Supplementary Information

The enantioselective benzoin condensation promoted by chiral triazolium precatalysts: stereochemical control via hydrogen bonding

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1.0 General

Proton Nuclear Magnetic Resonance spectra were recorded on 400 MHz and 600 MHz spectrometers in CDCl₃ referenced relative to residual CHCl₃ (δ = 7.26 ppm), DMSO-d₆ referenced relative to residual DMSO (H) (δ = 2.51 ppm) and CD₃CN referenced relative to residual CH₃CN (δ = 1.96 ppm). Chemical shifts are reported in ppm and coupling constants in Hertz. Carbon NMR spectra were recorded on the same instruments (100 MHz and 150 MHz) with total proton decoupling. All melting points are uncorrected. Infrared spectra were obtained using neat samples on a Perkin Elmer Spectrum 100 FT-IR spectrometer equipped with a universal ATR sampling accessory. Flash chromatography was carried out using silica gel, particle size 0.04-0.063 mm. TLC analysis was performed on precoated 60F₂₅₄ slides, and visualised by either UV irradiation or KMnO₄ staining. Optical rotation measurements were made on a Rudolph Research Analytical Autopol IV instrument, and are quoted in units of 10⁻¹ deg cm² g⁻¹. Toluene, ether and THF were distilled from sodium. Methylene chloride and triethylamine were distilled from calcium hydride. Analytical CSP-HPLC was performed using Daicel CHIRALCEL AD (4.6 mm x 25 cm) and CHIRALCEL OD-H (4.6 mm x 25 cm) and CHIRALCEL OJ-H (4.6 mm x 25 cm) columns. Unless otherwise stated, all chemicals were obtained from commercial sources and used as received. All reactions were carried out in oven-dried glassware with magnetic stirrers under an atmosphere of argon, unless specified.
2.0 Reaction Condition Sets

Condition Set A - K₂CO₃/KOH as Base

To a 5 cm³ round-bottomed flask, equipped with a magnetic stirring bar, were added K₂CO₃ (99.995%, anhydrous, 8.76 mg, 0.0634 mmol) and KOH (0.79 mg, 0.0141 mmol) that had both been finely ground using a mortar and pestle. The reaction vessel was put under a vacuum and heated with a heat gun for 4 one-minute intervals. When cooled to ambient temperature the appropriate catalyst (0.088 mmol) and (E)-stilbene (49.57 mg, 0.275 mmol) were added and the flask was fitted with a septum seal. The reaction was evacuated for 4 min and put under an atmosphere of Ar. The required aldehyde was washed in CH₂Cl₂ with aq. NaHCO₃. The lower organic layer was separated, dried over MgSO₄, filtered and solvent removed in vacuo. The aldehyde was distilled under vacuum and used directly. THF (1.78 cm³) was charged to the reaction, followed by the aldehyde (2.200 mmol). The reaction was stirred at room temperature for 48 h after which CH₂Cl₂ (3.0 cm³) and deionised H₂O (3.0 cm³) were added. The lower organic layer was removed and the aqueous layer was washed with CH₂Cl₂ (4 x 3.0 cm³). The organic layers were combined, dried (MgSO₄), filtered and the solvent removed under reduced pressure. The product was purified using column chromatography.

Condition Set B - KHMDS ‘Normal’ Addition

To a 5 cm³ round-bottomed flask, equipped with a magnetic stirring bar, was added the appropriate catalyst (0.220 mmol), and the flask was fitted with a septum seal. The reaction was evacuated for 4 min and put under an atmosphere of Ar. The required aldehyde was washed in CH₂Cl₂ with aq. NaHCO₃. The lower organic layer was separated, dried over MgSO₄, filtered and solvent removed in vacuo. The aldehyde was distilled under vacuum and used directly. Toluene (1.34 cm³) was charged to the reaction, followed by dropwise addition of the aldehyde (2.200 mmol). The reaction was stirred for 5 min and KHMDS (440 µL, 0.220 mmol, 0.5 M solution in toluene) was added via syringe over 15 min. The reaction was stirred at room temperature for the time indicated in Table 2. To quench the reaction EtOAc (6.0 cm³) and deionised H₂O (3.0 cm³) were added. The organic layer was removed and the aqueous layer was washed with EtOAc (4 x 6.0 cm³). The organic layers were combined, dried (MgSO₄), filtered
and the solvent removed under reduced pressure. The product was purified using column chromatography. Note: The internal standard \((E)\)-stilbene (49.57 mg, 0.275 mmol) was added to the reaction after the work-up (prior to removal of the solvent) due to poor solubility of the internal standard in toluene.

**Condition Set C - KHMDS ‘Inverse’ Addition**

To a 5 cm\(^3\) round-bottomed flask, equipped with a magnetic stirring bar, was added the appropriate catalyst (0.110 mmol), and the flask was fitted with a septum seal. The reaction was evacuated for 4 min and put under an atmosphere of Ar. The required aldehyde was washed in CH\(_2\)Cl\(_2\) with aq. NaHCO\(_3\). The lower organic layer was separated, dried over MgSO\(_4\), filtered and solvent removed in vacuo. The aldehyde was distilled under vacuum and used directly. Toluene (0.73 cm\(^3\)) was charged to the reaction, followed by addition via syringe of KHMDS (220 µL, 0.110 mmol, 0.5 M solution in toluene) over 7 min. The reaction was stirred for 15 min and the required aldehyde (1.100 mmol) was added dropwise to the reaction over 5 min. The reaction was stirred at room temperature for 16 h (unless otherwise indicated in Table 3). To quench the reaction EtOAc (6.0 cm\(^3\)) and deionised H\(_2\)O (3.0 cm\(^3\)) were added. The organic layer was removed and the aqueous layer was washed with EtOAc (4 x 6.0 cm\(^3\)). The organic layers were combined, dried (MgSO\(_4\)), filtered and the solvent removed under reduced pressure. The product was purified using column chromatography. Note: The internal standard \((E)\)-stilbene (24.78 mg, 0.138 mmol) was added to the reaction after the work-up (prior to removal of the solvent) due to poor solubility of the internal standard in toluene.
3.0 Characterisation Data

Synthesis of catalysts 15a-h and 16

\((1R,2R)-trans-N-(2-Azido-indan-1-yl)-2,3,4,5,6-pentafluoro-benzamide 23b\)

Prepared as per the synthesis of 23a using 21 (0.762 g, 3.615 mmol) in CH₂Cl₂ (6.0 cm³), triethylamine (2.51 cm³, 18.033 mmol) and a solution of 22b (0.60 cm³, 4.338 mmol) in CH₂Cl₂ (8 cm³). Purification by column chromatography (1:1 CH₂Cl₂-hexane, Rf 0.2) gave 23b (1.237 g, 93%) as a white solid, mp 211-212 °C. \([\alpha]_{D}^{20} = -27.9 \ (c \ 0.63 \ \text{in CHCl}_3)\).

\(\delta_H\) (600 MHz, DMSO-d₆) 2.87 (1H, dd, \(J\ 15.4, 8.4\)), 3.29 (1H, m, (under H₂O resonance)), 4.30-4.34 (1H, app. q) 5.43-5.45 (1H, app. t), 7.21 (1H, d, \(J\ 7.3\)), 7.31-7.32 (3H, m), 9.59 (1H, d, \(J\ 8.1\)). \(\delta_C\) (150 MHz, DMSO-d₆) 35.3, 59.4, 66.7, 112.0 (t, \(J\ 20.8\)), 123.4, 124.8, 127.3, 128.5, 136.0 (d of t, \(J\ 250.5, 14.7\)), 139.0, 139.5, 140.4 (d of m, \(J\ 257.7\)), 142.2 (d of m, \(J\ 251.7\)), 157.0. \(\nu_{\text{max}}\) (neat)/cm⁻¹ 3266, 2968, 2934, 2105, 1655, 1499, 1077, 988, 752. \(m/z\) (ES) 391.0579 (M⁺ + Na. C₁₆H₉N₄OF₅Na requires 391.0594).

\((1R,2R)-trans-1-Pentafluorobenzoylamino-indan-2-yl ammonium; chloride 24b\)
Prepared as per 24a using 23b (1.137 g, 3.089 mmol), triphenylphosphine (0.810 g, 3.089 mmol) in THF (28 cm³) and addition of water (4 cm³). Concentration of the aqueous layer produced a white solid which was purified by washing with ether to yield 24b (1.060 g, 91%) as a white solid, mp 277-279 °C. \([\alpha]_D^{20} = -26.7 \) (c 0.99 in MeOH).

