Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
This journal is © The Royal Society of Chemistry 2023

Tandem *Phospha*-Michael Addition/Cyclization/Dehydration of 2-Hydroxychalcones with *H*-Phosphine Oxides for Synthesis of 4-Phosphorylated 4*H*-Chromenes

Zhong Wen,[a] Kai-Cheng Yang,[a] Shi-Lu Zheng,[a] Yu-Shan Zhang,[a] Sheng-Jun Wang,[a] Hai-Liang Ni[b] and Long Chen*[a]

[a] Antibiotics Research and Re-evaluation Key Laboratory of Sichuan Province, Sichuan Industrial Institute of Antibiotics, School of Pharmacy, Chengdu University, 2025 Chengluo Avenue, Chengdu 610016, P. R. China

E-mail: chenlong@cdu.edu.cn

[b] College of Chemistry and Materials Science, Sichuan Normal University, 5 Jing An Road, Chengdu 610066, P. R. China

Table of Contents

1. General information:

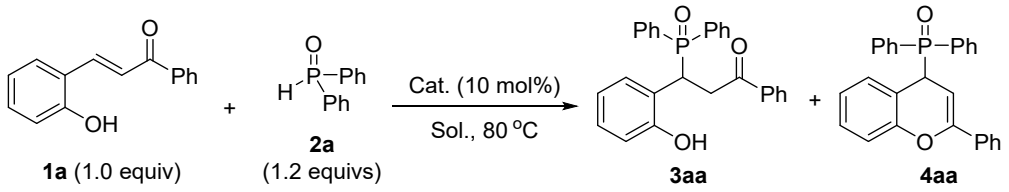
Reactions were monitored by thin layer chromatography using UV light to visualize the reaction course. Purification of reaction products were carried out by flash chromatography on silica gel H. Chemical yields refer to pure isolated substances. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker DPX-600 or DPX-400 spectrometer. The ^{19}F NMR spectra was recorded at JEOL 565 MHz. HRMS data were collected on a on a Thermo Scientific LTQ Orbitrap Discovery (Bremen, Germany). The linear ion trap (LTQ) part of the hybrid MS system was equipped with electrospray ionization (ESI) probe and operated in both positive and negative ion modes. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad.

All reactions were run under an atmosphere of air. Anhydrous THF, toluene and 1,4-dioxane were prepared by distillation over sodium-benzophenone ketyl prior to use. Anhydrous acetone was distilled over anhydrous $CaSO_4$ and stored over MS 4Å. Anhydrous halogenated solvents and CH_3CN were prepared by first distillation over P_2O_5 and then from CaH_2. Anhydrous ethyl acetate was prepared by first dried in anhydrous Na_2SO_4 and then distilled over P_2O_5 and stored over MS 4Å. Anhydrous CH_3NO_2 was prepared by first dried in anhydrous Na_2SO_4 and then distilled under reduced pressure. 2-Hydroxychalcones **1** were prepared according to the literature report.[1] $Hg(OTf)_2$ (99.998%) was purchased from Alfa-Aesar and used as received.

1 P. Saha, A. Biswas, N. Molleti and V. K. Singh, *J. Org. Chem.,* 2015, **80**, 11115.

2. Condition optimization

2.1 Catalyst and Solvent screening

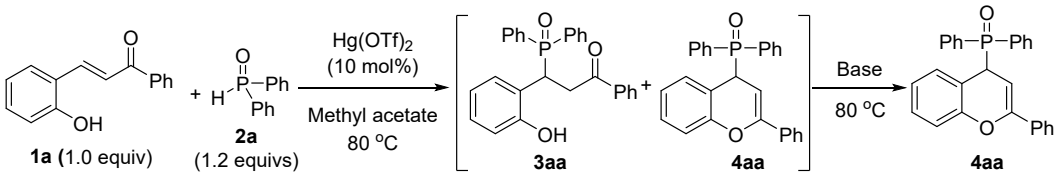


Entry[a]	Cat.	Time/h	Solvent	Yield/%[b]	
				3aa	**4aa**
1	HOTf	5	$ClCH_2CH_2Cl$	47	40
2	*p*-TsOH·H_2O	5	$ClCH_2CH_2Cl$	40	51
3	$HClO_4$ (70 wt%, aq.)	3.5	$ClCH_2CH_2Cl$	52	34
4	$Hg(ClO_4)_2·3H_2O$	11	$ClCH_2CH_2Cl$	53	39
5	$Zn(ClO_4)_2·6H_2O$	11	$ClCH_2CH_2Cl$	52	43
6[c]	$Cu(ClO_4)_2·6H_2O$	2	$ClCH_2CH_2Cl$	20	21
7	$Mg(ClO_4)_2·6H_2O$	15	$ClCH_2CH_2Cl$	70	23
8	$Mn(ClO_4)_2·6H_2O$	5	$ClCH_2CH_2Cl$	20	43
9	$Ga(OTf)_3$	5.5	$ClCH_2CH_2Cl$	57	34
10	$Y(OTf)_3$	4.5	$ClCH_2CH_2Cl$	57	39
11	$Bi(OTf)_3$	9	$ClCH_2CH_2Cl$	54	29
12	$Sc(OTf)_3$	7	$ClCH_2CH_2Cl$	55	22
13	$Sm(OTf)_3$	4	$ClCH_2CH_2Cl$	60	33
14	$La(OTf)_3$	5	$ClCH_2CH_2Cl$	59	35
15	$In(OTf)_3$	7	$ClCH_2CH_2Cl$	55	27
16	$Ni(OTf)_2$	23	$ClCH_2CH_2Cl$	49	31
17	$Hg(OTf)_2$	3.5	$ClCH_2CH_2Cl$	62	38
18	$Mg(OTf)_2$	6.5	$ClCH_2CH_2Cl$	47	37
19	$Zn(OTf)_2$	10	$ClCH_2CH_2Cl$	46	41
20	$Ca(OTf)_2$	12	$ClCH_2CH_2Cl$	45	41
21	$Cu(OTf)_2$	9	$ClCH_2CH_2Cl$	23	10
22[c]	CuOTf·toluene	2.5	$ClCH_2CH_2Cl$	11	8
23	AgOTf	20	$ClCH_2CH_2Cl$	14	23
24[d]	$Hg(OTf)_2$	3.5+24	$ClCH_2CH_2Cl$	60	37
25[d]	$Hg(OTf)_2$	2+24	Toluene	83	6
26[d]	$Hg(OTf)_2$	8+24	CH_3CN	49	36
27[e]	$Hg(OTf)_2$	24	CH_3NO_2	77	17
28[d]	$Hg(OTf)_2$	10+24	CH_3CO_2Et	9	78

29	$Hg(OTf)_2$	10	CH_3CO_2Et	14	72
30[f]	$Hg(OTf)_2$	10+24	CH_3CO_2Et	21	49
31	**$Hg(OTf)_2$**	**6+24**	**CH_3CO_2Me**	**12**	**85**
32	$Hg(OTf)_2$	2+24	$CH_3CO_2{}^nPr$	13	65
33	$Hg(OTf)_2$	2+24	$CH_3CO_2{}^nBu$	10	75

[a] 0.1 mmol scale; [b] NMR yield based on the disappearance of **1a**; [c] **2a** was consumed totally in 2.5 h; [d] Reaction was run for further 24 h after the disappearance of **1a**; [e] **1a** could not be consumed totally; [f] Temperature was increased to 100 °C after the disappearance of **1a** (10 h).

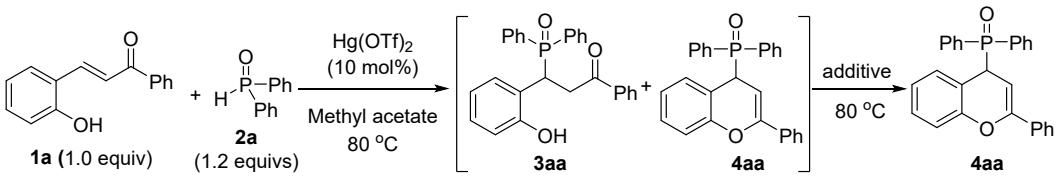
2.2 The addition of base after the disappearance of 1a



Entry[a]	Base (1.0 equiv)	Time/h[c]	Yield/%[b]	
			3aa	**4aa**
1	NEt_3	6+24	12	73
2	DMAP		22	43
3	DBU		23	66
4	DABCO		21	76
5	K_2CO_3		24	74
6	None		12	85

[a] 0.1 mmol scale; [b] NMR yield; [c] Reaction was run for further 24 h after the disappearance of **1a**.

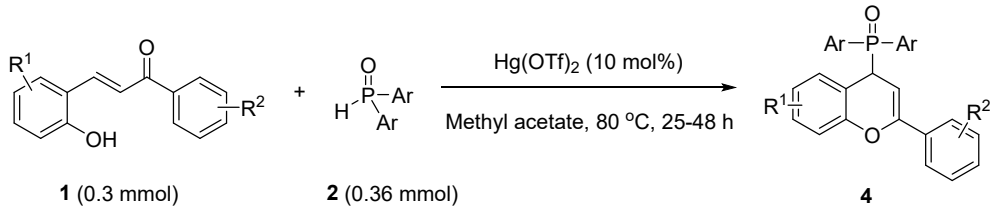
2.3 The addition of other additives after the disappearance of 1a



Entry[a]	Additive (1.0 equiv)	Time/h[c]	Yield/%[b]	
			3aa	**4aa**
1	KPF_6	6+24	9	79
2	$NaPF_6$		10	77
3	$NaBF_4$		13	77
4	NH_4PF_6		10	79
5	Bu_4NPF_6		10	76
6	None		12	85

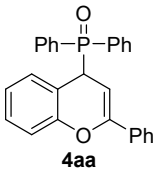
[a] 0.1 mmol scale; [b] NMR yield; [c] Reaction was run for further 24 h after the disappearance of **1a**.

3. General procedure for the tandem *phospha*-Michael addition/cyclization/dehydration to 4-phosphorylated 4*H*-chromenes



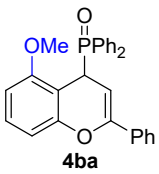
1 (0.3 mmol) **2** (0.36 mmol) **4**

The reaction was carried out under an air atmosphere. To a 35-mL sealed tube were added 2-hydroxychalcones **1** (0.3 mmol, 1.0 equiv), $Ar_2P(O)H$ **2** (0.36 mmol, 1.2 equivs) and 6.0 mL of anhydrous methyl acetate. After adding $Hg(OTf)_2$ (15.0 mg, 10 mol%), the reaction mixture was stirred at 80 °C till almost full conversion of **1** by TLC analysis and then further stirred for 24 hrs. The reaction mixture was cooled to room temperature and then directly subjected to column chromatography using dichloromethane/ethyl acetate (generally 40:1 to 5:1, v:v) as the eluent to afford the desired products **4**.



4aa

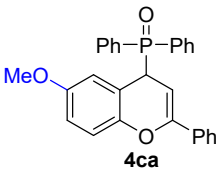
Column chromatography afforded the desired product **4aa** in 76% yield (93 mg) as yellow solid; Mp: 181-183 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.73-7.69 (m, 4H), 7.56-7.54 (m, 1H), 7.49-7.45 (m, 5H), 7.36-7.32 (m, 5H), 7.16-7.11 (m, 2H), 6.93 (t, J = 7.8 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 5.39 (dd, J = 5.4 Hz, 3.6 Hz, 1H), 4.66 (dd, J = 21.0 Hz, 5.4 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 152.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 151.1 (d, $J_{C\text{-}P}$ = 9.0 Hz), 133.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.09 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.06 (d, $J_{C\text{-}P}$ = 1.5 Hz), 132.02, 131.98 (d, $J_{C\text{-}P}$ =4.5 Hz), 130.3 (d, $J_{C\text{-}P}$ = 94.5 Hz), 129.8 (d, $J_{C\text{-}P}$ = 94.5 Hz), 129.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.9, 128.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.5 ($J_{C\text{-}P}$ = 12.0 Hz), 128.3, 128.2 (d, $J_{C\text{-}P}$ = 12.0 Hz), 124.8, 123.6 (d, $J_{C\text{-}P}$ = 1.5 Hz), 116.5 (d, $J_{C\text{-}P}$ = 1.5 Hz), 116.0 (d, $J_{C\text{-}P}$ = 3.0 Hz), 92.8 (d, $J_{C\text{-}P}$ = 6.0 Hz), 40.6 (d, $J_{C\text{-}P}$ = 67.5 Hz); ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 30.6; HRMS (ESI): Exact mass calcd for $C_{27}H_{21}O_2P$ $[M+H]^+$: 409.1352, Found: 409.1340.



4ba

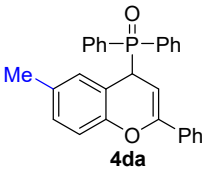
Column chromatography afforded the desired product **4ba** in 54% yield (72 mg) as yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.81-7.78 (m, 2H), 7.67-7.64 (m, 2H), 7.51-7.49 (m, 1H), 7.44-7.41 (m, 5H), 7.35-7.32 (m, 2H), 7.285-7.275 (m, 3H), 7.18-7.15 (m, 1H), 6.69 (d, J = 8.4 Hz, 1H), 6.37 (d, J = 7.8 Hz, 1H), 5.50 (dd, J = 5.4 Hz, 3.0 Hz, 1H), 4.90 (dd, J = 15.6 Hz, 6.0 Hz, 1H), 3.16 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 156.5 (d, $J_{C\text{-}P}$ = 3.0 Hz), 154.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 152.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 133.6 (d, $J_{C\text{-}P}$ = 4.5 Hz), 132.0 (d, $J_{C\text{-}P}$ = 91.5 Hz), 131.8 (d, $J_{C\text{-}P}$

= 1.5 Hz), 131.7, 131.45 (d, J_{C-P} = 6.0 Hz), 131.44 (d, J_{C-P} = 91.5 Hz), 131.4 , 128.71, 128.67 (d, J_{C-P} = 3.0 Hz), 128.1, 128.0 (d, J_{C-P} = 12.0 Hz), 127.8 (d, J_{C-P} = 10.5 Hz), 125.0 (d, J_{C-P} = 1.5 Hz), 109.3 (d, J_{C-P} = 1.5 Hz), 106.0 (d, J_{C-P} = 4.5 Hz), 104.9 (d, J_{C-P} = 1.5 Hz), 93.6 (d, J_{C-P} = 7.5 Hz), 54.6, 36.7 (d, J_{C-P} = 67.5 Hz); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 29.2; HRMS (ESI): Exact mass calcd for $C_{28}H_{23}O_3P$ $[M+H]^+$: 439.1458, Found: 439.1446.



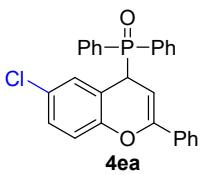
4ca

Column chromatography afforded the desired product **4ca** in 67% yield (88 mg) as brown solid; Mp: 134-136 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.76-7.69 (m, 4H), 7.56-7.54 (m, 1H), 7.51-7.49 (m, 1H), 7.48-7.44 (m, 4H), 7.40-7.37 (m, 2H), 7.34-7.31 (m, 3H), 6.82 (d, J = 9.0 Hz, 1H), 6.72-6.70 (m, 1H), 6.53-6.52 (m, 1H), 5.37 (dd, J = 5.4 Hz, 3.0 Hz, 1H), 4.64 (dd, J = 20.4 Hz, 5.4 Hz, 1H), 3.56 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 155.3 (d, J_{C-P} = 3.0 Hz), 151.3 (d, J_{C-P} = 9.0 Hz), 146.1 (d, J_{C-P} = 4.5 Hz), 133.7 (d, J_{C-P} = 3.0 Hz), 132.1 (d, J_{C-P} = 4.5 Hz), 132.0 (d, J_{C-P} = 9.0 Hz), 130.3 (d, J_{C-P} = 93.0 Hz), 130.1 (d, J_{C-P} = 93.0 Hz), 128.8, 128.5 (d, J_{C-P} = 10.5 Hz), 128.30 (d, J_{C-P} = 10.5 Hz), 128.28, 124.8 (d, J_{C-P} = 1.5 Hz), 117.4 (d, J_{C-P} = 3.0 Hz), 116.4 (d, J_{C-P} = 4.5 Hz), 115.6 (d, J_{C-P} = 3.0 Hz), 112.8 (d, J_{C-P} = 3.0 Hz), 91.7 (d, J_{C-P} = 7.5 Hz), 55.5, 41.1 (d, J_{C-P} = 67.5 Hz); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 30.5; HRMS (ESI): Exact mass calcd for $C_{28}H_{23}O_3P$ $[M+H]^+$: 439.1458, Found: 439.1450.



4da

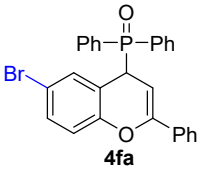
Column chromatography afforded the desired product **4da** in 52% yield (66 mg) as brown solid; Mp: 95-97 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.73-7.70 (m, 4H), 7.56-7.54 (m, 1H), 7.51-7.45 (m, 5H), 7.38-7.37 (m, 2H), 7.33-7.31 (m, 3H), 6.96-6.94 (m, 1H), 6.79-6.78 (m, 2H), 5.38-5.37 (m, 1H), 4.59 (dd, J = 20.4 Hz, 4.8 Hz, 1H), 2.16 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 151.2 (d, J_{C-P} = 9.0 Hz), 150.0 (d, J_{C-P} = 3.0 Hz), 133.7 (d, J_{C-P} = 3.0 Hz), 132.9 (d, J_{C-P} = 1.5 Hz), 132.1 (d, J_{C-P} = 7.5 Hz), 132.0 (d, J_{C-P} = 9.0 Hz), 131.9 (d, J_{C-P} = 3.0 Hz), 130.5 (d, J_{C-P} = 94.5 Hz), 130.1 (d, J_{C-P} = 94.5 Hz), 130.0 (d, J_{C-P} = 3.0 Hz), 129.2 (d, J_{C-P} = 3.0 Hz), 128.8, 128.4 (d, J_{C-P} = 10.5 Hz), 128.3, 128.1 (d, J_{C-P} = 10.5 Hz), 124.8, 116.2 (d, J_{C-P} = 3.0 Hz), 115.6 (d, J_{C-P} = 4.5 Hz), 92.6 (d, J_{C-P} = 6.0 Hz), 40.9 (d, J_{C-P} = 67.5 Hz), 20.6; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 30.3; HRMS (ESI): Exact mass calcd for $C_{28}H_{23}O_2P$ $[M+H]^+$: 423.1508, Found: 423.1501.



4ea

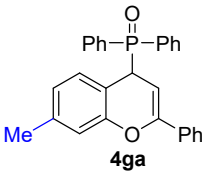
Column chromatography afforded the desired product **4ea** in 66% yield (78 mg) as green

solid; Mp: 180-182 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.74-7.71 (m, 4H), 7.59-7.56 (m, 1H), 7.53-7.47 (m, 3H), 7.46-7.44 (m, 2H), 7.41-7.38 (m, 2H), 7.33-7.32 (m, 3H), 7.11-7.09 (m, 1H), 7.00 (t, J = 1.8 Hz ,1H), 6.81 (d, J = 8.4 Hz, 1H), 5.36 (dd, J = 5.4 Hz, 3.0 Hz, 1H), 4.57 (dd, J = 19.8 Hz, 5.4 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 151.1 (d, $J_{C\text{-}P}$ = 9.0 Hz), 150.7 (d, $J_{C\text{-}P}$ = 4.5 Hz), 133.2 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.3 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.2 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 131.9 (d, $J_{C\text{-}P}$ = 9.0 Hz), 130.1 (d, $J_{C\text{-}P}$ = 96.0 Hz), 129.4 (d, $J_{C\text{-}P}$ = 96.0 Hz), 129.2 (d, $J_{C\text{-}P}$ = 3.0 Hz), 129.1, 128.7, 128.6 (d, $J_{C\text{-}P}$ = 4.5 Hz), 128.4, 128.3, 128.2 (d, $J_{C\text{-}P}$ = 3.0 Hz), 124.7, 117.8 (d, $J_{C\text{-}P}$ = 4.5 Hz), 117.7 (d, $J_{C\text{-}P}$ = 1.5 Hz), 92.4 (d, $J_{C\text{-}P}$ = 7.5 Hz), 40.7 (d, $J_{C\text{-}P}$ = 67.5 Hz); ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 30.1; HRMS (ESI): Exact mass calcd for $C_{27}H_{20}ClO_2P$ $[M+H]^+$: 443.0962, Found: 443.0953.



4fa

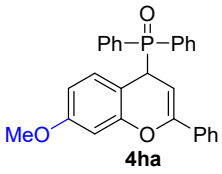
Column chromatography afforded the desired product **4fa** in 69% yield (100 mg) as yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.75-7.70 (m, 4H), 7.58-7.56 (m, 1H), 7.54-7.51 (m, 1H), 7.50-7.47 (m, 2H), 7.45-7.44 (m, 2H), 7.42-7.39 (m, 2H), 7.33-7.32 (m, 3H), 7.26-7.24 (m, 1H), 7.09 (s, 1H), 6.76 (d, J = 8.4 Hz, 1H), 5.37 (dd, J = 5.4 Hz, 3.6 Hz, 1H), 4.56 (dd, J = 19.2 Hz, 5.4 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 151.2 (d, $J_{C\text{-}P}$ = 4.5 Hz), 151.1 (d, $J_{C\text{-}P}$ = 9.0 Hz), 133.2 (d, $J_{C\text{-}P}$ = 4.5 Hz), 132.3 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.22 (d, $J_{C\text{-}P}$ = 1.5 Hz), 132.18 (d, $J_{C\text{-}P}$ = 1.5 Hz), 132.0 (d, $J_{C\text{-}P}$ = 7.5 Hz), 131.9 (d, $J_{C\text{-}P}$ = 9.0 Hz), 131.5 (d, $J_{C\text{-}P}$ = 1.5 Hz), 130.0 (d, $J_{C\text{-}P}$ = 94.5 Hz), 129.5 (d, $J_{C\text{-}P}$ = 96.0 Hz), 129.1, 128.6 (d, $J_{C\text{-}P}$ = 10.5 Hz), 128.37, 128.36 (d, $J_{C\text{-}P}$ = 12.0 Hz), 124.8 (d, $J_{C\text{-}P}$ = 1.5 Hz), 118.3 (d, $J_{C\text{-}P}$ = 4.5 Hz), 118.1 (d, $J_{C\text{-}P}$ = 1.5 Hz), 115.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 92.4 (d, $J_{C\text{-}P}$ = 6.0 Hz), 40.7 (d, $J_{C\text{-}P}$ = 67.5 Hz); ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 30.7; HRMS (ESI): Exact mass calcd for $C_{27}H_{20}BrO_2P$ $[M+H]^+$: 487.0457, Found: 487.0443.



4ga

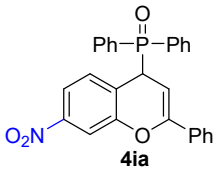
Column chromatography afforded the desired product **4ga** in 85% yield (107 mg) as yellow solid; Mp: 189-191 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.73-7.70 (m, 4H), 7.56-7.54 (m, 1H), 7.50-7.44 (m, 5H), 7.38-7.32 (m, 5H), 6.95 (dd, J = 7.2 Hz, 1.8 Hz, 1H), 6.74-6.72 (m, 2H), 5.39 (dd, J = 4.8 Hz, 3.6 Hz, 1H), 4.63 (dd, J = 20.4 Hz, 5.4 Hz, 1H), 2.27 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 151.9 (d, $J_{C\text{-}P}$ = 3.0 Hz), 151.1 (d, $J_{C\text{-}P}$ = 9.0 Hz), 138.8 (d, $J_{C\text{-}P}$ = 3.0 Hz), 133.7 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.1 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 131.9 (d, $J_{C\text{-}P}$ = 1.5 Hz), 130.5 (d, $J_{C\text{-}P}$ = 94.5 Hz), 130.1 (d, $J_{C\text{-}P}$ = 94.5 Hz), 129.3 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.8, 128.5 (d, $J_{C\text{-}P}$ = 10.5 Hz), 128.3, 128.2 (d, $J_{C\text{-}P}$ = 12.0 Hz), 124.8 (d, $J_{C\text{-}P}$ = 1.5 Hz), 124.5 (d, $J_{C\text{-}P}$ = 1.5 Hz),

117.0 (d, $J_{C\text{-}P}$ = 3.0 Hz), 112.8 (d, $J_{C\text{-}P}$ = 4.5 Hz), 92.9 (d, $J_{C\text{-}P}$ = 6.0 Hz), 40.4 (d, $J_{C\text{-}P}$ = 69.0 Hz), 21.1; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 30.3; HRMS (ESI): Exact mass calcd for $C_{28}H_{23}O_2P$ $[M+H]^+$: 423.1508, Found: 423.1498.



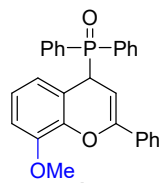
4ha

Column chromatography afforded the desired product **4ha** in 58% yield (76 mg) as yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.73-7.69 (m, 4H), 7.57-7.54 (m, 1H), 7.51-7.45 (m, 5H), 7.38-7.35 (m, 2H), 7.34-7.32 (m, 3H), 6.98 (dd, J = 9.0 Hz, 1.8 Hz, 1H), 6.52-6.50 (m, 1H), 6.44 (d, J = 2.4 Hz, 1H), 5.40 (dd, J = 5.4 Hz, 3.6 Hz, 1H), 4.61 (dd, J = 19.8 Hz, 5.4 Hz, 1H), 3.75 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 160.0 (d, $J_{C\text{-}P}$ = 1.5 Hz), 152.8 (d, $J_{C\text{-}P}$ = 4.5 Hz), 151.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 133.6 (d, $J_{C\text{-}P}$ = 4.5 Hz), 132.1 (d, $J_{C\text{-}P}$ = 7.5 Hz), 132.02, 132.015 (d, $J_{C\text{-}P}$ = 7.5 Hz), 131.95 (d, $J_{C\text{-}P}$ = 3.0 Hz), 130.4 (d, $J_{C\text{-}P}$ = 94.5 Hz), 130.2 (d, $J_{C\text{-}P}$ = 1.5 Hz), 130.0 (d, $J_{C\text{-}P}$ = 93.0 Hz), 128.9, 128.5 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.3, 128.2 (d, $J_{C\text{-}P}$ = 12.0 Hz), 124.8, 110.0, 107.8 (d, $J_{C\text{-}P}$ = 3.0 Hz), 101.8 (d, $J_{C\text{-}P}$ = 1.5 Hz), 93.2 (d, $J_{C\text{-}P}$ = 7.5 Hz), 55.4, 40.0 (d, $J_{C\text{-}P}$ = 67.5 Hz); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 31.2; HRMS (ESI): Exact mass calcd for $C_{28}H_{23}O_3P$ $[M+H]^+$: 439.1458, Found: 439.1457.



4ia

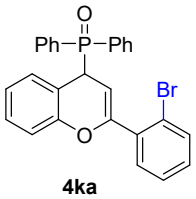
Column chromatography afforded the desired product **4ia** in 55% yield (75 mg) as yellow solid; Mp: 165-167 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.81-7.76 (m, 3H), 7.71-7.68 (m, 3H), 7.63-7.60 (m, 1H), 7.54-7.50 (m, 3H), 7.46-7.45 (m, 2H), 7.39-7.35 (m, 6H), 5.34 (dd, J = 5.4 Hz, 3.6 Hz, 1H), 4.71 (dd, J = 21.0 Hz, 5.4 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 152.3 (d, $J_{C\text{-}P}$ = 4.5 Hz), 151.1 (d, $J_{C\text{-}P}$ = 9.0 Hz), 148.0 (d, $J_{C\text{-}P}$ = 1.5 Hz), 132.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.5 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.1 (d, $J_{C\text{-}P}$ = 7.5 Hz), 131.8 (d, $J_{C\text{-}P}$ = 9.0 Hz), 130.4 (d, $J_{C\text{-}P}$ = 3.0 Hz), 129.9 (d, $J_{C\text{-}P}$ = 96.0 Hz), 129.5, 128.9 (d, $J_{C\text{-}P}$ = 10.5 Hz), 128.63, 128.55, 128.5 (d, $J_{C\text{-}P}$ = 96.0 Hz), 128.4 (d, $J_{C\text{-}P}$ = 10.5 Hz), 124.7, 123.9 (d, $J_{C\text{-}P}$ = 6.0 Hz), 118.2 (d, $J_{C\text{-}P}$ = 1.5 Hz), 111.8 (d, $J_{C\text{-}P}$ = 1.5 Hz), 92.6 (d, $J_{C\text{-}P}$ = 7.5 Hz), 40.9 (d, $J_{C\text{-}P}$ = 66.0 Hz); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 30.8; HRMS (ESI): Exact mass calcd for $C_{27}H_{20}NO_4P$ $[M+H]^+$: 454.1203, Found: 454.1196.



4ja

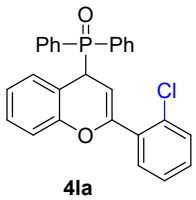
Column chromatography afforded the desired product **4ja** in 56% yield (74 mg) as yellow solid; Mp: 99-101 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.74-7.71 (m, 4H), 7.57-7.54 (m,

1H), 7.53-7.51 (m, 2H), 7.49-7.45 (m, 3H), 7.37-7.31 (m, 5H), 6.88-6.85 (m, 1H), 6.77 (d, J = 8.4 Hz, 1H), 6.72 (d, J = 7.8 Hz, 1H), 5.38 (dd, J = 5.4 Hz, 3.6 Hz, 1H), 4.67 (dd, J = 21.0 Hz, 5.4 Hz, 1H), 3.81 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 151.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 148.1 (d, $J_{C\text{-}P}$ = 1.5 Hz), 142.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 133.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.1 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.04 (d, $J_{C\text{-}P}$ = 4.5 Hz), 131.98 (d, $J_{C\text{-}P}$ = 4.5 Hz), 130.3 (d, $J_{C\text{-}P}$ = 94.5 Hz), 129.9 (d, $J_{C\text{-}P}$ = 94.5 Hz), 128.9, 128.5 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.4, 128.2 (d, $J_{C\text{-}P}$ = 10.5 Hz), 124.9, 123.2, 121.4 (d, $J_{C\text{-}P}$ = 3.0 Hz), 117.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 111.8, 92.8 (d, $J_{C\text{-}P}$ = 6.0 Hz), 56.4, 40.8 (d, $J_{C\text{-}P}$ = 67.5 Hz); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 31.1; HRMS (ESI): Exact mass calcd for $C_{28}H_{23}O_3P$ $[M+H]^+$: 439.1458, Found: 439.1451.



4ka

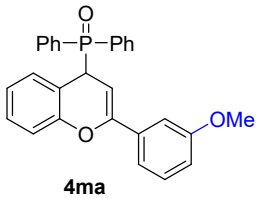
Column chromatography afforded the desired product **4ka** in 98% yield (142 mg) as yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.80-7.77 (m, 2H), 7.71-7.68 (m, 2H), 7.55-7.52 (m, 3H), 7.48-7.45 (m, 2H), 7.43-7.40 (m, 2H), 7.27-7.24 (m, 1H), 7.19-7.14 (m, 3H), 7.01-7.00 (m, 1H), 6.93-6.90 (m, 1H), 6.84 (d, J = 7.8 Hz, 1H), 5.26 (dd, J = 4.8 Hz, 3.0 Hz, 1H), 4.70 (dd, J = 20.4 Hz, 5.4 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 152.3 (d, $J_{C\text{-}P}$ = 3.0 Hz), 151.4 (d, $J_{C\text{-}P}$ = 7.5 Hz), 135.5 (d, $J_{C\text{-}P}$ = 3.0 Hz), 133.3, 132.21 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.15, 132.1 (d, $J_{C\text{-}P}$ = 7.5 Hz), 130.8 (d, $J_{C\text{-}P}$ = 1.5 Hz), 130.4, 130.1 (d, $J_{C\text{-}P}$ = 96.0 Hz), 129.9 (d, $J_{C\text{-}P}$ = 96.0 Hz), 129.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.7 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.3 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.2, 123.7 (d, $J_{C\text{-}P}$ = 1.5 Hz), 122.1 (d, $J_{C\text{-}P}$ = 3.0 Hz), 116.6, 116.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 98.0 (d, $J_{C\text{-}P}$ = 6.0 Hz), 40.9 (d, $J_{C\text{-}P}$ = 67.5 Hz); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 30.9; HRMS (ESI): Exact mass calcd for $C_{27}H_{20}BrO_2P$ $[M+H]^+$: 487.0457, Found: 487.0455.



4la

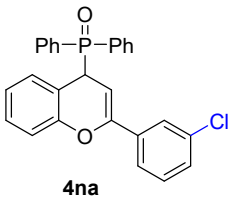
Column chromatography afforded the desired product **4la** in >99% yield (132 mg) as green oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.80-7.77 (m, 2H), 7.72-7.69 (m, 2H), 7.56-7.54 (m, 1H), 7.52-7.50 (m, 1H), 7.48-7.45 (m, 2H), 7.42-7.39 (m, 2H), 7.35-7.33 (m, 1H), 7.26-7.21 (m, 3H), 7.16-7.13 (m, 1H), 7.06 (d, J = 7.8 Hz, 1H), 6.94-6.92 (m, 1H), 6.81 (d, J = 8.4 Hz, 1H), 5.32 (dd, J = 4.8 Hz, 3.0 Hz, 1H), 4.70 (dd, J = 21.0 Hz, 4.8 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 152.2 (d, $J_{C\text{-}P}$ = 4.5 Hz), 149.9 (d, $J_{C\text{-}P}$ = 7.5 Hz), 133.4 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.7 (d, $J_{C\text{-}P}$ = 1.5 Hz), 132.2 (d, $J_{C\text{-}P}$ = 6.0 Hz), 132.12 (d, $J_{C\text{-}P}$ = 6.0 Hz), 132.06 (d, $J_{C\text{-}P}$ = 1.5 Hz), 130.39 (d, $J_{C\text{-}P}$ = 3.0 Hz), 130.36, 130.12 (d, $J_{C\text{-}P}$ = 96.0 Hz), 130.11 (d, $J_{C\text{-}P}$ = 15.0 Hz), 130.0 (d, $J_{C\text{-}P}$ = 96.0 Hz), 129.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.7 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.4 (d, $J_{C\text{-}P}$ = 30.0 Hz), 128.3 (d, $J_{C\text{-}P}$ = 30.0 Hz), 126.6,

123.7 (d, J_{C-P} = 1.5 Hz), 116.5 (d, J_{C-P} = 1.5 Hz), 116.0 (d, J_{C-P} = 3.0 Hz), 98.3 (d, J_{C-P} = 7.5 Hz), 40.9 (d, J_{C-P} = 67.5 Hz); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 30.7; HRMS (ESI): Exact mass calcd for $C_{27}H_{20}ClO_2P$ $[M+H]^+$: 443.0962, Found: 443.0953.



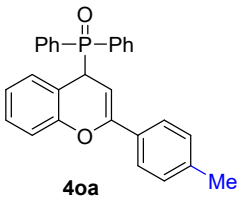
4ma

Column chromatography afforded the desired product **4ma** in 55% yield (73 mg) as yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.73-7.68 (m, 4H), 7.56-7.55 (m, 1H), 7.49-7.45 (m, 3H), 7.37-7.34 (m, 2H), 7.24 (t, J = 8.4 Hz, 1H), 7.14 (t, J = 7.8 Hz, 1H), 7.10 (d, J = 7.2 Hz, 1H), 7.05 (d, J = 7.8 Hz, 1H), 7.01 (s, 1H), 7.93 (t, J = 7.2 Hz, 1H), 6.88-6.85 (m, 2H), 5.38 (dd, J = 5.4 Hz, 3.6 Hz, 1H), 4.68 (dd, J = 21.0 Hz, 5.4 Hz, 1H), 3.80 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 159.6, 152.0 (d, J_{C-P} = 3.0 Hz), 150.9 (d, J_{C-P} = 9.0 Hz), 135.0 (d, J_{C-P} = 3.0 Hz), 132.06 (d, J_{C-P} = 13.5 Hz), 132.02 (d, J_{C-P} = 13.5 Hz), 130.4 (d, J_{C-P} = 94.5 Hz), 129.8 (d, J_{C-P} = 94.5 Hz), 129.6 (d, J_{C-P} = 1.5 Hz), 129.4, 128.6, 128.5 (d, J_{C-P} = 10.5 Hz), 128.2 (d, J_{C-P} = 12.0 Hz), 123.6, 117.3, 116.5, 116.0 (d, J_{C-P} = 4.5 Hz), 114.3, 110.6, 93.2 (d, J_{C-P} = 6.0 Hz), 55.3, 40.7 (d, J_{C-P} = 67.5 Hz); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 31.6; HRMS (ESI): Exact mass calcd for $C_{28}H_{23}O_3P$ $[M+H]^+$: 439.1458, Found: 439.1456.



4na

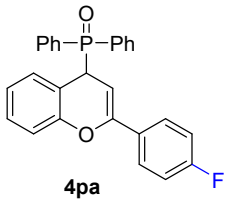
Column chromatography afforded the desired product **4na** in >99% yield (132 mg) as yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.71-7.66 (m, 4H), 7.57-7.55 (m, 1H), 7.52-7.49 (m, 1H), 7.47-7.44 (m, 3H), 7.39-7.36 (m, 2H), 7.34-7.33 (m, 1H), 7.29-7.28 (m, 1H), 7.26-7.23 (m, 1H), 7.17-7.14 (m, 1H), 7.03-7.02 (m, 1H), 6.93-6.91 (m, 1H), 6.87 (d, J = 7.8 Hz, 1H), 5.43 (dd, J = 4.8 Hz, 3.0 Hz, 1H), 4.65 (dd, J = 19.8 Hz, 5.4 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 151.9 (d, J_{C-P} = 4.5 Hz), 149.9 (d, J_{C-P} = 9.0 Hz), 135.3 (d, J_{C-P} = 3.0 Hz), 134.4, 132.2 (d, J_{C-P} = 1.5 Hz), 132.1 (d, J_{C-P} = 3.0 Hz), 132.0 (d, J_{C-P} = 9.0 Hz), 130.0 (d, J_{C-P} = 94.5 Hz), 129.8 (d, J_{C-P} = 94.5 Hz), 129.59, 129.57, 128.9, 128.7 (d, J_{C-P} = 3.0 Hz), 128.44 (d, J_{C-P} = 39.0 Hz), 128.36 (d, J_{C-P} = 39.0 Hz), 124.9, 123.7 (d, J_{C-P} = 1.5 Hz), 122.9 (d, J_{C-P} = 1.5 Hz), 116.5 (d, J_{C-P} = 1.5 Hz), 115.9 (d, J_{C-P} = 4.5 Hz), 94.0 (d, J_{C-P} = 6.0 Hz), 40.6 (d, J_{C-P} = 67.5 Hz); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 30.6; HRMS (ESI): Exact mass calcd for $C_{27}H_{20}ClO_2P$ $[M+H]^+$: 443.0962, Found: 443.0956.



4oa

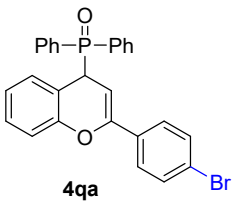
Column chromatography afforded the desired product **4oa** in 50% yield (63 mg) as yellow solid; Mp: 195-197 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.72-7.70 (m, 4H),

7.56-7.54 (m, 1H), 7.49-7.45 (m, 3H), 7.37-7.33 (m, 4H), 7.16-7.12 (m, 4H), 6.94-6.91 (m, 1H), 6.85 (d, J = 7.8 Hz, 1H), 5.33 (dd, J = 5.4 Hz, 3.0 Hz, 1H), 4.65 (dd, J = 20.4 Hz, 5.4 Hz, 1H), 2.35 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 152.1 (d, $J_{C\text{-}P}$ = 4.5 Hz), 151.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 138.9, 132.1 (d, $J_{C\text{-}P}$ = 7.5 Hz), 132.04 (d, $J_{C\text{-}P}$ = 3.0 Hz), 131.97, 131.95 (d, $J_{C\text{-}P}$ = 3.0 Hz), 130.8 (d, $J_{C\text{-}P}$ = 3.0 Hz), 130.4 (d, $J_{C\text{-}P}$ = 94.5 Hz), 129.8 (d, $J_{C\text{-}P}$ = 94.5 Hz), 129.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 129.0, 128.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.5 (d, $J_{C\text{-}P}$ = 10.5 Hz), 128.1 (d, $J_{C\text{-}P}$ = 10.5 Hz), 124.7, 123.5 (d, $J_{C\text{-}P}$ = 3.0 Hz), 116.5 (d, $J_{C\text{-}P}$ = 1.5 Hz), 116.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 91.9 (d, $J_{C\text{-}P}$ = 7.5 Hz), 40.6 (d, $J_{C\text{-}P}$ = 67.5 Hz), 21.3; $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 30.6; HRMS (ESI): Exact mass calcd for $C_{28}H_{23}O_2P$ $[M+H]^+$: 423.1508, Found: 423.1498.



4pa

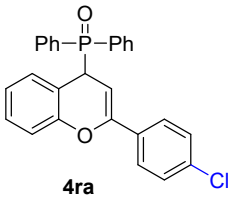
Column chromatography afforded the desired product **4pa** in 58% yield (75 mg) as yellow solid; Mp: 174-176 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.72-7.67 (m, 4H), 7.56-7.54 (m, 1H), 7.51-7.49 (m, 1H), 7.47-7.43 (m, 4H), 7.38-7.35 (m, 2H), 7.17-7.14 (m, 1H), 7.04-6.99 (m, 3H), 6.93-6.90 (m, 1H), 6.86 (d, J = 7.8 Hz, 1H), 5.34 (dd, J = 4.8 Hz, 3.0 Hz, 1H), 4.66 (dd, J = 19.8 Hz, 5.4 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 163.1 (d, $J_{C\text{-}F}$ = 97.5 Hz), 152.0 (d, $J_{C\text{-}P}$ = 3.0 Hz), 150.4 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.1 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.05 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.00 (d, $J_{C\text{-}P}$ = 4.5 Hz), 130.0 (d, $J_{C\text{-}P}$ = 94.5 Hz), 129.8 (d, $J_{C\text{-}P}$ = 94.5 Hz), 129.74 (d, $J_{C\text{-}P}$ = 6.0 Hz), 129.7, 129.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.7 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.2 (d, $J_{C\text{-}P}$ = 10.5 Hz), 126.7 (d, $J_{C\text{-}P}$ = 7.5 Hz), 123.6 (d, $J_{C\text{-}P}$ = 1.5 Hz), 116.5 (d, $J_{C\text{-}P}$ = 3.0 Hz), 116.0 (d, $J_{C\text{-}P}$ = 3.0 Hz), 115.3 (d, $J_{C\text{-}F}$ = 21.0 Hz), 92.5 (d, $J_{C\text{-}P}$ = 7.5 Hz), 40.5 (d, $J_{C\text{-}P}$ = 67.5 Hz); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 31.3; $^{19}F\{^{1}H\}$ NMR (564 MHz, $CDCl_3$): δ = -112.2 (1F); HRMS (ESI): Exact mass calcd for $C_{27}H_{20}FO_2P$ $[M+H]^+$: 427.1258, Found: 427.1252.



4qa

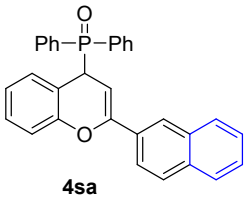
Column chromatography afforded the desired product **4qa** in 75% yield (110 mg) as white solid; Mp: 191-193 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.71-7.66 (m, 4H), 7.56-7.54 (m, 1H), 7.51-7.48 (m, 1H), 7.46-7.44 (m, 4H), 7.38-7.35 (m, 2H), 7.34-7.32 (m, 2H), 7.16-7.14 (m, 1H), 7.02 (d, J = 7.8 Hz, 1H), 6.92 (t, J = 7.8 Hz, 1H), 6.85 (d, J = 7.8 Hz, 1H), 5.41 (dd, J = 4.8 Hz, 3.0 Hz, 1H), 4.64 (dd, J = 19.8 Hz, 4.8 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 151.9 (d, $J_{C\text{-}P}$ = 3.0 Hz), 151.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.4 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.1, 132.04, 131.98 (d, $J_{C\text{-}P}$ = 3.0 Hz), 131.5, 130.0 (d, $J_{C\text{-}P}$ = 94.5 Hz), 129.9 (d, $J_{C\text{-}P}$ = 94.5 Hz), 129.6, 128.7, 128.5 (d, $J_{C\text{-}P}$ = 10.5 Hz), 128.2 (d, $J_{C\text{-}P}$ = 10.5 Hz), 126.3, 123.7, 123.0, 116.5, 115.9 (d, $J_{C\text{-}P}$ = 4.5

Hz), 93.3 (d, $J_{C\text{-}P}$ = 6.0 Hz), 40.6 (d, $J_{C\text{-}P}$ = 67.5 Hz); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 31.1; HRMS (ESI): Exact mass calcd for $C_{27}H_{20}BrO_2P$ $[M+H]^+$: 487.0457, Found: 487.0447.



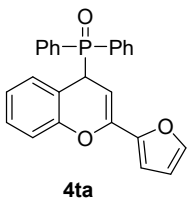
4ra

Column chromatography afforded the desired product **4ra** in 77% yield (102 mg) as white solid; Mp: 187-189 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.71-7.67 (m, 4H), 7.56-7.54 (m, 1H), 7.51-7.49 (m, 1H), 7.47-7.44 (m, 3H), 7.41-7.39 (m, 1H), 7.38-7.35 (m, 2H), 7.34-7.33 (m, 1H), 7.30-7.28 (m, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 5.41-5.40 (m, 1H), 4.64 (dt, *J* = 19.8 Hz, 4.8 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 151.9, 150.2 (d, $J_{C\text{-}P}$ = 7.5 Hz), 134.8, 132.4 (d, $J_{C\text{-}P}$ = 4.5 Hz), 132.1, 132.05 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.00 (d, $J_{C\text{-}P}$ = 3.0 Hz), 131.5, 130.1 (d, $J_{C\text{-}P}$ = 94.5 Hz), 129.9 (d, $J_{C\text{-}P}$ = 94.5 Hz), 129.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.7, 128.5 (d, $J_{C\text{-}P}$ = 10.5 Hz), 128.2 (d, $J_{C\text{-}P}$ = 10.5 Hz), 126.2 (d, $J_{C\text{-}P}$ = 39.0 Hz), 123.7, 123.0, 116.5, 116.0, 93.3 (d, $J_{C\text{-}P}$ = 15.0 Hz), 40.6 (d, $J_{C\text{-}P}$ = 67.5 Hz); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 31.1; HRMS (ESI): Exact mass calcd for $C_{27}H_{20}ClO_2P$ $[M+H]^+$: 443.0962, Found: 443.0956.



4sa

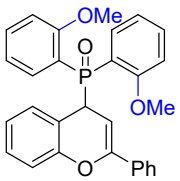
Column chromatography afforded the desired product **4sa** in 40% yield (59 mg) as brown oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.01 (s, 1H), 7.86-7.84 (m, 1H), 7.82-7.80 (m, 1H), 7.78-7.77 (m, 1H), 7.75-7.72 (m, 4H), 7.57-7.55 (m, 1H), 7.53-7.51 (m, 1H), 7.50-7.46 (m, 5H), 7.37-7.34 (m, 2H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 6.96-6.94 (m, 2H), 5.56 (dd, *J* = 5.4 Hz, 3.6 Hz, 1H), 4.71 (dd, *J* = 20.4 Hz, 5.4 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 152.1 (d, $J_{C\text{-}P}$ = 3.0 Hz), 151.0 (d, $J_{C\text{-}P}$ = 9.0 Hz), 133.4, 133.0, 132.1 (d, $J_{C\text{-}P}$ = 9.0 Hz), 132.0 (d, $J_{C\text{-}P}$ = 3.0 Hz), 130.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 130.1 (d, $J_{C\text{-}P}$ = 94.5 Hz), 129.8 (d, $J_{C\text{-}P}$ = 96.0 Hz), 129.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.7 (d, $J_{C\text{-}P}$ = 1.5 Hz), 128.54, 128.46 (d, $J_{C\text{-}P}$ = 1.5 Hz), 128.2 (d, $J_{C\text{-}P}$ = 10.5 Hz), 128.0, 127.6, 126.5 (d, $J_{C\text{-}P}$ = 15.0 Hz), 124.0, 123.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 122.3, 116.5 (d, $J_{C\text{-}P}$ = 3.0 Hz), 116.1 (d, $J_{C\text{-}P}$ = 4.5 Hz), 93.4 (d, $J_{C\text{-}P}$ = 6.0 Hz), 40.8 (d, $J_{C\text{-}P}$ = 67.5 Hz); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 31.3; HRMS (ESI): Exact mass calcd for $C_{31}H_{23}O_2P$ $[M+H]^+$: 459.1508, Found: 459.1500.



