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Electronic Supplementary Information for

Iridium complex immobilized on high-nitrogen containing covalent triazine

framework derived from 2,5-pyrazinedicarbonitrile as a recyclable catalyst for the

selective N-alkylation of aminobenzenesulfonamides with alcohols

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General Experimental Details. All reagents and materials used in this study were obtained from commercial sources and used as received unless mentioned otherwise. Quant 250 FEG operated at an accelerating voltage of 20.0 kV was used for the Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) measurements. X-ray Photoelectron Spectroscopy (XPS) analysis was performed on a PHI QUANTERA II using Mg Ka as the excitation source. All binding energy values were calibrated using the adventitious carbon C1s peak at 284.6 eV. XRD patterns were collected on a Bruker D8 Advanced Diffractometer using Cu K α irradiation (λ =0.15406 Å). TGA was performed on a Mettler 851e instrument with a heating rate of 10 °C min-1 in oxygen atmosphere. Metal contents in the Cp*Ir@CTF was determined by inductively coupled plasma optical emission spectrometry (ICP-MS) (iCAP-Q, Thermo Fisher Scientific) using microwave assisted acid digestion system (MARS6, CEM/U.S.A). BET surface area and N2 adsorption-desorption measurements were conducted at 77 K using an automated gas sorption system (ASAP 2020). ATR-IR measurements were recorded on a Thermo Fisher Scientific Nicolet iS 10 instrument. Melting points were measured on a X-6 micro-melting apparatus. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded at 500 MHz using a 500 spectrometer. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane or ppm relative to the center of the singlet at 2.50 ppm for DMSO-d₆. Coupling constants J values are reported in Hertz (Hz), and the splitting patterns were designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. Carbon-13 nuclear magnetic resonance (¹³C NMR) spectra were recorded at 125 MHz using a 500 spectrometer. Chemical shifts are reported in delta (δ) units, ppm relative to the center of the triplet at 39.52 ppm for DMSO-d6. ¹³C NMR spectra were routinely run with broadband decoupling. Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates. $[Cp*IrCl_2]_2^1$ and $[Cp*Ir(bpy)Cl]Cl^2$ were synthesized according to the previously reported methods.

Procedure for the synthesis of CTF.³ 2,5-pyrazinedicarbonitrile (0.30 g, 2.31 mmol) and zinc chloride (1.61 g, 11.8 mmol) were charged to a 20 mL ampoule under Ar atmosphere and closed with septum. The ampoule was then sealed under vacuum by flame and the contents were heated to 400 °C in a furnace for a period of 48 h. The heating rate was maintained to be 60 °C/h. The furnace was cooled to 20 °C after 48 h. The crude product was collected, ground well and stirred with 500 mL of water for 3 h. The black solid was filtered and washed with water and acetone. The resulting solid was

refluxed with 1 M HCl solution (500 mL) for 16 h, filtered and washed with 1 M HCl (3×100 mL), H₂O (3×100 mL), THF (3×100 mL) and acetone (3×100 mL). The black solid was dried under vacuum at 60 °C for 12 h.

Procedure for the synthesis of Cp*Ir@CTF. To a suspension of CTF (0.15 g) in mixed solution of 5.0 mL of dichloromethane was added [Cp*IrCl₂]₂ (0.10 g) under N₂ atm. The resulting suspension was reacted at 70 °C under N₂ atm for 12 h. After 12 h, the black solid was filtered and washed with an excess of dichloromethane (10×25 mL) to remove the unreacted metal precursor. The synthesized catalyst was dried under vacuum at 60 °C for 12 h for analysis and use as a catalyst.

General procedure for the N-alkylation of aminobenzenesulfonamides with alcohols catalyzed by Cp*Ir@CTF. Under a nitrogen atmosphere, to a 25-mL Schlenk tube were added aminobenzenesulfonamide (0.5 mmol), alcohol (0.6 mmol, 1.2 equiv), Cp*Ir@CTF (20 mg, 1 mol % Ir), Cs₂CO₃ (1 equiv) and *tert*-amyl alcohol (1 mL). The mixture was heated at 125 °C for 12 h and was then allowed to cool to ambient temperature. The reaction mixture was concentrated in vacuo and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding product.

