Supplementary Information

π-plane size dependent photocatalytic activity of radical-doped diimide covalent organic frameworks

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Supplementary Methods:

General methods

All air- and moisture-sensitive solutions and chemicals were handled under an argon atmosphere. Anhydrous solvents were purchased from Sigma-Aldrich and used without further purification. Unless otherwise stated, all reagents were commercially available and used as received without further purification. Chemicals were obtained from Sigma-Aldrich, Acros, TCI and Alfa-Aesar. TLC was performed with Merck TLC Silica gel60 F_{254} plates with detection under UV light at 254 nm. Silica gel (200-300 mesh, Qingdao) was used for flash chromatography. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker Avance III 400 at 400 MHz. Carbon-13 nuclear magnetic resonance (^{13}C NMR) was recorded on Bruker Avance III 400 spectrometer at 100 MHz. Chemical shifts were reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants were reported in hertz.

Powder X-ray diffraction (XRD) measurements was recorded on a Bruker D8 ADVANCE X-Ray diffractometer at room temperature using a graphite monochromator Cu-target tube. Solid-state UV-Vis spectra were performed on a Varian Cary 500 UV–Vis spectrophotometer. Thermostability of materials were performed on a Mettler Toledo TGA2 thermogravimetric system at N_2 atmosphere from 30 to 800 °C with a ramp rate of 10 °C/min.

The electrochemical measurements were carried out using a Princeton 2273 electrochemical workstation. Fourier transform infrared (FT-IR) spectra have been recorded on a Nicolet iS50 spectrometer using KBr disks dispersed with material powder. Scanning electron microscopy (SEM) images were obtained using Thermo Fisher Quattro S. Transmission electron microscopy (TEM) images were obtained using a JEM-1400 with the accelerating voltage of 100 kV. BET

surface area was measured at 77 K with a Micromeritics ASAP 2020 adsorption instrument.

Electrochemical Measurements

COF powder (10 mg) was ground with poly(vinylidene fluoride) (4 mg) and then ultrasonically dispersed in 3 mL of acetone. The resultant slurry was then drop-casted onto indium tin oxide (ITO) glass with an area of 0.5 × 0.5 cm^2. A Pt wire (counter electrode), an Ag/AgCl electrode (reference electrode), and a coated ITO conductive glass (working electrode) were assembled into a three-electrode system with 0.5 M Na_2SO_4 aqueous solution used as the electrolyte. The Mott-Schottky plots were collected in dark at 2000 Hz frequency. The photocurrent measurements were conducted under the irradiation of a 300 W xenon lamp with a 420 nm cut-off filter under a nitrogen-saturated atmosphere.

Structural modeling of PDI-COF, NDI-COF, and PBI-COF

Structural modeling of COFs were generated using the Materials Studio (ver. 7.0) suite of programs. Optimization of molecular geometry was performed with MS DMol3 module. The initial lattice was created by starting with the space group P6. The a and b lattice parameters were estimated according to the center-to-center distance between the opposite sides hexagon of the COFs. The constructed model was optimized using the Forcite module (Universal force fields, Ewald summations). Then the calculated PXRD pattern was generated with the Reflex Plus module. Finally, Pawley refinement was applied for profile fitting, producing the refined PXRD profile. A staggered arrangement of COFs was also constructed using similar to the above method wherein the stacked units were offset by a/2 and b/2. Comparison of the observed and the simulated PXRD patterns suggested that the preferable structures of COFs are the eclipsed arrangement.

DFT Computational details

All of the calculations were investigated with the Gaussian 16 software package. Structural optimizations and electronic properties were performed using the B3LYP functional with 6-311G(d, p) basis set (empirical dispersion correction GD3(BJ)). Calculations of frequency were accomplished at the parallel level of the theory (no imaginary frequency) to confirm the optimized-geometries as true minima.

Procedure and characterization for C-C coupling of *N*-aryl-tetrahydroisoquinoline with nitroalkanes and C-P coupling of *N*-aryl-tetrahydroisoquinoline with phosphite esters.

General Procedure A: C-C coupling of *N*-aryl-tetrahydroisoquinoline with nitroalkanes

An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with *N*-aryl-tetrahydroisoquinoline (0.2 mmol), COF (0.5 mol%), and nitroalkanes (1 mL). The reaction system was then exposed to air and stirred at room temperature for a period of 48-56 hours, while being irradiated by a 100 W white LED at a distance of 30 cm. Once the reaction was complete, the mixture was diluted with H_2O and ethyl acetate, the layers were separated and the aqueous phase was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with saturated brine solution (20 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. The crude products were purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 15:1→10:1) to give the corresponding C-C coupling products **3a**-**3i**.

General Procedure B: C-P coupling of *N*-aryl-tetrahydroisoquinoline with phosphite esters.

In a dry 10 mL Schlenk tube equipped with a stirring bar, *N*-aryl-tetrahydroisoquinoline (0.2 mmol), diethyl phosphite or diisopropyl phosphite (0.4 mmol), COF (0.5 mol%) and methyl

alcohol (1 mL) were added in air. The mixture was exposed to radiation under a 100 W white LED at a distance of 30 cm and stirred for 48-66 hours at room temperature. Once the reaction had been completed, the mixture was diluted with water and ethyl acetate. The layers were subsequently separated, and the aqueous phase was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with saturated brine solution (20 mL), dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude products were purified by column chromatography on silica gel (eluting with petroleum ether: thyl acetate = 15:1→7:1) to give the corresponding C-P coupling products **6a-6i**.

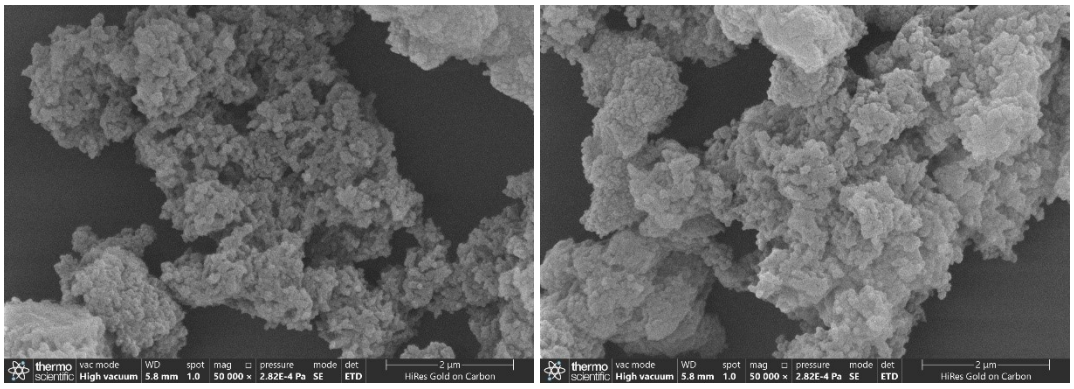


Figure S1. SEM images of the PDI-COF.

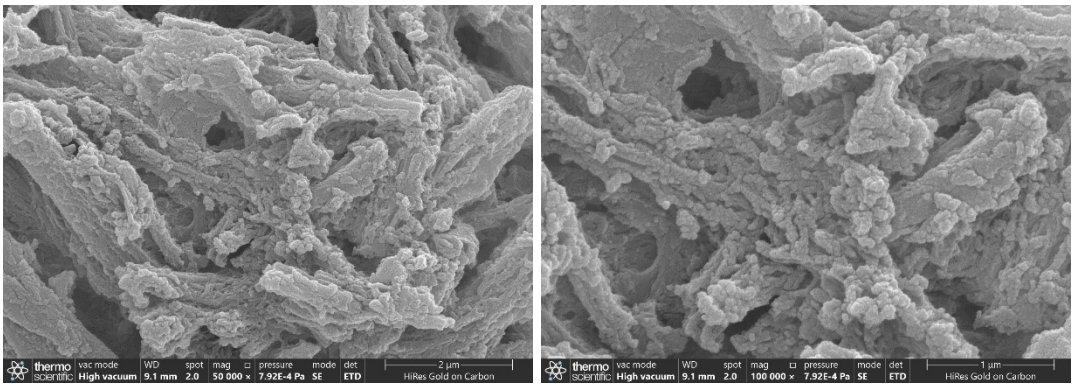


Figure S2. SEM images of the NDI-COF.

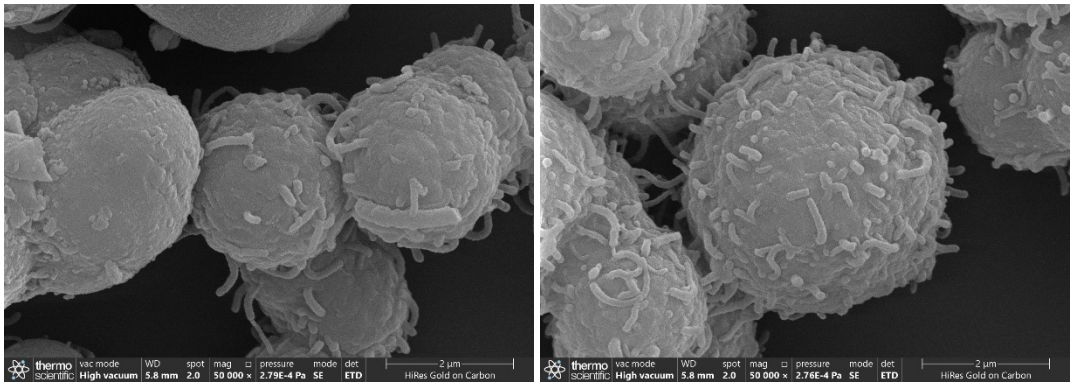


Figure S3. SEM images of the PBI-COF.

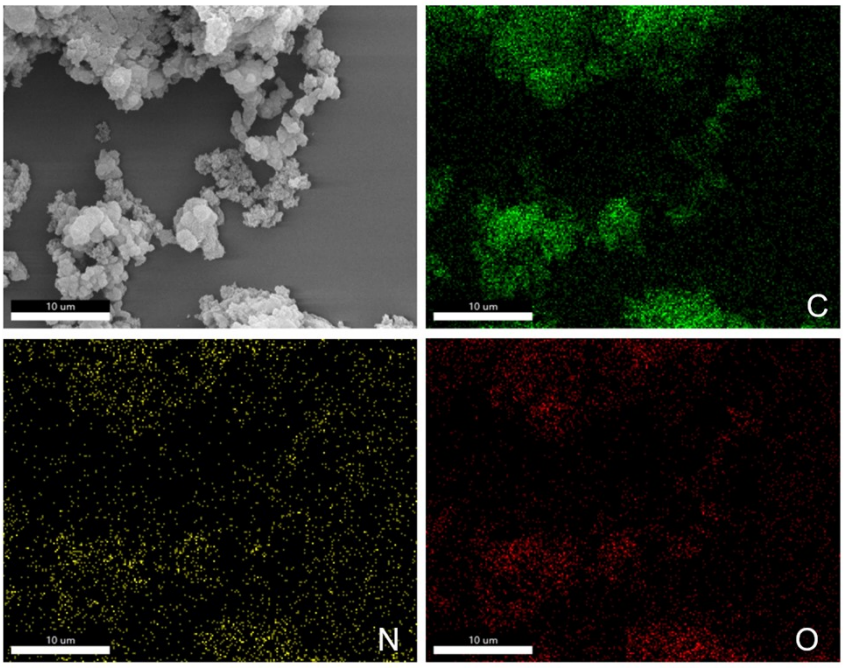


Figure S4. Elemental mapping images of PDI-COF.

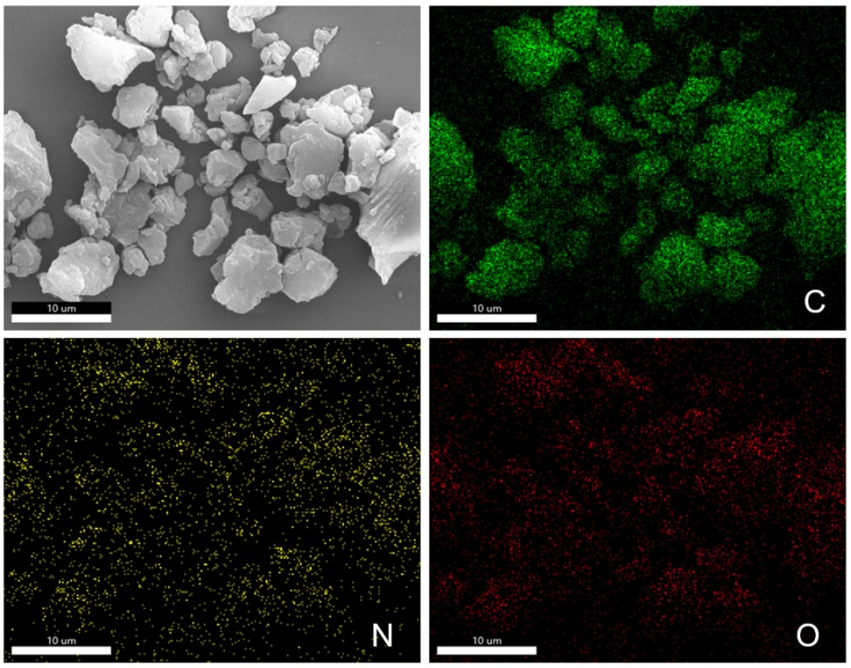


Figure S5. Elemental mapping images of NDI-COF.

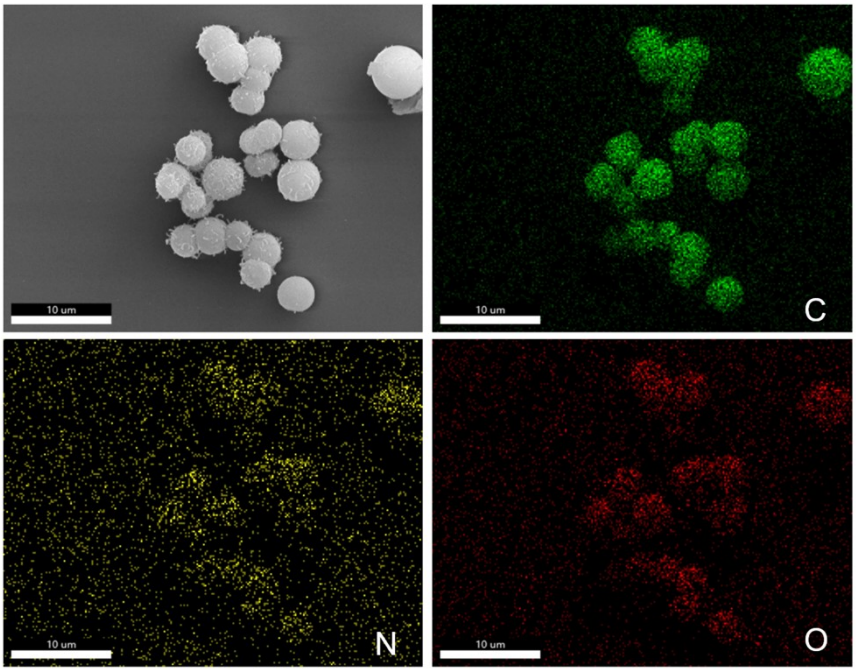


Figure S6. Elemental mapping images of PBI-COF.

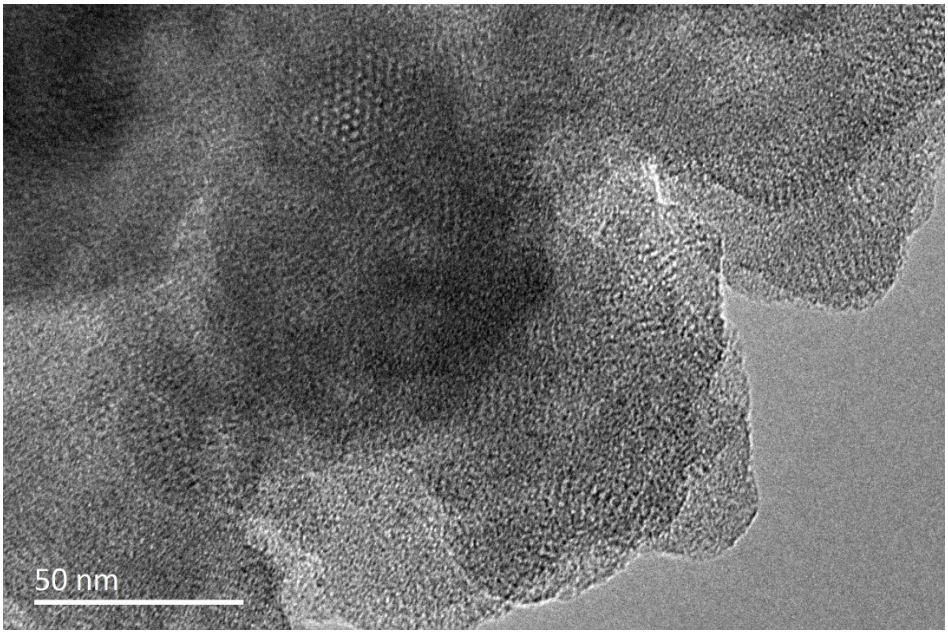


Figure S7. TEM images of the PDI-COF.

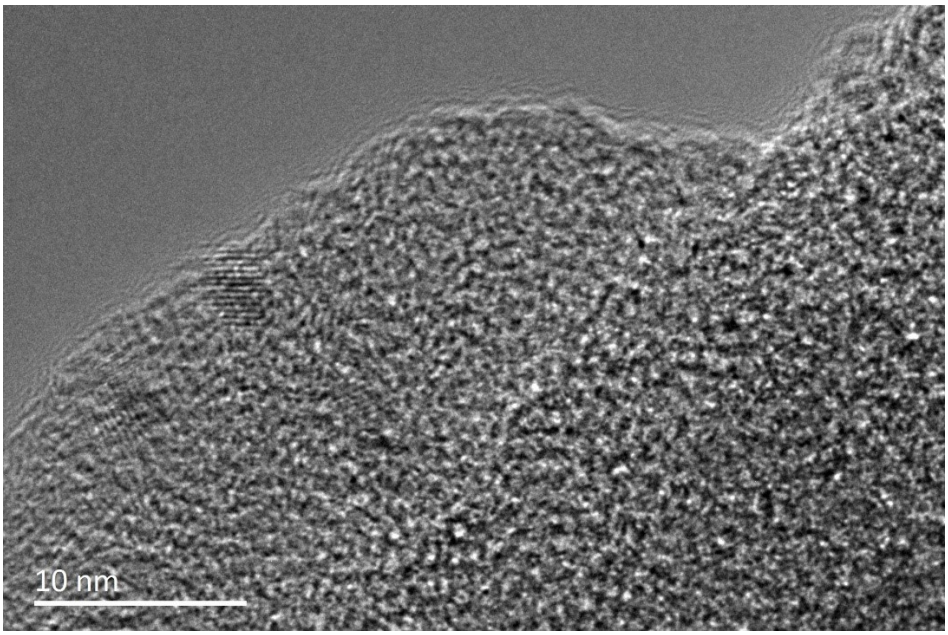


Figure S8. TEM images of the NDI-COF.

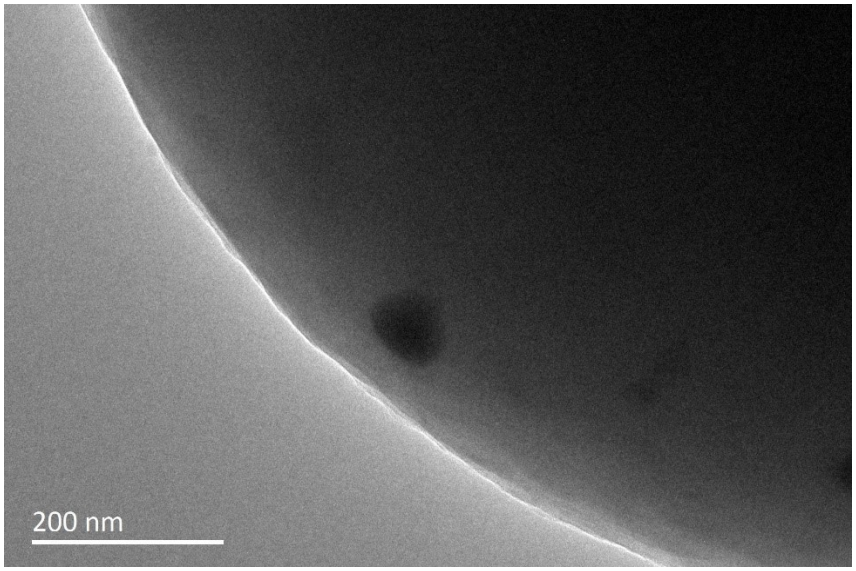


Figure S9. TEM images of the PBI-COF.

