

# Supporting Information

## Nickel Metallaphotoredox-Catalyzed C-O Bond Activation/Csp<sup>2</sup>-Csp<sup>3</sup> Coupling Enabled by Phosphine

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## 1. General Information

### A. Materials

All reactions were carried out in oven-dried glassware and under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. All the chemicals were purchased commercially and used without further purification.  $[\text{Ir}(\text{dFCF}_3\text{ppy})_2\text{dtbbpy}]\text{PF}_6$  was purchased from Laajoo.  $\text{NiBr}_2 \cdot \text{diglyme}$  and dtbbpy were purchased from Energy Chemical or Adamas. Triphenylphosphine, 2-bromobenzothiazole and 2,6-lutidine were purchased from Adamas. (*S*)-(+)-Ibuprofen, adapalene, indomethacin, vitamin E, estrone and benzyl alcohols were purchased from Energy Chemical or Adamas. Tetrabutylammonium iodide was purchased from Accela. *N,N*-Dimethylacetamide (DMA) was purchased from J&K (99.8%, SuperDry, with molecular sieves, J&K Seal) and stored under an argon atmosphere without additional drying. All other solvents were purchased as ACS reagents and used without further purification.

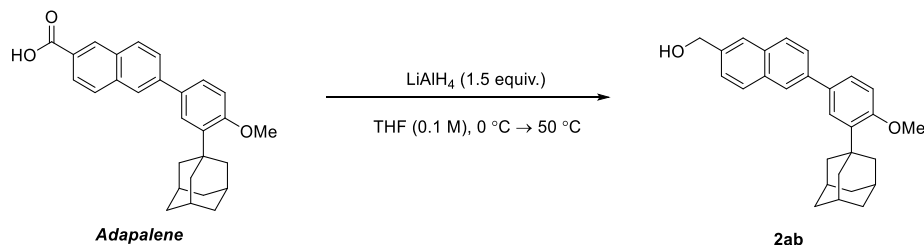
### B. Analytic Methods

Thin-layer chromatography (TLC) was conducted with 0.25 mm Tsingdao silica gel plates (60F-254) and visualized by exposure to UV light (254 nm) or chemical stained with basic potassium permanganate solution. Flash column chromatography was performed using Tsingdao silica gel (200-300 mesh) under a positive pressure of air. NMR spectra were recorded on Bruker Advance 500 ( $^1\text{H}$ : 500 MHz,  $^{13}\text{C}$ : 125 MHz).  $^1\text{H}$  NMR data are reported as follows: chemical shift (multiplicity, coupling constants, number of protons). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) analysis was performed using a Thermo Scientific Q Exactive Focus Orbitrap mass spectrometer equipped with an ESI source. Gas chromatography-mass spectra (GC-MS) were detected on an Agilent 8890-5977A

gas chromatography-mass spectrometry. Fluorescence quenching experiments were conducted on a Hitachi F-7100 Fluorescence Spectrophotometer using a quartz cuvette with 1 cm path length equipped with a septum cap. UV-Vis spectra were recorded on a TU-1950 UV-Vis Spectrophotometer.

## 2. Experimental Procedures and Spectral Data of Benzyl Alcohol Substrates

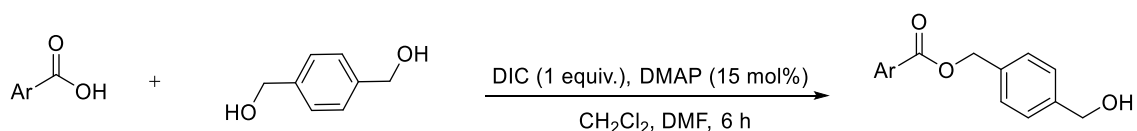
### Synthesis of Benzyl Alcohol 2ab



The title compound was prepared according to known literature procedure.<sup>[1]</sup> To an oven-dried 50 mL RBF placed with a solution of carboxylic acid (1.031 g, 2.5 mmol, 1 equiv.) in THF (25 mL) at 0 °C was added LiAlH<sub>4</sub> (0.142 g, 3.75 mmol, 1.5 equiv.) slowly. Then the reaction mixture was heated and stirred at 50 °C in the oil-bath and monitored by TLC. After the reaction was complete, the reaction was cooled to 0 °C and carefully quenched by the dropwise addition of H<sub>2</sub>O (0.14 mL, 1 mL per 1 g LiAlH<sub>4</sub>), 10% NaOH (0.14 mL, 1 mL per 1 g LiAlH<sub>4</sub>), and H<sub>2</sub>O (0.28 mL, 2 mL per 1 g LiAlH<sub>4</sub>) under stirring. Filtrated and the filtrate was concentrated *in vacuo* to give the crude product that purified by flash column chromatography on silica gel (hexane/EtOAc = 5:1) to give the corresponding product **2ab** (0.866 g, 87%) as white solid. The corresponding product **2ab** was known compound and spectral data match that reported in the previous literature.<sup>[1]</sup>

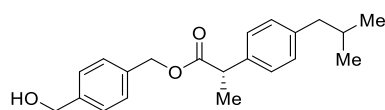
### Synthesis of Benzyl Alcohols 2ac, 2ad

#### General Procedure A:



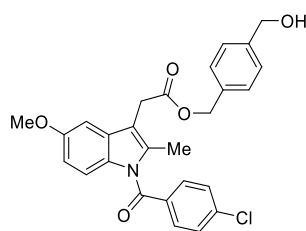
The title compound was prepared according to known literature procedure.<sup>[2]</sup> 1,4-Benzenedimethanol (0.331 g, 2.4 mmol, 1.5 equiv.), 4-dimethylaminopyridine (0.029 g, 0.24 mmol, 15 mol%) were added to a 25 mL RBF. CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and anhydrous

DMF (2 mL) were added and the resulting solution was cooled to 0 °C. A solution of carboxylic acid (1.6 mmol, 1 equiv.) and *N,N'*-diisopropylcarbodiimide (0.25 mL, 1.6 mmol, 1 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) were then added to the reaction. Over the course of six hours the reaction turned from a colorless homogeneous solution to heterogeneous mixture containing a white precipitate. The precipitate was removed by filtration and the filtrate was subsequently removed by rotary evaporation. The crude mixture was diluted with EtOAc (10 mL) and water (20 mL), and the aqueous and organic layers were separated. The aqueous layer was extracted with EtOAc (10 mL×2). The combined organic layers were washed with water (20 mL×2) and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to give product.



**2ac**

4-(hydroxymethyl)benzyl (S)-2-(4-isobutylphenyl)propanoate (**2ac**): Prepared according to General Procedure A. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) to give the corresponding product **2ac** as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.28 (d, *J* = 7.8 Hz, 2H), 7.20 (dd, *J* = 7.9, 4.3 Hz, 4H), 7.08 (d, *J* = 7.8 Hz, 2H), 5.32 – 4.80 (m, 2H), 4.64 (s, 2H), 3.73 (d, *J* = 7.2 Hz, 1H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.84 (dt, *J* = 13.6, 6.7 Hz, 1H), 1.49 (d, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 174.7, 140.8, 140.7, 137.6, 135.5, 129.4, 128.1, 127.3, 127.1, 66.2, 65.0, 45.2, 45.1, 30.3, 22.5, 18.5. ESI-MS calc'd for C<sub>21</sub>H<sub>26</sub>NaO<sub>3</sub> [M+Na]<sup>+</sup>: 349.1774, found 349.1772.

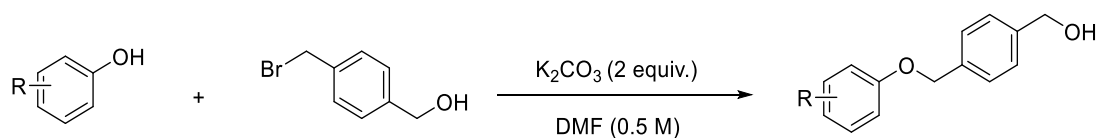


**2ad**

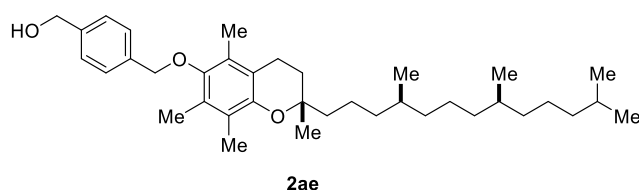
4-(hydroxymethyl)benzyl-2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl) acetate (**2ad**): Prepared according to General Procedure A. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 10:1) to give the corresponding product **2ad** as white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.70 – 7.60 (m, 2H), 7.53 – 7.43 (m, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.97 – 6.82 (m, 2H), 6.66 (dd, *J* = 9.1, 2.5 Hz, 1H), 5.13 (s, 2H), 4.69 (d, *J* = 4.2 Hz, 2H), 4.00 – 3.66 (m, 5H), 2.36 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 170.8, 168.4, 156.1, 141.2, 139.4, 136.0, 135.2, 133.9, 131.3, 130.9, 130.6, 129.2, 128.6, 127.2, 115.1, 112.6, 111.9, 101.3, 66.7, 65.1, 55.8, 30.6, 13.5. ESI-MS calc'd for C<sub>27</sub>H<sub>24</sub><sup>35</sup>ClNNaO<sub>5</sub> [M+Na]<sup>+</sup>: 500.1235, found 500.1236.

### Synthesis of Benzyl Alcohols **2ae**, **2af**

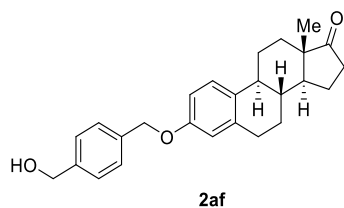
#### General Procedure B:



The title compound was prepared according to known literature procedure.<sup>[3]</sup> A solution of 4-(bromomethyl)benzyl alcohol (0.402 g, 2.0 mmol, 1 equiv.), phenolic compound (2.4 mmol, 1.2 equiv.), and potassium carbonate (0.553 g, 4.0 mmol, 2 equiv.) in DMF (4 mL) were stirred at room temperature for 9 h. The mixture was diluted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and water (20 mL), and the aqueous and organic layers were separated. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL×2). The combined organic layers were washed with water (20 mL×2) and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to give product.



