Supporting Information
for DOI: 10.1055/s-0038-1380687
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SUPPORTING INFORMATION

General

Experimental procedures and characterisation for 6-10, 12-14, 16, 17, S1 and S2

1H and 13C NMR spectra

References

S2

S3–S15

S16–S28

S29
**General**

All starting materials were purchased from commercial suppliers and used without further purification and all solvents used were dried and purified by standard techniques. Reactions requiring the exclusion of moisture were carried out under an atmosphere of argon or nitrogen in oven-dried glassware. Flash chromatography was carried out using Merck silica gel (35-70 µm) or on a Biotage Isolera Four platform using SNAP Ultra (25 µm) cartridges. Melting points were recorded on a Gallenkamp MPD350 apparatus. IR measurements were taken using a Perkin-Elmer 1600 FTIR spectrometer of solids (neat) and of oils (film). NMR spectra were recorded on Bruker DPX 300, Bruker DPX 400, Bruker DPX 500 or Oxford 300 spectrometer. $^1$H NMR spectra were measured at 250, 300, 400 and 500 MHz. $^{13}$C NMR spectra were measured at 75, 100, 125 and 150 MHz using CDCl$_3$ as the solvent and internal reference. Coupling constants $J$ are given in Hz. Multiplicity as follows: s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, sept = septet, m = multiplet, br = broad. Low Resolution Mass Spectrometry (LRMS) was carried out using a Varian Saturn 2 GC-MS, Waters LCR Premier XE TOF or Voyager DE-STR spectrometer. High Resolution Mass Spectrometry (HRMS) was carried out at the EPSRC National Mass Spectrometry Facility, Swansea. Optical rotations were measured with a UniPol L polarimeter and are quoted in units 10$^{-1}$ deg cm$^{-2}$ g$^{-1}$. High-performance liquid chromatography (HPLC) analysis was conducted using Shimadzu LC-10 AD coupled diode array-detector SPD-MA-10A-VP.
To a mixture of 1,3,5-trihydroxybenzene (2.03 g, 12.5 mmol), K$_2$CO$_3$ (8.65 g, 62.6 mmol) and activated 4 Å molecular sieves (7 g) in CH$_3$CN (15 mL) was added dropwise (S)-methyl 2-(methylsulfonyloxy)propanoate (8.00 g, 43.8 mmol) and the mixture heated at reflux for 5 days. The reaction was filtered, then water (15 mL) was added and organic material was extracted with ethyl acetate (3×20 mL). Combined organic extracts were dried (MgSO$_4$), filtered and concentrated under vacuum. Column chromatography (hexane:ethyl acetate) afforded a 1:1 diasteromeric mixture (predominantly $R,R,R$ and $R,R,S$) of the tris-methyl ester, 1.07 g, 22% ($R_f = 0.47$, hexane:ethyl acetate, 2:1).

This material was dissolved in THF (7 mL) and MeOH (7 mL), then 2M NaOH (10 mL) was added and the resulting mixture stirred for 16 h. After cooling to 0 °C, the reaction was acidified with 1M HCl and extracted with ethyl acetate (2×20 mL). Combined organic extracts were washed with brine (15 mL), dried (MgSO$_4$), filtered and concentrated under vacuum to give the tris-carboxylic acid, 924 mg, 97% as a 1:1 diasteromeric mixture. The acid (425 mg, 1.24 mmol) was stirred with thionyl chloride (1.64 g, 13.7 mmol) in toluene (10 mL) at reflux for 1h. The solvent then was evaporated (by benzene azeotrope). Dichloromethane (7 mL) was added and the solution cooled to 0 °C. 2,4,6-Trimethylaniline (588 mg, 4.35 mmol) was added and the mixture was stirred at room temperature for 16 h. 1M HCl (10 mL) was added and the aqueous phase was extracted with CH$_2$Cl$_2$ (3×20 mL). The combined organic layers were washed with 1M HCl (3×10 mL) brine (2x10 mL), dried over MgSO$_4$ and concentrated under vacuum.

The crude diastereomeric mixture was purified by multiple column chromatography (petroleum ether/ethyl acetate 3:1→1:1) to obtain (2R,2’R,2”R)-2,2’,2”-(Benzene-1,3,5-triyltris(oxy))tris(N-mesitylpropanamide) 9 (102 mg, 12%). Mp. 102-105.5 °C; $[\alpha]_D^{20} = -21.4$ ($c = 0.5$, CHCl$_3$); IR (neat) 3240, 2916, 1660, 1595, 1503, 1155, 732 cm$^{-1}$. 

S3
**1H NMR (400 MHz, CDCl₃):** δ = 7.50 (3H, br s), 6.84 (6H, s), 6.38 (3H, s), 4.83 (3H, q, J = 7 Hz), 2.25 (9H, s), 2.06 (18H, s), 1.72 (9H, d, J = 7 Hz) ppm; **13C NMR (125 MHz, CDCl₃):** δ = 170.3 (3C), 159.4 (3C), 137.4 (3C), 135.0 (6C), 129.9 (3C), 129.2 (6C), 97.0 (3C), 75.6 (3C), 21.0 (3C), 19.3 (3C), 18.2 (6C) ppm.

