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[Supporting Information]

Bandgap engineering in benzotrithiophene-based conjugated microporous polymers: A strategy for screening metal-free heterogeneous photocatalyts

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Section 1. Material and Characterization

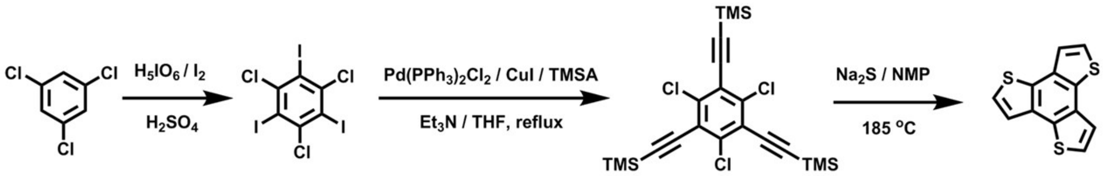
Materials. The 1,3,5-Trichlorobenzene, N-Bromosuccinimide, Trimethylsilylacetylene were obtained from Chembee Chemical Reagent. The tetrakis(triphenylphosphine)palladium (0), Benzene-1,4-diboronic acid Bis(triphenylphosphine)palladium (II) Dichloride, Benzaldehyde and its derivatives were obtained from Energy Chemical. The periodic acid, o-Phenylenediamine was obtained from Aladdin Chemical Reagent. The Copper iodide, Iodine, sodium sulfide were obtained from Sinopharm Chemical Reagent. Other organic solvents for reactions were distilled over appropriate drying reagents under nitrogen. Deuterated solvents for NMR measurement were obtained from Aladdin.

Instrumentations. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume on a JW-BK 132F analyzer at 77 K, the polymer was dried in vacuum at 80°C for more than 6 hours before measurement. Pore size distribution was estimated by Barrett-Joyner-Halenda (BJH) method. Fluorescence emission spectrum was recorded on FLUOROMAX-4 spectrometer and Cary Eclipse Fluorescence Spectrophotometer. The Nuclear Magnetic Resonance (NMR) spectroscopy were measured by an Avance III-400 NMR spectrometer, and the chemical shift (δ, ppm) is measured with the residual protons of the solvent as the standard. The powder X-ray diffraction (PXRD) data were carried out on a PANalytical BV Empyrean diffractometer, the powder was deposited on glass substrate with 2θ range of 1.5° to 45° at 298 K. The solid-state 13C CP/MAS NMR spectra was recorded on a Bruker AVANCE III 400 WB spectrometer with a CP contact time of 2 ms and a MAS rate of 5 kHz. The Fourier Transform Infrared (FT-IR) spectroscopy were recorded on an Avatar FT-IR 360 spectrometer by using KBr pellets within the wavenumber range 400 to 4000 cm^{-1}. The UV-vis absorption spectrum was recorded from 200–800 nm on a Shimadzu Corporation U-4100 Spectrophotometer. The thermogravimetric analysis (TGA) spectrum was recorded from 20 to 800 °C on a TA Q500 thermogravimeter at a rate of 10 °C min^{-1} under nitrogen. The Pd metal loading of obtained polymers was determined by Perkin-Elmer ICP-OES optima 3300DV spectroscopy. The electron paramagnetic resonance (EPR) spectra were measured by a JEOL JES-FA200 EPR spectrometer. The date of 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and 2,2,6,6-tetramethylpiperiding (TMP) solution with the concentration of 0.1 M were collected on the measurement parameters, scanning frequency: 9050 MHz; scanning power, 5 mW; central field, 323 mT; scanning width, 100 G; scanning temperature: 25 °C. The elemental analysis measurement was carried out on an Elementar model vario EL cube analyzer. The field emission scanning electron microscopy (FE-SEM) was carried out on a SU8020 model HITACHI microscope. The photocatalytic process is carried out under the irradiation of 30W blue LED lamp (460 nm, 36.2 ± 0.1 mW cm−2, distance app. 3 cm; 28.1 ± 0.1 mW cm^{-2}, distance app. 5 cm).

Electrochemical measurements. The photocurrent of the polymer was performed on a VersaSTAT 3 electrochemical workstation under irradiation of 300 W Xe lamp. Glassy carbon electrode, platinum wire electrode and saturated calomel electrode (SCE) are used as working electrode, assistant electrode and reference electrode respectively. The working electrode was prepared from the polymer and 5 wt% Nafion, the experiment was carried out in 0.1 M Na_2SO_4 aqueous solution. The Mott-Schottky analysis and electrochemical impedance spectra (EIS) was performed on a CHI760E electrochemical workstation at room temperature in the dark. Glassy carbon electrode, platinum wire electrode and saturated calomel electrode (SCE) are used as working electrode, assistant electrode and reference electrode respectively. The Mott-Schottky measurement was carried out in 0.1 M Na_2SO_4 aqueous solution at frequency of 1000 Hz. The electrochemical impedance spectra was obtained by immersing in a 0.1 M Na_2SO_4 aqueous solution.

Section 2. Synthesis and Photocatalysis

Synthesis of benzo[1,2-*b*:3,4-*b*′:5,6-*b*′′]trithiophene[1]

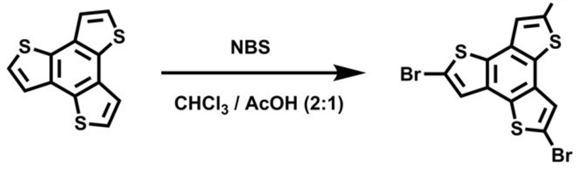


Synthesis of 1,3,5-trichloro-2,4,6-triiodobenzene: Dissolve periodic acid (4.3 g, 18.9 mmol) in concentrated H_2SO_4 (25 mL) with stirring. Iodine (14.1 g, 55.6 mmol) was added in three times to the clear liquid. After stirring for about 1h, the dark mixture was placed in an ice water bath. Then 1,3,5-trichlorobenzene (2.0 g, 11.02 mmol) was slowly added. The reaction was stirred to room temperature for 2 days. The mixture was then slowly added to an ice water bath to quench the excess H_2SO_4. The obtained solid was collected by suction filtration, and washed thoroughly with methanol. The crude product was purified by crystallization to obtain 1,3, 5-trichloro-2,4,6-triiodobenzene as white solid (4.5 g, yield: 72%). ^{13}C NMR (100 MHz, DMSO-d6): δ 101.4, 144.5 ppm.

Synthesis of 1,3,5-(trimethylsilyl) ethynyl-2,4,6-trichlorobenzene: Put 1,3,5-trichloro-2,4,6-triiodobenzene (2.0 g, 3.57 mmol), CuI (34.0 mg, 0.18 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (125 mg, 0.18 mmol) into the reflux Condenser 50 mL ampoules. Add trimethylsilylacetylene (3.0 ml, 21.43 mmol) under nitrogen atmosphere, and finally add triethylamine (15 mL) and THF (15mL) solvent. Degassed three times, return to room temperature, and the resulting mixture was refluxed for 48 hours. Diluted with water (10 mL), and extracted with chloroform (10 mL × 3). The extract was washed with saturated saltwater (50 mL × 3), and dried with $MgSO_4$. The solvent was evaporated, and the residue was purified by column chromatography to obtain 1,3,5-trichloro-2,4,6-tris[(trimethylsilyl)ethynyl] benzene as a yellow solid (1.54 g, yield: 88%). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.3, 97.4, 108.1, 122.7, 139.1 ppm.

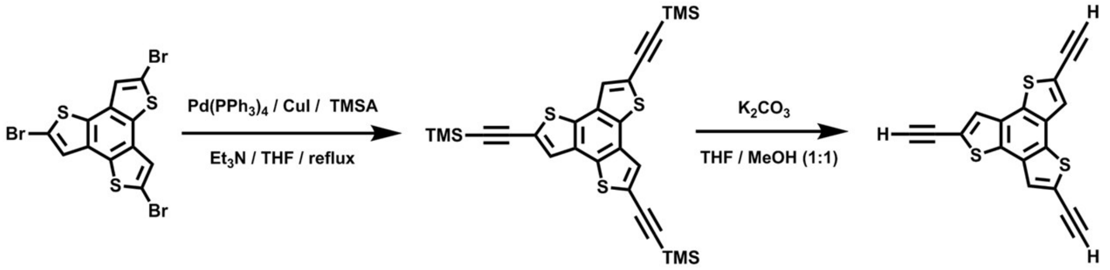
Synthesis of benzo[1,2-*b*:3,4-*b*′:5,6-*b*′′]trithiophene: Weigh sodium sulfide in a 150 mL two-neck flask, add *N*-Methyl pyrrolidone (NMP) to accelerate stirring for 30 min to make it suspension, then add 1,3,5-trichloro-2,4,6-tris[(trimethylsilyl)ethynyl]benzene and stirred at 185~195 °C for 24 h. The mixture was poured into 100 mL of saturated aqueous ammonium chloride solution. The resulting solid was collected by filtration and thoroughly diluted chloroform (210 mL). The solution was washed with saturated saltwater (300 mL × 4), and dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel to give benzo[1,2-*b*:3,4-*b*′:5,6-*b*′′]trithiophene as colorless microcrystals (0.26 g, yield: 35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 4 Hz, 3H), 7.64 (d, J = 4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 122.7, 125.4, 131.8, 132.2 ppm.

Synthesis of 2,5,8-tribromobenzo[1,2-*b*:3,4-*b*′:5,6-*b*″]trithiophene



Terthienobenzene (0.20 g, 0.81 mmol) was dissolved in a $CHCl_3$: AcOH (2:1) mixture along with *N*-bromosuccinimide (NBS) (0.43 g, 2.44 mmol) and The reaction mixture was stirred overnight at room temperature under nitrogen. The formed precipitate was filtered off and washed with $CHCl_3$ and water to give tribromo-terthienobenzene as off-white solid (0.30 g, yield: 78%). ^1H NMR (400 MHz, DMSO-d6): δ 8.07 (s, 3H) ppm.

Synthesis of 2,5,8-Triethynylbenzo[1,2-*b*:3,4-*b′*:5,6-*b″*]trithiophene



Synthesis of 2,5,8-Tri(trimethylsilylethynyl)benzo[1,2-*b*:3,4-*b′*:5,6-*b″*]trithiophene: To a solution mixture of 2,5,8-tribromobenzo[1,2-*b*:3,4-*b′*:5,6-*b″*]trithiophene (0.27 g, 0.56 mmol), copper(I) iodide (32 mg, 0.17 mmol) and tetrakis(triphenylphosphine)palladium(0) (97 mg, 0.08 mmol) in Et_3N:THF (4:1 v/v, 25 ml) was added trimethylsilylacetylene (0.56 mL, 3.94 mmol). The reaction mixture was rigorously stirred and heated to reflux overnight under nitrogen. This mixture was filtered and evaporated to dryness under reduced pressure. The crude product was purified by flash column chromatography on silica gel using hexane as eluent. Subsequent recrystallization by layering methanol onto a concentrated dichloromethane solution yielded the product as a white solid (0.26 g, Yield: 86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.3 (s, 27H), 7.66 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 97.5, 102.2, 123.1, 127.7, 130.7, 133.2 ppm.

Synthesis of 2,5,8-Triethynylbenzo[1,2-*b*:3,4-*b*′:5,6-*b*″]trithiophene: To a stirred solution of 2,5,8-tri(trimethylsilylethynyl)benzo[1,2-*b*:3,4-*b*′:5,6-*b*″]trithiophene (250 mg, 0.49 mmol) in THF:MeOH (1:1 v/v, 40 ml) was added potassium carbonate (0.42 g, 3.01 mmol). The reaction mixture was stirred overnight at room temperature under nitrogen. The yellow precipitate was filtered and washed with water and methanol. After drying under vacuum, the product was isolated as a pale yellow solid (94 mg, Yield: 88 %). ^{1}H NMR (400 MHz, $CHCl_3$): δ 3.53 (s, 3H), 7.72 (s, 3H) ppm.

Synthesis of BTT-CMP1. A 10 mL flask was charged with a solution mixture of 2,5,8-Triethynylbenzo[1,2-b:3,4-b':5,6-b"]trithiophene (50.0 mg, 0.157 mmol), copper (I) iodide (1.19 mg, 0.006 mmol) and bis(triphenylphosphine)palladium(II)dichloride (4.41 mg, 0.006 mmol). Further, anhydrous Et_3N-THF (1:1 v/v, 4.0 mL) solvent was added to dissolve, and then were degassed by three evacuation-N_2-backfill cycles and purged with N_2. The reaction medium was heated to 80 ^{o}C and stirred under N_2 for three days. And then cool to room temperature and precipitate was filtered. The obtained product was then filtered, washed thoroughly with aqueous HCl solution (2M), water, acetone, chloroform, tetrahydrofuran, methanol,and followed by Soxhlet extraction for 24h with tetrahydrofuran and methanol solution respectively. The desired polymer was collected and then dried in vacuum oven at 120 °C in vacuum oven to give a brown powder (yield: 97%). The Pd metal loading of BTT-CMP1 was determined by ICP to be 0.8%.

Synthesis of BTT-CMP2. A 10 mL flask was charged with Tribromo-benzotrithiophene (50.0 mg, 0.104 mmol), 1,4-phenylenediboronic acid (25.9 mg, 0.156 mmol), K_2CO_3 (1.5 mL, 2M) solution, dehydrated DMF (2 mL) and degassed by three evacuation-N_2-backfill cycles. After this, Tetrakis(triphenylphosphine)palladium(0)($[Pd(PPh_3)_4]$)(11.55mg,0.010mmol)was added to this solution and again degassed for 30 min and purged with N_2. This reaction mixture was then heated to 150 °C and vigorously stirred under N_2 gas for three days, reaction medium was cooled to room temperature and precipitate was filtered and washed with aqueous HCl solution (2M), water, acetone, tetrahydrofuran, ether, and methanol, respectively. Further, the sample was Soxhlet extracted with acetone and methanol solution for 24h, respectively. And finally dried at 120^0C in vacuum oven to give a yellow green powder (yield: 95%). The Pd metal loading of BTT-CMP2 was determined by ICP to be 2.1%.

Synthesis of BTT-CMP3. A 10 ml flask was charged with 2,5,8-Triethynylbenzo[1,2-b:3,4-b':5,6-b'']trithiophene (50.0 mg, 0.157 mmol), 1,4-Dibromobenzene(56.62 mg, 0.24 mmol), copper(I) iodide (0.91 mg, 0.005 mmol). Further, added anhydrous Et_3N-DMF (1:1 v/v, 4.0 ml) solvent to dissolve, and degassed by three evacuation-N_2-backfill cycles. After this, Tetrakis(triphenylphosphine)palladium(0) (18.48 mg, 0.016 mmol) was added to this solution and again degassed for 30 min and purged with N_2. And the mixture was heated at 80 °C and vigorously stirred under nitrogen atmosphere for three days. After cooling room temperature, the obtained product was then filtered, washed thoroughly with aqueous HCl solution (2M), water, acetone, tetrahydrofuran, chloroform, methanol and followed by Soxhlet extraction with tetrahydrofuran and methanol for 24h respectively to remove any unreacted substrates or catalyst residues. And finally, the product was dried in vacuum for 24h at 80 °C (yield: 96%). The Pd metal loading of BTT-CMP3 was determined by ICP to be 1.3%.

Synthesis of g-C_3N_4. The g-C_3N_4 powder was synthesized according to a procedure described in a previous literature.[2] In a typical synthesis, the dicyandiamide powder was placed in an alumina crucible, covered with cap and heated at 550 °C for 4 h in a muffle furnace with a ramp rate of 2.3 °C/min. The sample was then allowed to cool to room temperature before removal from the furnace. The obtained light yellow solid was ground to fine powders in a quartz mortar for further use.

Typical procedure for photocatalytic synthesis of benzimidazoles. The photosensitizer BTT-CMP (3.0 mg) was dispersed of 2.0 mL anhydrous ethanol in a 5.0 mL glass microwave tube. The reaction solvent was replaced with O_2. Then aldehyde (0.26 mmol) and *o*-phenylenediamine (0.26 mmol) were added and the mixture was stirred at room temperature under 30W blue LEDs (the tube was placed in the middle of the LED setup) until all starting substrates had been consumed. The progress of the reaction was monitored by TLC. After the reaction was completed, the heterogeneous catalyst could be filtered and thoroughly washed by tetrahydrofuran (4 mL × 3). The combined organic phase was evaporated at reduced pressure and the residue was purified by flash column chromatography using silica gel with petroleum ether/ethanol or petroleum ether/ethyl acetate mixture as eluent to give the target benzimidazole.