(4-((((S)-2,5,7,8-tetramethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)methyl)phenyl)methanol (**2ae**): Prepared according to General Procedure B. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 15:1) to give the corresponding product **2ae** as yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.50 (d, *J* = 7.7 Hz, 2H), 7.39 (d, *J* = 7.7 Hz, 2H), 4.70 (d, *J* = 10.1 Hz, 4H), 2.59 (t, *J* = 6.9 Hz, 2H), 2.27 – 2.01 (m, 9H), 1.82 – 1.77 (m, 2H), 1.57 – 1.47 (m, 3H), 1.39 (dt, *J* = 13.0, 5.6 Hz, 4H), 1.27 (d, *J* = 20.6 Hz, 11H), 1.17 – 1.03 (m, 6H), 0.85 (dd, *J* = 11.1, 6.4 Hz, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 148.2, 148.0, 140.6, 137.6, 128.1, 128.0, 127.2, 126.1, 123.1, 117.7, 75.0, 74.6, 65.3, 40.2, 39.5, 37.6, 37.6, 37.5, 37.4, 32.9, 32.8, 31.4, 28.1, 25.0, 24.6, 24.0, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 13.0, 12.2, 12.0. ESI-MS calc'd for C<sub>37</sub>H<sub>58</sub>NaO<sub>3</sub> [M+Na]<sup>+</sup>: 573.4278, found 573.4277.

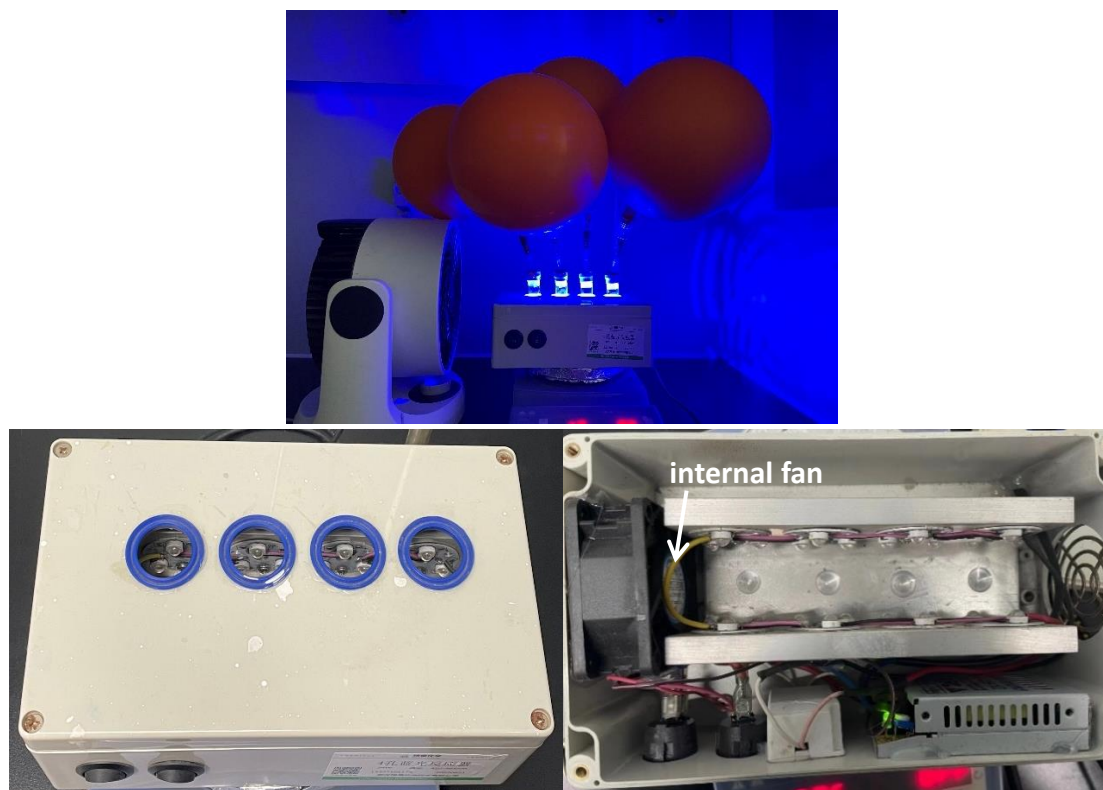


(8R,9S,13S,14S)-3-((4-(hydroxymethyl)benzyl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[*a*]phenanthren-17-one (**2af**): Prepared according to General Procedure B. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 2:1) to give the corresponding product **2af** as white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.48 – 7.35 (m, 4H), 7.20 (d, *J* = 8.6 Hz, 1H), 6.81 – 6.75 (m, 1H), 6.73 (s, 1H), 5.03 (s, 2H), 4.70 (s, 2H), 2.95 – 2.76 (m, 2H), 2.53 – 2.43 (m, 1H), 2.39 (d, *J* = 10.7 Hz, 1H), 2.30 – 2.17 (m, 1H), 2.18 – 1.91 (m, 4H), 1.64 – 1.37 (m, 6H), 0.90 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 221.3, 156.9, 140.7, 137.9, 136.7, 132.4, 127.8, 127.3, 126.5, 115.0, 112.4, 69.8, 65.2, 50.5, 48.1, 44.1, 38.4, 36.0, 31.6, 29.8, 26.6, 26.0, 21.7, 14.0. ESI-MS calc'd for C<sub>26</sub>H<sub>30</sub>NaO<sub>3</sub> [M+Na]<sup>+</sup>: 413.2087, found 413.2086.

### 3. Experimental Procedures and Spectral Data of Products

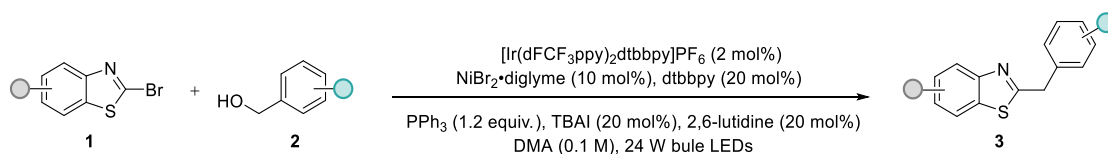


The photoreactors used in this research were bought from GeAo Chem (**Fig. S1**: blue LEDs, 1 W for every light bulb; every vial was irradiated by 6 light bulbs from the side). Gram-scale reaction was performed under irradiation of two 15 W blue LEDs, which is bought from Taobao ([www.taobao.com](http://www.taobao.com)) (**Fig. S2**) The metallaphotoredox reaction temperature was controlled between 22 °C and 30 °C by cooling with fans and air conditioner.



**Fig. S1** Reaction Set-up

### General Procedure C:



In an Ar-filled glovebox, dtbbpy (0.011 g, 0.04 mmol, 20 mol%), NiBr<sub>2</sub>•diglyme (0.007 g, 0.02 mmol, 10 mol%) were added to a 10 mL vial with a magnetic stir, then DMA (2.0 mL) was added via syringe. The reaction mixture was stirred for 0.5 h at room temperature. To another vial with a magnetic stir, 2-bromobenzothiazole **1** (0.2 mmol, 1 equiv.), benzyl alcohol **2** (0.6 mmol, 3 equiv.), triphenylphosphine (0.063 g, 0.24

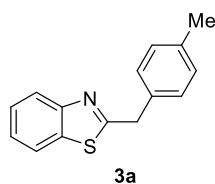
mmol, 1.2 equiv.), tetrabutylammonium iodide (0.015 g, 0.04 mmol, 20 mol%) and [Ir(dFCF<sub>3</sub>ppy)<sub>2</sub>dtbbpy]PF<sub>6</sub> (0.004 g, 0.004 mmol, 2 mol%) were added in the glovebox. The vial was capped and removed from the glovebox, 2,6-lutidine (0.004 mL, 0.04 mmol, 20 mol%) was added via micro-syringe and the above-mentioned freshly prepared solvent of nickel/ligand in DMA was added via syringe immediately. The resulting mixture was stirred under irradiation at a distance of ~1 cm from 4 x 6 W blue LEDs ( $\lambda = 450\text{-}465$  nm) for 3 h. The mixture was diluted with EtOAc (5 mL) and water (15 mL), and the aqueous and organic layers were separated. The aqueous layer was extracted with EtOAc (10 mL $\times$ 2). The combined organic layers were washed with water (20 mL $\times$ 2) and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The residue was purified by flash chromatography to give corresponding product **3**.

#### **General Procedure D:**

In an Ar-filled glovebox, dtbbpy (0.011 g, 0.04 mmol, 20 mol%), NiBr<sub>2</sub>•diglyme (0.007 g, 0.02 mmol, 10 mol%) were added to a 10 mL vial with a magnetic stir, then DMA (2.0 mL) was added via syringe. The reaction mixture was stirred for 0.5 h at room temperature. To another vial with a magnetic stir, 2-bromobenzothiazole **1** (0.2 mmol, 1 equiv.), triphenylphosphine (0.063 g, 0.24 mmol, 1.2 equiv.), tetrabutylammonium iodide (0.015 g, 0.04 mmol, 20 mol%) and [Ir(dFCF<sub>3</sub>ppy)<sub>2</sub>dtbbpy]PF<sub>6</sub> (0.004 g, 0.004 mmol, 2 mol%) were added in the glovebox. The vial was capped and removed from the glovebox, benzyl alcohol **2** (0.6 mmol, 3 equiv.) and 2,6-lutidine (0.004 mL, 0.04 mmol, 20 mol%) were added via micro-syringe, then the above-mentioned freshly prepared solvent of nickel/ligand in DMA was added via syringe immediately. The resulting mixture was stirred under irradiation at a distance of ~1 cm from 4 x 6 W blue LEDs ( $\lambda = 450\text{-}465$  nm) for 3 h. The mixture was diluted with EtOAc (5 mL) and water (15 mL), and the aqueous and organic layers were separated. The aqueous layer was extracted with EtOAc (10 mL $\times$ 2). The combined organic layers were washed with water (20 mL $\times$ 2) and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The residue was purified by flash chromatography to give corresponding product **3**.