HRMS (ES⁺) m/z calcld for C₄₂H₅₂IN₃O₆: 694.3856; found: 694.3858.

**Phenyl(2,4,6-tris((R)-1-(mesitylamino)-1-oxopropan-2-yloxy)phenyl)iodonium, 4-methylbenzenesulfonate (6a)**

![Diagram]

To a solution of 9 (90 mg, 0.13 mmol) in 2,2,2-trifluoroethanol (2 mL) was added [hydroxy(tosyloxy)iodo]benzene (51 mg, 0.13 mmol) and the resulting mixture was stirred for 4 h at room temperature. Methanol (2 mL) was added then the solvents were removed under vacuum. The product was precipitated with a mixture of methanol, diethyl ether and petroleum ether giving 6a as a light brown powder (125 mg, 90 %). Mp. 150-152.5 °C; [α]₀²⁰ = +10.0 (c = 0.4, MeOH); IR (neat) 3231, 2982, 1695, 1672, 1579, 1229, 1177, 684 cm⁻¹.

**1H NMR (400 MHz, MeOD):** δ = 8.15 (2H, d, J = 8 Hz), 7.48-7.55 (3H, m), 7.37 (2H, t, J = 8 Hz), 7.05 (2H, d, J = 8 Hz), 6.86 (4H, s), 6.63 (2H, s), 6.69 (2H, s), 5.28 (2H, q, J = 7 Hz), 5.20 (1H, q, J = 7 Hz), 2.30 (3H, s), 2.24 (9H, s), 2.08 (12H, s), 1.97 (6H, s), 1.74 (6H, d, J = 7 Hz), 1.68 (3H, d, J = 7 Hz) ppm; **13C NMR (100 MHz, MeOD):** δ = 172.1, 171.4 (2C), 165.7, 159.4 (2C), 143.2, 141.6 (2C), 138.4 (2C), 138.3, 136.5 (2C), 136.4 (2C), 133.2, 133.1, 132.8, 132.7 (2C), 131.8 (2C), 131.7 (2C), 129.8 (2C), 129.7 (4C), 126.7 (4C), 116.3 (2C), 96.6, 90.0, 76.7 (2C), 76.1, 21.3 (2C), 21.0 (4C), 19.4 (2C), 19.3, 18.6 (2C), 18.4, 18.3 ppm.

HRMS (ES⁺) m/z calcld for C₅₅H₆₃IN₃O₉S: 1068.3330; found: 1068.3326. 
(2,6-Bis((R)-1-(mesitylamino)-1-oxopropan-2-yloxy)phenyl)(phenyl)iodonium tetrafluoroborate (6b)

\[
\begin{align*}
\text{MesHN} & \quad \text{Ph} \quad - \quad \text{BF}_4^- \\
\text{O} & \quad \text{O} & \quad \text{O} & \quad \text{NHN} \\
\end{align*}
\]

To a solution of (2R,2'R)-2,2'(2-iodo-1,3-phenylene)bis(oxy)bis(N-mesitylpropanamide) 4a \(^1\) (60 mg, 0.10 mmol) and mCPBA (77%, 39 mg, 0.18 mmol) in dichloromethane (4 mL) at 0 °C was added dropwise BF\(_3\)•OEt\(_2\) (31 µL, 0.24 mmol) and the resulting mixture stirred at 0 °C for 2 h. Phenylboronic acid (21 mg, 0.18 mmol) was added in one portion. The reaction was allowed to warm to room temperature and stirred for 4 h. The crude reaction mixture was applied to a short silica plug (3 g). Unreacted starting material and impurities were eluted with dichloromethane (30 mL). The iodonium salt and polar impurities were eluted using with 5% MeOH in dichloromethane (15 mL). This fraction was concentrated under vacuum. Subsequent precipitation with MeOH/Et\(_2\)O yielded 6b (59 mg, 78%) as a light brown solid. Mp. 113.5-115 °C; [α]\(_D\)\(^{20}\) = -18.1 (c = 1.1, CHCl\(_3\)); IR (neat) 3340, 2995, 1659, 1510, 1464, 1256, 1096, 1059, 729 cm\(^{-1}\).

\(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta = 7.19 (2H, d, J = 7 \text{ Hz}), 7.63 (1H, t, J = 8 \text{ Hz}), 7.54 (1H, t, J = 7 \text{ Hz}), 7.42 (2H, t, J = 7 \text{ Hz}), 6.93 (2H, d, J = 9 \text{ Hz}), 6.90 (4H, s), 5.23 (2H, q, J = 7 \text{ Hz}), 2.25 (6H, s), 2.08 (12H, s), 1.80 (6H, d, J = 7 \text{ Hz}) \text{ ppm}; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 171.8 (2\text{C}), 158.6 (2\text{C}), 138.8 (2\text{C}), 136.6 (4\text{C}), 133.1 (2\text{C}), 131.8, 130.0 (4\text{C}), 125.7, 123.2 (4\text{C}), 120.7 (2\text{C}), 118.1, 108.7, 77.0 (2\text{C}), 21.1 (2\text{C}), 19.6 (2\text{C}), 18.6 (4\text{C}) \text{ ppm}; \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta = -154.1, -154.2 (3\text{F}) \text{ ppm.}\)

