Supporting Information

1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN)-based porous organic polymers for visible-light-driven organic transformations in water under aerobic oxidation

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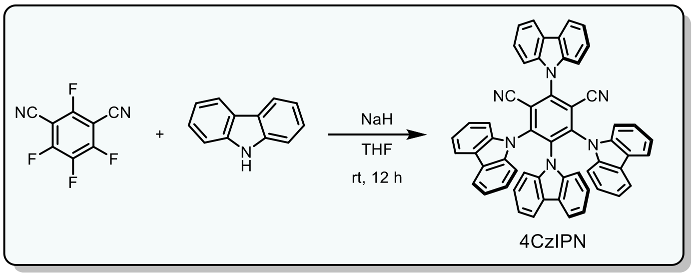
1. General Methods

All reagents were used without further purification. TLC was performed on silica gel plates (F254, 200-300 mesh) using UV light (254/366 nm) for detection and column chromatography was performed on neutral aluminum oxide (100-200 mesh). Liquid ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz or 151MHz), ^{19}F NMR (376 MHz), ^{31}P NMR (162 MHz) were measured on a Bruker Avance 400 MHz spectrometer. Proton chemical shifts δ were given in ppm using tetramethylsilane (TMS) as internal standard. All NMR spectra were recorded in $CDCl_3$ at room temperature (20 ± 3 °C). To display multiplicities and signal forms correctly the following abbreviations were used: s = singlet, d = doublet, t = triplet, m = multiplet. ^{1}H and ^{13}C chemical shifts are quoted in parts per million (ppm) downfield from TMS. High-resolution mass spectra (HRMS) were taken with a 3000-mass spectrometer, using Waters Q-Tof MS/MS system and the ESI technique. The ^{13}C CP/MAS NMR spectra were recorded by Bruker Avance (3) 400 WB. FT-IR spectra of the samples were recorded by Perkin Elmer. Gas sorption isotherms were obtained with Micromeritics ASAP 2460 2.01 accelerated surface area and porosimetry analyzers at certain temperature. Surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. The pore-size-distribution curves were obtained from the adsorption branches using non-local density functional theory (NLDFT) method. Field emission scanning electron microscopy (SEM) observations were performed on a Zeiss Merlin Compact microscope operated at an accelerating voltage of 15.0 kV. High-resolution transmission electron microscopy (HR-TEM, Tecnai G2 S-Twin F20, FEI), the energy-dispersive X-ray (EDX) spectroscopy, scanning TEM-EDX elemental mapping were performed on a HITACHI SU-8020 TEM. The XRD analysis was performed on a D/MAX-RC diffractometer operating at 50 kV and 200 mA with Cu Kα radiation (λ = 1.54056 Å). X-ray photoelectron spectroscopy (XPS) measurements were performed by a Thermo Fisher K-Alpha spectrometer, and the binding energies were calibrated using the carbonaceous C 1s line (284.8 eV) as the reference. EPR spectra were recorded with Bruker EMX-10/12 EPR spectrometer at room temperature. The thermal gravity analysis (TGA) measurement was conducted on Simultaneous. The UV-vis diffuse reflectance spectra (UV-vis DRS) were measured on a UV-vis-NIR spectrophotometer (Shimadzu UV-3600) detecting absorption over the range of 200-800 nm Cyclic voltammetry (CV) measurement was performed using Chen hua CHI 660E potentiostat/galvanostat (Metrohm) in a three-electrode-cell system.

2. Experimental Procedures

2.1 Preparation of Photocatalyst

2.1.1 Procedure for the synthesis of 4CzIPN photocatalyst[1]

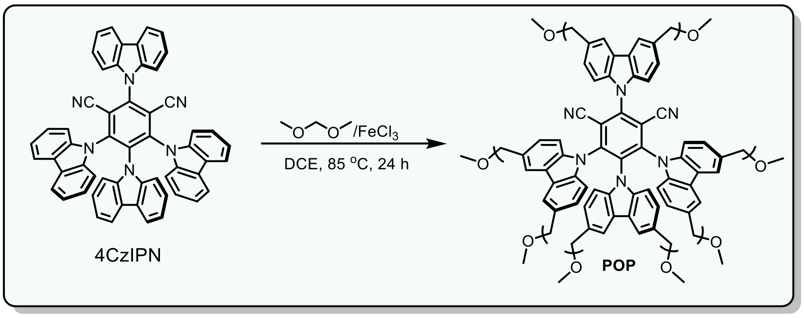


Scheme S1 Synthesis of 4CzIPN photocatalyst

Sodium hydride (60% suspension in mineral oil, 8.0 equiv) was added slowly to a stirred solution of carbazole (5.0 equiv) in dry THF (0.05 M) under a nitrogen atmosphere at rt. After 30 min, 2,4,5,6-

tetrafluoroisophthalonitrile (1.0 mmol, 1.0 equiv) was added. After stirring at rt for 12 h, 2 mL water was added to the reaction mixture to quench the excess NaH. The resulting mixture was then concentrated under reduced pressure and then the solid residue was washed with H_2O and EtOH to yield the crude product, which was purified by recrystallization from hexane/CH_2Cl_2 then filtered.

2.1.2 Synthesis of POPs *via* Friedel−Crafts alkylation reaction.

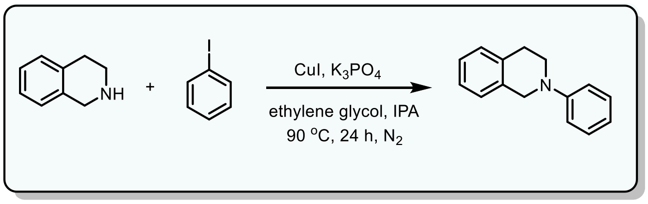


Scheme S2 Synthesis of POPs

$FeCl_3$ (5.84 g, 36 mmol, anhydrous) was added to a solution of 4CzIPN (3.15 g, 4 mmol) in 80 mL 1,2-dichloroethane (DCE). After being stirred at room temperature for 30 min, formaldehyde dimethyl acetal (FDA, 1.12 mL) was added. Then the resulting mixture was stirred first at 45 °C for 5 h and then at 80 °C for another 24 h to complete the cross-linking reaction, providing the crude **POP-1** solution. For the synthesis of **POP-2**, FDA (1.04 mL) was added again to the crude **POP-1** solution. The mixture was stirred at 80 °C for 24 h to complete the cross-linking reaction, providing the crude **POP-2** solution. Similarly, the addition of FDA (1.04 mL) to the crude **POP-2** solution and then stirring at 80 °C for 24 h will give the crude **POP-3** solution. For the further purification procedure, 30 mL methanol was added to the crude solution and stirred for 1 h. The resulting precipitate was washed with methanol three times. After filtration, the obtained solid was vigorously stirred in concentrated HCl for 2 h. Then, the suspension was filtered and washed with water and methanol. After extraction with methanol/dichloromethane in a Soxhlet extractor for 24 h and with tetrahydrofuran for another 24 h. The solid products were dried under vacuum at 60 ºC for 24 h, giving the desired **POP-1**, **POP-2**, and **POP-3**.

2.2 Preparation of Starting Materials

2.2.1 Synthesis of *N*-aryl-1,2,3,4-tetrahydroisoquinoline (exemplified by *N*-phenyl-1,2,3,4-tetrahydroisoquinoline)

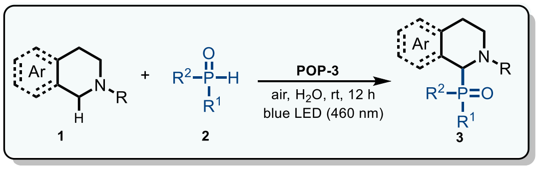


Scheme S3 Synthesis of *N*-phenyl -1,2,3,4-tetrahydroisoquinoline

A typical procedure is described as follows for the synthesis of *N*-phenyl-1,2,3,4-tetrahydroisoquinoline: To a two-neck round bottom flask, 400 mg CuI and 8.5 g anhydrous potassium phosphate was added. The flask was then connected with a condenser tube and the system was put into vacuum and recharged with N_2 to keep the system under an inert atmosphere. 20.0 mL 2-propanol (IPA), 2.2 mL ethylene glycol (EG), 4.0 mL 1,2,3,4-tetrahydroisoquinoline, and 2.6 mL iodine benzene was added into the flask *via* syringe. The mixture was refluxed for 24 h under 90 ºC and then left to cool to rt to pass a celite pad. The filtrate was mixed with 20.0 mL water and then extracted with ethyl acetate. The organic phase was collected and dried over anhydrous Na_2SO_4. The solvent was removed via rotary evaporation, and the remaining residue was purified by flash column chromatography on silica gel (petroleum ether/DCM (100:1~100:10) to afford the target compound.

2.3 Experimental procedures

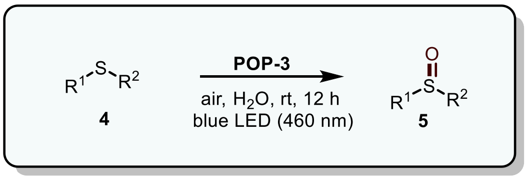
2.3.1 General Procedure for the Synthesis of 1-functionalized *N*-Aryl-tetrahydroisoquinolines



Scheme S4 Synthesis of the product 3aa

In a 10 mL reaction tube, a mixture of *N*-substituted THIQs **1** (0.2 mmol) and phosphorous reagents **2** (0.4 mmol), **POP-3** (2.0 mg) in 1.0 mL H_2O was allowed to stir with irradiation of 7 W blue LED (460 nm) in open air at rt for 12 h. The reaction was monitored by TLC. After substrate **1** was completely consumed, the reaction mixture was diluted with water (5.0 mL) and extracted with ethyl acetate (3 × 5.0 mL). The organic layers were combined, dried over anhydrous Na_2SO_4. and concentrated in *vacuo*. The residue was purified by chromatography on neutral aluminum oxide using petroleum ether/ethyl acetate as eluent to afford desired product **3**.

2.3.2 General Procedure for the Selective Oxidation of Sulfides to Sulfoxides



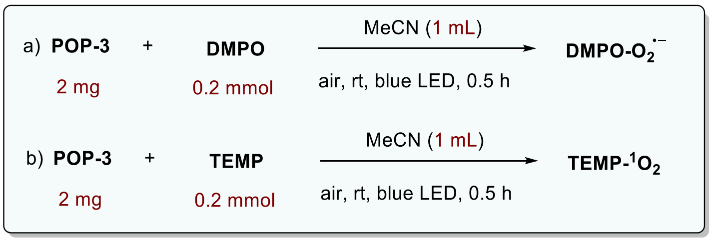
Scheme S5 Synthesis of the product Sulfoxides

In a 10 mL reaction tube, a mixture of sulfides **4** (0.2 mmol), **POP-3** (2.0 mg) in 1.0 mL H_2O was allowed to stir with irradiation of 7 W blue LED (460 nm) in open air at rt for 12 h. The reaction was monitored by TLC. After substrate **4** was completely consumed, the reaction mixture was diluted with water (5.0 mL) and extracted with ethyl acetate (3 × 5.0 mL). The organic layers were combined, dried over anhydrous Na_2SO_4. and concentrated in *vacuo*. The residue was purified by chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford desired product **5**.

2.4 Recycle experiment

In a 10 mL reaction tube, a mixture of *N*-phenyl-1,2,3,4-tetrahydroisoquinoline **1a** (0.2 mmol), diphenylphosphine oxide **2a** (0.4 mmol) **POP-3** (2.0 mg) in 1.0 mL H_2O was allowed to stir with irradiation of 7 W blue LEDs (460 nm) in the open air at rt for 12 h. After the reaction, the catalyst previously used was simply centrifuged at 10000 rpm for 10 min, and was washed with absolute ethanol (5 mL) for three times, the recyclable **POP-3** was dried under vacuum and directly reused for the next reaction cycle without any further purification.

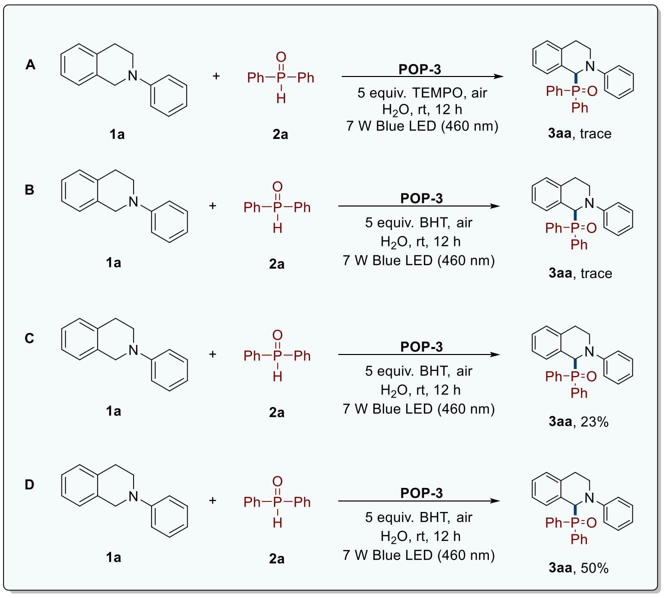
2.5 EPR experiment



Scheme S6 EPR experiments

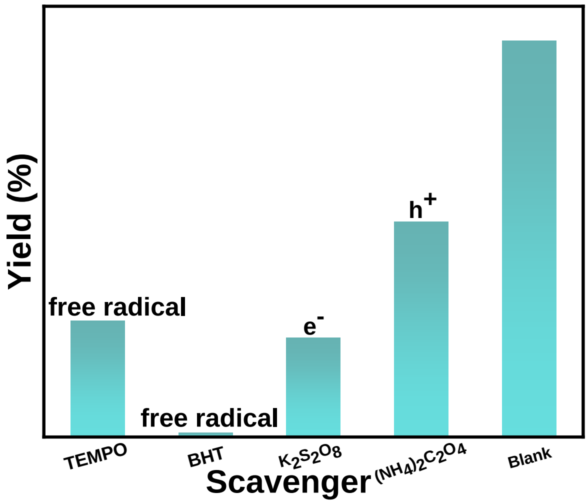
Reaction conditions: To a reaction tube, **POP-3** (2.0 mg), DMPO (5,5-dimethyl-1-pyrroline-*N*-oxide, 0.2 mmol) or TEMP (2,2,6,6-teteamethyl-piperidine) were dissolved in MeCN (1.0 mL), and then the solution was excited under the 7 W blue LED in open air at rt for 0.5 h. After reaction, the solution was directly detected by EPR, an obvious signal is detected. EPR spectroscopy is consistent with the previous report and clearly shows that superoxide free radicals or singlet oxygen are generated in the reaction process, suggesting a radical process was involved in this reaction.

2.6 Control experiments



Scheme S7 Control experiments

We carried out two control experiments using TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)- oxidanyl), BHT (2,6-di-tert-butyl-4-methylphenol) as radical scavengers, respectively (Scheme S7 A, B). As it can be seen, the two reactions were severely suppressed, reminding of a radical-involved process. Two more extra experiments were then carried out to gain deeper insight into the related photochemical process, in which ammonium oxalate as hole scavenger and $K_2S_2O_8$ as electron scavenger were added to the reaction system, respectively, and the product **3aa** was obtained in obviously lower yields in both cases, suggesting that both hole and electron in **POP-3** were heavily involved in the photocatalytic process (Scheme S7 C, D).



Reaction conditions: In a 10 mL reaction tube, *N*-phenyl-1,2,3,4-tetrahydroisoquinoline **1a** (0.2 mmol), diphenylphosphine oxide **2a** (0.4 mmol) and **POP-3** (2.0 mg) were added in H_2O (1.0 mL). Afterward, TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy)/2,6-ditert-butyl-4-methyl-phenol (BHT, 5.0 equiv.)/ ammonium oxalate (5.0 equiv.)/ $K_2S_2O_8$ (5.0 equiv.) was added in the mixture. The mixture was stirred under the irradiation of blue LED (460 nm) in open air at rt for 12 h.

2.7 Photograph of Photoreactor, Reaction Vial, and Spectrum of Blue LED Lamp

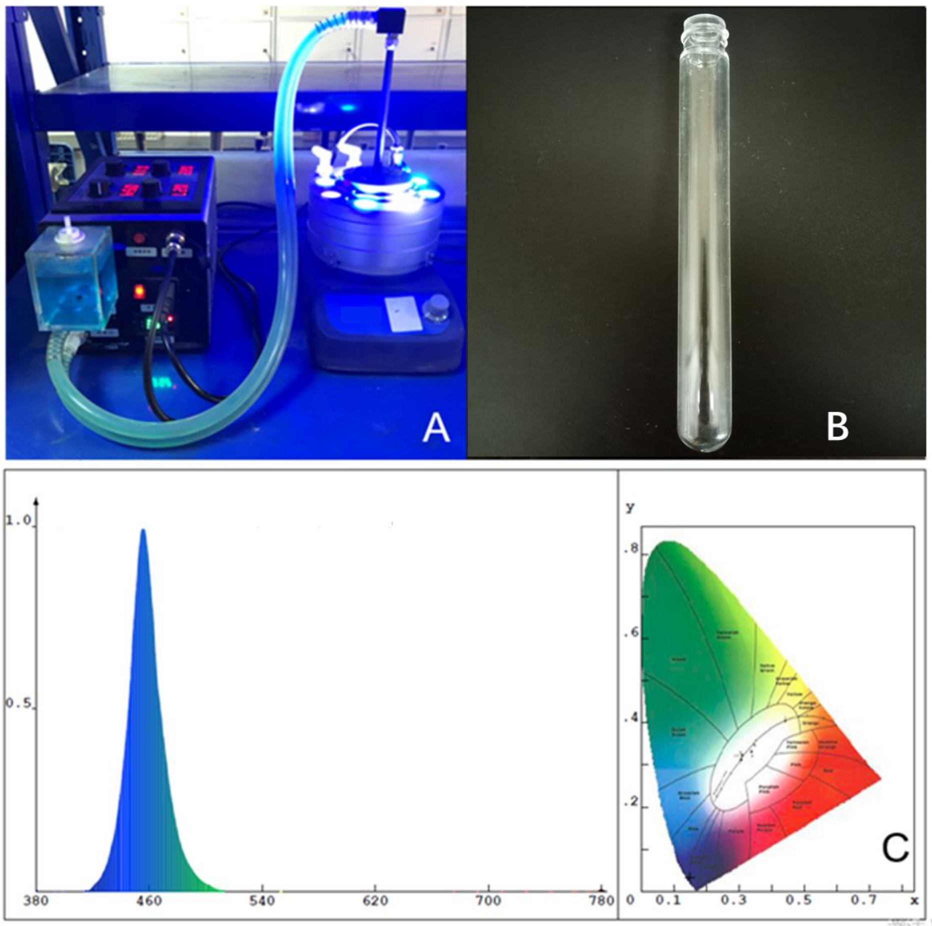


Figure S1 **A**: photoreactor; **B**: 10 mL reaction vial; **C**: spectrum of blue LED lamp.

2.8 Powder X-ray diffraction (XRD) spectra of ***POPs***

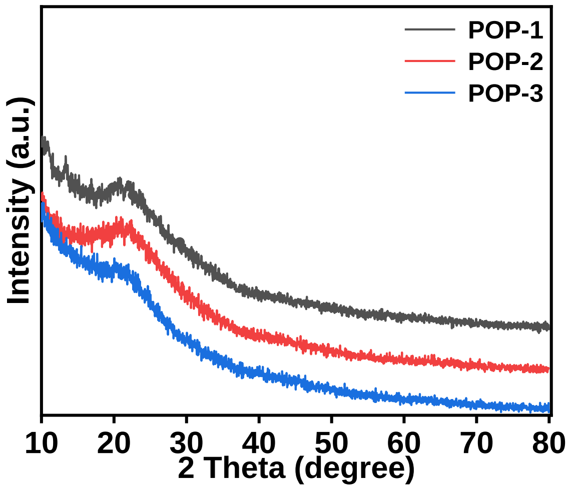


Figure S2 Powder X-ray diffraction spectra of the **POPs**. The crystalline structure of the samples was characterized by powder X-ray diffraction (XRD) with a Rigaku D/Max-2550 diffractometer using Cu Kα radiation (λ = 1.540598 Å) at 50 kV and 200 mA in the 2θ range of 10-80 ° at a scanning rate of 10 ° min^{-1}.

2.9 BET of ***POPs***

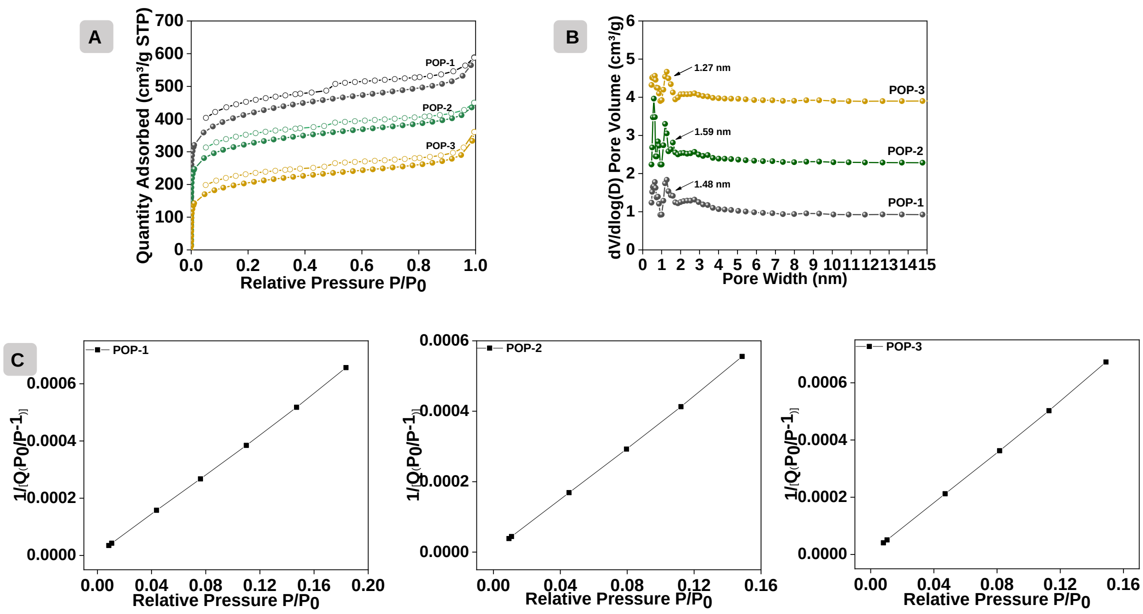


Figure S3 A: Adsorption (solid point) and desorption (hollow point) isotherms of N_2 at 77 K for **POPs**; B: Pore size distributions of **POPs** based on the calculation results of the NLDFT method. The samples were outgassed at 120 ºC for 12 h before the measurements. Surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods; C: BET plot of **POPs**.

2.10 Thermogravimetric analysis of the **POPs**

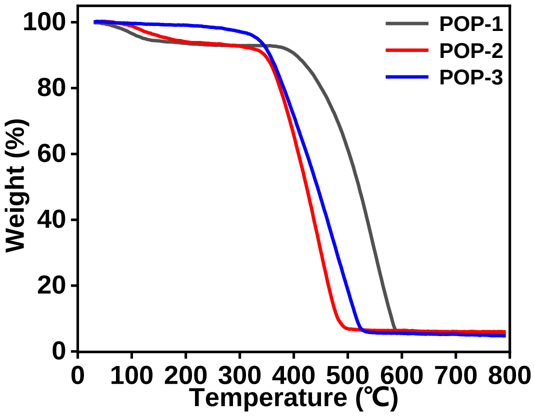


Figure S4 Thermogravimetric analysis of the **POPs**. TGA was applied in air atmosphere over the temperature range of 30 to 800 °C at a heating rate of 10 °C min^{-1}.

2.11 Cyclic voltammetry (CV) measurement of POPs

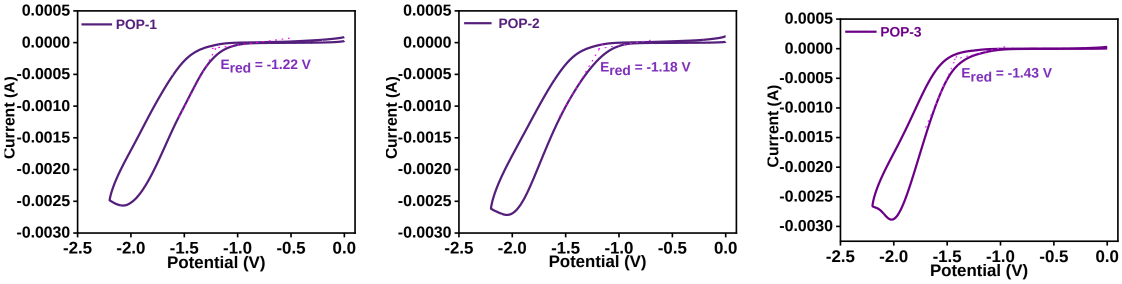
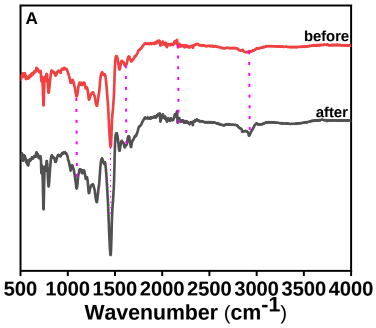


Figure S5 Cyclic voltammetry (CV) measurement of **POPs.** Cyclic voltammetry (CV) measurement was performed using Chenhua CHI660E potentiostat/galvanostat (Metrohm) in a three-electrode-cell system: as-prepared electrode film drop-casted with the polymers as the working electrode, Pt wire as the counter electrode, Hg/Hg_2Cl_2 (in saturated KCl solution) electrode as the reference electrode, Bu_4NPF_6 (0.1 M in MeCN) was used as electrolyte. For preparation of electrode film, 10 mg of catalysts were thoroughly mixed with 1.0 mL of ethanol and 30 μL of Nafion solution to get a slurry. Then, 30 μL of slurry was evenly dropped onto the FTO substrate and let the solvent evaporate. The measurement was carried out in a 0.1 M of Bu_4NPF_6 solution as supporting electrolyte in MeCN with a scan rate of 100 mV s^{-1}.

2.12 SEM image and FT-IR spectra of POP-3 Recycle



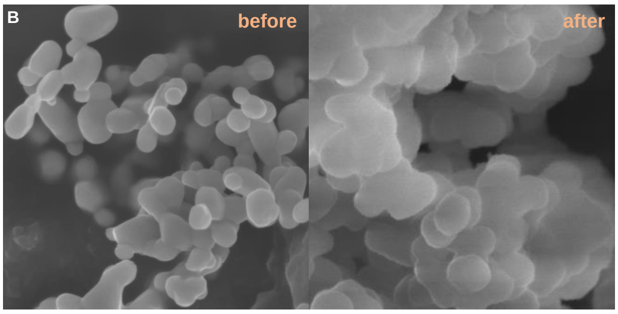
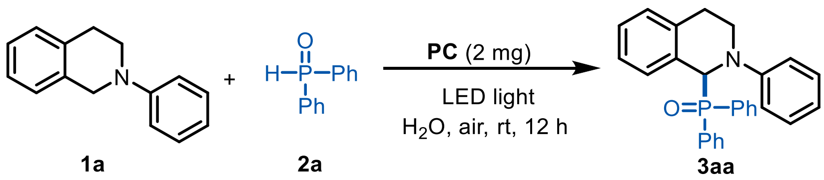


Figure S6 A: FT-IR spectra of **POP-3** and **POP-3**-after; B: SEM image of **POP-3** that refers to **POP-3** reused for 5 times, scale bar 200 nm.

2.13 Optimization of reaction condition

Table S1[a]

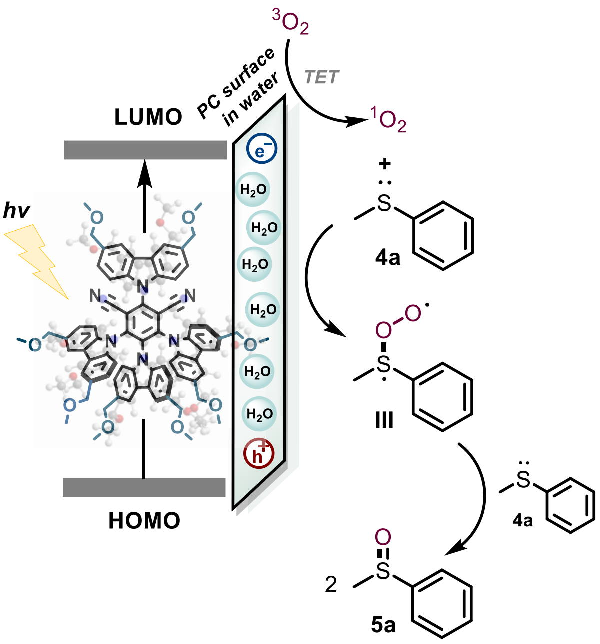


Entry	PC	Solvent	Light Source	Oxidant	Yield (%)
1[b]	**POP-1**	H_2O	Blue 5 W	air	60
2[b]	**POP-2**	H_2O	Blue 5 W	air	64
3[b]	**POP-3**	H_2O	Blue 5 W	air	76
4	**POP-3**	H_2O	Blue 5 W	air	86
5[c]	**POP-3**	H_2O	Blue 5 W	air	80
6[d]	**POP-3**	H_2O	Blue 5 W	air	80
7	**POP-3**	H_2O	Blue 3 W	air	86
8	**POP-3**	**H_2O**	**Blue 7 W**	**air**	**92**
9	**POP-3**	H_2O	Blue 10 W	air	87
10	**POP-3**	H_2O	Green 7 W	air	82
11[e]	**POP-3**	H_2O	Blue 7 W	air	54
12	**POP-3**	H_2O	Purple 7 W	air	64
13	**POP-3**	H_2O	Blue 7 W	O_2	62
14	**POP-3**	H_2O	Blue 7 W	N_2	trace
16[f]	--	H_2O	Blue 7 W	air	21
17[g]	**POP-3**	H_2O	Blue 7 W	air	32
18[h]	**POP-3**	H_2O	Blue 7 W	air	58
19[i]	**POP-3**	H_2O	Blue 7 W	air	80
20[j]	**POP-3**	H_2O	Blue 7 W	air	92

[a]Model reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol) and **POP-3** (2 mg) in H_2O (1.0 mL) under irradiation of 7 W blue LED (460 nm) in open air at rt for 12 h. Isolated yields are given. [b]4 mg of PC was used. [c]6 mg of PC was used. [d]10 mg of PC was used. [e]Reaction under irradiation of 7 W blue LED (430 nm). [f]None of **PC** was used. [g]Reaction time is 3h. [h]Reaction time is 6h. [i]Reaction time is 9h. [j]Reaction time is 15h.

2.14 Proposed mechanism for the selective oxidation of sulfide

A plausible mechanism for selective oxidation of sulfide was proposed. As shown in Scheme S8, Initially, upon visible light irradiation, **POP-3** promotes the generation of $^1O_2$ by triplet energy transfer (TET). Then sulfide **4a** can react with $^1O_2$ to furnish peroxysulfoxide diradical **III**, which can coexist with dipolar one during the reaction process. Finally, the active intermediate **III** can rapidly react with another sulfide **4a** to produce two sulfoxide products **5a**.



Scheme S8 Proposed mechanism for the selective oxidation of sulfide

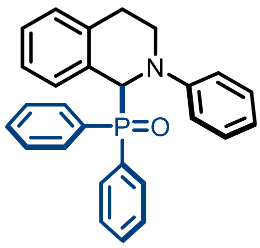
2.15 Oxygen elemental analysis testing

In order to indicate the amounts of the ether group in the three samples, a series of elemental analysis testing was performed. As shown in Table R1 below. the oxygen contents in **POP-1, POP-2** and **POP-3** are detected as 14.358%, 17.157%, 17.824%, respectively, indicating that the quantity of ether groups definitely grows with the continuous polymerization between 4CzIPN and FDA.

Table S2. Experimental results of oxygen contents analysis

Organic Elemental Analysis Test Results Report	
Test items	Organic element analyzer
Test mode	O mode
Instrument model	Elementar UNICUBLE
Sample serial number	**O (%)**
POP-1	14.358
POP-2	17.157
POP-3	17.824

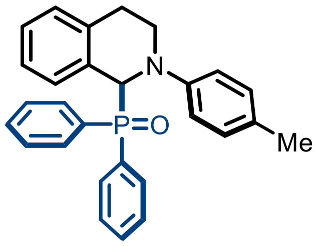
3. Characterization Data



3aa

diphenyl(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphine oxide (3aa)

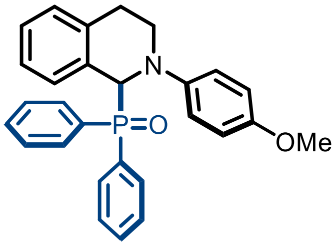
White solid (75.3 mg, 92% yield); m.p. 199.7 – 202.1 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.77 (m, 2H), 7.76 – 7.67 (m, 2H), 7.63 – 7.51 (m, 1H), 7.54 – 7.42 (m, 3H), 7.36 (td, J = 7.5, 3.0 Hz, 2H), 7.23 – 7.03 (m, 4H), 6.96 (t, J = 7.5 Hz, 1H), 6.84 – 6.78 (m, 3H), 6.68 (d, J = 7.7 Hz, 1H), 5.59 (d, J = 8.0 Hz, 1H), 4.20 – 3.84 (m, 1H), 3.64 – 3.58 (m, 1H), 2.95 – 2.58 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.0 (d, J = 7.8 Hz), 136.9 (d, J = 4.2 Hz), 132.30 (d, J = 92.7 Hz), 132.26 (d, J = 8.5 Hz), 131.9 (d, J = 2.9 Hz), 131.74, 131.65 (d, J = 1.9 Hz), 131.4 (d, J = 88.3 Hz), 123.0, 129.3 (d, J = 2.2 Hz), 129.1, 128.4 (d, J = 11.1 Hz), 128.3 (d, J = 11.3 Hz), 127. 8 (d, J = 3.3 Hz), 127.4 (d, J = 2.9 Hz), 125.5 (d, J = 2.6 Hz), 119.5, 116.8, 62.0 (d, J = 79.6 Hz), 45.2, 25.6. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 30.65. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{24}NNaOP$ 432.1488 found 432.1487.



3ab

***diphenyl(2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphine oxide (3ab)*[2]**

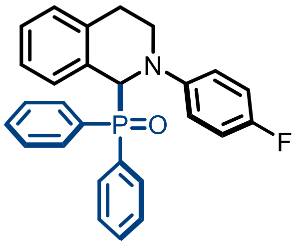
White solid (77.0 mg, 91% yield); m.p. 213.9 – 215.6 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.79 (m, 2H), 7.78 – 7.66 (m, 2H), 7.56 (t, J = 6.9 Hz, 1H), 7.49 – 7.45 (m, 3H), 7.38 (td, J = 7.5, 2.7 Hz, 2H), 7.17 (t, J = 7.4 Hz, 1H), 7.09 (d, J = 7.4 Hz, 1H), 7.02 – 6.92 (m, 3H), 6.75 (d, J = 8.4 Hz, 2H), 6.67 (d, J = 7.7 Hz, 1H), 5.51 (d, J = 11.5 Hz, 1H), 4.17 – 3.81 (m, 1H), 3.66 – 3.43 (m, 1H), 2.96 – 2.51 (m, 2H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.0 (d, J = 9.1 Hz), 136.9 (d, J = 4.3 Hz), 132.5 (d, J = 95.5 Hz), 132.2 (d, J = 8.4 Hz), 131.8 (d, J = 2.7 Hz), 131.74 (d, J = 8.6 Hz), 131.72 (d, J = 90.9 Hz), 131.6 (d, J = 2.7 Hz), 129.9, 129.7, 129.3 (d, J = 1.8 Hz), 128.4 (d, J = 11.1 Hz), 128.3 (d, J = 11.3 Hz), 127.8 (d, J = 3.1 Hz), 127.3 (d, J = 3.0 Hz), 125.4 (d, J = 2.6 Hz), 117.7, 62.0 (d, J = 80.6 Hz), 45.7, 25.1, 20.5. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 30.22.



3ac

***(2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)diphenylphosphine oxide (3ac)*[2]**

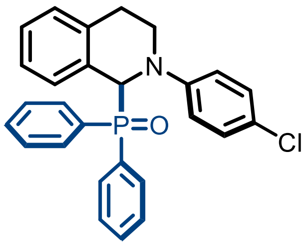
White solid (78.2 mg, 89% yield); m.p. 181.8 – 183.2 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.65 (m, 4H), 7.54 (t, J = 6.9 Hz, 1H), 7.51 – 7.41 (m, 3H), 7.38 (td, J = 7.5, 2.8 Hz, 2H), 7.23 – 7.04 (m, 2H), 6.96 (t, J = 7.4 Hz, 1H), 6.85 – 6.71 (m, 4H), 6.65 (d, J = 7.7 Hz, 1H), 5.40 (d, J = 11.9 Hz, 1H), 4.05 – 3.98 (m, 1H), 3.74 (s, 3H), 3.45 – 3.42 (m, 1H), 2.82 – 2.55 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.1, 144.6 (d, J = 10.2 Hz), 137.0 (d, J = 4.4 Hz), 132.5 (d, J = 96.1 Hz), 132.2 (d, J = 8.5 Hz), 131.9 (d, J = 90.8 Hz), 131.8 (d, J = 2.7 Hz), 131.7, 131.6 (d, J = 2.7 Hz), 129.7, 129.4 (d, J = 2.1 Hz), 128.4 (d, J = 11.1 Hz), 128.2 (d, J = 11.3 Hz), 127.8 (d, J = 3.1 Hz), 127.2 (d, J = 2.9 Hz), 125.5 (d, J = 2.8 Hz), 120.4, 114.4, 62.1 (d, J = 81.3 Hz), 55.5, 46.8, 24.8. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 30.94.



3ad

(2-(4-fluorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)diphenylphosphine oxide (3ad)

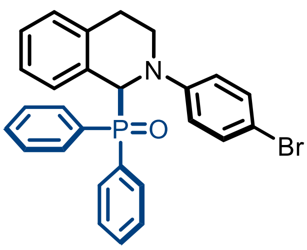
White solid (69.2 mg, 81% yield); m.p. 196.2 – 197.9 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.71 (m, 4H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.47 (d, *J* = 7.1 Hz, 3H), 7.40 – 7.36 (m, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 7.4 Hz,1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.86 (t, *J* = 8.6 Hz, 2H), 6.77 (dd, *J* = 8.9, 4.5 Hz, 2H), 6.63 (d, *J* = 7.6 Hz, 1H), 5.44 (d, *J* = 10.9 Hz, 1H), 4.21 – 3.93 (m, 1H), 3.59 – 3.35 (m, 1H), 2.89 – 2.54 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.1 (d, *J* = 239.4 Hz), 146.8 (dd, *J* = 8.7, 2.3 Hz), 136.9 (d, *J* = 4.3 Hz), 132.3 (d, *J* = 91.4 Hz), 132.2 (d, *J* = 8.5 Hz), 132.0 (d, *J* = 2.8 Hz), 131.71 (d, *J* = 2.4 Hz), 131.66 (d, *J* = 3.6 Hz), 131.4 (d, *J* = 86.5 Hz), 129.6, 129.3 (d, *J* = 2.1 Hz), 128.4 (d, *J* = 11.2 Hz), 128.3 (d, *J* = 11.1 Hz), 127.8 (d, *J* = 3.2 Hz), 127.5 (d, *J* = 2.9 Hz), 125.6 (d, *J* = 2.7 Hz), 119.2 (d, *J* = 7.6 Hz), 115.6 (d, *J* = 22.2 Hz), 62.3 (d, *J* = 80.1 Hz), 46.3, 25.3. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 30.73. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.11. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{23}FNNaOP$ 450.1394 found 450.1395.



3ae

(2-(4-chlorophenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)diphenylphosphine oxide (3ae)[2]

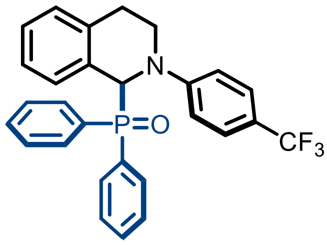
White solid (70.0 mg, 79% yield); m.p. 198.7 – 201.1 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.76 (m, 2H), 7.75 – 7.67 (m, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.54 – 7.43 (m, 3H), 7.37 (td, *J* = 7.7, 2.7 Hz, 2H), 7.24 – 7.16 (m, 3H), 7.11 (d, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.66 (dd, *J* = 17.2, 8.3 Hz, 3H), 5.50 (d, *J* = 10.0 Hz, 1H), 4.10 – 4.03 (m, 1H), 3.71 – 3.39 (m, 1H), 2.98 – 2.56 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.0 (d, *J* = 7.2 Hz), 136.7 (d, *J* = 4.3 Hz), 132.2 (d, *J* = 8.4 Hz), 132.1 (d, *J* = 2.9 Hz), 132.0 (d, *J* = 95.0 Hz), 131.9, 131.8 (d, *J* = 2.7 Hz), 131.6 (d, *J* = 8.8 Hz), 130.9 (d, *J* = 90.4 Hz), 129.6, 129.2 (d, *J* = 2.3 Hz), 128.5, 128.4 (d, *J* = 11.7 Hz), 127.7 (d, *J* = 3.3 Hz), 127.6 (d, *J* = 2.9 Hz), 125.7 (d, *J* = 2.7 Hz), 118.0, 111.5, 62.1 (d, *J* = 78.7 Hz), 45.1, 25.8. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 30.53.



3af

(2-(4-broPOPhenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)diphenylphosphine oxide (3af)[2]

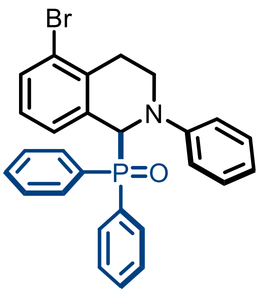
White solid (80.9 mg, 83% yield); m.p. 190.3 – 191.9 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.76 (m, 2H), 7.75 – 7.64 (m, 2H), 7.57 (t, *J* = 6.9 Hz, 1H), 7.55 – 7.44 (m, 3H), 7.37 (td, *J* = 7.6, 2.8 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.17 – 7.01 (m, 3H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 8.9 Hz, 2H), 6.65 (d, *J* = 7.7 Hz, 1H), 5.51 (d, *J* = 10.0 Hz, 1H), 4.10 – 4.03 (m, 1H), 3.53 (dt, *J* = 12.8, 4.8 Hz, 1H), 2.87 – 2.70 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.6 (d, *J* = 7.1 Hz), 136.7 (d, *J* = 4.2 Hz), 132.2 (d, *J* = 8.4 Hz), 132.1 (d, *J* = 2.7 Hz), 132.0 (d, *J* = 109.6 Hz), 131.8 (d, *J* = 2.9 Hz), 131.6 (d, *J* = 8.9 Hz), 130.1 (d, *J* = 84.7 Hz), 129.2 (d, *J* = 2.3 Hz), 129.0, 128.5, 128.4 (d, *J* = 1.5 Hz), 128.3, 127.8 (d, *J* = 3.3 Hz), 127.6 (d, *J* = 3.0 Hz), 125.7 (d, *J* = 2.6 Hz), 124.2, 117.7, 62.2 (d, *J* = 79.0 Hz), 45.2, 25.8. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 30.57.



3ag

diphenyl(2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphine oxide (3ag)

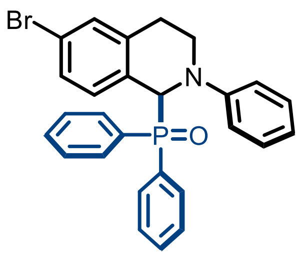
White solid (69.7 mg, 73% yield); m.p. 219.3 – 221.1 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (dt, *J* = 26.2, 9.2 Hz, 4H), 7.58 (t, *J* = 7.0 Hz, 1H), 7.56 – 7.42 (m, 3H), 7.37 (d, *J* = 8.3 Hz, 4H), 7.24 – 7.07 (m, 2H), 6.98 (t, *J* = 7.3 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 7.4 Hz, 1H), 5.69 (d, *J* = 8.4 Hz, 1H), 4.12 – 4.09 (m, 1H), 3.65 – 3.61 (m, 1H), 2.94 – 2.83 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.8 (d, *J* = 5.1 Hz), 136.5 (d, *J* = 4.0 Hz), 132.3 (d, *J* = 8.1 Hz), 132.2, 132.0 (d, *J* = 2.9 Hz), 131.7 (d, *J* = 94.2 Hz), 131.5 (d, *J* = 9.0 Hz), 130.2 (d, *J* = 90.8 Hz), 129.8, 129.1 (d, *J* = 2.3 Hz), 128.5 (d, *J* = 21.4 Hz), 127.9 (d, *J* = 2.9 Hz), 127.7 (d, *J* = 3.4 Hz), 126.3 (q, *J* = 3.8 Hz), 125.8 (d, *J* = 2.6 Hz), 124.7 (q, *J* = 270.5 Hz), 119.9 (q, *J* = 32.6 Hz), 114.2, 62.2 (d, *J* = 76.8 Hz), 44.3, 26.5. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 30.22. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -61.27. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{28}H_{23}F_3NNaOP$ 500.1362 found 500.1362.



3ah

(5-bromo-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)diphenylphosphine oxide (3ah)

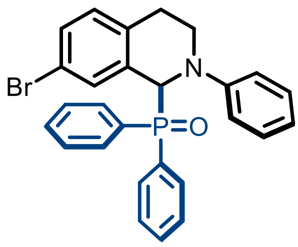
White solid (73.1 mg, 75% yield); m.p. 218.4 – 220.0 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.69 (m, 4H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.54 – 7.34 (m, 6H), 7.18 (t, *J* = 7.9 Hz, 2H), 6.90 – 6.78 (m, 4H), 6.58 (d, *J* = 7.7 Hz, 1H), 5.53 (d, *J* = 11.2 Hz, 1H), 4.18 – 4.11 (m, 1H), 3.74 – 3.71 (m, 1H), 2.75 – 2.72 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.7 (d, *J* = 9.0 Hz), 136.3 (d, *J* = 4.2 Hz), 132.5, 132.10 (d, *J* = 2.8 Hz), 132.08 (d, *J* = 8.5 Hz), 131.9 (d, *J* = 96.6 Hz), 131.8 (d, *J* = 2.8 Hz), 131.62 (d, *J* = 8.7 Hz), 131.56 (d, *J* = 91.5 Hz), 131.5 (d, *J* = 2.9 Hz), 129.3, 128.6 (d, *J* = 11.3 Hz), 128.4 (d, *J* = 11.4 Hz), 126.9 (d, J = 3.1 Hz), 126.6 (d, J = 2.7 Hz), 125.9 (d, J = 2.4 Hz), 120.1, 117.1, 61.7 (d, J = 79.4 Hz), 45.0, 26.0. ^{31}P NMR (162 MHz, Chloroform-d) δ 31.04. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{27}H_{23}BrNNaOP$ 510.0593 found 510.0592.



3ai

(6-bromo-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)diphenylphosphine oxide (3ai)

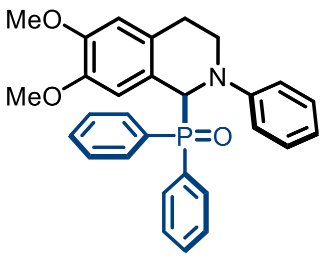
White solid (76.0 mg, 78% yield); m.p. 208.8 – 210.4 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.93 – 7.79 (m, 2H), 7.79 – 7.69 (m, 2H), 7.63 – 7.56 (m, 1H), 7.56 – 7.44 (m, 3H), 7.38 (td, J = 7.5, 3.0 Hz, 2H), 7.27 (s, 1H), 7.24 – 7.15 (m, 2H), 7.12 – 7.04 (m, 1H), 6.82 (dd, J = 17.5, 7.7 Hz, 3H), 6.51 – 6.49 (m, 1H), 5.49 (d, J = 10.8 Hz, 1H), 4.61 – 3.91 (m, 1H), 3.62 – 3.58 (m, 1H), 3.05 – 2.41 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 149.8 (d, J = 8.6 Hz), 139.2 (d, J = 4.2 Hz), 132.2 (d, J = 2.2 Hz), 132.1 (d, J = 3.0 Hz), 131.9 (d, J = 96.1 Hz), 131.8 (d, J = 2.8 Hz), 131.7 (d, J = 8.7 Hz), 131.3 (d, J = 91.4 Hz), 129.2 (d, J = 2.0 Hz), 128.9, 128.64 (d, J = 3.7 Hz), 128.58 (d, J = 4.9 Hz), 128.4, 128.3, 121.3 (d, J = 3.6 Hz), 120.1, 117.2, 61.3 (d, J = 79.8 Hz), 45.0, 25.2. ^{31}P NMR (162 MHz, Chloroform-d) δ 30.48. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{27}H_{23}BrNNaOP$ 510.0593 found 510.0594.