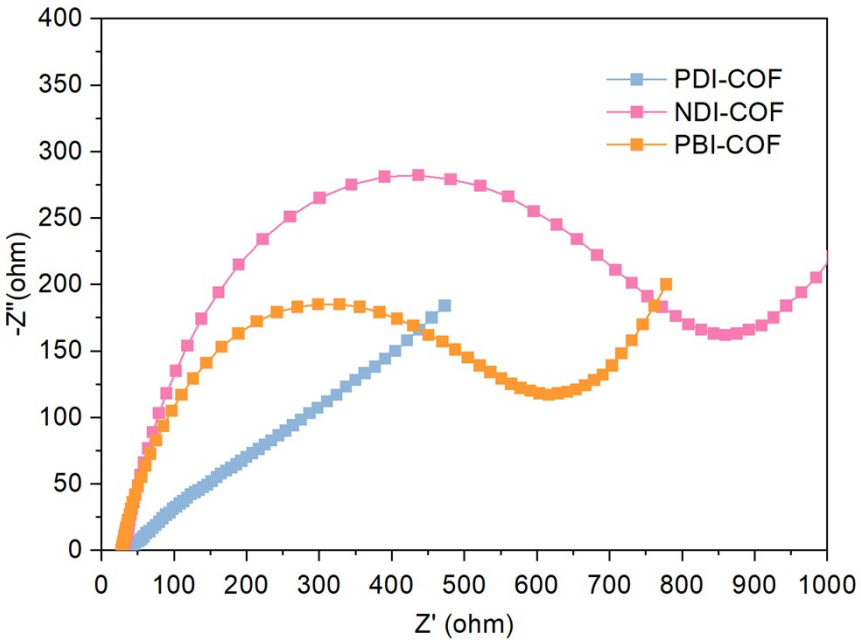


Figure S10. Electrochemical impedance spectra of PDI-COF, NDI-COF, and PBI-COF.

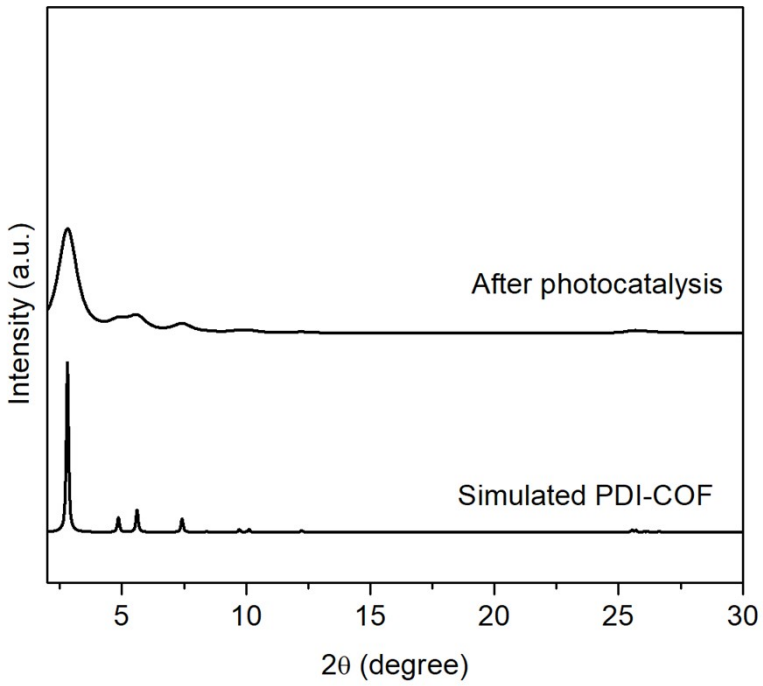


Figure S11. The PXRD patterns of PDI-COF after photocatalysis.

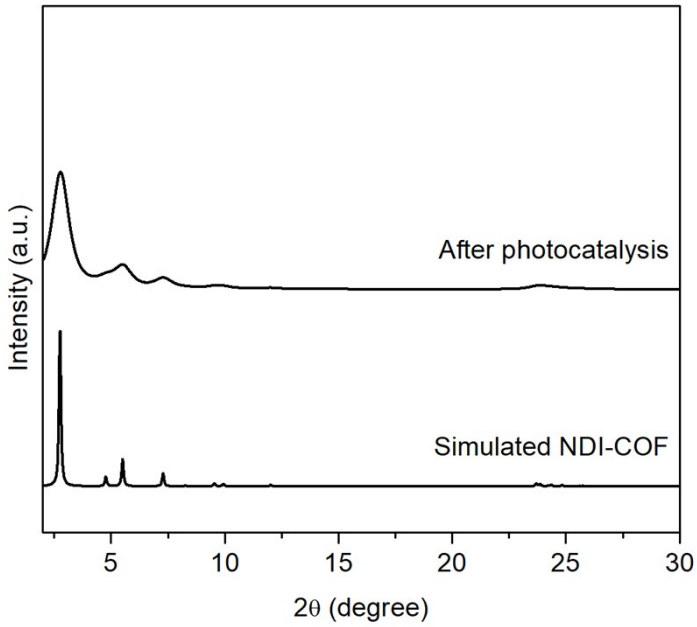


Figure S12. The PXRD patterns of NDI-COF after photocatalysis.

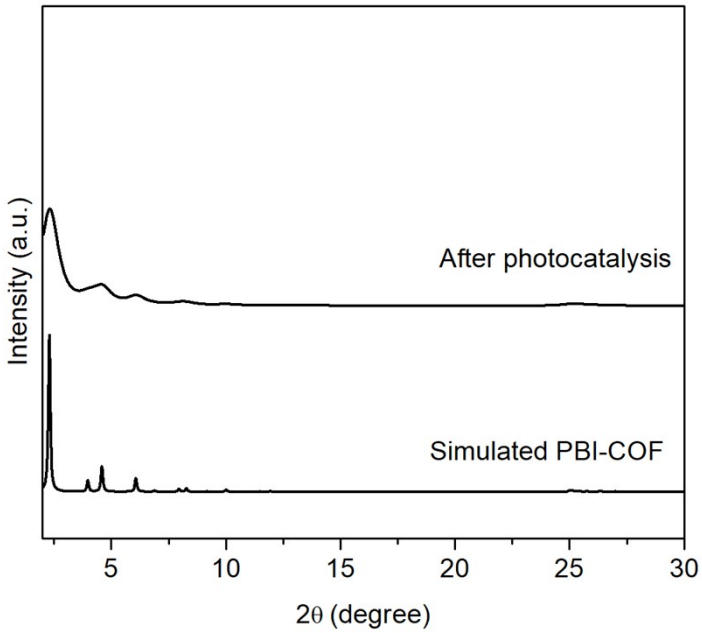


Figure S13. The PXRD patterns of PBI-COF after photocatalysis.

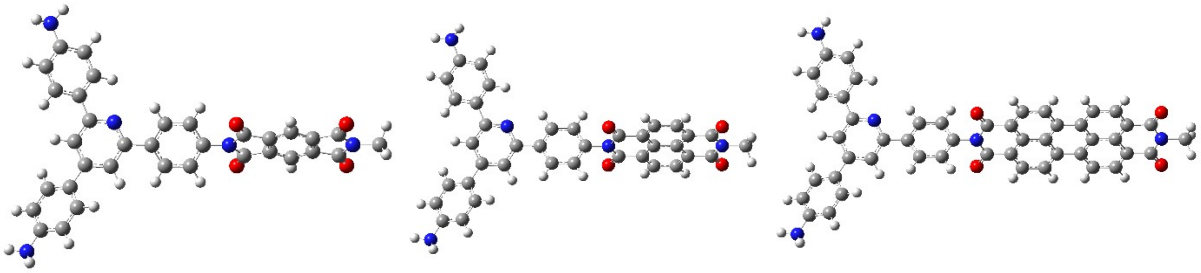
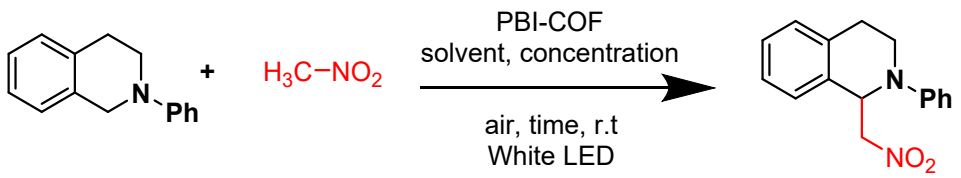


Figure S14. The optimized structural fragment of PdI-COF, NDI-COF, and PBI-COF. H: white; C: gray; N: blue; O: red.

Table S1. Reaction of between 2-aryl-tetrahydroisoquinoline and nitroalkanes [a,b,c].



1a **2a** **3a**

Entry	PBI-COF (mmol%)	Solvent	Time (h)	Yield (%)
1	0.5	THF	48	7
2	0.5	MeCN	48	26
3	0.5	MeOH	48	62
4	0.5	Toluene	48	23
5	0.5	1,4-Dioxane	48	6
6	0.25	CH_3NO_2	48	36
7	0.5	CH_3NO_2	48	58
8	0.5	CH_3NO_2	24	63
9	0.5	CH_3NO_2	48	97
10[d]	0.5	CH_3NO_2	48	10
11[e]	0.5	CH_3NO_2	48	0

[a] Reaction conducted on a 0.2 mmol scale using 1 equiv. of 1a and 2.0 equiv. of CH_3NO_2 (entry 1-5), solvent 1 mL.

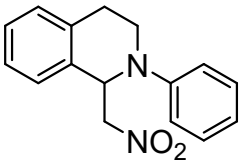
[b] assay yield determined by ^1H NMR spectroscopy of the crude reaction mixtures using CH_2Cl_2 as an internal standard.

[c] The light source is white LED (100W, Lamp spacing = 30 cm).

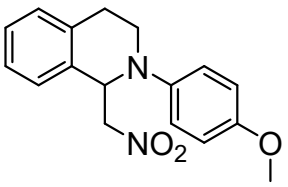
[d] N_2.

[e] In the dark.

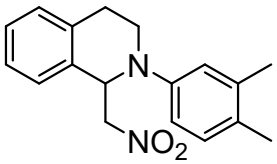
Characterization data of catalytic products

3a: 1-(nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline: The product is isolated by column chromatography on silica gel as Yellow oil liquid. 

1H NMR (400 MHz, CDCl3) δ 7.24 –6.96 (m, 10H), 6.88 (d, *J* = 8.3 Hz, 2H), 6.74 (t, *J* = 7.4 Hz, 1H), 5.44 (t, *J* = 7.4 Hz, 1H), 4.75 (dd, *J* = 11.8, 8.0 Hz, 1H), 4.44 (dd, *J* = 11.8, 6.8 Hz, 1H), 3.52 (dt, *J* = 13.8, 5.1 Hz, 2H), 3.08 – 2.78 (m, 1H), 2.67 (dd, *J* = 16.4, 4.7 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 148.50, 135.36, 132.97, 129.58, 129.28, 128.18, 127.07, 126.75, 119.47, 115.16, 78.81, 58.26, 42.07, 26.47.

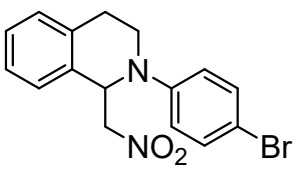
3b: 2-(4-methoxyphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline: The product is isolated by column chromatography on silica gel as Yellow liquid. 

1H NMR (400 MHz, CDCl3) δ 7.30 – 6.94 (m, 4H), 6.83 (d, *J* = 9.2 Hz, 2H), 6.73 (d, *J* = 9.1 Hz, 1H), 5.31 (dd, *J* = 8.7, 5.8 Hz, 1H), 4.74 (dd, *J* = 11.9, 8.7 Hz, 1H), 4.47 (dd, *J* = 11.9, 5.8 Hz, 1H), 3.66 (s, 3H), 3.55 – 3.39 (m, 2H), 2.93 (ddd, *J* = 16.3, 9.6, 6.5 Hz, 1H), 2.60 (dt, *J* = 16.5, 4.0 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 153.95, 143.07, 135.49, 132.85, 129.52, 127.94, 126.96, 126.65, 118.86, 114.69, 78.96, 58.94, 55.60, 43.10, 25.74.

3c: 2-(3,4-dimethylphenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline: The product is isolated by columnchromatography on silica gel as Yellow oil liquid. 

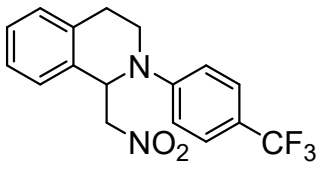
1H NMR (400 MHz, CDCl3) δ 7.16 (dddd, *J* = 27.2, 16.0, 7.2, 1.7 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 0H), 6.78 (d, *J* = 2.8 Hz, 0H), 6.75 – 6.48 (m, 0H), 5.95 – 5.26 (m, 0H), 4.82 (dd, *J* = 11.8, 8.1 Hz, 0H), 4.52 (dd, *J* = 11.8, 6.4 Hz, 0H), 3.76 – 3.40 (m, 0H), 3.04 (ddd, *J* = 15.6, 9.5, 5.6 Hz, 0H), 2.71 (d, *J* = 16.4 Hz, 0H), 2.22 (s, 1H), 2.16 (s, 1H). 13C NMR (101 MHz, CDCl3) δ 146.80, 137.64, 135.47, 133.02, 130.51, 129.35, 128.04, 127.93, 127.04, 126.65, 117.48, 113.22, 78.87, 58.41, 42.26, 26.28, 20.44, 18.83.

3d: 2-(4-bromophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline: The product is

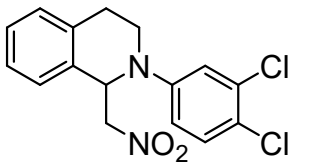


isolated by columnchromatography on silica gel as Orange liquid. 1H NMR (400 MHz, CDCl3) δ 7.39 – 7.24 (m, 1H), 7.23 – 7.08 (m, 2H), 7.06 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.87 – 6.64 (m, 1H), 5.49 – 5.33 (m, 0H), 4.77 (dd, *J* = 12.0, 8.1 Hz, 1H), 4.49 (dd, *J* = 12.0, 6.4 Hz, 1H), 3.58 – 3.49 (m, 1H), 3.07 – 2.91 (m, 1H), 2.71 (dt, *J* = 16.4, 4.9 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 147.51, 135.07, 132.45, 132.26, 129.33, 128.32, 127.01, 126.87, 116.79, 111.58, 78.64, 58.15, 42.10, 26.20.

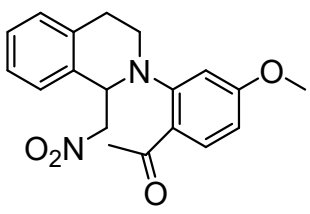
3e: 1-(nitromethyl)-2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline: The product is isolated by columnchromatography on silica gel as Yellow oil liquid. 1H NMR (400 MHz, CDCl3) δ 7.43 (d, *J* = 8.6 Hz, 1H), 7.29 – 7.11 (m, 1H), 7.09 – 7.05 (m, 1H), 6.93 (d, *J* = 8.6 Hz, 1H), 5.54 (t, *J* = 7.3 Hz, 1H), 4.80 (dd, *J* = 11.9, 7.7 Hz, 0H), 4.52 (dd, *J* = 11.9, 6.8 Hz, 0H), 3.65 – 3.57 (m, 1H), 3.04 (dt, *J* = 16.3, 6.3 Hz, 0H), 2.79 (dt, *J* = 16.3, 5.5 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 150.49, 134.91, 132.36, 129.22, 128.55, 126.96 (dd, *J* = 15.7, 3.9 Hz), 126.02, 123.33, 120.46 (d, *J* = 32.9 Hz), 113.31, 78.45, 57.82, 41.83, 26.60.



3f: 2-(3,4-dichlorophenyl)-1-(nitromethyl)-1,2,3,4-tetrahydroisoquinoline: The product is isolated by columnchromatography on silica gel as Orange liquid. 1H NMR (400 MHz, CDCl3) δ 7.31 – 7.16 (m, 1H), 7.01 (d, *J* = 2.8 Hz, 0H), 6.81 (dd, *J* = 8.9, 2.8 Hz, 0H), 5.63 – 5.40 (m, 0H), 4.83 (dd, *J* = 12.1, 8.2 Hz, 0H), 4.58 (dd, *J* = 12.1, 6.3 Hz, 0H), 3.61 (t, *J* = 6.0 Hz, 0H), 3.07 (dt, *J* = 15.3, 7.3 Hz, 0H), 2.80 (dt, *J* = 16.4, 5.0 Hz, 0H). 13C NMR (101 MHz, CDCl3) δ 134.86, 133.17, 132.08, 130.85, 129.37, 128.48, 127.00 (d, *J* = 2.2 Hz), 122.15, 78.50, 58.04, 42.06, 26.15.

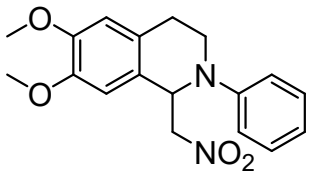


3g: 1-(4-methoxy-2-(1-(nitromethyl)-3,4-dihydroisoquinolin-2(1H)-yl)phenyl)ethan-1-one: The product is isolated by columnchromatography on silica gel as Yellow oil liquid. 1H NMR (400 MHz, CDCl3) δ 7.27 – 7.22 (m, 1H), 7.21 – 7.12 (m, 1H), 6.92 (d, *J* = 8.8 Hz, 0H), 6.59 (dd, *J* = 8.8, 2.9 Hz,



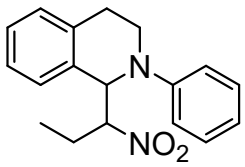
1H), 6.43 (d, *J* = 2.9 Hz, 1H), 5.20 (dd, *J* = 10.0, 4.8 Hz, 1H), 4.78 (dd, *J* = 11.9, 10.1 Hz, 1H), 4.56 (dd, *J* = 11.9, 4.8 Hz, 1H), 3.68 (s, 1H), 3.51 (dd, *J* = 9.9, 3.2 Hz, 1H), 2.85 (dt, *J* = 17.4, 9.5 Hz, 0H), 2.59 (dt, *J* = 16.7, 3.0 Hz, 1H), 2.12 (s, 1H). 13C NMR (101 MHz, CDCl3) δ 169.46, 157.79, 143.18, 138.94, 135.68, 132.54, 129.92, 127.90, 126.79, 126.60, 123.81, 110.51, 108.23, 78.95, 58.65, 55.46, 43.46, 25.48, 20.53.

3h: 6,7-dimethoxy-1-(nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline: The product is isolated by columnchromatography on silica gel as Yellow oil liquid.



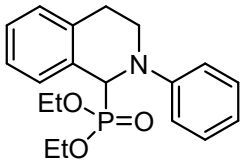
1H NMR (400 MHz, CDCl3) δ 7.19 (t, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.82 – 6.73 (m, 1H), 6.55 (d, *J* = 18.2 Hz, 1H), 5.39 (t, *J* = 7.2 Hz, 1H), 4.78 (dd, *J* = 11.8, 8.0 Hz, 1H), 4.50 (dd, *J* = 11.8, 6.4 Hz, 1H), 3.78 (d, *J* = 2.9 Hz, 4H), 3.60 (dt, *J* = 13.2, 5.1 Hz, 1H), 3.50 (ddd, *J* = 13.6, 9.5, 4.5 Hz, 1H), 2.93 (ddd, *J* = 15.5, 9.5, 5.5 Hz, 1H), 2.60 (dt, *J* = 16.2, 4.6 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 148.76, 148.62, 147.72, 129.49, 127.45, 124.55, 119.60, 115.54, 111.69, 109.57, 78.82, 58.04, 56.10, 55.94, 42.08, 25.82.

3i: 1-(1-nitropropyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline: The product is isolated by columnchromatography on silica gel as Yellow oil liquid.



1H NMR (400 MHz, CDCl3) δ 7.33 – 7.08 (m, 1H), 6.95 (dd, *J* = 15.4, 8.1 Hz, 0H), 6.87 – 6.72 (m, 0H), 5.18 (dd, *J* = 44.9, 9.5 Hz, 0H), 4.76 (dt, *J* = 74.7, 10.4 Hz, 0H), 3.92 – 3.40 (m, 0H), 3.22 – 2.94 (m, 0H), 2.95 – 2.64 (m, 0H), 2.32 – 1.65 (m, 0H), 0.92 (d, *J* = 3.3 Hz, 0H). 13C NMR (101 MHz, CDCl3) δ 149.10 (d, *J* = 9.5 Hz), 135.63, 134.80, 133.99, 132.60, 129.46 (d, *J* = 8.0 Hz), 129.27, 128.73 (d, *J* = 8.3 Hz), 128.29 (d, *J* = 4.5 Hz), 127.28, 126.69, 125.98, 119.45, 118.62, 115.88, 114.16, 96.24, 93.12, 62.26, 43.59, 42.33, 26.89, 25.76, 25.08, 24.72, 10.77 (d, *J* = 1.5 Hz).

6a: diethyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate: The product is isolated by columnchromatography on silica gel as Colorless oil liquid.

