Enantioselective synthesis of tertiary thiols by N→C aryl migration in lithiated thiocarbamates

Paul MacLellan and Jonathan Clayden,
School of Chemistry, University of Manchester, Oxford ROAD, Manchester M13 9PL, UK

SUPPORTING INFORMATION

2-4 General experimental procedures
5-11 Experimental data for synthesis of precursors
12-26 Experimental data for all compounds reported in the paper
27 Deuteration experiments to identify origin of loss of e.r.
28-101 Copies of NMR spectra
102-122 Copies of HPLC traces
GENERAL PROCEDURES

**General Procedure A** – *Preparation of N-methyl-N-aryl-1H-imidazole-1-carboxamides*

Substituted *N*-methyl aniline (1 eq) was added to a solution of carbonyldiimidazole (CDI) (2 eq) in THF. The mixture was heated to reflux with stirring until completion. The mixture was cooled to rt and the solvent removed under reduced pressure. The resulting residue was redissolved in dichloromethane and washed with water. The organic fraction was dried over magnesium sulfate, filtered and the solvent removed under reduced pressure to afford the *N*-methyl-*N*-aryl-1*H*-imidazole-1-carboxamide.

**General Procedure B** – *Preparation of 3-methyl-1-(methyl(aryl)carbamoyl)-1*H*-imidazol-3-i um iodides*

Iodomethane (4 eq) was added to a solution of *N*-methyl-*N*-aryl-1*H*-imidazole-1-carboxamide (1 eq) in acetonitrile. The mixture was heated to reflux with stirring until consummation of starting material was observed by TLC. The mixture was cooled to rt and the solvent was removed under reduced pressure to afford the 3-methyl-1-(methyl(aryl)carbamoyl)-1*H*-imidazol-3-i um iodide.

**General Procedure C** – *Preparation of thiocarbamates from thioesters*
Lithium aluminium hydride (1 eq, 1M in THF) was added dropwise to a solution of 1-arylethyl ethanethioate (1 eq) in diethyl ether. The mixture was heated to reflux with stirring for 1.5 h then cooled to rt. Aqueous HCl (1 M) was added with care. The phases were separated and the aqueous layer extracted with diethyl ether. The combined ethereal fractions were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude thiol was then dissolved in dichloromethane. 3-Methyl-1-(methyl(aryl)carbamoyl)-1*H*-imidazol-3-i um iodide (1.1 eq) and triethylamine (1.2 eq) were added. The mixture was stirred until completion was observed by TLC. The mixture was extracted with aqueous HCl, dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was then purified by flash column chromatography as required.
**General Procedure D – Preparation of thiocarbamates from thiols**

Benzylic thiol was dissolved in dichloromethane. 3-Methyl-1-(methyl(aryl)carbamoyl)-1H-imidazol-3-ium iodide (1.1 eq) and triethylamine (1.2 eq) were added. The mixture was stirred until completion was observed by TLC. The mixture was extracted twice with aqueous HCl (1M), dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was then purified by flash column chromatography as required.

**General Procedure E – Lithiation of benzylic thiocarbamates with LDA in THF**

*n*-Butyllithium (solution in hexanes, 2.5 eq) was added to a solution of diisopropylamine (3 eq) in THF (1 cm³) at 0 °C. This was stirred for 15 minutes and then cooled to -78 °C. This solution was added by cannula to a cooled (-78 °C) solution of benzylic thiocarbamate (0.05 g, 1 eq) in THF (1.5 cm³). The mixture was allowed to stir for 1 or 2 hours. Propionic acid (3 eq) was added and the mixture allowed to warm to room temperature. Water (10 cm³) and diethyl ether (10 cm³) were added and the phases separated. The aqueous fraction was extracted with diethyl ether (2 x 10 cm³) and the combined organic fractions dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was then purified by flash column chromatography as required.

**General Procedure F – Lithiation of benzylic thiocarbamates with LDA in THF/DMPU**

*n*-Butyllithium (solution in hexanes, 2.5 eq) was added to a solution of diisopropylamine (3 eq) in THF (1 cm³) at 0 °C. This was stirred for 15 minutes and then cooled to -78 °C. This solution was added by cannula to a cooled (-78 °C) solution of benzylic thiocarbamate (0.05 g, 1 eq) in THF (1 cm³) and DMPU (0.5 cm³). The mixture was allowed to stir for 1 or 2 hours. Propionic acid (3 eq) was added and the mixture allowed to warm to room temperature. Water (10 cm³) and diethyl ether (10 cm³) were added and the phases separated. The aqueous fraction was extracted with diethyl ether (2 x 10 cm³) and the combined organic fractions dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was then purified by flash column chromatography as required.

**General Procedure G – Lithiation of benzylic thiocarbamates with LiTMP in THF**

*n*-Butyllithium (solution in hexanes, 2.5 eq) was added to a solution of N,N,N′,N′-tetramethylpiperidine (3 eq) in THF (1 cm³) at 0 °C. This was stirred for 15 minutes and then cooled to -78 °C. This solution was added by cannula to a cooled (-78 °C) solution of benzylic thiocarbamate (0.05 g, 1 eq) in THF (1.5 cm³). The mixture was allowed to stir for 15 hours. Propionic acid (3 eq) was added and the mixture allowed to warm to room temperature. Water (10 cm³) and diethyl ether (10 cm³) were added and the phases separated. The aqueous fraction was extracted with diethyl ether (2 x 10 cm³) and the combined organic fractions dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was then purified by flash column chromatography as required.
General Procedure H – *One-pot lithiation/deprotection of benzylic thiocarbamates with LiTMP in THF*

*n*-Butyllithium (solution in hexanes, 2.5 eq) was added to a solution of \(N,N,N',N'\)-tetramethylpiperidine (3 eq) in THF (1 cm\(^3\)) at 0 °C. This was stirred for 15 minutes and then cooled to -78 °C. This solution was added by cannular to a cooled (-78 °C) solution of benzylic thiocarbamate (0.05 g, 1 eq) in THF (1.5 cm\(^3\)). The mixture was allowed to stir for 15 hours. Propionic acid (3 eq) was added and the mixture allowed to warm to room temperature. Sodium ethoxide solution (21 % w/w in ethanol, 5 eq) was added and the mixture stirred for a further 20 min. Water (10 cm\(^3\)) and diethyl ether (10 cm\(^3\)) were added and the phases separated. The aqueous fraction was extracted with diethyl ether (2 x 10 cm\(^3\)) and the combined organic fractions dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was then purified by flash column chromatography as required.

General Procedure I – *Benzylic thiols by deprotection of benzylic thiocarbamates*

Sodium ethoxide solution (21 % w/w in ethanol, 2 eq) was added to a solution of benzylic thiocarbamate (1 eq) in ethanol (1 cm\(^3\)) at 0 °C. This was stirred for 30 minutes and saturated ammonium chloride solution (1 cm\(^3\)) added. The mixture was allowed to warm to room temperature. Water (10 cm\(^3\)) and diethyl ether (10 cm\(^3\)) were added and the phases separated. The aqueous fraction was extracted with diethyl ether (2 x 10 cm\(^3\)) and the combined organic fractions dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was then purified by flash column chromatography as required.
s1: \((S\)-1-(4-Methoxyphenyl)ethanol\)


\[
\begin{align*}
\text{Triethylamine (2.02 cm}^3, 12.0 \text{ mmol) and formic acid (1.13 cm}^3, 30 \text{ mmol) were stirred} \\
\text{together at 0 °C and allowed to warm to room temperature. 4-Methoxycetophenone} \\
(0.751 \text{ g}, 5 \text{ mmol) and [(p-cymene)RuCl((S,S)-N-(p-toluenesulfonyl)-1,2-} \\
diphenylethlenediameine(1-)]) (0.156 \text{ g}, 0.025 mmol) were added and the mixture was} \\
\text{stirred for 72 hours. Water and EtOAc were added, the phases separated and the} \\
aqueous fraction extracted with EtOAc (3 x 10 cm). The combined organic fractions were} \\
dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/EtOAc, 4:1) and the title compound isolated as a colourless oil (0.728 g, 96%). \(R_F: 0.38 \) (petrol/EtOAc, 1:1); \([\alpha]_D^{22} -40.3^\circ \) (c. 1.2, CHCl₃); \(\text{MS m/z (EI)} \) 151 (100%, M⁺); \(\text{HRMS: found 137.0597, M-CH₃ requires 137.0597; IR } \nu_{\max} \) (film)/cm⁻¹ 3373 (OH); 1\(^{H}\)-NMR (CDCl₃, 400 MHz) δ 7.31 (d, J 8.8 Hz, 2H), 6.89 (d, J 8.8 Hz, 2H), 4.86 (q, J 4.8 Hz, 1H), 3.81 (s, 3H), 1.48 (d, J 4.8 Hz, 3H); \(^{13}C\)-NMR (CDCl₃, 100 MHz) δ 159.0, 138.0, 126.7, 113.8, 70.0, 55.3, 25.1.

s2: \((S\)-1-(3-Trifluoromethylphenyl)ethanol\)


\[
\begin{align*}
\text{Triethylamine (2.02 cm}^3, 12.0 \text{ mmol) and formic acid (1.13 cm}^3, 30 \text{ mmol) were stirred} \\
\text{together at 0 °C and allowed to warm to room temperature. 3-} \\
\text{Trifluoromethylacetonophene (0.68 cm}^3, 5 \text{ mmol) and [(p-cymene)RuCl((S,S)-N-(p-} \\
toluenesulfonyl)-1,2-diphenylethlenediameine(1-)]) (0.114 \text{ g}, 0.018 mmol) were} \\
\text{added and the mixture was stirred for 72 h. Water and EtOAc were added, the phases separated and the} \\
aqueous fraction extracted with EtOAc (3 x 10 cm). The combined organic fractions were} \\
dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/EtOAc, 4:1) and the title compound isolated as a colourless oil (0.764 g, 79%). \(R_F: 0.17 \) (petrol/EtOAc, 1:1); \([\alpha]_D^{22} -14.4^\circ \) (c. 1.1, CHCl₃); \(\text{MS m/z (ES-)} \) 189 (100%, M⁻); \(\text{HRMS: found 189.0525, M-H}^{-} \) requires 189.0527; \(\text{IR } \nu_{\max} \) (film)/cm⁻¹ 3349 (OH); 1\(^{H}\)-NMR (CDCl₃, 400 MHz) δ 7.66 (s, 1H), 7.58 - 7.45 (m, 3H), 4.97 (q, J 6.4 Hz, 1H), 2.01 (s, 1H), 1.52 (d, J 6.4 Hz, 3H); \(^{13}C\)-NMR (CDCl₃, 100 MHz) δ 146.7, 131.0, 130.6, 129.0, 128.8, 125.5, 124.3, 124.3, 122.8, 122.2, 69.9, 25.4.

s3: Thiocarbonylic acid S-\((S\)-1-phenylethyl) ester


\[
\begin{align*}
\text{Oxalyl chloride (0.85 cm}^3, 10 \text{ mmol) was added to a stirred solution of DMF (0.85 cm}^3, \\
31 \text{ mmol) in DCM (30 cm}^3 \) at 0 °C. The mixture was stirred for 5 minutes. (R)-1-} \\
\text{phenylethanethiol (1.2 cm}^3, 10 \text{ mmol), triethylamine (2.8 cm}^3, 20 \text{ mmol) and} \\
ethanethioic S-acid (0.5 cm}^3, 7 \text{ mmol) were added sequentially. The mixture was warmed to} \\
temperature and stirred for 17 h. Water (5 cm³) was added and the aqueous layer extracted with EtOAc. The combined organic fractions were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was subjected to flash column chromatography (40:1 petrol/diethyl ether) and the title compound isolated as a yellow oil (0.781 g, 62 %). \(R_F: 0.58 \) (9:1 petrol/diethyl ether); \([\alpha]_D^{22} -226.9^\circ \) (c. 1.3, CHCl₃); \(\text{MS m/z (EI)} \) 180 (20%, M⁺); \(\text{HRMS: found} \) 180.0602, M⁻ requires 180.0603; \(\text{IR } \nu_{\max} \) (film)/cm⁻¹ 1690 (\(\text{C=O}\)); 1\(^{H}\)-NMR (CDCl₃, 400 MHz) δ 7.24- \\
7.35 (m, 5H), 4.75 (q, J 7.2 Hz, 1H), 2.30 (s, 3H), 1.66 (d, J 7.2 Hz, 3H); \(^{13}C\)-NMR (CDCl₃, 100 MHz) δ 195.1, 142.6, 128.6, 127.3, 127.2, 43.0, 30.5, 22.2.

5
s4: Thioacetic acid S-((R)-1-phenylbutyl) ester

Oxalyl chloride (0.29 cm³, 3.3 mmol) was added to a stirred solution of DMF (0.28 cm³, 3.7 mmol) in DCM (20 cm³) at 0 °C. The mixture was stirred for 5 min. (S)-1-phenylbutan-1-ol (0.51 g, 3.3 mmol), triethylamine (0.93 cm³, 6.67 mmol) and ethanethioic S-acid (0.21 cm³, 3.00 mmol) were added sequentially. The mixture was warmed to room temperature and stirred for 18 h. Water (5 cm³) was added, the phases separated and the aqueous layer extracted with EtOAc. The combined organic fractions were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/diethyl ether, 40:1) and the title compound isolated as an amorphous pink solid (0.315 g, 45%). 

IR \( \nu_{\text{max}} \) (film)/cm\(^{-1}\): 1693 (C=O); \( \delta \) 7.33-7.19 (m, 5H), 4.56 (t, J 7.4 Hz, 1H), 2.27 (s, 3H), 1.88 (ap q, J 7.7 Hz, 2H), 0.88 (t, J 7.4 Hz, 3H); \(^{13}C\)-NMR (CDCl\(_3\), 100 MHz) \( \delta \) 194.9, 142.0, 128.5, 127.6, 127.2, 47.8, 38.3, 30.5, 20.7, 13.6.

s5: Thioacetic acid S-[(R)-1-(3-trifluoromethylphenyl)ethyl] ester

Oxalyl chloride (0.27 cm³, 3.1 mmol) was added to a stirred solution of DMF (0.26 cm³, 3.4 mmol) in DCM (20 cm³) at 0 °C. The mixture was stirred for 5 min. Triethylamine (0.87 cm³, 5.0 mmol) was added, the phases separated and the aqueous layer extracted with EtOAc. The combined organic fractions were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/diethyl ether, 40:1) and the title compound isolated as a yellow oil (0.110 g, 18%). 

IR \( \nu_{\text{max}} \) (film)/cm\(^{-1}\): 1690 (C=O); \( \delta \) 7.76 (br s, 1H), 7.55 (s, 1H), 7.35 (m, 8H), 7.01 (br s, 1H), 2.42 (s, 3H), 2.32 (s, 3H), 1.67 (d, J 7.1 Hz, 3H); \(^{1}H\)-NMR (CDCl\(_3\), 400 MHz) \( \delta \) 143.9, 130.8, 129.0, 128.8, 127.6, 127.2, 47.8, 38.3, 30.5, 20.7, 13.6.

s6: Naphthalen-1-ylcarbamic acid benzyl ester


Benzyl chloroformate (1.90 cm³, 13 mmol) was added dropwise to a stirred mixture of naphthalen-1-amine (1.557 g, 11 mmol) and pyridine (1.10 cm³, 14 mmol) at room temperature. The mixture was stirred for 20 h. The mixture was partitioned between saturated aqueous sodium bicarbonate solution and DCM and separated. The aqueous fraction was extracted with DCM (3 x 20 cm³), the combined organic fractions dried over sodium sulfate, filtered and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/EtOAc, 9:1) and the title compound isolated as an amorphous pink solid (2.857 g, 98%). 