3aj

(7-bromo-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)diphenylphosphine oxide (3aj)

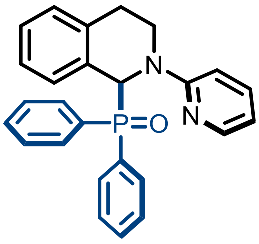
White solid (73.1 mg, 75% yield); m.p. 228.3 – 230.1 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.87 – 7.67 (m, 4H), 7.68 – 7.58 (m, 1H), 7.58 – 7.44 (m, 3H), 7.40 (td, J = 7.6, 3.0 Hz, 2H), 7.27 (s, 1H), 7.18 (t, J = 7.9 Hz, 2H), 6.98 (d, J = 8.1 Hz, 1H), 6.96 – 6.68 (m, 3H), 6.53 (s, 1H), 5.43 (d, J = 10.5 Hz, 1H), 4.25 – 4.18 (m, 1H), 3.67 – 3.63 (m, 1H), 3.02 – 2.38 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 149.9 (d, J = 9.1 Hz), 135.9 (d, J = 4.1 Hz), 132.2 (d, J = 2.9 Hz), 132.0 (d, J = 8.7 Hz), 131.8 (d, J = 3.4 Hz), 131.71 (d, J = 97.0 Hz), 131.68 (d, J = 8.7 Hz), 131.3 (d, J = 91.6 Hz), 130.9 (d, J = 2.1 Hz), 130.6 (d, J = 3.0 Hz), 130.3 (d, J = 2.9 Hz), 129.3, 128.7 (d, J = 11.3 Hz), 128.4 (d, J = 11.4 Hz), 120.3, 118.7 (d, J = 2.9 Hz), 117.5, 61.2 (d, J = 79.7 Hz), 45.3, 24.7. ^{31}P NMR (162 MHz, Chloroform-d) δ 32.21. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{27}H_{23}BrNNaOP$ 510.0593 found 510.0595.



3ak

(6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)diphenylphosphine oxide (3ak)

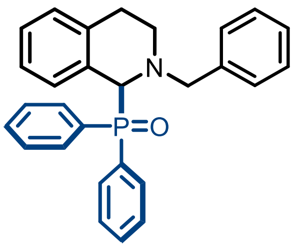
White solid (79.8 mg, 85% yield); m.p. 228.9 – 229.8 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (t, *J* = 8.9 Hz, 2H), 7.76 (t, *J* = 9.3 Hz, 2H), 7.55 – 7.44 (m, 4H), 7.39 – 7.35 (m, 2H), 7.17 (t, *J* = 7.1 Hz, 2H), 6.86 – 6.80 (m, 3H), 6.58 (s, 1H), 6.08 (s, 1H), 5.47 (d, *J* = 10.0 Hz, 1H), 4.15 (t, *J* = 10.6 Hz, 1H), 3.83 (s, 3H), 3.65 (d, *J* = 10.9 Hz, 1H), 3.38 (s, 3H), 3.00 – 2.35 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.3 (d, *J* = 9.2 Hz), 148.2 (d, *J* = 2.9 Hz), 146.5 (d, *J* = 2.6 Hz), 132.5 (d, *J* = 95.3 Hz), 132.3 (d, *J* = 8.5 Hz), 132.1 (d, *J* = 87.8 Hz), 131.8 (d, *J* = 2.8 Hz), 131.7 (d, *J* = 1.7 Hz), 131.6 (d, *J* = 2.2 Hz), 129.14, 129.11, 128.6 (d, *J* = 11.0 Hz), 128.3 (d, *J* = 11.3 Hz), 121.0, 119.9, 117.5, 112.0 (d, *J* = 2.2 Hz), 110.4 (d, *J* = 2.6 Hz), 61.2 (d, *J* = 81.3 Hz), 55.8, 55.3, 45.4, 24.7. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 23.07. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{29}H_{28}NNaO_3P$ 492.1699 found 492.1703.



3al

diphenyl(2-(pyridin-2-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphine oxide (3al)

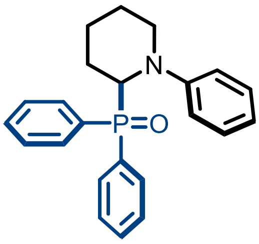
White solid (54.9 mg, 67% yield); m.p. 165.5 – 167.3 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.25 – 8.08 (m, 1H), 8.11 – 7.96 (m, 2H), 8.00 – 7.77 (m, 2H), 7.61 – 7.51 (m, 3H), 7.37 – 7.31 (m, 2H), 7.30 – 7.20 (m, 3H), 7.16 (q, *J* = 7.6 Hz, 2H), 7.01 – 6.80 (m, 1H), 6.57 (d, *J* = 7.7 Hz, 1H), 6.54 – 6.44 (m, 2H), 4.17 – 4.10 (m, 1H), 3.64 – 3.58 (m, 1H), 3.46 – 3.39 (m, 1H), 3.02 – 2.95 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.1 (d, *J* = 3.0 Hz), 147.3, 137.3, 136.9 (d, *J* = 3.8 Hz), 132.2 (d, *J* = 96.4 Hz), 132.0 (d, *J* = 8.6 Hz), 131.9 (d, *J* = 89.4 Hz), 131.8 (d, *J* = 2.8 Hz), 131.5 (d, *J* = 9.4 Hz), 131.3 (d, *J* = 2.9 Hz), 131.2, 128.7 (d, *J* = 2.3 Hz), 128.5 (d, *J* = 11.2 Hz), 127.7, 127.6 (d, *J* = 4.0 Hz), 127.4 (d, *J* = 2.9 Hz), 125.6 (d, *J* = 2.4 Hz), 112.7, 106.1, 56.7 (d, *J* = 76.1 Hz), 42.3, 27.4. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 33.32. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{26}H_{23}N_2NaOP$ 433.1440 found 433.1440.



3am

(2-benzyl-1,2,3,4-tetrahydroisoquinolin-1-yl)diphenylphosphine oxide (3am)

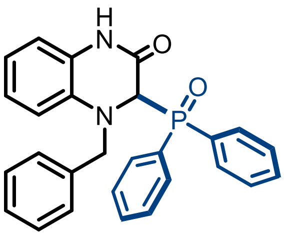
White solid (54.2 mg, 64% yield); m.p. 154.7 – 156.7 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.70 (m, 2H), 7.70 – 7.61 (m, 2H), 7.56 – 7.51 (m, 2H), 7.46 – 7.40 (m, 4H), 7.31 – 7.25 (m, 3H), 7.20 – 7.05 (m, 4H), 6.88 (t, *J* = 16.0 Hz 1H), 6.41 (d, *J* = 7.7 Hz, 1H), 4.61 (d, *J* = 11.2 Hz, 1H), 4.24 – 3.52 (m, 3H), 3.20 – 2.68 (m, 2H), 2.59 – 2.43 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.3, 136.7 (d, *J* = 4.4 Hz), 132.5 (d, *J* = 95.8 Hz), 132.1 (d, *J* = 8.3 Hz), 131.9 (d, *J* = 91.8 Hz), 131.8 (d, *J* = 8.3 Hz), 131.6 (d, *J* = 2.7 Hz), 131.4 (d, *J* = 2.6 Hz), 129.4, 129.3, 128.83, 128.79 (d, *J* = 1.5 Hz), 128.3 (d, *J* = 2.1 Hz), 128.23, 128.15 (d, *J* = 2.3 Hz), 127.3, 127.1 (d, *J* = 3.2 Hz), 125.2 (d, *J* = 2.9 Hz), 63.1 (d, *J* = 83.6 Hz), 59.3 (d, *J* = 12.5 Hz), 45.2, 23.4. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 31.32. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{27}NOP$ 423.1825 found 423.1825.



3an

diphenyl(1-phenylpiperidin-2-yl)phosphine oxide (3an)

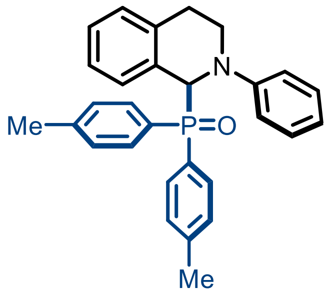
White solid (39.0 mg, 54% yield); m.p. 171.8 – 173.2 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.82 (m, 2H), 7.78 – 7.62 (m, 2H), 7.56 – 7.50 (m, 3H), 7.43 – 7.31 (m, 1H), 7.32 – 7.17 (m, 2H), 7.18 – 7.00 (m, 2H), 6.69 – 6.65 (m, 3H), 4.69 – 4.64 (m, 1H), 4.07 – 4.00 (m, 1H), 3.66 – 3.39 (m, 1H), 2.50 – 2.39 (m, 1H), 2.12 – 1.79 (m, 2H), 1.74 – 1.42 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.6 (d, *J* = 5.8 Hz), 132.8 (d, *J* = 86.5 Hz), 132.7 (d, *J* = 95.1 Hz), 131.6 (d, *J* = 2.8 Hz), 131.3 (d, *J* = 2.8 Hz), 131.1, 131.0 (d, *J* = 8.4 Hz), 129.1, 128.7 (d, *J* = 10.7 Hz), 128.1 (d, *J* = 11.2 Hz), 118.2, 115.9, 56.7 (d, *J* = 77.1 Hz), 46.1, 24.0 (d, *J* = 4.1 Hz), 23.6 (d, *J* = 1.7 Hz), 21.1 (d, *J* = 1.9 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 33.49. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{23}H_{24}NNaOP$ 384.1488 found 384.1487.



3ao

4-benzyl-3-(diphenylphosphoryl)-3,4-dihydroquinoxalin-2(1H)-one (3ao)

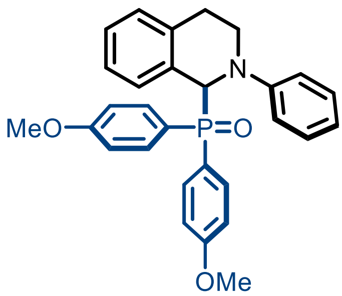
White solid (76.2 mg, 87% yield); m.p. 181.3 – 182.9 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 7.96 (m, 2H), 7.84 (s, 1H), 7.64 – 7.46 (m, 3H), 7.39 – 7.30 (m, 3H), 7.33 – 7.23 (m, 4H), 7.19 (td, *J* = 7.9, 2.9 Hz, 2H), 6.98 (dt, *J* = 15.4, 7.9 Hz, 2H), 6.67 (t, *J* = 7.7 Hz, 1H), 6.25 (d, *J* = 7.7 Hz, 1H), 5.32 (s, 1H), 5.00 (s, 1H), 4.88 (d, *J* = 7.8 Hz, 1H), 4.73 (dd, *J* = 14.6, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.0 (d, *J* = 8.8 Hz), 136.2, 134.1, 132.2 (d, *J* = 2.9 Hz), 132.0 (d, *J* = 91.0 Hz), 131.8, 131.7 (d, *J* = 3.9 Hz), 131.5 (d, *J* = 9.9 Hz), 130.6 (d, *J* = 89.1 Hz), 128.7, 128.7 (d, *J* = 11.8 Hz), 128.4, 127.8, 127.7 (d, *J* = 3.9 Hz), 126.3, 124.5, 119.8, 114.9, 114.2 (d, *J* = 1.6 Hz), 64.3 (d, *J* = 50.3 Hz), 53.8 (d, *J* = 70.3 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 31.42. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ $C_{27}H_{23}N_2NaO_2P$ 461.1389 found 461.1393.



3ba

(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)di-p-tolylphosphine oxide (3ba)

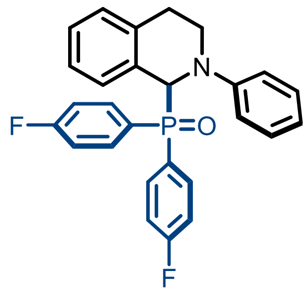
White solid (78.7 mg, 90% yield); m.p. 220.9 – 222.3 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (dd, *J* = 10.2, 8.1 Hz, 2H), 7.60 (dd, *J* = 10.5, 8.1 Hz, 2H), 7.28 (dd, *J* = 7.4, 2.2 Hz, 2H), 7.19 – 7.15 (m, 5H), 7.09 (d, *J* = 7.4 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.89 – 6.67 (m, 4H), 5.56 (d, *J* = 12.0 Hz, 1H), 4.07 – 4.00 (m, 1H), 3.77 – 3.51 (m, 1H), 2.97 – 2.61 (m, 2H), 2.43 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.1 (d, *J* = 7.8 Hz), 142.3 (d, *J* = 2.9 Hz), 142.0 (d, *J* = 2.8 Hz), 136.8 (d, *J* = 4.2 Hz), 132.3 (d, *J* = 8.7 Hz), 131.7 (d, *J* = 9.1 Hz), 130.2, 129.23 (d, *J* = 97.5 Hz), 129.21 (d, *J* = 2.8 Hz), 129.10, 129.08, 129.0 (d, *J* = 11.6 Hz), 128.1 (d, *J* = 93.8 Hz), 127.9 (d, *J* = 3.1 Hz), 127.3 (d, *J* = 2.9 Hz), 125.5 (d, *J* = 2.5 Hz), 119.3, 116.6, 62.1 (d, *J* = 79.7 Hz), 45.0, 25.6, 21.7, 21.6. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 31.00. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{29}H_{28}NNaOP$ 438.1981 found 438.1982.



3ca

bis(4-methoxyphenyl)(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphine oxide (3ca)[3]

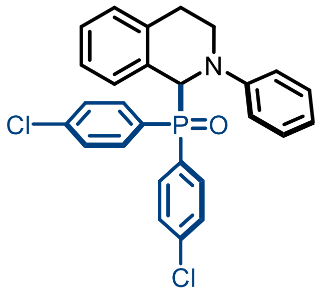
White solid (72.3 mg, 77% yield); m.p. 188.3 – 190.2 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (t, *J* = 9.3 Hz, 2H), 7.59 (t, *J* = 9.4 Hz, 2H), 7.17 (t, *J* = 7.7 Hz, 3H), 7.08 (d, *J* = 7.4 Hz, 1H), 7.02 – 6.96 (m, 3H), 6.87 – 6.83 (m, 4H), 6.78 (t, *J* = 7.8 Hz, 2H), 5.51 (d, *J* = 11.7 Hz, 1H), 4.01 – 3.94 (m, 1H), 3.87 (s, 3H), 3.80 (s, 3H), 3.62 – 3.58 (m, 1H), 2.97 – 2.76 (m, 1H), 2.72 – 2.59 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.4 (d, *J* = 2.8 Hz), 162.2 (d, *J* = 2.7 Hz), 150.0 (d, *J* = 7.4 Hz), 136.7 (d, *J* = 4.2 Hz), 134.2 (d, *J* = 9.5 Hz), 133.5 (d, *J* = 10.1 Hz), 130.4, 129.12, 129.10, 128.0 (d, *J* = 3.3 Hz), 127.3 (d, *J* = 2.9 Hz), 125.5 (d, *J* = 2.6 Hz), 123.9 (d, *J* = 101.0 Hz), 122.3 (d, *J* = 98.1 Hz), 119.2, 116.4, 114.0, 113.8 (d, *J* = 11.9 Hz), 62.4 (d, *J* = 80.8 Hz), 55.34, 55.27, 44.8, 25.7. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 30.37.



3da

bis(4-fluorophenyl)(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphine oxide (3da)

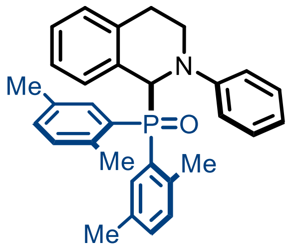
White solid (72.1 mg, 81% yield); m.p. 218.3 – 219.7 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.78 (m, 2H), 7.73 – 7.57 (m, 2H), 7.19 (q, *J* = 7.8 Hz, 5H), 7.13 – 6.92 (m, 4H), 6.86 – 6.67 (m, 4H), 5.54 (d, *J* = 11.1 Hz, 1H), 4.05 – 3.95 (m, 1H), 3.59 (dt, *J* = 12.8, 4.2 Hz, 1H), 3.03 – 2.42 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.2 (dd, *J* = 254.0, 3.2 Hz), 165.0 (dd, *J* = 253.7, 3.1 Hz), 149.9 (d, *J* = 8.0 Hz), 136.8 (d, *J* = 4.4 Hz), 134.9, 134.7 (d, *J* = 9.1 Hz), 134.2 (d, *J* = 8.5 Hz), 134.1 (d, *J* = 8.7 Hz), 129.4 (d, *J* = 13.4 Hz), 129.3 (d, *J* = 8.1 Hz), 128.0 (dd, *J* = 105.9, 3.2 Hz), 127.7 (dd, *J* = 13.8, 3.2 Hz), 127.0 (dd, *J* = 102.0, 3.6 Hz), 125.7 (d, *J* = 2.6 Hz), 120.0, 117.0, 116.0 (dd, *J* = 20.8, 12.2 Hz), 115.7 (d, *J* = 12.4 Hz), 62.2 (d, *J* = 81.5 Hz), 45.3, 25.6. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 29.38. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -106.31, -106.61. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{27}H_{22}F_2NNaOP$ 468.1299 found 468.1299.



3ea

bis(4-chlorophenyl)(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphine oxide (3ea)[2]

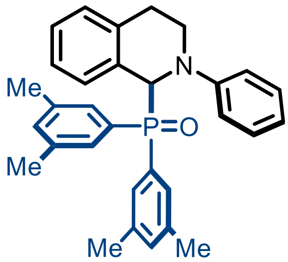
White solid (75.5 mg, 79% yield); m.p. 212.2 – 214.2 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.70 (m, 2H), 7.70 – 7.54 (m, 2H), 7.54 – 7.43 (m, 2H), 7.42 – 7.30 (m, 2H), 7.19 (q, *J* = 7.5, 7.0 Hz, 3H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.84 (t, *J* = 8.7 Hz, 3H), 6.75 (d, *J* = 7.6 Hz, 1H), 5.54 (d, *J* = 11.0 Hz,1H), 4.02 – 3.95 (m, 1H), 3.62 – 3.52 (m, 1H), 3.03 – 2.46 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.9 (d, *J* = 8.2 Hz), 138.8 (d, *J* = 3.5 Hz), 138.5 (d, *J* = 3.5 Hz), 136.8 (d, *J* = 4.4 Hz), 133.6 (d, *J* = 9.2 Hz), 133.0 (d, *J* = 9.5 Hz), 130.5 (d, *J* = 96.2 Hz), 129.7 (d, *J* = 91.1 Hz), 129.4 (d, *J* = 2.2 Hz), 129.3, 128.9 (d, *J* = 11.5 Hz), 128.7 (d, *J* = 11.8 Hz), 127.7 (d, *J* = 3.2 Hz), 125.8 (d, *J* = 2.6 Hz), 120.2, 117.3, 62.0 (d, *J* = 81.0 Hz), 45.5, 25.5. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 29.57.



3fa

bis(2,5-dimethylphenyl)(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphine oxide (3fa)

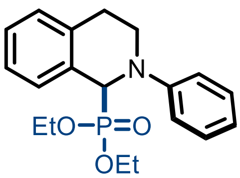
White solid (74.4 mg, 80% yield); m.p. 215.2 – 215.9 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 11.2 Hz, 1H), 7.28 (t, *J* = 7.9 Hz, 2H), 7.26 – 7.20 (m, 2H), 7.20 – 7.01 (m, 7H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.82 (t, *J* = 12.0 Hz, 1H), 6.18 (d, *J* = 8.0 Hz, 1H), 5.50 (d, *J* = 12.0 Hz, 1H), 4.82 – 4.53 (m, 1H), 3.75 (dd, *J* = 14.2, 5.9 Hz, 1H), 2.97 – 2.59 (m, 2H), 2.27 (s, 3H), 2.21 (s, 3H), 2.11 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.0 (d, *J* = 11.5 Hz), 140.1 (d, *J* = 7.8 Hz), 140.0 (d, *J* = 7.5 Hz), 137.7 (d, *J* = 4.3 Hz), 135.1 (d, *J* = 11.8 Hz), 134.3 (d, *J* = 11.1 Hz), 133.1 (d, *J* = 9.6 Hz), 132.9, 132.4 (d, *J* = 2.9 Hz), 132.1 (d, *J* = 2.7 Hz), 131.9 (d, *J* = 11.0 Hz), 131.7, 131.2 (d, *J* = 82.7 Hz), 130.6 (d, *J* = 88.2 Hz), 129.39 (d, *J* = 2.2 Hz), 129.35, 128.2 (d, *J* = 2.9 Hz), 127.0 (d, *J* = 3.0 Hz), 124.9 (d, *J* = 2.9 Hz), 120.9, 119.6, 59.1 (d, *J* = 80.6 Hz), 46.7, 24.7, 20.9, 20.83, 20.79, 20.7. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 36.10. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{31}H_{32}NNaOP$ 488.2114 found 488.2117.



3ga

bis(3,5-dimethylphenyl)(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphine oxide (3ga)

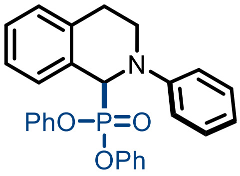
White solid (80.9 mg, 87% yield); m.p. 200.9 – 202.3 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 (dd, *J* = 17.3, 10.9 Hz, 4H), 7.27 – 7.14 (m, 4H), 7.11 – 7.08 (m, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 2H), 6.80 (t, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 5.56 (d, *J* = 10.6 Hz, 1H), 4.09 – 4.02 (m, 1H), 3.73 – 3.46 (m, 1H), 3.14 – 2.41 (m, 2H), 2.32 (s, 6H), 2.23 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.2 (d, *J* = 7.3 Hz), 138.0 (d, *J* = 11.8 Hz), 137.8 (d, *J* = 11.9 Hz), 137.0 (d, *J* = 4.2 Hz), 133.5 (d, *J* = 2.9 Hz), 133.3 (d, *J* = 2.9 Hz), 132.0 (d, *J* = 94.4 Hz), 131.2 (d, *J* = 89.6 Hz), 130.3, 129.8 (d, *J* = 8.5 Hz), 129.4 (d, *J* = 8.8 Hz), 129.1 (d, *J* = 2.2 Hz), 129.0, 127.9 (d, *J* = 3.2 Hz), 127.3 (d, *J* = 3.0 Hz), 125.3 (d, *J* = 2.6 Hz), 119.4, 117.0, 61.7 (d, *J* = 78.7 Hz), 45.2, 25.8, 21.3, 21.2. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 31.73. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{31}H_{32}NNaOP$ 488.2114 found 488.2117.



3ha

diethyl (2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (3ha)[4]

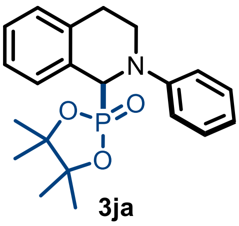
White solid (41.4 mg, 60% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.35 (m, 1H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.25 – 7.11 (m, 3H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.82 (t, *J* = 7.3 Hz, 1H), 5.23 (d, *J* = 20.0 Hz, 1H), 4.43 – 3.85 (m, 5H), 3.69 – 3.63 (m, 1H), 3.27 – 2.89 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.4 (d, *J* = 5.8 Hz), 136.5 (d, *J* = 5.6 Hz), 130.7, 129.2, 128.8 (d, *J* = 2.6 Hz), 128.2 (d, *J* = 4.6 Hz), 127.4 (d, *J* = 3.3 Hz), 125.9 (d, *J* = 2.9 Hz), 118.5, 114.8, 63.3 (d, J = 7.2 Hz), 62.3 (d, J = 7.7 Hz), 58.8 (d, J = 159.2 Hz), 43.5, 26.8, 16.5 (d, J = 5.5 Hz), 16.4 (d, J = 5.9 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 22.18.



3ia

diphenyl-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (3ia)[4]

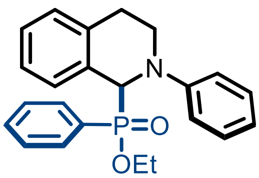
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, J = 7.4 Hz, 1H), 7.36 – 7.25 (m, 4H), 7.25 – 7.13 (m, 5H), 7.11 – 7.05 (m, 5H), 6.95 – 6.82 (m, 3H), 5.63 (d, J = 19.9 Hz, 1H), 4.13 – 4.07 (m, 1H), 3.70 (dt, J = 12.1, 5.4 Hz, 1H), 3.25 – 2.92 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.8 (d, J = 10.4 Hz), 150.3 (d, J = 11.3 Hz), 149.3 (d, J = 6.8 Hz), 136.8 (d, J = 6.0 Hz), 129.6, 129.5 (d, J = 1.6 Hz), 129.4, 129.3, 129.1 (d, J = 2.8 Hz), 128.4 (d, J = 5.0 Hz), 128.0 (d, J = 3.7 Hz), 126.2 (d, J = 3.2 Hz), 125.0 (d, J = 21.6 Hz), 120.7 (d, J = 4.3 Hz), 120.4 (d, J = 4.2 Hz), 119.2, 115.5, 59.2 (d, J = 160.7 Hz), 44.0, 26.6. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 14.76.



3ja

4,4,5,5-tetramethyl-2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)-1,3,2-dioxaphospholane 2-oxide (3ja)[4]

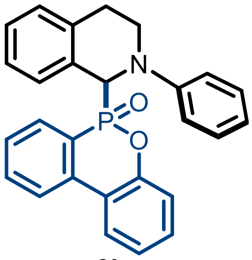
White solid (61.6 mg, 83% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.47 (m, 1H), 7.31 – 7.27 (m, 2H), 7.24 – 7.16 (m, 3H), 7.02 (d, J = 8.3 Hz, 2H), 6.84 (t, J = 7.3 Hz, 1H), 5.33 (d, J = 20.0 Hz 1H), 4.30 – 3.84 (m, 1H), 3.64 – 3.58 (m, 1H), 3.15 – 2.09 (m, 2H), 1.53 (s, 3H), 1.49 (s, 3H), 1.31 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.3 (d, J = 5.0 Hz), 136.2 (d, J = 5.6 Hz), 130.3, 129.1, 128.7 (d, J = 4.6 Hz), 128.6 (d, J = 2.6 Hz), 127.6 (d, J = 3.5 Hz), 126.2 (d, J = 2.9 Hz), 118.7, 114.9, 89.0 (d, J = 3.2 Hz), 88.2 (d, J = 2.5 Hz), 59.7 (d, J = 149.1 Hz), 43.8, 26.9, 25.5 (d, J = 2.2 Hz), 24.9 (d, J = 4.8 Hz), 24.2 (d, J = 4.1 Hz), 23.9 (d, J = 7.0 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 35.34.



3ka

ethyl phenyl(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphinate (3ka)[4]

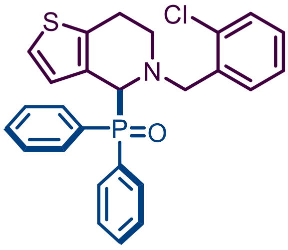
White solid (64.9 mg, 86% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.59 (m, 2H), 7.60 – 7.31 (m, 4H), 7.27 – 7.17 (m, 2H), 7.14 – 7.08 (m, 2H), 7.07 – 6.96 (m, 1H), 6.92 (d, J = 8.2 Hz, 1H), 6.85 – 6.66 (m, 2H), 5.25 (t, J = 13.6 Hz, 1H), 4.44 – 3.79 (m, 3H), 3.62 – 3.50 (m, 1H), 3.16 – 2.36 (m, 2H), 1.36 – 1.21 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.59, 149.55, 149.5, 136.8, 136.7, 136.51, 136.46, 132.6, 132.5, 132.4, 132.34, 132.31, 132.3, 132.19, 132.17, 131.0, 130.6, 130.4, 130.2, 129.8, 129.2, 129.01, 128.99, 128.96, 128.9, 128.54, 128.50, 128.44, 128.42, 128.33, 128.29, 128.25, 128.21, 128.17, 127.4, 127.33, 127.30, 125.73, 125.70, 125.7, 118.7, 118.3, 115.5, 114.6, 62.8, 61.7, 61.62, 61.59, 61.55, 61.3, 61.2, 60.5, 43.8, 43.7, 27.1, 25.9, 16.6, 16.5. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 37.70, 37.04.



3la

6-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (3la)[4]

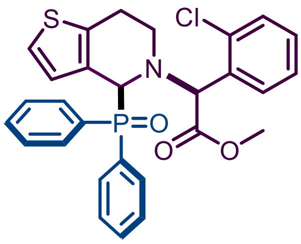
White solid (67.2 mg, 79% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.75 (m, 2H), 7.66 – 7.59 (m, 2H), 7.44 – 7.26 (m, 2H), 7.26 – 7.09 (m, 6H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.91 – 6.63 (m, 4H), 5.46 – 5.34 (m, 1H), 4.21 – 3.06 (m, 2H), 3.02 – 2.20 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.1, 150.0, 148.8, 148.7, 136.9, 136.8, 136.31, 136.25, 133.63, 133.61, 133.5, 132.3, 132.2, 130.4, 130.3, 129.13, 129.07, 128.9, 128.7, 128.53, 128.51, 128.4, 128.10, 128.05, 127.9, 127.79, 127.75, 126.51, 126.48, 125.7, 124.8, 124.7, 124.3, 124.1, 123.7, 123.1, 122.6, 121.8, 121.7, 120.7, 119.8, 119.7, 119.0, 118.8, 115.8, 114.8, 62.3, 61.2, 60.3, 44.5, 43.5, 26.9, 26.8. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 33.10, 32.03.



3ma

(5-(2-chlorobenzyl)-4,5,6,7-tetrahydrothieno[3,2-c]pyridin-4-yl)diphenylphosphine oxide (3ma)

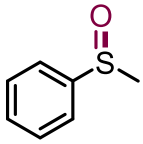
White solid (47.24 mg, 51% yield); m.p. 169.5 – 170.8 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.70 (m, 2H), 7.70 – 7.60 (m, 2H), 7.58 – 7.42 (m, 4H), 7.37 (td, *J* = 7.6, 2.8 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.26 – 7.16 (m, 1H), 7.17 – 7.00 (m, 2H), 6.92 (d, *J* = 5.2 Hz, 1H), 5.96 (d, *J* = 5.2 Hz, 1H), 4.65 (d, *J* = 11.0 Hz, 1H), 3.97 (dd, *J* = 13.9, 1.6 Hz, 1H), 3.89 – 3.47 (m, 2H), 3.08 – 2.98 (m, 2H), 2.66 – 2.59 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.9 (d, *J* = 7.0 Hz), 135.9, 134.6, 132.4 (d, *J* = 98.2 Hz), 131.84, 131.83 (d, *J* = 78.8 Hz), 131.8 (d, *J* = 2.8 Hz), 131.4, 131.3, 131.1, 129.5, 128.4 (d, *J* = 3.0 Hz), 128.3 (d, *J* = 2.3 Hz), 128.2, 126.64, 126.57, 126.3, 121.5 (d, *J* = 1.7 Hz), 61.0 (d, *J* = 85.9 Hz), 55.5 (d, *J* = 13.2 Hz), 46.0, 20.0. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 28.77. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{26}H_{24}ClNOPS$ 464.0999 found 464.0998.



3na

methyl 2-(2-chlorophenyl)-2-(4-(diphenylphosphoryl)-6,7-dihydrothieno[3,2-c]pyridin-5(4H)-yl)acetate (3na)

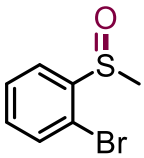
White solid (21.9 mg, 21% yield); m.p. 169.5 – 170.8 ºC; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 – 8.01 (m, 2H), 8.00 – 7.81 (m, 2H), 7.63 – 7.53 (m, 6H), 7.40 – 7.29 (m, 2H), 7.25 – 7.13 (m, 2H), 6.95 (d, *J* = 5.2 Hz, 1H), 5.97 (d, *J* = 5.1 Hz, 1H), 5.42 – 4.78 (m, 2H), 4.18 – 3.59 (m, 1H), 3.57 (s, 3H), 2.88 – 2.78 (m, 1H), 2.67 (dd, *J* = 14.6, 5.8 Hz, 1H), 2.51 (dt, *J* = 16.4, 4.3 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.6, 136.5 (d, *J* = 6.7 Hz), 134.4 (d, *J* = 25.0 Hz), 132.21 (d, *J* = 97.1 Hz), 132.20 (d, *J* = 8.9 Hz), 132.0 (d, *J* = 8.5 Hz), 131.9 (d, *J* = 2.8 Hz), 131.8 (d, *J* = 92.4 Hz), 131.5 (d, *J* = 2.8 Hz), 130.1, 129.8, 129.5, 128.5 (d, *J* = 11.2 Hz), 128.0 (d, *J* = 11.7 Hz), 127.3, 126.9, 126.3, 126.0, 122.0 (d, *J* = 1.7 Hz), 63.8 (d, *J* = 11.6 Hz), 60.7 (d, *J* = 82.1 Hz), 52.2, 43.0, 20.6. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 29.95. HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{28}H_{25}ClNNaO_3PS$ 544.0837 found 544.0837.



5a

(methylsulfinyl)benzene (5a)[5]

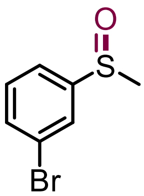
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.58 – 7.50 (m, 3H), 2.75 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.7, 131.0, 129.4, 123.5, 44.0.



5b

1-bromo-2-(methylsulfinyl)benzene (5b)[5]

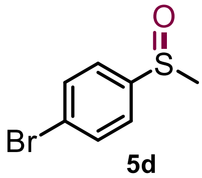
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.68 – 7.48 (m, 2H), 7.37 (td, *J* = 7.9, 1.5 Hz, 1H), 2.82 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.4, 132.9, 132.3, 128.7, 125.7, 118.4, 41.9.



5c

1-bromo-3-(methylsulfinyl)benzene (5c)[6]

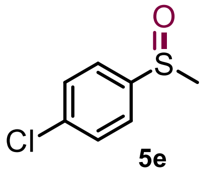
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (t, *J* = 1.7 Hz, 1H), 7.64 – 7.62 (ddd, *J* = 7.9, 1.8, 1.0 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 2.75 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.0, 134.1, 130.8, 126.5, 123.6, 122.1, 44.1.



5d

***1-bromo-4-(methylsulfinyl)benzene (5d)*[5]**

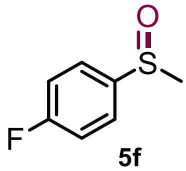
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 2.72 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.9, 132.6, 125.4, 125.1, 44.0.



5e

***1-chloro-4-(methylsulfinyl)benzene (5e)*[5]**

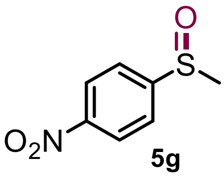
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.55 (m, 2H), 7.56 – 7.42 (m, 2H), 2.72 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.3, 137.2, 129.6, 125.0, 44.1.



5f

***1-fluoro-4-(methylsulfinyl)benzene (5f)*[6]**

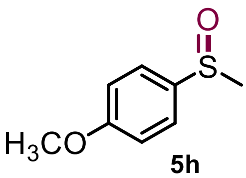
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.55 (m, 2H), 7.28 – 7.11 (m, 2H), 2.72 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.3 (d, *J* = 251.4 Hz), 141.2 (d, *J* = 3.2 Hz), 125.8 (d, *J* = 8.8 Hz), 116.7 (d, *J* = 22.5 Hz), 44.2 (d, *J* = 1.4 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -108.64.



5g

***1-(methylsulfinyl)-4-nitrobenzene (5g)*[7]**

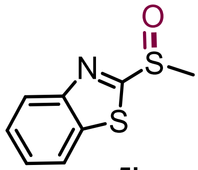
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.70 – 8.23 (m, 2H), 8.03 – 7.62 (m, 2H), 2.82 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.3, 149.5, 124.7, 124.5, 43.9.



5h

***1-methoxy-4-(methylsulfinyl)benzene (5h)*[6]**

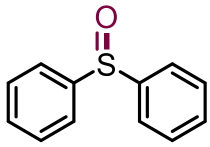
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.45 (m, 2H), 7.19 – 6.70 (m, 2H), 3.83 (s, 3H), 2.68 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.9, 136.6, 125.4, 114.8, 55.5, 44.0.



5i

2-(methylsulfinyl)benzo[d]thiazole (5i) [8]

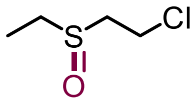
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 8.2 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.64 – 7.55 (m, 1H), 7.54 – 7.46 (m, 1H), 3.10 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.4, 153.8, 136.0, 127.0, 126.3, 122.4, 43.2.



5j

Sulfinyldibenzene (5j) [5]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 2.1 Hz, 2H), 7.66 – 7.64 (m, 2H), 7.46 (d, *J* = 3.6 Hz, 2H), 7.45 – 7.42 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.6, 131.1, 129.3, 124.8.



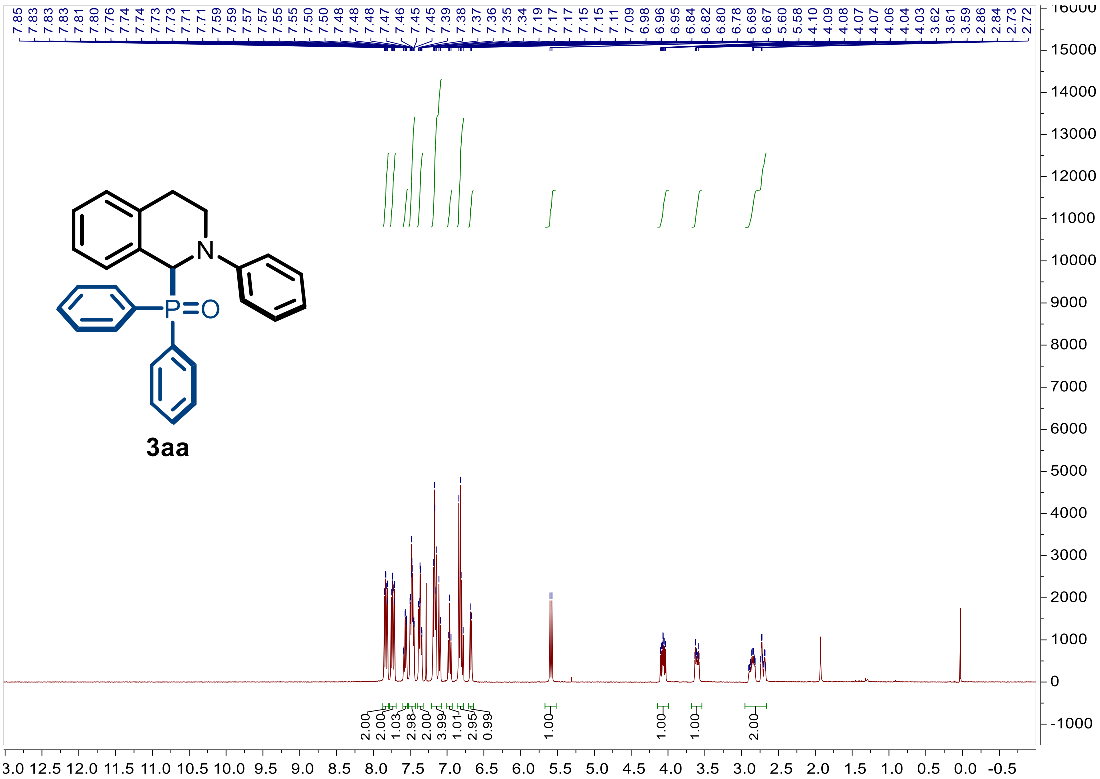
5k

1-chloro-2-(ethylsulfinyl)ethane (5k) [7]

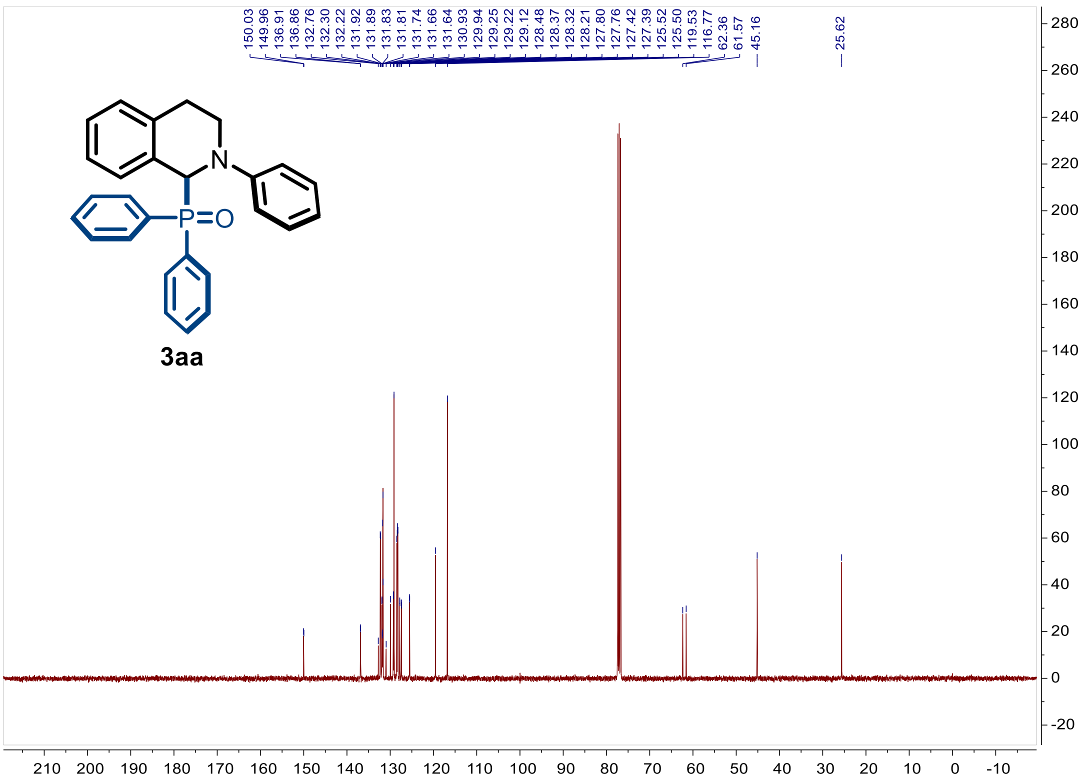
^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.17 – 3.73 (m, 2H), 3.29 – 3.01 (m, 2H), 2.82 (q, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 54.2, 46.1, 37.0, 6.8.

