Supporting Information

GENERATION OF MONOARYL-\(\lambda^3\)-IODANES FROM ARYL BORON COMPOUNDS THROUGH IPSO-SUBSTITUTION

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General information

General: NMR spectra were recorded on JEOL JNM-ECS400 spectrometers operating at 391.78 MHz for \(^1\)H NMR and 98.52 MHz for \(^{13}\)C NMR, JOEL JNM-ECX400 spectrometers, operating at 395.88 MHz for \(^1\)H NMR and 99.55 MHz for \(^{13}\)C NMR, and JNM-ECA500 spectrometers, operating at 500.16 MHz for \(^1\)H NMR and 125.77 MHz for \(^{13}\)C NMR and 470.54 MHz for \(^{19}\)F NMR. Chemical shifts were reported in the scale relative to TMS (0.00 ppm for \(^1\)H NMR), CHCl\(_3\) (7.26 ppm for \(^1\)H NMR), (CH\(_3\))\(_2\)SO (2.50 ppm for \(^1\)H NMR), (CH\(_3\))\(_2\)CO (2.05 ppm for \(^1\)H NMR), CDCl\(_3\) (77.0 ppm for \(^{13}\)C NMR), (CD\(_3\))\(_2\)SO (39.52 ppm for \(^{13}\)C NMR), (CD\(_3\))\(_2\)CO (29.84 ppm for \(^{13}\)C NMR), C\(_6\)F\(_6\) (–164.9 ppm for \(^{19}\)F NMR), C\(_6\)H\(_5\)CF\(_3\) (–63.7 ppm for \(^{19}\)F NMR) as an internal reference, respectively. ESI mass spectra were measured on JEOL JMS-T100LCP spectrometer. Silica gel column chromatography was performed with Kanto Silica gel 60 N (40-50 mesh). TLC analysis was carried out on Silicagel 70 F\(_{254}\) TLC Plate-Wako with visualization by UV light, anisaldehyde stain solution, phosphomolybdic acid stain solution, or ceric ammonium molybdate stain solution. All non-aqueous reactions were carried out in a flame-dried glassware under argon atmosphere unless otherwise noted.

Materials: Propionitrile was distilled from P\(_2\)O\(_5\) and then CaH\(_2\), and stored over activated molecular sieves 4A under argon atmosphere before use. Dichloromethane (DCM), tetrahydrofuran (THF) was purified by Glass Contour solvent purification system. Commercially available \(N,N\)-dimethylformamide (DMF, KANTO Chemical Co., Inc., dehydrated grade), \(N,N\)-dimethylacetamide (DMA, KANTO Chemical Co., Inc., dehydrated grade), and 1,4-dioxane (Wako Ltd., Super dehydrated) were used without further manipulation unless otherwise stated. [I(OCOCF\(_3\))\(_3\)]\(_2\)(OCOCF\(_3\))NO\(^{[1]}\) was synthesized according to the literature. Meldrum’s acid 3 was
synthesized according to the literature.\textsuperscript{[2]} Potassium aryltrifluoroborate derivatives 1\textsuperscript{[3]}, pinacol boronic ester 4\textsuperscript{a}\textsuperscript{[4]}, neopentylglycol boronic ester 5\textsuperscript{a}\textsuperscript{[5]}, MIDA boronate ester 7\textsuperscript{a}\textsuperscript{[6]}, triol borate 8\textsuperscript{a}\textsuperscript{[7]} were synthesized according to the reported procedures. All other reagents were commercially available and used as received.

Preparation of substrates

\textbf{General procedure for synthesis of potassium aryltrifluoroborate derivatives 1 (GP1):} \textsuperscript{[3]}

\begin{center}
\begin{align*}
\text{OH} & \quad \text{OH} \\
\text{R} \quad \text{R} & \quad \text{BF}_3\text{K}
\end{align*}
\end{center}

To a solution of a boronic acid or an aryl boronpinacol ester in MeOH (0.5 M) was added a solution of KHF\textsubscript{2} (3.98 equiv.) in H\textsubscript{2}O (1.0 M) dropwise. The mixture was vigorously stirred at room temperature for 15 min to 12 hours. The solvent was removed, and the resulting white solids were dried completely under high vacuum at 50 °C. The residual solids were extracted with boiling acetone three times, and the combined extracts were concentrated. The residue was again dissolved in acetone or boiling acetone, and then treated with Et\textsubscript{2}O to form white precipitates. The precipitates were filtered and dried under high vacuum at 50 °C to give the corresponding potassium aryltrifluoroborate.

benzo[d][1,3]dioxol-5-yltrifluoro-\textlambda\textsuperscript{4}-borane, potassium salt (1h)

Prepared according to GP1 from (3,4-methylenedioxophenyl)boronic acid (332 mg, 2.0 mmol). Purification of the crude product by recrystallization from Et\textsubscript{2}O/acetone afforded 1h as a colorless solid (458 mg, quant).