Recycle experiment. After the first run reaction was finished, the photocatalyst BTT-CMP2 was recovered by centrifugation, and then washed thoroughly with THF and chloroform to remove any residual products or unreacted substrates. The recovered BTT-CMP2 was dried under vacuum at 120 ^{o}C overnight. The used photocatalyst BTT-CMP2 was repeated use in next cycle under identical conditions

Section 3. ^{13}C NMR Spectra

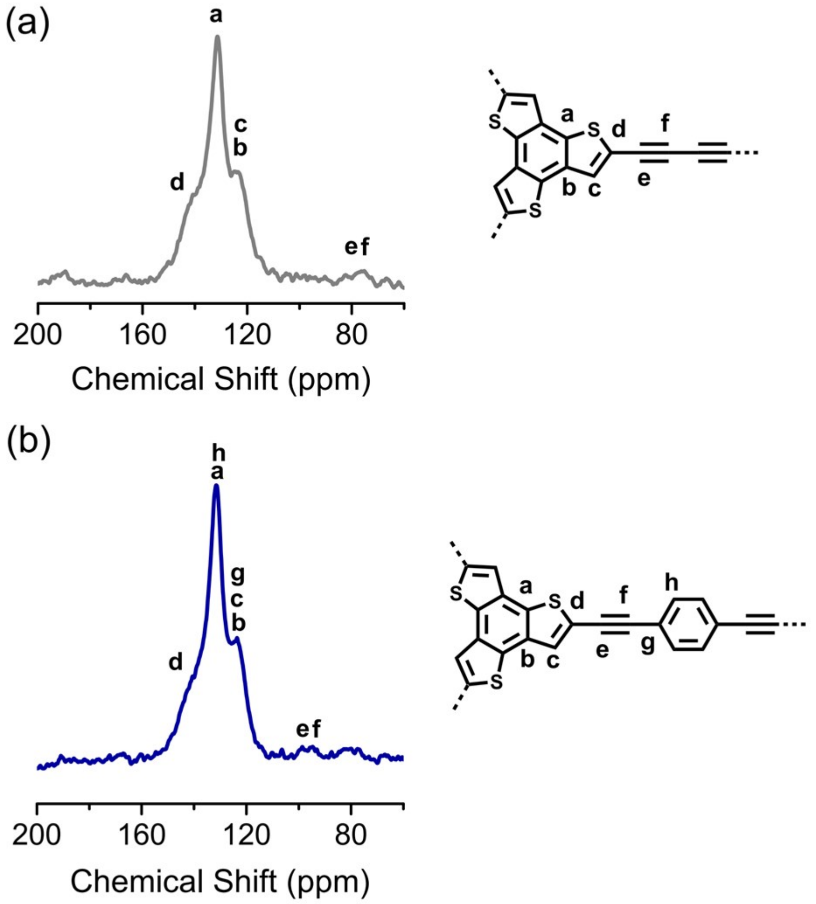


Figure S1. Solid state ^{13}C CP-MAS NMR spectra of BTT-CMP1 (a) and BTT-CMP3 (b).

Section 4. PXRD Spectra

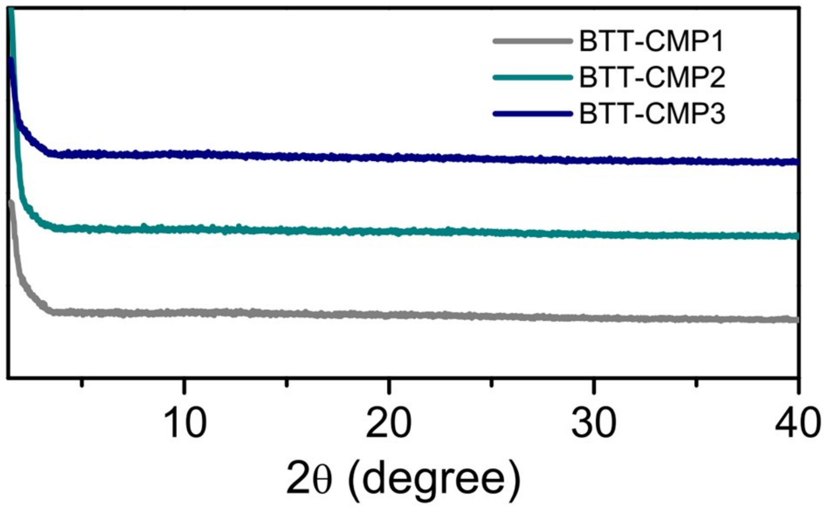


Figure S2. PXRD spectra of BTT-CMPs.

Section 5. SEM Images

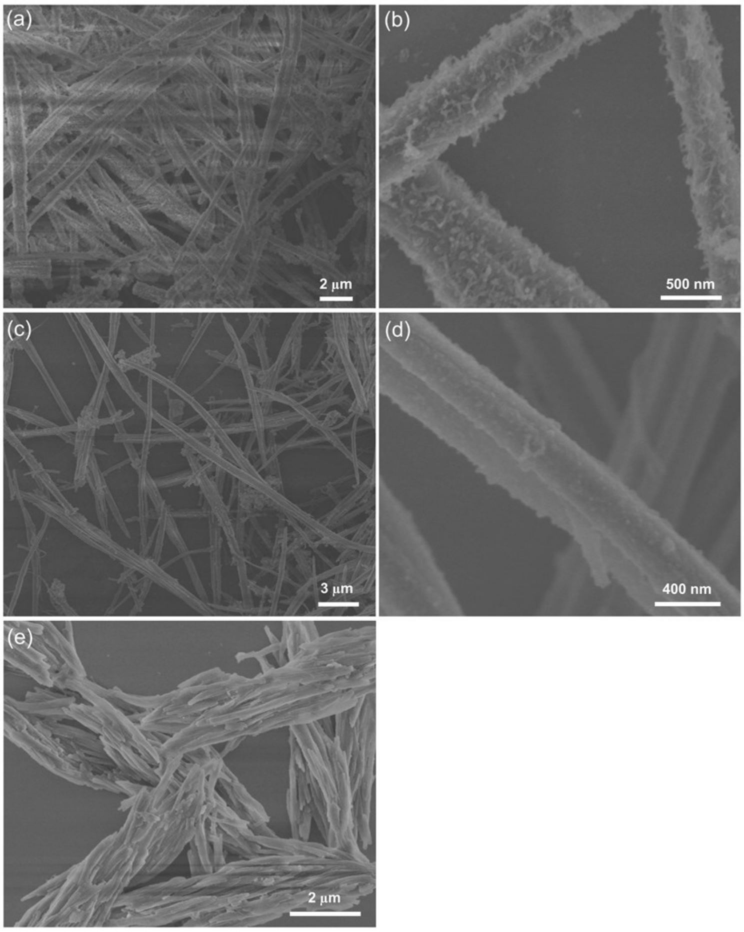


Figure S3. SEM image of BTT-CMP1 (a, b), BTT-CMP3 (c, d) and BTT-CMP2 (e).

Section 6. Catalytic Data

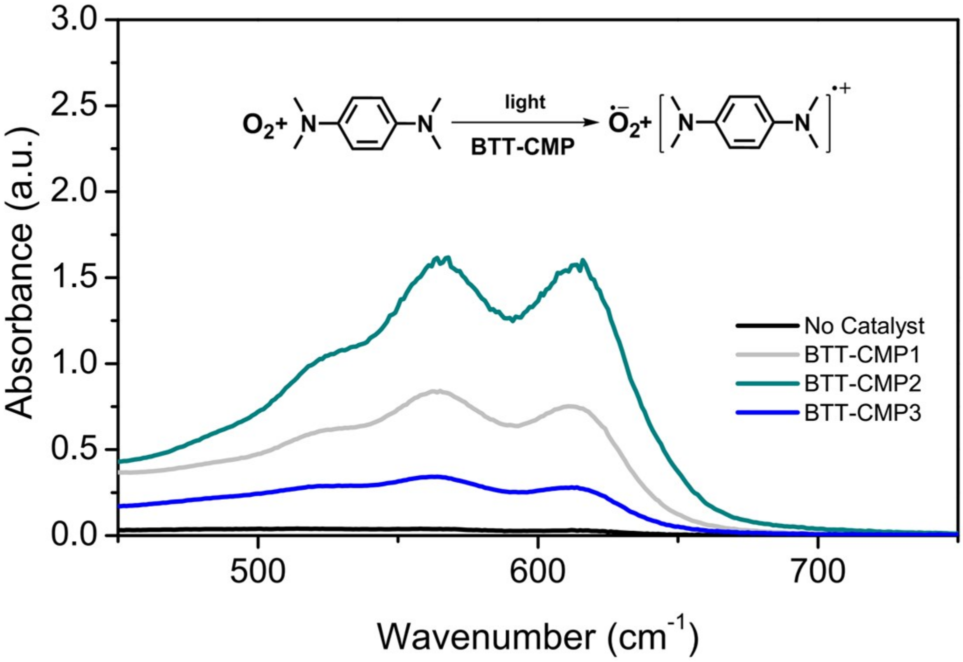
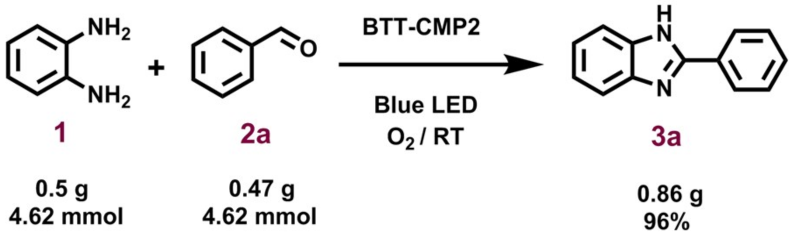
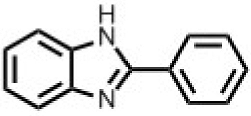


Figure S4. UV-vis absorption spectra of the cationic radical of TMPD generated by BTT-CMPs in the presence oxygen and light.

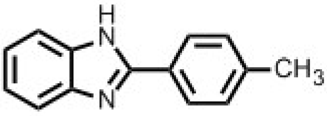
Scheme S1. Large-scale photocatalytic reaction using BTT-CMP2 as a Heterogeneous Photocatalyst.



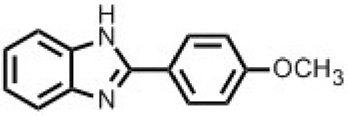
Section 7. Characterization Data of Catalytic Products



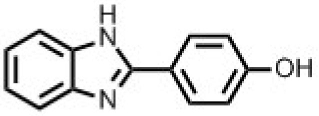
2-phenyl-1*H*-benzo[d]imidazole (3a): ^{1}H NMR (DMSO, 400 MHz)： δ 12.93 (s, 1H), 8.26–8.14 (m, 2H), 7.67–7.47 (m, 5H), 7.28–7.17 (m, 2H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 151.7, 143.2, 130.7, 130.3, 129.9, 129.5, 129.4, 129.2, 129.1, 126.9, 126.5, 126.2, 122.7 ppm.



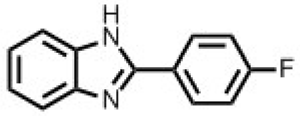
2-p-tolyl-1*H*-benzo[d]imidazole (3b): ^{1}H NMR (400 MHz, DMSO): δ 12.86 (s, 1H), 8.09 (s, 2H), 7.59 (s, 2H), 7.35 (s, 2H), 7.19 (s, 2H), 2.37 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO) δ 167.9, 151.9, 143.4, 140.0, 129.9, 129.8, 129.5, 128.6, 127.9, 126.9, 122.4, 21.4 ppm.



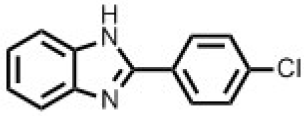
2-(4-methoxyphenyl)-1*H*-benzo[d]imidazole(3c): ^{1}H NMR (400 MHz, DMSO): δ 12.80 (s, 1H), 8.17 (d, *J* = 8.5 Hz, 2H), 7.59 (s, 2H), 7.19 (d, *J* = 2.6 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 161.1, 151.8, 128.5, 123.2, 122.2, 114.8, 55.8 ppm.



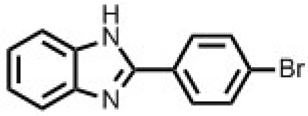
4-(1*H*-benzo[d]imidazol-2-yl)phenolde(3d): ^{1}H NMR (400 MHz, DMSO): δ 12.67 (s, 1H), 9.99 (s, 1H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.55 (dd, *J* = 4.6, 2.7 Hz, 2H), 7.16 (dd, *J* = 5.9, 3.1 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 159.6, 152.2, 139.7, 128.6, 122.1, 121.6, 116.2, 114.9 ppm.



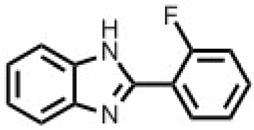
2-(4-fluorophenyl)-1*H*-benzo[d]imidazole (3e): ^{1}H NMR (400 MHz, DMSO): δ 12.99 (s, 1H), 8.20 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 4H), 7.22 (dd, *J* = 5.9, 3.1 Hz, 2H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 150.6 (d, *J* = 4.2 Hz), 144.2, 135.5, 134.9, 129.5, 128.6, 123.1, 122.3, 119.5, 112.0, 67.4, 25.6 ppm.



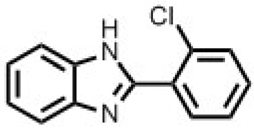
2-(4-chlorophenyl)-1*H*-benzo[d]imidazole(3f): ^{1}H NMR (400 MHz, DMSO): δ 13.02 (s, 1H), 8.21 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 6.9 Hz, 4H), 7.23 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ 150.6, 135.0, 129.5, 129.4, 128.6, 122.8, 118.1, 115.3 ppm.



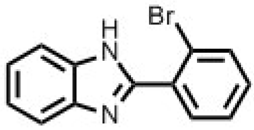
2-(4-bromophenyl)-1*H*-benzo[d]imidazole(3g): ^{1}H NMR (400 MHz, DMSO): δ 13.00 (s, 1H), 8.12 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.61 (s, 2H), 7.22 (dd, *J* = 5.9, 3.1 Hz, 2H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 150.6, 132.4, 129.8, 128.7, 123.7, 122.8, 99.9 ppm.



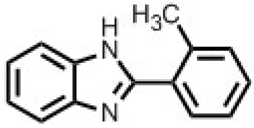
2-(2-fluorophenyl)-1*H*-benzo[d]imidazole(3h): ^{1}H NMR (400 MHz, DMSO): δ 12.61 (s, 1H), 8.24 (td, *J* = 7.7, 1.7 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 2H), 7.48–7.39 (m, 2H), 7.29–7.21 (m, 2H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 161.1, 158.7, 146.9 (d, *J* = 2.1 Hz), 132.3(d, *J* = 8.1 Hz), 130.6 (d, *J* = 2.5 Hz), 125.5 (d, *J* = 3.3 Hz), 122.9, 117.0, 116.8 ppm.



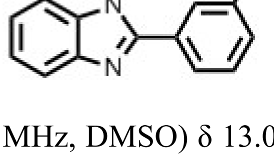
2-(2-chlorophenyl)-1*H*-benzo[d]imidazole(3i): ^{1}H NMR (400 MHz, DMSO): δ 12.78 (s, 1H), 7.94–7.91 (m, 1H), 7.72 (d, *J* = 6.0 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.59 (d, *J* = 6.8 Hz, 1H), 7.52 (dd, *J* = 12.3, 6.0 Hz, 2H), 7.25 (s, 2H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 150.9, 133.9, 132.7, 131.8, 129.4, 128.3, 126.9, 122.6, 122.0 ppm.



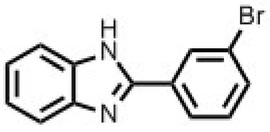
2-(2-bromophenyl)-1*H*-benzo[d]imidazole(3j): ^{1}H NMR (400 MHz, DMSO): δ 12.82 (s, 1H), 7.80 (dd, *J* = 14.4, 7.8 Hz, 2H), 7.64 (s, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.25 (dd, *J* = 5.9, 3.1 Hz, 2H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 150.9, 133.9, 132.9, 132.7, 131.8, 129.4, 128.3, 126.9, 122.0 ppm.



