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# **One-Pot Syntheses of Diaryliodonium Salts from Aryl Iodides Using Peracetic Acid as Green Oxidant**

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The rate-accelerating effects of fluoroalcohol solvents for generating trivalent hypervalent iodine species and the conversion into diaryliodonium(III) salts have been used for the first time to realize a facile and clean one-pot synthesis of diaryliodonium(III) salts **3** from aryl iodides **1** and suitable arene partners **2** with peracetic acid (PAA). The use of PAA as a green and practical oxidant is significantly effective in fluoroalcohol solvents. The scope and limitations of the methodology are elucidated by investigation of a wide variety of representative substrates.

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# Introduction

The diaryl- $\lambda^3$ -iodanes constitute one of the unique classes of hypervalent iodine compounds as represented by the classically known diaryliodonium(III) salts,  $ArI^+Ar'X^-$  (where, Ar and Ar' = aryls, and X = anionic counterion).<sup>[1]</sup> A broad range of specific applications, such as arylating agents and benzyne precursors in organic synthesis,<sup>[1a,b]</sup> active bactericides,<sup>[1c]</sup> a practical photoacid generator (PAG) for initiating cationic polymerization processes,<sup>[1d,e]</sup> etc., have been found. In combination with the expedient leaving ability of the aryl iodonio group,<sup>[1,2]</sup> the unusual physical properties and chemical behaviours compared with other onium salts has pioneered innovative research to allow novel metal-free carbon-carbon bond constructions<sup>[3]</sup> as well as other metal-involved transformations<sup>[4]</sup> in recent times. In such applications in organic synthesis and other fields of chemistry, the diaryliodonium(III) salts serve as useful and environmentally friendly chemical tools meeting the recent demands in green chemistry because of their salient features of typical hypervalent iodine compounds,<sup>[2]</sup> such as low toxicity, high stability, ready availability, easy handling, and unique reactivities similar to that of heavy metals.

Many synthetic routes are now available to obtain structural diversity in the available series of diaryliodonium(III) salts. The synthesis was originally carried out by the condensation of isolated trivalent iodine compounds and a suitable aromatic partner with a Brönsted acid.<sup>[5]</sup> However, such direct methods could only be achieved in a limited number of substrates and counterions using iodine(III) compounds activated with strong acids<sup>[5a,b]</sup> or reactive [hydroxy(tosyloxy)iodo]benzene (HTIB)<sup>[5c]</sup> in moderate yields with poor regioselectivities. Therefore, stepwise methods using a variety of organometallic aromatic compounds, i.e., lithio-, silyl-,

stannyl-, and boryl-arenes, have been used to circumvent the limitation of the original methodology.<sup>[6]</sup> More recently, synthetic interest has focussed on a more straightforward route, that is, the couplings starting from aryl iodides 1 and suitable arene partners 2 under oxidative conditions (Scheme 1),<sup>[7–11]</sup> otherwise, the former two routes require several further synthetic steps to the salts 3.<sup>[5,6]</sup> Chromium oxide,<sup>[7]</sup> sodium perborate,<sup>[8]</sup> potassium peroxodisulfate,<sup>[9]</sup> m-chloroperbenzoic acid,<sup>[10]</sup> and urea-hydrogen peroxide/ triflic anhydride,<sup>[11]</sup> have been employed as the concomitant oxidants in Scheme 1. Indeed, the stoichiometric use of these oxidants has realized facile and high-yielding syntheses of diaryliodonium(III) salts from the corresponding aryl iodides 1 and aromatic partners 2 with an acceptable substrate scope,\* however, the nature of the employed oxidants always caused the production of large amounts of inorganic and organic byproducts and/or toxic waste after the preparations despite being removable by aqueous workup. Thus, the synthetic hurdle at the present time is considered to be a replacement of the oxidants to other more favourable alternatives for decreasing the undesirable waste materials.

Based on this situation, we examined the use of peracetic acid (PAA) as an environmentally friendly and practical oxidant for the straightforward syntheses of diaryl iodonium salts **3** from aryl iodides **1** and the corresponding arene partners **2**. The important key for the successful transformation is that fluoroalcohols consistently act as extreme promoters during the



<sup>\*</sup>New straightforward protocols enabling the synthesis of diaryliodonium(III) salts from aromatic compounds in the presence of elemental iodine or inorganic periodate have been developed, however, their synthetic scope is strictly limited to obtaining symmetrical salts having the same aryl groups. See ref. [12].



Scheme 2. PAA = peracetic acid, Ts = p-toluenesulfonyl.

reaction. We now report the primary results obtained for the onepot syntheses of diaryliodonium salts **3** using PAA as the green oxidant.

Table 1. Solvent screening in the diaryliodonium salt formation 3aa-OTs<sup>A</sup>

# **Results and Discussion**

PAA is an extremely green oxidant and has frequently been used as a practical and environmentally friendly oxidant.<sup>[13]</sup> Its priority of use has been favoured in recent years in not only the laboratory, but also in industrial-scale processes because PAA only releases non-toxic co-products after its consumption, that is, easily removable acetic acid and water, making isolation of the products easy when using this organic oxidant. It is commercially available as dilute acetic acid solutions, or alternatively, can be prepared from hydrogen peroxide and acetic anhydride before use.<sup>[14]</sup> Also, a 0.2-0.3% aqueous solution of PAA is widely used as a disinfectant in medical situations because of its well confirmed safety toward humans.

