Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Effect of the functionalisation route on a Zr–MOF with an Ir–NHC complex for catalysis†

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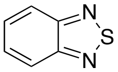
S1 General procedures

All starting materials and chemicals were purchased from commercial suppliers and used as purchased. Anhydrous CH_2Cl_2 and CH_3CN were obtained using a VAC solvent purifier system. Flash chromatography was carried out on Davisil silica gel 60 (35–70 μm). X-ray powder diffraction (XRPD) was carried out on a PANalytical X'Pert PRO diffractometer in reflectance Bragg-Brentano geometry equipped with a pixel detector and using Cu $K\alpha_1$ radiation. The samples were dispersed on zero-background Si plates. Fourier-transform infrared (FTIR) spectroscopy was performed on a Varian 670-IR spectrometer. N_2 sorption was carried out at 77 K on a Micromeritics ASAP2020 device. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA 7, equipped with a platinum pan, and all samples were heated at a rate of 2 °C/min in air. Medac Ltd in the UK carried out the elemental analysis. CHN analysis was performed on a Carlo Erba Flash 1112 elemental analyser and inductively coupled plasma-optical emission spectrometry (ICP-OES) was used for metal determination with a Varian Vista MPX ICP-OES. Scanning electron microscopy (SEM) was performed on a JEOL JSM-7000F field emission SEM operated at 4–6 kV. Cross-section polishing was performed using an argon ion milling system in a JEOL SM-09010 cross-section polisher operated at 5 kV/90 μA. The polishing time was set to 8 h. Extended X-ray absorption fine structure (EXAFS) spectroscopy was carried out on the Ir L_{III}-edge at beamline I811, MAX-lab, Lund, using a Si(111) double-crystal monochromator. The current of the storage ring was *ca* 200 mA. Samples were ground with BN as a binder and measured as a powder. The spectra were calibrated using Ge foil (Ge *K*-edge: 11103 eV) and the data were analysed using the Demeter package.[1] High resolution mass spectra (HRMS) were recorded on a Bruker microTOF ESI-TOF mass spectrometer. ^1H nuclear magnetic resonance (NMR) spectra were recorded at 400 MHz or 500 MHz, and ^{13}C spectra at 100 MHz, on a Bruker Avance 400 spectrometer. Chemical shifts (δ) are reported in ppm, using the residual non-deuterated solvent peaks in $CDCl_3$ (δ_H 7.26; δ_C 77.16) or DMSO-d_6 (δ_H 2.50; δ_C 39.52) as an internal reference; coupling constants (*J*) are given in Hz.

S2 Synthesis and characterisation of linkers

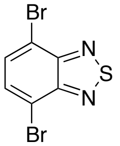
2,1,3-Benzothiadiazole (1):



The product was synthesised following the reported procedure.[2] *o*-Phenylenediamine (14.0 g, 129.5 mmol), was added to a flask containing CH_2Cl_2 (430 mL) and NEt_3 (72.2 mL, 518 mmol, 4 equiv.). The mixture was stirred until total dissolution of the diamine was observed. Then thionyl chloride (18.8 mL, 259 mmol, 2 equiv.) was added dropwise very slowly and the mixture was heated at reflux for 5 h. After cooling to room temperature, the solvent was removed under reduced pressure and water (1000 mL) was added. Concentrated HCl was added until pH 1. The product was purified by steam distillation. The distilled mixture was extracted with CH_2Cl_2 (5 × 150 mL), washed with brine (3 × 150 mL) and dried over $MgSO_4$, to afford **1** as a yellow solid (15.7 g, 89% yield).

^1H NMR (400 MHz, $CDCl_3$): δ = 8.02-8.00 (m, 2H, Ar–H), 7.60–7.58 (m, 2H, Ar–H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0, 129.5, 121.7.

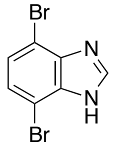
4,7-Dibromo-2,1,3-benzothiadiazole (2):



The product was synthesised following the reported procedure.[2] A 1000 mL two-necked flask was loaded with **1** (15.2 g, 112 mmol) and HBr (aq. 48%, 230 mL). A solution containing Br_2 (17,3 mL, 336 mmol) in HBr (aq., 48%, 150 mL) was added dropwise to the mixture. An additional 50 mL of HBr (aq., 48%, 50 mL) was added and the solution was heated at reflux for 6 h, resulting in the precipitation of an orange solid. After cooling to room temperature, $NaHSO_3$ (aq., sat., 400 mL) was added to consume excess Br_2. The mixture was filtered under vacuum and washed with water (200 mL), cold diethyl ether (200 mL) and dried overnight under vacuum to afford **3** as a yellow solid (27.25 g, 83% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.73 (s, 2H, Ar–H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 153.1, 132.5, 114.1.

4,7-Dibromobenzimidazole (3):

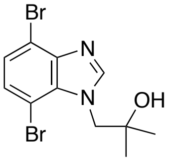


The product was synthesised by a modification of the reported procedures.[3,4] A 2000 mL two-necked flask was loaded with **2** (26.5 g, 90 mmol) and $CoCl_2 \cdot 6H_2O$ (214 mg, 0.90 mmol, 0.01 equiv.) followed by addition of THF (260 mL) and EtOH (510 mL). The resulting green solution was heated at reflux and $NaBH_4$ (10.2 g, 270 mmol, 3equiv.) was added in three portions over 3 h. After refluxing for 6 h, TLC showed no starting material left. The reaction was cooled to room temperature, and water (400 mL) was added and the mixture was stirred for 10 min. The reaction media was filtered through a pad of Celite® and the organic solvent was removed under reduced pressure. The product was extracted with CH_2Cl_2 (3 × 200 mL), washed with brine (3 × 100 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the product was purified by column chromatography (SiO_2; pentane/ EtOAc = 10:1 to 2:1) yielding an orange solid, which was used immediately in the subsequent reaction.

The diamine was dissolved in MeOH (220 mL) and $HC(OEt)_3$ (4.46 mL, 26.8 mmol) and NH_2SO_3H (108 mg, 1.12 mmol) were added. The mixture was stirred at room temperature overnight and a precipitate appeared. The solid was filtered off, washed with cold diethyl ether and dried under vacuum to give **3** (4.32 g, 70% two-step yield).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.26 (br s, 1H, N*H*), 8.40 (s, 1H, C*H* $_{\text{imidazole backbone}}$), 7.39 (s, 2H, Ar–H).

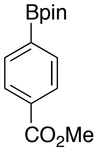
1-(4,7-Dibromo-1*H*-benzimidazol-1-yl)-2-methylpropan-2-ol (4):



4,7-Dibromobenzimidazole (**3**) (3.0 g, 10.9 mmol), K_2CO_3 (4.5 g, 32.7 mmol, 3 equiv.) and EtOH (60 mL) were added to a pressure tube. The mixture was stirred for 15 min at room temperature and 1-chloro-2-methyl-2-propanol (2.79 mL, 27.3 mmol, 2.5 equiv.) was dropwise added and the mixture was heated at 100 °C for 72 h. The product was extracted with CH_2Cl_2 (3 × 60 mL), washed with brine (3 × 40 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and **4** was obtained as white solid without further purification (3.8 g, 100% yield).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.28 (s, 1H, C*H*$_{\text{imidazole backbone}}$), 7.38 (s, 2H, C*H*$_{\text{phenyl ring}}$), 4.87 (s, 1H, O*H*), 4.55 (s, 2H, NC*H*$_2$C(CH$_3$)$_2$OH), 1.10 (s, 6H, (C*H*$_3$)$_2$OH); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 148.0, 143.0, 131.7, 128.4, 125.5, 112.6, 102.3, 69.0, 54.5, 26.8 ppm. HRMS (ES+): calcd. m/z for $C_{11}H_{13}N_2OBr_2$ $[M-H]^+$:343.9695; found 343.9697.

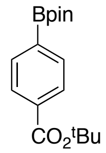
4-(Methoxycarbonyl)phenylboronic acid pinacol ester (5):



A mixture of 4-methoxycarbonylphenylboronic acid (14.8 g, 82.4 mmol) and pinacol (11.7 g, 98.8 mmol, 1.2 equiv.) was dissolved under nitrogen atmosphere in dry and degassed THF (300 mL) and the solution was heated at reflux for 5 h. The reaction media was diluted with EtOAc (200 mL), washed with brine (3 × 150 mL) and dried over $MgSO_4$. The solvent was removed under vacuum and **5** was isolated as a white solid (20.4 g, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.4 Hz, 2H, Ar–H), 7.87 (d, *J* = 8.4 Hz, 2H, Ar–H), 3.92 (s, 3H, COOC*H*$_3$), 1.36 (s, 12H, 4C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 134.8, 132.5, 128.7, 84.3, 52.3, 25.0.

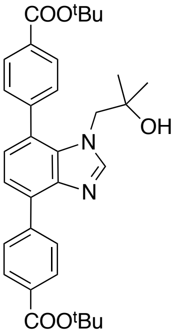
4-(Methoxycarbonyl)phenylboronic acid pinacol ester (6):



To a solution of **5** (20.2 g, 77.2 mmol) in dry and degassed Et_2O (770 mL), ^{t}BuOK (43.3 g, 386 mmol, 5 equiv.) was added portionwise under nitrogen atmosphere and the reaction mixture was stirred at room temperature for 1.5 h. The reaction media was quenched by the addition of H_2O (500 mL) and the product was diluted with EtOAc (150 mL), washed with brine (3 × 100 mL) and dried over $MgSO_4$.The solvent was removed under reduced pressure to give **6** as a white powder (14.4 g, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.4 Hz, 2H, Ar–H), 7.84 (d, *J* = 8.4 Hz, 2H, Ar–H), 1.60 (s, 9H, CH_{3tBu}), 1.36 (s, 12H, 4C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 134.9, 134.4, 128.6, 84.3, 81.3, 28.4, 25.0.

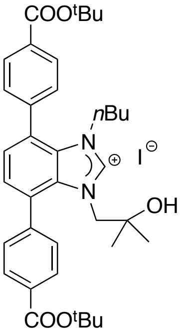
Di-tert-butyl-4,4'-(1-(2-hydroxy-2-methylpropyl)-1*H*-benzimidazol-1-yl-4,7-dibenzoate (7):



To a mixture of **4** (3.93 g, 11.3 mmol), **6** (7.21 g, 23.7 mmol, 2.1 equiv.), CsF (10.29 g, 67.7 mmol, 6 equiv.) and $PdCl_2(dppf)_2$ (413 mg, 0.565 mmol, 0.005 equiv.) degassed with N_2, a solution of dioxane / H_2O (2:1, 72 mL) pre-bubbled with N_2 for 1 h was added and the mixture was heated at 100 °C overnight under N_2. The product was extracted with CH_2Cl_2 (3 × 100 mL), washed with brine (3 × 70 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The product was purified by column chromatography (SiO_2 pre-treated with 5% NEt_3; pentane/EtOAc (20:1) to EtOAc to EtOAc/MeOH (100:2)) affording **7** as a white solid (3.44 g, 56 % yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (s, 1H, $NC\mathit{H}N_{\text{imidazole backbone}}$), 8.14–8.05 (m, 6H, Ar-H), 7.52–7.49 (m, 3H, Ar–H), 7.21–7.17 (m, 1H, Ar–H), 3.93 (s, 2H, $NC\mathit{H}_2C(CH_3)_2OH$), 1.65 (s, 9H, $3CH_{3\text{t-butyl}}$), 1.62 (s, 9H, $3CH_{3\text{t-butyl}}$), 0.84 (s, 6H, $(C\mathit{H}_3)_2OH$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 165.5, 146.4, 143.2, 142.4, 141.9, 132.2, 131.8, 131.6, 130.9, 130.0, 129.7, 129.6, 129.3, 126.1, 126.0, 121.7, 81.7, 81.0, 71.0, 55.7, 28.4, 28.4, 27.2. HRMS (ES+): calcd. m/z $C_{33}H_{38}O_5N_2Na$ [M+Na]+: 528.2678. Found: 565.2624.

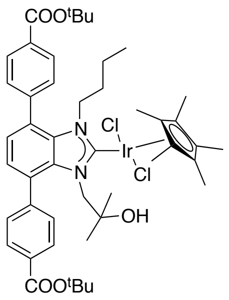
4,7-Bis(4-(tert-butoxycarbonyl)phenyl)-1-butyl-3-(2-hydroxy-2-methylpropyl)-1*H*-benzimidazol-3-ium iodide (8):



To a solution of **7** (3.33 g, 6.14 mmol) in dry CH_3CN (7 mL), *n*BuI (11.30 g, 61.4 mmol, 10 equiv.) was added and the mixture was heated in a pressure tube at 110°C overnight. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (3 × 30 mL), washed with brine (3 × 20 mL), and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure and the solid residue was washed with pentane to remove the excess of *n*BuI. Product **8** was isolated as a yellow solid (3.50 g, 95% yield).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 10.54 (s, 1H, NC*H*N$_{\text{imidazole backbone}}$), 8.17–8.15 (m, 4H, Ar-H), 7.59–7.50 (m, 4H, Ar–H), 7.43 (s, 2H, Ar–H), 4.45 (s, 2H, NC*H*$_2$C(CH$_3$)$_2$OH), 4.08 (t, 2H, *J* = 7.6 Hz, C*H*$_{2\text{n-butyl}}$), 1.64 (s, 18H, 6CH$_{3\text{t-butyl}}$), 1.62–1.56 (m, 2H, C*H*$_{2\text{n-butyl}}$), 1.06–0.97 (m, 2H, C*H*$_{2\text{n-butyl}}$), 0.90 (s, 6H, (C*H*$_3$)$_2$OH), 0.72 (t, 3H, *J* = 7.3 Hz, C*H*$_{3\text{n-butyl}}$); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 164.9, 164.9, 145.8, 139.9, 139.8, 133.1, 130.5, 130.0, 129.9, 129.8, 129.7, 129.4, 129.0, 128.9, 128.8, 82.2, 82.0, 69.8, 57.2, 50.0, 31.7, 28.3, 26.9, 19.5, 13.3. HRMS (ES+): calcd. m/z $C_{37}H_{48}IN_2O_5$ [M+H]+: 727.2608. Found: 727.2599.

(4,7-Bis(4-carboxyphenyl)-1-butyl-3-(2-hydroxy-2-methylpropyl)-1*H*-benzoimidazol-2-ylidene)(pentamethylcyclopentadienyl) iridium(III) dichloride (9):

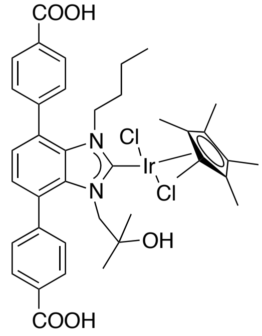


To a degassed solution of **8** (0.400 g, 0.55 mmol) in dry CH$_3$CN (40 mL), Ag$_2$O (0.255 g, 1.1 mmol, 2 equiv.) was added under a nitrogen atmosphere, and the reaction mixture was heated in dark at 35 °C for 3 h. The mixture was filtered through a pad of Celite®, the solvent was removed under reduced pressure and the product was used in the subsequent transmetallation reaction. A mixture of the silver carbene (0.55 mmol) and [IrCp*Cl$_2$]$_2$ (0.219 g, 0.275 mmol, 0.5 equiv.) was dissolved in dry CH$_2$Cl$_2$ (40 mL) and heated at 35 °C in dark, overnight. The reaction mixture was filtered through a pad of Celite® and the solvent was removed under reduced pressure. The product was purified by column chromatography (SiO$_2$; EtOAc/MeOH 100:0 to 15:1) affording **9** as a yellow solid (0.273 g, 49% yield, two steps).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.18–8.08 (m, 4H, Ar–H), 7.71–7.69 (m, 1H, Ar–H), 7.52–7.51 (m, 1H, Ar–H), 7.40–7.34 (m, 2H, Ar–H), 7.12–7.06 (m, 2H, Ar–H), 4.78–

4.66 (m, 1H, CH*H*$_{\text{n-butyl}}$) 3.77–3.70 (m, 1H, C*H*H$_{\text{n-butyl}}$), 3.62 (d, 1H, *J* = 13.6 Hz, NC*H*HC(CH$_3$)$_2$OH), 3.06 (d, 1H, *J* = 13.6 Hz, NCH*H*C(CH$_3$)$_2$OH), 2.64–2.45 (br s, 1H, O*H*), 1.75–1.78 (m, 2H, C*H*$_{2\text{n-butyl}}$), 1.65 (s, 18H, 6CH$_{3\text{t-butyl}}$), 1.62 (s, 15H, C$_5$(C*H*$_3$)$_5$), 1.21–1.12 (m, 1H, C*H*H$_{\text{nbutyl}}$), 1.03 (s, 3H, C(C*H*$_3$)$_2$OH), 0.94–0.82 (m, 1H, CH*H*$_{\text{n-butyl}}$), 0.61 (s, 3H, C(C*H*$_3$)$_2$OH), 0.56–0.45 (m, 4H, CH*H*$_{\text{n-butyl}}$, C*H*$_{3\text{n-butyl}}$); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 175.9, 165.4, 165.4, 142.8, 142.6, 133.8, 132.0, 131.9, 131.7, 130.0, 129.9, 129.5, 129.4, 129.3, 128.5, 126.3, 125.5, 125.4, 125.1, 88.6, 81.7, 81.7, 69.8, 61.9, 51.2, 33.3, 30.6, 28.4, 25.6, 19.6, 13.5, 9.1. HRMS (ES+): calcd. m/z $C_{47}H_{61}ClIrN_2O_5$: [M-Cl]$^+$: 961.3898. Found: 961.3904.