4. NMR Spectra

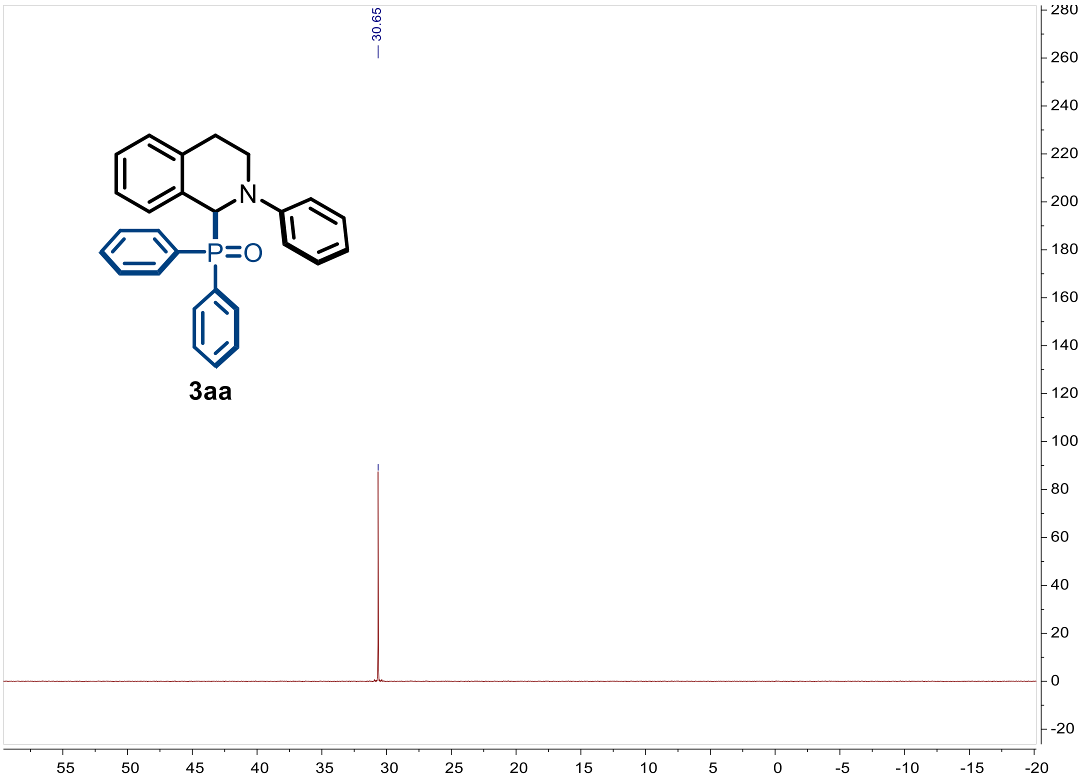
^{1}H NMR spectrum of 3aa



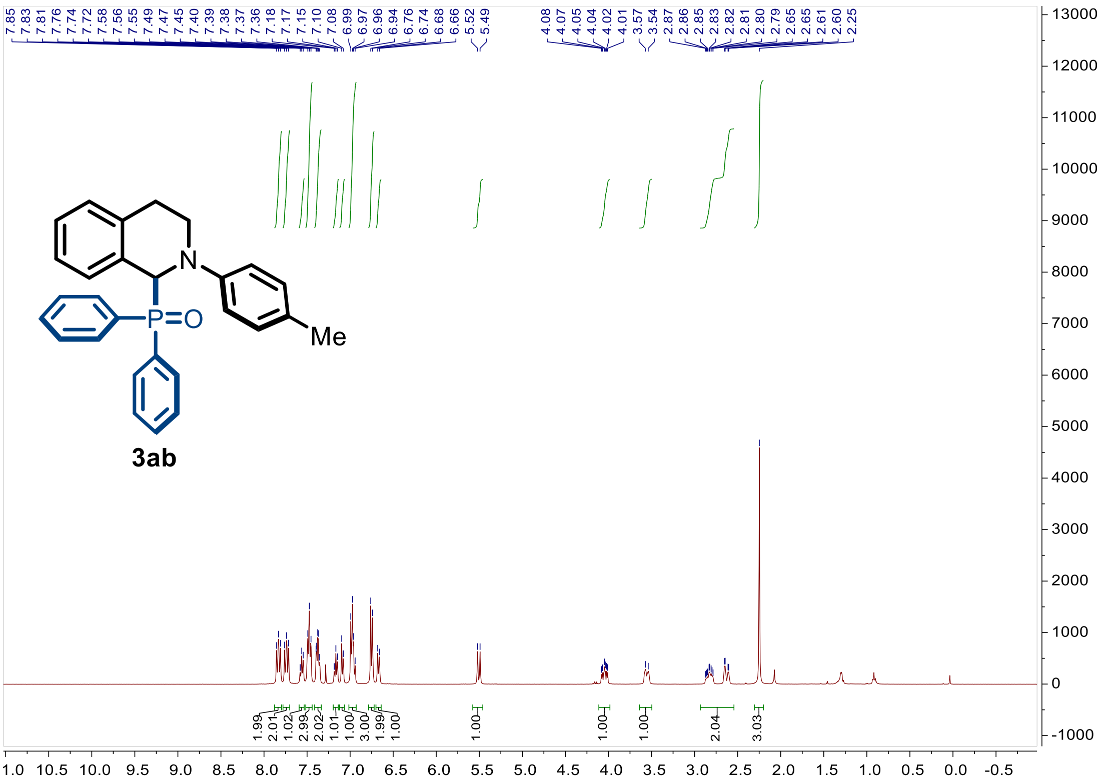
^{13}C NMR spectrum of 3aa



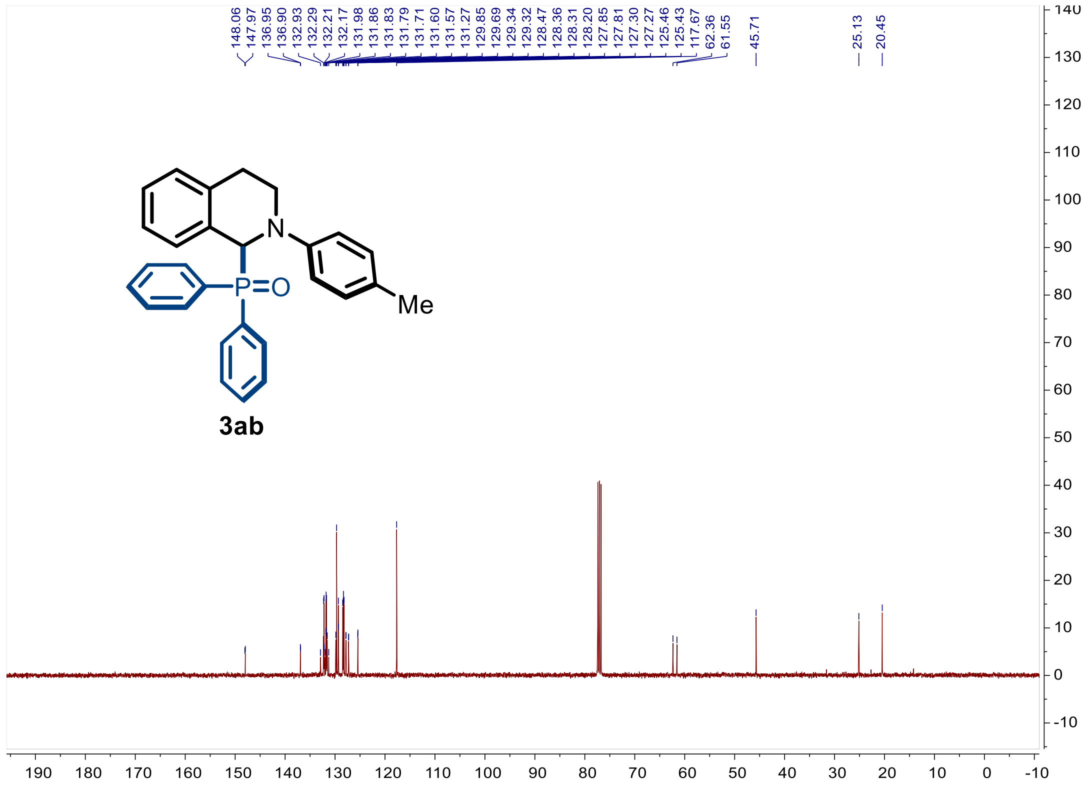
^{31}P NMR spectrum of 3aa



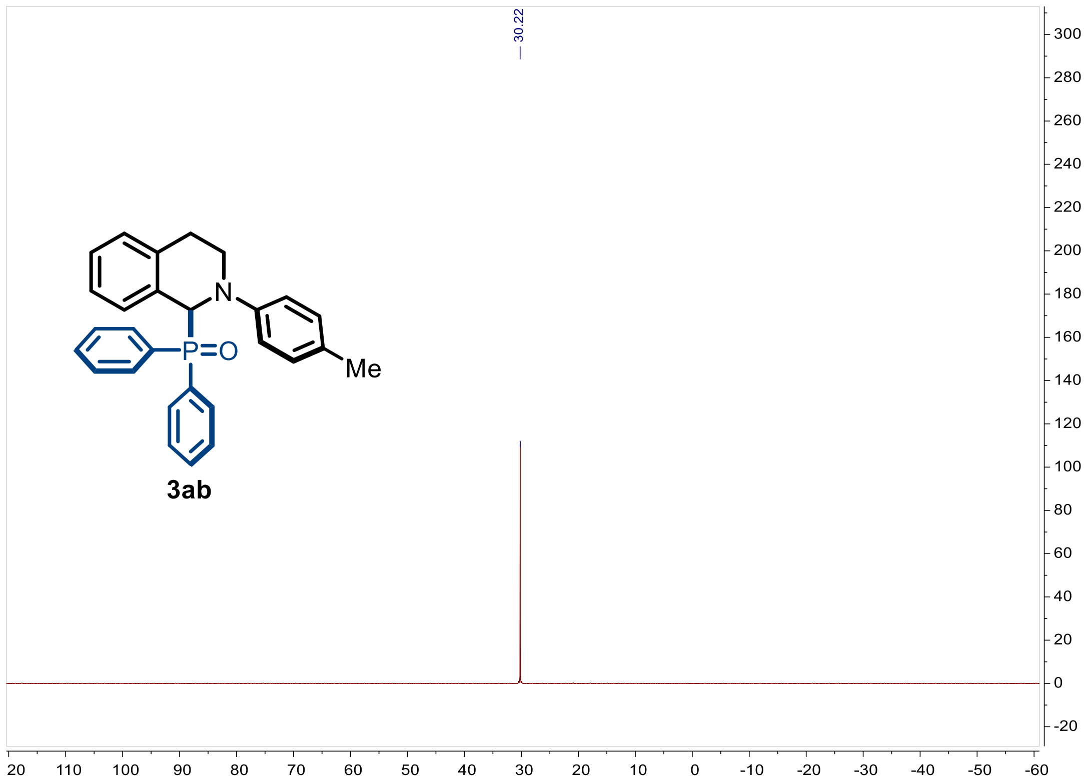
^{1}H NMR spectrum of 3ab



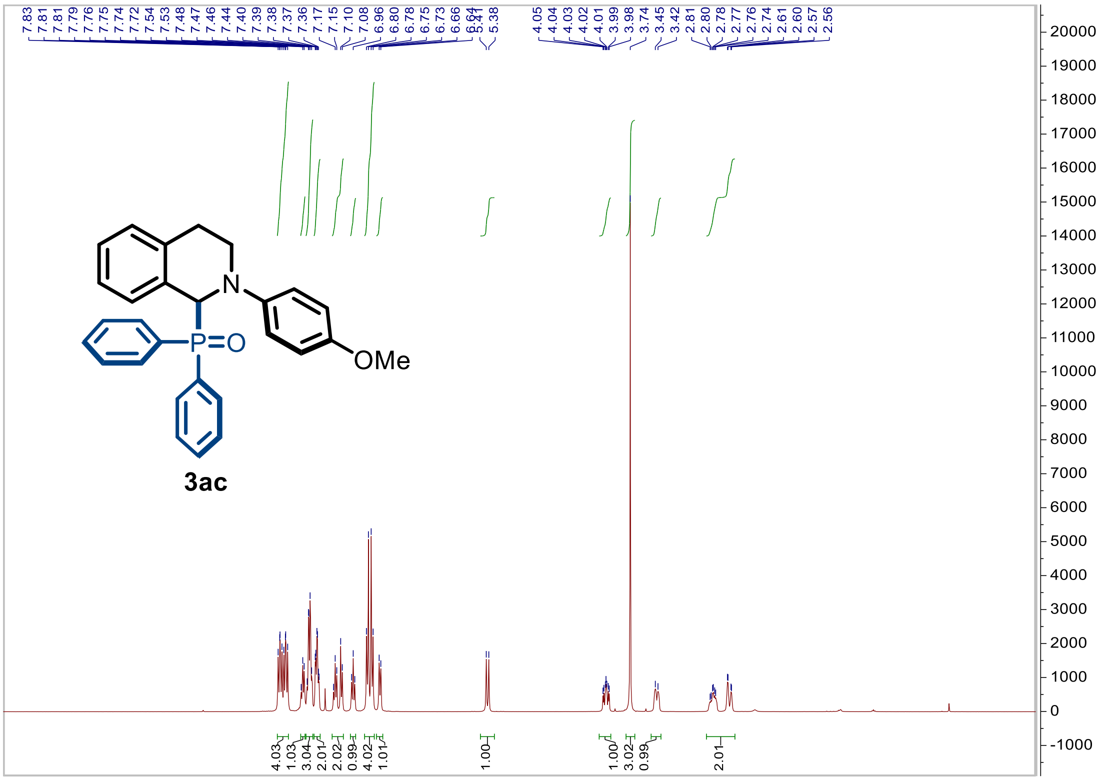
^{13}C NMR spectrum of 3ab



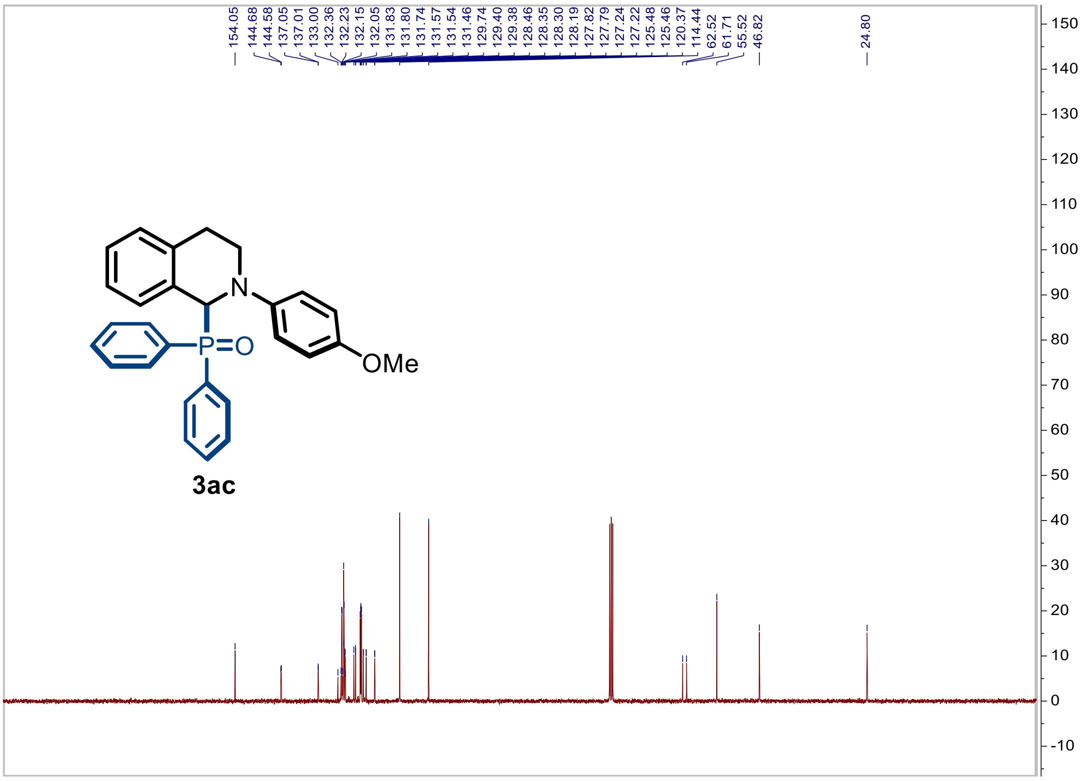
^{31}P NMR spectrum of 3ab



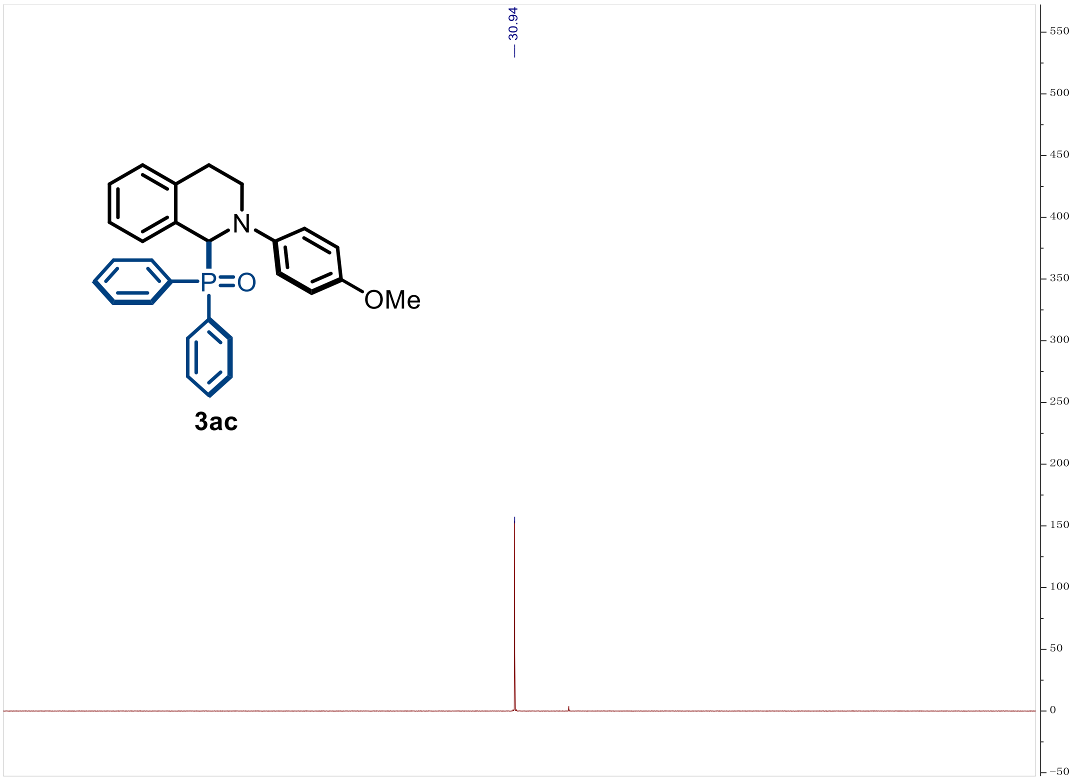
^{1}H NMR spectrum of 3ac



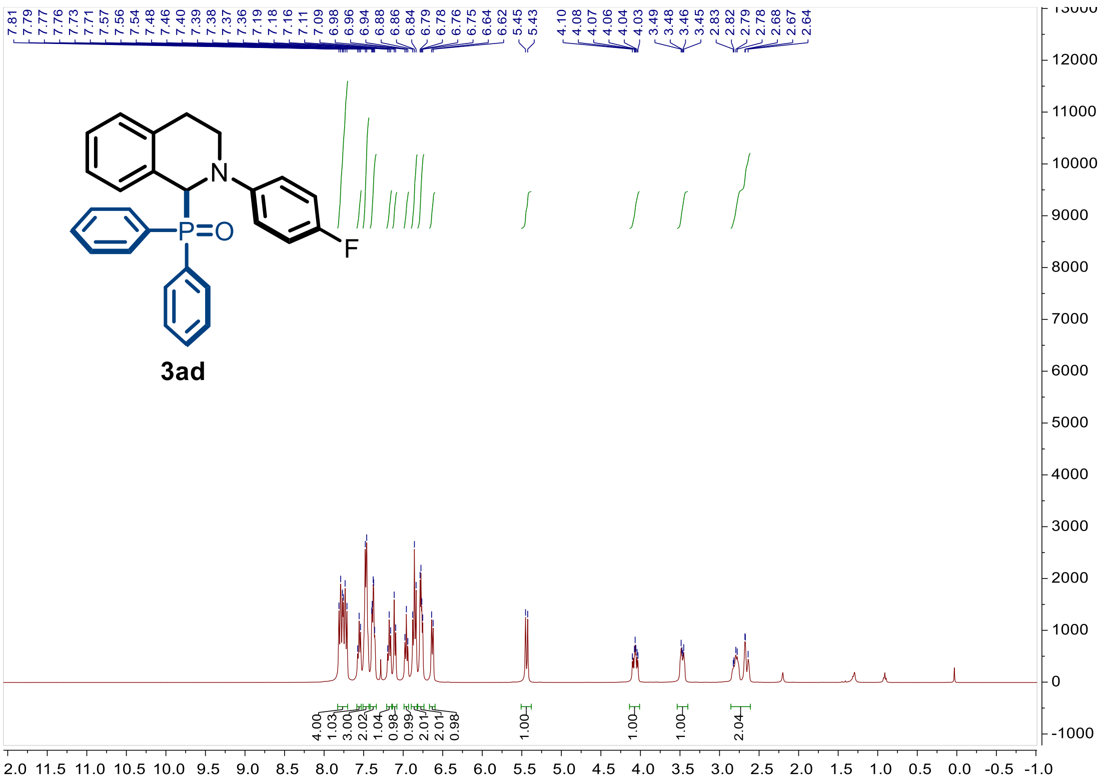
^{13}C NMR spectrum of 3ac



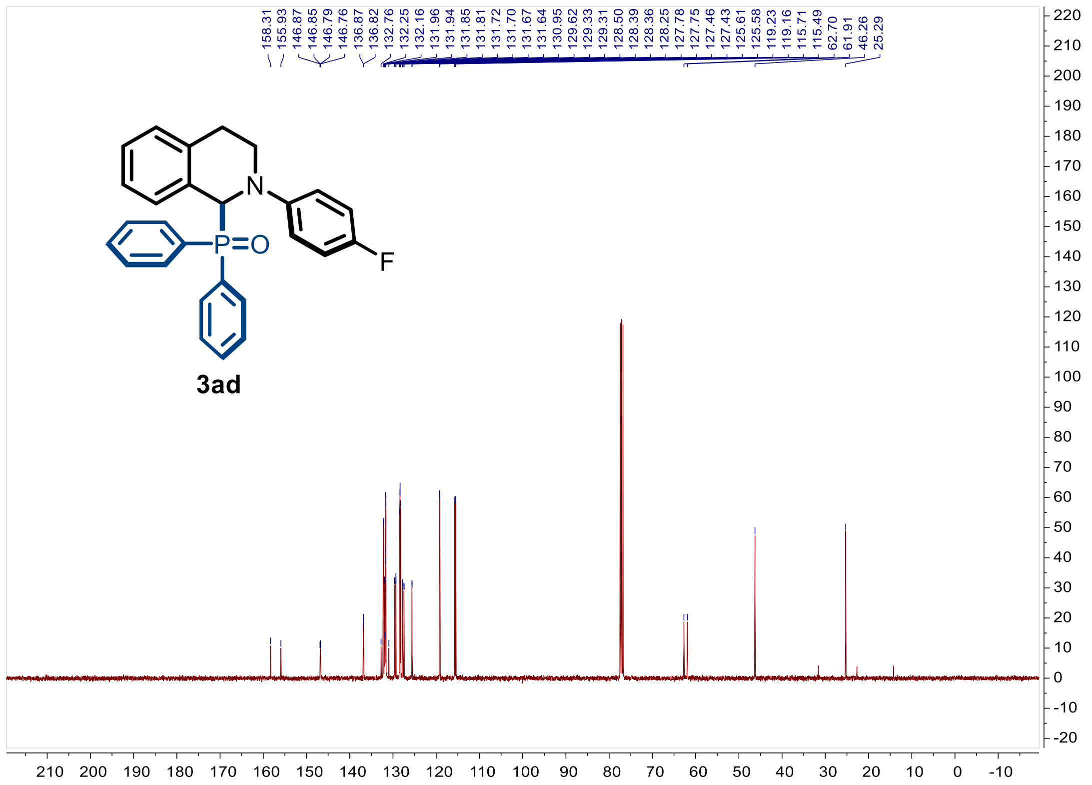
[31]P NMR spectrum of 3ac



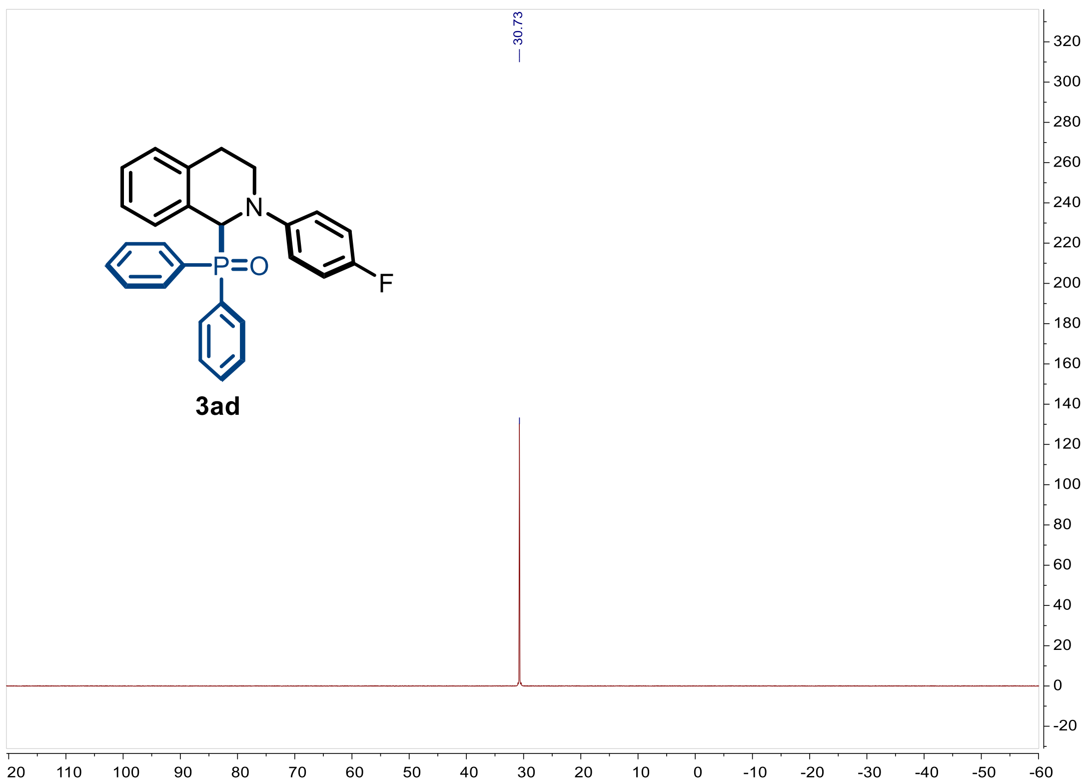
[1]H NMR spectrum of 3ad



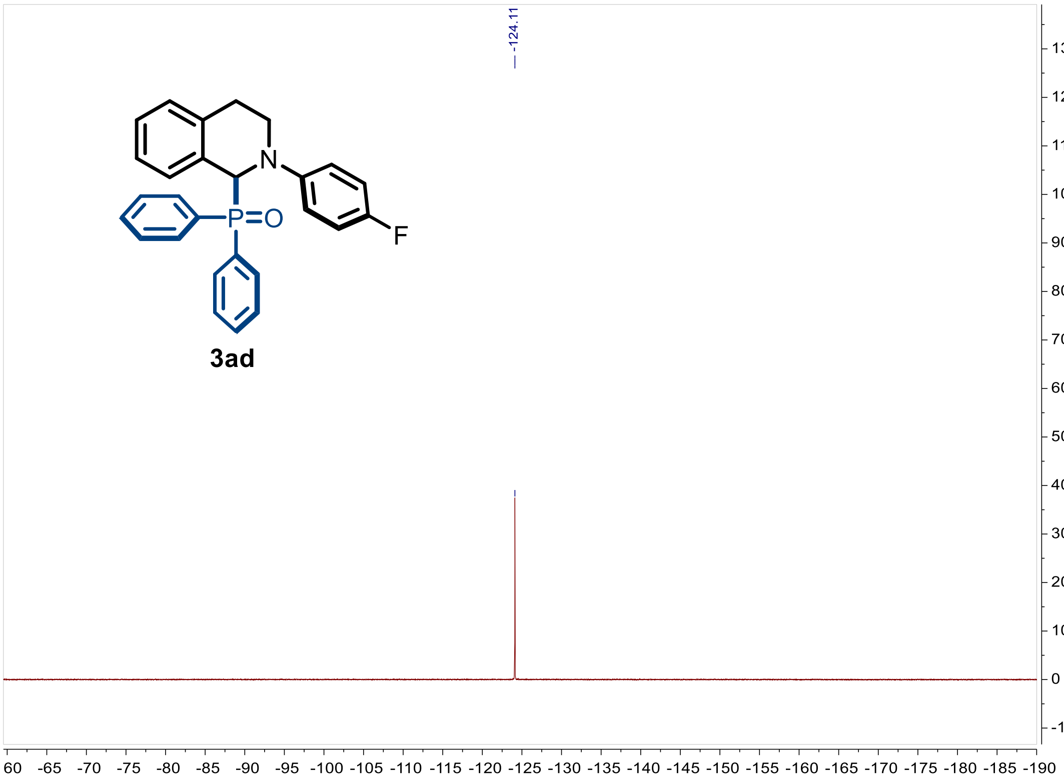
^{13}C NMR spectrum of 3ad



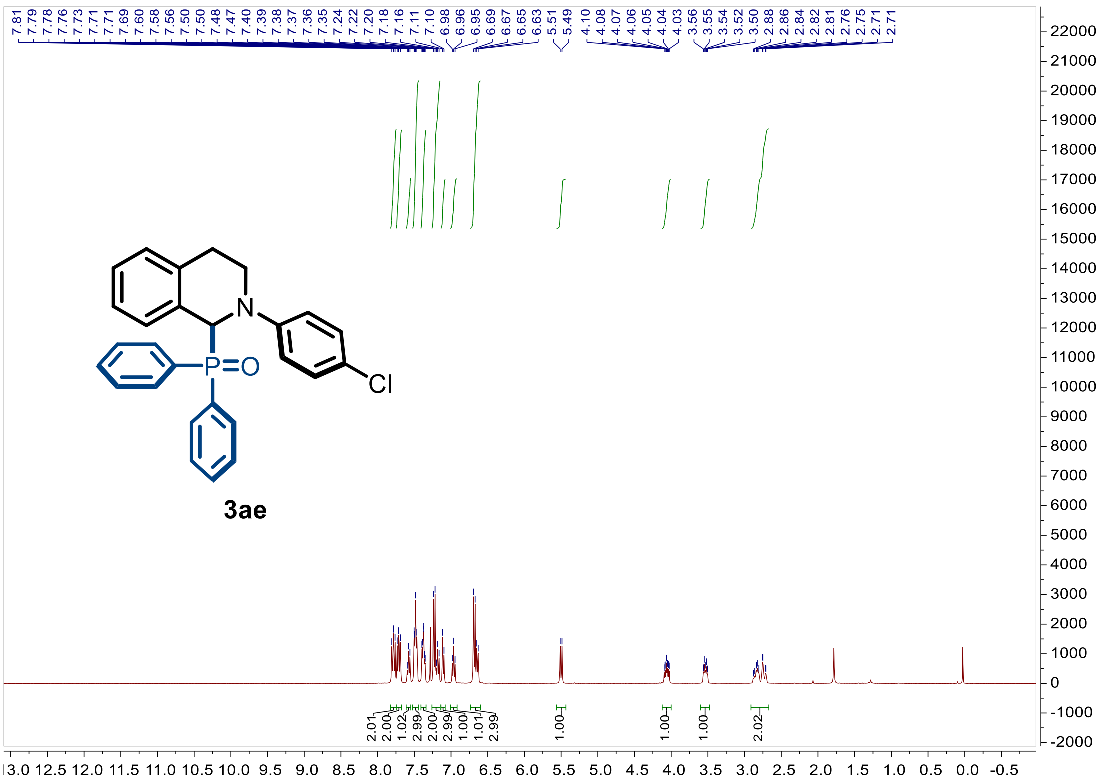
^{31}P NMR spectrum of 3ad



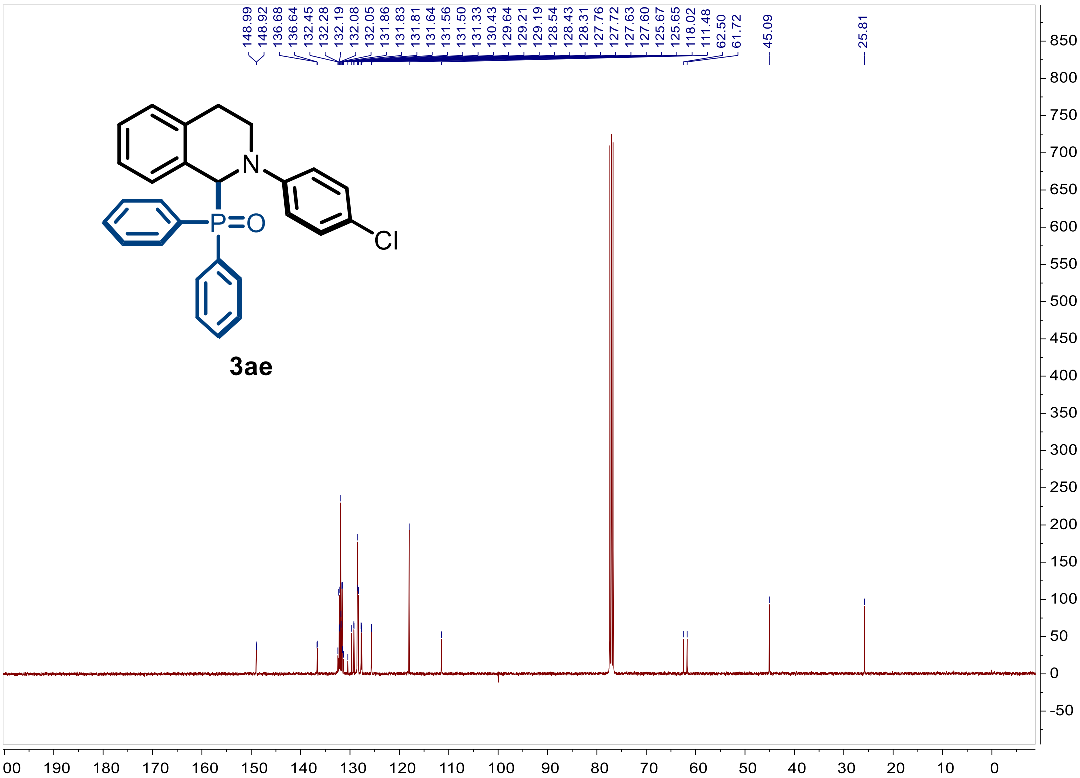
^{19}F NMR spectrum of 3ad



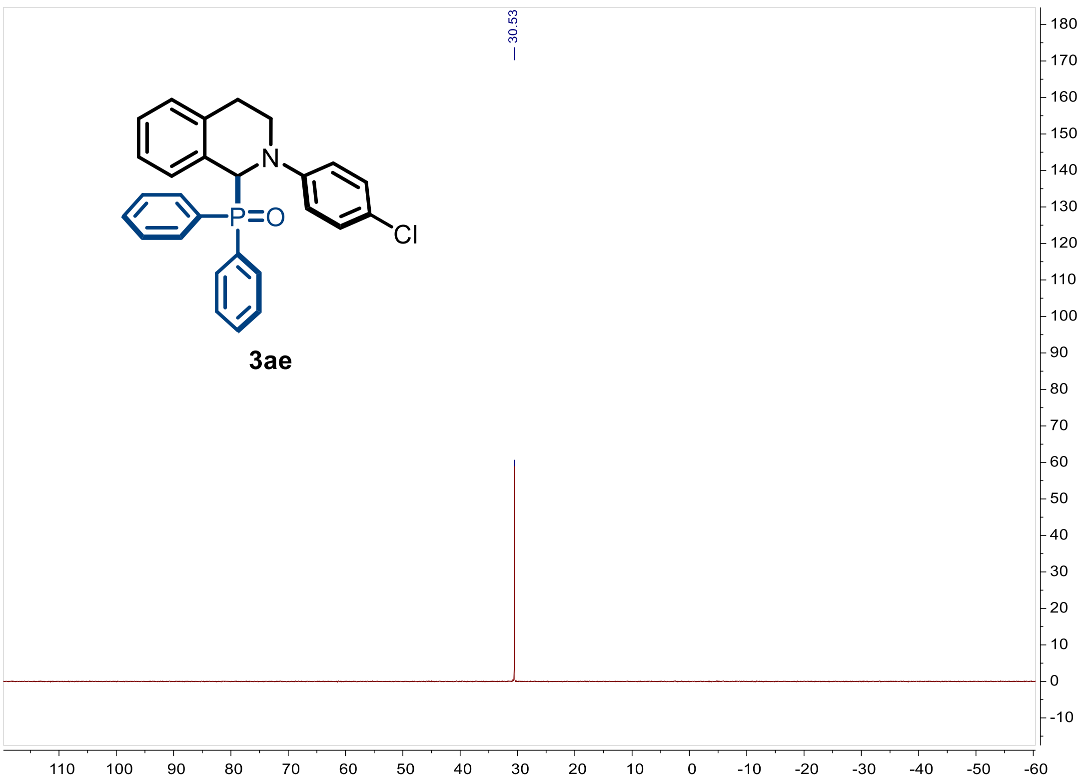
^{1}H NMR spectrum of 3ae



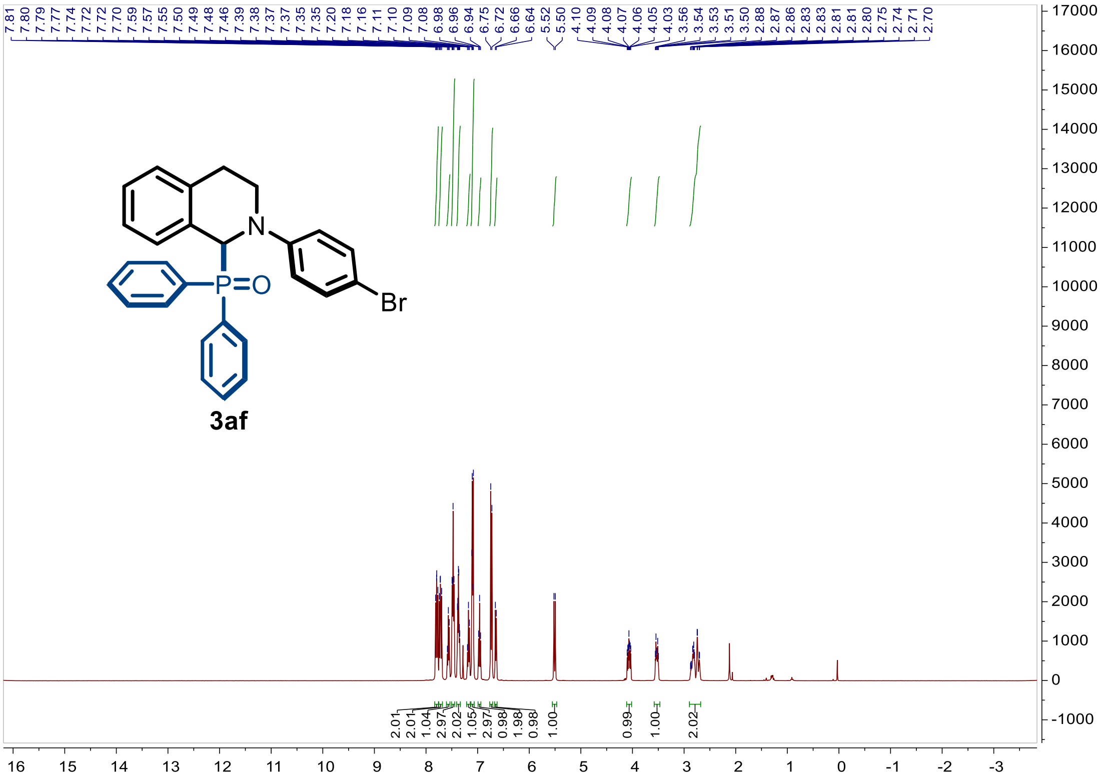
^{13}C NMR spectrum of 3ae



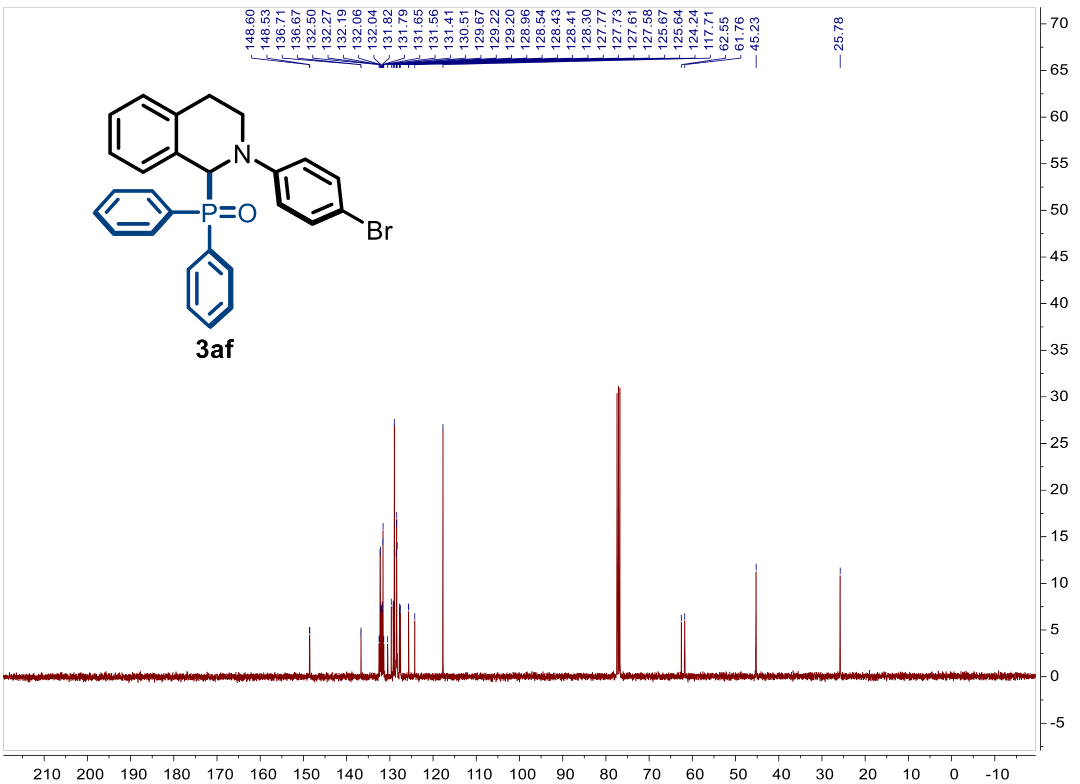
^{31}P NMR spectrum of 3ae



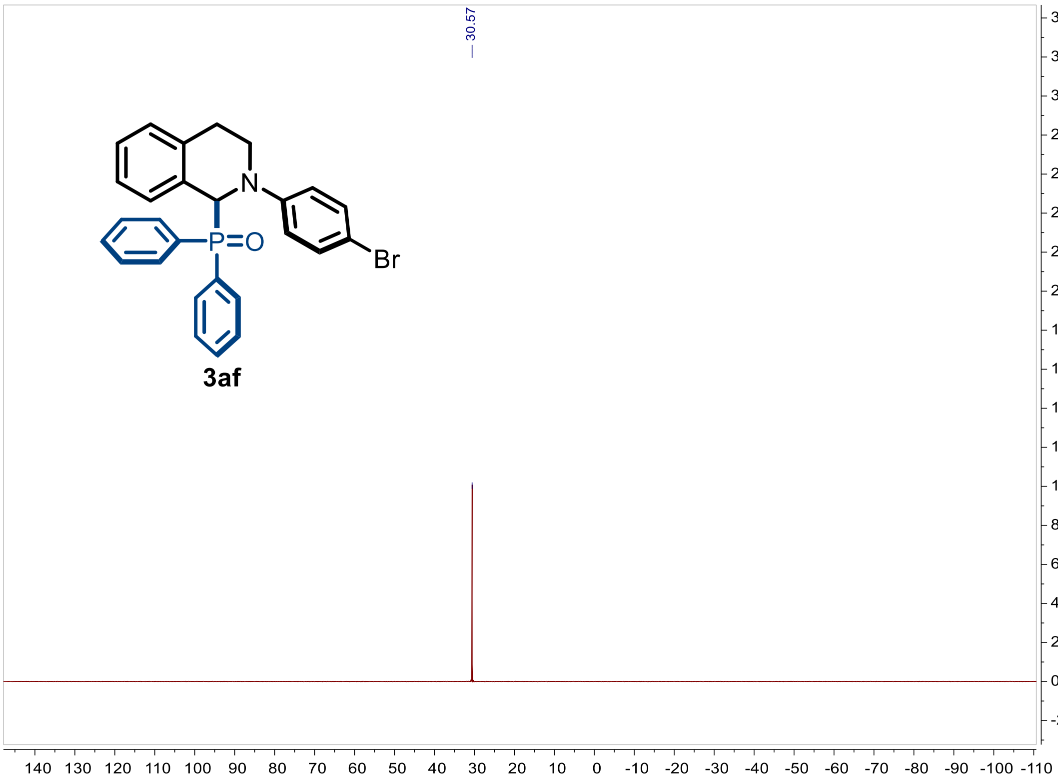
[1]H NMR spectrum of 3af



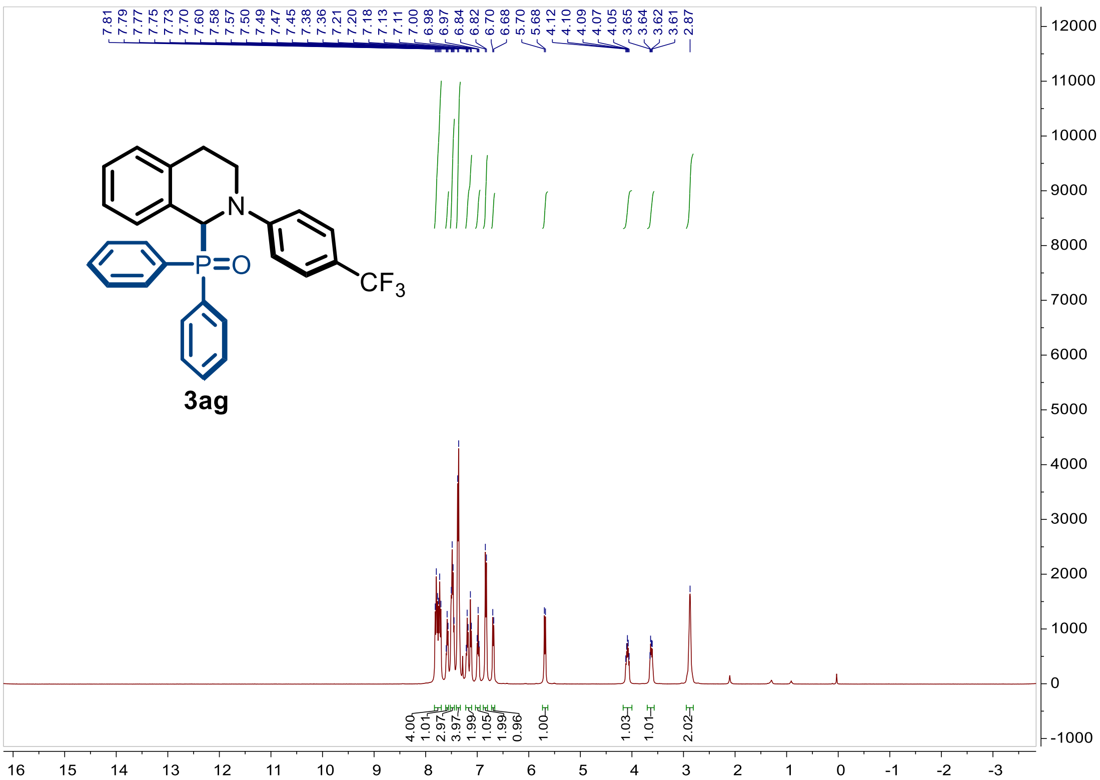
[13]C NMR spectrum of 3af