4ta

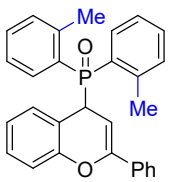
Column chromatography afforded the desired product **4ta** in 76% yield (49 mg) as yellow solid; Mp: 187-189 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.75-7.72 (m, 2H), 7.70-7.67 (m, 2H), 7.57-7.55 (m, 1H), 7.49-7.46 (m, 3H), 7.36-7.32 (m, 3H), 7.14-7.12 (m, 2H),

6.92 (td, J = 7.2 Hz, 1.2 Hz, 1H), 6.82-6.81 (m, 1H), 6.50 (d, J = 3.6 Hz, 1H), 6.39 (dd, J = 3.0 Hz, 1.8 Hz, 1H), 5.43 (dd, J = 5.4 Hz, 3.0 Hz, 1H), 4.62 (dd, J = 20.4 Hz, 5.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ = 151.6 (d, J_{C-P} = 3.0 Hz), 148.0 (d, J_{C-P} = 4.5 Hz), 144.0 (d, J_{C-P} = 9.0 Hz), 142.8, 132.1, 132.03 (d, J_{C-P} = 3.0 Hz), 131.95 (d, J_{C-P} = 3.0 Hz), 130.6 (d, J_{C-P} = 94.5 Hz), 129.8 (d, J_{C-P} = 3.0 Hz), 129.7 (d, J_{C-P} = 96.0 Hz), 128.62, 128.56 (d, J_{C-P} = 10.5 Hz), 128.1 (d, J_{C-P} = 10.5 Hz), 123.6 (d, J_{C-P} = 3.0 Hz), 116.4 (d, J_{C-P} = 3.0 Hz), 116.0 (d, J_{C-P} = 4.5 Hz), 111.2, 107.3 (d, J_{C-P} = 1.5 Hz), 91.6 (d, J_{C-P} = 7.5 Hz), 39.9 (d, J_{C-P} = 69.0 Hz); $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ = 30.2; HRMS (ESI): Exact mass calcd for $C_{25}H_{19}O_3P$ $[M+H]^+$: 399.1145, Found: 399.1135.



4ab

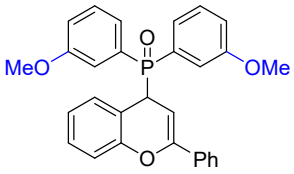
Column chromatography afforded the desired product **4ab** in 21% yield (30 mg) as white oil; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.70-7.66 (m, 1H), 7.50-7.42 (m, 4H), 7.40-7.38 (m, 1H), 7.31-7.27 (m, 3H), 7.24-7.22 (m, 1H), 7.05-7.02 (m, 1H), 6.98-6.92 (m, 3H), 6.88-6.87 (m, 1H), 6.79 (t, J = 7.2 Hz, 1H), 6.75 (dd, J = 8.4 Hz, 5.4 Hz, 1H), 5.53 (t, J = 4.8 Hz, 1H), 5.11 (dd, J = 25.2 Hz, 5.4 Hz, 1H), 3.77 (s, 3H), 3.54 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ = 160.7 (d, J_{C-P} = 6.0 Hz), 160.3 (d, J_{C-P} = 6.0 Hz), 151.6 (d, J_{C-P} = 6.0 Hz), 149.7 (d, J_{C-P} = 16.5 Hz), 135.8 (d, J_{C-P} = 9.0 Hz), 134.8 (d, J_{C-P} = 9.0 Hz), 134.4 (d, J_{C-P} = 4.5 Hz), 133.7 (d, J_{C-P} = 3.0 Hz), 133.6 (d, J_{C-P} = 3.0 Hz), 129.4 (d, J_{C-P} = 6.0 Hz), 128.4, 128.2, 127.9 (d, J_{C-P} = 3.0 Hz), 124.6 (d, J_{C-P} = 3.0 Hz), 123.0 (d, J_{C-P} = 3.0 Hz), 120.8 (d, J_{C-P} = 18.0 Hz), 120.6 (d, J_{C-P} = 16.5 Hz), 119.7 (d, J_{C-P} = 142.5 Hz), 118.4 (d, J_{C-P} = 141.0 Hz), 117.6 (d, J_{C-P} = 7.5 Hz), 116.0 (d, J_{C-P} = 3.0 Hz), 110.6 (d, J_{C-P} = 10.5 Hz), 109.9 (d, J_{C-P} = 10.5 Hz), 94.6 (d, J_{C-P} = 10.5 Hz), 55.5, 55.1, 41.6 (d, J_{C-P} = 106.5 Hz); $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ = 39.6; HRMS (ESI): Exact mass calcd for $C_{29}H_{25}O_4P$ $[M+H]^+$: 469.1563, Found: 469.1559.



4ac

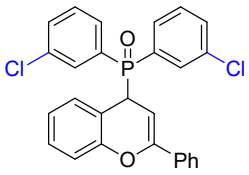
Column chromatography afforded **4ac** in 74% yield (96 mg) as yellow solid; Mp: 142-144 ^oC; ^1H NMR (600 MHz, $CDCl_3$): δ = 7.62-7.59 (m, 1H), 7.47-7.42 (m, 3H), 7.36-7.27 (m, 6H), 7.25-7.20 (m, 3H), 7.12-7.10 (m, 1H), 7.01-6.94 (m, 3H), 5.49 (dd, J = 5.4 Hz, 3.0 Hz, 1H), 4.80 (dd, J = 18.0 Hz, 5.4 Hz, 1H), 2.32 (s, 3H), 2.16 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ = 152.5 (d, J_{C-P} = 3.0 Hz), 151.5 (d, J_{C-P} = 9.0 Hz), 143.7 (d, J_{C-P} = 7.5 Hz), 143.4 (d, J_{C-P} = 6.0 Hz), 133.6 (d, J_{C-P} = 3.0 Hz), 132.3 (d, J_{C-P} = 10.5 Hz), 132.0 (d, J_{C-P} = 10.5 Hz), 131.8 (d, J_{C-P} = 3.0 Hz), 131.5 (d, J_{C-P} = 3.0 Hz), 131.0 (d, J_{C-P} = 10.5 Hz), 130.7 (d, J_{C-P} = 91.5 Hz), 130.6

(d, J_{C-P} = 3.0 Hz). 128.8, 128.6 (d, J_{C-P} = 3.0 Hz), 128.2, 125.4 (d, J_{C-P} = 12.0 Hz), 124.8, 124.5 (d, J_{C-P} = 12.0 Hz), 123.5 (d, J_{C-P} = 1.5 Hz), 116.3 (d, J_{C-P} = 1.5 Hz), 116.0 (d, J_{C-P} = 4.5 Hz), 93.6 (d, J_{C-P} = 7.5 Hz), 40.3 (d, J_{C-P} = 67.5 Hz), 21.4 (d, J_{C-P} = 4.5 Hz), 21.0 (d, J_{C-P} = 3.0 Hz); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 36.1; HRMS (ESI): Exact mass calcd for $C_{29}H_{25}O_2P$ $[M+H]^+$: 437.1665, Found: 437.1663.



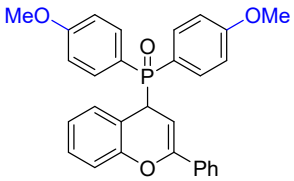
4ad

Column chromatography afforded **4ad** in 63% yield (89 mg) as yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70-7.66 (m, 1H), 7.50-7.42 (m, 4H), 7.40-7.38 (m, 1H), 7.30-7.27 (m, 3H), 7.24-7.23 (m, 1H), 7.05-7.02 (m, 1H), 6.97-6.92 (m, 3H), 6.88-6.87 (m, 1H), 6.81-6.78 (m, 1H), 6.75 (dd, J = 8.4 Hz, 5.4 Hz, 1H), 5.54 (t, J = 4.8 Hz, 1H), 5.12 (dd, J = 25.2 Hz, 4.8 Hz, 1H), 3.76 (s, 3H), 3.54 (s, 3H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 160.7 (d, J_{C-P} = 3.0 Hz), 160.2 (d, J_{C-P} = 3.0 Hz), 151.6, 149.6 (d, J_{C-P} = 15.0 Hz), 135.7 (d, J_{C-P} = 4.5 Hz), 134.8 (d, J_{C-P} = 7.5 Hz), 134.3 (d, J_{C-P} = 3.0 Hz), 133.6 (d, J_{C-P} = 21.0 Hz), 129.4 (d, J_{C-P} = 3.0 Hz), 128.4, 128.2, 127.9, 124.6, 123.0, 120.8 (d, J_{C-P} = 10.5 Hz), 120.6 (d, J_{C-P} = 10.5 Hz), 119.6 (d, J_{C-P} = 94.5 Hz), 118.3 (d, J_{C-P} = 94.5 Hz), 117.6 (d, J_{C-P} = 4.5 Hz), 116.0, 110.6 (d, J_{C-P} = 6.0 Hz), 109.9 (d, J_{C-P} = 6.0 Hz), 94.6, 55.5, 55.1, 41.6 (d, J_{C-P} = 70.5 Hz); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 39.6; HRMS (ESI): Exact mass calcd for $C_{29}H_{25}O_4P$ $[M+H]^+$: 469.1563, Found: 469.1558.



4ae

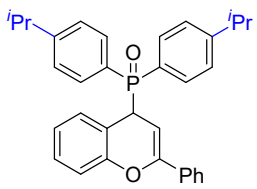
Column chromatography afforded **4ae** in 48% yield (68 mg) as yellow solid; Mp: 138-140 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.68-7.65 (m, 2H), 7.60-7.54 (m, 3H), 7.52-7.47 (m, 3H), 7.44-7.41 (m, 1H), 7.38-7.35 (m, 3H), 7.32-7.29 (m, 1H), 7.21-7.19 (m, 1H), 7.11-7.09 (m, 1H), 6.98 (t, J = 7.2 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H), 5.37 (dd, J = 5.4 Hz, 3.0 Hz, 1H), 4.65 (dd, J = 20.4 Hz, 5.4 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 152.0 (d, J_{C-P} = 4.5 Hz), 151.9 (d, J_{C-P} = 10.5 Hz), 135.2 (d, J_{C-P} = 15.0 Hz), 134.9 (d, J_{C-P} = 15.0 Hz), 133.2 (d, J_{C-P} = 3.0 Hz), 132.5 (d, J_{C-P} = 1.5 Hz), 132.4, 132.0 (d, J_{C-P} = 9.0 Hz), 131.8 (d, J_{C-P} = 9.0 Hz), 131.4. 130.1 (d, J_{C-P} = 12.0 Hz), 130.0 (d, J_{C-P} = 9.0 Hz), 129.9 (d, J_{C-P} = 7.5 Hz), 129.7 (d, J_{C-P} = 13.5 Hz), 129.5 (d, J_{C-P} = 3.0 Hz), 129.2, 129.1 (d, J_{C-P} = 3.0 Hz), 128.4, 124.9, 123.9 (d, J_{C-P} = 3.0 Hz), 116.7, 115.2 (d, J_{C-P} = 4.5 Hz), 91.9 (d, J_{C-P} = 7.5 Hz), 40.7 (d, J_{C-P} = 69.0 Hz); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 28.3; HRMS (ESI): Exact mass calcd for $C_{27}H_{19}Cl_2O_2P$ $[M+H]^+$: 477.0572, Found: 477.0565.



4af

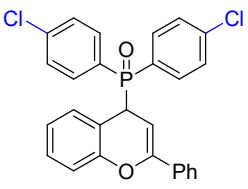
Column chromatography afforded the desired product **4af** in 34% yield (47 mg)

as white solid; Mp: 175-177 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.62-7.56 (m, 4H), 7.50-7.48 (m, 2H), 7.34-7.31 (m, 3H), 7.16-7.10 (m, 2H), 6.96-6.91 (m, 3H), 6.87-6.83 (m, 3H), 5.41 (dd, J = 7.8 Hz, 4.8 Hz, 1H), 4.59 (dd, J = 31.8 Hz, 8.4 Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 162.5, 152.0 (d, $J_{C\text{-}P}$ = 6.0 Hz), 150.8 (d, $J_{C\text{-}P}$ = 13.5 Hz), 134.0, 133.9 (d, $J_{C\text{-}P}$ = 1.5 Hz), 133.8, 133.7 (d, $J_{C\text{-}P}$ = 4.5 Hz), 129.7 (d, $J_{C\text{-}P}$ = 4.5 Hz), 128.8, 128.5 (d, $J_{C\text{-}P}$ = 4.5 Hz), 128.3, 124.8 (d, $J_{C\text{-}P}$ = 1.5 Hz), 123.5 (d, $J_{C\text{-}P}$ = 4.5 Hz), 121.5 (d, $J_{C\text{-}P}$ = 151.5 Hz), 121.2 (d, $J_{C\text{-}P}$ = 151.5 Hz), 116.5, 116.4 (d, $J_{C\text{-}P}$ = 3.0 Hz), 114.1 (d, $J_{C\text{-}P}$ = 19.5 Hz), 113.8 (d, $J_{C\text{-}P}$ = 18.0 Hz), 93.3 (d, $J_{C\text{-}P}$ = 10.5 Hz), 55.32, 55.26, 40.8 (d, $J_{C\text{-}P}$ = 103.5 Hz); ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 30.8; HRMS (ESI): Exact mass calcd for $C_{29}H_{25}O_4P$ $[M+H]^+$: 469.1563, Found: 469.1555.



4ag

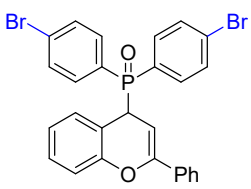
Column chromatography afforded **4ag** in 62% yield (58 mg) as yellow solid; Mp: 165-167 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.65-7.58 (m, 4H), 7.48-7.46 (m, 2H), 7.34-7.30 (m, 5H), 7.20-7.11 (m, 4H), 6.93-6.91 (m, 1H), 6.85 (d, J = 7.8 Hz, 1H), 5.40-5.39 (m, 1H), 4.61 (dd, J = 20.4 Hz, 5.4 Hz, 1H), 2.96-2.88 (m, 2H), 1.26 (d, J = 6.6 Hz, 6H), 1.22 (d, J = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 153.2 (d, $J_{C\text{-}P}$ = 1.5 Hz), 153.1 (d, $J_{C\text{-}P}$ = 1.5 Hz), 152.0 (d, $J_{C\text{-}P}$ = 3.0 Hz), 150.8 (d, $J_{C\text{-}P}$ = 9.0 Hz), 133.8 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.13 (d, $J_{C\text{-}P}$ = 18.0 Hz), 132.1, 129.7 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.8, 128.4 (d, $J_{C\text{-}P}$ = 1.5 Hz), 128.2, 127.6 (d, $J_{C\text{-}P}$ = 97.5 Hz), 127.0 (d, $J_{C\text{-}P}$ = 97.5 Hz), 126.6 (d, $J_{C\text{-}P}$ = 12.0 Hz), 126.3 (d, $J_{C\text{-}P}$ = 10.5 Hz), 124.8, 123.4 (d, $J_{C\text{-}P}$ = 1.5 Hz), 116.4 (d, $J_{C\text{-}P}$ = 1.5 Hz), 116.3 (d, $J_{C\text{-}P}$ = 4.5 Hz), 93.3 (d, $J_{C\text{-}P}$ = 6.0 Hz), 40.7 (d, $J_{C\text{-}P}$ = 67.5 Hz), 34.2, 34.1, 23.74, 23.68; ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 31.0; HRMS (ESI): Exact mass calcd for $C_{33}H_{33}O_2P$ $[M+H]^+$: 493.2291, Found: 493.2287.



4ah

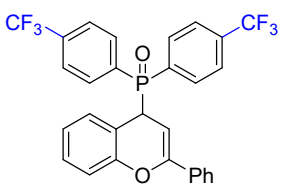
Column chromatography afforded the desired product **4ah** in 59% yield (85 mg) as white solid; Mp: 214-216 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.64-7.58 (m, 4H), 7.50-7.44 (m, 4H), 7.36-7.33 (m, 5H), 7.21-7.16 (m, 1H), 7.13-7.11 (m, 1H), 6.99-6.95 (m, 1H), 6.90 (d, J = 12.0 Hz, 1H), 5.37 (dd, J = 7.8 Hz, 4.8 Hz, 1H), 4.63 (dd, J = 31.2 Hz, 8.4 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 152.0 (d, $J_{C\text{-}P}$ = 6.0 Hz), 151.6 (d, $J_{C\text{-}P}$ = 15.0 Hz), 139.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 138.9 (d, $J_{C\text{-}P}$ = 4.5 Hz), 133.4 (d, $J_{C\text{-}P}$ = 10.5 Hz), 133.3 (d, $J_{C\text{-}P}$ = 10.5 Hz), 133.2, 129.6 (d, $J_{C\text{-}P}$ = 4.5 Hz), 129.2 (d, $J_{C\text{-}P}$ = 19.5 Hz), 129.00, 128.97, 128.7 (d, $J_{C\text{-}P}$ = 18.0 Hz), 128.54 (d, $J_{C\text{-}P}$ = 144.0 Hz), 128.48, 128.1 (d, $J_{C\text{-}P}$ = 144.0 Hz), 124.8 (d, $J_{C\text{-}P}$ = 1.5 Hz),

123.8 (d, $J_{C\text{-}P}$ = 3.0 Hz), 116.7 (d, $J_{C\text{-}P}$ = 3.0 Hz), 115.5 (d, $J_{C\text{-}P}$ = 6.0 Hz), 92.1 (d, $J_{C\text{-}P}$ = 9.0 Hz), 40.7 (d, $J_{C\text{-}P}$ = 103.5 Hz); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 29.1; HRMS (ESI): Exact mass calcd for $C_{27}H_{19}Cl_2O_2P$ $[M+H]^+$: 477.0572, Found: 477.0565.



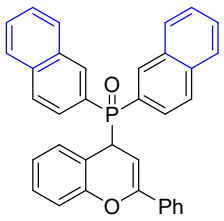
4ai

Column chromatography afforded the desired product **4ai** in 57% yield (96 mg) as white solid; Mp: 224-226 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.63-7.61 (m, 2H), 7.55-7.49 (m, 8H), 7.38-7.35 (m, 3H), 7.20-7.17 (m, 1H), 7.13-7.11 (m, 1H), 6.99-6.96 (m, 1H), 6.90 (d, J = 8.4 Hz, 1H), 5.37 (dd, J = 4.8 Hz, 3.0 Hz, 1H), 4.63 (dd, J = 20.4 Hz, 5.4 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 151.9 (d, $J_{C\text{-}P}$ = 3.0 Hz), 151.6 (d, $J_{C\text{-}P}$ = 9.0 Hz), 133.42 (d, $J_{C\text{-}P}$ = 18.0 Hz), 133.4, 133.2 (d, $J_{C\text{-}P}$ = 4.5 Hz), 131.9 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.6 (d, $J_{C\text{-}P}$ = 12.0 Hz), 129.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 129.2, 129.01 (d, $J_{C\text{-}P}$ = 94.5 Hz), 128.98 (d, $J_{C\text{-}P}$ = 1.5 Hz), 128.6 (d, $J_{C\text{-}P}$ = 94.5 Hz), 128.5, 127.61 (d, $J_{C\text{-}P}$ = 3.0 Hz), 127.56 (d, $J_{C\text{-}P}$ = 3.0 Hz), 124.8, 123.8 (d, $J_{C\text{-}P}$ = 3.0 Hz), 116.7 (d, $J_{C\text{-}P}$ = 3.0 Hz), 115.4 (d, $J_{C\text{-}P}$ = 6.0 Hz), 92.1 (d, $J_{C\text{-}P}$ = 7.5 Hz), 40.6 (d, $J_{C\text{-}P}$ = 69.0 Hz); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 29.3; HRMS (ESI): Exact mass calcd for $C_{27}H_{19}Br_2O_2P$ $[M+H]^+$: 564.9562, Found: 564.9562.



4aj

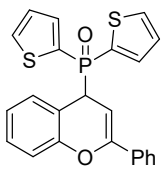
Column chromatography afforded the desired product **4aj** in 54% yield (88 mg) as white solid; Mp: 212-214 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.87-7.81 (m, 4H), 7.76-7.75 (m, 2H), 7.64-7.62 (m, 2H), 7.49-7.47 (m, 2H), 7.37-7.36 (m, 3H), 7.22-7.19 (m, 1H), 7.13 (d, J = 7.8 Hz, 1H), 7.00-6.98 (m, 1H), 6.90 (d, J = 8.4 Hz, 1H), 5.38 (dd, J = 5.4 Hz, 3.0 Hz, 1H), 4.72 (dd, J = 20.4 Hz, 5.4 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$): δ = 151.99 (d, $J_{C\text{-}F}$ = 12.0 Hz), 151.97, 134.6, 134.12 (qd, $J_{C\text{-}F}$ = 18.0 Hz, $J_{C\text{-}P}$ = 3.0 Hz), 134.08 (d, $J_{C\text{-}F}$ = 12.0 Hz), 133.5, 133.0 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.52 (d, $J_{C\text{-}P}$ = 4.5 Hz), 132.46 (d, $J_{C\text{-}P}$ = 6.0 Hz), 129.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 129.4, 129.2 (d, $J_{C\text{-}P}$ = 3.0 Hz), 128.5, 125.5 (dq, $J_{C\text{-}P}$ = 12.0 Hz, $J_{C\text{-}F}$ = 3.0 Hz), 125.2 (dq, $J_{C\text{-}P}$ = 12.0 Hz, $J_{C\text{-}F}$ = 3.0 Hz), 124.7, 124.0 (d, $J_{C\text{-}P}$ = 3.0 Hz), 123.4 (q, $J_{C\text{-}F}$ = 271.5 Hz), 116.8 (d, $J_{C\text{-}P}$ = 1.5 Hz), 115.0 (d, $J_{C\text{-}P}$ = 4.5 Hz), 91.6 (d, $J_{C\text{-}P}$ = 7.5 Hz), 40.7 (d, $J_{C\text{-}P}$ = 69.0 Hz); $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ = 28.0; $^{19}F\{^{1}H\}$ NMR (564 MHz, $CDCl_3$): δ = -63.20 (3F), -62.23 (3F); HRMS (ESI): Exact mass calcd for $C_{29}H_{19}F_6O_2P$ $[M+H]^+$: 545.1100, Found: 545.1099.



4ak

Column chromatography afforded the desired product **4ak** in 57% yield (85 mg) as

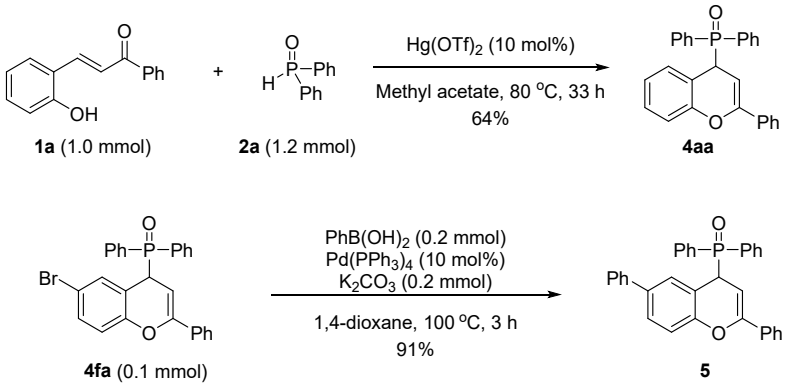
yellow solid; Mp: 84-86 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.75 (d, *J* = 8.4 Hz, 1H), 8.62 (d, *J* = 8.4 Hz, 1H), 8.04 (m, *J* = 8.4 Hz, 1H), 7.91-7.89 (m, 2H), 7.84-7.78 (m, 2H), 7.67-7.63 (m, 1H), 7.49-7.47 (m, 2H), 7.41-7.38 (m, 2H), 7.33-7.29 (m, 3H), 7.26-7.24 (m, 4H), 7.22-7.20 (m, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.90-6.88 (m, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 5.38-5.37 (m, 1H), 5.13 (dd, *J* = 21.0 Hz, 5.4 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 152.0 (d, J_{C-P} = 4.5 Hz), 150.9 (d, J_{C-P} = 9.0 Hz), 134.5 (d, J_{C-P} = 7.5 Hz), 134.1 (d, J_{C-P} = 9.0 Hz), 134.0 (d, J_{C-P} = 7.5 Hz), 133.8 (d, J_{C-P} = 9.0 Hz), 133.5 (d, J_{C-P} = 3.0 Hz), 133.2 (d, J_{C-P} = 3.0 Hz), 133.0 (d, J_{C-P} = 1.5 Hz), 132.4 (d, J_{C-P} = 10.5 Hz), 131.6 (d, J_{C-P} = 10.5 Hz), 130.3 (d, J_{C-P} = 3.0 Hz), 128.8 (d, J_{C-P} = 12.0 Hz), 128.6 (d, J_{C-P} = 1.5 Hz), 128.5, 128.3 (d, J_{C-P} = 91.5 Hz), 128.1, 127.4, 127.3 (d, J_{C-P} = 4.5 Hz), 126.7 (d, J_{C-P} = 67.5 Hz), 126.4 (d, J_{C-P} = 91.5 Hz), 126.1, 116.3 (d, J_{C-P} = 1.5 Hz), 116.2 (d, J_{C-P} = 4.5 Hz), 93.9 (d, J_{C-P} = 6.0 Hz), 41.2 (d, J_{C-P} = 67.5 Hz); ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 38.5; HRMS (ESI): Exact mass calcd for $C_{35}H_{25}O_2P$ [M+H]$^+$: 509.1665, Found: 509.1666.



4al

Column chromatography afforded the desired product **4al** in 79% yield (100 mg) as red solid; Mp: 194-196 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.80-7.79 (m, 1H), 7.67-7.63 (m, 2H), 7.60-7.59 (m, 2H), 7.51-7.49 (m, 1H), 7.39-7.36 (m, 3H), 7.31-7.30 (m, 1H), 7.25-7.23 (m, 1H), 7.22-7.19 (m, 1H), 7.091-7.086 (m, 1H), 7.05-7.02 (m, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 5.45 (dd, *J* = 4.8 Hz, 3.6 Hz, 1H), 4.54 (dd, *J* = 22.8 Hz, 5.4 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 151.9 (d, J_{C-P} = 4.5 Hz), 151.8 (d, J_{C-P} = 10.5 Hz), 137.3 (d, J_{C-P} = 9.0 Hz), 136.9 (d, J_{C-P} = 9.0 Hz), 134.4 (d, J_{C-P} = 4.5 Hz), 134.1 (d, J_{C-P} = 4.5 Hz), 133.6 (d, J_{C-P} = 3.0 Hz), 130.9 (d, J_{C-P} = 106.5 Hz), 130.0 (d, J_{C-P} = 3.0 Hz), 129.7 (d, J_{C-P} = 106.5 Hz), 129.1, 129.0 (d, J_{C-P} = 3.0 Hz), 128.4, 128.3 (d, J_{C-P} = 15.0 Hz), 128.0 (d, J_{C-P} = 13.5 Hz), 125.0, 123.8 (d, J_{C-P} = 3.0 Hz), 116.5 (d, J_{C-P} = 3.0 Hz), 115.4 (d, J_{C-P} = 4.5 Hz), 91.7 (d, J_{C-P} = 7.5 Hz), 43.0 (d, J_{C-P} = 76.5 Hz); ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 21.3; HRMS (ESI): Exact mass calcd for $C_{23}H_{17}O_2PS_2$ [M+H]$^+$: 421.0480, Found: 421.0475.

4. Scaled synthesis and product elaboration



4.1 Scaled synthesis

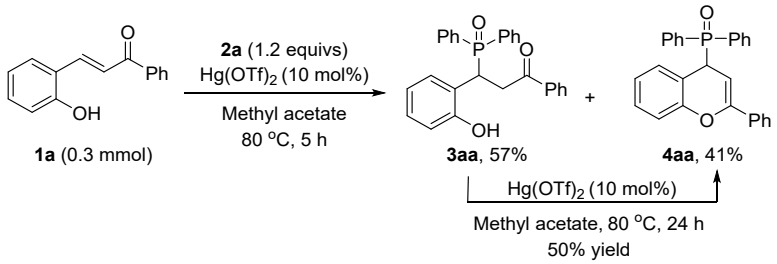
To a 35-mL sealed tube were added 2-hydroxychalcone **1a** (1.0 mmol, 224.2 mg, 1.0 equiv), $Ph_2P(O)H$ **2a** (1.2 mmol, 242.7 mg, 1.2 equivs) and 12.0 mL of anhydrous methyl acetate. After adding $Hg(OTf)_2$ (50.0 mg, 10 mol%), the reaction mixture was stirred at 80 °C till the almost full conversion of **1a** by TLC analysis and then further stirred for 24 hrs. The reaction mixture was cooled to room temperature and then directly subjected to column chromatography using dichloromethane/ethyl acetate (generally 40:1 to 5:1, v:v) as the eluent to afford the desired product **4aa** in 64% yield (0.26 g).

4.2 Product elaboration

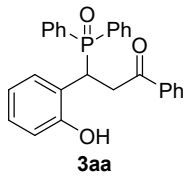
Compound **5** was prepared from **4fa** (60.1 mg, 0.1 mmol) and phenylboronic acid (24.4 mg, 0.2 mmol) according to the literature procedure.[2] Column chromatography afforded **5** in 91% yield (44 mg) as white solid. Mp: 193-195 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.80-7.77 (m, 2H), 7.74-7.71 (m, 2H), 7.56-7.53 (m, 2H), 7.51-7.50 (m, 2H), 7.48-7.45 (m, 2H), 7.43-7.40 (m, 3H), 7.36-7.33 (m, 5H), 7.30-7.28 (m, 3H), 7.21 (s, 1H), 6.97 (d, J = 9.0 Hz, 1H), 5.47 (dd, J = 5.4 Hz, 3.6 Hz, 1H), 4.72 (dd, J = 19.2 Hz, 5.4 Hz, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 151.6 (d, $J_{C\text{-}P}$ = 4.5 Hz), 151.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 139.9, 136.3 (d, $J_{C\text{-}P}$ = 3.0 Hz), 133.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.14 (d, $J_{C\text{-}P}$ = 7.5 Hz), 132.09, 132.06 (d, $J_{C\text{-}P}$ = 4.5 Hz), 132.0 (d, $J_{C\text{-}P}$ = 3.0 Hz), 130.4 (d, $J_{C\text{-}P}$ = 94.5 Hz), 129.9 (d, $J_{C\text{-}P}$ = 94.5 Hz), 128.9, 128.6 (d, $J_{C\text{-}P}$ = 10.5 Hz), 128.4 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.3, 128.1 (d, $J_{C\text{-}P}$ = 3.0 Hz), 127.2 (d, $J_{C\text{-}P}$ = 1.5 Hz), 127.0, 126.7, 124.8, 116.9 (d, $J_{C\text{-}P}$ = 3.0 Hz), 116.3 (d, $J_{C\text{-}P}$ = 4.5 Hz), 92.5 (d, $J_{C\text{-}P}$ = 7.5 Hz), 40.8 (d, $J_{C\text{-}P}$ = 67.5 Hz); ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 31.1; HRMS (ESI): Exact mass calcd for $C_{33}H_{25}O_2P$ $[M+H]^+$: 485.1665, Found: 485.1661.

5. Mechanism investigation

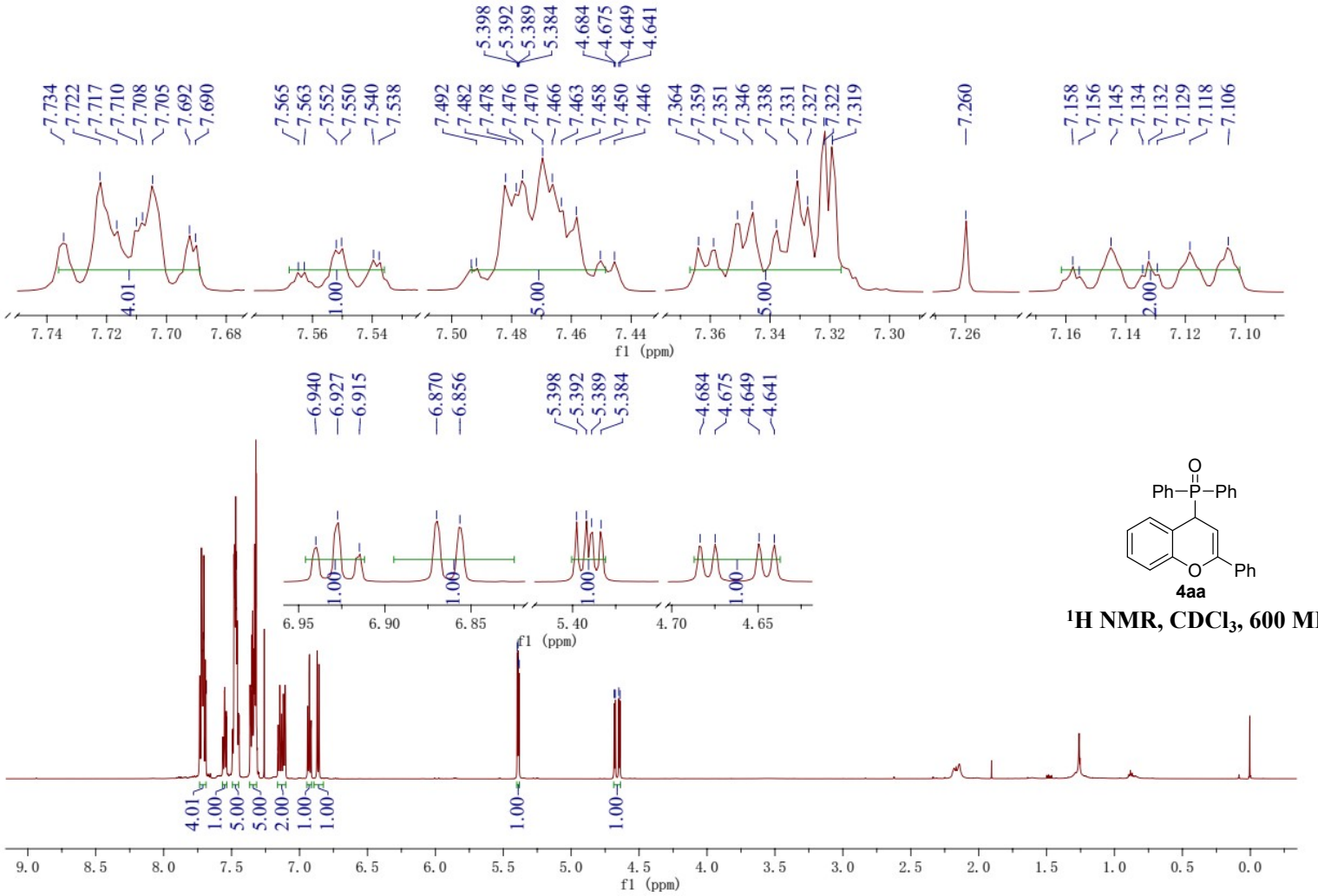
[2] N. Eleya, A. Mahal, M. Hein, A. Villiger and P. Langer, *Adv. Synth. Catal.* 2011, **353**, 2761.



To a 35-mL sealed tube were added 2-hydroxychalcone **1a** (0.3 mmol, 67.2 mg, 1.0 equiv), $Ph_2P(O)H$ **2a** (0.36 mmol, 72.8 mg, 1.2 equivs) and 6.0 mL of anhydrous methyl acetate. After adding $Hg(OTf)_2$ (15.0 mg, 10 mol%), the reaction mixture was stirred at 80 °C till almost full conversion of **1a** by TLC analysis. The reaction mixture was cooled to room temperature and then directly subjected to column chromatography using dichloromethane/ethyl acetate (generally 40:1 to 5:1, v:v) as the eluent to afford the intermediate **3aa** (73 mg, 57% yield) and product **4aa** (51 mg, 41% yield). To a 35-mL sealed tube were added intermediate **3aa** (0.1 mmol, 42.6 mg, 1.0 equiv), $Hg(OTf)_2$ (5.0 mg, 10 mol%) and 3.0 mL of anhydrous methyl acetate. The reaction mixture was stirred at 80 °C for 24 hrs. The reaction mixture was cooled to room temperature and then directly subjected to column chromatography using dichloromethane/ethyl acetate (generally 40:1 to 5:1, v:v) as the eluent to afford the desired product **4aa** in 50% yield (0.21 g).

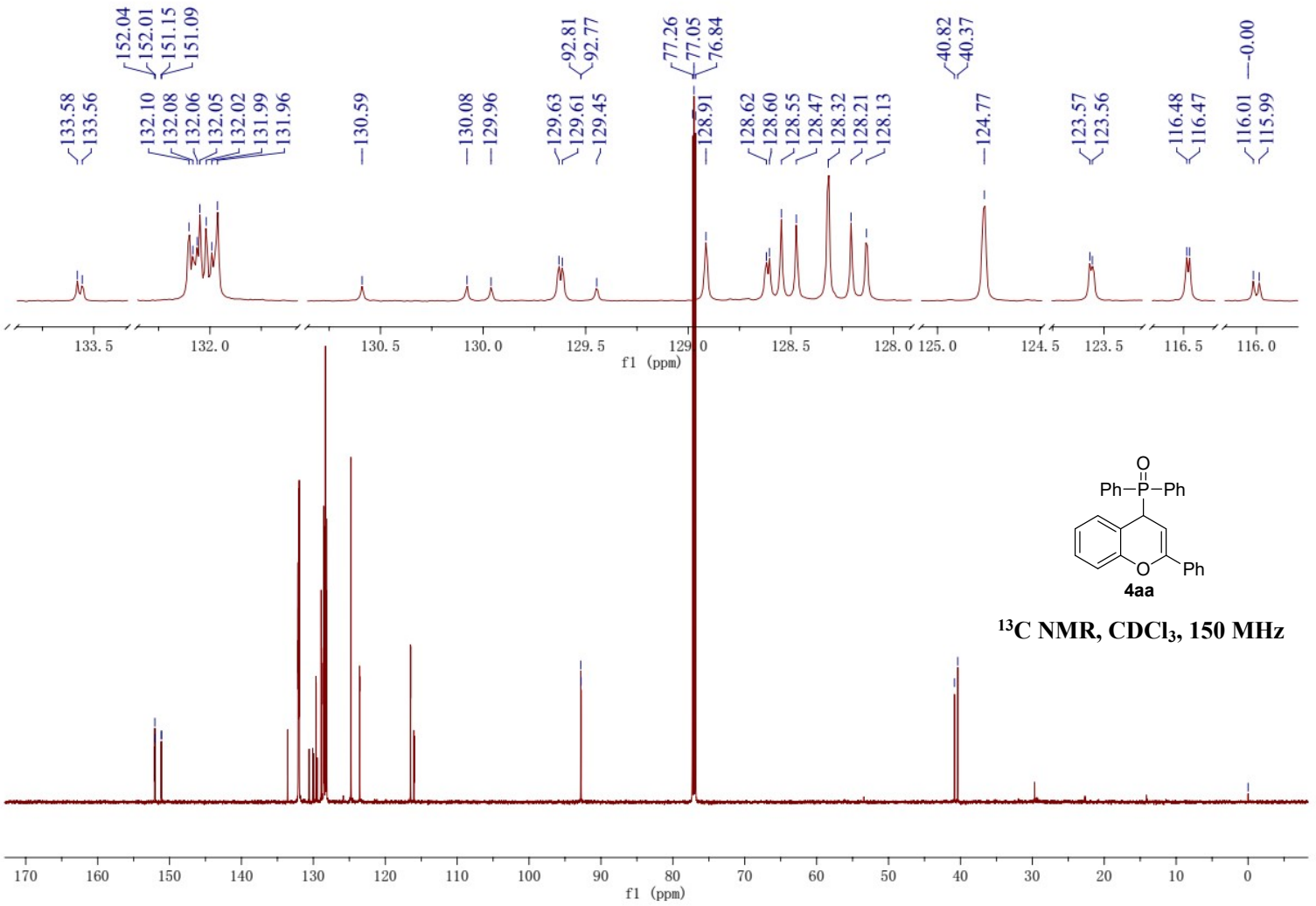

3aa

White solid; Mp: 181-183 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 10.25 (brs, 1H), 7.97-7.93 (m, 2H), 7.83-7.81 (m, 2H), 7.66-7.63 (m, 2H), 7.54-7.50 (m, 3H), 7.49-7.47 (m, 1H), 7.41-7.39 (m, 1H), 7.36-7.31 (m, 4H), 7.03-7.01 (m, 2H), 6.92-6.91 (m, 1H), 6.64-6.62 (m, 1H), 4.56 (td, J = 9.0 Hz, 2.4 Hz, 1H), 4.30-4.25 (m, 1H), 3.31-3.26 (m, 1H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 196.8, 156.0, 136.2, 133.5, 133.1, 132.6 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.1 (d, $J_{C\text{-}P}$ = 3.0 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.0 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.0 Hz), 130.3 (d, $J_{C\text{-}P}$ = 100.5 Hz), 129.5 (d, $J_{C\text{-}P}$ = 100.5 Hz), 129.25, 129.18 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.54, 128.53 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.2, 122.7 (d, $J_{C\text{-}P}$ = 6.0 Hz), 120.5, 120.0, 36.0; ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ = 42.2; HRMS (ESI): Exact mass calcd for $C_{27}H_{23}O_3P$ $[M+H]^+$: 427.1458, Found: 427.1455.