\textsuperscript{1}H NMR (500 MHz, DMSO-\textit{d}_6) δ 6.80 (d, J = 7.5 Hz, 1H), 6.79 (s, 1H), 6.65 (d, J = 7.4 Hz, 1H) 5.82 (s, 2H); \textsuperscript{13}C NMR (125 MHz, DMSO-\textit{d}_6) δ 145.7, 144.6, 123.9 (q, \textsuperscript{3}J_{C-F} = 1.9 Hz), 111.2 (q, \textsuperscript{3}J_{C-F} = 1.6 Hz), 106.9, 99.1; \textsuperscript{19}F NMR (400 MHz, DMSO-\textit{d}_6) δ -140.9 (br s). HRMS (ESI): m/z (M–K\textsuperscript{+}) calcd for C\textsubscript{7}H\textsubscript{5}O\textsubscript{2}BF\textsubscript{3}: 188.0376; found: 188.03742. IR (KBr): 3079, 2935, 1508, 1488, 1423, 1267, 1239, 1208, 1131, 1103, 980, 866, 813 cm\textsuperscript{-1}. Mp: over 200 °C.

1-tosyl-5-(trifluoro-\textlambda\textsuperscript{4}-boraneyl)-1H-indole, potassium salt (1i)

\begin{center}
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{S6} & \quad \text{S7} & \quad \text{BF}_3\text{K} \\
\text{N} & \quad \text{N} & \quad \text{N}
\end{align*}
\end{center}

B\textsubscript{2}pin\textsubscript{2} (2.0 equiv.), PdCl\textsubscript{2}(dppf)\textsubscript{2}CH\textsubscript{2}Cl\textsubscript{2} (1.4 mol%), KO\textsubscript{Ac} (5.0 equiv.), DMF (0.1 M) 90°C, 3 days. 1-tosyl-5-(trifluoro-\textlambda\textsuperscript{4}-boraneyl)-1H-indole, potassium salt (1i)
The transformation was performed based on the literature procedure.[8] A 30 mL dry round-bottomed flask was charged with 5-bromo-1-tosyl-1\textit{H}-indole S6[9] (350 mg, 1.0 mmol), bis(pinacolato)diborane (508 mg, 2.0 mmol), PdCl$_2$(dppf)•CH$_2$Cl$_2$ (11.4 mg, 14 μmol) and potassium acetate (491 mg, 5.0 mmol). The reaction vessel was purged with Ar gas three times. To the vessel was added DMF (10.0 mL), and the mixture was stirred at 90 °C for 3 days. After cooling to room temperature, the mixture was diluted with EtOAc, washed with water and brine, and then dried over Na$_2$SO$_4$. Filtration and concentration in vacuo furnished the crude product, which was filtered through a silica gel column (n-hexane/EtOAc = 8:1) to remove inorganic materials. The solvent was evaporated under reduced pressure and the residue was treated with KHF$_2$ according to GP1. Purification of the crude product by recrystallization from Et$_2$O/acetone afforded 1i as a colorless solid (223 mg, 59% yield, 2 steps).

1H NMR (500 MHz, DMSO-$d_6$) δ 7.80-7.70 (m, 2H), 7.65 (d, $J$ = 8.0 Hz, 1H), 7.54 (d, $J$ = 3.4 Hz, 1H), 7.46 (s, 1H), 7.33 (d, $J$ = 8.0 Hz, 2H), 7.30 (d, $J$ = 8.6 Hz, 1H), 6.68 (d, $J$ = 3.4 Hz, 1H), 2.29 (s, 3H); 13C NMR (125 MHz, DMSO-$d_6$) δ 145.0, 134.3, 133.0, 130.0, 129.5, 128.6 (q, $^3J$C–F = 1.5 Hz), 126.5, 125.2, 123.8 (q, $^3J$C–F = 1.7 Hz), 111.0, 110.1, 21.0; 19F NMR (400 MHz, DMSO-$d_6$) δ -140.9 (br s). HRMS (ESI): m/z (M–K$^+$) calcd for C$_{15}$H$_{12}$O$_2$NBF$_3$: 337.06757; found: 337.06823. IR (KBr): 3142, 1599, 1363, 1260, 1174, 1146, 1130, 996, 887, 818, 717, 671, 588 cm$^{-1}$. Mp: 191.2 °C (decomp.)

