Supporting Information

Synthesis of Polysubstituted Iodoarenes Enabled by Iterative Iodine-Directed *para* and *ortho* C–H Functionalization

*Yichen Wu, Sébastien Bouvet, Susana Izquierdo, and Alexandr Shafir**

anie_201809657_sm_miscellaneous_information.pdf

Table of Contents

TABLE OF CONTENTS	S1
MATERIALS AND METHODS	S2
EXPERIMENTAL PROCEDURES.....	S2
1. Synthesis of trimethylsilylmethylarene substrates	S2
2. Reductive <i>C-H</i> -benzylation.	S7
3. Reductive <i>C-H</i> (sulfonyl)allylation.	S16
4. Examples of iterative iodane-directed transformations	S18
5. Synthesis of the diaryliodonium salt.	S22
X-RAY DIFFRACTION STRUCTURAL DETERMINATION DETAILS.	S23
COMPUTATIONAL DETAILS.	S28
REFERENCES.	S35
NMR SPECTRA.	S36

Materials and Methods

Reagents. All commercially acquired reagents were used as received. Most of the (diacetoxyiodo)arenes used in Tables 2 and 4 were prepared following or adapting the previously published protocols.^[1] The iodane substrate used for preparing **4** (the NHCbz) was prepared as described by Zhu *et al.*^[2] The benzyltrimethylsilanes derivatives were prepared by the literature procedure.^[3]

Reaction conditions. Reactions requiring inert atmosphere were conducted under nitrogen using standard Schlenk line and glovebox techniques. Solvents were dried by passing through a column of activated molecular sieves. All other reactions were performed employing standard organic synthesis protocols.

Chromatography. Thin layer chromatography (TLC) was performed using Merck aluminium-backed plates of TLC Silica gel 60 F₂₅₄; the plates were revealed using UV light or KMnO₄ stain. Standard Flash Column chromatography was accomplished using silica gel (60 Å pore size, 230-400 µm mesh size). Alternatively, the CombiFlash® Rf⁺ from Teledyne Isco with 200-400 nm UV detector were employed for the separation of the products. An Agilent 6890N GC system equipped with an FID detector was used for routine gas chromatography analyses. Mixtures were spiked with known quantities of cyclohexanecarbonitrile, and the integration (peak area) results were corrected against this internal reference using previously determined GC response coefficients. GC-MS measurements were recorded on an Agilent 7890B chromatograph equipped with an Agilent 5977A MS detector.

NMR. Spectra were recorded using Bruker Avance 300, 400 or 500 spectrometers (*Nuclear Magnetic Resonance Unit*, ICIQ). For spectra recorded in CDCl₃, the ¹H chemical shifts are reported in ppm relative to the residual CHCl₃, while ¹³C are reported relative to the solvent resonance (7.26 ppm and 77.16 ppm, respectively). Similarly, spectra in other solvents are reported relative to the residual *protio* signal for ¹H and the solvent resonances for ¹³C. The ¹⁹F signals are reported relative to CFCl₃ (0.00 ppm).

IR Spectra were recorded at the Spectroscopy and Reaction Kinetics Unit at ICIQ on a Bruker Optics FT-IR Alpha spectrometer equipped with a DTGS detector, KBr beam splitter at 4 cm⁻¹ resolution using a one-bounce ATR accessory with at diamond windows.

Mass spectrometry. High resolution mass spectra were determined at the ICIQ High Resolution Mass Spectrometry facility by atmospheric pressure chemical ionization (APCI) or Electrospray ionization (ESI)

Experimental procedures.

1. Synthesis of trimethylsilylmethylarene substrates

The trimethylsilylmethylarenes were synthesized by adapting previously reported methods. While the Pd-catalyzed coupling of the organoindium species was used with only small modifications (method A)^[3a], some modifications were introduced into the Ni-based approach.^[3b] The details are shown as follows. In both cases, the standard Shlenk line technique was used.

Method A:^[3a] *Step 1: Preparation of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$.* A round-bottom flask equipped with a stirrer bar was charged with InCl_3 (10.14 mmol, 2.238 g) and was carefully dried under vacuum while heating with a heat gun. The flask was cooled, refilled with N_2 and dry THF (70 mL) was added. The resulting suspension was cooled to -78°C , and a solution of $\text{Me}_3\text{SiCH}_2\text{MgCl}$ (30 mmol, $\sim 1.33\text{ M}$ in Et_2O) was slowly added. The mixture was stirred for 30 min, at which point the cooling bath was removed and the flask was allowed to reach room temperature. The resulting solution of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ was used as obtained by assuming complete conversion of InCl_3 and a 100 mL total volume. *This THF solution of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ could be stored at room temp. for several weeks.*

Step 2. Formation of $\text{ArCH}_2\text{SiMe}_3$. A mixture of the iodoarene (1 equiv.) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.01 equiv.) in dry THF (0.25 M) was brought to reflux and to mixture a solution of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ (quantity as indicated, in THF/ Et_2O) was added. The resulting mixture was left under reflux (nitrogen atmosphere) until the product reached the highest yield as judged by GC. Although in most cases full consumption of the ArI could not be achieved, the reaction typically reached a plateau after 24 hours. **Note:** *it is important that the addition of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ take place once the reaction mixture had already been brought to reflux. Failure to do so results in a lower yield of the product.* The reaction was then quenched by the addition of few drops of MeOH. The mixture was concentrated under vacuum, and then Et_2O was added. The organic phase was washed with aqueous HCl (5%), saturated aqueous NaHCO_3 and brine, dried with Na_2SO_4 (anhydrous) and concentrated in vacuo. The residue was purified by flash chromatography.

Method B:^[3b] A solution of haloarene (1.0 equiv) and $\text{Ni}(\text{acac})_2$ (0.05 equiv) in dry THF (0.24 M) was stirred for 5 min at room temperature and then cooled to 0°C . A solution $\text{Me}_3\text{SiCH}_2\text{MgCl}$ of in Et_2O (1.5 equiv) was added via a cannula, and the mixture was allowed to stir at the indicated temperature for 2 h. At this point, the reaction was quenched with water and extracted with Et_2O three times. The combined organic layers were washed with water, brine, dried over Na_2SO_4 (anhydrous) and then concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography afforded benzyltrimentylsilane.

Substrates prepared

Following **Method B**, A solution of 2-bromoiodobenzene (5 mmol, 1.41 g) and $\text{Ni}(\text{acac})_2$ (0.25 mmol, 64.5 mg) in THF (21 mL) was stirred for 5 min at room temperature. A solution of $\text{Me}_3\text{SiCH}_2\text{MgCl}$ in Et_2O (5 mmol) was added. Column chromatography: silica gel, elution: cyclohexane; $R_f = 0.64$ in cyclohexane. Liquid, 620 mg. Yield: 51%.

^1H NMR (500 MHz, CDCl_3) δ 7.21 – 7.19 (m, 1H), 7.15 (t, $J = 1.9\text{ Hz}$, 1H), 7.07 (t, $J = 7.8\text{ Hz}$, 1H), 6.91 (dt, $J = 7.7, 1.3\text{ Hz}$, 1H), 2.05 (s, 2H), 0.00 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 143.26, 130.94, 129.77, 127.12, 126.77, 122.42, 27.10, -1.81 (SiMe_3).

Following **Method A**, a solution of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ (6.81 mmol in THF) was added to a refluxing mixture of 3-iodophenyl acetate (5 mmol, 1.31 g) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.05 mmol, 35 mg) in dry THF (20 mL). Column chromatography: silica gel, 20:1 of cyclohexane/ EtOAc ; $R_f = 0.33$ in 20:1, cyclohexane/ EtOAc . Liquid, 577 mg. Yield: 52%.

^1H NMR (400 MHz, CDCl_3) δ 7.21 (t, $J = 7.9\text{ Hz}$, 1H), 6.85 (dt, $J = 7.7, 1.0\text{ Hz}$, 1H), 6.79 (ddd, $J = 8.1, 2.4, 1.0\text{ Hz}$, 1H), 6.71 (t, $J = 2.0\text{ Hz}$, 1H), 2.28 (s, 3H), 2.09 (s, 2H), 0.00 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 169.63 (C=O), 150.78, 142.53, 129.09, 125.67, 121.15, 117.07, 27.25, 21.34 (COCH_3), -1.81.

Following **Method A**, a solution of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ (4.09 mmol in THF) was added to a refluxing mixture of 3-iodophenyl acetate (5 mmol, 1.87 g) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.05 mmol, 35 mg) in dry THF (20 mL). Column chromatography: silica gel, 20:1 of cyclohexane/EtOAc; $R_f = 0.23$ in 20:1, cyclohexane/EtOAc. Liquid, 832 mg. Yield: 50%.

^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, $J = 8.3$ Hz, 2H), 7.31 – 7.27 (m, 2H), 7.10 (t, $J = 7.9$ Hz, 1H), 6.85 (ddd, $J = 7.7, 1.6, 1.0$ Hz, 1H), 6.70 (ddd, $J = 8.1, 2.4, 1.0$ Hz, 1H), 6.65 – 6.62 (m, 1H), 2.43 (s, 3H), 2.01 (s, 2H), -0.09 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.82, 145.24, 143.02, 132.75, 129.83, 129.20, 128.65, 126.82, 121.75, 117.83, 27.17, 21.82 (SO_2PhCH_3), -1.89.

Following **Method A**, a solution of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ (5.45 mmol in THF) was added to a refluxing mixture of 1-(3-iodophenyl)ethanone (5 mmol, 1.23 g) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.05 mmol, 35 mg) in dry THF (20 mL). Column chromatography: silica gel, 10:1 of cyclohexane/EtOAc; $R_f = 0.41$ in 10:1, cyclohexane/EtOAc. Liquid, 608 mg. Yield: 59%.

^1H NMR (500 MHz, CDCl_3) δ 7.66 (dt, $J = 7.8, 1.4$ Hz, 1H), 7.59 (d, $J = 1.9$ Hz, 1H), 7.31 (t, $J = 7.6$ Hz, 1H), 7.20 (dt, $J = 7.7, 1.5$ Hz, 1H), 2.58 (s, 3H), 2.15 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 198.66 (C=O), 141.36, 137.26, 132.90, 128.46, 127.71, 124.37, 27.21, 26.83, -1.83 (SiMe_3).

Following **Method B**, a solution of 3-methylsulfonylbromobenzene (5 mmol, 1.175 g) and $\text{Ni}(\text{acac})_2$ (0.25 mmol, 64.5 mg) in THF (20 mL) was stirred for 5 min at room temperature. A solution of $\text{Me}_3\text{SiCH}_2\text{MgCl}$ in Et_2O (7.5 mmol) was added. Column chromatography: silica gel, 5:1 of cyclohexane/EtOAc; $R_f = 0.25$ in 5:1, cyclohexane /EtOAc. Solid, 1.02 g. Yield: 85%.

^1H NMR (300 MHz, CDCl_3) δ 7.65 (dt, $J = 7.7, 1.4$ Hz, 1H), 7.57 (t, $J = 1.9$ Hz, 1H), 7.41 (t, $J = 7.7$ Hz, 1H), 7.26 (dt, $J = 4.7, 1.4$ Hz, 1H), 3.03 (s, 3H), 2.19 (s, 2H), 0.00 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.92, 140.54, 133.28, 129.24, 126.43, 123.02, 44.67 (SO_2Me), 27.49, -1.89.

Following **Method B**, a solution of 3-trifluoromethyliodobenzene (5 mmol, 1.36 g) and $\text{Ni}(\text{acac})_2$ (0.25 mmol, 64.5 mg) in THF (21 mL) was stirred for 5 min at room temperature. A solution of $\text{Me}_3\text{SiCH}_2\text{MgCl}$ in Et_2O (7.8 mmol) was added. Column chromatography: silica gel, cyclohexane; $R_f = 0.76$ in cyclohexane. Liquid, 613 mg. Yield: 53%.

^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.31 (m, 2H), 7.25 – 7.22 (m, 1H), 7.18 – 7.15 (m, 1H), 2.15 (s, 2H), 0.00 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 141.76, 131.38, 128.60, 124.60, 124.56, 120.91, 120.87, 27.34, -1.90 (SiMe_3). ^{19}F NMR (376 MHz, CDCl_3) δ -62.40.

Following **Method A**, a solution of $\text{In}(\text{CH}_2\text{SiMe}_3)_3$ (1.16 mmol in THF) was added to a refluxing mixture of 3-methoxyiodobenzene (3 mmol, 702 mg) and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.03 mmol, 21 mg) in dry THF (12 mL). Column chromatography: silica gel, gradient elution: cyclohexane; $R_f = 0.30$ in cyclohexane. Liquid, 256 mg. Yield: 44%.

^1H NMR (500 MHz, CDCl_3) δ 7.13 (t, $J = 8$ Hz, 1 H), 6.63 (ddd, $J = 8.2, 2.6, 0.9$ Hz, 1H), 6.61 – 6.58 (m, 1H), 6.55 (t, $J = 2.1$ Hz, 1H), 3.78 (s, 3H), 2.06 (s, 2H), 0.00 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 159.64, 142.33, 129.13, 120.85, 113.99, 109.29, 55.21 (OCH_3), 27.36, -1.69.

Following **Method B**, a solution of ethyl 3-iodobenzoate (5 mmol, 1.38 g) and Ni(acac)₂ (0.25 mmol, 64.5 mg) in THF (20 mL) was stirred for 5 min at room temperature. A solution of Me₃SiCH₂MgCl in Et₂O (8 mmol) was added. Column chromatography: silica gel, 20:1 of cyclohexane/EtOAc; R_f = 0.25 in 5:1, cyclohexane /EtOAc. Liquid, 820 mg. Yield: 69%.

¹H NMR (400 MHz, CDCl₃) δ 7.75 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.68 (t, *J* = 2.4 Hz, 1H), 7.27 (t, *J* = 8 Hz, 1H), 7.20 – 7.14 (m, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.14 (s, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), -0.01 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 167.11 (C=O), 141.06, 132.58, 130.50, 129.04, 128.22, 125.35, 60.95 (COCH₂CH₃), 27.11, 14.50 (COCH₂CH₃), -1.82.

Ethyl 3-((trimethylsilyl)methyl) benzoate was dissolved in MeOH. After heating to 35 °C, KOH was added. The resulting mixture was kept at 35 °C for 20 hours. Water was added to dilute the reaction, the aqueous layer was washed by Et₂O (10 mL×2). The aqueous layer was then acidified to pH = 2, and extracted by Et₂O (3 x 10 mL). The combined organic layers were dried over Na₂SO₄. The product was purified by column chromatography: silica gel, 4:1 of cyclohexane/EtOAc; R_f = 0.26 in 3:1 of cyclohexane/EtOAc. Solid, 1.29 g. Yield: 73%.

¹H NMR (500 MHz, CDCl₃) δ 12.13 (s, br, 1H), 7.84 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.76 (s, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.27 – 7.23 (m, 1H), 2.16 (s, 2H), 0.01 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 172.23 (C=O), 141.33, 133.57, 129.63, 129.25, 128.42, 126.08, 27.15, -1.83.

Following **Method B**, a solution of 2-bromoethyl-3-iodobenzoate (12.33 mmol, 4.38 g) and Ni(acac)₂ (0.62 mmol, 158 mg) in THF (42 mL) was stirred for 5 min at room temperature. A solution of Me₃SiCH₂MgCl in Et₂O (19.7 mmol) was added. Column chromatography: silica gel, 10:1 of cyclohexane/EtOAc; R_f = 0.44 in 10:1 of cyclohexane/EtOAc. Liquid, 2.29 g. Yield: 59%.

¹H NMR (400 MHz, CDCl₃) δ 7.78 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.71 (t, *J* = 1.8 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.23 – 7.18 (m, 1H), 4.61 (t, *J* = 6.1 Hz, 2H), 3.64 (t, *J* = 6.2 Hz, 2H), 2.15 (s, 2H), 0.00 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 166.53 (C=O), 141.29, 133.08, 129.60, 129.22, 128.38, 125.59, 64.24 (CH₂O), 28.98, 27.14, -1.83.

