Electronic Supplementary Information

Covalent organic frameworks as metal-free heterogeneous photocatalysts for organic transformations

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1. General Procedures

^{1}H spectra were recorded on a Avance III-400 NMR spectrometer, where chemical shifts (δ in ppm) were determined with a residual proton of the solvent as standard. Solid-state ^{13}C CP/MAS NMR measurement was recorded using a Bruker AVANCE III 400 WB spectrometer at a MAS rate of 5 kHz and a CP contact time of 2 ms. Elemental analyses were carried out on an Elementar model vario EL cube analyzer. The infrared spectra were recorded from 400 to 4000 cm^{-1} on an Avatar FT-IR 360 spectrometer by using KBr pellets. UV/Vis spectra have been carried out on a Perkin Elmer Lambda 950 spectrophotometer within the wavelength range 200–700 nm. Field emission scanning electron microscopy was performed on a SU8020 model HITACHI microscope. Transmission electron microscopy was performed on a JEOL model JEM-2100 microscope. The sample was prepared by drop-casting a supersonicated methanol suspension of COF-JLU5 onto a copper grid. Powder X-ray diffraction data were recorded on a PANalytical BV Empyrean diffractometer diffractometer by depositing powder on glass substrate, from 2θ = 1.5° to 45° with 0.02° increment at 25 °C. Thermogravimetric analysis (TGA) was performed on a TA Q500 thermogravimeter by measuring the weight loss while heating at a rate of 10 °C min^{-1} from room temperature to 800 °C under nitrogen. Nitrogen sorption isotherms were measured at 77 K with a JW-BK 132F or ASIQ (iQ-2) analyzer. Before measurement, the samples were degassed in vacuum at 120 °C for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume. The nonlocal density functional theory (NLDFT) method was applied for the estimation of pore size distribution. Electrochemical measurements were performed in a three-electrode system with a CHI660E electrochemical workstation (CH Instruments, USA). The glass carbon electrode (GCE) was used as working electrode, a platinum wire electrode, and a saturated calomel electrode (SCE) as counter and reference electrode, respectively. Absolute fluorescence quantum yields were measured on an Edinburgh FLS920 steady state spectrometer using an integrating sphere. Luminescence decay experiments were carried out on an Edinburgh FLS920 spectrometer. To create measurable COF films, the COF was mixed and ground with 5wt % Nafion, the mixture was dropped on top of a glassy carbon working electrode, and the solvents were evaporated in a vacuum oven for at least 30 min. The

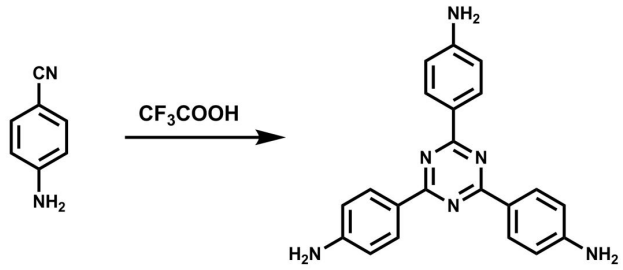
measurements were carried out in a 0.1 M solution of tetrabutylammonium phosphate in acetonitrile. A Pt counter electrode and a SCE reference electrode were used. Scan rate: 100 mV/s, T = 25 ^{o}C.

The EPR spectra were recorded on a JEOL JES-FA200 EPR spectrometer. Samples were quantitatively injected into specially made quartz capillaries for ESR analysis. The date of DMPO and TEMP solution with the concentration of 0.1 M were collected under this instrument parameters: scanning frequency, 9.05 GHz; central field, 323 mT; scanning width, 100 G; scanning power, 5 mW; scanning temperature: 293 K. All the irradiations were performed with >400 nm continuous laser.

2. Materials and Synthesis

Materials. The 1,4-Dimethoxybenzene, bromine, 4-aminobenzonitrile were obtained from Sinopharm Chemical Reagent. Trifluoromethanesulfonic acid and n-Butyllithium solution in hexanes (1.6 M) were obtained from J&K Scientific. Other organic solvents for reactions were distilled over appropriate drying reagents under nitrogen. Deuterated solvents for NMR measurement were obtained from Aladdin.

Synthesis of 1,3,5-tris-(4-aminophenyl)triazine



The 1,3,5-tris-(4-aminophenyl)triazine was prepared based on the reported procedure with minor modifications.[1] In a typical synthesis, 4-aminobenzonitrile (0.772 g, 6.538 mmol) was taken in a round bottom flask at 0 ºC. Then trifluoromethanesulfonic acid (2.0 mL, 22.2 mmol) was added dropwise for 20 min maintaining the temperature at 0 ºC. The resultant mixture was stirred for 24 h at room temperature in inert atmosphere. After that, distilled water (20 mL) was added to the mixture and it was neutralized by adding 2 M NaOH solution until the pH reaches to 7.0. Initially, with increase in pH, the orange precipitate dissolves to give a bright orange solution, which upon further increase in pH gives a pale yellow precipitate. The resultant pale yellow product was filtered and washed several times with distilled water. Yield: 90.6%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.34 (d, J = 8.0 Hz, 6H), 6.68 (d, J = 8.0 Hz, 6H), 5.90 (s, 6H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 169.6, 153.0, 130.1, 122.9, 113.1 ppm. FT-IR (KBr, cm^{-1}): 3313, 3211, 3128, 1633, 1605, 1502, 1428, 1370, 1293, 1175, 1148, 854, 814, 586, 518.

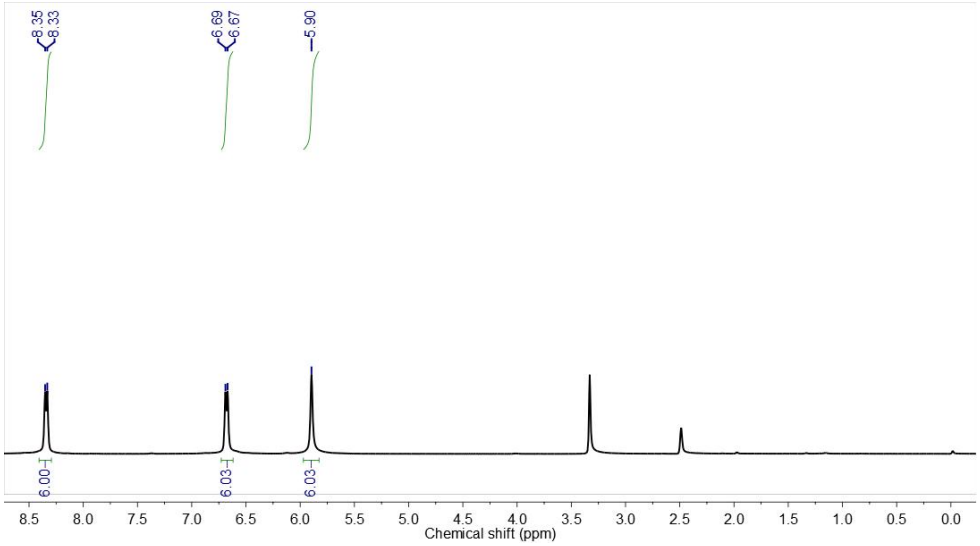


Figure: ^{1}H NMR spectrum of 1,3,5-tris-(4-aminophenyl)triazine.

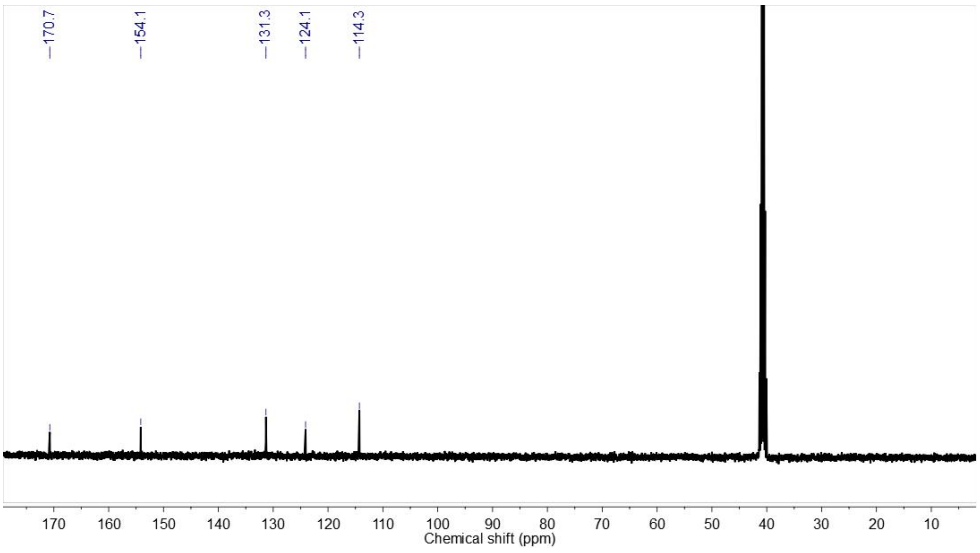
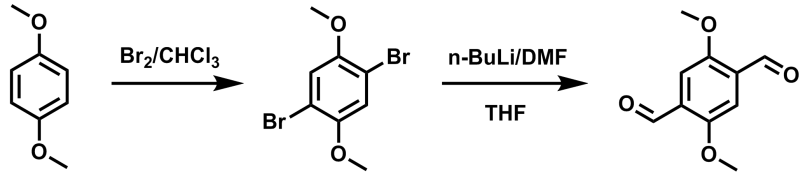


Figure: ^{13}C NMR spectrum of 1,3,5-tris-(4-aminophenyl)triazine.

Synthesis of 2,5-Dimethoxybenzene-1,4-dicarboxaldehyde[2]



To a mixture of a commercial reagent 1,4-dimethoxybenzene (5.0 g, 36.2 mmol) in $CHCl_3$ (25 mL) was added a solution of bromine (14.6 g, 91.75 mmol) in $CHCl_3$ (25 mL) at 0 °C, and the resulting mixture was stirred at room temperature for 24 h. The reaction mixture was diluted with $CHCl_3$ and washed successively with sat. $NaHSO_3$ aq., 1 mol/L NaOH aq., and water. The organic layer was dried over anhydrous Na_2SO_4, filtered, concentrated, and dried under reduced pressure to give 1,4-dibromo-2,5-dimethoxybenzene (10.4 g, 35.0 mmol) in 93.2% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (s, 2H, Ph-*H*), 3.84 (s, 6H, OC*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 117.2, 110.6, 57.1 ppm.

Under argon, to a solution of 1,4-dibromo-2,5-dimethoxybenzene (3.0 g, 10.0 mmol) in THF (50 mL) was added n-BuLi (14 mL, 1.6 mol L^{-1}, 22.0 mmol) at -78 °C, and the resulting mixture was stirred at that temperature for 2 h. Then, anhydrous DMF (2.0 mL, 25 mmol) was added to the solution and the mixture was gradually warmed up to room temperature. After the mixture was stirred further at room temperature for 3 h, 3.0 mol/L HCl aq. (15 mL) was added to precipitate the product, which was isolated by filtration and dried under reduced pressure to give 2,5-dimethoxyterephthalaldehyde (0.56 g, 2.88 mmol) in 28.9% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.50 (s, 2H, C*H*O), 7.46 (s, 2H, Ph-*H*), 3.94 (s, 6H, OC*H*$_3$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.5, 156.0, 129.4, 111.2 and 56.5 ppm. FT-IR (KBr, cm^{-1}): 3126, 2996, 2876, 1675, 1479, 1401, 1300, 1213, 1122, 1016, 879, 665, 564.

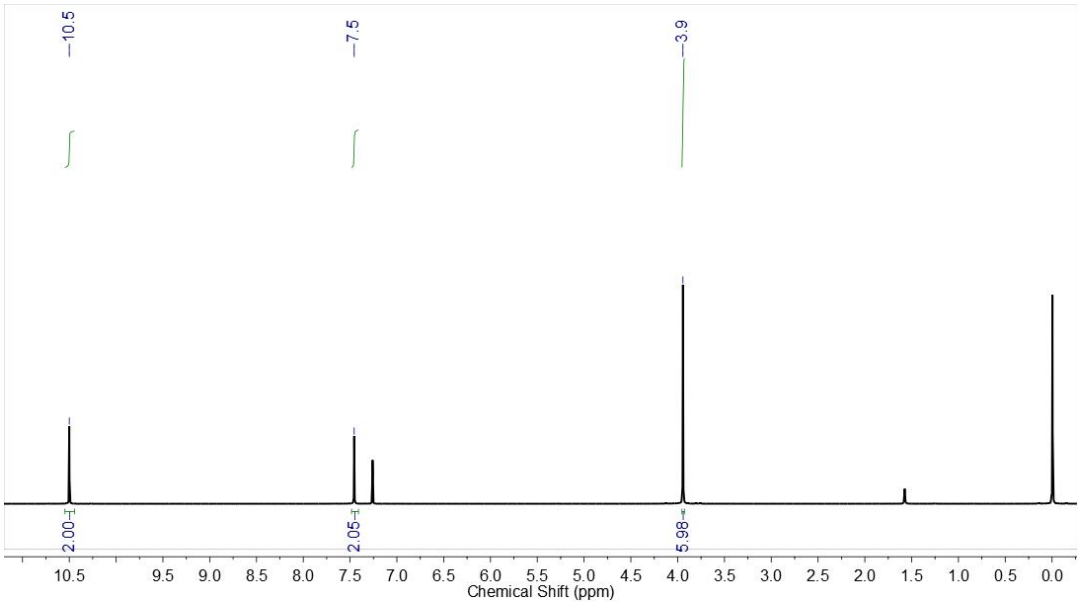


Figure: ^{1}H NMR spectrum of 2,5-Dimethoxybenzene-1,4-dicarboxaldehyde.

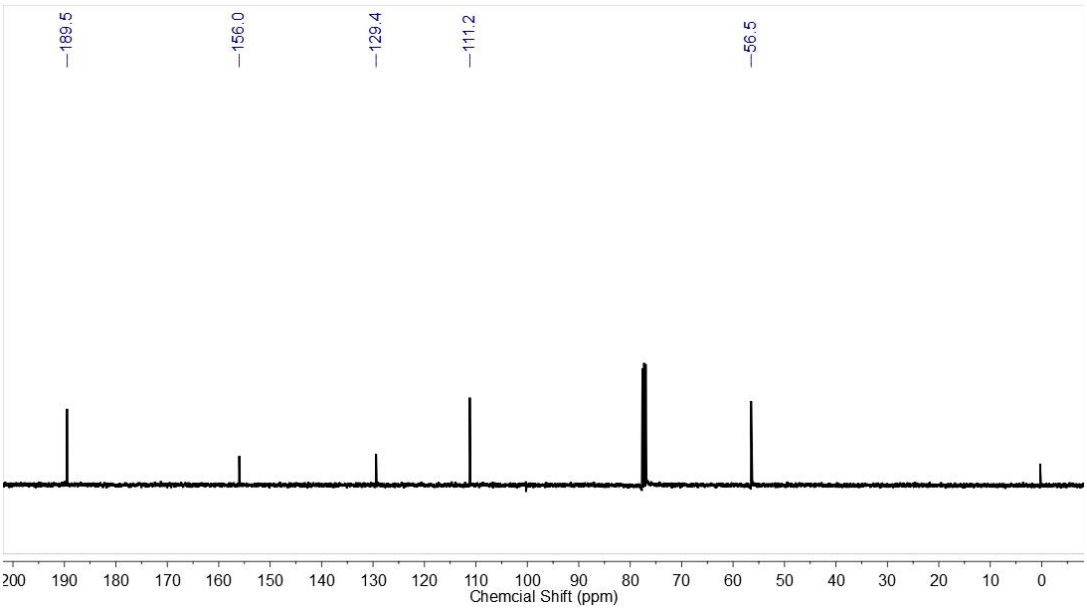
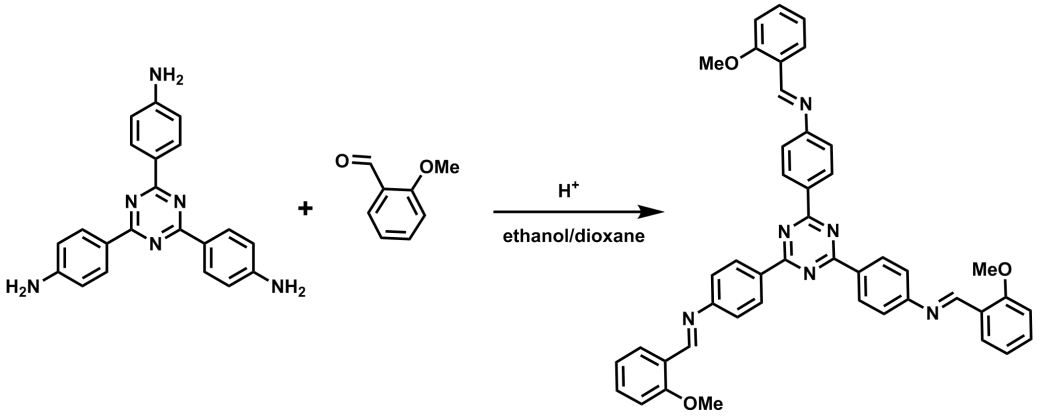


Figure: ^{13}C NMR spectrum of 2,5-Dimethoxybenzene-1,4-dicarboxaldehyde.

Synthesis of Model Compound.



This compound was synthesized by the reaction between 4,4',4''-(1,3,5-triazine-2,4,6-triyl)trianiline (236.0 mg, 0.667 mmol) and 2-methoxy-benzaldehyd (453.0 mg, 3.3 mmol) in 20 mL ethanol, 4.0 mL dioxane and 0.3 mL of aqueous acetic acid mixture under refluxing condition for one day. After that the solution was cooled to room temperature and the precipitate was collected by filtration, washed with ethanol to remove excess 2-methoxy-benzaldehyd, and dried under vacuum to give a light yellow solid compound (382.0 mg, 81%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.01 (s, 3H), 8.83 (d, J = 8.0 Hz, 6H), 8.21 (d, J = 8.0 Hz, 3H), 7.49 (t, J = 8.0 Hz, 3H), 7.39 (d, J = 8.0 Hz, 6H), 7.08 (t, J = 8.0 Hz, 3H), 6.99 (d, J = 8.0 Hz, 3H), 3.94 (s, 9H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.4, 160.0, 157.7, 157.0, 134.0, 133.5, 130.4, 128.1, 124.9, 121.6, 121.3, 111.5 and 55.9 ppm. FT-IR (KBr, cm^{-1}): 2944, 2834, 1587, 1514, 1415, 1366, 1301, 1284, 1256, 1171, 1140, 1106, 1028, 975, 890, 861, 814, 749, 655, 590, 554, 512.

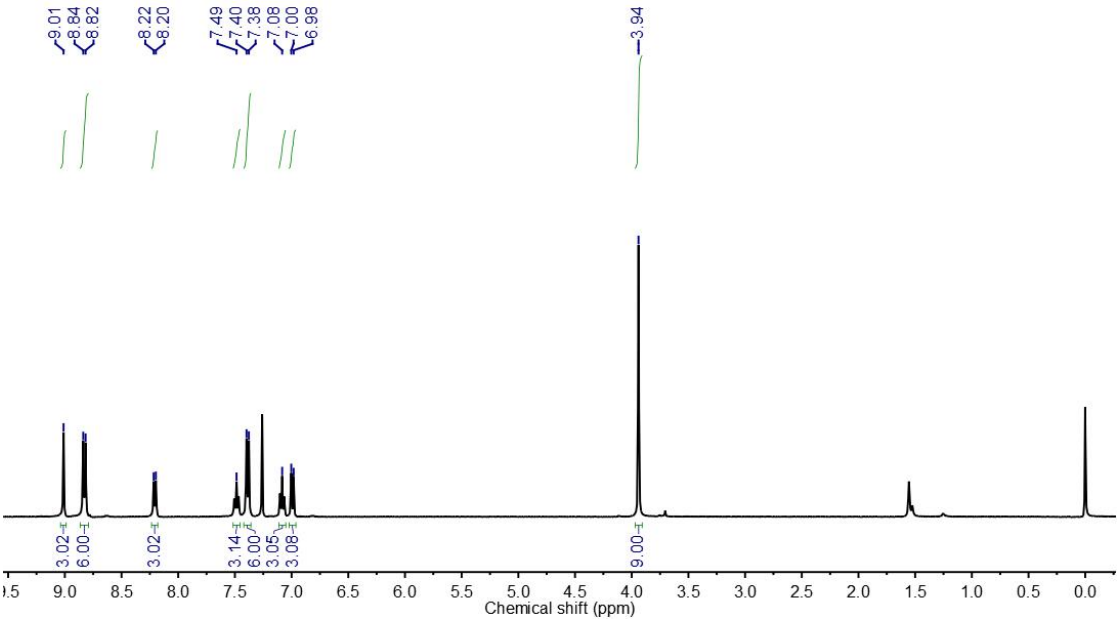


Figure: [1]H NMR spectrum of model compound.