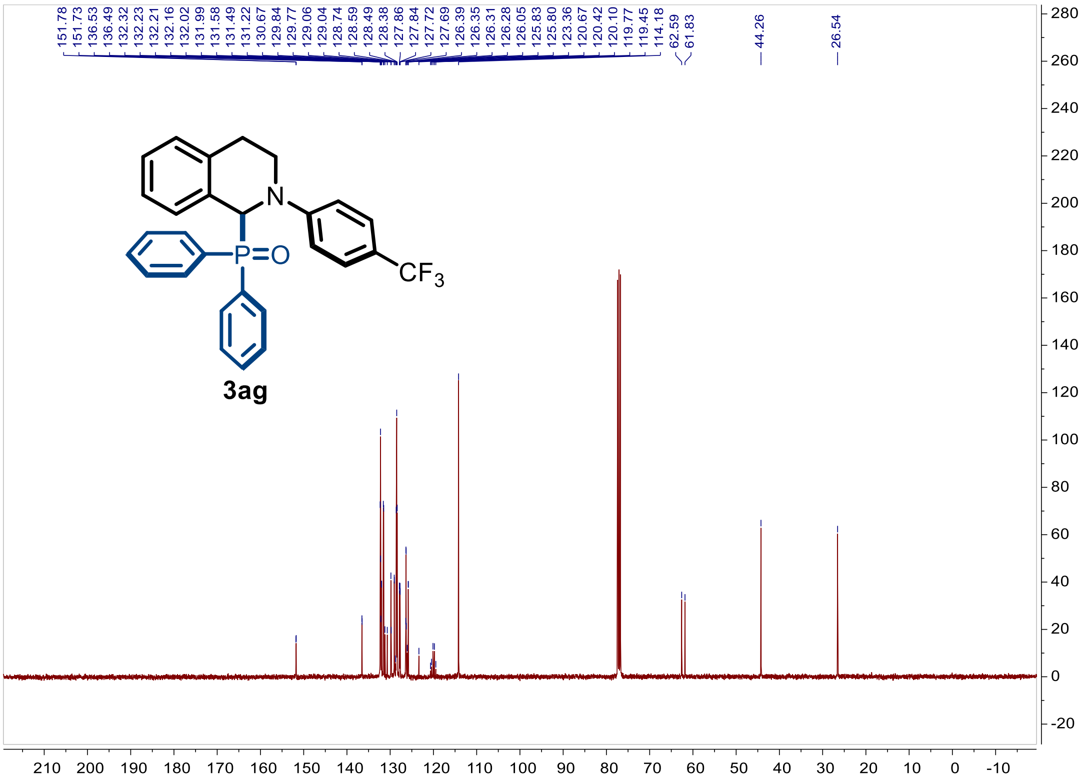
[31]P NMR spectrum of 3af



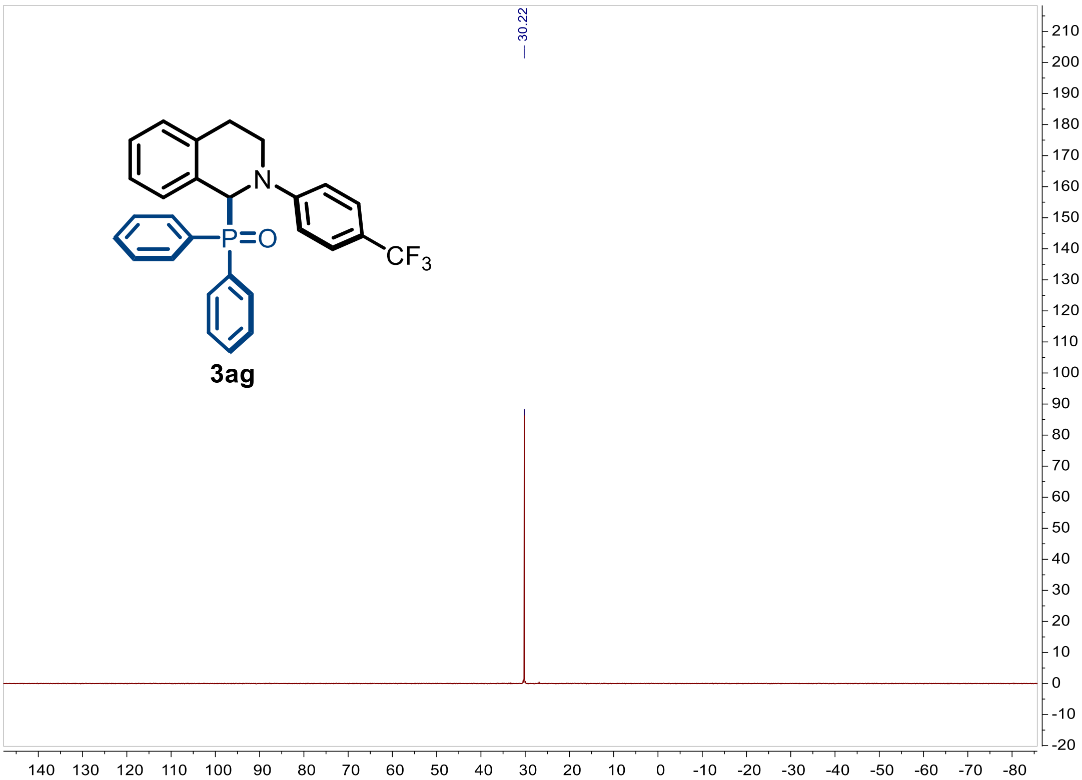
[1]H NMR spectrum of 3ag



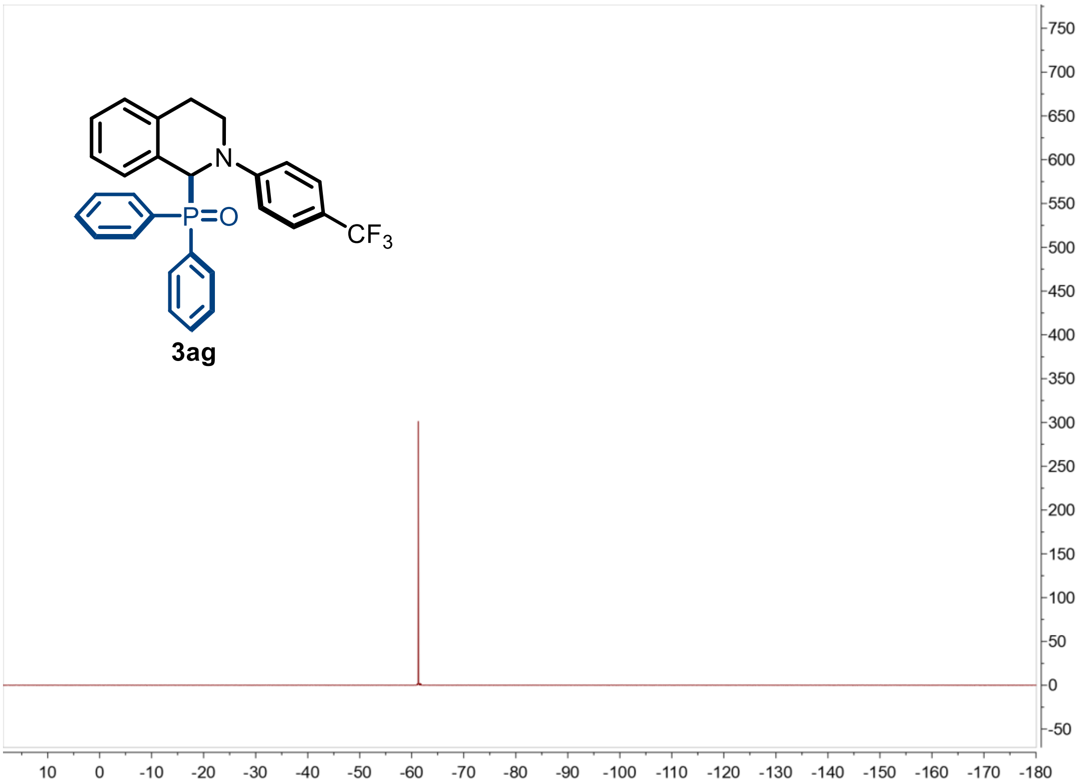
^{13}C NMR spectrum of 3ag



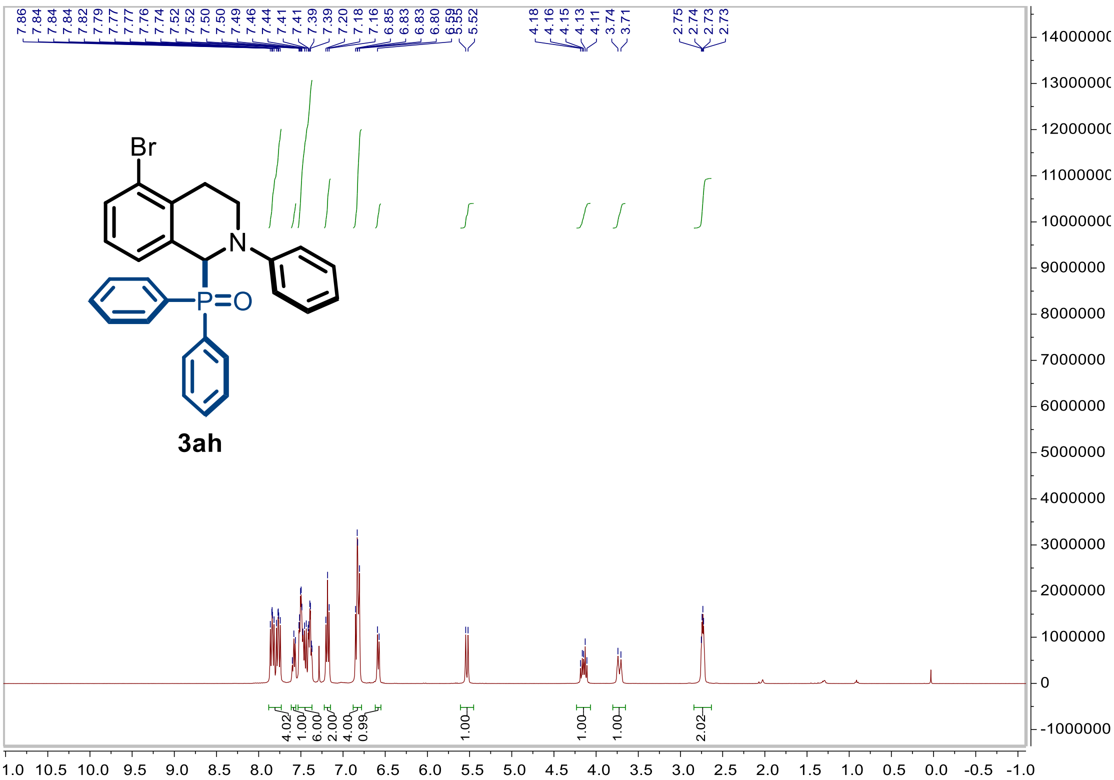
^{31}P NMR spectrum of 3ag



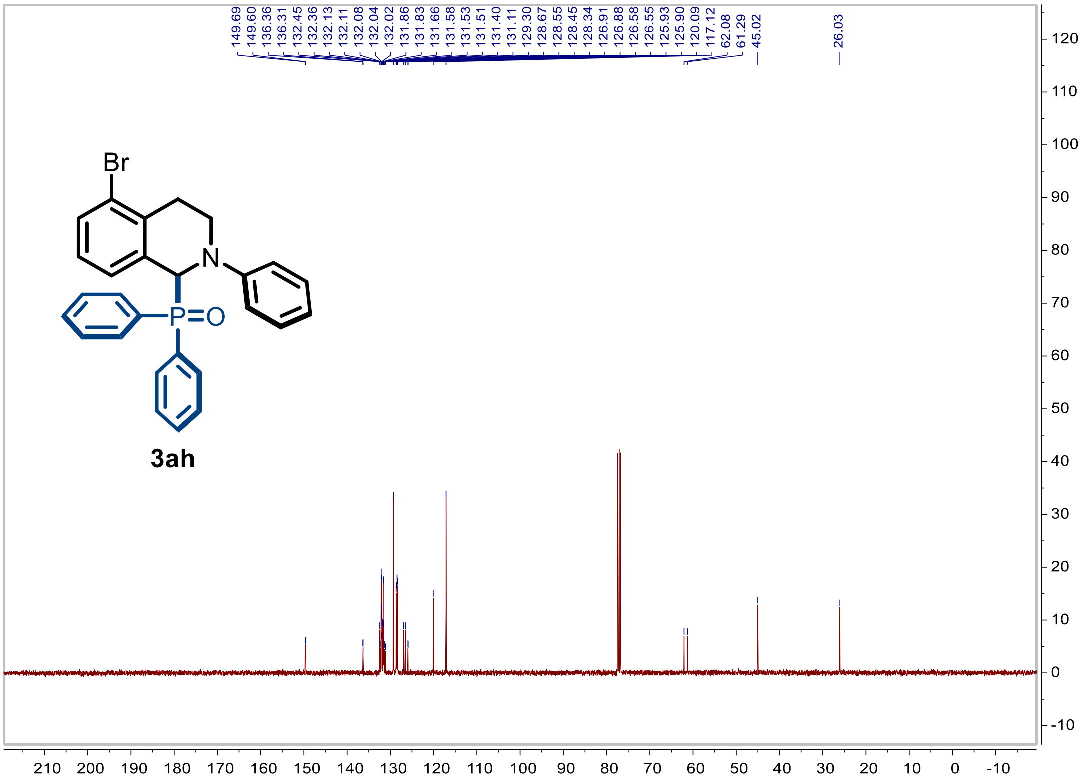
[19]F NMR spectrum of 3ag



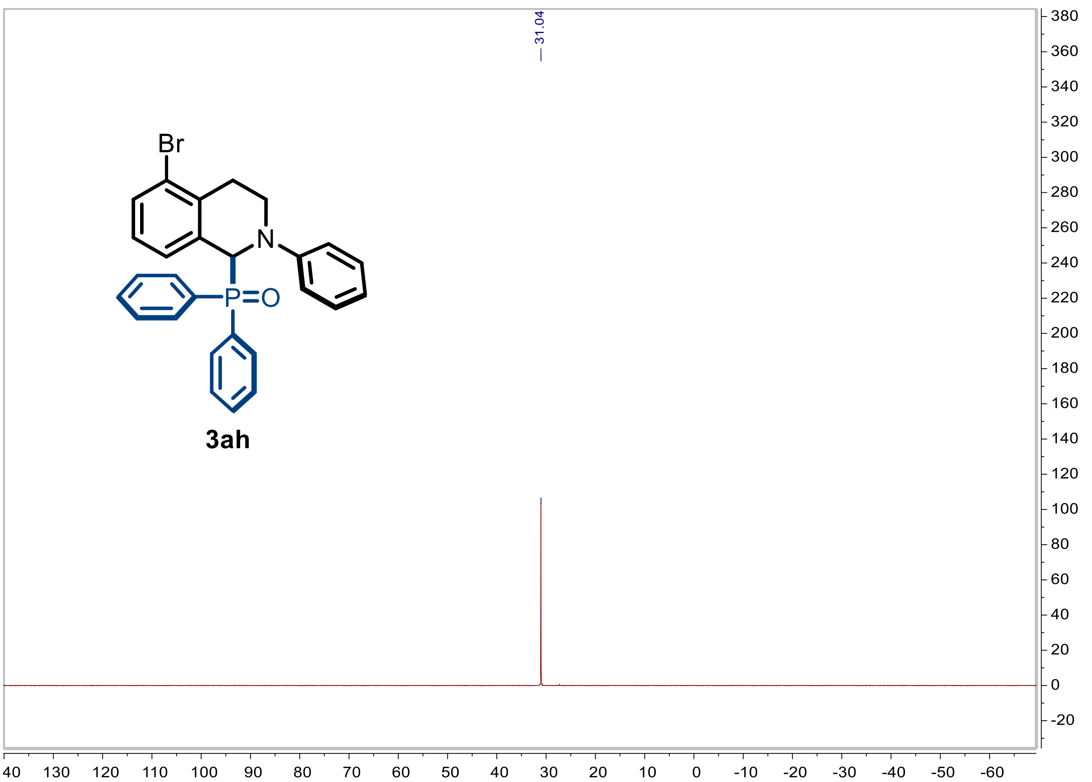
[1]H NMR spectrum of 3ah



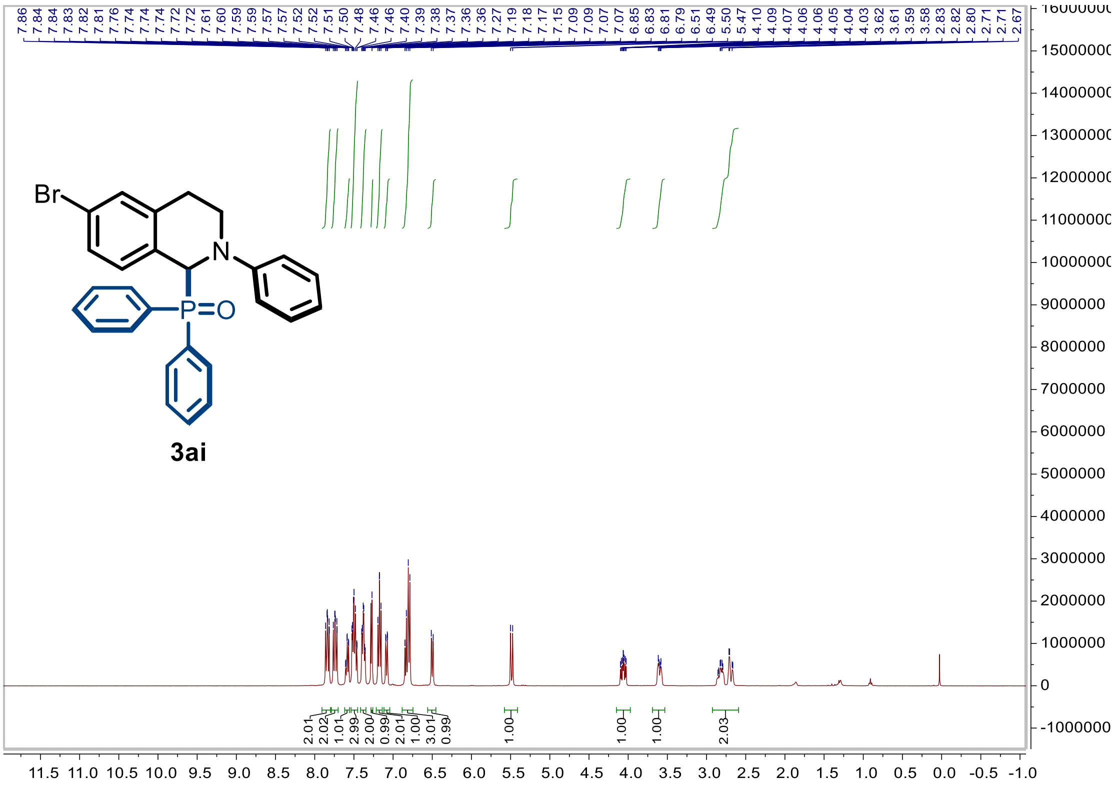
[13]C NMR spectrum of 3ah



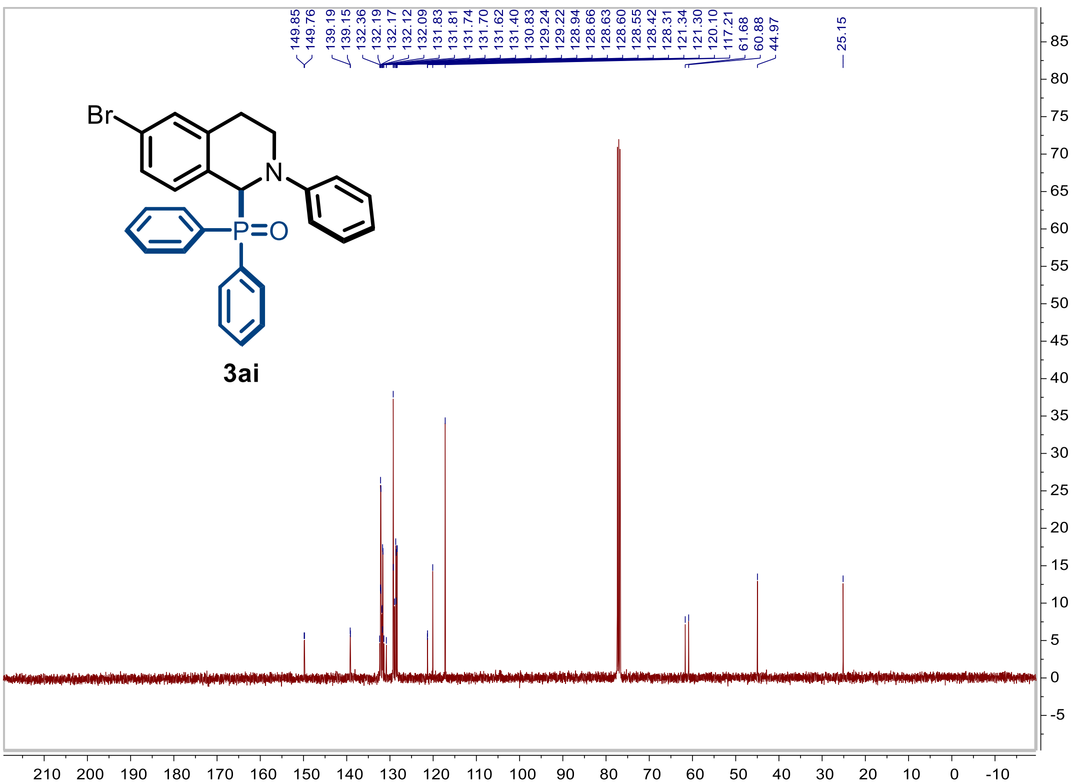
[31]P NMR spectrum of 3ah



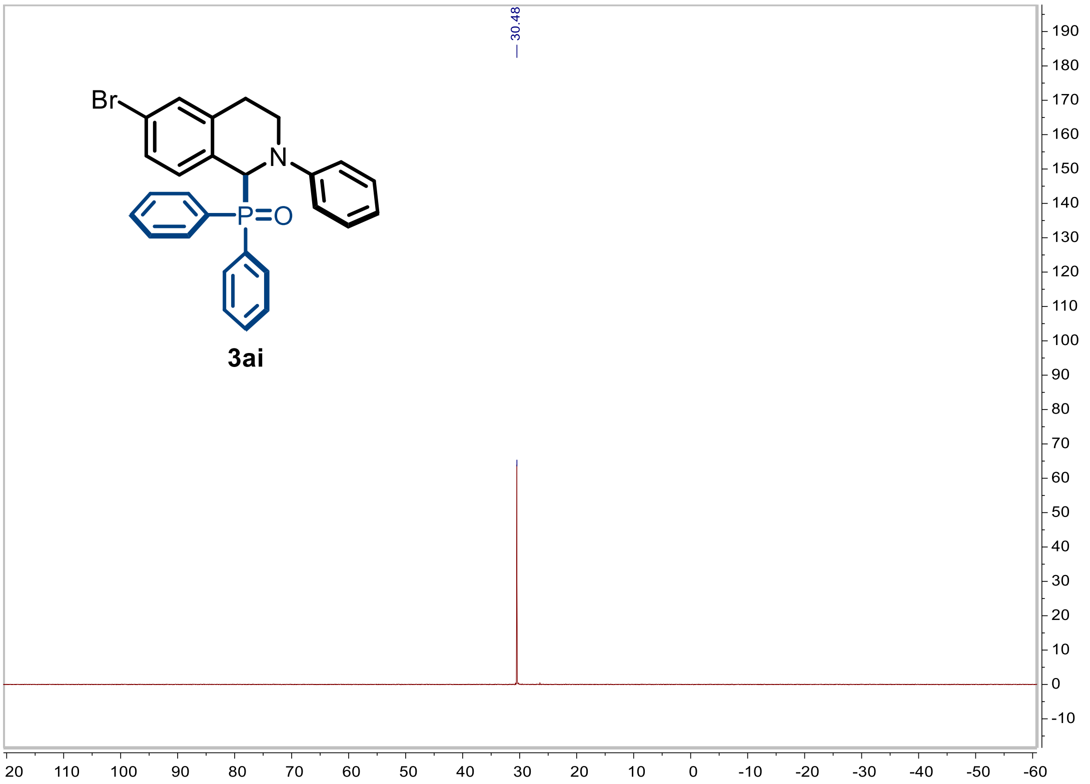
[1]H NMR spectrum of 3ai



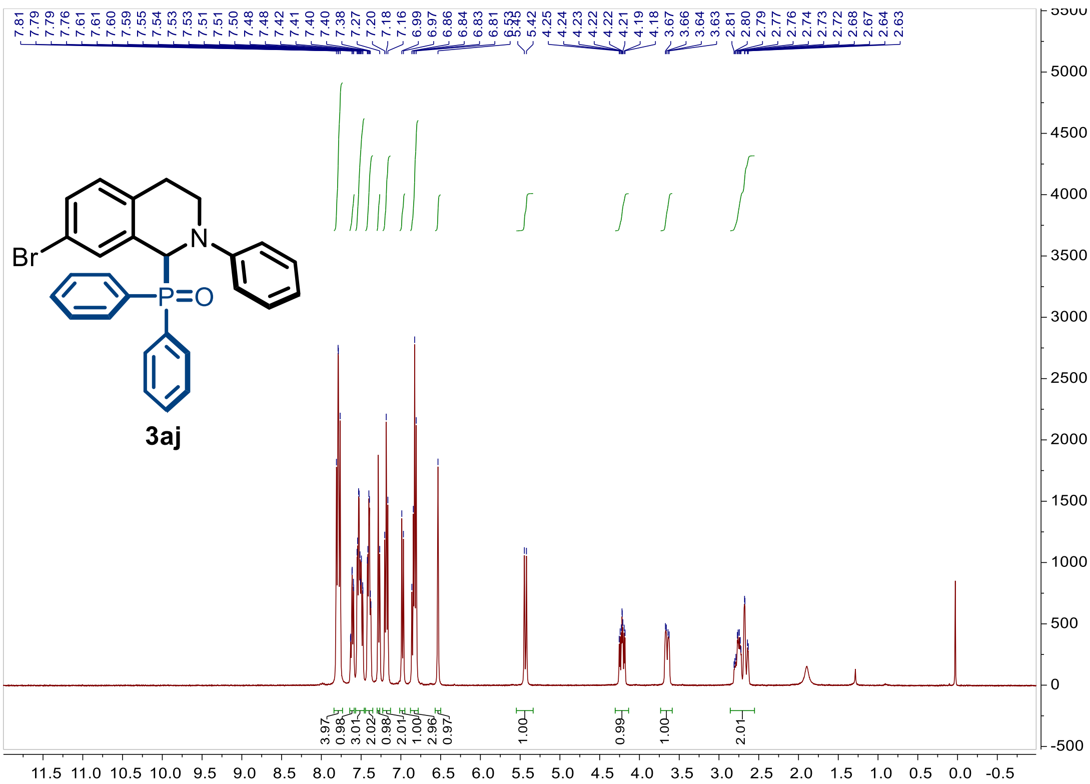
[13]C NMR spectrum of 3ai



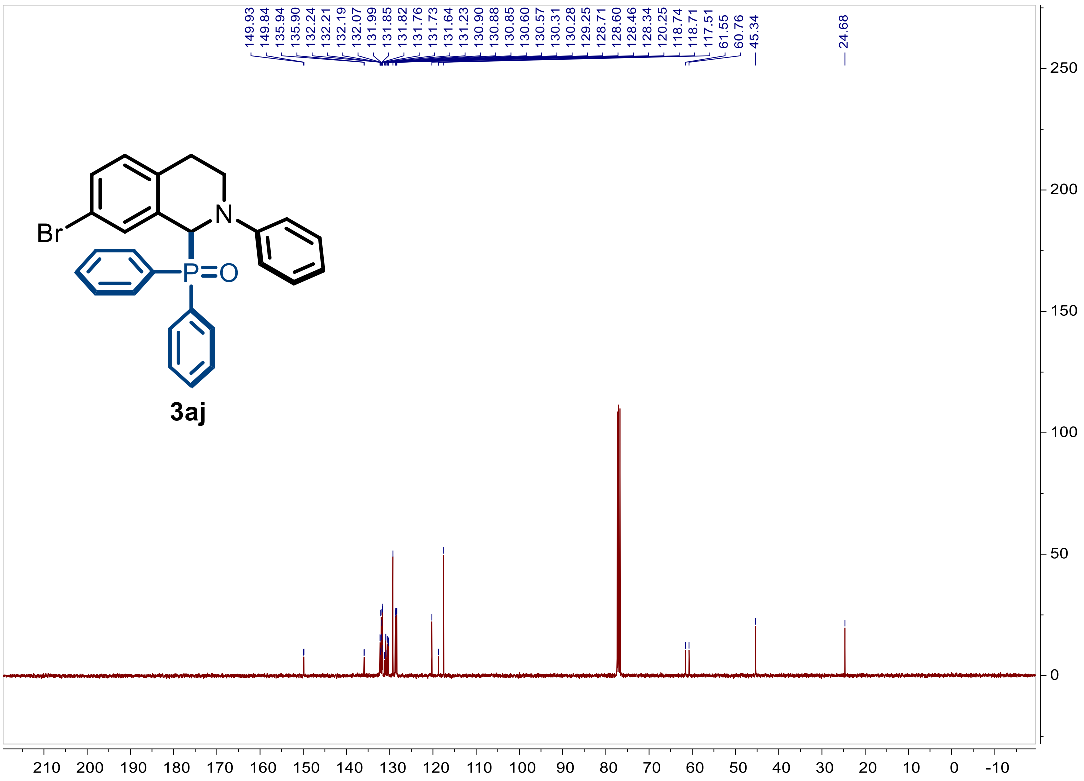
^{31}P NMR spectrum of 3ai



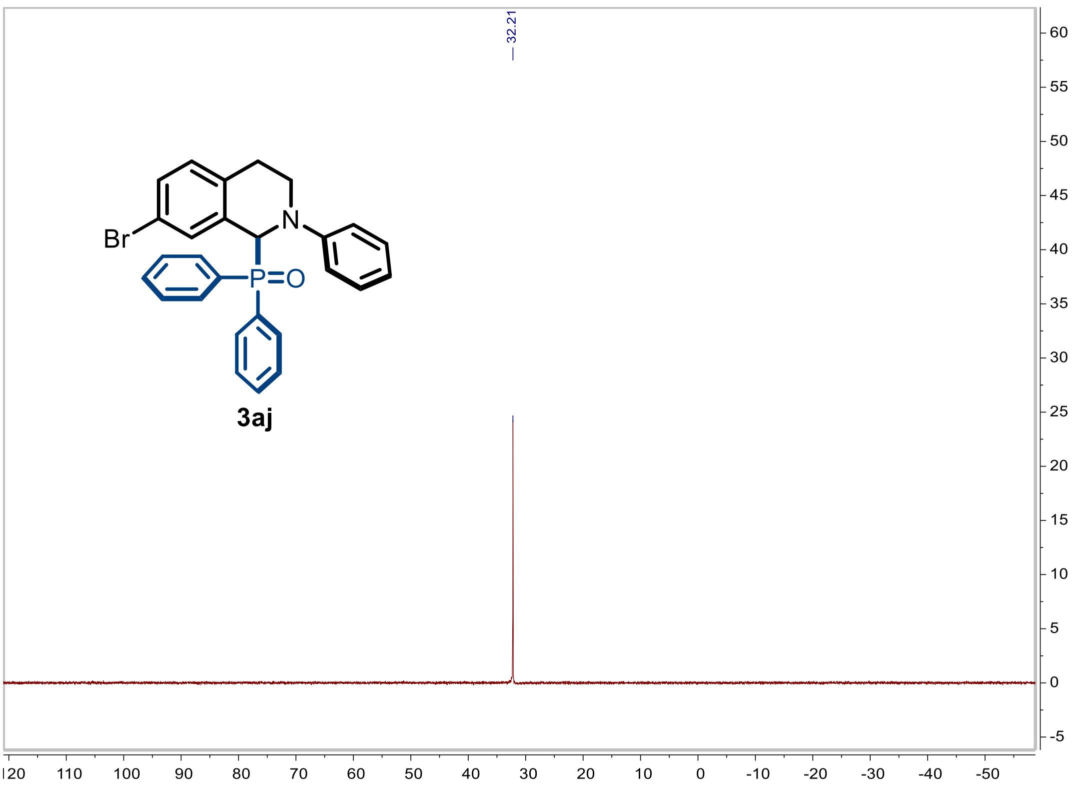
^{1}H NMR spectrum of 3aj



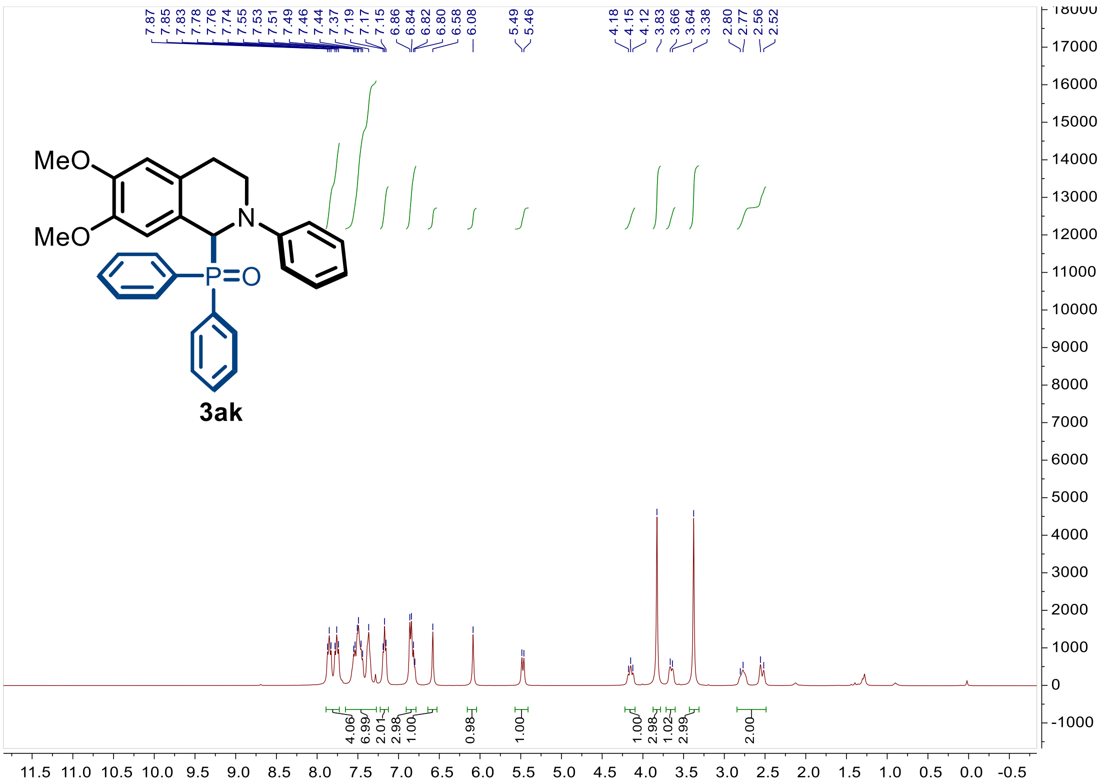
^{13}C NMR spectrum of 3aj



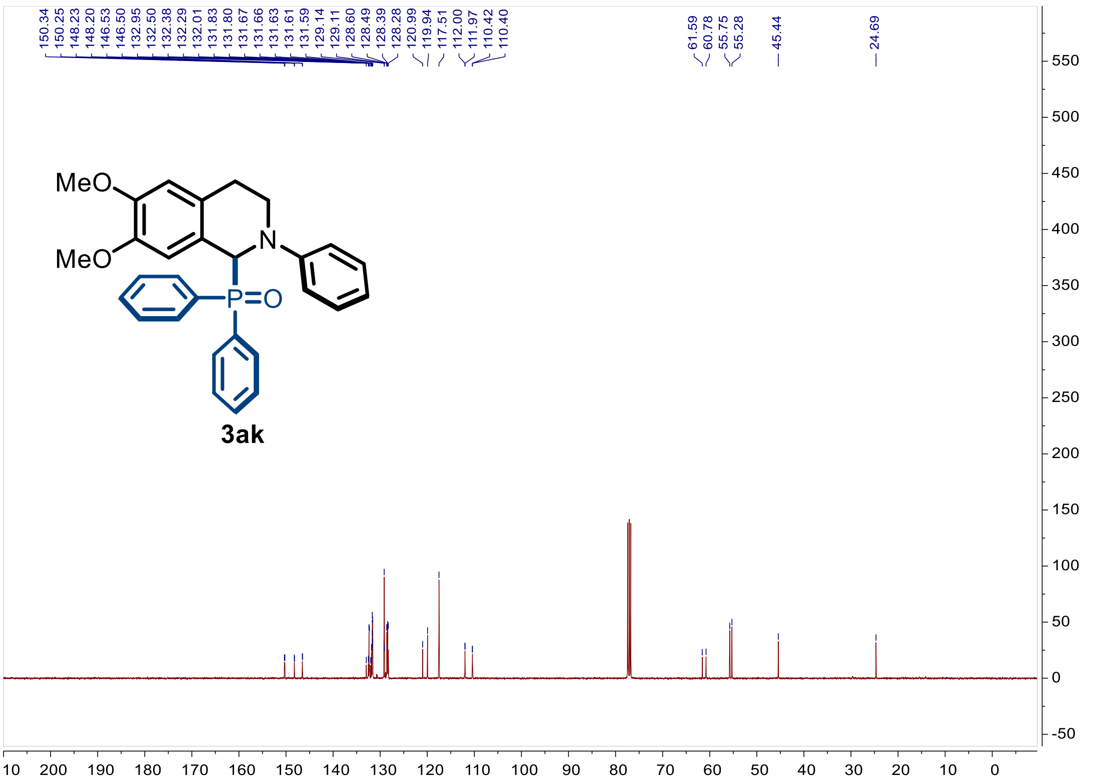
^{31}P NMR spectrum of 3aj



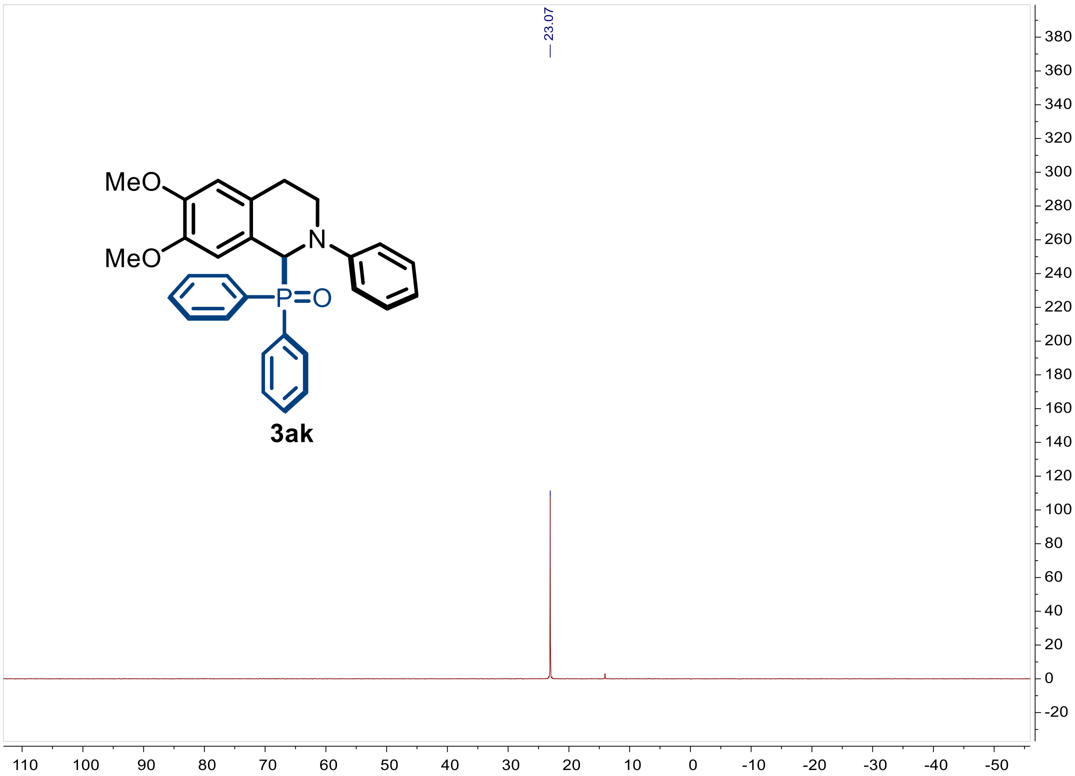
^{1}H NMR spectrum of 3ak



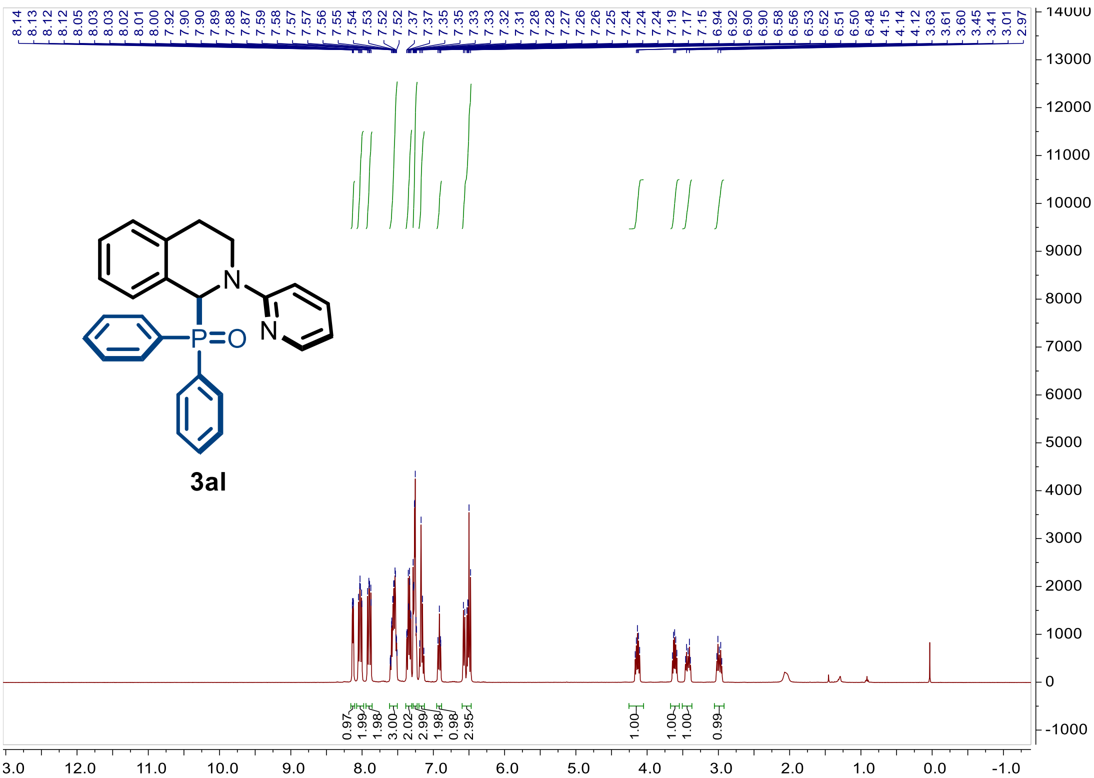
^{13}C NMR spectrum of 3ak



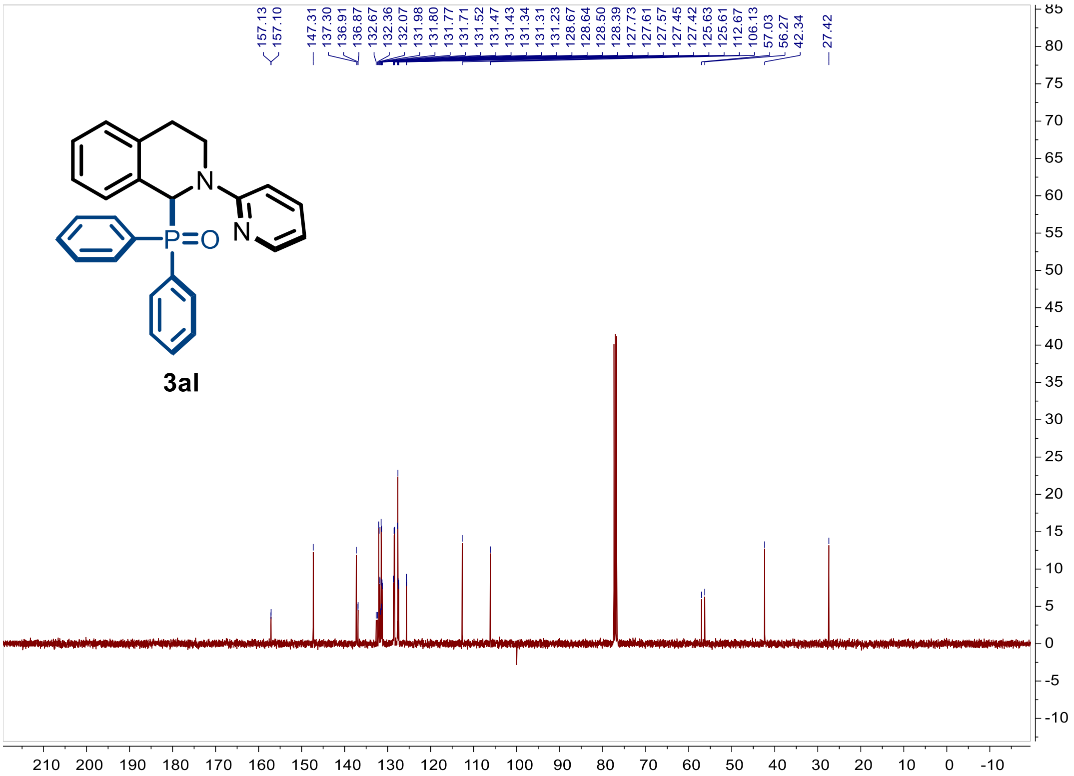
^{31}P NMR spectrum of 3ak



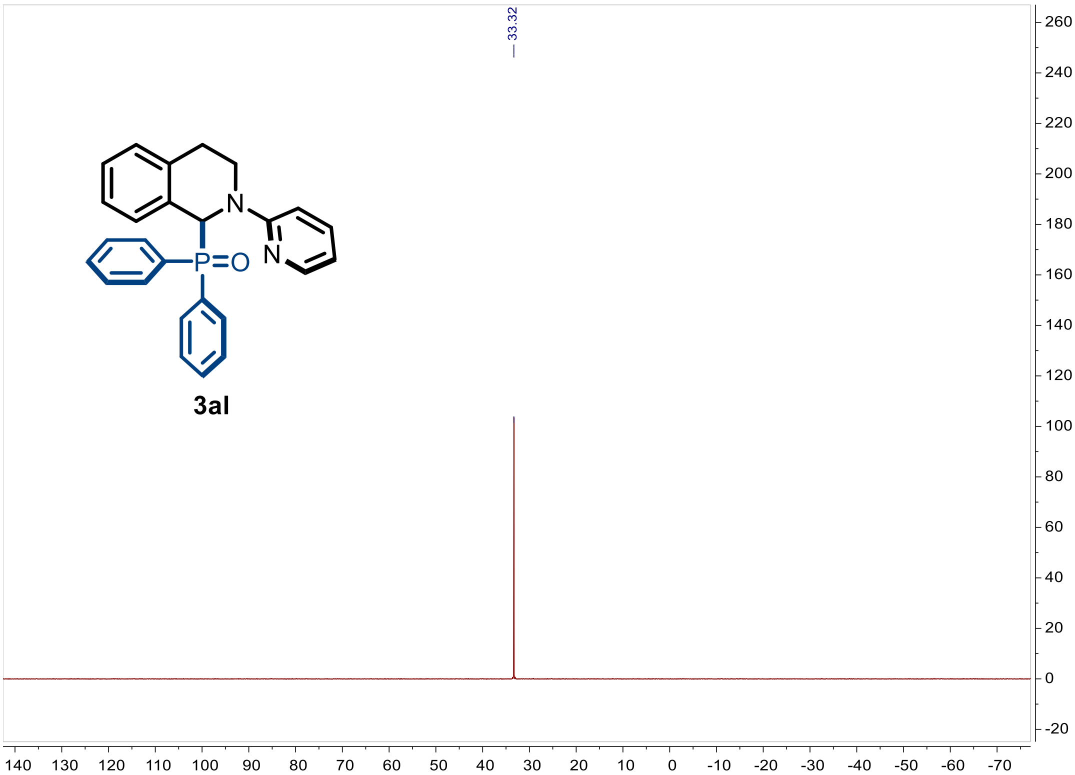
^{1}H NMR spectrum of 3al



