Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Organic Photoredox Catalytic *α*-C(sp^3)–H Phosphorylation of Saturated Aza-Heterocycles

Ming-Jun Yi, ‡[a] Teng-Fei Xiao, ‡[a] Wen-Hui Li, [a] Yi-Fan Zhang, [a] Pen-Ji Yan, [b]

Baoxin Zhang, [a] Peng-Fei Xu,[a][c] and Guo-Qiang Xu*[a]

[a] State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000 (P.R. China).

[b] Key Laboratory of Hexi Corridor Resources Utilization of Gansu Universities, College of Chemistry and Chemical Engineering, Hexi University, Zhangye 734000, (P.R. China)

[c] State Key Laboratory of Veterinary Etiological Biology, College of Veterinary Medicine, Lanzhou University, Lanzhou 730000 (P.R. China)

*Corresponding author (s): gqxu@lzu.edu.cn

Supporting Information Placeholder

This PDF file includes

Table of Contents

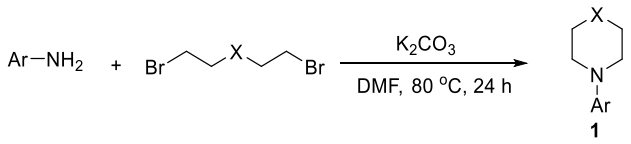
1. General information

All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 (400 MHz) or Agilent Inova 600 MHz. The spectra were recorded in $CDCl_3$ as solvent at room temperature, ^{1}H and ^{13}C NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.00 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q=quartet, m = multiplet, dd = doublet), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR are reported as chemical shift. HRMS were performed on a Bruker Apex II mass instrument (ESI).

2. Synthesis of substrates

2.1 Synthesis of Cyclic Amines

Cyclic amines were synthesized according to reported procedures with some modifications. [1]



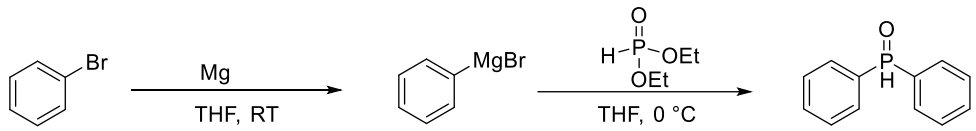
1

General procedure: K_2CO_3 (1.52 g, 11 mmol, 1.1 equiv.) was weighed into an oven-dried 25 mL round-bottom flask with magnetic stirring and DMF (10 mL, 1.0 M) was added. The appropriate aniline (10 mmol, 1.0 equiv.) was added into the reaction mixture *via* syringes. The reaction system was degassed (10 min) and backfilled with nitrogen. The corresponding dibromide (11 mmol, 1.1 equiv.) was added, and the reaction mixture was heated to 80 ºC for 24 h. After completion, the reaction mixture

was cooled to rt and diluted with EtOAc (20 mL) and H_2O (20 mL). The layers were separated, and the organic layer was extracted with 1 N HCl (3 x 10 mL). The acid layers were combined and adjusted to pH = 8 with 1N NaOH and then extracted with EtOAc (3 x 10 mL). The organic layers were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered, concentrated, and purified by flash chromatography.

2.2 Synthesis of diphenylphosphine oxide

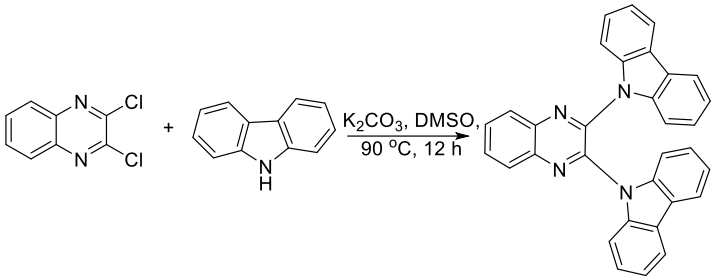
Phosphine Oxides were synthesized according to reported procedures with some modifications.[2]



General procedure: Diethylphosphite (1.29 mL, 10.0 mmol) was added dropwise at 0 ℃ to a solution of phenylmagnesium bromide in tetrahydrofuran which was prepared from aryl bromides (32.6 mmol) and magnesium (0.95 g, 39.6 mmol). The mixture was aged for 30 minutes at 0 ℃, then stirred at ambient temperature for 16 hours. After that it was cooled again to 0 ℃, and 75 mL NH_4Cl aqueous was then added slowly. The mixture was extracted with diethyl ether and the organic phase was washed with $NaHCO_3$ aqueous and brine, then it was dried over Na_2SO_4. After the solvent had been completely removed, the residue was purified by column chromatography on silica gel to give the product.

2.3 Synthesis and Characterization of Photocatalyst

2.3.1 Synthesis of DCQ



General procedure: A mixture of carbazole (2.1 mmol) and K_2CO_3 (2.2 mmol) dissolved in 7 mL DMSO and stirred for 20 min, then 2,3-dichloroquinoxaline (1 mmol) was added and the reaction mixture was stirred at 90 °C for 7 h. After completion, the

reaction mixture was cooled to room temperature, added 100 mL brine to the mixture and filtered. The crude compound was purified by flash column chromatography (n-Hexane/ethyl acetate 10:1) to give green crystals. 369 mg, 78% yield, R_f = 0.71 (PE:EA = 10:1); mp= 151-152 ^oC.

2.2 Characterization of Photocatalyst

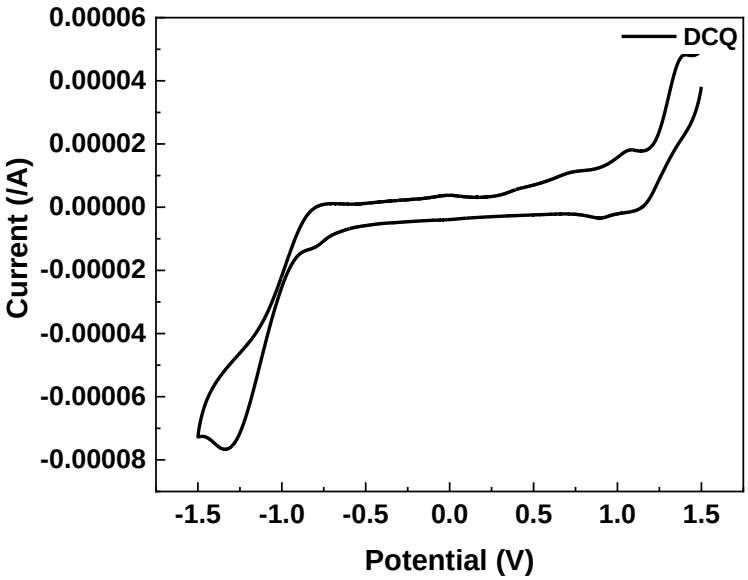


Figure S1. Cyclic voltammograms of DCQ. Recorded in MeCN containing 0.1 M *n*-Bu_4NPF_6 at 25 ± 2 ^oC at a 1 mm diameter GC electrode for 1 mM solutions of the analytes.

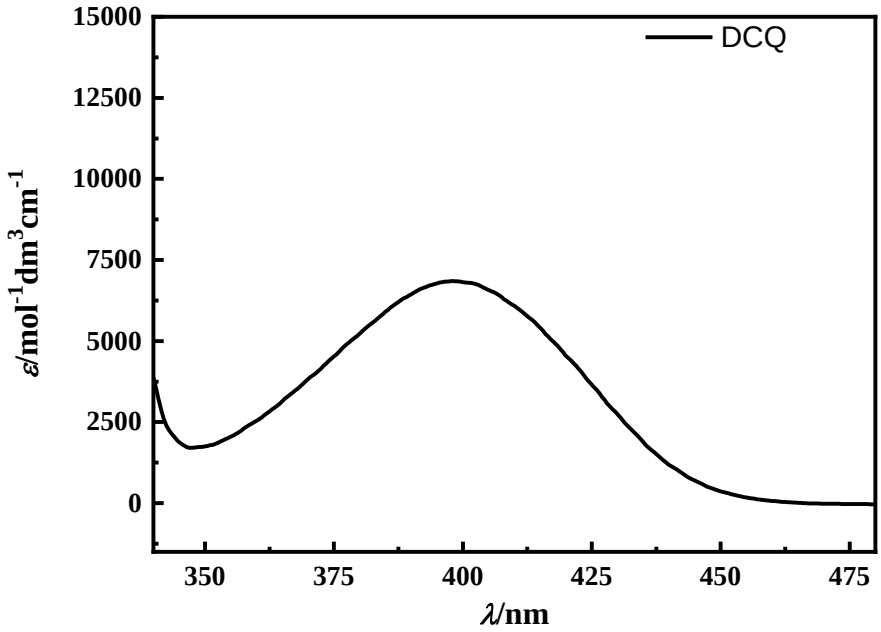


Figure S2. UV-vis spectrum of DCQ in toluene $3*10^{-4}$ M.

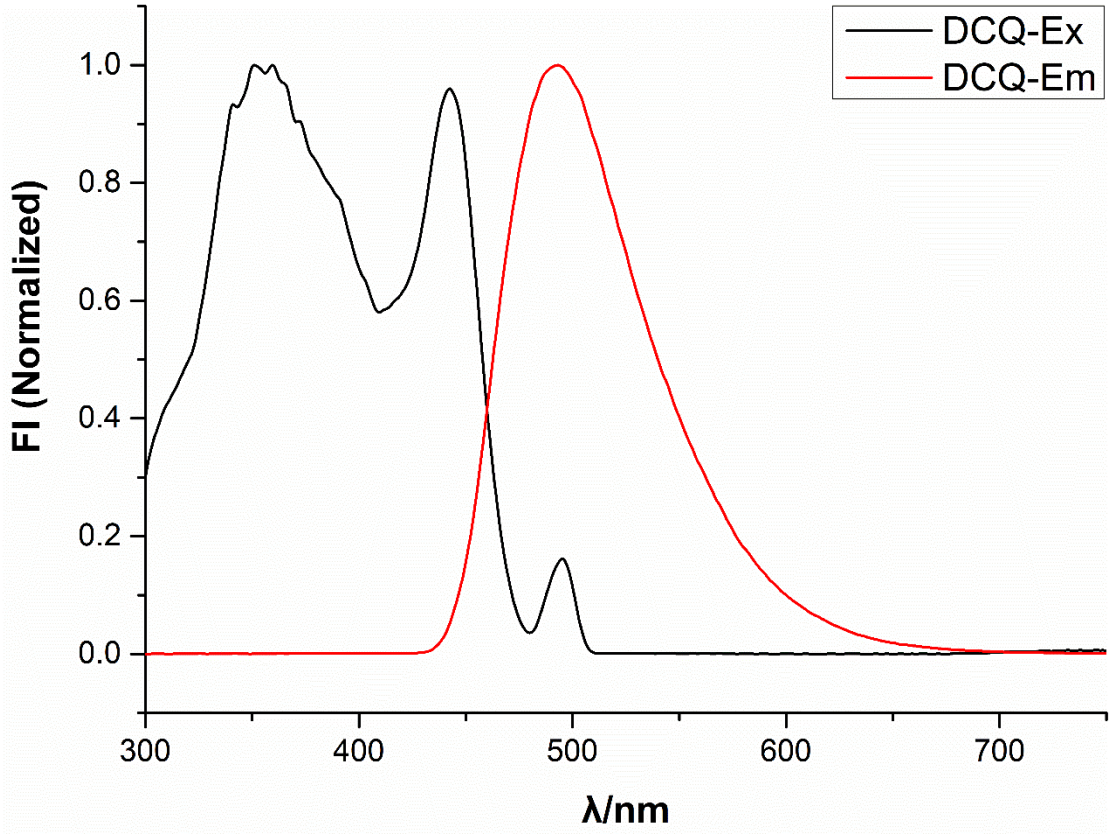


Figure S3. Excitation and emission spectra of DCQ in toluene.

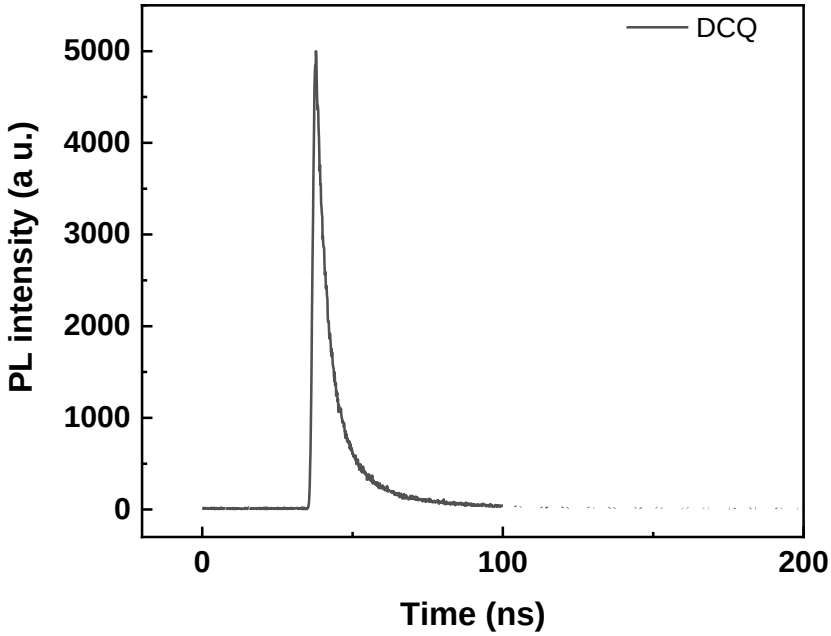


Figure S4. Transient emission decay profiles of DCQ.

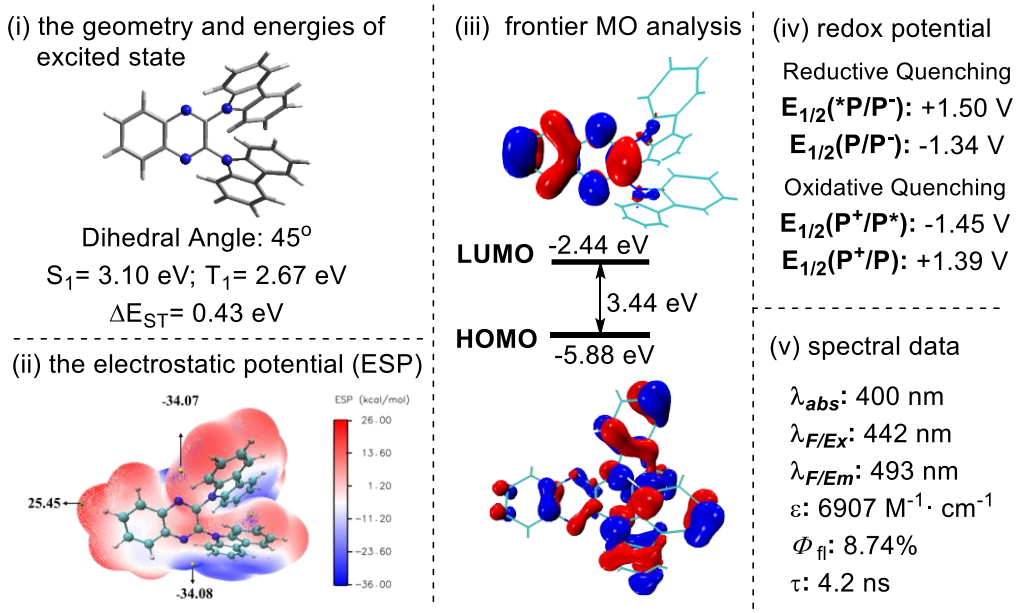


Figure S5. Characterization of DCQ.

DCQ HOMO-LUMO at B3PW91/def2TZVP level

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.290238	-0.659990	-0.301011

2	6	0	3.576351	-0.669576	-0.233377
3	6	0	3.576405	0.669354	0.233334
4	6	0	1.290298	0.659923	0.301014
5	1	0	4.779621	-2.358628	-0.816032
6	6	0	4.805475	-1.334669	-0.456903
7	6	0	4.805578	1.334346	0.456883
8	6	0	5.986039	0.670982	0.228109
9	6	0	5.985988	-0.671408	-0.228093
10	1	0	4.779809	2.358309	0.816008
11	1	0	6.932186	1.174070	0.400501
12	1	0	6.932096	-1.174573	-0.400463
13	7	0	2.404505	-1.302330	-0.516651
14	7	0	2.404606	1.302205	0.516580
15	6	0	-0.261412	-2.600259	-0.243493
16	6	0	-0.981729	-0.747411	-1.348018
17	6	0	0.474201	-3.534355	0.486165
18	6	0	-1.590564	-2.848732	-0.643818
19	6	0	-1.062819	0.474312	-2.015479
20	6	0	-2.049119	-1.667450	-1.351366
21	6	0	-0.153199	-4.734395	0.802961
22	1	0	1.498040	-3.339027	0.784225
23	6	0	-2.197920	-4.062926	-0.315574
24	6	0	-2.265494	0.785835	-2.638229
25	1	0	-0.222184	1.159350	-2.057446
26	6	0	-3.246690	-1.336102	-1.989741
27	6	0	-1.472860	-5.001288	0.407619
28	1	0	0.396580	-5.482187	1.366392
29	1	0	-3.221952	-4.262965	-0.617672
30	6	0	-3.351801	-0.102738	-2.619593
31	1	0	-2.359510	1.737269	-3.152977
32	1	0	-4.077480	-2.035888	-1.994422
33	1	0	-1.928847	-5.950532	0.670304
34	1	0	-4.276857	0.173072	-3.115711
35	6	0	-0.261179	2.600267	0.243525
36	6	0	-0.981642	0.747486	1.348080
37	6	0	0.474507	3.534283	-0.486153
38	6	0	-1.590328	2.848833	0.643806
39	6	0	-1.062819	-0.474205	2.015599
40	6	0	-2.048982	1.667592	1.351376
41	6	0	-0.152814	4.734350	-0.803006
42	1	0	1.498349	3.338899	-0.784181
43	6	0	-2.197611	4.063041	0.315490
44	6	0	-2.265542	-0.785638	2.638308
45	1	0	-0.222216	-1.159277	2.057663

46	6	0	-3.246603	1.336331	1.989706
47	6	0	-1.472471	5.001336	-0.407719
48	1	0	0.397037	5.482082	-1.366446
49	1	0	-3.221639	4.263146	0.617556
50	6	0	-3.351807	0.102992	2.619594
51	1	0	-2.359619	-1.737041	3.153102
52	1	0	-4.077355	2.036163	1.994320
53	1	0	-1.928398	5.950594	-0.670457
54	1	0	-4.276895	-0.172745	3.115694
55	7	0	0.092604	-1.304724	-0.644941
56	7	0	0.092739	1.304733	0.645023

---

0 imaginary frequencies

Zero-point Energies= -1449.548233

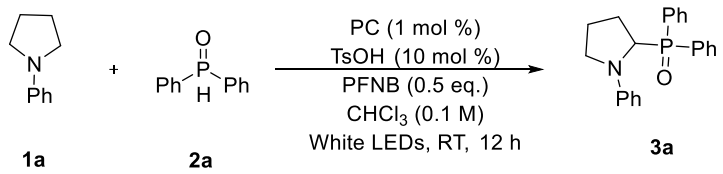
Thermal Energies= -1449.523463

Thermal Enthalpies= -1449.522519

Thermal Free Energies= -1449.602659

3. Screening of reaction conditions

Table S1. Optimization of the photocatalyst.[a]

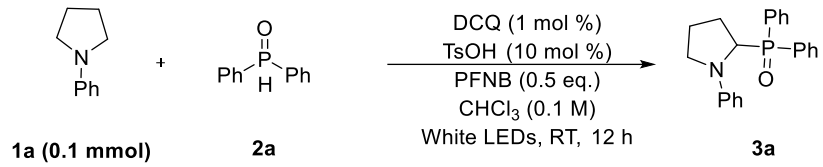


1a **2a** **3a**

Entry	PC (mol %)	Yield (%)[b]
1	Cz-NI-Ph	76
2	Cz-NI-Me	81
3	Cz-NI	71
4	DCQ	83
5	DCQ-^{t}Bu	82
6	dF-DCQ	32

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), PFNB (0.5 eq.), TsOH (10 mol %) and photocatalyst (1 mol %) in $CHCl_3$ (1 mL) at 25 ºC for 12 h under irradiation with white light. [b]Isolated yield after chromatography. PFNB = pentafluoronitrobenzene.

Table S2. Optimization of the loading of **2a**.[a]

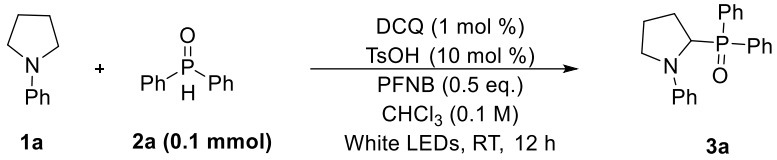


1a (0.1 mmol) **2a** **3a**

Entry	2a	Yield (%)[b]
1	0.1 mmol (1.0 eq.)	30
2	0.2 mmol (2.0 eq.)	56

[a]Reaction conditions: **1a** (0.1 mmol), **2a**, PFNB (0.5 eq.), TsOH (10 mol %) and DCQ (1 mol %) in $CHCl_3$ (1 mL) at 25 ºC for 12 h under irradiation with white light. [b]Isolated yield after chromatography. PFNB = pentafluoronitrobenzene.

Table S3. Optimization of the loading of **1a**.[a]

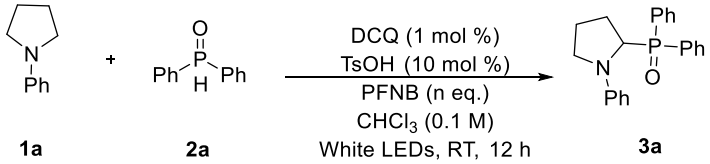


1a **2a (0.1 mmol)** **3a**

Entry	1a	Yield (%)[b]
1	0.12mmol (1.2 eq.)	41
2	0.13mmol (1.3 eq.)	89
3	0.14mmol (1.4 eq.)	84
4	0.15mmol (1.5 eq.)	85
5	0.20mmol (2.0 eq.)	82

[a]Reaction conditions: **1a** (0.1 mmol), PFNB（0.5 eq.）, TsOH (10 mol %) and DCQ (1 mol %) in $CHCl_3$ (1 mL) at 25 ºC for 12 h under irradiation with white light. [b]Isolated yield after chromatography. PFNB = pentafluoronitrobenzene.

Table S4. Optimization of the loading of PFNB.[a]

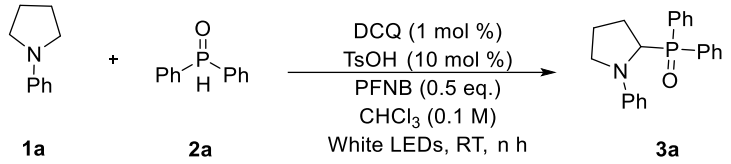


1a **2a** **3a**

Entry	PFNB	Yield (%)[b]
1	0.55 eq.	83
2	0.60 eq.	58

[a]Reaction conditions: **1a** (0.13 mmol), **2a** (0.1 mmol), PFNB, TsOH (10 mol %) and DCQ (1 mol %) in $CHCl_3$ (1 mL) at 25 ºC for 12 h under irradiation with white light. [b]Isolated yield after chromatography. PFNB = pentafluoronitrobenzene.

Table S5. Optimization of time.[a]



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

Entry	Time	Yield (%)[b]
1	2 h	83
2	4 h	81
3	6 h	88
4	8 h	99
5	10 h	97
6	14 h	91
7	18 h	80

[a]Reaction conditions: **1a** (0.13 mmol), **2a** (0.1 mmol), PFNB (0.5 eq.), TsOH (10 mol %) and DCQ (1 mol %) in $CHCl_3$ (1 mL) at 25 ºC for different time under irradiation with white light. [b]Isolated yield after chromatography. PFNB = pentafluoronitrobenzene.

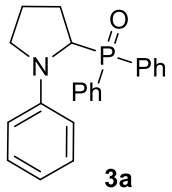
4. General procedure for the synthesis of product 3 and analytical data

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

General catalysis procedure: A dried 10 mL reaction tube was charged with the photocatalyst (0.001 mol, 0.46 mg), *p*-TSA (0.01 mmol, 1.9 mg), PFNB (0.05 mmol, 6.5 μL), 1-phenylpyrrolidine **1** (0.13 mmol, 1.3 equiv), diphenylphosphine oxide **2** (0.1 mmol, 1.0 equiv) and 1.0 mL $CHCl_3$. The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the vial was placed beside a white LED light. The reaction was stirred at 25 ºC for 8 h. After completion of the reaction as checked by TLC. The reaction mixture was purified by silica gel flash

column chromatography (PE/EA = 3:1 to PE/iPrOH = 10:1) to give the corresponding product**.**

Diphenyl (1-phenylpyrrolidin-2-yl)phosphine oxide (3a)



3a

Following the general procedure, compound **3a** was obtained as a white solid in 99% yield; mp = 188-190 ˚C; R_f = 0.51 (PE:*i*PrOH = 5:1);

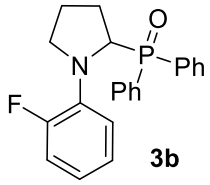
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-7.89 (m, 2H),7.78-7.74 (m, 2H), 7.58-7.54 (m, 1H), 7.51-7.45 (m, 2H), 7.45-7.41 (m, 1H), 7.35-7.31(m, 2H),6.96-6.92 (m, 2H), 6.57-6.93 (t, *J* = 7.28 Hz, 1H), 6.36-6.35 (d, *J* = 8.06 Hz, 2H), 4.69-4.65 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 147. 8, 131.91 (d, J_{C-P} = 2.7 Hz), 131.90 (d, J_{C-P} = 8.7 Hz), 131.81 (d, J_{C-P} = 89.3 Hz), 131.80 (d, J_{C-P} = 2.7 Hz), 131.7 (d, J_{C-P} = 8.4 Hz), 131.6 (d, J_{C-P} = 92.5 Hz), 128.6 (d, J_{C-P} = 10.8 Hz), 128.5, 128.2 (d, J_{C-P} = 11.0 Hz), 116.8, 113.2, 60.5 (d, J_{C-P} = 86.7 Hz), 50.9, 27.7, 24.2;

^{31}P NMR (162 MHz, $CDCl_3$): δ 27.3.

HRMS (ESI) for $C_{22}H_{23}NOP$ $[M+H]^+$ calcd.348.1512, found: 348.1512.

(1-(2-Fluorophenyl)pyrrolidin-2-yl)diphenylphosphine oxide (3b)



3b

Following the general procedure, compound **3b** was obtained as a white solid in 78% yield; mp = 142-144 ˚C; R_f = 0.53 (PE:*i*PrOH = 5:1);

1H NMR (400 MHz, $CDCl_3$): δ 7.91-7.73 (m, 1H), 7.45-7.30 (m, 1H), 7.29-7.19 (m, 1H), 6.79-6.49 (m, 1H), 4.94 (td, J = 9.1, 4.6 Hz, 1H), 3.81 (dt, *J* = 7.8, 6.4 Hz, 1H), 3.15 (dd, *J* = 15.1, 7.5 Hz, 1H), 2.45-2.21 (m, 1H), 2.09-1.93 (m, 1H), 1.93-1.72 (m, 1H);

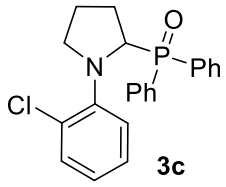
^{13}C NMR (101 MHz, $CDCl_3$): δ 154.1 (d, J_{C-F} = 243.4 Hz), 136.2 (d, J_{C-F} = 9.1 Hz), 132.1 (d, J_{C-P} = 90.9 Hz), 131.7 (d, J_{C-P} = 8.1 Hz), 131.4 (d, J_{C-P} = 2.0 Hz), 131.3 (d, J_{C-P} = 2.0 Hz), 131.1 (d, J_{C-P} = 8.1 Hz), 130.9 (d, J_{C-P} = 92.9 Hz), 128.2 (d, J_{C-P} = 11.1 Hz), 127.7 (d, J_{C-P} = 11.1 Hz), 123.7 (d, J_{C-F} = 3.0 Hz), 120.4 (t, J_{C-F} = 8.1 Hz), 119.5 (t, J_{C-F} = 4.0 Hz), 115.5 (t, J_{C-F} = 21.2 Hz), 58.8 (dd, J_{C-P} = 82.8 Hz, J_{C-F} = 5.0 Hz), 53.1 (t, J_{C-P} = 2.0 Hz), 27.2, 24.0;

^{31}P NMR (162 MHz, $CDCl_3$): δ 29.0;

^{19}F NMR (376 MHz, $CDCl_3$): δ -121.6.

HRMS (ESI) for $C_{22}H_{22}FNOP$ $[M+H]^+$ calcd. 382.1418, found: 382.1418.

(1-(2-Chlorophenyl)pyrrolidin-2-yl)diphenylphosphine oxide (3c)



3c

Following the general procedure, compound **3c** was obtained as a white solid in 73% yield; mp = 136-138 °C; R_f = 0.48 (PE:*i*PrOH = 5:1);

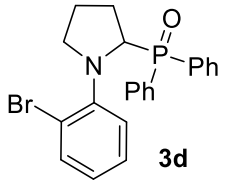
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15-7.97 (m, 2H), 7.79-7.58 (m, 2H), 7.49-7.39 (m, 1H), 7.39-7.33 (m, 2H), 7.33-7.25 (m, 1H), 7.26-7.17 (m, 2H), 7.12 - 7.00 (m, 1H), 6.99-6.83 (m, 2H), 6.82-6.66 (m, 1H), 4.99-4.70 (m, 1H), 3.89-3.61 (m, 1H), 3.15-2.82 (m, 1H), 2.70-2.36 (m, 1H), 2.36-2.04 (m, 1H), 1.91-1.69 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.8, 132.3 (d, J_{C-P} = 91.9 Hz), 132.0 (d, J_{C-P} = 8.2 Hz), 131.4 (d, J_{C-P} = 2.7 Hz), 131.2 (d, J_{C-P} = 2.7 Hz), 131.0 (d, J_{C-P} = 9.1 Hz), 130.09 (d, J_{C-P} = 93.9 Hz), 130.10, 129.0, 127.95 (d, J_{C-P} = 11.1 Hz), 127.88 (d, J_{C-P} = 11.1 Hz), 126.8, 123.4, 122.4, 59.4 (d, J_{C-P} = 89.0 Hz), 55.4 (d, J_{C-P} = 4.1 Hz), 27.3, 24.8 (d, J_{C-P} = 3.0 Hz);

^{31}P NMR (162 MHz, $CDCl_3$): δ 29.0.

HRMS (ESI) for $C_{22}H_{22}ClNOP$ $[M+H]^+$ calcd. 382.1122, found: 382.1122.

(1-(2-Bromophenyl)pyrrolidin-2-yl)diphenylphosphine oxide (3d)



3d

Following the general procedure, compound **3d** was obtained as a colorless oil in 64% yield; mp = 104-106 °C; R_f = 0.47 (PE:*i*PrOH = 5:1);

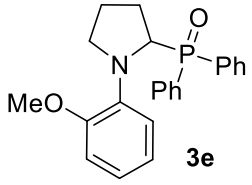
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17-8.00 (m, 1H), 7.75-7.59 (m, 1H), 7.53-7.42 (m, 1H), 7.42-7.35 (m, 1H), 7.34-7.26 (m, 1H), 7.26-7.14 (m, 1H), 7.03-6.93 (m, 1H), 6.76-6.51 (m, 1H), 4.90-4.70 (m, 1H), 3.87-3.57 (m, 1H), 3.14-2.74 (m, 1H), 2.74-2.38 (m, 1H), 2.37-2.12 (m, 1H), 1.93-1.63 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 148.6 (d, J_{C-P} = 2.2 Hz), 133.4, 132.3 (d, J_{C-P} = 8.3 Hz), 132.2 (d, J_{C-P} = 92.9 Hz), 131.5 (d, J_{C-P} = 2.7 Hz), 131.3 (d, J_{C-P} = 2.7 Hz), 131.2 (d, J_{C-P} = 8.9 Hz), 129.9 (d, J_{C-P} = 94.9 Hz), 128.0 (d, J_{C-P} = 11.1 Hz), 127.6, 124.2, 123.0, 120.2, 60.0 (d, J_{C-P} = 90.0 Hz), 56.1 (d, J_{C-P} = 4.5 Hz), 27.4, 24.9 (d, J_{C-P} = 3.1 Hz);

^{31}P NMR (162 MHz, $CDCl_3$): δ 29.5.

HRMS (ESI) for $C_{22}H_{22}BrNOP$ $[M+H]^+$ calcd. 426.0617, found: 426.0618.

(1-(2-Methoxyphenyl)pyrrolidin-2-yl)diphenylphosphine oxide (3e)



3e

Following the general procedure, compound **3e** was obtained as a yellow oil in 82% yield; R_f = 0.47 (PE:*i*PrOH = 5:1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79-7.72 (m, 1H), 7.72-7.66 (m, 1H), 7.41-7.33 (m, 1H), 7.33-7.28 (m, 1H), 7.25-7.17 (m, 1H), 6.87-6.79 (m, 1H), 6.75-6.66 (m, 1H), 6.66-6.59 (m, 1H), 6.45-6.28 (m, 1H), 5.12-4.98 (m, 1H), 3.84-3.70 (m, 1H), 3.66 (s, 1H), 3.16-2.98 (m, 1H), 2.47-2.33 (m, 1H), 2.33-2.19 (m, 1H), 1.92-1.72 (m, 1H);

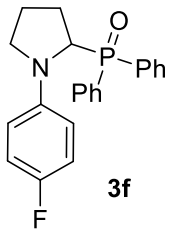
^{13}C NMR (151 MHz, $CDCl_3$): δ 152.4, 137.5, 133.4 (d, J_{C-P} = 88.6 Hz), 131.9 (d, J_{C-P} = 8.7 Hz), 131.2 (d, J_{C-P} = 1.6 Hz), 131.0 (d, J_{C-P} = 8.6 Hz), 130.9 (d, J_{C-P} = 2.9 Hz),

128.2 (d, $J_{C\text{-}P}$ = 10.8 Hz), 127.5 (d, $J_{C\text{-}P}$ = 11.0 Hz), 122.5, 121.5, 120.5, 110.6, 58.5 (d, $J_{C\text{-}P}$ = 81.4 Hz), 54.9, 53.5, 27.3, 24.1.

^{31}P NMR (243 MHz, $CDCl_3$): δ 30.2.

HRMS (ESI) for $C_{23}H_{25}NO_2P$ $[M+H]^+$ calcd. 378.1617, found: 378.1616.

(1-(4-Fluorophenyl)pyrrolidin-2-yl)diphenylphosphine oxide (3f)



3f

Following the general procedure, compound **3f** was obtained as a white solid in 96% yield; mp = 208-210 °C; R_f = 0.47 (PE:*i*PrOH = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.80 (m, 1H), 7.81-7.68 (m, 1H), 7.62-7.50 (m, 1H), 7.50-7.37 (m, 2H), 7.38-7.22 (m, 1H), 6.70-6.56 (m, 1H), 6.41-6.21 (m, 1H), 4.60 (t, J = 9.0 Hz, 1H), 3.61 (td, J = 8.4, 1.7 Hz, 1H), 3.14 (td, J = 9.7, 2.8 Hz, 1H), 2.51-2.29 (m, 1H), 2.27-2.04 (m, 1H), 2.04-1.78 (m, 1H);

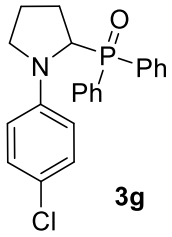
^{13}C NMR (101 MHz, $CDCl_3$): δ 155.1 (d, $J_{C\text{-}F}$ = 236.3 Hz), 144.3 (d, $J_{C\text{-}F}$ = 1.0 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.0 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.0 Hz), 131.68 (d, $J_{C\text{-}P}$ = 8.0 Hz), 131.6 (d, $J_{C\text{-}P}$ = 8.1 Hz), 131.5 (d, $J_{C\text{-}P}$ = 92.9 Hz), 131.4 (d, $J_{C\text{-}P}$ = 89.9 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.1 Hz), 128.2 (d, $J_{C\text{-}P}$ = 11.1 Hz), 114.7 (d, $J_{C\text{-}F}$ = 22.2 Hz), 113.8 (t, $J_{C\text{-}F}$ = 7.1 Hz), 59.6 (d, $J_{C\text{-}P}$ = 87.9 Hz), 51.3, 27.7, 24.2;

^{31}P NMR (162 MHz, $CDCl_3$): δ 27.5;

^{19}F NMR (376 MHz, $CDCl_3$): δ -128.8.

HRMS (ESI) for $C_{22}H_{22}FNOP$ $[M+H]^+$ calcd. 366.1418, found: 366.1415.

(1-(4-Chlorophenyl)pyrrolidin-2-yl)diphenylphosphine oxide (3g)



3g

Following the general procedure, compound **3c** was obtained as a white solid in 96% yield; mp = 200-202 °C; R_f = 0.48 (PE:iPrOH = 5:1);

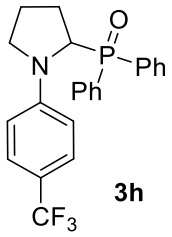
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97-7.84 (m, 1H), 7.81-7.67 (m, 1H), 7.66-7.54 (m, 1H), 7.55-7.47 (m, 1H), 7.46-7.40 (m, 1H), 7.39-7.28 (m, 1H), 7.00-6.65 (m, 1H), 6.25 (d, J = 9.0 Hz, 1H), 4.61 (t, J = 8.7 Hz, 1H), 3.67-3.53 (m, 1H), 3.23-3.11 (m, 1H), 2.53-2.35 (m, 1H), 2.34-2.06 (m, 1H), 2.04-1.82 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.3, 132.0 (d, J_{C-P} = 2.6 Hz), 131.9 (d, J_{C-P} = 2.7 Hz), 131.7 (d, J_{C-P} = 12.8 Hz), 131.6 (d, J_{C-P} = 12.3 Hz), 131.3 (d, J_{C-P} = 91.9 Hz), 128.7 (d, J_{C-P} = 10.9 Hz), 128.3 (d, J_{C-P} = 11.0 Hz), 128.1, 121.4, 114.1, 60.5 (d, J_{C-P} = 86.0 Hz), 50.8, 27.3 (d, J_{C-P} = 97.1 Hz), 24.1;

^{31}P NMR (162 MHz, $CDCl_3$): δ 27.6.

HRMS (ESI) for $C_{22}H_{22}ClNOP$ $[M+H]^+$ calcd. 382.1122, found: 382.1122.

Diphenyl(1-(4-(trifluoromethyl)phenyl)pyrrolidin-2-yl)phosphine oxide (3h)



3h

Following the general procedure, compound **3h** was obtained as a white solid in 66% yield; mp = 224-226 °C; R_f = 0.44 (PE:iPrOH = 5:1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97-7.83 (m, 1H), 7.74-7.65 (m, 1H), 7.64-7.54 (m, 1H), 7.56-7.49 (m, 1H), 7.45-7.37 (m, 1H), 7.35-7.28 (m, 1H), 7.11 (d, J = 18.4 Hz, 1H), 6.34 (d, J = 8.7 Hz, 1H), 4.72 (t, J = 9.0 Hz, 1H), 3.69-3.60 (m, 1H), 3.31-3.17 (m, 1H), 2.52-2.35 (m, 1H), 2.29-2.05 (m, 1H), 2.01-1.83 (m, 1H);

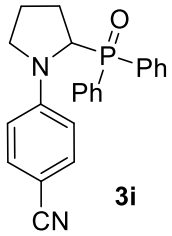
^{13}C NMR (151 MHz, $CDCl_3$): δ 149.7, 132.2 (d, J_{C-P} = 2.1 Hz), 132.1 (d, J_{C-P} = 2.7 Hz), 131.7 (d, J_{C-P} = 9.1 Hz), 131.6 (d, J_{C-P} = 9.1 Hz), 131.4 (d, J_{C-P} = 92.1 Hz), 131.2 (d, J_{C-P} = 89.1 Hz), 128.8 (d, J_{C-P} = 10.9 Hz), 128.4 (d, J_{C-P} = 11.0 Hz), 125.7 (q, J_{C-F} = 3.4 Hz), 124.8 (d, J_{C-F} = 270.3 Hz), 112.4, 60.1 (d, J_{C-P} = 83.9 Hz), 50.3, 27.9, 24.0;

^{31}P NMR (243 MHz, $CDCl_3$): δ 27.9;

^{19}F NMR (565 MHz, $CDCl_3$): δ -61.1.

HRMS (ESI): for $C_{23}H_{22}F_3NOP$ $[M+H]^+$ calcd.416.1386, found: 416.1385.

4-(2-(Diphenylphosphoryl)pyrrolidin-1-yl)benzonitrile (3i)



3i

Following the general procedure, compound **3i** was obtained as a white solid in 61% yield; mp = 260-262 °C; R_f = 0.22 (PE:*i*PrOH = 5:1);

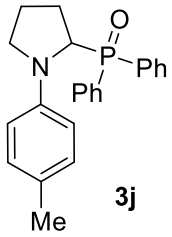
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.85 (m, 1H), 7.73-7.59 (m, 2H), 7.59-7.51 (m, 1H), 7.47-7.38 (m, 1H), 7.36-7.28 (m, 1H), 7.14 (d, J = 8.9 Hz, 1H), 6.29 (d, J = 8.9 Hz, 1H), 4.72 (t, J = 8.8 Hz, 1H), 3.76-3.54 (m, 1H), 3.41-3.10 (m, 1H), 2.51-2.37 (m, 1H), 2.34-2.08 (m, 1H), 2.03-1.93 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 150.0, 132.7, 132.4 (d, J_{C-P} = 2.7 Hz), 132.2 (d, J_{C-P} = 2.8 Hz), 131.6 (d, J_{C-P} = 3.3 Hz), 131.5 (d, J_{C-P} = 2.4 Hz), 131.3 (d, J_{C-P} = 93.7 Hz), 130.7 (d, J_{C-P} = 90.4 Hz), 128.9 (d, J_{C-P} = 11.0 Hz), 128.5 (d, J_{C-P} = 11.2 Hz), 120.4, 112.7, 98.1, 59.7 (d, J_{C-P} = 82.1 Hz), 50.0, 27.8, 23.8;

^{31}P NMR (162 MHz, $CDCl_3$): δ 28.0.

HRMS (ESI) for $C_{23}H_{22}N_2OP$ $[M+H]^+$ calcd.373.1464, found: 373.1464.

Diphenyl(1-(p-tolyl)pyrrolidin-2-yl)phosphine oxide (3j)



3j

Following the general procedure, compound **3j** was obtained as a white solid in 82% yield; mp = 78-80 °C; R_f = 0.46 (PE:*i*PrOH = 5:1);

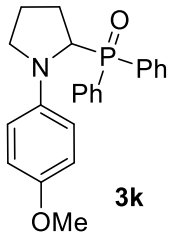
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.84 (m, 1H), 7.84-7.72 (m, 1H), 7.59-7.48 (m, 1H), 7.46-7.37 (m, 1H), 7.35-7.24 (m, 1H), 6.75 (d, J = 8.3 Hz, 1H), 6.27 (d, J = 8.4 Hz, 1H), 4.62 (t, J = 8.7 Hz, 1H), 3.73-3.43 (m, 1H), 3.30-2.75 (m, 1H), 2.55-2.36 (m, 1H), 2.23-1.97 (m, 2H), 1.94-1.73 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 145.7, 131.82 (d, J_{C-P} = 8.7 Hz), 131.79 (d, J_{C-P} = 89.3 Hz), 131.6 (d, J_{C-P} = 7.7 Hz), 131.5 (d, J_{C-P} = 8.1 Hz), 131.4 (d, J_{C-P} = 92.9 Hz), 128.8, 128.4 (d, J_{C-P} = 11.1 Hz), 128.1 (d, J_{C-P} = 10.1 Hz), 125.8, 113.1, 60.7 (d, J_{C-P} = 87.7 Hz), 51.1, 27.5, 26.7, 24.1, 20.0;

^{31}P NMR (162 MHz, $CDCl_3$): δ 27.30.

HRMS (ESI) for $C_{23}H_{25}NOP$ $[M+H]^+$ calcd. 362.1668, found: 362.1666.

(1-(4-Methoxyphenyl)pyrrolidin-2-yl)diphenylphosphine oxide (3k)



3k

Following the general procedure, compound **3k** was obtained as a white solid in 49% yield; mp = 160-162 °C; R_f = 0.76 (PE:*i*PrOH = 5:1);

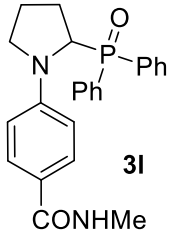
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.84 (m, 1H), 7.84-7.73 (m, 1H), 7.57-7.48 (m, 1H), 7.49-7.40 (m, 1H), 7.34 (M, 1H), 6.55 (d, J = 9.0 Hz, 1H), 6.34 (d, J = 8.9 Hz, 1H), 4.59 (t, J = 8.5 Hz, 1H), 3.67 (s, 1H), 3.64-3.51 (m, 1H), 3.22-3.04 (m, 1H), 2.51-2.34 (m, 1H), 2.15 (m, 1H), 1.95-1.76 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 151.5, 142.7, 132.0 (d, J_{C-P} = 89.5 Hz), 131.9 (d, J_{C-P} = 8.5 Hz), 131. (d, J_{C-P} = 2.7 Hz), 131.74, 131.7 (d, J_{C-P} = 8.2 Hz), 131.6 (d, J_{C-P} = 92.2 Hz), 128.5 (d, J_{C-P} = 10.8 Hz), 128.2 (d, J_{C-P} = 10.9 Hz), 114.6, 114.1, 61.1 (d, J_{C-P} = 88.5 Hz), 55.7, 51.9, 27.7, 24.4;

^{31}P NMR (162 MHz, $CDCl_3$): δ 27.2.

HRMS (ESI) for $C_{23}H_{25}NO_2P$ $[M+H]^+$ calcd. 378.1617, found: 378.1616.

4-(2-(Diphenylphosphoryl)pyrrolidin-1-yl)-N-methylbenzamide (3l)



3l

Following the general procedure, compound **3l** was obtained as a white solid in 47% yield; mp = 236-238 °C; R_f = 0.27 (PE:*i*PrOH = 5:1);

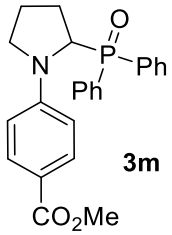
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95-7.81 (m, 1H), 7.76-7.66 (m, 1H), 7.63-7.53 (m, 1H), 7.53-7.46 (m, 1H), 7.46-7.38 (m, 1H), 7.33-7.22 (m, 1H), 6.40 (s, 1H), 6.27 (d, *J* = 8.7 Hz, 1H), 4.72 (t, *J* = 8.9 Hz, 1H), 3.61 (t, *J* = 8.0 Hz, 1H), 3.32-3.17 (m, 1H), 2.92 (t, *J* = 12.0 Hz, 1H), 2.50-2.37 (m, 1H), 2.24-1.99 (m, 1H), 1.92 (d, *J* = 4.8 Hz, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.9, 149.8, 132.2 (d, J_{C-P} = 2.0 Hz), 132.1 (d, J_{C-P} = 2.3 Hz), 131.7 (d, J_{C-P} = 14.9 Hz), 131.6 (d, J_{C-P} = 14.2 Hz), 131.34 (d, J_{C-P} = 86.1 Hz), 131.29 (d, J_{C-P} = 87.6 Hz), 128.8 (d, J_{C-P} = 10.9 Hz), 128.4 (d, J_{C-P} = 11.0 Hz), 127.8, 122.2, 112.3, 60.1 (d, J_{C-P} = 84.6 Hz), 50.4, 27.9, 26.6, 24.0;

^{31}P NMR (243 MHz, $CDCl_3$) δ 27.98.

HRMS (ESI) for $C_{24}H_{26}N_2O_2P$ $[M+H]^+$ calcd. 405.1726, found: 405.1728.

Methyl 4-(2-(diphenylphosphoryl)pyrrolidin-1-yl)benzoate (3m)



Following the general procedure, compound **3m** was obtained as a white solid in 52% yield; mp = 254-256 °C; R_f = 0.33 (PE:*i*PrOH = 5:1);

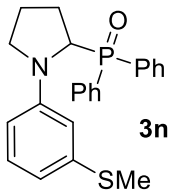
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01-7.82 (m, 1H), 7.83-7.71 (m, 1H), 7.71-7.63 (m, 1H), 7.58 (d, *J* = 8.9 Hz, 1H), 7.56-7.49 (m, 1H), 7.45-7.32 (m, 1H), 7.32-7.28 (m, 1H), 6.26 (d, *J* = 8.9 Hz, 1H), 4.74 (t, *J* = 8.7 Hz, 1H), 3.81 (s, 1H), 3.67 (t, *J* = 8.0 Hz, 1H), 3.39-3.19 (m, 1H), 2.55-2.33 (m, 1H), 2.33-2.05 (m, 1H), 2.05-1.81 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.2, 150.8, 132.3 (d, J_{C-P} = 2.1 Hz), 132.1 (d, J_{C-P} = 2.6 Hz), 131.7 (d, J_{C-P} = 18.5 Hz), 131.6 (d, J_{C-P} = 17.7 Hz), 131.2 (d, J_{C-P} = 93.6 Hz), 131.1 (d, J_{C-P} = 90.6 Hz), 130.5, 128.9 (d, J_{C-P} = 10.9 Hz), 128.4 (d, J_{C-P} = 11.0 Hz), 117.7, 112.0, 60.0 (d, J_{C-P} = 83.3 Hz), 51.4, 50.2, 27.8, 23.9;

^{31}P NMR (162 MHz, $CDCl_3$): δ 28.0.

HRMS (ESI) for $C_{24}H_{25}NO_3P$ $[M+H]^+$ calcd.406.1567, found: 406.1566.

(1-(3-(Methylthio)phenyl)pyrrolidin-2-yl)diphenylphosphine oxide (3n)



Following the general procedure, compound **3n** was obtained as a white solid in 82% yield; mp = 170-172 °C; R_f = 0.52 (PE:*i*PrOH = 5:1);

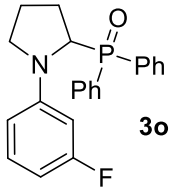
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95-7.84 (m, 1H), 7.81-7.71 (m, 1H), 7.59-7.52 (m, 1H), 7.51-7.45 (m, 1H), 7.45-7.39 (m, 1H), 7.38-7.29 (m, 1H), 6.85 (t, *J* = 8.0 Hz, 1H), 6.46 (d, *J* = 8.1 Hz, 1H), 6.24 (s, 1H), 6.16 (dd, *J* = 8.3, 2.2 Hz, 1H), 4.66 (t, *J* = 8.9 Hz, 1H), 3.66-3.54 (m, 1H), 3.33-3.11 (m, 1H), 2.53-2.38 (m, 1H), 2.29 (s, 1H), 2.21-2.05 (m, 1H), 2.05-1.94 (m, 1H), 1.93-1.76 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 147.9, 138.4, 131.8 (d, J_{C-P} = 20.7 Hz), 131.7 (d, J_{C-P} = 8.7 Hz), 131.6 (d, J_{C-P} = 86.1 Hz), 131.5 (d, J_{C-P} = 8.5 Hz), 131.4 (d, J_{C-P} = 93.6 Hz), 128.7, 128.6 (d, J_{C-P} = 10.7 Hz), 128.2 (d, J_{C-P} = 10.9 Hz), 115.1, 111.5, 110.4, 60.4 (d, J_{C-P} = 85.9 Hz), 50.7, 27.6, 24.0, 15.7;

^{31}P NMR (162 MHz, $CDCl_3$): δ 27.1.

HRMS (ESI) for $C_{23}H_{25}NOPS$ $[M+H]^+$ calcd. 394.1389, found: 394.1390.

(1-(3-Fluorophenyl)pyrrolidin-2-yl)diphenylphosphine oxide (3o)



3o

Following the general procedure, compound **3o** was obtained as a white solid in 75% yield; mp = 180-182 °C; R_f = 0.58 (PE:*i*PrOH = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01-7.85 (m, 1H), 7.79-7.69 (m, 1H), 7.63-7.55 (m, 1H), 7.55-7.46 (m, 1H), 7.46-7.39 (m, 1H), 7.37-7.29 (m, 1H), 6.90-6.75 (m, 1H), 6.39-6.16 (m, 1H), 6.08 (d, J = 8.3 Hz, 1H), 5.98 (d, J = 12.6 Hz, 1H), 4.75-4.49 (m, 1H), 3.76-3.50 (m, 1H), 3.29-3.02 (m, 1H), 2.57-2.31 (m, 1H), 2.30-1.99 (m, 1H), 1.99-1.76 (m, 1H);

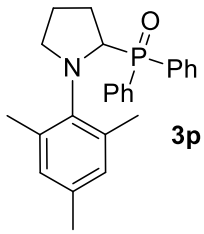
^{13}C NMR (101 MHz, $CDCl_3$): δ 163.3 (d, J_{C-F} = 243.4 Hz), 149.3 (d, J_{C-F} = 11.1 Hz), 132.1 (d, J_{C-P} = 3.0 Hz), 131.9 (dd, J_{C-P} = 3.0 Hz), 131.7 (d, J_{C-P} = 8.1 Hz), 131.6 (d, J_{C-P} = 8.1 Hz), 131.38 (d, J_{C-P} = 93.9 Hz), 131.37 (d, J_{C-P} = 90.9 Hz), 129.4 (d, J_{C-F} = 10.1 Hz), 128.7 (d, J_{C-P} = 11.1 Hz), 128.3 (d, J_{C-P} = 11.1 Hz), 108.8 (d, J_{C-F} = 2.0 Hz), 103.2 (d, J_{C-F} = 21.2 Hz), 100.1 (t, J_{C-F} = 21.2 Hz), 60.4 (d, J_{C-P} = 85.8 Hz), 50.7, 27.7, 24.0;

^{31}P NMR (162 MHz, $CDCl_3$): δ 27.5;

^{19}F NMR (376 MHz, $CDCl_3$): δ -113.3.

HRMS (ESI) for $C_{22}H_{22}FNOP$ $[M+H]^+$ calcd. 366.1418, found: 366.1418.

(1-Mesitylpyrrolidin-2-yl)diphenylphosphine oxide (3p)



3p

Following the general procedure, compound **3p** was obtained as a yellow oil in 54% yield; R_f = 0.70 (PE:*i*PrOH = 5:1);

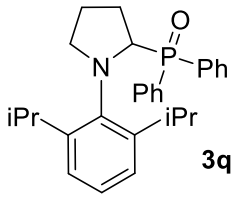
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71-7.62 (m, 1H), 7.61-7.49 (m, 1H), 7.45-7.36 (m, 1H), 7.36-7.24 (m, 2H), 7.16-7.04 (m, 1H), 6.74 (s, 1H), 6.39 (s, 1H), 4.64-4.50 (m, 1H), 3.48-3.33 (m, 1H), 3.14-2.89 (m, 1H), 2.44-2.32 (m, 1H), 2.31-2.17 (m, 2H), 2.15 (s, 1H), 2.01-1.87 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 142.5, 139.3, 134.6, 134.0, 133.6 (d, J_{C-P} = 86.9 Hz), 131.4 (d, J_{C-P} = 89.9 Hz), 131.1 (d, J_{C-P} = 8.6 Hz), 131.0, 130.8 (d, J_{C-P} = 34.9 Hz), 130.6 (d, J_{C-P} = 8.2 Hz), 129.6, 128.6, 128.2 (d, J_{C-P} = 10.5 Hz), 127.4 (d, J_{C-P} = 11.1 Hz), 60.5 (d, J_{C-P} = 92.1 Hz), 53.5 (d, J_{C-P} = 3.4 Hz), 27.4, 25.9, 20.5, 18.8, 18.5;

^{31}P NMR (162 MHz, $CDCl_3$): δ 28.1.

HRMS (ESI) for $C_{25}H_{29}NOP$ $[M+H]^+$ calcd. 390.1981, found: 390.1978.