4-amino-N-benzylbenzenesulfonamide (3aa).⁴ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 86% yield (113 mg); mp 186-187 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.63 (t, J = 6.4 Hz, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.30-7.21 (m, 5H), 6.61 (d, J = 8.6 Hz, 2H), 5.92 (s, 2H), 3.87 (d, J = 6.4 Hz, 2H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 152.8, 138.4, 128.8, 128.5, 127.8, 127.3, 125.9, 113.0, 46.4.

N-(3-methoxybenzyl)-4-aminobenzenesulfonamide (3ab).⁵ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 82% yield (120 mg); mp 100-101 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.62 (t, *J* = 6.4 Hz, 1H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 6.82-6.77 (m, 3H), 6.61 (d, *J* = 8.6 Hz, 2H), 5.91 (s, 2H), 3.86 (d, *J* = 6.3 Hz, 2H), 3.70 (s, 3H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 164.3, 157.5, 144.7, 134.3, 133.5, 130.7, 124.8, 118.0, 117.8, 117.5, 60.0, 51.1.

N-(4-methoxybenzyl)-4-aminobenzenesulfonamide (3ac).⁵ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 85% yield (124 mg); mp 130-131 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.53 (t, *J* = 6.4 Hz, 1H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.61 (d, *J* = 8.7 Hz, 2H), 5.91 (s, 2H), 3.79 (d, *J* = 6.4 Hz, 2H), 3.71 (s, 3H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 158.7, 152.7, 130.1, 129.2, 128.8, 126.0, 113.9, 113.0, 55.3, 45.9.

N-(4-methylbenzyl)-4-aminobenzenesulfonamide (3ad).⁵ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 88% yield (122 mg); mp 146-147 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.56 (t, *J* = 6.3 Hz, 1H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.10 (q, *J* = 8.0 Hz, 4H), 6.61 (d, *J* = 8.6 Hz, 2H), 5.91 (s, 2H), 3.81 (d, *J* = 6.3 Hz, 2H), 2.26 (s, 3H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 152.7, 136.4, 135.2, 129.0, 128.8, 127.8, 125.9, 113.0, 46.2, 20.9.

N-(4-isopropylbenzyl)-4-aminobenzenesulfonamide (3ae).⁵ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 85% yield (129 mg); mp 137-138 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.55 (t, *J* = 6.1 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.14 (s, 4H), 6.61 (d, *J* = 8.6 Hz, 2H), 5.91 (s, 2H), 3.83 (d, *J* = 6.3 Hz, 2H), 2.88-2.80 (m, 1H), 1.17 (d, *J* = 7.0 Hz, 6H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 152.7, 147.5, 135.6, 128.8, 127.9, 126.4, 125.9, 112.9, 46.2, 33.4, 24.2.

N-(4-bromobenzyl)-4-aminobenzenesulfonamide (3af).⁵ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 86% yield (147 mg); mp 186-187 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.69 (s, 1H), 7.48-7.41 (m, 4H), 7. 21 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 8.7 Hz, 2H), 5.94 (s, 2H), 3.84 (d, *J* = 6.6 Hz, 2H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 152.8, 138.0, 131.3, 130.0, 128.7, 125.7, 120.3, 113.0, 45.7.

N-(2-chlorobenzyl)-4-aminobenzenesulfonamide (3ag).⁵ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 85% yield (126 mg); mp 111-112 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.76 (t, J = 6.1 Hz, 1H), 7.54-7.48 (m, 3H), 7.37 (d, J = 7.7 Hz, 1H), 7.31-7.24 (m, 2H), 6.68 (d, J = 8.1 Hz, 2H), 5.96 (s, 2H), 4.01 (d, J = 5.9 Hz, 2H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 152.9, 135.6, 132.4, 129.9, 129.3, 129.1, 128.9, 127.3, 125.6, 113.1, 43.9.

N-(4-chlorobenzyl)-4-aminobenzenesulfonamide (3ah).⁶ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 87% yield (129 mg); mp 167-168 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.68 (t, J = 6.4 Hz, 1H), 7.43 (d, J = 8.6 Hz, 2H), 7. 33 (d, J = 8.2 Hz, 2H), 7. 26 (d, J = 8.2 Hz, 2H), 6.60 (d, J = 8.6 Hz, 2H), 5.93 (s, 2H), 3.86 (d, J = 6.4 Hz, 2H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 152.8, 137.5, 131.8, 129.7, 128.7, 128.4, 125.8, 113.0, 45.6.

