Sustainable and scalable one-pot synthesis of diaryliodonium salts

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Supporting information

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1. General experimental

All reagents were bought from commercial suppliers and used as received. Solvents were obtained as P.A. grade. Anhydrous EtOAc was produced via drying of EtOAc over 4 Å molecular sieves and stored overnight before use. Reactions using anhydrous EtOAc were carried out under nitrogen environment using standard Schlenk techniques.

*m*CPBA (Aldrich, 77 % active oxidant) was dried under vacuum for 4 hours, after which the amount of active oxidant was determined through an iodometric titration¹ and the purity was calculated by weight.

Melting points were measured using a STUART SMP3. NMR measurements were conducted using a 400 MHz Bruker AVANCE II with a BBO probe at 298 K. Chemical shifts (δ) are reported in parts per million (ppm) and referenced CDCl₃ (¹H: 7.26 ppm; ¹³C: 77.2 ppm), DMSO-*d*₆ (¹H: 2.50 ppm; ¹³C: 39.5 ppm) or MeOD-*d*₆ (¹H: 3.31 ppm; ¹³C: 49.0 ppm). Coupling constants (*J*) are given in Hertz (Hz) and refer to apparent multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and combinations thereof for example, dd = doublet of doublets). HRMS spectra were measured on a Bruker microTOF with electron spray ionization (ESI).

2. Optimization

2.1 Optimization for aryl(DMIX)iodonium triflates 2

DMIX-I **1a** was oxidized with *m*CPBA (89% purity) and TfOH in EtOAc (0.7 M) at the given time and temperature. Anisole was used as model substrate for the EAS to form iodonium salt **2a**, which was isolated via precipitation from diethyl ether and filtration. The reactions were performed under inert conditions with anhydrous EtOAc and the yield is based on DMIX-I **1a** if not otherwise stated. The detailed parameters of this optimization are given in Table S1.

		√.	<i>т</i> СРВА, Т	fOH	OMe		OTf	
		Ň≈(EtOAc	>	rt		1	
		1a	Oxidati	on	EAS	2a 0	1e	
Entry	TfOH (equiv)	Water (equiv)	<i>m</i> CPBA (equiv)	Anisole (equiv)	Ox. temp. (°C)	Ox. time (h)	EAS time (h)	Yield 2a (%)
1	4	4	1.3	1.3	0 to rt	2	2	36
2	3	3	1.3	1.3	0 to rt	2	2	46
3	2	3	1.3	1.3	–78 to rt	2	2	53
4	2	3	1.3	1.3	0 to rt	2	16	56
5	2	3	2	1.3	0 to rt	2	2	66
6	2	3	2.5	1.3	0 to rt	2	2	72
7	2	3	1.3	1.3	0 to 50	2	2	0
8	1.5	2.5	2	1.3	0 to rt	2	2	71
9	1	2	2	1.3	0 to rt	2	2	75
10	1	2	2	1.3	0 to rt	3	2	74
11	1	1	2	1.3	0 to rt	2	2	79
12	1	-	2	1.3	0 to rt	2	2	82
13	1	-	2	1	0 to rt	2	2	84
14 ¹	1	-	2	1	0 to rt	2	2	89
15 ¹	1	-	2	1	0	2	2	87
16 ¹	1	-	2	1	0 to rt	1	2	90
171	1	-	1.5	1	0 to rt	1	2	82, 83 ²
181	1	-	1.3	1	0 to rt	1	2	86, 83 ²
19 ¹	1	-	1.1	1	0 to rt	1	2	77
201,3	1	-	1.3	1	0 to rt	1	2	93
21	1	-	1.1	1.3	0 to rt	2	2	74
22	1	-	1.1	1	0 to rt	2	2	71
23 ¹	1	1	1.1	1	0 to rt	2	2	71

Table S1. Optimization for the synthesis of anisyl(DMIX)iodonium triflate (2a).

¹ Reaction open to air with non-dried EtOAc. ² Reaction was repeated to check reproducibility. ³ Yield based on anisole.

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The most important parameter for the reaction proved to be the amount of TfOH. In previous studies, an excess TfOH was required for the oxidation of electron poor iodoarenes,² but DMIX-I **1a** is electron-rich and did not need the extra activation by the acid. Water was added prior to anisole in entries 1-11. This has been shown to be efficient in synthesis of anisyl(heteroaryl)iodonium triflates when an excess of TfOH was used for the oxidation of the heteroaryl iodide.³ We found that by using only 1 equiv TfOH, the addition of water did not impact the yield (entries 11, 12). Presumably, the single equivalent of TfOH is consumed after the oxidation step and is therefore not available for further reactivity with anisole. Furthermore, we found that the reaction outcome does not change when the reaction is carried out open to air with non-dried EtOAc (entry 14). For sustainability reasons the loading of *m*CPBA was aimed to be as low as possible. This could be achieved by a slight increase of **1a** to 1.3 equiv, which resulted in 93% yield of **2a** (based on anisole, entry 20).

2.2 Solvent optimization for diaryliodonium triflate 3a

4-Nitroiodoarene was oxidized with *m*CPBA (87% purity) and TfOH in various solvents (0.7 м). Anisole was used as model substrate for the EAS to form iodonium salt **3a**, which was isolated via precipitation from diethyl and filtration. A brief optimization of solvents, selected based on their sustainability parameters,⁴ is displayed in Table S2.

The use of anhydrous EtOAc (5 ppm water) produced **3a** in 87% yield (entry 1). The use of wetter solvents did not affect the yield very much, as demonstrated by using an old bottle of EtOAc (120 ppm water), which produced 84% yield (entry 3). The reaction worked well also in the known green solvent diethyl carbonate (entry 4), whereas water and isopropanol were inefficient (entries 5, 6).



Table S2. Optimization for the synthesis of 3a.

Entry Solvent		Comments	Yield (%)
1	EtOAc	Anhydrous (5 ppm water)	87
2	EtOAc	Brand new bottle (66 ppm water)	87
3	EtOAc	Old bottle (120 ppm water)	84
4	Diethyl carbonate	-	73
5	Water	-	3
6	Isopropanol	<u>-</u>	2

Note: the use of anhydrous EtOAc proved beneficial in synthesis of some products, see section 2.4, the Note in section 5.2 and products 3e, 3r and 3u. Such conditions were only investigated early in the project and for certain low-yielding products, we have not screened other conditions for the main part of the scope.

2.3 Mini-optimization for diaryliodonium triflate 3q

A small optimization was carried out for **3q**, since this salt produced a lower yield than **3a**. 4-Nitroiodoarene was oxidized with *m*CPBA (87% purity) and TfOH in EtOAc (0.7 M). Benzene was used as model substrate for the EAS to form iodonium salt **3q**, which was isolated via precipitation from diethyl and filtration. A brief optimization of various parameters such as equivalents of triflic acid and temperature after addition of benzene is displayed in Table S3. Carrying out the reaction using the standard conditions produced **3q** in 46% yield (entry 1). An increase in EAS time or EAS temperature did not increase the temperature markedly (entries 2 and 3). However, increasing the equivalents of triflic acid to 3, EAS temp to 45 °C and EAS time to 4 h, resulted in an increased yield of 71% (entry 4).

	<i>m</i> CPBA (1.3 equiv) TfOH (x equiv)	(1.3 equiv)	O ₂ N-
NO ₂ (0.5 mmol)	EtOAc, 0 °C to rt, 2 h	<i>T</i> , t h	3q

Table S3. Optimization for the synthesis of 3q.

Entry	TfOH (equiv)	EAS temp (°C)	EAS time (h)	Yield (%)
1	2	RT	2	46
2	2	RT	20	50
3	2	45	2	45
4	3	45	4	71

2.4 Mini-optimization for diphenyliodonium triflate (3r)

A small optimization was carried out for 3r, since this salt produced a lower yield than 3a. Iodobenzene was oxidized with *m*CPBA (87% purity) and TfOH in EtOAc (0.7 M). Benzene was for the EAS to form iodonium salt 3r, which was isolated via precipitation from diethyl and filtration. A brief optimization of various parameters such as equivalents of triflic acid and temperature after addition of benzene is displayed in Table S4.

Carrying out the reaction using the standard conditions produced **3r** in just 39% yield (entry 1). The use of 3 equivalents TfOH, together with increased EAS time and temperature, increased the yield to 60% (entry 2). The use of anhydrous EtOAc led to 69% yield (entry 3), whereas increasing the EAS temperature from 45 °C to 77 °C during an overnight reaction did not influence the outcome (entry 4).

\downarrow	<i>m</i> CPBA (1.3 equiv) TfOH (x equiv)	(1.3 equiv)	
	EtOAc, 0 °C to rt, 2 h	<i>T</i> , t h	3r

Entry	TfOH (equiv)	EAS temp (°C)	EAS time (h)	Yield (%)
1	2	RT	2	39
2	3	45	4	60
3 ^{<i>a</i>}	3	45	4	69
4 ^{<i>a</i>}	3	45 (5 h) then 77 (overnight)	20	69

^{*a*} Use of anhydrous EtOAc under nitrogen atmosphere. All reagents added at the start of the reaction.

