Supporting Information

Synthesis of Dihydroindazo[2,3-f]phenanthridin-5(6H)-ones via Rh(III)-Catalyzed C–H Activation of 2-Aryl Indazoles and Annulation with Iodonium Ylides

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1. General information

All reactions were carried out under air with no precautions in dried glassware unless otherwise noted. All materials were obtained from commercial suppliers and used without further purification. Silica gel-G plates (Merck) were used for TLC analysis with a mixture of petroleum and ethyl acetate as the eluent. Column chromatography was performed with silica gel (200-300 mesh). Melting point of the products was measured on Büchi melting point apparatus, MPB-540. Open capillary tubes were used for the measurements and are uncorrected. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker Model Avance DMX 400 Spectrometer ($^1$H 400 MHz and $^{13}$C 100 MHz, respectively). Chemical shifts (δ) are given in ppm and are referenced to residual solvent peaks. High resolution mass spectrometry (HRMS) spectra were obtained on a Waters Xevo G2-XS Qtof Instrument. X-Ray single-crystal diffraction data were collected on an Agilent Technologies Gemini single-crystal diffractometer. UV-vis spectra were recorded on Agilent spectrophotometer. Fluorescence spectra and absolute quantum yields were collected on a Horiba JobinYvon-Edison Fluoromax-Plus fluorescence spectrometer with a calibrated integrating sphere system. Indazole$^1$ and iodonium ylides$^2$ were prepared according to literatures.

2. Optimization of the reaction conditions (Table S1)$^a$

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<th>Yield(%)$^b$</th>
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<td>Et$_2$O</td>
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$^a$ Reaction conditions: 1a (0.2 mmol, 1.0 equiv.), 2a (0.24 mmol, 1.2 equiv.), [RhCp*Cl$_2$]$_2$, (2.0 mol %) and AcOH (2.0 equiv.), solvents (2.0 mL), temperature, 18 $^\circ$C. $^b$ Isolated yield. $^c$ N.R. = no reaction.
3. General procedure for the synthesis of products 3

An oven-dried 10 mL reaction tube with a magnetic stir bar was charged with indazole 1 (0.2 mmol), iodonium ylides 2 (0.24 mmol, 1.2 equiv.), [RhCp*Cl₂]₂ (2 mol%), AgSbF₆ (4 mol%), AcOH (2.0 equiv.) and MeOH (2 mL) under air. The reaction was heated at 38 °C. The reaction was monitored by TLC, and upon completion of the reaction the solvent was evaporated under reduced pressure and the residue was directly purified by a silica gel column chromatography using ethyl acetate/petroleum as the eluent to afford product 3.

4. Gram-scale synthesis of 3aa

An oven-dried 50 mL reaction tube with a magnetic stir bar was charged with indazole 1a (3.5 mmol), iodonium ylides 2a (4.2 mmol, 1.2 equiv.), [RhCp*Cl₂]₂ (0.5 mol%), AgSbF₆ (2 mol%), AcOH (2 equiv.) and MeOH (2 mL) under air. The reaction mixture was stirred at 38°C until the 1a was consumed completely (12 h) detected by TLC. The product was filtered and washed with methanol, and provide the desired product 3aa (1.0802g, 98%).

The purity of the product is sufficient for NMR, UV and fluorescence characterization. The H-NMR, UV, and fluorescence data of the product were not substantially different from those of the product purified by column chromatography (Please see follow Fig. S1-S3).
Fig. S1. $^1$H-NMR of 3aa isolated with filtration and washed with methanol

Fig. S2. The comparison of UV absorbance of 3aa isolated from filtration and column chromatography
5. Recycling study of the catalytic system

An oven-dried 15 mL reaction flask with a magnetic stir bar was charged with indazole 1a (0.2 mmol), iodonium ylides 2a (0.24 mmol, 1.2 equiv.), [RhCp*Cl₂]₂ (2 mol%), AgSbF₆ (4 mol%), AcOH (2 equiv.) and MeOH (2 mL) under air. The reaction mixture was stirred at 38°C until the 1a was consumed completely detected by TLC. Afterwards, the product was filtered directly. The filtrate was transferred to the flask, and to which indazole 1a (0.2 mmol, 1.0 equiv.), iodonium ylides 2a (0.24 mmol, 1.2 equiv.) was added. The reaction mixture was stirred at 38°C until the 1a
was consumed completely detected by TLC. The product was filtered directly. The filtrate was transferred to the flask again for the next six times.

6. Derivatization reactions

An oven-dried 10 mL schlenk tube with a magnetic stir bar was charged with 3ga (0.1 mmol), PhB(OH)₂ (0.12 mmol, 1.2 equiv.), Pd(PPh₃)₄ (5 mol%), K₂CO₃ (0.6 mmol, 6 equiv.), 1,4-dioxane (0.5 mL) and H₂O (0.5 mL) under N₂. The reaction solution was heated at 100 °C for 3 h. Afterwards the reaction was quenched with H₂O (10 mL) and extracted with EtOAc (3×10 mL), washed with brine and dried over anhydrous Na₂SO₄. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product 4 (38.6 mg, 99%).

An oven-dried 10 mL reaction tube with a magnetic stir bar was charged with 3ab (0.2 mmol), NIS (0.22 mmol, 1.1 equiv.) and DMSO (2.0 mL) under air. The reaction solution was heated at 80 °C for 3 h. Afterwards the reaction was quenched with H₂O (10 mL) and extracted with EtOAc (3×10 mL), washed with brine and dried over anhydrous Na₂SO₄. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product 5 (41.2 mg, 50%).

7. Analytical data of the synthesized derivatives

7,7-Dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3aa)

Yellow solid; 62 mg, yield 99%; m.p. 179-180 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.44-9.38 (m, 1H), 8.50-8.43 (m, 1H), 8.27 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.63-7.58 (m, 2H), 7.53 (dt, J = 7.6, 0.8 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 3.54 (s, 2H), 2.67 (s, 2H), 1.24 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 198.4, 150.3, 145.5, 132.2, 128.6, 128.4, 127.9, 126.8, 125.3, 124.9, 122.5, 122.3, 121.7, 117.4, 116.7, 116.5, 53.6, 40.0, 32.4, 28.5; IR (KBr): 3446, 2961, 1672, 1627, 1520, 1486, 1466, 1367, 1326, 1282, 1233, 752 cm⁻¹; HRMS (ESI): m/z [M+H]⁺calcd for C₂₁H₁₈N₂O: 315.1492, found: 315.1484.