N-(3-fluorobenzyl)-4-aminobenzenesulfonamide (3ai).⁷ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 91% yield (127 mg); mp 107-108 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.72 (t, *J* = 6.4 Hz, 1H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.34-7.30 (m, 1H), 7.09-7.03 (m, 3H), 6.60 (d, *J* = 8.9 Hz, 2H), 5.94 (s, 2H), 3.91 (d, *J* = 6.7 Hz, 2H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 163.3, 161.4, 152.8, 141.5, (C-F, ³*J*_{C-F} = 7.2 Hz), 130.4 (C-F, ³*J*_{C-F} = 8.2 Hz), 128.7, 125.8, 123.7 (C-F, ⁴*J*_{C-F} = 2.5 Hz), 114.2 (C-F, ²*J*_{C-F} = 31.4 Hz), 112.9, 45.7.

N-(4-(trifluoromethoxy)benzyl)-4-aminobenzenesulfonamide (3aj).⁵ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 85% yield (147 mg); mp 151-152 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.70 (t, *J* = 6.4 Hz, 1H), 7.43 (d, *J* = 8.6 Hz, 2H), 7. 37 (d, *J* = 8.4 Hz, 2H), 7. 28 (d, *J* = 8.2 Hz, 2H), 6.60 (d, *J* = 8.6 Hz, 2H), 5.94 (s, 2H), 3.91 (d, *J* = 6.4 Hz, 2H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 152.8, 147.6, 138.0, 129.6, 128.7, 125.7, 121.1, 120.4 (C-F, ¹*J*_{C-F} = 256.0 Hz), 112.9, 45.6.

N-(3-(trifluoromethyl)benzyl)-4-aminobenzenesulfonamide (3ak).⁸ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 84% yield (139 mg); mp 176-177 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.80 (t, *J* = 6.2 Hz, 1H), 7.59-7.51 (m, 4H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 5.94 (s, 2H), 4.01 (d, *J* = 6.2 Hz, 2H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 152.9, 140.1, 131.9, 129.5, 129.2 (C-F, ²*J*_{C-F} = 31.2 Hz), 128.7, 125.7, 124.5 (C-F, ¹*J*_{C-F} = 272.2 Hz), 124.2, 124.0, 113.0, 45.7.

 2H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 152.9, 143.4, 128.8, 128.5, 127.9 (C-F, ²*J*_{C-F} = 31.6 Hz), 125.6, 125.3 (C-F, ³*J*_{C-F} = 3.7 Hz), 124.6 (C-F, ¹*J*_{C-F} = 268.8 Hz), 112.9, 45.8.

4-amino-N-(thiophen-2-ylmethyl)benzenesulfonamide (3am).⁵ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 81% yield (109 mg); mp 130-131 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.75 (t, J = 6.3 Hz, 1H), 7.44 (d, J = 8.6 Hz, 2H), 7.39-7.38 (d, J = 4.8 Hz, 1H), 6.91 (t, J = 5.0 Hz, 2H), 6.61 (d, J = 8.6 Hz, 2H), 5.93 (s, 2H), 4.05 (d, J = 6.3 Hz, 2H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 152.8, 141.4, 128.8, 127.0, 125.9, 125.7, 125.6, 113.0, 41.7.

4-amino-N-(naphthalen-1-ylmethyl)benzenesulfonamide (3an).⁵ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 89% yield (139 mg); mp 174-175 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 8.05 (t, *J* = 5.4 Hz, 1H), 7.94-7.92 (m, 1H), 7.86-7.84 (m, 1H), 7. 64 (t, *J* = 6.3 Hz, 1H), 7.54-7.51 (m, 4H), 7.45-7.40 (m, 2H), 6.65 (d, *J* = 8.6 Hz, 2H), 5.97 (s, 2H), 4.28 (d, *J* = 6.1 Hz, 2H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 152.9, 133.5, 133.3, 131.3, 128.9, 128.7, 128.3, 126.8, 126.5, 126.1, 125.6, 124.0, 113.0, 44.8.