IR \( \nu_{\text{max}} \) (film)/cm\(^{-1}\): 3277 (NH), 1690 (C=O); \( \delta \) 7.33-7.19 (m, 5H), 4.56 (t, J 7.4 Hz, 1H), 2.27 (s, 3H), 1.88 (ap q, J 7.7 Hz, 2H), 0.88 (t, J 7.4 Hz, 3H); \(^{13}C\)-NMR (CDCl\(_3\), 100 MHz) \( \delta \) 136.1, 134.1, 132.4, 128.8, 128.7, 128.4, 128.4, 126.3, 126.0, 125.8, 125.1, 120.4, 119.1, 67.3.
**s7: N-Methylnaphthalen-1-amine**

Iagarashi, T.; Shimokawa, M.; Iwasaki, M.; Nagata, K.; Fujii, M.; Sakurai, T. Synlett 2007, 9, 1436

Lithium aluminium hydride (6.8 cm³, 2 M in THF, 14 mmol) was added dropwise at 0 °C to a solution of s6 (2.481 g, 9 mmol) in THF (50 cm³). The mixture was heated to reflux and stirred for 4 hours then allowed to cool to room temperature. Water (0.5 cm³) was added dropwise followed by stirring for 10 minutes. Aqueous sodium hydroxide solution (15% w/w) was added followed by stirring for 30 min. Water (1.5 cm³) was added and the mixture stirred for 1 hour. The resulting suspension was filtered and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/EtOAc, 9:1) to afford the title compound as a brown oil (1.167 g, 82%). \( R_f \): 0.25 (9:1, Petrol:EtOAc); MS m/z (ES+) 158 (100%, M+H⁺); HRMS: found 158.0973, M+H⁺ requires 158.0964; \( ^1H \)-NMR (CDCl₃, 300 MHz) δ 7.78-7.83 (m, 2H), 7.36 (d, \( J \) 7.5 Hz, 1H), 6.62 (d, \( J \) 7.5 Hz, 1H), 4.45 (br s, 1H), 3.03 (s, 3H); \( ^13C \)-NMR (CDCl₃, 75 MHz) δ 144.6, 134.3, 127.2, 123.5, 119.8, 117.3, 101.9, 99.6, 60.2, 34.7.

**s8: N-Methyl-N-p-tolyl-1H-imidazole-1-carboxamide**

General procedure A was followed using N,N-dimethylbenzenamine (1.3 cm³, 10 mmol), CDI (3.244 g, 20 mmol) in THF (20 cm³) with stirring for 18 hours. The title compound was isolated as colourless prisms (1.7821 g, 83%). \( R_f \): 0.25 (9:1, Petrol:EtOAc); MS m/z (ES+) 158 (100%, M+H⁺); HRMS: found 158.0973, M+H⁺ requires 158.0964; \( ^1H \)-NMR (CDCl₃, 300 MHz) δ 7.53 (s, 1H), 7.16 (d, \( J \) 8.1 Hz), 6.99 (d, \( J \) 8.1 Hz), 6.87 (m, 1H), 6.80 (m, 1H), 3.45 (s, 3H), 2.34 (s, 3H); \( ^13C \)-NMR (CDCl₃, 100 MHz) δ 150.3, 140.3, 138.2, 137.7, 130.9, 128.9, 125.7, 124.7, 119.8, 117.3, 103.8, 31.1.

**s9: Imidazole-1-carboxylic acid methylphenylamide**


General procedure A was followed using methylphenylamine (1.09 cm³, 10 mmol), CDI (3.240 g, 20.0 mmol) in THF (20 cm³) with stirring for 20 hours. The title compound was isolated as colourless prisms (2.005 g, 99%). \( R_f \): 0.4 (EtOAc); Mpt: 55-57 °C (DCM); MS m/z (ES+) 202 (35%, M+H⁺); HRMS: found 202.0984, M+H⁺ requires 202.0975; \( ^1H \)-NMR (CDCl₃, 400 MHz) δ 7.58 (br s, 1H), 7.42 - 7.31 (m, 3H), 7.15 - 7.12 (m, 2H), 6.86 (m, 1H), 6.82 (m, 1H), 3.50 (s, 3H); \( ^13C \)-NMR (CDCl₃, 100 MHz) δ 150.3, 143.0, 137.7, 130.3, 129.0, 128.1, 126.0, 118.5, 40.2, 21.1.

**s10: N-(4-Methoxyphenyl)-N-methyl-1H-imidazole-1-carboxamide**

General procedure A was followed using 4-methoxy-N-methylbenzenamine (0.503 g, 3.67 mmol), CDI (1.130 g, 7.00 mmol) in THF (10 cm³) with stirring for 6 hours. The title compound was isolated as a pink amorphous solid (0.810 g, 95%). \( R_f \): 0.1 (1:1, Petrol:EtOAc); Mpt: 47-49 °C (DCM); MS m/z (ES+) 232 (20%, M+H⁺); HRMS: found 232.1074, M+H⁺ requires 232.1081; IR νₓmax(film)/cm⁻¹ 1698 (C=O); \( ^1H \)-NMR (CDCl₃, 400 MHz) δ 7.54 (s, 1H), 7.04 (d, \( J \) 9.0 Hz, 2H), 6.88 (m, 3H), 6.81 (s, 1H), 3.80 (s, 3H), 3.44 (s, 3H); \( ^13C \)-NMR (CDCl₃, 100 MHz) δ 159.1, 150.3, 137.8, 135.5, 128.9, 127.2, 118.6, 115.4, 55.5, 40.4.
s11: N-(2-Methoxyphenyl)-N-methyl-1H-imidazole-1-carboxamide

General procedure A was followed using 2-methoxy-N-methyl aniline (1.375 g, 10 mmol), CDI (3.244 g, 20 mmol) in THF (20 cm$^3$) with stirring for 48 h. The title compound was isolated as off-white prisms (2.180 g, 94 %). \( R_F \): 0.58 (EtOAc); \textbf{Mpt}: 60-62 °C (DCM); \textbf{MS m/z (ES+)} 232 (100%, M+H$^+$); \textbf{HRMS}: found 232.1085, M+H$^+$ requires 232.1081; \textbf{IR } \nu_{\text{max}}(\text{film})/\text{cm}^{-1} 1702 (\text{C=O}); \textbf{¹H-NMR (CDCl}_3, 100 MHz) \delta 7.59 (s, 1H), 7.29 (ddd, \textbf{J} 1.7, 7.6 and 8.3 Hz, 1H), 7.17 (dd, \textbf{J} 1.6 and 7.7 Hz, 1H), 6.97 (ddd, \textbf{J} 1.2, 7.6 and 7.6 Hz, 1H), 6.90, (m, 2H), 6.78 (s, 1H), 3.71 (s, 3H), 3.37 (s, 3H);

s12: N-(4-Chlorophenyl)-N-methyl-1H-imidazole-1-carboxamide

General procedure A was followed using 4-chloro-N-methylbenzenamine (1.20 cm$^3$, 10 mmol) and CDI (3.246 g, 20 mmol) in THF (20 cm$^3$) with stirring for 23 h. The title compound was isolated as an amorphous white solid (2.310 g, 99 %). \( R_F \): 0.37 (EtOAc); \textbf{Mpt}: 110-112 °C (DCM); \textbf{MS m/z (ES+)} 236 (100%, M+H$^+$); \textbf{HRMS}: found 236.0596, M+H$^+$ requires 236.0585; \textbf{IR } \nu_{\text{max}}(\text{film})/\text{cm}^{-1} 1700 (\text{C=O}); \textbf{¹H-NMR (CDCl}_3, 100 MHz) \delta 7.59 (s, 1H), 7.35 (m, 2H), 7.05 (m, 2H), 6.86 (m, 2H), 3.47 (s, 3H);

s13: Imidazole-1-carboxylic acid (3-chlorophenyl)methylamide

General procedure A was followed using (3-chlorophenyl)methylamine (1.73 cm$^3$, 14.12 mmol), CDI (4.580 g, 28.24 mmol) in THF (30 cm$^3$) with stirring for 2 days. The title compound was isolated as colourless prisms (3.30 g, 99 %). \( R_F \): 0.35 (EtOAc); \textbf{Mpt}: 73-75 °C (DCM); \textbf{MS m/z (ES+)} 236 (40%, M+H$^+$); \textbf{HRMS}: found 236.0595, M+H$^+$ requires 236.0585; \textbf{IR } \nu_{\text{max}}(\text{film})/\text{cm}^{-1} 1700 (\text{C=O}); \textbf{¹H-NMR (CDCl}_3, 100 MHz) \delta 7.63 (ap t, \textbf{J} 1.0 Hz, 1H), 7.32 - 7.30 (m, 2H), 7.19 (m, 1H), 7.00 - 6.97 (m, 1H), 6.89 - 6.88 (m, 1H), 6.86 (m, 1H), 3.42 (s, 3H);

s14: Imidazole-1-carboxylic acid (4-cyanophenyl)methylamide

General procedure A was followed using 4-methylaminobenzonitrile (1.518 g, 11.50 mmol), CDI (3.680 g, 22.72 mmol) in THF (20 cm$^3$) with stirring for 10 days. The title compound was isolated as colourless prisms (2.43 g, 95 %). \( R_F \): 0.35 (EtOAc); \textbf{Mpt}: 136-138 °C (DCM); \textbf{MS m/z (ES+)} 249 (35%, M+Na$^+$); \textbf{HRMS}: found 249.0747, M+Na$^+$ requires 249.0747; \textbf{IR } \nu_{\text{max}}(\text{film})/\text{cm}^{-1} 1700 (\text{C=O}), 2229 (\text{nitrile}); \textbf{¹H-NMR (CDCl}_3, 400 MHz) \delta 7.68 (d, J 8.8 Hz, 2H), 7.64 (br s, 1H), 7.22 (d, J 8.8 Hz, 2H), 6.89 (m, 1H), 6.86 (m, 1H), 3.54 (s, 3H); \textbf{¹C-NMR (CDCl}_3, 100 MHz) \delta 147.0, 137.4, 134.1, 132.9, 129.4, 128.3, 126.1, 124.1, 118.3, 118.1, 117.6, 111.4, 39.7.
s15: Imidazole-1-carboxylic acid methyl(2,4,6-trimethylphenyl)amide

General procedure A was followed using methyl(2,4,6-trimethylphenyl)amine (0.92 cm\(^3\), 5.77 mmol), CDI (1.957 g, 12.10 mmol) in THF (20 cm\(^3\)) with stirring for 4 days. The title compound was isolated as a white amorphous solid (1.00 g, 71 %). \(R_f\): 0.53 (EtOAc); Mpt: 92-94 ºC (DCM); MS m/z (ES+) 266 (70%, M+Na\(^+\)); HRMS: found 266.1250, M+Na\(^+\) requires 266.1264; \(\nu_{\text{max}}\) (film)/cm\(^{-1}\) 1698 (C=O); \(^1H\)-NMR (CDCl\(_3\), 300 MHz) \(\delta\) 7.44 (br s, 1H), 6.94 (s, 2H), 6.85 (s, 1H), 6.81 (s, 1H), 3.33 (s, 3H), 2.30 (s, 3H), 2.15 (s, 6H); \(^{13}C\)-NMR (CDCl\(_3\), 100 MHz) \(\delta\) 150.3, 139.2, 137.5, 137.4, 135.1, 130.3, 129.0, 118.3, 38.0, 21.0, 17.5.

s16: Imidazole-1-carboxylic acid methylnaphthalen-1-ylamide

General procedure A was followed using s7 (0.990 g, 6.37 mmol), CDI (2.064 g, 12.74 mmol) in THF (20 cm\(^3\)) with stirring for 2 days. The title compound was isolated as colourless prisms (1.22 g, 99 %). \(R_f\): 0.52 (EtOAc); Mpt: 107-109 ºC (DCM); MS m/z (ES+) 274 (100%, M+Na\(^+\)), 252 (15%, M+H\(^+\)); HRMS: found 252.1138, M+H\(^+\) requires 252.1131; \(\nu_{\text{max}}\) (film)/cm\(^{-1}\) 1682 (C=O); \(^1H\)-NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.97-7.89 (m, 3H), 7.67-7.60 (m, 2H), 7.52 (br s, 1H), 7.43 (t, \(J = 7.8\) Hz, 1H), 7.28-7.26 (m, 1H), 6.76 (br s, 1H), 6.69 (br s, 1H), 3.56 (s, 3H); \(^{13}C\)-NMR (CDCl\(_3\), 100 MHz) \(\delta\) 151.1, 138.9, 137.3, 134.8, 129.5, 129.2, 129.2, 128.7, 128.3, 127.3, 126.0, 125.1, 121.6, 118.2, 40.3.

s17: Imidazole-1-carboxylic acid (3-fluorophenyl)methylamide

General procedure A was followed using (3-fluorophenyl)methylamine (0.63 cm\(^3\), 5.60 mmol), CDI (1.810 g, 11.20 mmol) in THF (10 cm\(^3\)) with stirring for 4 days. The title compound was isolated as white cubes (1.22 g, 75 %). \(R_f\): 0.39 (EtOAc); Mpt: 56-58 ºC (DCM); MS m/z (ES+) 220 (30%, M+H\(^+\)); HRMS: found 220.0887, M+H\(^+\) requires 220.0881; \(\nu_{\text{max}}\) (film)/cm\(^{-1}\) 1703 (C=O); \(^1H\)-NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.62 (s, 1H), 7.32 - 7.38 (m, 1H), 7.01 - 7.07 (m, 1H), 6.86 - 6.91 (m, 4H), 3.49 (s, 3H); \(^{13}C\)-NMR (CDCl\(_3\), 100 MHz) \(\delta\) 164.5, 162.0, 150.1, 144.4, 144.3, 137.6, 131.6, 131.5, 129.4, 121.7, 118.3, 115.3, 115.1, 113.5, 113.3, 40.1.

s18: 3-Methyl-1-(methyl(p-tolyl)carbamoyl)-1H-imidazol-3-iium iodide

General procedure B was followed using s8 (2.137 g, 10 mmol) and iodomethane (2.49 cm\(^3\), 40 mmol) in acetonitrile (20 cm\(^3\)) with stirring for 4.5 hours. The title compound was isolated as a yellow amorphous solid (3.343 g, 94 %). \(R_f\): 0.04 (EtOAc); Mpt: 144-146 ºC (MeCN); MS m/z (ES+) 230 (100%, M+I\(^-\)); HRMS: found 230.1295, M-I requires 230.1288; \(\nu_{\text{max}}\) (film)/cm\(^{-1}\) 1731 (C=O); \(^1H\)-NMR (CDCl\(_3\), 400 MHz) \(\delta\) 9.73 (br s, 1H), 7.51 (br s, 1H), 7.31 (d, \(J = 8.3\) Hz), 7.23 (d, \(J = 8.3\) Hz), 7.00 (br s, 1H), 4.10 (s, 3H), 3.50 (s, 3H), 2.34 (s, 3H); \(^{13}C\)-NMR (CDCl\(_3\), 100 MHz) \(\delta\) 145.9, 139.7, 138.4, 137.9, 131.5, 126.4, 123.5, 121.0, 41.2, 38.1, 21.2.

s19: 1-Methyl-3-(methylphenylcarbamoyl)-3H-imidazol-1-iium iodide

General procedure B was followed using s9 (2.012 g, 10.00 mmol) and iodomethane (2.49 cm\(^3\), 40.00 mmol) in acetonitrile (20 cm\(^3\)) with stirring for 4 hours. The title compound was isolated as yellow prisms (3.204 g, 93 %). \(R_f\): 0.03 (EtOAc); Mpt: 104-106 ºC (DCM); MS m/z (ES+) 216 (100%, M-I); HRMS: found 216.1121, M-I.
s20: 1-((4-Methoxyphenyl)(methyl)carbamoyl)-3-methyl-1H-imidazol-3-iium iodide

