Substitution Effects of Hypervalent Iodine(III) Reagents in the Diamination of Styrene

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S *Supporting Information*

ABSTRACT: The influence of electronic parameters on the reaction performance of hypervalent iodine(III) reagents in the vicinal diamination of styrene has been investigated. It demonstrates the influence of the relative electron density on the aryl substituent of the hypervalent iodine reagent. In these cases, compounds with donor substituents outperform the corresponding acceptor-substituted systems. In line with this observation, a rapid enantioselective diamination was observed for a preformed chiral bisimidoiodine(III) reagent. For the first time, X-ray structural data could be obtained for an isolated chiral bisimidoiodine(III).
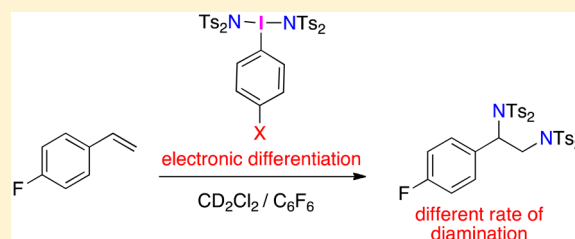
Hypervalent iodine(III) reagents represent versatile tools in modern organic oxidation chemistry[1] and in the development of new synthetic methodology have recently started to challenge traditional procedures based on transition metals.[2,3]

Recently, we introduced monomeric hypervalent iodine(III) compounds bearing defined iodine−nitrogen bonds with bissulfonylimides. As exemplified for bistosylimide, these compounds are best prepared through protonolysis events starting from (diacetoxy)iodobenzene PhI(OAc)$_2$ **1a** (Scheme 1).[4,5] In these

## Scheme 1. Phenyliodine(III)/Bistosylimide Pathways to Aminating Reagents
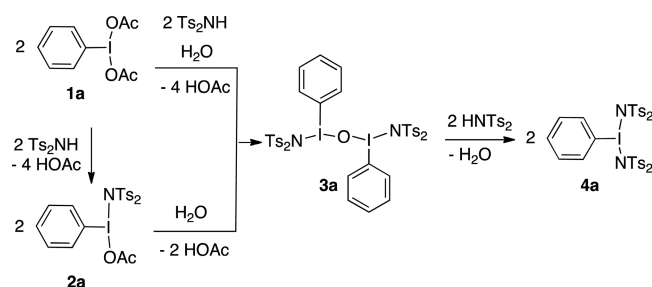
cases, treatment of **1a** with an equimolar amount of HNTs$_2$ formed the mixed reagent **2a** in an irreversible manner. The same reaction in the presence of water forms the μ-oxo-bridged dimer **3a**, which can also be accessed from **2a** upon controlled partial hydrolysis. Finally, saturation of the coordination sphere of iodine by introduction of an additional NTs$_2$ moiety generates the bisimido species **4a**.[4,6,7]

Successful applications of these aminating reagents involve allylic,[8,9] acetylenic,[10] and aromatic[11,12] amination events and the diamination of alkenes.[13] The overall series culminated in an enantioselective diamination of styrenes,[14] which is of unsurpassed efficiency in the field.[15,16]

For the simplest case of bismesylimide, a recent theoretical study has uncovered some details regarding the amination pathways involved in styrene amination using hypervalent iodine reagents.[17] We here report the effect of substituents on the arene ring of the central iodine(III), which gives additional insight into the mechanistic scenario and confirms the general trends from the theoretical study.

Regarding the diamination of styrene **5a** with an equimolar amount of the bistosylimide reagent **4a**, control experiments revealed a first-order dependence on iodine(III) reagent **4a** but a zero-order dependence on the alkene substrate (Scheme 2).[18]