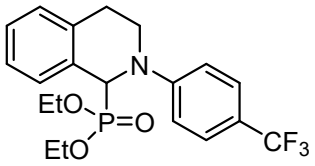


1H NMR (400 MHz, CDCl3) δ 7.43 – 7.32 (m, 1H), 7.31 – 7.11 (m, 4H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.79 (t, *J* = 7.3 Hz, 1H), 5.19 (d, *J* = 20.0 Hz, 1H), 4.27 – 3.81 (m, 2H), 3.63 (dt, *J* = 12.1, 5.5 Hz, 1H), 3.31 – 2.82 (m, 1H), 1.25 (td, *J* = 7.1, 1.7 Hz, 3H), 1.14 (td, *J* = 7.0, 1.7 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 149.42 (d, *J* = 5.8 Hz), 136.47 (d, *J* = 5.5 Hz), 130.66, 129.15, 128.77 (d, *J* = 2.6 Hz), 128.15 (d, *J* = 4.6 Hz), 127.45 (d, *J* = 3.5 Hz), 125.89 (d, *J* = 2.9 Hz), 118.47, 114.79, 63.36 (d, *J* = 7.1 Hz), 62.36 (d, *J* = 7.8 Hz), 59.61, 58.03, 43.49, 26.77, 16.43 (dd, *J* = 8.9, 5.7 Hz).

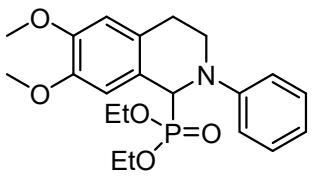
6b: diethyl (2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate: The product is isolated by columnchromatography on silica gel as White solid. 1H NMR (400 MHz, CDCl3) δ 7.44 – 7.38 (m, 1H), 7.25 – 7.11 (m, 3H), 6.98 – 6.91 (m, 3H), 6.89 – 6.79 (m, 2H), 5.05 (d, *J* = 21.5 Hz, 1H), 4.33 – 3.87 (m, 6H), 3.77 (s, 4H), 3.56 (dt, *J* = 12.8, 5.0 Hz, 1H), 3.28 – 2.87 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 4H), 1.18 (t, *J* = 7.1 Hz, 4H). 13C NMR (101 MHz, CDCl3) δ 153.12, 144.11 (d, *J* = 8.4 Hz), 130.48, 128.96 (d, *J* = 2.6 Hz), 128.20 (d, *J* = 4.4 Hz), 127.32 (d, *J* = 3.5 Hz), 125.85 (d, *J* = 2.9 Hz), 117.61, 114.48, 63.40 (d, *J* = 7.2 Hz), 62.27 (d, *J* = 7.7 Hz), 60.27, 58.69, 55.64, 44.69, 26.12, 16.49 (dd, *J* = 10.1, 5.7 Hz).

6c: diethyl (2-(3,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate: The product is isolated by columnchromatography on silica gel as Colorless oil liquid. 1H NMR (400 MHz, CDCl3) δ 7.41 – 7.33 (m, 1H), 7.22 – 7.07 (m, 3H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.79 (d, *J* = 2.8 Hz, 1H), 6.72 (dd, *J* = 8.3, 2.8 Hz, 1H), 3.06 – 2.91 (m, 2H), 2.22 (s, 3H), 2.16 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 147.86 (d, *J* = 7.3 Hz), 137.21, 136.50 (d, *J* = 5.6 Hz), 130.62 (d, *J* = 1.3 Hz), 130.20, 128.89 (d, *J* = 2.5 Hz), 128.18 (d, *J* = 4.4 Hz), 127.30 (d, *J* = 3.5 Hz), 126.82, 125.80 (d, *J* = 2.9 Hz), 116.88, 112.75, 63.43 (d, *J* = 7.2 Hz), 62.32 (d, *J* = 7.7 Hz), 59.91, 58.32, 43.73, 26.38, 20.37, 18.72, 16.50 (dd, *J* = 11.9, 5.8 Hz).

6d: diethyl (2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate:

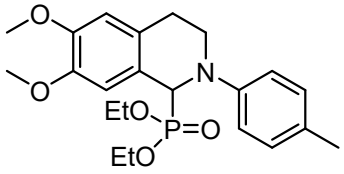


The product is isolated by columnchromatography on silica gel as White solid. 1H NMR (400 MHz, CDCl3) δ 7.54 – 7.45 (m, 1H), 7.46 – 7.35 (m, 1H), 7.33 – 7.18 (m, 1H), 7.03 (d, *J* = 9.1 Hz, 1H), 5.26 (d, *J* = 18.3 Hz, 0H), 4.26 – 3.79 (m, 3H), 3.62 (dd, *J* = 11.9, 6.5 Hz, 1H), 3.47 – 3.22 (m, 1H), 3.13 – 2.92 (m, 1H), 1.26 (td, *J* = 7.2, 2.7 Hz, 2H), 1.16 (td, *J* = 7.3, 2.6 Hz, 2H). 13C NMR (101 MHz, CDCl3) δ 151.24 (d, *J* = 3.6 Hz), 136.26 (d, *J* = 5.3 Hz), 130.36, 128.59 (d, *J* = 2.8 Hz), 128.13 (d, *J* = 4.9 Hz), 127.88 (d, *J* = 3.5 Hz), 126.37 (q, *J* = 3.7 Hz), 126.19 (d, *J* = 2.8 Hz), 123.56, 119.35 (q, *J* = 32.6 Hz), 113.09, 63.30 (d, *J* = 7.3 Hz), 62.64 (d, *J* = 7.7 Hz), 59.14, 57.55, 43.43, 27.27, 16.41 (dd, *J* = 8.8, 5.6 Hz).



6e: diethyl (6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate: The product is isolated by columnchromatography on silica gel as White solid. 1H NMR (400 MHz, CDCl3) δ 7.25 (dd, *J* = 8.5, 6.9 Hz, 1H), 7.03 – 6.88 (m, 1H), 6.80 (t, *J* = 7.2 Hz, 0H), 6.63 (s, 0H), 5.10 (d, *J* = 20.1 Hz, 0H), 4.16 – 3.89 (m, 1H), 3.86 (d, *J* = 5.0 Hz, 2H), 3.75 – 3.62 (m, 0H), 2.89 (dddd, *J* = 19.8, 15.8, 10.9, 5.3 Hz, 1H), 1.28 (t, *J* = 7.0 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 149.60 (d, *J* = 7.2 Hz), 148.27 (d, *J* = 3.4 Hz), 147.01 (d, *J* = 2.8 Hz), 129.19, 128.57 (d, *J* = 6.3 Hz), 121.98, 118.69, 115.22, 111.45 (d, *J* = 2.6 Hz), 110.93 (d, *J* = 3.6 Hz), 63.48 (d, *J* = 7.2 Hz), 62.07 (d, *J* = 7.7 Hz), 59.20, 57.61, 55.89 (d, *J* = 8.4 Hz), 43.43, 25.90, 16.55 (dd, *J* = 5.8, 2.9 Hz).

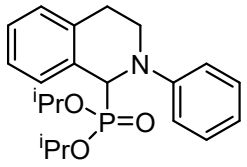
6f: diethyl (6,7-dimethoxy-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate: **The product is isolated by columnchromatography on silica gel as White solid.**



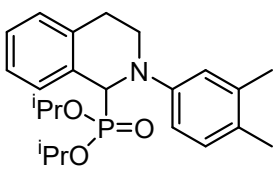
1H NMR (400 MHz, CDCl3) δ 6.97 (d, *J* = 8.4 Hz, 1H), 6.86 (d, *J* = 1.9 Hz, 0H), 6.80 (d, *J* = 8.6 Hz, 1H), 6.53 (s, 0H), 4.95 (d, *J* = 21.0 Hz, 1H), 4.26 – 3.82 (m, 2H), 3.78 (d, *J* = 8.9 Hz, 3H), 3.57 (dt, *J* = 13.2, 4.6 Hz, 1H), 2.82 (ddt, *J* = 14.8, 9.7, 4.7 Hz, 1H), 2.75 – 2.64 (m, 0H), 2.17 (s, 2H), 1.21 (t, *J* = 7.1 Hz, 2H), 1.10 (t, *J* = 7.1 Hz, 2H). 13C NMR (101 MHz, CDCl3) δ

148.19 (d, *J* = 3.4 Hz), 147.59 (d, *J* = 8.4 Hz), 146.97 (d, *J* = 2.9 Hz), 129.69, 128.59 (d, *J* = 6.5 Hz), 128.26, 121.92 (d, *J* = 1.4 Hz), 115.81, 111.49 (d, *J* = 2.5 Hz), 110.91 (d, *J* = 3.8 Hz), 63.52 (d, *J* = 7.2 Hz), 62.00 (d, *J* = 7.6 Hz), 59.40, 57.80, 55.86 (d, *J* = 8.4 Hz), 43.85, 25.52, 20.36, 16.59 (d, *J* = 4.9 Hz).

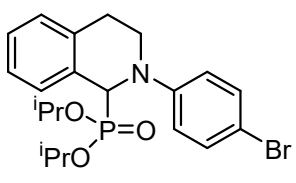
6g: diisopropyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate: The product is isolated by columnchromatography on silica gel as Yellow oil liquid. 1H NMR (400 MHz, CDCl3) δ 7.39 – 7.26 (m, 1H), 7.25 – 6.98 (m, 4H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.68 (t, *J* = 7.2 Hz, 1H), 5.06 (d, *J* = 21.0 Hz, 1H), 4.54 (d, *J* = 6.2 Hz, 1H), 4.08 – 3.82 (m, 1H), 3.63 – 3.39 (m, 1H), 2.90 (d, *J* = 16.1 Hz, 2H), 1.21 (t, *J* = 6.3 Hz, 6H), 1.08 (d, *J* = 5.3 Hz, 3H), 0.86 (d, *J* = 5.6 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 149.58 (d, *J* = 5.7 Hz), 136.47 (d, *J* = 4.4 Hz), 130.90, 129.04, 128.77, 128.47 (d, *J* = 3.5 Hz), 127.33 (d, *J* = 2.3 Hz), 125.68, 118.32, 115.07, 72.33 (d, *J* = 7.3 Hz), 70.91 (d, *J* = 7.7 Hz), 43.51, 26.60, 24.67, 24.20, 23.79 (d, *J* = 4.7 Hz), 23.36 (d, *J* = 4.6 Hz).



6h: diisopropyl (2-(3,4-dimethylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate: The product is isolated by columnchromatography on silica gel as Colorless oil liquid. 1H NMR (400 MHz, CDCl3) δ 7.55 – 7.31 (m, 1H), 7.15 (ddd, *J* = 5.7, 3.6, 1.9 Hz, 2H), 7.13 – 7.03 (m, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 6.76 (d, *J* = 2.8 Hz, 1H), 6.69 (dd, *J* = 8.3, 2.8 Hz, 1H), 5.07 (d, *J* = 22.3 Hz, 1H), 4.91 – 4.43 (m, 2H), 4.05 (ddd, *J* = 13.1, 9.5, 4.9 Hz, 1H), 3.64 (dt, *J* = 13.1, 4.9 Hz, 1H), 2.93 (tdt, *J* = 16.1, 11.8, 5.4 Hz, 2H), 2.21 (s, 3H), 2.15 (s, 3H), 1.30 (dd, *J* = 8.2, 6.2 Hz, 6H), 1.18 (d, *J* = 6.2 Hz, 3H), 0.98 (d, *J* = 6.2 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 148.00 (d, *J* = 8.4 Hz), 136.98, 136.47 (d, *J* = 5.7 Hz), 130.85 (d, *J* = 1.8 Hz), 130.06, 128.86 (d, *J* = 2.5 Hz), 128.51 (d, *J* = 4.4 Hz), 127.13 (d, *J* = 3.6 Hz), 126.63, 125.54 (d, *J* = 2.9 Hz), 117.20, 113.08, 72.29 (d, *J* = 7.6 Hz), 70.85 (d, *J* = 8.1 Hz), 59.86, 58.26, 43.74, 26.11, 24.67 (d, *J* = 2.9 Hz), 24.18 (d, *J* = 3.2 Hz), 23.79 (d, *J* = 5.8 Hz), 23.41 (d, *J* = 5.6 Hz), 20.31, 18.69.



6i: diisopropyl (2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate: The



product is isolated by columnchromatography on silica gel as Colorless oil liquid. 1H NMR (400 MHz, CDCl3) δ 7.38 (dt, *J* = 7.2, 2.2 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.25 – 7.06 (m, 3H), 6.93 – 6.60 (m, 2H), 5.06 (d, *J* = 20.3 Hz, 1H), 4.59 (dq, *J* = 13.6, 6.8 Hz, 1H), 3.99 (ddd, *J* = 12.9, 8.5, 4.7 Hz, 1H), 3.56 (dt, *J* = 12.0, 5.6 Hz, 1H), 3.11 (dq, *J* = 18.7, 3.9 Hz, 1H), 3.03 – 2.86 (m, 1H), 1.32 – 1.25 (m, 5H), 1.15 (d, *J* = 6.1 Hz, 3H), 0.94 (d, *J* = 6.2 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 148.48 (d, *J* = 5.5 Hz), 136.29 (d, *J* = 5.3 Hz), 131.68, 130.62, 128.67 (d, *J* = 2.7 Hz), 128.43 (d, *J* = 4.7 Hz), 127.53 (d, *J* = 3.3 Hz), 125.82 (d, *J* = 2.7 Hz), 116.37, 110.08, 72.35 (d, *J* = 7.8 Hz), 71.09 (d, *J* = 8.2 Hz), 59.57, 57.97, 43.61, 29.74, 26.76, 24.59 (d, *J* = 3.0 Hz), 24.18 (d, *J* = 3.1 Hz), 23.76 (d, *J* = 5.7 Hz), 23.38 (d, *J* = 5.4 Hz).

NMR spectra of catalytic products

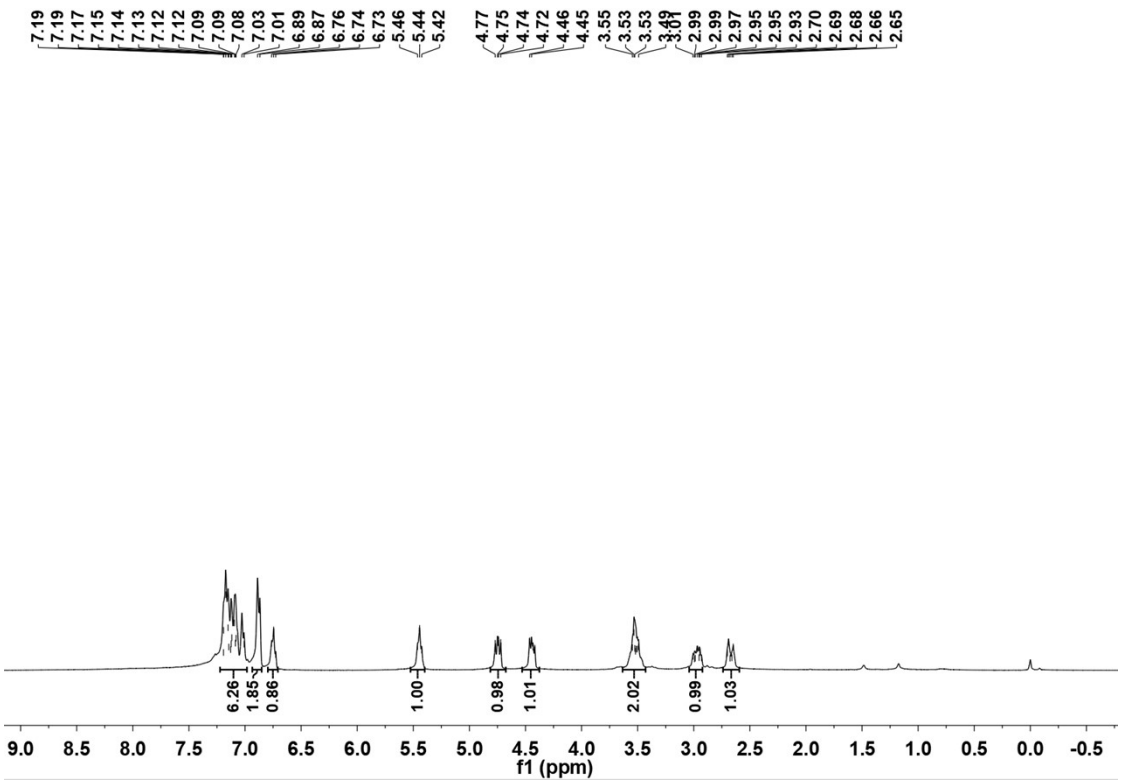


Figure S15. ^{1}H NMR spectrum of 3a (400MHz, $CDCl_3$).

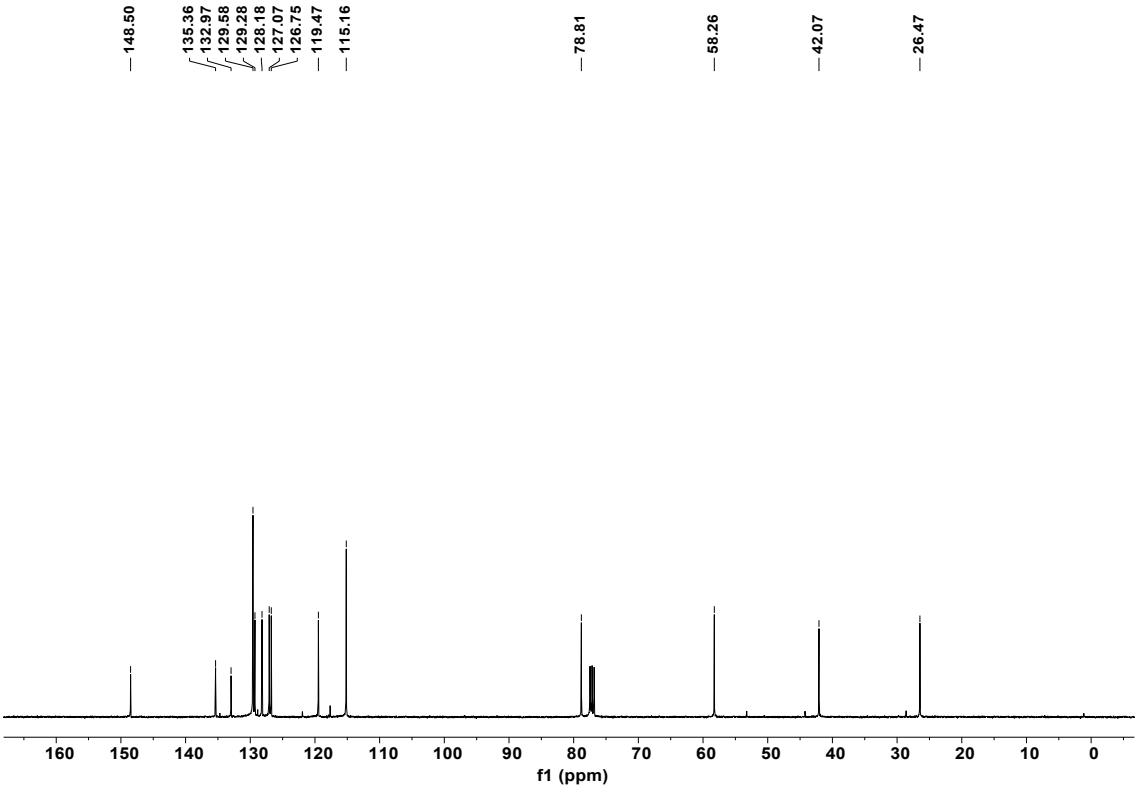


Figure S16. ^{13}C NMR spectrum of 3a (100MHz, $CDCl_3$).

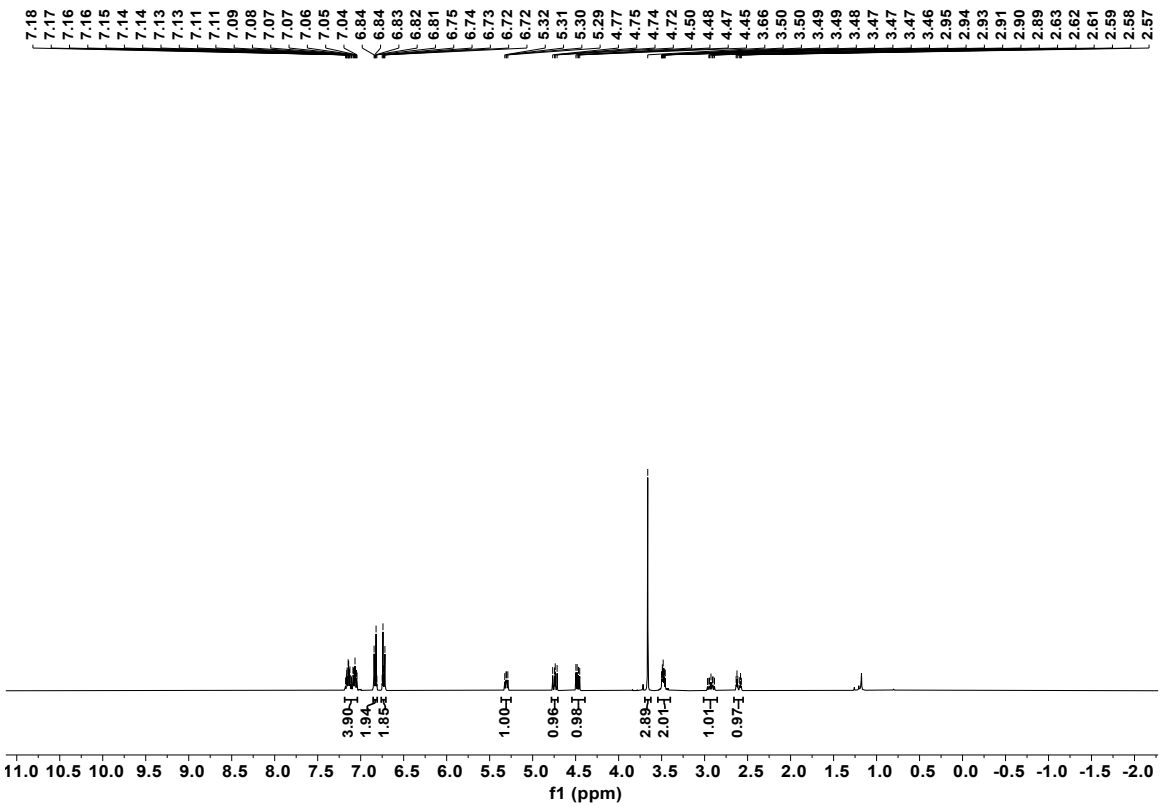


Figure S17. ^{1}H NMR spectrum of 3b (400MHz, $CDCl_3$).

