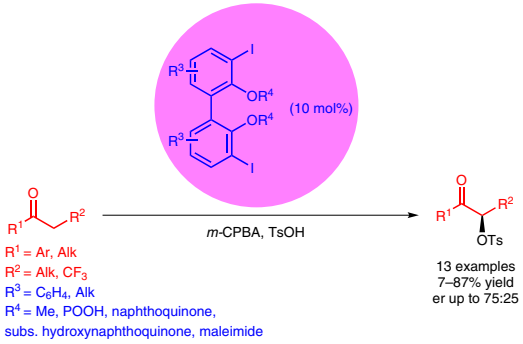
Synthesis S. Brenet et al. Paper

3,3′-Diiodobinaphthol and 3,3′-Diiodobiphenol Derivatives as Hypervalent Iodine Organocatalysts for the α-Oxytosylation of Ketones

Simon Brenet
Clémentine Minozzi
Bastien Clarens
Lilia Amiri
Florian Berthiol*

Département de Chimie Moléculaire (SERCO), UMR-5250, ICMG FR-2607, Université Joseph Fourier, 301 Rue de la Chimie, BP 53, 38041 Grenoble Cedex 9, France
florian.berthiol@ujf-grenoble.fr



Received: 22.07.2015
Accepted after revision: 24.08.2015
Published online: 17.09.2015
DOI: 10.1055/s-0035-1560267; Art ID: ss-2015-z0445-op

Abstract New series of enantiopure 3,3′-diiodobinaphthol- and 3,3′-diiodobiphenol-based molecules have been synthesized and used as chiral hypervalent iodine oxidation organocatalysts in the α-oxytosylation of propiophenone. When we compared these new organocatalysts to our previous series of 3,3′-diiodo-1,1′-binaphthalene-2,2′-diol-fused maleimides, we have made two important observations: the maleimide moiety is the best moiety for obtaining moderate enantioselectivities, and the presence of an aliphatic substituent on the biaryl part of the catalyst enhances the enantioselectivity.

Key words hypervalence, iodine, organocatalysis, imides, oxidation, stereoselective synthesis

Hypervalent iodine reagents are known for their ability to perform metal-like transformations, such as oxidation reactions[1,2] or the formation of carbon–carbon or carbon–heteroatom bonds.[3,4] Moreover hypervalent iodine reagents have the great advantage of low toxicity compared with transition-metal catalysts, making them good candidates for green and environmentally benign applications. Another of their advantages is the possibility of introducing a covalent chiral backbone on the iodine catalyst, thereby permitting the use of such compounds in asymmetric transformations. For all these reasons, numerous chiral hypervalent iodine reagents and catalysts have been synthesized and applied in various asymmetric reactions in recent years.[5] Among the various transformations that can be achieved by using hypervalent iodine species, the asymmetric α-oxytosylation of ketones is one of the most challenging.[6] Many attempts have been made to obtain the desired α-oxytosylated ketones with high enantiomeric excesses, but the enantioselectivities achieved have never exceeded 58%.[7] We recently reported the use of a new family of chiral hypervalent iodine organocatalysts in the catalytic asymmetric oxidation of ketones to give α-tosyloxy ketones (Figure 1).[7l] The enantioselectivities obtained with these 3,3′-diiodo-1,1′-binaphthalene-2,2′-diol (3,3′-diiodo-BINOL)-fused maleimides were close to the best reported ones obtained with other chiral hypervalent iodine catalysts.

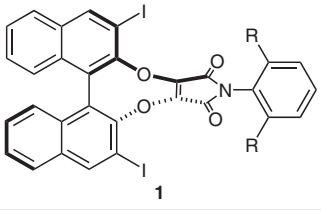


Figure 1 Previous series of organocatalysts **1**

The enantioselectivity was improved by tuning the *ortho* substituents of the phenyl group on the maleimide moiety. From this point, it was interesting to examine variations on this structure. In this report, we present further modifications on the previous structure in which the maleimide moiety was removed to determine whether its presence was necessary for enantioselectivity in oxidation reactions. The BINOL part was also replaced by a biphenol moiety to investigate the effect of such a change on the reactivity of these new organocatalysts. All these new molecules were applied in asymmetric α-oxytosylations of ketones.

First, it was necessary to determine whether the maleimide moiety of our previous catalyst series **1** (Figure 2) was essential for achieving enantioselectivity in oxytosylation reactions. We prepared a new series of maleimide-free organocatalysts (Figure 2; **2**–**5**), and we used them in a benchmark reaction, the α-oxytosylation of propiophenone (**6a**) (Table 1).

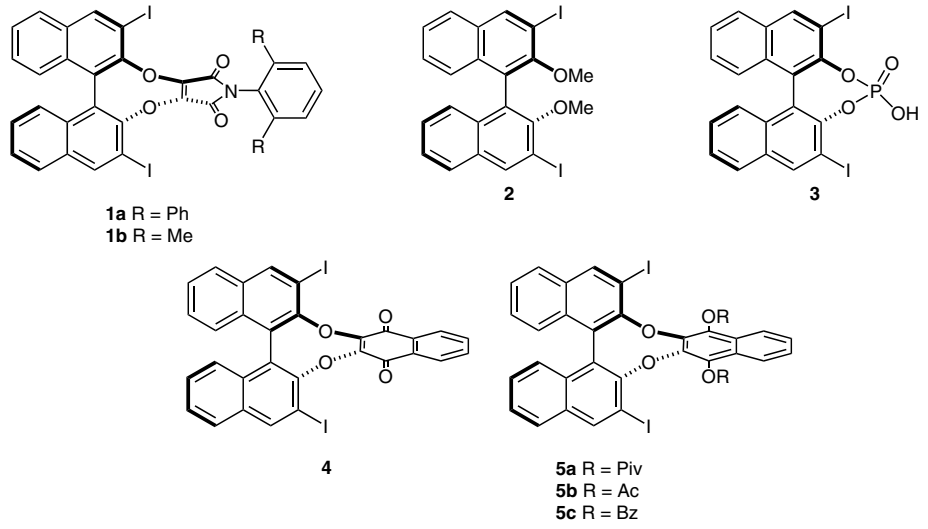
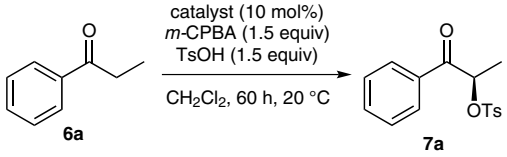


Figure 2 Previous series of organocatalysts **1** and new series of maleimide-free organocatalysts **2–5**

Table 1 Evaluation of Maleimide-Free Organocatalysts[a]



Entry	Catalyst	Yield (%)[b]	er[c]
1	**1a**	45	69:31
2	**2**	35	51:49
3	**3**	25	56:44
4	**4**	39	61:39
5	**5a**	51	52:48
6	**5b**	49	51:49
7	**5c**	45	50:50

[a] Reaction conditions: **6a** (0.05 mmol), catalyst (0.005 mmol; 10 mol%), *m*-CPBA (0.075 mmol; 1.5 equiv), TsOH (0.075 mmol, 1.5 equiv), CH_2Cl_2 (0.5 mL, 0.1 M).
[b] Determined by ^1H NMR in acetone-d_6 with Ph_3CH as internal reference.
[c] Determined by chiral HPLC analysis.

The first catalyst **2** was synthesized to verify whether the presence of a ring between the two oxygen atoms of the BINOL was important to the oxidation reaction. It was necessary to protect the phenol moieties, as they are known to be oxidized by hypervalent iodine reagents.[8] The reaction with catalyst **2** gave keto tosylate **7a** as a racemic mixture in low yield (Table 1, entry 2). Next, we synthesized catalyst **3** containing a phosphoric acid moiety to form a seven-membered ring between the two oxygen atoms of the BINOL moiety, and we used it in the oxytosylation reaction to give **7a** in 25% yield and 56:44 er (entry 3). This result confirmed that the presence of a ring in the scaffold provides better chiral induction. Functionalization at the position of the carbonyl group of the maleimide was of interest as a means of bringing bulky substituents closer to the iodine centers. It was therefore necessary to design a catalyst that contained a carbonyl substituent at a similar distance, but which could be further modified. To achieve this aim, we prepared a new series of functionalized 3,3′-diiodo-BINOL-fused hydronaphthoquinones **5** from the 3,3′-diiodo-BINOL-fused naphthoquinone **4** (Figure 2). We expected an enhancement of the enantioselectivity as a result of the presence of the R groups near the iodine centers, as demonstrated by simple 3D modelling of **5a** (Figure 3).

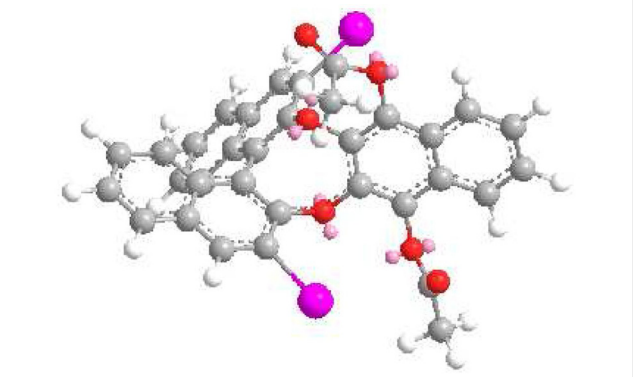


Figure 3 3D modelling of organocatalyst **5a**

Catalysts **4** and **5** were employed in the α-oxytosylation of propiophenone (Table 1, entries 4–9). With catalyst **4**, we obtained keto tosylate **7a** in 39% yield and 61:39 er (Table 1, entry 4). However, for catalysts **5**, even though moderate yields were obtained in all cases, the er values were far below expectation; no enantioselectivity was observed for catalyst **5a**, **5b**, or **5c** (entries 5–7). We observed that, unlike organocatalysts **1**, which could be recovered at the end of

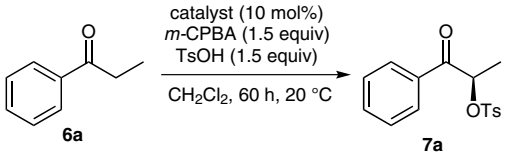
the reaction, catalysts **5** were not recoverable, as they were unstable under the reaction conditions. The previous series of 3,3′-diiodo-BINOL-fused maleimides give much better results in this reaction than did the new catalysts; the presence of the maleimide moiety is therefore necessary to achieve good enantioselectivity.

Having shown that the maleimide moiety is the best for obtaining moderate enantioselectivities in the oxidation reaction, we prepared a new series of 3,3′-diiodo-BINOL-fused maleimides bearing methylhydroxy arms in the *ortho* positions of the phenyl ring of the maleimide moiety (Table 2, catalysts **1c**–**m**). This type of catalyst can be quickly synthesized and can be easily functionalized on the hydroxy substituents, permitting the integration of various bulky functional groups that can have an influence on the iodine reactive centers. First, we examined the unsubstituted catalyst **1c** in the oxytosylation reaction, and this gave the expected product with a slightly lower 33% yield and a comparable enantioselectivity to that obtained with catalyst **1a** from the previous series (Table 2, entry 3 versus entry 1); this shows that the steric hindrance of the methylhydroxy group is more comparable to that of a phenyl group than that of a methyl group (entry 3 versus entries 1 and 2). The acetylated catalyst **1d** produced the same yield and enantioselectivity as **1c** (entry 4), showing that the acetyl group had no effect, probably because it was too far from the iodine reactive center. The reactivity of two catalysts bearing chiral ester groups, diastereoisomers **1e** and **1f**, was compared, but both catalysts gave keto tosylate **7a** with comparable yields and er values (entries 5 and 6). Subsequently, we prepared a range of catalysts bearing carbamate groups and evaluated them in the oxidation reaction. Catalyst **1g** bearing tolyl carbamate groups gave the expected product with 75:25 er, the best enantioselectivity ever obtained for a 3,3′-diiodo-BINOL-fused maleimide; however, the yield was quite low (entry 7). Catalysts **1h**–**k** gave yields in the range 17–46% and er values of about 70:30 (entries 8–11). Finally, catalysts **1l** and **1m** bearing protected amino ester groups were synthesized and used in the oxytosylation reaction; both gave keto tosylate **7a** with similar yields and er values (entries 12 and 13).

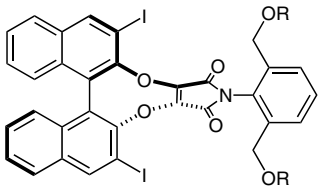
Because further modifications of the maleimide part of the catalysts had produced little improvement in the enantioselectivity of the oxytosylation reaction, it became important to investigate modifications to the BINOL part of this structure, on the basis that this might have more effect on the chiral induction.

Recently, Quideau and co-workers reported the synthesis of new biphenylic iodanes and their use in intermolecular asymmetric hydroxylative phenol dearomatization reactions.[9a] In their report they showed that dimethyl 2,2′-diiodosyl-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthalene-3,3′-dicarboxylate gave much better enantioselectivities in the oxidative dearomatization of 2-methylnaphthol than did 3,3′-Bis(methoxycarbonyl)-2,2′-diiodosyl-1,1′-binaphthyl. They also showed that for the binaphthalene compound, the iodine is oxidized to form a λ^3-iodane, whereas in the octahydrobinaphthalene compound, it is oxidized to form a λ^5-iodane. The improvement in enantioselectivity is almost certainly the result of this difference of in the degree of oxidation of the iodane centers. The change in the dihedral angle of the biaryl moiety or the change in the electronic properties of the aromatic ring might be responsible for the difference in the oxidative properties of the iodine precursors. These results supported our idea of investigating modifications of the BINOL part of our previous series of catalysts **1**.