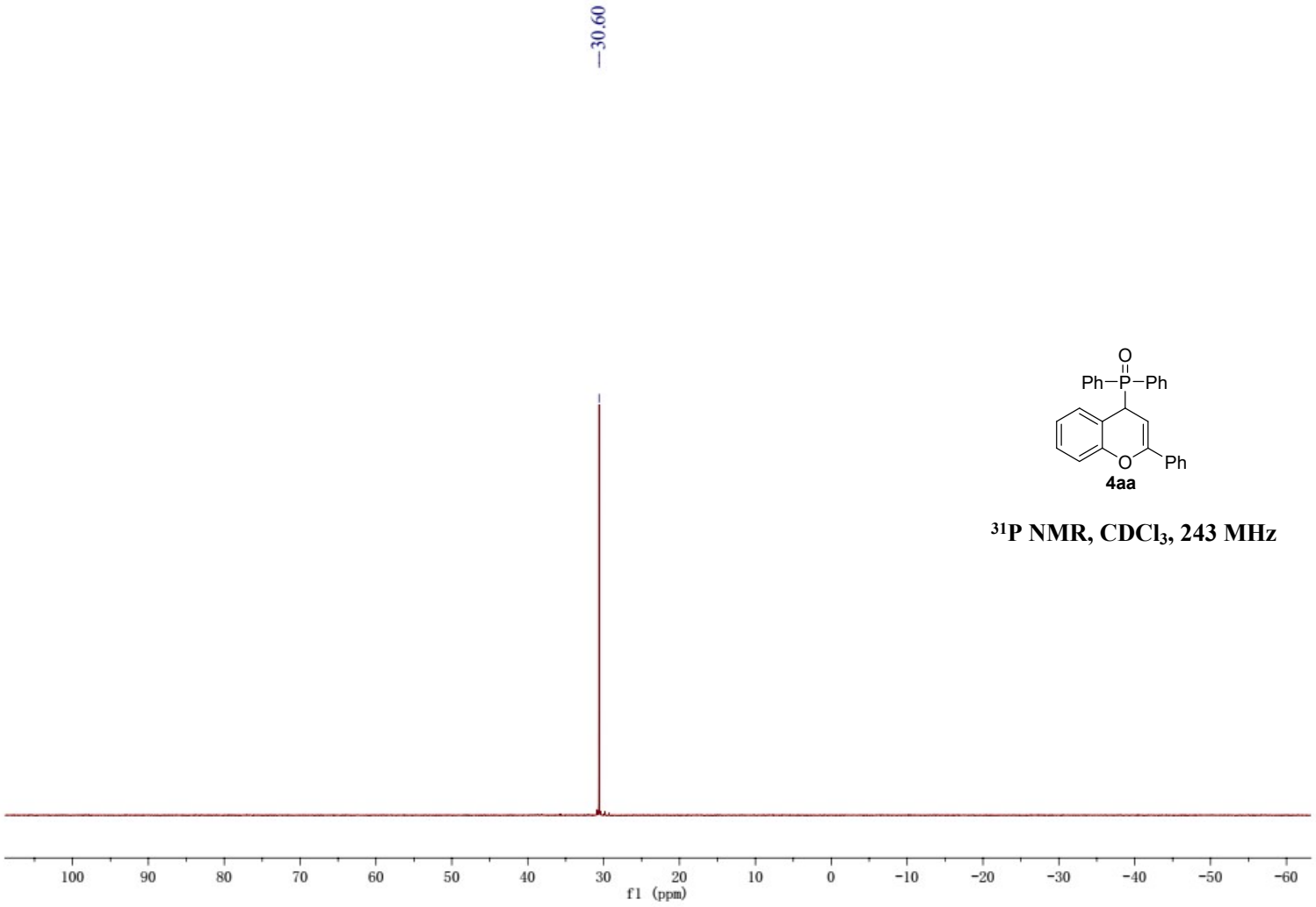
4aa

^{1}H NMR, $CDCl_3$, 600 MHz



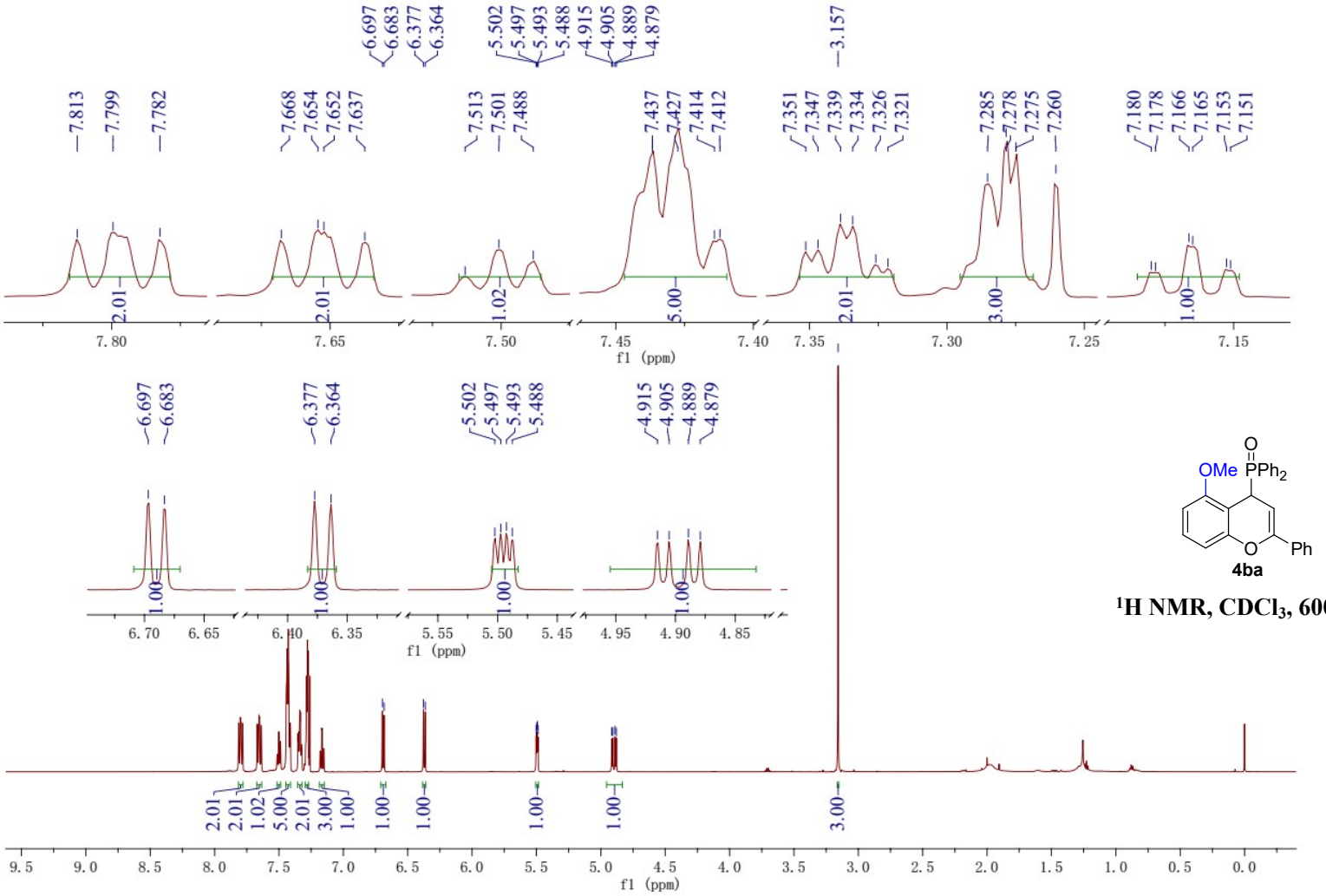
4aa

^{13}C NMR, $CDCl_3$, 150 MHz



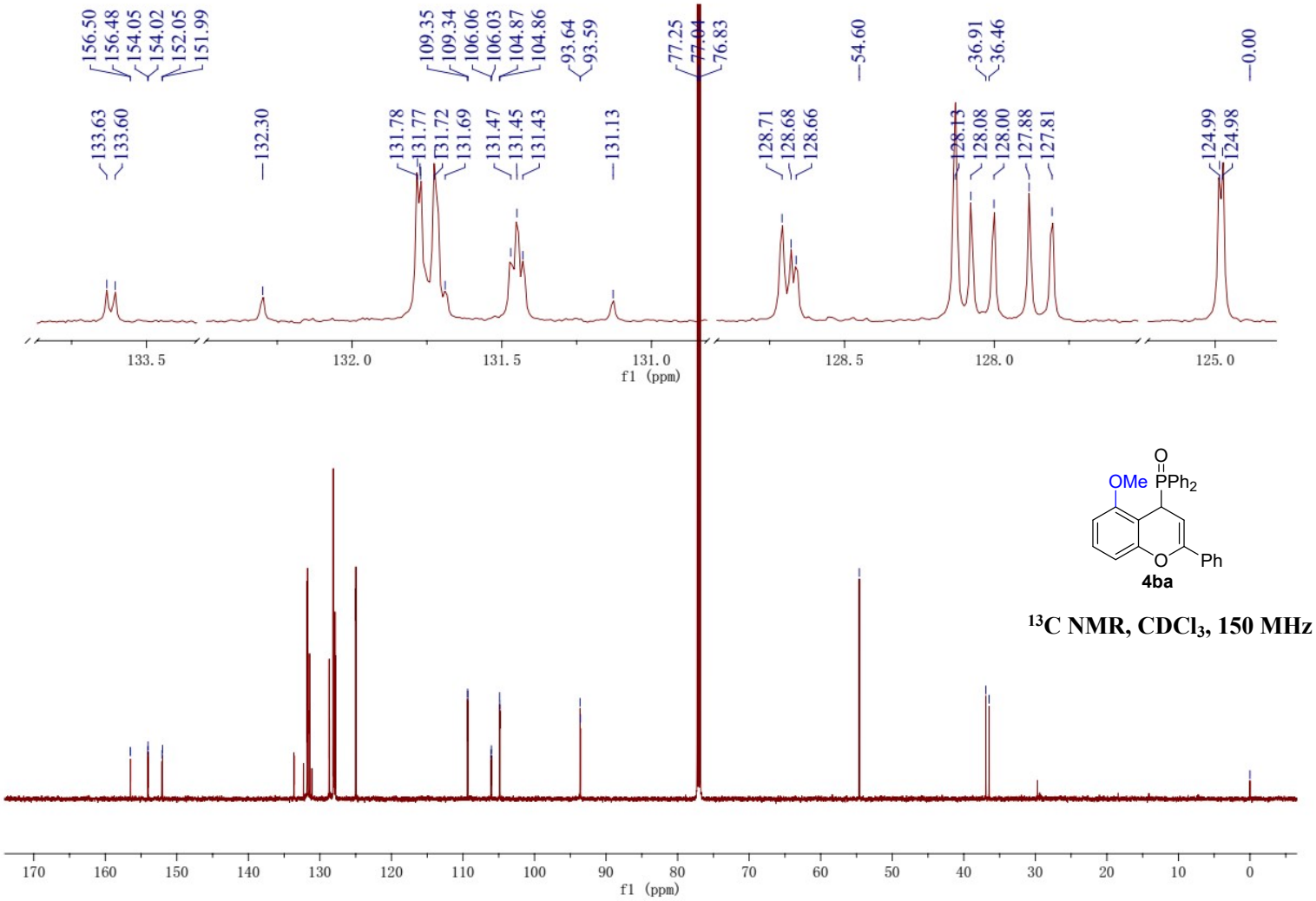
4aa

^{31}P NMR, $CDCl_3$, 243 MHz



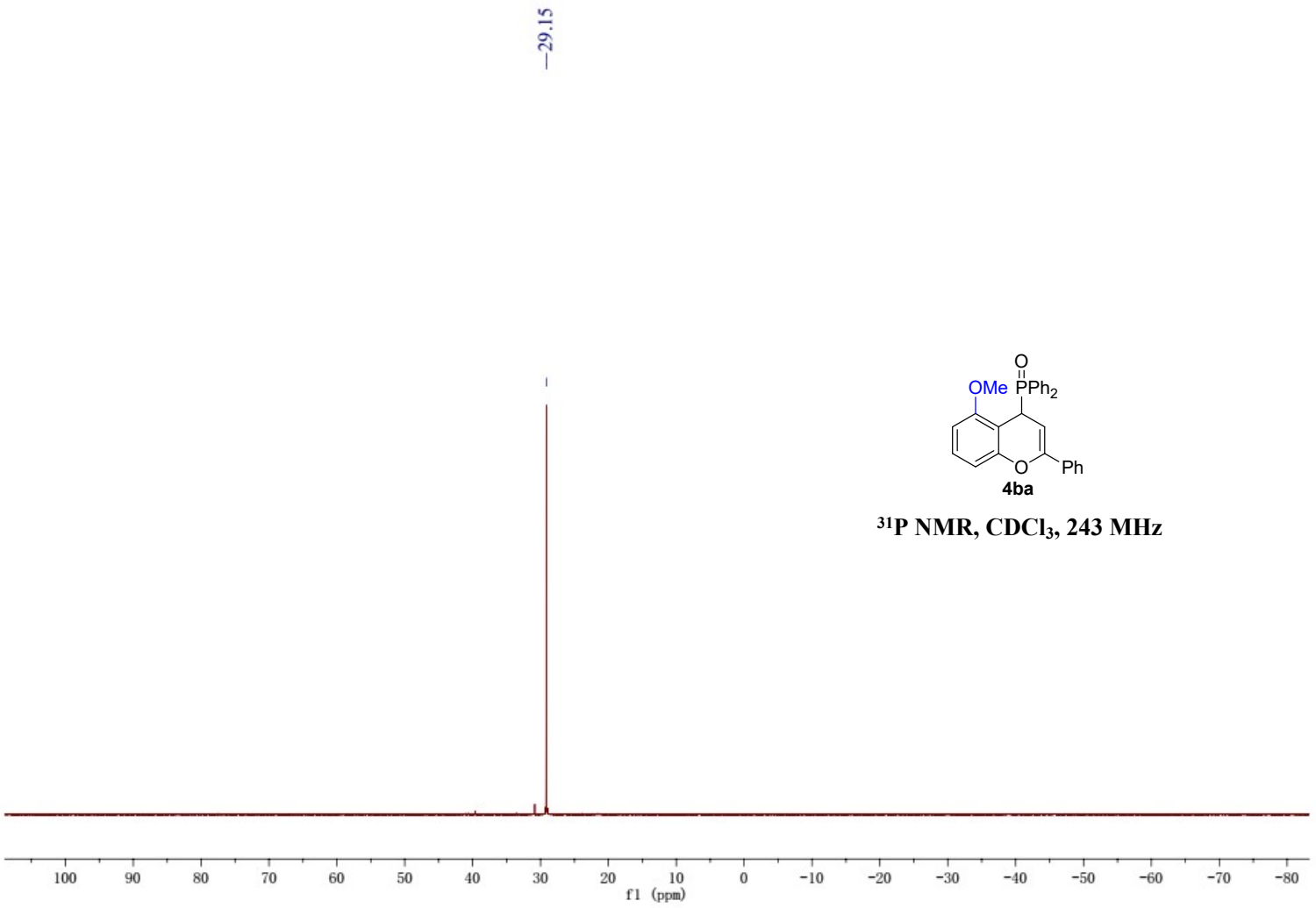
4ba

^{1}H NMR, $CDCl_3$, 600 MHz



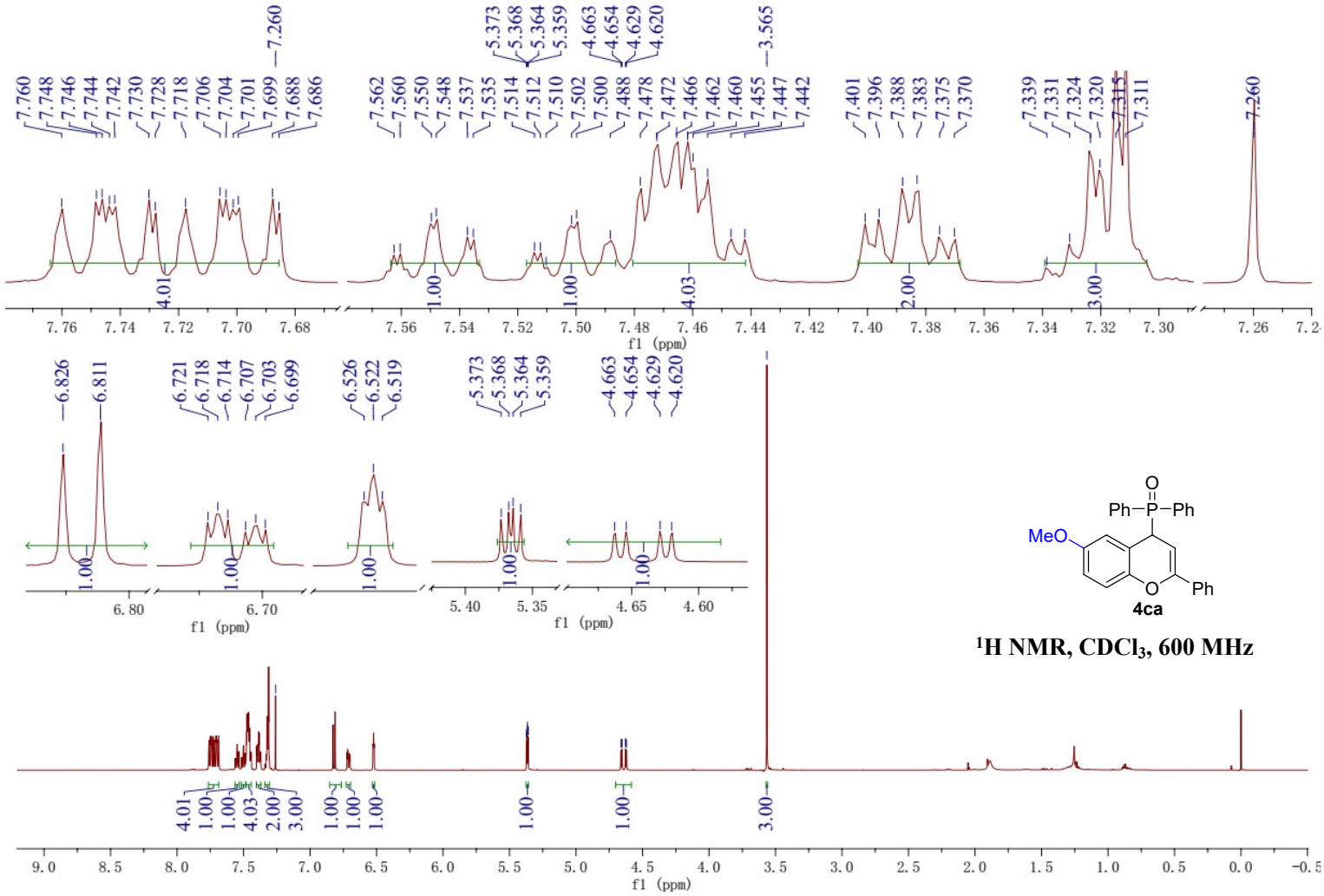
4ba

^{13}C NMR, $CDCl_3$, 150 MHz

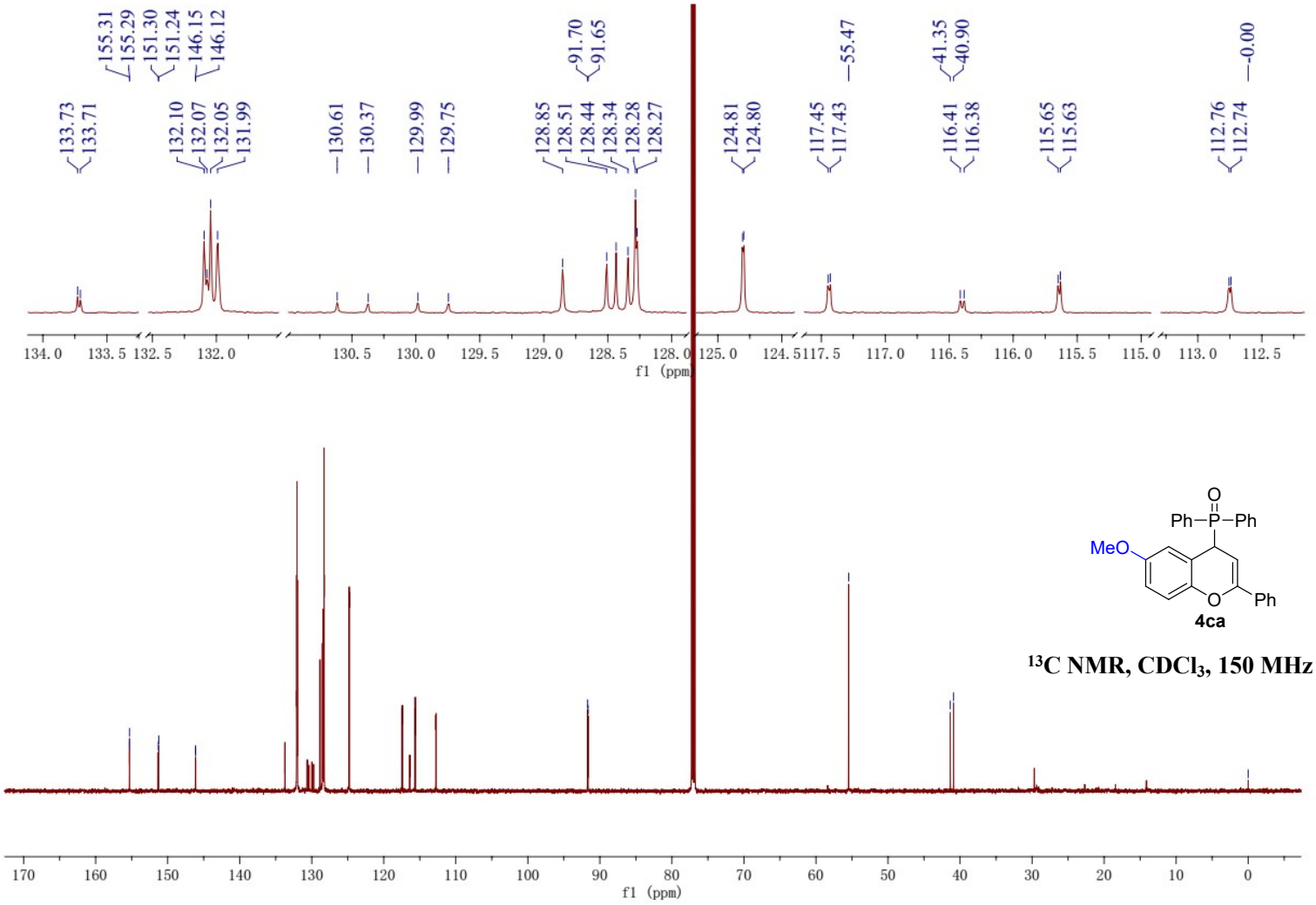


4ba

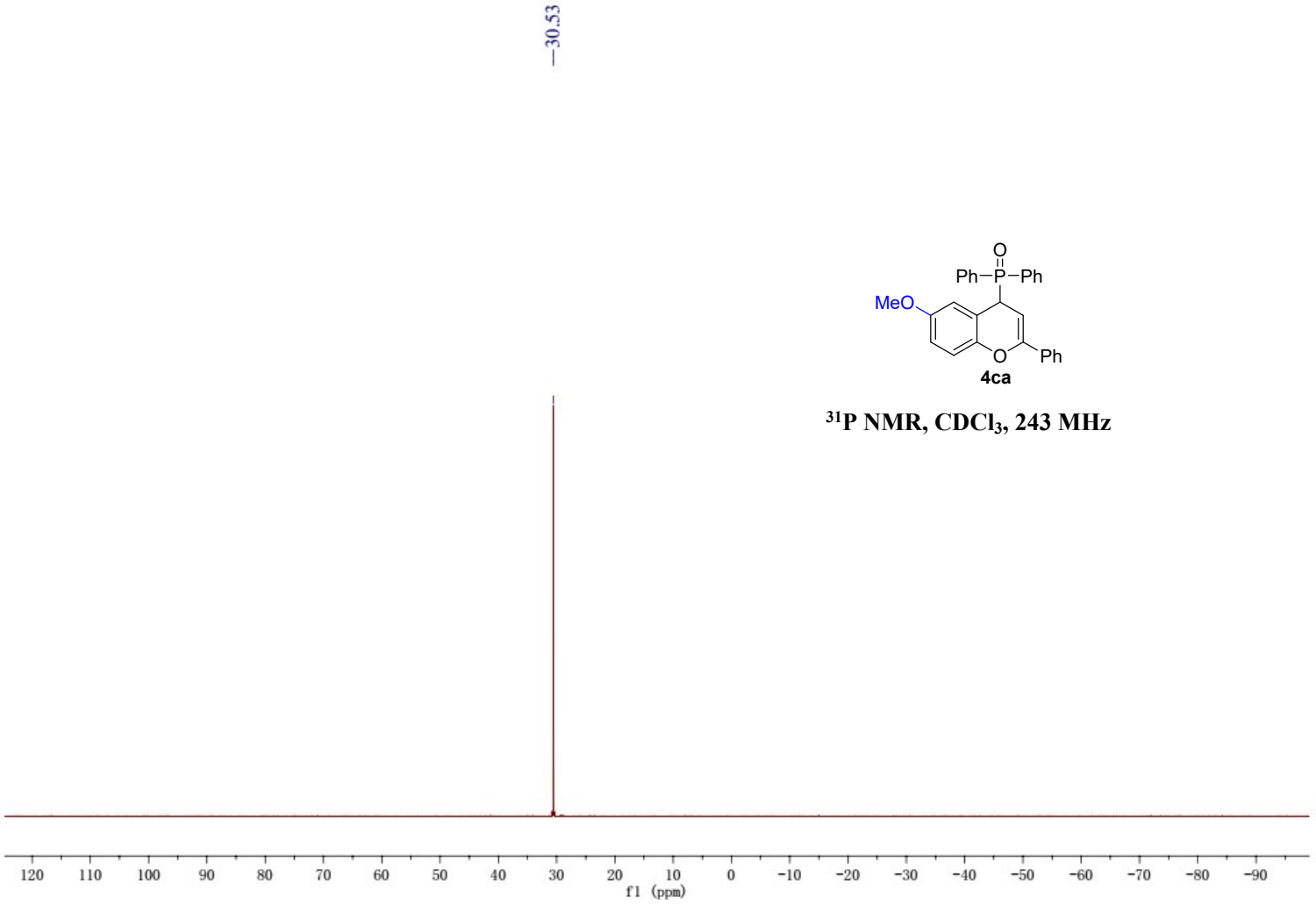
^{31}P NMR, $CDCl_3$, 243 MHz



^{1}H NMR, $CDCl_3$, 600 MHz

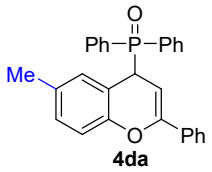


^{13}C NMR, $CDCl_3$, 150 MHz



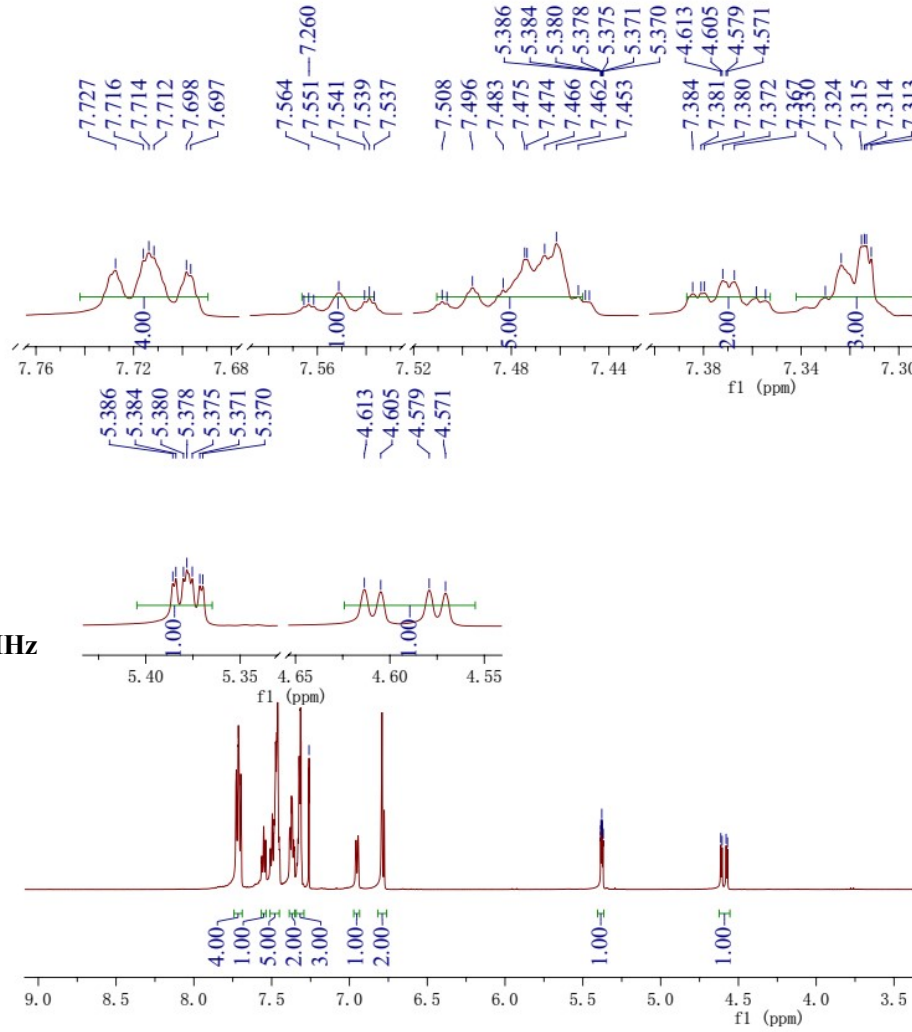
4ca

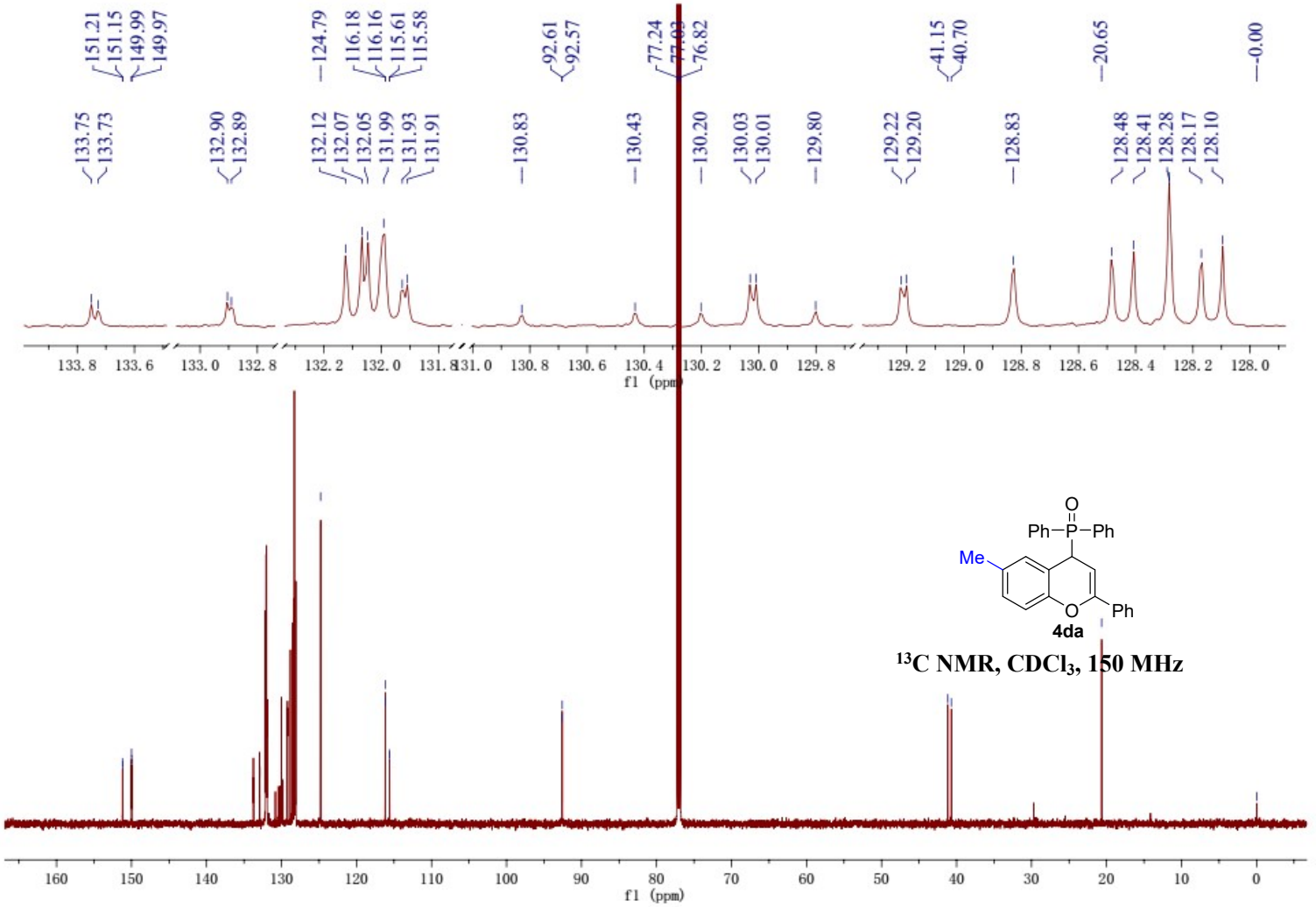
^{31}P NMR, $CDCl_3$, 243 MHz



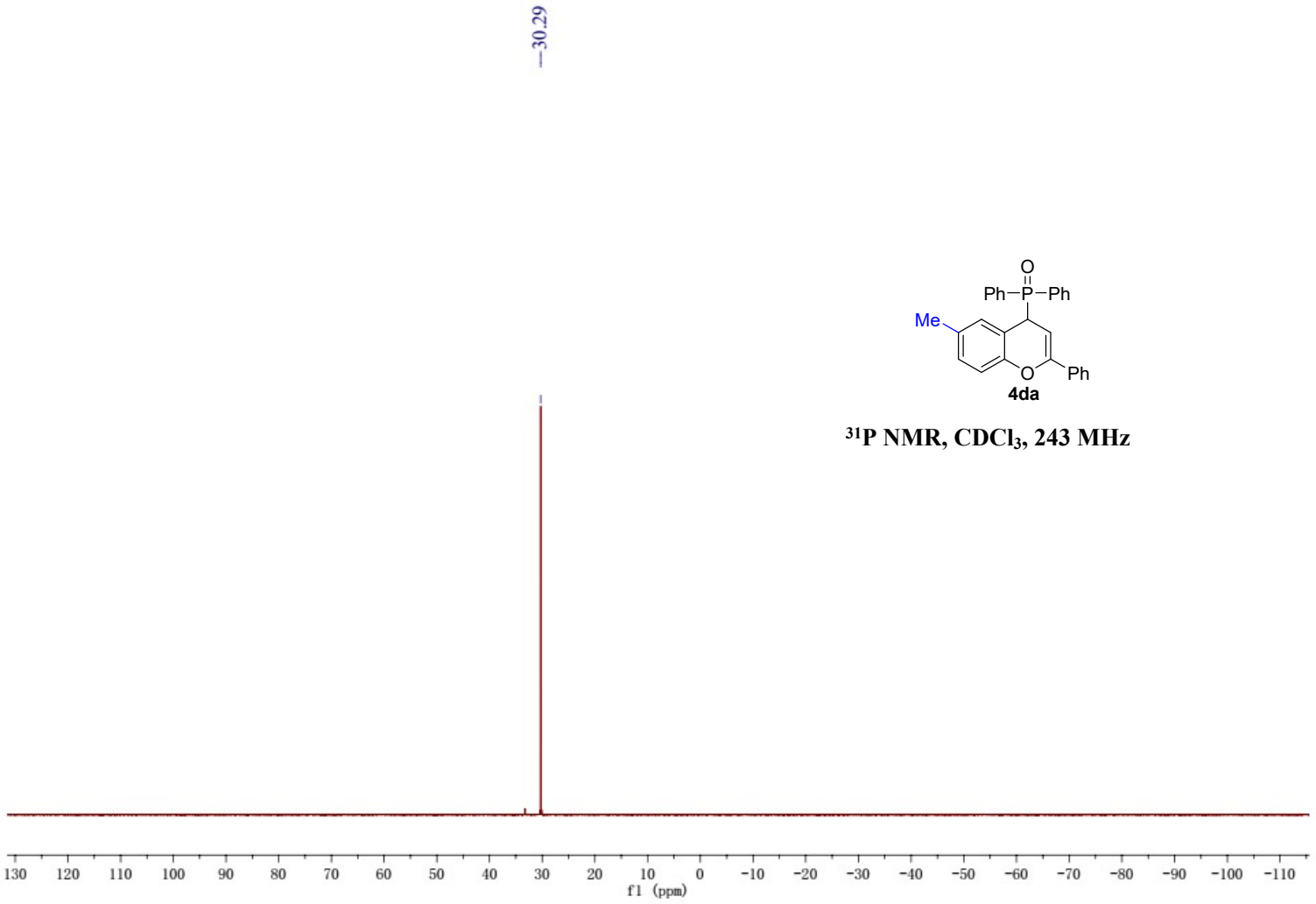
4da

^{1}H NMR, $CDCl_3$, 600 MHz

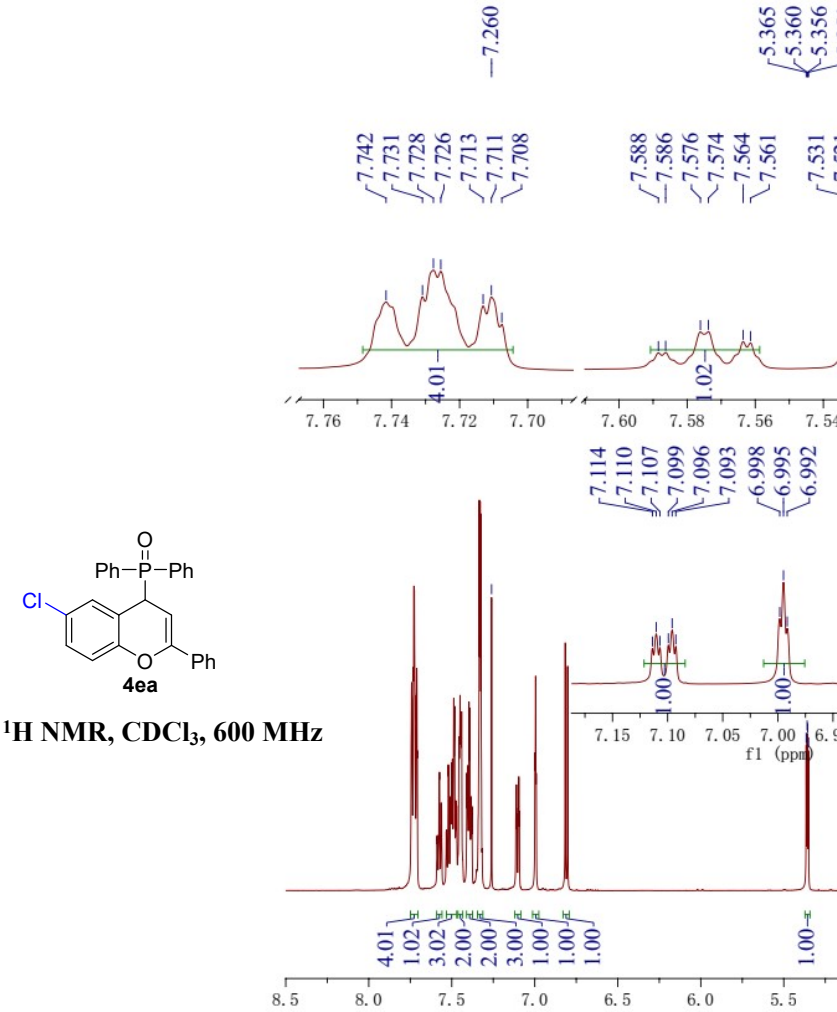




^{13}C NMR, $CDCl_3$, 150 MHz

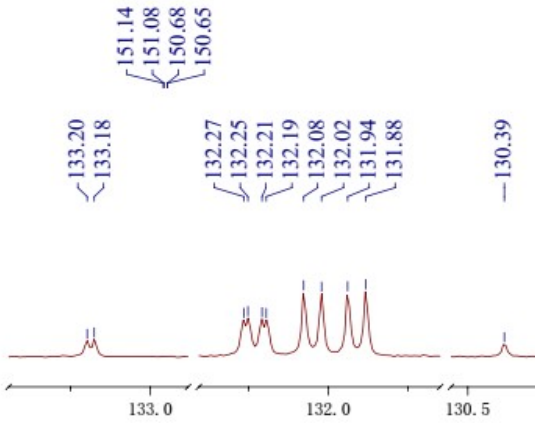


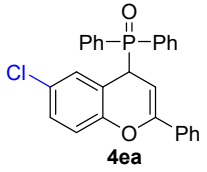
^{31}P NMR, $CDCl_3$, 243 MHz



4ea

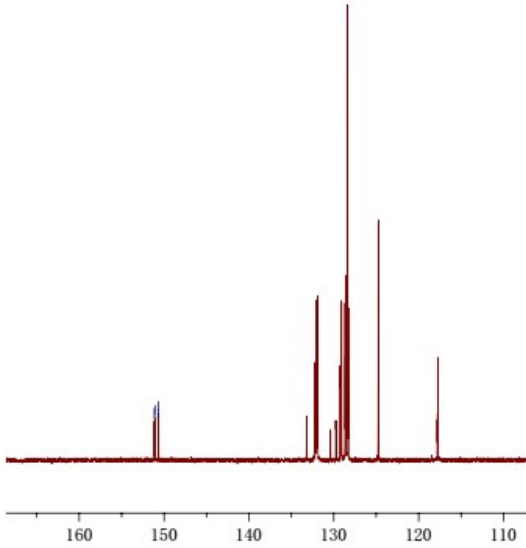
^{1}H NMR, $CDCl_3$, 600 MHz

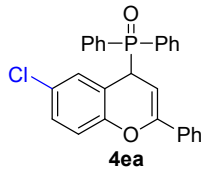




4ea

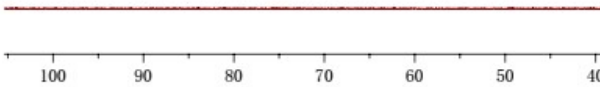
^{13}C NMR, $CDCl_3$, 150 MHz

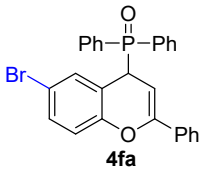




4ea

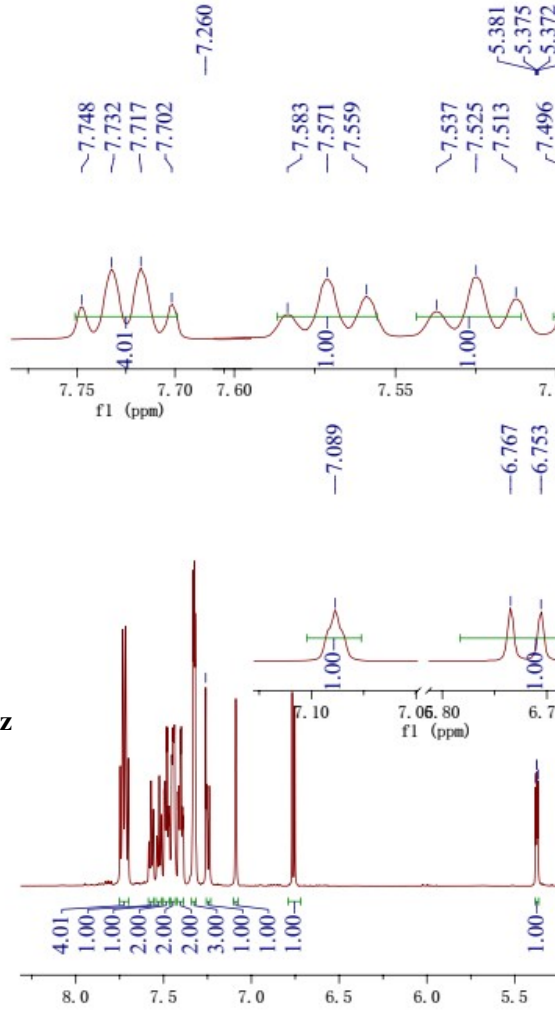
