Chiral Aryl Iodide-Catalyzed Enantioselective α-Oxidation of Ketones

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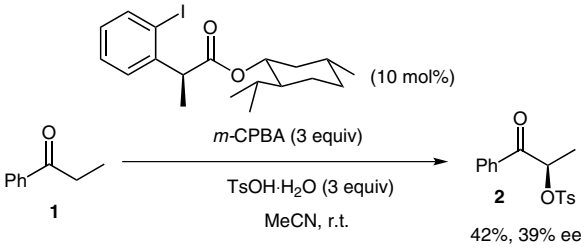
Abstract: Several chiral aryl iodides were synthesized and assessed as catalysts in the enantioselective α-oxytosylation of propiophenone and the oxidative cyclization of 5-oxo-5-phenylpentanoic acid to 5-benzoyldihydrofuran-2(3*H*)-one. The highest enantioselectivities obtained were 18 and 51% ee, respectively. The latter is the highest selectivity recorded to date for this reaction.

Key words: hypervalent iodine, enantioselectivity, oxidation, asymmetric catalysis, organocatalysis

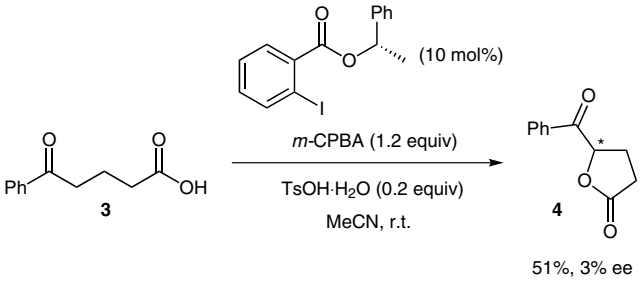
The α-functionalization of carbonyl compounds using hypervalent iodine reagents has received considerable attention; transformations including oxygenation, halogenation, arylation, alkylation, alkenylation and alkynylation have been reported.[1] An especially useful development in hypervalent iodine chemistry is the ability to use a catalytic amount of an aryl iodide and generate the iodine(III) species in situ.[2]

In particular, the α-oxytosylation of propiophenone **1** has received substantial interest.[3] Chiral hypervalent iodine reagents have been employed to perform this reaction enantioselectively,[4] however, an enantiomeric excess of 39%, reported by Wirth and co-workers, is the highest selectivity achieved to date (Scheme 1).[4c]



Scheme 1 Wirth's enantioselective α-oxytosylation of propiophenone

Another notable reaction is the oxidative cyclization of 5-oxo-5-phenylpentanoic acid (**3**) to 5-benzoyldihydrofuran-2(3*H*)-one (**4**).[5] Wirth and co-workers tested a sample of chiral aryliodides as catalysts for this lactonization process and reported enantioselectivities no greater than 3% (Scheme 2).[4b]



Scheme 2 Wirth's enantioselective lactonization

Over the past few years, several enantioselective hypervalent iodine mediated and catalyzed reactions have been reported, however, enantiomeric excesses of more than 90% have only been achieved in a handful of examples and these are predominantly additions to alkenes.[6]

We have been interested in synthesizing chiral aryl iodides and testing their efficacy in a range of enantioselective reactions for several years. Herein, we describe our results for the α-oxytosylation of propiophenone and the oxidative cyclization of 5-oxo-5-phenylpentanoic acid to 5-benzoyldihydrofuran-2(3*H*)-one.

We prepared a range of chiral aryl iodides using simple reactions including Mitsunobu reactions, esterifications and amidations. Lactic acid derived aryl iodides and iodanes have been shown to be successful catalysts/reagents in other reactions.[6a–e] Therefore, a number of such compounds were synthesized for our study (Figure 1).

