Sustainable Photoredox C(sp^3)–P Bond Formation via Nitrogen-Vacancy-Engineered Carbon Nitride

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Abbreviations

BQ: p-benzoquinone

CB: Conduction Band

CN: Carbon nitride

CP MAS NMR: Cross-polarization magic angle spinning nuclear magnetic resonance

DCM: Dichloromethane

DMF: Dimethylformamide

DMSO: Dimethyl Sulfoxide

DOPO: 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide

EIS: Electrochemical impedance spectroscopy

EPR: Electron paramagnetic resonance

EtOAc: Ethyl Acetate

FT-IR: Fourier-transform infrared spectroscopy

HAT: Hydrogen-atom transfer

ICP-MS: Inductively coupled plasma mass spectroscopy

IPA: Isopropanol

MeCN: Acetonitrile

NHE: Normal hydrogen electrode

***Nv*:** Nitrogen vacancy

***Nv*-CN(X)-TG:** Nitrogen vacant Carbon nitride synthesized from **X** precursor, annealed at **T** temperature under **G** atmosphere.

***Nv*-CN:** Nitrogen vacant Carbon nitride

PL: Photoluminescence

SEM: Scanning electron microscopy

SET: Single-electron transfer

TEM: Transmission electron microscopy

TEMPO: 2,2,6,6-tetramethylpiperidine-1-oxyl

TEOA: Triethanolamine

THF: Tetrahydrofuran

TPC: Transient photocurrent

TRPL: Time-resolved photoluminescence

UV-Vis DRS: Ultraviolet-visible diffuse reflectance spectroscopy

VB: Valance Band

XPS: X-ray photoelectron spectroscopy

XRD: X-Ray Diffraction

Experimental Section

Chemicals

Cyanamide (≥98%, Sigma-Aldrich), Dicyandiamide (≥99%, Sigma-Aldrich), Melamine (≥99%, Sigma-Aldrich), Copper (I) iodide (≥98%, Sigma-Aldrich), Potassium phosphate tribasic (≥98%, Sigma-Aldrich), Ethylene glycol (≥99%, Sigma-Aldrich), isopropanol (≥99.5%, IsoLab), 1,2,3,4-Tetrahydroisoquinoline (≥95%, Sigma-Aldrich), 4-iodoacetophenone (≥97%, Sigma-Aldrich), Acetonitrile (≥99%, IsoLab), Ethyl Acetate (≥99%, IsoLab), Cyclohexane (≥99%, IsoLab), Ethanol (≥99%, IsoLab), Toluene (≥99%, IsoLab), Dimethyl sulfoxide (≥99%, IsoLab), dimethyl formamide (≥99%, IsoLab), tetrahydrofuran (≥99%, IsoLab), 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (≥99%, Sigma-Aldrich), p-Benzoquinone (≥98%, Sigma-Aldrich), 2,2,6,6-tetramethylpiperidine-1-oxyl (≥99%, Sigma-Aldrich), Triethanolamine (≥99%, Sigma-Aldrich), Silver nitrate (≥99%, Sigma-Aldrich), Sodium Azide (≥99.5%, Chem Solute), Diethyl phosphite (≥99%, Sigma-Aldrich), Dibutyl phosphite (≥99%, Sigma-Aldrich), Diphenyl phosphite (≥99%, Sigma-Aldrich), Iodobenzene (≥99%, Sigma-Aldrich), 4-iodotoluene (≥99%, Sigma-Aldrich), Piperidine (≥99%, Sigma-Aldrich), 1,3-dinitrobenzene(97%, Sigma-Aldrich), Chloroform-d (99.8%, Sigma-Aldrich). Except as otherwise specified, all compounds and solvents were utilized without additional purification.

Characterization Instruments

The X-ray diffraction (XRD) measurements were performed by Bruker D2 Phaser X-ray diffractometer using Cu Kα radiation (1.54 Å). X-ray photoelectron spectroscopy (XPS) was carried out by Thermo K-Alpha XPS using Al Kα radiation (1486.6 eV). The Fourier-transform infrared spectroscopy (FT-IR) analyses were conducted by Thermo Scientific iS 10 FT-IR Spectrometer with ATR module. CHN elemental analyses were executed by Thermo Scientific Flash 2000. The diffuse reflectance spectroscopy (DRS) analyses were implemented by Shimadzu UV-3600 UV-vis-NIR spectrophotometer. Photoluminescence (PL) spectroscopy analyses were employed by Agilent Cary Eclipse PL at 320 nm. The nuclear magnetic resonance (NMR) analyses were performed by Bruker 500 MHz Ascend NMR spectrometer. NMR spectra were obtained in $CDCl_3$ using tetramethylsilane (TMS) as the internal standard. While chemical shifts are reported in parts per million (ppm), coupling constants (*J* values) are reported in Hz. The Bruker TopSpin 4.2.0 application was used to process the NMR spectra. For ssNMR analysis of ^{13}C, Bruker 500 MHz Ascend Neo NMR spectroscopy with MASSB-DR-BBLR CPMAS H/X VTN 4 mm double resonance probe for SB solid state was used.

Electron paramagnetic resonance (EPR) measurements were conducted on CIQTEK EPR200M with continues-wave X band frequency, where methanol was used as solvent and before recording radical signals, all samples were irradiated under light for 1 min. The Brunauer–Emmett–Teller (BET) measurements were employed on a Micromeritics Accelerated Surface Area and Porosimetry System ASAP 2020 HD (−195.804 °C). The electrochemical measurements were conducted on a CHI 660E electrochemical workstation using Hg/Hg_2Cl_2 reference and Pt wire counter electrodes. Prior to the measurements, 2.50 mg of CN(X) and *Nv*-CN(X)-TG derivatives were sonicated in 5 mL ethanol and spray coated on a 1 cm^2 area on ITO glasses to produce working electrodes. The measurements were performed in 0.1 M Na_2SO_4 solution. The Mott-Schottky analyses were employed at 1, 1.5, and 2 kHz with a potential range of −1.2 to 1.0 V. The EIS analyses were conducted at 1 V potential with the frequency range of 0.01 Hz to 100 kHz for the Nyquist plots. The inductively coupled plasma mass spectrometry (ICP-MS) analyses were conducted on an Agilent 7800 system (Agilent Technologies, Waldbronn, Germany).

Synthesis of Tertiary Amines

N-(4-acetylphenyl)-tetrahydroisoquinoline (**1**) was synthesized by a validated method.[1] In a 100-mL round bottom flask, 200 mg of copper(I) iodide (1.05 mmol, 10 mol%), 4.25 g of tribasic potassium phosphate (20 mmol, 2 equivalent), and 2.46 g of 4-iodoacetophenone (10 mmol, 10 equivalent) were put. The flask was first vacuumed and then filled with Ar gas. 20 mL of isopropanol, 1.1 mL of ethylene glycol (20.00 mmol, 2 equivalent), and 2.0 mL of 1,2,3,4-tetrahydroisoquinoline (15 mmol, 1.5 equivalent) were added. The mixture was heated at around 90°C for 24 hours under stirring. After the heating was stopped, the reaction mixture was allowed to cool to room temperature, filtered and 20 mL of DCM and 20 mL of water were added to the filtrate. The organic layer was extracted three times with DCM and collected organic phase was dried over anhydrous sodium sulfate. Compound **1** was purified from the organic phase by column chromatography on silica with cyclohexane/ethyl acetate eluent with 6:1 ratio. The compound was crystallized as yellow needles and verified by ^{1}H-NMR. Compounds **4**, **6**, and **8** were synthesized with the same methodology.

Characterization of Materials

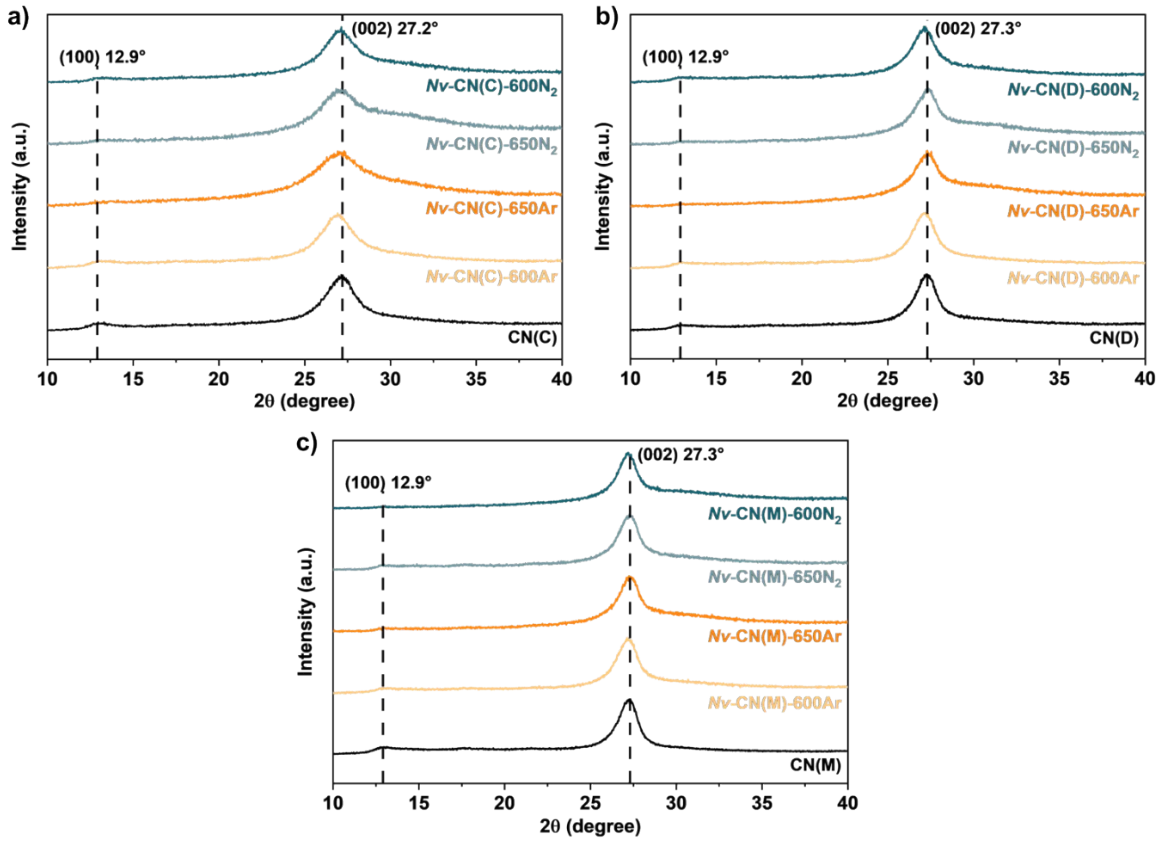


Figure S1. The XRD patterns of pristine and annealed CN derivatives using the precursor **a)** cyanamide, **b)** dicyandiamide, and **c)** melamine.

