One-Pot Synthesis and Conformational Analysis of 6-Membered Cyclic Iodonium Salts

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In this article we describe an efficient approach for the synthesis of cyclic diaryliodonium salts. The method is based on benzyl alcohols as starting materials and consists of an Friedel-Crafts-arylation/oxidation sequence. Besides a deep optimization, particular focusing on the choice and ratios of the utilized Bronsted-acids and oxidants, we explore the substrate scope of this transformation. We also discuss an interesting isomerism of cyclic iodonium salts substituted with aliphatic substituents at the bridge head carbon.

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Supporting Information

One-Pot Synthesis and Conformational Analysis of 6-Membered Cyclic Iodonium Salts

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1 General Information

Unless otherwise noted, all reactions were carried out under air. Reactions with chemicals sensitive to moisture or oxygen were carried out under a nitrogen atmosphere using standard Schlenk techniques. All chemicals were purchased from commercial suppliers and either used as received or purified according to "Purification of Laboratory Chemicals".^[1] Anhydrous tetrahydrofuran (THF) was obtained from an Inert PS-MD-6 solvent purification system. All other solvents were dried using standard methods if necessary.^[1]

Yields refer to isolated yields of compounds estimated to be > 95 % pure as determined by ¹H-NMR spectroscopy.

Thin layer chromatography was performed on fluorescence indicator marked precoated silica gel 60 plates (Macherey-Nagel, ALUGRAM Xtra SIL G/UV254) and visualized by UV light (254 nm/366 nm). Flash column chromatography was performed on silica gel (0.040 – 0.063 mm) with the solvents given in the procedures.

NMR spectra were recorded on a Bruker Avance DPX-200, a Bruker Avance 360WB spectrometer, a Bruker Avance Neo 600 MHz spectrometer with BBO probe head and a Bruker Avance Neo 600 MHz spectrometer with TXI probe head at 23 °C. Chemical shifts for ¹H-NMR spectra are reported as δ (parts per million) relative to the residual proton signal of CDCl₃ at 7.26 ppm (s), DMSO-*d*₆ at 2.50 ppm (quint) or MeOH-*d*₄ at 3.31 ppm (quint). Chemical shifts for ¹³C-NMR spectra are reported as δ (parts per million) relative to the signal of CDCl₃ at 77.0 ppm (t), DMSO-*d*₆ at 39.5 ppm (sept) or MeOH-*d*₄ at 49.0 ppm (sept). Chemical shifts for ¹⁹F-NMR spectra are reported as δ (parts per million) relative to the signal of Si(CH₃)₄ at 0.0 ppm. The following abbreviations are used to describe splitting patterns: br. = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet. Coupling constants *J* are given in Hz.

ESI and APCI mass spectra were recorded on an Advion Expression CMS^L via ASAP probe or direct inlet. Low resolution EI mass spectra were recorded on an Agilent 5977A Series GC/MSD system. High resolution (HR) EI mass spectra were recorded on a double focusing mass spectrometer ThermoQuest MAT 95 XL from Finnigan MAT. HR-ESI and HR-APCI mass spectra were recorded on a Bruker Impact II. All Signals are reported with the quotient from mass to charge *m/z*.

IR spectra were recorded on a Nicolet Thermo iS10 scientific spectrometer with a diamond ATR unit. The absorption bands $\tilde{\nu}$ are reported in cm⁻¹.

Melting points of solids were measured on a Büchi M-5600 Melting Point apparatus and are uncorrected. The measurements were performed with a heating rate of 2 °C/min and the melting point temperatures *T* are reported in °C.

Intensity data of suitable single crystals were collected on a Bruker Venture D8 diffractometer at 100 K with Mo-K α (0.71073 Å) radiation. All structures were solved by direct methods and refined based on F₂ by use of the SHELX program package as implemented in Olex 2.2 All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a rigid model. Figures were created using Olex2. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

2 Optimization of Reaction Conditions

2.1 Full Optimization Tables

2.1.1 Preliminary Method with *m*CPBA as Oxidant

Table S1: Preliminary optimization of the one-pot synthesis of 10*H*-dibenzo[*b,e*]iodinin-5-ium trifluoromethanesulfonate **7a**.

# ^a	TfOH (Eq.)	<i>m</i> CPBA (Eq.)	Solv. (0.1 M)	T / °C Step 1 / Step 2	Time Step 2	Yield (Purity ^b) / % (%)
1	2	1.1	1,2-DCE	80 / 0	2	79 (75 – 80)
2	3	1.1	1,2-DCE	rt / 0	2	79 (75 – 80)
3 ^c	3	1.1	DCM	rt / 0	2	68 (80 – 85)
4 ^{c,d}	3	1.1	DCM	rt / 0	---	---
5 ^c	3	1.1	DCM	0 / 0	2	76 (80 – 85)
6 ^c	3	1.5	DCM	0 / 0	1.5	75 (80 – 85)
7 ^e	3	1.5	DCM	0 / 0	1.5	85 (80 – 85)
8 ^{e,f}	3	1.5	DCM	0 / 0	1.5	64 (> 95)
9 ^{e,f}	3	1.5	DCM	0 / 0 – 40	1	65 (> 95)
10 ^{e,f}	2.5	1.5	DCM	0 / 0 – 40	1	66 (> 95)
11 ^{e,f}	3.5	1.5	DCM	0 / 0 – 40	1	60 (> 95)
12 ^{e,f,g}	2.5	1.5	DCM	0 / 0 – 40	1	73 (> 95)

^a All reactions were performed on a 0.1 mmol scale with benzene (10 eq.). in the given solvent (0.5 mL) were used in each of the reaction steps.

^b Approximate purity as molar fraction determined via ¹H-NMR spectroscopy.

^c Dropwise addition of *m*CPBA in DCM (0.5 mL) via syringe.

^d First addition of *m*CPBA in DCM and then TfOH in DCM.

^e Dropwise addition of *m*CPBA in 0.5 mL DCM via syringe-pump (rate: 50 μL/min).

^f Purification of the crude product via filtration over silica and washing with DCM/MeOH 25:1.

^g Dropwise addition of the benzylic alcohol in DCM (0.5 mL) to a solution of benzene in DCM (0.5 mL) via syringe pump (rate: 50 μL/min).

2.1.2 Preliminary Test Reactions for the Oxidation of 9a

Table S2: Optimization for the oxidation reaction of **9a** for the synthesis of 10H-dibenzo[b,e]iodinin-5-ium trifluoromethanesulfonate **7a**.

# ^a	[O] (Eq.)	HX (Eq.)	Solv. (c)	T / °C	Time / h	Yield ^b / %
1	mCPBA (1.2)	TfOH (2.5)	DCM (0.1 M)	rt	18	71
2	Oxone [®] (0.6)	TfOH (2.5)	DCM (0.1 M)	rt	18	57
3	K ₂ S ₂ O ₈ (1.2)	TfOH (2.5)	DCM (0.1 M)	rt	18	28
4	NaBO ₃ ·4H ₂ O (1.2)	TfOH (2.5)	DCM (0.1 M)	rt	18	8.3
5	Oxone [®] (0.6)	TfOH (2.5)	DCM (0.1 M)	0 – rt	18	20
6	Oxone [®] (1)	TfOH (2.5)	DCM (0.1 M)	0 – rt	18	39
7	Oxone [®] (1.5)	TfOH (2.5)	DCM (0.1 M)	0 – rt	18	26
8	Oxone [®] (1)	TfOH (2.5)	DCM/ACN (0.1 M)	rt	120	56
9	Oxone [®] (2)	TfOH (2.5)	DCM/ACN (0.1 M)	rt	18	Mult. Prods.
10	Oxone [®] (5)	TfOH (2.5)	DCM/ACN (0.1 M)	rt	18	Mult. Prods.
11	Oxone [®] (10)	TfOH (2.5)	DCM/ACN (0.1 M)	rt	18	15
12	Oxone [®] (1)	TfOH (3.5)	DCM/ACN (0.1 M)	rt	18	75
13	Oxone [®] (1)	TfOH (5)	DCM/ACN (0.1 M)	rt	18	91
14	Oxone [®] (2)	TfOH (5)	DCM/ACN (0.1 M)	rt	18	83
15	Oxone [®] (1)	H ₂ SO ₄ (5)	DCM/ACN (0.1 M)	rt	72	< 10
16	Oxone [®] (1)	HBf ₄ (5)	DCM/ACN (0.1 M)	rt	72	30
17	Oxone [®] (1)	HBf ₄ (5), H ₂ SO ₄ (5)	DCM/ACN (0.1 M)	rt	72	85
18	Oxone [®] (1)	TfOH (5), H ₂ SO ₄ (5)	DCM/ACN (0.1 M)	rt	2	92
19	Oxone [®] (1)	HBf ₄ (5), H ₂ SO ₄ (5)	DCM/ACN (0.1 M) ^c	rt – 40	24	4
20	Oxone [®] (1)	TfOH (5), H ₂ SO ₄ (5)	DCM/ACN (0.1 M) ^c	rt	1 – 2	87

^a All reactions were performed on a 0.2 mmol scale

^b Yield determined after isolation and purification of the product **7a**.

^c 5 % of TFE were added.

2.1.3 Final Method for Primary Alcohols with Oxone® as Oxidant

Table S3: Final optimization of the one-pot synthesis of 10H-dibenzo[b,e]iodinin-5-ium trifluoromethanesulfonate **7a**

# ^a	Benzene (Eq.)	HX (Eq.)	Solv. (c)	Time Step 1 / Step 2	Yield / %
1	benzene (3)	TfOH (5), H ₂ SO ₄ (5)	DCM/ACN (0.1 M)	5 min / 1.5 h	(39)
2	benzene (5)	TfOH (5), H ₂ SO ₄ (5)	DCM/ACN (0.1 M)	5 min / 1.5 h	77
3	benzene (10)	TfOH (5), H ₂ SO ₄ (5)	DCM/ACN (0.1 M)	5 min / 1.5 h	71
4 ^b	benzene (10)	TfOH (5), H ₂ SO ₄ (5)	DCM/ACN (0.1 M)	5 min / 1.5 h	89
5 ^{b, c}	benzene (10)	TfOH (5), H ₂ SO ₄ (5)	DCM (0.1 M)	5 min / 24 h	< 10
6 ^{b, d}	benzene (10)	TfOH (5), H ₂ SO ₄ (5)	ACN (0.1 M)	360 min / ---	0
7 ^b	benzene (10)	TfOH (5), H ₂ SO ₄ (5)	DCM/ACN/ HFIP ^e (0.1 M)	5 min / 1 h	89
8 ^b	benzene (10)	TfOH (3), H ₂ SO ₄ (5)	DCM/ACN (0.1 M)	5 min / 4 h	75
9 ^b	benzene (10)	TfOH (2), H ₂ SO ₄ (5)	DCM/ACN (0.1 M)	5 min / 4 h	53
10 ^b	benzene (10)	TfOH (1), H ₂ SO ₄ (5)	DCM/ACN (0.1 M)	3.5 h / 12 h	50
11 ^b	benzene (10)	TfOH (3), H ₂ SO ₄ (7.5)	DCM/ACN (0.1 M)	5 min / 4 h	81
12 ^b	benzene (10)	TfOH (3), H ₂ SO ₄ (10)	DCM/ACN (0.1 M)	5 min / 4 h	80
13 ^b	benzene (10)	TfOH (3), H ₂ SO ₄ (7.5)	DCM/ACN (0.1 M)	5 min / 2 h	(71)
14 ^b	benzene (10)	TfOH (5), H ₂ SO ₄ (7.5)	DCM/ACN (0.1 M)	5 min / 1.5 h	85
15 ^b	benzene (28)	TfOH (5), H ₂ SO ₄ (5)	DCM/ACN (0.1 M)	5 min / 2 h	90
16 ^b	benzene (5)	TfOH (5), H ₂ SO ₄ (5)	DCM/ACN (0.1 M)	5 min / 2 h	87 ^f
17 ^b	benzene (3)	TfOH (5), H ₂ SO ₄ (5)	DCM/ACN (0.1 M)	5 min / 1.3 h	92 ^f
18 ^{b, g}	benzene (28)	TfOH (5), H ₂ SO ₄ (5)	DCM/ACN (0.1 M)	5 min / 2 h	80
19 ^{b, h}	benzene (10)	TfOH (5), H ₂ SO ₄ (5)	DCM/ACN (0.1 M)	5 min / 2 h	93

Yields in parentheses indicate that the purity of the product was below 90 %

^a All reactions were performed on a 0.2 mmol scale with Oxone (2KHSO₅·KHSO₄·K₂SO₄, 1 eq.) in a tightly closed screw cap vial. Different colours in the table indicate that reagents were used in different steps of the reaction. **Step 1:** Acid A in solvent A (1 mL) with Nuc stirred at 0 °C. **Step 2:** Solvent B (1 mL) added, Acid B and Oxone added at 0 °C.

^b *o*-Iodobenzylalcohol was added dropwise in solvent (0.5 mL) to a solution of Nuc in solvent (0.5 mL).

^c No difference if H₂SO₄ is added before or after Oxone, very messy reaction in step 2.

^d No reaction in step 1.

^e HFIP (0.2 mL) in second step.

^f Purity between 90 and 95 %.

^g Open flask.

^h 5 mmol scale.

Table S4: Reoptimization for benzylic alcohols with electron-withdrawing groups.

# ^a	R	Deviation from standard condition	Yield / %
1	Br (5b)	---	57
2	Br	No H ₂ SO ₄ in step 2	52
3	Br	Addition of 0.2 mL HFIP in step 2	85
4	Br	TFA instead of MeCN	50
5	Br	2 mL MeCN in step 2	49
6	Br	Use of Pestled Oxone	78
7	Br	DCM instead of MeCN	< 5
8	Br	HFIP + Pestled Oxone	83
9 ^b	NO ₂ (5c)	---	40 – 50
10	NO ₂	40 °C in step 2, 2 nd eq. of Oxone after 16 h	35 – 45
11	NO ₂	40 °C, 2 eq. Oxone in step 2	27
12	NO ₂	# 10 with 7.5 eq. H ₂ SO ₄	30 – 40
13	NO ₂	# 10 with 10 eq. H ₂ SO ₄	27
14	NO₂	2nd eq. of Oxone and 5 eq. of H₂SO₄ after 16 h	84

^a Standard conditions: 0.2 mmol of alcohol **5** in DCM (1 mL) with benzene (10 eq.). Addition of TfOH (5 eq.) at 0 °C, stirring for 2 h (R = Br) or 5 h (R = NO₂), addition of MeCN (1 mL), H₂SO₄ (5 eq.) and Oxone (1 eq.). Stirring for 16 h at rt.

^b The standard conditions for R = NO₂ are identical to those in (a) with HFIP (0.2 mL) in step 2.

2.1.4 Preliminary Method for Secondary Alcohols with *m*CPBA as Oxidant

Table S5: Reoptimization for secondary benzylic alcohols with toluene.

# ^a	PhMe (eq.)	HBF ₄ (eq.) 1 st /2 nd step	[O] (eq.)	Deviation from standard condition	Yield / %
1 ^b	5	1 / 2	<i>m</i> CPBA (4)		97%
2	5	1 / 2	<i>m</i> CPBA (4)		67%
3	5	1 / 2	<i>m</i> CPBA (2)		83%
4 ^c	5	1 / 2	<i>m</i> CPBA (4)		53%
5 ^c	5	1 / 5	<i>m</i> CPBA (1)		58%
6 ^c	5	1 / 5	<i>m</i> CPBA (2)		70%
7 ^c	5	3 / 2	<i>m</i> CPBA (2)		81%
8 ^c	5	5 / 5	<i>m</i> CPBA (2)		82%
9 ^{bc}	3	3 / 2	<i>m</i> CPBA (1.5)		88%
10 ^c	3	3 / 2	<i>m</i> CPBA (1.5)		78%
11 ^c	3	3 / 3	<i>m</i> CPBA (1.5)		81%
12 ^c	3	5 / 0	<i>m</i> CPBA (1)		78%
13 ^c	3	5 / 0	<i>m</i> CPBA (2)		79%
14 ^{bc}	3	3 / 2	Oxone (1)	addition of H ₂ SO ₄ (2 eq.)	---
15 ^{bc}	3	3 / 5	Oxone (1)	addition of H ₂ SO ₄ (10 eq.)	50%
16 ^b	3	3 / 5	Oxone (1)	CH ₃ CN instead of DCM, addition of H ₂ SO ₄ (10 eq.)	22%
17 ^{bc}	3	3 / 0	Oxone (2)	addition of H ₂ SO ₄ (15 eq.)	8%

^a Standard conditions: 0.2 mmol of **5n** in 1 mL DCM with toluene (5 eq.). Addition of HBF₄·OEt₂ (1 eq.) at 0 °C, stirring till completion, addition of 1 mL MeCN, *m*CPBA, stirring for 10 min, addition of HBF₄·OEt₂ (2 eq.), stirring till completion at rt.

^b 0.1 mmol scale.

^c MeCN in the 2nd step.

3 Preparation of Starting Materials

3.1 General Procedures for the Synthesis of the Starting Materials

Scheme S1: General scheme for the synthesis of primary and secondary benzyl alcohol derivatives.

3.1.1 Sandmeyer-type Iodination of Anthranilic acids (GP1a)

In modification of a reported procedure,^[2] the anthranilic acid derivative (10.0 mmol, 1.00 eq.) and TsOH·H₂O (5.71 g, 30.0 mmol, 3.00 eq.) were suspended in MeCN (80 mL). The mixture was cooled to 10 – 15 °C. A solution of NaNO₂ (1.38 g, 20.0 mmol, 2.00 eq.) and KI (4.15 g, 25.0 mmol, 2.50 eq.) in H₂O (15 mL) was added dropwise over 1 h. After complete addition, the resulting dark coloured mixture stirred for another 1 h and then 1 N HCl (50 mL) and EtOAc (100 mL) were added. The phases were separated and the aqueous phases was extracted with EtOAc (2 x 50 mL). The combined organic phases were washed with water (50 mL), Na₂S₂O₃ (10 % w/w, 50 mL) and brine (20 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The residue was either purified by filtration over silica or by column chromatography.

3.1.2 Sandmeyer-type Iodination of Anthranilic acids (GP1b)

In modification of a reported procedure,^[3] the anthranilic acid derivative (10.0 mmol, 1.00 eq.) was suspended in aqueous H₂SO₄ (15 mL, 1:2 v/v) at 0 °C and MeOH (5 to 10 mL) was added until complete dissolution of the substrate. Then a solution of NaNO₂ (759 mg, 11.0 mmol, 1.10 eq.) in H₂O (2 mL) was added dropwise over 30 min. while maintaining a temperature between 0 and 5 °C. After complete addition the solution was stirred for further 60 min at 0 °C. Then the diazonium salt solution was added to a solution of KI (8.30 g, 50.0 mmol, 5.00 eq.) in H₂O (10 mL) at 60 °C over a period of 5 min. and stirred at that temperature for 1 h. Then 1 N HCl (50 mL) and EtOAc (100 mL) were added. The phases were separated and the aqueous phases was extracted with EtOAc (2 x 50 mL). The combined organic phases were washed with water (50 mL), Na₂S₂O₃ (10 % w/w, 50 mL) and brine (20 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The residue was either purified by filtration over silica or by column chromatography.

3.1.3 Borane-mediated Reduction of Carboxylic acids (GP2)

In modification of a reported procedure,^[4] the *o*-iodobenzoic acid derivative (**S1**, 1.00 eq.) was dissolved in dry THF (0.25M). After cooling to 0 °C, NaBH₄ (2.90 eq.) was added portion wise. To the resulting mixture I₂ (0.75 eq.) in THF (0.25M) was slowly added over 1 h. After the addition, the mixture was allowed to warm to rt and stirred overnight. After completion of the reaction, the mixture was cooled to 0 °C and water (1 mL/mmol) was carefully added. Afterwards, 3N HCl was slowly added until the solution was at pH 2 – 3. The resulting mixture was diluted with water (5 mL/mmol) and extracted with Et₂O (3 x 20 mL/mmol). The combined organic phases were washed with 1M Na₂CO₃ (2 x 20 mL/mmol) and brine (20 mL/mmol), dried over Na₂SO₄ and concentrated under reduced pressure to either give the desired product that could be purified (if necessary) by recrystallisation from cyclohexane or via a filtration column over silica in cyclohexane/ethyl acetate 4:1.

3.2 Synthesis of Starting Materials

3.2.1 Primary Benzyl Alcohols

The *o*-iodobenzoic acid derivatives **S1a**, **S1d** and **S1e** were commercially available and have been used as received for the synthesis of the corresponding alcohols.

(2-Iodophenyl)methanol (**5a**)

Following GP2, the reaction of *o*-iodobenzoic acid (**S1a**, 9.6 g, 200 mmol) with NaBH₄ (21.9 g, 580 mmol) and I₂ (38.1 g, 150 mmol) gave (2-iodophenyl)methanol (**5a**, 46.8 g, 200 mmol, quant.) as a colourless solid without further purification.

¹H-NMR (601 MHz, CDCl₃) δ = 7.83 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.46 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.37 (td, *J* = 7.5, 1.2 Hz, 1H), 7.00 (td, *J* = 7.6, 1.8 Hz, 1H), 4.68 (d, *J* = 6.3 Hz, 2H), 2.00 (t, *J* = 6.3 Hz, 1H). ¹³C-NMR

(151 MHz, CDCl₃) δ = 142.9, 139.5, 129.6, 128.8, 128.7, 97.7, 69.6. FTIR (ATR, neat) $\tilde{\nu}$ = 3262, 3061, 2887, 2843, 1434, 1321, 1195, 1033, 1009, 738. MS (EI, 70 eV) m/z = 234.0 [M]⁺. Mp T = 91. The analytical data is in accordance with literature data.^[5]

(5-Bromo-2-iodophenyl)methanol (5b)

o-Iodobenzoic acid (4.96 g, 20.0 mmol, 1.00 eq.) and *N*-bromosuccinimide (4.45 g, 25.0 mmol, 1.25 eq.) were suspended in H₂SO₄ (50 mL) and stirred for 2 h. The mixture was poured on ice (150 g). The resulting solid was collected by filtration and recrystallized from EtOH/H₂O (1:1, v/v) to obtain 5-bromo-2-iodobenzoic acid (**S1b**, 5.21 g, 15.9 mmol, 80 %) as a colourless solid.

¹H-NMR (360 MHz, CDCl₃) δ = 8.15 (d, J = 2.4 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.34 (dd, J = 8.4, 2.4 Hz, 1H). ¹³C-NMR (91 MHz, CDCl₃) δ = 169.9, 143.2, 136.6, 135.0, 134.5, 122.3, 92.8. FTIR (ATR, neat) $\tilde{\nu}$ = 3079, 1702, 1668, 1459, 1294, 1248, 1096, 1015, 898, 816, 776. HRMS (ESI-, MeOH) m/z = 324.82642. Calculated for C₇H₃BrIO₂: m/z = 324.83666. Mp T = 159 – 161. The analytical data is in accordance with literature data.^[6]

Following GP2, the reaction of 5-bromo-2-iodobenzoic acid (**S1b**, 1.63 g, 5.00 mmol) with NaBH₄ (549 mg, 14.5 mmol) and I₂ (952 mg, 3.75 mmol) gave after filtration over silica (cyclohexane/ethyl acetate 7:1) (5-bromo-2-iodophenyl)methanol (**5b**, 1.53 g, 4.87 mmol, 97 %) as a colourless solid.

¹H-NMR (360 MHz, CDCl₃) δ = 7.63 (d, J = 8.3 Hz, 1H), 7.61 (d, J = 1.9 Hz, 1H), 7.12 (dd, J = 8.3, 2.0 Hz, 1H), 4.61 (d, J = 6.0 Hz, 2H), 2.23 (t, J = 6.0, 6.0 Hz, 1H). ¹³C-NMR (91 MHz, CDCl₃) δ = 144.5, 140.3, 132.1, 131.1, 123.0, 94.6, 68.6. FTIR (ATR, neat) $\tilde{\nu}$ = 3206, 3076, 2908, 1435, 1387, 1190, 1089, 1005, 984, 878, 806. MS (EI, 70 eV) m/z = 311.9 [M]⁺, 233.0 [M-Br]⁺, 185.0 [M-I]⁺. Mp T = 107 – 109.

The analytical data is in accordance with literature data.^[7]

(2-Iodo-5-nitrophenyl)methanol (5c) and (2-Iodo-3-nitrophenyl)methanol (5c')

In modification of a reported procedure,^[3] nitric acid (7.4 mL, 10.1 g, 160 mmol, 8.00 eq.) was slowly added to H₂SO₄ (22.4 mL, 41.2 g, 420 mmol, 21 eq.) while maintaining a temperature between -10 and 0 °C. At this temperature, *o*-iodobenzoic acid (4.96 g,

20.0 mmol, 1.00 eq.) was added portionwise. The resulting mixture was stirred for 15 min, allowed to warm to rt and stirred for another 30 min and then heated to 135 °C for 1 h. After cooling to rt, the mixture was poured on ice (50 g) and the resulting solid was collected by filtration. The residue was dissolved in EtOAc (200 mL), washed with H₂O (50 mL), Na₂S₂O₃ (50 mL, w = 10 %), H₂O (50 mL), brine (50 mL), dried over Na₂SO₄ and concentrated under reduced pressure to give a 3:1 mixture of 2-iodo-5-nitro- (**S1c**) and 2-iodo-3-nitro-benzoic acid (**S1c'**, 5.46 g, 18.6 mmol, 93 %) as a yellow solid which was analysed via ¹H-NMR and used without further purification.

¹H-NMR (200 MHz, DMSO-*d*₆) δ = 8.40 (d, J = 2.7 Hz, 1H, **A**), 8.29 (d, J = 8.6 Hz, 1H, **A**), 8.00 (dd, J = 8.6, 2.8 Hz, 1H, **A**), 7.92 (dd, J = 7.8, 1.7 Hz, 1H, **B**), 7.78 (dd, J = 7.7, 1.7 Hz, 1H, **B**), 7.66 (dd, J = 7.7, 7.7 Hz, 1H, **B**). (3:1 mixture of **A** and **B**). The analytical data is in accordance with literature data.^[8]

Following GP2, the reaction of a 3:1 mixture of 2-iodo-5-nitrobenzoic acid (**S1c**) and 2-iodo-3-nitrobenzoic acid (**S1c'**) (2.49 g, 8.50 mmol) with NaBH₄ (933 mg, 24.7 mmol) and I₂ (1.62 g, 6.38 mmol) gave after separation of the isomers via column chromatography (silica, cyclohexane/ethyl acetate 10:1 → 4:1) (2-iodo-5-nitrophenyl)methanol (**5c**, 1.63 g, 5.85 mmol, 67 %) as a colourless solid and (2-iodo-3-nitrophenyl)methanol (**5c'**, 475 mg, 1.70 mmol, 20 %) as a yellow solid.