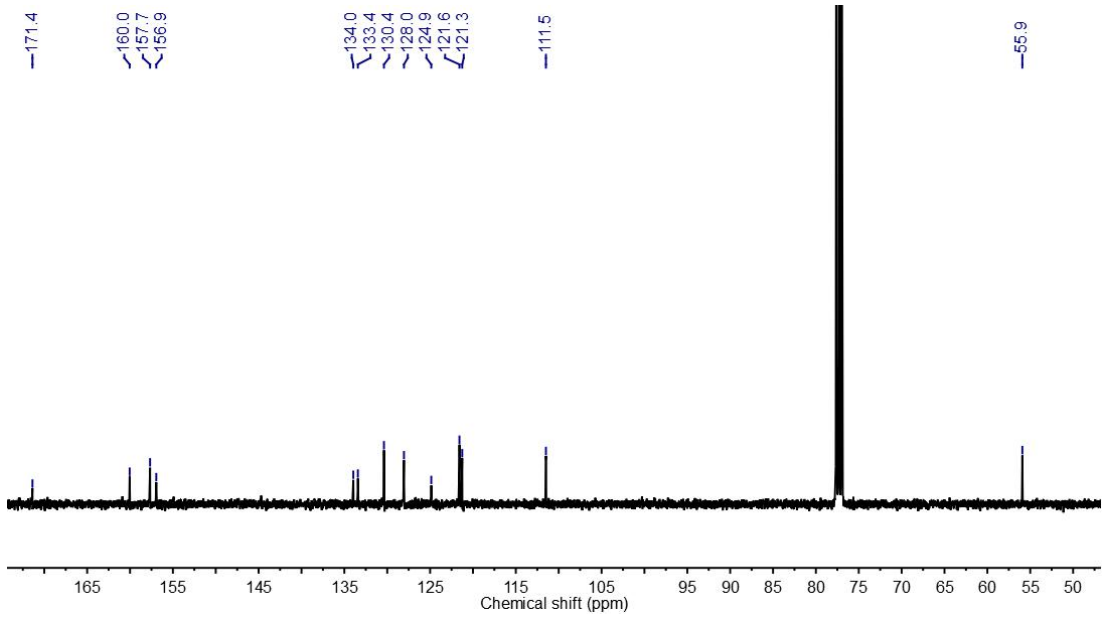
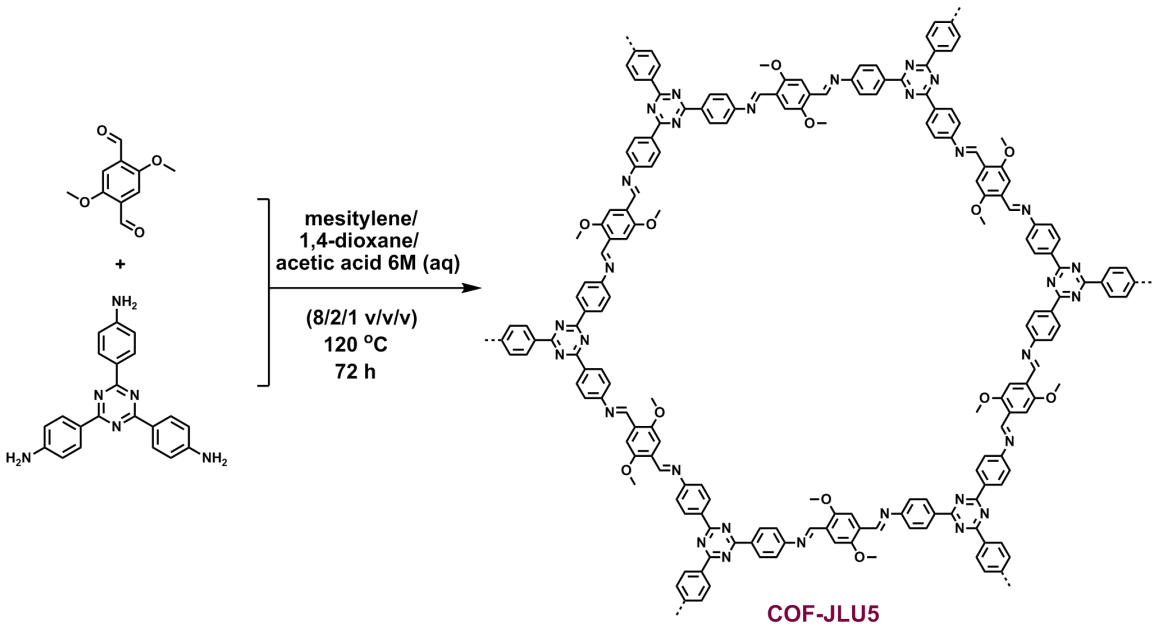


Figure: [13]C NMR spectrum of model compound.

Synthesis of COF-JLU5.



A dioxane/1,3,5-trimethylbenzene (0.4 mL/1.6 mL) mixture of 1,3,5-tris-(4-aminophenyl)triazine (56.6 mg, 0.16 mmol) and 1, 4-dimethoxy-terephthaldehyde (46.6 mg, 0.24 mmol), in the presence of an acetic acid catalyst (0.2 mL, 6 M) in a 10-mL Pyrex tube was degassed via three freeze–pump–thaw cycles. The tube was flame-sealed and heated at 120 °C for three days. The precipitate was collected through centrifugation, washed with anhydrous THF (3 x 5 mL) and anhydrous acetone (3 x 5 mL). The powder was collected and dried at 120 °C under vacuum overnight to produce COF-JLU5 as a yellow-green solid in 88% isolated yield. Anal. Cald for $(C_{12}H_9N_2O)_n$: C 73.08; H 4.60; N 14.20. Found: C 71.53; H 4.94; N 14.15.

3. General Procedure for Photocatalysis Reaction

3.1 The general procedure for the aerobic cross-dehydrogenative coupling reaction of tetrahydroisoquinoline with nitroalkanes

Tetrahydroisoquinoline derivatives (0.2 mmol), nitromethane or nitroethane or nitropropane (0.6 mmol), COF-JLU5 (4.0 mg) and methanol (2.0 mL) were mixed in a 10-mL reaction tube with magnetic stirring bar. The mixture was bubbled with a stream of oxygen for 30 min. The tube was then sealed and irradiated with a blue LEDs for 6 h at 25 ^{o}C. Thin layer chromatography (TLC) was used to monitor the progress of the reaction. After the completion of the reaction, the solvent was evaporated under reduced pressure. The residue was subjected to ^{1}H-NMR spectroscopic analysis and purified by column chromatography on silica gel using petroleum ether/ethyl acetate (10:1) as eluent.

3.2 The general procedure for the aerobic cross-dehydrogenative coupling reaction of tetrahydroisoquinoline with dialkyl malonates

Tetrahydroisoquinoline derivatives (0.2 mmol), dimethyl malonate or diethyl malonate (0.6 mmol), COF-JLU5 (4.0 mg) and methanol (2.0 mL) were mixed in a 10-mL reaction tube with magnetic stirring bar. The mixture was bubbled with a stream of oxygen for 30 min. The tube was then sealed and irradiated with a blue LEDs for 6 h at 25 ^{o}C. Thin layer chromatography (TLC) was used to monitor the progress of the reaction. After the completion of the reaction, the solvent was evaporated under reduced pressure. The residue was subjected to ^{1}H-NMR spectroscopic analysis and purified by column chromatography on silica gel using petroleum ether/ethyl acetate (10:1) as eluent.

3.3 The general procedure for the aerobic cross-dehydrogenative coupling reaction of tetrahydroisoquinoline with dialkyl phosphites

Tetrahydroisoquinoline derivatives (0.2 mmol), diethyl phosphite or diisopropyl phosphite (0.6 mmol), COF-JLU5 (4.0 mg) and methanol (2.0 mL) were mixed in a 10-mL reaction tube with magnetic stirring bar. The mixture was bubbled with a stream of oxygen for 30 min. The tube was then sealed and irradiated with a blue LEDs for 6 h at 25 ^{o}C. Thin layer chromatography (TLC) was used to

monitor the progress of the reaction. After the completion of the reaction, the solvent was evaporated under reduced pressure. The residue was subjected to ^{1}H-NMR spectroscopic analysis and purified by column chromatography on silica gel using petroleum ether/ethyl acetate (2:1) as eluent.

3.4 The general procedure for the Mannich reaction of tetrahydroisoquinoline with acetone

Tetrahydroisoquinoline derivatives (0.2 mmol), acetone (2 mmol), L-proline (0.06 mmol), COF-JLU5 (4.0 mg) and methanol (2.0 mL) were mixed in a 10-mL reaction tube with magnetic stirring bar. The mixture was bubbled with a stream of oxygen for 30 min. The tube was then sealed and irradiated with a blue LEDs for 6 h at 25 ^{o}C. Thin layer chromatography (TLC) was used to monitor the progress of the reaction. After the completion of the reaction, the solvent was evaporated under reduced pressure. The residue was subjected to ^{1}H-NMR spectroscopic analysis and purified by column chromatography on silica gel using petroleum ether/ethyl acetate (10:1) as eluent.

3.5 Recycle experiments for the aerobic cross-dehydrogenative coupling reaction of 2-phenyl-1,2,3,4-tetrahydroisoquinoline with nitromethane

After the first run reaction was finished, the photocatalyst COF-JLU5 was recovered by centrifugation, and then washed thoroughly with THF and CH_2Cl_2 to remove any residual products or unreacted substrates. The recovered COF-JLU5 was dried under vacuum at 100 ^{o}C overnight. The used photocatalyst COF-JLU5 was re-employed in next cycle under identical conditions.

3.6 Scaled-up reaction for the aerobic cross-dehydrogenative coupling reaction of 2-phenyl-1,2,3,4-tetrahydroisoquinoline with nitromethane

2-phenyl-1,2,3,4-tetrahydroisoquinoline (500 mg, 2.39 mmol), CH_3NO_2 (0.39 mL, 7.17 mmol), COF-JLU5 (20 mg) and methanol (30 mL) were mixed in the reaction tube with magnetic stirring bar. The tube was irradiated by blue LEDs for 10 h. After reaction the solvent was removed by rotary evaporation and purified by column chromatography on silica gel using petroleum ether/ethyl acetate (10:1) as eluent. An excellent yield (0.61g, 95%) was also afforded in the scaled-up reaction.

4. Infrared Spectra

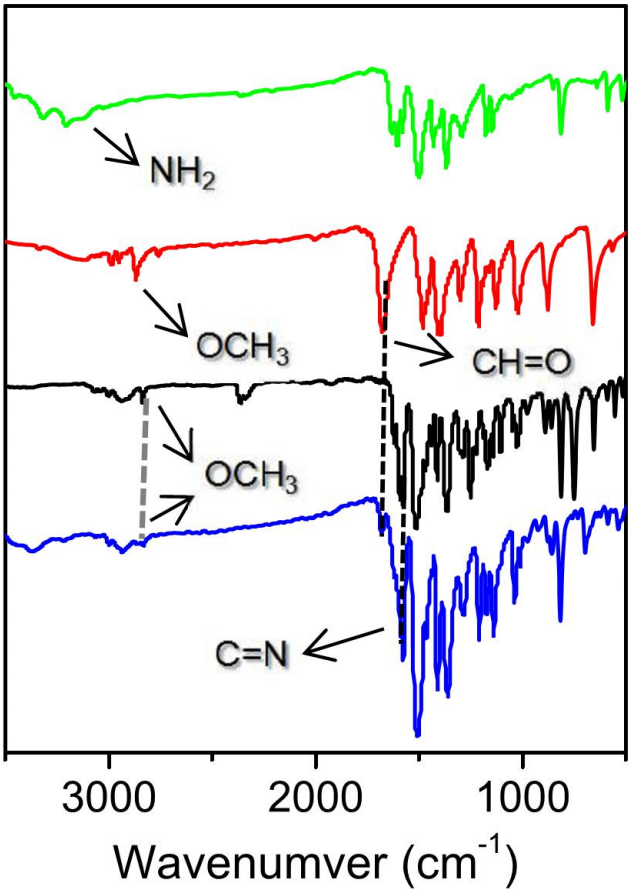


Figure S1. FT-IR spectra of the COF-JLU5 (***blue line***), model compound (***black line***) and monomers 1,3,5-tris-(4-aminophenyl)triazine (***green line***) and 2,5-dimethoxyterephthaldehyde (***red line***). The FT-IR spectrum of COF-JLU5 showed a –C=N– stretch at 1584 cm^{-1}, indicating the successful formation of imine bonds.

5. Solid State ^{13}C CP/MAS NMR

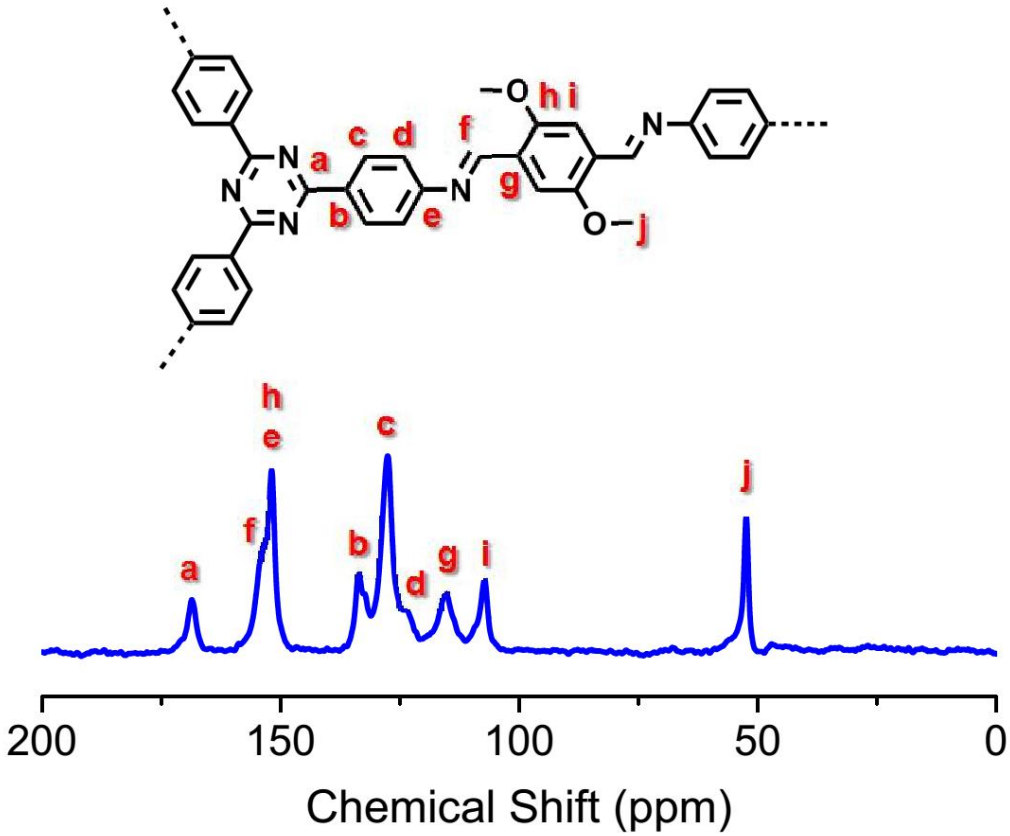


Figure S2. Solid state ^{13}C cross-polarization magic-angel spinning NMR spectrum of COF-JLU5. The assignments of ^{13}C chemical shifts of COF-JLU5 were indicated in the chemical structure. The well-resolved ^{13}C NMR peaks indicates the high crystallinity of COF-JLU5.

6. Electron Micrographs

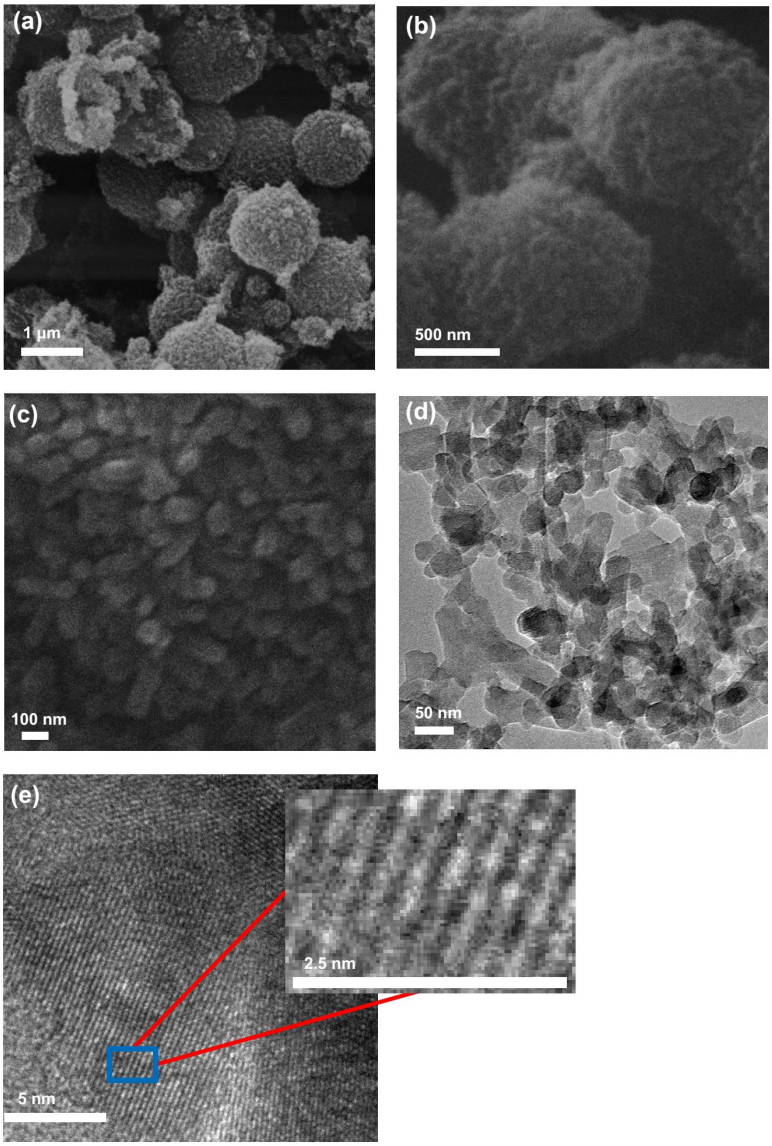


Figure S3. (a-c) The FE-SEM image of COF-JLU5; (d,e) HR-TEM image of COF-JLU5.

7. Thermogravimetric Analysis

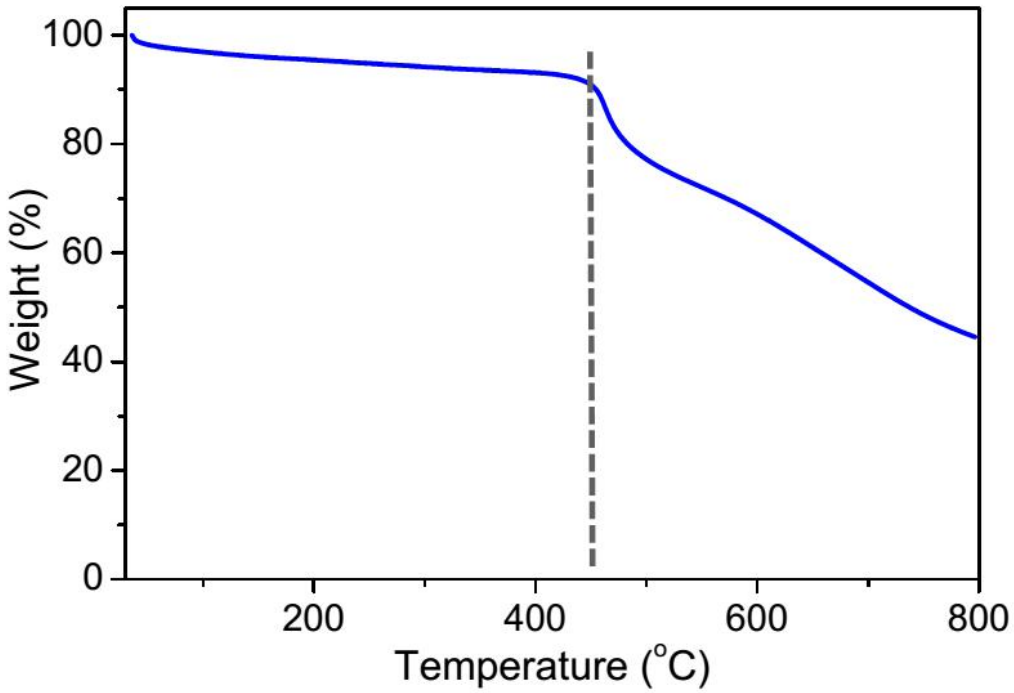


Figure S4. TGA data of COF-JLU5. TGA analysis indicates that COF-JLU5 is thermally stable up to about 445 °C.

8. IR and PXRD Spectra

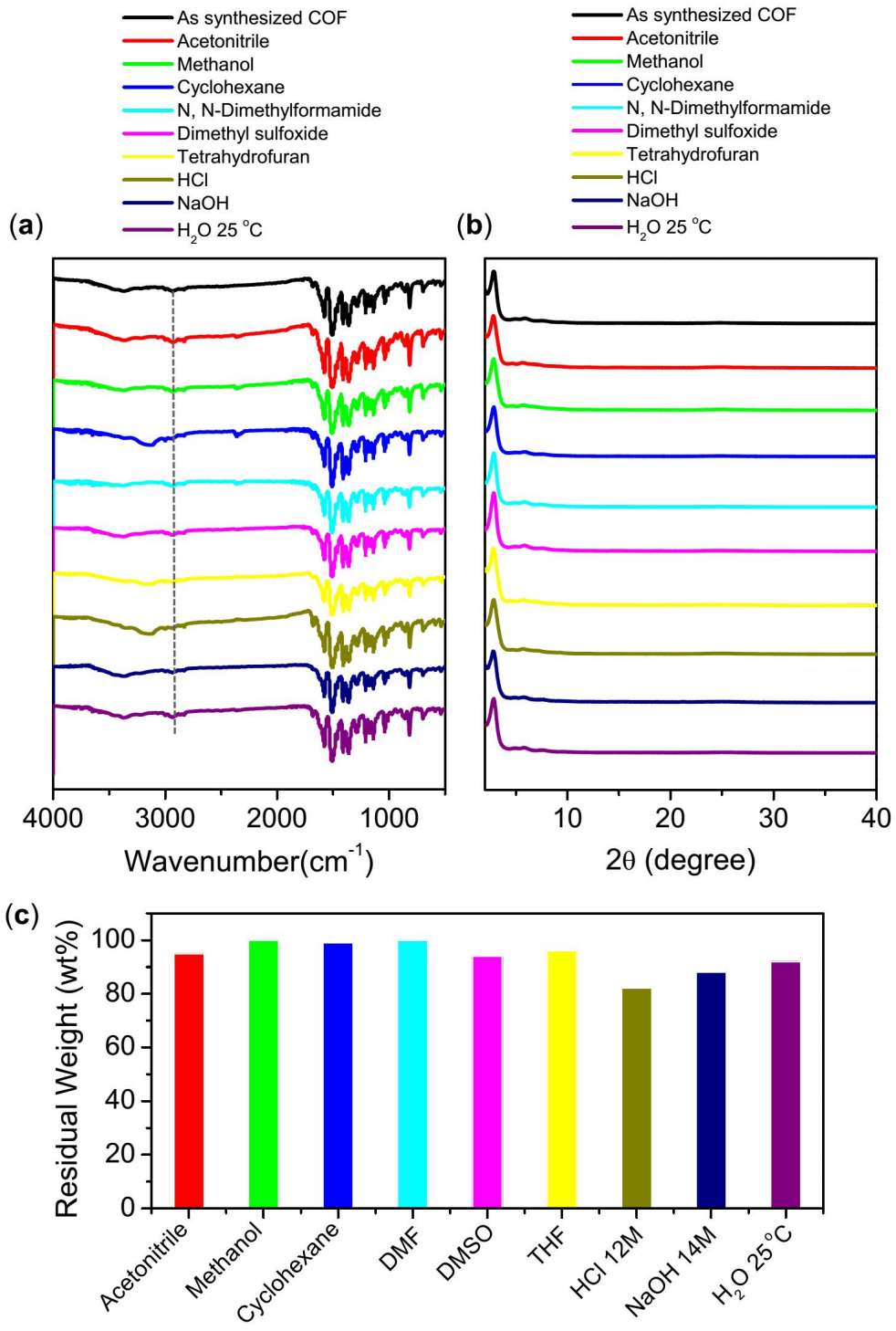


Figure S5. (a) IR spectra of COF-JLU5 after treatment in different solvents; (b) PXRD curves of COF-JLU5 after treatment in different solvents; (c) Residue weight percentage of COF-JLU5 after treatment in different solvents.