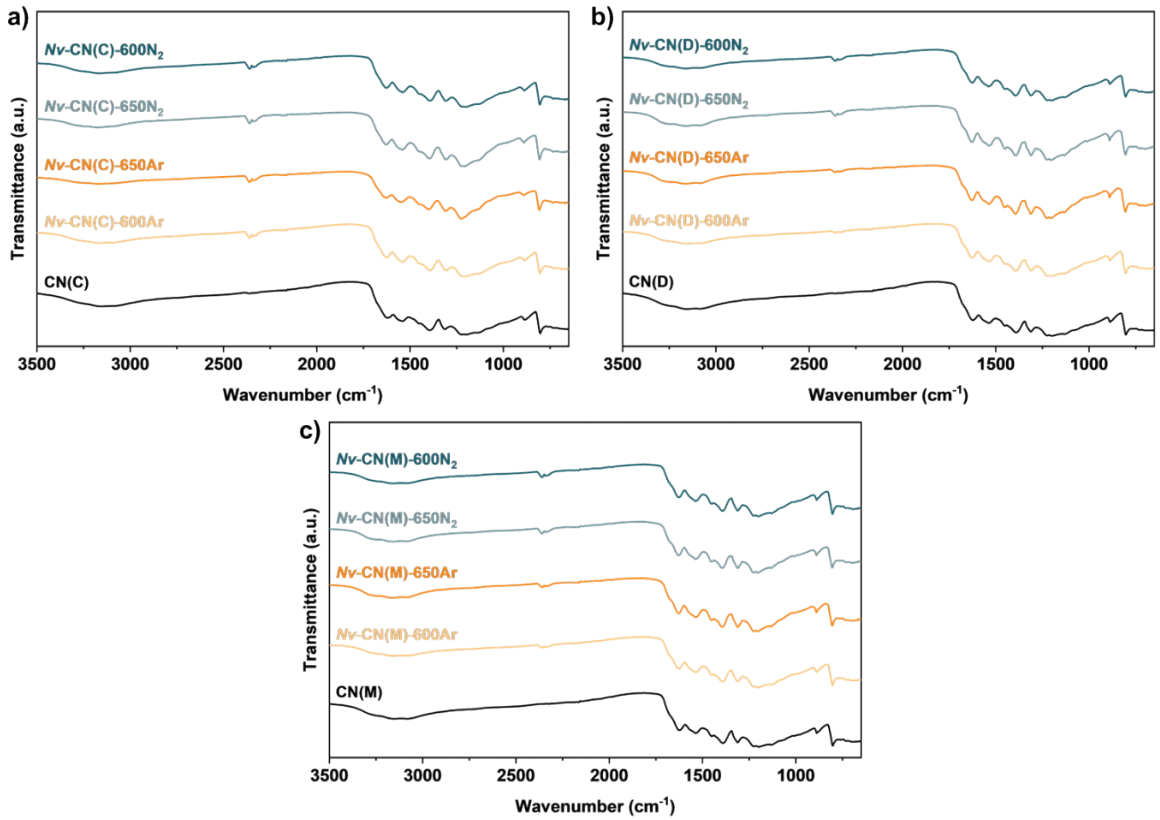


Figure S2. The FT-IR spectra of pristine and annealed CN derivatives using the precursor **a)** cyanamide, **b)** dicyandiamide, and **c)** melamine.

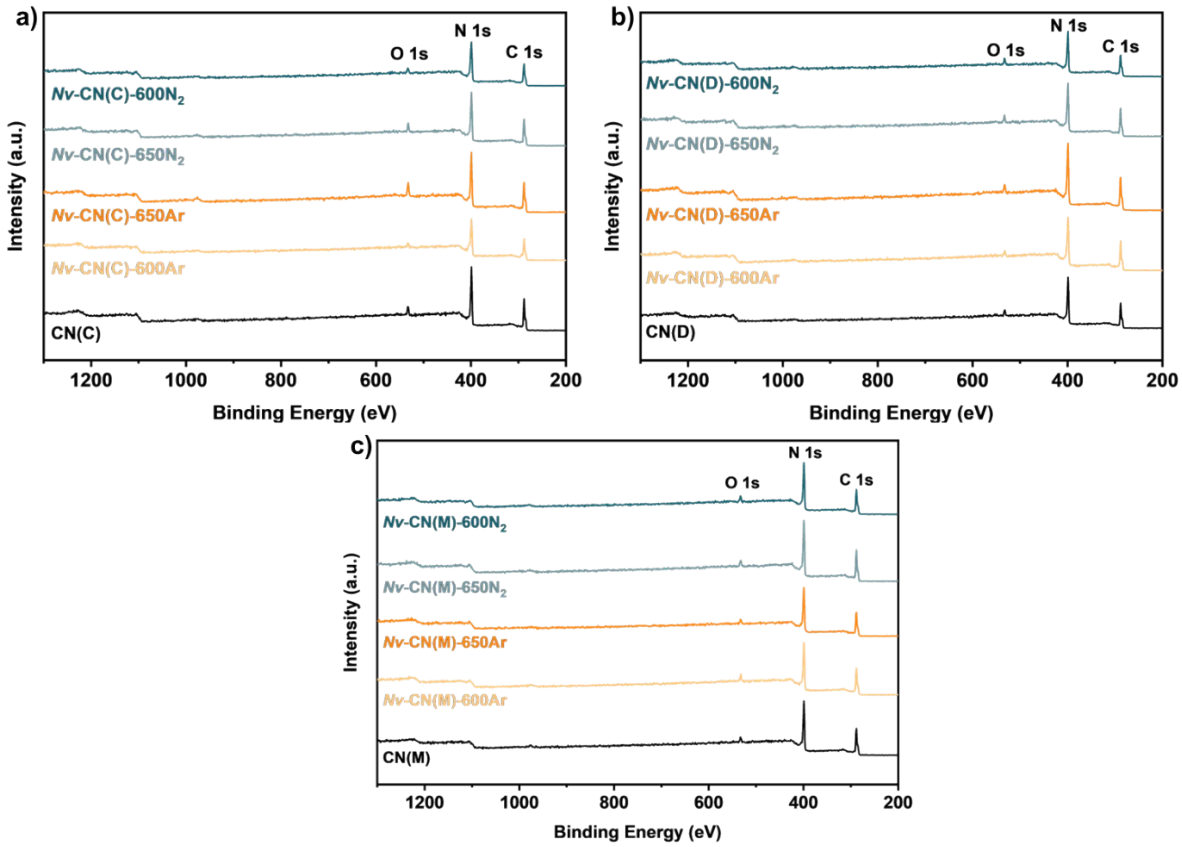


Figure S3. The XPS survey spectra of pristine and annealed CN derivatives using the precursor **a)** cyanamide, **b)** dicyandiamide, and **c)** melamine.

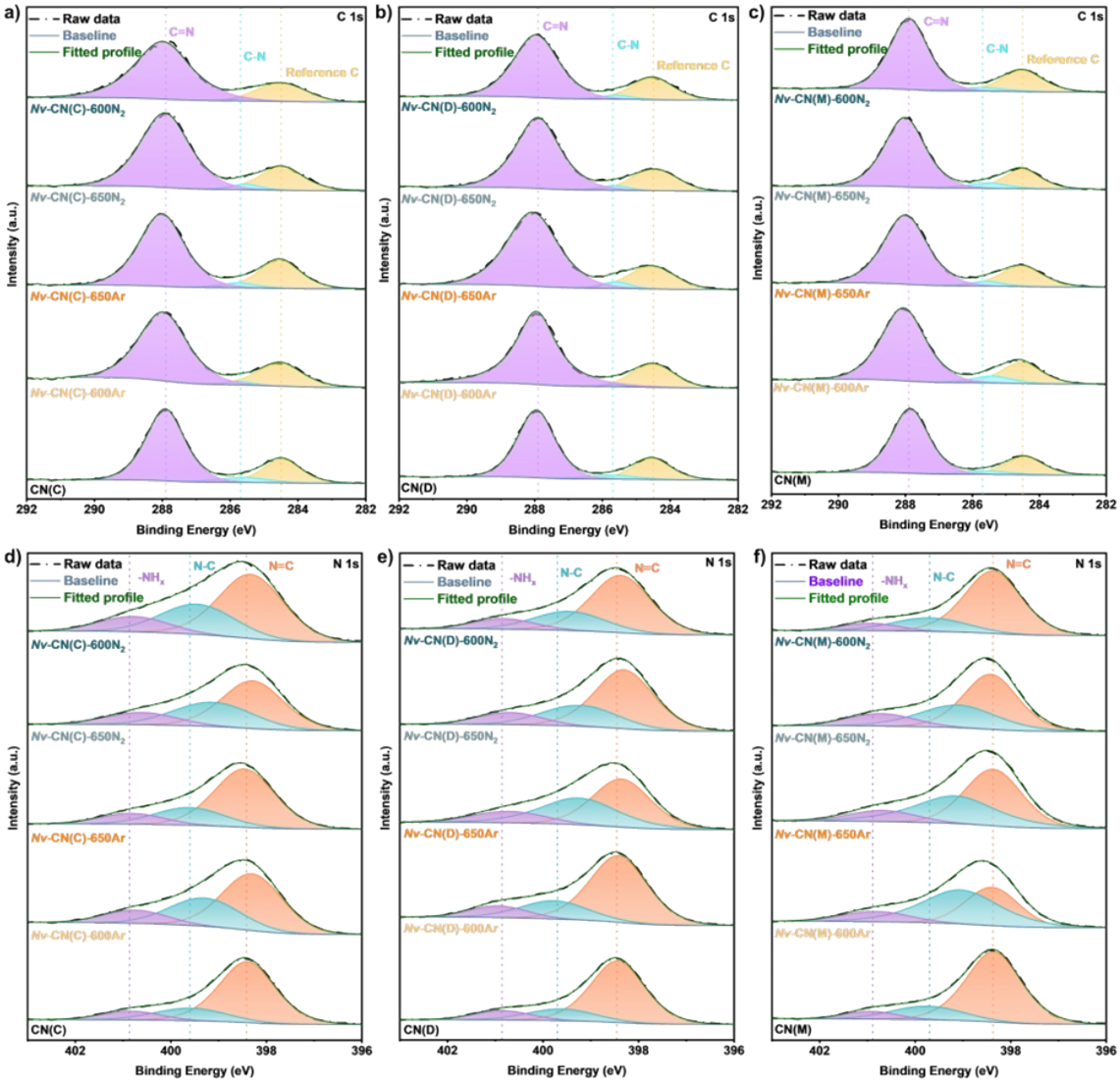


Figure S4. The high resolutions C 1s **a-c)** and N 1s **d-f)** XPS spectra of pristine and annealed CN derivatives using the precursor cyanamide, dicyandiamide, and melamine.

Table S1. Calculated C=N/–NH_x ratios of pristine and annealed CN derivatives by XPS peak area analysis.

Sample	Ratio	Sample	Ratio	Sample	Ratio
CN(C)	***6.95***	***CN(D)***	***6.54***	***CN(M)***	***10.25***
Nv-CN(C)600N_2	4.05	*Nv*-CN(D)600N_2	5.39	*Nv*-CN(M)600N_2	8.97
Nv-CN(C)600Ar	4.15	*Nv*-CN(D)600Ar	5.92	*Nv*-CN(M)600Ar	5.29
***Nv*-CN(C)650N_2**	**3.46**	***Nv*-CN(D)650N_2**	**4.62**	***Nv*-CN(M)650N_2**	**3.68**
***Nv*-CN(C)650Ar**	**3.14**	***Nv*-CN(D)650Ar**	**3.48**	***Nv*-CN(M)650Ar**	**4.47**

Table S2. Organic elemental composition (CHN) analysis of pristine and annealed CN derivatives.

Sample	C wt%	N wt%	H wt%	N/C ratio	Stoichiometry
CN(C)	***33.78***	***61.47***	***1.76***	***1.56***	$C_3N_{4.68}H_{1.85}$
Nv-CN(C)600N_2	34.14	61.23	1.63	1.54	$C_3N_{4.61}H_{1.70}$
Nv-CN(C)600Ar	34.04	60.09	1.64	1.51	$C_3N_{4.54}H_{1.72}$
***Nv*-CN(C)650N_2**	**33.64**	**57.90**	**1.73**	**1.47**	$\mathbf{C_3N_{4.43}H_{1.84}}$
***Nv*-CN(C)650Ar**	**32.35**	**56.05**	**1.90**	**1.49**	$\mathbf{C_3N_{4.47}H_{2.10}}$
CN(D)	***34.57***	***62.66***	***1.61***	***1.55***	$C_3N_{4.66}H_{1.66}$
Nv-CN(D)600N_2	34.29	61.51	1.60	1.54	$C_3N_{4.61}H_{1.67}$
Nv-CN(D)600Ar	34.41	61.99	1.57	1.54	$C_3N_{4.63}H_{1.63}$
Nv-CN(D)650N_2	34.47	60.62	1.61	1.51	$C_3N_{4.52}H_{1.67}$
***Nv*-CN(D)650Ar**	**34.42**	**59.97**	**1.59**	**1.49**	$\mathbf{C_3N_{4.48}H_{1.65}}$
CN(M)	***34.66***	***63.10***	***1.60***	***1.56***	$C_3N_{4.68}H_{1.64}$
Nv-CN(M)600N_2	34.56	61.80	1.55	1.53	$C_3N_{4.60}H_{1.60}$
Nv-CN(M)600Ar	34.46	61.20	1.55	1.54	$C_3N_{4.57}H_{1.61}$
Nv-CN(M)650N_2	34.41	61.41	1.61	1.53	$C_3N_{4.59}H_{1.67}$
***Nv*-CN(M)650Ar**	**34.41**	**61.04**	**1.57**	**1.52**	$\mathbf{C_3N_{4.56}H_{1.62}}$