MS (EI\(^+\)) \(m/z = 691 (M^+, 100)\); HRMS (APCI\(^+\)) \(m/z\) calcd for C\(_{36}\)H\(_{40}\)IN\(_2\)O\(_4\) (M\(^+\)) \(691.2033\); found: 691.2050.
(R)-2′-(Methoxymethoxy)-1,1′-binaphthyl-2-ol (S1)

Prepared from (R)-1,1′-bi-2-naphthol (1.00 g, 17.5 mmol, recrystallised from toluene) according to the literature. Obtained as a colourless oil (4.15 g, 72%)

1H NMR (500 MHz, CDCl3): δ = 7.94 (1H, d, J = 9 Hz), 7.82 (2H, d, J = 9 Hz), 7.78 (1H, d, J = 8 Hz), 7.51 (1H, d, J = 9 Hz), 7.31 (1H, q, J = 7 Hz), 7.28 (1H, d, J = 9 Hz), 7.24-7.19 (2H, m), 7.16-7.11 (2H, m), 7.00 (1H, d, J = 9 Hz), 5.02 (1H, d, J = 8 Hz), 4.97 (1H, d, J = 8 Hz), 4.89 (1H, br s), 3.09 (3H, s) ppm; 13C NMR (125 MHz, CDCl3): δ = 153.7, 151.3, 134.0, 133.9, 131.0, 129.8, 128.2 (2C), 128.1, 127.3 (2C), 126.5 (2C), 125.1, 124.9 (2C), 124.8, 123.3, 117.5, 117.2, 95.0, 56.2 ppm. Data in agreement with the literature.

(R)-Diethyl 2′-(methoxymethoxy)-1,1′-binaphthyl-2-yl phosphate (10)

To a solution (R)-2′-(methoxymethoxy)-1,1′-binaphthyl-2-ol (3.92 g, 11.8 mmol) in THF (25 mL) at −78 ºC was added n-BuLi (2.5 M in hexane, 5.46 mL, 13.66 mmol) The reaction was allowed to warm to 0 ºC, stirred for 1 h, then cooled to −78 ºC. Diethylchlorophosphate (1.97 mL, 13.66 mmol) was added dropwise and the reaction allowed to warm to room temperature over 1 h. The reaction was quenched with sat. NH4Cl and extracted with diethyl ether (3×15 mL). Combined organic extracts were washed with brine (15 mL), dried (MgSO4), filtered and concentrated under vacuum. Column chromatography (hexane:ethyl acetate) afforded 10 (4.93 g, 89%) as a colourless solid Mp. 71.5-73 ºC; [α]D 20 = 35.0 (c = 1.0, CHCl3).

1H NMR (400 MHz, CDCl3): δ = 7.96 (2H, t, J = 9 Hz), 7.91 (1H, d, J = 8 Hz), 7.85 (1H, d, J = 8 Hz), 7.77 (1H, d, J = 9 Hz), 7.58 (1H, d, J = 9 Hz), 7.44-7.40 (1H, m), 7.35 (1H, t, J = 7 Hz), 7.28-7.23 (3H, m), 7.18 (1H, d, J = 9 Hz), 5.08 (1H, d, J = 7 Hz), 5.04 (1H, d, J = 7 Hz), 3.65-3.49 (4H, m), 3.20 (3H, s), 1.00 (3H, t, J = 7 Hz), 0.88 (3H, t, J = 7 Hz) ppm.
\(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 152.8, 146.6, 146.5, 133.8, 131.0, 129.8, 129.7, 129.6, 128.1, 126.7, 126.5, 126.0, 125.7, 125.2, 124.2, 123.2, 123.1, 119.4, 116.6, 94.9, 64.1\) (2C), 55.9, 15.7 (2C) ppm.

MS (EI\(^+\)) \(m/z = 489\) ([M+Na]\(^+\), 100); HRMS (ES\(^+\)) \(m/z\) calcd for C\(_{26}\)H\(_{28}\)O\(_6\)P (M+H): 467.1624 found: 467.1607.

\((R)-2\)-Iodo-\(2\)'-(methoxymethoxy)-1,1'-binaphthyl (11) and \((S)-2\)-(methoxymethoxy)-1,1'-binaphthyl (11)

A solution of lithium naphthalenide (LiNAP) was prepared by dissolving freshly cut lithium metal (223 mg, 32.1 mmol) into a solution of naphthalene (4.12 g, 32.1 mmol) in THF (35 mL) under sonication and under an argon atmosphere. When all the lithium had dissolved, the resulting dark green solution was cooled to \(-78^\circ\)C. Under an argon atmosphere, a solution of phosphate (10) (3.75 g, 8.03 mmol) in THF (10 mL) at \(-78^\circ\)C was transferred via insulated cannula to the solution of LiNAP at \(-78^\circ\)C. After stirring for 30 minutes, powdered I\(_2\) (12.23 g, 48.2 mmol) was added in one portion, the resulting mixture stirred for 2 h, then allowed to warm to room temperature. Water (2 mL) was added dropwise to quench any remaining lithium reagent. The resulting solution was washed with 10\% Na\(_2\)S\(_2\)O\(_3\) solution (2×25 mL) and concentrated under vacuum. Column chromatography (hexane:ethyl acetate, 1:0→4:1) afforded 11 and 13 as a 5:1 mixture (\(R_f = 0.32\) in hexane:ethyl acetate, 4:1). Crystallisation with ethyl acetate/hexane afforded \((R)-2\)-iodo-\(2\)'-(methoxymethoxy)-1,1'-binaphthyl 11 (2.74 g, 77\%) as colourless needles. Mp. 156-156.5 \(^\circ\)C; \([\alpha]_D^{20} = 32.0\) (c = 0.3, CHCl\(_3\)).