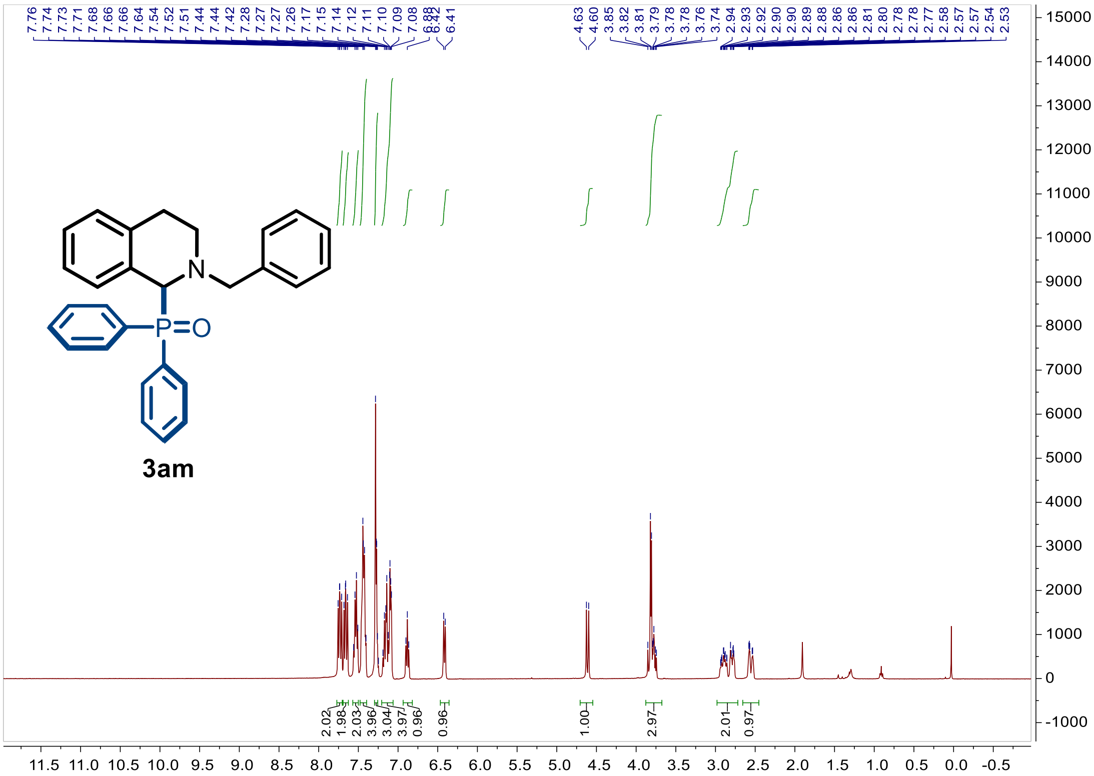
^{13}C NMR spectrum of 3al



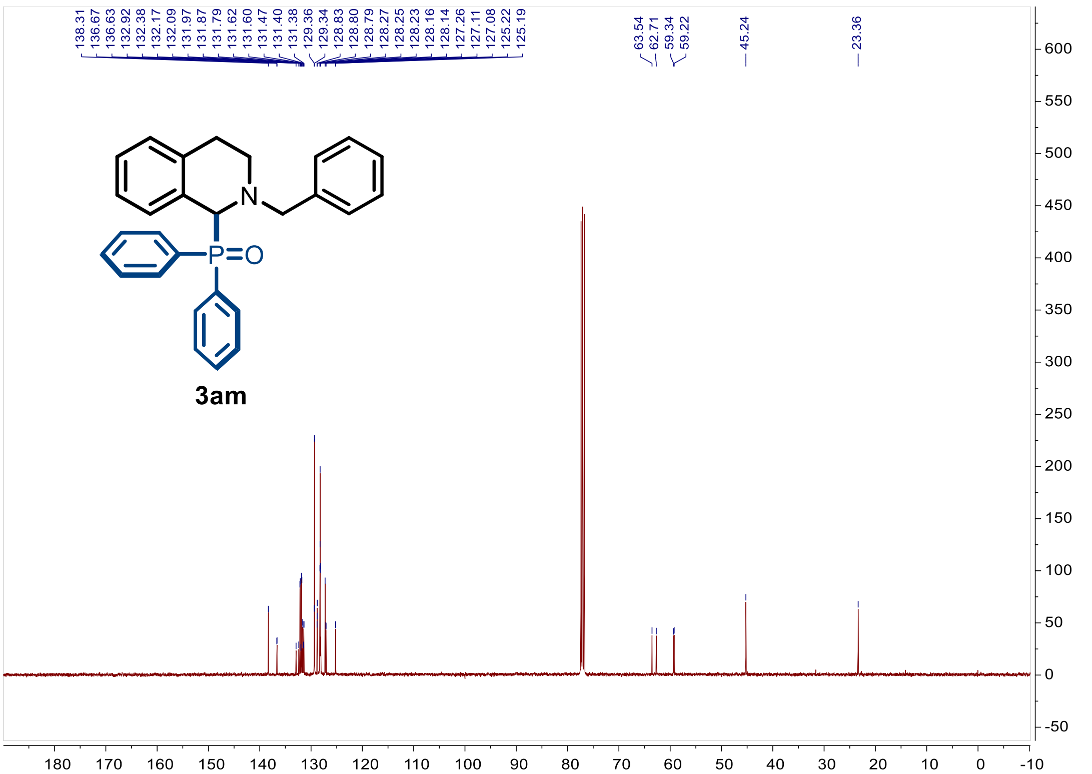
^{31}P NMR spectrum of 3al



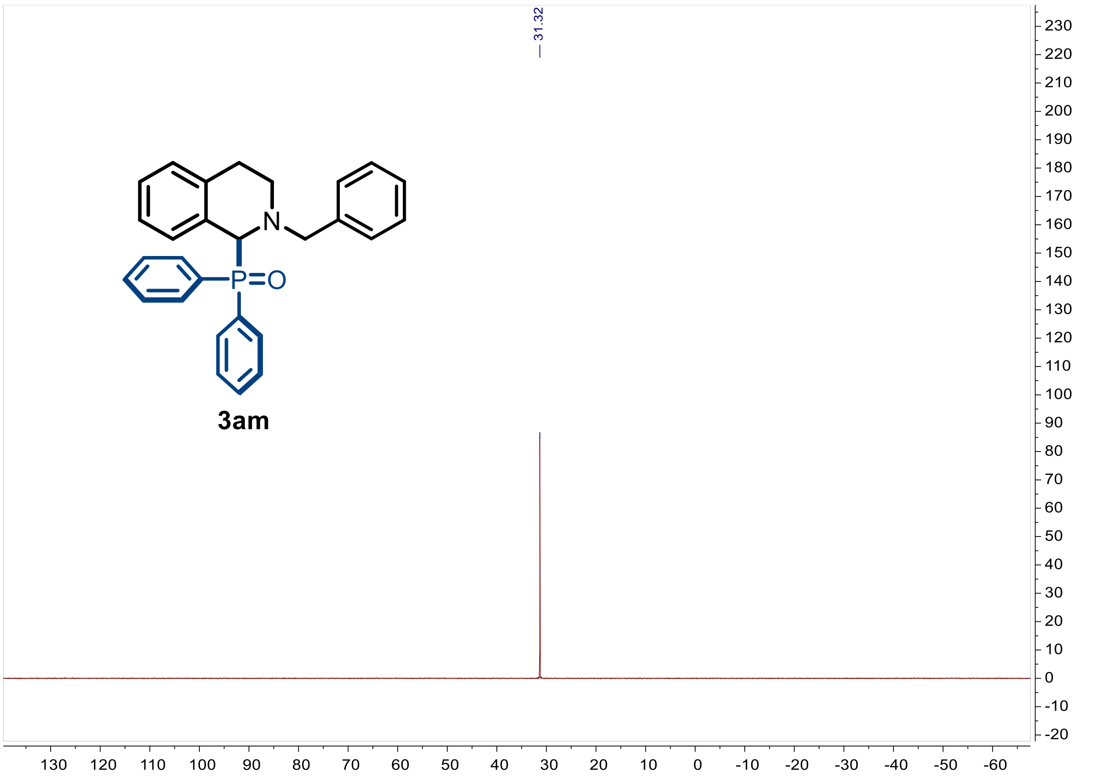
^{1}H NMR spectrum of 3am



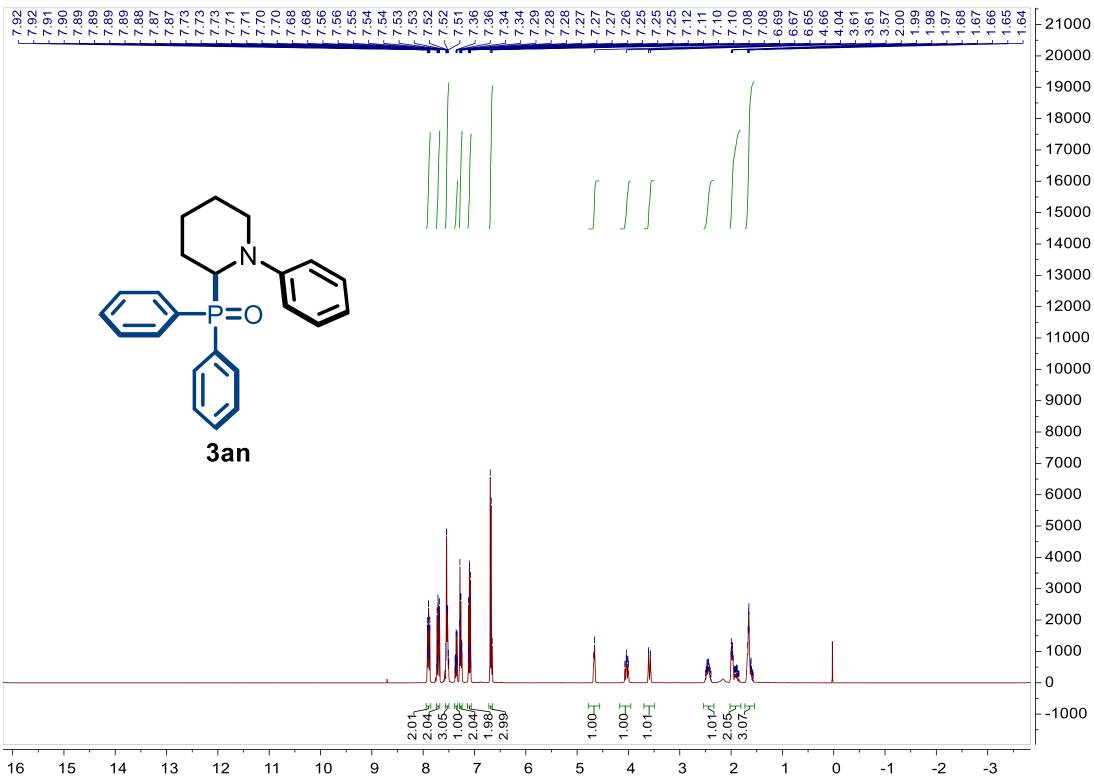
^{13}C NMR spectrum of 3am



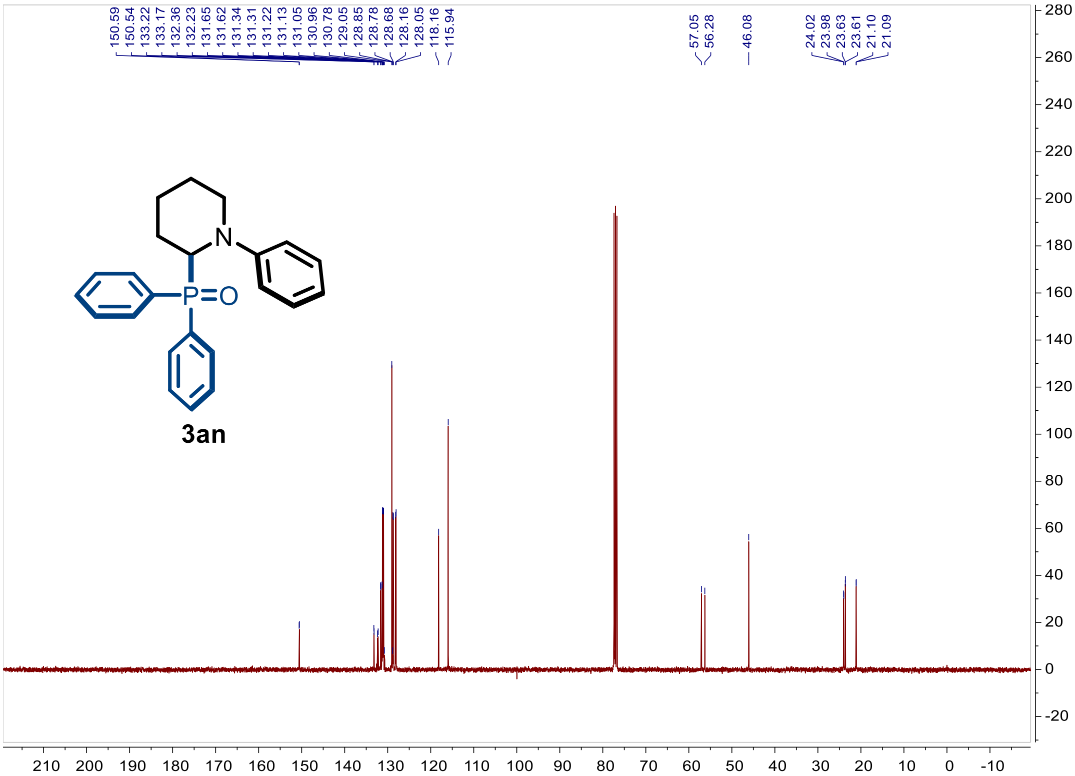
[31]P NMR spectrum of 3am



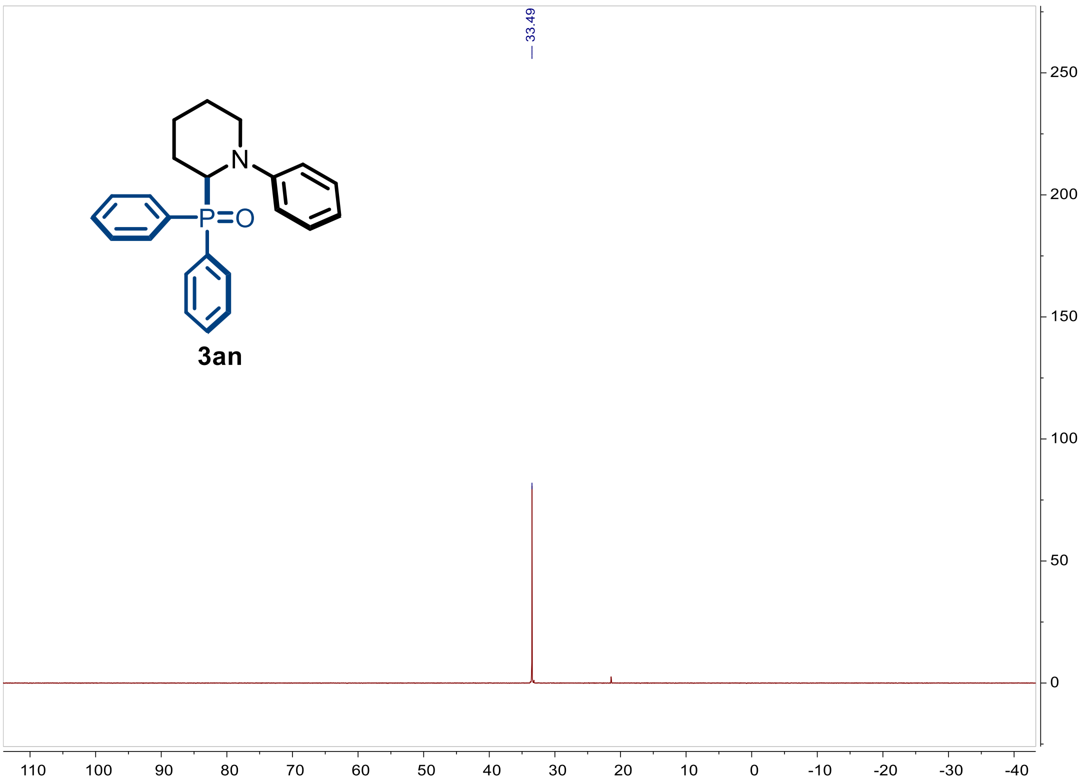
[1]H NMR spectrum of 3an



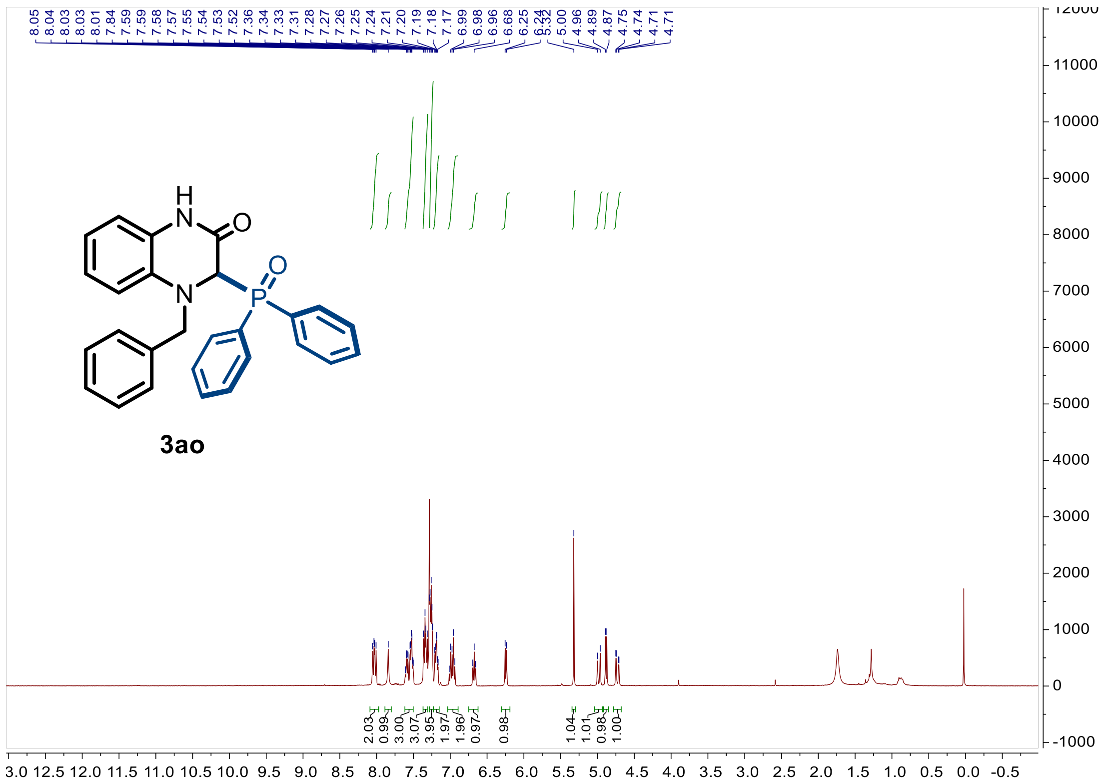
^{13}C NMR spectrum of 3an



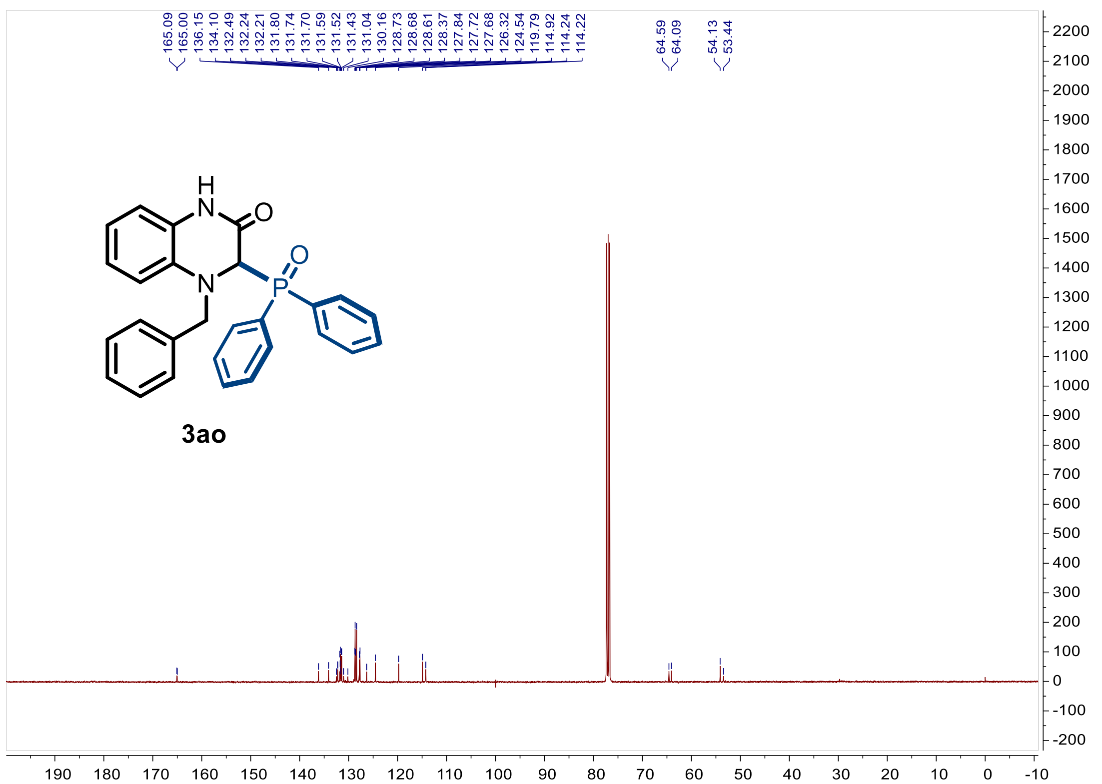
^{31}P NMR spectrum of 3an



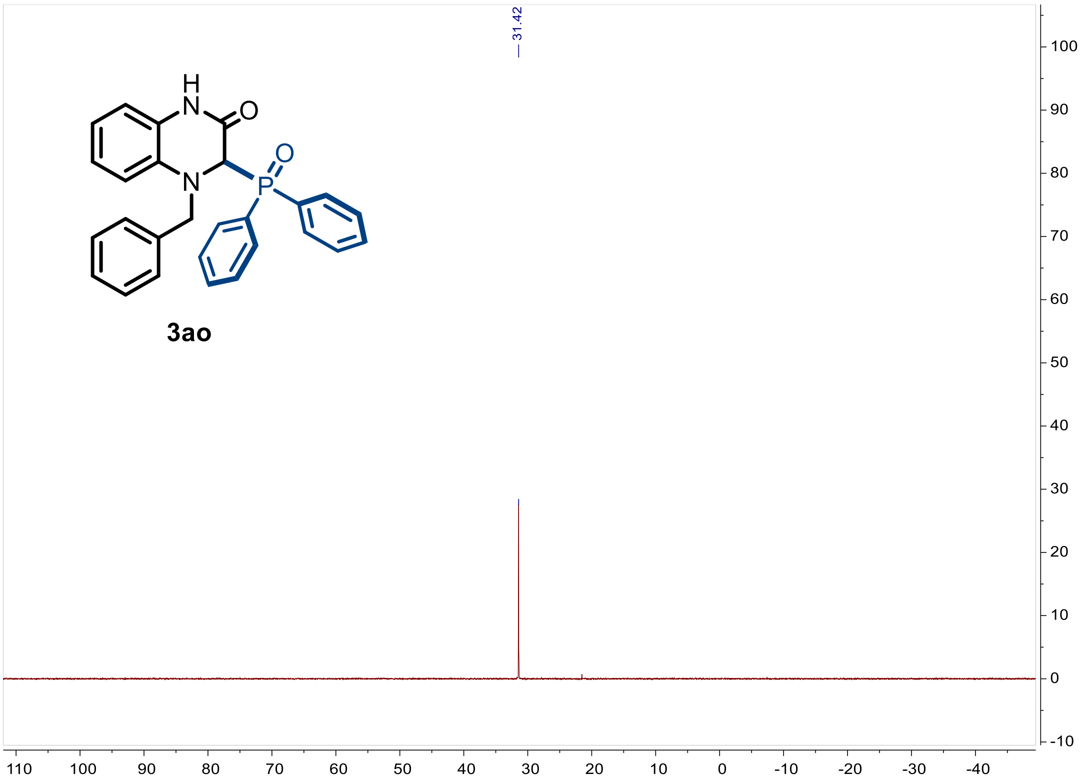
^{1}H NMR spectrum of 3ao



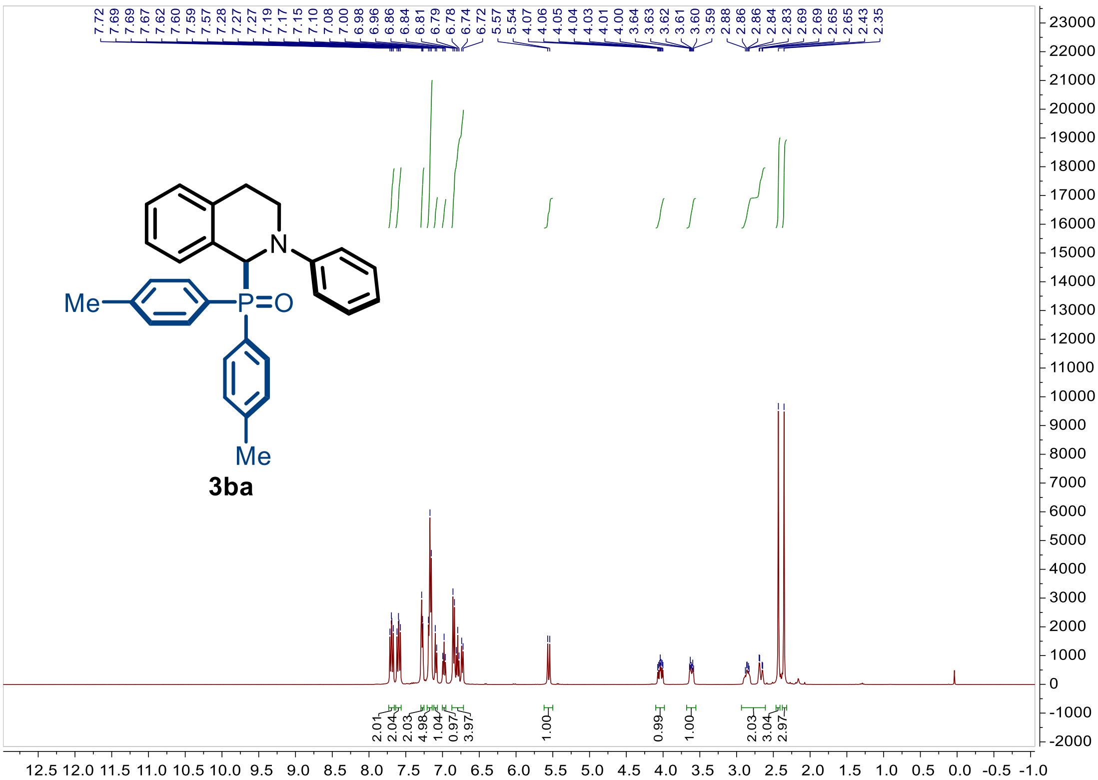
^{13}C NMR spectrum of 3ao



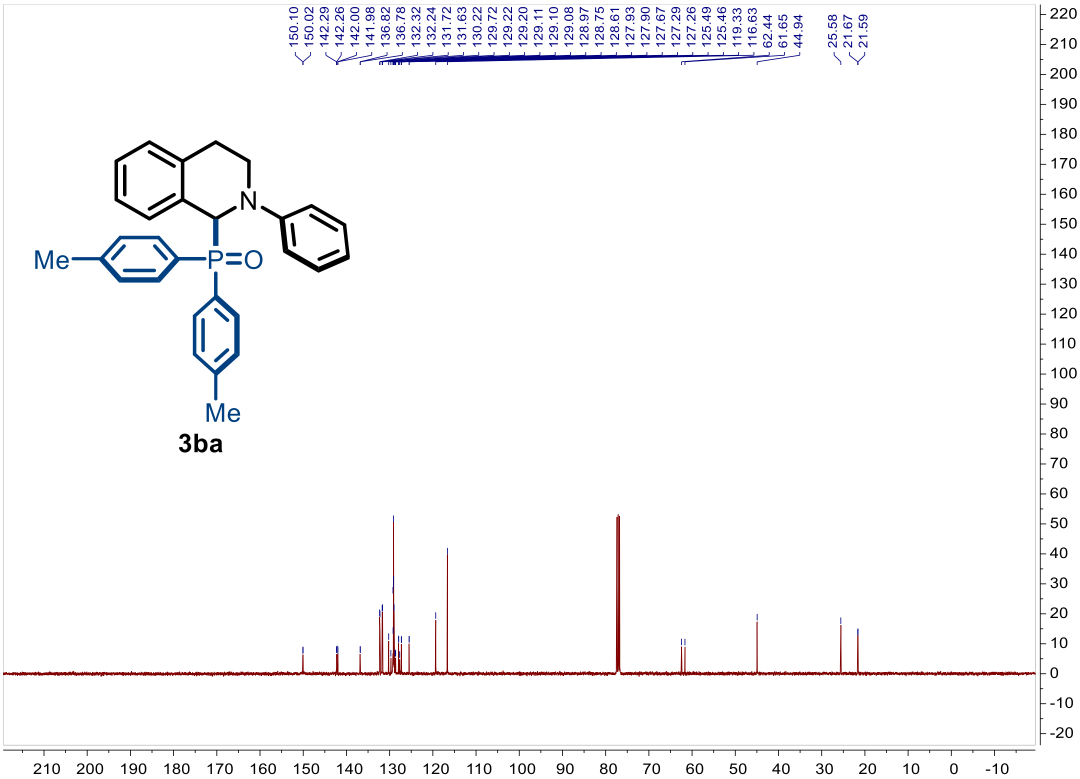
^{31}P NMR spectrum of 3ao



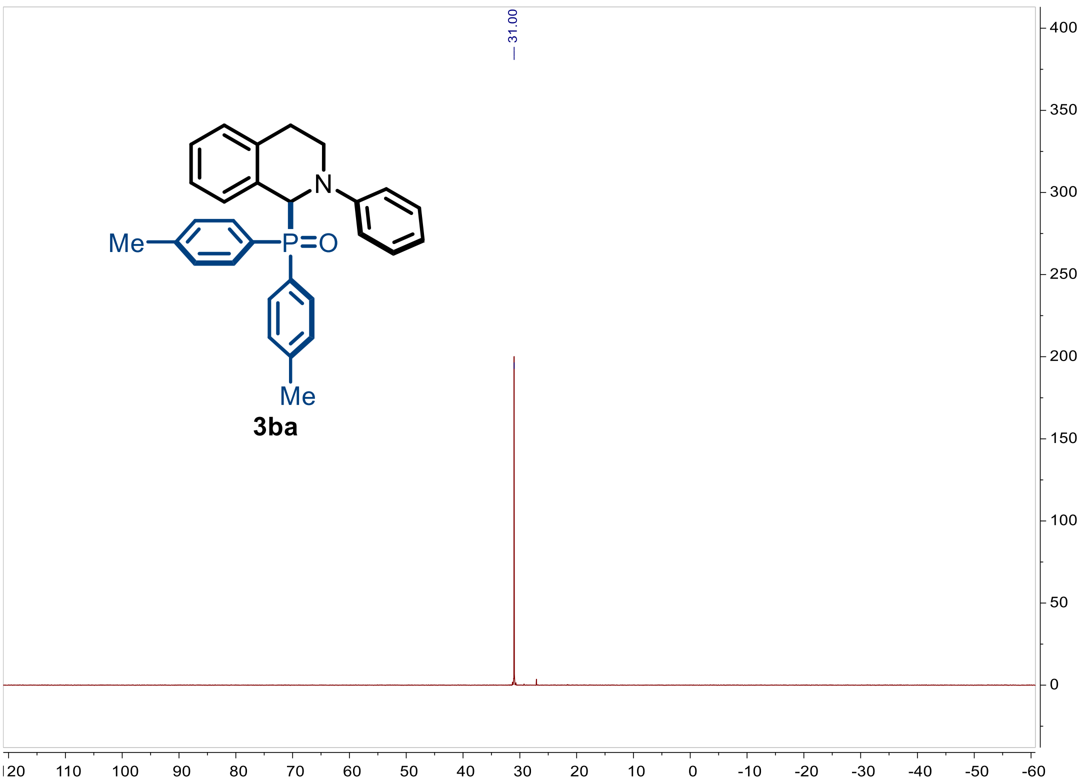
^{1}H NMR spectrum of 3ba



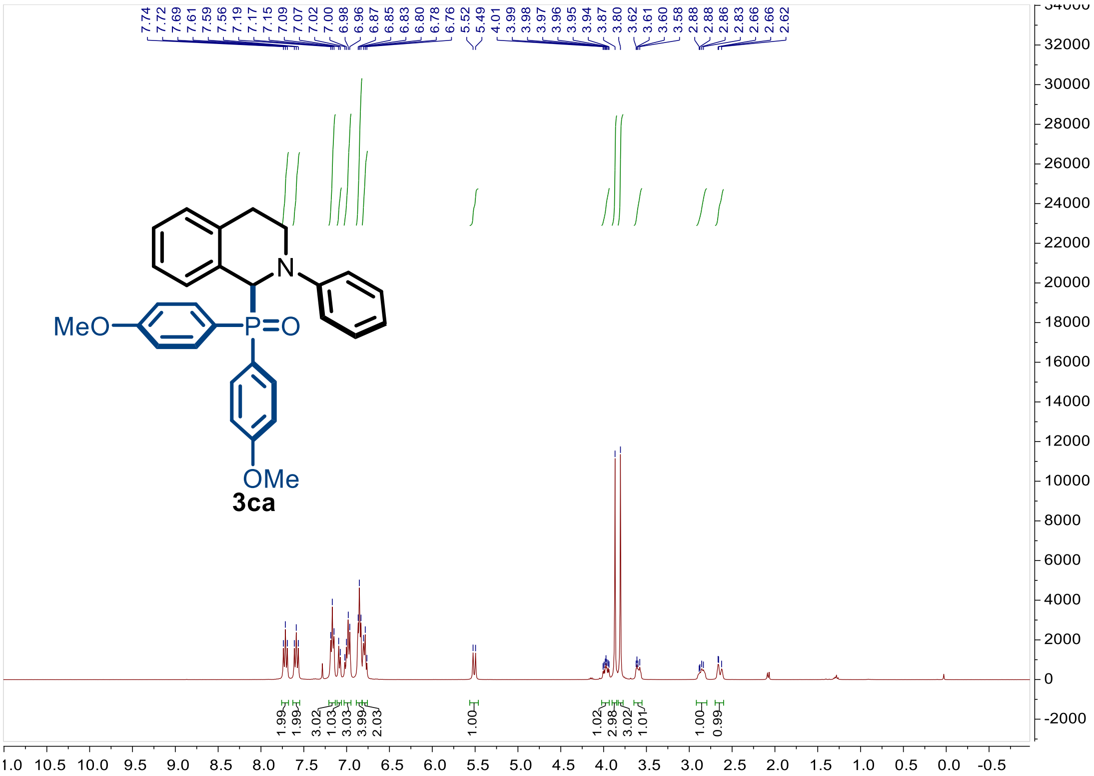
^{13}C NMR spectrum of 3ba



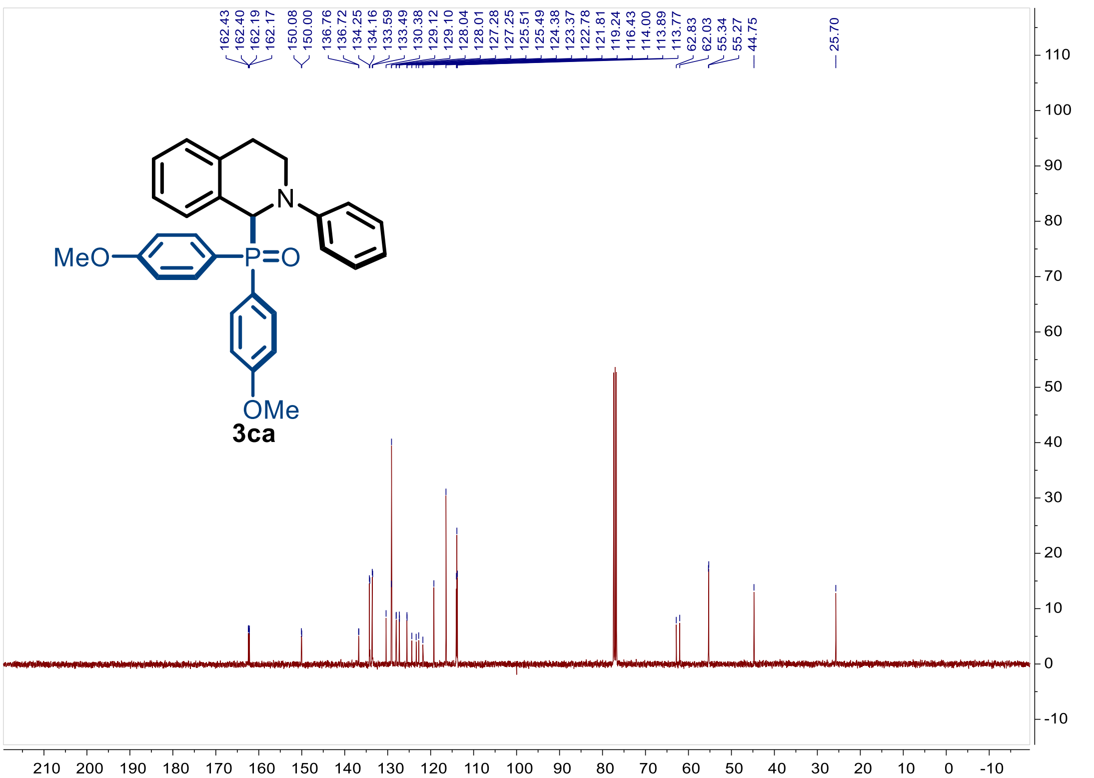
^{31}P NMR spectrum of 3ba



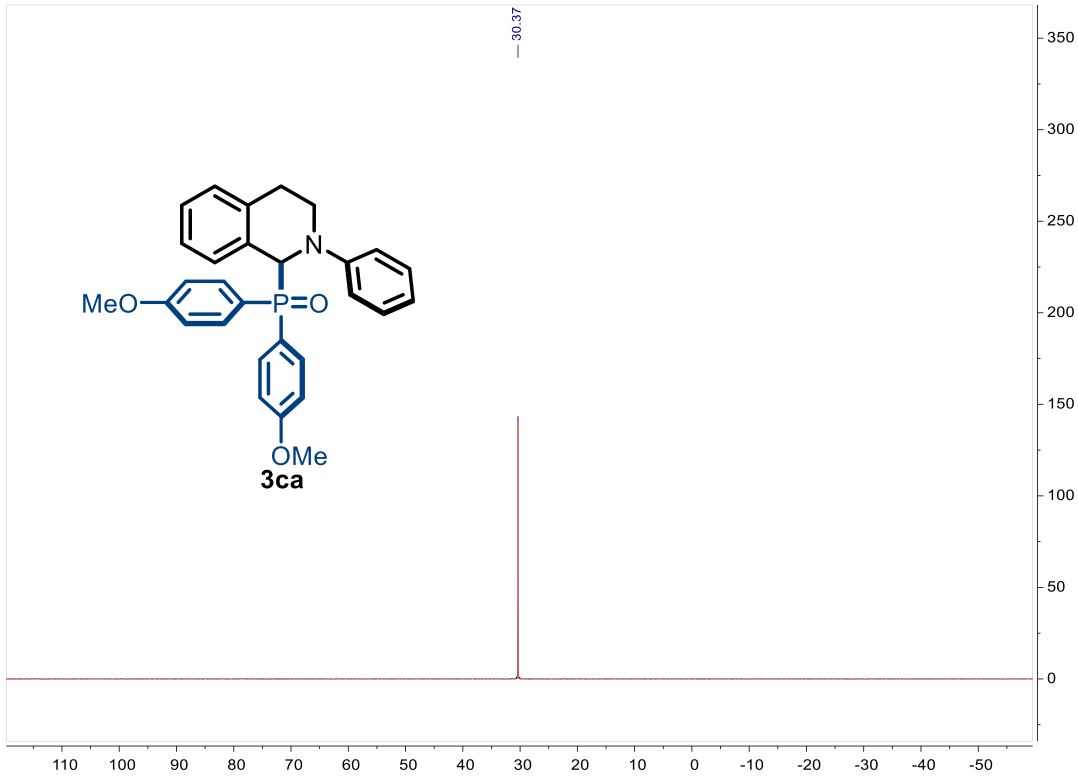
^{1}H NMR spectrum of 3ca



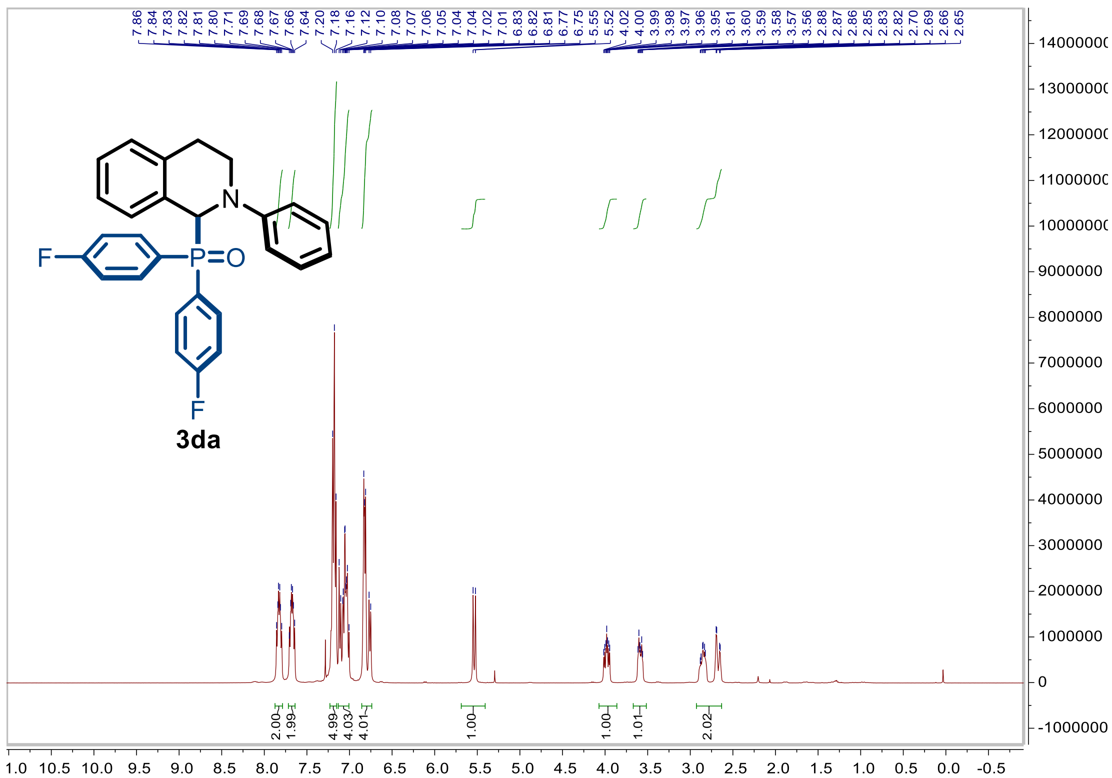
^{13}C NMR spectrum of 3ca



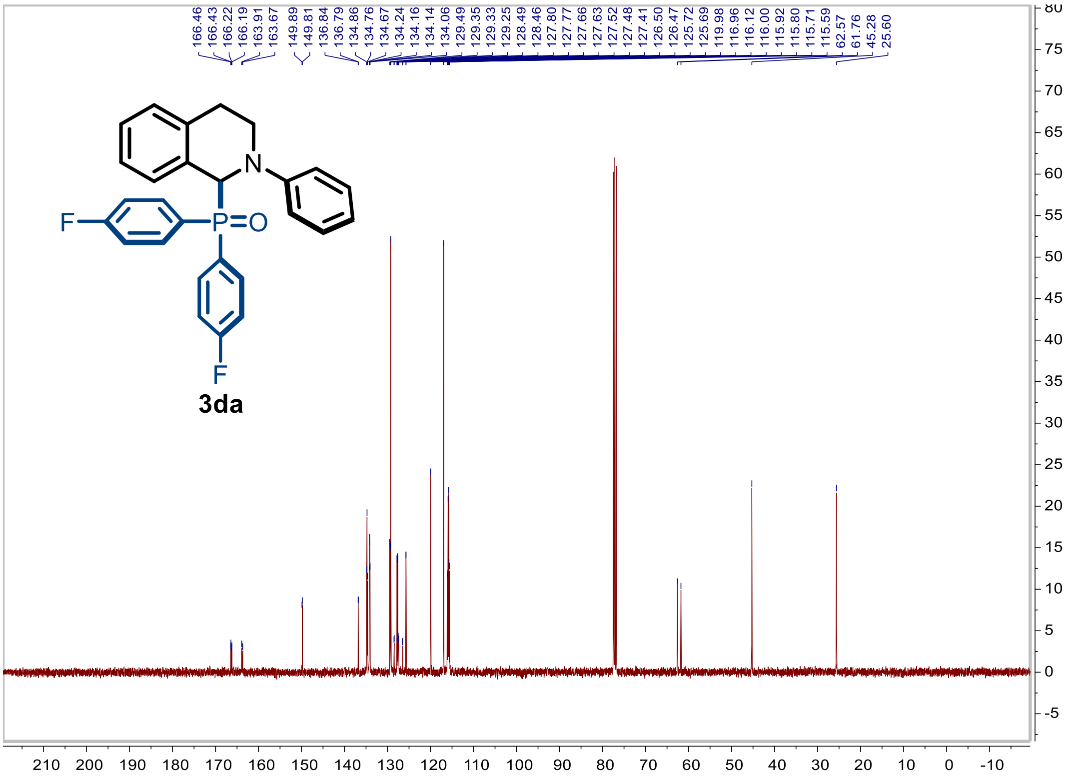
^{31}P NMR spectrum of 3ca



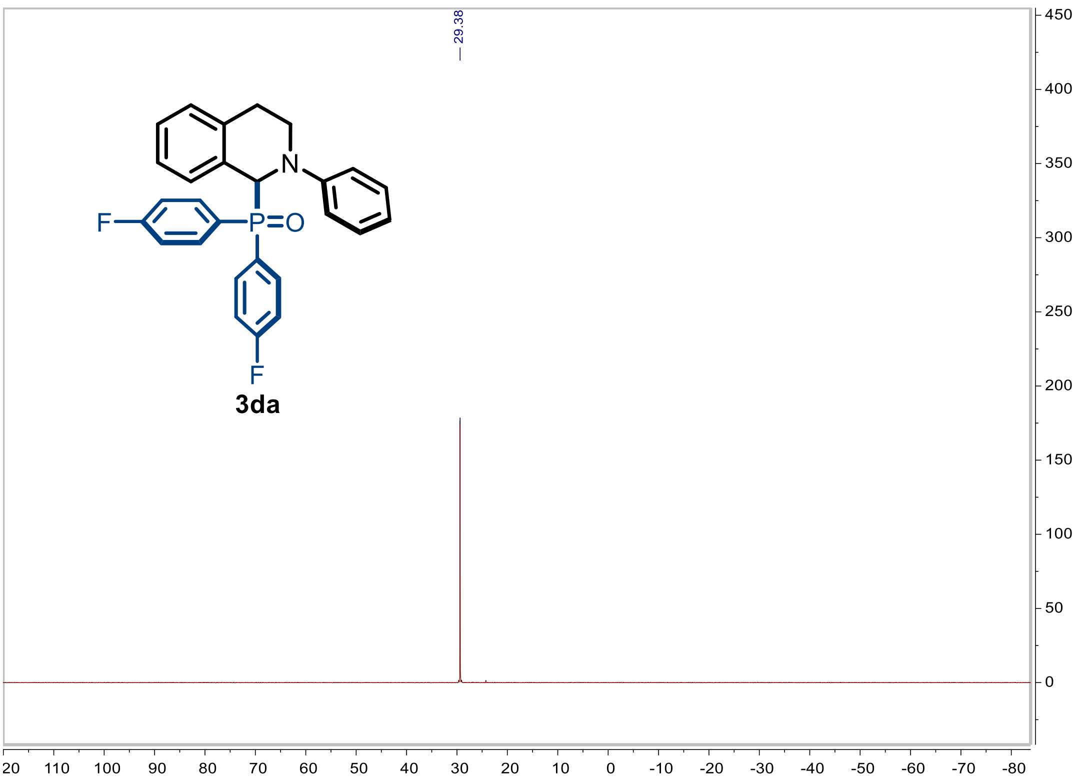
^{1}H NMR spectrum of 3da



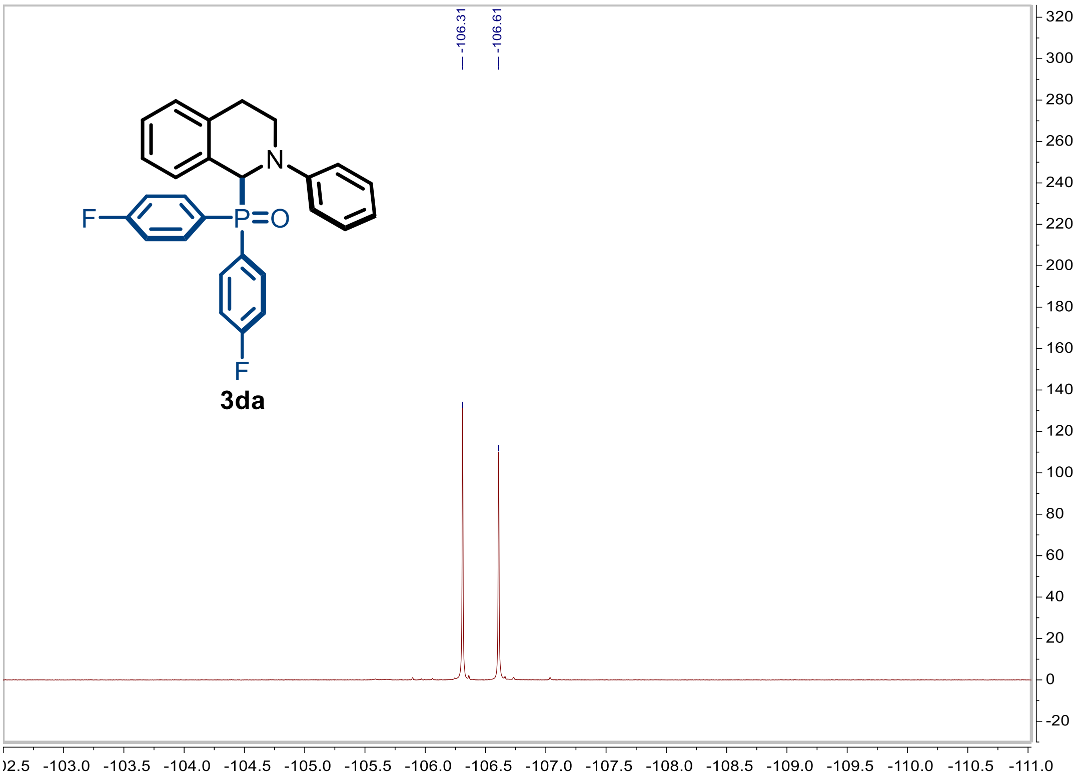