General procedure B was followed using s10 (0.520 g, 2.20 mmol) and iodomethane (0.54 cm³, 8.70 mmol) in acetonitrile (10 cm³) with stirring for 2 hours. The title compound was isolated as a dull green amorphous solid (0.7678 g, 95 %). Rf: 0.03 (EtOAc); Mpt: 139-141 °C (MeCN); MS m/z (ES+) 246 (100%, M-I); HRMS: found 246.1240, M-I requires 246.1237; IR νmax(film)/cm⁻¹ 1731 (C=O); ¹H-NMR (CDCl₃, 400 MHz) δ 9.77 (br s, 1H), 7.50-7.38 (m, 6H), 7.07 (br s, 1H), 4.10 (s, 3H), 3.56 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ 145.8, 140.5, 138.4, 130.9, 129.4, 126.7, 123.3, 121.0, 41.1, 38.1.

s21: 1-((2-Methoxyphenyl)(methyl)carbamoyl)-3-methyl-1H-imidazol-3-iium iodide

General procedure B was followed using s11 (1.161 g, 5 mmol) and iodomethane (1.25 cm³, 20 mmol) in acetonitrile (20 cm³) with stirring for 16 hours. The title compound was isolated as an orange amorphous solid (1.860 g, 99 %). Rf: 0.03 (EtOAc); Mpt: 158-160 °C (MeCN); MS m/z (ES+) 246 (100%, M-I); HRMS: found 246.1232, M-I requires 246.1237; IR νmax(film)/cm⁻¹ 1739 (C=O); ¹H-NMR (CDCl₃, 400 MHz) δ 9.71 (br s, 1H), 7.64 (br s, 1H), 7.59 (dd, J 1.6, 7.8 Hz, 1H), 7.34 (dt, J 1.6, 8.3 Hz, 1H), 7.16 (br s, 1H), 7.05 (dt, J 1.1, 7.7 Hz, 1H), 6.91 (dd, J 0.9, 8.3 Hz, 1H), 4.11 (s, 3H), 3.81 (s, 3H), 3.39 (s, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ 153.3, 147.1, 137.3, 131.1, 129.1, 128.5, 123.7, 122.5, 120.6, 112.6, 56.5, 40.0, 38.1.

s22: 1-((4-Chlorophenyl)(methyl)carbamoyl)-3-methyl-1H-imidazol-3-iium iodide


General procedure B was followed using s12 (1.184 g, 5 mmol) and iodomethane (1.25 cm³, 20 mmol) in acetonitrile (20 cm³) with stirring for 8 hours. The title compound was isolated as an orange amorphous solid (1.744 g, 92 %). Rf: 0.03 (EtOAc); Mpt: 120-122 °C (MeCN); MS m/z (ES+) 250 (100%, M-I); HRMS: found 250.0736, M-I requires 250.0742; IR νmax(film)/cm⁻¹ 1731 (C=O); ¹H-NMR (CD₂OD, 400 MHz) δ 9.29 (br s, 1H), 7.48-7.45 (m, 3H), 7.38 (d, J 8.7 Hz), 7.31 (br s, 1H), 3.91 (s, 3H), 3.53 (s, 3H); ¹³C-NMR (CD₂OD, 100 MHz) δ 147.6, 141.3, 135.7, 131.6, 129.3, 124.6, 122.8, 41.0, 37.3.

s23: 3-[(3-Chlorophenyl)methylcarbamoyl]-1-methyl-3H-imidazol-1-iium iodide

General procedure B was followed using s13 (3.009 g, 12.74 mmol) and iodomethane (3.17 cm³, 50.95 mmol) in acetonitrile (60 cm³) with stirring for 4 hours. The title compound was isolated as yellow prisms (4.786 g, 99 %). Rf: 0.03 (EtOAc); Mpt: 112-114 °C (DCM); MS m/z (ES+) 250 (100%, M-I); HRMS: found 250.0757, M-I requires 250.0742; IR νmax(film)/cm⁻¹ 1731 (C=O); ¹H-NMR (CDCl₃, 300 MHz) δ 9.99 (br s, 1H), 7.59 - 7.36 (m, 5H), 7.18 (br s, 1H), 4.14 (s, 3H), 3.57 (s, 3H); ¹³C-NMR (CDCl₃, 75.5 MHz) δ 141.7, 138.7, 135.9, 132.1, 129.7, 126.3, 125.8, 123.4, 121.0, 41.3, 38.1.
s24: 3-[(4-Cyanophenyl)methylcarbamoyl]-1-methyl-3\textit{H}-imidazol-1-ium iodide

General procedure B was followed using \textbf{s14} (2.209 g, 9.73 mmol) and iodomethane (2.43 cm³, 38.94 mmol) in acetonitrile (40 cm³) with stirring for 4 hours. The title compound was isolated as yellow prisms (3.532 g, 98 %). \textit{Rf}: 0.03 (EtOAc); \textit{Mpt}: 178-180 °C (DCM); \textit{MS} m/z (ES+) 241 (100%, M-\textit{I}); \textit{HRMS}: found 241.1077, M-I requires 241.1084; \textit{IR} \nu_{\text{max}}(\text{film})/cm⁻¹ 1729 (C=O), 2229 (nitrile); \textit{¹H-NMR} (CD₃OD, 400 MHz) δ 9.36 (br s, 1H, exchanges with MeOD), 7.83 (d, J 8.4 Hz, 2H), 7.60 (d, J 8.4 Hz, 2H), 7.50 (br s, 1H), 7.38 (br s, 1H), 3.94 (s, 3H), 3.59 (s, 3H); \textit{¹3C-NMR} (CD₃OD, 100 MHz) δ 147.6, 146.9, 145.8, 142.0, 141.9, 138.5, 132.3, 132.2, 123.6, 123.0, 118.7, 113.4, 40.7, 37.3.

s25: 1-Methyl-3-[(methyl(2,4,6-trimethylphenyl)carbamoyl]-3\textit{H}-imidazol-1-ium iodide

General procedure B was followed using \textbf{s15} (0.989 g, 4.10 mmol) and iodomethane (1.02 cm³, 16.45 mmol) in acetonitrile (20 cm³) with stirring for 4 hours. The title compound was isolated as yellow prisms (0.512 g, 96 %). \textit{Rf}: 0.05 (EtOAc); \textit{Mpt}: 160 °C (decomposition); \textit{MS} m/z (ES+) 258 (100%, M-I); \textit{HRMS}: found 258.1598, M-I requires 258.1601; \textit{IR} \nu_{\text{max}}(\text{film})/cm⁻¹ 1724 (C=O); \textit{¹H-NMR} (CDCl₃, 400 MHz) δ 9.38 (br s, 1H), 7.78 (m, 1H), 7.00 (s, 2H), 6.61 (m, 1H), 4.18 (s, 3H), 3.38 (s, 3H), 2.32 (s, 3H), 2.24 (s, 6H); \textit{¹3C-NMR} (CDCl₃, 100 MHz) δ 145.9, 140.7, 138.3, 135.2, 134.9, 131.0, 124.8, 120.2, 39.0, 38.7, 21.1, 18.1).

s26: 1-Methyl-3-[(methyl(1naphthalen-1-ylcarbamoyl)]-3\textit{H}-imidazol-1-ium iodide

General procedure B was followed using \textbf{s16} (1.005 g, 3.98 mmol) and iodomethane (0.99 cm³, 15.94 mmol) in acetonitrile (20 cm³) with stirring for 4 hours. The title compound was isolated as yellow prisms (1.498 g, 96 %). \textit{Rf}: 0.02 (EtOAc); \textit{Mpt}: 83-85 °C (DCM); \textit{MS} m/z (ES+) 266 (100%, M-I); \textit{HRMS}: found 266.1288, M-I requires 266.1289; \textit{IR} \nu_{\text{max}}(\text{film})/cm⁻¹ 1721 (C=O); \textit{¹H-NMR} (CDCl₃, 400 MHz) δ 9.86 (br s, 1H), 7.98-7.87 (m, 4H), 7.73-7.69 (m, 2H), 7.35 (m, 1H), 7.31 (dt, J 8.8, 2.0 Hz, 1H), 7.23 (br s, 1H), 7.12 - 7.08 (m, 1H), 4.07 (s, 3H), 3.50 (s, 3H); \textit{¹3C-NMR} (CDCl₃, 100 MHz) δ 146.9, 138.4, 136.2, 134.6, 130.5, 129.4, 129.1, 128.4, 127.6, 127.0, 126.7, 123.6, 120.9, 120.2, 41.0, 38.0.

s27: 3-[(3-Fluorophenyl)methylcarbamoyl]-1-methyl-3\textit{H}-imidazol-1-ium iodide

General procedure B was followed using \textbf{s17} (1.098 g, 5.00 mmol) and iodomethane (1.25 cm³, 20.00 mmol) in acetonitrile (20 cm³) with stirring for 4 hours. The title compound was isolated as yellow prisms (1.598 g, 88 %). \textit{Rf}: 0.03 (EtOAc); \textit{Mpt}: 115-117 °C (DCM); \textit{MS} m/z (ES+) 234 (100%, M-I); \textit{HRMS}: found 234.1035, M-I requires 234.1043; \textit{IR} \nu_{\text{max}}(\text{film})/cm⁻¹ 1731 (C=O); \textit{¹H-NMR} (CDCl₃, 400 MHz) δ 9.92 (br s, 1H), 7.52 (m, 1H), 7.45 (td, J 8.0, 6.4 Hz, 1H), 7.37 - 7.35 (m, 1H), 7.31 (dt, J 8.8, 2.0 Hz, 1H), 7.23 (br s, 1H), 7.12 - 7.08 (m, 1H), 4.07 (s, 3H), 3.50 (s, 3H); \textit{¹3C-NMR} (CDCl₃, 100 MHz) δ 164.3, 161.8, 145.8, 142.0, 141.9, 141.9, 138.5, 132.3, 132.2, 123.6, 123.0, 121.2, 116.7, 116.5, 114.3, 114.0, 41.3, 38.1.
EXPERIMENTAL DATA FOR COMPOUNDS REPORTED

5a: Methylphenylthiocarbamic acid S-(4-methylbenzyl) ester

General procedure D was followed using benzyl thiol (0.24 cm$^3$, 2.0 mmol), s18 (0.81 g, 2.2 mmol) and triethylamine (0.34 cm$^3$, 2.4 mmol) in DCM (10 cm$^3$) with stirring for 18 hours. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as a colourless oil (0.523 g, 95 %). $R_F$: 0.31 (8:1, Petrol:EtoAc); MS m/z (ES+) 294 (100%, M+Na$^+$); HRMS: found 294.0928, M+Na$^+$ requires 294.0923; IR $\nu_{\text{max}}$(film)/cm$^{-1}$ 1656 (C=O); $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 7.31-7.32 (m, 3H), 7.27-7.25 (m, 2H), 7.22 (d, $J$ 8.0 Hz, 2H), 6.79 (d, $J$ 8.0 Hz, 2H), 4.09 (s, 2H), 3.32 (s, 3H); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 168.7, 150.0, 134.8, 129.5, 128.7, 128.4, 128.3, 113.9, 55.3, 38.3, 35.0.

5b: Methylphenylthiocarbamic acid 4-methoxybenzyl ester

General procedure D was followed using (4-methoxyphenyl)methanethiol (0.61 cm$^3$, 4.4 mmol), s19 (1.507 g, 4.4 mmol) and triethylamine (0.73 cm$^3$, 5.3 mmol) in DCM (20 cm$^3$) with stirring for 18 hours. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as an amorphous white solid (1.192 g, 95 %). $R_F$: 0.11 (8:1, Petrol:EtoAc); Mpt: 76 °C (DCM); MS m/z (ES+) 310 (100%, M+Na$^+$); HRMS: found 310.0872, M+Na$^+$ requires 310.0869; IR $\nu_{\text{max}}$(film)/cm$^{-1}$ 1654 (C=O); $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 7.41-7.42 (m, 9H), 4.09 (s, 2H), 3.35 (s, 3H), 1.29 (s, 9H); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 168.7, 158.7, 142.0, 130.1, 130.0, 129.5, 128.4, 128.3, 113.9, 55.3, 38.3, 35.0.

5c: Methylphenylthiocarbamic acid 4-tert-butylbenzyl ester

General procedure D was followed using (4-tert-butylphenyl)methanethiol (0.52 cm$^3$, 2.8 mmol), s19 (1.078 g, 3.1 mmol) and triethylamine (0.58 cm$^3$, 4.1 mmol) in DCM (20 cm$^3$) with stirring for 18 hours. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 15:1) to afford the title compound as an amorphous colourless solid (0.845 g, 97 %). $R_F$: 0.28 (8:1, Petrol:EtoAc); Mpt: 67-69 °C (DCM); MS m/z (ES+) 336 (100%, M+Na$^+$); HRMS: found 336.1397, M+Na$^+$ requires 336.1398; IR $\nu_{\text{max}}$(film)/cm$^{-1}$ 1650 (C=O); $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 7.41-7.42 (m, 9H), 4.09 (s, 2H), 3.35 (s, 3H), 1.29 (s, 9H); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 168.7, 150.0, 134.8, 129.5, 128.7, 128.4, 128.3, 128.6, 128.3, 126.9, 38.4, 35.2, 34.5, 31.3.

5d: Methylphenylthiocarbamic acid 2-chlorobenzyl ester

General procedure D was followed using (2-chlorophenyl)methanethiol (0.41 cm$^3$, 3.2 mmol), s19 (1.197 g, 3.5 mmol) and triethylamine (0.66 cm$^3$, 4.7 mmol) in DCM (20 cm$^3$) with stirring for 18 hours. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 10:1) to afford the title compound as an amorphous colourless solid (0.787 g, 86 %). $R_F$: 0.24 (8:1, Petrol:EtoAc); Mpt: 67-78 °C (DCM); MS m/z (ES+) 314 (100%, M+Na$^+$), 292 (20%, M+H$^+$); HRMS: found 292.0557, M+H$^+$ requires 292.0547; IR $\nu_{\text{max}}$(film)/cm$^{-1}$ 1651 (C=O); $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 7.50-7.47 (m, 1H), 7.41-7.25 (m, 6H), 7.20-7.13 (m, 2H), 4.22 (s, 2H), 3.33 (s, 3H); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 168.4, 141.8, 136.0, 134.2, 131.3, 129.5, 129.4, 128.6, 128.3, 126.9, 38.5, 33.3.
6a: Methylthiocarbamic acid phenyl-p-tolylmethyl ester

General procedure F was followed using 5a (0.045 g, 0.17 mmol), diisopropylamine (0.08 cm³, 0.55 mmol), n-butyllithium (0.29 cm³, 1.6 M, 0.46 mmol) and propionic acid (0.04 cm³, 0.50 mmol) with stirring for 2 hours. The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as an amorphous colourless solid (0.032 g, 73 %). \( R_F \): 0.09 (8:1, petrol:EtOAc); \( \text{Mpt} \): 113-115 ºC (DCM); \( \text{MS} \ m/z \ (\text{ES}+) \ 294 \ (100\%, \ M+Na^+) \); HRMS: found 294.0924, \( M+Na^+ \) requires 294.0923; \( \text{IR} \ \nu_{\text{max}}(\text{film})/\text{cm}^{-1} \ 1648 \ (\text{C=O}) \); \( ^1\text{H}-\text{NMR} \ (\text{CDCl}_3, \ 400 \text{MHz}) \ \delta \ 7.39 \ (d, J 8.0 \text{ Hz}, 2H), 7.32-7.21 \ (m, 5H), 7.12 \ (d, J 8.0 \text{ Hz}, 2H), 5.94 \ (s, 1H), 5.24 \ (\text{br s}, 1H), 2.85 \ (d, J 4.0 \text{ Hz}, 3H), 2.32 \ (s, 3H); \( ^{13}\text{C}-\text{NMR} \ (\text{CDCl}_3, \ 100 \text{ MHz}) \ \delta \ 166.6, 141.6, 138.4, 136.9, 129.2, 128.5, 128.3, 128.2, 127.1, 52.8, 28.0, 21.1.