\(\delta_H\) (600 MHz, DMSO-\(d_6\)) 3.04 (1H, dd, \(J 15.8, 7.5\)), 3.39 (1H, dd, \(J 15.8, 8.3\)), 3.87-3.91 (1H, app. q), 5.62-5.65 (1H, app. t), 7.27 (1H, d, \(J 4.9\)), 7.32-7.36 (3H, m), 8.69 (3H, s (broad)), 9.66 (1H, d, \(J 7.9\)). \(\delta_C\) (150 MHz, DMSO-\(d_6\)) 35.3, 56.3, 58.5, 112.1 (t, \(J 20.1\)), 124.1, 125.3, 127.9, 129.0, 136.5 (d of t, \(J 249.9, 16.2\)), 139.2, 140.0, 140.7 (d of m, \(J 254.1\)), 142.7 (d of m, \(J 250.7\)), 157.5. \(\nu_{\max}\) (neat)/cm\(^{-1}\) 3299, 2856, 1661, 1552, 1518, 1496, 768, 738, 713. \(m/z\) (ES) 343.0858 (M+ - Cl. C\(_{16}\)H\(_{12}\)N\(_2\)OF\(_5\) requires 343.0870.

\((1R,2R)\)-trans-4-(1-Pentafluorobenzoylamino-indan-2-yl)-1-phenyl-4\(H\)-[1,2,4]triazol-1-ium; perchlorate 15b

Prepared as per 15a using 25 (0.330 g, 1.338 mmol), oven-dried molecular sieves (4Å, 1.30 g) and 24b (free-based amine, 0.458 g, 1.338 mmol) in CH\(_3\)CN (7 cm³). The reaction was heated under reflux for 4 d under an atmosphere of Ar. Filtration under a stream of Ar followed by removal of the filtrate in vacuo yielded a red-brown residue. Purification by column chromatography (1:1 EtOAc-hexane, \(R_f 0.2\)) gave 15b (0.321 g, 42%) as a yellow solid, mp 101-102 °C. \([\alpha]_D^{20} = -40.8 \) (c 2.42 in CHCl\(_3\)).

\(\delta_H\) (600 MHz, DMSO-\(d_6\)) 3.66 (1H, dd, \(J 15.8, 9.4\)), 3.71 (1H, dd, \(J 15.8, 8.7\)), 5.28 (1H, ddd, \(J 9.4, 8.7, 8.3\)), 6.09 (1H, dd, \(J 8.3, 7.9\)), 7.33-7.34 (1H, m), 7.44-7.47 (3H, m), 7.69 (1H, t, \(J 7.5\)), 7.75-7.77 (2H, app. t), 7.96 (2H, d, \(J 7.9\)), 9.70 (1H, s), 9.85 (1H, d, \(J 7.9\)), 11.29 (1H, s). \(\delta_C\) (150 MHz, DMSO-\(d_6\)) 36.1, 60.6, 65.3, 111.4 (t, \(J 33.6\)), 120.5, 123.6, 125.0, 127.9, 129.1,
130.3, 130.7, 134.9, 136.1 (d of m, J 250.9), 137.7, 137.9, 140.6 (d of m, J 252.1), 141.3, 142.4 (d of m, J 247.6), 144.6, 157.8. \( \nu_{\text{max}} \) (neat)/cm\(^{-1}\) 3290, 3127, 3077, 2925, 1657, 1570, 1542, 1516, 1501, 1461, 1072, 990, 756, 686. \( m/z \) (ES) 471.1238 (M\(^+\)-ClO\(_4\)). C\(_{24}\)H\(_{16}\)N\(_4\)OF\(_5\) requires 471.1244.

\((1R,2R)-\text{trans-}N-(2\text{-Azido-indan-1-yl})\text{-3,5-bis-trifluoromethyl-benzamide} \ 23c\)

\[
\begin{align*}
\text{NH} & \text{N}_3 \\
& \text{O} \\
& \text{CF}_3 \\
& \text{F}_3\text{C}
\end{align*}
\]

Prepared as per the synthesis of \(23a\) using \(21\) (1.200 g, 5.696 mmol) in CH\(_2\)Cl\(_2\) (10 cm\(^3\)), triethylamine (2.38 cm\(^3\), 17.089 mmol) and a solution of \(22c\) (1.23 cm\(^3\), 6.836 mmol) in CH\(_2\)Cl\(_2\) (8 cm\(^3\)). Purification by column chromatography (6:4 CH\(_2\)Cl\(_2\)-hexane, R\(_f\) 0.3) gave \(23c\) (2.161 g, 92%) as a white solid, mp 207-208 °C. \([\alpha]_{D}^{20} = -20.7\) (c 0.97 in CHCl\(_3\)).

\(\delta\)\(_H\) (600 MHz, DMSO-d\(_6\)) 2.89 (1H, dd, J 15.6, 7.3), 3.37 (1H, dd, J 15.6, 7.7), 4.39-4.43 (1H, m), 5.54-5.57 (1H, m), 7.26-7.33 (4H, m), 8.35 (1H, s), 8.60 (2H, s), 9.49 (1H, d, J 8.4). \(\delta\)\(_C\) (150 MHz, DMSO-d\(_6\)) 35.4, 59.7, 66.9, 120.4 (q, \(J = 272.9\)), 124.2, 124.7, 125.1 (septet, \(J = 3.3\)), 127.2, 128.2 (q, \(J = 3.0\)), 128.4, 130.2 (q, \(J = 33.2\)), 136.1, 139.3, 140.0, 163.6. \( \nu_{\text{max}} \) (neat)/cm\(^{-1}\) 3257, 3094, 2928, 2105, 1645, 1547, 1272, 1124, 910, 847, 701, 680. \( m/z \) (ES) 437.0807 (M\(^+\)+Na. C\(_{18}\)H\(_{12}\)N\(_4\)OF\(_6\)Na requires 437.0813).

\((1R,2R)-\text{trans-}1\text{-}(3,5\text{-Bis-trifluoromethyl-benzoylamino})\text{-inden-2-yl-ammonium; chloride} \ 24c\)
Prepared as per **24a** using **23c** (2.161 g, 5.215 mmol), triphenylphosphine (1.368 g, 5.215 mmol) in THF (44 cm³) and addition of water (6 cm³). Concentration of the aqueous layer produced a white solid which was purified by washing with ether to yield **24c** (2.105 g, 95%) as a white solid, mp 301-303 °C. \([\alpha]_D^{20} = -4.7\ (c\ 1.11\ \text{in MeOH})\).

\[
\delta_H (600\ \text{MHz, DMSO-d}_6)\ 3.06 (1\text{H, dd, } J\ 15.7,\ 9.2),\ 3.37 (1\text{H, dd, } J\ 15.7,\ 7.9),\ 3.97-4.03 (1\text{H, m}),\ 5.75-5.77 (1\text{H, app. t}),\ 7.26-7.40 (4\text{H, m}),\ 8.36 (1\text{H, s}),\ 8.63 (2\text{H, s}),\ 8.74 (3\text{H, broad s}),\ 9.57 (1\text{H, d, } J\ 8.3).\ \delta_C (150\ \text{MHz, DMSO-d}_6)\ 34.4,\ 56.6,\ 57.8,\ 120.4 (q,\ J\ 273.7),\ 123.9,\ 124.8,\ 124.9 (septet,\ J\ 3.3),\ 127.4,\ 128.4,\ 128.5 (q,\ J\ 3.8),\ 130.1 (q,\ J\ 33.1),\ 136.5,\ 138.5,\ 140.2,\ 164.2.\ \nu_{\text{max}} (\text{neat})/\text{cm}^{-1}\ 3280,\ 2861,\ 1646,\ 1621,\ 1544,\ 1278,\ 1124,\ 847,\ 742,\ 682.\ m/z\ (\text{ES})\ 389.1071\ (\text{M}^+ - \text{Cl}.\ C_{18}H_{15}N_2O_6\ \text{requires}\ 389.1089).
\]

**(1R,2R)-trans-4-[1-(3,5-Bistrifluoromethyl-benzoylamino)-indan-2-yl]-1-phenyl-4H-[1,2,4]triazol-1-ium; perchlorate 15c**

Prepared as per **15a** using **25** (0.285 g, 1.155 mmol), oven-dried molecular sieves (4Å, 1.10 g) and **24c** (free-based amine, 0.427 g, 1.100 mmol) in CH₃CN (10 cm³). The reaction was heated under reflux for 7 d under an atmosphere of Ar. Filtration under a stream of Ar followed by removal of the filtrate in vacuo yielded a red-brown residue. Purification by column
chromatography (7:3 EtOAc-hexane, R<sub>f</sub> 0.3) gave **15c** (0.597 g, 88%) as a yellow solid, mp 127-128 °C. [α]<sub>D</sub><sup>20</sup> = -78.9 (c 1.62 in CHCl₃).

δ<sub>H</sub> (600 MHz, DMSO-d<sub>6</sub>) 3.64 (1H, dd, J 15.8, 8.8), 3.75 (1H, dd, J 15.8, 8.8), 5.34 (1H, ddd, J 9.2, 8.8, 8.1), 6.18 (1H, dd, J 8.1, 7.3), 7.40-7.48 (4H, m), 7.66 (1H, t, J 7.3), 7.73-7.76 (2H, app. t), 7.96 (2H, d, J 8.1), 8.37 (1H, s), 8.57 (2H, s), 9.74 (1H, d, J 7.3), 9.78 (1H, s) 11.20 (1H, s) 11.20 (1H, s). δ<sub>C</sub> (150 MHz, DMSO-d<sub>6</sub>) 36.7, 60.8, 65.9, 120.7 (q, J 273.1), 120.9, 124.6, 125.1, 125.5 (septet, J 2.7), 128.1, 128.8 (q, J 4.1), 129.2, 130.4 (q, J 33.3), 130.6, 131.0, 135.3, 136.3, 138.3, 138.9, 141.8, 145.1, 164.9. ν<sub>max</sub> (neat)/cm<sup>-1</sup> 3318, 3133, 3076, 1655, 1621, 1570, 1534, 1461, 1277, 1128, 1069, 759, 681. m/z (ES) 517.1473 (M<sup>+</sup> - ClO₄. C<sub>26</sub>H<sub>19</sub>N₄OF₆ requires 517.1463).