¹H-NMR (200 MHz, CDCl₃) δ = 8.18 (d, *J* = 2.7 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 7.81 (dd, *J* = 8.5, 2.8 Hz, 1H), 5.85 (t, *J* = 5.4 Hz, 1H), 4.45 (d, *J* = 5.1 Hz, 2H). **¹³C-NMR (50 MHz, CDCl₃)** δ = 147.8, 146.3, 139.9, 122.7, 121.0, 105.5, 66.8. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3202, 3091, 2906, 1601, 1567, 1516, 1335, 1193, 1043, 1014, 907, 806, 736. **MS (EI, 70 eV)** *m/z* = 279.0 [M]⁺, 232.9 [M-NO₂]⁺, 152.0 [M-I]⁺. **Mp** *T* = 120 – 122 °C. The analytical data is in accordance with literature data.^[9]

¹H-NMR (200 MHz, CDCl₃) δ = 7.72 – 7.64 (m, 1H), 7.55 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 4.73 (s, 2H), 2.59 (s, 1H). **¹³C-NMR (50 MHz, CDCl₃)** δ = 154.5, 145.9, 130.5, 129.1, 123.4, 88.1, 69.7. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3277, 3075, 2926, 1586, 1523, 1418, 1345, 1048, 1018, 789. **MS (EI, 70 eV)** *m/z* = 279.0 [M]⁺, 262.0 [M-OH]⁺, 231.9 [M-HNO₂]⁺. **Mp** *T* = 91 – 92 °C. The analytical data is in accordance with literature data.^[9]

(5-Fluoro-2-iodophenyl)methanol (**5d**)

Following GP2, the reaction of 5-fluoro-2-iodobenzoic acid (665 mg, 2.50 mmol) with NaBH₄ (274 mg, 7.25 mmol) and I₂ (476 mg, 1.88 mmol) gave after filtration over silica (cyclohexane/ethyl acetate 4:1) (5-fluoro-2-iodophenyl)methanol (**5d**, 577 mg, 2.19 mmol, 87 %) as a colourless solid.

¹H-NMR (601 MHz, CDCl₃) δ = 7.74 (dd, *J* = 8.6, 3.1 Hz, 1H), 7.25 (dd, *J* = 9.3, 3.1 Hz, 1H), 6.76 (td, *J* = 8.3, 3.1 Hz, 1H), 4.63 (d, *J* = 6.1 Hz, 2H), 2.07 (t, *J* = 6.1 Hz, 1H). **¹³C-NMR (151 MHz, CDCl₃)** δ = 163.1 (d, *J* = 247.8 Hz), 145.0 (d, *J* = 6.9 Hz), 140.1 (d, *J* = 7.6 Hz), 116.4 (d, *J* = 22.0 Hz), 115.5 (d, *J* = 23.4 Hz), 89.1 (d, *J* = 2.7 Hz), 68.8. **¹⁹F-NMR (565 MHz, CDCl₃)** δ = -113.4. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3286, 1578, 1458, 1437, 1356, 1263, 1149, 1058, 1013, 808. **HRMS (EI, 70 eV)** *m/z* 251.94426. Calculated for C₇H₆FO⁺: *m/z* 251.94419. **Mp** *T* = 111.5 – 113. The analytical data is in accordance with literature data.^[10]

(2-Iodo-5-(trifluoromethyl)phenyl)methanol (**5e**)

Following GP2, the reaction of 2-iodo-(5-trifluoromethyl)benzoic acid (790 mg, 2.50 mmol) with NaBH₄ (274 mg, 7.25 mmol) and I₂ (476 mg, 1.88 mmol) gave after filtration over silica (cyclohexane/ethyl acetate 4:1) (2-iodo-5-(trifluoromethyl)phenyl)methanol (**5e**, 682 mg, 2.25 mmol, 90 %) as a colourless solid.

¹H-NMR (601 MHz, CDCl₃) δ = 7.94 (d, *J* = 8.2 Hz, 1H), 7.76 – 7.75 (m, 1H), 7.31 – 7.21 (m, 1H), 4.72 (d, *J* = 6.0 Hz, 2H), 2.07 (t, *J* = 6.1 Hz, 1H). **¹³C-NMR (151 MHz, CDCl₃)** δ = 143.7, 139.6, 131.0 (q, *J* = 32.7 Hz), 125.5 (q, *J* = 3.5 Hz), 124.5 (q, *J* = 3.5 Hz), 122.1 (q, *J* = 272.8 Hz), 100.8, 68.8. **¹⁹F-NMR (565 MHz, CDCl₃)** δ = -62.9. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3289, 1600, 1465, 1324, 1256, 1175, 1118, 1044, 1009, 897, 829, 743. **HRMS (EI, 70 eV)** *m/z* = 301.94107. Calculated for C₈H₆F₃IO⁺: *m/z* 301.94100. **Mp** *T* = 80.5 – 81.5. The analytical data is in accordance with literature data.^[11]

(5-Chloro-2-iodophenyl)methanol (**5f**)

Following GP1a, the reaction of 2-amino-5-chlorobenzoic acid (1.72 g) gave 5-chloro-2-iodobenzoic acid (**S1f**, 2.22 g, 7.87 mmol, 79 %) as a colourless solid which still contained some impurities (≈ 5 %) but was used without further purification.

¹H-NMR (600 MHz, DMSO-*d*₆) δ = 13.61 (brs, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 2.6 Hz, 1H), 7.32 (dd, *J* = 8.4, 2.6 Hz, 1H). **¹³C-NMR (151 MHz, DMSO-*d*₆)** δ = 167.0, 142.1, 138.9, 133.2, 132.2, 129.5, 92.1. **FTIR (ATR, neat)** $\tilde{\nu}$ = 1694, 1673, 1574, 1400, 1290, 1246, 1117, 1017, 780, 749. **HRMS (ESI-, MeOH)** *m/z* = 280.88690 [M-H]⁻. Calculated for C₇H₃ClIO₂⁻: *m/z* = 280.88717. **Mp** *T* = 154 – 157. The analytical data is in accordance with literature data.^[12]

Following GP2, the reaction of 5-chloro-2-iodobenzoic acid (**S1f**, 1.41 g, 5.00 mmol) with NaBH₄ (549 mg, 14.5 mmol) and I₂ (952 mg, 3.75 mmol) gave after column chromatography (silica, cyclohexane/ethyl acetate 10:1) (5-chloro-2-iodophenyl)methanol (**5f**, 1.08 g, 4.01 mmol, 80 %) as a colourless solid.

¹H-NMR (601 MHz, CDCl₃) δ = 7.71 (d, *J* = 8.3 Hz, 1H), 7.48 (d, *J* = 2.5 Hz, 1H), 6.99 (dd, *J* = 8.3, 2.6 Hz, 1H), 4.63 (s, 2H), 2.10 (s, 1H). **¹³C-NMR (151 MHz, CDCl₃)** δ = 144.3, 140.0, 135.0, 129.2, 128.2, 93.6, 68.7. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3289, 3212, 1452, 1436, 1391, 1193, 1101, 1055, 1007, 974, 808. **MS (EI, 70 eV)** *m/z* = 268.0 [M]⁺, 233.9 [M-Cl]⁺, 141.0 [M-I]⁺ **Mp** *T* = 118 – 119.5. The analytical data is in accordance with literature data.^[7]

3-(Hydroxymethyl)-4-iodobenzonitrile (**5g**)

In modification of a reported procedure,^[3] 2-Amino-5-bromobenzoic acid (5.40 g, 25.0 mmol, 1 eq.) was dissolved in MeOH (100 mL). After addition of H₂SO₄ (6.00 mL, 5.00 mmol, 0.2 eq., 98 % v/v) the mixture was heated under reflux for 16 h. The mixture was concentrated under reduced pressure and sat. Na₂CO₃ (50 mL) and EtOAc (50 mL) were added. The phases were separated, the aqueous phase was extracted with EtOAc (3 x 50 mL) and the combined organic phases were dried over Na₂SO₄ and concentrated under reduced pressure. After purification of the residue by column chromatography (silica, cyclohexane/ethyl acetate 7:1 → 4:1) methyl 2-amino-5-bromobenzoate (3.80 g, 16.7 mmol, 66 %) was obtained as a colourless solid.

¹H-NMR (600 MHz, CDCl₃) δ = 7.96 (d, *J* = 2.4 Hz, 1H), 7.31 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.55 (d, *J* = 8.8 Hz, 1H), 5.75 (s, 2H), 3.86 (s, 3H). **¹³C-NMR (151 MHz, CDCl₃)** δ = 167.4, 149.3, 136.7, 133.4, 118.3, 112.0, 107.3, 51.7. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3454, 3355, 1948, 1683, 1625, 1558, 1442, 1296, 1236, 1082, 967, 824, 786. **MS (EI, 70 eV)** *m/z* = 229.0 [M]⁺, 197.0 [M-MeOH]⁺, 170.0 [M-COOMe]⁺ **Mp** *T* = 72 – 73. The analytical data is in accordance with literature data.^[13]

In a pressure vial methyl 2-amino-5-bromobenzoate (1.15 g, 5.00 mmol, 1.00 eq.) and CuCN (493 mg, 5.50 mmol, 1.10 eq.) were suspended in dry DMF (20 mL) and stirred for 4 h at 160 °C. Et₂O (50 mL) and 2N Na₂CO₃ (50 mL) were added and the phases were separated. The aqueous phase was extracted with Et₂O (2 x 50 mL) and the combined organic phases were washed with H₂O (6 x 10 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified via column chromatography (silica, cyclohexane/ethyl acetate 5:1 → 3:1) to obtain methyl 2-amino-5-cyanobenzoate (484 mg, 2.75 mmol, 55 %) as a slightly yellow solid.

¹H-NMR (600 MHz, CDCl₃) δ = 8.19 (d, *J* = 2.0 Hz, 1H), 7.45 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.67 (d, *J* = 8.7 Hz, 1H), 6.29 (s, 2H), 3.90 (s, 3H). **¹³C-NMR (151 MHz, CDCl₃)** δ = 167.1, 153.0, 136.9, 136.3, 119.3, 117.0, 110.5, 98.7, 52.1. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3465, 3359, 2212, 1708, 1629, 1591, 1550, 1439, 1263, 1188, 1077, 821. **MS (EI, 70 eV)** *m/z* = 176.1 [M]⁺, 144.1 [M-MeOH]⁺, 117.0 [M-COOMe]⁺ **Mp** *T* = 129 – 131. The analytical data is in accordance with literature data.^[14]

Following GP1a, methyl 2-amino-5-cyanobenzoate (317 mg, 1.80 mmol, 1.00 eq.) and TsOH·H₂O (1.03 g, 5.40 mmol, 3.00 eq.) were suspended in Acetonitrile (8 mL). The mixture was cooled to 10 – 15 °C. A solution of NaNO₂ (278 mg, 3.60 mmol, 2 eq.) and KI (747 mg, 4.50 mmol, 2.50 eq.) in H₂O (1 mL) was added dropwise over 1 h. After complete addition, the resulting dark coloured mixture was allowed to stir for another 1 h and then 1 N HCl (10 mL) and EtOAc (20 mL) were added. The phases were separated and the aqueous phases was extracted with EtOAc (2 x 20 mL). The combined organic phases were washed with water (50 mL), Na₂S₂O₃ (10 % w/w, 50 mL) and brine (20 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by filtration over silica (cyclohexane/ethyl acetate 4:1) to obtain methyl 5-cyano-2-iodobenzoate (401 mg, 1.39 mmol, 78 %) as a colourless solid.

¹H-NMR (600 MHz, CDCl₃) δ = 8.15 (d, *J* = 8.2 Hz, 1H), 8.07 (d, *J* = 2.0 Hz, 1H), 7.39 (dd, *J* = 8.2, 2.0 Hz, 1H), 3.97 (s, 3H). **¹³C-NMR (151 MHz, CDCl₃)** δ = 165.1, 142.6, 136.2, 134.7, 134.0, 117.3, 112.5, 100.4, 53.1. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3057, 2233, 1729, 1584, 1431, 1298, 1245, 1195, 1104, 1020, 973, 828. **HRMS (EI, 70 eV)** *m/z* = 286.94331 Calculated for C₉H₆INO₂⁺: *m/z* = 286.94378 **Mp** *T* = 119 – 121.

Methyl 5-cyano-2-iodobenzoate (345 mg, 1.20 mmol, 1.00 eq.) was dissolved in MeOH/THF (2:1 v/v, 10 mL) and at 0 °C NaBH₄ (454 mg, 12.0 mmol, 10 eq.) was added portionwise over 2 h and the suspension was stirred for 1 h. Et₂O (50 mL), H₂O (10 mL) and 1N HCl (10 mL) were added, the phases were separated and the aqueous phase was extracted with Et₂O (2 x 50 mL). The combined organic phases were dried over Na₂SO₄, concentrated under reduced pressure and purified via column chromatography (cyclohexane/ethyl acetate 10:1) to obtain 3-(hydroxymethyl)-4-iodobenzonitrile (**5g**, 127 mg, 0.490 mmol, 41 %).

¹H-NMR (600 MHz, DMSO-*d*₆) δ = 8.05 (d, *J* = 8.0 Hz, 1H), 7.75 (s, 1H), 7.48 (dd, *J* = 8.0, 1.6 Hz, 1H), 5.70 (s, 1H), 4.42 (s, 2H). **¹³C-NMR (151 MHz, DMSO-*d*₆)** δ = 145.8, 139.8, 131.6, 129.9, 118.6, 111.0, 103.6, 66.8. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3460, 2234, 1583, 1427, 1394, 1299, 1221, 1055, 1010, 891, 821. **MS (EI, 70 eV)** *m/z* = 259.0 [M]⁺. **Mp** *T* = 147 – 148.5.

(4-Bromo-2-iodophenyl)methanol (**5h**)

Following GP1a, the reaction of 2-amino-4-bromobenzoic acid (2.16 g) gave 4-bromo-2-iodobenzoic acid (**51h**, 2.21 g, 7.06 mmol, 71 %) as a colourless solid.

¹H-NMR (600 MHz, DMSO-*d*₆) δ = 13.47 (s, 1H), 8.19 (d, *J* = 1.8 Hz, 1H), 7.70 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 1H). **¹³C-NMR (151 MHz, DMSO)** δ = 167.4, 142.1, 136.0, 131.5, 131.2, 125.0, 95.7. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3064, 1672, 1422, 1291, 1542, 1291, 1249, 1023, 838, 771. **HRMS (ESI-, MeOH)** *m/z* = 324.83636 Calculated for C₇H₃BrIO₂⁻ *m/z* = 324.83666. **Mp** *T* = 175 – 177.

Following GP2, the reaction of 4-bromo-2-iodobenzoic acid (**S1h**, 1.63 g, 5.00 mmol) with NaBH₄ (549 mg, 14.5 mmol) and I₂ (952 mg, 3.75 mmol) gave after filtration over silica (cyclohexane/ethyl acetate 4:1) (4-bromo-2-iodophenyl)methanol (**5h**, 1.39 g, 4.44 mmol, 87 %) as a colourless solid.

¹H-NMR (600 MHz, CDCl₃) δ = 7.96 (d, *J* = 1.9 Hz, 1H), 7.50 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 4.62 (d, *J* = 5.6 Hz, 2H), 2.06 (t, *J* = 6.0 Hz, 1H). **¹³C-NMR (151 MHz, CDCl₃)** δ = 141.6, 140.9, 131.5, 129.3, 121.7, 97.3, 68.6. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3315, 3226, 1572, 1550, 1467, 1377, 1056, 1008, 801, 705. **HRMS (EI)** *m/z* = 311.86442 Calculated for C₇H₆BrIO⁺ *m/z* = 311.86413 **Mp** *T* = 104 – 105.

(3-Bromo-2-iodophenyl)methanol (**5i**)

Following GP1a, the reaction of 2-amino-3-bromobenzoic acid (2.16 g) gave 3-bromo-2-iodobenzoic acid (**S1i**, 1.25 g, 3.83 mmol, 38 %) as a colourless solid which still contained some impurities ($\approx$ 5 %) but was used without further purification.

¹H-NMR (601 MHz, DMSO-*d*₆) δ = 13.54 (brs, 1H), 7.82 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.46 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H). **¹³C-NMR (151 MHz, DMSO-*d*₆)** δ = 169.0, 142.9, 133.9, 131.3, 129.9, 127.0, 100.8. **FTIR (ATR, neat)** $\tilde{\nu}$ = 2864, 1675, 1567, 1407, 1390, 1281, 1249, 1199, 967, 750. **HRMS (ESI-, MeOH)** *m/z* = 324.83636. Calculated for C₇H₃BrIO₂⁻ *m/z* = 324.83666. The analytical data is in accordance with literature data.^[15]

Following GP2, the reaction of 3-bromo-2-iodobenzoic acid (**S1i**, 817 mg, 2.50 mmol) with NaBH₄ (274 mg, 7.25 mmol) and I₂ (476 mg, 1.88 mmol) gave after filtration over silica (cyclohexane/ethyl acetate 4:1) (3-bromo-2-iodophenyl)methanol (**5i**, 611 mg, 1.95 mmol, 78 %) as a colourless solid.

¹H-NMR (600 MHz, CDCl₃) δ = 7.61 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 4.73 (d, *J* = 6.3 Hz, 2H), 2.19 (t, *J* = 6.3 Hz, 1H). **¹³C-NMR (151 MHz, CDCl₃)** δ = 146.2, 131.7, 131.0, 129.5, 126.2, 104.1, 71.0. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3295, 1428, 1397, 1345, 1215, 1172, 1133, 1048, 980, 769. **HRMS (EI, 70 eV)** *m/z* = 311.86442 Calculated for C₇H₆BrIO⁺ *m/z* = 311.86413 **Mp** *T* = 110 – 112.

(3,5-Dichloro-2-iodophenyl)methanol (**5j**)

Following GP1a, the reaction of 2-amino-3,5-dichlorobenzoic acid (2.06 g) gave 3,5-dichloro-2-iodobenzoic acid (**S1j**, 1.39 g, 4.39 mmol, 44 %) as a colourless solid which still contained some impurities ($\approx$ 5 %) but was used without further purification.

¹H-NMR (600 MHz, DMSO-*d*₆) δ = 13.85 (s, 1H), 7.87 (d, *J* = 2.4 Hz, 1H), 7.57 (d, *J* = 2.4 Hz, 1H). **¹³C-NMR (151 MHz, DMSO-*d*₆)** δ = 167.7, 143.8, 140.3, 134.0, 129.8, 126.6, 96.8. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3070, 1693, 1547, 1418, 1367, 1281, 1242, 1156, 1019, 870, 819. **HRMS (ESI-, MeOH)** *m/z* = 314.84790. Calculated for C₇H₂Cl₂IO₂⁻ *m/z* = 314.84820. **Mp** *T* = 177 – 179.

Following GP2, the reaction of 3,5-dichloro-2-iodobenzoic acid (**S1j**, 792 mg, 2.50 mmol) with NaBH₄ (274 mg, 7.25 mmol) and I₂ (476 mg, 1.88 mmol) gave after filtration over silica (cyclohexane/ethyl acetate 4:1) (3,5-dichloro-2-iodophenyl)methanol (**5j**, 744 mg, 2.46 mmol, 98 %) as a colourless solid.

¹H-NMR (601 MHz, CDCl₃) δ = 7.44 – 7.41 (m, 1H), 7.41 – 7.38 (m, 1H), 4.66 (d, J = 6.1 Hz, 2H), 2.15 (t, J = 6.1 Hz, 1H). **¹³C-NMR (151 MHz, CDCl₃)** δ = 146.9, 139.8, 135.3, 127.8, 125.9, 98.0, 69.8. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3183, 2889, 1551, 1418, 1399, 1384, 1216, 1171, 1094, 1058, 1008, 858. **HRMS (EI, 70 eV)** m/z = 301.87562. Calculated for C₇H₅Cl₂IO⁺ m/z = 301.87567. **Mp** T = 95.5 – 97.

3.2.2 Derivatives of Primary Benzyl Alcohols

2-Iodobenzyl acetate (10)

o-Iodobenzylalcohol (**5a**, 585 mg, 2.50 mmol, 1.00 eq.) was dissolved in dry DCM (12.5 mL), cooled to 0 °C and triethylamine (520 μ L, 3.75 mmol, 1.5 eq.) and Ac₂O (295 μ L, 3.13 mmol, 1.25 eq.) were added. The solution was warmed up to rt overnight. Water (10 mL) was added. The phases were separated and the aqueous phase was extracted with DCM (2 x 15 mL). The combined organic phases were washed with brine (15 mL), dried over Na₂SO₄ and concentrated under reduced pressure. Column chromatography of the crude product (silica, cyclohexane/ethyl acetate 5:1) afforded the product (**10**, 636 mg, 2.30 mmol, 92 %) as a colourless liquid.

¹H-NMR (600 MHz, CDCl₃) δ = 7.86 (d, J = 7.9 Hz, 1H), 7.38 (dd, J = 7.6, 1.9 Hz, 1H), 7.35 (td, J = 7.4, 0.9 Hz, 1H), 7.03 (td, J = 7.6, 1.9 Hz, 1H), 5.13 (s, 2H), 2.15 (s, 3H). **¹³C-NMR (151 MHz, CDCl₃)** δ = 170.6, 139.5, 138.3, 129.8, 129.5, 128.3, 98.4, 70.1, 20.9. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3056, 2953, 1732, 1566, 1437, 1378, 1360, 1218, 1012, 746. **MS (EI, 70 eV)** m/z = 276.0 [M]⁺, 149.1 [M-I]⁺. The analytical data is in accordance with literature data.^[16]

1-Iodo-2-(methoxymethyl)benzene (11)

In modification of a reported procedure,^[17] *o*-iodobenzylalcohol (**5a**, 585 mg, 2.50 mmol, 1.00 eq.) was dissolved in dry DMF (12.5 mL). After cooling to 0 °C, NaH (200 mg, 5.00 mmol, 60 % w/w in mineral oil, 2.00 eq.) was added and the resulting suspension was stirred for 10 min. Iodomethane (311 μ L, 710 mg, 5.00 mmol, 2.00 eq.) was added and the cooling bath was removed. After stirring for 1 h at rt, triethylamine (1 mL) was added and the suspension was stirred for another 30 min. Water (15 mL) was added, the phases were separated and the aqueous phase was extracted with DCM (2 x 15 mL). The combined organic phases were washed with water (30 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by filtration over silica (cyclohexane/ethyl acetate 10:1) to obtain the product (**11**, 615 mg, 2.48 mmol, 99 %) as a colourless liquid that solidifies at 4 °C.

¹H-NMR (601 MHz, CDCl₃) δ = 7.83 (dd, J = 7.9, 0.9 Hz, 1H), 7.43 – 7.39 (m, 1H), 7.35 (td, J = 7.6, 1.0 Hz, 1H), 7.01 – 6.96 (m, 1H), 4.45 (s, 2H), 3.47 (s, 3H). **¹³C-NMR (151 MHz, CDCl₃)** δ = 140.4, 139.2, 129.1, 128.6, 128.2, 97.7, 78.3, 58.6. **FTIR (ATR, neat)** $\tilde{\nu}$ = 2921, 1565, 1437, 1378, 1193, 1116, 1099, 1013, 973, 744. **MS (EI, 70 eV)** m/z = 248.0 [M]⁺, 217.0 [M-OMe]⁺, 121.1 [M-I]⁺. The analytical data is in accordance with literature data.^[17]

Ethyl (2-iodobenzyl) carbonate (12)

o-Iodobenzylalcohol (**5a**, 585 mg, 2.50 mmol) was dissolved in dry DCM (12.5 mL) and at 0 °C, dry pyridine (303 μ L, 297 mg, 3.75 mmol, 1.5 eq.) and ClCOOEt (298 μ L, 339 mg, 3.13 mmol, 1.25 eq.) were added. The cooling bath was removed and the solution was allowed to stir at rt over night. After completion of the reaction, sat. NaHCO₃ (15 mL) was added. The phases were separated and the aqueous phase was extracted with DCM (2 x 15 mL). The combined organic phases were washed with water (30 mL), dried over Na₂SO₄, concentrated under reduced pressure and the residue was purified by filtration over silica (cyclohexane) to obtain ethyl (2-iodobenzyl) carbonate (**12**, 665 mg, 2.17 mmol, 87 %) as a colourless solid.

¹H-NMR (600 MHz, CDCl₃) δ = 7.85 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.42 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.35 (td, *J* = 7.5, 1.1 Hz, 1H), 7.03 (td, *J* = 7.7, 1.6 Hz, 1H), 5.19 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). **¹³C-NMR (151 MHz, CDCl₃)** δ = 154.8, 139.5, 137.8, 130.0, 129.3, 128.4, 98.0, 73.0, 64.3, 14.3. **FTIR (ATR, neat)** $\tilde{\nu}$ = 2994, 1734, 1438, 1381, 1365, 1282, 1259, 1013, 976, 789, 744. **HRMS (EI, 70 eV)** *m/z* = 305.97500. Calculated for [C₁₀H₁₁O₃I]⁺: *m/z* = 305.97474. **Mp** *T* = 27 – 28.

1-(Chloromethyl)-2-iodobenzene (13)

In modification of a reported procedure,^[18] *o*-Iodobenzylalcohol (**5a**, 1.87 g, 8.00 mmol) was dissolved in dry DCM (40 mL) and SOCl₂ (0.73 mL, 1.19 g, 10.0 mmol, 1.25 eq.) was added dropwise at 0 °C. After complete addition, the cooling bath was removed and the mixture was allowed to warm to rt and stirred over night. Sat. NaCl (50 mL) was added, the phases were separated and the aqueous phase was extracted with DCM (2 x 50 mL). The combined organic phases were concentrated under reduced pressure and the residue was purified via column chromatography (silica, cyclohexane) to obtain the product (**13**, 1.22 g, 4.83 mmol, 60 %) as a colourless liquid.