Recently, we found a remarkable rate-accelerating effect of fluoroalcohol solvents, i.e., hexafluoroisopropanol (HFIP) and trifluoroethanol (TFE), for the dehydrative condensation of HTIB with various electron-sufficient aromatic rings to form the corresponding type 3 diaryliodonium(III) salts.<sup>[15,16]</sup> Thereafter, the fluoroalcohols were successfully introduced as effective solvents for enhancing the low activity of PAA to generate aryliodine(III) species and to construct hypervalent iodine(III)involved catalytic cycles.<sup>[17]</sup> Based on this knowledge, we now considered the effects of fluoroalcohols as the key to establishing a one-pot approach to diaryliodonium(III) salts 3 from the aryl iodide 1 and aromatic partners 2 with PAA that is shown in Scheme 2. The net conversion mainly consisted of two steps, i.e., the generation of aryliodine(III) diacetates 1' with PAA (step 1) followed by the condensation of 1' with aromatic rings of 2 in the presence of the appropriate anions,  $X^{-}$  (step 2), both of which would be accelerated by the use of the unique fluoroalcohol solvents.<sup>[18]</sup>

Based on this idea, we attempted the conversion of iodobenzene 1a into mesityl(phenyl)iodonium tosylate 3aa-OTs by selecting the mixed solvent system of HFIP/CH<sub>2</sub>Cl<sub>2</sub>  $(1/1, v/v)^{[17]}$ as the first choice. With a commercially available  $\sim 9\%$  (v/v) PAA solution in acetic acid (obtained from Sigma-Aldrich,  $\sim$ 5 equiv. was used), the reaction was performed around the temperature of 35°C for 1 h to suitably generate the aryliodine(III) diacetate 1' in situ. To the reaction mixture, p-toluenesulfonic acid (TsOH, 2 equiv.) and a slight excess amount of mesitylene 2a (1.5 equiv.) were added and mixed at room temperature for 3 h, from which the desired iodonium(III) salt 3aa-OTs could be obtained in 83% yield with high purity by precipitation in ether (Table 1, entry 1). Motivated by this encouraging result, we then screened minor modifications of the solvent systems using HFIP and TFE, all giving similar product yields of **3aa-OTs** as suggested by entries 2-4. Thus, the concentration of fluoroalcohols was less influential, and the reactions could be performed without any conversion losses of



Entry	Solvent	Time [h]	Yield of $3aa [\%]^{B}$
1	HFIP/CH <sub>2</sub> Cl <sub>2</sub> <sup>C</sup>	3	83
2	HFIP	3	89
3	TFE	3	89
4	TFE/CH2Cl2D	3	89
5	MeOH	24	n.d. <sup>E</sup>
6	$CH_2Cl_2$	24	57
7	CH <sub>3</sub> CN	24	42
8	AcOH	3	77

<sup>A</sup>Reactions were examined using **1a** (1 equiv.), **2a** (1.5 equiv.), 9% PAA solution ( $\sim$ 5 equiv. of PAA), and *p*-toluenesulfonic acid monohydrate (HOTs, 2 equiv.) under 0.2 M concentration of **1a**.

<sup>B</sup>Isolated yield based on **1a** used.

 $^{\rm C}$ 1/1 v/v of the solvents.

D10/1 v/v of TFE/CH<sub>2</sub>Cl<sub>2</sub>.

<sup>E</sup>Not determined because of a very low-yield of formation of **3aa** (<5%).

**1a** and **2a** using various ratios of the fluoroalcohols and dichloromethane (up to 1/1 v/v).

However, other conventional alcohols and polar or non-polar solvents, such as methanol, acetonitrile, and dichloromethane, generally gave inferior results as we expected (entries 5–7). The slightly higher formations of **3aa-OTs** in the case of acetonitrile (42%) and dichloromethane (57%) after prolonged reaction times are rationalized by the positive effect of the concomitant acetic acid in the PAA solution on the one-pot synthesis, although less effective than the fluoroalcohols, as implied in the better product yield when using the acetic acid solvent (entry 8). Our fast and greener synthetic method of producing diaryl iodonium(III) salts **3** with PAA has become the most successful of the fluoroalcohol systems based on these studies.

We next verified the versatility of the method in several kinds of aryl iodides 1 using the optimized conditions (Table 2). Among the examined fluoroalcohol systems, we selected for this examination TFE/CH<sub>2</sub>Cl<sub>2</sub> (10/1 v/v) to eliminate the solubility factor of the aryl iodides 1a-f in the solvent. A series of aryl iodides 1a-f are soluble enough in the solvent mixture, and the corresponding iodonium(III) salts 3 having different aryl rings could be obtained from the iodoarenes 1 except for 4-iodoanisole 1c (entries a-f). Thus, the problem seems to be the unavailability of the aryl iodide 1c having a strong resonancedonating group (entry c, see the discussion in Fig. 1). The use of HFIP was particularly beneficial in the case of the aryl iodide having a very strong electron-withdrawing group, such as a nitro group, because of the difficult smooth generation of the iodine(III)