**(1R,2R)-trans-Naphthalene-1-carboxylic acid (2-azido-indan-1-yl)-amide 23d**

![23d](image)

Prepared as per the synthesis of **23a** using **21** (1.500 g, 7.120 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>), triethylamine (2.97 cm<sup>3</sup>, 21.361 mmol) and a solution of **22d** (1.28 cm<sup>3</sup>, 8.545 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 cm<sup>3</sup>). Purification by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>, R<sub>f</sub> 0.4) gave **23d** (2.086 g, 89%) as an off-white solid, mp 204-205 °C. [α]<sub>D</sub><sup>20</sup> = -41.3 (c 0.93 in CHCl₃).

δ<sub>H</sub> (600 MHz, DMSO-d<sub>6</sub>) 2.87 (1H, dd, J 15.4, 8.4), 3.32-3.36 (1H, m, (under H<sub>2</sub>O resonance)), 4.40-4.44 (1H, app. q), 5.60-5.63 (1H, app. t), 7.29-7.33 (3H, m), 7.36 (1H, d, J 7.2), 7.58-7.64 (3H, m), 7.71 (1H, d, J 7.0), 8.00 (1H, d, J 8.1), 8.06 (1H, d, J 8.4), 8.33 (1H, d, J 8.4), 9.16 (1H, d, J 8.4). δ<sub>C</sub> (150 MHz, DMSO-d<sub>6</sub>) 35.3, 59.3, 66.7, 123.6, 124.7, 124.9, 125.25, 125.29, 126.3, 126.8, 127.2, 128.1, 128.2, 129.7, 130.0, 133.1, 134.2, 138.8, 140.8, 168.9. ν<sub>max</sub> (neat)/cm<sup>-1</sup> 3238, 3047, 2926, 2888, 2098, 1646, 1527, 1519, 773, 753. m/z (ES) 351.1210 (M<sup>+</sup> + Na. C<sub>20</sub>H<sub>16</sub>N<sub>4</sub>ONa requires 351.1222).

**((1R,2R)-trans-1-[(Naphthalene-1-carbonyl)-amino]-indan-2-yl-ammonium; chloride 24d**
Prepared as per 24a using 23d (1.986 g, 6.048 mmol), triphenylphosphine (1.586 g, 6.048 mmol) in THF (50 cm³) and addition of water (5 cm³). Concentration of the aqueous layer produced a white solid which was purified by washing with ether to yield 24d (1.915 g, 93%) as a white solid, mp 293-295 °C.  \([\alpha]_D^{20} = -72.2 \text{ (c 1.68 in MeOH)}\).

δ_H (600 MHz, DMSO-d_6) 3.03 (1H, dd, J 15.8, 8.7), 3.38 (1H, dd, J 15.8, 8.3), 3.94-4.01 (1H, app. q.), 5.76-5.79 (1H, app. t), 7.33-7.36 (4H, m), 7.59-7.65 (3H, m), 7.88 (1H, d, J 6.4), 8.01 (1H, d, J 7.9), 8.07 (1H, d, J 8.3), 8.43 (1H, d, J 8.3), 8.66 (3H, s (broad)), 9.12 (1H, d, J 8.3).  δ_C (150 MHz, DMSO-d_6) 35.1, 56.7, 58.0, 124.1, 125.1, 125.2, 126.0, 126.4, 126.6, 127.1, 127.8, 128.6, 128.7, 130.1, 130.6, 133.5, 134.2, 138.8, 141.1, 169.5.  ν_max (neat)/cm⁻¹ 3290, 2981, 2857, 1633, 1522, 1329, 1305, 1260, 1169, 783, 734.  m/z (ES) 303.1493 (M⁺ - Cl. C_{20}H_{19}N_{2}O requires 303.1497).

(1R,2R)-trans-4-\{1-[(Naphthalene-1-carbonyl)-amino]-indan-2-yl\}-1-phenyl-4H-\[1,2,4\]triazol-1-ium; perchlorate 15d

Prepared as per 15a using 25 (0.582 g, 2.360 mmol), oven-dried molecular sieves (4Å, 2.20 g) and 24d (free-based amine, 0.680 g, 2.248 mmol) in CH₃CN (30 cm³). The reaction was heated under reflux for 7 d under an atmosphere of Ar. Filtration under a stream of Ar followed by removal of the filtrate in vacuo yielded a red-brown residue. Purification by column
chromatography (7:3 hexane-EtOAc, Rf 0.1) gave 15d (0.616 g, 52%) as an off-white solid, mp 159-160 °C. $[\alpha]_D^{20} = -113.2$ (c 0.71 in MeOH).

$\delta$H (600 MHz, DMSO-$d_6$) 3.67 (1H, dd, $J$ 15.6, 9.4), 3.73 (1H, dd, $J$ 15.6, 8.3), 5.32-5.37 (1H, app. q), 6.18-6.21 (1H, app. t), 7.42-7.51 (5H, m), 7.56-7.61 (2H, m), 7.69 (1H, t, $J$ 7.5), 7.76-7.79 (2H, app. t), 7.85 (1H, d, $J$ 6.8), 7.99-8.02 (3H, m), 8.07 (1H, d, $J$ 8.3), 8.12 (1H, d, $J$ 8.3), 9.38 (1H, d, $J$ 7.9), 9.86 (1H, s), 11.35 (1H, s). $\delta$C (150 MHz, DMSO-$d_6$) 36.5, 60.6, 65.9, 120.9, 124.3, 125.15, 125.19, 125.5, 126.5, 126.6, 127.1, 128.1, 128.6, 129.0, 130.0, 130.7, 130.9, 131.1, 133.47, 133.52, 135.3, 138.1, 139.3, 141.9, 145.2, 170.1. $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 3294, 3136, 3104, 1640, 1593, 1569, 1530, 1505, 1485, 1078, 769. $m/z$ (ES) 431.1863 (M$^+$ -ClO$_4$). C$_{28}$H$_{23}$N$_4$O requires 431.1872.

(1R,2R)-trans-N-(2-Azido-indan-1-yl)-2,4,6-trimethyl-benzamide 23e

Prepared as per the synthesis of 23a using 21 (1.000 g, 4.747 mmol) in CH$_2$Cl$_2$ (8 cm$^3$), triethylamine (3.96 cm$^3$, 28.482 mmol) and a solution of 22e (2.670 g, 14.618 mmol) in CH$_2$Cl$_2$ (10 cm$^3$). Purification by column chromatography (1:1 CH$_2$Cl$_2$-hexane, Rf 0.1) gave 23e (1.116 g, 73%) as a red-brown solid, mp 149-150 °C. $[\alpha]_D^{20} = -61.3$ (c 1.03 in CHCl$_3$).

$\delta$H (400 MHz, CDCl$_3$) 2.29 (3H, s), 2.39 (6H, s), 2.98 (1H, dd, $J$ 15.7, 7.0), 3.32 (1H, dd, $J$ 15.7, 7.5), 4.12 (1H, ddd, $J$ 7.5, 7.0, 6.5), 5.60 (1H, dd, $J$ 8.0, 6.5), 5.92 (1H, d, $J$ 8.0), 6.87 (2H, s), 7.26-7.33 (4H, m). $\delta$C (100 MHz, CDCl$_3$) 18.9, 20.7, 35.8, 59.3, 67.9, 123.7, 124.6, 127.3, 127.8, 128.5, 133.7, 133.9, 138.3, 138.9, 139.3, 170.1. $\nu_{\text{max}}$ (neat)/cm$^{-1}$ 3242, 2951, 2912, 2099, 1639, 1518, 1458, 1260, 856, 748, 704, 682. $m/z$ (ES) 321.1725 (M$^+$ + H). C$_{19}$H$_{21}$N$_4$O requires 321.1715.
(1R,2R)-trans-1-(2,4,6-Trimethyl-benzoylamino)-indan-2-yl-ammonium chloride 24e

Prepared as per 24a using 23e (1.116 g, 3.483 mmol), triphenylphosphine (0.914 g, 3.483 mmol) in THF (29 cm³) and addition of water (4 cm³). Concentration of the aqueous layer produced a pale brown solid which was purified by washing with ether to yield 24e (0.641 g, 56%) as a white solid, mp 278-280 °C. \([\alpha]_D^{20} = -37.5\) (c 0.70 in MeOH).