9. IR and PXRD Spectra

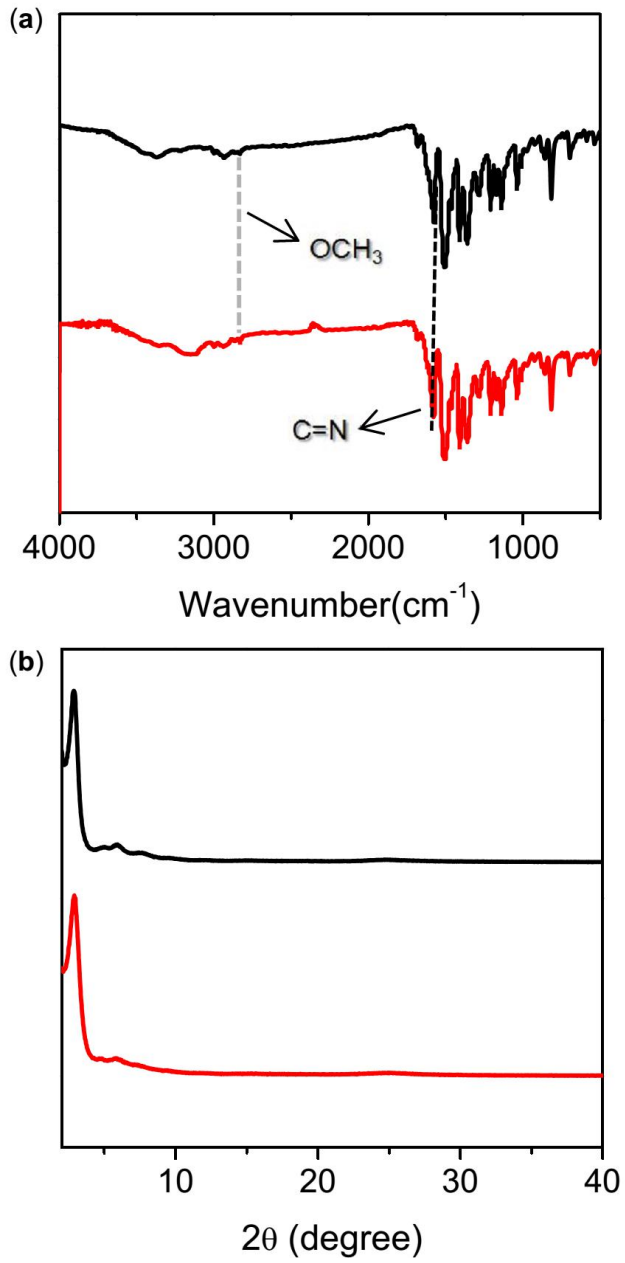


Figure S6. (a) IR spectra of COF-JLU5 (***black line***) and after treatment with light (***red line***); (b) PXRD curves of COF-JLU5 (***black line***) and after treatment with light (***red line***).

10. Electron absorption Spectra

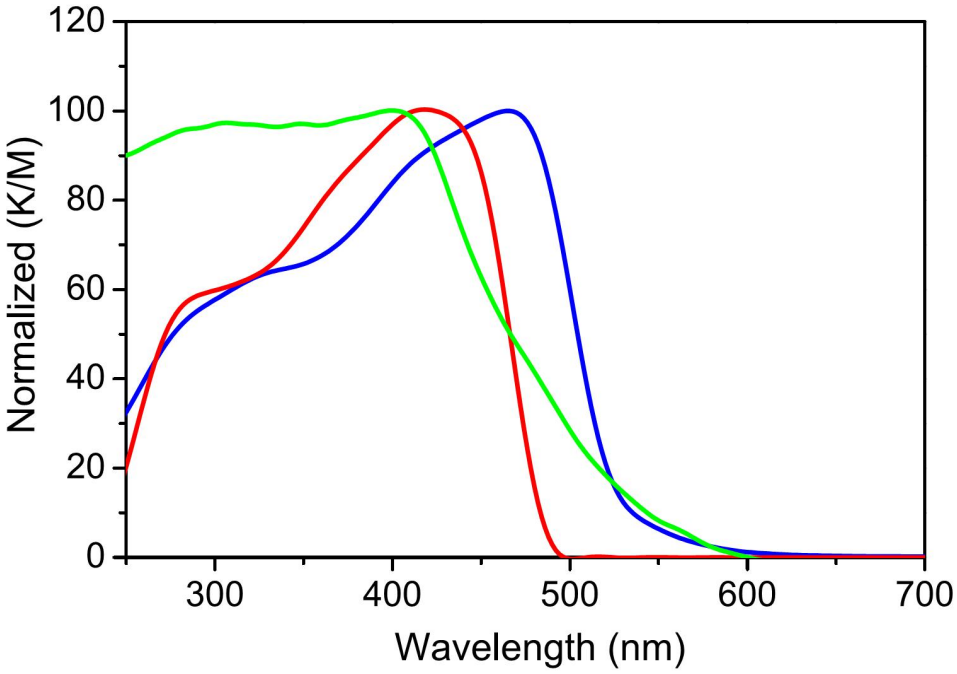


Figure S7. Electron absorption spectra of the COF-JLU5 (***blue line***) and its monomers 1,3,5-tris-(4-aminophenyl)triazine (***green line***) and 2,5-dimethoxyterephthaldehyde (***red line***). Compared with the monomers, the electron absorption spectrum of COF-JLU5 exhibits a rather broad absorption band and obvious red-shift, indicating the extended π-conjugation of COF-JLU5.

11. Kinetic Curves

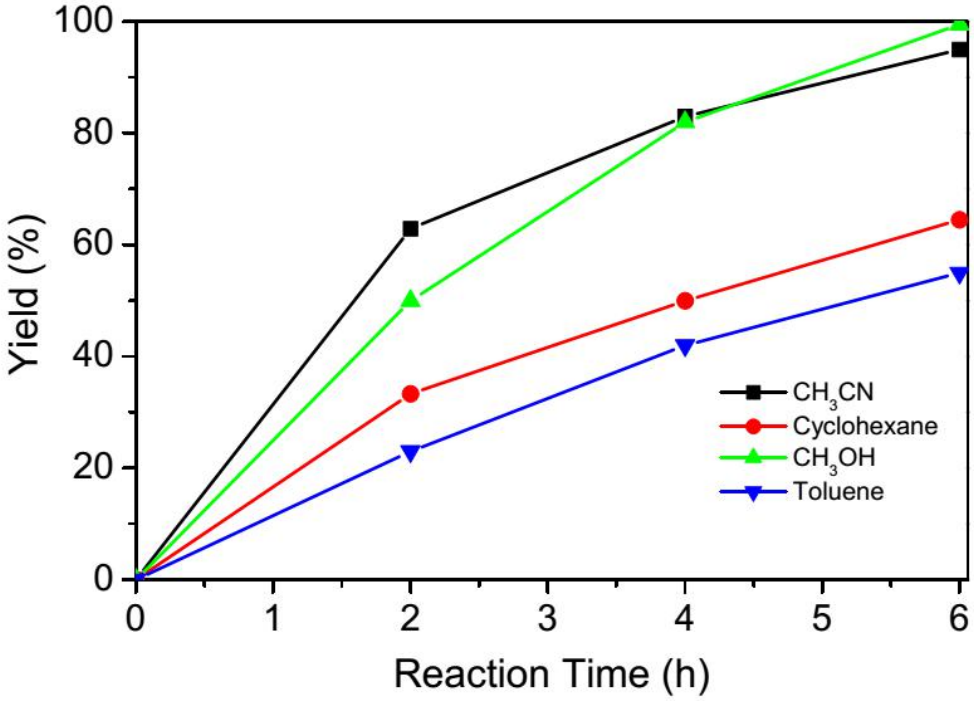


Figure S8. Reaction time vs yield (%) curves for photocatalytic CDC reaction by COF-JLU5 in different solvents. A general process: 2-phenyl-1,2,3,4-tetrahydroisoquinoline (41.8 mg, 0.2 mmol), CH_3NO_2 (32.5 μL, 0.6mmol), COF-JLU5 (4.0 mg) and a corresponding solvent (2.0 mL) were mixed in the reaction tube with magnetic stirring bar. The tube was irradiated by blue LEDs (460 nm, 30W) under air at room temperature for a period of time. The yields detected by ^{1}H-NMR spectroscopy.

12. Recycling Catalysis and Comparative Data

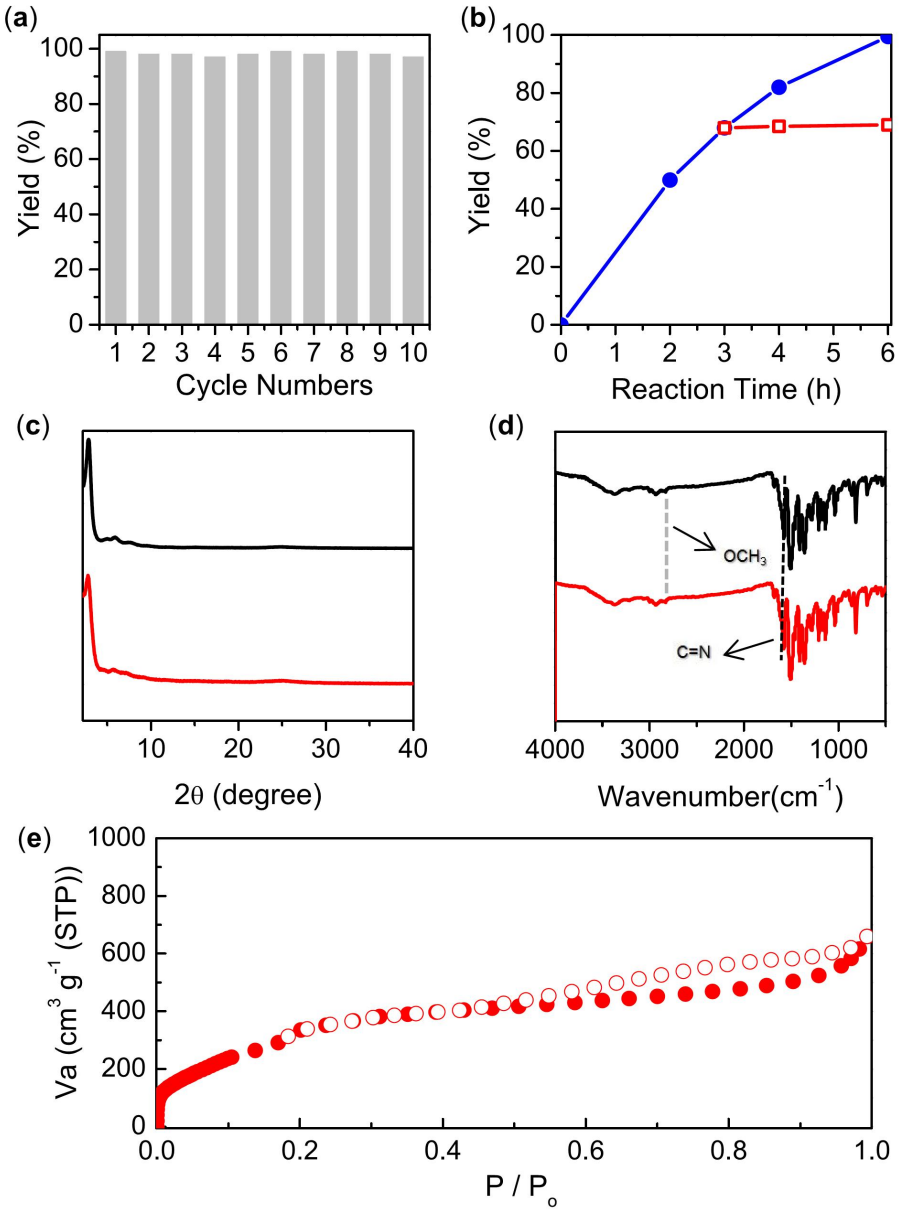


Figure S9. (a) The reusability of COF-JLU5 for aerobic CDC reaction of N-phenyl-1,2,3,4-tetrahydroisoquinoline with nitromethane at 25 °C for 6 h. (b) Reaction time vs yield (%) curve for the CDC reaction at 25 °C (***blue point***), after removing the COF at 68% product formation. (c) PXRD curves of COF-JLU5 before (***black line***) and after the tenth run (***red line***). (d) IR spectra of COF-JLU5 before (***black line***) and after the tenth run (***red line***). (e) Nitrogen sorption isotherm of COF-JLU5 samples after the tenth run (SA_{BET} = 1332 m^2 g^{-1}).

13. ^{1}H NMR Spectrum

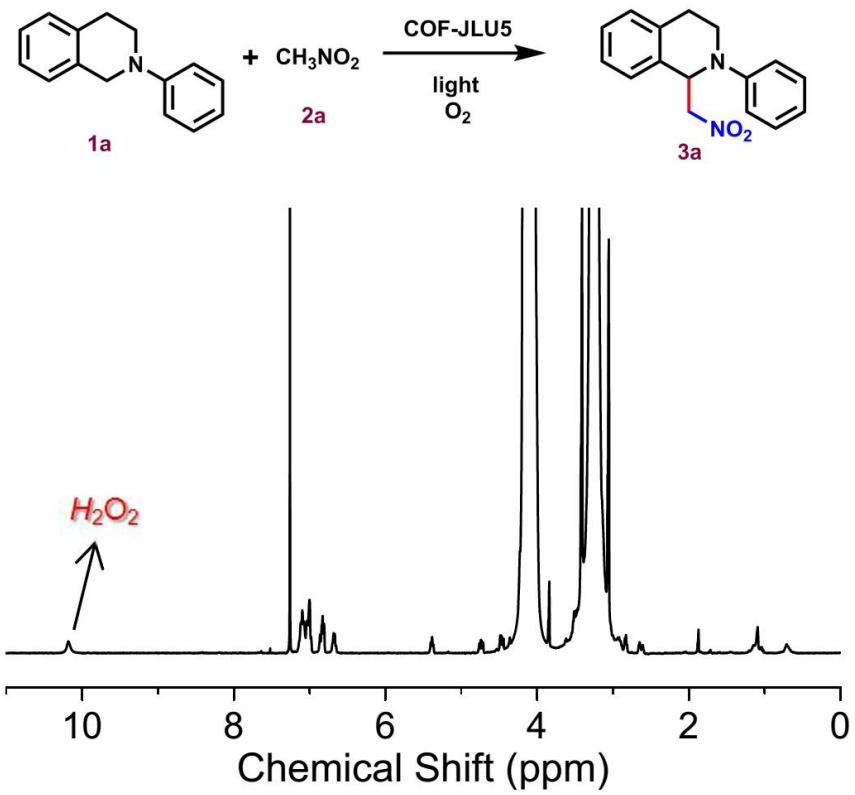
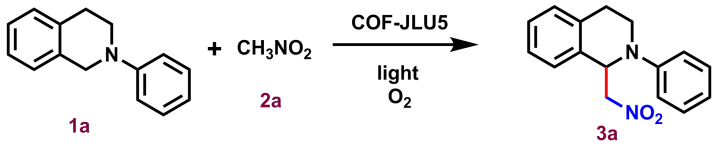


Figure S10. ^{1}H NMR determination of the H_2O_2 generated in the photocatalytic reactions of 3a. The peak at 10.20 ppm is due to H_2O_2 ($CDCl_3$, 400 MHz)

14. Photocatalytic Data

Table S1. The aerobic cross-dehydrogenative coupling reaction of N-aryltetrahydroisoquinolines using COF-JLU5 as photocatalyst[a]



Entry	Solvent	Temp. (°C)	Yield (%)[b]
1	Cyclohexane	25	65
2	Toluene	25	55
3	CH_3CN	25	97
4	Methanol	25	>99
5[c]	Methanol	25	< 1
6[d]	Methanol	25	4
7[e]	Methanol	25	10
8[f]	Methanol	25	42
9[g]	Methanol	25	61

[a]Reaction conditions: COF-JLU5 (4.0 mg), 1a (0.2 mmol), 2a (0.6 mmol), blue LEDs (460 nm, 30 w). The reaction with stirring was conducted in O_2 (1 bar) at 25 °C for 6 h. [b]Yield determined by ^{1}H-NMR using diphenylacetonitrile as an internal standard. [c]In dark, with COF-JLU5 and O_2. [d]No COF-JLU5, but with O_2 and under light irradiation. [e]No O_2, with COF-JLU5, under light irradiation. [f]TPB-DMTP-COF[3] (SA_{BET} = 1710 m^2 g^{-1}) instead of COF-JLU5 as photocatalyst. [g]TFB-COF[4] instead of COF-JLU5 as photocatalyst.

Scheme S1. Large-scale photocatalytic Reaction using COF-JLU5 as a Heterogeneous Photocatalyst.

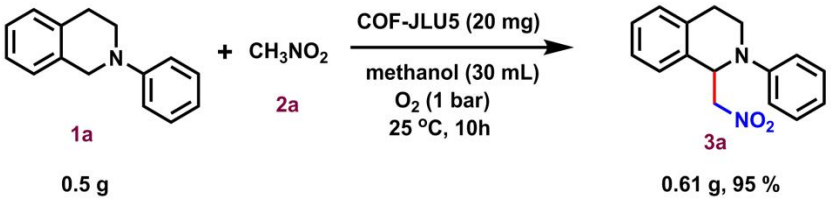


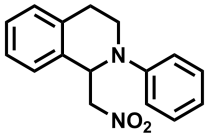
Table S2. Heterogeneous photocatalysis for 2-phenyl-1,2,3,4-tetrahydroisoquinoline with nitromethane reported to date

Catalyst	Solvent	Temp. (°C)	Time (h)	Lamp (w)	Yield (%)	Cycle Performance	SA (m^2/g)	Reference
Metal-Organic Frameworks								
Ir-PCP 1 mol % Ir-based catalyst	CH_3NO_2	R. T.	8	fluorescent lamp 26 W	94	four cycles	1547	*J. Am. Chem. Soc.* **2011**, *133*, 2056
MOF6 1 mol % catalyst	CH_3NO_2	R. T.	12	fluorescent lamp 26 W	86	After 3 cycles, the yield is obvious decreased.	1277	*J. Am. Chem. Soc.* **2011**, *133*, 13445
CRBPY-1 1 mol % catalyst	CH_3NO_2	R. T.	24	fluorescent lamp 18 W	90	After 3 cycles, the yield is slightly decreased, the crystallinity can be well maintained.	No description	*Chem. Sci.* **2015**, *6*, 1035
UiO-68M, 4 mg	CH_3NO_2	R. T.	4	blue LEDs 3 W	90	After 5 cycles, the yield and crystallinity can be maintained.	3500	*Inorg. Chem.* **2016**, *55*, 1005
UiO-68-BP 5 mg	CH_3NO_2	R. T.	3	green LEDs 3 W	89	After 3 cycles, the yield is obvious decreased.	No description	*RSC Adv.* **2016**, *6*, 23995
Porous Organic Polymers (Covalent Organic Frameworks)								
mpg-C_3N_4 15 mg	MeCN (10 equiv CH_3NO_2)	R. T.	22	cool daylight bulb 60 W	100	No description	No description	*Adv. Synth. Catal.* **2012**, *354*, 1909
Ru-CP 0.2 mol % catalyst	CH_3NO_2	R. T.	8	fluorescent lamp 26 W	97	No description	2.9	*ACS Appl. Mater. Interfaces* **2012**, *4*, 2288
1 0.2 mol % catalyst	CH_3NO_2	R. T.	8	fluorescent lamp 26w	85	No description	198	*ACS Catal.* **2012**, *2*, 417
RB-CMP1 2 mol % catalyst	CH_3NO_2	R. T.	15	household bulb 60 W	95	After 10 cycles, the yield is slightly decreased	833	*Macromolecules* **2013**, *46*, 8779
CPOP20 2 mol % catalyst	CH_3NO_2	R. T.	15	Bulb 23 W	88	After 3 cycles, the yield can be well maintained.	460	*Polym. Chem.* **2016**, *7*, 2299
EY-POP-1 10 mg	CH_3NO_2	R. T.	24	Household bulb 14 W	98	After 12 cycles, the yield and structure can be well maintained.	587	*RSC Adv.* **2017**, *7*, 408
TFB-COF 30 mg	CH_3NO_2	R. T.	36	energy-saving lamp 45 W	87	After 4 cycles, the yield and crystallinity are obvious decreased	1501	*ChemSusChem* **2017**, *10*, 664
COF-JLU5 4 mg	MeOH (3 equiv CH_3NO_2)	R. T.	6	blue LEDs 30 W	99	After 10 cycles, the yield and crystallinity can be well maintained.	1632	**This work**
Metallic Oxide								
TiO_2 (P25) 1 equiv	EtOH (10 equiv CH_3NO_2)	R. T.	40	fluorescent lamp 11 W	93	After 5 cycles, the yield and structure can be well maintained.	No description	*Chem. Eur. J.* **2012**, *18*, 3478
LP-Cu_2O (2 mg)	CH_3NO_2	R. T.	8	blue LEDs 4 W	90.3	After 5 cycles, the yield is slightly decreased, structure can be well maintained.	63.4	*Chem. Commun.* **2014**, *50*, 14237

Table S3. Homogeneous photocatalysis for 2-phenyl-1,2,3,4-tetrahydroisoquinoline with nitromethane reported to date

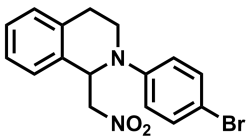
Catalyst	Solvent	Temp. (°C)	Time (h)	Lamp (w)	Yield (%)	Reference
Dye Molecules						
Eosin Y 2 mol %	CH_3NO_2	R. T.	8	green LEDs 1 W	80	*Org. Lett.* **2011***, 13, 3852.*
Rose Bengal 5 mol %	CH_3NO_2	R. T.	20	green LEDs 5 W	100	*Green Chem.* **2011**, *13*, 2682
TBA-eosin Y 2 mol %	CH_3NO_2	R. T.	4	High pressure mercury lamp 500 W	92	*Chem. Eur. J.* **2012**, *18*, 620
B-1 1 mol %	CH_3NO_2	R. T.	3	Xenon lamp 35 W	86	*RSC Adv.* **2013**, *3*, 23377
I_2 5 mol %	MeCN (5 equiv CH_3NO_2)	R. T.	12	fluorescent lamp 22 W	84	*RSC Adv.* **2013**, *3*, 10189
2-Cl-AQN 7 mol %	MeOH (5 equiv CH_3NO_2)	R. T.	20	green LEDs 5 W	80	*Synlett* **2014**, *25*, 1453
B-1 1 mol %	CH_3NO_2	R. T.	3	White LEDs 3 W	80	*Chem. Commun.* **2015**, *51*, 11256
Metal Complexes						
$Ir(ppy)_2(dtbbpy)PF_6$ 1.5 mol %	CH_3NO_2	R. T.	10	fluorescent lamp 15 W	92	*J. Am. Chem. Soc.* **2010**, *132*, 1464
$Ru(bpy)_3$-Cl_2 0.01 mol %	CH_3NO_2	R. T.	3	Blue LEDs 1W	95	*Org. Lett.* **2012***, 14,* 94
$PdF_{20}TPP$ 0.01 mol %	CH_3NO_2	R. T.	8	Xe lamp 300 W	91	*Chem. Eur. J.* **2013**, *19*, 5654
[Ir(piq)2(Hdpa)][PF6] 1 mol %	CH_3NO_2	R. T.	11	blue LED 2.4 W/m	69	*Org. Chem. Front.* **2014**, *1*, 639
C-1a 1 mol %	CH_3NO_2	R. T.	50 h	60 W cool daylight bulb	87	*Org. Chem. Front.* **2015**, *2*, 141
Cu3 1.5 mol %	CH_3NO_2	R. T.	8	Xenon lamp 300 W	91	*Chem. Eur. J.* **2015**, *21*, 1184
Pt3 1.5 mol %	CH_3NO_2	R. T.	8	Xe lamp 100 W	94	*ChemPlusChem* **2015**, 80, 1541
Gd-4 0.5 mol %	CH_3NO_2	R. T.	6	Xe lamp 500 W	66	*Chem. Eur. J.* **2016**, *22*, 9676

Section 15. Characterization Data of Catalytic Products



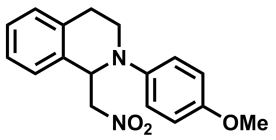
1-Nitromethyl-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3a)

^{1}H NMR ($CDCl_3$, 400 MHz): δ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.12 (m, 6H), 6.99 (d, J = 8.0 Hz, 2H), 6.86 (t, J = 7.1 Hz, 1H), 5.56 (t, J = 7.0 Hz, 1H), 4.94–4.82 (m, 1H), 4.57 (dd, J = 11.6, 6.7 Hz, 1H), 3.73–3.55 (m, 2H), 3.16–3.02 (m, 1H), 2.80 (d, J = 16.3 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.6, 135.4, 133.1, 129.6, 129.3, 128.3, 127.1, 126.8, 119.6, 115.2, 78.9, 58.3, 53.5, 42.2, 29.8 and 26.6 ppm.