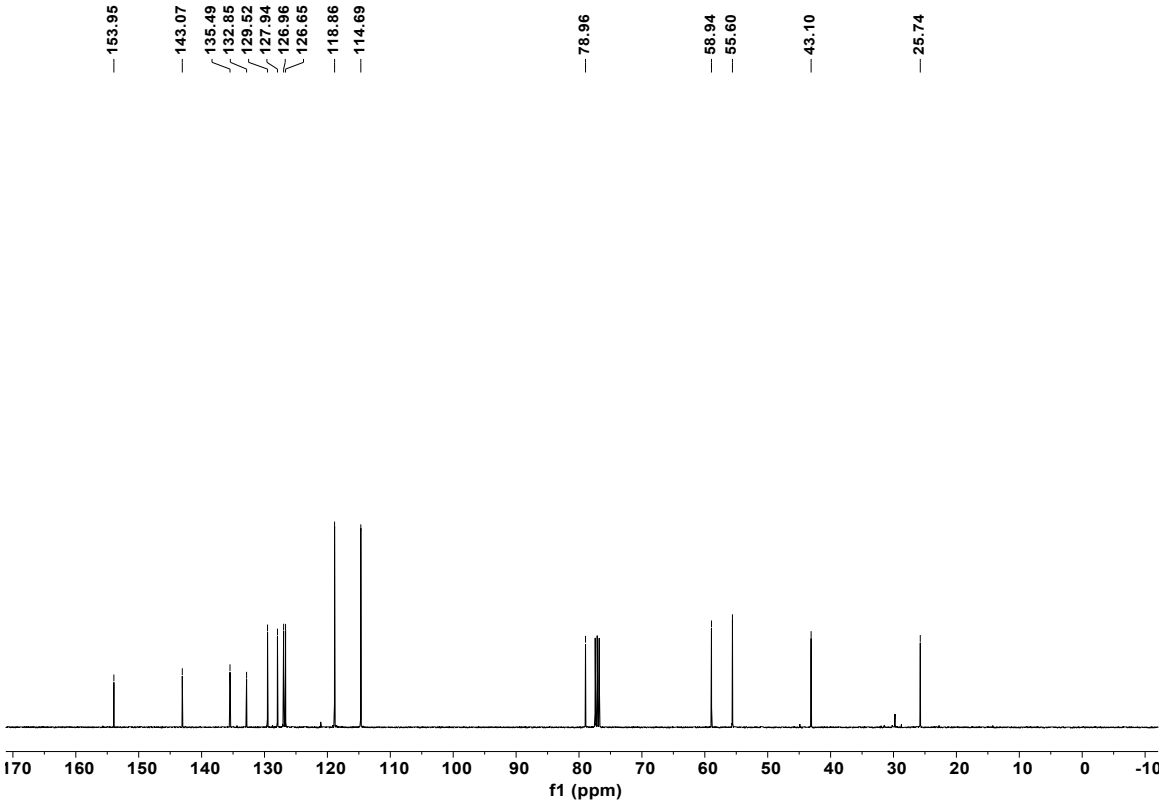


Figure S18. ^{13}C NMR spectrum of 3b (100MHz, $CDCl_3$).

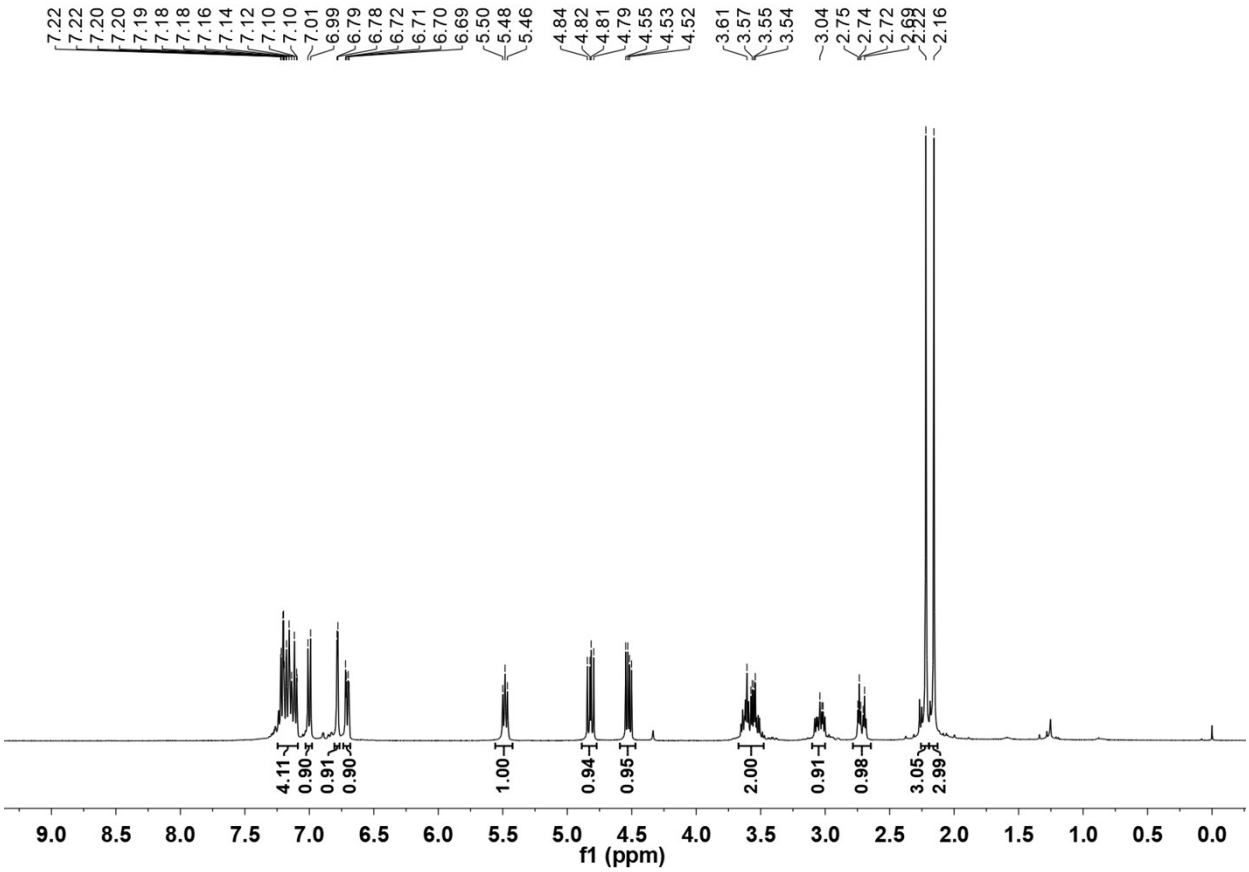


Figure S19. ^{1}H NMR spectrum of 3c (400MHz, $CDCl_3$).

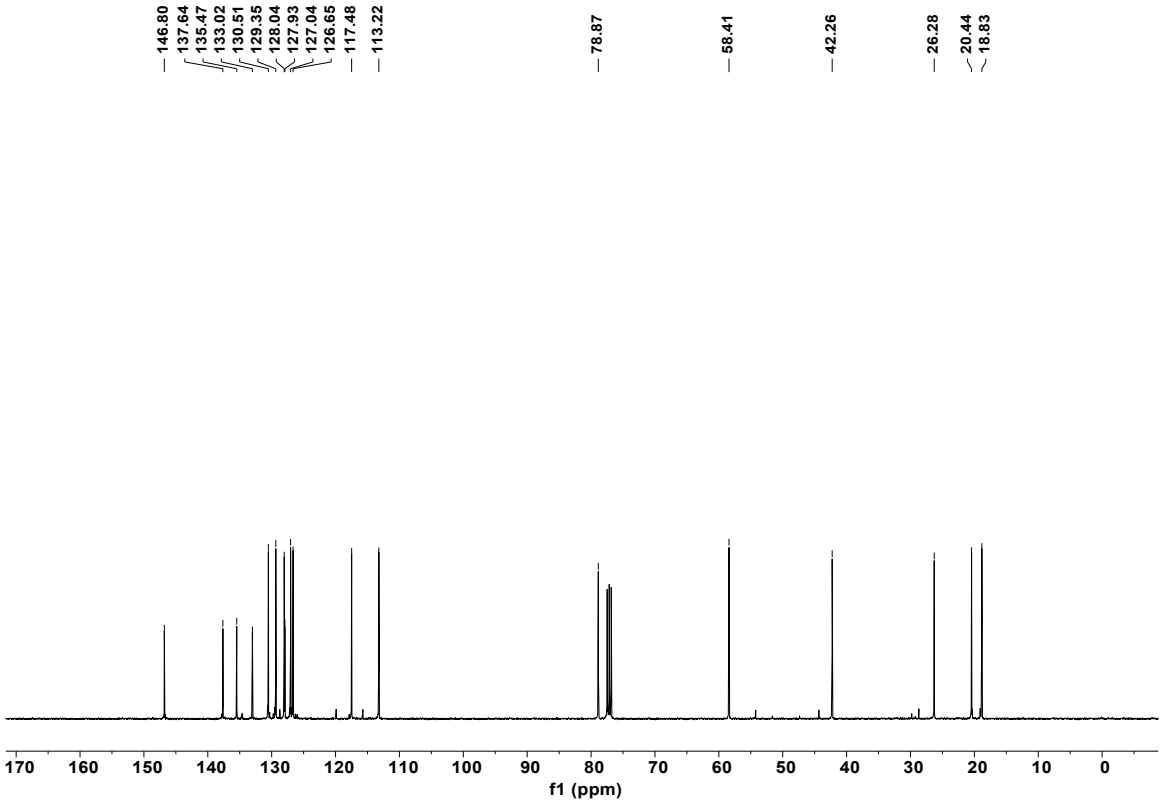


Figure S20. ^{13}C NMR spectrum of 3c (100MHz, $CDCl_3$).

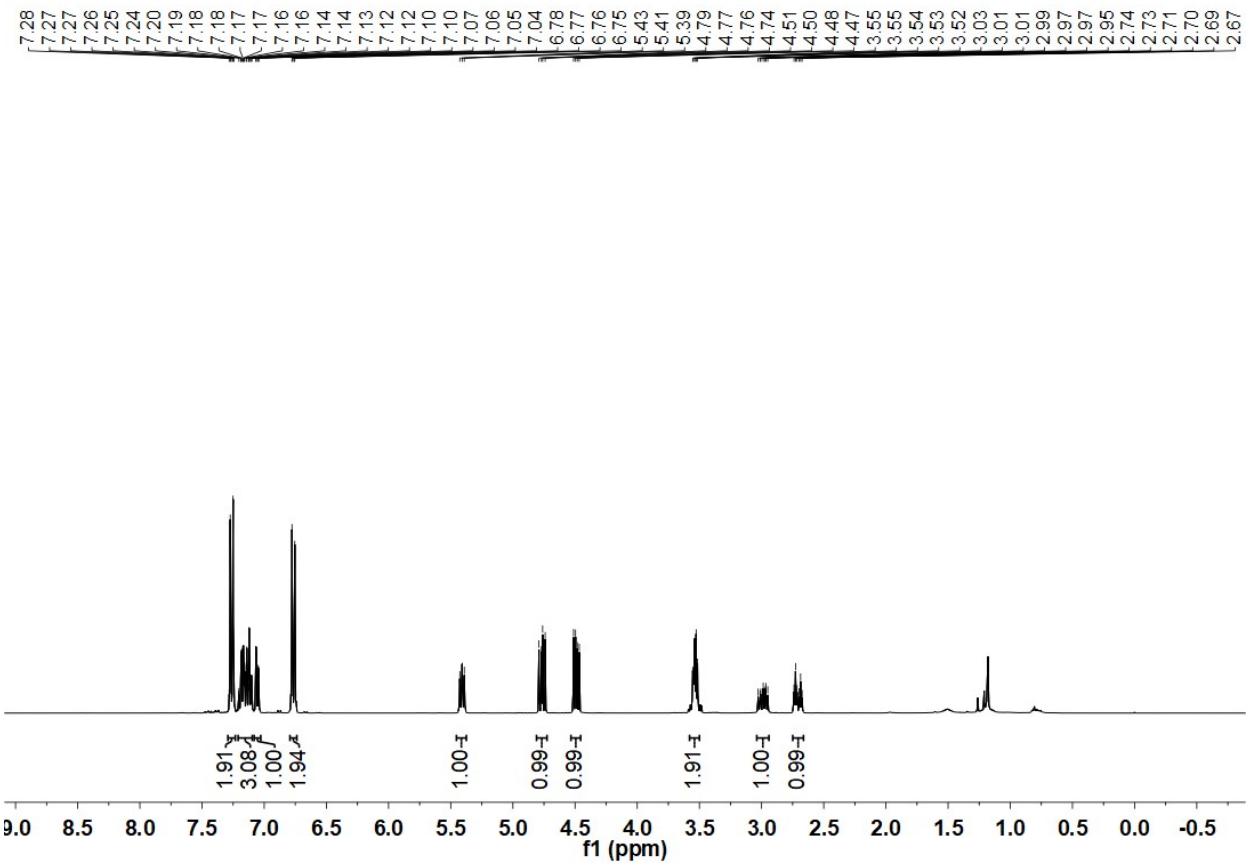


Figure S21. ^{1}H NMR spectrum of 3d (400MHz, $CDCl_3$).

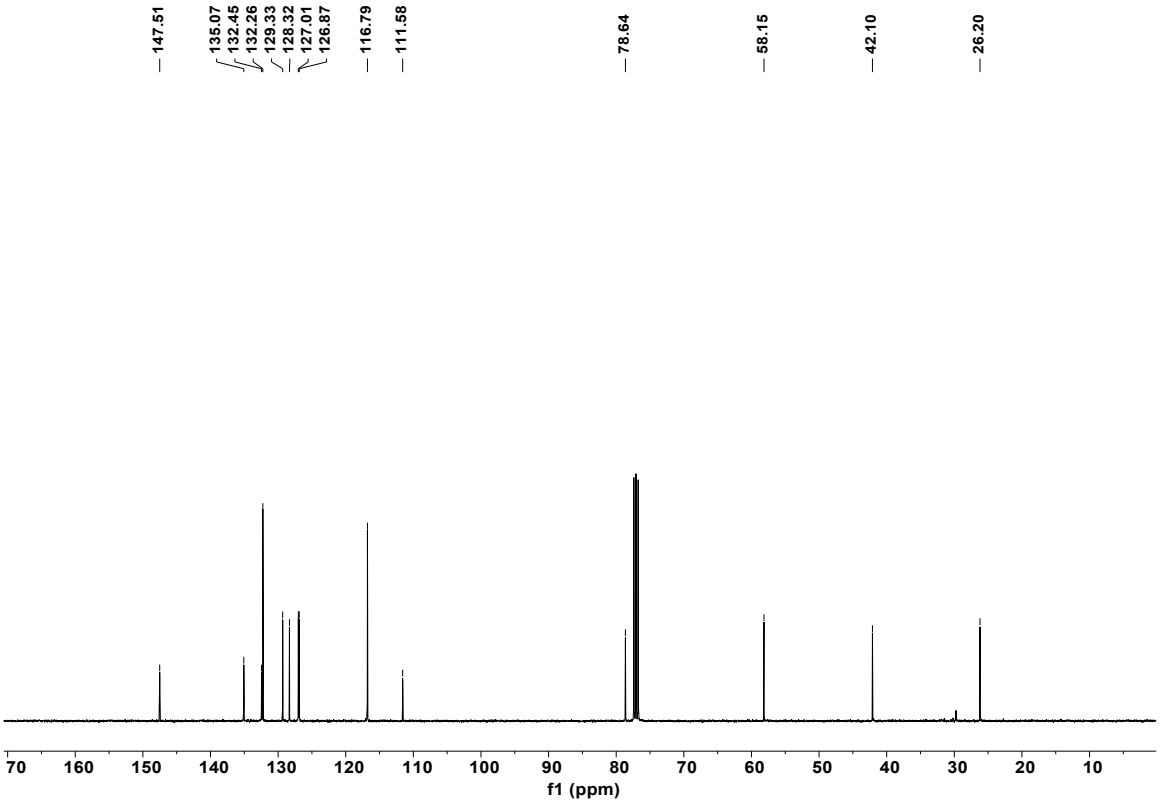


Figure S22. ^{13}C NMR spectrum of 3d (100MHz, $CDCl_3$).

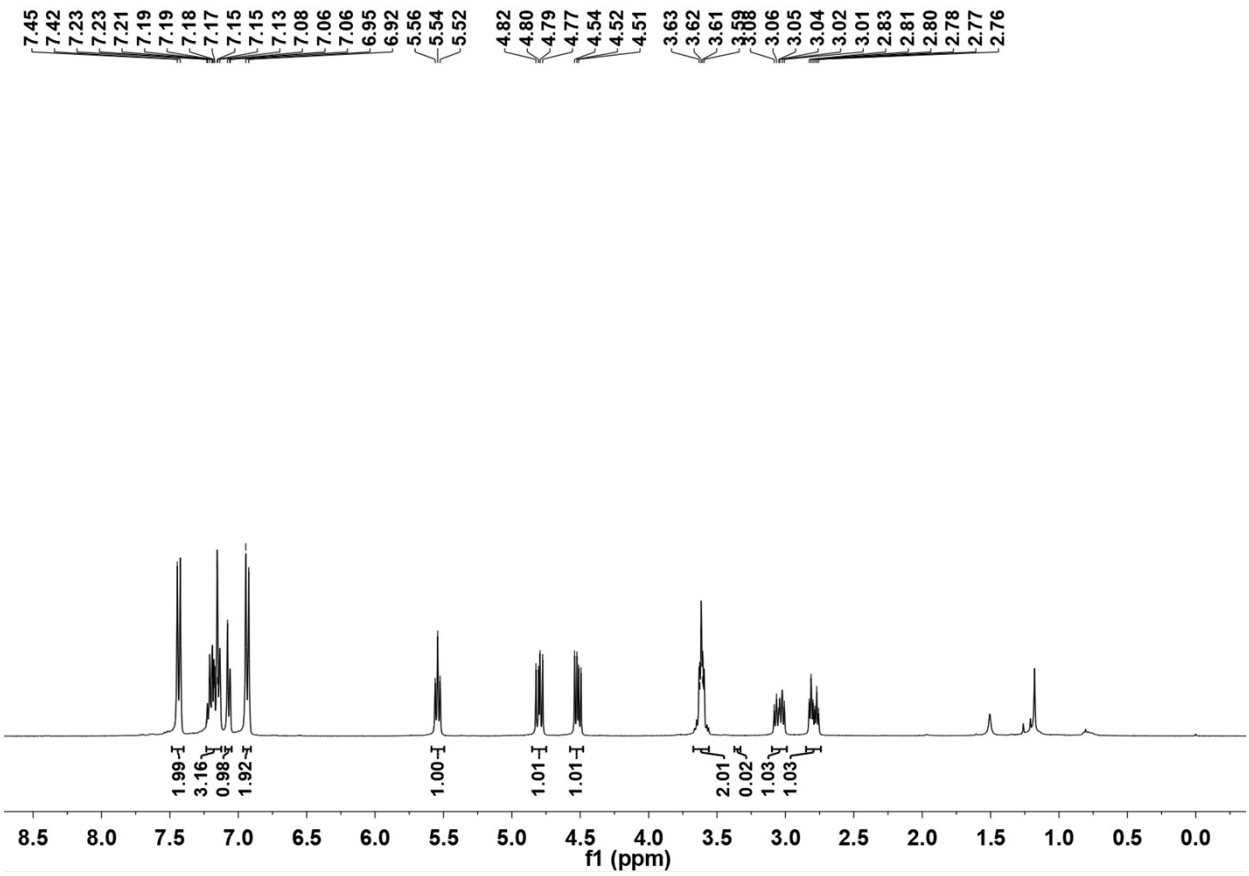


Figure S23. ^{1}H NMR spectrum of 3e (400MHz, $CDCl_3$).