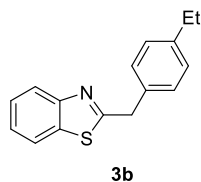
### General Procedure E:

In an Ar-filled glovebox, dtbbpy (0.011 g, 0.04 mmol, 20 mol%), NiBr<sub>2</sub>•diglyme (0.007 g, 0.02 mmol, 10 mol%) were added to a 10 mL vial with a magnetic stir, then DMA (2.0 mL) was added via syringe. The reaction mixture was stirred for 0.5 h at room temperature. Then benzyl alcohol **2** (0.4 mmol, 2 equiv.) was added via micro-syringe. To another vial with a magnetic stir, 2-bromobenzothiazole **1** (0.2 mmol, 1 equiv.), triphenylphosphine (0.063 g, 0.24 mmol, 1.2 equiv.), tetrabutylammonium iodide (0.015 g, 0.04 mmol, 20 mol%) and [Ir(dFCF<sub>3</sub>ppy)<sub>2</sub>dtbbpy]PF<sub>6</sub> (0.004 g, 0.004 mmol, 2 mol%) were added in the glovebox. The vial was capped and removed from the glovebox, and 2,6-lutidine (0.004 mL, 0.04 mmol, 20 mol%) was added via micro-syringe. Then the above-mentioned freshly prepared solvent of nickel/ligand and benzyl alcohol in DMA was added via syringe to the reaction vial immediately. The resulting mixture was stirred under irradiation at a distance of ~1 cm from 4 x 6 W blue LEDs ( $\lambda = 450\text{-}465\text{ nm}$ ) for 3 h. The mixture was diluted with EtOAc (5 mL) and water (15 mL), and the aqueous and organic layers were separated. The aqueous layer was extracted with EtOAc (10 mL×2). The combined organic layers were washed with water (20 mL×2) and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The residue was purified by flash chromatography to give corresponding product **3**.

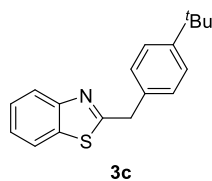


2-(4-methylbenzyl)benzo[*d*]thiazole (**3a**): Prepared according to General Procedure C. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 120:1) to yield product **3a** (0.032 g, 67%) as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.99 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.38 (m, 1H), 7.37 – 7.28 (m, 1H), 7.25 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 4.39 (s, 2H), 2.33 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  171.8, 153.4, 137.2, 135.8, 134.3, 129.7, 129.2,

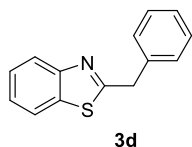
126.0, 124.9, 122.9, 121.6, 40.4, 21.2. ESI-MS calc'd for C<sub>15</sub>H<sub>14</sub>NS [M+H]<sup>+</sup>: 240.0841, found 240.0840.



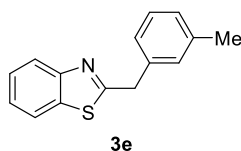
2-(4-ethylbenzyl)benzo[*d*]thiazole (**3b**): Prepared according to General Procedure D. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 130:1) to yield product **3b** (0.035 g, 69%) as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.99 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.76 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.49 – 7.38 (m, 1H), 7.35 – 7.26 (m, 3H), 7.20 – 7.15 (m, 2H), 4.40 (s, 2H), 2.63 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 171.7, 153.4, 143.5, 135.8, 134.5, 129.2, 128.5, 126.0, 124.9, 122.9, 121.6, 40.4, 28.6, 15.6. ESI-MS calc'd for C<sub>16</sub>H<sub>16</sub>NS [M+H]<sup>+</sup>: 254.0998, found 254.0998.



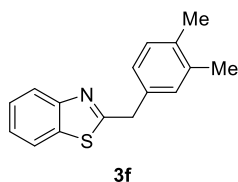
2-(4-(tert-butyl)benzyl)benzo[*d*]thiazole (**3c**): Prepared according to General Procedure E. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 140:1) to yield product **3c** (0.037 g, 66%) as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.41 (m, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.31 (dd, *J* = 8.2, 6.2 Hz, 3H), 4.41 (s, 2H), 1.31 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 171.6, 153.4, 150.4, 135.8, 134.3, 128.9, 126.1, 125.9, 124.9, 122.9, 121.6, 40.3, 34.6, 31.5. ESI-MS calc'd for C<sub>18</sub>H<sub>20</sub>NS [M+H]<sup>+</sup>: 282.1311, found 282.1310.



2-benzylbenzo[*d*]thiazole (**3d**): Prepared according to General Procedure D. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 130:1) to yield product **3d** (0.027 g, 60%) as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.78 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.39 – 7.32 (m, 5H), 7.32 – 7.25 (m, 1H), 4.44 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 171.3, 153.4, 137.3, 135.8, 129.3, 129.0, 127.5, 126.1, 124.9, 122.9, 121.6, 40.8. ESI-MS calc'd for C<sub>14</sub>H<sub>12</sub>NS [M+H]<sup>+</sup>: 226.0685, found 226.0684.

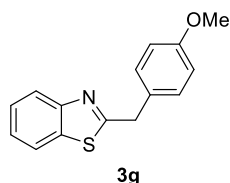


2-(3-methylbenzyl)benzo[*d*]thiazole (**3e**): Prepared according to General Procedure D. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 130:1) to yield product **3e** (0.031 g, 64%) as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.41 (m, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.28 – 7.21 (m, 1H), 7.17 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 7.5 Hz, 1H), 4.40 (s, 2H), 2.34 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 171.5, 153.4, 138.7, 137.2, 135.8, 130.0, 128.9, 128.2, 126.3, 126.1, 124.9, 122.9, 121.6, 40.7, 21.5. ESI-MS calc'd for C<sub>15</sub>H<sub>14</sub>NS [M+H]<sup>+</sup>: 240.0841, found 240.0841.

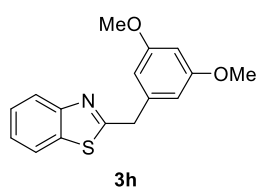


2-(3,4-dimethylbenzyl)benzo[*d*]thiazole (**3f**): Prepared according to General Procedure C. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 150:1) to yield product **3f** (0.032 g, 63%) as viscous oil. <sup>1</sup>H NMR

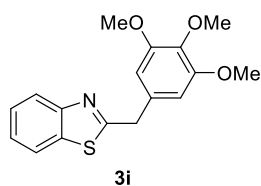
(500 MHz, CDCl<sub>3</sub>)  $\delta$  7.99 (d,  $J$  = 8.2 Hz, 1H), 7.76 (d,  $J$  = 8.0 Hz, 1H), 7.49 – 7.36 (m, 1H), 7.38 – 7.27 (m, 1H), 7.12 (d,  $J$  = 15.4 Hz, 3H), 4.36 (s, 2H), 2.24 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  172.0, 153.4, 137.2, 135.8, 135.8, 134.7, 130.5, 130.2, 126.6, 126.0, 124.8, 122.9, 121.6, 40.4, 19.9, 19.6. ESI-MS calc'd for C<sub>16</sub>H<sub>16</sub>NS [M+H]<sup>+</sup>: 254.0998, found 254.0997.



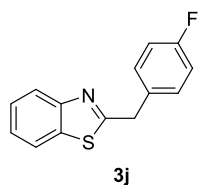
2-(4-methoxybenzyl)benzo[*d*]thiazole (**3g**): Prepared according to General Procedure D. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 70:1) to yield product **3g** (0.028 g, 55%) as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.99 (d,  $J$  = 8.1 Hz, 1H), 7.80 – 7.76 (m, 1H), 7.55 – 7.38 (m, 1H), 7.35 – 7.26 (m, 3H), 6.99 – 6.80 (m, 2H), 4.38 (s, 2H), 3.80 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  172.2, 159.0, 153.4, 135.8, 130.4, 129.4, 126.1, 124.9, 122.8, 121.6, 114.4, 55.4, 39.9. ESI-MS calc'd for C<sub>15</sub>H<sub>14</sub>NOS [M+H]<sup>+</sup>: 256.0791, found 256.0792.



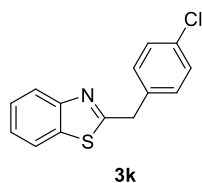
2-(3,5-dimethoxybenzyl)benzo[*d*]thiazole (**3h**): Prepared according to General Procedure C. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 20:1) to yield product **3h** (0.029 g, 51%) as viscous oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.99 (d,  $J$  = 8.2 Hz, 1H), 7.79 (d,  $J$  = 8.0 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.37 – 7.30 (m, 1H), 6.52 (d,  $J$  = 2.2 Hz, 2H), 6.39 (t,  $J$  = 2.3 Hz, 1H), 4.37 (s, 2H), 3.77 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  171.0, 161.2, 153.3, 139.4, 135.8, 126.1, 125.0, 122.9, 121.7, 107.3, 99.4, 55.5, 41.0. ESI-MS calc'd for C<sub>16</sub>H<sub>16</sub>NO<sub>2</sub>S [M+H]<sup>+</sup>: 286.0896, found 286.0895.



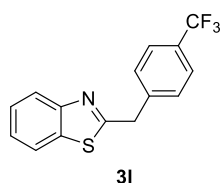
2-(3,4,5-trimethoxybenzyl)benzo[*d*]thiazole (**3i**): Prepared according to General Procedure D. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 8:1) to yield product **3i** (0.041 g, 65%) as white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.43 (m, 1H), 7.38 – 7.31 (m, 1H), 6.59 (s, 2H), 4.37 (s, 2H), 3.84 (d, *J* = 4.2 Hz, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 171.2, 153.6, 153.3, 137.3, 135.7, 132.8, 126.1, 125.0, 122.8, 121.7, 106.2, 61.0, 56.2, 41.0. ESI-MS calc'd for C<sub>17</sub>H<sub>17</sub>NNaO<sub>3</sub>S [M+Na]<sup>+</sup>: 338.0821, found 338.0819.



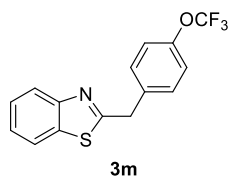
2-(4-fluorobenzyl)benzo[*d*]thiazole (**3j**): Prepared according to General Procedure D. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 150:1) to yield product **3j** (0.035 g, 72%) as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.40 (m, 1H), 7.36–7.32 (m, 3H), 7.09 – 6.99 (m, 2H), 4.41 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 170.9, 162.2 (d, *J* = 245.0 Hz), 153.4, 135.7, 133.0 (d, *J* = 2.5 Hz), 130.8 (d, *J* = 7.5 Hz), 126.2, 125.0, 123.0, 121.7, 115.9 (d, *J* = 21.2 Hz), 39.9. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -115.18. ESI-MS calc'd for C<sub>14</sub>H<sub>11</sub>FNS [M+H]<sup>+</sup>: 244.0591, found 244.0592.