(1-(2,6-Diisopropylphenyl)pyrrolidin-2-yl)diphenylphosphine oxide (3q)



3q

Following the general procedure, compound **3q** was obtained as a white solid in 50% yield; mp = 126-128 °C; R_f = 0.63 (PE:*i*PrOH = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.51 (m, 1H), 7.48-7.31 (m, 3H), 7.29-7.17 (m, 1H), 7.16-7.05 (m, 2H), 6.86-6.66 (m, 1H), 4.61-4.32 (m, 1H), 3.71-3.39 (m, 1H), 3.22-2.99 (m, 1H), 2.46-2.16 (m, 2H), 2.13-1.86 (m, 1H), 1.47 (d, J = 6.8 Hz, 1H), 1.22 (d, J = 6.8 Hz, 2H), 1.00 (d, J = 6.8 Hz, 1H), 0.34 (d, J = 6.8 Hz, 1H);

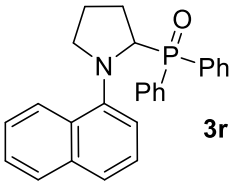
^{13}C NMR (101 MHz, $CDCl_3$): δ 150.6, 146.4, 143.5, 133.4 (d, J_{C-P} = 86.9 Hz), 132.3 (d, J_{C-P} = 91.9 Hz), 131.1 (d, J_{C-P} = 8.8 Hz), 130.9, 130.5 (d, J_{C-P} = 8.2 Hz), 128.4 (d,

J_{C-P} = 10.5 Hz), 127.9 (d, J_{C-P} = 11.1 Hz), 126.6, 124.5, 123.5, 62.3 (d, J_{C-P} = 91.4 Hz), 56.9 (d, J_{C-P} = 3.6 Hz), 28.1 (d, J_{C-P} = 9.6 Hz), 27.1 (d, J_{C-P} = 56.3 Hz), 26.2, 25.8, 23.7, 21.7;

^{31}P NMR (162 MHz, $CDCl_3$): δ 28.2.

HRMS (ESI) for $C_{28}H_{35}NOP$ $[M+H]^+$ calcd. 432.2451, found: 432.2448.

(1-(Naphthalen-1-yl)pyrrolidin-2-yl)diphenylphosphine oxide (3r)



3r

Following the general procedure, compound **3r** was obtained as white solid in 50% yield; mp = 160-162 °C; R_f = 0.49 (PE:*i*PrOH = 5:1);

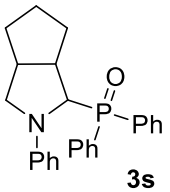
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.15-8.05 (m, 1H), 7.77-7.65 (m, 5H), 7.45-7.35 (m, 3H), 7.35-7.28 (m, 1H), 7.24-7.14 (m, 4H), 7.12-6.98 (m, 3H), 4.93-4.78 (m, 1H), 3.75-3.57 (m, 1H), 3.13-2.89 (m, 1H), 2.57-2.37 (m, 2H), 2.08-1.95 (m, 1H), 1.95-1.79 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 148.3 (d, J_{C-P} = 3.4 Hz), 134.5, 132.7 (d, J_{C-P} = 90.6 Hz), 131.5 (d, J_{C-P} = 8.6 Hz), 131.3, 131.0 (d, J_{C-P} = 8.7 Hz), 130.9 (d, J_{C-P} = 96.6 Hz), 130.2, 128.1 (d, J_{C-P} = 11.0 Hz), 127.7, 127.5 (d, J_{C-P} = 11.6 Hz), 125.6, 125.2, 125.0, 124.3, 123.5, 116.7, 61.1 (d, J_{C-P} = 91.0 Hz), 57.8, 26.9, 25.1;

^{31}P NMR (243 MHz, $CDCl_3$): δ 30.1.

HRMS (ESI) for $C_{26}H_{25}NOP$ $[M+H]^+$ calcd. 398.1668, found: 398.1665.

Diphenyl(2-phenyloctahydrocyclopenta[c]pyrrol-1-yl)phosphine oxide (3s)



3s

Following the general procedure, compound **3s** was obtained as a white solid in 74% yield; mp=212-214 °C; R_f = 0.58 (PE:*i*PrOH = 5:1); [1]

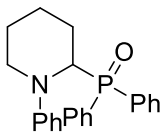
H NMR (400 MHz, $CDCl_3$): δ 7.97-7.83 (m, 1H), 7.72-7.62 (m, 1H), 7.58-7.52 (m, 1H), 7.51-7.43 (m, 1H), 7.40-7.30 (m, 1H), 7.30-7.23 (m, 1H), 6.95-6.82 (m, 1H), 6.48 (t, J = 7.2 Hz, 1H), 6.32 (d, J = 8.3 Hz, 1H), 4.68 (d, J = 9.4 Hz, 1H), 3.84 (t, J = 9.1 Hz, 1H), 3.08-2.98 (m, 1H), 2.98-2.88 (m, 1H), 2.82-2.63 (m, 1H), 2.03-1.92 (m, 1H), 1.88-1.74 (m, 1H), 1.74-1.55 (m, 1H), 1.56-1.41 (m, 1H), 1.41-1.25 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.3, 132.0 (d, J_{C-P} = 87.9 Hz), 131.8 (d, J_{C-P} = 90.9 Hz), 131.76 (d, J_{C-P} = 10.1 Hz), 131.73 (d, J_{C-P} = 20.2 Hz), 131.5 (d, J_{C-P} = 8.3 Hz), 128.7 (d, J_{C-P} = 10.7 Hz), 128.4, 128.1 (d, J_{C-P} = 11.0 Hz), 116.32, 113.1, 66.1 (d, J_{C-P} = 81.9 Hz), 57.0, 45.6 (d, J_{C-P} = 2.4 Hz), 42.0, 33.8 (d, J_{C-P} = 11.9 Hz), 32.6, 25.4;

^{31}P NMR (162 MHz, $CDCl_3$): δ 27.6.

HRMS (ESI) for $C_{25}H_{26}NOP$ $[M+H]^+$ calcd. 388.1825, found: 388.1825

Diphenyl(1-phenylpiperidin-2-yl)phosphine oxide (3t)



3t

Following the general procedure, compound **3t** was obtained as a white solid in 60% yield; mp = 168-170 °C; R_f = 0.60 (PE:*i*PrOH = 5:1);

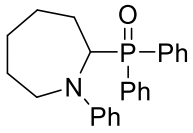
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04-7.81 (m, 1H), 7.78-7.63 (m, 1H), 7.60-7.42 (m, 2H), 7.38-7.28 (m, 1H), 7.28-7.18 (m, 1H), 7.11-7.04 (m, 1H), 6.74-6.52 (m, 1H), 4.78-4.35 (m, 1H), 4.20-3.74 (m, 1H), 3.71-3.42 (m, 1H), 2.50-2.31 (m, 1H), 2.03-1.78 (m, 1H), 1.76-1.52 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 150.4 (d, J_{C-P} = 5.8 Hz), 132.61 (d, J_{C-P} = 86.9 Hz), 132.5 (d, J_{C-P} = 96.0 Hz), 131.5 (d, J_{C-P} = 2.7 Hz), 131.2 (d, J_{C-P} = 2.7 Hz), 131.0 (d, J_{C-P} = 9.2 Hz), 130.9 (d, J_{C-P} = 8.3 Hz), 128.9, 128.6 (d, J_{C-P} = 10.7 Hz), 128.0 (d, J_{C-P} = 11.3 Hz), 118.0, 115.8, 56.5 (d, J_{C-P} = 77.2 Hz), 45.9, 23.9 (d, J_{C-P} = 4.2 Hz), 23.5 (d, J_{C-P} = 1.5 Hz), 21.0 (d, J_{C-P} = 1.7 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ 33.6.

HRMS (ESI) for $C_{23}H_{25}NOP$ $[M+H]^+$ calcd. 362.1668, found: 362.1671.

Diphenyl(1-phenylazepan-2-yl)phosphine oxide (3u)



3u

Following the general procedure, compound **3u** was obtained as a white solid in 96% yield; mp = 188-190 °C; R_f = 0.60 (PE:*i*PrOH = 5:1);

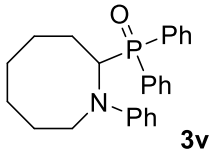
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.22 (m, 2H), 6.80 (t, J = 7.3 Hz, 1H), 6.60 (d, J = 7.8 Hz, 2H), 6.19 (s, 1H), 3.85-3.81 (m, 1H), 3.60 (d, J = 3.4 Hz, 1H), 2.95 (t, J = 8.2 Hz, 1H), 2.87-2.78 (m, 1H), 2.74-2.68 (m, 1H), 2.03-1.97 (m, 1H), 1.83-1.72 (m, 2H), 1.66-1.57 (m, 3H), 1.27 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5 (d, J_{C-P} = 2.0 Hz), 131.7 (d, J_{C-P} = 2.6 Hz), 131.6 (d, J_{C-P} = 85.8 Hz), 131.5 (d, J_{C-P} = 2.1 Hz), 131.4 (d, J_{C-P} = 2.7 Hz), 131.2 (d, J_{C-P} = 9.3 Hz), 131.0 (d, J_{C-P} = 8.7 Hz), 128.7, 128.5 (d, J_{C-P} = 10.7 Hz), 127.8 (d, J_{C-P} = 11.3 Hz), 115.8, 111.8, 56.2 (d, J_{C-P} = 80.6 Hz), 45.3, 29.4, 28.1 (d, J_{C-P} = 4.7 Hz), 25.5 (d, J_{C-P} = 3.2 Hz), 25.2 (d, J_{C-P} = 11.7 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.7.

HRMS (ESI) for $C_{24}H_{27}NOP$ $[M+H]^+$ calcd. 376.1825, found: 376.1824.

Diphenyl(1-phenylazocan-2-yl)phosphine oxide (3v)



3v

Following the general procedure, compound **3v** was obtained as a white solid in 73% yield; mp = 204-206 °C; R_f = 0.61 (PE:*i*PrOH = 5:1);

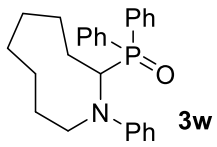
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.82 (m, 1H), 7.62-7.44 (m, 3H), 7.25 -7.17 (m, 1H), 7.14-7.07 (m, 1H), 7.05-6.97 (m, 1H), 6.62-6.45 (m, 2H), 4.68 (dt, J = 12.1, 2.8 Hz, 1H), 4.03-3.78 (m, 1H), 3.58 (d, J = 15.6 Hz, 1H), 2.61-2.38 (m, 1H), 1.94-1.68 (m, 1H), 1.58-1.40 (m, 3H), 1.39-1.23 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 132.2 (d, $J_{C\text{-}P}$ = 81.8 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.2 (d, $J_{C\text{-}P}$ = 2.7 Hz), 130.9 (d, $J_{C\text{-}P}$ = 9.9 Hz), 130.7 (d, $J_{C\text{-}P}$ = 8.7 Hz), 128.8, 128.7 (d, $J_{C\text{-}P}$ = 10.6 Hz), 127.6 (d, $J_{C\text{-}P}$ = 11.3 Hz), 116.0, 113.1, 58.2 (d, $J_{C\text{-}P}$ = 73.4 Hz), 43.7, 26.9 (d, $J_{C\text{-}P}$ = 13.4 Hz), 25.6, 24.89, 24.4, 23.7 (d, $J_{C\text{-}P}$ = 5.0 Hz);

^{31}P NMR (162 MHz, $CDCl_3$) δ 32.6.

HRMS (ESI) for $C_{25}H_{29}NOP$ $[M+H]^+$ calcd. 390.1981, found: 390.1979.

Diphenyl(1-phenylazonan-2-yl)phosphine oxide (3w)



3w

Following the general procedure, compound **3w** was obtained as a white solid in 36% yield; mp = 178-180 °C; R_f = 0.67 (PE:*i*PrOH = 5:1);

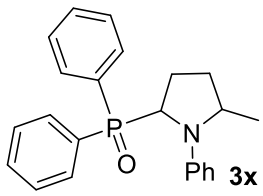
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.78 (m, 2H), 7.59-7.44 (m, 5H), 7.30-7.19 (m, 1H), 7.14-7.01 (m, 4H), 6.64-6.50 (m, 3H), 4.64 (d, J = 12.4 Hz, 1H), 3.89 (t, J = 13.2 Hz, 1H), 3.36 (d, J = 15.0 Hz, 1H), 2.48-2.27 (m, 1H), 1.86-1.55 (m, 2H), 1.51-1.38 (m, 3H), 1.38-1.25 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 148.2, 132.9 (d, $J_{C\text{-}P}$ = 82.8 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.5 (d, $J_{C\text{-}P}$ = 94.9 Hz), 131.2 (d, $J_{C\text{-}P}$ = 2.7 Hz), 130.9 (d, $J_{C\text{-}P}$ = 10.0 Hz), 130.4 (d, $J_{C\text{-}P}$ = 8.7 Hz), 128.8, 128.7 (d, $J_{C\text{-}P}$ = 10.7 Hz), 127.7 (d, $J_{C\text{-}P}$ = 11.3 Hz), 116.8, 114.3, 61.0 (d, $J_{C\text{-}P}$ = 68.0 Hz), 42.7, 25.6, 24.3, 23.6, 23.5 (d, $J_{C\text{-}P}$ = 4.8 Hz), 22.6, 22.1.

^{31}P NMR (162 MHz, $CDCl_3$): δ 32.4.

HRMS (ESI) for $C_{26}H_{31}NOP$ $[M+H]^+$ calcd. 404.2138, found: 404.2135.

(5-methyl-1-phenylpyrrolidin-2-yl)diphenylphosphine oxide (3x)



3x

Following the general procedure, compound **3x** was obtained as a white solid in 71% yield (dr = 2.4:1); mp = 120-122 °C; R_f = 0.31 (PE:iPrOH = 10:1);

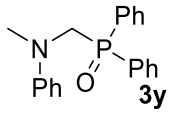
Major：**^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.96-7.91 (m, 2H), 7.74-7.70 (m, 2H), 7.61-7.52 (m, 3H), 7.72-7.67 (m, 1H), 7.32-7.25 (m, 2H), 6.98-6.94 (m, 2H), 6.61-6.57 (m, 1H), 6.40-6.38 (m, 2H), 4.64-4.60 (m, 1H), 3.82-3.79 (m, 1H), 2.30-2.23 (m, 1H), 2.12-1.98 (m, 3H), 1.43 (d, *J*=6.0 Hz, 3H); **minor**: **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.84-7.79 (m, 2H), 7.65-7.60 (m, 2H), 7.50-7.46 (m, 1H), 7.43-7.35 (m, 3H), 7.29-7.24 (m, 2H), 6.85-6.81 (m, 2H), 6.46-6.41 (m, 3H), 4.89-4.84 (m, 1H), 4.26-4.19 (m, 1H), 2.49-2.28 (m, 2H), 2.16-2.08 (m, 1H), 1.58-1.53 (m, 1H), 1.01 (d, *J*=6.0 Hz, 3H);

Major: ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.0 (d, J_{C-P} = 1.5 Hz), 131.94 (d, J_{C-P} = 93.5 Hz), 131.92 (d, J_{C-P} = 2.6 Hz), 131.87 (d, J_{C-P} = 2.4 Hz), 131.79, 131.7 (d, J_{C-P} = 2.6 Hz), 131.1 (d, J_{C-P} = 89.2 Hz), 128.6 (d, J_{C-P} = 10.8 Hz), 128.4, 128.2 (d, J_{C-P} = 10.8 Hz), 117.2, 113.5, 63.7 (d, J_{C-P} = 87.9 Hz), 57.8, 33.0, 27.1 (d, J_{C-P} = 1.8 Hz), 20.7; **Minor: ^{13}C NMR (101 MHz, $CDCl_3$):** δ 145.1, 132.5 (d, J_{C-P} = 87.7 Hz), 131.9 (d, J_{C-P} = 8.7 Hz), 131.6 (d, J_{C-P} = 2.5 Hz), 131.55 (d, J_{C-P} = 2.5 Hz), 131.47 (d, J_{C-P} = 90.9 Hz), 131.46 (d, J_{C-P} = 8.4 Hz), 128.4 (d, J_{C-P} = 10.9 Hz), 128.2, 127.9 (d, J_{C-P} = 10.9 Hz), 116.8, 58.9 (d, J_{C-P} = 81.1 Hz), 55.1, 31.5, 25.3, 17.8 (d, J_{C-P} = 3.0 Hz);

Major: ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.8; **Minor: ^{31}P NMR (162 MHz, $CDCl_3$)** δ 26.9.

HRMS (ESI) for $C_{23}H_{25}NOP$ $[M+H]^+$ calcd. 362.1668, found: 362.1665.

((methyl(phenyl)amino)methyl)diphenylphosphine oxide (3y)



3y

Following the general procedure, compound **3y** was obtained as a white solid in 37% yield; mp = 110-112 °C; R_f = 0.24 (PE:*i*PrOH = 10:1);

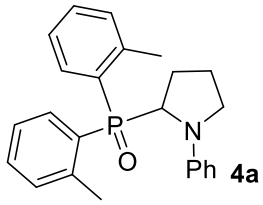
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83-7.80 (m, 4H), 7.54-7.52 (m, 2H), 7.47-7.44 (m, 4H), 7.14-7.12 (m, 2H), 6.72-6.69 (m, 3H), 4.19 (d, *J* = 3.6 Hz, 2H), 2.93 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 149.9 (d, J_{C-P} = 3 Hz), 132.0 (d, J_{C-P} = 2.1 Hz) 131.6 (d, J_{C-P} = 96.0 Hz), 131.3 (d, J_{C-P} = 9.0 Hz), 128.9, 128.6 (d, J_{C-P} = 10.5 Hz), 117.8, 113.4, 55.3 (d, J_{C-P} = 82.5 Hz), 39.9.

^{31}P NMR (243 MHz, $CDCl_3$): δ 32.4.

HRMS (ESI) for $C_{20}H_{21}NOP$ $[M+H]^+$ calcd. 322.1355, found: 322.1353.

(1-Phenylpyrrolidin-2-yl)di-o-tolylphosphine oxide (4a)



4a

Following the general procedure, compound **4a** was obtained as a white solid in 47% yield; mp = 138-140 °C; R_f = 0.68 (PE:*i*PrOH = 5:1);

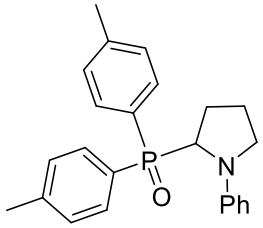
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63-7.51 (m, 1H), 7.49-7.40 (m, 1H), 7.34-7.26 (m, 2H), 7.23-7.14 (m, 2H), 7.14-7.01 (m, 1H), 6.96-6.87 (m, 3H), 6.51 (t, *J* = 7.2 Hz, 1H), 6.38 (d, *J* = 8.2 Hz, 2H), 5.06-4.81 (m, 1H), 3.69 (t, *J* = 8.5 Hz, 1H), 3.32-3.17 (m, 1H), 2.58-2.50 (m, 1H), 2.47 (d, *J* = 10.2 Hz, 5H), 2.41-2.23 (m, 2H), 2.01-1.85 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.6, 144.5 (d, J_{C-P} = 7.0 Hz), 144.1 (d, J_{C-P} = 5.8 Hz), 132.6 (d, J_{C-P} = 9.1 Hz), 131.9 (d, J_{C-P} = 10.1 Hz), 131.7 (d, J_{C-P} = 2.3 Hz), 131.5 (d, J_{C-P} = 2.6 Hz), 131.4 (d, J_{C-P} = 12.1 Hz), 131.2 (d, J_{C-P} = 10.1 Hz), 131.12 (d, J_{C-P} = 88.9 Hz), 131.11 (d, J_{C-P} = 86.9 Hz), 128.2, 125.1 (d, J_{C-P} = 7.1 Hz), 125.0 (d, J_{C-P} = 8.2 Hz), 116.4, 112.8, 58.9 (d, J_{C-P} = 86.9 Hz), 50.5, 28.9, 24.0, 21.6 (d, J_{C-P} = 3.9 Hz), 21.2 (d, J_{C-P} = 2.9 Hz);

^{31}P NMR (162 MHz, $CDCl_3$): δ 34.9.

HRMS (ESI) for $C_{24}H_{27}NOP$ $[M+H]^+$ calcd. 376.1825, found:376.1824.

(1-Phenylpyrrolidin-2-yl)di-p-tolylphosphine oxide (4b)



4b

Following the general procedure, compound **4b** was obtained as a white solid in 59% yield; mp = 172-174 °C; R_f = 0.58 (PE:*i*PrOH = 5:1);

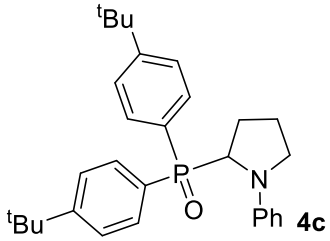
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82-7.69 (m, 1H), 7.70-7.60 (m, 1H), 7.30-7.20 (m, 1H), 7.17-7.08 (m, 1H), 7.00-6.90 (m, 1H), 6.55 (t, *J* = 7.2 Hz, 1H), 6.36 (d, *J* = 8.2 Hz, 1H), 4.62 (t, *J* = 8.5 Hz, 1H), 3.67-3.44 (m, 1H), 3.19 (td, *J* = 9.7, 2.7 Hz, 1H), 2.50-2.42 (m, 1H), 2.40 (s, 1H), 2.31 (s, 1H), 2.18-2.03 (m, 1H), 2.03-1.81 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 147.9, 142.2 (d, J_{C-P} = 2.5 Hz), 142.1 (d, J_{C-P} = 2.3 Hz), 131.9 (d, J_{C-P} = 8.8 Hz), 131.7 (d, J_{C-P} = 8.7 Hz), 129.3 (d, J_{C-P} = 11.0 Hz), 128.9 (d, J_{C-P} = 11.1 Hz), 128.7 (d, J_{C-P} = 92.2 Hz), 128.4, 128.4 (d, J_{C-P} = 94.9 Hz), 116.6, 113.2, 60.6 (d, J_{C-P} = 86.9 Hz), 50.8, 27.7, 24.1, 21.5 (d, J_{C-P} = 13.1 Hz);

^{31}P NMR (162 MHz, $CDCl_3$): δ 27.7.

HRMS (ESI) for $C_{24}H_{26}NOP$ $[M+H]^+$ calcd. 376.1825, found:376.1827.

Bis(4-(tert-butyl)phenyl)(1-phenylpyrrolidin-2-yl)phosphine oxide (4c)



4c

Following the general procedure, compound **4c** was obtained as a white solid in 82% yield; mp = 240-242 °C; R_f = 0.68 (PE:*i*PrOH = 5:1);

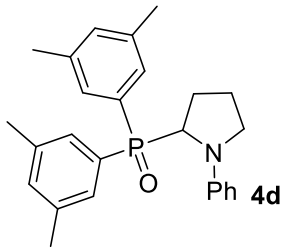
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.73 (m, 1H), 7.73-7.60 (m, 1H), 7.48 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.31 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.88 (t, *J* = 7.9 Hz, 1H), 6.50 (t, *J* = 7.2 Hz, 1H), 6.29 (d, *J* = 8.2 Hz, 1H), 4.62 (t, *J* = 8.8 Hz, 1H), 3.64 (t, *J* = 7.7 Hz, 1H), 3.45-2.95 (m, 1H), 2.58-2.33 (m, 1H), 2.29-1.94 (m, 1H), 1.94-1.78 (m, 1H), 1.33 (s, 4H), 1.25 (s, 4H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 155.3 (d, $J_{C\text{-}P}$ = 2.7 Hz), 155.2 (d, $J_{C\text{-}P}$ = 2.8 Hz), 147.8, 131.8 (d, $J_{C\text{-}P}$ = 9.0 Hz), 131.6 (d, $J_{C\text{-}P}$ = 8.6 Hz), 128.6 (d, $J_{C\text{-}P}$ = 91.8 Hz), 128.5 (d, $J_{C\text{-}P}$ = 95.2 Hz), 128.4, 125.6 (d, $J_{C\text{-}P}$ = 11.0 Hz), 125.2 (d, $J_{C\text{-}P}$ = 11.2 Hz), 116.5, 113.1, 60.4 (d, $J_{C\text{-}P}$ = 86.8 Hz), 50.8, 35.0, 34.9, 31.1, 31.1, 27.8, 24.2;

^{31}P NMR (162 MHz, $CDCl_3$): δ 27.3.

HRMS (ESI) for $C_{30}H_{39}NOP$ $[M+H]^+$ calcd. 460.2764, found: 460.2764.

Bis(3,5-dimethylphenyl)(1-phenylpyrrolidin-2-yl)phosphine oxide (4d)



4d

Following the general procedure, compound **4d** was obtained as a white solid in 45% yield; mp = 124-126 °C; R_f = 0.67 (PE:*i*PrOH = 5:1);

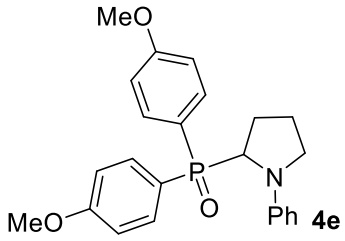
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 10.6 Hz, 1H), 7.31 (d, J = 10.9 Hz, 1H), 7.17 (s, 1H), 7.01 (s, 1H), 6.98-6.90 (m, 1H), 6.55 (t, J = 7.2 Hz, 1H), 6.36 (d, J = 8.2 Hz, 1H), 4.64 (t, J = 8.7 Hz, 1H), 3.73-3.57 (m, 1H), 3.32-3.11 (m, 1H), 2.47-2.37 (m, 1H), 2.34 (s, 3H), 2.19 (s, 3H), 2.16-2.00 (m, 1H), 1.97-1.75 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.8, 138.3 (d, $J_{C\text{-}P}$ = 11.4 Hz), 137.8 (d, $J_{C\text{-}P}$ = 11.7 Hz), 133.5 (d, $J_{C\text{-}P}$ = 2.8 Hz), 133. (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.5 (d, $J_{C\text{-}P}$ = 91.9 Hz), 131.3 (d, $J_{C\text{-}P}$ = 88.5 Hz), 129.4 (d, $J_{C\text{-}P}$ = 8.8 Hz), 129.3 (d, $J_{C\text{-}P}$ = 8.3 Hz), 128.3, 116.5, 113.2, 60.0 (d, $J_{C\text{-}P}$ = 85.8 Hz), 50.7, 27.8, 24.2, 21.3, 21.1;

^{31}P NMR (162 MHz, $CDCl_3$): δ 28.1.

HRMS (ESI) for $C_{26}H_{31}NOP$ $[M+H]^+$ calcd. 404.2138, found: 404.2136.

Bis(4-methoxyphenyl)(1-phenylpyrrolidin-2-yl)phosphine oxide (4e)



Following the general procedure, compound **4e** was obtained as a white solid in 44% yield; mp = 198-200 °C; R_f = 0.47 (PE:*i*PrOH = 5:1);

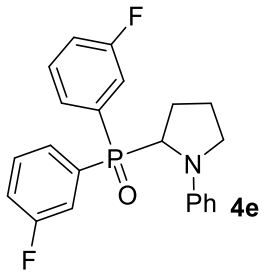
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86-7.74 (m, 1H), 7.72-7.61 (m, 1H), 7.02-6.91 (m, 2H), 6.83 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.56 (t, *J* = 7.2 Hz, 1H), 6.36 (d, *J* = 8.2 Hz, 1H), 4.59 (t, *J* = 8.3 Hz, 1H), 3.84 (s, 1H), 3.77 (s, 1H), 3.61-3.52 (m, 1H), 3.27-3.06 (m, 1H), 2.52-2.35 (m, 1H), 2.22-2.01 (m, 1H), 1.99-1.74 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 162.3 (d, J_{C-P} = 2.0 Hz), 147.8, 133.6 (d, J_{C-P} = 9.8 Hz), 133.4 (d, J_{C-P} = 9.6 Hz), 128.4, 123.1 (d, J_{C-P} = 96.1 Hz), 122.8 (d, J_{C-P} = 99.2 Hz), 116.6, 114.1 (d, J_{C-P} = 11.7 Hz), 113.8 (d, J_{C-P} = 11.8 Hz), 113.1, 61.0, 60.2, 55.2, 55.2, 50.8, 27.6, 24.1;

^{31}P NMR (162 MHz, $CDCl_3$): δ 27.4.

HRMS (ESI) for $C_{24}H_{27}NO_3P$ $[M+H]^+$ calcd. 408.1723, found: 408.1721.

Bis(3-fluorophenyl)(1-phenylpyrrolidin-2-yl)phosphine oxide (4f)



Following the general procedure, compound **4f** was obtained as a white solid in 77% yield; mp = 148-150 °C; R_f = 0.56 (PE:*i*PrOH = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.58 (m, 1H), 7.58-7.43 (m, 2H), 7.36-7.21 (m, 1H), 7.11 (td, *J* = 8.4, 2.2 Hz, 1H), 6.96 (t, *J* = 7.9 Hz, 1H), 6.58 (t, *J* = 7.3 Hz, 1H), 6.37 (d, *J* = 8.2 Hz, 1H), 4.69 (t, *J* = 9.3 Hz, 1H), 3.68 (td, *J* = 8.6, 1.8 Hz, 1H), 3.31-3.07 (m, 1H), 2.56-2.32 (m, 1H), 2.32-1.69 (m, 2H);

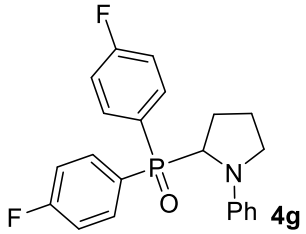
^{13}C NMR (101 MHz, $CDCl_3$): δ 162.6 (dd, J_{C-F} = 251.5 Hz, J_{C-P} = 15.3 Hz), 162.3 (d, J_{C-F} = 251.5 Hz, J_{C-P} = 15.3 Hz), 147.4, 133.9 (dd, J_{C-P} = 88Hz, J_{C-F} = 6 Hz), 133.8 (dd, J_{C-P} = 91 Hz, J_{C-F} = 6 Hz), 130.6 (dd, J_{C-F} = 13 Hz, J_{C-P} = 7 Hz), 130.1 (dd, J_{C-F} = 13 Hz, J_{C-P} = 8 Hz), 128.5, 127.4 (dd, J_{C-F} = 9 Hz, J_{C-P} = 3 Hz), 127.2 (dd, J_{C-F} = 8 Hz, J_{C-P} = 3 Hz), 119.17 (t, J_{C-F} = 20 Hz), 119.16 (t, J_{C-F} = 20 Hz), 118.7 (t, J_{C-F} = 9 Hz), 118.5 (t, J_{C-F} = 9 Hz), 117.3, 113.3, 60.1 (d, J_{C-p} = 87 Hz), 50.9, 27.5, 24.1;

^{31}P NMR (162 MHz, $CDCl_3$): δ 25.6;

^{19}F NMR (376 MHz, $CDCl_3$): δ -110.4 (d, J = 4.9 Hz), -111.2 (d, J = 5.3 Hz).

HRMS (ESI) for $C_{22}H_{21}F_2NOP$ $[M+H]^+$ calcd. 384.1323, found:384.1324.

Bis(4-fluorophenyl)(1-phenylpyrrolidin-2-yl)phosphine oxide (4g)



4g

Following the general procedure, compound **4g** was obtained as a white solid in 98% yield; mp = 222-224 °C; R_f = 0.55 (PE:*i*PrOH = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.81 (m, 1H), 7.81-7.62 (m, 1H), 7.17 (td, J = 8.6, 1.8 Hz, 1H), 7.11-6.87 (m, 2H), 6.59 (t, J = 7.3 Hz, 1H), 6.35 (d, J = 8.2 Hz, 1H), 4.64 (t, J = 8.9 Hz, 1H), 3.85-3.48 (m, 1H), 3.35-3.15 (m, 1H), 2.60-2.32 (m, 1H), 2.32-2.04 (m, 1H), 2.04-1.76 (m, 1H);

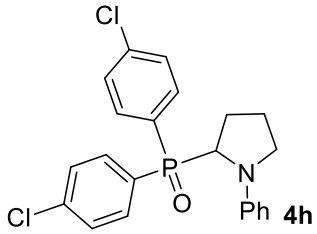
^{13}C NMR (101 MHz, $CDCl_3$): δ 165.13 (d, J_{C-F} = 254.5 Hz), 165.11 (d, J_{C-F} = 254.5 Hz), 147.6, 134.3 (t, J_{C-F} = 9.1 Hz), 134.1 (t, J_{C-F} = 9.1 Hz), 128.6, 127.5 (dd, J_{C-P} = 91.9 Hz, J_{C-F} = 3.0 Hz), 127.3 (dd, J_{C-P} = 95.9 Hz, J_{C-F} = 3.0 Hz), 117.2, 116.1 (dd, J_{C-F} = 21.2 Hz, J_{C-P} = 12.1 Hz), 115.7 (dd, J_{C-F} = 21.2 Hz, J_{C-P} = 11.1 Hz), 113.3, 60.4 (d, J_{C-P} = 88.9 Hz), 51.0. 27.5, 24.2;

^{19}F NMR (376 MHz, $CDCl_3$): δ -106.3, -106.7;

^{31}P NMR (162 MHz, $CDCl_3$): δ 26.2.

HRMS (ESI) for $C_{22}H_{21}F_2NOP$ $[M+H]^+$ calcd. 384.1323, found: 384.1321.

Bis(4-chlorophenyl)(1-phenylpyrrolidin-2-yl)phosphine oxide (4h)



4h

Following the general procedure, compound **4h** was obtained as a white solid in 79% yield; mp = 210-212 °C; R_f = 0.57 (PE:*i*PrOH = 5:1);

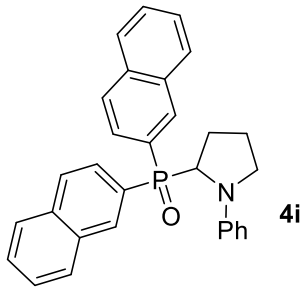
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.68 (m, 1H), 7.66-7.56 (m, 1H), 7.38 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.25 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.91 (t, *J* = 7.9 Hz, 1H), 6.54 (t, *J* = 7.3 Hz, 1H), 6.28 (d, *J* = 8.2 Hz, 1H), 4.57 (t, *J* = 9.0 Hz, 1H), 3.69-3.48 (m, 1H), 3.15 (qd, *J* = 8.7, 2.7 Hz, 1H), 2.63-2.25 (m, 1H), 2.19-1.95 (m, 1H), 1.95-1.69 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.5, 137.84 (d, J_{C-P} = 3.6 Hz), 137.79 (d, J_{C-P} = 3.5 Hz), 133.2 (d, J_{C-P} = 9.3 Hz), 133.0 (d, J_{C-P} = 9.1 Hz), 129.1 (d, J_{C-P} = 11.3 Hz), 128.7 (d, J_{C-P} = 11.3 Hz), 128.6, 117.4, 113.4, 60.4 (d, J_{C-P} = 87.4 Hz), 51.1, 27.6, 24.2;

^{31}P NMR (162 MHz, $CDCl_3$): δ 26.3.

HRMS (ESI) for $C_{22}H_{21}Cl_2NOP$ $[M+H]^+$ calcd. 416.0732, found: 416.0734.

Di(naphthalen-2-yl)(1-phenylpyrrolidin-2-yl)phosphine oxide (4i)



4i

Following the general procedure, compound **4i** was obtained as a white solid in 84% yield; mp = 178-180 °C; R_f = 0.58 (PE:*i*PrOH = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, *J* = 12.4 Hz, 1H), 8.42 (d, *J* = 12.6 Hz, 1H), 7.95-7.73 (m, 8H), 7.62-7.40 (m, 4H), 6.82 (t, *J* = 7.9 Hz, 2H), 6.59-6.18 (m, 3H), 4.86

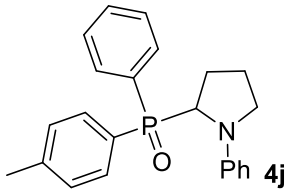
(t, *J* = 8.5 Hz, 1H), 3.64 (t, *J* = 7.7 Hz, 1H), 3.33-3.10 (m, 1H), 2.66-2.45 (m, 1H), 2.34-2.04 (m, 1H), 2.02-1.70 (m, 2H);

^{13}C NMR (101 MHz, CDCl$_3$): δ 147.9, 134.7 (d, J_{C-P} = 2.1 Hz), 134.7 (d, J_{C-P} = 2.0 Hz), 134.1 (d, J_{C-P} = 8.1 Hz), 133.9 (d, J_{C-P} = 7.7 Hz), 132.7 (d, J_{C-P} = 11.9 Hz), 132.5 (d, J_{C-P} = 12.2 Hz), 129.2 (d, J_{C-P} = 89.9 Hz), 129.0 (d, J_{C-P} = 7.2 Hz), 128.8 (d, J_{C-P} = 95.9 Hz), 128.8 (d, J_{C-P} = 7.1 Hz), 128.4, 128.3 (d, J_{C-P} = 10.1 Hz), 128.0 (d, J_{C-P} = 14.1 Hz), 127.9 (d, J_{C-P} = 11.1 Hz), 127.6 (d, J_{C-P} = 14.1 Hz), 126.69 (d, J_{C-P} = 25.2 Hz), 126.66 (d, J_{C-P} = 9.1 Hz), 126.4 (d, J_{C-P} = 9.1 Hz), 116.9, 113.3, 60.6 (d, J_{C-P} = 86.7 Hz), 50.9, 27.7, 24.2.

^{31}P NMR (162 MHz, CDCl$_3$): δ 27.7.

HRMS (ESI) for $C_{30}H_{27}NOP$ $[M+H]^+$ calcd. 448.1825, found: 448.1821.

Phenyl(1-phenylpyrrolidin-2-yl)(p-tolyl)phosphine oxide (4j)



4j

Following the general procedure, compound **4j** was obtained as a white solid in 99% yield; mp = 150-152 °C; R_f = 0.56 (PE:iPrOH = 5:1);

Major：**^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.80-7.77 (m, 2H), 7.75-7.72 (m, 2H), 7.51-7.37 (m, 2H, *overlapped*), 7.29-7.28 (m, 3H), 6.95-6.91 (m, 2H), 6.54 (q, *J*=7.2 Hz, 1H, *overlapped*), 6.36-6.34 (m, 2H, *overlapped*), 4.66-4.63 (m, 1H, *overlapped*), 3.62 (t, *J*=7.8 Hz, 1H), 3.20-3.18 (m, 1H, *overlapped*), 2.50-2.42 (m, 1H, *overlapped*), 2.40 (s, 3H), 2.15-2.01 (m, 3H); **minor**: **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.90-7.87 (m, 2H), 7.68-7.65 (m, 2H), 7.51-7.37 (m, 2H, *overlapped*), 7.15-7.14 (m, 3H), 6.95-6.91 (m, 2H, *overlapped*), 6.54 (q, *J*=7.2 Hz, 1H, *overlapped*), 6.36-6.34 (m, 2H, *overlapped*), 4.66-4.63 (m, 1H, *overlapped*), 3.57 (t, *J*=7.8 Hz, 1H), 3.20-3.18 (m, 1H, *overlapped*), 2.50-2.42 (m, 1H, *overlapped*), 2.32 (s, 3H), 1.90-1.86 (m, 3H);

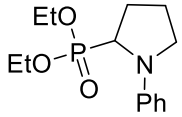
Major: ^{13}C NMR (151 MHz, CDCl$_3$): δ 147.8, 142.3 (d, J_{C-P} = 1.5 Hz), 132.0 (d, J_{C-P} = 88.5 Hz), 131.8 (d, J_{C-P} = 9 Hz), 131.6, 131.5(6) (d, J_{C-P} = 3.0 Hz), 129.3 (d, J_{C-P} =

10.5 Hz), 128.3, 128.2 (d, J_{C-P} = 88.5 Hz), 128.1 (d, J_{C-P} = 10.5 Hz), 116.6, 113.1, 60.6 (d, J_{C-P} = 87 Hz), 50.7, 27.7, 24.1, 21.5; **Minor: ^{13}C NMR (151 MHz, $CDCl_3$):** δ 147.8, 142.2 (d, J_{C-P} = 3 Hz), 132.2 (d, J_{C-P} = 88.5 Hz), 131.8 (d, J_{C-P} = 9 Hz), 131.7, 128.9 (d, J_{C-P} = 10.5 Hz), 128.5 (d, J_{C-P} = 10.5 Hz), 128.4, 128.0 (d, J_{C-P} = 94.5 Hz), 116.7, 113.2, 60.6 (d, J_{C-P} = 87 Hz), 50.8, 27.6, 24.1, 21.4;

^{31}P NMR (243 MHz, $CDCl_3$) δ 27.7, 27.3.

HRMS (ESI) for $C_{23}H_{25}BNOP$ $[M+H]^+$ calcd. 362.1668, found: 362.1668.

Diethyl (1-phenylpyrrolidin-2-yl)phosphonate (4k)



4k

Following the general procedure, compound **4k** was obtained as a colorless oil in 74% yield; R_f = 0.23 (PE:EA = 3:1);

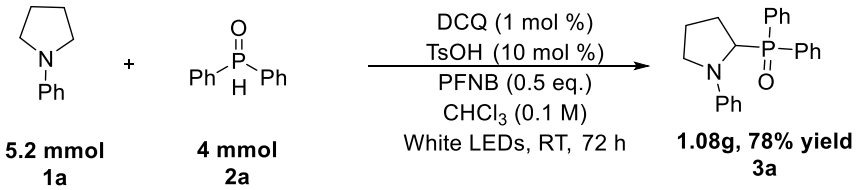
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25-7.22 (m, 2H), 6.82-6.80 (m, 2H), 6.75-6.73 (m, 1H), 4.16-4.10 (m, 2H), 4.09-4.04 (m, 2H), 3.95-3.89 (m, 1H), 3.60-3.58 (m, 1H), 3.21-3.16 (m, 1H), 2.42-2.34 (m, 2H), 2.11-2.02 (m, 2H), 1.31 (t, J_{C-P} = 7.2 Hz, 3H), 1.18 (t, J_{C-P} = 7.2 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$): δ 147.8, 128.8, 117.0, 113.2, 62.23 (d, J_{C-P} = 87.6 Hz), 62.18 (d, J_{C-P} = 87.6 Hz), 56.5 (d, J_{C-P} = 169.1 Hz), 49.7 (d, J_{C-P} = 1.5 Hz), 27.8, 24.3, 16.5 (t, J_{C-P} = 6.0 Hz).

^{31}P NMR (243 MHz, $CDCl_3$): δ 25.6.

HRMS (ESI) for $C_{14}H_{23}NO_3P$ $[M+H]^+$ calcd. 284.1416, found: 284.1415.

5. Gram-scale reaction



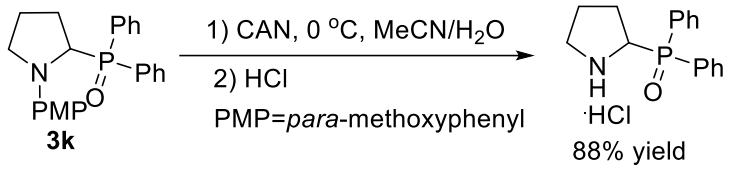
5.2 mmol
1a

4 mmol
2a

1.08g, 78% yield
3a

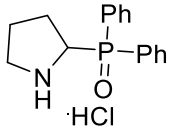
General procedure： A dried 10 mL reaction tube was charged with the photocatalyst (20.9 mg, 0.05 mmol, 1 mol %), *p*-TSA (0.5 mmol, 95 mg), PFNB (2.5 mmol, 0.33 mL), tertiary arylamine **1a** (5.2 mmol, 1.3 equiv, 0.6 mL), diphenylphosphine oxide **2** (4 mmol, 1.0 equiv, 0.81 g) and 40 mL $CHCl_3$. The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the reaction was under the irradiation of the white LEDs for 72 h. After completion of the reaction as checked by TLC. The reaction mixture was purified by silica gel flash column chromatography (petroleum ether/iPrOH) to give the corresponding product**.**

6. Transformations of product



To a solution of product **3k** (1 equiv) in acetonitrile (0.1 M), under N_2, at 0 °C, was slowly added a solution of ammonium cerium nitrate (5 equiv) in water (0.3 M to CAN). The reaction was allowed to stir for one hour at 0 °C, then two hours at rt. Upon complete consumption of the starting material (TLC), the reaction mixture was basified to pH ≈ 10 with an aqueous solution of NaOH 1M. Immediate precipitation of a dark red solidis observed and the reaction is extracted with DCM. Then, the combined organic phasesare acidified with aqueous HCl 2 M to pH ≈ 2 and washed with 2 M HCl one more time. The combined aqueous phases are concentrated under reduced pressure to afford a brown solid (NaCl), which after filtration washing with MeOH and concentration under reduced pressure affords the corresponding pyrrolidine hydrochloride salt as a white solid.

Diphenyl(pyrrolidin-2-yl)phosphine oxide hydrochloride (5)[3]



Compound **5** was obtained as a white solid in 88% yield;

^{1}H NMR (400 MHz, D_2O): δ 8.30-7.26 (m, 1H), 3.39 (d, *J* = 5.8 Hz, 1H), 2.37-1.88 (m, 1H);

^{13}C NMR (101 MHz, D_2O): δ 134.1 (d, J_{C-P} = 2.7 Hz), 134.0 (d, J_{C-P} = 2.5 Hz), 131.0 (d, J_{C-P} = 3.4 Hz), 130.9 (d, J_{C-P} = 3.5 Hz), 129.7 (d, J_{C-P} = 12.4 Hz), 129.5 (d, J_{C-P} = 12.7 Hz), 127.3 (d, J_{C-P} = 2.2 Hz), 126.3, 55.9 (d, J_{C-P} = 72.9 Hz), 48.1, 25.5, 24.1;

^{31}P NMR (162 MHz, D_2O): δ 32.9.

HRMS (ESI) for $C_{22}H_{27}N_3O_4$ $[M+H]^+$ calcd. 272.1199, found: 272.1198.

7. Mechanistic investigations

7.1 Luminescence quenching experiments

Stern-Volmer experiments were conducted on an Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer using the Cary Eclipse Scan Application. Rigorously purged (with nitrogen) solutions of each component were prepared prior to each set of experiments. Luminescence quenching experiments were run with $CHCl_3$ as the solvent. The solutions were irradiated at 410 nm and the luminescence was measured from 440 nm to 700 nm (emission maximum is at 530 nm). The concentration of DCQ stock solution was 0.3 mM in $CHCl_3$. After being stirred with a thin glass rod, the emission spectrum was collected. Linear regression of I0/I against concentration is done in Origin.

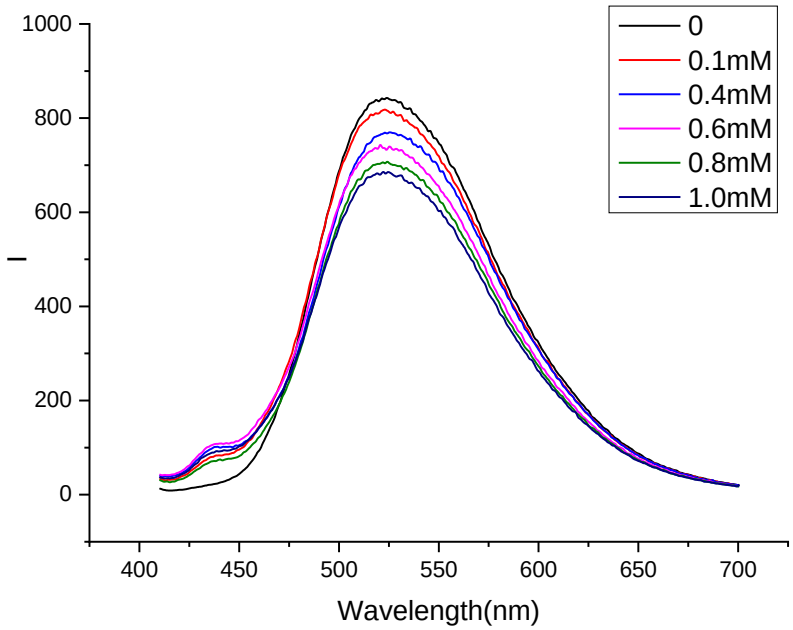


Figure S6. Fluorescence quenching data with DCQ and variable N-Ph pyrrolidine.

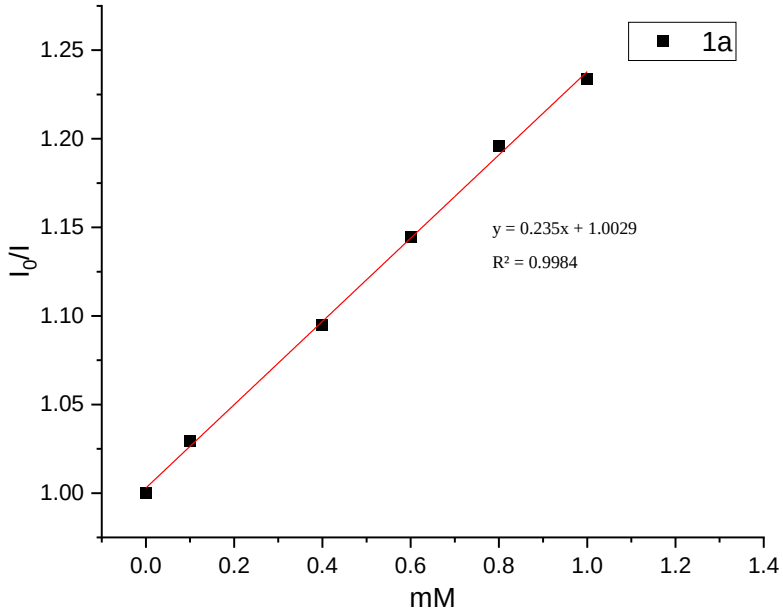


Figure S7. Stern-Volmer plot of DCQ with variable N-Ph pyrrolidine.

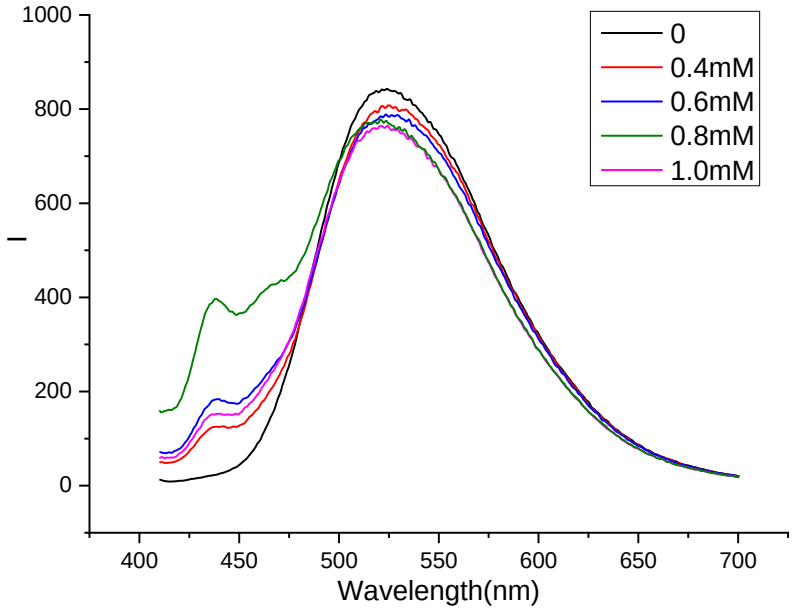


Figure S8. Fluorescence quenching data with DCQ and variable PFNB.

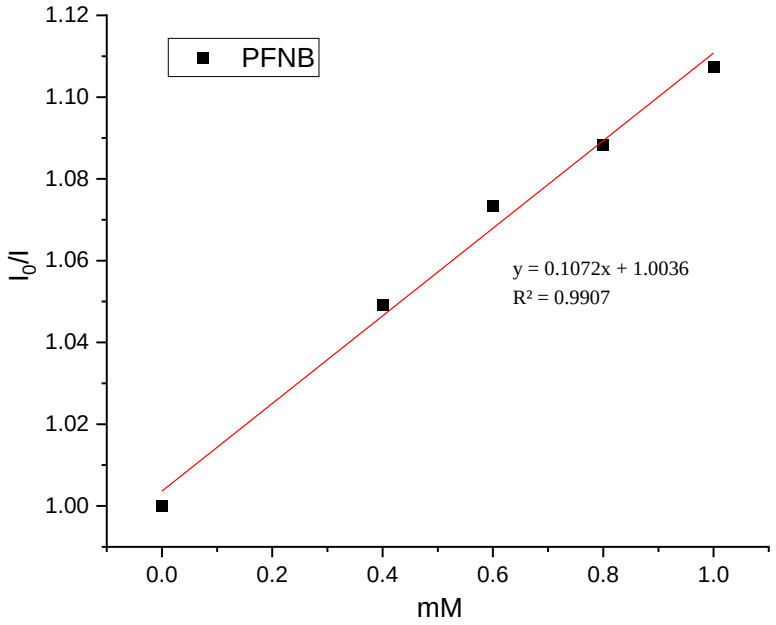


Figure S9. Stern-Volmer plot of DCQ with variable PFNB pyrrolidine.

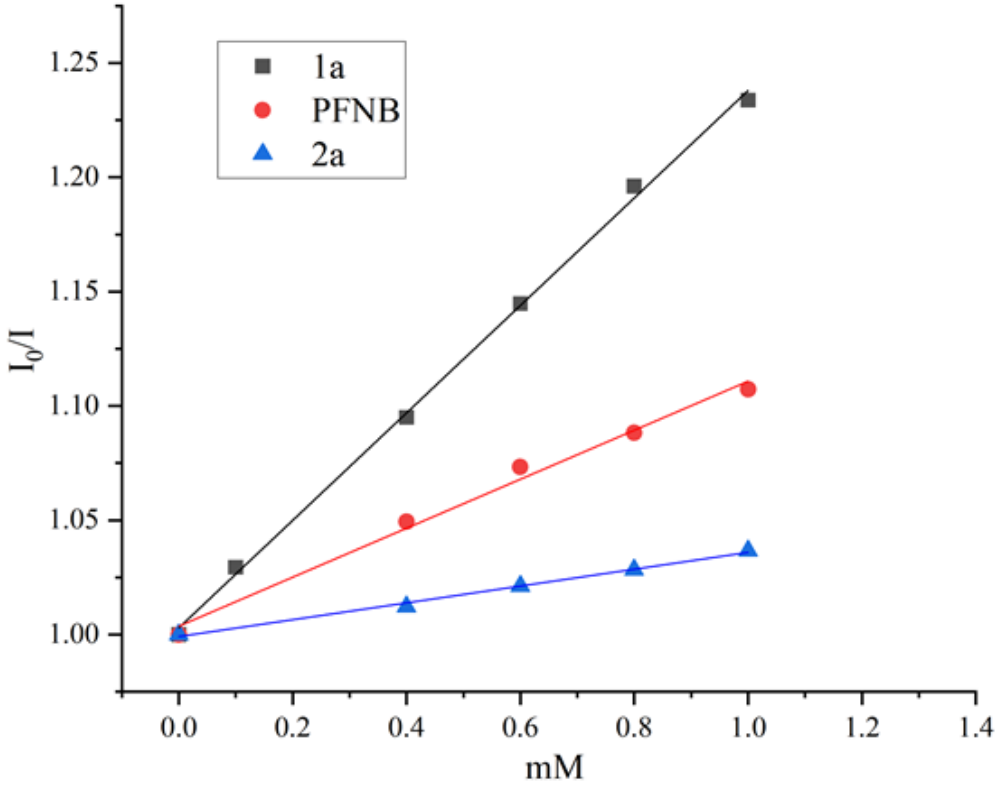
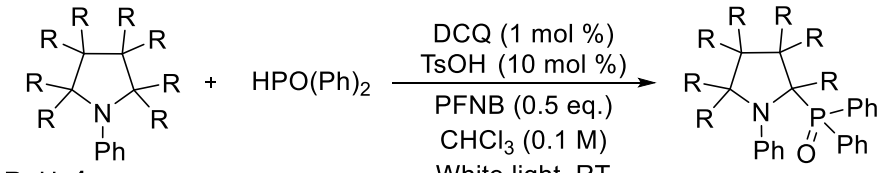


Figure S10. Stern-Volmer plot of DCQ with **1a**, **2a**, and PFNB.

7.2 Kinetic isotope effect



10 min: 21% conversion, k_H:k_D = 1:1
20 min: 27% conversion, k_H:k_D = 1:1

A dried 10 mL reaction tube was charged with the photocatalyst (0.001 mol, 0.4 mg), *p*-TSA (0.01 mmol, 1.9 mg), PFNB (0.05 mmol, 6.5 μL), tertiary arylamine **1a** (0.065 mmol, 0.65 equiv) and d_8-**1a**' (0.065 mmol, 0.65 equiv.), diphenylphosphine oxide **2a** (0.1mmol, 1.0 equiv.) and 1.0 mL $CHCl_3$. The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the vial was placed beside a white LED light. The reaction was stirred at 25 °C for 10 and 20 min. The yields and k_H/ k_D ratios were determined by the ^{1}H NMR spectrum.