Table S4. Optimization for the synthesis of 3r.

(0.5 mmol)

3. Compound table

3.1 lodoarenes and arenes used in study



1a Characterisation Spectra



1b Purchased 636-98-6



1c Purchased 3058-39-7



Purchased 589-87-7



1e Purchased 637-87-6



1f Purchased 591-50-4

. t-Bu

г-ви **1g** Purchased 35779-04-5



1h Purchased 610-97-9



1i Purchased 4387-36-4



1j Purchased 672-57-1



1k Method⁵ Data⁶



1I Method⁵ Data⁷

102

1m Method⁵ Data⁸



1n Purchased 887266-99-1

1o Purchased 69045-79-0

OMe

1p Purchased 100-66-3



Purchased 578-57-4



Purchased 101-84-8



.OMe MeO. OMe Purchased 621-23-8

Purchased 6231-18-1



Purchased

110-02-1



ÓMe

.OMe

Data⁹

 O_2H

Purchased 25812-30-0

Purchased

108-67-8



CO₂Me

ÓMe

Purchased

606-45-1

Purchased 71-43-2



Method¹⁰ Data¹¹



3.2 DMIX triflates 2

















2h Characterization Spectra





<u>Characterization</u> <u>Spectra</u> **2j** <u>Characterization</u> <u>Spectra</u>

3.3 Diaryliodonium salts 3



OMe

3e Characterization Spectra



3f <u>Characterization</u> <u>Spectra</u>







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4. Synthesis of starting materials

All iodoarenes except **1a** were either purchased or synthesized following literature procedures, see Section 3.1.

4.1 Synthesis of 4-iodo-3,5-dimethylisoxazole (1a)



3,5-dimethylisoxazole

Following a literature procedure,¹³ NH₂OH·HCl (16.9 g, 0.24 mol, 1.2 equiv) was dissolved in water (20 mL) and added to a solution of acetylacetone (25.5 mL, 0.20 mol, 1.0 equiv) in EtOH (20 mL). The reaction mixture was stirred at 100 °C for 3 h. Subsequently, the mixture was poured into ice water (60 mL), extracted with Et₂O (3×40 mL) and dried over anhydrous Na₂SO₄. The dying agent was filtered off and the solvent was removed under reduced pressure. The residue was purified by vacuum distillation (35 °C, 180 mbar) to obtain 3,5-dimethylisoxazole as a colourless liquid (12.0 g, 0.12 mol, 62%);

δ_H (400 MHz, CDCl₃) 5.80 (d, J = 1.0 Hz, 1H), 2.37 (d, J = 0.9 Hz, 3H), 2.25 (s, 3H);

δc (101 MHz, DMSO-d₆) 169.1, 159.9, 102.3, 12.09, 11.3;

HRMS (ESI) calculated C₅H₆NONa for (M+Na⁺)⁺: 120.0429; found: 120.0420.

The NMR data is consistent with literature precedent.¹³ Since no HRMS data was available, we have reported this value.

4-iodo-3,5-dimethylisoxazole (1a)

Following a literature procedure,¹⁴ conc. HNO₃ (8 mL) was added drop wise at 0 °C to a solution of iodine (10.2 g, 40 mmol, 1.0 equiv) in 3,5-dimethylisoxazole (8.29 g, 85.3 mmol, 2.1 equiv) and stirred for 2 h at room temperature. The mixture was poured on ice water (100 mL) and extracted with Et₂O (3×100 mL). The combined organic layers were washed with sat. Na₂S₂O₃, dried over Na₂SO₄ and filtered. The filtrate was collected and volatiles were removed under reduced pressure to obtain product **1a** as a light-yellow solid (17.3 g, 77.6 mmol, 97%); **δ_H (400 MHz, CDCl₃)** 2.42 (s, 1H), 2.23 (s, 1H);

δ_c (101 MHz, DMSO-d₆) 169.92, 161.43, 60.22, 12.51, 12.18;

HRMS (ESI) calculated C₅H₆INONa for (M+Na⁺)⁺: 245.9386; found: 245.9362; **Mp**: 51.5 – 56.0 °C.

The compound has been reported previously, but without full data.

5. General procedures

5.1 General procedure 1 (GP1) for the synthesis of DMIX salts 2



In prose:

DMIX-I (1a, 0.145 g, 0.65 mmol, 1.3 equiv) and ethyl acetate (0.71 mL) were added to a microwave vial followed by mCPBA (87% purity, 0.129 g, 0.65 mmol, 1.3 equiv). The vessel was capped with a rubber septum and whilst stirring, the mixture was cooled to 0 °C using an ice-bath. After stirring for 10 min at this temperature, trifluoromethanesulfonic acid (0.044 mL, 0.5 mmol, 1 equiv) was added dropwise. The ice bath was removed and the reaction was allowed to stir for 2 h at room temperature. The nucleophilic arene (0.5 mmol, 1.0 equiv) was then added dropwise, if liquid, or portion wise, if solid, at room temperature. The reaction was then allowed to stir for 1 h. Normally the reaction mixture was observed as a heterogenous mixture with solid particulates. EtOAc (~5 mL) was then used to wash out the contents of the microwave vial into a round-bottomed flask and then solvent was removed in vacuo but not to complete dryness. Diethyl ether (~15 mL) was added to the reaction mixture and then the flask was left in the freezer overnight to allow product precipitation. The solid diaryliodonium salt product 2 was isolated using filtration through a sintered glass funnel and washed with diethyl ether (3×5 mL). After collecting the solid from the funnel, there was sometimes some residue left on the funnel. This was then washed through the filter with some methanol, and the filtrate was concentrated to yield more of product 2.

In recipe style:

- DMIX-I (**1a**, 0.65 mmol, 1.3 equiv) and ethyl acetate (0.71 mL) are added to a microwave vial.
- *m*CPBA (87% purity, 0.129 mg, 0.65 mmol, 1.3 equiv) is added.
- The vessel is capped with a rubber septum.
- Whilst stirring, the mixture is cooled to 0 °C using an ice-bath.
- After stirring for 10 min at 0 °C, trifluoromethanesulfonic acid (0.044 mL, 0.5 mmol, 1.0 equiv) is added dropwise.
- The ice bath is removed.
- The reaction is allowed to stir for 2 h at room temperature.
- Water (0.027 mL, 1.5 mmol, 3.0 equiv) is then added.
- The reaction is allowed to stir for 10 min at room temperature.
- The nucleophilic arene (0.50 mmol, 1.0 equiv) is then added dropwise, if liquid, or portion-wise, if solid, at room temperature.
- The reaction is allowed to stir for 1 h.
- Normally the reaction mixture is observed as a heterogenous mixture with solid particulates. Methanol (~5 mL) is then used to wash out the contents of the microwave vial into a round-bottomed flask and then solvent is removed *in vacuo* but not to complete dryness.
- Diethyl ether (~15 mL) is added to the reaction mixture and then the flask is left in the freezer overnight to precipitate the product.

- The solid diaryliodonium salt product **2** is isolated using filtration through a sintered glass funnel.
- The solid is washed with diethyl ether (3×5 mL)
- After collecting the solid from the funnel, there can sometimes be some residue that is left on the funnel. This can be washed through with some methanol and the filtrate is concentrated to yield more of product **2**.

5.2 General procedure 2 (GP2) for the synthesis of diaryliodonium salts 3

This method is a modification of GP1, with different stoichiometry and reaction times, and the addition of water to quench the excess triflic acid.



In prose:

Iodoarene (0.50 mmol, 1.0 equiv) and ethyl acetate (0.71 mL) were added to a microwave vial followed by *m*CPBA (87% purity, 0.129 g, 0.65 mmol, 1.3 equiv). The vessel was capped with a rubber septum and whilst stirring, the mixture was cooled to 0 °C using an ice-bath. After stirring for 10 min at this temperature, trifluoromethanesulfonic acid (0.088 mL, 1.0 mmol, 2 equiv) was added dropwise. The ice bath was removed and the reaction was allowed to stir for 2 h at room temperature. Water (0.027 mL, 1.5 mmol, 3.0 equiv) was then added and the reaction was allowed to stir for 10 min. The arene (0.65 mmol, 1.3 equiv) was then added dropwise, if liquid, or in one portion, if solid, at room temperature. The reaction was then allowed to stir for 2 h. Normally the reaction mixture was observed as a heterogenous mixture with solid particulates. MeOH (~5 mL) was then used to wash out the contents of the microwave vial into a round-bottomed flask and then solvent was removed *in vacuo* but not to complete dryness. Diethyl ether (~15 mL) was added to the reaction mixture and then the flask was left in the freezer overnight to allow product precipitation. The solid diaryliodonium salt product **2** was isolated using filtration through a sintered glass funnel and washed with diethyl ether (3×5 mL). After collecting the solid from the funnel, there was sometimes some residue that is left on the funnel. This was washed through the filter with some methanol and the filtrate was concentrated to yield more of product **2**.

