

## Supporting Information

### Sulfonamides as new hydrogen atom transfer (HAT) catalysts for photoredox allylic and benzylic C-H arylations

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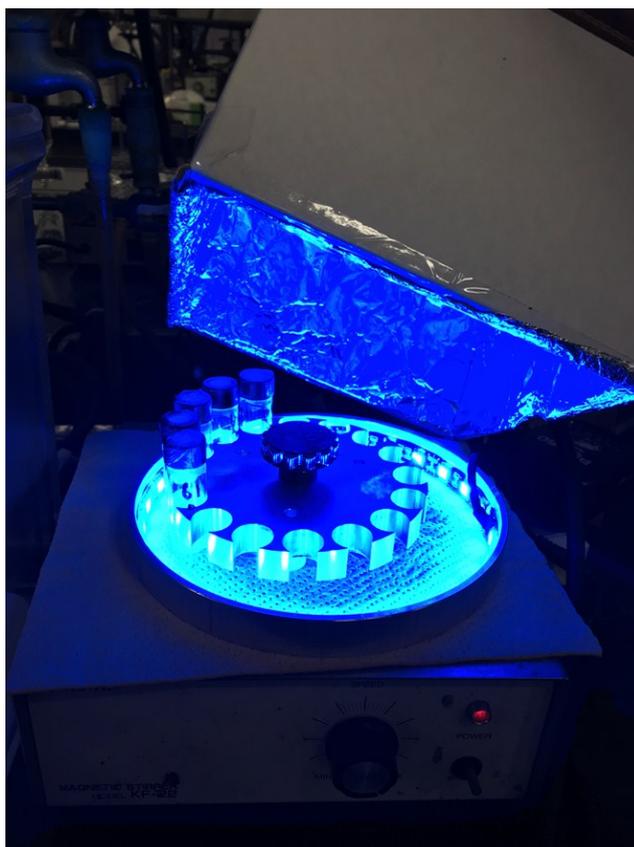
#### **1. General Method**

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on JEOL JNM-LA 500, JEOL ECX500 (500 MHz for <sup>1</sup>H NMR, 125 MHz for <sup>13</sup>C NMR), and JEOL ECS400 (400 MHz for <sup>1</sup>H NMR, 100 MHz for <sup>13</sup>C NMR) spectrometer. Chemical shifts were reported downfield from an internal standard (1,1,2,2-tetrachloroethane ( $\delta = 5.95$  ppm) or nitromethane ( $\delta = 4.33$  ppm)) or the solvent used as an internal reference for <sup>1</sup>H NMR or <sup>13</sup>C NMR. Column chromatographies were performed with silica gel Merck 60 (230-400 mesh ASTM) or by Biotage® Isolera™ One 3.0 with pre-packed column of Biotage® SNAP Ultra. Gel permeation chromatography was performed on a recycling preparative HPLC LC9210 NEXT system, Japan Analytical Industry Co., Ltd. All solvents and reagents were used without further purification (purchased from Aldrich, Tokyo Chemical Industry Co., Ltd. (TCI), Kanto Chemical Co., Inc., and Wako Pure Chemical Industries, Ltd.). NMR yield was calculated by <sup>1</sup>H NMR of crude product using an internal standard (1,1,2,2-tetrachloroethane or nitromethane).

## 2. General Procedure for the Arylation Reaction

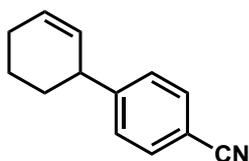
To a glass screw top vial (4 mL) with a cap equipped with a magnetic stirring bar were added potassium carbonate (0.01 mmol, 10 mol%), sulfonamide **4** (0.01 mmol, 10 mol%), and degassed acetone by freeze-pump-thaw (FPT) cycling. After the mixture was stirred at room temperature for 30 min, 1,4-dicyanobenzene (**1**, 0.1 mmol, 1.0 equiv), a substrate alkene or ether (**2**, 0.5 mmol, 5.0 equiv), and *tris*[2-(4,6-difluorophenyl)pyridinato-*C*<sub>2</sub>,*N*]iridium(III) (2 μmol, 2 mol%) were added to the mixture, and the vial was sealed under argon atmosphere. The reaction mixture was then placed in Aldrich® Micro Photochemical Reactor<sup>§</sup> and irradiated with blue LED lights for 24 hours at 40 °C. The reaction mixture was then diluted with water and brine, and products were extracted with AcOEt. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated by rotary evaporator after filtration. The residue was purified by a flash chromatography on silica gel to afford arylation product **3**.

<sup>§</sup>The reaction was performed inside of a cardboard box, of which inner walls are covered with aluminum foil to keep the internal temperature at 40 °C.