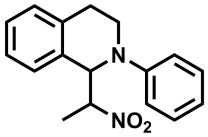
2-(4-Bromophenyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline (3b)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38–7.32 (m, 2H), 7.30–7.13 (m, 4H), 6.85 (t, J = 6.2 Hz, 2H), 5.53–5.47 (m, 1H), 4.84 (dd, J = 12.0, 8.1 Hz, 1H), 4.57 (dd, J = 12.0, 6.4 Hz, 1H), 3.65–3.59 (m, 2H), 3.13–3.02 (m, 1H), 2.79 (dt, J = 16.4, 4.8 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.6, 135.1, 132.5, 132.3, 129.4, 128.4, 127.0, 116.8, 111.6, 78.7, 58.2, 42.1 and 26.3 ppm.



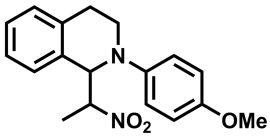
2-(4-Methoxyphenyl)-1-nitromethyl-1,2,3,4-tetrahydroisoquinoline (3c)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28–7.13 (m, 4H), 6.96–6.90 (m, 2H), 6.86–6.80 (m, 2H), 5.40 (dd, J = 8.6, 5.9 Hz, 1H), 4.83 (dd, J = 11.9, 8.6 Hz, 1H), 4.57 (dd, J = 11.9, 5.8 Hz, 1H), 3.76 (s, 3H), 3.61–3.54 (m, 2H), 3.02 (ddd, J = 16.2, 9.3, 6.7 Hz, 1H), 2.70 (dt, J = 16.6, 4.0 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.1, 143.2, 135.5, 133.0, 129.6, 128.0, 127.0, 126.7, 119.0, 114.8, 79.1, 59.0, 55.7, 43.2 and 25.9 ppm.



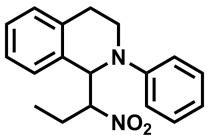
1-(1-Nitroethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3d)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30–7.10 (m, 6H), 7.00 (t, J = 7.9 Hz, 2H), 6.83 (m, 1H), 5.25 (t, J = 8.8 Hz, 1H), 5.10–4.85 (m, 1H), 3.89–3.52 (m, 2H), 3.12–2.83 (m, 2H), 1.63 (dd, J = 58.5, 5.6 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.2 , 148.9, 135.7, 132.1, 129.5, 129.2, 128.8, 128.4, 127.3, 126.7, 126.2, 119.4 , 118.9, 115.5, 114.6, 89.1, 85.5, 62.8, 61.3, 43.6, 42.8, 26.8, 26.5, 17.5 and 16.5 ppm.



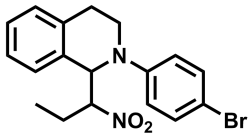
2-(4-Methoxyphenyl)-1-(1-Nitroethyl)-2-phenyl-1,2,3,4-tetra hydroisoquinoline (3e)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28–7.09 (m, 4H), 6.92 (t, J = 6.3 Hz, 2H), 6.86–6.77 (m, 2H), 5.09–4.83 (m, 2H), 3.77–3.73 (m, 3H), 3.58–3.46 (m, 1H), 2.99 (ddd, J = 15.2, 9.2, 5.9 Hz, 1H), 2.87–2.74 (m, 1H), 1.68 (d, J = 6.8 Hz, 1H), 1.54 (d, J = 6.1 Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.9, 143.6, 135.9, 132.2, 129.4, 129.1, 128.5, 128.12 (d, J = 4.0 Hz), 127.3, 126.6, 126.2, 119.0, 118.3, 114.75 (d, J = 12.5 Hz), 88.9, 85.9, 63.6, 62.3, 55.70 (d, J = 5.5 Hz), 45.1, 44.1, 26.4, 26.1, 17.2, 16.7 ppm.



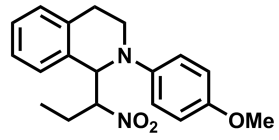
1-(1-Nitropropyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3f)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30 (d, J = 8 Hz, 2H), 6.89 (d, J = 8 Hz, 2H), 4.49 (dd, J = 8 Hz, J = 4 Hz, 1H), 4.20 (d, J = 16 Hz, 1H), 4.09 (d, J = 12 Hz, 1H), 2.28-2.35 (m, 1H), 2.06 (d, J = 16 Hz, 1H), 1.69 (s, 1H), 1.59 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.9, 134.8, 127.1, 124.5, 123.8, 113.7, 75.9, 70.3, 38.4, 18.3 and 13.8 ppm.



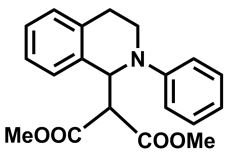
2-(4-Bromophenyl)-1-(1-Nitropropyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3g)

^{1}H NMR ($CDCl_3$, 400 MHz): δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.12 (m, 6H), 7.01 (t, J = 7.2 Hz, 1H), 6.88–6.77 (m, 2H), 5.18-5.07 (m, 1H), 4.87–4.62 (m, 1H), 3.88–3.42 (m, 2H), 3.11-2.85 (m, 2H), 2.23–1.99 (m, 2H), 1.81-1.76 (m) 2H, 0.96-0.91 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.2, 148.1, 135.4, 134.6, 133.7, 132.51–131.95 (t), 129.5, 128.8, 128.5 (d, J = 1.8 Hz), 127.3, 126.9, 126.2, 117.5, 115.8, 111.6, 96.1, 93.1, 62.3, 60.8, 43.8, 42.6, 26.9, 25.8, 25.1, 24.8, 10.8 ppm.



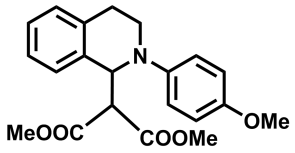
2-(4-Methoxyphenyl)-1-(1-Nitropropyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (3h)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29–7.12 (m, 4H), 6.84 (m, 4H), 4.97 (dd, J = 44.2, 9.3 Hz, 1H), 4.87–4.62 (m, 1H), 3.86–3.43 (m, 5H), 3.06–2.72 (m, 2H), 2.22–1.76 (m, 2H), 1.00–0.88 (m, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): 153.8, 143.9, 135.9, 135.0, 133.9, 132.6, 129.6, 128.9 (d, J = 9.5 Hz), 128.2, 126.7, 126.0, 119.2, 117.6, 114.9, 114.6, 96.2, 93.4, 63.1, 61.7, 55.7 (d, J = 10.3 Hz), 44.8, 43.7, 26.4, 25.4, 25.1, 24.8 and 10.83 (d, J = 7.2 Hz) ppm.



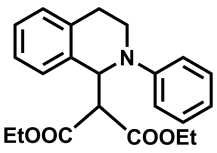
Dimethy-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate (3i)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.23–7.08 (m, 6H), 6.99 (d, J = 8.3 Hz, 2H), 6.77 (t, J = 7.2 Hz, 1H), 5.71 (d, J = 9.4 Hz, 1H), 3.94 (d, J = 9.3 Hz, 1H), 3.66 (s, 3H), 3.55 (s, 3H), 3.08 (ddd, J = 15.6, 8.7, 6.5 Hz, 1H), 2.88 (dt, J = 16.5, 5.1 Hz, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.4 , 167.5, 148.9, 135.8, 134.9, 129.2, 127.8, 127.2, 126.2, 118.8, 115.3, 76.8, 59.2, 58.3, 52.7, 42.3 and 26.2 ppm.



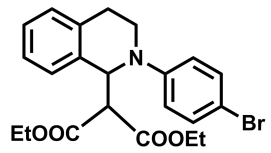
Dimethy-2-(2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate (3j)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.23–7.07 (m, 4H), 6.91 (d, J = 9.0 Hz, 2H), 6.77 (dd, J = 9.0 Hz, 2H) 5.49 (d, J = 9.4 Hz, 1H), 3.96 (d, J = 9.4 Hz, 1H), 3.73 (s, 3H), 3.62 (d, J = 11.3 Hz, 6H), 3.01 (m, 1H), 2.76 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.4, 167.7, 153.4, 143.6, 135.5, 134.9, 129.3, 127.6, 127.2, 126.1, 118.4, 114.6, 59.3 (d, J = 3.1 Hz), 55.7, 52.6 (d, J = 5.3 Hz), 43.2, 25.6 ppm.



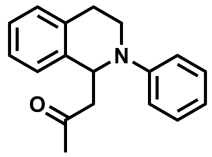
Diethyl-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate (3k)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24–7.07(m, 6H), 6.98 (d, J = 8.2 Hz, 2H), 6.74 (t, J = 7.3 Hz, 1H), 5.72 (d, J = 9.2 Hz, 1H), 4.17–3.93 (m, 4H), 3.89 (d, J = 9.2 Hz, 1H), 3.74–3.59 (m, 2H), 3.07 (m, 1H), 2.88 (m, 1H), 1.16 (t, J = 7.1 Hz, 3H), 1.08 (t, J = 7.1 Hz, 3H).^{13}C NMR ($CDCl_3$, 100 MHz): δ 168.1, 167.2, 148.9, 136.1, 134.9, 129.1, 127.6, 127.3, 126.1, 118.6, 115.2, 61.7, 59.7, 58.0, 42.4, 41.8, 26.2, 14.3, 13.9 ppm.



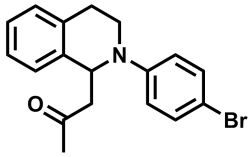
Diethyl-2-(2-(4-Bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate (3l)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32–7.13(m, 6H), 6.88 (d, J = 9.0 Hz, 2H), 5.69 (d, J = 9.3 Hz, 1H), 4.23–3.96 (m, 4H), 3.89 (d, J = 9.3 Hz, 1H), 3.75–3.53 (m, 2H), 3.14-2.89 (m, 2H), 1.20 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H).^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.9 , 167.1 , 147.9 , 135.8 , 134.7 , 131.9 , 129.0 , 127.8 , 127.2 , 126.3 , 116.5 , 110.4 , 61.8 , 59.6 , 57.9 , 42.6 , 26.2 , 14.0 ppm



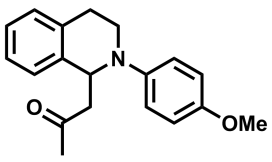
1-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (3m)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28–7.10 (m, 6H), 6.93 (d, J = 8.3 Hz, 2H), 6.77 (t, J = 7.2 Hz, 1H), 5.39 (t, J = 6.3 Hz, 1H), 3.68–3.60 (m, 1H), 3.56–3.47 (m, 1H), 3.09–2.99 (m, 2H), 2.86–2.76 (m, 2H), 2.06 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.4, 149.0, 138.4, 134.5, 129.5, 128.8, 126.9, 126.4, 118.4, 114.9, 54.9, 50.3, 42.2, 31.2 and 27.3 ppm.



1-(2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (3n)

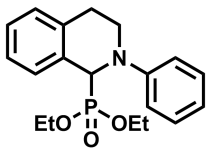
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 (d, J = 9.0 Hz, 2H), 7.21–7.12 (m, 4H), 6.81 (d, J = 8.9 Hz, 2H), 5.35 (t, J = 6.3 Hz, 1H), 3.55 (tdd, J = 12.8, 10.6, 5.1 Hz, 2H), 3.09–2.99 (m, 2H), 2.88–2.79 (m, 2H), 2.09 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.1, 147.9, 138.0, 134.3, 132.1, 128.8, 127.0, 126.5, 116.2, 110.1, 54.7, 50.2, 42.2, 31.3, 27.1 ppm.



1-(2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (3o)

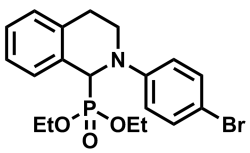
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.20–7.10 (m, 4H), 6.93 (d, J = 9.0 Hz, 2H), 6.83 (d, J = 9.0 Hz, 2H), 5.27 (t, J = 6.4 Hz, 1H), 3.76 (s, 3H), 3.61–3.53 (m, 1H), 3.51–3.43 (m, 1H), 3.06–2.97 (m, 2H), 2.76 (ddd, J = 14.7, 10.3, 5.0 Hz, 2H), 2.07 (s, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 207.4, 153.3, 143.7, 138.3, 134.4, 129.0, 126.8, 126.2, 118.4, 114.7, 56.0, 55.6, 50.0, 42.9, 30.9 and 26.8 ppm.

Diethyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (3p)

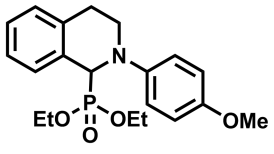


^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37 (m, 1H), 7.27–7.15 (m, 5H), 6.98 (d, J = 8.3 Hz, 2H), 6.79 (t, J = 7.2 Hz, 1H), 5.19 (d, J = 20.0 Hz, 1H), 4.18–3.82 (m, 5H), 3.69–3.58 (m, 1H), 3.17–2.92 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.5 (d, J = 5.8 Hz), 136.6 (d, J = 5.5 Hz), 130.8, 129.3 (s), 128.9 (d, J = 2.5 Hz), 128.3 (d, J = 4.6 Hz), 127.6 (d, J = 3.4 Hz), 126.0 (d, J = 2.8 Hz), 118.58, 114.91, 63.4 (d, J = 7.1 Hz), 62.5 (d, J = 7.7 Hz), 59.8, 58.2, 43.6, 26.9, 16.6 (d, J = 5.5 Hz), 16.4 (d, J = 6.1 Hz) ppm.

Diethyl (2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (3q)



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38–7.30 (m, 3H), 7.25–7.14 (m, 3H), 6.89–6.80 (m, 2H), 5.10 (d, J = 19.2 Hz, 1H), 4.11–3.82 (m, 5H), 3.57–3.50 (m, 1H), 3.20–3.11 (m, 1H), 3.02–2.92 (m, 1H), 1.24 (t, J = 7.1 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.43 (d, J = 4.9 Hz), 136.4 (d, J = 5.4 Hz), 131.9, 130.5, 128.8 (d, J = 2.6 Hz), 128.3 (d, J = 4.8 Hz), 127.8 (d, J = 3.4 Hz), 126.1 (d, J = 2.7 Hz), 116.2, 110.4, 63.4 (d, J = 7.3 Hz), 62.6 (d, J = 7.7 Hz), 59.7, 58.1, 43.8, 27.1, 16.48 (d, J = 5.4 Hz), 16.38 (d, J = 5.8 Hz) ppm.

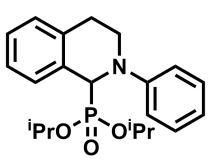


Diethyl-(2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoli n-1-yl)phosphonate (3s)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39 (d, J = 5.9 Hz, 1H), 7.23–7.09 (m, 3H), 6.92 (d, J = 9.0 Hz, 2H), 6.81 (d, J = 9.0 Hz, 2H), 5.03 (d, J = 21.5 Hz, 1H), 4.23–3.85 (m, 5H), 3.74 (s, 3H), 3.61–3.43 (m, 1H), 2.93 (s, 2H), 1.25 (t, J = 7.0 Hz, 3H), 1.16 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ

153.2, 144.2 (d, J = 8.2 Hz), 136.5 (d, J = 5.8 Hz), 130.6, 129.0 (d, J = 2.5 Hz), 128.2 (d, J = 4.4 Hz), 127.3 (d, J = 3.5 Hz), 125.9 (d, J = 2.9 Hz), 117.6, 114.6, 63.38 (d, J = 7.2 Hz), 62.27 (d, J = 7.6 Hz), 60.3, 58.7, 55.7, 44.7, 26.2, 16.50 (dd, J = 9.8, 5.7 Hz) ppm.

Diisopropyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (3t)



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37 (d, J = 7.1 Hz, 1H), 7.23–7.10 (m, 5H), 6.98 (d, J = 8.3 Hz, 2H), 6.79 (t, J = 7.2 Hz, 1H), 5.19 (d, J = 20.0 Hz, 1H), 4.62–4.55 (m, 2H), 4.13–3.98 (m, 1H), 3.67–3.60 (m, 1H), 3.09–2.90 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H).0.94 (d, J = 6.2 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.6 (d, J = 6.6 Hz), 136.5 (d, J = 5.6 Hz), 130.9, 129.1, 128.8 (d, J = 2.5 Hz), 128.5 (d, J = 4.6 Hz), 127.3 (d, J = 3.4 Hz), 125.7 (d, J = 2.8 Hz), 118.3, 115.1, 72.3 (d, J = 7.7 Hz), 70.9 (d, J = 8.2 Hz), 59.6, 58.0, 43.6, 26.6, 24.7 (d, J = 2.8 Hz), 24.2 (d, J = 3.2 Hz), 23.8 (d, J = 5.7 Hz), 23.4 (d, J = 5.6 Hz) ppm.

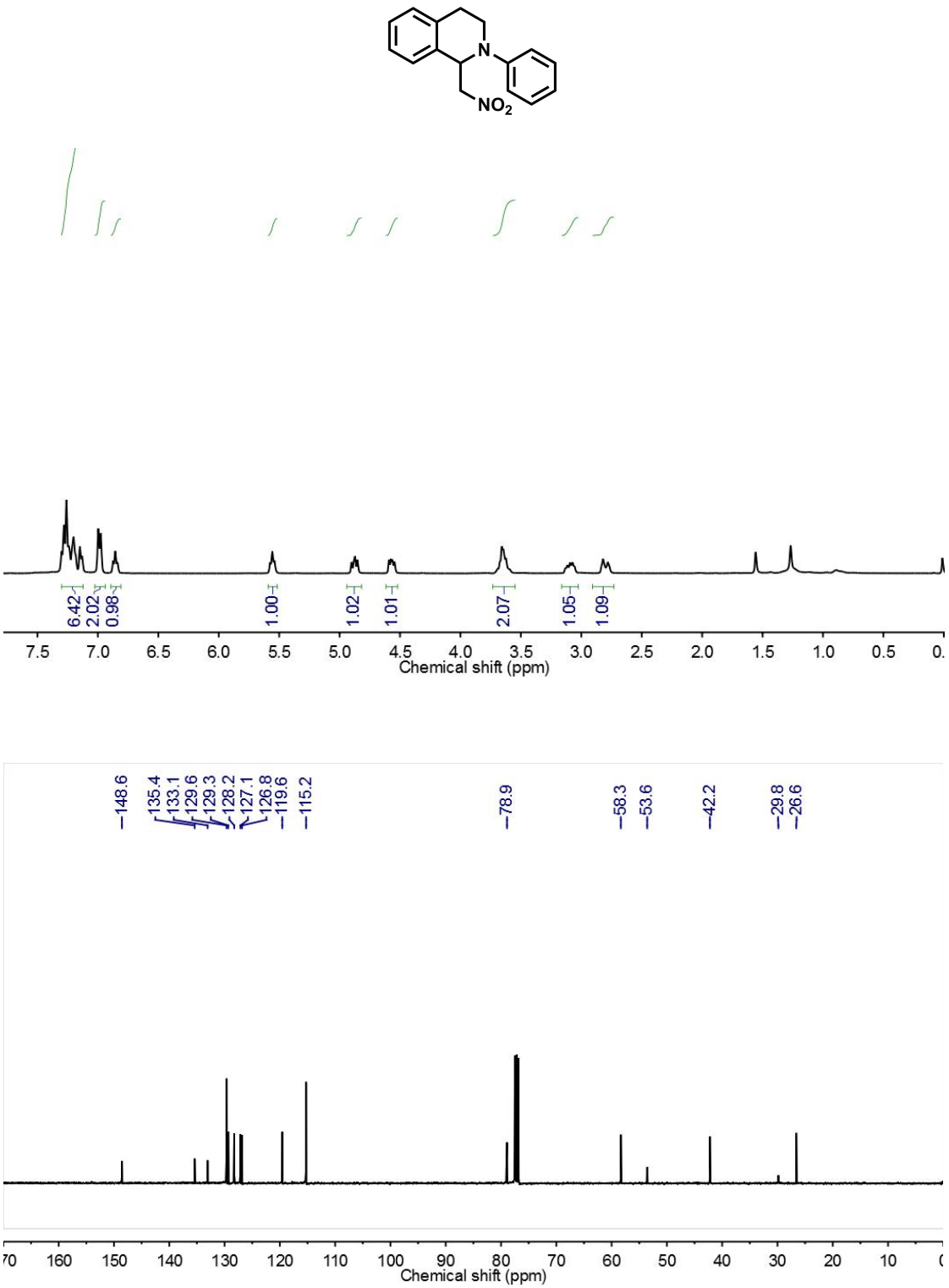
Diisopropyl(2-(4-bromophenyl)-1,2,3,4-tetrahydroisoquinoli n-1-yl)phosphonate (3u)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38 (d, J = 7.0 Hz, 1H), 7.33–7.27 (m, 2H), 7.23–7.12 (m, 3H), 6.86–6.79 (m, 2H), 5.05 (d, J = 20.3 Hz, 1H), 4.66–4.54 (m, 2H), 4.04–3.95 (m, 1H), 3.61–3.52 (m, 1H), 3.16–3.06 (m, 1H), 3.01–2.90 (m, 1H), 1.33–1.24 (m, 6H), 1.15 (d, J = 6.2 Hz, 3H), 0.94 (d, J = 6.2 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.6 (d, J = 5.6 Hz), 136.4 (d, J = 5.4 Hz), 131.8, 130.8, 128.7 (dd, J = 21.8, 3.7 Hz), 127.6 (d, J = 3.4 Hz), 125.9 (d, J = 2.7 Hz), 116.5, 110.2, 72.4 (d, J = 7.8 Hz), 71.2 (d, J = 8.2 Hz), 59.7, 58.1, 43.7, 26.9, 24.7 (d, J = 3.0 Hz), 24.3 (d, J = 3.2 Hz), 23.9 (d, J = 5.6 Hz), 23.5 (d, J = 5.4 Hz) ppm.