4-amino-N-octylbenzenesulfonamide (3ao).¹⁰ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 90% yield (128 mg); mp 113-114 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.40 (d, *J* = 8.8 Hz, 2H), 7.02 (t, *J* = 5.9 Hz, 1H), 6.60 (d, *J* = 8.7 Hz, 2H), 5.88 (s, 2H), 2.62 (q, *J* = 6.6 Hz, 2H), 1.33-1.29 (m, 2H), 1.24-1.16 (m, 10H), 0.84 (t, *J* = 7.1 Hz, 3H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 152.6, 128.7, 125.9, 112.9, 42.7, 31.5, 29.2, 28.9, 28.8, 26.4, 22.4, 14.2.

4-amino-N-pentylbenzenesulfonamide (3ap).¹¹ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 86% yield (104 mg); mp 115-116 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.40 (d, *J* = 8.7 Hz, 2H), 7.02 (t, *J* = 6.0 Hz, 1H), 6.60 (d, *J* = 8.6 Hz, 2H), 5.88 (s, 2H), 2.64-2.60 (m, 2H), 1.35-1.30 (m, 2H), 1.19-1.16 (m, 4H), 0.80 (t, *J* = 6.8 Hz, 3H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 152.6, 128.7, 126.0, 112.9, 42.7, 28.8, 28.6, 22.0, 14.1.

4-amino-N-butylbenzenesulfonamide (3aq).¹² Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); Pink solid; 82% yield (94 mg); mp 92-93 °C; ¹H NMR (500 MHz,

DMSO-d₆) δ 7.40 (d, *J* = 8.6 Hz, 2H), 7.03 (t, *J* = 5.9 Hz, 1H), 6.60 (d, *J* = 8.8 Hz, 2H), 5.89 (s, 2H), 2.62 (q, *J* = 6.7 Hz, 2H), 1.31 (q, *J* = 7.4 Hz, 2H), 1.22 (m, 2H), 0.78 (t, *J* = 7.1 Hz, 3H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 152.6, 128.7, 125.9, 112.9, 42.4, 31.2, 19.6, 13.8.

4-amino-N-(cyclohexylmethyl)benzenesulfonamide (3ar).⁵ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 83% yield (111 mg); mp 168-169 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.39 (d, J = 8.8 Hz, 2H), 7.05 (t, J = 6.2 Hz, 1H), 6.59 (d, J = 8.8 Hz, 2H), 5.88 (s, 2H), 2.46 (t, J = 6.7 Hz, 2H), 1.64-1.57 (m, 5H), 1.32-1.25 (m, 1H), 1.12-1.05 (m, 3H), 0.80-0.72 (m, 2H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 152.6, 128.6, 126.1, 112.9, 49.0, 37.4, 30.6, 26.3, 25.6.

4-amino-N-cyclohexylbenzenesulfonamide (3as).¹³ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 60% yield (76 mg); mp 84-85 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.41 (d, *J* = 8.6 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 8.7 Hz, 2H), 5.87 (s, 2H), 2.78 (s, 1H), 1.55 (s, 4H), 1.43 (d, *J* = 11.1 Hz, 1H), 1.13-1.00 (m, 5H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 152.5, 128.5, 127.6, 112.9, 52.1, 33.5, 25.2, 24.7.

4-amino-N-cyclopentylbenzenesulfonamide (3at).¹³ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 56% yield (67 mg); mp 104-105 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.10 (t, *J* = 7.0 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 2H), 5.88 (s, 2H), 3.28 (q, *J* = 6.7 Hz, 1H), 1.57-1.50 (m, 4H), 1.35-1.34 (m, 2H), 1.30-1.23 (m, 2H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 152.6, 128.7, 126.9, 112.9, 54.6, 32.7, 23.1.

4-amino-N-benzyl-3-bromobenzenesulfonamide (3ba).⁵ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 84% yield (143 mg); mp 136-137 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.85 (t, J = 6.4 Hz, 1H), 7.72 (d, J = 2.0 Hz, 1H), 7.50-7.47 (m, 1H), 7.28-7.21 (m, 5H), 6.86 (d, J = 6.6 Hz, 1H), 6.12 (s, 2H), 3.93 (d, J = 6.4 Hz, 2H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 149.6, 138.0, 131.4, 128.5, 128.3, 127.9, 127.7, 127.4, 114.5, 106.2, 46.4.

4-amino-N-benzyl-3,5-dibromobenzenesulfonamide (3ca).⁵ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 81% yield (170 mg); mp 183-184 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 8.02 (t, J = 6.4 Hz, 1H), 7.71 (s, 2H), 7.28-7.21 (m,

5H), 6.12 (s, 2H), 3.97 (d, J = 6.4 Hz, 2H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 146.5, 137.7, 130.6, 129.1, 128.4, 127.9, 127.4, 106.6, 46.5.

