

Pd-catalyzed Direct Diarylation of Sodium Hypophosphite Enables the Synthesis of Diarylphosphinates

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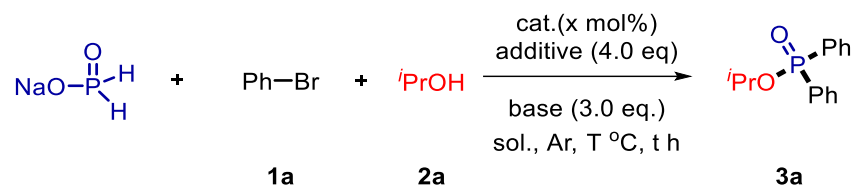
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1. Screening of Optimal Reaction Conditions



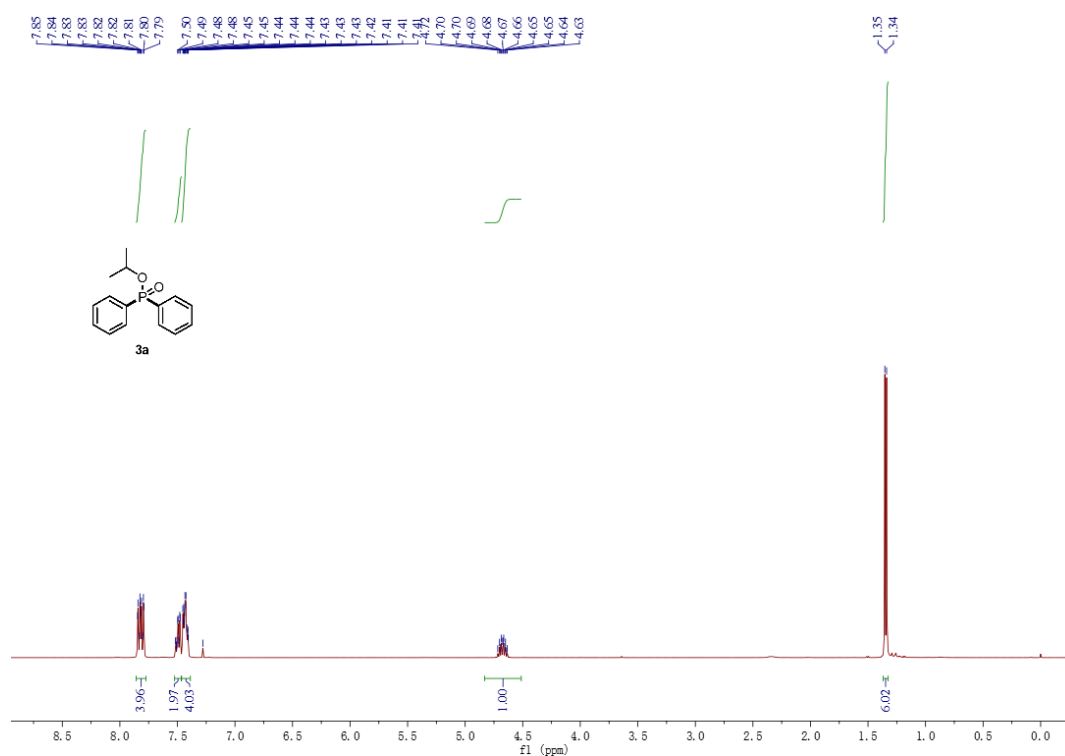
entry	additive	base	T/ °C	t/h	cat.	sol.	yield/% ^b
1	BzCl	DABCO	100	20	Pd(dppf)Cl ₂ /5 mol%	PhMe	n.r
2	CyC(O)Cl	DABCO	100	20	Pd(dppf)Cl ₂ /5 mol%	PhMe	19
3	TsCl	DABCO	100	20	Pd(dppf)Cl ₂ /5 mol%	PhMe	n.r
4	AcCl	DABCO	100	20	Pd(dppf)Cl ₂ /5 mol%	PhMe	38%
5	PivCl	DABCO	100	20	Pd(dppf)Cl ₂ /5 mol%	PhMe	48%
6	PivCl	DABCO	60	20	Pd(dppf)Cl ₂ /5 mol%	PhMe	n.r
7	PivCl	DABCO	80	20	Pd(dppf)Cl ₂ /5 mol%	PhMe	23
8	PivCl	DABCO	120	20	Pd(dppf)Cl ₂ /5 mol%	PhMe	48
9	PivCl	DABCO	100	12	Pd(dppf)Cl ₂ /5 mol%	PhMe	23
10	PivCl	DABCO	100	24	Pd(dppf)Cl ₂ /5 mol%	PhMe	58
11	PivCl	DABCO	100	28	Pd(dppf)Cl ₂ /5 mol%	PhMe	68
12	PivCl	DABCO	100	36	Pd(dppf)Cl ₂ /5 mol%	PhMe	61
13	PivCl	DABCO	100	28	Pd(dppf)Cl ₂ /1 mol%	PhMe	trace
14	PivCl	DABCO	100	28	Pd(dppf)Cl ₂ /2.5 mol%	PhMe	84
15	PivCl	DABCO	100	28	Pd(dppf)Cl ₂ /10 mol%	PhMe	45
16	PivCl	NaHCO ₃	100	28	Pd(dppf)Cl ₂ /2.5 mol%	PhMe	36
17	PivCl	KHCO ₃	100	28	Pd(dppf)Cl ₂ /2.5 mol%	PhMe	47
18	PivCl	NaOAc	100	28	Pd(dppf)Cl ₂ /2.5 mol%	PhMe	trace
19	PivCl	KOAc	100	28	Pd(dppf)Cl ₂ /2.5 mol%	PhMe	44
20	PivCl	DBU	100	28	Pd(dppf)Cl ₂ /2.5 mol%	PhMe	67
21	PivCl	Et ₃ N	100	28	Pd(dppf)Cl ₂ /2.5 mol%	PhMe	53
22	PivCl	DIPEA	100	28	Pd(dppf)Cl ₂ /2.5 mol%	PhMe	60
23 ^c	PivCl	DABCO	100	28	Pd(dppf)Cl ₂ /2.5 mol%	PhMe	74

24 ^d	PivCl	DABCO	100	28	Pd(dppf)Cl ₂ /2.5 mol%	PhMe	80
25 ^e	PivCl	DABCO	100	28	Pd(dppf)Cl ₂ /2.5 mol%	PhMe	71
26	PivCl	DABCO	100	28	Pd(dppe)Cl ₂ /2.5 mol%	PhMe	64
27	PivCl	DABCO	100	28	Pd(PPh ₃) ₂ Cl ₂ /2.5 mol%	PhMe	16
28	PivCl	DABCO	100	28	Ni(dppf)Cl ₂ /2.5 mol%	PhMe	n.r
29	PivCl	DABCO	100	28	Co(dppf)Cl ₂ /2.5 mol%	PhMe	n.r
30	PivCl	DABCO	100	28	Pd(dppf)Cl ₂ /2.5 mol%	xylene	74
31	PivCl	DABCO	100	28	Pd(dppf)Cl ₂ /2.5 mol%	dioxane	trace
32	PivCl	DABCO	100	28	Pd(dppf)Cl ₂ /2.5 mol%	THF	58
33	PivCl	DABCO	100	28	Pd(dppf)Cl ₂ /2.5 mol%	EtOAc	68
34	PivCl	DABCO	100	28	Pd(dppf)Cl ₂ /2.5 mol%	DCE	trace

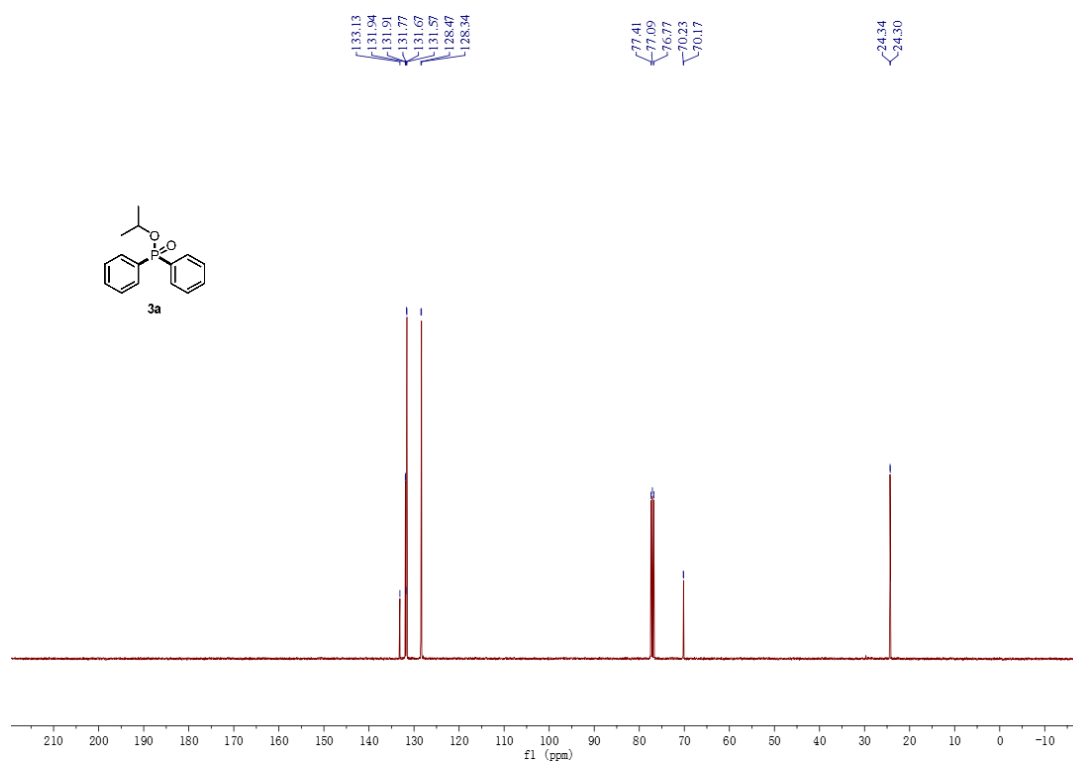
Table S1(a) Reaction conditions: bromobenzene (0.2 mmol), NaH₂PO₂ (0.4 mmol), *i*PrOH (1.6 mmol), PivCl (0.8 mmol), anhydrous solvent (2.0 mL); (b) Isolated yield; (c) 1.0 mL solvent; (d) 3.0 mL solvent; (e) 4.0 mL solvent.

2. Scanned ^1H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR Spectra of All products

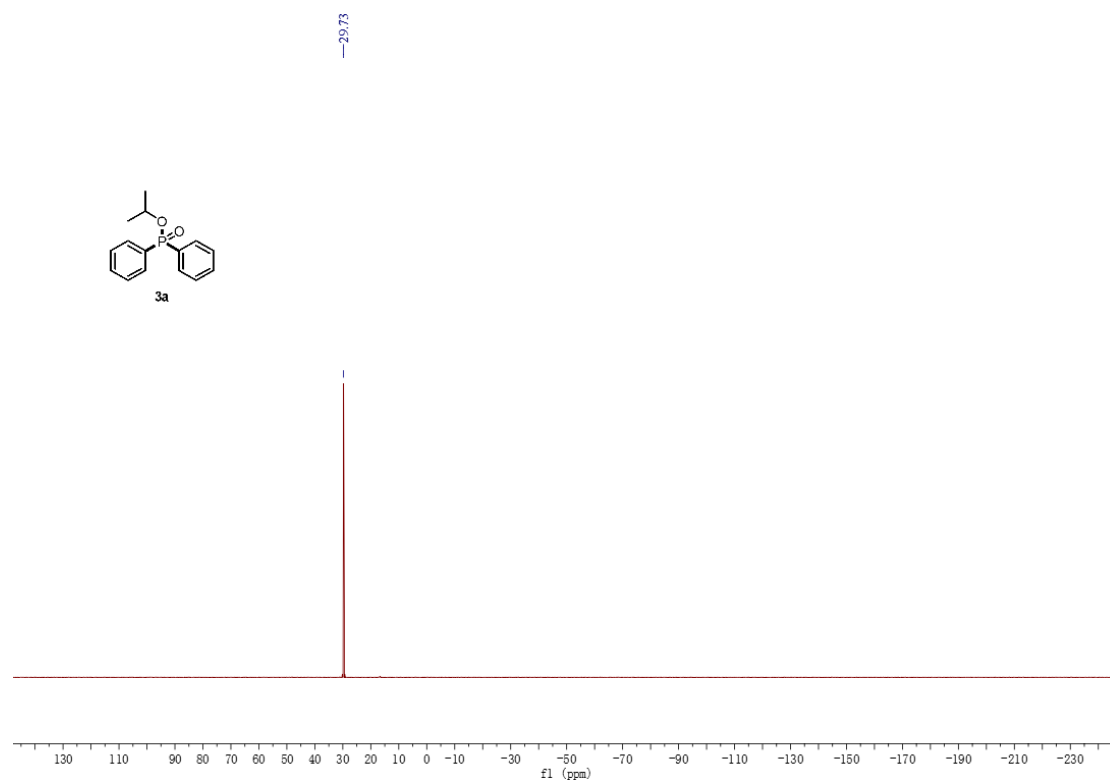
^1H NMR (400 MHz, CDCl_3) spectrum for 3a



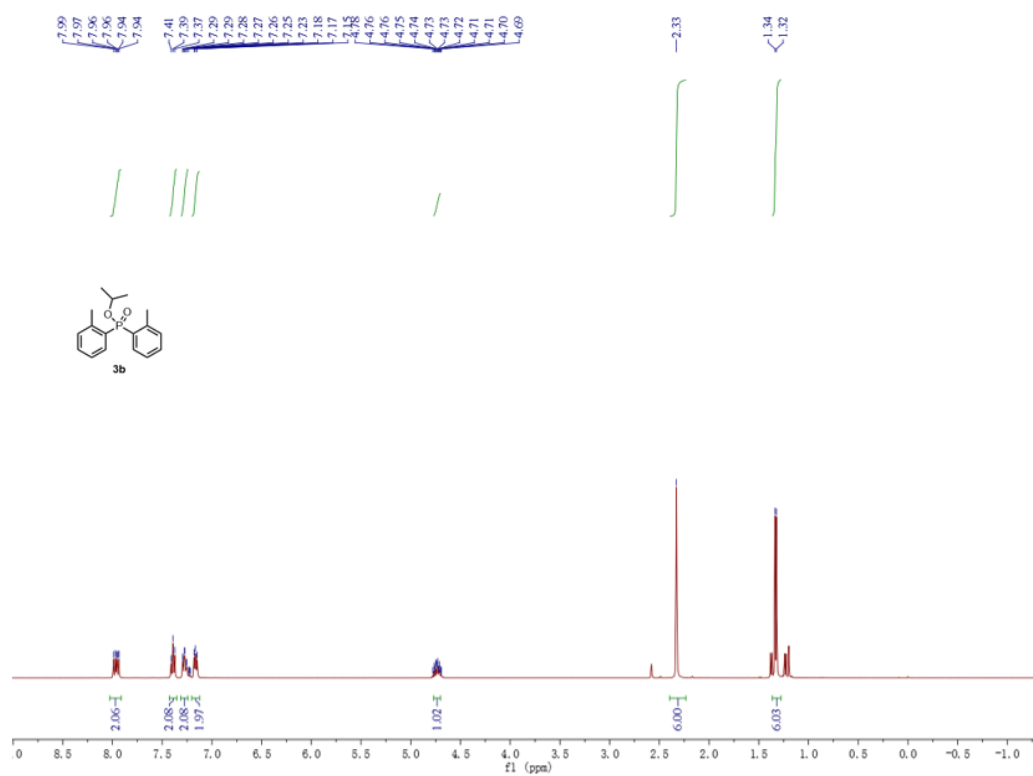
^{13}C NMR (101 MHz, CDCl_3) spectrum for 3a



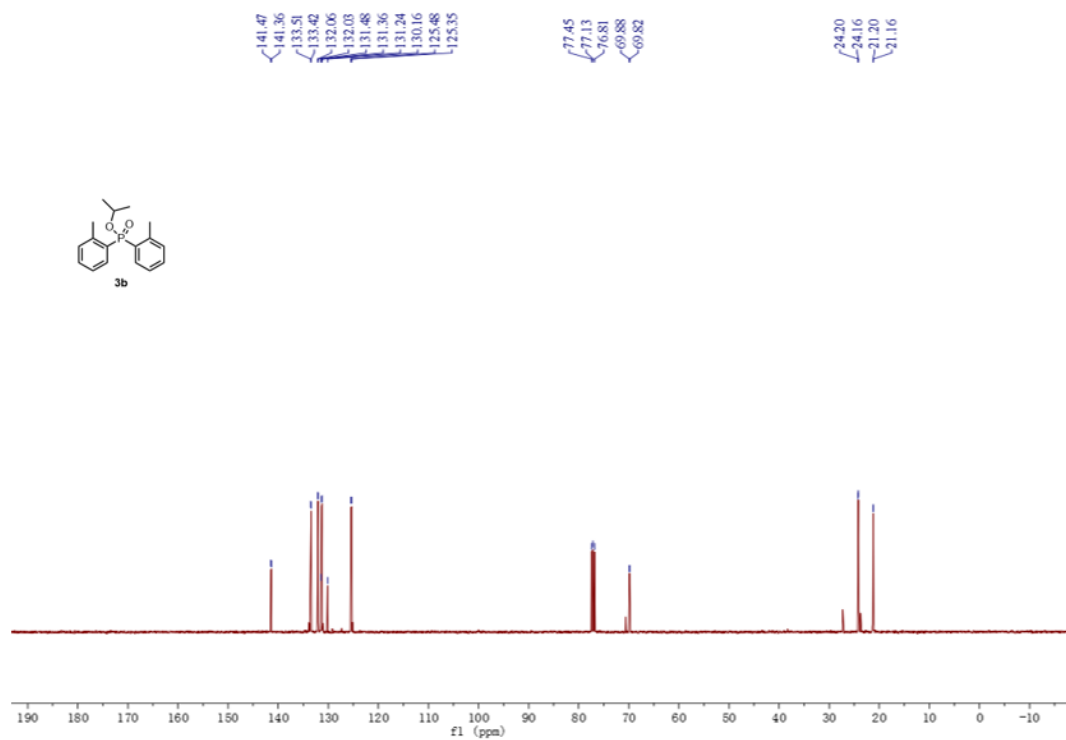
^{31}P NMR (121 MHz, CDCl_3) spectrum for 3a



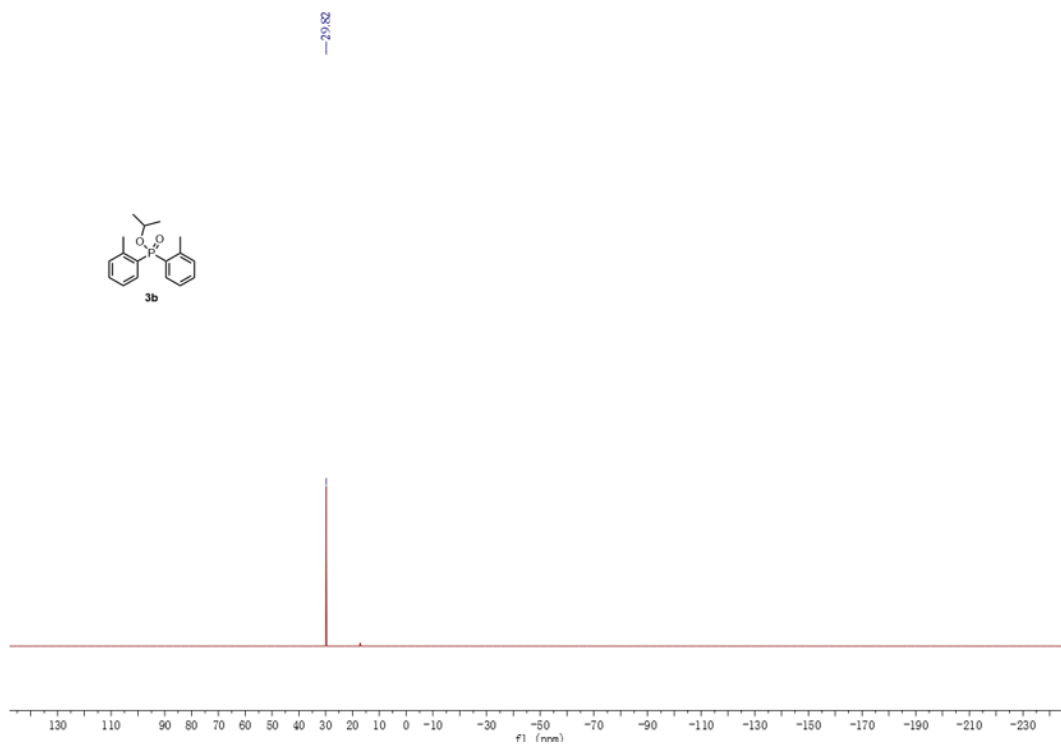
^1H NMR (400 MHz, CDCl_3) spectrum for 3b



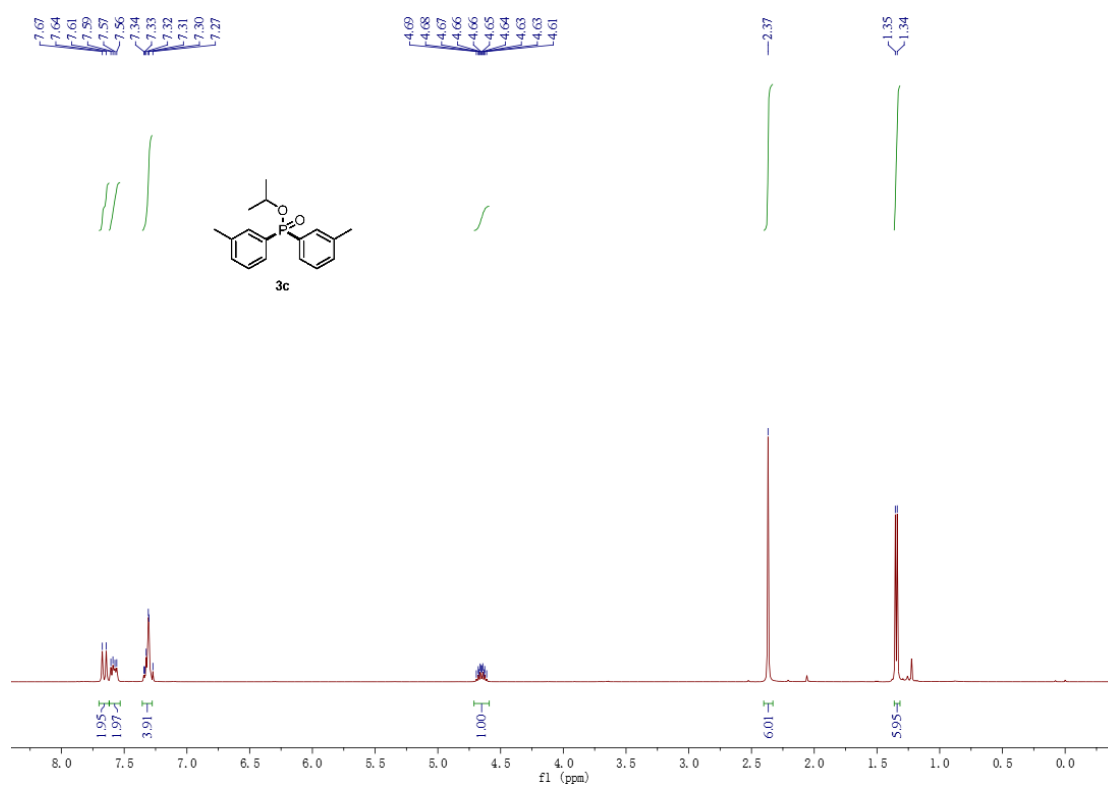
^{13}C NMR (101 MHz, CDCl_3) spectrum for 3b



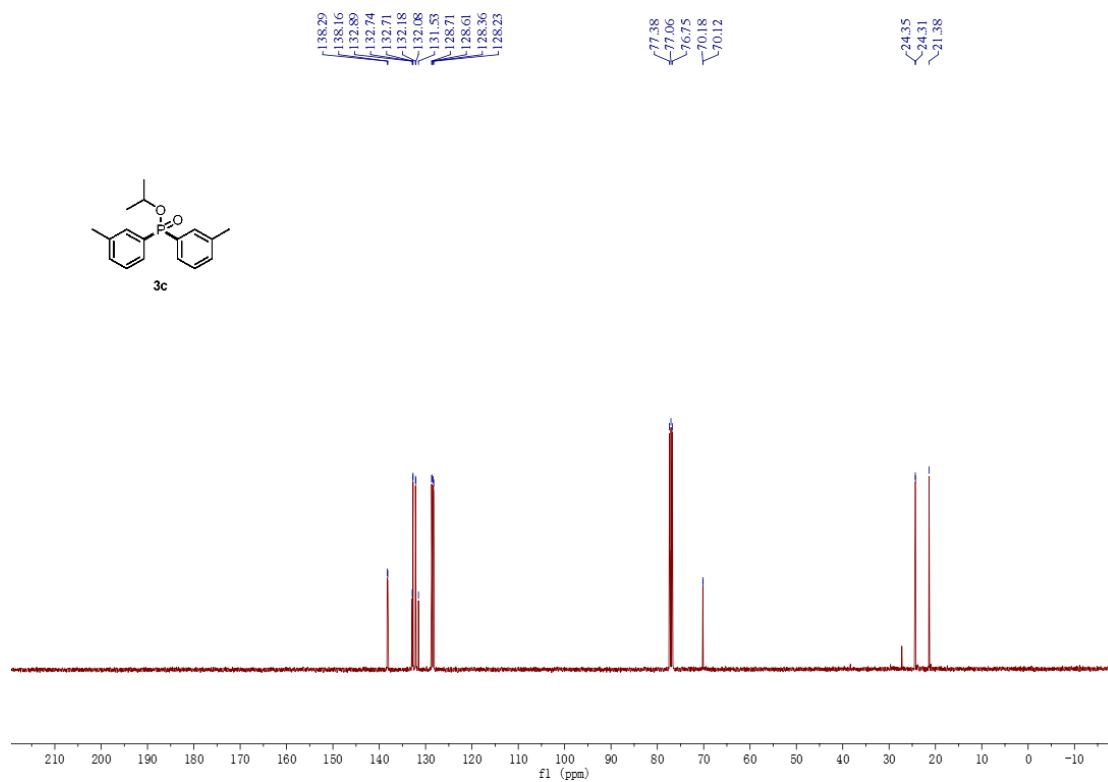
^{31}P NMR (121 MHz, CDCl_3) spectrum for 3b



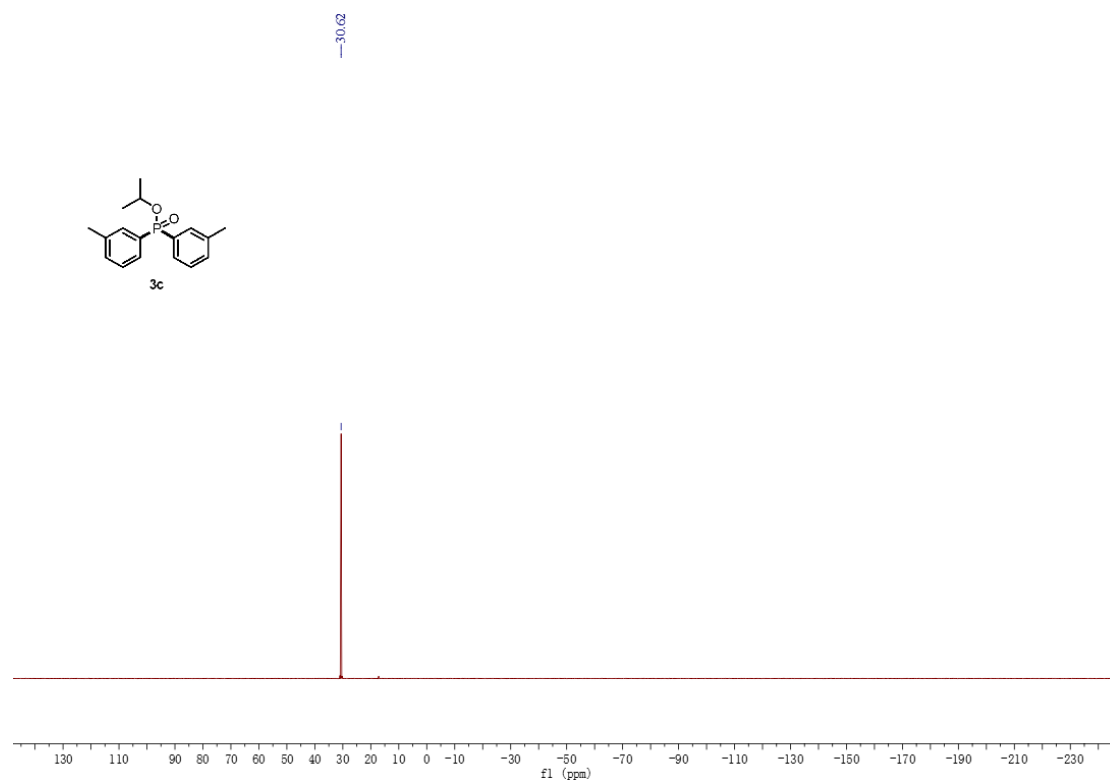
^1H NMR (400 MHz, CDCl_3) spectrum for 3c



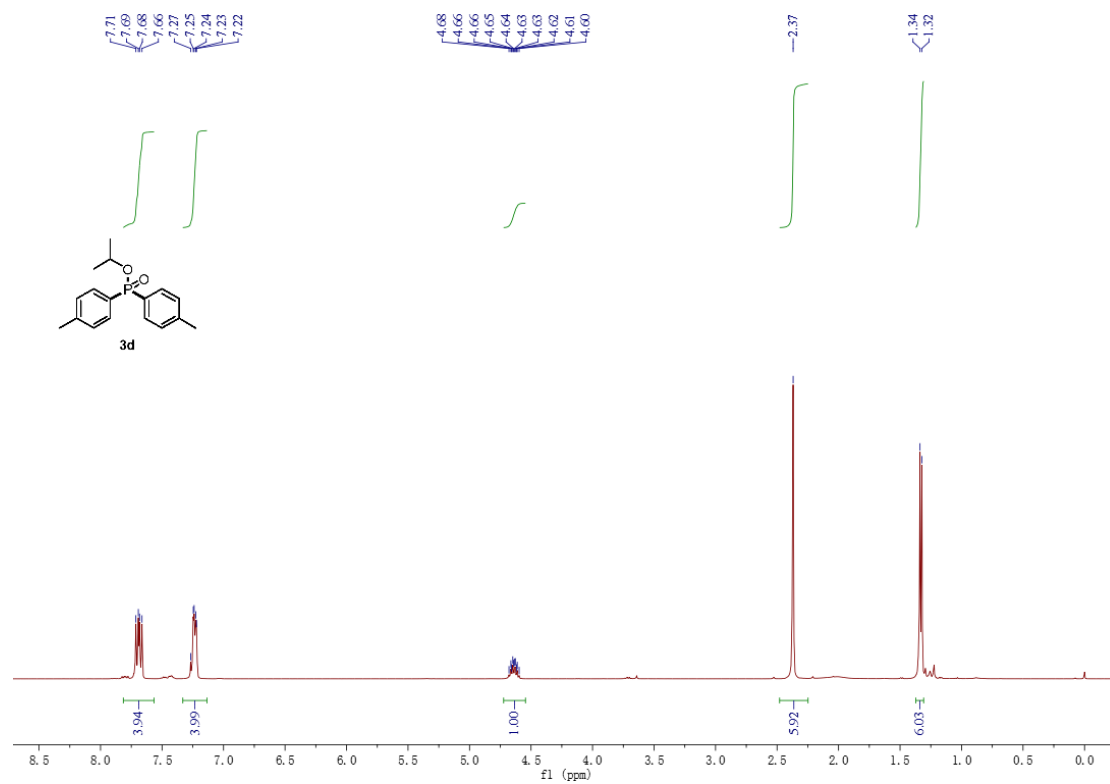
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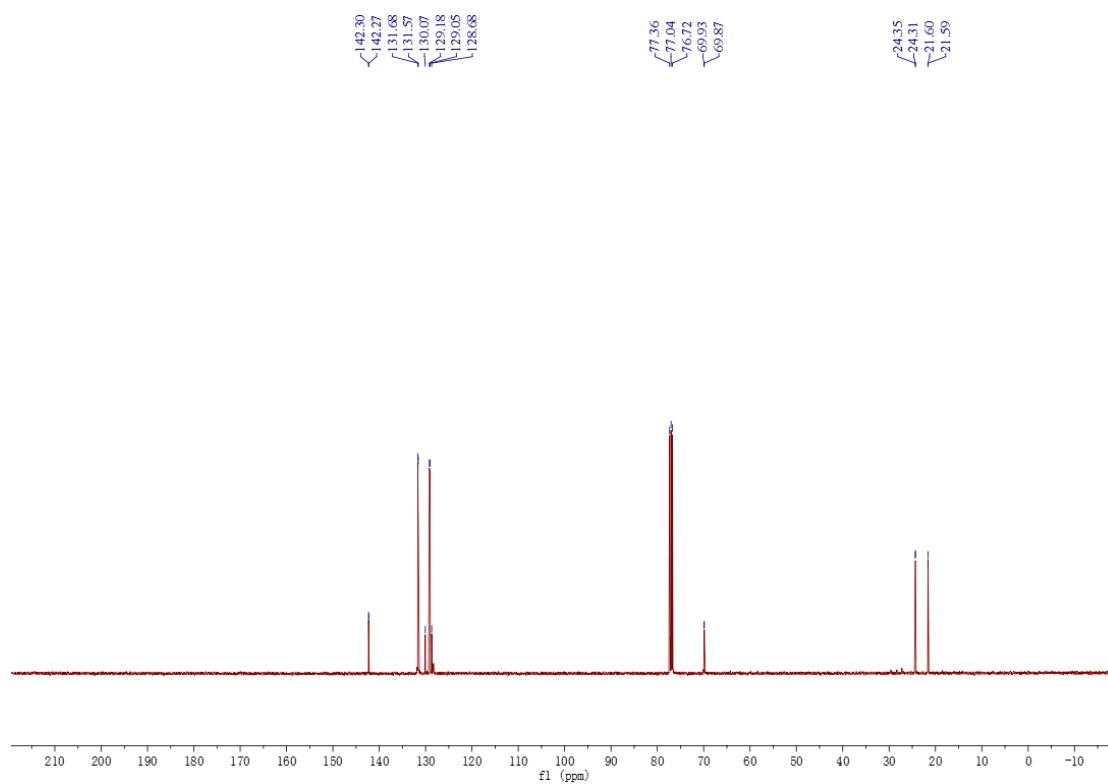
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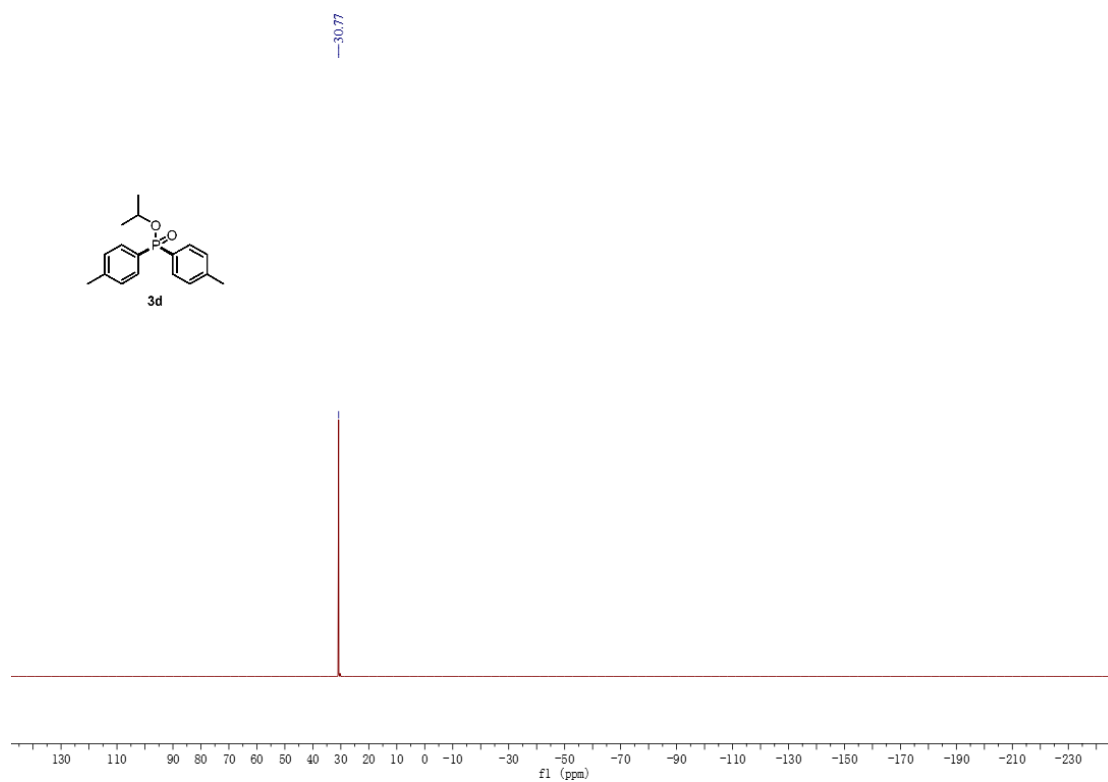
^1H NMR (400 MHz, CDCl_3) spectrum for 3d