¹H-NMR (601 MHz, CDCl₃) δ = 7.87 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.49 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.36 (td, *J* = 7.6, 1.0 Hz, 1H), 7.01 (td, *J* = 7.7, 1.6 Hz, 1H), 4.68 (s, 2H). **¹³C-NMR (151 MHz, CDCl₃)** δ = 139.9, 139.8, 130.2, 130.1, 128.8, 99.5, 51.0. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3067, 2966, 1587, 1564, 1462, 1441, 1256, 1206, 1013, 759, 719. **MS (EI, 70 eV)** *m/z* = 252.0 [M]⁺. The analytical data is in accordance with literature data.^[18]

3.2.3 Secondary Benzyl Alcohols

2-Iodobenzaldehyde

o-Iodobenzylalcohol (**5a**, 24.9 g, 106 mmol, 1 eq.) was dissolved in CHCl₃ (265 mL), activated MnO₂ (92.4 g, 1.06 mol, 10 eq.) was added and the suspension was stirred for 24 h at rt. The mixture was filtrated over Celite and the filter material was washed with ethyl acetate (300 mL). After removal of the solvent under reduced pressure, 2-iodobenzaldehyde (21.9 g, 94.4 mmol, 89 %) was obtained as a colourless solid.

¹H-NMR (600 MHz, CDCl₃) δ = 10.07 (d, *J* = 0.7 Hz, 1H), 7.96 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.89 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.29 (ddd, *J* = 7.9, 7.4, 1.8 Hz, 1H). **¹³C-NMR (151 MHz, CDCl₃)** δ = 196.0, 140.8, 135.7, 135.2, 130.4, 128.9, 100.9. **FTIR (ATR, neat)** $\tilde{\nu}$ = 2849, 2833, 2746, 1683, 1578,

1436, 1388, 1261, 1200, 1015, 748. **MS (EI, 70 eV)** m/z = 232.0 $[M]^+$, 203.0 $[M-CHO]^+$. **Mp** T = 34–35 °C. The analytical data is in accordance with literature data.^[19]

1-(2-Iodophenyl)ethan-1-ol (5n)

To a solution of 2-iodobenzaldehyde (3.02 g, 13.0 mmol, 1 eq.) in dry THF (26 mL) at 0 °C MeMgBr (4.8 mL, 3M in THF, 14.3 mmol, 1.1 eq.) was added at a rate of 0.8 mL/min. The mixture was allowed to warm to rt over night and sat. NH_4Cl (10 mL) and Et_2O (10 mL) were added. The phases were separated and the aqueous phase was extracted with Et_2O (2 x 10 mL). The combined organic phases were dried over Na_2SO_4 , concentrated under reduced pressure and the residue was purified via column chromatography (silica, cyclohexane/ethyl acetate 1:0 $\rightarrow$ 10: 1) to obtain 1-(2-iodophenyl)ethan-1-ol (**5n**, 2.84 g, 8.38 mmol, 88 %) as a colourless liquid.

1H -NMR (600 MHz, $CDCl_3$) δ = 7.80 (dd, J = 7.9, 1.2 Hz, 1H), 7.57 (dd, J = 7.8, 1.7 Hz, 1H), 7.38 (td, J = 7.6, 1.3 Hz, 1H) 6.97 (td, J = 7.7, 1.8 Hz, 1H), 5.08 (qd, J = 6.4, 3.3 Hz, 1H), 1.96 (d, J = 3.3 Hz, 1H), 1.47 (d, J = 6.4 Hz, 3H). **^{13}C -NMR (151 MHz, $CDCl_3$)** δ = 147.6, 139.5, 129.3, 128.9, 126.5, 97.4, 73.9, 23.9. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3312, 3057, 2970, 2924, 1584, 1563, 1462, 1435, 1367, 1260, 1199, 1124, 1086, 1067, 1045, 1007, 897, 751, 720, 652. **MS (EI, 70 eV)** m/z = 248.0 $[M]^+$, 233.0 $[M-CH_3]^+$. The analytical data is in accordance with literature data.^[7]

1-(2-Iodophenyl)propan-1-ol (5o)

To a suspension of Mg turnings (153 mg, 6.30 mmol, 1.4 eq.) in dry THF (1 mL) bromoethane (0.40 mL, 5.40 mmol, 1.2 eq.) was slowly added so that the reaction starts and keeps refluxing mildly. After complete formation of the Grignard reagent, dry THF (3.5 mL) was added and the resulting solution was added to a solution of 2-iodobenzaldehyde (1.04 g, 4.50 mmol, 1 eq.) in dry THF (18 mL) at 0 °C over 15 min. The ice bath was removed and after 30 min. of stirring sat. NH_4Cl (7 mL) and Et_2O (20 mL) were added. The phases were separated and the aqueous phase was extracted with Et_2O (2 x 20 mL). The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified via column chromatography (silica, cyclohexane/ethyl acetate 10:1) to obtain 1-(2-iodophenyl)propan-1-ol (**5o**, 560 mg, 2.13 mmol, 47 %) as colourless solid.

1H -NMR (200 MHz, $CDCl_3$) δ = 7.80 (dd, J = 7.9, 1.2 Hz, 1H), 7.49 (dd, J = 7.8, 1.9 Hz, 1H), 7.36 (ddd, J = 7.8, 7.2, 1.3 Hz, 1H), 6.96 (td, J = 7.5, 1.9 Hz, 1H), 4.82 (dt, J = 7.5, 3.8 Hz, 1H), 2.16 (d, J = 2.9 Hz, 1H), 1.96 – 1.50 (m, 2H), 1.02 (t, J = 7.4 Hz, 3H). **^{13}C -NMR (50 MHz, $CDCl_3$)** δ = 146.6, 139.4, 129.2, 128.6, 127.1, 98.0, 78.7, 30.9, 10.3. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3284, 3059, 2968, 2918, 1560, 1460, 1426, 1351, 1339, 1277, 1249, 1196, 1126, 1099, 1057, 1008, 972, 870, 809, 750, 722, 672. **HRMS (EI, 70 eV)** m/z = 261.98518 Calculated for $C_9H_{11}OI^+$ m/z = 261.98491. **Mp** T = 40.4 – 42.4 °C.

1-(2-Iodophenyl)-2-methylpropan-1-ol (5p)

Dry $ZnCl_2$ (636 mg, 4.66 mmol, 1.01 eq.) was suspended in dry THF (4.6 mL) and $iPrMgCl \cdot LiCl$ (7.1 mL, 1.3M in THF, 9.20 mmol, 2 eq.) was added dropwise over 15 min and the resulting mixture was stirred for 1 h. After cooling to 0 °C, a solution of 2-iodobenzaldehyde (1.07 g, 4.60 mmol, 1 eq.) in dry THF (4.6 mL) was added over 30 min. The reaction was warmed to rt over night and sat. NH_4Cl (5 mL) and $EtOAc$ (5 mL) were added. The phases were separated and the aqueous phase was extracted with $EtOAc$ (2 x 5 mL). The combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure to obtain 1-(2-iodophenyl)-2-methylpropan-1-ol (**5p**, 1.19 g, 4.31 mmol, 94 %) as a colourless liquid.

¹H-NMR (200 MHz, CDCl₃) δ = 7.79 (dd, J = 7.9, 1.2 Hz, 1H), 7.41 (dd, J = 7.8, 2.1 Hz, 1H), 7.38 – 7.28 (m, 1H), 6.94 (ddd, J = 7.8, 6.9, 2.1 Hz, 1H), 4.67 (d, J = 5.6 Hz, 1H), 2.40 (s, 1H), 2.02 (dq, J = 13.4, 6.7 Hz, 1H), 0.97 (d, J = 2.3 Hz, 3H), 0.93 (d, J = 2.1 Hz, 3H). **¹³C-NMR (50 MHz, CDCl₃)** δ = 145.8, 139.3, 129.1, 128.3, 128.0, 98.7, 81.8, 34.1, 19.7, 16.6. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3370, 3058, 2958, 2871, 1584, 1562, 1460, 1384, 1364, 1197, 1173, 1132, 1094, 1003, 943, 747. **HRMS (EI, 70 eV)** m/z = 276.00047. Calculated for C₁₀H₁₃O⁺ m/z = 276.00056. **MS (EI, 70 eV)** m/z = 276.0 [M]⁺, 233.0 [M-C₃H₇]⁺. The analytical data is in accordance with literature data.^[7]

1-(5-Bromo-2-iodophenyl)ethan-1-ol (5q)

(5-Bromo-2-iodophenyl)methanol (**5b**, 939 mg, 3.00 mmol, 1.00 eq.) was dissolved in CH₃Cl (12 mL), activated MnO₂ (5.22 g, 60.0 mmol, 20.0 eq.) was added and the resulting suspension was stirred for 24 h. The mixture was filtered over silica, the filter material washed with EtOAc (100 mL) and the organic phase was concentrated under reduced pressure to obtain 5-bromo-2-iodobenzaldehyde (882 mg, 2.84 mmol, 95 %) as a colourless solid.

¹H-NMR (360 MHz, CDCl₃) δ = 9.98 (s, 1H), 7.98 (d, J = 2.5 Hz, 1H), 7.80 (d, J = 8.4 Hz, 1H), 7.41 (dd, J = 8.4, 2.5 Hz, 1H). **¹³C-NMR (91 MHz, CDCl₃)** δ = 194.3, 141.8, 138.2, 136.2, 133.0, 123.4, 98.3. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3071, 2849, 1682, 1564, 1477, 1449, 1374, 1248, 1187, 1007, 823. **MS (EI, 70 eV)** m/z = 309.9 [M]⁺, 280.8 [M-CHO]⁺, 181.9 [M-I]⁺. **Mp** T = 91.5 – 92.5 °C. The analytical data is in accordance with literature data.^[9]

5-Bromo-2-iodobenzaldehyde (622 mg, 2.00 mmol, 1 eq.) was dissolved in dry THF (10 mL), cooled to -10 °C and MeMgBr (0.80 mL, 3M in THF, 2.40 mmol, 1.2 eq.) was added dropwise over 10 min. The cooling bath was removed and the mixture stirred for 30 min. Sat. NH₄Cl (10 mL) and Et₂O (10 mL) were added, the phases separated and the aqueous phase was extracted with Et₂O (2 x 10 mL). The combined organic phases were dried over Na₂SO₄ and concentrated under reduced pressure to obtain 1-(5-bromo-2-iodophenyl)ethan-1-ol (**5q**, 644 mg, 1.97 mmol, 98 %) as a colourless solid.

¹H-NMR (360 MHz, CDCl₃) δ = 7.68 (d, J = 2.4 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H), 7.09 (dd, J = 8.4, 2.5 Hz, 1H), 4.98 (dq, J = 6.2, 1.4 Hz, 1H), 2.33 (d, J = 1.8 Hz, 1H), 1.42 (d, J = 6.4 Hz, 3H). **¹³C-NMR (91 MHz, CDCl₃)** δ = 149.5, 140.4, 132.1, 129.6, 123.2, 94.7, 73.3, 23.7. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3292, 2978, 1439, 1367, 1185, 1081, 1005, 900, 800. **MS (EI, 70 eV)** m/z = 325.9 [M]⁺, 310.9 [M-Me]⁺. **Mp** T = 57 – 58 °C

(2-Iodophenyl)(phenyl)methanol (5k)

To a suspension of Mg turnings (115 mg, 4.73 mmol, 1.05 eq.) in dry Et₂O (1 mL) iodobenzene (0.56 mL, 4.95 mmol, 1.1 eq.) was slowly added so that the reaction starts and keeps refluxing mildly. After complete formation of the Grignard reagent, dry Et₂O (5 mL) was added and the resulting solution was added to a solution of 2-iodobenzaldehyde (1.04 g, 4.50 mmol, 1 eq.) in dry Et₂O (10 mL) at 0 °C over 15 min. The ice bath was removed and after 30 min. of stirring sat. NH₄Cl (10 mL) and EtOAc (10 mL) were added. The phases were separated and the aqueous phase was extracted with Et₂O (3 x 10 mL). The combined organic phases were dried over Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified via column chromatography (silica, cyclohexane/ethyl acetate 20:1) to obtain (2-iodophenyl)(phenyl)methanol (**5k**, 829 mg, 2.67 mmol, 59 %) as colourless liquid.

¹H-NMR (200 MHz, CDCl₃) δ = 7.84 (dd, J = 7.9, 1.2 Hz, 1H), 7.53 (dd, J = 7.8, 1.8 Hz, 1H), 7.49 – 7.24 (m, 6H), 7.00 (td, J = 7.7, 1.8 Hz, 1H), 6.06 (d, J = 3.6 Hz, 1H), 2.49 (dd, J = 3.7, 1.1 Hz, 1H). **¹³C-NMR (50 MHz, CDCl₃)** δ = 145.4, 142.2, 139.6, 129.5, 128.7, 128.6, 128.5, 127.9, 127.3, 98.8, 79.1. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3320, 3059, 3028, 1584, 1562, 1493, 1452, 1435, 1181, 1114, 1077, 1006, 916, 849, 918, 746, 697, 669. **MS (EI, 70 eV)** m/z = 310.0 [M]⁺. The analytical data is in accordance with literature data.^[20]

(3,5-Bis(trifluoromethyl)phenyl)(2-iodophenyl)methanol (5I)

3,5-Bis(trifluoromethyl)bromobenzene (806 mg, 2.75 mmol, 1.1 eq.) was dissolved in dry THF (20 mL) and cooled to -78 °C. *n*BuLi (1.1 mL, 2.5M in hexanes, 2.75 mmol, 1.1 eq.) was added dropwise over 10 min and the solution was stirred for 10 min. 2-Iodobenzaldehyde (580 mg, 2.50 mmol, 1.00 eq.) in dry THF (10 mL) was added dropwise over 30 min. via syringe pump. After complete addition the mixture was slowly warmed to rt. Sat. NH₄Cl (50 mL) and Et₂O (50 mL) were added, the phases were separated and the aqueous phase was extracted with Et₂O (2 x 50 mL). The combined organic phases were washed with brine (20 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified via column chromatography (cyclohexane/ethyl acetate 30:1) to obtain (3,5-bis(trifluoromethyl)phenyl)(2-iodophenyl)methanol (**5I**, 640 mg, 1.44 mmol, 57 %) as a yellow oil.

¹H-NMR (600 MHz, CDCl₃) δ = 7.91 (s, 2H), 7.89 (d, J = 8.0 Hz, 1H), 7.81 (s, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.37 (d, J = 7.7 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.22 (d, J = 3.1 Hz, 1H), 2.54 (d, J = 3.4 Hz, 1H). **¹³C-NMR (151 MHz, CDCl₃)** δ = 144.6, 144.2, 139.9, 131.7 (q, J = 33.3 Hz), 130.3, 129.2, 128.4, 127.5 – 126.4 (m), 123.3 (q, J = 272.9 Hz), 121.7 – 121.6 (m), 98.6, 77.9. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3289, 1374, 1274, 1165, 1123, 1010, 899, 844, 741, 705. **MS (EI, 70 eV)** m/z = 446.1 [M]⁺, 427.0 [M-F]⁺, 377.0 [M-CF₃]⁺. The analytical data is in accordance with literature data.^[21]

(5-Chloro-2-iodophenyl)(2-fluorophenyl)methanol (5m)

Following GP1a, (2-amino-5-chlorophenyl)(2-fluorophenyl)methanone (1.25 g, 5.00 mmol, 1.00 eq.) and TsOH·H₂O (2.85 g, 15.0 mmol, 3.00 eq.) were suspended in Acetonitrile (40 mL). The mixture was cooled to 10 – 15 °C and a solution of NaNO₂ (690 mg, 10.0 mmol, 2.00 eq.) and KI (2.08 g, 12.5 mmol, 2.50 eq.) in H₂O (6 mL) was added dropwise over 1 h. After complete addition, the resulting dark coloured mixture was allowed to stir for another 1 h and then 1 N HCl (25 mL) and EtOAc (50 mL) were added. The phases were separated and the aqueous phases was extracted with EtOAc (2 x 50 mL). The combined organic phases were washed with water (25 mL), Na₂S₂O₃ (10 % w/w, 25 mL) and brine (20 mL), dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (cyclohexane/ethyl acetate 50:1) to obtain (5-chloro-2-iodophenyl)(2-fluorophenyl)methanone (1.37 g, 3.81 mmol, 76 %).

¹H-NMR (360 MHz, CDCl₃) δ = 7.82 (d, J = 8.4 Hz, 1H), 7.77 (td, J = 7.6, 7.6, 1.7 Hz, 1H), 7.64 – 7.53 (m, 1H), 7.30 (d, J = 2.4 Hz, 1H), 7.27 (t, J = 7.6, 7.6 Hz, 1H), 7.15 (dd, J = 8.4, 2.5 Hz, 1H), 7.13 – 7.08 (m, 1H). **¹³C-NMR (91 MHz, CDCl₃)** δ = 192.6, 161.7 (d, J = 259 Hz), 146.3, 141.0, 135.6 (d, J = 9.0 Hz), 134.6, 131.9, 131.6, 128.5 (d, J = 1.1 Hz), 124.6 (d, J = 3.6 Hz), 124.4 (d, J = 10.2 Hz), 116.8 (d, J = 22.0 Hz), 88.7 (d, J = 1.2 Hz). **FTIR (ATR, neat)** $\tilde{\nu}$ = 3071, 1669, 1606, 1478, 1450, 1372, 1288, 1096, 944, 750. **HRMS (EI, 70 eV)** m/z = 359.92118 [M]⁺. Calculated for [C₁₃H₇OClFI]⁺: m/z = 359.92087. **Mp** T = 90 – 91.

(5-Chloro-2-iodophenyl)(2-fluorophenyl)methanone (721 mg, 2.00 mmol, 1.00 eq.) was dissolved in MeOH (4 mL) and at 0 °C NaBH₄ (37.8 mg, 1.00 mmol, 0.500 eq.) was added. After stirring for 30 min Et₂O (20 mL) and brine (5 mL) were added. The phases were separated, the aqueous phase was extracted with Et₂O (3 x 20 mL) and the combined organic phases were dried over Na₂SO₄ and concentrated under reduced pressure, to obtain (5-chloro-2-iodophenyl)(2-fluorophenyl)methanol (**5m**, 712 mg, 1.96 mmol, 98%) as a slightly yellow oil

¹H-NMR (200 MHz, CDCl₃) δ = 7.75 (d, J = 8.4 Hz, 1H), 7.55 (d, J = 2.6 Hz, 1H), 7.42 – 7.26 (m, 1H), 7.23 – 7.07 (m, 3H), 7.03 (dd, J = 8.4, 2.6 Hz, 1H), 6.20 (d, J = 3.5 Hz, 1H), 2.83 (d, J = 3.7 Hz, 1H). **¹³C-NMR (50 MHz, CDCl₃)** δ = 160.6 (d, J = 248.0 Hz), 145.6, 140.5, 134.9, 129.9 (d, J = 8.3 Hz), 129.6, 128.5, 128.4, 128.1 (d, J = 16.1 Hz), 124.3 (d, J = 3.5 Hz), 115.5 (d, J = 21.4 Hz), 95.2, 73.0 (d, J = 3.2 Hz). **FTIR (ATR, neat)** $\tilde{\nu}$ = 3264, 1614, 1586, 1487, 1452, 1385, 1227, 1093, 1007, 900, 807, 754. **HRMS (EI, 70 eV)** m/z = 361.93641 [M]⁺. Calculated for [C₁₃H₉OClFI]⁺: m/z = 361.93652.

4 Substrate synthesis

4.1 General Procedures for the One-Pot Reaction Utilizing Primary Benzyl Alcohols and Secondary Aromatic Benzyl Alcohols (OPP1)

4.1.1 Standard conditions (OPP1a)

The arene **6** (600 μ mol – 6.00 mmol, 3.00 – 30.0 eq.) was dissolved in DCM (0.5 mL) in a screw cap vial, cooled to 0 °C and TfOH (87.8 μ L, 150 mg, 1.00 mmol, 5.00 eq.) was added. To this solution, *o*-iodobenzylalcohol derivative **5** (200 μ mol, 1 eq.) in DCM (0.5 mL) was added by slowly rinsing it down the wall of the glass vial within one minute. If the alcohol **5** could not be dissolved in DCM it was added as solid in one portion. After complete consumption of **5**, MeCN (1 mL) and H₂SO₄ (53.3 μ L, 98.1 μ g, 1.00 mmol, 5.00 eq.) were added. Then Oxone® (123 mg, 200 μ mol, 1.00 eq.) was added in one portion, the vial was tightly closed and the suspension was stirred at room temperature for the indicated time. After completion of the reaction DCM (5 mL) and water (5 mL) were added and the phases were separated. The aqueous phase was extracted with DCM (2 x 5 mL) and the combined organic phases were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was washed with EtOAc/Cy (1:4) (2 x 2 mL), dried under reduced pressure and then washed with water (2 x 2 mL) to obtain the product after lyophilization.

4.1.2 Conditions for benzyl alcohols with electron withdrawing groups (OPP1b)

With benzyl alcohols carrying electron withdrawing groups, the oxidation may not be completed under the conditions described in OPP1a. In this case 0.2 mL of 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) is added just before addition of Oxone.

4.1.3 Conditions for benzyl alcohols with electron withdrawing groups (OPP1c)

When utilizing benzylalcohols with more strongly electron withdrawing groups, one equivalent of Oxone® may not be sufficient to complete the oxidation in the second step of the reaction, i.e. for example with NO₂-groups. In these cases, after 16 h reaction time in the oxidation step a second equivalent of Oxone® (123 mg, 200 µmol, 1.00 eq.) was added and the mixture was stirred for another 24 h.

4.2 Substrates from Primary Benzyl Alcohols and Secondary Aromatic Benzyl Alcohols

10*H*-Dibenzo[*b,e*]iodinin-5-ium trifluoromethanesulfonate (**7a**)

Following OPP1a, the reaction of *o*-iodobenzylalcohol (**5a**, 46.8 mg) with benzene (178 µL, 156 mg, 2.00 mmol, 10 eq.) gave after 5 min for the first reaction step and 2 h for the second reaction step the product **7a** (78.6 mg, 0.178 mmol, 89 %) as a colourless solid.

Upscaled reaction:

Benzene (**6a**, 4.44 mL, 3.91 g, 50.0 mmol, 10.0 eq.) was dissolved in DCM (12.5 mL) in a pressure vial, cooled to 0 °C and TfOH (2.19 mL, 3.75 g, 25.0 mmol, 5.00 eq.) was added. To this solution, *o*-iodobenzylalcohol (1.17 g, 5.00 mmol, 1.00 eq.) in DCM (12.5 mL) was added dropwise via a syringe within 5 min. After complete consumption of the substrate (5 min), MeCN (25 mL) and H₂SO₄ (1.33 mL, 2.45 g, 25.0 mmol, 5.00 eq.) were added. Then Oxone (3.07 g, 5.0 mmol, 1.00 eq.) was added in one portion, the vial was tightly closed and the suspension was stirred at room temperature for 2 h. After completion of the reaction, DCM (25 mL) and water (25 mL) were added and the phases were separated. The aqueous phase was extracted with DCM (2 x 25 mL) and the combined organic phases were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was washed with an EtOAc/Cy 1:4 mixture (3 x 10 mL), and dried under reduced pressure to obtain the product (2.06 g, 4.66 mmol, 93 %) as a colourless solid.

At this stage, the product was already sufficiently pure as estimated by NMR. To test the general procedure in a larger scale, the product was washed with water (3 x 10 mL) and lyophilized. To remove the water completely, the product had to be heated to 50 °C for 1 h at a pressure of approx. 0.1 mbar on the larger scale. No significant increase in purity was observed and the product was again obtained as a colourless solid (1.94 g, 4.39 mmol, 88 %).

Reaction with derivatives of *o*-iodobenzylalcohol:

Following OPP1a, the reaction of *o*-iodobenzylacetate (**10**, 55.2 mg) with benzene (178 µL, 156 mg, 2.00 mmol, 10 eq.) gave after 5 min for the first reaction step and 2 h for the second reaction step the product **7a** (76.6 mg, 0.173 mmol, 87 %) as a colourless solid.

Following OPP1a, the reaction of 1-iodo-2-(methoxymethyl)benzene (**11**, 49.6 mg) with benzene (178 µL, 156 mg, 2.00 mmol, 10 eq.) gave after 5 min for the first reaction step and 2 h for the second reaction step the product **7a** (70.2 mg, 0.159 mmol, 79 %) as a colourless solid.

Following OPP1a, the reaction of ethyl (2-iodobenzyl) carbonate (**12**, 61.2 mg) with benzene (178 μ L, 156 mg, 2.00 mmol, 10 eq.) gave after 5 min for the first reaction step and 2 h for the second reaction step the product **7a** (78.3 mg, 0.177 mmol, 89 %) as a colourless solid.

Following OPP1a, the reaction of *o*-iodobenzylchloride (**13**, 50.5 mg) with benzene (178 μ L, 156 mg, 2.00 mmol, 10 eq.) gave after 5 min. for the first reaction step and 2 h for the second reaction step a complex product mixture that contained **7a** in less than 10 % yield.

¹H-NMR (601 MHz, DMSO-*d*₆) δ = 8.10 (dd, *J* = 8.1, 1.2 Hz, 2H), 7.81 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.61 (td, *J* = 7.5, 1.2 Hz, 2H), 7.43 (td, *J* = 7.7, 1.6 Hz, 2H), 4.32 (s, 2H). **¹³C-NMR (151 MHz, DMSO-*d*₆)** δ = 138.9, 133.7, 131.8, 130.5, 129.1, 120.7 (q, *J* = 322.7 Hz), 116.0, 45.7. **¹⁹F-NMR (565 MHz, DMSO-*d*₆)** δ = -77.7. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3094, 3059, 1457, 1441, 1426, 1237, 1220, 1152, 1023, 751. **HRMS (ESI⁺, MeOH)** *m/z* = 292.98209 [M-OTf]⁺. Calculated for [C₁₃H₁₀I]⁺: *m/z* = 292.98217. **Mp** *T* = 219 – 221 °C (decomp.). The analytical data is in accordance with literature data.^[22]

2-Bromo-10*H*-dibenzo[*b,e*]iodinin-5-ium trifluoromethanesulfonate (**7b**)

Following OPP1b, the reaction of (5-bromo-2-iodophenyl)methanol (**5b**, 62.6 mg) with benzene (178 μ L, 156 mg, 2.00 mmol, 10 eq.) gave after 15 min for the first reaction step and 16 h for the second reaction step the product **7b** (88.3 mg, 0.169 mmol, 85 %) as a colourless solid.