Entry	Iodoarene (1)	Iodonium salt ( <b>3-X</b> )	Yield of $3-X [\%]^B$
	$R^1 \longrightarrow R^2$ $R^2$	$R^1 \longrightarrow \stackrel{R^2}{\underset{R^2}{\overset{-}{\underset{OTs}{\overset{-}{\underset{OTs}{\overset{-}{\underset{OTs}{\overset{-}{\underset{OTs}{\overset{-}{\underset{OTs}{\overset{-}{\underset{OTs}{\underset{OTs}{\overset{-}{\underset{OTs}{\underset{OTs}{\overset{-}{\underset{OTs}{\underset{OTs}{\overset{-}{\underset{OTs}{OTs}{\underset{OTs}{\underset{OTs}{OTs}{\underset{OTs}{\underset{OTs}{OTs}{\underset{OTs}{\underset{OTs}{OTs}{OTs}{}}}}}}}}}}}}}}}}}}}}}}}}$	
a	$R^1 = R^2 = H(1a)$	$R^1 = R^2 = H (3aa-OTs)$	89
b	$R^1 = R^2 = Me(1b)$	$R^1 = R^2 = Me (3ba-OTs)$	94
с	$R^1 = OMe, R^2 = H(1c)$	$R^1 = OMe, R^2 = H (3ca-OTs)$	Trace
d	$R^1 = Cl, R^2 = H(1d)$	$R^1 = Cl, R^2 = H (3da-OTs)$	89
e	$R^1 = CF_3, R^2 = H(1e)$	$R^1 = CF_3, R^2 = H$ ( <b>3ea-OTs</b> )	82
f	$R^1 = NO_2, R^2 = H(1f)$	$R^1 = NO_2, R^2 = H (3fa-OTs)$	18 (73) <sup>C</sup>

Table 2. Variation of starting iodoarenes 1 for the PAA method<sup>A</sup>

<sup>A</sup>Reactions were performed with the optimized experimental procedure and reaction time (3 h) described in Table 1, entry 4 unless otherwise noted. Reagents and conditions: iodoarene (1a–f; 1 equiv.), mesitylene (2a; 1.5 equiv.), 9% PAA ( $\sim$ 5 equiv.), HX (X = OTs; 2 equiv.) in TFE/CH<sub>2</sub>Cl<sub>2</sub> (10/1 v/v). <sup>B</sup>Isolated yield of the product 3 based on iodoarene (1a–f) used.

<sup>C</sup>HFIP was used as solvent.



Fig. 1. Summary of applicability of aromatic substrates.

species 1' for such an aryl iodide **1f** (entry f). As a large number of aryl iodides **1** are now commercially available, the variation of the aryl iodides **1** in the reaction can further expand the structural diversity of the obtained salts **3**.

Regarding the aromatic coupling partners 2, the new protocol provided the permissible options for the alkylbenzenes, phenylethers, and suitably protected aniline derivatives. To elucidate the selectivity and scope of the functional groups, we tested several types of aromatic compounds 2 for the reactions of iodobenzene 1a, and selected examples are shown in Table 3. Among the ring positions in the multi-substituted alkylbenzene 2b, the less hindered site exclusively reacted to give a salt 3ab-OTs as the single isomer (entry e). The reactions were usually para-selective to the donating substituents, but the 1,4-disubstituted benzene could give an iodonium salt 3ac-OTs during the reaction at the ortho-position of 2c, although HFIP was required for the transformation (entry f). As shown in entry g, a significantly electron-rich arene 2d was compatible and rather an excellent aromatic partner 2 in contrast to the result of the electron-rich aryl iodide 1c in Table 2. In turn, moderate electronwithdrawing functional groups, such as a halogen (entry h) and ester (entry i), on the anisole ring did not affect the reaction results. These substrate results are similar to those of the other straightforward systems.<sup>[7–11]</sup> For the diaryl ethers 2g and 2h, selective formations of mono-iodonium(III) salts **3ag-OTs** and **3ah-OTs** occurred on the one aryl ring without any production of the bisiodonium salt (entries j and k). A series of counterions,  $\neg$ OTf (Tf = trifluoromethanesulfonyl),  $\neg$ OMs (Ms = methanesulfonyl), and  $\neg$ OCs (Cs = (+)-10-camphorsulfonyl), were conveniently introduced into the product **3aa** using this methodology by changing the added sulfonic acids (entries a–d). Throughout the operations, no tedious workup and special equipment was necessary as the reactions only produced easily removable acetic acid and water as the main coproducts, which proved to be a distinct advantage of the PAA method.

Based on these investigations, the scope and limitation of our methodology are summarized in Fig. 1. For a wide range of aryl iodides **1** not having an oxidizable functionality, the one-pot preparation was effective, and even more versatile when compared with the reported methods except for **1c**.<sup>[5–16]</sup> The failure of the iodoanisole **1c** in Table 2 is rationalized by the expected in situ instability of the active iodonium(III) species. In the reaction profile depicted as Scheme 3, the conversions should take into account the formation of [hydroxyl(tosyloxy)iodo]arenes **1**'' (X = OTs) before starting the condensation with **2**, as the first generated aryliodine(III) diacetate **1**' can react very slowly with the aromatic coupling partners **2**.<sup>†</sup> In general, the aryliodonium(III) species are very unstable in the presence of strong

<sup>&</sup>lt;sup>†</sup>[Hydroxy(sulfonyloxy)iodo] arenes 1" can be generated rapidly from aryliodine(III) diacetates 1' and sulfonic acids in the presence of stoichiometric amounts of water. For preparative methods, see ref. [19].