\(^1\)H NMR (250 MHz, CDCl\(_3\)): \(\delta = 8.10\) (1H, d, \(J = 9\) Hz), 8.05 (1H, d, \(J = 9\) Hz), 7.94 (2H, dd, \(J = 8\), 2 Hz), 7.71 (1H, d, \(J = 9\) Hz), 7.64 (1H, d, \(J = 9\) Hz), 7.54-7.48 (1H, m), 7.41 (1H, t, \(J = 7\) Hz), 7.34-7.24 (3H, m), 7.05 (1H, m), 5.19 (1H, d, \(J = 7\) Hz), 5.12 (1H, d, \(J = 7\) Hz), 3.27 (3H, s) ppm; \(^{13}\)C NMR (50 MHz, CDCl\(_3\)): \(\delta = 151.9, 139.8, 135.6, 133.9, 133.0, 132.9, 130.1, 129.7, 129.2, 128.1\) (2C), 126.9 (2C), 126.8, 126.3, 124.9, 124.2, 116.5, 100.4, 94.7, 56.1, 40.4 ppm.

MS (EI\(^+\)) \(m/z = 463\) ([M+Na]\(^+\), 100). Data in agreement with the literature.\(^3\)
Concentration of the mother liquor yielded (S)-2-(Methoxymethoxy)-1,1'-binaphthyl 13 (430 mg, 17%).

\[
\begin{align*}
\text{H NMR (400 MHz, CDCl}_3\text{): } & \delta = 8.00 (2H, d, J = 8 \text{ Hz}), 7.99 (1H, d, J = 8 \text{ Hz}), 7.92 (1H, d, J = 8 \text{ Hz}), 7.66-7.63 (1H, m), 7.61 (1H, d, J = 9 \text{ Hz}), 7.53-7.48 (2H, m), 7.39 (2H, d, J = 8 \text{ Hz}), 7.34-7.26 (2H, m), 7.22 (1H, d, J = 8 \text{ Hz}), 5.09-5.05 (2H, m), 3.19 (3H, s) \text{ ppm. Data in agreement with the literature.}^3 
\end{align*}
\]

(R)-2'-Iodo-1,1'-binaphthyl-2-ol (S2)

To a solution (R)-2-iodo-2'-(methoxymethoxy)-1,1'-binaphthyl (11) (1.00 g, 2.27 mmol) in THF (10 mL) was added a solution of concentrated HCl in isopropanol (1:4) (15 mL) and the reaction stirred until completion (tlc). The reaction was concentrated to small volume under vacuum, then water (5 mL) and diethyl ether (15 mL) were added. The pH of the aqueous layer was adjusted to approx pH = 7 with aqueous sat. NaHCO\textsubscript{3}, the phases were separated, and the aqueous phase extracted with diethyl ether (2×15 mL). Combined organic extracts were washed with brine (15 mL), dried (MgSO\textsubscript{4}), filtered and concentrated under vacuum to give (R)-2'-iodo-1,1'-binaphthyl-2-ol S2 (846 mg, 94%) as a colourless solid. Mp. 78-80 °C; [\alpha]_D^{20} = −26.0 (c = 1.0, CHCl\textsubscript{3}); IR (neat) 2617, 1503, 1341, 1265, 1248, 799, 770 cm\textsuperscript{-1}.

\[
\begin{align*}
\text{H NMR (250 MHz, CDCl}_3\text{): } & \delta = 8.01 (1H, d, J = 9 \text{ Hz}), 7.85 (3H, app q, J = 9 \text{ Hz}), 7.65 (1H, d, J = 9 \text{ Hz}), 7.47-7.41 (1H, m), 7.30-7.15 (5H, m), 8.86 (1H, d, J = 9 \text{ Hz}), 4.67 (1H, br s) \text{ ppm; C NMR (50 MHz, CDCl}_3\text{): } \delta = 150.4, 136.7, 136.0 (2C), 134.0, 133.3, 132.7, 130.5 (2C), 129.1, 128.3, 128.2, 127.8, 127.0 (2C), 126.5, 124.3, 123.7, 121.9, 117.7 \text{ ppm.}
\end{align*}
\]

MS (EI\textsuperscript{+}) m/z = 396 (M\textsuperscript{+}, 100); HRMS (EI\textsuperscript{+}) m/z calcd for C\textsubscript{20}H\textsubscript{13}IO (M\textsuperscript{+}): 396.0011; found: 396.0016.
HPLC: Chiralcel OD-H column, hexane/i-PrOH = 98/2, 1.0 mL/min, 10 ºC, 260 nm; 
t_R (R) = 26.4 min, t_R (S) = 29.6 min; >99% ee.