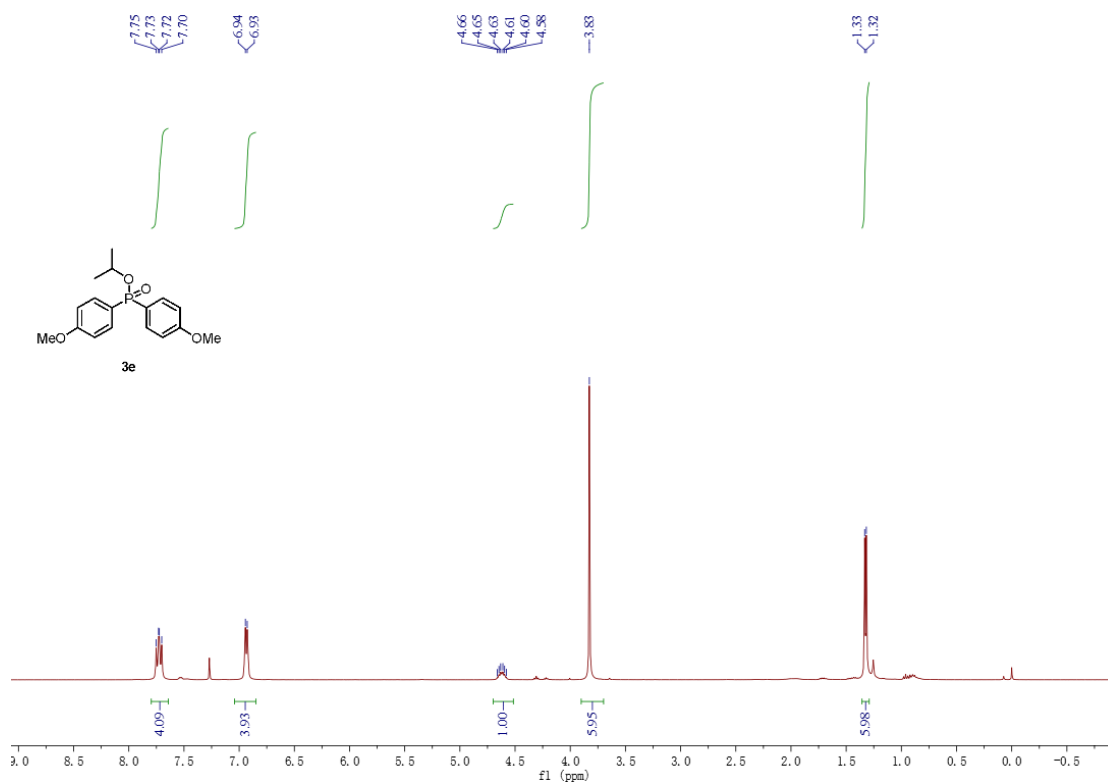
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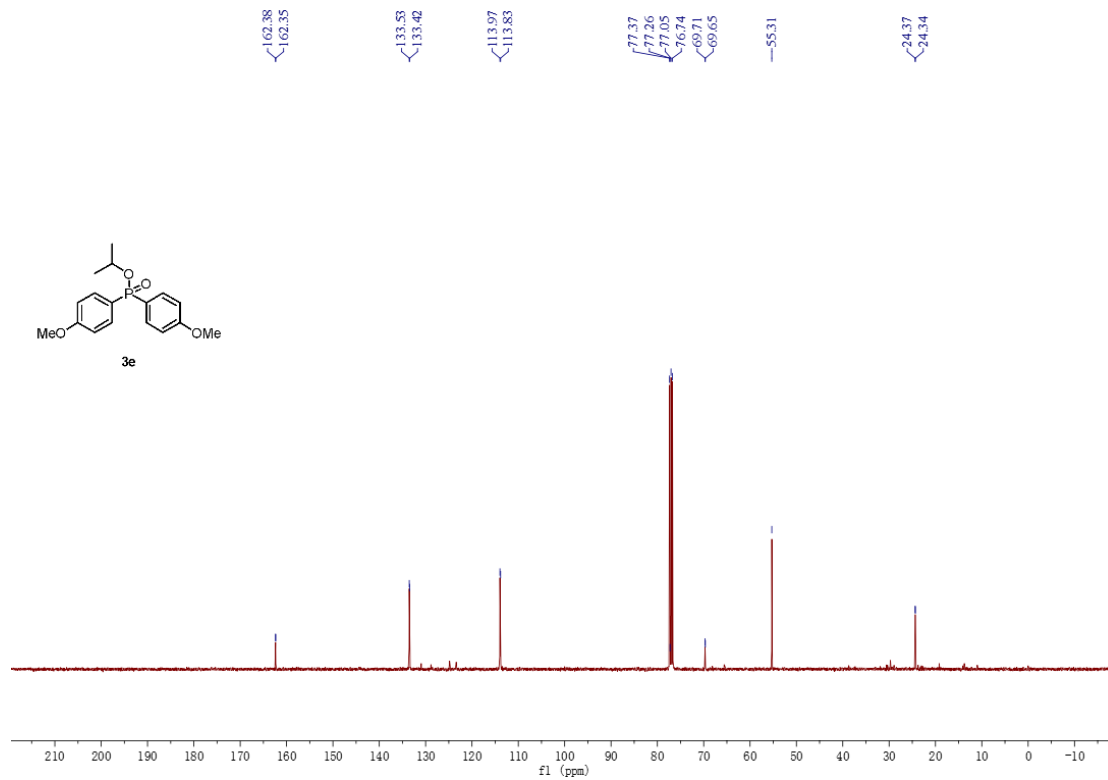
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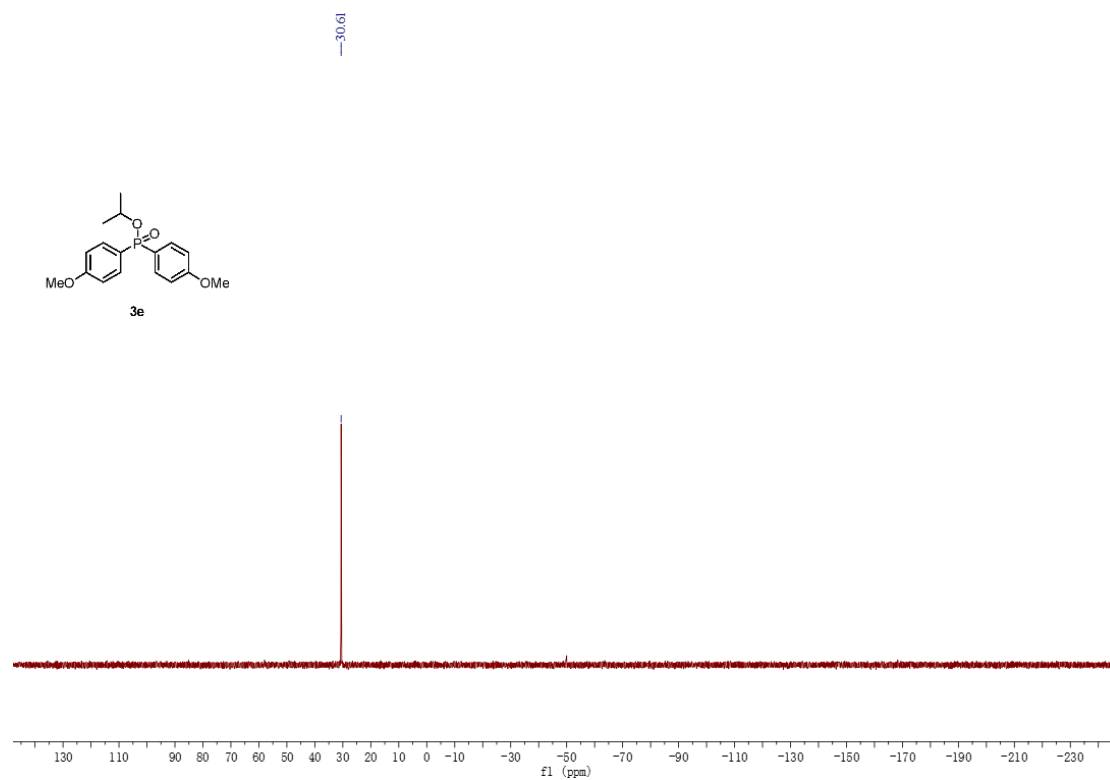
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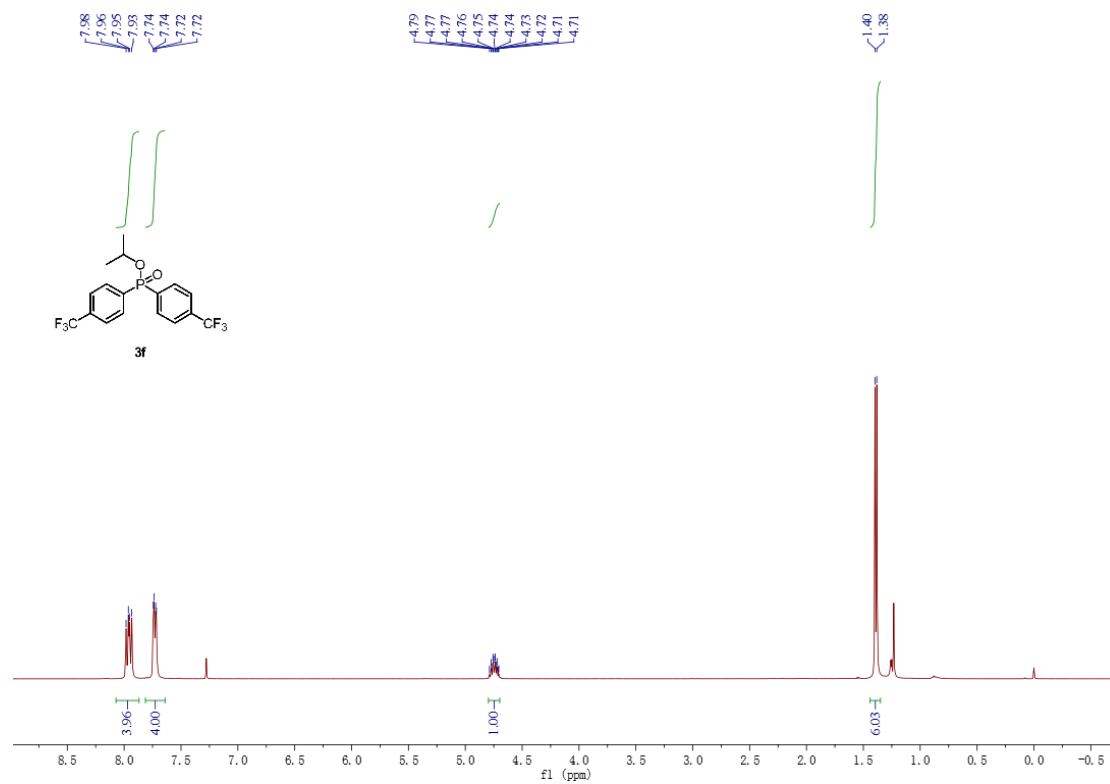
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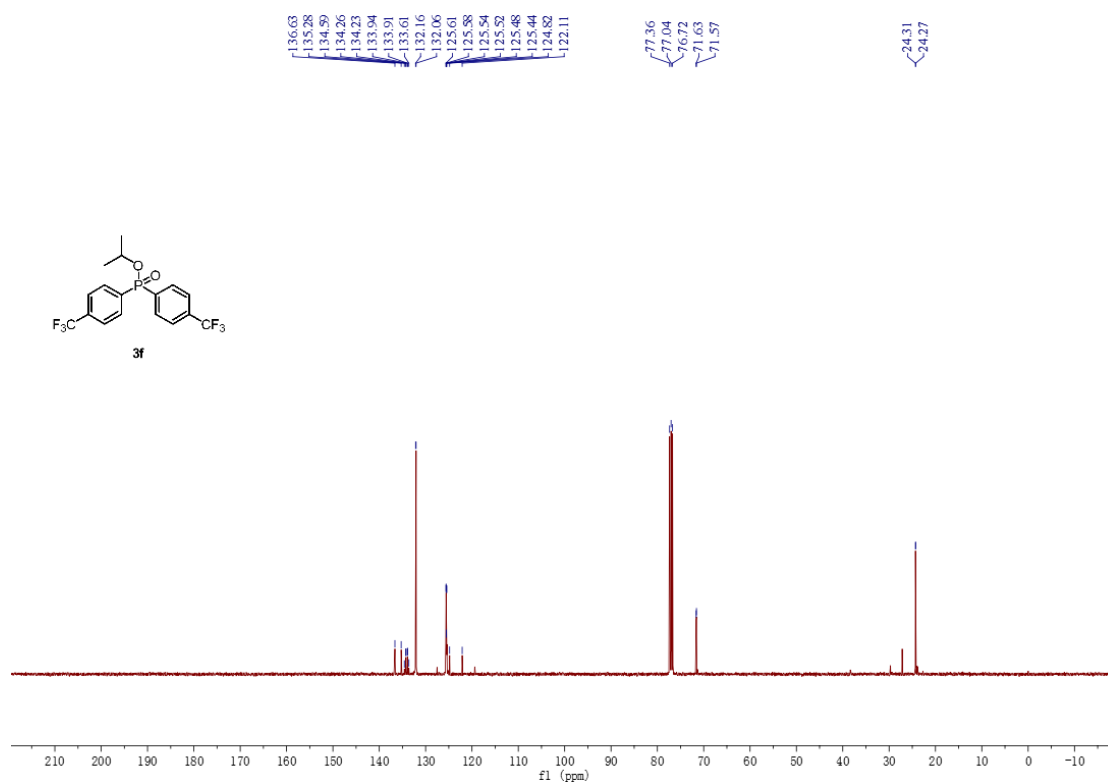
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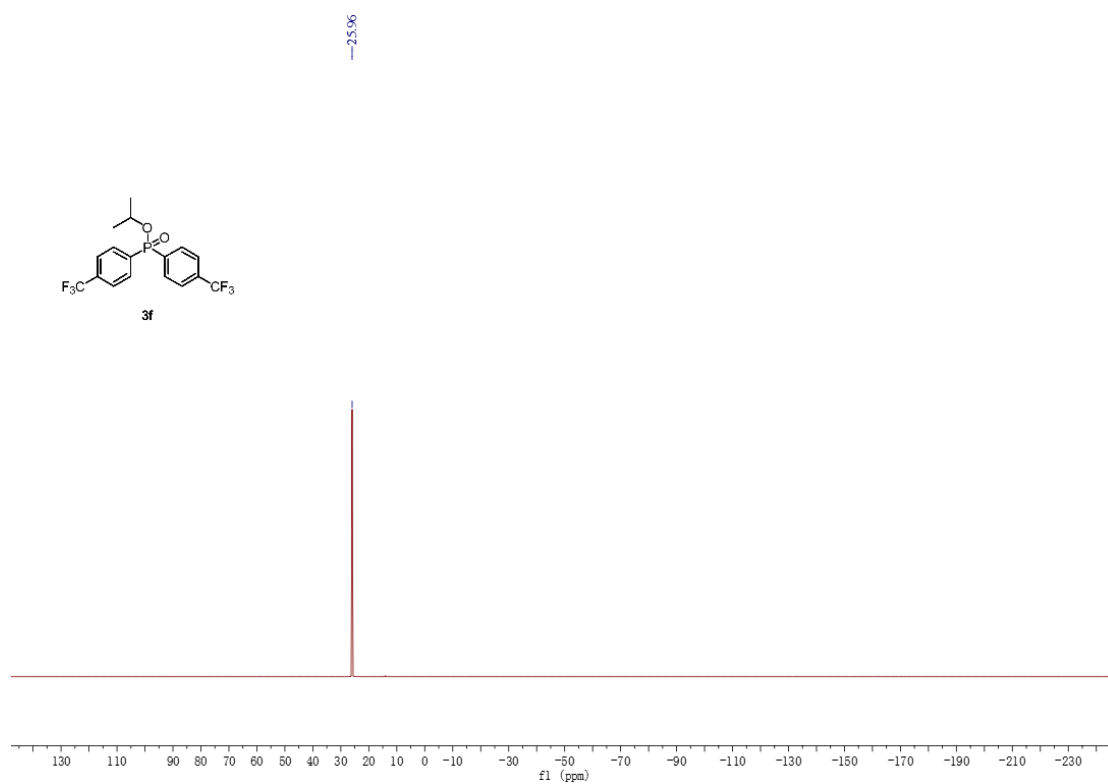
^1H NMR (400 MHz, CDCl_3) spectrum for 3f



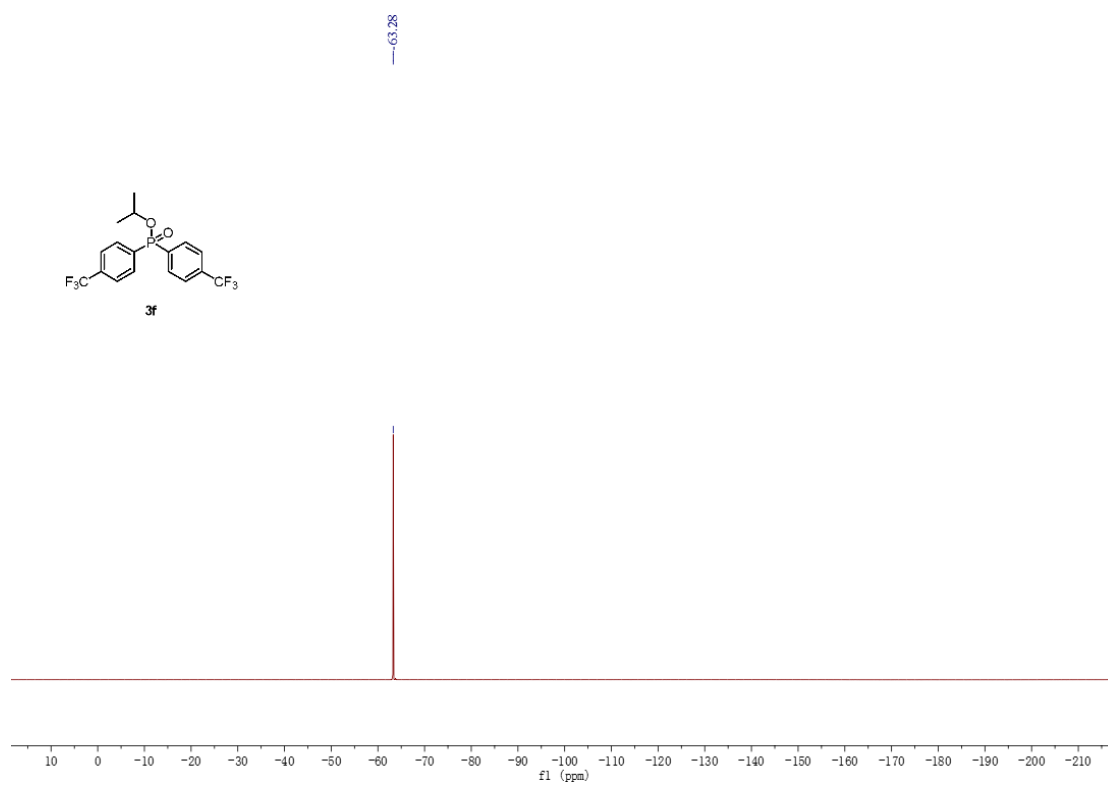
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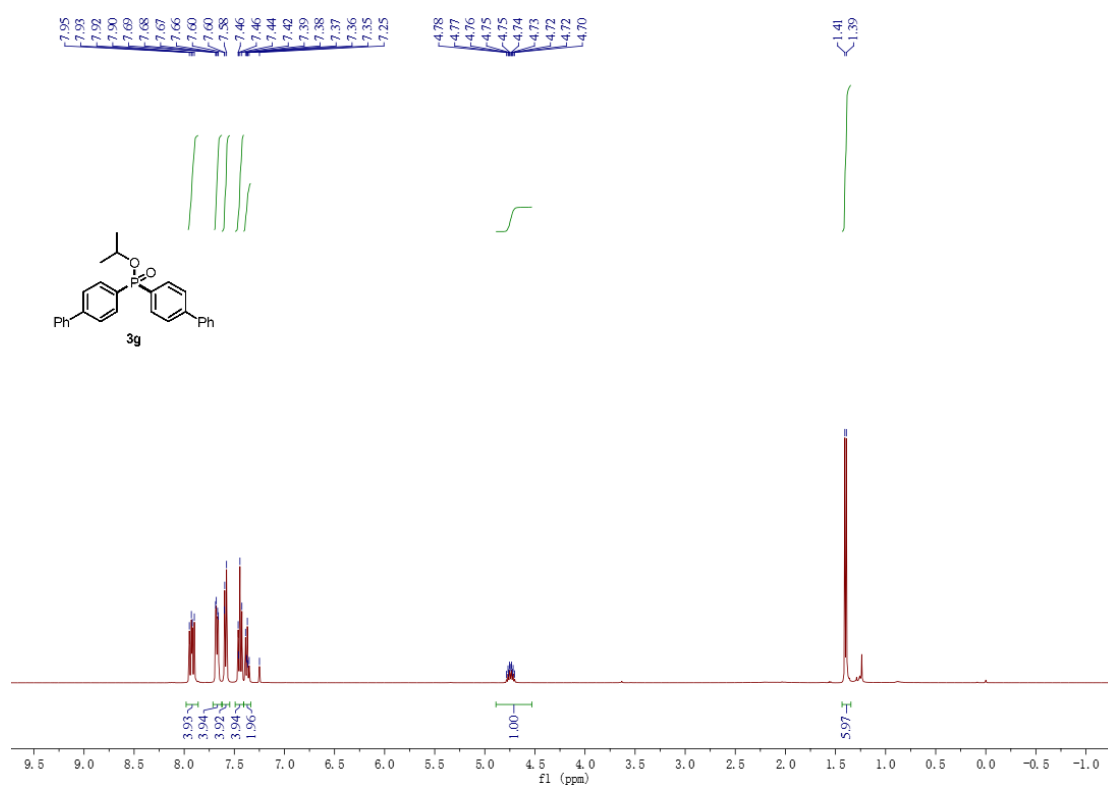
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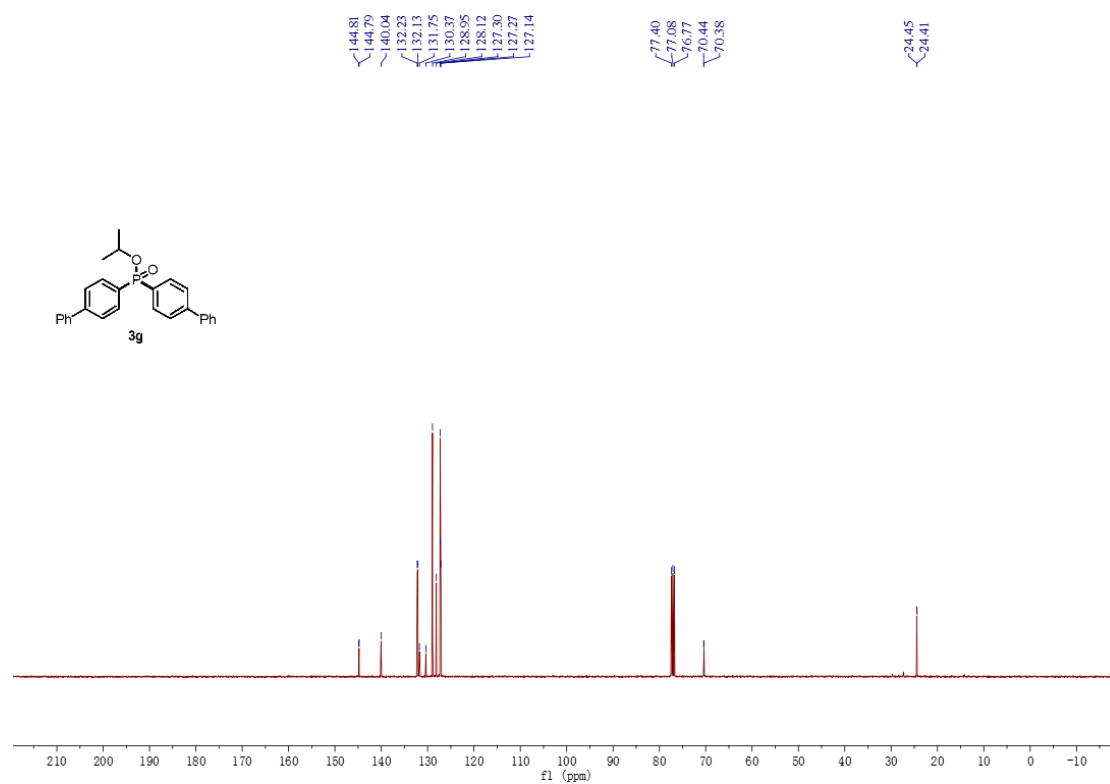
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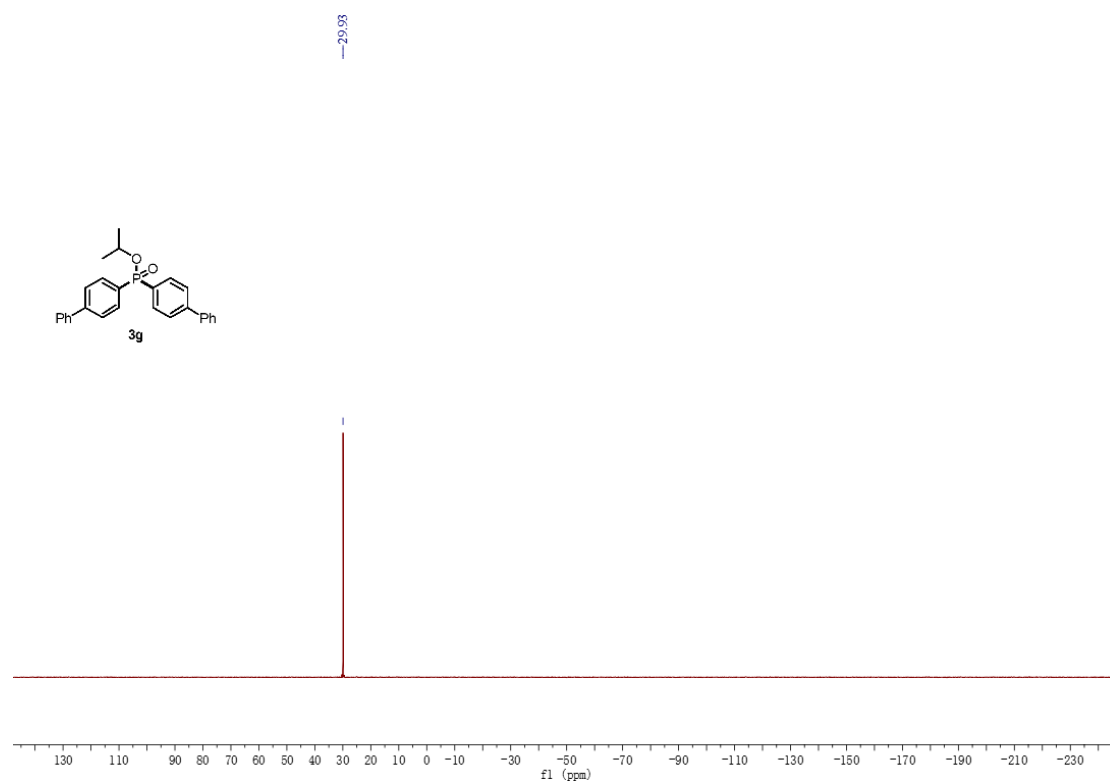
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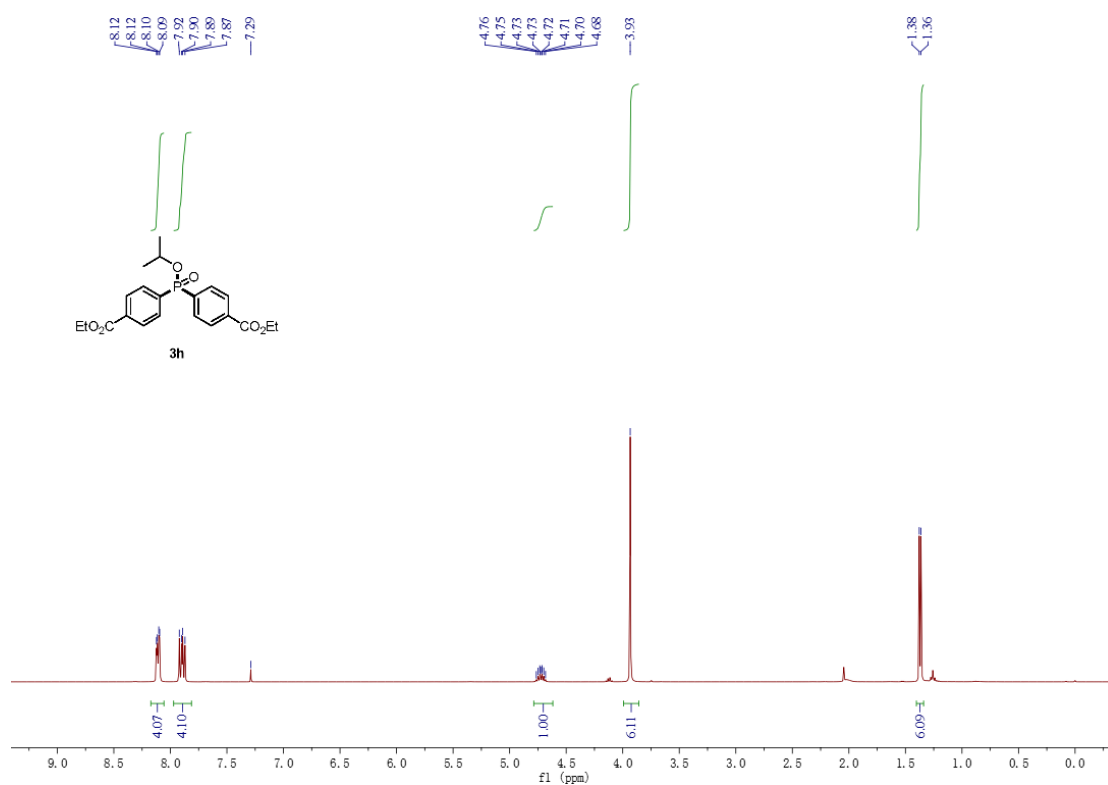
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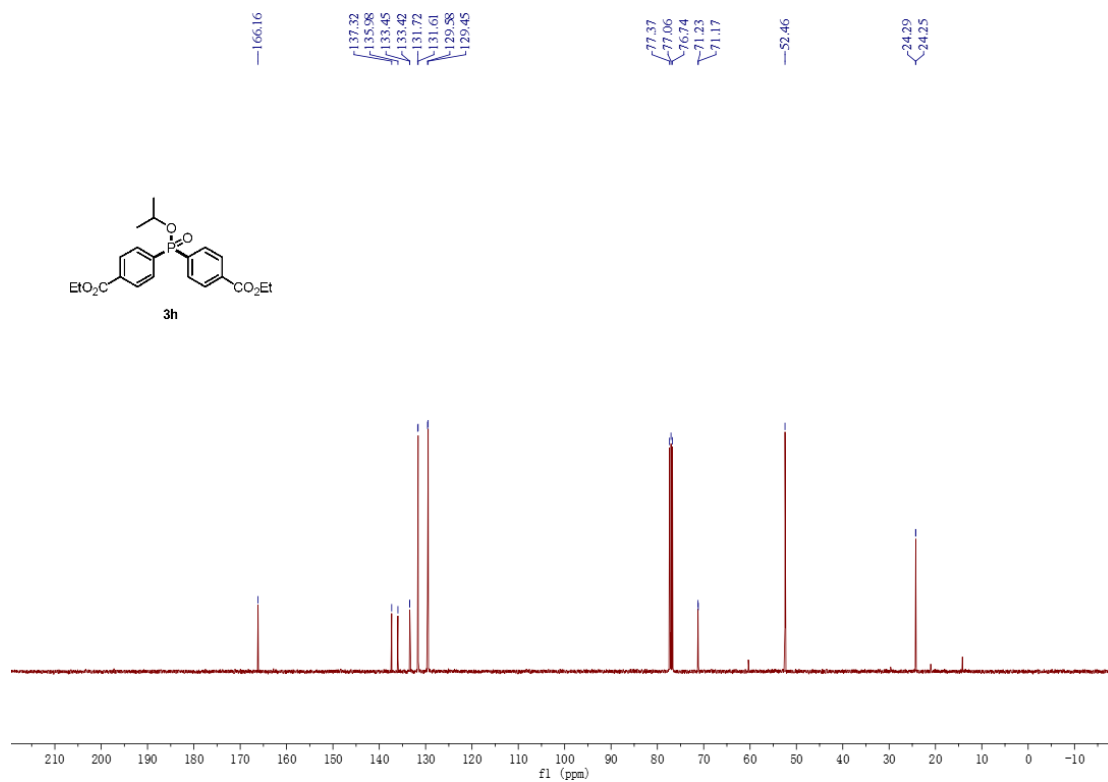
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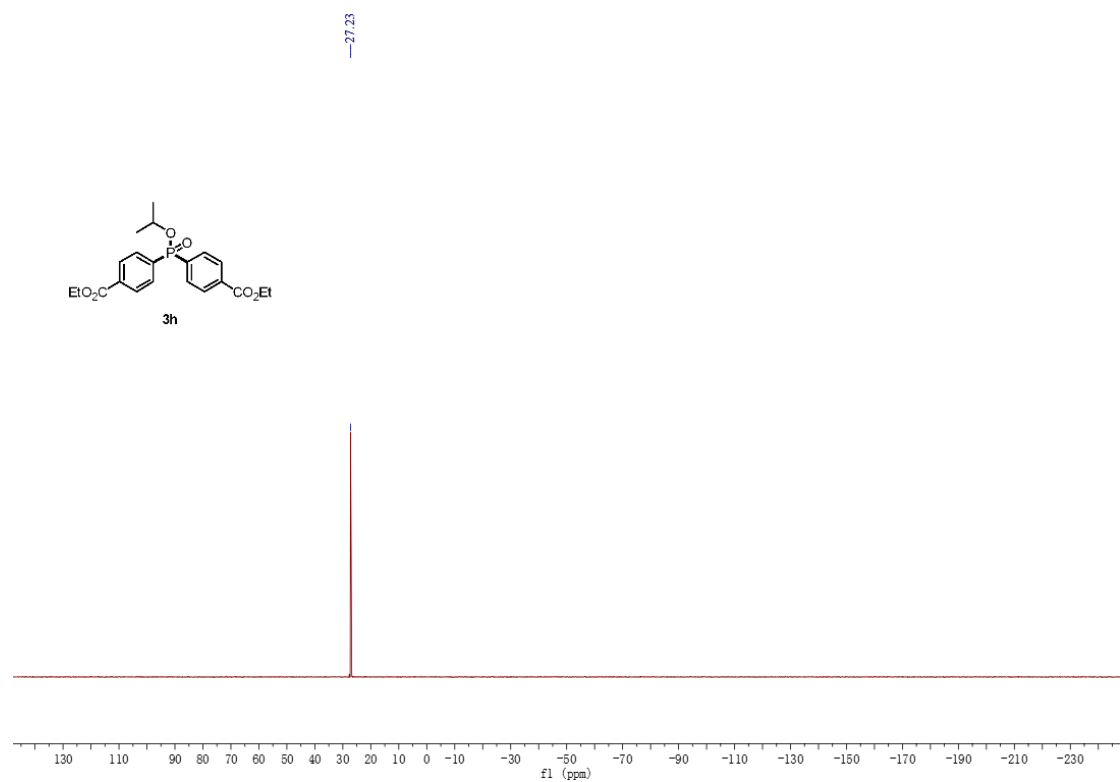
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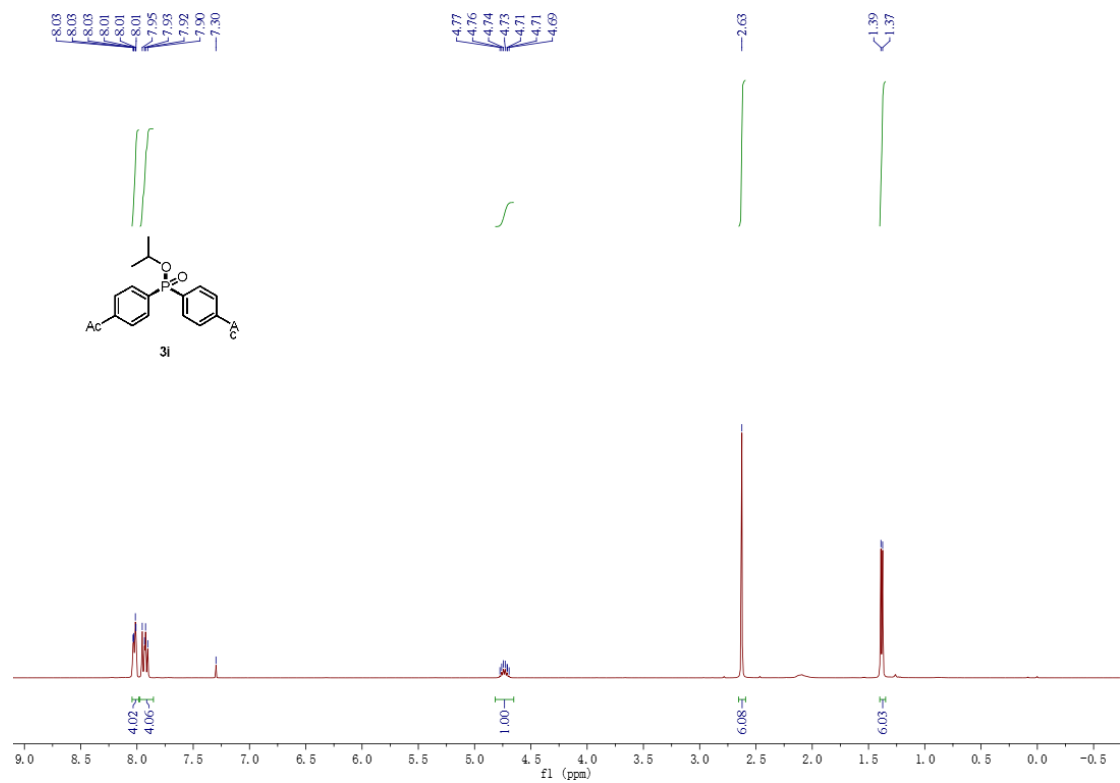
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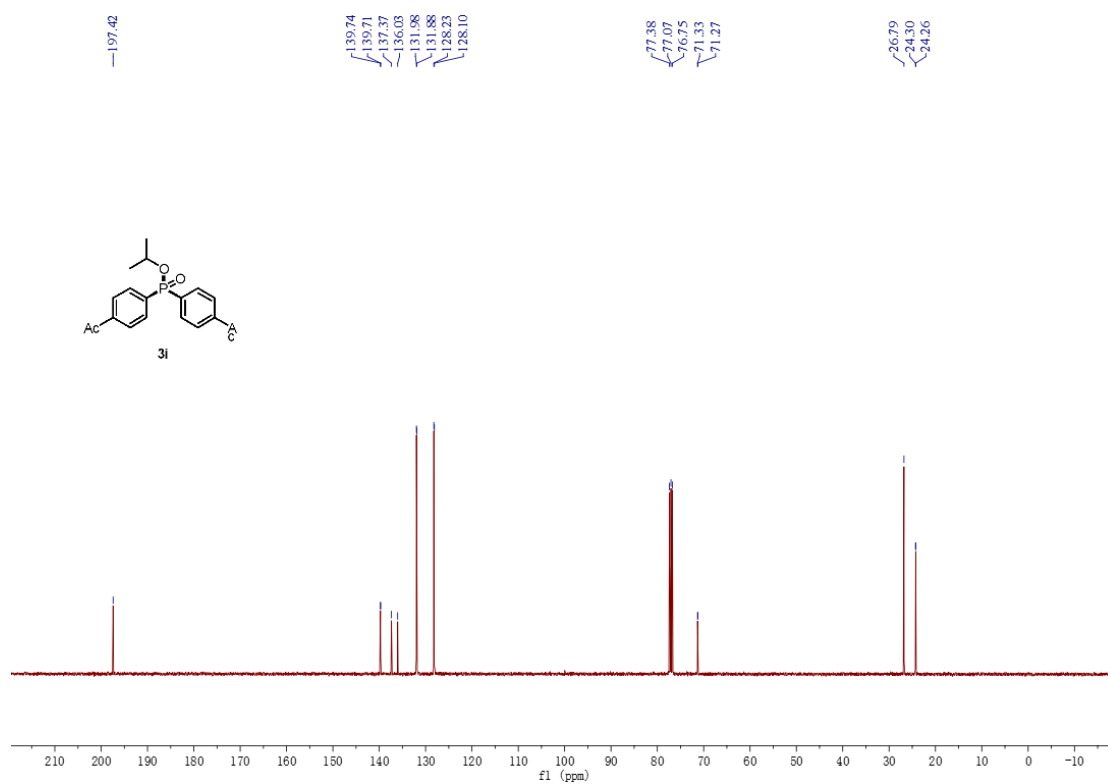
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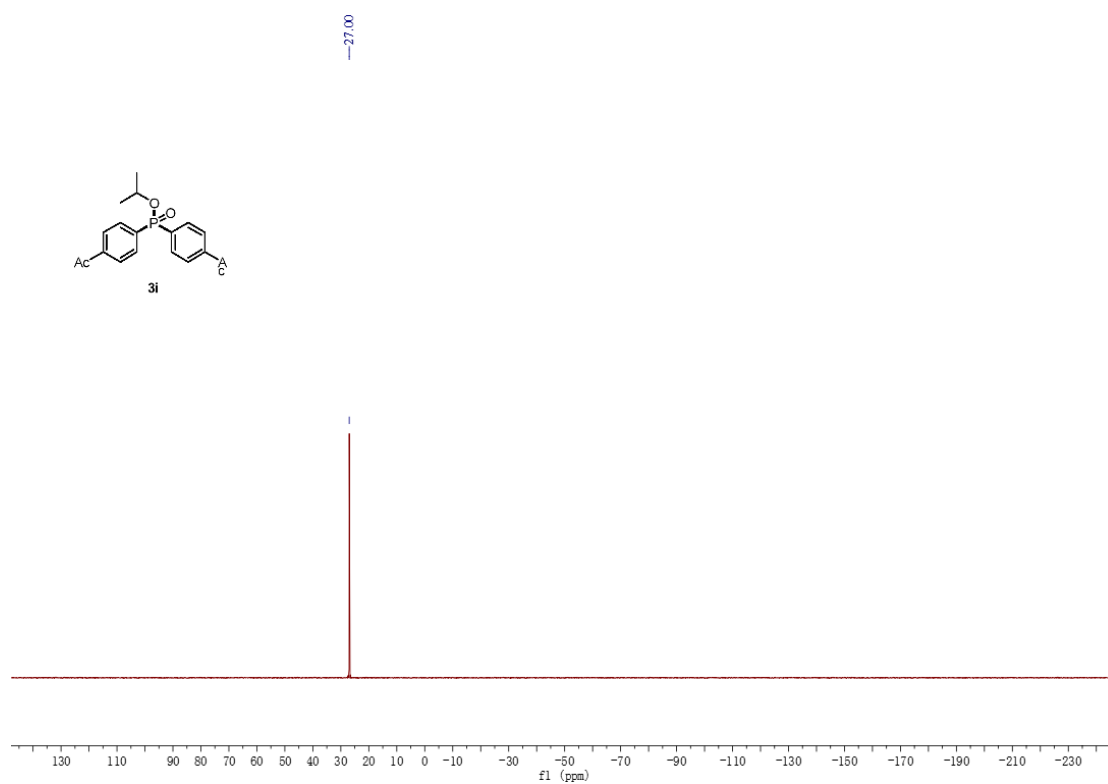
^1H NMR (400 MHz, CDCl_3) spectrum for 3i



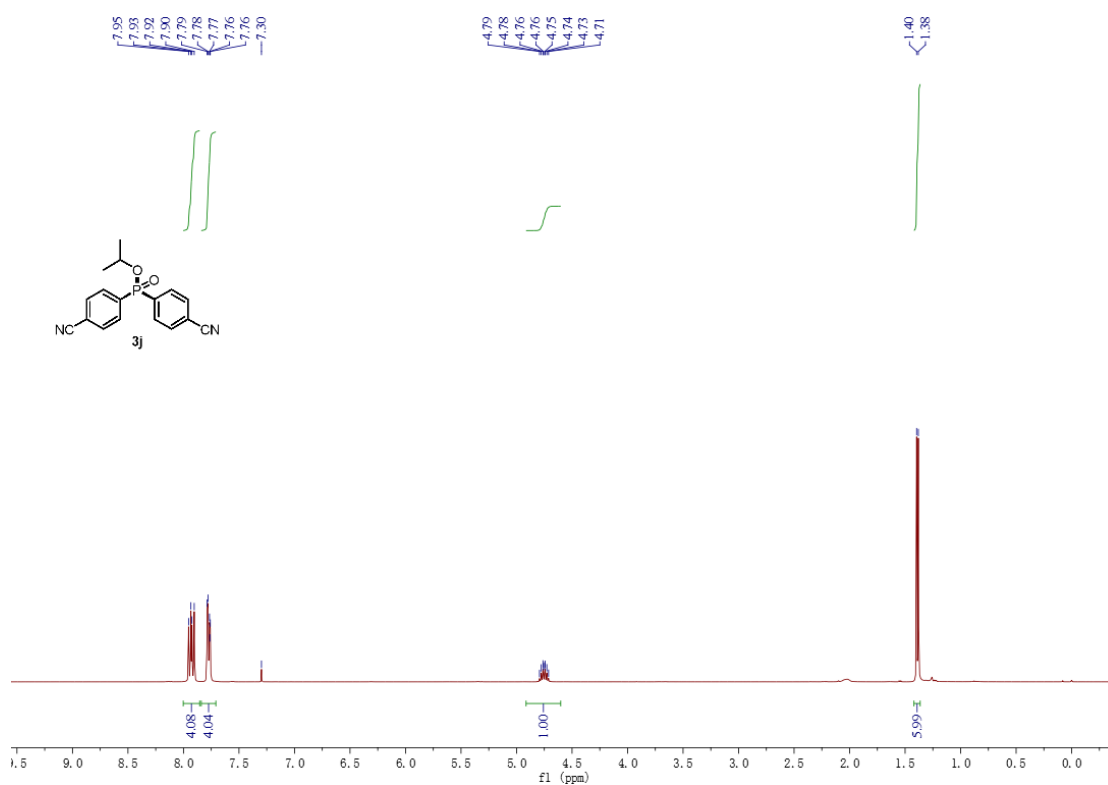
^{13}C NMR (101 MHz, CDCl_3) spectrum for 3i