¹H-NMR (601 MHz, DMSO-*d*₆) δ = 8.11 – 8.07 (m, 2H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.76 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.66 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.62 (td, *J* = 7.5, 1.2 Hz, 1H), 7.44 (td, *J* = 7.7, 1.6 Hz, 1H), 4.33 (s, 2H). **¹³C-NMR (151 MHz, DMSO-*d*₆)** δ = 141.6, 138.4, 135.3, 133.6, 132.9, 131.9, 131.7, 130.7, 129.2, 125.4, 120.7 (q, *J* = 322.3 Hz), 116.2, 114.9, 45.0. **¹⁹F-NMR (565 MHz, DMSO-*d*₆)** δ = -77.7. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3094, 1457, 1392, 1273, 1231, 1220, 1170, 1021, 992, 755. **HRMS (ESI⁺, MeOH)** *m/z* = 370.89224 [M-OTf]⁺. Calculated for [C₁₃H₉Br]⁺: *m/z* = 370.89268. **Mp** *T* = 210 – 215.

2-Nitro-10*H*-dibenzo[*b,e*]iodinin-5-ium trifluoromethanesulfonate (**7c**)

Following OPP1c, the reaction of (5-nitro-2-iodophenyl)methanol (**5c**, 55.8 mg) with benzene (178 μ L, 156 mg, 2.00 mmol, 10 eq.) gave after 5 h for the first reaction step and a total of 40 h for the second reaction step the product **7c** (81.7 mg, 0.168 mmol, 84 %) as a colourless solid.

¹H-NMR (601 MHz, DMSO-*d*₆) δ = 8.67 (d, *J* = 2.7 Hz, 1H), 8.36 (d, *J* = 8.8 Hz, 1H), 8.25 (dd, *J* = 8.8, 2.7 Hz, 1H), 8.11 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.81 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.64 (td, *J* = 7.5, 1.2 Hz, 1H), 7.46 (td, *J* = 7.8, 1.6 Hz, 1H), 4.52 (s, 2H). **¹³C-NMR (151 MHz, DMSO-*d*₆)** δ = 149.5, 141.4, 138.2, 135.2, 133.7, 132.0, 130.7, 129.4, 124.5, 123.4, 122.9, 120.7 (q, *J* = 322.5 Hz), 116.3, 45.0. **¹⁹F-NMR (565 MHz, DMSO-*d*₆)** δ = -77.7. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3086, 1537, 1344, 1275, 1224, 1166, 1025, 997, 818, 762. **HRMS (ESI⁺, MeOH)** *m/z* = 337.96690 [M-OTf]⁺. Calculated for [C₁₃H₉NO₂]⁺: *m/z* = 337.96725. **Mp** *T* = 215 – 220 (decomp.).

2-Fluoro-10*H*-dibenzo[*b,e*]iodinin-5-ium trifluoromethanesulfonate (**7d**)

Following OPP1b, the reaction of (5-fluoro-2-iodophenyl)methanol (**5d**, 50.4 mg) with benzene (178 μ L, 156 mg, 2.00 mmol, 10 eq.) gave after 20 min for the first reaction step and 16 h for the second reaction step the product **7d** (67.9 mg, 0.148 mmol, 74 %) as a colourless solid.

¹H-NMR (601 MHz, DMSO-*d*₆) δ = 8.12 (dd, *J* = 8.9, 5.3 Hz, 1H), 8.09 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.77 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.74 (dd, *J* = 9.3, 3.0 Hz, 1H), 7.62 (td, *J* = 7.5, 1.2 Hz,

1H), 7.44 (ddd, $J = 8.2, 7.4, 1.6$ Hz, 1H), 7.36 (td, $J = 8.7, 3.0$ Hz, 1H), 4.34 (s, 2H). **$^{13}\text{C-NMR}$ (151 MHz, DMSO- d_6)** $\delta = 163.8$ (d, $J = 249.8$ Hz), 142.2 (d, $J = 8.8$ Hz), 138.4, 135.7 (d, $J = 9.0$ Hz), 133.6, 131.8, 130.6, 129.2, 120.7 (q, $J = 322.3$ Hz), 117.6 (d, $J = 23.6$ Hz), 116.3 (d, $J = 24.2$ Hz), 116.2, 110.1 (d, $J = 2.4$ Hz), 45.3. **$^{19}\text{F-NMR}$ (565 MHz, DMSO- d_6)** $\delta = -77.7, -109.3$ (td, $J = 8.8, 5.3$ Hz). **FTIR (ATR, neat)** $\tilde{\nu} = 3098, 1573, 1460, 1272, 1220, 1173, 1021, 998, 817, 758$. **HRMS (ESI $^+$, MeOH)** $m/z = 310.97245$ [M-OTf] $^+$. Calculated for [C₁₃H₉IF] $^+$: 310.97275. **Mp** $T = 225 - 230$ (decomp.). The analytical data is in accordance with literature data.^[22]

2-(Trifluoromethyl)-10H-dibenzo[*b,e*]iodinin-5-ium trifluoromethanesulfonate (7e)

Following OPP1b, the reaction of (2-iodo-5-(trifluoromethyl)phenyl)methanol (**5e**, 60.4 mg) with benzene (178 μL , 156 mg, 2.00 mmol, 10 eq.) gave after 2 h for the first reaction step and 16 h for the second reaction step the product **7e** (60.1 mg, 0.118 mmol, 59 %) as a colourless solid.

Following OPP1c, the reaction of (2-iodo-5-(trifluoromethyl)phenyl)methanol (**5e**, 60.4 mg) with benzene (178 μL , 156 mg, 2.00 mmol, 10 eq.) gave after 2 h for the first reaction step and a total of 40 h for the second reaction step the product **7e** (67.0 mg, 0.131 mmol, 69 %) as a colourless solid.

$^1\text{H-NMR}$ (601 MHz, DMSO- d_6) $\delta = 8.32$ (d, $J = 8.4$ Hz, 1H), 8.23 (d, $J = 2.2$ Hz, 1H), 8.11 (dd, $J = 8.1, 1.2$ Hz, 1H), 7.83 (dd, $J = 8.6, 2.2$ Hz, 1H), 7.79 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.63 (td, $J = 7.5, 1.2$ Hz, 1H), 7.46 (ddd, $J = 8.2, 7.4, 1.6$ Hz, 1H), 4.45 (s, 2H). **$^{13}\text{C-NMR}$ (151 MHz, DMSO- d_6)** $\delta = 140.7, 138.3, 134.9, 133.7, 131.9, 131.6$ (q, $J = 32.6$ Hz), 130.7, 129.3, 126.8 (q, $J = 3.2$ Hz), 125.5 (d, $J = 3.1$ Hz), 124.4 (q, $J = 272.9$ Hz), 121.8 (q, $J = 322.3$ Hz), 120.7, 116.1, 45.2. **$^{19}\text{F-NMR}$ (565 MHz, DMSO- d_6)** $\delta = -61.4, -77.7$. **FTIR (ATR, neat)** $\tilde{\nu} = 3086, 1415, 1331, 1270, 1241, 1222, 1167, 1119, 1023, 826, 762, 747$. **HRMS (ESI $^+$, MeOH)** $m/z = 360.96921$ [M-OTf] $^+$. Calculated for [C₁₄H₉F₃I] $^+$: $m/z = 360.96955$. **Mp** $T = 179 - 181$.

2-Chloro-10H-dibenzo[*b,e*]iodinin-5-ium trifluoromethanesulfonate (7f)

Following OPP1b, the reaction of (5-chloro-2-iodophenyl)methanol (**5f**, 63.7 mg) with benzene (178 μL , 156 mg, 2.00 mmol, 10 eq.) gave after 15 min for the first reaction step and 16 h for the second reaction step the product **7f** (55.2 mg, 0.116 mmol, 58 %) as a colourless solid.

$^1\text{H-NMR}$ (601 MHz, DMSO- d_6) $\delta = 8.09$ (dd, $J = 8.1, 1.2$ Hz, 1H), 8.08 (d, $J = 8.6$ Hz, 1H), 7.95 (d, $J = 2.5$ Hz, 1H), 7.77 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.62 (td, $J = 7.5, 1.2$ Hz, 1H), 7.54 (dd, $J = 8.6, 2.5$ Hz, 1H), 7.44 (td, $J = 8.1, 1.6$ Hz, 1H), 4.33 (s, 2H). **$^{13}\text{C-NMR}$ (151 MHz, DMSO- d_6)** $\delta = 141.4, 138.4, 136.6, 135.2, 133.6, 131.9, 130.7, 130.1, 129.2, 128.8, 120.7$ (q, $J = 322.2$ Hz), 116.2, 114.1, 45.1. **$^{19}\text{F-NMR}$ (565 MHz, DMSO- d_6)** $\delta = -77.7$. **FTIR (ATR, neat)** $\tilde{\nu} = 3085, 1556, 1453, 1276, 1220, 1171, 1021, 993, 785, 756$. **HRMS (ESI $^+$, MeOH)** $m/z = 326.94288$ [M-OTf] $^+$. Calculated for [C₁₃H₉ClI] $^+$: $m/z = 326.94320$. **Mp** $T = 216 - 218$.

2-Cyano-10H-dibenzo[*b,e*]iodinin-5-ium trifluoromethanesulfonate (7g)

Following OPP1c, the reaction of 3-(hydroxymethyl)-4-iodobenzonitrile (**5g**, 51.8 mg) with benzene (178 μL , 156 mg, 2.00 mmol, 10 eq.) gave after 16 h for the first reaction step and a total of 48 h for the second reaction step the product **7g** (42.6 mg, 91.2 μmol , 46 %) as a pale yellow solid.

$^1\text{H-NMR}$ (601 MHz, DMSO- d_6) $\delta = 8.30$ (d, $J = 8.3$ Hz, 1H), 8.29 (d, $J = 1.9$ Hz, 1H), 8.10 (dd, $J = 8.2, 1.2$ Hz, 1H), 7.90 (dd, $J = 8.3, 2.0$ Hz, 1H), 7.79 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.63 (td, $J = 7.5, 1.2$ Hz, 1H), 7.46

(td, $J = 7.7, 1.6$ Hz, 1H), 4.39 (s, 2H). $^{13}\text{C-NMR}$ (151 MHz, DMSO- d_6) $\delta = 140.6, 138.1, 134.8, 133.7, 133.4, 132.1, 132.0, 130.7, 129.4, 121.6, 120.7$ (q, $J = 322.6$ Hz), 117.5, 116.2, 114.3, 45.1. $^{19}\text{F-NMR}$ (565 MHz, DMSO- d_6) $\delta = -77.7$. FTIR (ATR, neat) $\tilde{\nu} = 3090, 2234, 1522, 1461, 1273, 1236, 1156, 1024, 758, 741$. HRMS (ESI $^+$, MeOH) $m/z = 317.97716$ [M-OTf] $^+$. Calculated for [C₁₄H₉IN] $^+$: $m/z = 317.97742$. Mp $T = 165 - 170$ (decomp).

3-Bromo-10H-dibenzo[*b,e*]iodinin-5-ium trifluoromethanesulfonate (7h)

Following OPP1b, the reaction of (4-bromo-2-iodophenyl)methanol (5h, 62.6 mg) with benzene (178 μL , 156 mg, 2.00 mmol, 10 eq.) gave after 5 min for the first reaction step and 16 h for the second reaction step the product 7h (83.9 mg, 0.161 mmol, 81 %) as a colourless solid.

$^1\text{H-NMR}$ (601 MHz, DMSO- d_6) $\delta = 8.27$ (d, $J = 2.0$ Hz, 1H), 8.10 (dd, $J = 8.1, 1.2$ Hz, 1H), 7.83 (dd, $J = 8.1, 2.0$ Hz, 1H), 7.79 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.75 (d, $J = 8.2$ Hz, 1H), 7.62 (td, $J = 7.5, 1.2$ Hz, 1H), 7.44 (td, $J = 7.7, 1.7$ Hz, 1H), 4.30 (s, 2H). $^{13}\text{C-NMR}$ (151 MHz, DMSO- d_6) $\delta = 138.7, 138.5, 135.5, 134.5, 133.7, 131.9, 131.8, 130.6, 129.2, 121.75$ (q, $J = 322$ Hz), 120.4, 117.0, 116.2, 44.9. $^{19}\text{F-NMR}$ (565 MHz, DMSO- d_6) $\delta = -77.7$. FTIR (ATR, neat) $\tilde{\nu} = 3097, 1576, 1457, 1379, 1282, 1233, 1159, 1025, 842, 751$. HRMS (ESI $^+$, MeOH) $m/z = 370.89224$ [M-OTf] $^+$. Calculated for [C₁₃H₉BrI] $^+$: $m/z = 370.89269$. Mp $T = 210 - 215$ (decomp.).

4-Bromo-10H-dibenzo[*b,e*]iodinin-5-ium trifluoromethanesulfonate (7i)

Following OPP1b, the reaction of (3-bromo-2-iodophenyl)methanol (5i, 62.6 mg) with benzene (178 μL , 156 mg, 2.00 mmol, 10 eq.) gave after 10 min for the first reaction step and 16 h for the second reaction step the product 7i (57.2 mg, 0.110 mmol, 55 %) as a colourless solid.

$^1\text{H-NMR}$ (601 MHz, DMSO- d_6) $\delta = 8.17$ (dd, $J = 8.2, 1.1$ Hz, 1H), 7.85 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.82 (dd, $J = 7.6, 1.3$ Hz, 1H), 7.79 (dd, $J = 8.0, 1.3$ Hz, 1H), 7.63 (td, $J = 7.5, 1.2$ Hz, 1H), 7.57 (dd, $J = 7.7$ Hz, 1H), 7.45 (ddd, $J = 8.3, 7.4, 1.7$ Hz, 1H), 4.43 (s, 2H). $^{13}\text{C-NMR}$ (151 MHz, DMSO- d_6) $\delta = 143.2, 139.1, 134.3, 134.0, 132.5, 132.2, 131.0, 129.8, 129.7, 125.6, 122.0, 121.1$ (q, $J = 322.3$ Hz), 118.9, 48.0. $^{19}\text{F-NMR}$ (565 MHz, DMSO- d_6) $\delta = -77.7$. FTIR (ATR, neat) $\tilde{\nu} = 3084, 1556, 1442, 1284, 1233, 1218, 1161, 1021, 991, 785, 755$. HRMS (ESI $^+$, MeOH) $m/z = 370.89243$ [M-OTf] $^+$. Calculated for [C₁₃H₉BrI] $^+$: $m/z = 370.89269$. Mp $T = 205 - 210$.

2,4-Dichloro-10H-dibenzo[*b,e*]iodinin-5-ium trifluoromethanesulfonate (7j)

Following OPP1b, the reaction of (3,5-dichloro-2-iodophenyl)methanol (5j, 60.6 mg) with benzene (178 μL , 156 mg, 2.00 mmol, 10 eq.) gave after 4 h for the first reaction step and a total of 40 h for the second reaction step the product 7j (43.5 mg, 0.0890 mmol, 45 %) as a colourless solid.

$^1\text{H-NMR}$ (601 MHz, DMSO- d_6) $\delta = 8.15$ (dd, $J = 8.2, 1.1$ Hz, 1H), 7.96 (d, $J = 2.2$ Hz, 1H), 7.93 (d, $J = 2.2$ Hz, 1H), 7.80 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.64 (td, $J = 7.5, 1.2$ Hz, 1H), 7.46 (td, $J = 7.8, 1.7$ Hz, 1H), 4.44 (s, 2H). $^{13}\text{C-NMR}$ (151 MHz, DMSO- d_6) $\delta = 144.2, 138.2, 137.5, 136.1, 133.8, 132.1, 130.7, 129.4, 128.8, 128.0, 120.7$ (q, $J = 322.2$ Hz), 118.2, 117.0, 46.6. $^{19}\text{F-NMR}$ (565 MHz, DMSO- d_6) $\delta = -77.7$. FTIR (ATR, neat) $\tilde{\nu} = 3070, 1553, 1465, 1433, 1287, 1218, 1155, 1020, 863, 759$. HRMS (ESI $^+$, MeOH) $m/z = 360.90383$ [M-OTf] $^+$. Calculated for [C₁₃H₈Cl₂I] $^+$: $m/z = 360.90423$. Mp $T = 185.5 - 187.5$.

10-Phenyl-10*H*-dibenzo[*b,e*]iodinin-5-ium trifluoromethanesulfonate (7k)

Following OPP1a, the reaction of (2-iodophenyl)(phenyl)methanol (**5k**, 62.0 mg) with benzene (500 μ L, approx. 28 eq.) was completed after 5 min for the first reaction step and 2 h for the second reaction step. The combined organic phases were filtered over a small plug of silica which was washed with DCM/MeOH 25:1 10 mL). After removal of the solvents under reduced pressure and purification as described in OPP1a, the product **7k** (82.0 mg, 0.158 mmol, 79 %) was obtained as a colourless solid.

¹H-NMR (601 MHz, DMSO-*d*₆) δ = 8.13 (dd, *J* = 8.1, 1.2 Hz, 2H), 8.02 (dd, *J* = 7.6, 1.6 Hz, 2H), 7.76 (td, *J* = 7.5, 1.2 Hz, 2H), 7.53 (td, *J* = 7.7, 1.6 Hz, 2H), 7.34 – 7.25 (m, 3H), 6.80 – 6.77 (m, 2H), 6.22 (s, 1H). **¹³C-NMR (151 MHz, DMSO-*d*₆)** δ = 140.1, 138.0, 134.6, 132.9, 132.0, 129.7, 128.7, 127.7, 127.3, 120.7 (q, *J* = 322.2 Hz), 115.2, 57.6. **¹⁹F-NMR (565 MHz, DMSO-*d*₆)** δ = -77.7. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3086, 1493, 1461, 1440, 1245, 1156, 1025, 164, 758, 731. **HRMS (ESI⁺, MeOH)** *m/z* = 369.01317 [M-OTf]⁺. Calculated for [C₁₉H₁₄I]⁺: *m/z* = 369.01347. **Mp** *T* = 215 – 218 (decomp.). The analytical data is in accordance with literature data.^[22]

10-(3,5-Bis(trifluoromethyl)phenyl)-10*H*-dibenzo[*b,e*]iodinin-5-ium trifluoromethanesulfonate (7l)

Following OPP1a, the reaction of (3,5-bis(trifluoromethyl)phenyl)(2-iodophenyl)methanol (**5l**, 89.2 mg) with benzene (178 μ L, 156 mg, 2.00 mmol, 10.0 eq.) gave after 5 min for the first reaction step and 16 h for the second reaction step the product **7l** (95.4 mg, 0.146 mmol, 73 %) as a colourless solid.

¹H-NMR (601 MHz, DMSO-*d*₆) δ = 8.19 (dd, *J* = 8.1, 1.2 Hz, 2H), 8.17 (s, 1H), 8.11 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.82 (td, *J* = 7.5, 1.2 Hz, 2H), 7.60 (td, *J* = 7.8, 1.6 Hz, 2H), 7.36 (s, 2H), 6.45 (s, 1H). **¹³C-NMR (151 MHz, DMSO-*d*₆)** δ = 141.6, 138.5, 135.0, 133.1, 132.5, 130.8 (q, *J* = 32.9 Hz), 130.4, 128.0 – 127.8 (m), 122.9 (q, *J* = 273.1 Hz), 122.0 – 121.6 (m), 120.7 (q, *J* = 322.3 Hz), 115.2, 56.9. **¹⁹F-NMR (565 MHz, DMSO-*d*₆)** δ = -61.4, -77.8. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3068, 1487, 1454, 1272, 1235, 1221, 1163, 1025, 805, 756, 737. **HRMS (ESI⁺, MeOH)** *m/z* = 504.98785 [M-OTf]⁺. Calculated for [C₂₁H₁₂F₆I]⁺: *m/z* = 504.98824. **Mp** *T* = 188 – 190.

2-Chloro-10-(2-fluorophenyl)-10*H*-dibenzo[*b,e*]iodinin-5-ium trifluoromethanesulfonate (7m)

Following OPP1a, the reaction of (5-chloro-2-iodophenyl)(2-fluorophenyl)methanol (**5m**, 72.5 mg) with benzene (178 μ L, 156 mg, 2.00 mmol, 10.0 eq.) gave after 5 min for the first reaction step and 16 h for the second reaction step the product **7m** (67.1 mg, 0.118 mmol, 59 %) as a pale yellow solid.

¹H-NMR (601 MHz, DMSO-*d*₆) δ = 8.15 – 8.06 (m, 3H), 7.94 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.73 (td, *J* = 7.5, 1.3 Hz, 1H), 7.63 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.52 (td, *J* = 7.7, 1.6 Hz, 1H), 7.42 (tdd, *J* = 7.5, 5.0, 1.8 Hz, 1H), 7.23 (ddd, *J* = 11.6, 8.3, 1.3 Hz, 1H), 7.16 (td, *J* = 7.7, 1.3 Hz, 1H), 6.85 – 6.78 (m, 1H), 6.38 (s, 1H). **¹³C-NMR (151 MHz, DMSO-*d*₆)** δ = 160.9 (d, *J* = 248.0 Hz), 141.3, 138.4, 136.8, 136.0, 134.5, 132.9 (d, *J* = 2.7 Hz), 132.2 (d, *J* = 3.0 Hz), 132.0, 130.5 (d, *J* = 8.5 Hz), 129.9 (d, *J* = 3.5 Hz), 129.9, 129.5, 124.4 (d, *J* = 3.3 Hz), 123.2 (d, *J* = 12.2 Hz), 120.7 (q, *J* = 322.2 Hz), 116.8 (d, *J* = 21.5 Hz), 115.8, 113.7, 53.2. **¹⁹F-NMR (565 MHz, DMSO-*d*₆)** δ = -77.7, -109.4.

FTIR (ATR, neat) $\tilde{\nu}$ = 3068, 1487, 1454, 1272, 1235, 1221, 1163, 1025, 805, 756, 737. **HRMS (ESI⁺, MeOH)** m/z = 420.96470 [M-OTf]⁺. Calculated for [C₁₉H₁₂ClFI]⁺: m/z = 420.96508. **Mp** T = 205 – 210 (decomp.).

1,4-Dimethyl-10*H*-dibenzo[*b,e*]iodinin-5-ium trifluoromethanesulfonate (7n)

Following OPP1a, the reaction of *o*-iodobenzylalcohol (**5a**, 46.8 mg) with *p*-xylene (123 μ L, 106 mg, 1.00 mmol, 5.00 eq.) gave after 5 min for the first reaction step and 2 h for the second reaction step the product **7n** (87.3 mg, 0.186 mmol, 93 %) as a colourless solid.

¹H-NMR (601 MHz, DMSO-*d*₆) δ = 8.10 (dd, J = 8.1, 1.2 Hz, 1H), 7.94 (dd, J = 7.6, 1.6 Hz, 1H), 7.61 (td, J = 7.5, 1.2 Hz, 1H), 7.42 (td, J = 8.4, 7.8, 1.6 Hz, 1H), 7.38 (d, J = 7.7 Hz, 1H), 7.27 (d, J = 7.6 Hz, 1H), 4.31 (s, 2H), 2.59 (s, 3H), 2.56 (s, 3H).

¹³C-NMR (151 MHz, DMSO-*d*₆) δ = 139.1, 138.0, 137.4, 135.7, 133.6, 133.1, 131.8, 130.5, 128.9, 128.9, 122.1, 120.7 (q, J = 322.6 Hz), 117.6, 44.0, 24.6, 20.0. **¹⁹F-NMR (565 MHz, DMSO-*d*₆)** δ = -77.7. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3095, 3015, 1457, 1441, 1243, 1222, 1154, 818, 770, 753. **HRMS (ESI⁺, MeOH)** m/z = 321.01322 [M-OTf]⁺. Calculated for [C₁₅H₁₄I]⁺: m/z = 321.01347. **Mp** T = 207 – 210 (decomp.).

4.3 General Procedures for the One-Pot Reaction Utilizing Secondary Aliphatic Benzyl Alcohols (OPP2)

A solution of the secondary *o*-iodobenzyl alcohol (**5**, 200 μ mol, 1 eq.) and the arene (1.00 mmol, 5 eq.) in DCM (1 mL) was cooled to 0 °C and HBF₄ (29.5 μ L, 35.1 mg, 200 μ mol, 1 eq., 50 % w/w in Et₂O) was added. The solution was stirred until complete conversion of the alcohol as observed via TLC and then DCM (1 mL) and *m*CPBA (98.6 mg, 400 μ mol, 2 eq., 70 % w/w) were added and stirred for 10 min. Further HBF₄ (59.0 μ L, 70.3 mg, 400 μ mol, 1 eq., 50 % w/w in Et₂O) was added and stirred until complete conversion of the intermediate. H₂O (2 mL) was added, the phases separated and the aqueous phase was extracted with DCM (5 x 2 mL). The solvent of the combined organic phases was removed under reduced pressure. The residue was added to a small pad of silica, washed with DCM (120 mL) and afterwards eluted with EtOAc (80 mL). The ethyl acetate phase was evaporated to a minimum amount and the product precipitated by addition of Et₂O.

4.4 Substrates Derived from Secondary Aliphatic Benzyl Alcohols

3,10-Dimethyl-10*H*-dibenzo[*b,e*]iodinin-5-ium tetrafluoroborate (8a)

Following OPP2, 1-(2-iodophenyl)ethan-1-ol (**5n**, 49.6 mg) and toluene (106 μ L, 92.1 mg) gave after 10 min for the first reaction step and 2 h for the second reaction step the product **8a** (68.0 mg, 167 μ mol, 83 %) as a slightly yellow solid.

Upscaled reaction:

A solution of the 1-(2-iodophenyl)ethan-1-ol (**5n**, 1.24 g, 5.00 mmol, 1 eq.) and toluene (2.65 mL, 2.30 g, 25.0 mmol, 5 eq.) in DCM (25 mL) was cooled to 0 °C and HBF₄ (0.74 mL, 878 mg, 200 μ mol, 1 eq., 50 % w/w in Et₂O) was added in four portions over 5 min. The solution was stirred for 10 min and then DCM (25 mL) and *m*CPBA (2.47 g, 10 mmol, 2 eq., 70 % w/w) were added and stirred for 10 min. Further HBF₄ (1.48 mL, 1.76 g, 10.0 mmol, 2 eq., 50 % w/w in Et₂O) was slowly added and stirred at 0 °C for 3.5 h

until complete conversion of the intermediate. H₂O (50 mL) was added, the phases were separated and the aqueous phase was extracted with DCM (5 x 20 mL). The combined organic phases were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was added to a pad of silica, washed with DCM (600 mL) and afterwards eluted with EtOAc (300 mL). The ethyl acetate phase was evaporated to a minimum amount and the product precipitated by addition of Et₂O to obtain the product in approx. 90 % purity. After refluxing in EtOAc and slow cooling to 4 °C, the pure product **8a** was obtained as a colourless solid (717 mg, 1.76 mmol, 35 %).