In recipe style:

- Iodoarene (0.50 mmol, 1 equiv) and ethyl acetate (0.71 mL) are added to a microwave vial.
- *m*CPBA (87% purity, 0.129 mg, 0.65 mmol, 1.3 equiv) is added.
- The vessel is capped with a rubber septum.
- Whilst stirring, the mixture was cooled to 0 °C using an ice-bath.
- After stirring for 10 min at 0 °C, trifluoromethanesulfonic acid (0.088 mL, 1.0 mmol, 2.0 equiv) is added dropwise.
- The ice bath is removed.
- The reaction is allowed to stir for 2 h at room temperature.
- Water (0.027 mL, 1.5 mmol, 3.0 equiv) is then added.
- The reaction is allowed to stir for 10 min at room temperature.

- The nucleophilic arene (0.50 mmol, 1.0 equiv) is then added dropwise, if liquid, or portion wise, if solid, at room temperature.
- The reaction is allowed to stir for 2 h.
- Normally the reaction mixture is observed as a heterogenous mixture with solid particulates. Methanol (~5 mL) is then used to wash out the contents of the microwave vial into a round-bottomed flask and then solvent is removed *in vacuo* but not to complete dryness.
- Diethyl ether (~15 mL) is added to the reaction mixture and then the flask is left in the freezer overnight.
- The solid diaryliodonium salt product **2** is isolated using filtration through a sintered glass funnel.
- The solid is washed with diethyl ether (3×5 mL).
- After collecting the solid from the funnel, there can sometimes be some residue that is left on the funnel. This can be washed through with some methanol and the filtrate is concentrated to yield more of product **2**.

Note: During our studies, we observed that higher yields could be obtained for several compounds when a more complicated reaction setup was used, which entailed the use of cooling to -78 °C, use of inert atmosphere techniques and/or longer reaction times.

It was important for us to have a straightforward, easily scalable method, so we have reported the slightly lower yields obtained under standard conditions in the manuscript. The more complicated reaction setup and the higher yields obtained are detailed for individual compounds **3e** and **3u** in Section 6.

6. Synthetic details and analytical data of products 2 and 3

(3,5-Dimethylisoxazol-4-yl)(4-methoxyphenyl)iodonium triflate (2a)



Synthesized according to **GP1** from anisole (0.054 mL, 0.50 mmol, 1.0 equiv) to produce **2a** as an off-white solid (0.222 g, 0.463 mmol, 93%); δ_{H} (**400 MHz, DMSO-d₆**) 8.20 – 8.13 (m, 2H), 7.11 – 7.05 (m, 2H), 3.81 (s, 3H), 2.72 (s, 3H), 2.36 (s, 3H); δ_{F} (**376 MHz, DMSO-d₆**) –77.73;

δ_c (101 MHz, DMSO-d₆) 175.6, 162.1, 160.4, 137.1, 120.8 (q, *J* = 322.2 Hz), 117.6, 105.8, 86.1, 55.8, 12.3, 10.9;

HRMS (ESI) calculated $C_{12}H_{13}INO_2$ for (M-OTf⁻)⁺: 329.9985; found:

329.9989; **Mp** 173.7 – 177.6 °C.

(3-Bromo-4-methoxyphenyl)(3,5-dimethylisoxazol-4-yl)iodonium triflate (2b)



Synthesized according to **GP1** from 2-bromoanisole (0.063 mL, 0.50 mmol, 1.0 equiv) to produce **2b** as a beige solid (0.176 g, 0.315 mmol, 63%);

δ_H (400 MHz, DMSO-d₆) 8.58 (d, *J* = 2.2 Hz, 1H), 8.24 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.24 (d, *J* = 8.9 Hz, 1H), 3.91 (s, 3H), 2.73 (s, 3H), 2.37 (s, 3H); **δ_F (376 MHz, DMSO-d₆)** –77.74;

δ_c (101 MHz, DMSO-d₆) 175.9, 160.4, 158.5, 138.6, 136.5, 120.7 (q, J = 322.3 Hz), 115.6, 112.8, 105.8, 86.1, 56.9, 12.3, 10.9;

HRMS (ESI) calculated C₁₂H₁₂BrINO₂ for (M–OTf⁻)⁺: 407.9091; found: 407.9105; **Mp** 145.4 – 149.1 °C.

(2-Bromo-4-methoxyphenyl)(3,5-dimethylisoxazol-4-yl)iodonium triflate (2c)



Synthesized according to **GP1** from 3-bromoanisole (0.063 mL, 0.50 mmol, 1.0 equiv) to produce **2c** as an off-white solid (0.170 g, 0.304 mmol, 61%);

δ_H (400 MHz, DMSO-d₆) 8.44 (d, J = 8.9 Hz, 1H), 7.56 (d, J = 2.8 Hz, 1H), 7.10 (dd, J = 8.9, 2.9 Hz, 1H), 3.84 (s, 3H), 2.72 (s, 3H), 2.38 (s, 3H); δ_F (376 MHz, DMSO-d₆) –77.74;

OMe **δ**_c (101 MHz, DMSO-d₆) 175.8, 163.2, 160.4, 140.2, 127.9, 120.7 (q, *J* = 322.2 Hz), 119.4, 116.6, 111.4, 86.2, 56.3, 12.7, 11.1;

HRMS (ESI) calculated $C_{12}H_{13}INO_2$ for (M–OTf⁻)⁺: 407.9091; found: 407.9074; **Mp** 160.9 – 162.9 °C.

(3,5-Dimethylisoxazol-4-yl)(2,4,6-trimethoxyphenyl)iodonium triflate (2d)



Synthesized according **GP1** from trimethoxybenzene (0.084 g, 0.50 mmol, 1.0 equiv) to produce **2d** as an off-white solid (0.256 g, 0.475 mmol, 95%);

δ_H (400 MHz, DMSO-d₆) 6.47 (s, 2H), 3.97 (s, 6H), 3.87 (s, 3H), 2.65 (s, 3H), 2.33 (s, 3H);

δ_F (376 MHz, DMSO-d₆) -77.75;

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δ_c (101 MHz, DMSO-d₆) 175.5, 166.2, 160.4, 159.1, 120.7 (q, J = 322.3 Hz), 92.0, 87.6, 86.2, 57.2, 56.2, 12.2, 10.8; HRMS (ESI) calculated C₁₄H₁₇INO₄ for (M–OTf⁻)⁺: 390.0197; found: 390.0219; Mp 124.5 – 128.0 °C

(2,6-Dimethoxypyridin-3-yl)(3,5-dimethylisoxazol-4-yl)iodonium triflate (2e)



Synthesized according to **GP1** from 2,6-dimethoxypyridine (0.066 mL, 0.50 mmol, 1.0 equiv) to produce **2e** as a white solid (0.262 g, 0.513 mmol, quant.).

Large scale synthesis: DMIX-I **1a** (10.15 g, 45.5 mmol, 1.3 equiv) and ethyl acetate (40 mL) were added to a 250 mL 3-neck round bottomed flask and cooled to 0 °C. *m*CPBA (88% purity, 8.92 g, 45.5 mmol,

1.3 equiv) was then added portion-wise and the mixture was cooled to -20 °C. After stirring for 10 min at this temperature, TfOH (3.10 mL, 35.0 mmol, 1 equiv) as a solution in EtOAc (5 mL) was added dropwise via a dropping funnel over 15 min. The reaction was allowed to reach room temperature and stirred for 1.5 h. After this time, the reaction was cooled to -20 °C and 2,6-dimethoxypyridine (4.60 mL, 35 mmol, 1.0 equiv) as a solution in EtOAc (5 mL) was added dropwise via dropping funnel over 15 min. The reaction was concentrated until approximately 30 mL remained in the flask and cyclopentyl methyl ether (CPME, 40 mL) was added. The flask was left in the freezer overnight to precipitate the product. Then, the solid **2e** was isolated by filtration through a sintered glass funnel and the solid was washed with CPME (35 mL). The solid was left to air-dry for several hours to produce **2e** as a white solid (16.55 g, 32.43 mmol, 93%);

δ_H (400 MHz, DMSO-d₆) 8.61 (d, *J* = 8.5 Hz, 1H), 6.54 (d, *J* = 8.5 Hz, 1H), 4.01 (s, 3H), 3.92 (s, 3H), 2.70 (s, 3H), 2.37 (s, 3H);

δ_F (376 MHz, DMSO-d₆) -77.75;

δ_c (101 MHz, DMSO-d₆) 175.8, 165.7, 160.4, 159.6, 148.7, 120.7 (q, *J* = 322.3 Hz), 105.0, 89.1, 85.8, 55.3, 54.3, 12.2, 10.8;

HRMS (ESI) calculated $C_{12}H_{14}IN_2O_3$ for $(M-OTf^-)^+$: 361.0044; found: 361.0078; **Mp** 184.4 – 188.5 °C.