The synthesis was based on the methods reported by Alvarez *et al.*^[4] Sodium azide (3.3 mmol, 215 mg) was added to a flask containing DMSO (6.6 mL) and the mixture was stirred at room temperature for 24 hours in order to ensure full dissolution of the salt. To this solution was added 2-bromoethyl 3-((trimethylsilyl)methyl) benzoate (3 mmol, 945 mg) and the stirring was continued at room temperature for 23 h. The reaction diluted with water and the mixture was extracted with Et₂O (10 mL×3). The combined organic layers were washed with water, brine, and dried over MgSO₄. The product was used without further purification. Liquid, 761 mg. Yield: 92%.

¹H NMR (300 MHz, CDCl₃) δ 7.86 – 7.73 (m, 1H), 7.71 (s, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.21 (dt, *J* = 7.7, 1.5 Hz, 1H), 4.54 – 4.45 (m, 2H), 3.66 – 3.56 (m, 2H), 2.14 (s, 2H), -0.01 (s, 9H). ¹³C NMR (126 MHz,

CDCl₃) δ 166.74 (C=O), 141.34, 133.09, 129.53, 129.25, 128.41, 125.62, 63.71 (CH₂O), 50.19 (CH₂N₃), 27.15, -1.83.

Following **Method A**, a solution of In(CH₂SiMe₃)₃ (2.14 mmol in THF) was added to a refluxing mixture of 1-fluoro-2-iodobenzene (3 mmol, 0.66 g) and Pd(PPh₃)₂Cl₂ (0.03 mmol, 21 mg) in dry THF (12 mL). Column chromatography: silica gel, cyclohexane; R_f = 0.65 in cyclohexane. Liquid, 200 mg. Yield: 37%.

¹H NMR (500 MHz, CDCl₃) δ 7.07 – 6.94 (m, 4H), 2.08 (d, *J* = 1.9 Hz, 2H), 0.01 (d, *J* = 0.7 Hz, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 160.40 (d, *J* = 242.7 Hz), 130.46 (d, *J* = 5.1 Hz), 127.78 (d, *J* = 16.9 Hz), 125.55 (d, *J* = 7.7 Hz), 123.79 (d, *J* = 3.4 Hz), 115.13 (d, *J* = 22.3 Hz), 19.66 (d, *J* = 2.3 Hz), -1.70. ¹⁹F NMR (376 MHz, CDCl₃) δ -117.51.

Following **Method B**, A solution of 2-methyl-3-chloriodobenzene (5 mmol, 1.26 g) and Ni(acac)₂ (0.25 mmol, 64.5 mg) in THF (21 mL) was stirred for 5 min at room temperature. A solution of Me₃SiCH₂MgCl in Et₂O (8 mmol) was added. Column chromatography: silica gel, cyclohexane; R_f = 0.65 in cyclohexane. Liquid, 704 mg. Yield: 66%.

¹H NMR (500 MHz, CDCl₃) δ 7.13 – 7.08 (m, 1H), 6.97 (t, *J* = 7.8 Hz, 1H), 6.90 – 6.84 (m, 1H), 2.28 (s, 3H), 2.16 (s, 2H), 0.01 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 141.35, 135.17, 132.59, 127.43, 126.21, 125.31, 25.16, 17.12 (Me), -1.24.

Following **Method A**, a solution of In(CH₂SiMe₃)₃ (1.69 mmol in THF) was added to a refluxing mixture of the 3-cyanoiodobenzene (3 mmol, 687 mg) and Pd(PPh₃)₂Cl₂ (0.03 mmol, 21 mg) in dry THF (12 mL). Column chromatography: silica gel, 20:1 of cyclohexane/EtOAc; R_f = 0.29 in 20:1, cyclohexane/EtOAc. Liquid, 369 mg. Yield: 65%.

¹H NMR (500 MHz, CDCl₃) δ 7.37 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.27 – 7.26 (m, 1H), 7.21 (dt, *J* = 7.8, 1.3 Hz, 1H), 2.12 (s, 2H), 0.00 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 142.44, 132.57, 131.23, 129.01, 127.94, 119.42, 112.31, 27.24, -1.91.

Following **Method B** with modification. A solution of 3-bromobenzo[*b*]thiophene (10 mmol, 2.13 g) and Ni(acac)₂ (0.5 mmol, 129 mg) in dry THF was stirred for 5 min at room temperature and then cooled to 0 °C. A solution Me₃SiCH₂MgCl of in Et₂O (15 mmol) was added via a cannula, and the mixture was heated to 70 °C for 50 h. Column chromatography: silica gel, cyclohexane; R_f = 0.68 in cyclohexane. Liquid, 1.51 g. Yield: 69%.

¹H NMR (400 MHz, CDCl₃) δ 7.86 – 7.83 (m, 1H), 7.70 – 7.63 (m, 1H), 7.41 – 7.28 (m, 2H), 6.85 (d, *J* = 0.9 Hz, 1H), 2.32 (d, *J* = 0.9 Hz, 2H), 0.03 (d, *J* = 0.9 Hz, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 140.36, 139.50, 134.43, 123.95, 123.57, 122.87, 122.29, 118.43, 18.82, -1.18.

To the solution of 3-bromobenzo[*b*]thiophene (22.73 mmol, 4.84 g) in acetic acid (227 mL) was added the solid NaBO₃·4H₂O (227.3 mmol, 34.97 g) portionwise over a period of 30 minutes, and

the mixture was then heated to 50 °C for 14 h. Upon solvent removal, water was added and the CH₂Cl₂ was used to extract the aqueous layer. The organic fractions were then combined and dried over MgSO₄. After concentration, pentane was added leading to the appearance of a precipitate which was washed several times with pentane and then dried under vacuum to give 3-bromobenzo[*b*]thiophene 1,1-dioxide. White solid. 4.92 g. Yield: 88%.

¹H NMR (500 MHz, CDCl₃) δ 7.72 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.68 (td, *J* = 7.6, 1.2 Hz, 1H), 7.62 (td, *J* = 7.5, 1.1 Hz, 1H), 7.58 – 7.55 (m, 1H), 6.97 (s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 133.80, 131.62, 129.57, 124.69, 120.83.

Following **Method B** with a modification. A solution of 3-bromobenzo[*b*]thiophene 1,1-dioxide (15.63 mmol, 3.83 g) and Ni(acac)₂ (0.78 mmol, 201 mg) in THF (66 mL) was allowed to stir for 5 min at room temperature and then cooled to 0 °C. A solution Me₃SiCH₂MgCl of in Et₂O (25 mmol) was added via a cannula. The mixture was allowed to stir at 0 °C for 1h and then at room temp. for 14h. Column chromatography: silica gel, 7:1 of cyclohexane/EtOAc; R_f = 0.21 in 4:1 cyclohexane /EtOAc. Liquid, 1.96 g. Yield: 50%.

¹H NMR (500 MHz, CDCl₃) δ 7.71 (ddd, *J* = 7.3, 1.3, 0.6 Hz, 1H), 7.57 (td, *J* = 7.6, 1.3 Hz, 1H), 7.52 (td, *J* = 7.5, 1.1 Hz, 1H), 7.36 (dt, *J* = 7.5, 0.8 Hz, 1H), 6.23 (d, *J* = 1.2 Hz, 1H), 2.15 (d, *J* = 1.1 Hz, 2H), 0.10 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 146.40, 138.12, 133.33, 133.12, 130.45, 122.62, 121.82, 121.00, 19.57, -1.09.

The compound was synthesized following a reported procedure.^[5] A solution of 560 mg (5 mmol) of propargyltrimethylsilane (560 mg, 5 mmol) in THF (25 ml) was treated with Cp₂Zr(H)Cl (1.55 g, 6 mmol) and stirred at room temp. for 1h. After the addition of *p*-toluenesulfonyl chloride (1.14 g, 6 mmol), the reaction mixture was allowed to stir at 40 °C for 2h and then diluted with cyclohexane and stirred for a further 5 min. The mixture was then filtered through a short plug of silica gel. After concentration of the filtrate in vacuo, the residue was purified via silica gel flash column chromatography (10:1 of cyclohexane/EtOAc; R_f = 0.12 in 10:1, cyclohexane /EtOAc). Solid, 692 mg. Yield: 52%.

¹H NMR (500 MHz, CDCl₃) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.01 (dt, *J* = 14.9, 9.0 Hz, 1H), 6.11 (dt, *J* = 14.8, 1.3 Hz, 1H), 2.42 (s, 3H), 1.75 (dd, *J* = 9.1, 1.3 Hz, 2H), 0.03 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 145.96, 143.88, 138.78, 129.89, 127.95, 127.48, 24.41, 21.71, -1.68.

2. Reductive C-H-benylation.

Optimization protocol (for Table 1 in the main text).: A 15 mL reaction tube and was charged with (diacetoxyiodo)benzene (0.2 mmol, 64 mg) and a 3:7 mixture of CH₃CN/CH₂Cl₂ or HFIP (1.4 mL total). Then, benzyltrimethylsilane (0.3 mmol, 49 mg) and cyclohexanecarbonitrile (internal standard, 0.2 mmol) were added *via* syringe and the mixture was either cooled to -78°C in an acetone/CO₂ bath or kept at room temperature depending on the Table entry. At this temperature, the additive (0.24 mmol) was added and the solution was allowed to stir for 1 h at the same temperature. The yield was determined by GC analysis using cyclohexanecarbonitrile as internal standard. When indicated, the benzylation product was purified by column chromatography on silica gel (eluted with cyclohexane).

General procedure. Reactions were conducted in air without taking any special precautions;

described here for a 0.5 mmol scale reaction. A 15 mL reaction tube and was charged with the (diacetoxyiodo)arene (0.5 mmol) was charged in dissolved in a 3:7 mixture of CH₃CN/CH₂Cl₂ (3.5 mL total). Then, benzyltrimethylsilane (0.75 mmol) was added and the mixture was cooled at -78°C in an acetone/CO₂ bath. At this temperature, BF₃·Et₂O (0.6 mmol, 85 mg, 75 µl) was added and the solution was allowed to stir for 3h. After this time, the reaction was warmed up to room temperature and the solvent was removed by rotary evaporation. The product was isolated via silica gel flash column chromatography or by a CombiFlash set up on silica gel eluting with a cyclohexane:EtOAc mixture as indicated.

Following the general procedure, BF₃·Et₂O (0.6 mmol, 85 mg) was added to a premixed solution of PIDA (0.5 mmol, 161 mg) and benzyltrimethylsilane (0.75 mmol, 123 mg) in CH₂Cl₂ – MeCN. Column chromatography: silica gel, cyclohexane; R_f = 0.52, cyclohexane. Colorless oil, 113 mg. Yield: 77%.

¹H NMR (500 MHz, CDCl₃) δ 7.68 (pseudo d, *J* = 8.3 Hz, 2H), 7.40 – 7.34 (m, 2H), 7.32 – 7.27 (m, 1H), 7.25 – 7.23 (m, 2H), 7.01 (pseudo d, *J* = 8.2 Hz, 2H), 3.98 (s, 2H, CH₂). ¹³C NMR (126 MHz, CDCl₃) δ 140.84, 140.45, 137.57, 131.09, 128.95, 128.66, 126.39, 91.44 (C-I), 41.50.

The reaction has also been repeated on a 30 mmol scale scale: BF₃·Et₂O (36 mmol, 5.11 g) was added to a premixed solution of PIDA (30 mmol, 9.66 g) and benzyltrimethylsilane (45 mmol, 7.38 g) in CH₂Cl₂ – MeCN (210 mL, total). Yield: 6.12 g, 70%.

PIDA-*d*5

Step 1. A round-bottom flask was charged with AgOTf (1,285 g, 5.0 mmol), dichloromethane (20 mL), benzene-*d*6 (443 µL, 5.0 mmol, and I₂ (1.270 g, 5.0 mmol). Immediately, the resulting red mixture was covered with aluminum foil and allowed to stir for 1h. The resulting mixture was then filtered, transferred to a separatory funnel and washed with NH₄OH (aq) and NaHSO₃ (aq). The resulting solution was dried over MgSO₄ (anhydrous), and with care, most of the solvent was removed on rotary evaporator at ~300 mm Hg leaving behind crude PhI-*d*5 as an orange liquid. This residue was used directly in the next step.

Step 2. A round-bottom flask was charged with the crude PhI-*d*5 from the previous step, NaBO₃·4H₂O (7.7 g, 50 mmol) and glacial AcOH (50 mL). The mixture was heated to 45 °C for 16 hours. Upon solvent removal (rotary evaporation), water was added and the CH₂Cl₂ was used to extract the aqueous layer. The organic fractions were then combined and dried over MgSO₄. Upon concentration, pentane was added leading to the precipitation of PIDA-*d*5 as a white solid. This solid was isolated by filtration and dried in air. Yield: 1.12 g, 69%. ¹H NMR (500 MHz, CDCl₃) δ 2.01 (s, OAc). ¹³C NMR (126 MHz, CDCl₃) δ 176.52 (s, C=O), 134.65 (t, *J* = 25.9 Hz), 131.36 (t, *J* = 25.6 Hz), 130.57 (t, 25.0 Hz), 121.48 (C-I), 20.50 (Me).

^1H NMR (CDCl_3 , 500 MHz)

^{13}C NMR (CDCl_3 , 126 MHz) : PIDA- d_5 (top) and PIDA (bottom). Notice the cuts in the scale

Step 1. Synthesis of $\text{PhCD}_2\text{SiMe}_3$

Trimethylsilylchloride was freshly distilled and stored under N_2 . An oven-dried 20 mL Shlenk flask was charged with Mg (158 mg, 6.5 mmol), and the contents were flushed with Ar *via* 3 evacuate/refill cycles. THF (3 mL, anhydrous) was added, followed by TMSCl (824 μL , 6.5 mmol). The resulting mixture was allowed to stir for 90 min at room temp. At this point, $\text{BnBr-}d_2$ was added dropwise over 1h, initially at room temperature but cooling the reaction to 0°C when the mixture got too warm due to exothermicity. Once the addition was complete, the mixture was heated to 50°C for 20 min, at which point GC analysis showed complete conversion of BnBr to the desired product and some amount ($\sim 15\%$) of the bi-benzyl side product. Volatile fraction was removed by rotary evaporation, and the mixture was purified by column chromatography. Silica gel, pentane ($R_f = 0.7$ in hexanes). Colorless oil, yield: 539 mg, 65%. ^1H NMR is identical to that of non-deuterated species but with the CH_2 resonance at 2.08 ppm missing. EI-MS, $m/z = 166$ (M^+). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum lacks the CH_2 resonance at 22.2 ppm and has the difficult to observe *ipso* carbon at 140.6 ppm. Copies of spectra, compared to those of the non-deuterated BnSiMe_3 are shown in the Spectra section.

Step 2. *Para* C-H benzylation of $\text{PhI}(\text{OAc})_2$. Following the general procedure, $\text{BF}_3\cdot\text{Et}_2\text{O}$ (93 μL , 0.75

mmol) was added to a solution of $\text{PhI}(\text{OAc})_2$ (161 mg, 0.5 mmol) and $\text{PhCD}_2\text{SiMe}_3$ (125 mg, 0.75 mmol) that had been precooled to -78°C . Column chromatography: silica gel, pentane; $R_f = 0.48$, hexanes. Colorless oil, 110 mg. Yield: 74%. ^1H and ^{13}C spectra are comparable to those of the non-deuterated product but in both cases lack the CH_2 resonance, which for ^{13}C spectrum would be due to broadening by the neighboring D atoms. See copies of spectra in the Spectra section.

