Supporting Information

Sterically Congested 2,6-Disubstituted Anilines from Direct C–N Bond Formation at an Iodine(III) Center

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1. General Remarks

All solvents, reagents and all deuterated solvents were purchased from Aldrich, TCI, Alfa Aesar, Fluka, Fluorochem and Apollo Scientific commercial suppliers. Column chromatography was performed with silica gel (Merck, type 60, 0.063-0.2 mm). NMR spectra were recorded on a Bruker Avance 300 MHz, 400 MHz, and 500 MHz spectrometer, respectively. All chemical shifts in NMR experiments were reported as ppm downfield from TMS. The following calibrations were used: CDCl$_3$ $\delta$ = 7.26 and 77.0 ppm, CD$_3$OD $\delta$ = 31.0 and 49.0 ppm, DMSO-$d_6$ $\delta$ = 2.50 and 39.52 ppm. MS (ESI-LCMS) experiments were performed using an Agilent 1100 HPLC with a Bruker micro-TOF instrument (ESI). MS (EI) and HRMS were performed on a Kratos MS 50 within the service center at ICIQ. IR spectra were taken in a Bruker Alpha instrument in the solid state.

The following compounds were commercially available and used as received: (diacetoxyiodo)benzene, p-toluenesulfonic acid monohydrate 98%, 2,2,2-trifluoroethanol (TFE), iodine, diphenyliodonium hexafluorophosphate 98%, mesitylene, 2-bromomesitylene 98%, 1-tert-butyl-3,5-dimethylbenzene 98%, pentamethylbenzene 98%, mCPBA 77%, BF$_3$-OEt$_2$ 46%, phenylboronic acid 98%, trifluoromethanesulfonic acid 98%, 2,6-dichloriodobenzene 98%, 1-iodo-2,3,5,6-tetrachlorobenzene, 2-iodo-nitrotoluene 97%, acetic acid, peracetic acid 35 wt%, 2-iodo-1,3-dimethylbenzene 97%, 1,3,5-triethylbenzene, iodobenzene, 1,3,5-trisopropylbenzene, tetrafluorophthalimide, potassium phthalimide, sodium hydride 55 wt%, saccharin sodium salt, potassium tert-butoxide 97%, succinimide, 4-nitrophthalimide, 4-bromophthalimide, 1,8-naphthalimide, 2-oxazolidinone, 2-piperidone, pyrrolidone, benzene, ethylenediamine, potassium hydride 35 wt%, 2,6-dimethylbenzenedicarboxamide, 1-iodo-3,5-bis(trifluoromethyl)benzene 98%, copper iodide, potassium phosphate, racemic trans-1,2-diaminocyclohexane.
2. Synthesis of Diaryliodonium Salts

**General procedure for the synthesis of starting diaryliodonium salts (GP1).**\(^1\)

To a stirred solution of (diacetoxyiodo)benzene (1.0 equiv.) in a 2,2,2-trifluoroethanol (TFE) and CH\(_2\)Cl\(_2\) mixture (10/1, v/v) was added the arene (1.5 equiv.) and TsOH-H\(_2\)O (2.0 equiv.) and the solution was stirred at rt. After the disappearance of the arene (checked by TLC), water was added and the organic layer was extracted with CH\(_2\)Cl\(_2\) (3 x 10 mL), and then dried over anhydrous Na\(_2\)SO\(_4\). After filtration and evaporation of the solvent, the crude oily product was triturated with diethyl ether to afford the final diaryliodonium salt as solid.

**General procedure for the synthesis of starting diaryliodonium salts (GP2).**\(^2\)

In a flamed and dried Schlenk flask, the iodoarene (1.0 equiv.) was dissolved in 5.0 mL of dry CH\(_2\)Cl\(_2\). mCPBA 77% (1.08 equiv.) and BF\(_3\)-OEt\(_2\) 46% (2.48 equiv.) were added and the mixture was stirred at rt for 30 min. Then it was cooled down to 0 °C with an ice-bath and phenylboronic acid (1.08 equiv.) was added. The mixture was stirred warming to rt for 15 min. and then trifluoromethanesulfonic acid (1.08 equiv.) was added. The mixture was stirred for other 15 min. at rt and then the solvent was removed under reduced pressure. The crude oil was triturated with diethyl ether to afford the desired compound as solid.

**General procedure for the synthesis of (diacetoxyiodo)arenes (GP3).**\(^3\)

Arene (1.0 mmol, 1.0 equiv.) was dissolved in acetic acid (2.4 mL) and peracetic acid 35 wt% (2.6 equiv.) was added and the final mixture was stirred at rt for 20 h. The solvent was removed under reduced pressure. The (diacetoxyiodo)arene was recrystallized in CH\(_2\)Cl\(_2\)/n-hexane.
General procedure for the synthesis of starting diaryliodonium salts (GP4).\textsuperscript{[3]}

Arylboronic acid (1.1 equiv.) was dissolved in dry CH$_2$Cl$_2$ (3.0 mL) under inert atmosphere. At 0 °C, BF$_3$-OEt$_2$ 46% (1.5 equiv.) was added and the mixture was stirred at this temperature during 10 min. Then, (diacetoxyiodo)arene (1.0 equiv.) was added and the final mixture was stirred at rt for 1 h. After re-cooling again to 0 °C, trifluoromethanesulfonic acid (1.1 equiv.) was added and the mixture was stirred warming to rt for 30 min. The solvent was removed under reduced pressure and diethyl ether was added to the residual mixture. The resulting mixture was cooled to -20 °C overnight and the precipitate (diaryliodonium triflate) was collected by filtration and washed with cold diethyl ether.

General procedure for the synthesis of starting diaryliodonium salts (GP5).\textsuperscript{[4]}

1,3,5-Triisopropylbenzene (0.692 mL, 2.72 mmol) was added to a solution of iodobenzene (0.274 mL, 2.45 mmol) and mCPBA 77% (0.61 g, 2.72 mmol) in CH$_2$Cl$_2$ (10.0 mL) and the solution cooled to 0 °C. Trifluoromethanesulfonic acid (0.36 mL, 4.09 mmol) was added drop-wise over 5 min. and the reaction allowed to slowly warm to rt over the course of 2 h. The solvent was removed under reduced pressure and diethyl ether added. The crystallization was completed in the fridge and the white solid was collected by filtration.

General procedure for the synthesis of starting diaryliodonium salts (GP6).\textsuperscript{[5]}

Iodoarene (1.0 equiv.) was dissolved in CH$_2$Cl$_2$, and mCPBA 77% (1.1 equiv.), the arene (1.1 equiv.) were added. The mixture was cooled down to 0 °C with an ice-bath and trifluoromethanesulfonic acid (3.0 equiv.) was added drop-wise. The mixture was stirred for the indicated time while allowed warming to rt. The solvent was removed under reduced pressure and the crude was triturated with diethyl ether. After filtration the desired diaryliodonium salt was collected as
solid.
Mesityl(phenyl)iodonium tosylate 1b.

\[
\text{OTs}
\]

Synthesized by GP1. White solid, 93% yield. Spectroscopic data according to previous literature.[1]

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 2.31\) (s, 3H), 2.32 (s, 3H), 2.58 (s, 6H), 7.00-7.03 (m, 4H), 7.30-7.33 (m, 2H), 7.43-7.44 (m, 1H), 7.50-7.53 (m, 2H), 7.67-7.69 (m, 2H).

\(^13\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta = 21.2, 21.4, 27.3, 113.6, 122.0, 126.1, 128.5, 130.1, 131.2, 131.9, 133.1, 139.3, 142.5, 143.0, 143.8\).

(2,6-Dimethylphenyl)(phenyl)iodonium triflate 1c.

\[
\text{OTf}
\]

Synthesized by GP4. Brownish solid, 93% yield.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 2.69\) (s, 6H), 7.30-7.32 (m, 2H), 7.40-7.46 (m, 3H), 7.53-7.57 (m, 1H), 7.70-7.73 (m, 2H).

\(^19\)F-NMR (376 MHz, CDCl\(_3\)): \(\delta = -78.5\) (s, 3F).

\(^13\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta = 27.5, 111.7, 120.4\) (q, \(J_{C-F} = 319.8\) Hz), 124.5, 129.7, 132.1, 132.5, 133.4, 133.7, 142.9.

IR \(\nu (\text{cm}^{-1})\): 1469, 1239, 1219, 1159, 1024, 734, 633, 514.

HRMS (ESI\(^+\)): calc. for [C\(_{14}\)H\(_{14}\)I\(^+\)]\(^+\): 309.0135; found: 309.0136.

m.p.(\(^\circ\)C): 168-170 \(^\circ\)C.
Phenyl(2,3,5,6-tetramethylphenyl)iodonium triflate 1d.

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\begin{array}{c}
\text{OTf} \\
\text{I} \\
\text{Ph}
\end{array}
\]

Synthesized by GP4. Brownish solid, 60% yield.

\(^1\text{H-NMR (400 MHz, CDCl}_3\): \(\delta = 2.35\) (s, 6H), \(2.99\) (s, 6H), \(7.20\) (s, 1H), \(7.40-7.44\) (m, 2H), \(7.53-7.57\) (m, 1H), \(7.68-7.70\) (m, 2H).

\(^{19}\text{F-NMR (376 MHz, CDCl}_3\): \(\delta = -78.4\) (s, 3F).