^{31}P NMR, $CDCl_3$, 243 MHz

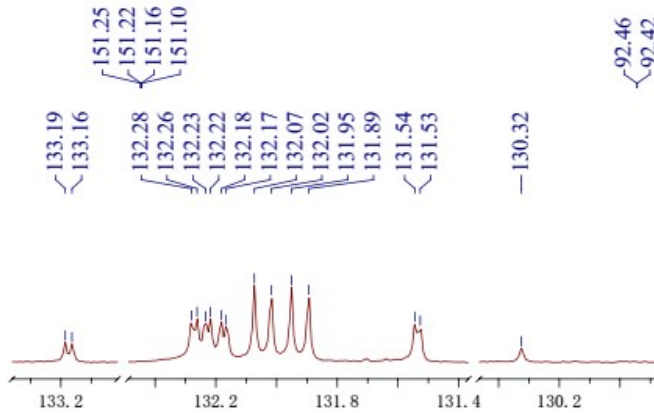


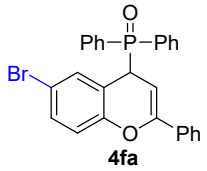


4fa

^{1}H NMR, $CDCl_3$, 600 MHz

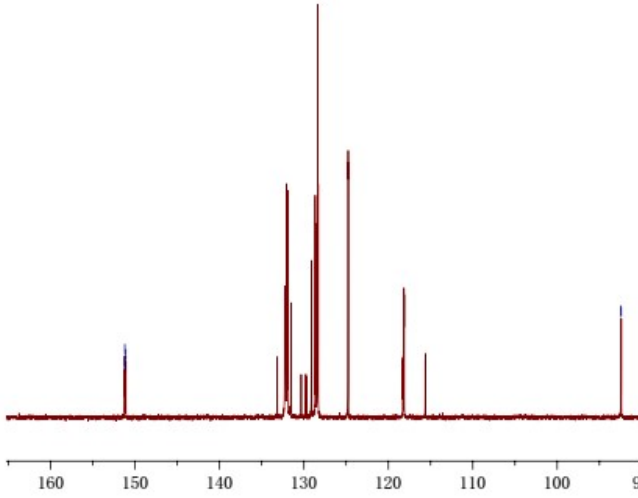


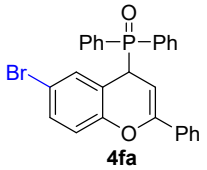




4fa

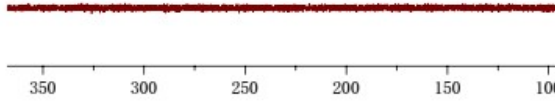
^{13}C NMR, $CDCl_3$, 150 MHz

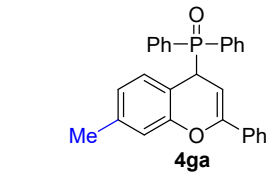




4fa

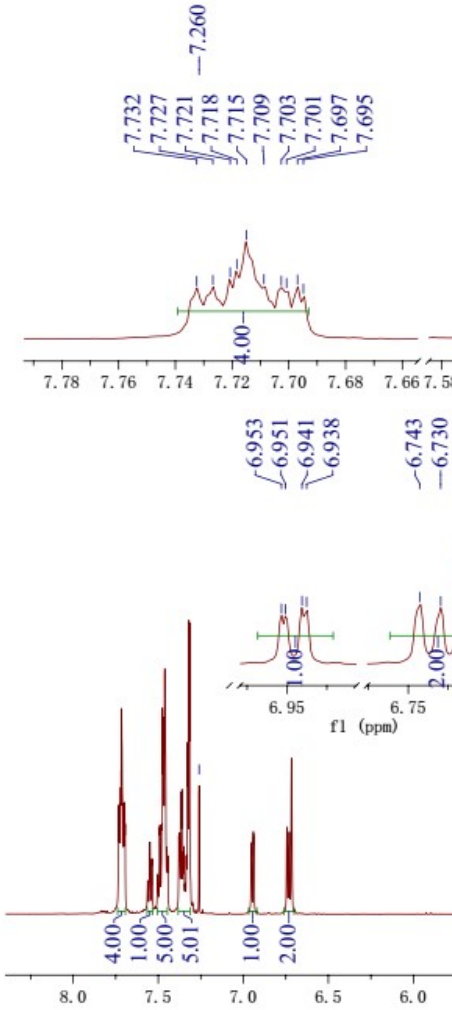
^{31}P NMR, $CDCl_3$, 243 MHz

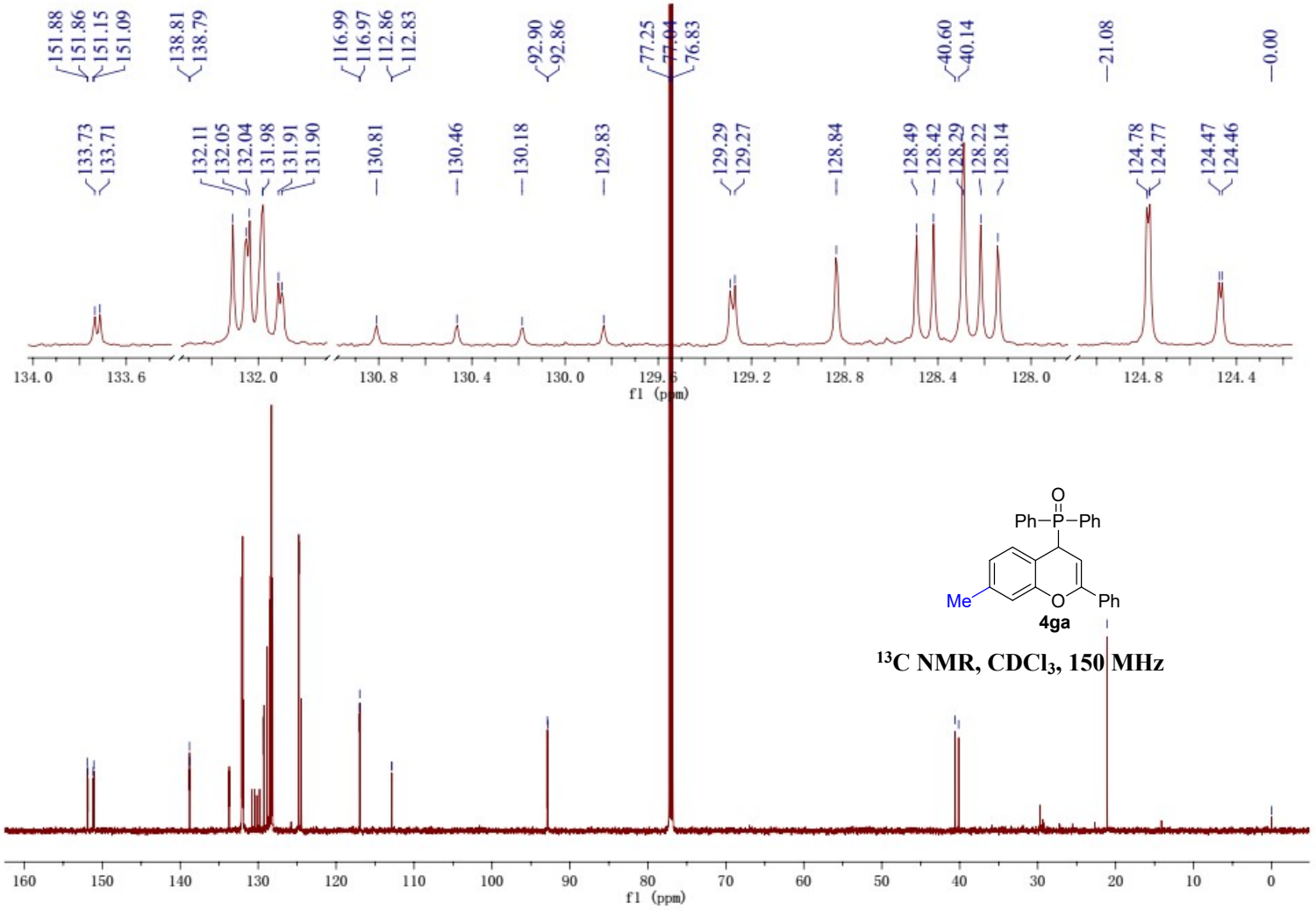




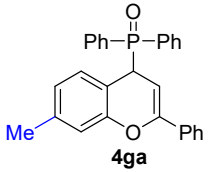
4ga

^{1}H NMR, $CDCl_3$, 600 MHz



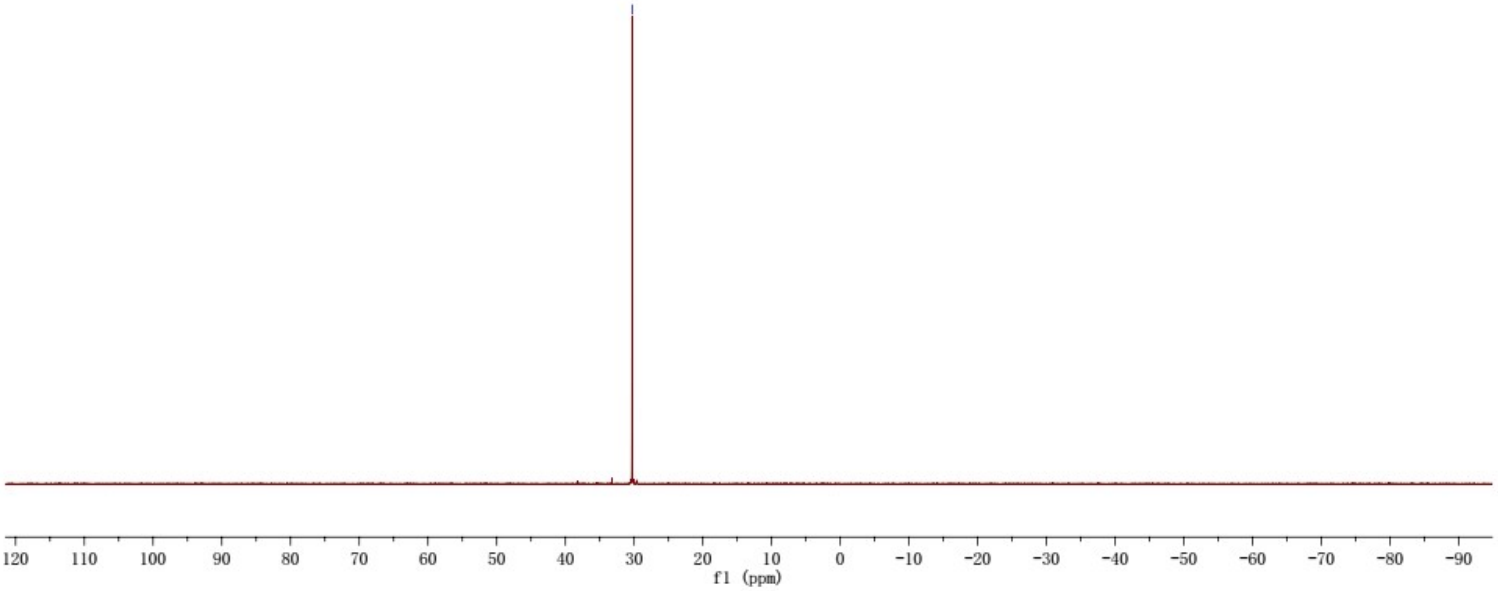


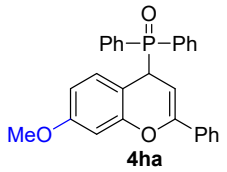
^{13}C NMR, $CDCl_3$, 150 MHz



4ga

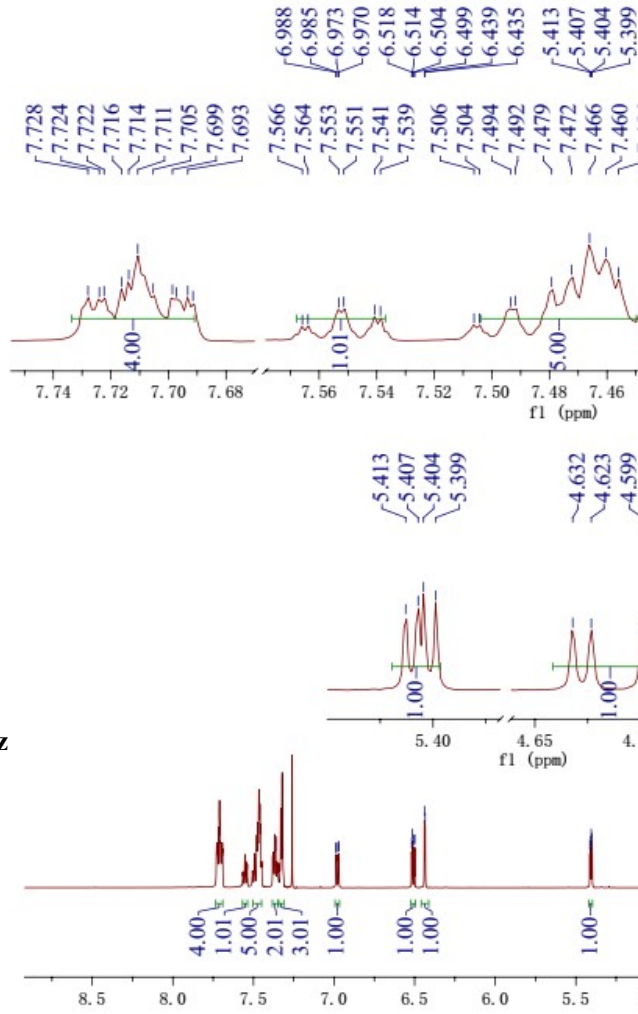
^{31}P NMR, $CDCl_3$, 243 MHz

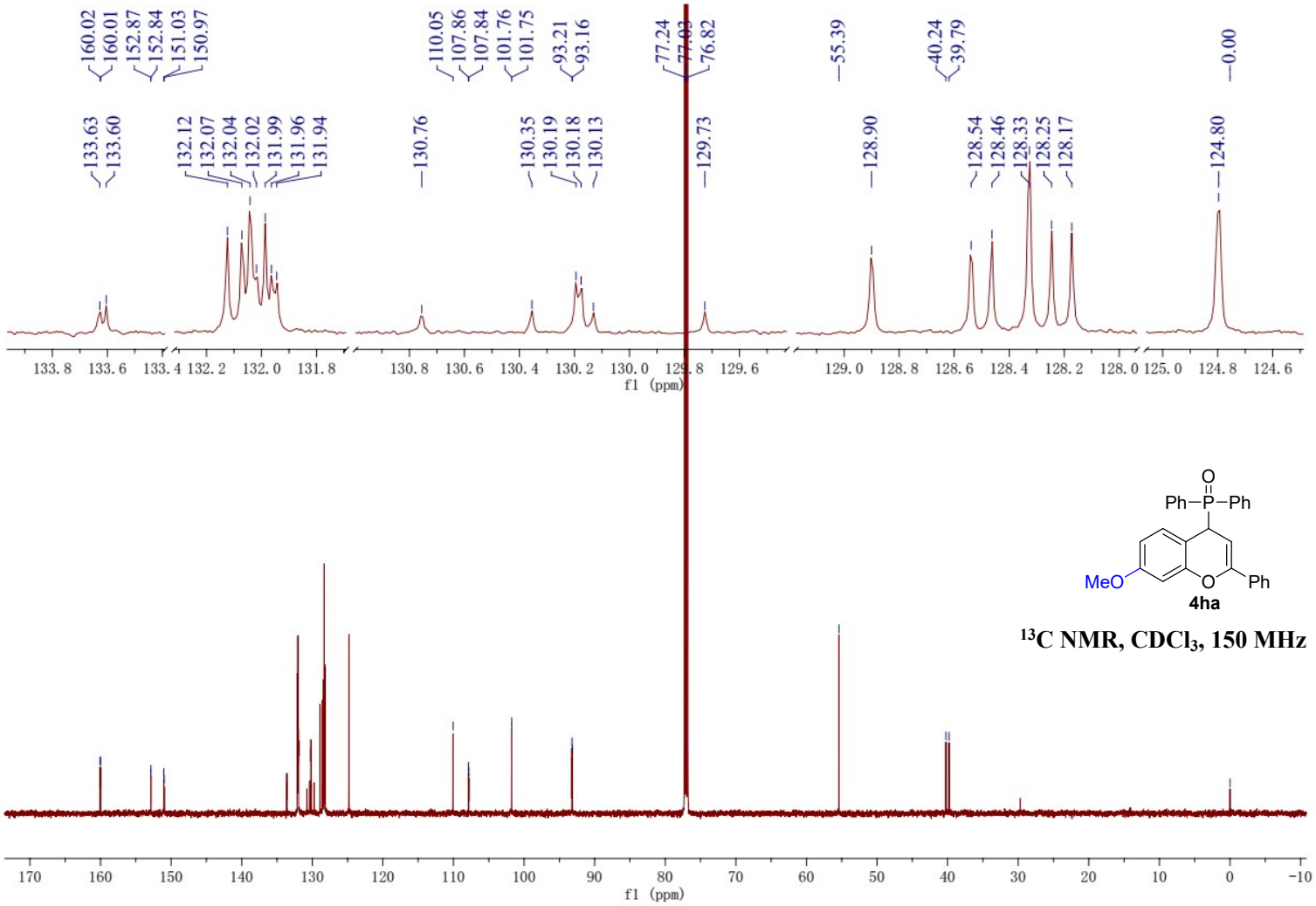


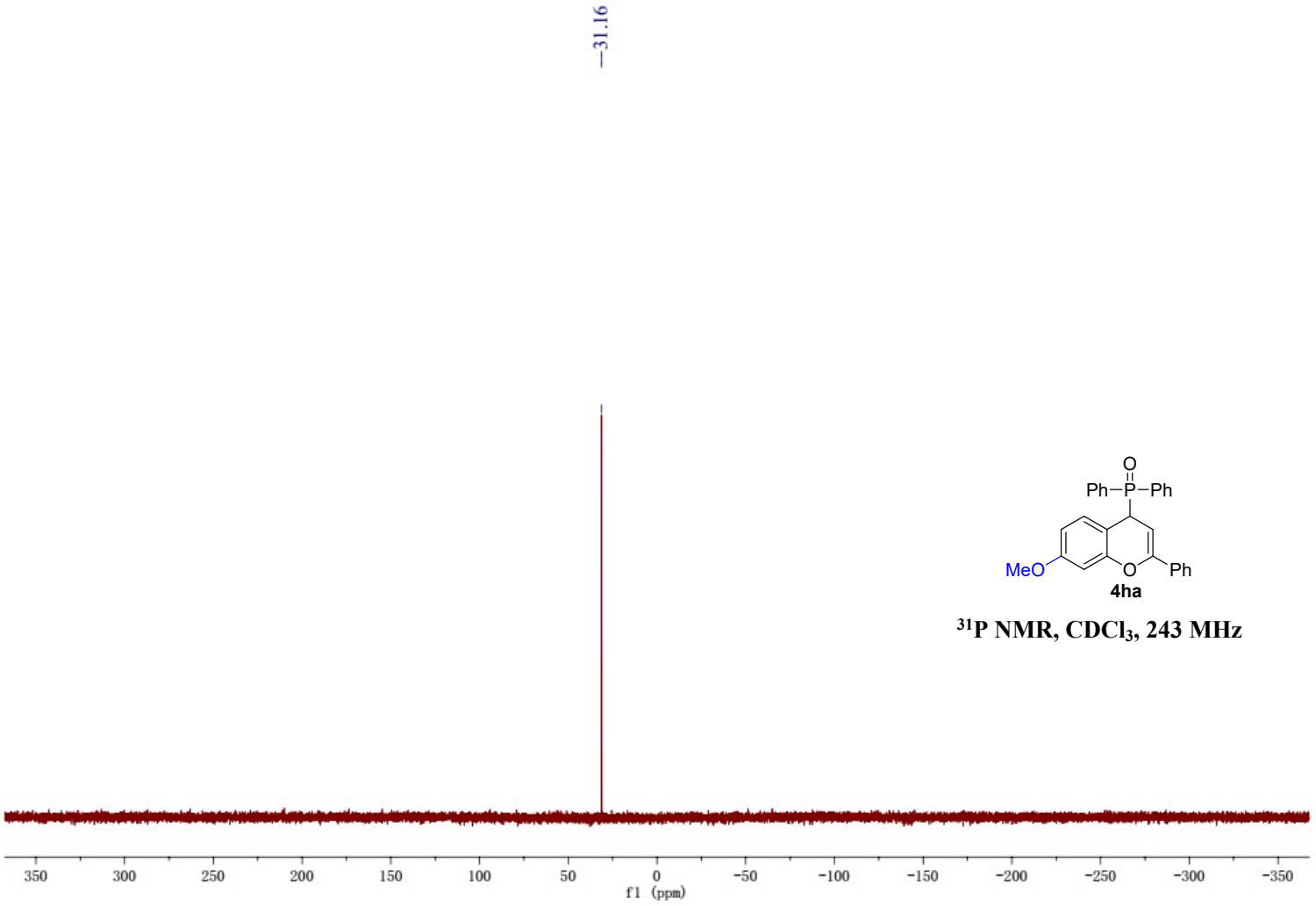


4ha

^{1}H NMR, $CDCl_3$, 600 MHz

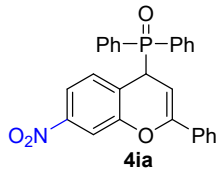



160.02
160.01
152.87
152.84
151.03
150.97
110.05
107.86
107.84
101.76
101.75
93.21
93.16
77.24
77.03
76.82
55.39
40.24
39.79
0.00
133.63
133.60
132.12
132.07
132.04
132.02
131.99
131.96
131.94
130.76
130.35
130.19
130.18
130.13
129.73
128.90
128.54
128.46
128.33
128.25
128.17
124.80
f1 (ppm)
O
Ph—P—Ph
MeO
O
Ph
4ha
^{13}C NMR, $CDCl_3$, 150 MHz