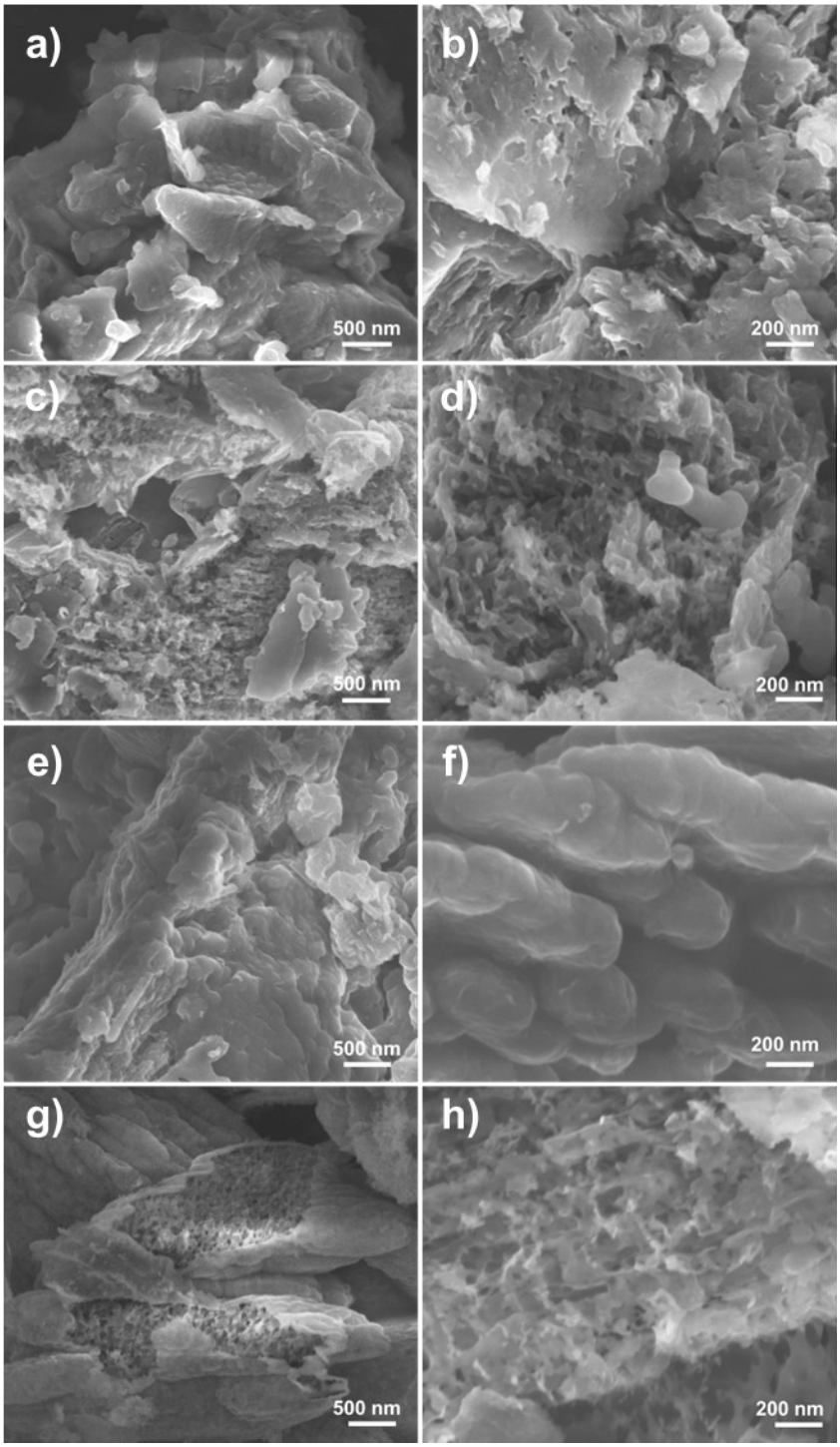


Figure S5. SEM images of **a** and **b)** CN(D), **c** and **d)** *Nv*-CN(D)600N_2, **e** and **f)** CN(M), **g** and **h)** *Nv*-CN(M)650Ar at different magnification.

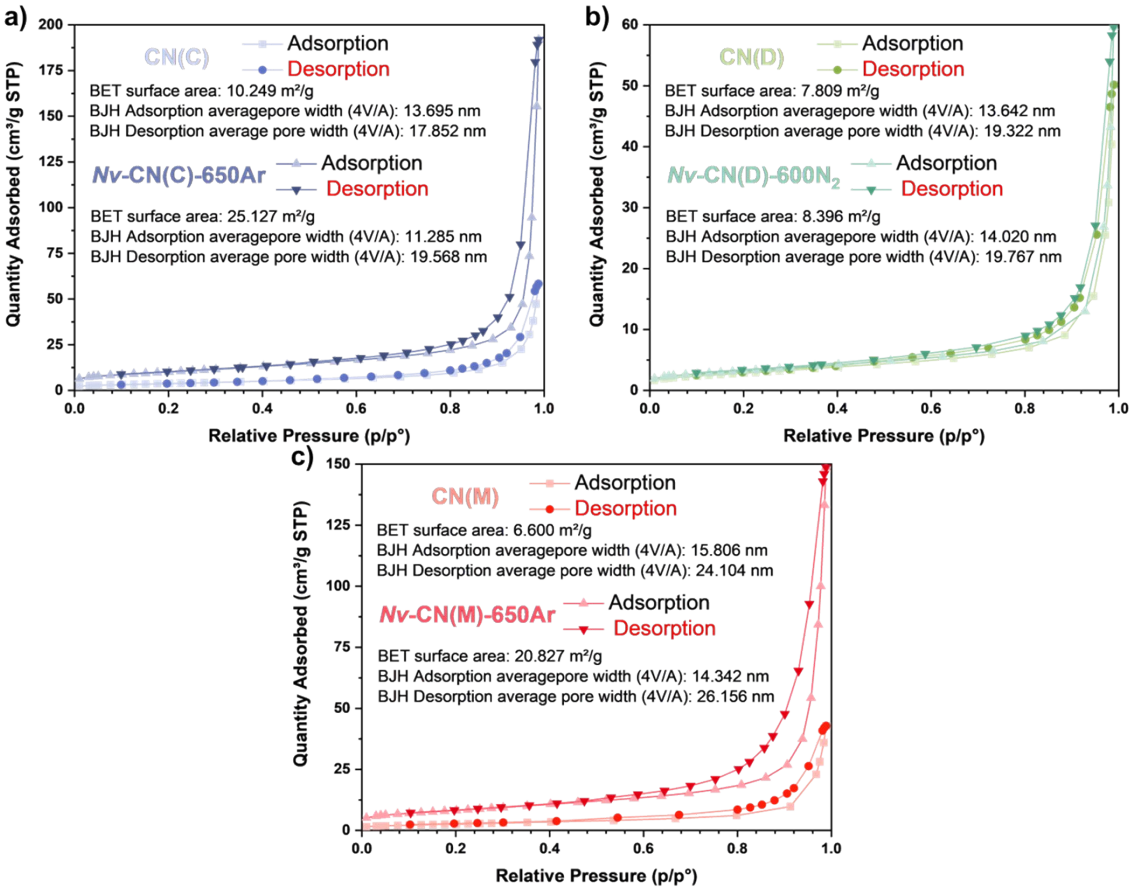


Figure S6. The Brunauer–Emmett–Teller (BET) N_2 adsorption/desorption isotherms of pristine and annealed CN derivatives using the precursor **a)** cyanamide, **b)** dicyandiamide, and **c)** melamine.

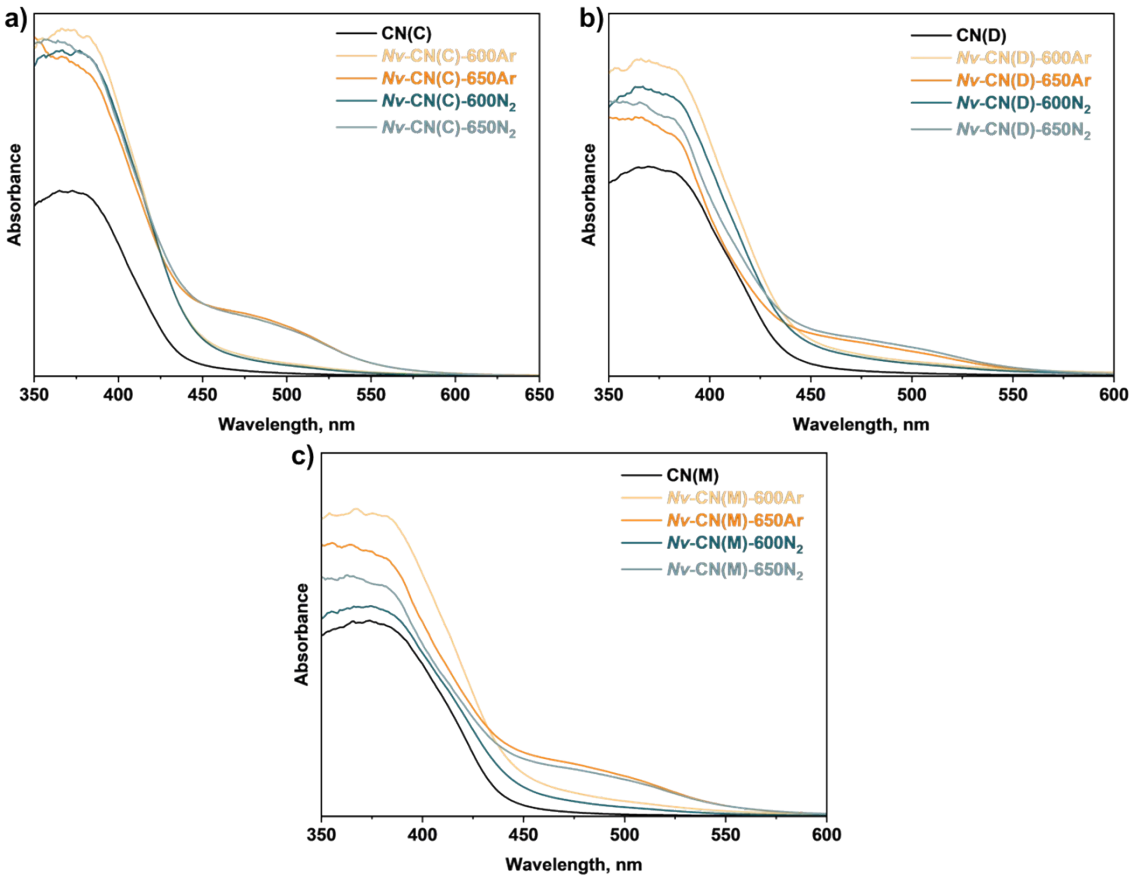


Figure S7. The UV-Vis absorption spectra of pristine and annealed CN derivatives using the precursor **a)** cyanamide, **b)** dicyandiamide, and **c)** melamine.