\(^{13}\text{C-NMR (75 MHz, CDCl}_3\): \(\delta = 21.9, 25.1, 111.9, 127.7, 132.1, 132.5, 133.2, 137.1, 137.5, 138.5\).

\(\text{IR } \nu(\text{cm}^{-1})\): \(1444, 1239, 1220, 1155, 1022, 727, 633, 516\).

\(\text{HRMS (ESI}^+\): \text{calc. for } [\text{C}_{16}\text{H}_{18}\text{I}]^+: 337.0448; \text{found: } 337.0436.

\(\text{m.p.(ºC): 178-179 ºC.}\)

(2,3,4,5,6-Pentamethylphenyl)(phenyl)iodonium tosylate 1e.

\[
\begin{array}{c}
\text{OTs} \\
\text{I} \\
\text{Ph}
\end{array}
\]

Synthesized by GP1 using 1.0 equiv. of arene. Brownish solid, 65% yield.

\(^1\text{H-NMR (400 MHz, CDCl}_3\): \(\delta = 2.26\) (s, 9H), \(2.30\) (s, 3H), \(2.62\) (s, 6H), \(7.00-7.02\) (m, 2H), \(7.29-7.34\) (m, 2H), \(7.44\) (tt, \(J = 1.1, 7.5\) Hz, 1H), \(7.52-7.55\) (m, 2H), \(7.66-7.69\) (m, 2H).

\(^{13}\text{C-NMR (75 MHz, CDCl}_3\): \(\delta = 17.6, 18.8, 21.4, 26.5, 113.7, 126.1, 127.0, 128.5, 131.2, 131.9, 133.1, 135.8, 137.3, 139.3, 141.1, 142.9\).

\(\text{IR } \nu(\text{cm}^{-1})\): \(2919, 1565, 1442, 1232, 1155, 1008, 739, 679, 560\).

\(\text{HRMS (ESI}^+\): \text{calc. for } [\text{C}_{17}\text{H}_{20}\text{I}]^+: 351.0604; \text{found: } 351.0594.

\(\text{m.p.(ºC): 157-159 ºC.}\)
**(4-**(Tert-butyl)-2,6-dimethylphenyl)(phenyl)iodonium tosylate 1f.**

Synthesized by GP1. White solid, 77% yield. Spectroscopic data according to previous literature.[8]

**1H-NMR (400 MHz, CDCl₃):** δ = 1.30 (s, 9H), 2.30 (s, 3H), 2.62 (s, 6H), 7.04 (d, J = 7.9 Hz, 2H), 7.20 (s, 2H), 7.32-7.36 (m, 2H), 7.44-7.49 (m, 1H), 7.52-7.55 (m, 2H), 7.70-7.72 (m, 2H).

**13C-NMR (100 MHz, CDCl₃):** δ = 21.4, 27.6, 31.2, 35.0, 113.5, 121.9, 126.1, 126.7, 128.6, 131.3, 131.9, 133.3, 139.4, 142.2, 143.0, 156.6.

**IR ν(cm⁻¹):** 1433, 1236, 1017, 821, 685, 572.

**HRMS (MALDI⁺):** calc. for [C₁₈H₂₂I]⁺: 365.0761; found: 365.0765.

**m.p.(°C):** 133-135 °C.

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**Phenyl(2,4,6-triethylphenyl)iodonium tosylate 1g.**

Synthesized by GP1 using CH₂Cl₂ as solvent. White solid, 67% yield.

**1H-NMR (400 MHz, CD₃OD):** δ = 1.24-1.29 (m, 9H), 2.36 (s, 3H), 2.72 (q, J = 7.6 Hz, 2H), 2.99 (q, J = 7.5 Hz, 4H), 7.21-7.23 (m, 2H), 7.30 (s, 2H), 7.48-7.52 (m, 2H), 7.61-7.65 (m, 1H), 7.69 (d, J = 7.9 Hz, 2H), 7.81-7.83 (m, 2H).

**13C-NMR (100 MHz, CD₃OD):** δ = 15.63, 15.65, 21.3, 29.5, 34.6, 114.5, 121.6, 127.0, 129.3, 129.8, 133.1, 133.3, 134.5, 141.6, 143.6, 149.1, 152.5.

**IR ν(cm⁻¹):** 1433, 1236, 1017, 821, 685, 572.

**HRMS (MALDI⁺):** calc. for [C₁₈H₂₂l]⁺: 365.0761; found: 365.0765.

**m.p.(°C):** 133-135 °C.
Phenyl(2,4,6-triisopropylphenyl)iodonium triflate 1h.

\[
\begin{align*}
\text{OTf} \\
\text{Synthetized by GP5. White powder, 65\% yield. Spectroscopic data according to previous literature.}^{[4]} \\
\end{align*}
\]

\[^1\text{H-NMR (400 MHz, CDCl}_3\text{)}: \delta = 1.27 (d, J = 6.7 \text{ Hz, 12H}), 1.30 (d, J = 6.9 \text{ Hz, 6H}), 2.99 (\text{hept, } J = 6.9 \text{ Hz, 1H}), 3.28 (\text{hept, } J = 6.7 \text{ Hz, 2H}), 7.21 (s, 2H), 7.43-7.48 (m, 2H), 7.55-7.59 (m, 1H), 7.68-7.71 (m, 2H).
\]^19\text{F-NMR (376 MHz, CDCl}_3\text{)}: \delta = -78.4 (s, 3F).

\[^13\text{C-NMR (100 MHz, CDCl}_3\text{)}: \delta = 23.8, 24.4, 34.4, 39.7, 113.0, 120.5, 125.5, 132.0, 132.5, 132.7, 152.5, 155.9.\]

(3-Bromo-2,4,6-trimethylphenyl)(phenyl)iodonium tosylate 1i.

\[
\begin{align*}
\text{OTs} \\
\text{Synthesized by GP1. White solid, 74\% yield.} \\
\end{align*}
\]

\[^1\text{H-NMR (500 MHz, CDCl}_3\text{)}: \delta = 2.31 (s, 3H), 2.40 (s, 3H), 2.61 (s, 3H), 2.83 (s, 3H), 6.99-7.01 (m, 2H), 7.11 (s, 1H), 7.29-7.32 (m, 2H), 7.40-7.44 (m, 3H), 7.71-7.73 (m, 2H).
\][13\text{C-NMR (100 MHz, CD}_3\text{OD): } \delta = 21.3, 24.4, 27.3, 29.7, 115.0, 125.8, 126.9, 129.8, 132.4, 133.4, 133.45, 133.49, 141.6, 142.1, 142.6, 143.5, 145.9.\]

\text{IR } \nu(\text{cm}^{-1}): 1439, 1224, 1165, 1028, 1006, 743, 678, 565.

\text{HRMS (ESI\textsuperscript{+}): calc. for [C}_{15}H_{15}BrI]\textsuperscript{+}: 400.9396; found: 400.9395.}

\text{m.p.(ºC): 171-173 ºC.}
(2,6-Dichlorophenyl)(phenyl)iodonium triflate 1j.

\[
\text{\begin{tikzpicture}
\draw[thick,fill=white] (0,0) circle (0.5cm);
\draw[thick,fill=white] (0.5,0) circle (0.5cm);
\draw[thick,fill=white] (1,0) circle (0.5cm);
\draw[thick,fill=white] (-0.5,0) circle (0.5cm);
\draw[thick,fill=white] (0,0.5) circle (0.5cm);
\draw[thick,fill=white] (0,-0.5) circle (0.5cm);
\draw[thick,fill=white] (-0.5,0.5) circle (0.5cm);
\draw[thick,fill=white] (-0.5,-0.5) circle (0.5cm);
\draw[thick,fill=white] (0.5,0.5) circle (0.5cm);
\draw[thick,fill=white] (0.5,-0.5) circle (0.5cm);
\end{tikzpicture}}
\]

Synthesized by GP2. White crystals, 29% yield.

\[^1\text{H-NMR (400 MHz, CD}_3\text{OD):}\ \delta = 7.56-7.60 \text{ (m, 2H), 7.64-7.68 (m, 1H), 7.71-7.76 (m, 3H), 8.20-8.22 (m, 2H).}\]
\[^{19}\text{F-NMR (376 MHz, CD}_3\text{OD):}\ \delta = -80.1 \text{ (s, 3F).}\]
\[^{13}\text{C-NMR (125 MHz, CD}_3\text{OD):}\ \delta = 116.9, 123.9, 130.2, 133.4, 134.2, 136.6, 136.9, 140.6.\]
\[\text{IR } \nu(\text{cm}^{-1}): 1428, 1238, 1221, 1158, 1024, 784, 741, 634, 514.\]
\[\text{HRMS (ESI\textsuperscript{+}): calc. for [C}_{12}\text{H}_8\text{Cl}_2\text{I}]^+: 348.9042; \text{ found: 348.9040.}\]
\[\text{m.p.}(\text{ºC}): 178-180 \text{ ºC.}\]

Phenyl(2,4,6-trichlorophenyl)iodonium triflate 1k.