## 3. Compound Characterization Data

4-(cyclohex-2-en-1-yl)benzonitrile (**3a**)



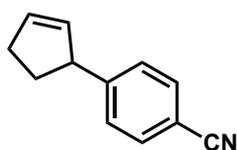
Prepared according to the general procedure, then the crude material was purified by flash column chromatography (SiO<sub>2</sub>, AcOEt / Hexane = 1:10) to afford **3a** as a colorless oil (85%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 5.98–5.92 (m, 1H), 5.68–5.62 (m, 1H), 3.49–3.42 (m, 1H), 2.14–2.06 (m, 2H), 2.06–1.97 (m, 1H), 1.77–1.68 (m, 1H), 1.68–1.58 (m, 1H), 1.57–1.47 (m, 1H).

All the spectroscopic data matches with the previously reported data.

Ref) J. D. Cuthbertson and D. W. C. MacMillan, *Nature*, 2015, **519**, 74.

#### 4-(cyclopent-2-en-1-yl)benzonitrile (**3b**)



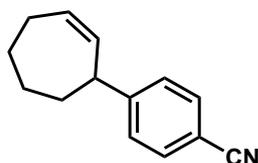
Prepared according to the general procedure, then the crude material was purified by flash column chromatography (SiO<sub>2</sub>, AcOEt / Hexanes = 1:10) to afford the **3b** as a colorless oil (95%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.57 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 6.01–5.99 (m, 1H), 5.73–5.72 (m, 1H), 3.94–3.91 (m, 1H), 2.55–2.40 (m, 3H), 1.72–1.58 (m, 1H)

All the spectroscopic data matches with the previously reported data.

Ref) J. D. Cuthbertson and D. W. C. MacMillan, *Nature*, 2015, **519**, 74.

#### 4-(cyclohept-2-en-1-yl)benzonitrile (**3c**)



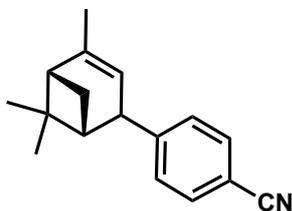
Prepared according to the general procedure, then the crude material was purified by flash column chromatography (SiO<sub>2</sub>, AcOEt / Hexanes = 1:10) to afford **3c** as a colorless oil (68%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.92–5.86 (m, 1H), 5.69–5.62 (m, 1H), 3.60–3.56 (m, 1H), 2.31–2.15 (m, 2H), 1.98–1.89 (m, 1H), 1.84–1.62 (m, 4H), 1.50–1.40 (m, 1H)

All the spectroscopic data matches with the previously reported data.

Ref) J. D. Cuthbertson and D. W. C. MacMillan, *Nature*, 2015, **519**, 74.

**4-((1R,5S)-4,6,6-trimethylbicyclo[3.1.1]hept-3-en-2-yl)benzotrile (3d)**



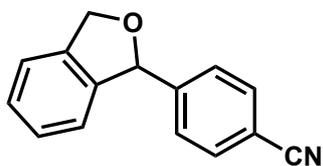
Prepared according to the general procedure, then the crude material was purified by flash column chromatography (SiO<sub>2</sub>, AcOEt / Hexanes = 1:10) to afford an inseparable mixture of the **3d** and minor uncharacterized isomeric products (54%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.32-5.29 (m, 1H), 3.63-3.59 (m, 1H), 2.13-2.04 (m, 3H), 1.80-1.78 (m, 3H), 1.33 (s, 3H), 1.22-1.17 (m, 1H), 1.00 (s, 3H).

All the spectroscopic data matches with the previously reported data.

Ref) J. D. Cuthbertson and D. W. C. MacMillan, *Nature*, 2015, **519**, 74.

**4-(1,3-dihydroisobenzofuran-1-yl)benzotrile (3e)**



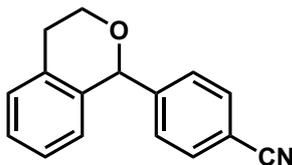
Prepared according to the general procedure, then the crude material was purified by flash column chromatography (SiO<sub>2</sub>, AcOEt / Hexanes = 1:4) to afford **3e** as a colorless oil (86%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.65 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.34-7.30 (m, 2H), 7.28-7.22 (m, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.20 (s, 1H), 5.37 (dd, *J* = 2.9, 12.0 Hz, 1H), 5.25 (dd, *J* = 1.7, 12.0 Hz, 1H).

All the spectroscopic data matches with the previously reported data.

Ref) K. Qvortrup, D. A. Rankic and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2014, **136**, 626.

**4-(isochroman-1-yl)benzotrile (3f)**



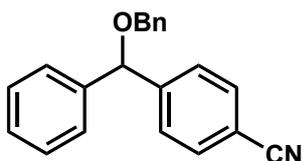
Prepared according to the general procedure, then the crude material was purified by flash column chromatography (SiO<sub>2</sub>, AcOEt / Hexanes = 1:4) to afford **3f** as a colorless oil (95%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 8.0$  Hz, 2H), 7.44 (d,  $J = 8.0$  Hz, 2H), 7.23-7.17 (m, 2H), 7.10 (dt,  $J = 5.8, 2.3$  Hz, 1H), 6.68 (d,  $J = 8.0$  Hz, 1H), 5.77 (s, 1H), 4.20-4.15 (m, 1H), 3.98-3.92 (m, 1H), 3.19-3.11 (m, 1H), 2.87-2.80 (m, 1H).