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(R)-2-Iodo-2'-phenoxy-1,1'-binaphthyl (12a)

![Image of molecule]

To a solution of (R)-2'-iodo-1,1'-binaphthyl-2-ol S2 (300 mg, 0.76 mmol) in THF (5 mL) at 0 ºC was added potassium tert-butoxide (93 mg, 0.83 mmol). The mixture stirred at 0 ºC for 30 minutes then diphenyliodonium triflate (391 mg, 0.91 mmol) was added in one portion, and the reaction mixture heated at 40 ºC for 4 h until completion as observed by tlc. The reaction was quenched with sat. NH₄Cl and extracted with diethyl ether (3×5 mL). Combined organic extracts were washed with brine (5 mL), dried (MgSO₄), filtered and concentrated under vacuum. Column chromatography (hexane:ethyl acetate, 9:1→4:1) afforded 12a (318 mg, 89 %) as a colourless solid. Mp. 158.5-160 ºC; [α]_D²⁰ = 130.0 (c = 1.0, CHCl₃); IR (neat) 3051, 1585, 1487, 1466, 1233, 974, 808 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 8.04 (1H, d, J = 9 Hz), 7.98 (1H, d, J = 9 Hz), 7.95 (1H, d, J = 8 Hz), 7.89 (1H, d, J = 8 Hz), 7.66 (1H, d, J = 9 Hz), 7.51-7.44 (2H, m), 7.37-7.23 (6H, m), 7.13 (1H, d, J = 8 Hz), 7.07-7.01 (3H, m) ppm; ¹³C NMR (75 MHz, CDCl₃): δ =
To a solution of \((R)-2\text{-iodo-2'}\text{-methoxy-1,1'}\text{-binaphthyl} \text{S2} \) (338 mg, 0.85 mmol) and K\(_2\)CO\(_3\) (259 mg, 1.88 mmol) in freshly distilled acetone (5 mL) was added dropwise iodomethane (106 µL, 1.71 mmol) and the mixture heated at reflux for 16 h. The mixture was concentrated under vacuum. Water (3 mL) and diethyl ether (5 mL) were added, the phases were separated, and the aqueous phase extracted with diethyl ether (2×15 mL). Combined organic extracts were washed with brine (15 mL), dried (MgSO\(_4\)), filtered and concentrated under vacuum to give \(12b\) (346 mg, 99%) as a light brown solid. Mp. 179-180 °C; \([\alpha]_{D}^{20} = -16.0\ (c = 1.0,\ CHCl_3)\); IR (neat) 2856, 1499, 1458, 1246, 1070, 800 cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.07\ (2H, dd, J = 8, 4\ Hz), 7.92\ (2H, dd, J = 8, 3\ Hz), 7.68\ (1H, d, J = 9\ Hz), 7.48\ (2H, d, J = 9\ Hz), 7.37\ (1H, t, J = 7\ Hz), 7.27\ (2H, t, J = 7\ Hz), 7.22\ (1H, d, J = 8\ Hz), 6.99\ (1H, d, J = 8\ Hz), 3.84\ (3H, s)\ ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta = 154.3, 139.8, 135.6\ (2C), 133.9, 133.0\ (2C), 130.1, 129.1\ (2C), 128.1, 128.0, 126.8\ (2C), 126.2, 125.8, 124.7, 123.8, 113.9, 100.5, 56.7\ ppm.

HRMS (EI\(^+\)) \(m/z\) calcd for C\(_{21}\)H\(_{13}\)IO (M\(^+\)): 410.0168; found: 410.0169.

\((R)-2\text{-((Diacetoxy)iodo-2'}\text {-phenoxy-1,1'}\text{-binaphthyl} \text{14a})

To a solution of \((R)-2\text{-iodo-2'}\text{-phenoxy-1,1'}\text{-binaphthyl} \text{12a} \) (50 mg, 0.11 mmol) in CH\(_3\)CN (3 mL) and AcOH (1mL) was added Selectfluor\(^{®}\) (188 mg, 0.53 mmol). The reaction was stirred at room temperature for 9 h then concentrated under vacuum. Water (5 mL) was
added, and the product extracted with dichloromethane (2×15 mL). Combined organic extracts were washed with water (5 mL), brine (5 mL) and concentrated under vacuum to give 14a (57 mg, 91 %) as a yellow oil which was used directly without further purification.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.44$ (1H, d, $J = 9$ Hz), 8.02 (2H, d, $J = 9$ Hz), 7.97 (2H, d, $J = 9$ Hz), 7.88 (2H, d, $J = 8$ Hz), 7.59 (1H, t, $J = 7$ Hz), 7.41-7.23 (5H, m), 7.06-6.97 (5H, m), 1.66 (3H, br s), 1.31 (3H, br s) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 176.7$ (br), 176.1 (br), 156.0, 152.6, 139.7, 134.8, 134.1, 133.1, 132.7, 131.4, 131.0, 129.7 (3C), 128.4 (2C), 128.2, 128.1, 127.8, 126.6, 126.5, 126.0, 124.7, 124.4, 123.7, 119.6 (2C), 117.7, 20.1 (br), 19.2 (br) ppm.