2-(4-chlorobenzyl)benzo[*d*]thiazole (**3k**): Prepared according to General Procedure C. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 20:1) to yield product **3k** (0.029 g, 56%) as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.04 – 7.88 (m, 1H), 7.80 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.38 – 7.28 (m, 5H), 4.40 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 170.4, 153.4, 135.7, 135.7, 133.4, 130.6, 129.1, 126.2, 125.1, 123.0, 121.7, 40.0. ESI-MS calc'd for C<sub>14</sub>H<sub>11</sub><sup>35</sup>CINS [M+H]<sup>+</sup>: 260.0295, found 260.0296.



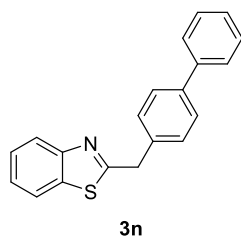
2-(4-(trifluoromethyl)benzyl)benzo[*d*]thiazole (**3l**): Prepared according to General Procedure D. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 150:1) to yield product **3l** (0.043 g, 73%) as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.01 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.48 (m, 3H), 7.42 – 7.36 (m, 1H), 4.49 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 169.4, 153.4, 141.2, 135.7, 129.8 (q, *J* = 32.5 Hz), 129.6, 126.3, 125.9 (q, *J* = 3.8 Hz), 125.2, 124.2 (q, *J* = 270.0 Hz), 123.1, 121.7, 40.4. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -62.50. ESI-MS calc'd for C<sub>15</sub>H<sub>11</sub>F<sub>3</sub>NS [M+H]<sup>+</sup>: 294.0559, found 294.0558.



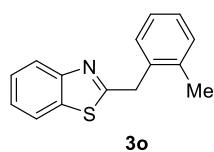
2-(4-(trifluoromethoxy)benzyl)benzo[*d*]thiazole (**3m**): Prepared according to General Procedure D. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 160:1) to yield product **3m** (0.038 g, 61%) as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.83 – 7.73 (m, 1H), 7.55 – 7.42 (m, 1H), 7.43 – 7.29 (m, 3H), 7.19 (d, *J* = 8.2 Hz, 2H), 4.43 (s, 2H). <sup>13</sup>C NMR (125



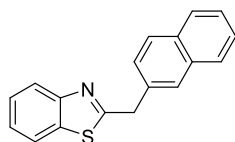
MHz, CDCl<sub>3</sub>)  $\delta$  170.1, 153.4, 148.6 (q,  $J = 1.25$  Hz), 136.0, 135.7, 130.6, 126.2, 125.1, 123.0, 121.7, 121.5, 120.6 (q,  $J = 255.0$  Hz), 39.9. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)  $\delta$  -57.86. ESI-MS calc'd for C<sub>15</sub>H<sub>11</sub>F<sub>3</sub>NOS [M+H]<sup>+</sup>: 310.0508, found 310.0510.



2-([1,1'-biphenyl]-4-ylmethyl)benzo[d]thiazole (**3n**): Prepared according to General Procedure C. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 130:1) to yield product **3n** (0.044 g, 73%) as white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 (d,  $J = 8.2$  Hz, 1H), 7.80 (d,  $J = 8.0$  Hz, 1H), 7.65 – 7.53 (m, 4H), 7.47 – 7.40 (m, 5H), 7.37 – 7.32 (m, 2H), 4.48 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  171.1, 153.4, 140.8, 140.4, 136.3, 135.8, 129.7, 128.9, 127.7, 127.5, 127.2, 126.1, 125.0, 122.9, 121.7, 40.4. ESI-MS calc'd for C<sub>20</sub>H<sub>16</sub>NS [M+H]<sup>+</sup>: 302.0998, found 302.0996.

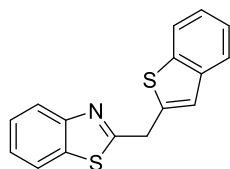


2-(2-methylbenzyl)benzo[d]thiazole (**3o**): Prepared according to General Procedure C. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 130:1) to yield product **3o** (0.028 g, 58%) as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.98 (d,  $J = 8.2$  Hz, 1H), 7.75 (d,  $J = 8.0$  Hz, 1H), 7.44 (t,  $J = 7.8$  Hz, 1H), 7.31 (t,  $J = 7.3$  Hz, 2H), 7.21 (q,  $J = 8.2, 7.4$  Hz, 3H), 4.43 (s, 2H), 2.33 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  171.7, 153.4, 137.1, 135.8, 135.7, 130.8, 130.3, 127.9, 126.6, 126.0, 124.8, 122.8, 121.6, 38.6, 19.8. ESI-MS calc'd for C<sub>15</sub>H<sub>14</sub>NS [M+H]<sup>+</sup>: 240.0841, found 240.0838.



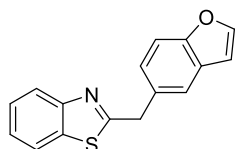
**3p**

2-(naphthalen-2-ylmethyl)benzo[*d*]thiazole (**3p**): Prepared according to General Procedure C. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 140:1) to yield product **3p** (0.034 g, 62%) as viscous oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.84 – 7.74 (m, 5H), 7.51 – 7.42 (m, 4H), 7.36 – 7.29 (m, 1H), 4.59 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 171.2, 153.4, 135.8, 134.8, 133.7, 132.7, 128.8, 128.0, 127.9, 127.8, 127.3, 126.4, 126.1, 126.1, 125.0, 122.9, 121.7, 40.9. ESI-MS calc'd for C<sub>18</sub>H<sub>14</sub>NS [M+H]<sup>+</sup>: 276.0841, found 276.0842.



**3q**

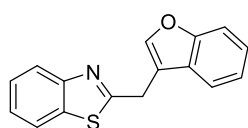
2-(benzo[*b*]thiophen-2-ylmethyl)benzo[*d*]thiazole (**3q**): Prepared according to General Procedure C. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 150:1) to yield product **3q** (0.034 g, 61%) as viscous oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.87 – 7.74 (m, 2H), 7.74 – 7.67 (m, 1H), 7.53 – 7.43 (m, 1H), 7.39 – 7.27 (m, 3H), 7.25 (d, *J* = 3.6 Hz, 1H), 4.71 (d, *J* = 1.1 Hz, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 169.2, 153.3, 140.2, 139.9, 139.9, 135.8, 126.3, 125.2, 124.6, 124.4, 123.6, 123.5, 123.1, 122.4, 121.8, 35.6. ESI-MS calc'd for C<sub>16</sub>H<sub>12</sub>NS<sub>2</sub> [M+H]<sup>+</sup>: 282.0406, found 282.0403.



**3r**

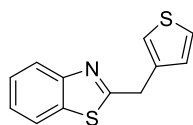
2-(benzofuran-5-ylmethyl)benzo[*d*]thiazole (**3r**): Prepared according to General

Procedure C. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 120:1) to yield product **3r** (0.032 g, 60%) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 8.2$  Hz, 1H), 7.76 (d,  $J = 8.0$  Hz, 1H), 7.60 (dd,  $J = 11.2, 2.0$  Hz, 2H), 7.51 – 7.41 (m, 2H), 7.36 – 7.25 (m, 2H), 6.72 (d,  $J = 2.1$  Hz, 1H), 4.52 (s, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  172.0, 154.4, 153.4, 145.7, 135.8, 131.9, 128.0, 126.0, 125.6, 124.9, 122.9, 121.8, 121.6, 111.8, 106.6, 40.6. ESI-MS calc'd for  $\text{C}_{16}\text{H}_{12}\text{NOS}$   $[\text{M}+\text{H}]^+$ : 266.0634, found 266.0634.



**3s**

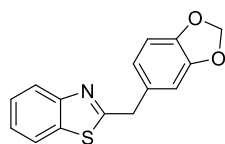
2-(benzofuran-3-ylmethyl)benzo[*d*]thiazole (**3s**): Prepared according to General Procedure C. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 120:1) to yield product **3s** (0.033 g, 62%) as white solid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 8.2$  Hz, 1H), 7.77 (d,  $J = 8.0$  Hz, 1H), 7.67 (s, 1H), 7.54 (d,  $J = 7.8$  Hz, 1H), 7.51 – 7.43 (m, 2H), 7.31 (dt,  $J = 16.6, 7.8$  Hz, 2H), 7.21 (t,  $J = 7.5$  Hz, 1H), 4.51 (s, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.9, 155.6, 153.4, 143.0, 135.7, 127.4, 126.2, 125.1, 124.8, 123.0, 122.9, 121.7, 119.9, 116.4, 111.8, 29.1. ESI-MS calc'd for  $\text{C}_{16}\text{H}_{12}\text{NOS}$   $[\text{M}+\text{H}]^+$ : 266.0634, found 266.0635.



**3t**

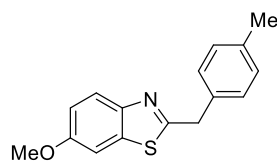
2-(thiophen-3-ylmethyl)benzo[*d*]thiazole (**3t**): Prepared according to General Procedure D. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 120:1) to yield product **3t** (0.024 g, 52%) as colorless liquid.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 – 7.91 (m, 1H), 7.80 (dd,  $J = 8.0, 1.1$  Hz, 1H), 7.53 – 7.37 (m, 1H), 7.37 – 7.30 (m, 2H), 7.22 (dd,  $J = 3.0, 1.3$  Hz, 1H), 7.08 (dd,  $J = 5.0, 1.3$  Hz,

1H), 4.46 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 170.8, 153.4, 137.1, 135.7, 128.4, 126.5, 126.1, 125.0, 123.2, 122.9, 121.7, 35.2. ESI-MS calc'd for C<sub>12</sub>H<sub>10</sub>NS<sub>2</sub> [M+H]<sup>+</sup>: 232.0249, found 232.0249.



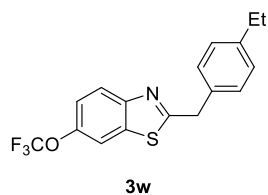
**3u**

2-(benzo[d][1,3]dioxol-5-ylmethyl)benzo[d]thiazole (**3u**): Prepared according to General Procedure C. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 80:1) to yield product **3u** (0.031 g, 57%) as white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.99 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.78 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.51 – 7.37 (m, 1H), 7.37 – 7.29 (m, 1H), 6.90 – 6.69 (m, 3H), 5.94 (s, 2H), 4.34 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 171.6, 153.4, 148.1, 147.0, 135.8, 131.0, 126.1, 125.0, 122.9, 122.5, 121.6, 109.7, 108.6, 101.2, 40.4. ESI-MS calc'd for C<sub>15</sub>H<sub>12</sub>NO<sub>2</sub>S [M+H]<sup>+</sup>: 270.0583, found 270.0582.