Table 2 Evaluation of Catalysts with Maleimide Moieties Bearing Bulky *Ortho* Substituents on Their Phenyl Rings[a]



6a **7a**



1c–m

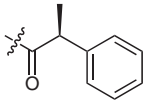
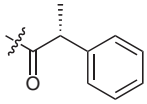
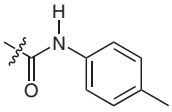
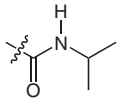
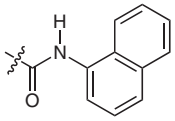
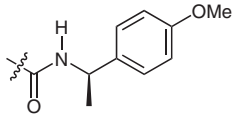
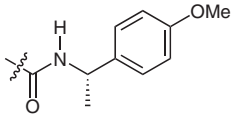
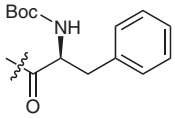
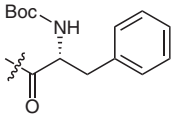
Entry	Catalyst	R	Yield[b] (%)	er[c]
1	**1a**	–	45	69:31
2	**1b**	–	27	64:36
3	**1c**	H	33	68:32
4	**1d**	Ac	32	68:32
5	**1e**		40	68:32
6	**1f**		45	69:31
7	**1g**		13	75:25
8	**1h**		46	70:30

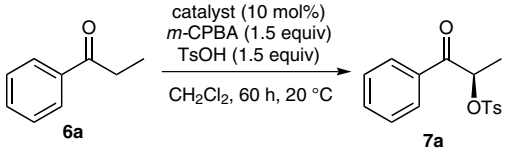
Table 2 (continued)

Entry	Catalyst	R	Yield[b] (%)	er[c]
9	**1i**		17	71:29
10	**1j**		29	71:29
11	**1k**		24	70:30
12	**1l**		30	71:29
13	**1m**		33	70:30

[a] Reaction conditions: **6a** (0.05 mmol), catalyst (0.005 mmol; 10 mol%), *m*-CPBA (0.075 mmol; 1.5 equiv), TsOH (0.075 mmol; 1.5 equiv), CH_2Cl_2 (0.5 mL, 0.1 M).
[b] Determined by ^{1}H NMR in acetone-d_6 with Ph_3CH as internal reference.
[c] Determined by chiral HPLC analysis.

From octahydro-BINOL, three new catalysts **8a**, **8b**, and **8c** (Figure 4) were quickly and easily obtained. When used in the oxytosylation reaction, catalyst **8a** gave keto tosylate **7a** with 31% yield and no er (Table 3, entry 1), a result similar to that obtained with the equivalent BINOL catalyst **2** (Table 1, entry 2). In the case of catalyst **8b**, the oxytosylated product was obtained in 38% yield and 61:39 er (Table 3, entry 2), an improvement in both yield and er compared with the equivalent BINOL catalyst **3** (Table 1, entry 3). Similarly, catalyst **8c** also gave keto tosylate **7a** with better results than did **1a** (Table 3, entry 3 versus Table 1, entry 1). To verify the effects of aliphatic substituents on the biphenol part of this new family of catalyst,[7i] catalyst **8d**, bearing six methyl groups on its biphenol part, was synthesized (Figure 2). Catalyst **8d** gave **7a** with the same yield and er as **8c** (Table 3, entry 4). To combine the best biphenol part with the best maleimide moiety, we synthesized catalyst **8e** (Figure 2). In the previous series of catalysts **1**, the 3,3′-diiodo-BINOL-fused maleimide that gave the best enantiomeric ratio contained the maleimide moiety shown in Figure 2. Keto tosylate **7a** was obtained with good yield and er with catalyst **8e** (Table 3, entry 5), but there was no improvement in yield and enantioselectivity compared with the equivalent BINOL catalyst. We also prepared catalyst **8f**, because its BINOL equivalent **1j** gave a lower yield but a better enantioselectivity (Table 2, entry 7). However, although this catalyst gave a greater yield than **1j**, the enantioselectivity was lower (Table 3, entry 6) and was comparable to that obtained with the other biphenol catalysts.

Table 3 Evaluation of Organocatalysts **8**[a]



6a **7a**

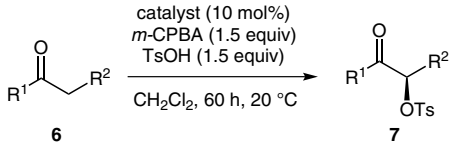
Entry	Catalyst	Yield[b] (%)	er[c]
1	**8a**	31	51:49
2	**8b**	38	61:39
3	**8c**	50	71:29
4	**8d**	51	71:29
5	**8e**	46	72:28
6	**8f**	52	70:30

[a] Reaction conditions: **6a** (0.05 mmol), catalyst (0.005 mmol, 10 mol%), *m*-CPBA (0.075 mmol, 1.5 equiv), PTSA (0.075 mmol, 1.5 equiv), CH_2Cl_2 (0.5 mL, 0.1 M).
[b] Determined by ^{1}H NMR in acetone-d_6 with Ph_3CH as internal reference.
[c] Determined by chiral HPLC analysis.

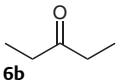
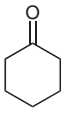
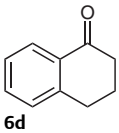
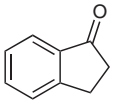
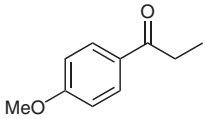
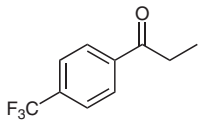
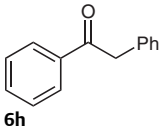
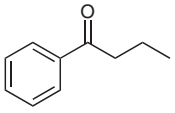
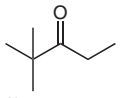
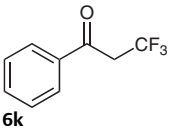
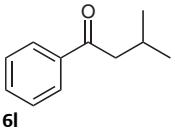
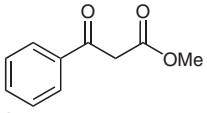
Among all the series of catalysts that we prepared, catalyst **8c** was the one that could be synthesized quickly and most easily on a large scale, and it gave one of the best results in the α-oxytosylation of propiophenone (**6a**). We therefore decided to use catalyst **8c** in α-oxytosylations of a range of ketones (Table 4). Whereas aliphatic ketones could not be oxidized by using the best catalyst of the previous series, catalyst **8c** was effective in the α-oxytosylation of such ketones (Table 4, entries 1 and 2), giving the products **7b** and **7c** in moderate to good yields but with no enantioselectivity. Keto tosylate **7d** was obtained in 21% yield and a 61:39 er (entry 3), the best result reported so far for this substrate in both terms of both yield and enantioselectivity.[7] Keto tosylate **7e** was obtained in good yield but with a lower er than expected (entry 4). Oxidation of **6f** to keto tosylate **7f** gave the expected low yield and low enantioselectivity (entry 5). Product **7g** was obtained with only 23% yield, but with an improved 69:31 er (entry 6). Keto tosylate **7h** was obtained with a high 87% yield but with no enantioselectivity (entry 7). Keto tosylate **7i** was obtained with a moderate 29% yield and a good 73:27 er (entry 8). Keto tosylate **7i** was obtained in only 11% yield and a 57:43 er (entry 9); this result is comparable to that obtained by Zhang and co-workers.[7g] To the best of our knowledge, ketones **6k**, **6l**, and **6m** have never been tested in the α-oxytosylation reaction before. Ketones **6k** and **6l** did not react at all, and were fully recovered from the reaction mixture (entries 10

and 11), whereas ketone **6m** was transformed in keto tosylate **7m** in good yield and 56:44 er (entry 12).

Table 4 Substrate Scope with Organocatalyst **8c**[a]



6 **7**

Entry	Substrate **6**	Yield[b] (%)	er[c]
1	 **6b**	64	51:49
2	 **6c**	17	52:48
3	 **6d**	21	61:39
4	 **6e**	64	57:43
5	 **6f**	7	63:37
6	 **6g**	23	69:31
7	 **6h**	87	51:49
8	 **6i**	29	73:27
9	 **6j**	11	57:43
10	 **6k**	0	–
11	 **6l**	0	–
12	 **6m**	72	56:44

[a] Reaction conditions: **6** (0.05 mmol), catalyst **8c** (0.005 mmol, 10 mol%), *m*-CPBA (0.075 mmol, 1.5 equiv), PTSA (0.075 mmol, 1.5 equiv), CH_2Cl_2 (0.5 mL, 0.1 M).
[b] Determined by ^1H NMR in acetone-d_6 with Ph_3CH as internal reference.
[c] Determined by chiral HPLC analysis.

In summary we have prepared several new families of hypervalent iodine oxidation organocatalysts. We showed that in these series, maleimide is the best moiety for achieving good enantioselectivities in the α-oxytosylation reaction of propiophenone, probably as a result of the enhanced stability of this structure under the reaction conditions. Moreover, we showed that the presence of a ring between the two oxygen atoms of the 3,3′-diiodo-BINOL or 3,3′-diiodobiphenol improved the enantioselectivity of the reaction. The enantioselectivity was also improved by replacing the BINOL segment with a biphenol. The 3,3′-diiodobiphenol-fused maleimide **8c** showed a broad substrate generality and was even capable of catalyzing the oxidation of aliphatic ketones. The use of 3,3′-diiodobiphenol-fused maleimides as organocatalysts in other hypervalent iodine-mediated asymmetric oxidation reactions is under study and will be reported in due course.

NMR spectra were recorded by using an Avance III 400 Bruker spectrometer at 293 K and 400 MHz. Chemical shifts are reported in ppm with the solvent as internal reference. High-resolution mass spectra were recorded on an Orbitrap apparatus with electrospray ionization. Reactions were monitored by TLC on commercial aluminum-backed silica gel plates. Unless otherwise noted, all reactions were performed under argon. All reagent-grade chemicals and solvents were obtained from commercial suppliers, and were used as received except for *m*-CPBA and PTSA. Ketones **6j**,[10] **6k**,[11] and **6m**[12] were prepared by the reported procedures. Chromatography purifications were performed by column chromatography on silica gel 60 (40–60 mesh). Melting points were obtained at a heating rate of 10 °C/min and are uncorrected. IR spectra were recorded by using a Fourier-transform spectrometer operated in the ATR mode for solid compounds. Solvents

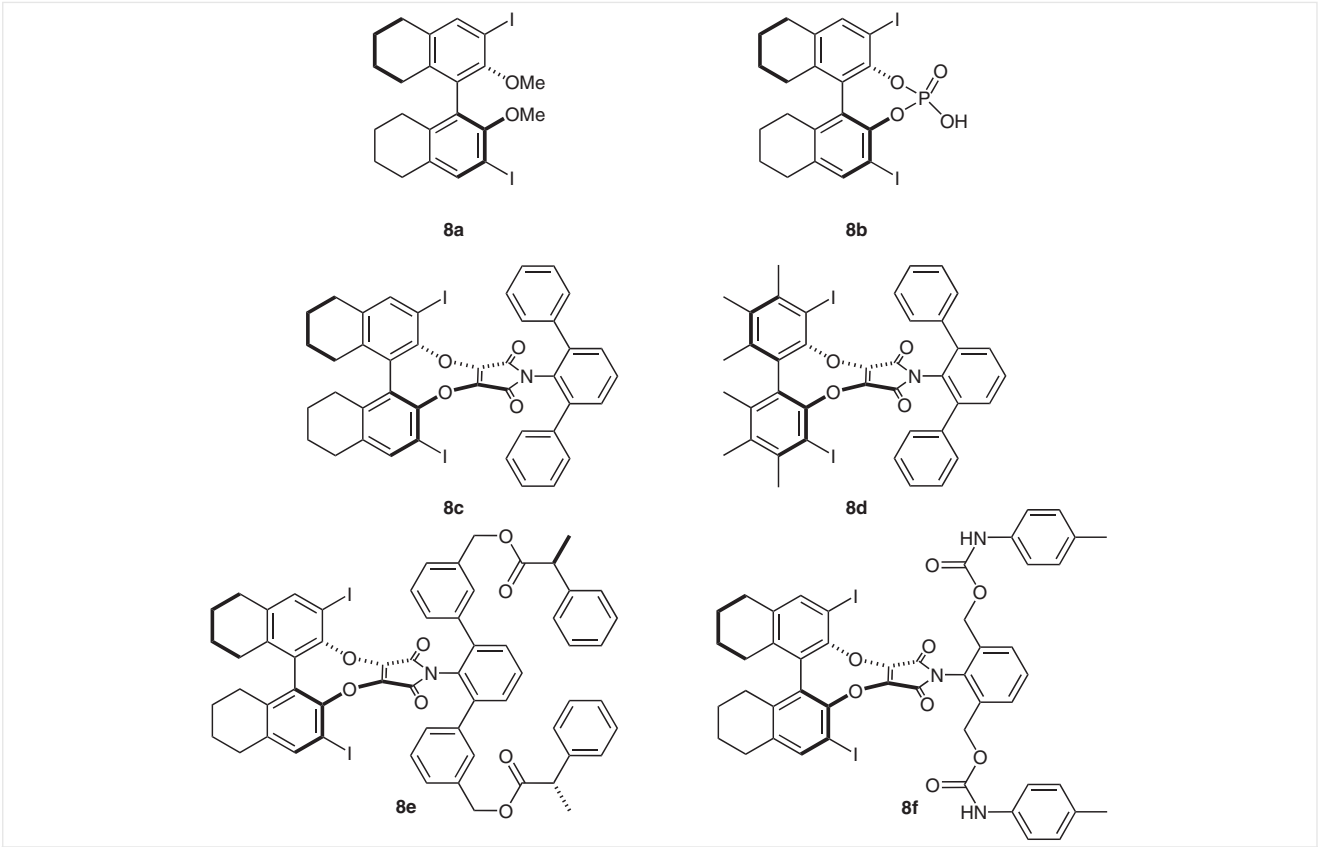


Figure 4 New series of 3,3′-diiodobiphenol organocatalysts **8**

and starting materials were obtained from Aldrich or Fisher Scientific, and were used without further purification, except for DMF, which was distilled over $MgSO_4$ before use. HPLC was performed on an Agilent Technologies 1260 Infinity apparatus using supercritical CO_2–MeOH as eluent. Optical rotations were determined with a Perkin-Elmer 341 polarimeter using solutions in $CHCl_3$.