Scheme 2. Dependence of the Diamination on Styrene 5a and on Iodine Reagent 4a
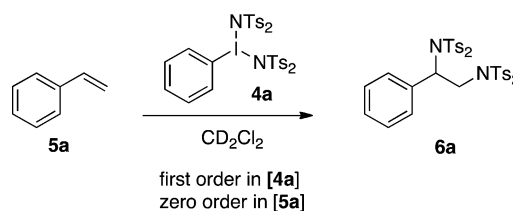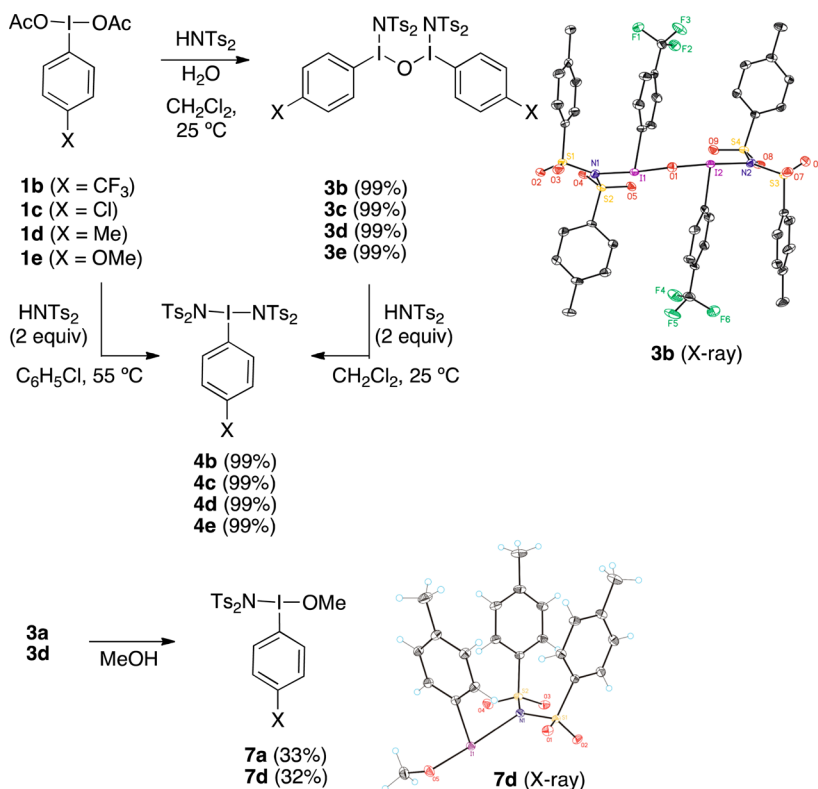

In order to gain a better understanding of this result, four derivatives **4b−e** with the 4-substituted aryliodine(III) core were prepared (Scheme 3). Following our literature protocol,[4] their synthesis comprises the initial formation of the corresponding dimeric μ-oxo-bridged iodine(III) derivatives **3b−e**, which were obtained quantitatively. Upon protonolysis with bistosylimide, compounds **3b−e** cleanly convert into the corresponding monomeric reagents **4b−e** in quantitative yields.

Scheme 3. Synthesis of 4-Substituted Aryliodine(III) Derivatives

1b (X = CF$_3$)
1c (X = Cl)
1d (X = Me)
1e (X = OMe)

3b (99%)
3c (99%)
3d (99%)
3e (99%)

3b (X-ray)

4b (99%)
4c (99%)
4d (99%)
4e (99%)

3a
3d → MeOH →

7a (33%)
7d (32%)

7d (X-ray)

Alternatively, these reagents **4b−e** can be equally accessed in a single transformation directly from **1b−e**.

The expected structures of compounds **3b−e** and **4b−e** match those for the parent series from Scheme 1. This was further shown from an X-ray analysis of **3b**.[18] Electronic effects render compound **4d** and particularly **4e** less stable than the parent compound **4a** as they are sensitive to hydrolysis. While the corresponding degradation products could not be characterized, the related reaction upon dissolution of compound **4d** in methanol was determined to provide the methoxy derivative **7d**. Starting from compounds **3a,d**, the expected new mixed iodine(III) derivatives **7a,d**, incorporating a single bistosylimido and a methoxy substituent, were obtained, and their structure was confirmed for **7d** by X-ray analysis.[18] These compounds are remarkably stable and serve as precursor to reactive imido-iodine(III) species upon treatment with bistosylimide.