\[\delta_H (600 \text{ MHz}, \text{DMSO-d}_6) 2.24 (3H, s), 2.27 (6H, s), 2.99 (1H, dd, \text{J} 16.6, 6.4), 3.42 (1H, dd, \text{J} 16.6, 8.1), 3.87-3.90 (1H, app. q), 5.57-5.59 (1H, app. t), 6.87 (2H, s), 7.30-7.32 (3H, m), 7.37 (1H, d, \text{J} 6.4), 8.53 (3H, s (broad)), 8.85 (1H, d, \text{J} 7.5). \delta_C (150 \text{ MHz}, \text{DMSO-d}_6) 19.1, 20.6, 35.4, 56.1, 58.2, 124.4, 124.8, 127.3, 127.7, 128.4, 133.8, 134.9, 137.4, 139.0, 140.5, 169.7. \nu_{\text{max}} (\text{neat})/\text{cm}^{-1} 3251, 2915, 1634, 1612, 1517, 1477, 1375, 848, 746. \ m/z (\text{ES}) 295.1815 (\text{M}^+ - \text{Cl}. \text{C}_{19}\text{H}_{23}\text{N}_2\text{O} \text{requires} \ 295.1810).\]

(1R,2R)-trans-1-phenyl-4-[1-(2,4,6-trimethyl-benzoylamino)-indan-2-yl]-4H-[1,2,4]triazol-1-ium; perchlorate 15e

Prepared as per 15a using 25 (0.416 g, 1.687 mmol), oven-dried molecular sieves (4Å, 1.60 g) and 24e (free-based amine, 0.473 g, 1.606 mmol) in CH₃CN (15 cm³). The reaction was heated under reflux for 5 d under an atmosphere of Ar. Filtration under a stream of Ar followed by
removal of the filtrate in vacuo yielded a red-brown residue. Purification by column chromatography (7:3 hexane-EtOAc, Rf 0.2) gave 15e (0.403 g, 48%) as a pale green solid, mp 143-144 °C. $[\alpha]_D^{20} = -94.1$ (c 2.22 in CHCl3).

δ$_H$ (600 MHz, DMSO-d$_6$) 2.18 (6H, s), 2.24 (3H, s), 3.57 (1H, dd, $J$ 15.7, 9.6), 3.68 (1H, dd, $J$ 15.7, 8.3), 5.24-5.29 (1H, app. q), 6.18-6.21 (1H, app. t), 6.88 (2H, s), 7.35-7.36 (1H, m), 7.40-7.43 (3H, m), 7.68 (1H, t, $J$ 7.5), 7.75-7.78 (2H, app. t), 7.96 (2H, d, $J$ 7.9), 9.13 (1H, d, $J$ 7.9), 9.77 (1H, s) 11.38 (1H, s). δ$_C$ (150 MHz, DMSO-d$_6$) 18.9, 20.6, 36.5, 59.6, 65.4, 120.5, 123.6, 124.9, 127.7, 127.8, 128.7, 130.3, 130.8, 133.4, 134.7, 134.8, 137.57, 137.60, 138.8, 141.5, 144.9, 170.3. ν$_{\text{max}}$ (neat)/cm$^{-1}$ 3284, 3128, 3029, 2922, 1639, 1610, 1569, 1501, 1487, 1460, 1379, 1084, 852, 755. m/z (ES) 423.2195 (M$^+$ -ClO$_4$. C$_{27}$H$_{27}$N$_4$O requires 423.2185).

(1R,2R)-trans-N-(2-Azido-indan-1-yl)-3,5-dimethyl-benzamide 23f

Prepared as per the synthesis of 23a using 21 (1.100 g, 5.222 mmol) in CH$_2$Cl$_2$ (10 cm$^3$), triethylamine (4.36 cm$^3$, 31.330 mmol) and a solution of 22f (2.807 g, 16.637 mmol) in CH$_2$Cl$_2$ (10 cm$^3$). Purification by column chromatography (CH$_2$Cl$_2$, Rf 0.1) gave 23f (1.469 g, 92%) as a yellow solid, mp 178-180 °C. $[\alpha]_D^{20} = -20.5$ (c 0.74 in CHCl$_3$).

δ$_H$ (400 MHz, CDCl$_3$) 2.38 (6H, s), 2.96 (1H, dd, $J$ 16.1, 6.5), 3.34 (1H, dd, $J$ 16.1, 7.5), 4.20-4.25 (1H, app. q), 5.62-5.66 (1H, app. t), 6.35 (1H, d, $J$ 7.5), 7.18 (1H, s), 7.29-7.33 (4H, m), 7.43 (2H, s). δ$_C$ (100 MHz, CDCl$_3$) 20.8, 35.8, 59.8, 67.7, 123.9, 124.4, 124.6, 127.3, 128.5, 133.0, 133.4, 138.0, 139.3, 139.5, 167.4. ν$_{\text{max}}$ (neat)/cm$^{-1}$ 3248, 3128, 3029, 2922, 2914, 2914, 2914, 2914, 1640, 1601, 1532, 1459, 861, 744, 683. m/z (ES) 307.1559 (M$^+$ + H. C$_{18}$H$_{19}$N$_4$O requires 307.1559).

(1R,2R)-trans-1-(3,5-Dimethyl-benzoylamino)-inden-2-yl-ammonium; chloride 24f
Prepared as per 24a using 23f (1.386 g, 4.525 mmol), triphenylphosphine (1.187 g, 4.525 mmol) in THF (38 cm³) and addition of water (5 cm³). Concentration of the aqueous layer produced a yellow solid which was purified by washing with ether to yield 24f (1.427 g, 99%) as a pale yellow solid, mp 265-266 °C (dec). \([\alpha]_D^{20} = -31.9 \ (c \ 0.91 \text{ in MeOH}).

\(\delta_H\) (600 MHz, DMSO-d₆) 2.33 (6H, s), 3.02 (1H, dd, \(J\ 15.4, 8.7\)), 3.34-3.39 (1H, m, (under H₂O resonance)), 3.97-3.99 (1H, app. q), 5.67-5.70 (1H, app. t), 7.16 (1H, d, \(J\ 7.2\)), 7.20 (1H, s), 7.24-7.31 (3H, m), 7.59 (2H, s), 8.64 (3H, broad s), 8.90 (1H, d, \(J\ 8.3\)). \(\delta_C\) (150 MHz, DMSO-d₆) 20.8, 34.5, 56.3, 57.5, 123.6, 124.6, 125.2, 127.3, 128.0, 132.6, 134.0, 137.2, 138.3, 140.9, 167.1. \(\nu_{\max}\) (neat)/cm⁻¹ 3306, 2947, 2920, 2838, 1641, 1601, 1521, 1475, 1343, 863, 769, 750, 691. m/z (ES) 281.1662 (M⁺ - Cl. C₁₈H₂₁N₂O requires 281.1654).

\((1R,2R)-trans-N-(2-Azido-indan-1-yl)-4-methoxy-benzamide \ 23g\)

Prepared as per the synthesis of \(23a\) using \(21\) (1.200 g, 5.696 mmol) in THF (10 cm³), triethylamine (2.38 cm³, 17.089 mmol), DMAP (0.035 g, 0.285 mmol) and a solution of \(22g\) (0.93 cm³, 6.836 mmol) in THF (13 cm³). Purification by column chromatography (CH₂Cl₂, \(R_f\) 0.3) gave \(23g\) (1.038 g, 59%) as an off-white solid, mp 174-175 °C. \([\alpha]_D^{20} = -26.1 \ (c \ 0.76 \text{ in CHCl}_3\)).
(1R,2R)-trans-1-(4-Methoxy-benzoylamino)-indan-2-yl-ammonium; chloride 24g

\[
\begin{align*}
\delta_H (600 \text{ MHz, DMSO-d}_6) & \ 2.84 (1\text{H}, \text{ dd, } J 15.4, 8.4), 3.28 (1\text{H}, \text{ m (under H}_2\text{O resonance)}), 3.83 (3\text{H}, \text{ s}), 4.38-4.42 (1\text{H}, \text{ app. q}), 5.50-5.53 (1\text{H}, \text{ app. t}), 7.03 (2\text{H}, \text{ d, } J 8.8), 7.16 (1\text{H}, \text{ d, } J 7.7), 7.24-7.29 (3\text{H}, \text{ m}), 7.92 (2\text{H}, \text{ d, } J 8.8), 8.83 (1\text{H}, \text{ d, } J 8.4). \ \\
\delta_C (150 \text{ MHz, DMSO-d}_6) & \ 35.2, 55.4, 59.2, 66.7, 113.5, 123.7, 124.6, 126.2, 127.1, 128.0, 129.2, 138.9, 141.1, 161.8, 166.1. \ \\
\nu_{\text{max}} (\text{neat})/\text{cm}^{-1} & \ 3279, 3025, 2913, 2847, 2097, 1634, 1507, 1259, 844, 750. \ \\
m/z (\text{ES}) & \ 331.1164 (\text{M}^+ + \text{Na. } \text{C}_{17}\text{H}_{16}\text{N}_4\text{O}_2\text{Na requires 331.1171}).
\end{align*}
\]