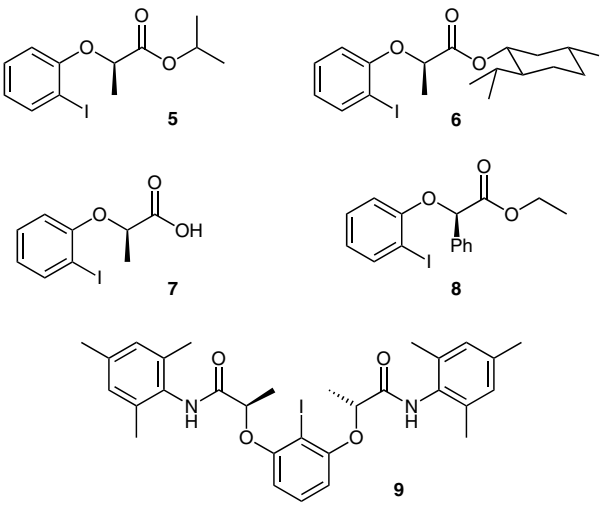


Figure 1 Aryl iodides prepared through Mitsunobu reactions

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A selection of novel aryl iodides was prepared from the corresponding acid chlorides through either esterification or amidation reactions (Figure 2).

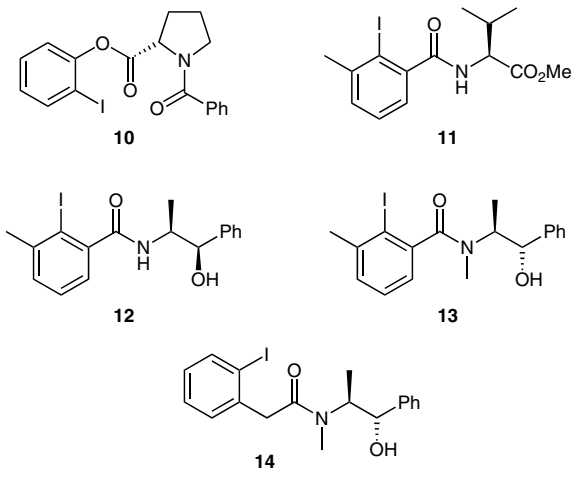


Figure 2 Aryl iodides prepared through esterification or amidation

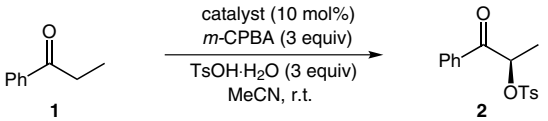
With these aryl iodides in hand, we investigated their use in the enantioselective α-oxytosylation of propiophenone **1** (Table 1) and the oxidative cyclization of 5-oxo-5-phenylpentanoic acid (**3**) to 5-benzoyldihydrofuran-2(3*H*)-one (**4**; Table 2).

Wirth's reported conditions for the α-oxytosylation of propiophenone worked well, providing good to very good yields of product for all of the aryliodide catalysts.[3] However, the enantioselectivities were disappointing in all cases, which is especially interesting because aryl iodide **9** has been shown to be a very effective catalyst in the oxidative spirolactonization of 1-naphthol derivatives.[6e] Also of interest is that the use of catalysts **5** and **6** led to the formation of major products with opposite configuration (Table 1, entries 1 and 2), highlighting the effect of distal stereocenters on enantioselectivity. The best result (18% ee) was obtained with norephedrine derivative **12** (entry 8). Interestingly, the structurally related pseudoephedrine derivatives **13** and **14** provided almost racemic products (entries 9 and 10).

The oxidative cyclization of 5-oxo-5-phenylpentanoic acid (**3**) to 5-benzoyldihydrofuran-2(3*H*)-one (**4**) was found to proceed under the same conditions as the α-oxytosylation of propiophenone **1**, however, the use of dichloromethane as solvent was generally found to lead to superior enantioselectivities.

The aryl iodide catalysts were screened for this lactonization process and it soon became apparent that the results were in stark contrast to the propiophenone oxidation. The reaction generally proceeded in moderate yields and low enantioselectivities for all of the catalysts, however, with pseudoephedrine derivative **13** an enantiomeric excess of 51% was obtained (entry 7). Norephedrine derivative **12** and pseudoephedrine derivative **14** were shown to be substantially inferior catalysts, providing only 9% ee in each case (entries 6 and 8).