 Table 3.
 Syntheses of diaryliodonium salts 3-X (X = OTs, OTf, OMs, OCs)<sup>A</sup> from iodobenzene 1a and various electron-rich arenes 2a–i using the PAA method<sup>B</sup>

Entry	Arene (2)	Iodonium salt ( <b>3-X</b> )	Yield of $3-X$ [%] <sup>C</sup>
а	2a	<b>3aa-OTs</b> $(X = OTs)$	89
b	2a	3aa-OTf(X = OTf)	87
с	2a	<b>3aa-OMs</b> $(X = OMs)$	89
d	2a	<b>3aa-OCs</b> $(X = OCs)$	90
e		√−l+ X− /Bu	
	2b	<b>3ab-OTs</b> $(X = OTs)$	91
f	$\geq$		
	2c	<b>3ac-OTs</b> $(X = OTs)$	37 (82) <sup>D</sup>
g	MeO ————————————————————————————————————	MeO I X - OMe	
	MeO		95
	20 Pr	3ad-01s (X=01s)	85
h	OMe		
	2e	<b>3ae-OTs</b> $(X = OTs)$	84
i	CO <sub>2</sub> Me		
	2f	3af-OTs (X = OTs)	84
j	-OBn	$-I^+$ OBn	
	2g	<b>3ag-OTs</b> ( $X = OTs$ )	91
k	-OPh	$-I^+_X$ -OPh	
	2h	<b>3ah-OTs</b> $(X = OTs)$	98
1		$ \underset{X^-}{\overset{l^+}{\longrightarrow}} \underset{N^-}{\overset{O}{\longrightarrow}} $	
	2i	<b>3ai-OTs</b> $(X = OTs)$	85

 $^{A}Tf = trifluoromethanesulfonyl;$  Ms = methanesulfonyl; Cs = (+)-10camphorsulfonyl.

<sup>B</sup>Reactions were performed with the optimized experimental procedure and reaction time (3 h) described in Table 1, entry 4 unless otherwise noted. Reagents and conditions: iodobenzene (**1a**; 1 equiv.), arene (**2a**–i; 1.5 equiv.), 9% PAA (~5 equiv.), HX (X = OTs, OTf, OMs, OCs; 2 equiv.) in TFE/CH<sub>2</sub>Cl<sub>2</sub> (10/1 v/v).

<sup>C</sup>Isolated yield of the product **3** based on iodobenzene (**1a**) used.

<sup>D</sup>HFIP was used as solvent.

acids once an electron-donating group is attached to the aryl ring.<sup> $\ddagger$ [20]</sup> Thus, the collapse of the intermediate 1", [hydroxyl (tosyloxy)iodo]anisole (R = 4-OMe, X = OTs), did not give the desired iodonium(III) salt **3ca-OTs**.

Electron-rich aromatic compounds 2 are the common excellent partners for the aryl iodides 1. In contrast, the presence of an electron-withdrawing group in the aromatic compounds 2 apparently retards the condensation with the [hydroxyl(tosyloxy)iodo]arenes 1', as seen in the other procedures. [5-16] Unfortunately, our effort to extend the one-pot strategy with PAA to the heteroaryl-involving iodonium(III) salt synthesis almost failed, resulting in the complex formation of unidentified oxidized products of heteroaromatic compounds. The limited successful cases include the aryl iodides 1 and electron-rich thiophenes, such as the combination of iodobenzene 1a and compound 2j or 2k (Scheme 4). For the five-membered heteroaromatics, the reactions usually occurred at the  $\alpha$ -position of the thiophene rings of 2j and 2k, in which the 2-position was more reactive than the other 5-position. It should be noted that the iodonium salts having these thienyl moieties are known to have special applications as the precursors of fluorinated aromatic compounds, organic non-linear optic materials, active bacteriocides, etc.<sup>[21]</sup>

### Conclusion

A practical and clean oxidant, PAA, has been used for the first time for the synthesis of diaryliodonium(III) salts 3 from aryl iodides 1. The transformation proceeded in exceptionally high yields with short reaction times for various types of substrate combinations, that is, various aryl iodide 1 except for those having an electron-rich aromatic moiety, and electron-rich aromatic partners 2, under mild conditions when using PAA in the fluoroalcohol solvents, HFIP and TFE. This study shows the importance of the fluoroalcohol solvents in the generation of hypervalent iodine(III) species, whose functions should make all the conversion steps to the salts 3 smooth and effective. The use of PAA results in the formation of only non-toxic acetic acid and water, and its applicability usually improves the cost and impact on the environment by reducing the undesirable waste. We believe that the present system, consistent with the recent direction of green chemistry, would become valuable for the production of industrial chemicals involving diaryliodonium(III) salts.

# Experimental

Melting points (mp) were measured using a Büchi B-545 apparatus. Infrared (IR) spectra were recorded on a Hitachi 270-50 spectrometer; absorptions are reported in reciprocal centimetres. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on JEOL JMN-300 or 400 spectrometers operating at 300 or 400 MHz in CD<sub>3</sub>OD at 25°C with tetramethylsilane as the internal standard. Data are reported as follows: chemical shift in ppm ( $\delta$ ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad singlet, m = multiplet), coupling constant [Hz], and integration. TLC was carried out on Merck Silica gel 60 (230– 400 mesh) using hexane/AcOEt as eluent; the spots were detected by UV irradiation (254, 365 nm). The 9% v/v PAA

<sup>&</sup>lt;sup>‡</sup>Interesting reactivities have been found by us for aryliodonium(III) species having electron-rich aryl moieties. See ref. [3].