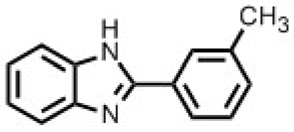
2-o-tolyl-1*H*-benzo[d]imidazole(3k): ^{1}H NMR (400 MHz, DMSO): δ 12.64 (s, 1H), 7.75 (d, *J* = 7.0 Hz, 1H), 7.61 (s, 2H), 7.41–7.34 (m, 3H), 7.24–7.18 (m, 2H), 2.62 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 152.4, 137.5, 131.7, 130.5, 129.9, 129.8, 126.4, 122.3, 21.5 ppm.



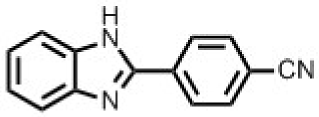
2-(3-chlorophenyl)-1*H*-benzo[d]imidazole(3l): ^{1}H NMR (400 MHz, DMSO) δ 13.06 (s, 1H), 8.24 (s, 1H), 8.16 (d, *J* = 7.1 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 9.0 Hz, 3H), 7.28–7.20 (m, 2H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 150.2, 144.1, 135.5, 134.2, 132.7, 131.3, 130.0, 126.5, 125.5, 123.4, 122.40, 119.5, 112.0 ppm.



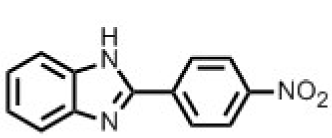
2-(2-bromophenyl)-1*H*-benzo[d]imidazole(3m): ^{1}H NMR (DMSO, 400 MHz): δ 13.07 (s, 1H), 8.30 (dd, *J* = 76.0, 7.4 Hz, 2H), 7.60 (dd, *J* = 57.2, 6.7 Hz, 4H), 7.23 (s, 2H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 150.1, 144.3, 135.6, 132.9, 131.6, 129.3, 125.8, 125.5, 123.3, 122.7, 122.5, 119.6, 112.0 ppm.



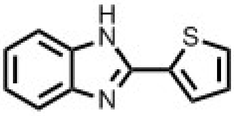
2-m-tolyl-1*H*-benzo[d]imidazole(3n): ^{1}H NMR (DMSO, 400 MHz): δ 12.93 (s, 1H), 8.06 (s, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.62 (s, 2H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.25–7.18 (m, 2H), 2.41 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 156.6, 151.8, 138.6, 130.9, 130.6, 129.3, 127.5, 124.1, 122.5, 21.5 ppm.

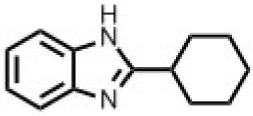


4-(1*H*-benzo[d]imidazol-2-yl)benzonitrile(3o): ^{1}H NMR (DMSO, 400 MHz): δ 13.21 (s, 1H), 8.34 (d, *J* = 8.4 Hz, 2H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 6.7 Hz, 1H), 7.58 (d, *J* = 7.1 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 2H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 149.8, 134.7, 133.3, 127.4, 123.2, 119.1, 112.3 ppm.

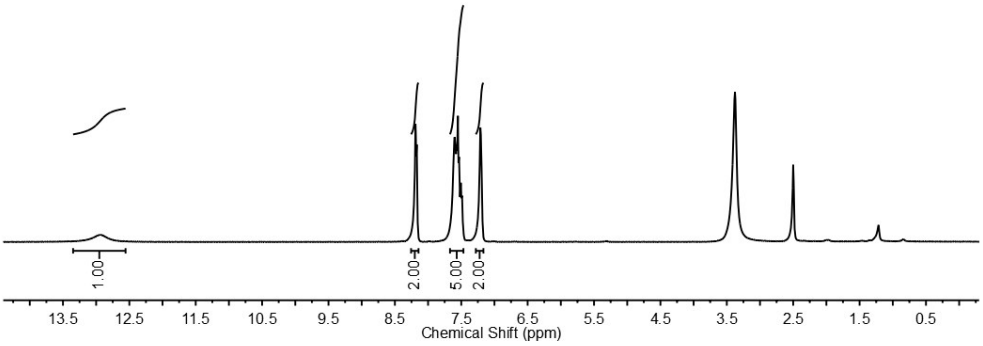


2-(4-nitrophenyl)-1*H*-benzo[d]imidazole(3p): ^{1}H NMR (DMSO, 400 MHz): δ 12.96 (s, 1H), 7.84 (d, *J* = 3.6 Hz, 1H), 7.72 (d, *J* = 5.0 Hz, 1H), 7.56 (s, 2H), 7.24–7.21 (m, 1H), 7.19 (dd, *J* = 5.9, 3.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 152.7, 147.5, 134.2, 129.2, 128.7, 127.2, 122.7 ppm.

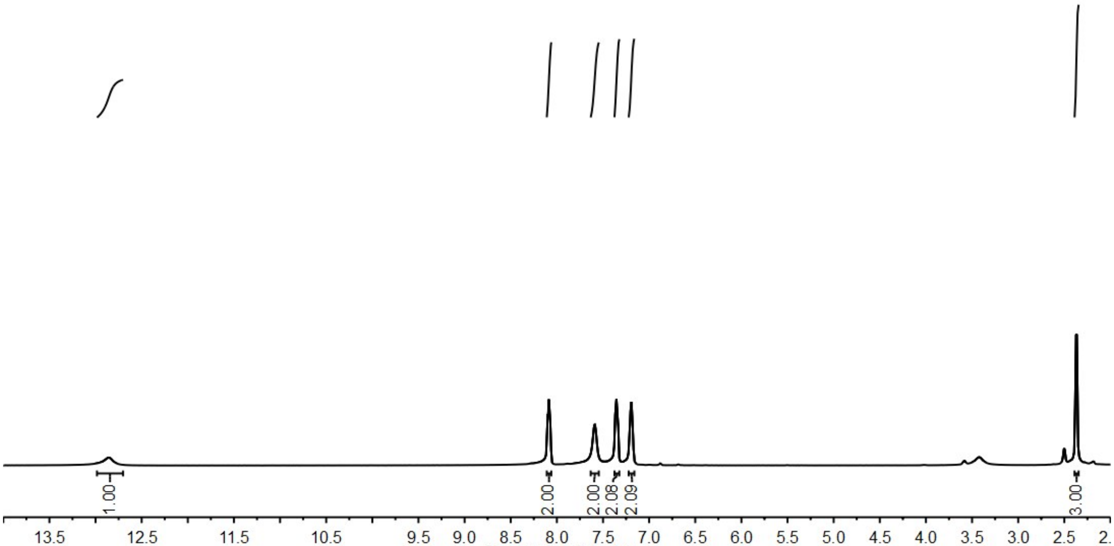
**2-(thiophen-2-yl)-1*H*-benzo[d]imidazole(3q):** ^{1}H NMR (DMSO, 400 MHz): δ 13.26 (s, 1H), 8.42–8.31 (m, 3H), 7.64 (s, 2H), 7.24 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO) δ 147.6, 139.8, 134.3, 129.1, 128.7, 127.2, 122.7, 115.5 ppm.

**2-cyclohexyl-1*H*-benzo[d]imidazole(3r):** ^{1}H NMR (DMSO, 400 MHz): δ 12.22 (s, 1H), 7.46 (dd, J = 5.6, 3.1 Hz, 2H), 7.11 (dd, J = 5.7, 3.1 Hz, 2H), 2.84 (t, J = 11.4 Hz, 1H), 2.02 (d, J = 12.1 Hz, 2H), 1.80 (d, J = 12.7 Hz, 2H), 1.61 (dd, J = 31.1, 19.0 Hz, 3H), 1.42–1.23 (m, 3H) ppm. ^{13}C NMR (100 MHz, DMSO) δ 159.4, 121.5, 115.1, 38.2, 31.7, 26.0 ppm.

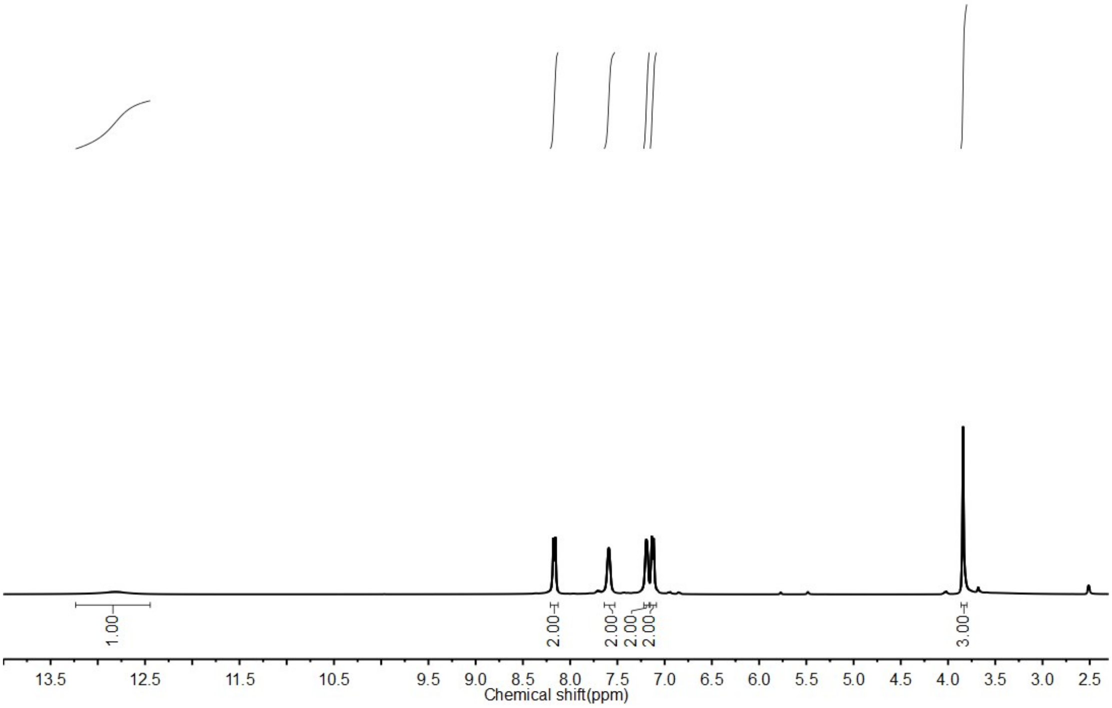
Section 8. NMR Spectra of Catalytic Products