With these compounds in hand, the reactivity of compounds **4a−e** in the diamination of 4-fluorostyrene **5b** in dichloromethane was monitored by ^{19}F NMR with hexafluorobenzene as internal standard (Figure 1).

While the highest rate was observed for the 4-methyl derivative **4d**, the corresponding initial rates for **4a** and **4e** were almost identical. In fact, the corresponding Hammett plot shows an almost identical outcome for donor substitution.[18] This matches with a recent screening on catalyst structure for enantioselective diacetoxylation of alkenes in which a 4-methyl substituent enhanced the rate of the catalysis.[19] In contrast, electron-deficient derivatives **4b,c** showed significantly lower conversion within a comparable reaction period.

These results are instructive as they present an unexpected electronic dependence. One expects a kinetic preference for electron-withdrawing substituents, which enhances the electrophilicity of the iodine(III) center in the initial alkene coordination
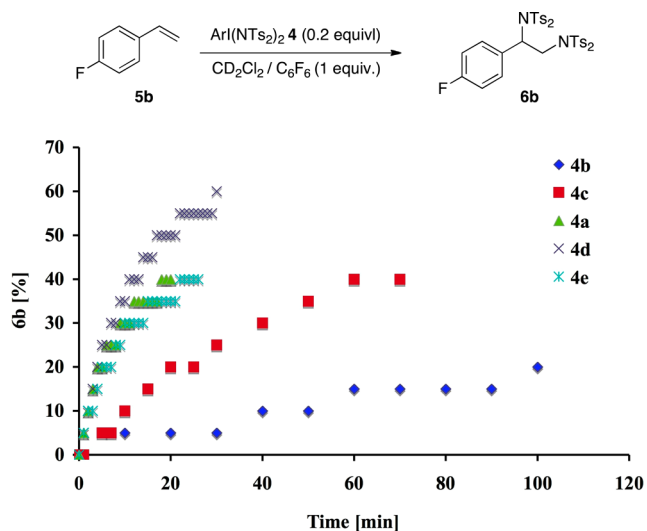

Figure 1. Kinetic profiles for diamination of **5b** with iodine(III) reagents **4a−e**.

and in the step of the reductive elimination, where the nucleophuge character of the iodine(III)[20] dominates the scenario. Instead, it appears that the reaction is accelerated by donor substitution. Based on the observations from Scheme 2 and Figure 1, we now propose that the decisive step in the diamination of alkenes with bistosylimide as nitrogen source consists of a dissociative pre-equilibrium (Figure 2). Previously, this dissociation context had been investigated experimentally for the neutral species **4a**[4] and had been identified by theory as the energetically most demanding step of the diamination reactions of styrene with related bismesylimide.[17] The data presented here imply that the enhanced acceleration with **4d** is
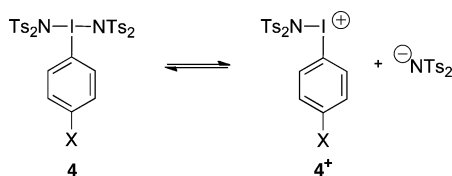
**Figure 2.** Electronic influence on I−N bond dissociation in reagents **4**.

based on an electronic donor stabilization of the involved cationic intermediate **4⁺**. The relation between donor substituent and overall rate needs to be balanced in a way that the electrophilic character at iodine is not reduced too much due to electronic stabilization as appears to be the case for the 4-methoxy substituent.

We then turned our attention toward the structures of chiral aryl iodides. Regarding the scenario of chirality, we had previously employed a chiral C_2-symmetric hypervalent iodine reagent bearing two lactate side chains in the enantioselective diamination of styrenes.[14a] In these cases, bismesylimide served as the best nitrogen source by providing the highest enantiomeric excesses of the final diamine products. Despite repeated attempts, we were unable to obtain any evidence for the incorporation of the bissulfonylimides into the coordination sphere of the iodine(III) center. Attempts were further hampered by the low solubility of the involved species. However, the anticipated sequential exchange of acetate for bistosylimide could be accomplished for the case of the chiral iodine(III) compound **1f**[21] bearing a single lactic ester side chain (Scheme 4). As in the case of the achiral derivatives **1a−e**, sequential replacement took place to initially generate the μ-oxo-bridged compound **3f**. The structure of **3f** was confirmed unambiguously by single-crystal X-ray analysis.[18] Its conversion into the bisimido derivative **4f** under standard protonolysis with free bistosylimide was possible but did not proceed in a quantitative manner. Instead, compound **4f** was better accessed through direct acetate for imide exchange at stage **1f**. It represents only the second iodine(III)−nitrogen derivative of a chiral iodine(III) reagent[14b] and the first for the successful class of lactate derivatives.[21]