Prepared as per 24a using 23g (0.938 g, 3.043 mmol), triphenylphosphine (0.798 g, 3.043 mmol) in THF (25 cm³) and addition of water (4 cm³). Concentration of the aqueous layer produced a white solid which was purified by washing with ether to yield 24g (0.925 g, 95%) as a white solid, mp 272-273 °C. \([\alpha]_{D}^{20} = -10.5 (c 0.87 \text{ in MeOH}). \]

\[
\begin{align*}
\delta_H (600 \text{ MHz, DMSO-d}_6) & \ 2.99 (1\text{H}, \text{ dd, } J 14.7, 7.9), 3.28-3.39 (1\text{H}, \text{ m (under H}_2\text{O resonance)}), 3.84 (3\text{H}, \text{ s}), 3.94-3.97 (1\text{H}, \text{ app. q}), 5.68-5.71 (1\text{H}, \text{ app. t}), 7.04 (2\text{H}, \text{ d, } J 7.7), 7.18 (1\text{H}, \text{ d, } J 6.4), 7.27-7.31 (3\text{H}, \text{ m}), 7.95 (2\text{H}, \text{ d, } J 7.7), 8.49 (3\text{H}, \text{ s (broad)}), 8.87 (1\text{H}, \text{ d, } J 7.2). \ \\
\delta_C (150 \text{ MHz, DMSO-d}_6) & \ 34.6, 55.4, 56.7, 57.7, 113.5, 123.8, 124.7, 126.2, 127.4, 128.2, 129.4, 138.4, 141.0, 161.8, 166.4. \ \\
\nu_{\text{max}} (\text{neat})/\text{cm}^{-1} & \ 3323, 2933, 2866, 2096, 1608, 1533, 1505, 1251, 842, 742. \ \\
m/z (\text{ES}) & \ 283.1450 (\text{M}^+ - \text{Cl. } \text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_2\text{ requires 283.1447}).
\end{align*}
\]

(1R,2R)-trans-4-[1-(4-Methoxy-benzoylamino)-indan-2-yl]-1-phenyl-4H-[1,2,4]triazol-1-ium; perchlorate 15g
Prepared as per 15a using 25 (0.355 g, 1.441 mmol), oven-dried molecular sieves (4Å, 1.40 g) and 24g (free-based amine, 0.388 g, 1.373 mmol) in CH₃CN (14 cm³). The reaction was heated under reflux for 7 d under an atmosphere of Ar. Filtration under a stream of Ar followed by removal of the filtrate in vacuo yielded a red-brown residue. Purification by column chromatography (7:3 EtOAc-hexane, Rf 0.2) gave 15g (0.533 g, 76%) as a pink solid, mp 123-124 °C. [α]D²⁰ = -88.9 (c 0.72 in CHCl₃).

δH (600 MHz, DMSO-d₆) 3.59 (1H, dd, J 16.1, 9.6), 3.72 (1H, dd, J 16.1, 8.3), 3.82 (3H, s), 5.31 (1H, ddd, J 9.6, 8.7, 8.3), 6.11 (1H, dd, J 8.7, 8.3), 7.02 (2H, d, J 8.7), 7.32 (1H, d, J 7.2), 7.37-7.44 (3H, m), 7.66 (1H, t, J 7.3), 7.73-7.75 (2H, app. t), 7.90 (2H, d, J 8.7), 7.95 (2H, d, J 7.5), 9.09 (1H, d, J 8.3), 9.74 (1H, s), 11.21 (1H, s). δC (150 MHz, DMSO-d₆) 36.4, 55.4, 60.1, 65.6, 113.5, 120.6, 123.9, 124.7, 125.7, 127.7, 128.6, 129.5, 130.3, 130.7, 135.0, 137.7, 139.4, 141.4, 144.7, 162.0, 166.9. νmax (neat)/cm⁻¹ 3363, 3123, 3074, 2841, 1640, 1605, 1571, 1498, 1460, 1253, 1075, 757, 687. m/z (ES) 411.1822 (M+ -ClO₄. C₂₅H₂₃N₄O₂ requires 411.1821).

(1R,2R)-trans-N-(2-Azido-indan-1-yl)-isobutyramide 23h

Prepared as per the synthesis of 23a using 21 (1.000 g, 4.747 mmol) in CH₂Cl₂ (8 cm³), triethylamine (1.98 cm³, 14.241 mmol) and a solution of 22h (0.60 cm³, 5.696 mmol) in CH₂Cl₂ (8 cm³). Purification by column chromatography (0.95:0.05 CH₂Cl₂-hexane, Rf 0.2) gave 23h (1.137 g, 98%) as a white solid, mp 177-178 °C. [α]D²⁰ = -15.3 (c 0.87 in CHCl₃).
\( \delta_H (600 \text{ MHz, DMSO-d}_6) \) 1.07 (3H, d, \( J 6.6 \)), 1.11 (3H, d, \( J 7.0 \)), 2.44-2.48 (1H, m), 2.77 (1H, dd, \( J 15.5, 8.4 \)), 3.24 (1H, dd, \( J 15.5, 7.5 \)), 4.17-4.21 (1H, app. q), 5.25-5.27 (1H, app. t), 7.10 (1H, d, \( J 7.0 \)), 7.24-7.28 (3H, m), 8.32 (1H, d, \( J 8.4 \)). \( \delta_C (150 \text{ MHz, DMSO-d}_6) \) 19.2, 19.6, 34.1, 35.2, 58.6, 66.7, 123.5, 124.6, 127.1, 128.0, 138.8, 141.0, 176.5. \( \nu_{\text{max}} \) (neat)/cm\(^{-1} \) 3269, 2973, 2877, 2100, 1644, 1524, 1460, 745. \( m/z \) (ES) 267.1209 (M\(^+\) + Na. C\(_{13}\)H\(_{16}\)N\(_4\)ONa requires 267.1222).

\( (1R,2R)-\text{trans}-1-(\text{Isobutyrylamino})-\text{indan-2-yl-ammonium; chloride 24h} \)

Prepared as per 24a using 23h (0.979 g, 4.009 mmol), triphenylphosphine (1.052 g, 4.009 mmol) in THF (33 cm\(^3\)) and addition of water (5 cm\(^3\)). Concentration of the aqueous layer produced a white solid which was purified by washing with ether to yield 24h (0.878 g, 86%) as a white solid, mp 274-276 °C. \( [\alpha]_D^{20} = -28.1 \) (c 0.76 in MeOH).

\( \delta_H (600 \text{ MHz, DMSO-d}_6) \) 1.10 (3H, d, \( J 6.8 \)), 1.12 (3H, d, \( J 6.8 \)) 2.46-2.51 (1H, m), 2.99 (1H, dd, \( J 15.8, 8.7 \)), 3.30 (1H, dd, \( J 15.8, 8.3 \)), 3.74 (1H, ddd, \( J 8.7, 8.3, 7.9 \)), 5.39 (1H, dd, \( J 7.9, 7.9 \)), 7.11 (1H, d, \( J 6.0 \)), 7.26-7.28 (3H, m), 8.41 (1H, d, \( J 7.9 \)), 8.65 (3H, s (broad)). \( \delta_C (150 \text{ MHz, DMSO-d}_6) \) 19.5, 20.3, 34.4, 34.9, 56.9, 57.4, 124.0, 125.0, 127.7, 128.5, 138.8, 141.3, 177.4. \( \nu_{\text{max}} \) (neat)/cm\(^{-1} \) 3301, 2966, 2831, 1643, 1596, 1522, 1474, 1354, 746. \( m/z \) (ES) 219.1488 (M\(^+\) - Cl. C\(_{13}\)H\(_{19}\)N\(_2\)O requires 219.1497).

\( (1R,2R)-\text{trans}-4-(1-\text{Isobutyrylamino})-\text{indan-2-yl}-1\text{-phenyl-4H-[1,2,4]}\text{triazol-1-ium; perchlorate 15h} \)
Prepared as per 15a using 25 (0.420 g, 1.705 mmol), oven-dried molecular sieves (4Å, 1.60 g) and 24h (free-based amine, 0.354 g, 1.624 mmol) in CH₃CN (11 cm³). The reaction was heated under reflux for 7 d under an atmosphere of Ar. Filtration under a stream of Ar followed by removal of the filtrate in vacuo yielded a red-brown residue. Purification by column chromatography (7:3 EtOAc-hexane, Rf 0.3) gave 15h (0.515 g, 71%) as a pale brown solid, mp 86-87 °C. \([\alpha]D^{20} = -2.3 \text{ (c 0.53 in CHCl}_3\).]