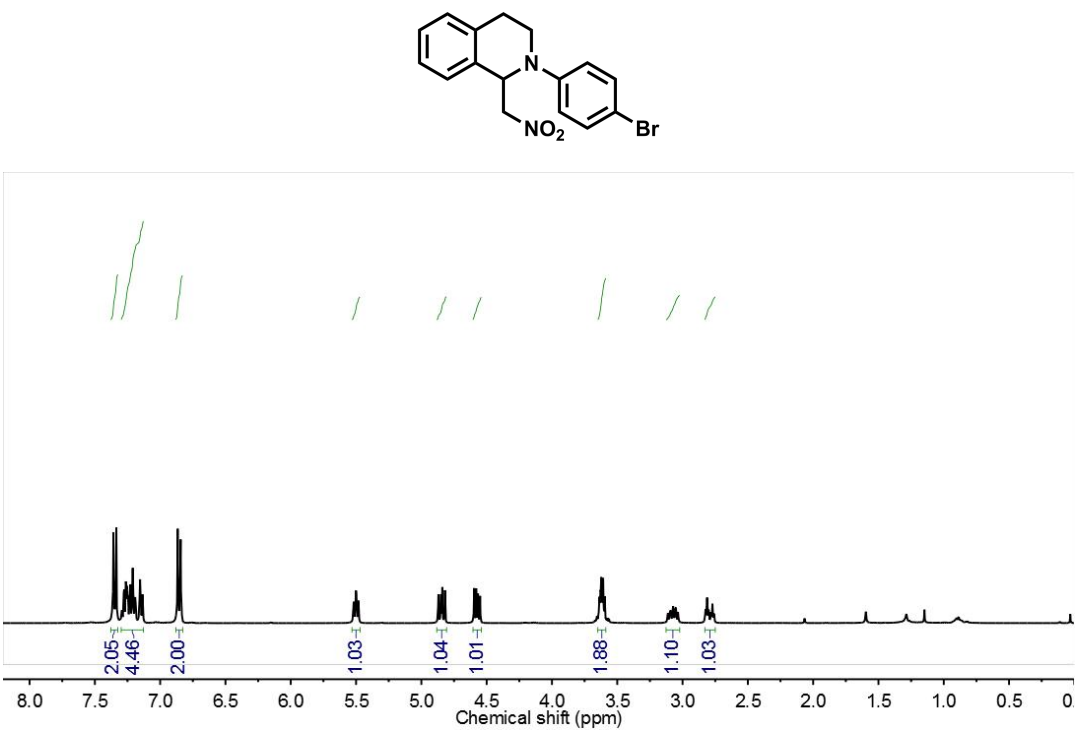
Diisopropyl(2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (3v)

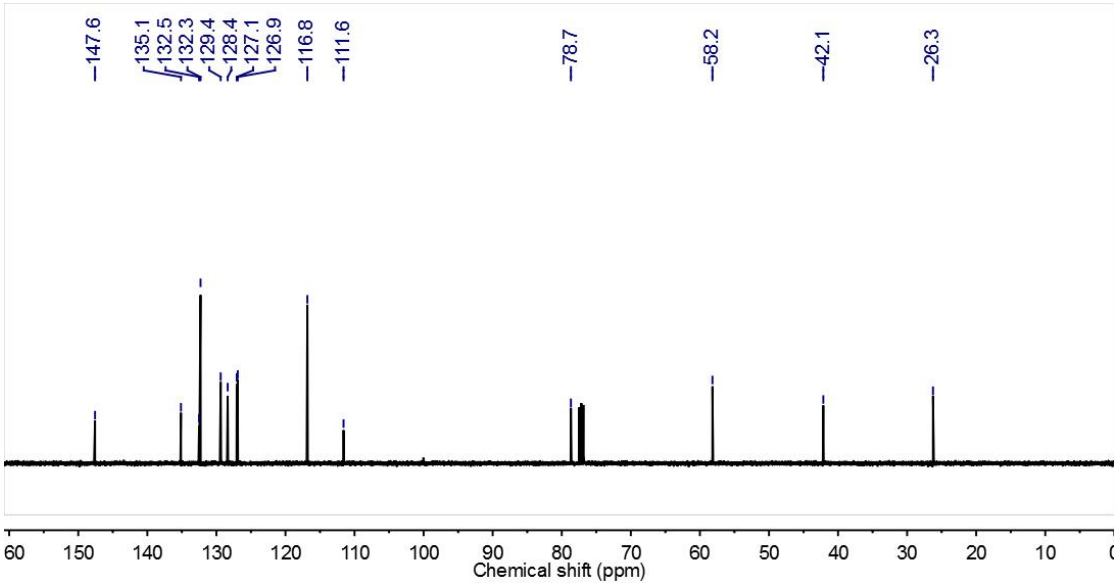
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46–7.38 (m, 1H), 7.17–7.1 (m, 3H), 6.92–6.86 (m, 2H), 6.82–6.75 (m, 2H), 4.96 (d, J = 22.9 Hz, 1H), 4.72–4.56 (m, 2H), 4.13–4.02 (m, 1H), 3.73 (s, 3H), 3.56 (dt, J = 12.9, 4.7 Hz, 1H), 2.95–2.80 (m, 2H), 1.34–1.27 (m, 6H), 1.18 (d, J = 6.2 Hz, 3H), 1.00 (d, J = 6.2 Hz, 3H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.04, 144.4 (d, J = 9.5 Hz), 136.5 (d, J = 5.8 Hz), 130.8, 128.9 (d, J = 2.4 Hz), 128.6 (d, J = 4.3 Hz), 127.2 (d, J = 3.5 Hz), 125.6 (d, J = 2.9 Hz), 117.9, 114.4, 72.2 (d, J = 7.7 Hz), 70.8 (d, J = 8.1 Hz), 60.2, 58.6, 55.6, 44.8, 25.87 (s), 24.7 (d, J = 2.7 Hz), 24.2 (d, J = 3.2 Hz), 23.8 (d, J = 5.7 Hz), 23.5 (d, J = 5.7 Hz) ppm.

Section 16. NMR Spectra of Catalytic Products

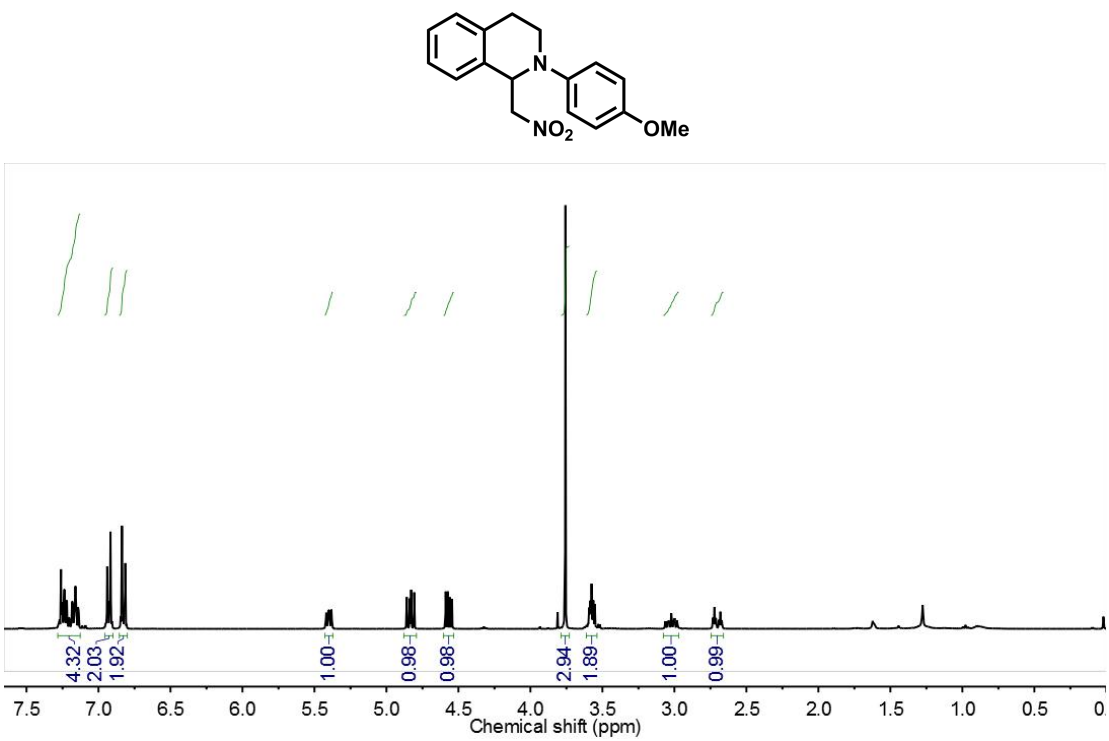


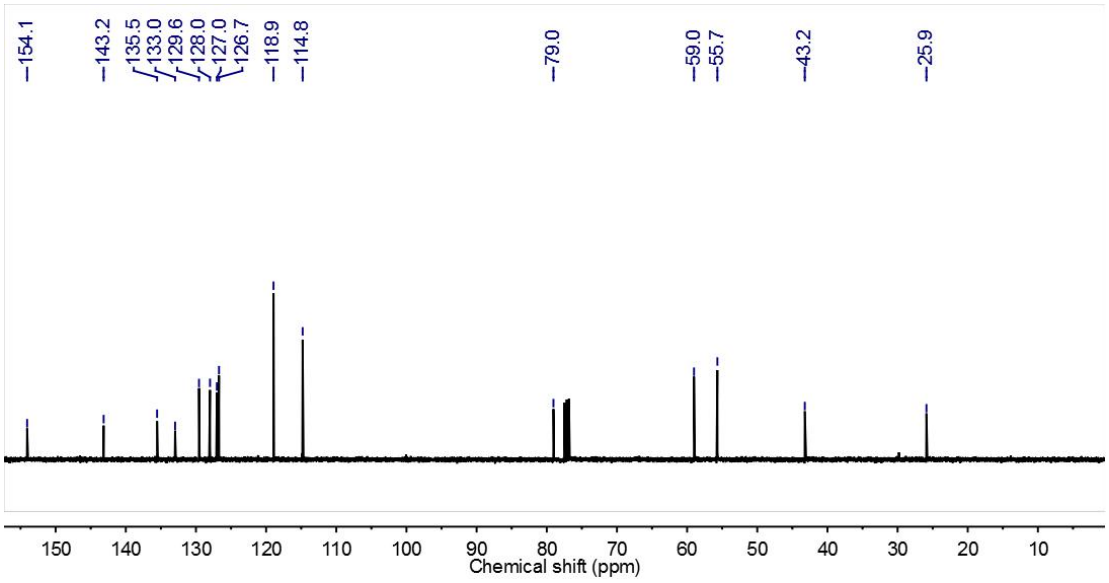
The ^{1}H-NMR and ^{13}C-NMR spectra of **3a**.



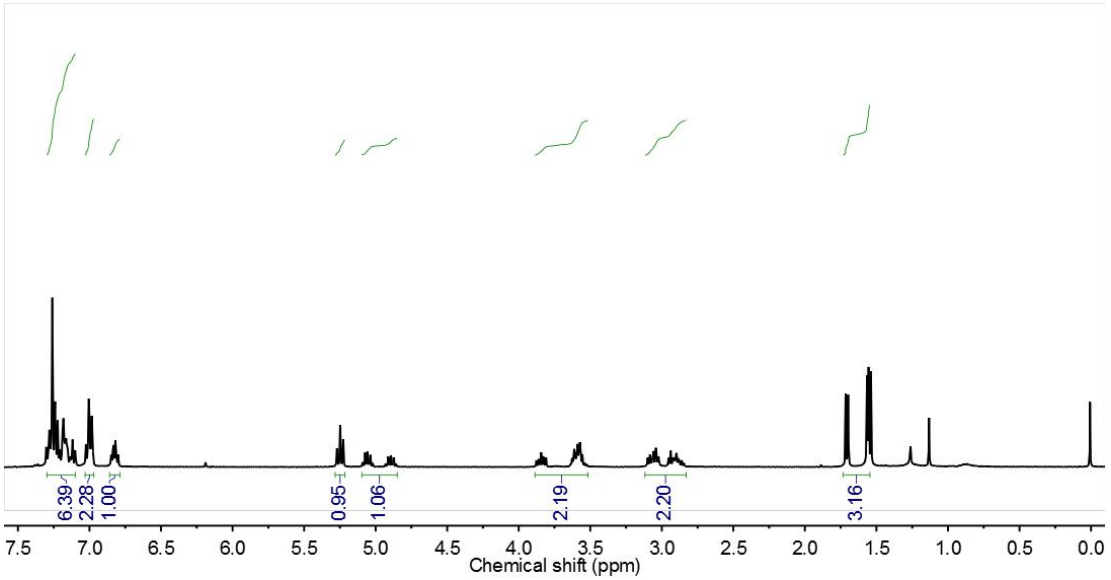


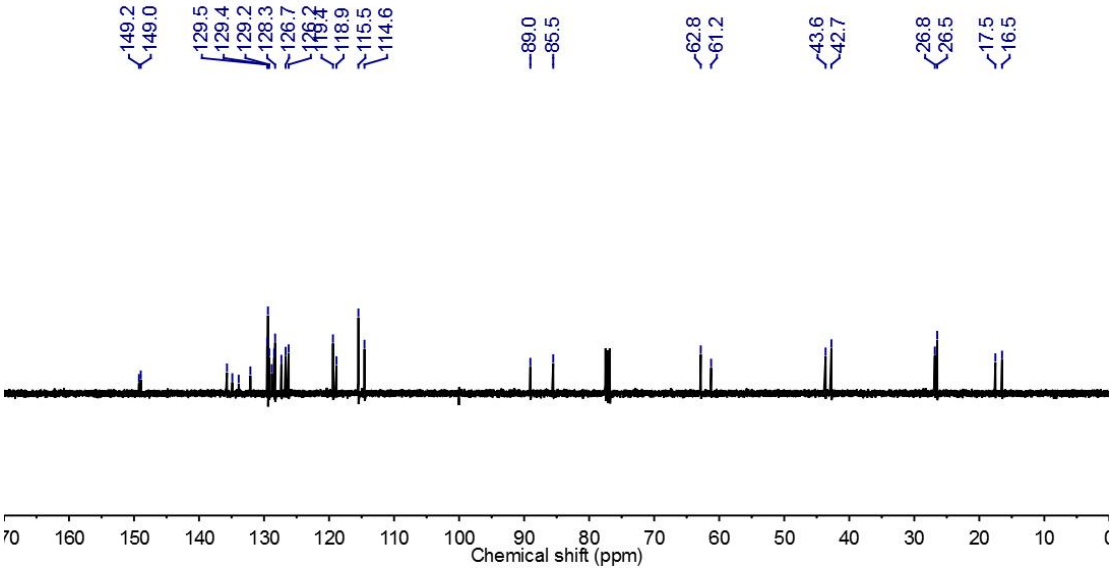
The ^{1}H-NMR and ^{13}C-NMR spectra of **3b**.



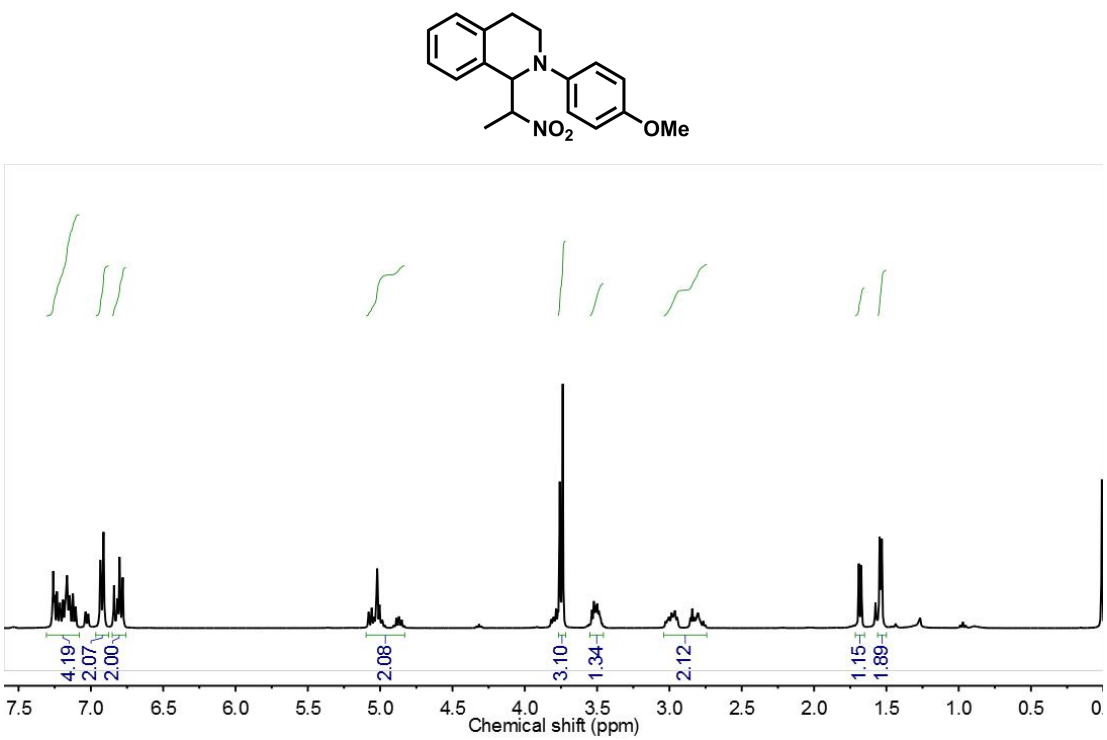


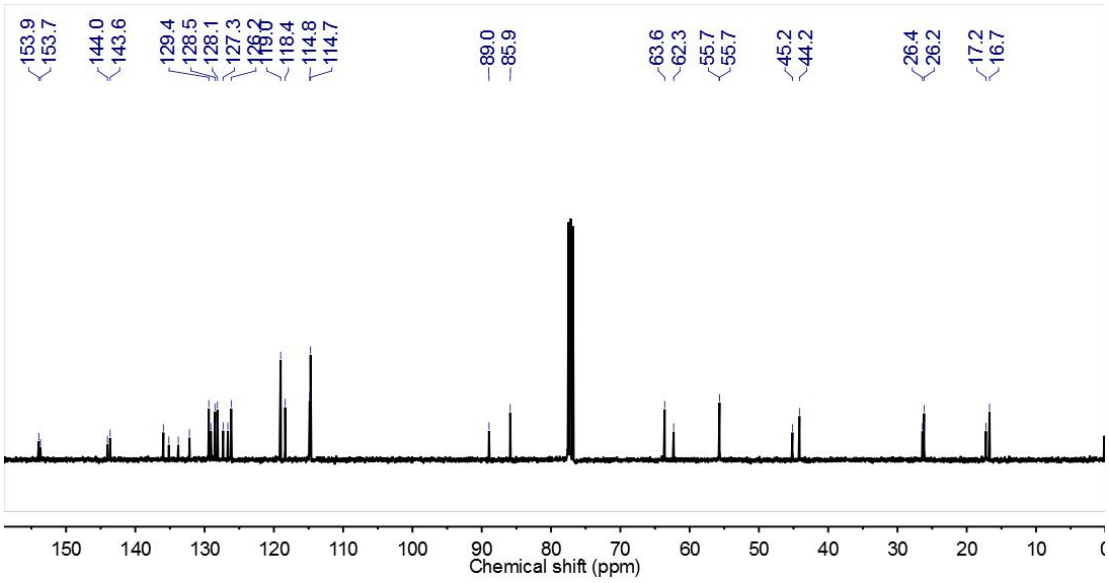
The ^{1}H-NMR and ^{13}C-NMR spectra of **3c**.



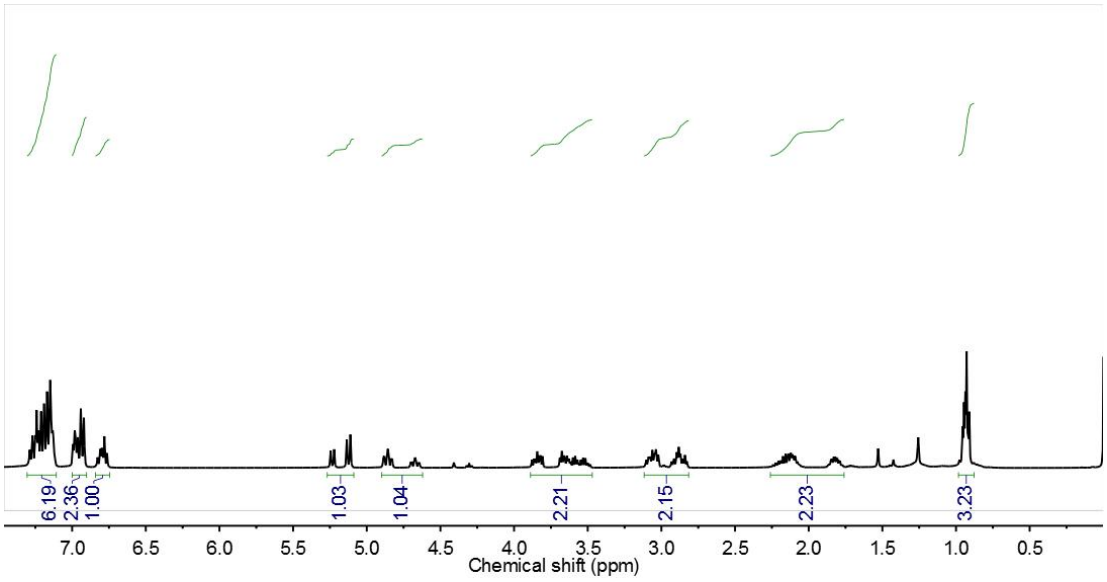


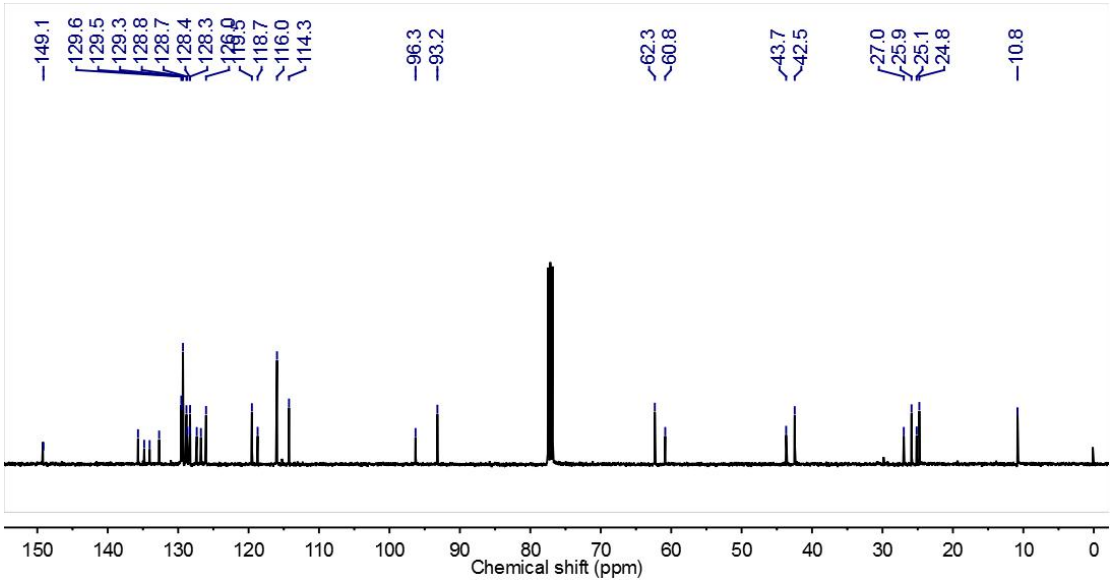
The ^{1}H-NMR and ^{13}C-NMR spectra of **3d**.