3-methyl-5-((trifluoro-λ$^4$-boraneyl)benzo[d]isoxazole, potassium salt (1k)

The transformation was performed based on the literature procedure.[10] A 30 mL dry round-bottomed flask was charged with 5-bromo-3-methylbenzo[d]isoxazole S4[10] (304 mg, 1.4 mmol), bis(pinacolato)diborane (726 mg, 2.9 mmol), PdCl$_2$(dppf) (31.4 mg, 43 μmol) and potassium acetate (422 mg, 4.3 mmol). The reaction vessel was purged with Ar gas three times. To the vessel was added 1,4-dioxane (7.2 mL), and the mixture was stirred at 80 °C for 15 hours. After cooling to room temperature, the mixture was diluted with CH$_2$Cl$_2$, washed with water and brine, and then dried over Na$_2$SO$_4$. Filtration and concentration in vacuo furnished the crude product, which was filtered through a silica gel column (n-hexane/EtOAc = 20:1 to 10:1) to remove inorganic compounds. The solvent was evaporated under reduced pressure and the residue was treated with KHF$_2$ according to GP1. Purification of the crude product by recrystallization from Et$_2$O/acetone afforded 1k as a colorless solid (134.1 mg, 37% yield, 2 steps).

1H NMR (400 MHz, acetone-$d_6$) δ 7.75 (s, 1H), 7.73 (d, $J$ = 8.2 Hz, 1H), 7.29 (d, $J$ = 8.5 Hz, 1H), 2.50 (s, 3H); 13C NMR (125 MHz, DMSO-$d_6$) δ 161.3, 154.6, 133.9 (q, $^3J$C–F = 1.4 Hz), 123.2 (q, $^3J$C–F = 1.5 Hz).
\( f = 1.8 \text{ Hz} \), 120.7, 106.9, 9.6; \(^{19}\text{F NMR} \) (400 MHz, DMSO-\( d_6 \)) \( \delta -140.8 \) (br s). HRMS (ESI): m/z (M–K\(^+\)) calcd for C\(_8\)H\(_6\)ONBF\(_3\): 199.05363; found: 199.05372. IR (KBr): 3047, 1614, 1446, 1303, 1203, 1078, 970, 897, 823, 776, 739, 588 cm\(^{-1}\). Mp: over 200 °C.

ethyl 2-methyl-2-(4-(trifluoro-\( \lambda^4 \)-boraneyl)phenoxy)propanoate, potassium salt (1m)

The transformation was performed based on the literature procedure.\(^{[11]}\) A 30 mL dry round-bottomed flask was charged with ethyl 2-(4-bromophenoxy)-2-methylpropanoate S2\(^{[12]}\) (504 mg, 1.8 mmol), bis(pinacolato)diborane (668 mg, 2.6 mmol), PdCl\(_2\)(dpff) (38.4 mg, 52 \( \mu \)mol) and potassium acetate (429 mg, 4.4 mmol). The reaction vessel was purged with Ar gas three times. To the vessel was added 1,4-dioxane (6.0 mL), and the mixture was stirred at 95 °C for 15 hours. After cooling to room temperature, the mixture was diluted with EtOAc, washed with water and brine, and then dried over Na\(_2\)SO\(_4\). Filtration and concentration in vacuo furnished the crude product, which was filtered through a silica gel column (\( n \)-hexane/EtOAc = 1:1) to remove inorganic materials. The solvent was evaporated under reduced pressure and the residue was treated with KHF\(_2\) according to GP1. Purification of the crude product by recrystallization from Et\(_2\)O/acetone afforded 1m as a colorless solid (320 mg, 67% yield, 2 steps).

\(^1\text{H NMR} \) (400 MHz, DMSO-\( d_6 \)) \( \delta \) 7.17 (d, \( J = 8.3 \text{ Hz} \), 2H), 6.54 (d, \( J = 7.9 \text{ Hz} \), 2H), 4.15 (q, \( J = 7.1 \text{ Hz} \), 2H), 1.45 (s, 6H), 1.18 (t, \( J = 7.1 \text{ Hz} \), 3H); \(^{13}\text{C NMR} \) (125 MHz, DMSO-\( d_6 \)) \( \delta \) 173.7, 152.7, 132.0 (q, \( ^3J_{C-F} = 1.6 \text{ Hz} \)), 117.5, 78.1, 60.7, 25.1, 13.9; \(^{19}\text{F NMR} \) (400 MHz, DMSO-\( d_6 \)) \( \delta -140.9 \) (br s). HRMS (ESI): m/z (M–2F+2(OMe)–K\(^+\)) calcd for C\(_{14}\)H\(_{21}\)BFO\(_5\): 299.14716; found: 299.14715. IR(KBr): 2994, 1732, 1599, 1274, 1205, 1151, 960, 832 cm\(^{-1}\). Mp: 101.9-103.0 °C.