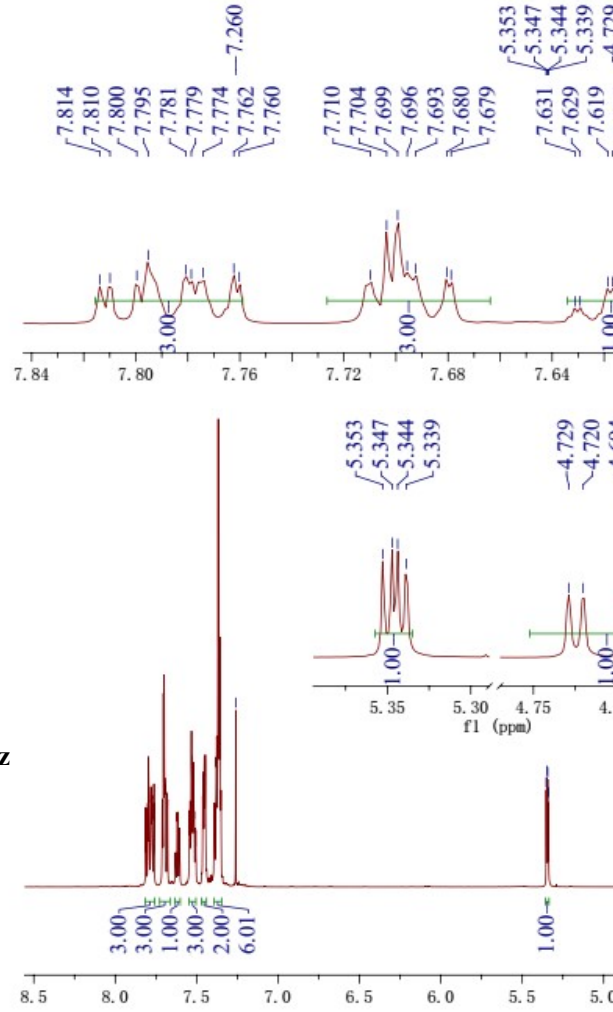
4ha

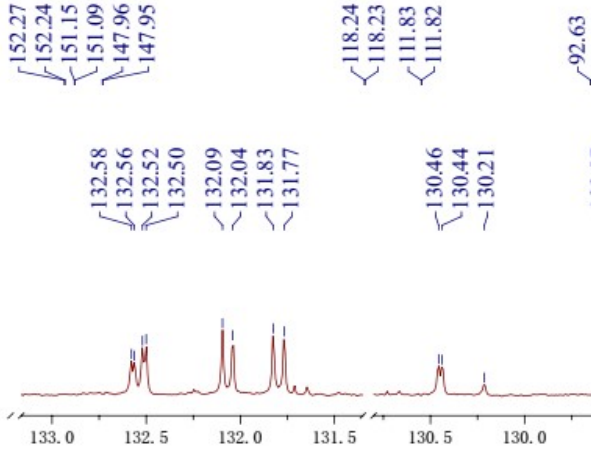
^{31}P NMR, $CDCl_3$, 243 MHz

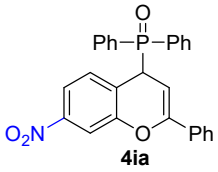


4ia

^{1}H NMR, $CDCl_3$, 600 MHz

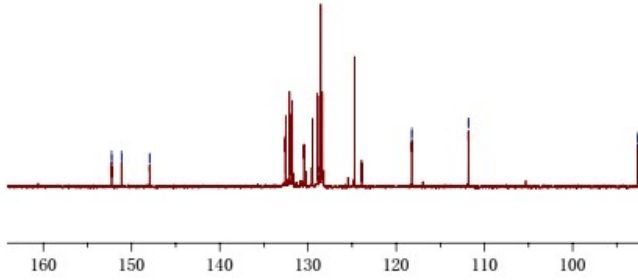


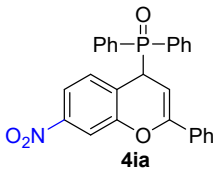




4ia

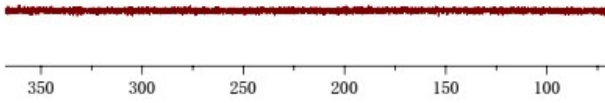
^{13}C NMR, $CDCl_3$, 150 MHz

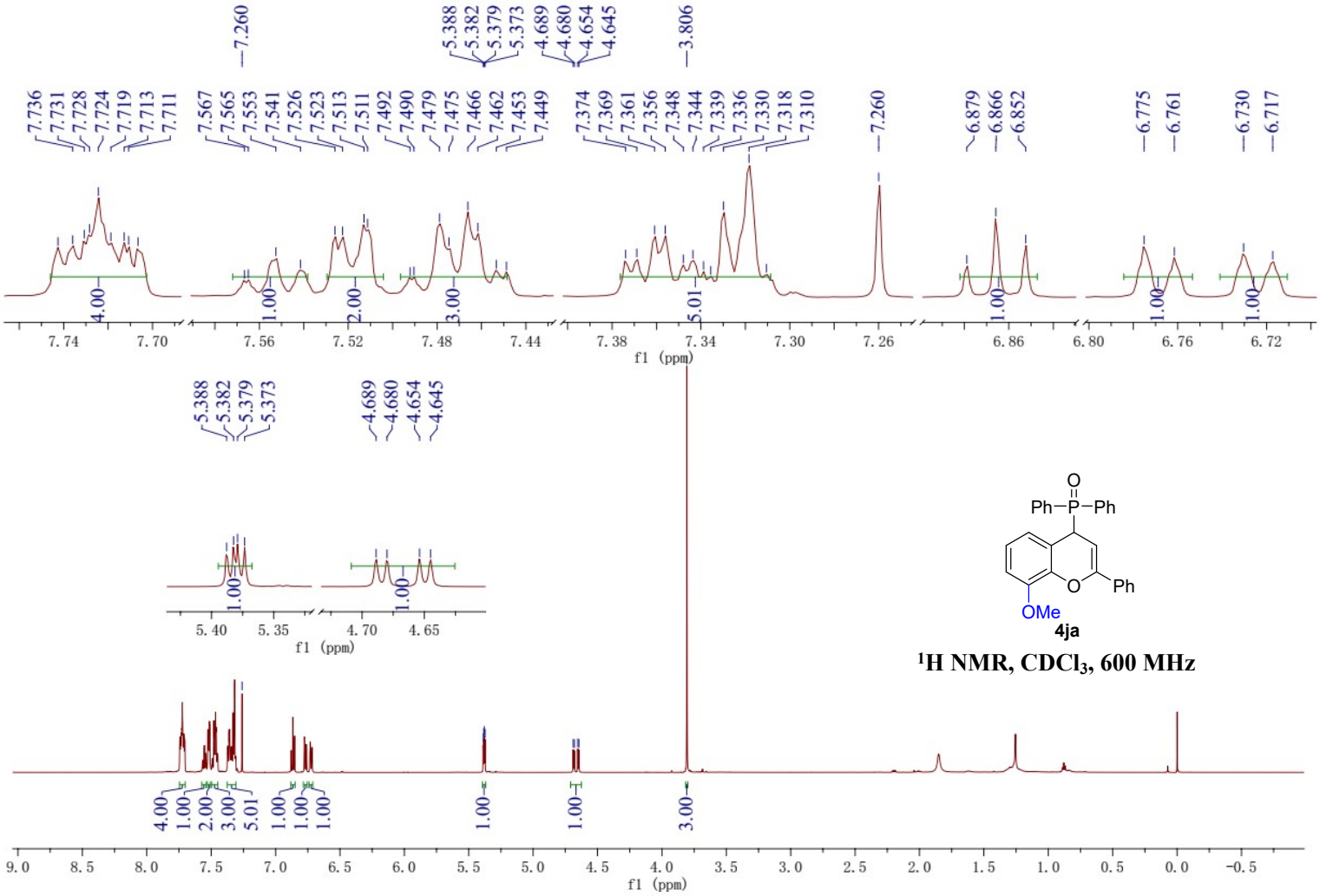




4ia

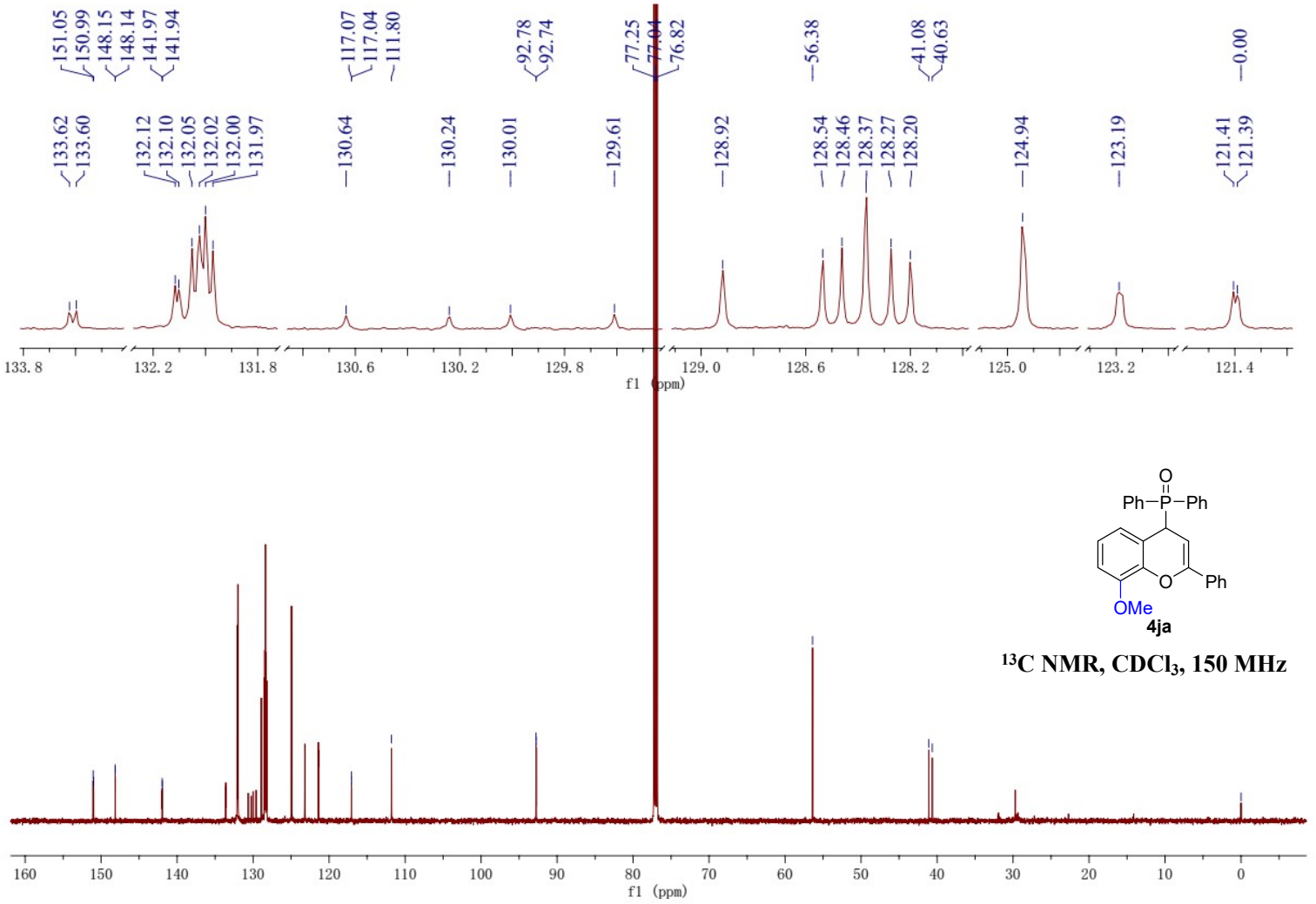
^{31}P NMR, $CDCl_3$, 243 MHz





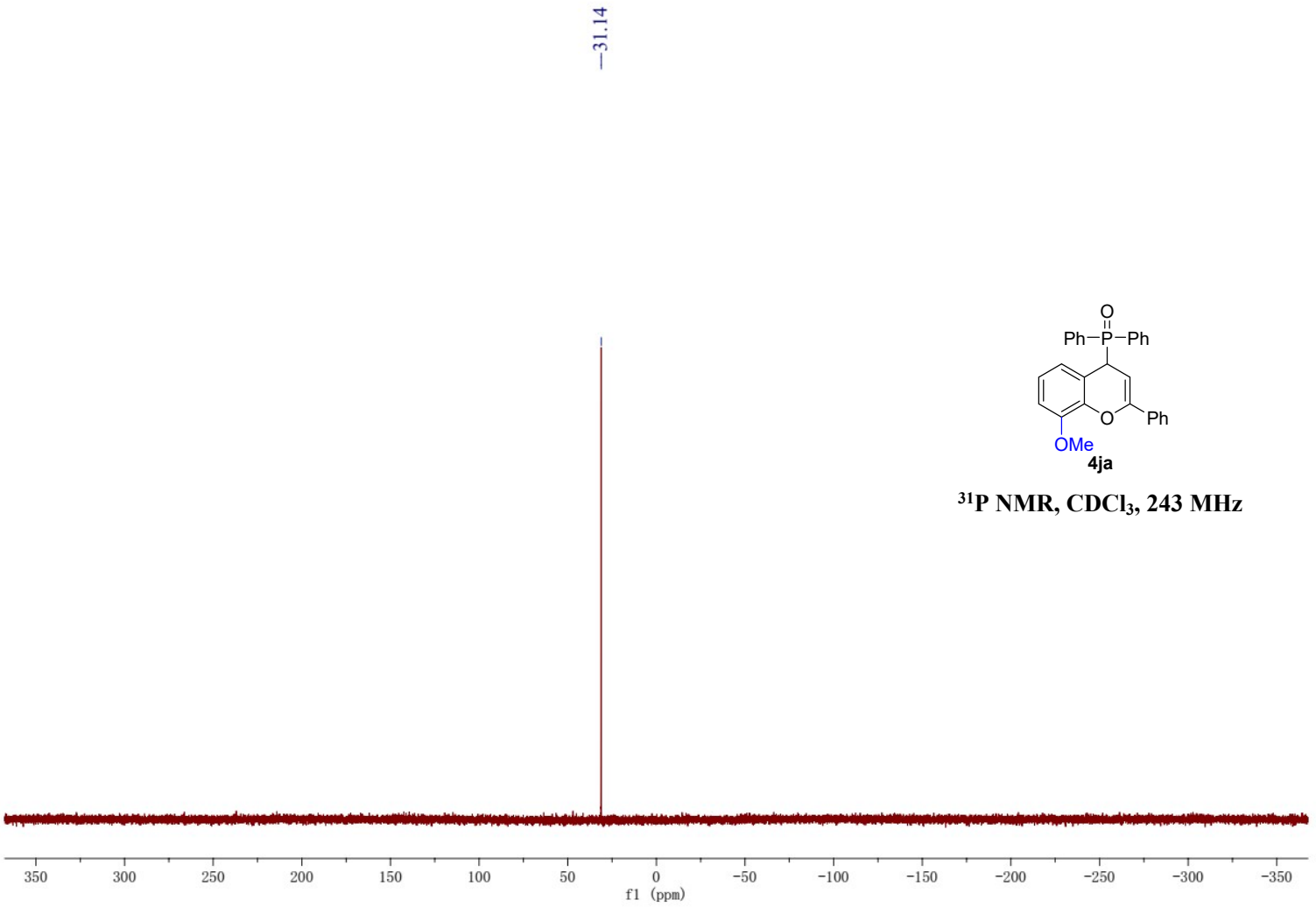
4ja

^{1}H NMR, $CDCl_3$, 600 MHz



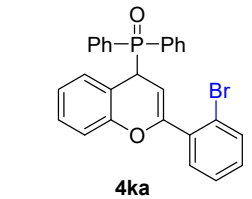
4ja

^{13}C NMR, $CDCl_3$, 150 MHz



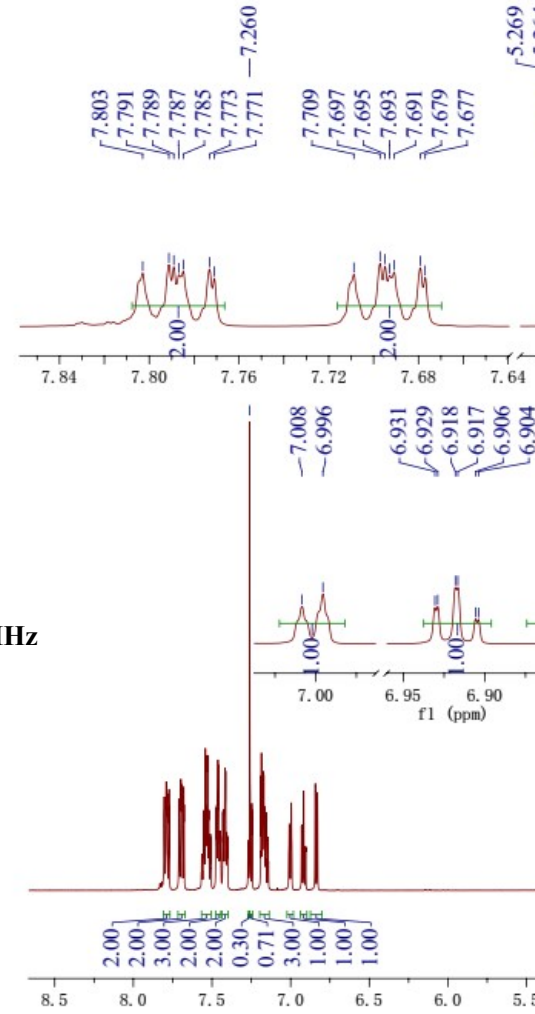
4ja

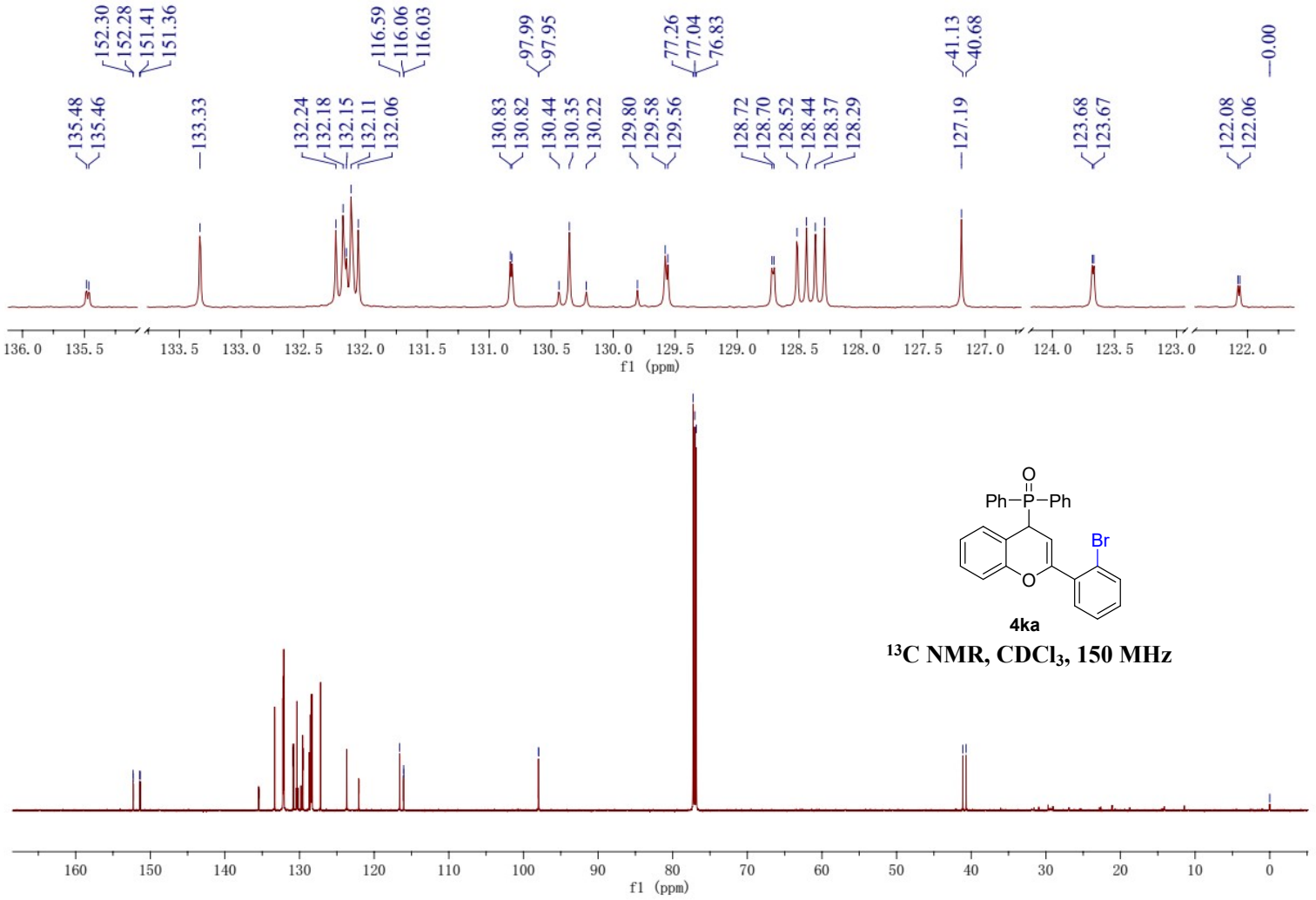
^{31}P NMR, $CDCl_3$, 243 MHz



4ka

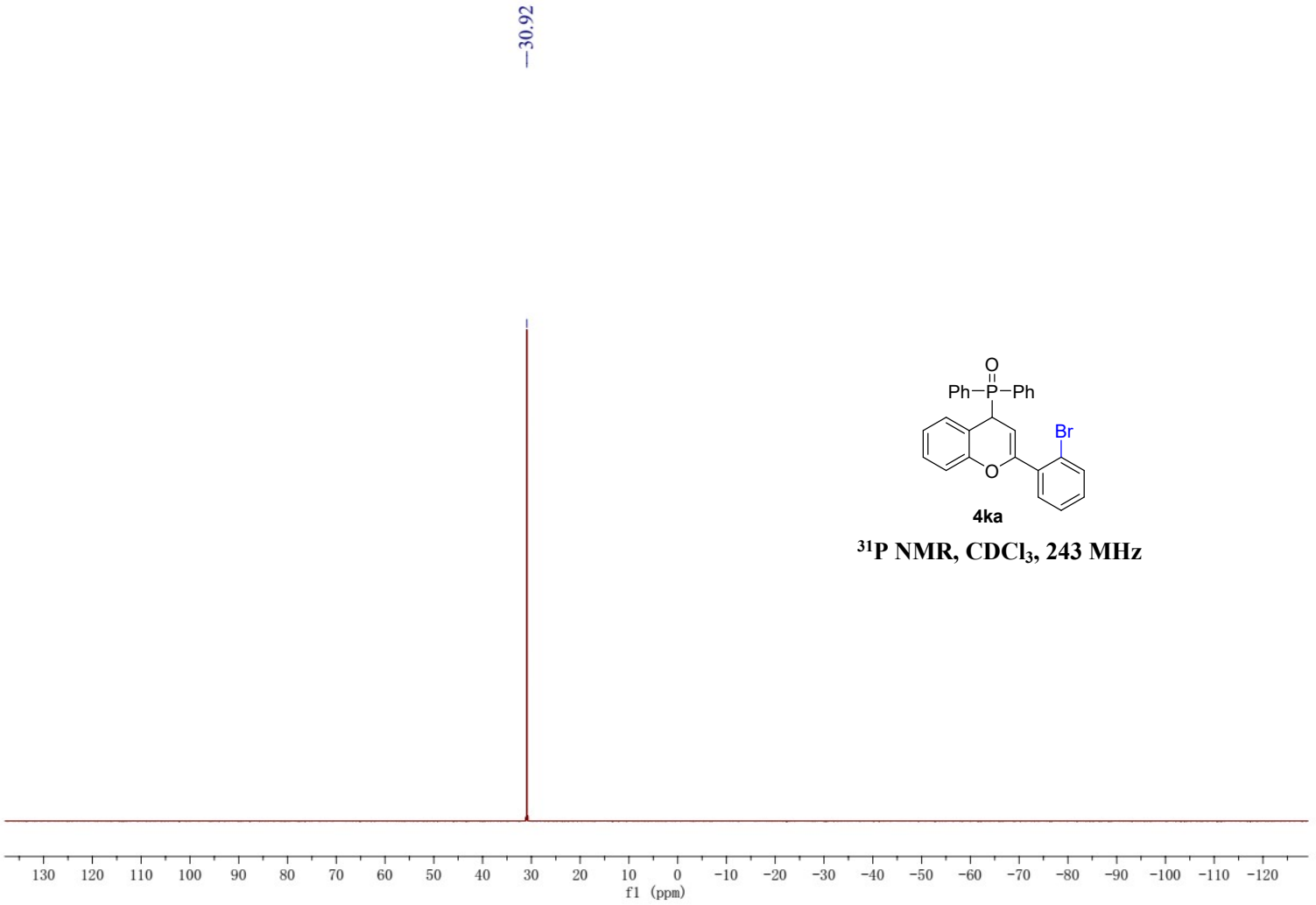
^{1}H NMR, $CDCl_3$, 600 MHz





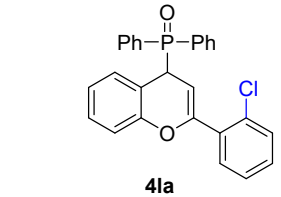
4ka

^{13}C NMR, $CDCl_3$, 150 MHz



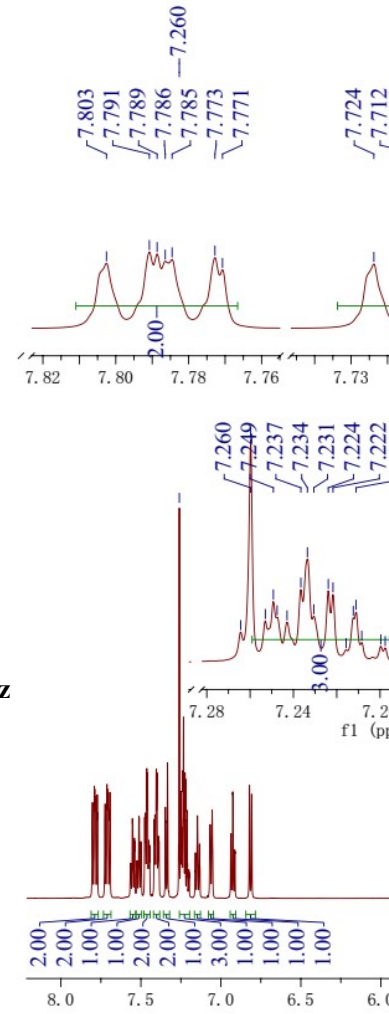
4ka

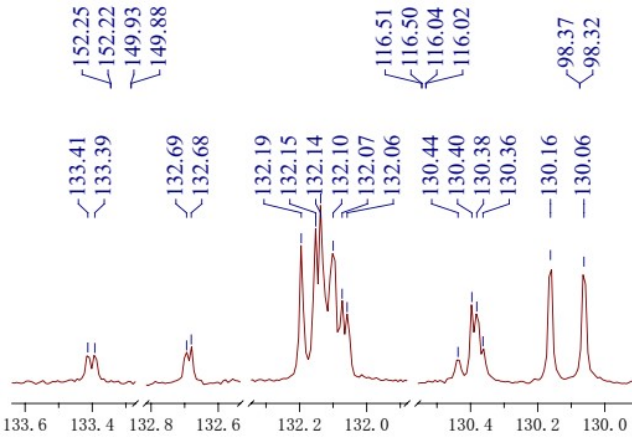
^{31}P NMR, $CDCl_3$, 243 MHz

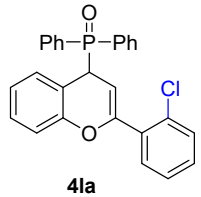


4la

^{1}H NMR, $CDCl_3$, 600 MHz

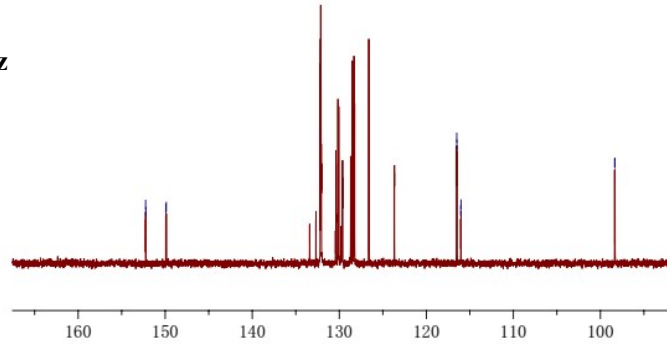


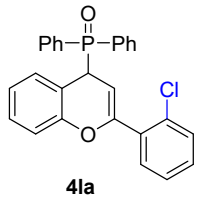




4la

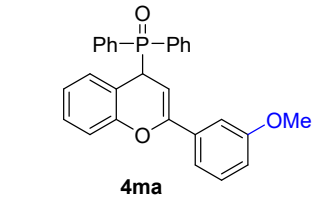
^{13}C NMR, $CDCl_3$, 150 MHz





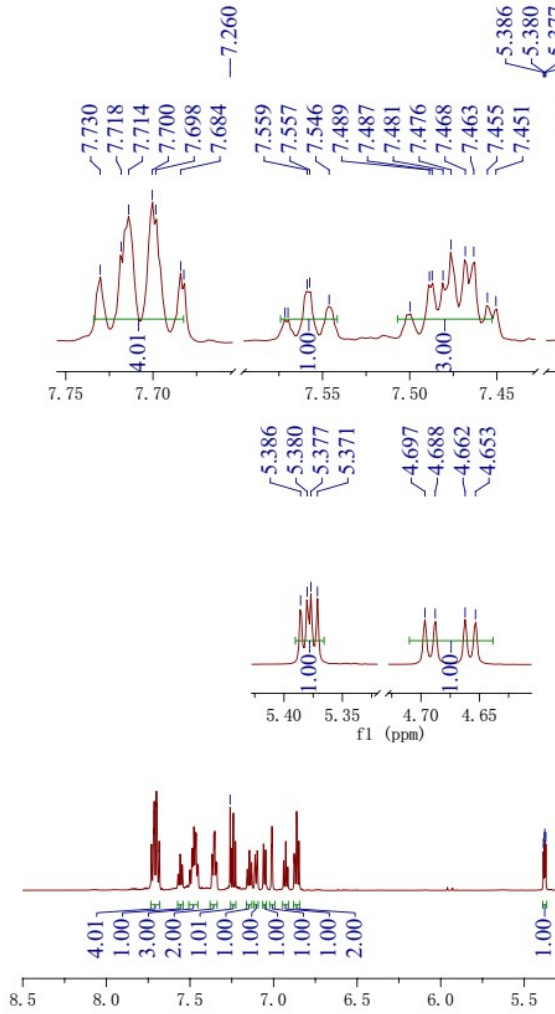
4la

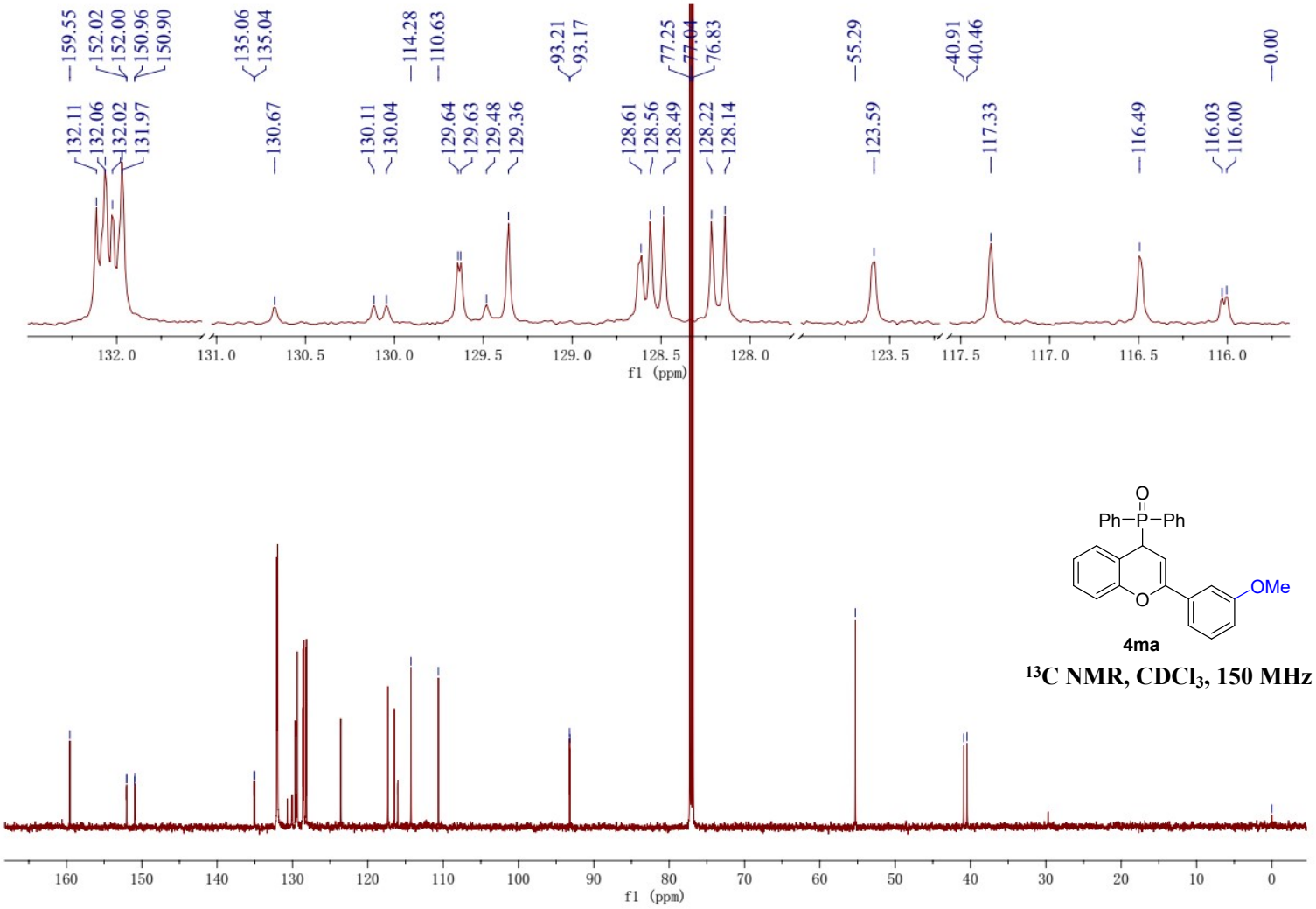
^{31}P NMR, $CDCl_3$, 243 MHz



4ma

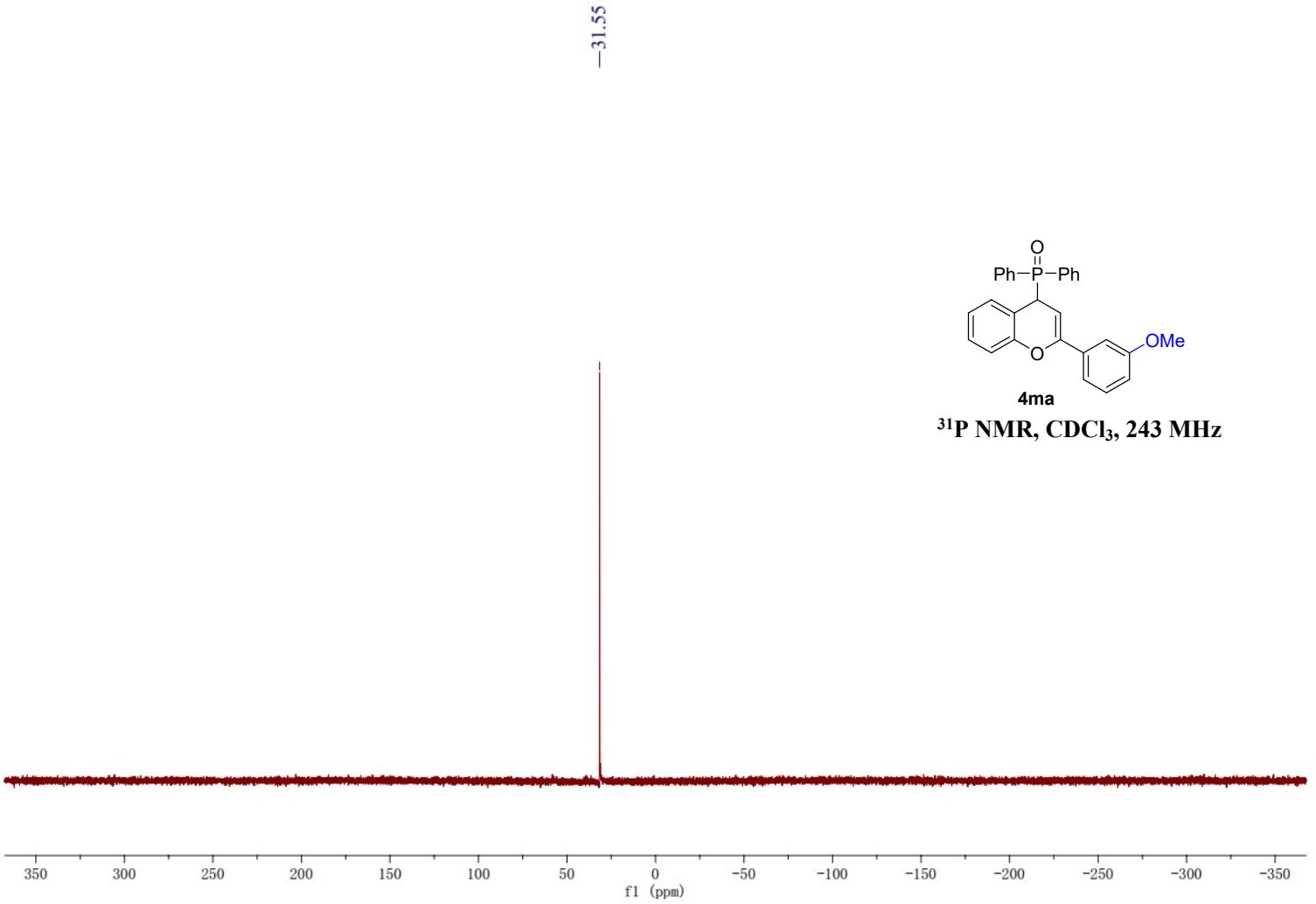
^{1}H NMR, $CDCl_3$, 600 MHz





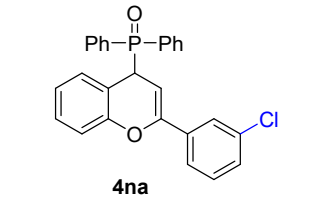
4ma

^{13}C NMR, $CDCl_3$, 150 MHz



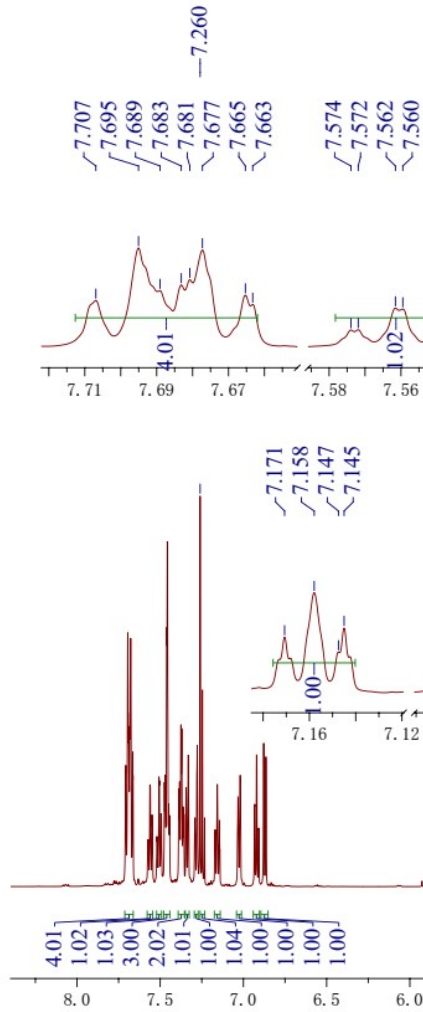
4ma

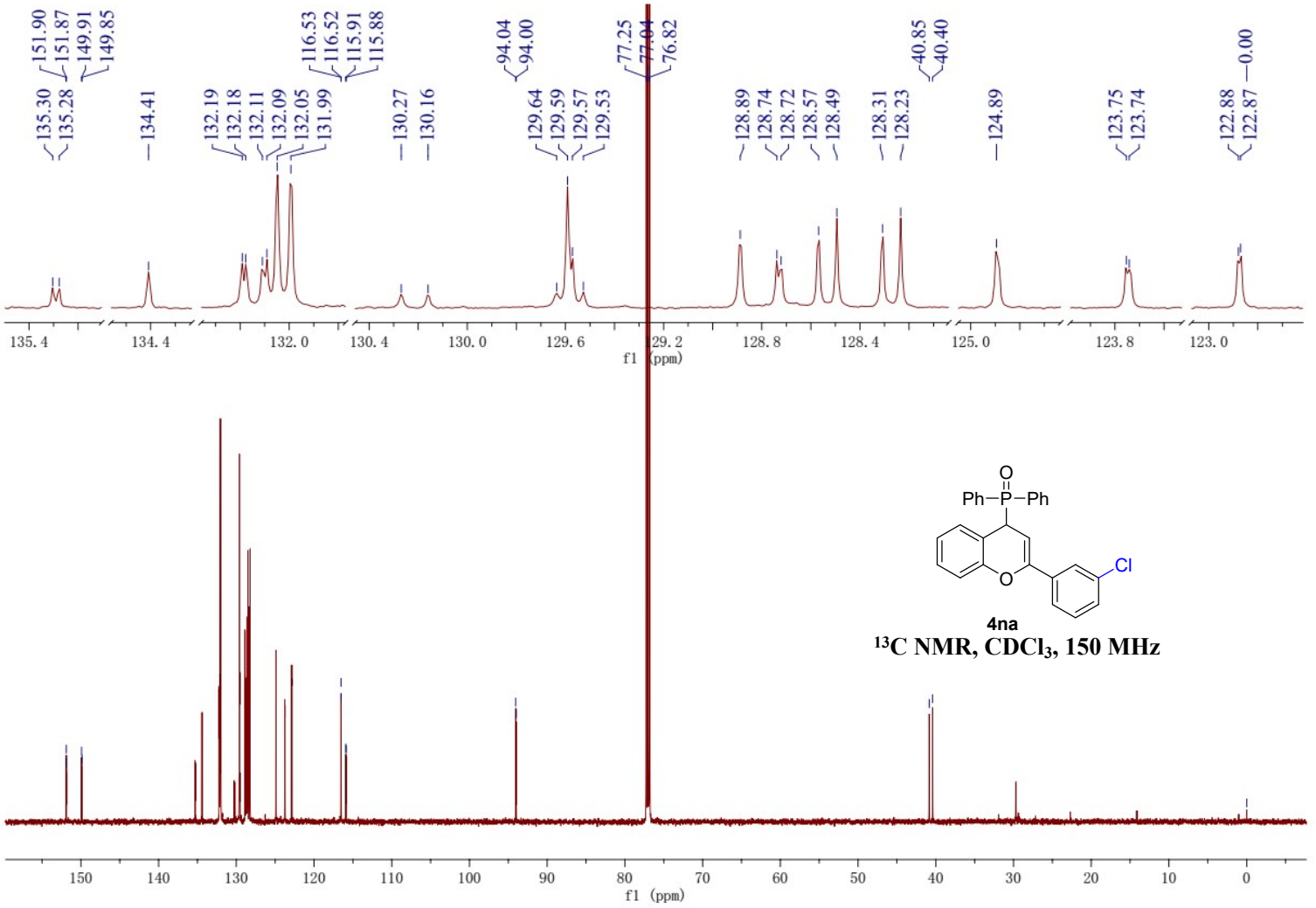
^{31}P NMR, $CDCl_3$, 243 MHz



4na

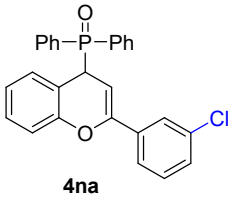
^{1}H NMR, $CDCl_3$, 600 MHz





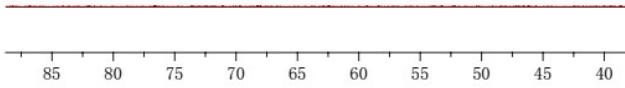
4na

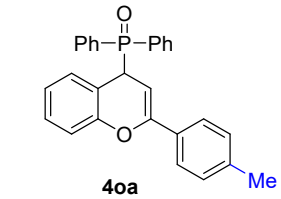
^{13}C NMR, $CDCl_3$, 150 MHz



4na

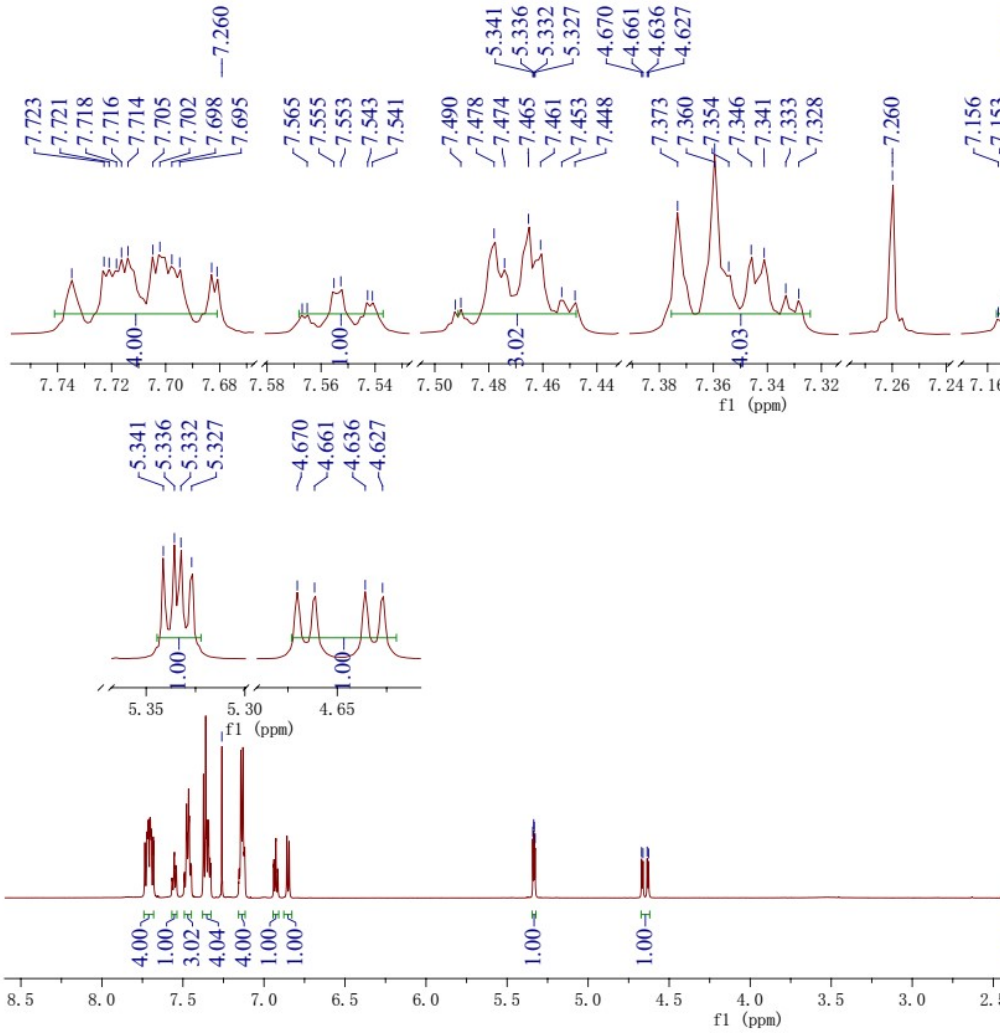
^{31}P NMR, $CDCl_3$, 243 MHz

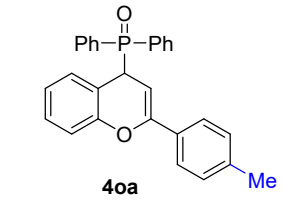




4oa

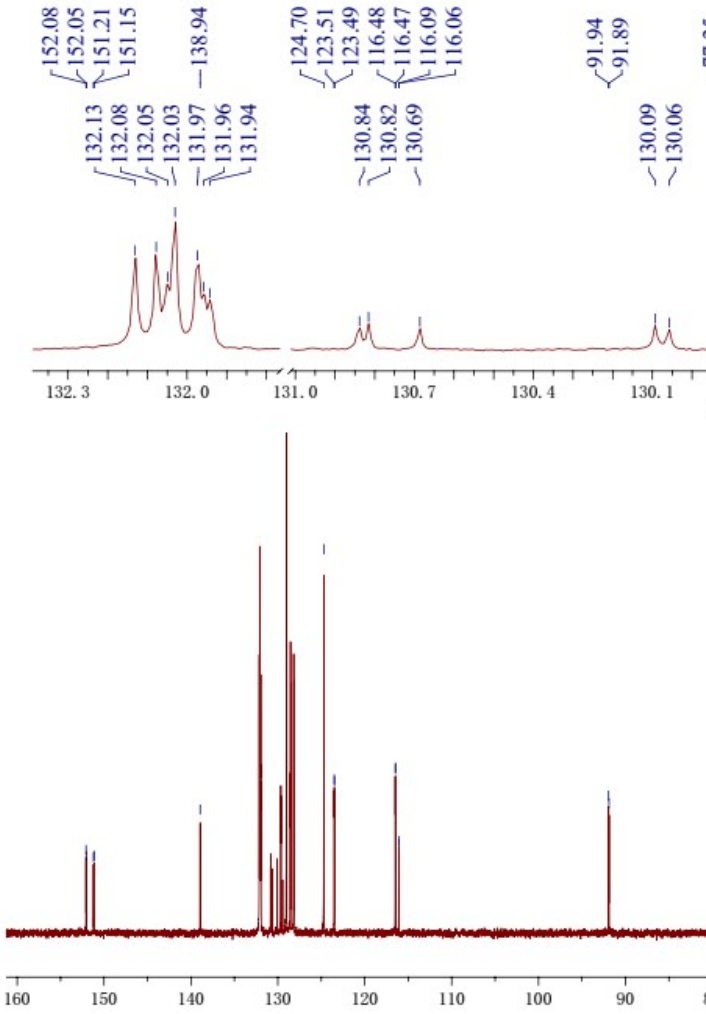
^{1}H NMR, $CDCl_3$, 600 MHz

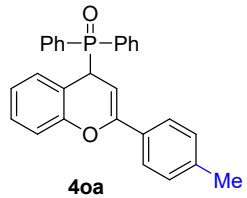




4oa

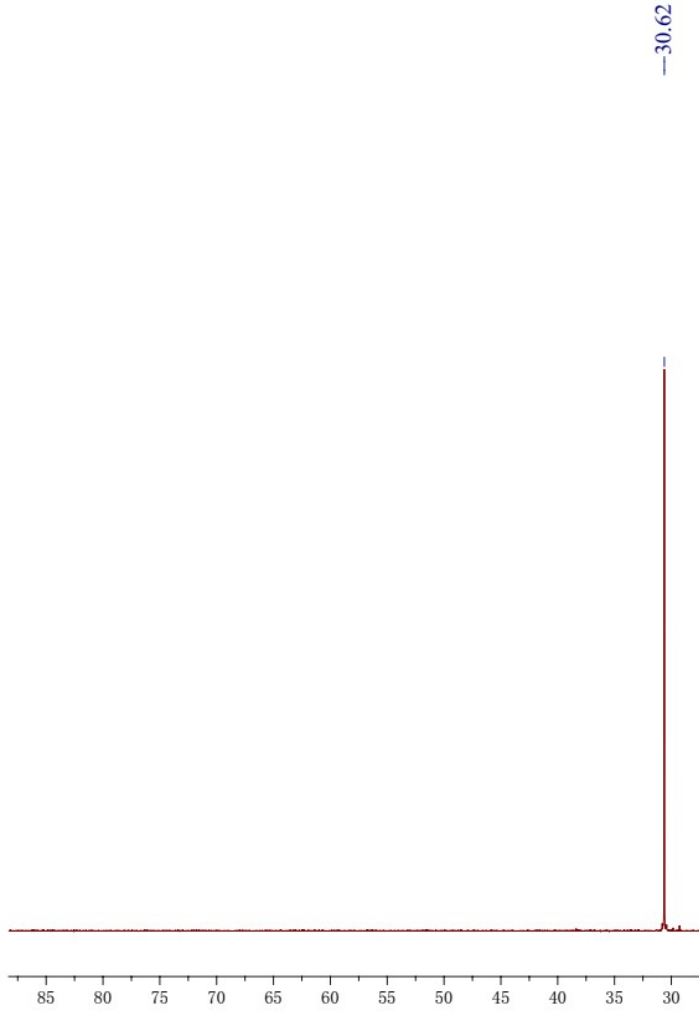
^{13}C NMR, $CDCl_3$, 150 MHz

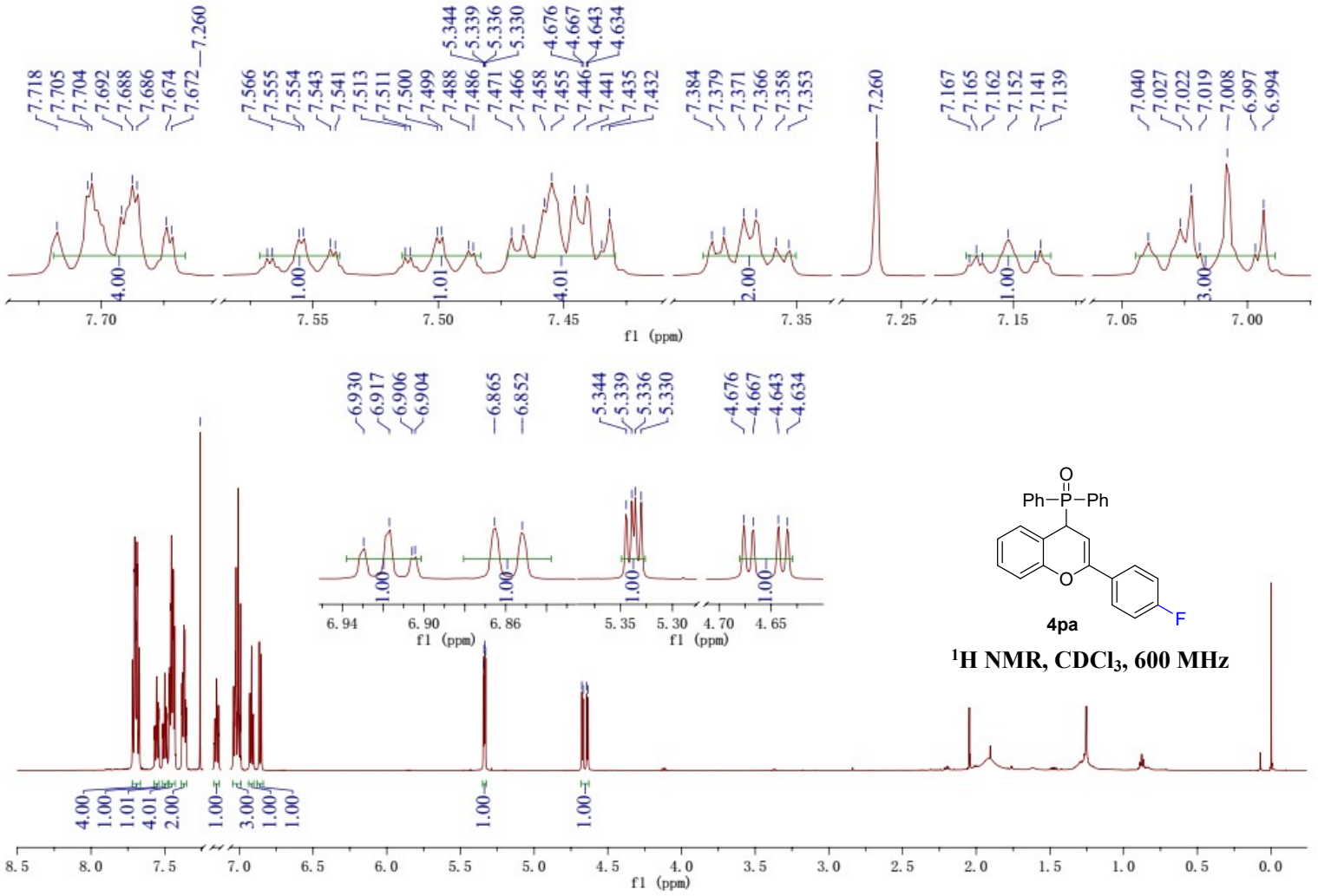




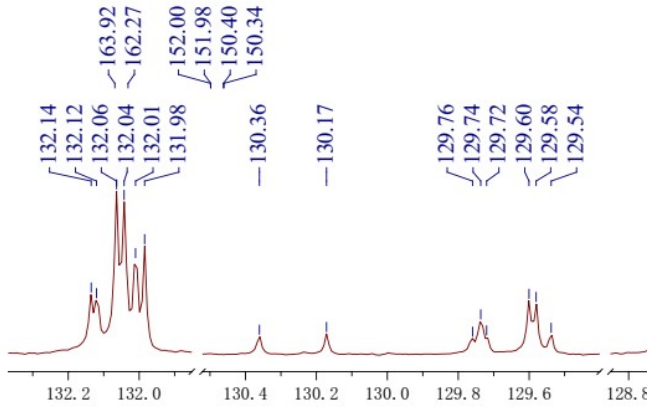
4oa

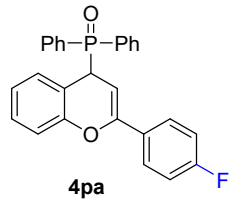
^{31}P NMR, $CDCl_3$, 243 MHz