(4,7-bis(4-(tert-butoxycarbonyl)phenyl)-1-butyl-3-(2-hydroxy-2-methylpropyl)-1H-benzoimidazol-2-ylidene)(pentamethylcyclopentadienyl) iridium(III) dichloride (10):

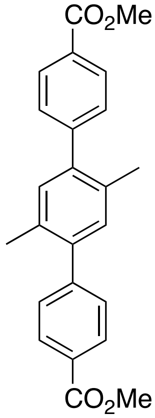


To a sealed vial containing **9** (100 mg, 0.099 mmol) at 0 °C, a solution of HCl in dioxane (4M, 0.5 mL) was added and allowed to warm to room temperature. Then the reaction mixture was stirred at room temperature for 5 h. The resulting solid was separated by centrifugation and washed with water (3 × 1mL) and CH$_2$Cl$_2$ (3 × 1 mL) to give **10** as a yellow solid (0.046 g, 51% yield).

^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ = 13.22 (br, 2H, CO$_2$*H*); 8.83 (s, 1H, O*H*), 8.16–8.10 (m, 4H, Ar–H); 7.86–7.58 (m, 4H, Ar–H); 7.35–7.28 (m, 2H, Ar–H); 4.37-4.32 (m, 1H, C*H*H$_{\text{n-butyl}}$); 3.92–3.87 (m, 1H, C*H*H$_{\text{n-butyl}}$), 3.61 (d, *J* = 14.8 Hz, 1H, NC*H*HCC(CH$_3$)$_2$OH), 3.38 (d, *J* = 14.8 Hz, 1H, NC*H*HCC(CH$_3$)$_2$OH), 1.60 (s, 15H,

$C_5(CH_3)_5$), 1.48–1.38 (m, 1H, $CHH_{\text{n-butyl}}$), 1.13–1.02 (m, 1H, $CHH_{\text{n-butyl}}$), 0.95 (s, 3H, $C(CH_3)_2OH$); 0.77–0.68 (m, 4H, $CHH_{\text{n-butyl}}$, $C(CH_3)_2OH$), 0.46-0.44 (m, 4H, $CHH_{\text{n-butyl}}$, $CH_{3\text{n-butyl}}$). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 173.9, 166.9, 166.8, 141.7, 141.3, 133.1, 130.9, 130.5, 130.5, 130.3, 129.6, 129.3, 128.7, 126.5, 126.2, 126.0, 125.4, 89.9, 72.9, 56.2 50.3, 32.4, 26.7, 22.7, 18.8, 12.9, 8.7. Elemental analysis calculated for $C_{39}H_{45}Cl_2IrN_2O_5$: C, 52.93; H, 5.13; N, 3.17; Found: C, 52.79; H, 4.99; N, 3.37.

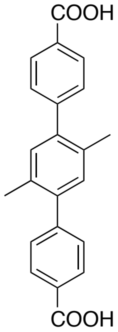
Dimethyl-2',5'-dimethyl-1,1':4',1''-terphenyl-4,4''-dicarboxylate (11):



The product was synthesised following the reported procedure.[5] 1,4-Dibromo-2,5-dimethylbenzene (6.7 g, 25.3 mmol), **5** (13.9 g, 53.0 mmol, 2.1 equiv.), CsF (23.1 g, 152 mmol, 6 equiv.) and $PdCl_2$(dppf) (926 mg, 1.27 mmol, 0.005 equiv.) were dissolved in a mixture of dioxane/ H_2O (2:1, 70 mL), previously degassed with N_2 for 1 h, and the mixture was heated at 100 °C overnight. After cooling to room temperature, the organic phase was extracted with CH_2Cl_2 (3 × 100 mL), washed with brine (3 × 50 mL) and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure and the resulting solid was purified by column chromatography (SiO_2; Pentane to CH_2Cl_2) to give **11** as a white powder (2.9 g, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12–8.10 (m, 4H, Ar–H), 7.46–7.44 (m, 4H, Ar–H), 7.16 (s, 2H, Ar-H), 3.96 (s, 6H, CO_2CH_3), 2.27 (s, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 146.5, 140.5, 132.8, 131.9, 129.6, 129.4, 128.9, 52.3, 20.0.

2',5'-Dimethyl-1,1':4',1''-terphenyl-4,4''-dicarboxylic acid (12):



To a solution of **11** (3.74 g, 9.98 mmol) in THF (200 mL), H_2O (200 mL) and NaOH (3.99 g, 99.8 mmol, 10 equiv.) were added and the solution was stirred at 50 °C overnight. After cooling to room temperature, the solvent was removed under reduced pressure and concentrated HCl was added dropwise, resulting in the precipitation of a white solid. H_2O (100 mL) was then added and the solid was filtered under vacuum and washed with water to give **12** as a white powder (3.35 g, 97% yield).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.97 (br, 2H, 2COO*H*), 8.01 (d, *J* = 8.4 Hz, 4H, Ar–H), 7.51 (d, *J* = 8.4 Hz, 4H, Ar–H), 7.19 (s, 2H, Ar–H), 2.25 (s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.2, 145.3, 139.8, 132.3, 131.6, 129.2, 19.6. Elemental analysis calculated for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24; Found: C, 75.95 H, 5.18.

S3 Synthesis of MOFs

UiO-68–2CH$_3$:

To a Teflon®-capped 20 mL scintillation vial, $ZrCl_4$ (47 mg, 0.20 mmol), benzoic acid (122 mg, 1.00 mmol, 5 equiv.) and anhydrous DMF (10 mL) were added and the mixture was sonicated for 10 min until total dissolution of the solids. Then, **12** (83 mg, 0.24 mmol) and H_2O (18 μL, 5 equiv.) were added and the mixture was further sonicated for 10 min until all the reactants were dissolved. The vial was placed in an isothermal oven at

70 °C for 72 h. After cooling to room temperature, the solid was isolated by centrifugation and washed with DMF (35 mL) (3 times per day over 3 days) and EtOH (35 mL) (3 times per day over 3 days). The resulting MOF was dried at 120 °C overnight under vacuum to give **UiO-68–2CH$_3$** as a white microcrystalline powder (44 mg, 48% yield).

UiO-68–2CH$_3$-L-*direct*:

To a Teflon®-capped 20 mL scintillation vial, $ZrCl_4$ (46 mg, 0.20 mmol), benzoic acid (122 mg, 1.00 mmol, 5 equiv.) and anhydrous DMF (10 mL) were added and the mixture was sonicated for 10 min until total dissolution of the solids. Then **12** (42 mg, 0.12 mmol), **10** (72 mg, 0.08 mmol) and H_2O (18 µL, 5 equiv.) were added and the mixture was further sonicated for 10 min until all the reactants were dissolved. The vial was placed in an isothermal oven at 70 °C for 72 h. After cooling to room temperature, the solid was isolated by centrifugation and washed with DMF (35 mL) (3 times per day over 3 days) and EtOH (35 mL) (3 times per day over 3 days). The resulting MOF was dried at 70 °C overnight under vacuum to give **UiO-68–2CH$_3$-L-*direct*** as a yellow microcrystalline powder (33 mg, 32% yield).

UiO-68–2CH$_3$-L-*PSE*:

UiO-68–2CH$_3$ (44 mg, 0.10 mmol) and **10** (40 mg, 0.04 mmol) and MeOH (6.5 mL) were added to a Teflon-capped 20 mL scintillation vial and the mixture was stirred at 60 °C for 24 h. After cooling to room temperature, the resulting MOF was separated by centrifugation and washed with fresh MeOH (35 mL) (3 times per day over 3 days) and EtOH (35 mL) (3 times per day over 3 days). The MOF was dried at 70 °C overnight under vacuum to give **UiO-68–2CH$_3$-L-*PSE*** as a yellow microcrystalline powder (44 mg, 71%) yield.

S4 Postsynthetic exchange experiments

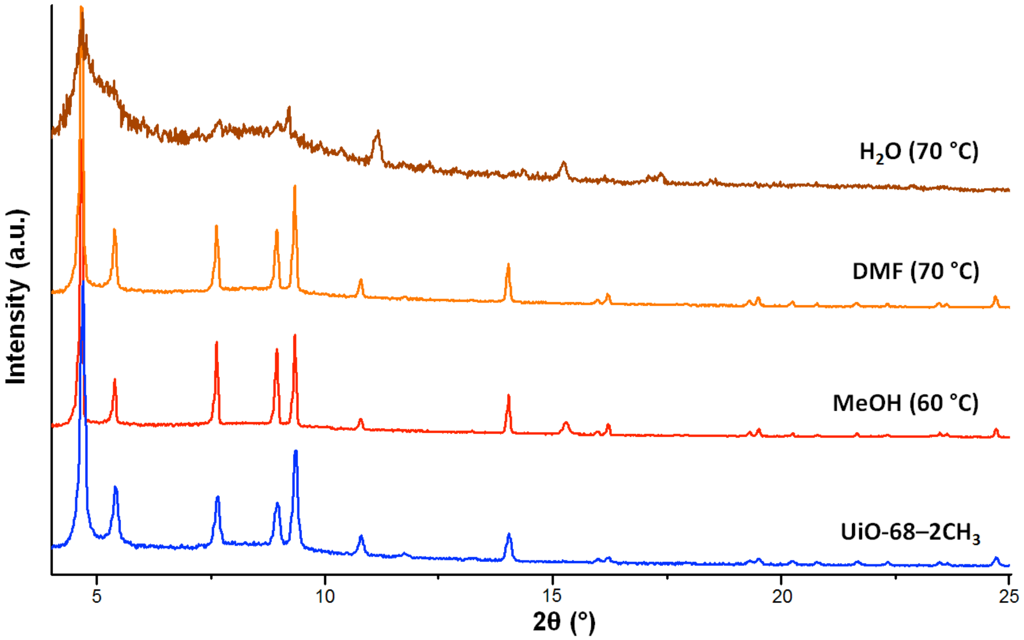


Figure S1. XRPD patterns of UiO-68–2CH_3 and UiO-68–2CH_3-**L**-*PSE* after postsynthetic exchange in MeOH at 60 °C, DMF at 70 °C and H_2O at 70 °C.

S5 Characterisation of MOFs

S5.1 LeBail refinement of UiO-68-2CH_3

Full pattern decomposition was done using LeBail refinement in Jana2006.[6] The data range was 2–30° 2θ and the background was fitted using 12th order Legendre polynomial. The space group used was $Fm\bar{3}m$ and the initial unit cell parameters were taken from PCN-56 (a = 32.60 Å).[7] The cell parameters and zero-shift were refined and a Pseudo-Voigt profile was used. The peak asymmetry was refined using correction by divergence (H/L = S/L). Convergence was reached, resulting in the following refined parameters: a = 32.902(1) Å, V = 35619(1) Å^3. Residuals: $\chi^2 = 2.03$, $R_p = 5.59\%$, $wR_p = 7.31\%$.

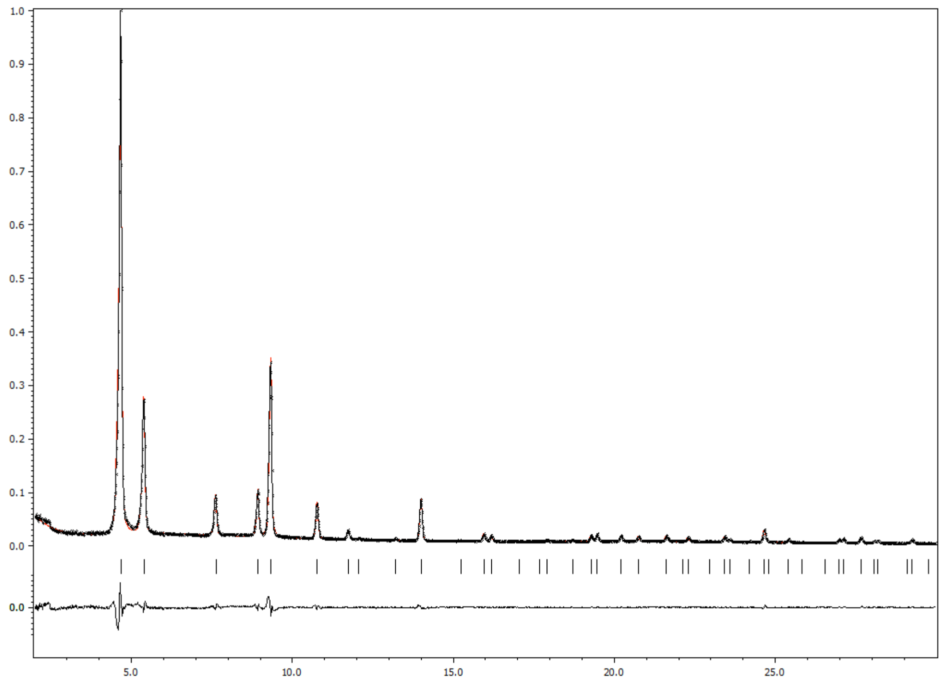


Figure S2. XRPD pattern of UiO-68–2CH_3 (black) showing the refined LeBail fitting (red), the calculated peak positions and the residual intensity below.

S5.2 Elemental analysis

UiO-68–2CH_3:

[C(%): 53.37 (obs), 52.77 (calcd); H(%): 3.46(obs), 4.10 (calcd); N(%): <0.10 (obs), 0 (calcd); Zr(%): 19.52 (obs), 19.88 (calcd) based on the chemical formula [$Zr_6O_5(OH)_3(dmtpdc)_{5.5}\cdot 10H_2O$].

***UiO-68–2CH_3-L-direct*:**

[C(%): 47.04 (obs), 45.55 (calcd); H(%): 3.97(obs), 4.99 (calcd); N(%): 0.78 (obs), 0.72 (calcd); Zr(%): 15.00 (obs), 15.06 (calcd); Ir(%): 4.17 (obs), 4.95(calcd) based on the chemical formula [$Zr_6O_5(OH)_3(dmtpdc)_{4.57}\mathbf{L}_{0.94}\cdot 30H_2O$].

UiO-68–2CH_3-L-*PSE*:

[C(%): 53.39 (obs), 51.24 (calcd); H(%): 3.89(obs), 4.49 (calcd); N(%): 1.20 (obs), 1.27 (calcd); Zr(%): 11.96 (obs), 13.20 (calcd); Ir(%): 7.39 (obs), 8.74 (calcd) based on the chemical formula [$Zr_6O_4(OH)_4(dmtpdc)_{4.62}\mathbf{L}_{1.38}.\cdot 0.5H_2\mathbf{L}\cdot 10H_2O$].

S5.3 Thermogravimetric analysis

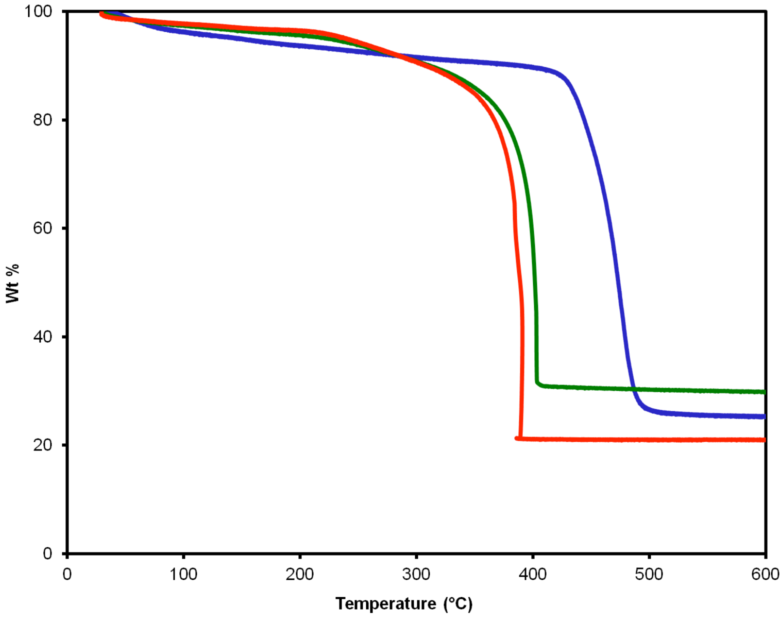


Figure S3. TGA curves for UiO-68–2CH$_3$ (blue), UiO-68–2CH$_3$-**L**-*direct* (green) and UiO-68–2CH$_3$-**L**-*PSE* (red) in air.