3,7,7-Trimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3ab)

Yellow solid; 65 mg, yield 99%; m.p. 195-197 °C; ¹H NMR (400 MHz, CDCl₃) δ 9.19 (s, 1H), 8.3 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.8 Hz,
1H), 7.51 (t, J = 8.0 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 3.50 (s, 2H), 2.63 (s, 2H), 2.53 (s, 3H), 1.22 (s, 6H); 13C NMR (100 MHz, CDCl3) δ 198.9, 150.4, 145.4, 138.7, 132.3, 129.4, 128.5, 126.4, 125.4, 122.7, 122.4, 121.9, 121.8, 117.2, 116.4, 116.2, 53.6, 40.0, 32.4, 28.5, 22.3; IR (KBr): 3459, 2957, 1681, 1666, 1626, 1520, 1411, 1367, 1281, 1230, 740 cm⁻¹; HRMS (ESI): m/z [M+H]⁺ calcd for C22H20N2O: 329.1648, found: 329.1648.

3-(tert-Butyl)-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3ca)

Yellow solid; 73 mg, yield 99%; m.p. 196-198 °C; 1H NMR (400 MHz, CDCl3) δ 9.60 (s, 1H), 8.56 (d, J = 8.8 Hz, 1H), 8.35 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 8.8 Hz, 1H), 7.80 (d, J = 8.8 Hz, 1H), 7.53 (t, J = 7.2 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 3.62 (s, 2H), 2.72 (s, 2H), 1.49 (s, 9H), 1.27 (s, 6H); 13C NMR (100 MHz, CDCl3) δ 199.2, 151.8, 150.5, 145.5, 132.4, 128.6, 126.2, 125.5, 123.0, 122.8, 122.4, 122.0, 117.2, 116.7, 116.6, 53.8, 40.1, 35.5, 32.5, 31.4, 28.5; IR (KBr): 3456, 2957, 1673, 1627, 1614, 1521, 1414, 1374, 1282, 1230, 739 cm⁻¹; HRMS (ESI): m/z [M+H]⁺ calcd for C25H26N2O: 371.2118, found: 371.2125.

3-Methoxy-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3da)

Yellow solid; 68 mg, yield 99%; m.p. 174-176 °C; 1H NMR (400 MHz, CDCl3) δ 8.98 (s, 1H), 8.34 (d, J = 8.8 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 7.51 (t, J = 6.8 Hz, 1H), 7.23-7.18 (m, 2H), 3.96 (s, 3H), 3.51 (s, 2H), 2.64 (s, 2H), 1.23 (s, 6H); 13C NMR (100 MHz, CDCl3) δ 199.1, 159.7, 150.5, 145.9, 132.5, 128.7, 127.1, 123.8, 121.8, 121.6, 119.1, 118.3, 117.0, 115.9, 115.6, 107.4, 55.4, 53.6, 40.0, 32.3, 28.4; IR (KBr): 3449, 2959, 1673, 1627, 1614, 1521, 1414, 1374, 1282, 1230, 739 cm⁻¹; HRMS (ESI): m/z [M+H]⁺ calcd for C22H20N2O: 345.1598, found: 345.1597.

3-Fluoro-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3ea)

Yellow solid; 66 mg, yield 99%; m.p. 197-199 °C; 1H NMR (400 MHz, CDCl3) δ 9.15 (dd, J = 12.0, 2.4 Hz, 1H), 8.32-8.24 (m, 1H), 8.09 (t, J = 8.8 Hz, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.52 (dd, J = 8.0, 1.2 Hz, 1H), 7.30-7.20 (m, 2H), 3.47 (s, 2H), 2.62 (s, 2H), 1.22 (s, 6H); 13C NMR (100 MHz, CDCl3) δ 198.4, 162.1 (d, J = 245.8 Hz), 150.3, 146.4, 131.7, 128.8, 126.9 (d, J = 10.6 Hz), 126.8, 124.3 (d, J = 9.0 Hz), 122.4, 121.4, 117.4, 116.7 (d, J = 24.2 Hz), 116.2, 115.4 (d, J = 4.4 Hz), 112.4 (d, J = 25.5 Hz), 53.2, 39.8, 32.2, 28.4; IR (KBr): 3462, 2957, 1670, 1628, 1558, 1426, 1369, 1295, 1282, 741 cm⁻¹; HRMS (ESI): m/z [M+H]⁺ calcd for C22H17FN2O: 333.1398, found: 333.1400.

3-Chloro-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3fa)

Yellow solid; 68 mg, yield 97%; m.p. 195-197 °C; 1H NMR (400 MHz, CDCl3) δ 9.39 (d, J = 1.6 Hz, 1H), 8.16-7.99 (m, 2H), 7.87 (d, J = 8.8 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.41 (d, J = 8.8 Hz, 1H), 7.28-7.20 (m, 1H), 3.44 (s, 2H), 2.61 (s, 2H), 1.21 (s, 6H); 13C NMR (100 MHz, CDCl3) δ 198.2, 150.3, 146.3, 134.5, 131.4, 128.8, 128.2, 126.3, 126.0, 123.4, 122.8, 122.6, 121.4, 117.4, 116.4, 115.1,
3-Bromo-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3ga)

Yellow solid; 70 mg, yield 89%; m.p. 211-213 °C; 1H NMR (400 MHz, CDCl₃) δ 9.55 (s, 1H), 8.05 (t, J = 7.2 Hz, 2H), 7.87 (d, J = 8.8 Hz, 1H), 7.56-7.49 (m, 2H), 7.24 (t, J = 7.2 Hz, 1H), 3.44 (s, 2H), 2.62 (s, 2H), 1.21 (s, 6H); 13C NMR (100 MHz, CDCl₃) δ 198.3, 150.4, 146.4, 131.4, 131.0, 129.4, 128.8, 126.3, 123.5, 123.1, 122.9, 122.6, 121.4, 117.5, 116.5, 115.1, 53.3, 39.9, 32.3, 28.4; IR (KBr): 3460, 2956, 1672, 1629, 1540, 1452, 1371, 1295, 1191, 808, 734 cm⁻¹; HRMS (ESI): m/z [M+H]+ calcd for C₂₁H₁₇BrN₂O: 349.1102, found: 349.1108.

7,7-Dimethyl-3-(trifluoromethyl)-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3ha)

Yellow solid; 65 mg, yield 85%; m.p. 216-218 °C; 1H NMR (400 MHz, CDCl₃) δ 9.80 (s, 1H), 8.48 (d, J = 8.4 Hz, 1H), 8.19 (d, J = 8.8 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 3.52 (s, 2H), 2.69 (s, 2H), 1.25 (s, 6H); 13C NMR (100 MHz, CDCl₃) δ 198.3, 150.3, 146.7, 131.0, 129.7 (q, J = 32.4 Hz), 129.2, 128.9, 126.5, 124.7, 124.5 (q, J = 4.5 Hz), 124.1 (q, J = 270.9 Hz), 124.0 (q, J = 3.3 Hz), 123.3, 122.9, 121.2, 117.7, 117.0, 115.8, 53.3, 39.9, 32.3, 28.4; IR (KBr): 3456, 2959, 1671, 1626, 1521, 1371, 1322, 1309, 1140, 1078, 748 cm⁻¹; HRMS (ESI): m/z [M+H]+ calcd for C₂₂H₁₇F₃N₂O: 383.1366, found: 383.1369.