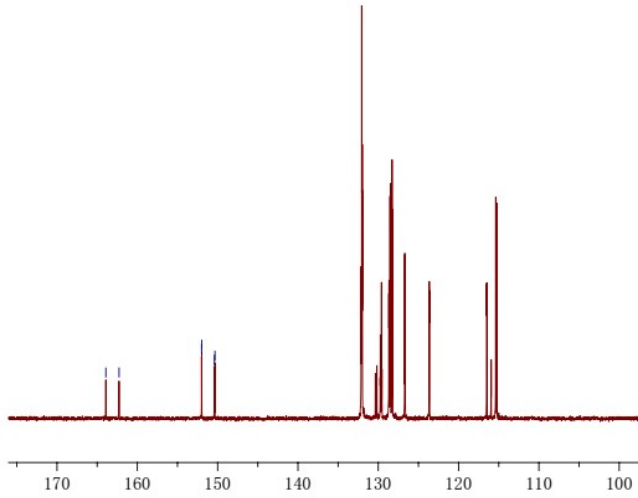
^{1}H NMR, $CDCl_3$, 600 MHz

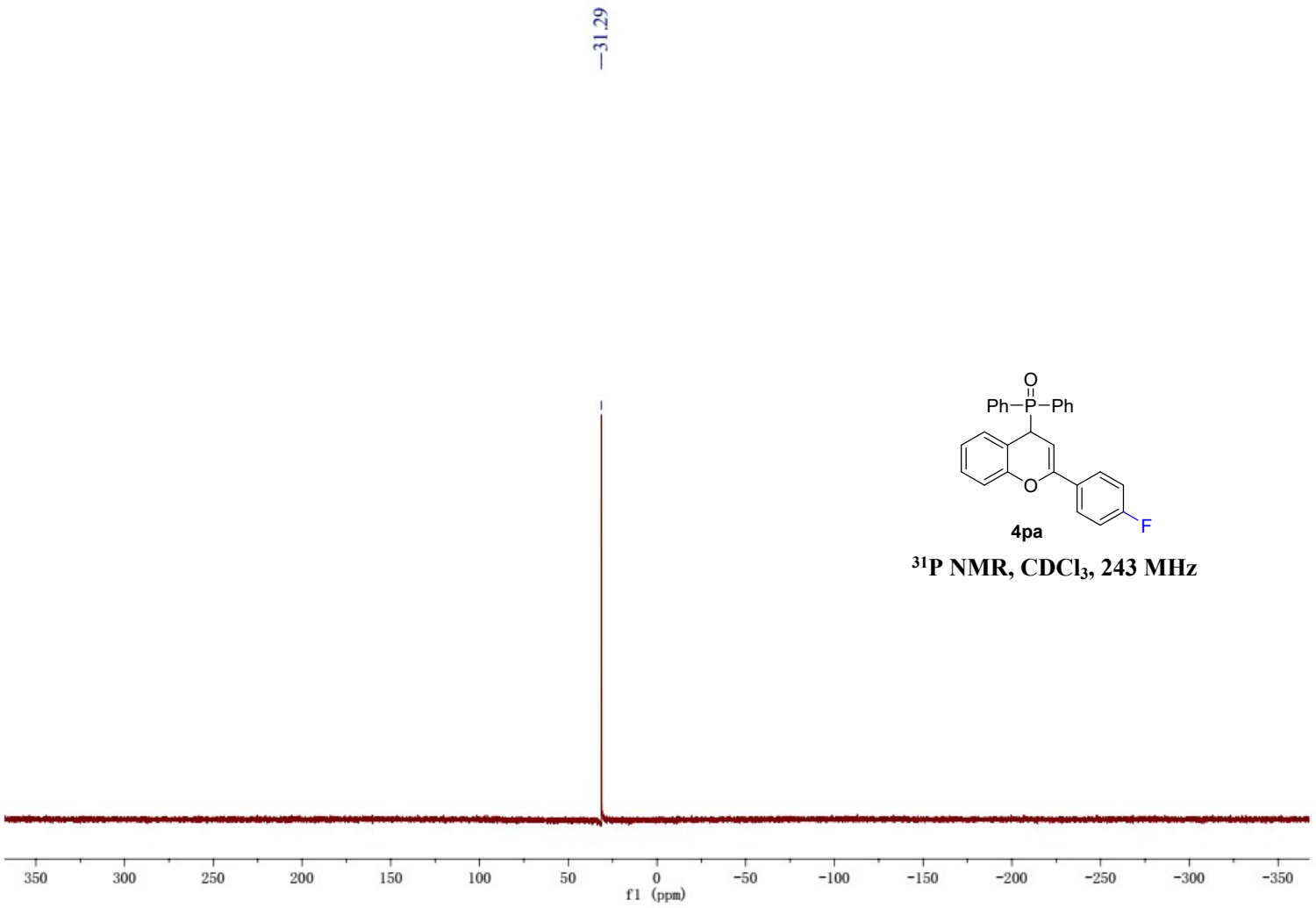




4pa

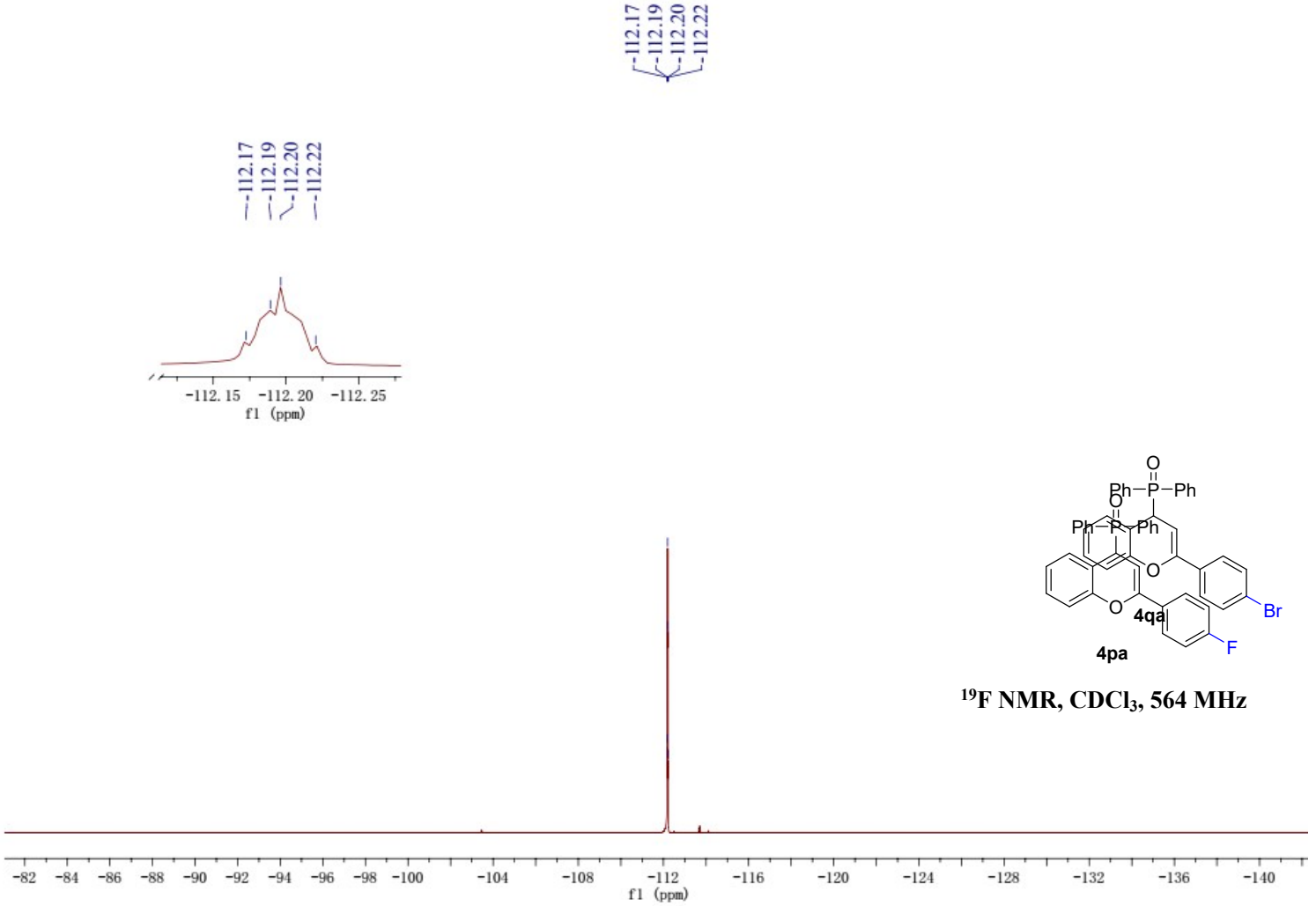
^{13}C NMR, $CDCl_3$, 150 MHz





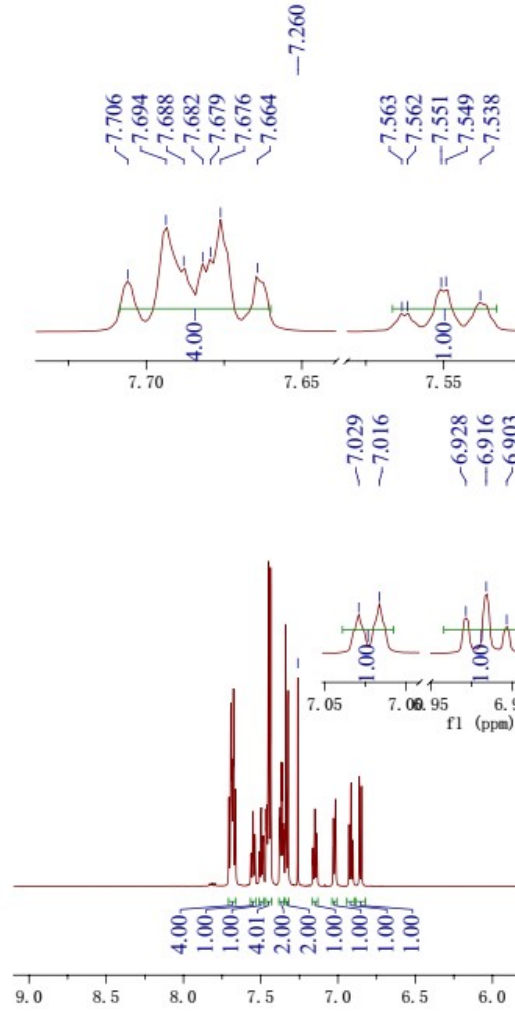
4pa

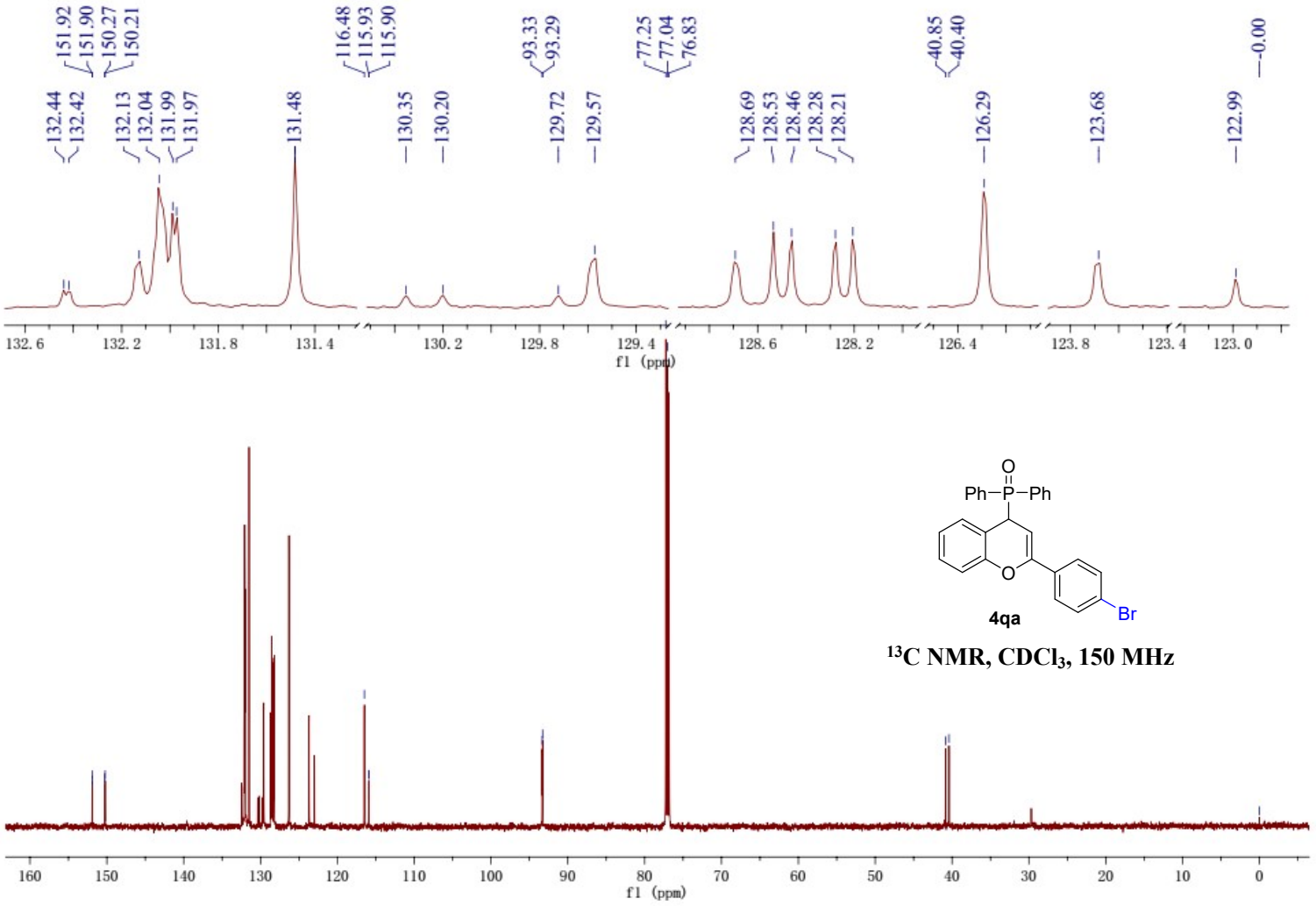
^{31}P NMR, $CDCl_3$, 243 MHz



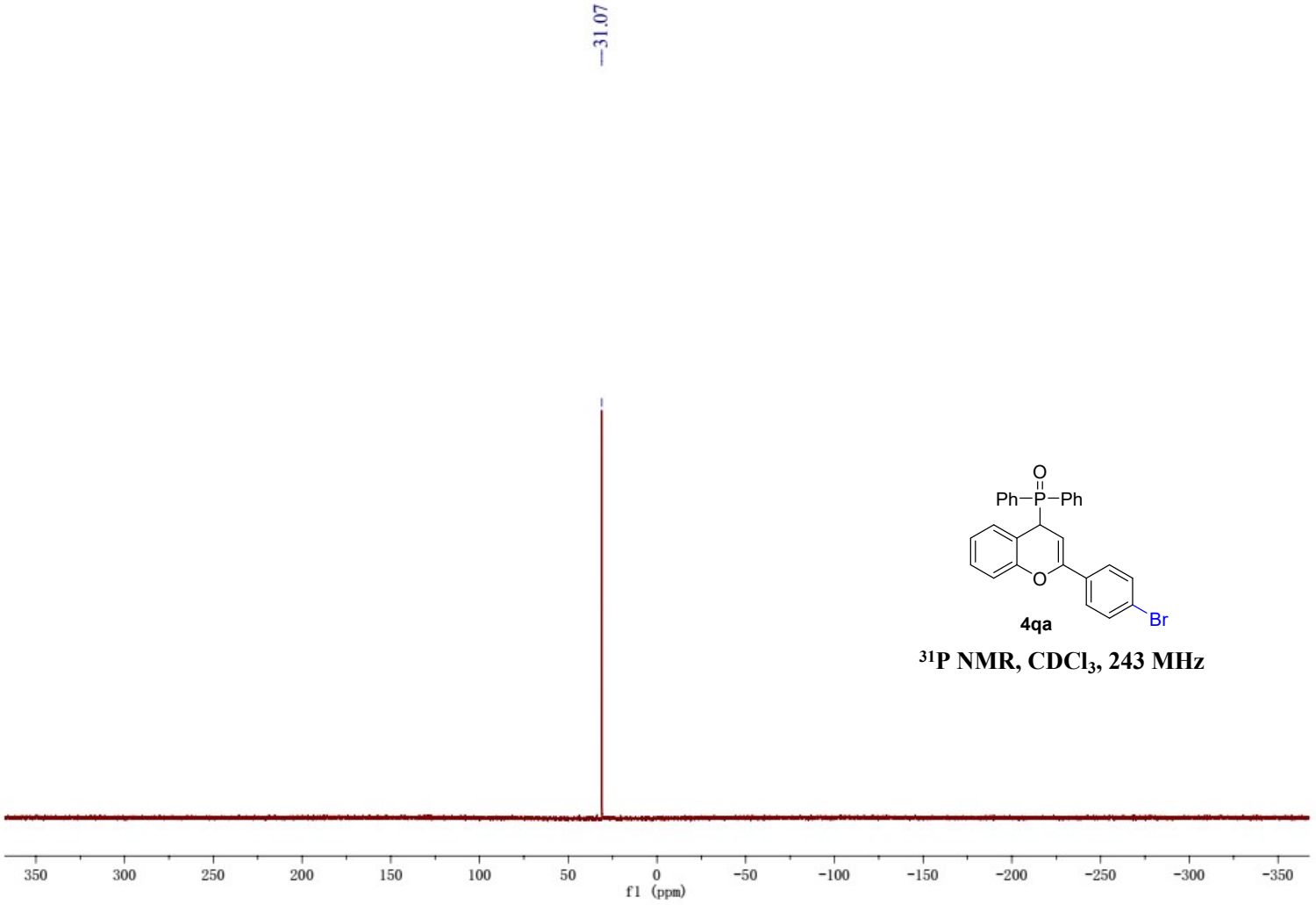
4pa

^{19}F NMR, $CDCl_3$, 564 MHz



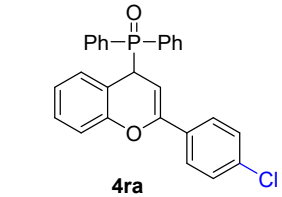


^{13}C NMR, $CDCl_3$, 150 MHz



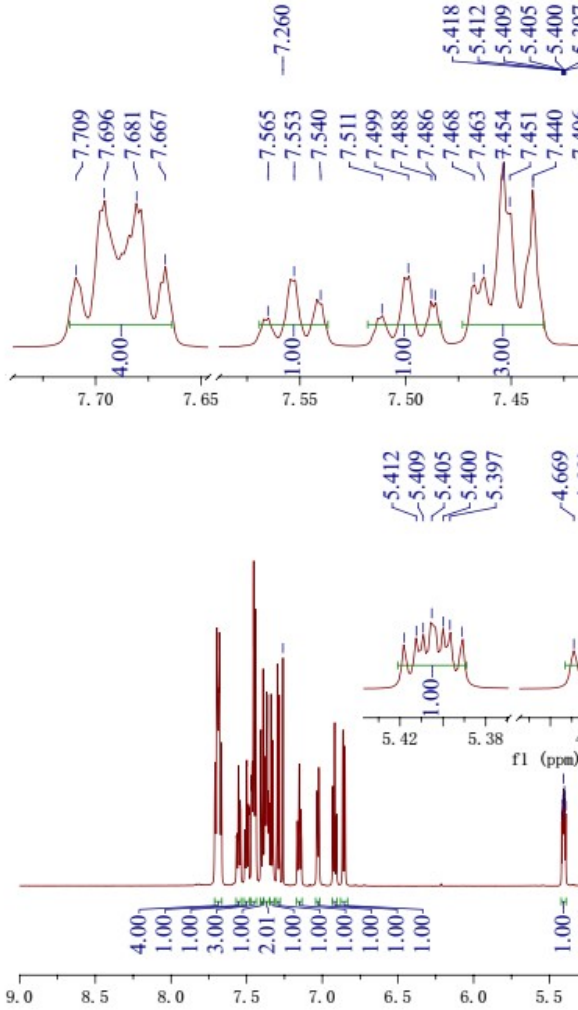
4qa

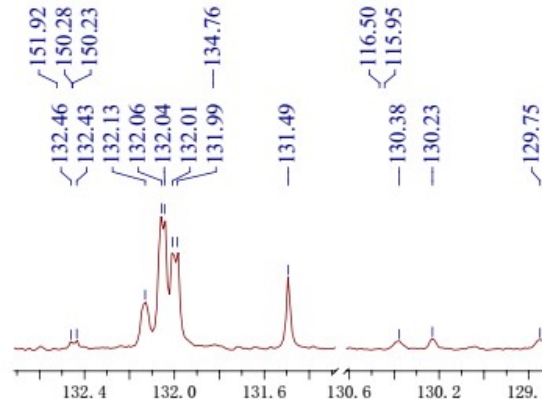
^{31}P NMR, $CDCl_3$, 243 MHz

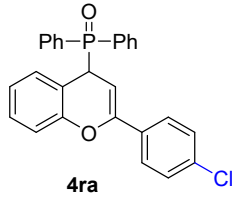


4ra

^{1}H NMR, $CDCl_3$, 600 MHz

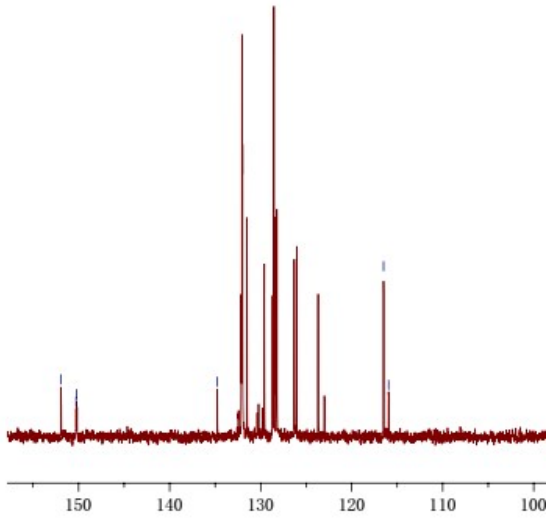


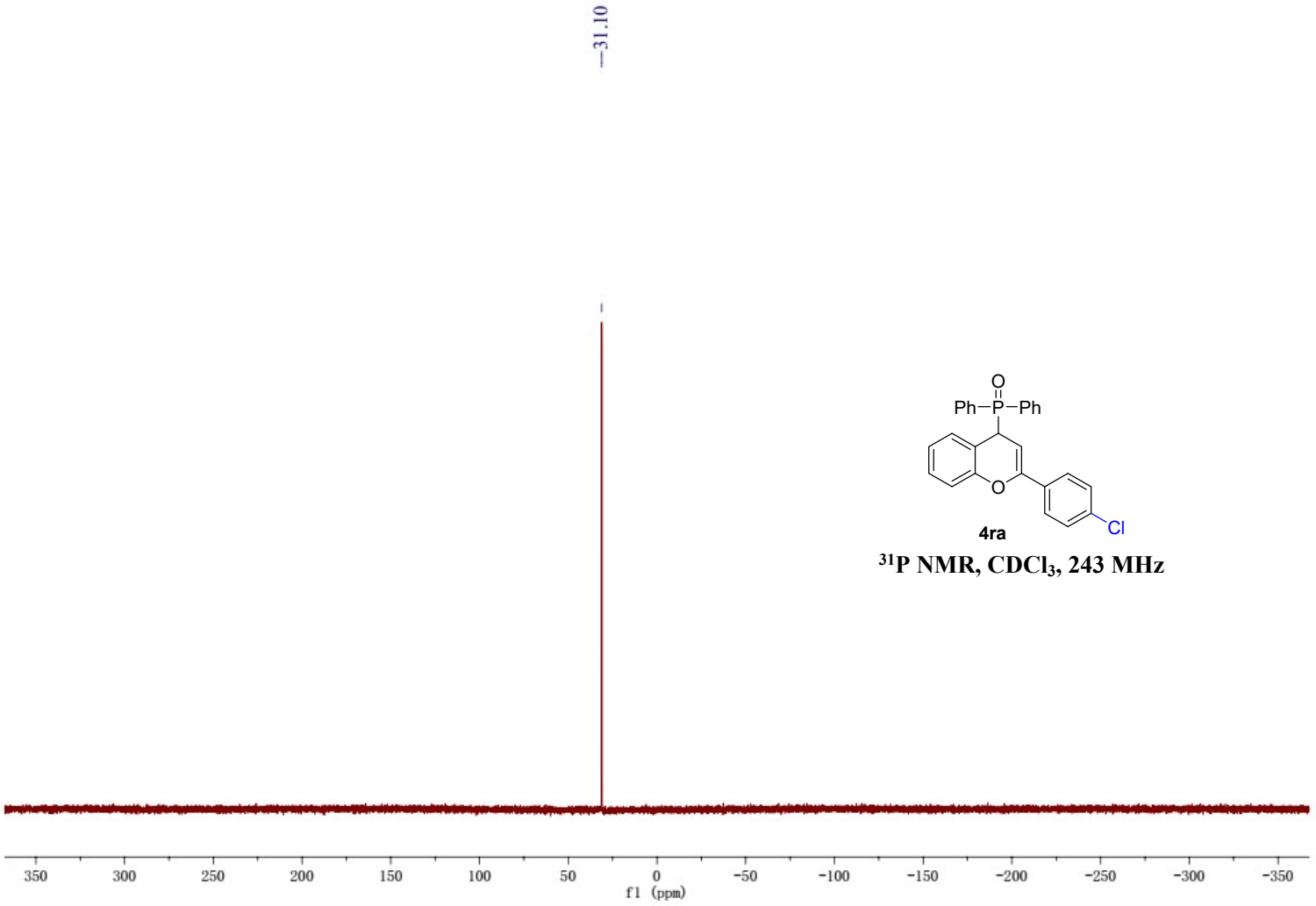




4ra

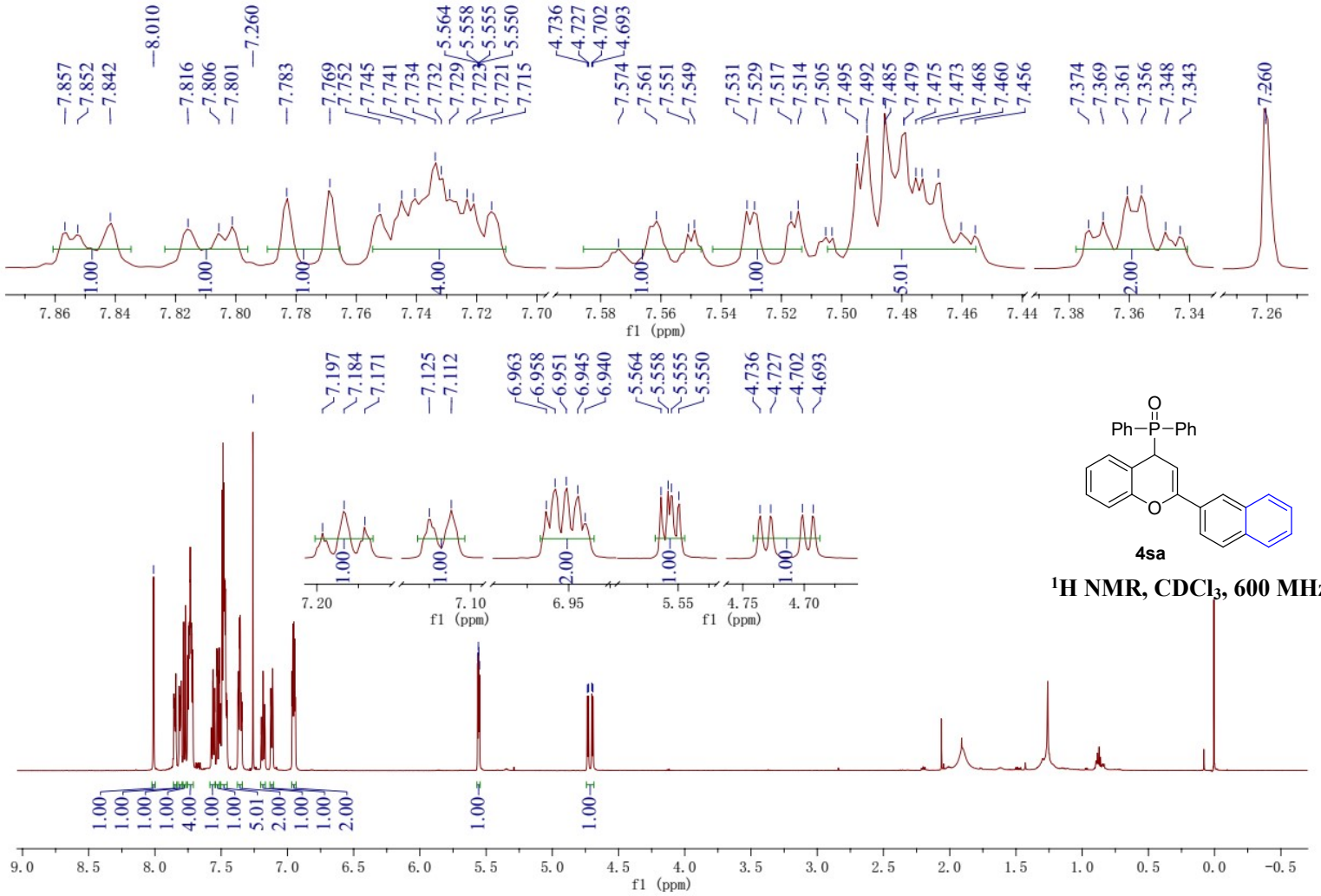
^{13}C NMR, $CDCl_3$, 150 MHz





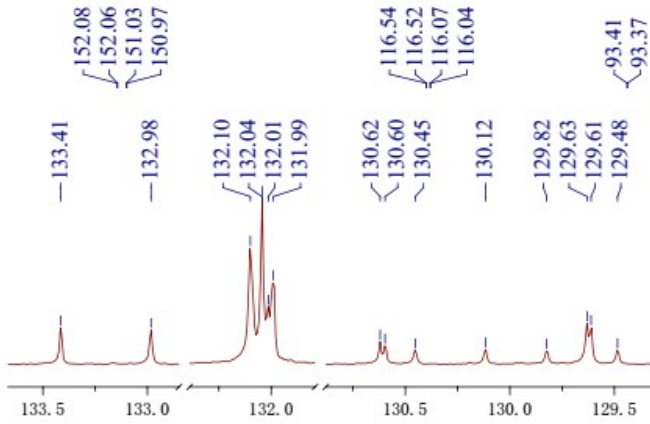
4ra

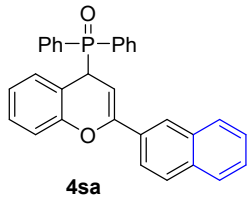
^{31}P NMR, $CDCl_3$, 243 MHz



4sa

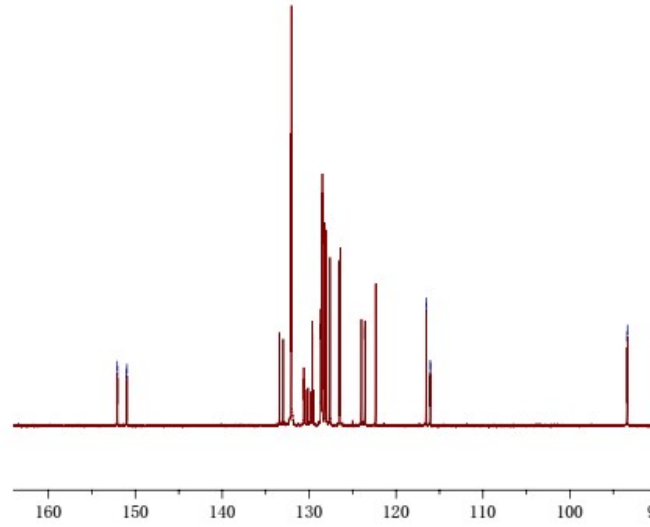
^{1}H NMR, $CDCl_3$, 600 MHz

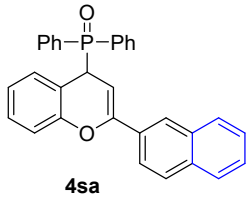




4sa

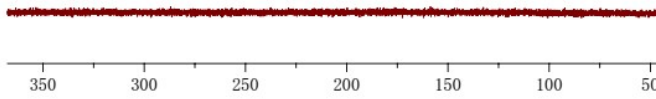
^{13}C NMR, $CDCl_3$, 150 MHz

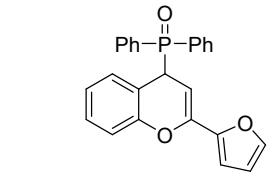




4sa

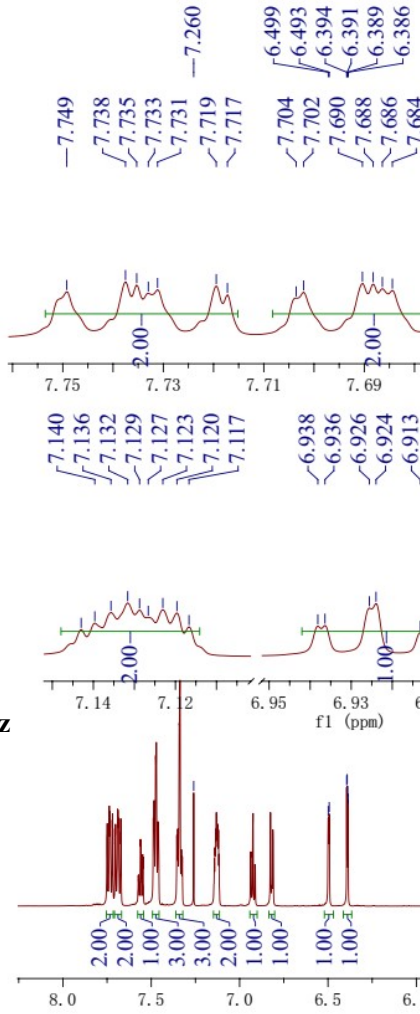
^{31}P NMR, $CDCl_3$, 243 MHz

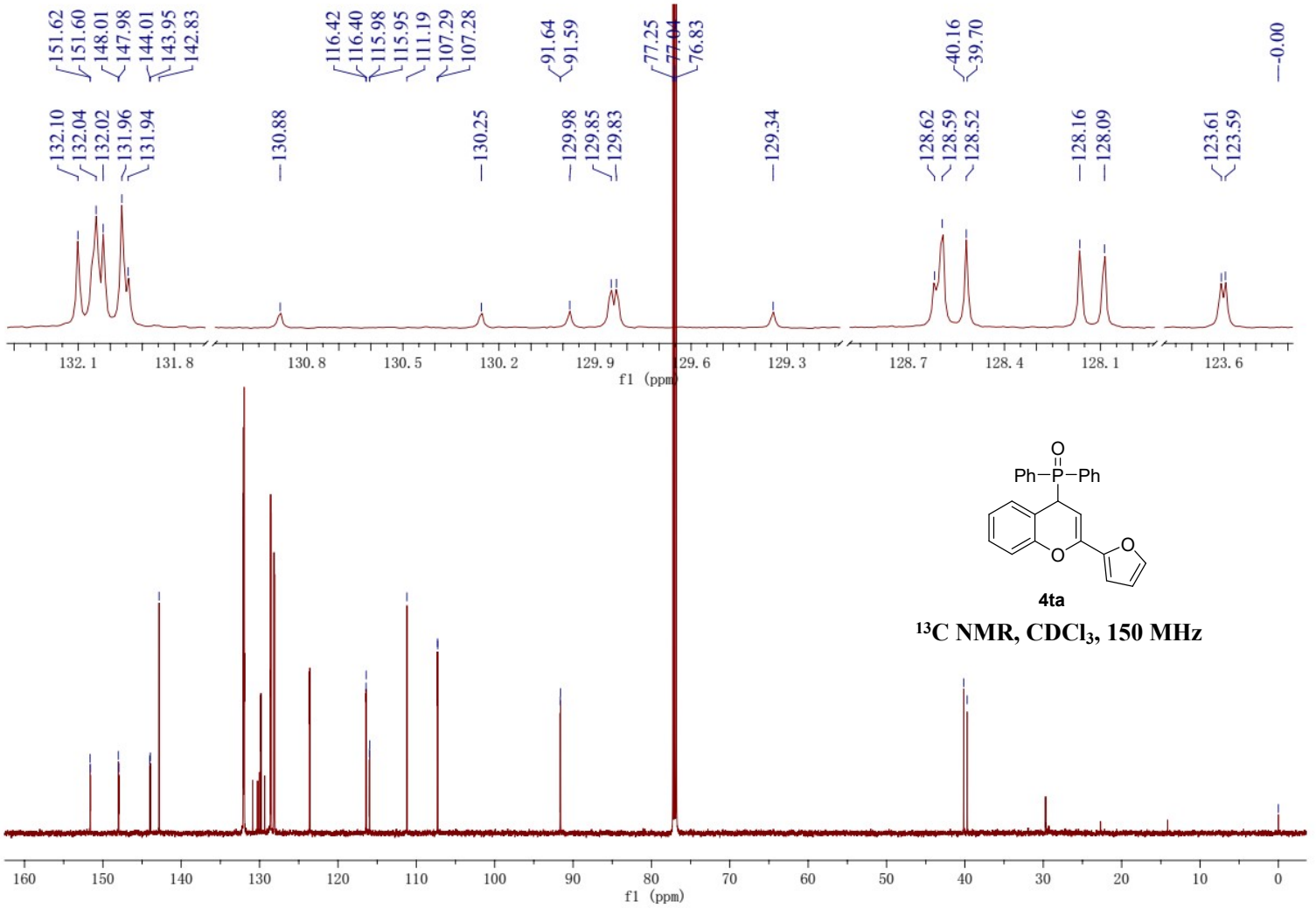


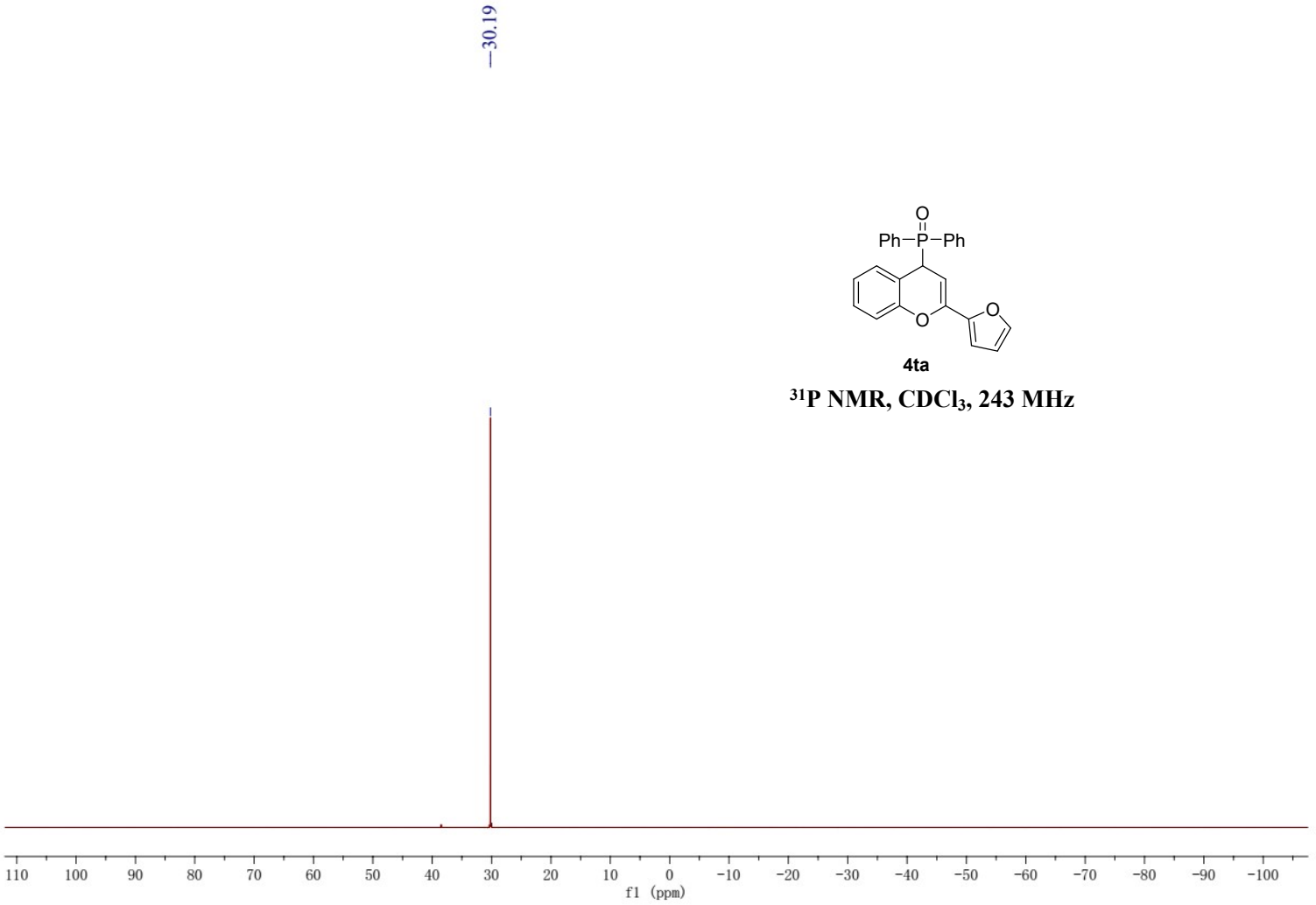


4ta

^{1}H NMR, $CDCl_3$, 600 MHz

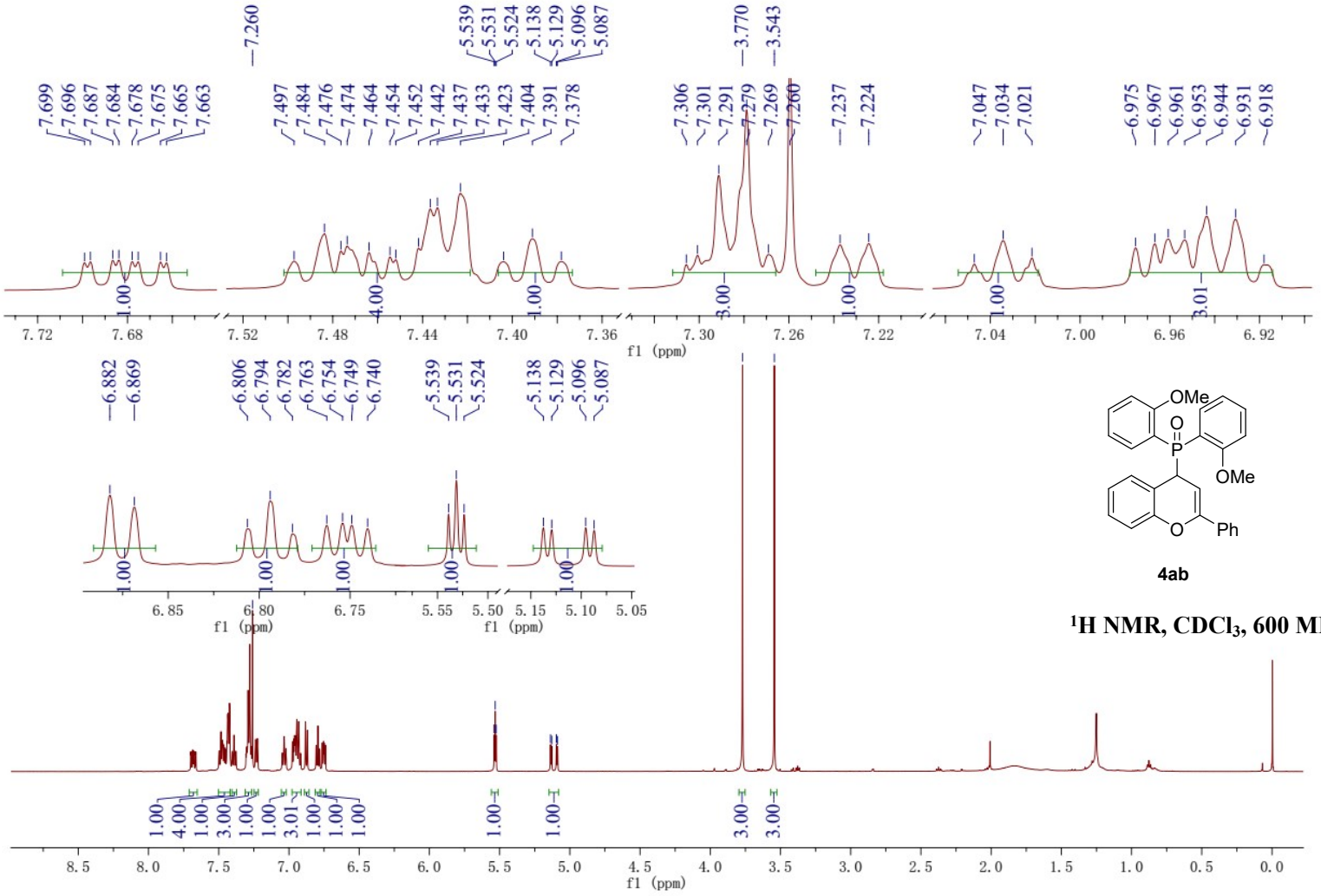


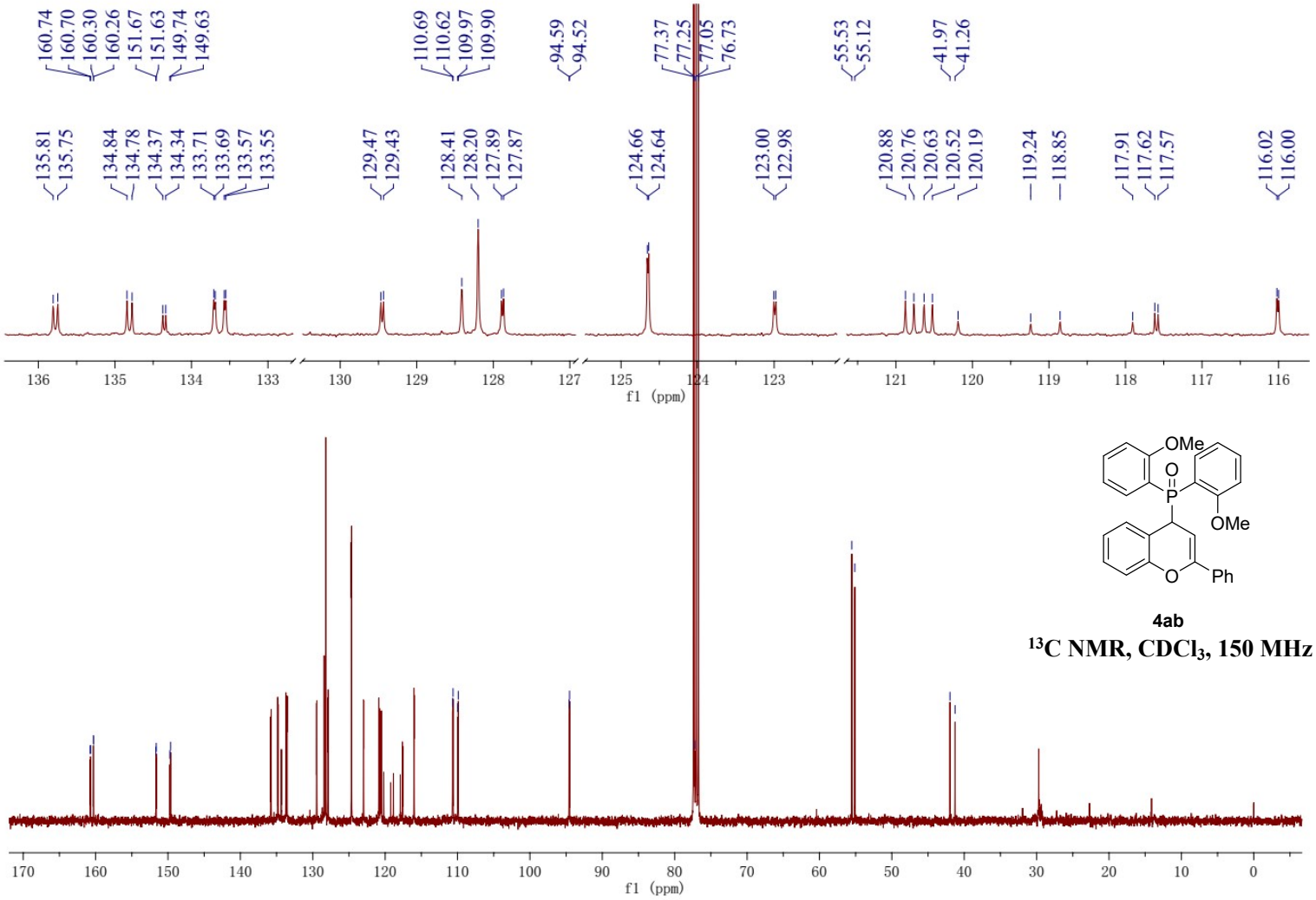

151.62
151.60
148.01
147.98
144.01
143.95
142.83
116.42
116.40
115.98
115.95
111.19
107.29
107.28
91.64
91.59
77.25
77.04
76.83
40.16
39.70
-0.00
132.10
132.04
132.02
131.96
131.94
130.88
130.25
129.98
129.85
129.83
129.34
128.62
128.59
128.52
128.16
128.09
123.61
123.59
f1 (ppm)
O
Ph—P—Ph
O
O
4ta
13C NMR, CDCl3, 150 MHz



4ta

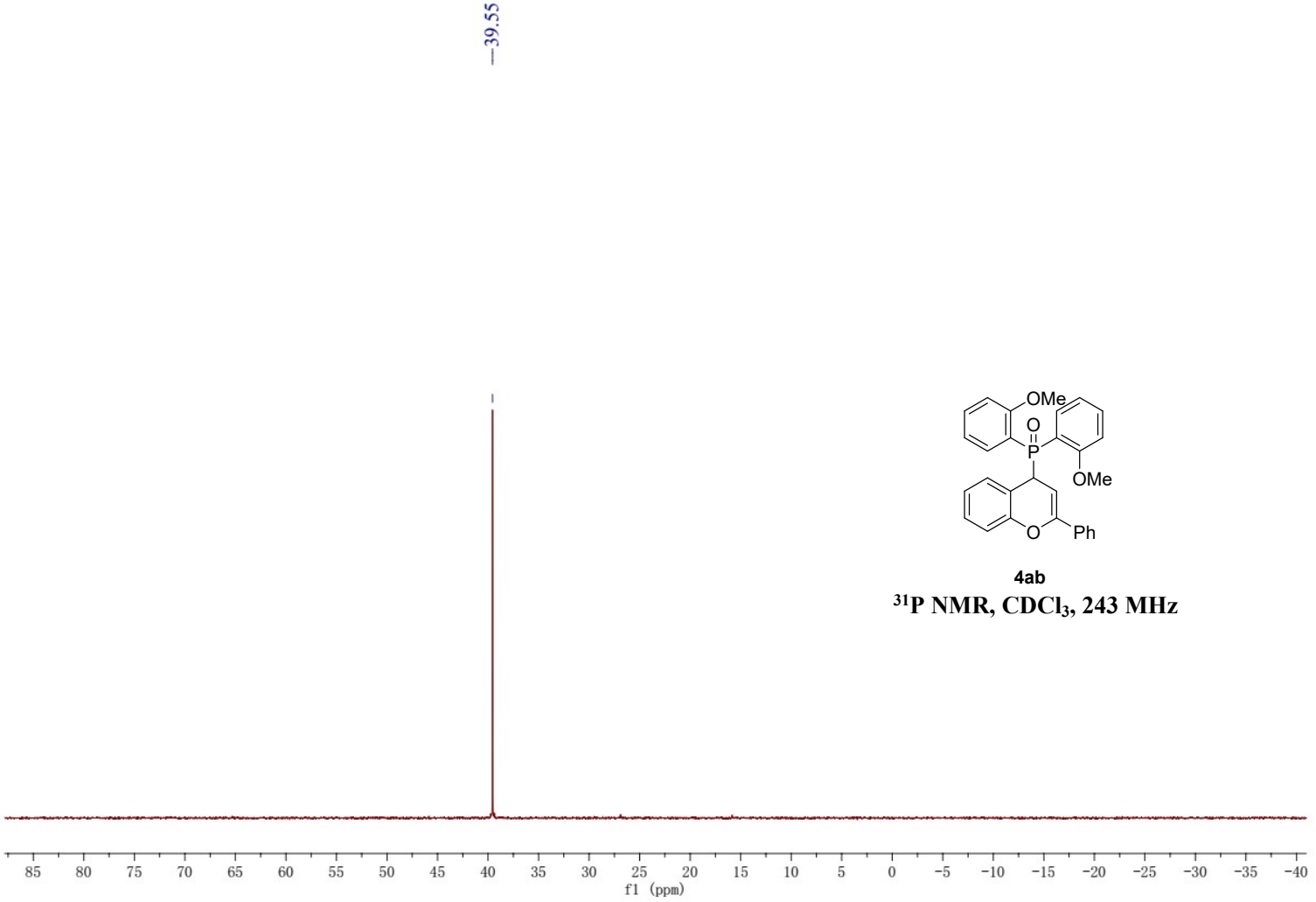
^{31}P NMR, $CDCl_3$, 243 MHz


7.260
5.539
5.531
5.524
5.138
5.129
5.096
5.087
3.770
3.543
7.699
7.696
7.687
7.684
7.678
7.675
7.665
7.663
7.497
7.484
7.476
7.474
7.464
7.454
7.452
7.442
7.437
7.433
7.423
7.404
7.391
7.378
7.306
7.301
7.291
7.279
7.269
7.260
7.237
7.224
7.047
7.034
7.021
6.975
6.967
6.961
6.953
6.944
6.931
6.918
f1 (ppm)
6.882
6.869
6.806
6.794
6.782
6.763
6.754
6.749
6.740
5.539
5.531
5.524
5.138
5.129
5.096
5.087
f1 (ppm)
f1 (ppm)
OMe
O
P
OMe
O
Ph
4ab
1H NMR, CDCl3, 600 MHz