(a*R*)-2,2′-Dimethoxy-1,1′-binaphthalene

K_2CO_3 (6.579 g, 47.6 mmol) and MeI (5.23 mL; 84.0 mmol) were successively added to a refluxing solution of (a*R*)-BINOL (4.000 g, 14.0 mmol) in acetone (30 mL). The mixture was stirred for 24 h, additional MeI (2.62 mL; 42.0 mmol) was added, and the mixture was stirred for another 12 h. The mixture was then allowed to cool down to r.t. H_2O (20 mL) was added, and the resulting suspension was stirred for 4 h at r.t. then filtered. The resulting product was washed with H_2O and dried in oven at 65 °C to give a white solid; yield: 4.347 g (13.8 mmol, 99%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 9.0 Hz, 2 H), 7.87 (d, *J* = 8.0 Hz, 2 H), 7.47 (d, *J* = 9.0 Hz, 2 H), 7.31 (dd, *J* = 7.0, 8.0 Hz, 2 H), 7.25–7.18 (m, 2 H), 7.12 (d, *J* = 8.5 Hz, 2 H), 3.77 (s, 6 H).

(a*R*)-3,3′-Diiodo-2,2′-dimethoxy-1,1′-binaphthalene (2)[13]

An oven-dried two-necked flask was charged with TMEDA (0.973 mL; 6.45 mmol) and anhyd Et_2O (50 mL) under an inert atmosphere. A 2.5 M solution of BuLi in hexane (4.89 mL, 11.72 mmol) was added at r.t., and the mixture was stirred for 20 min at r.t. (a*R*)-2,2′-dimethoxy-1,1′-binaphthalene (920 mg, 2.93 mmol) was added in one portion, and the resulting suspension was stirred for 3 h. The mixture was then cooled to –90 °C, a solution of I_2 (2.578 g, 9.96 mmol) in THF (20 mL) was added dropwise, and the mixture was slowly warmed to r.t. over 3 h and then stirred for another 16 h at r.t. Half-sat. aq $Na_2S_2O_3$ was added, and the mixture was stirred for 1 h. The aqueous layer was extracted with Et_2O (3 × 30 mL), and the organic layers were combined, dried ($MgSO_4$), filtered, and concentrated under vacuum. The product was purified by chromatography [silica gel, (60 g), toluene–cyclohexane (2:8 to 3:7)] to give a pale-yellow solid; yield: 1.258 g (2.22 mmol, 76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (s, 2 H), 7.80 (d, *J* = 8.1 Hz, 2 H), 7.41 (dd, *J* = 8.1, 7.1 Hz, 2 H), 7.28 (dd, *J* = 8.1, 7.1 Hz, 2 H), 7.07 (d, *J* = 8.1 Hz, 2 H), 3.42 (s, 6 H).

(a*R*)-3,3′-Diiodo-1,1′-binaphthalene-2,2′-diol

(a*R*)-3,3′-Diiodo-2,2′-dimethoxy-1,1′-binaphthalene (606 mg, 1.07 mmol) was dissolved in CH_2Cl_2 (20 mL) in an oven-dried two-necked flask. A solution of BBr_3 (0.420 mL; 4.28 mmol) in CH_2Cl_2 (5 mL) was then added dropwise at 0 °C. The mixture was stirred for 15 h at r.t., H_2O (20 mL) was added dropwise, and the mixture was stirred for a further 2 h. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL) and the organic layers were combined, dried ($MgSO_4$), filtered, and concentrated. Filtration over silica gel (EtOAc) gave an off-white solid; yield: 466 mg (0.87 mmol, 81%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (s, 2 H), 7.80 (d, *J* = 8.3 Hz, 2 H), 7.39 (dd, *J* = 6.9, 1.3 Hz, 2 H), 7.34 (dd, *J* = 4.1, 1.5 Hz, 2 H), 7.07 (d, *J* = 8.3 Hz, 2 H), 5.40 (s, 2 H).

(a*R*)-2,6-Diiododinaphtho[1,2-*f*:2′,1′-*d*][1,3,2]dioxaphosphepin-4-ol 4-Oxide (3)[14]

The product was obtained by following a modified version of the reported procedure originally applied to BINOL.[15] $POCl_3$ (125 μL, 1.4 equiv) was added to a solution of (a*R*)-3,3′-diiodo-[1,1′-binaphthalene]-2,2′-diol (0.490 g, 0.912 mmol) in pyridine (4 mL) at r.t., and the mixture was stirred at r.t. for 3 h. The reaction was quenched by addition of H_2O (100 μL) at 0 °C, and the mixture was stirred for 1 h at r.t. The pyridine was evaporated under vacuum and 6 M aq HCl (10 mL) was added to the residue at 0 °C. The mixture was refluxed with stirring for 2 h then cooled to 0 °C. The resulting solids were collected by filtration and washed with H_2O. The crude product was purified by precipitation from $CHCl_3$–pentane and collected by filtration to give a white solid; yield: 218 mg (0.363 mmol, 40%); mp 216 °C; $[\alpha]_D^{25}$ –32 (*c* 0.94, $CHCl_3$).

IR (neat): 3325.59, 3065.96, 1631.66, 1486.02, 1441.69, 1239.05, 1216.89, 1093.40, 1077.55, 966.65, 814.78, 745.12, 729.29, 669.13 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (s, 2 H), 8.01 (d, *J* = 8.2 Hz, 2 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.32 (t, *J* = 7.6 Hz, 2 H), 7.07 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 143.42, 139.46, 131.88, 131.74, 127.55, 127.00, 126.74, 126.04, 125.60, 92.22.

^{31}P NMR (400 MHz, $CDCl_3$): δ = 2.57.

HRMS (ESI): *m/z* $[M - H]^-$ calcd for $C_{20}H_{10}I_2O_4P$: 598.8406; found: 598.8416.

(a*R*)-1,12-Diiodotrinaphtho[1,2-*g*:2′,1′-*e*:2″,3″-*b*][1,4]dioxocine-14,19-dione (4)

(a*R*)-3,3′-Diiodo-[1,1′-binaphthalene]-2,2′-diol (538 mg, 1 mmol), 2,3-dichloro-1,4-naphthoquinone (227 mg, 1 mmol), and Na_2CO_3 (212 mg, 2.0 mmol) were dissolved in DMF (10 mL), and the mixture was stirred at 80 °C for 24 h. The DMF was evaporated under vacuum (3 Torr), and the resulting dark-red oil was directly purified by chromatography [silica gel (80 g), pentane–toluene–Et_3N (50:50:1 to 30:70:1 to 0:100:1) then silica gel (40 g), pentane–toluene (50:50 to 30:70 to 0:100)] to give a yellow solid; yield: 353 mg (0.51 mmol, 51%); mp 281 °C; $[\alpha]_D^{25}$ +716 (*c* 0.98, $CHCl_3$).

IR (neat): 3053.30, 2958.31, 2920.32, 2850.66, 1901.34, 1845.98, 1675.62, 1220.57, 979.23 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (s, 2 H), 8.20 (dd, *J* = 5.6, 3.3 Hz, 2 H), 7.84 (d, *J* = 8.2 Hz, 2 H), 7.77 (dd, *J* = 5.6, 3.3 Hz, 2 H), 7.54 (ddd, *J* = 8.2, 5.6, 2.5 Hz, 2 H), 7.41–7.33 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.89, 149.27, 146.55, 141.53, 134.39, 133.49, 131.71, 130.64, 127.84, 127.36, 127.22, 127.03, 126.89, 126.77, 87.72.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{30}H_{15}I_2O_4$: 692.9060; found: 692.9039.

(a*R*)-1,12-Diiodotrinaphtho[1,2-*g*:2′,1′-*e*:2″,3″-*b*][1,4]dioxocine-14,19-diyl Bis(2,2-dimethylpropanoate) (5a); Typical Procedure

Dione **4** (25 mg, 0.036 mmol) and $Na_2S_2O_4$ (253 mg, 1.45 mmol) were dissolved in degassed 1:1 $CHCl_3/H_2O$ (10 mL), and the mixture was vigorously stirred for 210 min at 75 °C and then allowed to cool to r.t. Under an argon atmosphere, most of the aqueous layer was removed with a syringe and the organic phase was dried ($MgSO_4$). The dried organic phase was filtered over silica gel, eluted with CH_2Cl_2, and degassed. (The entire filtration and elution operation should take no more than 5 min.)[16] DMAP (0.5 mg, 0.004 mmol), Et_3N (36 mg, 50 μL, 0.36 mmol), and PivCl (43 mg, 44 μL, 0.36 mmol) were added, and the solution was stirred at r.t. for 16 h. Half-sat. aq $NaHCO_3$ (5 mL) was added and the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The organic layers were combined, dried ($MgSO_4$), and evaporated under vacuum. The crude product was purified by chromatography [silica gel (10 g), toluene] to give a pale-yellow compound; yield: 31 mg (0.036 mmol, quant); mp 226 °C; $[\alpha]_D^{25}$ +331 (*c* 0.90, $CHCl_3$).

IR (neat): 3335.09, 3059.93, 2920.32, 2866.49, 2850.66, 1756.05, 1386.63, 1084.04, 978.72 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (s, 2 H), 7.86–7.75 (m, 4 H), 7.55–7.45 (m, 4 H), 7.40–7.32 (m, 4 H), 1.45 (s, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.88, 150.16, 141.86, 138.96, 135.53, 133.32, 131.72, 127.98, 127.45, 127.24, 126.91, 126.57, 126.47, 124.60, 121.32, 87.10, 39.54, 27.72.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{40}H_{32}I_2NaO_6$: 885.0186; found: 885.0181.

1,12-Diiodotrinaphtho[1,2-*g*:2′,1′-*e*:2″,3″-*b*][1,4]dioxocine-14,19-diyl Diacetate (5b)

Prepared by the typical procedure from dione **4** (25 mg, 0.036 mmol) by using AcCl (28 mg, 25 μL, 0.36 mmol) instead of PivCl, and purified by chromatography [silica gel (10 g), pentane–toluene (5:5 to 3:7 to 0:10)] to give a pale-yellow compound; yield: 20 mg (0.026 mmol, 71%); mp 340 °C; $[\alpha]_D^{25}$ +475 (*c* 0.16, $CHCl_3$).

IR (neat): 3341.42, 3056.46, 2957.26, 2925.69, 2860.16, 1751.98, 1673.61, 1605.55, 1386.14, 978.55 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (s, 2 H), 7.90–7.84 (m, 2 H) 7.81 (d, *J* = 8.1 Hz, 2 H), 7.51–7.45 (m, 4 H) 7.35–7.28 (m, 4 H) 2.43 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.83, 149.79, 141.46, 138.42, 135.22, 133.05, 131.58, 129.92, 127.60, 127.23, 127.20, 126.74, 126.55, 124.24, 121.32, 87.10, 21.10.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{34}H_{20}I_2NaO_6$: 800.9247; found: 800.9238.

1,12-Diiodotrinaphtho[1,2-*g*:2′,1′-*e*:2″,3″-*b*][1,4]dioxocine-14,19-diyl Dibenzoate (5c)

Prepared by the typical procedure from dione **4** (25 mg, 0.036 mmol) by using BzCl (51 mg, 42 μL, 0.36 mmol) instead of PivCl, and purified by chromatography [silica gel (10 g), pentane–toluene (3:7 to 0:10)] to give a pale-yellow compound; yield: 32 mg (0.036 mmol, quant); mp 142 °C; $[\alpha]_D^{25}$ +206 (*c* 0.34, $CHCl_3$).

IR (neat): 3341.42, 3062.80, 2955.15, 2920.32, 2853.83, 1741.51, 1387.99, 1209.92, 1079.09, 977.93 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (s, 2 H), 8.41–8.34 (m, 4 H), 7.97–7.90 (m, 2 H), 7.80 (d, *J* = 8.2 Hz, 2 H), 7.67–7.60 (m, 2 H) 7.56–7.42 (m, 8 H) 7.34–7.27 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.74, 149.97, 141.70, 139.16, 135.63, 133.83, 133.25, 131.68, 130.94, 130.72, 129.15, 128.63, 127.93, 127.37, 126.89, 126.75, 126.63, 124.64, 121.67, 87.36.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{44}H_{24}I_2NaO_6$: 924.9560; found: 924.9566.

2-Nitroisophthalic Acid[17]

1,3-Dimethyl-2-nitrobenzene (3.000 g, 19.84 mmol) was added to H_2O (150 mL) together with NaOH (1.200 g, 29.76 mmol), and the resulting suspension was stirred at 95 °C under air. $KMnO_4$ (12.00 g, 75.4 mmol) was then added directly to the mixture in portions over 3 h. The mixture was stirred at 95 °C for 20 h under air and then allowed to cool to r.t. The suspension was filtered over Celite and the mother liquor was acidified to pH 1 with 2 M aq HCl. The product was collected by filtration through frit and washed with 1 M aq HCl to give a white solid; yield: 3.69 g (88%).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 14.10 (s, 2 H), 8.18 (d, *J* = 7.8 Hz, 2 H), 7.82 (t, *J* = 7.8 Hz, 1 H).