\[
\text{\begin{tikzpicture}
\draw[thick,fill=white] (0,0) circle (0.5cm);
\draw[thick,fill=white] (0.5,0) circle (0.5cm);
\draw[thick,fill=white] (1,0) circle (0.5cm);
\draw[thick,fill=white] (-0.5,0) circle (0.5cm);
\draw[thick,fill=white] (0,0.5) circle (0.5cm);
\draw[thick,fill=white] (0,-0.5) circle (0.5cm);
\draw[thick,fill=white] (-0.5,0.5) circle (0.5cm);
\draw[thick,fill=white] (-0.5,-0.5) circle (0.5cm);
\draw[thick,fill=white] (0.5,0.5) circle (0.5cm);
\draw[thick,fill=white] (0.5,-0.5) circle (0.5cm);
\end{tikzpicture}}
\]

Synthesized by GP2. White solid, 23% yield.

\[^1\text{H-NMR (400 MHz, CD}_3\text{OD):}\ \delta = 7.57-7.61 \text{ (m, 2H), 7.72 -7.77 (m, 1H), 7.90 (s, 2H), 8.20-8.23 (m, 2H).}\]
\[^{19}\text{F-NMR (376 MHz, CD}_3\text{OD):}\ \delta = -80.1 \text{ (s, 3F).}\]
\[^{13}\text{C-NMR (100 MHz, CD}_3\text{OD):}\ \delta = 117.1, 121.8 \text{ (q, } J_{C,F} = 318.4 \text{ Hz), 122.4, 130.2, 133.5, 134.3, 136.6, 141.5, 142.4.}\]
\[\text{IR } \nu(\text{cm}^{-1}): 1546, 1220, 1020, 634, 514.\]
\[\text{HRMS (ESI\textsuperscript{+}): calc. for [C}_{12}\text{H}_7\text{Cl}_3\text{I}]^+: 382.8634; \text{ found: 382.8653.}\]
\[\text{m.p.}(\text{ºC}): 181-183 \text{ ºC.}\]
Phenyl(2,3,6-trichlorophenyl)iodonium triflate 1l.

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\begin{array}{c}
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\text{Cl} \\
\end{array}
\begin{array}{c}
\text{I} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\begin{array}{c}
\text{OTf} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\]

Synthesized by GP2. White solid, 30% yield.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.46-7.53 \text{ (m, 2H)}, 7.54 \text{ (d, } J = 8.7 \text{ Hz, 1H)}, 7.61-7.65 \text{ (m, 2H)}, 8.07-8.09 \text{ (m, 2H)}.\)

\(^19\)F-NMR (376 MHz, CDCl\(_3\)): \(\delta = -78.4 \text{ (s, 3F)}.\)

\(^{13}\)C-NMR (100 MHz, CD\(_3\)OD): \(\delta = 117.1, 121.8 \text{ (q, } J_{C-F} = 318.4 \text{ Hz)}, 125.2, 131.0, 133.3, 133.5, 134.4, 136.7, 137.0, 138.7, 139.1.\)

IR \(\nu(\text{cm}^{-1})\): 1421, 1274, 1219, 1160, 1019, 988, 734, 633, 515.

HRMS (ESI\(^+\)): calc. for [C\(_{12}\)H\(_7\)Cl\(_3\)I]\(^+\): 382.8653; found: 386.8657.

m.p.(\(^\circ\)C): 219-220 \(^\circ\)C.

Phenyl(2,3,5,6-tetrachlorophenyl)iodonium triflate 1m.

\[
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\begin{array}{c}
\text{I} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\begin{array}{c}
\text{OTf} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\]

Synthesized by GP2. Brownish solid, 36% yield.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.46-7.51 \text{ (m, 2H)}, 7.62-7.66 \text{ (m, 1H)}, 7.80 \text{ (s, 1H)}, 8.08-8.10 \text{ (m, 2H)}.\)

\(^19\)F-NMR (376 MHz, CDCl\(_3\)): \(\delta = -78.4 \text{ (s, 3F)}.\)

\(^{13}\)C-NMR (100 MHz, CD\(_3\)OD): \(\delta = 117.3, 121.8 \text{ (q, } J_{C-F} = 318.5 \text{ Hz)}, 126.1, 133.6, 133.8, 134.6, 136.8, 136.9, 137.6.\)

IR \(\nu(\text{cm}^{-1})\): 1391, 1212, 1162, 1018, 987, 633, 517.

HRMS (ESI\(^+\)): calc. for [C\(_{12}\)H\(_6\)Cl\(_4\)I]\(^+\): 416.8263; found: 416.8251.

m.p.(\(^\circ\)C): 208-209 \(^\circ\)C.
(Perchlorophenyl)(phenyl)iodonium triflate 1n.

Synthesized by GP2. Brownish solid, 29% yield.

\(^1\)H-NMR (400 MHz, CD\(_3\)OD): \(\delta = 7.59-7.63\) (m, 2H), 7.75-7.79 (m, 1H), 8.27-8.29 (m, 2H).

\(^19\)F-NMR (376 MHz, CD\(_3\)OD): \(\delta = -80.1\) (s, 3F).

\(^13\)C-NMR (100 MHz, CD\(_3\)OD): \(\delta = 117.4, 123.9, 133.5, 133.6, 134.6, 136.8, 138.2, 140.4\).

IR \(\nu\) (cm\(^{-1}\)): 1222, 987, 737, 635, 516.

HRMS (ESI\(^+\)): calc. for [C\(_{12}\)H\(_5\)Cl\(_5\)I]\(^+\): 450.7873; found: 450.7870.

m.p.(ºC): 213-215 ºC.

(2-Methyl-6-nitrophenyl)(phenyl)iodonium triflate 1o.

Synthesized by GP2. Beige solid, 40% yield.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 2.85\) (s, 3H), 7.42-7.47 (m, 2H), 7.56-7.61 (m, 1H), 7.64-7.68 (m, 1H), 7.73-7.75 (m, 1H), 7.98-8.04 (m, 3H).

\(^19\)F-NMR (376 MHz, CDCl\(_3\)): \(\delta = -77.9\) (s, 3F).
\(^{13}\text{C}-\text{NMR (100 MHz, CDCl}_3\):} \ \delta = 27.8, 110.9, 114.7, 120.0 \ (q, J_{C,F} = 319.8 \text{ Hz}), 124.6, 132.2, 132.7, 133.8, 135.1, 136.6, 145.9, 150.3.

\text{IR } \nu(\text{cm}^{-1}): \ 1536, 1223, 1154, 1024, 731, 633, 515.

\text{HRMS (MALDI\(^+\))}: \ \text{calc. for [C}_{13}\text{H}_{11}\text{INO}_2\]^+: 339.9829; found: 339.9824.

\text{m.p.(}^\circ\text{C)}: \ 128-130 ^\circ\text{C}.

\textit{Dimesityliodonium triflate 4a.}

\[
\begin{array}{c}
\text{Synthesized by GP6. White powder, 70% yield. Spectroscopic data according to previous literature.}\ [5]
\end{array}
\]

\(^1\text{H-NMR (500 MHz, CDCl}_3\):} \ \delta = 2.33 \ (s, 6\text{H}), 2.51 \ (s, 12\text{H}), 7.05 \ (s, 4\text{H}).

\(^{19}\text{F-NMR (376 MHz, CDCl}_3\):} \ \delta = -78.4 \ (s, 3\text{F}).

\(^{13}\text{C-NMR (100 MHz, CDCl}_3\):} \ \delta = 20.9, 26.1, 117.2, 120.5 \ (q, J_{C,F} = 320.2 \text{ Hz}), 130.9, 142.2, 143.8.

\textit{(2,6-Dimethylphenyl)-3-iodanediyl diacetate}

\[
\begin{array}{c}
\text{AcO—I—OAc}
\end{array}
\]

\[
\text{Synthesized by GP3. Yellowish solid, 94%. Spectroscopic data according to previous literature.}\ [3]
\]

\(^1\text{H-NMR (400 MHz, CDCl}_3\):} \ \delta = 1.97 \ (s, 6\text{H}), 2.75 \ (s, 6\text{H}), 7.28-7.30 \ (m, 2\text{H}), 7.38 \ (dd, J = 8.3, 6.6 \text{ Hz, 1H}).

\(^{13}\text{C-NMR (100 MHz, CDCl}_3\):} \ \delta = 20.4, 27.1, 128.3, 132.7, 133.1, 141.6, 176.6.

\textit{(2,4-Dimethylphenyl)-\( \lambda^3\)-iodanediyl diacetate}
Synthesized by GP3. Yellow solid, 95% yield.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 1.97$ (s, 6H), 2.40 (s, 3H), 2.67 (s, 3H), 7.03-7.06 (m, 1H), 7.30-7.31 (m, 1H), 8.04 (d, $J = 8.1$ Hz, 1H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta = 20.5$, 21.6, 25.5, 124.1, 129.3, 131.8, 137.3, 140.6, 143.7, 176.5.

IR $\nu$(cm$^{-1}$): 2928, 1643, 1367, 1265, 1008, 667.

HRMS (MALDI$^+$): calc. for [C$_{10}$H$_{12}$I$_2$]$^+$: 290.9876; found: 290.9875.

m.p.(°C): 120-122 °C.

$(2,3,5,6$-Tetramethylphenyl)-$\lambda^3$-iodanediyl diacetate

Synthesized by GP4. Yellow solid, 83%.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 1.97$ (s, 6H), 2.36 (s, 6H), 2.65 (s, 6H), 7.14 (s, 1H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta = 20.5$, 21.8, 24.7, 135.6, 136.0, 136.1, 137.1, 176.6.