Competition experiment for C-H benzylation using a 1:1 BnSiMe_3 and $\text{BnSiMe}_3\text{-}d_2$ mixture

The standard procedure was adapted so that $\text{BF}_3\cdot\text{Et}_2\text{O}$ (62 μL , 0.5 mmol, 2 equiv) was added to a solution containing $\text{PhI}(\text{OAc})_2$ (81 mg, 0.25 mmol), BnSiMe_3 (123 mg, 0.75 mmol, 3.0 equiv) and $\text{BnSiMe}_3\text{-}d_2$ (125 mg, 0.75 mmol, 3.0 equiv) at -78°C . Product was isolated following the standard protocol. Yield: 43 mg, 60% based on 1:1 H_2/D_2 ratio in the product. The benzylic resonance at 3.92 ppm (singlet) was found to integrate to 1.06 H with respect to resonance at 6.94 ppm, when the latter is set to 2H.

Substrate scope

Following the general procedure, $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.6 mmol, 85 mg) was added to a mixture of diacetoxyiodo-3,5-dimethylbenzene (0.5 mmol, 175 mg) and benzyltrimethylsilane (0.75 mmol, 123 mg) in CH_2Cl_2 – MeCN. Column chromatography: silica gel, cyclohexane; $R_f = 0.56$, cyclohexane. Colorless oil, 159 mg. Yield: 98%.

^1H NMR (400 MHz, CDCl_3) δ 7.48 (s, 2H), 7.32 – 7.26 (m, 2H, Bn), 7.25 – 7.18 (m, 1H, Bn), 7.09 – 7.00 (m, 2H, Bn), 4.04 (s, 2H, CH_2), 2.24 (s, 6H, Me). ^{13}C NMR (101 MHz, CDCl_3) δ 139.66, 139.08, 136.89, 136.80, 128.60, 127.88, 126.08, 91.85(C-I), 34.88, 19.93. HRMS (APCI $^+$) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{I}$ $[\text{M}]^+$ 322.0213, found: 322.0211.

Following the general procedure, $\text{BF}_3\cdot\text{Et}_2\text{O}$ (0.6 mmol, 85 mg) was added to a mixture of diacetoxyiodo-3-methoxybenzene (0.5 mmol, 176 mg) and benzyltrimethylsilane (0.75 mmol, 123 mg) in CH_2Cl_2 – MeCN. Column chromatography: silica gel, cyclohexane; $R_f = 0.19$, cyclohexane. White solid, 133 mg. Yield: 82%.

^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.34 (m, 2H), 7.33 – 7.24 (m, 5H, Bn), 6.88 (dd, $J = 7.9, 0.7$ Hz, 1H), 4.01 (s, 2H, CH_2), 3.88 (s, 3H, OMe). ^{13}C NMR (101 MHz, CDCl_3) δ 157.96, 140.34, 131.87, 129.74, 129.69, 128.96, 128.43, 126.07, 119.80, 91.64(C-I), 55.70, 35.63. HRMS (APCI $^+$) m/z calcd

for $C_{14}H_{13}IO$ $[M]^+$ 324.0006, found: 324.0012.

Following the general procedure, $BF_3 \cdot Et_2O$ (0.6 mmol, 85 mg) was added to a mixture of diacetoxiyodo-3-benzyl-(3-iodophenyl)carbamate (0.5 mmol, 236 mg) and benzyltrimethylsilane (0.75 mmol, 123 mg) in CH_2Cl_2 – MeCN. Column chromatography: silica gel, 10:1 in cyclohexane/EtOAc; R_f = 0.38, in 10: 1 of cyclohexane/EtOAc. White solid, 194 mg. Yield: 88%.

1H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.45 (dd, J = 8.0, 1.8 Hz, 1H), 7.43 – 7.34 (m, 5H), 7.33 – 7.24 (m, 3H), 7.18 – 7.10 (m, 2H), 6.91 (d, J = 8.0 Hz, 1H), 6.45 (s, 1H), 5.17 (s, 2H), 3.92 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.45, 138.11, 137.14, 136.01, 133.54, 132.24, 129.07, 128.67, 128.63, 128.48, 128.40, 128.22, 126.97, 92.24(C-I), 67.19, 37.74. HRMS (ESI $^+$) m/z calcd for $C_{21}H_{18}INaO_2$ $[M+Na]^+$ 466.0274, found: 466.0275. FTIR (ATR, neat) cm^{-1} : 3298 (NH), 1693 (CO).

Following the general procedure, $BF_3 \cdot Et_2O$ (0.6 mmol, 85 mg) was added to a mixture of diacetoxiyodo-2-methylbenzene (0.5 mmol, 168 mg) and benzyltrimethylsilane (0.75 mmol, 123 mg) in CH_2Cl_2 – MeCN. Column chromatography: silica gel, gradient elution: cyclohexane; R_f = 0.61, cyclohexane. Yellow oil, Total yield: 113 mg, 84% which based on 1H NMR includes 77% of the major and 7% of the minor isomers; these could not be separated.

Major isomer, 104 mg. Yield: 77% (determined by 1H NMR). 1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.0 Hz, 1H), 7.46 – 7.38 (m, 2H, Bn), 7.36 – 7.31 (m, 1H, Bn), 7.33 – 7.30 (m, 2H, Bn), 7.21 – 7.18 (m, 1H), 6.82 (ddd, J = 8.1, 2.2, 0.8 Hz, 1H), 4.01 (s, 2H, CH_2), 2.51 (s, 3H, Me). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.45, 141.40, 140.63, 139.00, 130.61, 128.93, 128.63, 128.27, 126.33, 98.29(C-I), 41.44, 28.13. HRMS (APCI $^+$) m/z calcd for $C_{14}H_{12}I$ $[M-H]^+$ 306.9978, found: 306.9973.

Following the general procedure, $BF_3 \cdot Et_2O$ (0.6 mmol, 85 mg) was added to a mixture of diacetoxiyodo-2,6-dimethylbenzene (0.5 mmol, 175 mg) and benzyltrimethylsilane (0.75 mmol, 123 mg) in CH_2Cl_2 – MeCN. Column chromatography: silica gel, cyclohexane; R_f = 0.6, cyclohexane. Colorless oil, 109 mg. Yield: 84% between two fractions (68% major and 16% minor).

Major. 1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 2H), 7.31 – 7.22 (m, 3H), 6.97 (s, 2H), 3.94 (s, 2H), 2.51 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.15, 140.82, 140.68, 128.96, 128.64, 127.82, 126.30, 105.55, 41.34, 29.72. HRMS (APCI $^+$) m/z calcd for $C_{15}H_{15}I$ $[M]^+$ 322.0213, found: 322.0217.

Minor. 1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.29 – 7.24 (m, 1H), 7.17 (d, J = 7.2 Hz, 2H), 7.14 – 7.04 (m, 2H), 4.13 (s, 2H), 2.56 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.65, 140.30, 140.28, 136.79, 130.02, 128.58, 127.14, 126.17, 110.93 (C-I), 30.34, 26.53.

Following the general procedure, TMSOTf (0.24 mmol, 53 mg) was added to a premixed CH_2Cl_2 and MeCN solution (1.4 mL) of diacetoxiyodo-3-bromobenzene (0.2 mmol, 80 mg) and benzyltrimethylsilane (0.3 mmol, 49 mg). Column chromatography: silica gel, cyclohexane; R_f = 0.5, cyclohexane. Colorless oil, 51 mg. Yield: 68%.

1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 1.8 Hz, 1H), 7.57 (dd, J = 8.1, 1.8 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.29 – 7.24 (m, 1H), 7.23 – 7.18 (m, 2H), 6.89 (d, J = 8.1 Hz, 1H), 4.09 (s, 2H). ^{13}C NMR (126

MHz, CDCl₃) δ 140.78, 140.36, 138.93, 136.65, 132.61, 129.07, 128.72, 126.61, 91.63, 41.46, 27.07. HRMS (APCI⁺) m/z calcd for C₁₃H₁₀BrI [M]⁺ 371.9005, found: 371.8998.

Following the general procedure, BF₃·Et₂O (0.6 mmol, 85 mg) was added to a mixture of diacetoxiyodo-2-bromo- 5-methylbenzene (0.5 mmol, 208 mg) and benzyltrimethylsilane (0.75 mmol, 123 mg) in CH₂Cl₂ – MeCN. Column chromatography: silica gel, cyclohexane; R_f = 0.39, cyclohexane. White solid, 160 mg. Yield: 83%.

¹H NMR (400 MHz, CDCl₃) δ 7.71 (s, 1H), 7.40 (s, 1H), 7.37 – 7.32 (m, 2H), 7.30 – 7.24 (m, 1H), 7.17 – 7.14 (m, 2H), 3.94 (s, 2H), 2.19 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 141.57, 141.25, 138.88, 137.76, 133.74, 128.69, 126.77, 126.47, 98.34 (C-I), 38.95, 18.86. HRMS (ESI⁺) m/z calcd for C₁₄H₁₂BrI [M]⁺ 385.9162, found: 385.9156.

Following the general procedure, BF₃·Et₂O (0.6 mmol, 85 mg) was added to a mixture of diacetoxiyodo-1-naphthalene (0.5 mmol, 186 mg) and benzyltrimethylsilane (0.75 mmol, 123 mg) in CH₂Cl₂ – MeCN. Column chromatography: silica gel, 50:1 of cyclohexane/EtOAc; R_f = 0.58, in 50:1 of cyclohexane/EtOAc. Yellow solid, 149 mg. Yield: 87%.

¹H NMR (400 MHz, CDCl₃) δ 8.24 – 8.19 (m, 1H), 8.08 (d, J = 7.5 Hz, 1H), 8.02 – 7.98 (m, 1H), 7.60 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.53 (ddd, J = 8.3, 6.8, 1.4 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.28 – 7.20 (m, 3H), 7.05 (d, J = 7.5 Hz, 1H), 4.47 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 140.09, 137.93, 137.32, 134.57, 133.10, 128.79, 128.67, 128.65, 128.57, 127.51, 126.99, 126.38, 124.97, 98.45, 38.98. HRMS (APCI⁺) m/z calcd for C₁₇H₁₃I [M]⁺ 344.0056, found: 344.0052.

Following the general procedure, BF₃·Et₂O (0.6 mmol, 85 mg) was added to a premixed CH₂Cl₂ - MeCN solution (3.5 mL) of diacetoxiyodo-4-methylbenzene (0.5 mmol, 168 mg) and benzyltrimethylsilane (0.75 mmol, 123 mg). Column chromatography: silica gel, cyclohexane. R_f = 0.56, in cyclohexane. Colorless oil. Total yield: 77 mg (50%).

Major isomer. 68 mg. Yield: 44% (determined by ¹H NMR). ¹H NMR (500 MHz, CDCl₃) δ 7.56 – 7.52 (m, 2H), 7.38 – 7.33 (m, 3H), 7.29 – 7.24 (m, 1H), 7.18 – 7.16 (m, 2H), 6.96 (d, J = 7.8 Hz, 1H), 3.98 (s, 2H), 2.25 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 141.56, 139.56, 138.66, 136.45, 135.59, 132.33, 128.74, 128.62, 126.31, 91.09, 39.23, 19.43. HRMS (APCI⁺) m/z calcd for C₁₄H₁₃I [M]⁺ 308.0056, found: 308.0047.

Minor isomer : ¹H NMR (500 MHz, CDCl₃) δ 7.79 (d, J = 8.0 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.31 – 7.26 (m, 3H), 7.03 (d, J = 2.2 Hz, 1H), 6.81 (dd, J = 8.0, 2.2 Hz, 1H), 4.15 (s, 2H), 2.31 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 143.34, 139.79, 139.34, 138.35, 131.37, 129.16, 129.11, 128.53, 126.28, 97.36, 46.36, 21.06.

Following the general procedure, BF₃·Et₂O (0.6 mmol, 85 mg) was added to a mixture of diacetoxiyodo-2,4,6-trimethylbenzene (0.5 mmol, 182 mg) and benzyltrimethylsilane

(0.75 mmol, 123 mg) in CH_2Cl_2 – MeCN. Column chromatography: silica gel, cyclohexane; R_f = 0.43, cyclohexane. White solid, 167 mg. Yield: 98%.

^1H NMR (500 MHz, CDCl_3) δ 7.35 – 7.32 (m, 2H), 7.28 – 7.25 (m, 1H), 7.15 – 7.06 (m, 3H), 4.23 (s, 2H), 2.57 (s, 3H), 2.55 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 140.42, 140.20, 139.49, 136.94, 134.93, 129.53, 128.56, 127.86, 126.01, 107.49, 36.70, 30.20, 27.05, 26.93, 20.14. HRMS (APCI $^+$) m/z calcd for $\text{C}_{16}\text{H}_{17}\text{I}$ $[\text{M}]^+$ 336.0369, found: 336.0379.

Following the general procedure, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.6 mmol, 85 mg) was added to a mixture of diacetoxyiodo-2-thiophene (0.5 mmol, 164 mg) and benzyltrimethylsilane (0.75 mmol, 123 mg) in CH_2Cl_2 – MeCN. Column chromatography: silica gel, cyclohexane; R_f = 0.65, cyclohexane. Yellow oil, 92 mg. Yield: 61%.

^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.35 (m, 2H), 7.32 – 7.27 (m, 3H), 7.11 (d, J = 3.6 Hz, 1H), 6.55 (d, J = 3.6 Hz, 1H), 4.17 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 150.41, 139.63, 136.74, 128.70, 128.61, 126.89, 126.78, 71.01, 36.32. HRMS (APCI $^+$) m/z calcd for $\text{C}_{11}\text{H}_{10}\text{IS}$ $[\text{M} + \text{H}]^+$ 300.9542, found: 300.9550.

Following the general procedure, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.6 mmol, 85 mg) was added to a mixture of diacetoxyiodobenzene (0.5 mmol, 161 mg) and 3-bromobenzyltrimethylsilane (0.75 mmol, 182 mg) in CH_2Cl_2 – MeCN. Column chromatography: silica gel, cyclohexane; R_f = 0.55, cyclohexane. Colorless oil, 133 mg. Yield: 71%.

^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 7.9 Hz, 1H), 7.33 (s, 1H), 7.17 (t, J = 7.7 Hz, 1H), 7.12 – 7.07 (m, 1H), 6.93 (d, J = 8.3 Hz, 2H), 3.89 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 142.77, 139.88, 137.73, 131.93, 131.05, 130.20, 129.56, 127.59, 122.76, 91.82, 41.08. HRMS (APCI $^+$) m/z calcd for $\text{C}_{13}\text{H}_{10}\text{BrI}$ $[\text{M}]^+$ 371.9005, found: 371.9010.

Following the general procedure, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.6 mmol, 85 mg) was added to a mixture of diacetoxyiodobenzene (0.5 mmol, 161 mg) and ethyl 3-((trimethylsilyl)methyl)phenyl acetate (0.75 mmol, 167 mg). Column chromatography: silica gel, 20:1 of cyclohexane/EtOAc; R_f = 0.2, 20:1 of cyclohexane/EtOAc. White solid, 80 mg. Yield: 45%.

^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, J = 7.9 Hz, 2H), 7.31 (t, J = 7.9, 1.2 Hz, 1H), 7.07 – 7.02 (m, 1H), 6.99 – 6.92 (m, 3H), 6.89 (d, J = 2.1 Hz, 1H), 3.93 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.48, 150.94, 142.16, 140.10, 137.67, 131.16, 129.55, 126.41, 122.03, 119.62, 91.65, 41.15, 21.23. HRMS (ESI $^+$) m/z calcd for $\text{C}_{15}\text{H}_{13}\text{INaO}_2$ $[\text{M} + \text{Na}]^+$ 374.9852, found: 374.9848. FTIR (ATR, neat) cm^{-1} : 1744 (CO).

Following the general procedure, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.6 mmol, 85 mg) was added to a mixture of diacetoxyiodobenzene (0.5 mmol, 161 mg) and 3-((trimethylsilyl)methyl)phenyl 4-methylbenzenesulfonate (0.75 mmol, 167 mg) in CH_2Cl_2 – MeCN. Column chromatography: silica gel, 10:1 of cyclohexane/EtOAc; R_f = 0.25, 10:1 of cyclohexane/EtOAc. Colorless oil, 180 mg. Yield: 78%.

