

Dearomative 1,6-addition of P(O)-H to *in situ* Formed *p*-QMs-like Ion Pair from 2-Benzofuryl-ols to C3-Phosphinoyl Hydrobenzofurans

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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. Chemical yields refer to pure isolated substances. ^1H and ^{13}C NMR spectra were obtained using a Bruker DPX-400 or JEOL-600 spectrometer. The ^{31}P NMR spectra were recorded at JEOL 243 MHz with 85% H_3PO_4 as external standard. The ^{19}F NMR spectra were recorded at JEOL 565 MHz. 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.

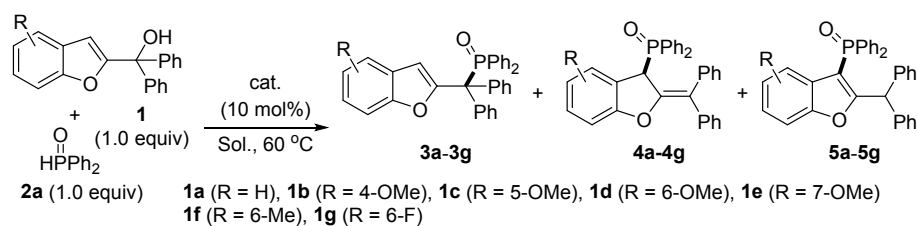
All reactions were run under an atmosphere of air. Anhydrous THF and toluene were prepared by distillation over sodium-benzophenone ketyl prior to use. Anhydrous halogenated solvents and CH_3CN were prepared by first distillation over P_2O_5 and then from CaH_2 . Anhydrous ethyl acetate was prepared 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. Anhydrous $\text{ClCH}_2\text{CH}_2\text{Cl}$ was prepared by dried in anhydrous Na_2SO_4 . 2-Benzofuryl-ols^{1a-c}, 2-benzothioenyl-ols^{1e}, 2-indolylmethols^{1f} and disubstituted phosphine oxides **2**² were prepared according to the literature report. $\text{Bi}(\text{OTf})_3$ (99.998%) was purchased from Alfa-Aesar and used as received.

¹ (a) Y. Zhou, X.-P. Xu, S.-J. Ji, *Org. Lett.*, 2019, **21**, 2039; (b) W. Chen, Z.-H. Zhou, H.-B. Chen, *Org. Biomol. Chem.*, 2017, **15**, 1530; (c) G. Kumaraswamy, G. Ramakrishna, R. Raju, M. Padmaja, *Tetrahedron*, 2010, **66**, 9814; (d) S. Dhiman, S. V. V. Ramasastry, *Org. Biomol. Chem.*, 2013, **11**, 4299; (e) A. B. Biró, A. Kotschy, *Eur. J. Org. Chem.*, 2007, 1364; (f) Y.-Y. He, X.-X. Sun, G.-H. Li, G.-J. Mei, F. Shi, *J. Org. Chem.*, 2017, **82**, 2462

²S. Molitor, J. Becker, V. H. Gessner, *J. Am. Chem. Soc.*, 2014, **136**, 15517.

2. Condition optimization

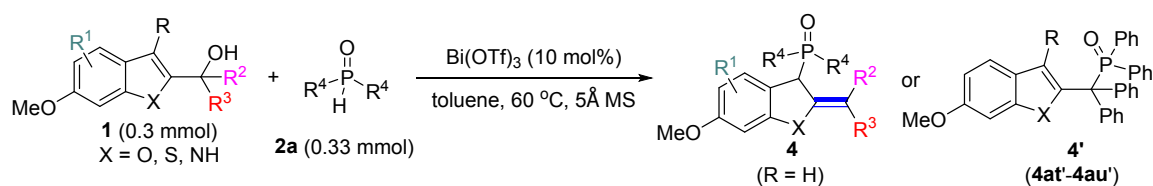
Table S1. Reaction condition optimization



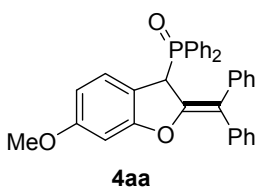
Entry ^a	1	Cat.	Solvent	Time/h	Yield[%] ^b			rr ^c	Entry ^a	1	Cat.	Solvent	Time/h	Yield[%] ^b		rr ^c
					3	4	3							4		
1	1a	TsOH:H ₂ O	DCE	24	23	49	1:2.1	20 ^d	1a	Bi(OTf) ₃	TFE	3	43	-	1:1.2 ^e	
2	1a	Tf ₂ NH	DCE	1.0	34	47	1:1.4	21	1a	Bi(OTf) ₃	Et ₂ O	9	21	60	1:2.9	
3	1a	Co(ClO ₄) ₂ ·6H ₂ O	DCE	8.0	31	55	1:1.8	22	1a	Bi(OTf) ₃	toluene	8	15	61	1:4.1	
4	1a	Zn(ClO ₄) ₂ ·6H ₂ O	DCE	8.0	26	45	1:1.7	23	1a	Bi(OTf) ₃	PhF	5.0	16	52	1:3.8	
5	1a	Ga(ClO ₄) ₃ ·6H ₂ O	DCE	7.0	31	30	1:1	24	1a	Bi(OTf) ₃	C ₆ F ₆	24	<10	<10	-	
6	1a	Mg(ClO ₄) ₂ ·6H ₂ O	DCE	8.0	29	53	1:1.8	25	1a	Bi(OTf) ₃	PhCF ₃	5.5	20	60	1:3.0	
7	1a	Mn(ClO ₄) ₂ ·6H ₂ O	DCE	8.0	29	47	1:1.6	26 ^f	1a	Bi(OTf) ₃	toluene	0.5	12	45	1:3.8	
8	1a	Fe(ClO ₄) ₃ ·xH ₂ O	DCE	1.5	31	48	1:1.5	27 ^g	1a	Bi(OTf) ₃	toluene	2.5	14	60	1:4.4	
9	1a	Ga(OTf) ₃	DCE	8	26	47	1:1.8	28 ^h	1a	Bi(OTf) ₃	toluene	2.5	14	63	1:4.4	
10	1a	Bi(OTf) ₃	DCE	8	26	57	1:2.2	29 ⁱ	1a	Bi(OTf) ₃	toluene	2.5	15	61	1:4.4	
11	1a	Ba(OTf) ₂	DCE	0.25	28	35	1:1.2	30 ^{g,h}	1b	Bi(OTf) ₃	toluene	0.25	12	79	1:6.6	
12	1a	Fe(OTf) ₃	DCE	3.5	26	50	1:1.9	31 ^{g,h}	1c	Bi(OTf) ₃	toluene	0.5	10	53	1:5.3	
13	1a	In(OTf) ₃	DCE	5.0	26	52	1:2.0	32 ^{g,h}	1d	Bi(OTf) ₃	toluene	0.25	<5	83	<20:1	
14	1a	BiBr ₃	DCE	8	31	43	1:1.4	33 ^{g,h}	1e	Bi(OTf) ₃	toluene	1.0	17	68	1:4.0	
15	1a	BF ₃ ·Et ₂ O	DCE	3.5	29	49	1:1.7	34 ^{g,h}	1f	Bi(OTf) ₃	toluene	3.5	15	64	1:4.3	
16	1a	Bi(OTf) ₃	EtOAc	3.5	19	60	1:3.2	35 ^{g,h}	1g	Bi(OTf) ₃	toluene	3.0	20	68	1:3.4	
17	1a	Bi(OTf) ₃	EtOH	12	30	35	1:1.2	36 ^{g,h}	1d	Bi(OTf) ₃	TFE	4.0	11	- ^j	1:6.3 ^e	
18	1a	Bi(OTf) ₃	CH ₃ CN	4	42	43	1:1	37 ^{g,h}	1d	Bi(OTf) ₃	toluene ^l	1.0	-	78 ^m	0:1 ^e	
19	1a	Bi(OTf) ₃	CH ₃ NO ₂	1.0	41	42	1:1									

^a **1** (0.1 mmol), **2a** (0.1 mmol); ^b NMR yield using trimethoxybenzene as internal standard; ^c rr (**3:4**) is the regioisomeric ratio and is determined by ¹H NMR analysis of crude products; ^d 54% yield of **5a** detected, TFE = CF₃CH₂OH; ^e rr of **3a:5a**; ^f 80 °C; ^g 5 Å MS was added; ^h **2a** (1.1 equivs); ⁱ **2a** (1.5 equivs); ^j 69% yield of **5a** detected; ^k 0.3 mmol scale; ^l TFE was added in place of toluene after the first step finished; ^m Isolated yield of **5d**.

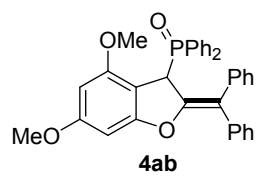
3. General procedure for dearomative C3-phosphorylation of 2-benzofuran-ols and analogues



The reaction was carried out under an air atmosphere. To a 10-mL vial were added alcohols **1** (0.3 mmol, 1.0 equiv), $\text{R}^4_2\text{P}(\text{O})\text{H}$ **2** (0.33 mmol, 1.1 equivs), $\text{Bi}(\text{OTf})_3$ (19.7 mg, 10 mol%) and 300 mg 5Å MS. After adding 3.0 mL of anhydrous toluene, the reaction mixture was stirred at 60 °C till almost full conversion of **1** by TLC analysis. The reaction mixture was directly subjected to column chromatography using petrol ether/ethyl acetate (generally 4:1 to 1:1, v:v) as the eluent to afford products **4** or **4'**.

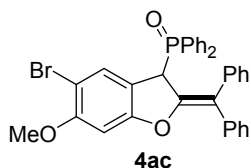


Column chromatography afforded the desired product **4aa** in 81% yield (125.0 mg) as white solid, Mp: 90-92 °C; ^1H NMR (600 MHz, CDCl_3): δ = 7.63-7.60 (m, 2H), 7.46-7.43 (m, 4H), 7.33-7.28 (m, 4H), 7.27-7.25 (m, 2H), 7.21-7.15 (m, 4H), 7.12-7.10 (m, 2H), 6.91-6.90 (m, 2H), 6.66-6.65 (m, 1H), 6.34-6.33 (m, 2H), 5.54 (d, J = 15.0 Hz, 1H), 3.70 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ = 160.9 (d, $J_{\text{C-P}}$ = 3.0 Hz), 159.7 (d, $J_{\text{C-P}}$ = 4.5 Hz), 149.4 (d, $J_{\text{C-P}}$ = 10.5 Hz), 139.7 (d, $J_{\text{C-P}}$ = 3.0 Hz), 139.2 (d, $J_{\text{C-P}}$ = 4.5 Hz), 131.72 (d, $J_{\text{C-P}}$ = 3.0 Hz), 131.66 (d, $J_{\text{C-P}}$ = 3.0 Hz), 131.6 (d, $J_{\text{C-P}}$ = 6.0 Hz), 131.5 (d, $J_{\text{C-P}}$ = 7.5 Hz), 130.4 (d, $J_{\text{C-P}}$ = 96.0 Hz), 130.3 (d, $J_{\text{C-P}}$ = 1.5 Hz), 129.74 (d, $J_{\text{C-P}}$ = 3.0 Hz), 129.71 (d, $J_{\text{C-P}}$ = 96.0 Hz), 128.6, 128.3 (d, $J_{\text{C-P}}$ = 12.0 Hz), 128.2 (d, $J_{\text{C-P}}$ = 12.0 Hz), 127.6, 126.7 (d, $J_{\text{C-P}}$ = 3.0 Hz), 125.8 (d, $J_{\text{C-P}}$ = 3.0 Hz), 120.8 (d, $J_{\text{C-P}}$ = 12.0 Hz), 113.6 (d, $J_{\text{C-P}}$ = 6.0 Hz), 107.8 (d, $J_{\text{C-P}}$ = 3.0 Hz), 96.2, 55.4, 47.3 (d, $J_{\text{C-P}}$ = 60.0 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): δ = 29.5; HRMS (ESI): Exact mass calcd for $\text{C}_{34}\text{H}_{27}\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 515.1771, Found: 515.1764.



Column chromatography afforded **4ab** in 80% yield (130.6 mg) as white solid; Mp: 180-182 °C; ^1H NMR (600 MHz, CDCl_3): δ = 7.54-7.51 (m, 2H), 7.42-7.36 (m, 4H), 7.31-7.28 (m, 2H), 7.28-7.26 (m, 3H), 7.25-7.23 (m, 3H), 7.20-7.17 (m, 1H), 7.13-7.08 (m, 3H), 6.88-6.86 (m, 2H), 6.22 (d, J = 1.8 Hz, 1H), 5.82 (d, J = 1.8 Hz, 1H), 5.44 (d, J = 10.8 Hz, 1H), 3.74 (s, 3H), 3.16 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ = 162.3, 160.3 (d, $J_{\text{C-P}}$ = 4.5 Hz), 155.9, 150.4 (d, $J_{\text{C-P}}$ = 10.5 Hz), 139.5 (d, $J_{\text{C-P}}$ = 3.0 Hz), 138.9 (d, $J_{\text{C-P}}$ =

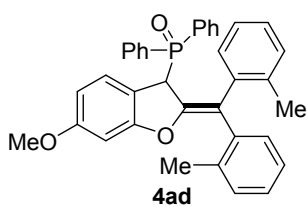
3.0 Hz), 132.3, 131.7 (d, $J_{C-P} = 16.5$ Hz), 131.5 (d, $J_{C-P} = 9.0$ Hz), 131.4 (d, $J_{C-P} = 9.0$ Hz), 131.2 (d, $J_{C-P} = 7.5$ Hz), 130.5, 129.7, 128.4, 127.9 (d, $J_{C-P} = 10.5$ Hz), 127.62, 127.55 (d, $J_{C-P} = 12.0$ Hz), 126.7 (d, $J_{C-P} = 30.0$ Hz), 120.8 (d, $J_{C-P} = 12.0$ Hz), 102.3 (d, $J_{C-P} = 7.5$ Hz), 92.4, 88.7, 55.6, 54.6, 47.4 (d, $J_{C-P} = 57.0$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 29.6$; HRMS (ESI): Exact mass calcd for $\text{C}_{35}\text{H}_{29}\text{O}_4\text{P}$ $[\text{M}+\text{H}]^+$: 545.1876, Found: 545.1869.



Column chromatography afforded the desired product **4ac** in 86% yield (153.0 mg)

as white solid; Mp: 184-186 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.62$ -7.59 (m, 2H), 7.50-7.46 (m, 2H), 7.45-7.43 (m, 2H), 7.35-7.33 (m, 2H), 7.32-7.29 (m, 2H), 7.27-7.26 (m, 1H), 7.26-7.25 (m, 1H), 7.21-7.19 (m, 3H), 7.17-7.15 (m, 1H), 7.11-

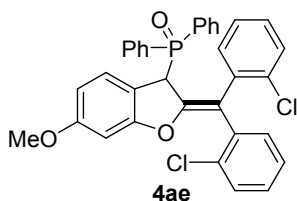
7.08 (m, 2H), 6.87-6.85 (m, 2H), 6.71 (d, $J = 2.4$ Hz, 1H), 6.42 (s, 1H), 5.51 (d, $J = 13.2$ Hz, 1H), 3.78 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 159.1$, 156.7, 149.1 (d, $J_{C-P} = 10.5$ Hz), 139.2 (d, $J_{C-P} = 64.5$ Hz), 131.9 (d, $J_{C-P} = 15.0$ Hz), 131.4 (d, $J_{C-P} = 9.0$ Hz), 130.19 (d, $J_{C-P} = 96.0$ Hz), 130.18, 129.8, 129.5 (d, $J_{C-P} = 109.5$ Hz), 129.3 (d, $J_{C-P} = 1.5$ Hz), 128.7, 128.4 (d, $J_{C-P} = 12.0$ Hz), 128.3 (d, $J_{C-P} = 12.0$ Hz), 127.7, 126.9 (d, $J_{C-P} = 10.5$ Hz), 121.4 (d, $J_{C-P} = 12.0$ Hz), 114.8 (d, $J_{C-P} = 7.5$ Hz), 103.1, 95.1, 56.4, 47.5 (d, $J_{C-P} = 58.5$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 29.0$; HRMS (ESI): Exact mass calcd for $\text{C}_{34}\text{H}_{26}\text{BrO}_3\text{P}$ $[\text{M}+\text{H}]^+$: 593.0876, Found: 593.0883.