methyl (S)-2-((tert-butoxycarbonyl)amino)-3-(4-(trifluoro-\( \lambda^4 \)-boraneyl)phenyl)propanoate, potassium salt (1n)

The transformation was performed based on the literature procedure.\(^{[13]}\) A 50 mL dry round-bottomed flask was charged with methyl N-(tert-butoxycarbonyl)-O-[(trifluoromethyl)sulfonyl]-L-tyrosinate
S0 (1.17 g, 2.7 mmol), bis(pinacolato)diborane (1.05 g, 4.1 mmol), PdCl2(dppf) (60.1 mg, 82 μmol) and potassium acetate (1.31 g, 13 mmol). The reaction vessel was purged with Ar gas three times. To the vessel was added DMF (14.0 mL), and the mixture was stirred at 95 °C for 16 hours. After cooling to room temperature, the mixture was diluted with EtOAc, washed with water and brine, and then dried over Na2SO4. Filtration and concentration in vacuo furnished the crude product, which was filtered through a silica gel column (n-hexane/EtOAc = 1:1) to remove inorganic materials. The solvent was evaporated under reduced pressure and the residue was treated with KHF2 according to GP1. Purification of the crude product by recrystallization from Et2O/acetone afforded 1n as a colorless solid (728 mg, 69% yield, 2 steps).

1H NMR (500 MHz, DMSO-d6) δ 7.23 (d, J = 7.5 Hz, 2H), 7.13 (d, J = 7.7 Hz, 1H), 6.93 (d, J = 7.4 Hz, 2H) 4.14-4.07 (m, 1H), 3.60 (s, 3H), 2.87 (dd, J = 13.7, 5.3 Hz, 1H) 2.77 (dd, J = 13.7, 9.6 Hz, 1H), 1.34 (s, 9H); 13C NMR (125 MHz, DMSO-d6) δ 172.9, 155.3, 133.5, 131.3 (q, 3J_C-F = 1.7 Hz), 126.9, 78.2, 55.5, 51.6, 36.5, 28.1; 19F NMR (400 MHz, DMSO-d6) δ -141.2 (br s). HRMS (ESI): m/z (M–K+)+ calcd for C15H20O4NBF3: 345.14793; found: 345.14837. IR (KBr): 3398, 2978, 1748, 1668, 1508, 1229, 1194, 1167, 1003, 975, 814 cm⁻¹. Mp: 167.8-168.2 °C.

methyl 3-methyl-5-(trifluoro-λ4-boraneyl)benzoate, potassium salt (1o)

The transformation was performed based on the literature procedure. In a glovebox, a sealed tube was charged with methyl 3-methylbenzoate 9o (300 mg, 2.0 mmol), [Ir(cod)(OMe)]2 (1.33 mg, 2.0 μmol), 4,4’-di-tert-butyl-2,2’-dipyridyl (1.1 mg, 4.1 μmol), bis(pinacolato)diborane (356 mg, 1.4 mmol) and THF (3.0 ml). The mixture was stirred at 80 °C for 16 h. After cooling to room temperature, the crude product was filtered through silica gel column (EtOAc) to remove inorganic materials. The solvent was evaporated under reduced pressure and the residue was treated with KHF2 according to GP1. Purification of the crude product by recrystallization from Et2O/acetone afforded 1o as a colorless solid (243.7 mg, 48% yield, 2 steps).

1H NMR (500 MHz, DMSO-d6) δ 7.79 (s, 1H), 7.48 (s, 1H), 7.40 (s, 1H), 3.80 (s, 3H), 2.28 (s, 3H); 13C NMR (125 MHz, DMSO-d6) δ 167.6, 137.4 (q, 3J_C-F = 1.6 Hz), 135.1, 129.7 (q, 3J_C-F = 1.7 Hz), 127.5, 126.5, 51.5, 21.0; 19F NMR (400 MHz, DMSO-d6) δ -141.9 (br s). HRMS (ESI): m/z (M–K+) calcd for C9H9O2BF3: 216.06895; found: 216.06919. IR(KBr): 3142, 1727, 1317, 1216, 965, 763 cm⁻¹. Mp: over 200 °C.
General procedure for synthesis of iodonium ylide (GP2):

\[
\text{Ar—BF}_3K \quad 1 \\
\begin{array}{c}
1) \text{ITT (0.60 equiv.)} \\
\text{DMF, 0 °C, 16 h}
\end{array} \\
\begin{array}{c}
2) \text{3, aq. Na}_2\text{CO}_3 \\
r.t., 1 \text{ h}
\end{array} \\
\rightarrow \\
\text{O}_{\text{O}} \text{O} \\
\text{Ar}
\]