6b: Methylthiocarbamic acid (4-methoxyphenyl)phenylmethyl ester

General procedure F was followed using 5b (0.057 g, 0.18 mmol), diisopropylamine (0.07 cm³, 0.52 mmol), n-butyllithium (0.29 cm³, 1.5 M, 0.43 mmol) and propionic acid (0.04 cm³, 0.50 mmol) with stirring for 2 hours. The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as an amorphous colourless solid (0.055 g, 96 %). \( R_F \): 0.06 (8:1, petrol:EtOAc); \( \text{Mpt} \): 84-86 ºC (DCM); \( \text{MS} \ m/z \ (\text{ES}+) \ 310 \ (100\%, \ M+Na^+) \); HRMS: found 310.0870, \( M+Na^+ \) requires 310.0872; \( \text{IR} \ \nu_{\text{max}}(\text{film})/\text{cm}^{-1} \ 1644 \ (\text{C=O}) \); \( ^1\text{H}-\text{NMR} \ (\text{CDCl}_3, \ 400 \text{ MHz}) \ \delta \ 7.40-7.38 \ (m, 2H), 7.33-7.21 \ (m, 5H), 6.84 \ (d, J 8.0 \text{ Hz}, 2H), 5.94 \ (s, 1H), 5.24 \ (\text{br s}, 1H), 3.79 \ (s, 3H), 2.85 \ (d, J 4.0 \text{ Hz}, 3H); \( ^{13}\text{C}-\text{NMR} \ (\text{CDCl}_3, \ 100 \text{ MHz}) \ \delta \ 166.6, 151.7, 133.5, 129.5, 128.5, 128.3, 128.2, 127.1, 113.9, 55.3, 52.5, 28.0.

6c: Methylthiocarbamic acid (4-tert-butylphenyl)phenylmethyl ester

General procedure F was followed using 5c (0.050 g, 0.16 mmol), diisopropylamine (0.07 cm³, 0.48 mmol), n-butyllithium (0.27 cm³, 1.5 M, 0.40 mmol) and propionic acid (0.04 cm³, 0.50 mmol) with stirring for 2 hours. The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as a colourless oil (0.042 g, 83 %). \( R_F \): 0.09 (8:1, petrol:EtOAc); \( \text{MS} \ m/z \ (\text{ES}+) \ 336 \ (100\%, \ M+Na^+) \); HRMS: found 336.1380, \( M+Na^+ \) requires 336.1393; \( \text{IR} \ \nu_{\text{max}}(\text{film})/\text{cm}^{-1} \ 1653 \ (\text{C=O}) \); \( ^1\text{H}-\text{NMR} \ (\text{CDCl}_3, \ 400 \text{ MHz}) \ \delta \ 7.42 \ (d, J 7.6 \text{ Hz}, 2H), 7.33-7.21 \ (m, 7H), 5.96 \ (s, 1H), 5.32 \ (\text{br s}, 1H), 2.83 \ (d, J 4.8 \text{ Hz}, 3H), 1.30 \ (s, 9H); \( ^{13}\text{C}-\text{NMR} \ (\text{CDCl}_3, \ 100 \text{ MHz}) \ \delta \ 165.6, 148.9, 140.7, 137.2, 127.4, 127.3, 126.9, 126.0, 124.4, 51.6, 33.4, 30.3, 26.9.

Supplementary Material (ESI) for Chemical Communications

This journal is (c) The Royal Society of Chemistry 2011
7a: Phenyl-p-tolylmethanethiol

General procedure I was followed using sodium ethoxide solution (0.04 cm$^3$, 0.10 mmol) and 6a (0.015 g, 0.06 mmol). The crude product was purified by flash column chromatography (n-pentane) and the title compound isolated as a colourless oil (0.007 g, 57 %). $R_F$: 0.55 (8:1, Petrol:EtOAc); MS m/z (ES-) 213 (55%, M-H$^-$), 181 (50%, M-SH$^{-}$); HRMS: found 214.0816, M requires 214.0811; IR $\nu_{max}(\text{film})$/cm$^{-1}$ 2560 (w, SH); $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 7.42 (d, $J$ 7.6 Hz, 2H), 7.34-7.22 (m, 5H), 7.14 (d, $J$ 8.0 Hz, 2H), 5.44 (d, $J$ 4.8 Hz, 1H), 2.34 (s, 3H), 2.27 (d, $J$ 5.0 Hz, 1H); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 143.6, 140.5, 136.9, 129.2, 128.5, 127.8, 127.1, 47.5, 21.0.

7b: (4-Methoxyphenyl)phenylmethanethiol

General procedure I was followed using sodium ethoxide solution (0.09 cm$^3$, 0.23 mmol) and 6b (0.033 g, 0.12 mmol). The crude product was purified by flash column chromatography (n-pentane) and the title compound isolated as a colourless oil (0.031 g, 99 %). The title compound was also isolated from the following procedure:

n-Butyllithium (0.29 cm$^3$, 1.5 M in hexanes, 0.44 mmol) was added to a solution of diisopropylamine (0.07 cm$^3$, 0.52 mmol) in THF (1 cm$^3$) at 0 °C. This was stirred for 15 minutes and then cooled to -78 °C. This solution was added by cannula to a cooled (-78 °C) solution of 5b (0.055 g, 0.19 mmol) in THF (1 cm$^3$) and DMPU (0.5 cm$^3$). The mixture was allowed to stir for 2 hours. Methanol (1 cm$^3$) was added and the mixture allowed to warm to room temperature. Water (10 cm$^3$) and diethyl ether (10 cm$^3$) were added and the phases separated. The aqueous fraction was extracted with diethyl ether (2 x 10 cm$^3$) and the combined organic fractions dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was then purified by flash column chromatography (petrol/EtOAc, 15:1) to afford the title compound as a colourless oil (0.027 g, 62 %). $R_F$: 0.40 (8:1, Petrol:EtOAc); MS m/z (EI) 229 (20%, M-H$^-$); HRMS: found 229.0685, M-H$^-$ requires 229.0682; IR $\nu_{max}(\text{film})$/cm$^{-1}$ 2559 (w, S-H); $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 7.42 (d, $J$ 4.0 Hz, 2H), 7.35-7.32 (m, 4H), 7.26-7.23 (m, 1H), 6.86 (d, $J$ 4.0 Hz, 2H), 5.44 (d, $J$ 4.0 Hz, 1H), 3.80 (s, 3H), 2.27 (d, $J$ 4.0 Hz, 1H); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 157.6, 142.7, 134.5, 127.9, 127.5, 126.7, 126.1, 112.8, 54.3, 46.2.

7c: (4-tert-Butylphenyl)phenylmethanethiol

General procedure I was followed using sodium ethoxide solution (0.07 cm$^3$, 0.18 mmol) and 6c (0.028 g, 0.09 mmol). The crude product was purified by flash column chromatography (n-pentane) and the title compound isolated as a colourless oil (0.018 g, 78 %). $R_F$: 0.54 (8:1, Petrol:EtOAc); MS m/z (EI) 223 (100%, M-SH$^{-}$); HRMS: found 223.1472, M-SH$^{-}$ requires 223.1481; IR $\nu_{max}(\text{film})$/cm$^{-1}$ 2558 (w, SH); $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 7.37 (d, $J$ 7.3 Hz, 2H), 7.32-7.11 (m, 7H), 5.37 (d, $J$ 4.0 Hz, 1H), 2.22 (d, $J$ 5.0 Hz, 1H), 1.24 (s, 9H); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 149.0, 142.5, 139.2, 127.5, 126.8, 126.3, 126.1, 124.4, 46.4, 33.4, 30.3.
n-Butyllithium (0.17 cm³, 0.43 mmol, 2.5 M in hexanes) was added to a solution of disopropylamine (0.07 cm³, 0.51 mmol) in THF (1 cm³) at 0 °C. This was stirred for 15 minutes and then cooled to -60 °C. This solution was added by cannular to a cooled (-60 °C) solution of 5d (0.053 g, 0.17 mmol) in THF (1 cm³) and DMPU (0.5 cm³). The mixture was allowed to stir for 15 hours. Propionic acid (0.04 cm³, 0.51 mmol) was added and the mixture allowed to warm to room temperature. Water (10 cm³) and diethyl ether (10 cm³) were added and the phases separated. The aqueous fraction was extracted with diethyl ether (2 x 10 cm³) and the combined organic fractions dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was then purified by flash column chromatography (petrol) to afford the title compound as a colourless oil (0.017 g, 41 %). 

The mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as a colourless oil (0.376 g, 79 %).

Methyl p-tolylthiocarbamic acid S-(S)-1-phenylethyl ester

General procedure C was followed using s3 (0.302 g, 1.67 mmol) and lithium aluminium hydride (1.67 cm³, 1.67 mmol, 1 M in THF) in diethyl ether (7 cm³) followed by s18 (0.585 g, 1.64 mmol) and triethylamine (0.23 cm³, 1.64 mmol) in DCM (10 cm³) with stirring for 24 hours. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as an amorphous white solid (0.376 g, 79 %). Rf: 0.30 (8:1, Petrol:EtoAc); [α]D 22: -8.4° (c. 1.1, CHCl3); Mpt: 76-78 °C (DCM); MS m/z (ES+) 286 (20%, M+H+), 308 (100%, M+Na+); HRMS: found 286.1268, M+Na+ requires 286.1266; IR νmax(film)/cm⁻¹ 1656 (C=O); 'H-NMR (CDCl3, 400 MHz) δ 7.33-7.11 (m, 9H), 4.67 (q, J 7.1 Hz, 1H), 3.28 (s, 3H), 2.36 (s, 3H), 1.63 (d, J 7.1 Hz, 3H); ¹³C-NMR (CDCl3, 100 MHz) δ 168.3, 143.4, 139.3, 130.1, 128.4, 128.1, 127.4, 127.0, 44.9, 38.3, 22.9, 21.2; HPLC: er 98:2, General conditions I: t 5.2 (maj), 6.0 (min).

(4-Methoxyphenyl)methylthiocarbamic acid S-((S)-1-phenylethyl) ester

General procedure C was followed using s3 (0.246 g, 1.34 mmol) and lithium aluminium hydride (1.34 cm³, 1.34 mmol, 1 M in THF) in diethyl ether (9 cm³) followed by s20 (0.483 g, 1.3 mmol) and triethylamine (0.18 cm³, 1.3 mmol) in DCM (10 cm³) with stirring for 26 hours. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 19:1) and the title compound isolated as a colourless oil (0.250 g, 62 %). Rf: 0.35 (8:1, Petrol:EtoAc); [α]D 21: 4.9° (c. 1.1, CHCl3); MS m/z (ES+) 302 (5%, M+H+); HRMS: found 302.1201, M+H+ requires 302.1209; IR νmax(film)/cm⁻¹ 1651 (C=O); 'H-NMR (CDCl3, 500 MHz) δ 7.34-7.18 (m, 5H), 7.15 (d, J 8.8 Hz, 2H), 6.88 (d, J 8.8 Hz, 2H), 4.66 (q, J 7.1 Hz, 1H), 3.81 (s, 3H), 3.27 (s, 3H), 1.62 (d, J 7.1 Hz, 3H); ¹³C-NMR (CDCl3, 100 MHz) δ 168.6, 143.4, 129.8, 129.7, 128.4, 127.4, 127.0, 114.6, 55.4, 44.9, 38.4, 23.0; HPLC: er 96:4, General conditions I: t 7.7 (maj), 8.8 (min).
8c: (2-Methoxyphenyl)methylthiocarbamic acid S-((S)-1-phenylethyl) ester

General procedure C was followed using s3 (0.270 g, 1.50 mmol) and lithium aluminium hydride (1.50 cm³, 1.50 mmol, 1 M in THF) in diethyl ether (7 cm³) followed by s21 (0.560 g, 1.50 mmol) and triethylamine (0.21 cm³, 1.50 mmol) in DCM (10 cm³) with stirring for 18 h. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as an amorphous white solid (0.283 g, 92%). \( R_F \): 0.17 (8:1, Petrol:EtOAc); \( [\alpha]_D^{22} \): -18° (c. 1.6, CHCl₃); \( \text{Mpt} \): 97-99 °C (petrol); \( \text{MS} \) m/z (ES+) 324 (100%, M+Na⁺); \( \text{HRMS} \): found 324.1022, M+Na⁺ requires 324.1029; \( \text{IR} \) \( \nu_{\max}(\text{film})/\text{cm}^{-1} \) 1656 (C=O); mixture of 2 rotamers \( ^1\text{H-NMR} \) (CDCl₃, 400 MHz) \( \delta \): 7.5 (min), 6.95 (maj), 7.9 (min). \( \nu_{\max}(\text{film})/\text{cm}^{-1} \) 1656 (C=O);

8d: (4-Chlorophenyl)methylthiocarbamic acid S-((S)-1-phenylethyl) ester

General procedure C was followed using s3 (0.482 g, 2.68 mmol) and lithium aluminium hydride (2.68 cm³, 2.68 mmol, 1 M in THF) in diethyl ether (10 cm³) followed by s22 (1.015 g, 2.70 mmol) and triethylamine (0.38 cm³, 2.70 mmol) in DCM (10 cm³) with stirring for 18 hours. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as an amorphous white solid (0.596 g, 73%). \( R_F \): 0.29 (8:1, Petrol:EtOAc); \( [\alpha]_D^{22} \): -6.5° (c. 1.1, CHCl₃); \( \text{MS} \) m/z (ES+) 328 (100%, M+Na⁺); \( \text{HRMS} \): found 328.0533, M+Na⁺ requires 328.0533; \( \text{IR} \) \( \nu_{\max}(\text{film})/\text{cm}^{-1} \) 1656 (C=O); \( ^1\text{H-NMR} \) (CDCl₃, 400 MHz) \( \delta \): 7.15 (m, 1H), 3.20 (s, 3H), 1.56 (d, \( J=7.2 \text{Hz} \), 3H); \( ^{13}\text{C-NMR} \) (CDCl₃, 100 MHz) \( \delta \): 169.0, 168.9, 156.2, 156.1, 143.6, 143.5, 130.8, 130.7, 130.1, 130.0, 128.4, 128.3, 127.4, 127.3, 126.9, 126.8, 120.8, 120.7, 112.2, 112.2, 55.7, 55.5, 44.6, 44.6, 36.8, 23.0, 22.9; \( \text{HPLC} \): er 97:3, General conditions I: \( t \), 9.1 (min), 10.9 (maj).
8f: (4-Cyanophenyl)methylthiocarbamic acid (S)-1-phenylethyl ester

General procedure C was followed using s3 (0.192 g, 1.00 mmol) and lithium aluminium hydride (1.00 cm³, 1.00 mmol, 1 M in THF) in diethyl ether (7 cm³) followed by s24 (0.405 g, 1.10 mmol), triethylamine (0.17 cm³, 1.20 mmol) and DCM (10 cm³) with stirring for 18 h. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as colourless prisms (0.238 g, 77%). Rf: 0.10 (petrol/EtOAc, 8:1); [α]D^22: -12.0º (c. 1, CHCl₃); Mpt: 98-100 ºC (DCM); MS m/z (ES+) 319 (100%, M+Na^+); HRMS: found 319.0866, M+Na^+ requires 319.0876; IR νmax (film)/cm⁻¹ 1654 (C=O); 'H-NMR (CDCl₃, 400 MHz) δ 7.84 (d, J 8.4 Hz, 2H), 7.41 (d, J 8.4 Hz, 2H), 7.36 - 7.22 (m, 5H), 4.72 (q, J 7.2 Hz, 1H), 3.34 (s, 3H) and 1.68 (d, J 7.2 Hz, 3H); ^13C-NMR (CDCl₃, 100 MHz) δ 168.1, 146.3, 142.7, 133.3, 128.6, 128.1, 127.3, 127.3, 118.2, 45.3, 37.7, 22.8; HPLC: er 98:2, General conditions I: t, 14.4 (maj), 18.9 (min).