7,7-Dimethyl-5-oxo-5,6,7,8-tetrahydroindazolo[2,3-f]phenanthridine-3-carbonitrile (3ia)

Yellow solid; 67 mg, yield 99%; m.p. up to 250 °C; 1H NMR (400 MHz, CDCl₃) δ 9.95 (s, 1H), 8.70 (d, J = 8.4 Hz, 1H), 8.39 (d, J = 8.8 Hz, 1H), 8.02 (d, J = 8.8 Hz, 1H), 7.65 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 3.68 (s, 2H), 2.77 (s, 2H), 1.30 (s, 6H); 13C NMR (100 MHz, CDCl₃) δ 198.3, 150.6, 147.3, 132.3, 129.9, 129.2, 127.0, 123.9, 123.3, 121.3, 118.1, 117.6, 115.5, 111.6, 100.0, 53.4, 40.1, 32.5, 28.5; IR (KBr): 3449, 2959, 2223, 1685, 1630, 1348, 1333, 1297, 1231, 1190, 756 cm⁻¹; HRMS (ESI): m/z [M+H]+ calcd for C₂₂H₁₇N₃O: 340.1444, found: 340.1453.

7,7-Dimethyl-3-nitro-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3ja)

Yellow solid; 71 mg, yield 99%; m.p. up to 250 °C; 1H NMR (400 MHz, CDCl₃) δ 10.51 (d, J = 2.4 Hz, 1H), 8.78 (d, J = 9.2 Hz, 1H), 8.54 (dd, J = 9.2, 2.4 Hz, 1H), 8.45 (d, J = 8.4 Hz, 1H), 8.05 (d, J = 8.8 Hz, 1H), 7.69-7.64 (m, 1H), 7.51-7.46 (m, 1H), 3.72 (s, 2H), 2.80 (s, 2H), 1.32 (s, 6H); 13C NMR (100 MHz, CDCl₃) δ 198.0, 150.7, 129.3, 128.4, 125.1, 124.2, 123.5, 123.4, 122.3, 121.2, 118.2, 117.8, 116.1, 53.3, 40.1, 32.5, 28.5; IR (KBr): 3450, 2953, 1672, 1626, 1522, 1348, 1333, 1297, 1231, 1190, 756 cm⁻¹; HRMS (ESI): m/z [M+H]+ calcd for C₂₂H₁₇N₃O: 360.1344, found: 360.1345.

2,7,7-Trimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3ka)
Yellow solid; 59 mg, yield 90%; m.p. 165-167 °C; 1H NMR (400 MHz, CDCl₃) δ 9.27 (d, J = 8.8 Hz, 1H), 8.27 (d, J = 8.4 Hz, 1H), 8.19 (s, 1H), 7.90 (d, J = 8.8 Hz, 1H), 7.54 (t, J = 7.2 Hz, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.28 (t, J = 7.2 Hz, 1H), 3.50 (s, 2H), 2.66 (s, 2H), 2.53 (s, 3H), 1.24 (s, 6H); 13C NMR (100 MHz, CDCl₃) δ 199.0, 150.2, 144.5, 137.9, 131.9, 130.1, 128.4, 126.6, 124.9, 123.0, 122.1, 122.0, 121.9, 117.3, 116.6, 116.4, 53.5, 39.9, 32.4, 28.5, 21.8; IR (KBr): 3453, 2958, 1672, 1628, 1522, 1496, 1372, 1325, 1297, 1229, 734 cm⁻¹; HRMS (ESI): m/z [M+H]⁺calcd for C₂₂H₂₅N₅O: 329.1648, found: 329.1641.

2-Fluoro-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3a₁)

Yellow solid; 60 mg, yield 90%; m.p. 191-193 °C; 1H NMR (400 MHz, CDCl₃) δ 8.19-8.15 (m, 2H), 7.88 (d, J = 8.8 Hz, 1H), 7.58-7.49 (m, 2H), 7.29-7.22 (m, 2H), 3.48 (s, 2H), 2.75 (s, 2H), 1.25 (s, 6H); 13C NMR (100 MHz, CDCl₃) δ 195.5, 158.5 (d, J = 256.7 Hz), 150.1, 143.7, 130.9, 129.2 (d, J = 9.3 Hz), 128.5, 126.9 (d, J = 5.0 Hz), 122.8, 121.3, 118.4 (d, J = 3.4 Hz), 118.3 (d, J = 5.8 Hz), 117.5, 116.7, 114.6 (d, J = 23.1 Hz), 113.08 (d, J = 14.6 Hz), 52.5, 39.5, 33.8, 29.0; IR (KBr): 3437, 2961, 1696, 1626, 1520, 1471, 1365, 1299, 1245, 1203, 749 cm⁻¹; HRMS (ESI): m/z [M+H]⁺calcd for C₂₁H₂₃FNO: 333.1398, found: 333.1389.

4-Fluoro-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3a₂)

Yellow solid; 6 mg, yield 9%; m.p. 219-222 °C; 1H NMR (400 MHz, CDCl₃) δ 9.53 (dd, J = 9.6, 6.0 Hz, 1H), 8.30 (d, J = 8.4 Hz, 1H), 8.19 (dd, J = 9.2, 2.4 Hz, 1H), 7.96 (d, J = 8.8 Hz, 1H), 7.59 (t, J = 7.2 Hz, 1H), 7.44-7.34 (m, 2H), 3.62 (s, 2H), 2.73 (s, 2H), 1.28 (s, 6H); 13C NMR (100 MHz, CDCl₃) δ 198.8, 161.7 (d, J = 265.6 Hz), 150.4, 144.9 (d, J = 2.2 Hz), 129.9 (d, J = 8.5 Hz), 128.7, 126.4 (d, J = 9.5 Hz), 122.9, 122.0 (d, J = 2.3 Hz), 121.3, 117.6, 117.2, 117.1 (d, J = 22.4 Hz), 117.0, 116.3, 107.8 (d, J = 23.1 Hz), 53.6, 40.0, 32.5, 28.5; IR (KBr): 3455, 2957, 1670, 1620, 1523, 1493, 1366, 1267, 1217, 839, 743 cm⁻¹; HRMS (ESI): m/z [M+H]⁺calcd for C₂₁H₁₇F₂NO: 333.1396, found: 333.1396.