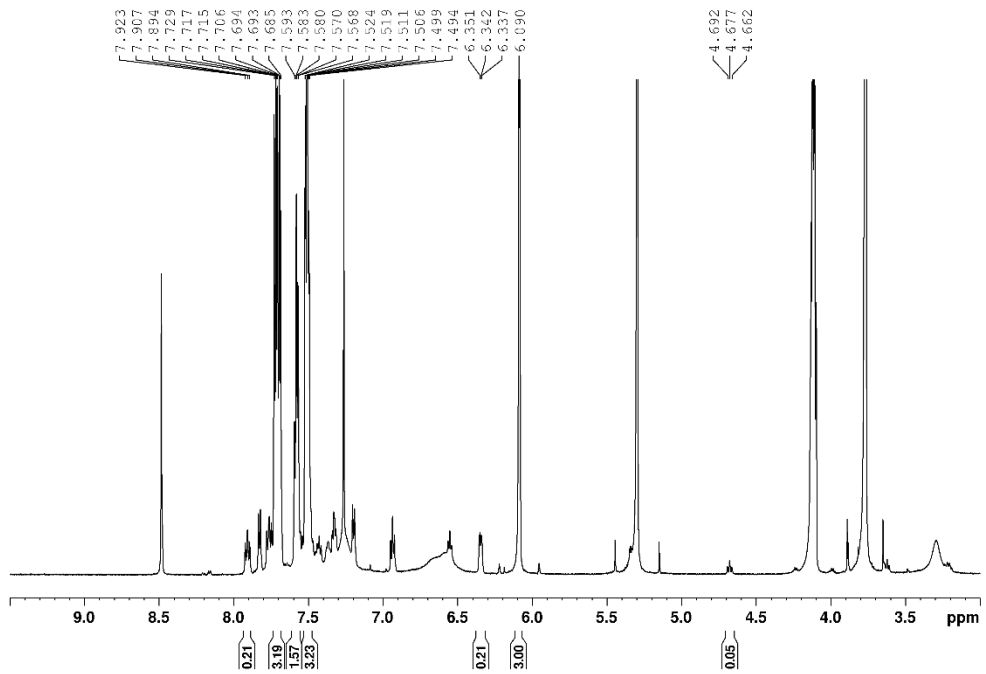


Figure S11. ^{1}H NMR of the reaction mixture after reacting 10 min.

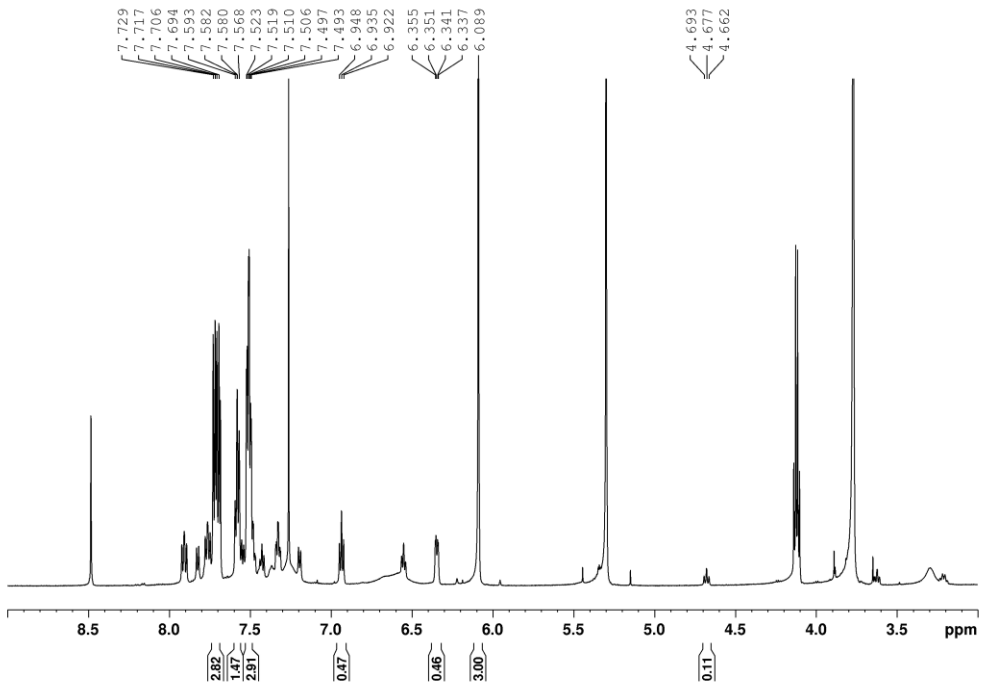
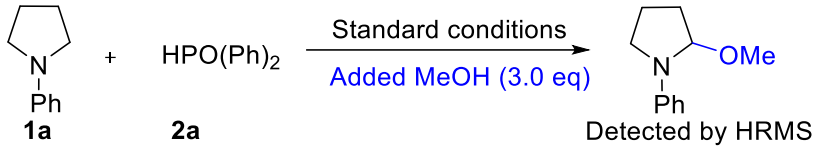
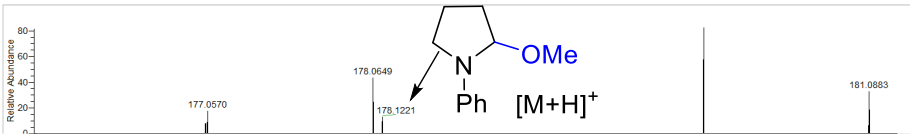


Figure S12. ^{1}H NMR of the reaction mixture after reacting 20 min.

7.3 MeOH-trapping experiments



A dried 10 mL reaction tube was charged with the photocatalyst (0.001 mol, 0.4 mg), *p*-TSA (0.01 mmol, 1.9 mg), PFNB (0.05 mmol, 6.5 μL), tertiary arylamine **1a** (0.13 mmol, 1.0 equiv) and MeOH (0.3 mmol, 3.0 equiv), diphenylphosphine oxide **2a** (0.1mmol, 1.0 equiv) and 1.0 mL $CHCl_3$. The reaction mixture was degassed by three cycles of freeze-pump-thaw. After the mixture was thoroughly degassed, the vial was placed beside a white LED light. The reaction was stirred at 25 °C for 8 h.



7.4 Determination of the Quantum Yield

1) Determination of the light intensity at 436 nm:

The photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry.[4-6] A 0.15 M solution of ferrioxalate was prepared by dissolving 1.84 g of potassium ferrioxalate hydrate in 25 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 25 mg of phenanthroline and 5.63 g of sodium acetate in 25 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at $\lambda = 420$ nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using eq. 1.

$$\text{mol Fe}^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon} \qquad \text{(eq.1)}$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, *l* is the path length (1.000 cm), and *ε* is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}).

The photon flux can be calculated using eq 2.

$$\text{photon flux} = \frac{\text{mol Fe}^{2+}}{\Phi \bullet t \bullet f} \qquad \text{(eq.2)}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.01 at λ=436 nm),[5] t is the time (90.0 s), and *f* is the fraction of light absorbed at λ = 436nm by the ferrioxalate actinometer. This value is calculated using eq. 3, where A436 nm is the absorbance of the ferrioxalate solution at 436 nm.

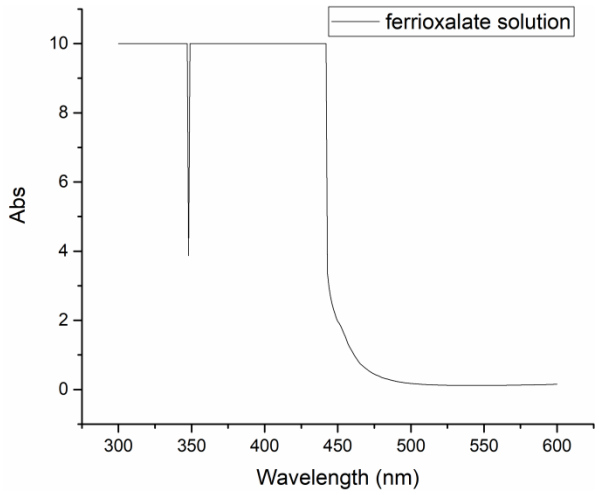
$$f = 1 - 10^{-A_{436nm}} \qquad \text{(eq.3)}$$

Sample calculation:

$$\text{mol Fe}^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon} = \frac{0.00235\ L \bullet 1.244}{1.0\ cm \bullet 11{,}100\ L \cdot mol^{-1} \cdot cm^{-1}} = 2.63 \times 10^{-7}\ mol$$

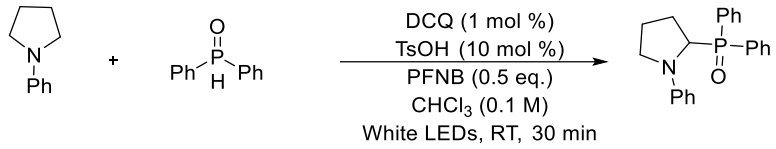
An absorption spectrum gave an A(436 nm) value of > 3, indicating that the fraction of absorbed light (f) is about 1.0.

$$f = 1 - 10^{-A_{436nm}} \approx 1.0$$



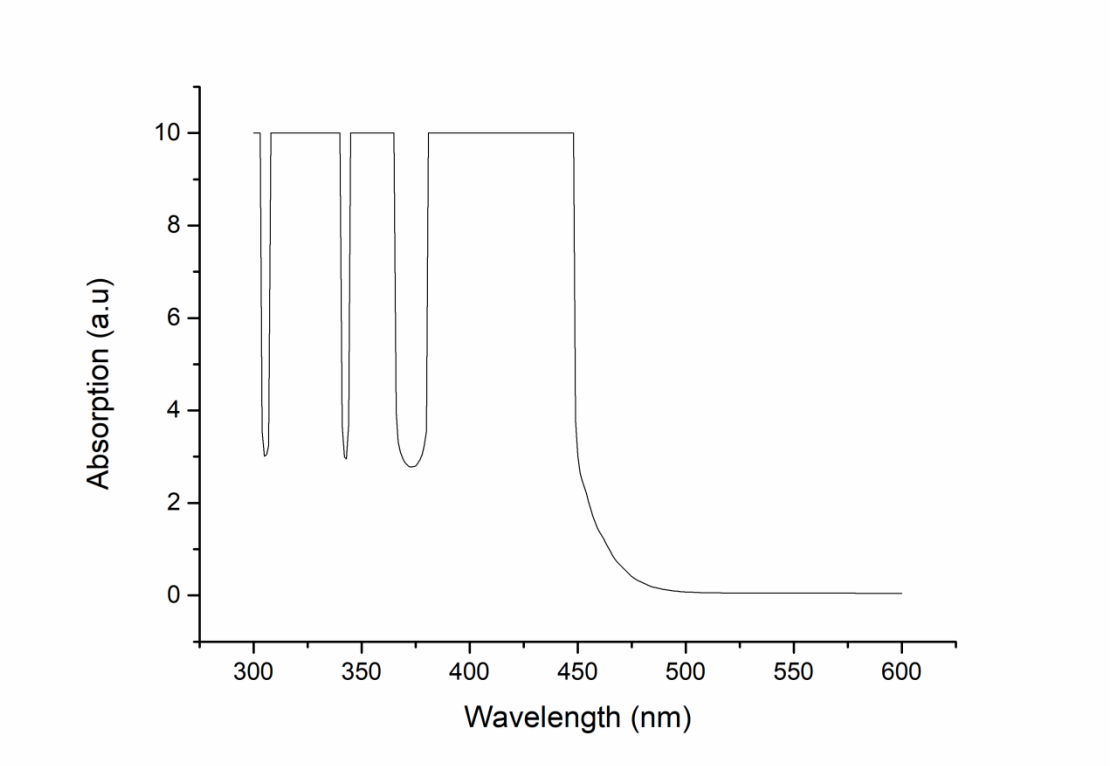
$$\text{photon flux} = \frac{\text{mol } Fe^{2+}}{\Phi \bullet t \bullet f} = \frac{2.63 \times 10^{-7}\, mol}{1.01 \cdot 90.0\, s \cdot 1.0} = 2.89 \times 10^{-9}\, einstein \cdot s^{-1}$$

2) Determination of the reaction quantum yield at 436 nm



A dried 10 mL reaction tube was charged with the photocatalyst (0.001 mol, 0.4 mg), *p*-TSA (0.01 mmol, 1.9 mg), PFNB (0.05 mmol, 6.5 μL), tertiary arylamine **1a** (0.13 mmol, 1.3 equiv), diphenylphosphine oxide **2a** (0.1mmol, 1.0 equiv) and 1.0 mL $CHCl_3$. The reaction mixture was degassed by three cycles of freeze-pump-thaw. The mixture was stirred under nitrogen atmosphere at room temperature while irradiated by blue light (420-425 nm) for 30 minutes (1800 s). The reaction was irradiated in Parallel Light Reactor (WP-TEC-1020). After irradiation, the yield of the product **3a** was determined by ^{1}H NMR based on a 1,3,5-trimethoxybenzene standard and the final yield was 15% ($1.5 \cdot 10^{-5}$ mol).

The reaction quantum yield (Φ) was determined using eq. 4, where the photon flux is 2.89 · 10-9 $E \cdot s^{-1}$ (determined by actinometry as described above), t is the reaction time (1800 s) and f is the fraction of incident light absorbed by the reaction mixture, determined using eq. 3. An absorption spectrum of the reaction mixture gave an absorbance value of 2.45 at 436 nm, indicating that essentially all the incident light (f > 0.999) is absorbed by the photocatalyst.

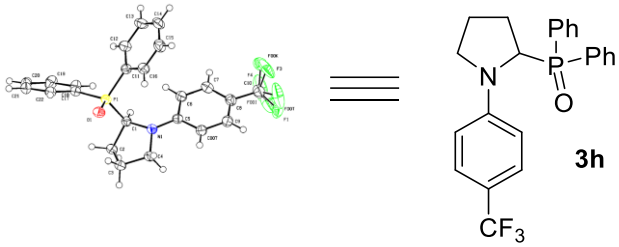


$$f = 1 - 10^{-A_{436nm}} = 1 - 10^{-2.45} = 0.996$$

$$\Phi = \frac{\text{mol of product formed}}{\text{photon flux} \cdot \text{t} \cdot \text{f}} = \frac{1.5\times10^{-5}}{2.89\times10^{-9}\times1800\text{s}\cdot0.996} = 2.9$$

8. X-Ray crystallographic data of product 3h:

The crystal structure **3h** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 2112791.



Bond precision:	C-C = 0.0021 A	Wavelength=1.54184	
Cell:	a=8.8027(1)	b=20.2100(2)	c=11.4809(1)
	alpha=90	beta=103.074(1)	gamma=90
Temperature:	150 K		
	Calculated	Reported	
Volume	1989.54(4)	1989.54(4)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C23 H21 F3 N O P	C23 H21 F3 N O P	
Sum formula	C23 H21 F3 N O P	C23 H21 F3 N O P	
Mr	415.38	415.38	
Dx,g cm-3	1.387	1.387	
Z	4	4	
Mu (mm-1)	1.595	1.595	
F000	864.0	864.0	
F000’	867.93		
h,k,lmax	11,25,14	11,25,14	
Nref	4161	3952	
Tmin,Tmax	0.875,0.938	0.718,1.000	
Tmin’	0.839		
Correction method= # Reported T Limits: Tmin=0.718 Tmax=1.000			
AbsCorr = MULTI-SCAN			
Data completeness= 0.950		Theta(max)= 76.137	
R(reflections)= 0.0377(3591)		wR2(reflections)= 0.1012(3952)	
S = 1.048		Npar= 289	

9. Mechanistic computational analysis

All the DFT calculations at the M062X(D3)/6-31G(d) [7-8] level for neutral molecules or UM062X(D3)/6-31G(d) level for radical ions with the SMD [9] solvation model and DCM as the solvent were carried out to study the mechanism by Gaussian 09[10]. Frequency calculations were carried out at the same level of theory to confirm their character as minima (no imaginary frequencies) or transition states (a single imaginary frequency). And the intrinsic reaction coordinate (IRC) calculations have confirmed that all stationary points were smoothly connected to each other. We have used Gauss View[11] programs to generate ball and stick geometries of optimized structures. The electron spin density with iso value of 0.02 are visualized by wave function analysis software Multiwfn-3.8[12] program and visualization software VMD [13] to generate the scheme of the electron spin density.

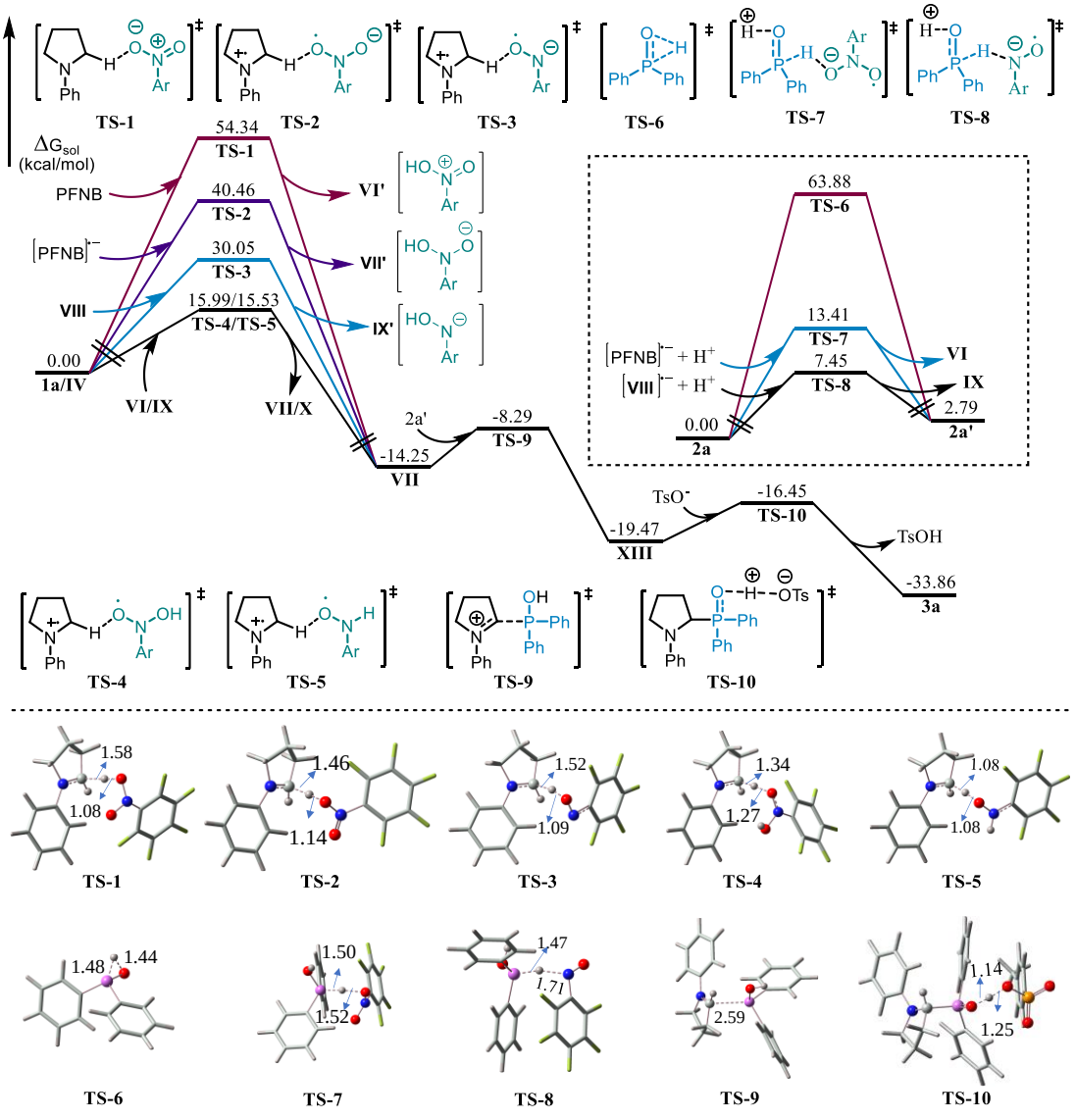
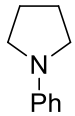


Figure S13. Free energy reaction profile of the proposed mechanism.

Table S6. Standard orientation of All Stationary Points and the only imaginary frequencies of each transition state



1. **1a** Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.057676	-0.692708	-0.326634
2	6	0	1.650060	-1.213893	-0.028405
3	6	0	1.650061	1.213775	0.028680
4	6	0	3.057988	0.692738	0.325543
5	1	0	3.837445	-1.353590	0.058448
6	1	0	3.191612	-0.595437	-1.409341
7	1	0	1.611204	-1.741980	0.936662
8	1	0	1.290653	-1.904126	-0.800714
9	1	0	1.610056	1.741083	-0.936789
10	1	0	1.291596	1.904632	0.800858
11	1	0	3.837321	1.353651	-0.060364
12	1	0	3.193001	0.595523	1.408122
13	7	0	0.844753	-0.000064	0.001147
14	6	0	-0.525146	-0.000014	0.000554
15	6	0	-1.253160	-1.205252	0.100386
16	6	0	-1.252987	1.205255	-0.099831
17	6	0	-2.642613	-1.193935	0.097398
18	1	0	-0.725663	-2.148795	0.191682
19	6	0	-2.642460	1.194030	-0.097880
20	1	0	-0.725378	2.148777	-0.190710
21	6	0	-3.355424	0.000081	-0.000506
22	1	0	-3.174462	-2.138338	0.177737
23	1	0	-3.174161	2.138477	-0.178679
24	1	0	-4.440469	0.000119	-0.000778

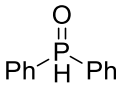
0 imaginary frequencies

Zero-point Energies= -443.241033

Thermal Energies= -443.231665

Thermal Enthalpies= -443.230721

Thermal Free Energies= -443.277302

2. **2a**  Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	0.001859	1.388039	0.329140
2	8	0	0.129950	2.592457	-0.555273
3	1	0	-0.120617	1.686606	1.701733
4	6	0	-1.444578	0.334180	0.067861
5	6	0	-1.503821	-0.509175	-1.047974
6	6	0	-2.521234	0.390777	0.956316
7	6	0	-2.634671	-1.287024	-1.270702
8	1	0	-0.662811	-0.559688	-1.735890
9	6	0	-3.651867	-0.391985	0.732243
10	1	0	-2.477739	1.045460	1.823663
11	6	0	-3.707185	-1.228544	-0.379909
12	1	0	-2.679787	-1.942378	-2.134979
13	1	0	-4.486685	-0.348975	1.424924
14	1	0	-4.588082	-1.839101	-0.554260
15	6	0	1.431973	0.281134	0.217353
16	6	0	1.465380	-0.944735	0.890220
17	6	0	2.521292	0.687435	-0.554335
18	6	0	2.589598	-1.757682	0.791010
19	1	0	0.613150	-1.267096	1.484596
20	6	0	3.643754	-0.132620	-0.656121
21	1	0	2.478681	1.641412	-1.072507
22	6	0	3.677410	-1.351398	0.016774
23	1	0	2.617488	-2.709410	1.312614
24	1	0	4.490180	0.180490	-1.259677
25	1	0	4.552436	-1.989736	-0.061569

---

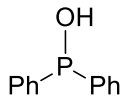
0 imaginary frequencies

Zero-point Energies= -880.037439

Thermal Energies= -880.025652

Thermal Enthalpies= -880.024708

Thermal Free Energies= -880.077481

3. **2a'**  Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	0.021878	1.451119	-0.594637
2	6	0	1.414339	0.325513	-0.166424
3	6	0	1.367486	-0.568599	0.911923
4	6	0	2.585085	0.414288	-0.925160
5	6	0	2.472944	-1.351615	1.226999
6	1	0	0.456645	-0.660850	1.500269
7	6	0	3.691781	-0.375972	-0.615971
8	1	0	2.629816	1.105584	-1.763423
9	6	0	3.635833	-1.256293	0.460836
10	1	0	2.428432	-2.041184	2.064821
11	1	0	4.594942	-0.302763	-1.214267
12	1	0	4.496698	-1.871977	0.704358
13	6	0	-1.398222	0.318970	-0.294205
14	6	0	-1.454909	-0.927974	-0.930425
15	6	0	-2.477987	0.728667	0.493402
16	6	0	-2.563366	-1.752749	-0.768826
17	1	0	-0.622132	-1.261156	-1.546287
18	6	0	-3.587020	-0.100915	0.658011
19	1	0	-2.452599	1.700230	0.979400
20	6	0	-3.632047	-1.341562	0.028437
21	1	0	-2.592505	-2.719945	-1.261947
22	1	0	-4.416801	0.226135	1.277900
23	1	0	-4.496146	-1.986750	0.155484
24	8	0	-0.074358	2.431393	0.746573
25	1	0	-0.083143	1.924193	1.579081

---

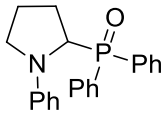
0 imaginary frequencies

Zero-point Energies= -880.032951

Thermal Energies= -880.020762

Thermal Enthalpies= -880.019817

Thermal Free Energies= -880.073029



4. **3a** Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.619465	-1.428532	-2.244215
2	6	0	0.383491	-0.737395	-1.625995
3	6	0	0.747658	-2.872534	-0.557529
4	6	0	1.384158	-2.909451	-1.945122
5	1	0	1.712872	-1.197623	-3.306239
6	1	0	2.537157	-1.095835	-1.745016
7	1	0	-0.378163	-0.564444	-2.400744
8	1	0	1.513485	-2.810772	0.229185
9	1	0	0.119397	-3.745151	-0.358291
10	1	0	2.303934	-3.498199	-1.973131
11	1	0	0.673435	-3.333765	-2.661850
12	7	0	-0.076052	-1.659845	-0.597306
13	6	0	-1.349094	-1.634351	-0.039956
14	6	0	-2.390452	-0.851294	-0.570280
15	6	0	-1.618217	-2.404693	1.107437
16	6	0	-3.641678	-0.836832	0.034453
17	1	0	-2.220960	-0.236849	-1.446681
18	6	0	-2.878884	-2.388345	1.695138
19	1	0	-0.826582	-3.003875	1.547590
20	6	0	-3.902052	-1.602940	1.169771
21	1	0	-4.423290	-0.216242	-0.395362
22	1	0	-3.054964	-2.991208	2.581707
23	1	0	-4.881693	-1.585349	1.636178
24	15	0	0.895998	0.931071	-0.998309
25	8	0	1.514447	1.738150	-2.106982
26	6	0	2.060116	0.615034	0.363675
27	6	0	1.805614	-0.233301	1.451475
28	6	0	3.297611	1.259156	0.266974
29	6	0	2.780204	-0.422881	2.427545
30	1	0	0.851966	-0.746751	1.536022

31	6	0	4.268584	1.067412	1.247557
32	1	0	3.490145	1.904898	-0.585281
33	6	0	4.010208	0.226700	2.327119
34	1	0	2.577686	-1.079391	3.268412
35	1	0	5.226269	1.572310	1.165730
36	1	0	4.766646	0.075273	3.091463
37	6	0	-0.572688	1.746912	-0.309105
38	6	0	-1.381130	2.425253	-1.229292
39	6	0	-0.952472	1.689253	1.033972
40	6	0	-2.575285	3.007376	-0.815683
41	1	0	-1.068489	2.496043	-2.268099
42	6	0	-2.146459	2.275493	1.445741
43	1	0	-0.325351	1.187174	1.763745
44	6	0	-2.962053	2.924961	0.521555
45	1	0	-3.201083	3.528673	-1.533751
46	1	0	-2.440196	2.222318	2.489552
47	1	0	-3.895286	3.376408	0.845100

---

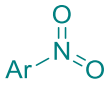
0 imaginary frequencies

Zero-point Energies= -1322.126339

Thermal Energies= -1322.105252

Thermal Enthalpies= -1322.104308

Thermal Free Energies= -1322.176938

5. **PFNB**  Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.167423	1.203483	0.039218
2	6	0	-0.219208	1.207224	0.029917
3	6	0	-0.916877	-0.000106	-0.000010
4	6	0	-0.218884	-1.207489	-0.029949
5	6	0	1.167538	-1.203326	-0.039122
6	6	0	1.858751	0.000235	0.000109
7	7	0	-2.374508	-0.000166	0.000087
8	8	0	-2.928696	-0.894509	0.608174

9	8	0	-2.928787	0.894184	-0.607967
10	9	0	-0.843398	-2.370989	-0.092119
11	9	0	1.833974	-2.349301	-0.089386
12	9	0	3.181019	0.000076	0.000094
13	9	0	1.833116	2.349885	0.089335
14	9	0	-0.843715	2.370734	0.091715

---

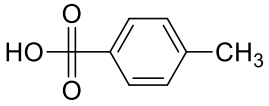
0 imaginary frequencies

Zero-point Energies= -932.475791

Thermal Energies= -932.464512

Thermal Enthalpies= -932.463568

Thermal Free Energies= -932.513456

6. **TsOH** 

Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	1.889581	0.004368	-0.121819
2	8	0	2.347490	-1.174902	-0.824288
3	8	0	2.358532	1.329196	-0.487989
4	8	0	2.303020	-0.254022	1.417337
5	1	0	2.336897	0.600384	1.893533
6	6	0	0.124317	0.009068	-0.081595
7	6	0	-0.551497	-1.210252	-0.041470
8	6	0	-1.937597	-1.199963	0.010647
9	6	0	-2.652212	0.006015	0.019382
10	6	0	-1.944551	1.209701	-0.025429
11	6	0	-0.553644	1.222847	-0.076158
12	1	0	0.000830	-2.144640	-0.059218
13	1	0	-2.479464	-2.141443	0.040126
14	1	0	-2.488178	2.150065	-0.025134
15	1	0	-0.004011	2.157496	-0.122190
16	6	0	-4.156407	-0.009404	0.058923
17	1	0	-4.561174	0.996473	0.193176
18	1	0	-4.561656	-0.417590	-0.873383
19	1	0	-4.519328	-0.640869	0.875906

---

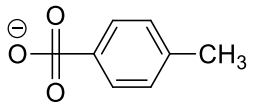
0 imaginary frequencies

Zero-point Energies= -894.989151

Thermal Energies= -894.978622

Thermal Enthalpies= -894.977678

Thermal Free Energies= -895.026461

7. **TsO**$^{-}$  Charge = -1 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	1.963622	-0.001054	0.005372
2	8	0	2.352821	-1.237483	-0.704496
3	8	0	2.358134	1.241821	-0.689830
4	8	0	2.315140	-0.010729	1.441659
5	6	0	0.166873	0.002593	-0.036328
6	6	0	-0.532102	-1.203228	-0.026672
7	6	0	-1.922262	-1.197326	-0.002817
8	6	0	-2.638111	0.005593	0.010010
9	6	0	-1.921508	1.204303	-0.002502
10	6	0	-0.528214	1.207268	-0.026795
11	1	0	0.021529	-2.137229	-0.051881
12	1	0	-2.465369	-2.140127	0.000465
13	1	0	-2.461690	2.148223	0.001564
14	1	0	0.026426	2.140665	-0.051357
15	6	0	-4.145538	-0.004197	0.016653
16	1	0	-4.548382	1.002809	0.155615
17	1	0	-4.540280	-0.396337	-0.927580
18	1	0	-4.533762	-0.640058	0.819273

---

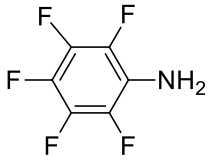
0 imaginary frequencies

Zero-point Energies= -894.540139

Thermal Energies= -894.530240

Thermal Enthalpies= -894.529296

Thermal Free Energies= -894.577049

8. **Ar-NH_2**  Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.447273	1.318674	0.000074
2	6	0	0.904535	1.012844	0.000033
3	6	0	1.371867	-0.301365	0.000004
4	6	0	0.413981	-1.313588	-0.000032
5	6	0	-0.945992	-1.029715	-0.000052
6	6	0	-1.376705	0.288058	0.000013
7	9	0	0.786691	-2.590872	-0.000074
8	9	0	-1.839791	-2.018073	-0.000098
9	9	0	-2.678022	0.564048	0.000024
10	9	0	-0.858414	2.586313	0.000132
11	9	0	1.786866	2.014896	0.000079
12	7	0	2.755112	-0.630942	0.000063
13	1	0	3.207678	-0.220953	-0.816059
14	1	0	3.208091	-0.218710	0.814822

---

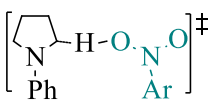
0 imaginary frequencies

Zero-point Energies= -783.383282

Thermal Energies= -783.373571

Thermal Enthalpies= -783.372627

Thermal Free Energies= -783.418341

9. **TS-1**  Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.719107	2.792358	1.399264
2	6	0	1.643787	1.353065	0.960501
3	6	0	3.798227	2.084393	0.417625

4	6	0	2.888063	3.308069	0.551551
5	1	0	0.785693	3.335747	1.241571
6	1	0	1.958007	2.825755	2.471650
7	1	0	0.747850	1.573321	-0.321871
8	1	0	0.976223	0.628557	1.420233
9	1	0	4.550520	2.031282	1.212743
10	1	0	4.299126	2.023767	-0.550553
11	1	0	3.406207	4.155383	1.002183
12	1	0	2.522968	3.604656	-0.435978
13	7	0	2.869406	0.946099	0.575000
14	6	0	3.240321	-0.366259	0.279505
15	6	0	2.285445	-1.394178	0.292971
16	6	0	4.578362	-0.660110	-0.037834
17	6	0	2.674749	-2.695514	-0.012240
18	1	0	1.248437	-1.190159	0.509427
19	6	0	4.946263	-1.963939	-0.330952
20	1	0	5.328397	0.122846	-0.045825
21	6	0	3.997403	-2.989573	-0.322812
22	1	0	1.924199	-3.480130	-0.010454
23	1	0	5.982848	-2.181556	-0.568860
24	1	0	4.292026	-4.007451	-0.557436
25	6	0	-2.980319	-1.522263	0.415880
26	6	0	-1.771845	-1.165010	-0.170623
27	6	0	-1.574746	0.120870	-0.692727
28	6	0	-2.659406	1.010804	-0.622327
29	6	0	-3.855576	0.657615	-0.024845
30	6	0	-4.026740	-0.619756	0.491419
31	7	0	-0.411799	0.507007	-1.403039
32	8	0	0.018828	1.740953	-1.095065
33	8	0	0.515196	-0.359687	-1.602859
34	9	0	-2.572376	2.228114	-1.153509
35	9	0	-4.858124	1.533263	0.028237
36	9	0	-5.178002	-0.966449	1.060880
37	9	0	-3.123389	-2.743533	0.929726
38	9	0	-0.814387	-2.092208	-0.149036

---

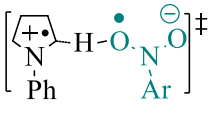
1 imaginary frequencies (748.85 icm^{-1})

Zero-point Energies= -1375.650435

Thermal Energies= -1375.628637

Thermal Enthalpies= -1375.627693

Thermal Free Energies= -1375.704167

10. **TS-2**  Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.960814	2.968186	1.455190
2	6	0	1.732276	1.514196	1.099090
3	6	0	3.889127	2.099977	0.316064
4	6	0	3.041023	3.367677	0.442573
5	1	0	1.051675	3.569319	1.374490
6	1	0	2.336814	3.054589	2.483827
7	1	0	0.768072	1.622398	0.003151
8	1	0	1.199656	0.856337	1.788479
9	1	0	4.697505	2.072081	1.058124
10	1	0	4.322948	1.965738	-0.678381
11	1	0	3.633141	4.229513	0.754943
12	1	0	2.574758	3.593055	-0.521521
13	7	0	2.930710	1.024256	0.604783
14	6	0	3.196601	-0.312021	0.326625
15	6	0	2.166649	-1.265872	0.356679
16	6	0	4.502047	-0.723072	0.008540
17	6	0	2.445564	-2.599560	0.084778
18	1	0	1.147972	-0.965782	0.566978
19	6	0	4.763076	-2.060501	-0.260895
20	1	0	5.311925	-0.002100	-0.014232
21	6	0	3.741015	-3.008345	-0.223656
22	1	0	1.633355	-3.320087	0.101510
23	1	0	5.778144	-2.362689	-0.500751
24	1	0	3.951173	-4.050836	-0.439793
25	6	0	-2.927211	-1.747125	0.114991
26	6	0	-1.732883	-1.253395	-0.390416
27	6	0	-1.591555	0.104479	-0.696471
28	6	0	-2.693508	0.943364	-0.490638

29	6	0	-3.880269	0.450379	0.026037
30	6	0	-4.003808	-0.899433	0.323570
31	7	0	-0.402151	0.622499	-1.257887
32	8	0	-0.012313	1.817066	-0.804940
33	8	0	0.420255	-0.128609	-1.834378
34	9	0	-2.640311	2.230801	-0.810246
35	9	0	-4.914553	1.266611	0.209754
36	9	0	-5.143680	-1.374139	0.812069
37	9	0	-3.031731	-3.038034	0.419447
38	9	0	-0.724098	-2.109860	-0.519702

---

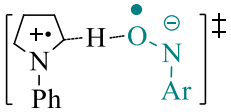
1 imaginary frequencies (708.14 icm^{-1})

Zero-point Energies= -1375.670631

Thermal Energies= -1375.648723

Thermal Enthalpies= -1375.647779

Thermal Free Energies= -1375.723559

11. T**S-3**  Charge =0 Multiplicity =1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.822236	2.367766	-0.822231
2	6	0	-1.355121	1.021398	-0.412570
3	6	0	-3.223634	2.422043	-0.663532
4	6	0	-1.986697	3.298347	-0.454870
5	1	0	0.114222	2.620262	-0.321651
6	1	0	-0.638435	2.365119	-1.905669
7	1	0	-0.815606	0.686318	0.970205
8	1	0	-0.873356	0.073280	-0.694291
9	1	0	-3.605437	2.480938	-1.689868
10	1	0	-4.038587	2.638997	0.030339
11	1	0	-2.019160	4.204342	-1.061312
12	1	0	-1.912200	3.584408	0.598056
13	7	0	-2.707547	1.061910	-0.426348
14	6	0	-3.543771	-0.048197	-0.234259
15	6	0	-3.022697	-1.243458	0.283528

16	6	0	-4.903580	0.041707	-0.559620
17	6	0	-3.864221	-2.337222	0.450438
18	1	0	-1.977659	-1.320307	0.569897
19	6	0	-5.729668	-1.061154	-0.377587
20	1	0	-5.311286	0.960684	-0.966452
21	6	0	-5.216826	-2.255393	0.124830
22	1	0	-3.454623	-3.258321	0.853168
23	1	0	-6.781383	-0.983772	-0.635472
24	1	0	-5.866630	-3.112851	0.266856
25	6	0	3.600323	-1.450328	-0.418669
26	6	0	2.327032	-1.633616	0.077530
27	6	0	1.576864	-0.594309	0.676602
28	6	0	2.221225	0.661044	0.735845
29	6	0	3.499652	0.849525	0.229610
30	6	0	4.201197	-0.197922	-0.344438
31	7	0	0.319166	-0.943868	1.120356
32	8	0	-0.303509	0.079966	1.723688
33	9	0	1.631493	1.747130	1.253632
34	9	0	4.061820	2.057804	0.299499
35	9	0	5.429313	-0.008613	-0.825401
36	9	0	4.259740	-2.467535	-0.974647
37	9	0	1.781023	-2.847617	-0.019526

---

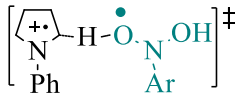
1 imaginary frequencies (539.37 icm^{-1})

Zero-point Energies= -1300.510683

Thermal Energies= -1300.489607

Thermal Enthalpies= -1300.488663

Thermal Free Energies= -1300.563109

12. **TS-4**  Charge = 1 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.185426	2.336322	1.176000
2	6	0	1.749634	0.941705	0.998173
3	6	0	3.139630	2.412098	-0.208946

4	6	0	1.763447	3.057137	-0.045484
5	1	0	0.096682	2.352018	1.221100
6	1	0	1.577220	2.753581	2.112034
7	1	0	0.957886	0.338197	0.107666
8	1	0	1.715965	0.204824	1.802050
9	1	0	3.904009	2.911536	0.398012
10	1	0	3.489283	2.342038	-1.240482
11	1	0	1.835679	4.136925	0.085969
12	1	0	1.147844	2.847686	-0.925249
13	7	0	2.944767	1.054722	0.344181
14	6	0	3.868992	0.022491	0.162803
15	6	0	3.499514	-1.310414	0.407909
16	6	0	5.168884	0.329042	-0.268477
17	6	0	4.436033	-2.318726	0.236970
18	1	0	2.481785	-1.564132	0.683784
19	6	0	6.093769	-0.693357	-0.426782
20	1	0	5.459971	1.356849	-0.454595
21	6	0	5.734971	-2.016623	-0.173284
22	1	0	4.146067	-3.348993	0.414529
23	1	0	7.101820	-0.453342	-0.747948
24	1	0	6.462166	-2.811403	-0.302525
25	6	0	-4.162769	-1.073523	0.143039
26	6	0	-2.863657	-1.515863	-0.041888
27	6	0	-1.820596	-0.609083	-0.298223
28	6	0	-2.149176	0.753153	-0.392402
29	6	0	-3.452665	1.186567	-0.211872
30	6	0	-4.466242	0.277458	0.052702
31	7	0	-0.516953	-1.062179	-0.544193
32	8	0	0.428836	-0.272786	-0.871064
33	9	0	-1.228521	1.684377	-0.625732
34	9	0	-3.724338	2.482298	-0.286980
35	9	0	-5.708290	0.694711	0.228679
36	9	0	-5.123056	-1.952714	0.392228
37	9	0	-2.644653	-2.823262	0.030288
38	8	0	-0.119202	-2.254656	-0.005579
39	1	0	-0.339603	-2.233047	0.951095

---

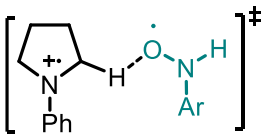
1 imaginary frequencies (1996.98 icm^{-1})

Zero-point Energies= -1376.074035

Thermal Energies= -1376.051874

Thermal Enthalpies= -1376.050930

Thermal Free Energies= -1376.127030

13. **TS-5**  Charge =1 Multiplicity =1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.995978	2.394990	-1.829950
2	6	0	-1.605988	1.061897	-1.446078
3	6	0	-3.304765	2.690017	-1.252184
4	6	0	-1.945314	3.380022	-1.139979
5	1	0	0.040287	2.490891	-1.503950
6	1	0	-1.029083	2.500603	-2.921127
7	1	0	-1.152095	0.783412	-0.253825
8	1	0	-1.325384	0.139232	-1.960591
9	1	0	-3.805747	2.915460	-2.201369
10	1	0	-3.988449	2.897611	-0.427450
11	1	0	-1.952072	4.367797	-1.601244
12	1	0	-1.668061	3.482811	-0.086214
13	7	0	-2.951836	1.255314	-1.261879
14	6	0	-3.878282	0.239938	-1.031852
15	6	0	-3.435783	-1.060980	-0.736963
16	6	0	-5.251803	0.523894	-1.087759
17	6	0	-4.366098	-2.065553	-0.519779
18	1	0	-2.375620	-1.275596	-0.652836
19	6	0	-6.167936	-0.495235	-0.869540
20	1	0	-5.598817	1.524423	-1.319943
21	6	0	-5.732523	-1.789821	-0.588326
22	1	0	-4.023975	-3.068649	-0.287449
23	1	0	-7.229186	-0.276215	-0.922353
24	1	0	-6.454853	-2.580919	-0.416833
25	6	0	3.666852	-1.046038	0.664952
26	6	0	2.309131	-1.234094	0.826663

27	6	0	1.412043	-0.157026	0.825566
28	6	0	1.929316	1.132890	0.652874
29	6	0	3.292739	1.322272	0.481553
30	6	0	4.164165	0.241800	0.491467
31	7	0	0.071462	-0.432606	1.008759
32	8	0	-0.841284	0.475291	0.944192
33	9	0	1.140901	2.204765	0.634979
34	9	0	3.766034	2.550289	0.312216
35	9	0	5.464018	0.434785	0.330573
36	9	0	4.492092	-2.083917	0.667919
37	9	0	1.821360	-2.465118	0.983576
38	1	0	-0.236869	-1.401559	1.089449

---

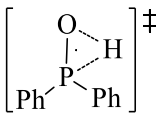
1 imaginary frequencies (1846.81 icm^{-1})

Zero-point Energies= -1300.941879

Thermal Energies= -1300.921691

Thermal Enthalpies= -1300.920747

Thermal Free Energies= -1300.991208

14. **Ts-6**  Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	0.020038	1.352561	-0.374053
2	8	0	-0.102205	2.564610	0.661836
3	1	0	0.110975	2.779874	-0.745221
4	6	0	1.448530	0.268552	-0.095119
5	6	0	1.395136	-0.826954	0.776448
6	6	0	2.650896	0.585959	-0.736403
7	6	0	2.536319	-1.589981	1.003914
8	1	0	0.464470	-1.081610	1.276649
9	6	0	3.790137	-0.181059	-0.508820
10	1	0	2.690876	1.432763	-1.417314
11	6	0	3.731461	-1.268011	0.361027
12	1	0	2.494045	-2.436953	1.681903

13	1	0	4.719983	0.066636	-1.011413
14	1	0	4.619111	-1.867938	0.538294
15	6	0	-1.430879	0.281205	-0.234520
16	6	0	-1.532345	-0.925077	-0.938880
17	6	0	-2.482922	0.712975	0.575854
18	6	0	-2.683701	-1.695436	-0.823871
19	1	0	-0.710400	-1.261847	-1.566484
20	6	0	-3.630888	-0.068740	0.694344
21	1	0	-2.388377	1.654342	1.110375
22	6	0	-3.732149	-1.267950	-0.006392
23	1	0	-2.764824	-2.631636	-1.367761
24	1	0	-4.446622	0.261018	1.330619
25	1	0	-4.629733	-1.872835	0.080973

---

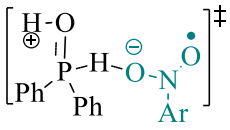
1 imaginary frequencies (1881.73 icm^{-1})

Zero-point Energies= -879.935757

Thermal Energies= -879.923743

Thermal Enthalpies= -879.922798

Thermal Free Energies= -879.975680

15. **TS-7**  Charge = 0 Multiplicity = 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-1.917666	0.799182	0.818949
2	1	0	-1.316190	-0.069175	1.880771
3	6	0	-3.349218	0.059733	0.034325
4	6	0	-4.109821	0.810583	-0.870808
5	6	0	-3.714452	-1.248085	0.367251
6	6	0	-5.241841	0.244409	-1.443965
7	1	0	-3.817387	1.827143	-1.122230
8	6	0	-4.849631	-1.806102	-0.215747
9	1	0	-3.092133	-1.823495	1.045883
10	6	0	-5.609177	-1.061820	-1.115255
11	1	0	-5.836691	0.817498	-2.147975

12	1	0	-5.137513	-2.822800	0.031551
13	1	0	-6.492984	-1.501453	-1.567741
14	6	0	-0.704978	1.279875	-0.416142
15	6	0	0.027014	2.459416	-0.238910
16	6	0	-0.396829	0.401076	-1.460643
17	6	0	1.071596	2.755815	-1.109565
18	1	0	-0.212658	3.131894	0.578292
19	6	0	0.654577	0.703578	-2.320721
20	1	0	-0.950736	-0.525925	-1.577091
21	6	0	1.389065	1.875898	-2.143586
22	1	0	1.643841	3.667902	-0.972727
23	1	0	0.902380	0.020411	-3.127062
24	1	0	2.213534	2.103389	-2.812869
25	8	0	-2.353220	2.240605	1.426815
26	1	0	-2.717464	2.174228	2.328803
27	6	0	3.252383	-1.405057	-0.577013
28	6	0	2.058465	-1.846207	-0.031737
29	6	0	1.343582	-1.061531	0.883856
30	6	0	1.886859	0.181528	1.234652
31	6	0	3.076856	0.624934	0.680056
32	6	0	3.768359	-0.165563	-0.225167
33	7	0	0.095571	-1.493073	1.356242
34	8	0	-0.332830	-1.042381	2.508696
35	8	0	-0.723760	-2.012332	0.518327
36	9	0	1.231665	1.029164	2.030384
37	9	0	3.531207	1.841875	0.979263
38	9	0	4.909711	0.264973	-0.760063
39	9	0	3.917348	-2.178139	-1.435495
40	9	0	1.618027	-3.050968	-0.384259

---

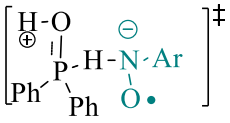
1 imaginary frequencies (367.50 cm^{-1})

Zero-point Energies= -1813.081062

Thermal Energies= -1813.055807

Thermal Enthalpies= -1813.054862

Thermal Free Energies= -1813.138741

16. **TS-8**  Charge =0 Multiplicity =2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-1.653578	-0.379767	1.192538
2	1	0	-0.807552	-1.524163	0.812597
3	6	0	-3.076612	-0.316037	0.114850
4	6	0	-4.098383	0.618959	0.325431
5	6	0	-3.162360	-1.253052	-0.921034
6	6	0	-5.205568	0.616793	-0.514287
7	1	0	-4.026161	1.339263	1.136491
8	6	0	-4.275435	-1.243736	-1.756867
9	1	0	-2.362197	-1.972553	-1.074391
10	6	0	-5.290964	-0.312316	-1.552670
11	1	0	-6.001810	1.337958	-0.360949
12	1	0	-4.348829	-1.964554	-2.564588
13	1	0	-6.158083	-0.308879	-2.206113
14	6	0	-0.689620	1.127641	1.134502
15	6	0	0.395208	1.230128	2.016085
16	6	0	-0.908629	2.101557	0.157314
17	6	0	1.253524	2.318474	1.920385
18	1	0	0.569222	0.463079	2.766137
19	6	0	-0.042602	3.188746	0.071467
20	1	0	-1.734662	2.006038	-0.541188
21	6	0	1.035530	3.294354	0.946684
22	1	0	2.096823	2.401425	2.598339
23	1	0	-0.203757	3.944966	-0.689869
24	1	0	1.714974	4.137365	0.867159
25	8	0	-2.122933	-0.445095	2.740437
26	1	0	-2.473426	-1.321734	2.991252
27	6	0	1.797522	0.554135	-1.444252
28	6	0	0.975365	-0.488433	-1.071446
29	6	0	1.397351	-1.576972	-0.281196
30	6	0	2.761637	-1.560124	0.078256
31	6	0	3.599096	-0.519755	-0.299351

32	6	0	3.132679	0.543634	-1.058932
33	7	0	0.417720	-2.489731	0.105610
34	8	0	0.847792	-3.553582	0.694083
35	9	0	3.307286	-2.516956	0.835160
36	9	0	4.880254	-0.534390	0.082084
37	9	0	3.948859	1.542820	-1.406944
38	9	0	1.321773	1.560625	-2.182731
39	9	0	-0.321529	-0.426336	-1.441793

---

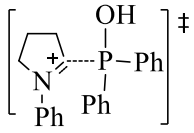
1 imaginary frequencies (79.18 icm^{-1})

Zero-point Energies= -1737.915530

Thermal Energies= -1737.890999

Thermal Enthalpies= -1737.890055

Thermal Free Energies= -1737.973212

17. **TS-9** 

Charge = 1 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.206827	-2.983663	-1.516852
2	6	0	-1.674210	-2.541463	-1.508406
3	6	0	-0.760997	-2.059601	0.571532
4	6	0	0.149514	-3.082021	-0.028892
5	1	0	-0.065089	-3.922037	-2.052855
6	1	0	0.410555	-2.213315	-1.988886
7	1	0	-2.374560	-3.381491	-1.538608
8	1	0	-1.925009	-1.835118	-2.302199
9	1	0	-0.798100	-1.803529	1.626736
10	1	0	1.203002	-2.909025	0.199251
11	1	0	-0.133361	-4.054321	0.397385
12	7	0	-1.809565	-1.868010	-0.192244
13	6	0	-2.888054	-0.995300	0.106622
14	6	0	-4.046637	-1.051328	-0.671767
15	6	0	-2.772954	-0.064192	1.144668
16	6	0	-5.095005	-0.178894	-0.400212
17	1	0	-4.138012	-1.774945	-1.474471

18	6	0	-3.831345	0.801290	1.401647
19	1	0	-1.871221	0.004763	1.746037
20	6	0	-4.992364	0.748487	0.634201
21	1	0	-5.996032	-0.227542	-1.002813
22	1	0	-3.738288	1.525500	2.204435
23	15	0	0.789432	0.018557	0.520459
24	6	0	0.582969	1.733717	-0.057998
25	6	0	-0.590939	2.069903	-0.740080
26	6	0	1.542645	2.722754	0.200897
27	6	0	-0.808856	3.382230	-1.154579
28	1	0	-1.336263	1.305658	-0.946745
29	6	0	1.318356	4.032779	-0.206833
30	1	0	2.466673	2.466461	0.713868
31	6	0	0.143191	4.361382	-0.884597
32	1	0	-1.720309	3.637719	-1.685761
33	1	0	2.060668	4.797728	-0.001755
34	1	0	-0.026537	5.384738	-1.205138
35	6	0	2.555479	-0.320839	0.237945
36	6	0	3.140239	-0.015093	-0.997969
37	6	0	3.302529	-0.996997	1.209246
38	6	0	4.463007	-0.365809	-1.248424
39	1	0	2.566430	0.510887	-1.757698
40	6	0	4.628370	-1.341367	0.954299
41	1	0	2.850472	-1.244522	2.166089
42	6	0	5.208531	-1.026971	-0.272436
43	1	0	4.914635	-0.118016	-2.203989
44	1	0	5.207206	-1.854582	1.716058
45	1	0	6.241614	-1.296089	-0.469367
46	8	0	0.674007	0.079984	2.168613
47	1	0	1.247206	0.755982	2.578412
48	1	0	-5.812116	1.428908	0.839876

---

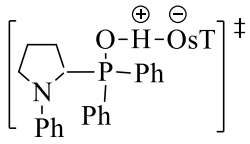
1 imaginary frequencies (78.31 icm^{-1})

Zero-point Energies= -1322.524483

Thermal Energies= -1322.502733

Thermal Enthalpies= -1322.501788

Thermal Free Energies= -1322.577433

18. **TS-10**  Charge =0 Multiplicity =1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.723232	-3.359426	-0.513848
2	6	0	3.615050	-2.276325	0.091982
3	6	0	2.059635	-1.221195	-1.425821
4	6	0	2.185127	-2.711219	-1.791884
5	1	0	3.286455	-4.271791	-0.720053
6	1	0	1.906695	-3.612914	0.167363
7	1	0	4.650459	-2.363426	-0.265894
8	1	0	3.629791	-2.320775	1.186507
9	1	0	2.232933	-0.585060	-2.302712
10	1	0	1.243473	-3.143406	-2.139936
11	1	0	2.916017	-2.796110	-2.601505
12	7	0	3.037827	-1.005873	-0.373254
13	6	0	3.776685	0.172271	-0.253962
14	6	0	4.859626	0.224987	0.643938
15	6	0	3.472293	1.333454	-0.988237
16	6	0	5.602840	1.391402	0.793247
17	1	0	5.120435	-0.646067	1.233903
18	6	0	4.225483	2.490717	-0.826757
19	1	0	2.635951	1.352556	-1.676877
20	6	0	5.297304	2.535609	0.061763
21	1	0	6.432670	1.397747	1.494344
22	1	0	3.959502	3.369629	-1.407429
23	15	0	0.345626	-0.826588	-0.851972
24	6	0	0.201173	0.948902	-0.594262
25	6	0	-0.090421	1.728708	-1.722291
26	6	0	0.512250	1.560544	0.623165
27	6	0	-0.043641	3.115750	-1.631605
28	1	0	-0.354042	1.254451	-2.663354
29	6	0	0.574679	2.949459	0.699237
30	1	0	0.711079	0.967445	1.509250
31	6	0	0.304534	3.724707	-0.425905