(2-Amino-1,3-phenylene)dimethanol

A solution of 2-nitroisophthalic acid (3.674 g, 17.41 mmol) in THF (60 mL) was added dropwise over 30 min at r.t. to a solution of $LiAlH_4$ (9.990 g, 52.24 mmol) in Et_2O (60 mL). The mixture was stirred at the reflux for 6 h then cooled to r.t. H_2O (5 mL) was carefully added, followed by 15% aq NaOH (5 mL) and H_2O (5 mL). The mixture was filtered through Celite, which was washed with CH_2Cl_2 and EtOAc. The mother liquors were evaporated under vacuum to give a beige solid; yield: 640 mg (24%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.06 (d, *J* = 7.5 Hz, 2 H), 6.66 (t, *J* = 7.5 Hz, 1 H), 4.75 (br, 2 H), 4.71 (d, *J* = 4.3 Hz, 4 H).[18]

[2-(3,4-Dibromo-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)-1,3-phenylene]di(methylene) Diacetate

(2-Amino-1,3-phenylene)dimethanol (333 mg, 2.5 mmol) and 3,4-dibromofuran-2,5-dione (584 mg, 2.5 mmol) were dissolved in AcOH (7 mL), and the mixture was stirred at the reflux for 16 h under air. The mixture was cooled to r.t. and the AcOH was removed under vacuum. Purification over silica gel (25 g, CH_2Cl_2) gave the desired compound as a pale-yellow solid; yield: 509 mg (43%); mp 132 °C.

IR (neat): 2977.31, 2955.15, 2913.98, 1723.48, 1590.50, 1473.35, 1372.03, 1229.55, 1102.90, 1030.08, 976.25, 824.27 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.48 (m, 3 H), 4.97 (s, 4 H), 1.98 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.30, 163.06, 135.90, 131.49, 130.66, 130.01, 129.51, 62.52, 20.57.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{16}H_{13}Br_2NNaO_6$: 495.9007; found: 495.9010.

(a*R*)-[2-(2,8-Diiodo-4,6-dioxo-4,6-dihydro-5*H*-dinaphtho[1′,2′:7,8;2″,1″:5,6][1,4]dioxocino[2,3-*c*]pyrrol-5-yl)-1,3-phenylene]di(methylene) Diacetate (1d)

(a*R*)-3,3′-Diiodo-[1,1′-binaphthalene]-2,2′-diol (435 mg, 0.81 mmol), [2-(3,4-dibromo-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)-1,3-phenylene]di(methylene) diacetate (500 mg, 1.05 mmol), and KF (470 mg, 8.1 mmol) were dissolved in DMF (10 mL), and the mixture was stirred at 70 °C for 16 h. The DMF was evaporated under vacuum (3 Torr), and the resulting dark-red oil was directly purified by chromatography [silica gel (50 g), toluene–EtOAc (100:0 to 95:5 to 90:10)] to give a pale-yellow solid; yield: 655 mg (94%); mp 320 °C; $[\alpha]_D^{25}$ +67 (*c* 1.26, $CHCl_3$).

IR (neat): 3056.46, 2964.64, 2926.65, 1729.82, 1685.49, 1568.34, 1495.51, 1470.18, 1381.53, 1318.21, 1232.72, 1197.89, 748.28 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.66 (s, 2 H), 7.89 (d, *J* = 7.9 Hz, 2 H), 7.56–7.48 (m, 5 H), 7.37–7.34 (m, 2 H), 7.10 (d, *J* = 8.5 Hz, 2 H), 5.10 (d, *J* = 12.8 Hz, 2 H), 5.04 (d, *J* = 12.8 Hz, 2 H), 1.91 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.48, 162.60, 149.36, 142.03, 137.68, 136.16, 133.47, 132.63, 130.71, 130.21, 128.47, 128.17, 127.50, 127.41, 126.72, 124.75, 87.67, 63.07, 21.05.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{36}H_{23}I_2NNaO_8$: 873.9406; found: 873.9411.

(a*R*)-5-[2,6-Bis(hydroxymethyl)phenyl]-2,8-diiodo-4*H*-dinaphtho[1′,2′:7,8;2″,1″:5,6][1,4]dioxocino[2,3-*c*]pyrrole-4,6(5*H*)-dione (1c)

Diacetate **1d** (596 mg, 0.7 mmol) was placed in a dry 25-mL round-bottom flask and purged under argon. Anhyd CH_2Cl_2 (4 mL), anhyd MeOH, (4 mL), and AcCl (277 mg, 250 μL, 3.5 mmol) were added, and the mixture was stirred at 40 °C for 16 h then allowed to cool to r.t. The solvent was evaporated and the residue was purified by chromatography [silica gel, (20 g), toluene–EtOAc (9:1 to 8:2)] to give a yellow solid; yield: 520 mg (96%); mp 225 °C; $[\alpha]_D^{25}$ +120 (*c* 1.00, $CHCl_3$).

IR (neat): 3268.60, 3062.80, 2970.98, 2929.82, 2860.16, 1729.82, 1685.49, 1571.50, 1460.69, 1444.85, 1381.53, 1318.21, 1229.55, 1204.22, 1071.24, 751.45 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (s, 2 H), 7.89 (d, *J* = 8.9 Hz, 2 H), 7.57–7.45 (m, 5 H), 7.38 (ddd, *J* = 8.7, 7.2, 1.3 Hz, 2 H), 7.12 (d, *J* = 8.5 Hz, 2 H), 4.59 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.42, 149.21, 141.89, 139.96, 137.47, 133.33, 132.42, 130.24, 129.19, 127.98, 127.30, 127.23, 126.60, 126.50, 124.65, 87.62, 62.76.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{32}H_{19}I_2NNaO_6$: 789.9191; found: 789.9199.

(a*R*)-[2-(2,8-Diiodo-4,6-dioxo-4,6-dihydro-5*H*-dinaphtho[1′,2′:7,8;2″,1″:5,6][1,4]dioxocino[2,3-*c*]pyrrol-5-yl)-1,3-phenylene]di(methylene) (2*S*,2′*S*)-Bis(2-phenylpropanoate) (1e); Typical Procedure

(2*S*)-2-Phenylpropanoic acid (30 mg, 0.2 mmol) was dissolved in anhyd CH_2Cl_2 (2 mL). DMF (1 μL) and oxalyl chloride (18 μL, 0.2 mmol) were added at 0 °C, and the mixture was stirred at 0 °C for 5 min and then at r.t. for 1 h. The mixture was then cooled at –20 °C and a solution of dione **1c** (36 mg, 0.047 mmol) in anhyd CH_2Cl_2 (1 mL) was added, followed by a mixture of anhyd Et_3N (30 μL, 0.22 mmol) and DMAP (0.6 mg, 0.005 mmol) in anhyd CH_2Cl_2 (1 mL). The mixture was stirred at r.t. for 24 h. Sat. aq $KHSO_4$ (2 mL) was added, and the aqueous phase was extracted with CH_2Cl_2 (2 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated under vacuum. Purification over silica gel [10 g, EtOAc–toluene (1:9)] gave a white solid; yield: 48 mg (99%); mp 95 °C; $[\alpha]_D^{25}$ +40 (*c* 1.44, $CHCl_3$).

IR (neat): 3059.63, 3050.13, 2970.98, 2926.65, 2850.66, 1726.65, 1682.32, 1454.35, 1381.53, 1318.21, 1229.55, 1194.72, 1147.23, 1064.91, 751.45 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (s, 2 H), 7.89 (d, *J* = 8.05 Hz, 2 H), 7.56 (t, *J* = 7.3 Hz, 2 H), 7.31–7.25 (m, 8 H), 7.17–7.05 (m, 9 H), 5.09 (d, *J* = 13.4 Hz, 2 H), 5.02 (d, *J* = 13.4 Hz, 2 H), 3.63 (q, *J* = 7.2 Hz, 2 H), 1.30 (d, *J* = 7.2 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.80, 162.11, 149.22, 141.81, 139.87, 138.60, 135.76, 133.29, 129.95, 129.89, 128.78, 128.46, 127.95, 127.57, 127.46, 127.29, 127.17, 127.02, 126.50, 124.58, 87.70, 63.11, 46.33, 18.55.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{50}H_{35}I_2NaNO_8$: 1054.0350; found: 1054.0355.

(a*R*)-(2-(5,16-Diiodo-1,3-dioxo-1*H*-dinaphtho[2′,1′:5,6;1″,2″:7,8][1,4]dioxocino[2,3-*c*]pyrrol-2(3*H*)-yl)-1,3-phenylene)bis(methylene) (2*R*,2′*R*)-Bis(2-phenylpropanoate) (1f)

Prepared by the typical procedure above from (2*R*)-2-phenylpropanoic acid (24 mg, 0.16 mmol), and purified over silica gel [10 g, EtOAc–toluene (0:100 to 2:98)] as a pale-yellow solid; yield: 14.4 mg (0.014 mmol; 36%); mp 179 °C; $[\alpha]_D^{25}$ –46 (*c* 1.04, $CHCl_3$).

IR (neat): 3069.13, 3040.63, 2967.81, 2932.98, 2847.49, 1729.82, 1682.32, 1568.34, 1476.52, 1448.02, 1384.70, 1318.21, 1188.39, 1147.23, 1115.57, 1071.24, 960.42, 884.43, 691.29 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.59 (s, 2 H), 7.93 (d, *J* = 8.2 Hz, 2 H), 7.61 (t, *J* = 7.4 Hz, 2 H), 7.44–7.33 (m, 5 H), 7.18–7.06 (m, 6 H), 6.91 (t, *J* = 7.7 Hz, 4 H), 6.77 (t, *J* = 7.4 Hz, 2 H), 5.18 (d, *J* = 12.9 Hz, 2 H), 4.91 (d, *J* = 12.9 Hz, 2 H), 3.57 (q, *J* = 7.3 Hz, 2 H), 1.37 (d, *J* = 7.3 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.84, 162.33, 149.29, 141.95, 139.98, 137.43, 136.09, 133.39, 132.43, 130.39, 130.06, 128.46, 128.28, 128.00, 127.37, 127.34, 127.26, 126.76, 126.65, 124.63, 87.67, 63.27, 45.20, 18.18.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{50}H_{35}I_2NNaO_8$: 1054.0350; found: 1054.0344.

(a*R*)-[2-(2,8-Diiodo-4,6-dioxo-4,6-dihydro-5*H*-dinaphtho[1′,2′:7,8;2″,1″:5,6][1,4]dioxocino[2,3-*c*]pyrrol-5-yl)-1,3-phenylene]di(methylene) Bis[(4-tolyl)carbamate] (1g)

Dione **1c** (20 mg, 0.026 mmol) was dissolved in anhyd $CHCl_3$ (1 mL) and 4-TolNCO (7.6 mg, 8 µL, 0.057 mmol) was added. The mixture was stirred at the reflux for 5 d then allowed to cool. The solvent was evaporated under vacuum and the crude product was directly purified by chromatography [silica gel (10 g), CH_2Cl_2–EtOAc (10:0 to 9:1)] to give an off-white solid; yield: 17 mg (62%); mp 132 °C; $[\alpha]_D^{25}$ +195 (*c* 0.20, $CHCl_3$).

IR (neat): 3328.76, 3027.97, 2961.48, 2920.32, 2850.66, 1729.82, 1679.16, 1596.83, 1517.68, 1384.70, 1311.87, 1201.06, 1052.24, 811.61, 745.12 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.65 (s, 2 H), 7.89 (d, *J* = 8.2 Hz, 2 H), 7.55–7.50 (m, 5 H), 7.37 (dd, *J* = 7.5, 1.4 Hz, 2 H), 7.11–7.10 (m, 6 H), 6.98 (d, *J* = 8.3 Hz, 4 H), 4.59 (d, *J* = 5.9 Hz, 4 H), 2.32 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.70, 152.76, 149.17, 141.88, 137.51, 136.41, 134.77, 134.43, 133.29, 132.92, 132.48, 131.53, 130.29, 129.30, 127.93, 127.34, 127.14, 126.54, 124.47, 118.85, 87.65, 63.79, 20.67.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{48}H_{33}I_2N_3NaO_8$: 1056.0255; found: 1056.0250.

(a*R*)-[2-(2,8-Diiodo-4,6-dioxo-4,6-dihydro-5*H*-dinaphtho[1′,2′:7,8;2″,1″:5,6][1,4]dioxocino[2,3-*c*]pyrrol-5-yl)-1,3-phenylene]di(methylene) Bis(isopropylcarbamate) (1h)

Dione **1c** (20 mg, 0.026 mmol) was dissolved in anhyd $CHCl_3$ (1 mL), and *i*-PrNCO (4.8 µL, 0.057 mmol) was added. The mixture was stirred for 10 d at reflux and then allowed to cool. The solvent was evaporated under vacuum, and the crude product was directly purified by chromatography [silica gel (10 g), toluene–EtOAc (9:1)] to give a beige solid; yield: 6.1 mg (25%); mp 140 °C; $[\alpha]_D^{25}$ +56 (*c* 0.62, $CHCl_3$). The product from monoaddition was also obtained; yield: 10.5 mg (47%).

IR (neat): 3072.30, 2964.64, 2917.15, 2869.66, 1726.65, 1685.49, 1571.50, 1498.68, 1454.35, 1381.53, 1321.37, 1229.55, 1197.89, 1068.07, 751.45 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.64 (s, 2 H), 7.87 (d, *J* = 8.4 Hz, 2 H), 7.60–7.40 (m, 5 H), 7.37 (t, *J* = 7.4 Hz, 2 H), 7.08 (d, *J* = 8.4 Hz, 2 H), 5.07 (d, *J* = 12.5 Hz, 2 H), 4.94 (d, *J* = 12.5 Hz, 2 H), 4.49–4.36 (m, 2 H), 3.60–3.47 (m, 2 H), 0.99 (d, *J* = 6.1 Hz, 6 H), 0.83 (d, *J* = 6.1 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.64, 154.85, 149.26, 141.83, 137.35, 136.73, 133.31, 132.49, 130.80, 130.09, 128.59, 127.96, 127.28, 127.19, 126.49, 124.54, 87.79, 63.27, 43.09, 22.80, 22.53.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{40}H_{33}I_2N_3NaO_8$: 960.0255; found: 960.0253.

