g**. —Method B was used with amide **5g** (80 mg, 0.24 mmol) to give a residue that was purified by flash chromatography (SiO_2; Petrol:EtOAc 50:50) to give the *amide* **6g** (40 mg, 59%) as colourless oil; R_f (70:30 Petrol:EtOAc) 0.86; ν_{max}/cm^{-1} 2938 (C-H), 1625 (C=O); δ_H(500 MHz; $CDCl_3$) 0.92 (3H, t, *J* 7, CH_3), 1.10 (3H, t, *J* 7, CH_3), 1.24 (9H, s, ^tBu), 2.52 (6H, s, NMe_2), 2.86 (1H, m, NCH_2), 2.91 (1H, m, NCH_2), 3.22 (1H, m, NCH_2), 3.59 (1H, m, NCH_2), 6.87 (1H, d, *J* 7, ArH), 7.07-7.13 (2H, m, ArH); δ_C(125 MHz; $CDCl_3$) 12.3, 13.2, 32.1, 36.9, 38.4, 43.2, 46.2, 118.1, 123.3, 128.7,

133.2, 148.1, 152.3, 171.8; *m/z* (CI) 277 (100%, M+H); Acc. mass found (M+H) 277.2265 ($C_{17}H_{28}N_2O$ requires (*M*) 277.2274).

2-sec-Butyl-6-(dimethylamino)-N,N-diethylbenzamide **6g'**. —*s*-BuLi (0.53 ml of a 1.3M solution in hexanes, 0.69 mmol) was added dropwise to sulfoxide **5g** (80 mg, 0.24 mmol) at –78 °C. After 20 minutes saturated ammonium chloride soln. (1 ml) was added and the mixture allowed to warm to room temperature. The mixture diluted with diethylether (30 ml), washed with saturated ammonium chloride solution (3 x 20 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromoatography (SiO_2; Petrol:EtOAc 80:20) to give the *amide* **6g'** (35 mg, 51%) as yellow crystals, m.p. >260 °C; R_f (70:30 Petrol:EtOAc) 0.65; ν_{max}/cm^{-1} 2962, 2933 (C-H), 1625 (C=O); δ_H(500 MHz; $CDCl_3$) 1:1 mixture of diastereoisomers, 0.75 (3H, t, *J* 7, CH_3), 0.80 (3H, t, *J* 7, CH_3), 0.90-1.00 (6H, m, NMe_2), 1.05 (3H, d, *J* 7, CH_3), 1.00-1.19 (9H, m, CH_3), 1.38-1.50 (2H, m, CH_2), 1.55-1.65 (2H, m, CH_2), 2.50-2.58 (2H, m, CHAr), 2.65 (12H, s, NMe_2), 2.90-3.05 (4H, m, NCH_2), 3.40-3.60 (4H, m, NCH_2), 6.78 (2H, m, ArH), 6.85 (2H, d, *J* 8, ArH), 7.15-7.19 (2H, m, ArH); δ_C(75 MHz; $CDCl_3$) mixture of diastereoisomers; *m/z* (CI) 277 (100%, M+H); Acc. mass found (M+H) 277.2279 ($C_{17}H_{28}N_2O$ requires (*M*) 277.2274).

N,N-Diisopropyl-2-(isopropylthio)naphthalene-1-carboxamide **7**. —By method A, **4d** (1.19 g, 4.70 mmol) and diisopropyldisulfide (0.97 ml, 6.10 mmol) gave a residue which was purified by flash chromatography (SiO_2; Petrol:EtOAc 70:30) to give the *sulfide* **7** (1.41 g, 92%) as white crystals, m.p. 72-74 °C; R_f (70:30 Petrol:EtOAc) 0.56; ν_{max}/cm^{-1} 2967, 2928 and 2867 (C-H), 1631 (C=O); δ_H(500 MHz; $CDCl_3$) 0.74 (3H, d, *J* 7, CH_3), 0.99 (3H, d, *J* 7, CH_3), 1.07-1.10 (6H, m, CH_3), 1.49 (3H, d, *J* 7, CH_3), 1.54 (3H, d, *J* 7, CH_3), 3.27 (1H, sept, *J* 7, NCH), 3.37-3.42 (2H, m, NCH), 7.25-7.34 (3H, m, ArH), 7.52-7.59 (3H, m, ArH); δ_C(125 MHz; $CDCl_3$) 20.6, 21.2, 21.2, 21.7, 23.4, 24.1, 39.9, 46.5, 51.7, 125.4, 126.8, 127.4, 128.2, 128.4, 128.9, 130.6, 131.2, 133.0, 140.3, 168.4; *m/z* (CI) 330 (100%, M+H); Acc. mass found (M+H) 330.1887 ($C_{20}H_{27}NSO$ requires (*M*) 330.1886).