IR $\nu$(cm$^{-1}$): 2919, 1650, 1269, 666, 494.

HRMS (MALDI$^+$): calc. for [C$_{12}$H$_{16}$I$_2$]$^+$: 319.0189; found: 319.0189.

m.p.(°C): 155-157 °C.

$p$-Tolyl-$\lambda^3$-iodanediyl diacetate
Synthesized by GP3. Yellow solid, 90% yield. Spectroscopic data according to previous literature.[7]

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 2.00$ (s, 6H), 2.44 (s, 3H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.97 (d, $J = 8.4$ Hz, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta = 20.6, 21.7, 118.5, 131.9, 135.1, 142.8, 176.6.$
Table S1. Metal-free C-N bond formation from diphenyliodonium salts: Reaction optimization.

![Diagram of chemical reaction]

| Entry | Amide (eq) | Solvent  | Time (h) | Temperature | Yield % |
|-------|------------|----------|----------|-------------|---------|
| 1     | Phthalimide (5.0) | CH₂Cl₂    | 44       | Reflux      | 9       |
| 2     | Phthalimide (5.0) | DCE       | 36       | 84 °C       | NR      |
| 3     | Phthalimide (4.0) | toluene   | 24       | 84 °C       | 60      |
| 4     | Phthalimide (3.0) | toluene   | 24       | 84 °C       | 54      |
| 5     | Phthalimide (3.0) | toluene   | 48       | 84 °C       | 49      |
| 6     | Phthalimide (3.0) | dry toluene | 24      | Reflux      | 67      |
| 7     | Phthalimide (3.0) | dry toluene | 24      | 100 °C      | 67      |
| 8     | Phthalimide (3.0) | DMF       | 24       | 130 °C      | NR      |
| 9     | Phthalimide (2.0) | dry Tol/PhCl | 24     | 100 °C      | 23      |
| 10    | Phthalimide (2.0) | dry Tol/PhCl | 24     | 110 °C      | 50      |
| 11    | Phthalimide (2.0) | dry Tol/PhCl | 24     | 120 °C      | 50      |
| 12    | Phthalimide (2.0) | dioxane   | 24       | 100 °C      | NR      |
| 13    | Phthalimide (3.0) | dry toluene | 24     | 100 °C      | 75      |

3. General procedure for the synthesis of protected anilines (GP7).

A Schlenk tube equipped with a stirrer bar was charged with the potassium or sodium salt of the amide (0.7 mmol, 3.0 equiv.) in 10.0 mL of dry toluene (0.24 M). The diaryliodonium salt (0.24 mmol, 1.0 equiv.) was added and the reaction mixture was stirred at 100 °C for the indicated time. After cooling to rt the suspension was filtered over a short pad of Celite® washing with CH₂Cl₂ and the solvent was removed under reduced pressure. After purification by column
chromatography (n-hexane/EtOAc, 95/5 v/v) the final protected aniline was isolated as solid.

Alternatively, the potassium salt of the amide may be generated in situ prior to the amination reaction. In this case, GP7 is modified as follows: A Schlenk tube equipped with a stirrer bar was charged with the free amide (0.7 mmol, 3.0 equiv.) and potassium tert-butoxide (0.7 mmol, 3.0 equiv.) followed by addition of 10.0 mL of dry toluene (0.24 M). After stirring for 1 h, the diaryliododnium salt was added following the procedure outlined before.

**2-Phenylisoindoline-1,3-dione 2a.**

![2-Phenylisoindoline-1,3-dione 2a](image)

Synthesized by GP7. White solid, 67% yield. Reaction time: 24 h. Spectroscopic data according to previous literature.\[10\]

\[^1H\text{-NMR (400 MHz, CDCl}_3\text{): }\delta = 7.39-7.43 (m, 1H), 7.44-7.46 (m, 2H), 7.49-7.53 (m, 2H), 7.79-7.80 (m, 2H), 7.95-7.97 (m, 2H).\]

\[^{13}C\text{-NMR (100 MHz, CDCl}_3\text{): }\delta = 123.9, 126.7, 128.2, 129.3, 131.9, 132.0, 134.5, 167.4.\]

**4,5,6,7-Tetrafluoro-2-phenylisoindoline-1,3-dione 3a.**

![4,5,6,7-Tetrafluoro-2-phenylisoindoline-1,3-dione 3a](image)

Synthesized by GP7. Yellowish solid, 75% yield. Reaction time: 24 h. Spectroscopic data according to previous literature.\[9\]

\[^1H\text{-NMR (400 MHz, CDCl}_3\text{): }\delta = 7.37-7.40 (m, 2H), 7.43-7.47 (m, 1H), 7.50-7.55 (m, 2H).\]
**19F-NMR (376 MHz, CDCl₃):** δ = -135.1 (q, J = 9.5 Hz, 2F), -141.6 (q, J = 9.5 Hz, 2F).

**13C-NMR (100 MHz, CDCl₃):** δ = 113.6-113.7 (m), 126.6, 129.0, 129.5, 130.6, 142.4-142.6 (m), 143.9-144.2 (m), 145.0-145.3 (m), 146.6-146.9 (m), 161.5.

**4,5,6,7-Tetrafluoro-2-mesitylisooindoline-1,3-dione 3b.**

![Structure Image]

Synthesized by GP7. Yellowish solid, 69% yield. Reaction time: 24 h.

**1H-NMR (400 MHz, CDCl₃):** δ = 2.10 (s, 6H), 2.34 (s, 3H), 7.51 (s, 2H).

**19F-NMR (376 MHz, CDCl₃):** δ = -134.8 (q, J = 9.6 Hz, 2F), -141.9 (q, J = 11.1 Hz, 2F).

**13C-NMR (125 MHz, CDCl₃):** δ = 18.0, 21.3, 113.83-113.88 (m), 126.0, 129.6, 136.3, 140.2, 142.38-142.43 (m), 144.0-144.2 (m), 145.0-145.2 (m), 146.7-146.8 (m), 161.5.

**IR ν(cm⁻¹):** 2924, 1725, 1498, 1400, 1362, 1138, 946, 885, 731, 533.

**HRMS (APCI⁺):** calc. for [C₁₇H₁₂F₄NO₂]⁺: 338.0799; found: 338.0798.

**m.p.(°C):** 155-157 °C.

**2-(2,6-Dimethylphenyl)-4,5,6,7-tetrafluorisoindoline-1,3-dione 3c.**

![Structure Image]

Synthesized by GP7. Yellowish solid, 79% yield. Reaction time: 24 h. Scale-up reaction (4.6 mmol), 78% yield.

**1H-NMR (400 MHz, CDCl₃):** δ = 2.15 (s, 6H), 7.19 (d, J = 7.6 Hz, 2H), 7.26-7.32 (m, 1H).
$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta = -134.7$ (q, $J = 9.6$ Hz, 2F), -141.8 (q, $J = 9.5$ Hz, 2F).

$^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta = 18.1$, 113.8, 128.75, 128.84, 136.8, 142.65-142.74 (m), 144.2-144.5 (m), 144.8-144.9 (m), 146.5-146.6 (m), 161.3.

IR $\nu$(cm$^{-1}$): 2978, 1715, 1504, 1359, 1091, 940, 756, 685, 541.

HRMS (MALDI$^*$): calc. for [C$_{16}$H$_9$F$_4$NO$_2$]: 323.0569; found: 323.0569.

m.p.(°C): 151-153 °C.

4,5,6,7-Tetrafluoro-2-(2,3,5,6-tetramethylphenyl)isoindoline-1,3-dione 3d.

Synthesized by GP7. Yellowish solid, 80% yield. Reaction time: 20 h.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 1.99$ (s, 6H), 2.27 (s, 6H), 7.10 (s, 1H).

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta = -134.7$ (q, $J = 9.4$ Hz, 2F), -141.9 (q, $J = 9.5$ Hz, 2F).

$^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta = 14.7$, 20.2, 113.8-113.9 (m), 128.5, 132.2, 133.5, 135.1, 142.6-142.8 (m), 144.2-144.5 (m), 144.8-144.9 (m), 146.3-146.6 (m), 161.7.

IR $\nu$(cm$^{-1}$): 2926, 1722, 1496, 1400, 1092, 944, 743, 649.

HRMS (ESI$^+$): calc. for [C$_{18}$H$_{13}$F$_4$NNaO$_2$]$^+$: 374.0775; found: 374.0784.

m.p.(°C): 193-195 °C.

4,5,6,7-Tetrafluoro-2-(2,3,4,5,6-pentamethylphenyl)isoindoline-1,3-dione 3e.

Synthesized by GP7. Pale yellow solid, 77% yield. Reaction time: 24 h.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 2.03$ (s, 6H), 2.25 (s, 6H), 2.27 (s, 3H).
$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta = -134.3$ (q, $J = 9.5$ Hz, 2F), -141.6 (q, $J = 9.4$ Hz, 2F).

$^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta = 15.6, 16.9, 17.2, 113.8-113.9$ (m), 126.1, 131.6, 114.0, 137.6, 142.6-142.7 (m), 144.2-144.4 (m), 144.8-144.9 (m), 146.3-146.5 (m), 161.8.

IR $\nu$(cm$^{-1}$): 2932, 1719, 1506, 1404, 1146, 1095, 943, 754, 650.