\[\delta H (600 MHz, DMSO-d_6) 1.02 (3H, d, J 6.6), 1.07 (3H, d, J 6.6), 2.47-2.51 (1H, m, (under DMSO resonance)), 3.56 (1H, dd, J 16.0, 9.5), 3.66 (1H, dd, J 16.0, 8.4), 5.09-5.13 (1H, app. q), 5.82-5.85 (1H, app. t), 7.27 (1H, d, J 7.3), 7.38-7.42 (3H, m), 7.67 (1H, t, J 7.3), 7.74-7.76 (2H, app. t.), 7.95 (2H, d, J 7.3), 8.62 (1H, d, J 8.1), 9.67 (1H, s), 11.20 (1H, s). \]

\[\delta C (150 MHz, DMSO-d_6) 19.3, 19.6, 33.9, 36.0, 59.5, 66.0, 120.5, 123.7, 124.8, 127.7, 128.7, 130.0, 130.7, 134.9, 137.7, 138.9, 141.3, 144.6, 177.7. \]

\[\nu_{\text{max}} \text{ (neat)/cm}^{-1} 3349, 3125, 2972, 1649, 1570, 1520, 1487, 1460, 1386, 1070, 756, 687. \]

\[m/z \text{ (ES) 347.1875 (M}^+ \text{-ClO}_4. \text{ C}_{21}\text{H}_{23}\text{N}_4\text{O requires 347.1872).} \]

\((1R,2R)-\text{trans-N-}(2-\text{Azido-indan-1-yl})-\text{N-methyl-benzamide 26}\)

An oven-dried 25 cm³ round bottomed flask equipped with a magnetic stirring bar was charged with 23a (1.200 g, 4.312 mmol) and put under an atmosphere of Ar (balloon). THF (6.5 cm³) was charged via syringe and the reaction was cooled to 0 °C. NaH (60% suspension, 0.198 g, 4.959 mmol) was added quickly from a clock glass, the reaction was returned to an atmosphere
of Ar and stirred for 30 min at 0 °C. Methyl iodide (0.30 cm³, 4.743 mmol) was added via syringe and the reaction left to return to ambient temperature overnight. Deionised water (15 cm³) and EtOAc (40 cm³) were added and the organic layer removed. The aqueous layer was washed with EtOAc (4 x 10 cm³) and the organic extracts combined, dried (MgSO₄) and concentrated in vacuo. Purification by column chromatography (8:2 CH₂Cl₂-hexane, Rf 0.2) gave 26 (0.850 g, 67%) as a yellow oil, [α]D²⁰ = -92.6 (c 1.10 in CHCl₃).

The ¹H and ¹³C NMR spectra of this compound indicate the presence of 2 rotameric species at rt in DMSO-d₆ - the ratio of these was found to be 0.40:0.60; δH (400 MHz, DMSO-d₆) 2.67 (1.2H, s), 2.69 (0.6H, dd, J 15.6, 9.5), 2.79 (1.8H, s), 2.84 (0.4H, dd, J 15.6, 9.5), 3.21 (0.6H, dd, J 15.6, 8.0), 3.39-3.36 (0.4H, m, (under H₂O resonance)), 4.60-4.66 (1H, m), 5.09 (0.6H, d, J 7.8), 6.15 (0.4H, d, J 7.8), 7.25-7.35 (4H, m), 7.44-7.55 (5H, m). δC (100 MHz, DMSO-d₆) 28.2, 32.9, 34.5, 35.5, 63.0, 63.2, 64.0, 69.1, 123.3, 123.7, 125.1, 125.2, 126.4, 126.8, 127.3, 127.6, 128.4, 128.5, 128.67, 128.7, 129.6, 129.7, 136.2, 136.4, 137.4, 137.8, 139.7, 171.5, 171.6. νmax (neat)/cm⁻¹ 3026, 2921, 2097, 1635, 1396, 748, 700. m/z (ES) 293.1404 (M⁺ + H. C₁₇H₁₇N₄O requires 293.1402).

(1R,2R)-trans-1-(Benzoyl-methyl-amino)-indan-2-yl-ammonium, chloride 27

![Structure of compound 27](image)

Prepared as per 24a using 26 (0.850 g, 2.907 mmol), triphenylphosphine (0.763 g, 2.907 mmol) in THF (24 cm³) and addition of water (4 cm³). Concentration of the aqueous layer produced an off-white solid which was purified by washing with ether to yield 27 (0.814 g, 93%) as an off-white solid, mp 254-255 °C. [α]D²⁰ = -66.4 (c 1.15 in MeOH).

The ¹H and ¹³C NMR spectra of this compound indicate the presence of 2 rotameric species at rt in DMSO-d₆ - the ratio of these was found to be 0.33:0.67. δH (600 MHz, DMSO-d₆) 2.68 (2.01H, s), 2.77 (0.99H, s), 2.85 (0.33H, dd, J 14.4, 8.0), 3.01 (0.67H, dd, J 14.4, 8.0), 3.24
(0.33H, dd, J 14.4, 7.5), 3.34-3.40 (0.66H, m, under H2O resonance)), 4.09-4.14 (1H, m), 5.33 (0.33H, d, J 8.0), 6.27 (0.67H, d, J 8.0), 7.22-7.70 (9H, m), 8.68 (0.99H, s (broad)), 8.83 (2.01H, s (broad)). δc (150 MHz, DMSO-d6) 28.5, 33.4, 34.3, 34.8, 53.0, 53.2, 62.5, 67.3, 123.5, 123.7, 125.4, 125.5, 126.90, 126.93, 127.8, 128.0, 128.5, 128.7, 129.0, 129.1, 129.5, 130.0, 136.7, 136.9, 138.0, 138.2, 138.8, 139.5, 171.8, 172.5.

νmax (neat)/cm⁻¹ 2924, 2851, 1622, 1598, 1481, 1386, 751, 731, 697. m/z (ES) 267.1506 (M⁺ - Cl. C₁₇H₁₉N₂O requires 267.1497).

(1R,2R)-trans-4-[1-(Benzoyl-methyl-amino)-indan-2-yl]-1-phenyl-4H-[1,2,4]triazol-1-ium; perchlorate 16

Prepared as per 15a using 25 (0.476 g, 1.932 mmol), oven-dried molecular sieves (4Å, 1.80 g) and 27 (free-based amine, 0.490 g, 1.840 mmol) in CH₃CN (5 cm³). The reaction was heated under reflux for 7 d under an atmosphere of Ar. Filtration under a stream of Ar followed by removal of the filtrate in vacuo yielded a red-brown residue. Purification by preparative thin layer chromatography (7:3 EtOAc-hexane, Rf 0.2) gave 16 (0.182 g, 20%) as an orange solid, mp 155-156 oC. [α]D²⁰ = -53.0 (c 0.82 in CHCl₃).

The ¹H NMR spectrum of this compound indicates the presence of 2 rotameric species at rt in CD₃CN - the ratio of these was found to be 0.20:0.80, the ¹³C spectrum indicates the major rotamer only. δH (600 MHz, CD₃CN) 2.83-2.97 (3H, m), 3.31 (0.20H, s (broad)), 3.55 (0.80H, s (broad)), 3.67 (0.20H, s (broad)), 3.90 (0.80H, s (broad)), 5.43-5.47 (1H, app. q), 5.88 (0.20H, s (broad)), 6.65 (0.80H, s (broad)), 7.16-7.62 (9H, m), 7.73-7.88 (5H, m), 8.80 (0.20H, s (broad)), 9.16 (0.80H, s (broad)), 9.78 (0.20H, s (broad)), 10.25 (0.80H, s (broad)). δC (150 MHz, CD₃CN) 34.2, 37.7, 63.4, 66.0, 122.0, 125.6, 126.4, 128.4, 129.1, 129.4, 130.3, 131.2, 131.4, 132.1, 136.0, 136.6, 137.0, 139.7, 141.4, 145.4, 174.6. νmax (neat)/cm⁻¹ 3131, 3068, 1623, 1600,
Synthesis of acyloins 6 and 43-51

(S)-2-Hydroxy-1,2-diphenyl-ethanone (S)-6 (Table 2, entry 19)

Prepared as per reaction condition set C using catalyst 15a (52.90 mg, 0.11 mmol), with addition of toluene (0.67 cm$^3$) and KHMDS (220 µL, 0.110 mmol, 0.5M solution in toluene) over 7 min. Benzaldehyde (111.7 µL, 1.100 mmol) was added dropwise over 5 min and the reaction was stirred at room temperature for 18 h. Purification by column chromatography (6:4 CH$_2$Cl$_2$:hexane, R$_f$ 0.2) gave (S)-6 (13.6 mg, 12%) as a white solid, mp 131-132 °C, lit.¹ 132-133 °C, 62% ee. \([\alpha]_D^{20} = +62.8 \text{ (c 0.20 in MeOH), lit.}^1 [\alpha]_D^{20}: +146.5 \text{ (c 1.0 in MeOH), for } S\text{ enantiomer with 90% } ee.\]

CSP-HPLC analysis. Chiralpak AD (4.6 mm x 25 cm), hexane/IPA: 9/1, 1.0 mL min$^{-1}$, RT, UV detection at 220 nm, retention times: 21.4 min (minor enantiomer) and 29.1 (major enantiomer).