Kinetic experiments reveal that **4f** reacts with 4-fluorostyrene in a rapid conversion leading to 50% diamination product **6b** within only 8 min reaction time.[18] Although this product is formed with a low 24% ee, this rate effect, which is attributed to

the electronically favorable 2-oxygenated substituent, is remarkable. It compares well with the observed rapid rate for related bislactamide derivatives, which were employed as catalysts in the homogeneous diacetoxylation of styrenes and which could effectively override potential background reactions from the terminal peracid oxidant.[19] For styrene itself, **4f** represents the active and only required reagent in the diamination reaction[14a] as demonstrated by the chemoselective formation of **6a** (Scheme 5). Here, the (S)-configured product is formed

Scheme 5. Enantioselective Diamination of Styrene
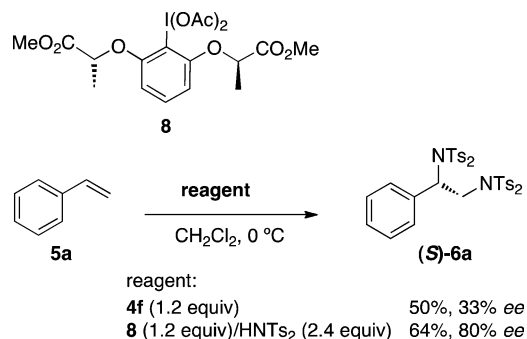
with 33% ee at a reaction temperature of 0 °C, while the corresponding in situ formed reagent from bislactate **8** generates (S)-**6a** with 80% ee. This value is comparable to reaction results at a slightly higher temperature as documented previously.[14a] In comparing the enantioinductions obtained with **4f** and **8**, the outcome suggests that ultimately both lactates within reagent **8** are required for high enantiocontrol in the diamination and confirms that the bislactate motif represents the currently most promising chiral iodine(III) reagent class.[14a,19,21,22]

In summary, we have succeeded in the synthesis and isolation of various structurally and electronically diversified hypervalent iodine(III) reagents. These compounds have led to two key insights, which round up the development of intermolecular amination reactions with hypervalent iodine(III) reagents. First, the diamination of styrenes with bistosylimides as nitrogen sources proceeds through a rate-determining preequilibrium with the formation of a cationic iodine(III) reagent that engages in styrene coordination as predicted from a theoretical investigation.[17]

Scheme 4. Synthesis of Enantiopure Iodine(III) Reagents with I−N Bonds
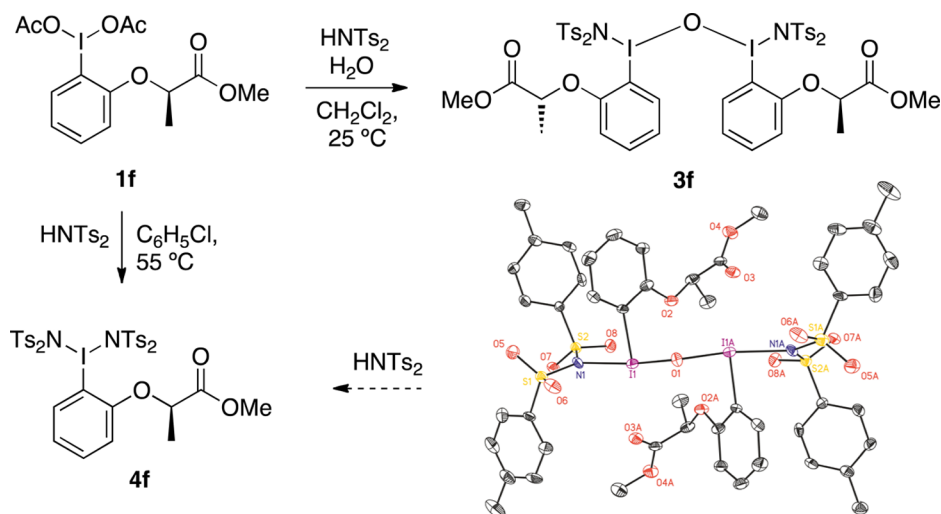
Related studies on a chiral, nonracemic iodine(III) derivative for the first time have allowed the isolation of reagents with defined iodine–nitrogen bonds. These compounds lend weight to the assumption that enantioselective amination processes such as the diamination of styrenes under the previously established in situ conditions involve the initial formation of imidoiodine(III) species.