32	1	0	-0.274236	3.719663	-2.503469
33	1	0	0.838041	3.423907	1.639435
34	1	0	0.356717	4.807451	-0.362450
35	6	0	0.008567	-1.750283	0.654590
36	6	0	0.791487	-1.624569	1.812676
37	6	0	-1.045254	-2.668819	0.611826
38	6	0	0.502130	-2.407234	2.924789
39	1	0	1.629624	-0.934577	1.841801
40	6	0	-1.323927	-3.449555	1.732111
41	1	0	-1.658521	-2.755366	-0.280769
42	6	0	-0.554431	-3.318176	2.884835
43	1	0	1.104508	-2.309419	3.822372
44	1	0	-2.146677	-4.156895	1.699867
45	1	0	-0.774904	-3.927832	3.755835
46	8	0	-0.595925	-1.284924	-2.000596
47	1	0	-1.605643	-0.773915	-2.156582
48	1	0	5.878952	3.443497	0.183005
49	16	0	-3.793170	-0.432358	-1.397133
50	8	0	-3.784885	-1.838653	-0.978680
51	8	0	-5.048944	0.105182	-1.914922
52	8	0	-2.663658	-0.152986	-2.391317
53	6	0	-3.333438	0.531911	0.027071
54	6	0	-3.105475	-0.093113	1.244967
55	6	0	-2.704508	0.672327	2.340690
56	6	0	-2.548724	2.053360	2.230812
57	6	0	-2.798726	2.663158	0.991787
58	6	0	-3.184693	1.914041	-0.108990
59	1	0	-3.238054	-1.166174	1.330425
60	1	0	-2.512429	0.183704	3.292631
61	1	0	-2.675216	3.739054	0.893670
62	1	0	-3.364554	2.390310	-1.068829
63	6	0	-2.125742	2.887194	3.410673
64	1	0	-2.961528	3.491751	3.780813
65	1	0	-1.774181	2.260498	4.234572
66	1	0	-1.323187	3.579269	3.135082

---

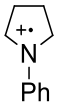
1 imaginary frequencies (107.91 icm^{-1})

Zero-point Energies= -2217.153449

Thermal Energies= -2217.122107

Thermal Enthalpies= -2217.121163

Thermal Free Energies= -2217.217229



19. **IV** Charge = 1 Multiplicity = 2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.506478	-0.689781	0.305625
2	6	0	-2.108558	-1.216352	-0.008219
3	6	0	-2.103912	1.219383	-0.023394
4	6	0	-3.504101	0.698255	-0.335994
5	1	0	-4.278846	-1.348710	-0.093113
6	1	0	-3.637704	-0.609471	1.388817
7	1	0	-2.055932	-1.669443	-1.005610
8	1	0	-1.723391	-1.924606	0.727482
9	1	0	-2.048483	1.671955	0.974087
10	1	0	-1.716927	1.926483	-0.759234
11	1	0	-4.273539	1.360175	0.063457
12	1	0	-3.636594	0.618507	-1.419073
13	7	0	-1.272798	-0.000071	-0.016417
14	6	0	0.070055	-0.002679	-0.017307
15	6	0	0.788265	-1.232726	-0.130987
16	6	0	0.793388	1.224486	0.095469
17	6	0	2.163820	-1.220346	-0.133568
18	1	0	0.249611	-2.166949	-0.234865
19	6	0	2.168856	1.206473	0.096515
20	1	0	0.258607	2.160885	0.199822
21	6	0	2.863308	-0.008363	-0.018871
22	1	0	2.709121	-2.152843	-0.228130
23	1	0	2.718098	2.136720	0.190486
24	1	0	3.948150	-0.010558	-0.019469

---

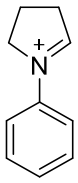
0 imaginary frequencies

Zero-point Energies= -443.055473

Thermal Energies= -443.046302

Thermal Enthalpies= -443.045358

Thermal Free Energies= -443.090676

20. **VII**  Charge = 1 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.101868	0.573042	0.465168
2	6	0	1.696439	1.153693	0.288515
3	6	0	1.620992	-1.040124	-0.423928
4	6	0	3.071321	-0.734783	-0.347007
5	1	0	3.868091	1.264986	0.117343
6	1	0	3.282597	0.351485	1.518898
7	1	0	1.622482	1.850625	-0.550620
8	1	0	1.275075	1.612937	1.182949
9	1	0	1.174118	-1.965043	-0.776418
10	1	0	3.630640	-1.559830	0.100438
11	1	0	3.441313	-0.612137	-1.374143
12	7	0	0.885256	-0.049133	-0.060594
13	6	0	-0.549155	-0.031591	-0.025162
14	6	0	-1.213814	1.168375	-0.268389
15	6	0	-1.243541	-1.205252	0.264563
16	6	0	-2.605024	1.179926	-0.245425
17	1	0	-0.661964	2.076516	-0.487703
18	6	0	-2.632807	-1.176589	0.280985
19	1	0	-0.708759	-2.119661	0.501318
20	6	0	-3.314149	0.011938	0.023893
21	1	0	-3.132592	2.107521	-0.440413
22	1	0	-3.181559	-2.083979	0.509969
23	1	0	-4.399010	0.028703	0.043257

---

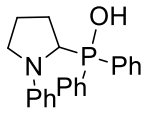
0 imaginary frequencies

Zero-point Energies= -442.479653

Thermal Energies= -442.470907

Thermal Enthalpies= -442.469963

Thermal Free Energies= -442.513740



22 **XIII** Charge =1 Multiplicity =1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.348807	-2.856675	0.014923
2	6	0	0.046639	-2.737804	0.623088
3	6	0	-0.132081	-1.182671	-1.207922
4	6	0	-1.153484	-2.313469	-1.401473
5	1	0	-1.705430	-3.888073	0.018870
6	1	0	-2.066026	-2.246017	0.572148
7	1	0	0.651536	-3.628651	0.407042
8	1	0	0.018360	-2.596544	1.707402
9	1	0	0.482750	-1.037844	-2.104102
10	1	0	-2.076917	-1.995537	-1.891445
11	1	0	-0.681296	-3.068207	-2.037537
12	7	0	0.637481	-1.563276	-0.041289
13	6	0	2.021203	-1.348281	0.027295
14	6	0	2.770440	-1.971838	1.039309
15	6	0	2.689518	-0.489028	-0.861719
16	6	0	4.138132	-1.741830	1.149917
17	1	0	2.287074	-2.634842	1.748022
18	6	0	4.056958	-0.269282	-0.737358
19	1	0	2.151805	0.033796	-1.644870
20	6	0	4.795543	-0.890763	0.266100
21	1	0	4.691163	-2.238854	1.941552
22	1	0	4.544353	0.402813	-1.437581
23	15	0	-0.921013	0.467016	-0.910783
24	6	0	0.248044	1.615835	-0.190183
25	6	0	0.664152	2.707625	-0.960750
26	6	0	0.802881	1.388486	1.078150
27	6	0	1.628157	3.575203	-0.456527
28	1	0	0.253575	2.874885	-1.951601
29	6	0	1.765440	2.261571	1.568933
30	1	0	0.512619	0.522458	1.664151
31	6	0	2.177575	3.351701	0.803433
32	1	0	1.952410	4.421708	-1.052680
33	1	0	2.203363	2.082621	2.545297
34	1	0	2.934300	4.027240	1.189693
35	6	0	-2.447685	0.379879	0.026366
36	6	0	-2.486925	0.668849	1.395271
37	6	0	-3.609497	-0.030932	-0.645709
38	6	0	-3.680894	0.518596	2.093317
39	1	0	-1.603645	1.021149	1.916679

40	6	0	-4.797680	-0.169958	0.061733
41	1	0	-3.591930	-0.232774	-1.712941
42	6	0	-4.830518	0.094735	1.430334
43	1	0	-3.712250	0.740566	3.154823
44	1	0	-5.697610	-0.483842	-0.456686
45	1	0	-5.759631	-0.020330	1.979503
46	8	0	-1.289507	0.940000	-2.401501
47	1	0	-1.884186	1.715233	-2.450477
48	1	0	5.861825	-0.712974	0.358357

---

0 imaginary frequencies

Zero-point Energies= -1322.543063

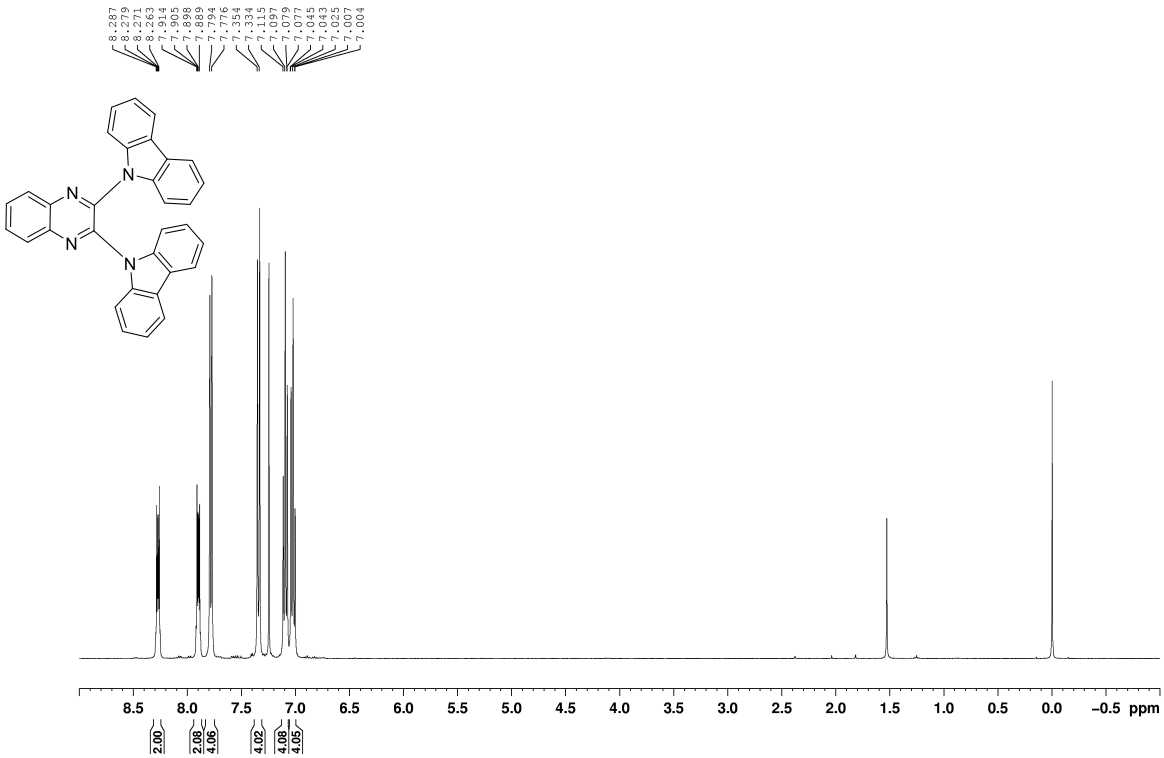
Thermal Energies= -1322.521545

Thermal Enthalpies= -1322.520601

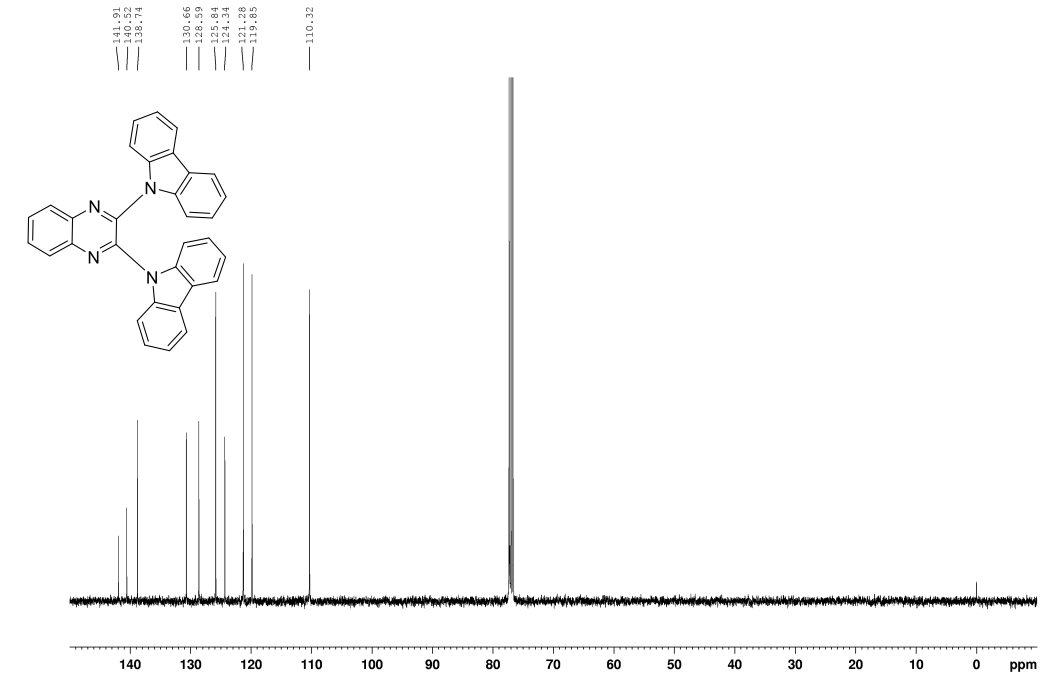
Thermal Free Energies= -1322.595093

10. NMR spectra of compound

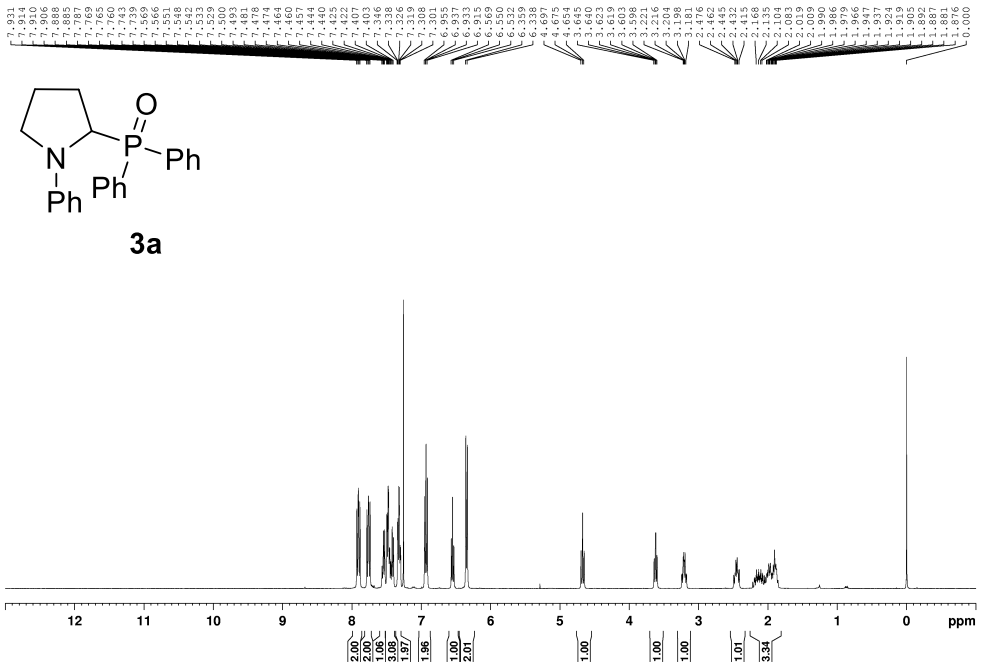
^{1}H NMR of **DCQ** ($CDCl_3$, 400 MHz)



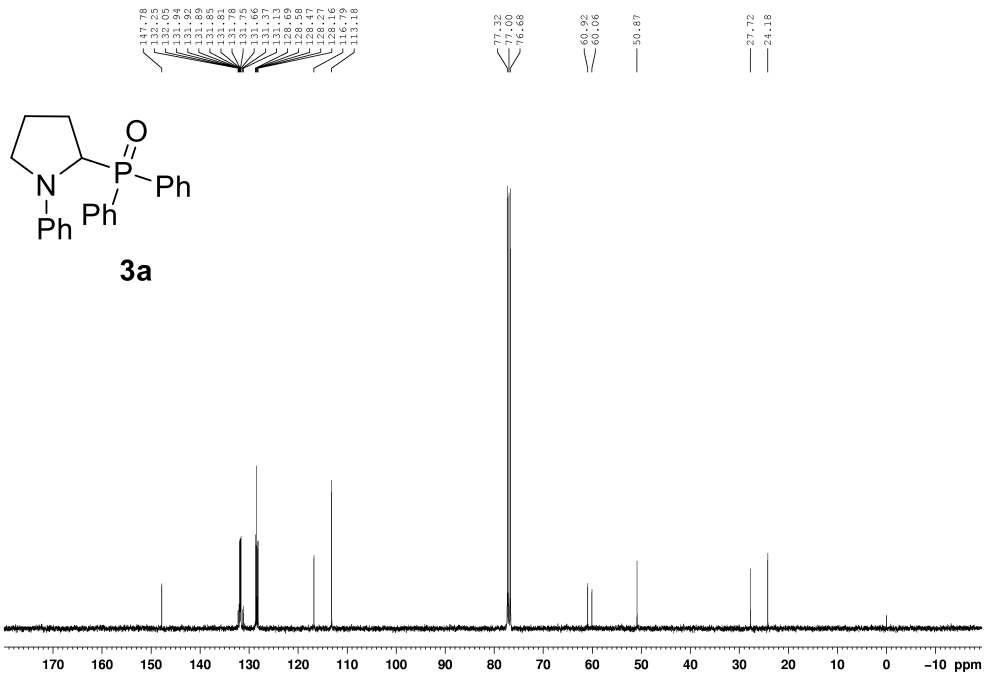
^{13}C NMR of **DCQ** ($CDCl_3$, 101 MHz)



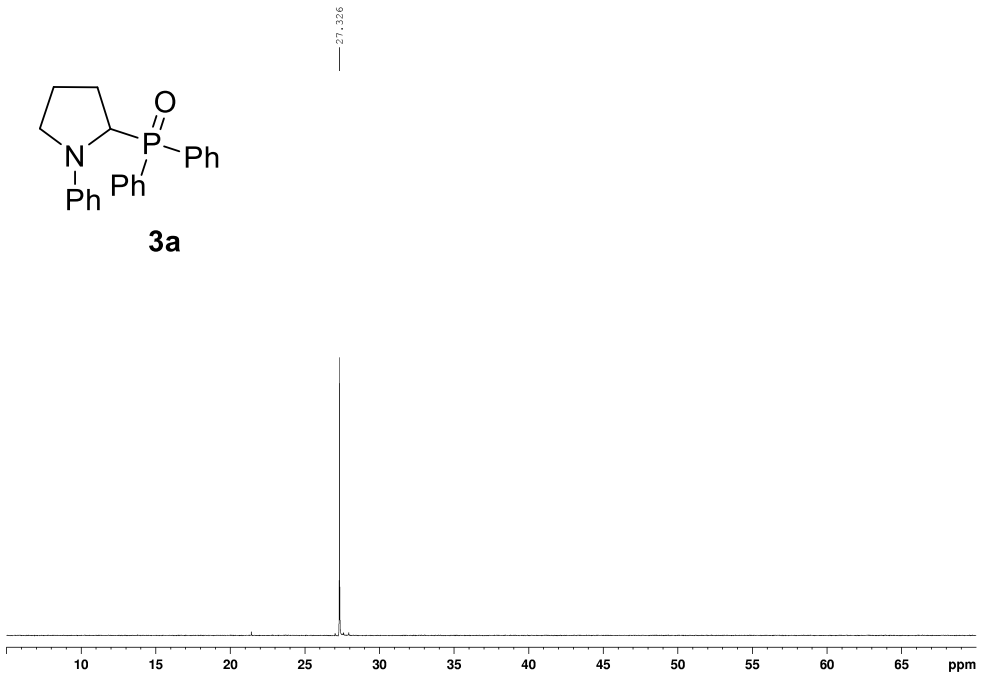
^{1}H NMR of **3a** ($CDCl_3$, 400 MHz)



^{13}C NMR of **3a** ($CDCl_3$, 101 MHz)

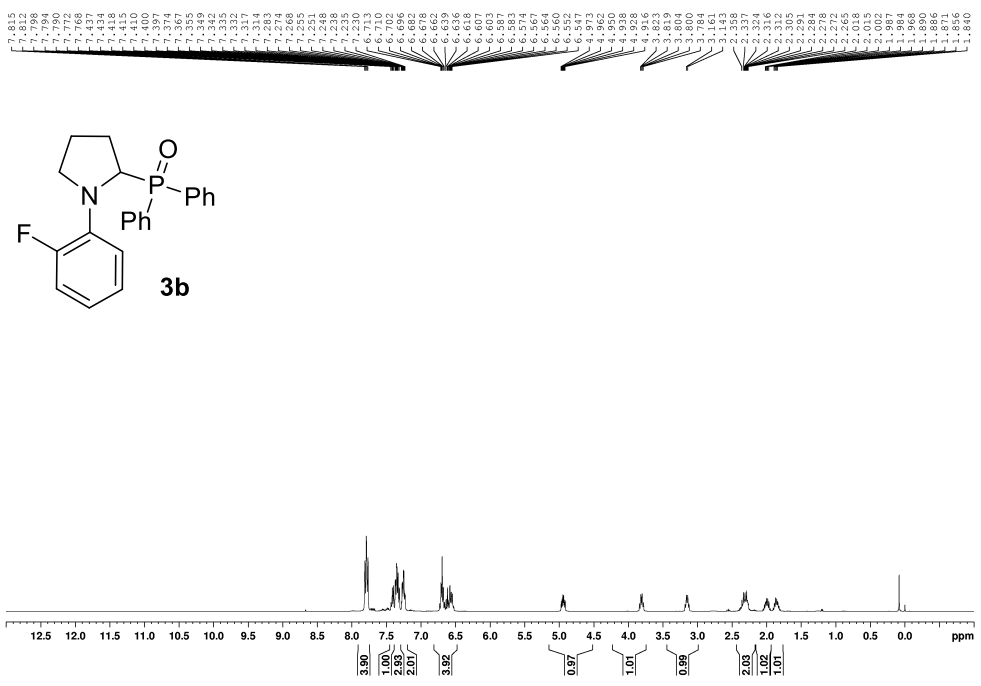


^{31}P NMR of **3a** ($CDCl_3$, 162 MHz)



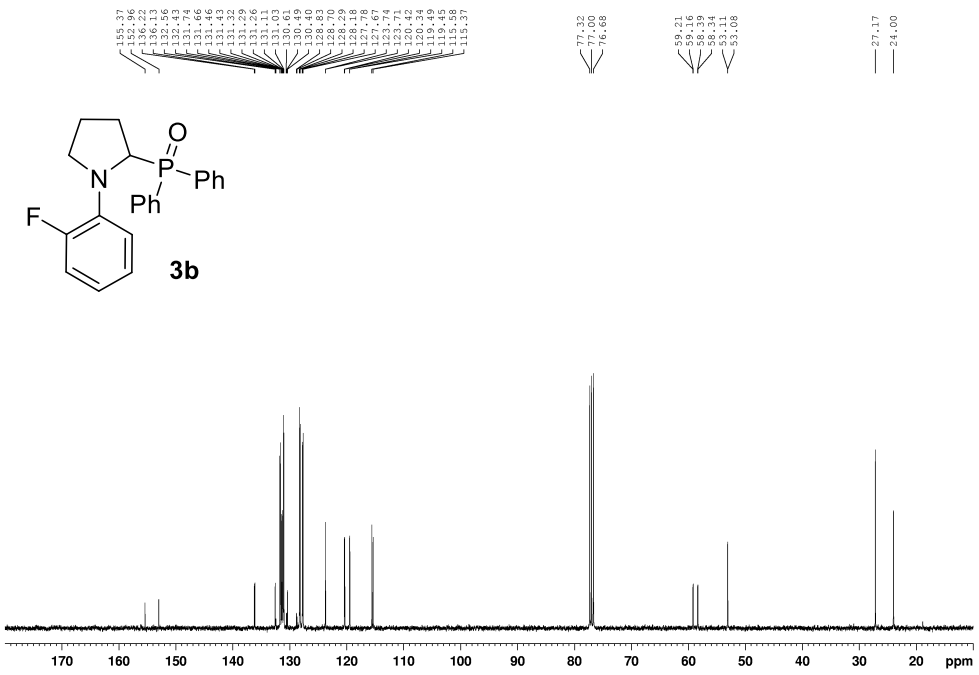
3a

^{1}H NMR of **3b** ($CDCl_3$, 400 MHz)

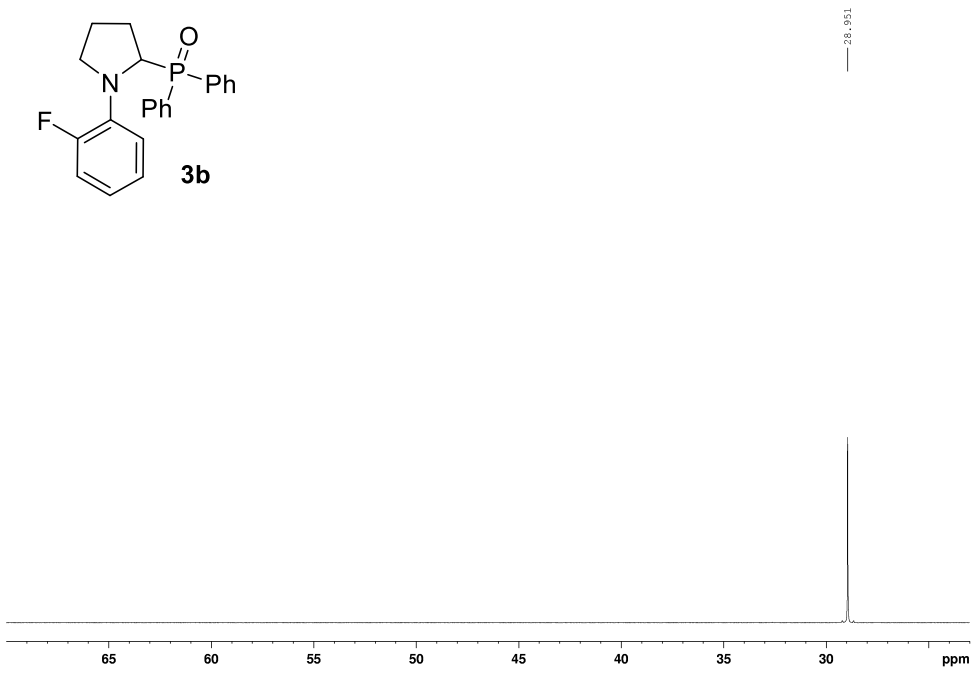


3b

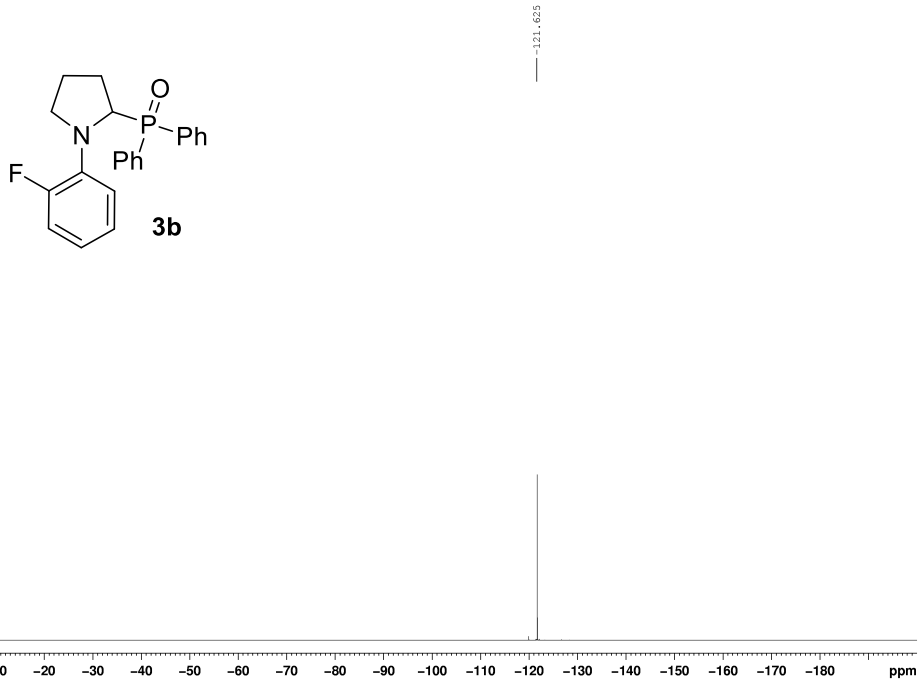
^{13}C NMR of **3b** ($CDCl_3$, 101 MHz)



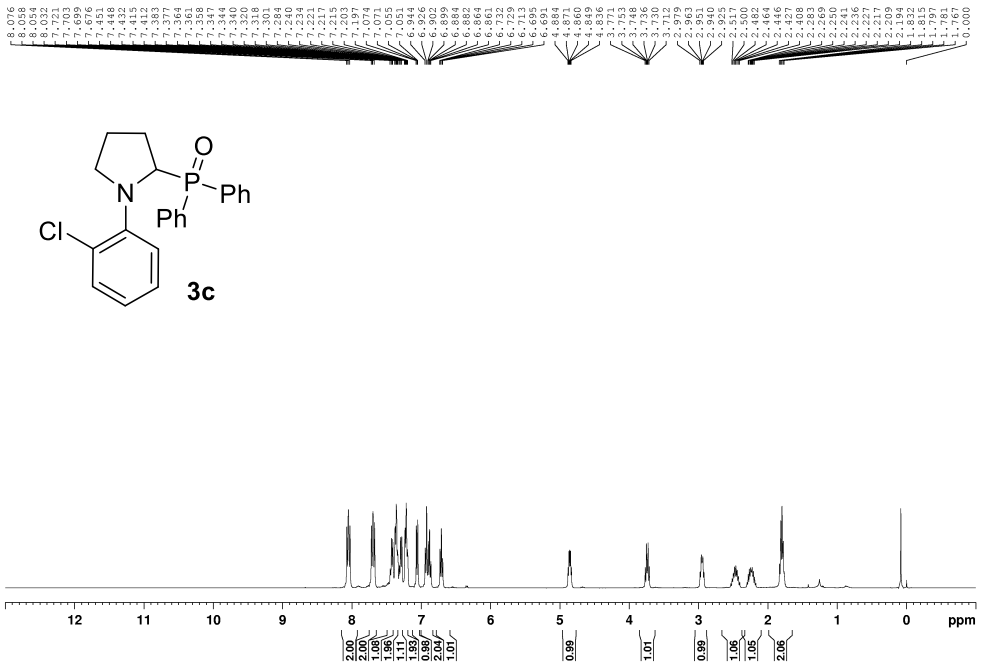
^{31}P NMR of **3b** ($CDCl_3$, 162 MHz)



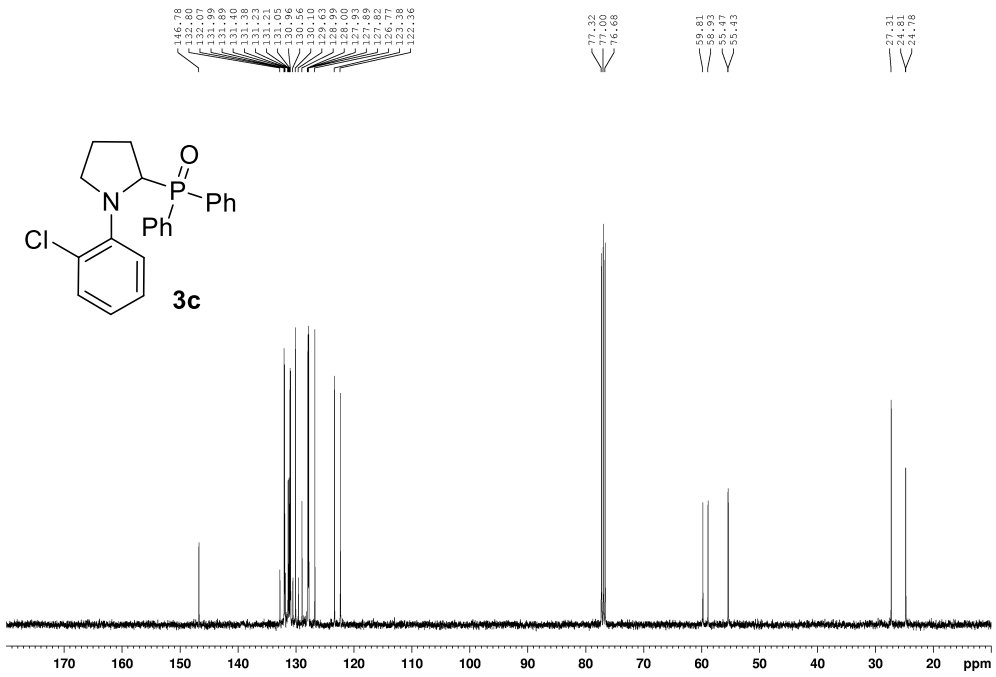
^{19}F NMR of **3b** ($CDCl_3$, 376 MHz)



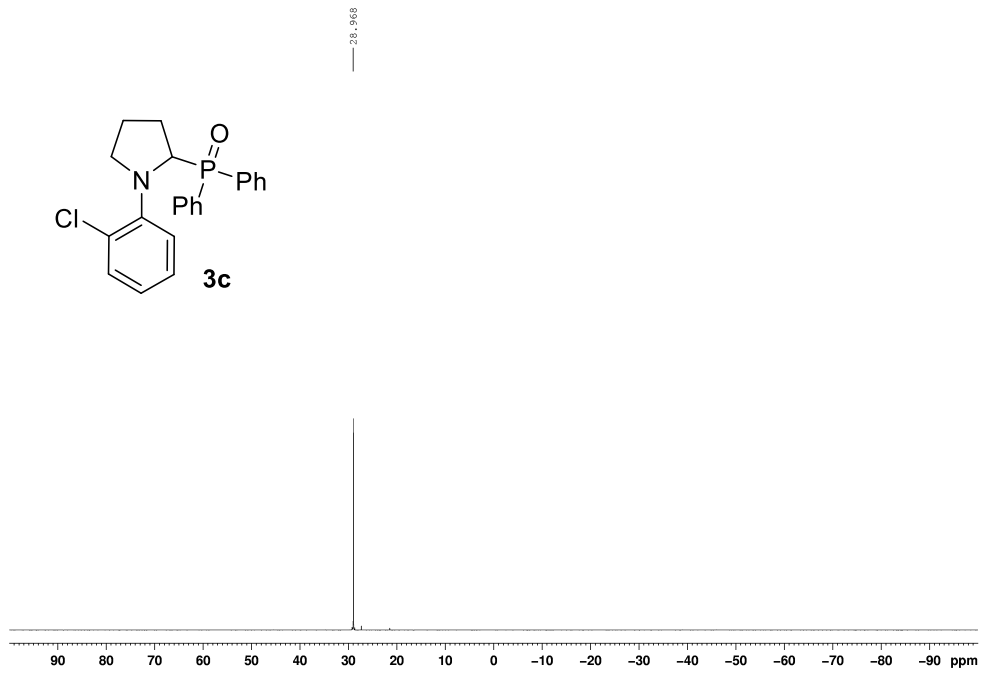
^{1}H NMR of **3c** ($CDCl_3$, 400 MHz)



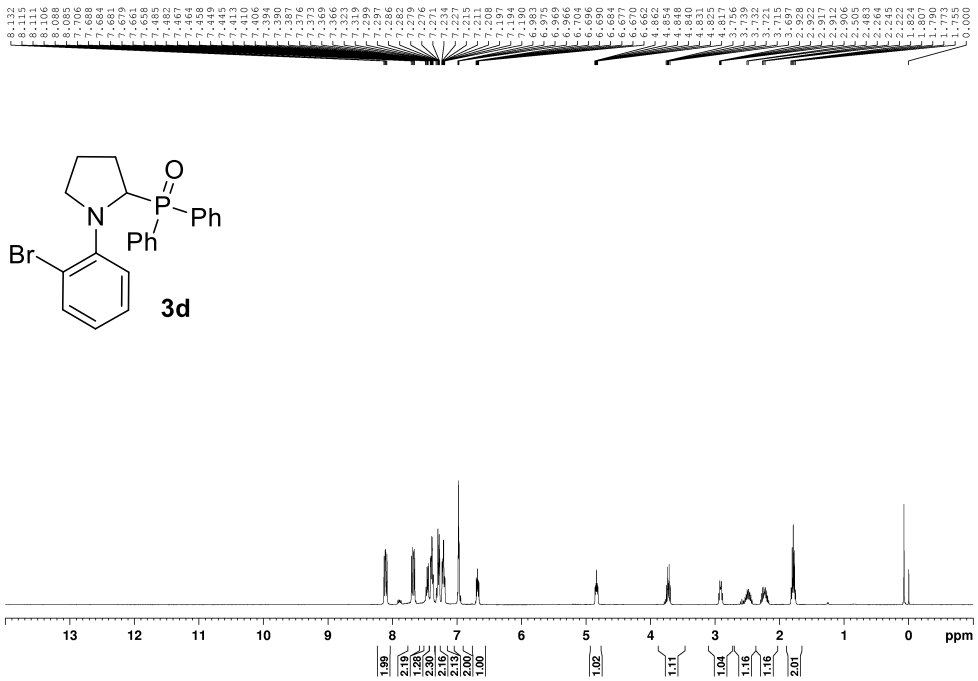
^{13}C NMR of **3c** ($CDCl_3$, 101 MHz)



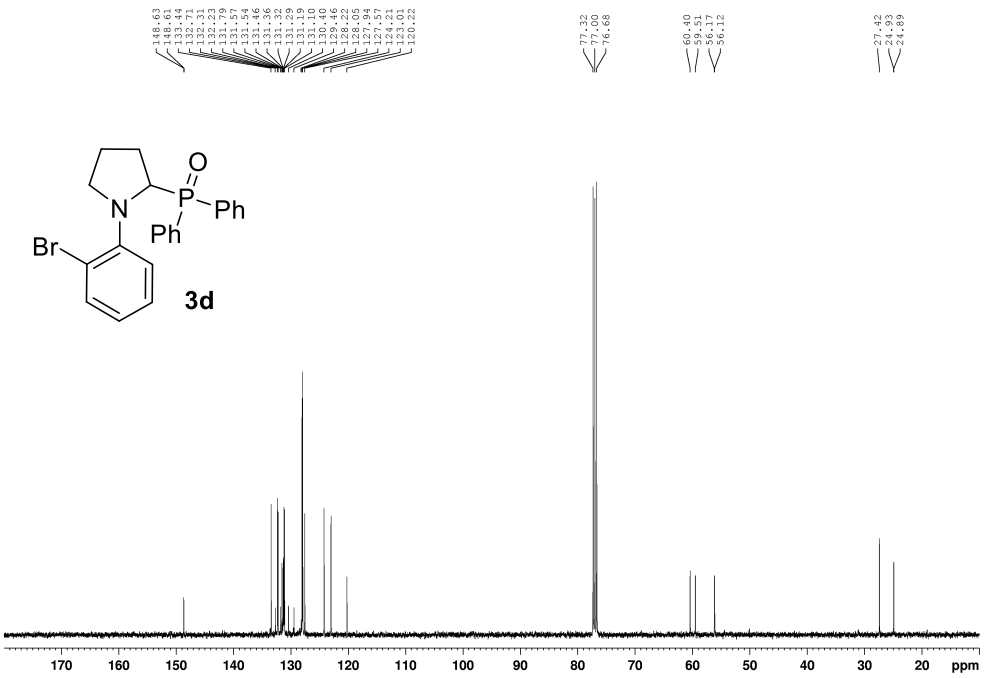
^{31}P NMR of **3c** ($CDCl_3$, 162 MHz)



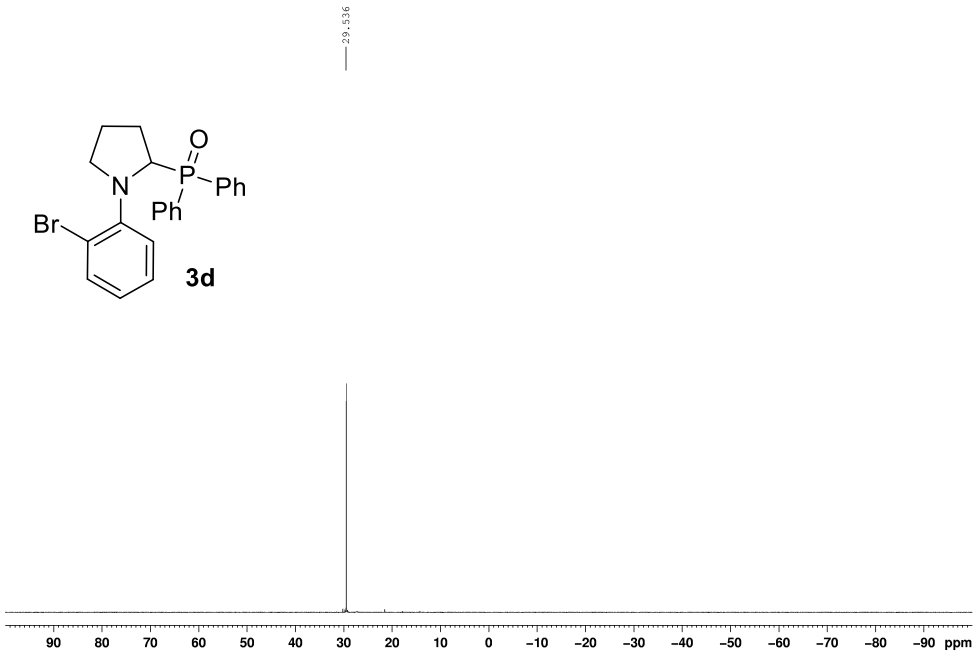
^{1}H NMR of **3d** ($CDCl_3$, 400 MHz)



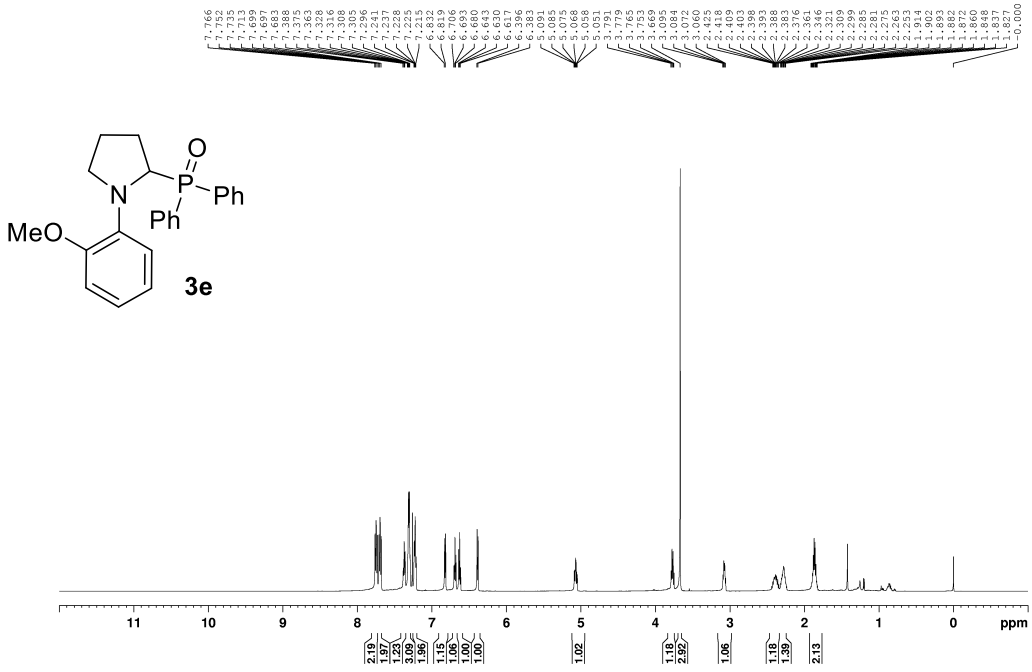
^{13}C NMR of **3d** ($CDCl_3$, 101 MHz)



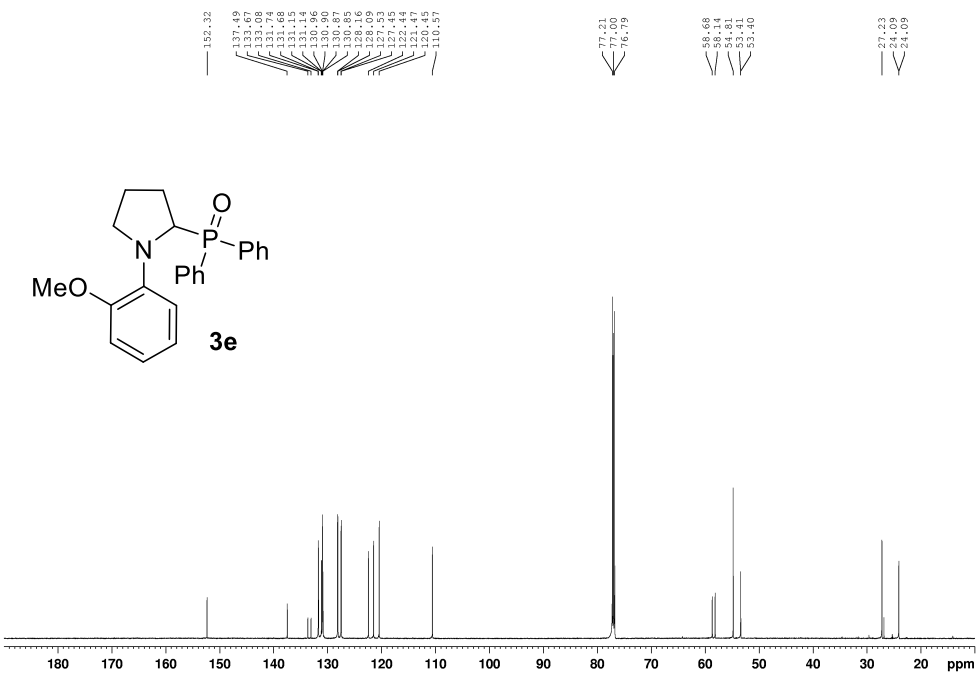
^{31}P NMR of **3d** ($CDCl_3$, 162 MHz)



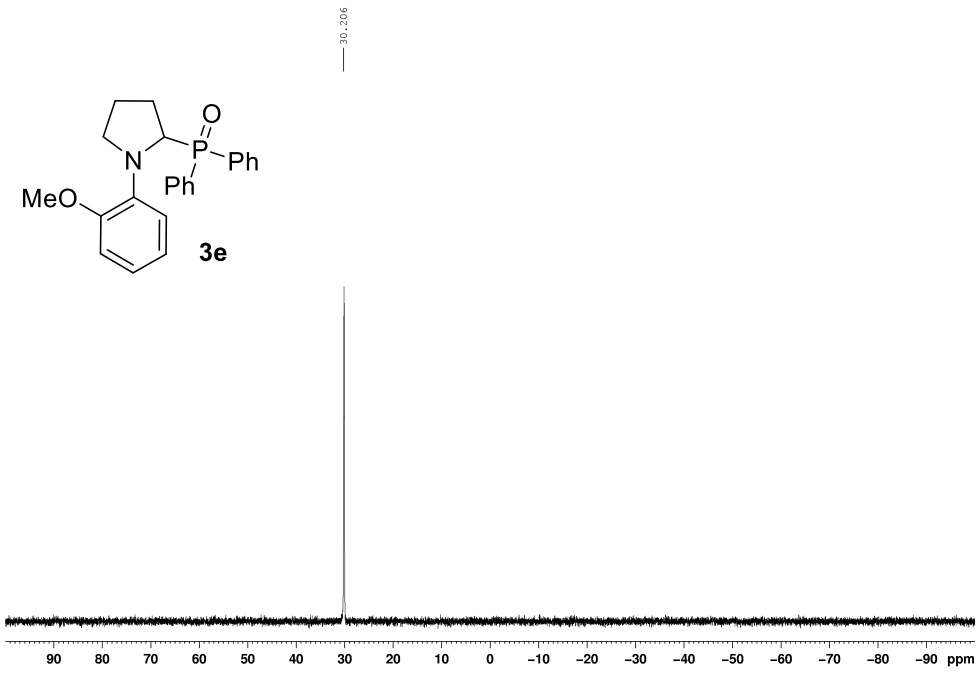
^{1}H NMR of **3e** ($CDCl_3$, 600 MHz)



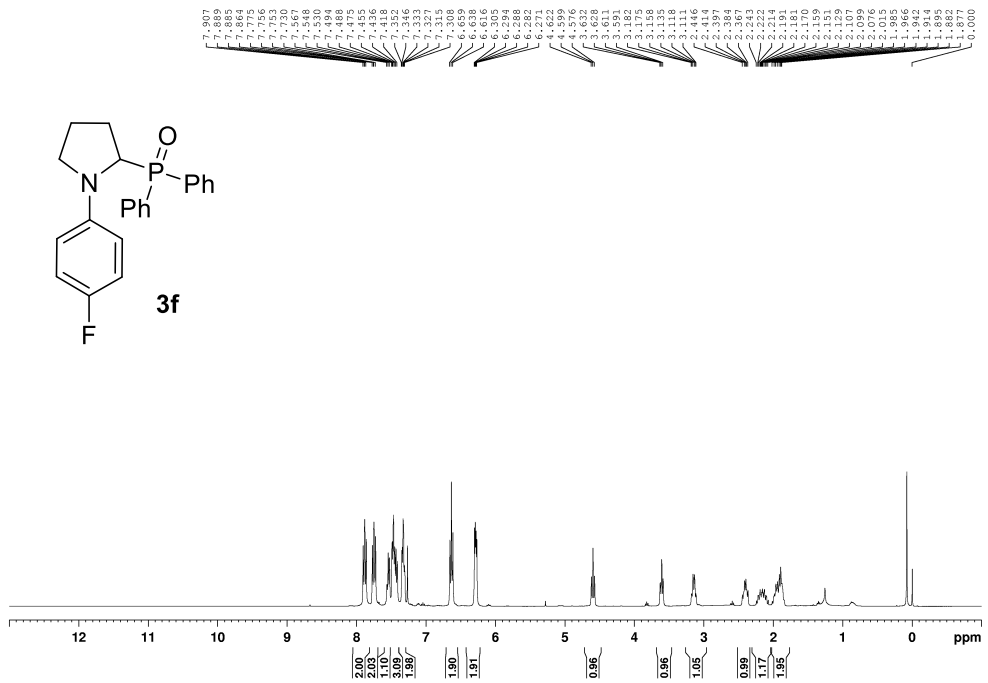
^{13}C NMR of **3e** ($CDCl_3$, 151 MHz)



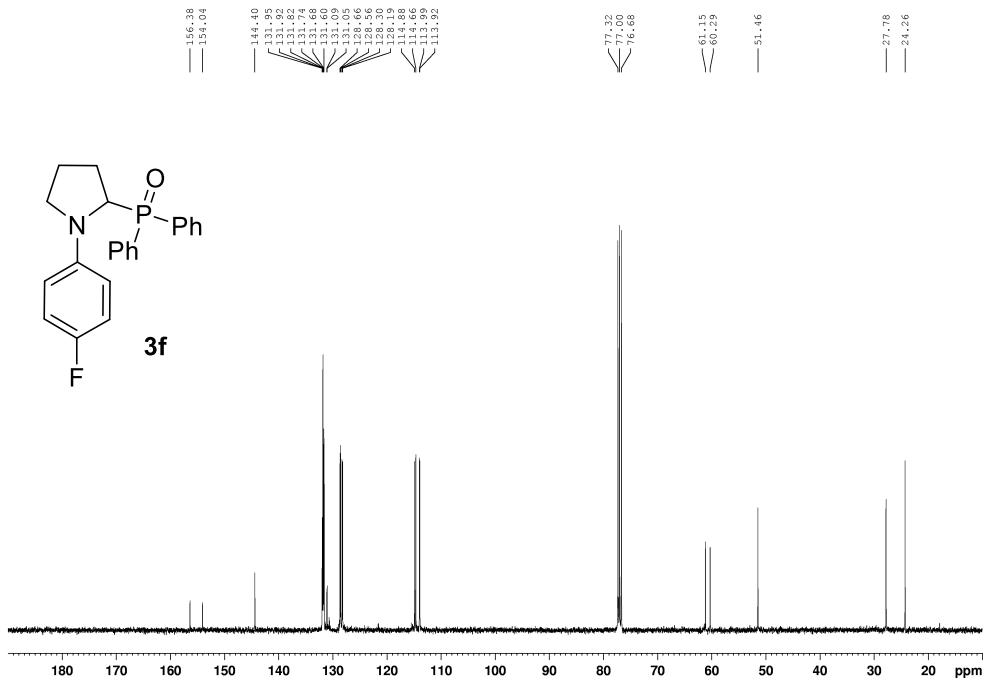
^{31}P NMR of **3e** ($CDCl_3$, 243 MHz)



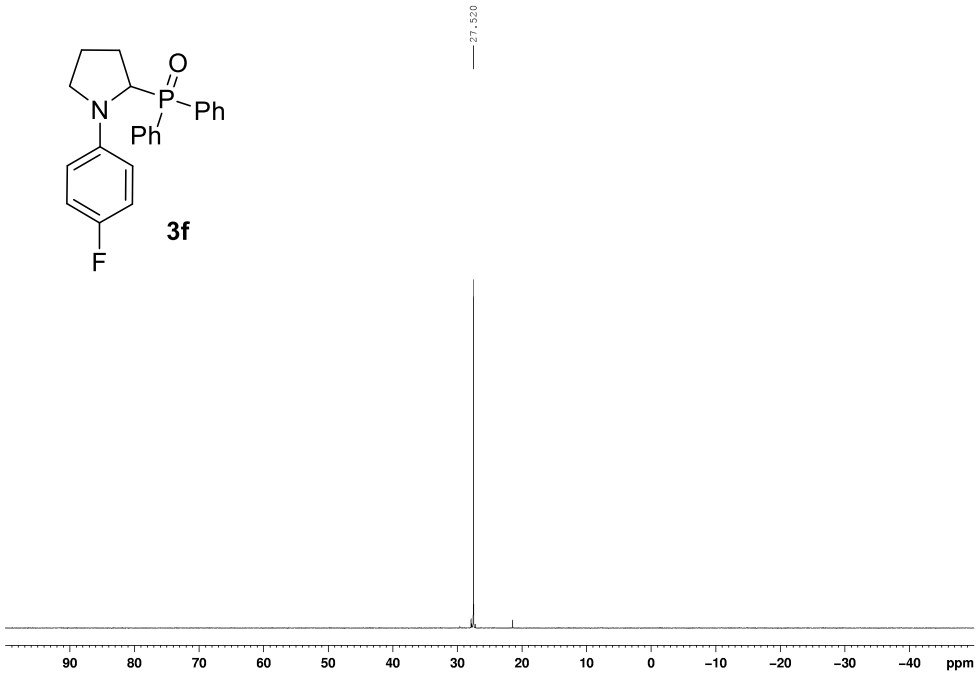
^{1}H NMR of **3f** ($CDCl_3$, 400 MHz)



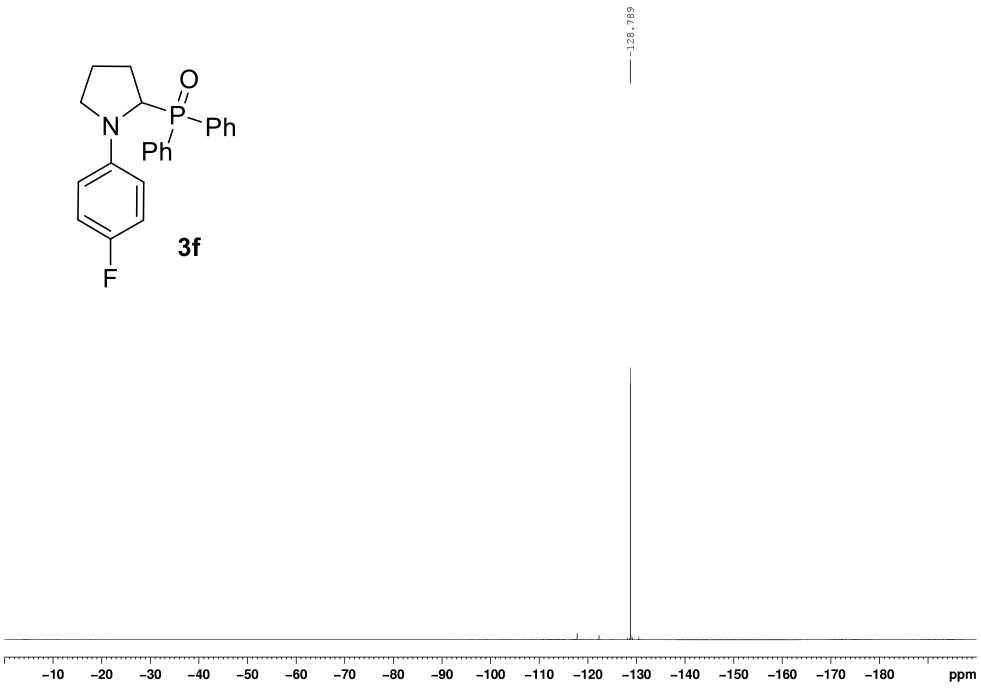
^{13}C NMR of **3f** ($CDCl_3$, 101 MHz)