(a*R*)-[2-(2,8-Diiodo-4,6-dioxo-4,6-dihydro-5*H*-dinaphtho[1′,2′:7,8;2″,1″:5,6][1,4]dioxocino[2,3-*c*]pyrrol-5-yl)-1,3-phenylene]di(methylene) Bis(1-naphthylcarbamate) (1i)

Dione **1c** (20 mg, 0.026 mmol) was dissolved in anhyd $CHCl_3$ (1 mL), and 1-naphthyl isocyanate (14 µL, 0.056 mmol) was added. The mixture was stirred for 10 d at the reflux and then allowed to cool. The solvent was evaporated under vacuum and the crude product was directly purified by chromatography [silica gel (10 g), toluene–EtOAc (9:1)] to give a mixture of the product and unidentified impurities. The solid product was dissolved in the minimum amount of CH_2Cl_2 and then precipitated by addition of pentane. The solid was collected by filtration on frit, washed with pentane, and dried to give a beige solid; yield: 21.5 mg (75%); mp 158 °C; $[\alpha]_D^{25}$ +19 (*c* 1.60, $CHCl_3$).

IR (neat): 3344.59, 3050.13, 2951.98, 2917.15, 2850.66, 1729.82, 1682.32, 1520.84, 1492.35, 1454.35, 1384.70, 1315.04, 1197.89, 1068.07, 748.28 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.45 (s, 2 H), 7.79 (d, *J* = 8.2 Hz, 2 H), 7.73 (t, *J* = 7.6 Hz, 2 H), 7.65 (d, *J* = 7.6 Hz, 2 H), 7.59 (d, *J* = 7.6 Hz, 2 H), 7.54–7.42 (m, 5 H), 7.38–7.25 (m, 6 H), 7.20 (t, *J* = 7.8 Hz, 2 H), 7.05–6.95 (m, 4 H), 5.26 (d, *J* = 12.6 Hz, 2 H), 5.19 (d, *J* = 12.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.21, 153.50, 149.09, 141.84, 137.56, 136.43, 133.86, 133.20, 132.47, 132.10, 131.72, 130.31, 129.77, 128.41, 127.91, 127.26, 127.20, 126.44, 126.31, 126.17, 125.84, 125.52, 124.88, 124.37, 120.55, 118.78, 87.57, 64.20.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{54}H_{33}I_2N_3NaO_8$: 1128.0255; found: 1128.0251.

(a*R*)-[2-(2,8-Diiodo-4,6-dioxo-4,6-dihydro-5*H*-dinaphtho[1′,2′:7,8;2″,1″:5,6][1,4]dioxocino[2,3-*c*]pyrrol-5-yl)-1,3-phenylene]di(methylene) Bis{[(1*R*)-1-(4-methoxyphenyl)ethyl]carbamate} (1j)

Dione **1c** (20 mg, 0.026 mmol) was dissolved in anhyd $CHCl_3$ (1 mL) and 1-[(1*R*)-1-isocyanatoethyl]-4-methoxybenzene (9 µL, 0.057 mmol) was added. The mixture was stirred for 10 d at reflux and then allowed to cool. The solvent was evaporated under vacuum, and the crude product was directly purified by chromatography [silica gel (10 g), toluene–EtOAc (9:1)] to give a mixture of the product and unidentified impurities. The solid product was dissolved in the minimum amount of CH_2Cl_2 and precipitated by addition of pentane. The precipitate was collected by filtration on frit, washed with pentane, and dried to give a white solid; yield: 15.5 mg (53%); mp 120 °C; $[\alpha]_D^{25}$ +111 (*c* 0.54, $CHCl_3$).

IR (neat): 3407.92, 3319.26, 3056.46, 2961.48, 2923.48, 2850.66, 1729.82, 1679.16, 1508.18, 1381.53, 1321.37, 1197.89, 1058.58, 745.12 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.62 (s, 2 H), 7.86 (d, *J* = 8.7 Hz, 2 H), 7.52 (t, *J* = 7.5 Hz, 2 H), 7.50–7.36 (m, 3 H), 7.33 (t, *J* = 7.5 Hz, 2 H), 7.06 (d, *J* = 6.9 Hz, 6 H), 6.78 (d, *J* = 6.9 Hz, 4 H), 5.25–5.09 (m, 2 H), 4.95–4.77 (m, 4 H), 4.60–4.45 (m, 2 H), 3.76 (s, 6 H), 1.22–1.07 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.76, 158.70, 154.82, 149.21, 141.84, 137.32, 136.66, 135.40, 133.30, 132.52, 131.04, 130.10, 129.02, 127.97, 127.28, 127.21, 127.07, 126.49, 124.45, 113.94, 87.83, 63.47, 55.26, 50.12, 21.92.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{52}H_{41}I_2N_3NaO_{10}$: 1144.0779; found: 1144.0769.

(a*R*)-[2-(2,8-Diiodo-4,6-dioxo-4,6-dihydro-5*H*-dinaphtho[1′,2′:7,8;2″,1″:5,6][1,4]dioxocino[2,3-*c*]pyrrol-5-yl)-1,3-phenylene]di(methylene) Bis{[(1*S*)-1-(4-methoxyphenyl)ethyl]carbamate} (1k)

Dione **1c** (20 mg, 0.026 mmol) was dissolved in anhyd $CHCl_3$ (1 mL), and 1-[(1*S*)-1-isocyanatoethyl]-4-methoxybenzene (9 μL, 0.057 mmol) was added. The mixture was stirred for 10 d at reflux and then allowed to cool. The solvent was evaporated under vacuum, and the crude product was directly purified by chromatography [silica gel (10 g), toluene–EtOAc (9:1)] to give a beige solid; yield: 17.2 mg (59%); mp 135 °C; $[\alpha]_D^{25}$ +86 (*c* 0.74, $CHCl_3$).

IR (neat): 3401.58, 3316.09, 2955.15, 2926.65, 2834.83, 1732.98, 1679.16, 1615.83, 1511.35, 1384.70, 1321.37, 1226.39, 1058.58, 827.44, 745.12 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.61 (s, 2 H), 7.86 (d, *J* = 8.1 Hz, 2 H), 7.52 (t, *J* = 7.6 Hz, 4 H), 7.44–7.36 (m, 1 H), 7.33 (t, *J* = 7.8 Hz, 2 H), 7.10 (d, *J* = 8.6 Hz, 4 H), 7.06 (d, *J* = 8.6 Hz, 2 H), 6.75 (d, *J* = 8.6 Hz, 4 H), 5.08–4.94 (m, 4 H), 4.90 (br s, 2 H), 4.68–4.57 (m, 2 H), 3.74 (s, 6 H), 1.42–1.28 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.61, 158.70, 154.94, 149.18, 141.84, 137.31, 136.58, 135.19, 133.30, 132.50, 131.23, 131.15, 130.05, 127.96, 127.27, 127.24, 127.17, 126.51, 124.49, 113.92, 87.78, 63.25, 55.24, 50.04, 21.96.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{52}H_{41}I_2N_3NaO_{10}$: 1144.0779; found: 1144.0773.

(a*R*)-[2-(2,8-Diiodo-4,6-dioxo-4,6-dihydro-5*H*-dinaphtho[1′,2′:7,8;2″,1″:5,6][1,4]dioxocino[2,3-*c*]pyrrol-5-yl)-1,3-phenylene]di(methylene) (2*S*,2′*S*)Bis{2-[(*tert*-butoxycarbonyl)amino]-3-phenylpropanoate} (1l); Typical Procedure

Dione **1c** (100 mg, 0.13 mmol) and DCC (54 mg, 0.26 mmol) were placed in a 10 mL flask, a solution of *N*-Boc-D-phenylalanine (70 mg, 0.26 mmol) in CH_2Cl_2 (2 mL) was added, and the mixture was stirred for 1 week at r.t. A further 140 mg of *N*-Boc-D-phenylalanine (0.52 mmol) was added, the solvent was evaporated under vacuum, and the crude product was directly purified by chromatography [silica gel (10 g), toluene–EtOAc (9:1)] to give a mixture of the product and unidentified impurities. The solid was dissolved in the minimum amount of Et_2O and precipitated by addition of pentane. The precipitate was collected by filtration on frit, washed with pentane, and dried. The mother liquor was concentrated, and the product was again dissolved in the minimum amount of Et_2O and precipitated by addition of pentane. After three precipitations, the product was obtained as a white solid; yield: 60 mg (37%); mp 114 °C; $[\alpha]_D^{25}$ +58 (*c* 0.48, $CHCl_3$).

IR (neat): 3065.96, 2970.98, 2929.82, 2863.32, 1729.82, 1679.16, 1571.50, 1495.51, 1454.35, 1384.70, 1318.21, 1229.55, 1197.89, 1153.56, 1068.07, 757.78 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (s, 2 H), 7.86–7.75 (m, 2 H), 7.44 (s, 3 H), 7.37–7.29 (m, 2 H), 7.15–6.99 (m, 8 H), 6.95–6.80 (m, 4 H), 5.20–5.03 (m, 4 H), 4.95–4.80 (m, 2 H), 4.60–4.45 (m, 2 H), 3.00–2.75 (m, 4 H), 1.32 (s, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.32, 162.39, 154.96, 149.22, 141.95, 137.60, 135.80, 135.48, 133.35, 132.43, 130.73, 130.25, 129.21, 128.37, 128.00, 127.31, 127.26, 126.77, 126.54, 124.63, 113.92, 87.57, 79.79, 63.06, 54.36, 38.07, 28.22.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{60}H_{53}I_2N_3NaO_{12}$: 1284.1616; found: 1284.1598.

(a*R*)-[2-(2,8-Diiodo-4,6-dioxo-4,6-dihydro-5*H*-dinaphtho[1′,2′:7,8;2″,1″:5,6][1,4]dioxocino[2,3-*c*]pyrrol-5-yl)-1,3-phenylene]di(methylene) (2*R*,2′*R*)-Bis{2-[(*tert*-butoxycarbonyl)amino]-3-phenylpropanoate} (1m)

Prepared by the typical procedure using *N*-Boc-L-phenylalanine (70 mg, 0.26 mmol) to give a white solid; yield: 97 mg (59%); mp 125 °C; $[\alpha]_D^{25}$ +9.6 (*c* 1.06, $CHCl_3$).

IR (neat): 3401.58, 3062.80, 3027.97, 2974.14, 2929.82, 1729.82, 1682.32, 1495.51, 1451.19, 1384.70, 1318.21, 1226.39, 1201.06, 1150.40, 1064.91, 748.28 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (s, 2 H), 7.85 (d, *J* = 8.5 Hz, 2 H), 7.51 (t, *J* = 7.4 Hz, 2 H), 7.45–7.40 (m, 3 H), 7.33 (t, *J* = 7.4 Hz, 2 H), 7.17–7.06 (m, 8 H), 6.95–6.85 (m, 4 H), 5.19 (d, *J* = 13.1 Hz, 2 H), 4.99 (d, *J* = 13.1 Hz, 2 H), 4.92–4.82 (m, 2 H), 4.60–4.45 (m, 2 H), 3.05–2.94 (m, 2 H), 2.92–2.80 (m, 2 H), 1.35 (s, 18 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.26, 162.29, 154.97, 149.23, 141.96, 137.58, 135.80, 135.43, 133.39, 132.44, 130.48, 130.19, 129.26, 128.44, 127.99, 127.94, 127.29, 126.81, 126.54, 124.66, 114.99, 87.65, 79.84, 63.07, 54.44, 38.10, 28.25.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{60}H_{53}N_3O_{12}NaI_2^+$: 1284.1616; found: 1284.1594.

(a*S*)-5,5′,6,6′,7,7′,8,8′-Octahydro-1,1′-binaphthalene-2,2′-diol[19]

The product was obtained by a modified version of the reported procedure.[9] A mixture of (a*S*)-[1,1′-binaphthalene]-2,2′-diol (5.328 g, 18.6 mmol) and PtO_2 (0.48 g, 2.1 mmol, 0.11 equiv) in AcOH (160 mL) was placed in a 500 mL flask under H_2 (balloon, 1 atm) and the mixture was stirred for 3 d at r.t. The mixture was then filtered through Celite, which was washed with $CHCl_3$ (270 mL). The organic phase was washed successively with H_2O (100 mL) and sat. aq $NaHCO_3$ (100 mL) then dried ($MgSO_4$), filtered, and evaporated to give a white solid; yield: 5.59 g (quant); mp 161 °C; $[\alpha]_D^{25}$ –47 (*c* 1.0, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.06 (d, *J* = 8.6 Hz, 2 H), 6.82 (d, *J* = 8.6 Hz, 2 H), 4.53 (s, 2 H), 2.74 (t, *J* = 6.4 Hz, 4 H), 2.23–2.34 (m, 2 H), 2.21–2.10 (m, 2 H), 1.79–1.61 (m, 8 H).

(a*S*)-3,3′-Diiodo-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthalene-2,2′-diol[20]

The product was obtained by the reported procedure;[20] mp 200 °C; $[\alpha]_D^{25}$ +5 (*c* 1.72, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (s, 2 H), 4.95 (s, 2 H), 2.72 (t, *J* = 5.8 Hz, 4 H), 2.20–2.33 (m, 2 H), 2.02–2.15 (m, 2 H), 1.57–1.80 (m, 8 H).