To a solution of [I(OCOCF\(_3\))]\(_2\) (193.5 mg, 0.18 mmol) in DMF (1.5 mL) was added potassium aryltrifluoroborate 1 (0.30 mmol) in DMF (1.5 mL) at –20 °C. The reaction mixture was stirred at 0 °C for 16 h. After the mixture was cooled to –10 °C [when the reaction temperature was different, the temperature was set to the reaction temperature – 10 °C], a solution of 6,10-dioxaspiro[4.5]decane-7,9-dione 3 (102 mg, 0.60 mmol) in Na\(_2\)CO\(_3\) aq. (15% w/v, 3.0 mL) was added. The pH of the reaction mixture was tested and adjusted with Na\(_2\)CO\(_3\) until the pH > 10. [We confirmed that the use of excess aqueous Na\(_2\)CO\(_3\) solution did not show any deleterious effects.] The reaction mixture was then stirred at room temperature for 1 h. The reaction mixture was diluted with EtOAc, and the organic layer was successively washed with sat. NaHCO\(_3\) aq., water (three times), and brine, and then dried over anhydrous Na\(_2\)SO\(_4\). Filtration and evaporation in vacuo furnished the crude product, which was purified by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1), or recrystallization from CH\(_2\)Cl\(_2\)/hexane to afford the corresponding iodonium ylide 2.

8-(p-tolyl-\(\lambda^3\)-iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (2a)

Prepared according to GP2 from potassium (4-methylphenyl)trifluoroborate 1a.[3c] Purification of the crude product by recrystallization from CH\(_2\)Cl\(_2\)/hexane afforded 2a as a colorless solid (85.7 mg, 74% yield).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta 7.69-7.63\) (m, 2H), 7.26 (d, \(J = 8.1\) Hz, 2H), 2.33 (s, 3H), 2.01-1.93 (m, 4H), 1.71-1.62 (m, 4H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)) \(\delta 163.5, 140.7, 132.5, 131.5, 112.7, 112.1, 58.6, 36.7, 22.7, 20.7\). HRMS (ESI): \(m/z\) (M+Na\(^+\)) calcd for C\(_{15}\)H\(_{14}\)IO\(_4\)Na: 408.99072; found: 408.99135. IR (KBr): 2962, 1689, 1641, 1609, 1338, 1284, 1104, 758 cm\(^{-1}\). Mp: 92.5 °C (decomp.).

8-(o-tolyl-\(\lambda^3\)-iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (2b)

Prepared according to GP2 from potassium (2-methylphenyl)trifluoroborate 1b.[3c] Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded 2b as a colorless solid (66.0 mg, 57% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.88\) (dd, \(J = 8.2, 0.9\) Hz, 1H), 7.47 (td, \(J = 7.4, 1.1\) Hz, 1H), 7.38 (dd, \(J = 7.7, 0.9\) Hz, 1H), 7.22 (td, \(J = 7.7, 1.2\) Hz, 1H), 2.67 (s, 3H), 2.23-2.07 (m, 4H), 1.87-1.73 (m, 4H); \(^{13}\)C NMR (125 MHz, DMSO-\(d_6\)) \(\delta 163.5, 139.9, 136.1, 131.6, 130.5, 128.3, 122.3, 112.0, 59.0, 36.7,
24.9, 22.7. HRMS (ESI): m/z (M+Na⁺) calcd for C₁₅H₁₅IO₄Na: 408.99072; found: 408.99138. IR (KBr): 2956, 2866, 1685, 1647, 1461, 1343, 1274, 1205, 1098, 763 cm⁻¹. Mp: 90.3 °C (decomp.).

8-(m-tolyl-λ³-iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (2c)
Prepared according to GP2 from potassium (3-methylphenyl)trifluoroborate 1c.[16] Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded 2c as a colorless solid (82.3 mg, 71% yield).

¹H NMR (400 MHz, DMSO-d⁶) δ 7.66-7.51 (m, 2H), 7.41-7.29 (m, 2H), 2.32 (s, 3H), 2.04-1.90 (m, 4H), 1.74-1.62 (m, 4H); ¹³C NMR (125 MHz, DMSO-d⁶) δ 163.5, 140.7, 132.5, 131.3, 130.7, 129.5, 116.2, 112.1, 58.4, 36.8, 22.7, 20.8. HRMS (ESI): m/z (M+Na⁺) calcd for C₁₅H₁₅IO₄Na: 408.99072; found: 408.99162. IR (KBr): 2967, 1748, 1685, 1588, 1471, 1338, 1280, 1195, 1098, 763, 683 cm⁻¹. Mp: 83.5 °C (decomp.).