^{13}C NMR spectrum of 3da



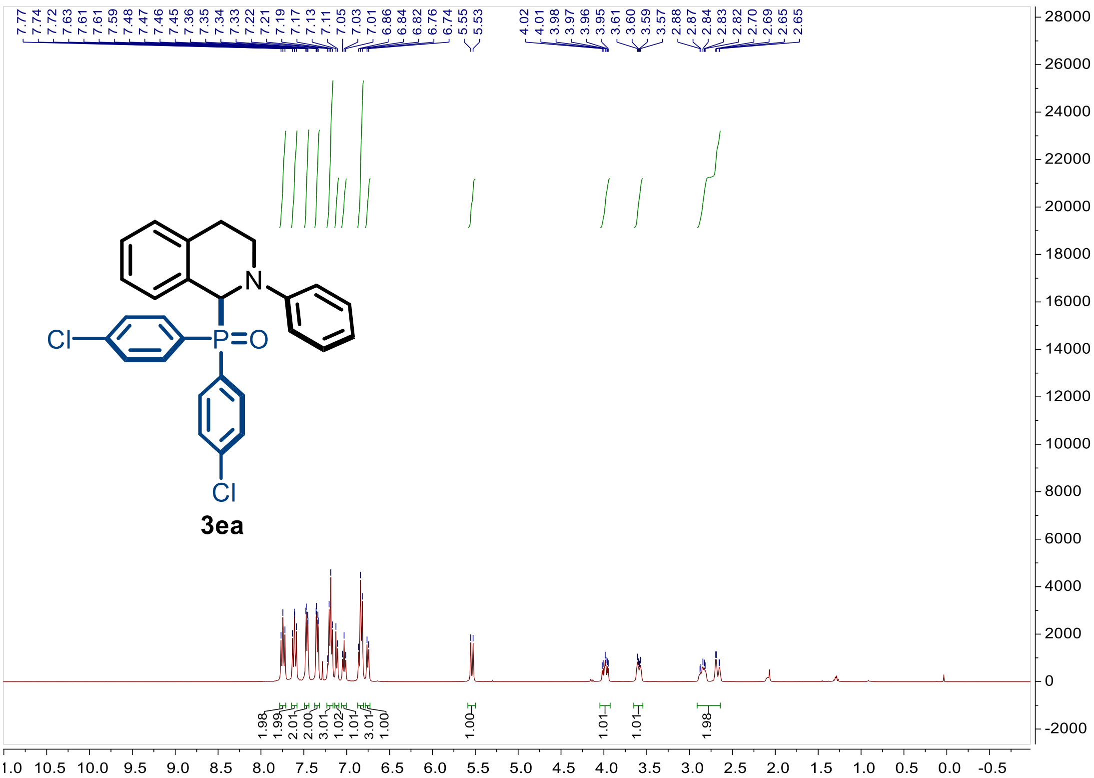
^{31}P NMR spectrum of 3da



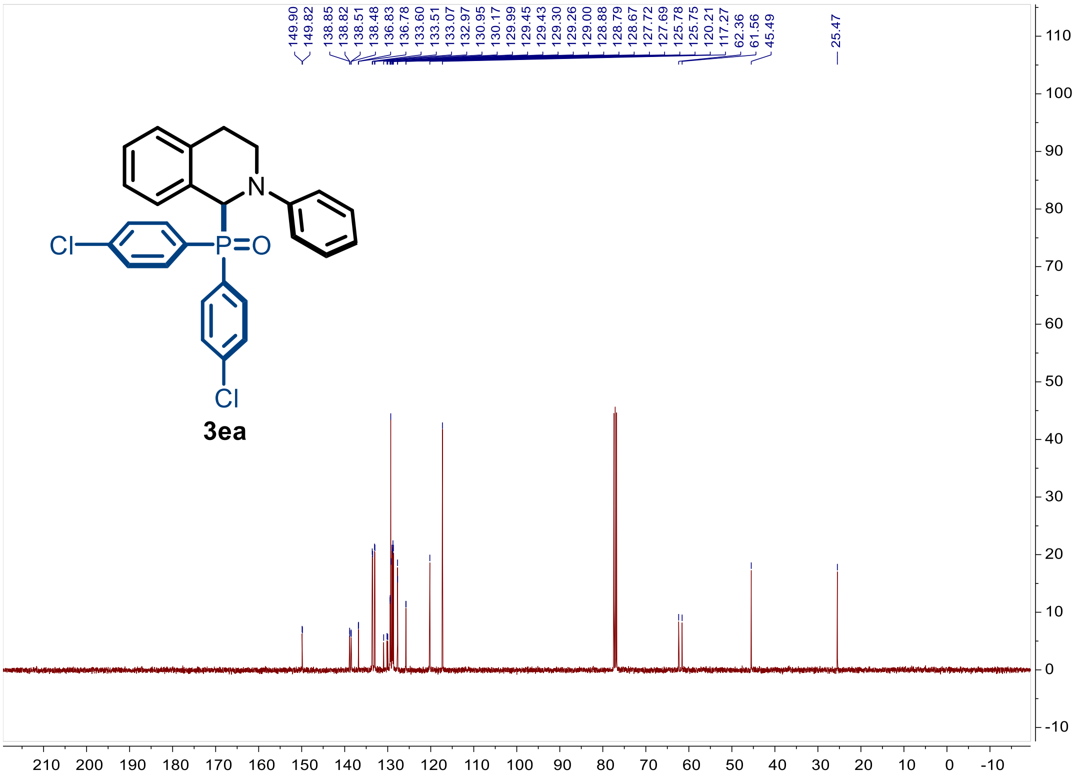
^{19}F NMR spectrum of 3da



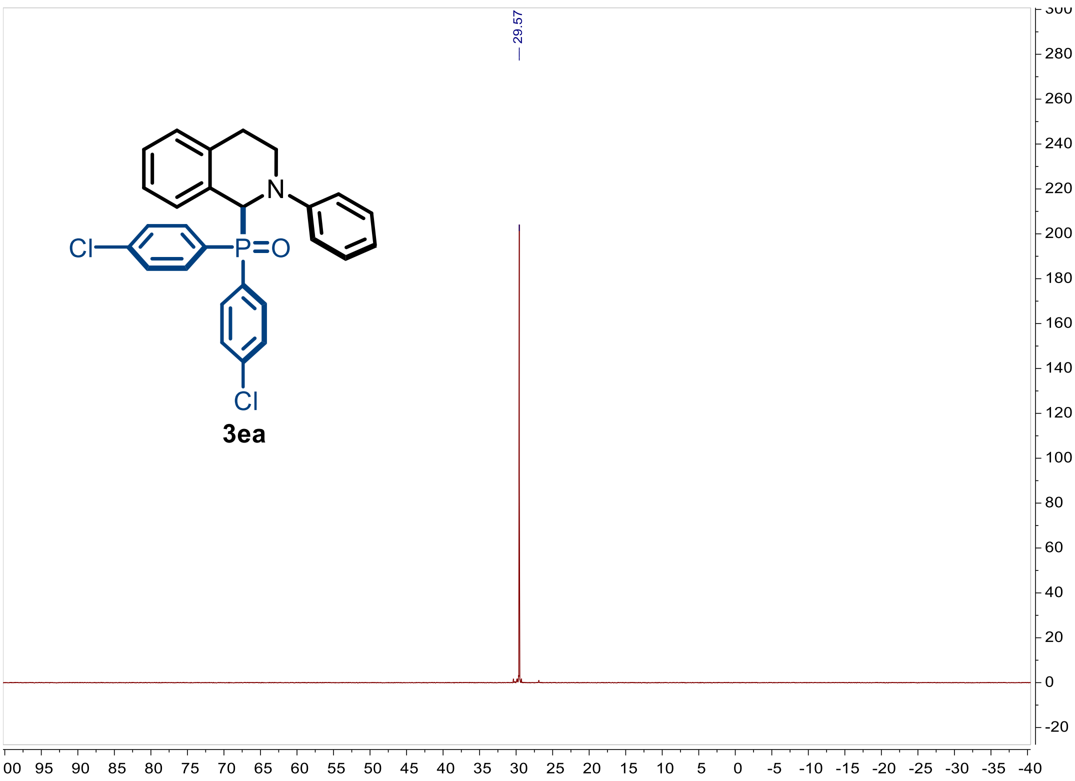
^{1}H NMR spectrum of 3ea



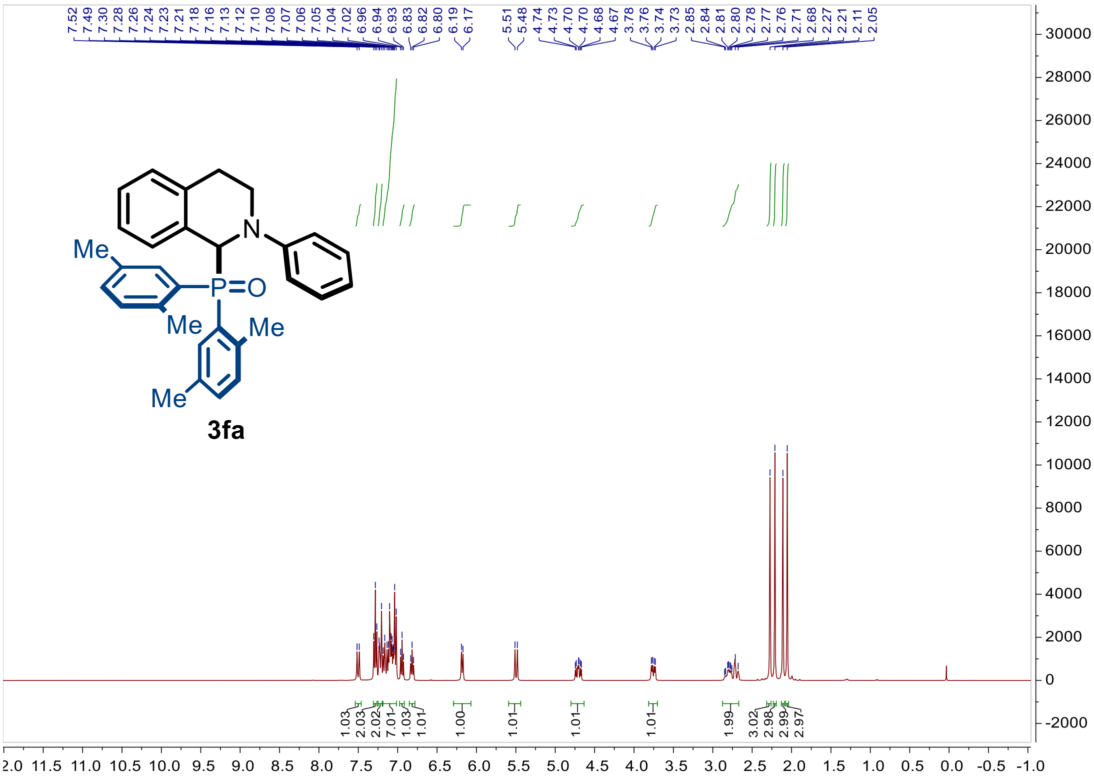
^{13}C NMR spectrum of 3ea



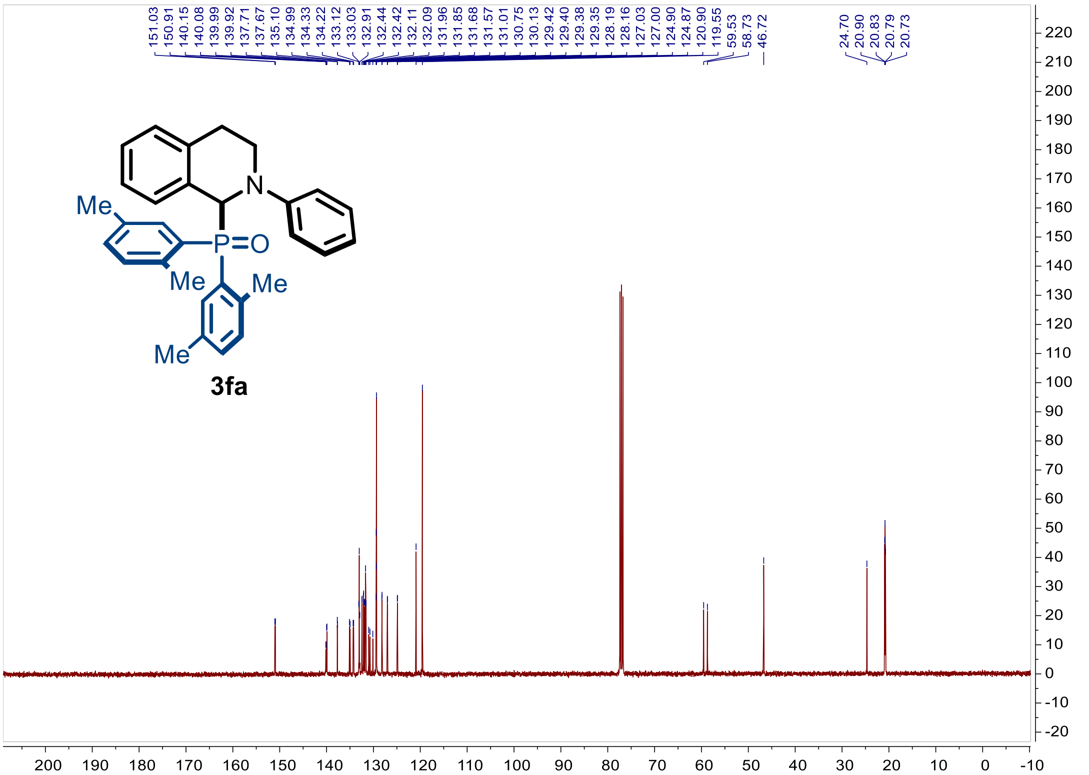
^{31}P NMR spectrum of 3ea



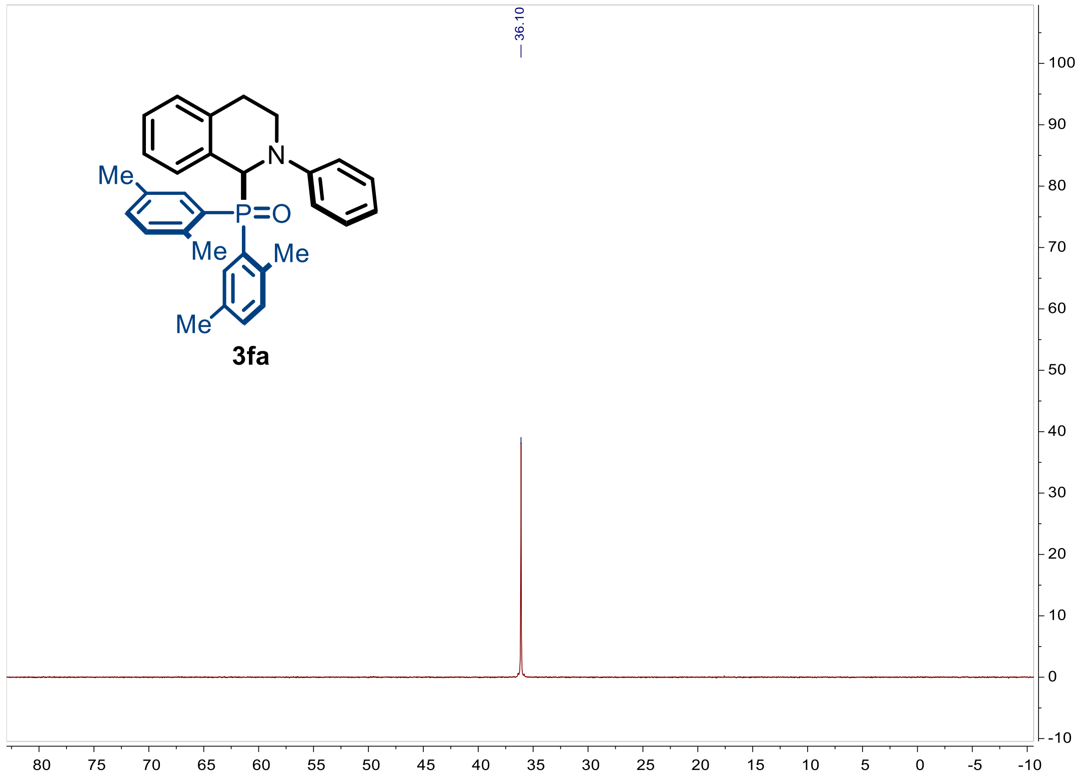
[1]H NMR spectrum of 3fa



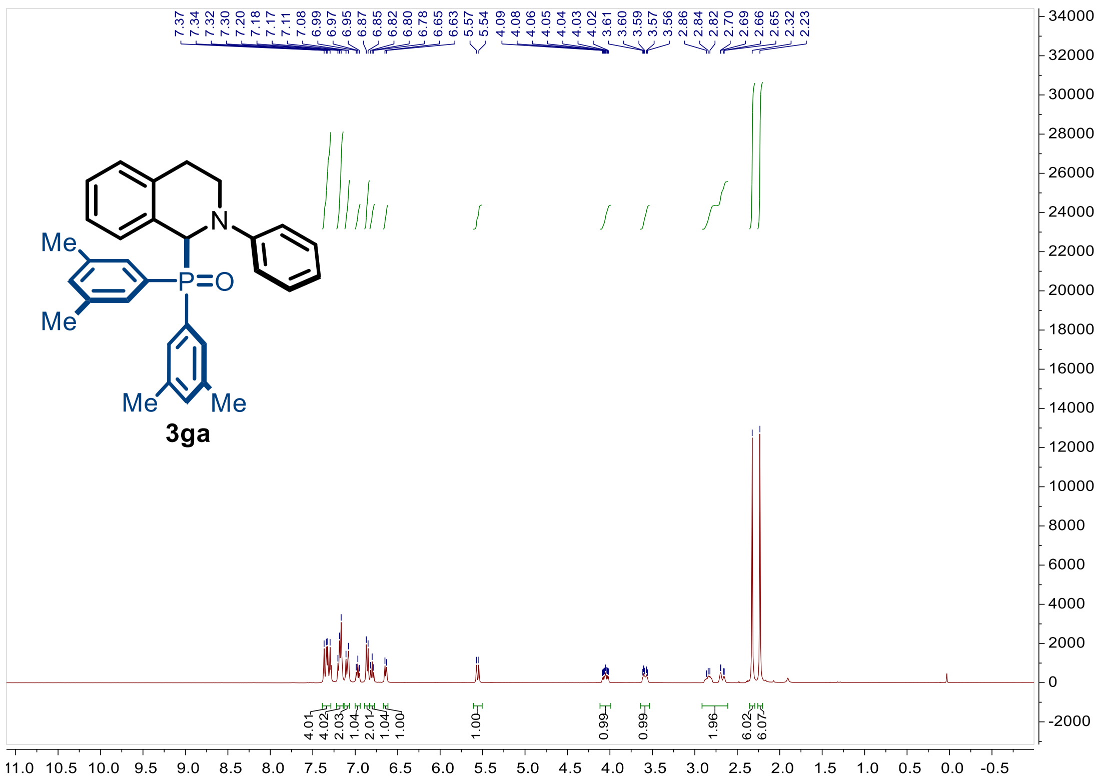
[13]C NMR spectrum of 3fa



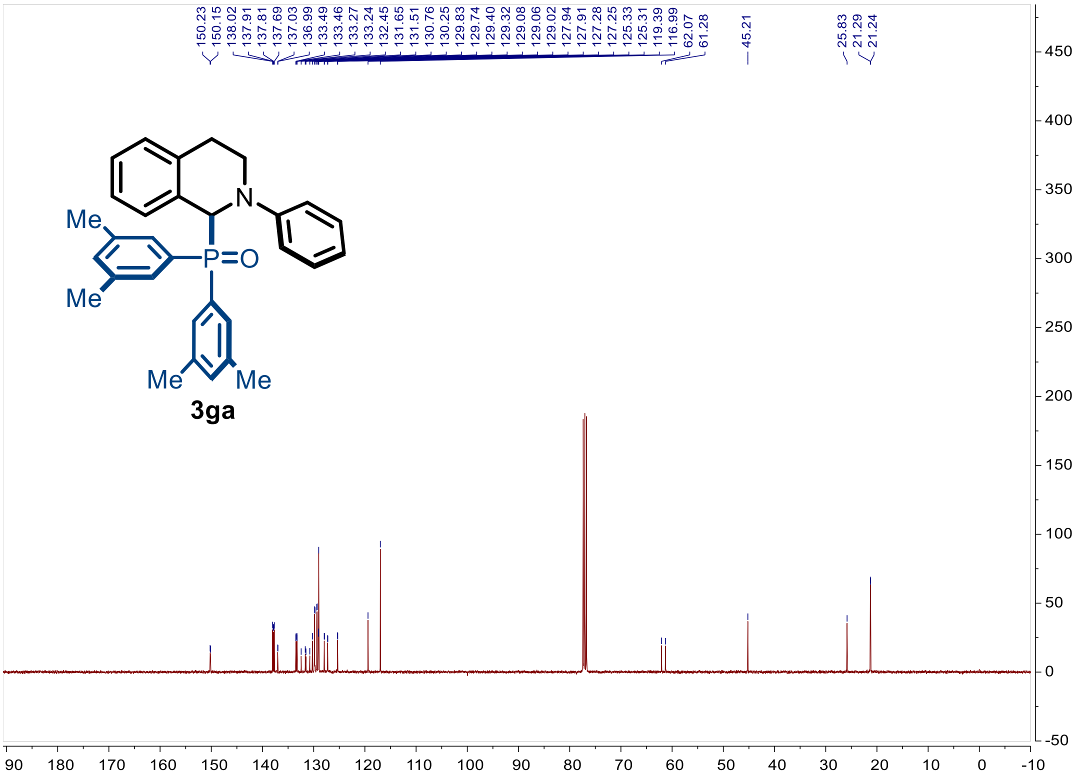
^{31}P NMR spectrum of 3fa



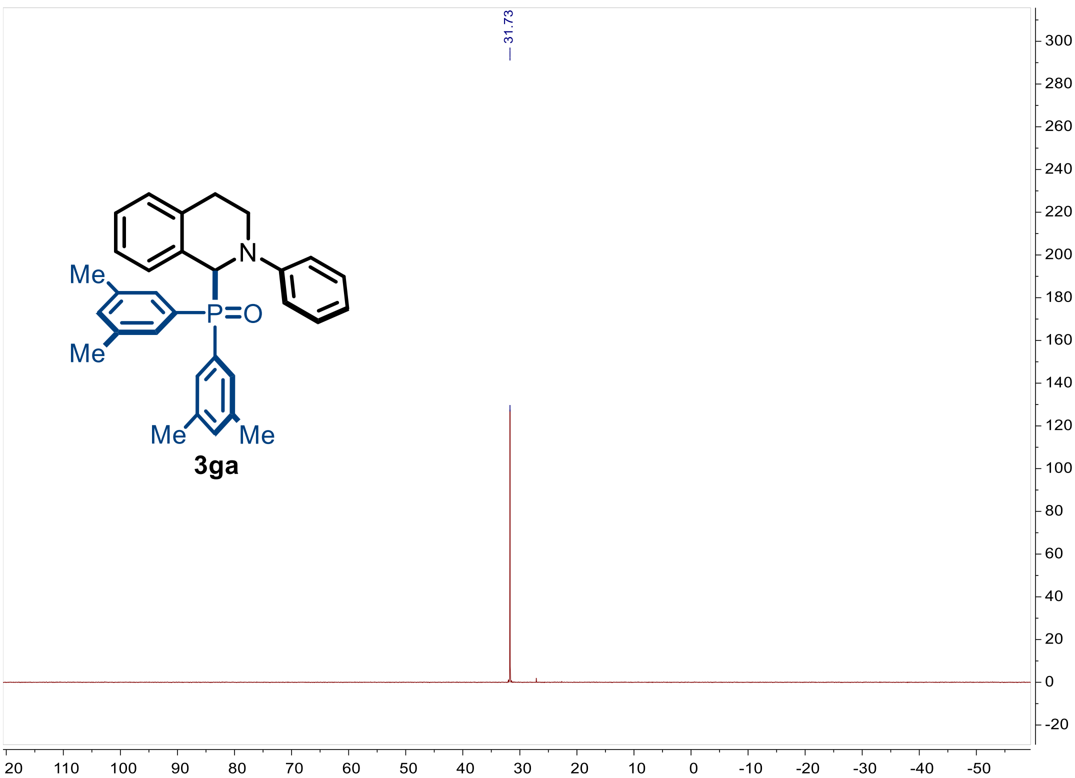
^{1}H NMR spectrum of 3ga



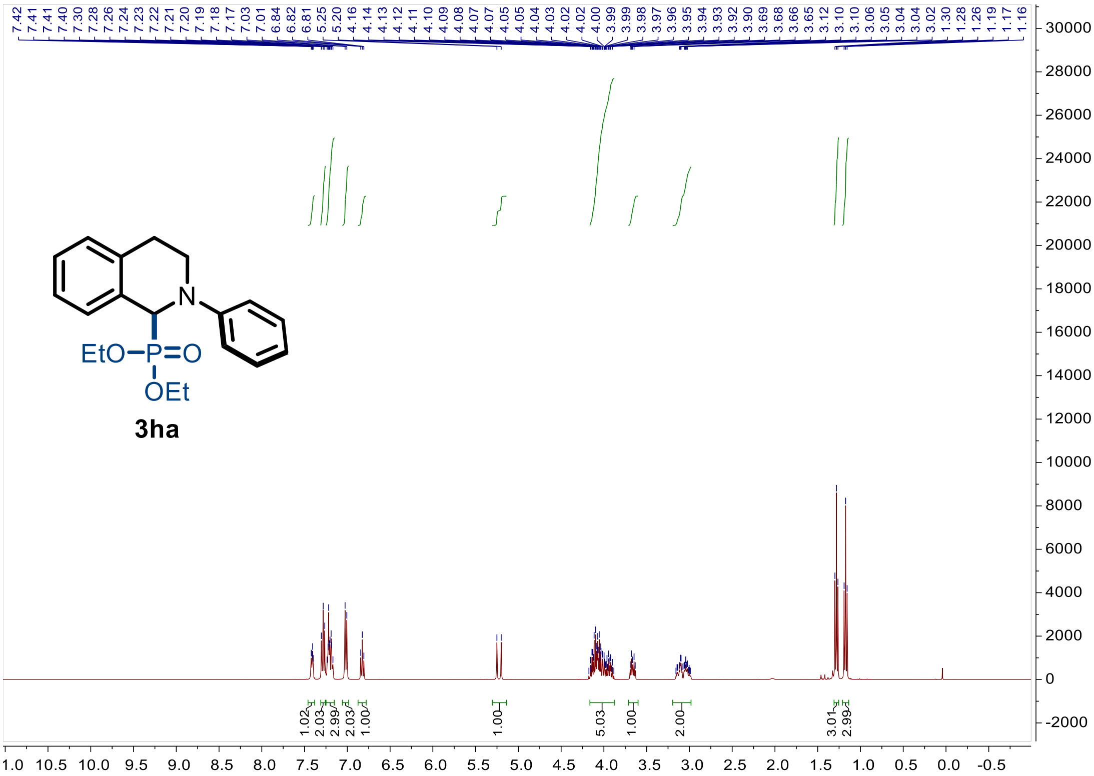
^{13}C NMR spectrum of 3ga



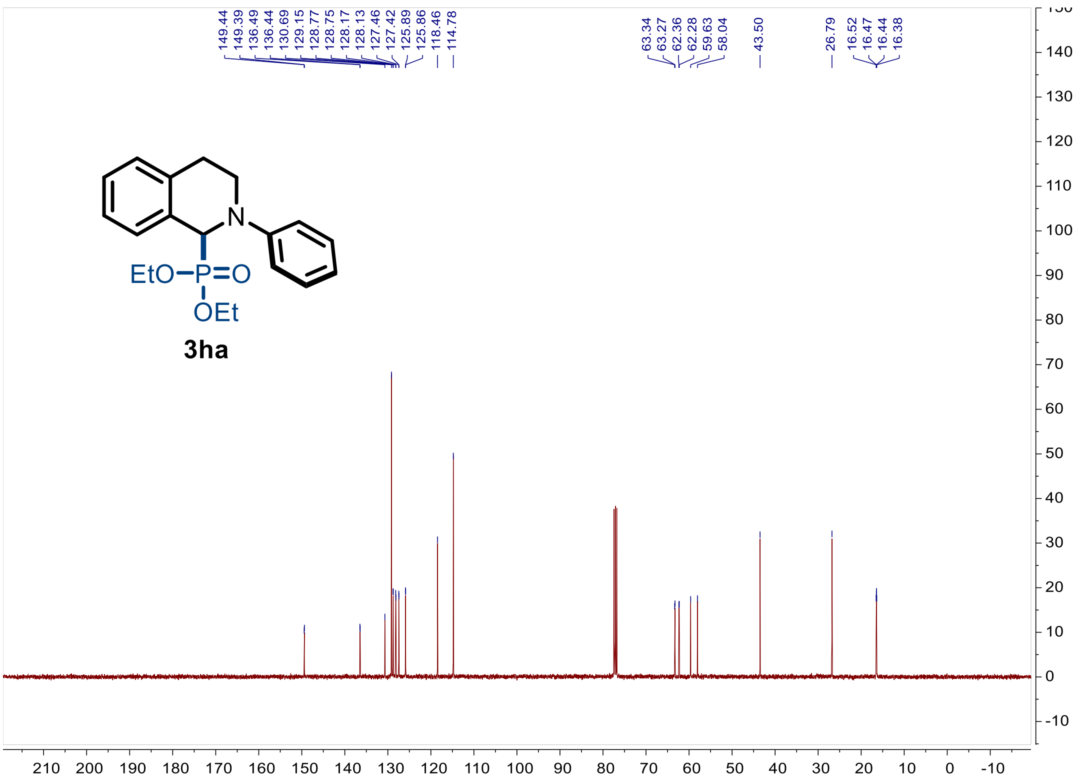
^{31}P NMR spectrum of 3ga



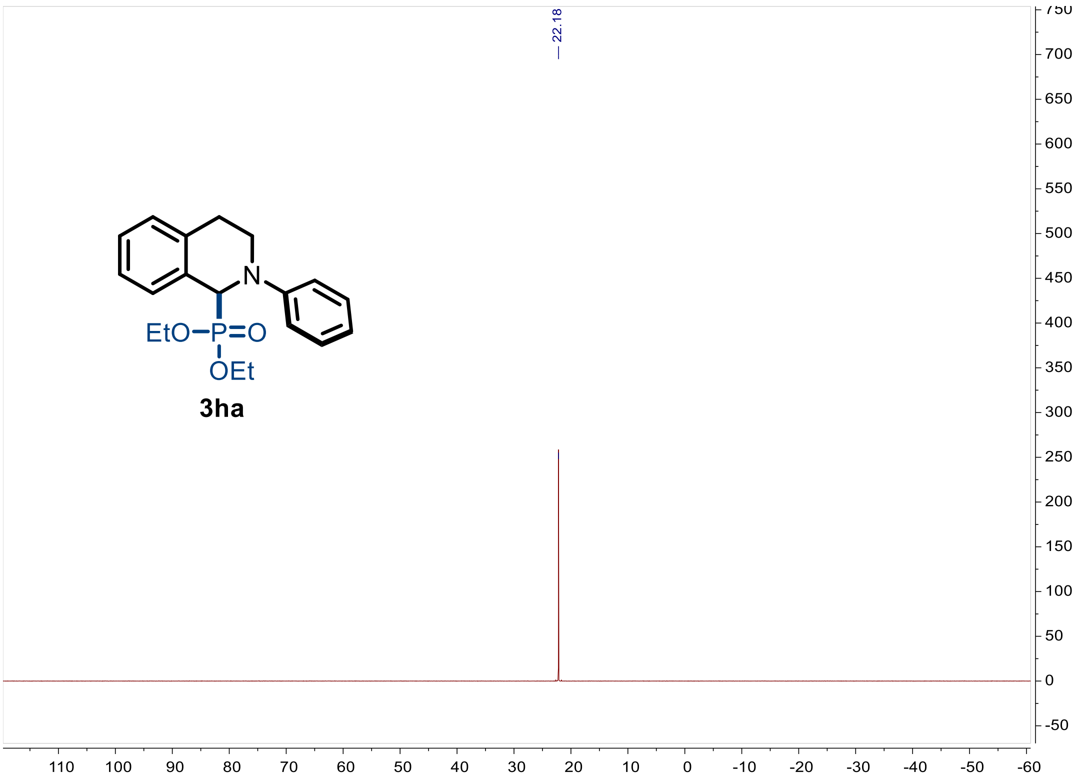
^{1}H NMR spectrum of 3ha



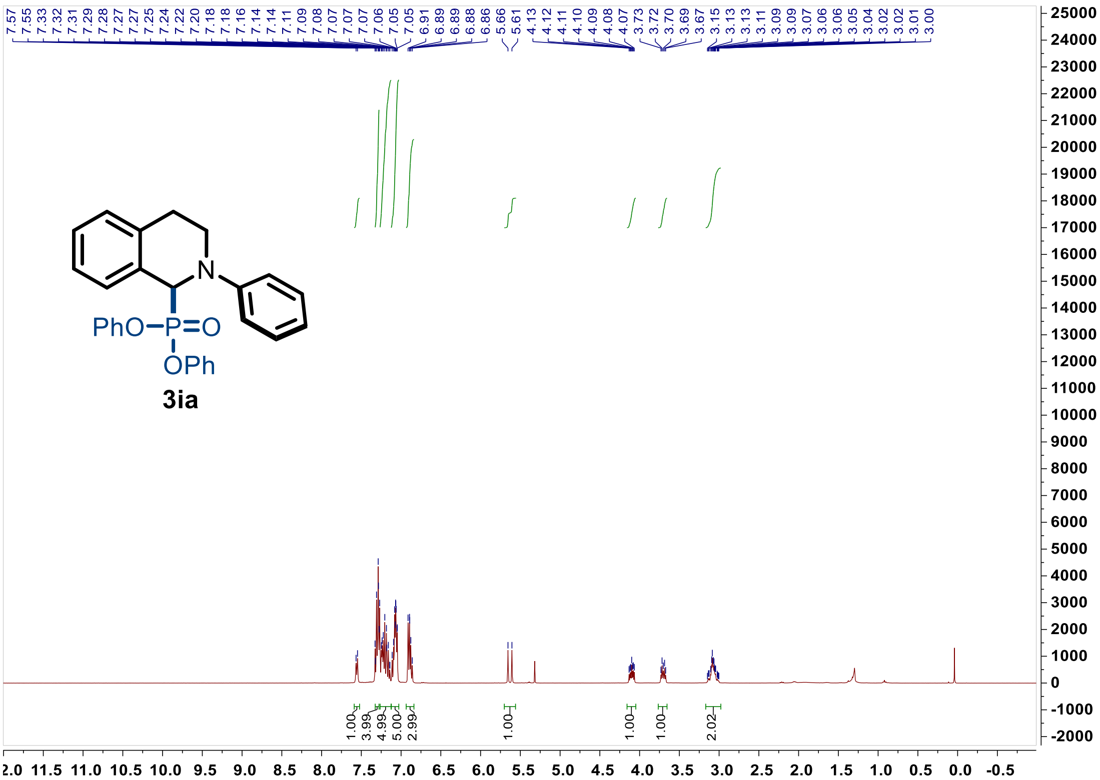
^{13}C NMR spectrum of 3ha



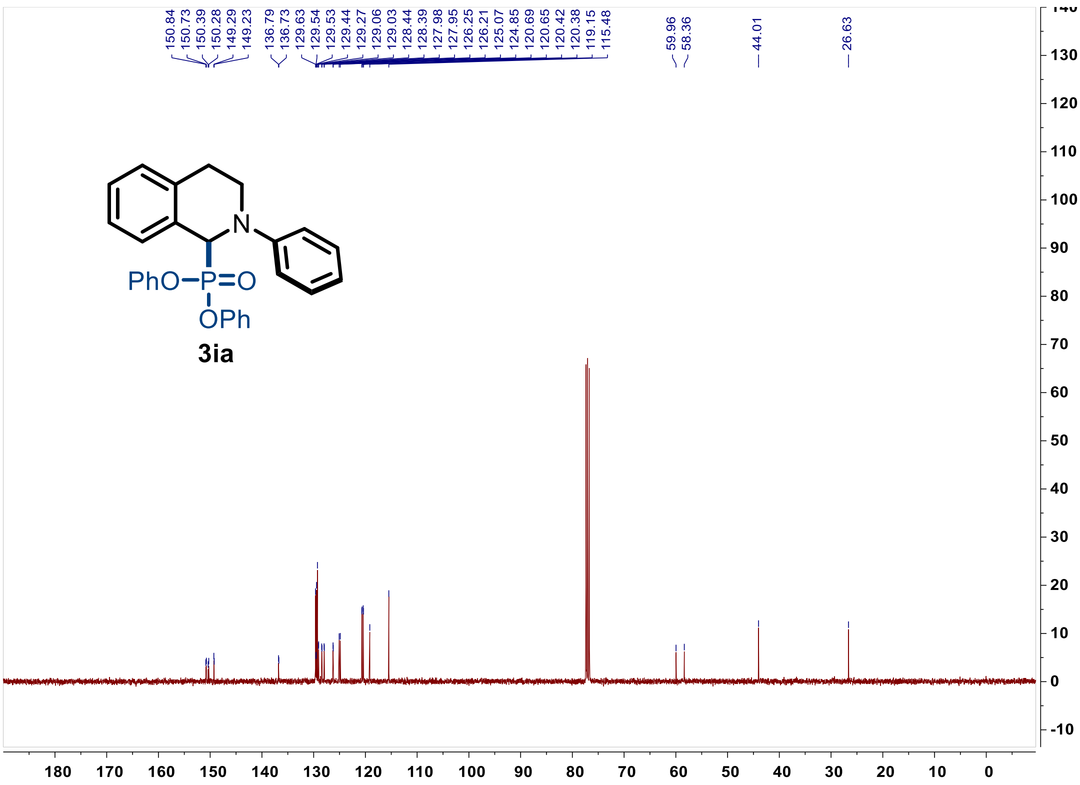
[31]P NMR spectrum of 3ha



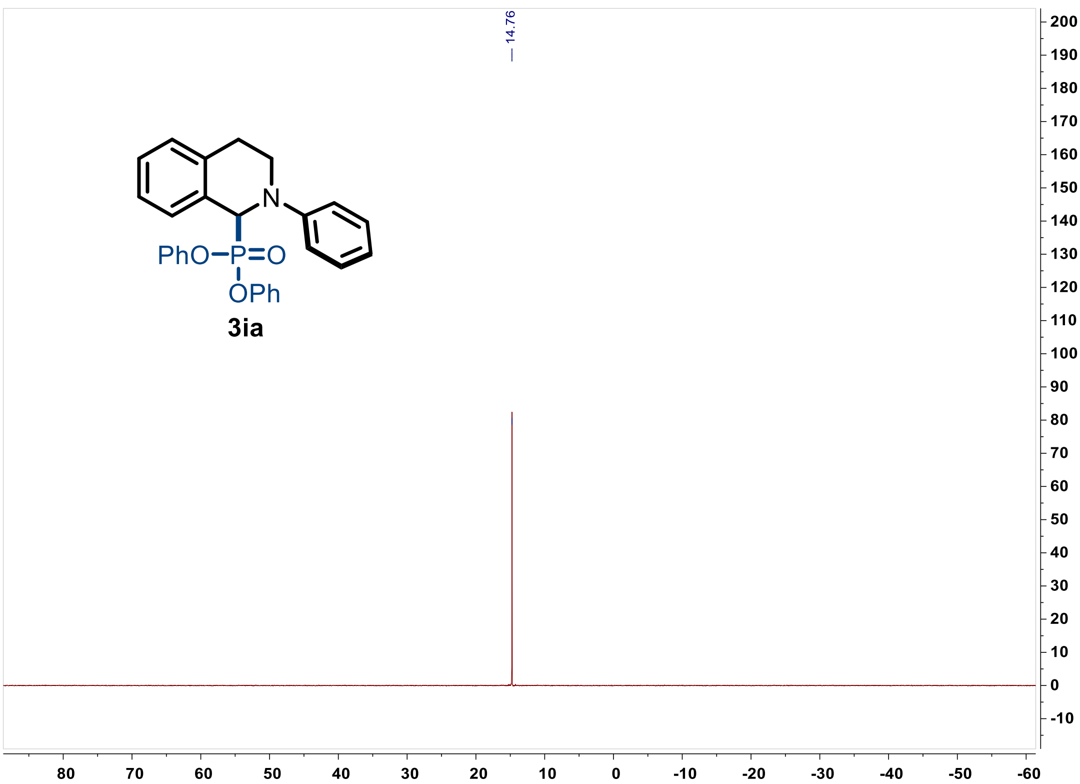
[1]H NMR spectrum of 3ia



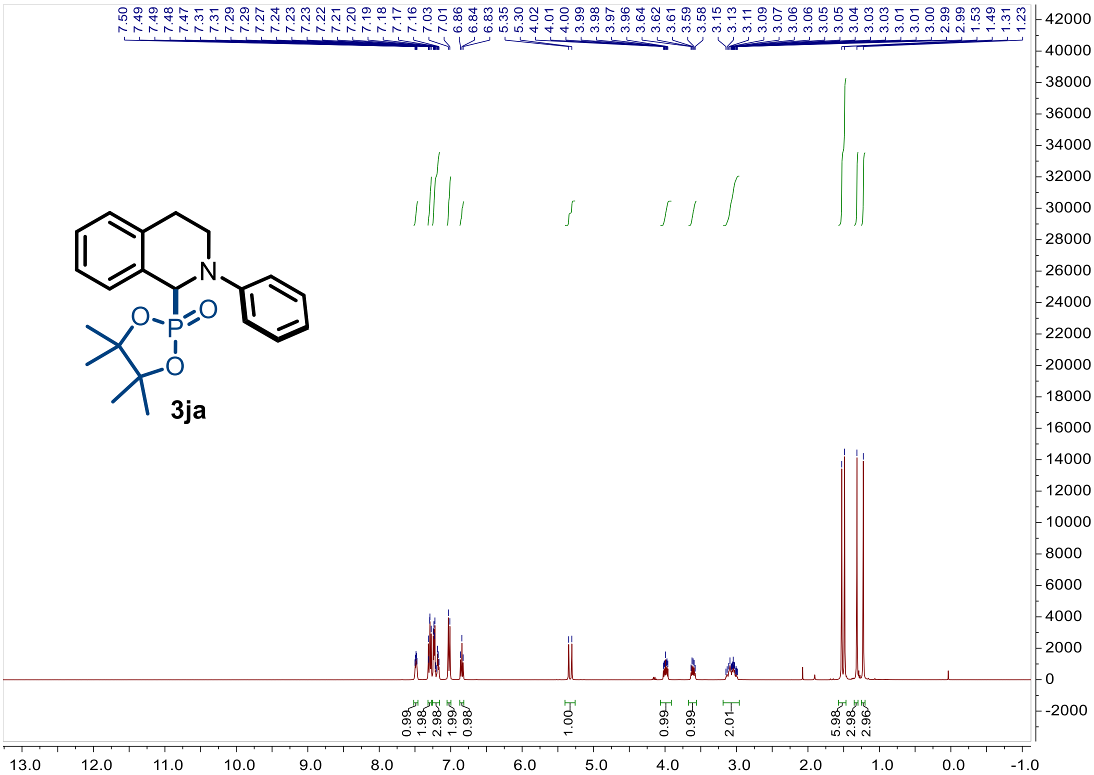
[13]C NMR spectrum of 3ia



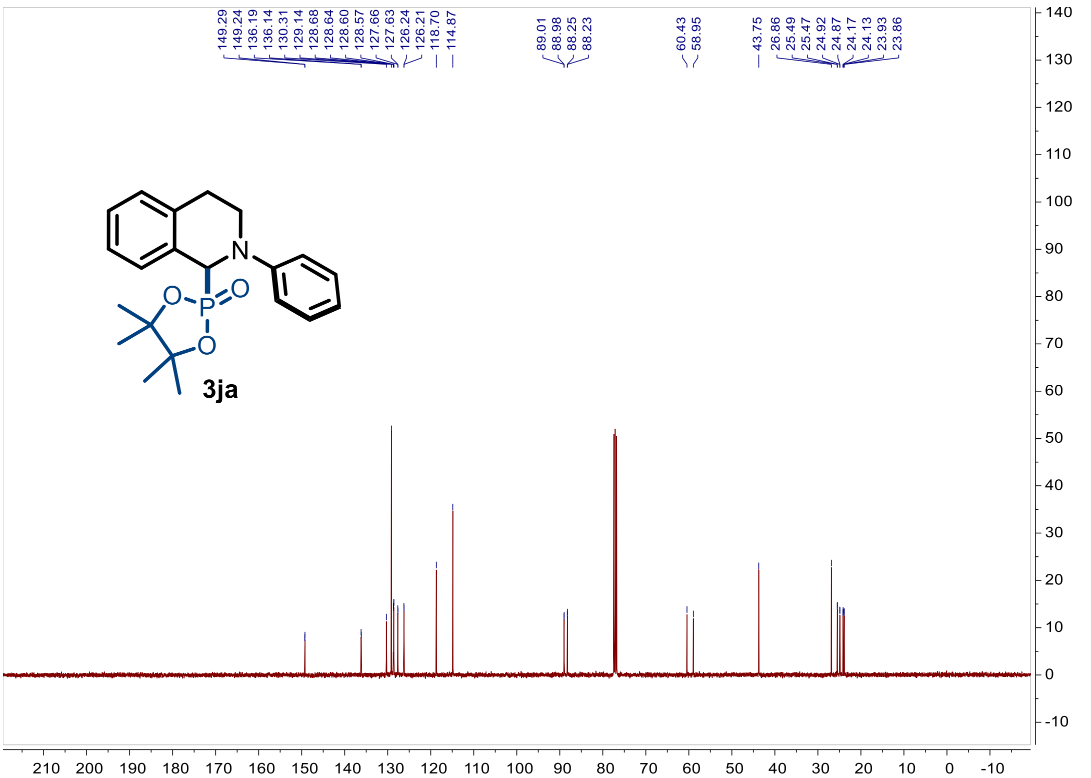
[31]P NMR spectrum of 3ia



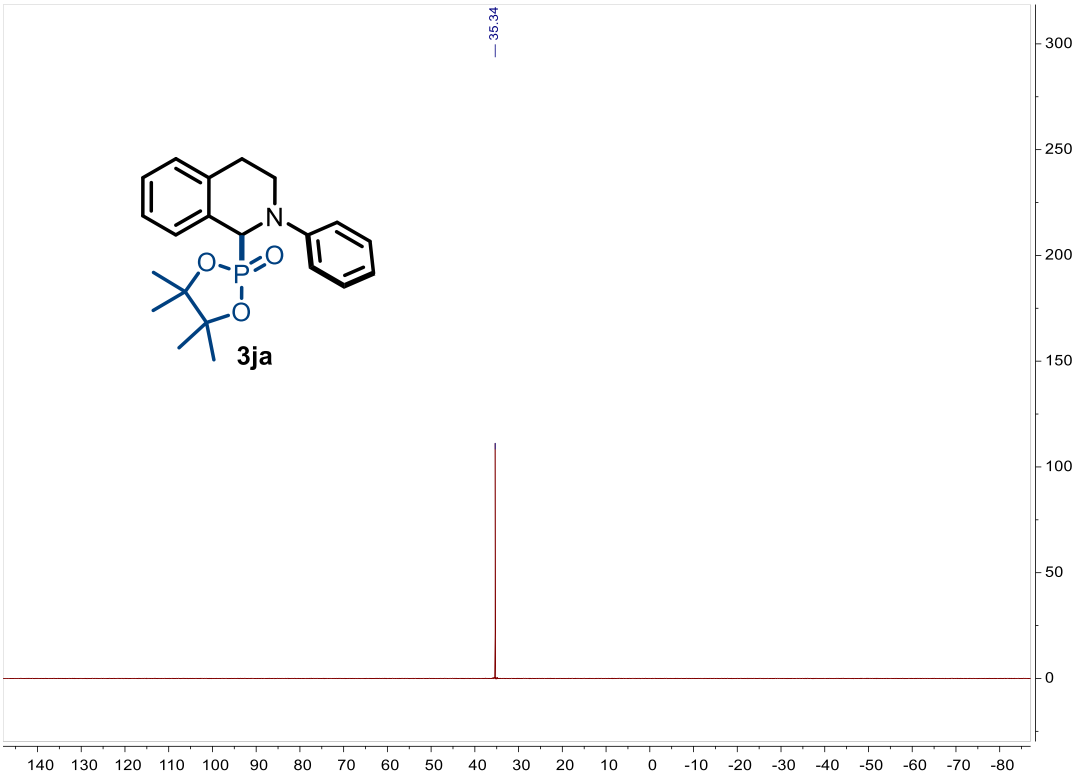