(3,5-Dimethylisoxazol-4-yl)(4-phenoxyphenyl)iodonium triflate (2f)



Synthesized according to **GP1** from diphenyl ether (0.079 mL, 0.50 mmol, 1.0 equiv) to produce **2f** as an off-white solid (0.183 g, 0.338 mmol, 68%); δ_{H} (**400 MHz, DMSO-d**₆) 8.23 – 8.16 (m, 2H), 7.52 – 7.42 (m, 2H), 7.27 (tt, J = 7.6, 1.2 Hz, 1H), 7.16 - 7.10 (m, 2H), 7.10 - 7.03 (m, 2H), 2.73 (s, 3H), 2.37 (s, 3H);

δ_F (376 MHz, DMSO-d₆) –77.74;

δ_c **(101 MHz, DMSO-d**₆**)** 175.8, 160.44, 160.43, 154.6, 137.4, 130.5, 125.2, 120.7 (q, *J* = 322.4 Hz), 120.5, 120.2, 108.3, 86.1, 12.3, 10.9;

HRMS (ESI) calculated $C_{17}H_{15}INO_2$ for (M–OTf⁻)⁺: 392.0142; found:

392.0168; **Mp** 157.7 – 158.7 °C.

(3,5-dimethylisoxazol-4-yl)(4-methoxy-3-(methoxycarbonyl)phenyl)iodonium triflate (2g)



Synthesized according to **GP1** from methyl 2-methoxybenzoate (0.072 mL, 0.50 mmol, 1.0 equiv) to produce **2g** as a white solid (0.081 g, 0.151 mmol, 30%);

δ_H (400 MHz, DMSO-d₆) 8.48 (d, *J* = 2.4 Hz, 1H), 8.36 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.29 (d, *J* = 9.1 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 2.73 (s, 3H), 2.36 (s, 3H);

δ_F (376 MHz, DMSO-d₆) –77.75;

δ_c (101 MHz, DMSO-d₆) 175.8, 164.4, 160.5, 160.4, 140.2, 137.2, 123.0, 120.7 (q, *J* = 322.4 Hz), 116.1, 105.1, 86.0, 56.5, 52.5, 12.3, 10.9;

HRMS (ESI) calculated C₁₄H₁₅INO₄ for (M–OTf⁻)⁺: 388.0040; found: 388.0024; **Mp** 151.2 – 153.7 °C.

(3,5-Dimethylisoxazol-4-yl)(thiophen-2-yl)iodonium triflate (2h)



Synthesized according to **GP1** from thiophene (0.040 mL, 0.50 mmol, 1.0 equiv) to produce **2h** as a grey solid (0.117 g, 0.256 mmol, 51%); $\delta_{\rm H}$ (400 MHz, DMSO-d₆) 8.09 (dd, J = 3.8, 1.3 Hz, 1H), 8.00 (dd, J = 5.3, 1.3 Hz, 1H), 7.19 (dd, J = 5.4, 3.8 Hz, 1H), 2.77 (s, 3H), 2.41 (s, 3H); $\delta_{\rm F}$ (376 MHz, DMSO-d₆) -77.73;

 δ_c (101 MHz, DMSO-d₆) 175.8, 160.1, 140.4, 137.2, 129.6, 120.7 (q, J = 322.4 Hz), 101.2, 88.6, 12.3, 10.9; HBMS (FSI) calculated CellalNOS for (M=OTf⁻)⁺: 305 9444: found: 305 9448:

HRMS (ESI) calculated C₉H₉INOS for (M−OTf⁻)⁺: 305.9444; found: 305.9448; **Mp** 146.2 − 148.0 °C.

(3,5-Dimethylisoxazol-4-yl)((8*R*,9*S*,13*S*,14*S*)-3-methoxy-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-2-yl)iodonium triflate (2i)



Synthesized according to **GP1** from estrone methyl ether (0.142 g, 0.50 mmol, 1.0 equiv). After evaporation of EtOAc a mixture of 4 mL *n*-pentane/diethyl ether (1:1) was added and the mixture was stirred for 10 min. The liquid phase removed with a pipet. The residue was then washed with a further 2 portions of 4 mL *n*-pentane/diethyl ether (1:1) to obtain **2i** as a brown solid (0.265 g, 0.404 mmol, 81%);

δ_H (400 MHz, CDCl₃) 7.81 (s, 1H), 6.75 (s, 1H), 3.90 (s, 3H), 2.96 (dd, J = 8.8, 4.4 Hz, 2H), 2.71 (s, 3H), 2.51 (dd, J = 19.0, 8.6 Hz,

1H), 2.40 (s, 3H), 2.35 – 2.19 (m, 2H), 2.14 (dd, *J* = 18.9, 9.1 Hz, 1H), 2.09 – 1.92 (m, 3H), 1.71 – 1.37 (m, 6H), 0.90 (s, 3H);

δ_F (376 MHz, CDCl₃) –78.48;

δ_c (101 MHz, CDCl₃) 220.9, 176.5, 160.6, 154.4, 145.5, 136.5, 134.0, 120.0 (d, *J* = 319.4 Hz), 112.9, 100.9, 81.5, 56.9, 50.2, 48.0, 43.7, 37.7, 35.9, 31.3, 30.0, 25.9, 25.6, 21.6, 13.8, 12.8, 11.2;

HRMS (ESI) calculated C₂₄H₂₉INO₃ for (M–OTf⁻)⁺: 506.1187; found: 506.1157; **Mp** 102.0 – 106.7 °C.

(4-((4-Carboxy-4-methylpentyl)oxy)-2,5-dimethylphenyl)(3,5-dimethylisoxazol-4-yl)iodonium triflate (2j)



Synthesized according to **GP1** from gemfibrozil (0.125 g, 0.50 mmol, 1.0 equiv). After evaporation of EtOAc a mixture of 4 mL *n*-pentane/diethyl ether (1:1) was added and the mixture was stirred for 10 min. The liquid phase removed with a pipet. The residue was then washed with a further 2 portions of 4 mL *n*-pentane/diethyl ether (1:1) to obtain **2j** as a low melting brown solid (0.170 g, 0.274 mmol, 55%);

δ_H (400 MHz, DMSO-d₆) 8.08 (d, J = 0.9 Hz, 1H), 7.13 (s, 1H), 4.00 (t, J = 6.0 Hz, 2H), 2.70 (s, 3H), 2.53 (s, 3H), 2.33 (s, 3H), 2.14 (s, 3H), 1.70 – 1.64 (m, 2H), 1.62 – 1.55 (m, 2H), 1.11 (s, 6H);

^H δ_F (376 MHz, DMSO-d₆) –77.74;

δ_c (101 MHz, DMSO-d₆) 178.8, 175.5, 160.5, 160.1, 140.2, 138.3, 127.7, 120.8 (q, *J* = 322.3 Hz), 114.1, 109.3, 84.9, 68.4, 41.1, 36.4, 25.0, 24.9, 24.6, 15.2, 12.6, 11.1;

HRMS (ESI) calculated C₂₀H₂₇INO₄ for (M–OTf⁻)⁺: 472.0979; found: 472.0951.

(4-Methoxyphenyl) (4-nitrophenyl)iodonium triflate (3a)



Synthesized according to **GP2** from 1-iodo-4-nitrobenzene (0.125 g, 0.50 mmol, 1.0 equiv) and anisole (0.071 mL, 0.65 mmol, 1.3 equiv) to produce **3a** as a white solid (0.220 g, 0.435 mmol, 87%);

δ_H (400 MHz, DMSO-d₆) 8.46 – 8.35 (2H, m), 8.33 – 8.26 (2H, m), 8.25-8.17 (2H, m), 7.13 – 7.04 (2H, m), 3.79 (3H, s);

δ_c (101 MHz, DMSO-d₆) 162.7, 149.7, 137.9, 136.5, 126.5, 123.5,

122.7, 119.5, 118.1, 105.9, 56.2; δ_F (376 MHz, DMSO-d₆) –77.73.

This data is consistent with literature precedent.¹⁵

(4-Cyanophenyl)(4-methoxyphenyl)iodonium triflate (3b)



Synthesized according to **GP2** from 1-iodo-4-cyanobenzene (0.115 g, 0.50 mmol, 1.0 equiv) and anisole (0.071 mL, 0.65 mmol, 1.3 equiv) to produce **3b** as an off-white solid (0.215 g, 0.442 mmol, 89%);

δ_H (400 MHz, DMSO-d₆) 8.36 (2H, d, J = 8.0 Hz), 8.21 (2H, d, J = 8.4 Hz), 7.99 (2H, d, J = 8.1 Hz), 7.10 (2H, d, J = 8.5 Hz), 3.80 (3H, s); **δ_F (376 MHz, DMSO-d₆)** –72.98;

δ_c (101 MHz, DMSO-d₆) 162.2, 137.5, 135.4, 134.9, 121.8, 120.5 (q, *J* = 321.4 Hz), 117.7, 117.5, 114.5, 105.5, 55.8.