(R)-2-(Diacetoxy)iodo-2'-methoxy-1,1'-binaphthyl (14b)

To a solution of (R)-2-iodo-2'-methoxy-1,1'-binaphthyl 12b (79 mg, 0.19 mmol) in CH$_3$CN (4 mL) and AcOH (1 mL) was added Selectfluor® (341 mg, 0.96 mmol). The reaction was stirred at room temperature for 5 h then concentrated under vacuum. Water (5 mL) was added, and the product extracted with dichloromethane (2×15 mL). Combined organic extracts were washed with water (5 mL), brine (5 mL) and concentrated under vacuum to give 14b (72 mg, 71 %) as an unstable yellow oil which was used promptly and without further purification.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.45$ (1H, d, $J = 9$ Hz), 8.07 (1H, d, $J = 9$ Hz), 8.02 (2H, t, $J = 7$ Hz), 7.87 (1H, d, $J = 8$ Hz), 7.60 (1H, t, $J = 7$ Hz), 7.45 (1H, d, $J = 9$ Hz), 7.38-7.30 (3H, m), 7.20 (1H, t, $J = 7$ Hz), 6.95 (1H, d, $J = 9$ Hz), 3.83 (3H, s), 2.01 (3H, br s), 1.32 (3H, br s) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 176.6$ (br), 176.1 (br), 154.2, 140.5, 134.9, 133.7, 133.0, 132.6, 131.8, 130.7, 128.5 (2C), 128.4, 128.3, 128.0, 127.8, 126.6, 126.5, 125.8, 123.7, 121.7, 112.7, 56.0, 20.6 (br), 20.4 (br) ppm.
(R)-(2'-Phenoxy-1,1'-binaphthyl-2-yl)(phenyl)iodonium tetrafluoroborate (7a)

To a solution of (R)-2-(diacetoxy)iodo-2'-phenoxy-1,1'-binaphthyl (14a) (107 mg, 0.18 mmol) in dichloromethane (4 mL) at −78 ºC was added dropwise BF$_3$ • OEt$_2$ (57 µL, 0.45 mmol). After 2 min, phenylboronic acid (24 mg, 0.20 mmol) was added in one portion. The reaction was allowed to warm to room temperature and stirred for 15 minutes at room temperature. The crude reaction mixture was applied to a short silica plug (1.6 g). Unreacted starting material and impurities were eluted with dichloromethane (20 mL). The iodonium salt was eluted using 5% MeOH in dichloromethane (15 mL). This fraction was concentrated under vacuum. Subsequent precipitation with MeOH/Et$_2$O yielded 7a (91 mg, 79%) as a light brown solid. Mp. 164.5-166 ºC; [α]$_D^{20}$ = 74.0 (c = 1.0, CHCl$_3$); IR (neat) 3061, 2363, 1489, 1235, 1053, 733 cm$^{-1}$.

$^1$H NMR (300 MHz, CDCl$_3$): δ = 8.51 (1H, d, $J$ = 9 Hz), 8.20 (2H, d, $J$ = 9 Hz), 8.09 (1H, d, $J$ = 8 Hz), 8.00 (1H, d, $J$ = 8 Hz), 7.65 (1H, t, $J$ = 8 Hz), 7.45-7.32 (7H, m), 7.22 (2H, t, $J$ = 8 Hz), 7.11 (2H, t, $J$ = 8 Hz), 7.04-6.98 (2H, m), 6.83-6.80 (2H, m), 6.46 (1H, d, $J$ = 9 Hz) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$): δ = 156.0, 152.5, 141.8, 140.5, 135.1, 134.9, 133.2 (2C), 132.0, 131.9 (2C), 131.5, 131.1, 130.1, 129.5, 129.0, 128.3, 128.2, 128.1, 127.7, 127.1, 126.2, 125.1, 124.1, 124.0, 123.7, 118.8 (2C), 118.2, 118.0, 112.6, 98.0 ppm. $^{19}$F NMR (282 MHz, CDCl$_3$): δ = −154.6 (4F) ppm.

MS (APCI$^+$) $m/z$ = 549 (M$^+$, 100); HRMS (ES$^+$) $m/z$ calcd for C$_{32}$H$_{22}$IO (M$^+$): 549.0710; found: 549.0699.

(R)-(2'-Methoxy-1,1'-binaphthyl-2-yl)(phenyl)iodonium tetrafluoroborate (7b)

To a solution of (R)-2-(diacetoxy)iodo-2'-methoxy-1,1'-binaphthyl (14b) (64 mg, 0.12 mmol)
in dry acetic acid (2 mL) was added sodium tetraphenylborate (83 mg, 0.24 mmol) and the reaction stirred for 4 h at 50 °C. After being concentrated under vacuum, the crude was dissolved in dichloromethane (5 mL) and filtered to give the crude product 7b (30 mg, 43%) as a brown solid. An analytic sample was prepared by recrystallisation from cold toluene. Mp. 106-108 °C (toluene); [α]_D^20 = −13.3 (c = 1.8, CHCl_3), IR (neat) 2967, 1721, 1591, 1487, 1238, 1159, 947, 813 cm⁻¹.