S5.4 SEM images of UiO-68–2CH$_3$

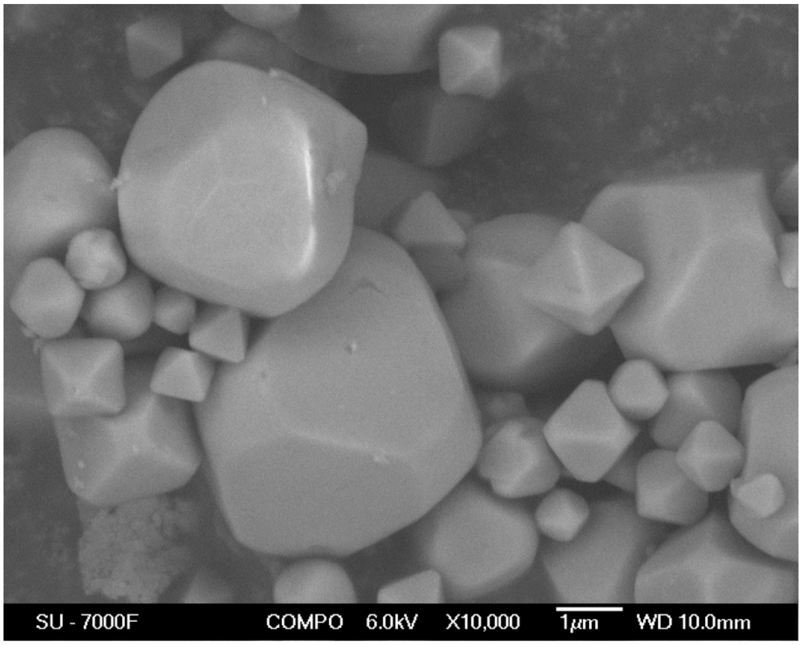


Figure S4. BSE image of UiO-68–2CH$_3$.

S5.5 FTIR spectroscopy

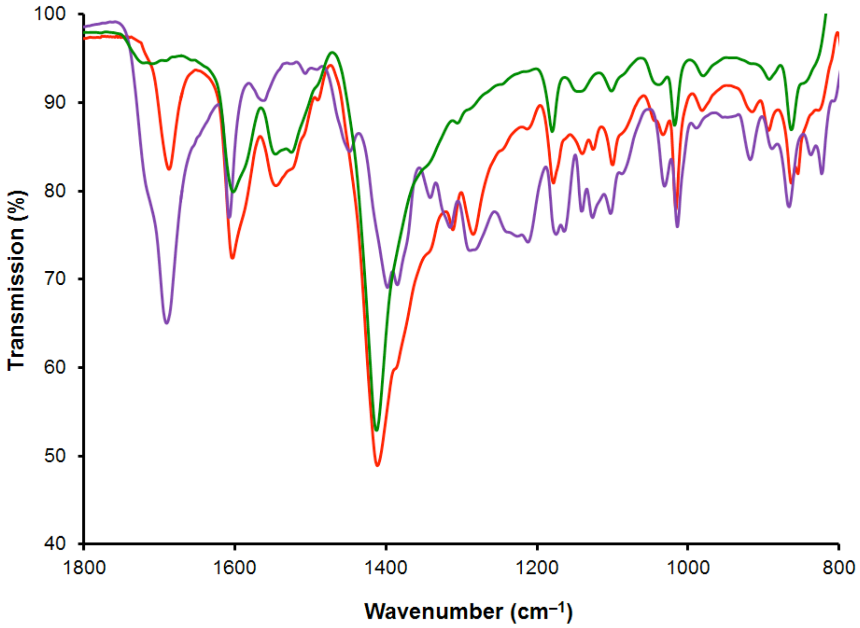


Figure S5. FTIR spectra of H_2**L** (purple), UiO-68–2CH$_3$-**L**-*direct* (green) and UiO-68–2CH$_3$-**L**-*PSE* (red).

S5.6 ^{1}H NMR spectroscopy of digested MOFs:

The ^{1}H NMR spectra were recorded at 500 MHz. Chemical shifts (δ) are reported in ppm, using the residual non-deuterated solvent peaks in DMSO-d_6 (δ_H 2.50; δ_C 39.52) as an internal reference.

Synthetic method	**Molar % Ir**
Direct synthesis	17
Post synthetic exchange	29

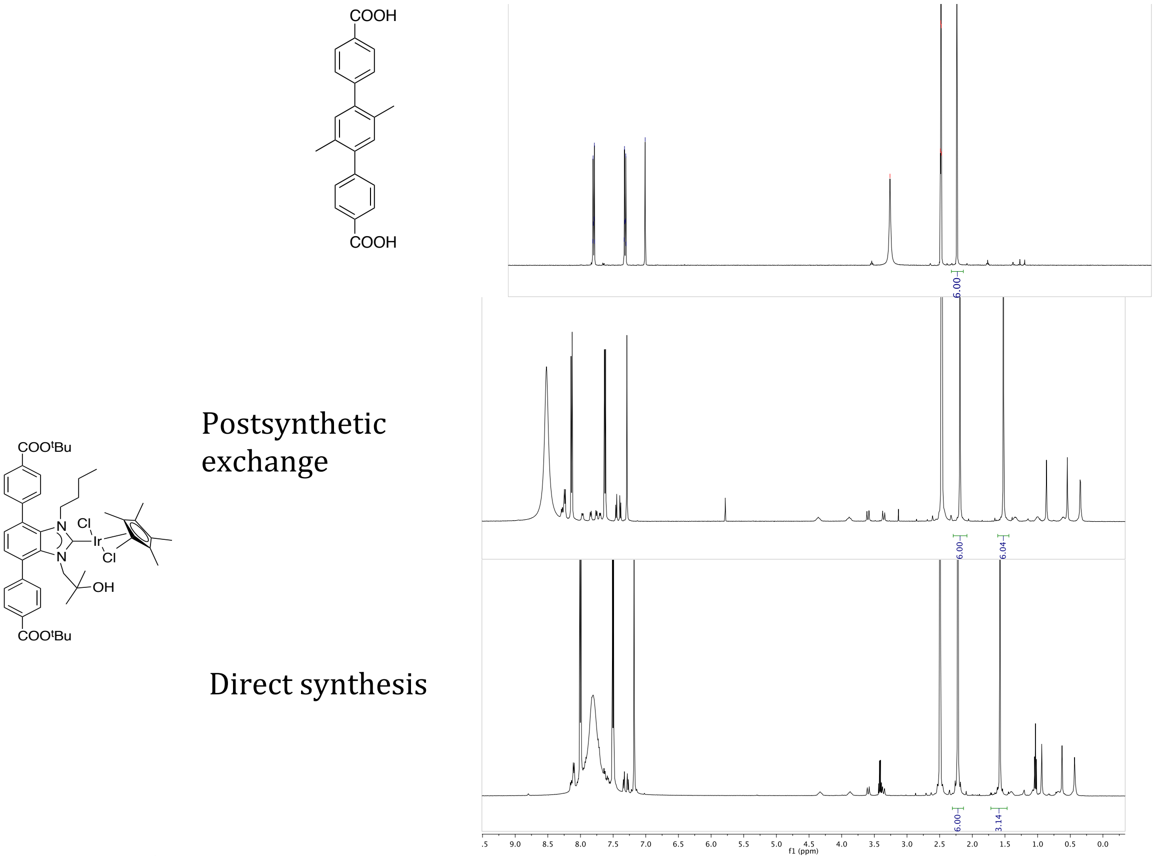


Figure S6. ^{1}H NMR spectra of (top) H_2dmtpdc and digested MOFs prepared *via* (middle) PSE and (bottom) direct synthesis.

S5.7 Cross-section polishing and EDS characterisation of MOFs

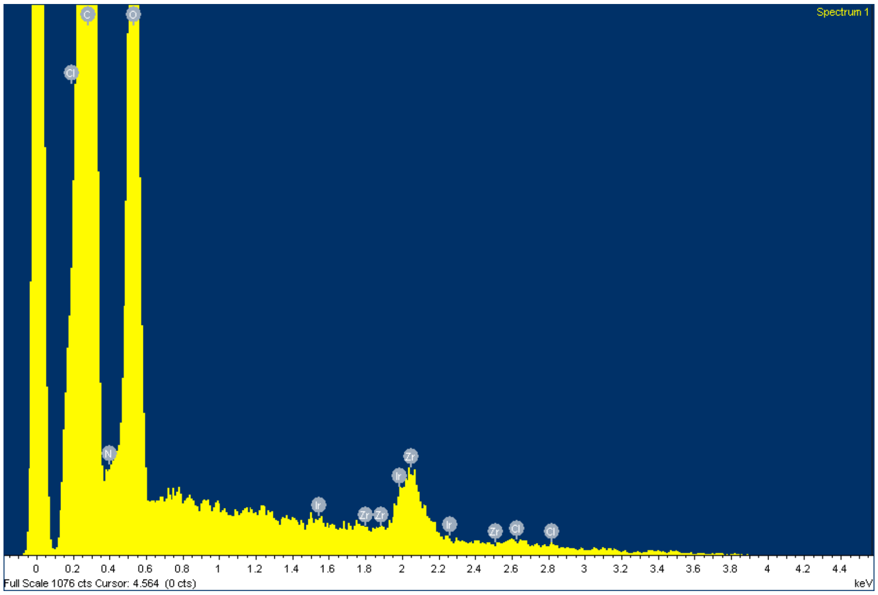


Figure S7. An EDS spectrum of UiO-68–$2CH_3$-**L**-*PSE*.

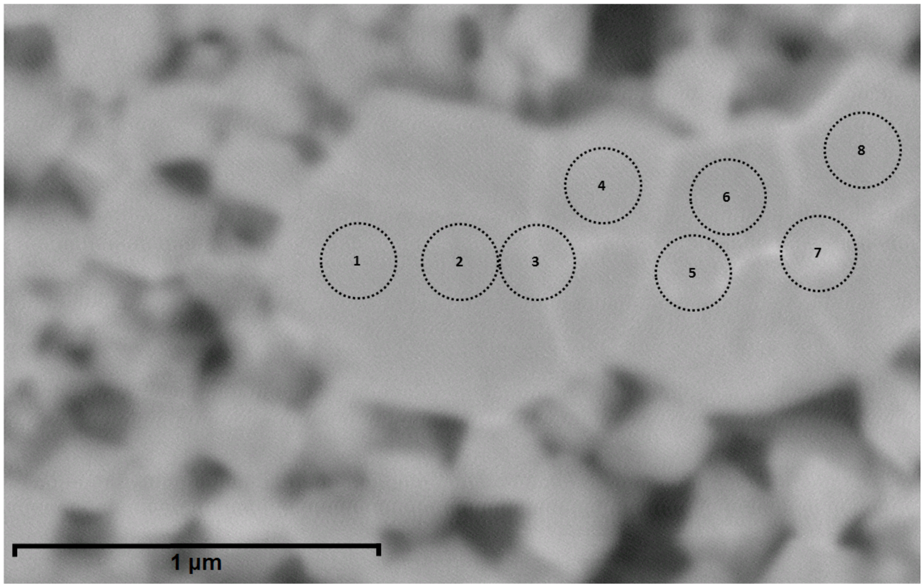


Figure S8. BSE image of UiO-68–2CH_3-**L**-*direct* prepared by cross-section polishing. The positions of the EDS measurements on the crystal are indicated and the numbers correspond to the spectra in Table S4. The accelerating voltage used for the measurement was 4 kV.

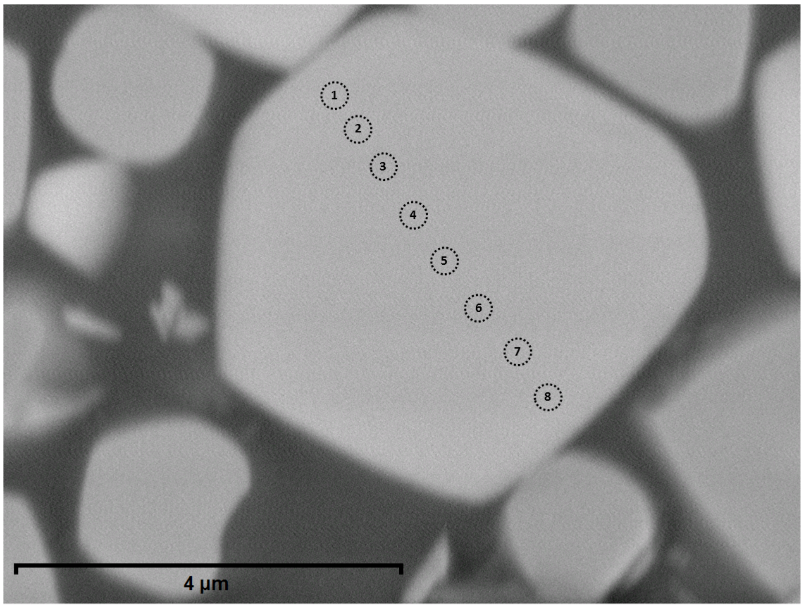


Figure S9. BSE image of UiO-68–2CH_3-**L**-*PSE* prepared by cross-section polishing. The positions of the EDS measurements on the crystal are indicated and the numbers correspond to the spectra in Table S3. The accelerating voltage used for the measurement was 4 kV.

Table S1. Element concentrations in UiO-68–2CH$_3$-**L**-*PSE* obtained from EDS.

	Spectrum	**Zr**	**Ir**	**Zr**[a]	**Ir**[a]
UiO-68–2CH$_3$-**L**-*direct*	1	3.73	0.81	1.00	0.22
	2	4.02	0.80	1.00	0.20
	3	4.73	0.74	1.00	0.16
	4	4.41	0.82	1.00	0.19
	5	5.27	0.99	1.00	0.19
	6	4.76	0.75	1.00	0.16
	7	4.31	1.02	1.00	0.24
	8	4.51	0.84	1.00	0.19
	Average	4.47±0.47[b]	0.85±0.10[b]	1.00±0.11[b]	0.19±0.02[b]
UiO-68–2CH$_3$-**L**-*PSE*	1	2.97	1.01	1.00	0.34
	2	3.81	1.38	1.00	0.36
	3	3.36	1.14	1.00	0.34
	4	2.45	0.84	1.00	0.34
	5	2.78	0.94	1.00	0.34
	6	3.15	1.27	1.00	0.40
	7	2.37	0.90	1.00	0.38
	8	2.53	0.95	1.00	0.38
	Average	2.93±0.50[b]	1.05±0.19[b]	1.00±0.17[b]	0.36±0.07[b]

[a] at.% normalised to Zr. [b] The error is based on the standard deviation of the measurements.

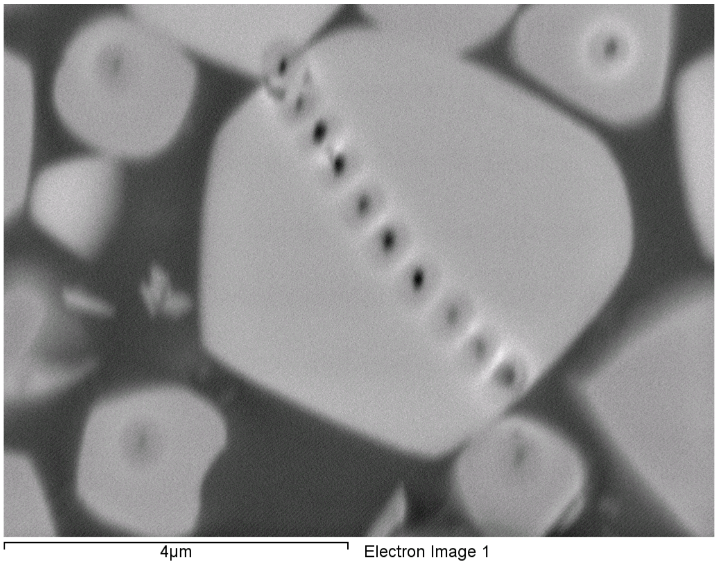


Figure S10. BSE image of UiO-68–2CH$_3$-**L**-*PSE* after EDS measurements illustrating beam damage on the crystal.