Table 1 α-Oxytosylation of Propiophenone **1**

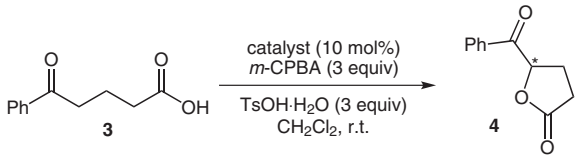


Entry	Catalyst	Yield (%)[a]	% ee (config.)[b]
1	**5**	74	6 (*S*)
2	**6**	76	5 (*R*)
3	**7**	87	5 (*S*)
4	**8**	49	1 (*S*)
5	**9**	82	14 (*S*)
6	**10**	68	7 (*S*)
7	**11**	35	11 (*S*)
8	**12**	67	18 (*S*)
9	**13**	59	3 (*S*)
10	**14**	81	5 (*S*)

[a] Yield of pure isolated product.
[b] Determined by chiral HPLC analysis (Chiralpak OB-H).

The effect of solvent on the enantioselectivity of the lactonization process with aryl iodide catalyst **13** was inves-

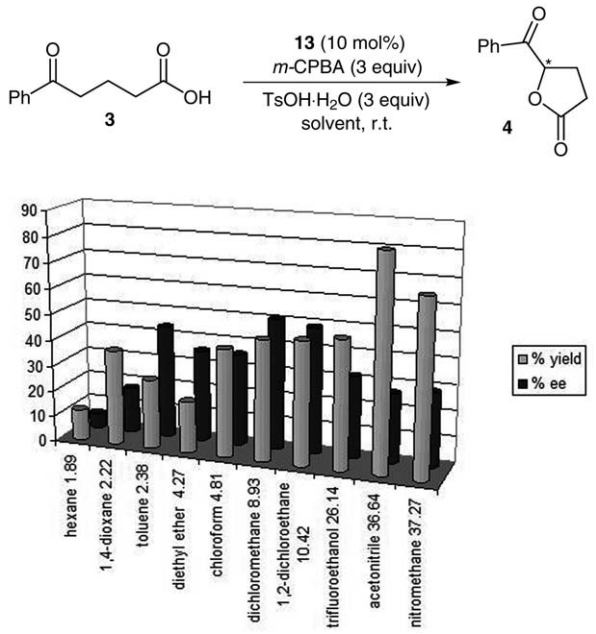
Table 2 Oxidative Cyclisation of 5-Oxo-5-phenylpentanoic Acid (**3**)



Entry	Catalyst	Yield (%)[a]	% ee[b]
1	**5**	31	12
2	**6**	29	12
3	**7**	25	2
4	**8**	35	0
5	**9**	45	0
6	**10**	62	2
7	**11**	26	7
8	**12**	30	9
9	**13**	47	51
10	**14**	58	9

[a] Yield of pure isolated product.
[b] Determined by chiral HPLC analysis (Chiralpak IB).

tigated (Scheme 3). Although there are probably other factors involved, a rough trend can be seen between the dielectric constant of the solvent used and the enantioselectivity observed. The enantioselectivity increases with dielectric constant up until dichloromethane and then decreases. Toluene appears to be an exception; perhaps, in this case, favorable π-interactions are responsible for the higher enantioselectivities observed. In addition, the observed yields generally increase with dielectric constant.



Scheme 3 Effect of solvent on enantioselectivity. Solvents given with dielectric constants. Yields are of pure isolated products. Enantioselectivities were determined by chiral HPLC analysis (Chiralpak IB).

In conclusion, ten chiral aryl iodides have been synthesised and assessed in the α-oxytosylation of propiophenone **1** and the oxidative cyclization of 5-oxo-5-phenylpentanoic acid (**3**) to 5-benzoyldihydrofuran-2(3*H*)-one (**4**). Only low enantioselectivities were obtained for the former, however, the highest reported enantioselectivity to date (51% ee) has been achieved for the latter process. Related studies are in progress and will be reported in due course.

NMR spectra were recorded with either a Bruker Avance DPX400 or a Bruker Avance 500 spectrometer. Mass spectrometry was performed with a Bruker MicroTOF LC operating in ESI mode, with only molecular ions reported. Infrared spectra were recorded with a Thermo Nicolet 380 spectrometer. Flash chromatography was performed on silica gel 60. Petroleum ether (PE) refers to the fraction boiling at 40–60 °C. All reactions were performed under a N_2 atmosphere unless otherwise noted. Catalysts **7**,[6d] **8**[6a] and **9**[6d] were prepared according to the published procedures and displayed satisfactory analytical data.