4-amino-N-benzyl-3-chlorobenzenesulfonamide (3da). Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 83% yield (123 mg); mp 103-104 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.84 (t, *J* = 6.3 Hz, 1H), 7.57-7.55 (m, 1H), 7.45-7.43 (m, 1H), 7.28-7.23 (m, 5H), 6.86 (d, *J* = 8.6 Hz, 1H), 6.19 (s, 2H), 3.92 (d, *J* = 6.5 Hz, 2H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 148.6, 138.0, 128.5, 128.2, 127.9, 127.4, 127.1, 117.4, 116.2, 114.6, 46.4. HRMS (ESI) m/z caled for C₁₃H₁₄ClN₂O₂S⁺[M⁺H⁺] 297.0465 found 297.0464.

4-amino-N-benzyl-3,5-dichlorobenzenesulfonamide (3ea).⁵ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 86% yield (142 mg); mp 184-185 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 8.02 (t, *J* = 6.1 Hz, 1H), 7.56 (s, 2H), 7.27-7.20 (m, 5H), 6.34 (s, 2H), 3.98 (d, *J* = 6.5 Hz, 2H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 144.9, 137.7, 128.4, 128.0, 127.8, 127.4, 126.9, 117.5, 46.5.

3-amino-N-benzylbenzenesulfonamide (3fa).⁵ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 85% yield (111 mg); mp 71-72 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.95 (t, *J* = 6.4 Hz, 1H), 7.32-7.18 (m, 6H), 7.04 (s, 1H), 6.93 (d, *J* = 6.5 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 5.58 (s, 2H), 3.95 (d, *J* = 6.4 Hz, 2H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 149.6, 141.4, 138.2, 129.9, 128.5, 127.8, 127.4, 117.5, 113.5, 111.4, 46.4.

5-amino-N-benzyl-2-methylbenzenesulfonamide (3ga).⁵ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 80% yield (111 mg); mp 82-83 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.99 (t, *J* = 6.4 Hz, 1H), 7.28 (t, *J* = 6.9 Hz, 2H), 7.23 (d, *J* = 7.3 Hz, 3H), 7.14 (d, *J* = 2.4 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.68-6.66 (m, 1H), 5.31 (s, 2H), 3.97 (d, *J* = 6.2 Hz, 2H), 2.37 (s, 3H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 147.1, 139.0, 138.5, 133.2, 128.4, 127.7, 127.4, 122.3, 117.6, 114.1, 46.1, 19.0.

2-amino-N-benzylbenzenesulfonamide (3ha).⁵ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid; 76% yield (100 mg); mp 55-56 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 8.06 (t, *J* = 5.9 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.29-7.21 (m, 6H), 6.83 (t, *J* = 8.3 Hz,

1H), 6.61 (t, J = 7.6 Hz, 1H), 5.94 (s, 2H), 3.94 (d, J = 5.9 Hz, 2H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 146.5, 138.0, 133.8, 129.4, 128.5, 127.8, 127.4, 120.3, 117.2, 115.4, 46.0.

Procedure for the reaction of aminobenzenesulfonamide (1a), benzylaldehyde (4) and 2-propanol (5) (Scheme 6). Under a nitrogen atmosphere, to a 25-mL Schlenk tube were added 1a (0.5 mmol), 4 (0.6 mmol, 1.2 equiv), 5 (1.5 mmol, 3 equiv), Cp*Ir@CTF (20 mg, 1 mol % Ir), Cs₂CO₃ (1 equiv) and *tert*-amyl alcohol (1 mL). The mixture was heated at 125 °C for 12 h and was then allowed to cool to ambient temperature. The reaction mixture was concentrated in vacuo and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding product 3aa in 82% yield (108 mg).

Procedure for the synthesis of 4-amino-N-phenethylbenzenesulfonamide (7). Under a nitrogen atmosphere, to a 25-mL Schlenk tube were added **1a** (1.72 g, 10 mmol), **6** (1.46 g, 12 mmol, 1.2 equiv), Cp*Ir@CTF (400 mg, 1 mol % Ir), Cs₂CO₃ (3.26 g, 10 mmol, 1 equiv) and *tert*-amyl alcohol (10 mL). The mixture was heated at 125 °C for 12 h and was then allowed to cool to ambient temperature. The reaction mixture was concentrated in vacuo and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding product.