S5.8 Ir L_{III}-edge EXAFS results of the metallolinker and the MOFs.

Athena and Artemis were used as part of the Demeter software package for data processing and EXAFS fitting.[1] The data were processed using Δk = 3.0–14.2 Å^{-1} and ΔR = 1.3–3.7 Å for H_2**L**, Δk = 3.0–14.0 Å^{-1} and ΔR = 1.3–4.0 Å for UiO-68–2CH_3-**L**-*direct*, and Δk = 3.0–12.1 Å^{-1} and ΔR = 1.3–4.0 Å for UiO-68–2CH_3-**L**-*PSE*. A Hanning window was used in the Fourier transform with a full sill width of 1.0 Å^{-1}. The data and Fourier transform ranges resulted in 18 degrees of freedom and 14 variables in the fit for H_2**L**, 18 degrees of freedom and 14 variables in the fit for UiO-68–2CH_3-**L**-*direct,* and 16 degrees of freedom and 14 variables in the fit for UiO-68–2CH_3-**L**-*PSE*. ΔE_0 and S_0^2 were 7.7(2.4) and 0.80(18) for H_2**L**, 8.5(1.9) and 0.80(13) for UiO-68–2CH_3-**L**-*direct* and 9.6(2.7) and 0.90(42) for UiO-68–2CH_3-**L**-*PSE*.

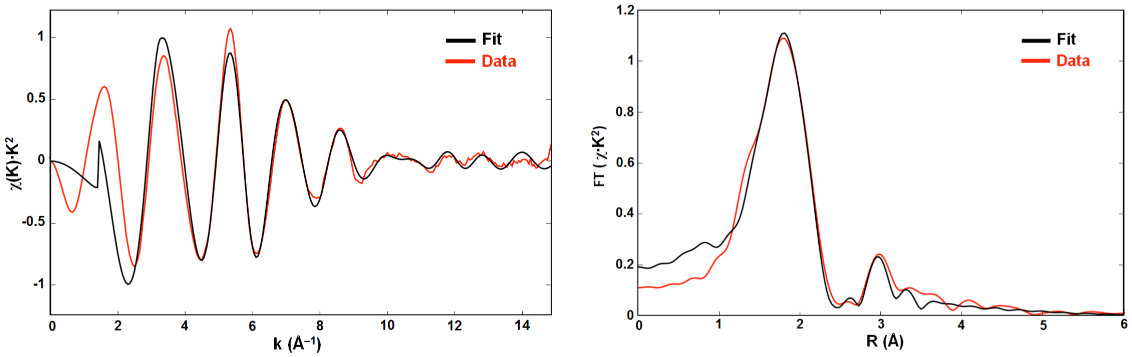


Figure S11. Left: XAFS $\chi(k)k^2$ data (red) and best-fit model (black) for H_2**L**. Right: Magnitude of the Fourier transform of $\chi(k)k^2$ (red) and best-fit model (black).

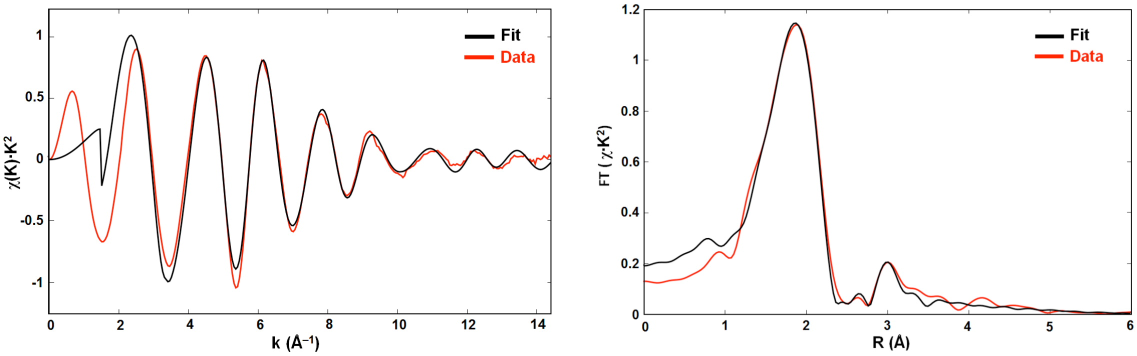


Figure S12. Left: XAFS $\chi(k)k^2$ data (red) and best-fit model (black) for UiO-68–2CH_3-**L**-*direct*. Right: Magnitude of the Fourier transform of $\chi(k)k^2$ (red) and best-fit model (black).

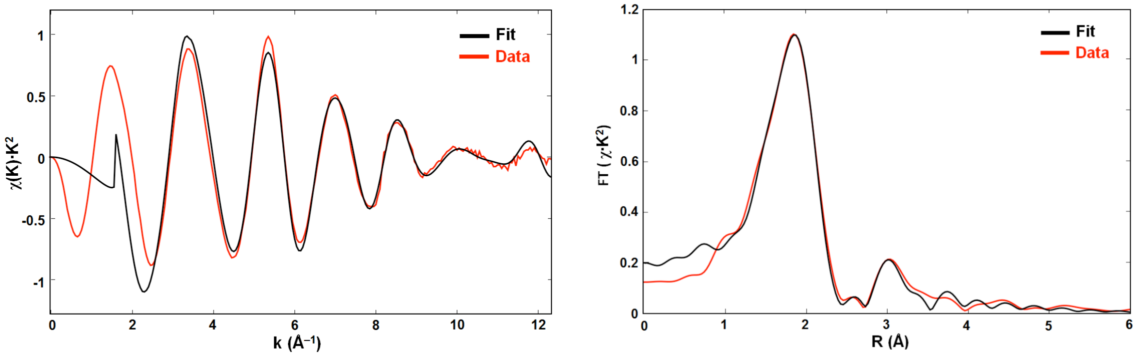


Figure S13. Left: XAFS $\chi(k)k^2$ data (red) and best-fit model (black) for UiO-68–2CH_3-**L**-*PSE*. Right: Magnitude of the Fourier transform of $\chi(k)k^2$ (red) and best-fit model (black).

Table S2. Information from Ir L_{III}-edge EXAFS studies of H_2**L**, UiO-68–2CH$_3$-**L**-*direct* and UiO-68–2CH$_3$-**L**-*PSE*.

			H_2**L**		UiO-68–2CH$_3$-**L**-*direct*		UiO-68–2CH$_3$-**L**-*PSE*	
Interaction	*N*	R_{cryst}[a] [Å]	R_{EXAFS} [Å]	σ^2 [Å^2]	R_{EXAFS} [Å]	σ^2 [Å^2]	R_{EXAFS} [Å]	σ^2 [Å^2]
Ir–C$_{\text{carbene}}$	1	2.040	2.01(5)	0.001(8)	2.02(4)	0.002(5)	2.07(3)	0.003(2)
Ir–C$_{\text{Cp* aromatic}}$	5	2.150	2.16(2)	0.003(4)	2.16(2)	0.003(3)	2.20(5)	0.008(3)
Ir–Cl	2	2.420	2.39(2)	0.005(3)	2.38(1)	0.003(2)	2.37(3)	0.006(3)
Ir–N$_{\text{im}}$[b]	2	3.074	3.03(5)	0.003(4)	3.05(3)	0.003(3)	3.03(7)	0.001(6)
Ir–C$_{\text{Cp* methyl}}$	5	3.365	3.27(3)	0.005(4)	3.29(3)	0.007(3)	3.27(5)	0.004(6)
Ir–C$_{CH_2}$	2	3.516	3.80(10)	0.005(13)	3.77(9)	0.007(13)	3.78(7)	0.001(8)
Ir–C–N$_{\text{(carbene–im)}}$	4	3.239	3.30(10)	0.004(12)	3.17(7)	0.005(8)	3.23(10)	0.004(8)
Ir–C–C $_{\text{(Cp* aromatic–methyl)}}$	10	3.554	3.52(5)	0.008(8)	3.53(5)	0.010(6)	3.47(10)	0.008(9)

[a] Crystallographic distances taken from reference [8]. [b] im = imidazole.

S5.9 N$_2$ sorption

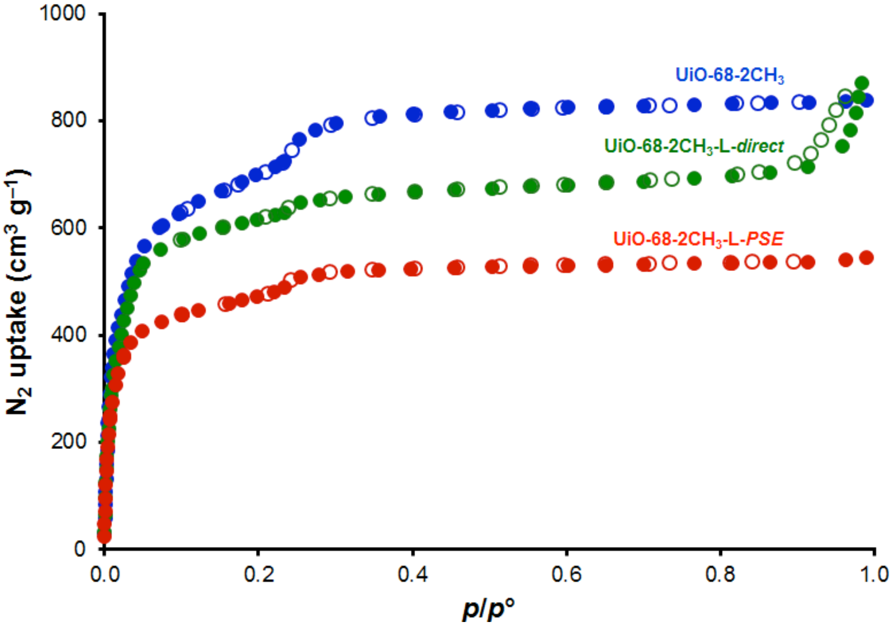


Figure S14. N$_2$ adsorption (●) and desorption (○) isotherms of UiO-68–2CH$_3$ (blue), UiO-68–2CH$_3$-**L**-*direct* (green) and UiO-68–2CH$_3$-**L**-*PSE* (red) measured at 77 K.

Table S3. Textural properties of the MOFs.

Material	BET surface area (m^2/g)	Pore volume (cm^3/g)
UiO-68–2CH_3	2470	1.30
UiO-68–2CH_3-**L**-*direct*	2040	1.35
UiO-68–2CH_3-**L**-*PSE*	1600	0.84

S6 Catalysis experiments

General procedure for the isomerisation of 1-octen-3-ol:

In a microwave tube, the catalyst (4 mol% Ir) was dispersed in dry toluene (1mL) under an argon atmosphere and 1-octen-3-ol (0.1 mmol, 14 μL) and any additive (see table S4) were added. The reaction mixture was stirred at 100 °C for the time given in Table 1 and then cooled to room temperature. For catalytic tests with MOFs the solid was separated by centrifugation and the yield was determined by ^{1}H-NMR of the supernatant.

Table S4. Comparison of different catalysts and additives for isomerisation of 1-octen-3-ol.

Catalyst	Additive	Time	Yield
UiO-68–2CH_3	-	24	0
Metallolinker (**9**)	-	24	99
UiO-68–2CH_3-**L**-*direct*	-	48	64
UiO-68–2CH_3-**L**-*PSE*	-	48	65
UiO-68–2CH_3-**L**-*PSE*	$AgBF_4$	24	80
UiO-68–2CH_3-**L**-*PSE*	$NaHCO_3$	24	99
UiO-68–2CH_3-**L**-*PSE*	K_2CO_3	24	99

Procedure for large-scale catalyst recycling tests:

The reaction was carried out using a sealed microwave tube. The tube was charged with UiO-68–2CH$_3$-**L**-*PSE* (50 mg, 0.045 mmol, 4 mol% Ir), 1-octen-3-ol (0.38 mmol, 57 µL) and toluene (5 mL). The reaction mixture was stirred at 100 °C for 48 h. After cooling to room temperature the solid was separated by centrifugation, the supernatant was collected and the yield was determined by ^{1}H NMR spectroscopy. The MOF was washed three times with CH$_2$Cl$_2$ (3 × 2 mL), dried at room temperature under vacuum for 16 h and then reused for another cycle.

Table S5. Recycling data.

Entry	**Cycle**	**Yield (%)**
1	I	99
2	II	99
3	III	99

Procedure for heterogeneity tests:

The isomerisation of 1-octen-3-ol was carried out as described in the general procedure with UiO-68–2CH$_3$-**L**-*PSE*. After 3 h, the solid was removed by centrifugation and the yield determined by ^{1}H NMR spectroscopy (0 % yield of 3-octanone). The supernatant was filtered through a short pad of celite and the filtrate was stirred at 100 °C as before. After 18 h, the yield did not increase any further.

S7 XRPD analysis of MOFs after catalysis

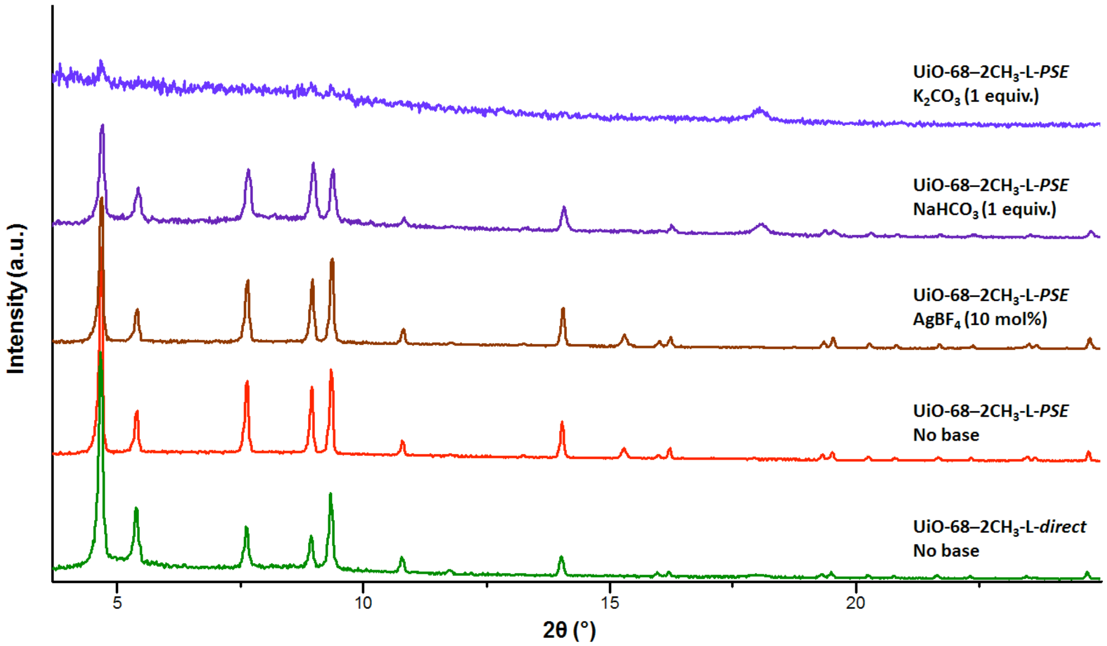


Figure S15. XRPD patterns of MOFs after catalysis under different conditions.