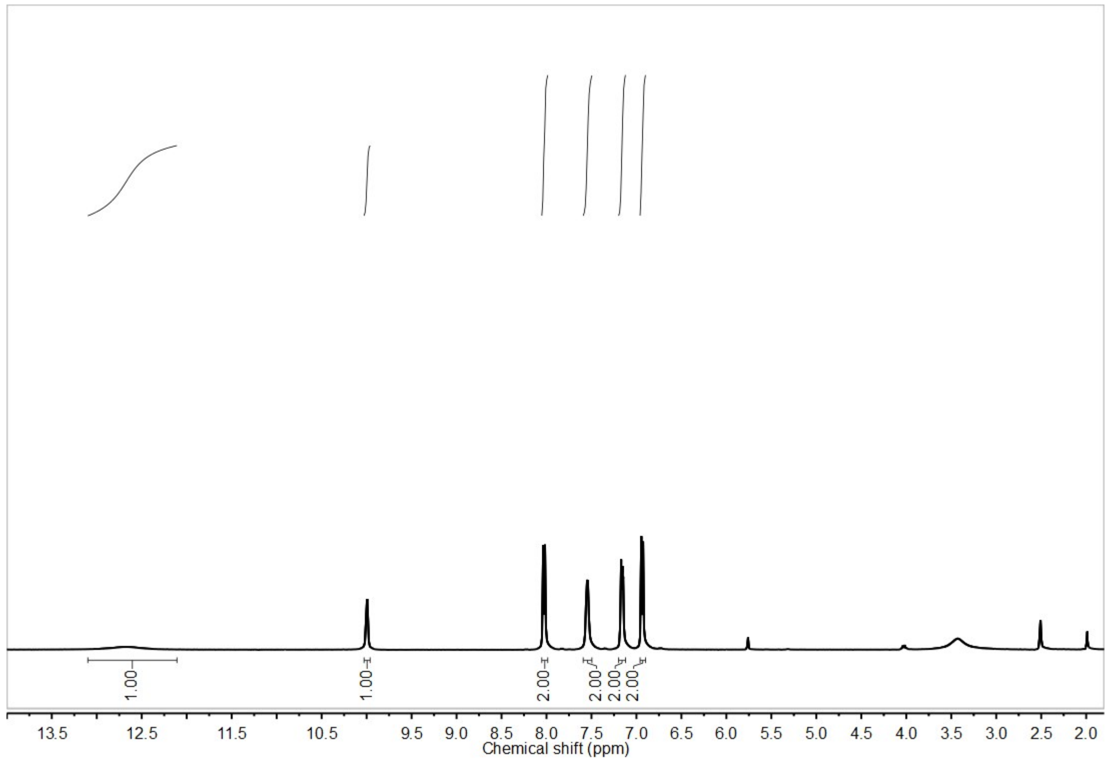
The ^{1}H-NMR spectrum of 3a



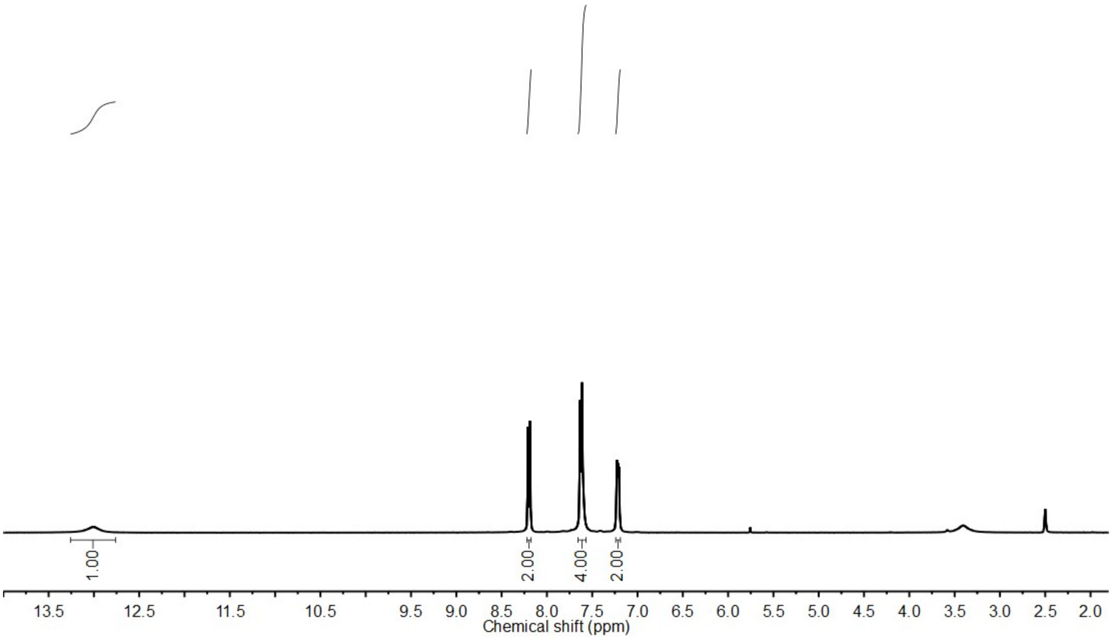
The ^{1}H-NMR spectrum of 3b



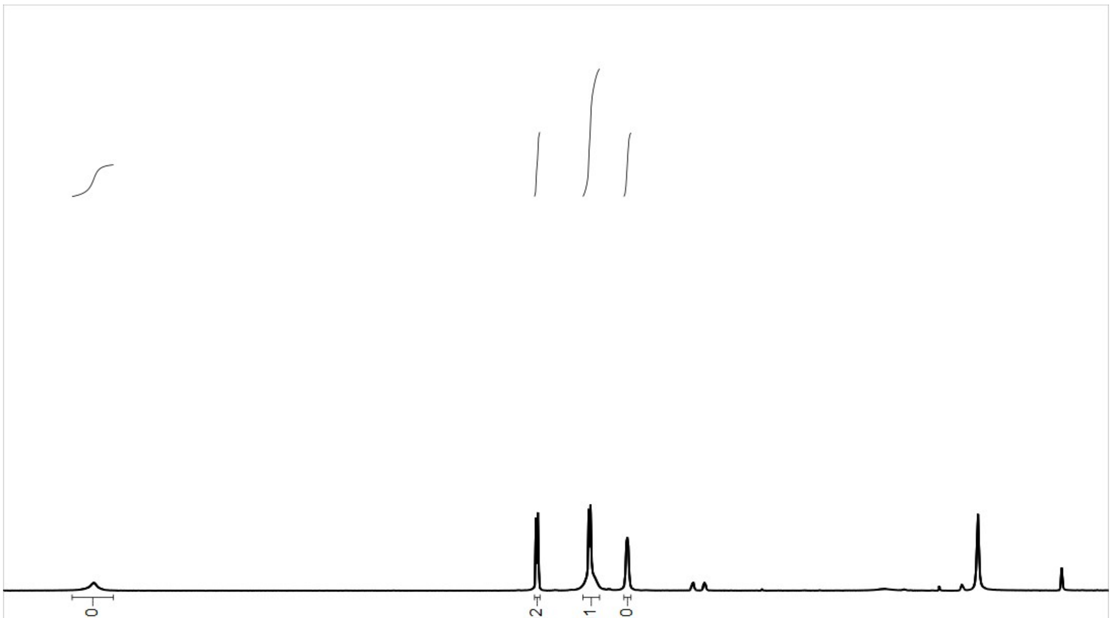
The ^{1}H-NMR spectrum of 3c



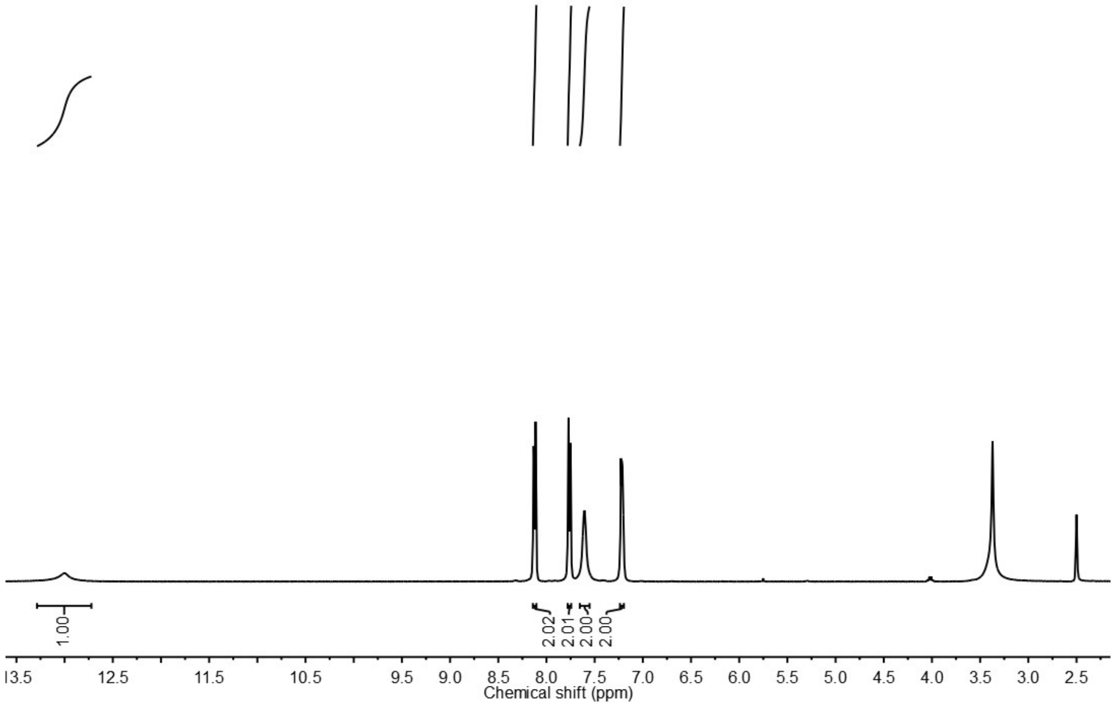
The ^{1}H-NMR spectrum of 3d



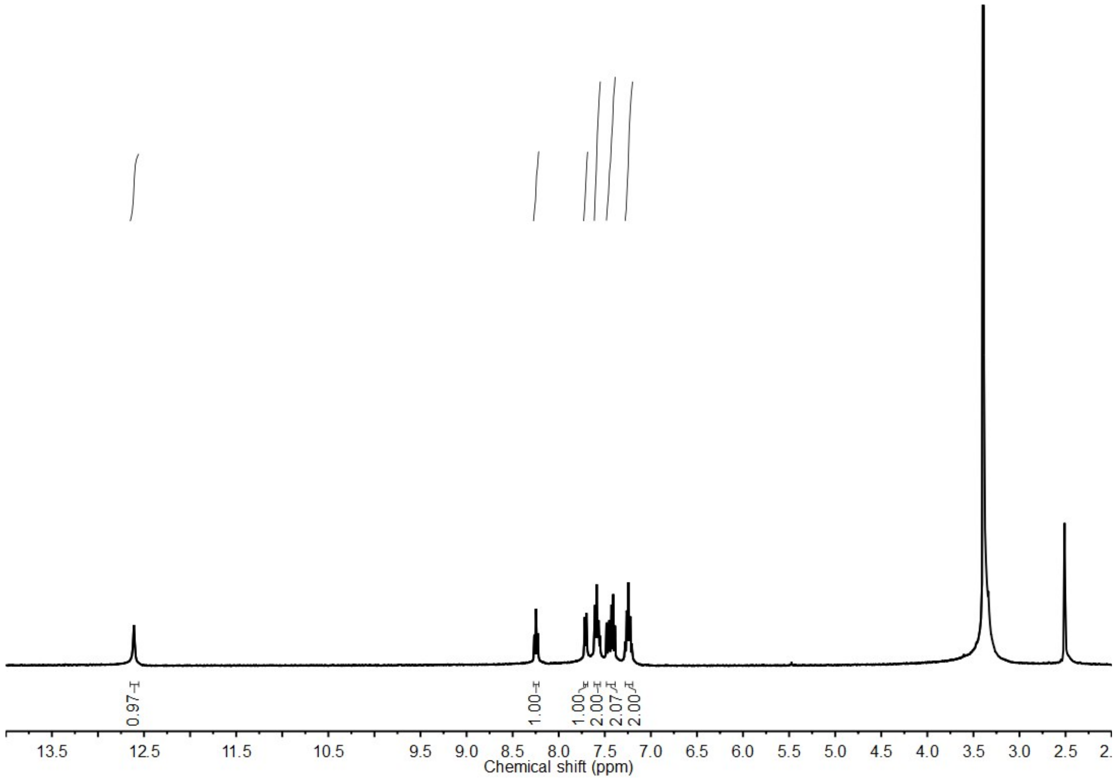
The ^{1}H-NMR spectrum of 3e



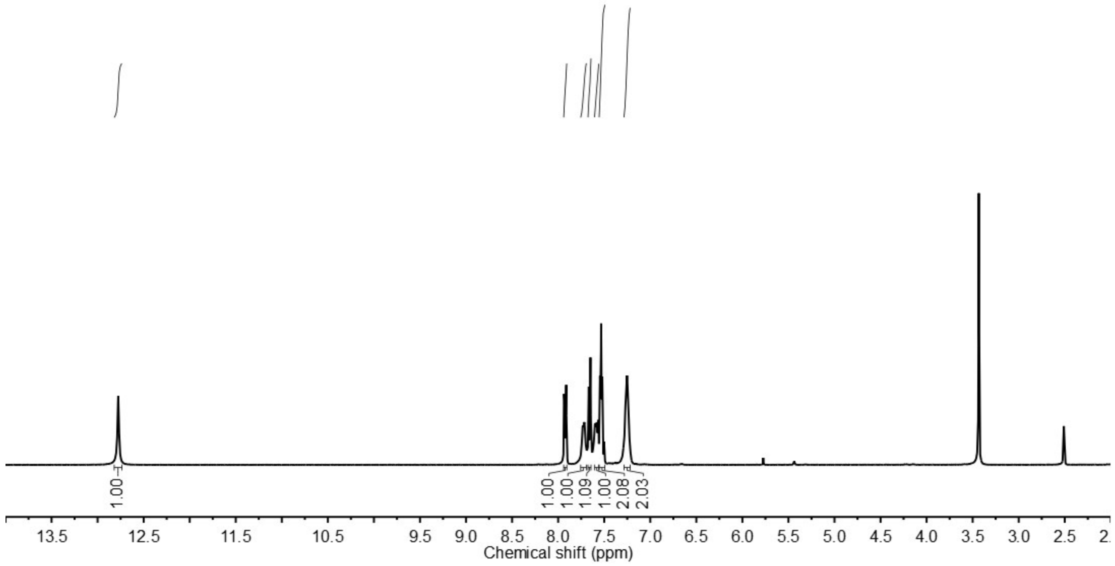
The ^{1}H-NMR spectrum of 3f



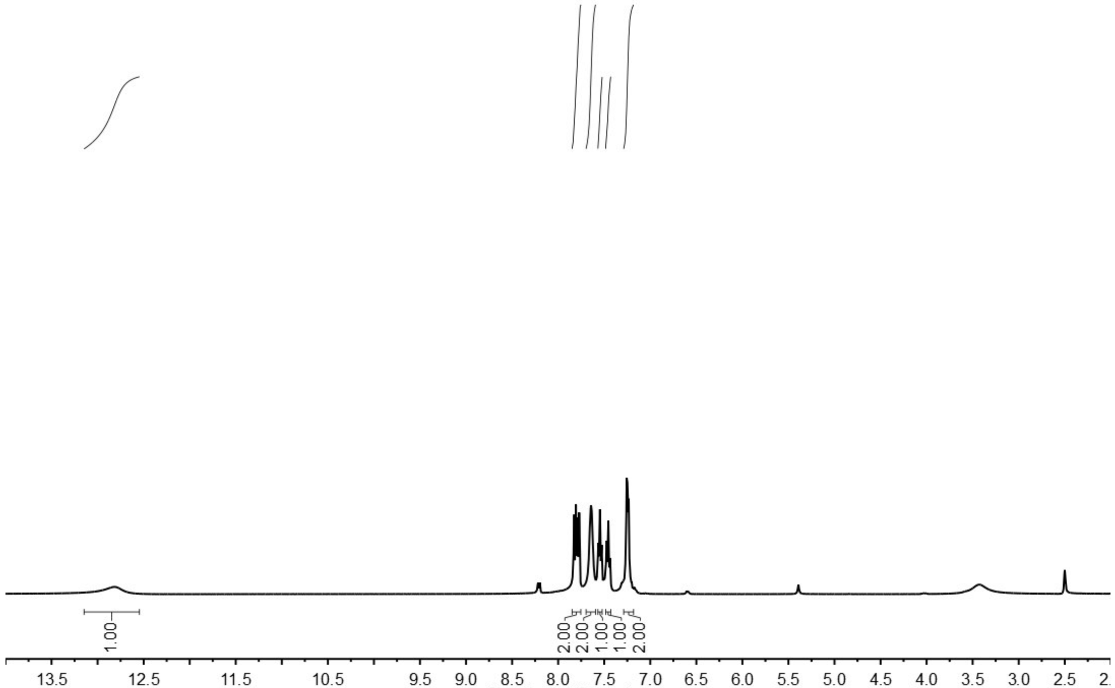
The ^{1}H-NMR spectrum of 3g



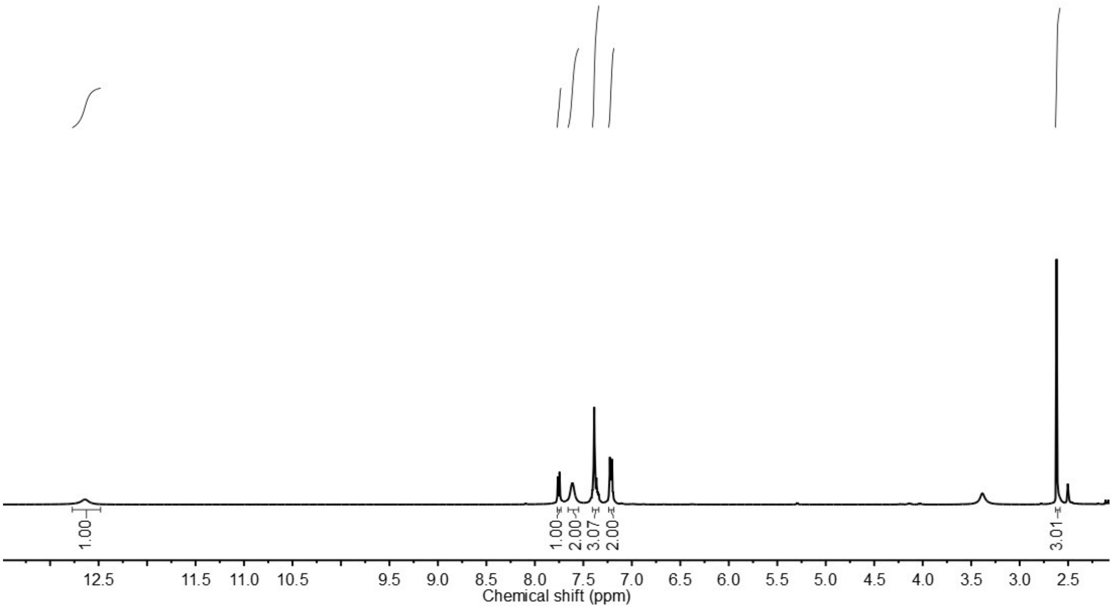
The ^{1}H-NMR spectrum of 3h



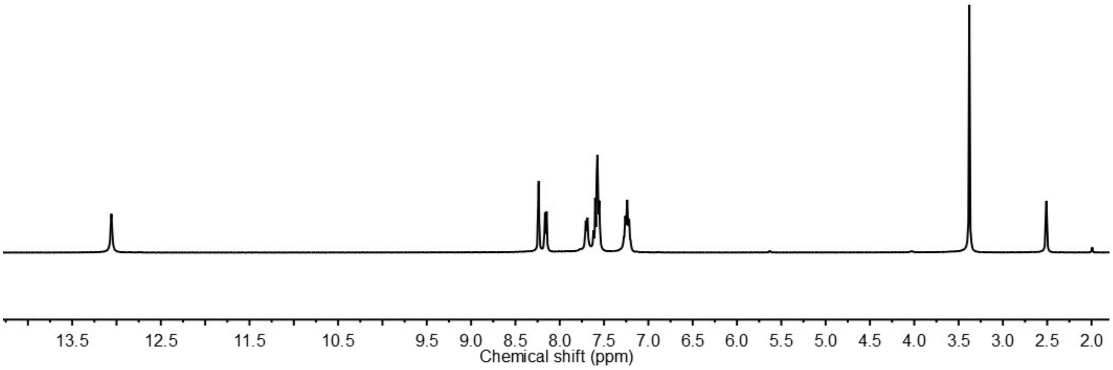