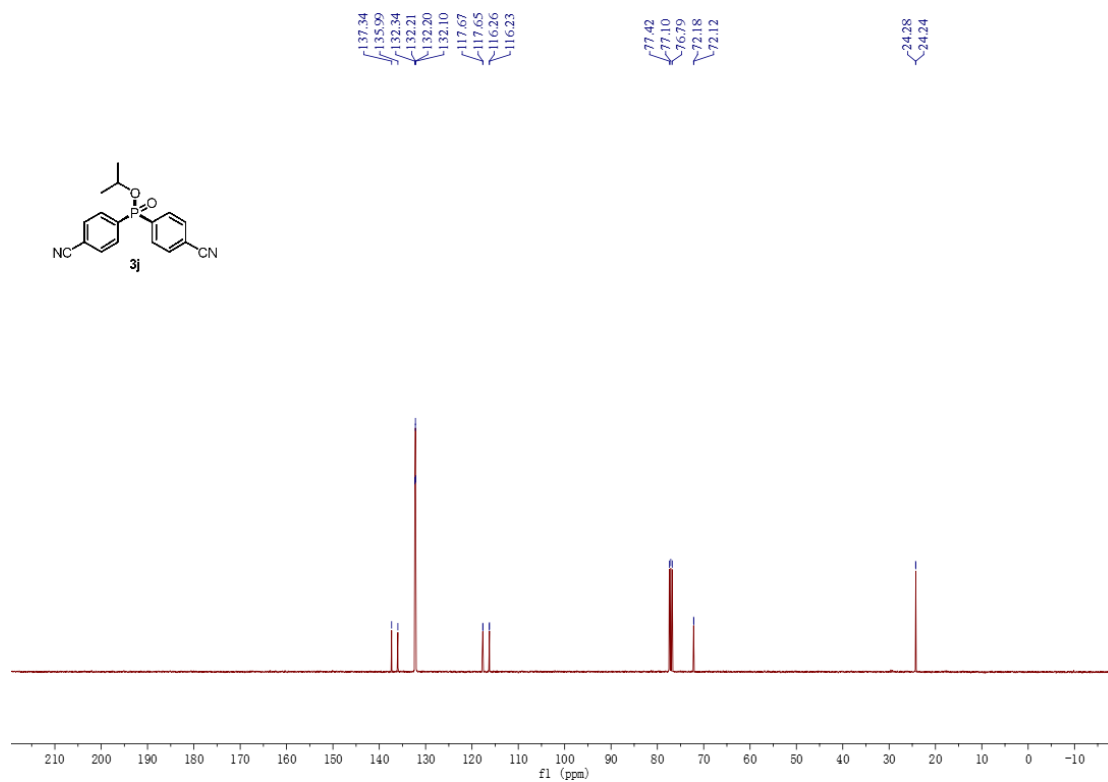
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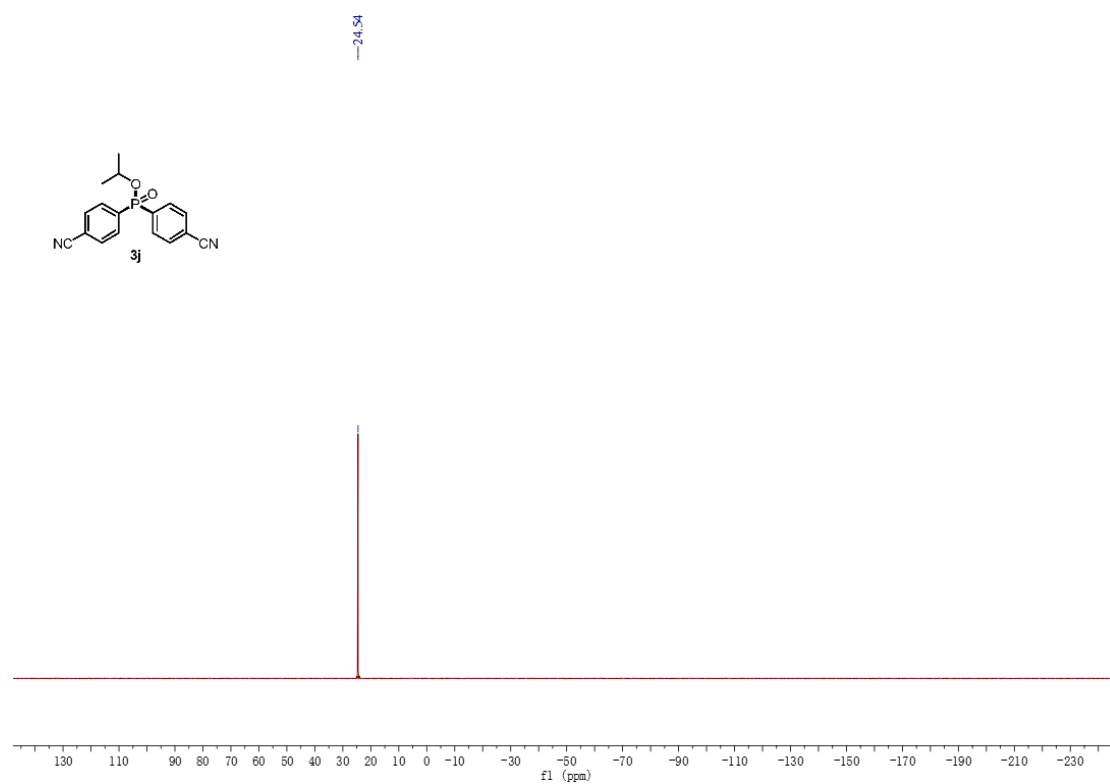
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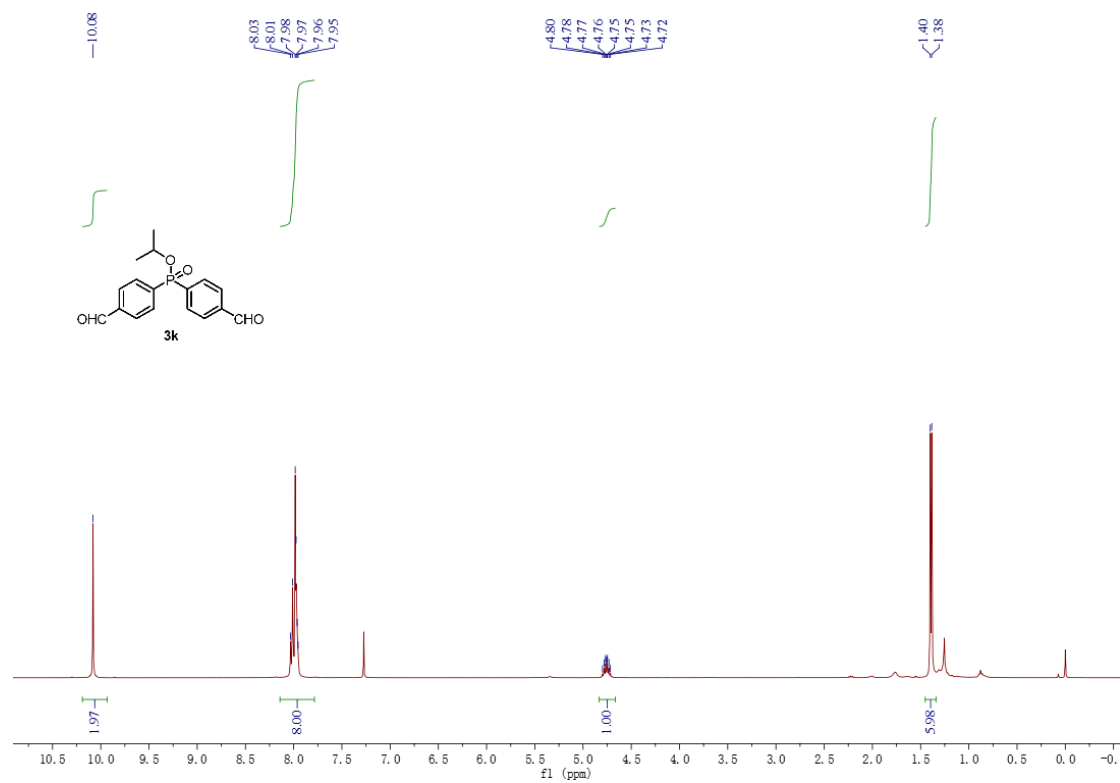
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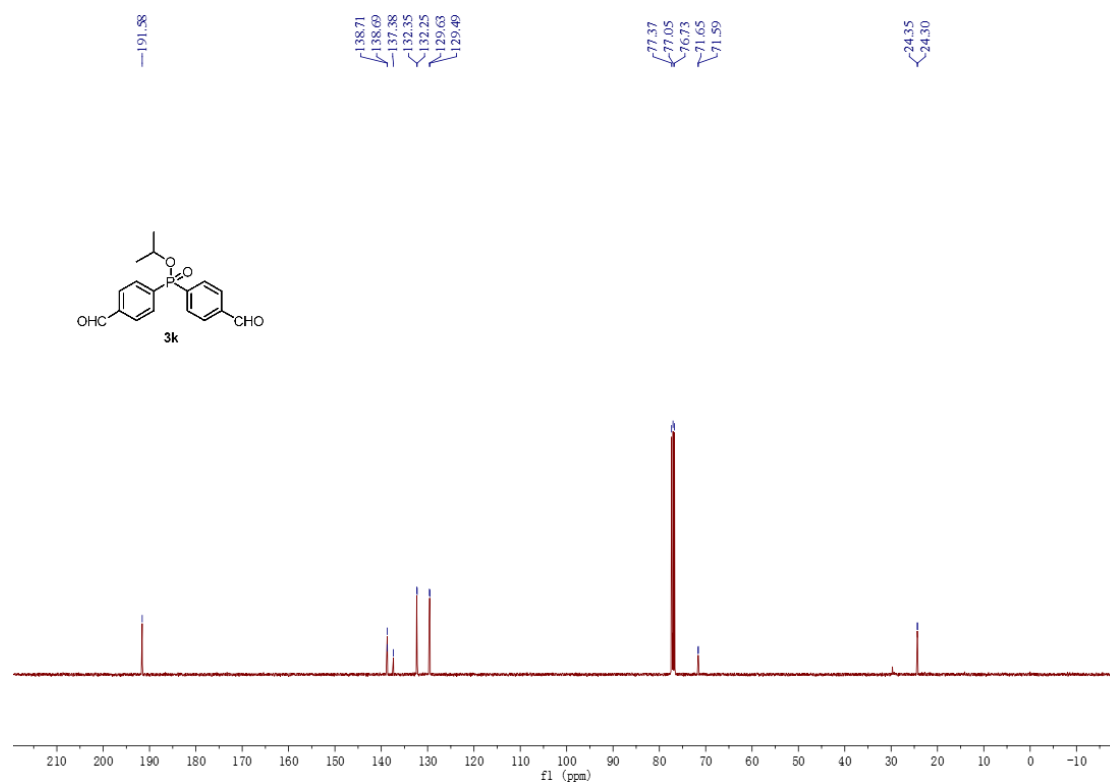
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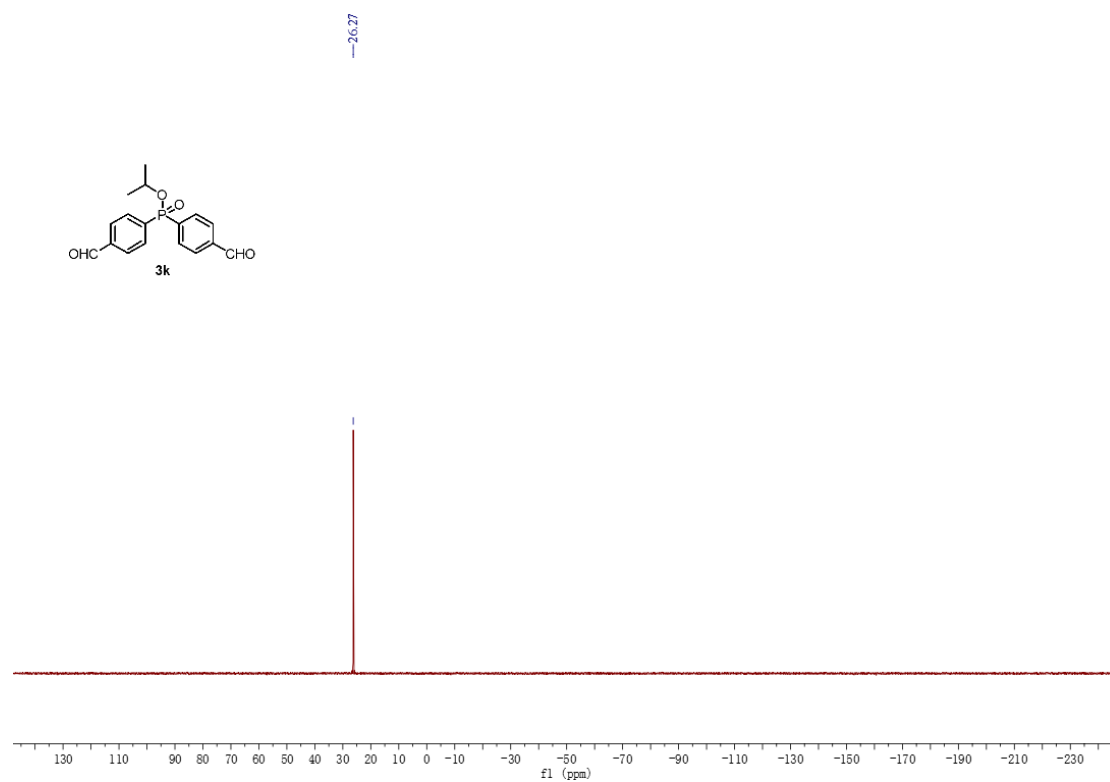
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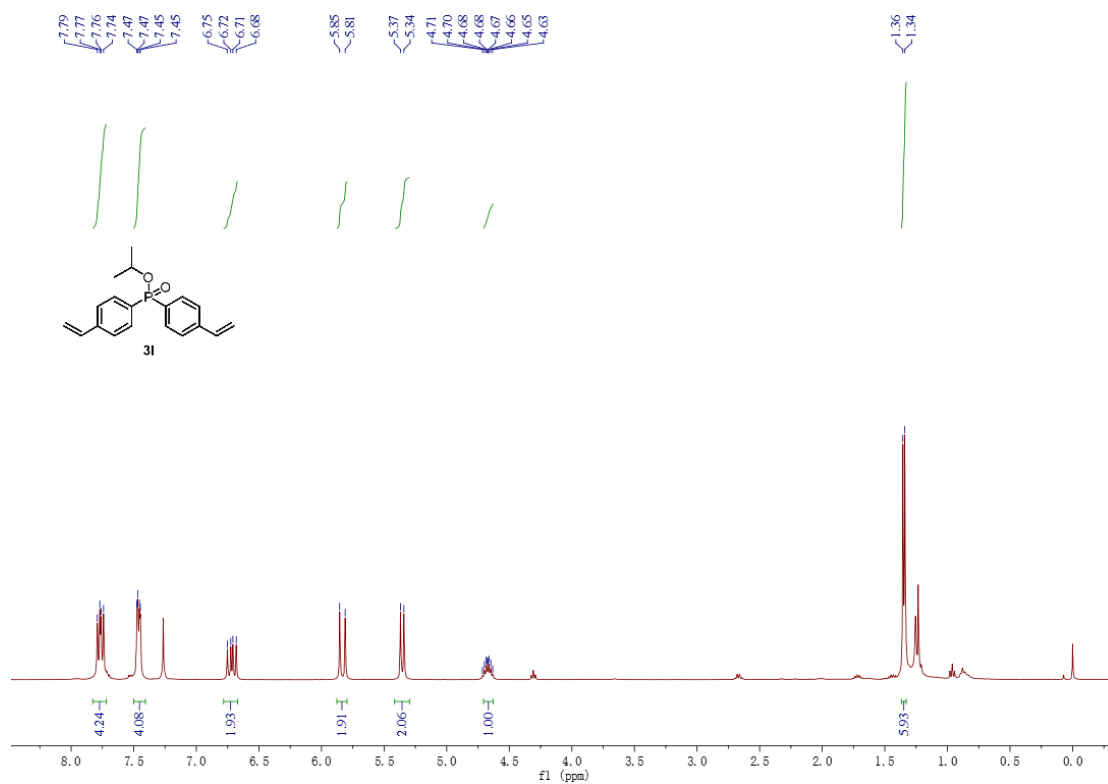
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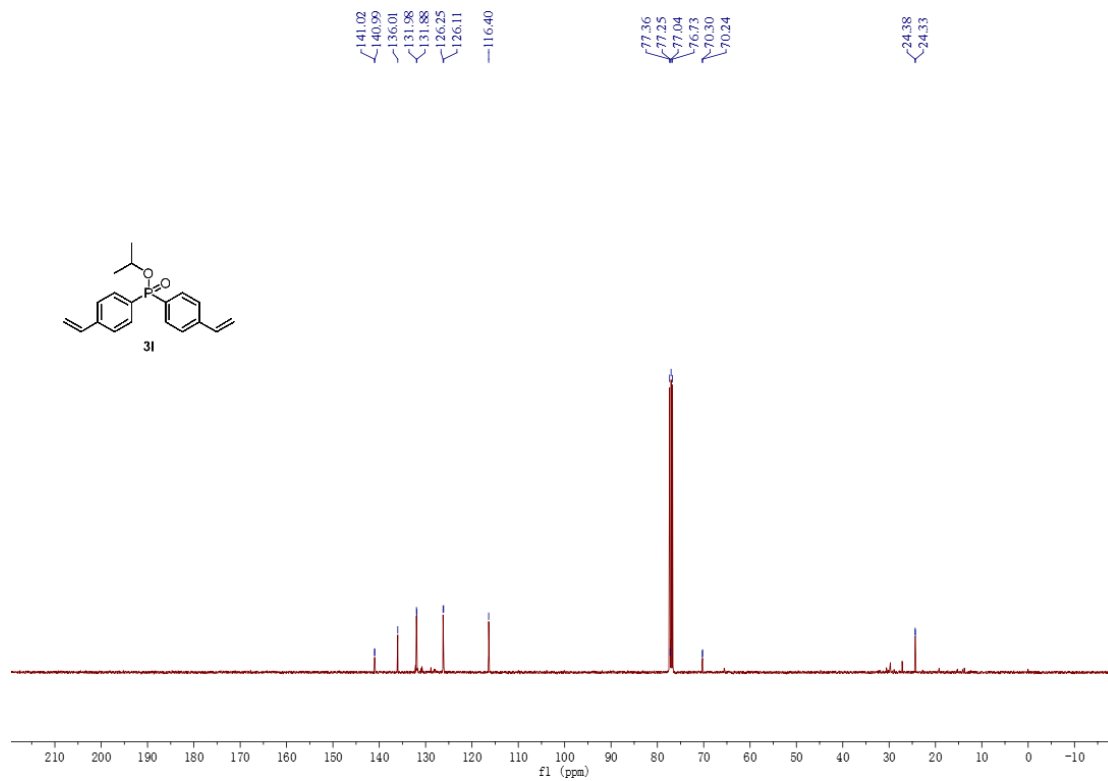
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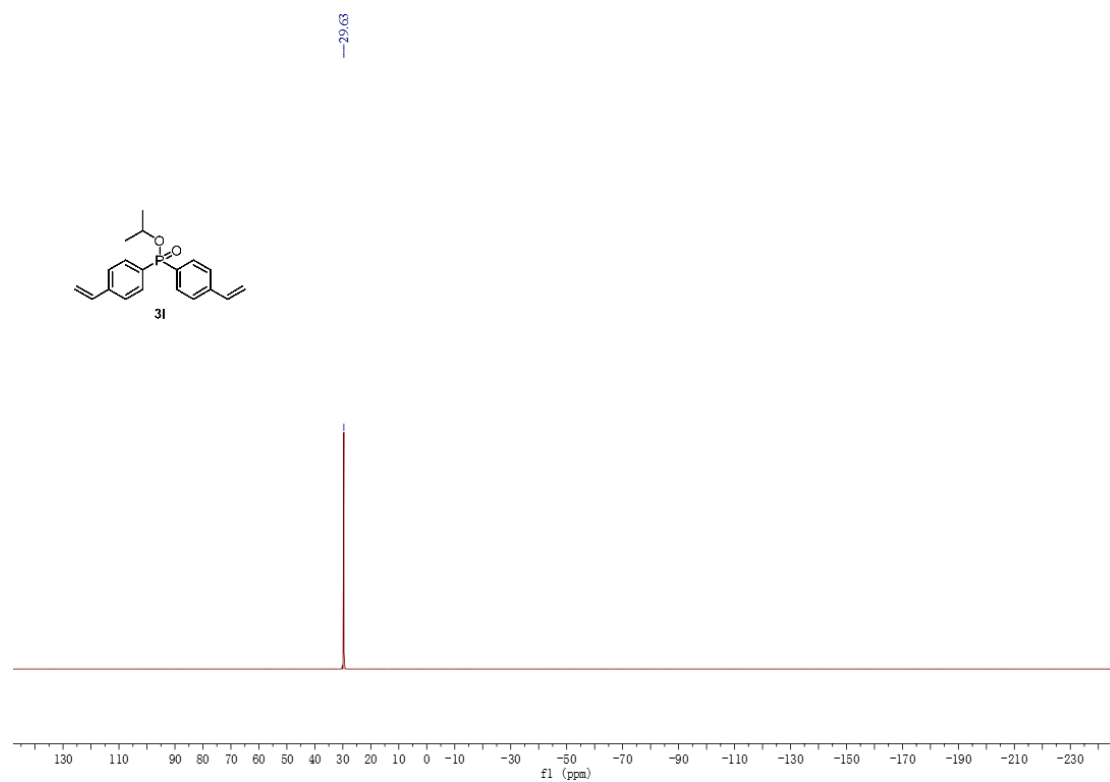
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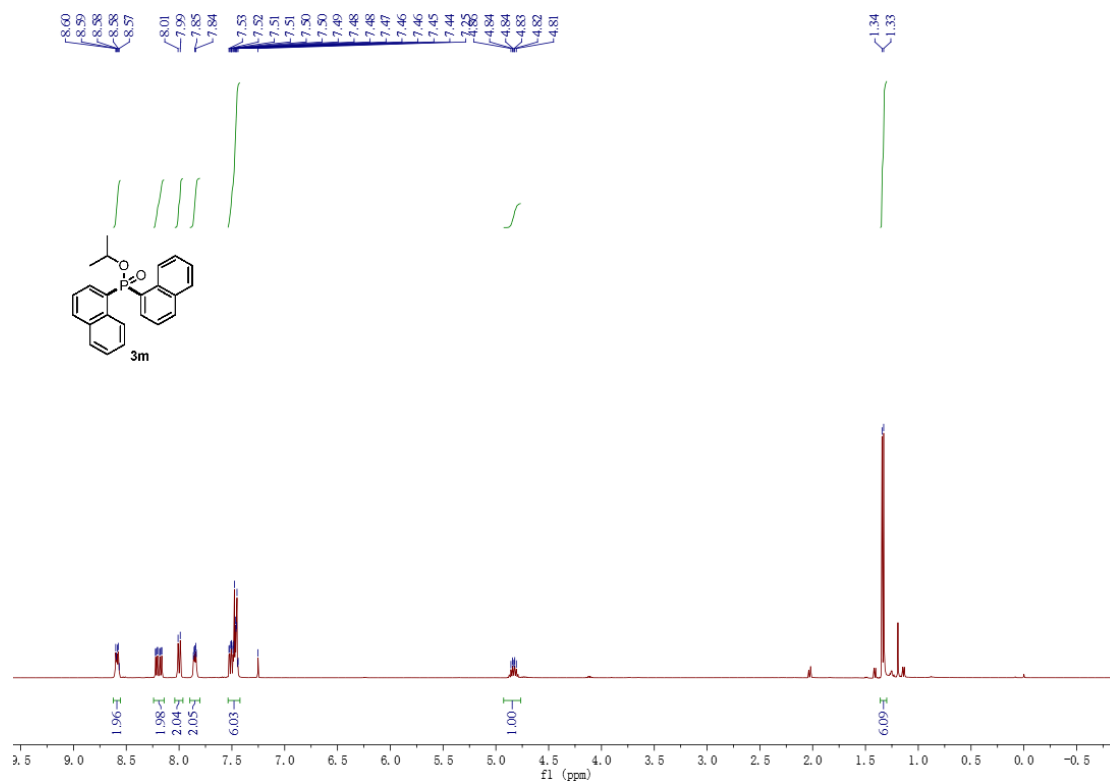
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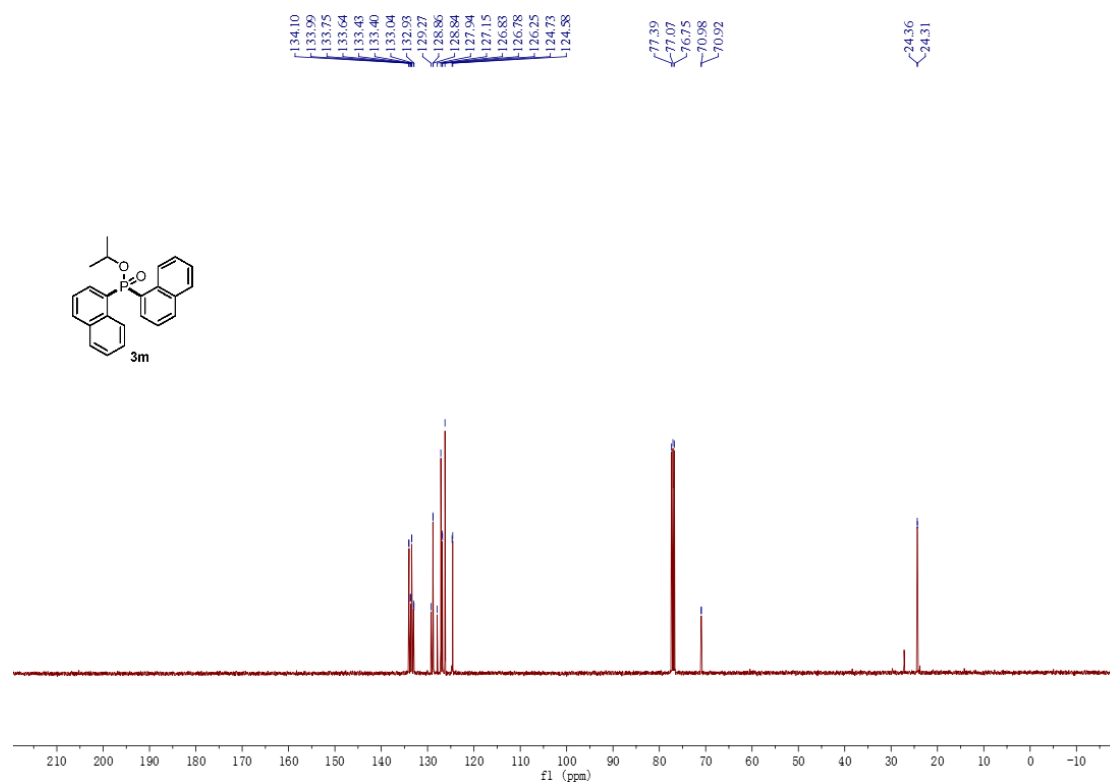
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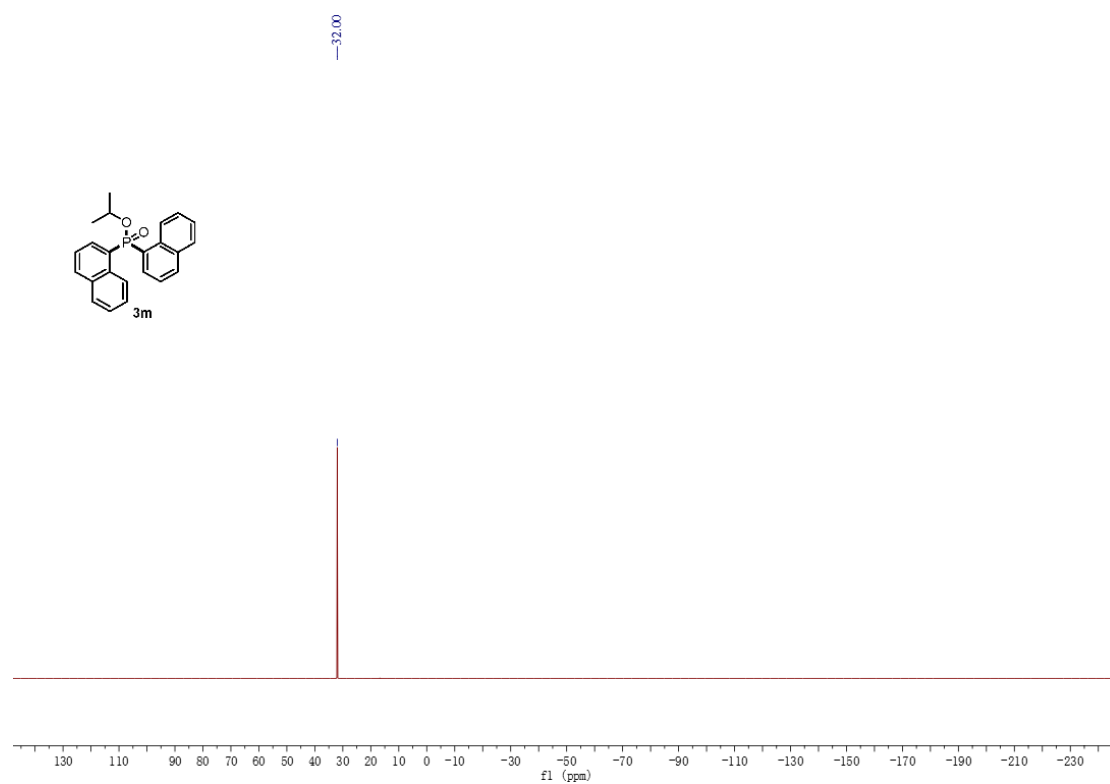
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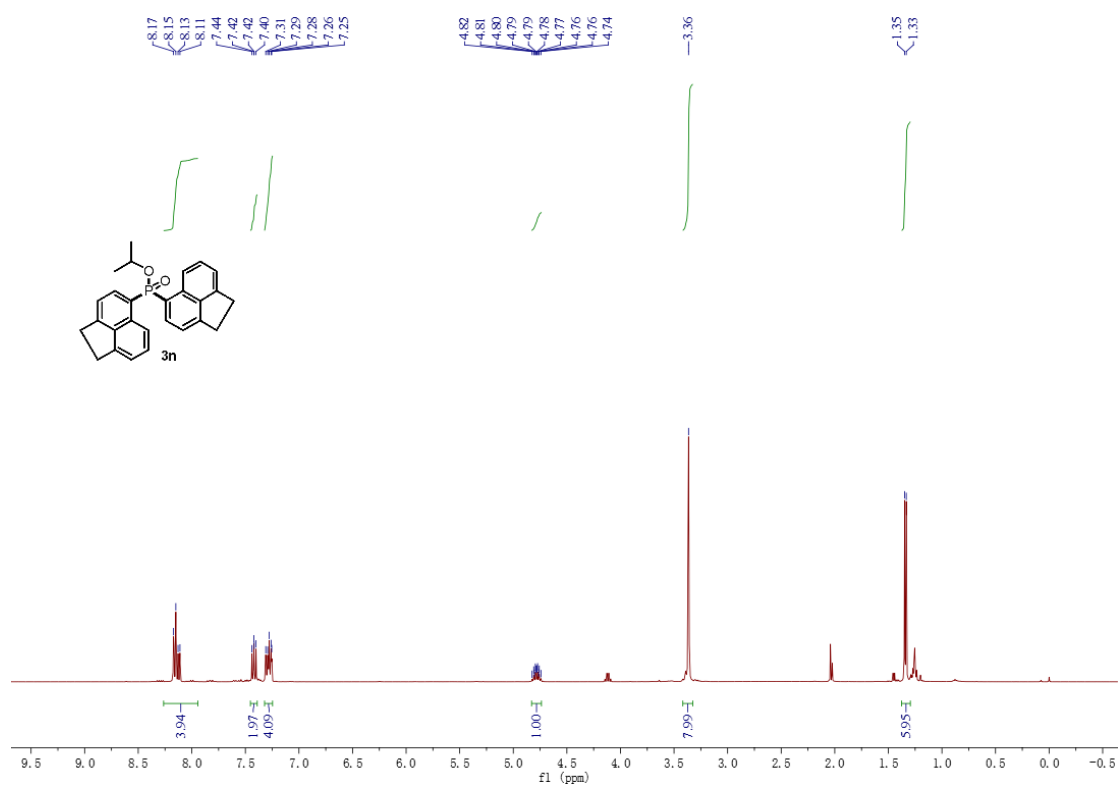
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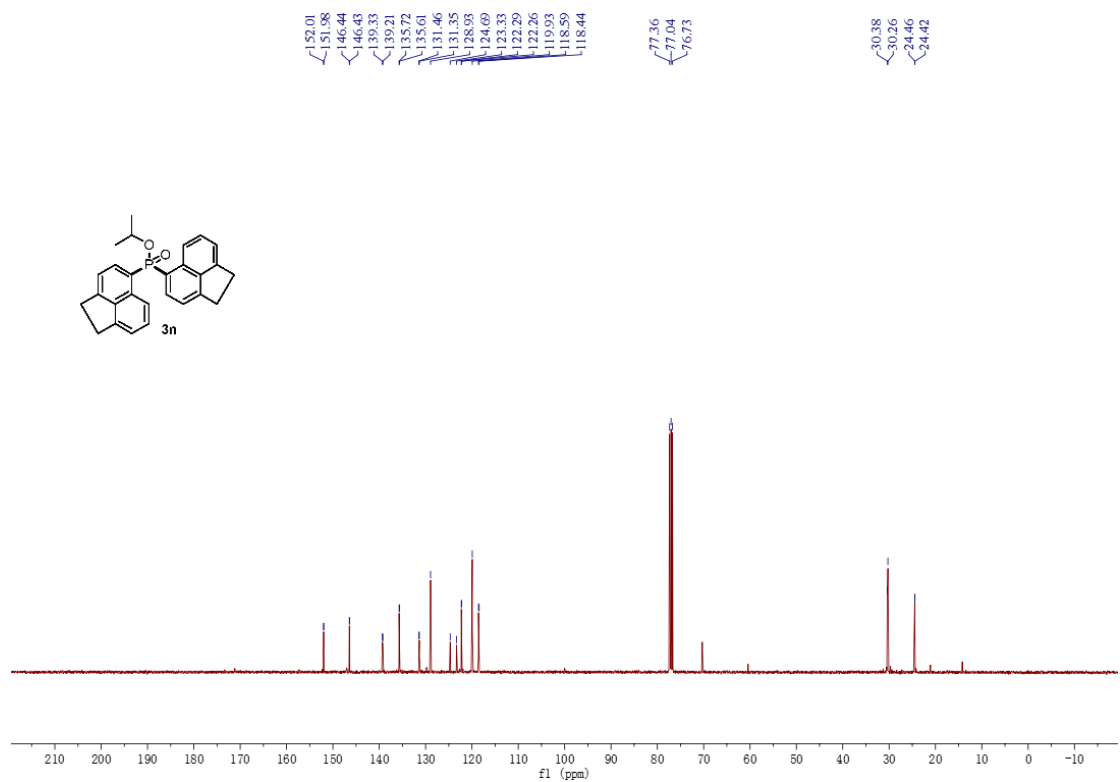
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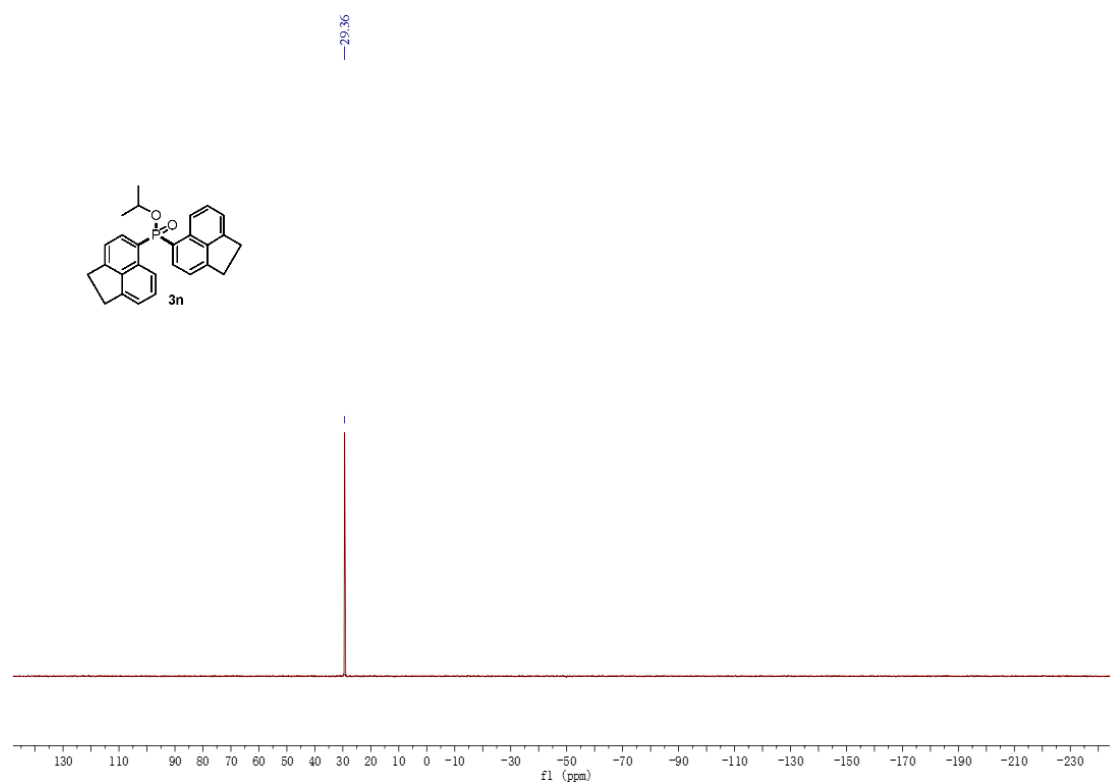
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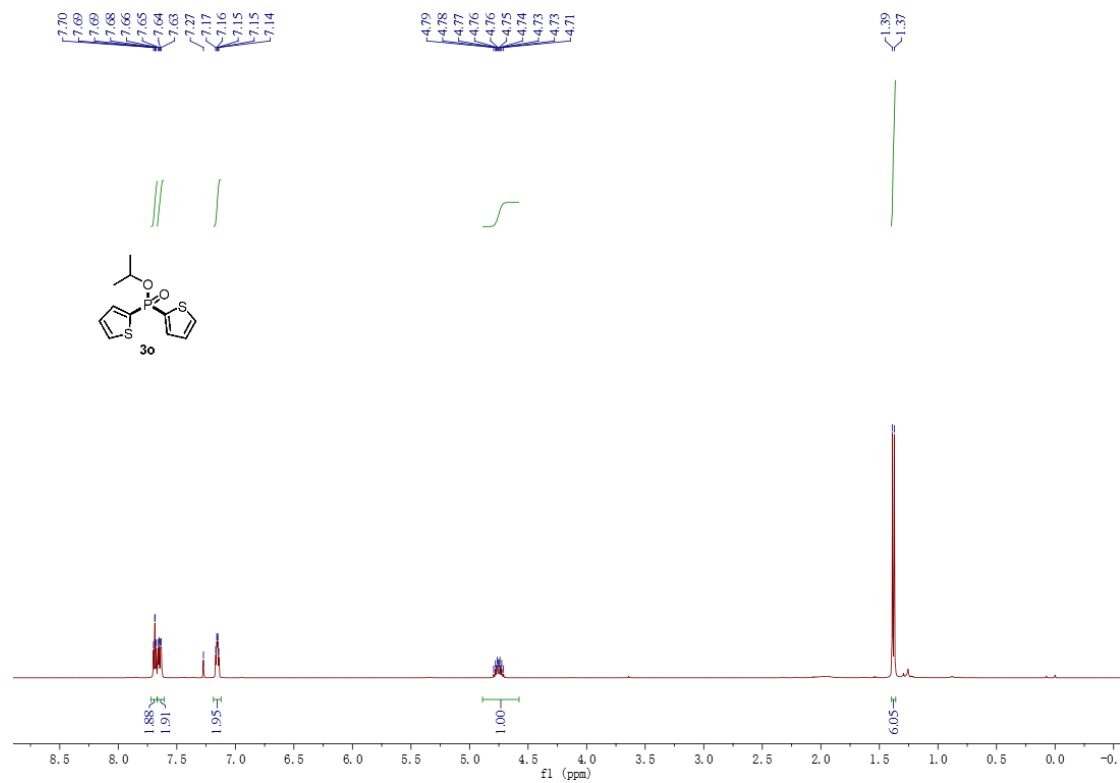
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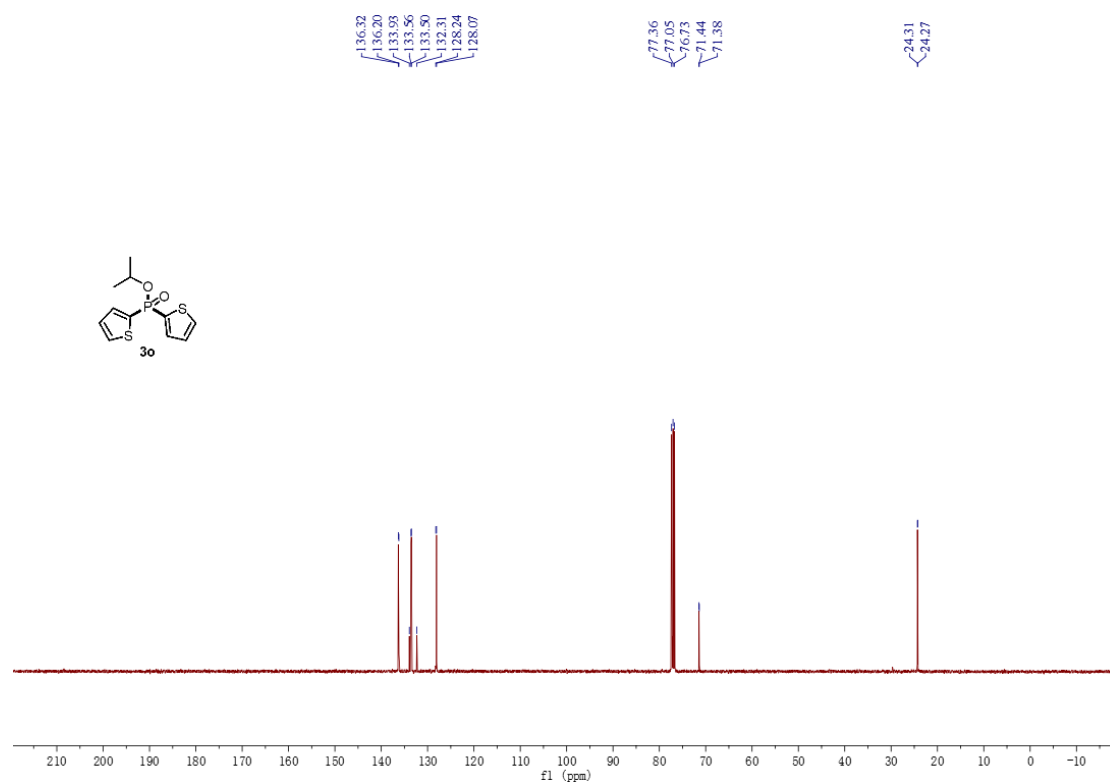
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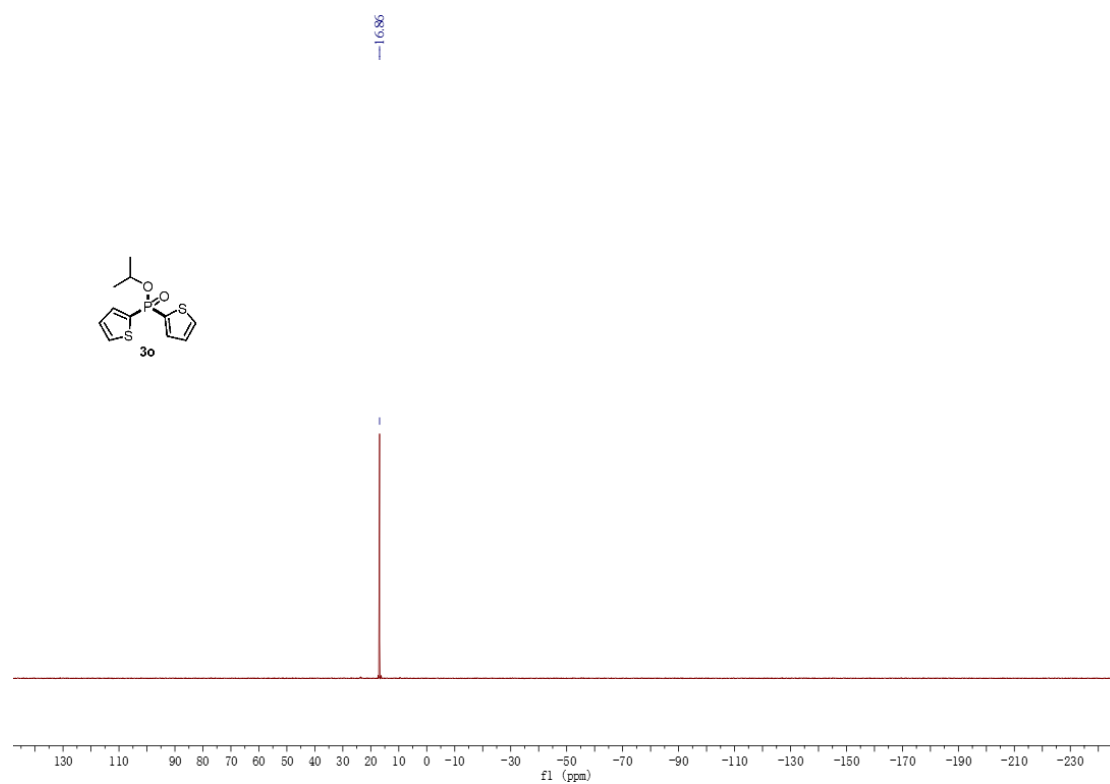
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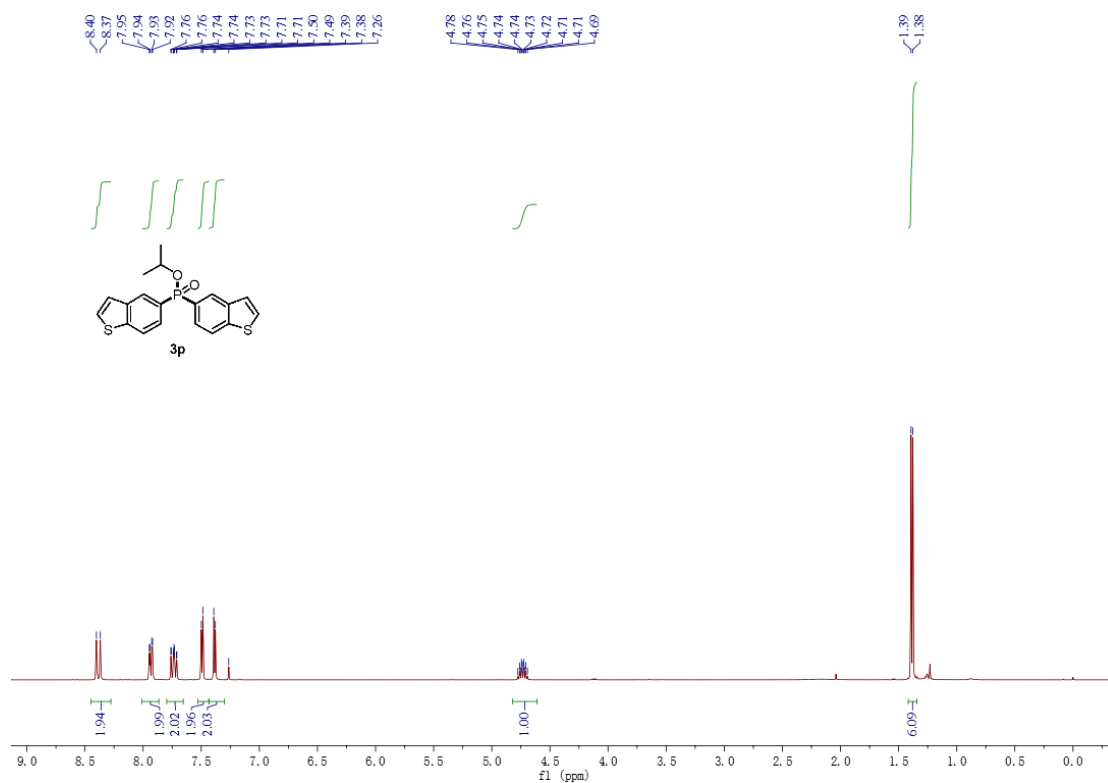
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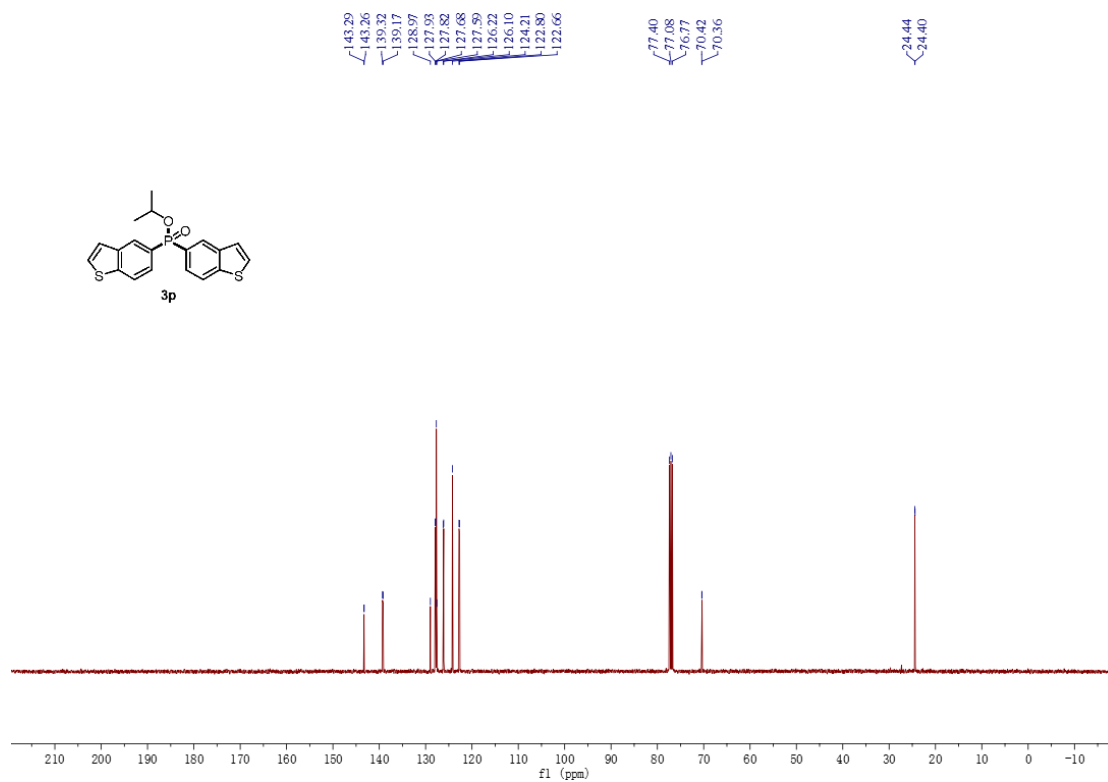
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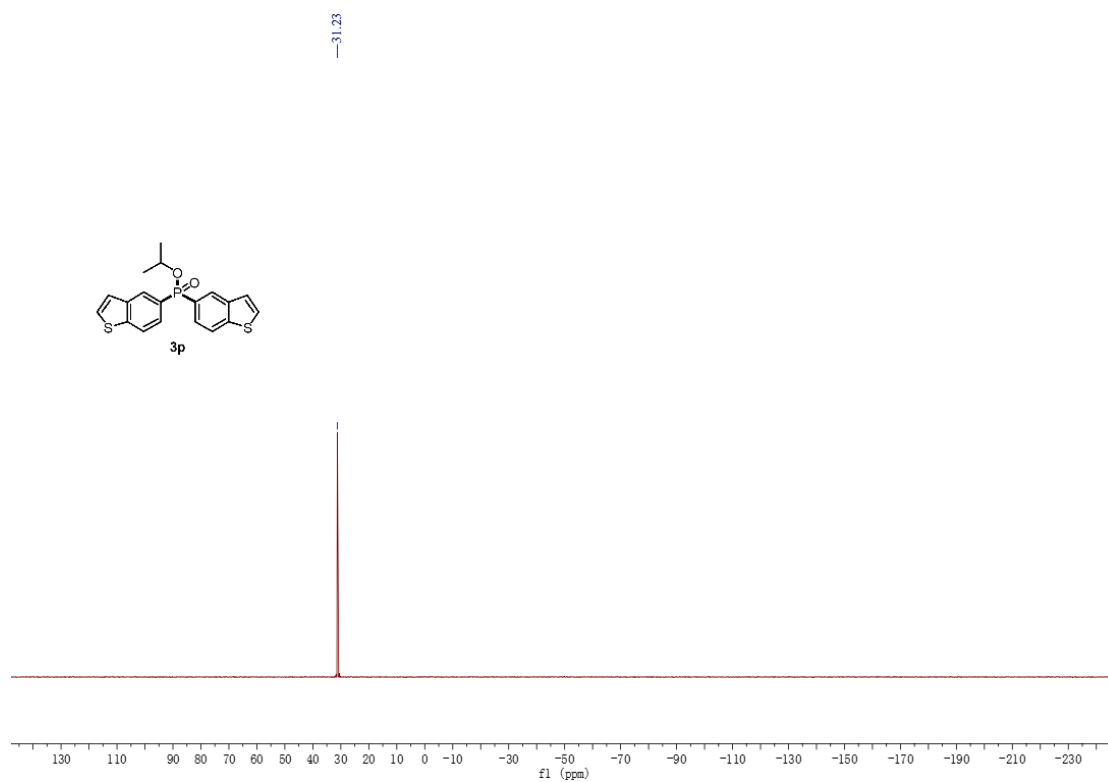
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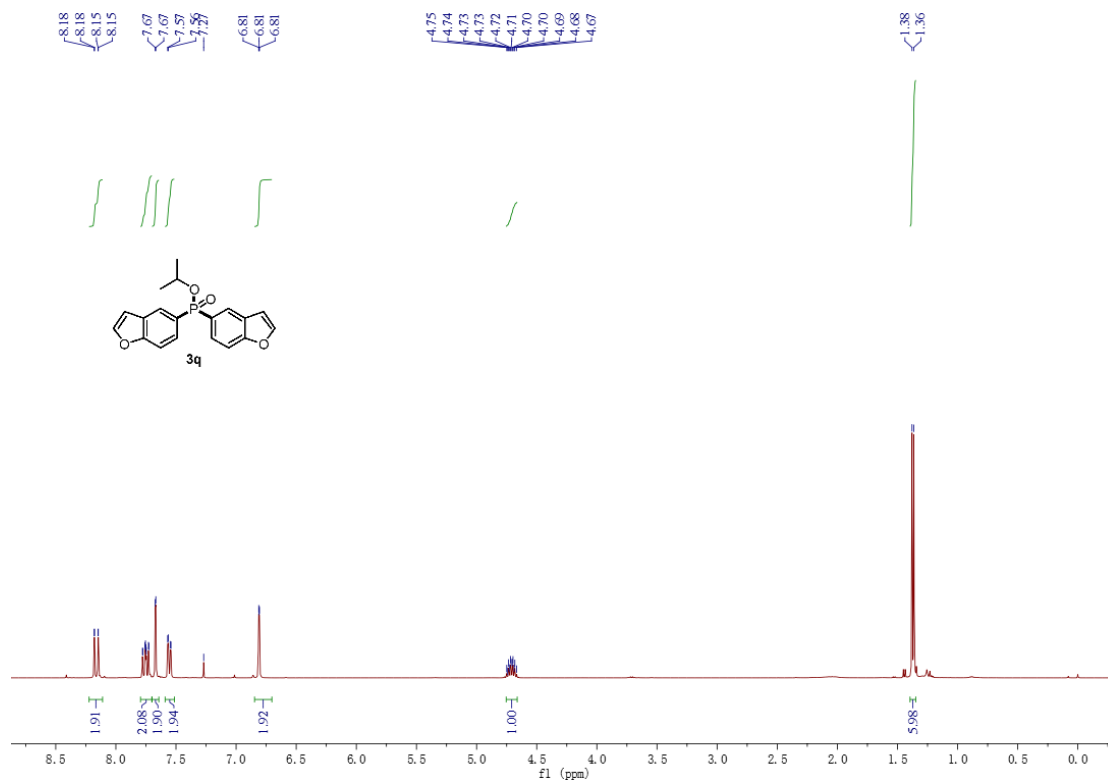
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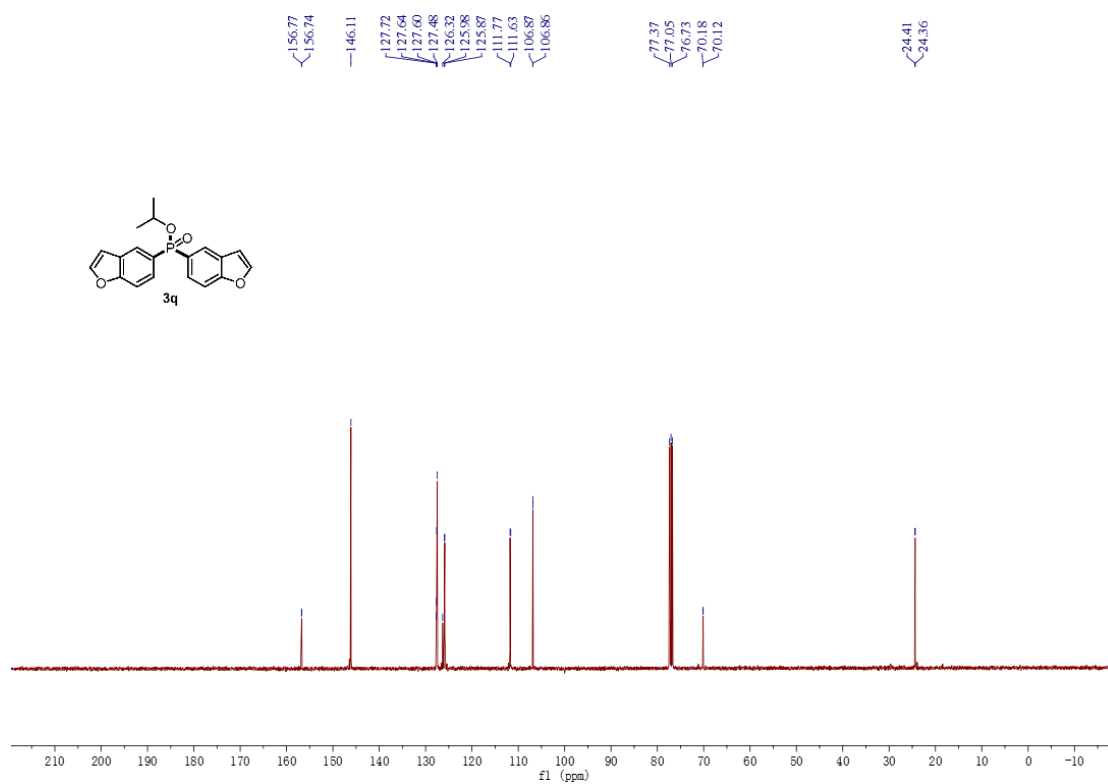
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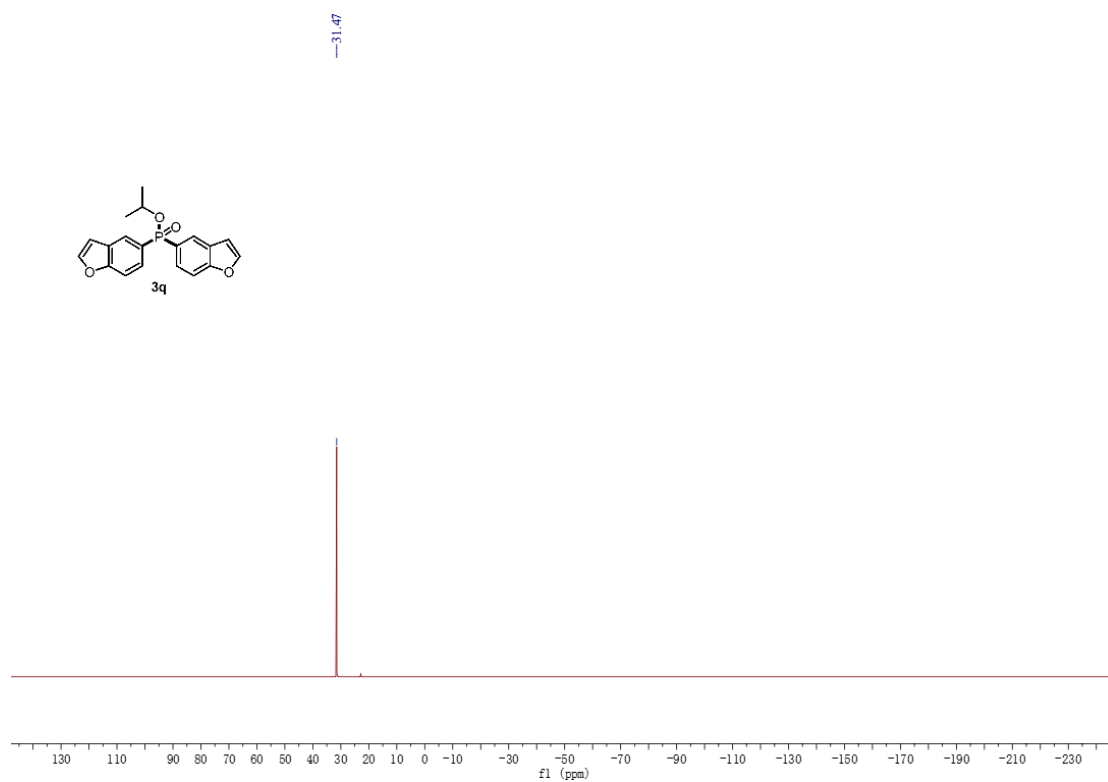
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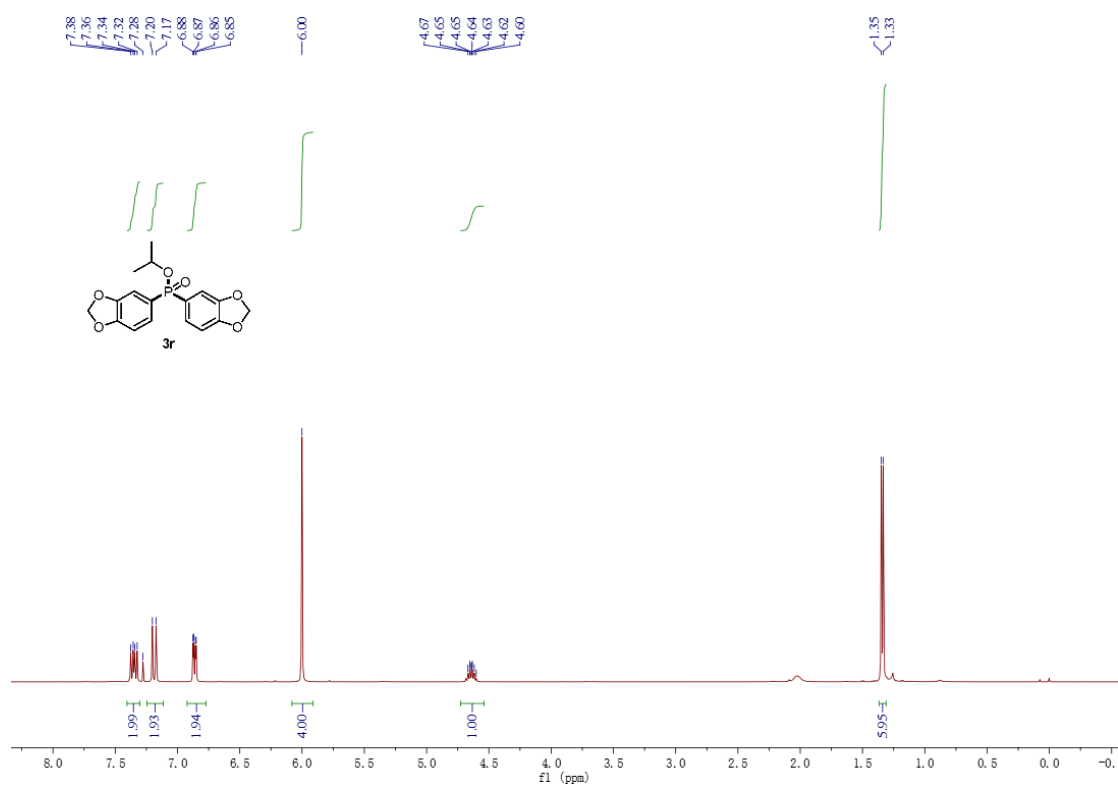
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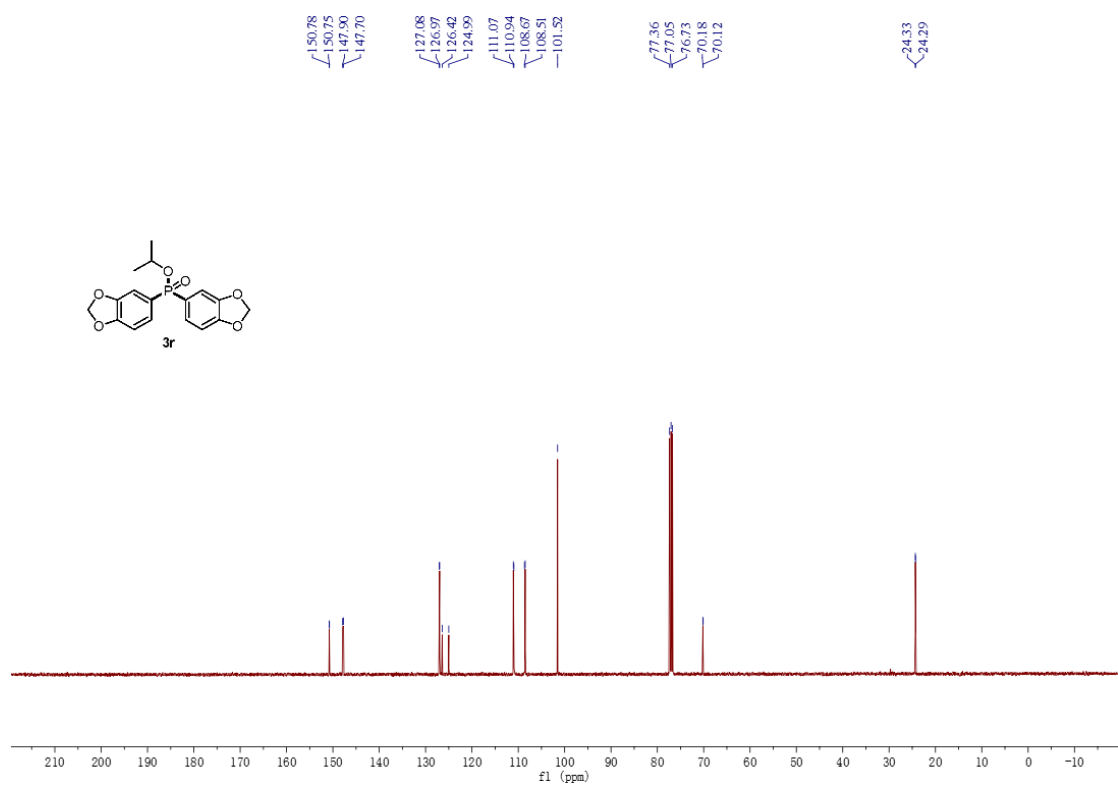
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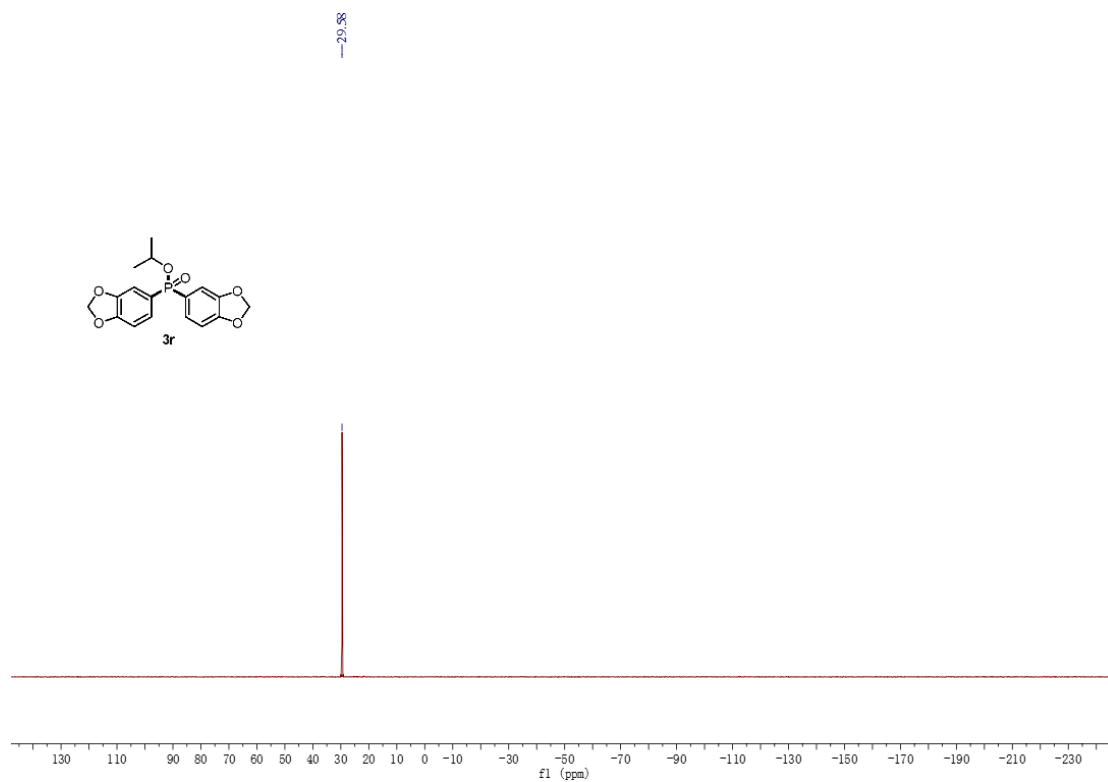
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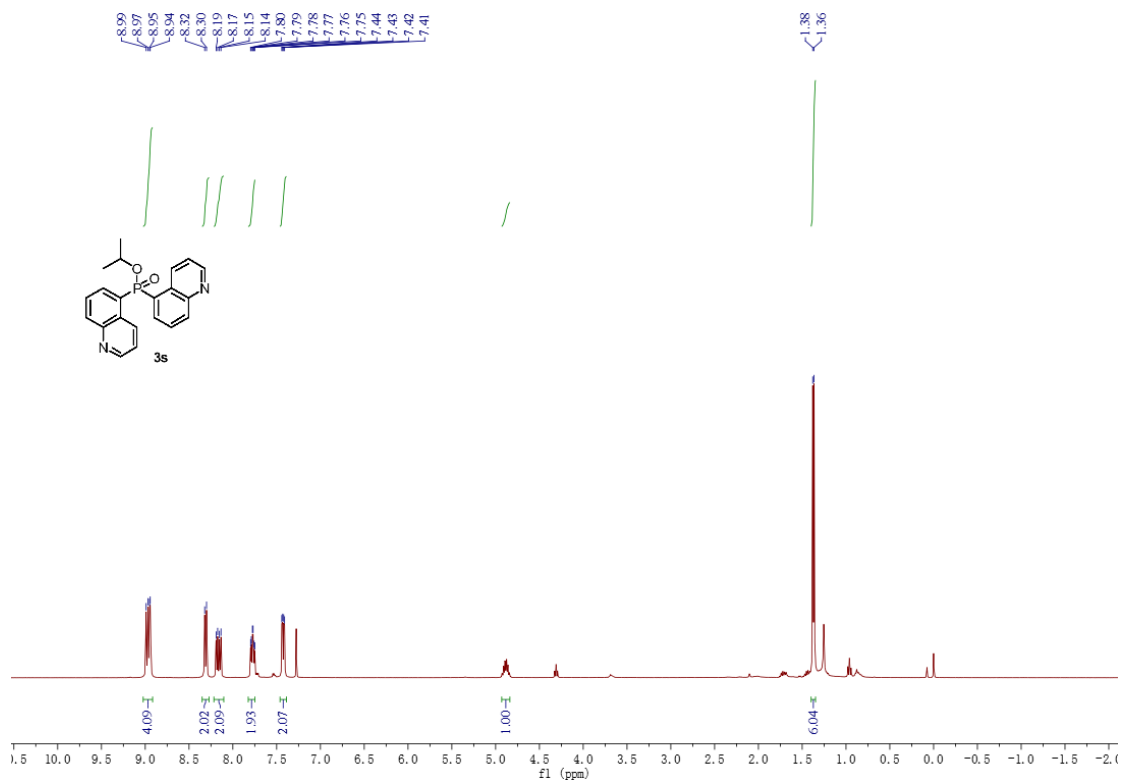
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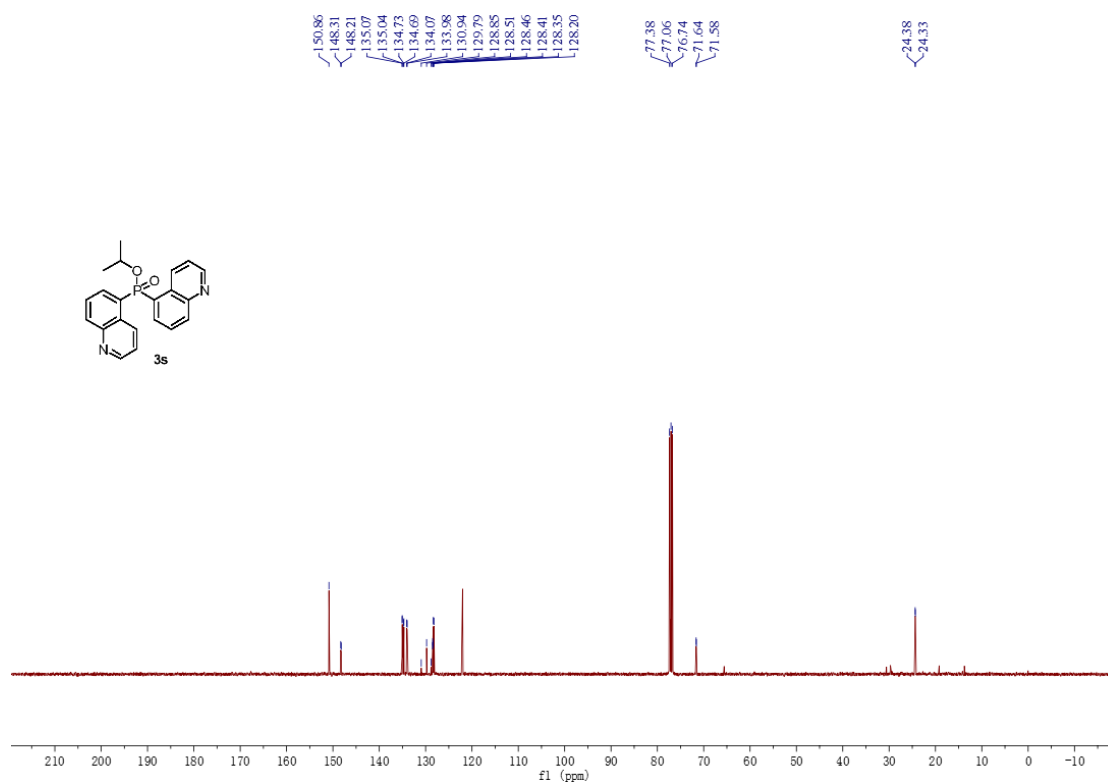
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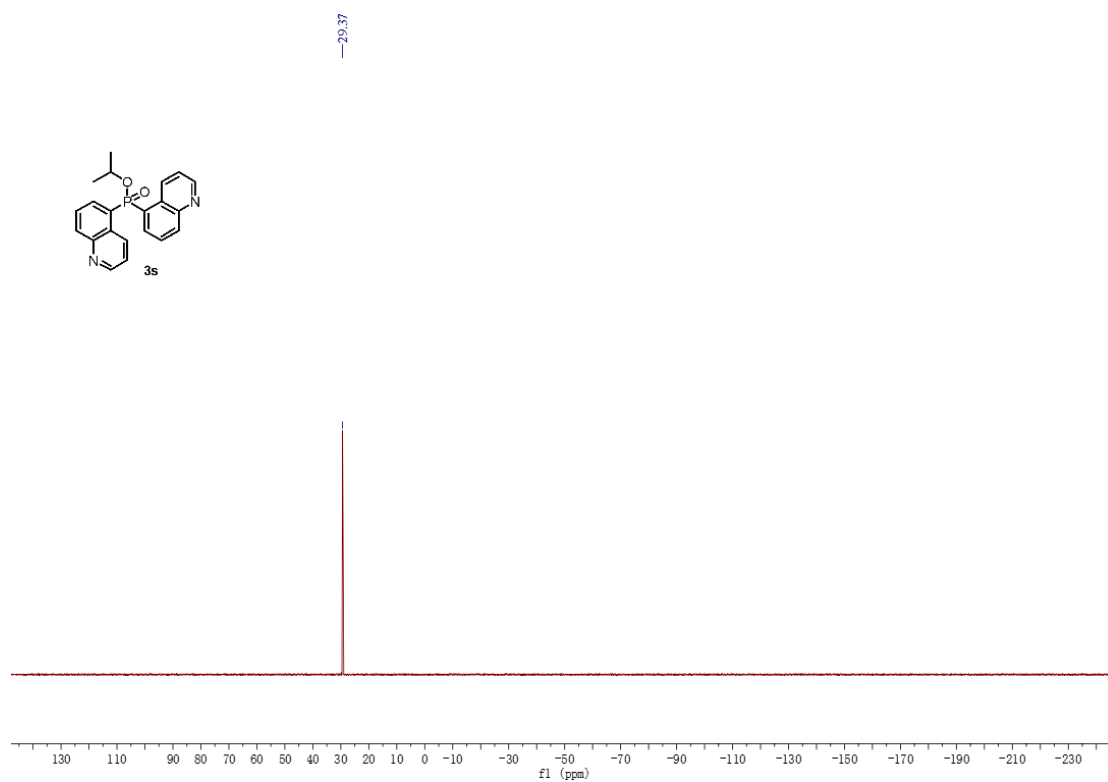
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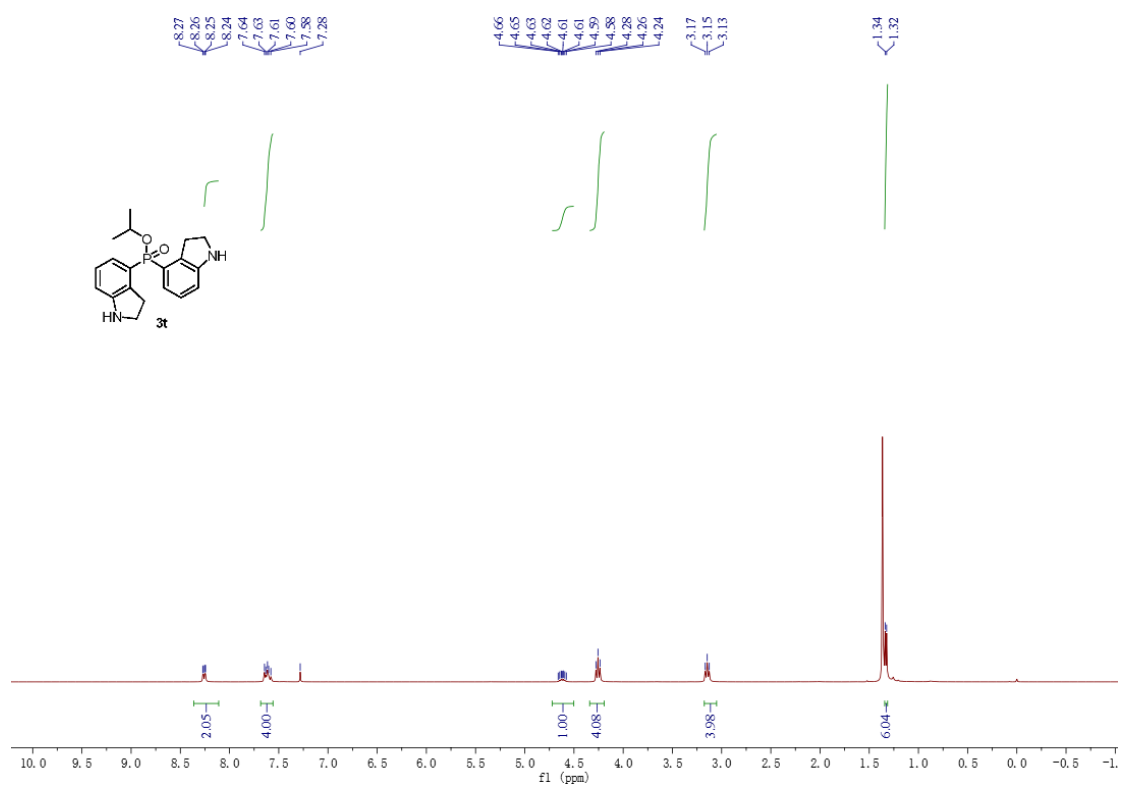
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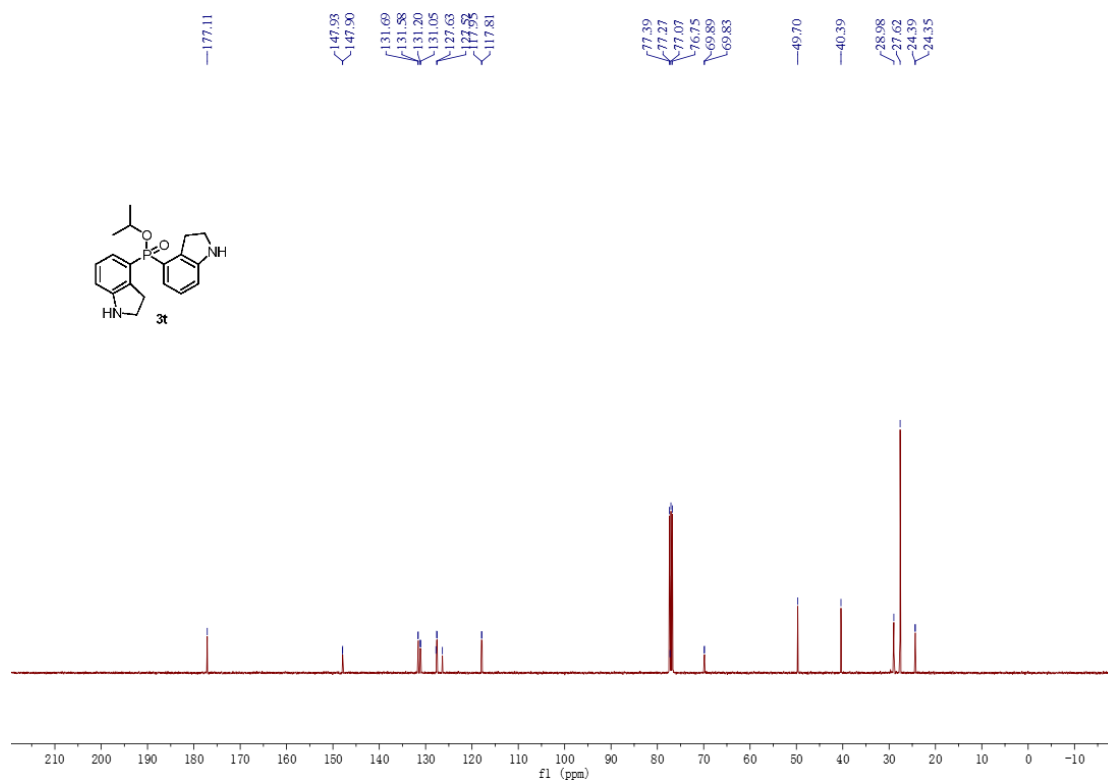
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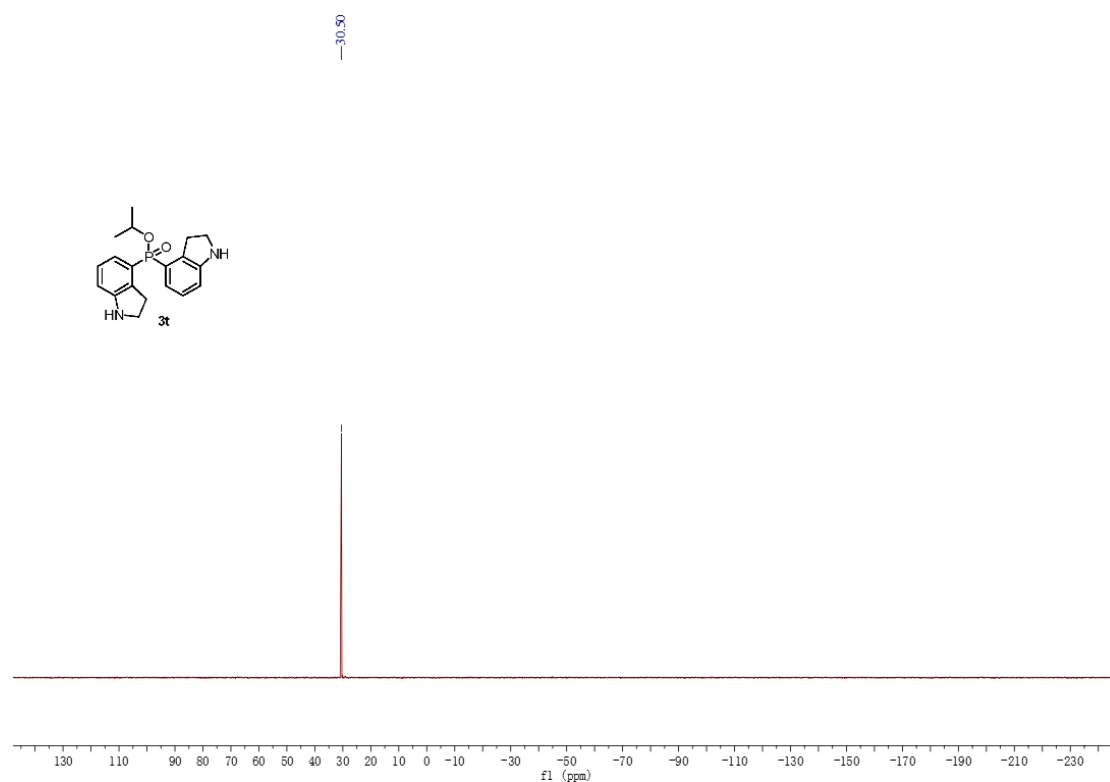
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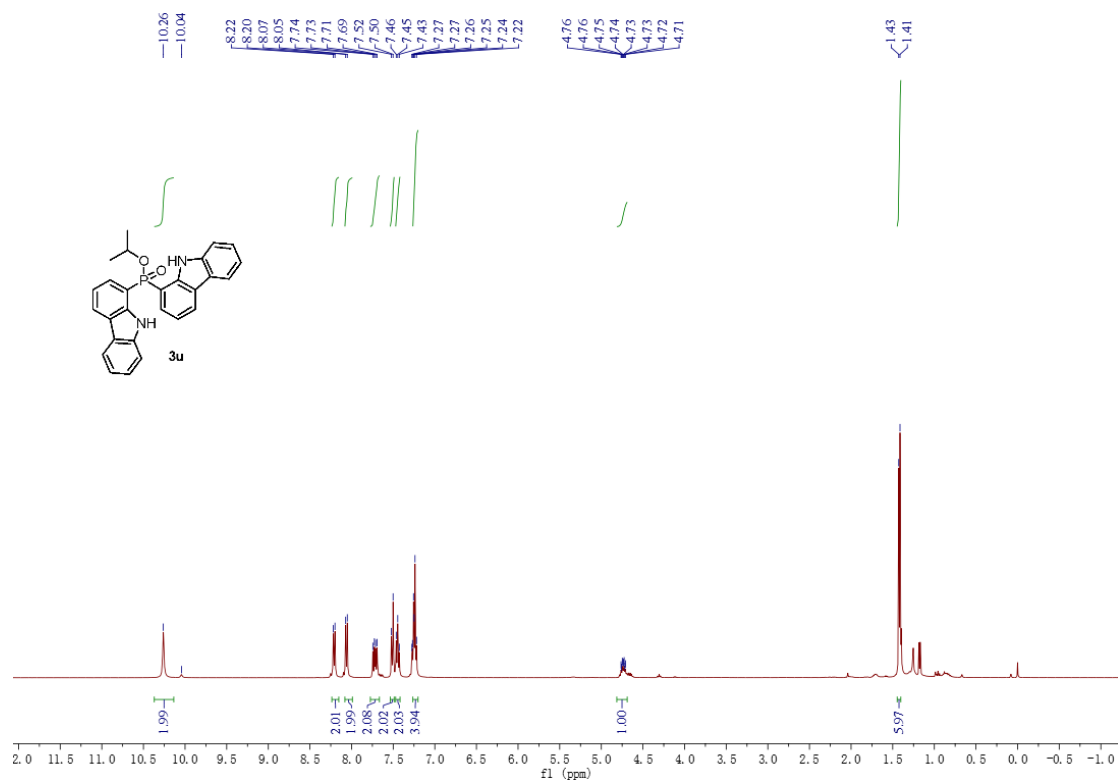
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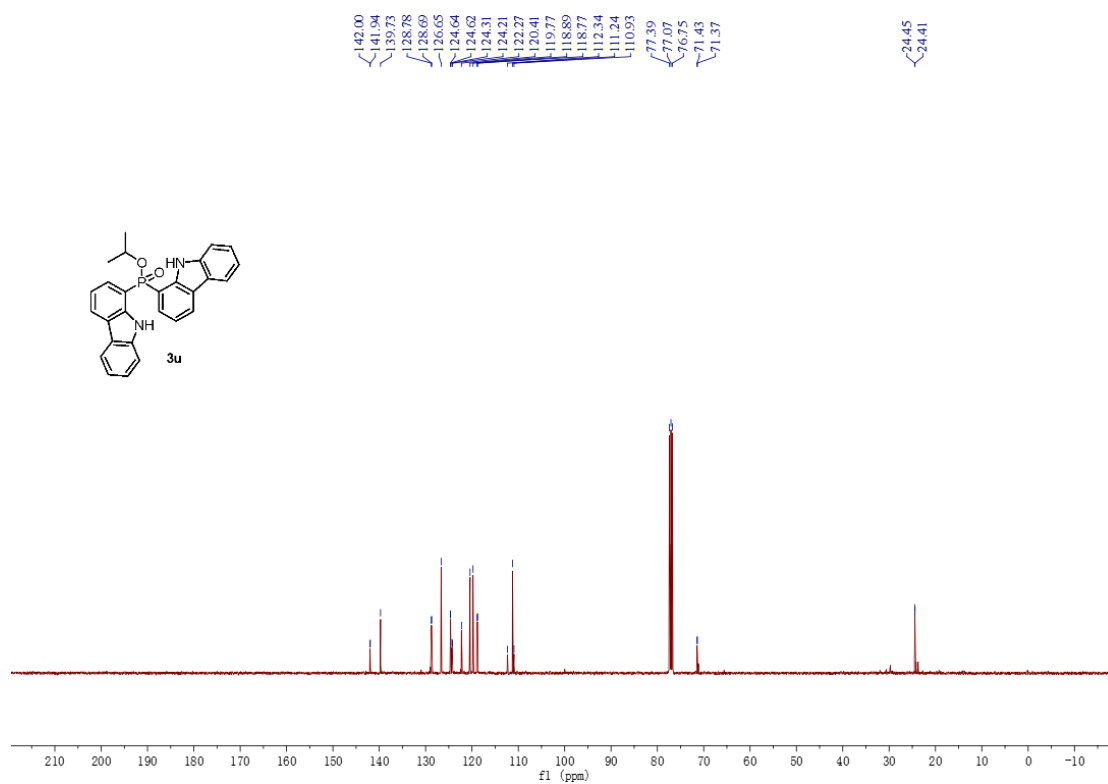
^{31}P NMR (121 MHz, CDCl_3) spectrum for 3t