N,N-Diisopropyl-2-(isopropylsulfinyl)naphthalene-1-carboxamide **8**. —The sulfide **7** (1.10 g, 3.34 mmol in 10 ml dry dichloromethane) was added dropwise to a stirred solution of ~50% mCPBA (1.15 g, 6.68 mmol) in dry dichloromethane (30 ml) at 0 °C. After 2 hours the reaction

was quenched with 10% aq. sodium sulfite, diluted with 30 ml dichloromethane and washed with saturated bicarbonate solution (3 x 15 ml), dried ($MgSO_4$) and solvents evaporated under reduced pressure. The residue was purified by flash chromoatography (SiO_2; Petrol:EtOAc 80:20) to give the *sulfoxide* **8** (800 mg, 70%) as white crystals, m.p. 92-96 °C; R_f (70:30 Petrol:EtOAc) 0.42; ν_{max}/cm^{-1} 2971, 2933, 2871 (C-H), 1626 (C=O); δ_H(500 MHz; $CDCl_3$) 0.80 (3H, d, *J* 7, CH_3), 0.95 (3H, d, *J* 7, CH_3), 0.99 (3H, d, *J* 7, CH_3), 1.15 (3H, d, *J* 7, CH_3), 1.45 (3H, d, *J* 7, CH_3), 1.53 (3H, d, *J* 7, CH_3), 3.07 (1H, sept, *J* 7, CH), 3.29 (1H, sept, *J* 7, CH), 3.43 (1H, sept, *J* 7, CH), 7.38-7.40 (2H, m, ArH), 7.64 (1H, sept, *J* 7, CH), 7.72 (1H, sept, *J* 7, CH), 7.77-7.83 (2H, sept, *J* 7, CH); δ_C(125 MHz; $CDCl_3$) 13.2, 18.2, 20.5, 20.9, 21.2, 21.4, 46.9, 52.0, 54.5, 120.7, 125.6, 128.2, 128.4, 129.0, 129.4, 129.4, 134.9, 135.3, 136.3, 166.7; *m/z* (CI) 346 (100%, M+H), 245 (60%); Acc. mass found (M+H) 346.1834 ($C_{20}H_{27}NSO_2$ requires (*M*) 346.1835).

2-(^{13}*C-tert-Butylsulfinyl)-N,N-diisopropylnaphthalene-1-carboxamide* **^{13}C-5d**. —LDA (0.60 ml of a 1.8 M solution in hexanes, 1.09 mmol) was added dropwise to amide **8** (250 mg, 0.72 mmol) at –78 °C giving a reddish-brown solution. After 30 minutes $^{13}CH_3I$ (68 μL, 1.09 mmol) was added and the mixture was raised to room temperature giving a yellow solution. The mixture diluted with diethyl ether (30 ml), washed with saturated ammonium chloride solution (3 x 20 ml), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromoatography (SiO_2; Petrol:EtOAc 50:50) to give the sulfoxide **^{13}C-5d** (232 mg, 88%) as yellow crystals, m.p. 35-36 °C; R_f (70:30 Petrol:EtOAc) 0.20; ν_{max}/cm^{-1} 2973, 2934 (C-H), 1633 (C=O); δ_H(500 MHz; $CDCl_3$) 0.83 (3H, d, *J* 7, CH_3), 1.16 (3H, d, *J* 7, CH_3), 1.21 (3H, d, *J* 128, $^{13}C\underline{H}_3$), 1.22 (6H, s, CH_3), 1.57 (3H, d, *J* 7, CH_3), 1.65 (3H, d, *J* 7, CH_3), 3.33 (1H, sept, *J* 7, NCH), 3.52 (1H, sept, *J* 7, NCH), 7.49-7.53 (2H, m, ArH), 7.80-7.89 (4H, m, ArH); δ_C(125 MHz; $CDCl_3$) 20.4, 20.9, 21.0, 21.6, 23.2 (major), 46.8, 51.8, 58.5, 121.9, 126.2, 128.1, 128.7, 128.8, 129.0, 129.5, 134.3, 135.2, 137.9, 166.7; *m/z* (CI) 361 (100%, M+H); Acc. mass found (M+H) 361.2036 ($^{13}CC_{20}H_{29}NO_2S$ requires (*M*) 361.2025).

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