HRMS (ESI$^+$): calc. for [C$_{19}$H$_{15}$F$_4$NNaO$_2$]$^+$: 388.0931; found: 388.0927.

m.p.(°C): 223-225 °C.

2-(4-(Tert-butyl)-2,6-dimethylphenyl)-4,5,6,7-tetrafluoroisoindoline-1,3-dione 3f.

![Structure of 2-(4-(Tert-butyl)-2,6-dimethylphenyl)-4,5,6,7-tetrafluoroisoindoline-1,3-dione 3f.]

Synthesized by GP7. Yellowish solid, 70% yield. Reaction time: 24 h.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 1.32$ (s, 9H), 2.13 (s, 6H), 7.18 (s, 2H).

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta = -134.8$ (q, $J = 9.4$ Hz, 2F), -142.0 (q, $J = 9.5$ Hz, 2F).

$^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta = 18.4, 31.4, 34.7, 113.8-113.9$ (m), 125.96, 126.0, 135.8, 142.6-142.7 (m), 144.2-144.4 (m), 144.8-144.9 (m), 146.3-146.6 (m), 153.0, 161.5.

IR $\nu$(cm$^{-1}$): 2973, 1721, 1500, 1365, 1140, 1090, 943, 713, 536.

HRMS (ESI$^+$): calc. for [C$_{20}$H$_{17}$F$_4$NNaO$_2$]$^+$: 402.1088; found: 402.1085.

m.p.(°C): 182-184 °C.

4,5,6,7-Tetrafluoro-2-(2,4,6-triethylphenyl)isoindoline-1,3-dione 3g.

![Structure of 4,5,6,7-Tetrafluoro-2-(2,4,6-triethylphenyl)isoindoline-1,3-dione 3g.]

Synthesized by GP7. Yellow amorphous solid, 90% yield. Reaction time: 20 h.
$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 1.13$ (t, $J = 7.5$ Hz, 6H), 1.27 (t, $J = 7.6$ Hz, 3H), 2.39 (q, $J = 7.6$ Hz, 4H), 2.67 (q, $J = 7.7$ Hz, 2H), 7.05 (s, 2H).

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta = -134.7$ (q, $J = 9.6$ Hz, 2F), -141.9 (q, $J = 9.4$ Hz, 2F).

$^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta = 14.6$, 15.4, 24.8, 28.9, 113.7-113.8 (m), 124.9, 126.6, 142.1, 142.2-142.4 (m), 143.9-144.2 (m), 144.7-145.1 (m), 146.6, 146.6-146.9 (m), 162.2.

IR $\nu$(cm$^{-1}$): 2968, 1727, 1367, 1094, 947.

HRMS (ESI$^+$): calc. for [C$_{20}$H$_{17}$F$_4$NNaO$_2$]$^+$: 402.1088; found: 402.1085.

m.p.(ºC): 105-107 ºC.

4,5,6,7-Tetrafluoro-2-(2,4,6-triisopropylphenyl)isoindoline-1,3-dione 3h.

Synthesized by GP7. Yellowish solid, 70% yield. Reaction time: 24 h.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 1.16$ (d, $J = 6.9$ Hz, 12H), 1.29 (d, $J = 7.0$ Hz, 6H), 2.60 (hept, $J = 7.2$ Hz, 2H), 2.95 (hept, $J = 7.1$ Hz, 1H), 7.11 (s, 2H).

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta = -134.2$ (q, $J = 9.5$ Hz, 2F), -141.6 (q, $J = 9.5$ Hz, 2F).

$^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta = 24.1$, 24.2, 29.6, 34.5, 113.76-113.83 (m), 122.4, 123.2, 142.6-142.7 (m), 144.2-144.5 (m), 144.8-144.9 (m), 146.7, 151.3, 162.5.

IR $\nu$(cm$^{-1}$): 2965, 1728, 1502, 1366, 1092, 944, 720, 552.

HRMS (ESI$^+$): calc. for [C$_{23}$H$_{25}$F$_4$NNaO$_2$]$^+$: 444.1557; found: 444.1552.

m.p.(ºC): 174-176 ºC.

2-(3-Bromo-2,4,6-trimethylphenyl)-4,5,6,7-tetrafluoroisoindoline-1,3-dione 3i.
Synthesized by GP7. White solid, 73% yield. Reaction time: 24 h.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 2.07$ (s, 3H), 2.23 (s, 3H), 2.44 (s, 3H), 7.12 (s, 1H).

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta = -134.3$ (q, $J = 9.8$ Hz, 2F), -141.3 (q, $J = 9.6$ Hz, 2F).

$^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta = 18.0, 19.4, 24.2, 113.6-113.7$ (m), 125.8, 127.0, 130.5, 135.3, 137.0, 140.7, 142.7-142.8 (m), 144.3-144.6 (m), 144.9-145.0 (m), 146.5-146.7 (m), 161.2.

IR $\nu$(cm$^{-1}$): 2928, 1723, 1501, 1402, 1094, 942, 753, 541.

HRMS (ESI$^+$): calc. for [C$_{18}$H$_{14}$BrF$_4$NNaO$_3$]$^+$: 469.9985; found: 469.9985.

m.p.(ºC): 122-124 ºC.

2-(2,6-Dichlorophenyl)-4,5,6,7-tetrafluoroisoindoline-1,3-dione 3j.

Synthesized by GP7. Yellowish solid, 51% yield. Reaction time: 24 h.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 7.40-7.45$ (m, 1H), 7.49-7.51 (m, 2H).

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta = -133.9$ (q, $J = 9.9$ Hz, 2F), -141.1 (q, $J = 9.8$ Hz, 2F).

$^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta = 113.7-113.8$ (m), 126.9, 128.9, 132.0, 135.5, 142.9-143.0 (m), 144.4-144.6 (m), 145.0-145.1 (m), 146.7-146.8 (m), 159.8.

IR $\nu$(cm$^{-1}$): 2963, 1731, 1506, 1463, 1089, 941, 777, 645.

HRMS (ESI$^+$): calc. for [C$_{15}$H$_7$Cl$_2$F$_4$NNaO$_3$]$^+$: 417.9631; found: 417.9634.

m.p.(ºC): 159-161 ºC.
4,5,6,7-Tetrafluoro-2-(2,4,6-trichlorophenyl)isoindoline-1,3-dione 3k.

Synthesized by GP7. Yellow solid, 61% yield. Reaction time: 19 h.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.52\) (s, 2H).

\(^{19}\)F-NMR (376 MHz, CDCl\(_3\)): \(\delta = -133.6\) (q, \(J = 10.0\) Hz, 2F), \(-140.8\) (q, \(J = 9.9\) Hz, 2F).

\(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \(\delta = 113.6-113.7\) (m), 125.7, 129.1, 136.1, 137.5, 142.6-142.8 (m), 144.2-144.5 (m), 145.3-145.5 (m), 146.9-147.2 (m), 159.6.

IR \(\nu(\text{cm}^{-1})\): 1737, 1471, 1401, 1095, 947, 817.

HRMS (ESI\(^+\)): calc. for \([C_{15}H_{6}Cl_{3}F_{4}NaO_{3}]^+\): 451.9242; found: 451.9244.

m.p.(\(^\circ\)C): 186-188 \(^\circ\)C.

4,5,6,7-Tetrafluoro-2-(2,3,6-trichlorophenyl)isoindoline-1,3-dione 3l.

Synthesized by GP7. White solid, 67% yield. Reaction time: 17 h.

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.45\) (d, \(J = 8.8\) Hz, 1H), 7.59 (d, \(J = 8.8\) Hz, 1H).

\(^{19}\)F-NMR (376 MHz, CDCl\(_3\)): \(\delta = -133.5\) (q, \(J = 9.9\) Hz, 2F), \(-140.7\) (q, \(J = 9.9\) Hz, 2F).

\(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \(\delta = 113.6-113.7\) (m), 128.4, 128.8, 132.6, 133.0, 133.8, 134.5, 142.95-143.0 (m), 144.6-144.8 (m), 145.1-145.2 (m), 146.8-146.9 (m), 159.5.

IR \(\nu(\text{cm}^{-1})\): 1731, 1502, 1402, 1093, 942, 795, 653.

HRMS (ESI\(^+\)): calc. for \([C_{15}H_{6}Cl_{3}F_{4}NaO_{3}]^+\): 451.9242; found: 451.9233.
m.p.(°C): 127-129 °C.

4,5,6,7-Tetrafluoro-2-(2,3,5,6-tetrachlorophenyl)isoindoline-1,3-dione 3m.

Synthesized by GP7. Yellowish solid, 75% yield. Reaction time: 20 h.

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ = 7.79 (s, 1H).
$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta$ = -133.1 (q, $J$ = 10.1 Hz, 2F), -140.3 (q, $J$ = 10.0 Hz, 2F).
$^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ = 113.5-113.6 (m), 129.5, 132.87, 132.89, 133.0, 142.7-142.9 (m), 144.3-144.6 (m), 145.5-145.6 (m), 147.0-147.3 (m), 159.3.

IR $\nu$(cm$^{-1}$): 1738, 1504, 1404, 1091, 946, 738, 525.

HRMS (ESI$^+$): calc. for [C$_{15}$H$_5$Cl$_4$F$_4$NNaO$_3$]$^+$: 485.8852; found: 485.8854.

m.p.(°C): 256-258 °C.