^1H NMR (500 MHz, CDCl_3) δ 7.67 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H),

7.24 (t, $J = 7.9$ Hz, 1H), 7.07 (d, $J = 7.6, 1.2$ Hz, 1H), 6.94 – 6.89 (m, 1H), 6.83 (d, $J = 8.2$ Hz, 2H), 6.74 (d, $J = 2.0$ Hz, 1H), 3.85 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 149.87, 145.36, 142.40, 139.79, 137.59, 132.41, 130.94, 129.75, 128.49, 127.66, 122.70, 120.43, 91.64, 40.95, 21.85. HRMS (ESI^+) m/z calcd for $\text{C}_{20}\text{H}_{17}\text{I}\text{NaO}_3\text{S}$ [$\text{M} + \text{Na}$] $^+$ 486.9835, found: 486.9840. FTIR (ATR, neat) cm^{-1} : 1369 (SO_2), 1175 (SO_2).

Following the general procedure, Tf_2O (0.6 mmol, 169 mg) was added to a mixture of diacetoxiodobenzene (0.5 mmol, 161 mg) and 1-(3-((trimethylsilyl)methyl)phenyl)ethan-1-one (0.75 mmol, 155 mg) in CH_2Cl_2 – MeCN. Column chromatography: silica gel, 10:1 of cyclohexane/EtOAc; $R_f = 0.26$, 10:1 of cyclohexane/EtOAc. Colorless oil, 100 mg. Yield: 59%.

^1H NMR (500 MHz, CDCl_3) δ 7.81 – 7.79 (m, 2H), 7.59 (d, $J = 8.0$ Hz, 2H), 7.40 – 7.33 (m, 2H), 6.93 (d, $J = 8.0$ Hz, 2H), 3.96 (s, 2H), 2.57 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 198.10, 141.04, 140.13, 137.70, 137.51, 133.65, 130.98, 128.91, 128.56, 126.63, 91.70, 41.29, 26.76. HRMS (ESI^+) m/z calcd for $\text{C}_{15}\text{H}_{14}\text{IO}$ [$\text{M} + \text{H}$] $^+$ 337.0084, found: 337.0086. FTIR (ATR, neat) cm^{-1} : 1680 (CO).

Following the general procedure, Tf_2O (0.6 mmol, 169 mg) was added to a mixture of diacetoxiodobenzene (0.5 mmol, 161 mg) and 3-methylsulfonyl benzyl trimethylsilane (0.75 mmol, 182 mg) in CH_2Cl_2 – MeCN. Column chromatography: silica gel, 5:1 of cyclohexane/EtOAc; $R_f = 0.14$, 5:1 of cyclohexane/EtOAc. White solid, 86 mg. Yield: 46%.

^1H NMR (500 MHz, CDCl_3) δ 7.81 – 7.73 (m, 2H), 7.65 – 7.56 (m, 2H), 7.48 (t, $J = 7.7$ Hz, 1H), 7.44 – 7.40 (m, 1H), 6.92 (d, $J = 8.3$ Hz, 2H), 3.99 (s, 2H), 3.03 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 142.36, 140.95, 139.27, 137.88, 134.22, 131.01, 129.73, 127.47, 125.44, 92.04, 44.55, 41.16. HRMS (ESI^+) m/z calcd for $\text{C}_{14}\text{H}_{13}\text{I}\text{NaO}_2\text{S}$ [$\text{M} + \text{Na}$] $^+$ 394.9573, found: 394.9571. FTIR (ATR, neat) cm^{-1} : 1295 (SO_2), 1137 (SO_2).

Following the general procedure, Tf_2O (0.6 mmol, 169 mg) was added to a mixture of diacetoxiodobenzene (0.5 mmol, 161 mg) and 3-trifluoromethyl benzyltrimethylsilane (0.75 mmol, 174 mg) in CH_2Cl_2 – MeCN. Column chromatography: silica gel, cyclohexane; $R_f = 0.38$, cyclohexane. Colorless oil, 80 mg. Yield: 44%.

^1H NMR (500 MHz, CDCl_3) δ 7.67 – 7.60 (m, 2H), 7.49 (d, $J = 7.8$ Hz, 1H), 7.45 (s, 1H), 7.41 (t, $J = 7.7$ Hz, 1H), 7.34 (d, $J = 7.7$ Hz, 1H), 6.96 – 6.91 (m, 2H), 3.98 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 141.43, 139.78, 137.87, 132.37, 131.07, 131.04 (q, $J = 21.5$ Hz), 129.16, 125.64 (q, $J = 3.8$ Hz), 124.25 (q, $J = 216.5$ Hz), 123.40 (q, $J = 3.8$ Hz), 91.91, 41.28. ^{19}F NMR (376 MHz, CDCl_3) δ -62.29. HRMS (APCI $^+$) m/z calcd for $\text{C}_{14}\text{H}_{10}\text{F}_3\text{I}$ [M] $^+$ 361.9774, found: 361.9774.

Following the general procedure, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.6 mmol, 85 mg) was added to a mixture of diacetoxiodobenzene (0.5 mmol, 161 mg) and ethyl 3-((trimethylsilyl)methyl) benzoate (0.75 mmol, 177 mg) in CH_2Cl_2 – MeCN. Column chromatography: silica gel, 20:1 of cyclohexane/EtOAc; $R_f = 0.16$, 20:1 of cyclohexane/EtOAc. Colorless oil, 124 mg. Yield: 68%.

^1H NMR (400 MHz, CDCl_3) δ 7.95 – 7.84 (m, 2H), 7.64 – 7.57 (m, 2H), 7.41 – 7.30 (m, 2H), 6.96 – 6.88 (m, 2H), 4.37 (q, $J = 7.1$ Hz, 2H), 3.95 (s, 2H), 1.39 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3)

δ 166.54, 140.71, 140.21, 137.65, 133.37, 130.97, 130.87, 129.97, 128.66, 127.65, 91.63, 61.04, 41.22, 14.42. HRMS (ESI⁺) m/z calcd for C₁₆H₁₅INaO₂ [M + Na]⁺ 389.0009, found: 389.0002. FTIR (ATR, neat) cm⁻¹: 1712 (CO).

Following the general procedure, TfOH (0.6 mmol, 90 mg) was added to a mixture of diacetoxyiodobenzene (0.5 mmol, 161 mg) and 3-((trimethylsilyl) methyl)benzoic acid (0.75 mmol, 156 mg) in CH₂Cl₂ – MeCN. Column chromatography: silica gel, 3:1 of cyclohexane/EtOAc; R_f = 0.14, 3:1 of cyclohexane/EtOAc. White solid, 83 mg. Yield: 49%.

¹H NMR (500 MHz, CDCl₃) δ 12.18 (s, br, 1H), 7.98 (td, J = 4.7, 1.7 Hz, 1H), 7.94 (d, J = 1.6 Hz, 1H), 7.62 (d, J = 8.3 Hz, 2H), 7.43 – 7.37 (m, 2H), 6.98 – 6.91 (m, 2H), 3.99 (s, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 172.28, 141.10, 140.11, 137.83, 134.49, 131.08, 130.66, 129.73, 128.95, 128.46, 91.80, 41.29. HRMS (ESI⁺) m/z calcd for C₁₄H₁₀IO₂ [M – H]⁺ 336.9731, found: 336.9729. FTIR (ATR, neat) cm⁻¹: 1683 (CO).

Following the general procedure, TfOH (0.6 mmol, 90 mg) was added to a premixed CH₂Cl₂/MeCN solution (3.5 mL) of diacetoxyiodobenzene (0.5 mmol, 161 mg) and 2-bromoethyl 3-((trimethylsilyl)methyl) benzoate (0.75 mmol, 236 mg). Column chromatography: silica gel, 10:1 of cyclohexane/EtOAc; R_f = 0.39, 10:1 of cyclohexane/EtOAc. Yellow solid, 90 mg. Yield: 41%.

¹H NMR (400 MHz, CDCl₃) δ 7.96 – 7.92 (m, 1H), 7.90 (s, 1H), 7.64 – 7.57 (m, 2H), 7.43 – 7.33 (m, 2H), 6.99 – 6.89 (m, 2H), 4.61 (t, J = 6.1 Hz, 2H), 3.97 (s, 2H), 3.63 (t, J = 6.1 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 166.04, 140.96, 140.10, 137.72, 133.88, 131.02, 130.18, 130.00, 128.85, 127.90, 91.73, 64.30, 41.22, 28.89. HRMS (ESI⁺) m/z calcd for C₁₆H₁₄BrINaO₂ [M + Na]⁺ 466.9114, found: 466.9113. FTIR (ATR, neat) cm⁻¹: 1716 (CO).

Following the general procedure, TMSOTf (0.6 mmol, 133 mg) was added to a premixed CH₂Cl₂ / MeCN solution (3.5 mL) of diacetoxyiodobenzene (0.5 mmol, 161 mg) and 2-azidoethyl 3-((trimethylsilyl)methyl) benzoate (0.75 mmol, 208 mg). Column chromatography: silica gel, 10:1 of cyclohexane/EtOAc; R_f = 0.24, 10:1 of cyclohexane/EtOAc. Colorless oil, 82 mg. Yield: 40%.

¹H NMR (500 MHz, CDCl₃) δ 7.97 – 7.88 (m, 2H), 7.63 – 7.58 (m, 2H), 7.43 – 7.35 (m, 2H), 6.96 – 6.90 (m, 2H), 4.51 – 4.47 (m, 2H), 3.96 (s, 2H), 3.58 (dd, J = 5.8, 4.4 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 166.23, 141.03, 140.14, 137.73, 133.88, 131.02, 130.23, 129.95, 128.89, 127.93, 91.71, 63.79, 50.06, 41.27. HRMS (ESI⁺) m/z calcd for C₁₆H₁₄IN₃NaO₂ [M + Na]⁺ 430.0023, found: 430.0023. FTIR (ATR, neat) cm⁻¹: 2099 (N₃), 1717 (CO).

Following the general procedure, BF₃·Et₂O (0.24 mmol, 34 mg) was added to a premixed CH₂Cl₂ / MeCN solution (1.5 mL) of diacetoxyiodobenzene (0.2 mmol, 64 mg) and 2-fluorobenzyl trimethylsilane (0.3 mmol, 55 mg). Column chromatography: silica gel, cyclohexane; R_f = 0.41, cyclohexane. Colorless oil, 60 mg. Yield: 63%.

^1H NMR (400 MHz, CDCl_3) δ 7.66 – 7.58 (m, 2H), 7.24 – 7.18 (m, 1H), 7.13 (td, J = 7.7, 1.9 Hz, 1H), 7.09 – 7.02 (m, 2H), 6.99 – 6.94 (m, 2H), 3.94 (d, J = 1.3 Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 161.03 (d, J = 245.7 Hz), 139.68, 137.68, 131.04 (d, J = 4.6 Hz), 130.96, 128.36 (d, J = 8.0 Hz), 127.51 (d, J = 15.8 Hz), 124.31 (d, J = 3.7 Hz), 115.56 (d, J = 21.9 Hz), 91.60, 34.56 (d, J = 3.1 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -117.82. HRMS (APCI $^+$) m/z calcd for $\text{C}_{13}\text{H}_{10}\text{FI}$ $[\text{M}]^+$ 311.9806, found: 311.9814.

Following the general procedure, TfOH (0.6 mmol, 90 mg) was added to a premixed CH_2Cl_2 - MeCN solution (3.5 mL) of diacetoxyiodobenzene (0.5 mmol, 161 mg) and 2-methyl-3-chloro benzyltrimethylsilane (0.75 mmol, 160 mg). Column chromatography: silica gel, cyclohexane; R_f = 0.47, cyclohexane. Yellow oil, 121 mg. Yield: 71%.

^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, J = 8.3 Hz, 2H), 7.30 (dd, J = 8.0, 1.4 Hz, 1H), 7.13 – 7.07 (m, 1H), 7.02 (d, J = 7.6 Hz, 1H), 6.90 – 6.83 (m, 2H), 3.98 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.20, 139.61, 137.64, 135.38, 134.76, 130.72, 128.70, 127.89, 126.77, 91.49, 39.87, 16.38. HRMS (APCI $^+$) m/z calcd for $\text{C}_{14}\text{H}_{11}\text{ClI}$ $[\text{M} - \text{H}]^+$ 340.9589, found: 340.9592.

3. Reductive C-H (sulfonyl)allylation.

Following the general procedure, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.6 mmol, 85 mg) was added to a premixed CH_2Cl_2 and MeCN solution (3.5 mL) of diacetoxyiodobenzene (0.5 mmol, 161 mg) and 3-((trimethylsilyl)methyl) benzo[*b*]thiophene 1,1-dioxide (0.5 mmol, 126 mg). Column chromatography: silica gel, 4:1 cyclohexane/EtOAc; R_f = 0.22 in 4:1 of cyclohexane/EtOAc. White solid, 187 mg. Yield: 98%.

^1H NMR (400 MHz, CDCl_3) δ 7.90 (dd, J = 8.0, 1.3 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.64 – 7.51 (m, 2H), 7.50 – 7.44 (m, 1H), 7.39 – 7.32 (m, 1H), 7.25 (dd, J = 7.7, 1.7 Hz, 1H), 7.02 (td, J = 7.6, 1.8 Hz, 1H), 6.07 (t, J = 1.9 Hz, 1H), 4.03 (d, J = 1.9 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 145.33, 140.09, 138.65, 138.07, 133.61, 132.27, 130.79, 130.27, 129.49, 129.00, 127.04, 122.54, 121.27, 100.91, 39.55. HRMS (ESI $^+$) m/z calcd for $\text{C}_{15}\text{H}_{11}\text{INaO}_2\text{S}$ $[\text{M} + \text{Na}]^+$ 404.9417, found: 404.9413. FTIR (ATR, neat) cm^{-1} : 1286 (SO_2), 1178 (SO_2).

Following the general procedure, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.36 mmol, 51 mg) was added to a premixed CH_2Cl_2 - MeCN solution (2.1 mL) of (diacetoxy)-4-chloro-iodobenzene (0.3 mmol, 107 mg) and 3-((trimethyl silyl)methyl)benzo[*b*]thiophene 1,1-dioxide (0.3 mmol, 76 mg). Column chromatography: silica gel, 4:1 cyclohexane/EtOAc; R_f = 0.23 in 4:1 of cyclohexane/EtOAc. White solid, 117 mg. Yield: 93%.

^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, J = 8.4 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.68 – 7.57 (m, 2H), 7.51 – 7.45 (m, 1H), 7.31 – 7.21 (m, 1H), 7.06 (dd, J = 8.4, 2.5 Hz, 1H), 6.11 (t, J = 1.9 Hz, 1H), 4.03 (d, J = 1.9 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.50, 141.11, 140.56, 138.09, 135.34, 133.69, 132.07, 130.99, 130.29, 129.82, 127.25, 122.42, 121.47, 97.92, 39.37. HRMS (ESI $^+$) m/z calcd for $\text{C}_{15}\text{H}_{10}\text{ClINaO}_2\text{S}$ $[\text{M} + \text{Na}]^+$ 438.9027, found: 438.9026.

Following the general procedure, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.36 mmol, 51 mg) was added to a premixed CH_2Cl_2 - MeCN solution (2.1 mL) of (diacetoxy)-4-trifluoromethyl-iodobenzene (0.3 mmol, 117 mg) and 3-((trimethyl silyl)methyl)benzo[*b*]thiophene 1,1-dioxide (0.3 mmol, 76mg). Column chromatography: silica gel, 5:1 cyclohexane/EtOAc; R_f = 0.23 in 5:1 of cyclohexane/EtOAc. White solid, 115 mg. Yield: 85%.