α-Oxytosylation of Propiophenone 1; General Procedure

Propiophenone **1** (40 μL, 0.3 mmol) was added to a solution of chiral aryl iodide (0.03 mmol, 0.1 equiv), MCPBA (155 mg, 0.9 mmol) and 4-toluenesulfonic acid monohydrate (171 mg, 0.9 mmol) in MeCN (1 mL) at r.t., open to air, and the solution was stirred until precipitation occurred (typically 16–72 h). The reaction mixture was then quenched by addition of sat. aq sodium thiosulfate (10 mL), extracted with CH_2Cl_2 (3 × 10 mL), washed with sat. aq $NaHCO_3$ (10 mL), dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography (silica gel; PE–EtOAc, 9:1) to provide **2** as a white solid. Analytical data was similar to that reported.[4c]

HPLC [Chiralpak OB-H; hexanes–2-propanol (40:60); 0.25 mL/min; 40 °C; 254 nm]: t_R = 28.6 (*R*), 34.4 (*S*) min.

Lactonisation of 5-Oxo-5-phenylpentanoic Acid (3); General Procedure

5-Oxo-5-phenylpentanoic acid (**3**; 50 mg, 0.26 mmol) was added to a solution of chiral aryl iodide (0.052 mmol, 0.2 equiv), MCPBA (135 mg, 0.78 mmol) and 4-toluenesulfonic acid monohydrate (148 mg, 0.78 mmol) in CH_2Cl_2 (1 mL) at r.t., open to air, and the solution was stirred until precipitation occurred (typically 16–72 h). The reaction was quenched by addition of sat. aq. sodium thiosulfate (10 mL), extracted with CH_2Cl_2 (3 × 10 mL), washed with sat. aq $NaHCO_3$ (10 mL), dried ($MgSO_4$), filtered and concentrated. The residue was purified by flash chromatography (silica gel; PE–EtOAc, 9:1) to provide **4** as a white solid. Analytical data was similar to that reported.[5b]

HPLC [Chiralpak IB; hexanes–2-propanol (85:15); 1.0 mL/min; r.t.; 254 nm]: t_R = 20.6, 25.7 min.

(*R*)-Isopropyl 2-(2-Iodophenoxy)propanoate (5)

Diisopropyl azodicarboxylate (0.45 mL, 2.3 mmol) was added to a solution of 2-iodophenol (0.50 g, 2.3 mmol), (*S*)-isopropyl lactate (0.30 mL, 2.3 mmol) and Ph_3P (595 mg, 2.3 mmol) in THF (20 mL) at r.t. After stirring overnight, the reaction mixture was concentrated and purified by flash chromatography (silica gel; PE–EtOAc, 9:1) to provide **5**.

Yield: 597 mg (79%); colorless oil.

IR (neat): 1091 (s), 1470 (s), 1748 (m), 1749 (m), 1774 (w), 2981 (w) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.16 (d, *J* = 6.3 Hz, 3 H), 1.26 (d, *J* = 6.3 Hz, 3 H), 1.67 (d, *J* = 6.8 Hz, 3 H), 4.72 (q, *J* = 6.8 Hz, 1 H), 5.05 (hept, *J* = 6.3 Hz, 1 H), 6.68–6.73 (m, 2 H), 7.20–7.25 (m, 1 H), 7.77 (dd, *J* = 7.7, 1.5 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.8, 21.9, 22.0, 69.3, 74.5, 87.6, 113.7, 123.7, 129.6, 140.0, 157.0, 171.4.

MS: *m*/*z* = 357.0 [M + Na].

HRMS: *m*/*z* calcd for $C_{12}H_{15}INaO_3$: 356.9958; found: 356.9951.

(*R*)-[(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl] 2-(2-Iodophenoxy)propanoate (6)

Diisopropyl azodicarboxylate (0.45 mL, 2.3 mmol) was added to a solution of 2-iodophenol (0.50 g, 2.3 mmol), (–)-menthyl lactate (0.53 g, 2.3 mmol) and Ph_3P (595 mg, 2.3 mmol) in THF (20 mL) at r.t. After stirring overnight, the reaction mixture was concentrated and purified by flash chromatography (silica gel; PE–EtOAc, 5:1) to provide **6**.

Yield: 816 mg (82%); white solid; mp 53–55 °C.