Column chromatography afforded the **4ad** in 90% yield (146.5 mg) as white

solid; Mp: 175-177 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.53$ -7.50 (m, 2H), 7.47-7.38 (m, 5H), 7.34-7.31 (m, 2H), 7.26-7.23 (m, 3H), 7.16-7.08 (m, 4H), 6.98-6.83 (m, 3H), 6.39 (s, 1H), 6.19 (d, $J = 7.2$ Hz, 1H), 5.73 (d, $J = 312.0$

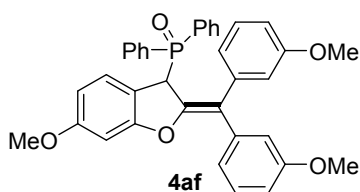
Hz, 1H), 3.68 (s, 3H), 2.31 (brs, 3H), 1.56 (brs, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 160.9$, 160.1, 131.82, 131.75, 131.3, 130.9 (d, $J_{C-P} = 9.0$ Hz), 130.3, 130.1, 128.3 (d, $J_{C-P} = 12.0$ Hz), 128.2 (d, $J_{C-P} = 12.0$ Hz), 127.5, 126.7, 125.5 (d, $J_{C-P} = 40.5$ Hz), 124.8, 113.4 (d, $J_{C-P} = 6.0$ Hz), 107.6, 96.1, 55.4, 46.4 (d, $J_{C-P} = 64.5$ Hz), 20.5, 20.0; $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 28.1$; HRMS (ESI): Exact mass calcd for $\text{C}_{36}\text{H}_{31}\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 543.2084, Found: 543.2078.



Column chromatography afforded the desired product **4ae** in 88% yield

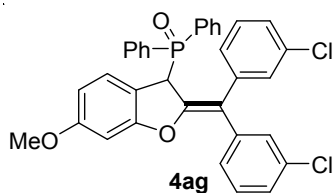
(154.0 mg) as white solid; Mp: 102-104 °C; ^1H NMR (600 MHz, CDCl_3): $\delta =$

7.67-7.64 (m, 2H), 7.50-7.48 (m, 1H), 7.47-7.42 (m, 4H), 7.35-7.32 (m, 7H), 7.16-7.13 (m, 4H), 6.33 (brs, 2H), 6.29-6.27(m, 1H), 5.44 (d, $J = 17.4$ Hz, 1H), 3.68 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 161.1, 159.6$ (d, $J_{\text{C-P}} = 4.5$ Hz), 133.4, 132.2 (d, $J_{\text{C-P}} = 7.5$ Hz), 132.0 (d, $J_{\text{C-P}} = 10.5$ Hz), 131.5 (d, $J_{\text{C-P}} = 9.0$ Hz), 129.8, 128.6, 128.5, 128.4 (d, $J_{\text{C-P}} = 3.0$ Hz), 128.3, 126.9, 126.3, 125.8, 114.0, 108.0, 96.3, 55.6, 48.6 (d, $J_{\text{C-P}} = 60.0$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 29.4$; HRMS (ESI): Exact mass calcd for $\text{C}_{34}\text{H}_{25}\text{Cl}_2\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 583.0991, Found: 583.0989.



Column chromatography afforded the desired product **4af** in 86% yield (148.2 mg) as white solid; Mp: 172-174 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.66$ -7.63 (m, 2H), 7.46-7.42 (m, 4H), 7.34-7.31 (m, 2H), 7.30-7.27 (m, 2H), 7.18-7.16 (m, 1H), 7.11-7.08 (m, 1H), 6.78-6.74 (m, 3H), 6.72-

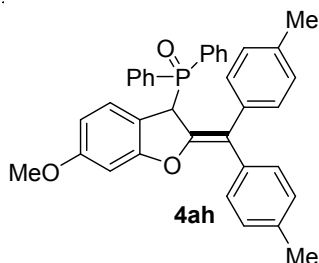
6.68 (m, 3H), 6.35-6.32 (m, 2H), 6.24 (s, 1H), 5.60 (d, $J = 15.6$ Hz, 1H), 3.74 (s, 3H), 3.69 (s, 3H), 3.64 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 160.9, 159.6$ (d, $J_{\text{C-P}} = 4.5$ Hz), 159.2 (d, $J_{\text{C-P}} = 96.0$ Hz), 149.7 (d, $J_{\text{C-P}} = 10.5$ Hz), 140.9, 140.4 (d, $J_{\text{C-P}} = 4.5$ Hz), 131.7 (d, $J_{\text{C-P}} = 13.5$ Hz), 131.6, 131.4 (d, $J_{\text{C-P}} = 9.0$ Hz), 130.6 (d, $J_{\text{C-P}} = 96.0$ Hz), 129.4, 129.3 (d, $J_{\text{C-P}} = 96.0$ Hz), 128.5, 128.2 (d, $J_{\text{C-P}} = 12.0$ Hz), 128.0 (d, $J_{\text{C-P}} = 10.5$ Hz), 126.0 (d, $J_{\text{C-P}} = 1.5$ Hz), 122.4 (d, $J_{\text{C-P}} = 6.0$ Hz), 120.4 (d, $J_{\text{C-P}} = 10.5$ Hz), 115.8 (d, $J_{\text{C-P}} = 54.0$ Hz), 113.5 (d, $J_{\text{C-P}} = 7.5$ Hz), 112.5 (d, $J_{\text{C-P}} = 90.0$ Hz), 107.8, 96.1, 55.4, 55.2, 54.9, 47.3 (d, $J_{\text{C-P}} = 58.5$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 29.6$; HRMS (ESI): Exact mass calcd for $\text{C}_{36}\text{H}_{31}\text{O}_5\text{P}$ $[\text{M}+\text{H}]^+$: 575.1982, Found: 575.1981.



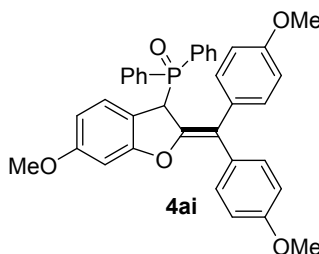
Column chromatography afforded the desired product **4ag** in 87% yield (152.3 mg) as white solid; Mp: 78-80 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.63$ -7.60 (m, 2H), 7.52-7.46 (m, 4H), 7.36-7.32 (m, 4H), 7.21-7.12 (m, 5H), 7.02-6.98 (m, 2H), 6.69 (s, 1H), 6.58 (dd, $J = 6.0$ Hz, 2.4 Hz, 1H), 6.38-

6.37 (m, 1H), 6.34 (dd, $J = 6.0$ Hz, 2.4 Hz, 1H), 5.50 (d, $J = 15.0$ Hz, 1H), 3.71 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 161.0, 159.4$ (d, $J_{\text{C-P}} = 4.5$ Hz), 151.2 (d, $J_{\text{C-P}} = 9.0$ Hz), 141.1 (d, $J_{\text{C-P}} = 3.0$ Hz), 140.4 (d, $J_{\text{C-P}} = 3.0$ Hz), 134.1 (d, $J_{\text{C-P}} = 126.0$ Hz), 132.1, 131.5 (d, $J_{\text{C-P}} = 9.0$ Hz), 131.4 (d, $J_{\text{C-P}} = 9.0$ Hz), 130.5, 130.3, 129.85, 129.6, 129.4 (d, $J_{\text{C-P}} = 97.5$ Hz), 129.0, 128.3 (d, $J_{\text{C-P}} = 13.5$ Hz), 128.2, 127.9, 127.3 (d, $J_{\text{C-P}} = 66.0$ Hz), 125.7 (d, $J_{\text{C-P}} = 1.5$ Hz), 118.2 (d, $J_{\text{C-P}} = 10.5$ Hz), 113.2 (d, $J_{\text{C-P}} = 7.5$ Hz),

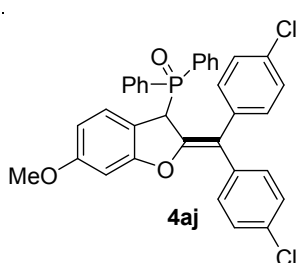
108.2, 96.2, 55.5, 47.6 (d, $J_{C-P} = 58.5$ Hz); $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): $\delta = 29.3$; HRMS (ESI): Exact mass calcd for $C_{34}H_{25}Cl_2O_3P$ $[M+H]^+$: 583.0991, Found: 583.0989.



Column chromatography afforded the desired product **4ah** in 84% yield (136.7 mg) as white solid; Mp: 232-234 °C; 1H NMR (600 MHz, $CDCl_3$): $\delta = 7.65-7.62$ (m, 2H), 7.46-7.42 (m, 4H), 7.33-7.30 (m, 2H), 7.29-7.26 (m, 2H), 7.11-7.06 (m, 4H), 6.88 (AB, $J = 7.8$ Hz, 2H), 6.78 (AB, $J = 7.8$ Hz, 2H), 6.72-6.71 (m, 1H), 6.35-6.33 (m, 2H), 5.54 (d, $J = 15.0$ Hz, 1H), 3.70 (s, 3H), 2.34 (s, 3H), 2.32 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): $\delta = 160.9$, 159.8, 148.7 (d, $J_{C-P} = 10.5$ Hz), 136.6 (d, $J_{C-P} = 37.5$ Hz), 136.2 (d, $J_{C-P} = 52.5$ Hz), 131.6 (d, $J_{C-P} = 7.5$ Hz), 131.4 (d, $J_{C-P} = 9.0$ Hz), 130.7 (d, $J_{C-P} = 96.0$ Hz), 129.8 (d, $J_{C-P} = 73.5$ Hz), 129.6 (d, $J_{C-P} = 96.0$ Hz), 129.4, 128.4, 128.2 (d, $J_{C-P} = 10.5$ Hz), 128.0 (d, $J_{C-P} = 12.0$ Hz), 120.5 (d, $J_{C-P} = 10.5$ Hz), 113.7 (d, $J_{C-P} = 7.5$ Hz), 107.6, 96.1, 55.4, 47.2 (d, $J_{C-P} = 60.0$ Hz), 21.24, 21.18; $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): $\delta = 29.4$; HRMS (ESI): Exact mass calcd for $C_{36}H_{31}O_3P$ $[M+H]^+$: 543.2084, Found: 543.2079.

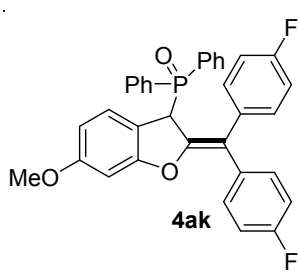


Column chromatography afforded the desired product **4ai** in 83% yield (143.1 mg) as white solid; Mp: 198-200 °C; 1H NMR (600 MHz, $CDCl_3$): $\delta = 7.65-7.62$ (m, 2H), 7.46-7.42 (m, 4H), 7.34-7.27 (m, 4H), 7.15 (AB, $J = 8.4$ Hz, 2H), 6.81-6.79 (m, 4H), 6.71-6.69 (m, 1H), 6.61 (AB, $J = 8.4$ Hz, 2H), 6.34-6.33 (m, 2H), 5.51 (d, $J = 15.0$ Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.70 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): $\delta = 160.9$, 159.8, 158.2 (d, $J_{C-P} = 12.0$ Hz), 148.0 (d, $J_{C-P} = 10.5$ Hz), 132.0 (d, $J_{C-P} = 3.0$ Hz), 131.9 (d, $J_{C-P} = 4.5$ Hz), 131.7 (d, $J_{C-P} = 4.5$ Hz), 131.6, 131.4 (d, $J_{C-P} = 9.0$ Hz), 131.1 (d, $J_{C-P} = 69.0$ Hz), 130.8 (d, $J_{C-P} = 96.0$ Hz), 129.7 (d, $J_{C-P} = 97.5$ Hz), 128.2 (d, $J_{C-P} = 12.0$ Hz), 128.1 (d, $J_{C-P} = 12.0$ Hz), 125.9 (d, $J_{C-P} = 3.0$ Hz), 114.1, 113.7 (d, $J_{C-P} = 7.5$ Hz), 113.0, 107.6, 96.1, 55.4, 55.2, 55.1, 47.2 (d, $J_{C-P} = 60.0$ Hz); $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): $\delta = 29.3$; HRMS (ESI): Exact mass calcd for $C_{36}H_{31}O_5P$ $[M+H]^+$: 575.1982, Found: 575.1981.



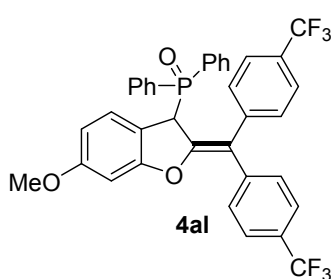
Column chromatography afforded **4aj** in 83% yield (145.3 mg) as white solid; Mp: 228-230 °C; 1H NMR (600 MHz, $CDCl_3$): $\delta = 7.62-7.58$ (m, 2H), 7.51-7.43 (m, 4H), 7.35-7.32 (m, 4H), 7.23-7.21 (m, 2H), 7.12-7.10 (m, 2H), 7.06-

7.04 (m, 2H), 6.85-6.83 (m, 2H), 6.55-6.53 (m, 1H), 6.362-6.359 (m, 1H), 6.33-6.31 (m, 1H), 5.45 (d, $J = 14.4$ Hz, 1H), 3.70 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 161.0, 159.5$ (d, $J_{\text{C-P}} = 4.5$ Hz), 150.3 (d, $J_{\text{C-P}} = 9.0$ Hz), 137.8, 137.2 (d, $J_{\text{C-P}} = 3.0$ Hz), 132.7 (d, $J_{\text{C-P}} = 45.0$ Hz), 131.8, 131.5 (d, $J_{\text{C-P}} = 12.0$ Hz), 131.2 (d, $J_{\text{C-P}} = 52.5$ Hz), 130.2 (d, $J_{\text{C-P}} = 96.0$ Hz), 129.7 (d, $J_{\text{C-P}} = 96.0$ Hz), 129.0, 128.4 (d, $J_{\text{C-P}} = 7.5$ Hz), 128.3 (d, $J_{\text{C-P}} = 7.5$ Hz), 128.0, 125.8 (d, $J_{\text{C-P}} = 3.0$ Hz), 118.4 (d, $J_{\text{C-P}} = 10.5$ Hz), 113.1 (d, $J_{\text{C-P}} = 6.0$ Hz), 108.0, 96.2, 55.5, 47.3 (d, $J_{\text{C-P}} = 58.5$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 29.1$; HRMS (ESI): Exact mass calcd for $\text{C}_{34}\text{H}_{25}\text{Cl}_2\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 583.0991, Found: 583.0991.