(a*S*)-3,3′-Diiodo-2,2′-dimethoxy-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthalene (8a)

K_2CO_3 (430 mg, 3.4 equiv) and Me I (342 μL, 6 equiv) were successively added to a refluxing solution of (a*S*)-3,3′-diiodo-5,5′,6,6′,7,7′,8,8′-octahydro-[1,1′-binaphthalene]-2,2′-diol (0.5 g, 0.916 mmol) in acetone (2 mL). The mixture was stirred for 24 h then additional MeI (171 μL, 3 equiv) was added and the mixture was stirred for another 12 h. The mixture was then allowed to cool to r.t. and H_2O (1.3 mL) was added. The resulting suspension was stirred for 4 h at r.t. then fil-

tered. The resulting white solid was washed with H_2O and dried in an oven at 65 °C to give a white solid; yield: 497 mg (0.886 mmol, 95%); mp 114 °C; $[\alpha]_D^{25}$ +43 (*c* 1.03, $CHCl_3$).

IR (neat): 2996.31, 2926.65, 2853.83, 2831.66, 1454.35, 1429.02, 1413.19, 1410.03, 1378.36, 1299.21, 1264.38, 1242.22, 1074.41, 1033.25, 925.25, 912.93, 868.60, 786.28 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.55 (s, 2 H), 3.50 (s, 6 H), 2.84–2.66 (m, 4 H), 2.37–2.19 (m, 2 H), 2.18–1.98 (m, 2 H), 1.80–1.55 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.34, 139.17, 137.29, 135.55, 131.42, 86.26, 60.44, 29.05, 27.44, 22.68, 22.66.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{22}H_{24}I_2NaO_2$: 596.9763; found: 596.9758.

(a*S*)-2,6-Diiodo-8,9,10,11,12,13,14,15-octahydrodinaphtho[1,2-*f*:2′,1′-*d*][1,3,2]dioxaphosphepin-4-ol 4-Oxide (8b)

The product was obtained by a modification of the reported procedure originally applied to BINOL.[15] $POCl_3$ (125 µL, 1.4 equiv) was added to a solution of (a*S*)-3,3′-diiodo-5,5′,6,6′,7,7′,8,8′-octahydro-[1,1′-binaphthalene]-2,2′-diol (0.501 g, 0.918 mmol) in pyridine (4 mL) at r.t., and the mixture was stirred for 3 h at r.t. The reaction was quenched with H_2O (100 µL) at 0 °C, and the mixture was stirred for 1 h at r.t. After evaporation of the pyridine under vacuum, the residue was treated with 6 M aq HCl (10 mL) at 0 °C, and the resulting mixture was stirred for 2 h at the reflux then cooled to 0 °C. The solids were collected by filtration and washed with H_2O. The crude product was purified by precipitation from $CHCl_3$–pentane and filtration to give a white solid; yield: 230 mg (0.378 mmol, 41%); mp 225 °C; $[\alpha]_D^{25}$ +250 (*c* 0.2, $CHCl_3$).

IR (neat): 3344.59, 2932.98, 2920.32, 2853.83, 2834.83, 1726.65, 1669.66, 1637.99, 1444.85, 1410.03, 1223.22, 1020.58, 1007.92, 954.09, 868.60, 707.12 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.55 (s, 2 H), 2.85–2.62 (m, 4 H), 2.60–2.45 (m, 2 H), 2.26–2.10 (m, 2 H), 1.83–1.65 (m, 6 H), 1.60–1.40 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.36, 139.52, 138.56, 136.98, 126.99, 85.89, 28.70, 27.66, 22.28, 22.15.

^{31}P NMR (400 MHz, $CDCl_3$): δ = 1.38.

HRMS (ESI): *m/z* $[M + K]^+$ calcd for $C_{20}H_{18}I_2KO_4NaP$: 668.8567; found: 668.8554.

(a*S*)-2,8-Diiodo-5-(1,1′:3′,1″-terphenyl-2′-yl)-10,11,12,13,14,15,16,17-octahydro-4*H*-dinaphtho[1′,2′:7,8;2″,1″:5,6][1,4]dioxocino[2,3-*c*]pyrrole-4,6(5*H*)-dione (8c)

The product was obtained by a similar procedure to that used to prepare **1a**.[7l] (a*S*)-3,3′-Diiodo-5,5′,6,6′,7,7′,8,8′-octahydro-[1,1′-binaphthalene]-2,2′-diol (401.8 mg, 0.736 mmol), 3,4-dibromo-1-(1,1′:3′,1″-terphenyl-2′-yl)-1*H*-pyrrole-2,5-dione (462.2 mg, 1.3 equiv), and KF (426.9 mg, 10 equiv) were dissolved in DMF (11 mL), and the mixture was stirred at 80 °C for 16 h. The DMF was evaporated under vacuum (3 Torr), and the resulting dark-red oil was directly purified by chromatography [silica gel (10 g), cyclohexane–toluene (3:7 to 0:10)]. The resulting product, containing an unidentified impurity, was precipitated from $CHCl_3$–pentane to afford the pure compound as a pale-yellow solid; yield: 518.6 mg (0.598 mmol, 81%); mp 273 °C; $[\alpha]_D^{25}$ –248 (*c* 0.82, $CHCl_3$).

IR (neat): 3056.46, 3027.97, 2926.65, 2856.99, 1726.65, 1672.82, 1460.69, 1432.19, 1416.36, 1375.20, 1315.04, 1296.04, 1121.90, 1058.58, 757.78, 694.46 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.59 (s, 2 H), 7.52 (t, *J* = 7.7 Hz, 1 H), 7.41 (d, *J* = 7.5 Hz, 2 H), 7.37–7.23 (m, 10 H), 2.75 (t, *J* = 6.2 Hz, 4 H), 2.30–2.16 (m, 2 H), 2.16–2.02 (m, 2 H), 1.83–1.50 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.00, 149.45, 143.08, 140.59, 138.63, 138.42, 137.72, 136.94, 129.94, 129.61, 128.49, 128.28, 127.72, 126.89, 125.75, 84.78, 28.88, 27.15, 22.21 (2C).

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{42}H_{31}I_2NNaO_4$: 890.0240; found: 890.0244.

Anal. Calcd for $C_{42}H_{31}I_2NO_4$: C, 58.15; H, 3.61; N, 1.62. Found: C, 58.18; H, 3.61; N, 1.55.

(a*S*)-4,4′,5,5′,6,6′-Hexamethylbiphenyl-2,2′-diol

The racemic[21] and enantiopure[22] {$[\alpha]_D^{25}$ –43 (*c* 0.68, $CHCl_3$)} compound were obtained by following the reported procedures; mp 243 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.82 (s, 2 H), 2.33 (s, 6 H), 2.20 (s, 6 H), 1.97 (s, 6 H).

(a*S*)-3,3′-Diiodo-4,4′,5,5′,6,6′-hexamethylbiphenyl-2,2′-diol

The product was obtained by the same procedure as that used to prepare 3,3′-diiodo-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthalene-2,2′-diol.[20] Morpholine (660 µL, 6 equiv) and I_2 (636 mg, 2 equiv) were successively added to a solution of (a*S*)-4,4′,5,5′,6,6′-hexamethylbiphenyl-2,2′-diol (338 mg, 1.252 mmol) in CH_2Cl_2 (11 mL) at r.t. The mixture was stirred for 5 h at r.t., and CH_2Cl_2 (10 mL) and 1 M aq HCl (10 mL) were added. The aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL), and the organic layers were combined, washed successively with sat. aq $Na_2S_2O_3$ and brine (10 mL), dried ($MgSO_4$), filtered, and concentrated to give an orange solid; yield: 494 mg (76%); mp 73 °C; $[\alpha]_D^{25}$ +37 (*c* 1.16, $CHCl_3$).

IR (neat): 3461.74, 3376.25, 3325.59, 2974.14, 2923.48, 2850.66, 1736.15, 1692.86, 1622.16, 1574.67, 1514.51, 1441.69, 1283.38, 1194.72, 1159.89, 1045.91, 745.12 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 5.06 (br s, 2 H), 2.56 (s, 6 H), 2.29 (s, 6 H), 1.91 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.88, 139.96, 136.73, 128.41, 120.12, 90.59, 26.58, 17.58, 16.98.

HRMS (ESI): *m/z* $[M - H]^-$ calcd for $C_{18}H_{19}I_2O_2$: 520.9465; found: 520.9474.

(a*S*)-5,12-Diiodo-6,7,8,9,10,11-hexamethyl-2-(1,1′:3′,1″-terphenyl-2′-yl)-1*H*-dibenzo[5,6:7,8][1,4]dioxocino[2,3-*c*]pyrrole-1,3(2*H*)-dione (8d)

The product was obtained by a similar procedure to that used to prepare **1a**.[7l] (a*S*)-3,3′-Diiodo-4,4′,5,5′,6,6′-hexamethylbiphenyl-2,2′-diol (494 mg, 0.947 mmol), 3,4-dibromo-1-(1,1′:3′,1″-terphenyl-2′-yl)-1*H*-pyrrole-2,5-dione (595 mg, 1.3 equiv), and KF (549 mg, 10 equiv) were dissolved in DMF (12 mL), and the mixture was stirred at 80 °C for 16 h. The DMF was evaporated under vacuum (3 Torr), and the resulting dark-red oil was directly purified by chromatography [silica gel (10 g), pentane–toluene (1:1 to 2:8 to 0:10) then EtOAc–toluene (4:1)] to give a pale yellow solid; yield: 326 mg (0.388 mmol, 41%); mp 145 °C; $[\alpha]_D^{25}$ +161 (*c* 0.72, $CHCl_3$).

IR (neat): 3056.46, 3018.47, 2993.14, 2904.49, 1729.82, 1675.99, 1644.33, 1460.69, 1429.02, 1368.87, 1324.54, 1261.21, 1134.56, 1071.24, 868.60, 757.78, 694.46 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (dd, *J* = 8.3, 6.7 Hz, 1 H), 7.41 (d, *J* = 7.5 Hz, 2 H), 7.37–7.13 (m, 10 H), 2.59 (s, 6 H), 2.31 (s, 6 H), 1.85 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.92, 149.88, 143.09, 141.85, 138.69, 137.55, 136.74, 134.60, 129.89, 129.49, 128.39, 128.32, 128.14, 127.79, 127.62, 94.26, 26.81, 17.94, 17.19.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{40}H_{32}I_2NO_4$: 844.0421; found: 844.0420.

Anal. Calcd for $C_{40}H_{31}I_2NO_4$: C, 56.95; H, 3.71; N, 1.66. Found: C, 57.13; H, 3.94; N, 1.85.

(a*S*)-[2′-(2,8-Diiodo-4,6-dioxo-4,6,10,11,12,13,14,15,16,17-decahydro-5*H*-dinaphtho[1′,2′:7,8;2″,1″:5,6][1,4]dioxocino[2,3-*c*]pyrrol-5-yl)-1,1′:3′,1″-terphenyl-3,3″-diyl]di(methylene) Diacetate

This intermediate was obtained by following the same procedure at that used to obtain **1a**:[7l] (a*S*)-3,3′-diiodo-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthalene-2,2′-diol (1.065 g, 1.9 mmol), [2′-(3,4-dibromo-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)-1,1′:3′,1″-terphenyl-3,3″-diyl]di(methylene) diacetate (1.589 g, 1.3 equiv), and KF (1.13 g, 10 equiv) were dissolved in DMF (22 mL), and the mixture was stirred at 80 °C for 16 h. The DMF was evaporated under vacuum (3 Torr), and the resulting dark-red oil was directly purified by chromatography [silica gel (25 g), cyclohexane–toluene (3:7 to 0:10)] to give a pale-yellow solid; yield: 846.6 mg (0.837 mmol, 43%); mp 87 °C; $[\alpha]_D^{25}$ +134 (*c* 0.98, $CHCl_3$).

IR (neat): 2923.48, 2850.66, 1729.82, 1672.82, 1448.02, 1416.36, 1375.20, 1315.04, 1299.21, 1216.89, 1128.23, 1026.91, 700.79 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (s, 2 H), 7.58–7.51 (m, 1 H), 7.45–7.40 (m, 2 H), 7.36–7.10 (m, 8 H), 5.11 (d, *J* = 12.6 Hz, 2 H), 5.04 (d, *J* = 12.6 Hz, 2 H), 2.83–2.76 (m, 4 H), 2.33–2.17 (m, 2 H), 2.08 (s, 6 H), 2.15–2.03 (m, 2 H), 1.80–1.58 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.76, 162.87, 149.50, 142.62, 140.65, 139.11, 138.55, 137.09, 136.20, 130.25, 129.73, 129.70, 128.98, 128.78, 128.06, 127.90, 127.72, 84.85, 66.12, 28.92, 27.20, 26.90, 22.26, 20.91.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{48}H_{39}I_2NNaO_8$: 1034.0663; found: 1034.0631.

(a*S*)-5-[3,3″-Bis(hydroxymethyl)-1,1′:3′,1″-terphenyl-2′-yl]-2,8-diiodo-10,11,12,13,14,15,16,17-octahydro-4*H*-dinaphtho[1′,2′:7,8;2″,1″:5,6][1,4]dioxocino[2,3-*c*]pyrrole-4,6(5*H*)-dione

(a*S*)-[2′-(2,8-Diiodo-4,6-dioxo-4,6,10,11,12,13,14,15,16,17-decahydro-5*H*-dinaphtho[1′,2′:7,8;2″,1″:5,6][1,4]dioxocino[2,3-*c*]pyrrol-5-yl)-1,1′:3′,1″-terphenyl-3,3″-diyl]di(methylene) diacetate (688 mg, 0.68 mmol) was placed in a dry 25 mL round-bottomed flask and purged with argon. Anhyd CH_2Cl_2 (4 mL), anhyd MeOH (4 mL), and AcCl (266 mg, 240 μL, 3.39 mmol) were added, and the mixture was stirred at 40 °C for 16 h then allowed to cool to r.t. The solvent was evaporated to give a yellow solid; yield: 646.5 mg (0.68 mmol, quant.); mp 170 °C; $[\alpha]_D^{25}$ +136 (*c* 1.02, $CHCl_3$). This was used without further purification in the next step.