¹H-NMR (DMSO-*d*₆, 601 MHz) δ = 8.11 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.93 (s, 1H), 7.73 (d, *J* = 6.9 Hz, 1H), 7.63 (td, *J* = 8.4, 7.6, 0.9 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.42 (td, *J* = 8.0, 1.4 Hz, 1H), 4.21 (bs, 1H), 2.36 (s, 3H) 1.72 (bs, 3H). **¹³C-NMR (DMSO-*d*₆, 151 MHz)** δ = 141.8, 138.8, 138.6, 133.9, 133.8, 132.4, 131.8, 129.0, 128.7, 128.4, 115.5 (2 C), 47.3, 20.2, 16.3. **¹⁹F-NMR (DMSO-*d*₆, 565 MHz)** δ = -148.3. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3096, 2976, 2926, 1458, 1438, 1386, 1015, 831, 769, 745. **HRMS (ESI⁺, MeOH)** *m/z* = 321.01281 [M-BF₄]⁺. Calculated for C₁₅H₁₄I⁺: *m/z* = 321.01347. **Mp** *T* = 170.

10-Ethyl-3-methyl-10*H*-dibenzo[*b,e*]iodinin-5-ium tetrafluoroborate (**8b**)

Following OPP2, 1-(2-iodophenyl)propan-1-ol (**5o**, 52.4 mg) and toluene (106 μ L, 92.1 mg) gave after 10 min for the first reaction step and 2 h for the second reaction step the product **8b** (49.8 mg, 118 μ mol, 59 %) as a colourless solid.

¹H-NMR (DMSO-*d*₆, 601 MHz) δ = 8.11 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.92 (s, 1H), 7.72 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.62 (td, *J* = 7.4, 1.2 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.47 - 7.42 (m, 2H), 4.37 (bs, 1H), 2.36 (s, 3H), 1.86 (bs, 2H), 0.88 (bs, 3H). **¹³C-NMR (DMSO-*d*₆, 151 MHz)** δ = 140.4, 139.2, 137.1, 134.0, 133.9, 132.3, 131.7, 129.3, 111.5 (2 C), 54.8, 25.0, 20.3, 12.2. Due to conformational broadening not all signals were obtained. **¹⁹F-NMR (DMSO-*d*₆, 565 MHz)** δ = -148.3. **FTIR (ATR, neat)** $\tilde{\nu}$ = 2973, 2934, 2881, 2858, 1489, 1460, 1020, 984, 827, 760. **HRMS (ESI⁺, MeOH)** *m/z* = 335.02878 [M-BF₄]⁺. Calculated for C₁₆H₁₆I⁺: *m/z* = 335.02912. **Mp** *T* = 205.

10-Isopropyl-3-methyl-10*H*-dibenzo[*b,e*]iodinin-5-ium tetrafluoroborate (**8c**)

Following OPP2, 1-(2-iodophenyl)-2-methylpropan-1-ol (**5p**, 55.2 mg) and toluene (106 μ L, 92.1 mg) gave after 10 min for the first reaction step and 2 h for the second reaction step the product **8c** (38.6 mg, 88.5 μ mol, 44 %) as a colourless solid.

¹H-NMR (DMSO-*d*₆, 601 MHz) δ = 8.11 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.92 (d, *J* = 1.1 Hz, 1H), 7.68 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.60 (td, *J* = 7.5, 1.2 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.48 - 7.40 (m, 2H), 4.14 (d, *J* = 11.0 Hz, 1H), 2.37 (s, 3H), 2.31 - 2.20 (m, 1H), 0.83 (d, *J* = 5.6 Hz, 3H), 0.82 (d, *J* = 5.6 Hz, 3H). **¹³C-NMR (DMSO-*d*₆, 151 MHz)** δ = 140.1, 139.2, 136.9, 134.1, 134.0, 133.1, 132.7, 132.0, 131.3, 129.4, 111.9, 111.8, 60.8, 28.3, 21.2, 21.2, 20.3. **¹⁹F-NMR (DMSO-*d*₆, 565 MHz)** δ = -148.3. **FTIR (ATR, neat)** $\tilde{\nu}$ = 2971, 2933, 2906, 2877, 1607, 1463, 1024, 988, 823, 761. **HRMS (ESI⁺, MeOH)** *m/z* = 349.04439 [M-BF₄]⁺. Calculated for C₁₇H₁₈I⁺: *m/z* = 349.04477. **Mp** *T* = 250 (decomp.).

3-Methyl-10-phenyl-10*H*-dibenzo[*b,e*]iodinin-5-ium tetrafluoroborate (8d)

Following OPP2, (2-iodophenyl)(phenyl)methanol (**5k**, 62.0 mg) and toluene (106 μ l, 92.1 mg) gave after 30 min for the first reaction step and 2 h for the second reaction step the product **8d** (34.5 mg, 73.4 μ mol, 37 %) as a colourless solid.

¹H-NMR (601 MHz, DMSO-*d*₆) δ = 8.12 (dd, *J* = 8.1, 1.2 Hz, 1H), 8.00 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.95 – 7.92 (m, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.75 (td, *J* = 7.5, 1.2 Hz, 1H), 7.57 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.52 (td, *J* = 8.0, 1.6 Hz, 1H), 7.32 – 7.26 (m, 3H), 6.79 (d, *J* = 7.9 Hz, 2H), 6.16 (s, 1H), 2.41 (s, 3H). **¹³C-NMR (151 MHz, DMSO-*d*₆)** δ = 140.4, 139.6, 138.2, 137.1, 134.6, 134.6, 132.8, 132.6, 132.5, 132.0, 129.6, 128.7, 127.7, 127.2, 115.1, 115.1, 57.2, 20.4. **¹⁹F-NMR (565 MHz, DMSO-*d*₆)** δ = -148.3. **¹H-NMR (CD₃OD, 601 MHz)** δ = 8.10 (dd, *J* = 8.1, 1.2 Hz, 1H), 8.01 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.93 (s, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.77 (td, *J* = 7.5, 1.2 Hz, 1H), 7.59 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.51 (td, *J* = 7.8, 1.6 Hz, 1H), 7.29 – 7.22 (m, 3H), 6.84 (dt, *J* = 7.9, 1.3 Hz, 2H), 6.02 (s, 1H), 2.47 (s, 3H). **¹³C-NMR (CD₃OD, 151 MHz)** δ = 142.1, 142.1, 139.3, 138.7, 135.5, 135.5, 134.4, 134.2, 134.0, 133.5, 131.1, 129.8, 129.1, 128.6, 115.2, 115.1, 60.1, 20.9. **¹⁹F-NMR (CD₃OD, 565 MHz)** δ = -154.8. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3028, 1601, 1488, 1463, 1287, 1020, 835, 822, 760, 730. **HRMS (ESI⁺, MeOH)** *m/z* = 383.02881 [M-BF₄]⁺. Calculated for C₂₀H₁₆I⁺: *m/z* = 383.02912. **Mp** *T* = 230 (decomp.).

2-Bromo-7,10-dimethyl-10*H*-dibenzo[*b,e*]iodinin-5-ium tetrafluoroborate (8e)

Following OPP2, 1-(5-bromo-2-iodophenyl)ethan-1-ol (**5q**, 65.4 mg) and toluene (106 μ l, 92.1 mg) gave after 2 h for the first reaction step and 4 h for the second reaction step the product **8e** (16.9 mg, 40.1 μ mol, 20 %) as a colourless solid.

¹H-NMR (601 MHz, DMSO-*d*₆) δ = 8.03 (d, *J* = 8.5 Hz, 1H), 7.92 (dd, *J* = 1.6, 0.7 Hz, 1H), 7.90 (s, 1H), 7.66 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.46 (ddd, *J* = 7.9, 1.7, 0.8 Hz, 1H), 4.24 (s, 1H), 2.36 (s, 3H), 1.72 (s, 3H). **¹³C-NMR (151 MHz, DMSO-*d*₆)** δ = 144.5, 139.0, 138.1, 135.6, 133.8, 132.5, 131.7, 125.7, 47.0, 20.2. **¹⁹F-NMR (565 MHz, DMSO-*d*₆)** δ = -148.3. **¹H-NMR (CD₃OD, 601 MHz)** δ = 7.98 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 2.3 Hz, 1H), 7.91 (s, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.61 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 4.25 (bs, 1H), 2.42 (s, 3H), 1.78 (bs, 3H). **¹³C-NMR (CD₃OD, 151 MHz)** δ = 136.2, 132.3, 129.9, 126.6, 125.3, 124.8, 124.0, 120.9, 118.6, 11.3, 7.6. Due to conformational broadening not all signals were obtained. **¹⁹F-NMR (CD₃OD, 565 MHz)** δ = -155.0. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3107, 2978, 1546, 1484, 1393, 1021, 875, 823, 765. **HRMS (ESI⁺, MeOH)** *m/z* = 398.92363 [M-BF₄]⁺. Calculated for C₁₅H₁₃BrI⁺: *m/z* = 398.92399. **Mp** *T* = 206 (decomp.).

2,3,10-Trimethyl-10*H*-dibenzo[*b,e*]iodinin-5-ium (8f)

Following OPP2, 1-(2-iodophenyl)ethan-1-ol (**5n**, 49.6 mg) and toluene (121 μ l, 106 mg) gave after 10 min for the first reaction step and 2 h for the second reaction step the product **8f** (47.5 mg, 0.113 μ mol, 56 %) as a colourless solid.

¹H-NMR (601 MHz, DMSO-*d*₆) δ = 8.10 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.85 (s, 1H), 7.72 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.62 (td, *J* = 7.5, 1.3 Hz, 1H), 7.52 (s, 1H), 7.41 (td, *J* = 7.7, 1.6 Hz, 1H). **¹³C-NMR (151 MHz, DMSO-*d*₆)** δ = 142.4, 141.3, 139.3, 138.2, 134.3, 134.2, 132.2, 130.0, 129.4, 129.2, 116.0, 112.4, 47.7, 19.7, 19.3, 16.8. **¹⁹F-NMR (565 MHz, DMSO-*d*₆)** δ = -148.3. **FTIR (ATR, neat)** $\tilde{\nu}$ = 3627, 3543, 2987, 2926, 1622, 1483, 1456, 1437, 1390, 1286, 1257. **HRMS (ESI⁺, MeOH)** *m/z* = 335.02885 [M-BF₄]⁺. Calculated for C₁₆H₁₆I⁺: *m/z* = 335.02912. **Mp** *T* = 189 – 190.

1,4,10-Trimethyl-10*H*-dibenzo[*b,e*]iodinin-5-ium tetrafluoroborate (8g)

Following OPP2, 1-(2-iodophenyl)ethan-1-ol (**5n**, 49.6 mg) and *p*-xylene (123 μ l, 103 mg) gave after 2 h for the first reaction step and 4 h for the second reaction step the product **8g** (16.9 mg, 40.1 μ mol, 20 %) as colourless solid.

¹H-NMR (CD₃OD, 601 MHz) δ = 8.11 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.42 (d, J = 7.7 Hz, 1H), 7.31 (d, J = 7.7 Hz, 1H), 5.08 (q, J = 7.5 Hz, 1H), 2.62 (s, 3H), 2.60 (s, 3H), 1.57 (d, J = 7.6 Hz, 3H). **¹³C-NMR (CD₃OD, 151 MHz)** δ = 142.9, 140.7, 139.3, 138.2, 135.3, 134.8, 133.8, 133.2, 131.1, 130.9, 117.2, 111.5, 47.2, 25.3, 20.3, 17.5. **¹⁹F-NMR (CD₃OD, 565 MHz)** δ = -155.1. **FTIR (ATR, neat)** $\tilde{\nu}$ = 2935, 1599, 1560, 1472, 1454, 1439, 1394, 1019, 834, 764. **HRMS (ESI⁺, MeOH)** m/z = 335.02897 [M-BF₄]⁺. Calculated for C₁₆H₁₆I⁺: m/z = 335.02912. **Mp** T = 234 (decomp.).

4.5 Substrates that could not be successfully synthesized

OPP1

OPP2

Figure S1: Substrates that could not successfully be synthesized with OPP1 or OPP2.

5 Computational Details

For DFT calculations the Orca 4.2.0 program suite was utilized. Structures optimizations and frequency calculations were performed with PBE0 functional^[23] and Becke-Johnson damping^[24] using the def2-SVP basis set^[25] and an auxiliary basis set for the RI approximation.^[26] On the optimized structures, single point calculations were performed with DSD-BLYP functional^[27] and Becke-Johnson Damping as parametrized in GMTKN55 benchmark set^[28] using a def2-TZVPP basis set^[25] and auxiliary basis sets for the RI-approximation.^[26,29] Transition state structures contain exactly one imaginary frequency and the connection of two minima was confirmed with IRC calculations.

Table S6: Energies for iodonium salt conformers as calculated on CPCM(DCM)/RI-DSD-BLYP/TZVPP//RI-PBE0/SVP level of theory.

#	R	Conformer	G / Eh	G / kcal	ΔE / kcal (to axial conformer with same R-group)
1	Me	Ax	-1261.6898	-791723.0	0.0
2	Me	Eq	-1261.6888	-791722.3	0.6
3	Me	TS	-1261.6697	-791710.4	12.6
4	Et	Ax	-1300.9385	-816351.9	0.0
5	Et	Eq	-1300.9357	-816350.1	1.8
6	Et	TS	-1300.9118	-816335.2	16.8
7	<i>i</i> Pr	Ax	-1340.1866	-840980.5	0.0
8	<i>i</i> Pr	Eq	-1340.1798	-840976.2	4.3
9	<i>i</i> Pr	Ts	-1340.1512	-840958.3	22.2
10	<i>t</i> Bu	Ax	-1379.4280	-865604.9	0
11	<i>t</i> Bu	Eq	-1379.4179	-865598.8	6.4
12	<i>t</i> Bu	Ts	---	---	---
13	Ph	Ax	-1453.2043	-911900.2	0.0
14	Ph	Eq	-1453.1983	-911896.4	3.8
15	Ph	Ts	-1453.1853	-911888.3	11.9

Table S7: Energies for iodonium salt conformers as calculated on CPCM(DMSO)/RI-DSD-BLYP/TZVPP//RI-PBE0/SVP level of theory.

#	R	Conformer	G / Eh	G / kcal	ΔE / kcal (of axial conformer with same R-group)
1	Me	Ax	-1261.6935	-791725.3	0
2	Me	Eq	-1261.6925	-791724.7	0.6
3	Me	TS	-1261.6733	-791712.6	12.6
4	Et	Ax	-1300.9399	-816352.8	0
5	Et	Eq	-1300.9370	-816351.0	1.8
6	Et	TS	-1300.9154	-816337.4	15.4
7	<i>i</i> Pr	Ax	-1340.1879	-840981.3	0
8	<i>i</i> Pr	Eq	-1340.1811	-840977.1	4.2
9	<i>i</i> Pr	Ts	-1340.1548	-840960.5	20.8
10	<i>t</i> Bu	Ax	-1379.4294	-865605.7	0
11	<i>t</i> Bu	Eq	-1379.4192	-865599.3	6.4
12	<i>t</i> Bu	Ts	---	---	---
13	Ph	Ax	-1453.2058	-911901.2	0
14	Ph	Eq	-1453.1997	-911897.3	3.8
15	Ph	Ts	-1453.1892	-911890.7	10.4

Table S8: Energies for iodonium salt conformers as calculated on CPCM(MeOH)/RI-DSD-BLYP/TZVPP//RI-PBE0/SVP level of theory.

#	R	Conformer	G / Eh	G / kcal	ΔE / kcal (of axial conformer with same R-group)
1	Me	Ax	-1261.6931	-791725.0	0.0
2	Me	Eq	-1261.6921	-791724.4	0.6
3	Me	TS	-1261.6729	-791712.4	12.6
4	Et	Ax	-1300.9395	-816352.5	0.0
5	Et	Eq	-1300.9366	-816350.7	1.8
6	Et	TS	-1300.9150	-816337.2	15.4
7	iPr	Ax	-1340.1875	-840981.1	0.0
8	iPr	Eq	-1340.1807	-840976.8	3.7
9	iPr	Ts	-1340.1544	-840960.3	20.2
10	tBu	Ax	-1379.4290	-865605.5	0.0
11	tBu	Eq	-1379.4188	-865599.1	6.4
12	tBu	Ts	---	---	---
13	Ph	Ax	-1453.2054	-911900.9	0.0
14	Ph	Eq	-1453.1993	-911897.1	3.8
15	Ph	Ts	-1453.1888	-911890.5	10.4

Coordinates of #1 R = Me (8a'), axial conformer

32

symmetry c1

C	-3.446174000	2.022300000	-0.838332000
C	-2.613878000	3.116658000	-1.062506000
H	-3.140248000	1.014989000	-1.131174000
C	-5.077625000	3.522396000	0.105188000
H	-5.348447000	1.381601000	-0.056271000
C	-2.972706000	4.424432000	-0.726541000
C	-4.686539000	2.230362000	-0.240167000
C	-1.495713000	5.670141000	-2.353870000
C	-0.825312000	4.616776000	-2.974766000
C	-0.230592000	4.687203000	-4.225886000
C	-0.318033000	5.894057000	-4.915973000
H	0.320858000	3.842925000	-4.639237000
C	-0.994664000	6.972463000	-4.352607000
H	0.156598000	5.981075000	-5.895017000
C	-1.574351000	6.857319000	-3.092544000
H	-1.064990000	7.917922000	-4.894535000
H	-2.092656000	7.711881000	-2.649378000
I	-0.715603000	2.776114000	-1.924710000
C	-4.233244000	4.601004000	-0.143443000
H	-4.550742000	5.612546000	0.123825000
H	-6.052202000	3.693405000	0.567349000
C	-2.062935000	5.613057000	-0.951663000
H	-2.696282000	6.505767000	-0.842014000
C	-0.952111000	5.715009000	0.106053000
H	-0.217762000	4.900571000	0.028657000
H	-1.386560000	5.698017000	1.116094000
H	-0.399706000	6.655992000	-0.026175000
B	2.550074000	3.390372000	-2.740356000

F	1.452833000	2.481828000	-3.158607000
F	2.846915000	4.184277000	-3.828248000
F	2.000018000	4.147901000	-1.692449000
F	3.598907000	2.618136000	-2.318956000

Coordinates of #2 R = Me (8a'), equatorial conformer

32			
symmetry c1			
C	-2.513554000	0.811780000	-1.109222000
C	-2.275715000	2.150828000	-0.849718000
H	-1.779285000	0.194606000	-1.626241000
C	-4.606166000	1.073335000	0.060082000
H	-3.918478000	-0.786057000	-0.807357000
C	-3.126884000	2.995023000	-0.134966000
C	-3.707477000	0.270972000	-0.635828000
C	-2.552656000	5.198337000	-1.147721000
C	-1.599230000	4.768036000	-2.078522000
C	-1.369420000	5.412989000	-3.289118000
C	-2.117128000	6.549163000	-3.593146000
H	-0.624833000	5.037162000	-3.994508000
C	-3.080106000	7.000327000	-2.694186000
H	-1.950206000	7.071975000	-4.537162000
C	-3.296930000	6.331504000	-1.490494000
H	-3.674255000	7.885569000	-2.931126000
H	-4.056646000	6.704874000	-0.802486000
I	-0.493302000	3.037429000	-1.575554000
C	-4.319719000	2.414622000	0.307844000
H	-5.030596000	3.017631000	0.874080000
H	-5.540854000	0.648180000	0.431735000
C	-2.739883000	4.436606000	0.154570000
C	-3.648254000	5.129512000	1.153983000
H	-4.679464000	5.228415000	0.783243000
H	-3.270961000	6.136614000	1.379945000
H	-3.678376000	4.564499000	2.095662000
H	-1.734358000	4.375065000	0.617667000
B	0.511034000	0.468317000	0.432094000
F	-0.400349000	-0.547262000	0.637008000
F	0.480024000	0.790275000	-1.016853000
F	0.098864000	1.652072000	1.066940000
F	1.795233000	0.128987000	0.761300000

Coordinates of #3 R = Me (8a'), transition state conformer

32			
symmetry c1			
C	-2.472238000	2.047526000	-0.218552000
C	-2.250797000	3.189601000	-0.993119000
H	-1.831229000	1.168950000	-0.332856000
C	-4.337947000	3.147889000	0.794331000
H	-3.696578000	1.139864000	1.303352000
C	-3.004399000	4.359740000	-0.879238000
C	-3.518487000	2.027336000	0.693081000

C	-1.497649000	5.899573000	-2.425997000
C	-0.521272000	4.968510000	-2.793858000
C	0.675924000	5.276174000	-3.438030000
C	0.913227000	6.594242000	-3.806459000
H	1.403960000	4.492734000	-3.657005000
C	-0.055825000	7.555249000	-3.540289000
H	1.845182000	6.851888000	-4.312855000
C	-1.217512000	7.209633000	-2.861453000
H	0.091423000	8.591106000	-3.853114000
H	-1.944308000	7.997029000	-2.667431000
I	-0.827319000	2.902461000	-2.506639000
C	-4.076356000	4.278426000	0.030402000
H	-4.746079000	5.130610000	0.141643000
H	-5.189033000	3.149039000	1.478431000
C	-2.795901000	5.673888000	-1.639103000
H	-3.611773000	5.718606000	-2.386476000
C	-2.994189000	6.847915000	-0.660828000
H	-2.178399000	6.868303000	0.076861000
H	-3.942559000	6.776173000	-0.119125000
H	-3.015903000	7.814374000	-1.174320000
B	1.763384000	1.720723000	-3.983415000
F	0.693190000	2.526713000	-4.572057000
F	2.400982000	2.575365000	-3.071678000
F	1.117519000	0.688605000	-3.289710000
F	2.598089000	1.270250000	-4.962750000

Coordinates of #4 R = Et (8b'), axial conformer

35

symmetry c1

C	-3.478680000	1.998848000	-0.879018000
C	-2.646055000	3.096511000	-1.085222000
H	-3.165669000	0.993881000	-1.172420000
C	-5.129118000	3.490660000	0.043717000
H	-5.390935000	1.349497000	-0.128981000
C	-3.012469000	4.402191000	-0.748989000
C	-4.728728000	2.200874000	-0.299263000
C	-1.523409000	5.659395000	-2.350301000
C	-0.841932000	4.611885000	-2.969309000
C	-0.232063000	4.691644000	-4.212556000
C	-0.315352000	5.902272000	-4.896572000
H	0.327412000	3.851768000	-4.624160000
C	-1.002472000	6.975128000	-4.335121000
H	0.170778000	5.996699000	-5.869265000
C	-1.596744000	6.850787000	-3.082813000
H	-1.069404000	7.923514000	-4.872362000
H	-2.122931000	7.700881000	-2.640413000
I	-0.738010000	2.764997000	-1.928431000
C	-4.283734000	4.572382000	-0.187169000
H	-4.607657000	5.581763000	0.079541000
H	-6.111435000	3.657409000	0.490783000
C	-2.100875000	5.591993000	-0.954541000
H	-2.734169000	6.484736000	-0.836479000

C	-0.981578000	5.702164000	0.105671000
H	-0.242593000	4.896639000	-0.030450000
H	-0.430017000	6.630738000	-0.111139000
B	2.536045000	3.387950000	-2.701431000
F	1.446832000	2.479602000	-3.138677000
F	2.845027000	4.188944000	-3.780853000
F	1.971277000	4.138281000	-1.655890000
F	3.581566000	2.616011000	-2.270879000
C	-1.495262000	5.712776000	1.533724000
H	-1.993920000	4.767272000	1.796752000
H	-0.665816000	5.858648000	2.240673000
H	-2.219785000	6.527051000	1.698224000

Coordinates of #5 R = Et (8b'), equatorial conformer

35

symmetry c1

C	-2.505130000	0.790363000	-1.188070000
C	-2.269350000	2.118558000	-0.875294000
H	-1.750771000	0.182325000	-1.686768000
C	-4.662345000	1.047636000	-0.140243000
H	-3.942959000	-0.797393000	-1.012977000
C	-3.146526000	2.949685000	-0.177731000
C	-3.729728000	0.251449000	-0.798942000
C	-2.574066000	5.158465000	-1.131235000
C	-1.598027000	4.754788000	-2.050974000
C	-1.368004000	5.410028000	-3.255731000
C	-2.142963000	6.526387000	-3.565753000
H	-0.604266000	5.057131000	-3.952374000
C	-3.133546000	6.945688000	-2.681016000
H	-1.977164000	7.057449000	-4.505362000
C	-3.349183000	6.267947000	-1.482041000
H	-3.750988000	7.812489000	-2.926522000
H	-4.131955000	6.613402000	-0.805040000
I	-0.475539000	3.034611000	-1.538320000
C	-4.375489000	2.376541000	0.165206000
H	-5.115469000	2.975884000	0.697755000
H	-5.625659000	0.626472000	0.155053000
C	-2.751693000	4.378700000	0.159850000
C	-3.625257000	5.060399000	1.206683000
H	-4.680209000	5.059876000	0.883207000
H	-3.328467000	6.120280000	1.252981000
H	-1.738967000	4.297475000	0.604604000
B	0.475627000	0.467855000	0.490515000
F	-0.457515000	-0.534146000	0.662266000
F	0.499613000	0.792351000	-0.957127000
F	0.058453000	1.656487000	1.114405000
F	1.742215000	0.109042000	0.864390000
C	-3.485390000	4.450533000	2.593976000
H	-3.758886000	3.385850000	2.612637000
H	-2.445817000	4.520892000	2.948878000
H	-4.123826000	4.975792000	3.319089000

Coordinates of #6 R = Et (8b'), transition state conformer

35

symmetry c1			
C	-2.355584000	1.636939000	-0.425088000
C	-2.082586000	2.888537000	-0.985308000
H	-1.850353000	0.741104000	-0.796742000
C	-3.928723000	2.684428000	1.045705000
H	-3.497774000	0.559169000	1.047563000
C	-2.663293000	4.073765000	-0.535379000
C	-3.280350000	1.532960000	0.604530000
C	-1.218914000	5.763141000	-1.972831000
C	-0.414670000	4.856758000	-2.666407000
C	0.694758000	5.204839000	-3.436268000
C	1.000579000	6.550916000	-3.589473000
H	1.299708000	4.433943000	-3.917052000
C	0.187799000	7.506384000	-2.986668000
H	1.863885000	6.839721000	-4.191694000
C	-0.882607000	7.112921000	-2.194780000
H	0.390910000	8.570626000	-3.122950000
H	-1.491711000	7.887193000	-1.726603000
I	-0.877563000	2.798053000	-2.702632000
C	-3.616832000	3.917694000	0.489126000
H	-4.140070000	4.800089000	0.860645000
H	-4.680837000	2.625413000	1.835137000
C	-2.405558000	5.488138000	-1.048376000
H	-3.297958000	5.732273000	-1.656818000
C	-2.390026000	6.489153000	0.150799000
H	-2.398955000	5.923606000	1.092611000
H	-1.429268000	7.021596000	0.162555000
B	1.351298000	1.735693000	-4.754425000
F	0.312865000	2.733362000	-5.012298000
F	2.218186000	2.339610000	-3.833783000
F	0.690624000	0.659092000	-4.143947000
F	1.965987000	1.393754000	-5.922506000
C	-3.534738000	7.489438000	0.142429000
H	-4.515483000	6.988483000	0.182859000
H	-3.473501000	8.170093000	1.004579000
H	-3.531124000	8.106913000	-0.770131000