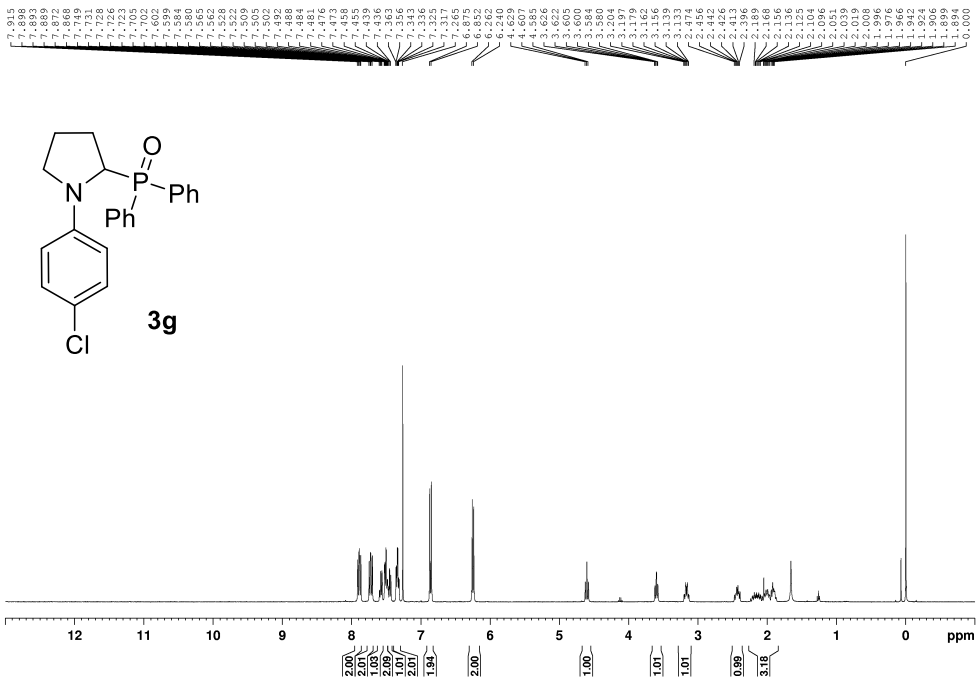
^{31}P NMR of **3f** ($CDCl_3$, 162 MHz)



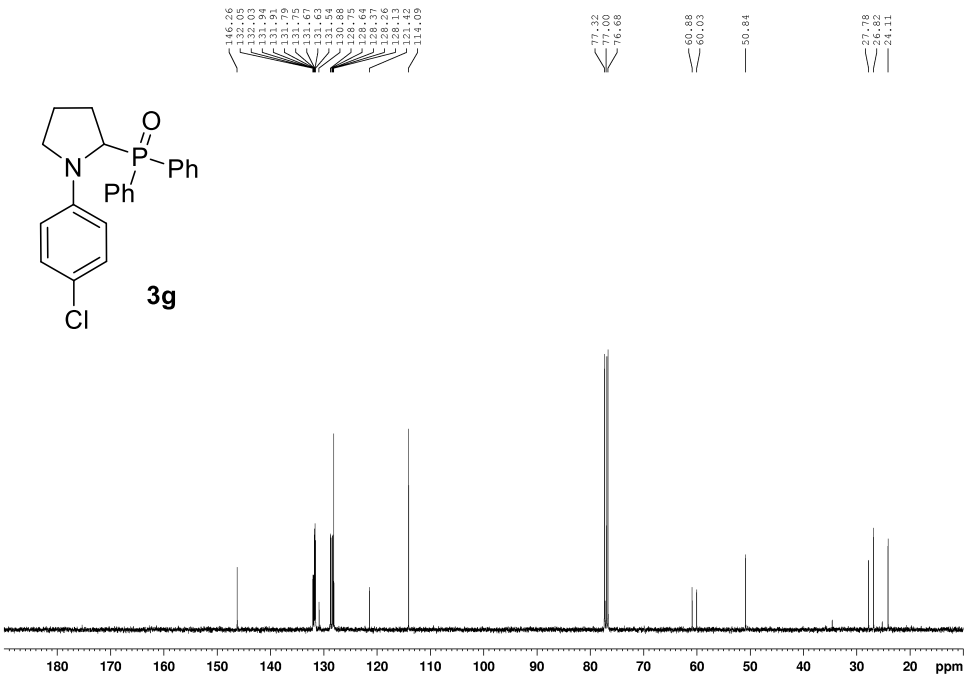
^{19}F NMR of **3f** ($CDCl_3$, 376 MHz)



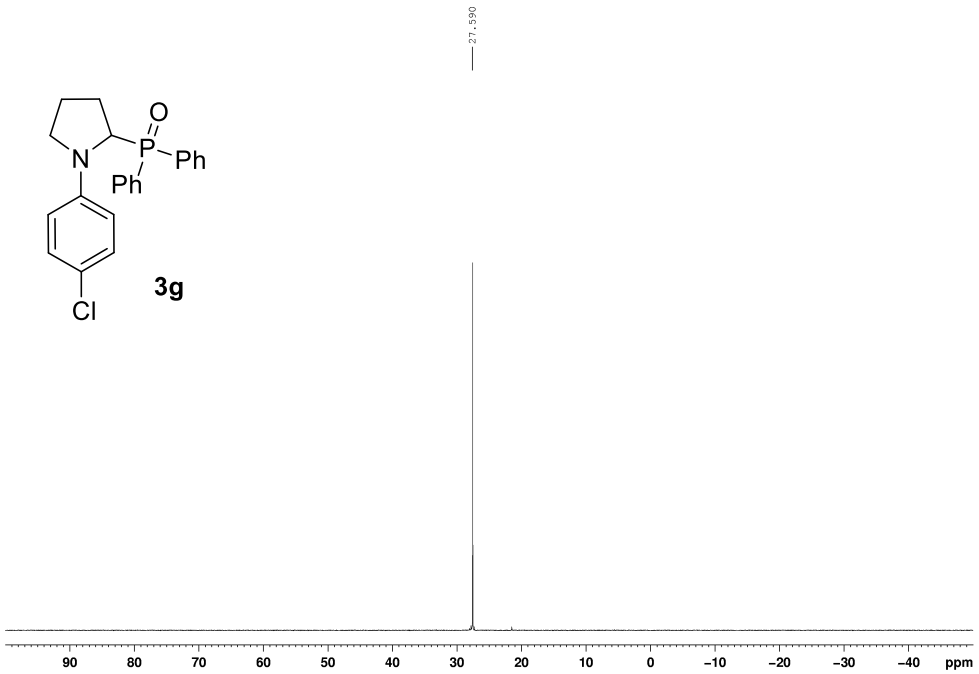
^{1}H NMR of **3g** ($CDCl_3$, 400 MHz)



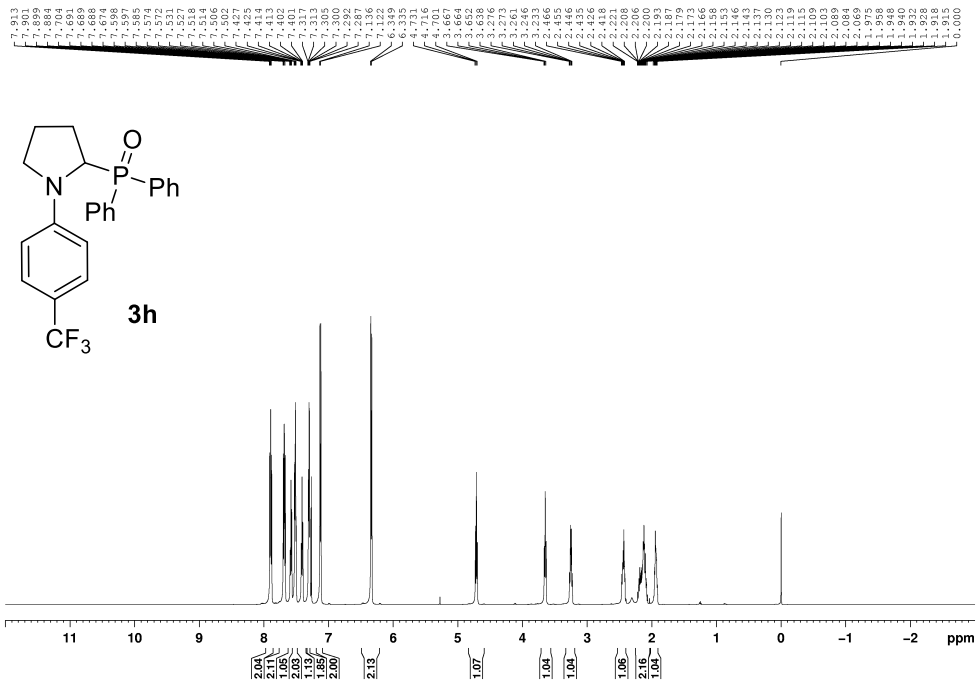
^{13}C NMR of **3g** ($CDCl_3$, 101 MHz)



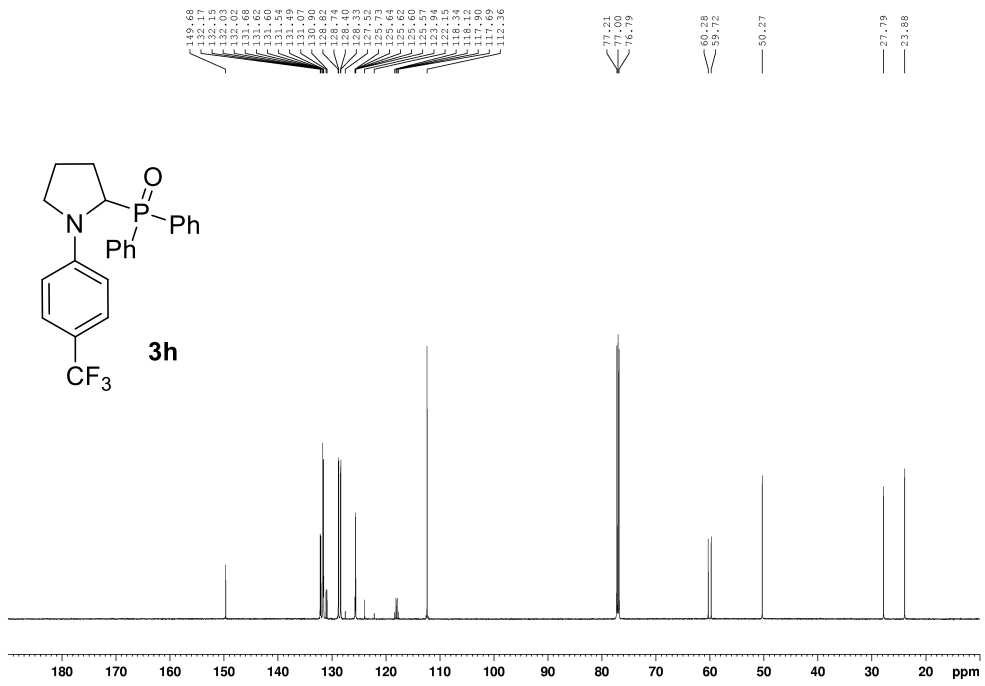
^{31}P NMR of **3g** ($CDCl_3$, 162 MHz)



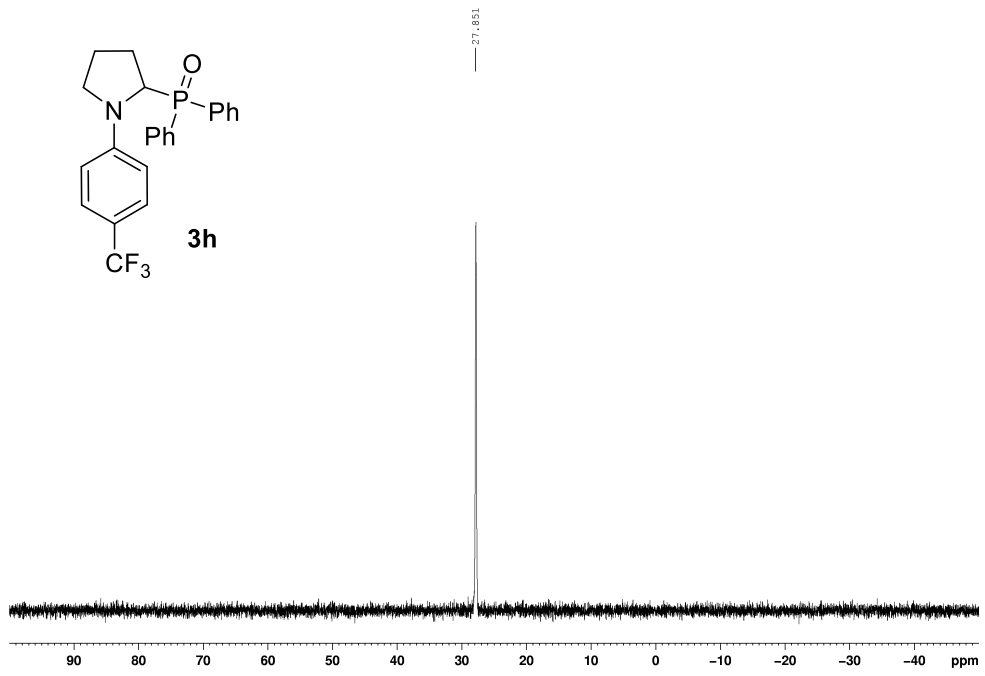
^{1}H NMR of **3h** ($CDCl_3$, 600 MHz)



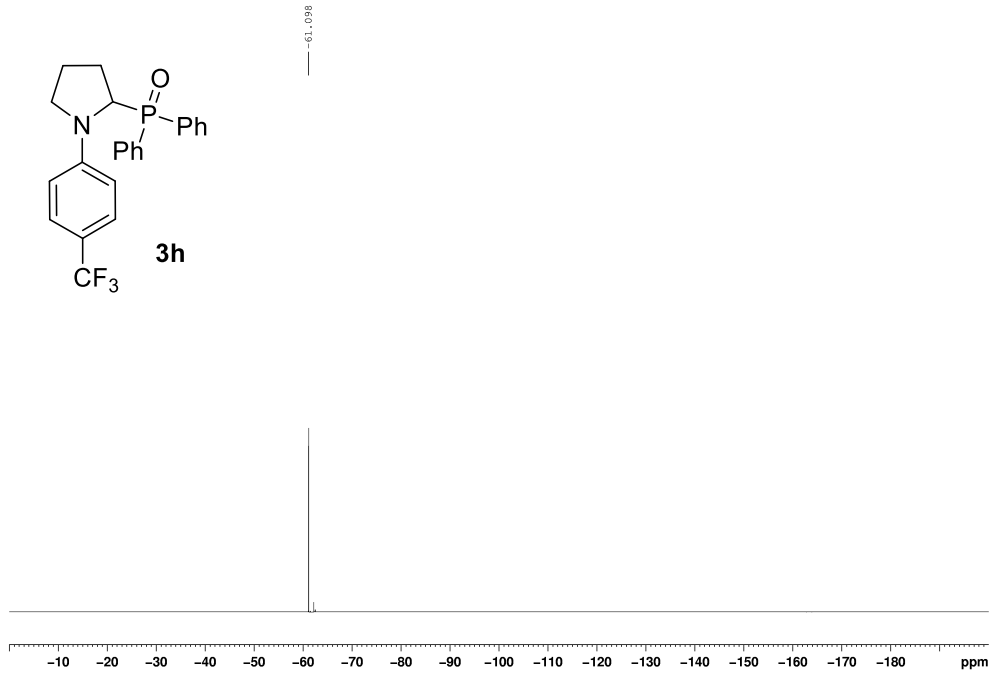
^{13}C NMR of **3h** ($CDCl_3$, 151 MHz)



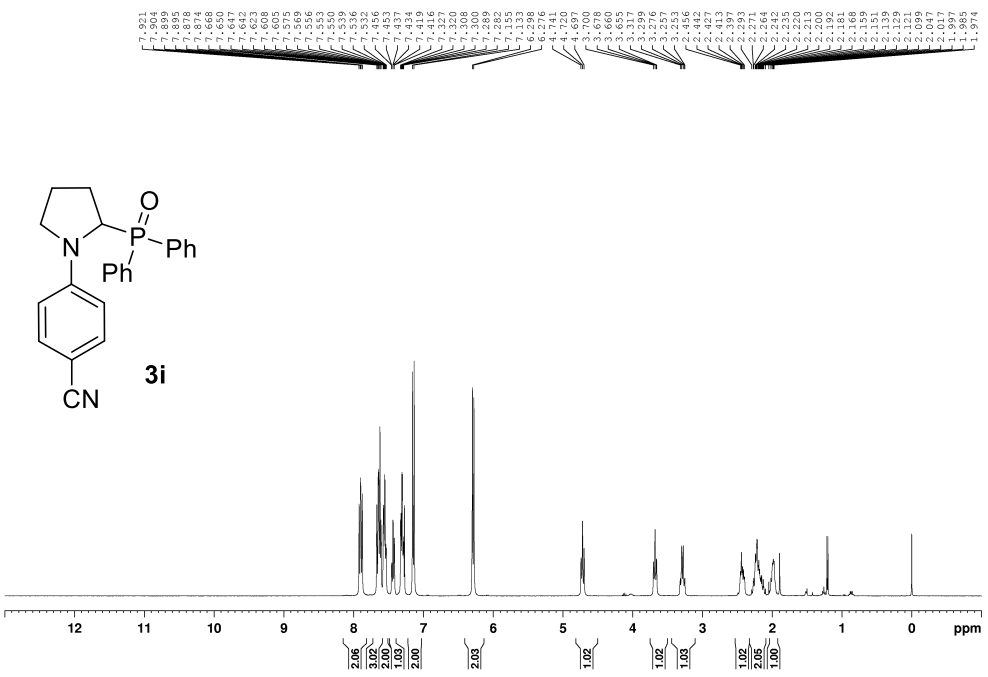
^{31}P NMR of **3h** ($CDCl_3$, 243 MHz)



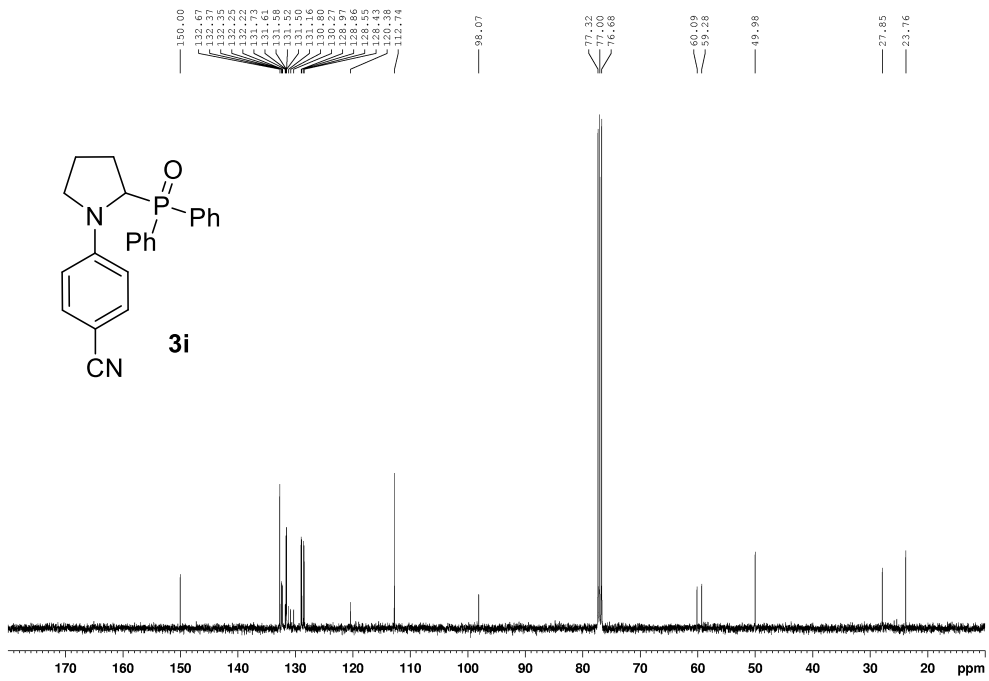
^{19}F NMR of **3h** ($CDCl_3$, 376 MHz)



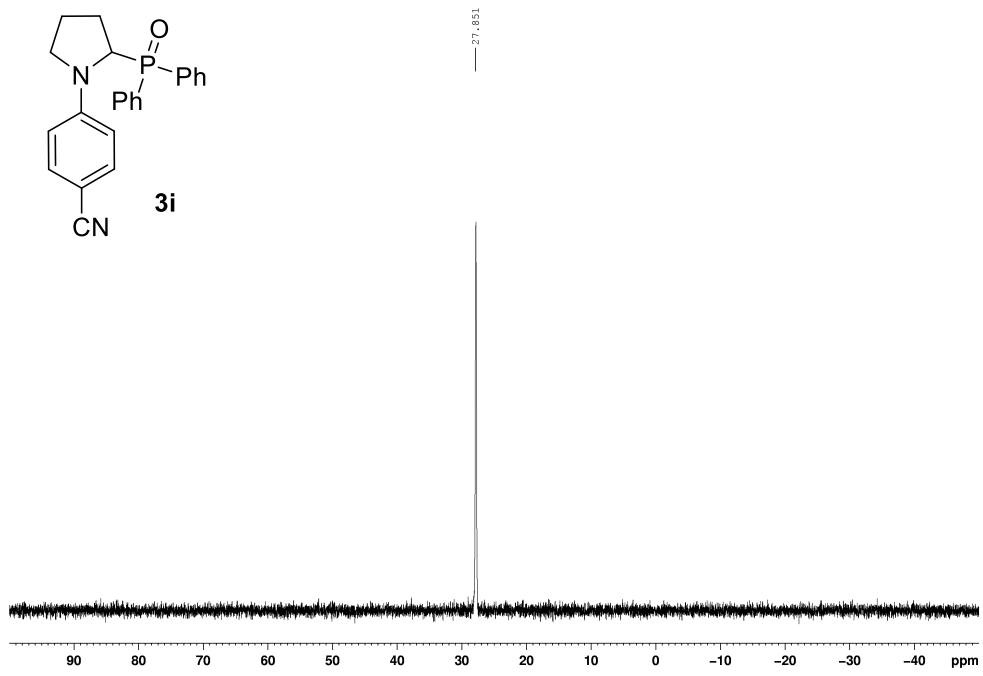
^{1}H NMR of **3i** ($CDCl_3$, 400 MHz)



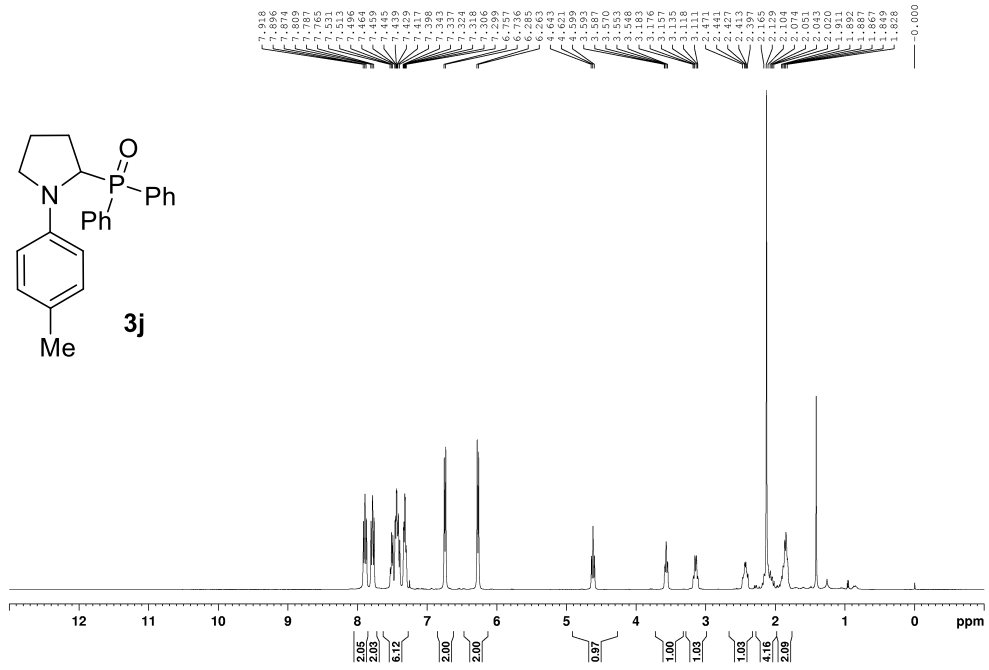
^{13}C NMR of **3i** ($CDCl_3$, 101 MHz)



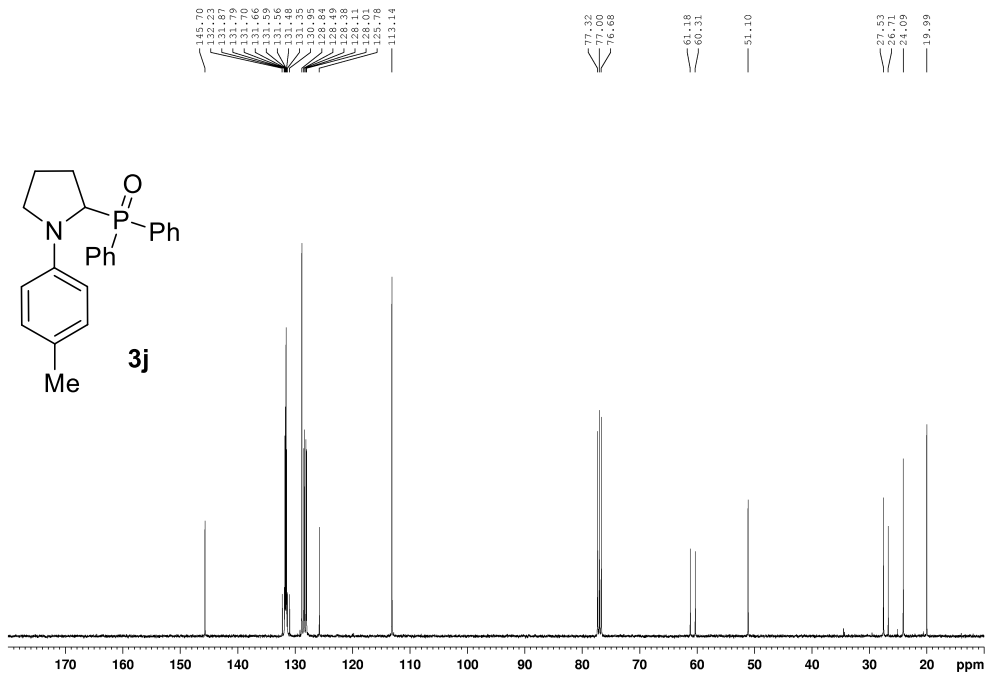
^{31}P NMR of **3i** ($CDCl_3$, 162 MHz)



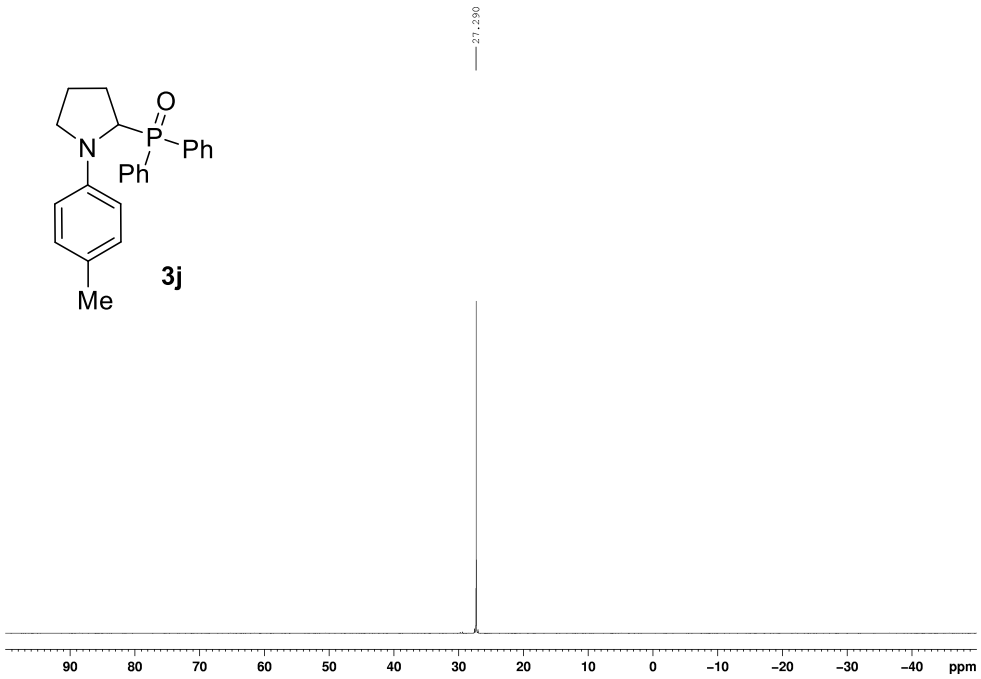
^{1}H NMR of **3j** ($CDCl_3$, 400 MHz)



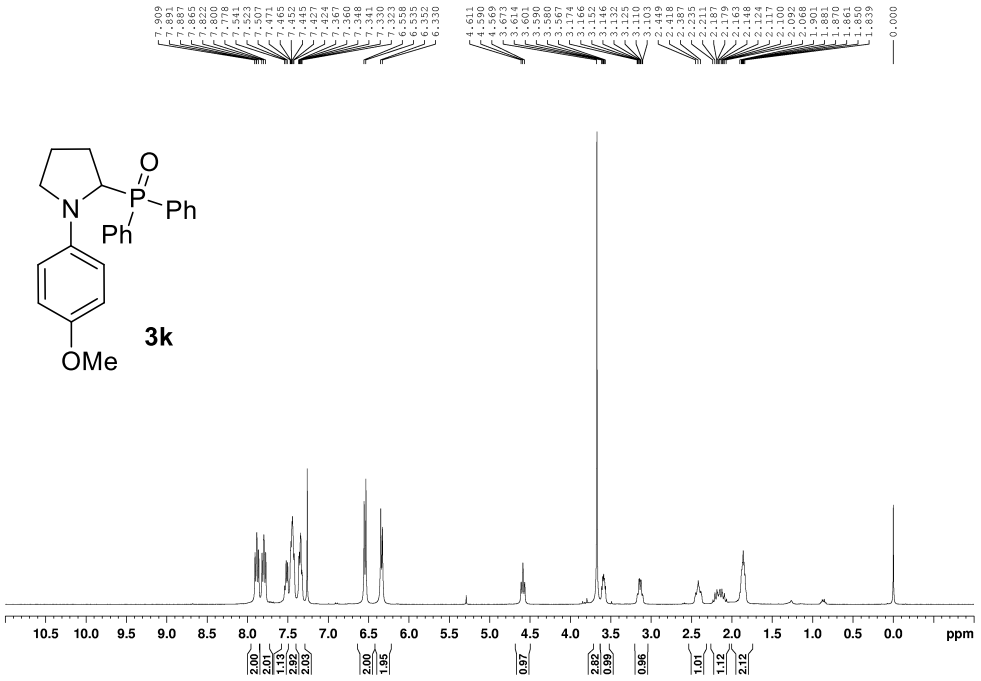
^{13}C NMR of **3j** ($CDCl_3$, 101 MHz)



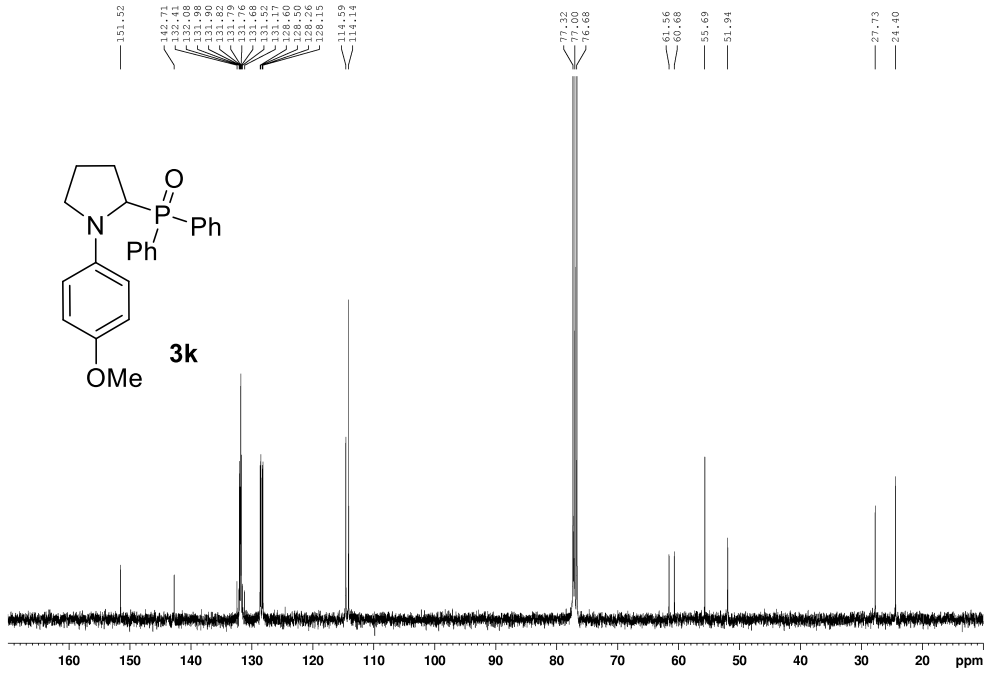
^{31}P NMR of **3j** ($CDCl_3$, 162 MHz)



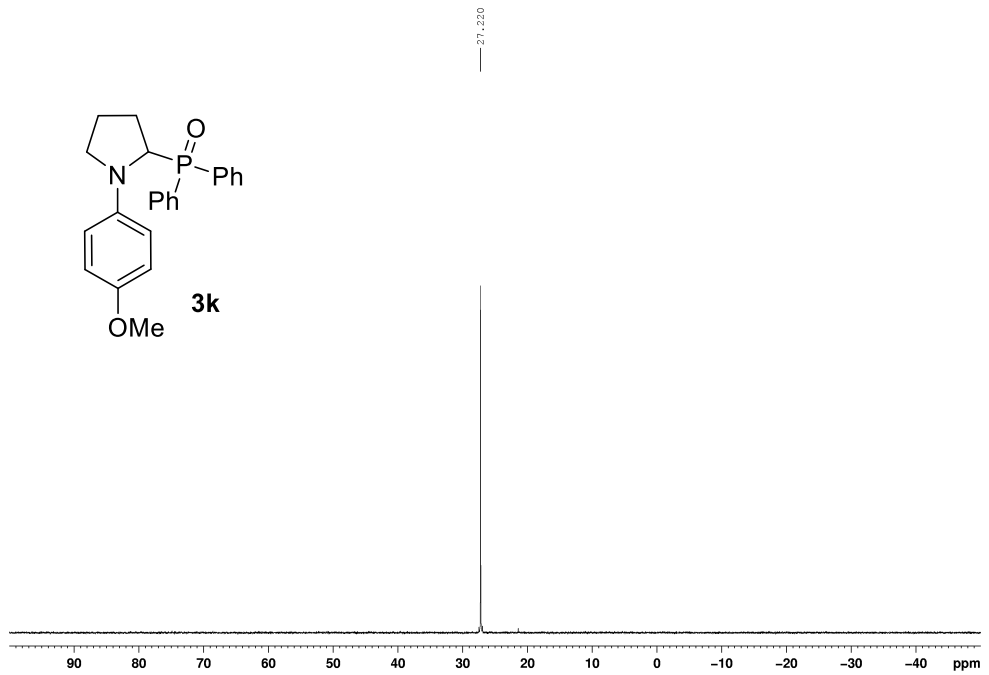
^{1}H NMR of **3k** ($CDCl_3$, 400 MHz)



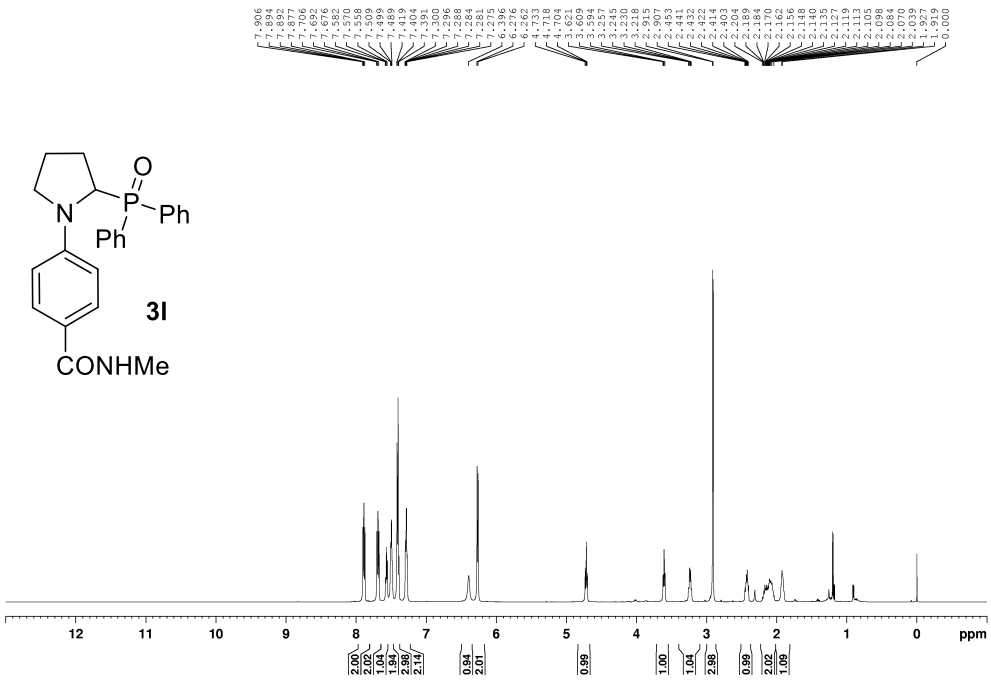
^{13}C NMR of **3k** ($CDCl_3$, 101 MHz)



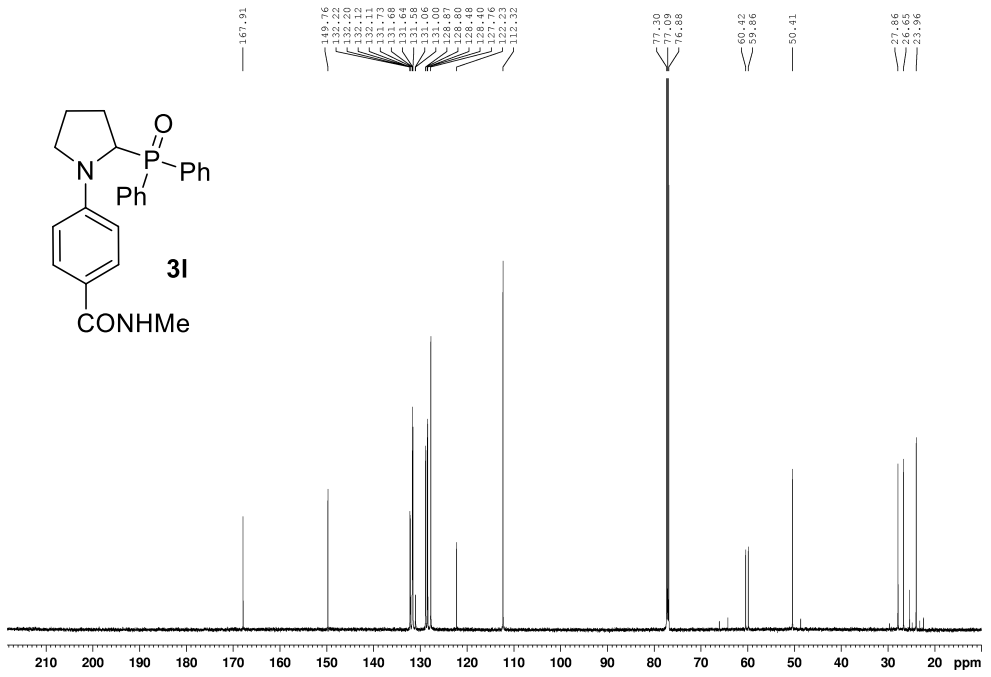
^{31}P NMR of **3k** ($CDCl_3$, 162 MHz)



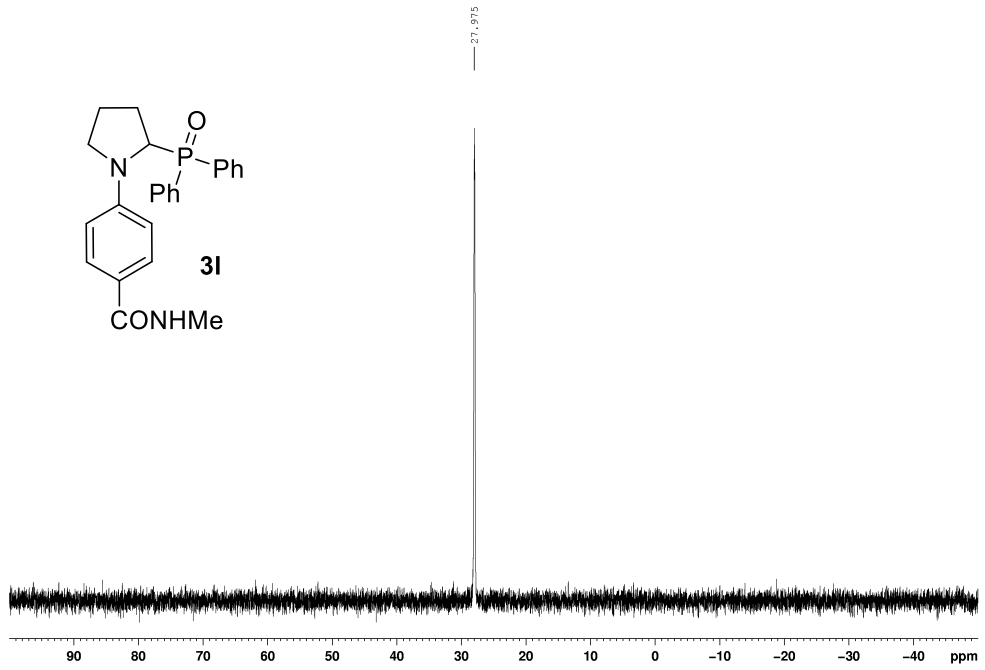
^{1}H NMR of **3l** ($CDCl_3$, 600 MHz)



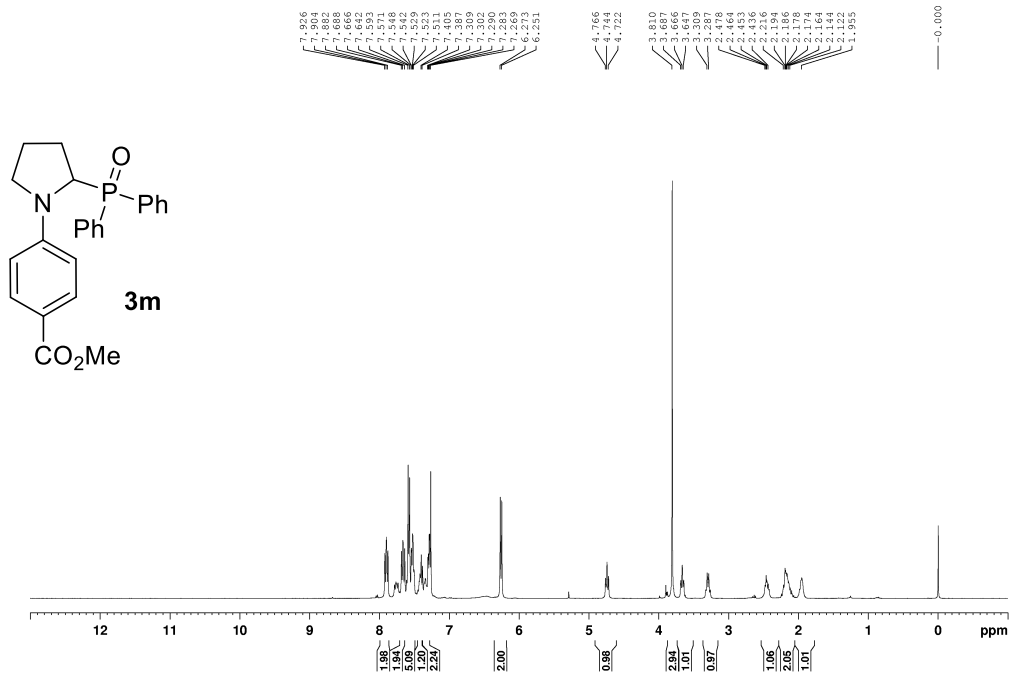
^{13}C NMR of **3l** ($CDCl_3$, 151 MHz)



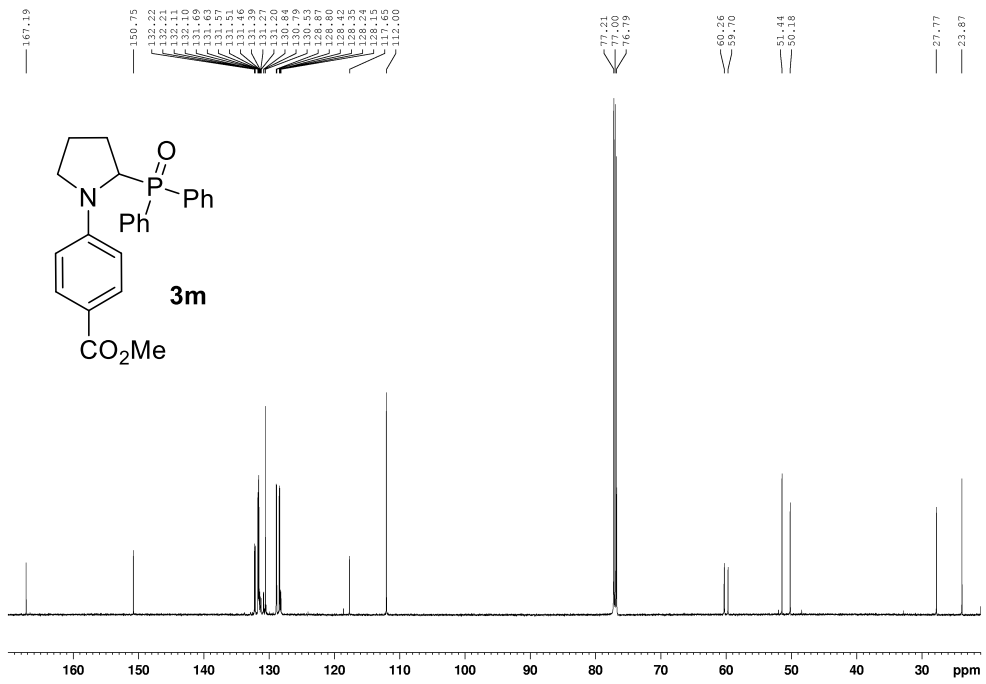
^{31}P NMR of **3l** ($CDCl_3$, 243 MHz)



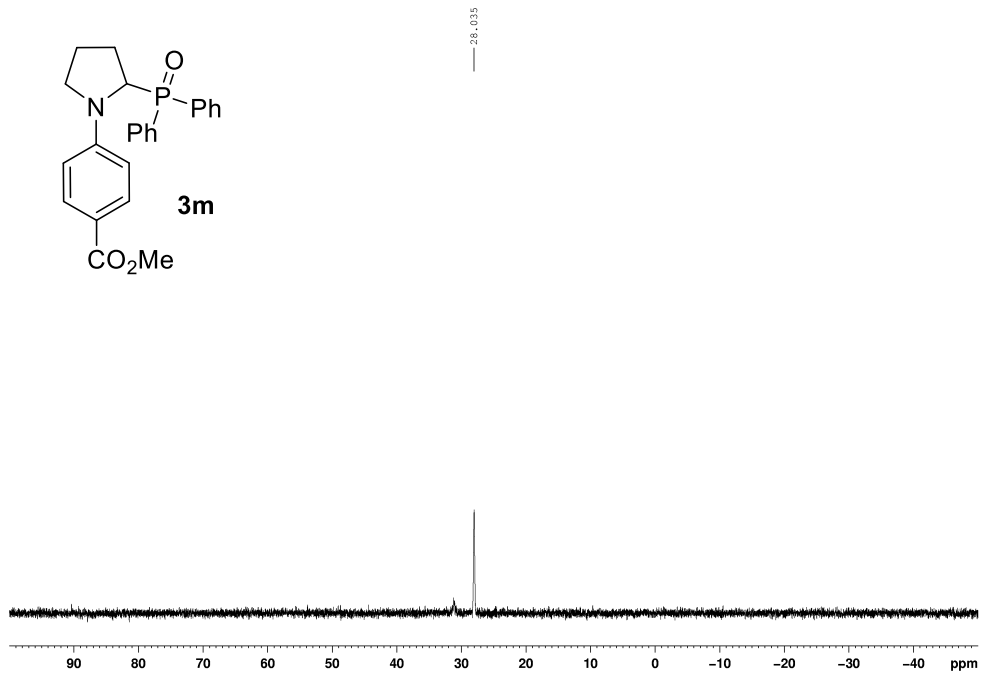
^{1}H NMR of **3m** ($CDCl_3$, 400 MHz)



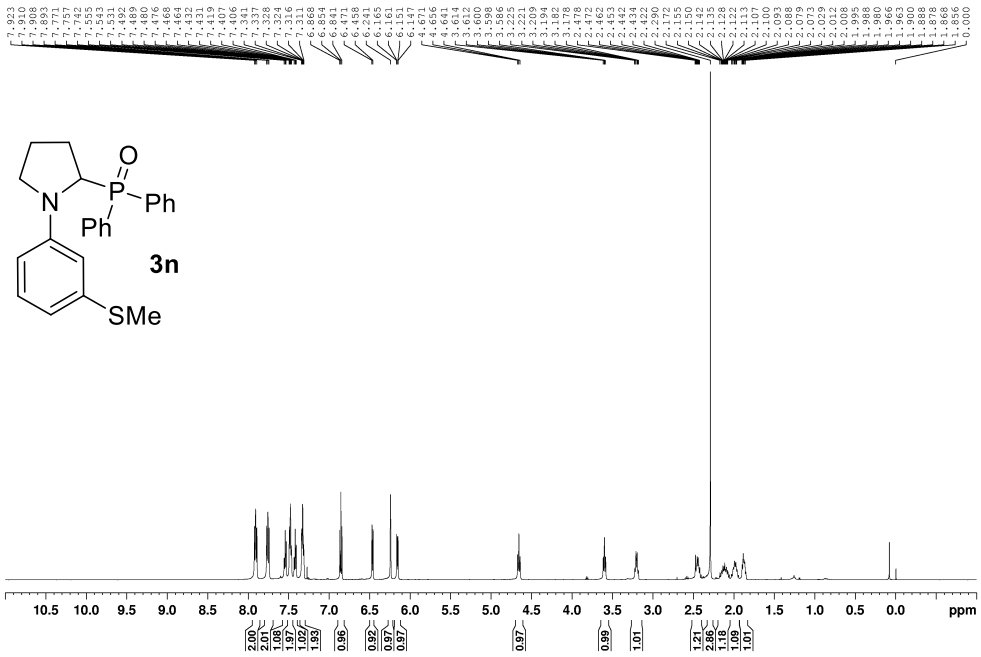
^{13}C NMR of **3m** ($CDCl_3$, 101 MHz)



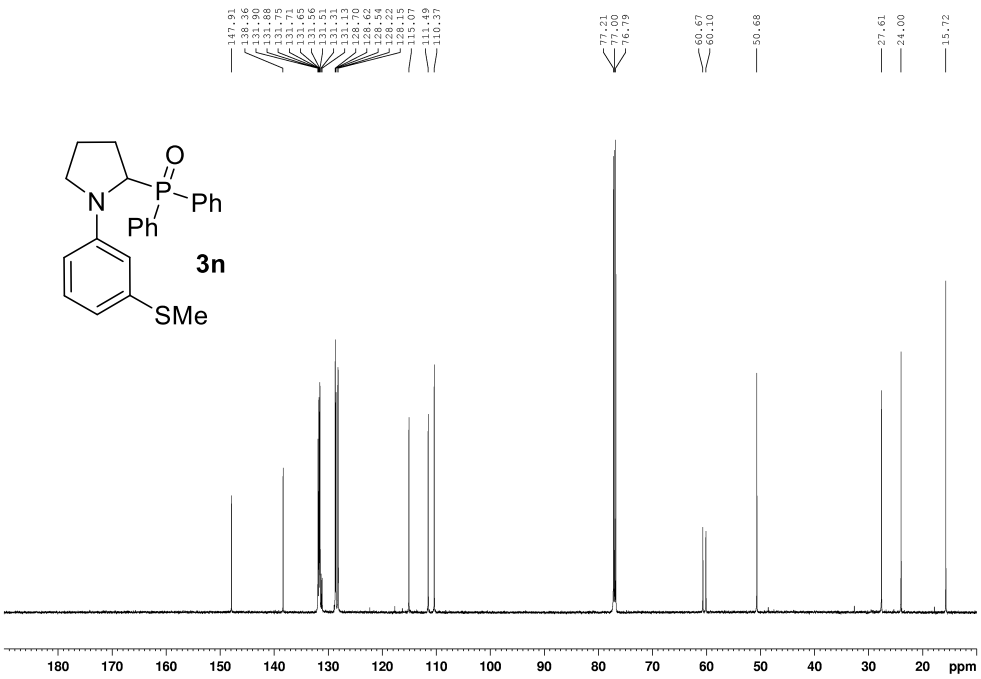
^{31}P NMR of **3m** ($CDCl_3$, 162 MHz)



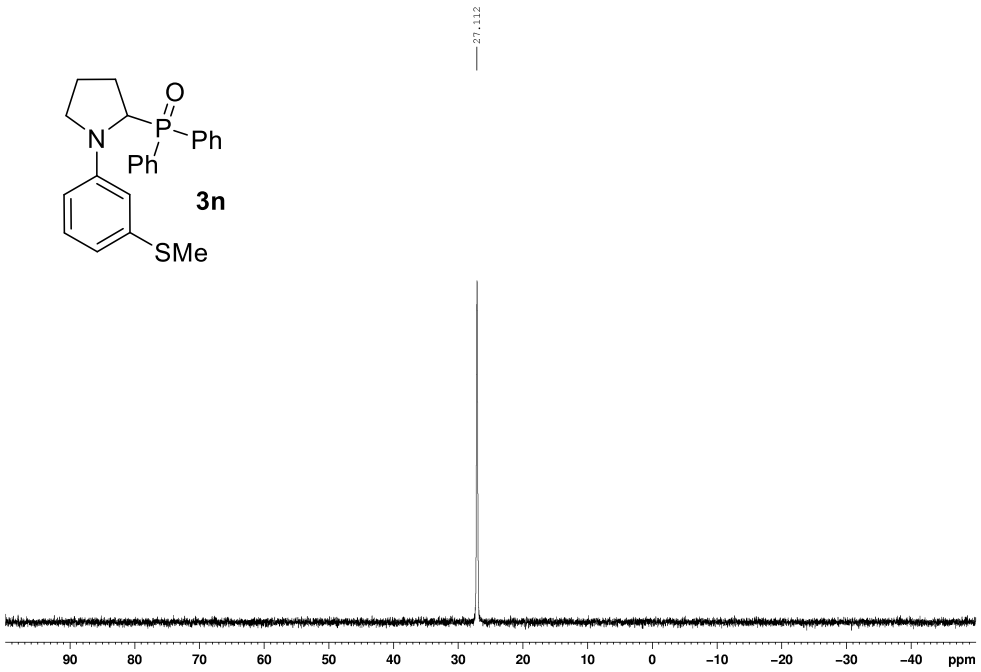
^{1}H NMR of **3n** ($CDCl_3$, 400 MHz)