4,5,6,7-Tetrafluoro-2-(perchlorophenyl)isoindoline-1,3-dione 3n.

Synthesized by GP7. Yellow solid, 67% yield. Reaction time: 17 h.

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta$ = -135.0 (q, $J$ = 9.4 Hz, 2F), -142.0 (q, $J$ = 9.3 Hz, 2F).

$^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ = 113.5-113.6 (m), 127.3, 133.0, 133.7, 136.8, 143.05-143.14 (m), 144.7-145.3 (m), 146.8-147.0 (m), 159.2.

IR $\nu$(cm$^{-1}$): 1732, 1502, 1402, 1094, 944, 755, 558.

HRMS (ESI$^+$): calc. for [C$_{15}$H$_6$Cl$_4$F$_4$NNaO$_3$]$^+$: 519.8462; found: 519.8467.

m.p.(°C): 151-153 °C.
4,5,6,7-Tetrafluoro-2-(2-methyl-6-nitrophenyl)isoindole-1,3-dione 3o.

Synthesized by GP7. White foam, 87% yield. Reaction time: 17 h. Purification by column chromatography (CH$_2$Cl$_2$/MeOH, 200/1 v/v)

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 2.33$ (s, 3H), 7.59 (t, $J = 8.0$ Hz, 1H), 7.68-7.70 (m, 1H), 8.07-8.09 (m, 1H).

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta = -133.9$ (q, $J = 10.0$ Hz, 2F), -141.0 (q, $J = 9.9$ Hz, 2F).

$^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta = 18.2$, 113.96-114.0 (m), 123.6, 124.1, 130.7, 136.6, 140.8, 142.9-143.0 (m), 144.5-144.7 (m), 145.0-145.1 (m), 146.4, 146.7-146.8 (m), 160.8.

IR $\nu$(cm$^{-1}$): 1731, 1501, 1340, 1089, 944, 809, 728, 652.

HRMS (ESI$^+$): calc. for [C$_{15}$H$_6$F$_4$N$_2$NaO$_4$]$^+$: 377.0156; found: 377.0151.

m.p.(°C): 167-169 °C.

2-Mesityl-5-nitroisoindole-1,3-dione 5a.

Synthesized by GP7. Yellowish solid, 80% yield. Reaction time: 20 h.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 2.11$ (s, 6H), 2.35 (s, 3H), 7.03 (s, 2H), 8.16 (d, $J = 8.1$ Hz, 1H), 8.68 (dd, $J = 8.1$ Hz, 1.9 Hz, 1H), 8.78-8.79 (m, 1H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta = 18.1$, 21.3, 119.4, 125.2, 126.5, 129.6, 129.7, 133.5, 136.3, 136.5, 140.1, 152.1, 165.1, 165.4.

IR $\nu$(cm$^{-1}$): 3101, 1720, 1537, 1343, 1106, 1030.

HRMS (ESI$^+$): calc. for [C$_{17}$H$_{14}$N$_2$NaO$_4$]$^+$: 333.0846; found: 333.0852.
m.p. (°C): 214-216 °C.

5-Bromo-2-mesitylisodoline-1,3-dione 5b.

![Chemical Structure](image)

Synthesized by GP7. White solid, 67% yield. Reaction time: 15 h.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 2.10$ (s, 6H), 2.33 (s, 3H), 7.00 (s, 2H), 7.82 (dd, $J = 7.9$, 0.6 Hz, 1H), 7.94 (dd, $J = 7.9$, 1.7 Hz, 1H), 8.10 (dd, $J = 1.7$, 0.6 Hz, 1H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta = 18.1$, 21.3, 125.3, 126.9, 127.3, 129.4, 129.5, 130.6, 133.8, 136.5, 137.4, 139.7, 166.2, 166.7.

IR $\nu$(cm$^{-1}$): 2917, 1709, 1370, 1096, 853, 744.

HRMS (ESI$^+$): calc. for [C$_{17}$H$_{14}$BrNNaO$_2$]$^+$: 366.0100; found: 366.0104.

m.p. (°C): 194-196 °C.

1-Mesitylpyrrolidine-2,5-dione 5c.

![Chemical Structure](image)

Synthesized by GP7. White solid, 43% yield. Reaction time: 20 h. Purification by column chromatography ($n$-hexane/EtOAc, 3/2 v/v). Spectroscopic data according to previous literature.$^{[1]}$

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta = 2.07$ (s, 6H), 2.30 (s, 3H), 2.93 (s, 4H), 6.97 (s, 2H).

$^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta = 17.8$, 21.2, 28.8, 127.6, 129.5, 135.4, 139.6, 176.3.

2-Mesitylbenzo[d]isothiazol-3(2H)-one-1,1-dioxide 5d.
Synthesized by GP7. White solid, 72% yield. Reaction time: 24 h. Purification by column chromatography (n-hexane/CH$_2$Cl$_2$ 1/4 v/v).

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 2.29 (s, 6H), 2.34 (s, 3H), 7.03 (s, 2H), 7.91 (dtd, J = 18.0, 7.4, 1.3 Hz, 2H), 7.99-8.01 (m, 1H), 8.16-8.18 (m, 1H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 18.5, 21.3, 121.4, 123.6, 125.8, 127.2, 130.1, 134.5, 135.1, 138.6, 139.6, 140.9, 158.5.

IR $\nu$(cm$^{-1}$): 2927, 1725, 1463, 1262, 1183, 984, 747, 580, 505.

HRMS (ESI$^+$): calc. for [C$_{16}$H$_{16}$NO$_3$S]$^+$: 302.0845; found: 302.0847.

m.p.(ºC): 207-209 ºC.

2-Mesityl-1H-benzo[de]isoquinoline-1,3(2H)-dione 5e.

Synthesized by GP7. Yellowish solid, 59% yield. Reaction time: 16 h. Purification by column chromatography (n-hexane/EtOAc, 85/15 v/v).

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 2.12 (s, 6H), 2.36 (s, 3H), 7.04 (s, 2H), 7.81 (dd, J = 8.2, 7.3 Hz, 2H), 8.29 (dd, J = 8.3, 1.1 Hz, 2H), 8.68 (dd, J = 7.3, 1.2 Hz, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 17.9, 21.3, 122.9, 127.1, 129.0, 129.5, 131.4, 131.8, 132.0, 134.4, 135.4, 138.6, 163.7.

IR $\nu$(cm$^{-1}$): 2920, 1659, 1347, 1234, 774, 526.

HRMS (ESI$^+$): calc. for [C$_{21}$H$_{18}$NO$_2$]$^+$: 316.1332; found: 316.1333.

m.p.(ºC): 232-234 ºC.

3-Mesityloxazolidin-2-one 5f.
Synthesized by GP7. White solid, 95% yield. Reaction time: 16 h. Purification by column chromatography (n-hexane/EtOAc, 65/35 v/v).

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta =$ 2.24 (s, 6H), 2.28 (s, 3H), 3.79-3.83 (m, 2H), 4.51-4.55 (m, 2H), 6.92 (s, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta =$ 17.8, 21.1, 46.4, 62.5, 129.6, 131.6, 136.5, 138.6, 156.9.

IR $\nu$(cm$^{-1}$): 2921, 1744, 1411, 1111, 758, 618.

HRMS (ESI$^+$): calc. for [C$_{12}$H$_{16}$NO$_2$]$^+$: 206.1176; found: 206.1174.

m.p.(ºC): 87-89 ºC.

1-Mesitylpyrrolidin-2-one 5g.

Synthesized by GP7. Colorless solid, 77% yield. Reaction time: 16 h. Purification by column chromatography (CH$_2$Cl$_2$/MeOH, 97/3 v/v).

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta =$ 2.17 (s, 6H), 2.22-2.25 (m, 2H), 2.27 (s, 3H), 2.57 (t, $J =$ 8.1 Hz, 2H), 3.59 (t, $J =$ 7.0 Hz, 2H), 6.91 (s, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta =$ 17.8, 19.5, 21.1, 31.0, 49.1, 129.4, 133.3, 135.7, 138.0, 174.6.

IR $\nu$(cm$^{-1}$): 2915, 1680, 1404, 1283, 867, 500.

HRMS (ESI$^+$): calc. for [C$_{13}$H$_{18}$NO]$^+$: 204.1383; found: 204.1381.

m.p.(ºC): 77-79 ºC.

1-Mesitylpiperidin-2-one 5h.
Synthesized by GP7. White solid, 94% yield. Reaction time: 14 h. Purification by column chromatography (CH$_2$Cl$_2$/MeOH, 96/4 v/v).

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 1.94-1.96 (m, 4H), 2.15 (s, 6H), 2.27 (s, 3H), 2.56-2.58 (m, 2H), 3.37-3.39 (m, 2H), 6.91 (s, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 17.6, 21.1, 21.7, 23.7, 32.6, 49.7, 129.6, 134.7, 137.4, 138.1, 169.4.

IR $\nu$(cm$^{-1}$): 2944, 2922, 1637, 1435, 1301, 1161, 859.

HRMS (ESI$^+$): calc. for [C$_{14}$H$_{20}$NO]$^+$: 218.1539; found: 218.1532.

m.p.(°C): 103-105 °C.

**N-mesityl-toluenesulfonamide 5i**[12]

Synthesized by GP7. White solid, 56% yield. Reaction time: 14 h. Purification by column chromatography (CH$_2$Cl$_2$/MeOH, 96/4 v/v).