Column chromatography afforded the desired product **4ak** in 89% yield (147.0 mg) as white solid; Mp: 210-212 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.62$ -7.59 (m, 2H), 7.50-7.44 (m, 4H), 7.35-7.32 (m, 4H), 7.15-7.13 (m, 2H), 6.96-6.93 (m, 2H), 6.90-6.88 (m, 2H), 6.82-6.79 (m, 2H), 6.55-6.53 (m, 1H), 6.36-6.35 (m, 1H), 6.32-6.31 (m, 1H), 5.44 (d, $J = 14.4$ Hz, 1H), 3.70 (s, 3H);

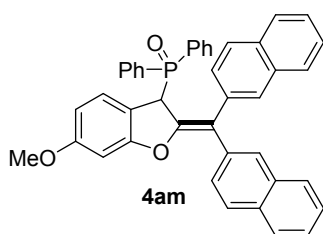
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 162.4$ (d, $J_{\text{C-F}} = 16.5$ Hz), 161.0, 160.7 (d, $J_{\text{C-P}} = 18.0$ Hz), 159.6 (d, $J_{\text{C-P}} = 4.5$ Hz), 149.6 (d, $J_{\text{C-P}} = 10.5$ Hz), 135.2 (d, $J_{\text{C-F}} = 72.0$ Hz), 131.8, 131.6 (d, $J_{\text{C-P}} = 9.0$ Hz), 131.4 (d, $J_{\text{C-P}} = 9.0$ Hz), 131.3 (d, $J_{\text{C-P}} = 6.0$ Hz), 130.2 (d, $J_{\text{C-P}} = 97.5$ Hz), 130.0 (d, $J_{\text{C-P}} = 96.0$ Hz), 128.33 (d, $J_{\text{C-P}} = 3.0$ Hz), 128.26 (d, $J_{\text{C-P}} = 4.5$ Hz), 125.8, 118.7 (d, $J_{\text{C-P}} = 10.5$ Hz), 115.7 (d, $J_{\text{C-P}} = 21.0$ Hz), 114.6 (d, $J_{\text{C-P}} = 21.0$ Hz), 113.3 (d, $J_{\text{C-P}} = 7.5$ Hz), 107.9, 96.2, 55.5, 47.3 (d, $J_{\text{C-P}} = 60.0$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 29.1$; $^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, CDCl_3): $\delta = -114.75, -114.85$; HRMS (ESI): Exact mass calcd for $\text{C}_{34}\text{H}_{25}\text{F}_2\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 551.1582, Found: 551.1580.



Column chromatography afforded product **4al** in 68% yield (132.7 mg) as white solid; Mp: 145-147 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.61$ -7.58 (m, 2H), 7.53-7.44 (m, 6H), 7.37-7.28 (m, 8H), 7.05-7.04 (m, 2H), 6.50 (dd, $J = 8.4$ Hz, 1.8 Hz, 1H), 6.39 (d, $J = 2.4$ Hz, 1H), 6.33 (dd, $J = 8.4$ Hz, 1.8 Hz, 1H), 5.49 (d, $J = 13.8$ Hz, 1H), 3.71 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz,

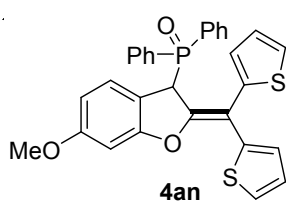
CDCl_3): $\delta = 161.1, 159.4, 152.0$ (d, $J_{\text{C-P}} = 10.5$ Hz), 142.6 (d, $J_{\text{C-F}} = 138.0$ Hz), 132.1 (d, $J_{\text{C-P}} = 9.0$ Hz), 131.5 (d, $J_{\text{C-P}} = 9.0$ Hz), 131.3 (d, $J_{\text{C-P}} = 9.0$ Hz), 130.3 (d, $J_{\text{C-P}} = 76.5$ Hz), 130.0 (d, $J_{\text{C-P}} = 97.5$ Hz), 129.7 (d, $J_{\text{C-P}} = 97.5$ Hz), 128.8 (qd, $J_{\text{C-F}} = 10.5$ Hz, 6.0 Hz), 128.4 (d, $J_{\text{C-P}} = 12.0$ Hz), 125.7 (d, $J_{\text{C-P}} = 7.5$ Hz), 124.8, 124.1 (qd, $J_{\text{C-F}} = 270.0$ Hz, 9.0 Hz), 118.2 (d, $J_{\text{C-P}} = 10.5$ Hz), 112.9 (d, $J_{\text{C-P}} = 7.5$ Hz), 108.3,

96.3, 55.5, 47.5 (d, $J_{C-P} = 57.0$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 28.9$; $^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, CDCl_3): $\delta = -62.41, -62.42$; HRMS (ESI): Exact mass calcd for $\text{C}_{36}\text{H}_{25}\text{F}_6\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 651.1518, Found: 651.1517.



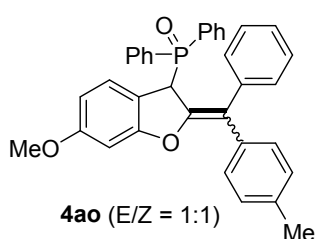
Column chromatography afforded the desired product **4am** in 81% yield (149.4 mg) as white solid; Mp: 213-215 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.81-7.78$ (m, 2H), 7.75-7.71 (m, 3H), 7.63-7.60 (m, 3H), 7.57-7.56 (m, 1H), 7.52-7.46 (m, 2H), 7.46-7.39 (m, 5H), 7.36-7.28 (m, 3H), 7.16-7.13 (m, 2H), 7.11-7.08 (m, 2H), 7.06-7.04 (m, 1H), 6.71-6.69 (m, 1H), 6.39-6.36 (m,

2H), 5.74 (d, $J = 14.4$ Hz, 1H), 3.71 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 161.0, 159.8$ (d, $J_{C-P} = 4.5$ Hz), 150.3 (d, $J_{C-P} = 9.0$ Hz), 136.9 (d, $J_{C-P} = 91.5$ Hz), 133.3 (d, $J_{C-P} = 84.0$ Hz), 132.4 (d, $J_{C-P} = 10.5$ Hz), 131.7 (d, $J_{C-P} = 22.5$ Hz), 131.5 (d, $J_{C-P} = 9.0$ Hz), 131.3 (d, $J_{C-P} = 9.0$ Hz), 130.7 (d, $J_{C-P} = 96.0$ Hz), 129.4 (d, $J_{C-P} = 97.5$ Hz), 129.2 (d, $J_{C-P} = 31.5$ Hz), 128.3 (d, $J_{C-P} = 9.0$ Hz), 128.1 (d, $J_{C-P} = 3.0$ Hz), 128.0, 127.9 (d, $J_{C-P} = 12.0$ Hz), 127.5 (d, $J_{C-P} = 15.0$ Hz), 127.0, 126.0, 125.9, 120.6 (d, $J_{C-P} = 10.5$ Hz), 113.4 (d, $J_{C-P} = 7.5$ Hz), 107.9, 96.1, 55.4, 47.3 (d, $J_{C-P} = 58.5$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 29.2$; HRMS (ESI): Exact mass calcd for $\text{C}_{42}\text{H}_{31}\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 615.2084, Found: 615.2083.

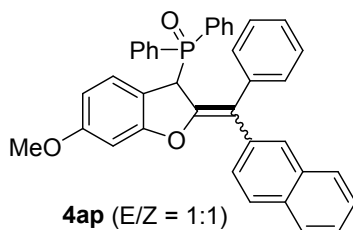


Column chromatography afforded the **4an** in 73% yield (115.3 mg) as white solid; Mp: 168-170 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.64-7.61$ (m, 2H), 7.48-7.43 (m, 4H), 7.36-7.29 (m, 4H), 7.26-7.25 (m, 1H), 7.19-7.18 (m, 1H), 6.97-6.94 (m, 2H), 6.79 (dd, $J = 8.4$ Hz, 2.4 Hz, 1H), 6.76-6.74 (m, 1H), 6.494-

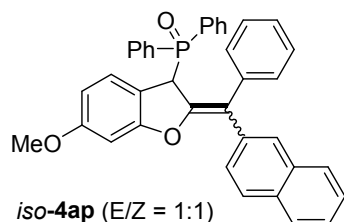
6.489 (m, 1H), 6.430-6.426 (m, 1H), 6.39 (dd, $J = 8.4$ Hz, 2.4 Hz, 1H), 5.59 (d, $J = 16.8$ Hz, 1H), 3.72 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 161.0, 159.1$ (d, $J_{C-P} = 4.5$ Hz), 150.1 (d, $J_{C-P} = 10.5$ Hz), 141.4 (d, $J_{C-P} = 6.0$ Hz), 138.4, 131.7 (d, $J_{C-P} = 27.0$ Hz), 131.6, 131.4 (d, $J_{C-P} = 9.0$ Hz), 130.6 (d, $J_{C-P} = 96.0$ Hz), 129.7, 129.0 (d, $J_{C-P} = 97.5$ Hz), 128.4 (d, $J_{C-P} = 12.0$ Hz), 128.2 (d, $J_{C-P} = 10.5$ Hz), 127.6, 127.0 (d, $J_{C-P} = 1.5$ Hz), 126.2 (d, $J_{C-P} = 9.0$ Hz), 125.6, 125.4, 113.8 (d, $J_{C-P} = 7.5$ Hz), 108.2, 108.0 (d, $J_{C-P} = 10.5$ Hz), 96.2, 55.5, 48.5 (d, $J_{C-P} = 58.5$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 29.3$; HRMS (ESI): Exact mass calcd for $\text{C}_{30}\text{H}_{23}\text{O}_3\text{PS}_2$ $[\text{M}+\text{H}]^+$: 527.0899, Found: 527.0894.



Column chromatography afforded the desired product **4ao** in 84% yield (133.2 mg) as white solid; Mp: 211-213 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.64-7.63 (m, 1H), 7.62-7.60 (m, 1H), 7.45-7.41 (m, 4H), 7.32-7.26 (m, 4H), 7.25-7.23 (m, 1H), 7.20-7.13 (m, 2H), 7.11-7.06 (m, 3H), 6.890-6.888 (m, 1H), 6.878-6.875 (m, 1H), 6.79-6.78 (m, 1H), 6.71-6.69 (m, 0.5 H), 6.67-6.65 (m, 0.5 H), 6.34-6.32 (m, 2H), 5.54 (d, *J* = 15.0 Hz, 0.5 H), 5.53 (d, *J* = 15.0 Hz, 0.5 H), 3.68 (s, 3H), 2.33 (s, 1.5 H), 2.32 (s, 1.5 H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 160.9, 159.8, 149.2 (d, *J*_{C-P} = 9.0 Hz), 149.0 (d, *J*_{C-P} = 10.5 Hz), 139.5 (d, *J*_{C-P} = 72.0 Hz), 136.6 (d, *J*_{C-P} = 3.0 Hz), 136.5, 136.3 (d, *J*_{C-P} = 4.5 Hz), 136.2, 131.6 (d, *J*_{C-P} = 7.5 Hz), 131.5, 131.4 (d, *J*_{C-P} = 6.0 Hz), 130.8 (d, *J*_{C-P} = 33.0 Hz), 130.2 (d, *J*_{C-P} = 30.0 Hz), 129.9, 129.7 (d, *J*_{C-P} = 13.5 Hz), 129.4, 129.2, 128.5 (d, *J*_{C-P} = 31.5 Hz), 128.3 (d, *J*_{C-P} = 12.0 Hz), 128.2 (d, *J*_{C-P} = 7.5 Hz), 128.1 (d, *J*_{C-P} = 7.5 Hz), 128.0, 127.6, 126.6 (d, *J*_{C-P} = 3.0 Hz), 125.9 (d, *J*_{C-P} = 30.0 Hz), 120.8 (d, *J*_{C-P} = 12.0 Hz), 120.6 (d, *J*_{C-P} = 10.5 Hz), 113.63, 113.59, 107.7, 96.2, 96.1, 55.4, 47.3 (d, *J*_{C-P} = 58.5 Hz), 47.2 (d, *J*_{C-P} = 58.5 Hz), 21.23, 21.18; ³¹P{¹H} NMR (243 MHz, CDCl₃): δ = 28.8; HRMS (ESI): Exact mass calcd for C₃₅H₂₉O₃P [M+H]⁺: 529.1927, Found: 529.1920.

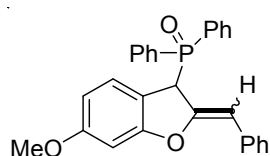


Column chromatography afforded the desired product **4ap+iso-4ap** in 83% yield (140.6 mg) as white solid; Mp: 226-228 °C; Spectra data for **4ap**: ¹H NMR (600 MHz, CDCl₃): δ = 7.78-7.77 (m, 1H), 7.61-7.56 (m, 3H), 7.54-7.52 (m, 1H), 7.49-7.44 (m, 2H), 7.40 (s, 1H), 7.35-7.31 (m, 3H), 7.28-7.24 (m, 5H), 7.23-7.19 (m, 1H), 7.16-7.13 (m, 2H), 7.04-6.98 (m, 3H), 6.74-6.72 (m, 1H), 6.36-6.35 (m, 2H), 5.66 (d, *J* = 15.0 Hz, 1H), 3.70 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 161.0, 159.7 (d, *J*_{C-P} = 4.5 Hz), 149.9 (d, *J*_{C-P} = 10.5 Hz), 139.2 (d, *J*_{C-P} = 4.5 Hz), 137.2, 133.5, 132.1 (d, *J*_{C-P} = 88.5 Hz), 131.5 (d, *J*_{C-P} = 9.0 Hz), 131.3 (d, *J*_{C-P} = 9.0 Hz), 130.7 (d, *J*_{C-P} = 96.0 Hz), 129.9, 129.3 (d, *J*_{C-P} = 96.0 Hz), 129.2, 128.3, 128.04 (d, *J*_{C-P} = 4.5 Hz), 127.93 (d, *J*_{C-P} = 12.0 Hz), 127.7, 127.5, 126.8, 126.0, 125.9 (d, *J*_{C-P} = 18.0 Hz), 120.5 (d, *J*_{C-P} = 12.0 Hz), 113.5 (d, *J*_{C-P} = 7.5 Hz), 107.8, 96.1, 55.5, 47.3 (d, *J*_{C-P} = 58.5 Hz); ³¹P{¹H} NMR (243 MHz, CDCl₃): δ = 29.3; HRMS (ESI): Exact mass calcd for C₃₈H₂₉O₃P [M+H]⁺: 565.1927, Found: 565.1920.



Spectra data for *iso-4ap*: ¹H NMR (600 MHz, CDCl₃): δ = 7.78-7.74 (m, 2H), 7.71-7.70 (m, 1H), 7.68-7.64 (m, 3H), 7.52-7.46 (m, 3H), 7.45-7.42

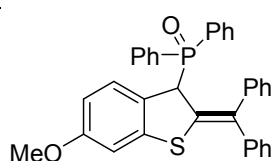
(m, 3H), 7.35-7.32 (m, 4H), 7.29-7.27 (m, 1H), 7.20-7.18 (m, 1H), 7.15-7.12 (m, 2H), 6.96-6.94 (m, 2H), 6.63-6.61 (m, 1H), 6.36-6.33 (m, 2H), 5.61 (d, $J = 14.4$ Hz, 1H), 3.70 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 161.0, 159.8, 149.9$ (d, $J_{\text{C-P}} = 10.5$ Hz), 139.8, 136.7, 132.6 (d, $J_{\text{C-P}} = 106.5$ Hz), 131.7, 131.6 (d, $J_{\text{C-P}} = 9.0$ Hz), 130.4 (d, $J_{\text{C-P}} = 94.5$ Hz), 130.38, 129.9 (d, $J_{\text{C-P}} = 96.0$ Hz), 128.9, 128.7, 128.4 (d, $J_{\text{C-P}} = 12.0$ Hz), 128.2 (d, $J_{\text{C-P}} = 12.0$ Hz), 128.1, 127.9, 127.4, 126.9 (d, $J_{\text{C-P}} = 27.0$ Hz), 125.8 (d, $J_{\text{C-P}} = 3.0$ Hz), 120.9 (d, $J_{\text{C-P}} = 10.5$ Hz), 113.6 (d, $J_{\text{C-P}} = 7.5$ Hz), 107.9, 96.2, 55.4, 47.4 (d, $J_{\text{C-P}} = 58.5$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 29.4$; HRMS (ESI): Exact mass calcd for $\text{C}_{38}\text{H}_{29}\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 565.1927, Found: 565.1920.