2-Chloro-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3a₃) and 4-chloro-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3a₄) (78:22)

Yellow solid; 69 mg, yield 99%; m.p. 174-176 °C; 1H NMR (400 MHz, CDCl₃) δ 9.34 (d, J = 8.8 Hz, 0.78Hz), 8.39 (d, J = 8.0 Hz, 0.22Hz), 8.30 (d, J = 1.6 Hz, 0.78Hz), 8.20 (d, J = 8.8 Hz, 0.22Hz), 8.13 (d, J = 8.4 Hz, 0.78Hz), 7.78 (d, J = 8.8 Hz, 1H), 7.63 (d, J = 8.4 Hz, 0.22Hz), 7.57-7.49 (m, 2H), 7.29 (d, J = 8.0 Hz, 1H), 3.50 (s, 2H), 2.80 (s, 0.44Hz), 2.67 (s, 1.56Hz), 1.30 (s, 1.32Hz), 1.25 (s, 4.68Hz); 13C NMR (100 MHz, CDCl₃) δ 198.6, 195.9, 150.3, 150.2, 145.6, 144.2, 133.9, 132.2, 131.0, 130.7, 130.2, 128.7, 128.6, 128.5, 128.4, 127.4, 125.7, 123.4, 122.9, 122.8, 122.7, 121.6, 121.2, 121.1, 120.5, 117.7, 117.5, 116.8, 116.6, 115.9, 53.4, 52.3, 39.9, 39.4, 33.7, 32.4, 29.2, 28.5; IR (KBr): 2955, 2867, 1693, 1626, 1519, 1484, 1367, 1285, 1187, 788, 749 cm⁻¹; HRMS (ESI): m/z [M+H]⁺calcd for C₂₁H₁₇Cl₂NO: 349.1102, found: 349.1092.
2-Bromo-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3na)

Yellow solid; 73 mg, yield 93%; m.p. 212-214 °C; ^1H NMR (400 MHz, CDCl₃) δ 9.28 (d, J = 9.2 Hz, 1H), 8.50 (s, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.53 (t, J = 7.2 Hz, 1H), 7.30 (t, J = 7.2 Hz, 1H), 3.50 (s, 2H), 2.67 (s, 2H), 1.25 (s, 6H); ^13C NMR (100 MHz, CDCl₃) δ 198.5, 150.2, 145.7, 131.4, 130.5, 128.7, 128.6, 126.0, 124.8, 123.7, 122.9, 122.3, 121.2, 117.5, 116.6, 115.9, 53.4, 39.9, 32.4, 28.5; IR (KBr): 3077, 2954, 1667, 1625, 1518, 1478, 1369, 1320, 1135, 758 cm⁻¹; HRMS (ESI): m/z [M+H]^+ caleld for C₂₁H₁₃BrN₂O: 393.0597, found: 393.0597.

1-Fluoro-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3pa)

Yellow solid; 66 mg, yield 99%; m.p. 175-177 °C; ^1H NMR (400 MHz, CDCl₃) δ 9.22 (d, J = 8.4 Hz, 1H), 8.45 (d, J = 8.8 Hz, 1H), 7.84 (d, J = 8.8 Hz, 1H), 7.56-7.46 (m, 2H), 7.29 (dd, J = 12.4, 8.0 Hz, 1H), 7.20 (t, J = 8.0 Hz 1H), 3.56 (s, 2H), 2.68 (s, 2H), 1.25 (s, 6H); ^13C NMR (100 MHz, CDCl₃) δ 198.4, 157.0 (d, J = 249.2 Hz), 150.7, 146.4, 129.3 (d, J = 1.4 Hz), 128.7,128.6,127.0 (d, J = 4.1 Hz), 124.0 (d, J = 34.7 Hz), 122.4 (d, J = 3.5 Hz), 122.2 (d, J = 6.4 Hz), 117.4, 116.9, 115.9 (d, J = 1.0 Hz), 114.0 (d, J = 16.6 Hz), 113.6 (d, J = 22.0 Hz), 53.6, 40.4, 32.3, 28.5; IR (KBr): 2958, 1672, 1622, 1513, 1476, 1466, 1369, 1325, 1244, 747 cm⁻¹; HRMS (ESI): m/z [M+H]^+ caleld for C₂₁H₁₃F₂N₂O: 333.1398, found: 333.1393.

1-Chloro-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3qa)

Yellow solid; 47 mg, yield 68%; m.p. 202-204 °C; ^1H NMR (400 MHz, CDCl₃) δ 9.43 (d, J = 7.6 Hz, 1H), 8.69 (d, J = 8.8 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 6.8 Hz, 1H), 7.60-7.51 (m, 2H), 7.25 (t, J = 7.2 Hz, 1H), 3.66 (s, 2H), 2.72 (s, 2H), 1.27 (s, 6H); ^13C NMR (100 MHz, CDCl₃) δ 198.3, 150.7, 146.2, 131.1, 130.2, 128.6, 128.4, 128.1, 126.3, 125.1, 121.3, 117.9, 117.3, 116.2, 53.7, 40.5, 32.3, 28.5; IR (KBr): 3123, 2949, 1680, 1619, 1538, 1466, 1365, 1320, 1198, 1135, 758 cm⁻¹; HRMS (ESI): m/z [M+H]^+ caleld for C₂₁H₁₃ClN₂O: 349.1102, found: 349.1106.

6,6-Dimethyl-6,7-dihydro-[1,3]dioxolo[4,5-k]indazolo[2,3-f]phenanthridin-4(5H)-one (3ta₁)

Yellow solid; 64 mg, yield 89%; m.p. 212-214 °C; ^1H NMR (400 MHz, CDCl₃) δ 8.20 (d, J = 8.8 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.50 (t, J = 7.2 Hz, 1H), 7.28-7.21 (m, 2H), 6.16 (s, 2H), 3.53 (s, 2H), 2.73 (s, 2H), 1.26 (s, 6H); ^13C NMR (100 MHz, CDCl₃) δ 195.6, 150.2, 147.2, 144.0, 142.7, 132.2, 128.5, 122.1, 121.6, 120.8, 117.3, 117.2, 116.1, 110.6, 109.3, 101.4, 52.6, 39.6, 33.6, 28.9; IR (KBr): 3089, 2947, 1672, 1633, 1526, 1350, 1303, 1286, 1223, 741 cm⁻¹; HRMS (ESI): m/z [M+H]^+ caleld for C₂₂H₁₈N₂O₄: 359.1390, found: 359.1393.

7,7-Dimethyl-7,8-dihydro-[1,3]dioxolo[4,5-j]indazolo[2,3-f]phenanthridin-5(6H)-one (3ta₂)

Yellow solid; 7 mg, yield 10%; m.p. 239-241 °C; ^1H NMR (400 MHz, CDCl₃) δ 9.01 (s, 1H), 8.28 (d, J = 8.8 Hz, 1H), 7.96-7.90 (m, 2H), 7.59-7.54 (m, 1H),
7.29 (t, J = 8.0 Hz, 1H), 6.15 (s, 2H), 3.60 (s, 2H), 2.70 (s, 2H), 1.26 (s, 6H); ^13^C NMR (100 MHz, CDCl\textsubscript{3}) δ 199.04, 150.6, 149.3, 148.4, 143.7, 132.4, 128.6, 122, 121.6, 121.6, 121.3, 117.1, 116.2, 116.1, 105.3, 102.0, 100.6, 53.7, 40.0, 32.4, 28.5; IR (KBr): 3463, 2955, 1664, 1628, 1495, 1469, 1377, 1300, 1035, 732 cm\textsuperscript{-1}; HRMS (ESI): m/z [M+H]\textsuperscript{+} calecd for C\textsubscript{22}H\textsubscript{18}N\textsubscript{2}O\textsubscript{3}: 359.1390, found: 359.1383.