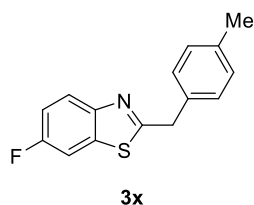


**3v**

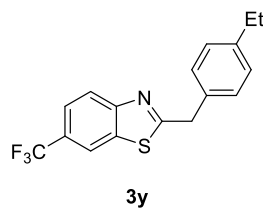
6-methoxy-2-(4-methylbenzyl)benzo[d]thiazole (**3v**): Prepared according to General Procedure C. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 80:1) to yield product **3v** (0.033 g, 61%) as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.86 (d, *J* = 8.9 Hz, 1H), 7.40 – 7.20 (m, 3H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.03 (dd, *J* = 8.9, 2.6 Hz, 1H), 4.34 (s, 2H), 3.82 (s, 3H), 2.33 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 169.1, 157.5, 147.8, 137.1, 137.0, 134.4, 129.6, 129.1, 123.3, 115.1, 104.3, 55.9, 40.2, 21.2. ESI-MS calc'd for C<sub>16</sub>H<sub>16</sub>NOS [M+H]<sup>+</sup>: 270.0947, found 270.0946.



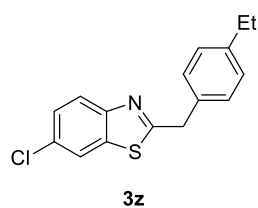
2-(4-ethylbenzyl)-6-(trifluoromethoxy)benzo[*d*]thiazole (**3w**): Prepared according to General Procedure D. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 170:1) to yield product **3w** (0.036 g, 54%) as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.97 (d, *J* = 8.9 Hz, 1H), 7.70 – 7.59 (m, 1H), 7.31 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.40 (s, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 173.2, 152.0, 146.3 (q, *J* = 1.2 Hz), 143.7, 136.6, 134.1, 129.2, 128.6, 123.7, 120.6 (q, *J* = 256.2 Hz), 120.0, 114.3, 40.4, 28.6, 15.6. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -58.06. ESI-MS calc'd for C<sub>17</sub>H<sub>15</sub>F<sub>3</sub>NOS [M+H]<sup>+</sup>: 338.0821, found 338.0820.



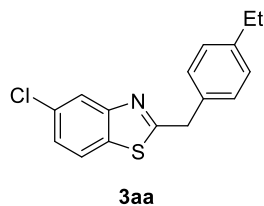
6-fluoro-2-(4-methylbenzyl)benzo[*d*]thiazole (**3x**): Prepared according to General Procedure C. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 130:1) to yield product **3x** (0.026 g, 51%) as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.91 (dd, *J* = 8.9, 4.8 Hz, 1H), 7.44 (dd, *J* = 8.2, 2.6 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.14 (m, 3H), 4.37 (s, 2H), 2.34 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 171.5 (d, *J* = 3.7 Hz), 160.3 (d, *J* = 243.7 Hz), 150.0 (d, *J* = 2.5 Hz), 137.3, 136.7 (d, *J* = 11.2 Hz), 134.0, 129.7, 129.2, 123.7 (d, *J* = 10.0 Hz), 114.6 (d, *J* = 25.0 Hz), 107.8 (d, *J* = 26.3 Hz), 40.3, 21.2. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -116.67. ESI-MS calc'd for C<sub>15</sub>H<sub>13</sub>FNS [M+H]<sup>+</sup>: 258.0747, found 258.0748.



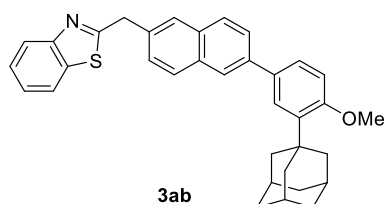
2-(4-ethylbenzyl)-6-(trifluoromethyl)benzo[*d*]thiazole (**3y**): Prepared according to General Procedure D. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 160:1) to yield product **3y** (0.031 g, 48%) as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.07 (dd, *J* = 5.1, 3.4 Hz, 2H), 7.69 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 4.43 (s, 2H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.24 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 175.3, 155.5, 143.8, 135.9, 134.0, 129.3, 128.6, 127.1 (q, *J* = 32.5 Hz), 124.3 (q, *J* = 270.0 Hz), 123.3, 123.1 (q, *J* = 3.7 Hz), 119.3 (q, *J* = 5.0 Hz), 40.5, 28.6, 15.6. <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -61.37. ESI-MS calc'd for C<sub>17</sub>H<sub>15</sub>F<sub>3</sub>NS [M+H]<sup>+</sup>: 322.0872, found 322.0873.



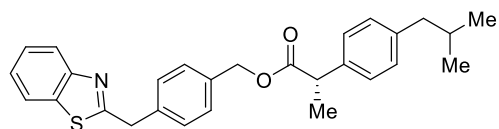
6-chloro-2-(4-ethylbenzyl)benzo[*d*]thiazole (**3z**): Prepared according to General Procedure D. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 170:1) to yield product **3z** (0.034 g, 59%) as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.88 (d, *J* = 8.7 Hz, 1H), 7.74 (d, *J* = 2.1 Hz, 1H), 7.40 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.31 – 7.21 (m, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 4.38 (s, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 172.4, 152.0, 143.7, 137.0, 134.2, 130.8, 129.2, 128.6, 126.8, 123.6, 121.2, 40.4, 28.6, 15.6. ESI-MS calc'd for C<sub>16</sub>H<sub>15</sub><sup>35</sup>ClNS [M+H]<sup>+</sup>: 288.0608, found 288.0608.



5-chloro-2-(4-ethylbenzyl)benzo[*d*]thiazole (**3aa**): Prepared according to General Procedure D. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 170:1) to yield product **3aa** (0.036 g, 63%) as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 2.0 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 1H), 7.31 – 7.24 (m, 3H), 7.18 (d, *J* = 7.8 Hz, 2H), 4.38 (s, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 173.9, 154.3, 143.7, 134.2, 134.1, 132.0, 129.2, 128.5, 125.4, 122.8, 122.3, 40.4, 28.6, 15.6. ESI-MS calc'd for C<sub>16</sub>H<sub>15</sub><sup>35</sup>ClNS [M+H]<sup>+</sup>: 288.0608, found 288.0607.

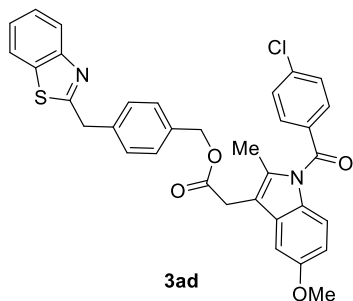


2-((6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)methyl) benzo[*d*]thiazole (**3ab**): Prepared according to General Procedure C. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 50:1) to yield product **3ab** (0.055 g, 53%) as white solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 1.9 Hz, 1H), 7.89 – 7.80 (m, 3H), 7.78 – 7.71 (m, 2H), 7.58 (d, *J* = 2.4 Hz, 1H), 7.52 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.37 – 7.30 (m, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 4.61 (s, 2H), 3.89 (s, 3H), 2.18 (d, *J* = 2.9 Hz, 6H), 2.11 – 1.99 (m, 3H), 1.80 (d, *J* = 3.5 Hz, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 171.4, 158.7, 153.4, 139.3, 139.0, 135.9, 134.4, 133.2, 133.1, 132.5, 128.9, 128.2, 127.8, 127.6, 126.3, 126.1, 126.0, 125.7, 125.0, 122.9, 121.7, 112.2, 55.3, 41.0, 40.7, 37.3, 37.3, 29.2. ESI-MS calc'd for C<sub>35</sub>H<sub>34</sub>NOS [M+H]<sup>+</sup>: 516.2356, found 516.2356.



**3ac**

4-(benzo[*d*]thiazol-2-ylmethyl)benzyl (S)-2-(4-isobutylphenyl)propanoate (**3ac**): Prepared according to General Procedure C. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 30:1) to yield product **3ac** (0.062 g, 70%) as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.31 (dd, *J* = 19.8, 7.7 Hz, 3H), 7.24 – 7.13 (m, 4H), 7.07 (d, *J* = 7.8 Hz, 2H), 5.08 (d, *J* = 2.9 Hz, 2H), 4.41 (s, 2H), 3.74 (q, *J* = 7.1 Hz, 1H), 2.42 (d, *J* = 7.2 Hz, 2H), 1.82 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.50 (d, *J* = 7.2 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 174.6, 170.8, 153.4, 140.7, 137.7, 137.1, 135.8, 135.3, 129.4, 129.3, 128.4, 127.3, 126.1, 125.0, 122.9, 121.6, 66.0, 45.2, 45.1, 40.4, 30.3, 22.5, 18.5. ESI-MS calc'd for C<sub>28</sub>H<sub>29</sub>NNaO<sub>2</sub>S [M+Na]<sup>+</sup>: 466.1811, found 466.1810.

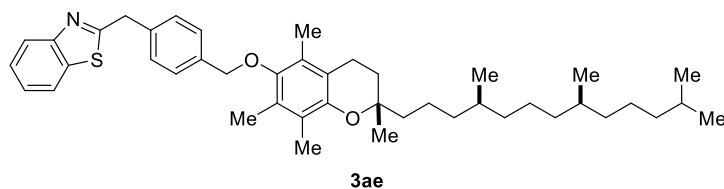


**3ad**

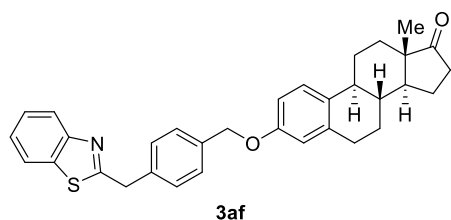
4-(benzo[*d*]thiazol-2-ylmethyl)benzyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (**3ad**): Prepared according to General Procedure C. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 8:1) to yield product **3ad** (0.057 g, 48%) as yellow viscous oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.44 (dd, *J* = 8.4, 2.3 Hz, 3H), 7.37 – 7.30 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 2.5 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 1H), 6.66 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.13 (s, 2H), 4.43 (s, 2H), 3.72 (d, *J* = 21.6 Hz, 5H), 2.36 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 170.8, 170.7,



168.4, 156.2, 153.4, 139.4, 137.5, 136.1, 135.7, 135.0, 134.0, 131.3, 130.9, 130.7, 129.5, 129.2, 128.8, 126.2, 125.0, 123.0, 121.7, 115.1, 112.6, 112.0, 101.3, 66.5, 55.8, 40.4, 30.5, 13.5. ESI-MS calc'd for  $C_{34}H_{27}^{35}ClN_2NaO_4S$   $[M+Na]^+$ : 617.1272, found 617.1275.