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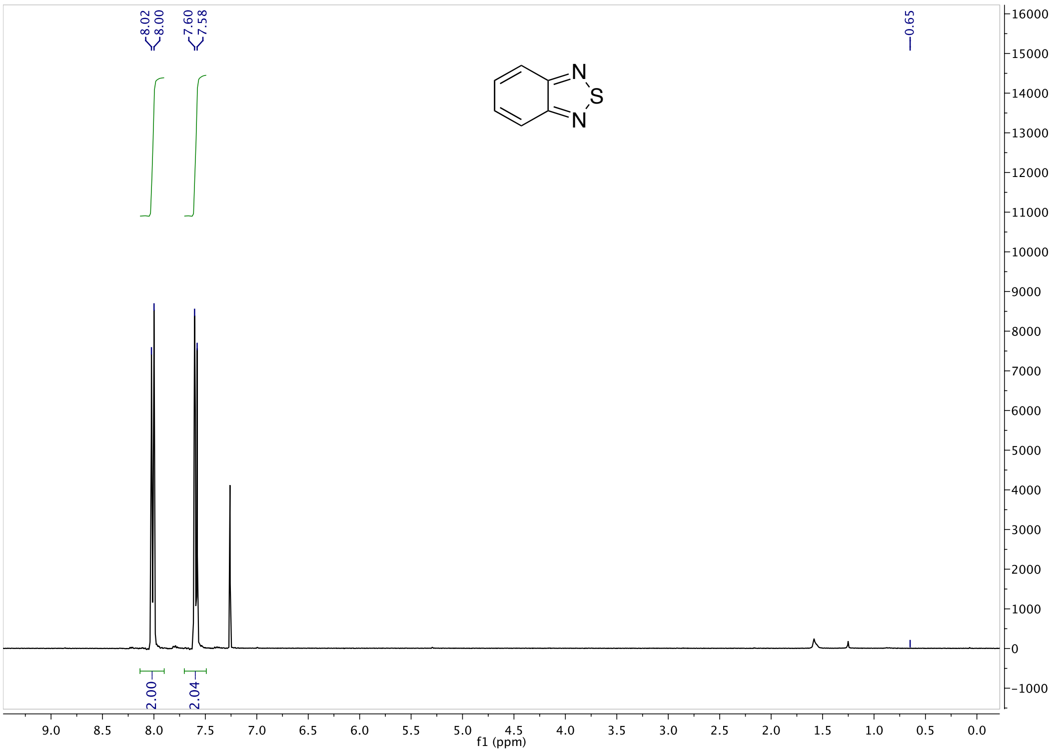
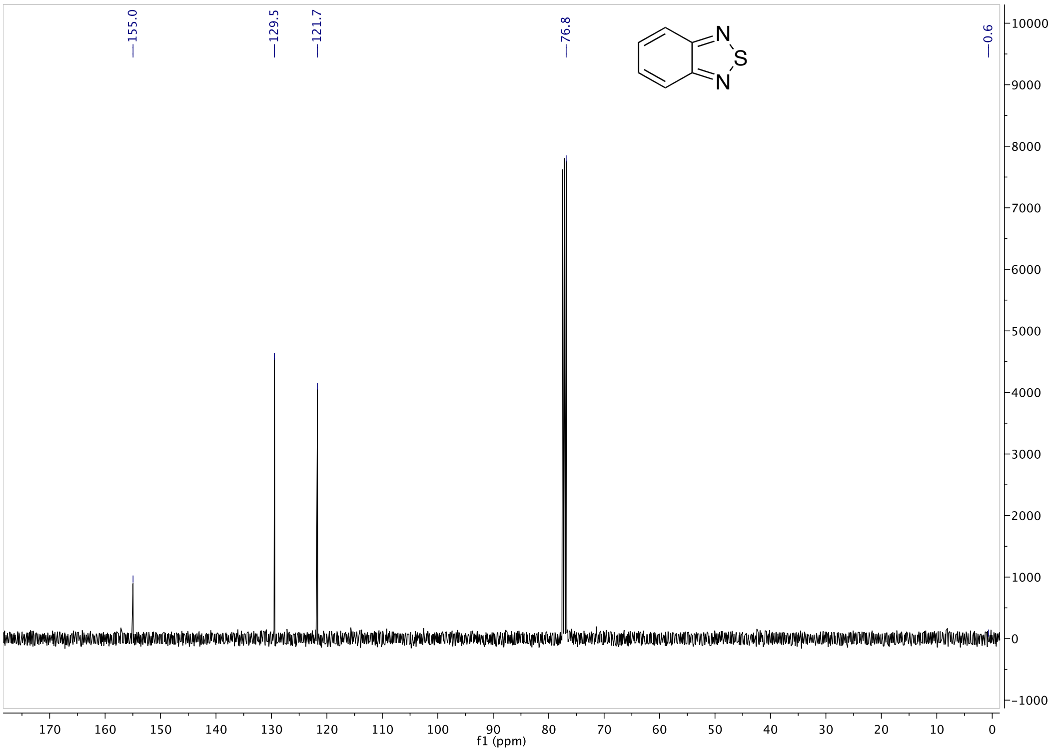
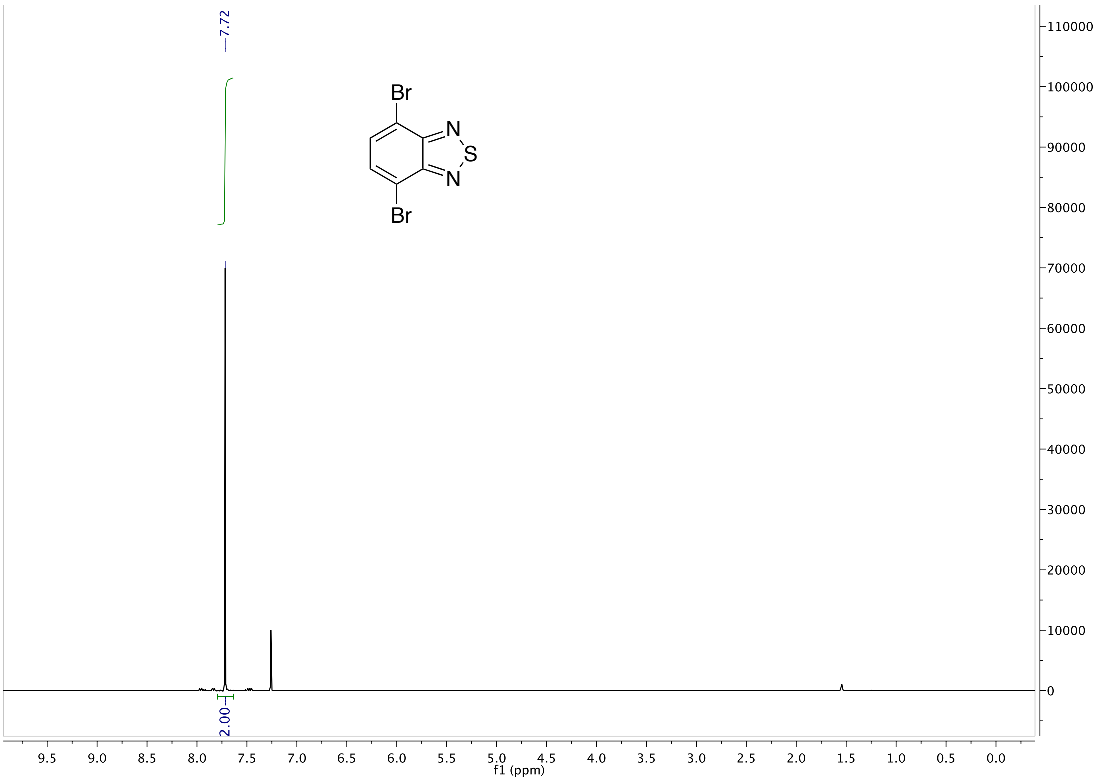
S8 ^{1}H (upper) and ^{13}C (lower) NMR spectra of isolated products



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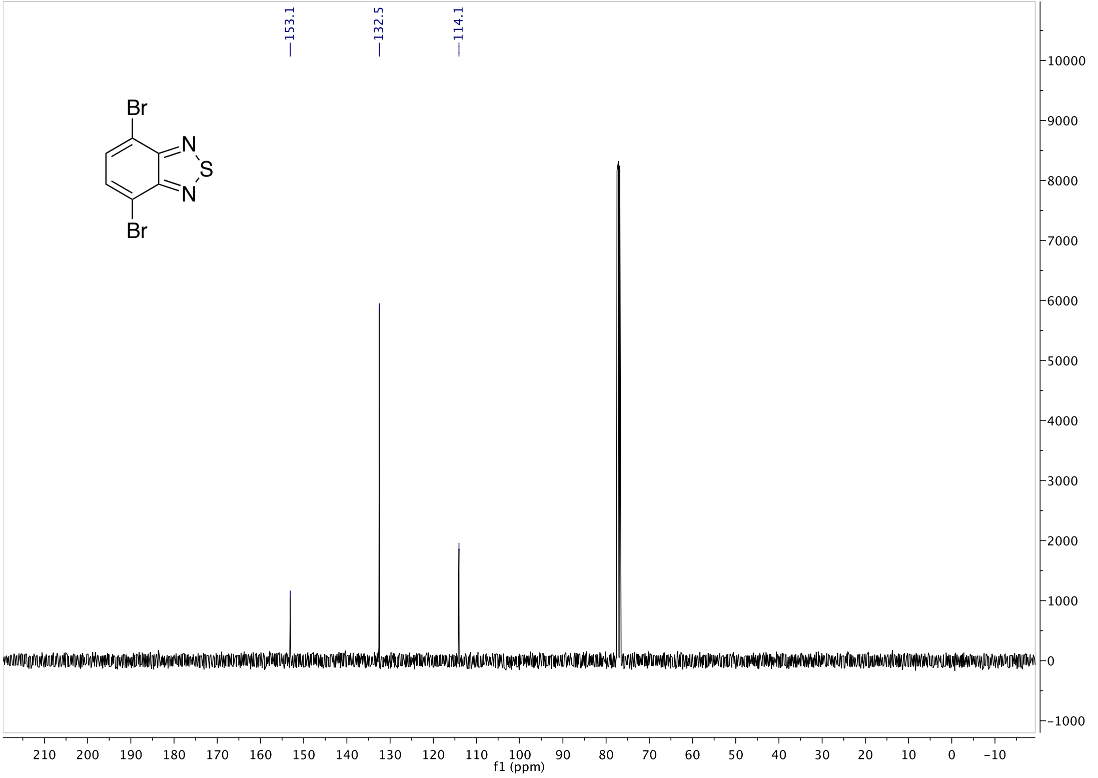
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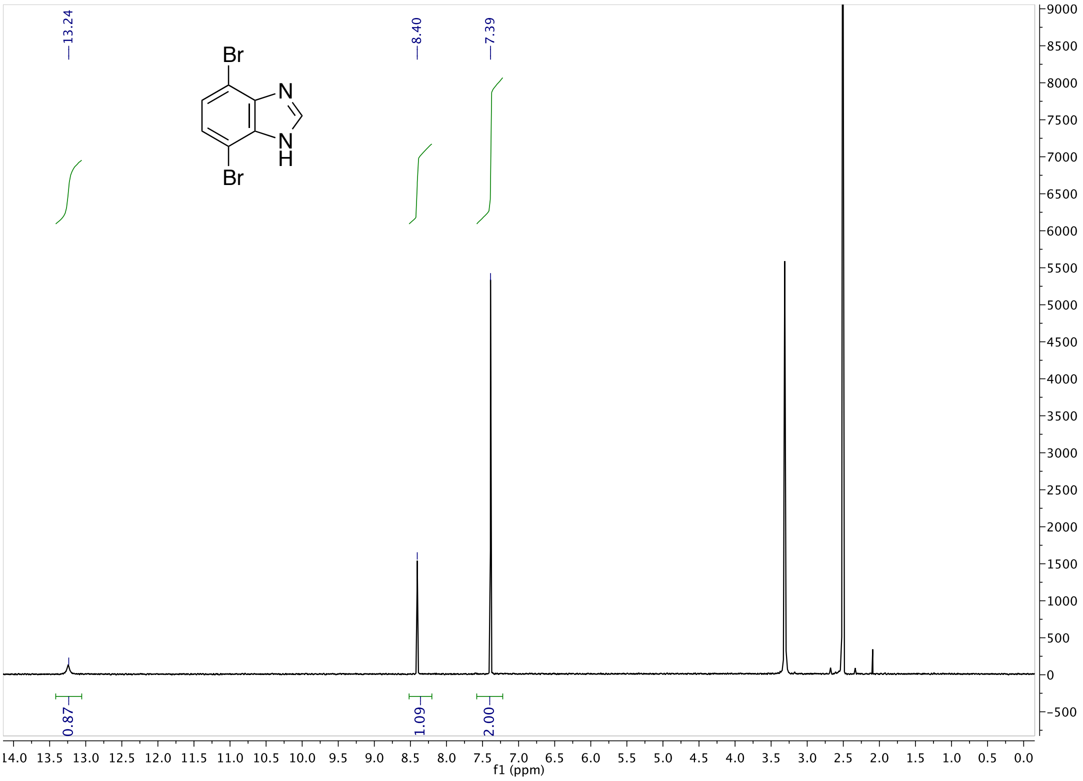
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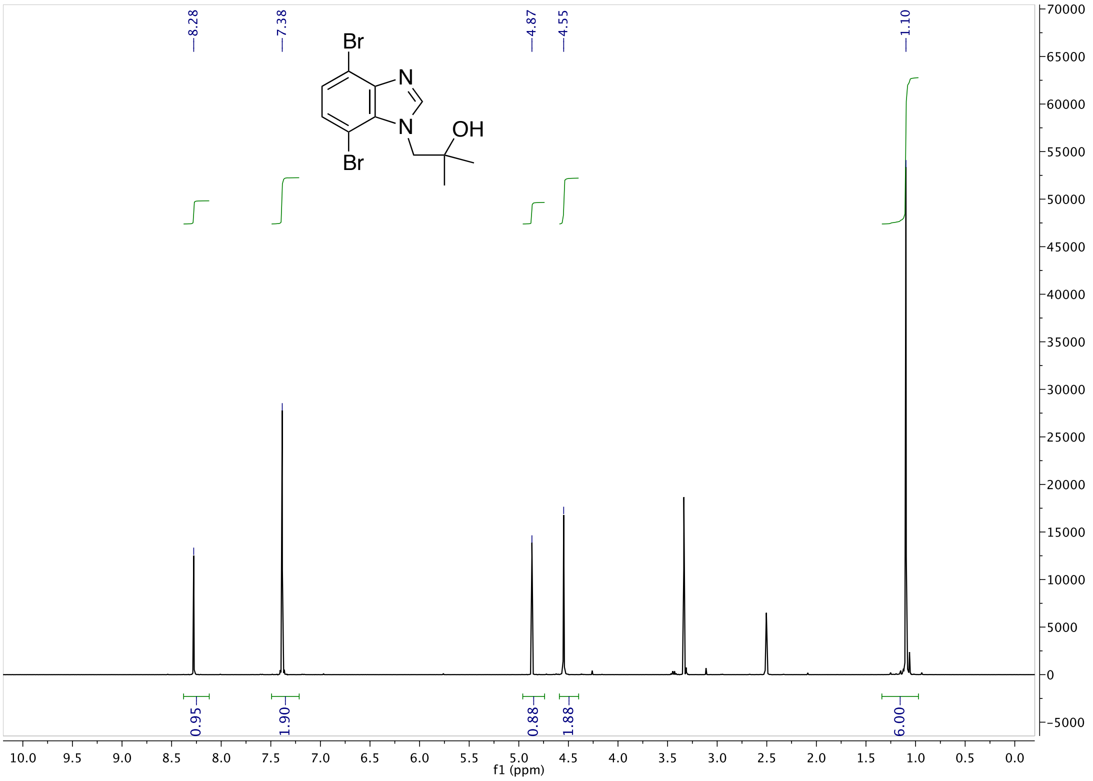
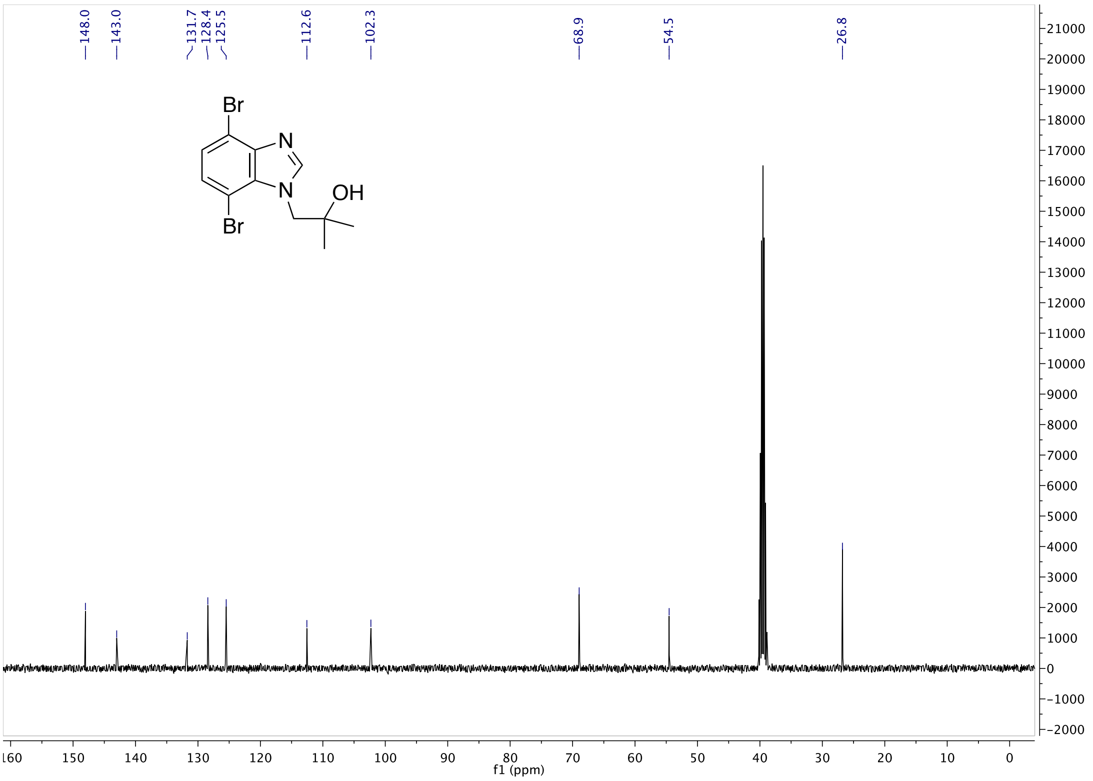
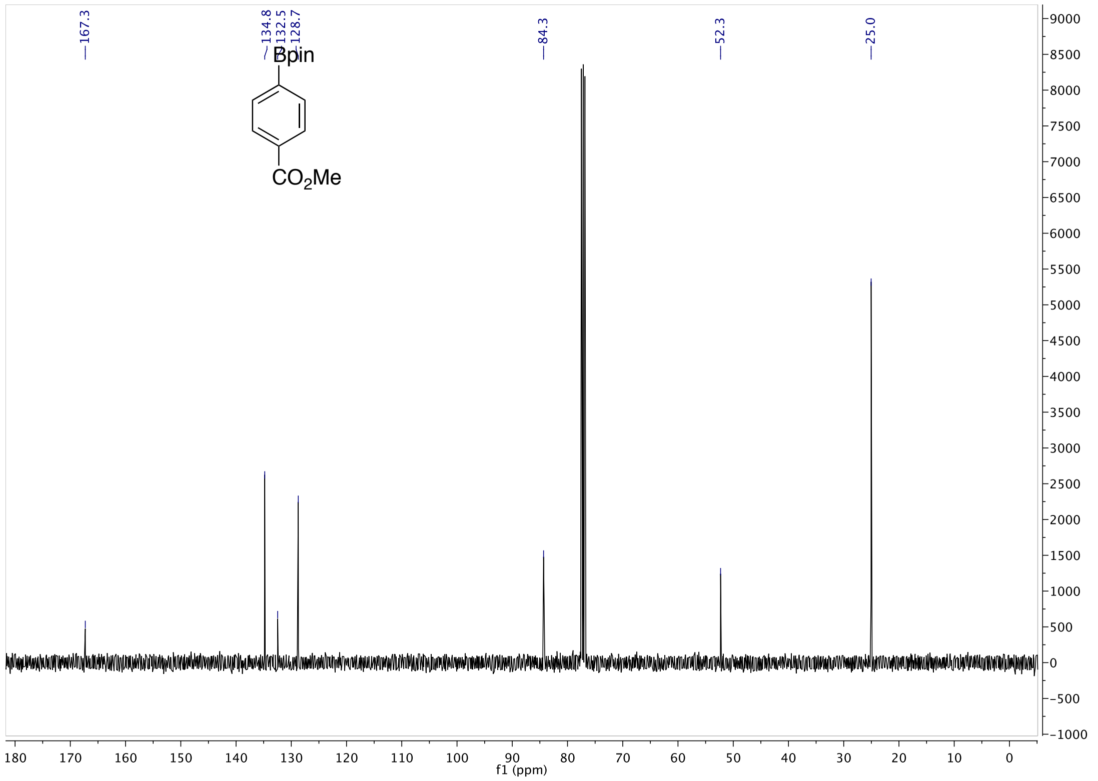
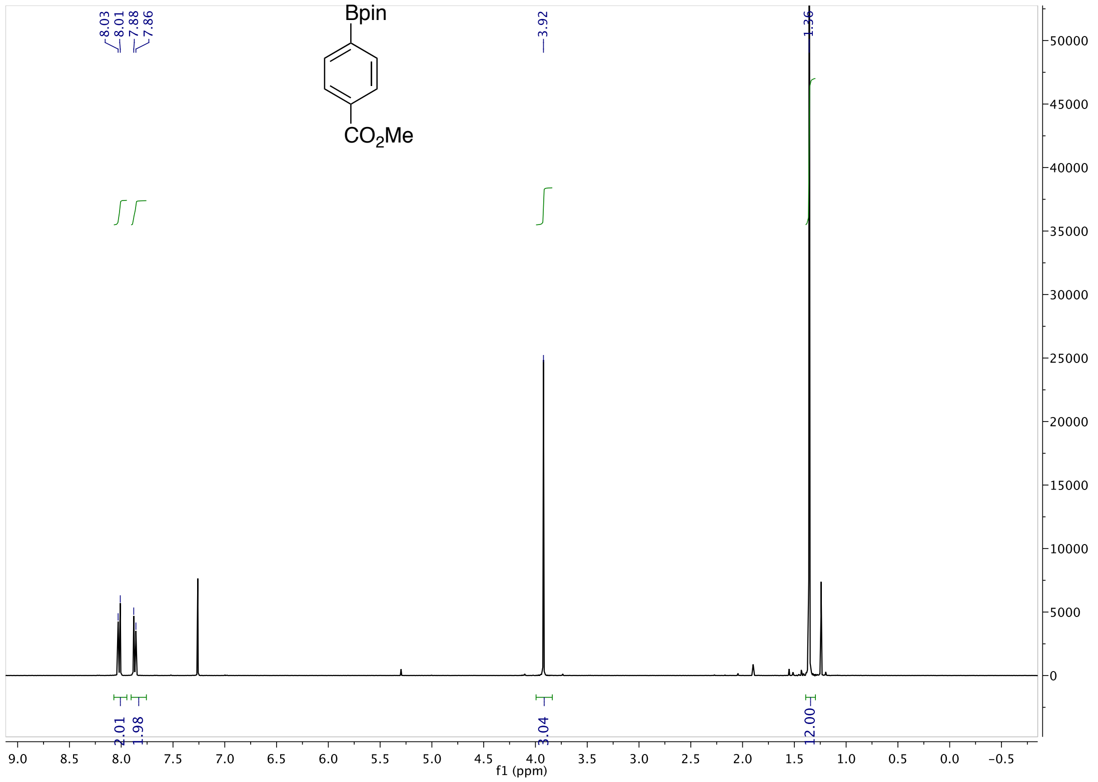
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