4ar (E/Z > 20:1)

Column chromatography afforded product **4ar** in 50% yield (65.8 mg) as white solid; Mp: 232-239 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.84$ -7.81 (m, 2H), 7.50-7.44 (m, 3H), 7.42-7.37 (m, 3H), 7.34-7.30 (m, 3H), 7.29-7.25 (m, 2H), 7.19-7.16 (m, 3H), 6.96 (s, 1H), 6.843-6.840 (m, 1H), 6.78-6.76 (m, 1H), 5.02 (d,

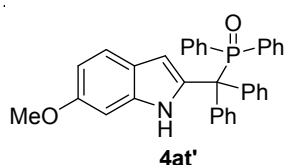
$J = 11.4$ Hz, 1H), 3.77 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 157.7, 155.3, 151.8, 133.6$ (d, $J_{\text{C-P}} = 4.5$ Hz), 132.0 (d, $J_{\text{C-P}} = 13.5$ Hz), 131.7 (d, $J_{\text{C-P}} = 33.0$ Hz), 131.3, 131.2 (d, $J_{\text{C-P}} = 3.0$ Hz), 129.9 (d, $J_{\text{C-P}} = 4.5$ Hz), 128.5 (d, $J_{\text{C-P}} = 12.0$ Hz), 128.3, 128.1 (d, $J_{\text{C-P}} = 10.5$ Hz), 127.4, 121.9, 121.0, 111.5, 106.4 (d, $J_{\text{C-P}} = 4.5$ Hz), 95.7, 55.6, 47.8 (d, $J_{\text{C-P}} = 66.0$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 30.2$; HRMS (ESI): Exact mass calcd for $\text{C}_{28}\text{H}_{23}\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 439.1458, Found: 439.1459.



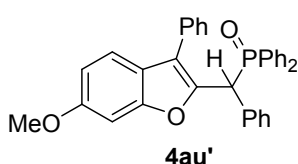
4as

Column chromatography afforded **4as** in 84% yield (133.7 mg) as white solid; Mp: 68-70 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.58$ -7.55 (m, 2H), 7.53-7.48 (m, 3H), 7.42-7.39 (m, 3H), 7.32-7.26 (m, 5H), 7.23-7.21 (m, 1H), 7.20-7.17 (m, 2H), 7.14-7.13 (m, 2H), 6.74-6.73 (m, 2H), 6.66-6.65 (m, 1H), 6.52 (dd, $J = 8.4$

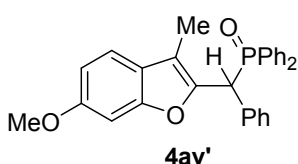
Hz, 2.4 Hz, 1H), 6.40 (dd, $J = 8.4$ Hz, 2.4 Hz, 1H), 5.62 (d, $J = 12.6$ Hz, 1H), 3.70 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 159.9, 143.9$ (d, $J_{\text{C-P}} = 3.0$ Hz), 142.0, 140.6, 138.7 (d, $J_{\text{C-P}} = 10.5$ Hz), 134.8 (d, $J_{\text{C-P}} = 10.5$ Hz), 132.1 (d, $J_{\text{C-P}} = 7.5$ Hz), 131.8 (d, $J_{\text{C-P}} = 15.0$ Hz), 131.6 (d, $J_{\text{C-P}} = 13.5$ Hz), 131.2 (d, $J_{\text{C-P}} = 96.0$ Hz), 129.8, 129.7 (d, $J_{\text{C-P}} = 93.0$ Hz), 129.0 (d, $J_{\text{C-P}} = 1.5$ Hz), 128.5, 128.3 (d, $J_{\text{C-P}} = 10.5$ Hz), 128.2 (d, $J_{\text{C-P}} = 10.5$ Hz), 128.0, 127.8, 127.0, 125.5, 124.7 (d, $J_{\text{C-P}} = 7.5$ Hz), 110.4, 107.5, 55.4, 55.3 (d, $J_{\text{C-P}} = 55.5$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 31.9$; HRMS (ESI): Exact mass calcd for $\text{C}_{34}\text{H}_{27}\text{O}_2\text{PS}$ $[\text{M}+\text{H}]^+$: 531.1542, Found: 531.1540.



4at' was obtained in 36% yield (55.7 mg) as white solid; Mp: 104-106 °C; ¹H NMR (600 MHz, CDCl₃): δ = 10.18 (brs, 1H), 7.47-7.44 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.28-7.24 (m, 6H), 7.17-7.14 (m, 8H), 7.01-6.99 (m, 4H), 6.95-6.94 (m, 1H), 6.78 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.19 (s, 1H), 3.87 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 156.4, 139.1, 137.4, 137.0, 133.0 (d, *J*_{C-P} = 9.0 Hz), 132.0 (d, *J*_{C-P} = 3.0 Hz), 131.5, 130.9 (d, *J*_{C-P} = 4.5 Hz), 128.2 (d, *J*_{C-P} = 12.0 Hz), 127.9, 127.6, 121.3, 121.0, 109.9, 105.7 (d, *J*_{C-P} = 6.0 Hz), 94.4, 60.9 (d, *J*_{C-P} = 63.0 Hz), 55.5; ³¹P{¹H} NMR (243 MHz, CDCl₃): δ = 36.8; HRMS (ESI): Exact mass calcd for C₃₄H₂₈NO₂P [M+Na]⁺: 536.1750, Found: 536.1752.

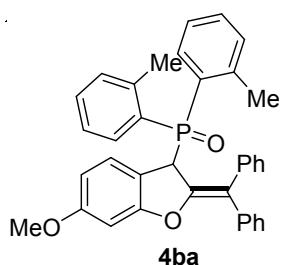


Column chromatography afforded **4au'** in 44% yield (67.0 mg) as white solid; Mp: 165-167 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.60-7.58 (m, 2H), 7.53-7.50 (m, 2H), 7.47-7.40 (m, 5H), 7.39-7.36 (m, 2H), 7.29-7.26 (m, 3H), 7.25-7.22 (m, 5H), 7.17-7.16 (m, 2H), 7.132-7.129 (m, 1H), 6.80-6.78 (m, 1H), 5.08 (d, *J* = 13.2 Hz, 1H), 3.84 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 157.9, 155.6, 147.2 (d, *J*_{C-P} = 9.0 Hz), 133.8 (d, *J*_{C-P} = 4.5 Hz), 132.0, 131.8, 131.6 (dd, *J*_{C-P} = 7.5 Hz, 3.0 Hz), 131.3 (t, *J*_{C-P} = 9.0 Hz), 131.1 (d, *J*_{C-P} = 4.5 Hz), 130.5, 130.1 (d, *J*_{C-P} = 4.5 Hz), 129.0, 128.9, 128.5, 128.1 (d, *J*_{C-P} = 9.0 Hz), 128.0 (d, *J*_{C-P} = 9.0 Hz), 127.6, 127.4 (d, *J*_{C-P} = 1.5 Hz), 121.0, 120.0 (d, *J*_{C-P} = 7.5 Hz), 119.7, 112.0, 96.0, 55.6, 46.8 (d, *J*_{C-P} = 63.0 Hz); ³¹P{¹H} NMR (243 MHz, CDCl₃): δ = 30.2; HRMS (ESI): Exact mass calcd for C₃₄H₂₇O₃P [M+H]⁺: 515.1771, Found: 515.1776



Column chromatography afforded **4av'** in 50% yield (67.8 mg) as white solid; Mp: 135-137 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.71-7.68 (m, 2H), 7.65-7.62 (m, 2H), 7.54-7.52 (m, 2H), 7.43-7.40 (m, 2H), 7.34-7.31 (m, 4H), 7.23-7.16 (m, 4H), 6.98 (d, *J* = 2.4 Hz, 1H), 6.79 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H), 5.00 (d, *J* = 13.8 Hz, 1H), 3.80 (s, 3H), 1.94 (d, *J* = 1.8 Hz, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 157.7, 155.1, 146.5 (d, *J*_{C-P} = 9.0 Hz), 134.0 (d, *J*_{C-P} = 4.5 Hz), 131.9 (d, *J*_{C-P} = 13.5 Hz), 131.7 (d, *J*_{C-P} = 3.0 Hz), 131.6 (d, *J*_{C-P} = 3.0 Hz), 131.4 (d, *J*_{C-P} = 7.5 Hz), 131.3, 131.2 (d, *J*_{C-P} = 15.0 Hz), 130.6 (d, *J*_{C-P} = 12.0 Hz), 130.1 (d, *J*_{C-P} = 6.0 Hz), 128.9 (d, *J*_{C-P} = 13.5 Hz), 128.3, 128.14, 128.13 (d, *J*_{C-P} = 22.5 Hz),

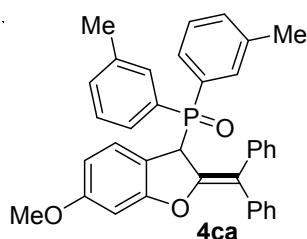
127.3, 122.8, 119.1, 112.9 (d, $J_{C-P} = 7.5$ Hz), 111.2, 95.9, 55.6, 47.3 (d, $J_{C-P} = 63.0$ Hz), 8.01; $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 29.9$; HRMS (ESI): Exact mass calcd for $\text{C}_{29}\text{H}_{25}\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 453.1614, Found: 453.1606.



Column chromatography afforded **4ba** in 91% yield (148.1 mg) as white solid;

Mp: 161-163 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.37$ -7.33 (m, 1H), 7.31-7.28 (m, 2H), 7.27-7.24 (m, 2H), 7.23-7.17 (m, 4H), 7.16-7.11 (m, 3H), 7.08-7.02 (m, 4H), 6.93-6.91 (m, 3H), 6.45-6.44 (m, 1H), 6.38 (dd, $J = 9.0$ Hz, 2.4 Hz, 1H), 5.70 (d, $J = 11.4$ Hz, 1H), 3.71 (s, 3H), 2.22 (s, 3H), 2.16 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR

(150 MHz, CDCl_3): $\delta = 160.9$ (d, $J_{C-P} = 1.5$ Hz), 160.2 (d, $J_{C-P} = 4.5$ Hz), 150.2 (d, $J_{C-P} = 10.5$ Hz), 144.0 (d, $J_{C-P} = 6.0$ Hz), 143.3 (d, $J_{C-P} = 7.5$ Hz), 139.7 (d, $J_{C-P} = 3.0$ Hz), 139.2 (d, $J_{C-P} = 4.5$ Hz), 132.4 (d, $J_{C-P} = 10.5$ Hz), 132.3 (d, $J_{C-P} = 9.0$ Hz), 132.0 (d, $J_{C-P} = 10.5$ Hz), 131.7 (d, $J_{C-P} = 12.0$ Hz), 131.43 (d, $J_{C-P} = 3.0$ Hz), 131.39 (d, $J_{C-P} = 3.0$ Hz), 130.5 (d, $J_{C-P} = 1.5$ Hz), 130.0 (d, $J_{C-P} = 93.0$ Hz), 129.8 (d, $J_{C-P} = 1.5$ Hz), 129.4 (d, $J_{C-P} = 93.0$ Hz), 128.7, 127.6, 126.8 (d, $J_{C-P} = 34.5$ Hz), 126.1 (d, $J_{C-P} = 4.5$ Hz), 125.0 (d, $J_{C-P} = 12.0$ Hz), 124.6 (d, $J_{C-P} = 12.0$ Hz), 121.1 (d, $J_{C-P} = 10.5$ Hz), 114.0 (d, $J_{C-P} = 6.0$ Hz), 107.9 (d, $J_{C-P} = 1.5$ Hz), 96.3 (d, $J_{C-P} = 1.5$ Hz), 55.5, 46.6 (d, $J_{C-P} = 57.0$ Hz), 21.6 (d, $J_{C-P} = 3.0$ Hz), 21.3 (d, $J_{C-P} = 3.0$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 36.0$; HRMS (ESI): Exact mass calcd for $\text{C}_{36}\text{H}_{31}\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 543.2084, Found: 543.2078.

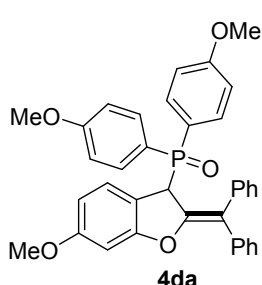


Column chromatography gave **4ca** in 80% yield (130.2 mg) as white solid;

Mp: 64-66 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.44$ -7.40 (m, 2H), 7.28-7.26 (m, 2H), 7.25-7.23 (m, 3H), 7.22-7.20 (m, 4H), 7.19-7.18 (m, 2H), 7.16-7.13 (m, 1H), 7.10-7.08 (m, 2H), 6.89-6.88 (m, 2H), 6.71-6.69 (m, 1H), 6.35-6.34 (m, 2H), 5.51 (d, $J = 15.0$ Hz, 1H), 3.70 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H);

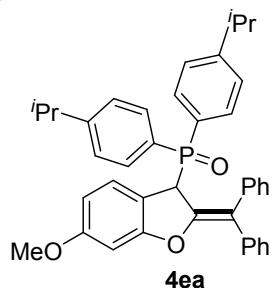
$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 160.8$, 159.7 (d, $J_{C-P} = 4.5$ Hz), 149.6 (d, $J_{C-P} = 10.5$ Hz), 139.5 (d, $J_{C-P} = 3.0$ Hz), 139.2 (d, $J_{C-P} = 4.5$ Hz), 138.2 (d, $J_{C-P} = 10.5$ Hz), 137.8 (d, $J_{C-P} = 10.5$ Hz), 132.6, 132.3 (d, $J_{C-P} = 7.5$ Hz), 132.1 (d, $J_{C-P} = 7.5$ Hz), 130.3, 130.2 (d, $J_{C-P} = 96.0$ Hz), 129.7, 129.5 (d, $J_{C-P} = 97.5$ Hz), 128.6 (d, $J_{C-P} = 9.0$ Hz), 128.42, 128.37, 128.03 (d, $J_{C-P} = 9.0$ Hz), 127.95 (d, $J_{C-P} = 9.0$ Hz), 127.6, 126.7, 126.6, 125.8 (d, $J_{C-P} = 3.0$ Hz), 120.6 (d, $J_{C-P} = 12.0$ Hz), 113.8 (d, $J_{C-P} = 7.5$ Hz), 107.7, 96.1, 55.4,

47.4 (d, $J_{C-P} = 58.5$ Hz), 21.4; $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 30.2$; HRMS (ESI): Exact mass calcd for $\text{C}_{36}\text{H}_{31}\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 543.2084, Found: 543.2081.