All the spectroscopic data matches with the previously reported data.

Ref) K. Qvortrup, D. A. Rankic and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2014, **136**, 626.

#### 4-((benzyloxy)(phenyl)methyl)benzonitrile (**3g**)



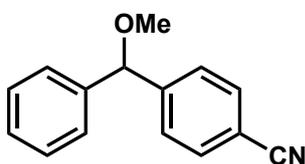
Prepared according to the general procedure, then the crude material was purified by flash column chromatography ( $\text{SiO}_2$ , AcOEt / Hexanes = 1:10) to afford **3g** as a colorless oil (82%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (d,  $J = 8.0$  Hz, 2H), 7.50 (d,  $J = 8.6$  Hz), 7.40-7.28 (m, 10 H), 5.46 (s, 1H), 4.57 (d,  $J = 12.0$  Hz, 1H), 4.50 (d,  $J = 12.0$  Hz, 1H).

All the spectroscopic data matches with the previously reported data.

Ref) K. Qvortrup, D. A. Rankic and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2014, **136**, 626.

#### 4-(methoxy(phenyl)methyl)benzonitrile (**3h**)



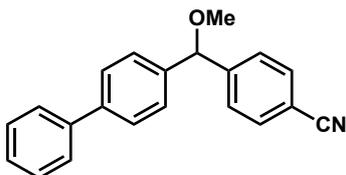
Prepared according to the general procedure, then the crude material was purified by flash column chromatography ( $\text{SiO}_2$ , AcOEt / Hexanes = 1:10) to afford **3h** as a colorless oil (99%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (d,  $J = 8.0$  Hz, 2H), 7.43 (d,  $J = 8.0$  Hz, 2H), 7.35-7.22 (m, 5H), 5.23 (s, 1H), 3.04 (s, 3H).

All the spectroscopic data matches with the previously reported data.

Ref) K. Qvortrup, D. A. Rankic and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2014, **136**, 626.

#### 4-([1,1'-biphenyl]-4-yl(methoxy)methyl)benzonitrile (**3i**)



Prepared according to the general procedure, then the crude material was purified by flash column

chromatography (SiO<sub>2</sub>, AcOEt / Hexanes = 1:10) to afford **3i** as a white solid (48%).

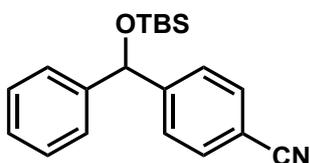
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.63 (d, *J* = 8.6 Hz, 2H), 7.60-7.55 (m, 4H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.38-7.34 (m, 1H), 5.32 (s, 1H), 3.42 (s, 3H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 147.5, 141.1, 140.5, 139.6, 132.3, 128.8, 127.4, 127.4, 127.3, 127.0, 118.8, 111.2, 84.4, 57.1, 22.6.

IR (KBr) cm<sup>-1</sup> 3424, 2932, 2361, 2227, 1607, 1486, 1407, 1193, 1092, 830, 754, 698.

HRMS (ESI) *m/z* calc. for C<sub>21</sub>H<sub>17</sub>NONa ([M+Na]<sup>+</sup>) 322.1208, found 322.1227.

#### 4-(((*tert*-butyldimethylsilyloxy)(phenyl)methyl)benzonitrile (**3j**))



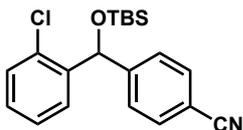
Prepared according to the general procedure, then the crude material was purified by flash column chromatography (SiO<sub>2</sub>, AcOEt / Hexanes = 1:10) to afford **3j** as a colorless oil (74%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.33-7.22 (m, 5H), 5.76 (s, 1H), 0.91 (s, 9H), 0.01 (s, 3H), -0.04 (s, 3H).

All the spectroscopic data matches with the previously reported data.

Ref) K. Qvortrup, D. A. Rankic and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2014, **136**, 626.

#### 4-(((*tert*-butyldimethylsilyloxy)(2-chlorophenyl)methyl)benzonitrile (**3k**))



Prepared according to the general procedure, then the crude material was purified by flash column chromatography (SiO<sub>2</sub>, AcOEt / Hexanes = 1:10) to afford **3k** as a colorless oil (41%).

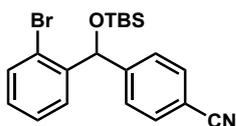
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.60-7.52 (m, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.20 (m, 1H), 6.25 (s, 1H), 0.90 (s, 9H), 0.03 (s, 3H), -0.04 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 149.27, 141.4, 132.1, 131.4, 129.3, 128.8, 128.4, 127.3, 126.8, 118.9, 110.8, 71.8, 25.7, 18.2, -4.9, -5.1.

IR (KBr) cm<sup>-1</sup> 2935, 2929, 2856, 2228, 1607, 1472, 1252, 1078, 1003, 884, 835, 774.