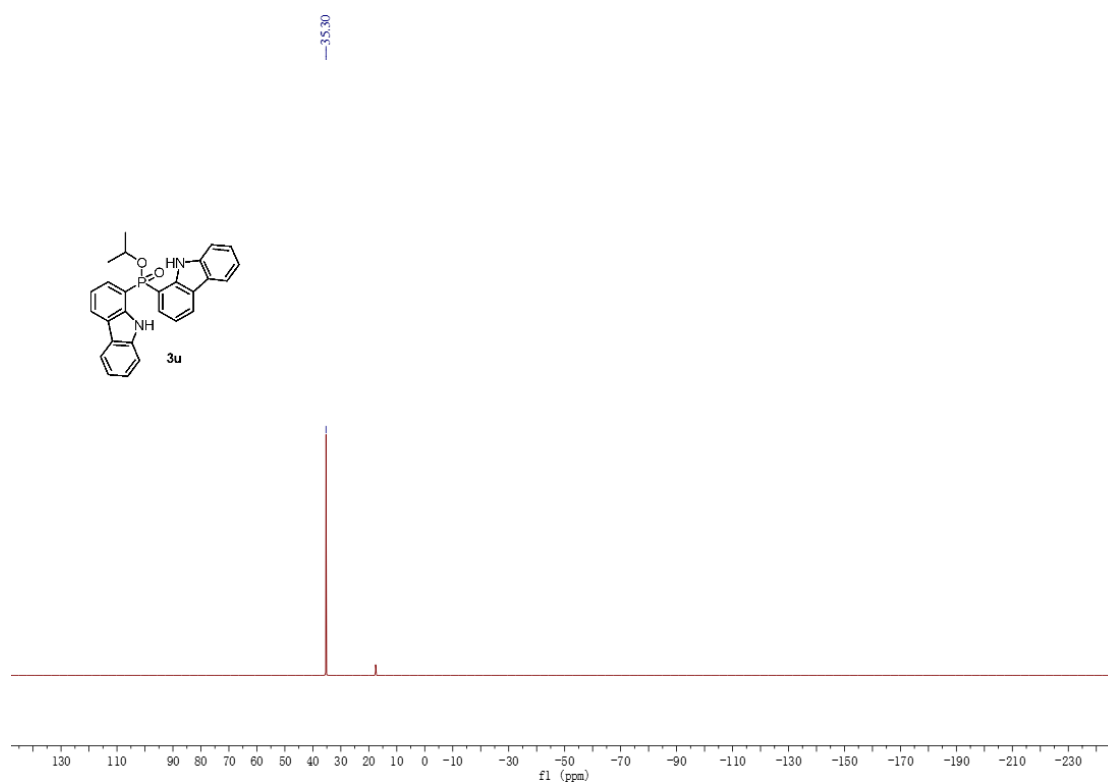
^1H NMR (400 MHz, CDCl_3) spectrum for 3u



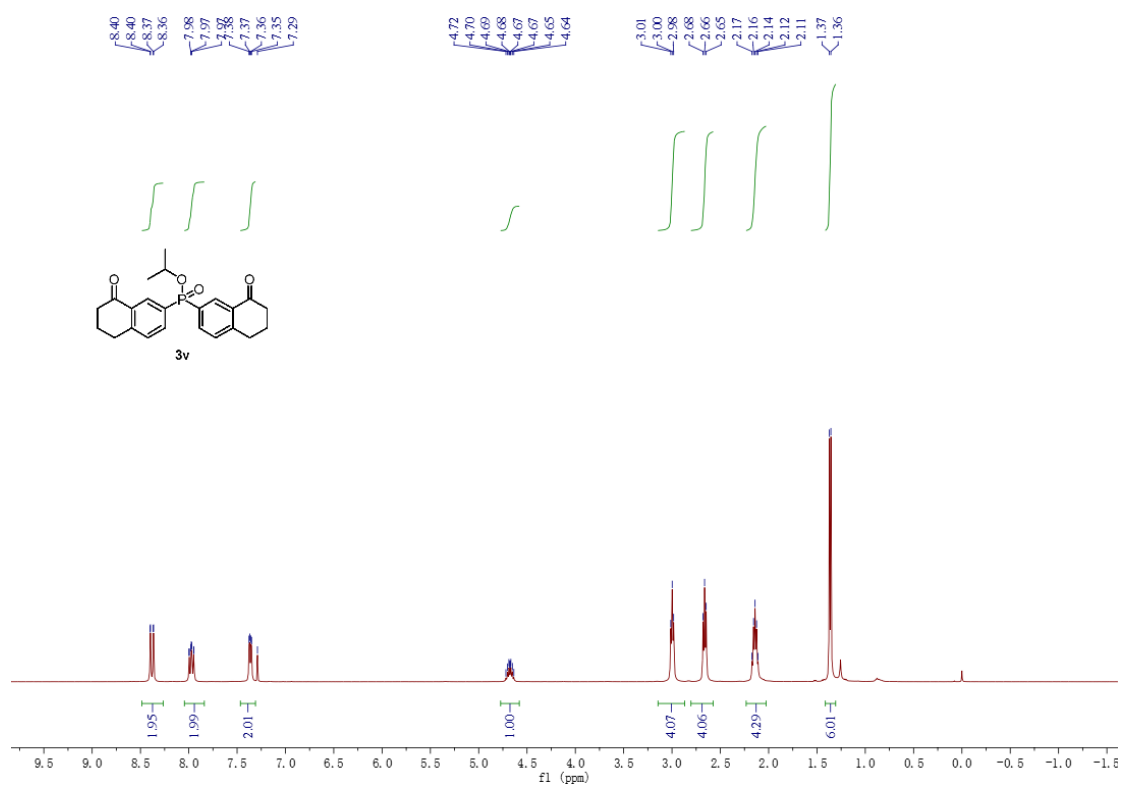
^{13}C NMR (101 MHz, CDCl_3) spectrum for 3u