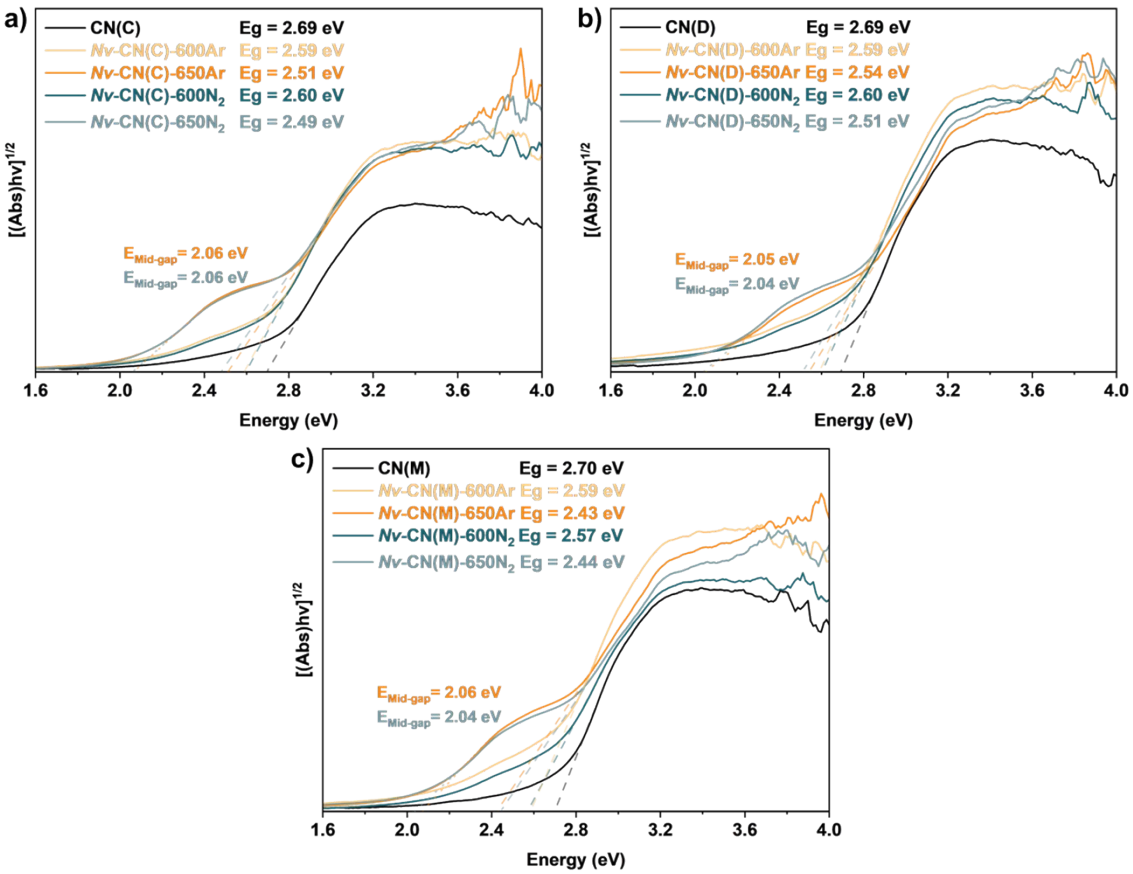


Figure S8. The Tauc plots of pristine and annealed CN derivatives using the precursor **a)** cyanamide, **b)** dicyandiamide, and **c)** melamine.

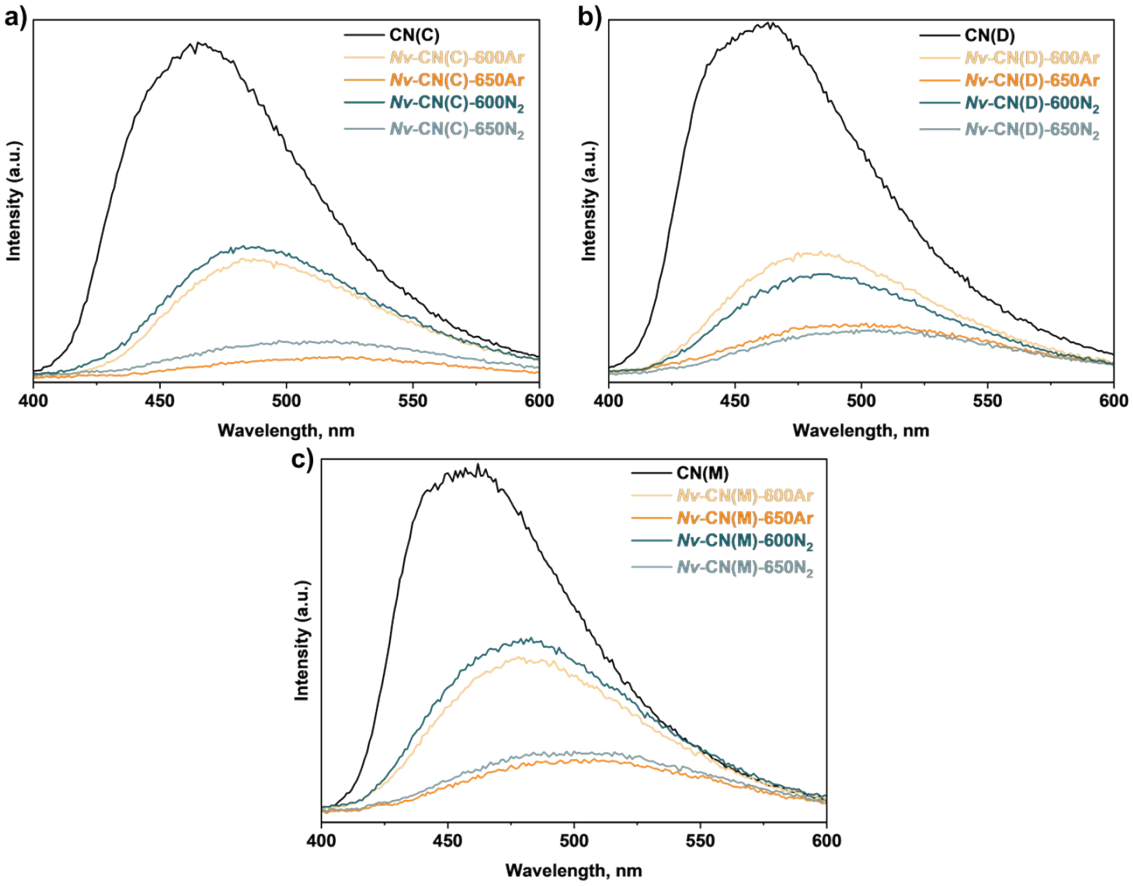


Figure S9. The PL spectra of pristine and annealed CN derivatives using the precursor **a)** cyanamide, **b)** dicyandiamide, and **c)** melamine.

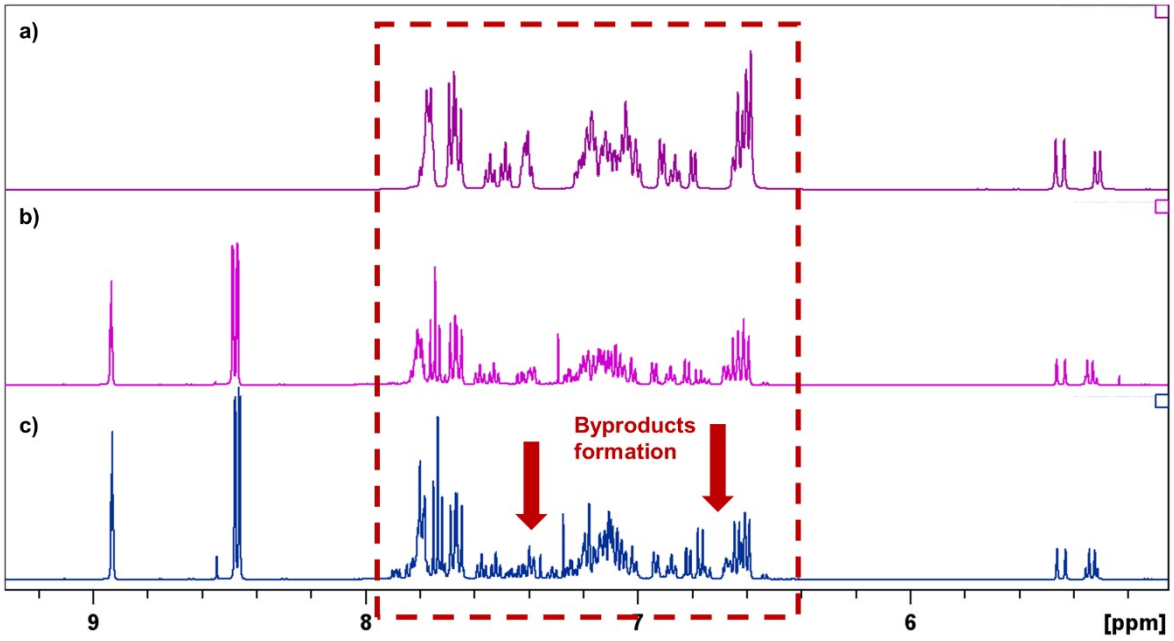


Figure S10. ^{1}H NMR of compound **5 a)** pure, **b)** reaction time is 2 h and **c)** reaction time is 5 h (control experiments showing the possible degradation of compound **5** for longer period of reaction. Note* ^{1}H NMR in **b)** and **c)** contain internal standard 1,3-dinitrobenzene).

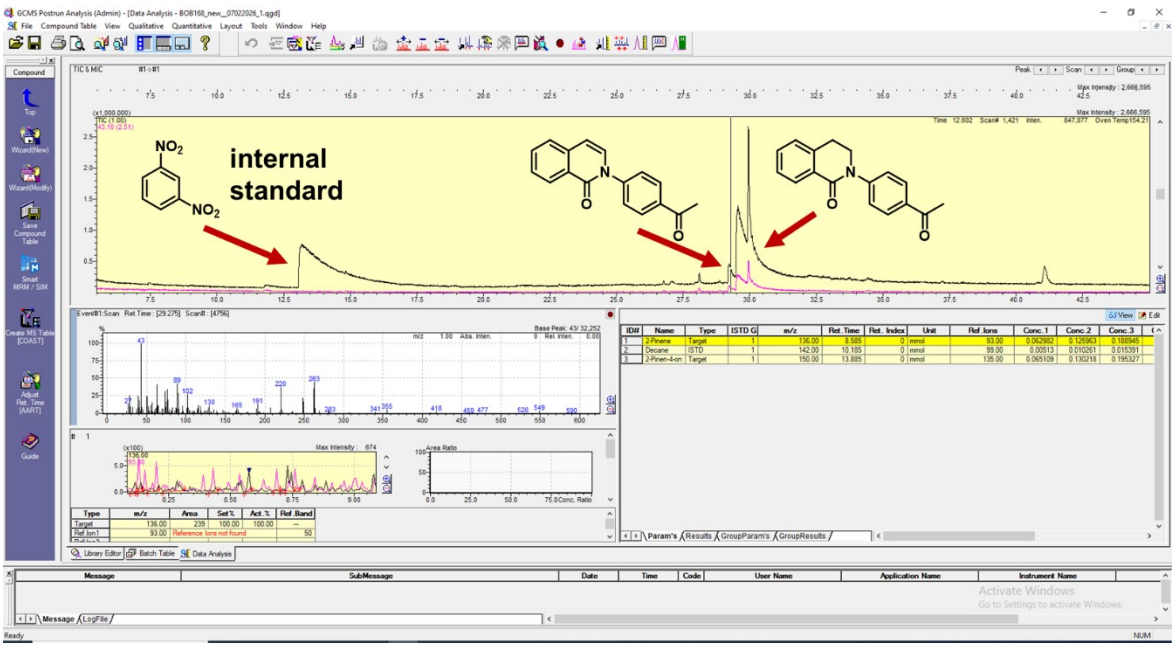


Figure S11. GC-MS of byproducts (compound **5** after treating under optimized conditions with longer duration).

Experimental procedure for degradation reaction: 0.03 mmol of purified compound **3** in 10 mL of 9:1 MeCN/DMSO mixture in the presence of 3 mg *Nv*-CN(C)-650Ar was irradiated with blue LED for 5 hours. At the end of the irradiation, 0.03 mmol of 1,3-dinitrobenzene was added to the mixture, then the mixture was filtrated through a syringe filter. After extraction of the filtrate with EtOAc, the organic phase was concentrated and then analyzed.

Table S3. Optimization table for the model reaction.