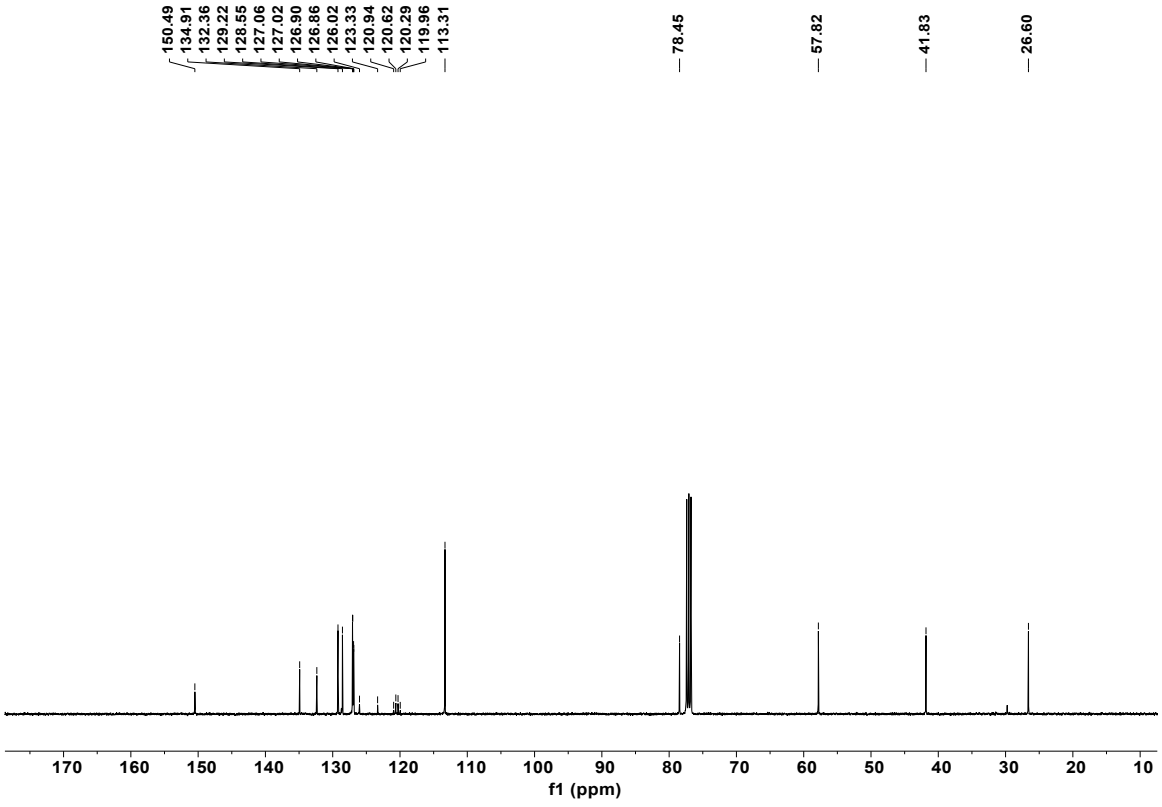


Figure S24. 13C NMR spectrum of 3e (100MHz, $CDCl_3$).

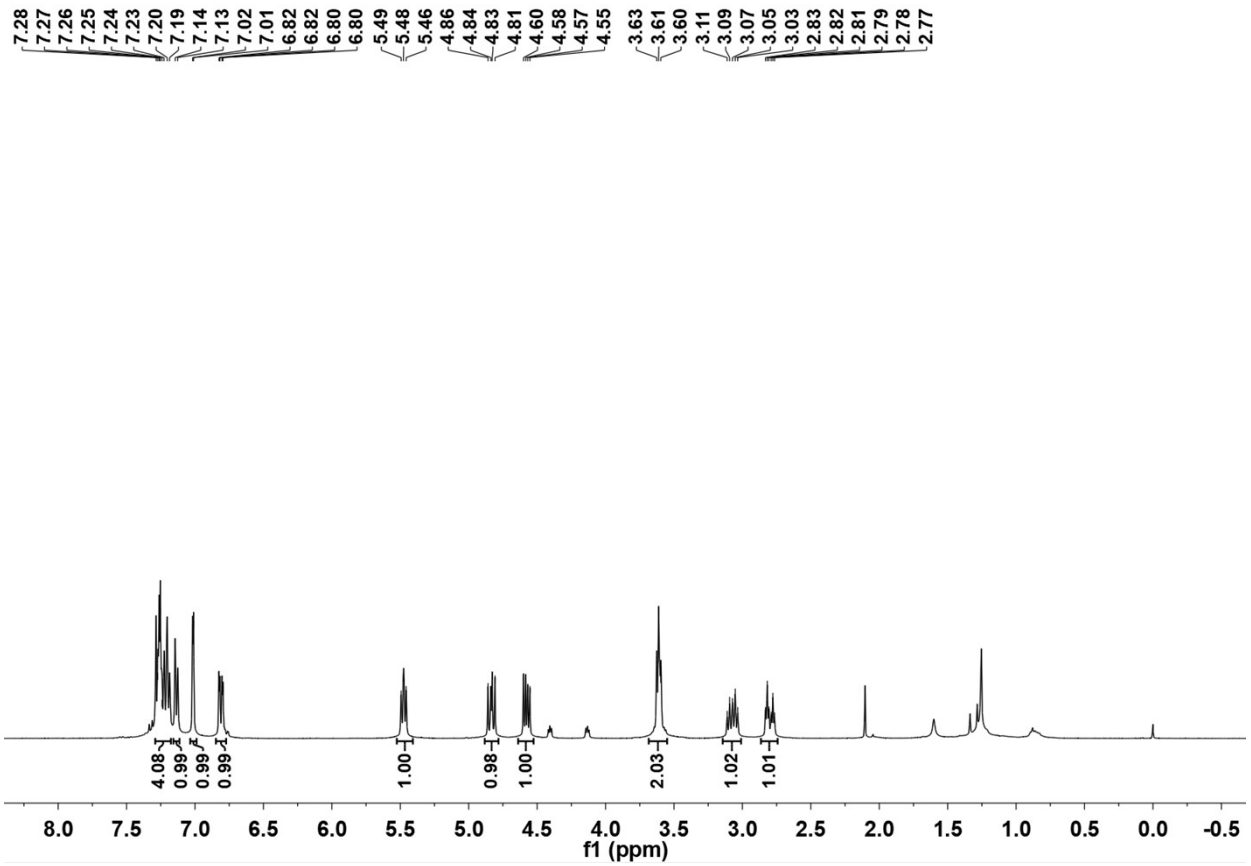


Figure S25. ^{1}H NMR spectrum of 3f (400MHz, $CDCl_3$).

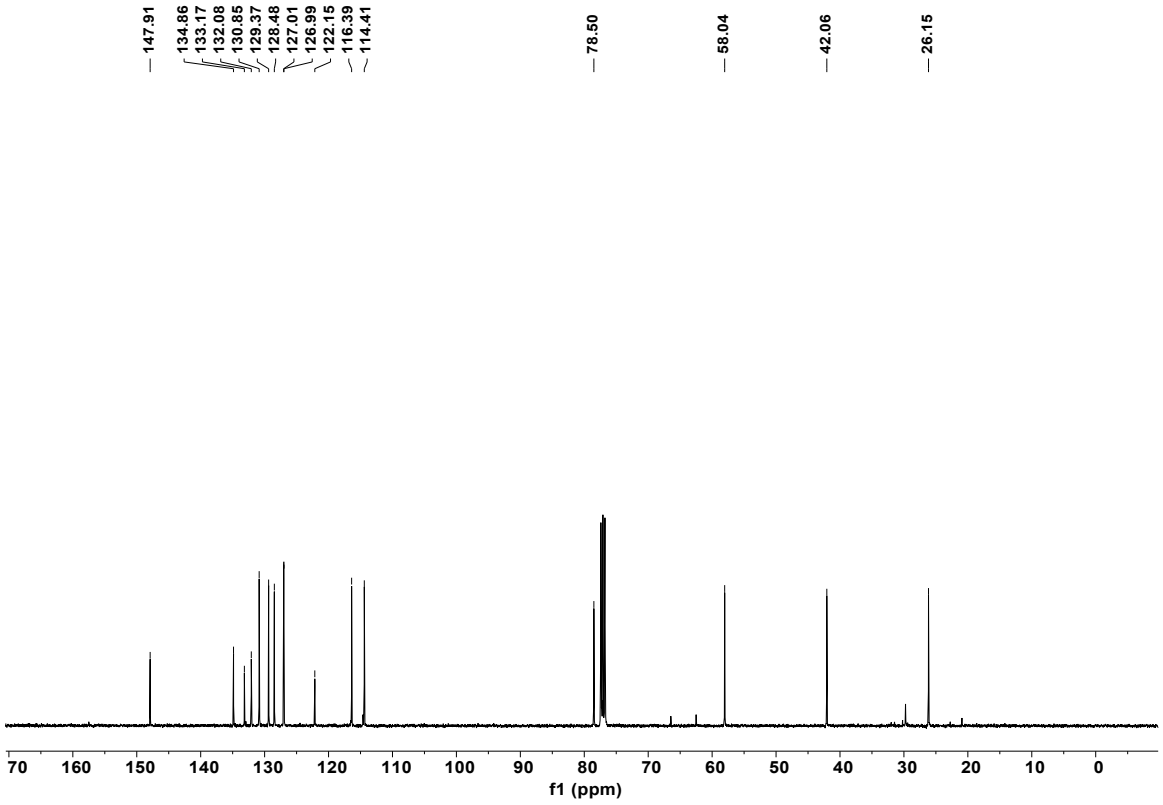


Figure S26. ^{13}C NMR spectrum of 3f (100MHz, $CDCl_3$).

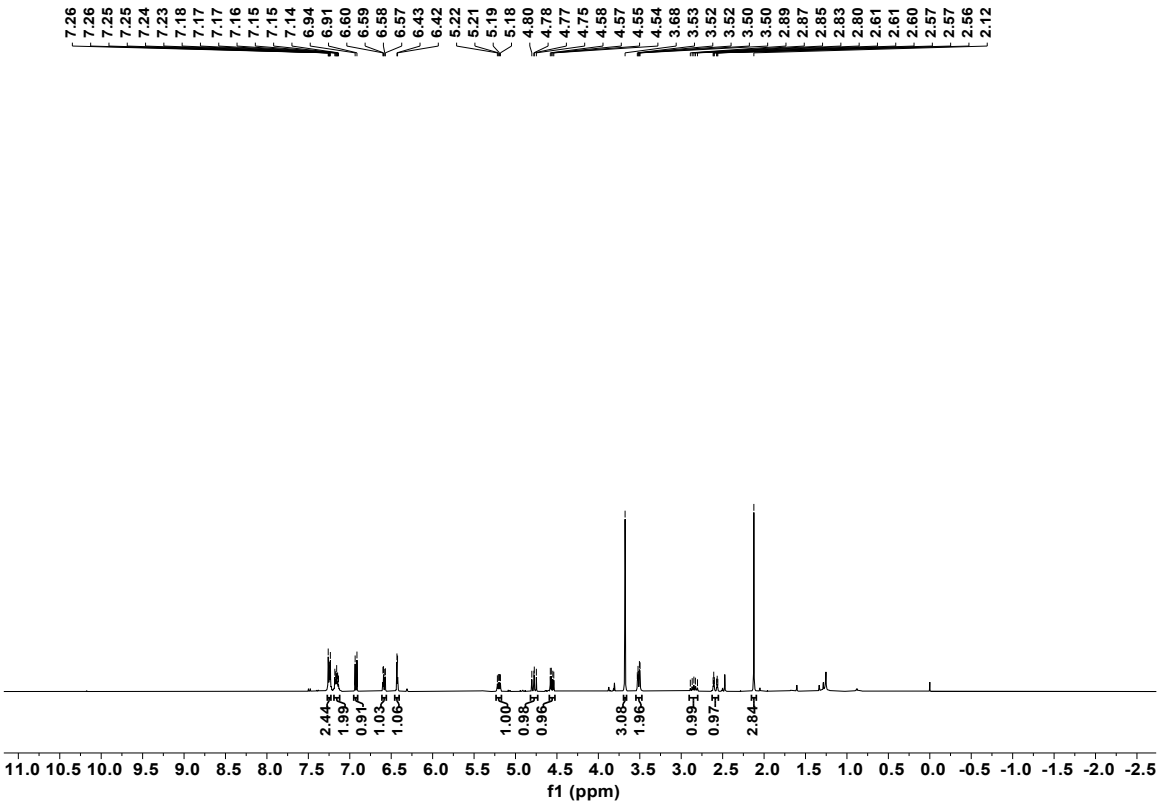


Figure S27. ^{1}H NMR spectrum of 3g (400MHz, $CDCl_3$).

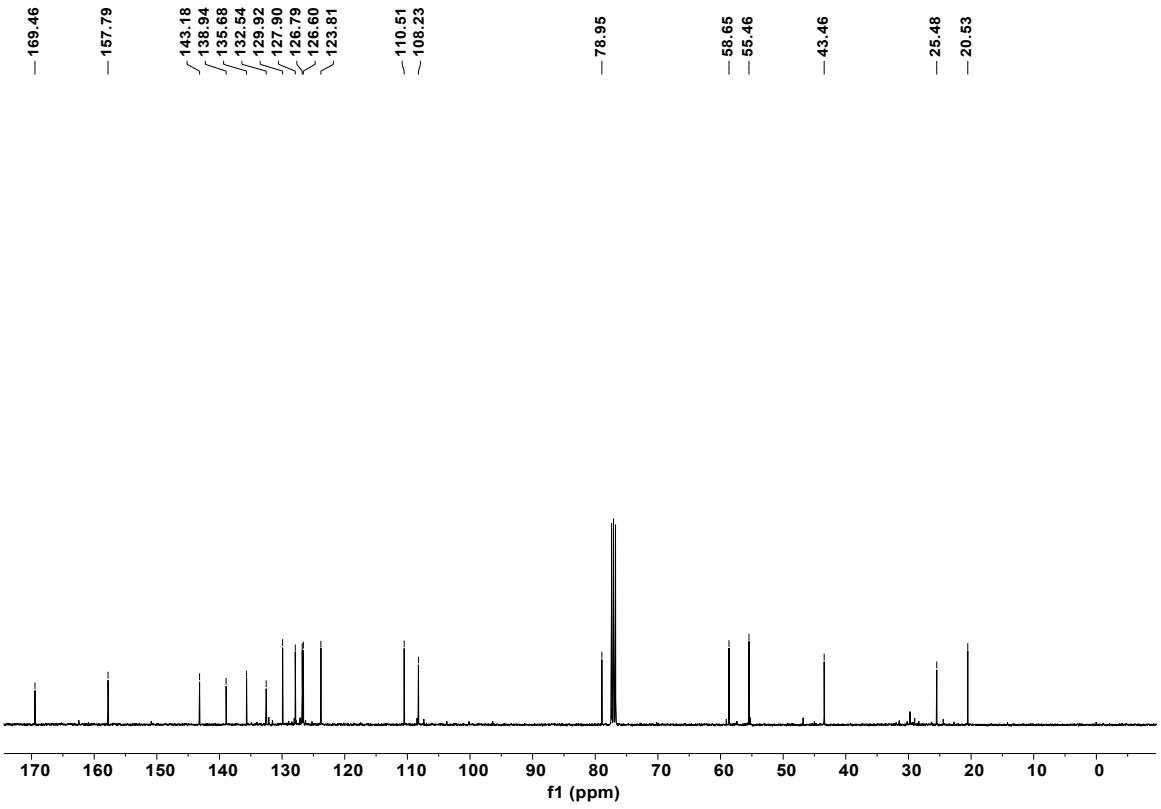


Figure S28. ^{13}C NMR spectrum of 3g (100MHz, $CDCl_3$)

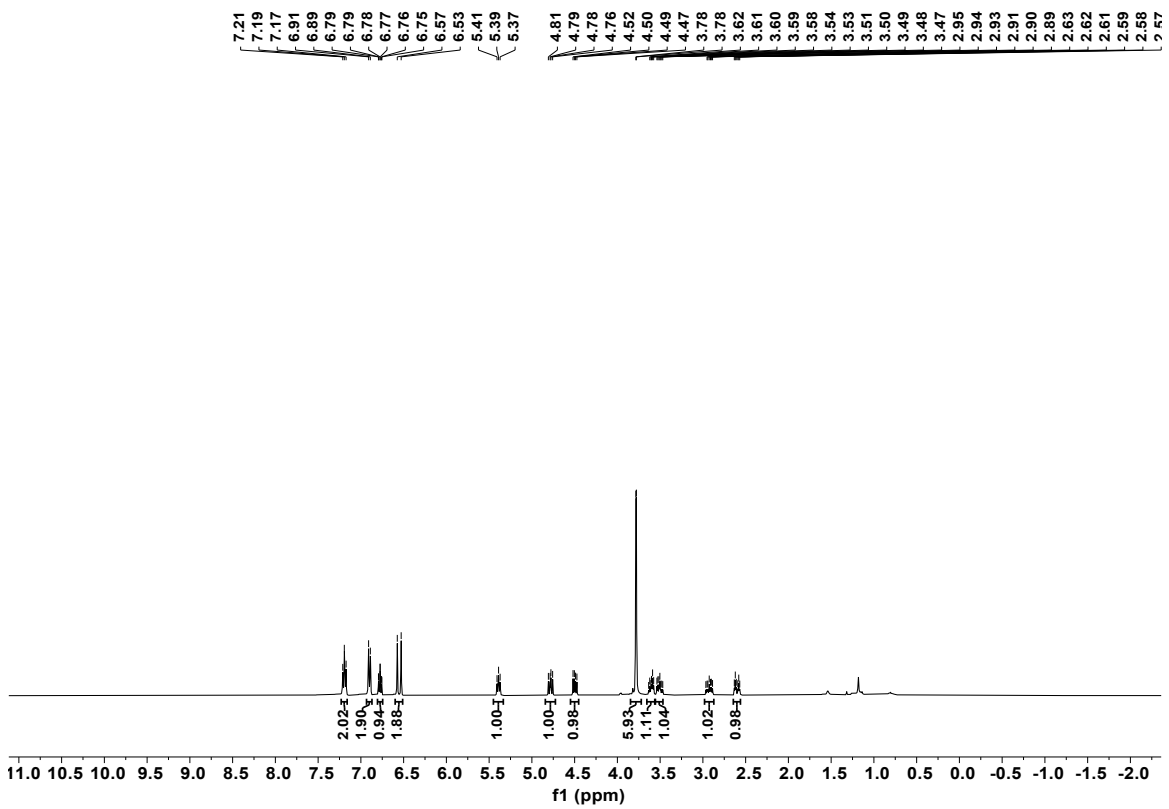


Figure S29. ^{1}H NMR spectrum of 3h (400MHz, $CDCl_3$).

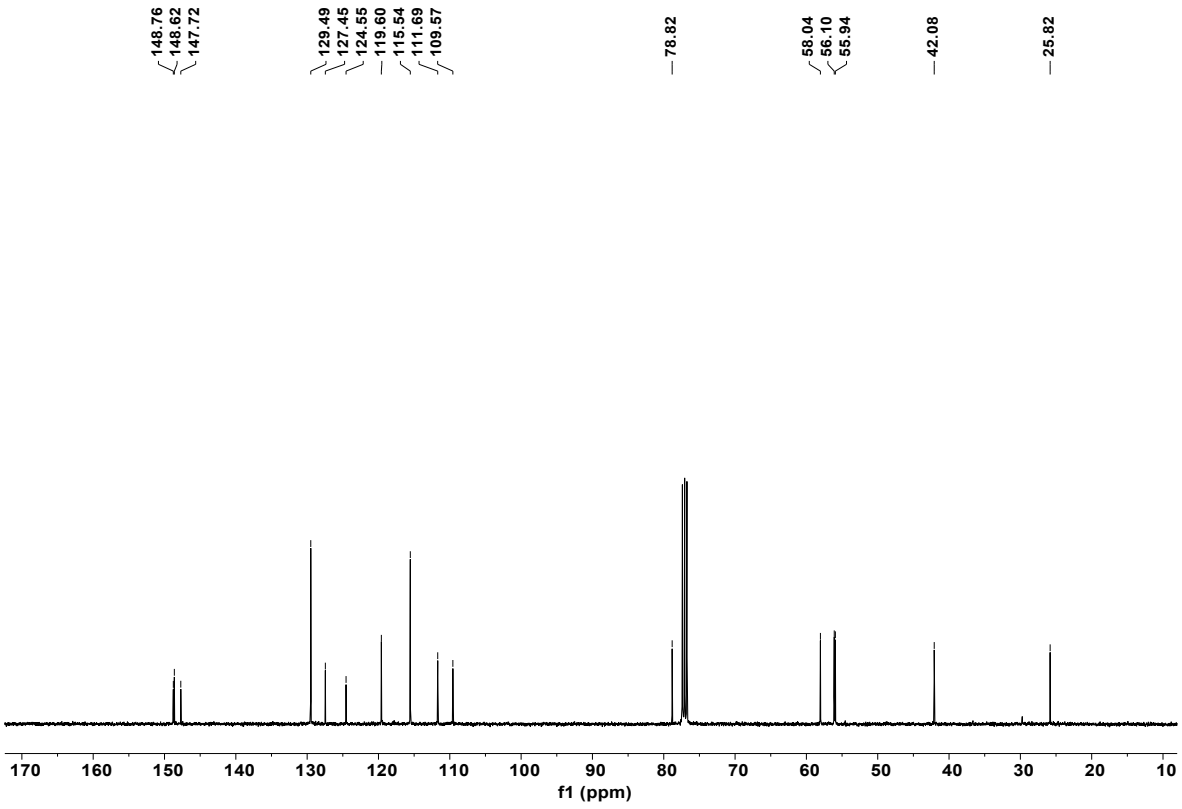


Figure S30. ^{13}C NMR spectrum of 3h (100MHz, $CDCl_3$).