HRMS (ESI) *m/z* calc. for C<sub>20</sub>H<sub>24</sub>ClNOSiNa ([M+Na]<sup>+</sup>) 380.1208, found 380.1212.

#### 4-(((2-bromophenyl)((*tert*-butyldimethylsilyloxy)methyl)benzonitrile (**3l**))



Prepared according to the general procedure, then the crude material was purified by flash column chromatography (SiO<sub>2</sub>, AcOEt / Hexanes = 1:10) to afford as a colorless oil (36%).

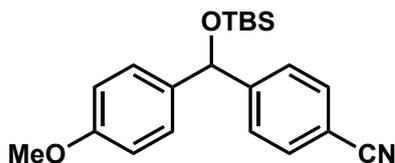
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60-7.49 (m, 6H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.12 (dt, *J* = 1.4, 8.2 Hz, 1H), 6.23 (s, 1H), 0.90 (s, 9H), 0.05 (s, 3H), -0.05 (s, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 149.3, 143.0, 132.6, 132.1, 129.2, 129.0, 128.0, 126.8, 121.7, 118.9, 110.8, 74.0, 25.7, 18.2, -4.8, -5.0.

IR (KBr) cm<sup>-1</sup> 3636, 2930, 2857, 2229, 1699, 1646, 1470, 1362, 1254, 1085, 1022, 839, 779.

HRMS (ESI) *m/z* calc. for C<sub>20</sub>H<sub>24</sub>BrNOSiNa ([M+Na]<sup>+</sup>) 424.0703, found 424.0715.

#### 4-((*tert*-butyldimethylsilyloxy)(4-methoxyphenyl)methyl)benzotrile (**3m**)



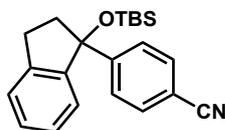
Prepared according to the general procedure, then the crude material was purified by flash column chromatography (SiO<sub>2</sub>, AcOEt / Hexanes = 1:10) to afford **3m** as a colorless oil (89%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 9.2 Hz, 2H), 6.84 (d, *J* = 9.2 Hz, 2H), 5.73 (s, 1H), 3.78 (s, 3H), 0.91 (s, 9H), 0.01 (s, 3H), -0.06 (s, 3H).

All the spectroscopic data matches with the previously reported data.

Ref) Y. Deng, Q. Liu and A. B. Smith, III, *J. Am. Chem. Soc.*, 2017, **139**, 9487.

#### 4-(1-((*tert*-butyldimethylsilyloxy)-2,3-dihydro-1H-inden-1-yl)methyl)benzotrile (**3n**)



Prepared according to the general procedure, then the crude material was purified by flash column chromatography (SiO<sub>2</sub>, AcOEt / Hexanes = 1:10) to afford **3n** as a colorless oil (76%).

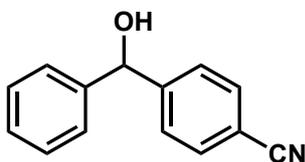
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.59 (d, *J* = 8.7 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.31-7.28 (m, 2H), 7.23-7.17 (m, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 3.16 (ddd, *J* = 7.8, 7.8, 16.0 Hz, 1H), 2.96 (ddd, *J* = 4.1, 8.7, 16.5 Hz, 1H), 2.49 (ddd, *J* = 4.1, 8.2, 13.7 Hz, 1H), 2.37 (ddd, *J* = 7.7, 7.8, 14.7 Hz, 1H), 0.93 (s, 9H), -0.24 (s, 3H), -0.41 (s, 3H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.0, 146.5, 144.5, 131.7, 128.9, 126.9, 126.5, 125.3, 125.0, 119.1, 110.2, 87.2, 45.6, 30.1, 25.9, 18.4, -3.3, -4.2.

IR (KBr)  $\text{cm}^{-1}$  2953, 2929, 2856, 2228, 1607, 1472, 1252, 1078, 1003, 884, 835, 774.

HRMS (ESI)  $m/z$  calc. for  $\text{C}_{22}\text{H}_{27}\text{NOSiNa}$  ( $[\text{M}+\text{Na}]^+$ ) 372.1754, found 372.1771.

#### 4-(hydroxy(phenyl)methyl)benzonitrile (**3o**)



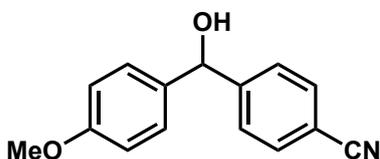
Prepared according to the general procedure, then the crude material was purified by flash column chromatography ( $\text{SiO}_2$ , AcOEt / Hexanes = 1:4) to afford a mixture of **3o** and benzyl alcohol, due to tough purification. The yield was determined by  $^1\text{H}$  NMR in the presence of 1,1,2,2-tetrachloroethane as an internal standard (43%)

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (d,  $J = 8.6$  Hz, 2H), 7.50 (d,  $J = 8.0$  Hz, 2H), 7.39-7.28 (m, 5H), 5.85 (s, 1H), 2.61 (bs, 1H).