The ^{1}H-NMR spectrum of 3i



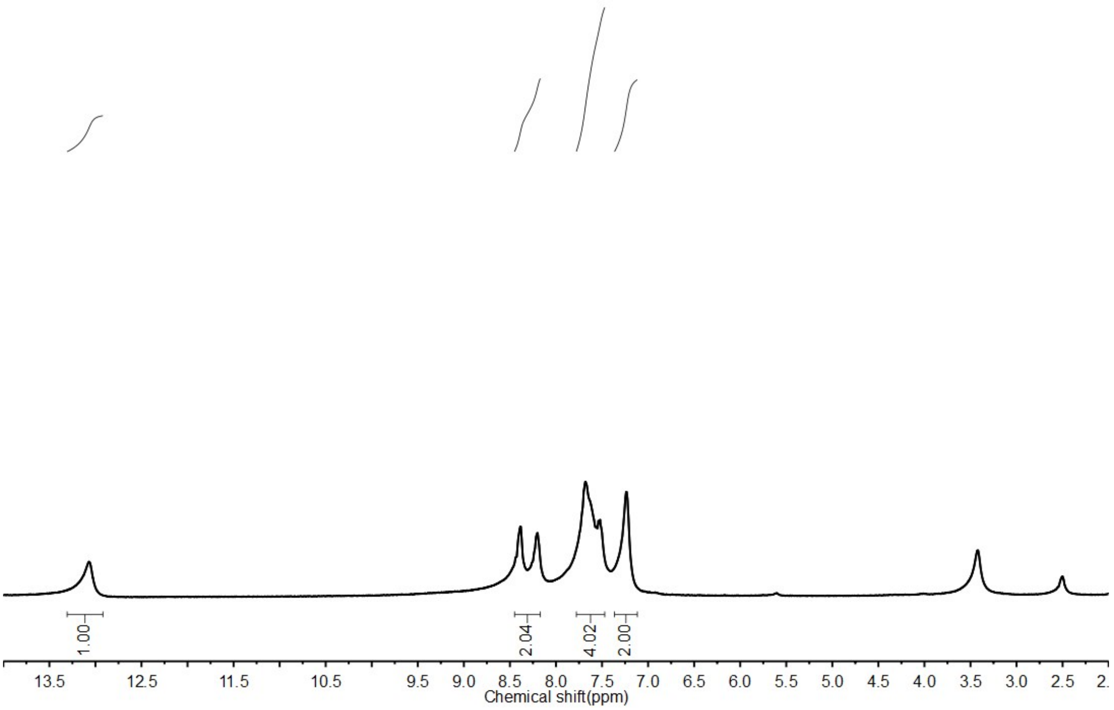
The ^{1}H-NMR spectrum of 3j



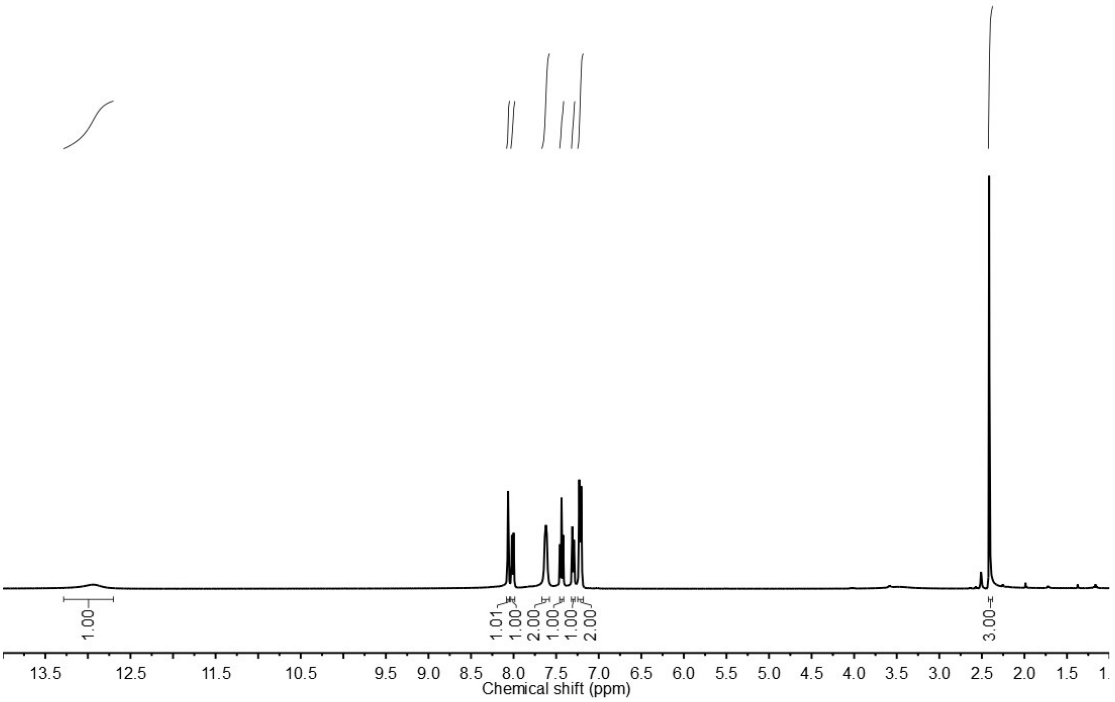
The ^{1}H-NMR spectrum of 3k



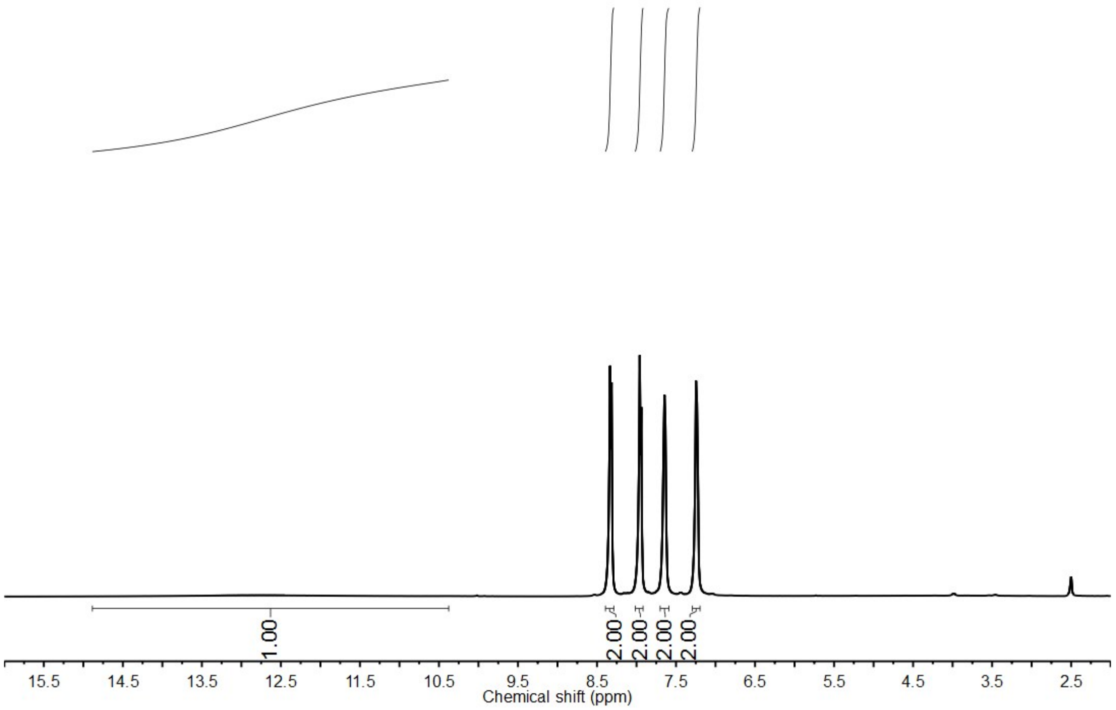
The ^{1}H-NMR spectrum of 3l



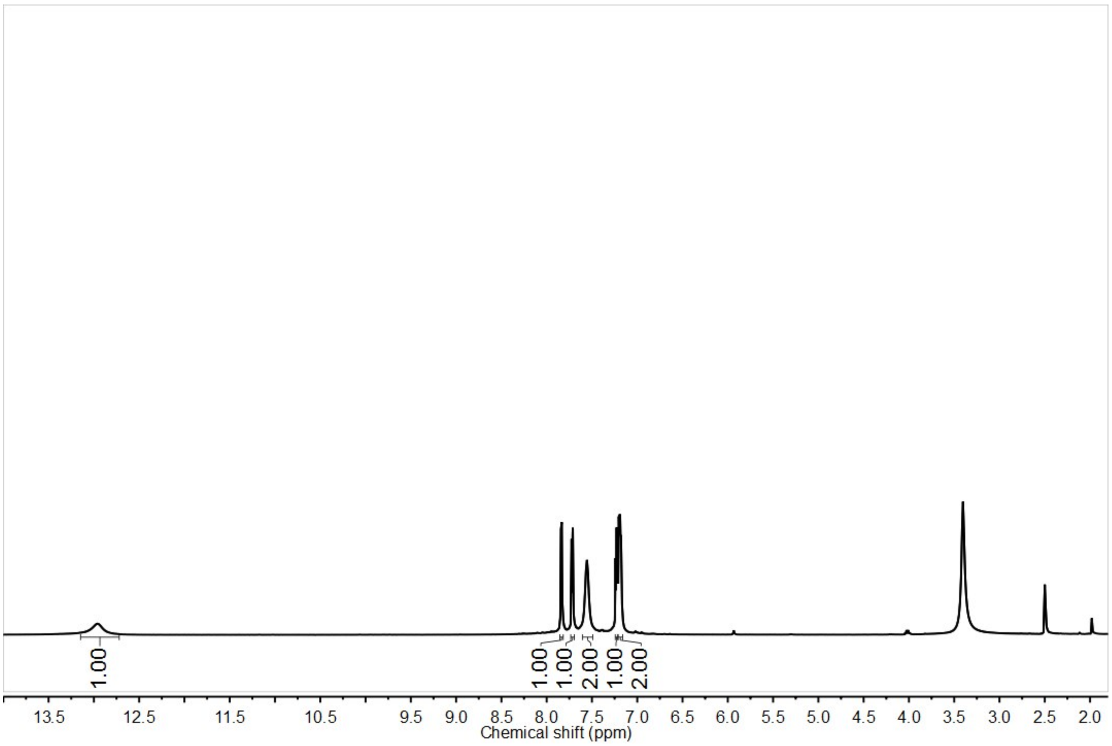
The ^{1}H-NMR spectrum of 3m



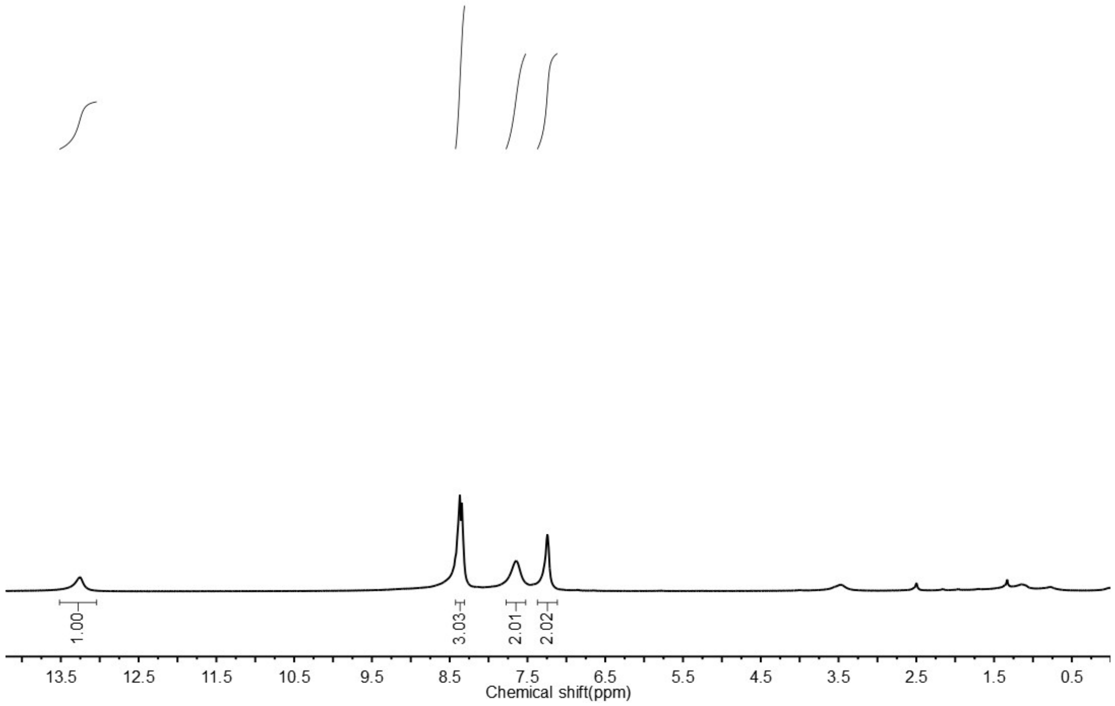
The ^{1}H-NMR spectrum of 3n



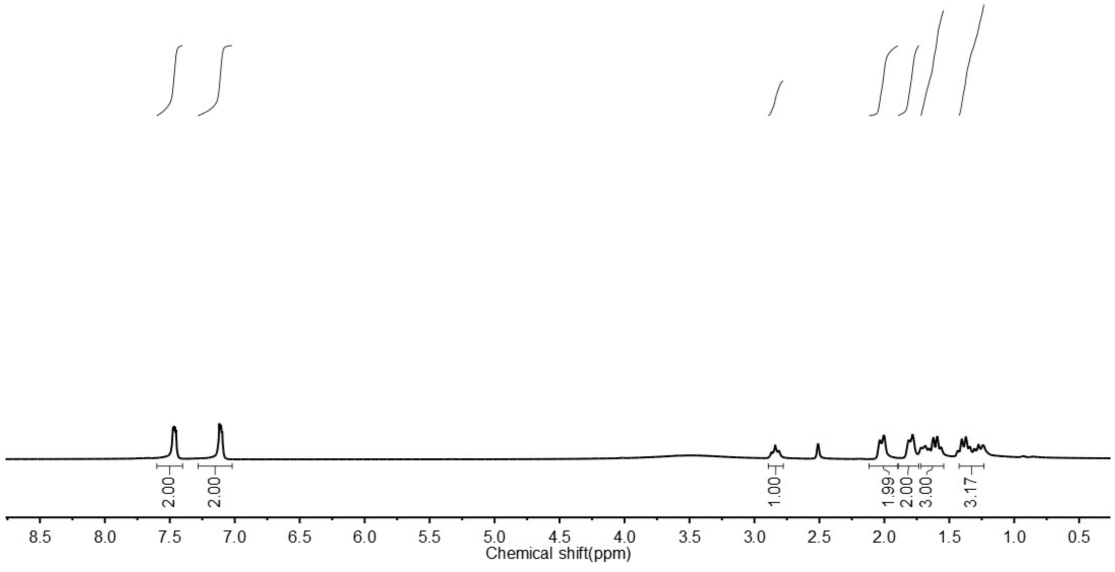
The ^{1}H-NMR spectrum of 3o



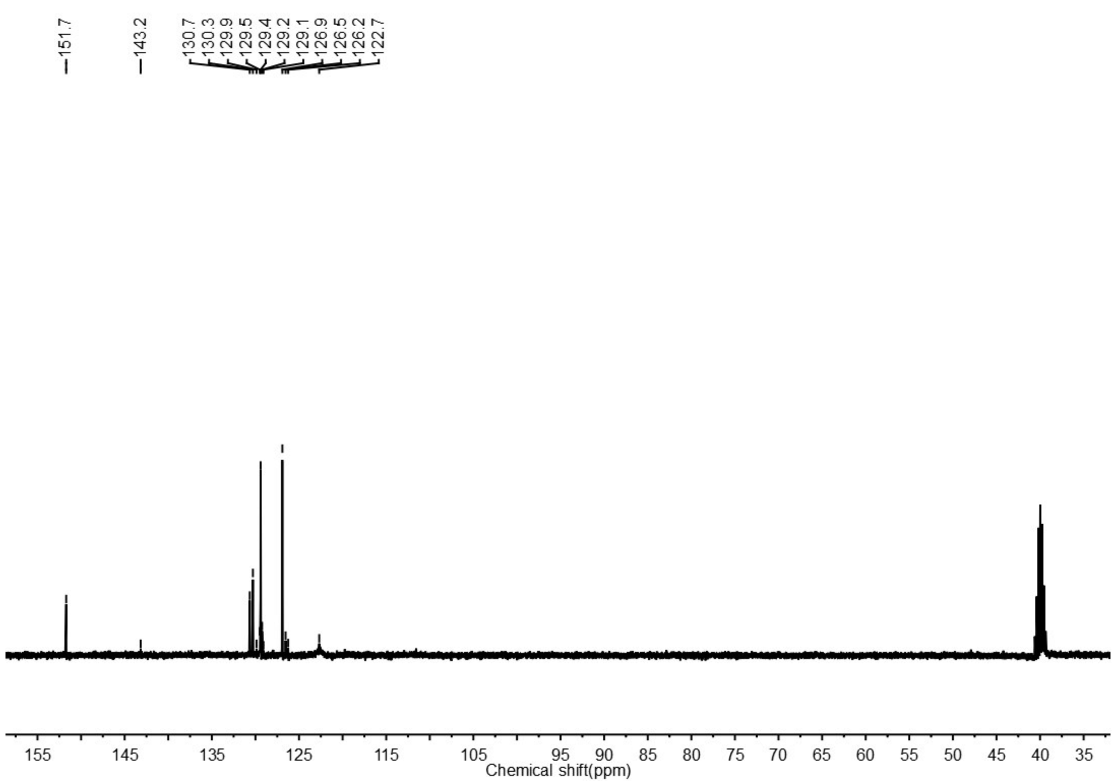
The ^{1}H-NMR spectrum of 3p



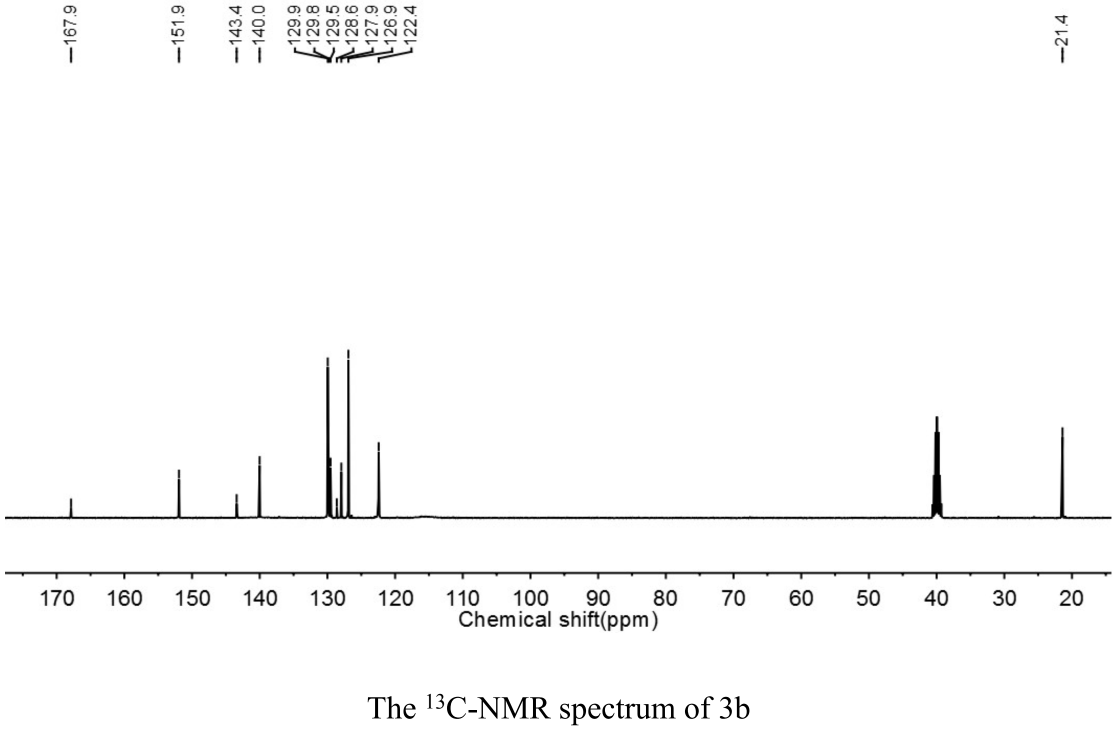