δ$_H$ (400 MHz, CDCl$_3$) 4.58 (1H, d, \(J = 5.8\)), 5.98 (1H, d, \(J = 5.8\)), 7.29-7.44 (5H, m (overlapping with CHCl$_3$ resonance)), 7.41-7.44 (2H, app. t), 7.53 (1H, t, \(J = 7.0\)), 7.93 (2H, d, \(J = 7.1\))

(S)-2-Hydroxy-1,2-di-naphthalen-2-yl-ethanone (S)-43 (Table 3, entry 1)

δ$_H$ (400 MHz, CDCl$_3$) 4.58 (1H, d, \(J = 5.8\)), 5.98 (1H, d, \(J = 5.8\)), 7.29-7.44 (5H, m (overlapping with CHCl$_3$ resonance)), 7.41-7.44 (2H, app. t), 7.53 (1H, t, \(J = 7.0\)), 7.93 (2H, d, \(J = 7.1\))
Prepared as per reaction condition set C using catalyst 15a (52.90 mg, 0.11 mmol), with addition of toluene (0.40 cm³) and KHMDS (220 µL, 0.110 mmol, 0.5M solution in toluene) over 7 min. Aldehyde 34 (171.80 mg, 1.100 mmol) in toluene (0.38 cm³) was added dropwise over 5 min and the reaction was stirred at room temperature for 16 h. Purification by column chromatography (6:4 CH₂Cl₂:hexane, Rₜ 0.1) gave (S)-43 (62.6 mg, 36%) as a pale yellow solid, mp 127-128 °C, lit.,³ 127 °C, 35% ee. 

\[ \alpha_d^{20} = -6.8 \text{ (c 0.63 in CHCl}_3) \text{, lit.,}^4 \alpha_d^{20} = +21.0 \text{ (c 1.1 in CHCl}_3) \text{, for R enantiomer with 99} \% \text{ ee.} \]

CSP-HPLC analysis. Chiralpak AD (4.6 mm x 25 cm), hexane/IPA: 8/2, 1.0 mL min⁻¹, RT, UV detection at 254 nm, retention times: 28.1 min (minor enantiomer) and 47.7 (major enantiomer).

δH (400 MHz, CDCl₃) 4.75 (1H, s (broad)), 6.30 (1H, s), 7.45-7.61 (5H, m), 7.78-7.85 (5H, m), 7.89 (1H, d, \( J = 8.5 \)), 7.94 (1H, s), 8.01 (1H, d, \( J = 8.5 \)), 8.53 (1H, s)

(5)-2-Hydroxy-1,2-bis-(4-methylphenyl)ethanone (S)-45 (Table 3, entry 3)

Prepared as per reaction condition set C using catalyst 15a (52.90 mg, 0.11 mmol), with addition of toluene (0.65 cm³) and KHMDS (220 µL, 0.110 mmol, 0.5M solution in toluene) over 7 min. Substrate 36 (129.7 µL, 1.100 mmol) was added dropwise over 5 min and the reaction was stirred at room temperature for 18 h. Purification by column chromatography (6:4 CH₂Cl₂:hexane, Rₜ 0.1) gave (S)-45 (12.8 mg, 10%) as a yellow solid, mp 90-91 °C, lit.,⁵ 89-90 °C, 45% ee. \[ \alpha_d^{20} = +51.3 \text{ (c 0.18 in MeOH) , lit.,}^6 \alpha_d^{20} = -130.8 \text{ (c 1.0 in MeOH) , for R enantiomer with 82} \% \text{ ee.} \]

CSP-HPLC analysis. Chiralpak AD (4.6 mm x 25 cm), hexane/IPA: 9/1, 0.8 mL min⁻¹, RT, UV detection at 254 nm, retention times: 29.3 min (minor enantiomer) and 33.8 (major enantiomer).
δ_H (400 MHz, CDCl₃) 2.31 (3H, s), 2.38 (3H, s), 4.60 (1H, s, (broad)), 5.92 (1H, s (broad)), 7.13-7.34 (6H, m (overlapping with CHCl₃ resonance)), 7.83 (2H, d, J 8.0)

(S)-2-Hydroxy-1,2-bis-(2-methoxy-phenyl)ethanone (S)-46 (Table 3, entry 4)

\[
\begin{align*}
\text{(S)-46} \\
\text{H}_2\text{CO} & \quad \text{O} \\
\text{OCH}_3 & 
\end{align*}
\]

Prepared as per reaction condition set C using catalyst 15a (52.90 mg, 0.11 mmol), with addition of toluene (0.48 cm³) and KHMDS (220 µL, 0.110 mmol, 0.5M solution in toluene) over 7 min. Substrate 37 (149.77 mg, 1.100 mmol) in toluene (0.30 cm³) was added dropwise over 5 min and the reaction was stirred at room temperature for 24 h. Purification by column chromatography (CH₂Cl₂, Rf 0.2) gave (S)-46 (42.9 mg, 29%) as an off-white solid, mp 98-99 °C, lit., 54% ee. [α]₂⁰ = +39.1 (c 0.43 in CHCl₃), lit., +123.0 (c 1.0 in CHCl₃), for S enantiomer with 98% ee.

CSP-HPLC analysis. Chiralpak OD-H (4.6 mm x 25 cm), hexane/IPA: 85/15, 0.5 mL min⁻¹, RT, UV detection at 254 nm, retention times: 30.8 min (major enantiomer) and 43.7 (minor enantiomer).

δ_H (400 MHz, CDCl₃) 3.74 (3H, s), 3.75 (3H, s), 4.50 (1H, s (broad)), 6.13 (1H, s), 6.76-6.81 (2H, app. t), 6.84-6.88 (1H, app. t), 6.93-6.97 (1H, app. t), 7.17-7.22 (2H, m (overlapping with CHCl₃ resonance)), 7.37-7.41 (1H, app. t), 7.70 (1H, d, J 7.5)

(S)-1,2-Bis-(2-chloro-phenyl)-2-hydroxy-ethanone (S)-48 (Table 3, entry 6)

\[
\begin{align*}
\text{(S)-48} \\
\text{Cl} & \quad \text{O} \\
\text{Cl} & 
\end{align*}
\]
Prepared as per reaction condition set C using catalyst 15a (52.90 mg, 0.11 mmol), with addition of toluene (0.66 cm³) and KHMDS (220 µL, 0.110 mmol, 0.5M solution in toluene) over 7 min. Substrate 39 (123.9 µL, 1.100 mmol) was added dropwise over 5 min and the reaction was stirred at room temperature for 16 h. Purification by column chromatography (6:4 CH₂Cl₂:hexane, Rf 0.2) gave (S)-48 (11.6 mg, 8%) as a colourless solid, mp 61-62 °C, lit., 5 63-64 °C, 28% ee. [α]D²⁰ = +9.3 (c 0.17 in CHCl₃), lit., 4 [α]D²⁰: -46.0 (c 1.0 in CHCl₃), for R enantiomer with 97% ee.

CSP-HPLC analysis. Chiralpak AD (4.6 mm x 25 cm), hexane/IPA: 9/1, 0.8 mL min⁻¹, RT, UV detection at 254 nm, retention times: 22.8 min (major enantiomer) and 25.8 (minor enantiomer).

δH (400 MHz, CDCl₃) 3.30 (1H, s (broad)), 6.31 (1H, s), 7.15-7.23 (5H, m (overlapping with CHCl₃ resonance)), 7.31-7.34 (3H, m)

(S)-1,2-Bis-(3-chloro-phenyl)-2-hydroxy-ethanone (S)-49 (Table 3, entry 7)

Prepared as per reaction condition set C using catalyst 15a (52.90 mg, 0.11 mmol), with addition of toluene (0.66 cm³) and KHMDS (220 µL, 0.110 mmol, 0.5M solution in toluene) over 7 min. Substrate 40 (124.60 µL, 1.100 mmol) was added dropwise over 5 min and the reaction was stirred at room temperature for 16 h. Purification by column chromatography (6:4 CH₂Cl₂:hexane, Rf 0.3) gave (S)-49 (73.1 mg, 47%) as an off-white solid, mp 75-76 °C, lit., 5 76-77 °C, 1% ee. [α]D²⁰ = +2.4 (c 0.73 in CHCl₃), lit., 4 [α]D²⁰: -31.0 (c 1.2 in CHCl₃), for R enantiomer with 99% ee.

CSP-HPLC analysis. Chiralpak AD (4.6 mm x 25 cm), hexane/IPA: 9/1, 0.8 mL min⁻¹, RT, UV detection at 254 nm, retention times: 19.7 min (minor enantiomer) and 26.9 (major enantiomer).
\(\delta_H\) (400 MHz, CDCl\(_3\)) 4.50 (1H, d, \(J\ 5.5\)), 5.90 (1H, d, \(J\ 5.5\)), 7.23-7.41 (5H, m), 7.53 (1H, d, \(J\ 8.0\)), 7.76 (1H, d, \(J\ 7.5\)), 7.93 (1H, s)

\((S)-1,2\)-Bis-(4-chloro-phenyl)-2-hydroxy-ethanone \((S)-50\) (Table 3, entry 8)

\[
\begin{array}{c}
\text{HO} \\
\text{Cl} \\
\text{Cl}
\end{array}
\]

Prepared as per reaction condition set C using catalyst 15a (52.90 mg, 0.11 mmol), with addition of toluene (0.40 cm\(^3\)) and KHMDS (220 µL, 0.110 mmol, 0.5M solution in toluene) over 7 min. Substrate 41 (154.63 mg, 1.100 mmol) in toluene (0.38 cm\(^3\)) was added dropwise over 5 min and the reaction was stirred at room temperature for 16 h. Purification by column chromatography (6:4 CH\(_2\)Cl\(_2\):hexane, R\(_f\) 0.3) gave \((S)-50\) (48.8 mg, 32%) as an off-white solid, mp 88-89 °C, lit.,\(^5\) 87-88 °C, 6% ee. \([\alpha]\)\(_D\)^{20} = +1.4 (c 0.49 in MeOH), lit.,\(^9\) \([\alpha]\)\(_D\)^{20}: -12.3 (c 1.0 in MeOH), for \(R\) enantiomer with 29% ee.