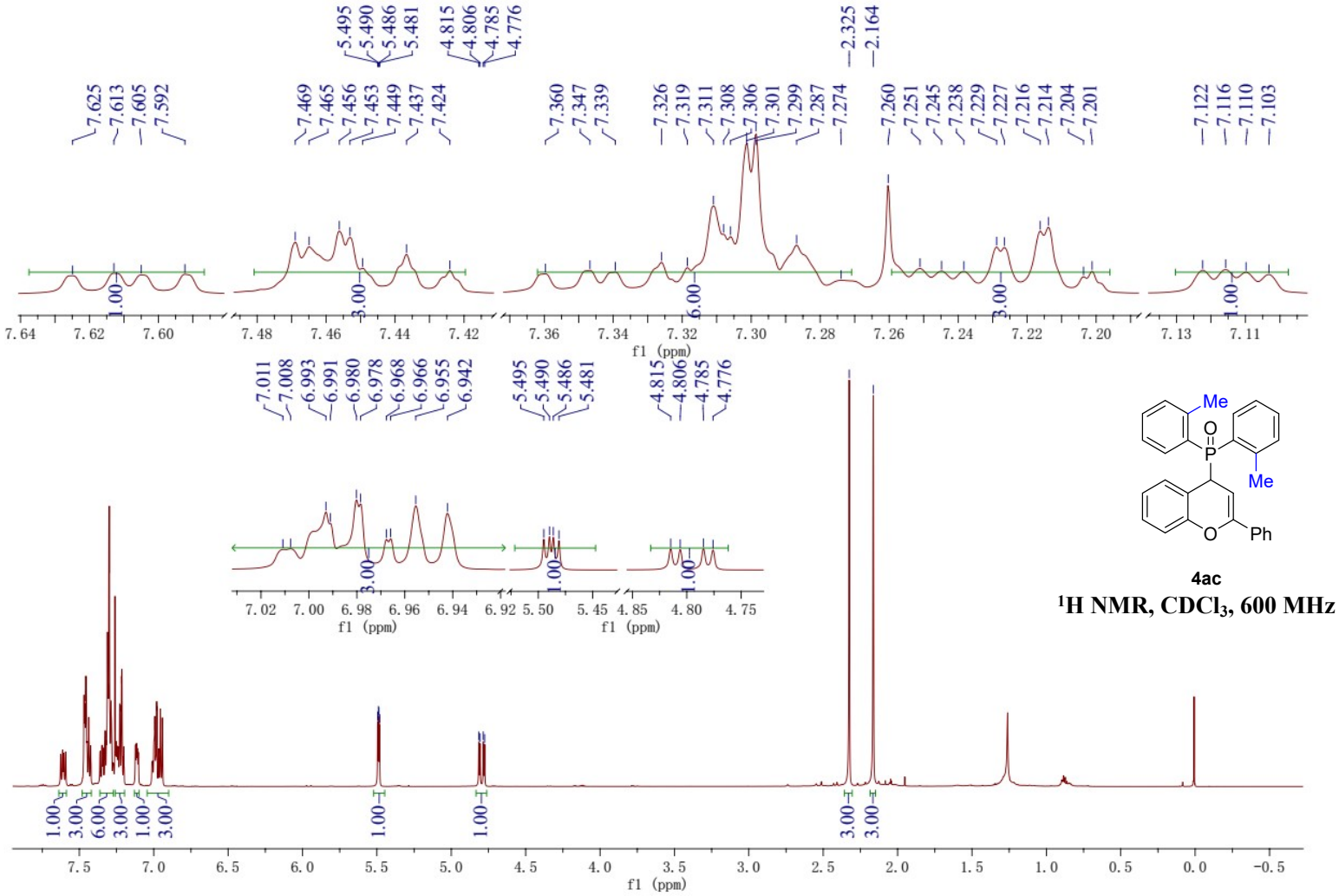
4ab

^{13}C NMR, $CDCl_3$, 150 MHz



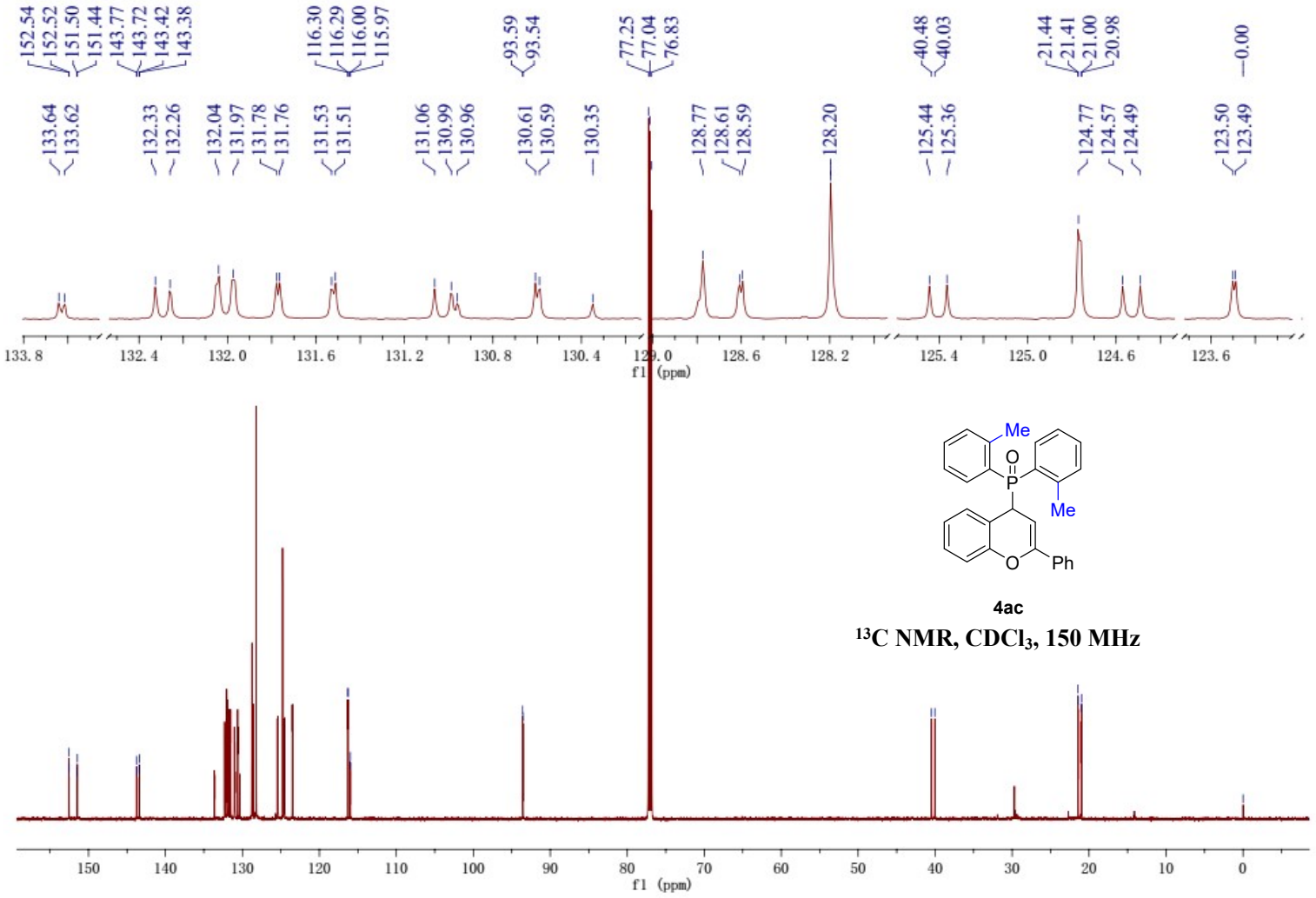
4ab

^{31}P NMR, $CDCl_3$, 243 MHz



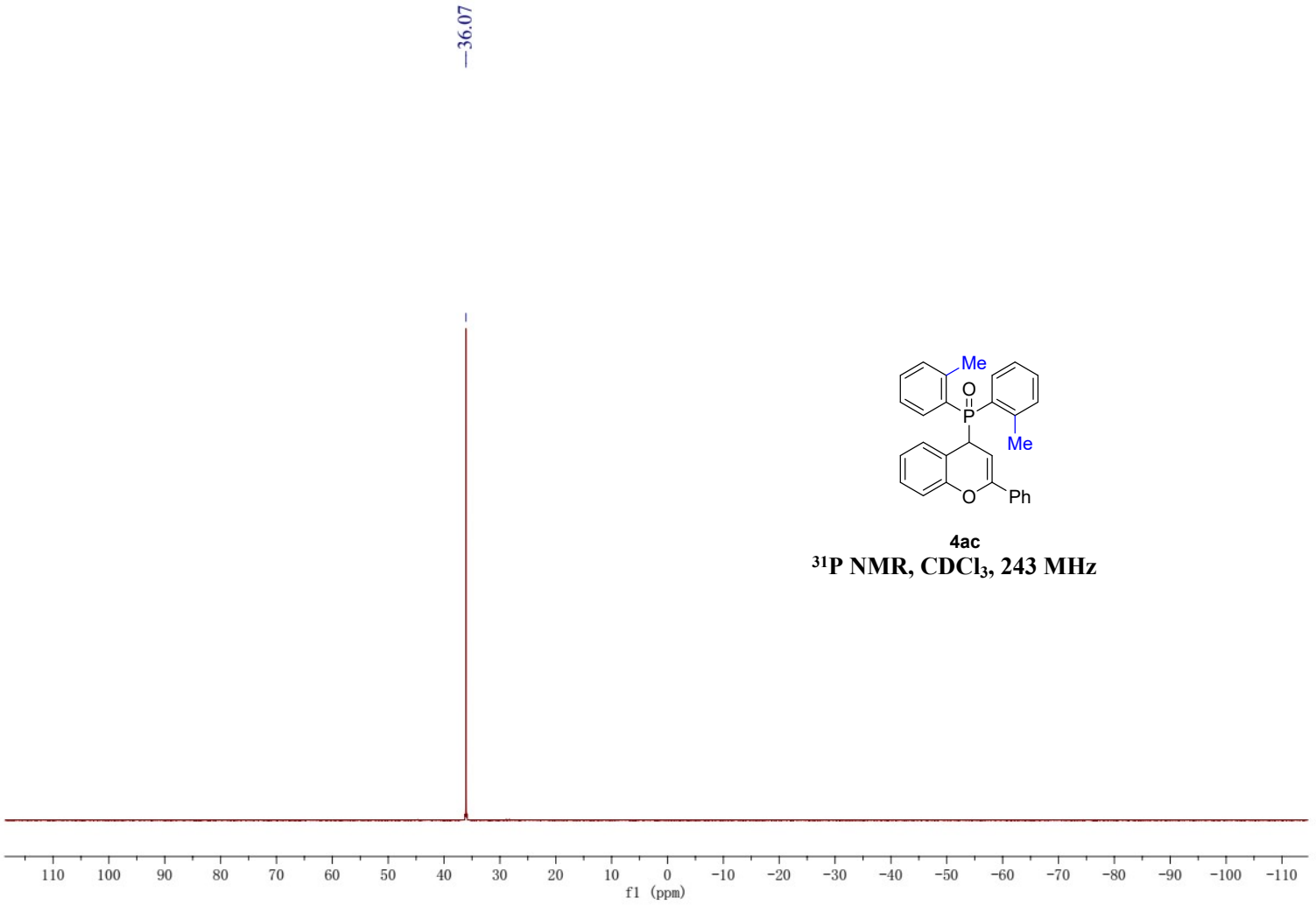
4ac

^{1}H NMR, $CDCl_3$, 600 MHz



4ac

^{13}C NMR, $CDCl_3$, 150 MHz

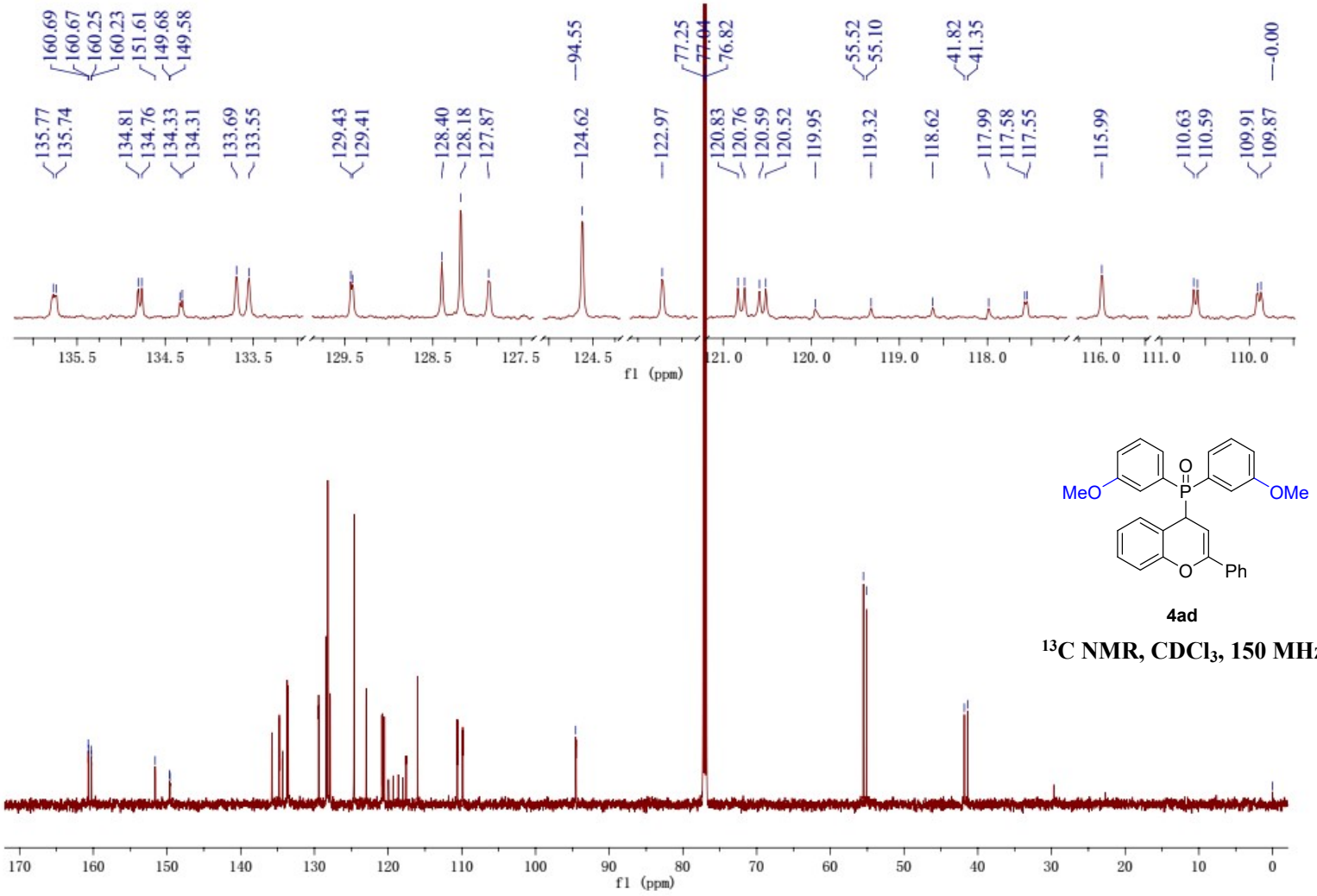


4ac

^{31}P NMR, $CDCl_3$, 243 MHz

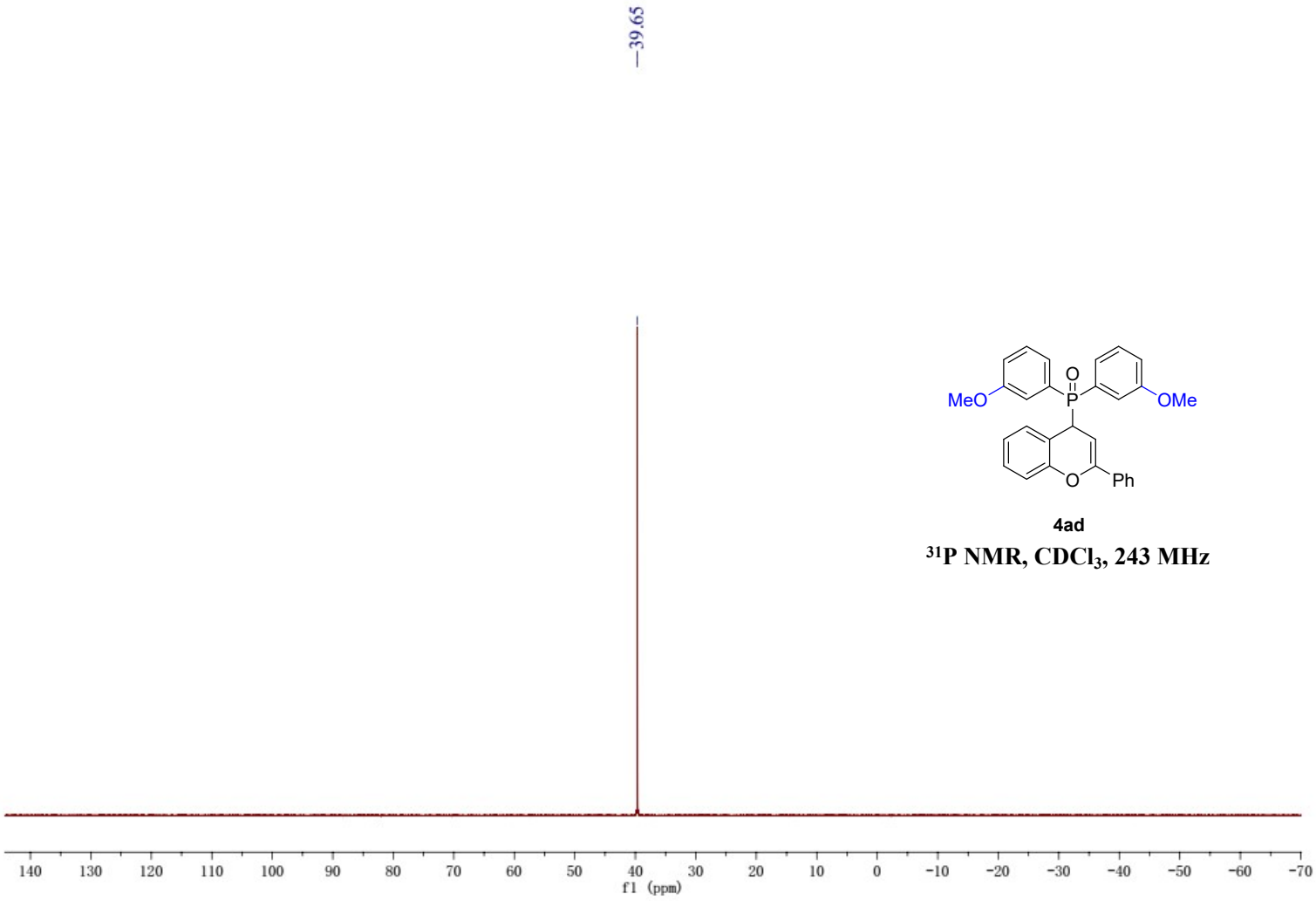
4ad

^{1}H NMR, $CDCl_3$, 600 MHz



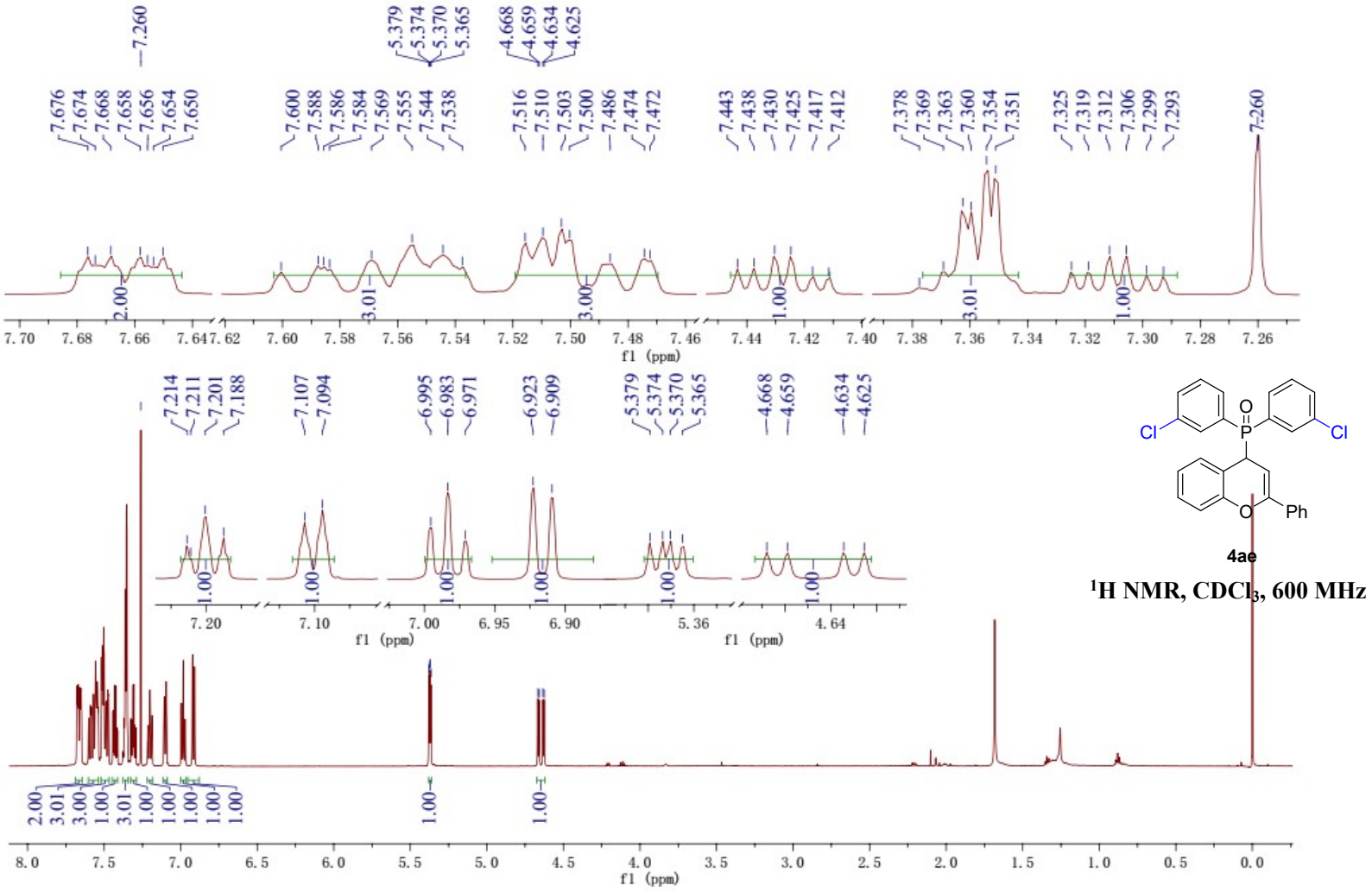
4ad

^{13}C NMR, $CDCl_3$, 150 MHz



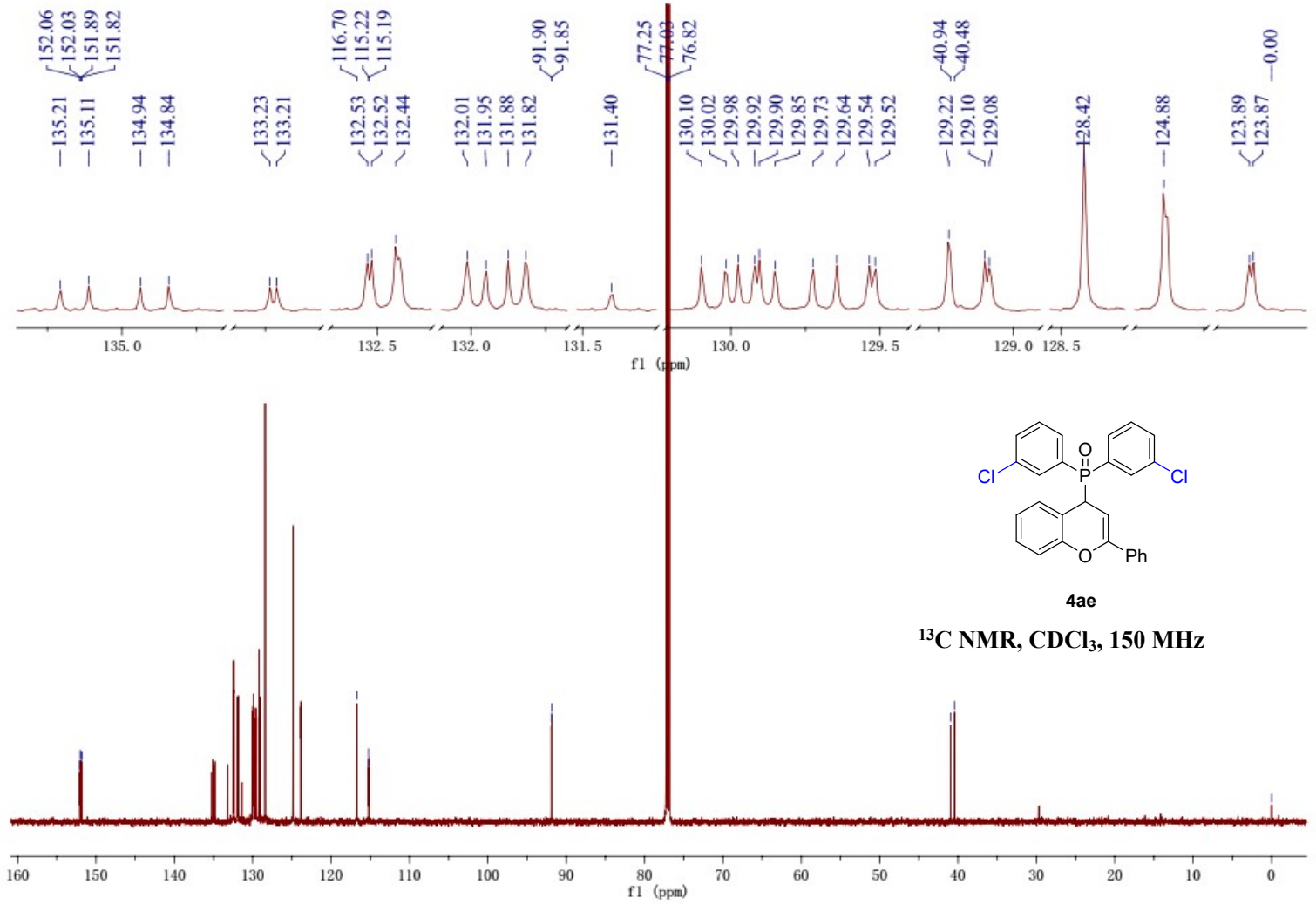
4ad

^{31}P NMR, $CDCl_3$, 243 MHz



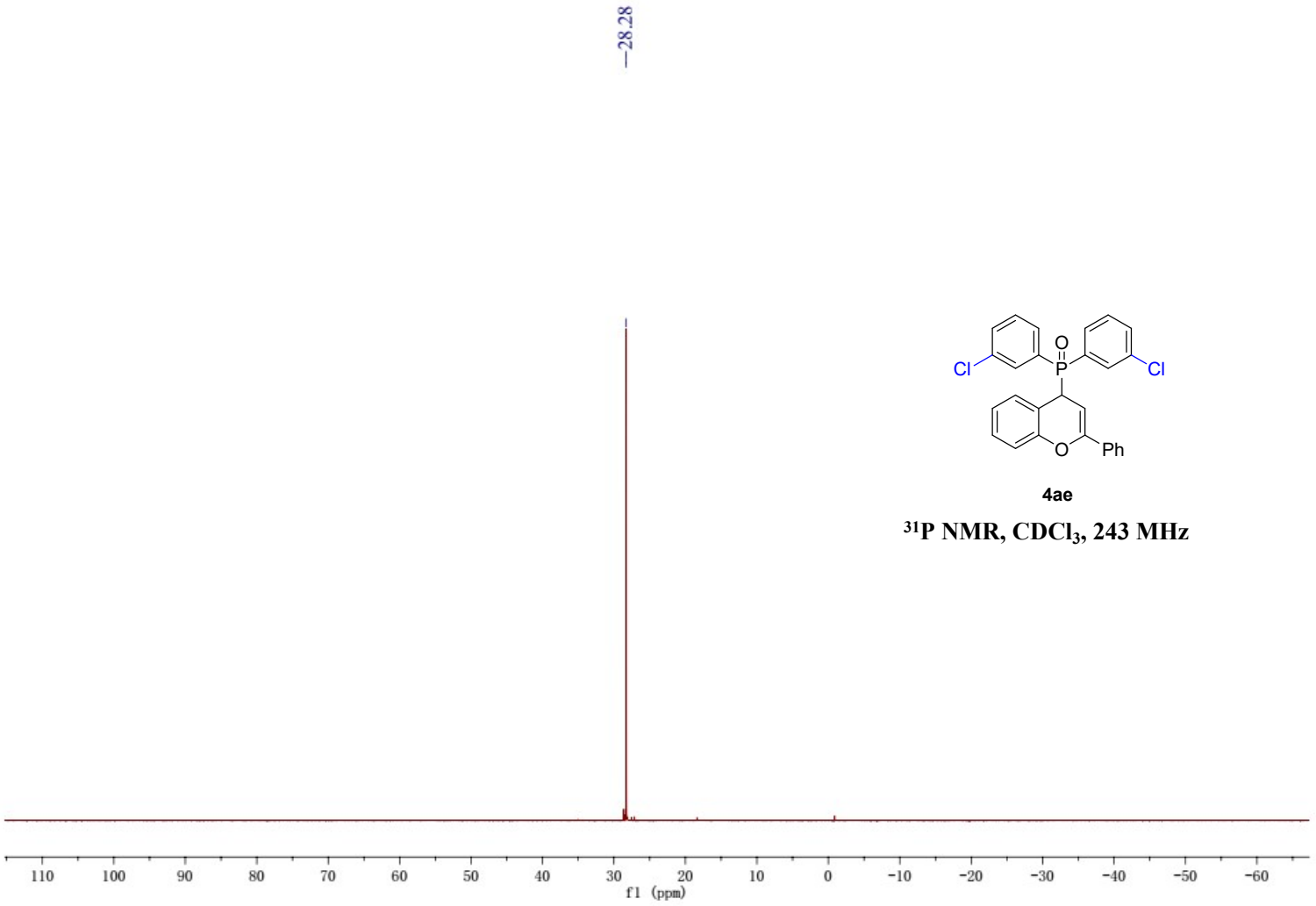
4ae

^{1}H NMR, $CDCl_3$, 600 MHz



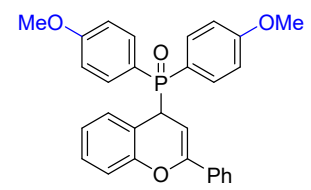
4ae

^{13}C NMR, $CDCl_3$, 150 MHz



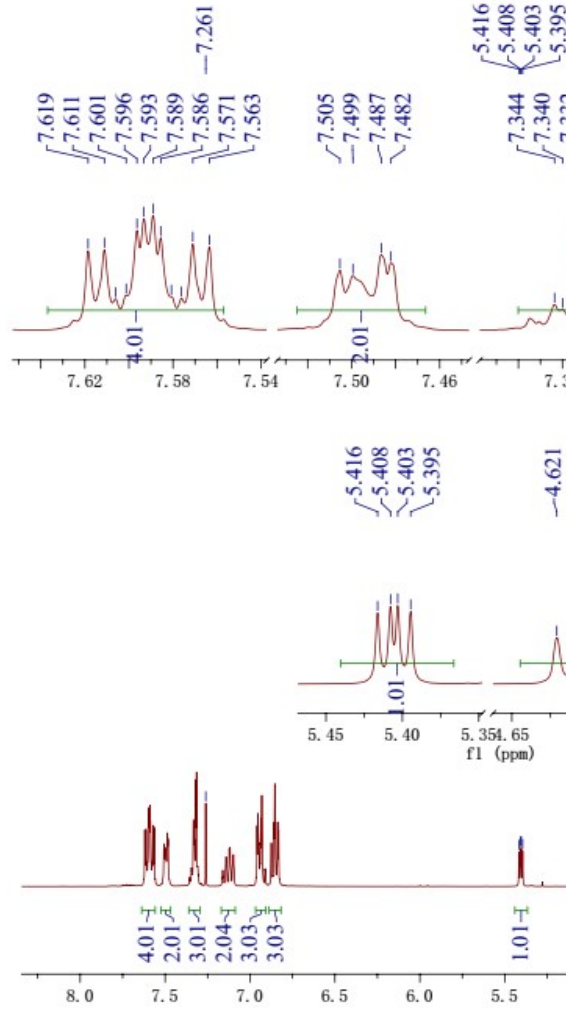
4ae

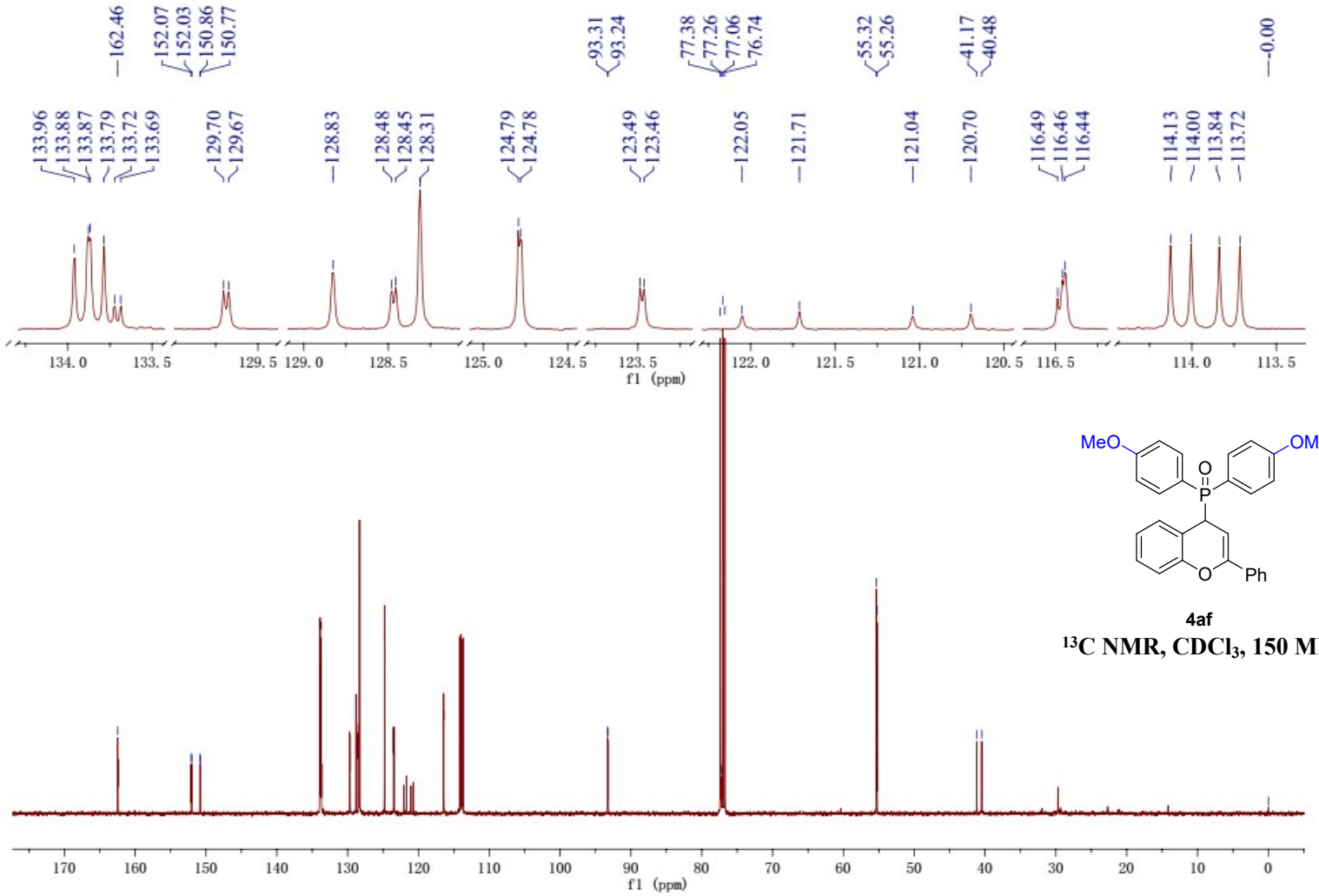
^{31}P NMR, $CDCl_3$, 243 MHz



4af

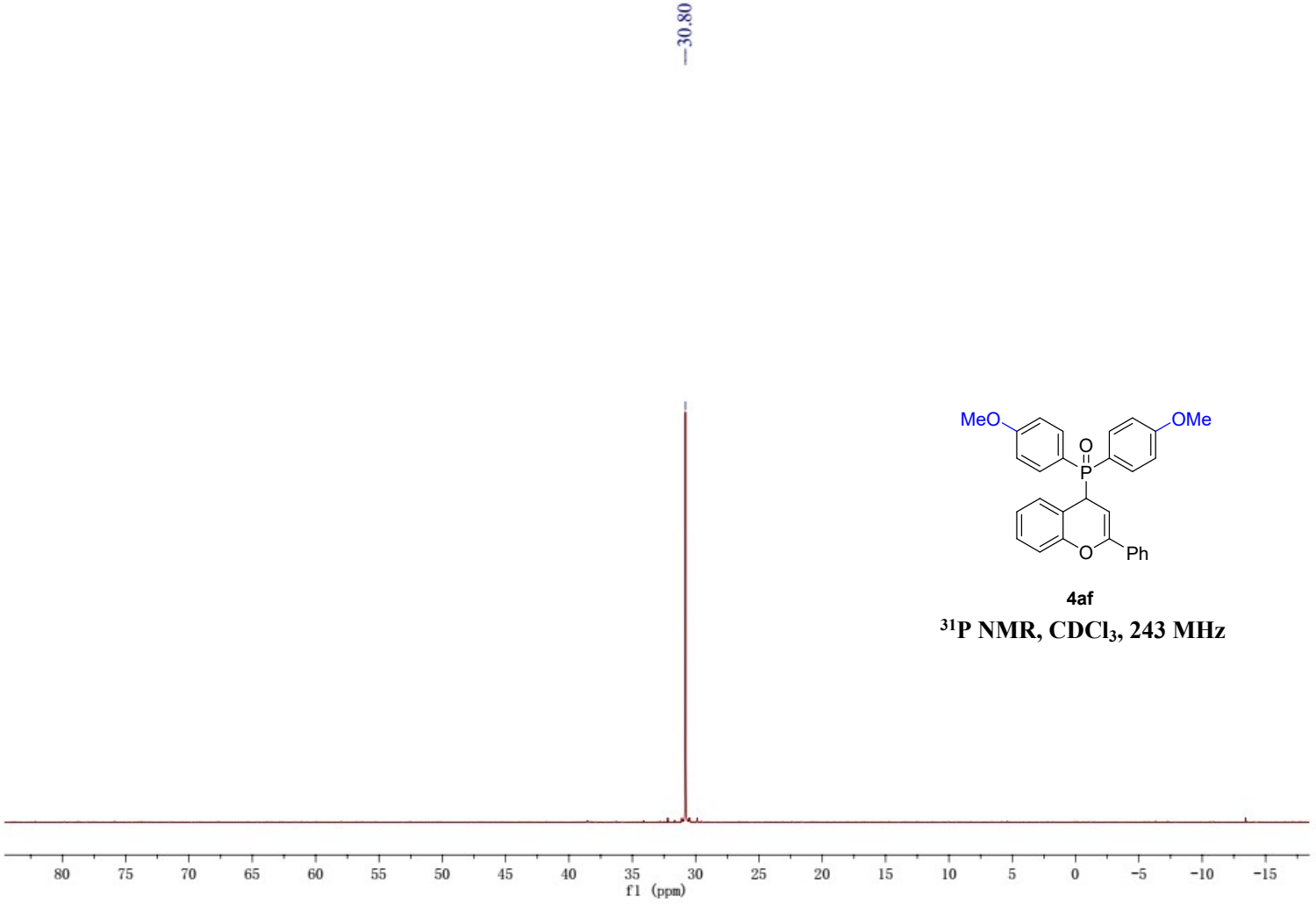
^{1}H NMR, $CDCl_3$, 600 MHz





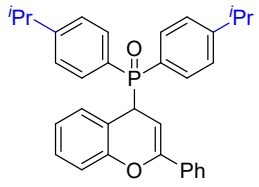
4af

^{13}C NMR, $CDCl_3$, 150 MHz



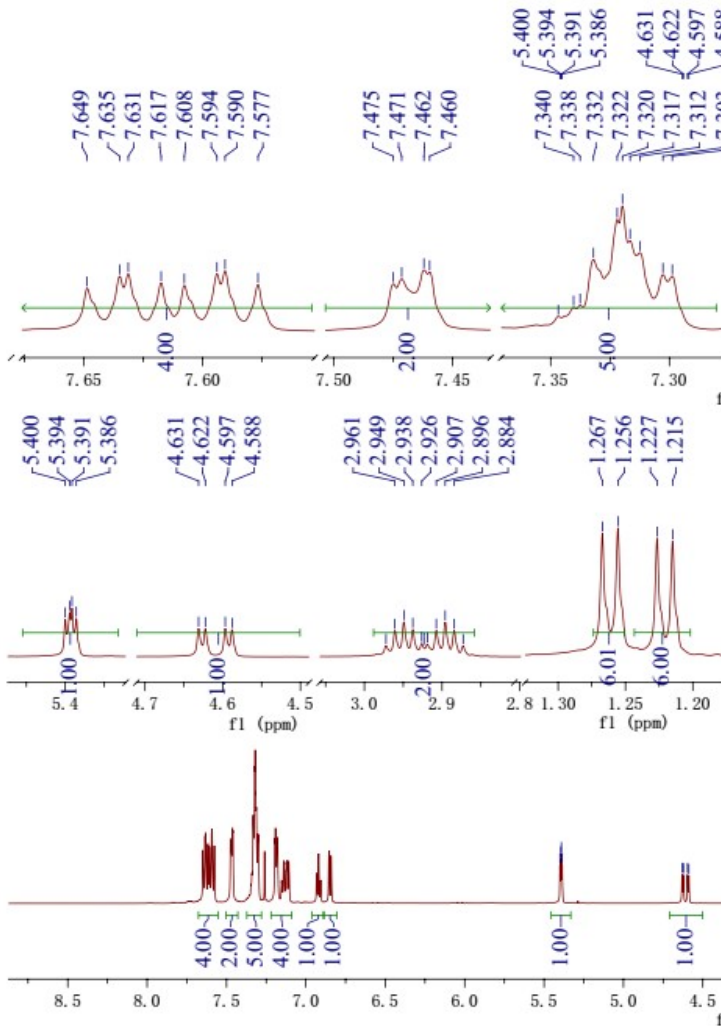
4af

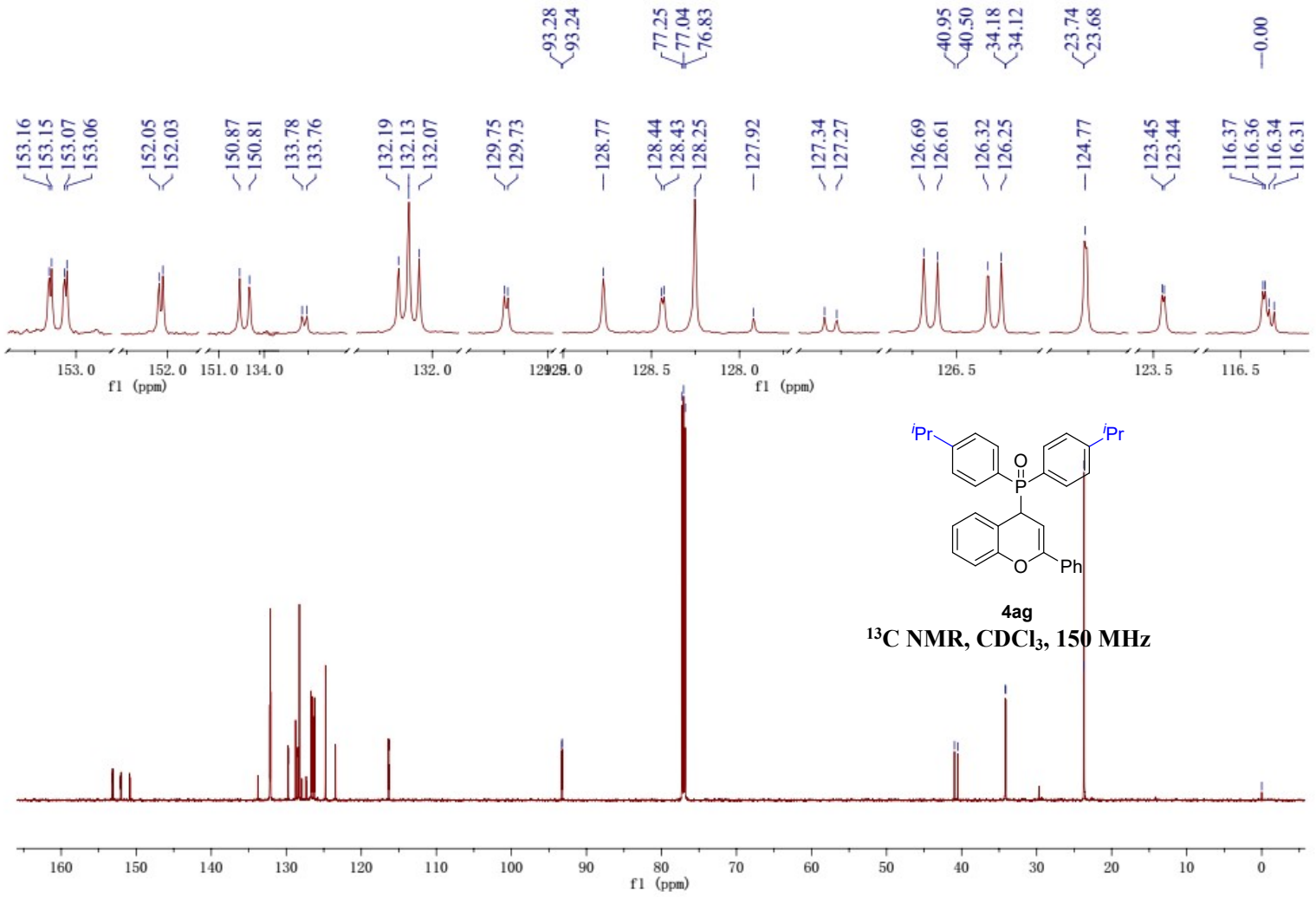
^{31}P NMR, $CDCl_3$, 243 MHz



4ag

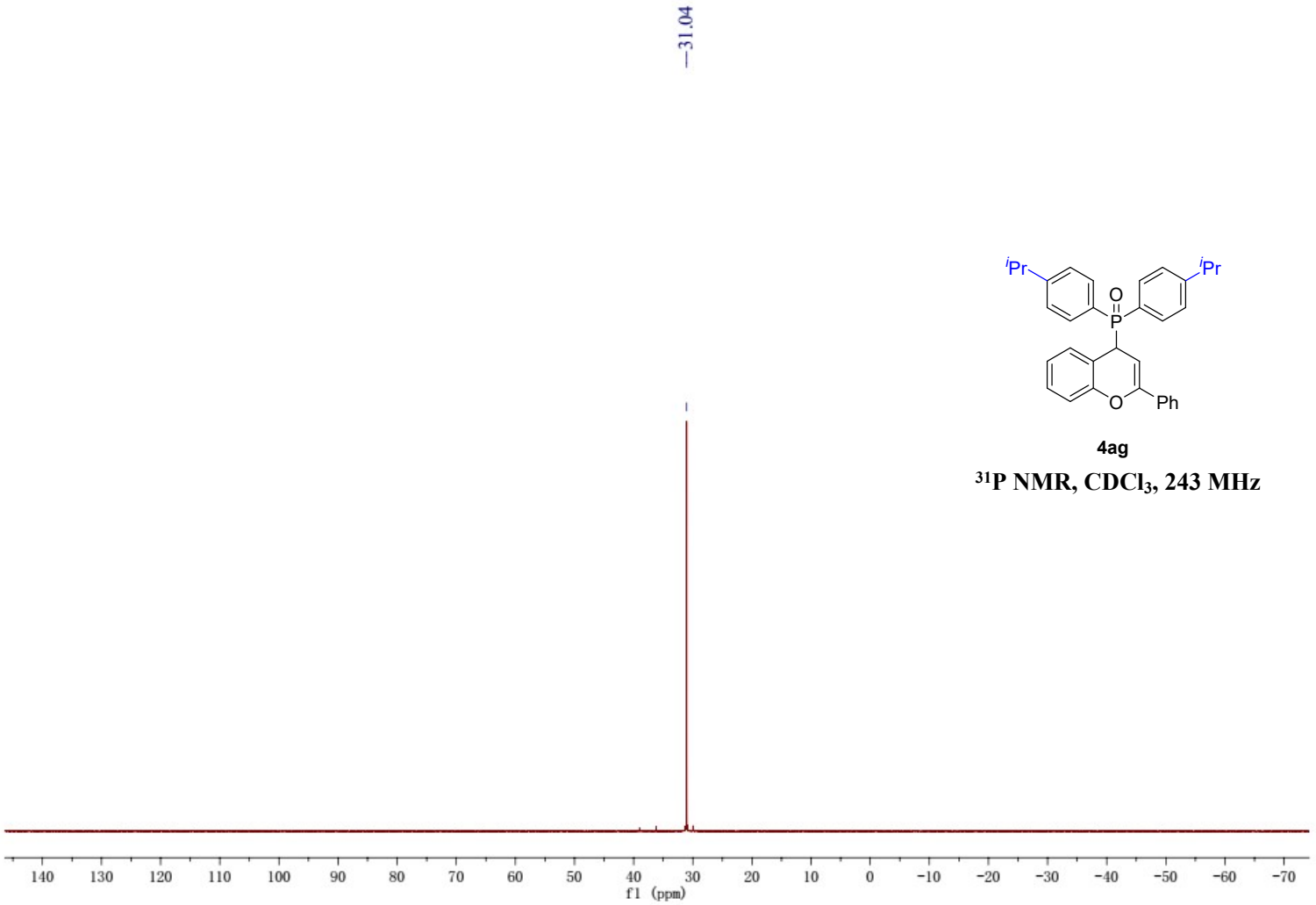
^{1}H NMR, $CDCl_3$, 600 MHz





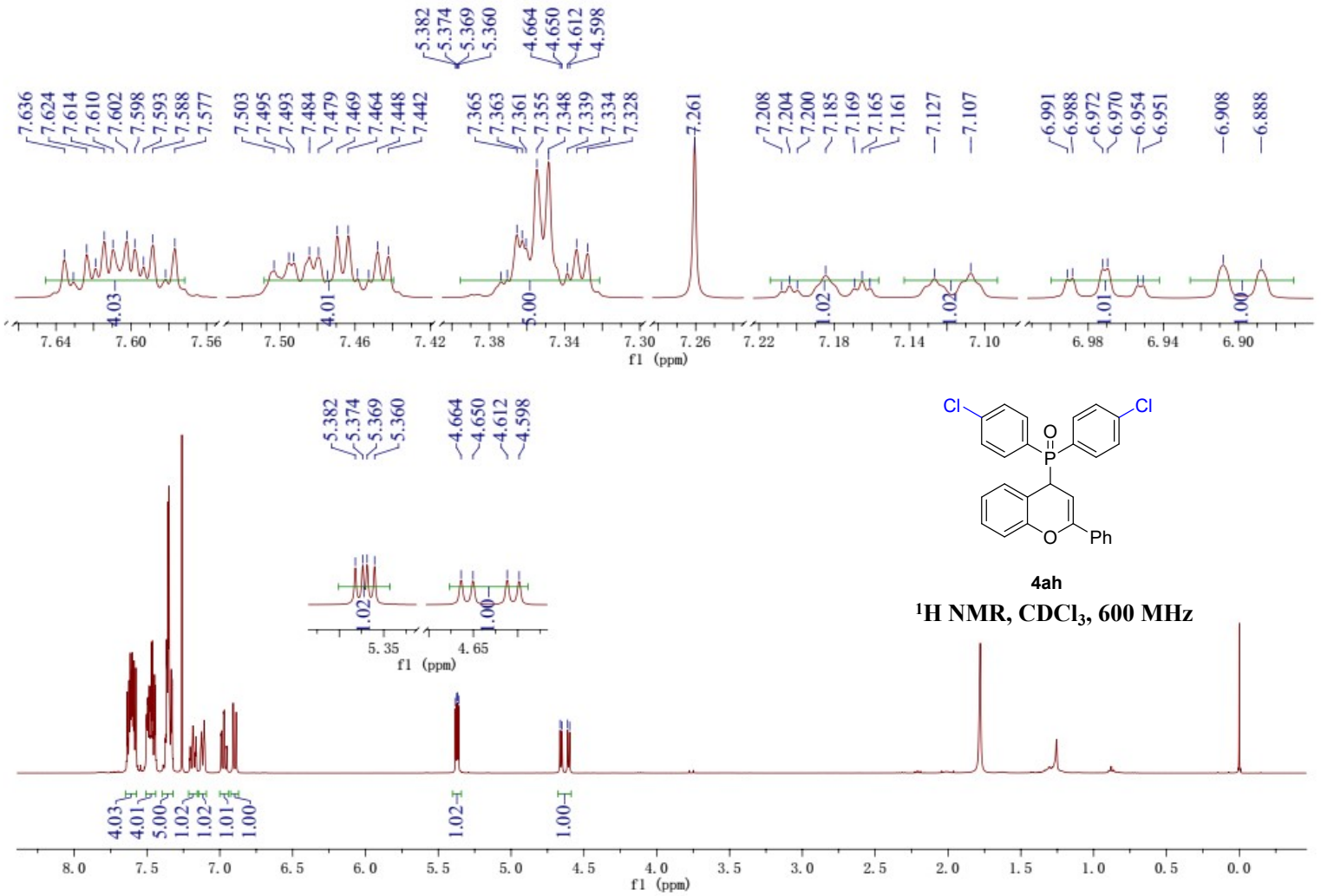
4ag

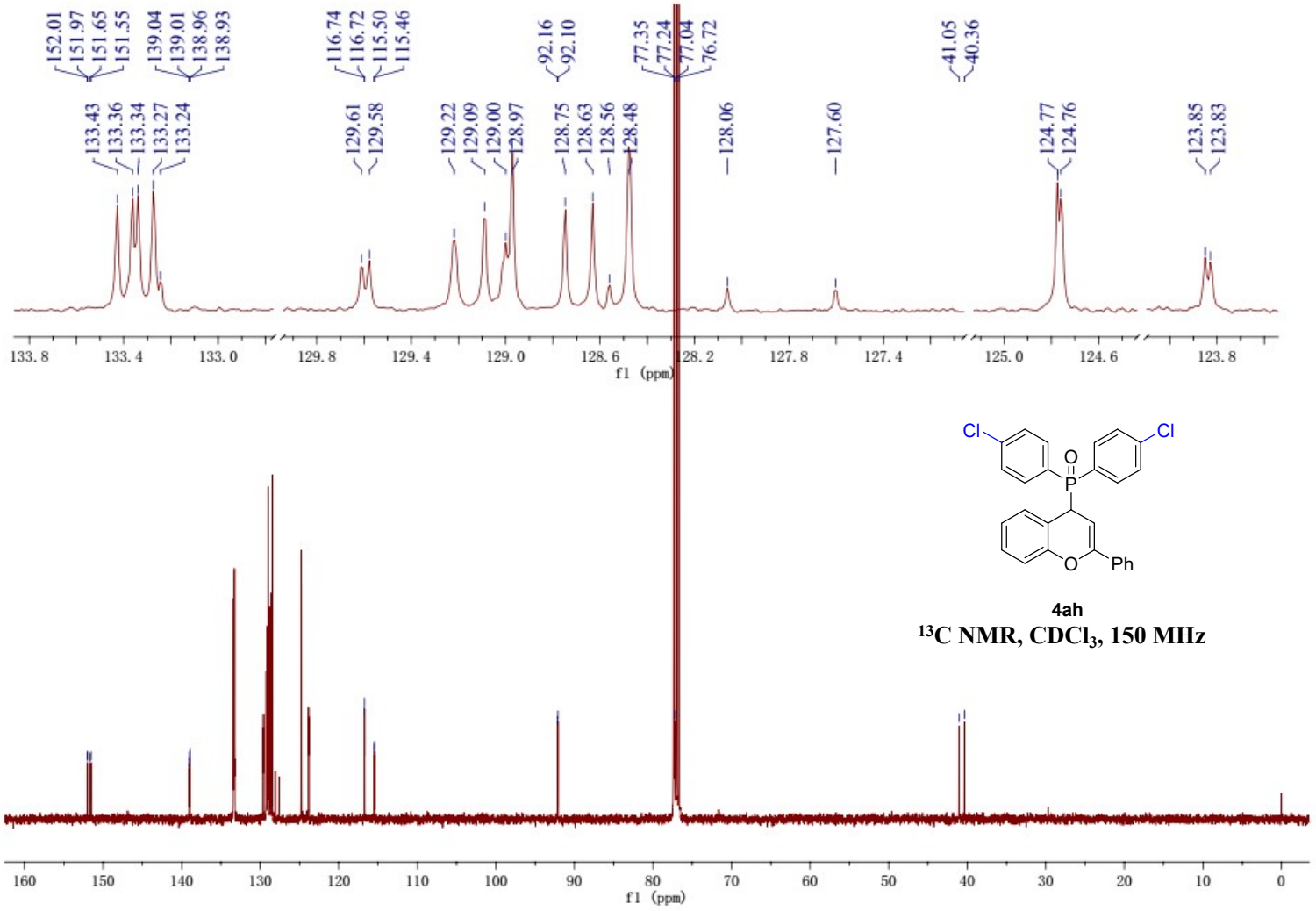
^{13}C NMR, $CDCl_3$, 150 MHz



4ag

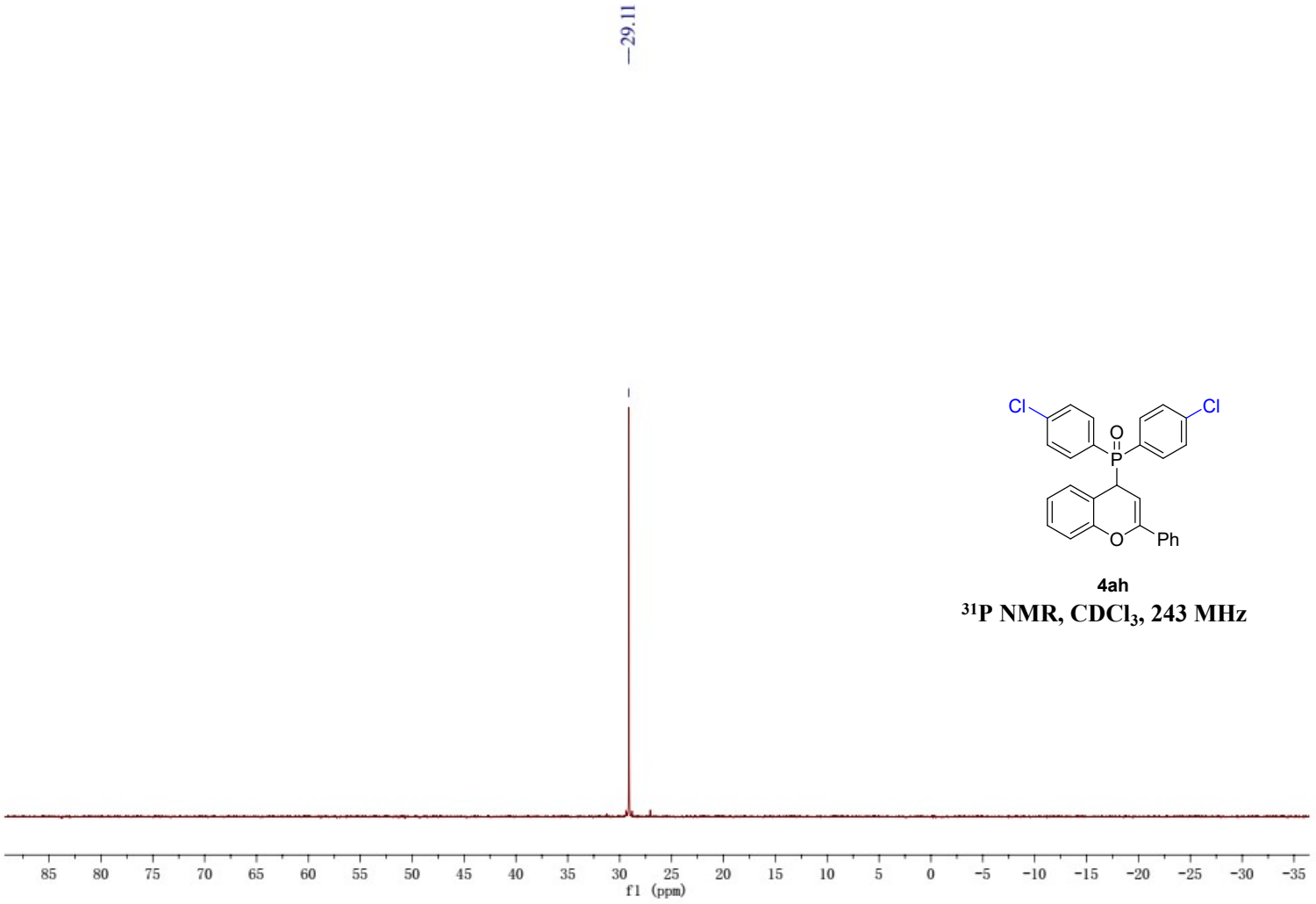
^{31}P NMR, $CDCl_3$, 243 MHz


5.382
5.374
5.369
5.360
4.664
4.650
4.612
4.598
7.636
7.624
7.614
7.610
7.602
7.598
7.593
7.588
7.577
7.503
7.495
7.493
7.484
7.479
7.469
7.464
7.448
7.442
7.365
7.363
7.361
7.355
7.348
7.339
7.334
7.328
7.261
7.208
7.204
7.200
7.185
7.169
7.165
7.161
7.127
7.107
6.991
6.988
6.972
6.970
6.954
6.951
6.908
6.888
4.03
4.01
5.00
1.02
1.02
1.01
1.00
f1 (ppm)
Cl
Cl
O
P
O
Ph
4ah
1H NMR, CDCl3, 600 MHz