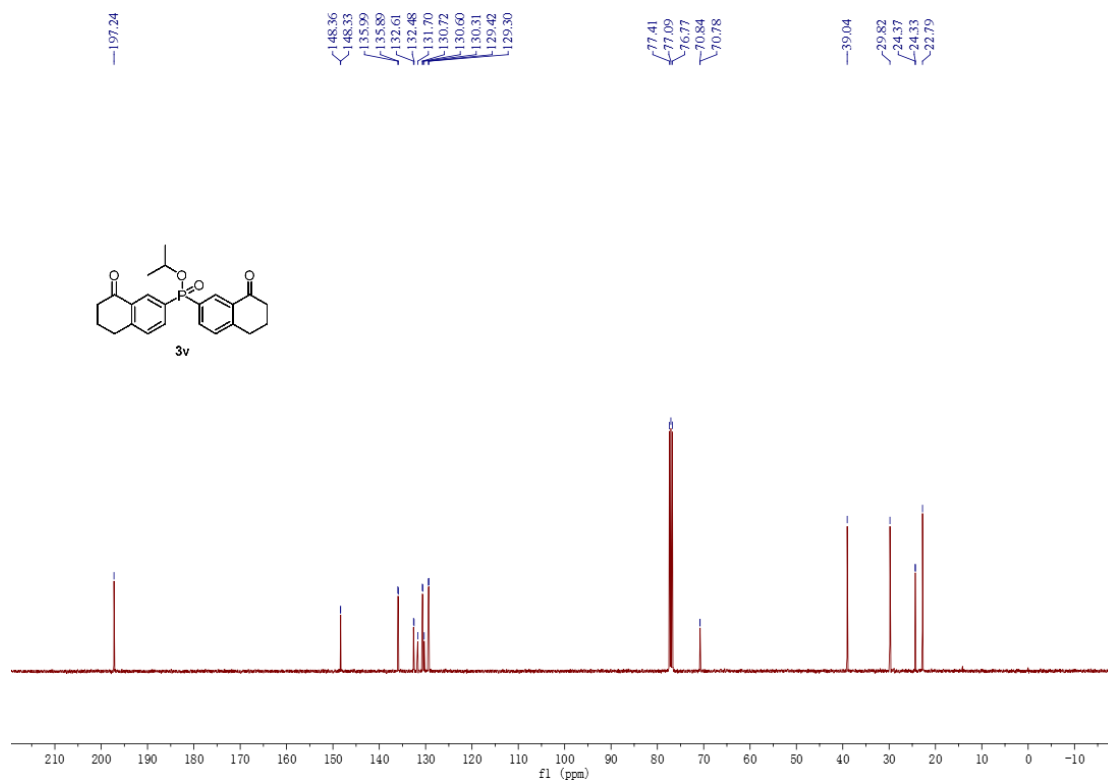
^{31}P NMR (121 MHz, CDCl_3) spectrum for 3u



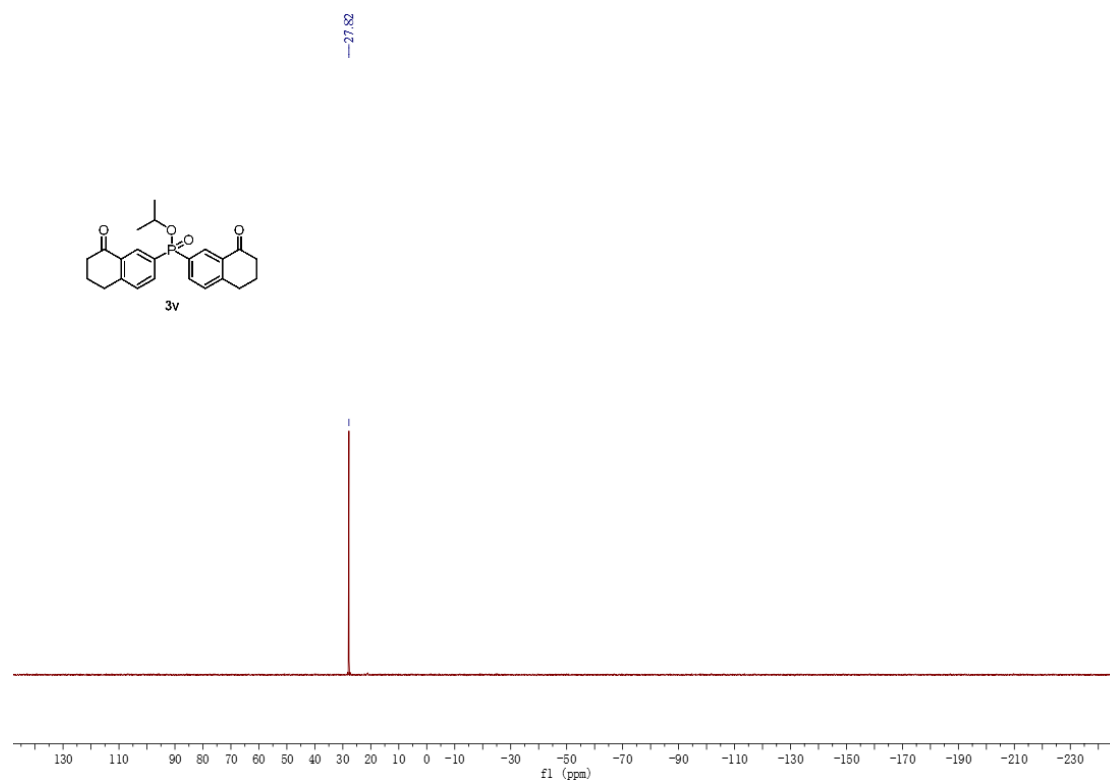
^1H NMR (400 MHz, CDCl_3) spectrum for 3v



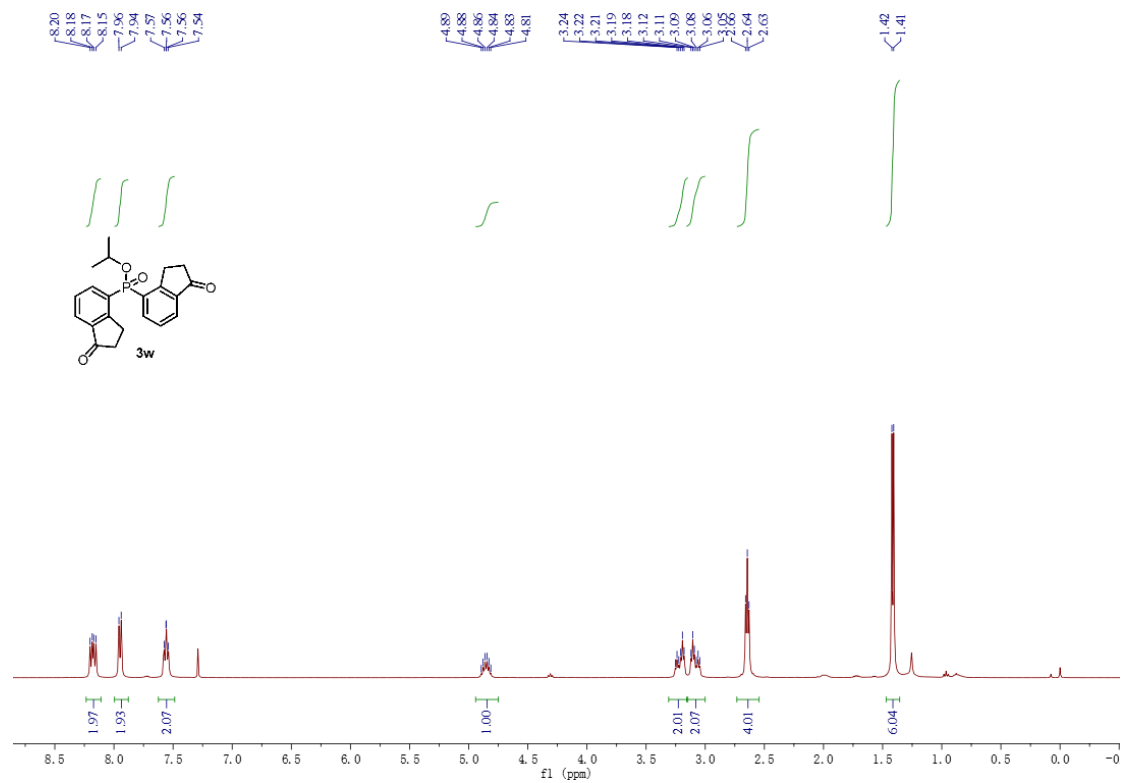
^{13}C NMR (101 MHz, CDCl_3) spectrum for 3v



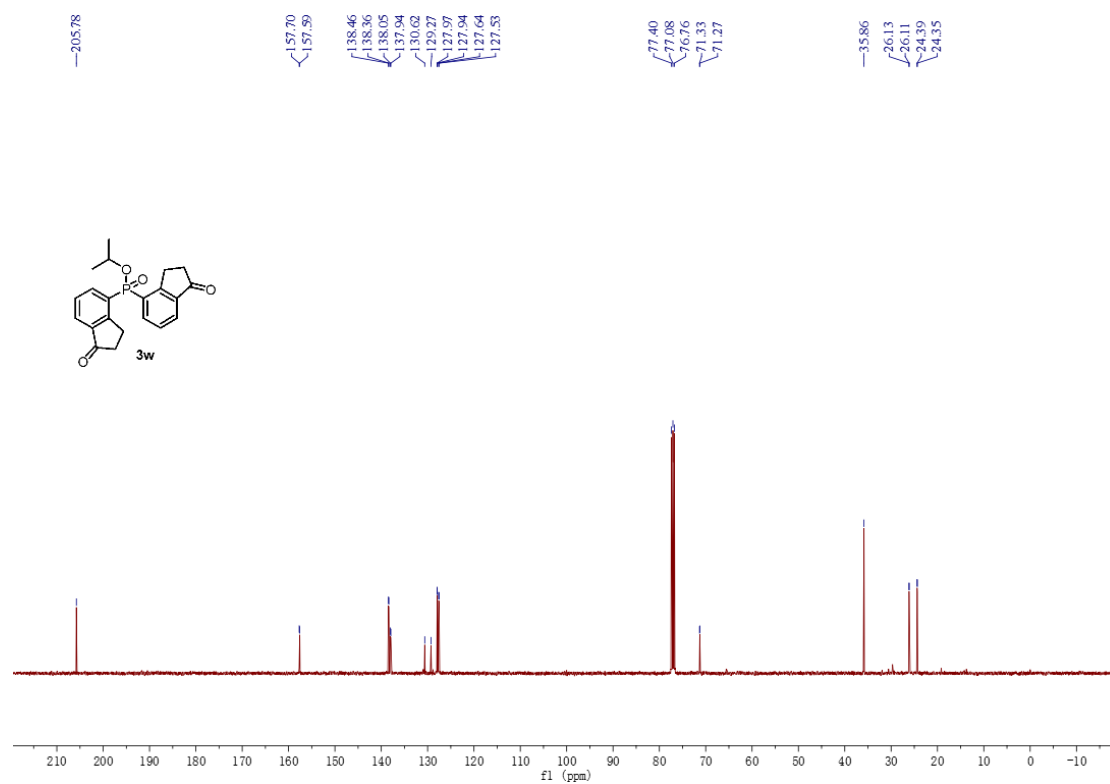
^{31}P NMR (121 MHz, CDCl_3) spectrum for 3v



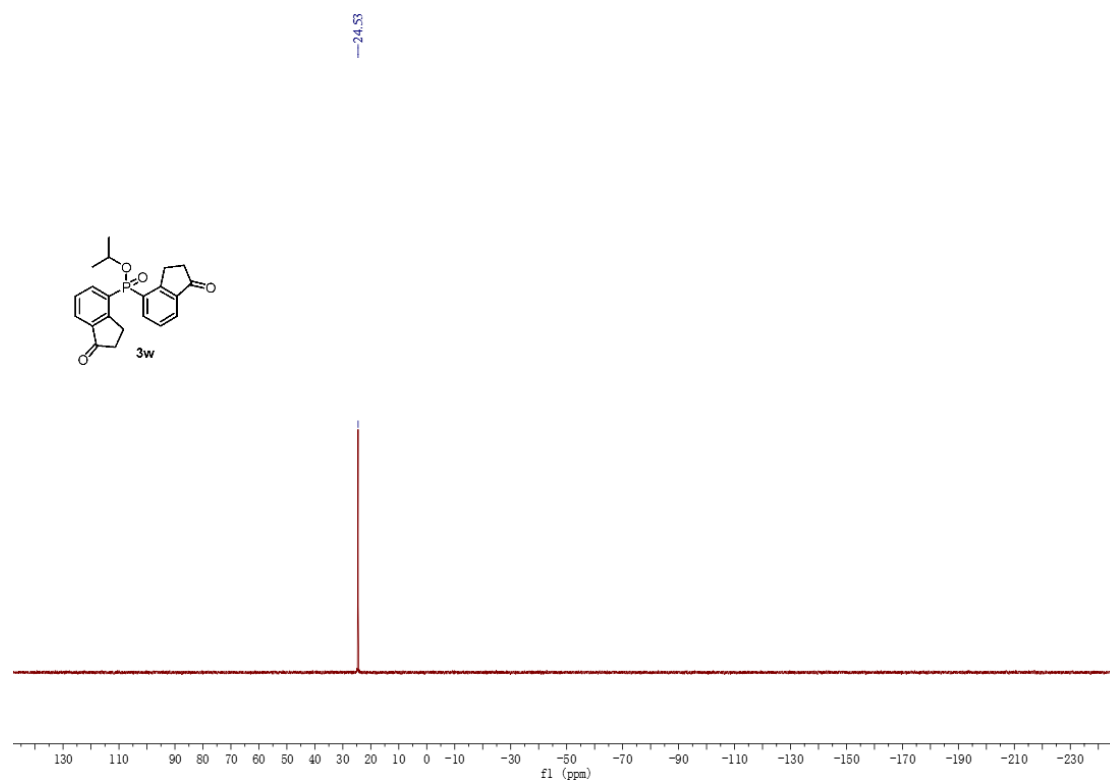
^1H NMR (400 MHz, CDCl_3) spectrum for 3w



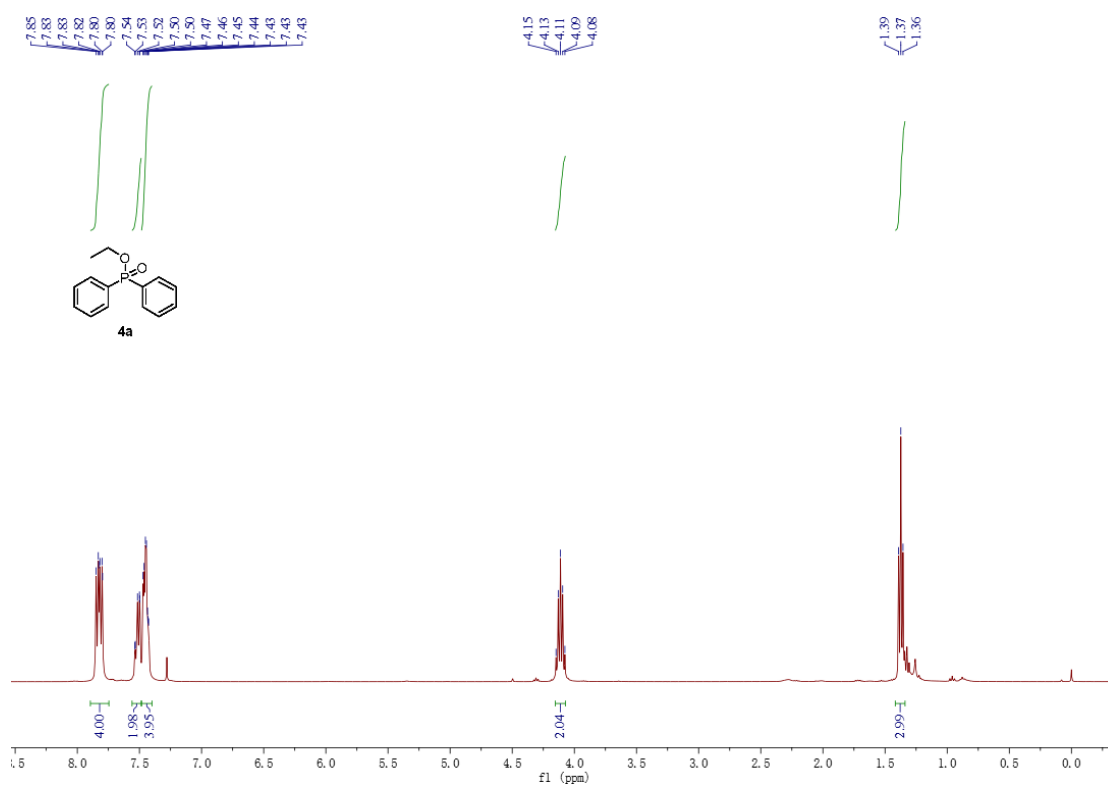
^{13}C NMR (101 MHz, CDCl_3) spectrum for 3w



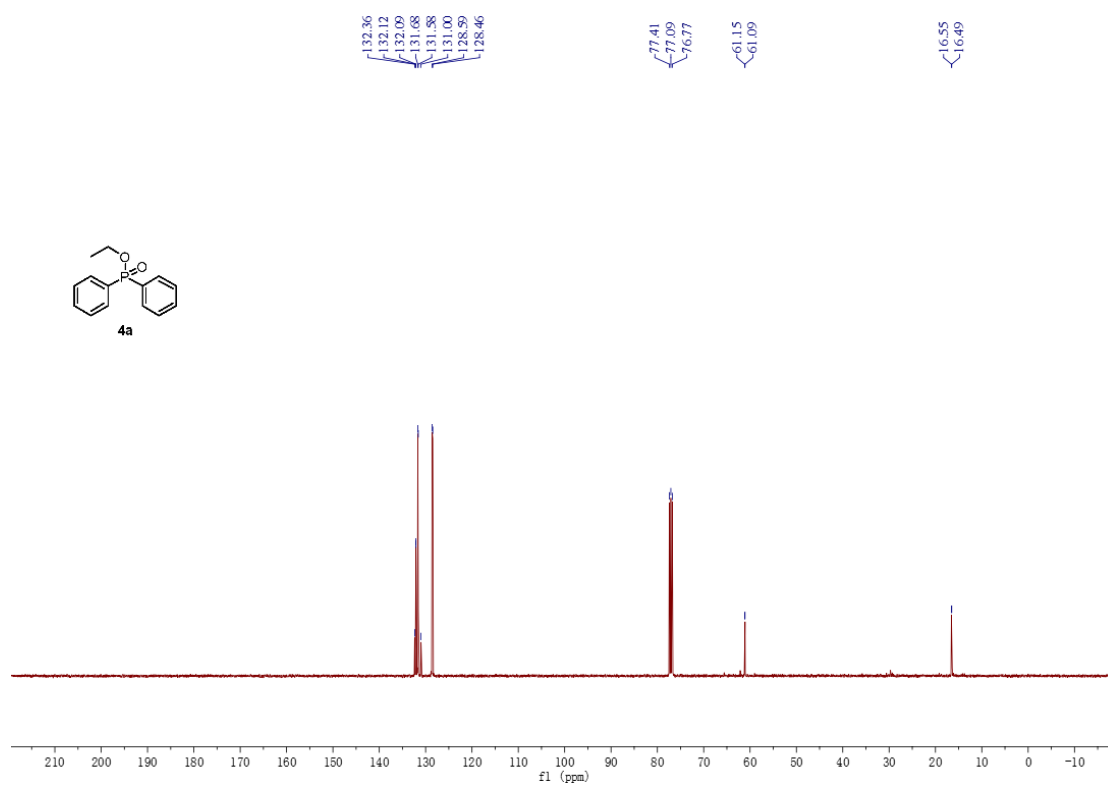
^{31}P NMR (121 MHz, CDCl_3) spectrum for 3w



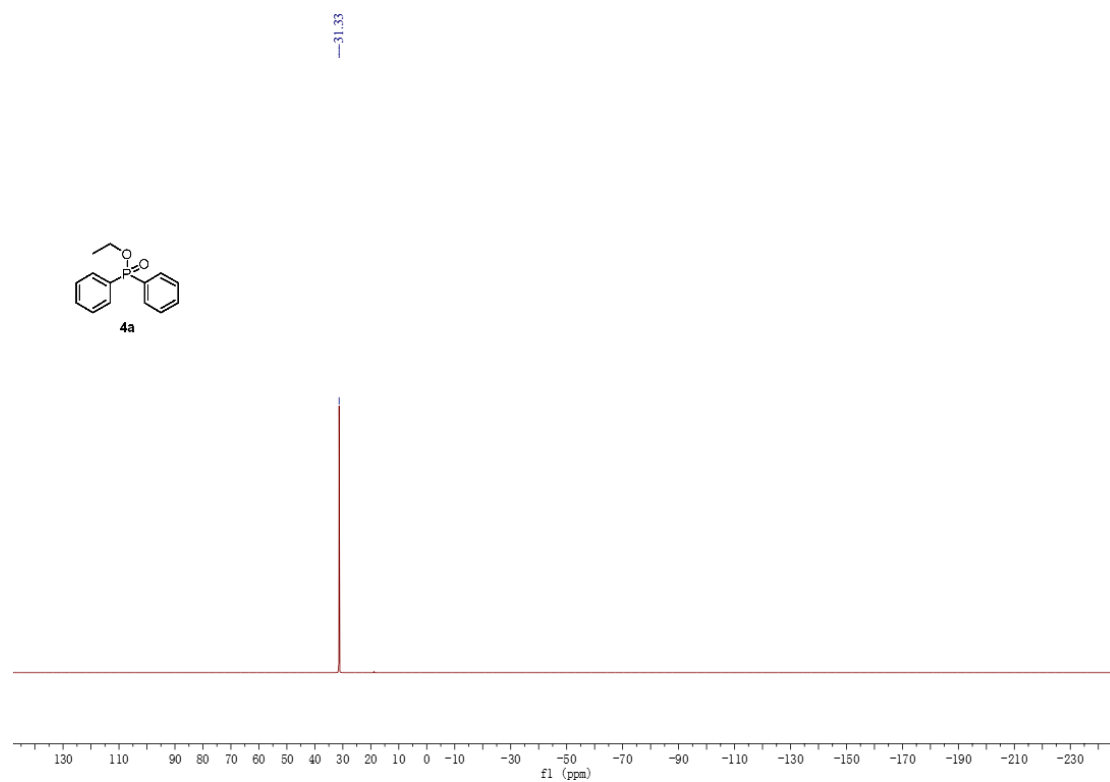
^1H NMR (400 MHz, CDCl_3) spectrum for 4a



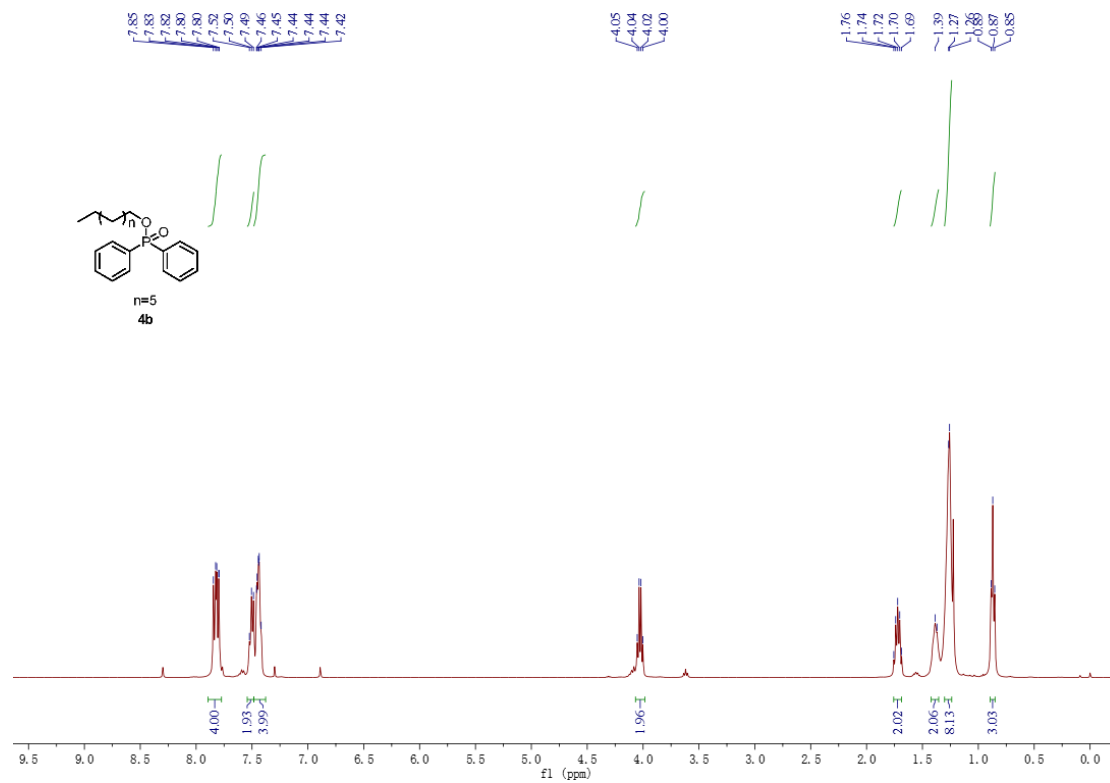
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4a



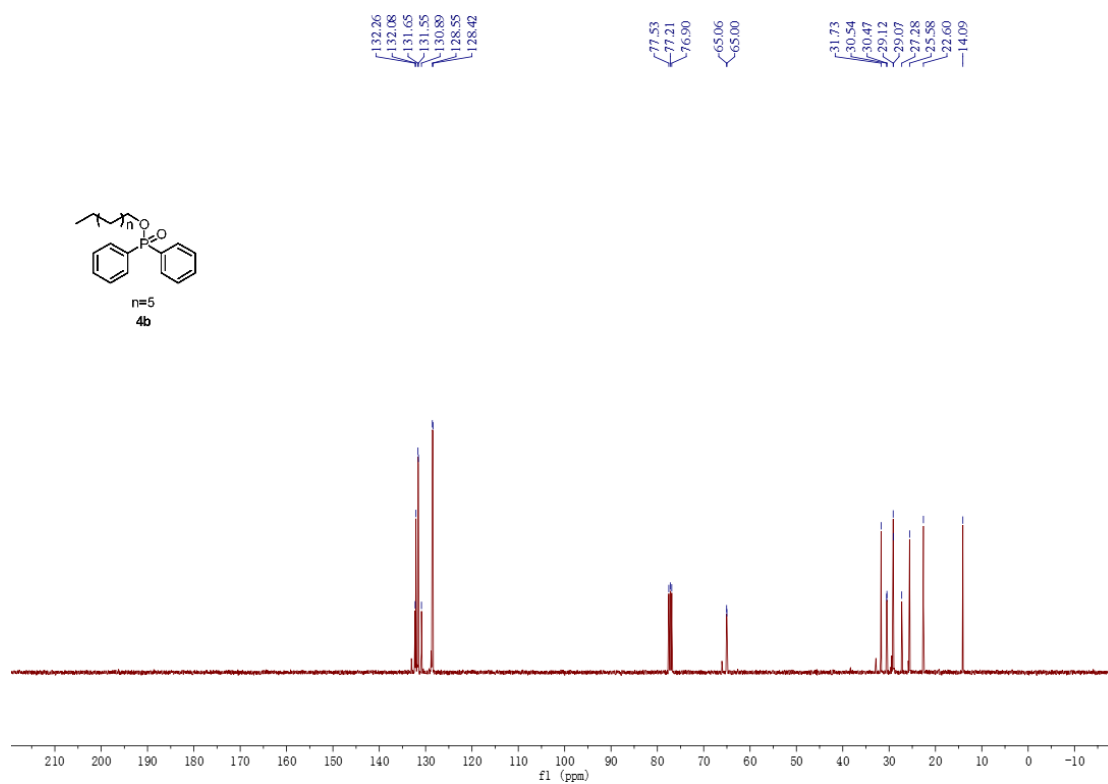
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4a



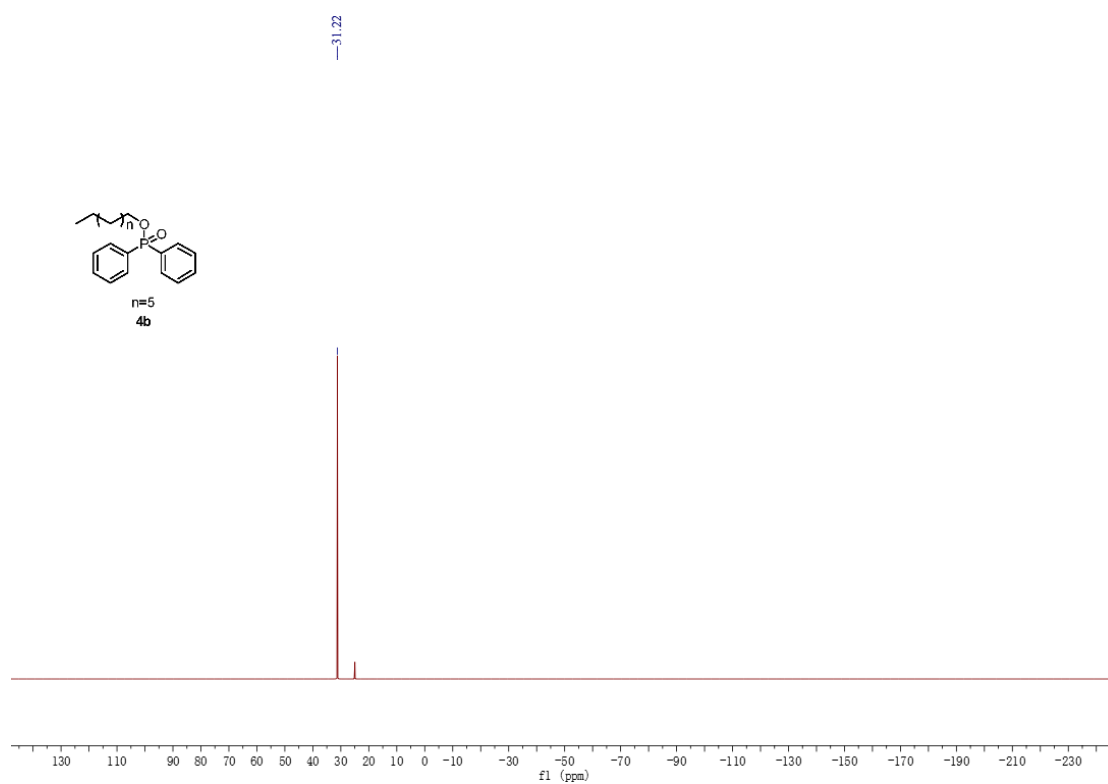
^1H NMR (400 MHz, CDCl_3) spectrum for 4b



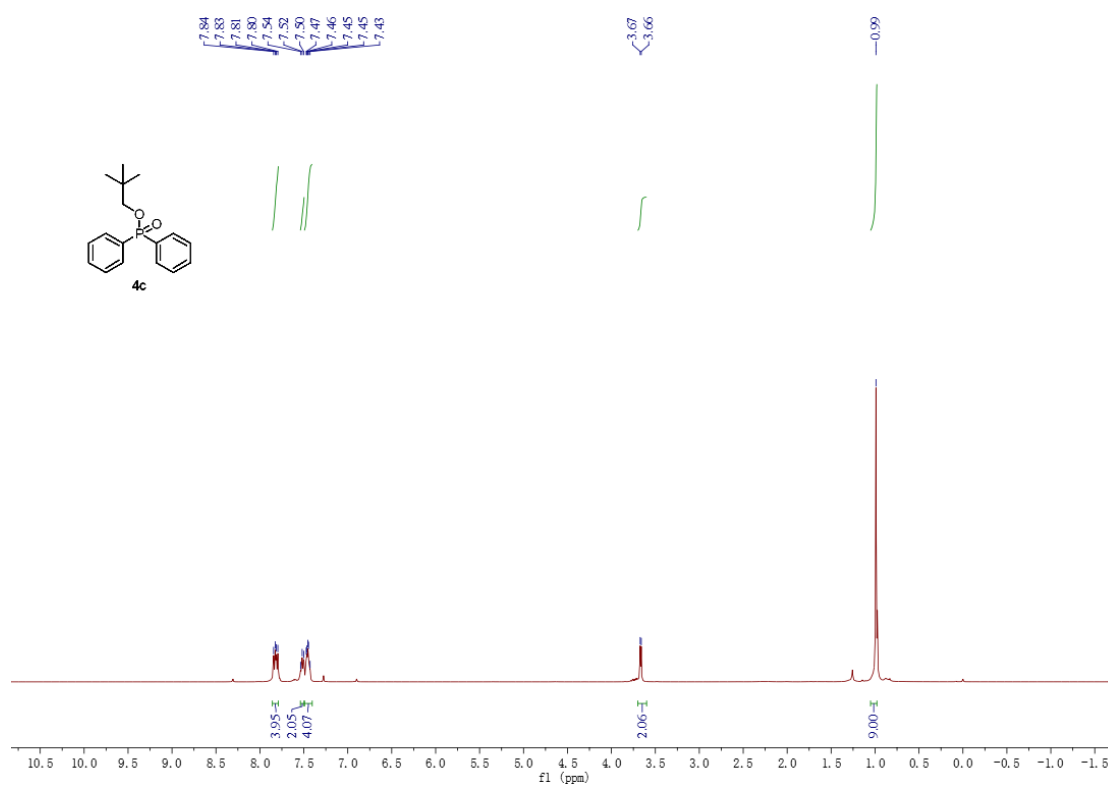
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4b



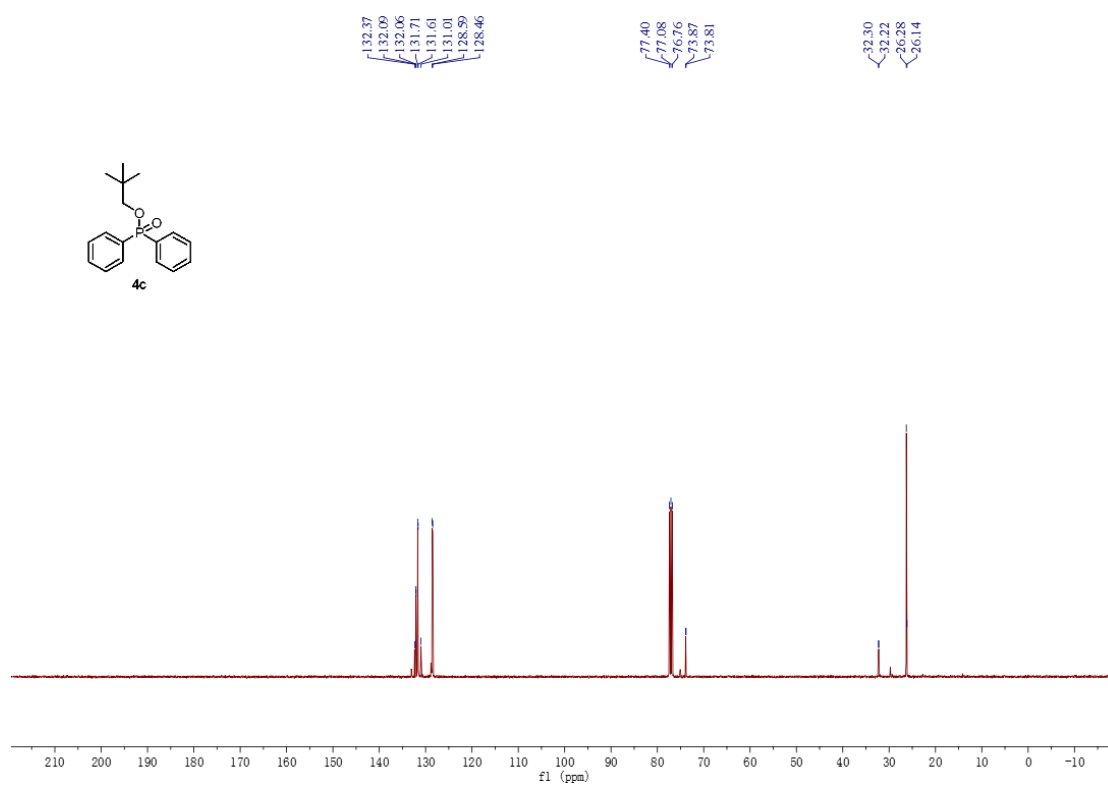
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4b



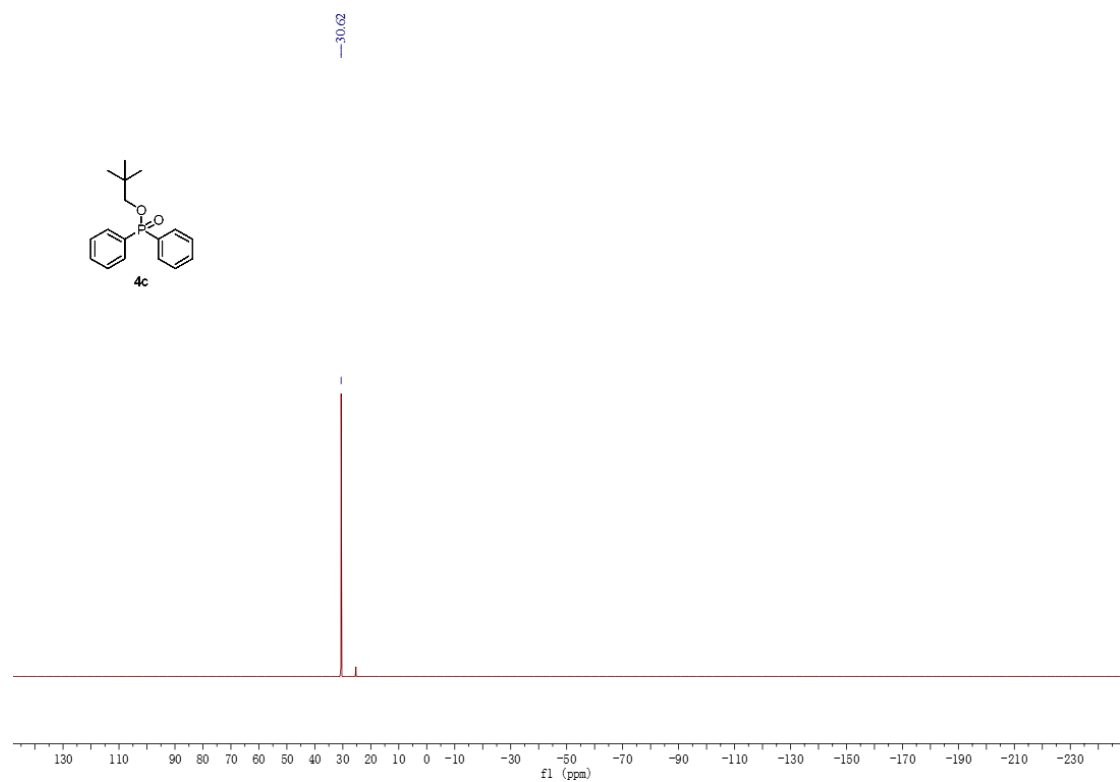
^1H NMR (400 MHz, CDCl_3) spectrum for 4c



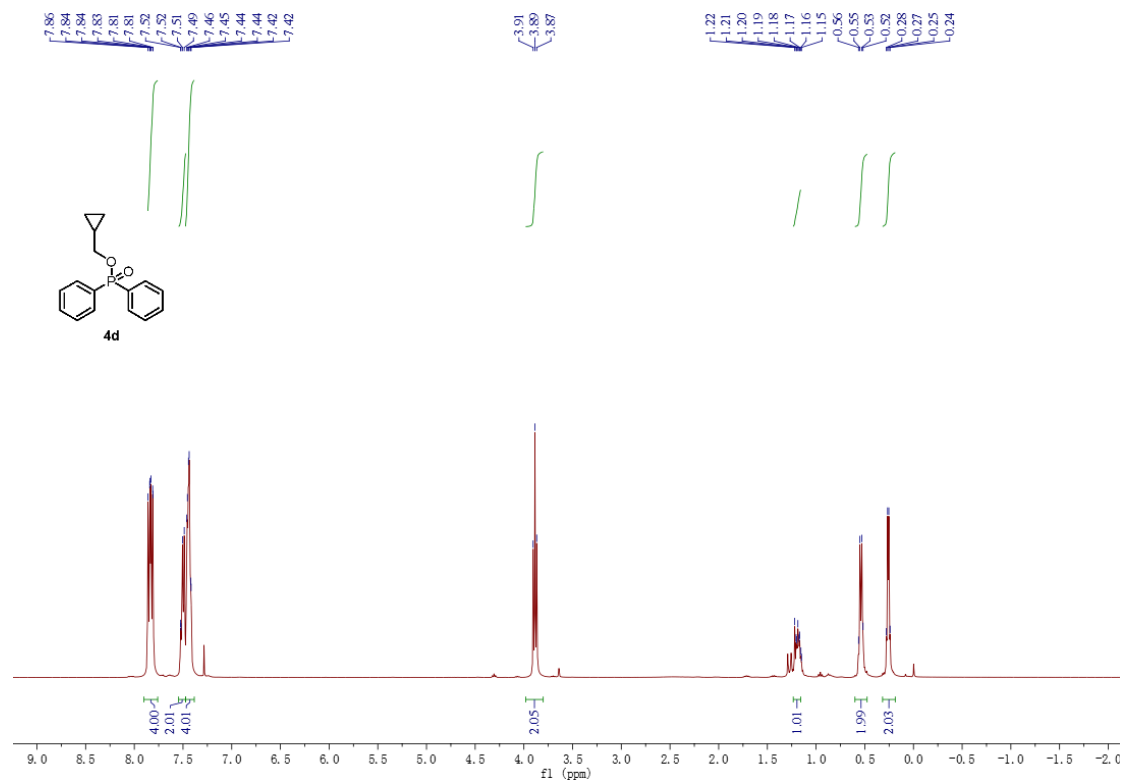
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4c



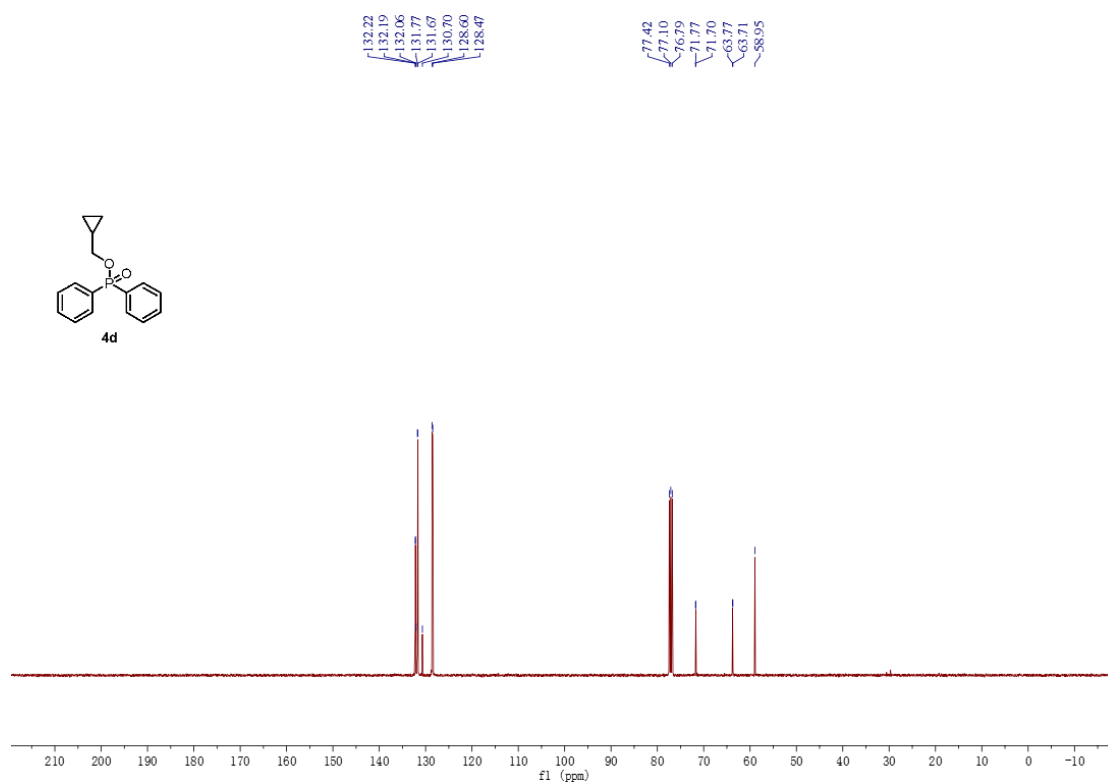
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4c