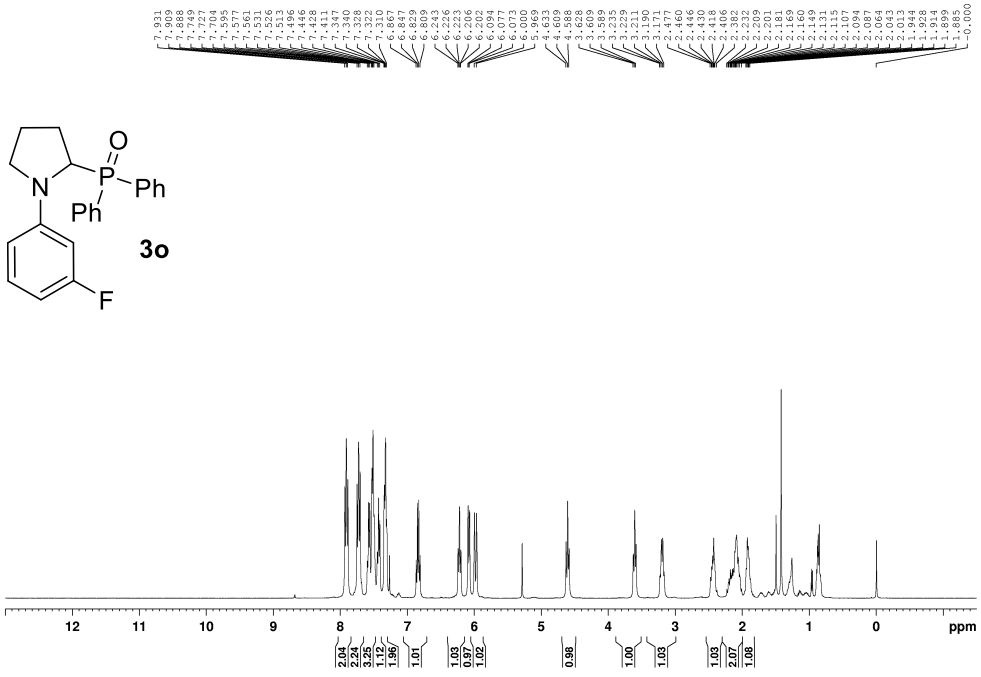
^{13}C NMR of **3n** ($CDCl_3$, 101 MHz)



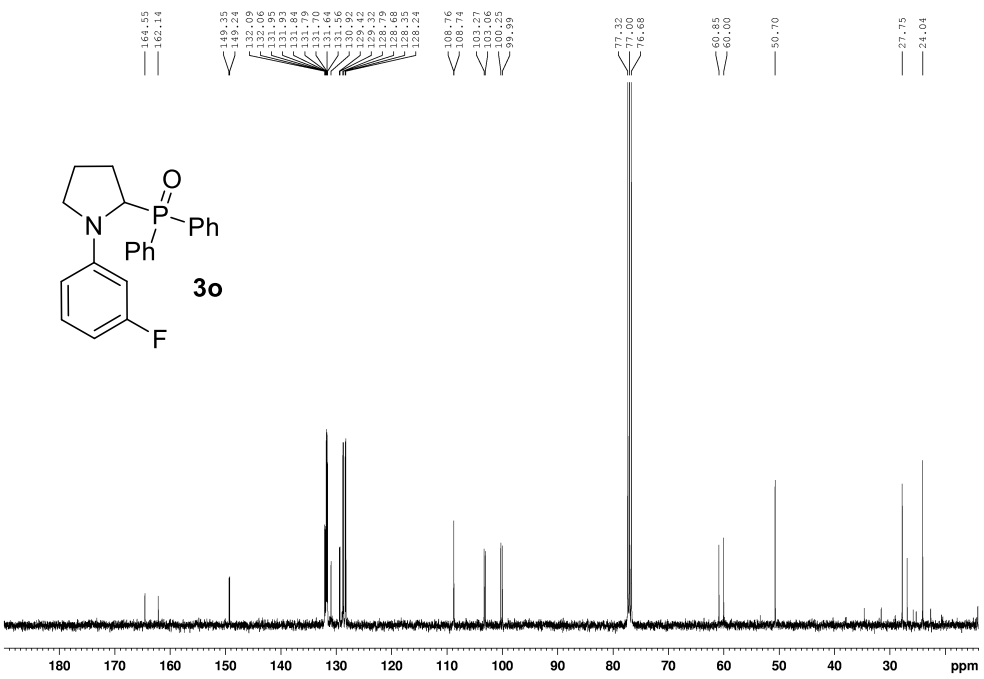
^{31}P NMR of **3n** ($CDCl_3$, 162 MHz)



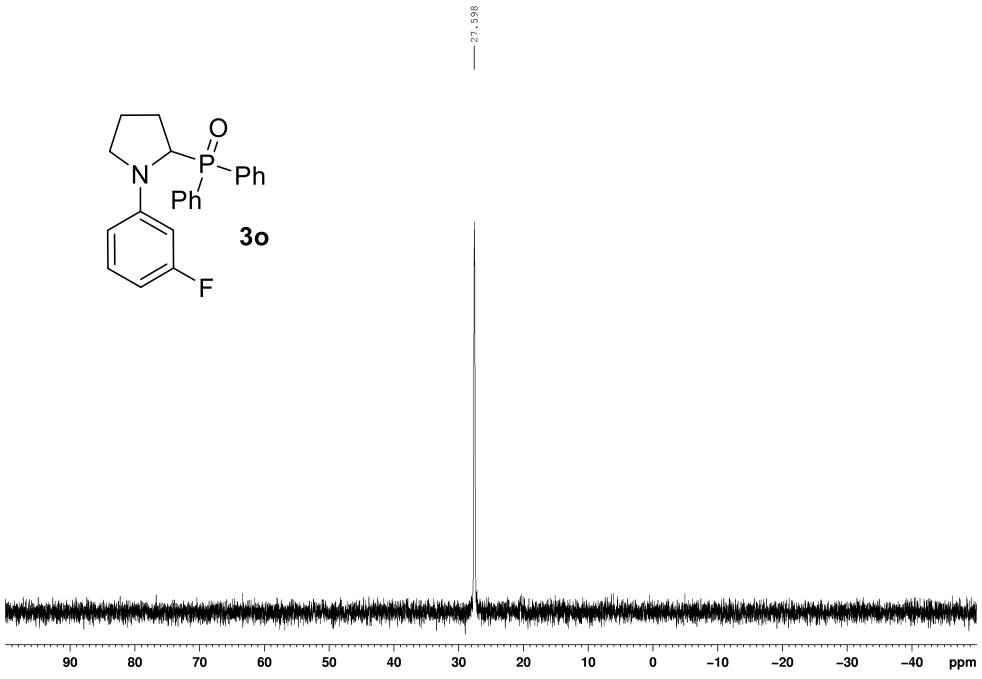
^{1}H NMR of **3o** ($CDCl_3$, 400 MHz)



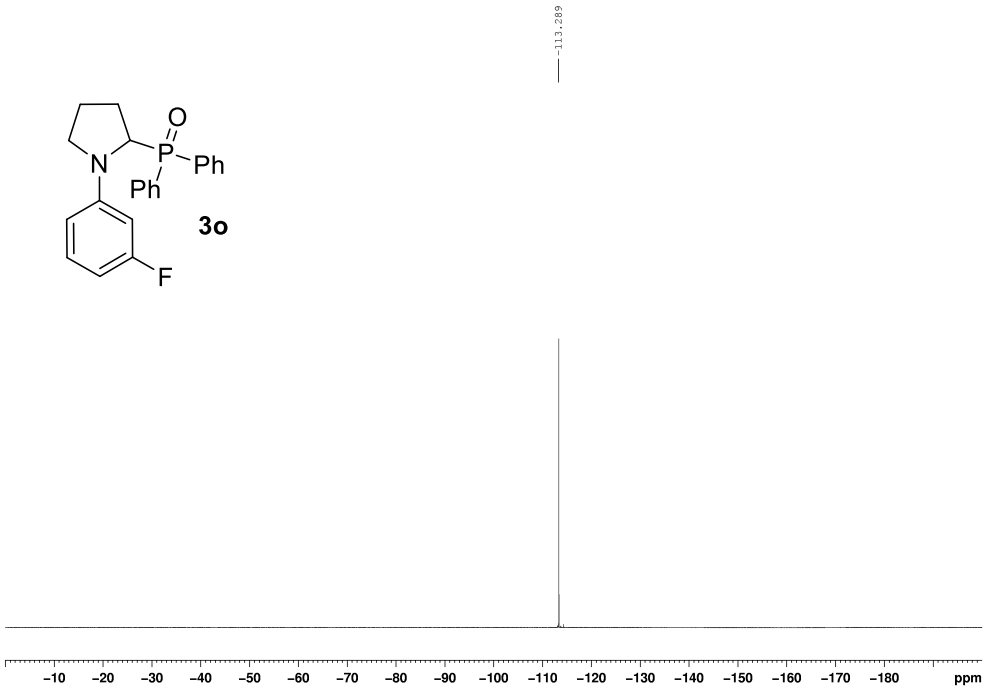
^{13}C NMR of **3o** ($CDCl_3$, 101 MHz)



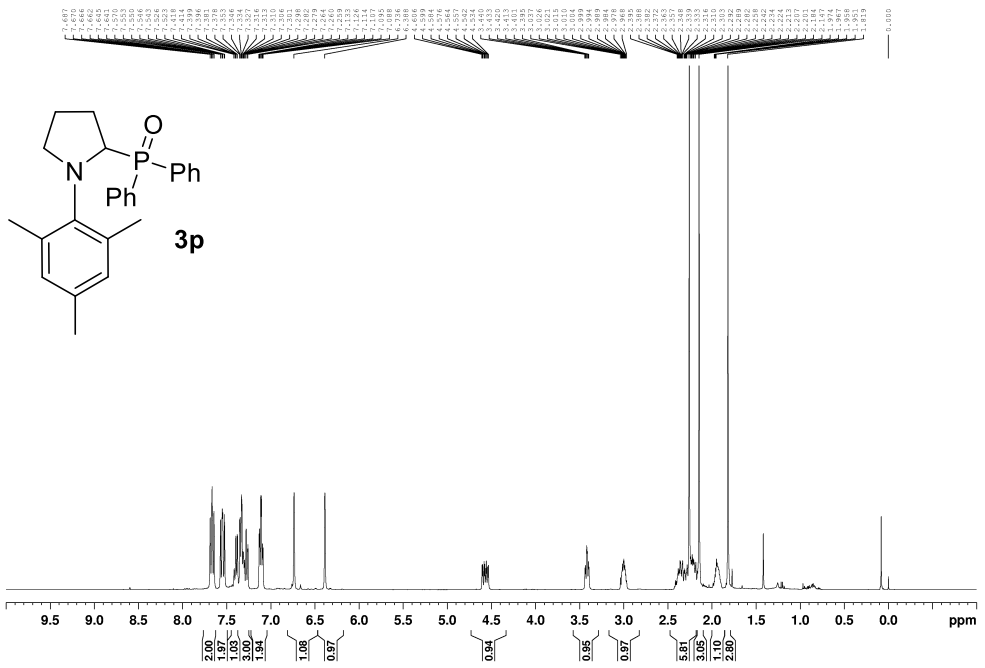
^{31}P NMR of **3o** ($CDCl_3$, 162 MHz)



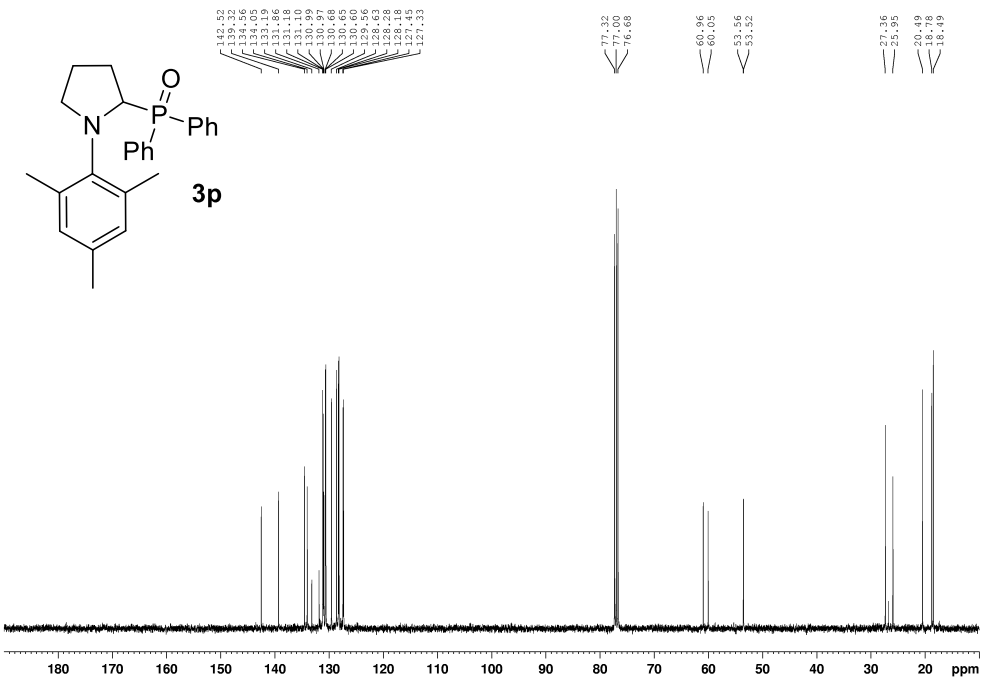
^{19}F NMR of **3o** ($CDCl_3$, 376 MHz)



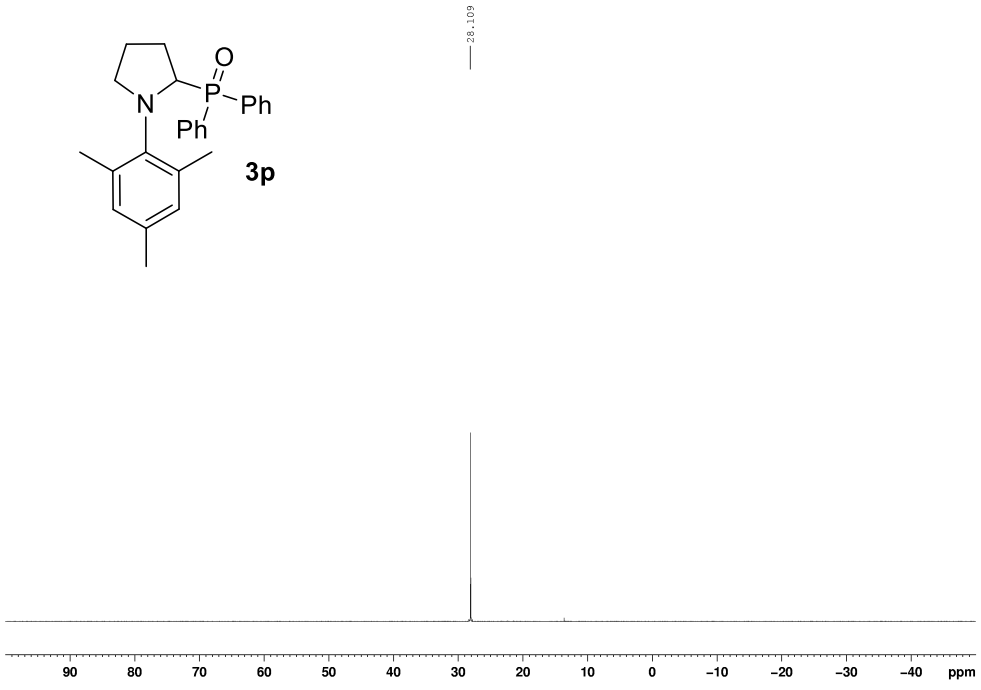
^{1}H NMR of **3p** ($CDCl_3$, 400 MHz)



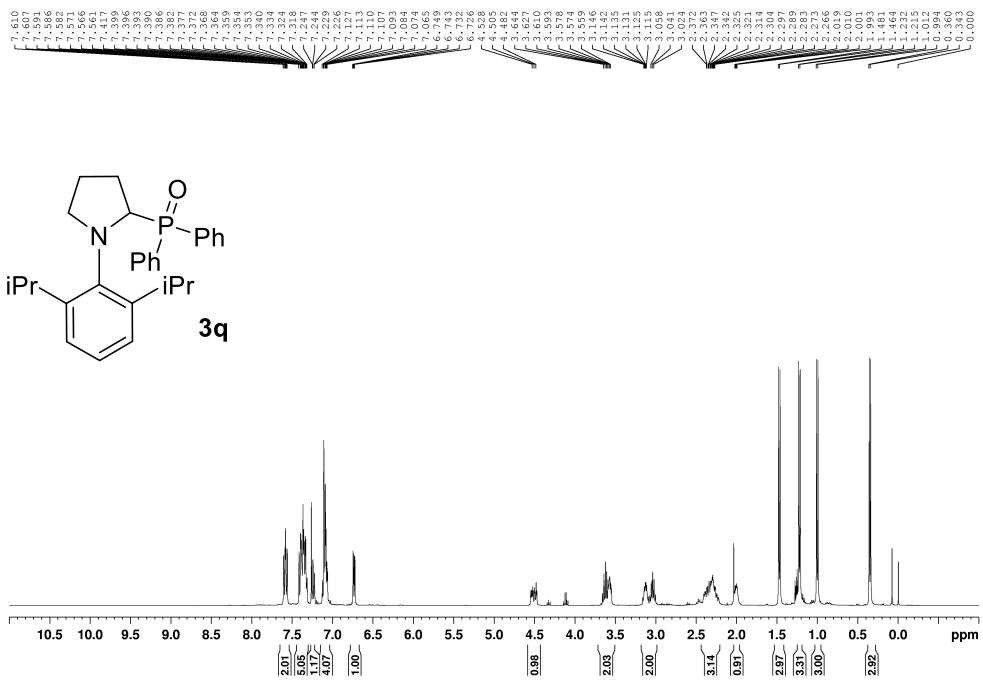
^{13}C NMR of **3p** ($CDCl_3$, 101 MHz)



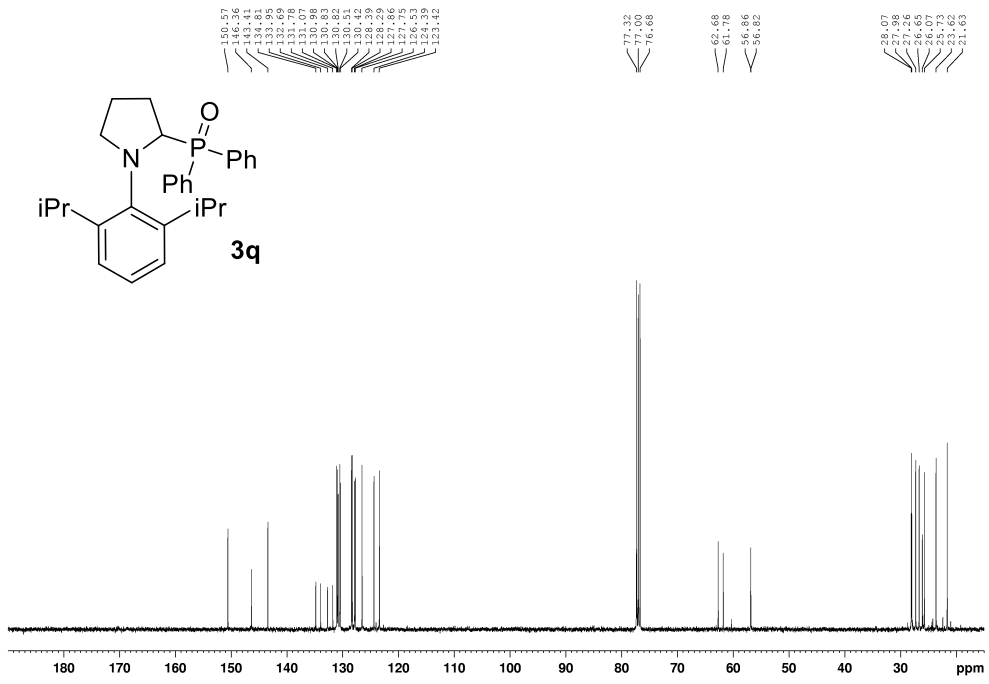
^{31}P NMR of **3p** ($CDCl_3$, 162 MHz)



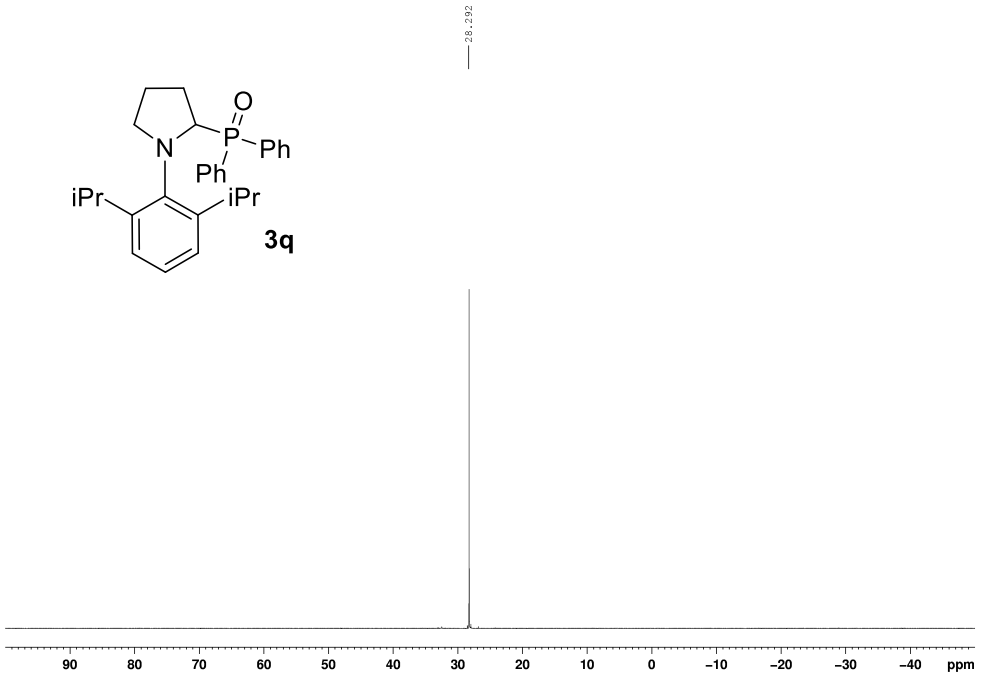
^{1}H NMR of **3q** ($CDCl_3$, 400 MHz)



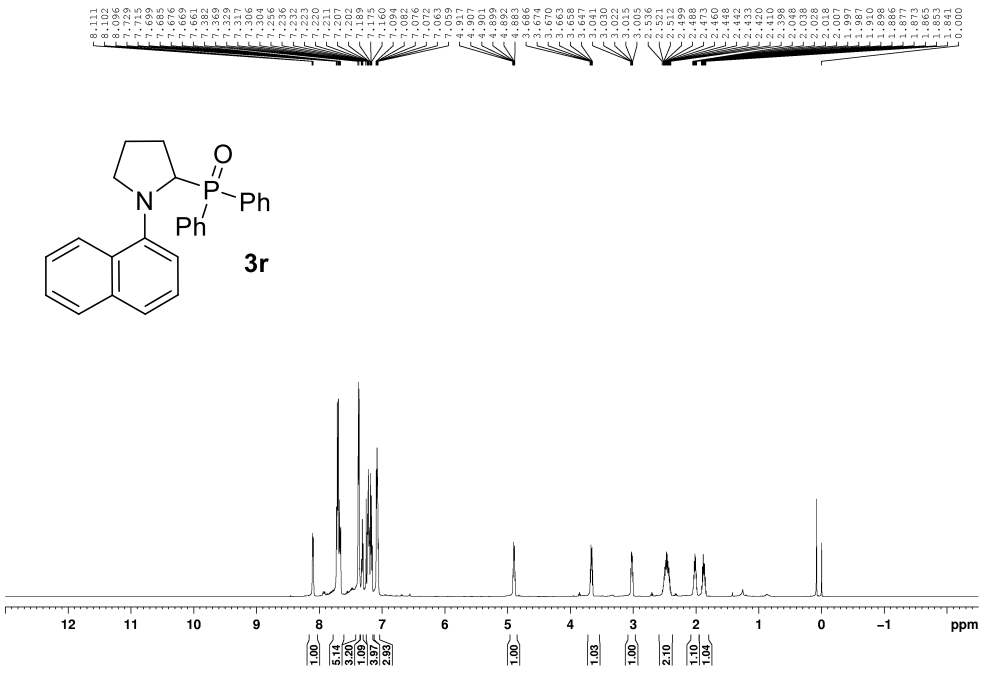
^{13}C NMR of **3q** ($CDCl_3$, 101 MHz)



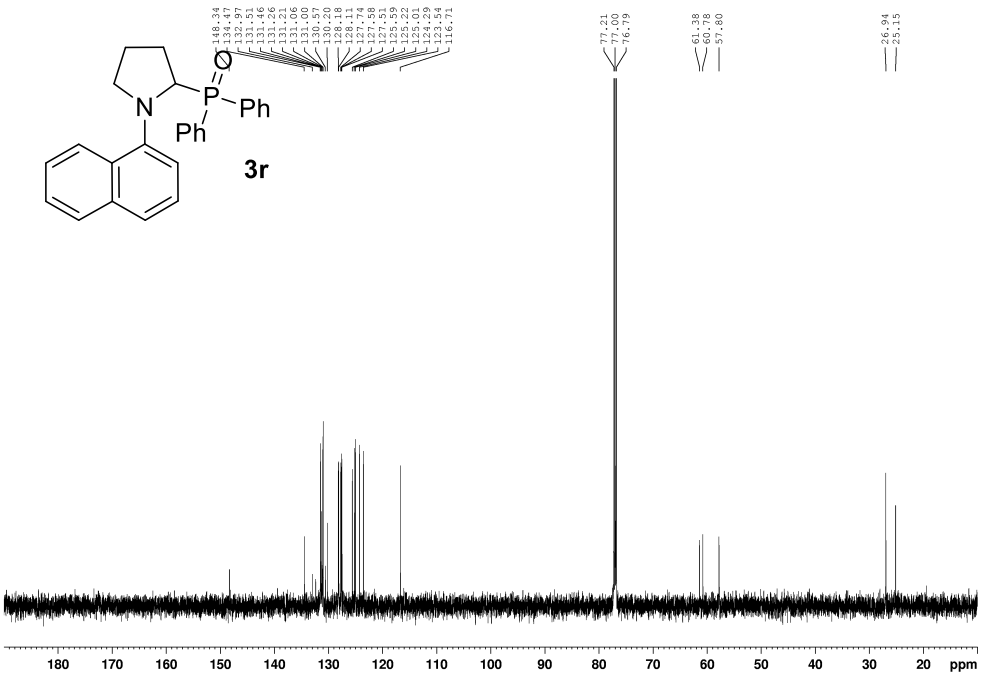
^{31}P NMR of **3q** ($CDCl_3$, 162 MHz)



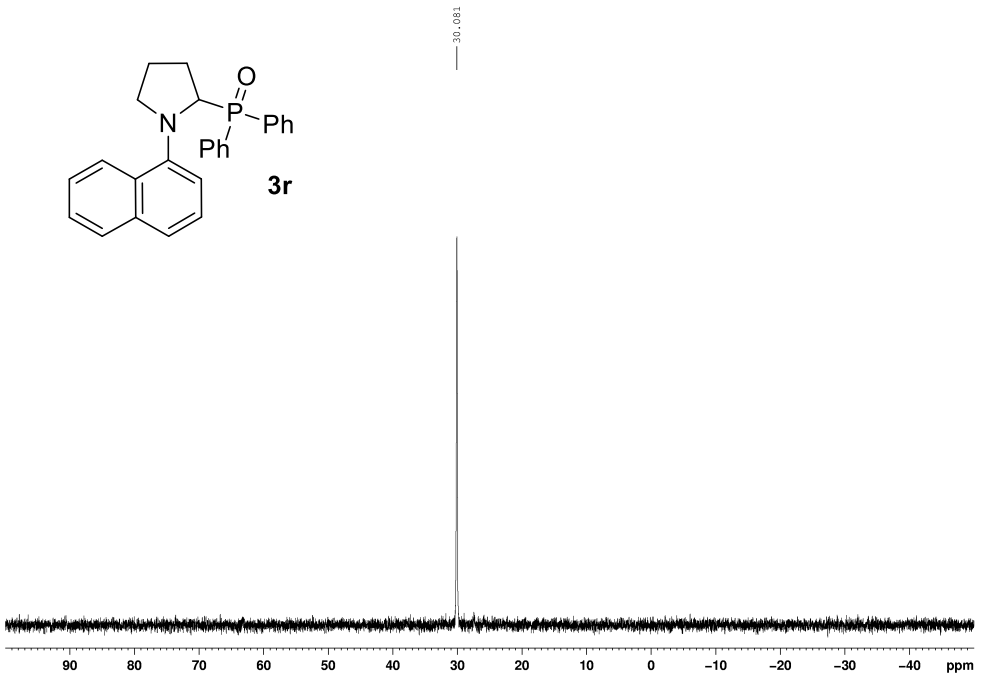
^{1}H NMR of **3r** ($CDCl_3$, 600 MHz)



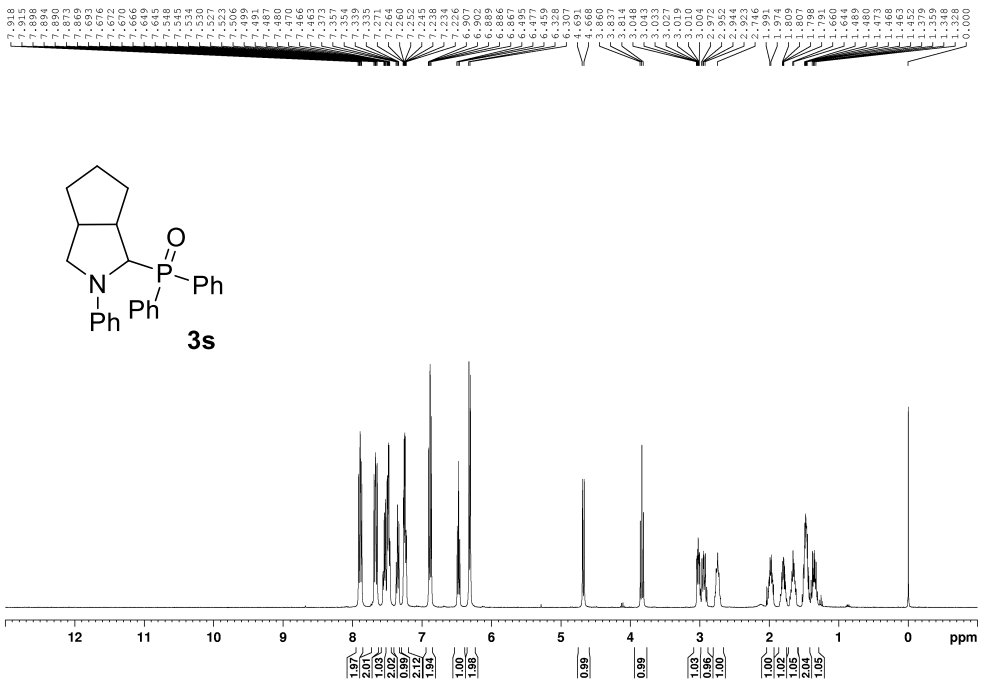
^{13}C NMR of **3r** ($CDCl_3$, 151 MHz)



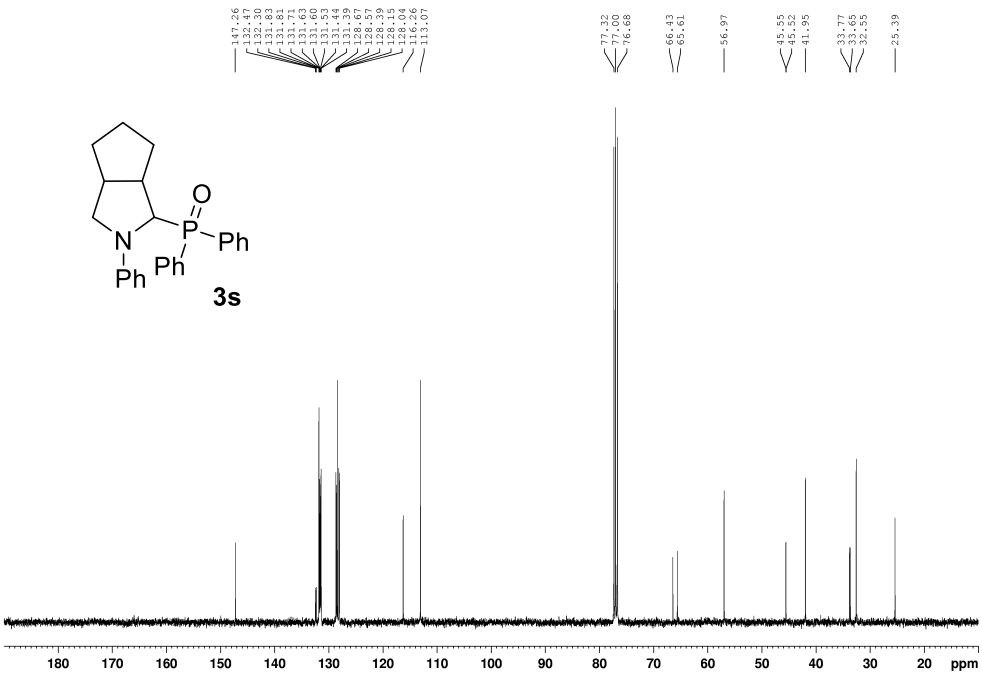
^{31}P NMR of **3r** ($CDCl_3$, 243 MHz)



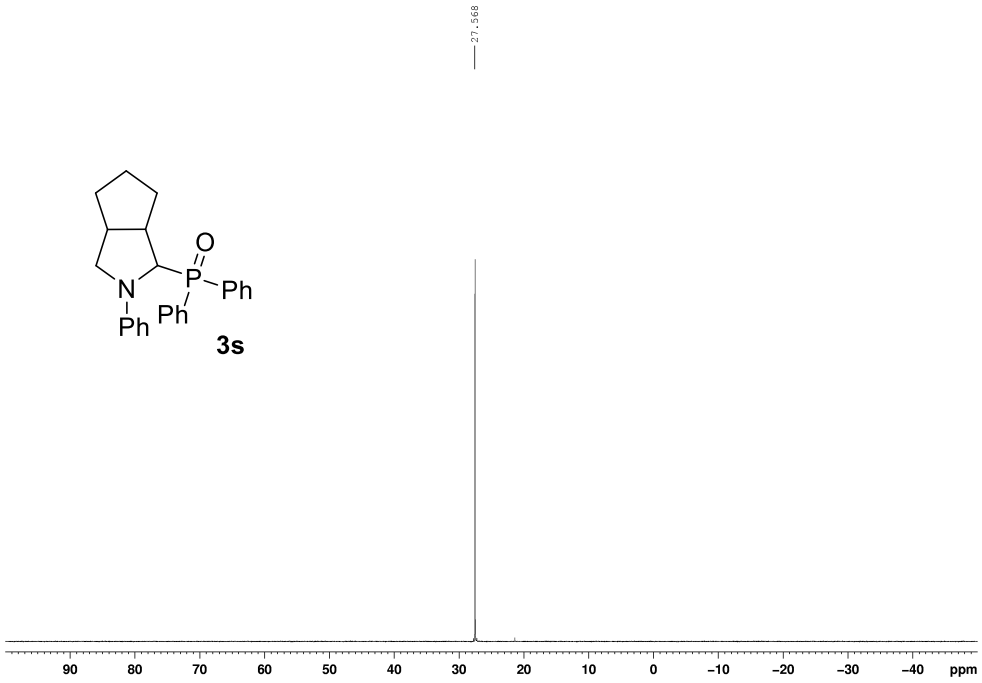
^{1}H NMR of **3s** ($CDCl_3$, 400 MHz)



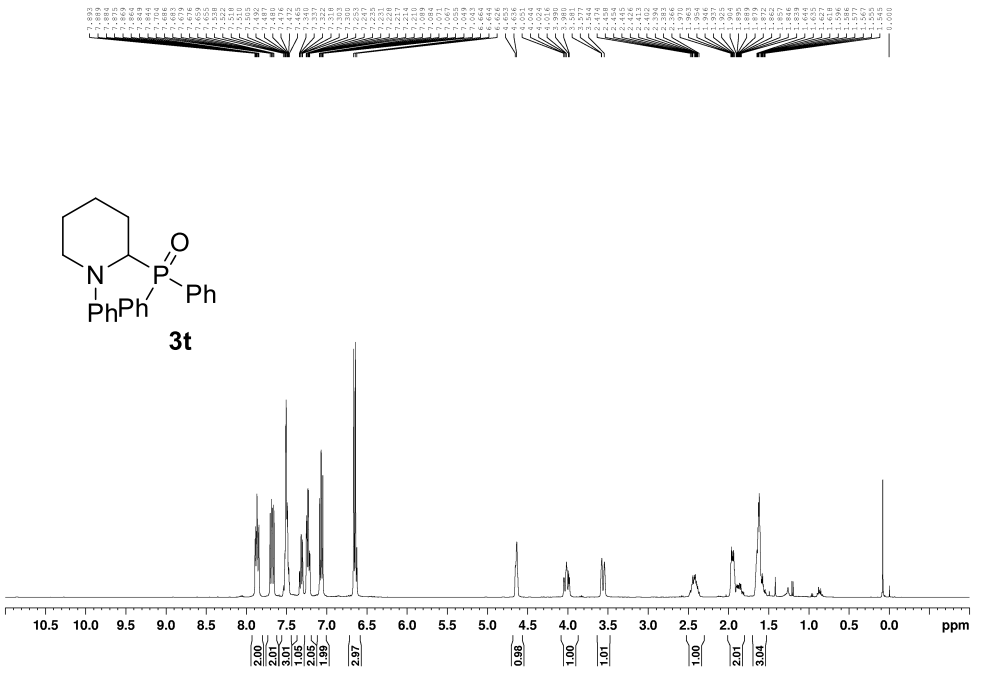
^{13}C NMR of **3s** ($CDCl_3$, 101 MHz)



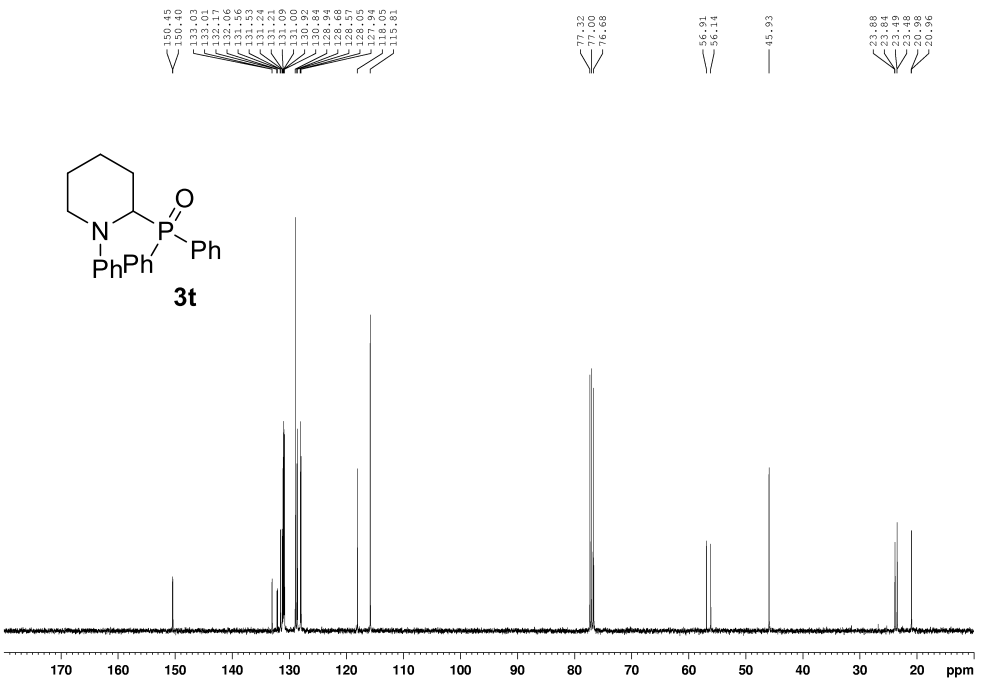
^{31}P NMR of **3s** ($CDCl_3$, 162 MHz)



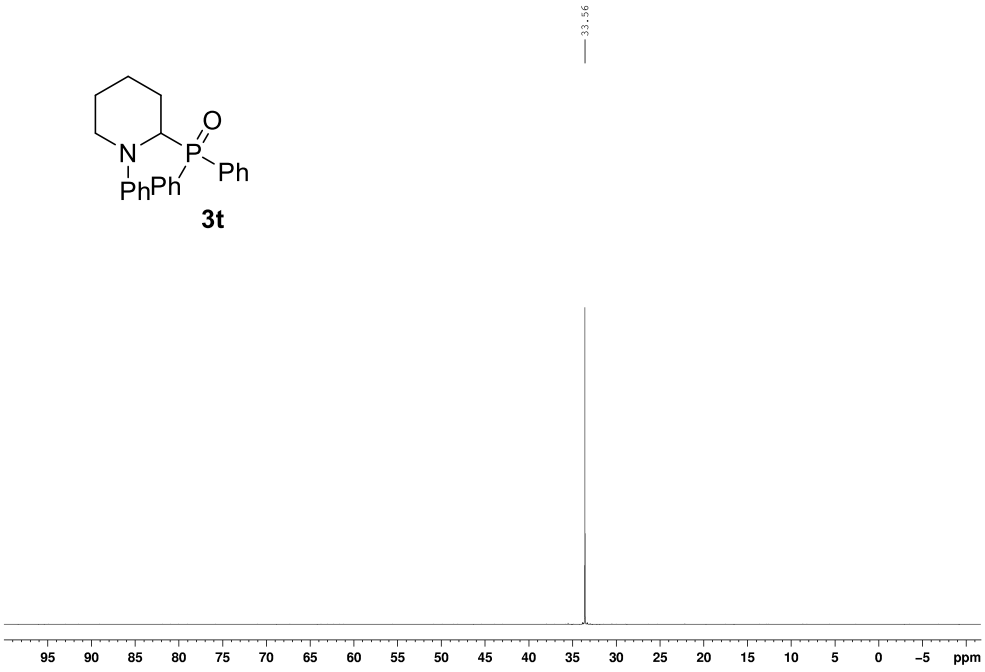
^{1}H NMR of **3t** ($CDCl_3$, 400 MHz)



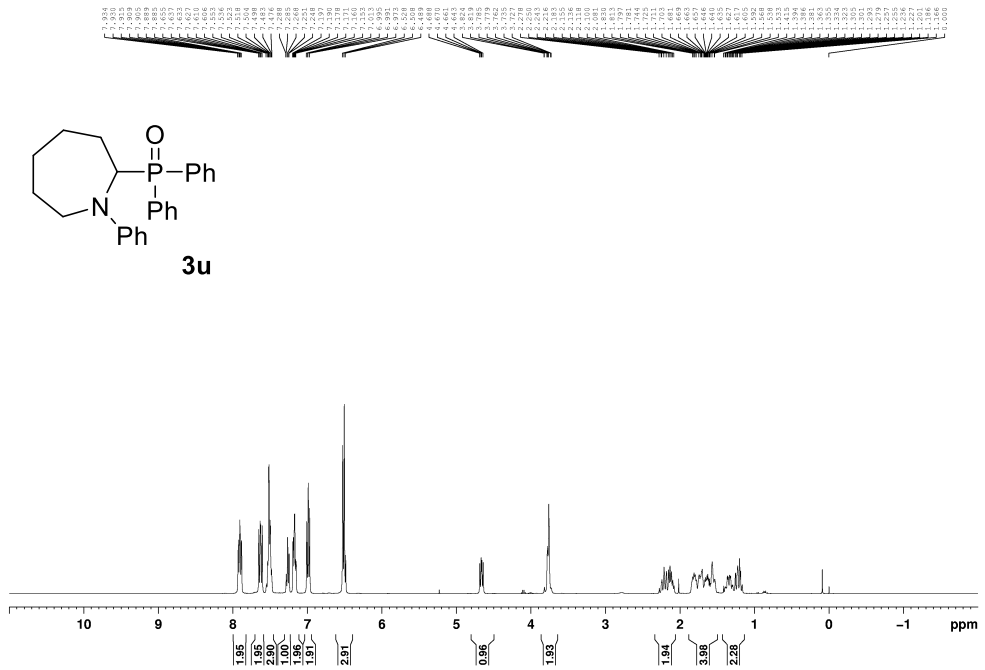
^{13}C NMR of **3t** ($CDCl_3$, 101 MHz)



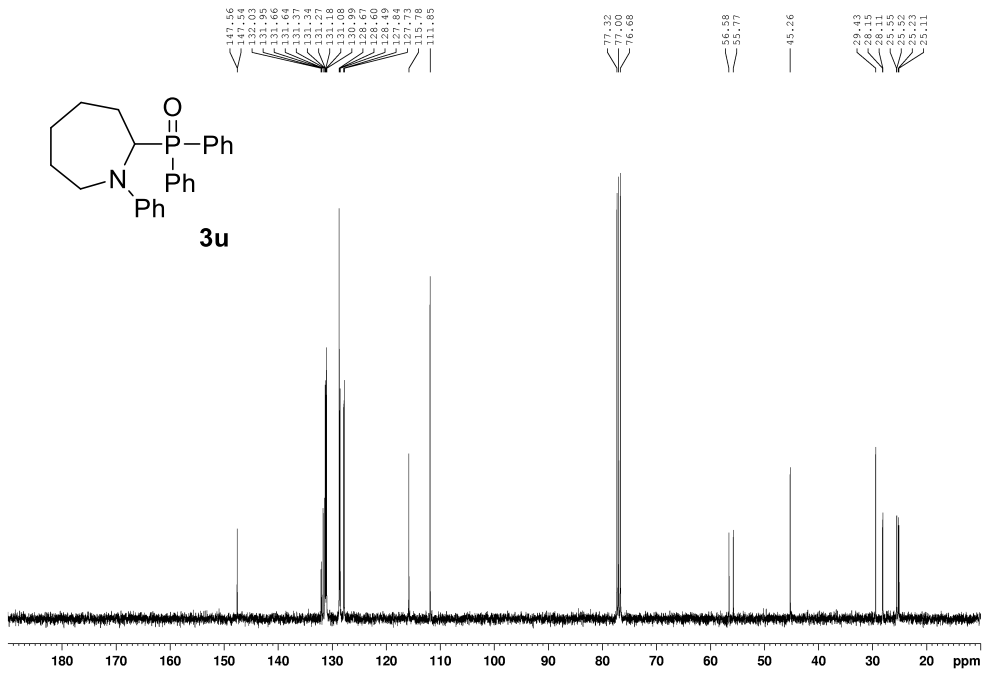
^{31}P NMR of **3t** ($CDCl_3$, 162 MHz)



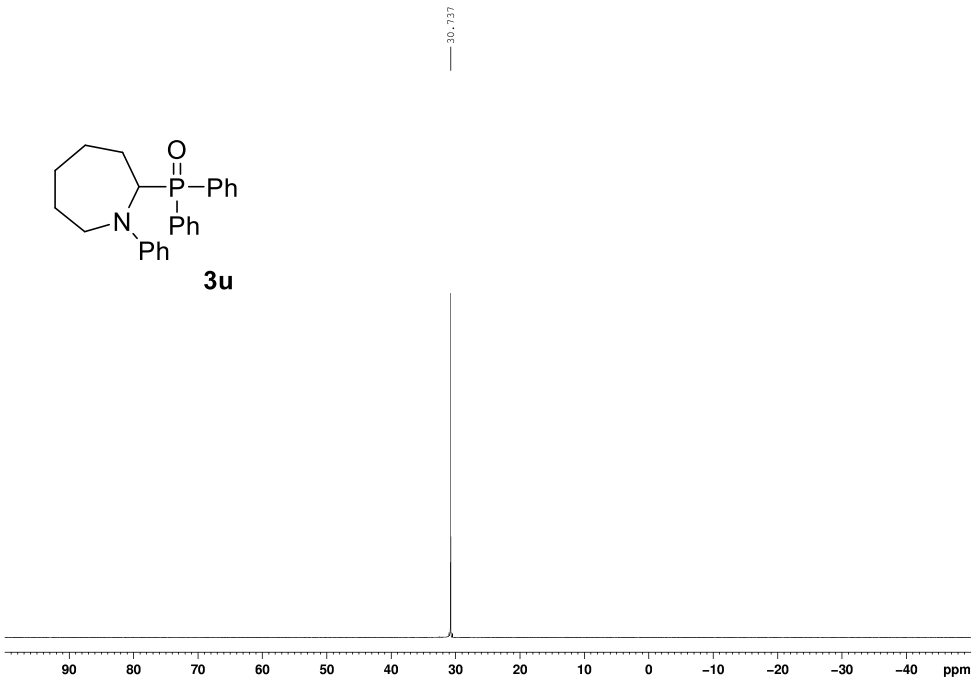
^{1}H NMR of **3u** ($CDCl_3$, 400 MHz)



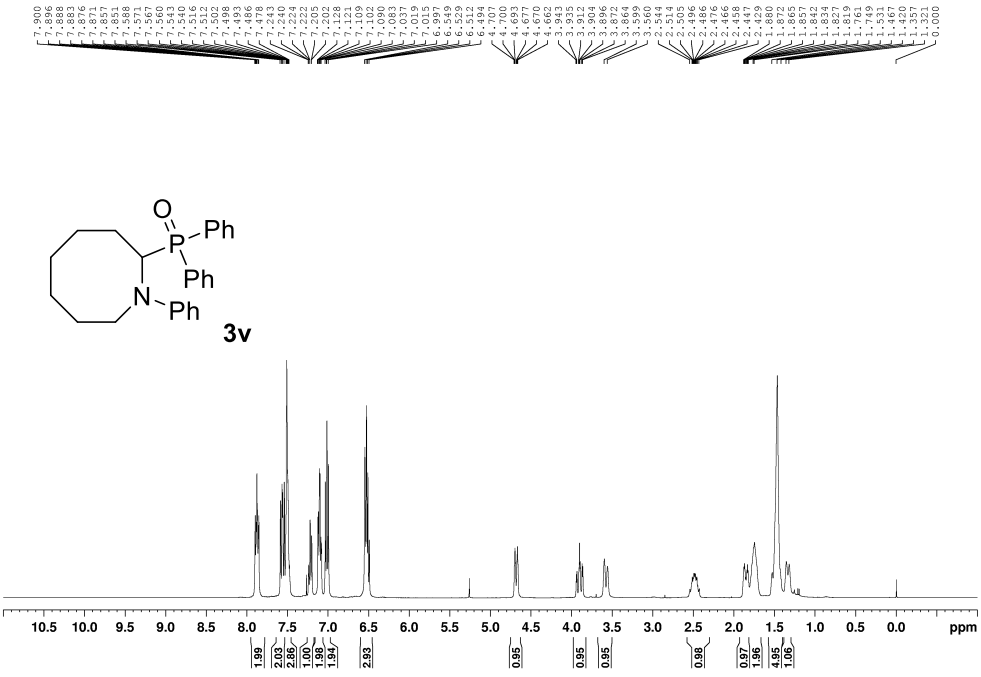
^{13}C NMR of **3u** ($CDCl_3$, 101 MHz)



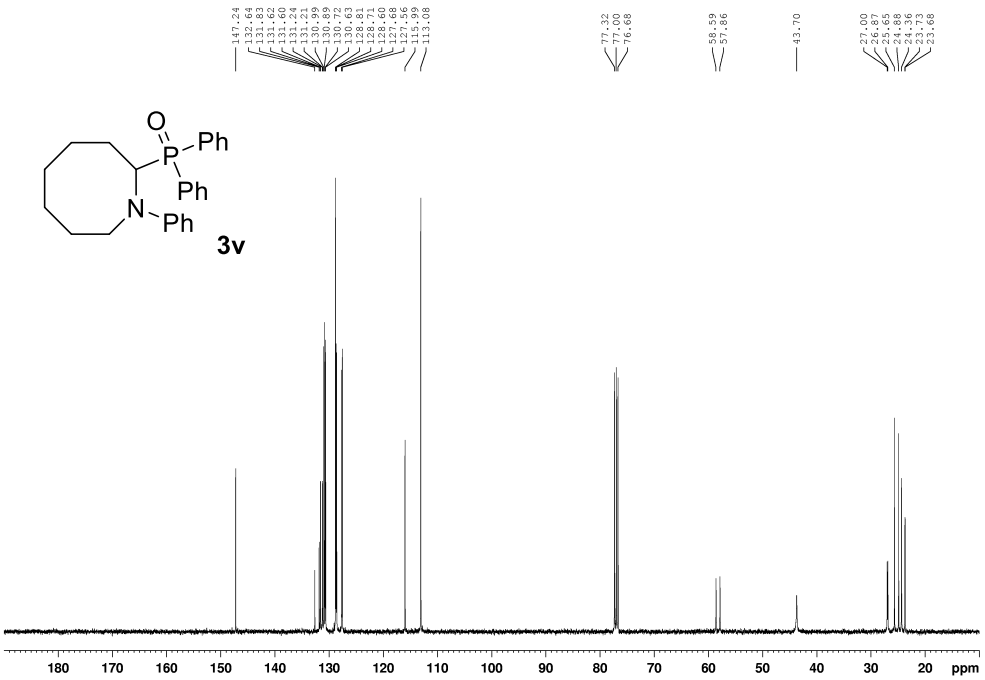
^{31}P NMR of **3u** ($CDCl_3$, 162 MHz)



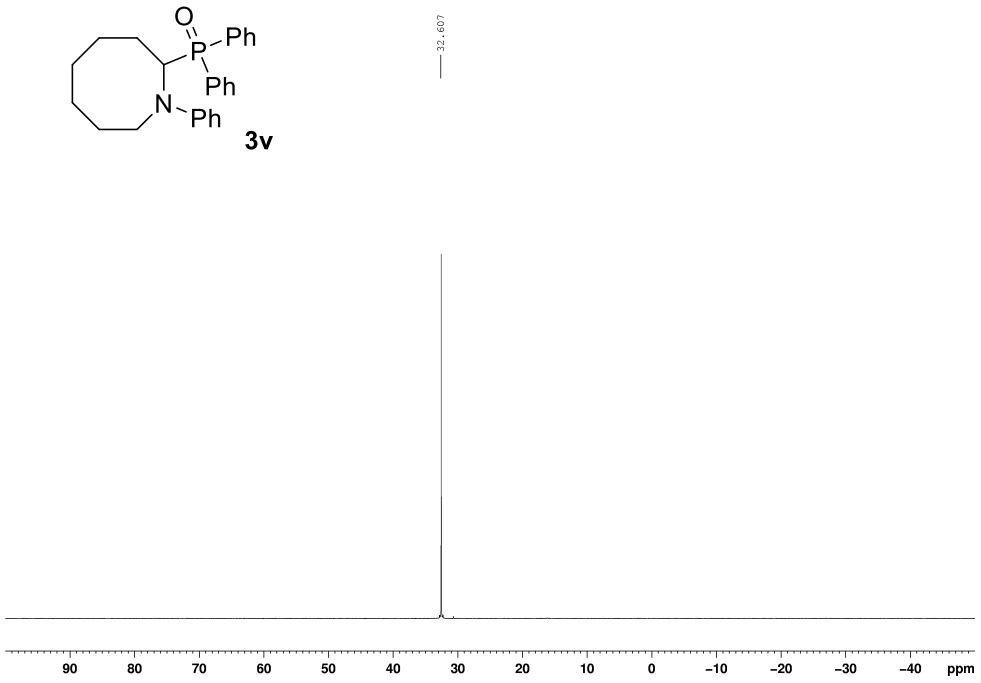
^{1}H NMR of **3v** ($CDCl_3$, 400 MHz)