^1H NMR (400 MHz, CDCl_3) δ 8.09 – 8.01 (m, 1H), 7.77 – 7.73 (m, 1H), 7.64 (td, J = 7.6, 1.3 Hz, 1H), 7.59 (td, J = 7.5, 1.1 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.30 (dd, J = 8.3, 2.2 Hz, 1H), 6.00 (t, J = 2.0 Hz, 1H), 4.10 (d, J = 2.0 Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 144.36, 140.90, 140.01, 138.06, 133.71, 132.00, 131.66 (q, J = 33.1 Hz), 131.06, 127.15, 126.81 (q, J = 3.7 Hz), 126.12 (q, J = 3.6 Hz), 123.64 (q, J = 272.5 Hz), 122.31, 121.49, 105.22, 39.48. ^{19}F NMR (471 MHz, CDCl_3) δ -62.96. HRMS (ESI $^+$) m/z calcd for $\text{C}_{16}\text{H}_{10}\text{F}_3\text{I}\text{NaO}_2\text{S}$ 482.8524 [$\text{M} + \text{Na}$] $^+$ 472.9291, found: 472.9284.

Following the general procedure, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.36 mmol, 51 mg) was added to a premixed CH_2Cl_2 - MeCN solution (2.1 mL) of (diacetoxy)-2-bromo-iodobenzene (0.3 mmol, 120 mg) and 3-((trimethyl silyl)methyl)benzo[*b*]thiophene 1,1-dioxide (0.3 mmol, 76 mg). Column chromatography: silica gel, 5:1 cyclohexane/EtOAc; R_f = 0.16 in 5:1 of cyclohexane/EtOAc. White solid, 127 mg. Yield: 92%.

^1H NMR (400 MHz, CDCl_3) δ 7.74 – 7.72 (m, 1H), 7.63 – 7.53 (m, 3H), 7.46 – 7.42 (m, 1H), 7.24 – 7.14 (m, 2H), 6.10 (t, J = 1.8 Hz, 1H), 4.16 (d, J = 1.9 Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 144.94, 142.19, 138.11, 133.66, 132.20, 132.14, 130.93, 129.89, 128.38, 127.19, 122.50, 121.42, 108.46, 42.18. HRMS (ESI $^+$) m/z calcd for $\text{C}_{15}\text{H}_{10}\text{BrI}\text{NaO}_2\text{S}$ [$\text{M} + \text{Na}$] $^+$ 482.8522, found: 482.8524.

Following the general procedure, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.36 mmol, 51 mg) was added to a premixed CH_2Cl_2 - MeCN solution (2.1 mL) of (diacetoxy)-1-iodonaphthalene (0.3 mmol, 112 mg) and 3-((trimethyl silyl)methyl)benzo[*b*]thiophene 1,1-dioxide (0.3 mmol, 76 mg). Column chromatography: silica gel, 5:1 cyclohexane/EtOAc; R_f = 0.21 in 5:1 of cyclohexane/EtOAc. White solid, 89.2 mg. Yield: 68%.

^1H NMR (500 MHz, CDCl_3) δ 8.26 (dd, J = 8.5, 1.0 Hz, 1H), 7.85 – 7.79 (m, 2H), 7.78 – 7.73 (m, 1H), 7.65 – 7.59 (m, 2H), 7.58 – 7.54 (m, 2H), 7.53 – 7.51 (m, 1H), 7.35 (d, J = 8.3 Hz, 1H), 6.08 (t, J = 1.9 Hz, 1H), 4.36 (d, J = 1.9 Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 145.41, 138.12, 137.94, 135.34, 133.63, 133.27, 133.00, 132.36, 130.81, 129.59, 128.48, 127.16, 127.08, 127.01, 122.59, 121.29, 106.72, 41.67. HRMS (ESI $^+$) m/z calcd for $\text{C}_{19}\text{H}_{13}\text{I}\text{NaO}_2\text{S}$ [$\text{M} + \text{Na}$] $^+$ 454.9573, found: 454.9567.

Following the general procedure, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.36 mmol, 51 mg) was added to a premixed CH_2Cl_2 - MeCN solution (2.1 mL) of (diacetoxy)-2-iodothiophene (0.3 mmol, 98 mg) and 3-((trimethylsilyl)methyl)benzo[*b*]thiophene 1,1-dioxide (0.3 mmol, 76 mg). Column chromatography: silica gel, 5:1 cyclohexane/EtOAc; R_f = 0.40 in 5:1 of cyclohexane/EtOAc. White solid, 102.2 mg.

Yield: 88%.

^1H NMR (500 MHz, CDCl_3) δ 7.76 – 7.71 (m, 1H), 7.61 (td, J = 7.6, 1.3 Hz, 1H), 7.56 (td, J = 7.5, 1.1 Hz, 1H), 7.49 – 7.47 (m, 1H), 7.28 (d, J = 5.3 Hz, 1H), 7.08 (d, J = 5.3 Hz, 1H), 6.32 (t, J = 1.7 Hz, 1H), 4.09 (d, J = 1.7 Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 144.13, 138.14, 135.95, 135.43, 133.64, 131.91, 130.90, 127.23, 127.19, 122.52, 121.46, 82.86, 30.93. HRMS (ESI^+) m/z calcd for $\text{C}_{13}\text{H}_9\text{I}\text{NaO}_2\text{S}_2$ [$\text{M} + \text{Na}$] $^+$ 410.8981, found: 410.8975.

Following the general procedure, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.36 mmol, 51 mg) was added to a premixed CH_2Cl_2 and MeCN solution (2.1 mL) of (diacetoxy)-2,6-dimethyl-iodobenzene (0.3 mmol, 105 mg) and 3-((trimethyl silyl)methyl)benzo[*b*]thiophene 1,1-dioxide (0.3 mmol, 76 mg). Column chromatography: silica gel, gradient elution: 5:1 cyclohexane/EtOAc; R_f = 0.26 in 5:1 of cyclohexane/EtOAc. White solid. Total yield: 93 mg (75%), with a 10:1 selectivity as determined by ^1H NMR.

Major isomer. 84 mg. Yield: 68% (determined by ^1H NMR). ^1H NMR (500 MHz, CDCl_3) δ 7.74 – 7.71 (m, 1H), 7.61 (td, J = 7.5, 1.3 Hz, 1H), 7.56 (td, J = 7.5, 1.1 Hz, 1H), 7.48 (d, J = 7.4 Hz, 1H), 7.08 (d, J = 7.6 Hz, 1H), 7.02 (d, J = 7.7 Hz, 1H), 5.99 (t, J = 2.0 Hz, 1H), 3.95 (d, J = 2.0 Hz, 2H), 2.50 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 146.17, 142.28, 140.02, 138.16, 133.58, 132.29, 131.39, 130.82, 129.79, 127.63, 126.76, 122.31, 121.27, 110.88, 33.83, 30.38, 26.48. HRMS (ESI^+) m/z calcd for $\text{C}_{17}\text{H}_{15}\text{I}\text{NaO}_2\text{S}$ [$\text{M} + \text{Na}$] $^+$ 432.9730, found: 432.9725.

Following the general procedure, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.42 mmol, 60 mg) was added to a premixed CH_2Cl_2 - MeCN solution (2.45 mL) of (diacetoxy)-iodobenzene (0.35 mmol, 112 mg) and (E)-2-tosylvinyltrimethylsilane (0.39 mmol, 105 mg). Column chromatography: silica gel, 7:1 cyclohexane/EtOAc; R_f = 0.24 in 7:1 of cyclohexane/EtOAc. Colorless oil, 129 mg. Yield: 92%.

^1H NMR (500 MHz, CDCl_3) δ 7.79 (dd, J = 7.9, 1.3 Hz, 1H), 7.73 (d, J = 8.3 Hz, 2H), 7.33 – 7.25 (m, 3H), 7.14 (dd, J = 7.6, 1.7 Hz, 1H), 7.05 (dt, J = 15.1, 6.2 Hz, 1H), 6.92 (td, J = 7.6, 1.7 Hz, 1H), 6.20 (dt, J = 15.1, 1.6 Hz, 1H), 3.65 (dd, J = 6.2, 1.7 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 144.31, 143.23, 139.81, 139.54, 137.40, 132.42, 130.12, 129.88, 128.98, 128.82, 127.67, 100.52, 42.39, 21.66. HRMS (ESI^+) m/z calcd for $\text{C}_{16}\text{H}_{15}\text{I}\text{NaO}_2\text{S}$ [$\text{M} + \text{Na}$] $^+$ 420.9730, found: 420.9735. FTIR (ATR, neat) cm^{-1} : 1284 (SO_2), 1141 (SO_2).

4. Examples of iterative iodane-directed transforations

The synthesis was based on the methods reported by Shreeve *et al.*^[6] The 4-benzyl-iodobenzene (2.33 mmol, 685 mg) was dissolved in a mixture of HOAc (2.9 mL) and CH_3CN (58 mL). To this solution Selectfluor[®] (6.06 mmol, 2.15 g) was added and the mixture was stirred at room temperature for 20 h. The solvent was then removed and H_2O was added. The aqueous layer was extracted with CH_2Cl_2 and the combined organic fraction was dried over MgSO_4 . Upon

concentration, pentane was added inducing the formation of a precipitate, which was washed with pentane several times and dried under vacuum. White solid, 749 mg, yield: 78%.

^1H NMR (300 MHz, CDCl_3) δ 8.02 – 7.95 (m, 2H), 7.39 – 7.24 (m, 6H), 7.21 – 7.18 (m, 2H), 4.05 (s, 2H), 2.00 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 176.55, 145.79, 139.46, 135.27, 131.56, 129.22, 128.92, 126.85, 119.03, 41.90, 20.55.

The reaction has also been repeated on a ~17 mmol scale. Selectfluor® (43.5 mmol, 15.4 g) was added to a CH_3CN (416 mL) and HOAc (21 mL) solution of 4-benzyl-iodobenzene (16.73 mmol, 4.92 g). Yield: 79%, (includes 20 mol% in the μ -oxo dimer form).

Following the general procedure, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.96 mmol, 278 mg) was added to a premixed CH_2Cl_2 -MeCN solution (7:3, 11.4 mL) of (diacetoxy)-4-benzyl-iodobenzene (1.63 mmol, purity: 79%, dimer as impurity, 604 mg) and 3-((trimethyl silyl)methyl)benzo[*b*]thiophene 1,1-dioxide (1.63 mmol, 411 mg). Column chromatography: silica gel, 5:1 cyclohexane/EtOAc; R_f = 0.29 in 5:1 of cyclohexane/EtOAc. White solid, 493 mg. Yield: 64%.

^1H NMR (500 MHz, CDCl_3) δ 7.80 (d, J = 8.1 Hz, 1H), 7.75 – 7.72 (m, 1H), 7.61 – 7.52 (m, 2H), 7.45 (dd, J = 7.0, 1.1 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.24 – 7.19 (m, 1H), 7.16 – 7.12 (m, 2H), 7.09 (d, J = 2.2 Hz, 1H), 6.87 (dd, J = 8.1, 2.2 Hz, 1H), 6.05 (t, J = 1.9 Hz, 1H), 3.98 (d, J = 1.9 Hz, 2H), 3.92 (s, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 145.33, 142.50, 140.05, 140.02, 138.67, 138.06, 133.54, 132.27, 130.96, 130.73, 130.20, 128.89, 128.75, 126.95, 126.53, 122.47, 121.23, 97.78, 41.29, 39.40. HRMS (ESI $^+$) m/z calcd for $\text{C}_{22}\text{H}_{17}\text{INaO}_2\text{S}$ [$\text{M} + \text{Na}$] $^+$ 494.9886, found: 494.9895.

Reaction was conducted under nitrogen atmosphere; the first step (oxidation) was conducted following the Selectfluor-based protocol reported by DiMaggio et al.^[7] Selectfluor® (0.36 mmol, 128 mg) was charged in a 10 mL Schlenk tube under N_2 atmosphere and dissolved in CH_3CN (2.4 mL). Then, TMSOAc (0.73 mmol, 96 mg, 109 μL) and 3-(5-benzyl-2-iodobenzyl)benzo[*b*]thiophene 1,1-dioxide (0.24 mmol, 114 mg) were added and the mixture was allowed to stir at room temperature for 16h. Then, 2 mL of H_2O was added. The aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic fraction was dried over MgSO_4 . The solvent was removed almost to dryness, and the crude λ^3 -iodane was dissolved in a mixture 7:3 CH_2Cl_2 : CH_3CN (3.4 mL). At this point, propargyl(trimethyl)silane (0.36 mmol, 41 mg) was added and the mixture was cooled to -78°C in an acetone/ CO_2 bath. At this temperature, the $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.29 mmol, 41 mg, 36 μL) was added and the solution was stirred at -78°C for 4 h, allowed to warm to room temp. and allowed to stir for an additional 1.5 h. After this time, the solvent was removed and the product isolated by column chromatography: CombiFlash, silica gel cartridge (gradient eluent: 10:1 pentane/diethyl ether to 2:1 pentane/diethyl ether; R_f = 0.18 in 2:1 pentane/diethyl ether). White solid, 51 mg, yield: 42%.

^1H NMR (500 MHz, CDCl_3) δ 7.74 – 7.73 (m, 1H), 7.61 – 7.53 (m, 2H), 7.45 – 7.44 (m, 2H), 7.30 – 7.27 (m, 3H), 7.23 – 7.19 (m, 1H), 7.16 – 7.13 (m, 2H), 6.97 (d, J = 2.2 Hz, 1H), 4.05 (d, J = 1.9 Hz, 2H), 3.95 (s, 2H), 3.70 (d, J = 2.7 Hz, 2H), 2.30 (t, J = 2.7 Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 145.47, 142.34, 140.70, 140.03, 139.78, 138.17, 133.59, 132.38, 130.81, 129.56, 129.15, 128.95, 128.83, 127.00, 126.60, 122.44, 121.36, 103.66, 81.12, 72.21, 41.31, 40.70, 32.62. HRMS (ESI $^+$) m/z calcd for $\text{C}_{25}\text{H}_{19}\text{INaO}_2\text{S}$ [$\text{M} + \text{Na}$] $^+$ 533.0043, found: 533.0044. FTIR (ATR, neat) cm^{-1} : 3262 (CCH), 1290 (SO_2), 1168 (SO_2)

For I(III)-**1**, the purification was tested in 1.93 mmol scale: TMSOAc (5.02 mmol, 662 mg, 751 μL) and 3-(5-benzyl-2-iodobenzyl)benzo[*b*]thiophene 1,1-dioxide (1.93 mmol, 910 mg) were added to a CH_3CN (12 mL) solution of Selectfluor $^{\text{®}}$ (2.51 mmol, 889 mg) at room temp. After 13 h, the solvent was then removed and H_2O was added. The aqueous layer was extracted with CH_2Cl_2 and the combined organic fraction was dried over MgSO_4 . Upon concentration, pentane and a small amount of CH_2Cl_2 were added inducing the formation of a precipitate, which was washed with pentane several times and dried under vacuum. Light yellow solid, 1.12 g, yield: 98%, purity: 81% (impurity: 3-(5-benzyl-2-iodobenzyl)benzo[*b*]thiophene 1,1-dioxide and CH_2Cl_2). I(III)-**1** proved unstable when isolated, and quickly turned to dark brown sticky goo after 30h at room temp.

I(III)-**1**: ^1H NMR (300 MHz, CDCl_3) δ 8.18 (d, J = 8.2 Hz, 1H), 7.75 – 7.72 (m, 1H), 7.61 – 7.55 (m, 2H), 7.51 – 7.45 (m, 1H), 7.35 – 7.27 (m, 3H), 7.25 – 7.19 (m, 2H), 7.20 – 7.13 (m, 2H), 6.14 (t, J = 1.9 Hz, 1H), 4.26 (d, J = 1.9 Hz, 2H), 4.03 (s, 2H, Bn), 1.95 (s, 6H, OAc).