IR (neat): 1204 (s), 1472 (s), 1731 (s), 2956 (m) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.52 (d, *J* = 6.9 Hz, 3 H), 0.73 (d, *J* = 6.9 Hz, 3 H), 0.80–0.90 (m, 1 H), 0.90 (d, *J* = 6.6 Hz, 3 H), 0.93–1.07 (m, 2 H), 1.29–1.40 (m, 2 H), 1.41–1.52 (m, 1 H), 1.58–1.66 (m, 2 H), 1.69 (d, *J* = 6.8 Hz, 3 H), 1.95–2.03 (m, 1 H), 4.62 (td, *J* = 11, 4.4 Hz, 1 H), 4.77 (q, *J* = 6.8 Hz, 1 H), 6.68–6.73 (m, 2 H), 7.20–7.25 (m, 1 H), 7.78 (dd, *J* = 8.1, 1.7 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.9, 18.9, 21.2, 22.4, 23.3, 25.9, 31.7, 34.5, 40.8, 47.1, 74.4, 75.9, 87.3, 113.1, 123.6, 129.7, 140.2, 156.9, 171.8.

MS: *m*/*z* = 453.1 [M + Na].

HRMS: *m*/*z* calcd for $C_{19}H_{27}INaO_3$: 453.0897; found: 453.0911.

(*S*)-2-Iodophenyl 1-Benzoylpyrrolidine-2-carboxylate (10)
N-Benzoyl-L-proline[7] (1.0 g, 8.7 mmol), 2-iodophenol (0.84 g, 3.8 mmol), diisopropylcarbodiimide (0.47 mL, 3.0 mmol), and DMAP (23 mg, 0.19 mmol) were dissolved in CH_2Cl_2 (3 mL) and stirred at r.t. overnight. The reaction mixture was cooled to 0 °C and filtered through Celite. The filtrate was washed with H_2O (30 mL), sat. aq $NaHCO_3$ (20 mL) and cold 1N HCl (20 mL), then dried ($MgSO_4$), filtered and concentrated. Purification by flash chromatography (silica gel; PE–EtOAc, 5:1) provided **10**.

Yield: 0.95 g (59%); white solid; mp 78–80 °C.

IR (neat): 1129 (s), 1410 (m), 1615 (m), 1774 (m) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.95–2.05 (m, 1 H), 2.17–2.27 (m, 1 H), 2.44–2.55 (m, 2 H), 3.58–3.65 (m, 1 H), 3.71–3.79 (m, 1 H), 4.91 (dd, *J* = 8.0, 6.2 Hz, 1 H), 6.98 (td, *J* = 7.8, 1.5 Hz, 1 H), 7.25–7.29 (m, 1 H), 7.33–7.46 (m, 4 H), 7.57–7.62 (m, 2 H), 7.82 (dd, *J* = 8.0, 1.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.9, 29.7, 50.4, 59.9, 90.1, 123.8, 127.7 (2C), 128.1, 128.7 (2C), 130.0, 130.7, 136.3, 139.6, 146.1, 170.2, 170.3.

MS: *m*/*z* = 444.0 [M + Na].

HRMS: *m*/*z* calcd for $C_{18}H_{16}INNaO_3$: 444.0067; found: 444.0077.

(*S*)-Methyl 2-(2-Iodo-3-methylbenzamido)-3-methylbutanoate (11)
2-Iodo-3-methylbenzoic acid[8] (0.5 g, 1.9 mmol) was dissolved in CH_2Cl_2 (19 mL) at r.t., and oxalyl chloride (0.32 mL, 3.8 mmol) and DMF (0.01 mL) were added sequentially. The reaction mixture was stirred overnight then concentrated under vacuum. The residue was dissolved in CH_2Cl_2 (9.6 mL) and cooled to 0 °C. L-Valine methyl ester hydrochloride (320 mg, 1.9 mmol) and Et_3N (0.53 mL, 3.8 mmol) were added and the mixture was allowed to warm to r.t. overnight. The reaction was quenched with H_2O (20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The organic layer was washed sequentially with 10% aq. HCl and 5% aq. NaOH solutions, then dried ($MgSO_4$), filtered and concentrated. Purification by flash chromatography (silica gel; PE–EtOAc, 5:1) provided **11**.

Yield: 228 mg (32%); white solid ; mp 95–97 °C.