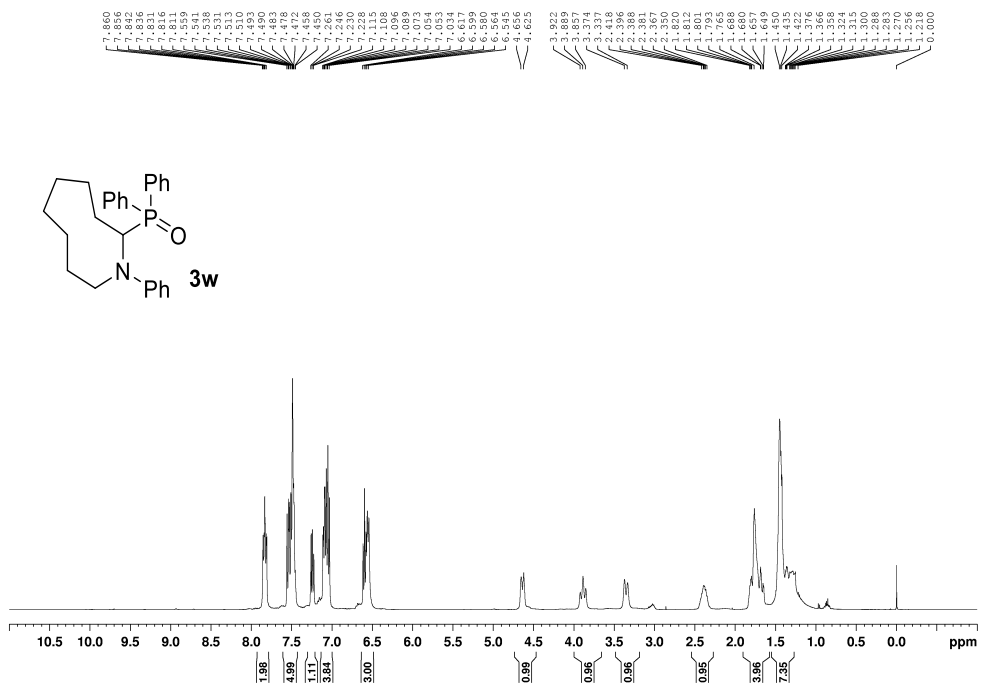
^{13}C NMR of **3v** ($CDCl_3$, 101 MHz)



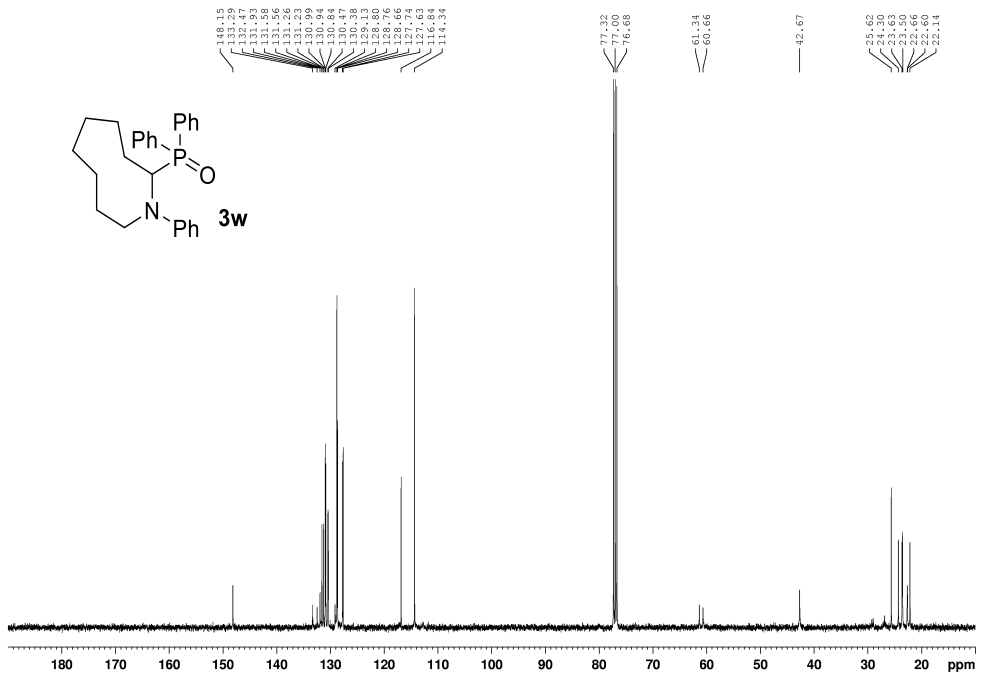
^{31}P NMR of **3v** ($CDCl_3$, 162 MHz)



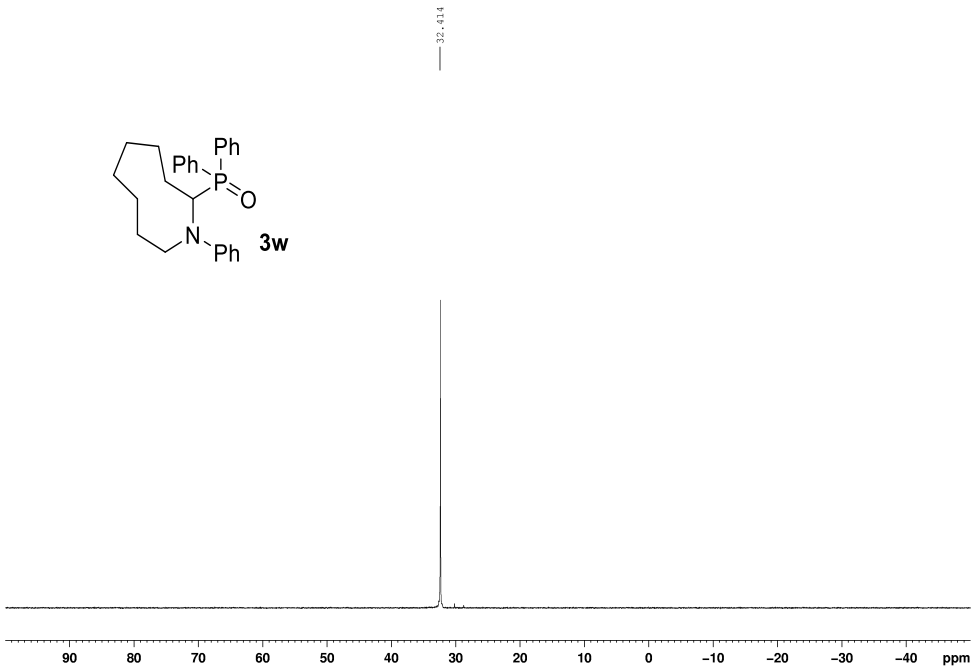
^{1}H NMR of **3w** ($CDCl_3$, 400 MHz)



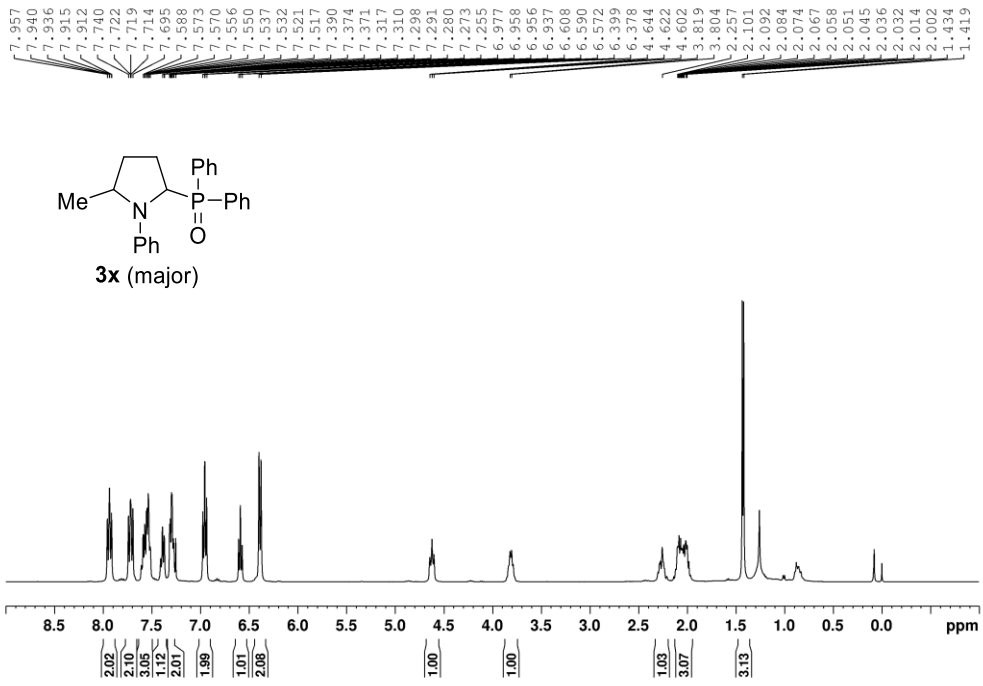
^{13}C NMR of **3w** ($CDCl_3$, 101 MHz)



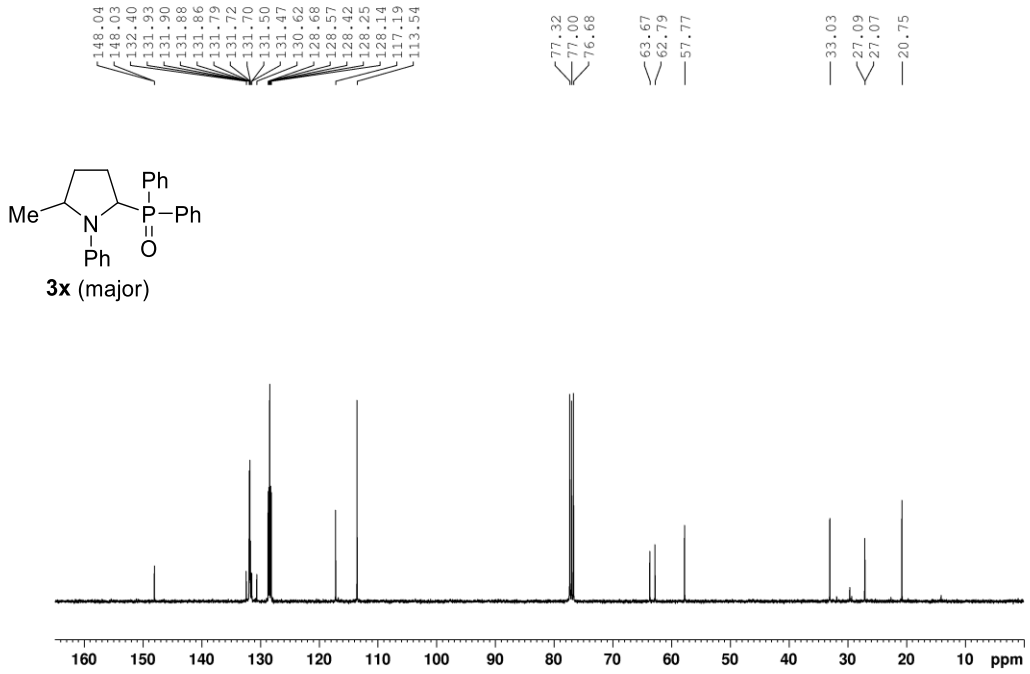
^{31}P NMR of **3w** ($CDCl_3$, 162 MHz)



^{1}H NMR of **3x** (major) ($CDCl_3$, 400 MHz)

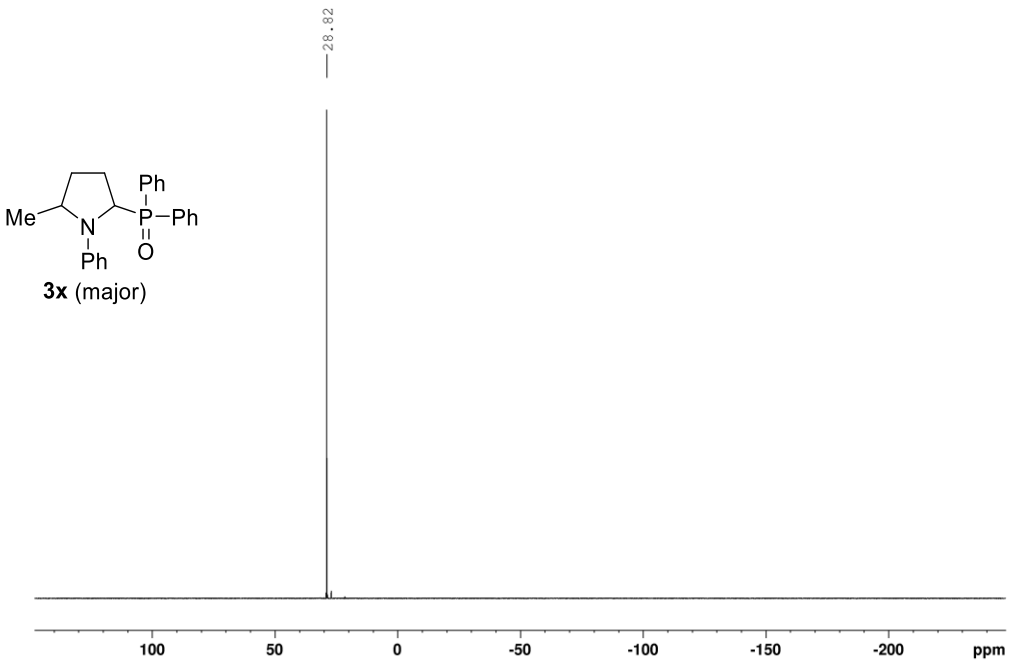


^{13}C NMR of **3x** (major) ($CDCl_3$, 101 MHz)



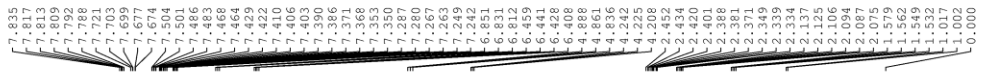
3x (major)

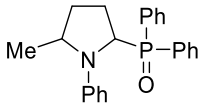
^{31}P NMR of **3x** (major) ($CDCl_3$, 162 MHz)



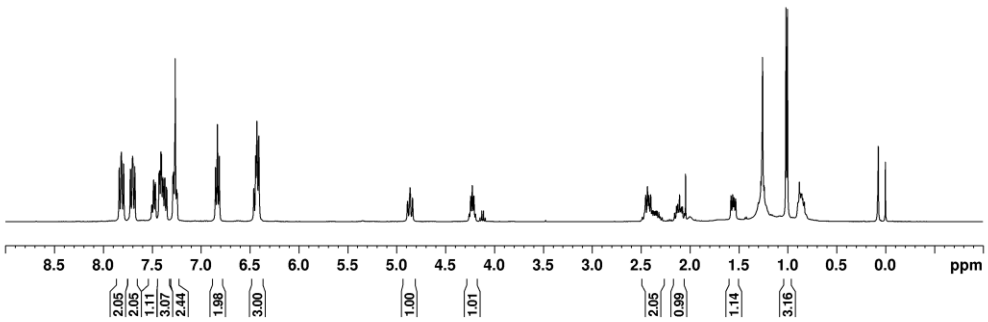
3x (major)

^{1}H NMR of **3x** (minor) ($CDCl_3$, 400 MHz)

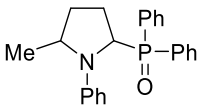




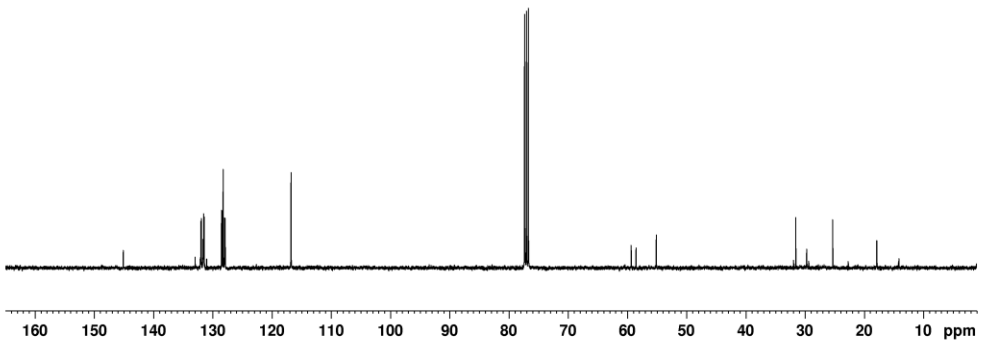
3x (minor)



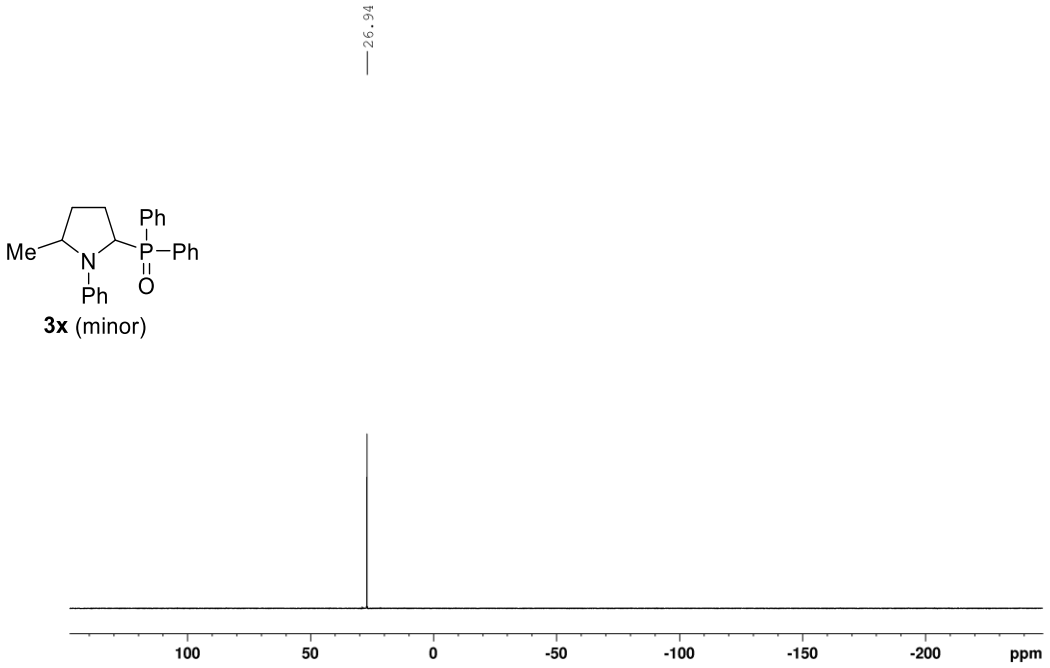
^{13}C NMR of **3x** (minor) ($CDCl_3$, 101 MHz)



3x (minor)

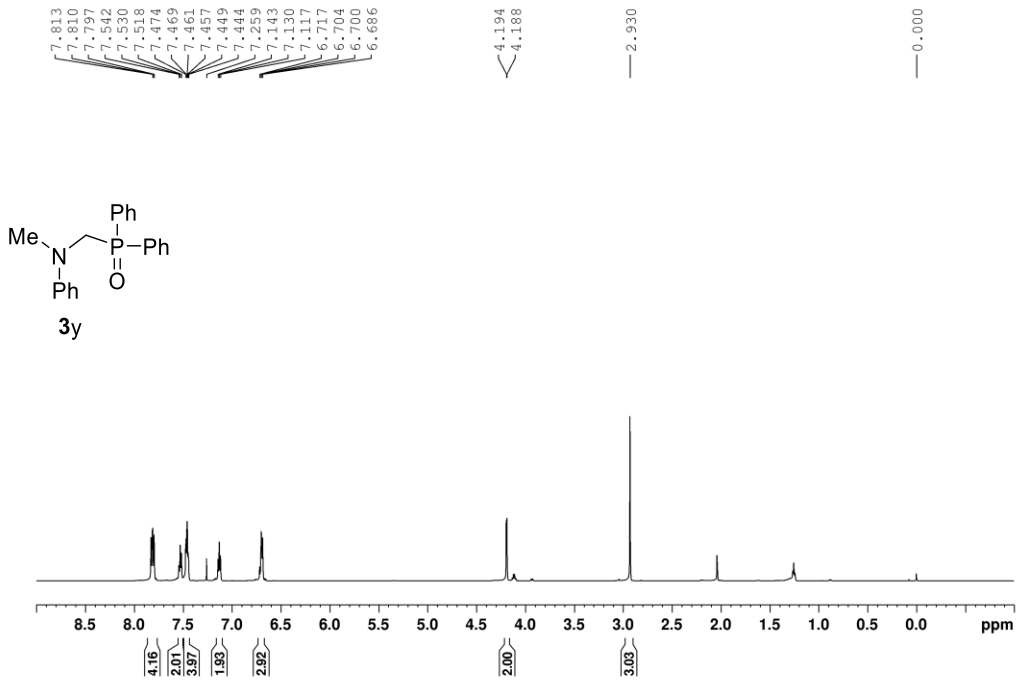


^{31}P NMR of **3x** (minor) ($CDCl_3$, 162 MHz)



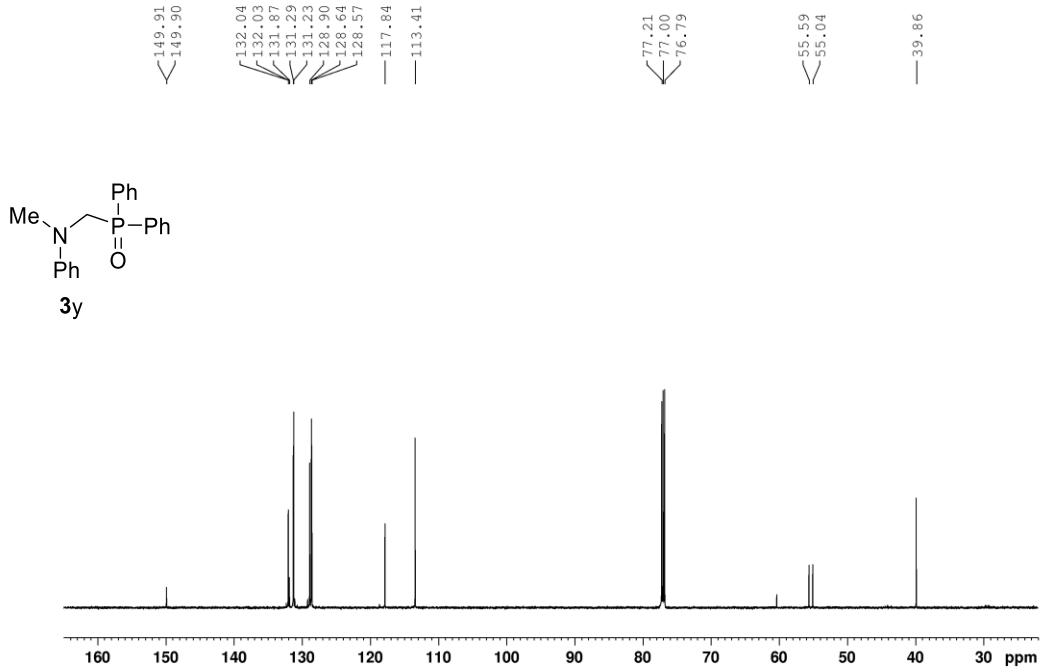
3x (minor)

^{1}H NMR of **3y** ($CDCl_3$, 600 MHz)

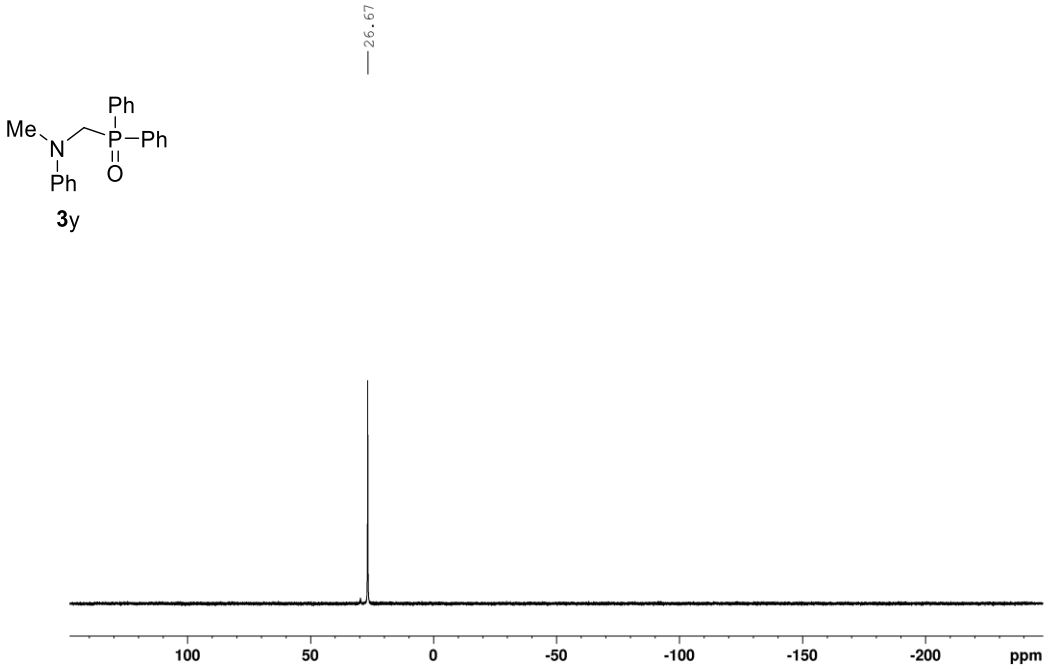


3y

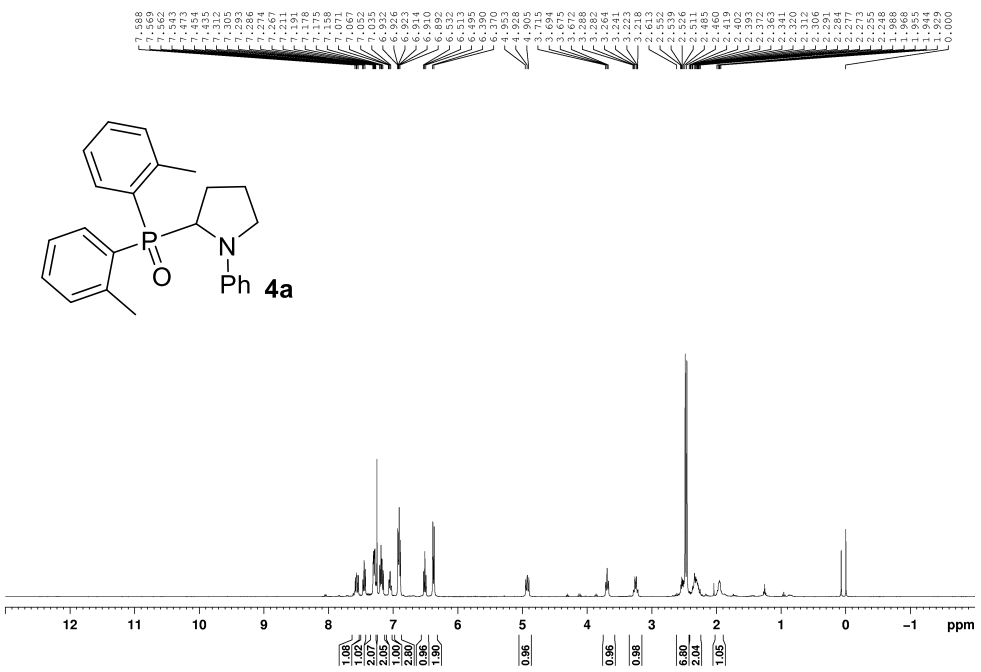
^{13}C NMR of **3y** ($CDCl_3$, 151 MHz)



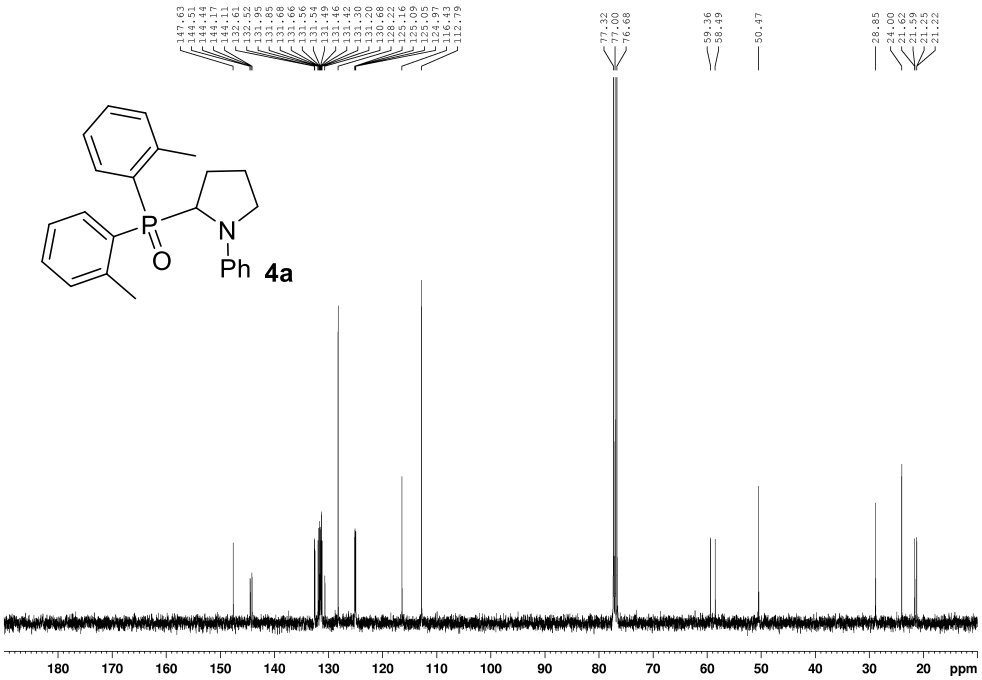
^{31}P NMR of **3y** ($CDCl_3$, 243 MHz)



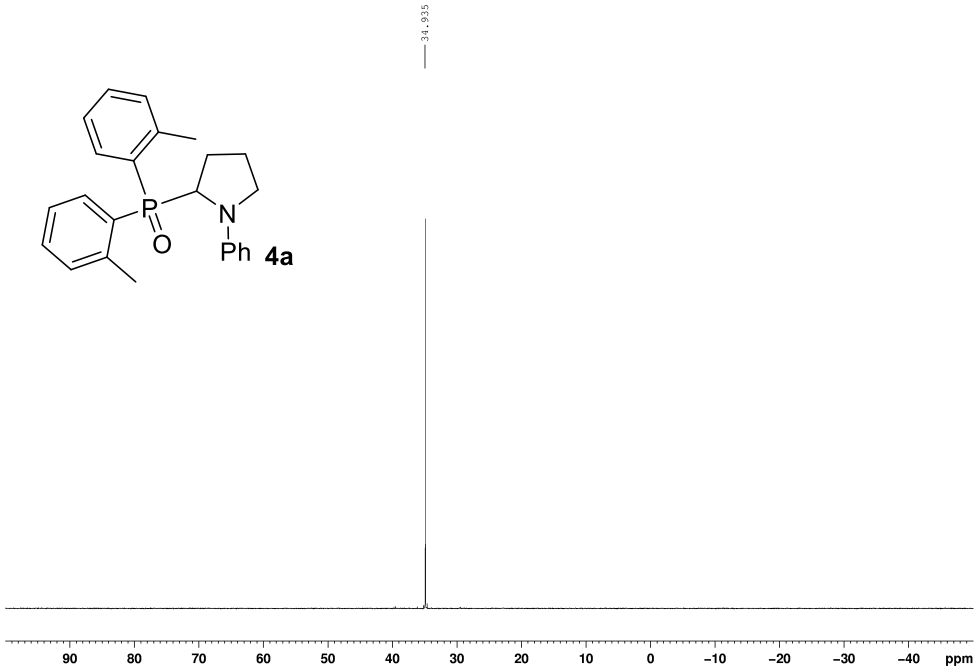
^{1}H NMR of **4a** ($CDCl_3$, 400 MHz)



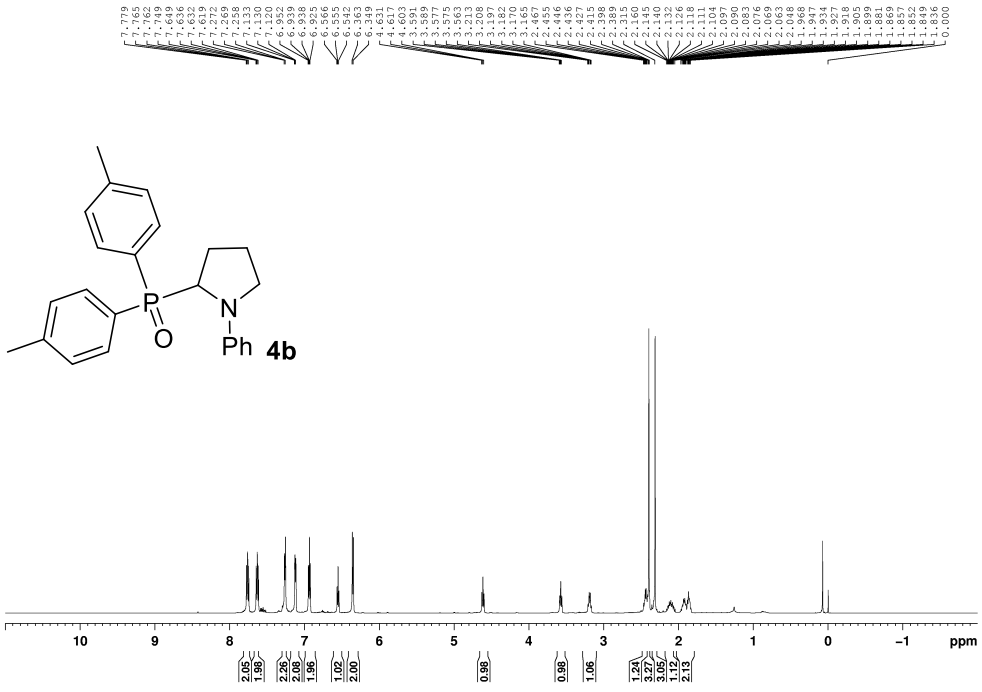
^{13}C NMR of **4a** ($CDCl_3$, 101 MHz)



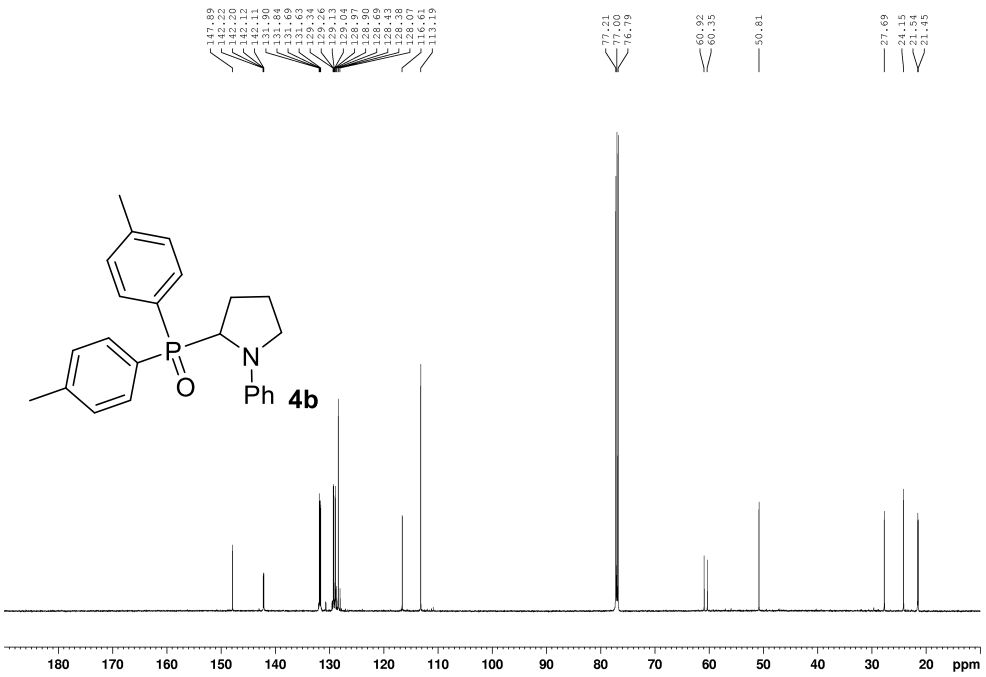
^{31}P NMR of **4a** ($CDCl_3$, 162 MHz)



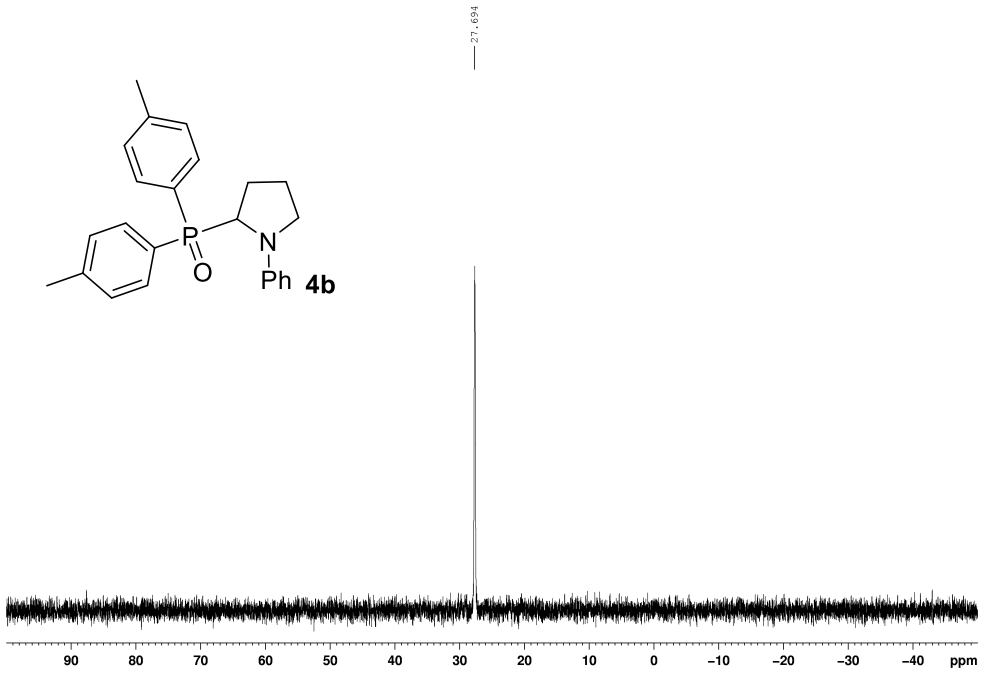
^{1}H NMR of **4b** ($CDCl_3$, 600 MHz)



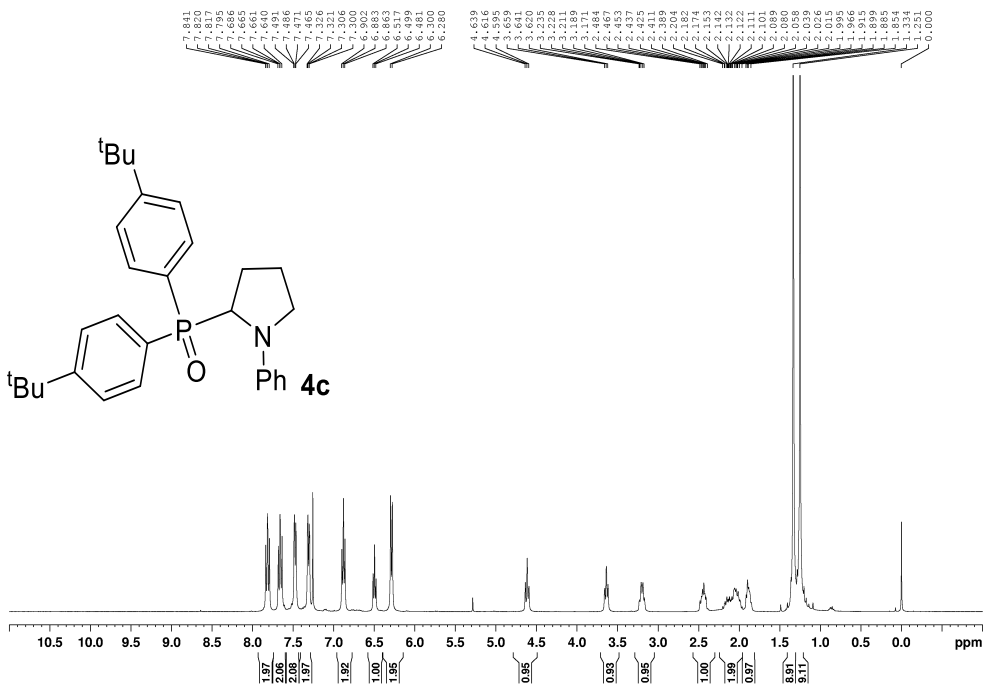
^{13}C NMR of **4b** ($CDCl_3$, 151 MHz)



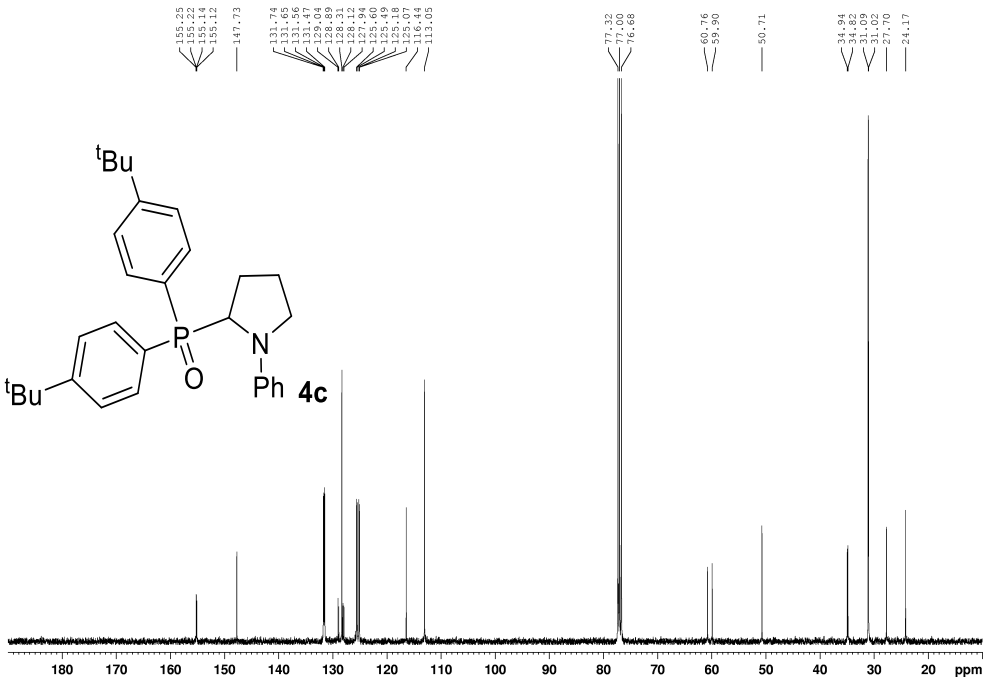
^{31}P NMR of **4b** ($CDCl_3$, 243 MHz)



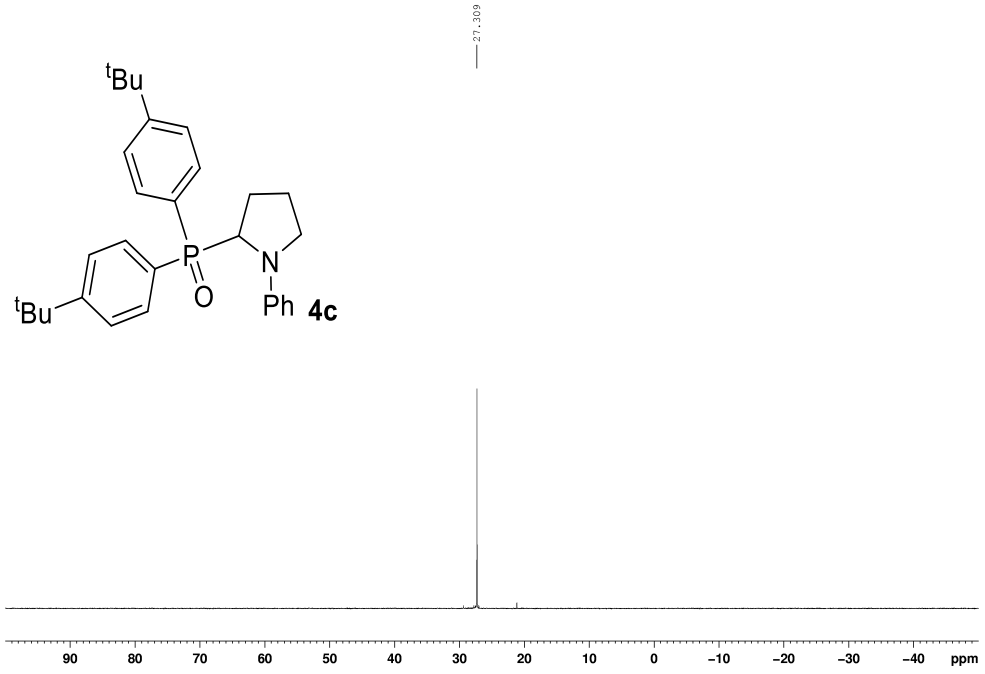
^{1}H NMR of **4c** ($CDCl_3$, 400M)



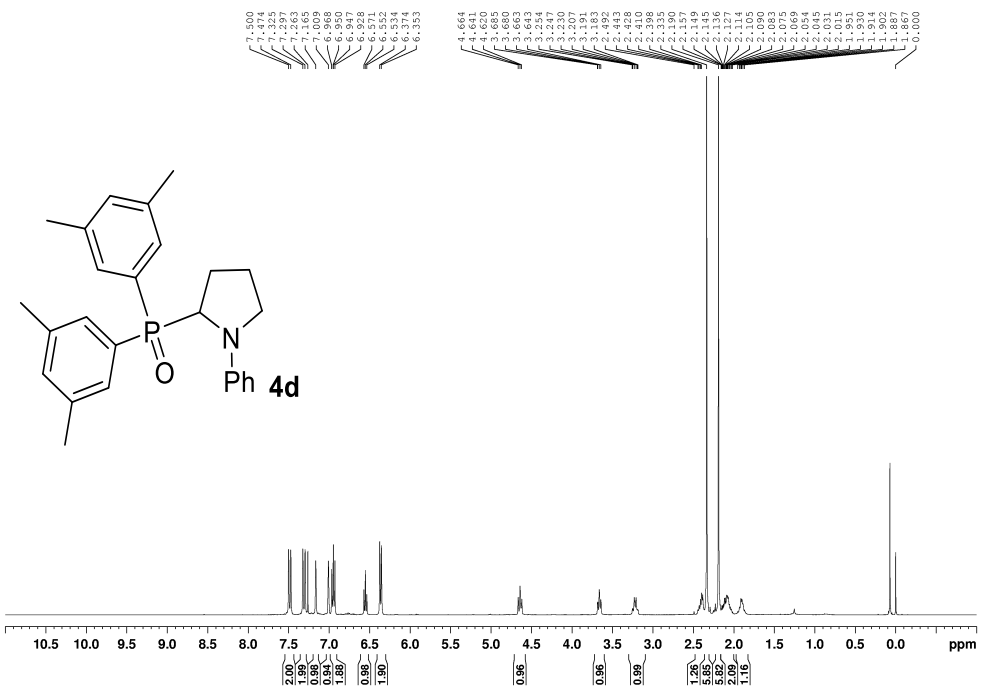
^{13}C NMR of **4c** ($CDCl_3$, 101M)



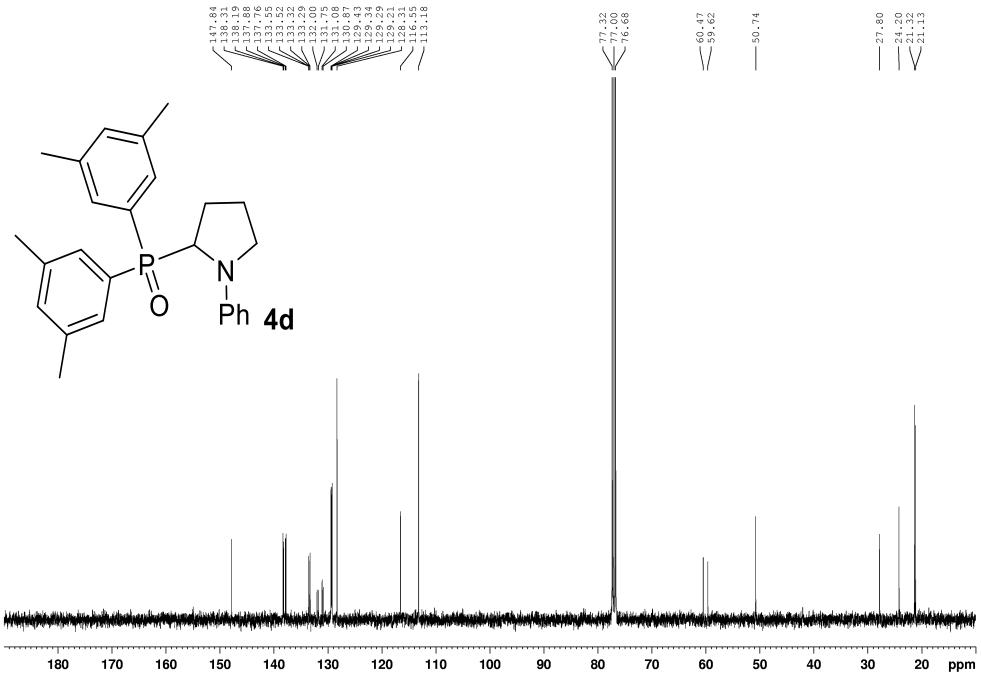
^{31}P NMR of **4c** ($CDCl_3$, 162 MHz)



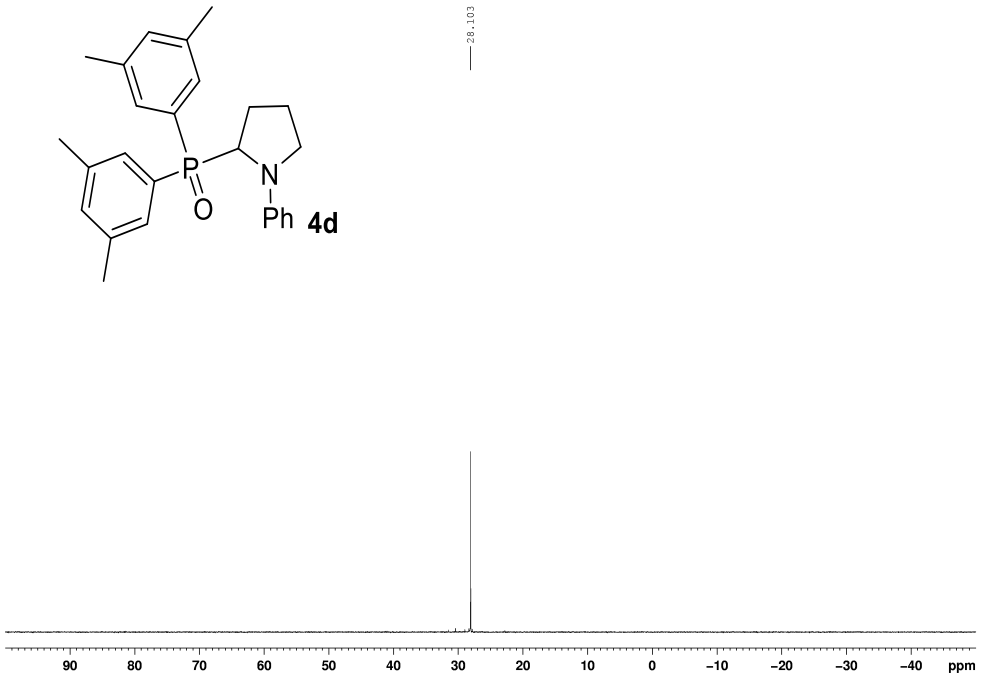
^{1}H NMR of **4d** ($CDCl_3$, 101M)



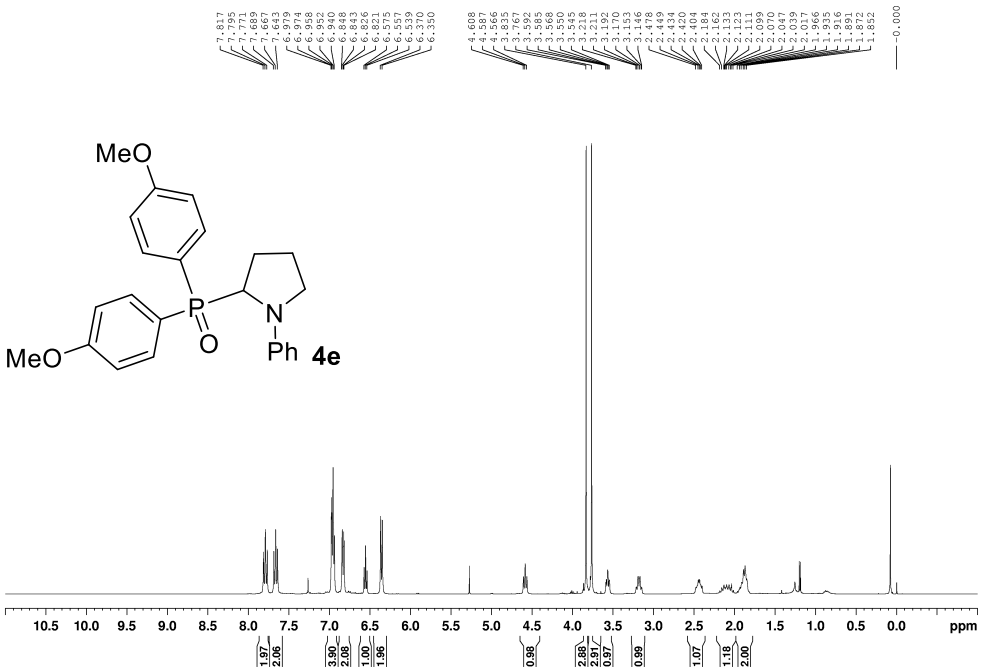
^{13}C NMR of **4d** in $CDCl_3$



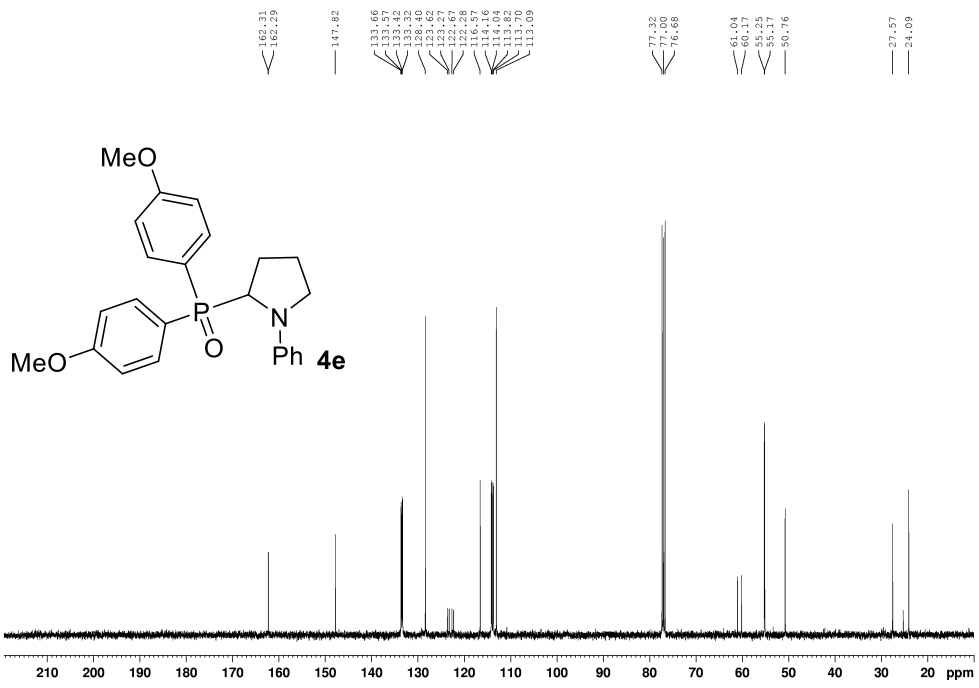
^{31}P NMR of **4d** ($CDCl_3$, 162 MHz)