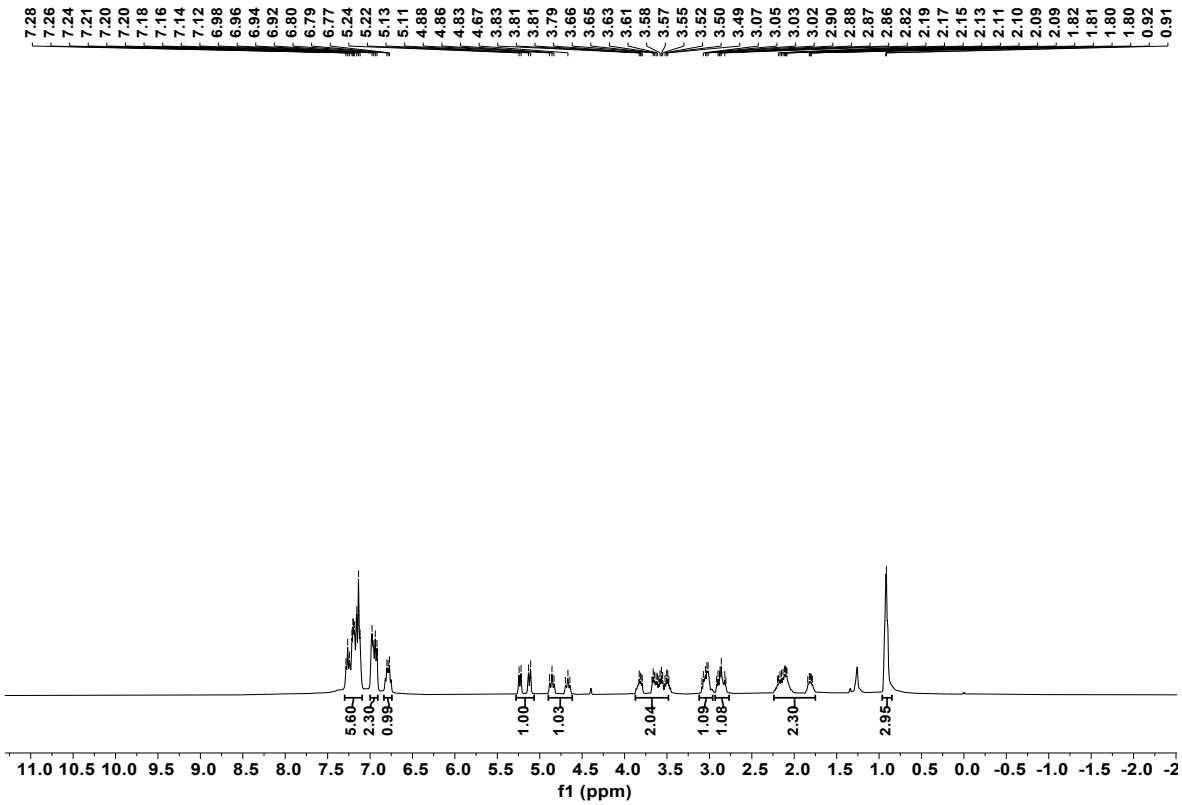


Figure S31. ^{1}H NMR spectrum of 3i (400MHz, $CDCl_3$).

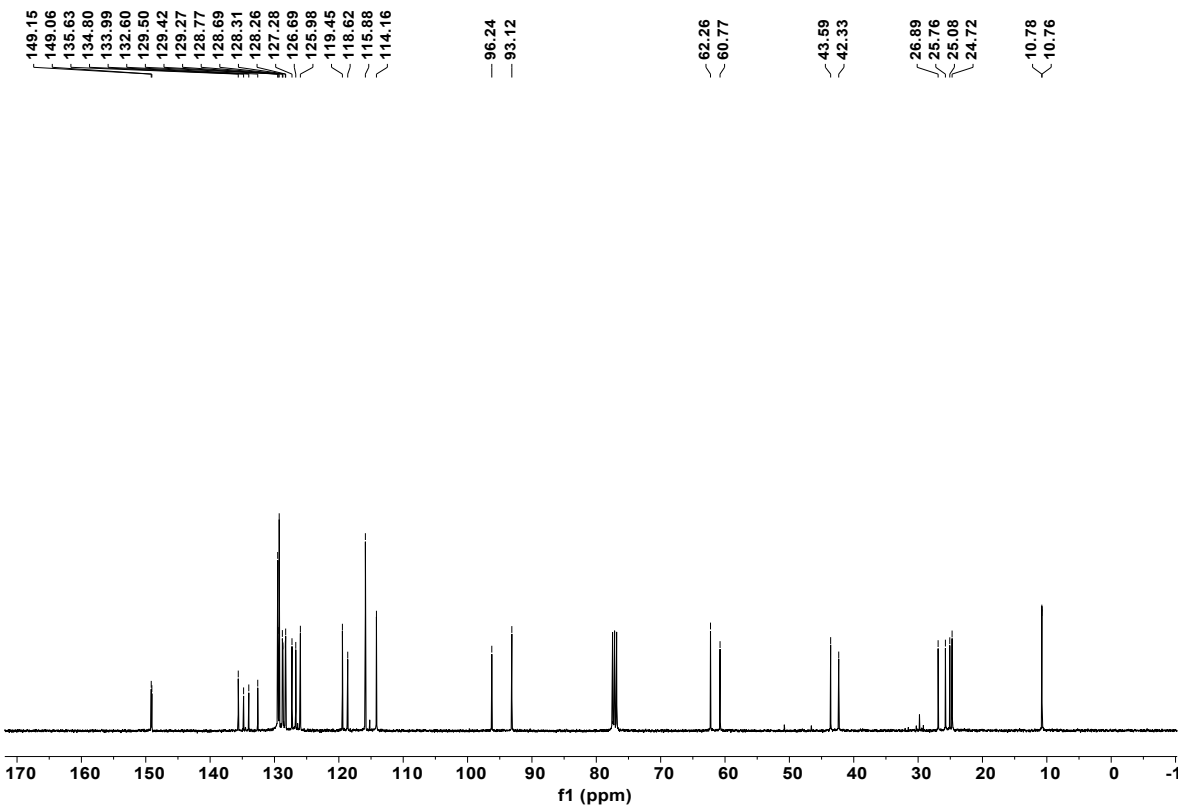


Figure S32. ^{13}C NMR spectrum of 3i (100MHz, $CDCl_3$).

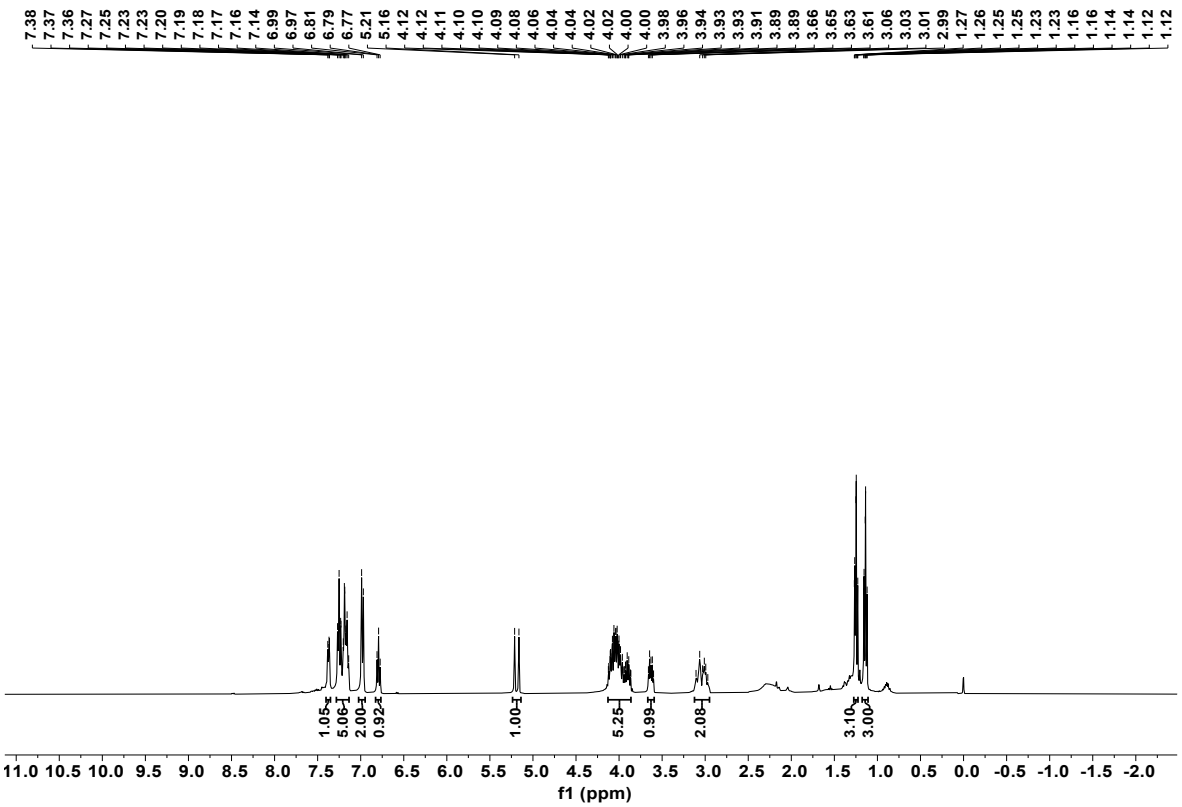


Figure S33. ^{1}H NMRspectrum of 6a (400MHz, $CDCl_3$).

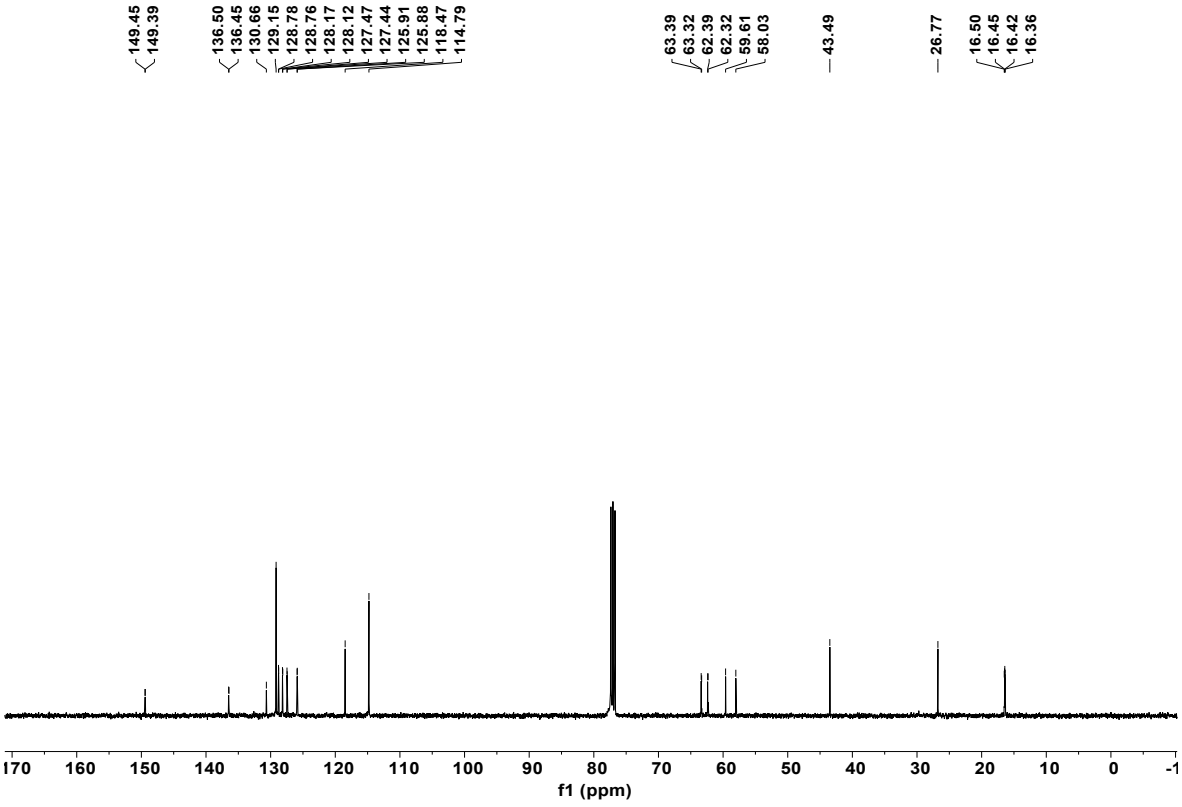


Figure S34. ^{13}C NMR spectrum of 6a (100MHz, $CDCl_3$).

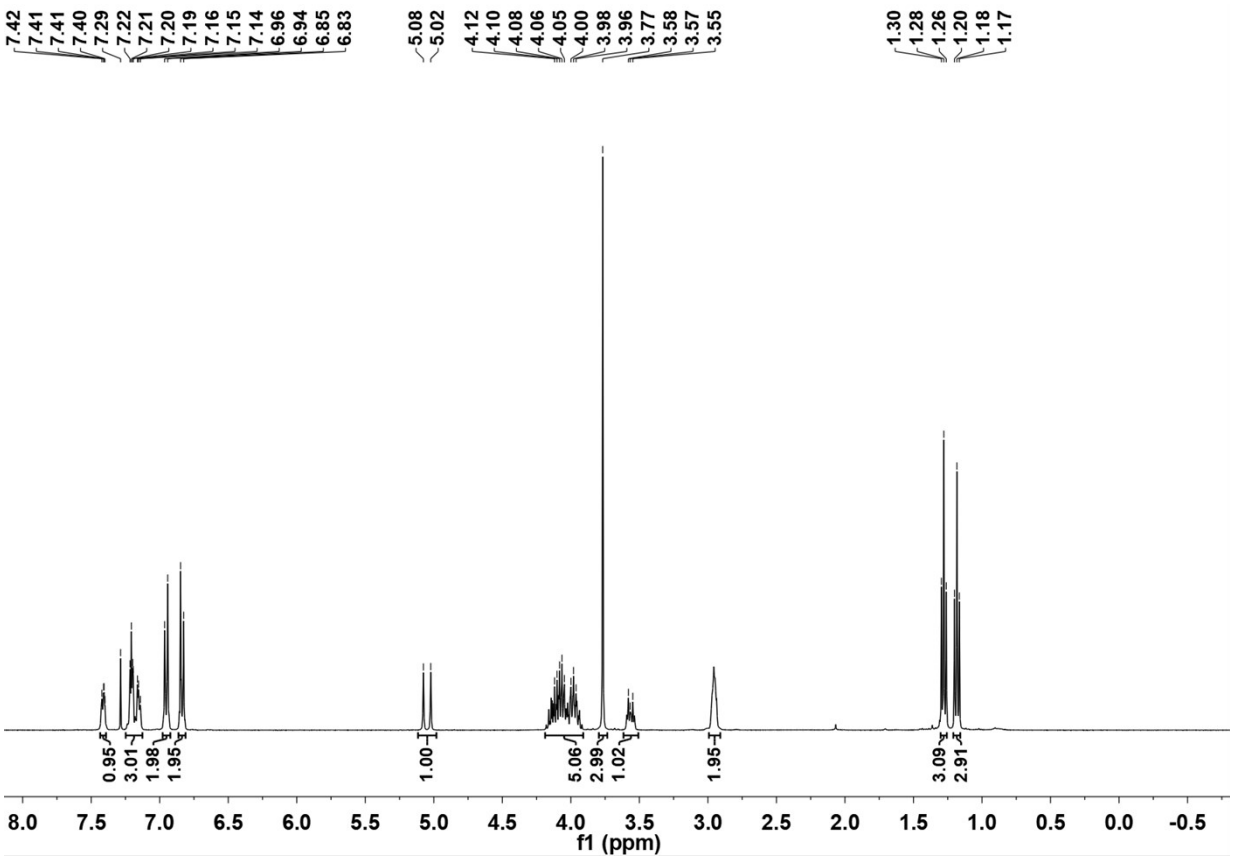


Figure S35. ^{1}H NMR spectrum of 6b (400MHz, $CDCl_3$).

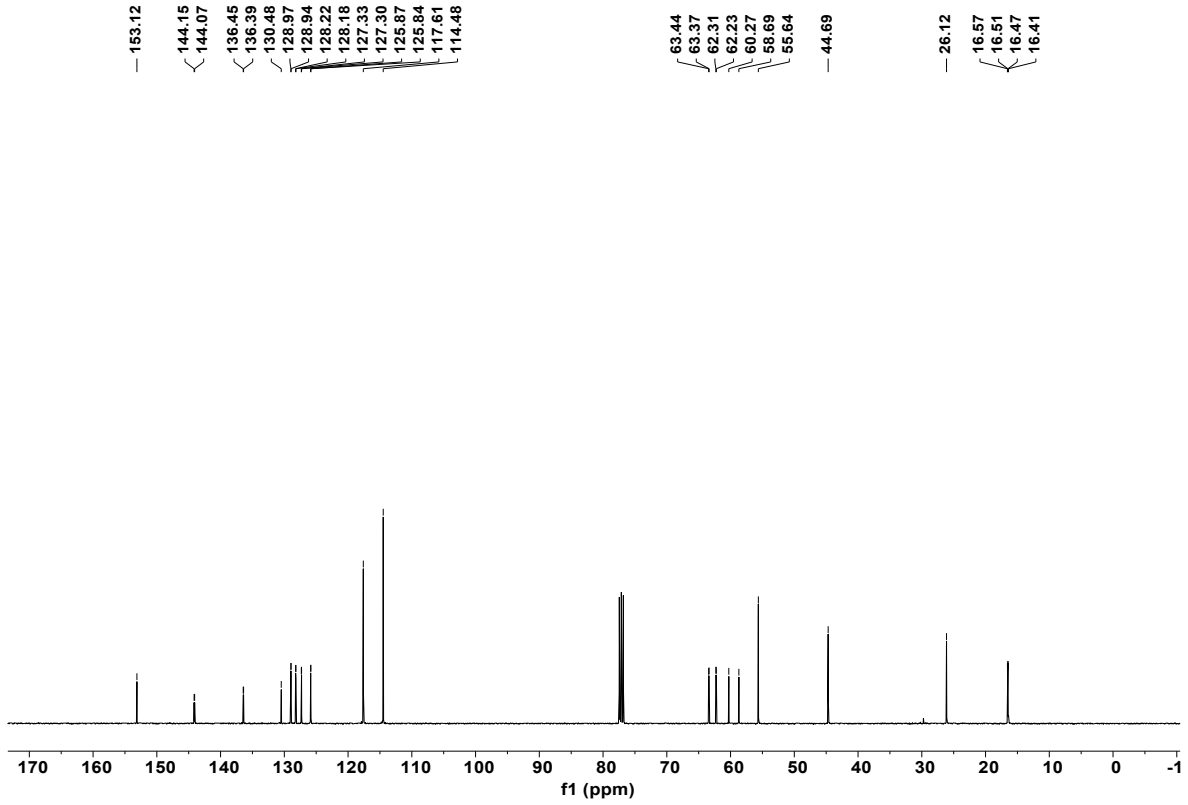


Figure S36. ^{13}C NMR spectrum of 6b (100MHz, $CDCl_3$).