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 2.44 (s, 6H), 2.69 (s, 3H), 2.86 (s, 3H), 6.74 (s, 1H), 7.67-7.70 (m, 2H), 8.05-8.08 (m, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 18.6, 20.8, 21.5, 127.1, 129.4, 129.5, 129.9, 137.4, 137.9, 143.4.
4. General procedure for the deprotection of protected anilines (GP8).

![Chemical structure of 3c and 3c']

To a solution of 2-(2,6-dimethylphenyl)-4,5,6,7-tetrafluoroisoindoline-1,3-dione 3c (1.0 equiv.) in ethanol (2.0 mL) was added ethylenediamine (21.1 equiv.). The mixture was heated at 65 °C for 14 h. After cooling the reaction mixture to rt, it was concentrated under reduced pressure and the crude purified by column chromatography (CH$_2$Cl$_2$) to afford the aniline 4c as yellow oil in 99% of yield.

**2,6-Dimethylaniline 4c.**

![Chemical structure of 4c]

Yellow oil, 99% yield.

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 2.20$ (s, 6H), 3.57 (bs, 1H), 6.66 (t, $J = 7.5$ Hz, 1H), 6.96 (d, $J = 7.4$ Hz, 2H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta = 17.7, 118.1, 121.8, 128.4, 142.8.$
5. Application of the methodology to the synthesis of 9

In a flamed and dried Schlenk tube under argon atmosphere, NaH 55 wt% (0.035 g, 6.9 equiv.) was washed with 20.0 mL of dry hexane. After that the solvent was removed, dry THF (5.0 mL) and 5-oxopyrrolidine-3-carboxamide 6 (0.045 g, 3.0 equiv.) were added at 0 °C. The reaction mixture was stirred for 1 h warming to rt. The solvent was removed under reduced pressure and the iodonium salt 1c (0.055 g, 1.0 equiv.) and dry DMF (2.5 mL) were added. The reaction was stirred for 16 h at 100 °C. The solvent was removed under reduced pressure warming to 60 °C and the crude was dissolved in EtOAc, filtered over a short pad of Celite and concentrated under reduced pressure. The crude was used without further purification in the following step.

1-(2,6-Dimethylphenyl)-5-oxopyrrolidine-3-carboxamide 7.

Brownish solid. For the X-ray analysis the compound was purified by Al₂O₃ column chromatography (CH₂Cl₂/MeOH, 92.5/7.5 v/v) and re-crystallized (CH₂Cl₂/n-hexane, 33% isolated yield).

¹H-NMR (400 MHz, CDCl₃): δ = 2.17 (s, 3H), 2.21 (s, 3H), 2.79-2.85 (m, 1H), 2.90-2.95 (m, 1H), 3.30-3.36 (m, 1H), 3.72 (dd, J = 10.1, 8.6 Hz, 1H), 3.92 (dd, J = 10.1, 6.7 Hz, 1H), 7.09-7.11 (m, 2H), 7.14-7.17 (m, 1H).

¹³C-NMR (100 MHz, CDCl₃): δ = 17.89, 17.94, 34.7, 38.0, 50.9, 128.6, 129.0, 135.2, 135.9, 136.7, 171.9, 173.9.

IR (cm⁻¹): 3407, 3207, 2921, 1679, 1650, 1483, 1277, 789, 612.

HRMS (ESI⁺): calc. for [C₁₃H₁₆N₂NaO₂]⁺: 255.1104; found: 255.1107.
m.p.(°C): 215-217 °C.

Table S-1. Crystal data and structure refinement for 7.

| Identification code         | mo_NL1678_0m                      |
|----------------------------|-----------------------------------|
| Empirical formula          | C13 H16 N2 O2                     |
| Formula weight             | 232.28                            |
| Temperature                | 100(2) K                          |
| Wavelength                 | 0.71073 Å                         |
| Crystal system             | Monoclinic                        |
| Space group                | P2(1)/n                           |
| Unit cell dimensions       | a = 9.2926(11) Å, b = 10.7562(14) Å, c = 12.5718(16) Å |
| Volume                     | 1210.3(3) Å³                     |
| Z                          | 4                                |
| Density (calculated)       | 1.275 Mg/m³                       |
| Absorption coefficient     | 0.087 mm⁻¹                        |
| F(000)                     | 496                              |
| Crystal size               | 0.20 x 0.12 x 0.08 mm³            |
| Theta range for data collection | 2.439 to 28.724°                 |
| Index ranges               | -12<=h<=6,-14<=k<=14,-16<=l<=16   |
Reflections collected 14409
Independent reflections 3131 [R(int) = 0.0503]
Completeness to theta =28.724° 99.7%
Absorption correction Empirical
Max. and min. transmission 0.993 and 0.934
Refinement method Full-matrix least-squares on F^2
Data / restraints / parameters 3131/ 3/ 162
Goodness-of-fit on F^2 1.034
Final R indices [I>2sigma(I)] R1 = 0.0491, wR2 = 0.1095
R indices (all data) R1 = 0.0777, wR2 = 0.1235
Largest diff. peak and hole 0.315 and -0.225 e.Å^-3

\( N-(3,5\text{-bis(trifluoromethyl)phenyl})\text{-1-(2,6-dimethylphenyl)-5-oxopyrrolidine-3-carboxamide} \, 9. \)\(^{[13]}[14]\)

In a flamed and dried Schlenk tube under argon atmosphere, 1-(2,6-dimethylphenyl)-5-oxopyrrolidine-3-carboxamide 7 (1.0 equiv.), potassium phosphate (2.0 equiv.) and Cul (10 mol%) were dissolved in 1.0 mL of dry dioxane. 1-Iodo-3,5-bis(trifluoromethyl)benzene 8 (1.2 equiv.) and racemic \textit{trans}-1,2-diaminocyclohexane (20 mol%) were added and the reaction was stirred for 21 h at 110 °C. The mixture was cooled down to rt, filtered over a short pad of Celite\(^\text{®}\) washing with EtOAc and concentrated under reduced pressure. The crude compound was purified by column chromatography (n-hexane/EtOAc, 3/7 v/v).
Brownish solid, 45% yield over two steps (0.024 g).

**$^1$H-NMR (400 MHz, DMSO-$d_6$):** $\delta = 2.15$ (s, 3H), 2.17 (s, 3H), 2.69-2.85 (m, 2H), 3.55-3.62 (m, 1H), 3.71-3.75 (m, 1H), 3.81-3.86 (m, 1H), 7.10-7.18 (m, 3H), 7.79 (s, 1H), 8.29 (s, 2H), 10.8 (s, 1H).

**$^{19}$F-NMR (376 MHz, DMSO-$d_6$):** $\delta = -61.8$ (s, 6F).

**$^{13}$C-NMR (125 MHz, DMSO-$d_6$):** $\delta = 17.2$, 17.3, 33.6, 38.1, 50.2, 116.2-116.3 (m), 119.0-119.1 (m), 123.2 (q, $J_{C,F} = 272.8$ Hz), 127.9, 128.2 (d, $J_{C,F} = 10.2$ Hz), 130.8 (q, $J_{C,F} = 32.8$ Hz), 135.7, 135.9, 136.2, 140.8, 171.4, 172.4.

**IR $\nu$(cm$^{-1}$):** 3293, 2925, 1671, 1382, 1276, 1130, 776.

**HRMS (ESI$^+$):** calc. for [C$_{21}$H$_{18}$F$_6$N$_2$O$_2$]$^+$: 467.1165; found: 467.1181.

**m.p.(ºC):** 233-235 ºC.

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**Table S-2.** Crystal data and structure refinement for 9.

| Identification code       | mo_NL1699 |
|---------------------------|-----------|
| Empirical formula         | C$_{21}$H$_{18}$F$_6$N$_2$O$_2$ |
| Formula weight            | 444.37    |
| Temperature               | 100(2) K  |
| Wavelength                | 0.71073 Å |
| Crystal system            | Monoclinic |
| Space group               | P2(1)/c   |
| Unit cell dimensions      | a = 11.1092(5)Å  
                          | b = 16.8278(8)Å |
|                           | a = 90°,  
                          | b = 95.0660(16)° |
c = 10.6784(4) Å

\[ g = 90^\circ \].

Volume 1988.46(15) Å³

Z 4

Density (calculated) 1.484 Mg/m³

Absorption coefficient 0.134 mm⁻¹

F(000) 912

Crystal size 0.20 x 0.10 x 0.05 mm³

Theta range for data collection 1.840 to 25.426°.

Index ranges -13<=h<=12,-20<=k<=18,-12<=l<=12

Reflections collected 20676

Independent reflections 3561[R(int) = 0.0317]

Completeness to theta =25.426° 97.1%

Absorption correction Multi-scan

Max. and min. transmission 0.993 and 0.764

Refinement method Full-matrix least-squares on F²

Data / restraints / parameters 3561/ 18/ 282

Goodness-of-fit on F² 1.044

Final R indices [I>2sigma(I)] R1 = 0.0502, wR2 = 0.1317

R indices (all data) R1 = 0.0650, wR2 = 0.1399

Largest diff. peak and hole 0.712 and -0.417 e.Å⁻³
6. Synthesis of diphenyliodonium ditosylamide 11a.