4-amino-N-phenethylbenzenesulfonamide (7).¹³ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); White solid, 81% yield (2.24 g); mp 130-131 °C; ¹H NMR (500 MHz, DMSO-d₆) δ 7.42 (d, *J* = 8.6 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.21-7.17 (m, 2H), 7.14 (d, *J* = 7.2 Hz, 2H), 6.62 (d, *J* = 8.6 Hz, 2H), 5.92 (s, 2H), 2.87 (q, *J* = 6.7 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 152.7, 139.2, 128.9, 128.8, 128.6, 126.5, 125.6, 113.0, 44.4, 35.5.

Procedureforthesynthesisof4-(3-chloro-1,4-dioxo-1,4-dihydronaphthalen-2-ylamino)-N-phenethylbenzenesulfonamide (9). Ina round-bottomed flask with a condenser tube were added 7 (1.38 g, 5 mmol), 8 (1.14 g, 5 mmol) andethanol (20 mL). The mixture was heated under reflux for 24 h and was then allowed to cool toambient temperature. The reaction mixture was concentrated in vacuo and purified by flash columnchromatography with hexanes/ethyl acetate to afford the corresponding product.

4-((3-chloro-1,4-dioxo-1,4-dihydronaphthalen-2-yl)amino)-N-phenethylbenzenesulfonamide

(9).¹⁴ Purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 2/1); Orange solid, 56% yield (1.30 g); ¹H NMR (500 MHz, DMSO-d₆) δ 9.54 (s, 1H), 8.05 (d, *J* = 7.5 Hz, 2H), 7.88 (t, *J* = 7.4 Hz, 1H), 7.83 (t, *J* = 7.4 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 5.7 Hz, 1H), 7.28-7.17 (m, 5H), 7.15 (d, *J* = 7.3 Hz, 2H), 2.97 (q, *J* = 6.6 Hz, 2H), 2.66 (t, *J* = 7.5 Hz, 2H); ¹³C {¹H} NMR (125 MHz, DMSO-d₆) δ 180.2, 177.2, 143.1, 143.0, 139.0, 135.0, 134.8, 133.8, 132.0, 130.7, 128.9, 128.6, 127.0, 126.9, 126.5, 122.8, 118.7, 44.4, 35.5.

References

(1) R. G. Ball, W. A. G. Graham, D. M. Heinekey, J. K. Hoyano, A. D. McMaster, B. M. Mattson and S. T. Michel, *Inorg, Chem.*, 1990, **29**, 2023-2025.

(2) R. Ziessel, J. Chem. Soc. Chem. Commun., 1988, 1, 16-17.

(3) M. Soorholtz, L. C. Jones, D. Samuelis, C. Weidenthaler, R. J. White, M. Titirici, D. A. Cullen, T. Zimmermann, M. Antonietti, J. Maier, R. Palkovits, B. F. Chmelka and F. Schüth, *ACS Catal.*, 2016, **6**, 2332-2340.

(4) E. M. Bissinger, R. Heinke, A. Spannhoff, A. Eberlin, E. Metzger, V. Cura, P. Hassenboehler, J. Cavarelli, R. Schule, M. T. Bedford, W. Sippl and M. Jung, *Bioorg. Med. Chem.*, 2011, **19**, 3717-3731.

(5) L. Lu, J. Ma, P. Qu and F. Li, Org. Lett., 2015, 17, 2350-2353.

(6) P. Wang, C. Liu, T. Sanches, Y. Zhong, B. Liu, J. Xiong, N. Neamati and G. Zhao, *Bioorg. Med. Chem. Lett.*, 2009, **19**, 4574-4578.

(7) Y. S. Lai, F. Wang, Y. Zou, Q. Xu, W. J. Guo, Y. Wang, Q. R. Sun and Y. Z. Li, WO2018161892, **2018**.

(8) F. Habens, N. Srinivasan, F. Oakley, D. A. Mann, A. Ganesan and G. Packham, *Apoptosis*, 2005, 10, 481-491.

(9) Lukin, V. Gramlich, R. Kandre, I. Zhun, T. Felder, C. A. Schalley and G.Dolgonos, *J. Am. Chem. Soc.*, 2006, **128**, 8964-8974.