Coordinates of #7 R = *i*Pr (8c'), axial conformer

38

symmetry c1			
C	-3.480999000	2.008879000	-0.881025000
C	-2.642146000	3.103607000	-1.075613000
H	-3.164894000	1.002019000	-1.164105000
C	-5.145995000	3.509956000	-0.000022000
H	-5.410275000	1.368592000	-0.167338000
C	-3.010283000	4.412500000	-0.750307000
C	-4.742098000	2.217198000	-0.327866000
C	-1.539727000	5.648992000	-2.357158000

C	-0.855654000	4.599360000	-2.968185000
C	-0.276097000	4.657845000	-4.226772000
C	-0.398621000	5.848739000	-4.938675000
H	0.287783000	3.817443000	-4.630751000
C	-1.096491000	6.920830000	-4.388815000
H	0.062951000	5.928486000	-5.924542000
C	-1.658355000	6.817692000	-3.119817000
H	-1.196262000	7.853137000	-4.948621000
H	-2.189154000	7.668935000	-2.686104000
I	-0.719213000	2.777867000	-1.890330000
C	-4.293008000	4.588486000	-0.217176000
H	-4.618562000	5.599758000	0.039804000
H	-6.137228000	3.681422000	0.425092000
C	-2.087528000	5.594890000	-0.948790000
H	-2.704625000	6.498576000	-0.822014000
C	-0.968857000	5.688771000	0.130340000
H	-0.336826000	4.787779000	0.062444000
B	2.526072000	3.605686000	-2.607052000
F	1.517739000	2.601215000	-3.024576000
F	2.769110000	4.409481000	-3.701865000
F	1.902239000	4.331381000	-1.576655000
F	3.632842000	2.934353000	-2.161933000
C	-1.575450000	5.738247000	1.526615000
H	-2.181866000	4.848495000	1.751646000
H	-0.780646000	5.801279000	2.284244000
H	-2.219522000	6.625780000	1.647781000
C	-0.062905000	6.885062000	-0.128068000
H	0.692098000	6.962635000	0.667568000
H	0.477631000	6.790331000	-1.079756000
H	-0.637966000	7.826702000	-0.140160000

Coordinates of #8 R = *i*Pr (8c'), equatorial conformer

38

symmetry c1

C	-2.488679000	0.848695000	-1.203551000
C	-2.246194000	2.170910000	-0.872211000
H	-1.724862000	0.232682000	-1.677551000
C	-4.690664000	1.141654000	-0.259467000
H	-3.961816000	-0.713295000	-1.102772000
C	-3.135623000	3.008088000	-0.198518000
C	-3.739019000	0.330109000	-0.872311000
C	-2.596385000	5.173803000	-1.169402000
C	-1.602335000	4.783157000	-2.076257000
C	-1.423304000	5.382751000	-3.318305000
C	-2.278479000	6.419965000	-3.685478000
H	-0.643112000	5.041257000	-4.002153000
C	-3.306338000	6.803956000	-2.826423000
H	-2.153643000	6.908581000	-4.654017000
C	-3.468386000	6.183354000	-1.589270000
H	-3.996765000	7.596030000	-3.124381000
H	-4.286410000	6.493170000	-0.936619000
I	-0.444955000	3.097079000	-1.512610000

C	-4.395040000	2.462527000	0.070897000
H	-5.150067000	3.077461000	0.563696000
H	-5.677247000	0.738157000	-0.021848000
C	-2.716668000	4.426395000	0.148009000
C	-3.497949000	5.115892000	1.274548000
H	-4.551428000	5.240911000	0.961481000
H	-1.683450000	4.329977000	0.538074000
B	0.439442000	0.600500000	0.625878000
F	-0.504912000	-0.392434000	0.786752000
F	0.524035000	0.884971000	-0.828273000
F	0.003213000	1.807127000	1.201514000
F	1.687920000	0.247116000	1.060903000
C	-3.457779000	4.277700000	2.552644000
H	-3.896319000	3.279059000	2.433422000
H	-2.416319000	4.134726000	2.882294000
H	-3.998279000	4.791043000	3.361539000
C	-2.910166000	6.493830000	1.578878000
H	-3.475586000	6.978963000	2.388100000
H	-1.867053000	6.393706000	1.920089000
H	-2.910478000	7.171796000	0.715150000

Coordinates of #9 R = *i*Pr (8c'), transition state conformer

38

symmetry c1

C	-1.983575000	1.699641000	-0.275041000
C	-1.884832000	2.932488000	-0.925501000
H	-1.391677000	0.847098000	-0.619158000
C	-3.635268000	2.641750000	1.165569000
H	-2.931200000	0.595886000	1.316027000
C	-2.572163000	4.085130000	-0.526992000
C	-2.851050000	1.553641000	0.798386000
C	-1.230109000	5.778183000	-2.050501000
C	-0.407492000	4.871444000	-2.729033000
C	0.713309000	5.206051000	-3.486854000
C	1.033306000	6.548489000	-3.642343000
H	1.317193000	4.428971000	-3.961331000
C	0.213339000	7.505453000	-3.056353000
H	1.906820000	6.829724000	-4.233286000
C	-0.875163000	7.120006000	-2.283769000
H	0.420020000	8.569405000	-3.190272000
H	-1.482684000	7.901366000	-1.841876000
I	-0.871627000	2.819754000	-2.757366000
C	-3.491390000	3.863735000	0.518299000
H	-4.150282000	4.668658000	0.841241000
H	-4.370885000	2.547282000	1.967050000
C	-2.439551000	5.492309000	-1.146490000
H	-3.330389000	5.609247000	-1.794480000
C	-2.586699000	6.559336000	-0.003201000
H	-3.307718000	6.113816000	0.685618000
B	1.200650000	1.861397000	-5.082859000
F	0.085009000	2.813366000	-5.127415000
F	2.209477000	2.506159000	-4.357454000

F	0.721816000	0.760809000	-4.359798000
F	1.577571000	1.544033000	-6.354399000
C	-3.257021000	7.888871000	-0.375366000
H	-4.002968000	7.763914000	-1.175385000
H	-3.785088000	8.285775000	0.505045000
H	-2.560333000	8.680734000	-0.685013000
C	-1.311615000	6.734131000	0.814565000
H	-1.516883000	7.336542000	1.712476000
H	-0.920578000	5.760109000	1.147325000
H	-0.513057000	7.237710000	0.251376000

Coordinates of #10 R = tBu, axial conformer

41

symmetry c1			
C	-3.425270000	1.913711000	-0.980925000
C	-2.591495000	3.014237000	-1.180774000
H	-3.136478000	0.921942000	-1.337768000
C	-5.020583000	3.368809000	0.076298000
H	-5.302113000	1.236014000	-0.170548000
C	-2.924954000	4.306598000	-0.764888000
C	-4.643633000	2.091581000	-0.333821000
C	-1.432657000	5.619838000	-2.333468000
C	-0.793055000	4.594136000	-3.030378000
C	-0.191556000	4.735630000	-4.274621000
C	-0.234802000	5.985938000	-4.882687000
H	0.329376000	3.903370000	-4.747979000
C	-0.892525000	7.039210000	-4.252865000
H	0.248383000	6.122525000	-5.851788000
C	-1.482355000	6.850390000	-3.008879000
H	-0.944469000	8.019490000	-4.731159000
H	-1.992960000	7.684202000	-2.521397000
I	-0.767182000	2.652023000	-2.178976000
C	-4.177681000	4.451372000	-0.148484000
H	-4.489929000	5.450304000	0.164864000
H	-5.983213000	3.525688000	0.567481000
C	-2.053339000	5.529855000	-0.954361000
H	-2.750760000	6.380590000	-0.912390000
C	-1.057501000	5.817866000	0.237586000
B	2.515800000	3.054648000	-3.177154000
F	1.322405000	2.265271000	-3.556809000
F	2.837688000	3.842054000	-4.263998000
F	2.089094000	3.841908000	-2.092092000
F	3.507947000	2.183624000	-2.815347000
C	-1.877433000	5.976323000	1.520905000
H	-2.382490000	5.042123000	1.807380000
H	-1.212229000	6.259759000	2.350261000
H	-2.640850000	6.765323000	1.423704000
C	-0.326763000	7.133402000	-0.039154000
H	0.302860000	7.392546000	0.825206000
H	0.329835000	7.061441000	-0.917825000
H	-1.030587000	7.966158000	-0.198590000
C	-0.019488000	4.718907000	0.452377000

H	0.609015000	4.982820000	1.317023000
H	-0.491975000	3.752714000	0.687813000
H	0.658848000	4.594641000	-0.404274000

Coordinates of #11 R = tBu, equatorial conformer

41

symmetry c1			
C	-2.403908000	0.804688000	-1.297850000
C	-2.254903000	2.139705000	-0.962030000
H	-1.595100000	0.243668000	-1.765278000
C	-4.612793000	0.937455000	-0.349872000
H	-3.762924000	-0.859045000	-1.207433000
C	-3.202791000	2.924416000	-0.300480000
C	-3.613850000	0.196658000	-0.973925000
C	-2.701140000	5.144213000	-1.247988000
C	-1.667060000	4.783147000	-2.125675000
C	-1.434388000	5.409701000	-3.345183000
C	-2.267649000	6.459494000	-3.724456000
H	-0.623868000	5.082536000	-4.000132000
C	-3.318633000	6.833549000	-2.891185000
H	-2.102188000	6.969699000	-4.675594000
C	-3.535964000	6.181948000	-1.678441000
H	-3.987189000	7.644425000	-3.188493000
H	-4.369810000	6.494635000	-1.053941000
I	-0.473548000	3.140722000	-1.525478000
C	-4.412179000	2.276247000	-0.019944000
H	-5.207221000	2.816551000	0.490495000
H	-5.564788000	0.464834000	-0.099163000
C	-2.849781000	4.364875000	0.053070000
C	-3.583531000	5.027669000	1.251256000
H	-1.814650000	4.278245000	0.437559000
B	0.354835000	0.784227000	0.794892000
F	-0.553527000	-0.245697000	0.925109000
F	0.542235000	1.015155000	-0.658707000
F	-0.179710000	1.988485000	1.289394000
F	1.580669000	0.509214000	1.338658000
C	-3.441448000	4.084213000	2.457251000
H	-4.044269000	3.172088000	2.360796000
H	-2.395395000	3.768916000	2.595318000
H	-3.765639000	4.603437000	3.371819000
C	-2.827347000	6.316722000	1.602614000
H	-3.301049000	6.805066000	2.467786000
H	-1.782136000	6.099950000	1.873493000
H	-2.819552000	7.038271000	0.772570000
C	-5.072414000	5.367435000	1.021146000
H	-5.555444000	4.744542000	0.256610000
H	-5.637818000	5.240698000	1.956620000
H	-5.212849000	6.415337000	0.718268000

Coordinates of #12 R = tBu, transition state conformer

A transition state for R = tBu could not be found.

Coordinates of #13 R = Ph (8d'), axial conformer

39

symmetry c1			
C	-3.436390000	1.995177000	-0.895504000
C	-2.587162000	3.084840000	-1.061763000
H	-3.119022000	0.986983000	-1.172024000
C	-5.123564000	3.505617000	-0.066345000
H	-5.390000000	1.366317000	-0.238957000
C	-2.963597000	4.392540000	-0.744776000
C	-4.713373000	2.211739000	-0.379846000
C	-1.476992000	5.640400000	-2.317862000
C	-0.826453000	4.585401000	-2.959927000
C	-0.284713000	4.653034000	-4.233588000
C	-0.407727000	5.858923000	-4.922505000
H	0.254048000	3.810527000	-4.666455000
C	-1.064159000	6.936795000	-4.335487000
H	0.026148000	5.944691000	-5.920408000
C	-1.592607000	6.825316000	-3.051337000
H	-1.157527000	7.880505000	-4.876958000
H	-2.091653000	7.679863000	-2.587228000
I	-0.661030000	2.771160000	-1.874763000
C	-4.259107000	4.582080000	-0.255155000
H	-4.585594000	5.595525000	-0.007358000
H	-6.127491000	3.680228000	0.326486000
C	-2.001873000	5.550500000	-0.902597000
H	-2.578222000	6.471711000	-0.722782000
B	2.574953000	3.291247000	-3.018703000
F	1.420937000	2.406250000	-3.284238000
F	2.721572000	4.107029000	-4.126325000
F	2.194652000	4.036222000	-1.891933000
F	3.670046000	2.507109000	-2.772341000
C	-0.885422000	5.497444000	0.144701000
C	-1.184052000	5.097472000	1.453510000
C	0.424381000	5.870329000	-0.165823000
C	-0.191903000	5.072041000	2.429074000
C	1.420085000	5.832054000	0.808509000
C	1.115900000	5.436091000	2.107655000
H	-2.201610000	4.794204000	1.712159000
H	0.691970000	6.160275000	-1.182837000
H	-0.440358000	4.756258000	3.445170000
H	2.443563000	6.093472000	0.533463000
H	1.898924000	5.399638000	2.868483000

Coordinates of #14 R = Ph (8d'), equatorial conformer

39

symmetry c1			
C	-2.478933000	0.749669000	-1.099763000
C	-2.325438000	2.110448000	-0.889554000
H	-1.712646000	0.165292000	-1.608373000
C	-4.545722000	0.904696000	0.124123000

H	-3.759961000	-0.931271000	-0.712080000
C	-3.221042000	2.925409000	-0.193722000
C	-3.619775000	0.143026000	-0.580258000
C	-2.675132000	5.177064000	-1.236280000
C	-1.695945000	4.742604000	-2.137918000
C	-1.401921000	5.403095000	-3.327142000
C	-2.097336000	6.569474000	-3.636460000
H	-0.640197000	5.017405000	-4.008666000
C	-3.061805000	7.044331000	-2.752304000
H	-1.879889000	7.102782000	-4.564178000
C	-3.345789000	6.358527000	-1.572813000
H	-3.603504000	7.965388000	-2.978145000
H	-4.094003000	6.758645000	-0.888276000
I	-0.567850000	3.039635000	-1.611666000
C	-4.347869000	2.270350000	0.316456000
H	-5.069340000	2.839765000	0.902464000
H	-5.431468000	0.429815000	0.551221000
C	-2.923270000	4.404162000	0.059651000
H	-1.949855000	4.402951000	0.589123000
B	0.557104000	0.510401000	0.397136000
F	-0.259785000	-0.584213000	0.591433000
F	0.504345000	0.837029000	-1.049787000
F	0.039097000	1.649956000	1.035627000
F	1.865386000	0.285593000	0.731804000
C	-3.913030000	5.067512000	0.986675000
C	-5.255312000	5.250389000	0.623319000
C	-3.495714000	5.506209000	2.245102000
C	-6.151435000	5.860070000	1.497071000
C	-4.391306000	6.117067000	3.122447000
C	-5.720915000	6.296546000	2.750343000
H	-5.604525000	4.907627000	-0.354371000
H	-2.454402000	5.362020000	2.545584000
H	-7.193857000	5.993379000	1.198397000
H	-4.045342000	6.451220000	4.103134000
H	-6.424365000	6.773724000	3.436461000

Coordinates of #15 R = Ph (8d'), transition state conformer

39

symmetry c1

C	-2.808614000	1.500779000	-1.092620000
C	-2.282512000	2.747434000	-1.448871000
H	-2.570280000	0.607875000	-1.677624000
C	-3.939424000	2.542813000	0.749040000
H	-4.052570000	0.425397000	0.294211000
C	-2.541913000	3.907997000	-0.727312000
C	-3.641014000	1.396603000	0.012406000
C	-1.034962000	5.581731000	-2.134716000
C	-0.516105000	4.720927000	-3.101651000
C	0.411134000	5.096858000	-4.072538000
C	0.836699000	6.419099000	-4.105837000
H	0.805984000	4.386444000	-4.800502000
C	0.328582000	7.330666000	-3.184207000

H	1.565973000	6.719496000	-4.860435000
C	-0.578119000	6.910110000	-2.222931000
H	0.647286000	8.374864000	-3.204256000
H	-0.947604000	7.625703000	-1.485292000
I	-1.141725000	2.695398000	-3.215992000
C	-3.392363000	3.763991000	0.384539000
H	-3.612187000	4.649387000	0.984908000
H	-4.596040000	2.483005000	1.619364000
C	-2.013098000	5.308122000	-0.997372000
H	-2.904922000	5.916399000	-1.230153000
B	1.305947000	2.055901000	-5.585377000
F	-0.096225000	2.511902000	-5.536375000
F	2.054876000	3.139414000	-6.023117000
F	1.624143000	1.743595000	-4.255581000
F	1.384143000	0.968787000	-6.410616000
C	-1.430592000	5.863346000	0.297003000
C	-2.046974000	6.920165000	0.968986000
C	-0.263744000	5.305446000	0.829791000
C	-1.508556000	7.414797000	2.158172000
C	0.274296000	5.797126000	2.014291000
C	-0.347594000	6.853655000	2.682698000
H	-2.958489000	7.364486000	0.557896000
H	0.228637000	4.480403000	0.307634000
H	-2.000126000	8.243136000	2.673613000
H	1.187000000	5.354482000	2.419720000
H	0.076625000	7.239274000	3.612490000

6 NMR-Spectra

6.1 NMR Spectra of New Substrates

Figure S2: 600 MHz ^1H -NMR spectrum of compound **S1h**.

Figure S3: 151 MHz ^{13}C -NMR spectrum of compound **S1h**.

Figure S4: 600 MHz ¹H-NMR spectrum of compound **5h**.

Figure S5: 151 MHz ¹³C-NMR spectrum of compound **5h**.

Figure S6: 600 MHz ¹H-NMR spectrum of compound **5i**.

Figure S7: 151 MHz ¹³C-NMR spectrum of compound **5i**.

Figure S8: 600 MHz ¹H-NMR spectrum of compound **S1j**.

Figure S9: 151 MHz ¹³C-NMR spectrum of compound **S1j**.

Figure S10: 600 MHz ^1H -NMR spectrum of compound **5j**.

Figure S11: 151 MHz ^{13}C -NMR spectrum of compound **5j**.

Figure S12: 600 MHz ^1H -NMR spectrum of methyl 5-cyano-2-iodobenzoate.

Figure S13: 151 MHz ^{13}C -NMR spectrum of methyl 5-cyano-2-iodobenzoate.

Figure S14: 600 MHz ¹H-NMR spectrum of compound **5g**.

Figure S15: 151 MHz ¹³C-NMR spectrum of compound **5g**.

Figure S16: 600 MHz ^1H -NMR spectrum of compound **12**.

Figure S17: 151 MHz ^{13}C -NMR spectrum of compound **12**.

Figure S18: 200 MHz ^1H -NMR spectrum of compound **5o**.

Figure S19: 50 MHz ^{13}C -NMR spectrum of compound **5o**.

Figure S20: 360 MHz ¹H-NMR spectrum of compound **5q**.

Figure S21: 90 MHz ¹³C-NMR spectrum of compound **5q**.

Figure S22: 360 MHz ¹H-NMR spectrum of compound (5-chloro-2-iodophenyl)(2-fluorophenyl)methanone.

Figure S23: 90 MHz ¹³C-NMR spectrum of compound (5-chloro-2-iodophenyl)(2-fluorophenyl)methanone.

Figure S24: 200 MHz ¹H-NMR spectrum of compound **5m**.

Figure S25: 50 MHz ¹³C-NMR spectrum of compound **5m**.

6.3 NMR-Spectra of Iodoniumsalts 7 and 8

Figure S26: 600 MHz ^1H -NMR spectrum of compound **7a**.

Figure S27: 151 MHz ^{13}C -NMR spectrum of compound **7a**.

Figure S28: 600 MHz ¹H-NMR spectrum of compound **7b**.

Figure S29: 151 MHz ¹³C-NMR spectrum of compound **7b**.

Figure S30: 600 MHz ¹H-NMR spectrum of compound **7c**.

Figure S31: 151 MHz ¹³C-NMR spectrum of compound **7c**.

Figure S32: 600 MHz ¹H-NMR spectrum of compound **7d**.

Figure S33: 151 MHz ¹³C-NMR spectrum of compound **7d**.

Figure S34: 600 MHz ¹H-NMR spectrum of compound **7e**.

Figure S35: 151 MHz ¹³C-NMR spectrum of compound **7e**.

Figure S36: 600 MHz ¹H-NMR spectrum of compound **7f**.

Figure S37: 151 MHz ¹³C-NMR spectrum of compound **7f**.

Figure S38: 600 MHz ¹H-NMR spectrum of compound **7g**.

Figure S39: 151 MHz ¹³C-NMR spectrum of compound **7g**.

Figure S40: 600 MHz ¹H-NMR spectrum of compound **7h**.

Figure S41: 151 MHz ¹³C-NMR spectrum of compound **7h**.

Figure S42: 600 MHz ¹H-NMR spectrum of compound **7i**.

Figure S43: 151 MHz ¹³C-NMR spectrum of compound **7i**.

Figure S44: 600 MHz ¹H-NMR spectrum of compound **7j**.

Figure S45: 151 MHz ¹³C-NMR spectrum of compound **7j**.

Figure S46: 600 MHz ¹H-NMR spectrum of compound **7k**.

Figure S47: 151 MHz ¹³C-NMR spectrum of compound **7k**.

Figure S48: 600 MHz ¹H-NMR spectrum of compound **7I**.

Figure S49: 151 MHz ¹³C-NMR spectrum of compound **7I**.

Figure S50: 600 MHz ¹H-NMR spectrum of compound **7m**.

Figure S51: 151 MHz ¹³C-NMR spectrum of compound **7m**.

Figure S52: 600 MHz ^1H -NMR spectrum of compound **7n**.

Figure S53: 151 MHz ^{13}C -NMR spectrum of compound **7n**.

Figure S54: 600 MHz ^1H -NMR spectrum of compound **8a**.

Figure S55: 151 MHz ^{13}C -NMR spectrum of compound **8a**.

Figure S56: 600 MHz ^1H -NMR spectrum of compound **8b**.

Figure S57: 151 MHz ^{13}C -NMR spectrum of compound **8b**.

Figure S60: 600 MHz ^1H -NMR spectrum of compound **8d**.

Figure S61: 151 MHz ^{13}C -NMR spectrum of compound **8d**.

Figure S62: 600 MHz ¹H-NMR spectrum of compound **8e**.

Figure S63: 151 MHz ¹³C-NMR spectrum of compound **8e**.

Figure S64: 600 MHz ^1H -NMR spectrum of compound **8f**.

Figure S65: 151 MHz ^{13}C -NMR spectrum of compound **8f**.

Figure S66: 600 MHz ^1H -NMR spectrum of compound **8g**.

Figure S67: 151 MHz ^{13}C -NMR spectrum of compound **8g**.

7 Crystallographic Data

Crystallographic data for compound 7k

Table S9: Crystal data and structure refinement for 7k.