IR (neat): 3502.90, 2923.48, 2850.66, 1726.65, 1672.82, 1448.02, 1416.36, 1378.36, 1315.04, 1302.37, 1235.88, 1210.55, 1131.40, 1061.74, 783.11, 700.79 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (s, 2 H), 7.56–7.48 (m, 1 H), 7.43–7.36 (m, 2 H), 7.33–7.21 (m, 6 H), 7.21–7.14 (m, 2 H), 4.61 (s, 4 H), 2.79–2.70 (m, 4 H), 2.29–2.16 (m, 2 H), 2.15–2.02 (m, 2 H), 1.78–1.54 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.94, 149.44, 142.79, 141.22, 140.60, 138.96, 138.60, 137.89, 137.00, 130.08, 129.66, 128.97, 128.75, 127.42, 127.00, 126.58, 125.75, 84.76, 65.23, 28.93, 27.19, 26.90, 22.23.

HRMS (ESI): *m/z* $[M + Na]^+$ calcd for $C_{44}H_{35}I_2NNaO_6$: 950.0451; found: 950.0449.

(a*S*)-[2′-(2,8-Diiodo-4,6-dioxo-4,6,10,11,12,13,14,15,16,17-decahydro-5*H*-dinaphtho[1′,2′:7,8;2″,1″:5,6][1,4]dioxocino[2,3-*c*]pyrrol-5-yl)-1,1′:3′,1″-terphenyl-3,3″-diyl]di(methylene) (2*S*,2′*S*)-Bis(2-phenylpropanoate) (8e)

DMF (3 μL) and oxalyl chloride (50 μL, 0.55 mmol) were added to a solution of (2*S*)-2-phenylpropanoic acid (82.4 mg, 0.55 mmol) in anhyd CH_2Cl_2 (6 mL), and the mixture was stirred at 0 °C for 5 min and then at r.t. for 1 h. The mixture was cooled to –20 °C, and a solution of (a*S*)-5-[3,3″-bis(hydroxymethyl)-1,1′:3′,1″-terphenyl-2′-yl]-2,8-diiodo-10,11,12,13,14,15,16,17-octahydro-4*H*-dinaphtho[1′,2′:7,8;2″,1″:5,6][1,4]dioxocino[2,3-*c*]pyrrole-4,6(5*H*)-dione (100 mg, 0.108 mmol) in anhyd CH_2Cl_2 (3 mL) was added, followed by a mixture of anhyd Et_3N (82 μL, 0.6 mmol) and DMAP (1.6 mg, 0.013 mmol) in anhyd CH_2Cl_2 (3 mL). The mixture was stirred at –20 °C for 2 h and then at r.t. for 24 h. Sat. aq $KHSO_4$ (6 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (2 × 6 mL). The organic phase was dried ($MgSO_4$), filtered, and concentrated in vacuum. The residue was purified by chromatography [silica gel (25 g), cyclohexane–toluene (70:30) then toluene–EtOAc (95: 5 to 90:10)] to give a pale-yellow solid; yield: 100.4 mg (0.084 mmol, 78%); mp 79 °C; $[\alpha]_D^{25}$ +123 (*c* 1.02, $CHCl_3$).

IR (neat): 3059.63, 3024.80, 2929.82, 2869.66, 1808.97, 1729.82, 1672.82, 1489.18, 1448.02, 1416.36, 1375.20, 1311.87, 1299.21, 1197.89, 1153.56, 1128.23, 1061.74, 783.11, 694.46 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (s, 2 H), 7.56–7.48 (m, 1 H), 7.37–7.11 (m, 20 H), 5.10 (d, *J* = 12.8 Hz, 2 H), 4.98 (d, *J* = 12.8 Hz, 2 H), 3.77 (q, *J* = 7.2 Hz, 2 H), 2.80–2.67 (m, 4 H), 2.31–2.13 (m, 2 H), 2.13–1.99 (m, 2 H), 1.80–1.56 (m, 8 H), 1.52 (d, *J* = 7.2 Hz, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.24, 162.85, 149.48, 142.61, 140.66, 140.37, 139.00, 138.54, 137.81, 136.39, 130.22, 128.97, 128.70, 128.65, 128.61, 127.77, 127.67, 127.62, 127.56, 127.38, 127.21, 127.10, 84.78, 66.20, 45.51, 28.93, 27.18, 22.25, 18.49, 18.22.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{62}H_{52}I_2NO_8$: 1192.1782; found: 1192.1756.

[2-(2,8-Diiodo-4,6-dioxo-4,6,10,11,12,13,14,15,16,17-decahydro-5*H*-dinaphtho[1′,2′:7,8;2″,1″:5,6][1,4]dioxocino[2,3-*c*]pyrrol-5-yl)-1,3-phenylene]di(methylene) Diacetate

This intermediate was obtained by following a procedure similar to that used to prepare **1a**.[7l] (a*S*)-3,3′-Diiodo-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthalene-2,2′-diol (57.0 mg, 0.104 mmol), [2-(3,4-dibromo-2,5-dioxo-2,5-dihydro-1*H*-pyrrol-1-yl)-1,3-phenylene]di(methylene) diacetate (64.2 mg, 1.3 equiv), and KF (60.3 mg, 10 equiv) were dissolved in DMF (1 mL), and the mixture was stirred at 80 °C for 16 h. The DMF was evaporated under vacuum (3 Torr) and the resulting dark-red oil was directly purified by chromatography [silica gel (25 g), cyclohexane–toluene (3:7 to 0:10)] to give a pale-yellow solid; yield: 31.7 mg (0.0369 mmol, 35%); mp 167 °C; $[\alpha]_D^{25}$ –12.2 (*c* 0.87, $CHCl_3$).

IR (neat): 2932.98, 2850.66, 1729.82, 1679.16, 1473.35, 1444.85, 1432.19, 1416.36, 1378.36, 1315.04, 1210.55, 1131.40, 1026.91, 935.09, 792.61, 745.12 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (s, 2 H), 7.51–7.41 (m, 3 H), 5.04 (d, *J* = 13.0 Hz, 2 H), 4.97 (d, *J* = 13.0 Hz, 2 H), 2.85–2.75 (m, 4 H), 2.41–2.13 (m, 4 H), 1.93 (s, 6 H), 1.84–1.58 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.32, 162.79, 149.70, 140.97, 138.785, 138.03, 135.97, 130.31, 129.95, 129.21, 129.02, 128.21, 85.20, 62.86, 29.00, 27.30, 22.35, 22.31, 20.90.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{36}H_{31}I_2NNaO_8$: 882.0037; found: 882.0032.

(a*S*)-5-[2,6-Bis(hydroxymethyl)phenyl]-2,8-diiodo-10,11,12,13,14,15,16,17-octahydro-4*H*-dinaphtho[1′,2′:7,8;2″,1‴:5,6][1,4]dioxocino[2,3-*c*]pyrrole-4,6(5*H*)-dione

[2-(2,8-Diiodo-4,6-dioxo-4,6,10,11,12,13,14,15,16,17-decahydro-5*H*-dinaphtho[1′,2′:7,8;2″,1‴:5,6][1,4]dioxocino[2,3-*c*]pyrrol-5-yl)-1,3-phenylene]di(methylene) diacetate (23 mg, 0.027 mmol) was placed in a dry 10 mL round-bottomed flask and purged with argon. Anhyd CH_2Cl_2 (1 mL), anhyd MeOH (1 mL), and AcCl (2 μL, 0.028 mmol) were added. The mixture was stirred at 40 °C for 16 h then allowed to cool to r.t. The solvent was evaporated to give a pale-yellow solid; yield: 14.9 mg (0.019 mmol, 71%); mp 145 °C; $[\alpha]_D^{25}$ –33 (*c* 0.84, $CHCl_3$). This was used without further purification in the next step.

IR (neat): 3445.91, 2923.48, 2853.83, 1723.48, 1675.99, 1463.85, 1416.36, 1381.53, 1318.21, 1299.21, 1258.05, 1239.05, 1216.89, 1163.06, 1112.40, 1061.74, 1017.41, 935.09, 786.28, 745.12 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (s, 2 H), 7.55–7.42 (m, 3 H), 4.53 (s, 4 H), 2.85–2.75 (m, 4 H), 2.40–2.15 (m, 4 H), 1.83–1.50 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.92, 149.75, 141.02, 139.96, 138.86, 138.07, 137.65, 130.29, 129.45, 129.29, 126.74, 85.30, 62.22, 29.69, 29.00, 27.32, 22.30.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{32}H_{27}I_2NNaO_6$: 797.7825; found: 797.7823.

(a*S*)-[2-(2,8-Diiodo-4,6-dioxo-4,6,10,11,12,13,14,15,16,17-decahydro-5*H*-dinaphtho[1′,2′:7,8;2″,1‴:5,6][1,4]dioxocino[2,3-*c*]pyrrol-5-yl)-1,3-phenylene]di(methylene) Bis[(4-tolyl)carbamate] (8f)

(a*S*)-5-[2,6-Bis(hydroxymethyl)phenyl]-2,8-diiodo-10,11,12,13,14,15,16,17-octahydro-4*H*-dinaphtho[1′,2′:7,8;2″,1‴:5,6][1,4]dioxocino[2,3-*c*]pyrrole-4,6(5*H*)-dione (7.5 mg, 0.0097 mmol) was dissolved in anhyd $CHCl_3$ (1 mL), and 4-TolNCO (2.8 mg, 2.7 μL, 0,0213 mmol) was added. The mixture was stirred for 7 d at reflux then additional 4-TolNCO (2.8 mg, 2.7 μL, 0.0213 mmol) was added. The mixture was stirred for a further 3 d then allowed to cool. The solvent was evaporated under vacuum, and the crude product was directly purified by chromatography [silica gel (10 g), CH_2Cl_2–EtOAc (9:1 to 1:1)] to give an off-white solid; yield: 4.5 mg (45%); $[\alpha]_D^{25}$ –62 (*c* 0.9, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (s, 2 H), 7.58–7.52 (m, 2 H), 7.46–7.40 (m, 1 H), 7.16 (d, *J* = 8.4 Hz, 4 H), 7.04 (d, *J* = 8.4 Hz, 4 H), 6.52 (br s, 2 H), 5.10 (d, *J* = 12.7 Hz, 2 H), 5.05 (d, *J* = 12.7 Hz, 2 H), 2.82–2.66 (m, 4 H), 2.37–2.10 (m, 4 H), 2.27 (s, 6 H), 1.80–1.60 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.67, 163.28, 149.56, 141.02, 139.26, 138.77, 138.00, 137.56, 136.28, 134.93, 133.03, 131.39, 130.24, 129.44, 129.10, 118.94, 85.22, 63.66, 29.69, 28.92, 27.30, 22.26, 20.74.

HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{48}H_{41}I_2N_3NaO_8$: 1064.0881; found: 1064.0892.

α-Oxytosylation of Ketones; General Procedure

The appropriate catalyst (10 mol%; 0.01 M), PTSA (13 mg, 0.075 mmol), and *m*-CPBA (13 mg, 0.075 mmol)[23] were added to a sealed flask and purged with argon. A 0.1 M solution of substrate **6** in CH_2Cl_2 (0.5 mL, 0.05 mmol) was added, and the mixture was stirred at r.t. for 60 h then evaporated under vacuum. Yields were determined by ^{1}H NMR analysis in acetone-d_6 with Ph_3CH as an internal reference. The mixture was purified by semi-preparative TLC on silica gel (cyclohexane–EtOAc, 90:10) and analyzed by chiral column chromatography. In all cases, the NMR spectra were the same as those obtained in full analyses of the products.

(1*R*)-1-Methyl-2-oxo-2-phenylethyl Tosylate (7a)

^{1}H NMR (400 MHz, $CDCl_3$): δ = = 7.89 (d, *J* = 7.5 Hz, 2 H), 7.77 (d, *J* = 8.1 Hz, 2 H), 7.59 (t, *J* = 7.5 Hz, 1 H), 7.45 (t, *J* = 8.1 Hz, 2 H), 7.27 (d, *J* = 8.1 Hz, 2 H), 5.79 (q, *J* = 7.0 Hz, 1 H), 2.41 (s, 3 H), 1.60 (d, *J* = 7.0 Hz, 3 H).

HPLC: Column: ID-3 (4.6 × 250 mm), CO_2/MeOH: 80:20, 1.5 mL/min, 40 °C; t_R = 4.3 min (*R*), 4.6 min (*S*).

1-Methyl-2-oxobutyl Tosylate (7b)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.2 Hz, 2 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 4.77 (q, *J* = 7.0 Hz, 1 H), 2.54 (dq, *J* = 7.0, 4.0 Hz, 2 H), 2.40 (s, 3 H), 1.30 (d, *J* = 7.0 Hz, 3 H), 0.97 (t, *J* = 7.0 Hz, 3 H).

HPLC: Column: ID-3 (4.6 × 250 mm), CO_2/MeOH: 80:20, 1.5 mL/min, 40 °C; t_R = 3.0 min (minor), 3.1 min (major).

2-Oxocyclohexyl Tosylate (7c)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.2 Hz, 2 H), 7.30 (d, *J* = 8.2 Hz, 2 H), 4.86 (dd, *J* = 10.7, 6.0 Hz, 1 H), 2.55–2.45 (m, 1 H), 2.40 (s, 3 H), 2.33–2.20 (m, 2 H), 2.02–1.78 (m, 3 H), 1.75–1.54 (m, 2 H).