Entry	Photocatalyst	Catalyst Amount	Reaction Time	Solvent	Light Source	Yield%[a]
1	-	-	1h	1 mL MeCN	Low Mode Blue LED	14
2	CN(C)	3 mg	1h	1 mL MeCN	Low Mode Blue LED	20
3	*Nv*-CN(C)-600N_2	3 mg	1h	1 mL MeCN	Low Mode Blue LED	27
4	*Nv*-CN(C)-600Ar	3 mg	1h	1 mL MeCN	Low Mode Blue LED	21
5	*Nv*-CN(C)-650N_2	3 mg	1h	1 mL MeCN	Low Mode Blue LED	27
6	*Nv*-CN(C)-650Ar	3 mg	1h	1 mL MeCN	Low Mode Blue LED	30
7	CN(D)	3 mg	1h	1 mL MeCN	Low Mode Blue LED	15
8	*Nv*-CN(D)-600N_2	3 mg	1h	1 mL MeCN	Low Mode Blue LED	25
9	*Nv*-CN(D)-	3 mg	1h	1 mL MeCN	Low	25

	600Ar				Mode Blue LED	
10	*Nv*-CN(D)-650N_2	3 mg	1h	1 mL MeCN	Low Mode Blue LED	24
11	*Nv*-CN(D)-650Ar	3 mg	1h	1 mL MeCN	Low Mode Blue LED	20
12	CN(M)	3 mg	1h	1 mL MeCN	Low Mode Blue LED	14
13	*Nv*-CN(M)-600N_2	3 mg	1h	1 mL MeCN	Low Mode Blue LED	17
14	*Nv*-CN(M)-600Ar	3 mg	1h	1 mL MeCN	Low Mode Blue LED	26
15	*Nv*-CN(M)-650N_2	3 mg	1h	1 mL MeCN	Low Mode Blue LED	26
16	*Nv*-CN(M)-650Ar	3 mg	1h	1 mL MeCN	Low Mode Blue LED	27
17	*Nv*-CN(C)-650Ar	3 mg	1h	5 mL MeCN	Low Mode Blue LED	37
18	*Nv*-CN(C)-	3 mg	1h	5 mL MeCN	High	70

	650Ar				Mode Blue LED	
19	*Nv*-CN(C)-650Ar	5 mg	1h	5 mL MeCN	High Mode Blue LED	61
20	*Nv*-CN(C)-650Ar	7 mg	1h	5 mL MeCN	High Mode Blue LED	65
21	*Nv*-CN(D)-600N_2	3 mg	1h	5 mL MeCN	Low Mode Blue LED	36
22	*Nv*-CN(D)-600N_2	3 mg	1h	5 mL MeCN	High Mode Blue LED	63
23	*Nv*-CN(M)-650Ar	3 mg	1h	5 mL MeCN	Low Mode Blue LED	29
24	*Nv*-CN(M)-650Ar	3 mg	1h	5 mL MeCN	High Mode Blue LED	51
25	*Nv*-CN(C)-650Ar	3 mg	1h	5 mL Toluene	High Mode Blue LED	33
26	*Nv*-CN(C)-650Ar	3 mg	1h	7 mL MeCN	High Mode Blue LED	68
27	*Nv*-CN(C)-	3 mg	1h	10 mL MeCN	High	76

	650Ar				Mode Blue LED	
28	*Nv*-CN(C)-650Ar	3 mg	1h	10 mL (9:1) MeCN:DMF	High Mode Blue LED	57
29	*Nv*-CN(C)-650Ar	3 mg	1h	10 mL (9:1) MeCN:THF	High Mode Blue LED	77
30	*Nv*-CN(C)-650Ar	3 mg	1h	10 mL (9.5:0.5) MeCN:DMSO	High Mode Blue LED	73
31	*Nv*-CN(C)-650Ar	3 mg	1h	10 mL (9:1) MeCN:DMSO	High Mode Blue LED	92
32	*Nv*-CN(C)-650Ar	3 mg	1h	15 mL MeCN	High Mode Blue LED	62
33	*Nv*-CN(C)-650Ar	3 mg	0.5h	10 mL (9:1) MeCN:DMSO	High Mode Blue LED	63
34	*Nv*-CN(C)-650Ar	3 mg	2h	10 mL (9:1) MeCN:DMSO	High Mode Blue LED	73
35	*Nv*-CN(C)-650Ar	3 mg	1h	10 mL (9:1) MeCN:DMSO	High Mode Cyan LED	44
36	*Nv*-CN(C)-	3 mg	1h	10 mL (9:1)	High	25

	650Ar			MeCN:DMSO	Mode Green LED	
37	*Nv*-CN(C)-650Ar	3 mg	1h	10 mL (9:1) MeCN:DMSO	High Mode White LED	59
38	*Nv*-CN(C)-650Ar	3 mg	1h	10 mL (9:1) MeCN:DMSO	DARK	0

[a]0.25 mmol of **1** and **2** were used. Solvents were gassed with oxygen beforehand. Yields were determined by ^{1}H-NMR using 0.25 mmol 1,3-dinitrobenzene as the internal standard.

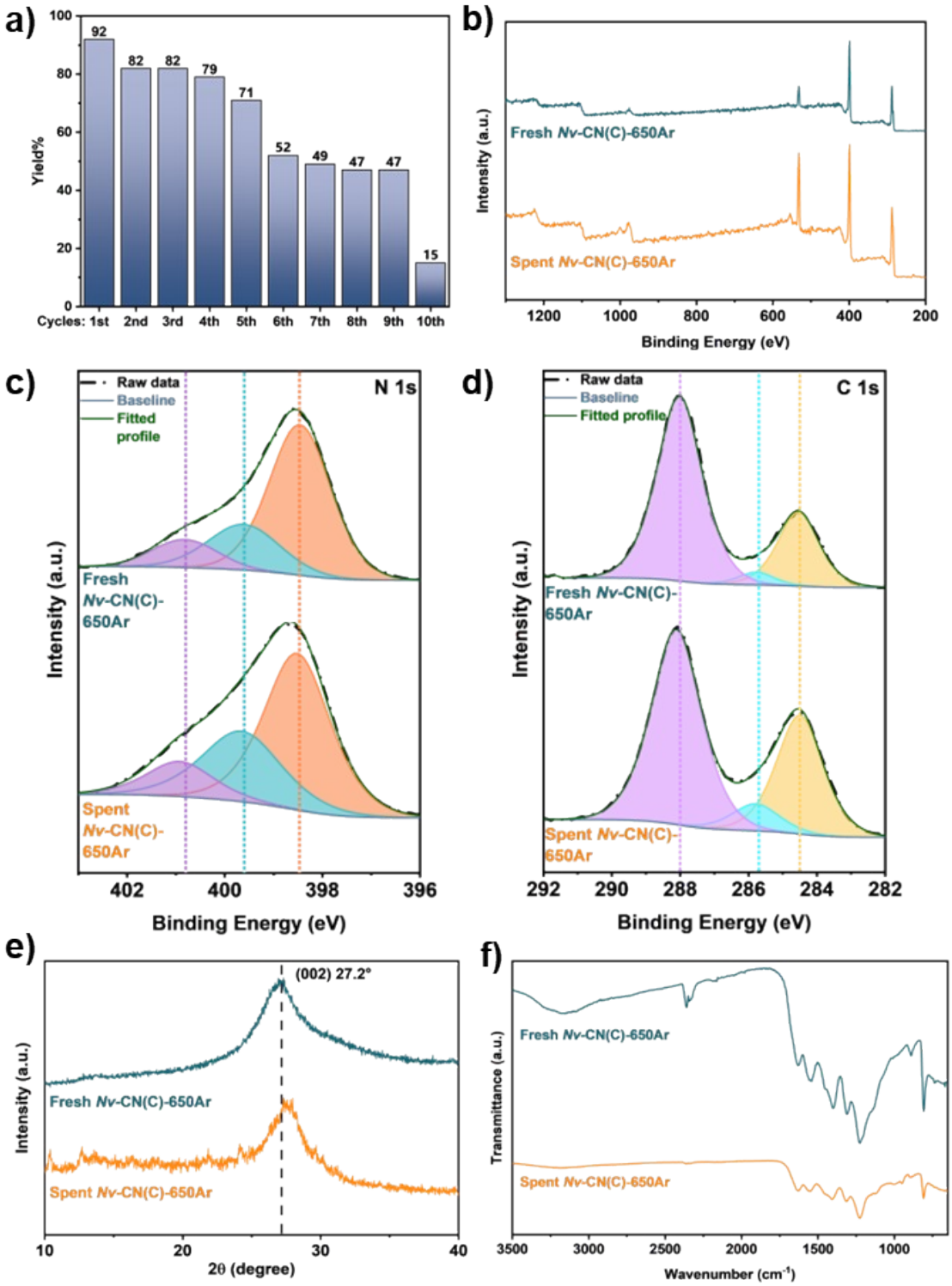


Figure S12. a) The reusability trials for ten consecutive cycles, **b)** The XPS survey spectra, The high resolutions **c)** C 1s and **d)** N 1s XPS spectra, **e)** The XRD pattern, and **f)** The FT-IR spectra of *Nv*-CN(C)-650Ar before and after use in ten consecutive cycles.

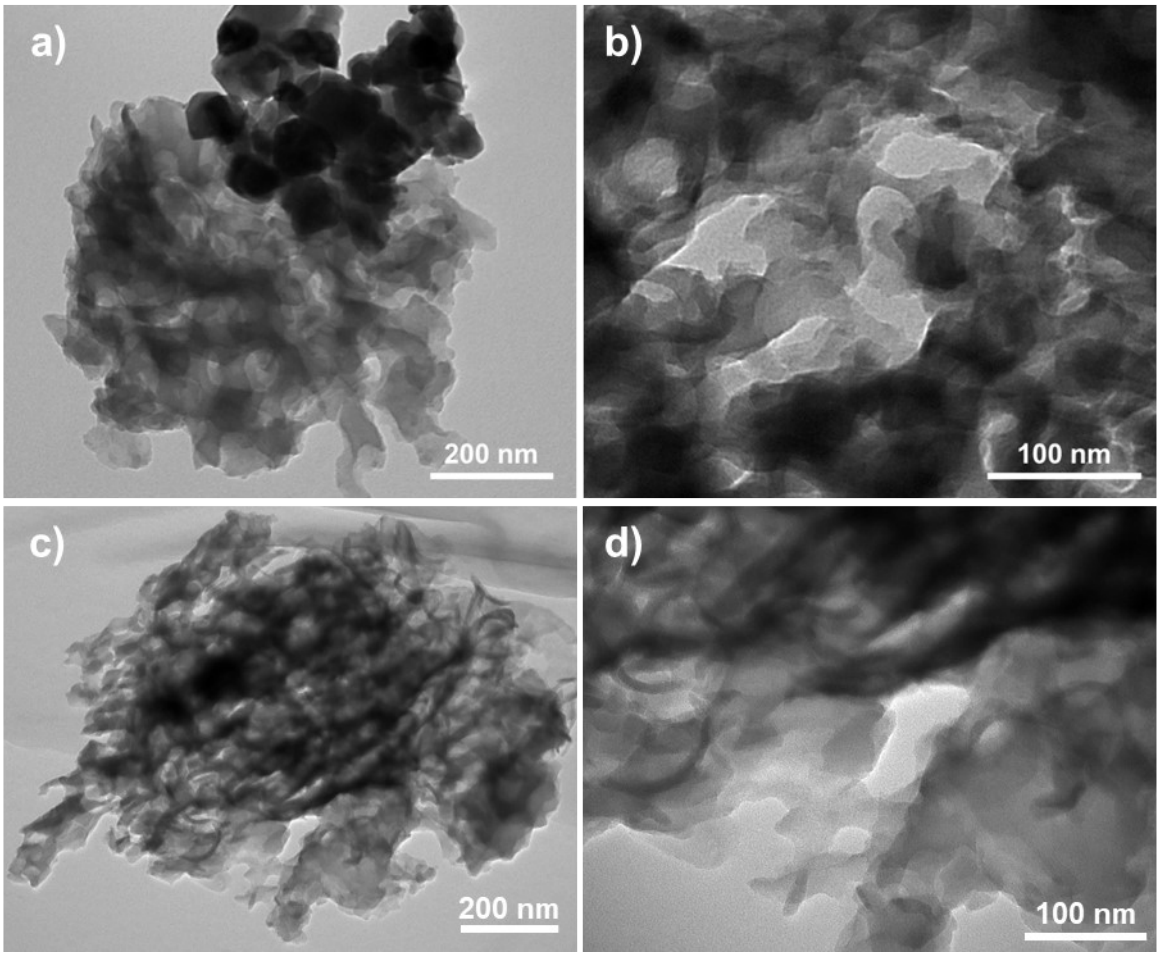
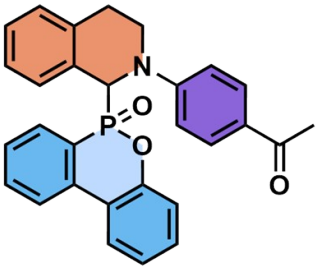


Figure S13. The TEM image of photocatalyst *Nv*-CN(C)-650Ar after **a-b)** five consecutive cycles of, and **c-d)** ten consecutive cycles of reusability experiments.

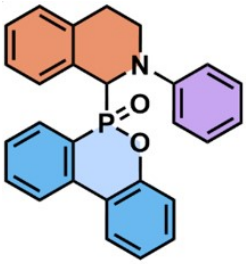
NMR Results



3, 92%

1-(4-(1-(6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)-3,4-dihydroisoquinolin-2(1H)-yl)phenyl)ethan-1-one (**3**), (92% yield, 1:3 d.r.)