8-((4-chlorophenyl)-λ³-iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (2d)
Prepared according to GP2 from potassium (4-chlorophenyl)trifluoroborate 1d.[17] Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded 2d as a pale brown solid (80.5 mg, 66% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.85-7.78 (m, 2H), 7.44-7.34 (m, 2H), 2.20-2.06 (m, 4H), 1.85-1.73 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 164.4, 139.4, 134.9, 132.3, 114.4, 111.0, 57.4, 37.5, 23.5. The ¹H and ¹³C NMR spectra were in agreement with those reported in the literature.[18]

8-((4-methoxyphenyl)-λ³-iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (2e)
Prepared according to GP2 from potassium (4-methoxyphenyl)trifluoroborate 1e.[16] Purification of the crude product by recrystallization CH₂Cl₂/hexane afforded 2e as a colorless solid (62.7 mg, 52% yield).

¹H NMR (500 MHz, CDCl₃) δ 7.91-7.82 (m, 2H), 6.95-6.88 (m, 2H), 3.84 (s, 3H), 2.19-2.08 (m, 4H), 1.84-1.73 (m, 4H); ¹³C NMR (100 MHz, DMSO-d⁶) δ 163.5, 161.1, 134.6, 116.6, 112.0, 105.6, 59.2, 55.5, 36.7, 22.7. The ¹H and ¹³C NMR spectra were in agreement with those reported in the literature.[18]
8-[[1,1′-biphenyl]-4-yl-λ³-iodanylidene]-6,10-dioxaspiro[4.5]decane-7,9-dione (2f)
Prepared according to GP2 [−20 °C instead of 0 °C] from potassium (4-
biphenyl)trifluoroborate 1f.[16] Purification of the crude product by silica gel
column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded 2f as a
colorless solid (99.5 mg, 74% yield).

1H NMR (400 MHz, CDCl₃) δ 7.98-7.92 (m, 2H), 7.64-7.59 (m, 2H), 7.57-7.52 (m, 2H), 7.51-7.45 (m,
2H), 7.45-7.40 (m, 1H), 2.21-2.14 (m, 4H), 1.83-1.77 (m, 4H); 13C NMR (125 MHz, CDCl₃) δ 164.4,
145.8, 138.9, 134.2, 130.7, 129.3, 128.9, 127.4, 114.3, 112.2, 57.2, 37.6, 23.5. The ¹H and ¹³C NMR
spectra were in agreement with those reported in the literature.[18]

8-(naphthalen-2-yl-λ³-iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (2g)
Prepared according to GP2 from Potassium 2-naphthyltrifluoroborate 1g.[16]
Purification of the crude product by recrystallization from CH₂Cl₂/hexane
afforded 2g as a pale orange solid (72.2 mg, 57% yield).

1H NMR (400 MHz, CDCl₃) δ 8.42 (s, 1H), 7.94-7.79 (m, 4H), 7.69-7.57 (m, 2H), 2.20-2.12 (m, 4H),
1.86-1.72 (m, 4H); ¹³C NMR (125 MHz, DMSO-d₆) δ 163.6, 133.6, 133.1, 132.8, 130.6, 128.5, 128.1,
127.9, 127.9, 127.5, 113.5, 112.2, 58.9, 36.8, 22.7. The ¹H and ¹³C NMR spectra were in agreement
with those reported in the literature.[18]

8-(benzo[d][1,3]dioxol-5-yl-λ³-iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (2h)
Prepared according to GP2 [ITT (0.53 equiv.)] from potassium (3,4-
methylenedioxyphenyl)trifluoroborate 1h.[16] Purification of the crude product
by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded
2h as a colorless solid (68.7 mg, 55% yield).

1H NMR (400 MHz, CDCl₃) δ 7.43 (dd, J = 8.2, 2.1 Hz, 1H), 7.39 (d, J = 2.1 Hz, 1H), 6.83 (d, J = 8.2
Hz, 1H), 6.08 (s, 2H), 2.19-2.11 (m, 4H), 1.82-1.76 (m, 4H); ¹³C NMR (125 MHz, acetone-d₆) δ 164.4,
151.7, 150.3, 129.1, 114.2, 113.4, 111.4, 105.1, 103.6, 58.6, 37.9, 23.9. The ¹H and ¹³C NMR spectra
were in agreement with those reported in the literature.[18]

8-((1-tosyl-1H-indol-5-yl)-λ³-iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (2i)
Prepared according to GP2 [−10 °C instead of 0 °C] from potassium [1-[(4-
methylphenyl)sulfonyl]-indol-5-yl]trifluoroborate 1i. Purification of the crude
product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded 2i as a pale brown solid (103.5 mg, 61% yield).
$^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.08 (d, $J = 1.8$ Hz, 1H), 8.02 (d, $J = 9.1$ Hz, 1H), 7.99-7.82 (m, 3H), 7.72 (dd, $J = 8.6$, 1.8 Hz, 1H), 7.38 (d, $J = 8.2$ Hz, 2H), 6.96 (d, $J = 3.6$ Hz, 1H), 2.31 (s, 3H), 1.98-1.91 (m, 4H), 1.73-1.59 (m, 4H); $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ 163.6, 146.1, 134.7, 133.8, 132.2, 130.5, 128.8, 128.4, 126.9, 126.6, 115.5, 112.3, 110.4, 109.0, 59.2, 36.8, 22.8, 21.1. The $^1$H and $^{13}$C NMR spectra were in agreement with those reported in the literature.[19]