8.28
7.38
4.87
4.55
1.10
Br
N
N
OH
Br
0.95
1.90
0.88
1.88
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
70000 65000 60000 55000 50000 45000 40000 35000 30000 25000 20000 15000 10000 5000 0 −5000

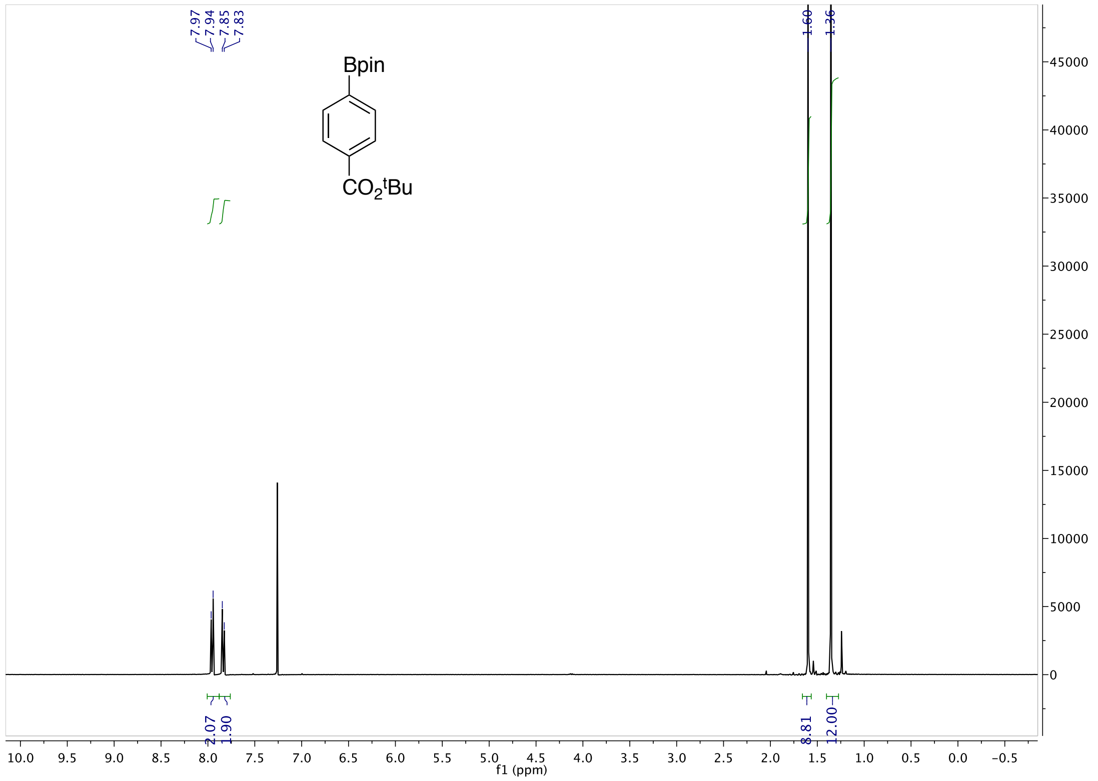

148.0
143.0
131.7
128.4
125.5
112.6
102.3
68.9
54.5
26.8
Br
N
N
OH
Br
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
21000 20000 19000 18000 17000 16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 −1000 −2000

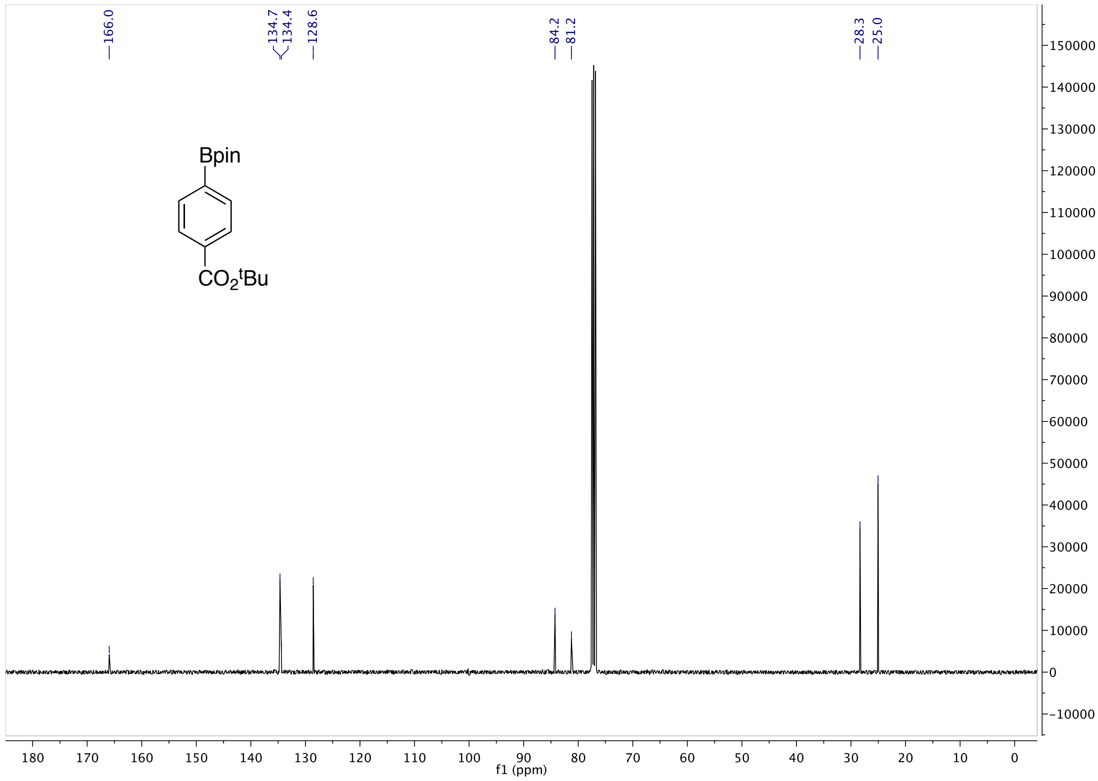


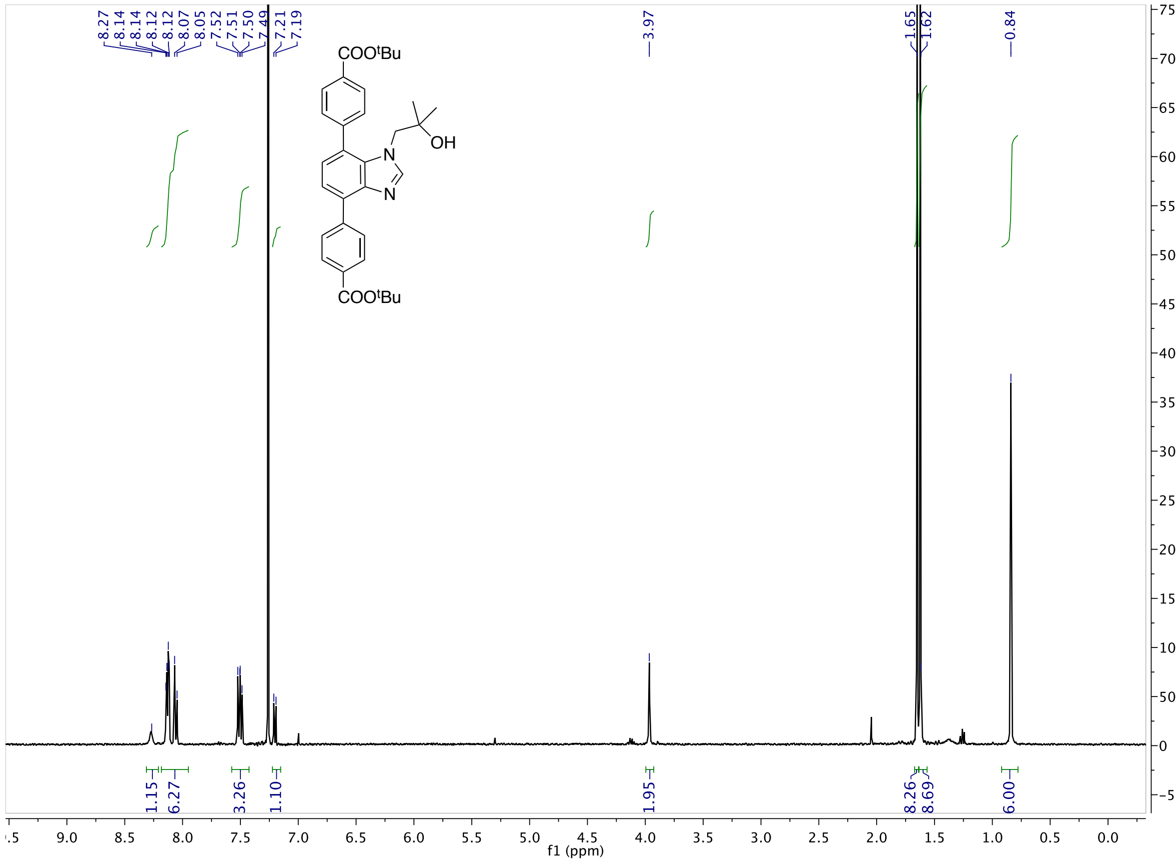
167.3
134.8
132.5
128.7
84.3
52.3
25.0
Bpin
CO2Me
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
−1000
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