■ EXPERIMENTAL SECTION

General Remarks. Chemicals and solvents for chromatography were used as received. Solvents were obtained from a solvent purification system. Reactions that were monitored by TLC were visualized by a dual short wave/long wave UV lamp. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded using an internal deuterium lock on a 300 or a 500 MHz spectrometer. All chemical shifts in NMR experiments are reported as ppm downfield from TMS. J couplings are reported in hertz. The following calibrations were used: CDCl$_3$ δ = 7.26 and 77.0 ppm, DMSO-d_6 δ = 2.50 and 39.5 ppm. Infrared spectra were recorded on a FT-IR fitted with an ATR accessory. Absorptions are given in wavenumbers (cm^{-1}). High-resolution mass spectra were obtained on a HRMS-TOF spectrometer.

General Procedure for Synthesis of μ-Oxobis[(4-methyl)-N-tosylbenzenesulfonamidyl(aryl)iodine(III)] (3). To a solution of the corresponding (diacetoxyiodo)arene **1** (0.3 mmol, 2 equiv) in CH$_2$Cl$_2$ (0.6 mL) was added HNTs$_2$ (0.3 mmol, 2 equiv) in one portion, and the reaction mixture was stirred at room temperature overnight. Then cyclohexane was added, and the solvent was removed under reduced pressure. Twice more, CH$_2$Cl$_2$ and cyclohexane were added and removed under reduced pressure. After being dried at reduced pressure, the corresponding iodine(III) compound was obtained in quantitative yield.

General Procedure for Synthesis of Bis[(4-methyl)-N-tosylbenzenesulfonamidyl]iodosoarene (4). To a solution of the corresponding (diacetoxyiodo)arene **1** (0.3 mmol, 1 equiv) in chlorobenzene (1.5 mL) was added HNTs$_2$ (0.6 mmol, 2 equiv), and the reaction mixture was stirred at 55 °C. The solvent was removed under reduced pressure. Chlorobenzene was added and removed three times under reduced pressure. After drying at reduced pressure, the corresponding iodine(III) compound was obtained in quantitative yield.

General Procedure for Synthesis of Methoxy((4-methyl)-N-tosylbenzenesulfonamidyl)iodosoarene (7). To a solution of diacetoxyiodoarene **1** (1 mmol, 1 equiv) in chlorobenzene (3.7 mL) and H$_2$O (1 equiv) was added HNTs$_2$ (1 equiv), and the reaction mixture was stirred at 55 °C. The solvent was removed under reduced pressure. Chlorobenzene was added and removed three times under reduced pressure. After drying at reduced pressure, the corresponding iodine(III) compound **3** was obtained as a yellow solid. To this solid was added MeOH until a white suspension formed at 4 °C. Filtration provided the title compounds in pure form.

Kinetic Measurement of Diamination Reaction with Different Iodine(III) Reagents 4. In an NMR tube were dissolved the respective reagent ArI(NTs$_2$)$_2$ **4** (1 equiv), C$_6$F$_6$ (5 equiv), and 4-fluorostyrene **5b** (0.2 mmol, 5 equiv) in CD$_2$Cl$_2$ (0.6 mL). The reaction progress was monitored by ^{19}F NMR spectroscopy, with individual spectra recorded within a time interval of 1 min.