Following the general procedure, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (3.09 mmol, 439 mg) was added to a premixed CH_2Cl_2 - MeCN solution (7:3, 18.1 mL) of (diacetoxy)-4-benzyl-iodobenzene (2.58 mmol, contains 21% of the μ -oxo form, 955 mg) and (*E*)-2-tosylvinyltrimethylsilane (2.58 mmol, 692 mg). Column chromatography: silica gel, 7:1 cyclohexane/EtOAc; R_f = 0.33 in 7:1 of cyclohexane/EtOAc. White solid, 670 mg. Yield: 53%.

^1H NMR (500 MHz, CDCl_3) δ 7.75 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.1 Hz, 1H), 7.34 – 7.27 (m, 4H), 7.24 – 7.19 (m, 1H), 7.16 – 7.12 (m, 2H), 7.04 (dt, J = 15.1, 6.2 Hz, 1H), 7.00 (d, J = 2.2 Hz, 1H), 6.78 (dd, J = 8.1, 2.2 Hz, 1H), 6.22 (dt, J = 15.0, 1.7 Hz, 1H), 3.90 (s, 2H), 3.62 (dd, J = 6.2, 1.8 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 144.20, 143.25, 142.14, 140.03, 139.71, 139.49, 137.40, 132.30, 130.69, 129.81, 129.67, 128.77, 128.57, 127.59, 126.33, 97.40, 42.19, 41.16, 21.60. HRMS (ESI $^+$) m/z calcd for $\text{C}_{23}\text{H}_{21}\text{INaO}_2\text{S}$ [$\text{M} + \text{Na}$] $^+$ 511.0199, found: 511.0203.

Reaction was conducted under nitrogen atmosphere. Selectfluor® (0.31 mmol, 110 mg) was charged in a 10 mL Schlenk tube under N₂ atmosphere and dissolved in CH₃CN (1.4 mL). Then, the trimethylsilyl acetate (0.62 mmol, 82 mg, 93 µL) and (E)-((3-(5-benzyl-2-iodophenyl)prop-1-Tosyl-1-en (0.238 mmol, 116 mg) were added and the mixture was allowed to stir at room temperature for 16 h. The solvent was removed and H₂O was added. The aqueous layer was extracted with CH₂Cl₂ and the combined organic fraction was dried over MgSO₄. Upon solvent removal, the residue was dissolved in a 3:7 mixture of CH₃CN - CH₂Cl₂ (1.7 mL total). The 3-((trimethylsilyl)methyl)benzo [b]thiophene 1,1-dioxide (0.238 mmol, 60 mg) was then added and the mixture was cooled to -78°C in an acetone/CO₂ bath. At this temperature, the BF₃ Et₂O (0.286 mmol, 41 mg, 35 µL) was added and the solution was allowed to stir at -78°C for 2 h. After this time, the solvent was removed. The product was isolated by column chromatography on silica gel (3:1 cyclohexane/EtOAc; R_f = 0.11 in 4:1 of cyclohexane/EtOAc). White solid, 122 mg, yield: 76%.

¹H NMR (500 MHz, CDCl₃) δ 7.73 (td, *J* = 6.7, 1.7 Hz, 3H), 7.63 – 7.51 (m, 2H), 7.42 (dd, *J* = 7.0, 1.4 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.23 (m, 2H), 7.24 – 7.18 (m, 1H), 7.14 – 7.07 (m, 2H), 7.04 (dt, *J* = 15.0, 6.2 Hz, 1H), 6.98 – 6.94 (m, 2H), 6.25 (dt, *J* = 15.1, 1.7 Hz, 1H), 5.99 (d, *J* = 2.0 Hz, 1H), 4.02 (d, *J* = 1.8 Hz, 2H), 3.89 (s, 2H), 3.73 (dd, *J* = 6.3, 1.6 Hz, 2H), 2.43 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 145.24, 144.52, 143.06, 142.61, 141.68, 140.40, 139.68, 138.09, 137.43, 133.58, 132.80, 132.22, 130.81, 130.03, 129.94, 129.85, 128.88, 128.84, 127.75, 126.97, 126.65, 122.44, 121.29, 104.43, 43.70, 41.09, 40.79, 21.73. HRMS (ESI⁺) *m/z* calcd for C₃₂H₂₇IO₄S₂Na [M + Na]⁺ 689.0288, found: 689.0304.

A Schlenk tube was charged with a magnetic stir bar, the ArI (42 mg, 63 µmol), PdCl₂(PPh₃)₂ (4.4 mg, 6 µmol) and CuI (2.5 mg, 13 µmol). The contents of the tube were flushed with N₂, and under a nitrogen counterflow Et₃N (not dried, 300 µL) was added, followed by THF (400 µL). The tube was sealed and the reaction mixture was heated to 60 °C for 14h. At this point, the mixture was diluted with EtOAc and diluted aqueous hydrochloric acid (0.1M). The organic fraction was collected, and the aqueous fraction was extracted with 2x 5 mL of EtOAc. The combined organic fraction was evaporated and then purified by column chromatography. Silica gel, gradient 10:1 -> 2:1 cyclohexane:EtOAc. R_f = 0.52 in 2:1 cyclohexane:EtOAc. Yellow solid, yield: 31 mg, 49 µmol (78%).

¹H NMR (500 MHz, CDCl₃) δ 7.79 – 7.73 (m, 4H), 7.67 – 7.62 (m, 2H), 7.56 – 7.51 (m, 1H), 7.38 – 7.25 (m, 6H), 7.18 (d, *J* = 6.8 Hz, 2H), 6.94 (d, *J* = 1.9 Hz, 1H, benzo[thiophene] CH-SO₂), 6.88 (d, *J* = 16.0 Hz, 1H, SO₂CH=CH), 6.23 (dt, *J* = 15.8, 7.6 Hz, 1H, SO₂CH=CH), 4.13 (d, *J* = 2.3 Hz, 2H, CH₂-benzoth.), 4.00 (s, 2H, CH₂Ph), 3.98 (dd, *J* = 7.6, 1.3 Hz, 2H, CH₂C=C), 2.43 (s, 3H, Me), 0.19 (s, 9H, SiMe₃). ¹³C NMR (101 MHz, CDCl₃) δ 144.95 (C), 142.00 (C), 139.77 (C), 138.64 (C), 138.22 (C), 137.00 (C), 136.59 (CH), 135.69 (C), 133.84 (CH), 130.48 (CH), 129.88 (CH), 129.03 (CH), 128.98 (CH), 128.59 (CH), 128.05 (CH), 126.89 (CH), 126.86 (C), 126.10 (CH), 125.87 (CH), 121.92 (CH), 121.74 (CH), 120.48 (C), 118.50 (CH), 106.61 (CC), 100.68 (CC), 60.95 (CH₂), 54.86 (CH₂), 41.89 (CH₂), 21.80 (ArCH₃), 0.03 (SiMe₃).

5. Synthesis of the diaryliodonium salt.

A 15 mL oven-dried reaction tube was charged with $\text{PhI}(\text{OAc})_2$ (5.1 mmol, 1.64 g), followed by injection of dry dichloromethane (25.5 mL) and acetonitrile (10.2 mL) and 4-(tributylstannyl)benzyltrimethylsilane (5.1 mmol, 2.3 g). The reaction mixture was then cooled to -78°C and $\text{BF}_3\cdot\text{Et}_2\text{O}$ (6.12 mmol, 638 μL) was added dropwise. The reaction was first stirred at -78°C for 1 hour and then gradually warmed to room temperature. The reaction was stopped after overnight stirring. The solvent was removed and Et_2O was added together with a small amount of CH_2Cl_2 to get precipitate. White solid. Yield: 604 mg, 26%.

^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 8.5$ Hz, 2H), 7.87 (d, $J = 8.5$ Hz, 1H), 7.60 (t, $J = 7.5$ Hz, 1H), 7.45 (t, $J = 7.9$ Hz, 2H), 7.45 (t, $J = 7.9$ Hz, 2H), 2.14 (s, 2H), 2.14 (s, 9H). ^{13}C NMR (126 MHz, CDCl_3) δ 148.10, 135.71, 135.05, 132.78, 132.58, 132.18, 112.65, 105.67, 28.15, -1.87. ^{19}F NMR (376 MHz, CDCl_3) δ -146.48. ^{11}B NMR (128 MHz, CDCl_3) δ -114.04 – -127.54 (m). HRMS (ESI^+) m/z calcd for $\text{C}_{16}\text{H}_{20}\text{Si} [\text{M} - \text{OAc}]^+$ 367.0374, found 367.0375.

X-Ray diffraction structural determination details.

Table S1. Crystal data and structure refinement for mo_WYC076P_0m

Identification code	mo_WYC076P_0m	
Empirical formula	C ₁₄ H ₁₂ Br I	
Formula weight	387.05	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.7846(6) Å	α = 90°.
	b = 8.3291(5) Å	β = 102.6874(19)°.
	c = 16.0372(10) Å	γ = 90°.
Volume	1275.07(14) Å ³	
Z	4	
Density (calculated)	2.016 Mg/m ³	
Absorption coefficient	5.615 mm ⁻¹	
F(000)	736	
Crystal size	0.25 x 0.15 x 0.05 mm ³	
Theta range for data collection	2.242 to 32.529°.	
Index ranges	-14 ≤ h ≤ 14, -10 ≤ k ≤ 11, -12 ≤ l ≤ 23	
Reflections collected	14076	
Independent reflections	4133 [R(int) = 0.0259]	
Completeness to theta = 32.529°	89.3%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.767 and 0.606	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4133/ 0/ 181	
Goodness-of-fit on F ²	0.642	
Final R indices [I > 2σ(I)]	R1 = 0.0208, wR2 = 0.0725	
R indices (all data)	R1 = 0.0272, wR2 = 0.0814	
Largest diff. peak and hole	0.640 and -0.561 e.Å ⁻³	

Table S2. Crystal data and structure refinement for mo_WYCCO968_0m.

Identification code	mo_WYCCO968_0m	
Empirical formula	C16 H20 B F4 I Si	
Formula weight	454.12	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 8.8109(4) Å	$\alpha = 69.6574(12)^\circ$
	b = 10.3861(5) Å	$\beta = 81.4168(11)^\circ$
	c = 11.3746(5) Å	$\gamma = 70.8107(11)^\circ$
Volume	921.03(7) Å ³	
Z	2	
Density (calculated)	1.637 Mg/m ³	
Absorption coefficient	1.835 mm ⁻¹	
F(000)	448	
Crystal size	0.20 x 0.20 x 0.20 mm ³	
Theta range for data collection	1.911 to 31.581°	
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 9, -16 ≤ l ≤ 16	
Reflections collected	16964	
Independent reflections	6016 [R(int) = 0.0200]	
Completeness to theta = 31.581°	97.6%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.710 and 0.633	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6016/ 0/ 211	
Goodness-of-fit on F ²	1.056	
Final R indices [I > 2σ(I)]	R1 = 0.0225, wR2 = 0.0532	
R indices (all data)	R1 = 0.0258, wR2 = 0.0547	
Largest diff. peak and hole	1.108 and -0.573 e.Å ⁻³	

Table S3. Crystal data and structure refinement for mo_WYC0853P_0m.

Identification code	mo_WYC0853P_0m	
Empirical formula	C15 H11 I O2 S	
Formula weight	382.20	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.6829(5) Å	$\alpha = 81.5859(12)^\circ$
	b = 8.2002(6) Å	$\beta = 87.0418(13)^\circ$
	c = 11.0181(8) Å	$\gamma = 80.6573(11)^\circ$
Volume	677.30(8) Å ³	
Z	2	
Density (calculated)	1.874 Mg/m ³	
Absorption coefficient	2.512 mm ⁻¹	
F(000)	372	
Crystal size	0.20 x 0.20 x 0.15 mm ³	
Theta range for data collection	1.869 to 33.432°	
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -10 ≤ l ≤ 17	
Reflections collected	9929	
Independent reflections	4654 [R(int) = 0.0223]	
Completeness to theta = 33.432°	88.1%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.704 and 0.484	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4654 / 172 / 228	
Goodness-of-fit on F ²	1.137	
Final R indices [I > 2σ(I)]	R1 = 0.0225, wR2 = 0.0583	
R indices (all data)	R1 = 0.0233, wR2 = 0.0587	
Largest diff. peak and hole	1.013 and -0.717 e.Å ⁻³	

Table S4. Crystal data and structure refinement for WYC1077.

Identification code	WYC1077	
Empirical formula	C13 H9 I O2 S2	
Formula weight	388.22	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 7.6942(9)Å	$\alpha = 83.906(3)^\circ$
	b = 8.0833(9)Å	$\beta = 87.646(3)^\circ$
	c = 10.9346(12)Å	$\gamma = 78.932(3)^\circ$
Volume	663.50(13) Å ³	
Z	2	
Density (calculated)	1.943 Mg/m ³	
Absorption coefficient	2.717 mm ⁻¹	
F(000)	376	
Crystal size	0.25 x 0.20 x 0.15 mm ³	
Theta range for data collection	1.873 to 31.544°	
Index ranges	-9<= <i>h</i> <=11, -11<= <i>k</i> <=10, -15<= <i>l</i> <=12	
Reflections collected	8703	
Independent reflections	4283[R(int) = 0.0259]	
Completeness to theta =31.544°	96.8%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.686 and 0.528	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4283/ 0/ 163	
Goodness-of-fit on F ²	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0220, wR2 = 0.0563	
R indices (all data)	R1 = 0.0244, wR2 = 0.0578	
Largest diff. peak and hole	0.532 and -0.725 e.Å ⁻³	

Table S5. Crystal data and structure refinement for mo_WYC1098_0m.

Identification code	mo_WYC1098_0m	
Empirical formula	C ₂₅ H ₁₉ I O ₂ S	
Formula weight	510.36	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.4495(4) Å	α = 85.8720(10)°.
	b = 8.8324(4) Å	β = 86.8370(10)°.
	c = 13.8514(6) Å	γ = 76.8730(10)°.
Volume	1003.29(8) Å ³	
Z	2	
Density (calculated)	1.689 Mg/m ³	
Absorption coefficient	1.720 mm ⁻¹	
F(000)	508	
Crystal size	0.20 x 0.15 x 0.10 mm ³	
Theta range for data collection	1.475 to 33.779°.	
Index ranges	-12 ≤ h ≤ 13, -8 ≤ k ≤ 13, -21 ≤ l ≤ 21	
Reflections collected	19574	
Independent reflections	7135 [R(int) = 0.0295]	
Completeness to theta = 33.779°	88.700005%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.847 and 0.644	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7135/ 0/ 263	
Goodness-of-fit on F ²	1.116	
Final R indices [I > 2σ(I)]	R1 = 0.0252, wR2 = 0.0590	
R indices (all data)	R1 = 0.0278, wR2 = 0.0602	
Largest diff. peak and hole	1.270 and -0.907 e.Å ⁻³	

Computational details.

All calculations were performed using Gaussian 09^[8] by adapting a method described by Vasdev, Liang and co-workers for a series of iodine(III)-containing species.^[9]

Geometry optimizations. All calculations were performed at the DFT level using the B3LYP functional with an ultrafine integration grid. The 6-31+G(d,p) basis set was used for C,H,O and S, while using for iodine the augmented LANL2DZ(dp) set described by Gilbert, Sunderlin and co-workers.^[10] Empirical dispersion was applied using the D3 version of Grimme dispersion with Becke-Johnson damping (gd3BJ keyword).^[11] All structures were fully optimized in dichloromethane using the SMD continuum model. Transition states were identified by having one imaginary frequency in the Hessian matrix. It was confirmed that transition states connect with the corresponding intermediates by means of application of the eigenvector corresponding to the imaginary frequency and subsequent optimization of the resulting structures. All energies collected in the text are Gibbs energies in solvent at 298 K.

Single point energy calculations. Energy calculations were performed for the previously optimized structures using the PBE0 functional and the Aug-cc-pvtz basis set for C,H,O and S atoms and the DB-aug-cc-pVTZ for iodine. Calculations were performed in dichloromethane (SMD continuum model) and applying the D3 version of Grimme dispersion with Becke-Johnson damping (gd3BJ keyword).