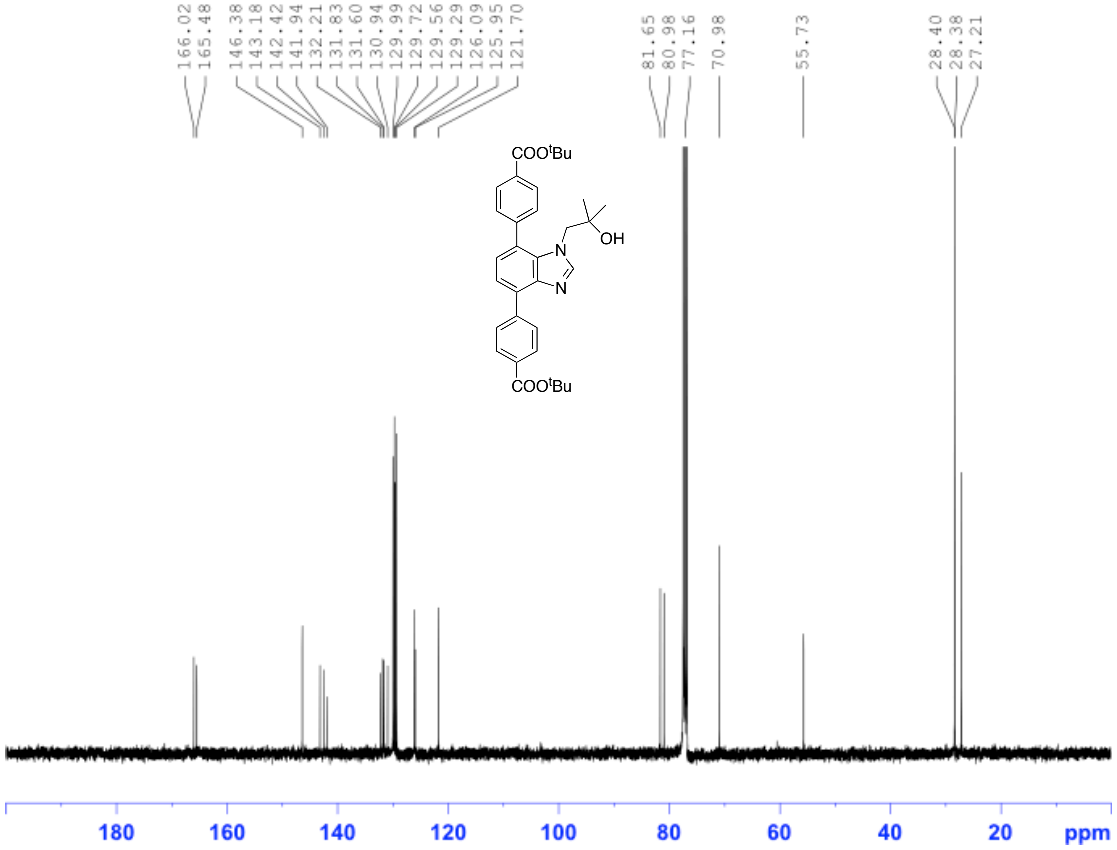


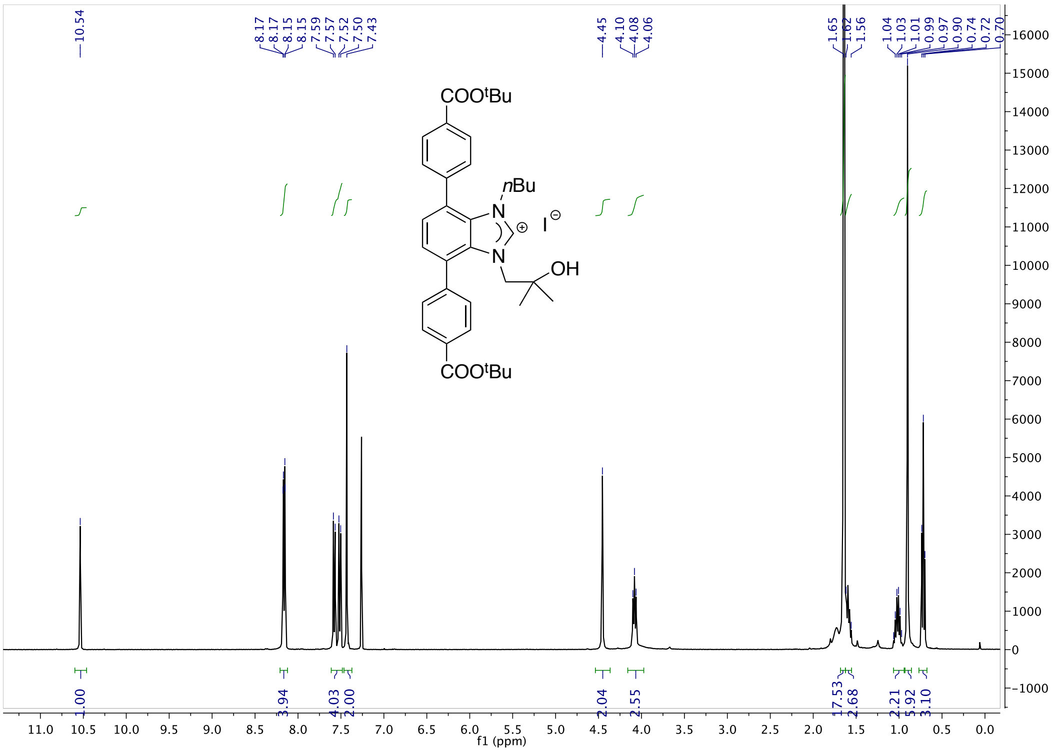
8.03
8.01
7.88
7.86
3.92
1.36
Bpin
CO2Me
2.01
1.98
3.04
12.00
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

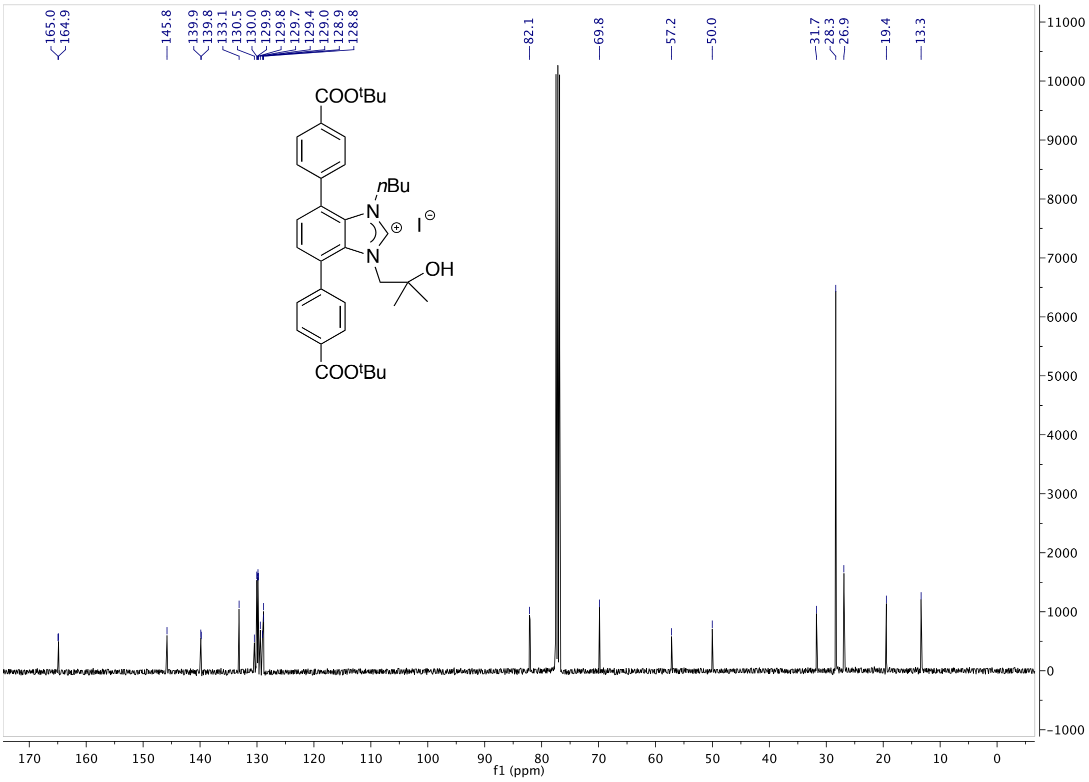

7.97
7.94
7.85
7.83
1.60
1.36
Bpin
CO$_2$^{t}Bu
2.07
1.90
8.81
12.00
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

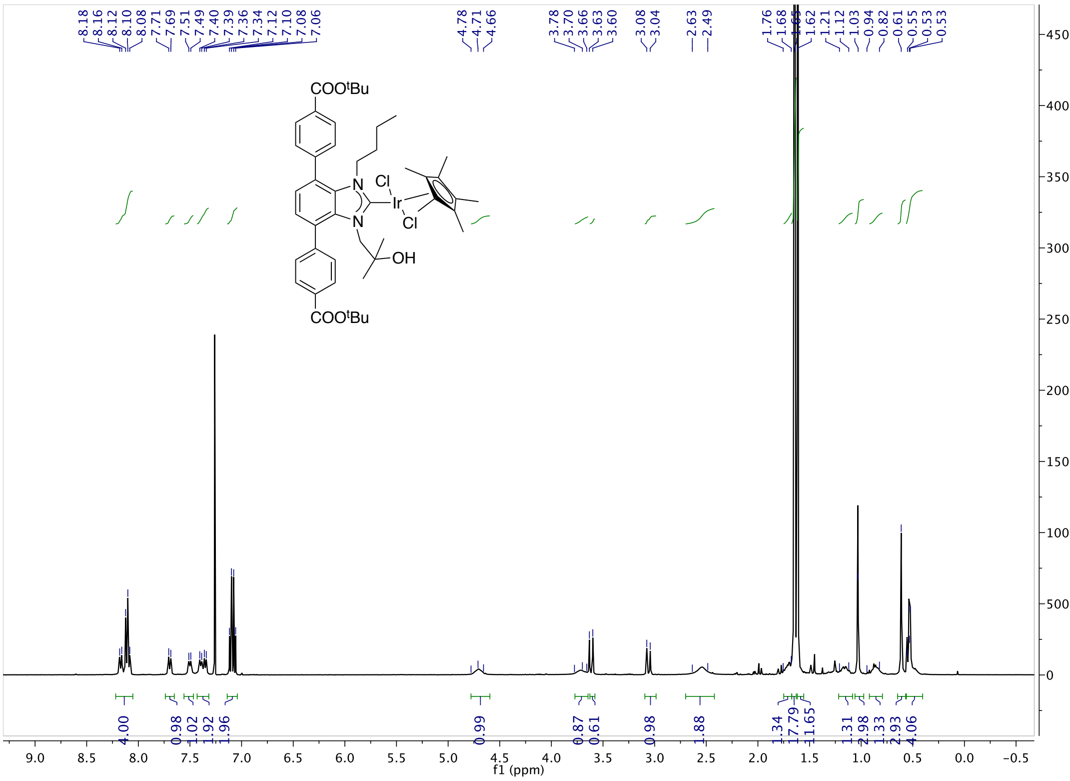

166.0
134.7
134.4
128.6
84.2
81.2
28.3
25.0
Bpin
CO$_2$^{t}Bu
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

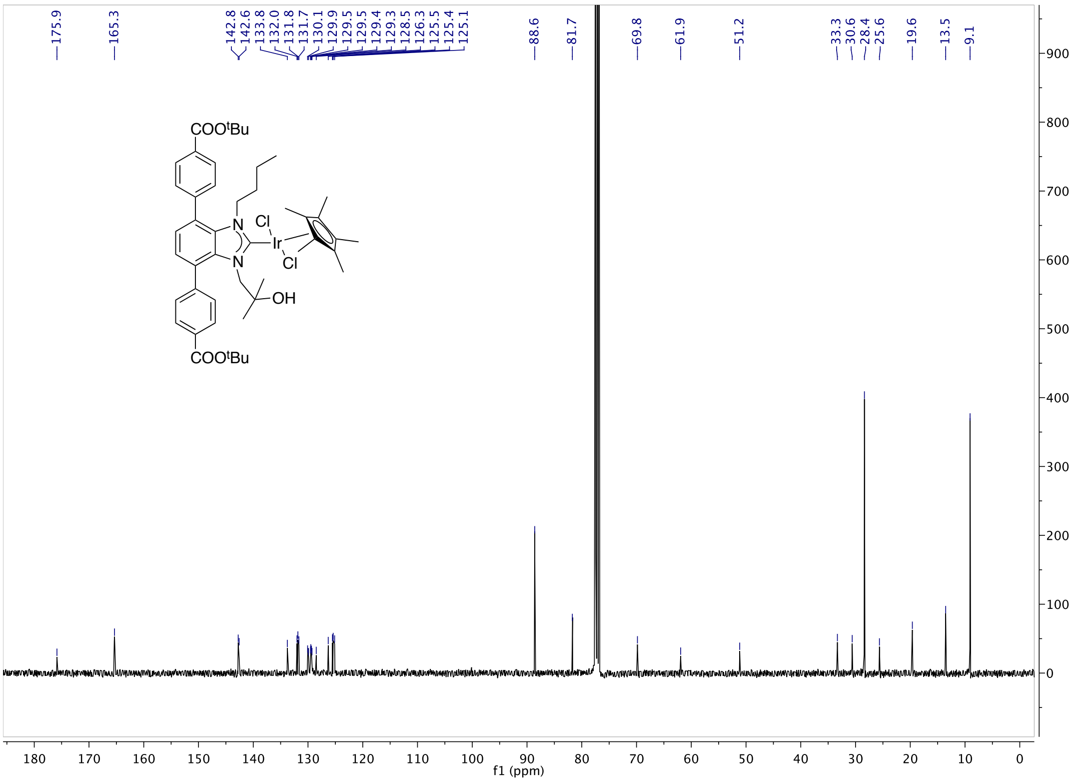

8.27
8.14
8.14
8.12
8.12
8.07
8.05
7.52
7.51
7.50
7.49
7.21
7.19
3.97
1.65
1.62
0.84
COOtBu
N
N
OH
COOtBu
1.15
6.27
3.26
1.10
1.95
8.26
8.69
6.00
f1 (ppm)

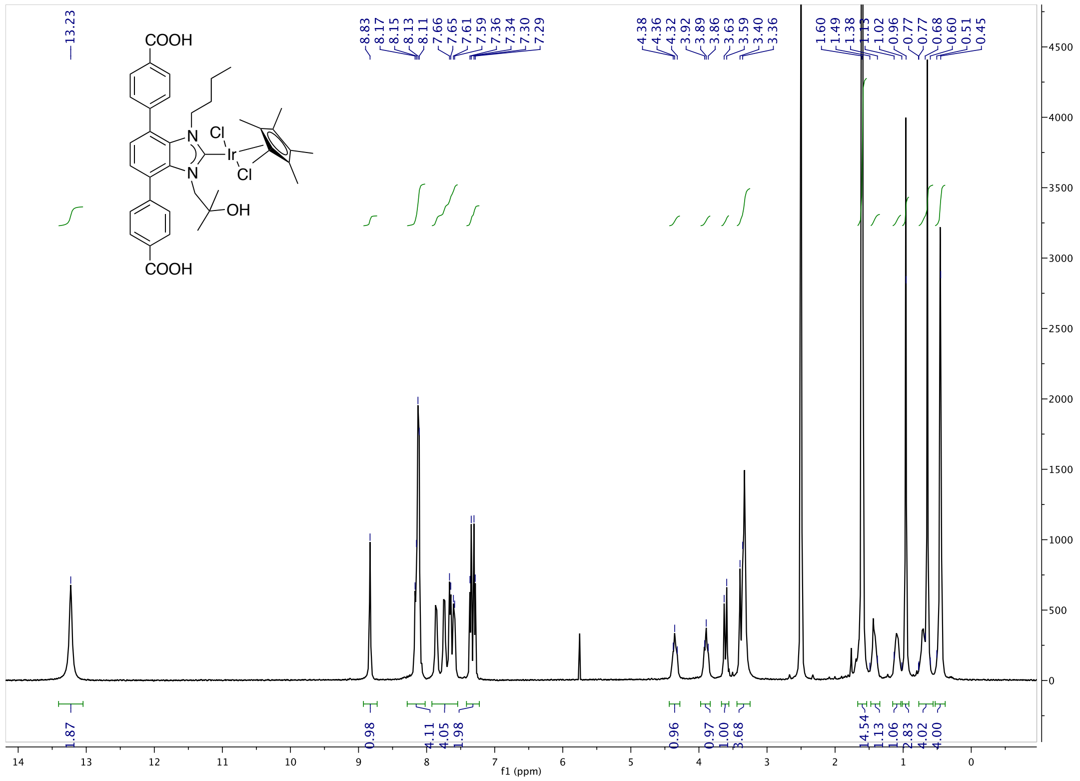

166.02
165.48
146.38
143.18
142.42
141.94
132.21
131.83
131.60
130.94
129.99
129.72
129.56
129.29
126.09
125.95
121.70
81.65
80.98
77.16
70.98
55.73
28.40
28.38
27.21
COOtBu
N
N
OH
COOtBu
ppm