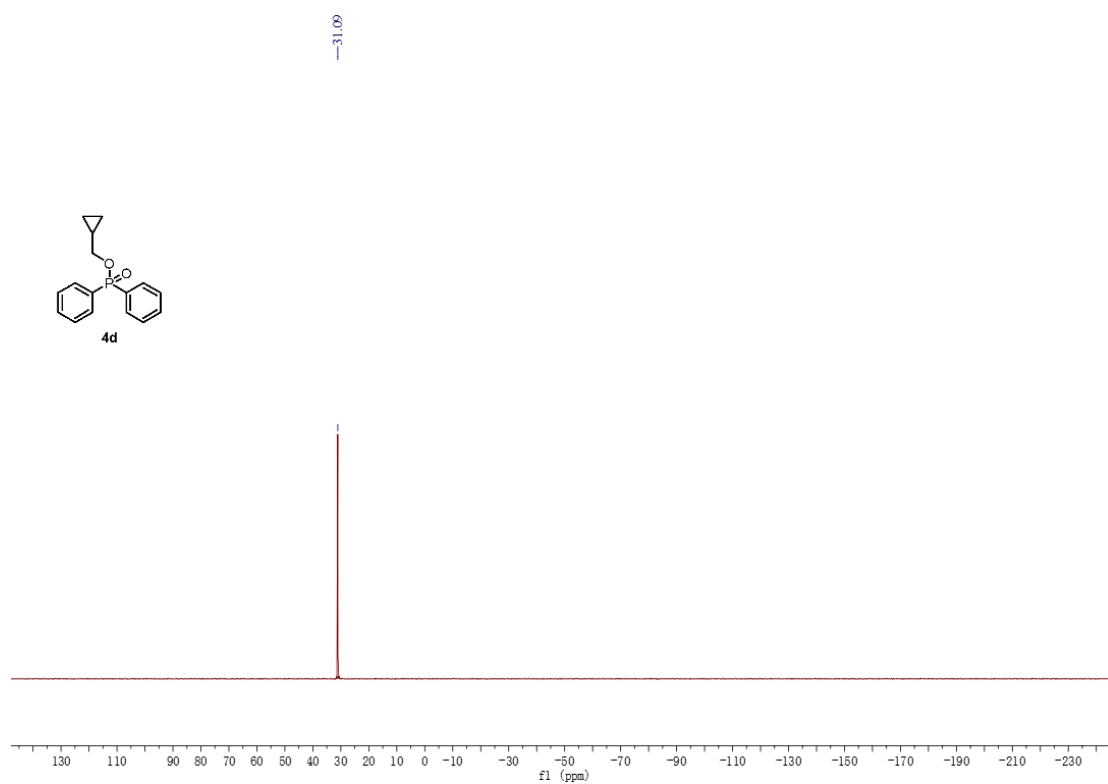
^1H NMR (400 MHz, CDCl_3) spectrum for 4d



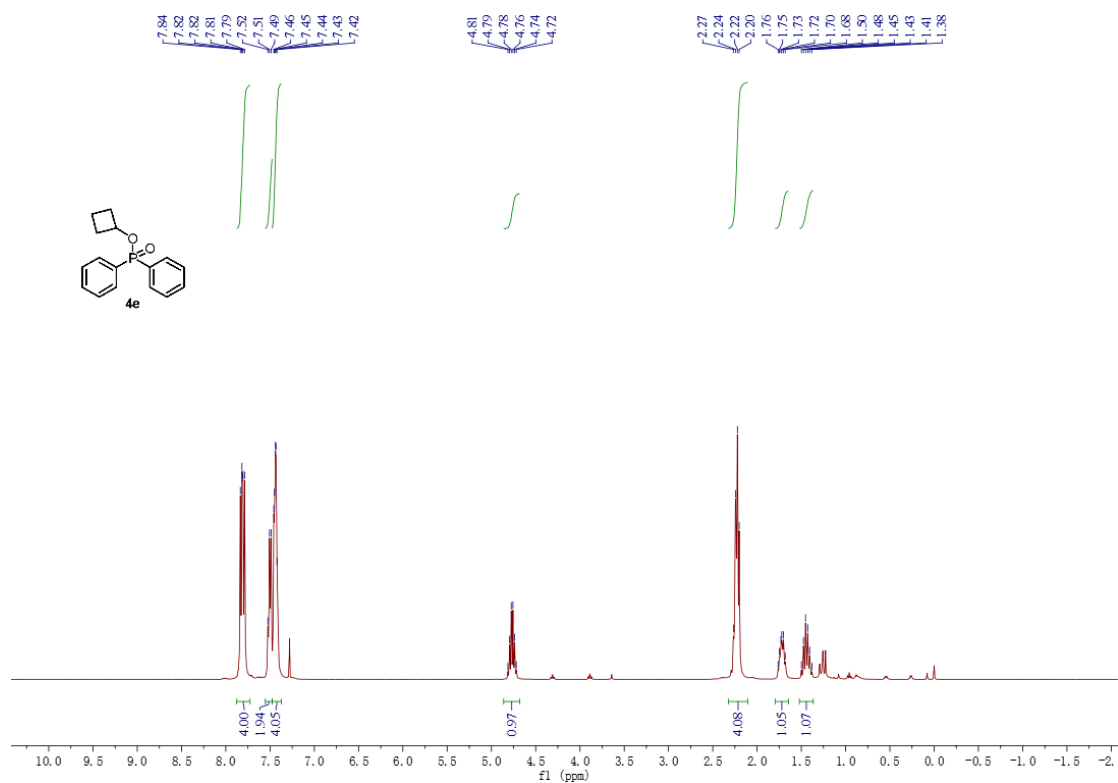
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4d



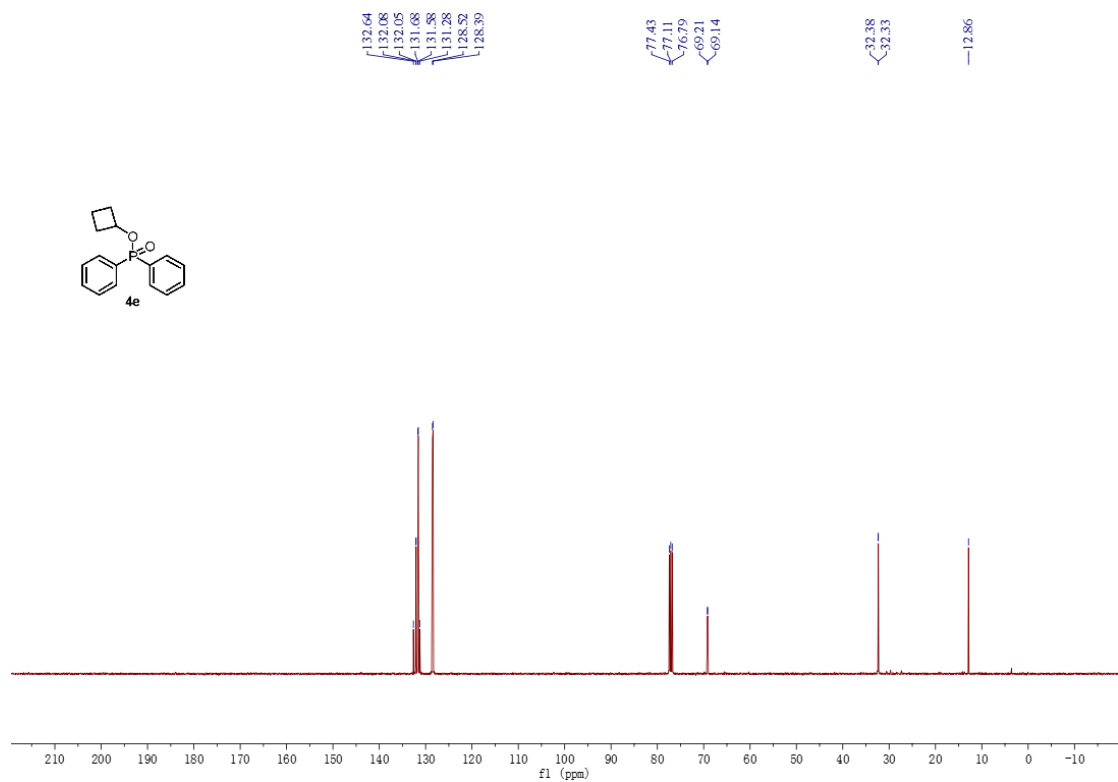
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4d



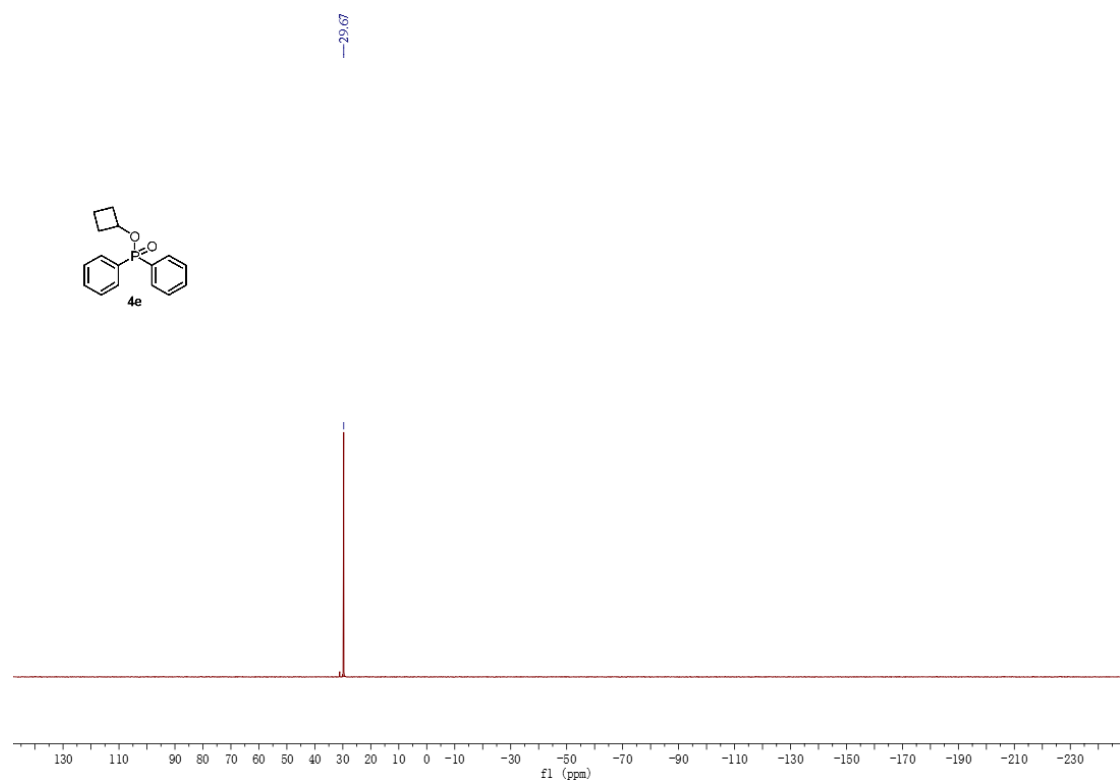
^1H NMR (400 MHz, CDCl_3) spectrum for 4e



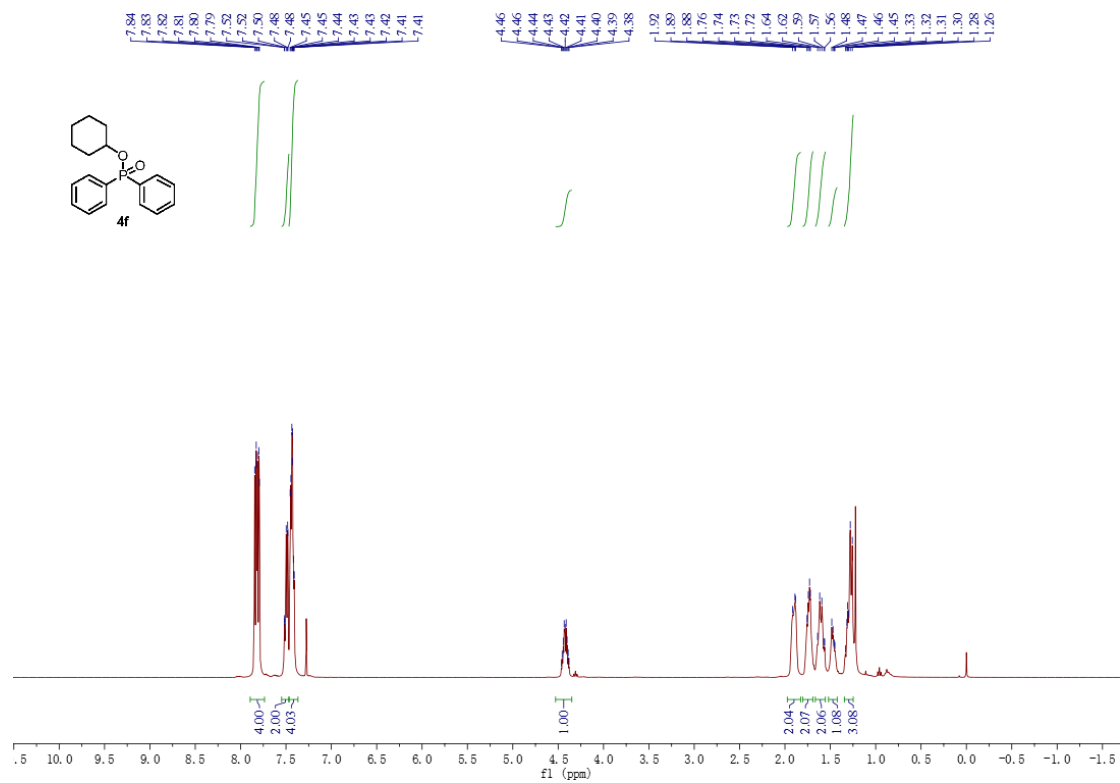
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4e



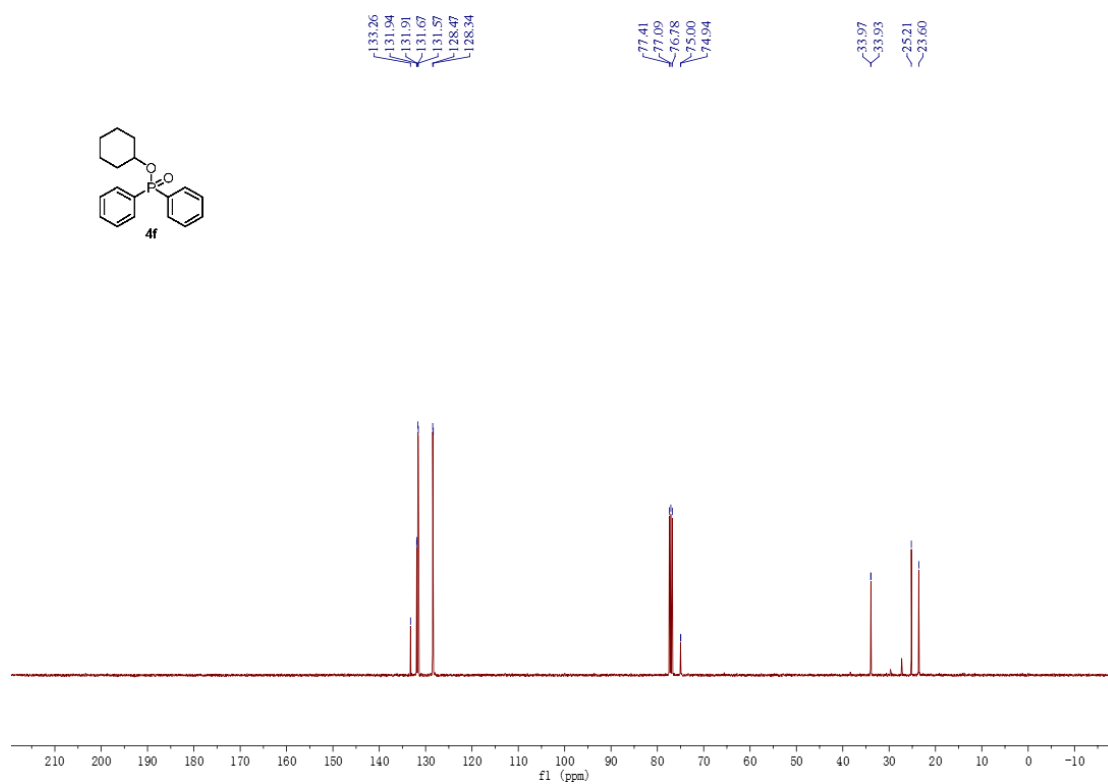
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4e



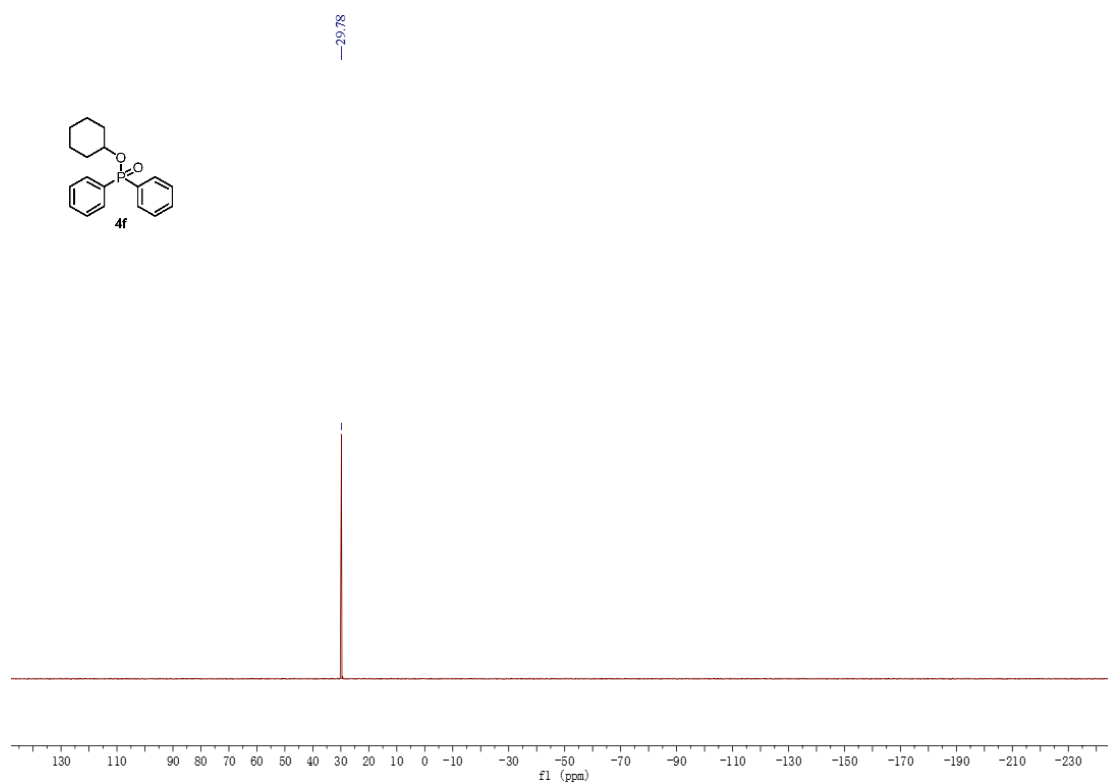
^1H NMR (400 MHz, CDCl_3) spectrum for 4f



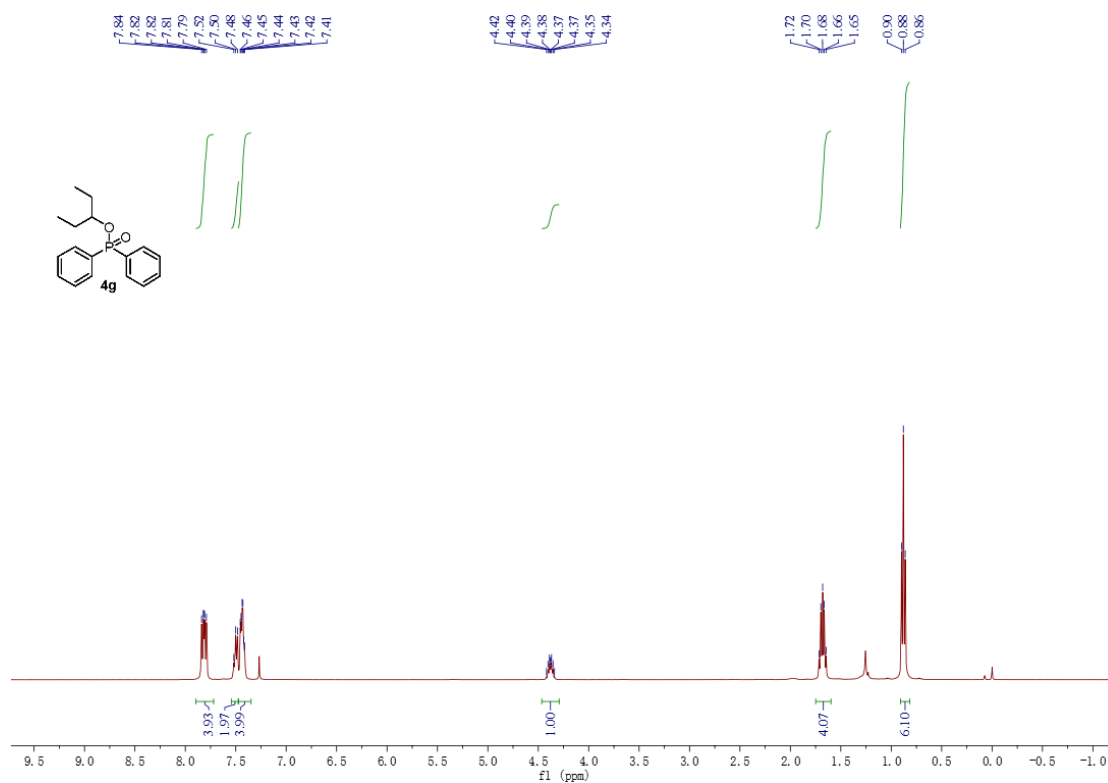
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4f



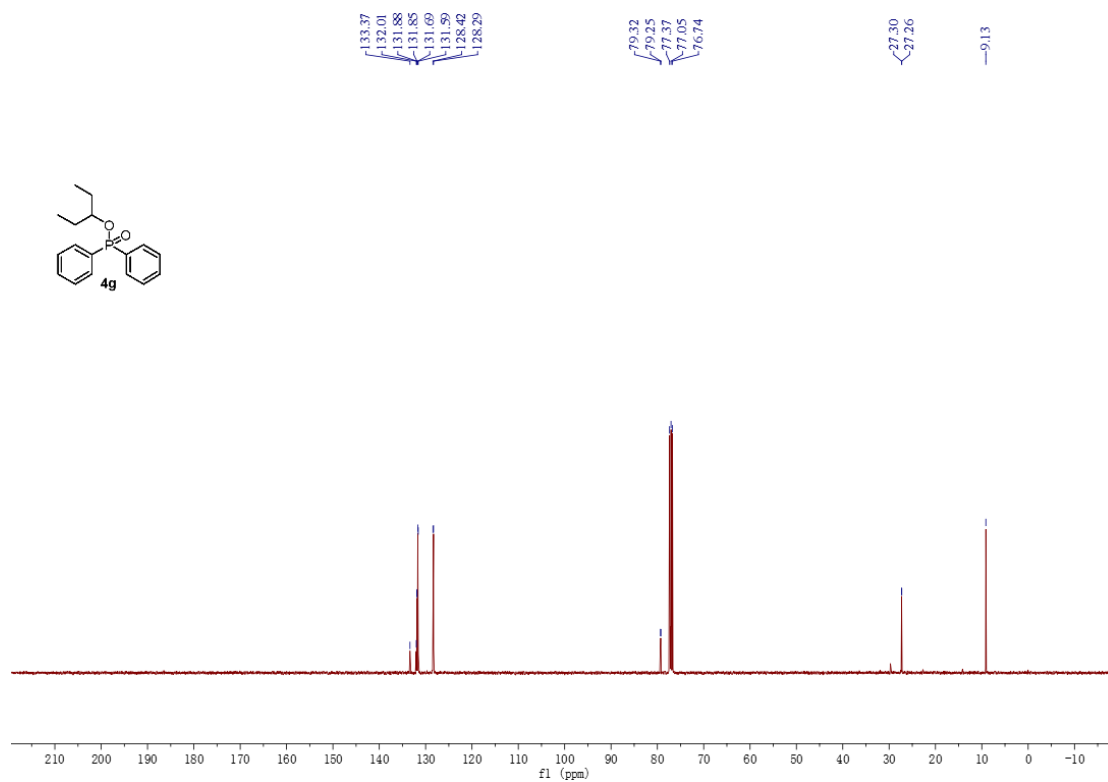
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4f



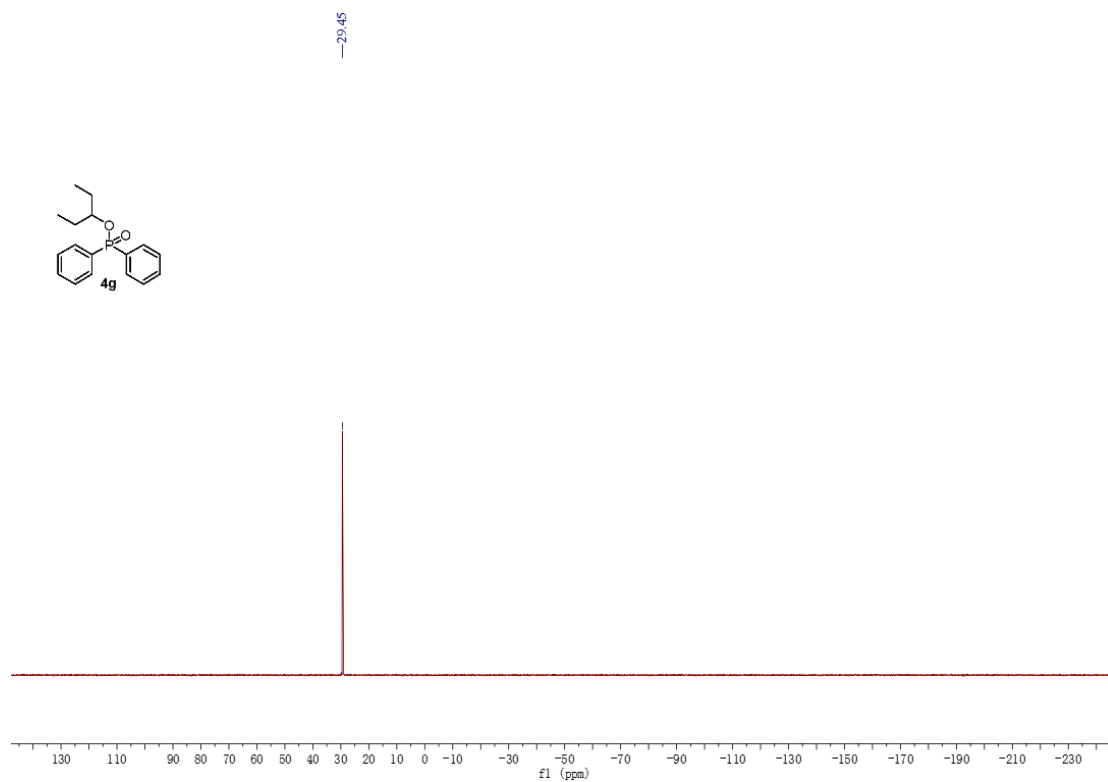
^1H NMR (400 MHz, CDCl_3) spectrum for 4g



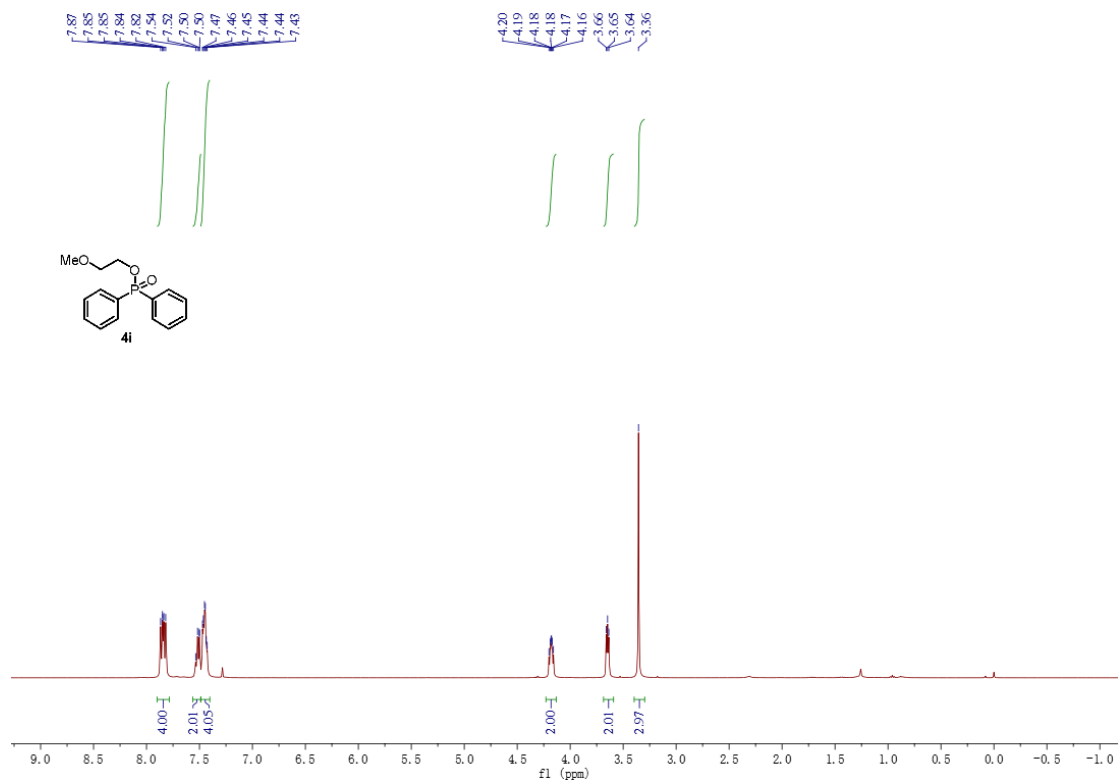
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4g



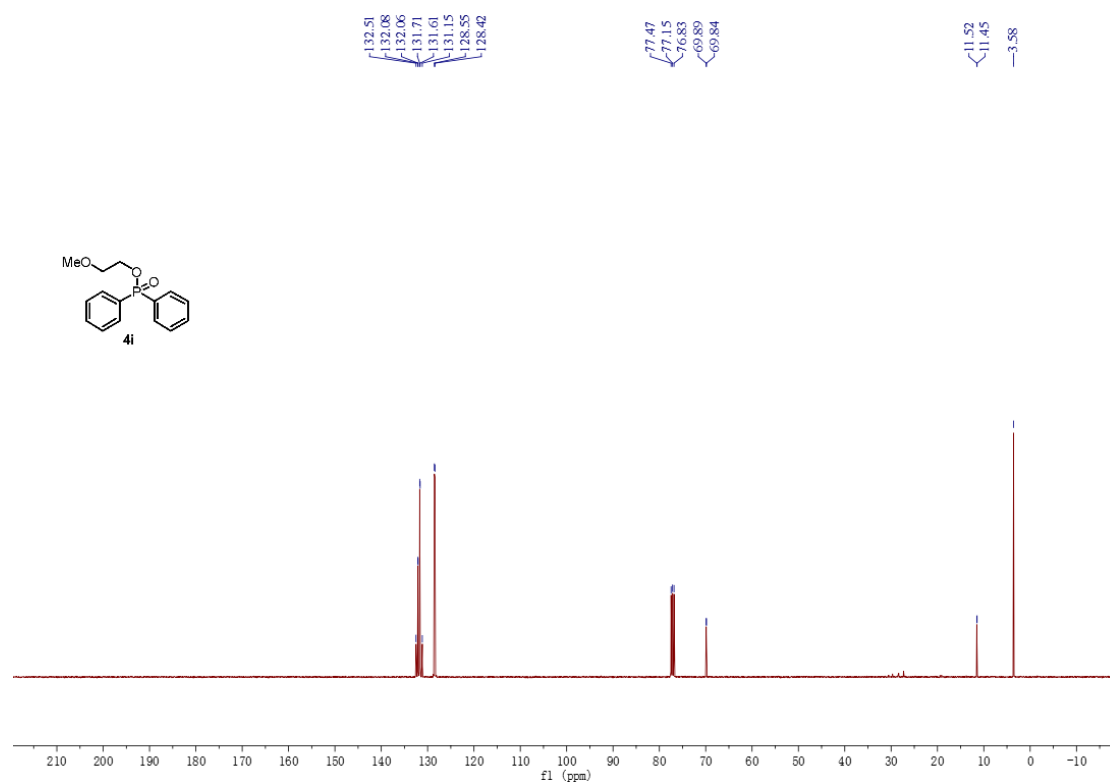
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4g



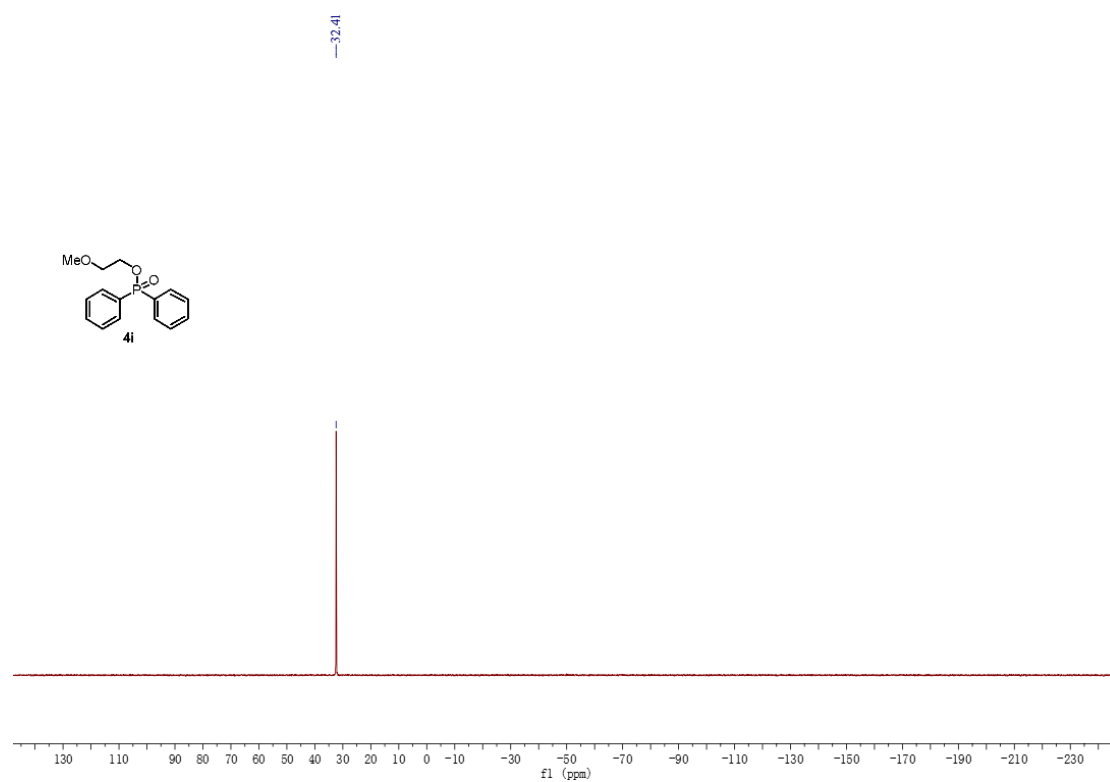
^1H NMR (400 MHz, CDCl_3) spectrum for 4i



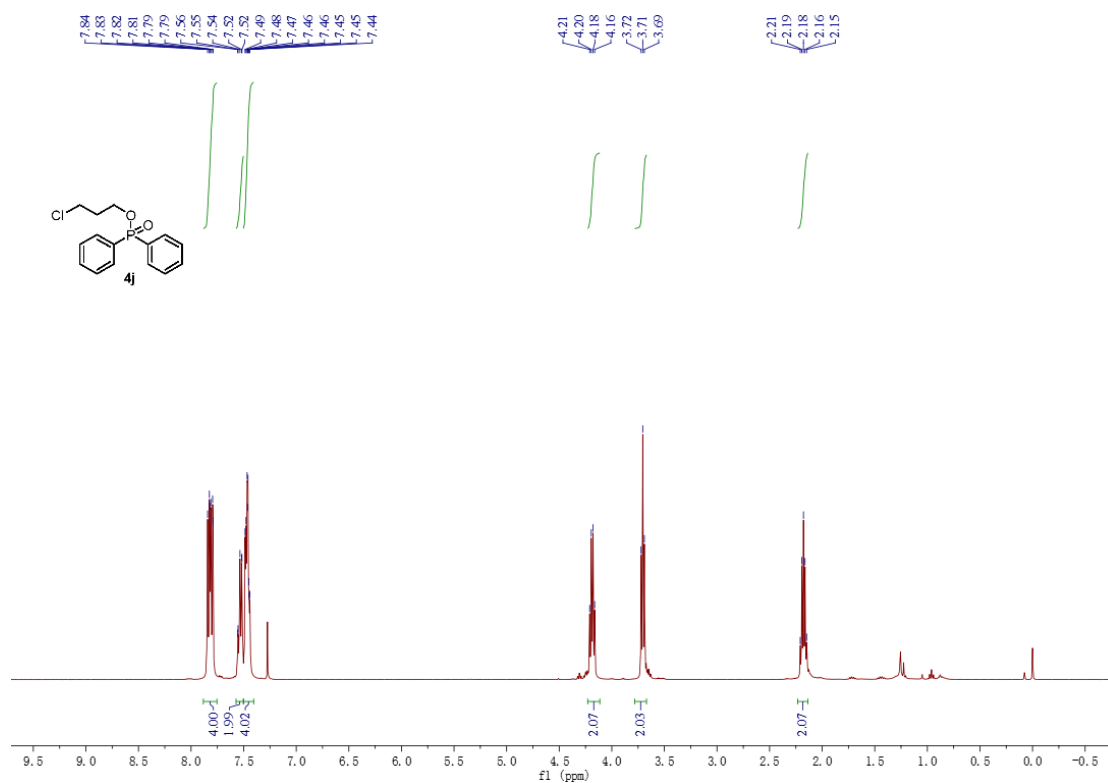
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4i



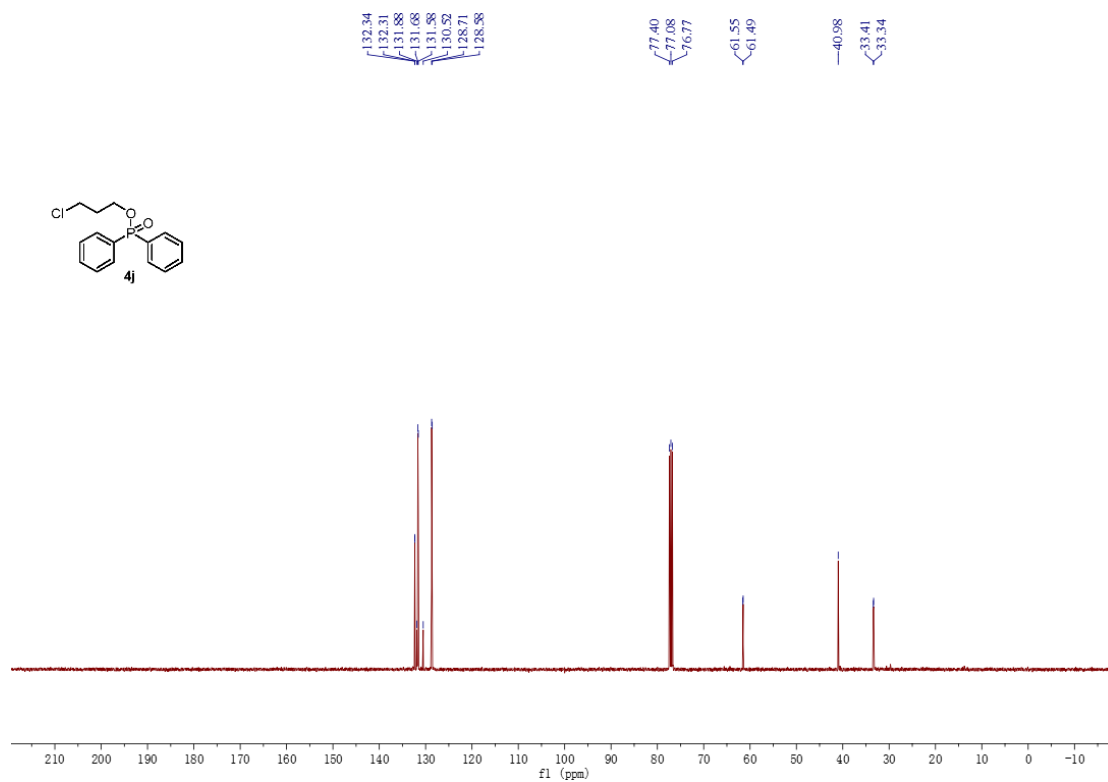
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4i



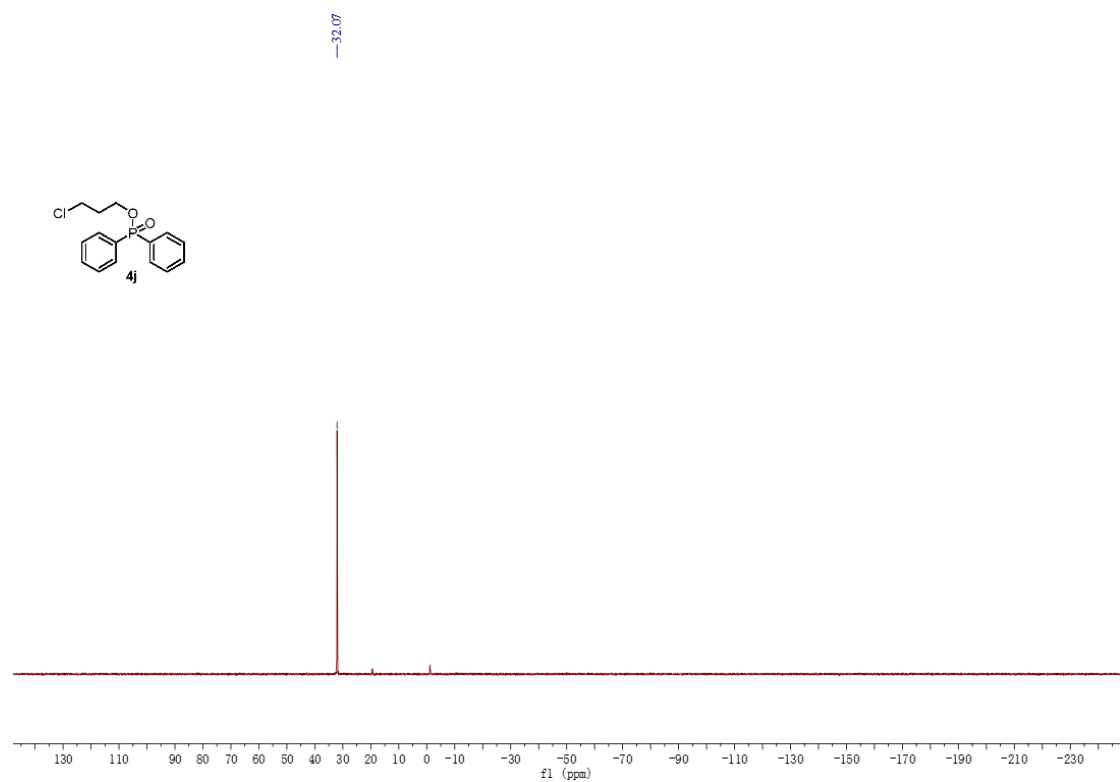
^1H NMR (400 MHz, CDCl_3) spectrum for 4j



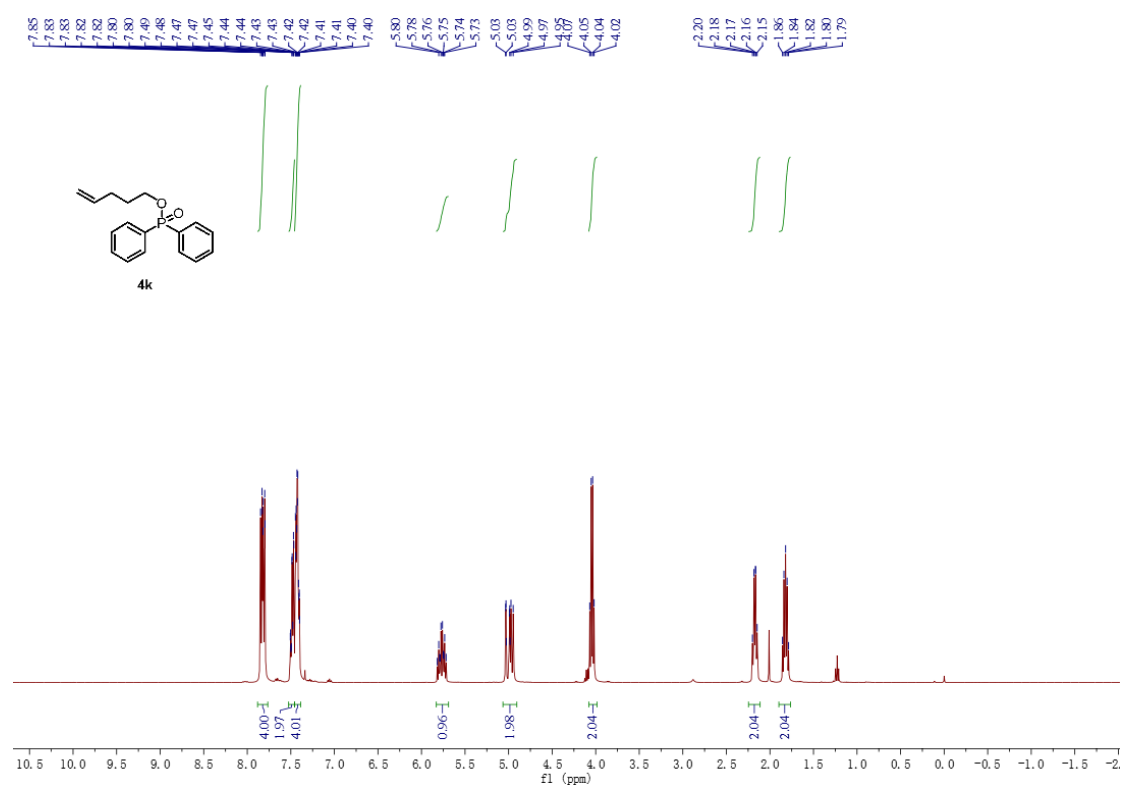
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4j