One-Pot Syntheses of Diaryliodonium Salts









solution was purchased from Sigma–Aldrich, Japan. All aryl iodides and other chemicals were commercially available, and were used as received without further purification.

# General Experimental Procedure for the Syntheses of Diaryliodonium Salts **1** from Aryl Iodides **2** (Tables 1–3, Scheme 4)

To a stirred solution of iodobenzene (204 mg, 1.0 mmol) in 5 mL of 2,2,2-trifluoroethanol (TFE) and dichloromethane (10:1) was added the commercially available PAA solution (9% v/v in acetic acid, 2.2 mL,  $\sim 5 \text{ mmol of PAA}$ ). The reaction mixture was then stirred for 1 h while the reaction temperature was maintained around 35°C. After cooling to room temperature, mesitylene (180 mg, 1.5 mmol) and TsOH·H<sub>2</sub>O (380 mg, 2.0 mmol) were added to the mixture, and then stirred for 3 h at room temperature. After the disappearance of mesitylene (checked by TLC), CH<sub>2</sub>Cl<sub>2</sub> was added to the mixture and the organic layer was washed with water, and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After filtration, evaporation of the solvents under vacuum afforded an oily crude product 3aa-OTs, which was further purified by the addition of Et<sub>2</sub>O with stirring. The precipitate was collected and dried under vacuum to give the pure 3aa-OTs (438.5 mg, 0.89 mmol) in 89% yield. The solvents could be reused repeatedly after distillation.

Iodonium salts **3aa-X** (X = OTf, OMs, OCs) having other counterions could be prepared by replacement of *p*-toluene-sulfonic acid monohydrate (*p*-TsOHH<sub>2</sub>O) with the appropriate sulfonic acids (HX).

# Compound Data for Table 3

**3aa/OTs**: <sup>[15a]</sup> a colourless solid; mp 153–157°C.  $v_{max}$  (KBr)/cm<sup>-1</sup> 3045, 2951, 1566, 1469, 1438, 1230, 1192, 1132, 1045, 989, 737, 696.  $\delta_{\rm H}$  (CD<sub>3</sub>OD, 300 MHz) 2.32 (s, 3H), 2.33 (s, 3H), 2.62 (s, 6H), 7.16–7.18 (m, 4H), 7.45 (d, *J* 7.5, 1H), 7.48 (d, *J* 7.5, 1H), 7.58–7.65 (m, 3H), 7.87 (d, *J* 7.8, 2H).  $\delta_{\rm C}$  (CD<sub>3</sub>OD, 75 MHz) 21.0, 21.3, 27.0, 114.1, 122.4, 126.9, 129.8, 131.2, 133.1, 133.2, 135.2, 141.5, 143.4, 143.6, 145.6. **3aa/OTf**:<sup>[15a]</sup> a colourless solid; mp 148°C.  $v_{max}$  (KBr)/cm<sup>-1</sup> 3053, 2983, 1622, 1566, 1469, 1379, 1259, 1163, 1029, 989, 746, 638.  $\delta_{\rm H}$  (CD<sub>3</sub>OD, 300 MHz) 2.35 (s, 3H), 2.65 (s, 6H), 7.23 (s, 2H), 7.50 (t, *J* 7.5, 2H), 7.63 (t, *J* 7.5, 1H), 7.90 (d, *J* 7.5, 2H).  $\delta_{\rm C}$  (CD<sub>3</sub>OD, 75 MHz) 21.0, 27.0, 114.0, 119.7, 122.2, 131.3, 133.2, 133.3, 135.2, 143.5, 145.8.

 $\begin{array}{l} \textbf{3aa/OMs}.^{[15a]} \text{ a colourless solid; mp 135-136°C. } \nu_{max} \\ \textbf{(KBr)/cm}^{-1} \ 3018, \ 2950, \ 1566, \ 1438, \ 1218, \ 1058, \ 995, \ 750. \\ \delta_{H} \ \textbf{(CD_{3}OD, \ 300 \ MHz) \ 2.34} \ \textbf{(s, 3H)}, \ 2.53 \ \textbf{(s, 3H)}, \ 2.65 \ \textbf{(s, 6H)}, \\ \textbf{7.08} \ \textbf{(s, 2H)}, \ \textbf{7.38} \ \textbf{(t, J7.5, 2H)}, \ \textbf{7.49} \ \textbf{(t, J7.5, 1H)}, \ \textbf{7.75} \ \textbf{(d, J7.8, 2H)}. \\ \delta_{C} \ \textbf{(CD_{3}OD, \ 75 \ MHz) \ 21.0, \ 26.9, \ 39.0, \ 113.3, \ 121.7, \ 129.8, \\ 131.0, \ 131.6, \ 132.9, \ 142.1, \ 143.5. \end{array}$ 