CSP-HPLC analysis. Chiralpak OJ-H (4.6 mm x 25 cm), hexane/IPA: 95/5, 0.6 mL min\(^{-1}\), RT, UV detection at 220 nm, retention times: 34.7 min (major enantiomer) and 37.8 (minor enantiomer).

\(\delta_H\) (400 MHz, CDCl\(_3\)) 4.49 (1H, s (broad)), 5.90 (1H, s), 7.26-7.27 (2H, d, (overlapping with CHCl\(_3\) resonance)), 7.32 (2H, d, \(J\ 8.0\)), 7.40 (2H, d, \(J\ 7.8\)), 7.84 (2H, d, \(J\ 7.8\))

\((S)-1,2\)-Di-furan-2-yl-2-hydroxy-ethanone \((S)-51\) (Table 3, entry 9)

\[
\begin{array}{c}
\text{HQ} \\
\text{O} \\
\text{O}
\end{array}
\]

\((S)-51\)
Prepared as per reaction condition set C using catalyst $15a$ (52.90 mg, 0.11 mmol), with addition of toluene (0.69 cm$^3$) and KHMDS (220 µL, 0.110 mmol, 0.5M solution in toluene) over 7 min. Substrate $42$ (90.72 µL, 1.100 mmol) was added dropwise over 5 min and the reaction was stirred at room temperature for 18 h. Purification by column chromatography (CH$_2$Cl$_2$, R$_f$ 0.2) gave (S)-$51$ (51.3 mg, 49%) as a pale yellow solid, mp 134-135 °C, lit.,$^{10}$ 135-136 °C, 1% ee. $\left[\alpha\right]_D^{20} = +0.6$ (c 0.51 in MeOH), lit.,$^4$ $\left[\alpha\right]_D^{20} = -21.6$ (c 0.1 in MeOH), for $R$ enantiomer with 92% ee.

CSP-HPLC analysis. Chiralpak AD (4.6 mm x 25 cm), hexane/IPA: 9/1, 0.8 mL min$^{-1}$, RT, UV detection at 254 nm, retention times: 33.3 min (major enantiomer) and 40.9 (minor enantiomer).

$\delta_H$ (400 MHz, CDCl$_3$) 4.22 (1H, s (broad)), 5.82 (1H, s, (broad)), 6.37 (1H, dd, $J$ 3.3, 1.5), 6.42 (1H, d, $J$ 3.5), 6.56 (1H, dd, $J$, 3.5, 1.5), 7.27 (1H, m (overlapping with CHCl$_3$ resonance)), 7.40 (1H, d, $J$ 1.5), 7.64 (1H, app. s)
4.0 NMR spectra

$^1$H NMR spectrum (600 MHz, DMSO) of catalyst 15a

$^{13}$C NMR spectrum (150 MHz, CDCl$_3$) of catalyst 15a
$^1$H NMR spectrum (600 MHz, DMSO) of catalyst 15b

$^{13}$C NMR spectrum (150 MHz, DMSO) of catalyst 15b
\(^1\)H NMR spectrum (600 MHz, DMSO) of catalyst 15c

\(^{13}\)C NMR spectrum (150 MHz, DMSO) of catalyst 15c
$^1$H NMR spectrum (600 MHz, DMSO) of catalyst 15d

$^{13}$C NMR spectrum (150 MHz, DMSO) of catalyst 15d
$^1$H NMR spectrum (600 MHz, DMSO) of catalyst 15e

$^{13}$C NMR spectrum (150 MHz, DMSO) of catalyst 15e
$^1$H NMR spectrum (600 MHz, DMSO) of catalyst 15g

$^{13}$C NMR spectrum (150 MHz, DMSO) of catalyst 15g
$^1$H NMR spectrum (600 MHz, DMSO) of catalyst 15h

$^{13}$C NMR spectrum (150 MHz, DMSO) of catalyst 15h
\( ^1\)H NMR spectrum (600 MHz, CD\(_3\)CN) of catalyst 16

\( ^{13}\)C NMR spectrum (150 MHz, CD\(_3\)CN) of catalyst 16
$^1$H NMR spectrum (400 MHz, CHCl$_3$) of benzoin ($S$)-6

$^1$H NMR spectrum (400 MHz, CHCl$_3$) of acyloin ($S$)-43
$^1$H NMR spectrum (400 MHz, CHCl$_3$) of acyloin (S)-45

$^1$H NMR spectrum (400 MHz, CHCl$_3$) of acyloin (S)-46
$^1$H NMR spectrum (400 MHz, CHCl$_3$) of acyloin (S)-48

$^1$H NMR spectrum (400 MHz, CHCl$_3$) of acyloin (S)-49
$^1$H NMR spectrum (400 MHz, CHCl$_3$) of acyloin (S)-50

$^1$H NMR spectrum (400 MHz, CHCl$_3$) of acyloin (S)-51
5.0 HPLC Chromatograms – acyloin products

HPLC Chromatograms of benzoin 6
Chiralpak AD (4.6 mm x 25 cm),
Hexane/IPA: 90/10, 1.0 mL min\(^{-1}\),
RT, UV detection at 220 nm

<table>
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<th>Ret. Time (min)</th>
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Resolved HPLC chromatogram for benzoin 6 – racemate

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Resolved HPLC chromatogram for enantioenriched benzoin (S)-6
HPLC Chromatograms of acyloin 43

Chiralpak AD (4.6 mm x 25 cm),
Hexane/IPA: 80/20, 1.0 mL min\(^{-1}\),
RT, UV detection at 254 nm

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Resolved HPLC chromatogram for acyloin 43 – racemate

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Resolved HPLC chromatogram for enantioenriched (S)-43
HPLC Chromatograms of acyloin 45
Chiralpak AD (4.6 mm x 25 cm),
Hexane/IPA: 90/10, 0.8 mL min⁻¹,
RT, UV detection at 254 nm

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Resolved HPLC chromatogram for acyloin 45 – racemate

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Resolved HPLC chromatogram for enantioenriched acyloin (S)-45
HPLC Chromatograms of acyloin \(46\)
Chiralpak OD-H (4.6 mm x 25 cm),
Hexane/IPA: 85/15, 0.5 mL min\(^{-1}\),
RT, UV detection at 254 nm

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Resolved HPLC chromatogram for acyloin \(46\) – racemate

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Resolved HPLC chromatogram for enantioenriched acyloin \((S)-46\)
HPLC Chromatograms of acyloin 48
Chiralpak AD (4.6 mm x 25 cm),
Hexane/IPA: 90/10, 0.8 mL min\(^{-1}\),
RT, UV detection at 254 nm

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Resolved HPLC chromatogram for acyloin 48 – racemate

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Resolved HPLC chromatogram for enantioenriched acyloin (S)-48
HPLC Chromatograms of acyloin 49
Chiralpak AD (4.6 mm x 25 cm),
Hexane/IPA: 90/10, 0.8 mL min⁻¹,
RT, UV detection at 254 nm

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Resolved HPLC chromatogram for acyloin 49 – racemate

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Resolved HPLC chromatogram for enantioenriched acyloin (S)-49
HPLC Chromatograms of acyloin 50
Chiralpak OJ-H (4.6 mm x 25 cm),
Hexane/IPA: 95/5, 0.6 mL min\(^{-1}\),
RT, UV detection at 220 nm

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Resolved HPLC chromatogram for acyloin 50 – racemate

<table>
<thead>
<tr>
<th>Peak No</th>
<th>Result</th>
<th>Ret. Time (min)</th>
<th>Area (counts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.8564</td>
<td>22.192</td>
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<tr>
<td>2</td>
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<td>3</td>
<td>43.8779</td>
<td>37.747</td>
<td>365590048</td>
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</tbody>
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Resolved HPLC chromatogram for enantioenriched acyloin (S)-50
HPLC Chromatograms of acyloin 51
Chiralpak AD (4.6 mm x 25 cm),
Hexane/IPA: 90/10, 0.8 mL min⁻¹,
RT, UV detection at 254 nm

<table>
<thead>
<tr>
<th>Peak No</th>
<th>Result (min)</th>
<th>Ret. Time (min)</th>
<th>Area (counts)</th>
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</thead>
<tbody>
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<td>2</td>
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Resolved HPLC chromatogram for acyloin 51 – racemate

<table>
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<tbody>
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</tbody>
</table>

Resolved HPLC chromatogram for enantioenriched acyloin (S)-51
5.0 References