8g: Methyl(2,4,6-trimethylphenyl)thiocarbamic acid (S)-1-phenyl-ethyl ester

General procedure C was followed using s3 (0.186 g, 1.03 mmol) and lithium aluminium hydride (1.03 cm³, 1.03 mmol, 1 M in THF) in diethyl ether (7 cm³) followed by s25 (0.423 g, 1.10 mmol), triethylamine (0.17 cm³, 1.20 mmol) and DCM (10 cm³) with stirring for 20 h. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as colourless prisms (0.185 g, 55%). Rf: 0.10 (petrol/EtOAc, 8:1); [α]D^22: -3.9º (c. 0.9, CHCl₃); Mpt: 45-47 ºC (DCM); MS m/z (ES+) 336 (100%, M+Na^+); HRMS: found 336.1394, M+Na^+ requires 336.1393; IR νmax (film)/cm⁻¹ 1656 (C=O); 'H-NMR (CDCl₃, 400 MHz) δ 7.33 - 7.16 (m, 5H), 6.93 (s, 1H), 6.88 (s, 1H), 4.67 (q, J 7.2 Hz, 1H), 3.16 (s, 3H), 2.29 (s, 3H), 2.23 (s, 3H), 2.07 (s, 3H) and 1.61 (d, J 7.2 Hz, 3H); ^13C-NMR (CDCl₃, 100 MHz) δ 168.5, 143.5, 138.8, 137.0, 136.8, 136.2, 129.6, 129.5, 128.3, 127.4, 126.9, 44.3, 35.3, 22.8, 21.1, 17.6, 17.5. Conditions for resolution on chiral HPLC were not found.

8h: Methylanaphthalen-1-ylthiocarbamic acid (S)-1-phenylethyl ester

General procedure C was followed using s3 (0.209 g, 1.16 mmol) and lithium aluminium hydride (1.16 cm³, 1.16 mmol, 1 M in THF) in diethyl ether (7 cm³) followed by s26 (0.501 g, 1.27 mmol), triethylamine (0.18 cm³, 1.27 mmol) and DCM (10 cm³) with stirring for 15 hours. The crude mixture was purified by flash column chromatography (petrol/DCM, 9:1) to afford the title compound as an amorphous white solid (0.274 g, 73 %). Rf: 0.06 (9:1, Petrol:DCM); [α]D^21: +1º (c. 1.2, CHCl₃); Mpt: 87-89 ºC (DCM); MS m/z (ES+) 344 (100%, M+Na^+); HRMS: found 344.1068, M+Na^+ requires 344.1080; IR νmax (film)/cm⁻¹ 1654 (C=O); mixture of 2 rotamers 'H-NMR (CDCl₃, 500 MHz) δ 7.96-7.84 (m, 4H), 7.68-7.35 (m, 10H), 7.29-7.17 (m, 10H), 4.72-7.65 (m, 2H), 3.42 (s, 3H), 3.40 (s, 3H), 1.60-1.52 (m, 6H); ^13C-NMR (CDCl₃, 75.5 MHz) δ 169.2, 143.4, 143.3, 134.7, 134.7, 128.4, 127.4, 126.9, 125.4, 122.6, 122.5, 44.9, 44.8, 38.1, 22.9, 22.8; HPLC: er 97:3, General conditions III: t, 7.8 (min), 9.7 (maj).
18

8i: Methyl(2,4,6-trimethylphenyl)thiocarbamic acid (S)-1-phenylethyl ester

General procedure C was followed using s3 (0.191 g, 0.40 mmol) and lithium aluminium hydride (0.36 cm³, 0.36 mmol, 1 M in THF) in diethyl ether (5 cm³) followed by s18 (0.144 g, 0.40 mmol), triethylamine (0.06 cm³, 0.43 mmol) and DCM (10 cm³) with stirring for 18 h. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as a colourless prisms (0.075 g, 69%). Rf: 0.33 (petrol/EtOAc, 8:1); [α]D20: 29.4° (c. 2.2, CHCl₃); Mpt: 37-39 °C (DCM); MS m/z (ES+) 336 (100%, M+Na⁺), 314 (15%, M+H⁺); HRMS: found 336.0815, M+Na⁺; IR νmax(film)/cm⁻¹: 7.38 - 7.21 (m, 6H), 7.08 - 6.98 (m, 3H), 4.70 (q, J 7.2 Hz, 1H), 3.31 (s, 3H) and 1.66 (d, J 7.2 Hz, 3H); ¹H-NMR (CDCl₃, 400 MHz) δ 7.21 (m, 6H), 7.08 (m, 4H), 7.25 (m, 2H), 4.74 (q, J 6.6, 8.8 Hz, 1H), 3.27 (s, 3H), 2.37 (s, 3H), 1.97-1.79 (m, 2H), 1.38-1.15 (m, 3H), 0.87 (t, J 7.3 Hz, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ 167.4, 141.6, 129.0, 127.4, 127.3, 127.1, 126.8, 125.8, 48.8, 38.0, 37.3, 20.2, 19.8, 12.7; HPLC: er 99:1, General conditions III: t, 5.2 (maj), 6.1 (min).

8j: Methyl-p-tolylthiocarbamic acid S-((R)-1-phenylbutyl) ester

General procedure C was followed using s4 (0.075 g, 0.36 mmol) and lithium aluminium hydride (0.36 cm³, 0.36 mmol, 1 M in THF) in diethyl ether (5 cm³) followed by s18 (0.144 g, 0.40 mmol), triethylamine (0.06 cm³, 0.43 mmol) and DCM (10 cm³) with stirring for 18 h. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as colourless prisms (0.078 g, 69%). Rf: 0.33 (petrol/EtOAc, 8:1); [α]D20: 29.4° (c. 2.2, CHCl₃); Mpt: 37-39 °C (DCM); MS m/z (ES+) 336 (100%, M+Na⁺), 314 (15%, M+H⁺); HRMS: found 336.1393, M+Na⁺ requires 336.1393; IR νmax(film)/cm⁻¹ 1649 (C=O); ¹H-NMR (CDCl₃, 400 MHz) δ 7.34 - 7.25 (m, 4H), 7.23-7.18 (m, 3H), 7.11 (d, J 8.3 Hz, 2H), 4.52 (dd, J 6.6, 8.8 Hz, 1H), 3.27 (s, 3H), 2.37 (s, 3H), 1.97-1.79 (m, 2H), 1.38-1.15 (m, 3H), 0.87 (t, J 7.3 Hz, 3H); ¹³C-NMR (CDCl₃, 100 MHz) δ 167.4, 141.6, 129.0, 127.4, 127.3, 127.1, 126.8, 125.8, 48.8, 38.0, 37.3, 20.2, 19.8, 12.7; HPLC: er 99:1, General conditions III: t, 5.2 (maj), 6.1 (min).

8k: Methyl(3-trifluoromethylphenyl)thiocarbamic acid (R)-1-phenylethyl ester

General procedure C was followed using s5 (0.399 g, 1.59 mmol) and lithium aluminium hydride (1.60 cm³, 1.60 mmol, 1 M in THF) in diethyl ether (8 cm³) followed by s19 (0.600 g, 1.75 mmol) and triethylamine (0.27 cm³, 1.91 mmol) in DCM (10 cm³) with stirring for 18 hours. The crude mixture was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as an amorphous white solid (0.436 g, 80%). Rf: 0.17 (8:1, Petrol/EtOAc); [α]D20: -18° (c. 1.6, CHCl₃); Mpt: 97-99 °C (petrol); MS m/z (ES+) 324 (100%, M+Na⁺); HRMS: found 324.1022, M+Na⁺ requires 324.1029; IR νmax(film)/cm⁻¹ 1656 (C=O); ¹H-NMR (CDCl₃, 500 MHz) δ 7.59 (br s, 1H), 7.53 (d, J 7.6 Hz, 1H), 7.47 (d, J 7.9 Hz, 1H), 7.43-7.36 (m, 4H), 7.26-7.25 (m, 2H), 4.74 (q, J 7 Hz, 1H), 3.31 (s, 3H), 1.63 (d, J 7.3 Hz, 3H); ¹³C-NMR (CDCl₃, 75.5 MHz) δ 167.7, 144.8, 141.9, 131.0, 131.0, 130.5, 129.5, 128.8, 128.5, 128.3, 124.1-123.8 (m), 44.3, 38.3, 22.6; HPLC: er 96:4, General conditions I: t, 5.9 (min), 6.5 (maj).
8l: Methyl-\(\text{p}\)-tolylthiocarbamic acid 1-(4-methoxyphenyl)ethyl ester

Oxaly chloride (0.34 cm\(^3\), 4.00 mmol, 1 eq) was added to a stirred solution of DMF (0.33 cm\(^3\), 4.30 mmol, 1.1 eq) in DCM (10 cm\(^3\)) at 0 °C. The mixture was stirred for 5 min. (S)-1-(4-methoxyphenyl)ethanol (0.54 g, 3.60 mmol, 1 eq), triethylamine (1.10 cm\(^3\), 7.90 mmol, 2 eq) and ethanethioic S-acid (0.25 cm\(^3\), 3.60 mmol, 1 eq) were added sequentially. The mixture was warmed to room temperature and stirred for 18 h. Water (5 cm\(^3\)) was added, the phases separated and the aqueous layer extracted with EtOAc (3 x 10 cm\(^3\)). The combined organic fractions were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude thioacetate was dissolved in diethyl ether (7 cm\(^3\)) and the title compound isolated as a waxy colourless oil (0.954 g, 52 %). HRMS: found 320.1074, M+Na\(^+\) requires 320.1080; \(\Delta\nu_{\text{max}}(\text{film})/\text{cm}^{-1}\) 1649 (C=O); \(\nu\text{C-NMR} (\text{CDCl}_3, 75.5 \text{MHz}) \delta\) 168.5, 125.5, 135.4, 130.1, 128.5, 113.7, 55.2, 44.4, 38.3, 23.0, 21.2.

Optically pure (S)-1-(4-methoxy-phenyl)-ethanol was used in this procedure. The product, however, was isolated as a racemic mixture. It is though that the electron rich nature of the benzylic ring promotes S\(_N1\) nucleophilic addition of ethanethioic S-acid over the desired S\(_N2\) mechanism.

8m: Methyl-\(\text{p}\)-tolylthiocarbamic acid (S)-inden-1-yl ester

Oxaly chloride (0.54 cm\(^3\), 6.16 mmol, 1 eq) was added to a stirred solution of DMF (0.52 cm\(^3\), 6.77 mmol, 1.1 eq) in DCM (50 cm\(^3\)) at 0 °C. The mixture was stirred for 5 min. (R)-inden-1-ol (0.83 g, 6.16 mmol, 1 eq), triethylamine (1.72 cm\(^3\), 12.3 mmol, 2 eq) and ethanethioic S-acid (0.44 cm\(^3\), 6.16 mmol, 1 eq) were added sequentially. The mixture was warmed to room temperature and stirred for 18 h. Water (20 cm\(^3\)) was added, the phases separated and the aqueous layer extracted with EtOAc (3 x 10 cm\(^3\)). The combined organic fractions were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude thioacetate was dissolved in diethyl ether (20 cm\(^3\)). Lithium aluminium hydride (6.16 cm\(^3\), 1 M in THF, 6.16 mmol, 1 eq) was added dropwise. The mixture was heated to reflux with stirring for 1.5 h then cooled to room temperature. Aqueous HCl (3 cm\(^3\), 1 M) was added with care. The phases were separated and the aqueous layer extracted with diethyl ether (3 x 10 cm\(^3\)). The combined organic fractions were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude thiol was then dissolved in DCM (10 cm\(^3\)). \(\text{8l} (0.283 g, 0.79 mmol, 1.1 eq) and triethylamine (0.11 cm\(^3\), 0.80 mmol, 1.2 eq) were added and the mixture was stirred for 72 h. The mixture was washed with aqueous HCl (2 x 7 cm\(^3\), 1M), dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as a yellow oil (0.954 g, 52 %). \(\text{Rf}\) 0.19 (8:1, Petrol:EtOAc); \(\text{MS m/z (ES+)}\) 338 (100%, M+Na\(^+\)), 316 (20%, M+H\(^+\)); \(\text{IR }\nu_{\text{max}}(\text{film})/\text{cm}^{-1}\) 1654 (C=O); \(\text{H-NMR} (\text{CDCl}_3, 400 \text{MHz}) \delta\) 7.25 (d, J 8.8 Hz, 2H), 7.18 (d, J 8.1 Hz, 2H), 7.12 (d, J 8.6 Hz, 2H), 6.80 (d, J 8.8 Hz, 2H), 4.65 (q, J 7.3 Hz, 1H), 3.77 (s, 3H), 3.29 (s, 3H), 2.36 (s, 3H), 1.62 (d, J 7.3 Hz, 3H); \(\text{\(^{13}\text{C-NMR} (\text{CDCl}_3, 75.5 \text{MHz}) \delta\) 168.5, 125.5, 135.4, 130.1, 128.5, 113.7, 55.2, 44.4, 38.3, 23.0, 21.2.\)
(C=O); \textsuperscript{1}H-NMR (CDCl\textsubscript{3}, 400 MHz) \(\delta\) 7.34-7.32 (m, 1H), 7.25-7.12 (m, 7H), 5.01 (dd, J 4.8, 7.6 Hz, 1H), 3.35 (s, 3H), 3.03-2.95 (m, 1H), 2.89-2.82 (m, 1H), 2.70-2.61 (m, 1H), 2.36 (s, 3H), 2.18-2.10 (m, 1H); \textsuperscript{13}C-NMR (CDCl\textsubscript{3}, 100 MHz) \(\delta\) 169.1, 143.9, 142.4, 139.5, 130.3, 130.1, 128.1, 127.6, 126.6, 125.1, 124.5, 49.6, 38.3, 34.7, 30.9, 21.2; HPLC: er 79:21, General conditions I: \(\tau\), 7.3 (maj), 8.7 (min).

9a: Methylthiocarbamic acid (S)-1-phenyl-1-\(p\)-tolylethyl ester

General procedure G was followed using \(n\)-BuLi (0.18 cm\(^3\), 0.44 mmol, 2.5 M in hexanes), TMP (0.09 cm\(^3\), 0.53 mmol), \(8a\) (0.050 g, 0.18 mmol) and propionic acid (0.04 cm\(^3\), 0.53 mmol). The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as an amorphous white solid (0.042 g, 83%).

9b: (\(\pm\))-Methylthiocarbamic acid 1-(4-methoxyphenyl)-1-phenylethyl ester

General procedure F was followed using \(8b\) (0.021 g, 0.07 mmol), diisopropylamine (0.03 cm\(^3\), 0.21 mmol), \(n\)-BuLi (0.09 cm\(^3\), 2.0 M, 0.18 mmol) and propionic acid (0.02 cm\(^3\), 0.27 mmol) with stirring for 4 hours. The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) to afford the title compound as an amorphous white solid (0.044 g, 89%).