All the spectroscopic data matches with the previously reported data.

Ref) K. Qvortrup, D. A. Rankic and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2014, **136**, 626.

#### 4-(hydroxy(4-methoxyphenyl)methyl)benzonitrile (**3p**)



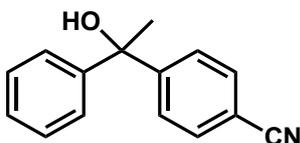
Prepared according to the general procedure, then the crude material was purified by flash column chromatography ( $\text{SiO}_2$ , AcOEt / Hexanes = 1:4) to afford a mixture of **3p** and *p*-methoxybenzyl alcohol, due to tough purification. The yield was determined by  $^1\text{H}$  NMR in the presence of 1,1,2,2-tetrachloroethane as an internal standard (46%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (d,  $J = 8.3$  Hz, 2H), 7.50 (d,  $J = 8.3$  Hz, 2H), 7.23 (d,  $J = 8.8$  Hz, 2H), 6.89 (d,  $J = 8.8$  Hz, 2H), 5.82 (s, 1H), 3.79 (s, 3H), 2.33 (s, 1H).

All the spectroscopic data matches with the previously reported data.

Ref) M. Chen, X. Zhao, C. Yang and W. Xia, *Org. Lett.*, 2017, **19**, 3807.

#### 4-(1-hydroxy-1-phenylethyl)benzonitrile (**3q**)



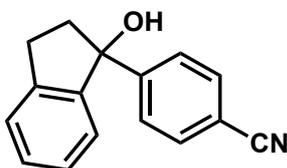
Prepared according to the general procedure, then the crude material was purified by flash column chromatography (SiO<sub>2</sub>, AcOEt / Hexanes = 1:4) to afford a mixture of **3q** and 1-phenylethan-1-ol, due to tough purification. The yield was determined by <sup>1</sup>H NMR in the presence of nitromethane as an internal standard (35%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.58 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.38-7.30 (m, 4H), 7.26 (t, *J* = 6.9 Hz, 1H), 2.25 (s, 1H), 1.94 (s, 3H).

All the spectroscopic data matches with the previously reported data.

Ref) K. Qvortrup, D. A. Rankic and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2014, **136**, 626.

#### 4-(1-hydroxy-2,3-dihydro-1H-inden-1-yl)benzotrile (**3r**)



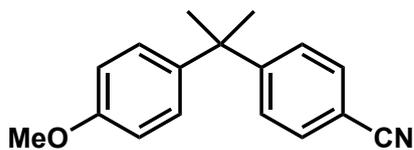
Prepared according to the general procedure, then the crude material was purified by flash column chromatography (SiO<sub>2</sub>, AcOEt / Hexanes = 1:4) to afford a mixture of **3r** and 2,3-dihydro-1H-inden-1-ol, due to tough purification. The yield was determined by <sup>1</sup>H NMR in the presence of 1,1,2,2-tetrachloroethane as an internal standard (56%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.60 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.37-7.22 (m, 3H), 7.01 (d, *J* = 7.4 Hz, 1H), 3.20 (dt, *J* = 12.7, 16.6 Hz, 1H), 3.05-2.95 (m, 1H), 2.51-2.42 (m, 2H), 2.20-2.12 (brs, 1H).

All the spectroscopic data matches with the previously reported data.

Ref) M. Chen, X. Zhao, C. Yang and W. Xia, *Org. Lett.*, 2017, **19**, 3807.

#### 4-(2-(4-methoxyphenyl)propan-2-yl)benzotrile (**3s**)



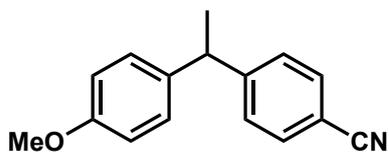
Prepared according to the general procedure, then the crude material was purified by flash column chromatography (SiO<sub>2</sub>, AcOEt / Hexanes = 1:10) to afford **3s** as a colorless oil (21%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 2H), 7.07 (d, *J* = 9.2 Hz, 2H), 6.80 (d, *J* = 9.2 Hz, 2H), 3.77 (s, 3H), 1.64 (s, 6H).

All the spectroscopic data matches with the previously reported data.

Ref) P. Maslak, W. H. Chapman, Jr., *Tetrahedron*, 1990, **46**, 2715.

#### 4-(1-(4-methoxyphenyl)ethyl)benzonitrile (**3t**)



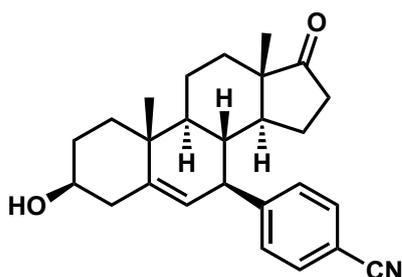
Prepared according to the general procedure, then the crude material was purified by flash column chromatography (SiO<sub>2</sub>, AcOEt / Hexanes = 1:10) to afford **3t** as a colorless oil (3%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.56 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 4.14 (q, *J* = 7.4 Hz, 1H), 3.78 (s, 3H), 1.61 (d, *J* = 7.4 Hz, 3H).