^1^H NMR (400 MHz, CDCl_3): δ = 8.23 (1H, d, J = 9 Hz), 8.00 (1H, d, J = 8 Hz), 7.96 (1H, d, J = 8 Hz), 7.88 (1H, d, J = 9 Hz), 7.62 (1H, t, J = 7 Hz), 7.50-7.34 (12H, m), 7.29-7.25 (1H, m), 7.20-7.16 (2H, m), 7.07 (2H, t, J = 8 Hz), 6.92 (8H, t, J = 7 Hz), 6.83 (2H, d, J = 7 Hz), 6.76 (4H, t, J = 7 Hz), 6.43 (1H, d, J = 8 Hz), 3.78 (3H, s) ppm; ^13^C NMR (75 MHz, CDCl_3): δ = 164.5 (4C, q, J_B-C = 49 Hz), 154.4, 140.2, 137.9, 136.2 (8C), 134.9 (2C), 132.5, 132.1, 131.9, 131.5 (2C), 129.6, 129.2, 129.0 (2C), 128.6, 128.4, 128.2 (2C), 128.1, 127.7, 126.3 (8C), 125.3, 124.5, 123.5, 122.3 (4C), 118.1, 113.2, 112.8, 56.3 ppm.

HRMS (ES⁺) m/z calcd for C_{27}H_{20}IO (M⁺): 487.0553; found: 487.0557.

(R)-5,5',6,6',7,7',8,8'-Octahydro-1,1'-binaphthyl-2,2'-diamine (16)

Prepared according to the method of Gou.⁴ (R)-1,1'-Binaphthyl-2,2'-diamine (500 mg, 1.76 mmol) and isopropanol (100 mL) were added to a flask containing nickel-aluminium alloy (1:1 wt, 3.53 g, 41.2 mmol) in water (100 mL). The suspension was heated to reflux under stirring, and then 1% aqueous NaOH (200 mL) was added dropwise over 1 h. The reaction was stirred for a further 36 h. It was then cooled and filtered through paper (Caution). The filter cake was washed with ethyl acetate, and the combined organic phases were dried (MgSO_4), filtered and concentrated under vacuum, affording 16 (426 mg, 83 %) as a colourless solid. Mp. 207-210 °C; [α]_D^20 = 130.0 (c = 1.0, pyridine).

^1^H NMR (400 MHz, CDCl_3): δ = 6.92 (2H, d, J = 8 Hz), 6.63 (1H, d, J = 8 Hz), 3.38 (4H, br s), 2.78-2.73 (4H, m), 2.31-2.10 (4H, m), 1.76-1.65 (8H, m) ppm; ^13^C NMR (75 MHz, CDCl_3): δ = 141.7 (2C), 136.3 (2C), 129.3 (2C), 127.8 (2C), 122.2 (2C), 131.3 (2C), 29.4 (2C), 27.0 (2C), 23.3 (2C), 23.4 (2C) ppm.
Data in agreement with the literature.\textsuperscript{5,6}

\((R)-2,2'\text{-Diodo-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (17)}\)

![Structure of (R)-2,2'-Diodo-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (17)](image)

Prepared according to the literature.\textsuperscript{7} A mixture of \((R)-5,5',6,6',7,7',8,8'-\text{octahydro-1,1'-binaphthyl}-2,2'\text{-diamine 16 (156 mg, 0.53 mmol), sodium nitrite (294 mg, 4.27 mmol)}\) and potassium iodide (886 mg, 5.33 mmol) in dimethyl sulfoxide (15 mL) was immersed in a room temperature water bath, then 47\% aqueous HBr (0.75 mL) was added dropwise with intense stirring. The water bath was removed and the reaction stirred for 2 h. It was then poured into 50\% aqueous sat. NaHCO\textsubscript{3} (15 mL) and then extracted with dichloromethane (2×15 mL). Combined organic extracts were washed with 10\% Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} solution (2×10 mL), water (2×10 mL), brine (5 mL), then dried (MgSO\textsubscript{4}), filtered and concentrated under vacuum. Column chromatography (hexane) afforded partially pure 17 (184 mg, 67 \%) as a colourless solid, containing c. 10\% re-aromatised products. This material was used directly in the next step. \([\alpha]_D^{20} = -20.0 (c = 1.0, \text{CHCl}_3)\).

\(^1\text{H NMR (300 MHz, CDCl}_3\]): \(\delta = 7.70 \text{ (2H, d, } J = 8 \text{ Hz)}, 6.86 \text{ (2H, d, } J = 8 \text{ Hz)}, 2.91-2.74 \text{ (4H, m)}, 2.39-2.30 \text{ (2H, m)}, 2.16-2.07 \text{ (2H, m)}, 1.80-1.62 \text{ (8H, m) ppm}; ^{13}\text{C NMR (125 MHz, CDCl}_3\]): \(\delta = 147.1 \text{ (2C)}, 138.0 \text{ (2C)}, 136.7 \text{ (2C)}, 135.9 \text{ (2C)}, 130.4 \text{ (2C)}, 97.1 \text{ (2C)}, 29.7 \text{ (2C)}, 28.8 \text{ (2C)}, 23.3 \text{ (2C)}, 22.5 \text{ (2C) ppm.}\)