9c: Methylthiocarbamic acid (S)-1-(2-methoxyphenyl)-1-phenylethyl ester

General procedure G was followed using \(n\)-BuLi (0.17 cm\(^3\), 0.42 mmol, 2.5 M in hexanes), TMP (0.09 cm\(^3\), 0.50 mmol), \(8c\) (0.049 g, 0.17 mmol) and propionic acid (0.04 cm\(^3\), 0.53 mmol). The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as an amorphous white solid (0.044 g, 89%).
9d: Methylthiocarbamic acid (S)-1-(4 chlorophenyl)-1-phenylethyl ester

General procedure G was followed using n-BuLi (0.17 cm³, 0.41 mmol, 2.5 M in hexanes), TMP (0.08 cm³, 0.49 mmol), 8d (0.046 g, 0.16 mmol) and propionic acid (0.04 cm³, 0.53 mmol). The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as an amorphous white solid (0.044 g, 94%). \( R_f \): 0.07 (8:1, Petrol:EtOAc); \( [\alpha]_D^{22} \) -18.8° (c. 1.5, CHCl₃); MS m/z (ES⁺) 328 (100%, M⁺Na⁺); HRMS: found 328.0527, M+Na⁺ requires 328.0533; IR \( \nu_{\text{max}} \)(film)/cm⁻¹ 1660 (C=O); \( ^{1}H\)-NMR (CDCl₃, 400 MHz) δ 7.40-7.23 (m, 9H), 5.27 (d, J 4.5 Hz, 3H), 2.76 (s, 3H); \( ^{13}C\)-NMR (CDCl₃, 125 MHz) δ 151.0, 144.5, 131.8, 129.0, 128.4, 127.5, 118.8, 110.6, 59.3, 29.8, 27.6; HPLC: er 96:4, General conditions II: tₚ 8.9 (maj), 10.7 (min).

9e: Methylthiocarbamic acid (S)-1-(3-chlorophenyl)-1-phenylethyl ester

General procedure G was followed using n-BuLi (0.17 cm³, 0.41 mmol, 2.5 M in hexanes), TMP (0.08 cm³, 0.49 mmol), 8e (0.049 g, 0.16 mmol) and propionic acid (0.04 cm³, 0.53 mmol). The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as a colourless oil (0.037 g, 78%). \( R_f \): 0.10 (8:1, Petrol:EtOAc); \( [\alpha]_D^{22} \) -10.3° (c. 0.9, CHCl₃); MS m/z (ES⁺) 328 (100%, M⁺Na⁺); HRMS: found 328.0531, M+Na⁺ requires 328.0533; IR \( \nu_{\text{max}} \)(film)/cm⁻¹ 1651 (C=O); \( ^{1}H\)-NMR (CDCl₃, 400 MHz) δ 7.37-7.21 (m, 8H), 5.21 (br s, 1H), 2.76 (d, J 4.8 Hz, 3H), 2.38 (s, 3H); \( ^{13}C\)-NMR (CDCl₃, 75.5 MHz) δ 165.7, 147.6, 144.9, 134.0, 129.2, 128.3, 128.2, 127.7, 127.2, 127.1, 126.2, 59.2, 30.0, 27.6; HPLC: er 96:4, General conditions II: tₚ 11.0 (min), 15.9 (maj).

9f: Methylthiocarbamic acid (S)-1-(4-cyanophenyl)-1-phenylethyl ester

General procedure G was followed using n-BuLi (0.17 cm³, 0.42 mmol, 2.5 M in hexanes), TMP (0.09 cm³, 0.51 mmol), 8f (0.048 g, 0.17 mmol) and propionic acid (0.04 cm³, 0.53 mmol). The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as an amorphous white solid (0.038 g, 69%). \( R_f \): 0.10 (8:1, Petrol:EtOAc); \( [\alpha]_D^{22} \) -3.8° (c. 1.6, CHCl₃); MS m/z (ES⁺) 319 (80%, M⁺Na⁺); HRMS: found 319.0875, M+Na⁺ requires 319.0876; IR \( \nu_{\text{max}} \)(film)/cm⁻¹ 2227 (CN), 1674 (C=O); \( ^{1}H\)-NMR (CDCl₃, 500 MHz) δ 7.61 (s, 4H), 7.34-7.24 (m, 5H), 5.25 (br s, 1H), 2.76 (d, J 4.5 Hz, 3H), 2.38 (s, 3H); \( ^{13}C\)-NMR (CDCl₃, 125 MHz) δ 151.0, 144.5, 131.8, 129.0, 128.4, 127.5, 118.8, 110.6, 59.3, 29.8, 27.6; HPLC: er 97:3, General conditions II: tₚ 12.3 (min), 13.8 (maj).

9h: Methylthiocarbamic acid (S)-1-naphthalen-1-yl-1-phenylethyl ester

General procedure G was followed using n-BuLi (0.19 cm³, 0.40 mmol, 2.12 M in hexanes), TMP (0.08 cm³, 0.48 mmol), 8h (0.052 g, 0.16 mmol) and propionic acid (0.04 cm³, 0.53 mmol). The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as an amorphous white solid (0.051 g, 98%). \( R_f \): 0.07 (8:1, Petrol:EtOAc); \( [\alpha]_D^{21} \) -218.6° (c. 0.3, CHCl₃); Mpt: 59-61 °C (DCM); MS m/z (ES⁺) 344 (100%, M⁺Na⁺); HRMS: found 322.1252, M+H⁺ requires 322.1260; IR \( \nu_{\text{max}} \)(film)/cm⁻¹ 1667 (C=O); \( ^{1}H\)-NMR (CDCl₃,
500 MHz) δ 7.96 (d, J 7.3 Hz, 1H), 7.84 (ap t, J 8.6 Hz, 2H), 7.71 (d, J 8.8 Hz, 1H), 7.54 (ap t, J 7.7 Hz, 1H), 7.36-7.30 (m, 3H), 7.27-7.15 (m, 4H), 5.11 (br s, 1H), 2.61 (d, J 4.1 Hz, 3H), 2.52 (s, 3H); \(^1\)C-NMR (CDCl\(_3\), 125 MHz) δ 165.8, 147.0, 138.9, 135.0, 130.5, 129.3, 129.0, 128.5, 128.1, 126.8, 126.6, 124.9, 124.6, 124.5, 60.2, 33.0, 27.4; HPLC: er 96:4, General conditions II: t 9.1 (maj), 10.0 (min).

9j: Methylthiocarbamic acid (R)-1-phenyl-1-p-tolybutyl ester

General procedure G was followed using n-BuLi (0.16 cm\(^3\), 0.41 mmol, 2.5 M in hexanes), TMP (0.08 cm\(^3\), 0.49 mmol), 8j (0.051 g, 0.16 mmol) and propionic acid (0.04 cm\(^3\), 0.49 mmol). The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as an amorphous white solid (0.038 g, 74%). \(R_F\): 0.12 (8:1, Petrol:EtOAc); [\(\alpha\)]\(^D\): -2.0º (c 1, CHCl\(_3\)); \(\text{Mpt:} 97-99 \degree \text{C} \) (petrol); MS m/z (ES\(^+\)) 336 (100%, M+Na\(^+\)); HRMS: found 336.1401, M+Na\(^+\) requires 336.1393; IR \(\nu_{\text{max}}\) (film)/cm\(^{-1}\) 1659 (C=O); \(\text{\(^1\)H-NMR} \) (CDCl\(_3\), 400 MHz) δ 7.39 (d, J 7.3 Hz, 1H), 7.71 (m, 4H), 7.12 (d, J 7.8 Hz, 1H), 7.43 (ap t, J 7.8 Hz, 1H), 7.35-7.25 (m, 5H), 5.24 (br s, 1H), 2.75 (d, J 4.3 Hz, 3H), 2.42 (s, 3H); \(\text{\(^1\)C-NMR} \) (CDCl\(_3\), 100 MHz) δ 145.2, 142.0, 136.3, 128.4, 128.3, 127.7, 126.6, 63.6, 42.7, 21.0, 18.8, 14.3; HPLC: er 98:2, General conditions II: t 10.5 (min), 11.5 (maj).

9k: Methylthiocarbamic acid (S)-1-phenyl-1-(3-trifluoromethylphenyl)ethyl ester

General procedure G was followed using n-BuLi (0.15 cm\(^3\), 0.37 mmol, 2.5 M in hexanes), TMP (0.08 cm\(^3\), 0.44 mmol), 8k (0.053 g, 0.15 mmol) and propionic acid (0.04 cm\(^3\), 0.53 mmol). The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as an amorphous white solid (0.045 g, 85%). \(R_F\): 0.06 (8:1, Petrol:EtOAc); [\(\alpha\)]\(^D\)\(^{20}\): -5.4º (c 1.4, CHCl\(_3\)); \(\text{Mpt:} 82-84 \degree \text{C} \) (DCM); MS m/z (ES\(^+\)) 362 (100%, M+Na\(^+\)); HRMS: found 340.0976, M+H\(^+\) requires 340.0977; IR \(\nu_{\text{max}}\) (film)/cm\(^{-1}\) 1659 (C=O); \(\text{\(^1\)H-NMR} \) (CDCl\(_3\), 400 MHz) δ 7.45 (d, J 7.8 Hz, 1H), 7.64 (d, J 7.8 Hz, 1H), 7.51 (d, J 7.8 Hz, 1H), 7.43 (ap t, J 7.8 Hz, 1H), 7.35-7.25 (m, 5H), 5.24 (br s, 1H), 2.75 (d, J 4.3 Hz, 3H), 2.42 (s, 3H); \(\text{\(^1\)C-NMR} \) (CDCl\(_3\), 75.5 MHz) δ 165.6, 146.6, 144.8, 131.5, 130.5, 130.1, 128.5, 128.3, 127.6, 127.3, 124.7, 124.7, 123.8, 123.7, 59.3, 30.0, 27.6; HPLC: er 67:33, General conditions II: t 5.6 (min), 6.6 (maj).

9l: (±)-Methylthiocarbamic acid 1-(4-methoxyphenyl)-1-p-tolyethyl ester

General procedure E was followed using n-BuLi (0.22 cm\(^3\), 0.40 mmol, 1.8 M in hexanes), diisopropylamine (0.07 cm\(^3\), 0.48 mmol), 8l (0.040 g, 0.16 mmol) and propionic acid (0.04 cm\(^3\), 0.53 mmol). The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as a slightly yellow amorphous solid (0.034 g, 86%). \(R_F\): 0.06 (8:1, Petrol:EtOAc); \(\text{Mpt:} 91-93 \degree \text{C} \) (DCM); MS m/z (ES\(^+\)) 225 (100%, M-(SCONHCH\(_3\))) 338 (45%, M+Na\(^+\)); HRMS: found 338.1186, M+Na\(^+\) requires 338.1186; IR \(\nu_{\text{max}}\) (film)/cm\(^{-1}\) 1656 (C=O); \(\text{\(^1\)H-NMR} \) (CDCl\(_3\), 400 MHz) δ 7.35-7.29 (m, 4H), 7.12 (d, J 8.1 Hz, 2H), 6.84 (d, J 8.8 Hz, 2H), 5.20 (br d, J 3.5 Hz, 1H), 3.80 (s, 3H), 2.73 (d, J 4.5 Hz, 3H), 2.36 (s, 3H), 2.33 (s, 3H); \(\text{\(^1\)C-NMR} \) (CDCl\(_3\), 75.5 MHz) δ 166.6, 158.3, 142.7, 137.6, 136.6, 129.1, 128.8, 127.7, 113.4, 59.2, 55.2, 30.3, 27.5, 21.0.
9m: Methylthiocarbamic acid (R)-1-\textit{p}‐tolylindan-1-yl ester

General procedure G was followed using \textit{n}‐BuLi (0.18 cm$^3$, 0.40 mmol, 2.3 M in hexanes), TMP (0.06 cm$^3$, 0.48 mmol), \textbf{8m} (0.056 g, 0.16 mmol) and propionic acid (0.04 cm$^3$, 0.50 mmol). The crude product was purified by flash column chromatography (petrol/EtOAc, 8:1) and the title compound isolated as a colourless oil (0.013 g, 87%). $R_f$: 0.63 (9:1 Petrol/EtOAc); $[\alpha]_D^{21}:-3.6^\circ$ (c. 1.3, CHCl$_3$); \textbf{Mpt: 96–98 °C (DCM)}; \textbf{MS m/z (ES+)} 320 (100%, M+Na$^+$); \textbf{HRMS:} found 320.1086, M+Na$^+$ requires 320.1080; \textbf{IR $\nu$ (film)/cm$^{-1}$ 1654 (C=O); $^{1}$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 7.41–7.37 (m, 3H), 7.30–7.20 (m, 3H), 7.13 (d, $J$ 8.0 Hz, 2H), 5.20 (br s, 1H), 3.14-2.89 (m, 3H), 2.82-2.73 (m, 4H), 2.33 (s, 3H); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 145.7, 143.6, 140.8, 136.5, 128.9, 127.9, 127.3, 126.7, 125.7, 124.8, 66.1, 42.8, 30.5, 27.5, 21.0; \textbf{HPLC:} $t$ 74:26, General conditions II: $t$ 8.0 (min), 10.4 (maj).

10a: (S)-1-(4-Methylphenyl)-1-phenylethanol

General procedure I was followed using sodium ethoxide solution (0.08 cm$^3$, 0.21 mmol) and \textbf{9a} (0.029 g, 0.10 mmol). The crude product was purified by flash column chromatography (n-pentane) and the title compound isolated as a colourless oil (0.015 g, 63 %). $R_f$: 0.63 (9:1 Petrol/EtOAc); $[\alpha]_D^{21}:-3.6^\circ$ (c. 1.3, CHCl$_3$); \textbf{MS m/z (ES-)} 227 (100%, M-H$^-$); \textbf{HRMS:} found 227.0915, M-H$^-$ requires 227.0900; \textbf{IR $\nu$ (film)/cm$^{-1}$ 3256 (w, SH); $^{1}$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 7.42–7.38 (m, 2H), 7.19-7.30 (m, 5H), 7.08 (d, $J$ 8.0 Hz, 2H), 2.45 (s, 1H), 2.30 (s, 3H), 2.11 (s, 3H); $^{13}$C-NMR (CDCl$_3$, 125 MHz) $\delta$ 148.5, 145.4, 136.3, 128.8, 128.1, 127.1, 127.0, 126.6, 53.4, 34.8, 20.9.

10b: (±)-1-(4-Methoxyphenyl)-1-phenylethanol

General procedure I was followed using sodium ethoxide solution (0.02 cm$^3$, 0.07 mmol) and \textbf{9b} (0.018 g, 0.06 mmol). The crude product was purified by flash column chromatography (n-pentane) and the title compound isolated as a colourless oil (0.013 g, 94 %). $R_f$: 0.53 (8:1, Petrol:EtoAc); \textbf{MS m/z (EI)} 211 (100%, M-H$^+$); \textbf{HRMS:} found 211.1123, M-SH requires 211.1117; \textbf{IR $\nu$ (film)/cm$^{-1}$ 3258 (w, SH); $^{1}$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 7.46-7.43 (m, 2H), 7.37-7.21 (m, 5H), 6.84 (d, $J$ 8.8 Hz, 2H), 3.81 (s, 3H), 2.50 (s, 1H), 2.15 (s, 1H); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 158.2, 148.6, 140.5, 128.3, 128.1, 127.1, 126.6, 113.3, 55.3, 53.2, 35.0.