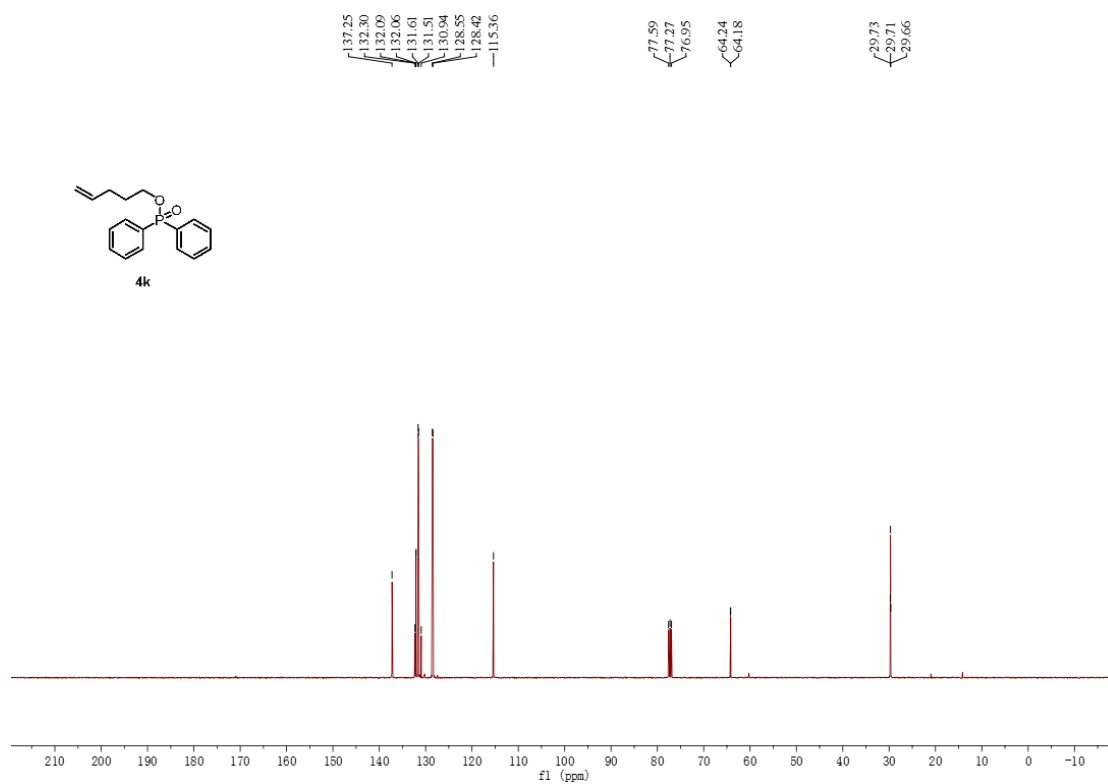
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4j



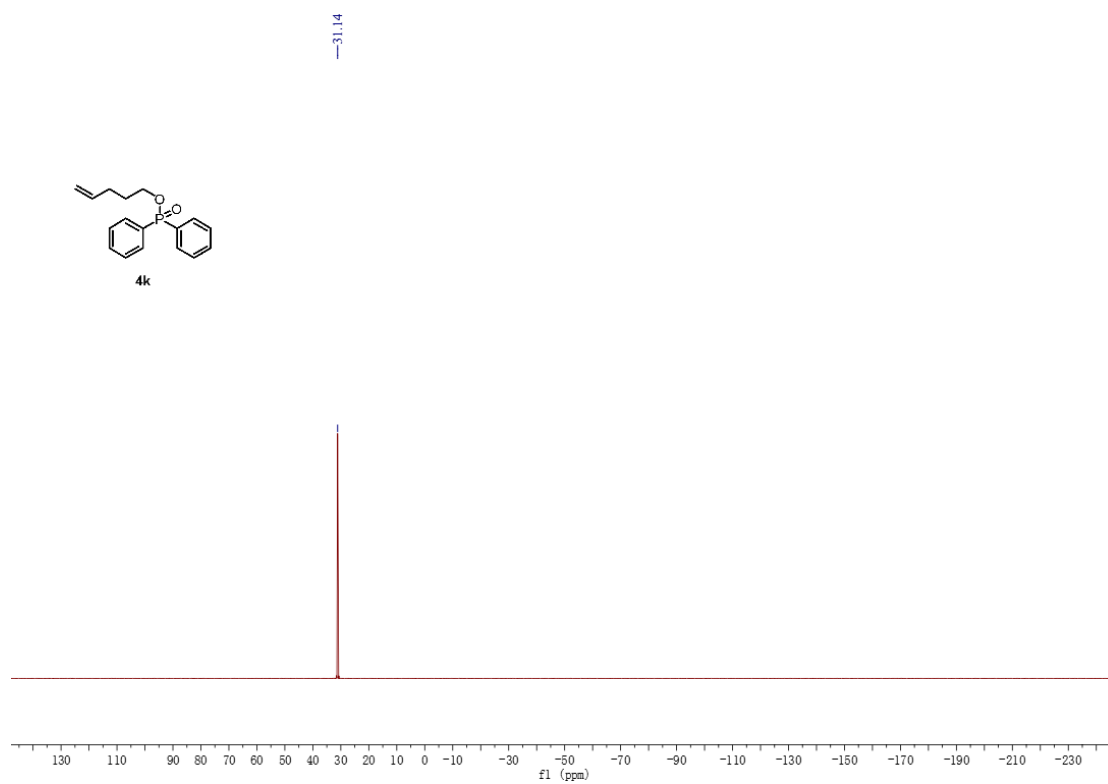
^1H NMR (400 MHz, CDCl_3) spectrum for 4k



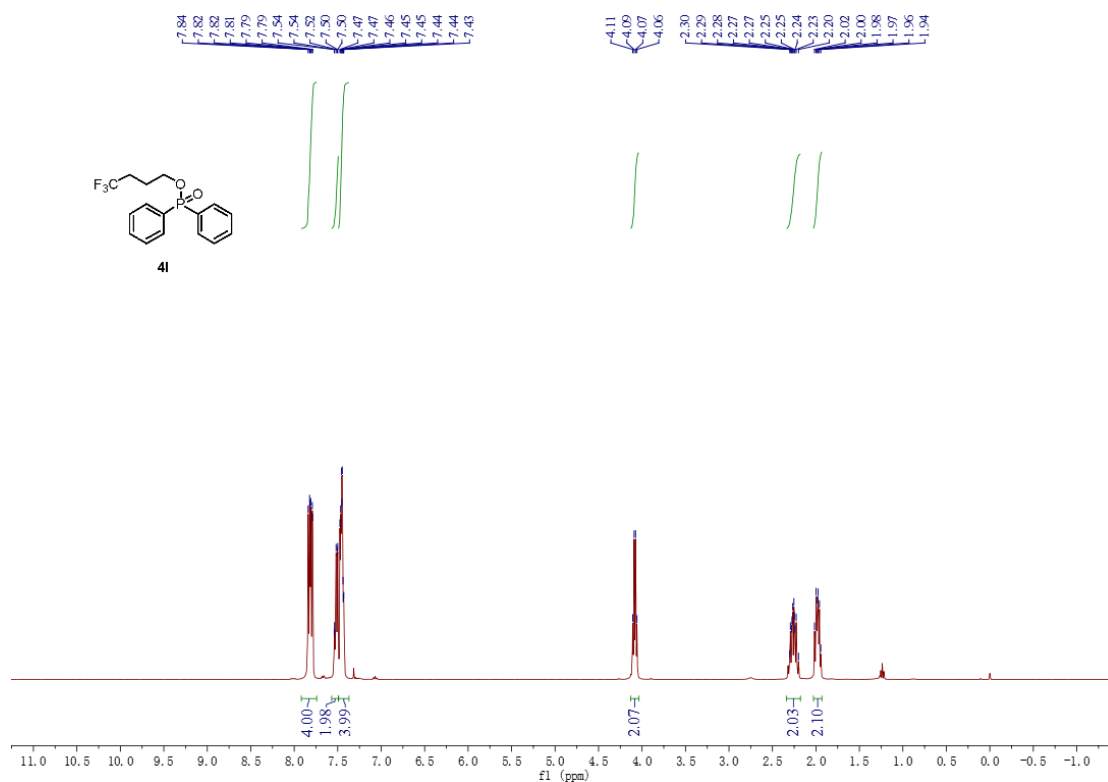
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4k



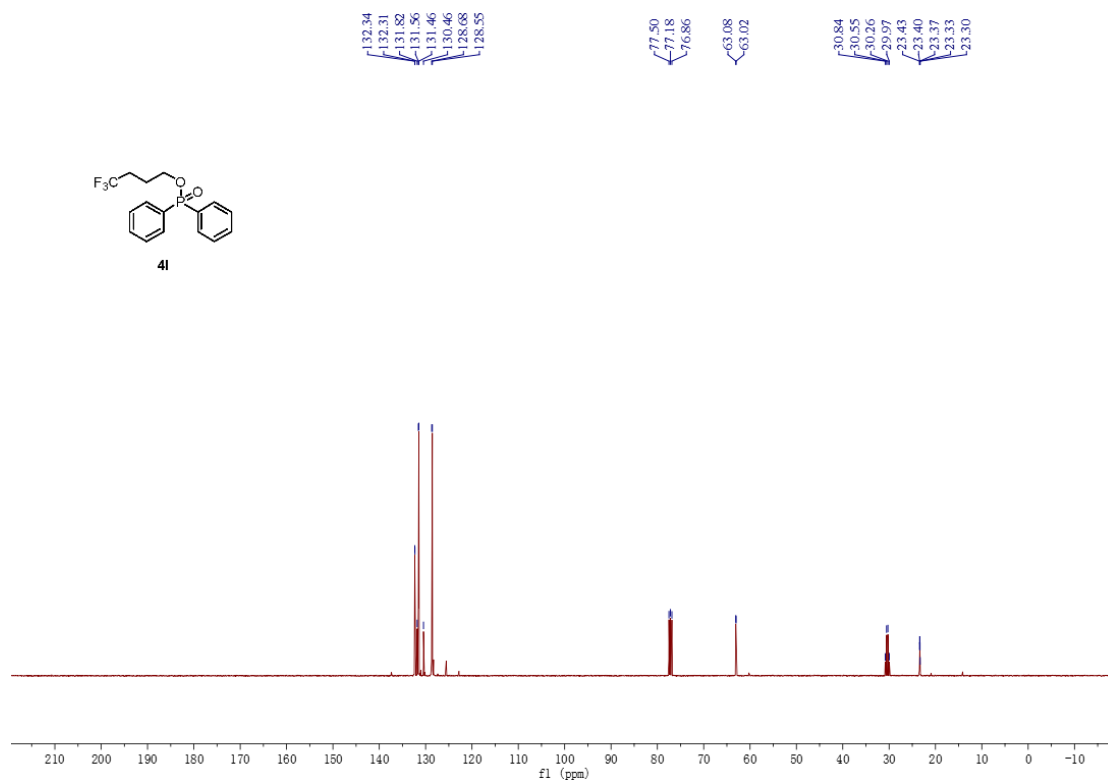
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4k



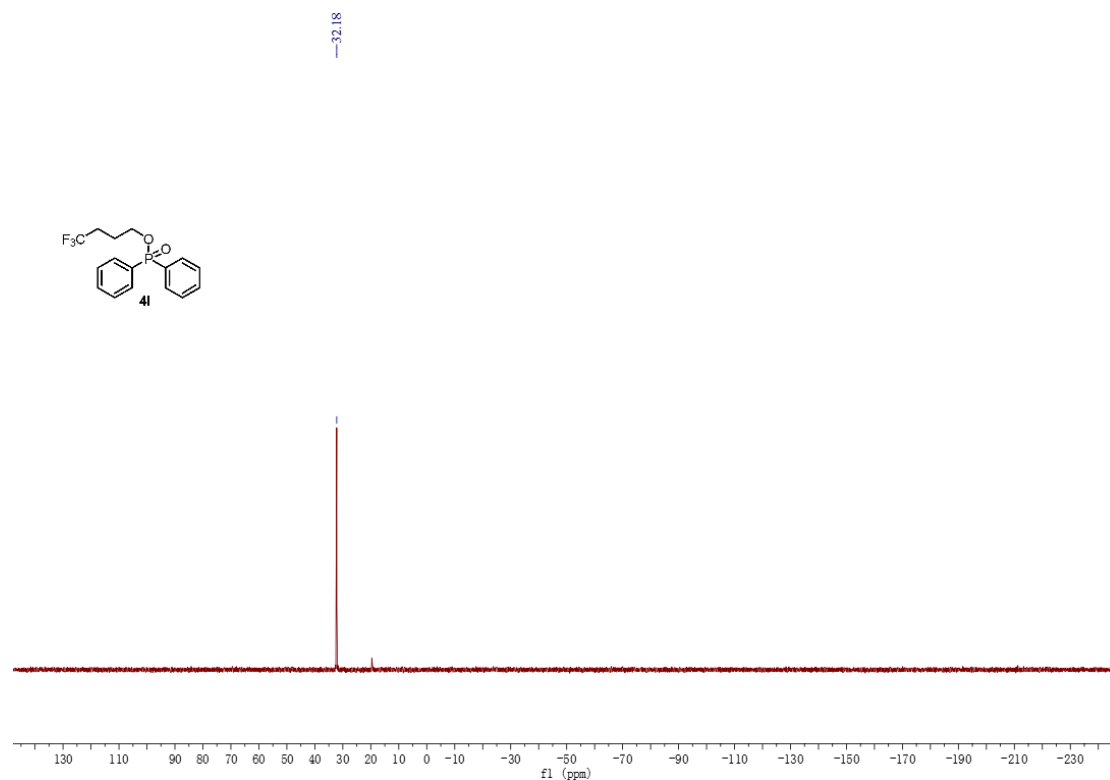
^1H NMR (400 MHz, CDCl_3) spectrum for 4l



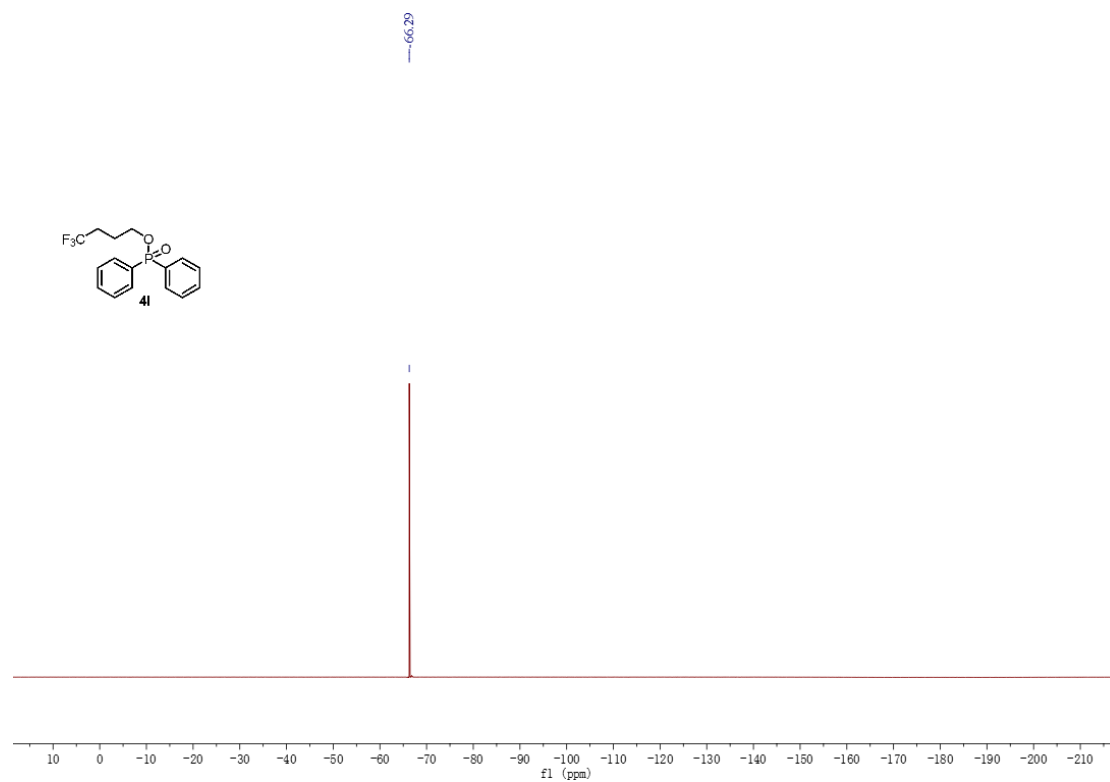
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4l



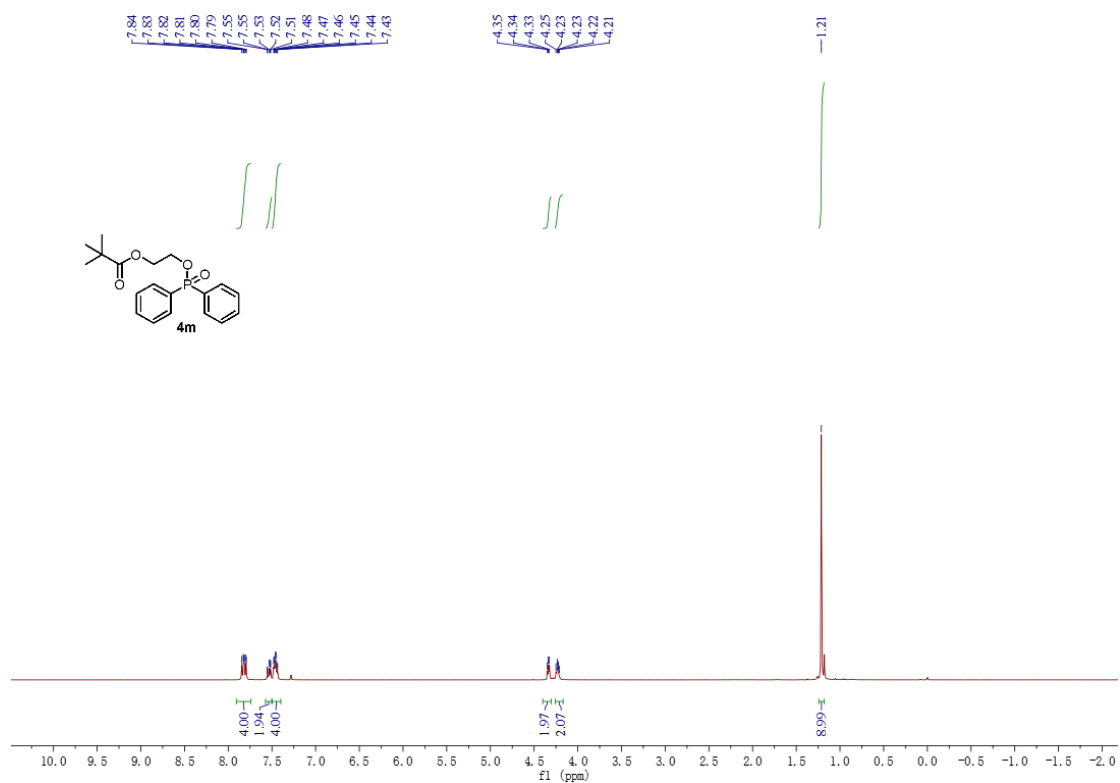
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4l



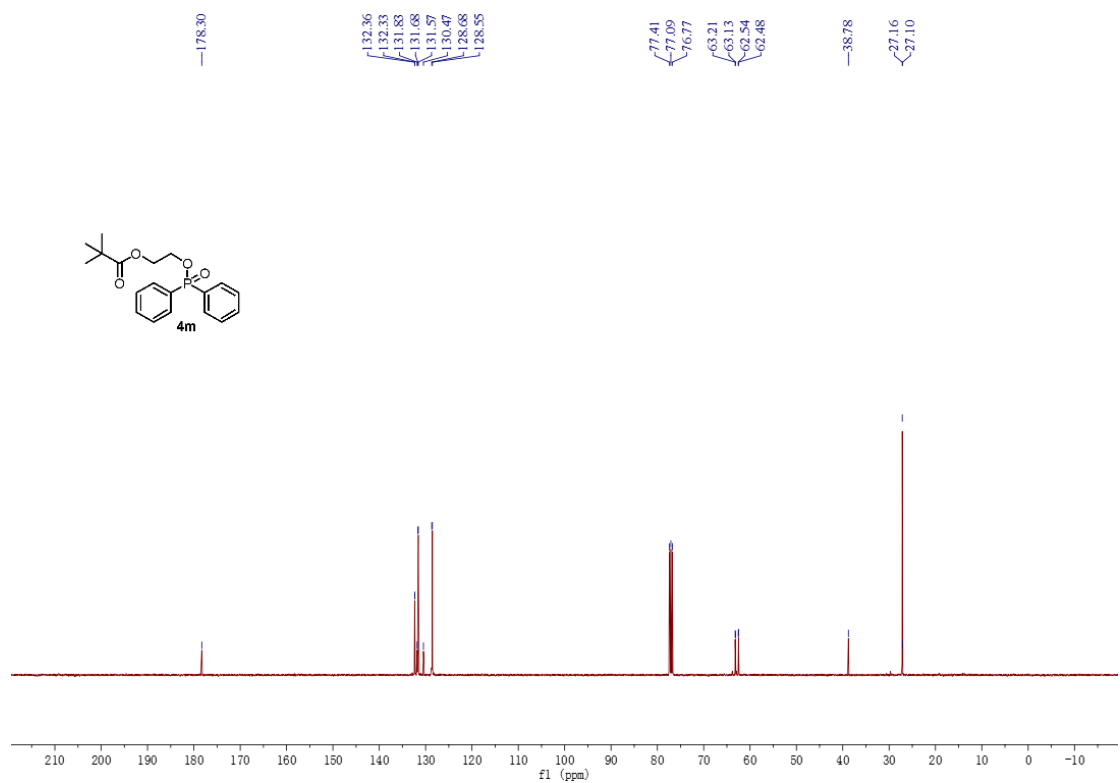
^{19}F NMR (282 MHz, CDCl_3) spectrum for 4l



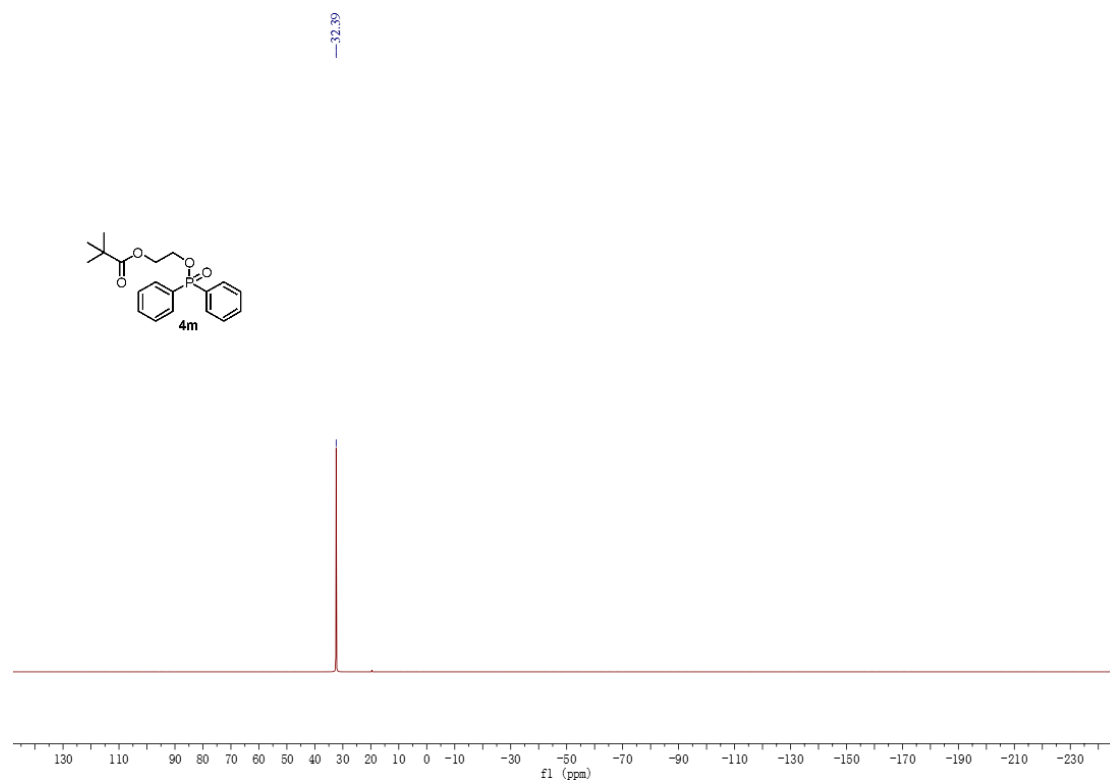
^1H NMR (400 MHz, CDCl_3) spectrum for 4m



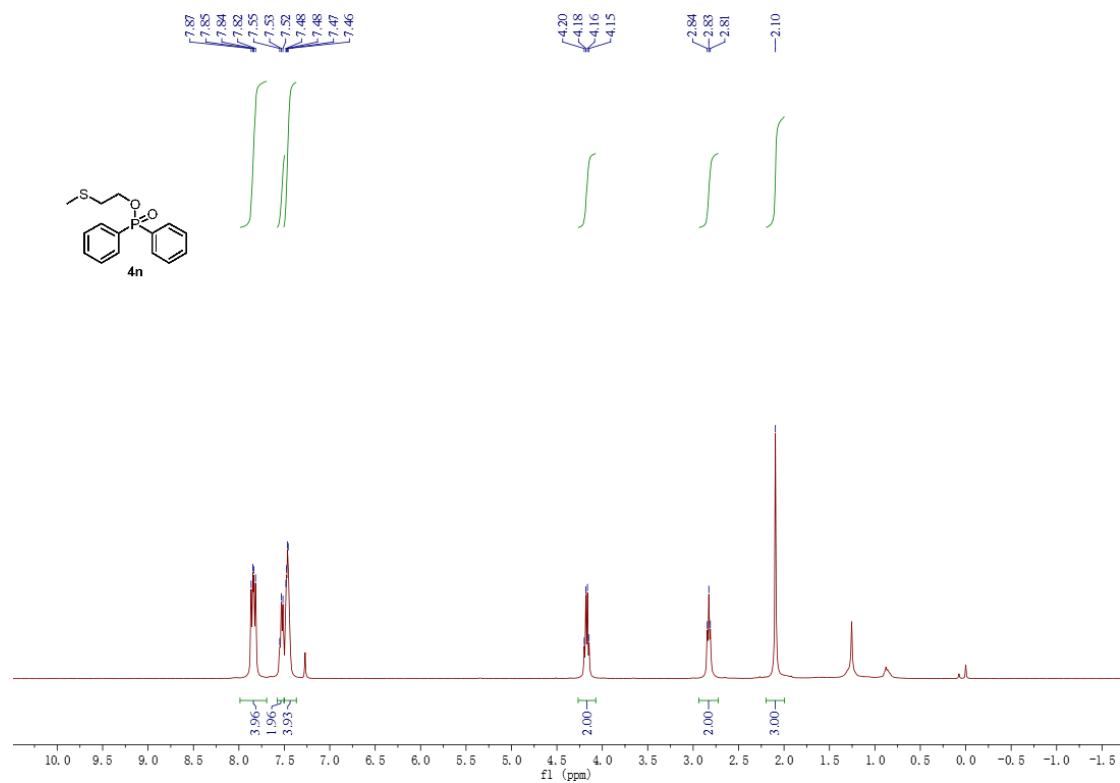
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4m



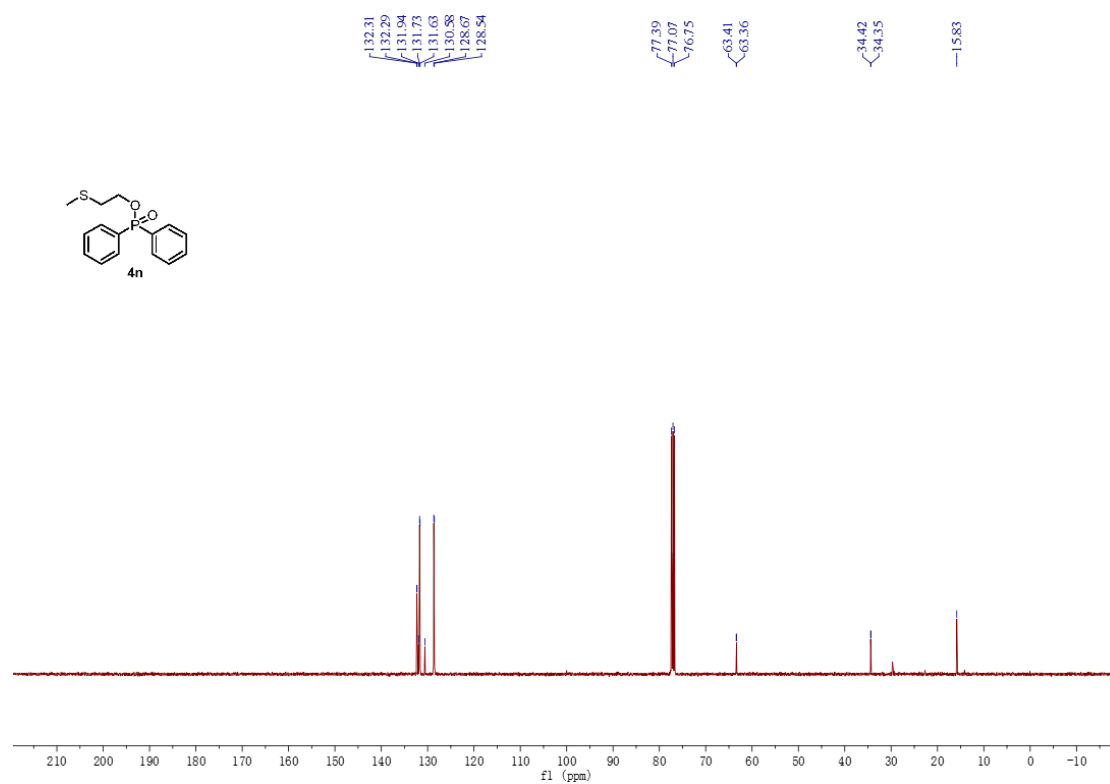
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4m



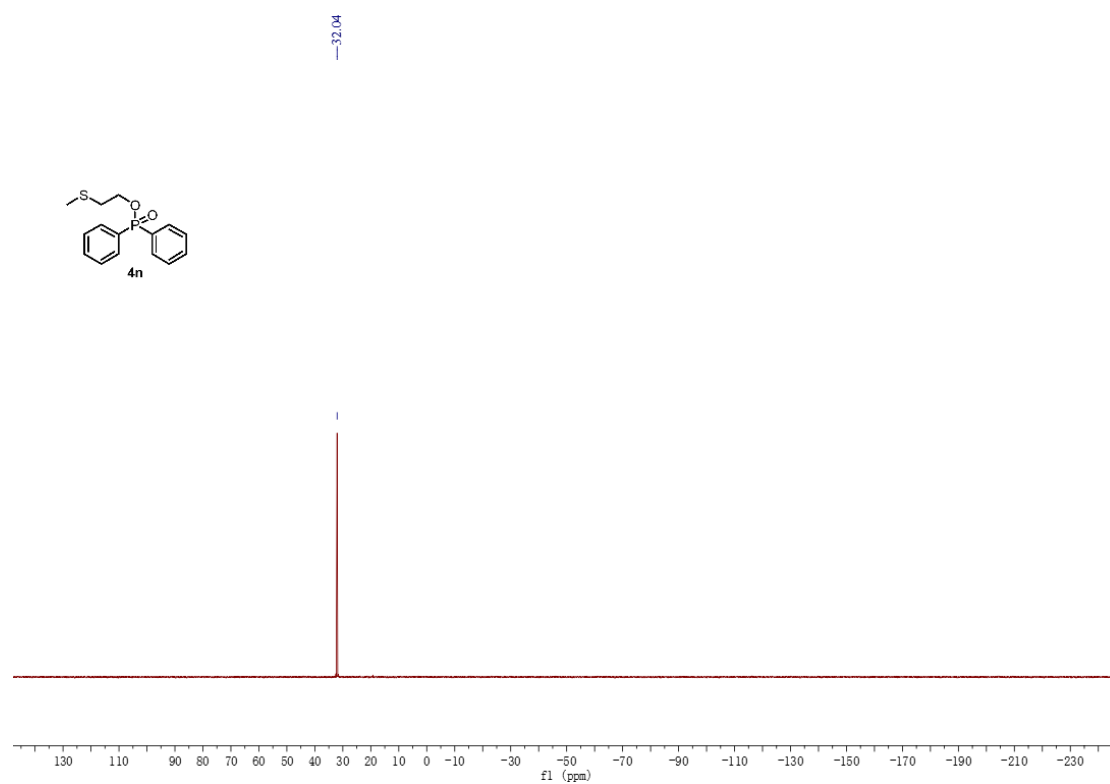
^1H NMR (400 MHz, CDCl_3) spectrum for 4n



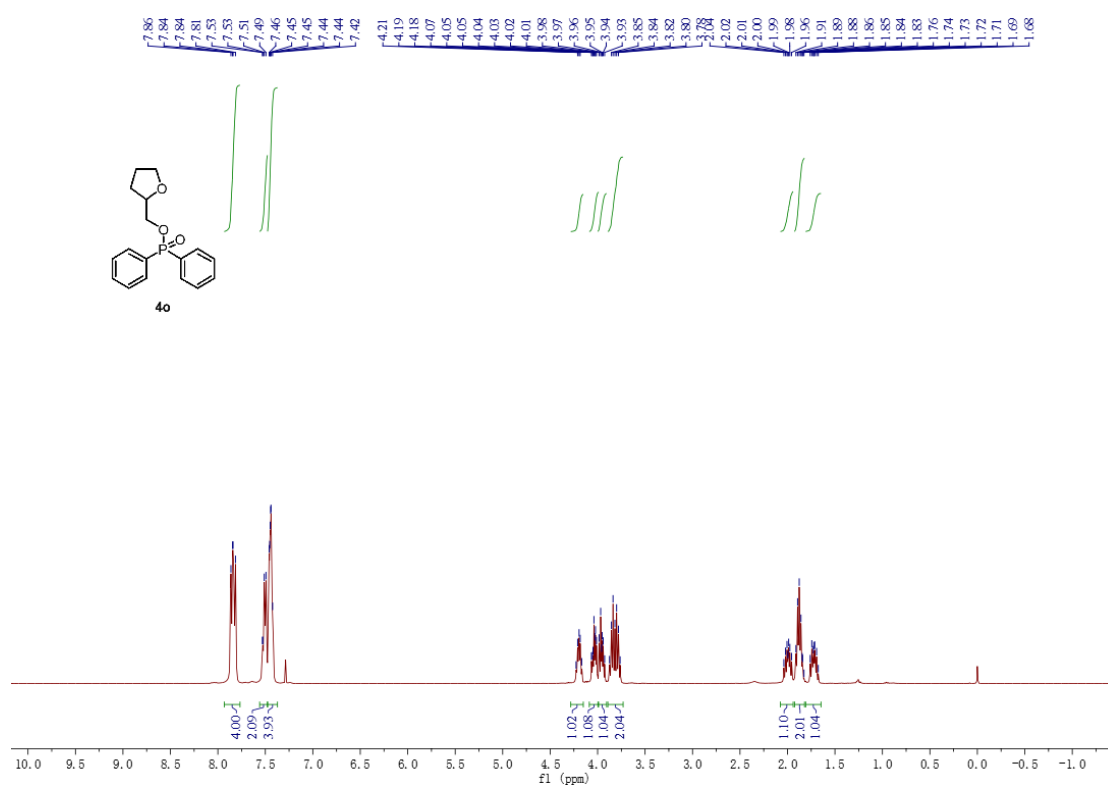
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4n



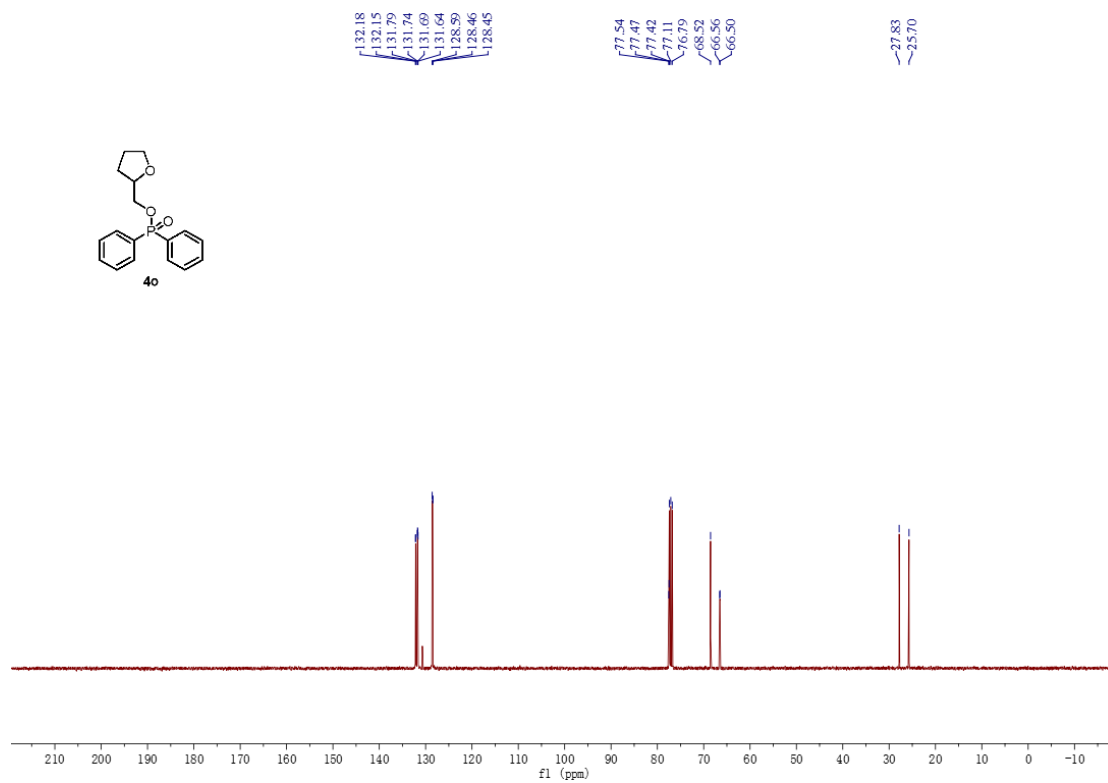
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4n



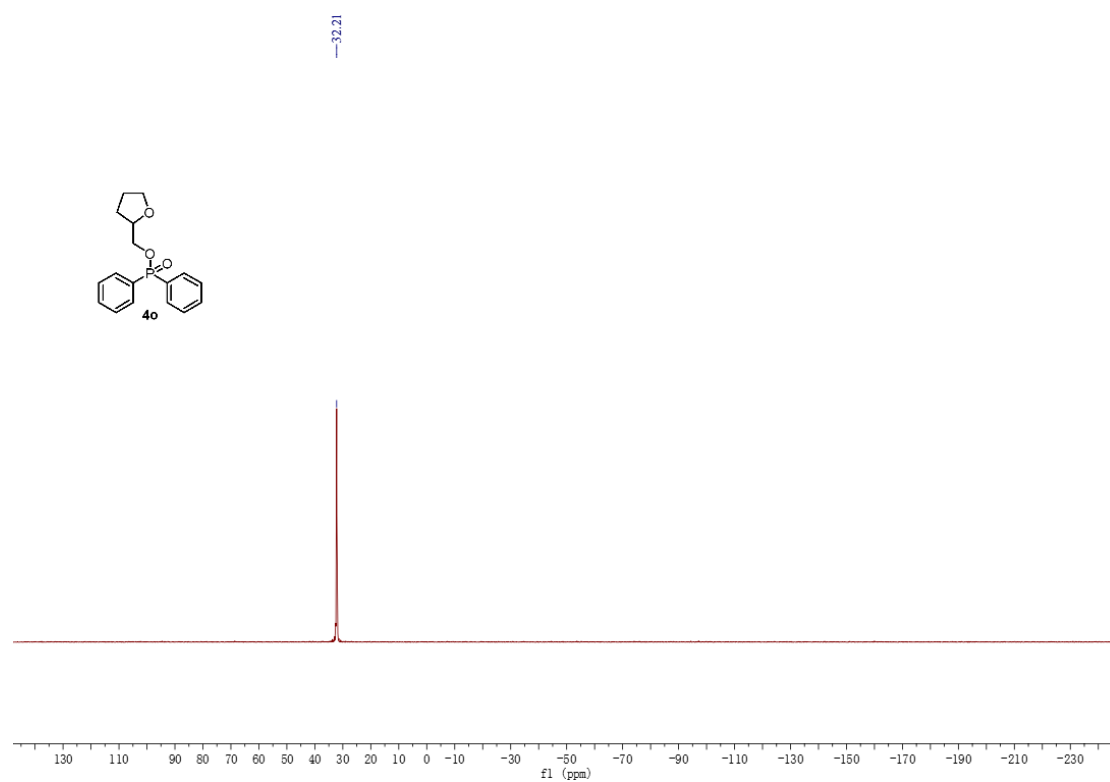
^1H NMR (400 MHz, CDCl_3) spectrum for 4o



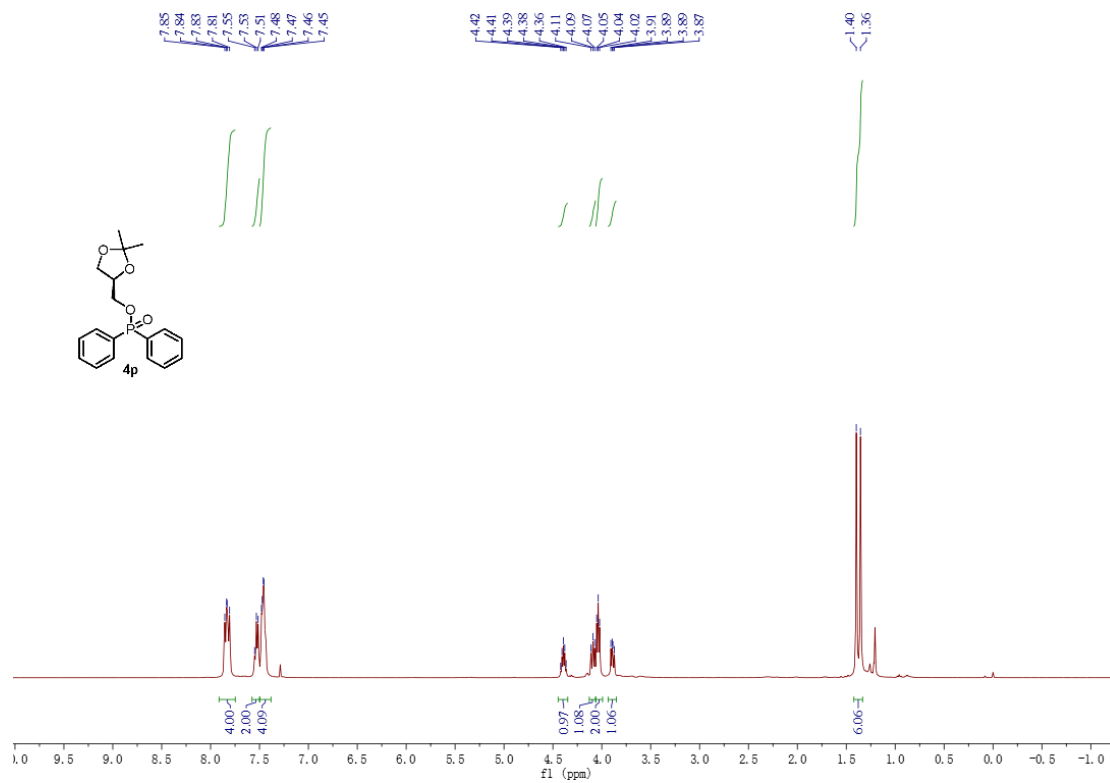
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4o



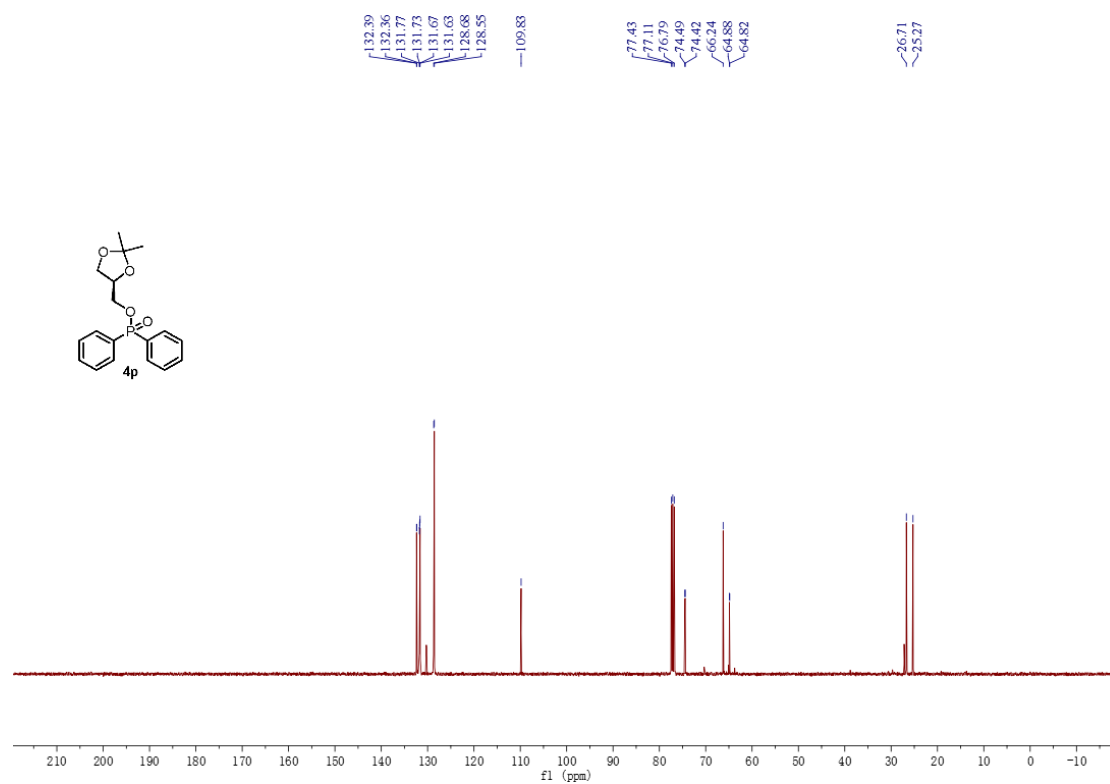
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4o



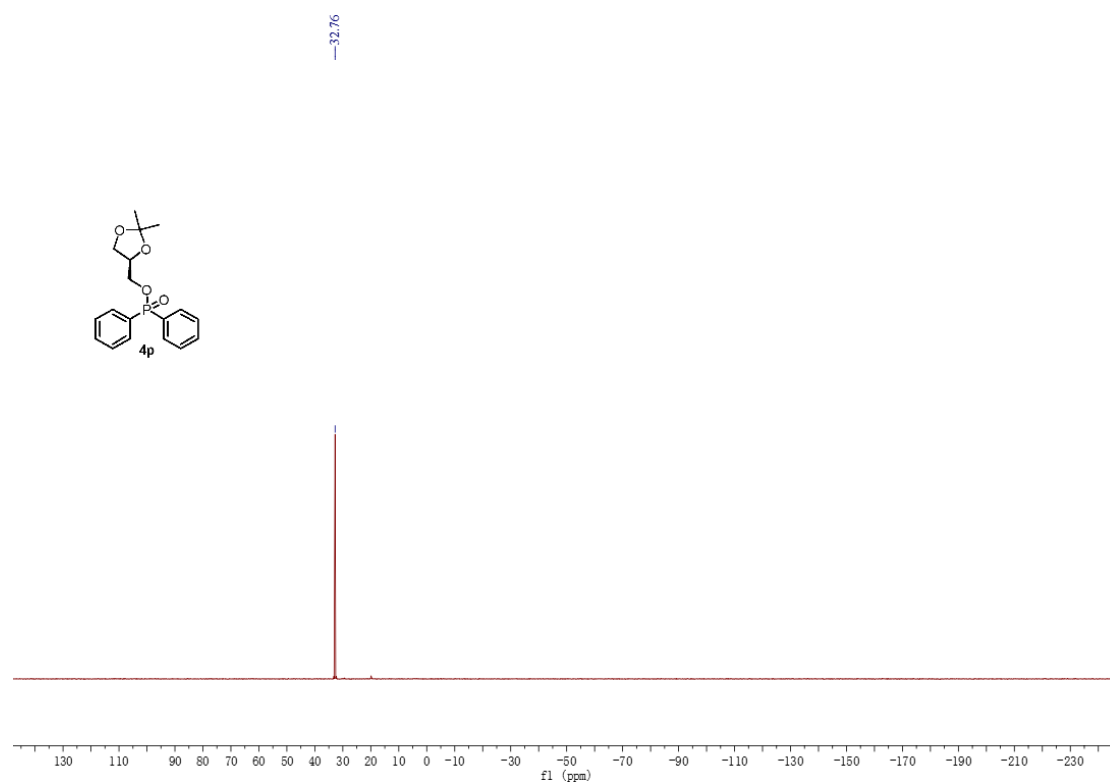
^1H NMR (400 MHz, CDCl_3) spectrum for 4p



^{13}C NMR (101 MHz, CDCl_3) spectrum for 4p



^{31}P NMR (121 MHz, CDCl_3) spectrum for 4p



Chemical structure of **4q** is shown in the top left. The ^1H NMR spectrum (CDCl₃) is displayed below, with chemical shifts (ppm) and integration values indicated.