**3aa/OCs**:<sup>[15a]</sup> a colourless solid; mp 173–174°C.  $\nu_{max}$  (KBr)/cm<sup>-1</sup> 2955, 1741, 1566, 1454, 1415, 1265, 1190, 1045, 995, 750.  $\delta_{\rm H}$  (CD<sub>3</sub>OD, 300 MHz) 0.81 (s, 3H), 1.09 (s, 3H), 1.32–1.39 (m, 1H), 1.50–1.58 (m, 1H), 1.85 (d, *J* 18.3, 1H), 1.98–2.02 (m, 2H), 2.28–2.35 (m, 4H), 2.57–2.72 (m, 8H), 3.26 (d, *J* 15.0, 1H), 7.23 (s, 2H), 7.50 (t, *J* 7.8, 2H), 7.64 (t, *J* 7.5, 1H), 7.91 (d, *J* 7.8, 2H).  $\delta_{\rm C}$  (CD<sub>3</sub>OD, 75 MHz) 20.1, 20.5, 21.0, 25.7, 27.1, 27.8, 43.6, 44.0, 48.1, 59.5, 114.2, 122.4, 131.3, 133.2, 133.2, 135.3, 143.5, 145.7, 218.1.

**3ab/OTs**:<sup>[15a]</sup> a colourless solid; mp 157°C.  $v_{max}$  (KBr)/cm<sup>-1</sup> 3018, 2968, 1568, 1472, 1219, 1132, 1045, 928, 772, 665, 627.  $\delta_{\rm H}$  (CD<sub>3</sub>OD, 300 MHz) 1.30 (s, 9H), 2.34 (s, 3H), 2.68 (s, 6H), 7.18 (d, *J* 8.4, 2H), 7.42–7.50 (m, 4H), 7.57–7.66 (m, 3H), 7.90 (d, *J* 8.4, 2H).  $\delta_{\rm C}$  (CD<sub>3</sub>OD, 75 MHz) 21.3, 27.3, 31.3, 35.8, 114.1, 122.5, 126.9, 127.9, 129.8, 133.2, 133.3, 135.3, 141.5, 143.2, 143.6, 158.3.

**3ac/OTs**:<sup>[16]</sup> a colourless solid; mp 143°C.  $v_{max}$  (KBr)/cm<sup>-1</sup> 3027, 2973, 2919, 1787, 1601, 1578, 1563, 1491, 1633, 1471, 1440, 1377, 1321, 1274, 1193, 1129, 1039, 1012, 991, 8897, 845, 812, 738, 688, 650.  $\delta_{\rm H}$  (CD<sub>3</sub>OD, 400 MHz) 2.35 (s, 3H), 2.36 (s, 3H), 2.58 (s, 3H), 7.21 (d, *J* 8.0, 2H), 7.42 (s, 2H), 7.50 (t, *J* 8.0, 2H), 7.65–7.68 (m, 3H), 8.07 (d, *J* 8.0, 2H), 8.13 (s, 1H).  $\delta_{\rm C}$  (CD<sub>3</sub>OD, 100.75 MHz) 20.5, 21.3, 25.1, 115.1, 120.7, 126.9, 129.8, 1332.5, 133.2, 133.4, 135.3, 136.1, 138.6, 139.2, 141.4, 141.6, 143.6.

**3ad/OTs**:<sup>[16]</sup> a slightly yellow solid; mp 178–180°C.  $\nu_{max}$  (KBr)/cm<sup>-1</sup> 2942, 2840, 2595, 2067, 1587, 1469, 1413, 1342, 1229, 1125, 1065, 1045, 1014, 992, 947, 913, 815, 740, 695, 642.  $\delta_{\rm H}$  (CD<sub>3</sub>OD, 400 MHz) 2.34 (s, 3H), 3.88 (s, 3H), 3.96 (s, 6H), 6.40 (s 2H), 7.20 (d, *J* 8.0, 2H), 7.44 (t, *J* 8.0, 2H), 7.60 (t, *J* 8.0, 1H), 7.68 (d, *J* 8.0, 2H), 7.93 (d, *J* 8.0, 2H).  $\delta_{\rm C}$  (CD<sub>3</sub>OD, 75 MHz) 21.3, 56.7, 57.7, 86.2, 92.8, 115.9, 126.9, 129.8, 132.7, 133.0, 135.8, 141.6, 143.6, 161.4, 168.7.

**3ae/OTs**:<sup>[16]</sup> a colourless solid; mp 158–159°C.  $v_{max}$  (KBr)/ cm<sup>-1</sup> 3050, 3015, 2936, 1566, 1476, 1439, 1379, 1292, 1271, 1255, 1207, 1192, 1155, 1132, 1045, 1015, 991, 816, 758, 692.  $\delta_{\rm H}$  (CD<sub>3</sub>OD, 300 MHz) 2.30 (s, 3H), 3.84 (s, 3H), 6.80 (d, *J*7.8, 100)

1H), 7.00 (d, *J* 7.8, 2H), 7.30 (t, *J* 7.8, 2H), 7.40–7.47 (m, 3H), 8.11–8.15 (m, 3H), 8.37 (d, *J* 2.1, 1H).  $\delta_{\rm C}$  (CDCl<sub>3</sub>, 75 MHz) 21.3, 56.4, 104.3, 113.8, 114.3, 116.2, 125.9, 128.5, 130.7, 131.4, 131.5, 134.9, 136.9, 139.1, 139.6, 158.6.