All the spectroscopic data matches with the previously reported data.

Ref) C. -M. Chu, W. -J. Huang, J. -T. Liu and C. -F. Yao, *Tetrahedron Lett.*, 2007, **48**, 6881.

#### 4-((3*S*,7*R*,8*R*,9*S*,10*R*,13*S*,14*S*)-3-hydroxy-10,13-dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-7-yl)benzonitrile (**3u**)



Prepared according to the general procedure without extraction, then the crude material was purified by gel permeation chromatography to afford **3u** (82%, >10:1) and a minor uncharacterized isomer, as a white solid.

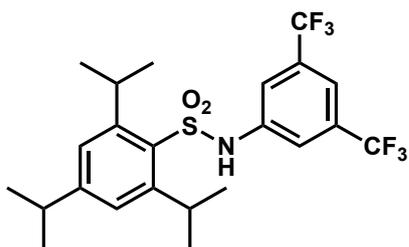
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.00 (s, 1H), 3.57-3.51 (m, 1H), 3.20 (d, *J* = 9.7 Hz, 1H), 2.25 (d, *J* = 8.0 Hz, 2H), 2.21 (d, *J* = 9.2 Hz, 1H), 2.06 (ddd, *J* = 10.3 Hz, 1H), 1.96-1.77 (m, 5H), 1.58-1.46 (m, 5H), 1.43-1.37 (m, 1H), 1.32-1.22 (m, 2H), 1.20 (s, 3H), 1.18-1.14 (m, 1H), 0.81 (s, 3H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 220.6, 152.4, 141.0, 132.5, 129.3, 125.3, 119.0, 110.4, 71.4, 52.1, 50.3, 50.0, 48.2, 42.0, 38.1, 37.2, 36.4, 35.8, 31.7, 31.3, 31.1, 24.3, 20.6, 19.9, 13.8.

IR (KBr) cm<sup>-1</sup> 3447(br), 2936, 2857, 2226, 1737, 1605, 1503, 1455, 1376, 1266, 1174, 1131, 1058, 993, 865, 838, 737, 703.

HRMS (ESI) *m/z* calc. for C<sub>26</sub>H<sub>31</sub>NO<sub>2</sub>Na ([M+Na]<sup>+</sup>) 412.2247, found 412.2235.

#### *N*-(3,5-bis(trifluoromethyl)phenyl)-2,4,6-triisopropylbenzenesulfonamide (**4**)



To a solution of 2,4,6-triisopropylbenzenesulfonyl chloride (1.21 g, 4 mmol) and pyridine (0.97 mL, 12 mmol) in THF (20 mL) was added 3,5-bis(trifluoromethyl)aniline (0.929 mL, 6 mmol) at room temperature. The mixture was stirred at room temperature for 21 hours then concentrated by rotary evaporator. The residue was purified by flash chromatography on silica gel (AcOEt / hexane = 1 / 15), then recrystallized from Et<sub>2</sub>O – *n*-hexane to give **4** as a white solid (1.4 g, 71%).

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.54 (s, 1H), 7.32 (s, 2H), 7.33-7.27 (brm, 1H), 7.19 (s, 2H), 4.12 (sep, *J* = 6.9 Hz, 2H), 2.90 (sep, *J* = 6.9 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 18H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.0, 150.9, 139.0, 132.6 (q, *J* = 24.3 Hz), 131.0, 124.3, 122.7 (q, *J* = 27.5 Hz), 119.38-119.27 (m), 117.7-117.5 (m), 34.2, 30.0, 24.6, 23.4.

IR (KBr) cm<sup>-1</sup> 3253, 2964, 2931, 2355, 1702, 1620, 1507, 1470, 1414, 1378, 1280, 1185, 1148, 970, 883, 653.

HRMS (ESI) *m/z* calc. for C<sub>23</sub>H<sub>27</sub>F<sub>6</sub>NO<sub>2</sub>SNa ([M+Na]<sup>+</sup>) 518.1559, found 518.1574.

#### 4. Optimization of Reaction Conditions

First, using Ir (ppy)<sub>3</sub>, we obtained diarylsulfonamide **4** as a promising HAT candidate, which consists of a sterically hindered, electron-donating 2,4,6-triisopropylphenyl sulfone and a strongly electron-withdrawing 3,5-bis(trifluoromethyl)aniline. Then, Ir (Fppy)<sub>3</sub> was found to be an optimal photoredox catalyst for sulfonamide **4** (Figure S1). Further screening of the base revealed that potassium is the best counterion of the HAT catalyst (Table S1). Changing the stoichiometry of reactants proved that using 5 equivalents of **2a** and 1 equivalent of **1** are the best conditions (Table S2).