Chemical shifts (ppm): 7.54, 7.52, 7.51, 7.49, 7.49, 7.46, 7.44, 7.43, 7.42, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.28, 7.26, 7.25, 4.34, 4.33, 4.31, 4.09, 4.07, 4.06.

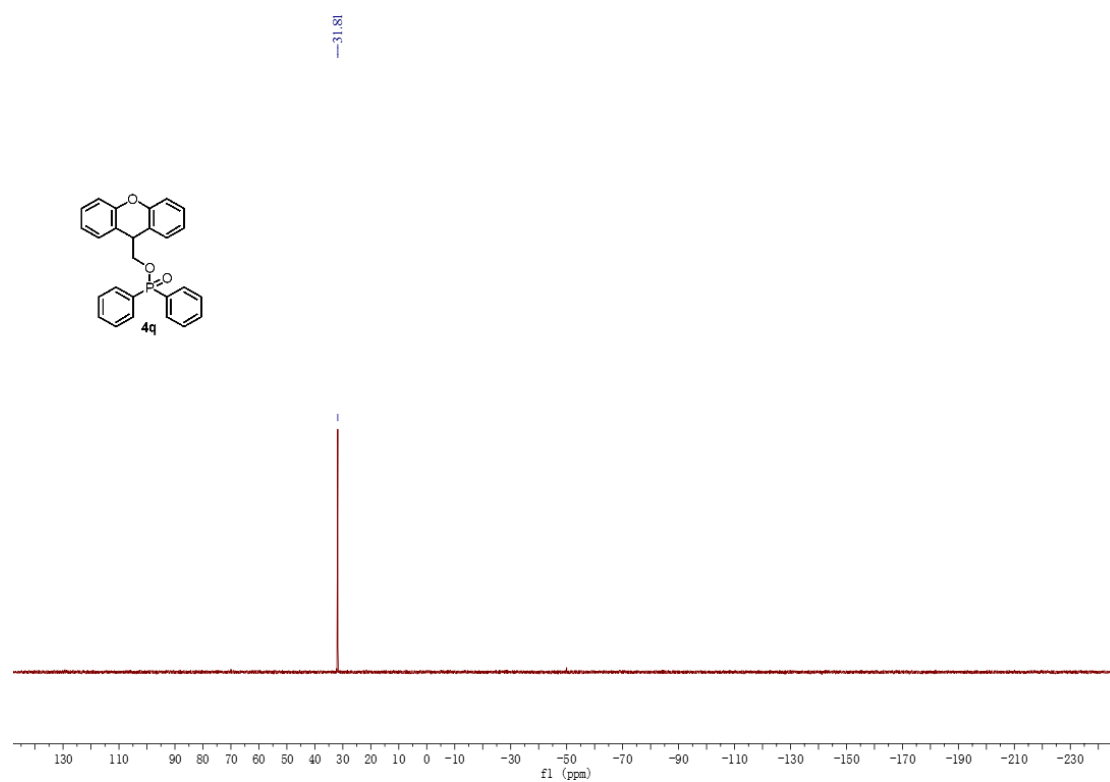
Integration values: 5.92, 3.93, 4.01, 1.00, 1.99, 1.00.

Chemical structure of **4q** is shown above the ^{13}C NMR spectrum.

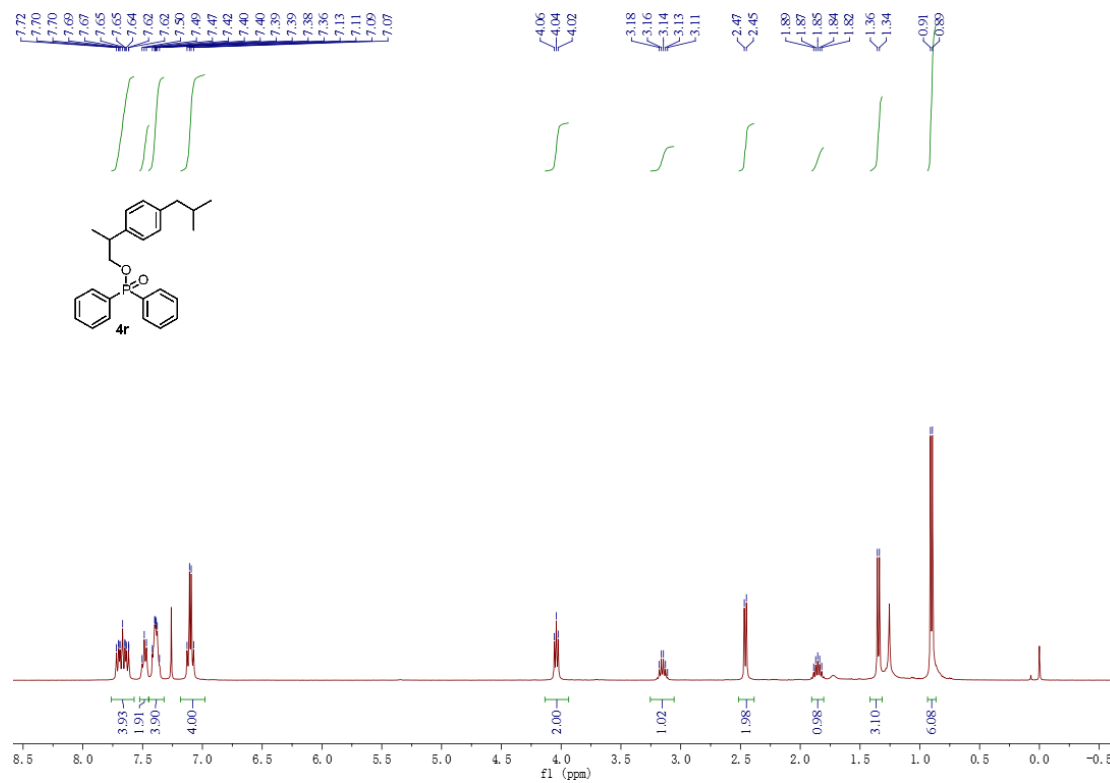
^{13}C NMR spectrum (ppm) peaks (from top to bottom):

- 152.49
- 132.06
- 132.03
- 131.72
- 131.58
- 131.48
- 130.46
- 129.46
- 128.54
- 128.41
- 123.31
- 121.17
- 116.50
- 77.37
- 77.05
- 76.73
- 69.62
- 69.56
- 40.30
- 40.22

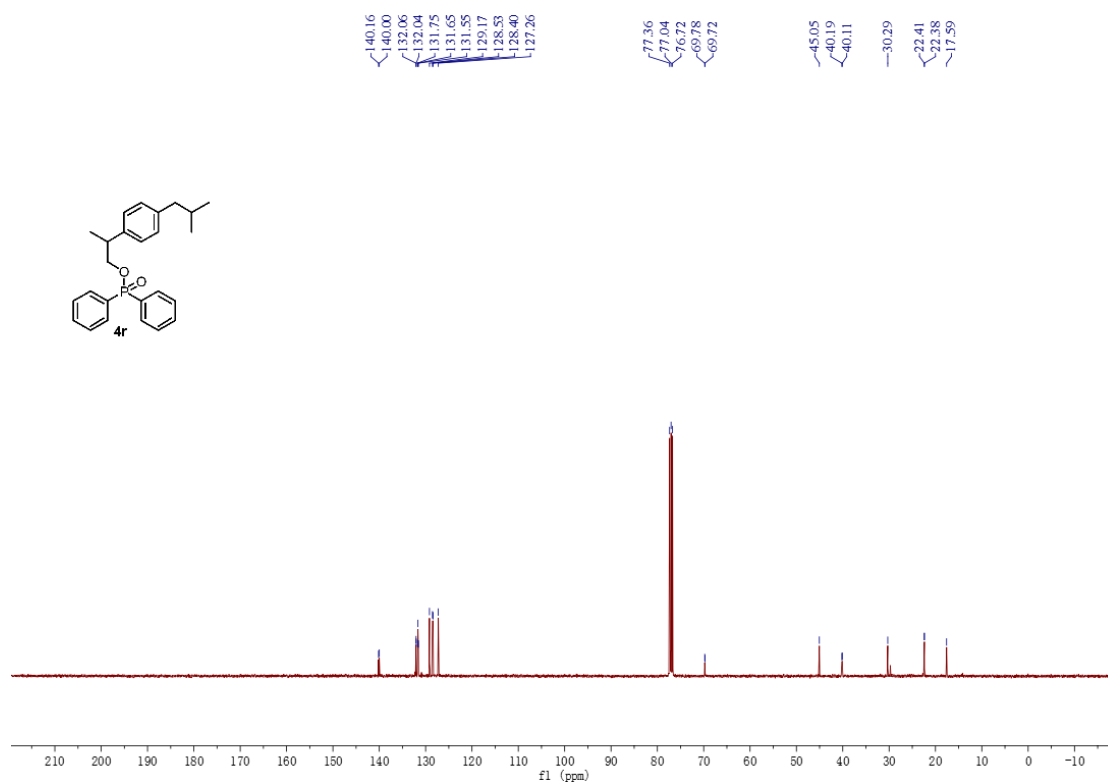
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4q



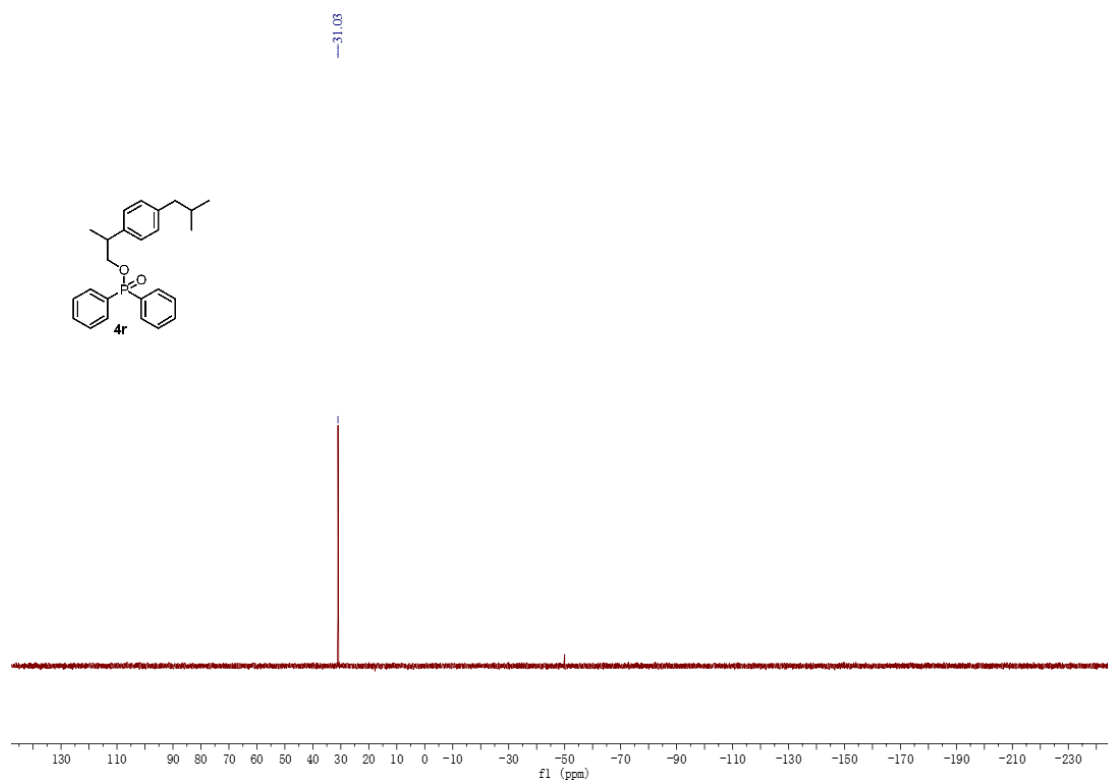
^1H NMR (400 MHz, CDCl_3) spectrum for 4r



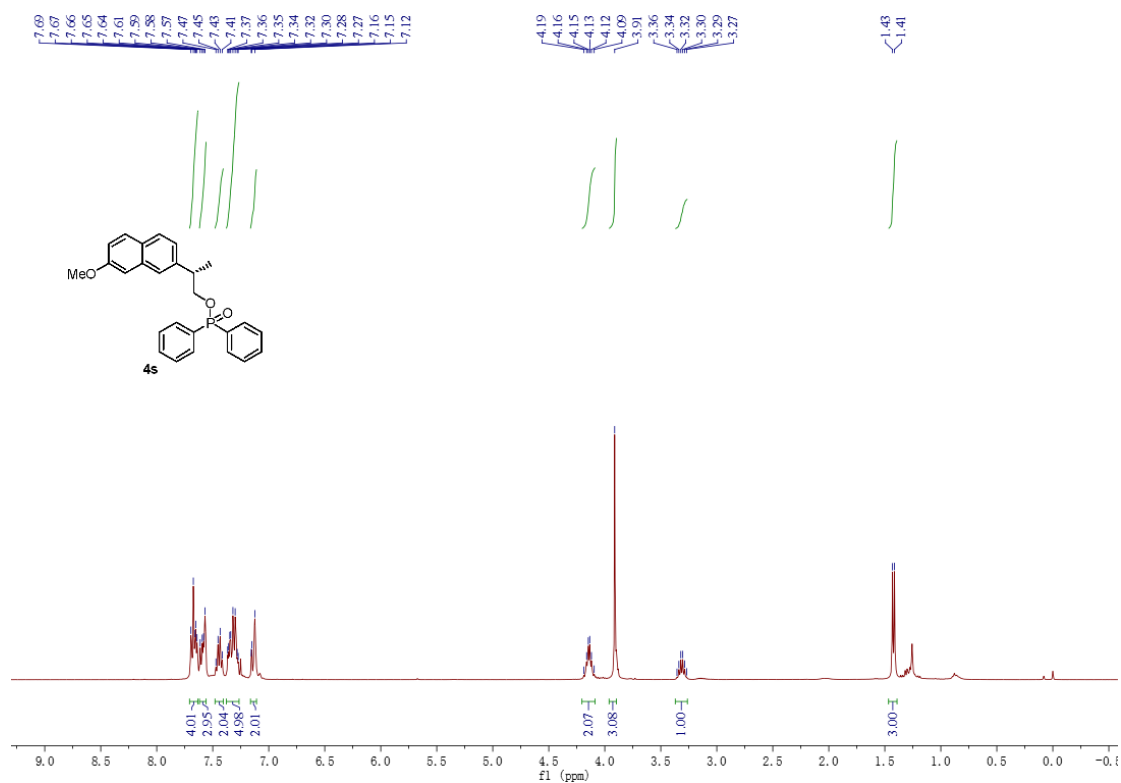
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4r



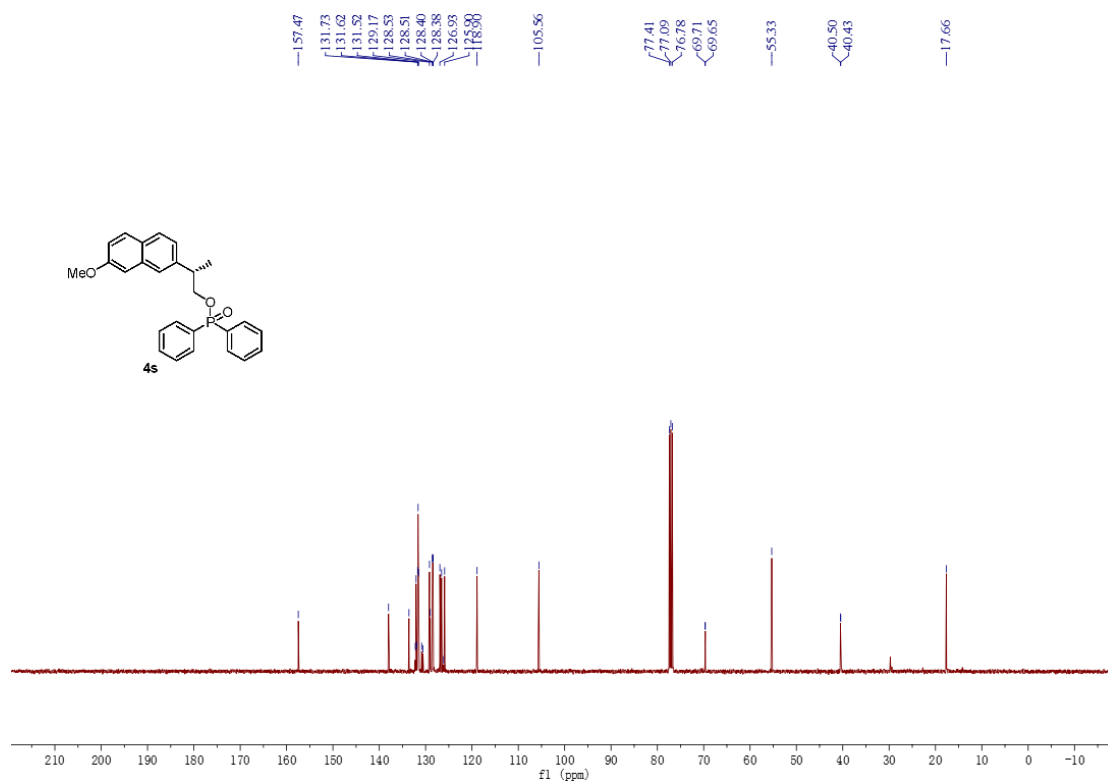
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4r



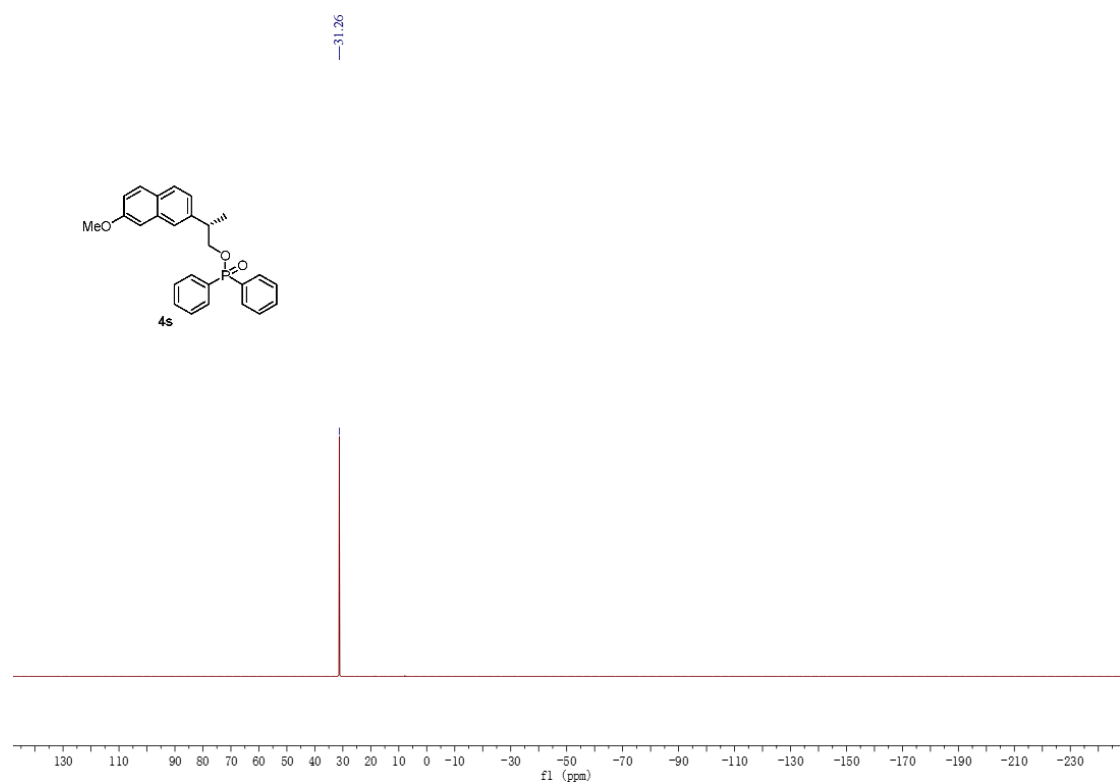
^1H NMR (400 MHz, CDCl_3) spectrum for 4s



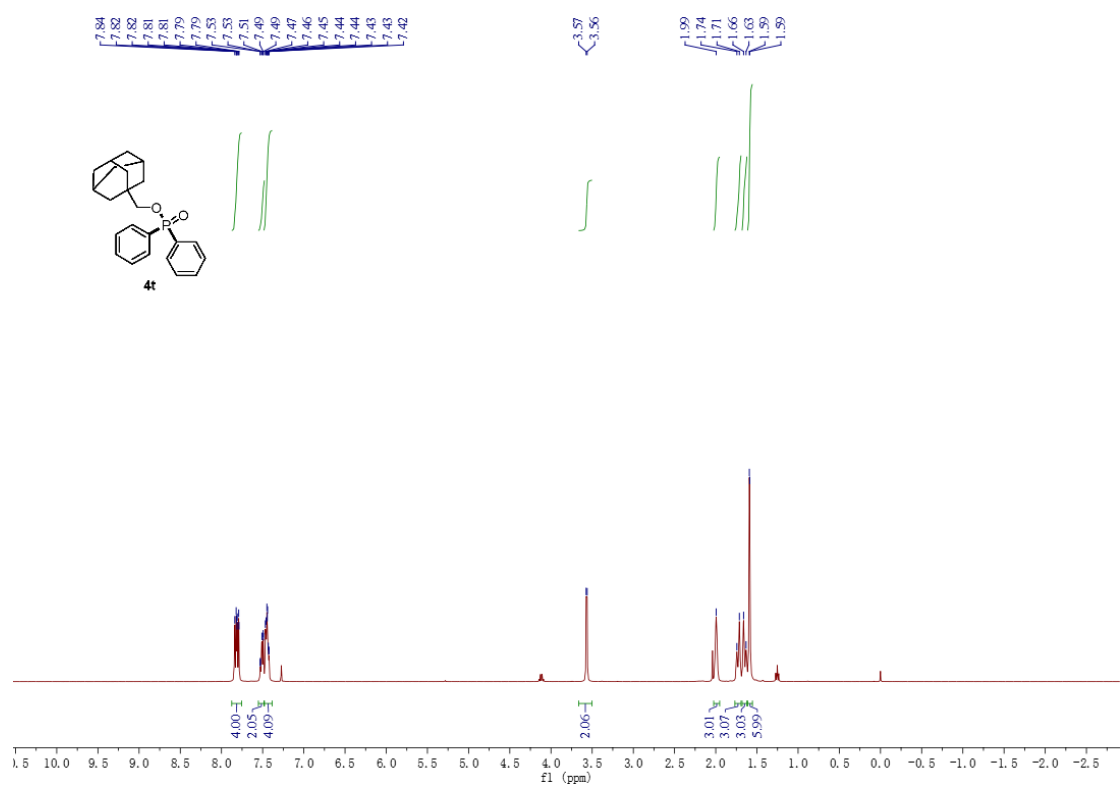
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4s



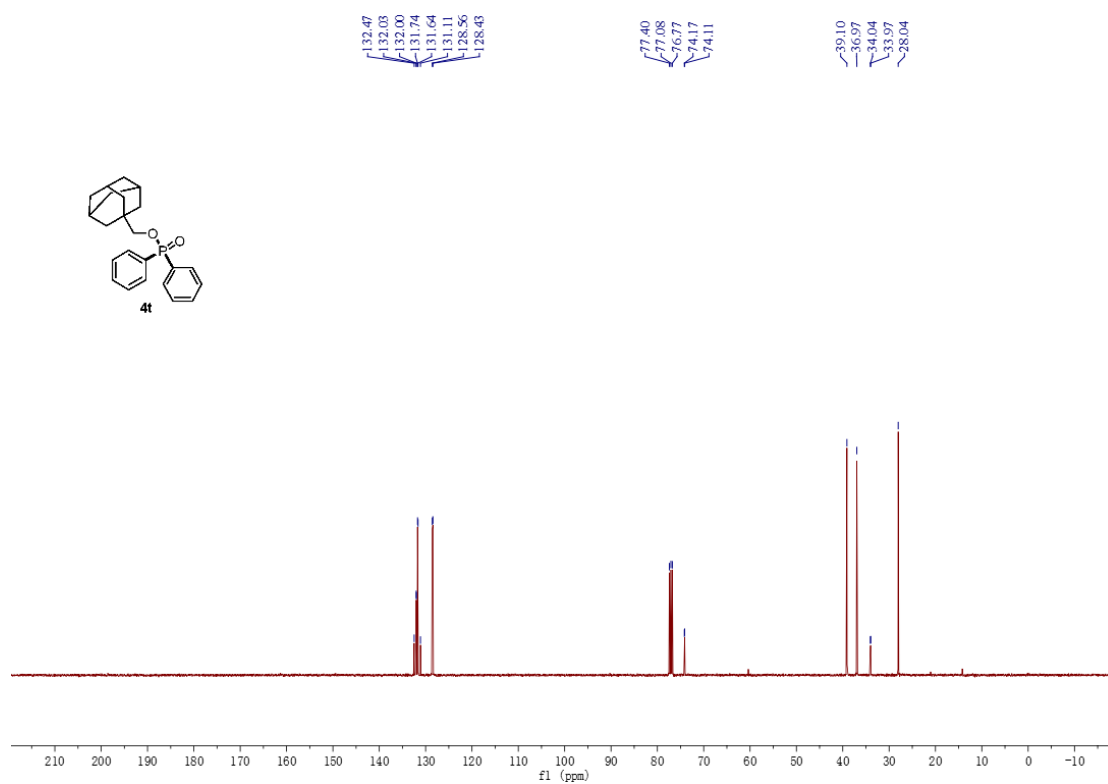
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4s



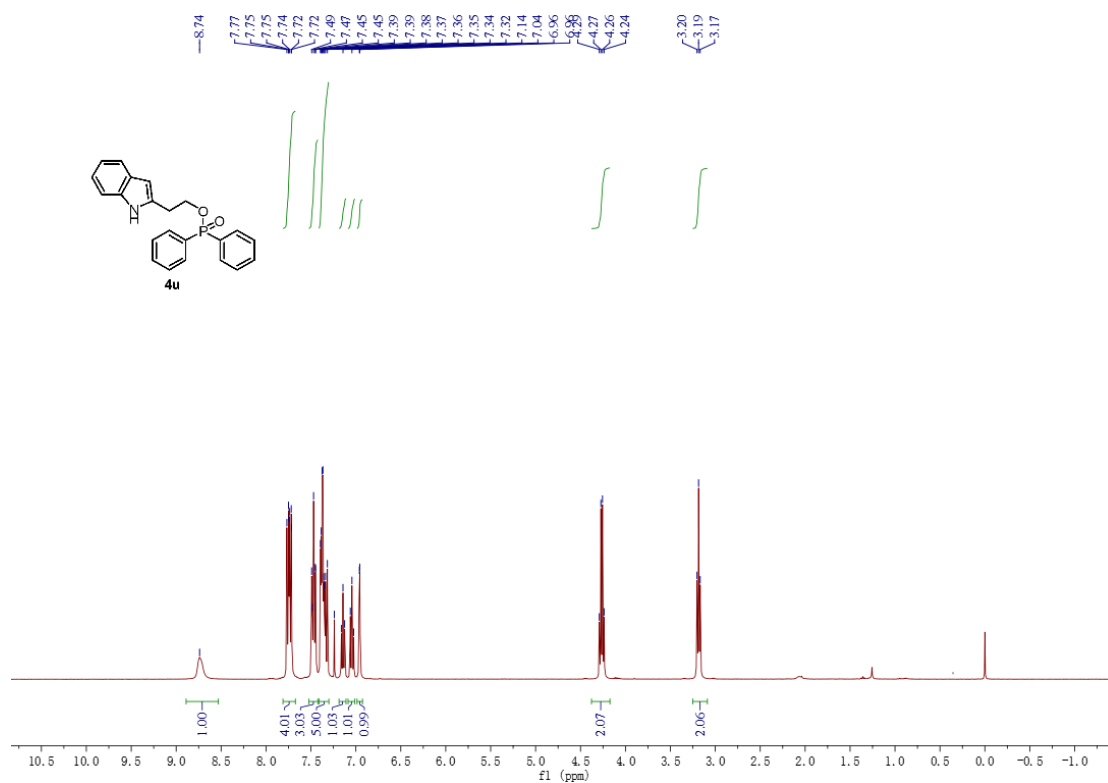
^1H NMR (400 MHz, CDCl_3) spectrum for 4t



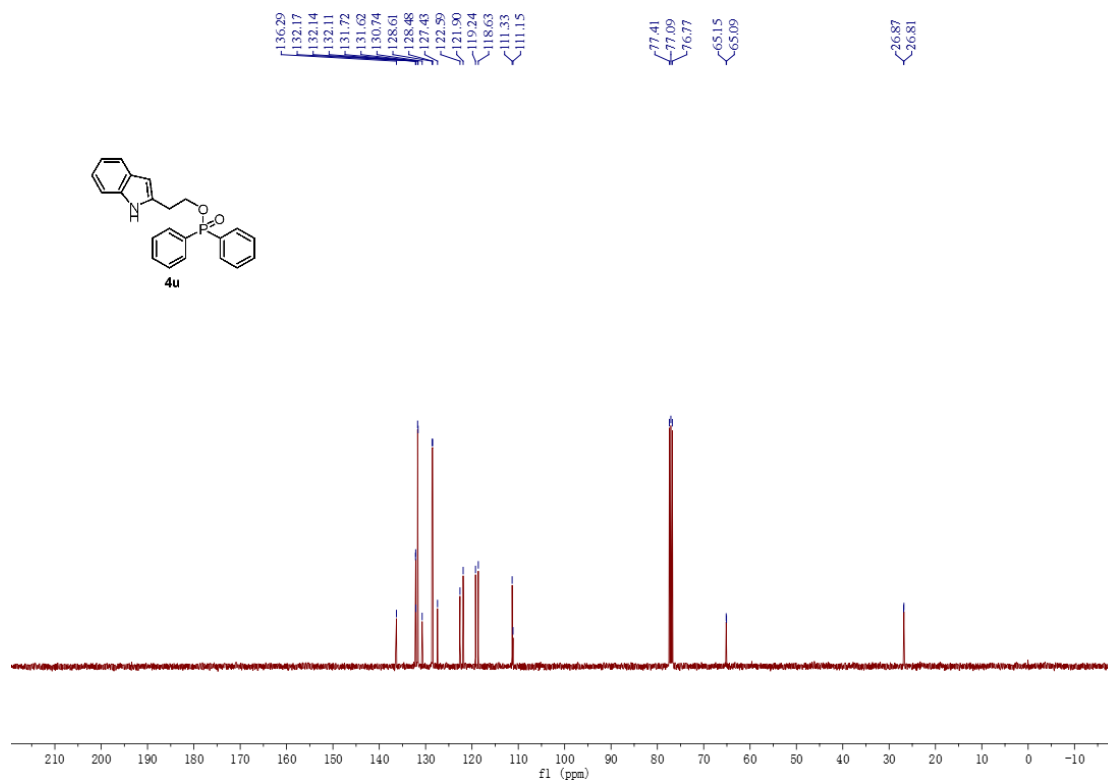
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4t



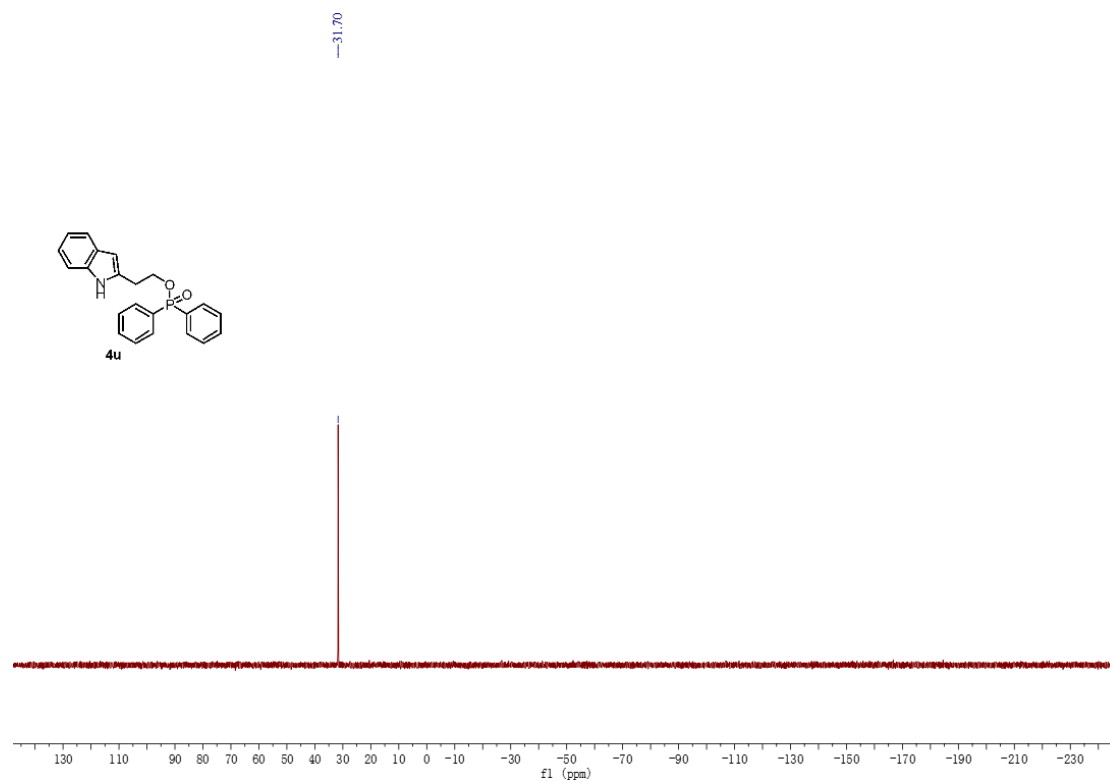
^1H NMR (400 MHz, CDCl_3) spectrum for 4u



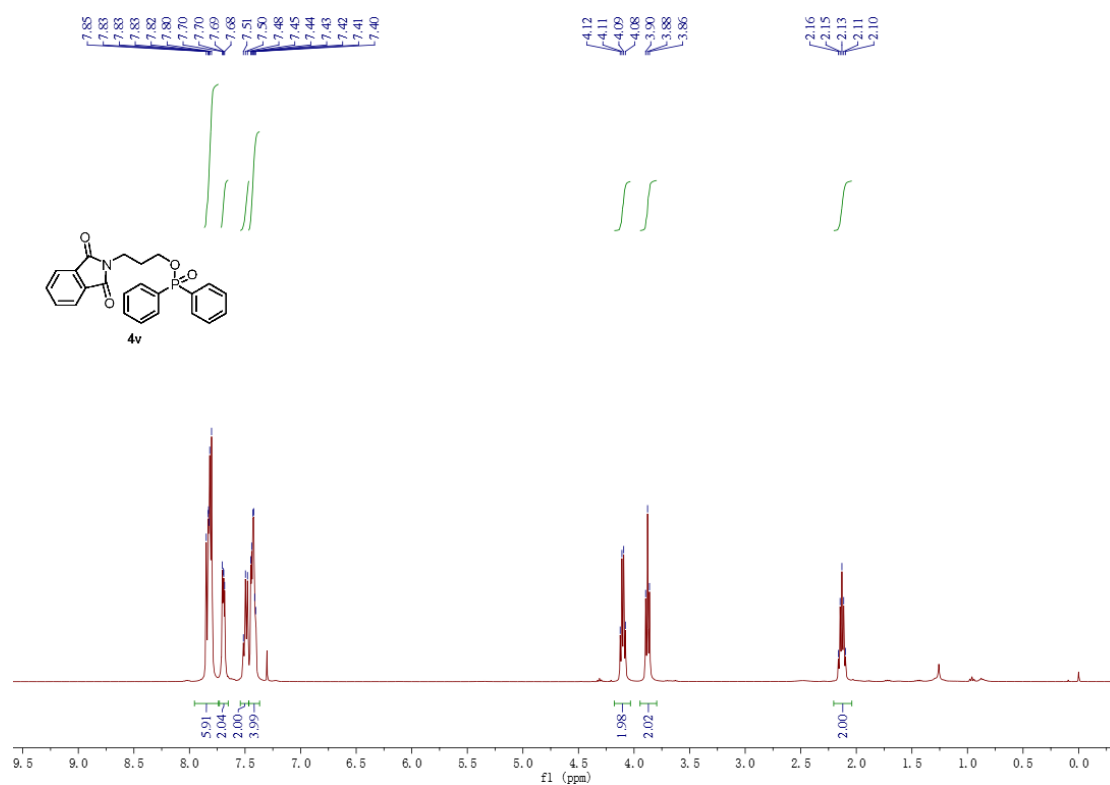
^{13}C NMR (101 MHz, CDCl_3) spectrum for 4u



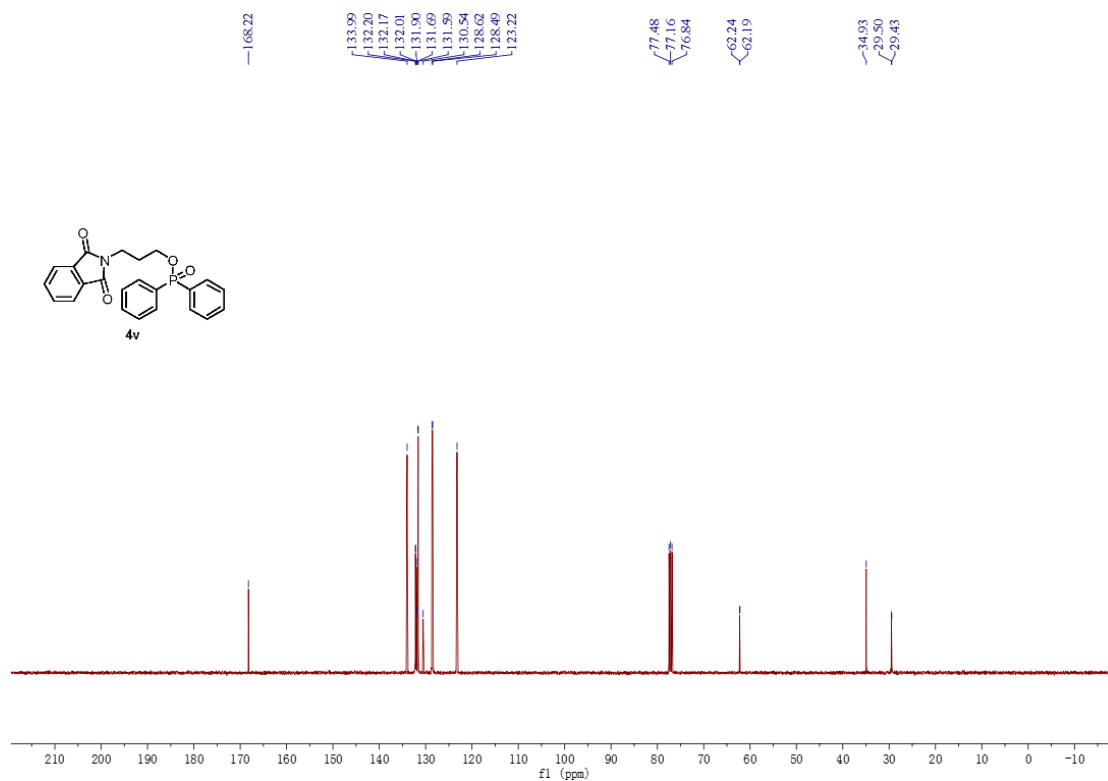
^{31}P NMR (121 MHz, CDCl_3) spectrum for 4u



^1H NMR (400 MHz, CDCl_3) spectrum for 4v



^{13}C NMR (101 MHz, CDCl_3) spectrum for 4v



^{31}P NMR (121 MHz, CDCl_3) spectrum for 4v