**3af/OTs**:<sup>[15a]</sup> a colourless solid; mp 170°C.  $v_{max}$  (KBr)/cm<sup>-1</sup> 3018, 1585, 1487, 1434, 1265, 1218, 771, 667.  $\delta_{\rm H}$  (CD<sub>3</sub>OD, 300 MHz) 2.34 (s, 3H), 3.86 (s, 3H), 3.90 (s, 3H), 7.21 (t, *J* 8.7, 3H), 7.50 (t, *J* 7.8, 2H), 7.67 (d, *J* 7.8, 3H), 8.15 (d, *J* 7.8, 2H), 8.28 (d, *J* 9.0, 1H), 8.49 (d, *J* 1.8, 1H).  $\delta_{\rm C}$  (CD<sub>3</sub>OD, 75 MHz) 21.3, 53.1, 57.1, 104.1, 116.7, 117.1, 124.5, 126.9, 129.8, 133.1, 133.6, 136.2, 139.5, 141.6, 142.0, 143.6, 163.2, 166.0.

 $\begin{array}{l} \textbf{3ag/OTs:}^{[16]} \text{ a colourless solid; mp 183–185°C. } \nu_{max} \\ (\text{KBr})/\text{cm}^{-1} 3071, 3046, 2934, 1578, 1567, 1482, 1454, 1442, 1402, 1381, 1291, 1235, 1193, 1131, 1043, 1013, 1003, 858, 832, 314, 756, 736, 696. \\ \delta_{\text{H}} (\text{CD}_{3}\text{OD}, 300 \text{ MHz}) 2.34 (s, 3\text{H}), 5.13 (s, 2\text{H}), 7.11 (d, J 8.0, 2\text{H}), 7.20 (d, J 8.0, 2\text{H}), 7.33–7.41 (m, 5\text{H}), 7.50 (t, J 8.0, 2\text{H}), 7.67 (t, J 8.0, 3\text{H}), 8.05–8.11 (m, 4\text{H}). \\ \delta_{\text{C}} (\text{CD}_{3}\text{OD}, 75 \text{ MHz}) 21.3, 71.5, 104.7, 116.5, 119.7, 127.0, 128.7, 129.3, 129.6, 129.8, 133.0, 133.5, 136.0, 137.5, 138.5, 141.6, 143.6, 163.5. \\ \textbf{3ah/OTs:}^{[15a]} \text{ a colourless solid; mp 138–139°C. } \nu_{max} \end{array}$ 

**3ah/OTs**:<sup>[15a]</sup> a colourless solid; mp 138–139°C.  $\nu_{max}$  (KBr)/cm<sup>-1</sup> 3020, 1568, 1479, 1440, 1217, 1132, 1043, 815, 752, 692.  $\delta_{\rm H}$  (CD<sub>3</sub>OD, 300 MHz) 2.30 (s, 3H), 6.94–7.02 (m, 4H), 7.16–7.24 (m, 3H), 7.37–7.49 (m, 4H), 7.59–7.70 (m, 3H), 8.08–8.15 (m, 4H).  $\delta_{\rm C}$  (CD<sub>3</sub>OD, 75 MHz) 21.3, 106.9, 116.5, 121.3, 121.5, 126.3, 126.9, 129.8, 131.4, 133.0, 133.4, 136.2, 138.8, 141.6, 143.6, 156.1, 162.8.

**3ai/OTs**:<sup>[15a]</sup> a colourless solid; mp 79°C.  $v_{max}$  (KBr)/cm<sup>-1</sup> 3051, 2981, 1693, 1579, 1487, 1384, 1303, 1191, 1130, 1043, 817, 746, 694.  $\delta_{\rm H}$  (CD<sub>3</sub>OD, 300 MHz) 2.13 (m, 2H), 2.34 (s, 3H), 2.58 (t, *J* 8.1, 2H), 3.86 (t, *J* 6.9, 2H), 7.20 (d, *J* 7.8, 2H), 7.49 (t, *J* 7.8, 2H), 7.63–7.69 (m, 3H), 7.80 (d, *J* 8.7, 2H), 8.13 (d, *J* 8.7, 4H).  $\delta_{\rm C}$  (CD<sub>3</sub>OD, 75 MHz) 18.6, 21.3, 35.6, 108.9, 116.5, 123.7, 126.9, 129.8, 133.1, 133.5, 136.2, 137.3, 141.6, 143.6, 144.5, 177.5.

# Compound Data for Table 2

**3ba/OTs**:<sup>[15a]</sup> a colourless solid; mp 138–142°C.  $v_{max}$  (KBr)/cm<sup>-1</sup> 3022, 2976, 1454, 1191, 1132, 1045, 985, 732, 694.  $\delta_{\rm H}$  (CD<sub>3</sub>OD, 300 MHz) 2.33 (s, 6H), 2.35 (s, 3H), 2.51 (s, 12H), 7.17–7.22 (m, 6H), 7.66 (d, *J* 7.8, 2H).  $\delta_{\rm C}$  (CD<sub>3</sub>OD, 75 MHz) 20.8, 21.3, 26.1, 119.1, 126.9, 129.7, 131.7, 141.5, 143.6, 143.6, 145.2.