6,6-Dimethyl-6,7-dihydroindazolo[2,3-a]thieno[2,3-c]quinolin-4(5\textsubscript{H})-one (3ua)

Yellow solid; 63 mg, yield 99%; m.p. 228-230 °C; ^1H NMR (400 MHz, CDCl\textsubscript{3}) δ 8.57 (d, J = 5.2 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.57 (t, J = 7.2 Hz, 1H), 3.55 (s, 2H), 2.67 (s, 2H), 1.25 (s, 6H); ^13^C NMR (100 MHz, CDCl\textsubscript{3}) δ 197.3, 150.7, 142.9, 131.7, 130.8, 129.4, 128.4, 128.1, 125.3, 121.3, 120.9, 116.4, 115.9, 114.8, 52.2, 39.3, 32.8, 28.6; IR (KBr): 3475, 2948, 1672, 1634, 1526, 1380, 1350, 1303, 1287, 1224, 741 cm\textsuperscript{-1}; HRMS (ESI): m/z [M+H]\textsuperscript{+} calecd for C\textsubscript{19}H\textsubscript{16}N\textsubscript{2}O: 321.1056, found: 321.1054.

12,13-Dimethoxy-7,7-dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6\textsubscript{H})-one (3va)

Yellow solid; 74 mg, yield 99%; m.p. 209-230 °C; ^1H NMR (400 MHz, CDCl\textsubscript{3}) δ 9.40 (d, J = 7.2 Hz, 1H), 8.18-8.12 (m, 1H), 7.59-7.52 (m, 2H), 7.20 (s, 1H), 3.99 (s, 6H), 3.39 (s, 2H), 2.63 (s, 2H), 1.20 (s, 6H); ^13^C NMR (100 MHz, CDCl\textsubscript{3}) δ 198.7, 152.9, 148.0, 147.5, 145.7, 131.0, 127.9, 127.4, 126.8, 125.3, 124.4, 122.0, 114.6, 110.6, 98.5, 95.3, 56.1, 56.0, 53.4, 39.8, 32.2, 28.5; IR (KBr): 3385, 2965, 1668, 1639, 1528, 1504, 1461, 1323, 1231, 1202, 810 cm\textsuperscript{-1}; HRMS (ESI): m/z [M+H]\textsuperscript{+} calecd for C\textsubscript{23}H\textsubscript{22}N\textsubscript{2}O\textsubscript{3}: 375.1703, found: 375.1669.

10,10-Dimethyl-10,11-dihydropyrazolo[1,5-f]phenanthridin-8(9\textsubscript{H})-one (3wa)

White solid; 11 mg, yield 20%; m.p. 100-101 °C; ^1H NMR (400 MHz, CDCl\textsubscript{3}) δ 9.39 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 2.0 Hz, 1H), 8.07 (dd, J = 7.6, 0.8 Hz, 1H), 7.64-7.59 (m, 1H), 7.58-7.52 (m, 1H), 7.04 (d, J = 2.0 Hz, 1H), 3.45 (s, 2H), 2.66 (s, 2H), 1.24 (s, 6H); ^13^C NMR (100 MHz, CDCl\textsubscript{3}) δ 198.6, 146.4, 143.6, 140.0, 129.2, 127.4, 126.9, 126.1, 123.4, 123.2, 113.8, 99.28, 53.6, 39.5, 32.3, 28.5; IR (KBr): 2962, 1667, 1600, 1483, 1427, 1409, 1333, 1296, 757 cm\textsuperscript{-1}; HRMS (ESI): m/z [M+H]\textsuperscript{+} calecd for C\textsubscript{17}H\textsubscript{16}N\textsubscript{2}O: 265.1335, found: 265.1331.

7,7-Dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6\textsubscript{H})-one (3ab)

Yellow solid; 56 mg, yield 98%; m.p. 211-213 °C; ^1H NMR (400 MHz, CDCl\textsubscript{3}) δ 9.37 (d, J = 8.4 Hz, 1H), 8.38 (d, J = 6.8 Hz, 1H), 8.21 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.61-7.49 (m, 3H), 7.25 (t, J = 6.8 Hz, 1H), 3.62 (t, J = 6.4 Hz, 2H), 2.81 (t, J = 6.0 Hz, 2H), 2.39-2.30 (m, 2H); ^13^C NMR (100 MHz, CDCl\textsubscript{3}) δ 198.5, 150.3, 147.1, 131.8, 128.4, 128.2, 127.8, 126.9, 125.3, 124.7, 122.4, 121.2, 121.7, 117.3, 117.2, 116.6, 39.9, 26.4, 20.8; IR (KBr): 3455, 2964, 2361, 1680, 1628, 1522, 1486, 1372, 1326, 766 cm\textsuperscript{-1}; HRMS (ESI): m/z [M+H]\textsuperscript{+} calecd for C\textsubscript{19}H\textsubscript{16}N\textsubscript{2}O: 287.1179, found: 287.1175.
7-Methyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3ac)

Yellow solid; 59 mg, yield 99%; m.p. 188-190 °C; 1H NMR (400 MHz, CDCl₃) δ 9.32 (d, J = 8.0 Hz, 1H), 8.29 (d, J = 7.2 Hz, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.56-7.46 (m, 3H), 7.22 (t, J = 7.6 Hz, 1H), 3.89 (d, J = 18.8 Hz, 1H), 2.90 (dd, J = 18.4, 9.6 Hz, 1H), 2.79 (d, J = 11.2 Hz, 1H), 2.54-2.40 (m, 2H), 1.27 (d, J = 3.6 Hz, 3H); 13C NMR (100 MHz, CDCl₃) δ 198.6, 150.2, 146.4, 131.7, 128.4, 128.2, 127.7, 126.7, 125.1, 124.5, 122.3, 122.1, 121.7, 117.3, 116.7, 116.5, 47.9, 34.2, 28.3, 21.3; IR (KBr): 3450, 2955, 1669, 1627, 1521, 1487, 1375, 1293, 1209, 754 cm⁻¹; HRMS (ESI): m/z [M+H]+ calcd for C₂₀H₁₆N₂O: 301.1335, found: 301.1337.