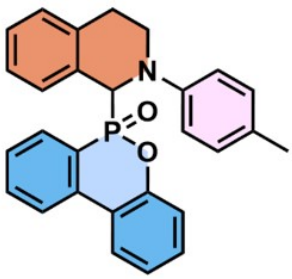
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89-7.86 (m, 2H), 7.78 (d, *J* = 9.1 Hz, 2H), 7.61-7.58 (m, 1H), 7.53-7.49 (m, 1H), 7.31-7.14 (m, 5H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.72-6.67 (m, 4H), 5.56 (d, *J* = 15.50 Hz 1H), 3.38-3.33 (m, 1H), 3.31-3.25 (m, 1H), 2.75-2.70 (m, 1H), 2.51-2.44 (m, 1H), 2.50 (s, 3H).
^{13}C NMR (125.7 MHz, $CDCl_3$): 196.52, 151.96, 151.67, 149.69, 136.85, 135.70, 135.66, 133.94, 132.17, 130.52, 130.10, 128.75, 128.30, 128.21, 128.10, 127.98, 127.17, 126.80, 124.71, 124.43, 123.21, 123.13, 119.66, 119.61, 112.66, 61.46, 42.94, 27.17, 26.11.
^{31}P NMR (202.4 MHz, $CDCl_3$): δ 31.82, 31.47.



5, 80%

6-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**5**), (80% yield, 1:3 d.r.)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88-7.85 (m, 2H), 7.59-7.55 (m, 2H), 7.31-7.10 (m, 6H), 7.00 (d, *J* = 7.30 Hz, 1H), 6.78-6.72 (m, 4H), 6.68 (d, *J* = 8.43 Hz, 2H), 5.42 (d, *J* = 17.56 Hz 1H), 3.38-3.33 (m, 1H), 3.22-3.18 (m, 1H), 2.72-2.66 (m, 1H), 2.36-2.31 (m, 1H).
^{13}C NMR (125.7 MHz, $CDCl_3$): 150.05, 149.98, 148.70, 148.67, 136.79, 136.24, 133.57, 132.25, 132.18, 130.23, 129.00, 128.85, 128.46, 128.04, 128.00, 127.98, 127.89, 127.73, 127.70, 126.46, 126.44, 124.57, 124.06, 123.04, 62.06, 44.43, 26.79.
^{31}P NMR (202.4 MHz, $CDCl_3$): δ 33.14, 32.05.



7, 76%

6-(2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (**7**), (76% yield, 1:6 d.r.)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90-7.87 (m, 2H), 7.61-7.55 (m, 2H), 7.42-7.38 (m, 1H), 7.28-7.15 (m, 6H), 7.01 (d, *J* = 7.45 Hz, 1H), 6.93 (d, *J* = 8.50 Hz, 2H), 6.86 (dd, *J* = 7.66 Hz, *J* = 1.67 Hz, 2H), 5.32 (d, *J* = 18.27 Hz, 1H), 3.41-3.36 (m, 1H), 3.21-3.16 (m, 1H), 2.71-2.67 (m, 1H), 2.36-2.30 (m, 1H), 2.21 (s, 3H).
^{13}C NMR (125.7 MHz, $CDCl_3$): 150.12, 146.49, 140.52, 138.27, 136.07, 131.92, 130.84, 130.26,

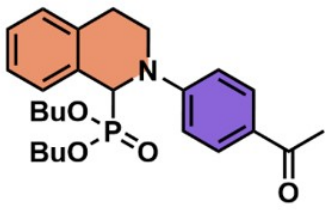
130.12, 129.75, 129.53, 129.38, 128.70, 128.05, 127.14, 125.19, 124.61, 124.29, 124.03, 120.69, 120.38, 119.86, 116.63, 115.65, 62.30, 44.04, 28.61, 20.27.
^{31}P NMR (202.4 MHz, $CDCl_3$): δ 33.25, 31.73.

diethyl (2-(4-acetylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (**11**),
(83% yield)

11, 83%

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (d, *J* = 9.05 Hz, 2H), 7.36 (d, *J* = 9.05 Hz, 1H), 7.24-7.18 (m, 3H), 6.96 (d, *J* = 9.05 Hz, 2H), 5.32 (d, *J* = 17.95 Hz 1H), 4.13 (q, *J* = 7.05 Hz 4H), 3.86-3.80 (m, 1H), 3.68-3.63 (m, 1H), 3.35-3.29 (m, 1H), 3.04-2.98 (m, 1H), 2.46 (s, 3H), 1.26 (t, *J* = 7.07 Hz 6H).
^{13}C NMR (125.7 MHz, $CDCl_3$): 196.47, 152.68, 137.41, 136.34, 134.39, 130.31, 129.08 128.52, 128.09, 127.93, 126.94, 126.21, 124.58, 63.29, 58.59, 43.39, 29.67, 27.44, 16.43.
^{31}P NMR (202.4 MHz, $CDCl_3$): δ 21.32.

dibutyl (2-(4-acetylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (**13**),
(76% yield)



13, 76%

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, *J* = 9.05 Hz, 2H), 7.30 (d, *J* = 7.45 Hz, 1H), 7.25-7.16 (m, 3H), 6.88 (d, *J* = 8.96 Hz, 2H), 5.26 (d, *J* = 18.06 Hz 1H), 3.99-3.86 (m, 3H), 3.83-3.76 (m, 1H), 3.71-3.59 (m, 2H), 3.29-3.23 (m, 1H), 2.99-2.93 (m, 1H), 2.44 (s, 3H), 1.51-1.45 (m, 2H), 1.40-1.35 (m, 2H), 1.26-1.11 (m, 4H), 0.81 (t, *J* = 7.35 Hz 3H), 0.75 (t, *J* = 7.44 Hz 3H).
^{13}C NMR (125.7 MHz, $CDCl_3$): 197.11, 164.15, 147.20, 138.23, 134.33, 132.43, 130.36, 129.38, 128.89, 127.45, 127.02, 124.57, 112.30, 66.89, 58.51, 57.25, 43.33, 32.48, 29.67, 27.47, 26.74, 18.61, 18,57, 13.53, 13.48.
^{31}P NMR (202.4 MHz, $CDCl_3$): δ 21.46.

diphenyl (2-(4-acetylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (**15**)
(71% yield)

15, 71%

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, *J* = 9.01 Hz, 2H), 7.51-7.49 (m, 1H), 7.32-7.22 (m, 5H), 7.17-7.11 (m, 3H), 7.07-7.03 (m, 3H), 6.97 (d, *J* = 8.53 Hz, 2H), 6.82 (d, *J* = 8.53 Hz, 2H), 5.76 (d, *J* = 17.62 Hz 1H), 4.06-4.01 (m, 1H), 3.74-3.69 (m, 1H), 3.34-3.30 (m, 1H), 3.08-3.03 (m, 1H), 2.53 (s, 3H).

^{13}C NMR (125.7 MHz, $CDCl_3$): 196.49, 152.08, 150.46, 150.37, 150.17, 150.08 136.40, 136.35, 130.45, 129.66, 129.52, 129.29, 128.79, 128.45, 128.42, 128.36, 128.31, 127.45, 126.55, 126.53, 125.22, 125.03, 120.46, 120.12, 112.74, 59.03, 43.61, 29.67, 27.37.

^{31}P NMR (202.4 MHz, $CDCl_3$): δ 13.81.

NMR Spectra

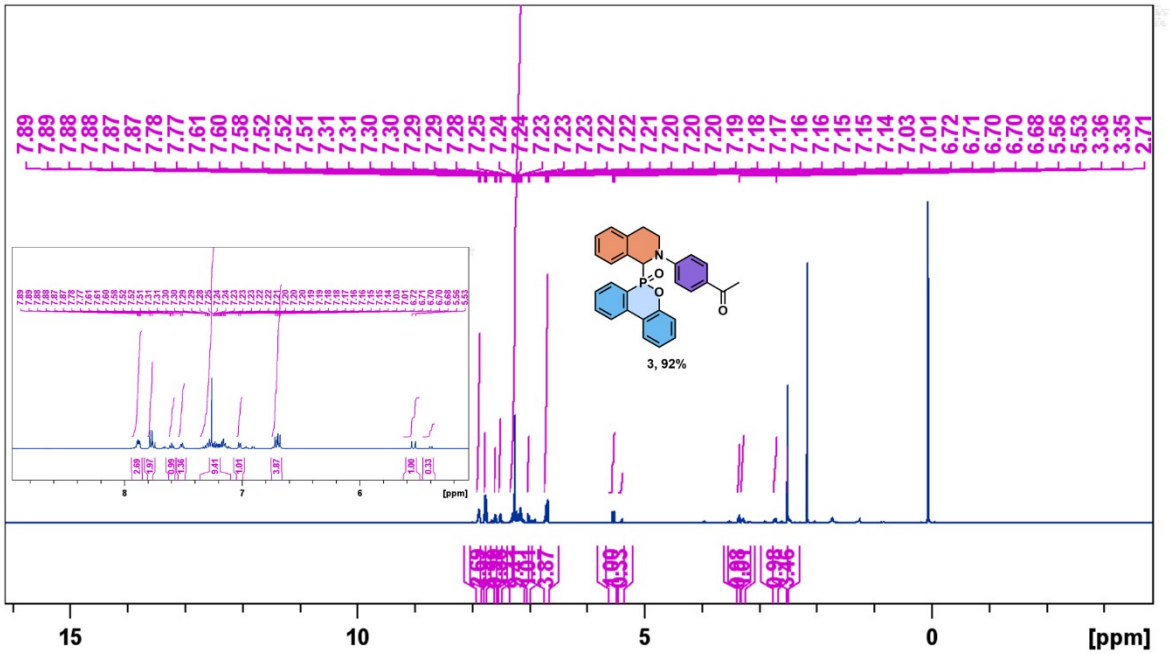


Figure S14. ^{1}H NMR of compound **3** ($CDCl_3$).

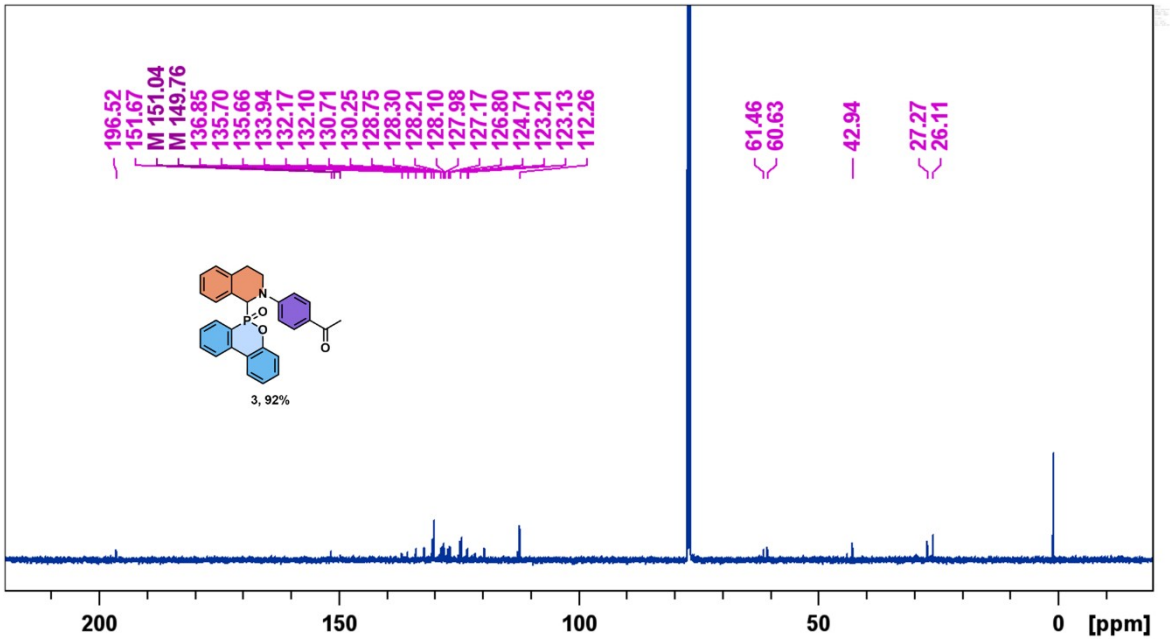


Figure S15. ^{13}C NMR of compound **3** ($CDCl_3$).