Figure S1. Optimization of sulfonamides

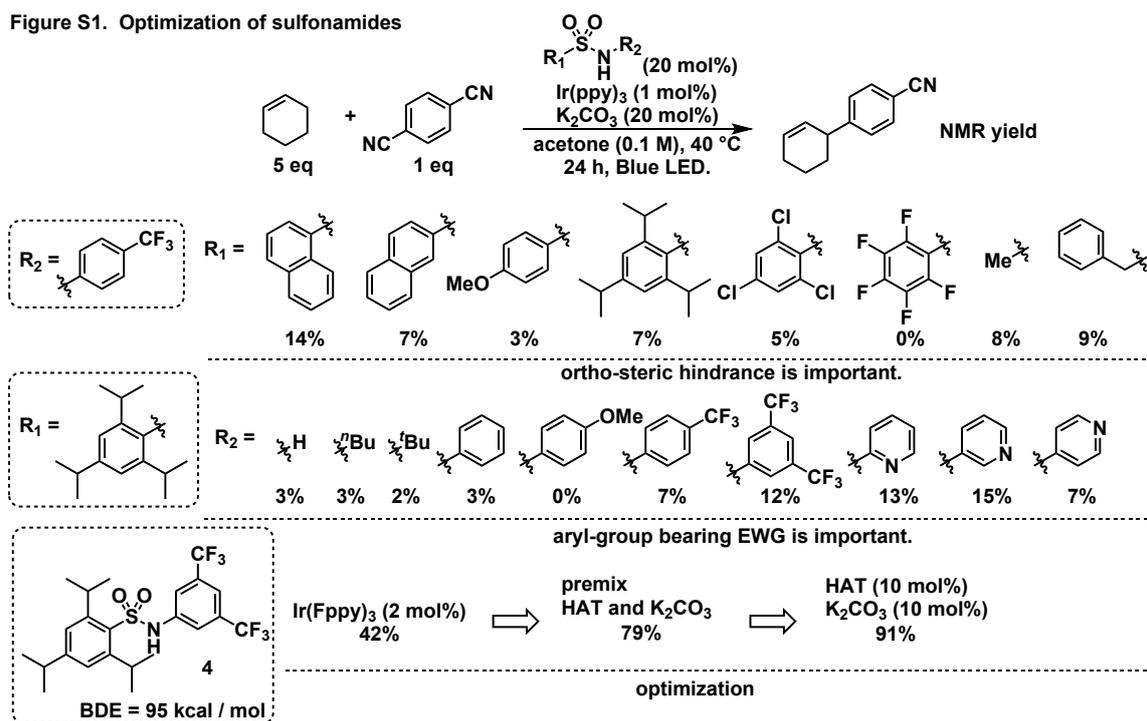
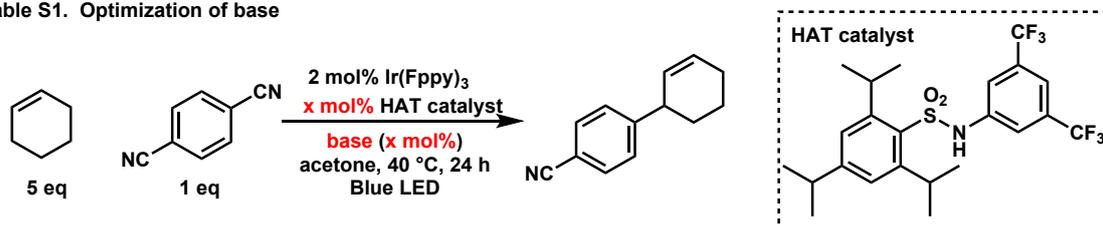


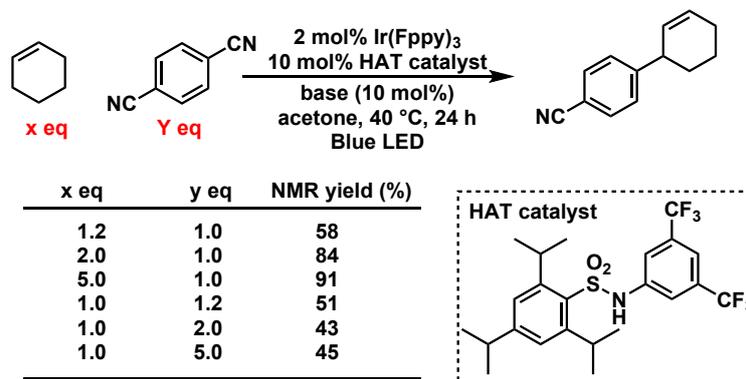
Table S1. Optimization of base



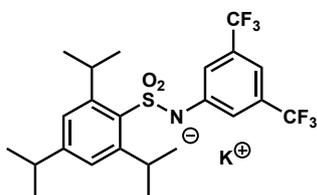
base	x mol%	yield (%) <sup>a</sup>	SM rec. (%) <sup>a</sup>
$N^+Bu_4O^+P(O)(OBu)_2$	20	30	61
KOH	20	85	5
LiOH	20	53	45
$Cs_2CO_3$	20	65	36
$K_2CO_3$	20	79	3
$Na_2CO_3$	20	13	87
$K_2HPO_4$	20	17	49
KOtBu	20	64	29
KOH	10	91	5
KOH	5	90	6
KOH	1	20	81
$K_2CO_3$	10	91	1
$K_2CO_3$	5	87	5
$K_2CO_3$	1	42	57
$K_2CO_3$	20 <sup>b</sup>	77 <sup>b</sup>	12 <sup>b</sup>

<sup>a</sup> NMR yield, <sup>b</sup> at r.t.