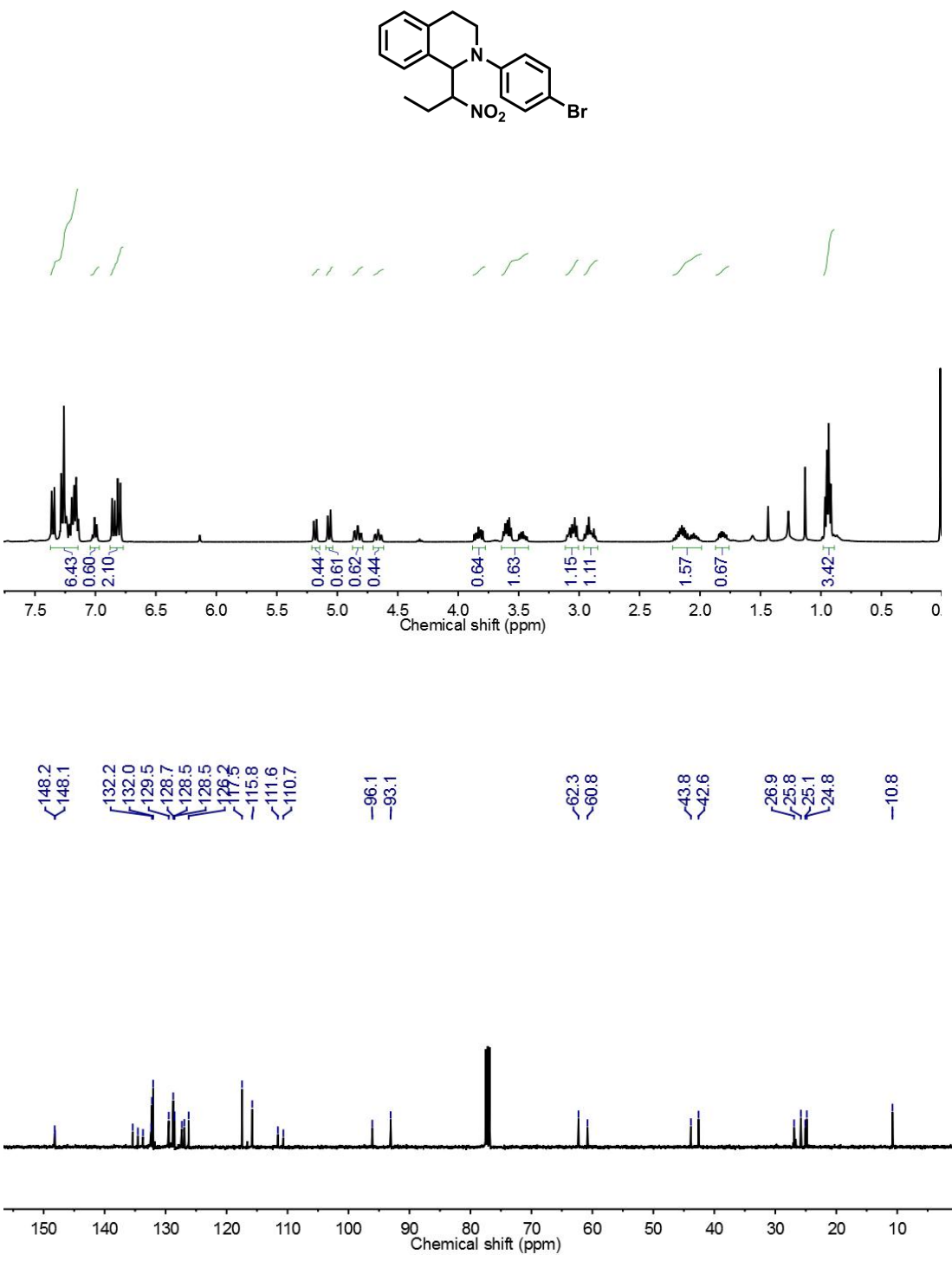


The ^{1}H-NMR and ^{13}C-NMR spectra of **3e**.

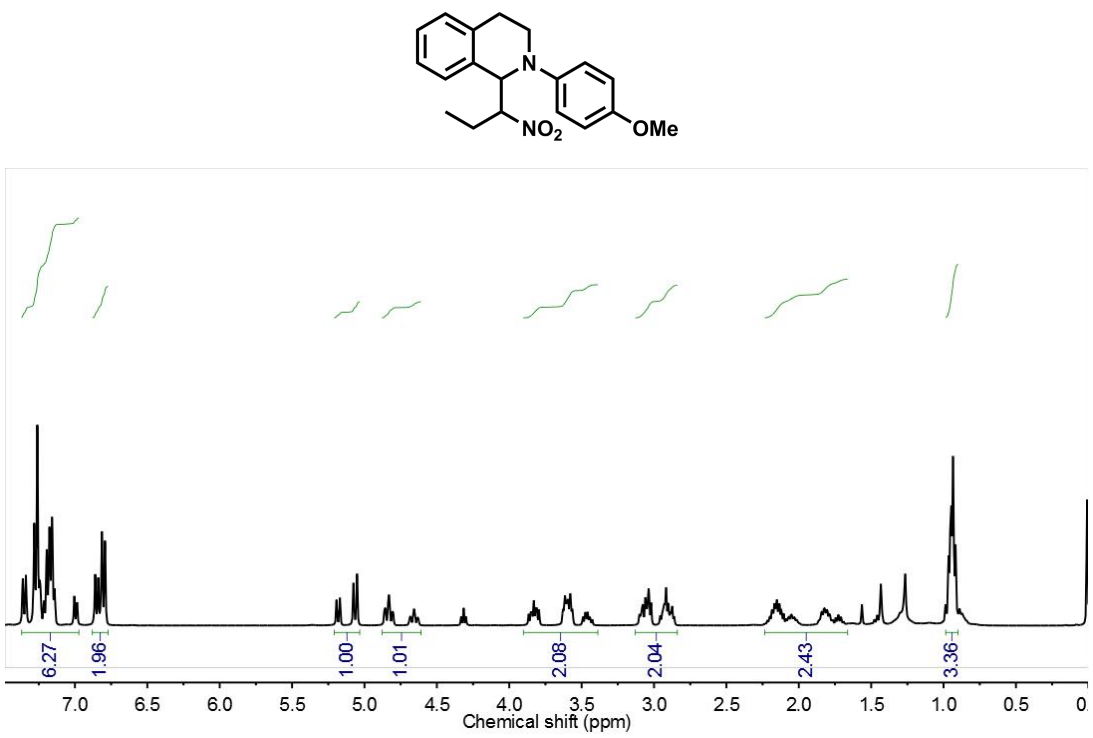


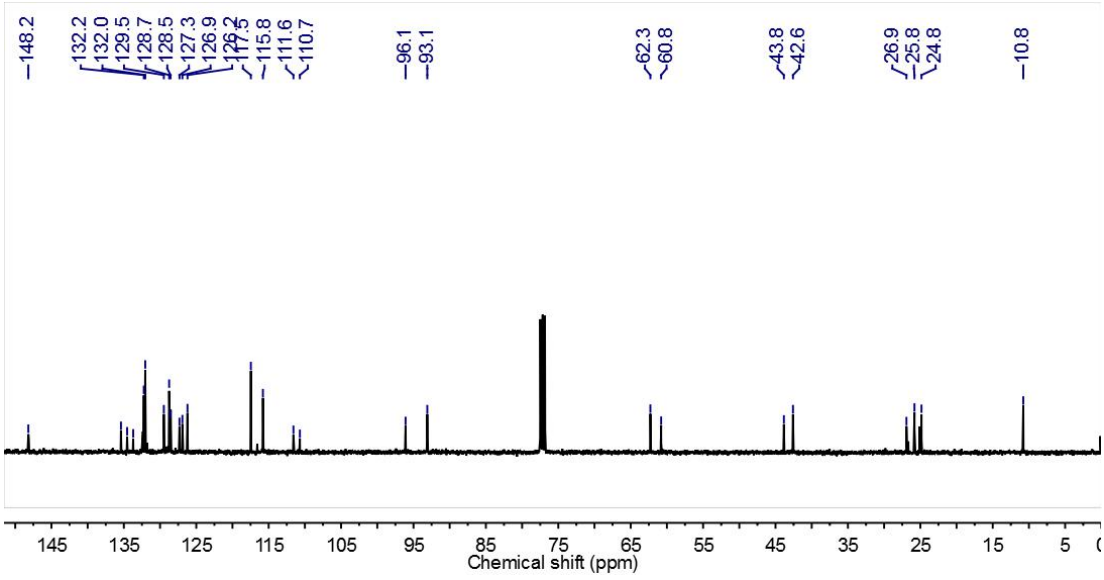


The ^{1}H-NMR and ^{13}C-NMR spectra of **3f**.

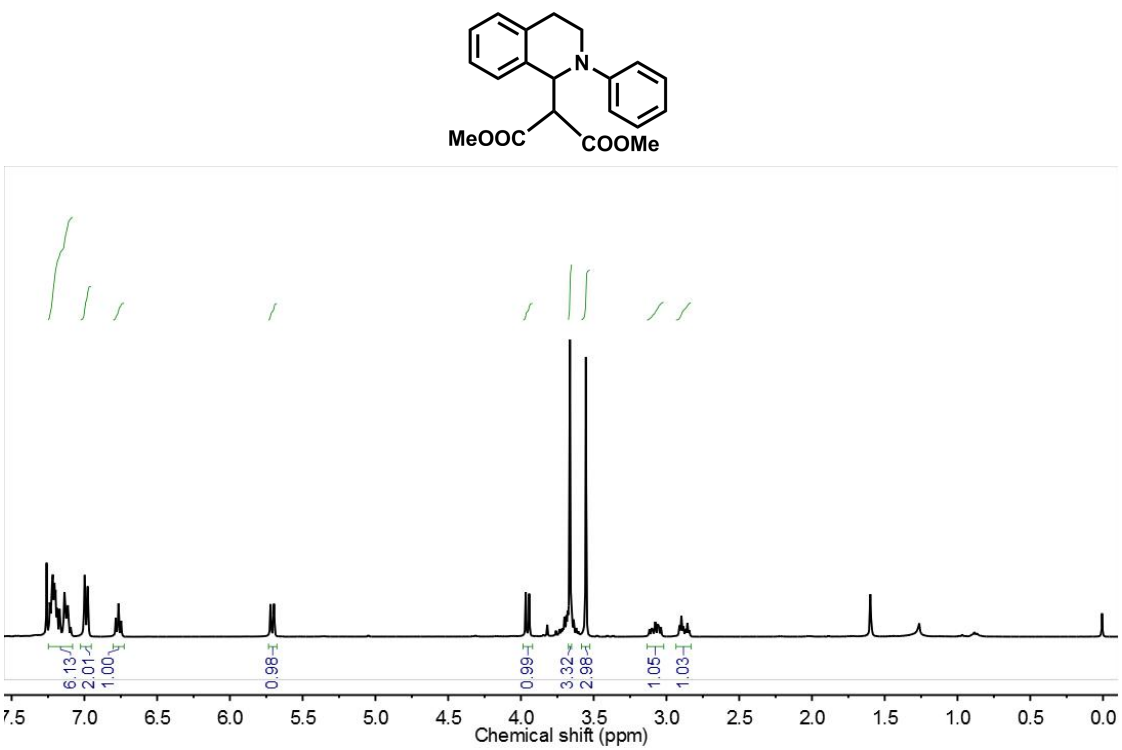


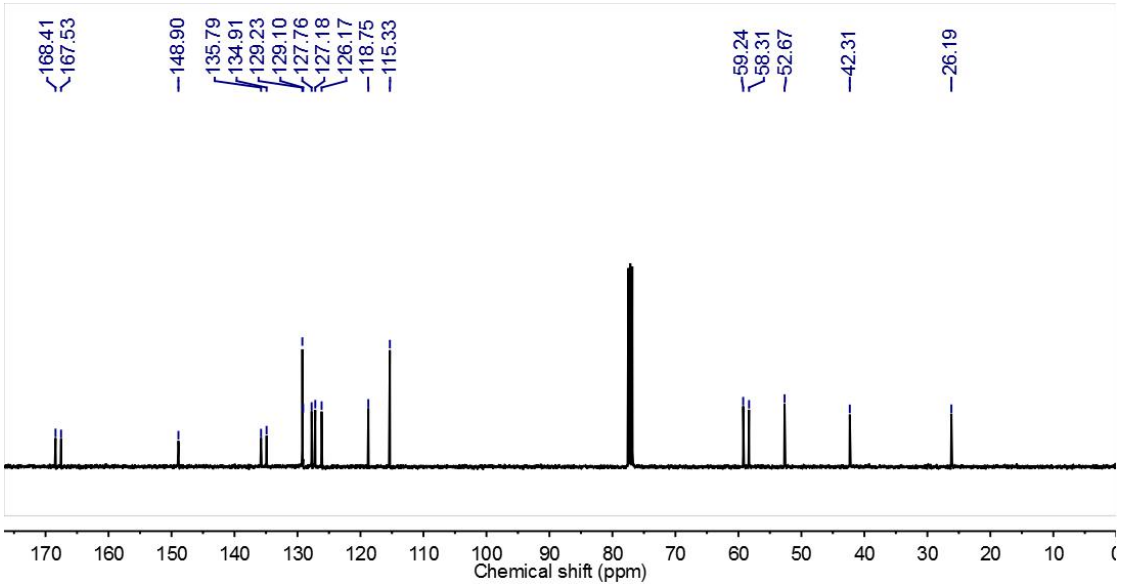
The ^{1}H-NMR and ^{13}C-NMR spectra of **3g**.



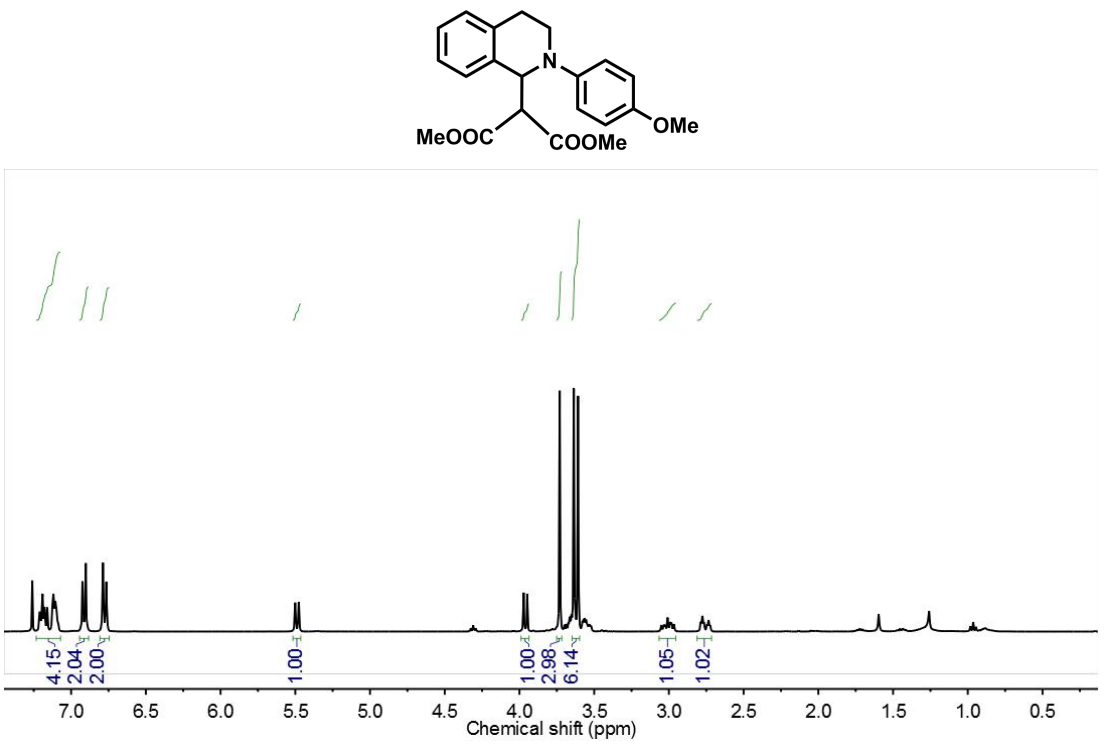


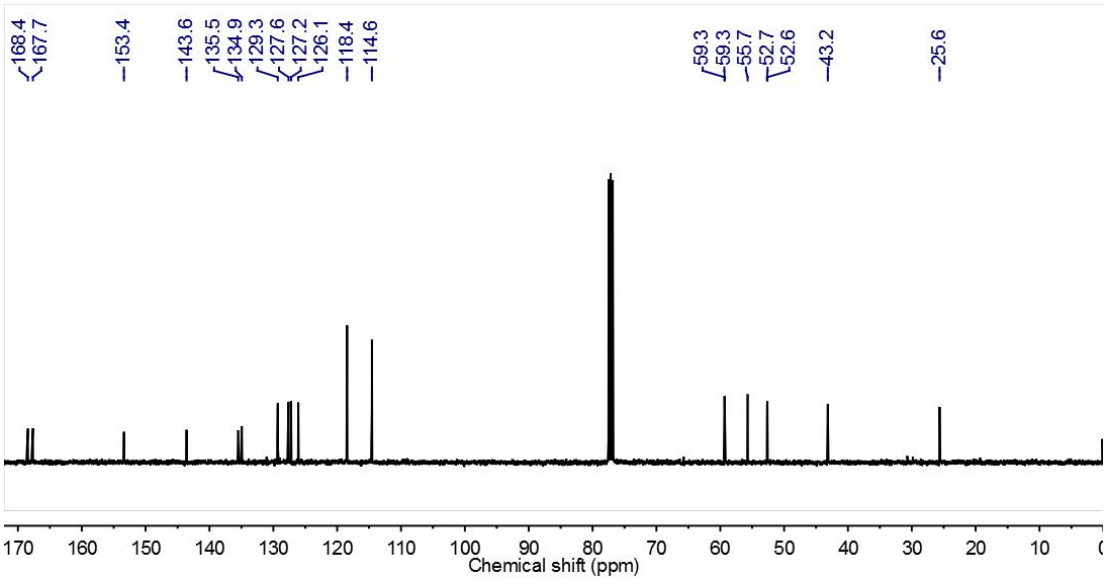
The ^{1}H-NMR and ^{13}C-NMR spectra of **3h**.



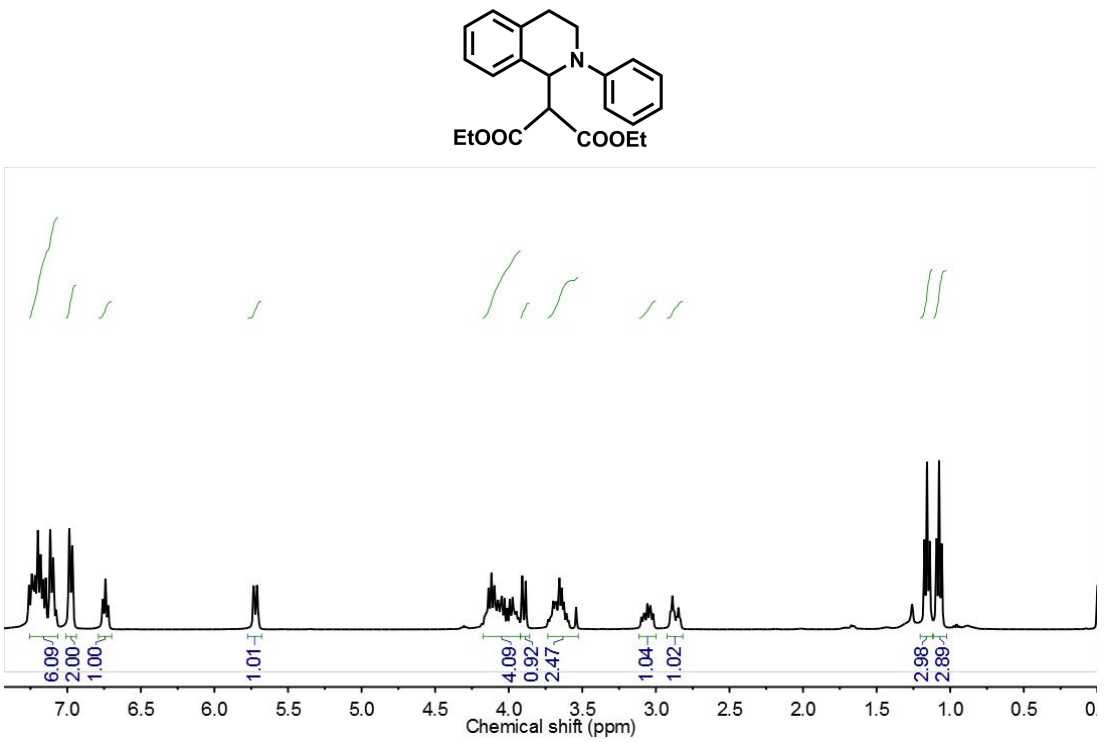


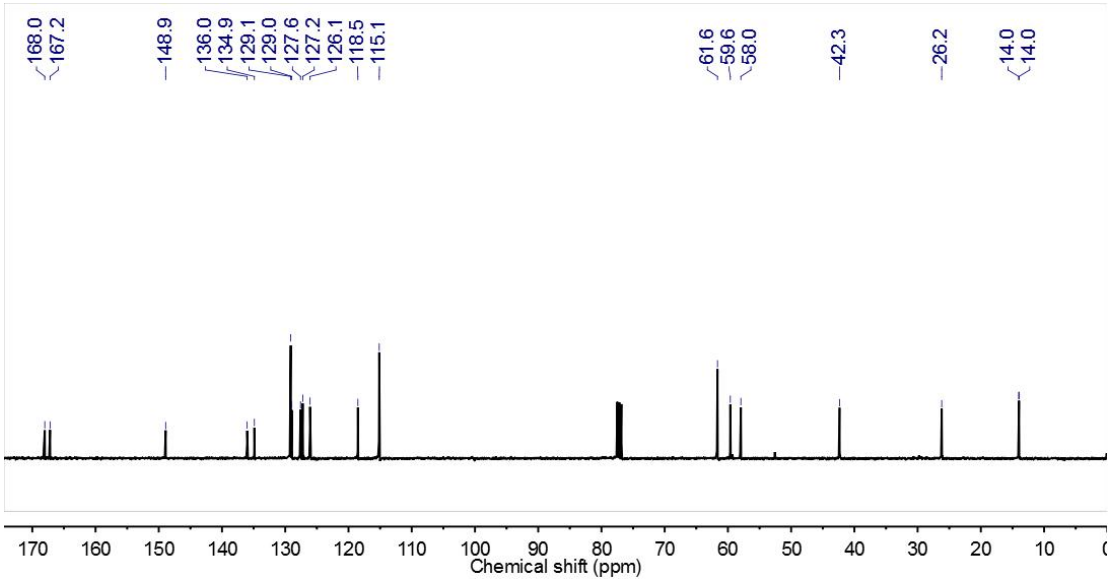
The ^{1}H-NMR and ^{13}C-NMR spectra of **3i**.