8-(thiophen-2-yl-l3-iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (2j)

Prepared according to GP2 [– 40°C instead of 0 °C, ITT (0.53 equiv.)] from potassium (thiophen-2-yl)trifluoroborate 1j.[3c] Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded 2j as a colorless solid (52.2 mg, 46% yield).

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.84 (dd, $J = 5.3$, 1.1 Hz, 1H), 7.60 (dd, $J = 3.7$, 1.1 Hz, 1H), 7.08 (dd, $J = 5.3$, 3.7 Hz, 1H), 1.97-1.90 (m, 4H), 1.70-1.63 (m, 4H); $^{13}$C NMR (125 MHz, DMSO-$d_6$): δ 163.2, 136.7, 134.3, 128.6, 112.1, 101.7, 62.2, 36.8, 22.7. The $^1$H and $^{13}$C NMR spectra were in agreement with those reported in the literature.[20]

8-((3-methylbenzo[d]isoxazol-5-yl)-l3-iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (2k)

Prepared according to GP2[ – 20°C instead of 0 °C] from potassium (3-methyl-1,2-benzoazol-5-yl)trifluoroborate 1k. Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded 2k as a colorless solid (87.1 mg, 68% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.33 (d, $J=$1.3 Hz, 1H), 8.10 (dd, $J = 9.0$, 1.6 Hz, 1H), 7.64 (d, $J = 8.1$ Hz, 1H), 2.63 (s, 3H), 2.19-2.11 (m, 4H), 1.83-1.77 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$): δ 164.4, 164.1, 155.1, 134.8, 129.2, 125.5, 114.5, 113.7, 106.7, 58.4, 37.5, 23.5, 10.2. The $^1$H and $^{13}$C NMR spectra were in agreement with those reported in the literature.[18]

8-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)-l3-iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione (2l)

Prepared according to GP2 from (8R,9S,13S,14S)-13-methyl-3-((trifluoro-$\lambda^4$-boraneyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one, potassium salt 1i.[20] Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded 2l as a colorless solid (126.7 mg, 77% yield).
**ethyl 2-(4-((7,9-dioxo-6,10-dioxaspiro[4.5]decan-8-ylidene)-1,3-iodanyl)phenoxy)-2-methylpropanoate (2m)**

Prepared according to GP2 from potassium (4-((1-ethoxy-2-methyl-1-oxopropan-2-yl)oxy)phenyl)trifluoroborate 1m. Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded 2m as a colorless solid (111.5 mg, 74% yield).

**methyl (S)-2-((tert-butoxycarbonyl)amino)-3-(4-((7,9-dioxo-6,10-dioxaspiro[4.5]decan-8-ylidene)-1,3-iodanyl)phenyl)propanoate (2n)**

Prepared according to GP2 from potassium (S)-(4-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)phenyl)trifluoroborate 1n. Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded 2n as a colorless solid (111.8 mg, 65% yield).

**methyl 3-((7,9-dioxo-6,10-dioxaspiro[4.5]decan-8-ylidene)-1,3-iodanyl)-5-methylbenzoate (2o)**

Prepared according to GP2 from potassium (3-methoxycarbonyl-5-methylphenyl)trifluoroborate 1o. Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100:0 to 99:1) afforded 2o as a colorless solid (66.6 mg, 50% yield).
$^1$H NMR (500 MHz, DMSO-$d_6$) δ 8.14 (s, 1H), 7.91 (s, 1H), 7.87 (s, 1H), 3.86 (s, 3H), 2.40 (s, 3H), 2.06-1.97 (m, 4H), 1.74-1.66 (m, 4H); $^{13}$C NMR (125 MHz, DMSO-$d_6$) δ 164.7, 163.5, 141.4, 136.7, 131.7, 131.6, 129.6, 116.0, 112.3, 58.7, 52.6, 36.8, 22.8, 20.6. HRMS (ESI): m/z (M+Na$^+$) calcd for C$_{17}$H$_7$INaO$_6$: 466.9962; found: 466.99696. IR (KBr): 2956, 1721, 1641, 1434, 1349, 1280, 1200, 1093, 758 cm$^{-1}$. Mp: 191.2 °C (decomp.).