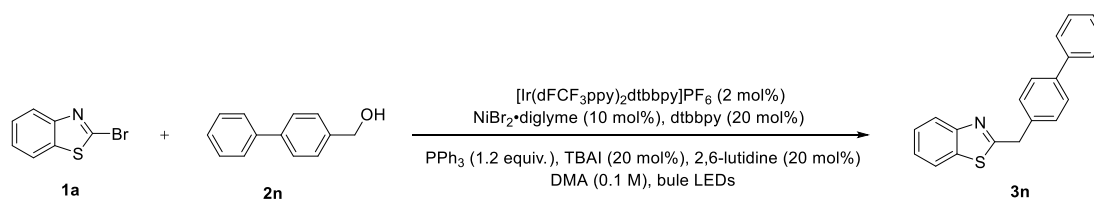
2-(4-(((S)-2,5,7,8-tetramethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)methyl)benzyl)benzo[*d*]thiazole (**3ae**): Prepared according to General Procedure C. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 50:1) to yield product **3ae** (0.081 g, 61%) as colorless oil.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.00 (d,  $J = 8.2$  Hz, 1H), 7.78 (d,  $J = 8.0$  Hz, 1H), 7.50 – 7.42 (m, 3H), 7.40 (d,  $J = 7.8$  Hz, 2H), 7.32 (t,  $J = 7.6$  Hz, 1H), 4.68 (s, 2H), 4.45 (s, 2H), 2.58 (t,  $J = 6.9$  Hz, 2H), 2.33 – 1.98 (m, 9H), 1.89 – 1.67 (m, 2H), 1.53 (dd,  $J = 13.6, 6.7$  Hz, 3H), 1.39 (td,  $J = 11.0, 5.0$  Hz, 4H), 1.25 (d,  $J = 9.5$  Hz, 11H), 1.17 – 1.03 (m, 6H), 0.85 (dd,  $J = 10.5, 6.3$  Hz, 12H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  171.2, 153.4, 148.2, 148.1, 137.4, 136.8, 135.8, 129.4, 128.3, 128.0, 126.1, 126.0, 124.9, 123.1, 122.9, 121.6, 117.7, 74.9, 74.4, 40.5, 40.2, 39.5, 37.6, 37.6, 37.5, 37.4, 32.9, 32.8, 31.4, 28.1, 24.9, 24.7, 24.0, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 13.0, 12.1, 12.0. ESI-MS calc'd for  $C_{44}H_{61}NNaO_2S$   $[M+Na]^+$ : 690.4315, found 690.4315.



(8R,9S,13S,14S)-3-((4-(benzo[*d*]thiazol-2-ylmethyl)benzyl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (**3af**): Prepared according to General Procedure C. The residue was purified by flash column

chromatography on silica gel (hexane/EtOAc = 7:1) to yield product **3af** (0.059 g, 58%) as white viscous oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 7.0 Hz, 4H), 7.20 (d, *J* = 8.6 Hz, 1H), 7.15 (d, *J* = 8.5 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 1H), 6.72 (s, 1H), 6.69 – 6.59 (m, 1H), 5.02 (s, 2H), 4.45 (s, 2H), 2.94 – 2.82 (m, 2H), 2.38 (dd, *J* = 10.2, 5.1 Hz, 1H), 2.24 (d, *J* = 9.7 Hz, 1H), 2.15 (dt, *J* = 18.5, 8.7 Hz, 1H), 2.10 – 1.86 (m, 4H), 1.63 – 1.42 (m, 6H), 0.91 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 221.4, 171.2, 156.9, 153.2, 138.0, 136.9, 136.5, 135.7, 132.5, 129.5, 128.1, 126.5, 126.2, 125.0, 122.9, 121.7, 115.0, 112.4, 69.7, 50.5, 48.2, 44.1, 40.4, 38.4, 36.0, 31.6, 29.8, 26.6, 26.0, 21.7, 14.0. ESI-MS calc'd for C<sub>33</sub>H<sub>33</sub>NNaO<sub>2</sub>S [M+Na]<sup>+</sup>: 530.2124, found 530.2127.

#### 4. Gram-Scale Synthesis



In an Ar-filled glovebox, dtbbpy (0.107 g, 0.4 mmol, 20 mol%), NiBr<sub>2</sub>·diglyme (0.070 g, 0.2 mmol, 10 mol%) were added to a 50 mL RBF with a magnetic stir, then DMA (20.0 mL) was added via syringe. The reaction mixture was stirred for 0.5 h at room temperature. To another RBF with a magnetic stir, 2-bromobenzothiazole **1a** (0.428 g, 2 mmol, 1 equiv.), biphenyl-4-methanol **2n** (1.105 g, 6 mmol, 3 equiv.), triphenylphosphine (0.629 g, 2.4 mmol, 1.2 equiv.), tetrabutylammonium iodide (0.148 g, 0.4 mmol, 20 mol%) and [Ir(dFCF<sub>3</sub>ppy)<sub>2</sub>dtbbpy]PF<sub>6</sub> (0.045 g, 0.04 mmol, 2 mol%) were added in the glovebox. The RBF was capped and removed from the glovebox, 2,6-lutidine (0.047 mL, 0.4 mmol, 20 mol%) was added via micro-syringe and the above-mentioned freshly prepared solvent of nickel/ligand in DMA was added via syringe immediately. The mixture was stirred under irradiation at a distance of ~5 cm from two 15 W blue LEDs for 3 h, and the temperature was controlled at approximately 30 °C by cooling with a fan and air conditioner. The mixture was diluted with EtOAc

(25 mL) and water (50 mL), and the aqueous and organic layers were separated. The aqueous layer was extracted with EtOAc (25 mL×2). The combined organic layers were washed with water (50 mL×2) and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 120:1) to give the corresponding product **3n** (0.401 g, 67%) as white solid.



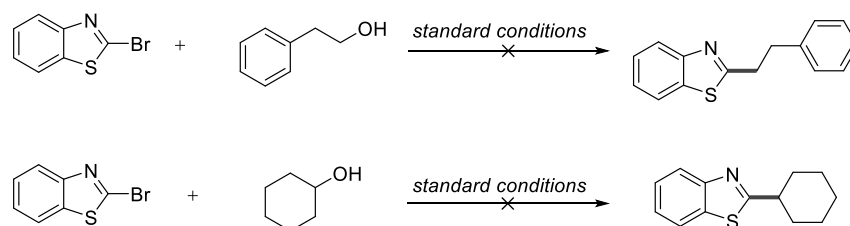
Fig. S2 Reaction setup for gram-scale synthesis

## 5. Unsuccessful Substrates

A) reaction using phenyl bromide:



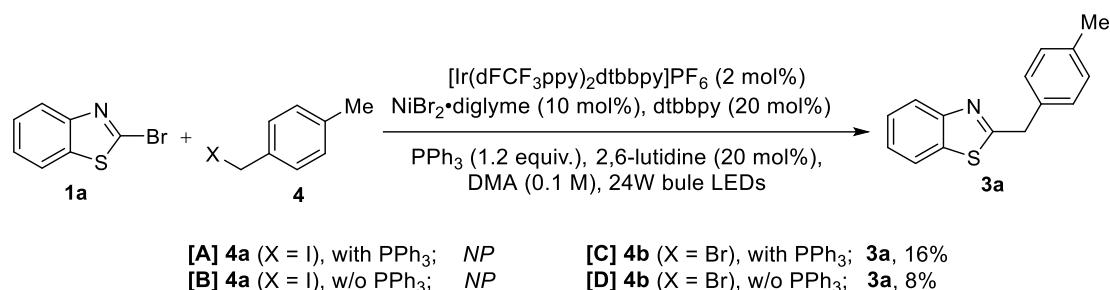
B) reaction using inactive alkyl alcohol (*primary or secondary*):



The phenyl bromide and inactive primary or secondary alkyl alcohols were individually explored under standard conditions, however, all of them failed to give a product.

## 6. Mechanistic Studies

### 6.1 Experiment with Benzyl Halide

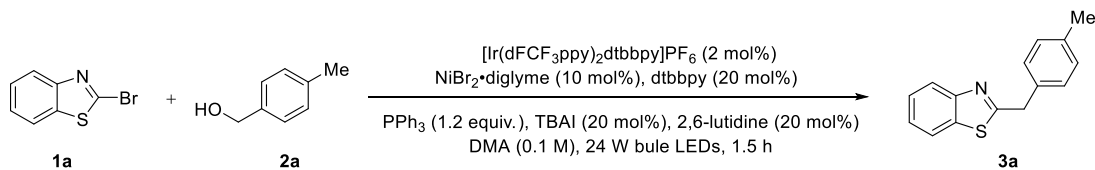


In an Ar-filled glovebox, dtbbpy (0.011 g, 0.04 mmol, 20 mol%), NiBr<sub>2</sub>·diglyme (0.007 g, 0.02 mmol, 10 mol%) were added to a 10 mL vial with a magnetic stir, then DMA (2.0 mL) was added via syringe. The reaction mixture was stirred for 0.5 h at room temperature. To another vial with a magnetic stir, 2-bromobenzothiazole **1a** (0.043 g, 0.2 mmol, 1 equiv.), benzyl halide **4** (0.6 mmol, 3 equiv.), [A][C] triphenylphosphine (0.063 g, 0.24 mmol, 1.2 equiv.)/[B][D] without triphenylphosphine, and [Ir(dFCF<sub>3</sub>ppy)<sub>2</sub>dtbbpy]PF<sub>6</sub> (0.004 g, 0.004 mmol, 2 mol%) were added in the glovebox. The vial was capped and removed from the glovebox, 2,6-lutidine (0.004 mL, 0.04 mmol, 20 mol%) was added via micro-syringe and the above-mentioned freshly prepared solvent of nickel/ligand in DMA was added via syringe immediately. The resulting mixture was stirred under irradiation at a distance of ~1 cm from 4 x 6 W blue LEDs ( $\lambda = 450\text{-}465$  nm) for 3 h.