Species: cationic PhI-benzyl⁺ σ adduct

Stoichiometry: C₁₃H₁₂I⁺

Charge: 1 Multiplicity: 1

Coordinates (xyz)

C	0.43026800	1.12503100	-0.17354400
C	-0.41774900	1.05638000	-1.28250300
C	0.16186600	1.95765700	0.91940400
C	-1.57504600	1.83790600	-1.28358600
H	-0.19129400	0.40794100	-2.12010200
C	-0.99482700	2.73890600	0.89138500
H	0.83239100	1.99507300	1.76994900
C	-1.86384500	2.67476100	-0.20224100
H	-2.24948400	1.78665500	-2.13192700
H	-1.21764000	3.38941400	1.73078500
H	-2.76534300	3.27856400	-0.21214900
I	2.12194800	-0.11656200	-0.11767100
C	0.57668600	-2.17900000	0.75460100
H	1.07036400	-2.89666600	0.10825900
H	0.97762300	-2.06868800	1.75562800
C	-0.74464300	-1.76971600	0.47536800
C	-1.45633200	-0.96175400	1.40400900
C	-1.37180700	-2.14402100	-0.74568700
C	-2.75512300	-0.56503000	1.12777300
H	-0.97281500	-0.66440400	2.32849500
C	-2.67494900	-1.75429600	-1.00450600
H	-0.81990300	-2.74203800	-1.46380500
C	-3.36281200	-0.96136800	-0.07176400
H	-3.29764600	0.05476300	1.83248700
H	-3.16005000	-2.04847300	-1.92859300
H	-4.37957000	-0.64708700	-0.28468800

Imaginary frequencies: none

E(RPBE1PBE)=	-513.397394 Hartrees
Thermal correction to Gibbs Free Energy=	0.166444
Sum of electronic and thermal Free Energies=	-513.230950

Species: cationic PhI-benzyl⁺ π adduct

Stoichiometry: C₁₃H₁₂I⁺

Charge: 1 Multiplicity: 1

Coordinates (xyz)

C	-0.17855828	-1.11699168	0.00008873
C	0.45478072	-1.39171192	-1.22399103
C	0.45489040	-1.39136985	1.22419127
C	1.74442096	-1.91318735	-1.21610151
H	-0.05304484	-1.19706478	-2.16133667
C	1.74453505	-1.91283899	1.21633498
H	-0.05284888	-1.19645713	2.16152811
C	2.40924275	-2.14164823	0.00011740
H	2.24451065	-2.12145328	-2.15626257
H	2.24471530	-2.12083940	2.15650685
H	3.41037155	-2.56007185	0.00013287
I	-2.10753273	-0.30154561	0.00005685
C	3.30196881	0.44873048	-0.00030689
H	3.80540854	0.19488887	0.92576223
H	3.80508506	0.19459065	-0.92647282
C	2.13935782	1.19629045	-0.00021283
C	1.51972288	1.57862321	-1.23523047
C	1.52015947	1.57902148	1.23490214
C	0.36218900	2.32846602	-1.22805909
H	1.98117053	1.27673037	-2.16929781
C	0.36263534	2.32887648	1.22789897
H	1.98194971	1.27745007	2.16890404
C	-0.22098853	2.69303430	-0.00003559
H	-0.10996103	2.62203572	-2.15835537
H	-0.10918475	2.62275551	2.15826479
H	-1.13507537	3.27758614	0.00003682

Imaginary frequencies: none

E(RPBE1PBE)=	-513.392321	Hartrees
Thermal correction to Gibbs Free Energy=	0.167020	
Sum of electronic and thermal Free Energies=	-513.225301	

Species: transition state in going from π -cation to 1H⁺

Stoichiometry: C₁₃H₁₂I⁺

Charge: 1 Multiplicity: 1

Coordinates (xyz)

C	0.33378540	-1.13170009	-0.00017211
C	-0.27873161	-1.44998655	1.23467145
C	-0.27894470	-1.44931235	-1.23508415

C	-1.57079768	-1.92136503	1.23031774
H	0.25478642	-1.29468426	2.16442135
C	-1.57100142	-1.92070836	-1.23074902
H	0.25440248	-1.29350946	-2.16484832
C	-2.30849079	-1.99043428	-0.00017461
H	-2.07767260	-2.13695523	2.16534193
H	-2.07803194	-2.13580123	-2.16580439
H	-3.23639763	-2.55526774	-0.00027819
I	2.17272338	-0.17224060	-0.00007190
C	-3.13786145	-0.21566496	0.00044143
H	-3.72187350	-0.34388376	-0.90551002
H	-3.72133613	-0.34420754	0.90669231
C	-2.16518418	0.86019258	0.00034521
C	-1.67694880	1.38892201	1.21603775
C	-1.67784699	1.38943243	-1.21548770
C	-0.74117732	2.41685684	1.21529866
H	-2.04049208	0.98705308	2.15655338
C	-0.74207737	2.41736278	-1.21501785
H	-2.04211453	0.98794847	-2.15588928
C	-0.26375570	2.92424453	0.00007212
H	-0.37387219	2.81681027	2.15430617
H	-0.37546929	2.81771055	-2.15413038
H	0.47792740	3.71650127	-0.00003726

Imaginary frequencies: one

E(RPBE1PBE)=	-513.392321	Hartrees
Thermal correction to Gibbs Free Energy=	0.169417	
Sum of electronic and thermal Free Energies=	-513.222698	

Species: rearranged species 1H+. Corresponds to protonated *para*-benzyl iodobenzene

Stoichiometry: C₁₃H₁₂I⁺

Charge: 1 Multiplicity: 1

Coordinates (xyz)

C	-0.59904400	-1.06701300	-0.00009100
C	-0.03002300	-1.45784900	-1.24105600
C	-0.03025200	-1.45829000	1.24084100
C	1.20535600	-2.04282200	-1.23751500
H	-0.55489600	-1.25732300	-2.16690600
C	1.20513900	-2.04323200	1.23733600
H	-0.55531900	-1.25812700	2.16666100
C	1.97651600	-2.16278800	-0.00003600
H	1.68631200	-2.30773300	-2.17398300
H	1.68590000	-2.30852200	2.17379600
H	2.66728900	-3.00928500	-0.00009400
I	-2.28992200	0.11174800	-0.00006300
C	3.03926600	-0.85579600	0.00006100
H	3.65172100	-1.01463200	0.88836900
H	3.65168300	-1.01448500	-0.88829200
C	2.36518000	0.47657900	0.00014200
C	2.03010400	1.10984200	-1.20816600
C	2.02952900	1.10948700	1.20845900
C	1.37227400	2.33968400	-1.21023900
H	2.28335700	0.63493300	-2.15184000
C	1.37169600	2.33934100	1.21057500
H	2.28235900	0.63434300	2.15212500
C	1.03352500	2.95323800	0.00018200
H	1.12011700	2.81547400	-2.15256800
H	1.11908000	2.81483600	2.15292900
H	0.51265400	3.90557200	0.00019000

Imaginary frequencies: none

E(RPBE1PBE)=	-513.396485 Hartrees
Thermal correction to Gibbs Free Energy=	0.170177
Sum of electronic and thermal Free Energies=	-513.226307516

Species: cationic PhI-allyl⁺

Stoichiometry: C₉H₁₀I

Charge: 1 Multiplicity: 1

Coordinates (xyz)

I	-1.34502361	-0.71164933	-0.13486059
C	2.77709213	0.21818777	-1.13036300
C	3.48204349	-0.15279643	0.01657160
C	2.81139250	-0.70783878	1.11201394
C	1.42873909	-0.89839876	1.07090440
C	0.74769971	-0.51577794	-0.08737154
C	1.39085524	0.04353681	-1.19493450
H	3.29721091	0.64796334	-1.97993987
H	4.55687421	-0.01082786	0.05880551
H	3.36043406	-0.99531331	2.00258242
H	0.90517630	-1.32978529	1.91587199
H	0.83846267	0.33183227	-2.08090523
C	-1.69059702	1.46575097	0.76265302
H	-2.77336801	1.49622251	0.67193763
H	-1.33785958	1.27338603	1.77281590
C	-0.92408365	2.39971004	-0.03856990
H	-1.38750240	2.78393462	-0.94302780
C	0.33010750	2.76131200	0.29719801
H	0.82013486	2.36286593	1.18131568
H	0.88719431	3.47502224	-0.30045714

Imaginary frequencies: none

E(RPBE1PBE)=	-359.859424357 Hartrees
Thermal correction to Gibbs Free Energy=	0.122941
Sum of electronic and thermal Free Energies=	-359.736483

Species: TS for [3,3] rearrangement in cationic PhI-allyl⁺

Stoichiometry: C₉H₁₀I

Charge: 1 Multiplicity: 1

Coordinates (xyz)

I	-1.55731989	-0.58818529	-0.15118929
C	2.67311945	0.13957070	-0.98127881
C	3.32383918	-0.64108412	-0.04999629
C	2.57217506	-1.34624067	0.91039317
C	1.17459283	-1.31269074	0.91655971
C	0.50928670	-0.54920577	-0.03995465
C	1.24672009	0.29839568	-0.93505243
H	3.22861802	0.69339084	-1.73091020
H	4.40454072	-0.72362248	-0.05915711
H	3.08410034	-1.94852306	1.65412531
H	0.62096948	-1.90223608	1.63745414

H	0.74811835	0.67371233	-1.82296881
C	-0.97702939	2.43323105	1.04398098
H	-1.96872591	2.87231092	1.01157092
H	-0.69970843	1.89997359	1.94884040
C	-0.10046811	2.60154067	0.02487761
H	-0.40442405	3.13512775	-0.87145704
C	1.23464700	2.07608753	0.07315863
H	1.61042643	1.71779274	1.02720033
H	1.97274219	2.55826747	-0.55779314

Imaginary frequencies: one (-224.8 cm^{-1})

E(RPBE1PBE)=	-359.847779 Hartrees
Thermal correction to Gibbs Free Energy=	0.124334
Sum of electronic and thermal Free Energies=	-359.723446

Species: protonated (rearranged non-aromatic) *ortho*-allyl C₆H₅⁺

Stoichiometry: C₉H₁₀I

Charge: 1 Multiplicity: 1

Coordinates (xyz)

I	-1.52115718	-0.67223760	-0.14215461
C	2.69671954	0.32664080	-0.85881987
C	3.36233118	-0.56228511	-0.06353627
C	2.61941112	-1.38165144	0.81899160
C	1.21915644	-1.37479049	0.85112391
C	0.52584924	-0.51635470	0.01331423
C	1.23649205	0.51642157	-0.76908975
H	3.23758977	0.99171460	-1.52503819
H	4.44200327	-0.64610978	-0.09870794
H	3.14760538	-2.06660723	1.47540133
H	0.69471823	-2.07518557	1.48983230
H	0.78920874	0.67107177	-1.75579011
C	-1.02847270	2.76198886	1.03524677
H	-2.00970824	3.22282587	0.97694738
H	-0.66069399	2.50204934	2.02475016
C	-0.30085268	2.53545647	-0.06526608
H	-0.70021033	2.79156489	-1.04475075
C	1.08073237	1.98352397	-0.03010256
H	1.45312971	1.87281018	0.98982534
H	1.75948876	2.63075928	-0.58944715

Imaginary frequencies: none

E(RPBE1PBE)=	-359.855759121 Hartrees
Thermal correction to Gibbs Free Energy=	0.125592
Sum of electronic and thermal Free Energies=	-359.730167

Species: cationic PhI-allyl-Tos⁺

Stoichiometry: C₁₀H₁₂IO₂S

Charge: 1 Multiplicity: 1

Coordinates (xyz)

I	-0.01341538	-1.25239685	-0.01308556
C	-3.63321317	0.73283975	1.32129640
C	-4.38861770	0.85343539	0.15111782
C	-3.90207585	0.35727821	-1.06236029
C	-2.65331920	-0.26575698	-1.11998613

C	-1.91829317	-0.37069067	0.06461961
C	-2.38070987	0.11576587	1.29107669
H	-4.01314912	1.11790349	2.26168677
H	-5.36059914	1.33430200	0.18505845
H	-4.49109277	0.45043943	-1.96855717
H	-2.27316912	-0.65476791	-2.05718597
H	-1.79046054	0.02043696	2.19450895
C	1.07736910	0.73478507	-0.53125842
H	1.04136126	0.71023422	-1.62078198
C	0.39962470	1.86939796	0.07953230
H	0.50897336	2.02751345	1.14809796
C	-0.39076731	2.67490896	-0.65196557
H	-0.53797329	2.51810241	-1.71644167
H	-0.89881175	3.51807268	-0.19610025
S	2.82602016	0.37958289	-0.08670703
O	3.62735072	1.32082876	-0.88389868
O	2.99113926	-1.07858482	-0.27434654
C	2.99326082	0.76914927	1.65467828
H	4.01099264	0.47272981	1.91660108
H	2.85970102	1.84119224	1.79513463
H	2.27144997	0.18291941	2.22428418

Imaginary frequencies: none

E(RPBE1PBE)=	-947.535067488 Hartrees
Thermal correction to Gibbs Free Energy=	0.153340
Sum of electronic and thermal Free Energies=	-947.381727

Species: TS for [3,3] rearrangement in cationic PhI·[allyl-Tosyl]⁺

Stoichiometry: C₁₀H₁₂IO₂S

Charge: 1 Multiplicity: 1

Coordinates (xyz)

I	-0.24833874	-1.56072581	0.20892120
C	-3.32340800	1.45339454	0.91757720
C	-4.11419618	1.38116189	-0.21615916
C	-3.78139895	0.48254295	-1.24693233
C	-2.67689348	-0.36260947	-1.14117695
C	-1.88725904	-0.30470731	0.01131907
C	-2.15876773	0.65047511	1.02936593
H	-3.56643211	2.13684148	1.72426408
H	-4.99232363	2.00998644	-0.31094958
H	-4.39629289	0.43602666	-2.13974495
H	-2.44644162	-1.06304291	-1.93508881
H	-1.62151663	0.61305728	1.97030154
C	1.23232871	1.02613402	-0.48888103
H	0.85829630	0.83643398	-1.49171649
C	0.56457541	1.81220780	0.41276304
H	0.99900573	2.03559143	1.38144690
C	-0.72649197	2.28821407	0.13398148
H	-1.15743858	2.17457811	-0.85435063
H	-1.16490494	3.03351606	0.78511728
S	2.95763251	0.53697600	-0.33933543
O	3.70068369	1.58393374	-1.06742388
O	3.05572899	-0.86123346	-0.79079032
C	3.35632619	0.61776482	1.40660738
H	4.38595822	0.26036867	1.47501352
H	3.29418109	1.64979140	1.75085330
H	2.68755103	-0.04536970	1.95632278

Imaginary frequencies: two

E(RPBE1PBE)=	-947.523232 Hartrees
Thermal correction to Gibbs Free Energy=	0.158476
Sum of electronic and thermal Free Energies=	-947.364756

Species: protonated (rearranged non-aromatic) *ortho*-tosylallyl C₆H₅⁺

Stoichiometry: C₁₀H₁₂IO₂S

Charge: 1 Multiplicity: 1

Coordinates (xyz)

I	-0.59484363	-1.66874987	0.19067957
C	-2.99992178	1.98996448	0.73102580
C	-3.99973709	1.82846126	-0.18264517
C	-3.93895249	0.73316013	-1.07798848
C	-2.93017441	-0.23791504	-1.01590143
C	-1.93011626	-0.12159159	-0.06662589
C	-1.81994121	1.09491061	0.78104233
H	-2.99905629	2.83661745	1.41056731
H	-4.82957872	2.52314623	-0.23478466
H	-4.71764778	0.61895922	-1.82631066
H	-2.96998259	-1.09259188	-1.68049415
H	-1.59998400	0.82142949	1.82040481
C	1.60072119	1.20055818	-0.49455136
H	1.36125980	1.41328550	-1.53351715
C	0.75955988	1.41029763	0.51914060
H	1.03843024	1.17178462	1.54178697
C	-0.58493872	2.02995727	0.32003148
H	-0.74379528	2.31724904	-0.72058863
H	-0.65738541	2.92497944	0.94388141
S	3.22838850	0.49194951	-0.34912257
O	4.18819020	1.47911557	-0.88906258
O	3.17458375	-0.84609952	-0.97942581
C	3.54415420	0.28388025	1.40640978
H	4.54982516	-0.13716953	1.46176868
H	3.51351332	1.25574415	1.89943587
H	2.82078668	-0.41511052	1.82607545

Imaginary frequencies: none

E(RPBE1PBE)=	-947.541951 Hartrees
Thermal correction to Gibbs Free Energy=	0.157046
Sum of electronic and thermal Free Energies=	-947,384905

References.