The ^{1}H-NMR spectrum of 3q



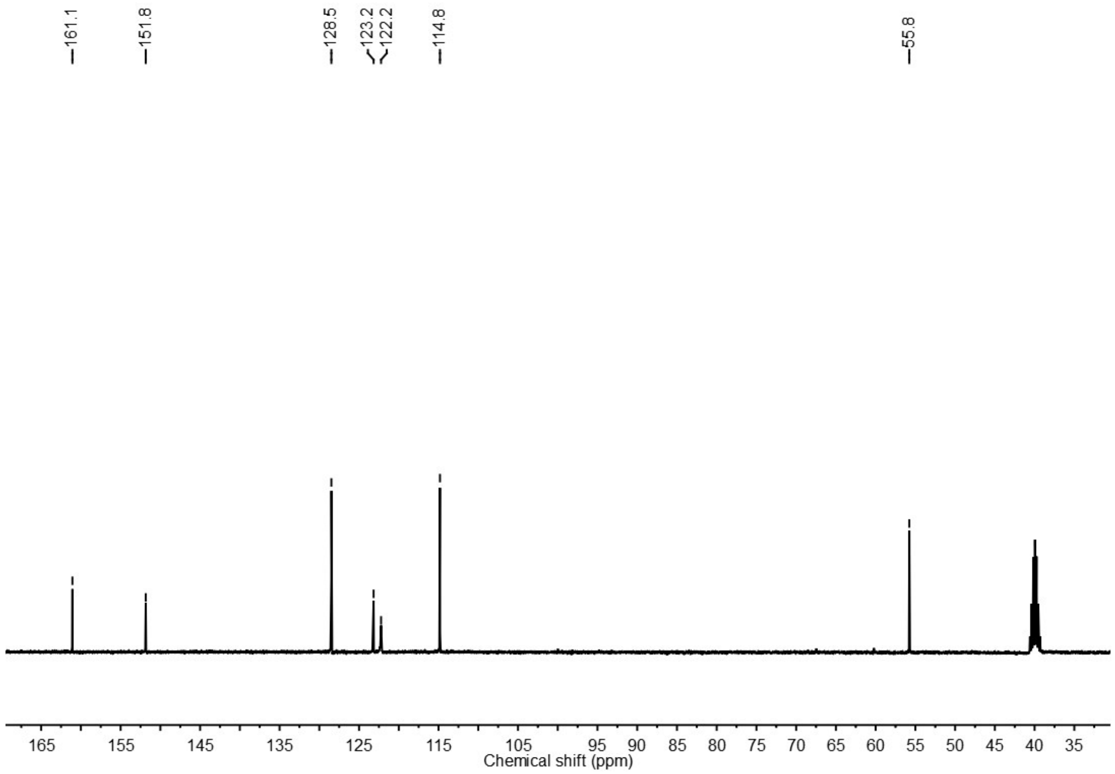
The ^{1}H-NMR spectrum of 3r



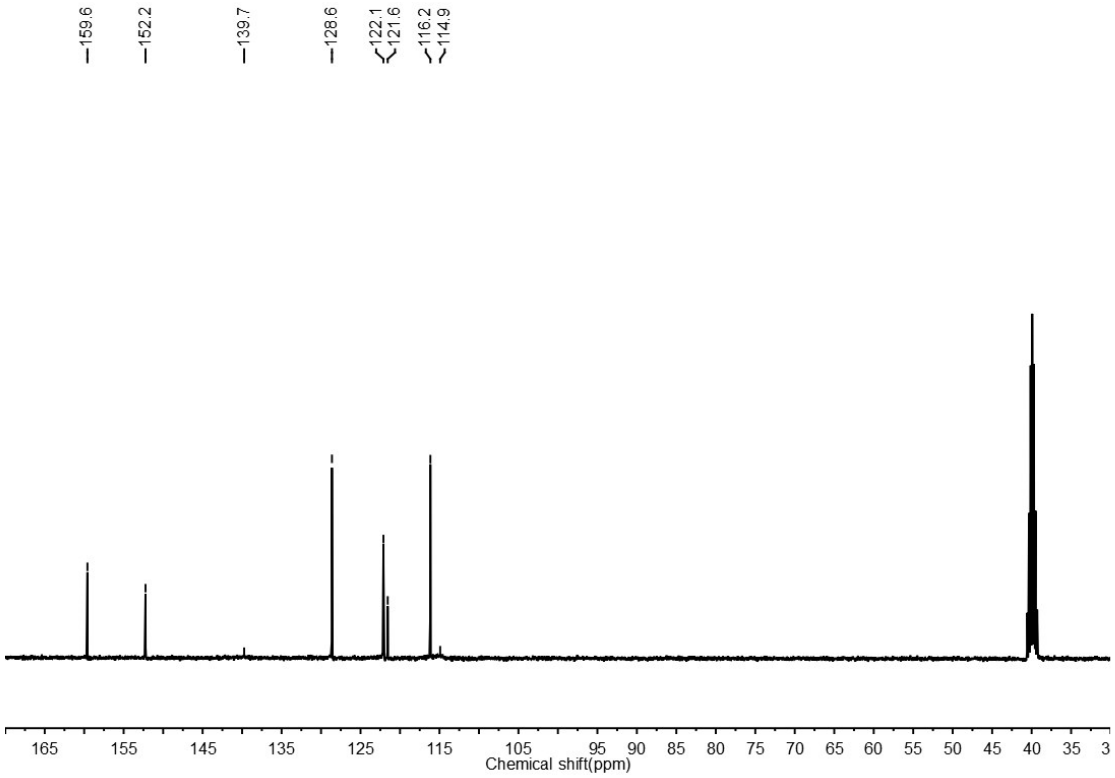
The ^{13}C-NMR spectrum of 3a



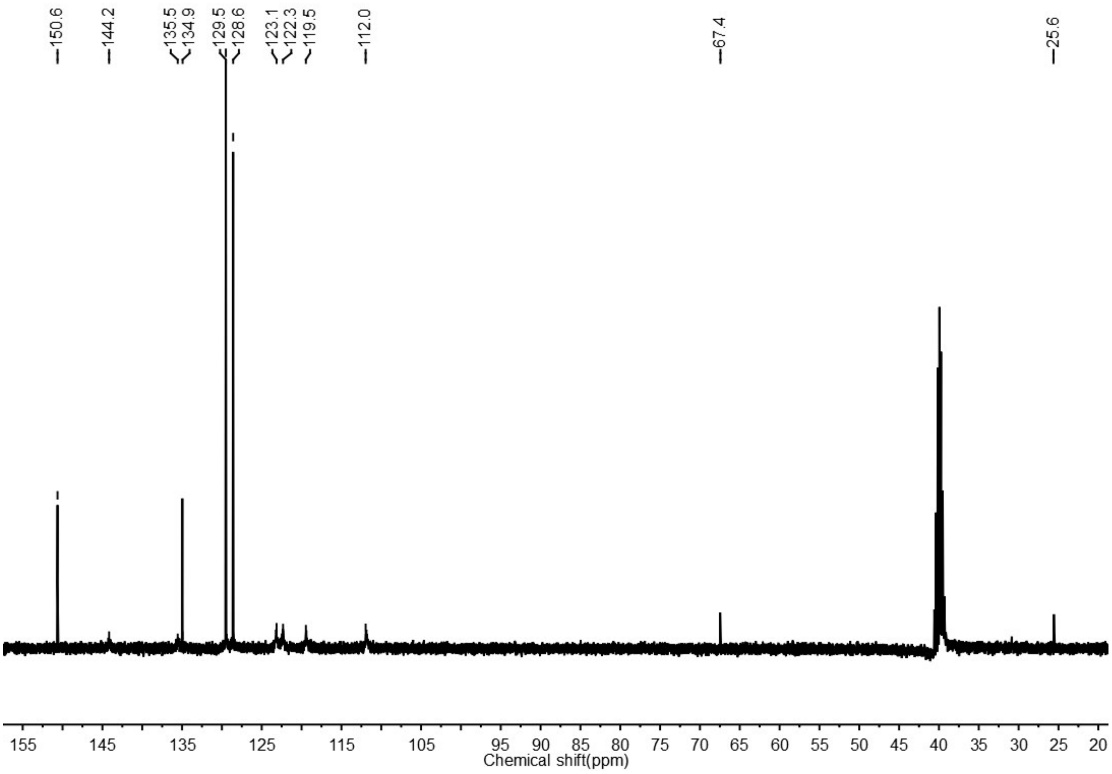
The ^{13}C-NMR spectrum of 3b



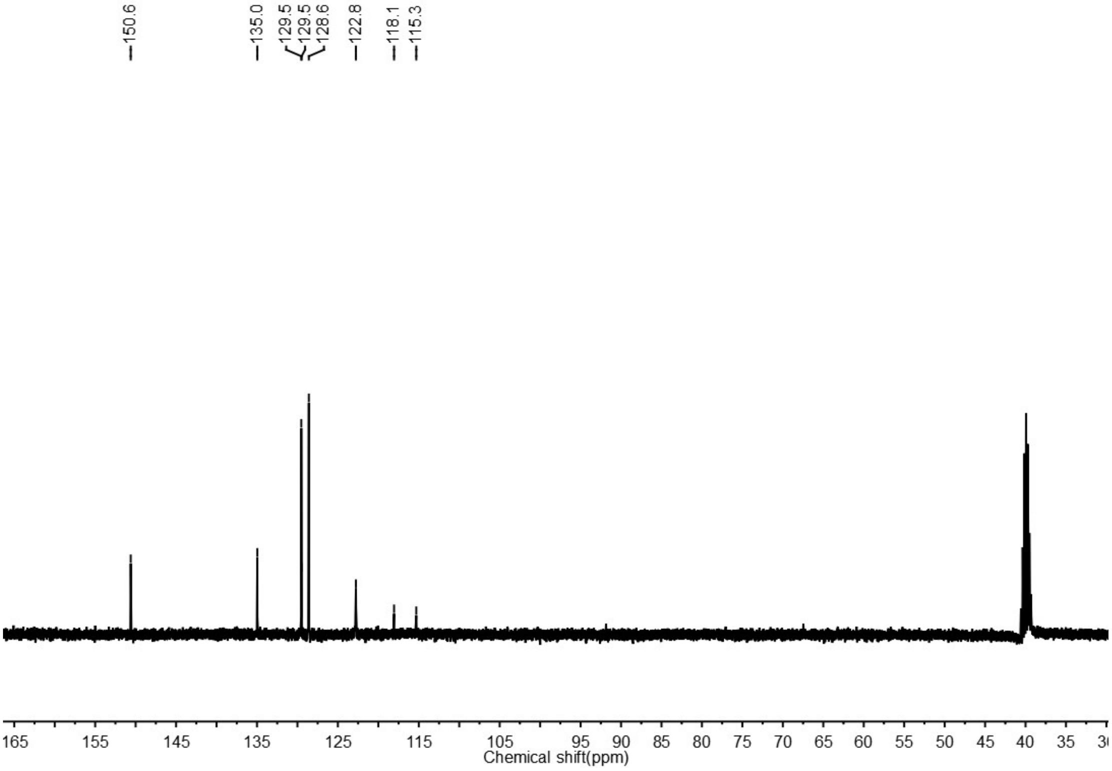
The ^{13}C-NMR spectrum of 3c



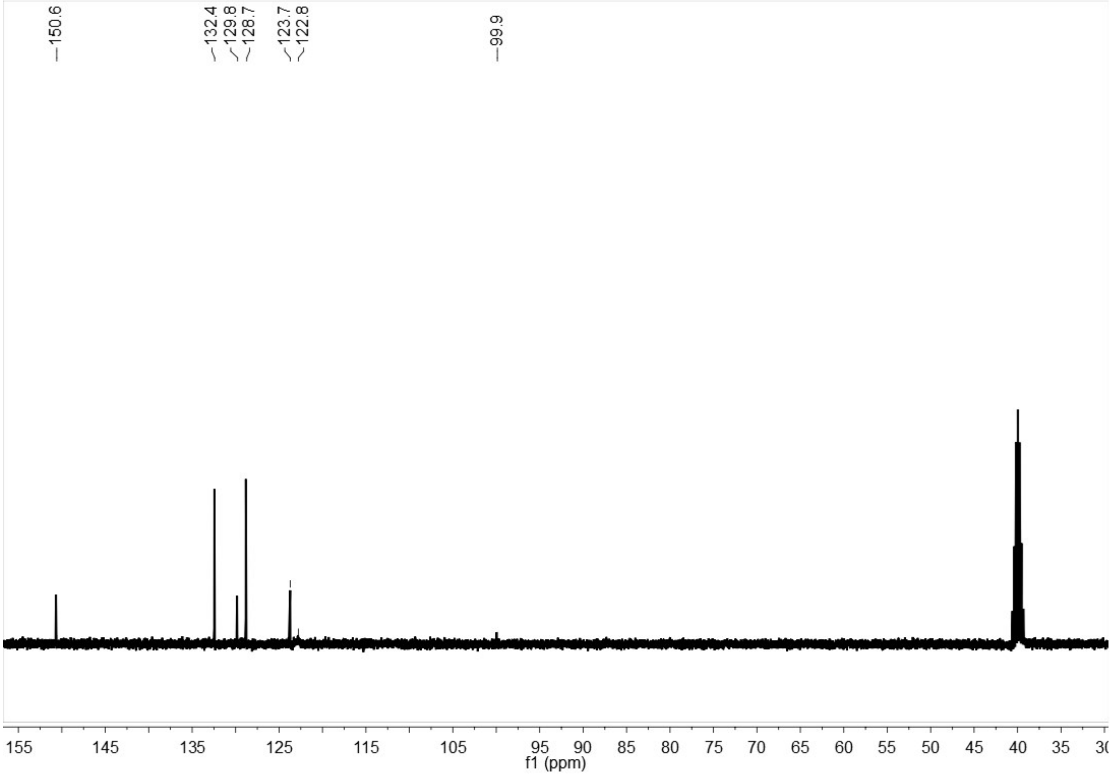
The ^{13}C-NMR spectrum of 3d



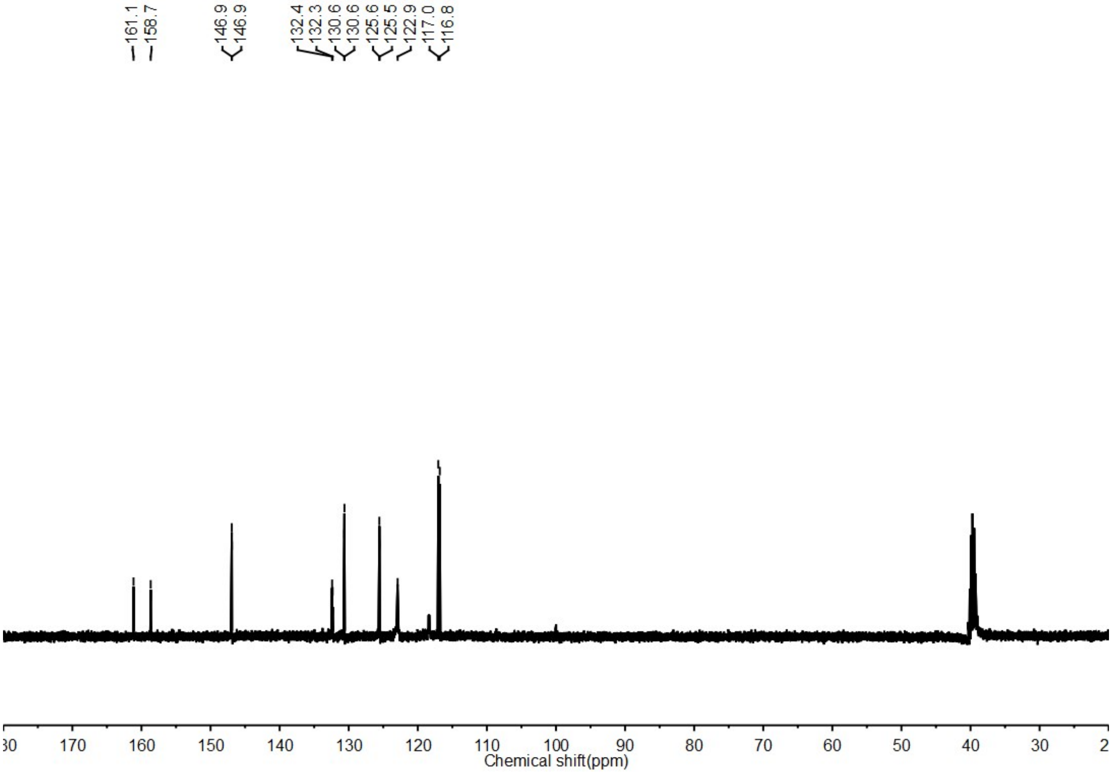
The ^{13}C-NMR spectrum of 3e



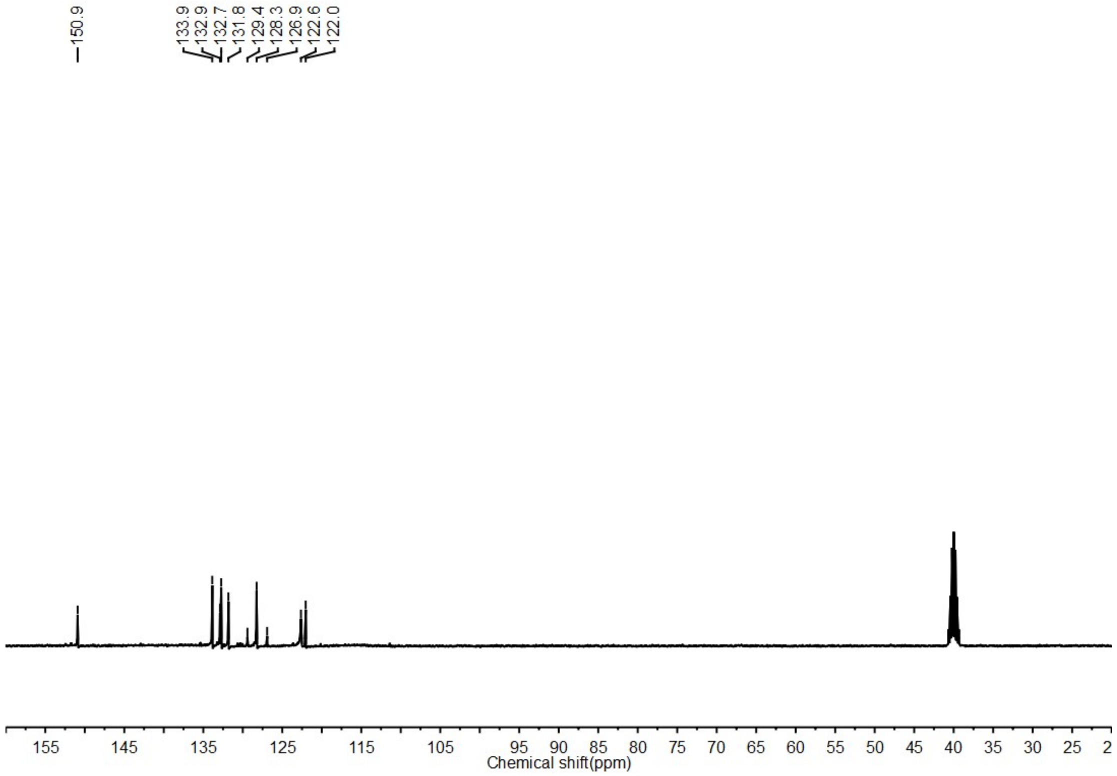
The ^{13}C-NMR spectrum of 3f



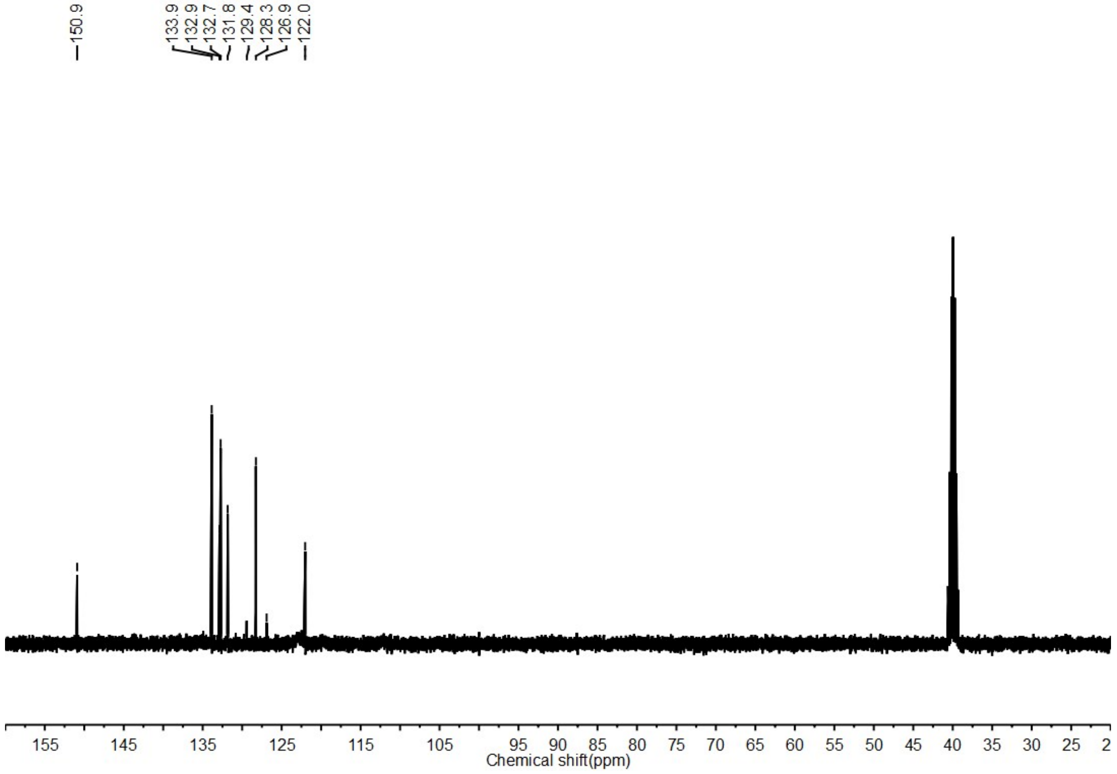
The ^{13}C-NMR spectrum of 3g