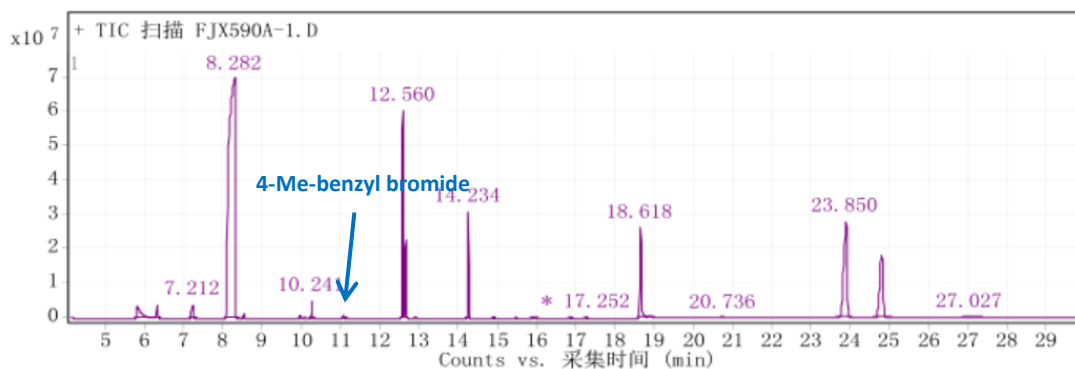
*No desired product **3a** formed when benzyl iodide **4a** was employed, thereby excluding the involvement of benzyl iodide species in the catalysis.*

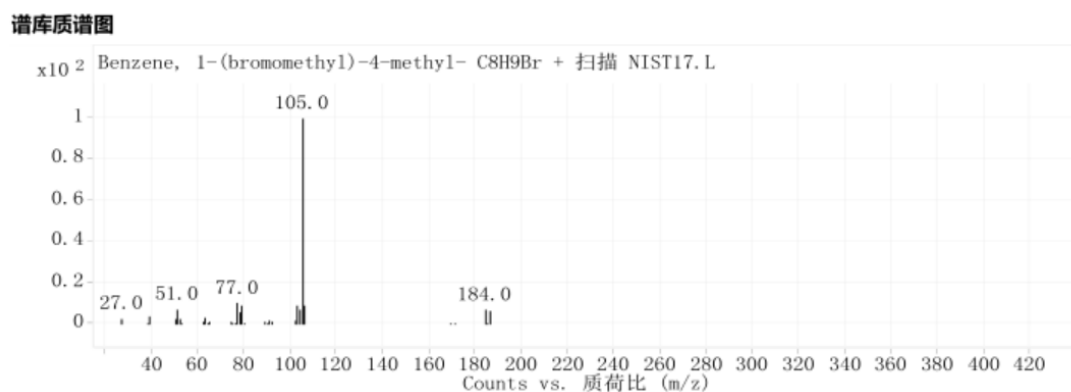
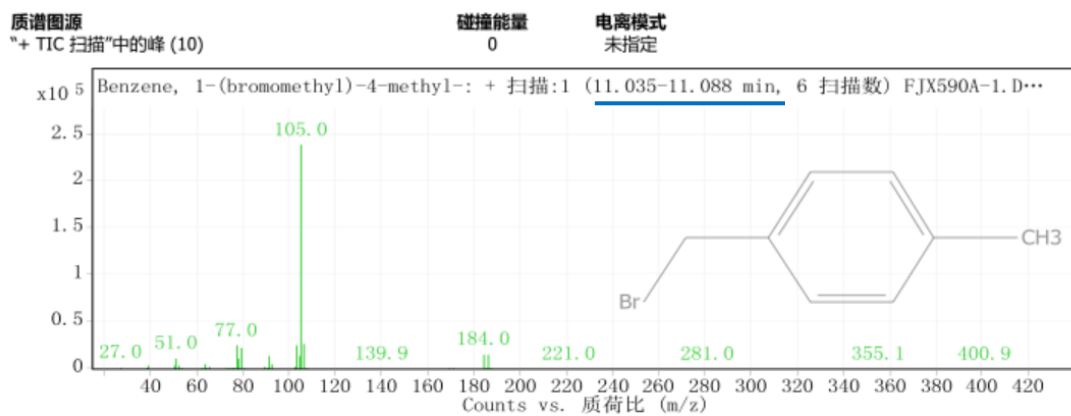
*When benzyl bromide **4b** was employed, the desired product **3a** was formed in yields of 16% and 8%, respectively, alluding that it might be involved as an intermediate.*

### 6.2 GC-MS Analysis for Probing Benzyl Bromide Intermediacy

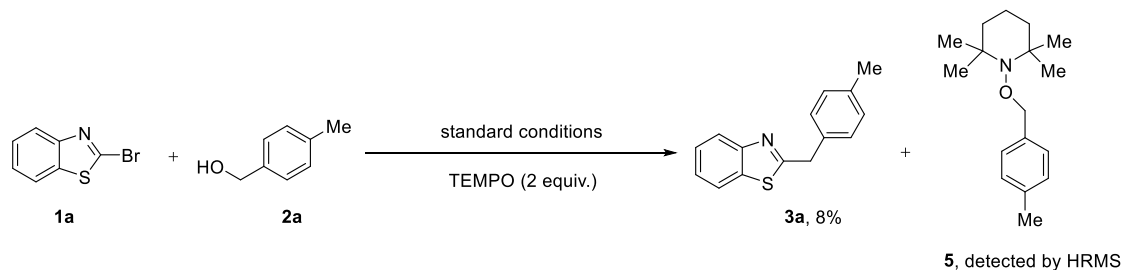


In an Ar-filled glovebox, dtbbpy (0.011 g, 0.04 mmol, 20 mol%),  $\text{NiBr}_2\cdot\text{diglyme}$  (0.007 g, 0.02 mmol, 10 mol%) were added to a 10 mL vial with a magnetic stir, then DMA (2.0 mL) was added via syringe. The reaction mixture was stirred for 0.5 h at room temperature. To another vial with a magnetic stir, 2-bromobenzothiazole **1a** (0.043 g, 0.2 mmol, 1 equiv.), 4-methylbenzyl alcohol **2a** (0.073 g, 0.6 mmol, 3 equiv.), triphenylphosphine (0.063 g, 0.24 mmol, 1.2 equiv.), tetrabutylammonium iodide (0.015 g, 0.04 mmol, 20 mol%) and  $[\text{Ir}(\text{dFCF}_3\text{ppy})_2\text{dtbbpy}]\text{PF}_6$  (0.004 g, 0.004 mmol, 2 mol%) were added in the glovebox. The vial was capped and removed from the glovebox, and 2,6-lutidine (0.004 mL, 0.04 mmol, 20 mol%) was added via microsyringe and the above-mentioned freshly prepared solvent of nickel/ligand in DMA was added via syringe immediately. The resulting mixture was stirred under irradiation at a distance of  $\sim 1$  cm from 4 x 6 W blue LEDs ( $\lambda = 450\text{-}465$  nm) for 1.5 h. *The reaction mixture was analyzed by GC-MS, and benzyl bromide was detected, further supporting that benzyl bromide might be a crucial intermediate in the catalysis.*



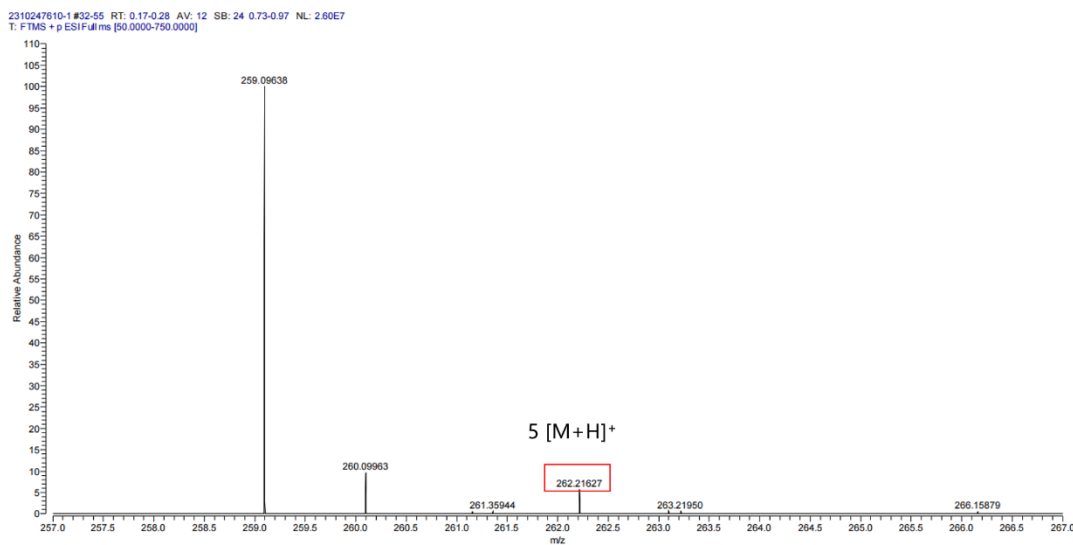


### 6.3 TEMPO Radical-Trapping Experiment



To probe the radical intermediate in our metallaphotoredox reaction, a TEMPO radical-trapping experiment was performed. In an Ar-filled glovebox, dtbbpy (0.011 g, 0.04 mmol, 20 mol%), NiBr<sub>2</sub>•diglyme (0.007 g, 0.02 mmol, 10 mol%) were added to a 10 mL vial with a magnetic stir, then DMA (2.0 mL) was added via syringe. The reaction mixture was stirred for 0.5 h at room temperature. To another vial with a magnetic stir, 2-bromobenzothiazole **1a** (0.043 g, 0.2 mmol, 1 equiv.), 4-methylbenzyl alcohol **2a** (0.073 g, 0.6 mmol, 3 equiv.), triphenylphosphine (0.063 g, 0.24 mmol, 1.2 equiv.), tetrabutylammonium iodide (0.015 g, 0.04 mmol, 20 mol%), [Ir(dFCF<sub>3</sub>ppy)<sub>2</sub>dtbbpy]PF<sub>6</sub> (0.004 g, 0.004 mmol, 2 mol%) and TEMPO (0.062 g, 0.4

mmol, 2 equiv.) were added in the glovebox. The vial was capped and removed from the glovebox, and 2,6-lutidine (0.004 mL, 0.04 mmol, 20 mol%) was added via microsyringe and the above-mentioned freshly prepared solvent of nickel/ligand in DMA was added via syringe immediately. The resulting mixture was stirred under irradiation at a distance of ~1 cm from 4 x 6 W blue LEDs ( $\lambda = 450\text{-}465\text{ nm}$ ) for 3 h. The mixture was diluted with EtOAc (5 mL) and water (15 mL), and the aqueous and organic layers were separated. The aqueous layer was extracted with EtOAc (10 mL $\times$ 2). The combined organic layers were washed with water (20 mL $\times$ 2) and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel (hexane/EtOAc = 120:1) to give the corresponding product **3a** (0.004 g, 8%) as colorless liquid. The TEMPO radical-trapping experiment dramatically halted the generation of the product, whereas benzyl-trapped TEMPO adduct **5** was detected by HRMS (ESI, m/z). Calcd for C<sub>17</sub>H<sub>28</sub>NO [M+H]<sup>+</sup>: 262.2165, found: 262.2163. *The result implied that benzyl radical might be involved in the reaction.*