(10) P. G. Baraldi, A. R. Moorman and P. A. Borea, US 20090233878, 2009.

(11) D. Rennison, D. Conole, M. D. Tingle, J. Yang, C. T. Eason and M. A. Brimble, *Bioorg. Med. Chem. Lett.*, 2013, 23, 6629-6635.

(12) P. G. Baraldi, A. R. Moorman, and P. A. Borea, WO 2005028489, 2005.

(13) M. Schlitzer, M. Bohm, I. Sattler and H. M. Dahse, Bioorg. Med. Chem., 2000, 8, 1991-2006.

(14) R. Pingaew, V. Prachayasittikul, A. Worachartcheewan, C. Nantasenamat, S. Prachayasittikul,S. Ruchirawat and V. Prachayasittikul, *Eur. J. Med. Chem.*, 2015, **103**, 446-459.



Fig. S1. FT-IR spectra of (a) 2,5-pyridinedicarbonitrile; (b) CTF; (c) Cp*Ir@CTF; (d) recovered Cp*Ir@CTF.



Fig. S2. XRD of CTF



Fig. S3. TGA of CTF





Fig. S4. TEM image of CTF.



Fig. S5. SEM image of CTF.



Fig. S6. TEM image of Cp*Ir@CTF (left) and recovered Cp*Ir@CTF (right).



Fig. S7. SEM image of Cp*Ir@CTF (left) and recovered Cp*Ir@CTF (right).



Fig. S8. SEM image of Cp*Ir@CTF (a). EDS mapping of (b) Ir; (c) Cl; (d) N; (e) C and (f) O atoms in Cp*Ir@CTF.



Fig. S9. SEM image of recovered Cp*Ir@CTF (a). EDS mapping of (b) Ir; (c) Cl; (d) N; (e) C and (f) O atoms in recovered Cp*Ir@CTF.



Fig. S10. The structure of [Cp*Ir(bpy)Cl]Cl



Fig. S11. XPS of Cp*Ir@CTF (a) and [Cp*Ir(bpy)Cl]Cl (b).

| Element | Before catalysis (Wt%) | After 6 cycles (Wt%) |
|---------|------------------------|----------------------|
| С | 72.41 | 65.07 |
| N | 6.34 | 10.42 |
| 0 | 16.34 | 22.00 |
| Cl | 1.27 | 0.03 |
| lr | 3.64 | 2.47 |
| Total | 100.00 | 100.00 |

Table S1. Atomic composition by SEM-EDS.

Table S2. BET analysis of CTF and Cp*Ir@CTF, and ICP-MS data.

| Material | S _{BET} (m ² /g) | Pore volume (cm ³ /g) | Pore size (nm) | wt% of Ir content |
|-----------|--------------------------------------|----------------------------------|----------------|-------------------|
| CTF | 623 | 0.21 | 1.38 | |
| Cp*Ir@CTF | 421 | 0.12 | 1.17 | 4.80 |

4-amino-N-benzylbenzenesulfonamide Proton DMSO-d6





4-amino-N-benzylbenzenesulfonamide C13CPD DMSO-d6



N-(3-methoxybenzyl)-4-aminobenzenesulfonamide Proton DMSO-d6



N-(3-methoxybenzyl)-4-aminobenzenesulfonamide C13CPD DMSO-d6



N-(4-methoxybenzyl)-4-aminobenzenesulfonamide Proton DMSO-d6



N-(4-methoxybenzyl)-4-aminobenzenesulfonamide C13CPD DMSO-d6

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55.344 45.908 40.230 39.985 39.985 39.730 39.730 39.563 39.563 39.229 N-(4-methylbenzyl)-4aminobenzenesulfonamide Proton DMSO-d6







N-(4-isopropylbenzyl)-4-aminobenzenesulfonamide Proton DMSO-d6



N-(4-isopropylbenzyl)-4-aminobenzenesulfonamide C13CPD DMSO-d6



N-(4-bromobenzyl)-4-aminobenzenesulfonamide Proton DMSO-d6





N-(2-chlorobenzyl)-4-aminobenzenesulfonamide Proton DMSO-d6





7.5 8.5 8.0 7.0 6.5 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 6.0 0.0 ppm 3.03 2.05 2.04 **2.11** 2.01