HPLC: Column: ID-3 (4.6 × 250 mm), CO_2/MeOH: 80:20, 1.7 mL/min, 40 °C; t_R = 6.9 min (major), 7.5 min (minor).

1-Oxo-1,2,3,4-tetrahydronaphthalen-2-yl Tosylate (7d)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.4 Hz, 2 H), 7.71 (d, *J* = 8.1 Hz, 1 H), 7.63 (t, *J* = 7.6 Hz, 1 H), 7.45–7.33 (m, 4 H), 4.86 (dd, *J* = 7.9, 5.2 Hz, 1 H), 3.63 (dd, *J* = 17.1, 7.9 Hz, 2 H), 3.24 (dd, *J* = 17.1, 5.2 Hz, 2 H), 2.45 (s, 3 H).

HPLC: Column: ID-3 (4.6 × 250 mm), CO_2/MeOH: 80:20, 1.5 mL/min, 40 °C; t_R = 8.2 min (minor), 8.9 min (major).

1-Oxo-2,3-dihydro-1*H*-inden-2-yl Tosylate (7e)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 8.3 Hz, 2 H), 7.73 (d, *J* = 7.7 Hz, 1 H), 7.64 (t, *J* = 7.5 Hz, 1 H), 7.43 (d, *J* = 8.6 Hz, 1 H), 7.38 (d, *J* = 8.3 Hz, 3 H), 5.12 (dd, *J* = 8.0, 4.8 Hz, 1 H), 3.64 (dd, *J* = 17.2, 8.0 Hz, 1 H), 3.26 (dd, *J* = 17.2, 4.7 Hz, 1 H), 2.46 (s, 3 H).

HPLC: Column: ID-3 (4.6 × 250 mm), CO_2/MeOH: 80:20, 1.7 mL/min, 40 °C; t_R = 8.0 min (minor), 8.4 min (major).

2-(4-Methoxyphenyl)-1-methyl-2-oxoethyl Tosylate (7f)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 9.1 Hz, 2 H), 7.75 (d, *J* = 8.5 Hz, 2 H), 7.25 (d, *J* = 8.5 Hz, 2 H), 6.91 (d, *J* = 9.1 Hz, 2 H), 5.73 (q, *J* = 7.0 Hz, 1 H), 3.87 (s, 3 H), 2.40 (s, 3 H), 1.57 (d, *J* = 7.0 Hz, 3 H).

HPLC: Column: ID-3 (4.6 × 250 mm), CO_2/MeOH: 80:20, 1.7 mL/min, 40 °C; t_R = 5.1 min (major), 5.9 min (minor).

1-Methyl-2-oxo-2-[4-(trifluoromethyl)phenyl]ethyl Tosylate (7g)

White solid; mp 88 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.4 Hz, 2 H), 7.73 (d, *J* = 7.3 Hz, 2 H), 7.70 (d, *J* = 7.3 Hz, 2 H), 7.27 (d, *J* = 8.4 Hz, 2 H), 5.70 (q, *J* = 6.9 Hz, 1 H), 2.41 (s, 3 H), 1.60 (d, *J* = 6.9 Hz, 3 H).

HPLC: Column: ID-3 (4.6 × 250 mm), CO_2/MeOH: 80:20, 1.7 mL/min, 40 °C; t_R = 2.9 min (major), 3.1 min (minor).

2-Oxo-1,2-diphenylethyl Tosylate (7h)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.0 Hz, 2 H), 7.64 (d, *J* = 8.0 Hz, 2 H), 7.44 (t, *J* = 7.6 Hz, 1 H), 7.33–7.28 (m, 4 H), 7.23–7.20 (m, 3 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 6.60 (s, 1 H), 2.31 (s, 3 H).

HPLC: Column: ID-3 (4.6 × 250 mm), CO_2/MeOH: 80:20, 1.7 mL/min, 40 °C; t_R = 7.7 min (minor), 8.4 min (major).

1-Benzoylpropyl Tosylate (7i)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.2 Hz, 2 H), 7.74 (d, *J* = 8.3 Hz, 2 H), 7.58 (t, *J* = 7.4 Hz, 1 H), 7.44 (t, *J* = 7.7 Hz, 2 H), 7.25 (t, *J* = 7.0 Hz, 2 H), 5.55 (dd, *J* = 7.9, 5.0 Hz, 1 H), 2.40 (s, 3 H), 2.00–1.85 (m, 2 H), 0.98 (t, *J* = 7.4 Hz, 3 H).

HPLC: Column: ID-3 (4.6 × 250 mm), CO_2/MeOH: 80:20, 1.5 mL/min, 40 °C; t_R = 4.3 min (major), 4.7 min (minor).

1,3,3-Trimethyl-2-oxobutyl Tosylate (7j)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.4 Hz, 2 H), 7.33 (t, *J* = 8.4 Hz, 2 H), 5.42 (q, *J* = 6.7 Hz, 1 H), 2.43 (s, 3 H), 1.40 (d, *J* = 6.7 Hz, 3 H), 1.23 (s, 9 H).

HPLC: Column: ID-3 (4.6 × 250 mm), CO_2/MeOH: 80:20, 1.7 mL/min, 40 °C; t_R = 3.3 min (minor), 3.8 min (major).

Methyl 3-Oxo-3-phenyl-2-(tosyloxy)propanoate (7m)

Light yellow solid; mp 68 °C.

IR (neat): 1761.48, 1691.82, 1596.83, 1492.35, 1451.19, 1432.19, 1372.03, 1299.21, 1242.22, 1191.56, 1172.56, 1045.91, 960.42, 735.62, 694.46, 672.30 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.88 (m, 2 H), 7.78 (d, *J* = 8.4 Hz, 2 H), 7.59 (tt, *J* = 7.4, 1.3 Hz, 1 H), 7.48–7.39 (m, 2 H), 7.29 (d, *J* = 8.4 Hz, 2 H), 6.00 (s, 1 H), 3.70 (s, 3 H), 2.41 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.07, 164.64, 145.68, 134.40, 133.27, 132.37, 129.82, 129.37, 128.75, 128.26, 77.90, 53.29, 21.62.

HRMS (ESI): *m/z* $[M + H]^+$ calcd for $C_{17}H_{17}O_6S$: 349.0746; found: 349.0757.

HPLC: Column: ID-3 (4.6 × 250 mm), CO_2/MeOH: 80:20, 1.7 mL/min, 40 °C; t_R = 5.1 min (minor), 5.5 min (major).

Acknowledgment

Financial support from CNRS and Université Joseph Fourier is gratefully acknowledged. S.B. thanks Université Joseph Fourier for a Ph.D. grant.

References

(1) Varvoglis, A. *Tetrahedron* **1997**, *53*, 1179.
(2) Finkbeiner, P.; Nachtsheim, B. J. *Synthesis* **2013**, *45*, 979.
(3) Wirth, T. *Angew. Chem. Int. Ed.* **2005**, *44*, 3656.
(4) Brown, M.; Farid, U.; Wirth, T. *Synlett* **2013**, *24*, 424.
(5) (a) Ngatimin, M.; Lupton, D. W. *Aust. J. Chem.* **2010**, *63*, 653. (b) Liang, H.; Ciufolini, M. A. *Angew. Chem. Int. Ed.* **2011**, *50*, 11849. (c) Uyanik, M.; Ishihara, K. *J. Synth. Org. Chem., Jpn.* **2012**, *70*, 1116. (d) Parra, A.; Reboredo, S. *Chem. Eur. J.* **2013**, *19*, 17244. (e) Berthiol, F. *Synthesis* **2015**, 587. (f) Kumar, R.; Wirth, T. *Top. Curr. Chem.* **2015**, in press.
(6) (a) Merritt, E. A.; Olofsson, B. *Synthesis* **2011**, 517. (b) Dong, D.-Q.; Hao, S.-H.; Wang, Z.-L.; Chen, C. *Org. Biomol. Chem.* **2014**, *12*, 4278.
(7) (a) Wirth, T.; Hirt, U. H. *Tetrahedron: Asymmetry* **1997**, *8*, 23. (b) Hirt, U. H.; Spingler, B.; Wirth, T. *J. Org. Chem.* **1998**, *63*, 7674. (c) Hirt, U. H.; Schuster, M. F. H.; French, A. N.; Wiest, O. G.; Wirth, T. *Eur. J. Org. Chem.* **2001**, 1569. (d) Richardson, R. D.; Page, T. K.; Altermann, S.; Paradine, S. M.; French, A. N.; Wirth, T. *Synlett* **2007**, 538. (e) Altermann, S. M.; Richardson, R. D.; Page, T. K.; Schmidt, R. K.; Holland, E.; Mohammed, U.; Paradine, S. M.; French, A. N.; Richter, C.; Bahar, A. M.; Witulski, B.; Wirth, T. *Eur. J. Org. Chem.* **2008**, 5315. (f) Farooq, U.; Schäfer, S.; Ali Shah, A.-ul-H.; Freudendahl, D. M.; Wirth, T. *Synthesis* **2010**, 1023. (g) Yu, J.; Cui, J.; Hou, X.-S.; Liu, S.-S.; Gao, W.-C.; Jiang, S.; Tian, J.; Zhang, C. *Tetrahedron: Asymmetry* **2011**, *22*, 2039. (h) Rodríguez, A.; Moran, W. J. *Synthesis* **2012**, *44*, 1178. (i) Guibault, A.-A.; Legault, C. Y. *ACS Catal.* **2012**, *2*, 219. (j) Guibault, A.-A.; Basdevant, B.; Wanie, V.; Legault, C. Y. *J. Org. Chem.* **2012**, *77*, 11283. (k) Thérien, M.-E.; Guibault, A.-A.; Legault, C. Y. *Tetrahedron: Asymmetry* **2013**, *24*, 1193. (l) Brenet, S.; Berthiol, F.; Einhorn, J. *Eur. J. Org. Chem.* **2013**, 8094.
(8) Pouységu, L.; Deffieux, D.; Quideau, S. *Tetrahedron* **2010**, *66*, 2235.
(9) (a) Bosset, C.; Coffinier, R.; Peixoto, P. A.; El Assal, M.; Miqueu, K.; Sotiropoulos, J.-M.; Pouységu, L.; Quideau, S. *Angew. Chem. Int. Ed.* **2014**, *53*, 9860. For reports on hypervalent iodine compounds based on a binaphthyl motif, see also: (b) Quideau, S.; Lyvinec, G.; Marguerit, M.; Bathany, K.; Ozanne-Beaudenon, A.; Buffeteau, T.; Cavagnat, D.; Chénedé, A. *Angew. Chem. Int. Ed.* **2009**, *48*, 4605. (c) Brown, M.; Delorme, M.; Malmedy, F.; Malmgren, J.; Olofsson, B.; Wirth, T. *Synlett* **2015**, *26*, 1573.
(10) Sparling, B. A.; Moslin, R. M.; Jamison, T. F. *Org. Lett.* **2008**, *10*, 1291.
(11) Lu, Q.; Liu, C.; Huang, Z.; Ma, Y.; Zhang, J.; Lei, A. *Chem. Commun.* **2014**, *50*, 14101.
(12) Yang, P.; Xu, H.; Zhou, J. *Angew. Chem. Int. Ed.* **2014**, *53*, 12210.
(13) Bremner, J. B.; Coates, J. A.; Coghlan, D. R.; David, D. M.; Keller, P. A.; Pyne, S. G. *New J. Chem.* **2002**, *26*, 1549.
(14) Hua, J.; Li, W. *Org. Lett.* **2004**, *6*, 861.
(15) Yamanaka, M.; Itoh, J.; Fuchibe, K.; Akiyama, T. *J. Am. Chem. Soc.* **2007**, *129*, 6756.
(16) The intermediate hydroxynaphthoquinone is oxidized by oxygen with $t_{1/2} \approx 2$ h in an NMR tube.
(17) Harvey, I. W.; McFarlane, M. D.; Moody, D. J.; Smith, D. M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1939.
(18) Zhang, Y.; Yin, Q.; Yin, L.; Ma, L.; Tang, L.; Cheng, J. *Angew. Chem. Int. Ed.* **2013**, *52*, 6435.
(19) Cram, D. J.; Helgeson, R. C.; Peacock, S. C.; Kaplan, L. J.; Domeier, L. A.; Moreau, P.; Koga, K.; Mayer, J. M.; Chao, Y.; Siegel, M. G.; Hoffman, D. H.; Sogah, G. D. Y. *J. Org. Chem.* **1978**, *43*, 1930.
(20) Pousse, G.; Devineau, A.; Dalla, V.; Humphreys, L.; Lasne, M.-C.; Rouden, J.; Blanchet, J. *Tetrahedron* **2009**, *65*, 10617.
(21) Henschke, J. P.; Burk, J. M.; Malan, C. G.; Herzberg, D.; Peterson, J. A.; Wildsmith, A. J.; Cobley, C. J.; Casy, G. *Adv. Synth. Catal.* **2003**, *345*, 300.

(22) Takemura, T.; Emoto, G.; Satoh, J.; Kobayashi, Y.; Yaginuma, C.; Yuta, T.; Utsukihara, T.; Horiuchi, C. A. *J. Mol. Catal. B: Enzym.* **2008**, *55*, 104.
(23) Commercial *m*-CPBA containing 15% of *m*-chlorobenzoic acid was dried by the following procedure. The commercial product was dissolved in CH_2Cl_2 and dried over Na_2SO_4. The resulting mixture was filtered through a pad of cotton and evaporated under vacuum to give a white powder. The *m*-chlorobenzoic acid was not removed, because pure *m*-CPBA is known to be explosive; see: *Purification of Laboratory Chemicals*, 3rd ed. Perrin, D. D.; Armarego, W. L. F., Eds.; Pergamon: Oxford, **1988**.