## 6.4 Benzylic Radical Probe Experiment with Cyclopropanemethanol





## 6.5 Stern-Volmer Quenching Experiments

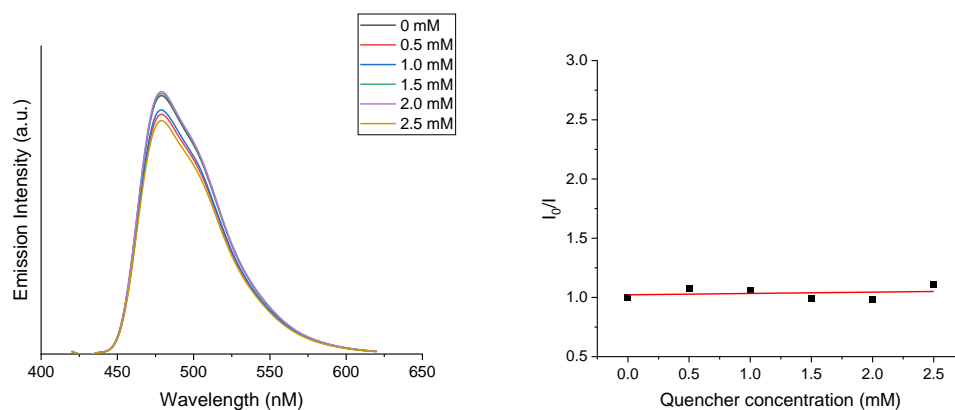
### Formulation Solution:

All solutions and samples were prepared in an Ar-filled glovebox, sealed well with electrical tape and analyzed immediately. A stock solution of  $[\text{Ir}(\text{dFCF}_3\text{ppy})_2\text{dtbbpy}]\text{PF}_6$  (14 mg in 5 mL DMA,  $2.5 \times 10^{-3}$  M) was diluted 0.5 mL into DMA (4.5 mL) for a concentration of  $[\text{Ir}]$  ( $2.5 \times 10^{-4}$  M). This stock solution ( $2.5 \times 10^{-4}$  M) was diluted 2 mL into DMA (18 mL) for an active concentration of  $[\text{Ir}]$  ( $2.5 \times 10^{-5}$  M).

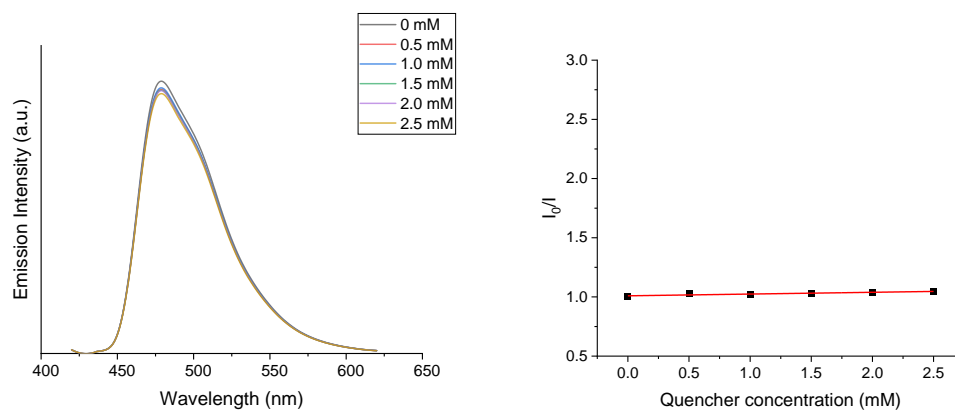
Stock solutions of  $\text{PPh}_3$ , 2,6-lutidine, 2-bromobenzothiazole, 4-methylbenzyl alcohol and TBAI were all dissolved in DMA (2 mL) to set the concentration to be 0.1 M.

### Experimental Procedure:

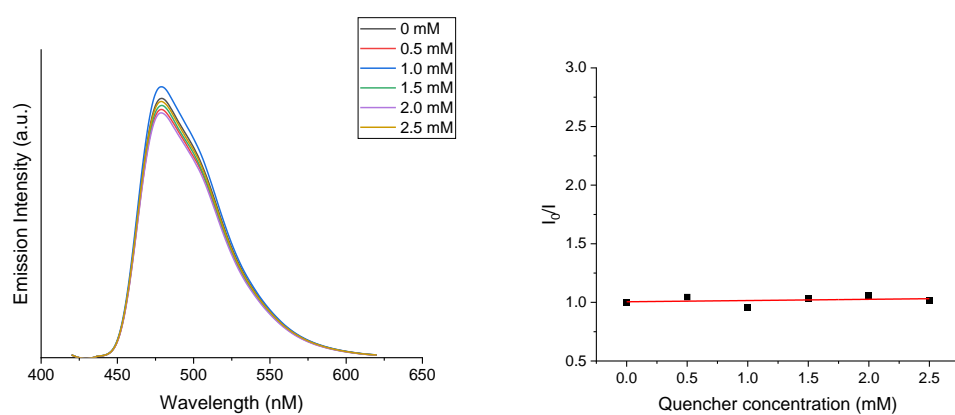
The resulting  $[\text{Ir}(\text{dFCF}_3\text{ppy})_2\text{dtbbpy}]\text{PF}_6$  solution ( $2.5 \times 10^{-5}$  M, 2 mL) was added to cuvette, and into this solution, 10.0  $\mu\text{L}$  of quencher solution was successively added and uniformly mixed. For the emission quenching, the solutions were irradiated at 320 nm and fluorescence was measured from 420 nm to 620 nm. The emission intensities at the maximum emission wavelength ( $\lambda = 477$  nm) were recorded for different concentrations of quencher (Q), where  $[\text{Q}] = 0\text{--}2.5$  mM. Fluorescence emission spectra were recorded (3 trials per sample). Follow this method and make changes to the amount to obtain the Stern–Volmer relationship in turn.



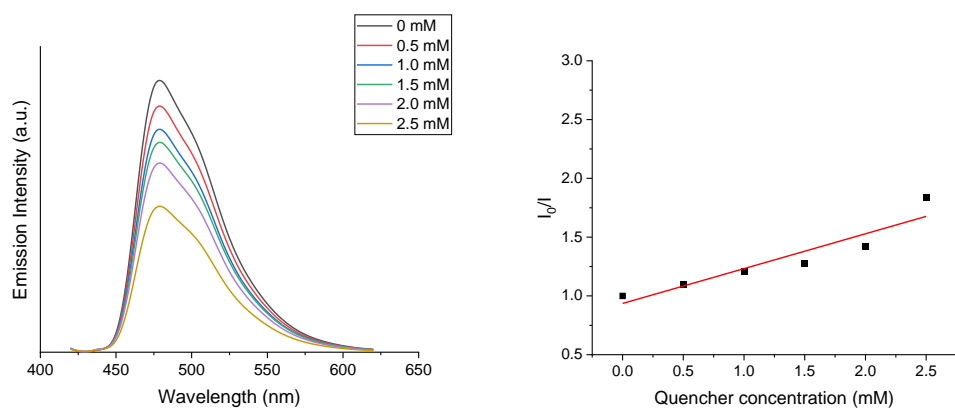
**Fig. S3** Fluorescence quenching of  $[\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2[\text{dtbbpy}]]\text{PF}_6$  by 2,6-lutidine



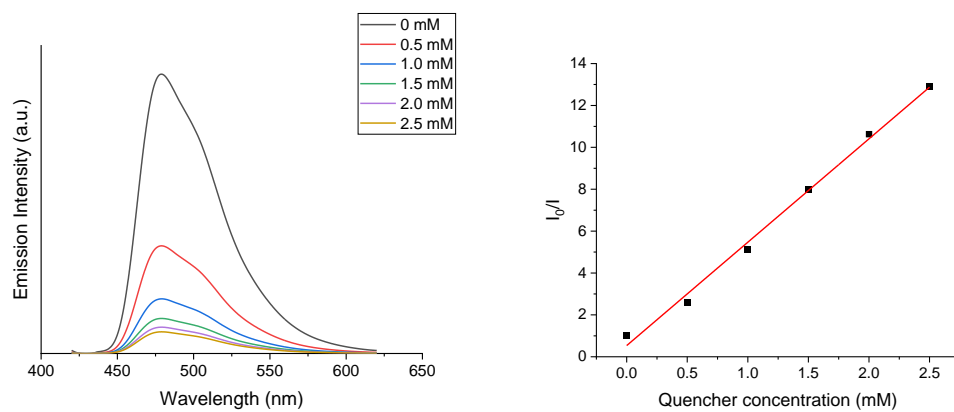
**Fig. S4** Fluorescence quenching of  $[\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2[\text{dtbbpy}]]\text{PF}_6$  by 4-methylbenzyl alcohol



**Fig. S5** Fluorescence quenching of  $[\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2[\text{dtbbpy}]]\text{PF}_6$  by 2-bromobenzothiazole



**Fig. S6** Fluorescence quenching of  $[\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2[\text{dtbbpy}]]\text{PF}_6$  by  $\text{PPh}_3$



**Fig. S7** Fluorescence quenching of  $[\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2[\text{dtbbpy}]]\text{PF}_6$  by TBAI

## 7. References

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- [3] Hanson, S.K.; Wu, R.; Silks, L.A. *Angew. Chem. Int. Ed.* **2012**, *51*, 3410–3413.

## 8. NMR Spectra