Empirical formula	C₂₀H₁₄F₃IO₃S
Formula weight	518.27
Temperature/K	100.0
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	13.6314(4)
b/Å	19.2653(5)
c/Å	14.8884(4)
α/°	90
β/°	90
γ/°	90
Volume/Å³	3909.89(19)
Z	8
ρ_{calc}/cm³	1.761
μ/mm⁻¹	1.791
F(000)	2032.0
Crystal size/mm³	0.2 × 0.2 × 0.15
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.57 to 72.828
Index ranges	-22 ≤ h ≤ 22, -32 ≤ k ≤ 31, -17 ≤ l ≤ 24
Reflections collected	91480
Independent reflections	19037 [R _{int} = 0.0351, R _{sigma} = 0.0334]
Data/restraints/parameters	19037/0/506

Goodness-of-fit on F²	1.029
Final R indexes [I>=2σ (I)]	R ₁ = 0.0266, wR ₂ = 0.0497
Final R indexes [all data]	R ₁ = 0.0372, wR ₂ = 0.0530
Largest diff. peak/hole / e Å⁻³	1.07/-0.75
Flack parameter	0.391(10)

Table S10: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **7k**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
I1	2955.8(2)	2530.2(2)	5226.5(2)	10.97(3)
I002	4015.6(2)	2542.9(2)	8613.3(2)	14.30(3)
S21	2603.8(5)	3949.8(3)	6917.7(5)	17.81(12)
F21	2893(2)	5233.1(10)	6414.8(17)	51.0(6)
F22	4084(2)	4548.1(14)	6120.7(18)	56.1(7)
F23	3830.7(18)	4895.7(11)	7478.9(15)	42.8(6)
O21	3285(2)	3432.6(11)	7245.4(16)	32.5(5)
O22	1903.5(18)	4191.2(12)	7568.7(16)	31.1(5)
O23	2201.9(16)	3795.8(10)	6040.5(14)	24.5(4)
C0AA	4018(2)	1190.8(13)	9635(2)	23.5(5)
C1	4525(2)	1200.7(14)	3391.7(18)	19.7(5)
C2	3903(2)	635.5(14)	3287.9(19)	22.5(5)
C3	3042(2)	584.5(13)	3771.8(18)	21.0(5)
C4	2767(2)	1119.5(12)	4342.9(18)	17.0(5)
C4A	3389.7(19)	1684.1(12)	4423.2(18)	13.8(4)
C5	3090(2)	3835.9(12)	4089.3(18)	19.2(5)
C5A	3572(2)	3221.5(12)	4286.0(17)	14.4(5)
C6	3511(3)	4273.9(14)	3457(2)	25.8(6)
C7	4377(3)	4093.4(15)	3043(2)	26.9(6)
C8	4854(2)	3471.8(15)	3252.5(18)	22.6(5)
C8A	4457.6(19)	3023.7(13)	3893.1(17)	15.8(4)
C9	4961.2(17)	2347.7(12)	4144.9(15)	15.4(4)
C9A	4283.6(19)	1739.1(13)	3982.5(17)	14.8(4)
C10	5324.7(17)	2355.1(13)	5123.0(16)	17.5(5)
C11	5500(2)	1726.6(16)	5563.5(19)	20.5(5)
C11'	5492(2)	2973.8(16)	5578(2)	21.1(5)
C12	5831(2)	1720.7(18)	6450(2)	25.5(6)
C12'	5825(2)	2964.9(18)	6466(2)	26.1(6)
C13	5994.1(19)	2340.3(18)	6897.0(18)	29.0(7)
C21	5142(2)	3947.0(14)	10627.8(19)	21.2(5)
C22	4523(2)	4519.4(15)	10543(2)	25.4(6)
C23	3767(2)	4528.0(14)	9923.7(19)	23.5(5)
C24	3623(2)	3957.3(13)	9367.2(17)	17.4(4)
C24A	4258.2(19)	3396.9(13)	9458.7(17)	15.2(4)
C25A	4451(2)	1843.4(13)	9629.2(18)	18.0(5)
C26	4320(2)	726.5(15)	10293(2)	29.9(7)
C27	5016(3)	920.7(16)	10922(2)	29.8(7)
C28	5422(2)	1579.8(15)	10907.1(19)	23.3(5)
C28A	5161.9(18)	2058.9(13)	10235.8(18)	17.5(4)
C29	5699.0(18)	2746.0(13)	10174.5(17)	16.6(4)
C29A	5023.3(18)	3366.3(13)	10076.7(16)	16.0(4)
C30	6509.9(18)	2708.3(13)	9448.3(16)	16.4(4)

C31	6817(2)	3301.9(14)	8996.0(19)	21.8(5)
C31'	7000(2)	2086.7(15)	9284.8(18)	21.7(5)
C32	7607(2)	3270.3(16)	8398(2)	25.5(6)
C32'	7791(2)	2061.4(15)	8690.4(19)	23.1(5)
C33	8092.6(19)	2652.5(15)	8249.3(17)	22.5(5)
C34	3393(3)	4698.5(17)	6722(2)	27.5(7)
S1	2752.5(5)	1141.1(3)	7135.5(5)	18.84(13)
F1	2491.0(18)	-45.0(11)	6329.0(19)	48.1(6)
F2	3635.4(17)	-59.0(10)	7319.5(15)	38.0(5)
F3	3890.8(18)	432.3(10)	6048.8(14)	34.2(5)
O1	3647.3(18)	1472.2(12)	7441.6(18)	36.1(6)
O2	2091.8(18)	941.0(11)	7837.6(15)	30.6(5)
O3	2297.6(17)	1469.9(10)	6371.8(15)	26.7(4)
C14	3225(3)	326.2(15)	6683(2)	24.0(6)

Table S11: Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for **7k**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
I1	10.04(5)	9.58(5)	13.30(5)	-0.60(6)	1.36(4)	0.13(5)
I002	16.35(6)	14.15(6)	12.41(5)	-0.88(6)	-1.07(4)	0.07(6)
S21	24.1(3)	13.5(2)	15.9(3)	-2.7(2)	1.2(2)	0.6(2)
F21	77.7(18)	18.8(8)	56.6(14)	13.0(9)	-	-4.7(10)
F22	50.8(16)	66.7(16)	50.9(15)	-8.3(12)	18.0(14)	-
F23	46.7(13)	43.5(12)	38.0(12)	-5.1(10)	28.3(13)	21.9(13)
O21	50.9(15)	21.7(10)	24.7(11)	1.1(8)	-	-
O22	30.0(12)	32.6(11)	30.8(12)	-14.5(9)	12.5(10)	21.0(10)
O23	31.2(11)	21.6(9)	20.7(9)	-6.5(7)	-8.4(10)	12.5(10)
C0AA	25.7(13)	18.2(11)	26.6(14)	1.5(10)	11.3(10)	-6.2(9)
C1	19.7(12)	24.2(12)	15.1(11)	-3.4(9)	-5.8(8)	1.9(8)
C2	28.1(14)	19.8(11)	19.5(13)	-7.0(9)	6.3(11)	-3.3(10)
C3	28.7(14)	11.9(9)	22.3(13)	-3.6(8)	-1.8(9)	8.5(10)
C4	20.0(12)	12.0(9)	19.1(11)	-0.9(8)	-6.5(11)	8.3(10)
C4A	15.4(11)	11.9(9)	14.0(11)	-1.6(8)	-8.3(11)	2.0(9)
C5	23.3(13)	13.1(9)	21.0(12)	1.0(9)	-3.3(9)	0.1(8)
C5A	18.2(12)	11.9(9)	13.3(11)	2.9(8)	-2.2(9)	3.0(8)
C6	38.3(17)	15.3(11)	23.8(14)	5.0(10)	-6.4(10)	0.1(9)
C7	40.9(17)	20.9(12)	18.9(13)	6.8(10)	-3.7(9)	-2.8(8)
C8	25.4(13)	25.3(13)	17.0(12)	1.0(10)	-7.5(13)	-5.3(11)
C8A	15.5(11)	19.0(11)	12.8(11)	-0.1(8)	-2.4(12)	-
C9	11.3(9)	22.1(11)	12.9(9)	-1.7(8)	-	12.0(12)
C9A	14.9(10)	16.8(10)	12.6(10)	-1.0(8)	2.4(10)	-
C10	11.1(9)	26.6(13)	14.7(10)	-0.1(9)	-	10.2(11)
C11	12.9(11)	30.5(14)	18.2(12)	2.3(11)	0.1(8)	-5.5(9)
C11'	11.9(11)	30.5(14)	20.8(13)	-4.6(11)	0.8(7)	-0.1(8)
C12	14.0(12)	42.4(16)	20.0(13)	5.0(12)	-2.1(8)	3.2(8)
C12'	15.5(12)	42.6(16)	20.1(13)	-	-1.9(7)	-1.2(8)
				11.7(13)	-1.1(9)	0.8(10)
					-1.8(9)	0.2(10)
					-3.5(10)	2.0(11)
					-0.6(10)	-2.6(11)

C13	13.4(10)	59(2)	14.7(10)	-1.1(12)	-1.2(9)	-2.7(12)
C21	22.6(13)	23.5(12)	17.3(12)	-3.2(10)	-2.8(10)	-5.2(10)
C22	34.8(16)	19.7(12)	21.7(13)	-5.2(10)	-3.1(12)	-2.8(11)
C23	34.0(15)	15.3(10)	21.3(13)	-1.3(9)	-2.2(11)	2.9(10)
C24	20.4(12)	16.1(10)	15.7(11)	0.6(8)	-1.5(9)	2.3(9)
C24A	17.6(11)	16.4(10)	11.7(10)	-0.6(8)	-0.3(8)	-2.0(8)
C25A	19.3(12)	17.0(10)	17.7(12)	3.8(9)	3.8(9)	2.2(9)
C26	34.4(16)	19.7(12)	35.5(17)	8.4(12)	13.2(14)	1.6(11)
C27	34.4(16)	26.4(13)	28.4(15)	15.1(12)	11.9(13)	11.1(12)
C28	22.9(13)	27.6(13)	19.6(12)	9.4(10)	4.4(10)	6.1(10)
C28A	17.1(11)	20.5(10)	14.9(10)	4.7(9)	4.1(9)	1.8(8)
C29	14.1(10)	22.6(10)	13.1(10)	1.4(9)	-0.8(8)	1.4(8)
C29A	15.3(10)	19.3(10)	13.3(10)	0.6(8)	0.1(8)	-1.0(8)
C30	13.8(10)	22.9(11)	12.6(10)	2.1(8)	-2.3(8)	-1.9(8)
C31	24.0(13)	19.6(11)	21.9(13)	0.0(10)	4.9(10)	-4.5(9)
C31'	17.1(11)	26.5(12)	21.5(12)	8.4(10)	1.6(10)	4.2(10)
C32	27.8(14)	26.2(13)	22.6(13)	0.5(10)	7.2(11)	-8.8(11)
C32'	16.0(12)	30.6(13)	22.7(13)	4.1(11)	1.8(10)	5.8(10)
C33	14.4(10)	34.7(15)	18.4(11)	0.4(10)	3.2(8)	-3.6(9)
C34	32.6(17)	24.3(13)	25.6(15)	1.2(11)	1.1(13)	-6.7(12)
S1	22.1(3)	15.1(2)	19.3(3)	-0.3(2)	5.7(2)	-1.2(2)
F1	45.2(13)	25.0(9)	74.2(17)	-	-	-8.1(9)
				18.1(11)	13.0(13)	
F2	44.5(13)	31.1(10)	38.3(12)	12.0(8)	5.5(10)	15.1(9)
F3	44.8(12)	29.3(9)	28.4(10)	-1.8(8)	13.8(9)	8.4(9)
O1	31.7(13)	33.8(12)	42.8(14)	-	3.0(11)	-
				19.6(11)		10.1(10)
O2	31.9(12)	31.1(10)	29.0(11)	11.7(9)	14.8(10)	5.5(9)
O3	32.6(11)	21.4(9)	26.1(10)	9.5(8)	7.7(9)	4.8(8)
C14	29.0(16)	16.3(11)	26.8(15)	0.5(10)	0.4(11)	-0.8(10)

Table S12: Bond Lengths for **7k**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	C4A	2.106(2)	C11	C12	1.395(4)
I1	C5A	2.107(3)	C11'	C12'	1.398(4)
I002	C24A	2.098(2)	C12	C13	1.384(5)
I002	C25A	2.111(3)	C12'	C13	1.383(5)
S21	O21	1.447(2)	C21	C22	1.395(4)
S21	O22	1.438(2)	C21	C29A	1.397(4)
S21	O23	1.447(2)	C22	C23	1.383(4)
S21	C34	1.823(3)	C23	C24	1.391(4)
F21	C34	1.317(4)	C24	C24A	1.390(4)
F22	C34	1.332(4)	C24A	C29A	1.392(4)
F23	C34	1.330(4)	C25A	C28A	1.388(4)
C0AA	C25A	1.389(4)	C26	C27	1.384(5)
C0AA	C26	1.390(4)	C27	C28	1.385(4)
C1	C2	1.389(4)	C28	C28A	1.406(4)
C1	C9A	1.399(4)	C28A	C29	1.515(4)

C2	C3	1.381(4)	C29	C29A	1.516(3)
C3	C4	1.388(3)	C29	C30	1.548(3)
C4	C4A	1.385(4)	C30	C31	1.391(4)
C4A	C9A	1.388(4)	C30	C31'	1.392(4)
C5	C5A	1.385(3)	C31	C32	1.399(4)
C5	C6	1.388(4)	C31'	C32'	1.396(4)
C5A	C8A	1.395(4)	C32	C33	1.380(4)
C6	C7	1.377(5)	C32'	C33	1.377(4)
C7	C8	1.398(4)	S1	O1	1.450(2)
C8	C8A	1.396(4)	S1	O2	1.433(2)
C8A	C9	1.519(3)	S1	O3	1.442(2)
C9	C9A	1.512(3)	S1	C14	1.826(3)
C9	C10	1.538(3)	F1	C14	1.337(4)
C10	C11	1.398(4)	F2	C14	1.328(4)
C10	C11'	1.390(4)	F3	C14	1.326(4)

Table S13: Bond Angles for **7k**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4A	I1	C5A	89.99(10)	C24	C24A	I002	116.88(18)
C24A	I002	C25A	91.51(11)	C24	C24A	C29A	124.3(2)
O21	S21	C34	102.70(16)	C29A	C24A	I002	118.78(18)
O22	S21	O21	114.94(15)	C0AA	C25A	I002	117.5(2)
O22	S21	O23	115.05(14)	C28A	C25A	I002	118.14(18)
O22	S21	C34	104.10(15)	C28A	C25A	C0AA	124.3(2)
O23	S21	O21	113.97(13)	C27	C26	C0AA	120.4(3)
O23	S21	C34	103.98(14)	C26	C27	C28	120.7(3)
C25A	C0AA	C26	117.4(3)	C27	C28	C28A	120.8(3)
C2	C1	C9A	120.5(3)	C25A	C28A	C28	116.2(2)
C3	C2	C1	121.1(2)	C25A	C28A	C29	124.0(2)
C2	C3	C4	119.8(2)	C28	C28A	C29	119.6(2)
C4A	C4	C3	118.1(3)	C28A	C29	C29A	113.6(2)
C4	C4A	I1	118.99(19)	C28A	C29	C30	110.3(2)
C4	C4A	C9A	123.9(2)	C29A	C29	C30	113.8(2)
C9A	C4A	I1	117.12(18)	C21	C29A	C29	120.3(2)
C5A	C5	C6	117.9(3)	C24A	C29A	C21	116.2(2)
C5	C5A	I1	119.5(2)	C24A	C29A	C29	123.5(2)
C5	C5A	C8A	123.7(2)	C31	C30	C29	120.9(2)
C8A	C5A	I1	116.82(18)	C31	C30	C31'	118.6(2)
C7	C6	C5	120.3(3)	C31'	C30	C29	120.3(2)
C6	C7	C8	121.1(3)	C30	C31	C32	120.2(3)
C8A	C8	C7	120.1(3)	C30	C31'	C32'	120.7(2)
C5A	C8A	C8	116.9(2)	C33	C32	C31	120.6(3)
C5A	C8A	C9	121.5(2)	C33	C32'	C31'	120.3(3)
C8	C8A	C9	121.6(2)	C32'	C33	C32	119.6(2)
C8A	C9	C10	111.8(2)	F21	C34	S21	111.6(3)
C9A	C9	C8A	110.44(19)	F21	C34	F22	107.6(3)
C9A	C9	C10	110.8(2)	F21	C34	F23	107.6(3)
C1	C9A	C9	122.1(2)	F22	C34	S21	110.7(2)
C4A	C9A	C1	116.5(2)	F23	C34	S21	110.8(2)
C4A	C9A	C9	121.3(2)	F23	C34	F22	108.3(3)

C11	C10	C9	119.4(2)	O1	S1	C14	101.41(15)
C11'	C10	C9	121.5(2)	O2	S1	O1	114.70(16)
C11'	C10	C11	119.1(2)	O2	S1	O3	115.05(14)
C12	C11	C10	120.4(3)	O2	S1	C14	105.05(14)
C10	C11'	C12'	120.2(3)	O3	S1	O1	114.61(15)
C13	C12	C11	120.0(3)	O3	S1	C14	103.79(14)
C13	C12'	C11'	120.2(3)	F1	C14	S1	110.0(2)
C12'	C13	C12	120.0(3)	F2	C14	S1	111.4(2)
C22	C21	C29A	120.7(3)	F2	C14	F1	107.3(3)
C23	C22	C21	121.4(3)	F3	C14	S1	111.8(2)
C22	C23	C24	119.5(3)	F3	C14	F1	108.3(3)
C24A	C24	C23	117.9(2)	F3	C14	F2	107.8(3)

Table S14: Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for **7k**.

Atom	x	y	z	U(eq)
H0AA	3533.29	1066.65	9204.9	28
H1	5118.69	1222.03	3058.98	24
H2	4072.94	277.81	2877.13	27
H3	2639.06	184.65	3714.05	25
H4	2168.92	1099.1	4669.28	20
H5	2491.12	3953.66	4377.66	23
H6	3199.31	4700.16	3309.99	31
H7	4654.43	4396.1	2608.49	32
H8	5450.02	3354.35	2958.06	27
H9	5545.72	2290.98	3745.73	19
H11	5393.2	1300.62	5257.22	25
H11'	5380.33	3404.41	5284.22	25
H12	5945.42	1291.8	6747.13	31
H12'	5935.14	3389.37	6774.68	31
H13	6221.94	2336.51	7500	35
H21	5650.46	3952.21	11064.47	25
H22	4621.95	4911.62	10919	30
H23	3349.22	4921	9878.52	28
H24	3107.68	3950.51	8938.12	21
H26	4047.79	272.89	10312.04	36
H27	5216.78	598.69	11369.02	36
H28	5881.94	1709.63	11355.99	28
H29	6045.58	2807	10761.17	20
H31	6488.46	3730.27	9093.89	26
H31'	6792.92	1675.21	9581.1	26
H32	7810.55	3677.86	8090.94	31
H32'	8122.71	1634.81	8589.74	28
H33	8631.6	2635.01	7845.45	27

8 Literature

- [1] Wilfred L. F. Armarego, Christina Li Lin Chai, *Purification of Laboratory Chemicals*, Elsevier, **2009**.
- [2] E. Krasnokutskaya, N. Semenischeva, V. Filimonov, P. Knochel, *Synthesis* **2007**, 2007, 81.
- [3] R. Beckert, E. Fanghänel, W. D. Habicher, H.-J. Knölker, P. Metz, K. Schwetlick, *Organikum. Organisch-chemisches Grundpraktikum*, Wiley-VCH Verlag, Weinheim, **2015**.
- [4] R. Imbos, A. J. Minnaard, B. L. Feringa, *J. Am. Chem. Soc.* **2002**, 124, 184.
- [5] R. Quach, D. P. Furkert, M. A. Brimble, *Tetrahedron Lett.* **2013**, 54, 5865.
- [6] S. Wang, L. Liu, X. Guo, G. Li, X. Wang, H. Dong, Y. Li, W. Zhao, *RSC Adv.* **2019**, 9, 13878.
- [7] T. Fukuyama, T. Bando, I. Ryu, *Synthesis* **2018**, 50, 3015.
- [8] J. C. Gonzalez-Gomez, N. P. Ramirez, T. Lana-Villarreal, P. Bonete, *Org. Biomol. Chem.* **2017**, 15, 9680.
- [9] M. Barbasiewicz, K. Błocki, M. Malińska, R. Pawłowski, *Dalton Trans.* **2013**, 42, 355.
- [10] E. Coya, N. Sotomayor, E. Lete, *Adv. Synth. Catal.* **2015**, 357, 3206.
- [11] M. Sickert, H. Weinstabl, B. Peters, X. Hou, M. Lautens, *Angew. Chem. Int. Ed.* **2014**, 53, 5147.
- [12] a) T.-S. Mei, R. Giri, N. Maugel, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2008**, 47, 5215; b) Xing Chen, Marc Poirier, Yee-Shing Wong, Guang-Zhong Wu, EP0977739, **2003**.
- [13] H.-Y. Zhao, X.-Y. Yang, H. Lei, M. Xin, S.-Q. Zhang, *Synth. Commun.* **2019**, 49, 1406.
- [14] K. S. Yang, G. Budin, C. Tassa, O. Kister, R. Weissleder, *Angew. Chem. Int. Ed.* **2013**, 52, 10593.
- [15] F. Gohier, J. Mortier, *J. Org. Chem.* **2003**, 68, 2030.
- [16] T.-C. Chang, S. J. Yu, *Synth. Commun.* **2014**, 45, 651.
- [17] A. J. Blake, A. Novak, M. Davies, R. I. Robinson, S. Woodward, *Synth. Commun.* **2009**, 39, 1065.
- [18] R. Bedford, T. Gallagher, D. Pye, W. Savage, *Synthesis* **2015**, 47, 1761.
- [19] A. Boelke, E. Lork, B. J. Nachtsheim, *Chem. Eur. J.* **2018**, 24, 18653.
- [20] J. Cvengroš, D. Stolz, A. Togni, *Synthesis* **2009**, 2009, 2818.
- [21] S. Bhattacharjee, A. Guin, R. N. Gaykar, A. T. Bijju, *Org. Lett.* **2019**, 21, 4383.
- [22] D. Zhu, M. Li, Z. Wu, Y. Du, B. Luo, P. Huang, S. Wen, *Eur. J. Org. Chem.* **2019**, 2019, 4566.
- [23] C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, 110, 6158.
- [24] a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, 132, 154104; b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, 32, 1456.
- [25] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, 7, 3297.
- [26] F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, 8, 1057.
- [27] S. Kozuch, D. Gruzman, J. M. L. Martin, *J. Phys. Chem. C* **2010**, 114, 20801.
- [28] L. Goerigk, A. Hansen, C. Bauer, S. Ehrlich, A. Najibi, S. Grimme, *Phys. Chem. Chem. Phys.* **2017**, 19, 32184.
- [29] A. Hellweg, C. Hättig, S. Höfener, W. Klopper, *Theor. Chem. Acc.* **2007**, 117, 587.

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One-Pot Synthesis and Conformational Analysis of 6-Membered Cyclic Iodonium Salts

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Abstract

Two one-pot procedures for the construction of carbon-bridged diaryliodonium triflates and tetrafluoroborates are described. Strong Brønsted acids enable the effective Friedel-Crafts alkylation with diversely substituted *o*-iodobenzylalcohol derivatives, providing diphenylmethane scaffolds which are subsequently oxidized and cyclized to the corresponding dibenzo[*b,e*]iodinium salts. Based on NMR-investigations and DFT-calculations we could verify a so far undescribed existence of two stable isomers in cyclic iodonium salts substituted with aliphatic side chains in the carbon bridge.

Keywords

hypervalent iodine • iodonium salts • one-pot synthesis • Friedel-Crafts synthesis • I-heterocycles

Introduction

The last decades have witnessed extensive developments in the chemistry of hypervalent iodine compounds (HVIs).^[1] Even in the delicate field of total synthesis^[2] or in organo-^[3] and photocatalysis,^[4] HVIs have found widespread applications. An important subclass of HVIs are diaryl- λ^3 -iodanes or diaryliodonium salts (DIS, **1**, Figure 1).^[5] Bearing iodobenzene as potent leaving group (hypernucleofuge)^[6] they have become frequently utilized reagents in a plethora of C(spⁿ)-H and Het-H arylation reactions.^[7] Despite their outstanding performance as electrophilic group transfer reagents in transition metal-mediated and metal-free arylations their time-consuming multi-step synthesis often impedes their application.^[8] Albeit various λ^3 -iodane mediated reactions have been performed in a catalytic manner and diverse atom-economic conversions have been described for different types of (recyclable) HVIs, most DIS are utilized generating equimolar amounts of waste.

Figure 1: Schematic presentation of DIS **1** (left) and CDIS **2 – 4** (right).

A subclass of DIS are cyclic diaryliodonium salts (CDIS) where the aryl moieties are directly connected or bridged with carbon- or heteroatoms (**2 – 4**, Figure 1).^[9] While comprising a comparable reactivity towards carbon and heteroatom nucleophiles as their acyclic counterparts, CDIS are promising candidates for the effective synthesis of doubly functionalized diaryl-based systems. The aryl-moieties are chemically bound and are, after an initial ring-opening reaction, readily available for a second inter- or intramolecular coupling event. Various transformations have been described with these iodacycles providing numerous highly functionalized biaryls and polycyclic (hetero)arenes (Scheme 1). Here, tricyclic dibenzo[*b,d*]iodol-5-ium salts **3** were widely applied. They have been utilized in enantioselective ring opening reactions to give *o,o'*-difunctionalized biaryls (Scheme 1, **a**)^[10] and in effective double functionalizations for the efficient synthesis of carbazoles, fluorenes, dibenzothio- and dibenzoselenophenes (**b**),^[11,12,13] giving a fast access to a wide range of pharmacophores and functional materials. 6-Membered dibenzo[*b,e*]iodinium salts **4** were commonly utilized as well. Effective ring-opening reactions with high enantioselectivities (**c**),^[14] and the synthesis of (oxidized) thioxanthenes (**d**),^[12] acridines (**e**)^[13] and xanthen(on)es (**f**)^[15] have been described, emphasizing their wide range of applications.

Scheme 1: Synthetic applications of cyclic diaryliodonium salts.

Compared to their acyclic counterparts, CDIS are much less frequently utilized in organic synthesis. Apart from their specialized need as substrates for the synthesis of heteroatom- or carbon-bridged *o,o'*-disubstituted biaryl systems, one reason for this issue may be the availability of efficient protocols for their synthesis. The synthesis of iodonium salts **3** and their precursors is commonly achieved *via* cross-coupling reactions of *o*-haloanilines followed by a Sandmeyer-type iodination (Scheme 2, **A**).^[13] The preparation of homologues iodonium salts **4** is less standardized: A selective mono-metalation of *o*-diiodobenzenes and 1,2-addition to aromatic aldehydes with a subsequent dehydroxylation enables the synthesis of various diphenylmethanes (Scheme 2, **B1**).^[13] Different *p*-toluidine derivatives have been *o*-alkylated in order to obtain diversely aminated 2,2-diphenylpropanes which were transformed into precursors for CDIS *via* Sandmeyer iodination (**B2**).^[12] Unsubstituted diphenylmethanes can be modified with electron-withdrawing groups, thus enabling a selective electrophilic iodination at the methylene *o*-position (**B3**).^[16]

A) Common pathway for the synthesis of *o*-iodobiphenyls

B) Conventional synthesis of dibenzo[*b,e*]iodinium precursors

C) Our approach: One-pot Friedel-Crafts/oxidation sequence

Scheme 2: Common pathways for the precursor synthesis of cyclic diaryliodonium salts.

All these routes need at least two independent steps to obtain the *o*-iodinated diphenyl-compounds which then need to be further oxidized to the desired CDIS **3** or **4**. Herein, we describe the effective synthesis of dibenzo[*b,e*]iodinium salts **4** in a one-step Friedel-Crafts/oxidation sequence to give iodonium triflates and tetrafluoroborates **7** and **8** (Scheme 2, **C**).

Results and Discussion

For the initial Friedel-Crafts alkylation with *o*-iodobenzyl alcohols **5** different procedures in dipolar aprotic solvents were known under Brønsted or Lewis-acidic conditions.^[17] We decided to utilize a strong but weakly coordinating Brønsted acid that promotes the coupling step to the diphenylmethane **9** (Table 1) and the concluding oxidation to the final dibenzo[*b,e*]iodinium salt **4** to serve as the activator in both steps and as a the final counter anion in the CDIS. In preliminary optimizations with trifluoromethanesulfonic acid (TfOH) and *m*CPBA as oxidant (see SI, Table S1) the desired one-pot reaction was effectively performed. However, the utilization of *m*CPBA gave undesired side products that complicated the work-up of the reaction. Therefore, we decided to conduct a second optimization with Oxone[®] as oxidant, that enabled an easier, extraction-based work-up procedure.