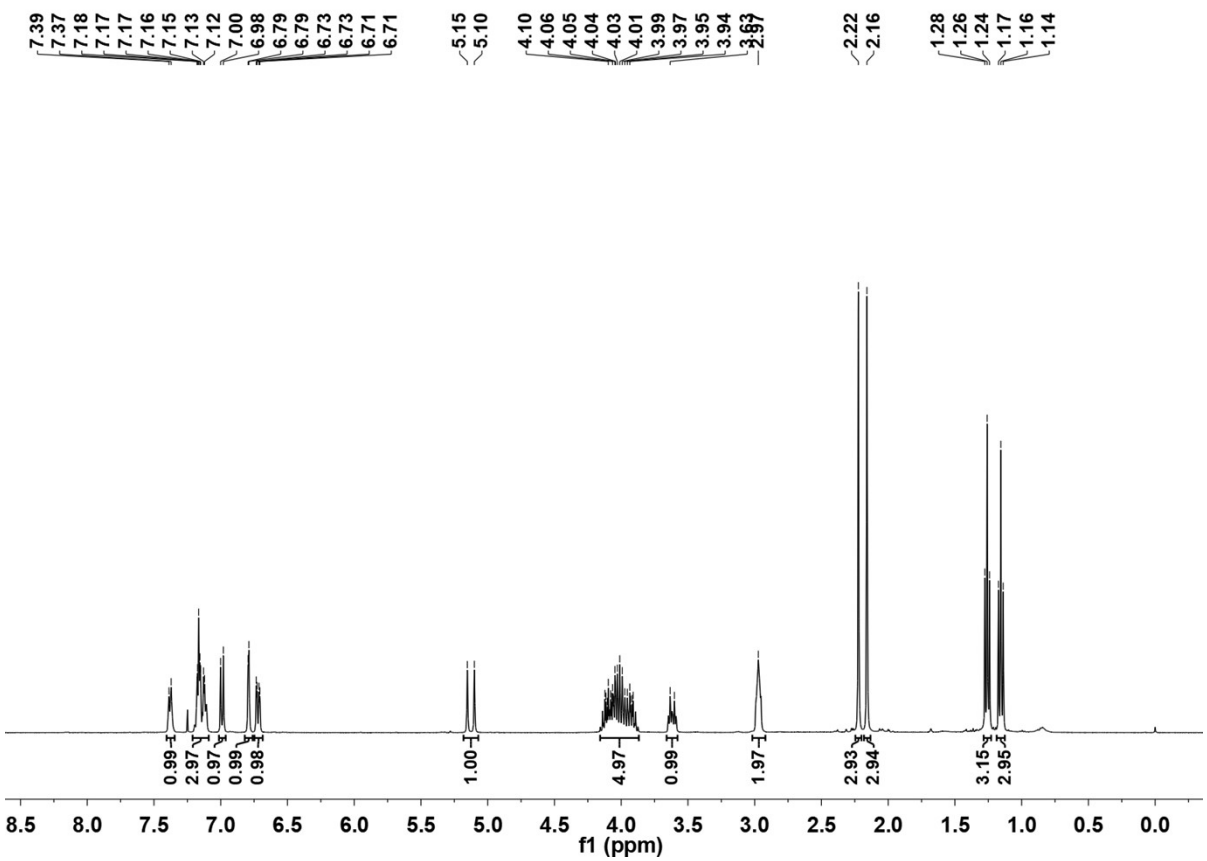


Figure S37. ^{1}H NMRspectrum of 6c (400MHz, $CDCl_3$).

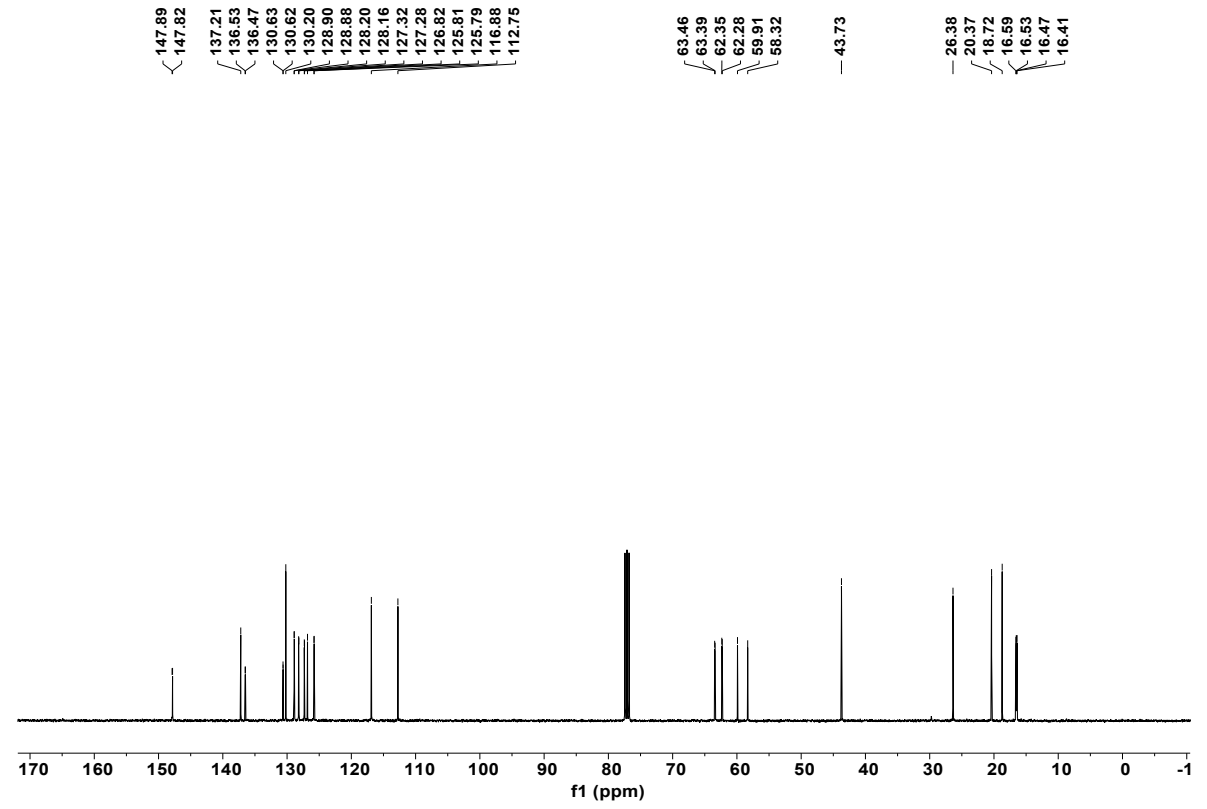


Figure S38. ^{13}C NMR spectrum of 6c (100MHz, $CDCl_3$).

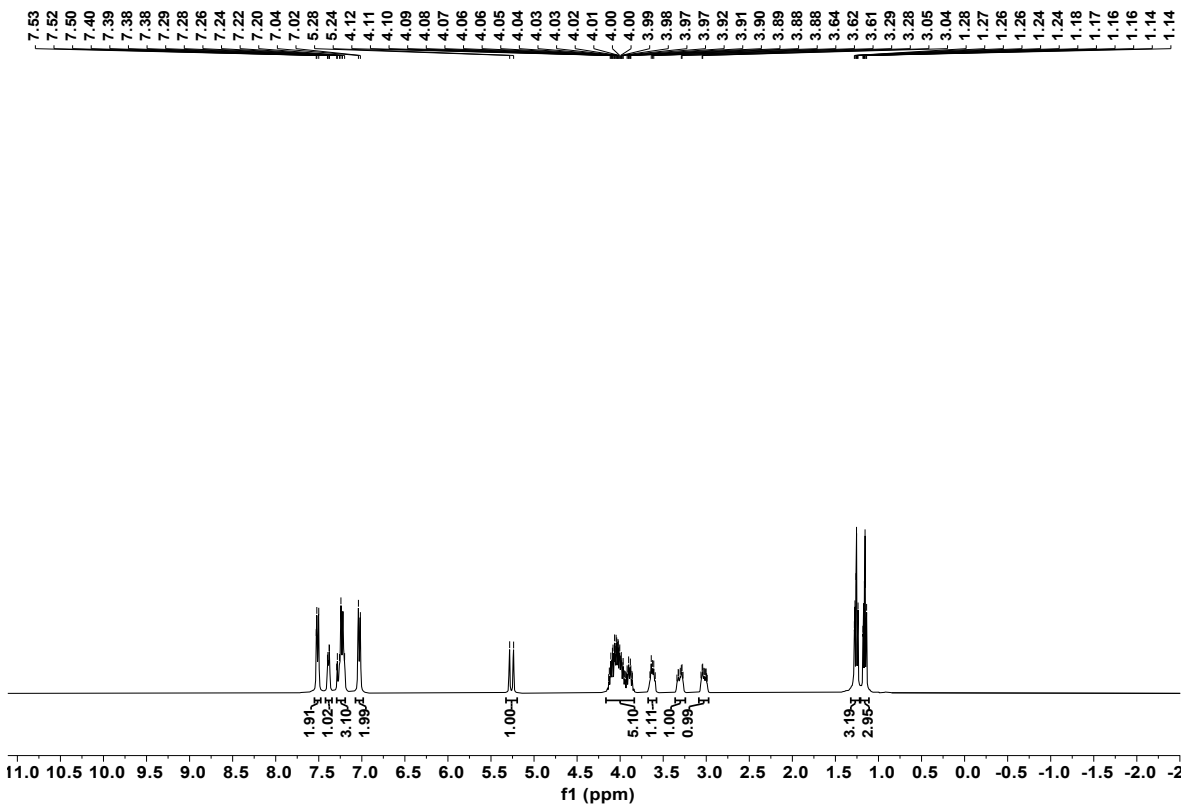


Figure S39. ^{1}H NMR spectrum of 6d (400MHz, $CDCl_3$).

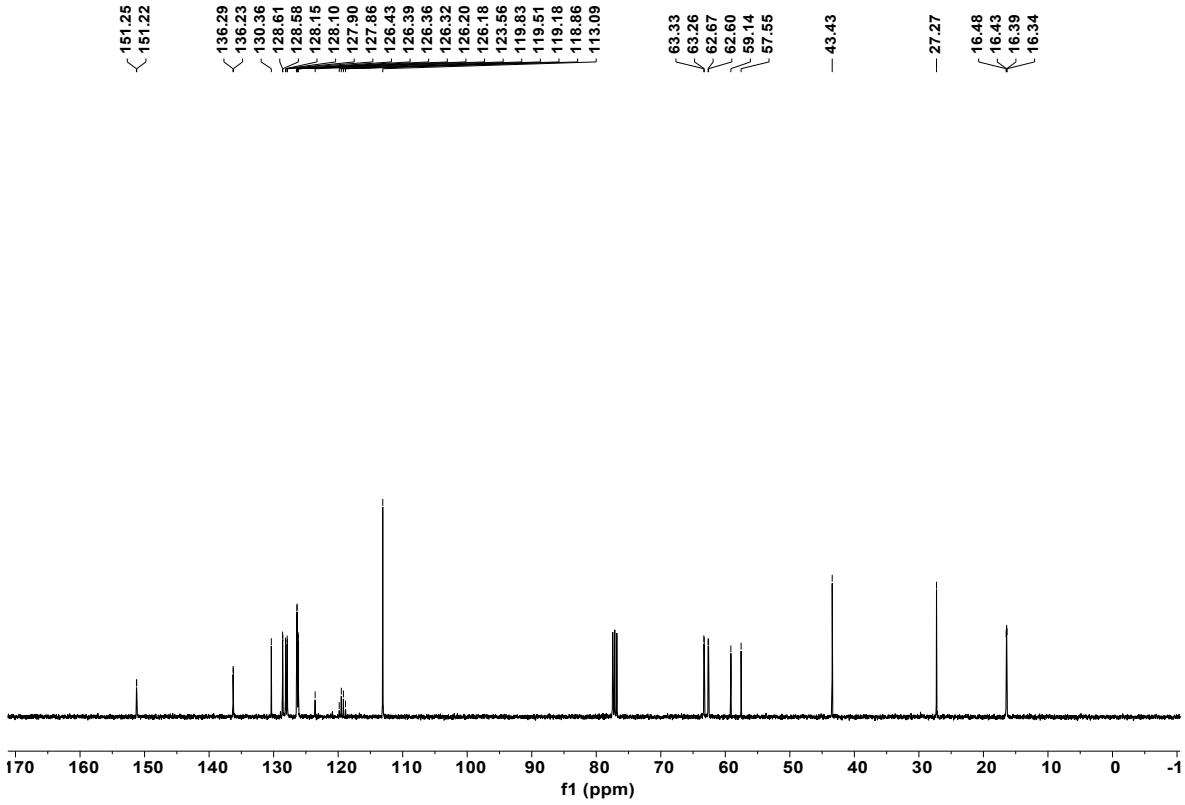


Figure S40. ^{13}C NMR spectrum of 6d (100MHz, $CDCl_3$).

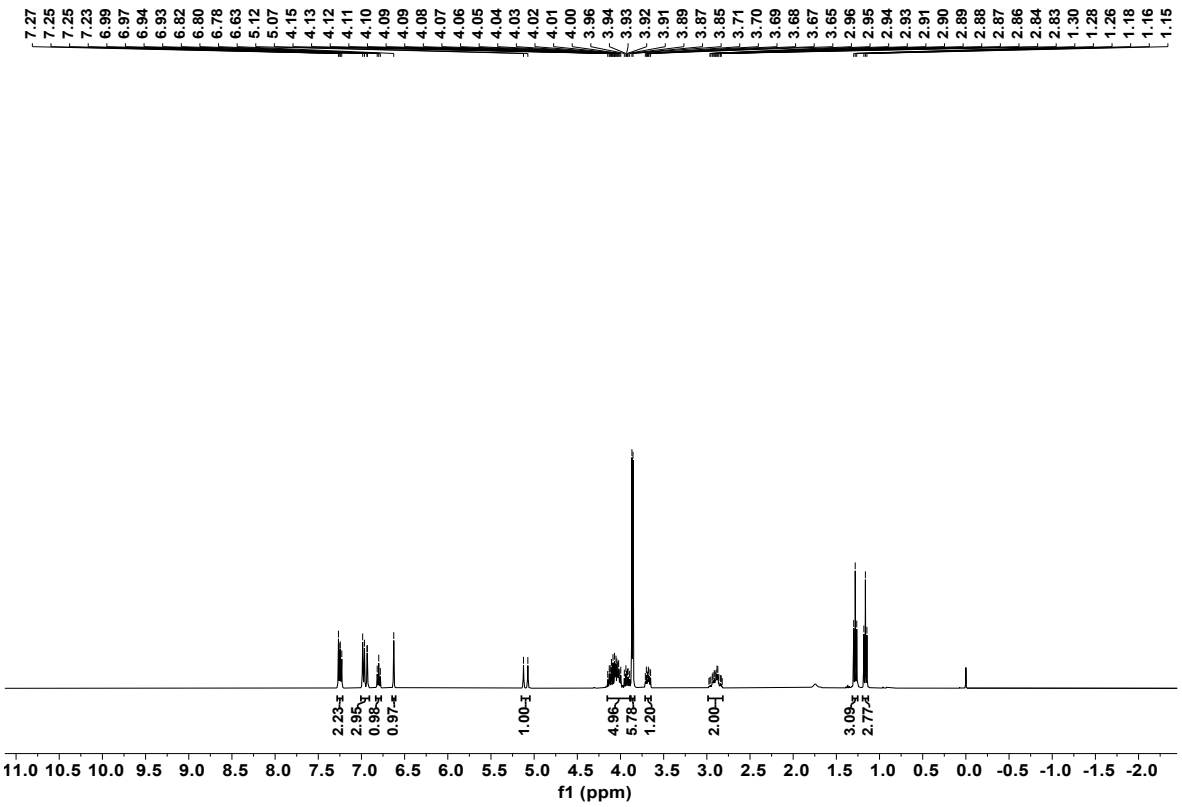


Figure S41. ^{1}H NMR spectrum of 6e (400MHz, $CDCl_3$).

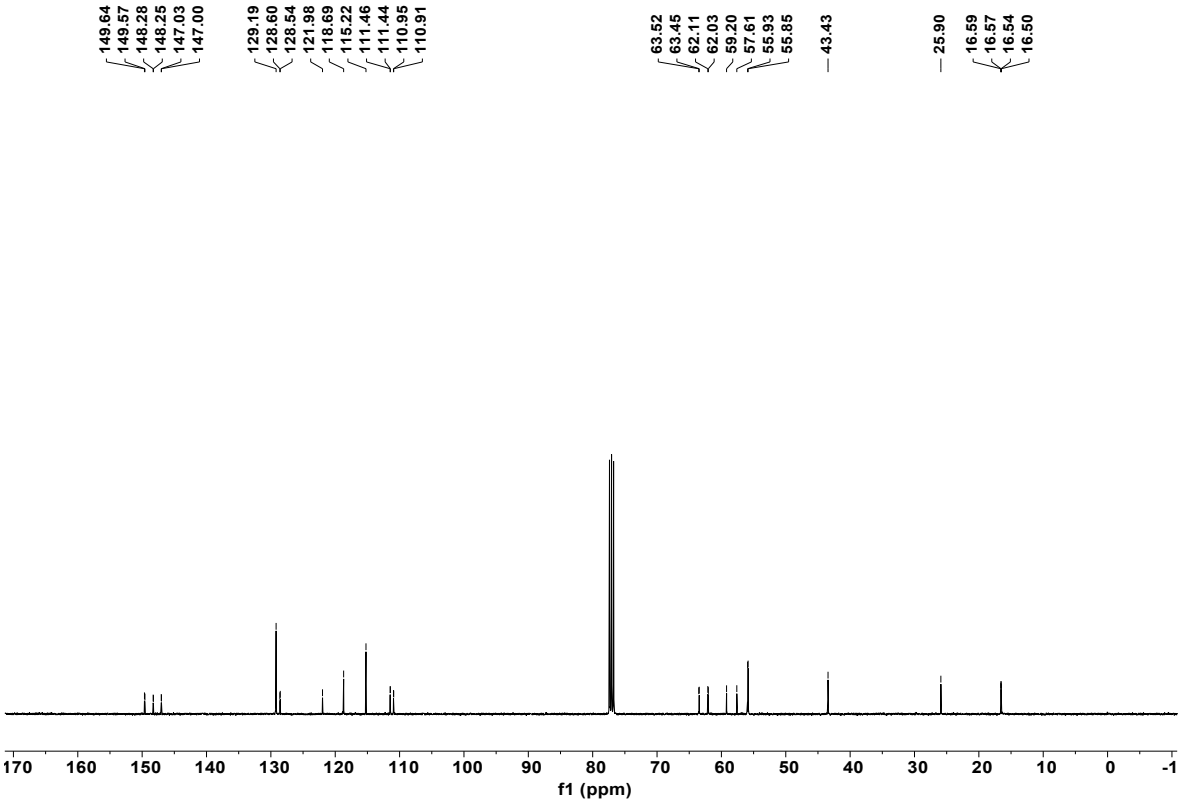


Figure S42. ^{13}C NMR spectrum of 6e (100MHz, $CDCl_3$).

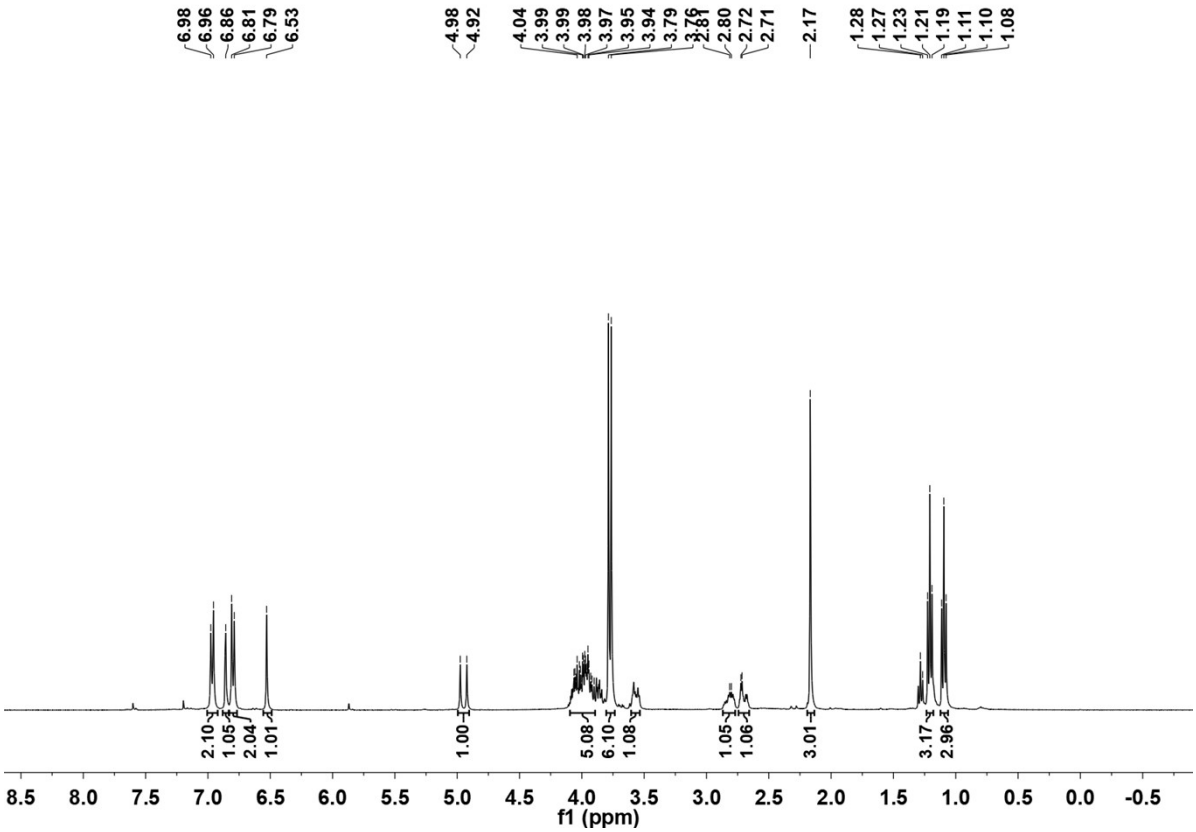


Figure S43. ^{1}H NMR spectrum of 6f (400MHz, $CDCl_3$).