μ-Oxobis[(4-methyl)-N-tosylbenzenesulfonamidyl(p-trifluoromethylphenyl)iodine(III)] (3b). White solid (0.181 g, 0.15 mmol, 99%). ^1H NMR (400 MHz, DMSO-d_6): δ = 2.32 (s, 12H), 7.15 (d, J = 8.0 Hz, 8H), 7.52 (d, J = 8.1 Hz, 8H), 7.99 (d, J = 8.3 Hz, 4H), 8.39 (d, J = 8.1 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.8, 123.4 (q, J = 272 Hz), 126.2, 127.9 (q, J = 4 Hz), 128.3, 131.9 (q, J = 33 Hz), 134.7, 138.2, 139.8, 143.3. ^{19}F-NMR (376 MHz, DMSO-d_6): δ = −61.3. IR ν (cm^{-1}): 3095, 3048, 2924, 1595, 1398, 1335, 1316, 1142, 1081, 1065, 938. HRMS (MALDI+): calcd for [C$_{21}$H$_{18}$F$_3$INO$_4$S$_2$]$^+$ 595.9668, found 595.9671. Mp: 147–148 °C.

Bis[(4-methyl)-N-tosylbenzenesulfonamidyl]iodoso-p-trifluoromethylbenzene (4b). White solid (0.276 mg, 0.3 mmol, 99%). ^1H NMR (400 MHz, DMSO-d_6): δ = 2.33 (s, 12H), 7.18 (d, J = 8.0 Hz, 8H), 7.54 (d, J = 8.1 Hz, 8H), 7.99 (d, J = 8.4 Hz, 2H), 8.39 (d, J = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 20.9,

123.5 (q, J = 273 Hz), 126.5, 127.8, 128.7, 131.9 (q, J = 33 Hz), 134.9, 138.3, 141.3, 141.4. ^{19}F-NMR (376 MHz, DMSO-d_6): δ = −61.3. IR ν (cm^{-1}): 3157, 3097, 1595, 1493, 1448, 1399, 1359, 1336, 1316, 1164, 1143, 1082, 1065, 1044, 1020, 999. HRMS (MALDI+): calcd for [C$_{21}$H$_{18}$F$_3$INO$_4$S$_2$]$^+$ 595.9668, found 595.9705. Mp: 162–165 °C.

μ-Oxobis[(4-methyl)-N-tosylbenzenesulfonamidyl(p-chlorophenyl)iodine(III)] (3c). White solid (0.171 g, 0.15 mmol, 99%). ^1H NMR (400 MHz, DMSO-d_6): δ = 2.31 (s, 12H), 7.14 (d, J = 7.8 Hz, 8H), 7.52 (d, J = 7.8 Hz, 8H), 7.68 (d, J = 8.0 Hz, 4H), 8.20 (d, J = 7.6 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.9, 121.4, 126.2, 128.2, 131.2, 136.3, 137.4, 139.6, 143.8. IR ν (cm^{-1}): 3089, 2919, 1596, 1494, 1469, 1390, 1332, 1306, 1288, 1143, 1082, 1020, 997. HRMS (MALDI+): calcd for [C$_{20}$H$_{18}$ClNO$_4$S$_2$I]$^+$ 561.9405, found 561.9368. Mp: 169–170 °C.

Bis[(4-methyl)-N-tosylbenzenesulfonamidyl]iodoso-p-chlorobenzene (4c). White solid (0.266 mg, 0.3 mmol, 99%). ^1H NMR (400 MHz, DMSO-d_6): δ = 2.33 (s, 12H), 7.18 (d, J = 7.9 Hz, 8H), 7.54 (d, J = 8.1 Hz, 8H), 7.69 (d, J = 8.6 Hz, 2H), 8.22 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.9, 126.3, 128.5, 130.6 131.2, 136.3, 138.9, 140.6, 142.2. IR ν (cm^{-1}): 3156, 2921, 1596, 1494, 1469, 1359, 1334, 1305, 1164, 1143, 1082, 1019, 998. HRMS (MALDI+): calcd for [C$_{20}$H$_{18}$ClINO$_4$S$_2$]$^+$ 561.9405, found 561.9379. Mp: 154–156 °C.