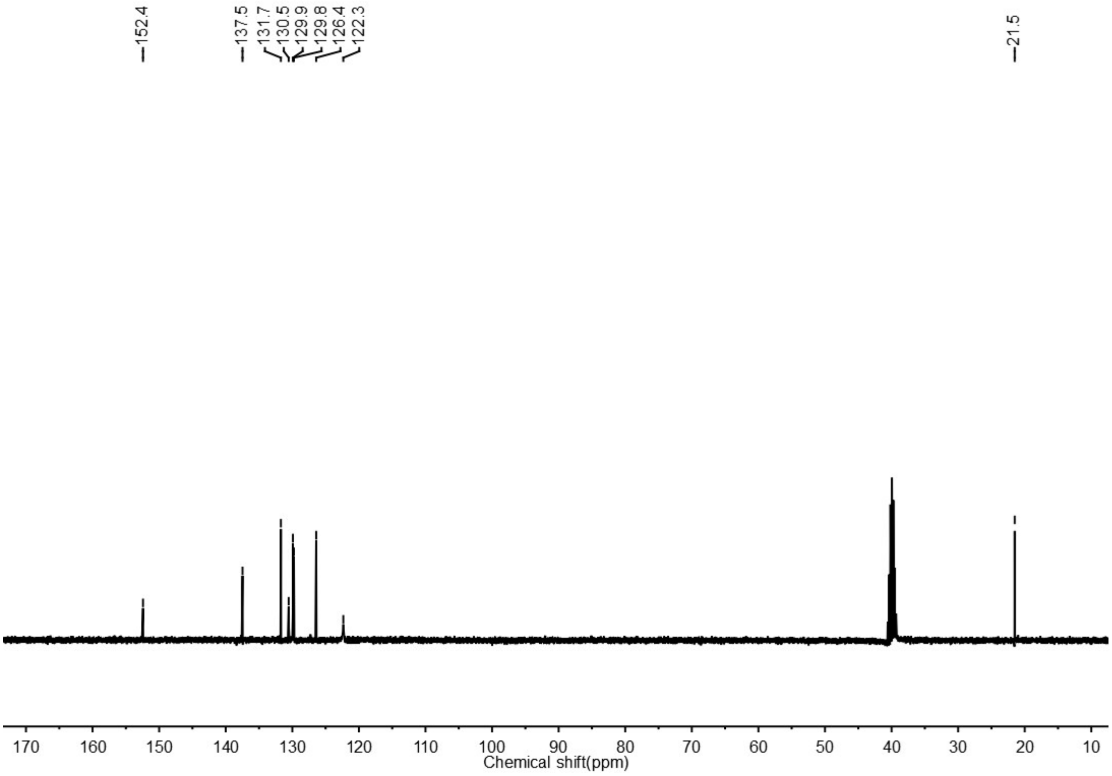
The ^{13}C-NMR spectrum of 3h



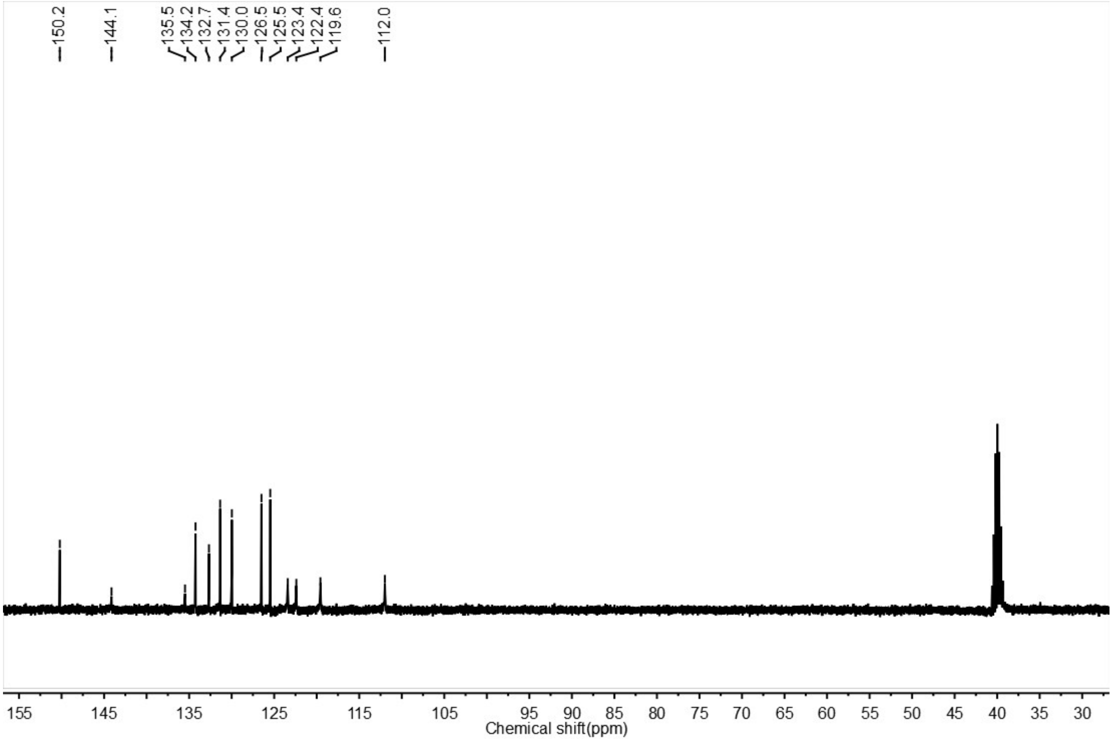
The ^{13}C-NMR spectrum of 3i



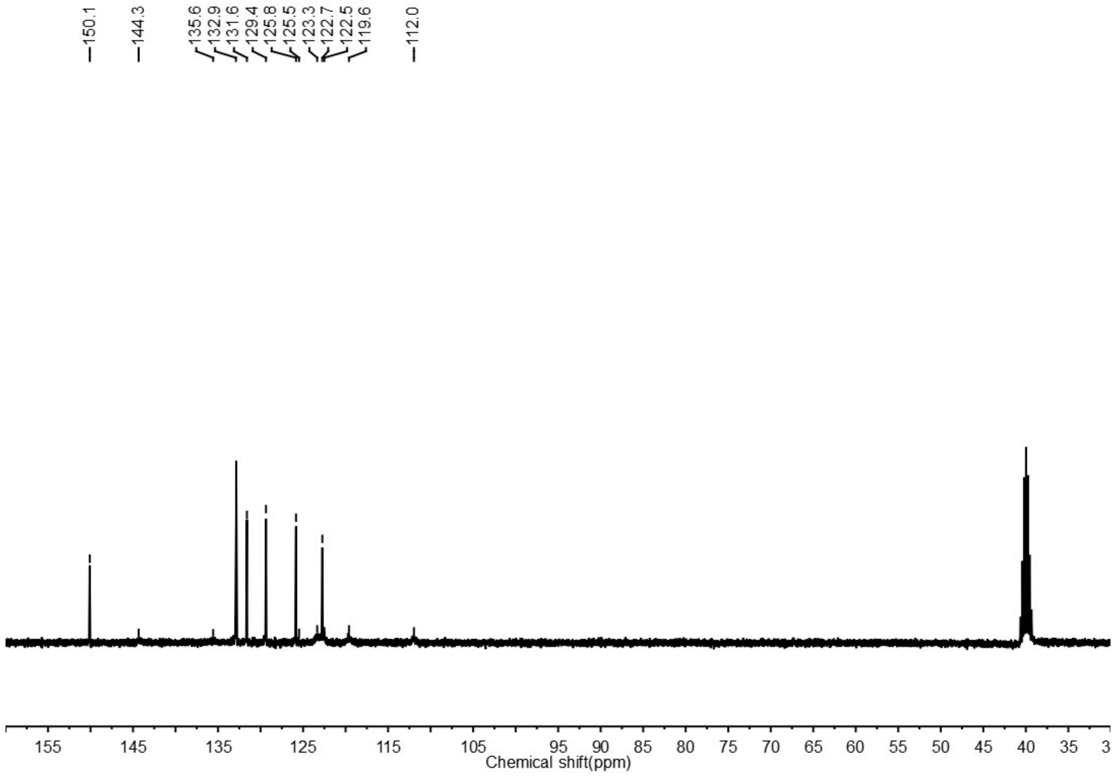
The ^{13}C-NMR spectrum of 3j



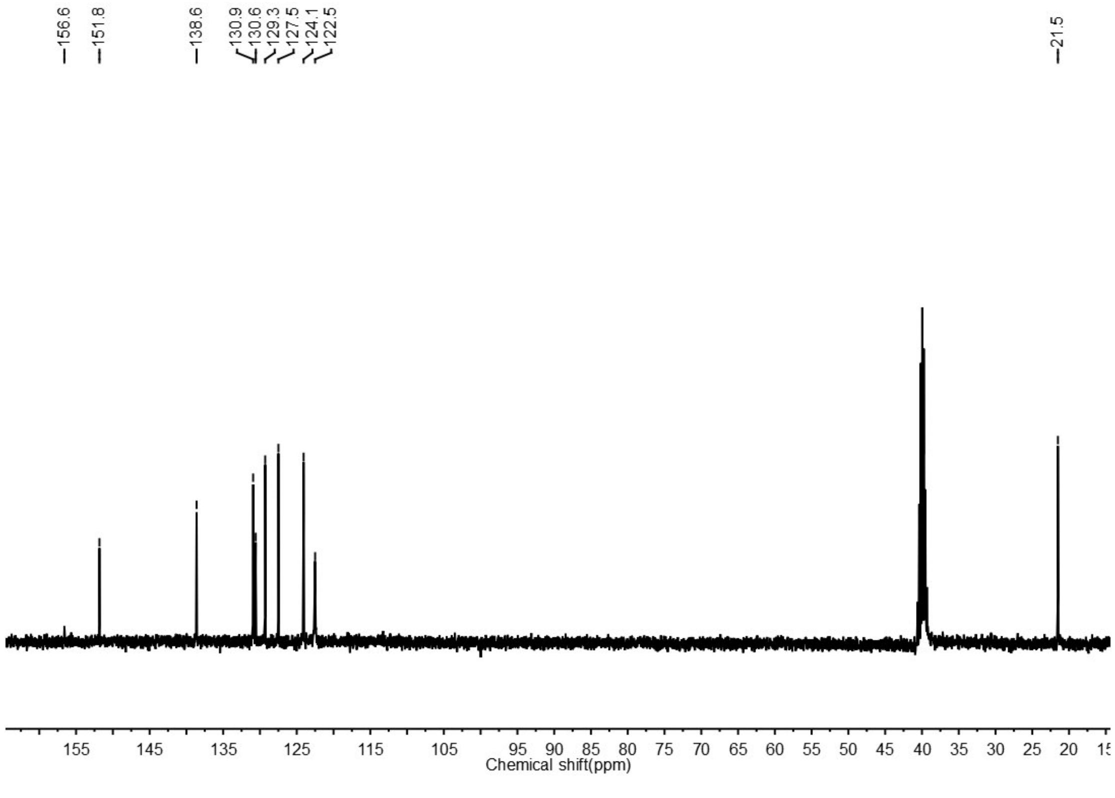
The ^{13}C-NMR spectrum of 3k



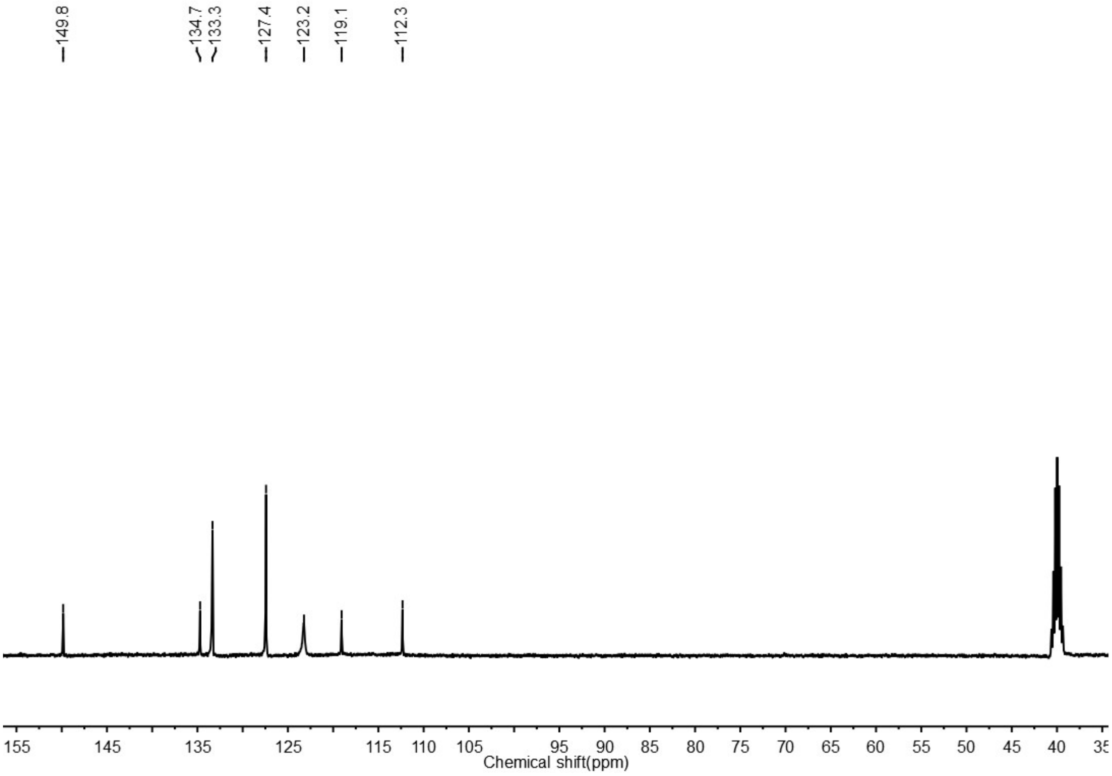
The ^{13}C-NMR spectrum of 3l



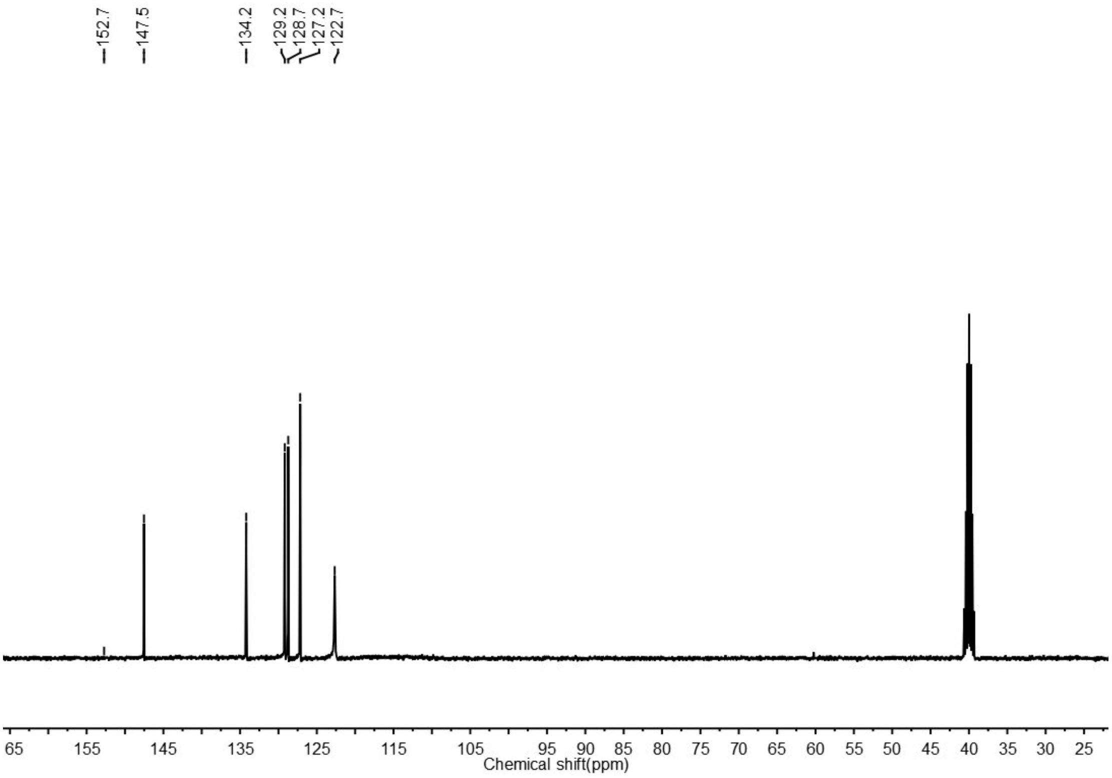
The ^{13}C-NMR spectrum of 3m



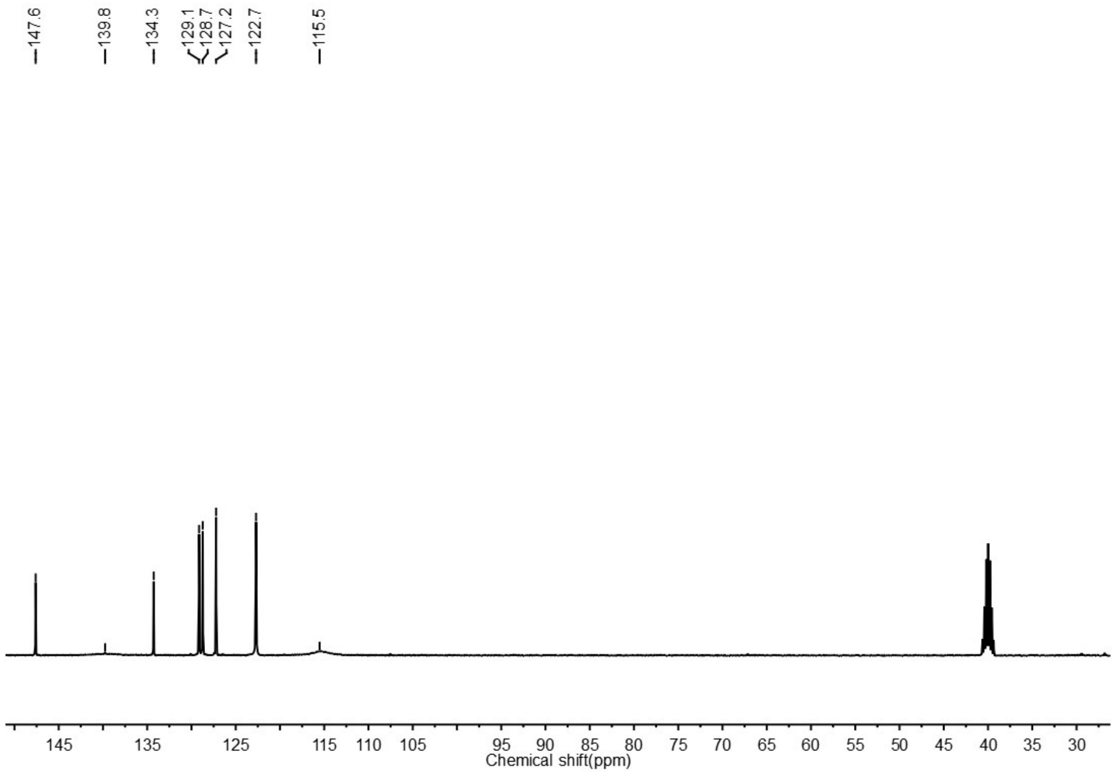
The ^{13}C-NMR spectrum of 3n



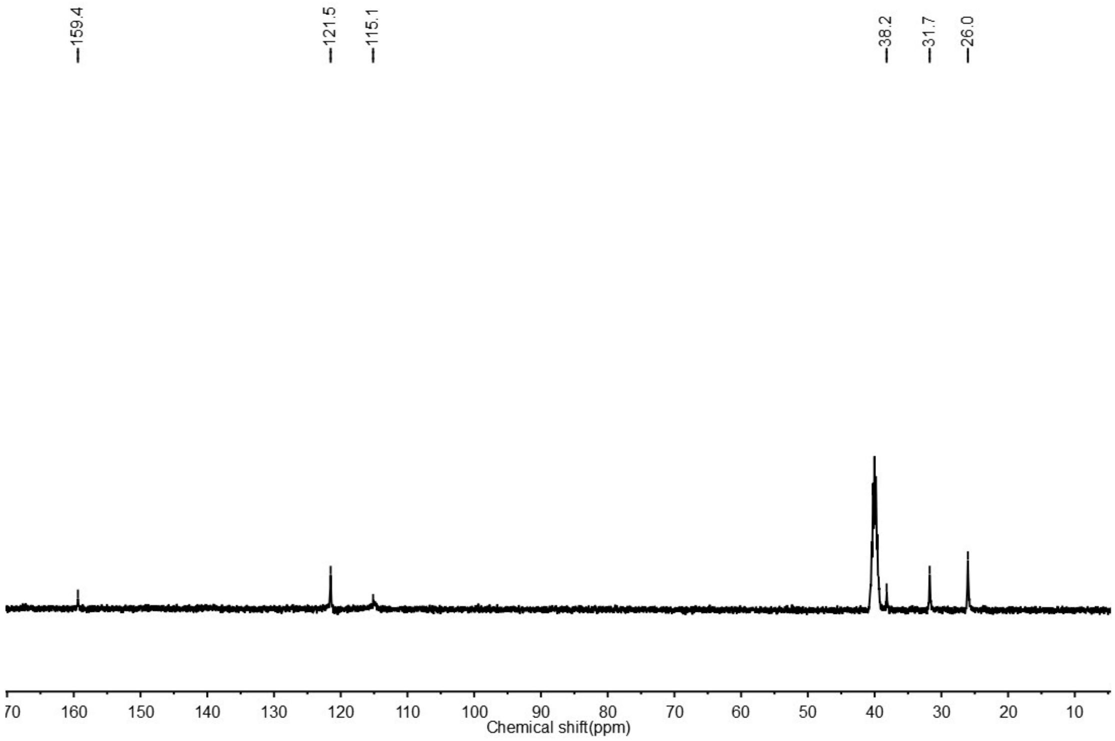
The ^{13}C-NMR spectrum of 3o



The ^{13}C-NMR spectrum of 3p



The ^{13}C-NMR spectrum of 3q



The ^{13}C-NMR spectrum of 3r

Section 9. References

[1] Li, Z.; Zhi, Y.; Shao, P.; Xia, H.; Li, G.; Feng, X.; Chen, X.; Shi, Z.; Liu, X. Covalent Organic Framework as An Efficient, Metal-Free, Heterogeneous Photocatalyst for Organic Transformations under Visible Light. *Appl. Catal. B: Environ.* **2019**, 245, 334−342.

[2] Wang, X.; Maeda, K.; Thomas, A.; Takanabe, K.; Xin, G.; Carlsson, J.; Domen, K.; Antonietti, M. A Metal-Free Polymeric Photocatalyst for Hydrogen Production from Water under Visible Light, *Nat. Mater.* **2009**, 8, 76−80.