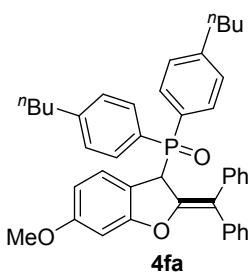
4da was obtained in 66% yield (111.8 mg) as white solid; Mp: 84-86 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.56-7.52$ (m, 2H), 7.35-7.32 (m, 2H), 7.27-7.25 (m, 2H), 7.20-7.19 (m, 3H), 7.15-7.14 (m, 1H), 7.13-7.11 (m, 2H), 6.92-6.91 (m, 2H), 6.82-6.80 (m, 2H), 6.77-6.75 (m, 3H), 6.37-6.36 (m, 1H), 6.34-6.33 (m, 1H), 5.48 (d, $J = 15.6$ Hz, 1H), 3.825 (s, 3H), 3.823 (s, 3H), 3.70 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$

NMR (150 MHz, CDCl_3): $\delta = 162.2$ (d, $J_{C-P} = 24.0$ Hz), 160.8, 159.6 (d, $J_{C-P} = 4.5$ Hz), 149.8 (d, $J_{C-P} = 10.5$ Hz), 140.0, 139.4 (d, $J_{C-P} = 3.0$ Hz), 133.4 (d, $J_{C-P} = 10.5$ Hz), 133.2 (d, $J_{C-P} = 10.5$ Hz), 130.0 (d, $J_{C-P} = 78.0$ Hz), 128.4, 127.6, 126.6 (d, $J_{C-P} = 3.0$ Hz), 125.8, 122.1, 121.3 (d, $J_{C-P} = 42.0$ Hz), 120.4 (d, $J_{C-P} = 10.5$ Hz), 114.1, 114.0 (d, $J_{C-P} = 13.5$ Hz), 113.8 (d, $J_{C-P} = 12.0$ Hz), 107.7, 96.1, 55.4, 55.2, 47.6 (d, $J_{C-P} = 60.0$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 28.9$; HRMS (ESI): Exact mass calcd for $\text{C}_{36}\text{H}_{31}\text{O}_5\text{P}$ $[\text{M}+\text{H}]^+$: 575.1982, Found: 575.1976.



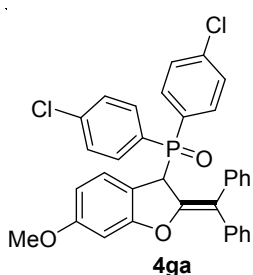
Column chromatography afforded the desired product **4ea** in 72% yield (129.3 mg) as white solid; Mp: 150-152 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.53-7.50$ (m, 2H), 7.38-7.34 (m, 2H), 7.26-7.23 (m, 2H), 7.20-7.17 (m, 2H), 7.16-7.13 (m, 6H), 7.12-7.09 (m, 2H), 6.91-6.90 (m, 2H), 6.66-6.64 (m, 1H), 6.33-6.32 (m, 2H), 5.49 (d, $J = 15.0$ Hz, 1H), 3.70 (s, 3H), 2.94-2.87 (m, 2H), 1.26-1.24 (m, 12H);

$^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 160.8$ (d, $J_{C-P} = 3.0$ Hz), 159.7 (d, $J_{C-P} = 4.5$ Hz), 152.65 (d, $J_{C-P} = 3.0$ Hz), 152.57 (d, $J_{C-P} = 3.0$ Hz), 149.9 (d, $J_{C-P} = 10.5$ Hz), 139.8 (d, $J_{C-P} = 3.0$ Hz), 139.4 (d, $J_{C-P} = 4.5$ Hz), 131.7 (d, $J_{C-P} = 9.0$ Hz), 131.6 (d, $J_{C-P} = 10.5$ Hz), 130.4 (d, $J_{C-P} = 3.0$ Hz), 129.8 (d, $J_{C-P} = 1.5$ Hz), 128.5, 128.1, 127.6, 127.4 (d, $J_{C-P} = 22.5$ Hz), 126.7 (d, $J_{C-P} = 3.0$ Hz), 126.5 (d, $J_{C-P} = 12.0$ Hz), 126.3 (d, $J_{C-P} = 10.5$ Hz), 125.9 (d, $J_{C-P} = 3.0$ Hz), 120.5 (d, $J_{C-P} = 10.5$ Hz), 114.0 (d, $J_{C-P} = 7.5$ Hz), 107.7 (d, $J_{C-P} = 1.5$ Hz), 96.0, 55.4, 47.6 (d, $J_{C-P} = 58.5$ Hz), 34.1, 23.71, 23.68, 23.6; $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 29.2$; HRMS (ESI): Exact mass calcd for $\text{C}_{40}\text{H}_{39}\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 599.2710, Found: 599.2708.

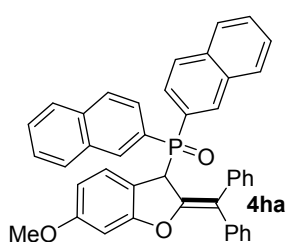


Column chromatography afforded product **4fa** in 88% yield (165.5 mg) as white solid; Mp: 154-156 °C; ^1H NMR (600 MHz, CDCl_3): δ = 7.52-7.49 (m, 2H), 7.35-7.32 (m, 2H), 7.26-7.24 (m, 2H), 7.20-7.15 (m, 4H), 7.12-7.08 (m, 6H), 6.91-6.90 (m, 2H), 6.67-6.65 (m, 1H), 6.34-6.32 (m, 2H), 5.50 (d, J = 15.0 Hz, 1H), 3.70 (s, 3H), 2.63-2.60 (m, 4H), 1.62-1.56 (m, 4H), 1.39-1.31 (m, 4H), 0.95-

0.92 (m, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ = 160.8 (d, $J_{\text{C-P}}$ = 3.0 Hz), 159.7 (d, $J_{\text{C-P}}$ = 3.0 Hz), 149.8 (d, $J_{\text{C-P}}$ = 10.5 Hz), 146.9 (d, $J_{\text{C-P}}$ = 3.0 Hz), 146.8 (d, $J_{\text{C-P}}$ = 3.0 Hz), 139.9 (d, $J_{\text{C-P}}$ = 4.5 Hz), 139.4 (d, $J_{\text{C-P}}$ = 4.5 Hz), 131.6 (d, $J_{\text{C-P}}$ = 9.0 Hz), 131.5 (d, $J_{\text{C-P}}$ = 10.5 Hz), 130.4 (d, $J_{\text{C-P}}$ = 1.5 Hz), 129.8 (d, $J_{\text{C-P}}$ = 1.5 Hz), 128.44, 128.36, 128.2 (d, $J_{\text{C-P}}$ = 12.0 Hz), 127.6, 127.4 (d, $J_{\text{C-P}}$ = 97.5 Hz), 126.8 (d, $J_{\text{C-P}}$ = 99.0 Hz), 126.6, 125.8 (d, $J_{\text{C-P}}$ = 3.0 Hz), 120.5 (d, $J_{\text{C-P}}$ = 10.5 Hz), 114.0 (d, $J_{\text{C-P}}$ = 7.5 Hz), 107.7, 96.1, 55.4, 47.6 (d, $J_{\text{C-P}}$ = 58.5 Hz), 35.6, 33.2, 22.3, 22.2, 13.9; $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): δ = 30.1; HRMS (ESI): Exact mass calcd for $\text{C}_{42}\text{H}_{43}\text{O}_3\text{P}$ [$\text{M}+\text{H}$] $^+$: 627.3023, Found: 627.3022.

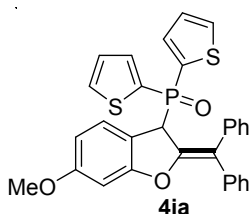


Column chromatography afforded the product **4ga** in 87% yield (152.3 mg) as white solid; Mp: 204-206 °C; ^1H NMR (600 MHz, CDCl_3): δ = 7.57-7.54 (m, 2H), 7.37-7.34 (m, 2H), 7.30-7.28 (m, 3H), 7.27-7.22 (m, 4H), 7.21-7.18 (m, 3H), 7.15-7.13 (m, 2H), 6.87-6.86 (m, 2H), 6.80-6.78 (m, 1H), 6.39-6.36 (m, 2H), 5.55 (d, J = 15.6 Hz, 1H), 3.70 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ = 161.2 (d, $J_{\text{C-P}}$ = 3.0 Hz), 159.6 (d, $J_{\text{C-P}}$ = 4.5 Hz), 148.8 (d, $J_{\text{C-P}}$ = 10.5 Hz), 139.6 (d, $J_{\text{C-P}}$ = 4.5 Hz), 139.0 (d, $J_{\text{C-P}}$ = 4.5 Hz), 138.7 (d, $J_{\text{C-P}}$ = 4.5 Hz), 138.6 (d, $J_{\text{C-P}}$ = 3.0 Hz), 132.8 (d, $J_{\text{C-P}}$ = 9.0 Hz), 132.6 (d, $J_{\text{C-P}}$ = 10.5 Hz), 130.2 (d, $J_{\text{C-P}}$ = 1.5 Hz), 129.7 (d, $J_{\text{C-P}}$ = 3.0 Hz), 129.2, 128.8 (d, $J_{\text{C-P}}$ = 12.0 Hz), 128.7, 128.6, 127.83, 127.78, 127.2, 126.9 (d, $J_{\text{C-P}}$ = 16.5 Hz), 125.9 (d, $J_{\text{C-P}}$ = 3.0 Hz), 121.1 (d, $J_{\text{C-P}}$ = 12.0 Hz), 112.9 (d, $J_{\text{C-P}}$ = 7.5 Hz), 108.1 (d, $J_{\text{C-P}}$ = 3.0 Hz), 96.3 (d, $J_{\text{C-P}}$ = 1.5 Hz), 55.5, 47.3 (d, $J_{\text{C-P}}$ = 61.5 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): δ = 27.3; HRMS (ESI): Exact mass calcd for $\text{C}_{34}\text{H}_{25}\text{Cl}_2\text{O}_3\text{P}$ [$\text{M}+\text{H}$] $^+$: 583.0991, Found: 583.0993.

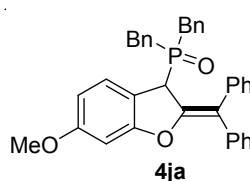


Column chromatography afforded product **4ha** in 85% yield (156.7 mg) as white solid; Mp: 118-120 °C; ^1H NMR (600 MHz, CDCl_3): δ = 8.27-8.24 (m, 1H), 8.16-8.14 (m, 1H), 7.85-7.84 (m, 2H), 7.81-7.79 (m, 1H), 7.78-7.76 (m, 3H), 7.75-7.72 (m, 1H), 7.60-7.57 (m, 2H), 7.53-7.49 (m, 3H), 7.25-7.22 (m,

4H), 7.20-7.15 (m, 1H), 6.91-6.88 (m, 1H), 6.78-6.74 (m, 5H), 6.341-6.338 (m, 1H), 6.30-6.29 (m, 1H), 5.76 (d, $J = 15.0$ Hz, 1H), 3.65 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 161.0$ (d, $J_{\text{C-P}} = 3.0$ Hz), 159.8 (d, $J_{\text{C-P}} = 4.5$ Hz), 149.5 (d, $J_{\text{C-P}} = 10.5$ Hz), 139.4 (d, $J_{\text{C-P}} = 4.5$ Hz), 139.2 (d, $J_{\text{C-P}} = 4.5$ Hz), 134.6 (d, $J_{\text{C-P}} = 4.5$ Hz), 134.0 (d, $J_{\text{C-P}} = 7.5$ Hz), 130.1 (d, $J_{\text{C-P}} = 1.5$ Hz), 129.8 (d, $J_{\text{C-P}} = 3.0$ Hz), 129.0 (d, $J_{\text{C-P}} = 10.5$ Hz), 128.3 (d, $J_{\text{C-P}} = 7.5$ Hz), 128.2 (d, $J_{\text{C-P}} = 3.0$ Hz), 128.1 (d, $J_{\text{C-P}} = 10.5$ Hz), 127.9 (d, $J_{\text{C-P}} = 10.5$ Hz), 127.7, 127.5, 126.83, 126.76, 126.6 (d, $J_{\text{C-P}} = 10.5$ Hz), 126.1 (d, $J_{\text{C-P}} = 10.5$ Hz), 126.0 (d, $J_{\text{C-P}} = 10.5$ Hz), 125.8 (d, $J_{\text{C-P}} = 3.0$ Hz), 120.9 (d, $J_{\text{C-P}} = 10.5$ Hz), 113.6 (d, $J_{\text{C-P}} = 7.5$ Hz), 108.0, 96.3 (d, $J_{\text{C-P}} = 1.5$ Hz), 55.4, 47.5 (d, $J_{\text{C-P}} = 58.5$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 29.1$; HRMS (ESI): Exact mass calcd for $\text{C}_{42}\text{H}_{31}\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 615.2084, Found: 615.2076.

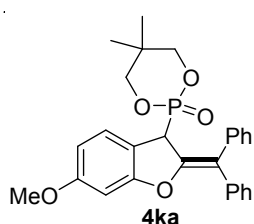


Column chromatography afforded the product **4ia** in 40% yield (63.2 mg) as white solid; Mp: 204-206 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.67$ -7.65 (m, 1H), 7.61-7.60 (m, 1H), 7.49-7.48 (m, 1H), 7.29-7.27 (m, 1H), 7.261-7.255 (m, 1H), 7.24-7.20 (m, 4H), 7.18-7.16 (m, 3H), 7.10-7.09 (m, 1H), 7.02-6.99 (m, 3H), 6.88-6.86 (m, 1H), 6.43 (dd, $J = 8.4$ Hz, 2.4 Hz, 1H), 6.330-6.326 (m, 1H), 5.48 (d, $J = 19.2$ Hz, 1H), 3.71 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 161.2$ (d, $J_{\text{C-P}} = 3.0$ Hz), 159.8 (d, $J_{\text{C-P}} = 4.5$ Hz), 148.7 (d, $J_{\text{C-P}} = 12.0$ Hz), 139.6 (d, $J_{\text{C-P}} = 4.5$ Hz), 139.2 (d, $J_{\text{C-P}} = 6.0$ Hz), 136.4 (d, $J_{\text{C-P}} = 10.5$ Hz), 136.2 (d, $J_{\text{C-P}} = 9.0$ Hz), 133.98 (d, $J_{\text{C-P}} = 4.5$ Hz), 133.96 (d, $J_{\text{C-P}} = 4.5$ Hz), 131.0 (d, $J_{\text{C-P}} = 61.5$ Hz), 130.32 (d, $J_{\text{C-P}} = 3.0$ Hz), 130.27 ($J_{\text{C-P}} = 63.0$ Hz), 129.8 (d, $J_{\text{C-P}} = 3.0$ Hz), 128.6, 128.5 (d, $J_{\text{C-P}} = 13.5$ Hz), 128.0 (d, $J_{\text{C-P}} = 15.0$ Hz), 127.7, 126.8 (d, $J_{\text{C-P}} = 24.0$ Hz), 126.1 (d, $J_{\text{C-P}} = 3.0$ Hz), 121.8 (d, $J_{\text{C-P}} = 13.5$ Hz), 113.3 (d, $J_{\text{C-P}} = 7.5$ Hz), 107.9 (d, $J_{\text{C-P}} = 3.0$ Hz), 96.2 (d, $J_{\text{C-P}} = 3.0$ Hz), 55.5, 50.0 (d, $J_{\text{C-P}} = 69.0$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 18.9$; HRMS (ESI): Exact mass calcd for $\text{C}_{30}\text{H}_{23}\text{O}_3\text{PS}_2$ $[\text{M}+\text{H}]^+$: 527.0899, Found: 527.0893.