μ-Oxobis[(4-methyl)-N-tosylbenzenesulfonamidyl(p-methylphenyl)iodine(III)] (3d). White solid (0.165 g, 0.15 mmol, 99%). ^1H NMR (400 MHz, DMSO-d_6): δ = 2.31 (s, 12H), 2.42 (s, 6H), 7.14 (d, J = 7.9 Hz, 8H), 7.41 (d, J = 8.7 Hz, 4H), 7.52 (d, J = 8.0 Hz, 8H), 8.10 (d, J = 8.7 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.9, 21.1, 120.2, 126.1, 128.2, 131.7, 134.8, 139.5, 143.1, 143.8. IR ν (cm^{-1}): 3029, 2919, 1596, 1493, 1399, 1329, 1305, 1288, 1207, 1187, 1159, 1143, 1119, 1082, 1020, 1000, 956. HRMS (MALDI+): calcd for [C$_{21}$H$_{21}$INO$_4$S$_2$]$^+$ 541.9951, found 541.9922. Mp: 160–161 °C.

Bis[(4-methyl)-N-tosylbenzenesulfonamidyl]iodoso-p-methylbenzene (4d). White solid (0.260 g, 0.3 mmol, 99%). ^1H NMR (400 MHz, DMSO-d_6): δ = 2.32 (s, 12H), 2.42 (s, 3H), 7.17 (d, J = 8.0 Hz, 8H), 7.42 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 8.2 Hz, 8H), 8.11 (d, J = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): δ = 20.9, 21.1, 126.4, 128.7, 131.5, 131.8, 134.9, 136.9, 141.2, 141.4. IR ν (cm^{-1}): 3050, 2925, 1908, 1710, 1595, 1491, 1472, 1452, 1395, 1343, 1326, 1305, 1231, 1207, 1184, 1148, 1120, 1081, 1043, 1017, 993. HRMS (MALDI+): calcd for [C$_{21}$H$_{21}$INO$_4$S$_2$]$^+$ 541.9951, found 541.9956. Mp: 136–141 °C.

μ-Oxobis[(4-methyl)-N-tosylbenzenesulfonamidyl(p-methoxyphenyl)iodine(III)] (3e). White solid (0.170 g, 0.15 mmol, 99%). ^1H NMR (400 MHz, DMSO-d_6): δ = 2.31 (s, 12H), 3.85 (s, 6H), 7.10–7.16 (m, 12H), 7.52 (d, J = 8.1 Hz, 8H), 8.16 (d, J = 6.8 Hz, 4H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.9, 55.8, 113.5, 116.7, 126.2, 128.2, 137.5, 139.7, 143.7, 162.3. IR ν (cm^{-1}): 2920, 1572, 1487, 1457, 1403, 1328, 1301, 1250, 1175, 1141, 1080, 1019, 946. MS (MALDI+): 558.1. Mp: 132–134 °C.

Bis[(4-methyl)-N-tosylbenzenesulfonamidyl]iodoso-p-methoxybenzene (4e). White solid (0.265 g, 0.3 mmol, 99%). ^1H NMR (400 MHz, DMSO-d_6): δ = 2.33 (s, 12H), 3.84 (s, 3H), 7.13 (d, J = 8.8 Hz, 2H), 7.19 (d, J = 7.8 Hz, 8H), 7.55 (d, J = 7.9 Hz, 8H), 8.18 (d, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.9, 55.8, 113.5, 116.8, 126.4, 128.6, 137.6, 140.8, 142.0, 162.4. IR ν (cm^{-1}): 3096, 2922, 1595, 1569, 1484, 1442, 1403, 1346, 1330, 1302, 1253, 1145, 1120, 1081, 1018, 918. MS (MALDI+): 558.1. Mp: 131–132 °C.