7-Phenyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3ad)

Yellow solid; 72 mg, yield 99%; m.p. 249-251 °C; 1H NMR (400 MHz, CDCl₃) δ 9.57 (dd, J = 8.0, 1.2 Hz, 1H), 8.72 (dd, J = 8.0, 1.2 Hz, 1H), 8.46 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.8 Hz, 1H), 7.80-7.72 (m, 2H), 7.56-7.46 (m, 3H), 7.43-7.33 (m, 6H), 4.44 (dd, J = 18.0, 4.0 Hz, 1H), 3.78-3.72 (m, 1H), 3.64 (dd, J = 18.0, 11.2 Hz, 1H), 3.18-3.16 (m, 2H); 13C NMR (100 MHz, CDCl₃) δ 197.9, 150.6, 146.4, 142.1, 132.3, 128.9, 128.7, 128.6, 128.2, 127.4, 127.2, 126.8, 125.6, 125.2, 122.8, 122.5, 121.8, 117.6, 117.3, 116.9, 46.7, 39.0, 34.2; IR (KBr): 3445, 1668, 1627, 1522, 1384, 1365, 1385, 748 cm⁻¹; HRMS (ESI): m/z [M+H]+ calcd for C₂₅H₁₈N₂O: 363.1492, found: 363.1496.

7-([p]-Tolyl)-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3ae)

Yellow solid; 74 mg, yield 99%; m.p. 230-232 °C; 1H NMR (400 MHz, CDCl₃) δ 9.51 (d, J = 6.0 Hz, 1H), 8.60 (d, J = 5.2 Hz, 1H), 8.37 (d, J = 8.8 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.72-7.67 (m, 2H), 7.56 (t, J = 6.8 Hz, 1H), 7.35-7.28 (m, 3H), 7.35-7.19 (m, 3H), 4.34 (d, J = 18.4 Hz, 1H), 3.72-3.64 (m, 1H), 3.53 (dd, J = 18.4, 11.6 Hz, 1H), 3.10 (d, J = 8.4 Hz, 2H), 2.38 (s, 3H); 13C NMR (100 MHz, CDCl₃) δ 198.1, 150.5, 146.6, 139.3, 136.9, 132.1, 129.5, 128.6, 128.2, 127.4, 127.2, 126.8, 125.6, 125.2, 122.8, 122.5, 121.8, 117.6, 117.3, 116.9, 46.8, 38.5, 34.1, 21.1; IR (KBr): 3457, 1664, 1627, 1516, 1485, 1371, 1291, 764 cm⁻¹; HRMS (ESI): m/z [M+H]+ calcd for C₂₆H₂₀N₂O: 377.1648, found: 377.1655.

7-(4-Methoxyphenyl)-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3af)

Yellow solid; 78 mg, yield 99%; m.p. 236-238 °C; 1H NMR (400 MHz, CDCl₃) δ 9.56 (dd, J = 8.0, 1.2 Hz, 1H), 8.72 (dd, J = 7.6, 1.2 Hz, 1H), 8.37 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.72-7.67 (m, 2H), 7.56 (t, J = 6.8 Hz, 1H), 7.35-7.28 (m, 3H), 6.94 (d, J = 8.4 Hz, 2H), 4.42 (dd, J = 18.0, 4.0 Hz, 1H), 3.83 (s, 3H), 3.75-3.67 (m, 1H), 3.60 (dd, J = 18.0, 11.2 Hz, 1H), 3.13 (d, J = 9.2 Hz, 2H); 13C NMR (100 MHz, CDCl₃) δ 198.1, 150.5, 146.6, 139.3, 136.9, 132.1, 129.5, 128.6, 128.1, 127.1, 126.7, 125.4, 125.0, 122.6, 122.4, 121.8, 117.5, 117.1, 116.8, 46.8, 38.5, 34.1, 21.1; IR (KBr): 3457, 1664, 1627, 1516, 1485, 1384, 1371, 1291, 764 cm⁻¹; HRMS (ESI): m/z [M+H]+ calcd for C₂₆H₂₀N₂O₂: 393.1598, found: 393.1590.
6,6-Dimethyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (3ag)

Yellow solid; 60 mg, yield 95%; m.p. 140-143 °C; 1H NMR (400 MHz, CDCl₃) δ 9.34-9.27 (m, 1H), 8.48-8.44 (m, 1H), 8.26 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.63-7.58 (m, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.26 (t, J = 8.4 Hz, 1H), 3.64 (t, J = 6.4 Hz, 2H), 2.21 (t, J = 6.4 Hz, 2H), 1.31 (s, 6H); 13C NMR (100 MHz, CDCl₃) δ 203.5, 150.3, 145.1, 131.8, 128.4, 128.2, 127.8, 127.0, 125.8, 125.1, 122.6, 122.1, 121.7, 117.3, 116.6, 116.1, 42.4, 34.0, 24.5, 23.21; IR (KBr): 3459, 2921, 1627, 1522, 1487, 1370, 1074, 773, 749 cm⁻¹; HRMS (ESI): m/z [M+H]+ calcd for C₂₁H₁₈N₂O: 315.1492, found: 315.1489.

6,7-Dihydro-5H-cyclopenta[c]indazolo[3,2-a]isoquinolin-5-one (3ah)

Yellow solid; 54 mg, yield 99%; m.p. up to 250 °C; 1H NMR (400 MHz, CDCl₃) δ 9.13 (d, J = 7.6, 1.2, 1.2 Hz, 1H), 8.70 (d, J = 8.0 Hz, 1H), 8.46 (d, J = 8.8 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.781-7.72 (m, 2H), 7.61 (t, J = 8.0 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 3.70-3.67 (m, 2H), 3.05-3.02 (m, 2H). 13C NMR (100 MHz, CDCl₃) δ 203.0, 151.4, 142.5, 134.6, 130.5, 128.8, 128.7, 124.6, 124.4, 124.0, 123.0, 122.8, 121.6, 117.8, 117.3, 35.9, 39.0, 23.5; IR (KBr): 3450, 1702, 1637, 1531, 1371, 1286, 1238, 1096, 779, 734 cm⁻¹; HRMS (ESI): m/z [M+H]+ calcd for C₁₈H₁₂N₂O: 273.1022, found: 273.1028.

6,7,8,9-Tetrahydro-5H-cyclohepta[c]indazolo[3,2-a]isoquinolin-5-one (3ai)

Yellow solid; 20 mg, yield 33%; m.p. 142-144 °C; 1H NMR (400 MHz, CDCl₃) δ 8.67 (d, J = 8.0 Hz, 1H), 8.42 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.8 Hz, 1H), 7.70 (t, J = 7.2 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 8.0 Hz, 1H), 7.33 (t, J = 7.2 Hz, 1H), 3.86 (t, J = 6.4 Hz, 2H), 2.92 (t, J = 6.0 Hz, 2H), 2.18-2.07 (m, 2H), 2.03-1.95 (m, 2H); 13C NMR (100 MHz, CDCl₃) δ 206.2, 149.5, 139.2, 131.2, 128.0, 128.7, 125.4, 125.2, 124.9, 122.9, 121.9, 121.5, 117.3, 117.0, 42.8, 27.0, 22.9, 22.6; IR (KBr): 3051, 2929, 1673, 1627, 1520, 1370, 1283, 1239, 1152, 751 cm⁻¹; HRMS (ESI): m/z [M+H]+ calcd for C₂₀H₁₆N₂O: 301.1335, found: 301.1339.