- [1] a) Y. Wu, S. Izquierdo, P. Vidossich, A. Lledós, A. Shafir, *Angew. Chem. Int. Ed.* **2016**, *55*, 7152-7156; b) A. McKillop, D. Kemp, *Tetrahedron* **1989**, *45*, 3299-3306; c) P. Kazmierczak, L. Skulski, L. Kraszkiewicz, *Molecules*, **2001**, *6*, 881-891; d) M. D. Hossain, T. Kitamura, *J. Org. Chem.* **2005**, *70*, 6984-6986.
- [2] H. R. Khatri, J. Zhu, *Chem.-Eur. J.* **2012**, *18*, 12232-12236.
- [3] a) I. Pérez, J. P.; Sestelo, L. A. Sarandeses, *J. Am. Chem. Soc.* **2001**, *123*, 4155-4160; b) Y. Wu, L. Li, H. Li, L. Gao, H. Xie, Z. Zhang, Z. Su, C. Hu, Z. Song, *Org. Lett.* **2014**, *16*, 1880-1883.
- [4] S. G. Alvarez, M. T. Alvarez, *Synthesis* **1997**, 413-414.
- [5] D.-H. Duan, X. Huang *Synlett* **1999**, 317-318.
- [6] C. Ye, B. Twamley, J. M. Shreeve, *Org. Lett.* **2005**, *7*, 3961-3964.3.
- [7] L. Qin, B. Hu, K. D. Neumann, E. J. Linstad, K. McCauley, J. Veness, J. J. Kempinger, S. G. DiMagno, *Eur. J. Org. Chem.* **2015**, 5919-5924.
- [8] Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
- [9] B. H. Rotstein, L. Wang, R. Y. Liu, J. Patteson, E. E. Kwan, N. Vasdev, S. H. Liang, *Chem. Sci.*, **2016**, *7*, 4407-4417.
- [10] C. E. Check, T. O. Faust, J. M. Bailey, B. J. Wright, T. M. Gilbert, L. S. Sunderlin, *J. Phys. Chem. A* **2001**, *105*, 8111-8116.

NMR Spectra.

¹H NMR (500 MHz, CDCl₃)

¹³C NMR (126 MHz, CDCl₃)

^1H NMR (400 MHz, CDCl_3)

Comparison with $\text{PhCH}_2\text{SiMe}_3$

^{13}C NMR (101 MHz, CDCl_3)

Comparison with $\text{PhCH}_2\text{SiMe}_3$

^1H NMR (400 MHz, CDCl_3)

Comparison with $\text{PhCH}_2\text{C}_6\text{H}_4\text{I}$ (upper trace)

^{13}C NMR (101 MHz, CDCl_3)

Comparison with $\text{PhCH}_2\text{C}_6\text{H}_4\text{I}$ (upper trace)

¹H NMR (500 MHz, CDCl₃)

¹³C NMR (126 MHz, CDCl₃)

¹H NMR (500 MHz, CDCl₃)

¹³C NMR (126 MHz, CDCl₃)

¹H NMR (400 MHz, CDCl₃)

¹³C NMR (101 MHz, CDCl₃)

¹H NMR (400 MHz, CDCl₃)

WYC0721_P_0214_H.10.fid

ResearchGroup Shafir

ICIQ_1H12p8s CDCl₃ /opt/topspin ywu 39

¹³C NMR (101 MHz, CDCl₃)

WYC0721-P-C.10.fid

ResearchGroup Shafir

ICIQ_13C{1H}512s CDCl₃ /opt/topspin ywu 72

Gradient HMQC experiment CDCl₃)

HMBC experiment

1D NOE experiment: irradiation of the benzylic position

WYC1101_P_H.10.fid
ResearchGroup Shafir
ICIQ_1H12p8s CDCl₃ /opt/topspin ywu 45

¹³C NMR (126 MHz, CDCl₃)

WYC1101_P_C.10.fid
ResearchGroup Shafir
ICIQ_13C(1H)512s CDCl₃ /opt/topspin ywu 45

wyc0868_Pa_H.10.fid
 ResearchGroup Shafir
 ICIQ_1H12p8s CDCl₃ /opt/topspin ywu 56

¹³C NMR (126 MHz, CDCl₃)

wyc0868_Pa_C.10.fid
 ResearchGroup Shafir
 ICIQ_13C(1H)512s CDCl₃ /opt/topspin ywu 56

WYC0727-P-H.10.fid
 ResearchGroup Shafir
 ICIQ_1H12p8s CDCl₃ /opt/topspin ywu 73

WYC0727-P-C.10.fid
 ResearchGroup Shafir
 ICIQ_13C(1H)512s CDCl₃ /opt/topspin ywu 73

WYC0763_2_P_1028.10.fid
ResearchGroup Shafir
ICIQ_1H12p8s CDCl_3 /opt/topspin ywu 43

^{13}C NMR (126 MHz, CDCl_3)

WYC0763_2_P_C_1029.10.fid
ResearchGroup Shafir
ICIQ_13C{1H}512s CDCl_3 /opt/topspin ywu 43

WYC0833-P-H.10.fid
 ResearchGroup Shafir
 ICIQ_1H12p8s CDCl₃ /opt/topspin ywu 71

¹³C NMR (101 MHz, CDCl₃)

WYC0833-P-C.10.fid
 ResearchGroup Shafir
 ICIQ_13C(1H)512s CDCl₃ /opt/topspin ywu 71

WYC0880_Pa_H2.10.fid
ResearchGroup Shafir
ICIQ_1H12p8s CDCl₃ /opt/topspin ywu 41

WYC0880_P_C.10.fid
ResearchGroup Shafir
ICIQ_13C{1H}512s CDCl₃ /opt/topspin ywu 50

WYC0888_P_H.10.fid
 ResearchGroup Shafir
 ICIQ_1H12p8s CDCl₃ /opt/topspin ywu 41

¹³C NMR (126 MHz, CDCl₃)

WYC0888_P_C.10.fid
 ResearchGroup Shafir
 ICIQ_13C(1H)512s CDCl₃ /opt/topspin ywu 41

WYC883_P_1027.10.fid
 ResearchGroup Shafir
 ICIQ_1H12p8s CDCl₃ /opt/topspin ywu 33

¹³C NMR (126 MHz, CDCl₃)

WYC0883_P_C.10.fid
 ResearchGroup Shafir
 ICIQ_13C(1H)512s CDCl₃ /opt/topspin ywu 1

WYC0887_P_H.10.fid
ResearchGroup Shafir
ICIQ_1H12p8s CDCl₃ /opt/topspin ywu 30

¹³C NMR (126 MHz, CDCl₃)

WYC0887_P_C.10.fid
ResearchGroup Shafir
ICIQ_13C{1H}512s CDCl₃ /opt/topspin ywu 30

¹⁹F NMR (376 MHz, CDCl₃)

WYC0886_1_F.10.fid
ResearchGroup Shafir
ICIQ_19F{1H} CDCl₃ /opt/topspin ywu 7

WYC0942_P_H.10.fid
 ResearchGroup Shafir
 ICIQ_1H20p8s CDCl₃ /opt/topspin ywu 21

WYC0942_P_C.10.fid
 ResearchGroup Shafir
 ICIQ_13C(1H)512s CDCl₃ /opt/topspin ywu 21

WYC0920_P_H.10.fid
ResearchGroup Shafir
ICIQ_1H12p8s CDCl₃ /opt/topspin ywu 51

¹³C NMR (101 MHz, CDCl₃)

WYC0920_P_C.10.fid
ResearchGroup Shafir
ICIQ_13C(1H)512s CDCl₃ /opt/topspin ywu 51

WYC0929_P_H.10.fid
 ResearchGroup Shafir
 ICIQ_1H12p8s CDCl3 /opt/topspin ywu 1

¹³C NMR (126 MHz, CDCl₃)

166.23, 141.03, 140.14, 137.73, 133.88, 131.02, 130.23, 129.95, 128.89, 127.93, 91.71, 77.41, 77.16, 76.91, 63.79, 50.06, 41.27

WYC0929_P_C.10.fid
 ResearchGroup Shafir
 ICIQ_13C(1H)512s CDCl3 /opt/topspin ywu 1

WYC0777-P2-H.10.fid
ResearchGroup Shafir
ICIQ_1H12p8s CDCl₃ /opt/topspin ywu 47

¹³C NMR (126 MHz, CDCl₃)

WYC0777-P2-C.10.fid
ResearchGroup Shafir
ICIQ_13C(1H)512s CDCl₃ /opt/topspin ywu 47

¹⁹F NMR (376 MHz, CDCl₃)

WYC0777-P-F.10.fid
ResearchGroup Shafir
ICIQ_19F CDCl₃ /opt/topspin ywu 61

WYC0897_P_H.10.fid
 ResearchGroup Shafir
 ICIQ_1H12p8s CDCl₃ /opt/topspin ywu 1

¹³C NMR (101 MHz, CDCl₃)

WYC0897_P_C.10.fid
 ResearchGroup Shafir
 ICIQ_13C{1H}512s CDCl₃ /opt/topspin ywu 1

¹H NMR (400 MHz, CDCl₃)

WYC0853-P-H.10.fid
ResearchGroup Shafir
ICIQ_1H12p8s CDCl3 /opt/topspin ywu 97

¹³C NMR (101 MHz, CDCl₃)

WYC0853-P-C.10.fid
ResearchGroup Shafir
ICIQ_13C(1H)512s CDCl3 /opt/topspin ywu 37

WYC1081_P_H.10.fid
ResearchGroup Shafir
ICIQ_1H12p8s CDCl₃ /opt/topspin ywu 6

¹³C NMR (126 MHz, CDCl₃)

144.51, 141.10, 140.55, 138.07, 135.33, 133.69, 132.06, 130.98, 130.29, 129.82, 127.23, 122.42, 121.46, 97.92, 77.41, 77.16, 76.91, 39.36

WYC1081_P_C.10.fid
ResearchGroup Shafir
ICIQ_13C{1H}512s CDCl₃ /opt/topspin ywu 6

WYC1114_Pa_H.10.fid

ResearchGroup Shafir

ICIQ_1H12p8sTBFO CDCl₃ /opt/topspin ywu 28

¹³C NMR (126 MHz, CDCl₃)

¹⁹F NMR (471 MHz, CDCl₃)

WYC1114_Pa_F2.10.fid

ResearchGroup Shafir

ICIQ_19F{1H}TBFO CDCl₃ /opt/topspin ywu 28

1H NMR spectrum of compound 10 in CDCl₃. The spectrum shows peaks in the aromatic region (7.1-7.8 ppm) and a reference peak at 0 ppm. Integration values are provided below the peaks: 1.01, 3.07, 1.00, 2.03, 1.02, and 2.08. An inset shows a zoomed-in view of the peak at 6.10 ppm with integration values 6.11 and 6.10.

WYC1113_P_C.10.fid
ResearchGroup Shafir
ICIQ_13C{1H}512s CDCl3 /opt/topspin ywu 31

144.94
142.19
138.11
133.66
132.20
132.14
130.93
129.89
128.38
127.19
122.50
121.42
108.46
77.41
77.16
76.91
42.18

f1 (ppm)

WYC1079_P_H_180126.10.fid

ResearchGroup Shafir

ICIQ_1H12p8s CDCl₃ /opt/topspin ywu 51

¹³C NMR (126 MHz, CDCl₃)

WYC1079_P_C.10.fid

ResearchGroup Shafir

ICIQ_13C(1H)512s CDCl₃ /opt/topspin ywu 29

¹H NMR (500 MHz, CDCl₃)

WYC1077_P_H.10.fid
ResearchGroup Shafir
ICIQ_1H12p8s CDCl₃ /opt/topspin ywu 28

¹³C NMR (126 MHz, CDCl₃)

WYC1077_P_C.10.fid
ResearchGroup Shafir
ICIQ_13C{1H}512s CDCl₃ /opt/topspin ywu 32

with isomer, ^1H NMR (500 MHz, CDCl_3)

WYC1115_Pa2_H.10.fid
ResearchGroup Shafir
ICIQ_1H12p8sTBFO CDCl_3 /opt/topspin ywu 36

^{13}C NMR (101 MHz, CDCl_3)

WYC1115_P_C.10.fid
ResearchGroup Shafir
ICIQ_13C(1H)512s CDCl_3 /opt/topspin ywu 15

¹H NMR (500 MHz, CDCl₃)

¹³C NMR (126 MHz, CDCl₃)

¹H NMR (300 MHz, CDCl₃)

8.00 7.97 7.97 7.36 7.35 7.34 7.33 7.32 7.31 7.30 7.30 7.29 7.28 7.27 7.27 7.26 7.25 7.21 7.21 7.19 7.19 7.18

WYC1011-r.10.fid
ResearchGroup Shafir
ICIQ_1H20p8s CDCl₃ (C:\Bruker\TopSpin3.1) ywu 60

¹³C NMR (101 MHz, CDCl₃)

176.55 145.79 139.46 135.27 131.96 129.22 128.92 126.85 119.03 77.48 77.16 76.84 41.90 20.55

WYC1002_P_C.10.fid
ResearchGroup Shafir
ICIQ_13C(1H)512s CDCl₃ /opt/topspin ywu 7

¹H NMR (500 MHz, CDCl₃)

WYC1076_P_H.10.fid
ResearchGroup Shafir
ICIQ_1H12p8s CDCl₃ /opt/topspin ywu 31

¹³C NMR (126 MHz, CDCl₃)

WYC1076_P_C.10.fid
ResearchGroup Shafir
ICIQ_13C(1H)512s CDCl₃ /opt/topspin ywu 31

WYC1098_2_0216_H.10.fid
ResearchGroup Shafir
ICIQ_1H12p32s CDCl_3 /opt/topspin ywu 1

WYC1098_2a_C.10.fid
ResearchGroup Shafir
ICIQ_13C(1H)512s CDCl_3 /opt/topspin ywu 1

(unstable!) ^1H NMR (300 MHz, CDCl_3)

WYC1110_P_H.10.fid
ResearchGroup Shafir
ICIQ_1H20p8s CDCl3 {C:\Bruker\TopSpin3.1} ywu 34

144.20
143.25
142.14
140.03
139.71
139.49
137.40
132.30
130.69
129.81
129.67
128.77
128.57
127.59
126.33

WYC1092_P_wash1_C.10.fid
ResearchGroup Shafir
ICIQ_13C{1H}512s CDC13 /opt/topspin ywu 20

WYC1121_P_C.10.fid
ResearchGroup Shafir
ICIQ_13C{1H}512sTBFO CDCI3 /opt/topspin ashafir 32

145.24
144.52
143.06
142.61
141.68
140.40
139.68
138.09
137.43
135.58
132.80
132.22
130.81
130.03
129.94
129.85
128.88
128.84
127.75
126.97
126.65
122.44
121.29
104.43

77.41
77.16
76.91

43.70
41.09
40.79

21.73

f1 (ppm)

¹³C{¹H} NMR, CDCl₃, 101 MHz

DEPT135 vs ^{13}C NMR,