10c: (S)-1-(2-Methoxyphenyl)-1-phenylethanol

General procedure I was followed using sodium ethoxide solution (0.04 cm$^3$, 0.12 mmol) and \textbf{9c} (0.031 g, 0.10 mmol). The crude product was purified by flash column chromatography (n-pentane) and the title compound isolated as a colourless oil (0.024 g, 97 %). $R_f$: 0.49 (8:1, Petrol:EtoAc); $[\alpha]_D^{21}:-53.0^\circ$ (c. 1.7, CHCl$_3$); \textbf{MS m/z (ES-)} 243 (100%, M-H$^-$); \textbf{HRMS:} found 244.0922, M-H$^-$ requires 244.0916; \textbf{IR $\nu$ (film)/cm$^{-1}$ 2589 (w, SH); $^{1}$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 7.63 (dd, $J$ 7.8, 1.8 Hz, 1H), 7.43-7.40 (m, 2H), 7.31-7.15 (m, 4H), 7.03 (td, $J$ 7.6, 1.3 Hz, 1H), 6.87 (dd, $J$ 8.1, 1.0 Hz, 1H), 3.46 (s, 3H), 3.17 (q, $J$ 1.3 Hz, 1H), 2.04 (d, $J$ 1.3 Hz, 3H); $^{13}$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 157.0, 149.4, 136.5, 128.6, 127.7, 126.5, 125.8, 125.7, 120.5, 112.7, 55.3, 51.7, 32.9.

23
10d: (S)-1-(4-Chlorophenyl)-1-phenylethanethiol

General procedure I was followed using sodium ethoxide solution (0.06 cm$^3$, 0.16 mmol) and 9d (0.016 g, 0.05 mmol). The crude product was purified by flash column chromatography (n-pentane) and the title compound isolated as a colourless oil (0.012 g, 97 %). $R_F$: 0.63 (8:1, Petrol:EtOAc); $[\alpha]_D^{22}$: 5.1° (c. 0.8, CHCl$_3$); MS m/z (EI) 215 (100%, M-SH); HRMS: found 215.0622, M-SH$^+$ requires 215.0616; IR $\nu_{max}$(film)/cm$^{-1}$ 2557 (w, SH); $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 7.41-7.22 (m, 9H), 2.48 (s, 1H), 2.13 (s, 3H); $^1$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 146.7, 145.9, 135.1, 130.4, 128.9, 128.4, 127.8, 127.0, 125.9, 52.1, 37.3.

10e: (S)-1-(3-Chlorophenyl)-1-phenylethanethiol

General procedure H was followed using 8e (0.046 g, 0.16 mmol), n-butyllithium (0.26 cm$^3$, 0.41 mmol, 1.6 M in hexanes), TMP (0.08 cm$^3$, 0.41 mmol, 1.6 M in hexanes), and sodium ethoxide (0.05 cm$^3$, 0.16 mmol) and propionic acid (0.03 cm$^3$, 0.47 mmol) and sodium ethoxide (0.25 cm$^3$, 0.82 mmol, 21 % w/w in ethanol). The crude product was purified by column chromatography (petrol/EtOAc, 20:1) and the title compound isolated as a colourless oil (0.016 g, 41 %). $R_F$: 0.53 (8:1, Petrol:EtOAc); $[\alpha]_D^{22}$: 7.3° (c. 0.2, CHCl$_3$); MS m/z (ES-): 247 (100%, M-H$^+$); HRMS: found 247.0361, M-H$^+$ requires 247.0353; IR $\nu_{max}$(film)/cm$^{-1}$ 2292 (CH); $^1$H-NMR (CDCl$_3$, 500 MHz) $\delta$ 7.47 (s, 1H), 7.41 (d, J 7.9 Hz, 2H), 7.34-7.21 (m, 6H), 2.50 (s, 1H), 2.14 (s, 3H); $^1$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 150.6, 147.5, 134.0, 129.4, 128.3, 127.4, 127.0, 126.9, 125.6, 53.3, 34.5;

10f: 4-((S)-1-phenyl-1-sulfanyl ethyl)benzonitrile

General procedure I was followed using sodium ethoxide solution (0.05 cm$^3$, 0.17 mmol) and 9f (0.017 g, 0.06 mmol). The crude product was purified by flash column chromatography (n-pentane) and the title compound isolated as a colourless oil (0.013 g, 98 %). $R_F$: 0.40 (8:1, Petrol:EtOAc); $[\alpha]_D^{21}$: 7.8° (c. 1.3, CHCl$_3$); MS m/z (EI) 206 (100%, M-SH); HRMS: found 206.0967, M-SH$^+$ requires 206.0964; IR $\nu_{max}$(film)/cm$^{-1}$ 2228 (w, SH); $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 7.61 (d, J 8.8 Hz, 2H), 7.56 (d, J 8.8 Hz, 2H), 7.40-7.25 (m, 5H), 2.51 (s, 1H), 2.15 (s, 3H); $^1$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 153.9, 146.8, 132.0, 128.4, 128.0, 127.2, 126.9, 118.7, 110.6, 53.4, 34.3.

10h: (S)-1-Naphthalen-1-yl-1-phenylethanethiol

General procedure I was followed using sodium ethoxide solution (0.04 cm$^3$, 0.09 mmol) and 9h (0.015 g, 0.05 mmol). The crude product was purified by flash column chromatography (n-pentane) and the title compound isolated as a colourless oil (0.006 g, 51 %). $R_F$: 0.58 (8:1, Petrol:EtOAc); $[\alpha]_D^{22}$: -11.4° (c. 0.8, CHCl$_3$); MS m/z (EI) 231 (100%, M-SH); HRMS: found 231.1165, M-SH$^+$ requires 231.1168; IR $\nu_{max}$(film)/cm$^{-1}$ 2568 (w, SH); $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 7.92-7.90 (m, 1H), 7.84 (d, J 7.8 Hz, 2H), 7.62 (d, J 8.1 Hz, 1H), 7.54-7.50 (m, 1H), 7.44-7.42 (m, 2H), 7.38-7.34 (m, 1H), 7.27-7.17 (m, 4H), 2.78 (s, 1H), 2.26 (s, 3H); $^1$C-NMR (CDCl$_3$, 100 MHz) $\delta$ 148.9, 142.5, 135.1, 130.4, 128.9, 128.4, 127.8, 126.4, 126.1, 125.1, 124.8, 123.8, 53.8, 37.5.
10j: (R)-1-Phenyl-1-p-tolylbutane-1-thiol

General procedure I was followed using sodium ethoxide solution (0.02 cm$^3$, 0.05 mmol) and 9j (0.009 g, 0.03 mmol). The crude product was purified by flash column chromatography (n-pentane) and the title compound isolated as a colourless oil (0.007 g, 98 %). $R_f$: 0.72 (8:1, Petrol:EtOAc); [α]$^D_{20}$: -5.6° (c. 0.5, CHCl$_3$); MS m/z (EI) 223 (100%, M-H$_2$SH); HRMS: found 223.0812, M requires 223.0808; IR ν$_{max}$ (film)/cm$^{-1}$ 2954 (w, SH); $^1$H-NMR (CDCl$_3$, 500 MHz) δ 7.40-7.37 (m, 2H), 7.33-7.28 (m, 2H), 7.25-7.19 (m, 3H), 7.10 (d, J 8.1 Hz, 2H), 2.43-2.39 (m, 2H), 2.33 (s, 3H); $^13$C-NMR (CDCl$_3$, 100 MHz) δ 146.7, 143.7, 135.1, 127.6, 126.9, 126.6, 126.5, 125.4, 45.6, 28.7, 19.9, 17.8, 13.3.

10k: (S)-1-Phenyl-1-(3-trifluoromethylphenyl)ethanethiol

General procedure I was followed using sodium ethoxide solution (0.06 cm$^3$, 0.16 mmol) and 9k (0.027 g, 0.08 mmol). The crude product was purified by flash column chromatography (n-pentane) and the title compound isolated as a colourless oil (0.018 g, 76 %). $R_f$: 0.58 (8:1, Petrol:EtOAc); [α]$^D_{20}$: 2.5° (c. 1.8, CHCl$_3$); MS m/z (ES-) 281 (100%, M-H$^+$); HRMS: found 281.0614, M-H$^+$ requires 281.0617; IR ν$_{max}$ (film)/cm$^{-1}$ 2557 (w, SH); $^1$H-NMR (CDCl$_3$, 400 MHz) δ 7.77.9 (s, 1H), 7.58 (d, J 7.8 Hz, 1H), 7.51 (d, J 7.6 Hz, 1H), 7.44-7.40 (m, 3H), 7.33 (t, J 7.4 Hz, 2H), 7.28-7.25 (m, 1H), 2.54 (s, 1H), 2.18 (s, 3H); $^13$C-NMR (CDCl$_3$, 100 MHz) δ 149.5, 147.3, 130.9, 130.3, 128.6, 128.4, 127.1, 127.0, 123.7, 123.6, 122.8, 53.3, 34.6, 29.7.

10l: (±)-1-(4-Methoxyphenyl)-1-p-tolylethanethiol

General procedure I was followed using sodium ethoxide solution (0.05 cm$^3$, 0.13 mmol) and 9l 0.020 g, 0.06 mmol). The crude product was purified by flash column chromatography (n-pentane) and the title compound isolated as a colourless oil (0.012 g, 75 %). $R_f$: 0.59 (8:1, Petrol:EtOAc); MS m/z (EI) 224 (90%, M-H$_2$SH); HRMS: found 2241.199, M-H$_2$SH requires 2241.1996; IR ν$_{max}$ (film)/cm$^{-1}$ 2553 (w, SH); $^1$H-NMR (CDCl$_3$, 400 MHz) δ 7.36 (d, J 8.8 Hz, 2H), 7.33 (d, J 8.3 Hz, 2H), 7.12 (d, J 8.1 Hz, 2H), 6.83 (d, J 9.1 Hz, 2H), 3.81 (s, 3H), 2.48 (s, 1H), 2.34 (s, 3H), 2.14 (s, 3H); $^13$C-NMR (CDCl$_3$, 100 MHz) δ 157.1, 144.6, 139.6, 135.2, 127.7, 127.2, 125.9, 112.2, 54.2, 52.0, 34.0, 19.9.

10m: (R)-1-p-Tolylinadan-1-thiol

General procedure I was followed using sodium ethoxide solution (0.05 cm$^3$, 0.12 mmol) and 9m (0.018 g, 0.06 mmol). The crude product was purified by flash column chromatography (n-pentane) and the title compound isolated as a colourless oil (0.013 g, 99 %). $R_f$: 0.57 (8:1, Petrol:EtOAc); [α]$^D_{20}$: -10.0° (c. 1.3, CHCl$_3$); MS m/z (EI) 206 (100%, M-H$_2$S); HRMS: found 206.1090, M-H$_2$S requires 206.1090; IR ν$_{max}$ (film)/cm$^{-1}$ 2563 (w, SH); $^1$H-NMR (CDCl$_3$, 400 MHz) δ 7.37-7.30 (m, 6H), 7.12 (d, J 8.1 Hz, 2H), 3.07 (ddd, J 15.6, 7.6, 6.8 Hz, 1H), 2.88 (ddd, J 15.6, 7.3, 6.3 Hz, 1H), 2.73 (ddd, J 13.1, 7.6, 6.3 Hz, 1H), 2.57 (ddd, J 13.6, 7.8, 6.1 Hz, 1H), 2.36 (s, 1H), 2.34 (s, 3H); $^13$C-NMR (CDCl$_3$, 100 MHz) δ 149.2, 143.1, 142.5, 136.5, 128.8, 127.5, 127.1, 127.0, 124.9, 124.7, 60.2, 48.0, 30.4, 20.9.
11: 4-Nitrothiobenzoic acid S-((S)-1-phenyl-1-p-tolylethyl) ester

Sodium hydride (0.004 g, 0.10 mmol, 60 % in mineral oil) was added to a solution of 10a (0.015 g, 0.06 mmol) in THF (3 cm$^3$) at 0 °C. The mixture was stirred for 3 minutes and 4-nitro-benzoyl chloride (0.024 g, 0.13 mmol) was added. The mixture was warmed to room temperature and stirred for 18 hours. The mixture was cooled to 0 °C and water (2 cm$^3$) was added with care. The mixture was partitioned between saturated aqueous ammonium chloride and EtOAc and the phases separated. The aqueous fraction was extracted with EtOAc (3 x 10 cm$^3$). The combined organic fractions were dried over magnesium sulfate, filtered and the solvent removed under reduced pressure. The crude product was purified by flash column chromatography (petrol/EtOAc, 15:1) and the title compound isolated as colourless prisms (0.016 g, 66 %). $R_F$: 0.43 (8:1, Petrol:EtoAc); Mpt: 85-87 °C (DCM); $[\alpha]_D^{22}$: -7.2° (c. 0.9, CHCl$_3$); MS m/z (ES+) 400 (60%, M+Na$^+$); HRMS: found 400.0964, M+Na$^+$ requires 400.0978; IR $\nu_{\text{max}}$(film)/cm$^{-1}$ 1664 (C=O), 1529 (NO$_2$ sy), 1350 (NO$_2$ as); $^1$H-NMR (CDCl$_3$, 400 MHz) $\delta$ 8.26 (d, J 8.8 Hz, 2H), 8.06 (d, J 8.8 Hz, 2H), 7.44 (d, J 8.6 Hz, 2H), 7.36-7.26 (m, 5H), 7.15 (d, J 8.3 Hz, 2H), 2.46 (s, 3H), 2.35 (s, 3H); $^{13}$C-NMR (CDCl$_3$, 75.5 MHz) $\delta$ 188.8, 150.3, 144.6, 142.2, 141.5, 137.1, 129.0, 128.3, 128.2, 127.7, 127.6, 127.3, 123.8, 61.3, 28.7, 21.0.
DEUTERATION EXPERIMENTS

$n$-Butyllithium (solution in hexanes, 2.5 eq) was added to a solution of diisopropylamine (3 eq) in THF (1 cm$^3$) at 0 °C. This was stirred for 15 minutes and then cooled to -78 °C. This solution was added by cannula to a cooled (-78 °C) solution of 8a (0.05 g, 1 eq) in THF (1.5 cm$^3$). The mixture was allowed to stir for the time specified in the table (below). CD$_3$OD (3 eq) was added dropwise followed immediately by propionic acid (5 eq) and the mixture allowed to warm to room temperature. Water (10 cm$^3$) and diethyl ether (10 cm$^3$) were added and the phases separated. The aqueous fraction was extracted with diethyl ether (2 x 10 cm$^3$) and the combined organic fractions dried over magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was then purified by flash column chromatography as required.

![Diagram]

<table>
<thead>
<tr>
<th>Reaction time (min)</th>
<th>Yield er</th>
<th>%D NMR$^a$</th>
<th>%D MS$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>nd</td>
<td>95:5</td>
<td>11</td>
</tr>
<tr>
<td>10</td>
<td>72</td>
<td>80:20</td>
<td>39</td>
</tr>
<tr>
<td>20</td>
<td>64</td>
<td>77:23</td>
<td>41</td>
</tr>
<tr>
<td>30</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>15</td>
<td>54:46</td>
<td>35</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Yield er</th>
<th>%D NMR$^a$</th>
<th>%D MS$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>94:6</td>
<td>10</td>
</tr>
<tr>
<td>19</td>
<td>63:7</td>
<td>2</td>
</tr>
<tr>
<td>64</td>
<td>88:12</td>
<td>3</td>
</tr>
<tr>
<td>76</td>
<td>88:12</td>
<td>2</td>
</tr>
</tbody>
</table>

$^a$% deuteration calculated by integration in $^1$H NMR.