μ-Oxo-Bridged Chiral Iodine(III) 3f. White solid (0.191 g, 0.15 mmol, 99%). ^1H NMR (400 MHz, DMSO-d_6): δ = 1.63 (d, J = 6.8 Hz, 6H), 2.31 (s, 12H), 3.72 (s, 6H), 5.30 (q, J = 6.8 Hz, 2H), 7.14–7.16 (m, 10H), 7.24 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 8.2 Hz, 8H), 7.62–7.71 (m, 2H), 8.30 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 18.0, 20.9, 52.5, 73.4, 113.8, 115.4, 123.6, 126.1, 128.2, 135.6, 138.0, 139.6, 143.8, 154.4, 171.0. IR ν (cm^{-1}): 2953, 1736, 1651, 1586, 1569, 1493, 1470, 1448, 1385, 1360, 1326, 1282, 1248, 1217, 1186, 1143, 1099, 1080, 1051, 1017, 981. HRMS (MALDI+): calcd for [C$_{24}$H$_{25}$INO$_7$S$_2$]$^+$ 630.0112, found 630.0131. Mp: 139–141 °C. [α]$^{27}_D$: −290.1 (c = 0.10, CH$_2$Cl$_2$).

Chiral iodine(III) 4f. White solid (0.286 g, 0.3 mmol, 99%) ^1H NMR (400 MHz, DMSO-d_6): δ = 1.63 (d, J = 6.7 Hz, 3H), 2.33 (s, 12H),

3.72 (s, 3H), 5.30 (q, J = 6.7 Hz, 1H), 7.13−7.26 (m, 10H), 7.55 (d, J = 7.9 Hz, 8H), 7.67 (t, J = 7.6 Hz, 1H), 8.30 (d, J = 9.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 18.0, 20.9, 52.5, 73.4, 113.8, 115.4, 123.6, 126.3, 128.5, 135.6, 138.0, 140.7, 142.2, 154.4, 171.0. IR ν (cm^{-1}): 3155, 1738, 1595, 1493, 1469, 1377, 1356, 1330, 1282, 1216, 1162, 1144, 1081, 1053, 1017, 980. HRMS (MALDI+): calcd for $[C_{24}H_{25}INO_7S_2]^+$ 630.0112, found 630.0001. Mp: 146−147 °C. $[\alpha]^{27}_D$: −233.0 (c = 0.10, CH$_2$Cl$_2$).

Methoxy((4-methyl)-N-tosylbenzenesulfonamidyl)iodosobenzene (7a). White solid (0.185 g, 0.33 mmol, 33%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.31 (s, 6H), 3.17 (s, 3H), 7.14 (d, J = 8.0 Hz, 4H), 7.52 (d, J = 8.1 Hz, 4H), 7.60−7.64 (m, 2H), 7.69−7.73 (m, 1H), 8.22 (d, 7.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.9, 63.2, 122.1, 126.2, 128.3, 131.4, 133.1, 135.5, 139.9, 143.4. IR ν (cm^{-1}): 2919; 2813, 1595, 1493, 1469, 1446, 1334, 1148, 1080, 1019, 989. HRMS (MALDI+): calcd for $[C_{20}H_{19}INO_4S_2]^+$ 527.9795, found 527.9859. Mp: 163−167 °C.

Methoxy((4-methyl)-N-tosylbenzenesulfonamidyl)-4-methyliodosobenzene (7d). White solid (0.184 mg, 0.32 mmol, 32%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.32 (s, 6H), 2.42 (s, 3H), 3.17 (s, 3H), 7.16 (d, J = 8.0 Hz, 4H), 7.42 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 8.1 Hz, 4H), 8.11 (d, J = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.9, 21.1, 48.6, 126.2, 128.3, 131.5, 131.7, 134.8, 136.9, 139.9, 143.1. IR ν (cm^{-1}): 3026, 2957, 2921, 1597, 1482, 1447, 1399, 1317, 1283, 1138, 1079, 960, 805, 771, 664, 547, 506, 483. HRMS (MALDI +): calcd for $[C_{21}H_{21}INO_4S_2]^+$ 541.9957, found 541.9983. Mp: 132−134 °C.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01070.

  Full experimental description of control experiments and ^{1}H and ^{13}C NMR spectra of new compounds (PDF)
  X-ray crystallographic data for **7d** (CIF)
  X-ray crystallographic data for **3f** (CIF)
  X-ray crystallographic data for **3b** (CIF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

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