Data in agreement with the literature.\textsuperscript{7}

\((R)\text{-}2'\text{-Iodo-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2-yl}(\text{phenyl})\text{jodonium tetrafluoroborate (8)}\)

![Structure of (R)-2'-Iodo-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2-yl}(\text{phenyl})jodonium tetrafluoroborate (8)](image)
To a solution of (R)-2,2'-diiodo-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl (17) (210 mg, 0.41 mmol) in CH$_3$CN (6 mL) and AcOH (2 mL) was added Selectfluor® (868 mg, 2.45 mmol). The reaction was stirred at room temperature for 9 h then concentrated under vacuum. Water (5 mL) was added, and the product extracted with dichloromethane (2×15 mL). Combined organic extracts were washed with water (5 mL), brine (5 mL) and concentrated under vacuum to give 18 (264 mg, 86 %) as a yellow oil. $^1$H NMR showed the presence of a broad acetate signal ($\delta = 1.75$ ppm) with integration consistent with 18. This crude material was promptly dissolved in dichloromethane (4 mL) and cooled to $-78 \, ^{\circ}C$. BF$_3$ • OEt$_2$ (223 $\mu$L, 1.76 mmol) was added dropwise, followed after 2 minutes by phenylboronic acid (45 mg, 0.37 mmol) in one portion. The reaction was allowed to warm to room temperature and stirred for 15 minutes. The crude reaction mixture was applied to a short silica plug (2 g). Unreacted starting material and impurities were eluted with hexane/dichloromethane (1:0 $\rightarrow$ 0:1). The iodonium salt was eluted using with 10% MeOH in dichloromethane (10 mL). Subsequent precipitation with dichloromethane/ Et$_2$O yielded 19 (135 mg, 65%) as a colourless solid. Mp. 116-118 °C; $[\alpha]_{D}$ 20 = $-85.0$ (c = 1.0, CHCl$_3$); IR (neat) 2940, 1443, 1267, 1051, 729, 700 cm$^{-1}$.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.84$ (2H, d, $J = 8$ Hz), 7.70 (1H, d, $J = 8$ Hz), 7.67 (1H, d, $J = 8$ Hz), 7.59 (1H, t, $J = 7$ Hz), 7.41 (2H, t, $J = 8$ Hz), 7.19 (1H, d, $J = 8$ Hz), 6.96 (1H, d, $J = 8$ Hz), 2.92-2.76 (4H, m), 2.34-2.26 (1H, m), 2.13-2.00 (2H, m), 1.92-1.84 (1H, m), 1.80-1.67 (8H, m) ppm; $^{13}$C NMR (125 MHz, d$_4$-MeOD): $\delta = 148.1$, 146.3, 144.5, 140.6 (2C), 138.8, 138.0, 137.4 (2C), 135.7, 134.1, 133.7, 133.4, 133.2 (2C), 115.1, 113.2, 98.2, 30.8, 30.4, 29.9, 29.6, 23.8 (2C), 23.2, 23.1 ppm; $^{19}$F NMR (282 MHz, CDCl$_3$): $\delta = -149.0$ (4F) ppm.

MS (EI$^+$) $m/z = 591$ (M$^+$, 100); HRMS (APCI$^+$) $m/z$ calcd for C$_{26}$H$_{25}$I$_2$ (M$^+$): 591.0046; found: 591.0051.
$^1$H and $^{13}$C NMR spectra

$(2R,2'R,2''R)$-$2,2',2''-(Benzene-1,3,5-triyltris(oxy))tris(N-mesitylpropanamide) (9)
Phenyl(2,4,6-tris((R)-1-(mesitylamino)-1-oxopropan-2-yloxy)phenyl)iodonium, 4-methylbenzenesulfonate (6a)
(2,6-Bis((R)-1-(mesitylamino)-1-oxopropan-2-yloxy)phenyl)(phenyl)iodonium tetrafluoroborate (6b)
(R)-Diethyl 2'-(methoxymethoxy)-1,1'-binaphthyl-2-yl phosphate (10)

![Chemical Shift Diagram]
(R)-2-Iodo-2’-(methoxymethoxy)-1,1’-binaphthyl (11)
(R)-2'-Iodo-1,1'-binaphthyl-2-ol (S2)
(R)-2-Iodo-2'-phenoxy-1,1'-binaphthyl (12a)
(R)-2-Iodo-2'-methoxy-1,1'-binaphthyl (12b)
(R)-2-(Diacetoxy)iodo-2'-phenoxy-1,1'-binaphthyl (14a)
(R)-2-(Diacetoxy)iodo-2'-methoxy-1,1'-binaphthyl (14b)
(R)-(2'-Phenoxy-1,1'-binaphthyl-2-yl)(phenyl)iodonium tetrafluoroborate (7a)
(R)-(2’-Methoxy-1,1’-binaphthyl-2-yl)(phenyl)iodonium tetrafluoroborate (7b)
(R)-(2'-Iodo-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2-yl)(phenyl)iodonium tetrafluoroborate (8)
References