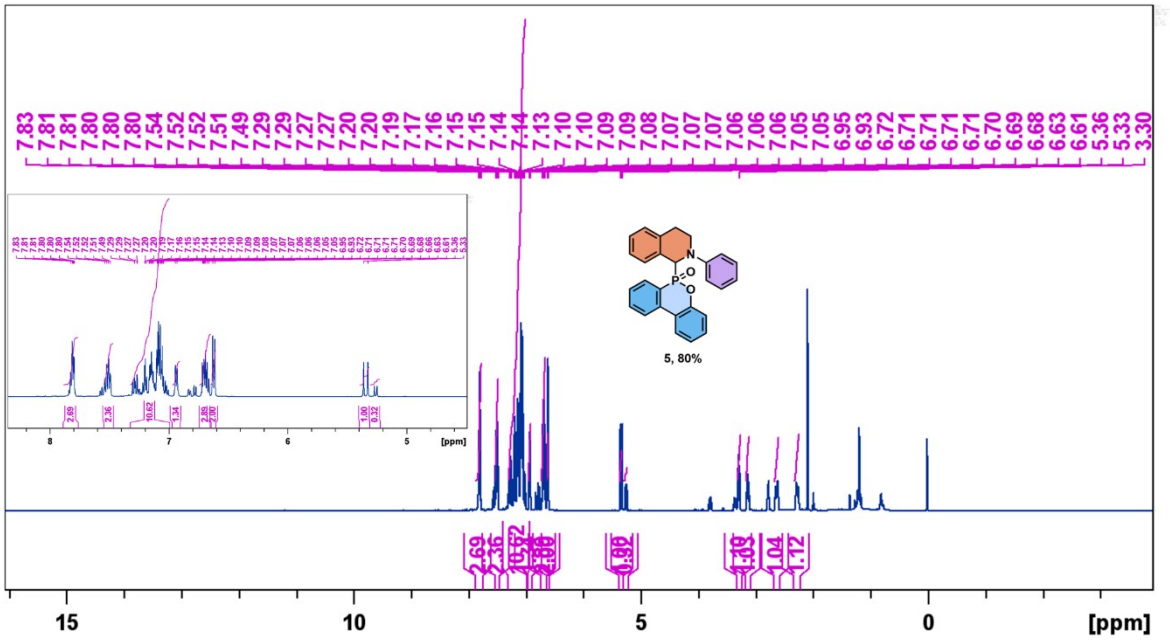


Figure S16. ^{1}H NMR of compound **5** ($CDCl_3$).

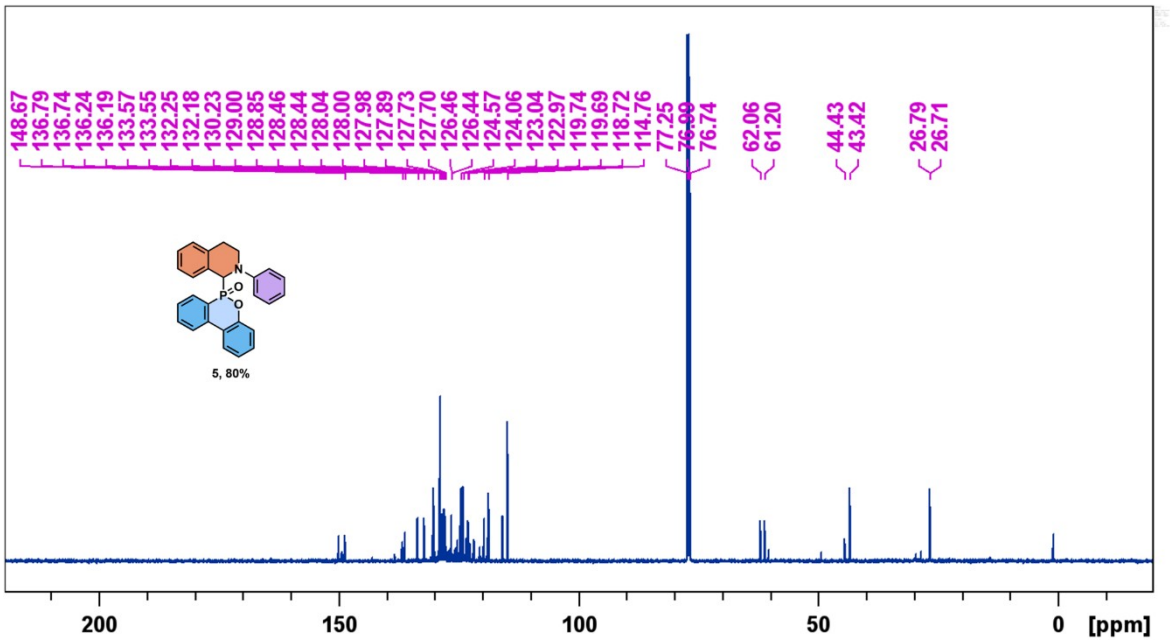


Figure S17. ^{13}C NMR of compound **5** ($CDCl_3$).

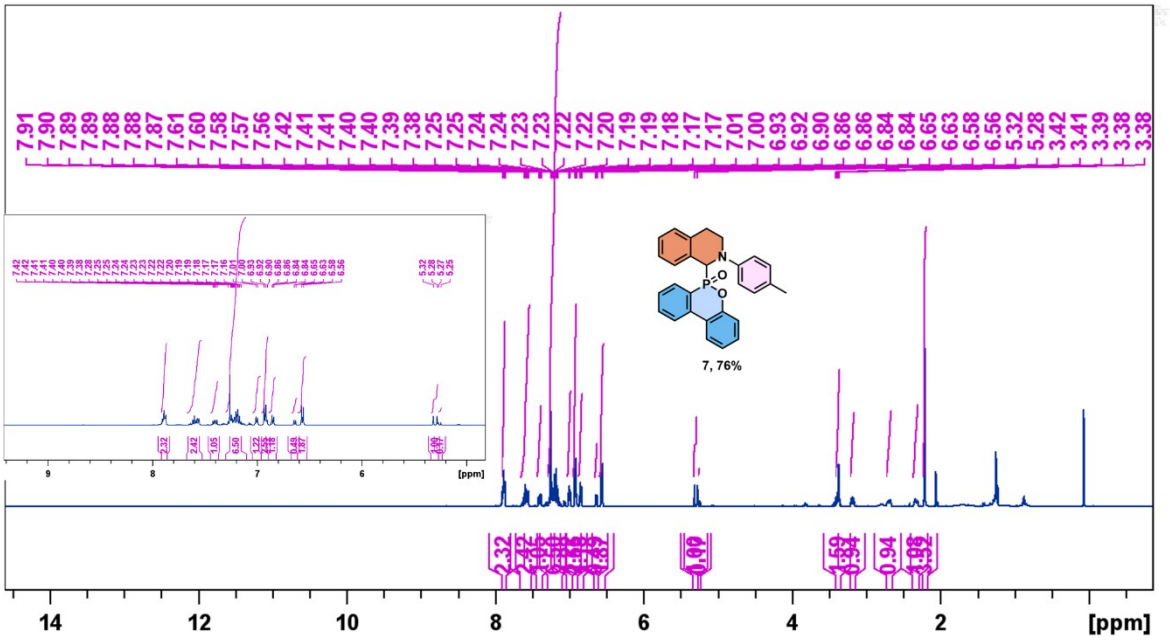


Figure S18. ^{1}H NMR of compound **7** ($CDCl_3$).

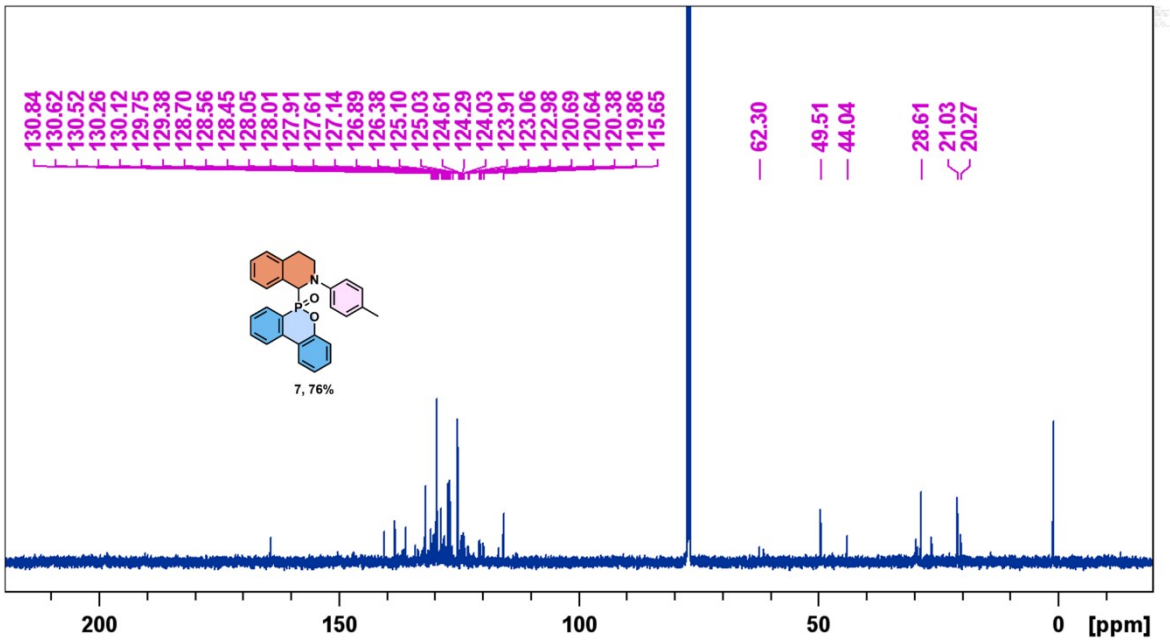


Figure S19. ^{13}C NMR of compound **7** ($CDCl_3$).

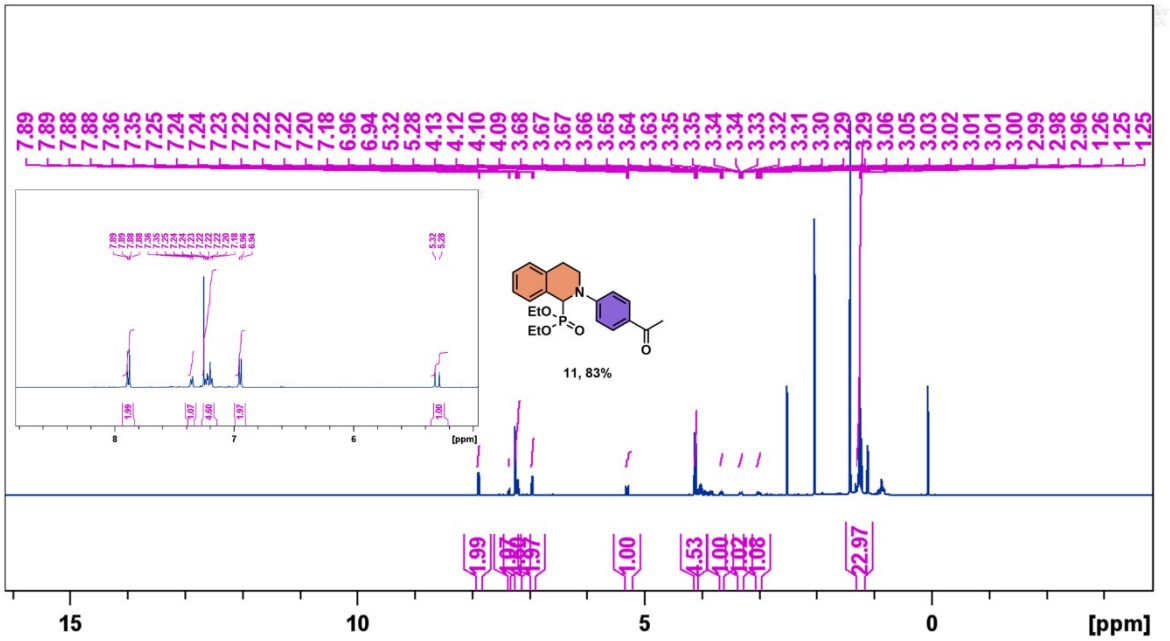


Figure S20. ^{1}H NMR of compound **11** ($CDCl_3$).