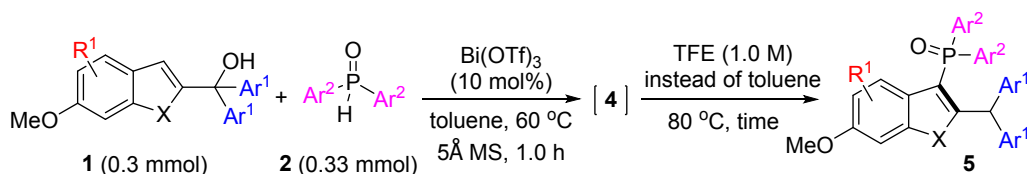
Column chromatography afforded the desired product **4ja** in 63% yield (102.5 mg) as white solid; Mp: 184-186 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.45$ -7.40 (m, 4H), 7.37-7.36 (m, 4H), 7.35-7.33 (m, 1H), 7.30-7.28 (m, 1H), 7.21-7.19 (m, 1H), 7.18-7.16 (m, 3H), 7.09-7.07 (m, 3H), 6.96-6.94 (m, 2H), 6.86-6.85 (m, 2H), 6.52-6.50 (m, 1H), 6.434-6.430 (m, 1H), 5.14 (d, $J = 17.4$ Hz, 1H), 3.76 (s, 3H), 2.98 (d, $J = 12.6$ Hz, 2H), 2.55 (ABd, $J = 15.0$ Hz, 9.0 Hz, 1H), 2.36 (ABd, $J = 15.0$ Hz, 9.0 Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz,

CDCl₃): δ = 161.0, 159.0 (d, J_{C-P} = 4.5 Hz), 150.1 (d, J_{C-P} = 7.5 Hz), 140.1 (d, J_{C-P} = 3.0 Hz), 138.9 (d, J_{C-P} = 3.0 Hz), 131.3 (d, J_{C-P} = 9.0 Hz), 131.0 (d, J_{C-P} = 6.0 Hz), 130.8 (d, J_{C-P} = 1.5 Hz), 130.0 (d, J_{C-P} = 4.5 Hz), 129.9 (d, J_{C-P} = 1.5 Hz), 129.7 (d, J_{C-P} = 6.0 Hz), 129.4, 128.3 (d, J_{C-P} = 18.0 Hz), 127.9, 127.0, 126.74 (d, J_{C-P} = 3.0 Hz), 126.69 (d, J_{C-P} = 3.0 Hz), 126.4 (d, J_{C-P} = 1.5 Hz), 120.2 (d, J_{C-P} = 10.5 Hz), 113.7 (d, J_{C-P} = 7.5 Hz), 108.3, 96.4 (d, J_{C-P} = 1.5 Hz), 55.5, 46.0 (d, J_{C-P} = 52.5 Hz), 35.1 (d, J_{C-P} = 58.5 Hz), 32.7 (d, J_{C-P} = 60.0 Hz); ³¹P{¹H} NMR (243 MHz, CDCl₃): δ = 42.3; HRMS (ESI): Exact mass calcd for C₃₆H₃₁O₃P [M+H]⁺: 543.2084, Found: 543.2081.



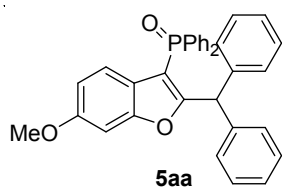
4ka was obtained in 33% yield (45.7 mg) as white solid; Mp: 54-56 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.42-7.40 (m, 2H), 7.38-7.35 (m, 2H), 7.33-7.29 (m, 5H), 7.26-7.23 (m, 2H), 6.56-6.55 (m, 2H), 5.04 (d, J = 25.2 Hz, 1H), 4.01 (t, J = 10.2 Hz, 1H), 3.77 (s, 3H), 3.75-3.73 (m, 1H), 3.69 (t, J = 12.0 Hz, 1H), 3.25-3.21 (m, 1H), 0.932 (s, 3H), 0.928 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 161.1, 159.6 (d, J_{C-P} = 6.0 Hz), 148.4 (d, J_{C-P} = 13.5 Hz), 140.2 (d, J_{C-P} = 4.5 Hz), 138.8 (d, J_{C-P} = 6.0 Hz), 130.2 (d, J_{C-P} = 115.5 Hz), 128.2 (d, J_{C-P} = 121.5 Hz), 127.0 (d, J_{C-P} = 52.5 Hz), 125.5 (d, J_{C-P} = 3.0 Hz), 120.2 (d, J_{C-P} = 12.0 Hz), 112.7 (d, J_{C-P} = 9.0 Hz), 108.3, 96.7, 76.0 (d, J_{C-P} = 6.0 Hz), 75.7 (d, J_{C-P} = 6.0 Hz), 75.2 (d, J_{C-P} = 6.0 Hz), 55.5, 42.0 (d, J_{C-P} = 135.0 Hz), 32.3, 32.2, 21.43, 21.36; ³¹P{¹H} NMR (243 MHz, CDCl₃): δ = 15.6; HRMS (ESI): Exact mass calcd for C₂₇H₂₇O₅P [M+H]⁺: 463.1669, Found: 463.1663.

4. General procedure for tandem dearomative C3-phosphorylation/aromatization



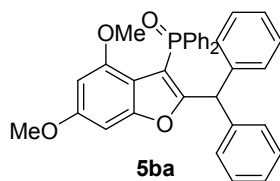
The reaction was carried out under an air atmosphere. To a 25-mL Schlenk tube were added alcohols **1** (0.3 mmol, 1.0 equiv), Ar₂P(O)H **2** (0.33 mmol, 2.0 equivs), Bi(OTf)₃ (19.7 mg, 10 mol%) and 300 mg 5 Å MS. After adding 3.0 mL of anhydrous toluene, the reaction mixture was stirred at 60 °C till almost full conversion of **1** by TLC analysis. Then, toluene was removed under vacuum and TFE (3.0

mL) was added. After stirring at 80 °C for indicated time in the main text, the reaction mixture was directly subjected to column chromatography using petrol ether/ethyl acetate (generally 4:1, v:v) as the eluent to afford products **5**.



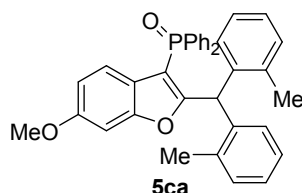
Column chromatography afforded the desired product **5aa** in 78% yield (120.4 mg) as white solid; Mp: 54-56 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.70-7.66 (m, 4H), 7.54-7.51 (m, 2H), 7.42-7.39 (m, 4H), 7.25-7.19 (m, 10H), 7.00 (s, 1H), 6.66-6.61 (m, 2H), 6.29 (s, 1H), 3.76 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃):

δ = 165.4 (d, *J*_{C-P} = 16.5 Hz), 157.9, 155.6 (d, *J*_{C-P} = 12.0 Hz), 140.7, 132.9 (d, *J*_{C-P} = 108.0 Hz), 132.1, 131.7 (d, *J*_{C-P} = 10.5 Hz), 129.1, 128.6 (d, *J*_{C-P} = 13.5 Hz), 128.2, 126.6, 121.4, 121.2 (d, *J*_{C-P} = 10.5 Hz), 112.4, 107.1 (d, *J*_{C-P} = 118.5 Hz), 96.0, 55.6, 48.8; ³¹P{¹H} NMR (243 MHz, CDCl₃): δ = 22.0; HRMS (ESI): Exact mass calcd for C₃₄H₂₇O₃P [M+H]⁺: 515.1771, Found: 515.1768.



Column chromatography afforded the desired product **5ba** in 76% yield (124.2 mg) as white solid; Mp: 224-226 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.71-7.67 (m, 4H), 7.48-7.45 (m, 2H), 7.39-7.36 (m, 4H), 7.30-7.28 (m, 4H), 7.27-7.24 (m, 4H), 7.21-7.19 (m, 2H), 6.88 (s, 1H), 6.65-6.64 (m, 1H), 6.13 (d,

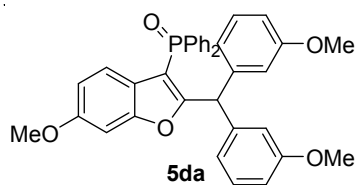
J = 2.4 Hz, 1H), 3.77 (s, 3H), 3.12 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 165.5 (d, *J*_{C-P} = 16.5 Hz), 159.3, 156.4 (d, *J*_{C-P} = 10.5 Hz), 153.1, 141.5, 134.4 (d, *J*_{C-P} = 111.0 Hz), 131.5 (d, *J*_{C-P} = 10.5 Hz), 131.3, 129.2, 128.2, 128.0 (d, *J*_{C-P} = 13.5 Hz), 126.5, 111.3 (d, *J*_{C-P} = 9.0 Hz), 105.5 (d, *J*_{C-P} = 115.5 Hz), 95.0, 88.4, 55.7, 54.2, 48.2; ³¹P{¹H} NMR (243 MHz, CDCl₃): δ = 25.4; HRMS (ESI): Exact mass calcd for C₃₃H₂₉O₄P [M+H]⁺: 545.1876, Found: 545.1880.



Column chromatography afforded the desired product **5ca** in 85% yield (138.4 mg) as white solid; Mp: 210-212 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.60-7.57 (m, 4H), 7.49-7.46 (m, 2H), 7.35-7.32 (m, 4H), 7.14-7.09 (m, 4H), 7.06-7.03 (m, 2H), 6.993-6.991 (m, 1H), 6.93-6.92 (m, 2H), 6.68-6.66 (m, 1H), 6.62-6.60 (m, 2H), 3.76 (s, 3H), 2.16 (s, 6H); ¹³C{¹H} NMR (150 MHz,

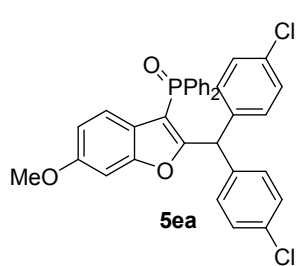
CDCl₃): δ = 165.5 (d, *J*_{C-P} = 18.0 Hz), 157.8, 155.4 (d, *J*_{C-P} = 12.0 Hz), 139.2, 136.8, 132.7 (d, *J*_{C-P} = 109.5 Hz), 131.9, 131.5 (d, *J*_{C-P} = 10.5 Hz), 130.2, 128.8, 128.4 (d, *J*_{C-P} = 13.5 Hz), 126.7, 125.6, 121.4,

121.3, 112.6, 106.0 (d, $J_{C-P} = 117.0$ Hz), 96.0, 55.6, 43.9, 19.7; $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 21.2$; HRMS (ESI): Exact mass calcd for $\text{C}_{36}\text{H}_{31}\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 543.2084, Found: 543.2089.



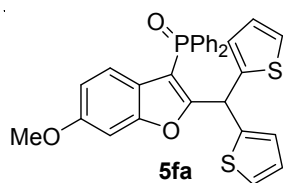
Column chromatography afforded the desired product **5da** in 84% yield (144.8 mg) as white solid; Mp: 79-81 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.70$ -7.67 (m, 4H), 7.54-7.52 (m, 2H), 7.43-7.40 (m, 4H), 7.15 (t, $J = 7.8$ Hz, 2H), 7.014-7.009 (m, 1H), 6.82-6.81 (m, 2H), 6.77-6.76 (m, 2H),

6.75-6.73 (m, 2H), 6.66-6.64 (m, 1H), 6.61-6.60 (m, 1H), 6.26 (s, 1H), 3.77 (s, 3H), 3.69 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 165.2$ (d, $J_{C-P} = 18.0$ Hz), 159.4, 158.0, 155.6 (d, $J_{C-P} = 10.5$ Hz), 142.0, 132.9 (d, $J_{C-P} = 108.0$ Hz), 132.1, 131.7 (d, $J_{C-P} = 10.5$ Hz), 129.2, 128.6 (d, $J_{C-P} = 12.0$ Hz), 121.5, 121.4, 121.2 (d, $J_{C-P} = 9.0$ Hz), 114.9, 112.5, 112.1, 107.1 (d, $J_{C-P} = 117.0$ Hz), 96.0, 55.6, 55.1, 48.8; $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 22.1$; HRMS (ESI): Exact mass calcd for $\text{C}_{36}\text{H}_{31}\text{O}_5\text{P}$ $[\text{M}+\text{H}]^+$: 575.1982, Found: 575.1985.



Column chromatography afforded **5ea** in 56% yield (98.0 mg) as white solid; Mp: 132-134 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.69$ -7.65 (m, 4H), 7.57-7.54 (m, 2H), 7.44-7.41 (m, 4H), 7.21 (AB, $J = 8.4$ Hz, 4H), 7.14 (AB, $J = 8.4$ Hz, 4H), 7.00 (t, $J = 1.8$ Hz, 1H), 6.66 (dd, $J = 8.4$ Hz, 2.4 Hz, 1H), 6.50-6.47 (m, 2H), 3.78 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 164.5$ (d, $J_{C-P} =$

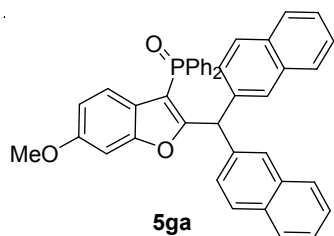
18.0 Hz), 158.1, 155.6 (d, $J_{C-P} = 12.0$ Hz), 138.8, 133.0, 132.7, 132.3 (d, $J_{C-P} = 1.5$ Hz), 131.6 (d, $J_{C-P} = 10.5$ Hz), 130.3, 128.7 (d, $J_{C-P} = 12.0$ Hz), 128.5, 121.3, 120.8 (d, $J_{C-P} = 10.5$ Hz), 112.7, 107.6 (d, $J_{C-P} = 115.5$ Hz), 96.0, 55.6, 47.6; $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 21.5$; HRMS (ESI): Exact mass calcd for $\text{C}_{34}\text{H}_{25}\text{Cl}_2\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 583.0991, Found: 583.0993.



Column chromatography afforded product **5fa** in 73% yield (115.3 mg) as lilac solid; Mp: 119-121 °C; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.74$ -7.71 (m, 4H), 7.57-7.55 (m, 2H), 7.47-7.44 (m, 4H), 7.18 (dd, $J = 4.8$ Hz, 1.2 Hz, 2H), 7.06 (d, $J = 1.8$ Hz, 1H), 6.96-6.95 (m, 2H), 6.90-6.89 (m, 2H), 6.82 (s, 1H), 6.67 (d, $J =$

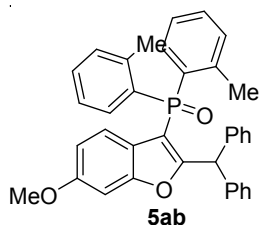
2.4 Hz, 2H), 3.78 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 163.5$ (d, $J_{C-P} = 18.0$ Hz), 158.2, 155.5 (d, $J_{C-P} = 12.0$ Hz), 143.1, 132.6 (d, $J_{C-P} = 109.5$ Hz), 132.3 (d, $J_{C-P} = 1.5$ Hz), 131.7 (d, $J_{C-P} = 10.5$ Hz),

128.7 (d, $J_{C-P} = 12.0$ Hz), 126.5 (d, $J_{C-P} = 10.5$ Hz), 125.0, 121.6, 120.9 (d, $J_{C-P} = 10.5$ Hz), 112.8, 106.3 (d, $J_{C-P} = 117.0$ Hz), 96.0, 55.6, 39.7; $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 21.4$; HRMS (ESI): Exact mass calcd for $\text{C}_{30}\text{H}_{23}\text{O}_3\text{PS}_2$ $[\text{M}+\text{H}]^+$: 527.0899, Found: 527.0904.