A Schlenk tube equipped with a stirrer bar was charged with PhI(OAc)(NTs₂) 10 (0.1 g, 0.17 mmol) and dry CH₂Cl₂ (2.0 mL) was added under argon atmosphere. In the order were added benzene (1.0 equiv.) and trifluoromethanesulfonic acid (1.0 equiv.) and the reaction mixture was stirred at rt for 24 h. The mixture was quenched with NaHCO₃ sat., extracted with CH₂Cl₂ (3 x 10 mL) and dried over anhydrous MgSO₄. After concentration under reduced pressure, the crude oil was triturated with diethyl ether. The crystallization was completed inside the fridge. The desired diphenyliodonium salt 11a was collected as brownish solid in 82% yield after filtration.

¹H-NMR (400 MHz, DMSO-d₆): δ = 2.32 (s, 6H), 7.15 (d, J = 7.9 Hz, 4H), 7.50-7.58 (m, 8H), 7.65-7.71 (m, 2H), 8.22-8.24 (m, 4H).

¹³C-NMR (100 MHz, DMSO-d₆): δ = 20.8, 116.5, 126.1, 128.1, 131.8, 132.0, 135.1, 139.4, 144.0.

IR ν(cm⁻¹): 1127, 1108, 1076, 1030, 1009, 741, 662, 553.

HRMS (ESI⁺): calc. for [C₁₂H₁₀I]⁺: 280.9822; found: 280.9829.

m.p.(°C): 201-203 °C.
Table S-3. Crystal data and structure refinement for 11a.

| Property                              | Value                           |
|---------------------------------------|---------------------------------|
| Identification code                   | mo_NL209_0m                     |
| Empirical formula                     | C26 H24 I N O4 S2               |
| Formula weight                        | 605.48                          |
| Temperature                           | 100(2) K                        |
| Wavelength                            | 0.71073 Å                       |
| Crystal system                        | Triclinic                       |
| Space group                           | P-1                             |
| Unit cell dimensions                  | a = 13.0359(8)Å, b = 13.3667(8)Å, c = 14.4397(9)Å |
| Volume                                | 2467.0(3) Å³                    |
| Z                                      | 4                               |
| Density (calculated)                  | 1.630 Mg/m³                     |
| Absorption coefficient                | 1.501 mm⁻¹                      |
| F(000)                                | 1216                            |
| Crystal size                          | 0.25 x 0.20 x 0.20 mm³          |
| Theta range for data collection       | 1.546 to 30.156°                |
| Index ranges                          | -18<=h<=18, -17<=k<=18, -18<=l<=20 |
| Reflections collected                 | 89262                           |
| Independent reflections               | 12850[R(int) = 0.0216]          |
| Completeness to theta = 30.156°       | 88.1%                           |
| Absorption correction                 | Empirical                       |
| Max. and min. transmission            | 0.753 and 0.663                 |
| Refinement method                     | Full-matrix least-squares on F² |
| Data / restraints / parameters        | 12850/0/617                     |
| Goodness-of-fit on F²                 | 1.045                           |
| Final R indices [I>2σ(I)]             | R1 = 0.0203, wR2 = 0.0532       |
R indices (all data)  
R1 = 0.0223, wR2 = 0.0550

Largest diff. peak and hole  
1.369 and -0.624 eÅ⁻³

Table S2. Attempted metal-free C-N bond formation from diphenylidonium ditosylamide.

| Entry | Solvent        | Time (h) | Temperature | Yield% |
|-------|----------------|----------|-------------|--------|
| 1     | THF            | 13       | 100 °C      | NR     |
| 2     | DCE            | 24       | 80 °C       | NR     |
| 3     | DCE            | 48       | 80 °C       | NR     |
| 4     | DCE            | 13       | 100 °C      | NR     |
| 5     | DMF            | 24       | 100 °C      | NR     |
| 6     | dry toluene    | 24       | 100 °C      | NR     |
| 7     | m-xylene       | 24       | 100 °C      | NR     |
| 8     | dry CH₃CN      | 48       | 80 °C       | NR     |
| 9     | t-BuOH         | 48       | 80 °C       | NR     |
| 10    | benzene        | 24       | 100 °C      | NR     |
| 11    | dioxane        | 24       | 100 °C      | NR     |
7. Synthesis of Diphenyliodonium 4,5,6,7-tetrafluoro-1,3-dioxiisoindolin-2-ide 11b.

The potassium salt of tetrafluorophthalimide was previously prepared stirring the amide (1.0 equiv.) with KH 35 wt% (1.0 equiv.) in dry THF for 1 h, from 0°C to rt.

A Schlenk tube equipped with a stirrer bar was charged with [Ph₂I]NTs₂ 11a (0.19 g, 0.29 mmol) and dry CH₂Cl₂ (20.0 mL) was added under argon atmosphere. The potassium salt of tetrafluorophthalimide (1.5 g, 5.8 mmol) was added and the slurry was stirred at rt overnight. The mixture was filtrated over a short pad of Celite® washing with dry CH₂Cl₂. After concentration under reduced pressure the crude oil was triturated with dry diethyl ether to afford the desired diphenyliodonium salt 11b as brownish solid in 34% yield.

In an identical manner, compound 11b can be generated from parent compound 1a (67% yield).

¹H-NMR (400 MHz, DMSO-d₆): δ = 7.51 (t, J = 7.7 Hz, 4H), 7.62-7.66 (m, 2H), 8.22 (d, J = 7.7 Hz, 4H).

¹⁹F-NMR (376 MHz, DMSO-d₆): δ = -144.38- -144.43 (m, 2F), -151.19- -151.22 (m, 2F).

¹³C-NMR (100 MHz, DMSO-d₆, 313 K): δ = 119.0 (m), 126.6, 128.6, 131.8, 135.4, 139.2-139.4 (m), 141.2-141.4 (m), 143.1-143.4 (m), 176.4.

IR ν(cm⁻¹): 3052, 1639, 1615, 1489, 1262, 1063, 915, 731, 681, 556, 466.

HRMS (ESI⁺): calc. for [C₁₂H₁₀I]⁺: 280.9822; found: 280.9825.

HRMS (ESI⁻): calc. for [C₈F₄NO₂]⁻: 217.9871; found: 217.9873.
m.p.(°C): 139-141 °C.

Table S-4. Crystal data and structure refinement for 11b.

| Parameter                                    | Value                              |
|----------------------------------------------|------------------------------------|
| Identification code                          | mo_NL1064_0m                       |
| Empirical formula                            | C32 H20 Cl F4 I2 N O2              |
| Formula weight                               | 815.74                             |
| Temperature                                  | 100(2) K                           |
| Wavelength                                   | 0.71073 Å                          |
| Crystal system                               | Triclinic                          |
| Space group                                  | P-1                                |
| Unit cell dimensions                         | a = 11.7732(10)Å, b = 12.2213(10)Å, c = 13.1241(10)Å |
| Volume                                        | 1521.6(2) Å³                       |
| Z                                             | 2                                  |
| Density (calculated)                         | 1.780 Mg/m³                        |
| Absorption coefficient                       | 2.209 mm⁻¹                         |
| F(000)                                       | 788                                |
| Crystal size                                 | 0.25 x 0.15 x 0.04 mm³             |
| Theta range for data collection              | 1.851 to 30.560°                   |
| Index ranges                                 | -16<=h<=15,-17<=k<=15,-12<=l<=18   |
| Reflections collected                        | 28705                              |
| Independent reflections                      | 9225[R(int) = 0.0292]              |
| Completeness to theta =30.560°               | 98.799995%                         |
| Absorption correction                        | Empirical                          |
| Max. and min. transmission                   | 0.917 and 0.761                    |
| Refinement method          | Full-matrix least-squares on F^2 |
|---------------------------|----------------------------------|
| Data / restraints / parameters | 9225/ 0/ 380                     |
| Goodness-of-fit on F^2    | 1.032                            |
| Final R indices [I>2sigma(I)] | R1 = 0.0269, wR2 = 0.0620       |
| R indices (all data)      | R1 = 0.0350, wR2 = 0.0664        |
| Largest diff. peak and hole | 1.164 and -0.695 eÅ^3          |
8. Thermodynamic data for the reductive elimination reaction.

To calculate the activation barrier for the reductive elimination, the reaction was carried out in a NMR tube using a mixture PhCl/1,2,4-trichlorobenzene (2/1, v/v), \( N,N \)-dimethyl-formamide-\( d_7 \) as reference, at different temperatures (353 K, 368 K, 373 K, 378 K) to determine the corresponding reaction rates.

Reaction rate at 80 °C (353 K):
Reaction rate at 95 °C (368 K):

![Graph showing the reaction rate at 95 °C with the equation y = -0.0145x + 7E-05 and R² = 0.99987.]

Reaction rate at 100 °C (373 K):

![Graph showing the reaction rate at 100 °C with the equation y = -0.0272x - 0.0019 and R² = 0.97101.]

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Reaction rate at 105 °C (378 K):
Arrhenius plot (lnK vs 1/T):

\[ E_A = 17499 \times 8.31 \times 2.39 \times 10^{-5} = 34.77 \text{ Kcal/mol} \]
Eyring plot (lnK/T vs 1/T):

\[ \Delta H = 17135 \times 8.31 \times 2.39 \times 10^{-5} = 34.06 \text{ Kcal/mol} \]

\[ \Delta S = 105.5 \text{ J/K} \]
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