(4-Bromophenyl)(4-methoxyphenyl)iodonium triflate (3c)



Synthesized according to **GP2** from 1-iodo-4-bromobenzene (0.142 g, 0.50 mmol, 1.0 equiv) and anisole (0.071 mL, 0.65 mmol, 1.3 equiv) to produce **3c** as a beige solid (0.210 g, 0.390 mmol, 78%);

δ_H (400 MHz, DMSO-d₆) 8.19 – 8.15 (2H, m), 8.13 – 8.10 (2H, m), 7.76 – 7.71 (2H, m), 7.11 – 7.06 (2H, m), 3.80 (3H, s);

δ_F (376 MHz, DMSO-d₆) -72.97;

δ_c (101 MHz, DMSO-d₆) 162.1, 137.3, 136.7, 134.5, 126.0, 120.7 (q, *J* = 322.4 Hz), 117.5, 115.5, 105.6, 55.7.

This data is consistent with literature precedent.¹⁵

(4-Chlorophenyl)(4-methoxyphenyl)iodonium triflate (3d)



Synthesized according to **GP2** from 1-iodo-4-chlorobenzene (0.119 g, 0.50 mmol, 1.0 equiv) and anisole (0.071 mL, 0.65 mmol, 1.3 equiv) to produce **3d** as a white solid (0.214 g, 0.433 mmol, 87%);

δ_H (400 MHz, DMSO-d₆) 8.25 – 8.13 (4H, m), 7.68 – 7.55 (2H, m), 7.13 – 7.03 (2H, m), 3.80 (3H, s);

δ_F (376 MHz, DMSO-d₆) -72.97;

δ_c (101 MHz, DMSO-d₆) 162.1, 137.3, 137.2, 136.6, 131.6, 120.7 (q, *J* = 322.7 Hz), 117.5, 114.8, 105.6, 55.7.

This data is consistent with literature precedent.¹⁵

(4-Methoxyphenyl)(phenyl)iodonium triflate (3e)



OTf Synthesized according to **GP2** from iodobenzene (0.058 mL, 0.50 mmol, 1.0 equiv) and anisole (0.071 mL, 0.65 mmol, 1.3 equiv) to produce **3e** as a white solid (0.180 g, 0.391 mmol, 78%);

δ_H (400 MHz, DMSO-d₆) 8.18 (4H, dd, *J* = 9.9, 8.2 Hz), 7.65 (1H, t, *J* = 7.4 Hz), 7.52 (2H, t, *J* = 7.7 Hz), 7.12 – 7.03 (2H, m), 3.79 (3H, s);

δ_F (376 MHz, DMSO-d₆) –72.97;

δ_c **(101 MHz, DMSO-d**₆**)** 162.0, 137.2, 134.8, 131.9, 131.7, 120.7 (q, *J* = 321.1 Hz), 117.5, 117.0, 105.3, 55.7.

This data is consistent with literature precedent.¹⁵

Note: **3e** was obtained in 85% when anhydrous EtOAc and a nitrogen atmosphere was used throughout the reaction.

(4-(tert-Butyl)phenyl)(4-methoxyphenyl)iodonium triflate (3f)



Synthesized according to **GP2** from 1-iodo-4-*tert*-butyl benzene (0.130 g, 0.50 mmol, 1.0 equiv) and anisole (0.071 mL, 0.65 mmol, 1.3 equiv) to produce **3f** as a beige solid (0.231 g, 0.447 mmol, 90%);

δ_H (400 MHz, DMSO-d₆) 8.17 (2H, d, *J* = 8.5 Hz), 8.10 (2H, d, *J* = 8.2 Hz), 7.53 (2H, d, *J* = 8.3 Hz), 7.07 (2H, d, *J* = 8.5 Hz), 3.79 (3H, s), 1.25 (9H, s);

δ_F (376 MHz, DMSO-d₆) -72.98;

Contents table

 δ_c (101 MHz, DMSO-d₆) 162.0, 161.6, 155.0, 137.2, 134.6, 128.8, 120.5 (q, *J* = 319.8 Hz), 117.5, 113.5, 105.3, 55.7, 34.9, 30.7. This data is consistent with literature precedent.¹⁵

(2-(Methoxycarbonyl)phenyl)(4-methoxyphenyl)iodonium triflate (3g)



Synthesized according to **GP2** from methyl 2-iodobenzoate (0.131 g, 0.50 mmol, 1.0 equiv) and anisole (0.071 mL, 0.65 mmol, 1.3 equiv) to produce **3g** as a light orange solid (0.183 g, 0.353 mmol, 71%); $\delta_{\rm H}$ (400 MHz, DMSO-d₆) 8.36 - 8.14 (4H, m), 7.82 - 7.70 (2H, m), 7.34 - 7.13 (3H, m), 4.06 (3H, s), 3.91 (3H, s); $\delta_{\rm F}$ (376 MHz, DMSO-d₆) -72.89; $\delta_{\rm C}$ (101 MHz DMSO-d₆) 167.8 163.1 139.1 137.0 132.5 131.4 131.0

δ_c **(101 MHz, DMSO-d**₆**)** 167.8, 163.1, 139.1, 137.0, 132.5, 131.4, 131.0, 127.0, 125.9 (q, *J* = 322.2 Hz), 118.3, 116.6, 99.9, 55.9, 54.5.

This data is consistent with literature precedent.¹⁶

(2-Cyanophenyl)(4-methoxyphenyl)iodonium triflate (3h)



Synthesized according to **GP2** from 1-iodo-2-cyanobenzene (0.115 g, 0.50 mmol, 1.0 equiv) and anisole (0.071 mL, 0.65 mmol, 1.3 equiv) to produce **3h** as beige solid (0.207 g, 0.427 mmol, 85%); $\delta_{\rm H}$ (400 MHz, DMSO-d₆) 8.62 (1H, dd, J = 5.8, 3.4 Hz), 8.19 – 8.10 (3H,

m), 7.86 (2H, dd, J = 5.9, 3.4 Hz), 7.11 (2H, d, J = 8.7 Hz), 3.80 (3H, s);

δ_F (376 MHz, DMSO-d₆) -72.96;

OMe δ_c (101 MHz, DMSO-d₆) 162.3, 137.2, 137.1, 136.3, 135.5, 133.0, 120.8 (q, J = 322.4 Hz), 120.6, 118.0, 117.9, 116.4, 106.2, 55.8.

This data is consistent with literature precedent.¹⁷

(2-Chloro-5-(trifluoromethyl)phenyl)(4-methoxyphenyl)iodonium triflate (3i)



Synthesized according to **GP2** from 1-iodo-2-chloro-5trifluoromethylbenzene (0.153 mg, 0.50 mmol, 1.0 equiv) and anisole (0.071 mL, 0.65 mmol, 1.3 equiv) to produce **3i** as a white solid (0.243 g, 0.432 mmol, 86%);

δ_H (400 MHz, DMSO-d₆) 9.06 (1H, d, *J* = 1.9 Hz), 8.26 – 8.18 (2H, m), 8.10 – 8.00 (2H, m), 7.15 – 7.06 (2H, m), 3.79 (3H, s);

δ_F (376 MHz, DMSO-d₆) –56.32 (3F, s), –73.01 (3F, s);

δ_c **(101 MHz, DMSO-d**₆**)** 162.3, 140.5, 137.4, 135.4 – 135.3 (m), 135.3 – 135.1 (m), 131.1, 129.8 (q, *J* = 33.3 Hz), 122.6 (q, *J* = 273.3 Hz), 120.8, 120.7 (q, *J* = 322.4 Hz),

117.7, 105.9, 55.7.