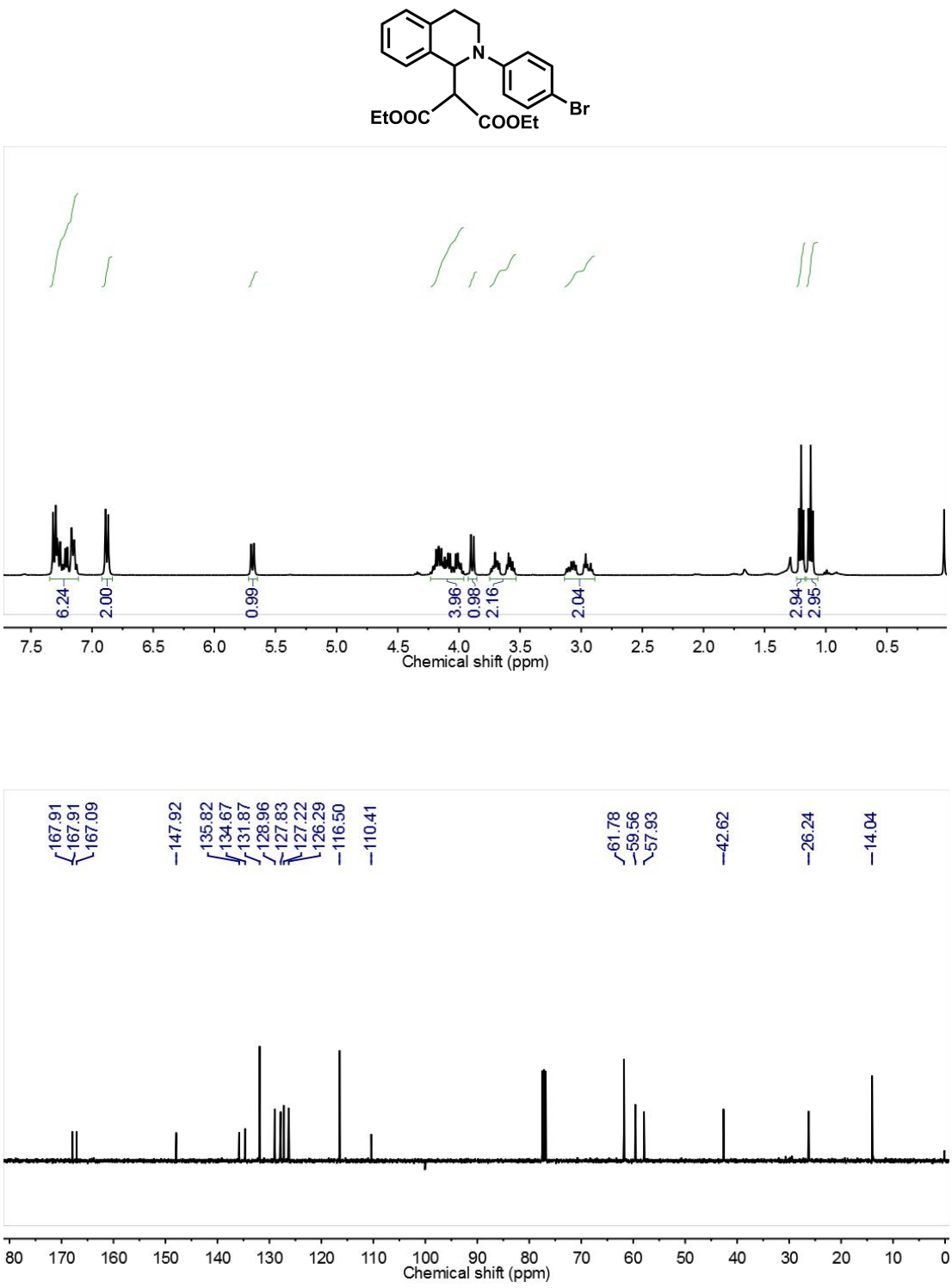


The ^{1}H-NMR and ^{13}C-NMR spectra of **3j**.

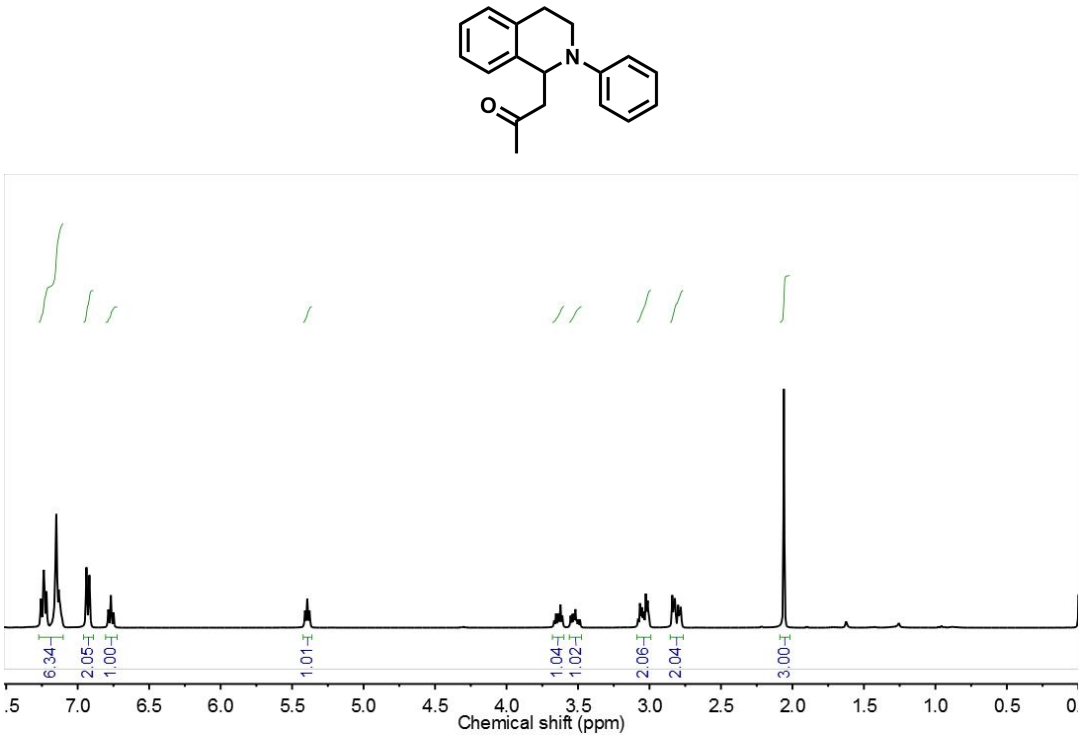


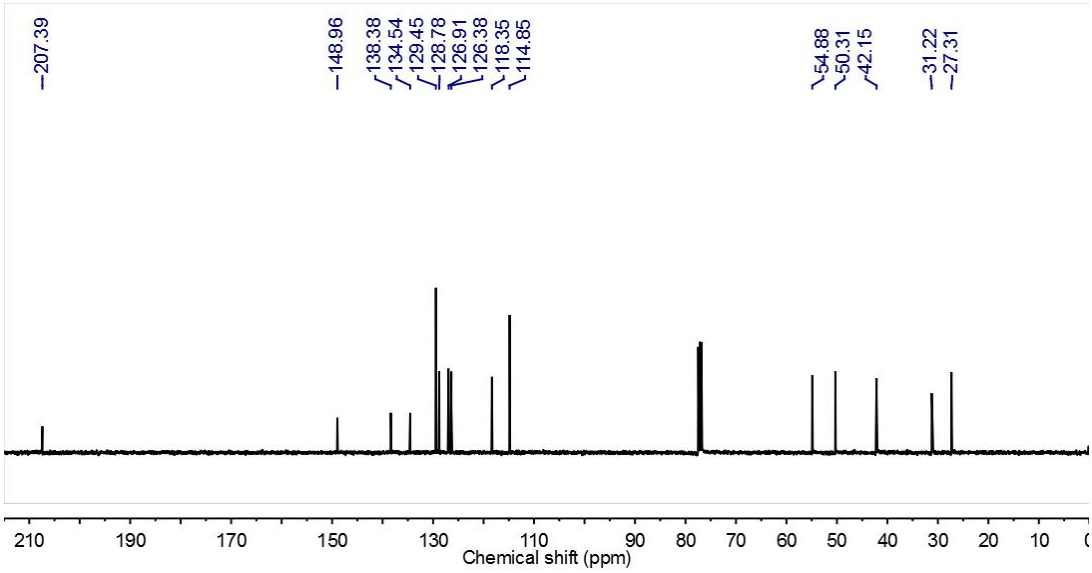


The ^{1}H-NMR and ^{13}C-NMR spectra of **3k**.

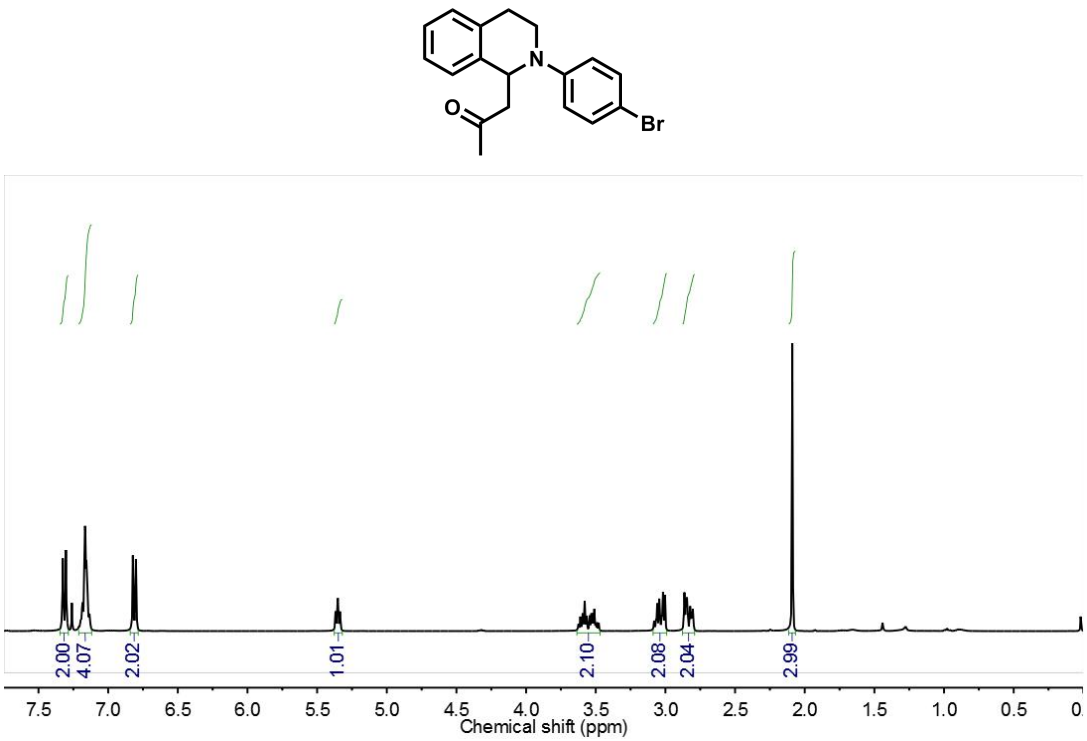


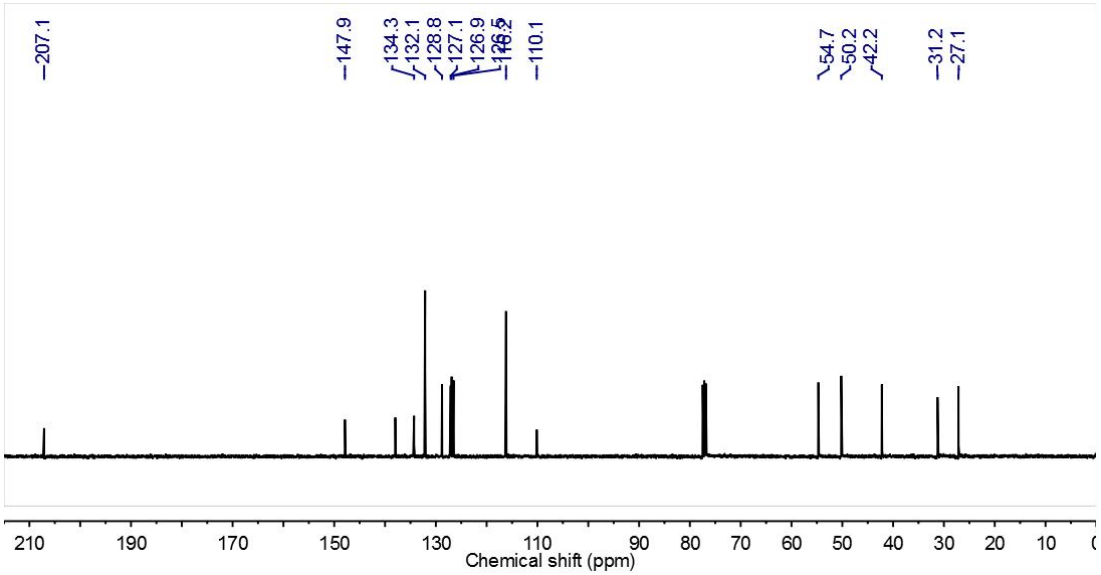
The ^{1}H-NMR and ^{13}C-NMR spectra of **3l**.



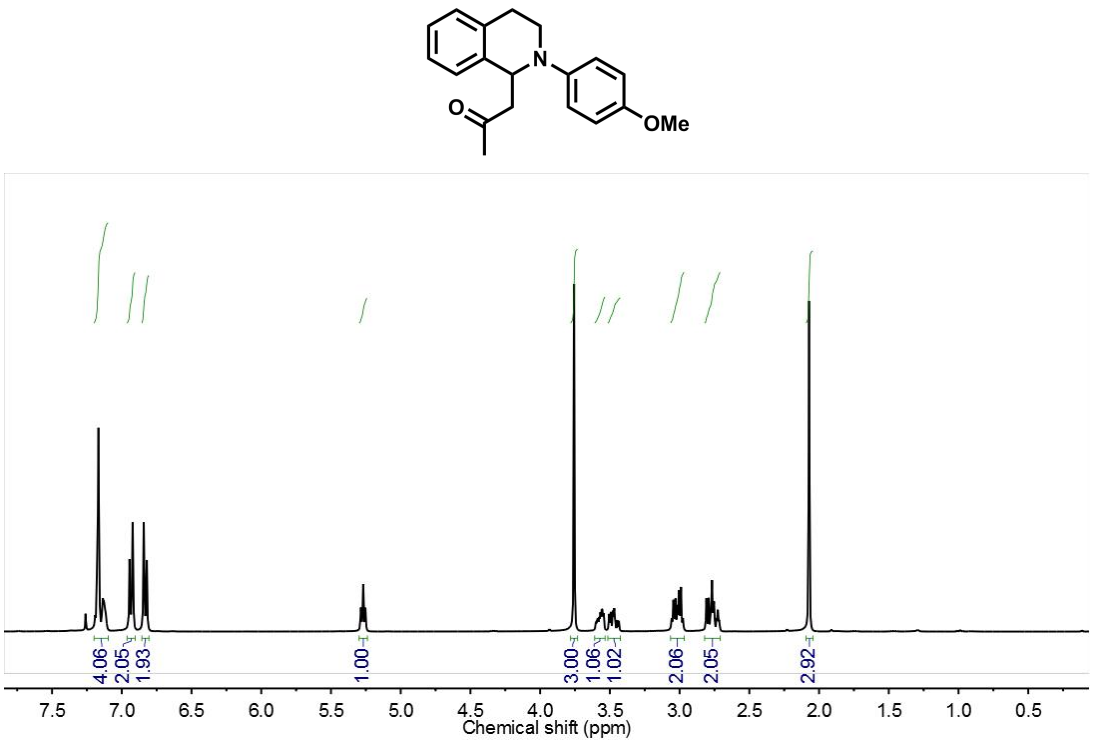


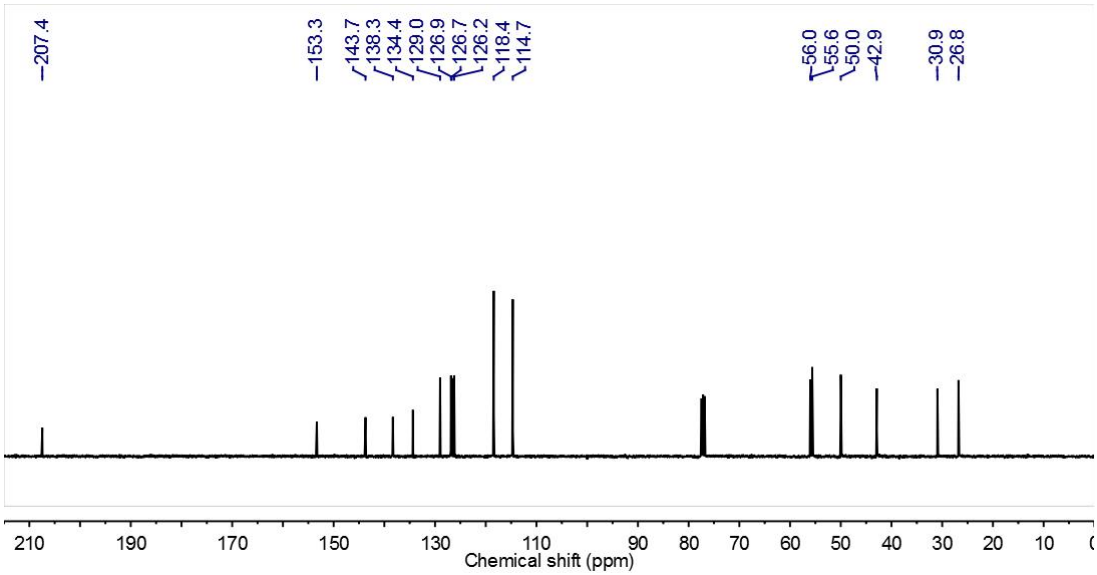
The ^{1}H-NMR and ^{13}C-NMR spectra of **3m**.



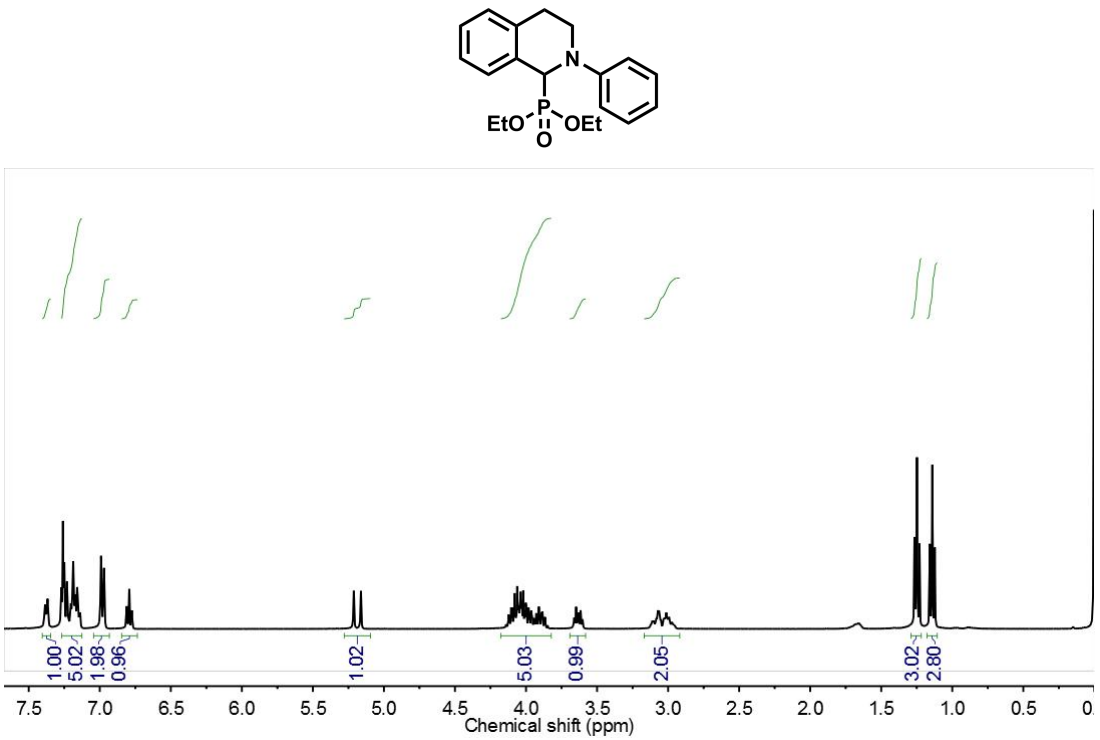


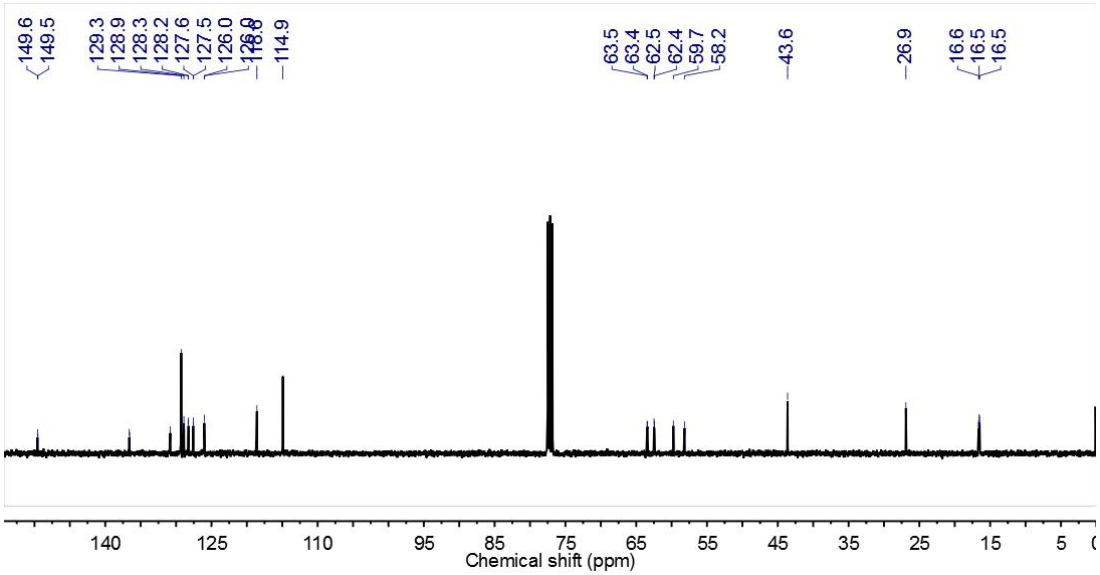
The ^{1}H-NMR and ^{13}C-NMR spectra of **3n**.