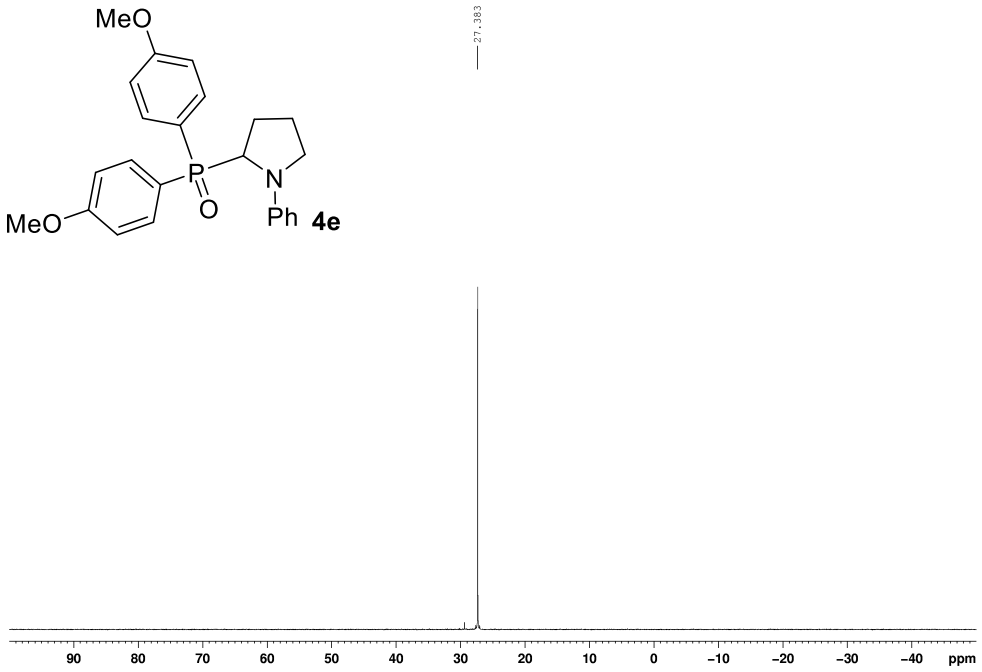
^{1}H NMR of **4e** ($CDCl_3$, 400 MHz)



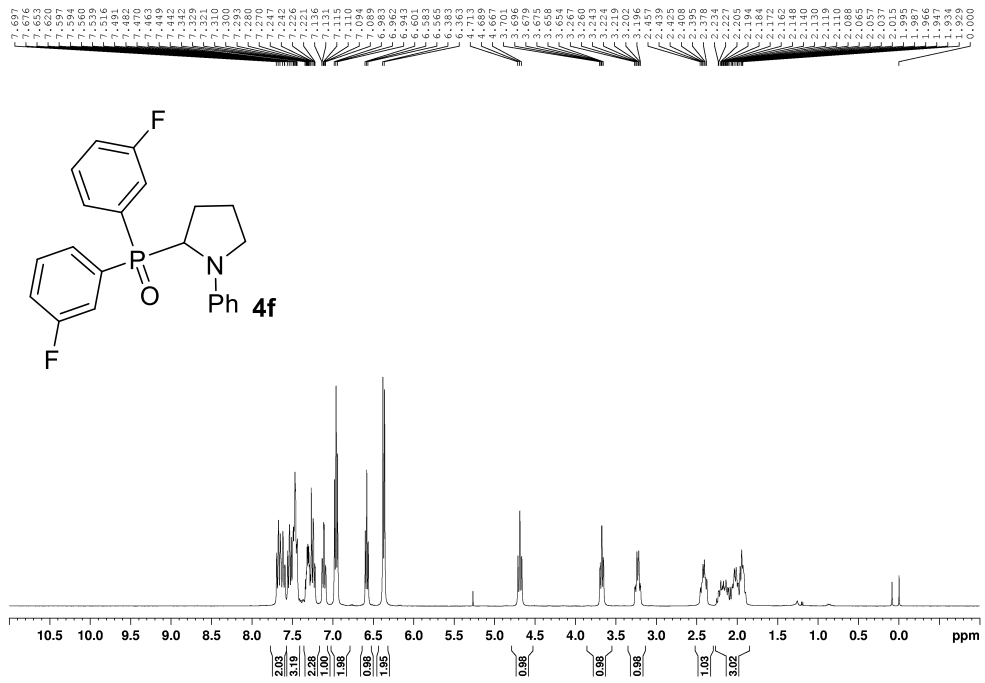
^{13}C NMR of **4e** ($CDCl_3$, 101 MHz)



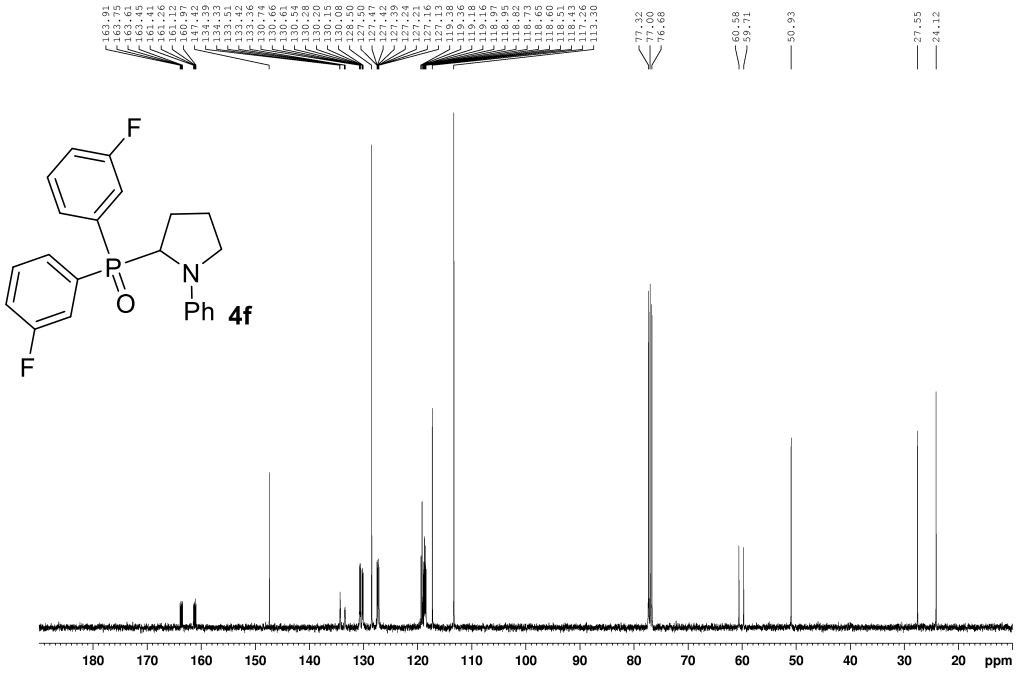
^{31}P NMR of **4e** ($CDCl_3$, 162 MHz)



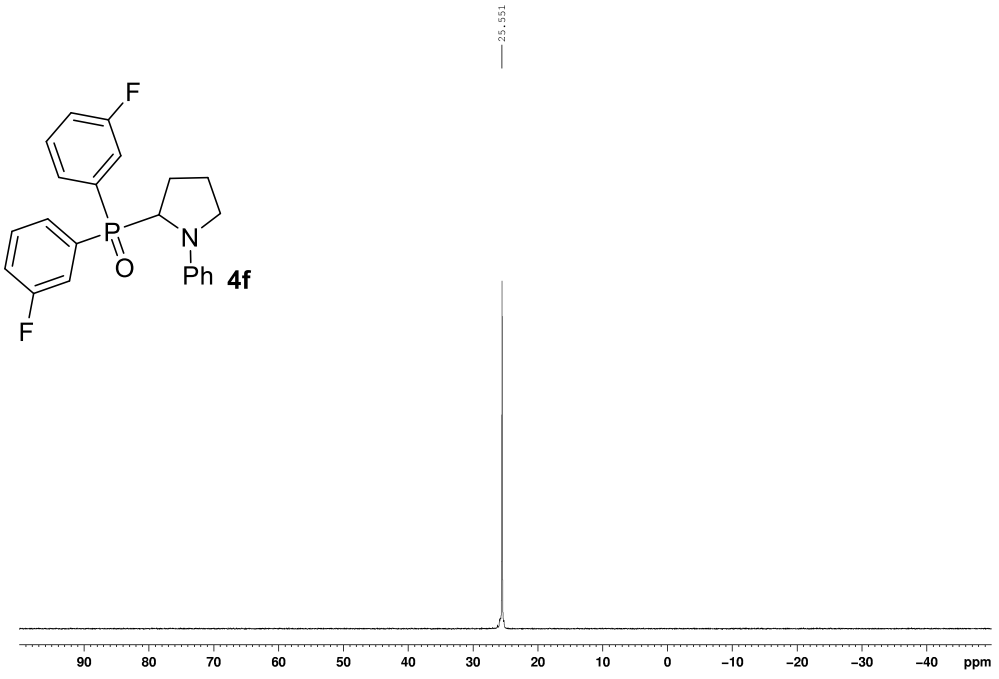
^{1}H NMR of **4f** ($CDCl_3$, 400 MHz)



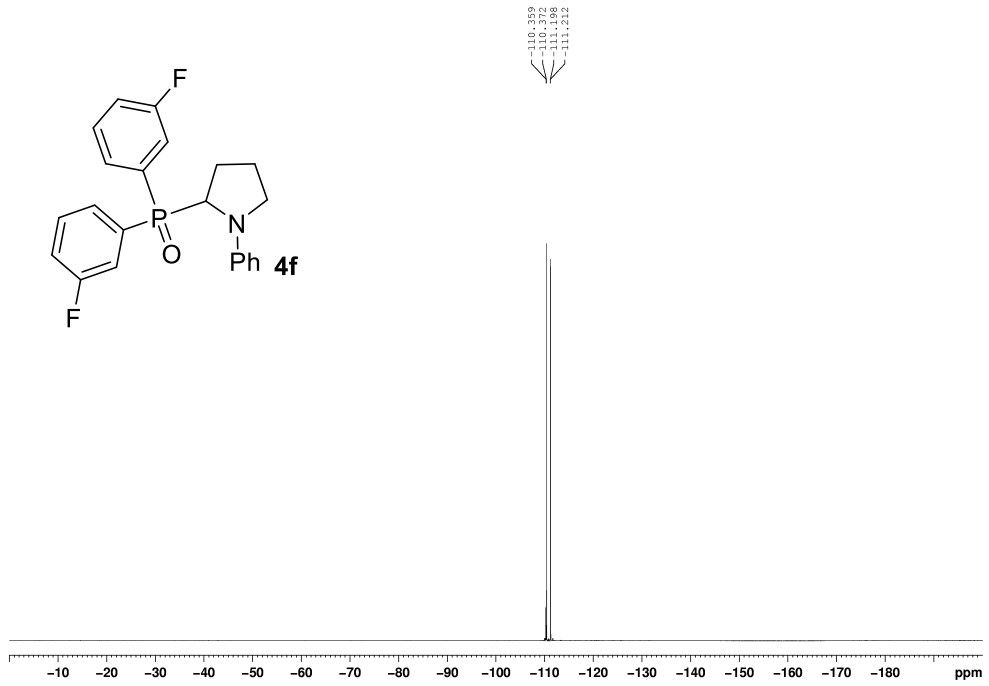
^{13}C NMR of **4f** ($CDCl_3$, 101 MHz)



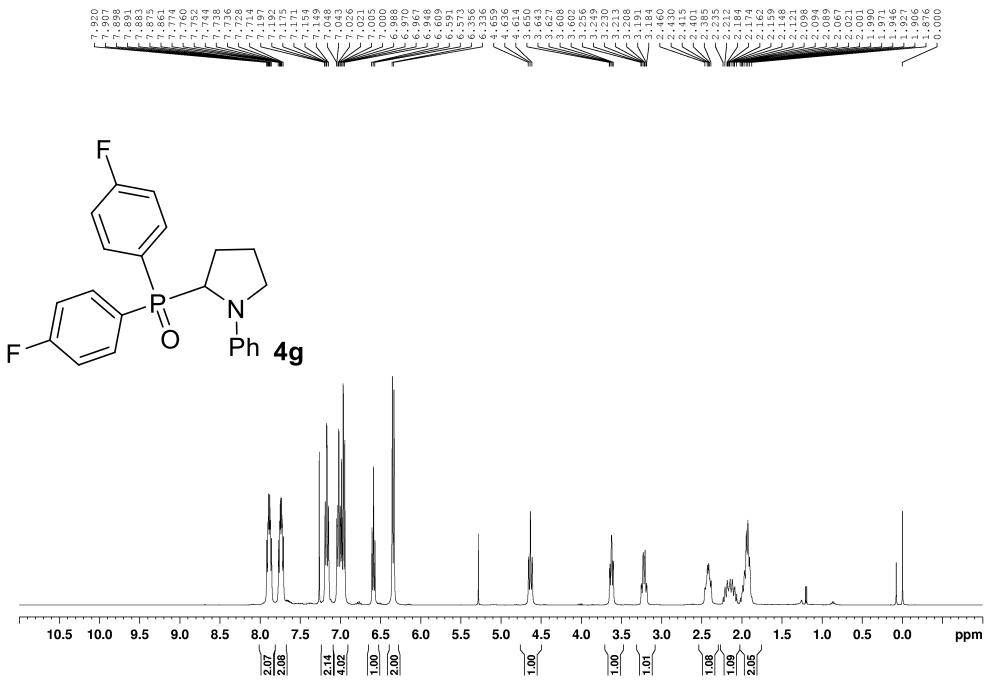
^{31}P NMR of **4f** ($CDCl_3$, 162 MHz)



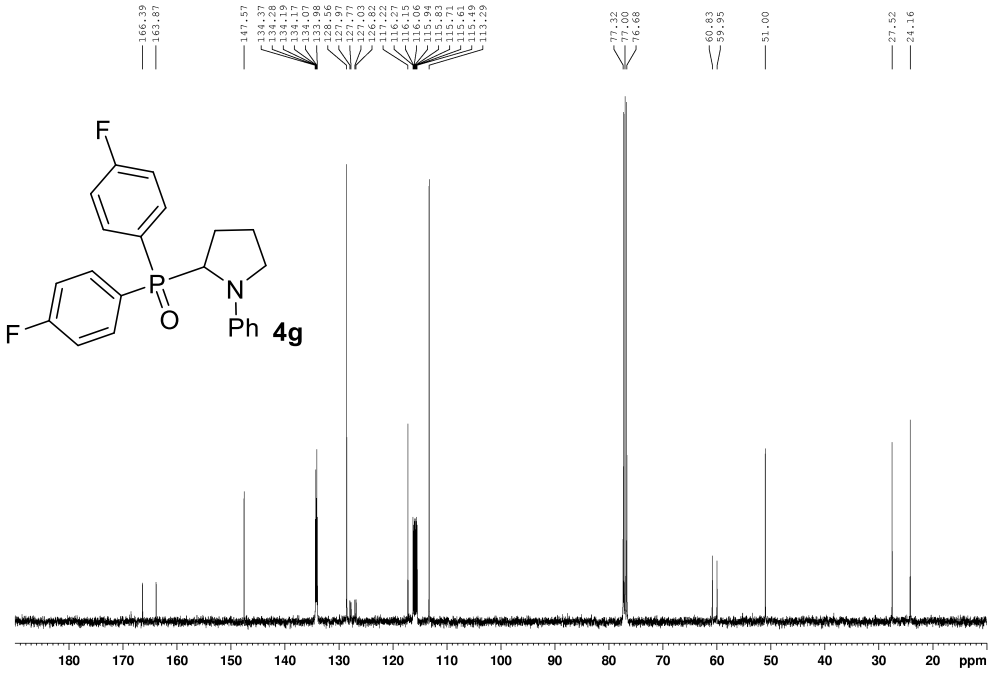
^{19}F NMR of **4f** ($CDCl_3$, 376 MHz)



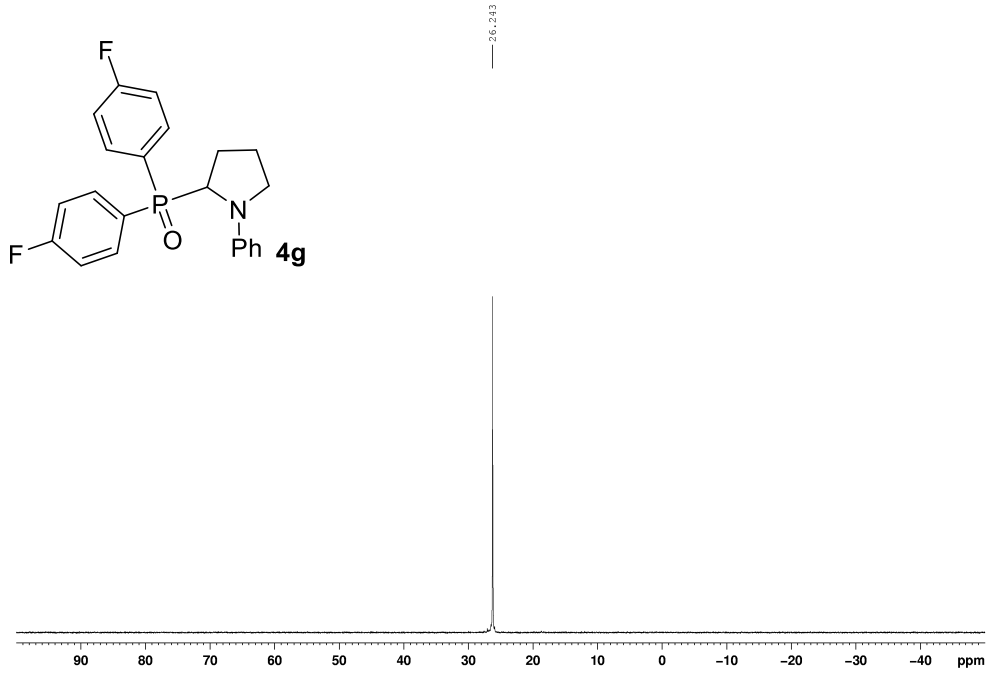
^{1}H NMR of **4g** ($CDCl_3$, 400 MHz)



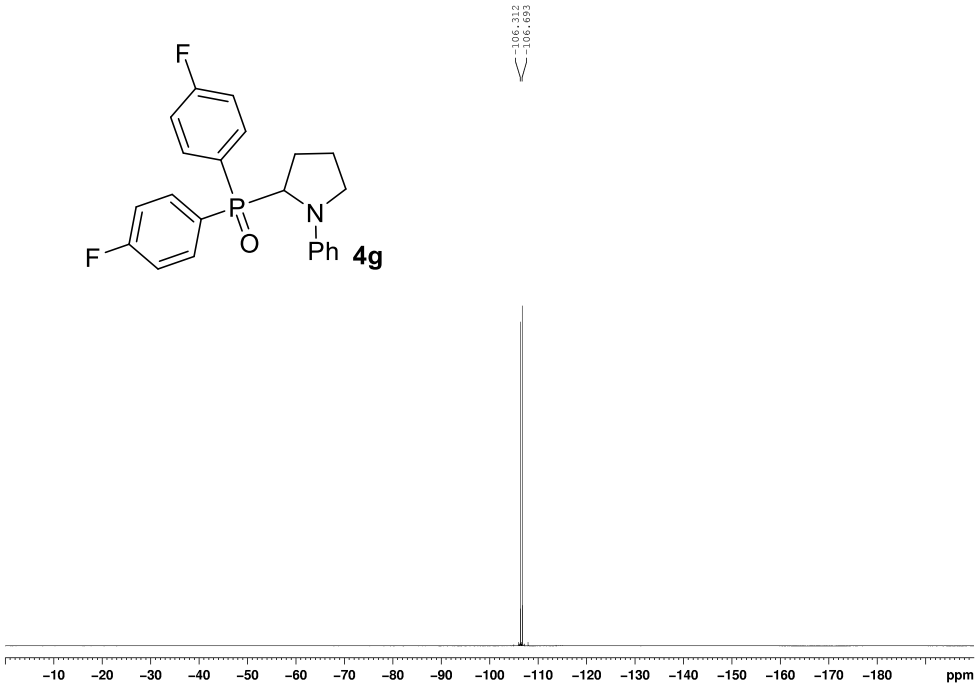
^{13}C NMR of **4g** ($CDCl_3$, 101 MHz)



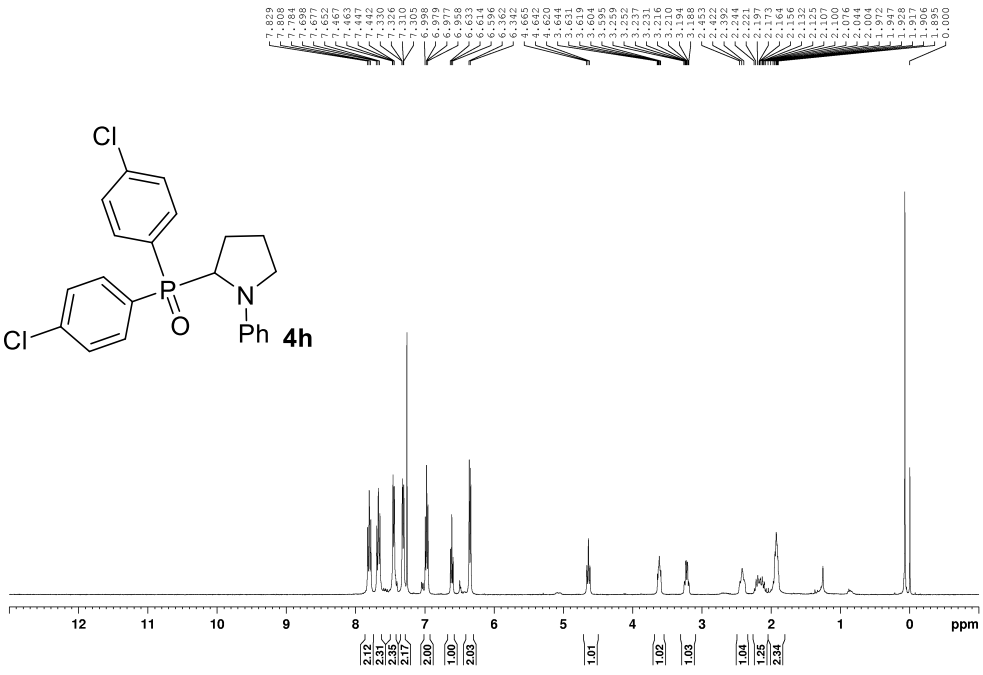
^{31}P NMR of **4g** ($CDCl_3$, 162 MHz)



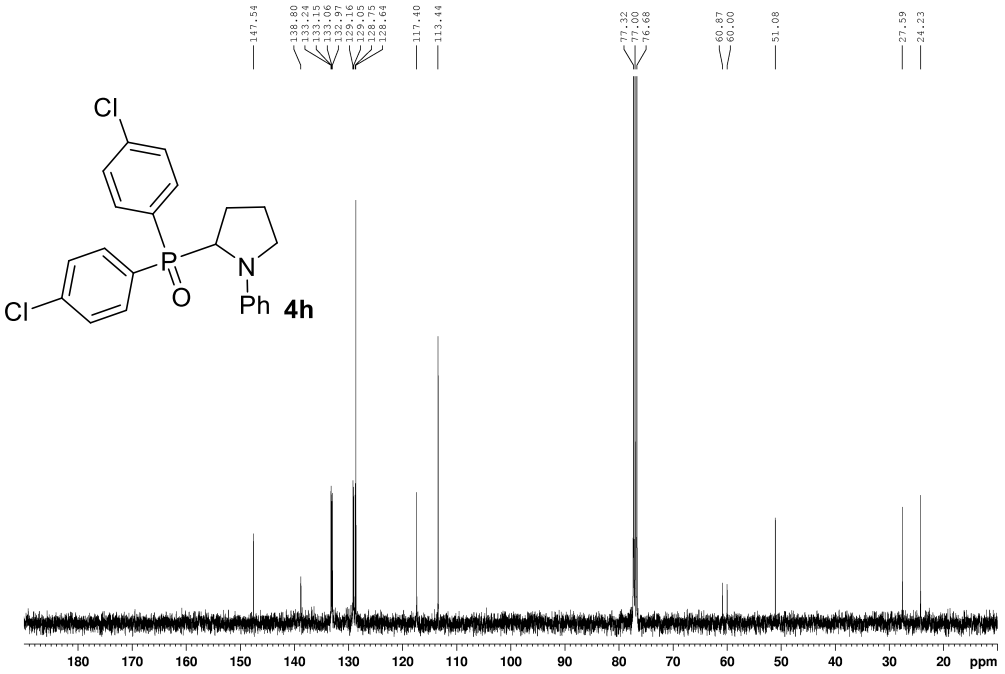
^{19}F NMR of **4g** ($CDCl_3$, 376 MHz)



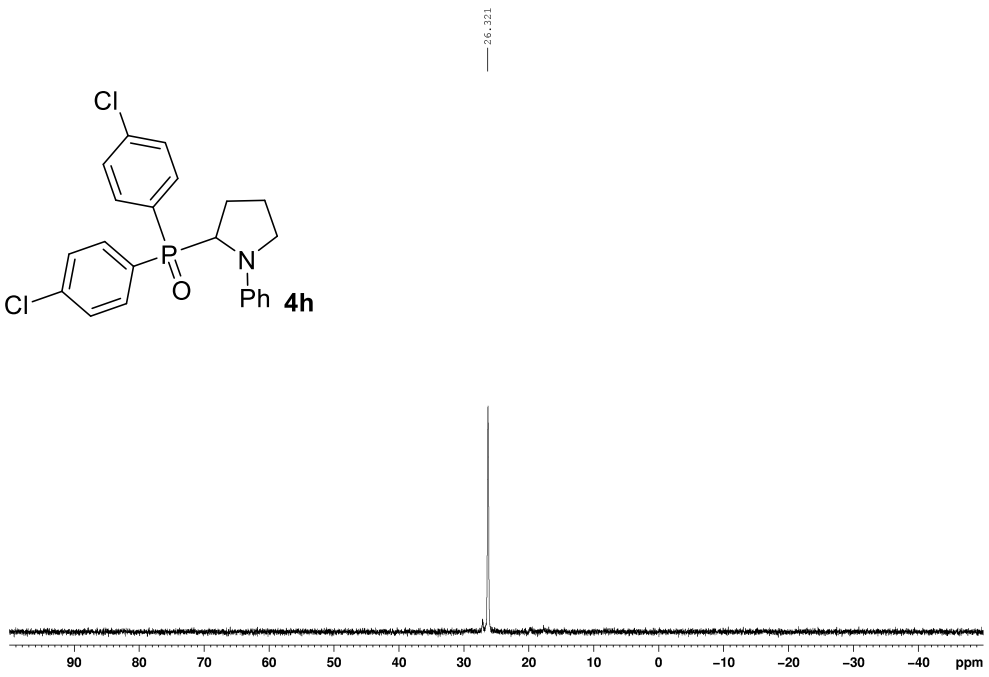
^{1}H NMR of **4h** ($CDCl_3$, 400 MHz)



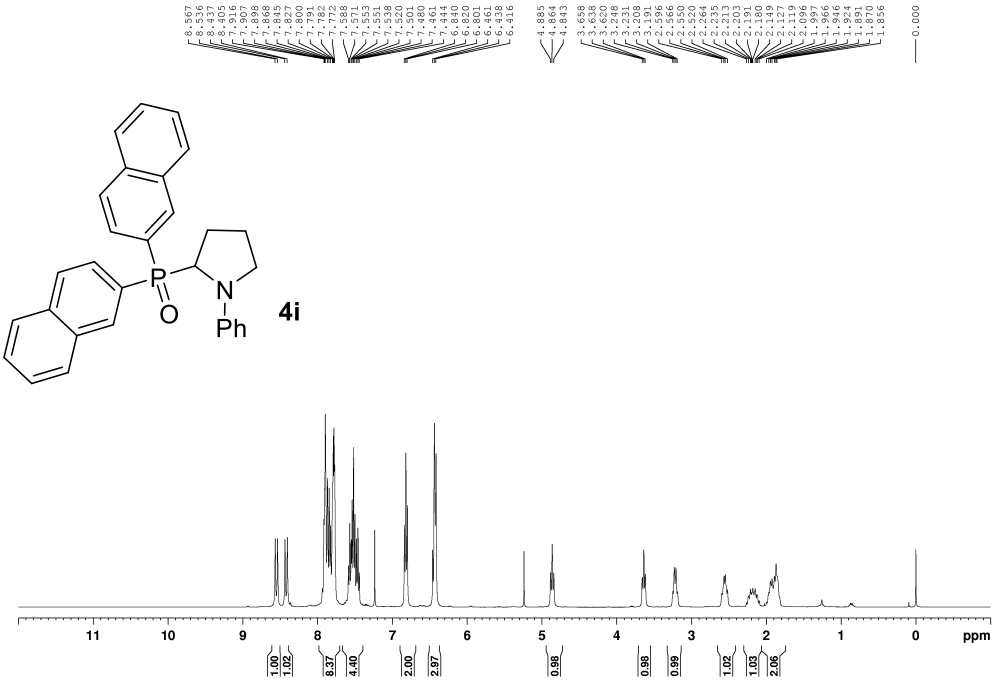
^{13}C NMR of **4h** ($CDCl_3$, 101 MHz)



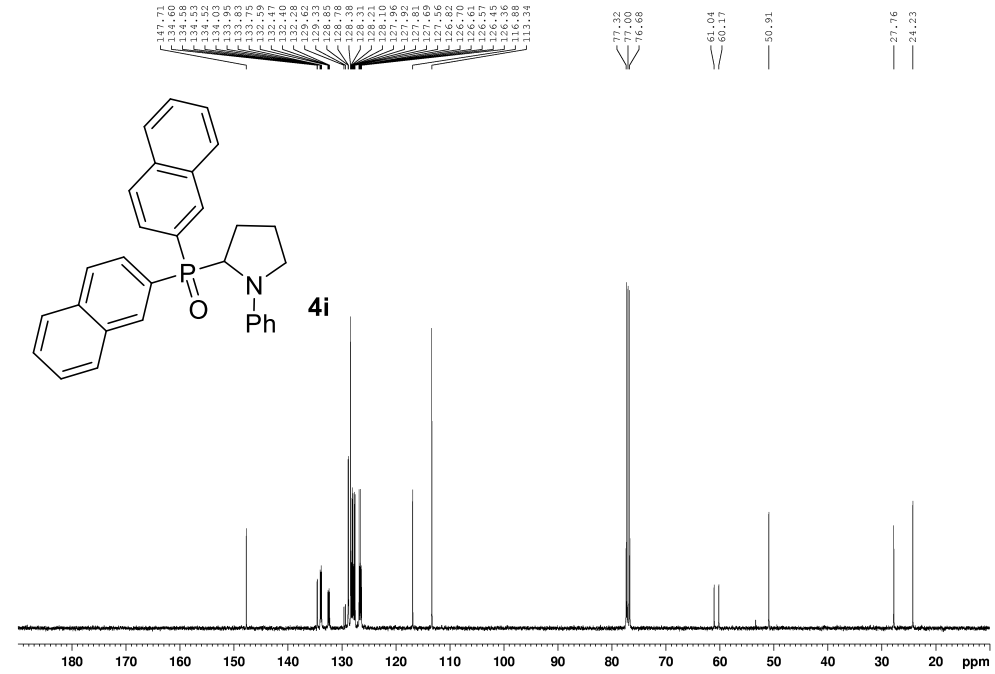
^{31}P NMR of **4h** ($CDCl_3$, 162 MHz)



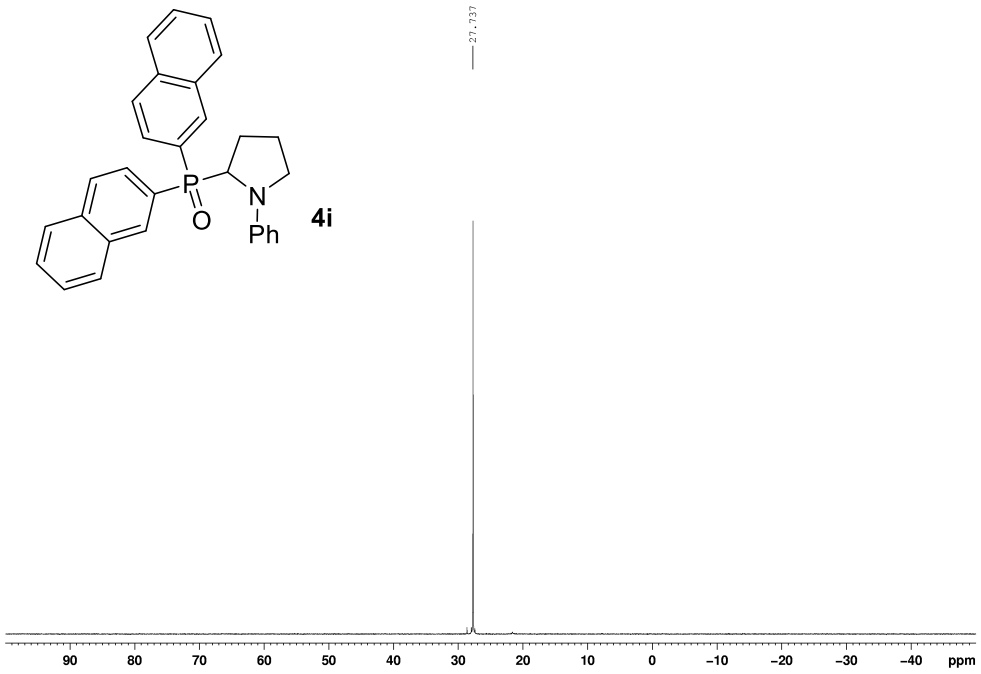
^{1}H NMR of **4i** ($CDCl_3$, 400 MHz)



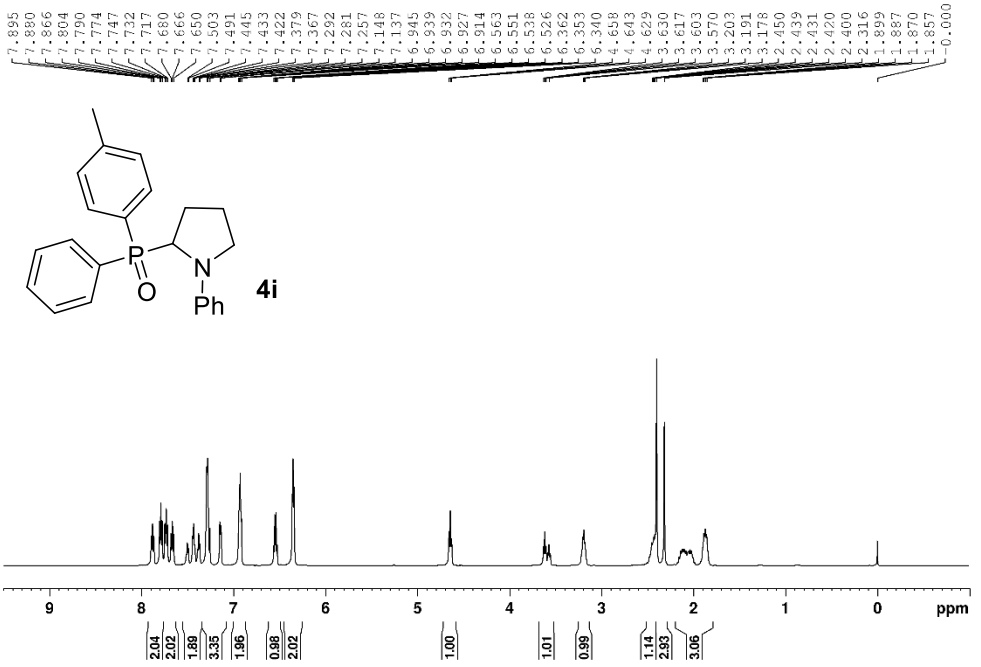
^{13}C NMR of **4i** ($CDCl_3$, 101 MHz)



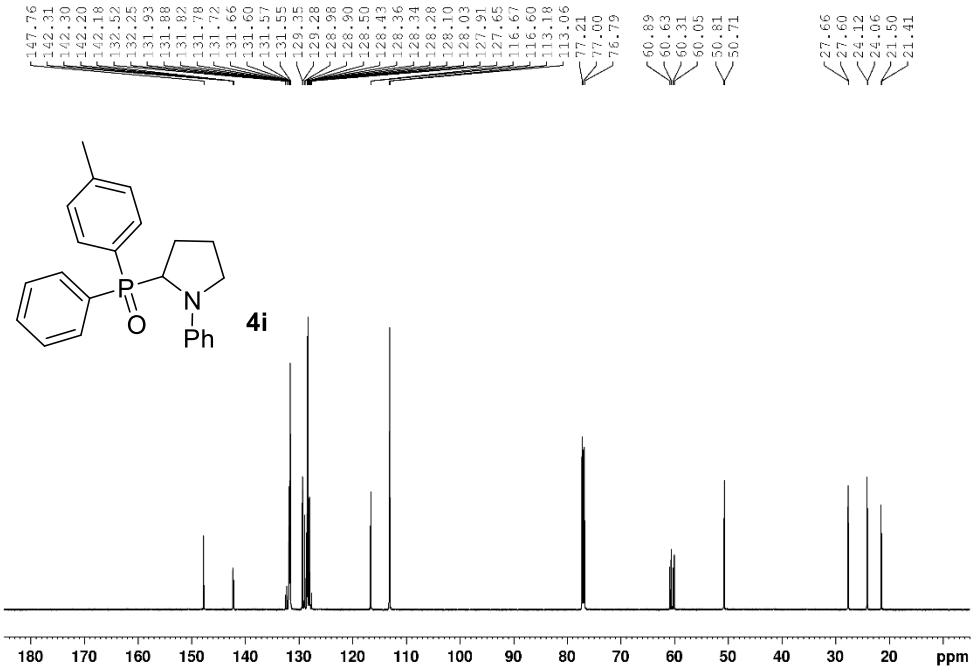
^{31}P NMR of **4i** ($CDCl_3$, 162 MHz)



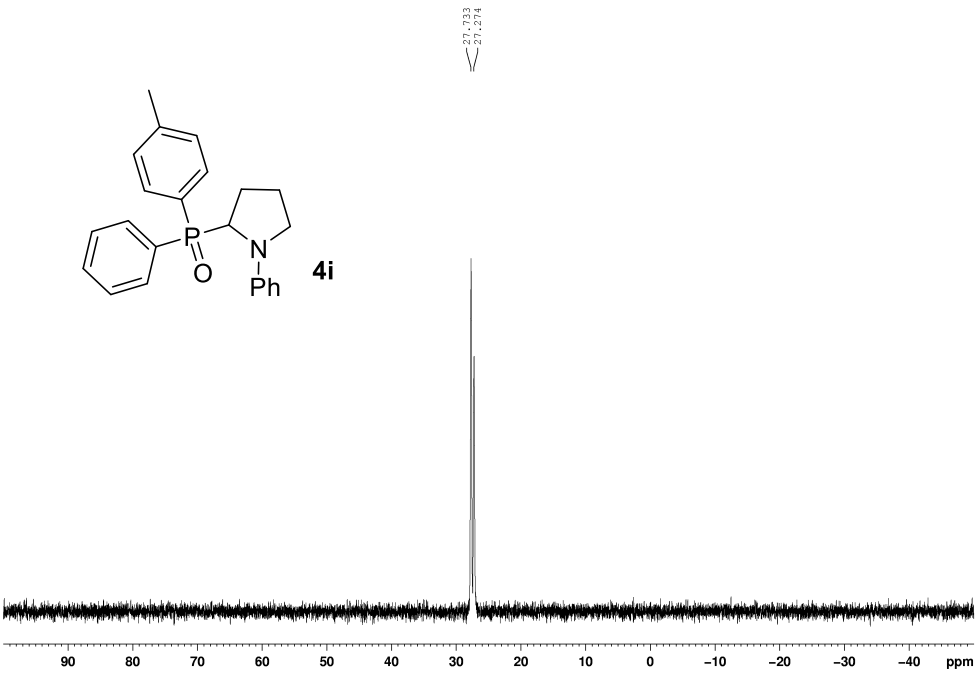
^{1}H NMR of **4j** ($CDCl_3$, 600M)



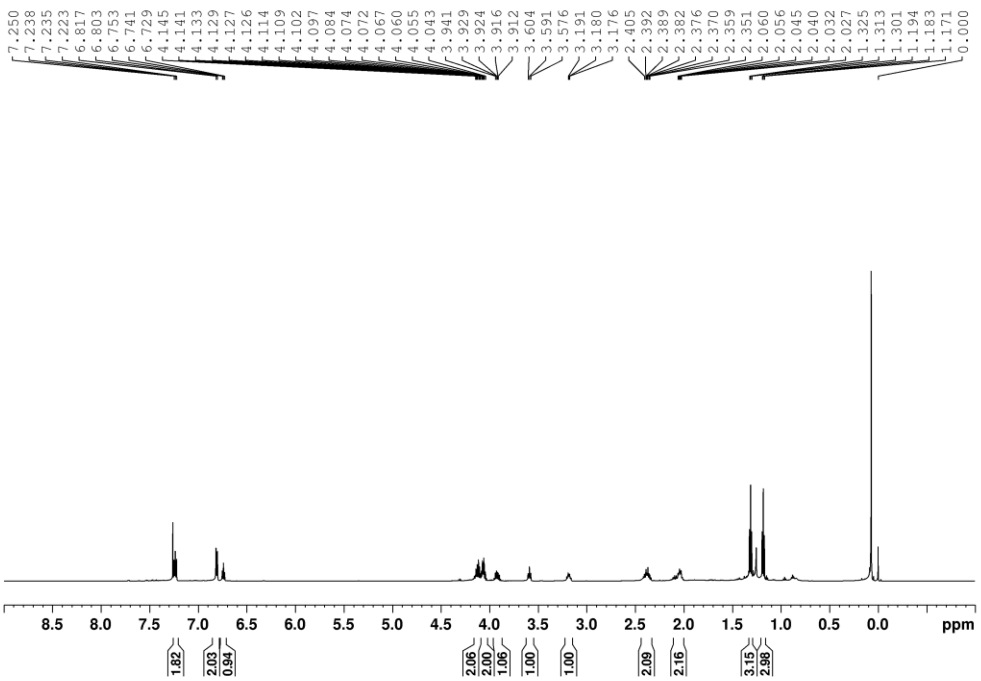
^{13}C NMR of **4j** ($CDCl_3$, 151 MHz)



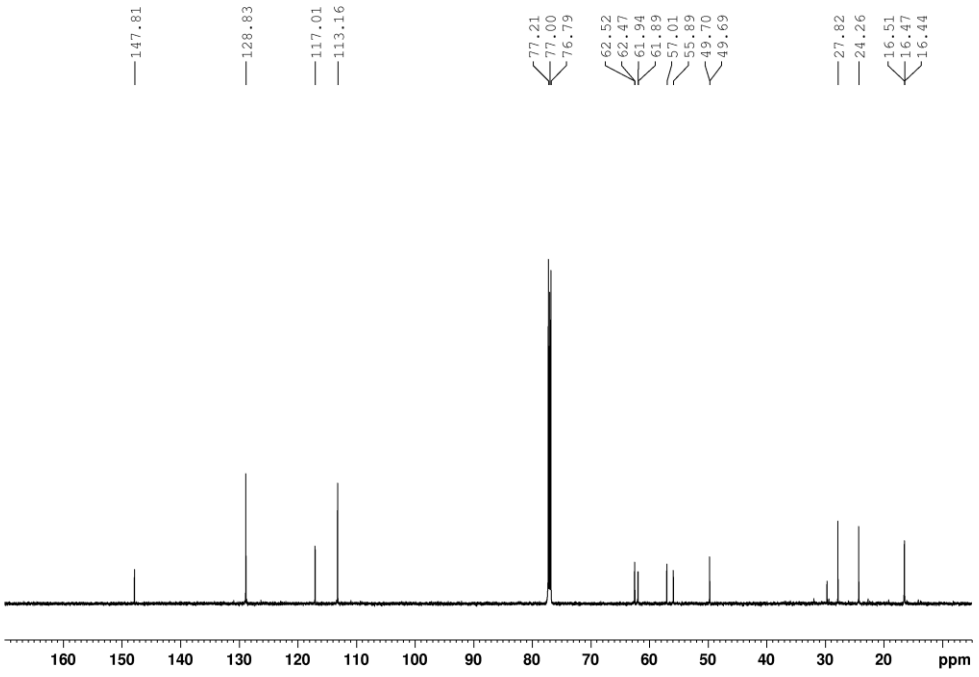
^{31}P NMR of **4j** ($CDCl_3$, 243 MHz)



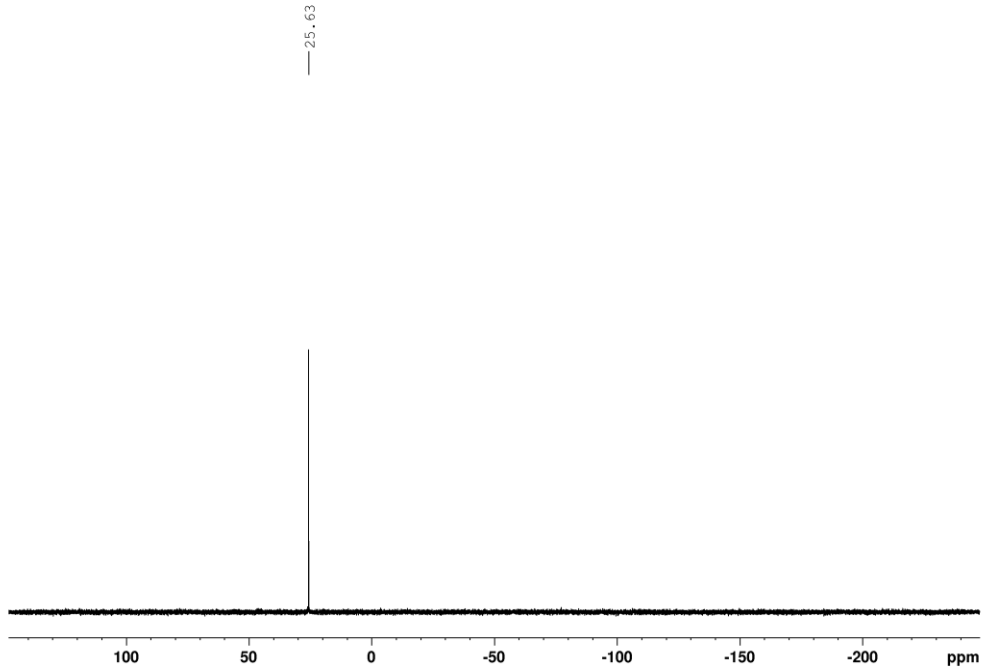
^{1}H NMR of **4k** ($CDCl_3$, 600 MHz)



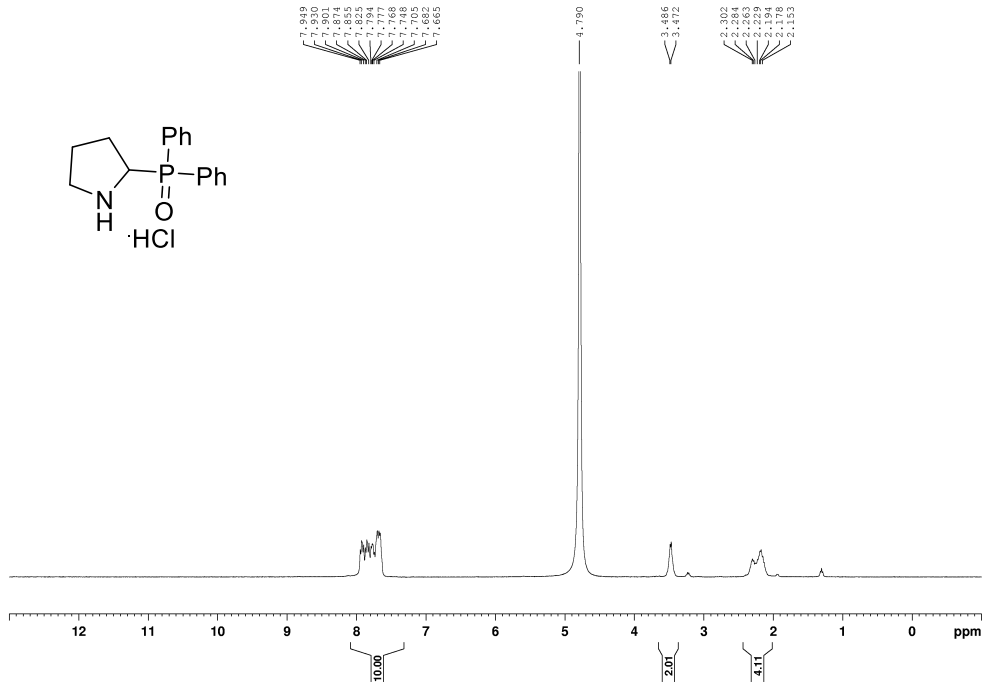
^{13}C NMR of **4j** ($CDCl_3$, 151 MHz)



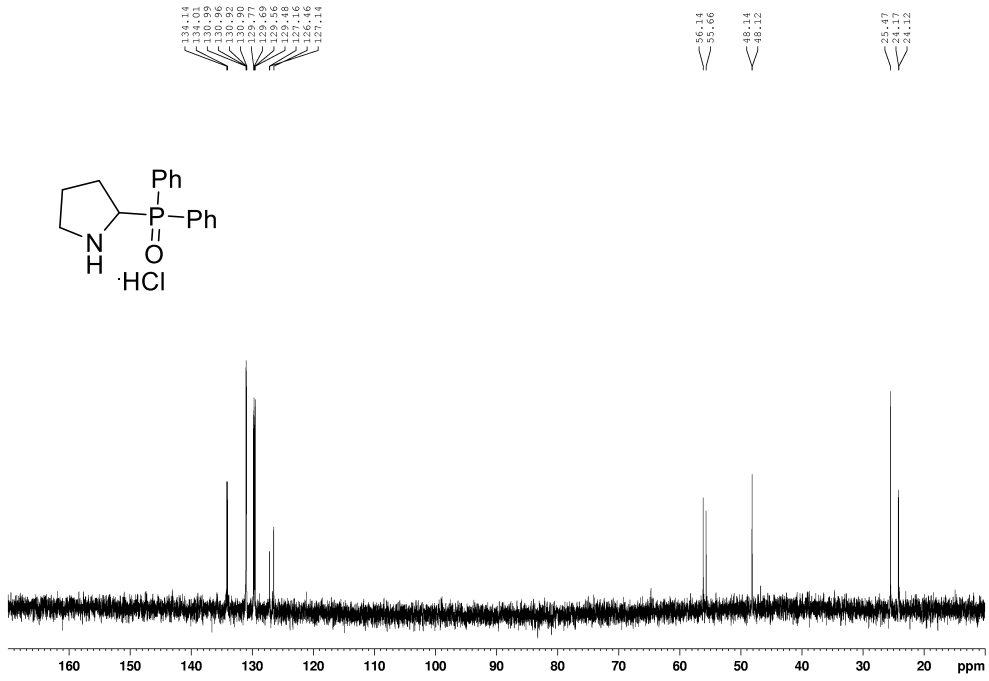
^{31}P NMR of **4j** ($CDCl_3$, 243 MHz)



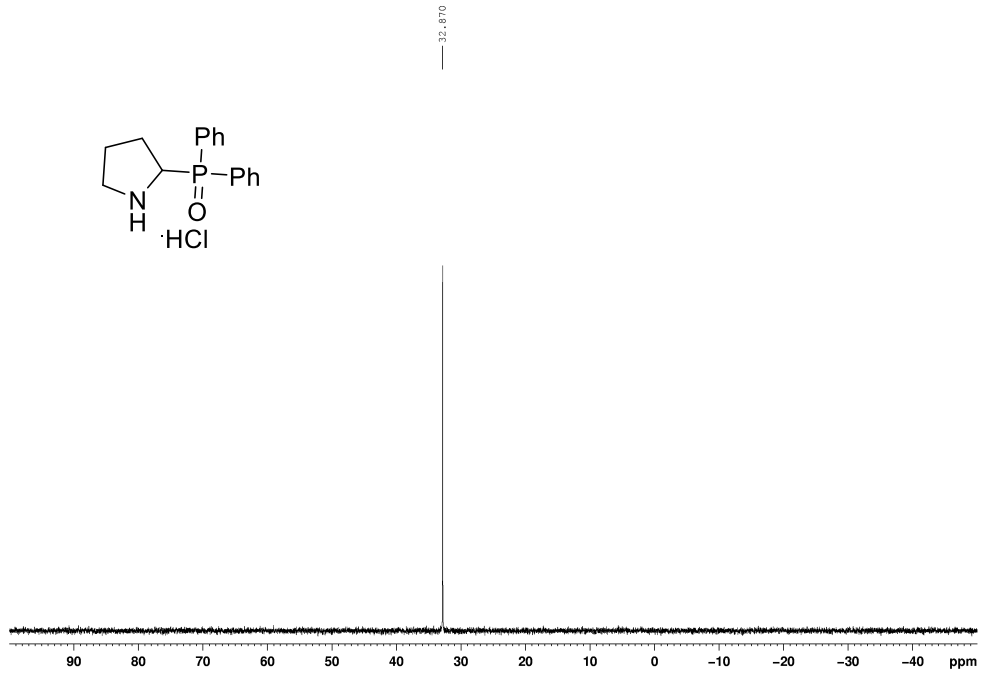
^{1}H NMR of **5** (D_2O, 400 MHz)



^{13}C NMR of **5** in (D_2O, 101 MHz)



^{31}P NMR of **5** (D_2O, 162 MHz)



11. References

[1] a) A. McNally, A.; Prier, C. K.; MacMillan, D. W. C. Discovery of an α-Amino C–H Arylation Reaction Using the Strategy of Accelerated Serendipity. *Science* **2011**, *334*, 1114-1117. b) Takasu, N.; Oisaki, K.; Kanai, M. Iron-Catalyzed Oxidative C(sp^3)–H Functionalization of Amines. *Org. Lett.* **2013**, *15*, 1918-1921.

[2] C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei, C. H. Senanayake, A Superior Method for the Reduction of Secondary Phosphine Oxides, *Org. Lett.* **2005**, *7*, 4277-4280.

[3] Jurberg, I. D.; Peng, B.; Wostefeld, E.; Wasserloos, M.; Maulide, N., Intramolecular redox-triggered C-H functionalization. *Angew. Chem. Int. Ed.* **2012**, *51*, 1950-3.

[4] Cismesiaa, M. A.; Yoon, T. P. Correction: Characterizing chain processes in visible light photoredox catalysis. *Chem. Sci.* **2015**, *6*, 6019–6019.

[5] Hatchard, C. G.; Parker, C. A. *Proc. Roy. Soc. (London)* **1956**, *A235*, 518-536.

[6] a) Kuhn, H. J.; Braslavsky, S. E.; Schmidt, R. *Pure Appl.* Chemical actinometry (IUPAC Technical Report) *Chem.* **2004**, *76*, 2105–2146. b) Monalti, M. *Chemical Actinometry. Handbook of Photochemistry*, 3rd Ed; Taylor & Francis Group, LLC. Boca Raton, FL, **2006**, 601–616.

[7] Y. Zhao, D. G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, *Theor. Chem. Acc.* **2008**, *120*, 215–241.

[8] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *J. Chem. Phys.* **2010**, *132*, 154104-15423.

[9] A. V. Marenich, C. J. Cramer, D. G. Truhlar, Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions, *J. Phys. Chem. B.* **2009**, *113*, 6378–6396.

[10] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, D. J. Fox, Gaussian 09 Revision A.1. Gaussian Inc. 2009.

[11] R. Dennington, T. Keith, J. Millam, Semichem Inc., Shawnee Mission KS, GaussView, Version 5, 2009

[12] T. Lu, F. Chen, Multiwfn: A multifunctional wavefunction analyzer, *J. Comput.Chem.* **2012**, *33*, 580–592.

[13] W. Humphrey, A. Dalke and K. Schulten, VMD: visual molecular dynamics, *J. Mol. Graphics*, **1996**, *14*, 33–38.