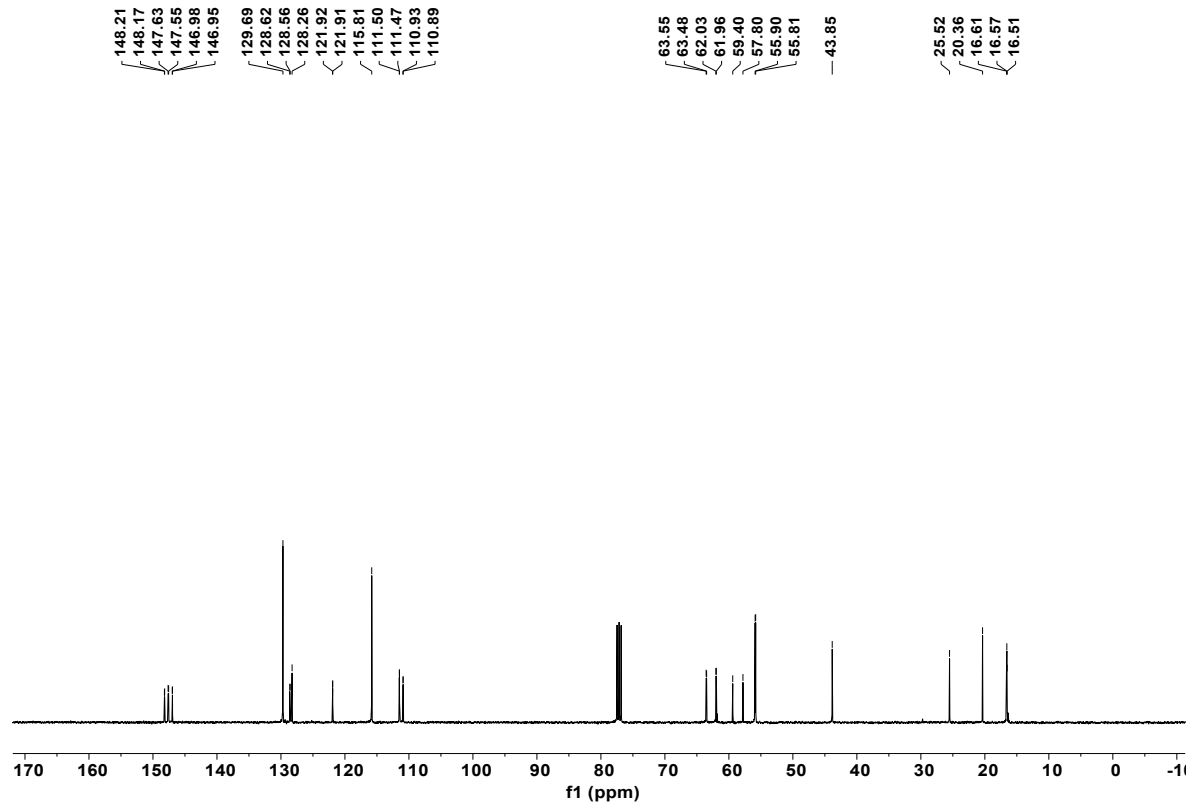


Figure S44. ^{13}C NMR spectrum of 6f (100MHz, $CDCl_3$).

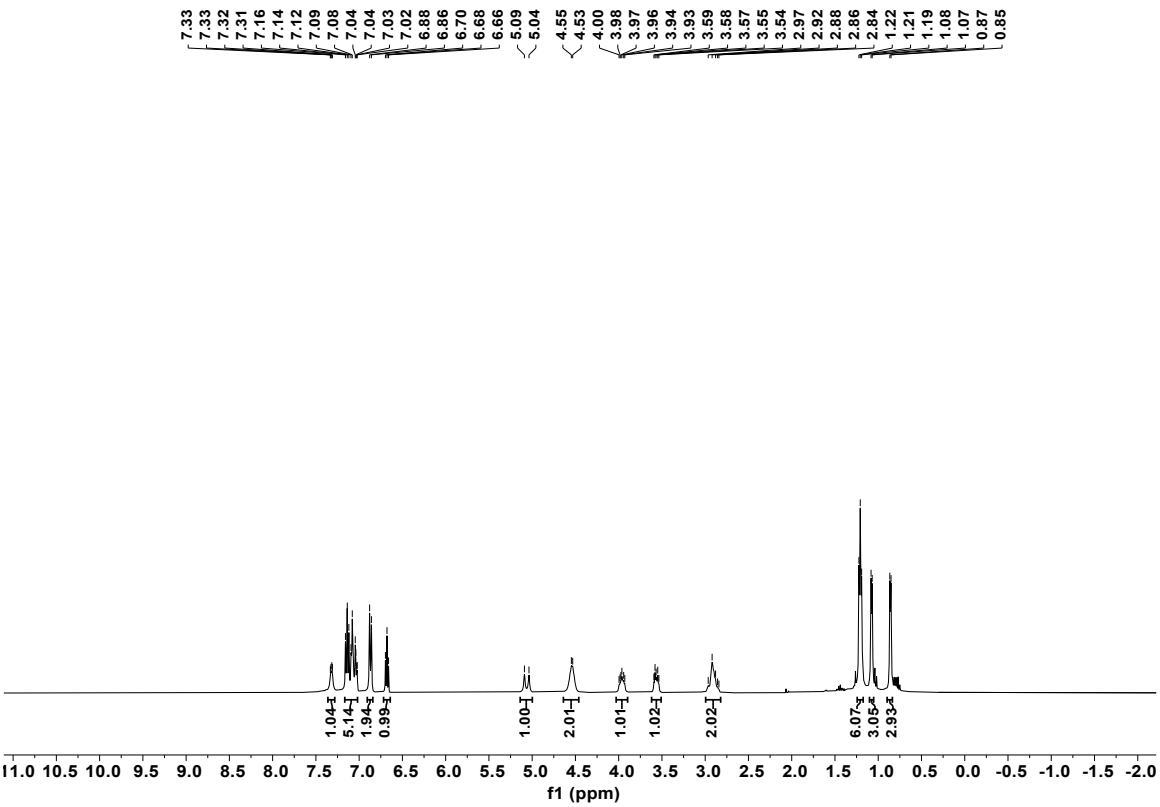


Figure S45. ^{1}H NMR spectrum of 6g (400MHz, $CDCl_3$).

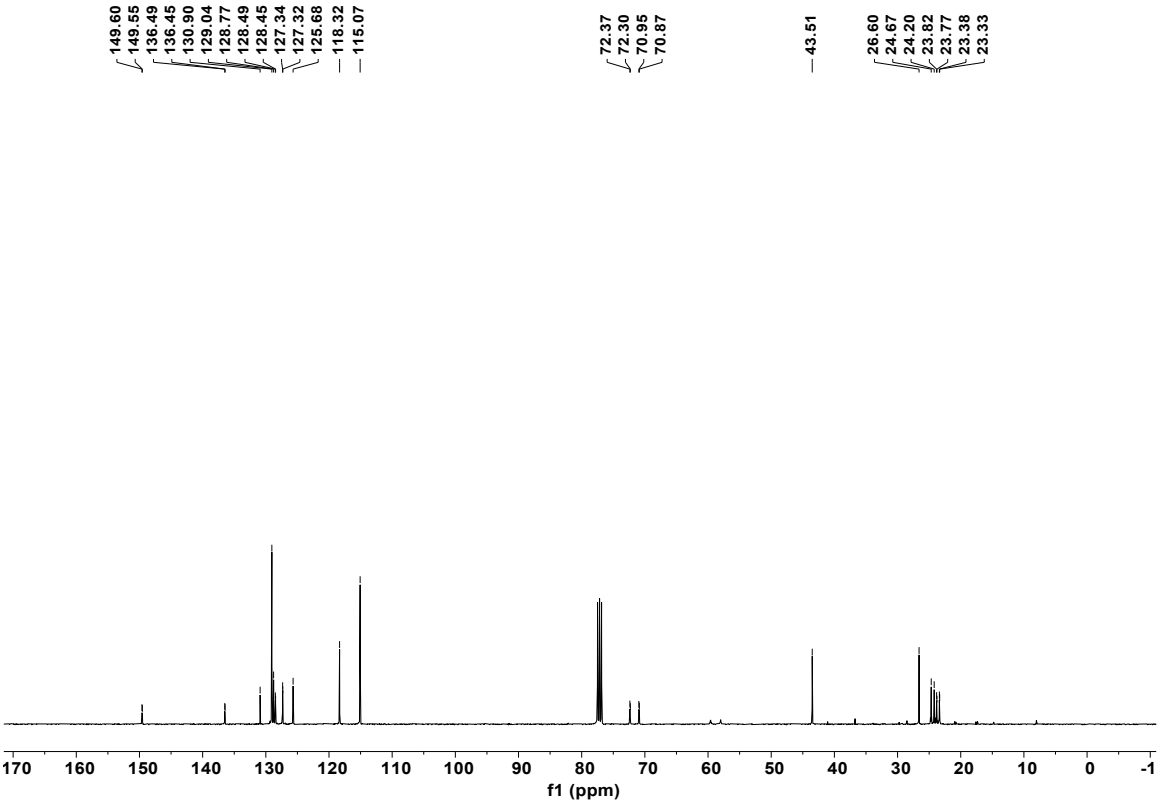


Figure S46. ^{13}C NMR spectrum of 6g (100MHz, $CDCl_3$)

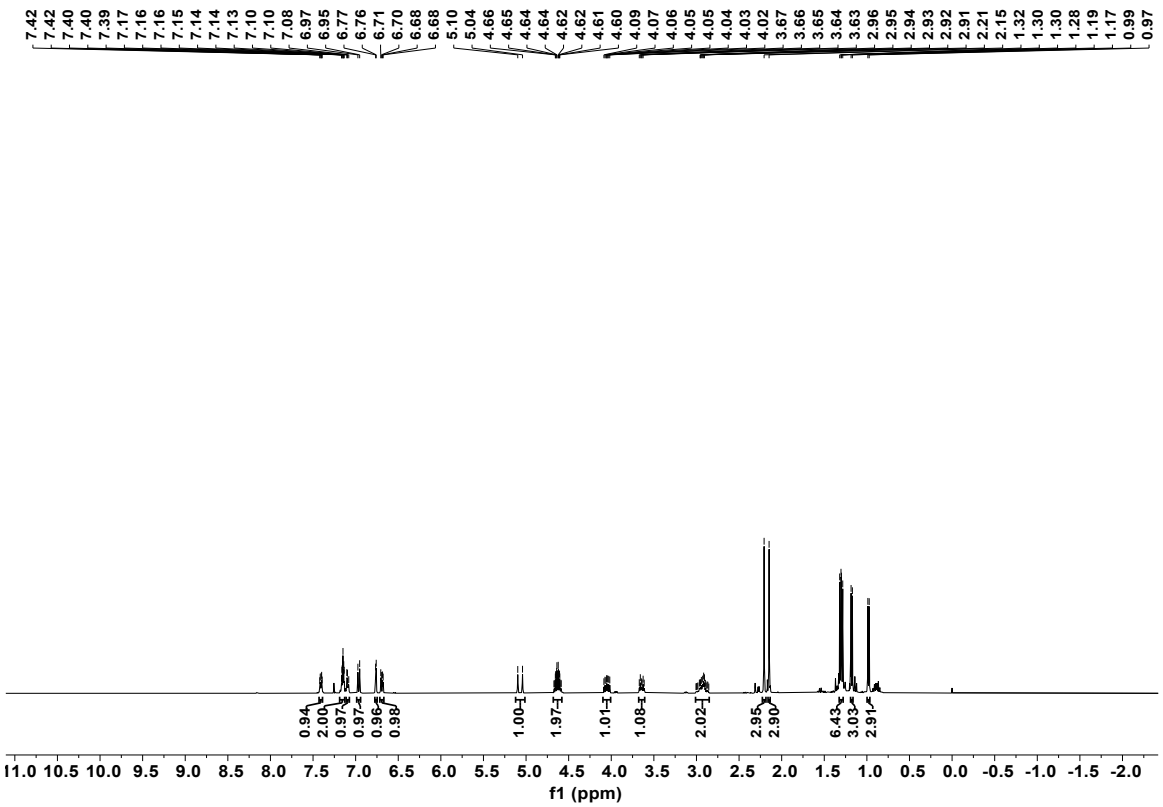


Figure S47. ^{1}H NMR spectrum of 6h (400MHz, $CDCl_3$).

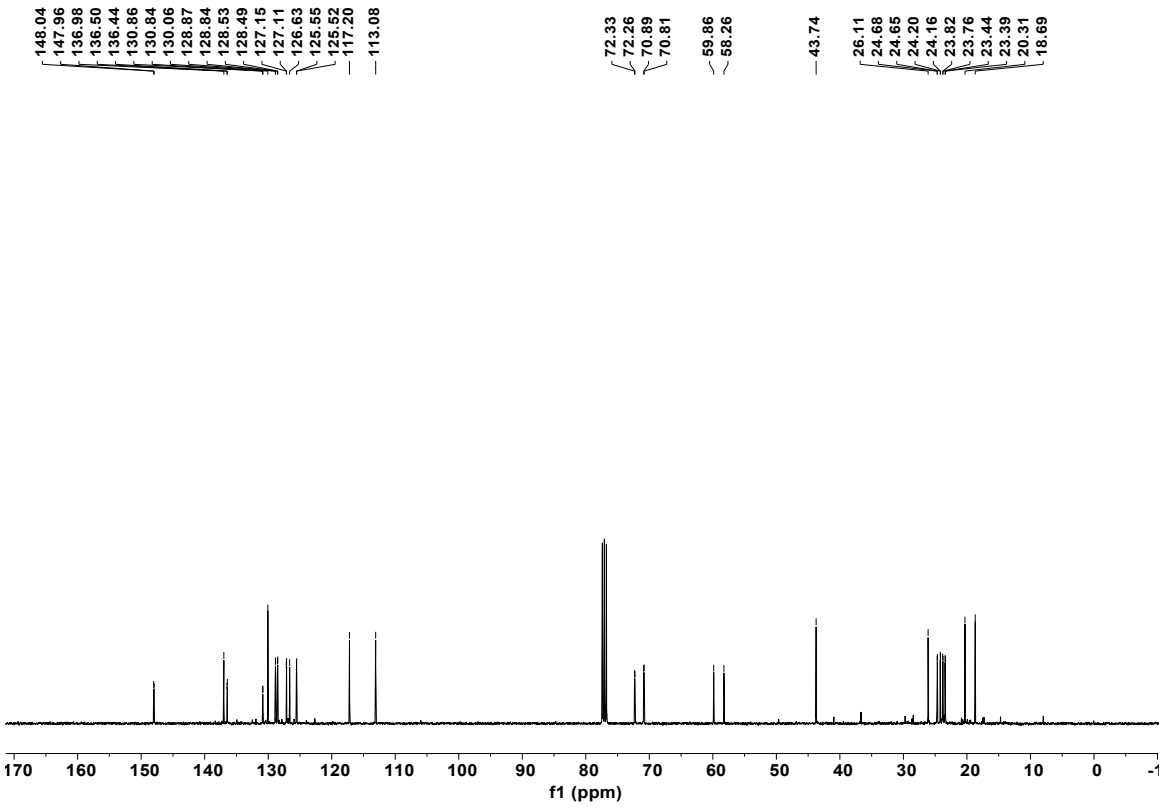


Figure S48. ^{13}C NMR spectrum of 6h (100MHz, $CDCl_3$).

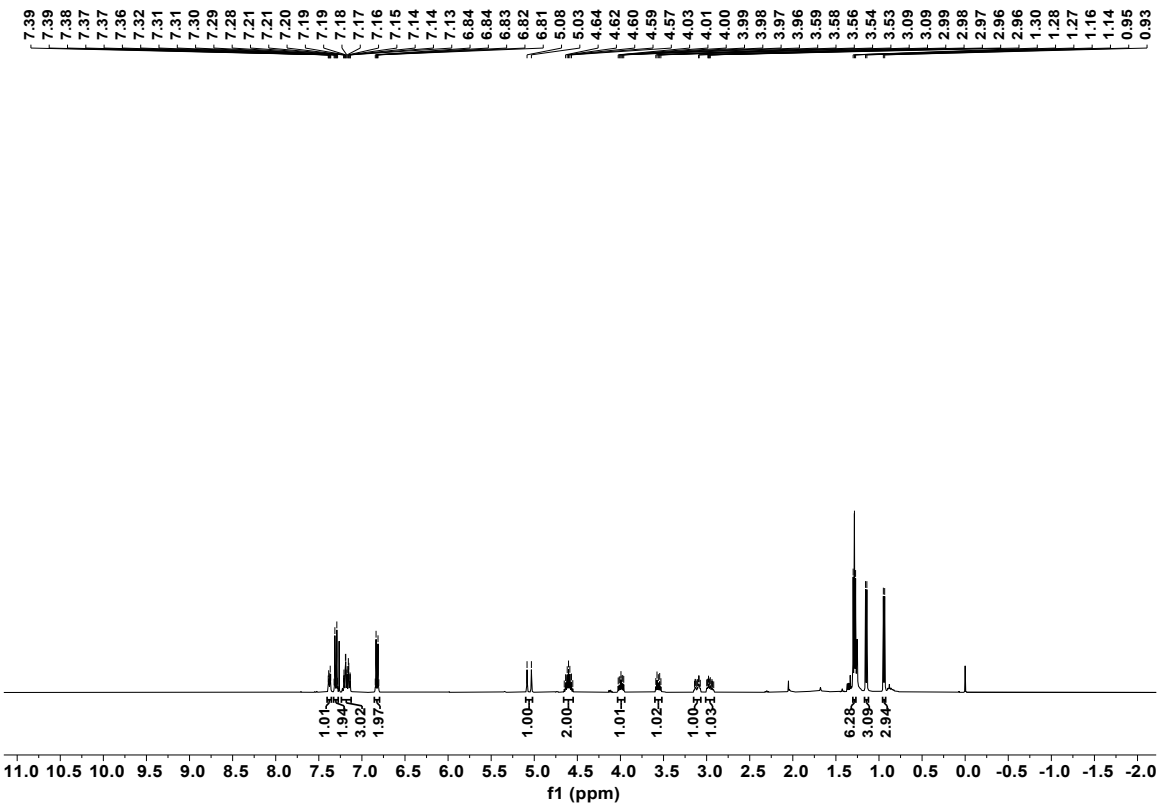


Figure S49. ^{1}H NMR spectrum of 6i (400MHz, $CDCl_3$).

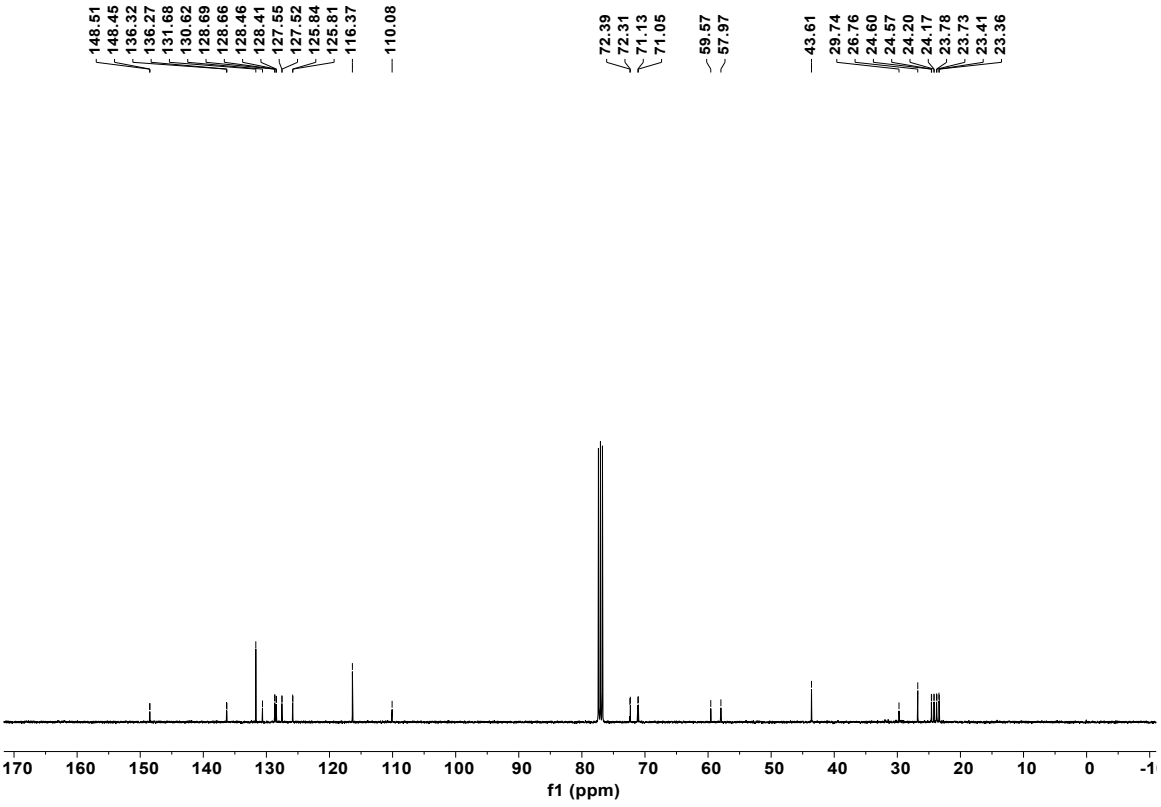


Figure S50. ^{13}C NMR spectrum of 6i (100MHz, $CDCl_3$).