(2-Fluoro-5-nitrophenyl)(4-methoxyphenyl)iodonium triflate (3j)



Synthesized according to **GP2** from 1-fluoro-2-iodo-4-nitrobenzene (0.134 g, 0.50 mmol, 1.0 equiv) and anisole (0.071 mL, 0.65 mmol, 1.3 equiv) to produce **3j** as a light orange solid (0.200 g, 0.382 mmol, 77%);

Large scale synthesis: 1-fluoro-2-iodo-4-nitrobenzene (18.69 g, 70.0 mmol, 1.0 equiv) and EtOAc (90 mL) were added to a 250 mL 3-neck round bottomed flask and cooled to 0 °C. *m*CPBA (88% purity,

17.84 g, 91.0 mmol, 1.3 equiv) was then added portion-wise and the mixture was cooled to -20 °C. After stirring for 10 min at this temperature, TfOH (12.40 mL, 140 mmol, 2 equiv) as a solution in EtOAc (10 mL) was added dropwise via a dropping funnel over 15 min. The reaction was allowed to reach room temperature and the reaction was stirred for 2.5 h. After this time, water (3.80 mL, 210 mmol, 3 equiv) was added and the reaction mixture was allowed to stir for 10 min. The reaction was cooled to -20 °C and anisole (9.90 mL, 91 mmol, 1.3 equiv) as a solution in EtOAc (10 mL) was added dropwise via a dropping funnel over 15 min. The reaction was allowed to reach room temperature and the reaction was stirred for 2.5 h. After this time, the crude mixture was concentrated until approximately 60 mL remained in the flask and CPME (50 mL) was added. The flask was then left in the freezer overnight to precipitate the product. The solid diaryliodonium salt product was isolated by filtration through a sintered glass funnel and the solid was washed with CPME (130 mL). This product was then left to airdry for several hours to produce **3j** as a white solid (24.50 g, 46.8 mmol, 67%);

δ_H (400 MHz, DMSO-d₆) 9.36 (1H, dd, *J* = 4.9, 2.8 Hz), 8.54 (1H, ddd, *J* = 9.1, 4.5, 2.8 Hz), 8.27 – 8.19 (2H, m), 7.83 (1H, dd, *J* = 9.2, 7.5 Hz), 7.13 – 7.06 (2H, m), 3.80 (3H, s);

δ_F (376 MHz, DMSO-d₆) -72.97 (3F, s), -84.24 - -84.32 (1F, m);

δ_c (101 MHz, DMSO-d₆) 162.8 (d, *J* = 258.2 Hz), 162.3, 144.8 (d, *J* = 2.8 Hz), 137.5, 132.4 (d, *J* = 9.1 Hz), 130.8 (d, *J* = 11.9 Hz), 120.7 (q, *J* = 321.7 Hz), 118.0, 117.7, 105.9, 105.0 (d, *J* = 27.0 Hz), 55.8.

This data is consistent with literature precedent.⁶

(4-Cyano-2-fluorophenyl)(4-methoxyphenyl)iodonium triflate (3k)



Synthesized according to **GP2** from 5-fluoro-4-iodobenzonitrile OTf (0.124 g, 0.50 mmol, 1.0 equiv) and anisole (0.071 mL, 0.65 mmol, 1.3 equiv) to produce **3m** as an off-white solid (0.201 g, 0.399 mmol, 80%);

δ_H (400 MHz, DMSO-d₆) 8.57 (1H, dd, *J* = 8.2, 6.0 Hz), 8.30 – 8.17 (3H, m), 7.88 (1H, dd, *J* = 8.1, 1.8 Hz), 7.15 – 7.05 (2H, m), 3.80 (3H, s);

δ_F (376 MHz, DMSO-d₆) –72.99 (3F, s), –90.64 – –90.74 (1F, m);

 δ_{c} (101 MHz, DMSO-d₆) 162.3, 158.8 (d, J = 250.7 Hz), 137.8, 137.5, 131.2 (d, J = 3.6 Hz), 120.7 (d, J = 27.1 Hz), 120.3 (q, J = 320.7 Hz), 117.8, 117.1 (d, J = 9.7 Hz), 116.4 (d, J = 2.8 Hz), 110.1 (d, J = 24.2 Hz), 105.8, 55.8.

(4-Fluoro-3-nitrophenyl)(4-methoxyphenyl)iodonium triflate (3I)



Synthesized according to **GP2** from 1-fluoro-4-iodo-2-nitrobenzene (0.134 g, 0.50 mmol, 1.0 equiv) and anisole (0.071 mL, 0.65 mmol, 1.3 equiv) to produce **3I** as a light orange solid (0.222 g, 0.424 mmol, 85%);

δ_H (400 MHz, DMSO-d₆) 8.55 (1H, dd, *J* = 10.0, 1.7 Hz), 8.30 – 8.17 (4H, m) 7.12 (2H, d, *J* = 8.8 Hz), 3.81 (3H, s);

δ_F (376 MHz, DMSO-d₆) –72.99 (3F, s), –109.28 (1F, t, J = 8.8 Hz);

δ_c (101 MHz, DMSO-d₆) 162.3, 154.1 (d, *J* = 268.8 Hz), 139.1 (d, *J* = 7.4 Hz), 137.6, 131.4 (d, *J* = 4.5 Hz), 128.8 (d, *J* = 2.7 Hz), 124.8 (d, *J* = 24.1 Hz), 121.9 (d, *J* = 7.1 Hz), 120.5 (q, *J* = 322.8 Hz), 117.8, 105.9, 55.8;

HRMS (ESI) calculated C₁₃H₁₀IFNO₃ for (M–OTf⁻)⁺: 373.9684; found: 373.9682; **Mp** 160.6 – 163.9 °C.

(3-Cyano-4-fluorophenyl)(4-methoxyphenyl)iodonium triflate (3m)



Synthesized according to **GP2** from 2-fluoro-5-iodo-benzonitrile (0.124 g, 0.50 mmol, 1.0 equiv) and anisole (0.071 mL, 0.65 mmol, 1.3 equiv) to produce **3k** as an off-white solid (0.209 g, 0.415 mmol, 83%);

δ_H (400 MHz, DMSO-d₆) 8.90 (1H, dd, J = 6.0, 2.3 Hz), 8.61 (1H, ddd, J = 9.0, 4.9, 2.3 Hz), 8.20 (2H, d, J = 8.8 Hz), 7.71 (1H, t, J = 9.1 Hz),

7.15 - 7.06 (2H, m), 3.80 (3H, s);

δ_F (376 MHz, DMSO-d₆) –72.99 (3F, s), –97.22 – –97.34 (1F, m);

δ_c (101 MHz, DMSO-d₆) 169.3 (d, *J* = 262.5 Hz), 167.4, 147.9 (d, *J* = 9.6 Hz), 145.6, 142.5, 125.9 (q, *J* = 322.2 Hz),125.2 (d, *J* = 20.8 Hz), 122.8, 117.6, 116.7 (d, *J* = 3.6 Hz), 111.3, 108.5 (d, *J* = 16.4 Hz), 61.0;

HRMS (ESI) calculated C₁₄H₁₀IFNO for (M–OTf⁻)⁺: 353.9786; found: 353.9810; **Mp** 157.3 – 163.2 °C.

(6-Chloropyridin-3-yl)(4-methoxyphenyl)iodonium triflate (3n)



Synthesized according to **GP2** from 2-chloro-5-iodopyridine (0.120 g, 0.50 mmol, 1.0 equiv) and anisole (0.071 mL, 0.65 mmol, 1.3 equiv) to produce **3n** as a white solid (0.192 g, 0.387 mmol, 78%);

δ_H (400 MHz, DMSO-d₆) 9.13 (1H, d, *J* = 2.5 Hz), 8.64 (1H, dd, *J* = 8.4, 2.5 Hz), 8.20 (2H, d, *J* = 8.6 Hz), 7.73 (1H, dd, *J* = 8.6, 3.0 Hz), 7.10 (2H, d, *J* = 8.6 Hz), 3.80 (3H, s);

δ_F (376 MHz, DMSO-d₆) -72.98;

δ_c **(101 MHz, DMSO-d**₆**)** 162.2, 154.0, 153.2, 145.3, 137.3, 127.5, 120.7 (q, *J* = 322.4 Hz), 117.7, 114.6, 105.7, 55.8.

Mesityl(4-nitrophenyl)iodonium triflate (30)



Synthesized according to **GP2** from 1-iodo-4-nitrobenzene (0.125 g, 0.50 mmol, 1.0 equiv) and mesitylene (0.090 mL, 0.65 mmol, 1.3 equiv) with no addition of water to produce **3o** as an off-white solid (0.235 g, 0.416 mmol, 83%);

δ_H (400 MHz, DMSO-d₆) 8.26 (2H, d, *J* = 8.7 Hz), 8.18 (2H, d, *J* = 8.7 Hz), 7.26 (2H, s), 2.60 (6H, s), 2.31 (3H, s);

δ_F (376 MHz, DMSO-d₆) –72.99 (3F);

δ_c (101 MHz, DMSO-d₆) 149.3, 143.6, 141.8, 135.5, 130.0, 126.3, 122.8, 120.7, 120.6 (q, *J* = 321.7 Hz), 26.3, 20.6.

This data is consistent with literature precedent.¹⁵

1,3,5-Trimethoxyphenyl (4-nitrophenyl)iodonium triflate (3p)



Synthesized according to **GP2** from 1-iodo-4-nitrobenzene (0.125 g, 0.50 mmol, 1.0 equiv) and 1,3,5-trimethoxybenzene (109 mg, 0.65 mmol, 1.3 equiv) to produce **3p** as an off-white solid (0.239 g, 0.423 mmol, 85%);

δ_H (400 MHz, DMSO-d₆) 8.27 – 8.21 (2H, m), 8.18 – 8.10 (2H, m), 6.50 (2H, s), 3.95 (6H, s), 3.88 (3H, s);

δ_F (376 MHz, DMSO-d₆) –72.99;

δ_c (101 MHz, DMSO-d₆) 166.6, 159.5, 149.2, 135.4, 126.1, 122.3, 120.7 (q, *J* = 320.4 Hz), 92.2, 87.0, 57.4, 56.3.