7,7-Dimethyl-3-phenyl-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (4)

Yellow solid; 38.6 mg, yield 99%; m.p. 222-224 °C; 1H NMR (400 MHz, CDCl₃) δ 9.79 (d, J = 1.2 Hz, 1H), 8.59 (d, J = 8.8 Hz, 1H), 8.35 (d, J = 8.4 Hz, 1H), 7.96-7.93 (m, 1H), 7.91 (dd, J = 8.4, 1.6 Hz, 1H), 7.81-7.78 (m, 2H), 7.59-7.54 (m, 1H), 7.51 (t, J = 7.2 Hz, 2H), 7.42-7.38 (m, 1H), 7.33-7.29 (m, 1H), 3.60 (s, 2H), 2.70 (s, 2H), 1.25 (s, 6H); 13C NMR (100 MHz, CDCl₃) δ 198.9, 150.5, 145.8, 140.7, 140.4, 132.1, 129.0, 128.7, 127.8, 127.5, 126.9, 126.8, 125.7, 124.9, 122.8, 122.3, 121.8, 117.4, 116.8, 116.5, 53.6, 40.0, 32.4, 28.5; IR (KBr): 3057, 2958, 2360, 1673, 1627, 1520, 1370, 1283, 1239, 1152, 751 cm⁻¹; HRMS (ESI): m/z [M+H]+ calcd for C₂₇H₂₂N₂O: 391.1805, found: 391.1810.

6-Iodo-7,8-dihydroindazolo[2,3-f]phenanthridin-5(6H)-one (5)

Yellow solid; 41.2 mg, yield 50%; m.p. 231-233°C; 1H NMR (400 MHz, CDCl₃) δ 9.47-9.44 (m, 1H), 8.73 (s, 1H), 8.50-8.47 (m, 1H), 7.77-7.67 (m,
4H), 3.71 (t, J = 6.4 Hz, 2H), 2.90-2.85 (m, 2H), 2.44-2.37 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 198.4, 148.9, 147.0, 136.9, 130.9, 130.6, 128.9, 128.3, 127.3, 125.7, 124.7, 122.5, 119.4, 118.9, 117.9, 86.0, 39.9, 26.5, 20.9; IR (KBr): 3447, 2923, 2360, 1679, 1620, 1509, 1392, 1360, 1267, 1233, 802, 767 cm$^{-1}$; HRMS (ESI): m/z [M+H]$^+$ calcld for C$_{19}$H$_{13}$IN$_2$O: 413.0145, found: 413.0147.

7. Mechanistic study

(a) H/D exchange experiments

An oven-dried 10 mL reaction tube with a magnetic stir bar was charged with 3-Phenyl-1H-indazole 1 (0.2 mmol, 1.0 equiv.), [RhCp*Cl)$_2$ (2 mol%), AgSbF$_6$ (4 mol%), AcOH (2 equiv.) and MeOD (2 mL) under air. The reaction was heated at 38 °C for 1h. Afterwards the reaction solution was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product. The deuterated ratio was calculation from $^1$H NMR analysis.
An oven-dried 10 mL reaction tube with a magnetic stir bar was charged with 3-Phenyl-1H-indazole 1 (0.2 mmol, 1.0 equiv.), iodonium ylides 2 (0.24 mmol, 1.2 equiv.), [RhCp*Cl₂]₂ (2 mol%), AgSbF₆ (4 mol%), AcOH (2 equiv.) and MeOD (2 mL) under air. The reaction was heated at 38 °C for 30 min. Afterwards the reaction solution was concentrated and the residue was purified by column chromatography on silica gel to provide the desired [D₆]-3aa and [D₆]-1a. The deuterated ratio was calculated from ¹H NMR analysis.
(b) Competition experiment

An oven-dried 10 mL reaction tube with a magnetic stir bar was charged with 1a (0.2 mmol, 1.0 equiv.), 1f (0.2 mmol, 1.0 equiv.), iodonium ylide 2a (0.2 mmol, 1.0 equiv.), [RhCp*Cl₂]₂ (2 mol%), AgSbF₆ (4 mol%), AcOH (2 equiv.) and MeOH (2 mL) under air. The reaction is heated for sufficient time at 38°C. Afterwards the reaction solution was concentrated and the residue was purified by column chromatography on silica gel to provide the desired mixture of 3aa and 3af. The proportion of 3aa and 3af was calculated by NMR analysis (3aa: 3af = 5:2).
8. X-ray crystallography date of 3va.

The crystal structure was deposited into the CCDC database (CCDC No. 2189691). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

By slowly volatilizing the CDCl$_3$ solvent, single crystals 3va suitable for X-ray analysis were obtained. The detailed characteristics and data are shown below.

**Figure S2.** Crystal structure of compound 3va

**Table S2** Crystal data and structure refinement for 3va (CCDC No. 2189691)
Identification code 3va

Empirical formula C24 H23 Cl3 N2 O3
Formula weight 493.79
Temperature 293(2) K
Wavelength 0.71073 Å

Crystal system Triclinic
Space group P-1

Unit cell dimensions
\[a = 5.8190(2) \text{ Å}, \quad b = 9.8242(4) \text{ Å}, \quad c = 20.3104(10) \text{ Å},\]
Volume 1153.44(8) Å³

Z 2
Density (calculated) 1.422 Mg/m³
Absorption coefficient 0.427 mm⁻¹
F(000) 512

Crystal size 0.210 x 0.190 x 0.180 mm³
Theta range for data collection 3.520 to 25.096°.

Index ranges -6≤h≤6, -11≤k≤11, -23≤l≤24
Reflections collected 12533
Independent reflections 4077 [R(int) = 0.0229]
Completeness to theta = 25.096° 99.8%

Absorption correction Semi-empirical from equivalents
Max. and min. transmission 1.00000 and 0.31974
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 4077 / 0 / 293
Goodness-of-fit on F² 1.047

Final R indices [I>2σ(I)]
R1 = 0.0428, wR2 = 0.1082
R indices (all data) R1 = 0.0544, wR2 = 0.1154
Extinction coefficient n/a

Largest diff. peak and hole 0.249 and -0.334 e.Å⁻³

9. Photophysical properties

a. The summarized photophysical properties of 3aa-3aj

<table>
<thead>
<tr>
<th>Product</th>
<th>λ_{abs} (nm)</th>
<th>λ_{em} Max (nm)</th>
<th>Stokes shift(nm)</th>
<th>Φ_F (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3aa</td>
<td>406</td>
<td>481</td>
<td>75</td>
<td>21.33</td>
</tr>
<tr>
<td>3ba</td>
<td>411</td>
<td>489</td>
<td>78</td>
<td>24.62</td>
</tr>
<tr>
<td>3ca</td>
<td>410</td>
<td>489</td>
<td>79</td>
<td>24.60</td>
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<td>3da</td>
<td>424</td>
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<td>50.44</td>
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<td>3ea</td>
<td>412</td>
<td>490</td>
<td>78</td>
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<tr>
<td>3fa</td>
<td>411</td>
<td>488</td>
<td>77</td>
<td>14.84</td>
</tr>
</tbody>
</table>
b. The UV-Vis and fluorescence spectra of 3ja and its emission picture in different solvents.