**3ca/OTs**: trace amount of formation was confirmed by <sup>1</sup>H NMR;  $\delta_{\rm H}$  (CD<sub>3</sub>OD, 300 MHz) 2.31 (s, 3H), 2.33 (s, 3H), 2.63 (s, 6H), 3.79 (s, 3H), 7.00 (d, *J* 7.8, 2H), 7.15 (s, 2H), 7.17 (d, *J* 7.8, 2H), 7.64 (d, *J* 7.8, 2H), 7.83 (d, *J* 7.8, 2H).

**3da/OTs:** a slightly yellow solid; mp 185–186°C.  $v_{max}$  (KBr)/cm<sup>-1</sup> 3040, 2979, 1496, 1467, 1382, 1302, 1191, 1131, 1109, 1085, 1041, 1014, 1001, 850, 815, 695.  $\delta_{\rm H}$  (CD<sub>3</sub>OD, 400 MHz) 2.34 (s, 3H), 2.35 (s, 3H), 2.62 (s, 6H), 7.19 (d, *J* 8.8, 2H), 7.20 (s, 2H), 7.48 (d, *J* 8.8, 2H), 7.63 (d, *J* 8.8, 2H), 7.86 (d, *J* 8.8, 2H).  $\delta_{\rm C}$  (CD<sub>3</sub>OD, 100.53 MHz) 21.0, 21.3, 27.0, 111.6, 122.6, 126.9, 129.8, 131.3, 133.2, 136.9, 139.8, 141.6, 143.5 (× 2), 145.9.

**3ea/OTs**:<sup>[16]</sup> a colourless solid; mp 165–166°C.  $\nu_{max}$  (KBr)/cm<sup>-1</sup> 3034, 2969, 2920, 1593, 1449, 1393, 1323, 1300, 1188, 1132, 1103, 1067, 1045, 1015, 1003, 991, 853, 827, 816, 772, 754, 696.  $\delta_{\rm H}$  (CD<sub>3</sub>OD, 300 MHz) 2.34 (s, 3H × 2), 2.63 (s, 6H), 7.18 (d, *J* 7.8, 2H), 7.22 (s, 2H), 7.62 (d, *J* 7.8, 2H), 7.76 (d, *J* 7.8, 2H), 8.06 (d, *J* 7.8, 2H).  $\delta_{\rm C}$  (CD<sub>3</sub>OD, 75 MHz) 21.1, 21.3, 27.1, 118.1, 122.5, 124.7 (q, *J* 271), 126.9, 129.7

(q, J 3.8), 129.8, 131.4, 134.6 (q, J 33.6), 135.9, 141.6, 143.5, 143.6, 146.1.

**3fa/OTs:**<sup>[16]</sup> a colourless solid; mp 163–165°C.  $\nu_{max}$  (KBr)/cm<sup>-1</sup> 2969, 1601, 1568, 1530, 1468, 1350, 1343, 1312, 1300, 1192, 1132, 1043, 1005, 849, 816, 752, 734, 696.  $\delta_{\rm H}$  (CD<sub>3</sub>OD, 300 MHz) 2.34 (s, 3H), 2.35 (s, 3H), 2.63 (s, 6H), 6.39 (d, *J* 7.8, 2H), 7.24 (s, 2H), 7.62 (d, *J* 7.8, 2H), 8.09 (d, *J* 7.8, 2H), 8.24 (d, *J* 7.8, 2H).  $\delta_{\rm C}$  (CD<sub>3</sub>OD, 75 MHz) 21.1, 21.3, 27.1, 120.0, 122.6, 126.9, 127.5, 129.8, 131.5, 136.3, 141.7, 143.5, 143.7, 146.3, 151.3.

#### Compound Data for Scheme 4

**3aj/OTs**:<sup>[15b]</sup> an off-white solid; mp 165°C.  $v_{max}$  (KBr)/cm<sup>-1</sup> 3051, 1575, 1469, 1440, 1377, 1191, 1132, 1045, 1014, 991, 815, 746, 680.  $\delta_{\rm H}$  (CD<sub>3</sub>OD, 300 MHz) 2.33 (s, 3H), 2.49 (s, 3H), 7.03 (d, *J* 5.1, 1H), 7.19 (d, *J* 7.2, 2H), 7.46–7.49 (m, 2H), 7.59– 7.67 (m, 3H), 7.83 (d, *J* 5.1, 1H), 8.05 (d, *J* 7.8, 2H).  $\delta_{\rm C}$  (CD<sub>3</sub>OD, 75 MHz) 17.5, 21.3, 98.4, 118.4, 126.9, 129.8, 131.0, 133.0, 133.1, 133.4, 135.4, 137.7, 141.6, 150.0.

**3ak/OTs**: <sup>[15b]</sup> a colourless solid; mp 49°C.  $v_{max}$  (KBr)/cm<sup>-1</sup> 3045, 1562, 1469, 1438, 1373, 1330, 1191, 1130, 1043, 1014, 860, 815, 740, 692.  $\delta_{\rm H}$  (CD<sub>3</sub>OD, 300 MHz) 2.35 (s, 3H), 7.19–7.24 (m, 3H), 7.53 (t, *J* 7.8, 2H), 7.67 (d, *J* 7.8, 3H), 7.98 (d, *J* 5.7, 1H), 8.16 (d, *J* 7.8, 2H).  $\delta_{\rm C}$  (CD<sub>3</sub>OD, 75 MHz) 21.3, 119.2, 125.6, 126.9, 129.8, 132.1, 133.2, 133.9, 135.9, 139.8, 141.4, 141.7, 143.5.

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