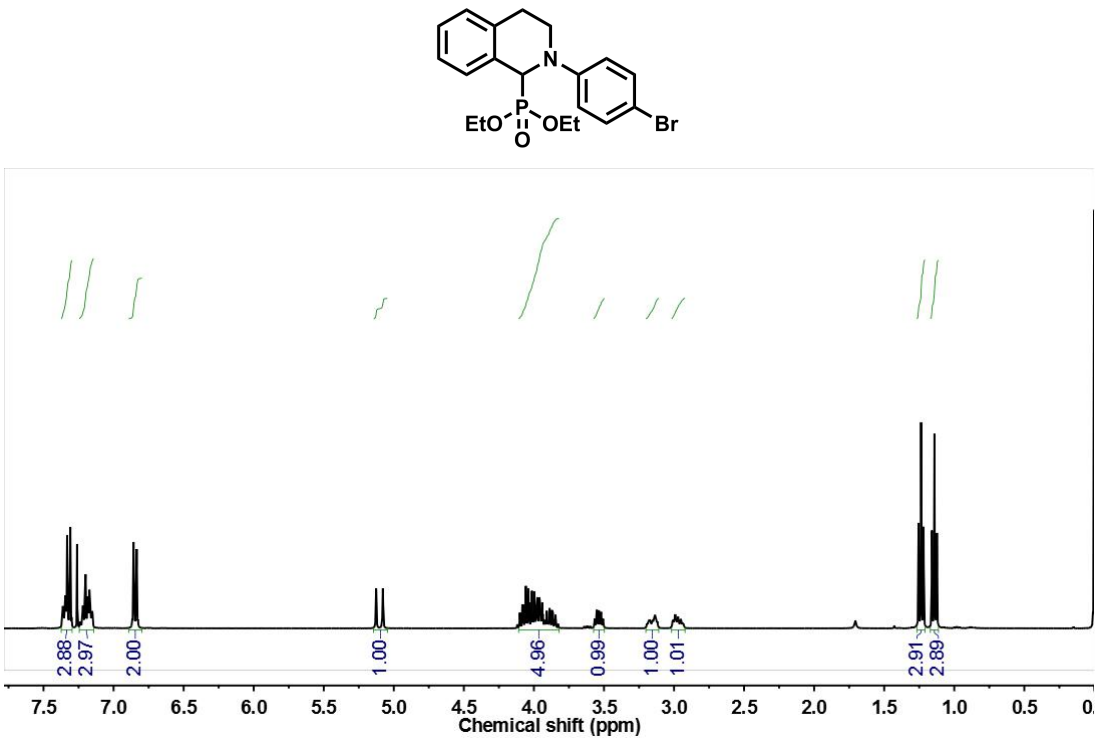


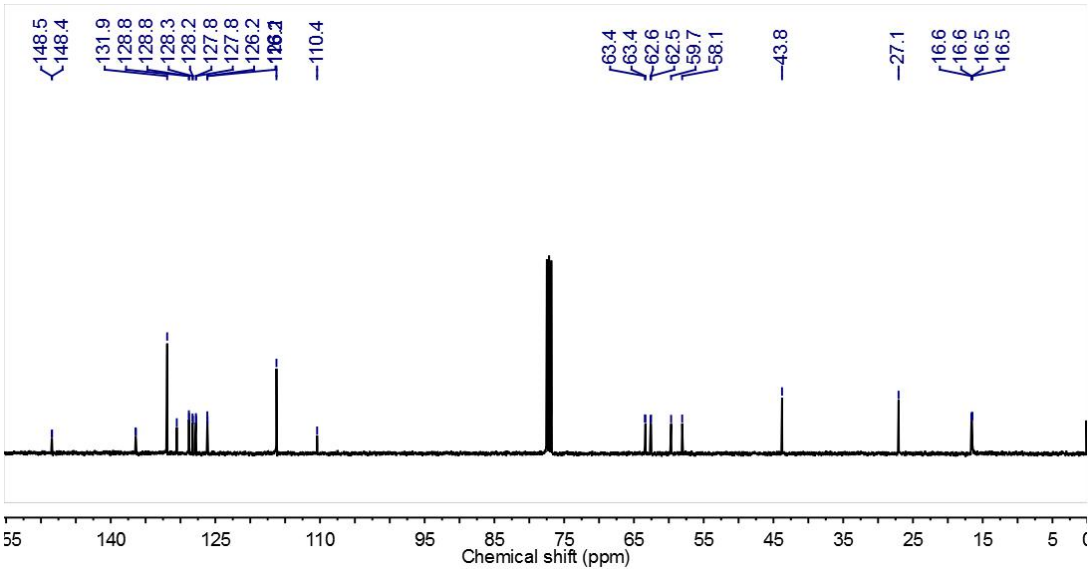
The ^{1}H-NMR and ^{13}C-NMR spectra of **3o**.



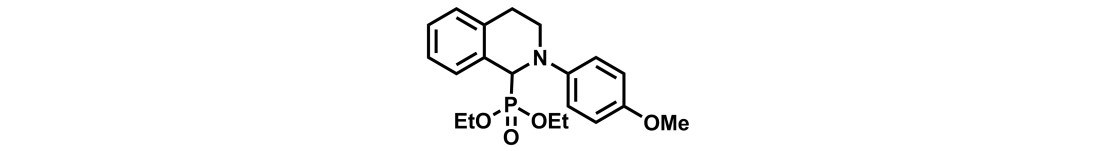


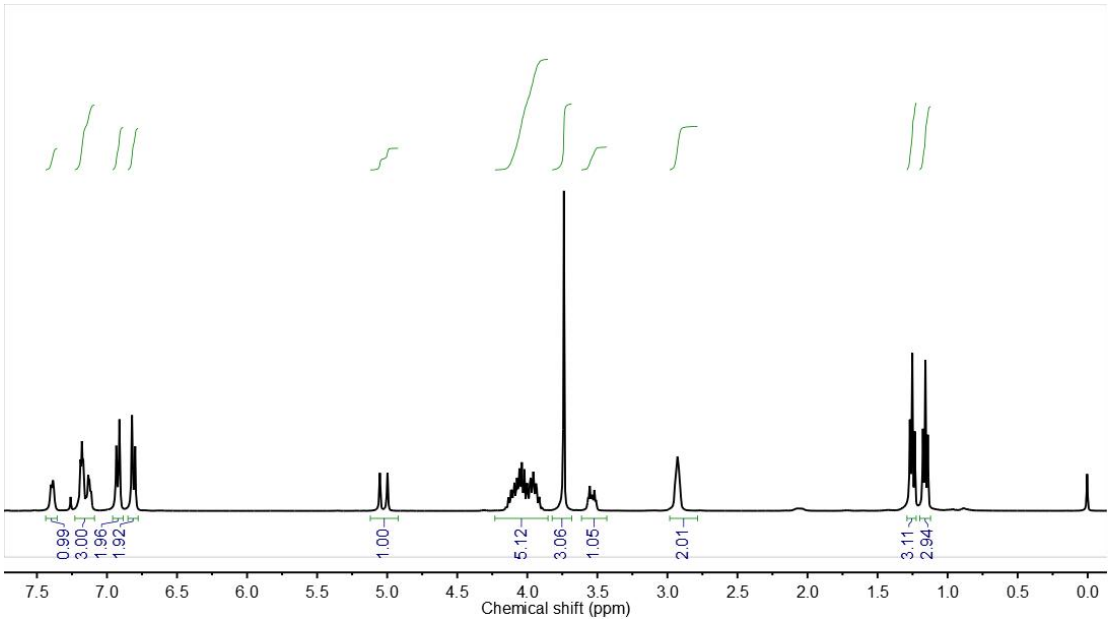
The ^{1}H-NMR and ^{13}C-NMR spectra of **3p**.

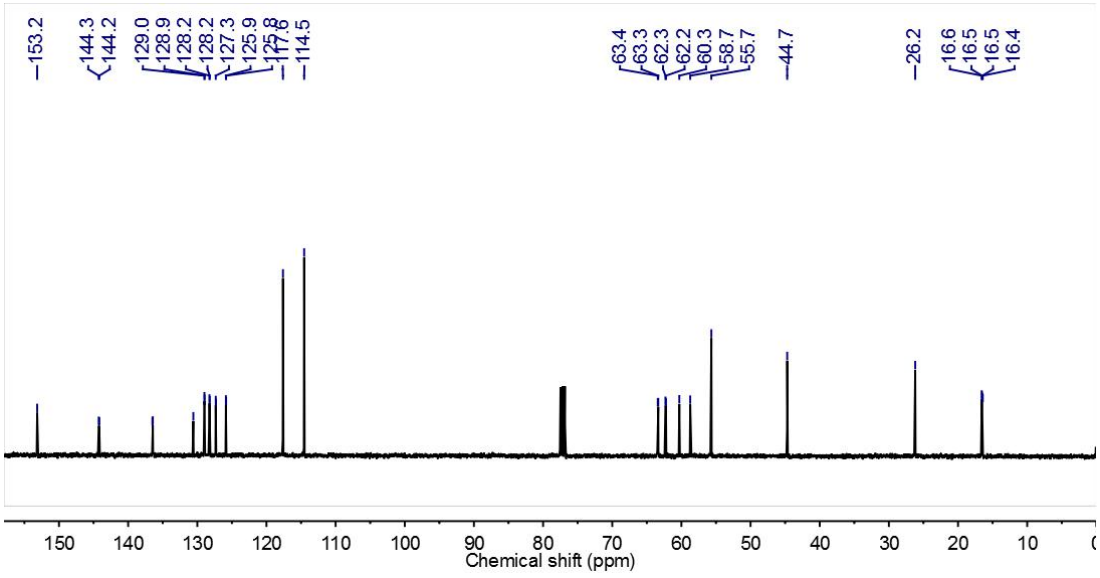




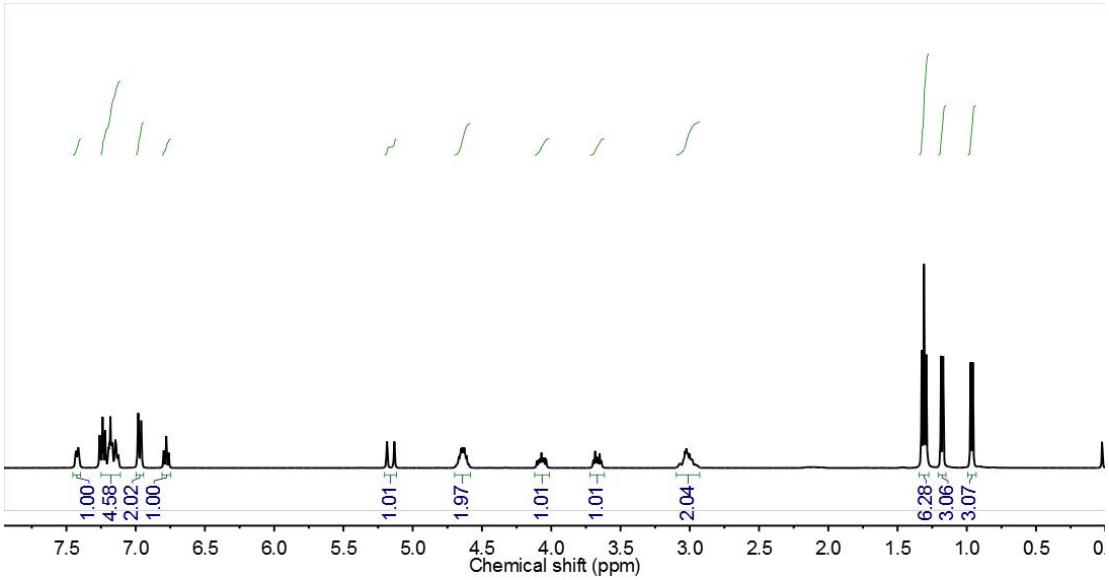
The ^{1}H-NMR and ^{13}C-NMR spectra of **3q**.

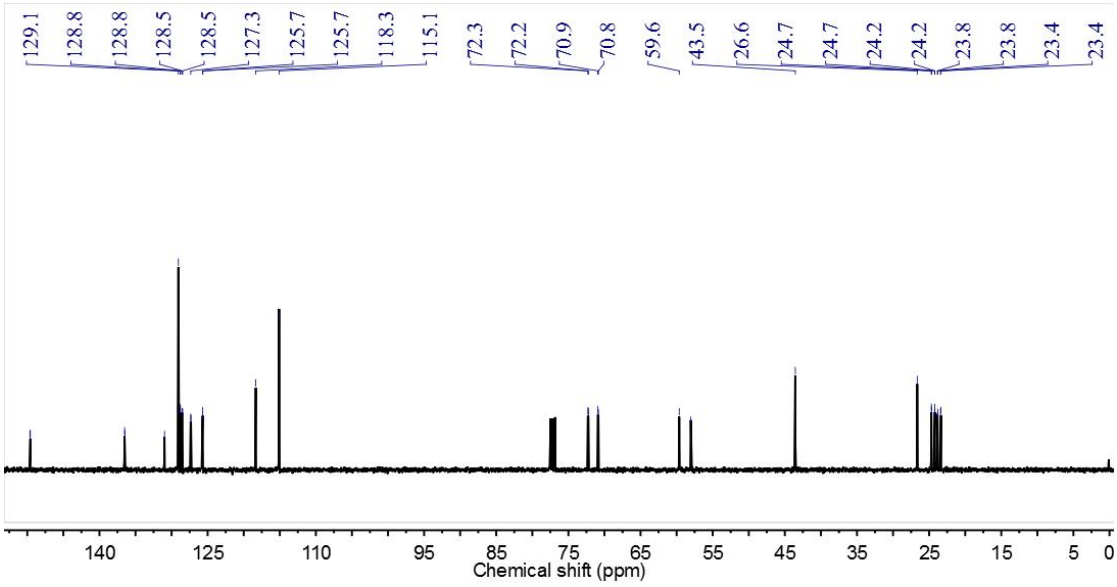




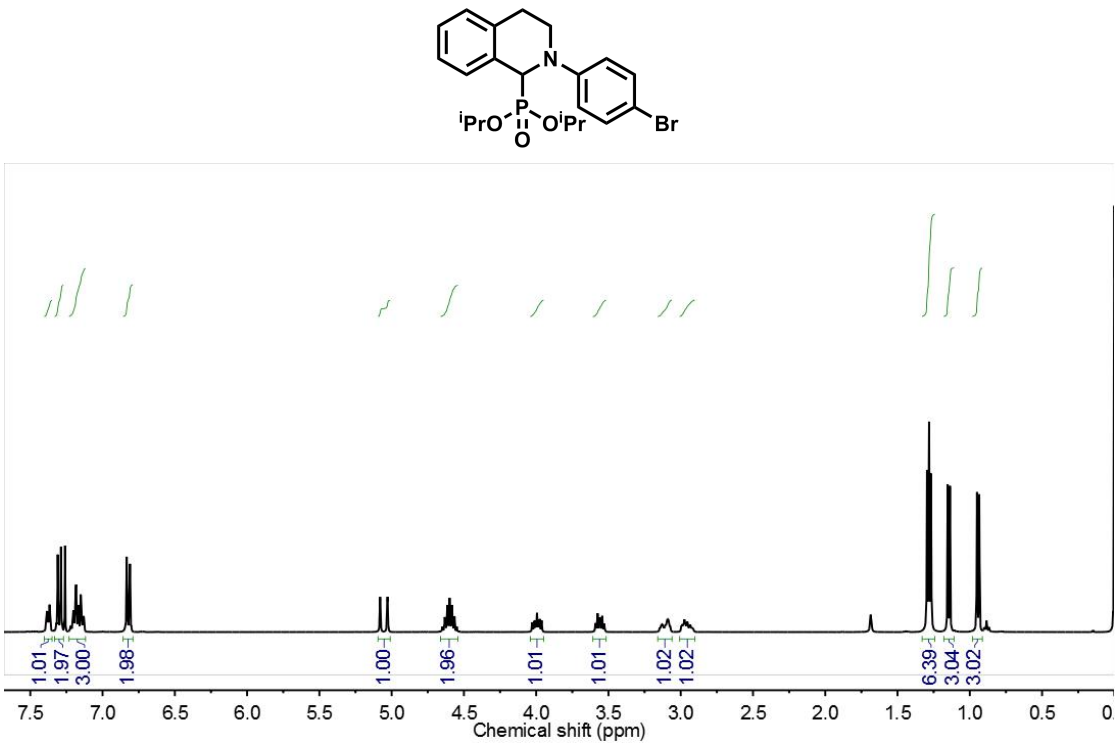


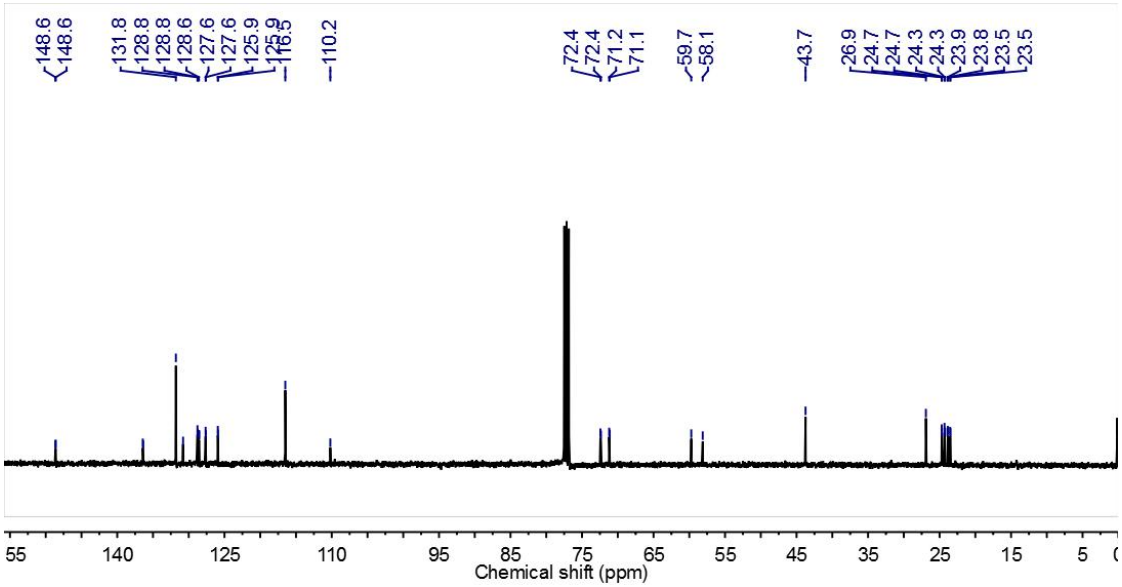
The ^{1}H-NMR and ^{13}C-NMR spectra of **3s**.



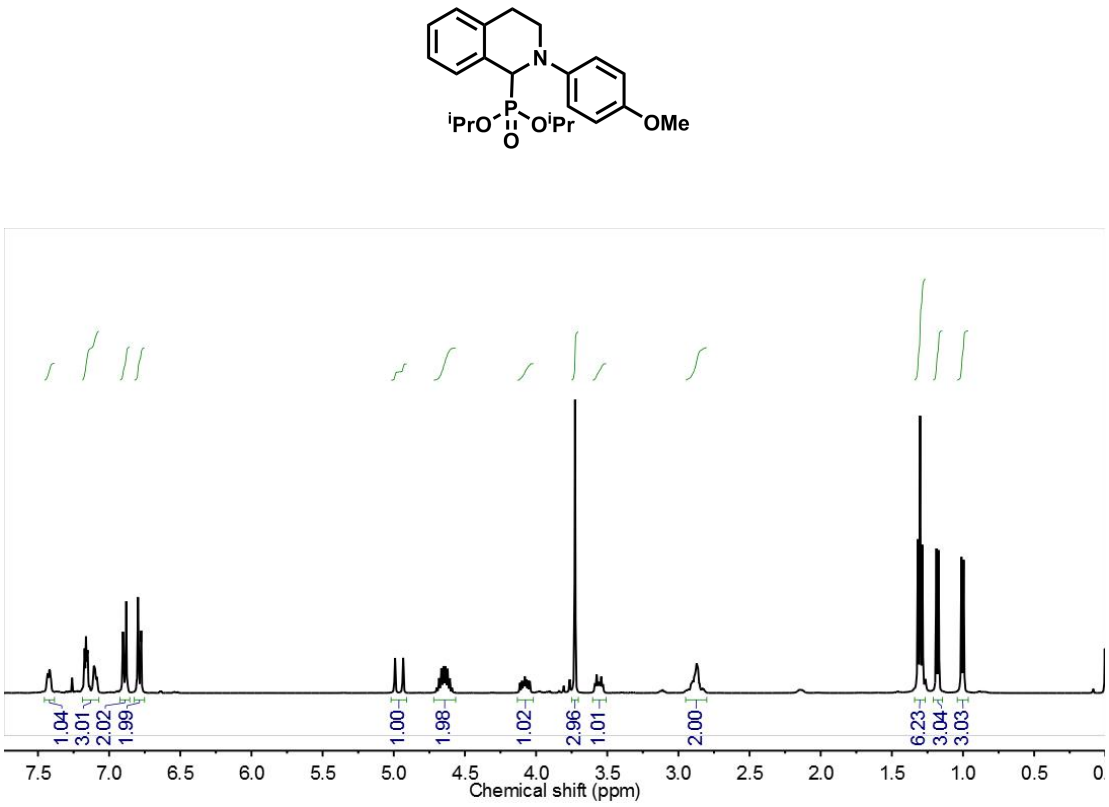


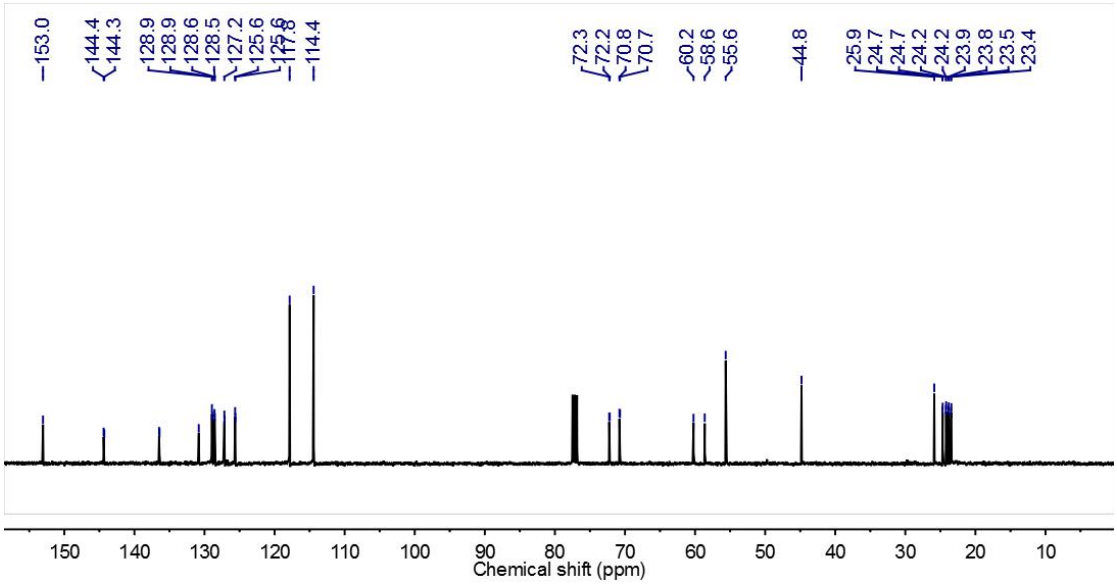
The ^{1}H-NMR and ^{13}C-NMR spectra of **3t**.





The ^{1}H-NMR and ^{13}C-NMR spectra of **3u**.





The ^{1}H-NMR and ^{13}C-NMR spectra of **3v**.

17. References

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