Table S2. Optimization of reactant ratio



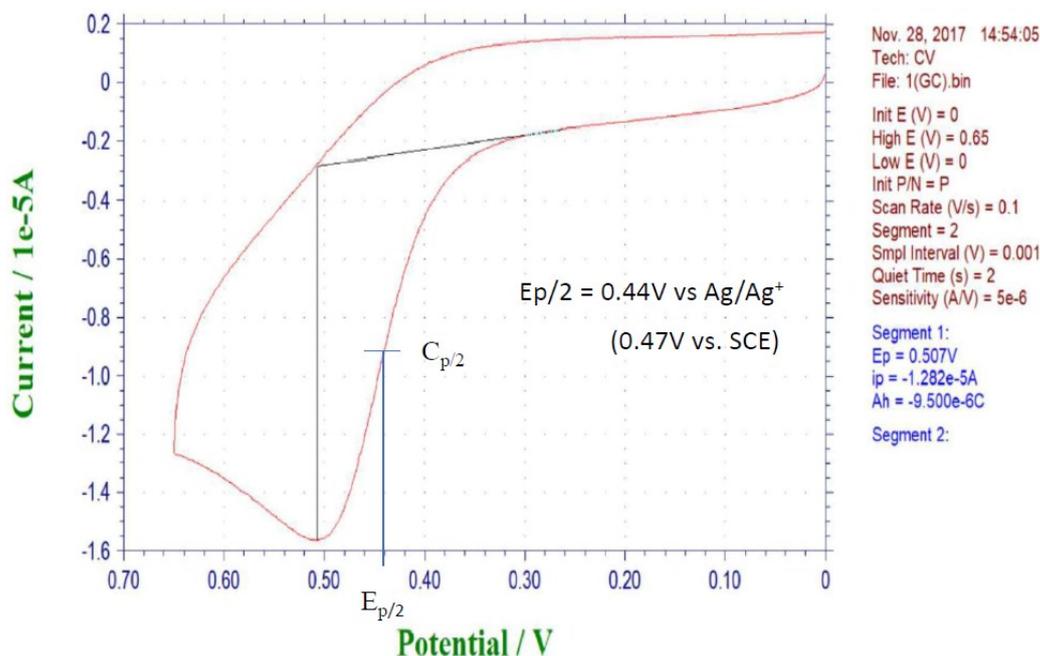
## 5. Cyclic Voltammetry (CV) Measurement



A potassium salt of **4** was prepared by following method.

To a solution of *N*-(3,5-bis(trifluoromethyl)phenyl)-2,4,6-triisopropylbenzenesulfonamide (**4**, 25 mg, 0.05 mmol) in CH<sub>3</sub>CN (2 mL) was added potassium *tert*-butoxide (5.6 mg, 0.05 mmol). The mixture was stirred at room temperature for 3 hours then concentrated by rotary evaporator. The residue was dissolved in acetonitrile to the optimum concentration to measure the CV.

The  $E_{p/2}$  was determined at the half current ( $C_{p/2}$ )<sup>a</sup>. The obtained value was referenced to Ag/Ag<sup>+</sup> and converted to SCE<sup>b</sup>.



- (a) H. G. Roth, N. A. Romero, D. A. Nicewicz, *Synlett*, 2016, **27**, 714.  
 (b) V. V. Pavlishchuk, A. W. Addison, *Inorg. Chim. Acta.*, 2000, **298**, 97.

## 6. Bond Dissociation Energy (BDE) Calculation of Sulfonamides

Molecular modeling studies using a Merck molecular force field 94S (MMFF94S) were performed by CONFLEX<sup>®</sup> 7. Geometry optimization with the density functional theory (DFT) method was performed by the Gaussian 16 program package. Ground-state geometry was optimized at the B3LYP/6-31G(d) level of theory in the gas phase, geometry optimization for open shell species were performed at UB3LYP/6-31G(d) level of theory and the total energies of individual conformers were obtained. These having minimum energies were confirmed by frequency calculation. Subsequent single point calculations have been performed at the B3LYP/6-31(d) or ROB3PLYP/6-31G(d) with the SMD continuum solvation model (SMD, acetone).

$$BDE = \Delta_f H^0_{Radical} + \Delta_f H^0_H - \Delta_f H^0_{Molecule}$$

Ref) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J.V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D.

Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A., Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian 16, Revision A. 03; Gaussian, Inc.: Wallingford, CT, 2016.