![Normalized absorption and emission spectra of 3ja in DCM solution.](image)

**Figure S3** Normalized absorption and emission spectra of 3ja in DCM solution.

![Fluorescence emission image of 3ja in different solvent.](image)

**Figure S4** The fluorescence emission image of 3ja in different solvent, demonstrating a remarkable solvatochromic effect.

c. The photophysical properties of the selected F-containing samples

<table>
<thead>
<tr>
<th>Product</th>
<th>λ_{abs}</th>
<th>λ_{em,Max}</th>
<th>Stokes Shift</th>
<th>Φ_F %</th>
<th>CIE coordinate</th>
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</thead>
<tbody>
<tr>
<td>3aa</td>
<td>406</td>
<td>481</td>
<td>75</td>
<td>21.33</td>
<td>0.16, 0.31</td>
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<tr>
<td>3ea</td>
<td>412</td>
<td>490</td>
<td>78</td>
<td>28.92</td>
<td>0.19, 0.37</td>
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<tr>
<td>3la_1</td>
<td>394</td>
<td>472</td>
<td>78</td>
<td>8.28</td>
<td>0.17, 0.31</td>
</tr>
<tr>
<td>3la_2</td>
<td>404</td>
<td>477</td>
<td>73</td>
<td>15.07</td>
<td>0.17, 0.30</td>
</tr>
</tbody>
</table>

*Note: 5 × 10^{-6} M in CH_2Cl_2.*
### Table S1

<table>
<thead>
<tr>
<th>Compound</th>
<th>λmax (nm)</th>
<th>QY (a.u.)</th>
<th>Emission Color</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3pa</td>
<td>402</td>
<td>0.21</td>
<td>Blue</td>
<td>310</td>
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<tr>
<td></td>
<td>485</td>
<td>0.41</td>
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<td></td>
</tr>
<tr>
<td>a: 5 × 10^{-6} M in CH$_2$Cl$_2$.</td>
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</table>

**Figure S5** Normalized absorption and emission spectra of 3aa, 3ea, 3la$_1$, 3la$_2$, and 3pa in DCM solution.

**Figure S6** Emission color coordinates of compounds in DCM solutions in the CIE 1931 chromaticity diagram. Inset picture: the DCM solution of selected compounds under daylight and under the irradiation of 365 nm UV-Vis light.

### 10. References


11. Copy of NMR

3aa $^1$H NMR (400 MHz, CDCl$_3$)
$\text{3aa} \ ^{13}\text{C NMR (100 MHz, CDCl}_3)$
$^{1}$H NMR (400 MHz, CDCl$_3$)
3ba $^{13}$C NMR (100 MHz, CDCl$_3$)
$3\text{ca} \ ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3)$
$^{13}$C NMR (100 MHz, CDCl$_3$)
$3\text{da} \, {^1\text{H}} \text{NMR (400 MHz, CDCl}_3)$
3da $^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl₃)
3ea $^{13}$C NMR (100 MHz, CDCl$_3$)
3fa $^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}{H}$ NMR (400 MHz, CDCl$_3$)

3ga
$^{13}$C NMR (100 MHz, CDCl$_3$)

3g

S35
$^1$H NMR (400 MHz, CDCl$_3$)
$3ha^{13}$C NMR (100 MHz, CDCl$_3$)
$\text{H NMR} \ (400 \text{ MHz, CDCl}_3)$

$\text{3ia } ^1\text{H NMR (400 MHz, CDCl}_3)$
3ia $^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)
3ja $^{13}$C NMR (100 MHz, CDCl$_3$)
$3ka^1H$ NMR (400 MHz, CDCl$_3$)
$3ka^{13}$C NMR (100 MHz, CDCl$_3$)
$3\text{la}_1$ $^1\text{H NMR (400 MHz, CDCl}_3)$
$3\text{la}_1$, $^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

3la$_2$
$31a_2^{13}$C NMR (100 MHz, CDCl$_3$)
$3\text{ma}_1$ and $3\text{ma}_2$ $^1\text{H}$ NMR (400 MHz, CDCl$_3$)
$3\text{ma}_1$ and $3\text{ma}_2$ $^{13}\text{C}$ NMR (100 MHz, CDCl$_3$)
$3n\text{a}^1\text{H NMR (400 MHz, CDCl}_3\text{)}$
$^{13}$C NMR (100 MHz, CDCl$_3$)

3na $^{13}$C NMR (100 MHz, CDCl$_3$)
$3\text{pa}^1\text{H NMR (400 MHz, CDCl}_3$)
3na $^{13}$C NMR (100 MHz, CDCl$_3$)
3qa $^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)
$3\text{ta}_1$ $^{13}\text{C NMR (100 MHz, CDCl}_3$}
$^1$H NMR (400 MHz, CDCl$_3$)

3ta$_2$
$^{13}$C NMR (100 MHz, CDCl$_3$)
$\text{3ua } ^1\text{H NMR (400 MHz, CDCl}_3\text{)}$
$^{13}$C NMR (100 MHz, CDCl$_3$)

3ua $^{13}$C NMR (100 MHz, CDCl$_3$)
3va $^1$H NMR (400 MHz, CDCl$_3$)
3va $^{13}$C NMR (100 MHz, CDCl$_3$)
$3wa\ ^1H\ NMR\ (400\ MHz,\ CDCl_3)$
$^{13}$C NMR (100 MHz, CDCl$_3$)
$3ab \ ^1H \text{ NMR (400 MHz, CDCl}_3\)$
$\text{3ab }^{13}\text{C NMR (100 MHz, CDCl}_3\text{)}$
$^{1}$H NMR (400 MHz, CDCl$_3$)
$3\text{ac}^{13}\text{C NMR (100 MHz, CDCl}_3)$
$^{1}$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$3ag^{1}H$ NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$3ai \ ^1H \text{NMR (400 MHz, CDCl}_3)$
\textbf{3ai} $^{13}\text{C} \text{ NMR (100 MHz, CDCl}_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^1$C NMR (100 MHz, CDCl$_3$)
12. UV-Vis and emission spectrum

![Absorbance and Emission Spectra](image-url)