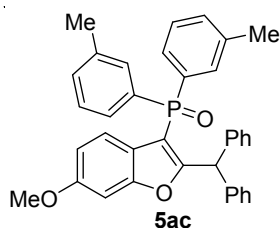
Product **5ga** was obtained in 80% yield (147.5 mg) as white solid; Mp: 196-198 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.81$ -7.79 (m, 2H), 7.74-7.72 (m, 5H), 7.70-7.68 (m, 3H), 7.63 (s, 2H), 7.52-7.49 (m, 2H), 7.46-7.40 (m, 6H), 7.39-7.36 (m, 4H), 7.04-7.03 (m, 1H), 6.69-6.68 (m, 2H), 6.64-6.62 (m, 1H), 3.78 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 165.3$ (d, $J_{C-P} = 18.0$

Hz), 158.0, 155.7 (d, $J_{C-P} = 12.0$ Hz), 138.1, 133.3, 132.8 (d, $J_{C-P} = 108.0$ Hz), 132.3, 132.2 (d, $J_{C-P} = 3.0$ Hz), 131.7 (d, $J_{C-P} = 10.5$ Hz), 128.6 (d, $J_{C-P} = 13.5$ Hz), 127.9, 127.8, 127.5 (d, $J_{C-P} = 1.5$ Hz), 125.8 (d, $J_{C-P} = 25.5$ Hz), 121.4, 121.2 (d, $J_{C-P} = 10.5$ Hz), 112.6, 107.4 (d, $J_{C-P} = 117.0$ Hz), 96.0, 55.6, 49.2; $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 21.5$; HRMS (ESI): Exact mass calcd for $\text{C}_{42}\text{H}_{31}\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 615.2084, Found: 615.2084.



Column chromatography afforded the desired product **5ab** in 90% yield (146.5 mg) as white solid; Mp: 80-82 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.42$ -7.40 (m, 2H), 7.26-7.10 (m, 16H), 7.04 (s, 1H), 6.59-6.58 (m, 1H), 6.53 (s, 1H), 6.46-6.44 (m, 1H), 3.78 (s, 3H), 2.52 (brs, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 165.4$ (d, $J_{C-P} = 18.0$ Hz), 157.9, 155.6 (d, $J_{C-P} = 12.0$ Hz), 143.7 (d, $J_{C-P} = 7.5$ Hz), 140.7,

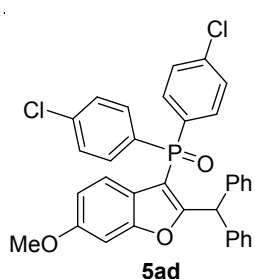
132.0 (d, $J_{C-P} = 10.5$ Hz), 129.2, 128.2, 126.6, 125.5 (d, $J_{C-P} = 12.0$ Hz), 121.4 (d, $J_{C-P} = 10.5$ Hz), 121.1, 112.4, 106.8 (d, $J_{C-P} = 117.0$ Hz), 96.0, 55.6, 48.8, 21.6; $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 28.3$; HRMS (ESI): Exact mass calcd for $\text{C}_{36}\text{H}_{31}\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 543.2084, Found: 543.2088.



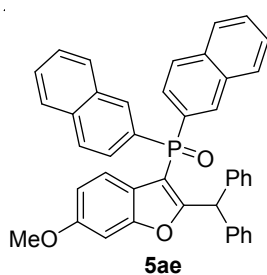
Product **5ac** was obtained in 78% yield (127.1 mg) as white solid; Mp: 77-79 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.57$ -7.55 (m, 2H), 7.44-7.41 (m, 2H), 7.34-7.32 (m, 2H), 7.31-7.28 (m, 2H), 7.25-7.23 (m, 4H), 7.21-7.19 (m, 2H), 7.17-7.16 (m, 4H), 7.02-7.01 (m, 1H), 6.80-6.79 (m, 1H), 6.69-6.68 (m, 1H), 6.01 (s, 1H), 3.78 (s, 3H), 2.27 (s, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 164.5$ (d,

$J_{C-P} = 18.0$ Hz), 157.9, 155.6 (d, $J_{C-P} = 12.0$ Hz), 140.7, 138.6 (d, $J_{C-P} = 12.0$ Hz), 132.9, 132.7 (d, $J_{C-P} =$

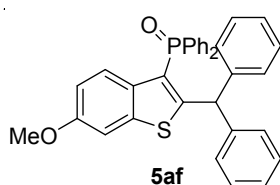
108.0 Hz), 132.2 (d, $J_{C-P} = 9.0$ Hz), 129.0, 128.7 (d, $J_{C-P} = 10.5$ Hz), 128.4 (d, $J_{C-P} = 13.5$ Hz), 128.2, 126.6, 121.8, 121.4 (d, $J_{C-P} = 10.5$ Hz), 112.4, 107.6 (d, $J_{C-P} = 117.0$ Hz), 96.0, 55.6, 48.9, 21.3; $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 22.3$; HRMS (ESI): Exact mass calcd for $\text{C}_{36}\text{H}_{31}\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 543.2084, Found: 543.2089.



Column chromatography afforded the desired product **5ad** in 50% yield (87.5 mg) as white solid; Mp: 81-83 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.60$ -7.56 (m, 4H), 7.39-7.37 (m, 4H), 7.26-7.18 (m, 10H), 7.02 (t, $J = 1.8$ Hz, 1H), 6.69 (dd, $J = 9.0$ Hz, 2.4 Hz, 1H), 6.58 (d, $J = 9.0$ Hz, 1H), 6.34 (s, 1H), 3.78 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 166.1$ (d, $J_{C-P} = 19.5$ Hz), 158.1, 155.7 (d, $J_{C-P} = 13.5$ Hz), 140.4, 139.0, 133.0 (d, $J_{C-P} = 12.0$ Hz), 131.1 (d, $J_{C-P} = 109.5$ Hz), 129.1 (d, $J_{C-P} = 13.5$ Hz), 129.0, 128.4, 126.8, 121.0, 120.7 (d, $J_{C-P} = 10.5$ Hz), 112.8, 106.2 (d, $J_{C-P} = 120.0$ Hz), 96.2, 55.7, 49.0; $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 20.5$; HRMS (ESI): Exact mass calcd for $\text{C}_{34}\text{H}_{25}\text{Cl}_2\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 583.0991, Found: 583.0994.



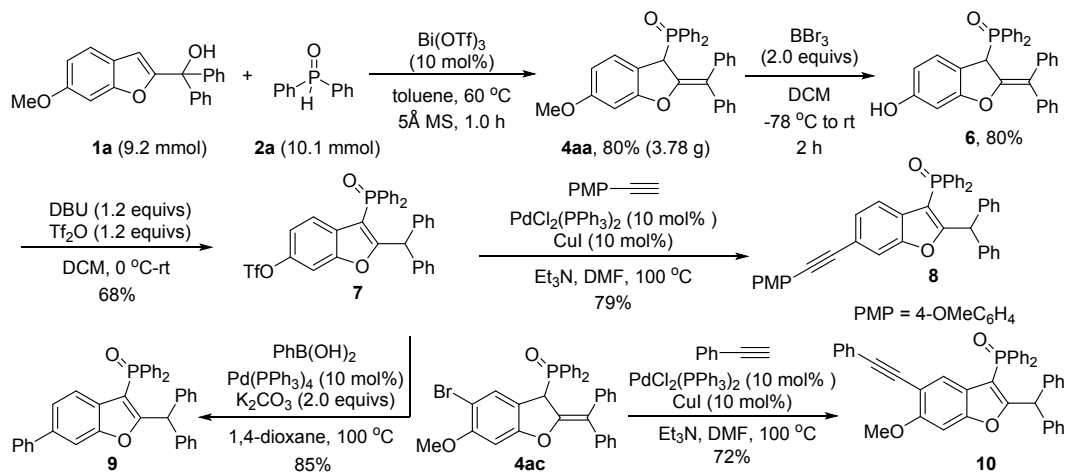
Column chromatography afforded the desired product **5ae** in 83% yield (153.1 mg) as white solid; Mp: 184-186 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 8.29$ -8.27 (m, 2H), 7.88-7.87 (m, 4H), 7.77-7.73 (m, 4H), 7.61-7.59 (m, 2H), 7.54-7.51 (m, 2H), 7.19-7.14 (m, 10H), 7.04 (s, 1H), 6.76 (d, $J = 8.4$ Hz, 1H), 6.61 (dd, $J = 8.4$ Hz, 2.4 Hz, 1H), 6.25 (s, 1H), 3.76 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 165.3$ (d, $J_{C-P} = 19.5$ Hz), 158.0, 155.7 (d, $J_{C-P} = 12.0$ Hz), 140.6, 134.8, 133.7 (d, $J_{C-P} = 10.5$ Hz), 132.5 (d, $J_{C-P} = 13.5$ Hz), 130.1 (d, $J_{C-P} = 108.0$ Hz), 129.0 (d, $J_{C-P} = 7.5$ Hz), 128.6 (d, $J_{C-P} = 12.0$ Hz), 128.3 (d, $J_{C-P} = 6.0$ Hz), 127.8, 126.8 (d, $J_{C-P} = 30.0$ Hz), 126.6 (d, $J_{C-P} = 10.5$ Hz), 121.6, 121.3 (d, $J_{C-P} = 10.5$ Hz), 112.5, 107.2 (d, $J_{C-P} = 117.0$ Hz), 96.1, 55.6, 49.1; $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 22.2$; HRMS (ESI): Exact mass calcd for $\text{C}_{42}\text{H}_{31}\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 615.2084, Found: 615.2084.



Column chromatography afforded the desired product **5af** in 68% yield (108.3 mg) as white solid; Mp: 65-67 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.57$ -7.54 (m, 4H), 7.49-7.47 (m, 2H), 7.36-7.33 (m, 4H), 7.22-7.18 (m, 8H), 7.11-7.10 (m,

4H), 6.74 (s, 1H), 6.73-6.71 (m, 1H), 3.77 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ = 160.3 (d, $J_{\text{C-P}}$ = 12.0 Hz), 157.1, 143.4, 140.9 (d, $J_{\text{C-P}}$ = 13.5 Hz), 134.4 (d, $J_{\text{C-P}}$ = 15.0 Hz), 133.2 (d, $J_{\text{C-P}}$ = 105.0 Hz), 132.0, 131.8 (d, $J_{\text{C-P}}$ = 9.0 Hz), 129.4, 128.6 (d, $J_{\text{C-P}}$ = 12.0 Hz), 128.2, 126.8, 125.5, 121.8 (d, $J_{\text{C-P}}$ = 102.0 Hz), 114.3, 104.5, 55.6, 49.8; $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): δ = 24.6; HRMS (ESI): Exact mass calcd for $\text{C}_{34}\text{H}_{27}\text{O}_2\text{PS}$ $[\text{M}+\text{H}]^+$: 531.1542, Found: 531.1546.

5. Gram-scale synthesis and product elaboration



1) Gram-scale synthesis

The gram-scale reaction was carried out under an air atmosphere. To a 100 mL three-necked flask was added **1a** (3.03 g, 9.2 mmol, 1.0 equiv), Ph₂P(O)H **2a** (2.04 g, 10.1 mmol, 1.1 equivs), Bi(OTf)₃ (603 mg, 10 mol%) and 9 g 5 Å MS. After adding 50.0 mL of anhydrous toluene, the reaction mixture was stirred at 60 °C till almost full conversion of **1a** by TLC analysis. The reaction mixture was directly subjected to column chromatography using petroleum ether/ethyl acetate (4:1 to 1:1, v:v) as the eluent to afford product **4aa** in 80% yield (3.78 g).

2) Product elaboration

2a) The cleavage of the methyl group for the synthesis of **6**

Compound **6** was prepared according to the literature procedure.³ To a dried Schlenk tube was added sequentially **4aa** (514.0 mg, 1 mmol, 1.0 equiv) and anhydrous CH₂Cl₂ (6 mL) under nitrogen. The reaction mixture was cooled to -78 °C and then BBr₃ (0.2 mL, 2.0 mmol, 2.0 equivs) was added, followed by stirring at room temperature until full conversion of **4aa** by TLC analysis. Then, the reaction solution was slowly poured to a flask containing crush ice, extracted with dichloromethane (3*20 mL) and washed with saturated NaHCO₃ solution. After dried with anhydrous Na₂SO₄, the organic layer was concentrated in vacuo to give the crude product, which was further subjected to column chromatography using CH₂Cl₂/MeOH (30:1, v:v) as the eluent to afford product **6** in 80% yield (400.0 mg) as pale pink solid. Mp: 224-226 °C; ¹H NMR (600 MHz, DMSO-*d*₆): δ = 9.69 (s, 1H), 7.69-7.66 (m, 2H), 7.64-7.62

³ W. Chen, W. Du, Y.-Z. Duan, Y. Wu, S.-Y. Yang, Y.-C. Chen, *Angew. Chem. Int. Ed.*, 2007, **46**, 7667.

(m, 1H), 7.59-7.56 (m, 2H), 7.53-7.50 (m, 2H), 7.48-7.46 (m, 1H), 7.38-7.35 (m, 2H), 7.33-7.27 (m, 3H), 7.19-7.16 (m, 3H), 7.13-7.10 (m, 2H), 6.91-6.90 (m, 2H), 6.36-6.34 (m, 1H), 6.32-6.31 (m, 1H), 6.23-6.21 (m, 1H), 5.99 (d, $J = 10.8$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, DMSO- d_6): $\delta = 159.3, 158.5, 149.8$ (d, $J_{\text{C-P}} = 10.5$ Hz), 139.4 (d, $J_{\text{C-P}} = 61.5$ Hz), 131.8, 131.44, 131.35, 131.2 (d, $J_{\text{C-P}} = 7.5$ Hz), 130.8, 130.6 (d, $J_{\text{C-P}} = 9.0$ Hz), 129.6 (d, $J_{\text{C-P}} = 28.5$ Hz), 128.5, 128.4, 128.3, 128.2, 127.8, 126.5 (d, $J_{\text{C-P}} = 57.0$ Hz), 125.6, 119.8 (d, $J_{\text{C-P}} = 12.0$ Hz), 112.0 (d, $J_{\text{C-P}} = 7.5$ Hz), 104.5, 97.0, 45.6 (d, $J_{\text{C-P}} = 58.5$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, DMSO- d_6): $\delta = 28.3$; HRMS (ESI): Exact mass calcd for $\text{C}_{33}\text{H}_{25}\text{O}_3\text{P}$ $[\text{M}+\text{H}]^+$: 501.1614, Found: 501.1611.

2b) Procedure for the synthesis of 7

To a 50 mL three-necked flask were added **6** (250.0 mg, 0.5 mmol, 1.0 equiv) and anhydrous CH_2Cl_2 (15 mL) under nitrogen. The reaction mixture was then cooled to 0 °C and DBU (90 μL , 0.6 mmol, 1.2 equivs), Tf_2O (101 μL , 0.6 mmol, 1.2 equivs) were added sequentially, followed by stirring at room temperature for 1.0 h until full conversion of **6** by TLC analysis. The reaction mixture was directly subjected to column chromatography using petroleum ether/ethyl acetate (3:1, v:v) as the eluent to afford product **7** in 68% yield (215.0 mg). Mp: 113-115 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.69$ -7.66 (m, 4H), 7.58-7.56 (m, 2H), 7.46-7.42 (m, 5H), 7.26-7.25 (m, 2H), 7.24-7.21 (m, 4H), 7.16-7.14 (m, 4H), 6.99-6.97 (m, 1H), 6.88-6.86 (m, 1H), 6.17 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): $\delta = 168.6$ (d, $J_{\text{C-P}} = 16.5$ Hz), 154.0 (d, $J_{\text{C-P}} = 12.0$ Hz), 146.5, 139.9, 132.7, 131.9, 131.8 (d, $J_{\text{C-P}} = 9.0$ Hz), 129.1, 129.0, 128.9, 128.6, 127.1, 122.4, 118.8 (q, $J_{\text{C-F}} = 318.0$ Hz), 117.3, 108.4, 107.6, 105.8, 49.2; $^{31}\text{P}\{^1\text{H}\}$ NMR (243 MHz, CDCl_3): $\delta = 21.4$; $^{19}\text{F}\{^1\text{H}\}$ NMR (565 MHz, CDCl_3): $\delta = -72.6$; HRMS (ESI): Exact mass calcd for $\text{C}_{34}\text{H}_{24}\text{F}_3\text{O}_5\text{PS}$ $[\text{M}+\text{Na}]^+$: 655.0926, Found: 655.0925.