8-((3,5-dimethylphenyl)-2,3-iodanylidene)-6,10-dioxaspiro[4.5]decane-7,9-dione ($2p$)
The transformation was performed based on the literature procedure.$^{[21]}$ In a glovebox, a sealed tube was charged with $m$-xylene $9p$ (618 µL, 5.0 mmol), [Ir(cod)(OMe)]$_2$ (16.6 mg, 25 µmol), 4,4′-di-tert-butyl-2,2′-dipyridyl (13.4 mg, 50 µmol), bis(pinacolato)diborane (889 mg, 3.5 mmol) and THF (7.5 ml). The mixture was stirred at 80 °C for 16 h. After cooling to room temperature, the crude product was filtered through silica gel column (EtOAc) to remove inorganic materials. The solvent was evaporated under reduced pressure and the residue was treated with KHF$_2$ according to GP1. Purification of the crude product by recrystallization from Et$_2$O/acetone afforded potassium (3,5-dimethylphenyl)trifluoroborate $1p$ as a colorless solid (414 mg, 39% yield, 2 steps).

Prepared $2p$ according to GP2 from $1p$. Purification of the crude product by silica gel column chromatography (AcOEt/MeOH = 100 : 0 to 99 : 1) afforded $2p$ as a colorless solid (82.8 mg, 69% yield). $^1$H NMR (500 MHz, DMSO-$d_6$) δ 7.41 (s, 2H), 7.18 (s, 1H), 2.28 (s, 6H), 2.01-1.95 (m, 4H), 1.71-1.66 (m, 4H); $^{13}$C NMR (125 MHz, DMSO-$d_6$) δ 163.5, 140.4, 132.1, 129.7, 116.1, 112.1, 58.3, 36.7, 22.7, 20.7. HRMS (ESI): m/z (M+Na$^+$) calcd for C$_{16}$H$_7$INaO$_4$: 423.00637; found: 423.00731. IR (KBr): 2952, 1685, 1631, 1343, 1284, 1104, 758 cm$^{-1}$. Mp: 126.0 °C (decomp.).

Supplementary references

S11


$^1$H NMR spectrum of 1h

![NMR spectrum of 1h](image)
$^{13}$C NMR spectrum of 1h
$^{19}$F NMR spectrum of $1h$
$^1$H NMR spectrum of 1i
$^{13}$C NMR spectrum of 1\textit{i}
$^{19}$F NMR spectrum of $1i$
$^1$H NMR spectrum of 1k
$^{13}$C NMR spectrum of 1k
$^{19}$F NMR spectrum of $1k$
1H NMR spectrum of \textbf{1m}
$^{13}$C NMR spectrum of 1m
$^{19}$F NMR spectrum of 1m

![Chemical Structure of 1m](image)

PPM
$^1$H NMR spectrum of 1n
$^{13}$C NMR spectrum of $1n$
$^{19}$F NMR spectrum of 1n
$^1$H NMR spectrum of 1o
$^{13}$C NMR spectrum of 1o
$^{19}$F NMR spectrum of $10$
$^1$H NMR spectrum of 2a
\[ ^{13}\text{C} \text{ NMR spectrum of } 2a \]
$^1$H NMR spectrum of 2b
$^{13}$C NMR spectrum of 2b
$^1$H NMR spectrum of 2c
\textsuperscript{13}C NMR spectrum of 2c
$^1$H NMR spectrum of 2d
$^{13}$C NMR spectrum of $2d$
$\text{H NMR spectrum of 2e}$
$^{13}$C NMR spectrum of 2e
$^1$H NMR spectrum of 2f
$^{13}$C NMR spectrum of 2f
$^1$H NMR spectrum of 2g
$^{13}$C NMR spectrum of $2g$
\( ^1H \) NMR spectrum of \( 2h \)
$^{13}$C NMR spectrum of $2h$
$^1$H NMR spectrum of 2i
$^{13}$C NMR spectrum of 2i
$^1$H NMR spectrum of 2j
$^{13}$C NMR spectrum of 2j
$^1$H NMR spectrum of 2k
$^{13}$C NMR spectrum of 2k
$^1$H NMR spectrum of 2l
\text{^13}C NMR spectrum of 2l

\begin{center}
\includegraphics[width=\textwidth]{s54.png}
\end{center}

X: parts per Million: 13C

S54
$^1$H NMR spectrum of 2m
$^{13}$C NMR spectrum of $2m$
$^1$H NMR spectrum of 2n
$^{13}$C NMR spectrum of 2n
$^1$H NMR spectrum of 2o

[Chemical structure and NMR spectrum image]
$^{13}$C NMR spectrum of 2o
$^1$H NMR spectrum of 2p
$^{13}\text{C}$ NMR spectrum of $2\text{p}$