HRMS (ESI) calculated C₁₅H₁₅IFNO₅ for (M–OTf⁻)⁺: 415.9989; found: 415.9992; **Mp** 157.6 – 161.2 °C.

(4-Nitrophenyl)(phenyl)iodonium triflate (3q)



Synthesized according to a modified version of **GP2** from 1-iodo-4-nitrobenzene (0.125 g, 0.50 mmol, 1.0 equiv) and benzene (0.058 mL, 0.65 mmol, 1.3 equiv), with 3 equiv TfOH. After the oxidation step, benzene was added (no water addition) and the reaction was heated to 45 °C for 2 hours to produce **3q** as a white solid (0.168 g, 0.35 mmol, 71%);

δ_H (400 MHz, DMSO-d₆) 8.53 – 8.44 (2H, m), 8.36 – 8.26 (4H, m), 7.73 – 7.67 (1H, m), 7.57 (2H, t, *J* = 7.8 Hz);

δ_F (376 MHz, DMSO-d₆) –72.97;

 $δ_c$ (101 MHz, DMSO-d₆) 149.4, 136.4, 135.5, 132.4, 132.0, 126.3, 122.6, 120.70 (q, J = 322.3 Hz), 116.9.

This data is consistent with literature precedent.¹⁵

Diphenyliodonium triflate (3r)



Synthesized according to a modified version of **GP2** using iodobenzene (0.060 mL, 0.50 mmol, 1.0 equiv), benzene (0.058 mL, 0.65 mmol, 1.3 equiv), TfOH (3 equiv) and EtOAc (1 mL), which were all added at the start of the reaction (no water addition). The reaction was heated to 45 °C for 4 hours to produce **3r** as white solid (0.149 g, 0.346 mmol, 69%);

δ_H **(400 MHz, CD**₃**OD)** 8.37 − 8.20 (4H, m), 7.74 − 7.60 (2H, m), 7.59 − 7.43 (4H, m); **δ**_F **(376 MHz, CD**₃**OD)** −72.92;

Contents table

δ_c (101 MHz, CD₃OD) 135.2, 132.1, 131.8, 120.8 (q, *J* = 322.2 Hz), 116.5. This data is consistent with literature precedent.²

(2-Fluoro-5-nitrophenyl)(mesityl)iodonium trifluoromethanesulfonate (3s)



Synthesized according to **GP2** from 1-fluoro-2-iodo-4-nitrobenzene OTf (0.134 g, 0.50 mmol, 1.0 equiv) and mesitylene (0.091 mL, 0.65 mmol, 1.3 equiv) with no addition of water to produce **3s** as white solid (0.181 g, 0.338 mmol, 68%);

δ_H (400 MHz, CD₃OD) 9.09 – 9.02 (1H, m), 8.65 – 8.51 (1H, m), 7.72 (1H, t, *J* = 8.5 Hz), 7.27 (2H, s), 2.74 (6H, s), 2.37 (3H, s);

δ_F (376 MHz, CD₃OD) –80.03 (3F, s), -89.77 – -89.85 (1F, m);

δ_c (101 MHz, CD₃OD) 165.2 (d, J = 259.2 Hz), 146.8, 146.7, 146.3, 143.7, 133.6 (d, J = 3.2 Hz), 132.0 (d, J = 10.4 Hz), 131.5, 122.7, 121.8 (q, J = 318.3 Hz), 101.3 (d, J = 26.7 Hz), 26.9, 21.0. This data is consistent with literature precedent.⁶

Mesityl(phenyl)iodonium triflate (3t)



Synthesized according to **GP2** from iodobenzene (0.055 mL, 0.50 mmol, 1.0 equiv) and mesitylene (0.091 mL, 0.65 mmol, 1.3 equiv) with no addition of water to produce **3t** as white solid (0.194 g, 0.411 mmol, 82%);

δ_H (400 MHz, CD₃OD) 7.92 (2H, d, *J* = 8.0 Hz), 7.67 (1H, t, *J* = 7.5 Hz), 7.53 (2H, t, *J* = 7.8 Hz), 7.26 (2H, s), 2.68 (6H, s), 2.38 (3H, s);

δ_F (376 MHz, CD₃OD) -80.00;

δ_c (101 MHz, CD₃OD) 145.9, 143.5, 135.2, 133.3, 131.3, 122.2, 121.6 (q, *J* = 323.1 Hz), 114.1, 27.0, 21.0.

This data is consistent with literature precedent.¹⁸

(4-Methoxyphenyl)(4-nitrophenyl)iodonium tosylate (3a-OTs)



Synthesized according to **GP2** from 4-nitroiodobenzene (0.125 g, 0.50 mmol, 1.0 equiv), anisole (0.071 mL, 0.65 mmol, 1.3 equiv), toluenesulfonic acid monohydrate (0.190 g, 1.00 mmol, 2 equiv) instead of triflic acid, no addition of water and the reaction was heated to 60 °C to produce **3a-OTs** as white solid (0.221 g, 0.419 mmol, 84%);

δ_H **(400 MHz, DMSO-d**₆**)** 8.42 (2H, d, *J* = 8.5 Hz), 8.25 (4H, dd, *J* = 16.9, 8.6 Hz), 7.47 (2H, d, *J* = 7.7 Hz), 7.17 – 7.05 (4H, m), 3.80 (3H, s), 2.28 (3H, dd, *J* = 4.0, 2.1 Hz);

δ_c (101 MHz, DMSO-d₆) 162.2, 149.3, 145.7, 137.6, 137.6, 136.1, 128.1, 126.1, 125.5, 123.2, 117.6, 105.7, 55.8, 20.8.

(2-chloro-5-(trifluoromethyl)phenyl)(4-methoxyphenyl)iodonium tosylate (3i-OTs)



Synthesized according to **GP2** from 1-iodo-2-chloro-5trifluoromethylbenzene (0.153 g, 0.50 mmol, 1.0 equiv), anisole (0.071 mL, 0.65 mmol, 1.3 equiv) toluenesulfonic acid monohydrate (0.190 g, 1.00 mmol, 2 equiv) instead of triflic acid, no addition of water and the reaction was heated to 60 °C to produce **3i-OTs** as white solid (0.225 g, 0.385 mmol, 77%);

 δ_{H} (400 MHz, CD₃OD) 8.81 (1H, s), 8.18 - 8.11 (2H, m), 8.02 - 7.87 (2H, m), 7.66 (2H, d, J = 7.7 Hz), 7.20 (2H, d, J = 7.7 Hz), 7.06 (2H, d, J = 8.5 Hz), 3.83 (3H, s), 2.35 (3H, s);

δ_F (376 MHz, CD₃OD) -64.00;

δ_c (101 MHz, CD₃OD) 164.7, 143.5, 142.5, 141.6, 138.9, 136.6 – 136.3 (m), 133.0 (q, *J* = 34.1 Hz), 132.5 (q, *J* = 3.8 Hz), 132.4, 129.8, 126.9, 123.9 (q, *J* = 272.4 Hz), 120.0, 119.0, 105.1, 56.4, 21.3;

HRMS (ESI) calculated C₁₄H₁₀ClF₃IO for (M–OTf⁻)⁺: 412.9411 found: 412.9432; **Mp** 161.6 – 168.2 °C.

Dibenzo[b,d]iodol-5-ium triflate (3u)



Synthesized according to a modification of **GP2** from 2-iodo-1,1'-biphenyl (0.140 g, 0.50 mmol, 1.0 equiv), without addition of arene or water to produce **3u** as an off-white solid (0.195 g, 0.455 mmol, 91%);

δ_H (400 MHz, DMSO-d₆) 8.46 (2H, dd, J = 8.0, 1.5 Hz), 8.20 (2H, dd, J = 8.3, 1.1 Hz), 7.84 (2H, td, J = 7.6, 1.1 Hz), 7.70 (2H, ddd, J = 8.5, 7.3, 1.4 Hz); **δ_F (376 MHz, DMSO-d₆)** –72.96;

δ_c (101 MHz, DMSO-d₆) 141.7, 131.1, 130.7, 130.6, 127.0, 121.6 120.7 (q, J = 320.1 Hz). This data is consistent with literature precedent.²⁰

Note: **3u** was obtained in 97% when addition of triflic acid took place at -78 °C, and anhydrous EtOAc and nitrogen atmosphere was used throughout the reaction.