IR (neat): 1199 (s), 1533 (s), 1644 (s), 1740 (s), 3263 (br) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.02 (d, *J* = 6.9 Hz, 3 H), 1.11 (d, *J* = 6.8 Hz, 3 H), 2.28–2.41 (m, 1 H), 2.51 (s, 3 H), 3.80 (s, 3 H), 4.79 (dd, *J* = 8.8, 4.8 Hz, 1 H), 6.48 (d, *J* = 8.7 Hz, 1 H), 7.13–7.19 (m, 1 H), 7.26–7.33 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.2, 19.3, 29.4, 31.6, 52.4, 57.8, 99.3, 125.3, 128.3, 130.7, 143.0, 143.6, 170.2, 172.2.

MS: *m*/*z* = 398.0 [M + Na].

HRMS: *m*/*z* calcd for $C_{14}H_{18}INNaO_3$: 398.0224; found: 398.0223.

***N*-[(1*S*,2*S*)-1-Hydroxy-1-phenylpropan-2-yl]-2-iodo-3-methylbenzamide (12)**
2-Iodo-3-methylbenzoic acid[8] (1 g, 3.8 mmol) was dissolved in CH_2Cl_2 (38 mL) at r.t. and oxalyl chloride (0.65 mL, 7.6 mmol) and DMF (0.01 mL) were added sequentially. The reaction mixture was stirred overnight then concentrated under vacuum. The residue was dissolved in CH_2Cl_2 (5 mL) and added dropwise to a solution of (1*R*,2*S*)-norephedrine (578 mg, 3.8 mmol) and Et_3N (0.53 mL, 3.8 mmol) in CH_2Cl_2 (5 mL) at 0 °C. The mixture was allowed to warm to r.t. overnight and then quenched with H_2O (30 mL) and extracted with CH_2Cl_2 (3 × 20 mL), dried ($MgSO_4$), filtered and concentrated. Purification by flash chromatography (silica gel; PE–EtOAc, 1:1) provided **12**.

Yield: 1.09 g (72%); white solid; mp 66–68 °C.

IR (neat): 1626 (s), 3288 (br) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.13 (d, *J* = 7.0 Hz, 3 H), 2.49 (s, 3 H), 3.10 (br, 1 H), 4.45–4.57 (m, 1 H), 5.07 (d, *J* = 2.9 Hz, 1 H), 5.91 (d, *J* = 8.0 Hz, 1 H), 7.07–7.13 (m, 1 H), 7.23–7.32 (m, 3 H), 7.34–7.39 (m, 2 H), 7.40–7.45 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 29.4, 51.8, 75.7, 99.6, 125.2, 126.4 (2C), 127.6, 128.3, 128.4 (2C), 130.6, 141.2, 142.9, 143.8, 170.9.

MS: *m*/*z* = 394.0 [M – 1].

***N*-[(1*R*,2*S*)-1-Hydroxy-1-phenylpropan-2-yl]-2-iodo-*N*,3-dimethylbenzamide (13)**
2-Iodo-3-methylbenzoic acid[8] (0.5 g, 1.9 mmol) was dissolved in CH_2Cl_2 (19 mL) at r.t. and oxalyl chloride (0.32 mL, 3.9 mmol) and DMF (0.01 mL) were added sequentially. The reaction mixture was stirred overnight then concentrated under vacuum. The residue was dissolved in THF (10 mL) and added dropwise to a solution of (1*S*,2*S*)-pseudoephedrine hydrochloride (313 mg, 1.6 mmol) and Et_3N (0.5 mL, 3.6 mmol) in THF (10 mL) at 0 °C. The mixture was allowed to warm to r.t. overnight and then quenched with H_2O (20 mL) and extracted with EtOAc (3 × 20 mL), dried ($MgSO_4$), filtered and concentrated. Purification by flash chromatography (silica gel; PE–EtOAc, 1:1) provided **13** as four amide rotamers (A/B/C/D ratio 15:9:2:1 in DMSO).

Yield: 280 mg (44%); white solid; mp 181–185 °C.