From literature and our preliminary test reactions we recognized that for a successful oxidation of iodoarenes with Oxone[®], combinations of TfOH and H₂SO₄ are best in terms of reactions times and yields (SI, Table 2) and therefore focused on this combination.^[18] We started our investigation with *o*-iodobenzyl alcohol **5a** (R = H, Table 1) as the model substrate. Coupling with TfOH and 3 eq. of benzene (**6a**) in DCM and subsequent oxidation with Oxone[®] and H₂SO₄ after addition of MeCN yielded the desired iodonium salt **7a** in 36% (entry 1). While the yield was still moderate, the product could be easily purified by extraction and washing. Utilizing 5 eq. of **6a** enhanced the yield to 77% (entry 2) while the use 10 eq. improved the product purity due to a lowered side product profile in the coupling step (entry 3). A dropwise addition of **5a** to the acidic solution led to a more selective generation of **9a** and could increase the yield to 89% (entry 4). Performing the first step in a 1:1 mixture of benzene and DCM did not show a significant improvement (entry 5). Further experiments revealed, that MeCN was necessary in the second step to ensure a clean conversion of the intermediate (entry 6) while the generation of **9a** could not be achieved in pure MeCN (entry 7). Addition of low amounts of 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) in the second reaction step slightly improved the reaction time (entry 8).

When we then started to investigate our substrate scope, we observed a significant dropdown in yield with brominated *o*-iodobenzyl alcohol **5b** (entry 9). Addition of HFIP in the second step could increase the oxidation rate and product **7b** was obtained in

85% (entry 10). With NO₂-substituted alcohol **5c** addition of HFIP was not sufficient to completely convert the intermediate **9c** (entry 11). Possibly due to diminished stability of the oxidant under these strongly acidic conditions, the addition of further Oxone[®] and H₂SO₄ after an initial oxidation period was necessary which finally increased the yield of **7c** to 84% (entry 12).

Table 1: Optimization of the One-Pot Procedure with Oxone[®] as Oxidant.

Entry ^[a]	R	Benzene (eq.)	Solvent A	Solvent B	t ₁ / t ₂ [min] / [h]	Yield of 7 ^[b] [%]
1	H (5a)	3	DCM	MeCN	5 / 1.5	36
2	H	5	DCM	MeCN	5 / 1.5	77
3	H	10	DCM	MeCN	5 / 1.5	71 ^[c]
4^[d]	H	10	DCM	MeCN	5 / 2	89
5 ^[d]	H	28	DCM	MeCN	5 / 2	90
6 ^[d]	H	10	DCM	DCM	5 / 24	< 10
7 ^[d]	H	10	MeCN	MeCN	360 / ---	0
8 ^[d]	H	10	DCM	MeCN^[e]	5 / 1	89
9	Br (5b)	10	DCM	MeCN	120 / 16	57
10	Br	10	DCM	MeCN^[e]	120 / 16	85
11	NO₂ (5c)	10	DCM	MeCN ^[e]	300 / 16	40 – 50
12^[f]	NO₂	10	DCM	MeCN^[e]	300 / 40	84

[a] Reaction conditions: Step 1: **5a** (0.2 mmol), benzene, TfOH (5 eq.), solvent A (1 mL), 5 min, 0 °C; Step 2: solvent B (1 mL), H₂SO₄ (5 eq.), Oxone[®] (1 eq.), tightly closed screw cap vial, 0 °C – rt. [b] Isolated yield after purification, purity > 97% [c] Fluctuation in yield comes from washing process. 10 eq. of arene were kept as purity improved from > 95% to > 98%. [d] Dropwise addition of **5a** to **6a** in DCM and TfOH. [e] HFIP (0.2 mL) was added. [f] Addition of Oxone[®] (1 eq.) and H₂SO₄ (5 eq.) after 16 h of step 2.

With optimized conditions for different benzylic alcohols **5** in hand, we started to further investigate the scope and scalability of the reaction (Scheme 3). Performing the reaction on a 5 mmol scale, gave **7a** in slightly improved yield of 93%. We then investigated other leaving groups than Y = OH. When utilizing o-iodobenzyl acetate **10**, **7a** was obtained in 87% yield, whereas with methyl ether **11** or ethyl carbonate **12** iodonium salt **7a** was isolated in 79% and 89% yield. With chloride **13** a complex mixture was obtained during the oxidation step which drastically reduced isolated yield of **7a** to less than 10%.

Scheme 3: Substrate scope using the optimized conditions of Table 1: Step 1: **5** (0.2 mmol), **6** (10 eq.), TfOH (5 eq.), DCM (1 mL), 5 min, 0 °C; Step 2: MeCN (1 mL), H₂SO₄ (5 eq.), Oxone® (1 eq.), tightly closed screw cap vial, 0 °C – rt. [a] Reaction was performed on a 5.0 mmol scale. [b] HFIP (0.2 mL) was used in step 2. [c] 0.2 mL HFIP were used in step 2. After 16 h additional Oxone® (1 eq.) and H₂SO₄ (5 eq.) were added. [d] Only 5 eq. of **6** were used.

As already discussed in Table 1, 5-Br and 5-NO₂ derivatives were viable as well, although under slightly different reaction conditions. Under these conditions F- and CF₃-substituted derivatives **7d** and **7e** could be obtained in up to 74%. Cl-substitution led to a diminished yield of 58% for **7f**. CN-substituted iodonium salt **7g** was generated in 45%, albeit the rate for both reaction steps was significantly reduced. A variation of the substitution pattern was viable as 4- and 3-Br-substituted derivatives **7h** and **7i** were isolated in 81% and 55% respectively, indicating that steric effects may be relevant during the oxidation step. Thus, the lowered yield for the (Cl)₂-substituted salt **7j** (42%) in comparison to **7f** might be due to electronic or steric effects. The utilization of secondary aliphatic benzyl alcohols was difficult due to significant styrene formation during the Friedel-Crafts step (see SI, Figure S1) while secondary diphenylmethanols were suitable. Here, the Ph-substituted salt **7k** could be obtained in 79% yield. Even substrates with electron withdrawing substituents such as bis-(CF₃)- and Cl,F-disubstituted diphenylmethanols were viable for a selective cyclization and yielded **7l** and **7m** in up to 73% yield.

Reaction of **5a** with *p*-xylene successfully lead to the formation of **7n** in 93% yield. However, arenes with an unsymmetrical substitution pattern or more electron donating groups were problematic due to inseparable isomer formation and decomposition during the oxidation step. Substrates that could not successfully be synthesized are found in the SI (Figure S1).

While the selectivities in Friedel-Crafts alkylations and the decomposition of electron rich substrates were intrinsic problems of our methodology, we tried to reoptimize our one-pot procedure to enable the transformation of secondary, aliphatic benzyl alcohols. In preexaminations we found, that 1-(2-iodophenyl)ethan-1-ol (**5n**, Table 2) reacts in DCM with toluene in excellent *para*-selectivity under mild conditions (0 °C) with 1 eq. of HBF₄·OEt₂. When adding more acid after the addition of *m*CPBA as oxidant, the desired alkyl substituted iodonium salt **8a** could be obtained in 67% (Table 2, entry 1). TLC-MS and GC-MS investigations indicated the formation of side products during the oxidation step. Thus, a reduction of oxidant lead to a significant increase in yield (83%, entry 2). However, the reaction mixtures still contained a significant amount of dark-coloured impurities which made an unwanted filtration necessary during the work-up. Hence, we tried to modify our oxidation conditions by addition of MeCN. First,

this resulted in a reduction in yield (entry 3). The addition of more HBF₄ during the oxidation step enabled at least a moderate yield of 70% (entry 4). Reduction of the amount of oxidant was also not successful (entry 5 and SI, Table S5). We then reevaluated the acid stoichiometry and recognized that addition of 3 eq. HBF₄ at the beginning of the reaction was beneficial for its total outcome, yielding 81% of **8a** (entry 6). We now were satisfied with the reaction performance and stopped our optimization at this point to investigate a preliminary substrate scope. Here we decided to use DCM as sole solvent due to its higher efficiency in terms of applied amount of HBF₄.

Table 2: Re-optimization with 1-(2-iodophenyl)ethan-1-ol (**5n**) for the synthesis of iodonium salt **8a**.

Entry ^[a]	PhMe (eq.)	HBF ₄ (eq.) 1 st / 2 nd step	mCPBA (eq.)	Solvent 2 nd step	Yield of 8a ^[b] [%]
1	5	1 / 2	4	DCM	67
2	5	1 / 2	2	DCM	83
3	5	1 / 2	2 ^[c]	MeCN	53
4	5	1 / 5	2	MeCN	70
5	5	1 / 5	1	MeCN	58
6	5	3 / 2	2	MeCN	81

[a] Standard conditions: **5n** (0.2 mmol) in DCM (1 mL) with toluene (5 eq.). Addition of HBF₄·OEt₂ at 0 °C, stirring till completion, addition of DCM (1 mL), mCPBA, stirring for 10 min, addition of HBF₄·OEt₂, stirring till completion at rt. [b] Isolated yield after purification, purity > 97%. [c] mCPBA (2 eq.) was added, as the intermediate was not completely converted in the 2nd step.

When the reaction of **5n** was performed with toluene on a 5 mmol scale under the optimized conditions, pure **8a** was obtained in 35% (Scheme 4). When exchanging the Me-substituent to Et- or *i*Pr-moieties the corresponding products **8b** and **8c** were

isolated in yields of up to 59%. The reduced yields may be attributed to a more stabilized, sterically demanding benzylic cation and a higher lability to oxidants due to the increased electron density at the benzylic position. While diphenylmethanols are well tolerated under the previously optimized conditions, the Ph-derivative **8d** could only be obtained in 37%. A reduction of the electron density of the secondary alcohol **5** was detrimental for the reaction outcome and substrate **8e** was obtained in only 22%. Due to the increased steric demand of secondary benzyl cations, the coupling with *o*-xylene was moderately selective and yielded 56% of **8f**. The same effect was disadvantageous for the reaction with *p*-xylene giving **8g** in 20%. With benzene as coupling partner the Friedel-Crafts step could not be performed. Also, with tertiary alcohols no product was obtained due to major side reactions during the initial Friedel-Crafts-step (see SI, Figure 1).

Scheme 4: Substrate scope for the optimized conditions of Table 2: Step 1: **5** (0.2 mmol), **6** (5 eq.), HBF₄·OEt₂ (1 eq.), DCM (1 mL), 5 min, 0 °C; Step 2: DCM (1 mL), HBF₄·OEt₂ (2 eq.), mCPBA (2 eq.), tightly closed screw cap vial, 0 °C – rt. [a] Reaction was performed on a 5.0 mmol scale.

During our method development we observed that the ¹H-NMR-spectra of the newly obtained iodonium salts showed interesting exchange effects (Figure 2). Compounds **8a** and **8b** showed an unusual signal broadening, of the benzylic proton and all other

protons in the benzylic aliphatic side chain. In contrast, the corresponding protons of the *i*Pr-group in **8c** and the benzylic proton of **8d** showed well-resolved signals. As these effects were also visible in the corresponding ^{13}C -spectra (see SI, Chapter 6) and some previously published literature spectra,^[14] we were interested in the origin of these observations. At this point two causes were taken into account: First, a coordination or even deprotonation of the benzylic protons by the counter-anion of the iodonium salt or traces of water in the NMR-solvent was considered. But the spectra in Figure 2 showed no significant effect on the peak shape or chemical shift of the aromatic methyl groups at 2.4 ppm (green area) and a computational study of Hoffmann *et al.* suggested that a potential zwitterionic iodabenzene structure was very unlikely for our structures under the examined conditions.^[19] Therefore, conformational changes of our substrates were more likely to be the reason for the observed signal broadening and we investigated potential conformers via DFT calculations.

Figure 2: 600 MHz ^1H -NMR-spectra of compounds **8a-d**. The signals of the benzylic- (●) as well as alkyl-protons (Δ) are broadened in compounds **8a** and **8b**.

As the aromatic Me-groups were unlikely to have a severe effect on conformational changes at the benzylic position, we performed our calculations on the simplified

tetrafluoroborates **8a'-d'** (Figure 3). When optimizing the structure of the Me-derivative **8a'** at RI-PBE0-D3BJ/SVP level of theory, we were able to minimize two conformational isomers **8a'**_{ax} and **8a'**_{eq} in which the central 6-membered iodoninium-ring adopts a boat-like structure with the methyl group in an either axial or equatorial position. When reevaluating the energies of the conformers at CPCM(DMSO)/RI-DSD-BLYP/TZVPP level of theory we found that **8a'**_{ax} was only 0.6 kcal/mol lower in energy than the equatorial conformer **8a'**_{eq}. This corresponds to an equilibrium constant of $K \approx 3$ that would provide a significant amount of both conformers at room temperature. While the availability of a reasonable amount of > 1% of both species is a prerequisite for the occurrence of dynamic effects in NMR-spectra (besides a significant chemical shift difference for the observed protons H_{ax} and H_{eq} in both conformers) we were furthermore interested in an approximate activation energy for the process.

Figure 3: Relative energies in kcal/mol for conformational isomers of dibenzo[*b,e*]iodinium tetrafluoroborates **8a'-d'** (R = Me, Et, *i*Pr, Ph). Energies were calculated on CPCM(DMSO)/RI-DSD-BLYP/TZVPP//RI-PBE0-D3BJ/SVP level of theory. The corresponding structures for the

methyl derivative are shown, the BF_4^- anions were omitted for clarity. For the coordinates of all optimized structures see SI.

An optimization and energy evaluation for a transition state **8a'**_{TS} implied a free activation energy $G^\ddagger$ of 12.6 kcal/mol that is reasonable for the observed dynamic process at room temperature. As we could not conclusively account either the free activation energy $G^\ddagger$ or the free energy difference ΔG between the axial and equatorial conformers for the availability of sharp NMR signals, we conducted similar calculations with Et-, *i*Pr- and Ph-substituted compounds **8b'**-**8d'**. Since the calculated free activation energy $G^\ddagger$ of each compound was in a range between 10.4 and 20.8 kcal/mol, exchange processes should be reasonably fast. Our calculated free energy values ΔG for the conformers are in good agreement with observed signal broadenings in the spectra as the ethyl derivative **8b'** gives with a ΔG of ≈ 1.8 kcal/mol rise to an equilibrium constant of $K \approx 20$. Calculations for **8c'** and **8d'** result in values of $K \approx 660$ and $K \approx 1300$. Thus, the most reasonable explanation for the observed signal broadening was the availability or absence of both equilibrium conformers **8ax** and **8eq**. Interestingly, a transition state for a potential *t*Bu-substituted derivative could not be found which may indicate a non-interconvertibility of both isomers. This circumstance is still under ongoing investigation.

Figure 4: Top: Temperature dependant 360 MHz ^1H -NMR-spectra of 10-methyl-10*H*-dibenzo-*[b,e]*iodinin-5-ium trifluoromethanesulfonate **14** in $\text{MeOH-}d_4$ (for synthesis see SI). Bottom: Axial and equatorial conformer of the cation of **14** as optimized on RI-PBE0-D3BJ/SVP level of theory.

To back up the results of our DFT calculations we synthesized the triflate **14** as it was better soluble than the corresponding tetrafluoroborate and performed temperature dependant 360 MHz- ^1H -NMR measurements in a range between -80 and +55 °C (Figure 4). At elevated temperatures the benzylic proton and the methyl groups gave a well separated single quartet at 4.31 ppm and a single doublet at 1.81 ppm. Both signals showed coalescence at $T \approx 0$ °C and became very distinct at -60 °C showing two quartets in a 1:2.8 ratio at 4.78 and 3.94 ppm and two corresponding doublets at 2.02 and 1.54 ppm. The ratio changed to 1:3.6 at -80 °C what most likely originates from a different solubility of the conformers at low temperatures.

The observed conformer ratios and the previously calculated equilibrium constant of $K \approx 3$ are in good agreement. An approximate determination of the free activation energy from the measured spectra resulted in a $\Delta G^\ddagger$ value of ≈ 12.5 kcal/mol, which is in first approximation in excellent agreement with the calculated value for **8a'**. However, at this point we cannot clearly allocate the measured signals to their corresponding conformers. All attempts to assign the structures via low temperature NOE-measurements or to synthetically fix the conformation of the iodonium salt did not give resilient results and are still under current investigation.

Summary

In summary, we developed two one-pot procedures for the synthesis of 6-membered cyclic iodonium triflates and tetrafluoroborates. With a Friedel-Crafts alkylation followed by an oxidative cyclization, primary *o*-iodobenzyl alcohols and secondary *o*'-iododiphenylmethanols were successfully transformed into a variety of tricyclic dibenzo[*b,e*]iodinium triflates in moderate to excellent yields. Delicate aliphatic 1-(2-iodophenyl) alcohols could be utilized as starting materials using a modified procedure with HBF₄ as the Brønsted acid. Depending on the substitution of the bridging carbon atom, we observed significant signal broadenings in the corresponding ¹H-NMR and ¹³C-NMR spectra and verified via DFT-calculations and temperature-dependent NMR-measurements that a fast and so far undescribed conformational switch between two stable isomers bearing the aliphatic side chain either in an axial or equatorial position are the rational for this behaviour.

Experimental Section

Detailed optimization studies, experimental procedures, analytical data (¹H-, ¹³C- and ¹⁹F-NMR-chemical shifts, IR-bands, melting points) including the corresponding NMR-spectra as well as coordinates of the calculated structures can be found in the supporting information.

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References

- [1] a) L. D. Caspers, B. J. Nachtsheim, *Chem. Asian. J.* **2018**, *13*, 1231; b) J. Charpentier, N. Früh, A. Togni, *Chem. Rev.* **2015**, *115*, 650; c) X. Li, P. Chen, G. Liu, *Beilstein J. Org. Chem.* **2018**, *14*, 1813; d) G. K. Murphy, L. Racicot, M. S. Carle, *Asian J. Org. Chem.* **2018**, *7*, 837; e) A. Yoshimura, V. V. Zhdankin, *Chem. Rev.* **2016**, *116*, 3328; f) Y. Yoshimura, H. Wakamatsu, Y. Natori, Y. Saito, N. Minakawa, *Beilstein J. Org. Chem.* **2018**, *14*, 1595.
- [2] a) M. Ciufolini, N. Braun, S. Canesi, M. Ousmer, J. Chang, D. Chai, *Synthesis* **2007**, *2007*, 3759; b) S. Ghosh, S. Pradhan, I. Chatterjee, *Beilstein J. Org. Chem.* **2018**, *14*, 1244; c) H. Hamamoto, Y. Shiozaki, H. Nambu, K. Hata, H. Tohma, Y. Kita, *Chem. Eur. J.* **2004**, *10*, 4977; d) G. Jacquemot, G. Maertens, S. Canesi, *Chem. Eur. J.* **2015**, *21*, 7713; e) G. Maertens, C. L'Homme, S. Canesi, *Front. Chem.* **2014**, *2*, 115; f) L. F. Silva, B. Olofsson, *Nat. Prod. Rep.* **2011**, *28*, 1722.
- [3] a) A. H. Abazid, B. J. Nachtsheim, *Angew. Chem. Int. Ed.* **2020**, *59*, 1479; b) A. Boelke, B. J. Nachtsheim, *Adv. Synth. Catal.* **2020**, *362*, 184; c) E. Cots, A. Flores, R. M. Romero, K. Muñiz, *ChemSusChem* **2019**, *12*, 3028; d) A. Flores, E. Cots, J. Bergès, K. Muñiz, *Adv. Synth. Catal.* **2019**, *361*, 2; e) C. Gelis, A. Dumoulin, M. Bekkaye, L. Neuville, G. Masson, *Org. Lett.* **2017**, *19*, 278; f) L. Massignan, X. Tan, T. H. Meyer, R. Kuniyil, A. M. Messinis, L. Ackermann, *Angew. Chem. Int. Ed.* **2020**, *59*, 3184; g) P. Mizar, A. Laverny, M. El-Sherbini, U. Farid, M. Brown, F. Malmedy, T. Wirth, *Chem. Eur. J.* **2014**, *20*, 9910.
- [4] a) A. Baralle, L. Fensterbank, J.-P. Goddard, C. Ollivier, *Chem. Eur. J.* **2013**, *19*, 10809; b) N. Declas, F. Le Vaillant, J. Waser, *Org. Lett.* **2019**, *21*, 524; c) F. Le Vaillant, M. Garreau, S. Nicolai, G. Gryn'ova, C. Corminboeuf, J. Waser, *Chem. Sci.* **2018**, *9*, 5883; d) L. Li, S. Guo, Q. Wang, J. Zhu, *Org. Lett.* **2019**, *21*, 5462; e) S. Mukherjee, R. A. Garza-Sanchez, A. Tlahuext-Aca, F. Glorius, *Angew. Chem. Int. Ed.* **2017**, *56*, 14723; f) D. Wang, J. Mao, C. Zhu, *Chem. Sci.* **2018**, *9*, 5805.
- [5] a) K. Aradi, B. Tóth, G. Tolnai, Z. Novák, *Synlett* **2016**, *27*, 1456; b) E. A. Merritt, B. Olofsson, *Angew. Chem. Int. Ed.* **2009**, *48*, 9052.
- [6] T. Okuyama, T. Takino, T. Sueda, M. Ochiai, *J. Am. Chem. Soc.* **1995**, *117*, 3360.
- [7] a) S. K. Bhunia, A. Polley, R. Natarajan, R. Jana, *Chem. Eur. J.* **2015**, *21*, 16786; b) L. Y. Chan, L. Cheong, S. Kim, *Org. Lett.* **2013**, *15*, 2186; c) Z. Chen, W.-F.

- Wang, H. Yang, X.-F. Wu, *Org. Lett.* **2020**, 22, 1980; d) R. Ghosh, E. Lindstedt, N. Jalalian, B. Olofsson, *ChemistryOpen* **2014**, 3, 54; e) N. Jalalian, E. E. Ishikawa, L. F. Silva, B. Olofsson, *Org. Lett.* **2011**, 13, 1552; f) D. Kumar, M. Pilania, V. Arun, S. Pooniya, *Org. Biomol. Chem.* **2014**, 12, 6340; g) D. Li, C. Liang, Z. Jiang, J. Zhang, W.-T. Zhuo, F.-Y. Zou, W.-P. Wang, G.-L. Gao, J. Song, *J. Org. Chem.* **2020**, 85, 2733; h) R. J. Mayer, A. R. Ofial, H. Mayr, C. Y. Legault, *J. Am. Chem. Soc.* **2020**; i) S. G. Modha, M. F. Greaney, *J. Am. Chem. Soc.* **2015**, 137, 1416; j) X. Pang, Z. Lou, M. Li, L. Wen, C. Chen, *Eur. J. Org. Chem.* **2015**, 2015, 3361; k) M. Reitti, P. Villo, B. Olofsson, *Angew. Chem. Int. Ed.* **2016**, 55, 8928; l) D.-T. D. Tang, K. D. Collins, J. B. Ernst, F. Glorius, *Angew. Chem. Int. Ed.* **2014**, 53, 1809; m) B. R. Vaddula, R. S. Varma, J. Leazer, *Eur. J. Org. Chem.* **2012**, 2012, 6852; n) A. M. Wagner, M. S. Sanford, *J. Org. Chem.* **2014**, 79, 2263; o) D. Wang, B. Ge, L. Li, J. Shan, Y. Ding, *J. Org. Chem.* **2014**, 79, 8607; p) K. Yin, R. Zhang, *Org. Lett.* **2017**, 19, 1530.
- [8] A. Boelke, P. Finkbeiner, B. J. Nachtsheim, *Beilstein J. Org. Chem.* **2018**, 14, 1263.
- [9] a) N. Chatterjee, A. Goswami, *Eur. J. Org. Chem.* **2017**, 2017, 3023; b) V. V. Grushin, *Chem. Soc. Rev.* **2000**, 29, 315.
- [10] a) M. Hou, R. Deng, Z. Gu, *Org. Lett.* **2018**, 20, 5779; b) Q. Li, M. Zhang, S. Zhan, Z. Gu, *Org. Lett.* **2019**, 21, 6374; c) S. Xu, K. Zhao, Z. Gu, *Adv. Synth. Catal.* **2018**, 360, 3877; d) K. Zhao, L. Duan, S. Xu, J. Jiang, Y. Fu, Z. Gu, *Chem* **2018**, 4, 599; e) K. Zhu, K. Xu, Q. Fang, Y. Wang, B. Tang, F. Zhang, *ACS Catal.* **2019**, 9, 4951.
- [11] a) S. Riedmüller, B. J. Nachtsheim, *Beilstein J. Org. Chem.* **2013**, 9, 1202; b) M. Shimizu, M. Ogawa, T. Tamagawa, R. Shigitani, M. Nakatani, Y. Nakano, *Eur. J. Org. Chem.* **2016**, 2016, 2785; c) D. Zhu, Y. Wu, B. Wu, B. Luo, A. Ganesan, F.-H. Wu, R. Pi, P. Huang, S. Wen, *Org. Lett.* **2014**, 16, 2350.
- [12] M. Wang, S. Chen, X. Jiang, *Org. Lett.* **2017**, 19, 4916.
- [13] M. Wang, Q. Fan, X. Jiang, *Org. Lett.* **2018**, 20, 216.
- [14] B. Li, Z. Chao, C. Li, Z. Gu, *J. Am. Chem. Soc.* **2018**, 140, 9400.
- [15] D. Zhu, M. Li, Z. Wu, Y. Du, B. Luo, P. Huang, S. Wen, *Eur. J. Org. Chem.* **2019**, 2019, 4566.
- [16] F. M. Beringer, L. Kravetz, G. B. Topliss, *J. Org. Chem.* **1965**, 30, 1141.
- [17] a) C. He, X. Zhang, R. Huang, J. Pan, J. Li, X. Ling, Y. Xiong, X. Zhu, *Tetrahedron Lett.* **2014**, 55, 4458; b) J. A. McCubbin, O. V. Krokhn, *Tetrahedron Lett.* **2010**, 51,

- 2447; c) X. Mo, J. Yakiwchuk, J. Dansereau, J. A. McCubbin, D. G. Hall, *J. Am. Chem. Soc.* **2015**, *137*, 9694; d) M. Rueping, B. J. Nachtsheim, W. leawsuwan, *Adv. Synth. Catal.* **2006**, *348*, 1033; e) M. Wilsdorf, D. Lechnitz, H.-U. Reissig, *Org. Lett.* **2013**, *15*, 2494.
- [18] a) N. Soldatova, P. Postnikov, O. Kukurina, V. V. Zhdankin, A. Yoshimura, T. Wirth, M. S. Yusubov, *Beilstein J. Org. Chem.* **2018**, *14*, 849; b) N. Soldatova, P. Postnikov, O. Kukurina, V. V. Zhdankin, A. Yoshimura, T. Wirth, M. S. Yusubov, *ChemistryOpen* **2017**, *6*, 18.
- [19] A. M. Rawashdeh, P. Chakkingal Parambil, T. Zeng, R. Hoffmann, *J. Am. Chem. Soc.* **2017**, *139*, 7124.

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