$^b$% deuteration measured in mass spectrometry (ES$^+$) with correction for $^{13}$C.
s1: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
s2: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
s3: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
s4: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
s5: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
s6: $^1$H-NMR: 300 MHz, $^{13}$C-NMR: 100 MHz

![NMR Spectra](image)
s7: $^1$H-NMR: 300 MHz, $^{13}$C-NMR: 75 MHz
s8: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
s9: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
s10: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
s11: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
s12: $^1$H-NMR: 300 MHz, $^{13}$C-NMR: 100 MHz
s13: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
s14: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
s15: $^1$H-NMR: 300 MHz, $^{13}$C-NMR: 100 MHz
s16: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
s17: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
s18: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
s19: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
s20: $^1$H-NMR: 500 MHz, $^{13}$C-NMR: 100 MHz
s21: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
s22: ¹H-NMR: 400 MHz, ¹³C-NMR: 100 MHz
s23: $^1$H-NMR: 300 MHz, $^{13}$C-NMR: 75 MHz
s24: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
s25: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
s26: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
s27: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
5a: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
5b: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
5c: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
5d: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
6a: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
6b: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
6c: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
7a: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
7b: £H-NMR: 400 MHz, £C-NMR: 100 MHz
7c: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
7d: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
8a: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
8b: $^1$H-NMR: 500 MHz, $^{13}$C-NMR: 100 MHz
8c: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
8d: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
8e: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
8f: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz

![NMR Spectroscopy Image](image-url)
8g: \(^1\)H-NMR: 400 MHz, \(^{13}\)C-NMR: 100 MHz
8h: $^1$H-NMR: 500 MHz, $^{13}$C-NMR: 75.5 MHz
8i: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
8j: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
8k: $^1$H-NMR: 500 MHz, $^{13}$C-NMR: 75.5 MHz
8l: $^1\text{H-NMR}$: 400 MHz, $^{13}\text{C-NMR}$: 75.5 MHz
8m: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
9a: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 75.5 MHz
9b: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
9c: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
9d: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 125 MHz
9e: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 75.5 MHz

![Chemical structure and NMR spectra]
9f: $^1$H-NMR: 500 MHz, $^{13}$C-NMR: 125 MHz
9h: $^1$H-NMR: 500 MHz, $^{13}$C-NMR: 125 MHz
9j: \( ^1\text{H-NMR} \): 400 MHz, \( ^{13}\text{C-NMR} \): 100 MHz
9k: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 75.5 MHz
9l: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 75.5 MHz
9m: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
10a: $^1$H-NMR: 300 MHz, $^{13}$C-NMR: 125 MHz
10b: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
10c: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
10d: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
10e: $^1$H-NMR: 500 MHz, $^{13}$C-NMR: 100 MHz
10f: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
10h: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz

![NMR Spectra](image)
10j: $^1$H-NMR: 500 MHz, $^{13}$C-NMR: 100 MHz
10k: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
10l: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz

[Chemical structure image]
10m: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 100 MHz
11: $^1$H-NMR: 400 MHz, $^{13}$C-NMR: 75.5 MHz
Racemic standard:

Signal 1: DAD1 C, Sig=214,4 Ref-550,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.054</td>
<td>VB</td>
<td>0.1364</td>
<td>7417.34375</td>
<td>828.77435</td>
<td>40.9555</td>
</tr>
<tr>
<td>2</td>
<td>7.113</td>
<td>PB</td>
<td>0.1647</td>
<td>7427.54932</td>
<td>694.90533</td>
<td>50.0344</td>
</tr>
</tbody>
</table>
### Racemic Standard:

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.559</td>
<td>0.282</td>
<td>3.81195e4</td>
<td>2251.11377</td>
<td>95.7023</td>
</tr>
<tr>
<td>2</td>
<td>14.717</td>
<td>0.348</td>
<td>1711.84241</td>
<td>83.38615</td>
<td>4.2977</td>
</tr>
</tbody>
</table>

---

**Signal 1: DAD1 C, Sig-214,4 Ref-550,100**

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.706</td>
<td>0.248</td>
<td>1.10583e4</td>
<td>696.09546</td>
<td>50.0089</td>
</tr>
<tr>
<td>2</td>
<td>14.999</td>
<td>0.319</td>
<td>1.16667e4</td>
<td>557.80151</td>
<td>49.9911</td>
</tr>
</tbody>
</table>
**Racemic standard:**

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.746</td>
<td>BB</td>
<td>0.1901</td>
<td>2.3515e+4</td>
<td>2055.49119</td>
<td>95.7523</td>
</tr>
<tr>
<td>2</td>
<td>8.792</td>
<td>BB</td>
<td>0.2315</td>
<td>1130.52744</td>
<td>69.72172</td>
<td>4.3072</td>
</tr>
</tbody>
</table>
Racemic standard:

Signal 1: DAD C, Sig=214,4 Ref=550,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td></td>
<td>[min]</td>
<td>[mAU*s]</td>
<td>[mAU]</td>
<td>[mAU]</td>
</tr>
<tr>
<td>1</td>
<td>9.072</td>
<td>BP</td>
<td>0.1830</td>
<td>1025.82043</td>
<td>86.08256</td>
<td>2.9383</td>
</tr>
<tr>
<td>2</td>
<td>10.926</td>
<td>YV</td>
<td>0.2361</td>
<td>3.40056e4</td>
<td>2253.46045</td>
<td>97.0717</td>
</tr>
</tbody>
</table>

Signal 1: DAD C, Sig=214,4 Ref=550,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td></td>
<td>[min]</td>
<td>[mAU*s]</td>
<td>[mAU]</td>
<td>[mAU]</td>
</tr>
<tr>
<td>1</td>
<td>9.270</td>
<td>BP</td>
<td>0.1712</td>
<td>1.32093e4</td>
<td>1211.34646</td>
<td>50.0543</td>
</tr>
<tr>
<td>2</td>
<td>9.205</td>
<td>BB</td>
<td>0.2079</td>
<td>1.31753e4</td>
<td>986.13293</td>
<td>49.9387</td>
</tr>
</tbody>
</table>
Signal 1: DAD 1 C, Sig-214,4 Ref-550,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.593</td>
<td>BE</td>
<td>0.2027</td>
<td>1.0007e4</td>
<td>1405.90096</td>
<td>91.0293</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>12.406</td>
<td>VS</td>
<td>0.2723</td>
<td>1893.56443</td>
<td>104.64934</td>
<td>8.9707</td>
<td></td>
</tr>
</tbody>
</table>

Racemic standard:

Signal 1: DAD 1 C, Sig-214,4 Ref-550,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.591</td>
<td>W</td>
<td>0.1995</td>
<td>1599.86506</td>
<td>123.22392</td>
<td>50.0633</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>12.368</td>
<td>BP</td>
<td>0.2574</td>
<td>1594.53088</td>
<td>94.25573</td>
<td>49.9162</td>
<td></td>
</tr>
</tbody>
</table>
Signal 1: DAD1 A, Sig=254.4 Ref=550,100

<table>
<thead>
<tr>
<th>Peak RefTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.944 PB</td>
<td>0.1347</td>
<td>1458.14587</td>
<td>165.60994</td>
<td>97.9949</td>
<td></td>
</tr>
<tr>
<td>7.924 B</td>
<td>0.1764</td>
<td>25.85662</td>
<td>2.55404</td>
<td>2.0051</td>
<td></td>
</tr>
</tbody>
</table>

Racemic standard:

Signal 1: DAD1 A, Sig=254.4 Ref=550,100

<table>
<thead>
<tr>
<th>Peak RefTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.917 BD</td>
<td>0.1361</td>
<td>4042.82666</td>
<td>457.61425</td>
<td>49.9791</td>
<td></td>
</tr>
<tr>
<td>7.966 BD</td>
<td>0.1900</td>
<td>4041.20650</td>
<td>350.78778</td>
<td>50.0209</td>
<td></td>
</tr>
</tbody>
</table>
9d

Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2011

Racemic standard:

Signal 1: VWD1 A, Wavelength=254 nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time (min)</th>
<th>Type</th>
<th>Width (min)</th>
<th>Height (AU)</th>
<th>Area (mAU*s)</th>
<th>Area (mAU)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.931</td>
<td>VR</td>
<td>0.192</td>
<td>193.30365</td>
<td>2505.80054</td>
<td></td>
<td>95.9564</td>
</tr>
<tr>
<td>2</td>
<td>10.655</td>
<td>BB</td>
<td>0.252</td>
<td>6.39132</td>
<td>105.55557</td>
<td></td>
<td>4.0436</td>
</tr>
</tbody>
</table>

Signal 1: VWD1 A, Wavelength=254 nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time (min)</th>
<th>Type</th>
<th>Width (min)</th>
<th>Height (AU)</th>
<th>Area (mAU*s)</th>
<th>Area (mAU)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.004</td>
<td>VR</td>
<td>0.2027</td>
<td>54.69103</td>
<td>720.47180</td>
<td></td>
<td>50.4221</td>
</tr>
<tr>
<td>2</td>
<td>10.729</td>
<td>BB</td>
<td>0.2425</td>
<td>45.52840</td>
<td>708.46808</td>
<td></td>
<td>49.5779</td>
</tr>
</tbody>
</table>
Racemic standard:

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.272</td>
<td>BP</td>
<td>0.1411</td>
<td>4898.31836</td>
<td>543.63306</td>
<td>97.9129</td>
</tr>
<tr>
<td>2</td>
<td>7.516</td>
<td>BP</td>
<td>0.1815</td>
<td>104.41408</td>
<td>9.11720</td>
<td>2.0871</td>
</tr>
</tbody>
</table>

Signal 1: DAD1, Sig=254,4 Ref=550,100
Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2011

Racemic standard:

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.982</td>
<td>VB</td>
<td>0.3134</td>
<td>1004.04181</td>
<td>41.98306</td>
<td>4.1493</td>
</tr>
<tr>
<td>2</td>
<td>15.559</td>
<td>VV</td>
<td>0.4020</td>
<td>2.31939e+4</td>
<td>911.10040</td>
<td>95.8507</td>
</tr>
</tbody>
</table>

Signal 1: 
Wavelength=210 nm

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.764</td>
<td>VB</td>
<td>0.2630</td>
<td>1.49609e4</td>
<td>890.53448</td>
<td>48.6367</td>
</tr>
<tr>
<td>2</td>
<td>15.186</td>
<td>VV</td>
<td>0.3515</td>
<td>1.57966e4</td>
<td>699.50018</td>
<td>51.3833</td>
</tr>
</tbody>
</table>
Racemic standard:

Signal 1: VUD1 A, Wavelength=254 nm

<table>
<thead>
<tr>
<th>#</th>
<th>Ret Time [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU's]</th>
<th>Height [mAU]</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.403</td>
<td>BB</td>
<td>0.453</td>
<td>2.68337e4</td>
<td>872.99139</td>
<td>98.0062</td>
</tr>
<tr>
<td>2</td>
<td>18.904</td>
<td>BB</td>
<td>0.464</td>
<td>545.90395</td>
<td>15.00963</td>
<td>1.9938</td>
</tr>
</tbody>
</table>
Racemic standard:

Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2011
Racemic standard:
Racemic standard:

<table>
<thead>
<tr>
<th>#</th>
<th>Ret Time [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.100</td>
<td>UV</td>
<td>0.2093</td>
<td>4950.50195</td>
<td>367.16678</td>
<td>95.9788</td>
</tr>
<tr>
<td>2</td>
<td>9.292</td>
<td>UV</td>
<td>0.2350</td>
<td>207.40020</td>
<td>13.22161</td>
<td>4.0212</td>
</tr>
</tbody>
</table>
Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2011

Racemic standard:

---

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.021</td>
<td>BB</td>
<td>0.1306</td>
<td>4190.14893</td>
<td>495.74654</td>
<td>97.7847</td>
</tr>
<tr>
<td>2</td>
<td>7.038</td>
<td>BB</td>
<td>0.1619</td>
<td>94.92862</td>
<td>8.79970</td>
<td>2.2153</td>
</tr>
</tbody>
</table>

---

Signal 1: DAD 1 & Sig=254,4 Ref=550,100

---

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.085</td>
<td>BB</td>
<td>0.1323</td>
<td>4997.20215</td>
<td>561.43939</td>
<td>50.0015</td>
</tr>
<tr>
<td>2</td>
<td>7.113</td>
<td>BB</td>
<td>0.1594</td>
<td>4996.89600</td>
<td>468.42007</td>
<td>49.9985</td>
</tr>
</tbody>
</table>
Supplementary Material (ESI) for Chemical Communications

This journal is (c) The Royal Society of Chemistry 2011

Racemic standard:

Supplementary Material (ESI) for Chemical Communications

This journal is (c) The Royal Society of Chemistry 2011
Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2011

Signal 1: DAD 1 C, Sig=214,4 Ref=556,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime Type</th>
<th>Width</th>
<th>Area (mAU^2)</th>
<th>Height (mAU)</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.551</td>
<td>0.2092</td>
<td>15.09872</td>
<td>2.3468</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>11.502</td>
<td>0.2420</td>
<td>512.41595</td>
<td>97.4532</td>
<td></td>
</tr>
</tbody>
</table>

Racemic standard:

Signal 1: DAD 1 C, Sig=214,4 Ref=556,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime Type</th>
<th>Width</th>
<th>Area (mAU^2)</th>
<th>Height (mAU)</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.579</td>
<td>0.2179</td>
<td>441.47629</td>
<td>49.9220</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>11.520</td>
<td>0.2422</td>
<td>403.20587</td>
<td>50.0580</td>
<td></td>
</tr>
</tbody>
</table>
Racemic standard:

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.943</td>
<td>BP</td>
<td>0.1258</td>
<td>195.42192</td>
<td>243.1819</td>
<td>3.6047</td>
</tr>
<tr>
<td>2</td>
<td>5.539</td>
<td>VB</td>
<td>0.1403</td>
<td>5225.90430</td>
<td>563.06769</td>
<td>96.3953</td>
</tr>
</tbody>
</table>

Signal 1: DADB C, Sig=214,4 Ref=550,100

Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2011
Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2011

Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2011

Racemic standard:

Signal 1: DaBi C, Sig=214,4 Ref=550,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.62 W</td>
<td>0.11</td>
<td>7327</td>
<td>948.46</td>
<td>982990</td>
<td>38.26</td>
</tr>
<tr>
<td>2</td>
<td>5.62 V</td>
<td>0.14</td>
<td>1425</td>
<td>148929</td>
<td>150944</td>
<td>66.74</td>
</tr>
</tbody>
</table>

Signal 1: DaBi C, Sig=214,4 Ref=550,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.65 W</td>
<td>0.12</td>
<td>7083</td>
<td>2139</td>
<td>42187</td>
<td>49.12</td>
</tr>
<tr>
<td>2</td>
<td>6.65 V</td>
<td>0.16</td>
<td>9659</td>
<td>1843</td>
<td>32483</td>
<td>50.87</td>
</tr>
</tbody>
</table>
Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2011

Signal 1: DAD1 C, Sig=214,4 Ref=550,100

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU*sec]</td>
<td>[mAU]</td>
</tr>
<tr>
<td>1</td>
<td>7.250</td>
<td>0.1705</td>
<td>1.1711E6</td>
<td>957.9333</td>
</tr>
<tr>
<td>2</td>
<td>8.721</td>
<td>0.2257</td>
<td>3011.08684</td>
<td>207.03917</td>
</tr>
</tbody>
</table>

Racemic standard:

Signal 1: DAD1 C, Sig=214,4 Ref=550,100

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU*sec]</td>
<td>[mAU]</td>
</tr>
<tr>
<td>1</td>
<td>7.193</td>
<td>0.1693</td>
<td>9327.82520</td>
<td>841.88147</td>
</tr>
<tr>
<td>2</td>
<td>8.611</td>
<td>0.2195</td>
<td>9289.3828</td>
<td>546.97845</td>
</tr>
</tbody>
</table>
Supplementary Material (ESI) for Chemical Communications

This journal is (c) The Royal Society of Chemistry 2011

9m

Racemic standard:

11
Racemic standard:

Signal 2: DAD1 C, Sig=214,4 Ref=550,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21.082</td>
<td>VP</td>
<td>0.4045</td>
<td>5660.93848</td>
<td>214.01173</td>
<td>50.3711</td>
</tr>
<tr>
<td>2</td>
<td>23.270</td>
<td>BV</td>
<td>0.441</td>
<td>5577.53418</td>
<td>195.39821</td>
<td>49.6289</td>
</tr>
</tbody>
</table>

9b