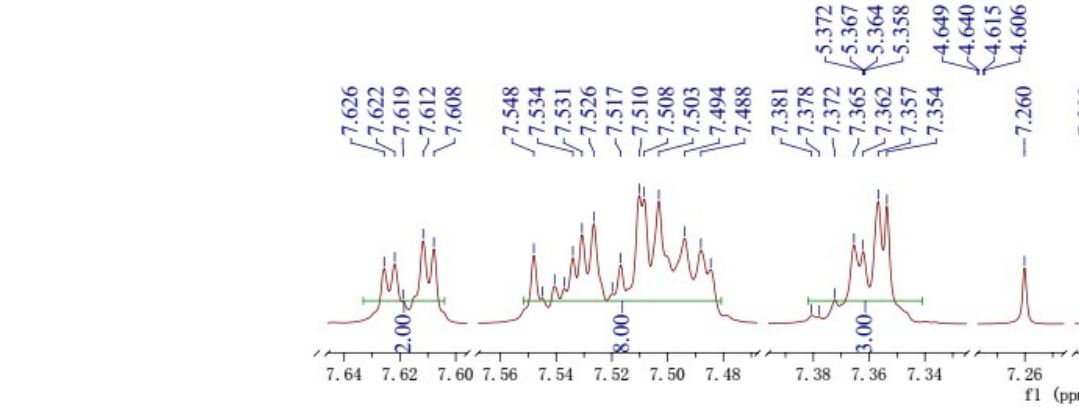
4ah

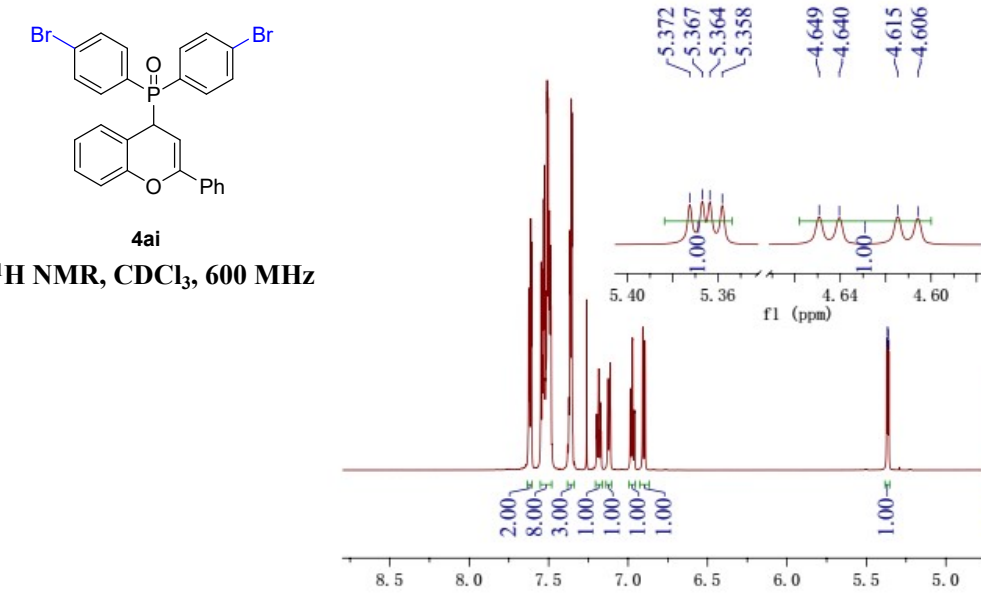
^{13}C NMR, $CDCl_3$, 150 MHz



4ah

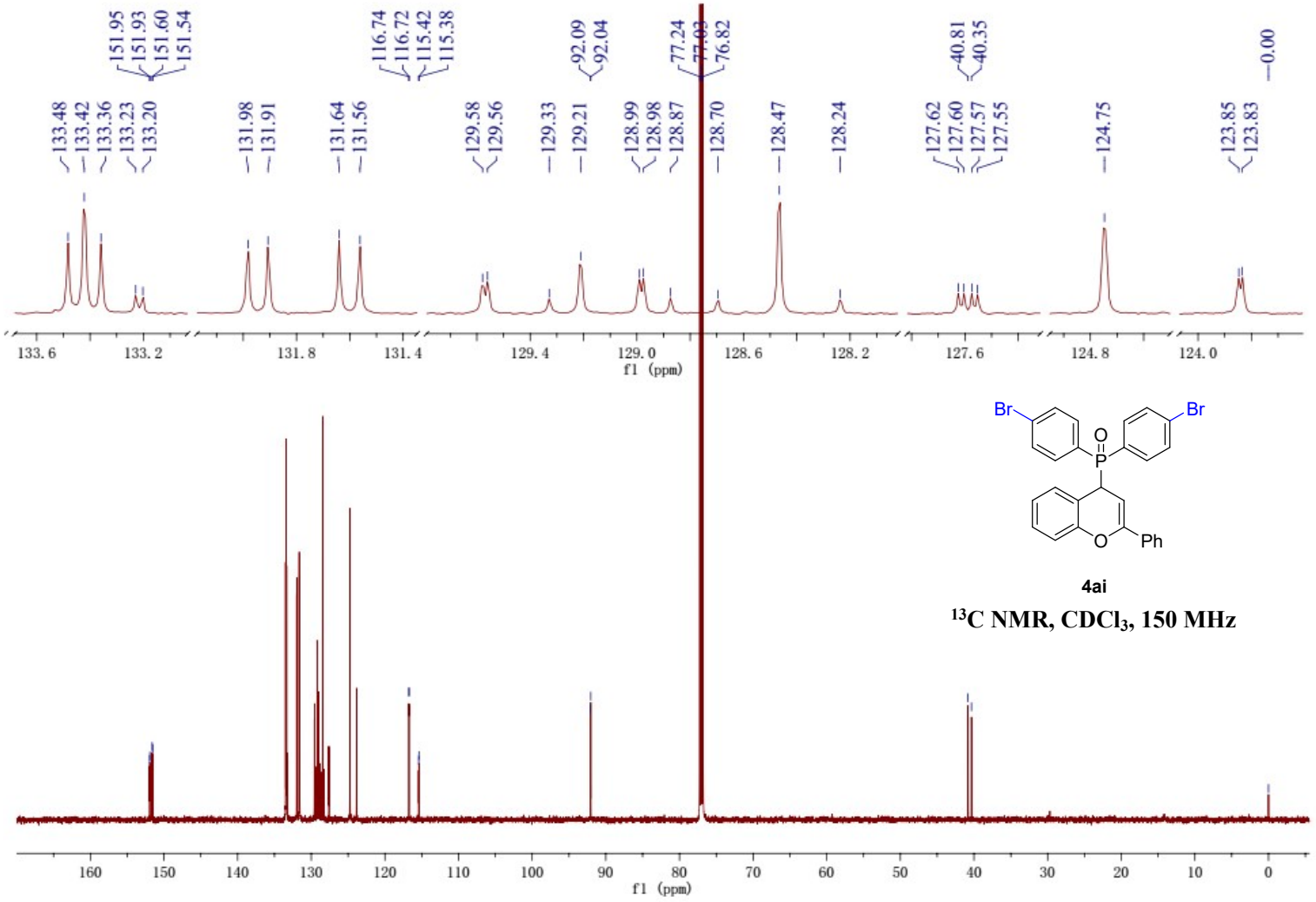
^{31}P NMR, $CDCl_3$, 243 MHz





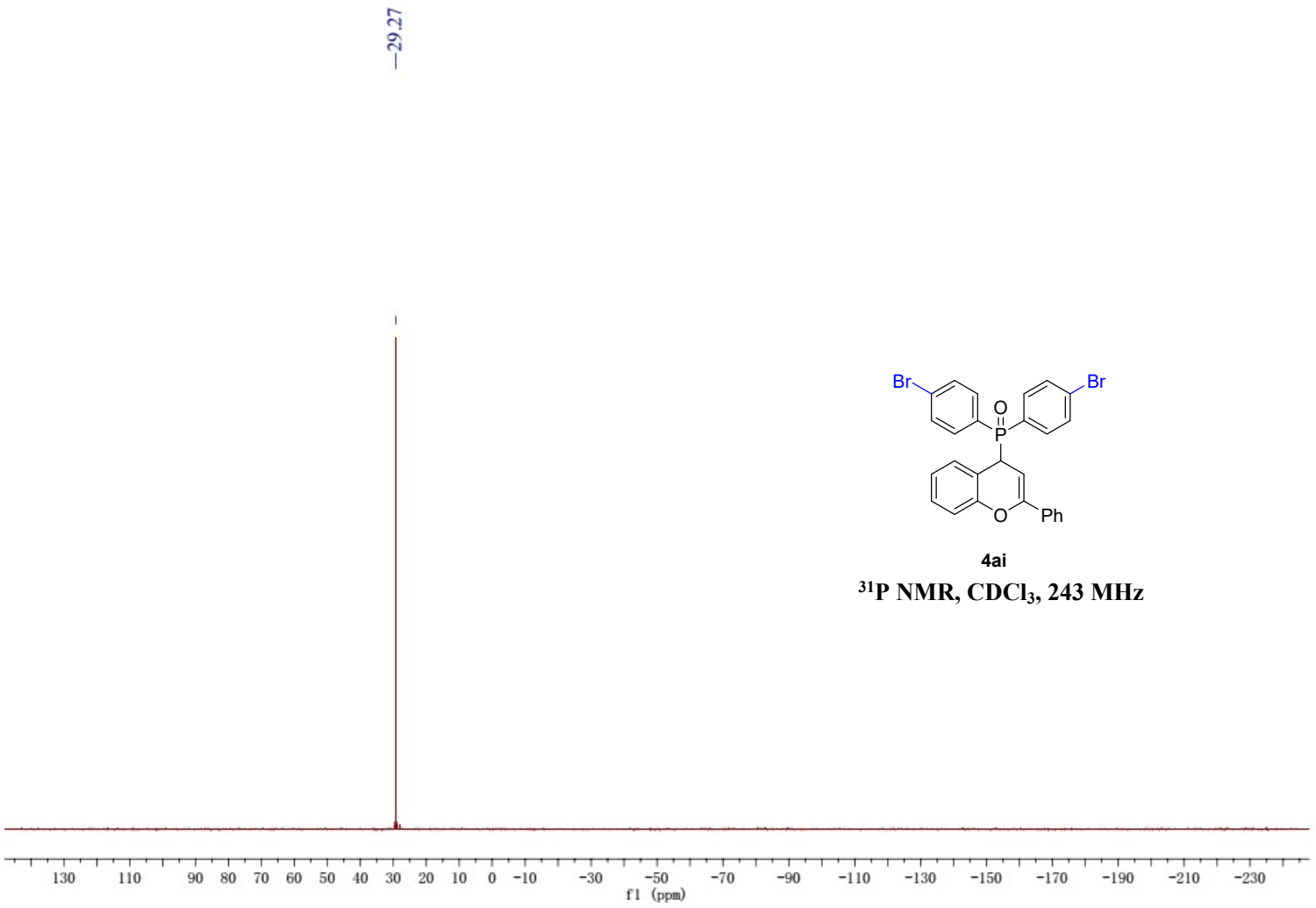
4ai

^{1}H NMR, $CDCl_3$, 600 MHz



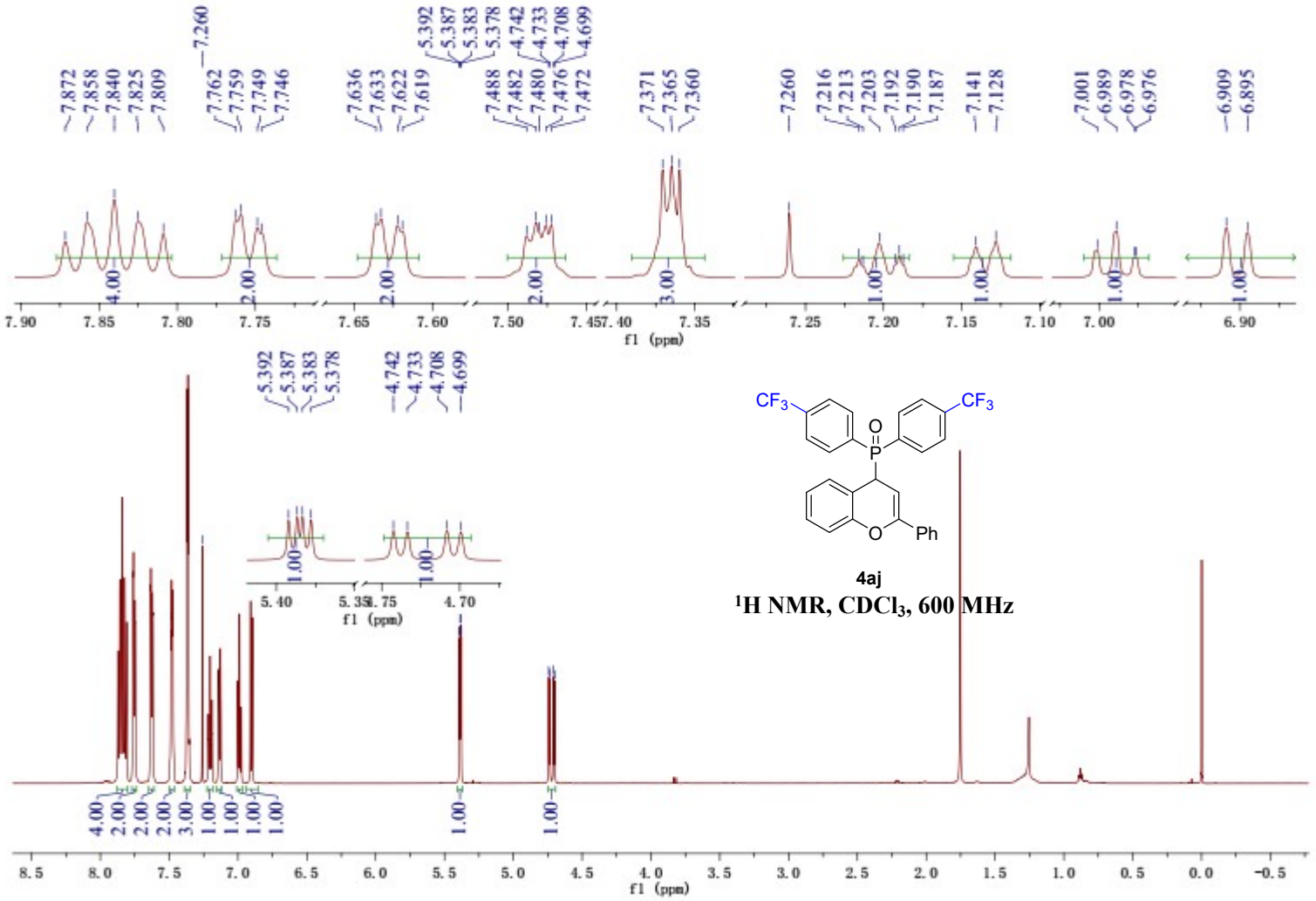
4ai

^{13}C NMR, $CDCl_3$, 150 MHz



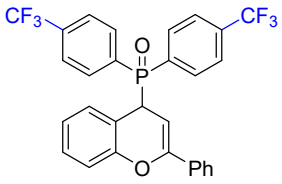
4ai

^{31}P NMR, $CDCl_3$, 243 MHz



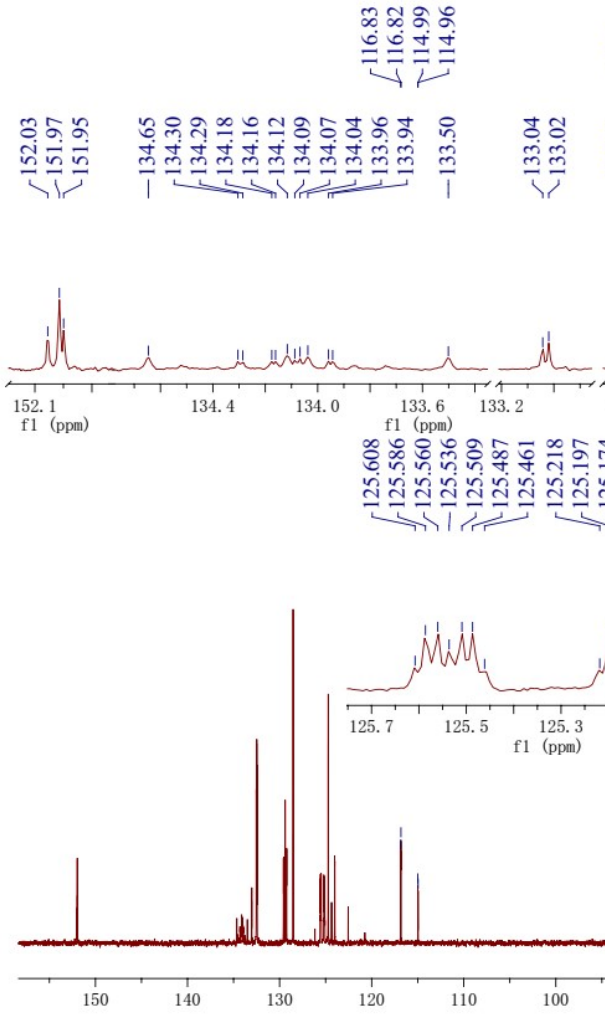
4aj

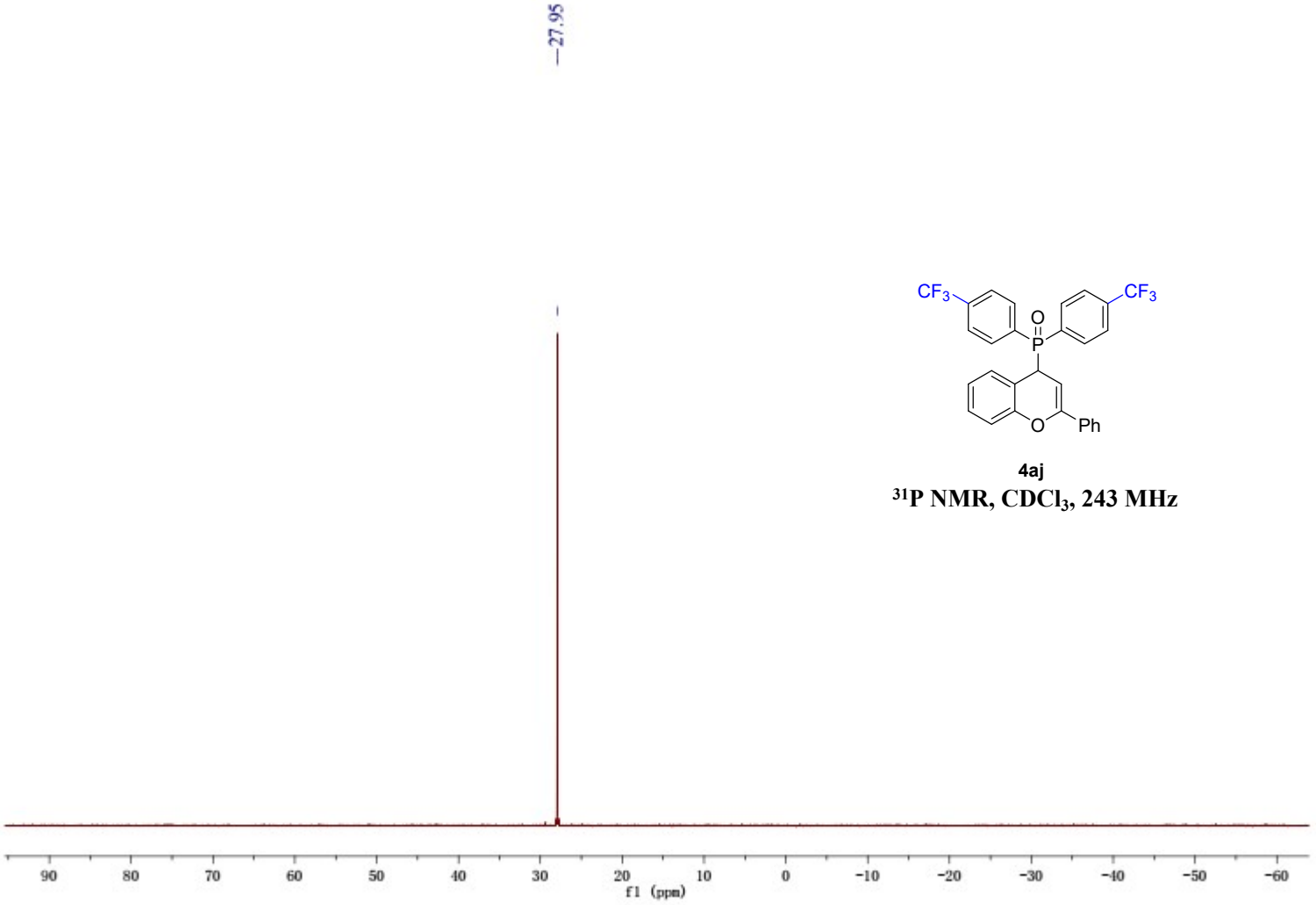
^{1}H NMR, $CDCl_3$, 600 MHz



4aj

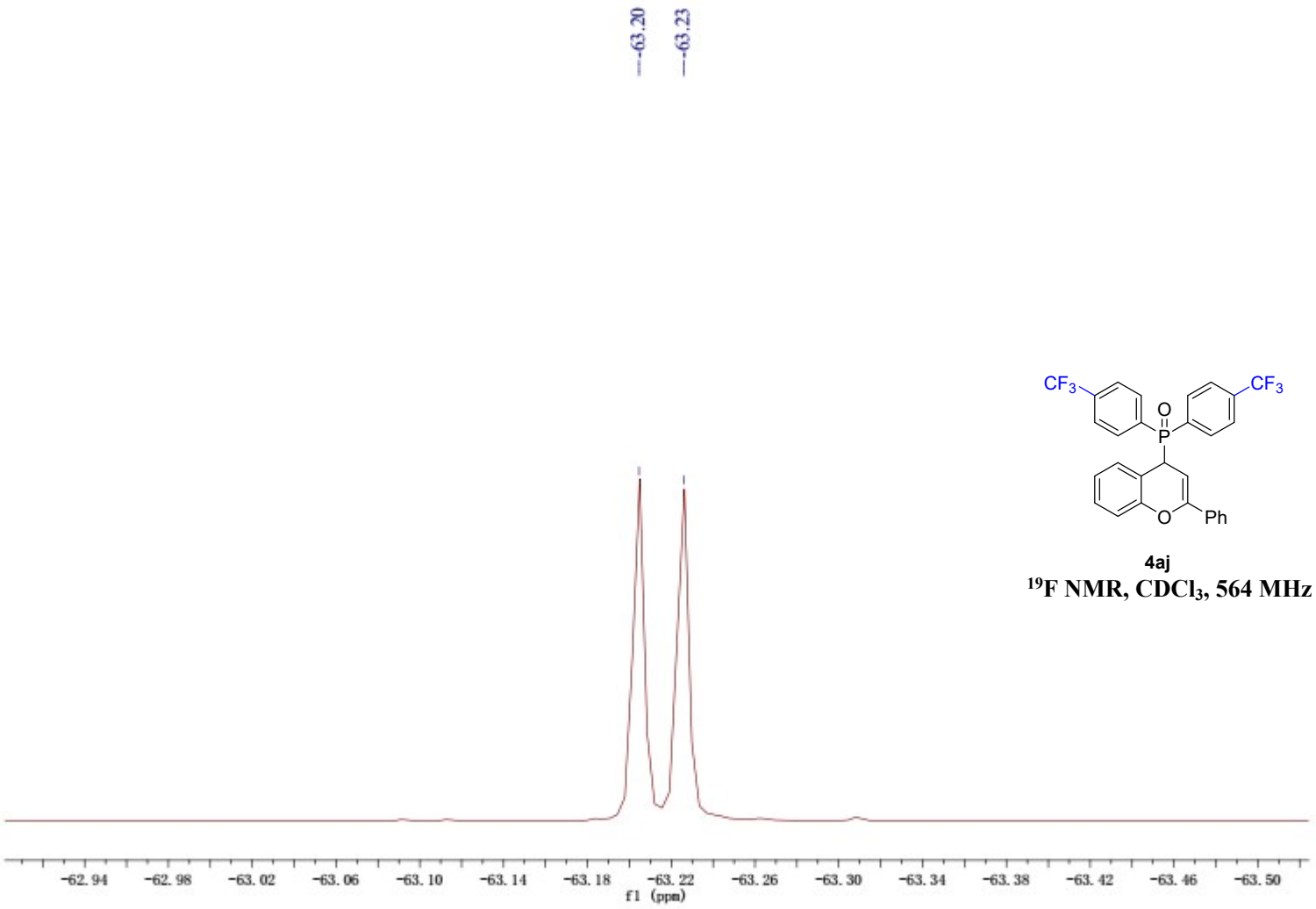
^{13}C NMR, $CDCl_3$, 150 MHz





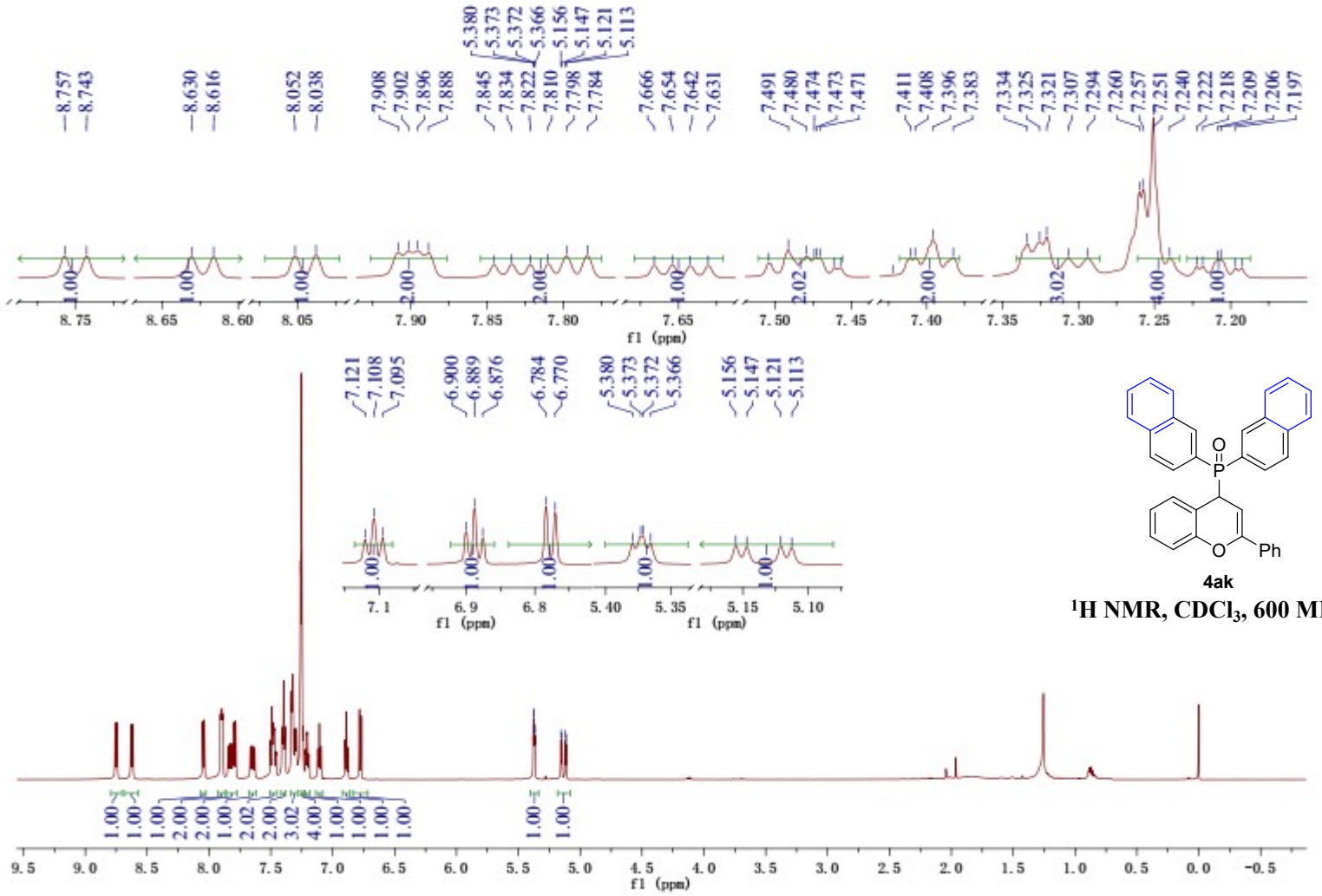
4aj

^{31}P NMR, $CDCl_3$, 243 MHz



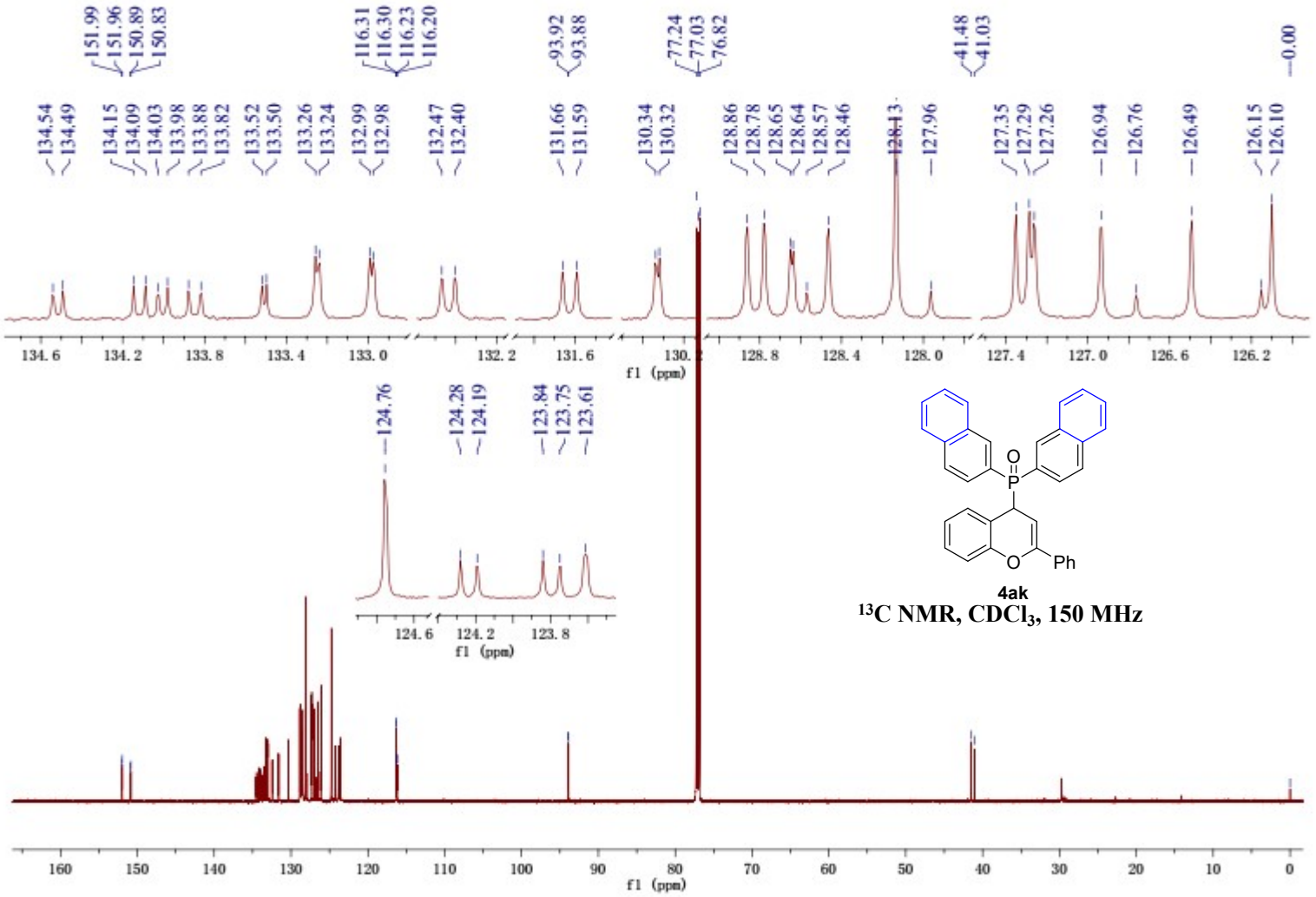
4aj

^{19}F NMR, $CDCl_3$, 564 MHz



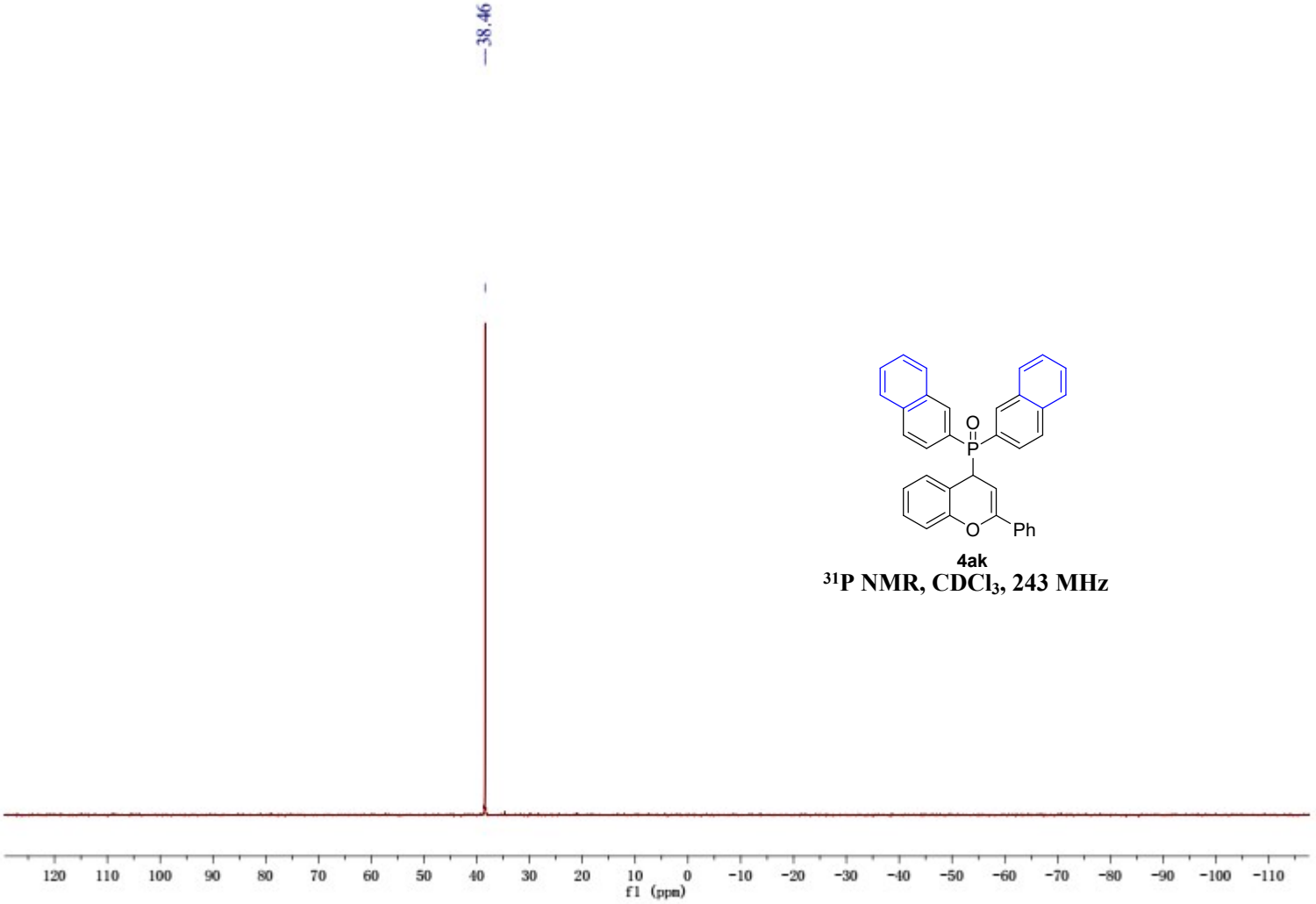
4ak

^{1}H NMR, $CDCl_3$, 600 MHz



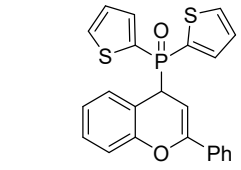
4ak

^{13}C NMR, $CDCl_3$, 150 MHz



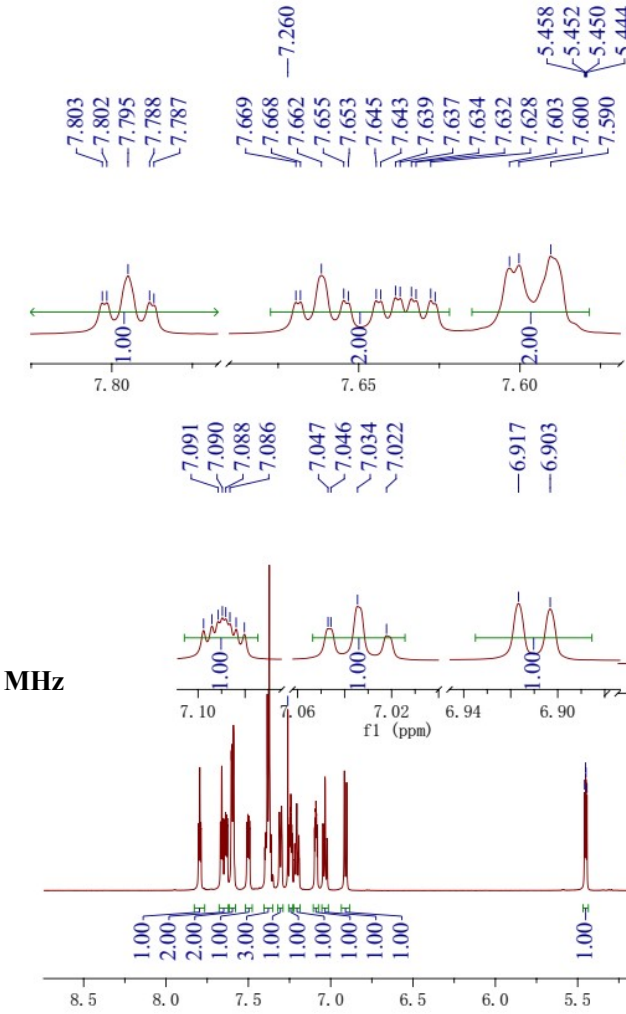
4ak

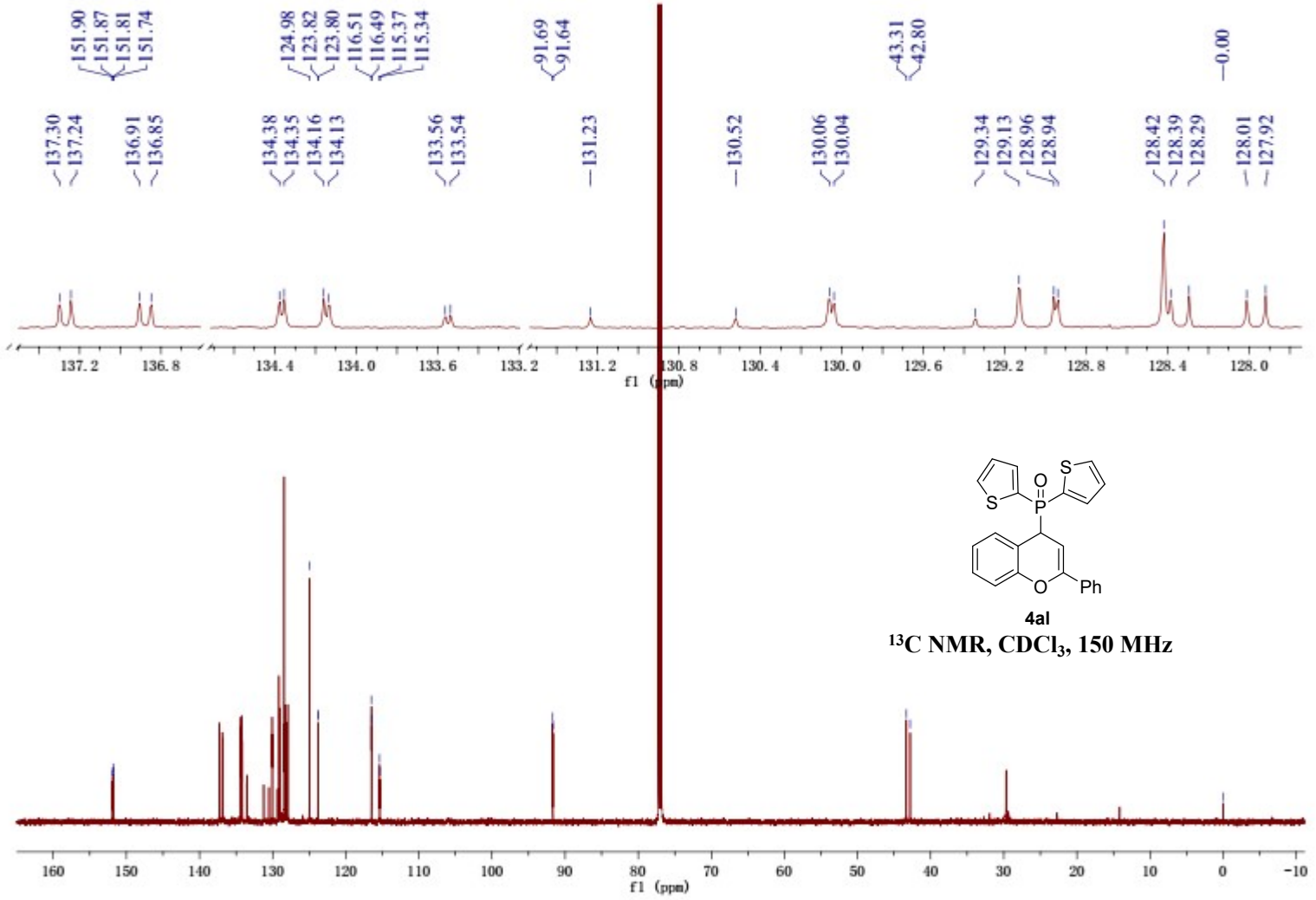
^{31}P NMR, $CDCl_3$, 243 MHz



4al

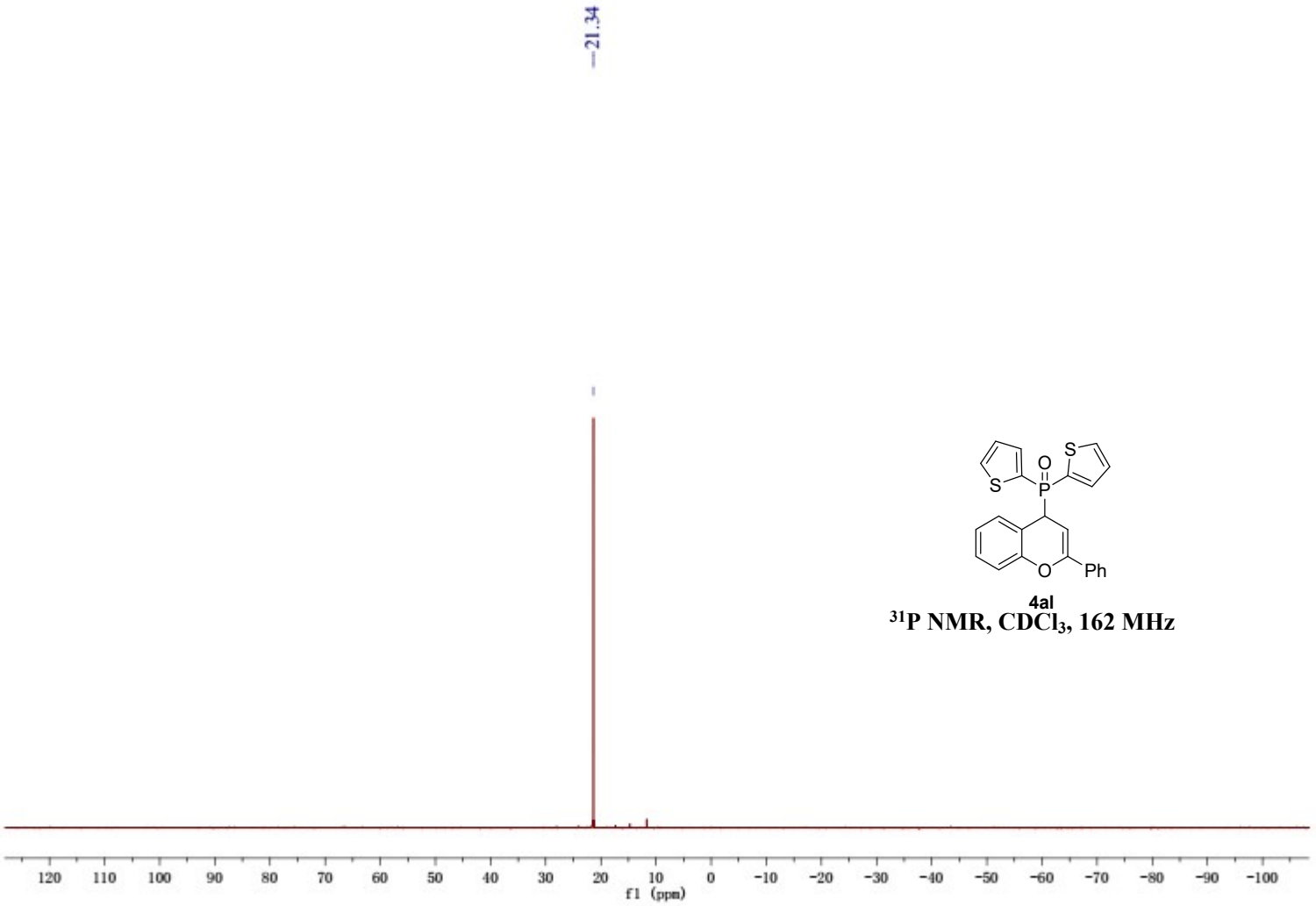
^{1}H NMR, $CDCl_3$, 400 MHz





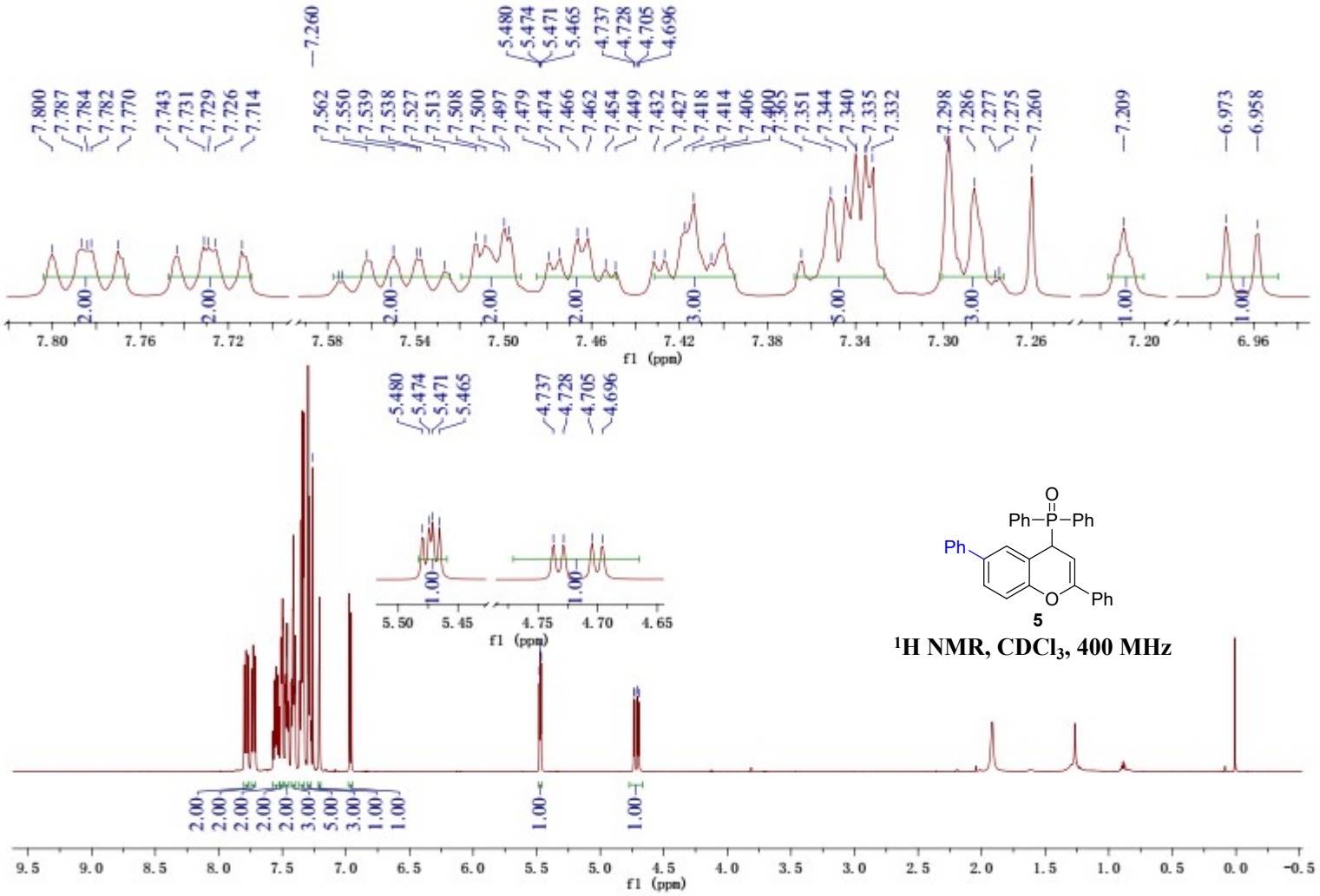
4al

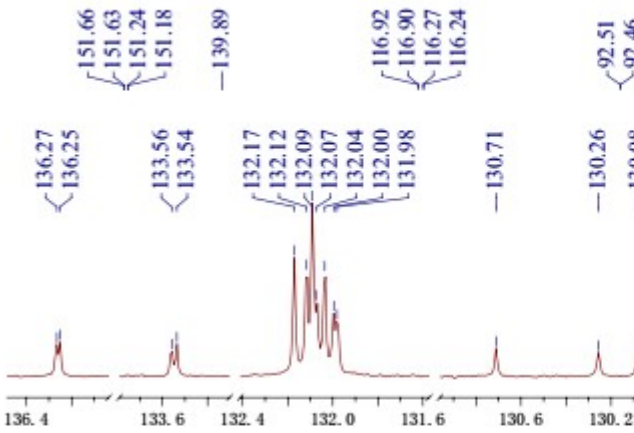
^{13}C NMR, $CDCl_3$, 150 MHz

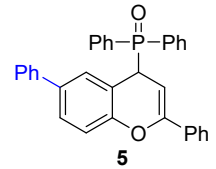


4al

^{31}P NMR, $CDCl_3$, 162 MHz

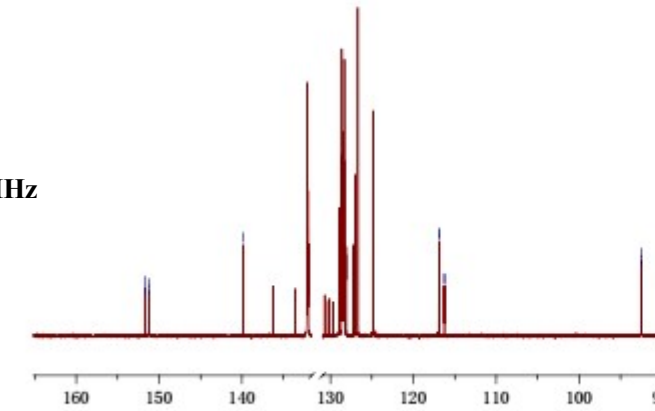

7.260
5.480
5.474
5.471
5.465
4.737
4.728
4.705
4.696
7.800
7.787
7.784
7.782
7.770
7.743
7.731
7.729
7.726
7.714
7.562
7.550
7.539
7.538
7.527
7.513
7.508
7.500
7.497
7.479
7.474
7.466
7.462
7.454
7.449
7.432
7.427
7.418
7.414
7.406
7.400
7.365
7.351
7.344
7.340
7.335
7.332
7.298
7.286
7.277
7.275
7.260
7.209
6.973
6.958
f1 (ppm)
Ph
Ph
Ph
O
O
5
1H NMR, CDCl3, 400 MHz

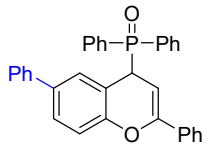




5

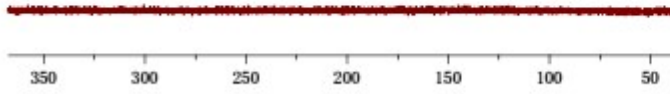
^{13}C NMR, $CDCl_3$, 150 MHz

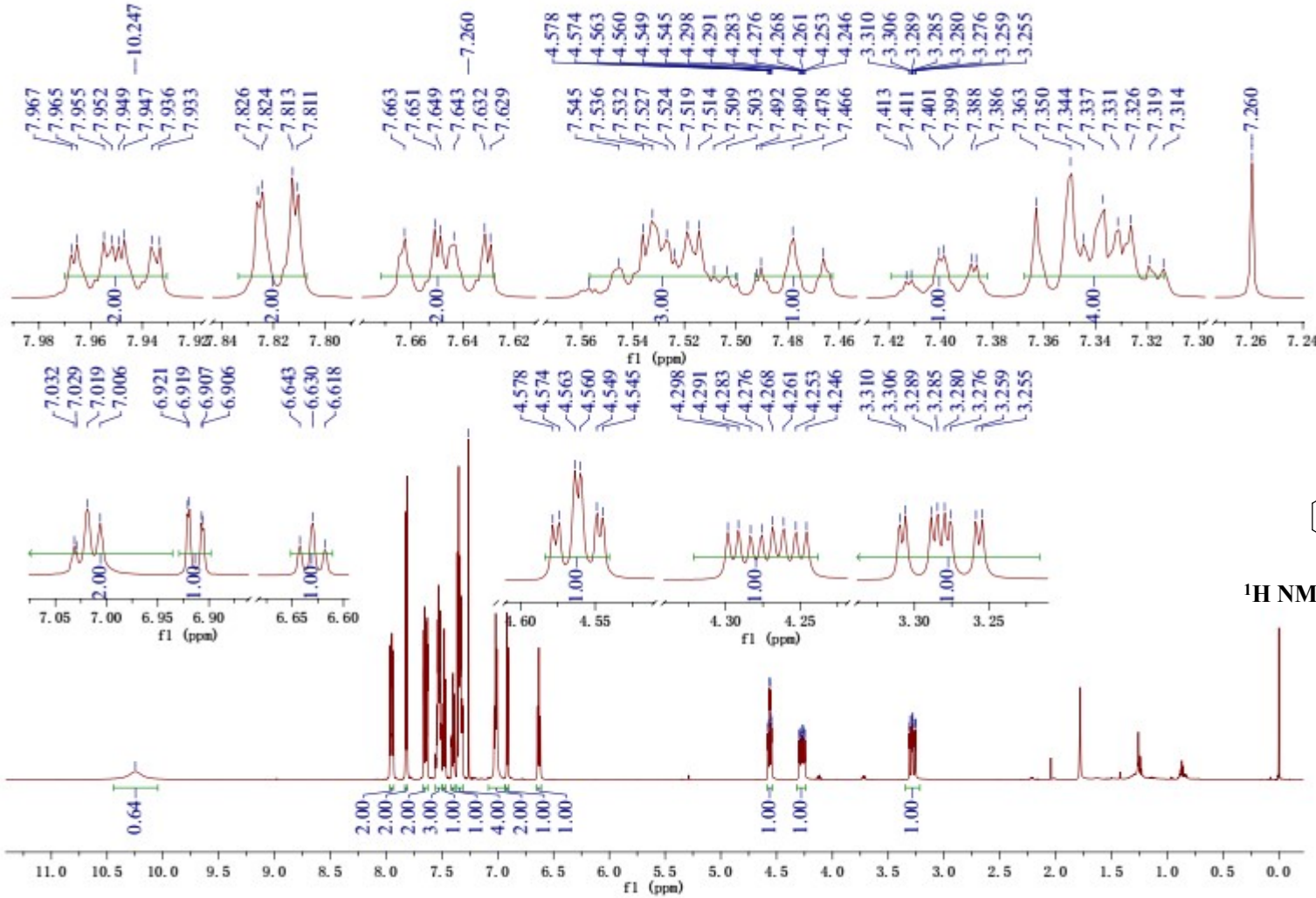


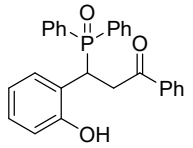


5

^{31}P NMR, $CDCl_3$, 243 MHz

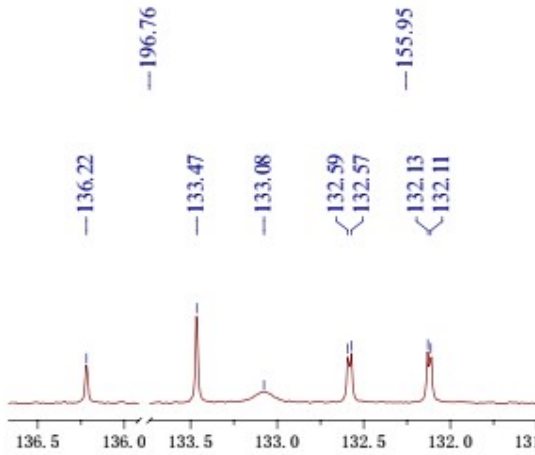


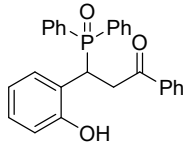




3aa

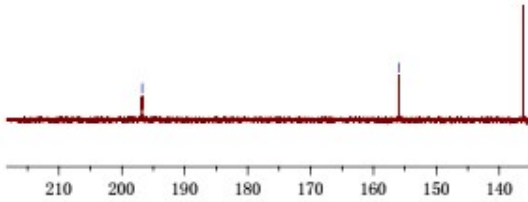
^{1}H NMR, $CDCl_3$, 600 MHz

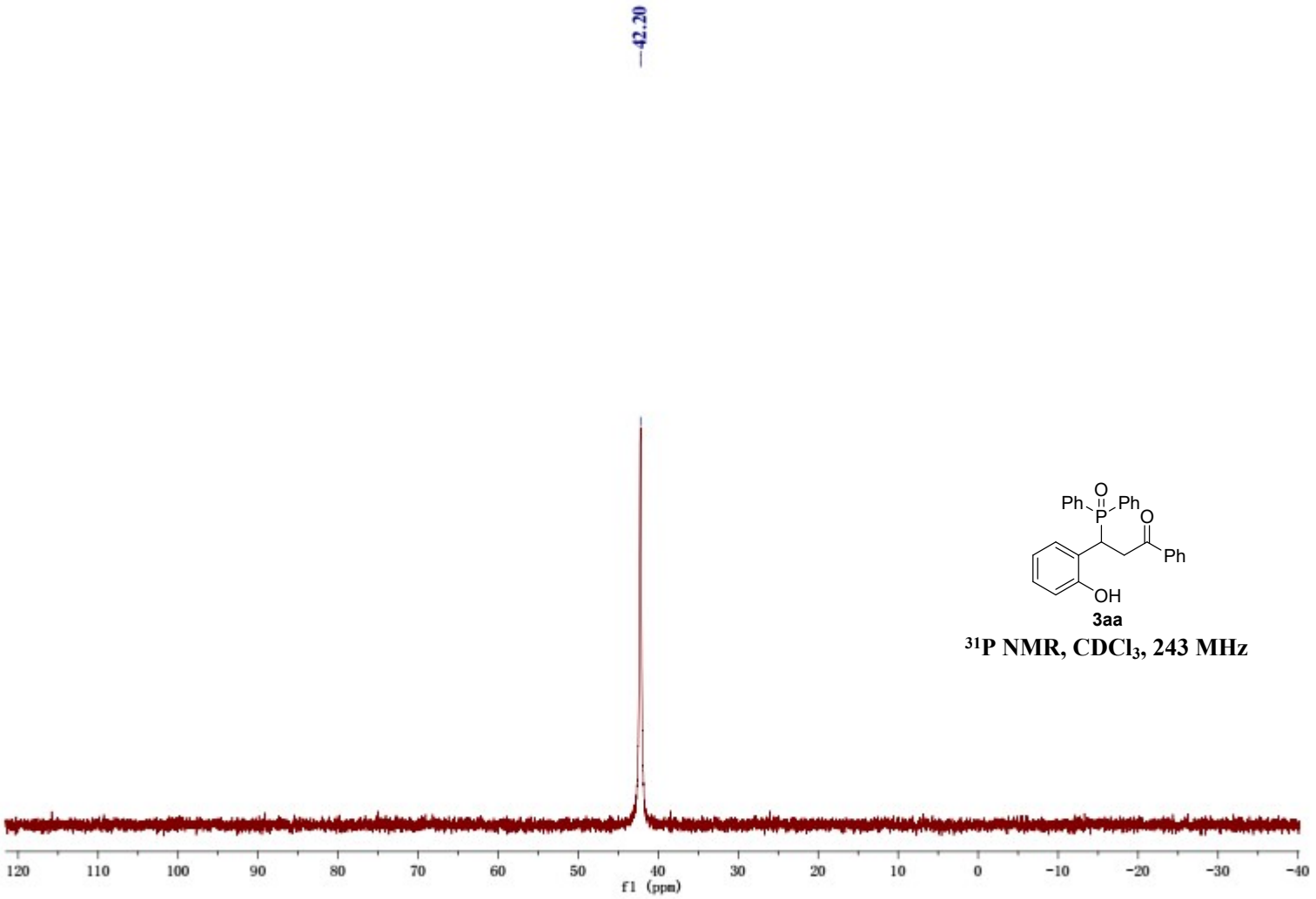




3aa

^{13}C NMR, $CDCl_3$, 150 MHz





3aa

^{31}P NMR, $CDCl_3$, 243 MHz