^{1}H NMR spectrum of 3ja



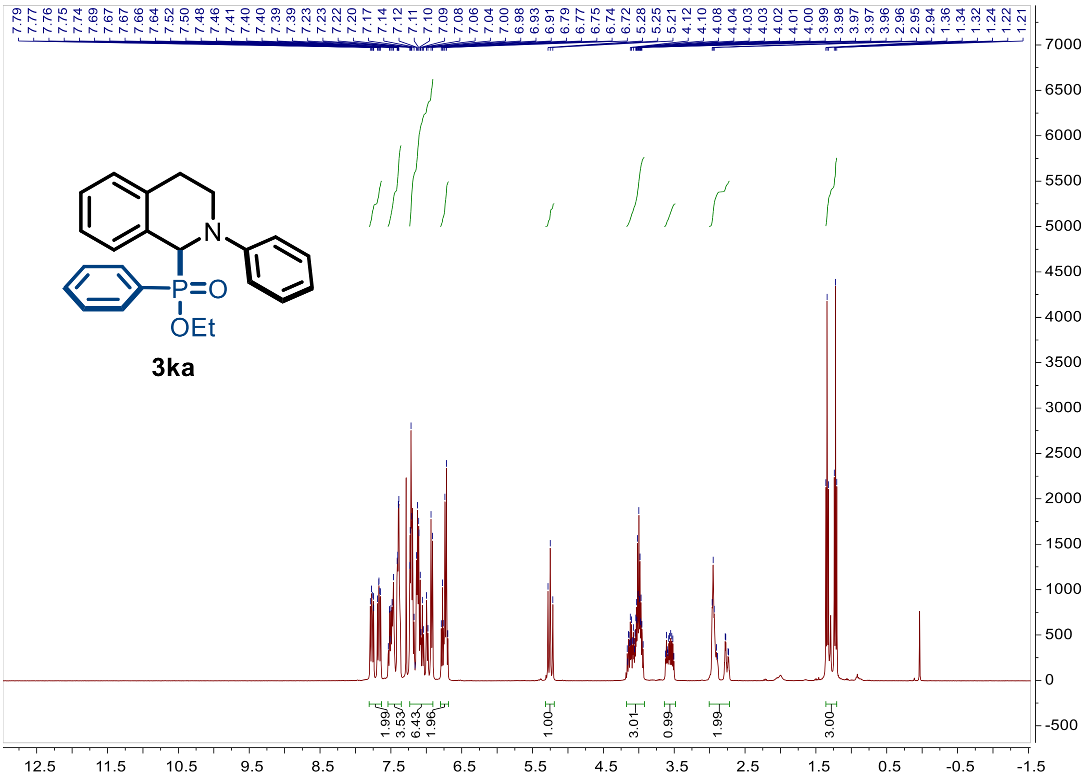
^{13}C NMR spectrum of 3ja



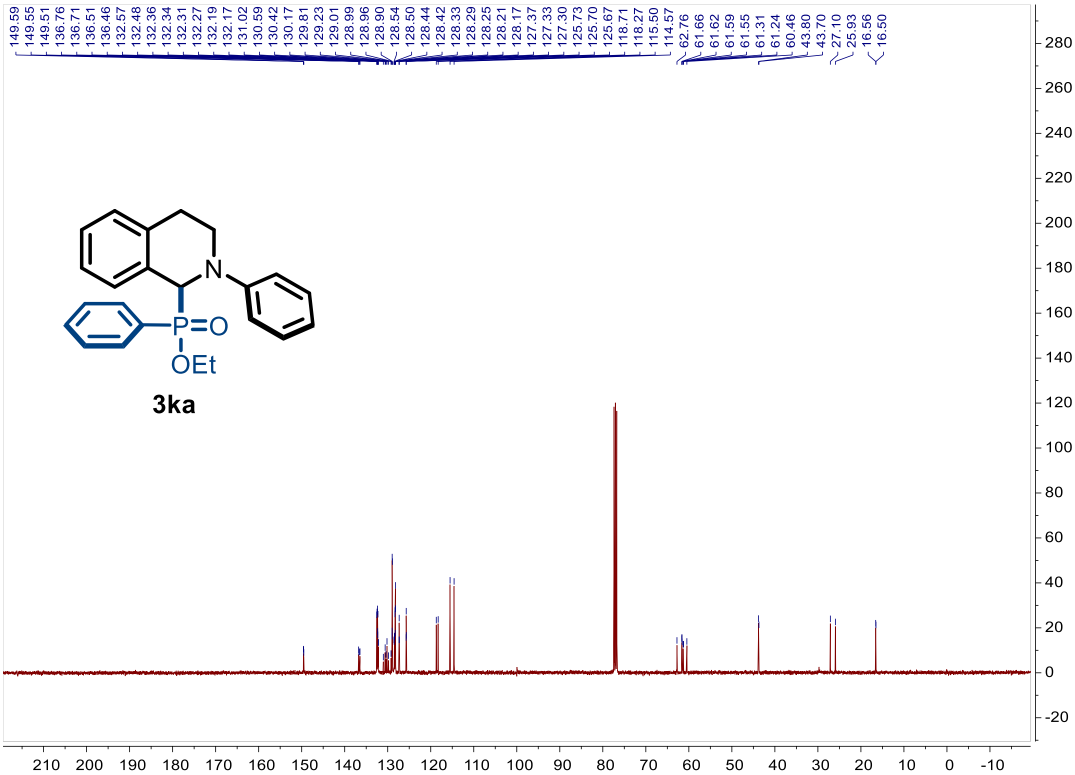
^{31}P NMR spectrum of 3ja



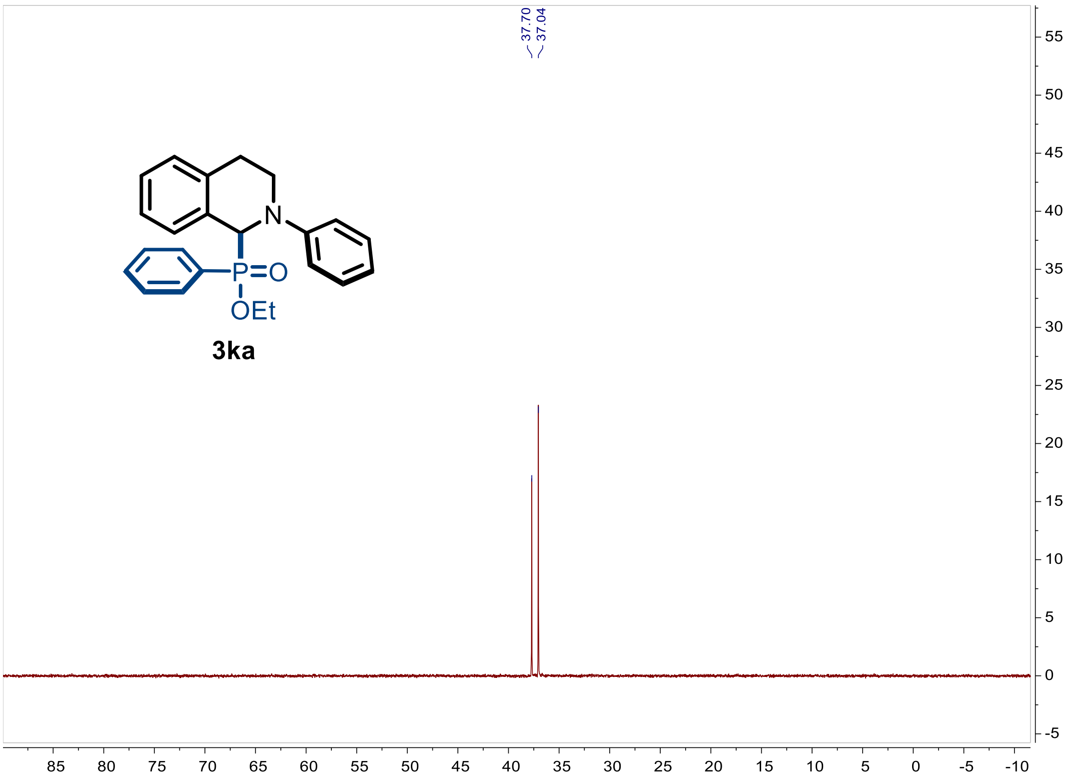
^{1}H NMR spectrum of 3ka



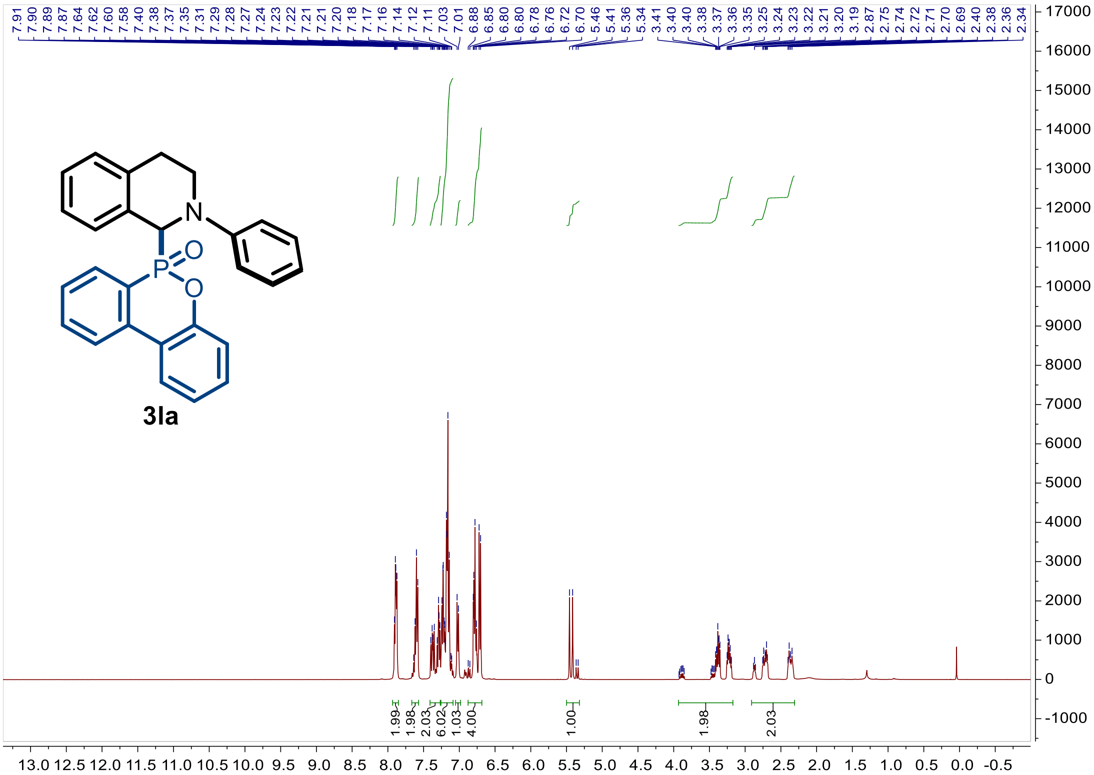
^{13}C NMR spectrum of 3ka



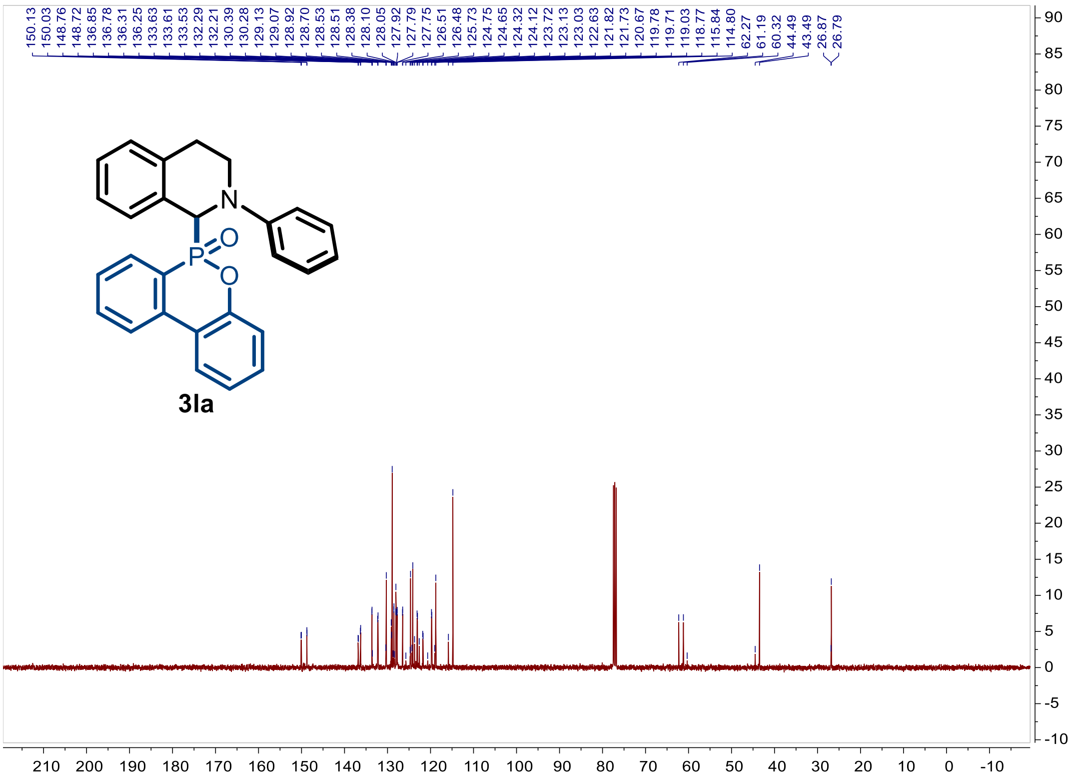
^{31}P NMR spectrum of 3ka



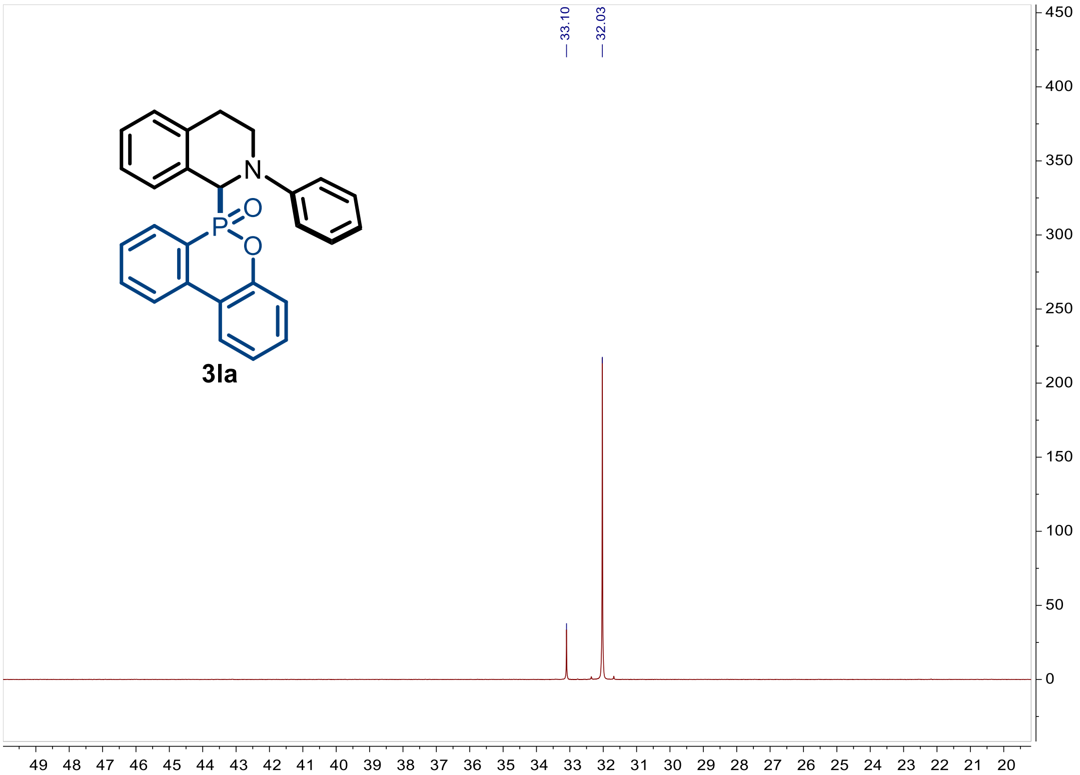
^{1}H NMR spectrum of 3la



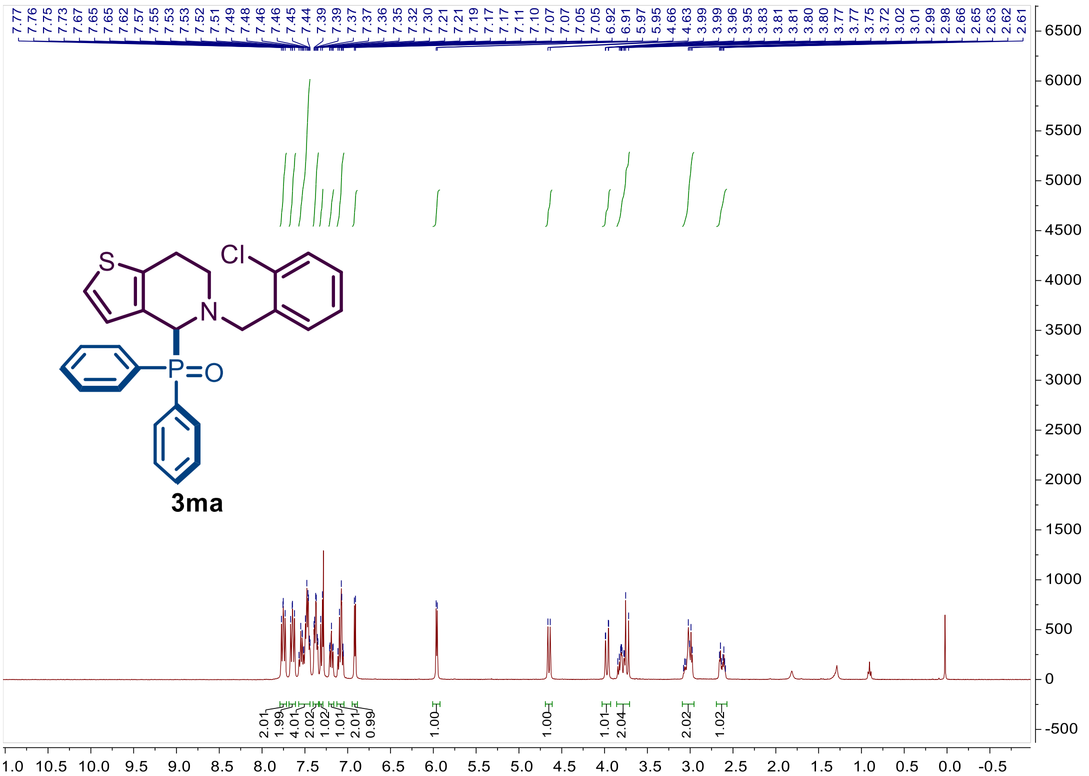
^{13}C NMR spectrum of 3la



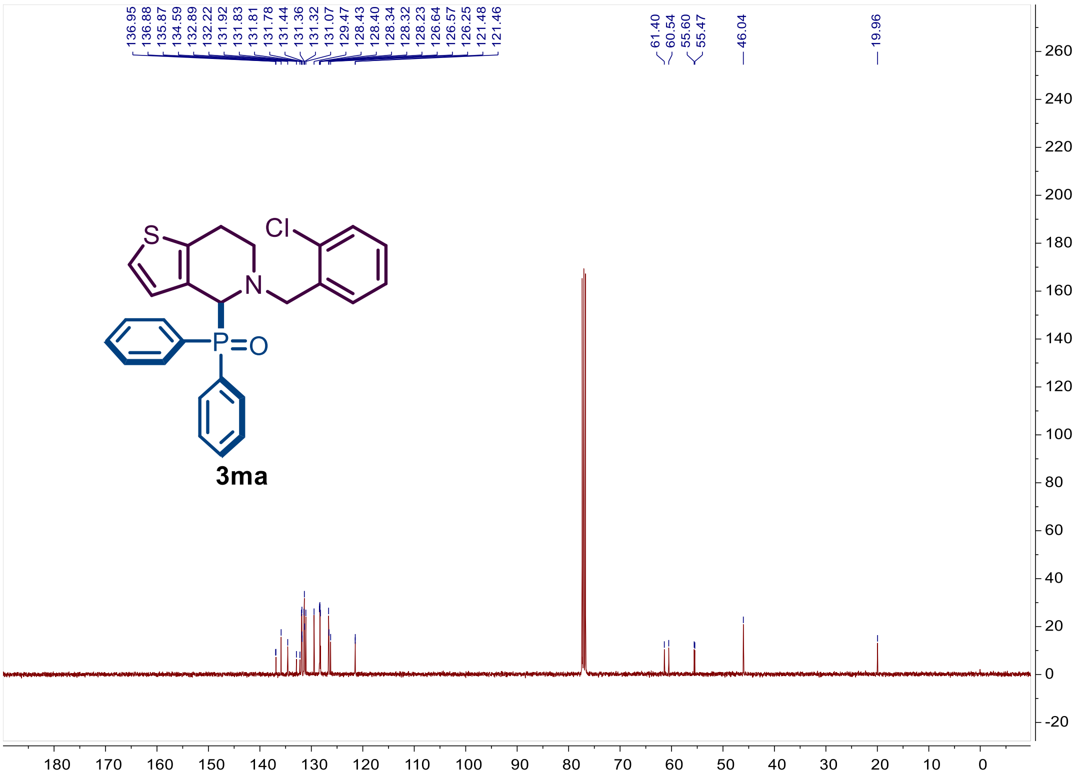
^{31}P NMR spectrum of 3la



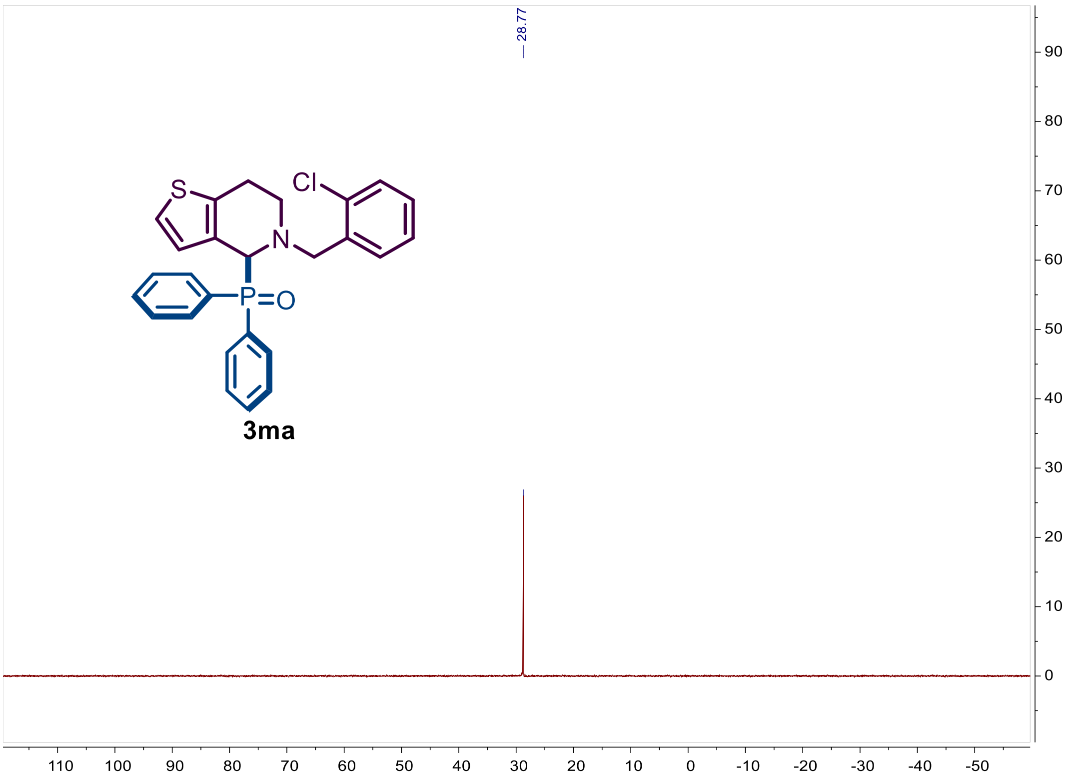
^{1}H NMR spectrum of 3ma



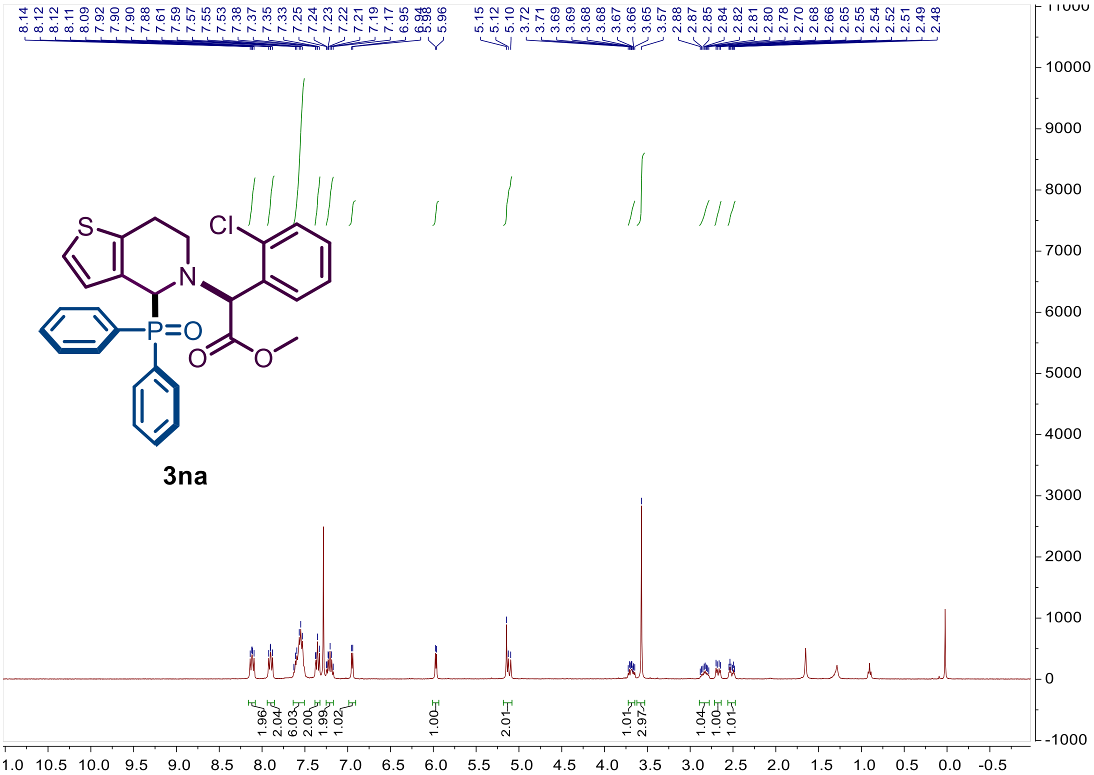
[13]C NMR spectrum of 3ma



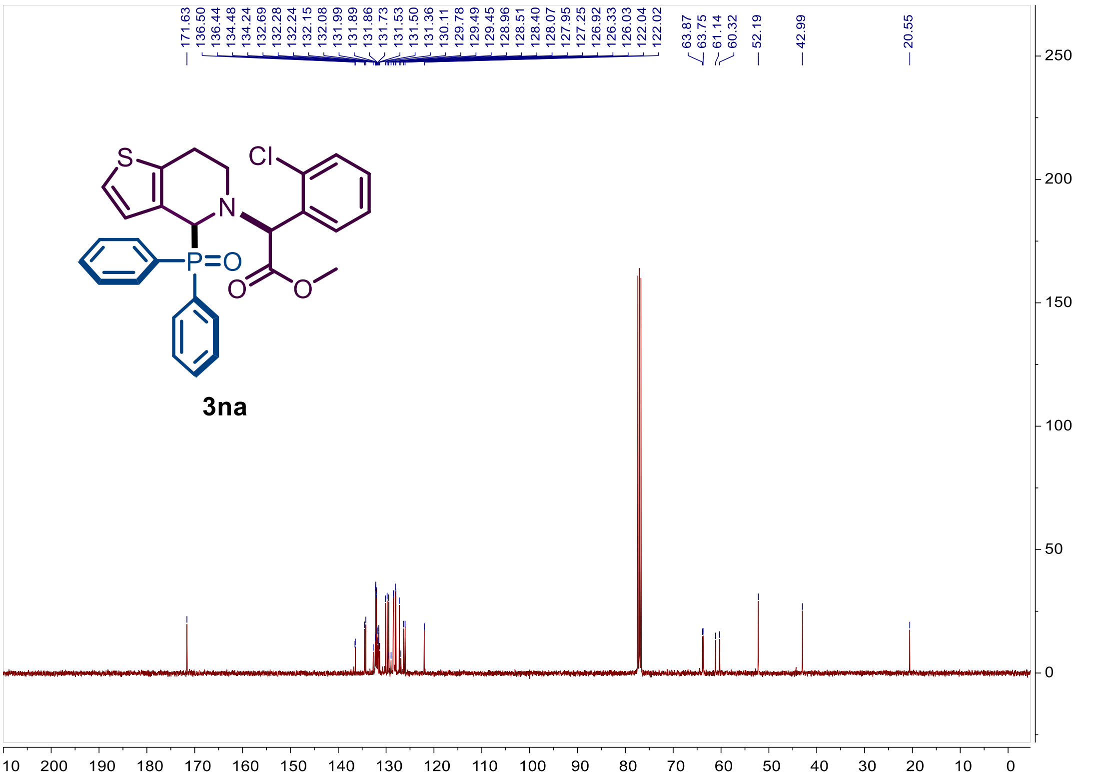
[31]P NMR spectrum of 3ma



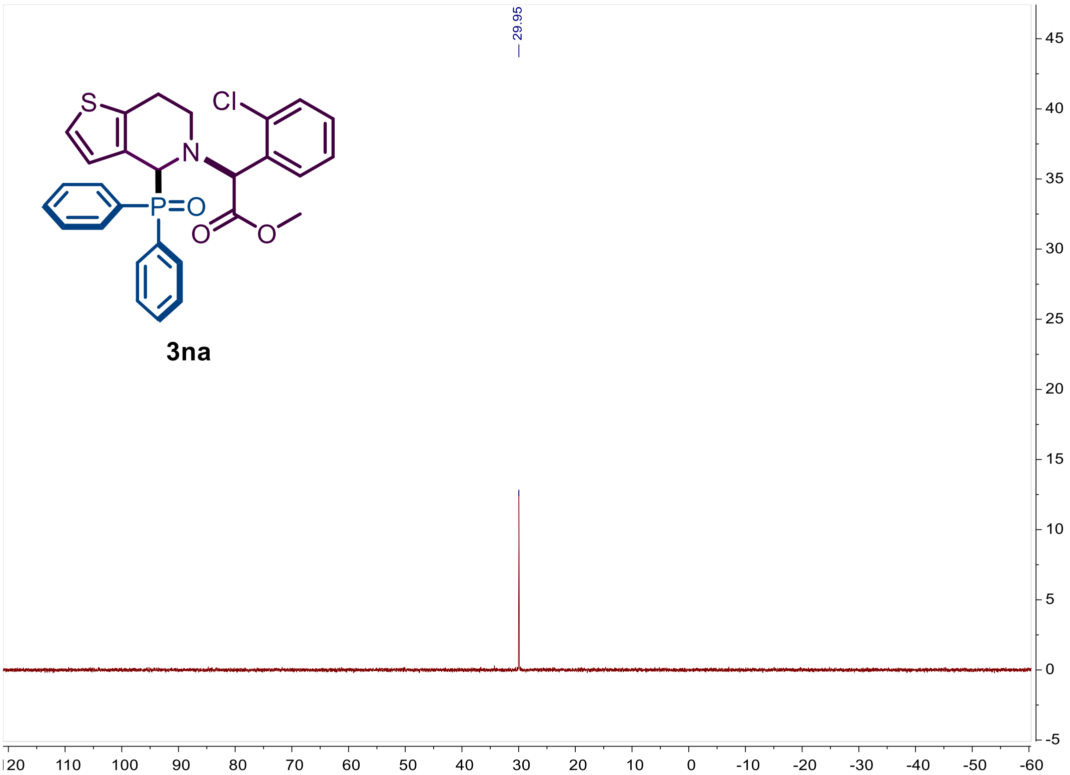
[1]H NMR spectrum of 3na



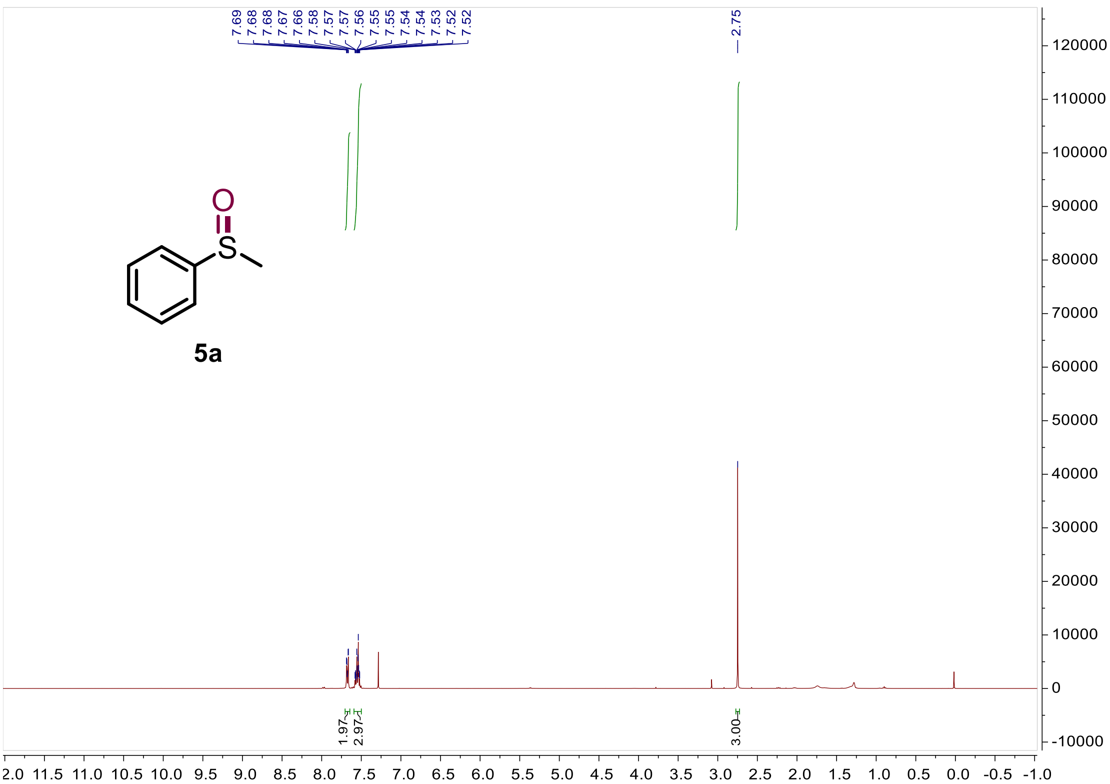
[13]C NMR spectrum of 3na



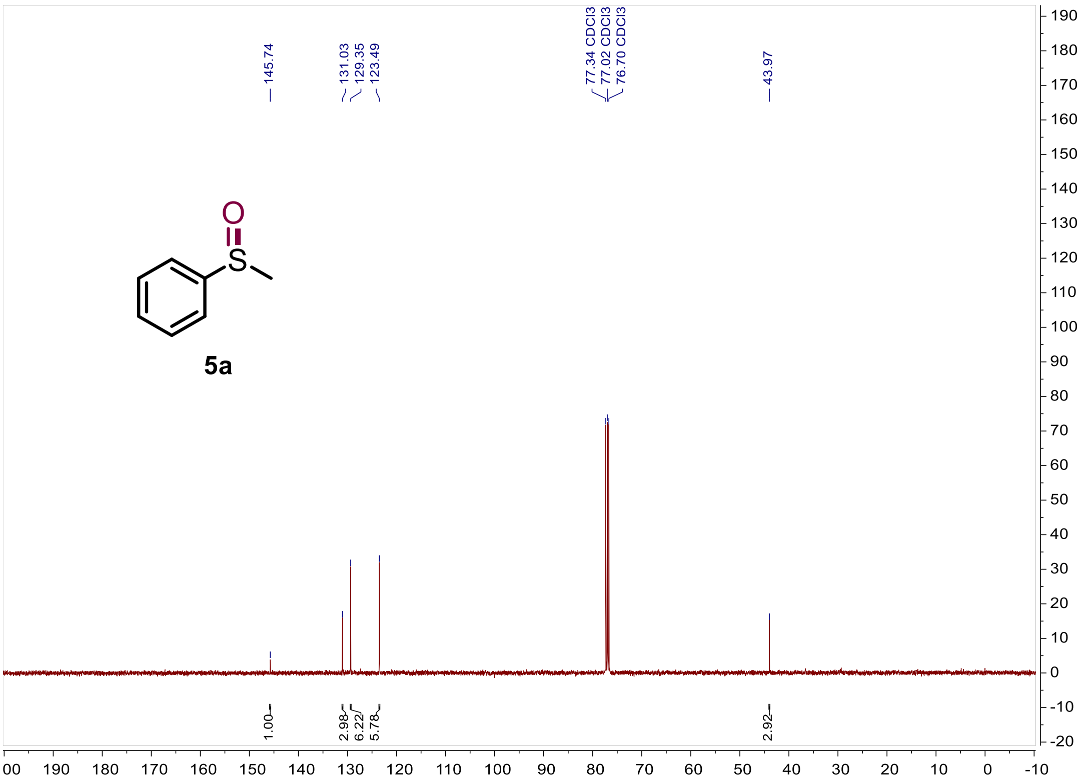
^{31}P NMR spectrum of 3na



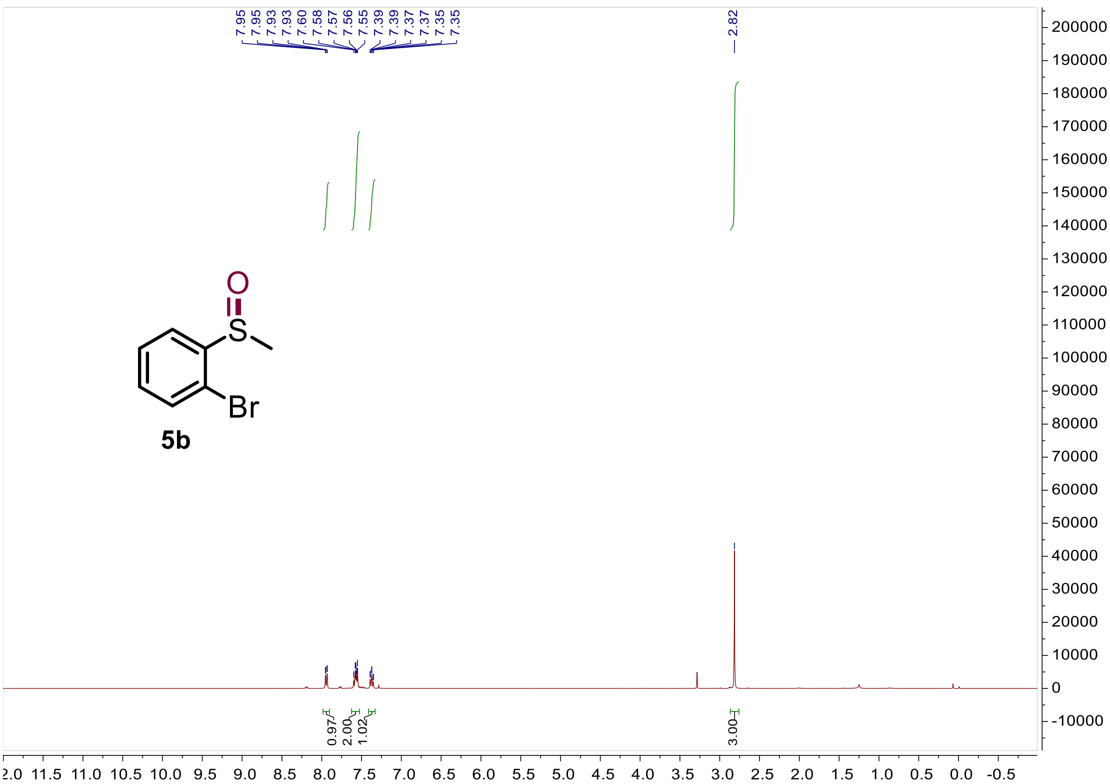
^{1}H NMR spectrum of 5a



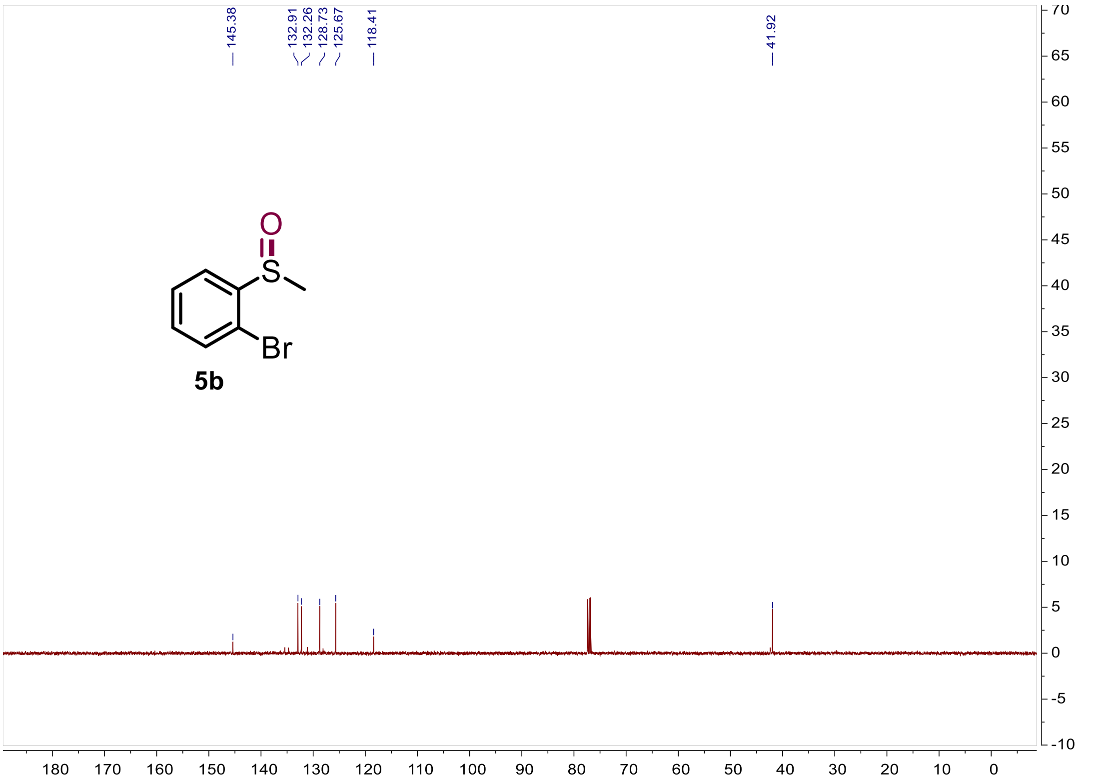
[13]C NMR spectrum of 5a



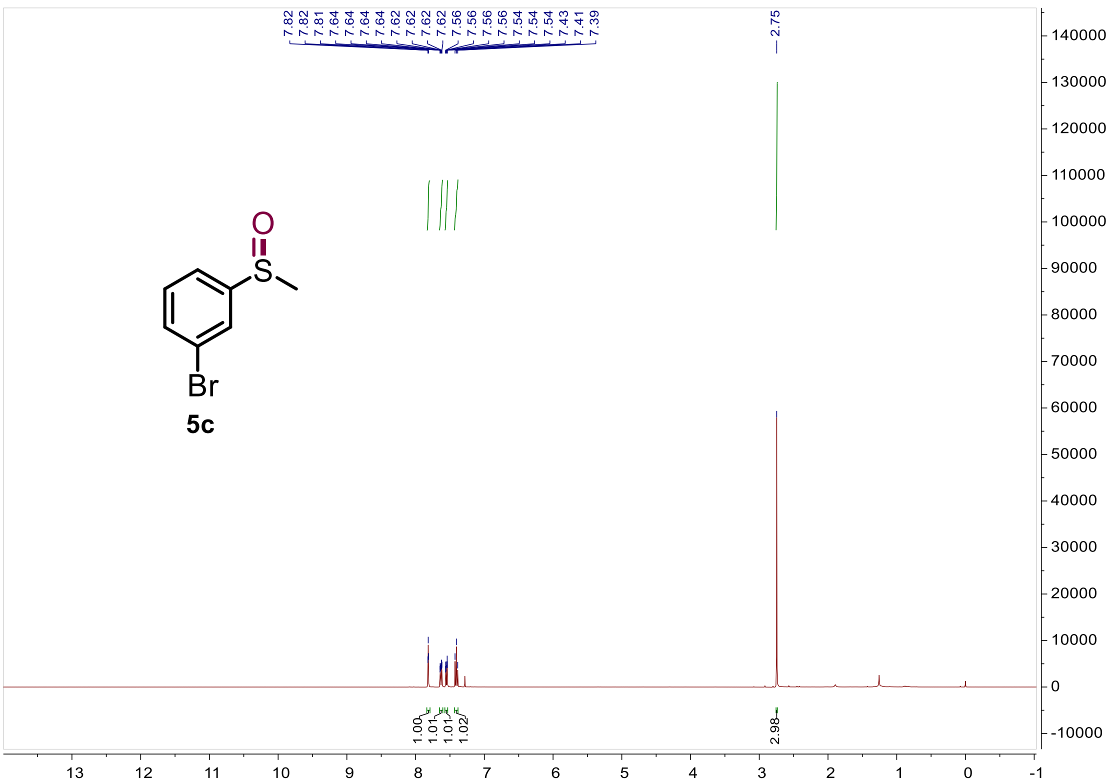
[1]H NMR spectrum of 5b



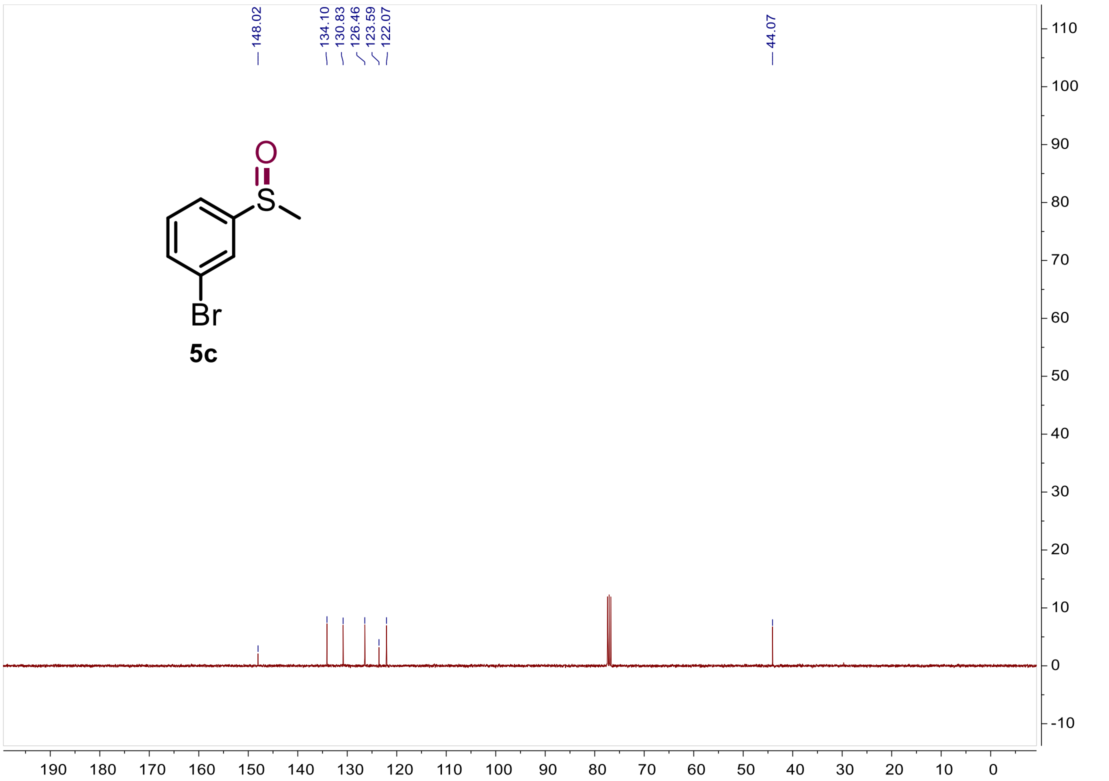
^{13}C NMR spectrum of 5b