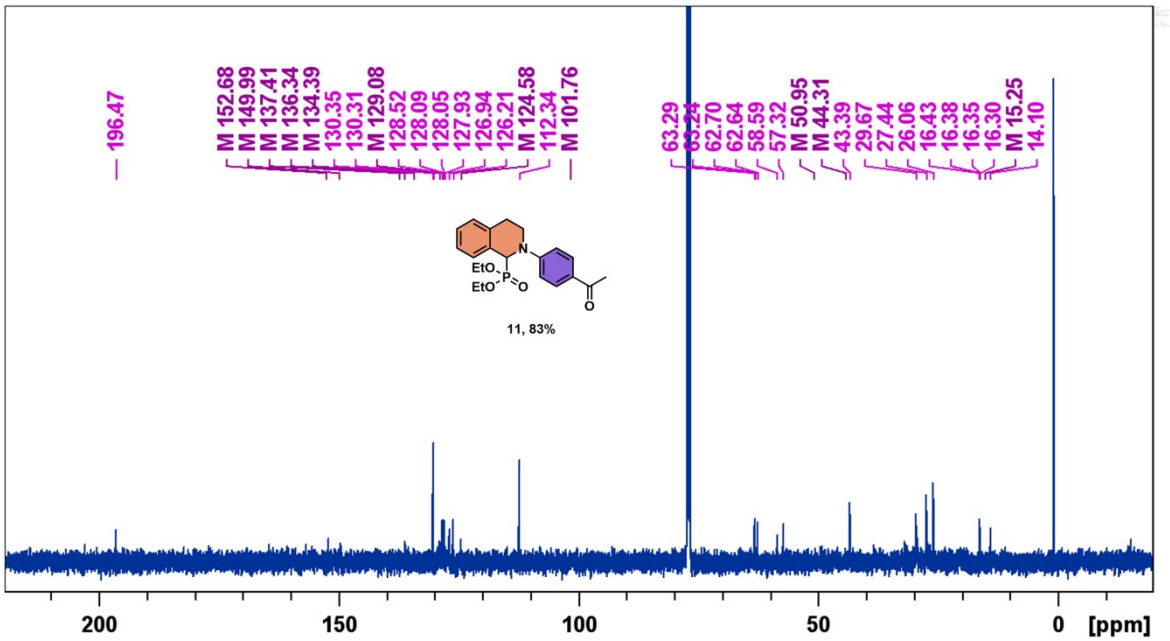


Figure S21. ^{13}C NMR of compound **11** ($CDCl_3$).

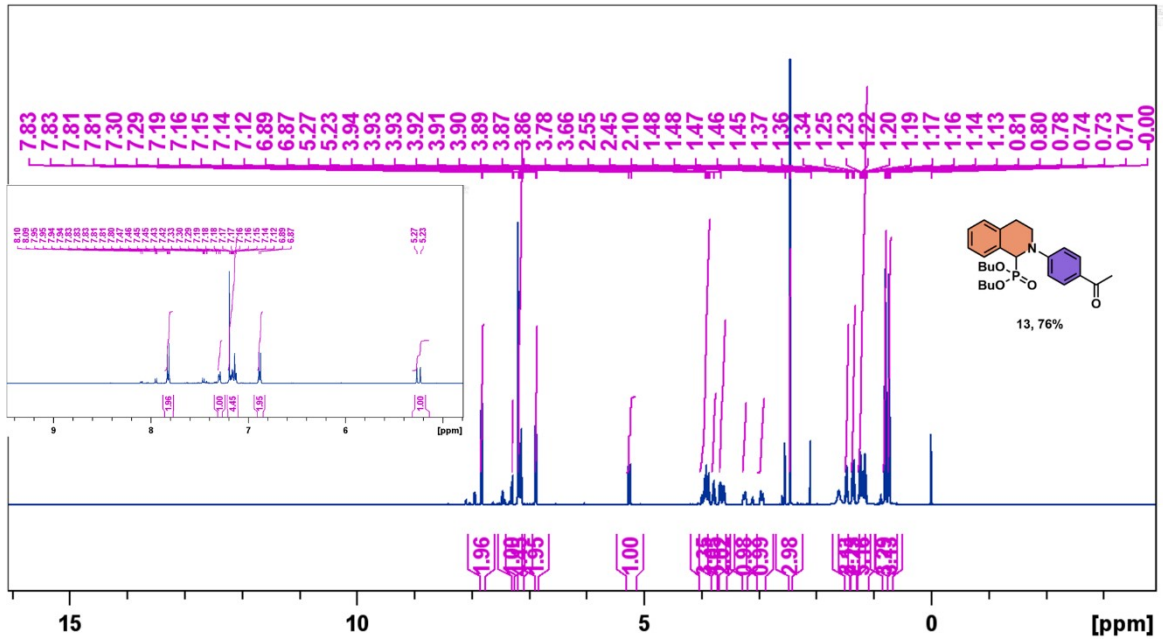


Figure S22. ^{1}H NMR of compound **13** ($CDCl_3$).

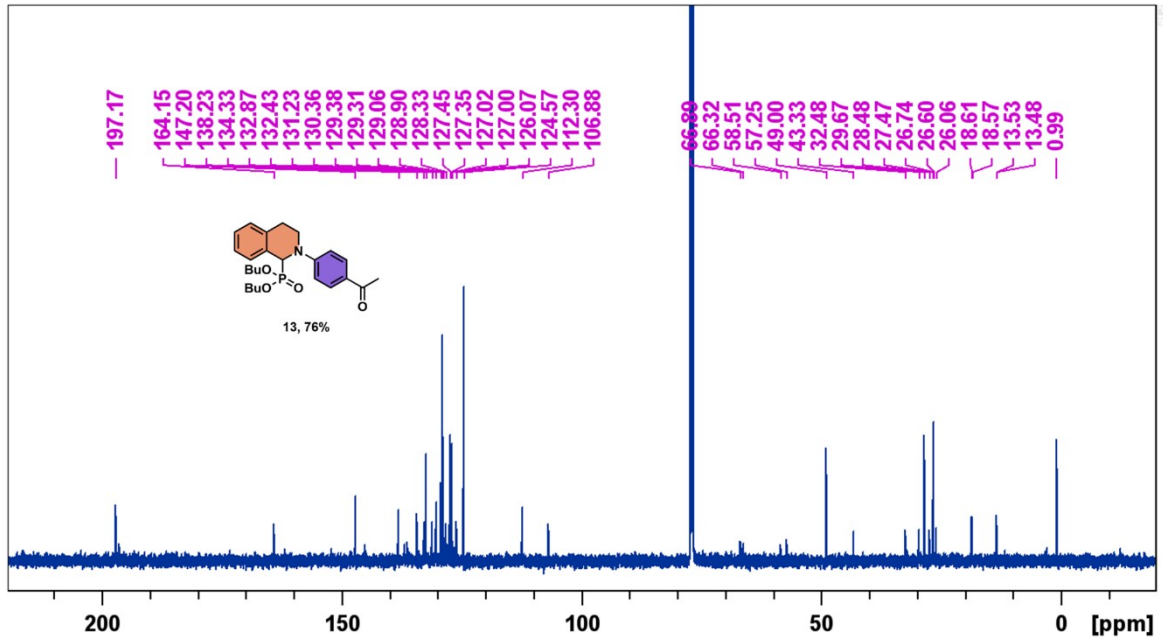


Figure S23. ^{13}C NMR of compound **13** ($CDCl_3$).

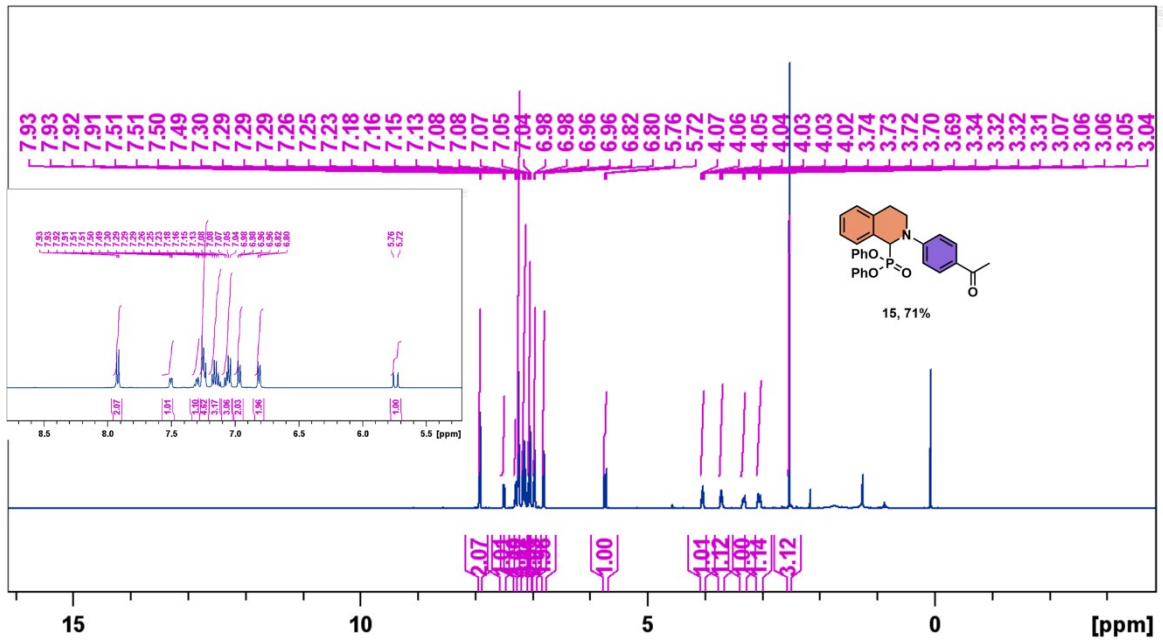


Figure S24. ^{1}H NMR of compound **15** ($CDCl_3$).

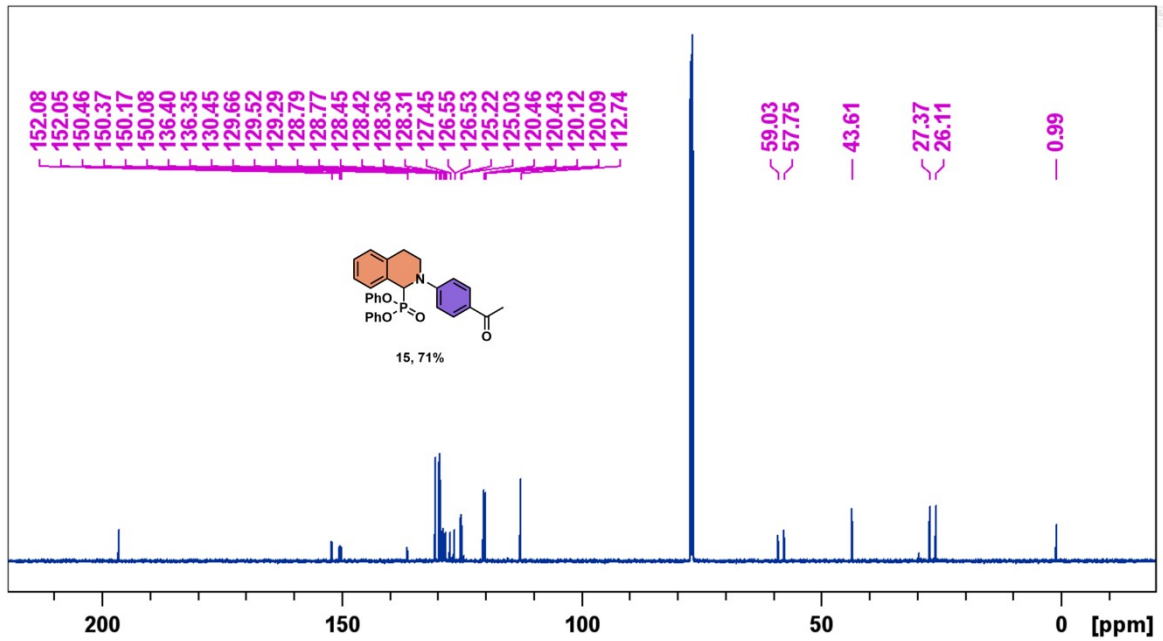


Figure S25. ^{13}C NMR of compound **15** ($CDCl_3$).

References

1 F. Y. Kwong, A. Klapars and S. L. Buchwald, *Org Lett*, 2002, **4**, 581–584.