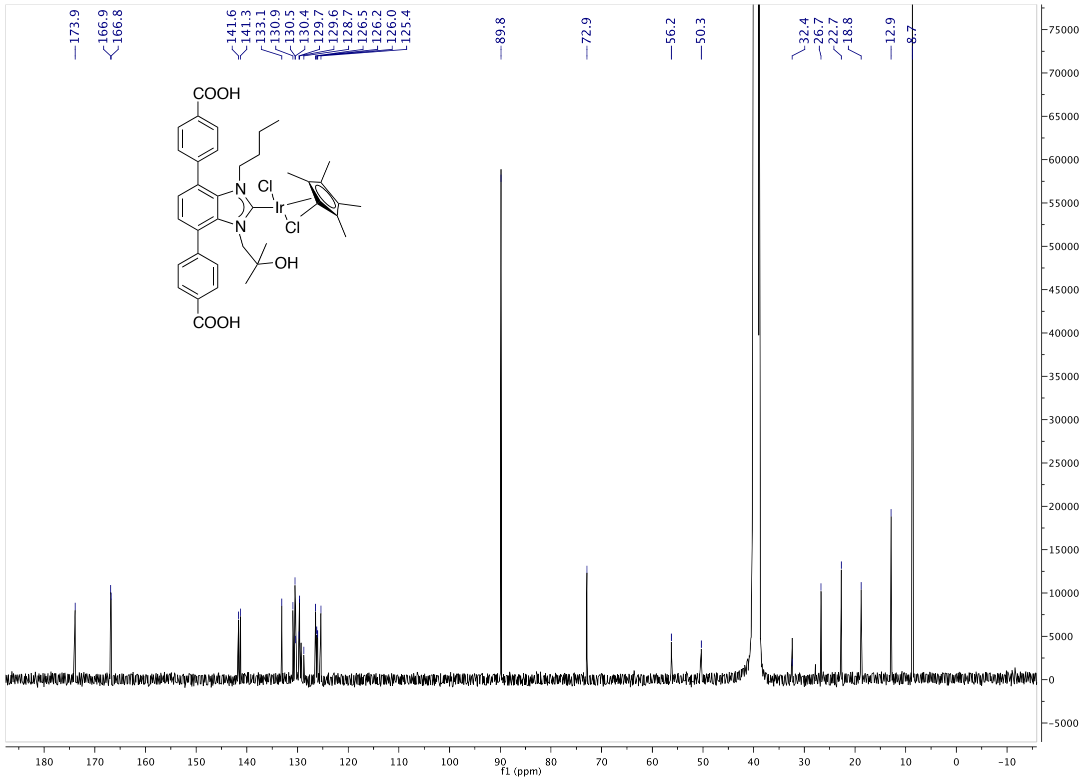

10.54
8.17
8.17
8.15
8.15
7.59
7.57
7.52
7.50
7.43
4.45
4.10
4.08
4.06
1.65
1.62
1.56
1.04
1.03
1.01
0.99
0.97
0.90
0.74
0.72
0.70
COOᵗBu
nBu
N
N
⊕
I⊖
OH
COOᵗBu
1.00
3.94
4.03
2.00
2.04
2.55
17.53
2.68
2.21
5.92
3.10
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

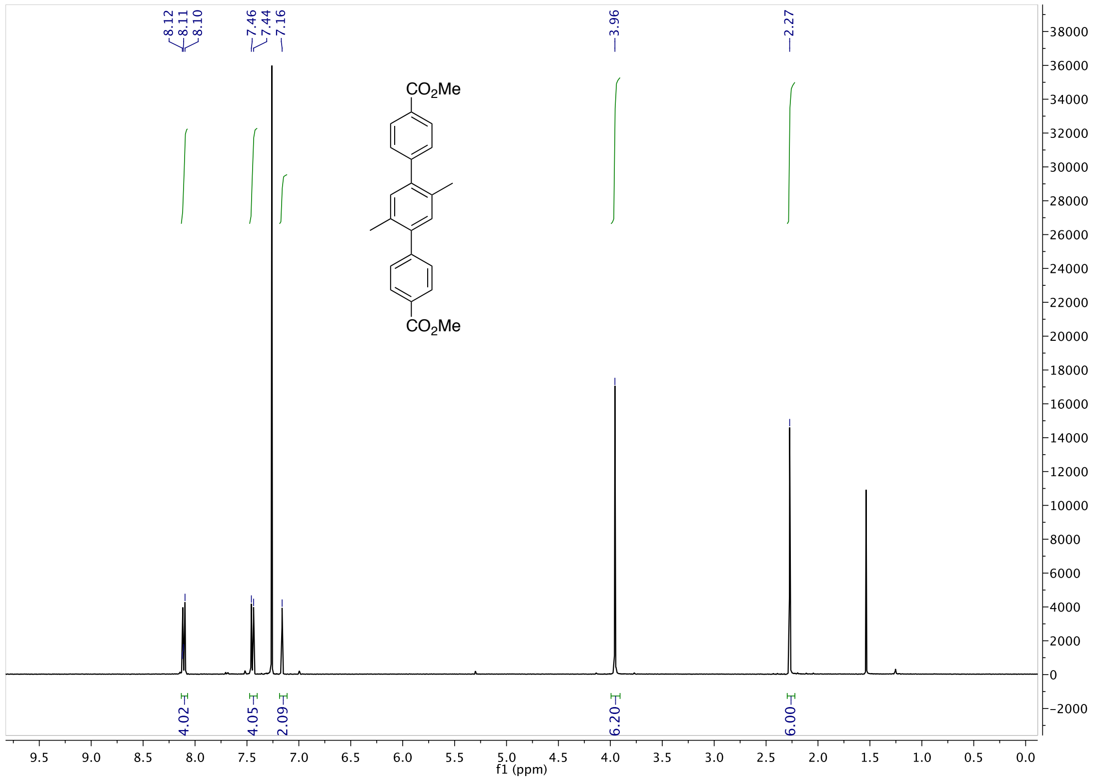

165.0
164.9
145.8
139.9
139.8
133.1
130.5
130.0
129.9
129.8
129.7
129.4
129.0
128.9
128.8
82.1
69.8
57.2
50.0
31.7
28.3
26.9
19.4
13.3
COOᵗBu
nBu
N
N
⊕
I⊖
OH
COOᵗBu
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

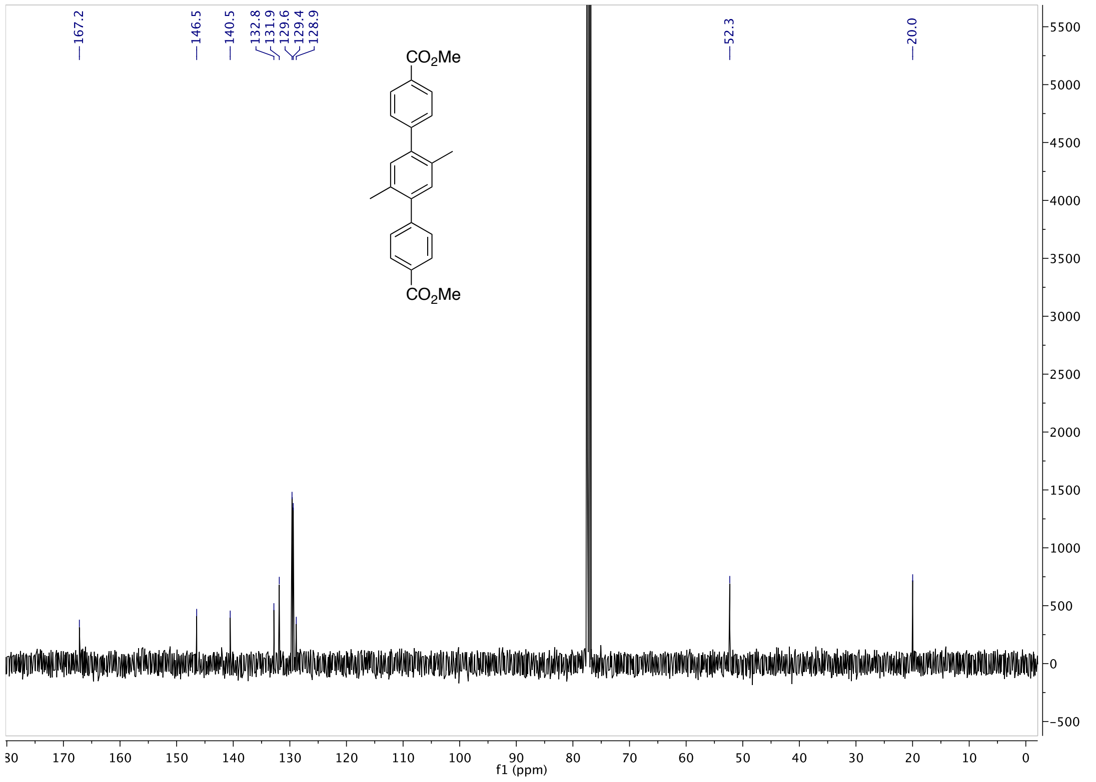

8.18 8.16 8.12 8.10 8.08 7.71 7.69 7.51 7.49 7.40 7.39 7.36 7.34 7.12 7.10 7.08 7.06
4.78 4.71 4.66
3.78 3.70 3.66 3.63 3.60
3.08 3.04
2.63 2.49
1.76 1.68 1.65 1.62 1.21 1.12 1.03 0.94 0.82 0.61 0.55 0.53 0.53
COO^tBu
N
Cl
Ir
Cl
N
OH
COO^tBu
4.00 0.98 1.02 1.92 1.96 0.99 0.87 0.61 0.98 1.88 1.34 17.79 1.65 1.31 2.98 1.33 2.93 4.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
45000 40000 35000 30000 25000 20000 15000 10000 5000 0

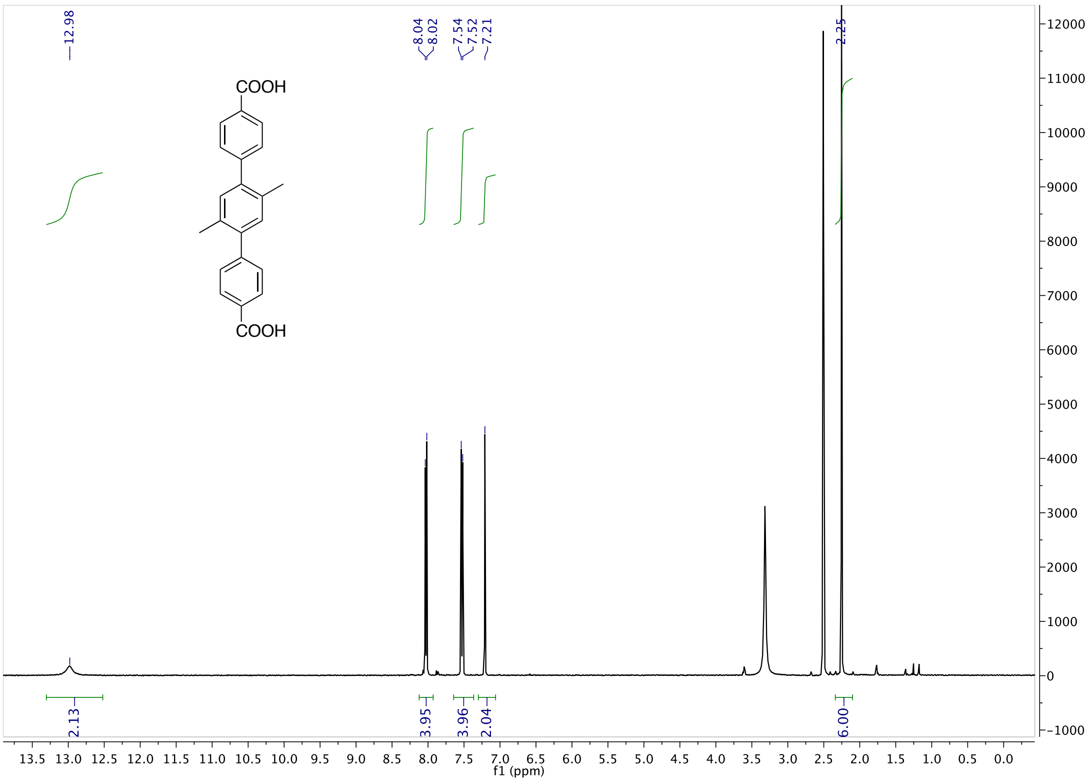

175.9
165.3
142.8 142.6 133.8 132.0 131.8 131.7 130.1 129.9 129.5 129.4 129.3 128.5 126.3 125.5 125.4 125.1
88.6
81.7
69.8
61.9
51.2
33.3 30.6 28.4 25.6
19.6
13.5
9.1
COO^tBu
N
Cl
Ir
Cl
N
OH
COO^tBu
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
90000 80000 70000 60000 50000 40000 30000 20000 10000 0

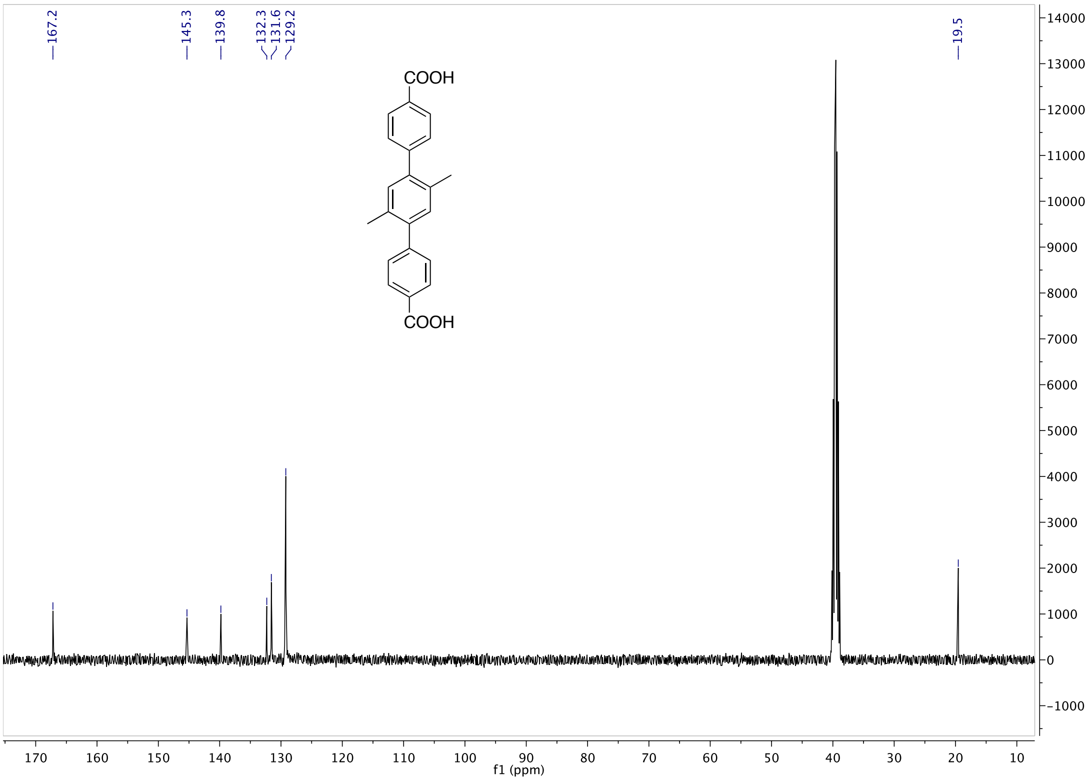

13.23
8.83
8.17
8.15
8.13
8.11
7.66
7.65
7.61
7.59
7.36
7.34
7.30
7.29
4.38
4.36
4.32
3.92
3.89
3.86
3.63
3.59
3.40
3.36
1.60
1.49
1.38
1.15
1.02
0.96
0.77
0.68
0.60
0.51
0.45
COOH
N
Cl
Ir
Cl
N
OH
COOH
1.87
0.98
4.11
4.05
1.98
0.96
0.97
1.00
3.68
14.54
1.13
1.06
2.83
4.02
4.00
f1 (ppm)


173.9
166.9
166.8
141.6
141.3
133.1
130.9
130.5
130.4
129.7
129.6
128.7
126.5
126.2
126.0
125.4
89.8
72.9
56.2
50.3
32.4
26.7
22.7
18.8
12.9
8.7
COOH
N
Cl
Ir
Cl
N
OH
COOH
f1 (ppm)


8.12
8.11
8.10
7.46
7.44
7.16
3.96
2.27
CO2Me
CO2Me
4.02
4.05
2.09
6.20
6.00
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
−2000
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.2
146.5
140.5
132.8
131.9
129.6
129.4
128.9
52.3
20.0
CO2Me
CO2Me
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


12.98
8.04
8.02
7.54
7.52
7.21
2.25
COOH
COOH
2.13
3.95
3.96
2.04
6.00
f1 (ppm)
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 −1000


167.2
145.3
139.8
132.3
131.6
129.2
19.5
COOH
COOH
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 −1000