IR (neat): 1011 (m), 1402 (m), 1614 (s), 3380 (br) cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ (data for two major rotamers A and B) = 1.00 (d, *J* = 6.8 Hz, 3 H, A), 1.05 (d, *J* = 6.9 Hz, 3 H, B), 2.39 (s, 3 H, A), 2.40 (s, 3 H, B), 2.64 (s, 3 H, B), 2.99 (s, 3 H, A), 3.38–3.46 (m, 1 H, A), 4.48 (dd, *J* = 8.2, 3.6 Hz, 1 H, A), 4.68 (dd, *J* = 7.5, 4.6 Hz, 1 H, B), 4.84–4.92 (m, 1 H, B), 5.53 (d, *J* = 4.5 Hz, 1 H, B), 5.63 (d, *J* = 3.6 Hz, 1 H, A), 6.63–6.68 (m, 1 H, B), 6.77–6.83 (m, 1 H, A), 7.09 (d, *J* = 6.7 Hz, 2 H, A), 7.21–7.45 (m, 7 H, B and 5 H, A).

^{13}C NMR (126 MHz, DMSO-d_6): δ (data for two major rotamers A and B) = 13.9^B, 15.7^A, 27.1^A, 28.6^B, 28.9^A, 31.3^B, 53.1^B, 59.5^A, 74.1^B, 74.3^A, 99.8^B, 100.3^A, 124.2^B, 126.4^A, 127.2^B (2C), 127.3^A (2C), 127.6^B, 127.9^A, 128.2^A, 128.4^B (2C), 128.6^A (2C), 129.0^B, 129.5^A, 129.5^B, 142.0^A, 142.3^B, 143.8^A, 143.9^B, 144.7^A, 145.0^B, 170.8^B, 171.4^A.

MS: *m*/*z* = 432.0 [M + Na].

HRMS: *m*/*z* calcd for $C_{18}H_{20}INNaO_2$: 432.0431; found: 432.0427.

***N*-[(1*S*,2*S*)-1-Hydroxy-1-phenylpropan-2-yl]-2-(2-iodophenyl)-*N*-methylacetamide (14)**
2-Iodophenylacetic acid (0.50 g, 1.9 mmol) was dissolved in CH_2Cl_2 (10 mL) at r.t. and oxalyl chloride (0.32 mL, 3.9 mmol) and DMF (0.01 mL) were added sequentially. The reaction mixture was stirred overnight then concentrated under vacuum. The residue was dissolved in THF (10 mL) and added dropwise to a solution of (1*S*,2*S*)-pseudoephedrine hydrochloride (313 mg, 1.6 mmol) and Et_3N (0.5 mL, 3.6 mmol) in THF (10 mL) at 0 °C. The mixture was allowed to warm to r.t. overnight and then quenched with H_2O (20 mL) and extracted with EtOAc (3 × 20 mL), dried ($MgSO_4$), filtered and concentrated. Purification by flash chromatography (silica gel; PE–EtOAc, 1:1) provided **14** as two amide rotamers (A/B ratio 3:1 in $CDCl_3$).

Yield: 546 mg (75%); pale-yellow gum.

IR (neat): 1012 (s), 1620 (s), 2925 (w), 3366 (br) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.91 (d, *J* = 6.7 Hz, 3 H, B), 1.14 (d, *J* = 7.0 Hz, 3 H, A), 2.89 (s, 3 H, A), 2.97 (s, 3 H, B), 3.75–3.81 (m, 2 H, B, 2 H, A), 3.88–3.98 (m, 1 H, B), 4.45–4.57 (m, 1 H, A), 4.57 (d, *J* = 8.8 Hz, 1 H, B), 4.64 (d, *J* = 7.9 Hz, 1 H, A), 6.89–6.98 (m, 1 H, B, 1 H, A), 7.15–7.20 (m, 1 H, A), 7.23–7.40 (m, 7 H, B, 6 H, A), 7.80–7.86 (m, 1 H, A, 1 H, B).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 14.8^{A}, 15.6^{B}, 27.4^{B}, 36.0^{A}, 46.2^{B}, 47.1^{A}, 59.2^{A}, 69.5^{B}, 75.9^{B}, 76.8^{A}, 101.5^{A+B}, 126.8^{2A}, 127.3^{2B}, 128.1^{A}, 128.8^{2A}, 128.9^{A+2B}, 129.0^{A}, 129.1^{2B}, 130.2^{B}, 130.4^{A+B}, 128.8^{B}, 139.1^{B}, 139.7^{2A+B}, 142.6^{A}, 171.7^{A+B}.

MS: *m*/*z* = 408.0 [M – 1].

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