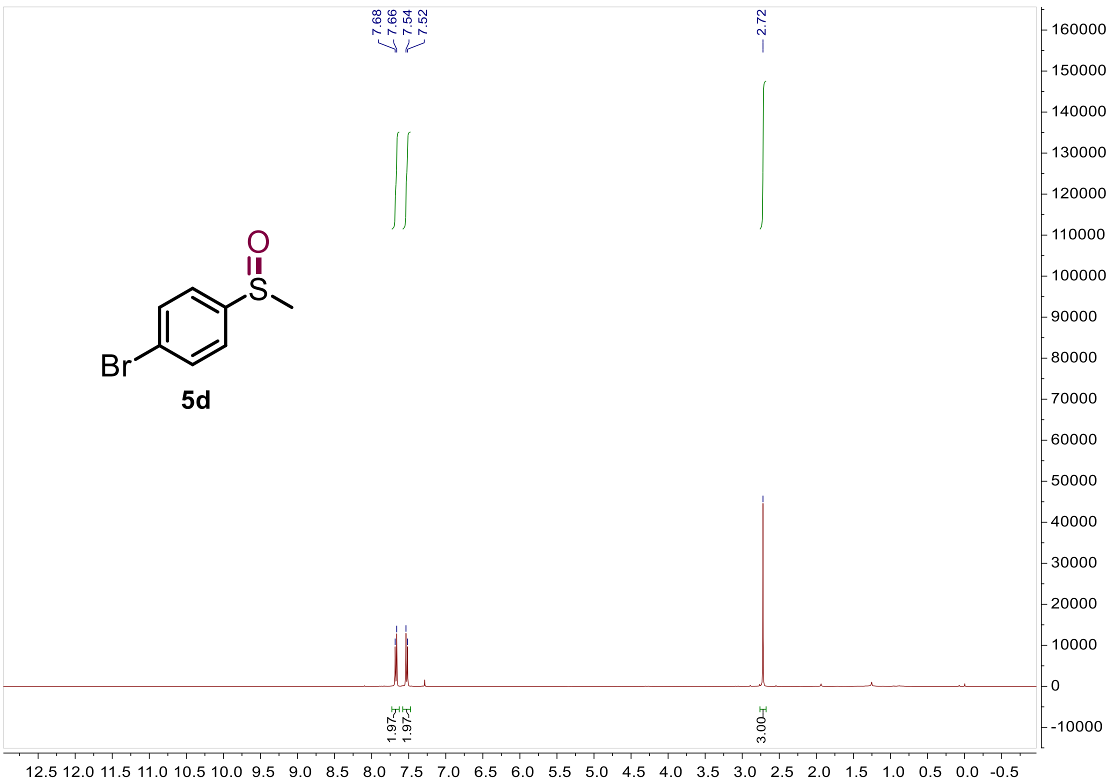
^{1}H NMR spectrum of 5c



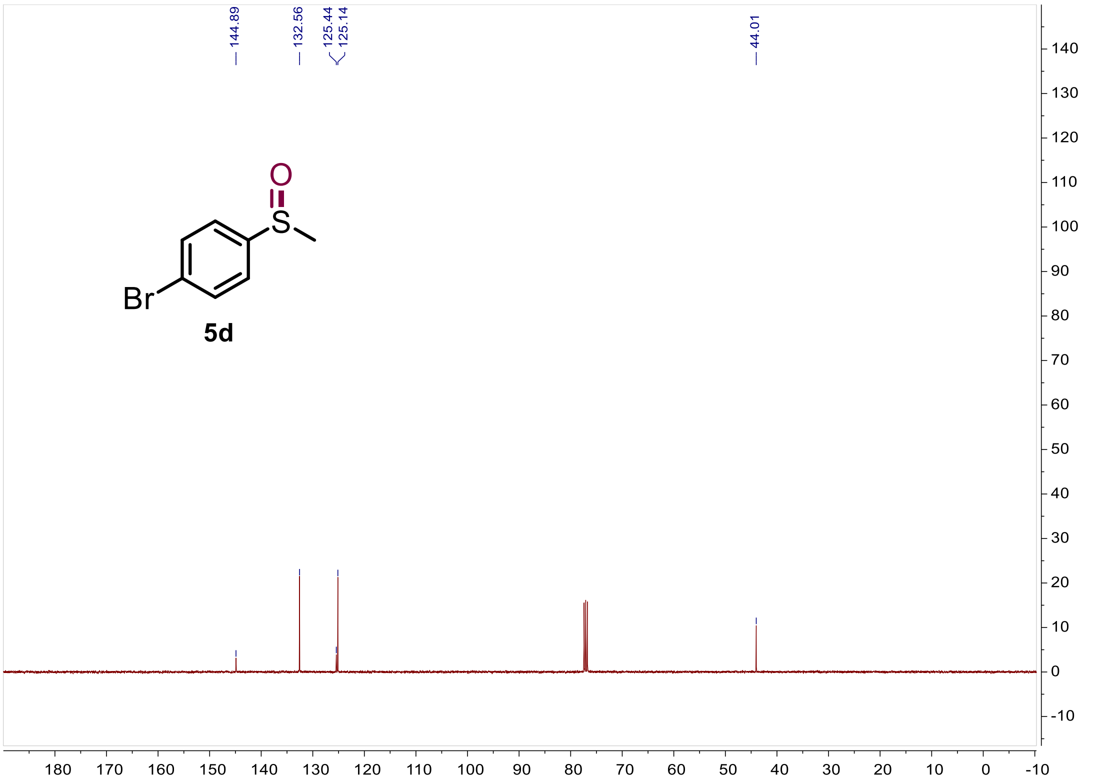
[13]C NMR spectrum of 5c



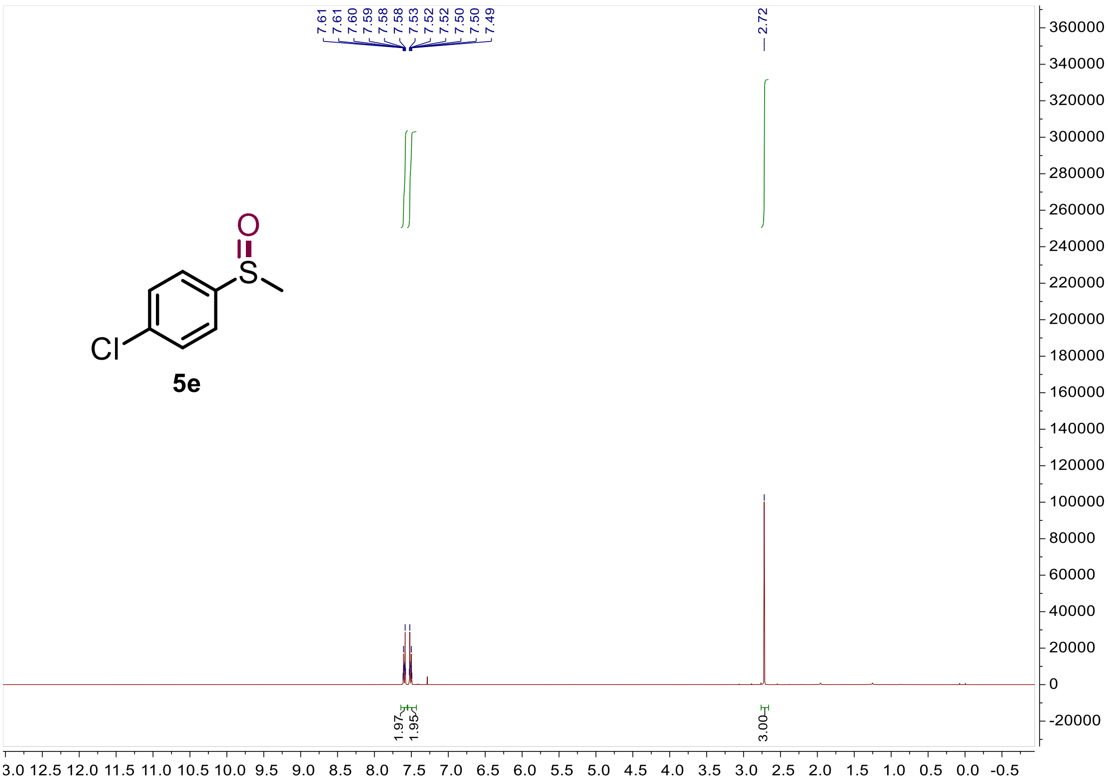
[1]H NMR spectrum of 5d



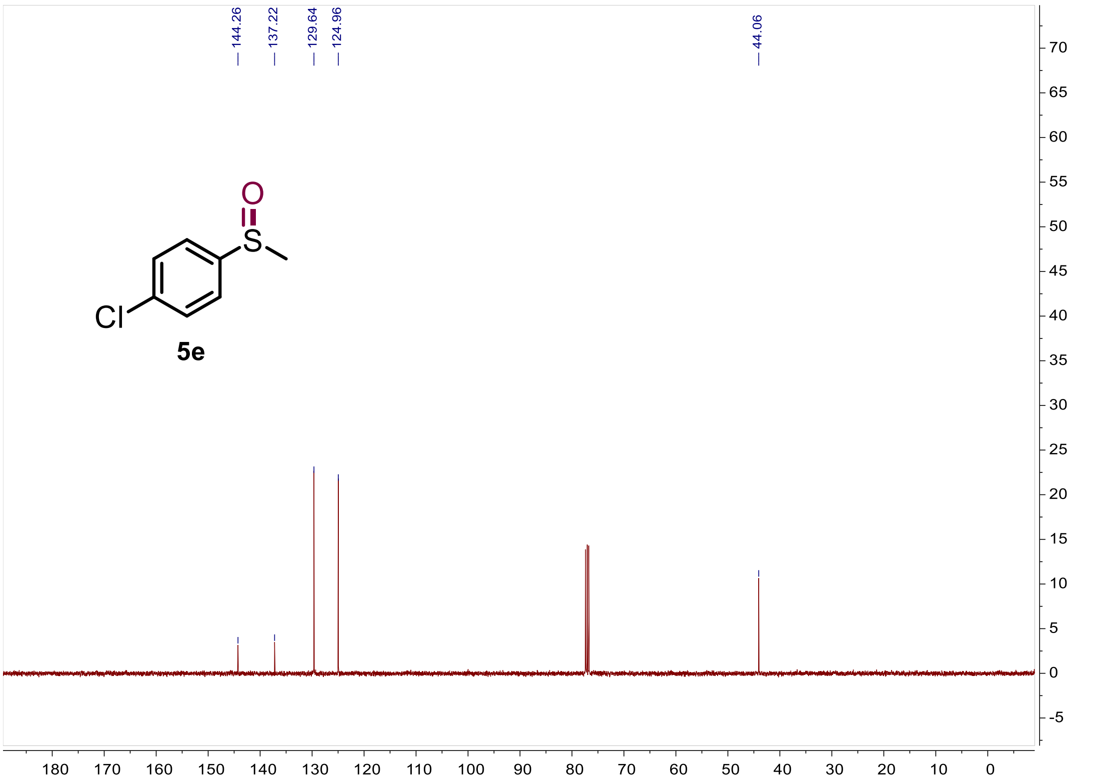
^{13}C NMR spectrum of 5d



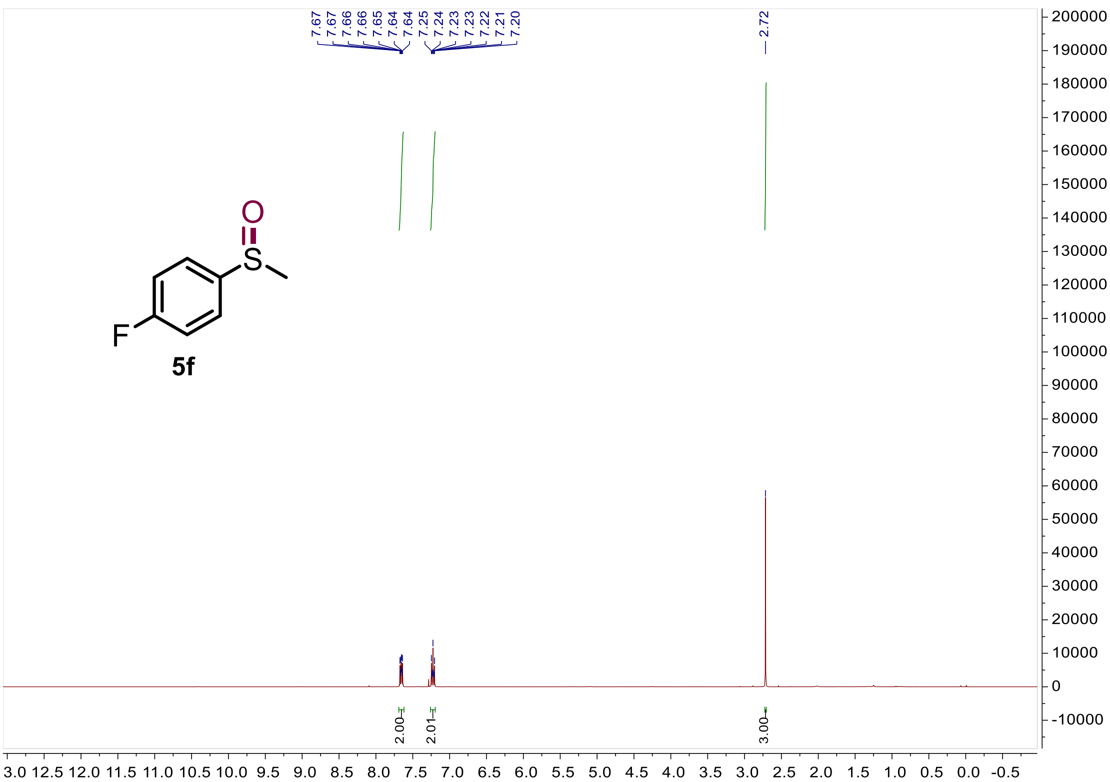
^{1}H NMR spectrum of 5e



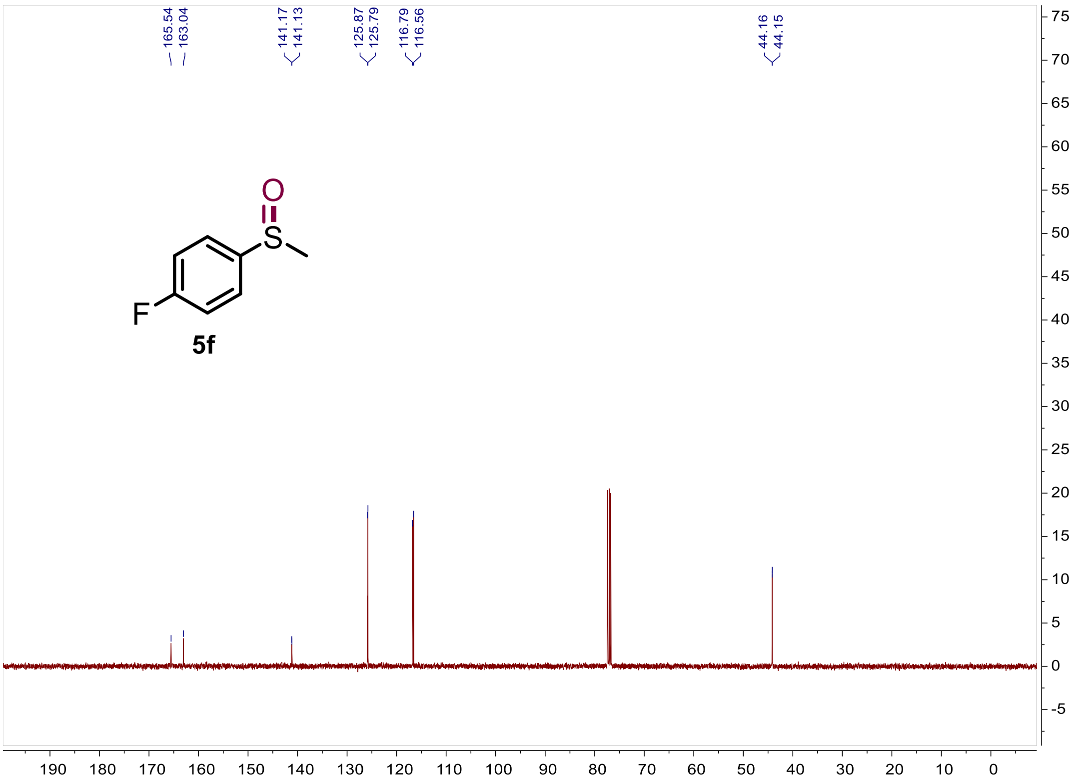
[13]C NMR spectrum of 5e



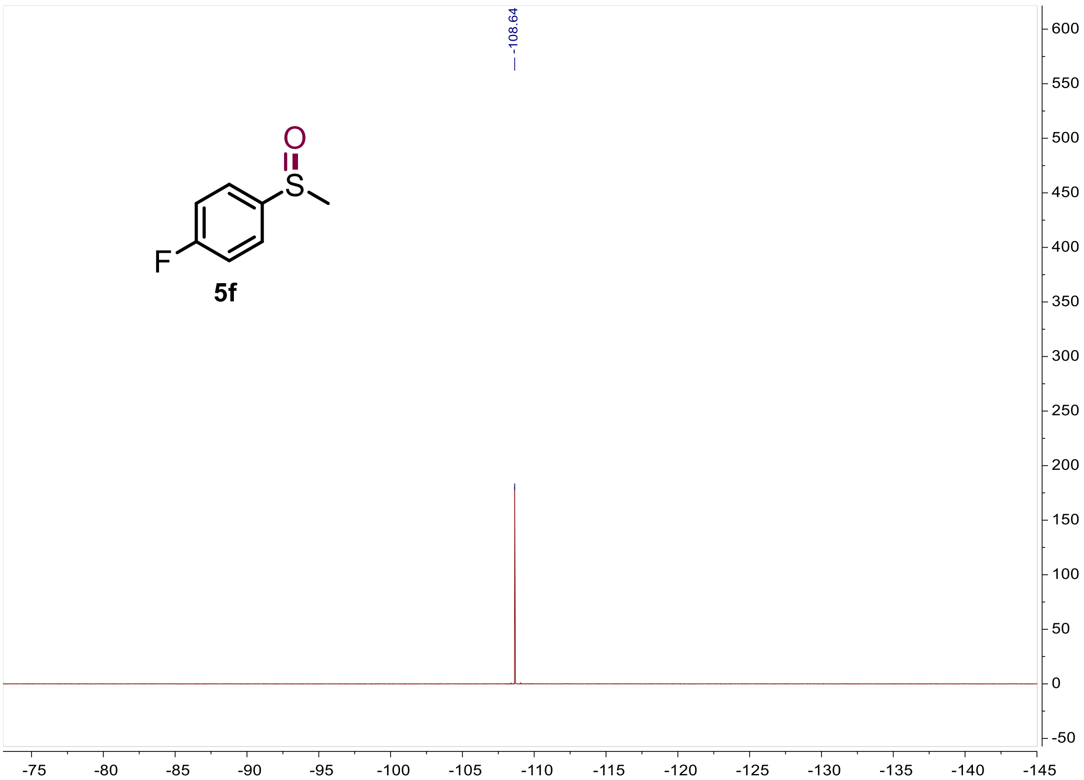
[1]H NMR spectrum of 5f



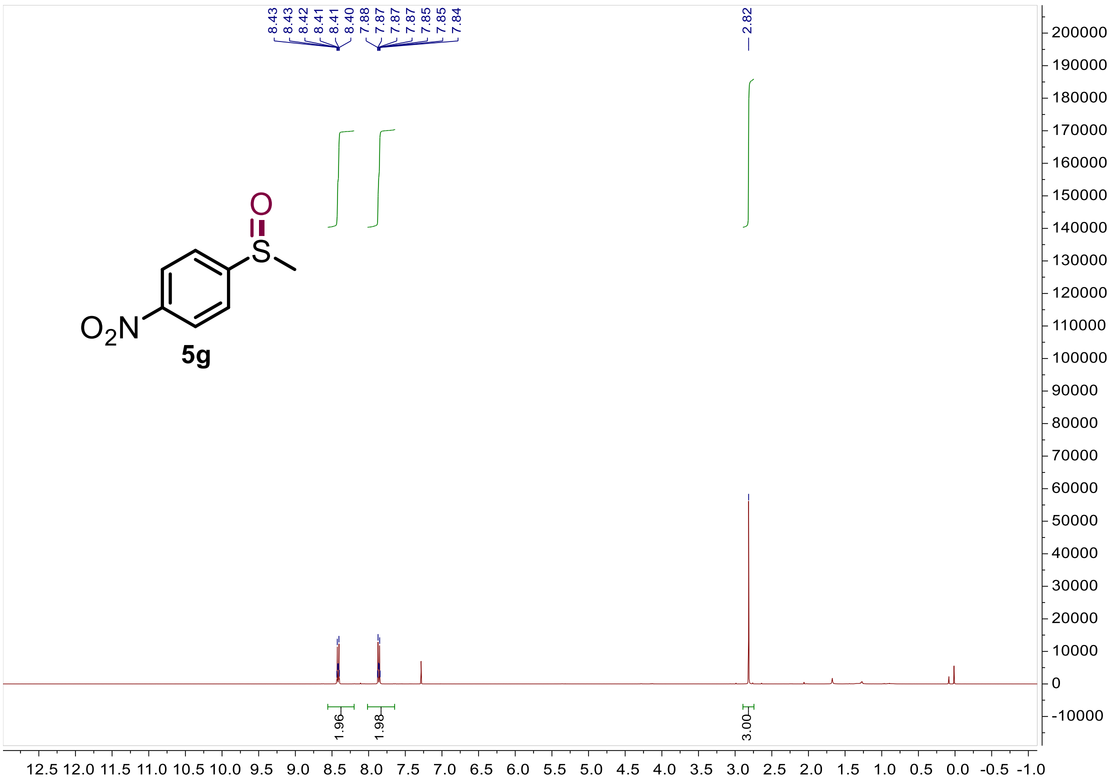
^{13}C NMR spectrum of 5f



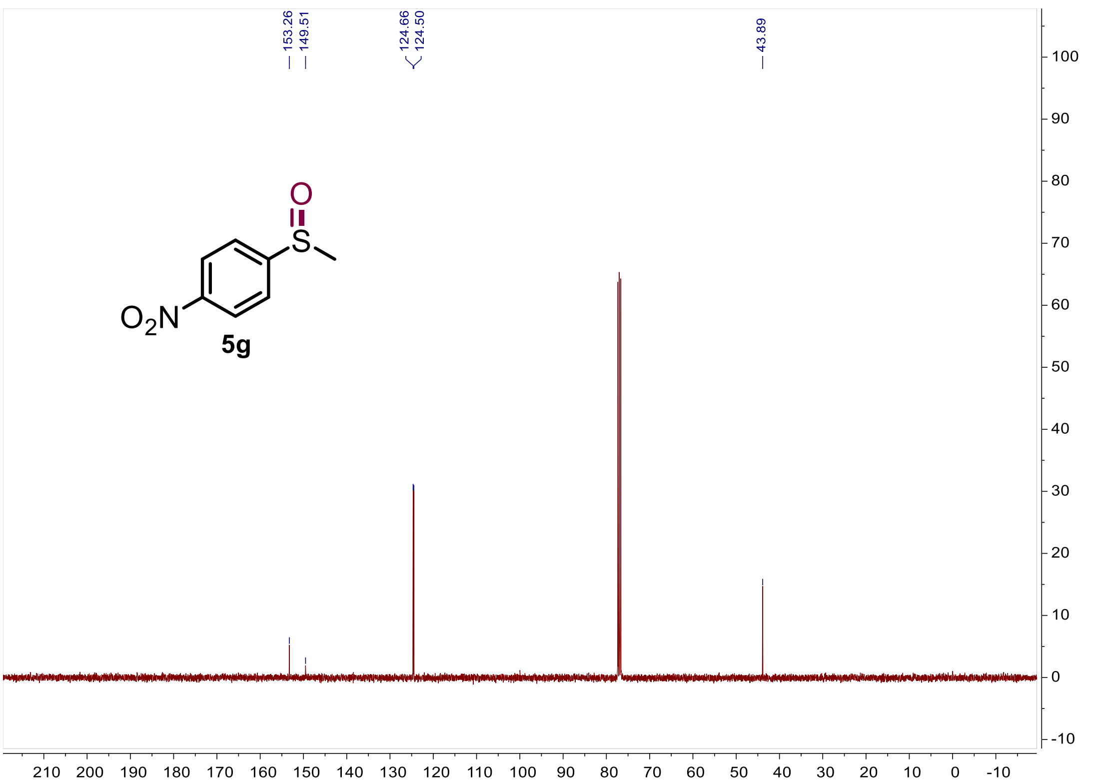
^{19}F NMR spectrum of 5f



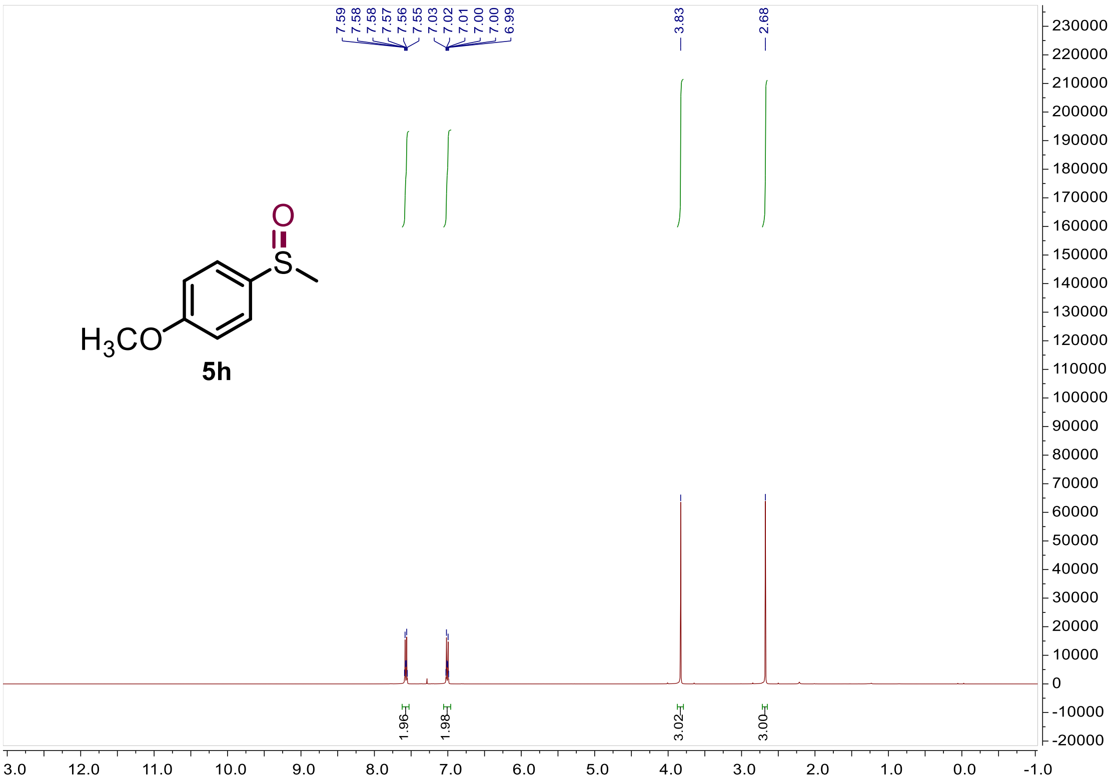
[1]H NMR spectrum of 5g



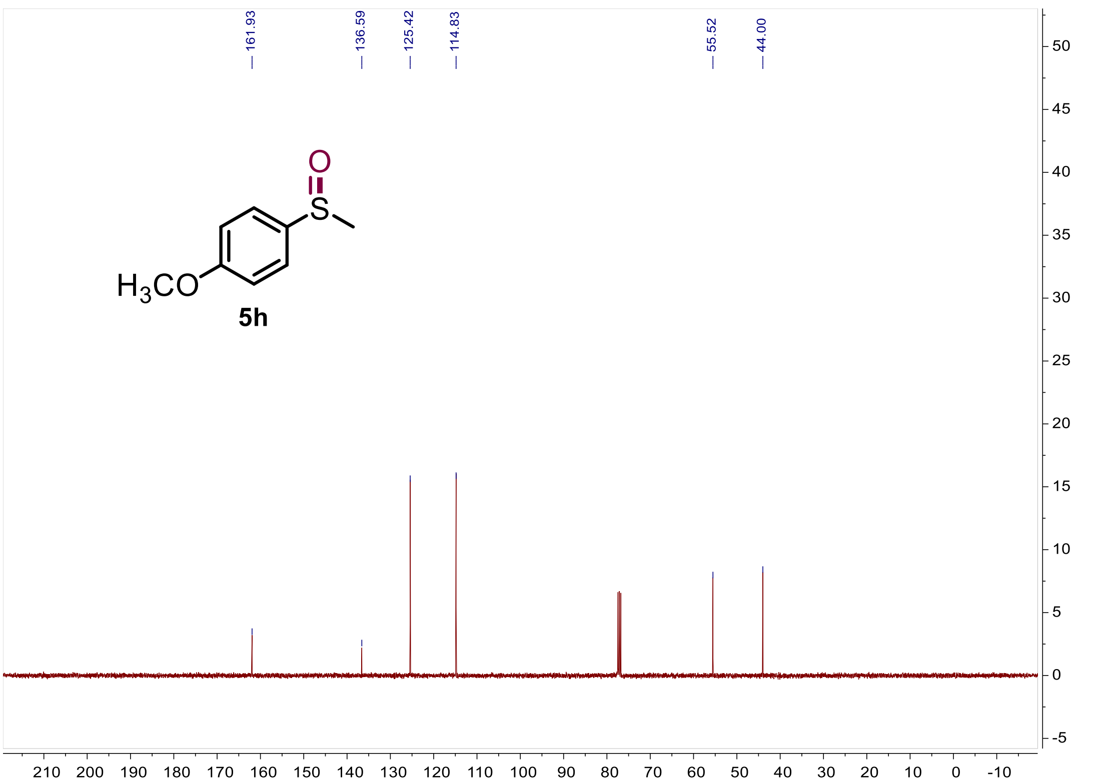
[13]C NMR spectrum of 5g



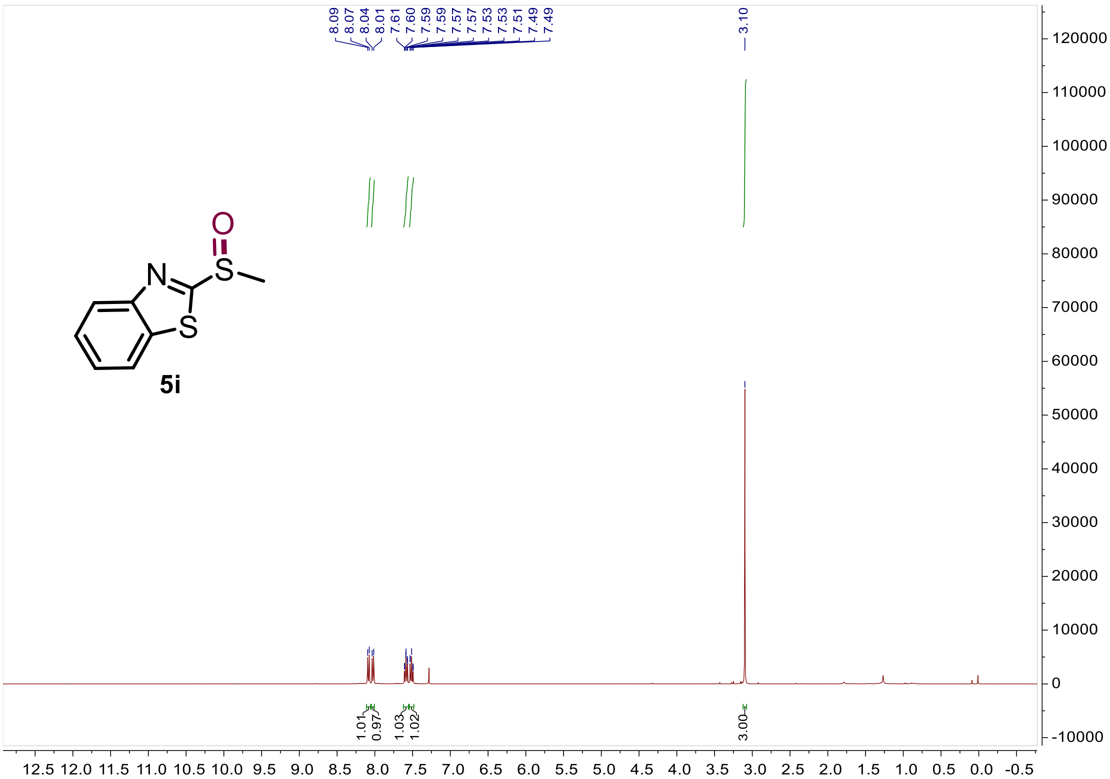
^{1}H NMR spectrum of 5h



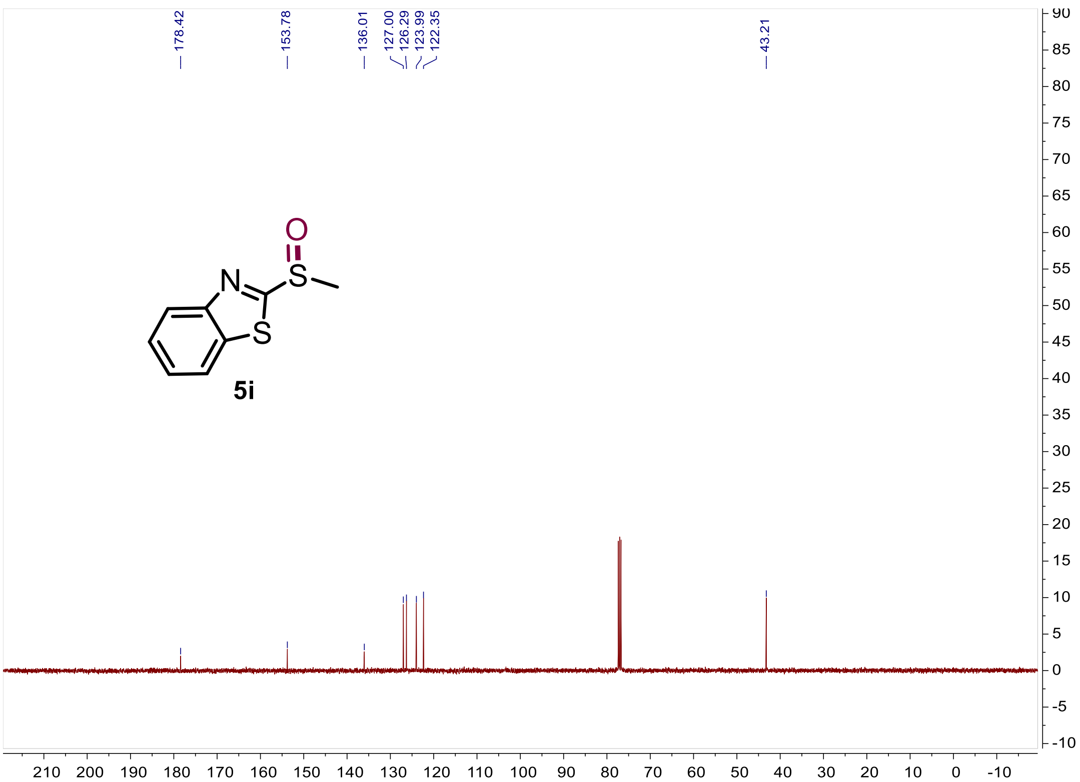
^{13}C NMR spectrum of 5h



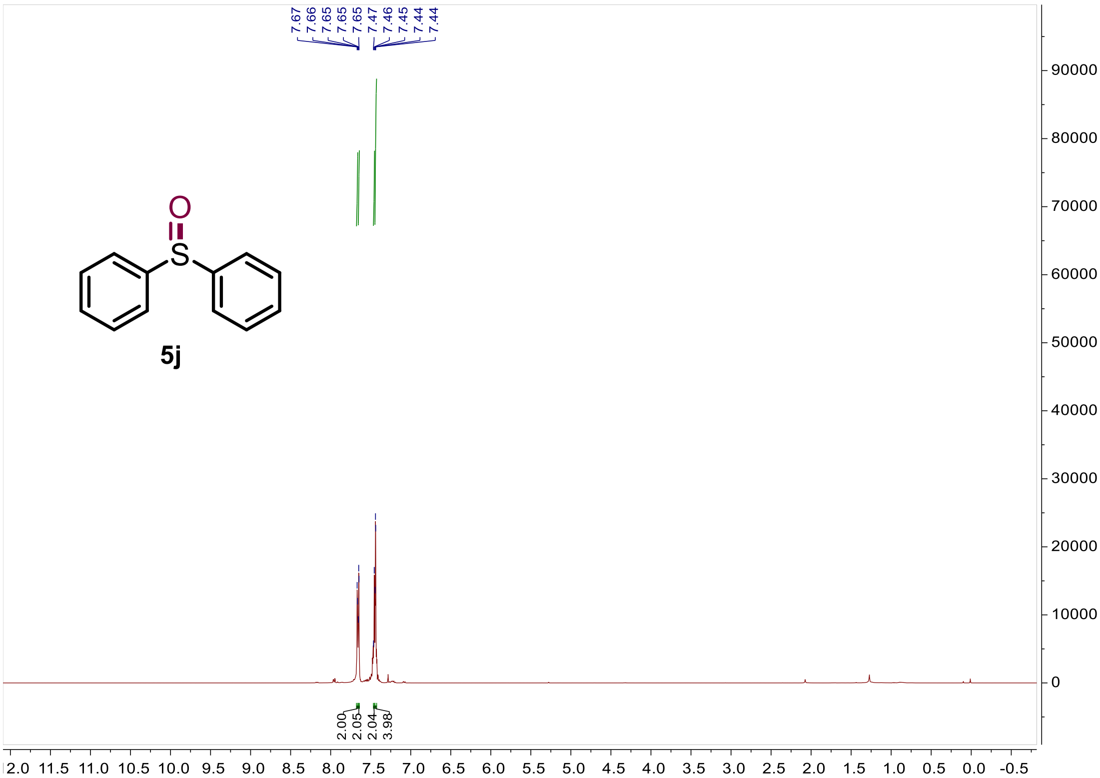
[1]H NMR spectrum of 5i



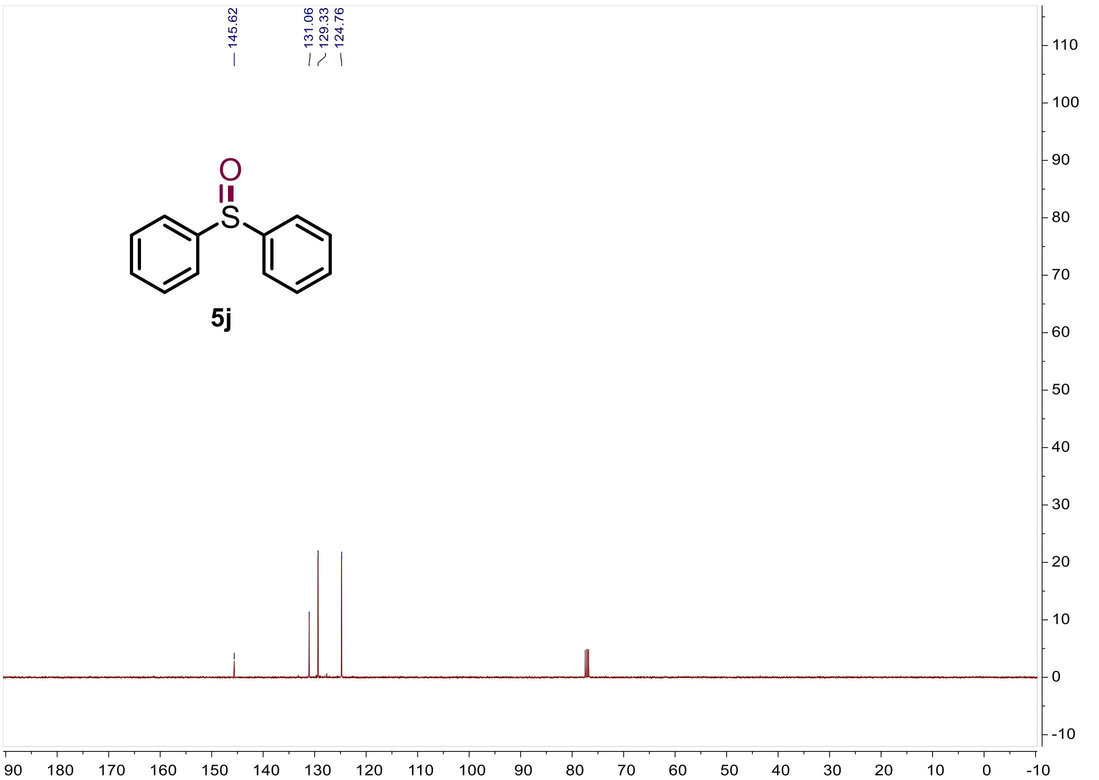
[13]C NMR spectrum of 5i



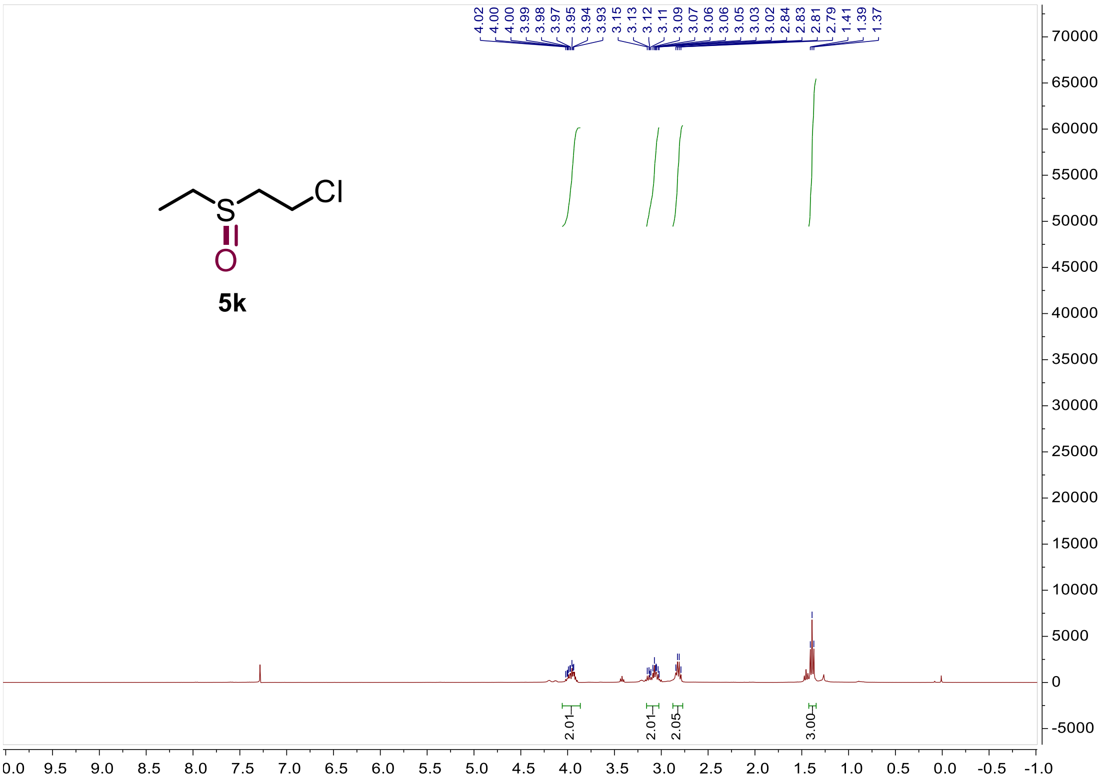
[1]H NMR spectrum of 5j



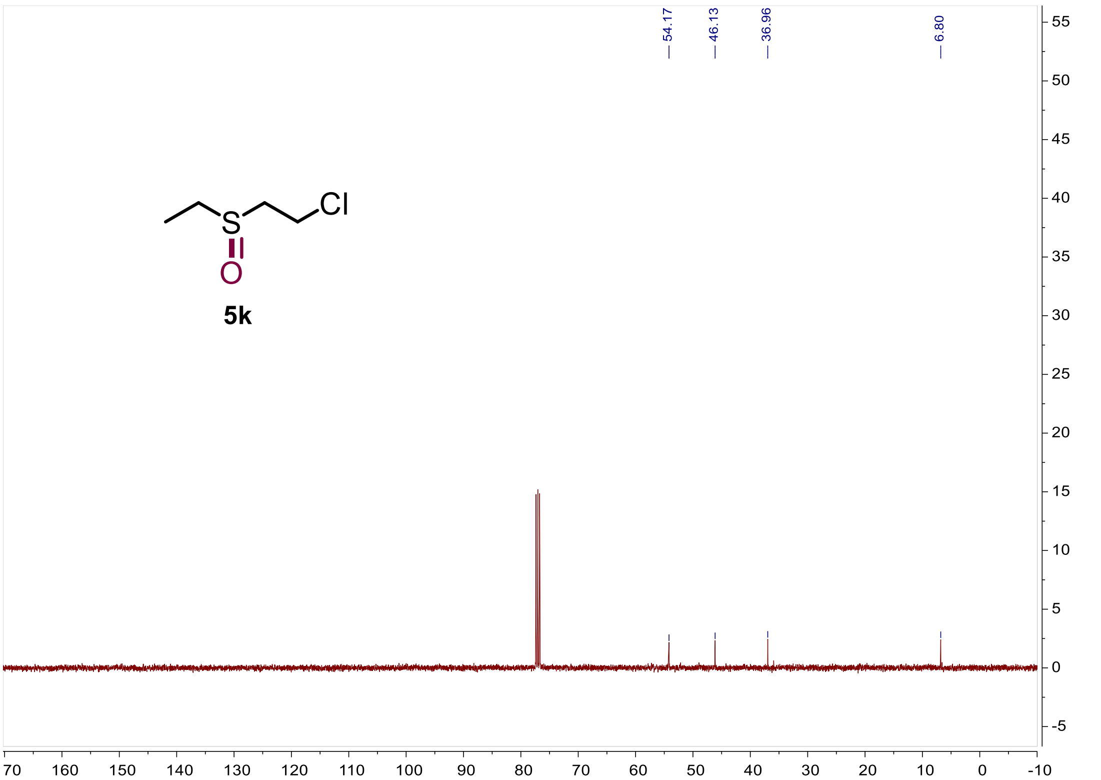
[13]C NMR spectrum of 5j



[1]H NMR spectrum of 5k



[13]C NMR spectrum of 5k



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