10,10-Bis(ethoxycarbonyl)-3-nitro-10*H*-dibenzo[*b,e*]iodinin-5-ium triflate (3v)



Synthesized according to a modification of **GP2** from diethyl 2-(2iodophenyl)-2-(4-nitrophenyl)malonate (0.242 g, 0.50 mmol, 1.0 equiv) without addition of arene or water to produce **3v** as an off-white solid (0.231 g, 0.394 mmol, 79%);

δ_H (400 MHz, DMSO-d₆) 9.00 (1H, d, J = 2.5 Hz), 8.52 (1H, dd, J = 8.9, 2.5 Hz), 8.23 – 8.19 (1H, m), 8.03 (1H, d, J = 8.9 Hz), 7.78 – 7.72 (2H, m), 7.63 (1H, ddd, J = 8.6, 6.1, 2.8 Hz), 4.42 (4H, q, J = 7.1 Hz), 1.23 (6H, t, J = 7.1 Hz);

δ_F (376 MHz, DMSO-d₆) -72.99;

δ_c (101 MHz, DMSO-d₆) 166.4, 147.0, 142.8, 135.5, 134.6, 132.2, 132.1, 131.5, 131.0, 129.2, 126.4, 120.6 (q, *J* = 323.5 Hz), 114.3, 113.8, 73.4, 64.0, 13.5. This data is consistent with literature precedent.¹²

7. E-factor calculations

The E-factors for the large-scale reactions were calculated according to the equation below:²¹

$$E - factor = \frac{waste mass(g)}{product(g)} = \frac{total mass of everything used(g) - product(g)}{product(g)}$$

 Table S3. E-factor calculation of scale-up of DMIX triflate 2e.



Compound	<i>M</i> r (g/mol)	Amount	equiv	density (g/mL)	mass (g)
DMIX-I 1a	223	45.5 mmol	1.3	/	10.15
<i>m</i> CPBA	173	45.5 mmol	1.3	/	8.92
TfOH	151	35 mmol	1	1.696	5.25
2,6-Dimethoxypyridine	108	35 mmol	1	1.054	4.87
EtOAc	88	50 mL		0.901	45.05
СРМЕ	100	75 mL		0.863	64.72
Total mass of everything use	ed during the	reaction and	l purificat	tion (g)	138.96
Product 2e	510	32.4		/	16.54
١	Vaste mass (g)		-	122.42
	E-factor				7.40

Table S4. E-factor calculation of scale-up of anisyl triflate 3j.



Compound	M _r (g/mol)	Amount	equiv	density (g/mL)	mass (g)
Iodoarene	267	70 mmol	1	/	18.69
<i>m</i> CPBA	173	91 mmol	1.3	/	17.84
TfOH	151	140 mmol	2	1.696	21.01
Anisole	108	91 mmol	1.3	0.994	9.84
H ₂ O	18	210 mmol	3	1.000	3.80
EtOAc	88	110 mL		0.901	99.11
CPME	100	180 mL		0.863	155.34
Total mass of	everything	<mark>g used during th</mark>	e reaction and p	ourification (g)	325.63
Product 3j	523	46.8		/	24.50
Waste mass (g)					301.13
	12.29				

8. Benchmarking studies

Comparison of our yields to those in literature. To acquire the literature yields, we have conducted a literature search using ScifinderTM to find the highest yields of each compound. The vast majority were synthesized using the aforementioned one-pot method,^{2, 22} with the exception of **3h**, which were synthesized using an anion exchange method from the appropriate tosylate salt and triflic acid.¹⁷



Scheme S1. Yield comparison between EtOAc and DCM methods. Yields in DCM are the best found in the literature: (**3a-3d**, **3f**, **3i**, **3k**, **3n-3o**, **3q**, **3u**),¹⁵ (**3e**),²² (**3g**),¹⁶ (**3h**),¹⁷ (**3j**, **3s**),⁶ (**3r**),²³ (**3t**),²⁴ (**3a-OTs**),²⁵ (**3u**),²⁰ (**3v**).¹²

9. NMR spectra 3,5-dimethylisoxazole



 δ_{H} (400 MHz, CDCl₃) - 7.26 CDCI3 5.80 5.80 2.37 2.37 2.25 1.00-I 3.16_⊈ 3.15₄ 2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 (ppm) δ_C (101 MHz, CDCl₃) - 77.2 CDCI3 — 159.9 — 169.1 - 102.3 ×12.1 11.3 210 200 190 180 170 160 150 140 130 120 110 100 (ppm) 0 -10 90 70 60 50 30 20 10 80 40



(3,5-Dimethylisoxazol-4-yl)(4-methoxyphenyl)iodonium trifluoromethanesulfonate (2a)



 δ_{H} (400 MHz, DMSO-d₆)





250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 (ppm)

(3-Bromo-4-methoxyphenyl)(3,5-dimethylisoxazol-4-yl)iodonium trifluoromethanesulfonate (2b)





20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 (ppm)


(2-Bromo-4-methoxyphenyl)(3,5-dimethylisoxazol-4-yl)iodonium trifluoromethanesulfonate (2c)



 δ_{H} (400 MHz, DMSO-d₆)





(3,5-Dimethylisoxazol-4-yl)(2,4,6-trimethoxyphenyl)iodonium trifluoromethanesulfonate (2d)



δ_H (400 MHz, DMSO-d₆)





250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 (ppm)

(2,6-Dimethoxypyridin-3-yl)(3,5-dimethylisoxazol-4-yl)iodonium trifluoromethanesulfonate (2e)



 δ_{H} (400 MHz, DMSO-d₆)



10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 (ppm)



(3,5-Dimethylisoxazol-4-yl)(4-phenoxyphenyl)iodonium trifluoromethanesulfonate (2f)



 δ_{H} (400 MHz, DMSO-d₆)







44

(3,5-Dimethylisoxazol-4-yl)(4-methoxy-3-(methoxycarbonyl)phenyl)iodonium triflate (2g)



δ_H (400 MHz, DMSO-d₆)





(3,5-Dimethylisoxazol-4-yl)(thiophen-2-yl)iodonium trifluoromethanesulfonate (2h)









(3,5-Dimethylisoxazol-4-yl)((8*R*,9*S*,13*S*,14*S*)-3-methoxy-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-2-yl)iodonium trifluoromethanesulfonate (2i)





(ppm)

----78.48



(4-((4-Carboxy-4-methylpentyl)oxy)-2,5-dimethylphenyl)(3,5-dimethylisoxazol-4-yl)iodonium trifluoromethanesulfonate (2j)



 δ_{H} (400 MHz, DMSO-d₆)



---77.74

δ_F (376 MHz, DMSO-d₆)

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 (ppm)

Compounds table



(4-Methoxyphenyl)(4-nitrophenyl)iodonium trifluoromethanesulfoante (3a)



 δ_{H} (400 MHz, DMSO-d₆)









240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

56





(4-Chlorophenyl)(4-methoxyphenyl)iodonium trifluoromethanesulfonate (3d)







10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)



f1 (ppm)





210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 f1 (ppm)

(4-(Tert-butyl)phenyl)(4-methoxyphenyl)iodonium trifluoromethanesulfonate (3f)





---72.98

 δ_F (376 MHz, DMSO-d₆)





240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

64





240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

66





240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm) (2-Chloro-5-(trifluoromethyl)phenyl)(4-methoxyphenyl)iodonium trifluoromethanesulfonate (3i)









210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 f1 (ppm)





 $\delta_{\rm H}$ (400 MHz, DMSO-d₆)







f1 (ppm)
(4-Cyano-2-fluorophenyl)(4-methoxyphenyl)iodonium trifluoromethanesulfonate (3k)



 δ_{H} (400 MHz, DMSO-d₆)



20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -22 f1 (ppm)



240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

 δ_C (101 MHz, DMSO-d₆)



δ_H (400 MHz, DMSO-d₆)





240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

3-Cyano-4-fluorophenyl)(4-methoxyphenyl)iodonium trifluoromethanesulfonate (3m)



δ_H (400 MHz, DMSO-d₆)





240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

(6-Chloropyridin-3-yl)(4-methoxyphenyl)iodonium trifluoromethanesulfonate (3n)







240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm) Mesityl(4-nitrophenyl)iodonium trifluoromethanesulfonate (30)







1,3,5-Trimethoxyphenyl (4-nitrophenyl)iodonium trifluoromethanesulfonate (3p)









240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

(4-Nitrophenyl)(phenyl)iodonium trifluoromethanesulfonate (3q)





10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 f1 (ppm)

Diphenyliodonium trifluoromethanesulfonate (3r)







240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)





Mesityl(phenyl)iodonium trifluoromethanesulfonate (3t)





δ_F (376 MHz, CD₃OD)





250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

(4-Methoxyphenyl)(4-nitrophenyl)iodonium toluenesulfonate (3a-OTs)





(2-Chloro-5-(trifluoromethyl)phenyl)(4-methoxyphenyl)iodonium toluenesulfonate (3i-OTs)







250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

Dibenzo[*b*,*d*]iodol-5-ium trifluoromethanesulfonate (3u)









210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 f1 (ppm)

10,10-Bis(ethoxycarbonyl)-3-nitro-10H-dibenzo[b,e]iodinin-5-ium trifluoromethanesulfonate (3v)





10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)



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