N-(2-chlorobenzyl)-4-aminobenzenesulfonamide C13CPD DMSO-d6

N-(4-chlorobenzyl)-4-aminobenzenesulfonamide Proton DMSO-d6





S32

N-(3-fluorophenyl)-4-aminobenzenesulfonamide Proton DMSO-d6





N-(3-fluorophenyl)-4-aminobenzenesulfonamide C13CPD DMSO-d6

N-(4-(trifluoromethoxy)benzyl)-4-aminobenzenesulfonamide Proton DMSO-d6

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4.5 8.5 8.0 7.5 7.0 6.5 **6.0** 5.5 5.0 **4.0** 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm 2.10 2.08 2.08 2:07

N-(4-(trifluoromethoxy)benzyl)-4-aminobenzenesulfonamide C13CPD DMSO-d6


N-(3-(trifluoromethyl)benzyl)-4-aminobenzenesulfonamide Proton DMSO-d6

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N-(4-(trifluoromethyl)benzyl)-4-aminobenzenesulfonamide Proton DMSO-d6



N-(4-(trifluoromethyl)benzyl)-4-aminobenzenesulfonamide C13CPD DMSO-d6



4-amino-N-(thiophen-2-ylmethyl)benzenesulfonamide Proton DMSO-d6



4-amino-N-(thiophen-2-ylmethyl)benzenesulfonamide C13CPD DMSO



4-amino-N-(naphthalen-1-ylmethyl)benzenesulfonamide Proton DMSO-d6



4-amino-N-(naphthalen-1-ylmethyl)benzenesulfonamide C13CPD DMSO-d6



4-amino-N-octylbenzenesulfonamide Proton DMSO-d6



4-amino-N-octylbenzenesulfonamide C13CPD DMSO-d6



4-amino-N-pentylbenzenesulfonamide Proton DMSO-d6







3ap ¹H NMR (500 MHz, DMSO-d6)







4-amino-N-butylbenzenesulfonamide Proton DMSO-d6



8.5 8.0 7.5 6.5 5.5 5.0 4.5 3.5 3.0 2.5 2.0 1.5 1.0 0.5 7.0 6.0 4.0 0.0 ppm 2.00 1.03 2.03 **2.12** 2.07 2.06 2.04 3.02

4-amino-N-butylbenzenesulfonamide C13CPD DMSO-d6





4-amino-N-(cyclohexylmethyl)benzenesulfonamide Proton DMSO-d6









4-amino-N-cyclohexylbenzenesulfonamide Proton DMSO-d6



4-amino-N-cyclohexylbenzenesulfonamide C13CPD DMSO-d6



4-amino-N-cyclopentylbenzenesulfonamide Proton DMSO-d6



4-amino-N-cyclopentylbenzenesulfonamide C13CPD DMSO-d6



4-amino-N-benzyl-3-bromobenzenesulfonamide Proton DMSO-d6





4-amino-N-benzyl-3-bromobenzenesulfonamide C13CPD DMSO-d6

4-amino-N-benzyl-3,5-dibromobenzenesulfonamide Proton DMSO-d6







4-amino-N-benzyl-3-chlorobenzenesulfonamide Proton DMSO-d6



4-amino-N-benzyl-3-chlorobenzenesulfonamide C13CPD DMSO-d6



4-amino-N-benzyl-3,5-dichlorobenzenesulfonamide Proton DMSO-d6

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3-amino-N-benzylbenzenesulfonamide Proton DMSO-d6

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3f a ¹H NMR (500 MHz, DMSO-d6)



3-amino-N-benzylbenzenesulfonamide Proton DMSO-d6



5-amino-N-benzyl-2-methylbenzenesulfonamide Proton DMSO-d6



5-amino-N-benzyl-2-methylbenzenesulfonamide C13CPD DMSO-d6



2-amino-N-benzylbenzenesulfonamide Proton DMSO-d6



2-amino-N-benzylbenzenesulfonamide C13CPD DMSO-d6







3ha ¹³C {¹H} NMR (125 MHz, DMSO-d6)



4-amino-N-phenethylbenzenesulfonamide Proton DMSO-d6



4-amino-N-phenethylbenzenesulfonamide C13CPD DMSO-d6


4-((3-chloro-1,4-dioxo-1,4-dihydronaphthalen-2-yl)amino)-N-phenethylbenzenesulfonamide Proton DMSO-d6







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0 ppm