2c) Sonogashira coupling reaction for the synthesis of 8

Compound **8** was prepared from **7** (63.0 mg, 0.1 mmol) and 1-ethynyl-4-methoxybenzene (39.6 mg, 0.3 mmol) according to the literature procedure.⁴ Column chromatography afforded the desired product **8** in 79% yield (48.6 mg) as yellow solid. Mp: 48-50 °C; ^1H NMR (600 MHz, CDCl_3): $\delta = 7.71$ -7.67 (m, 4H), 7.63 (s, 1 H), 7.56-7.53 (m, 2H), 7.44-7.40 (m, 6H), 7.26-7.23 (m, 4H), 7.21-7.17 (m, 7H), 6.86 (d, $J = 9.0$ Hz, 2H), 6.73 (d, $J = 8.4$ Hz, 1H), 6.33 (s, 1H), 3.80 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (150

⁴Q.-Y. Chen, Z.-Y. Yang, *Tetrahedron Lett.*, 1986, **27**, 1171.

MHz, CDCl₃): δ = 167.4 (d, J_{C-P} = 18.0 Hz), 159.6, 154.2 (d, J_{C-P} = 10.5 Hz), 140.3, 134.0, 133.0, 132.2, 131.7 (d, J_{C-P} = 10.5 Hz), 129.0, 128.7 (d, J_{C-P} = 12.0 Hz), 128.3, 128.1 (d, J_{C-P} = 9.0 Hz), 127.1, 126.8, 121.1, 119.9, 115.1, 114.3, 114.1, 114.0, 107.6 (d, J_{C-P} = 117.0 Hz), 89.6, 87.8, 55.2, 48.9; ³¹P{¹H} NMR (243 MHz, CDCl₃): δ = 21.9; HRMS (ESI): Exact mass calcd for C₄₂H₃₁O₃P [M+Na]⁺: 637.1903, Found: 637.1901.

2d) Suzuki coupling reaction for the synthesis of 9

Compound **9** was prepared from **7** (63.0 mg, 0.1 mmol) and phenylboronic acid (24.4 mg, 0.2 mmol) according to the literature procedure.⁵ Column chromatography afforded the desired product **9** in 85% yield (47.5 mg) as white solid. Mp: 62-64 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.73-7.70 (m, 5H), 7.55-7.52 (m, 4H), 7.44-7.38 (m, 6H), 7.32-7.30 (m, 1H), 7.28-7.26 (m, 1H), 7.24-7.23 (m, 8H), 7.21-7.18 (m, 2H), 6.80 (d, J = 8.4 Hz, 1H), 6.40 (s, 1H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 167.0 (d, J_{C-P} = 18.0 Hz), 155.2 (d, J_{C-P} = 12.0 Hz), 140.5 (d, J_{C-P} = 15.0 Hz), 138.3, 132.8 (d, J_{C-P} = 108.0 Hz), 132.2, 131.7 (d, J_{C-P} = 9.0 Hz), 129.1, 128.8, 128.7, 128.6, 128.3, 127.32, 127.27, 127.2, 126.7, 123.0, 121.4, 110.0, 107.3 (d, J_{C-P} = 117.0 Hz), 49.0; ³¹P{¹H} NMR (243 MHz, CDCl₃): δ = 22.1; HRMS (ESI): Exact mass calcd for C₃₉H₂₉O₂P [M+Na]⁺: 583.1797, Found: 583.1799.

2e) Sonogashira coupling reaction for the synthesis of 10

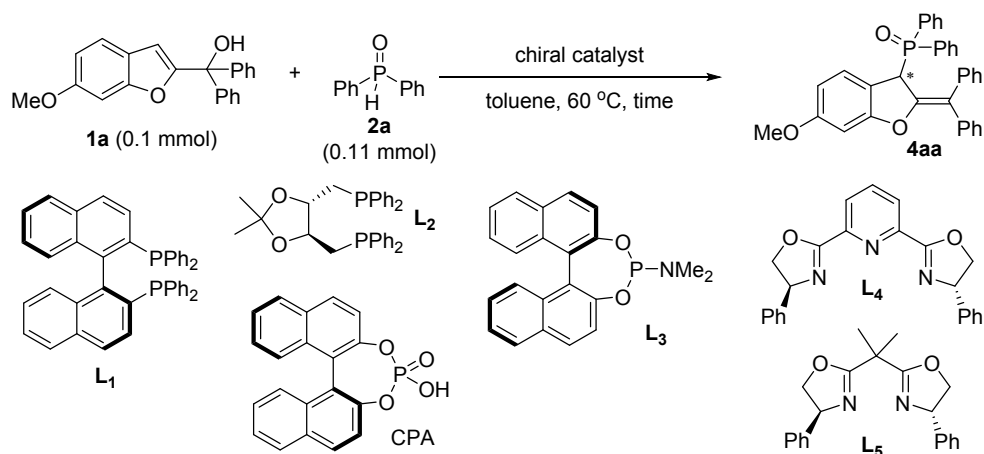
Compound **10** was prepared from **4ac** (59.3 mg, 0.1 mmol) and phenylacetylene (30.6 mg, 0.3 mmol) according to the literature procedure.⁴ Column chromatography afforded the desired product **13** in 72% yield (44.2 mg) as yellow solid. Mp: 173-175 °C; ¹H NMR (600 MHz, CDCl₃): δ = 7.71-7.67 (m, 4H), 7.57-7.55 (m, 2H), 7.48-7.46 (m, 2H), 7.45-7.42 (m, 4H), 7.32-7.29 (m, 3H), 7.26-7.23 (m, 4H), 7.22-7.20 (m, 2H), 7.17-7.16 (m, 4H), 7.023-7.022 (m, 1H), 6.95 (s, 1H), 6.13 (s, 1H), 3.89 (s, 3H); ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 165.6 (d, J_{C-P} = 16.5 Hz), 158.4, 155.4 (d, J_{C-P} = 12.0 Hz), 140.5, 132.4 (d, J_{C-P} = 109.5 Hz), 132.3, 131.8, 131.7, 131.5, 129.0, 128.8 (d, J_{C-P} = 13.5 Hz), 128.3, 128.2, 128.0, 126.8, 125.8, 123.4, 121.1 (d, J_{C-P} = 10.5 Hz), 109.5, 107.2 (d, J_{C-P} = 115.5 Hz), 94.7, 92.6, 85.6, 56.2, 48.9; ³¹P{¹H} NMR (243 MHz, CDCl₃): δ = 22.1; HRMS (ESI): Exact mass calcd for C₄₂H₃₁O₃P [M+H]⁺: 615.2084, Found: 615.2083.

⁵ N. Eleya, A. Mahal, M. Hein, A. Villiger, P. Langer, *Adv. Synth. Catal.*, 2011, **353**, 2761.

6. Asymmetric feasibility of this dearomative C3-phosphorylation of 2-benzofuran-ol

The asymmetric version of the dearomative C3-phosphorylation of 2-benzofuran-ol **1a** with $\text{Ph}_2\text{P(O)H}$ (**2a**) was investigated by brief screening typical N- and P- ligands **L**₁-**L**₅ and chiral phosphoric acid (CPA), and the results were shown in Table S2.

Table S2. Brief screening chiral ligand



entry ^a	Chiral catalyst	time/h	yield ^b /%	ee ^c /%
1	$\text{Bi}(\text{OTf})_3$ (10 mol%)+ L ₁ (11 mol%)	0.5	82	1.0
2	$\text{Bi}(\text{OTf})_3$ (10 mol%)+ L ₂ (11 mol%)	4.0	68	2.5
3	$\text{Bi}(\text{OTf})_3$ (10 mol%)+ L ₃ (11 mol%)	0.5	83	1.0
4	$\text{Bi}(\text{OTf})_3$ (10 mol%)+ L ₄ (11 mol%)	2.0	86	1.5
5	$\text{Bi}(\text{OTf})_3$ (10 mol%)+ L ₅ (11 mol%)	5.0	82	2.0
6	$\text{Bi}(\text{OTf})_3$ (10 mol%)+CPA (11 mol%)	0.5	80	0.0
7	CPA (10 mol%)	12.0	68	0.0

^a 0.1 mmol scale; ^b isolated yield; ^c determined by chiral HPLC.

7. X-ray Crystallographic Data of 4aa

Data intensity of **4aa** was collected on a 'Bruker APEX-II CCD' diffractometer at 299 K. Data collection and reduction were done by using Olex2 and the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization. Hydrogen atoms were added at their geometrically ideal positions and refined isotropically. Crystal data for **4aa**: C₃₄H₂₇O₃P, *T* = 299 K, triclinic, space group P-1 (no. 2), *a* = 5.7794(2) Å, *b* = 10.4840(4) Å, *c* = 22.3150(10) Å, α = 91.944(2) deg, β = 90.968(2) deg, γ = 101.813(2) deg, *V* = 1322.30(9) Å³. *Z* = 2, *d*_{calc} = 1.292 g/m³. 44658 reflections measured (4.308° ≤ 2 θ ≤ 58.34°), 7068 unique [*R*_{int} = 0.1511, *R*_{sigma} = 0.1194] which were used in all calculations. The final *R*₁ was 0.0746 (*I* > 2 σ (*I*)) and *wR*₂ was 0.2060 (all data).

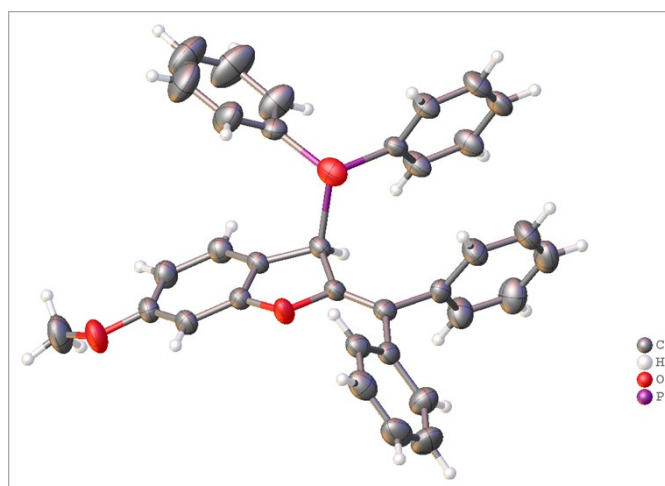


Table S3. Crystal data and structure refinement for mo_CL-ZH-65_0m.

Identification code	mo_CL_ZH_65_0m
Empirical formula	C ₃₄ H ₂₇ O ₃ P
Formula weight	514.52
Temperature/K	299.0
Crystal system	triclinic
Space group	P-1
<i>a</i> /Å	5.7794(2)
<i>b</i> /Å	10.4840(4)
<i>c</i> /Å	22.3150(10)
α /°	91.944(2)
β /°	90.968(2)
γ /°	101.813(2)
Volume/Å ³	1322.30(9)

Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.292
μ/mm^{-1}	0.138
F(000)	540.0
Crystal size/ mm^3	$0.4 \times 0.2 \times 0.1$
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	4.308 to 58.34
Index ranges	$-7 \leq h \leq 7, -14 \leq k \leq 14, -30 \leq l \leq 30$
Reflections collected	44658
Independent reflections	7068 [$R_{\text{int}} = 0.1511, R_{\text{sigma}} = 0.1194$]
Data/restraints/parameters	7068/0/344
Goodness-of-fit on F^2	1.029
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0746, wR_2 = 0.1770$
Final R indexes [all data]	$R_1 = 0.1233, wR_2 = 0.2060$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.63/-0.72

Table S4. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for mo_CL-ZH-65_0m. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
P001	2667.1(9)	2880.5(5)	2963.9(3)	31.65(18)
O002	3000(3)	6088.3(13)	2478.5(7)	38.2(4)
O003	186(3)	3068.5(15)	2966.9(8)	44.0(4)
O003	186(3)	3068.5(15)	2966.9(8)	44.0(4)
O004	8077(3)	8921.7(16)	3865.6(8)	54.1(5)
C005	2171(4)	4607(2)	1647.4(10)	34.5(5)
C006	5863(3)	5323.4(18)	2996.2(10)	30.7(4)
C007	3170(4)	4906.4(18)	2186.0(10)	33.0(5)
C008	4757(4)	6357.8(19)	2917.2(10)	31.9(5)
C009	4650(3)	4213.0(18)	2580.2(10)	31.4(5)
C00A	802(4)	5469(2)	1347.8(10)	36.6(5)
C00B	-915(4)	5972(2)	1650.6(11)	39.4(5)
C00C	2414(4)	3384(2)	1305.4(10)	34.8(5)
C00D	2946(3)	1370.1(18)	2590.3(10)	31.8(5)
C00E	7789(4)	5488(2)	3380.7(11)	37.8(5)
C00F	3805(4)	2824(2)	3714.7(11)	39.7(5)
C00G	5437(4)	7548(2)	3212.4(10)	37.9(5)
C00H	7413(4)	7705(2)	3596.3(10)	38.1(5)
C00I	4948(4)	1176(2)	2301.6(12)	41.9(6)
C00J	8579(4)	6684(2)	3680.1(11)	41.3(5)

C00K	2976(4)	-1000(2)	2004.7(12)	45.3(6)
C00L	986(4)	349(2)	2601.3(11)	40.8(5)
C00M	4947(4)	-2(2)	2002.7(12)	45.5(6)
C00N	1023(4)	-830(2)	2313.1(12)	48.2(6)
C00O	-2233(4)	6747(2)	1366.9(13)	49.9(6)
C00P	4419(4)	3292(3)	998.8(12)	50.3(6)
C00Q	527(4)	2324(2)	1273.4(12)	47.6(6)
C00R	1145(5)	5778(3)	752.5(12)	53.7(7)
C00S	-1839(5)	7054(3)	783.4(14)	59.3(8)
C00T	688(5)	1197(2)	944.8(13)	58.5(7)
C00U	2668(5)	1122(3)	645.2(13)	57.7(7)
C00V	4558(5)	2164(3)	670.6(14)	59.4(7)
C00W	5538(5)	2139(3)	3858.0(14)	65.4(8)
C00X	2813(6)	3421(3)	4171.8(13)	65.4(8)
C00Y	-149(6)	6581(3)	477.1(14)	66.1(8)
C00Z	10288(5)	9232(3)	4175.7(15)	69.1(9)
C010	5234(7)	2673(4)	4893.1(16)	87.8(11)
C011	3548(7)	3367(4)	4759.8(16)	88.3(11)
C012	6221(6)	2079(5)	4449.5(16)	95.1(13)

Table S5. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for mo_CL-ZH-65_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*2U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P001	32.5(3)	24.7(3)	38.0(4)	2.9(2)	3.2(2)	5.89(19)
O002	50.4(9)	25.6(7)	38.4(9)	-4.6(6)	-13.9(7)	9.4(6)
O003	35.5(8)	39.5(9)	59.7(11)	2.2(8)	7.1(7)	13.6(6)
O004	63.7(11)	36.2(9)	58.7(12)	-17.0(8)	-15.9(9)	6.5(7)
C005	37.2(11)	29.2(10)	34.2(12)	2.8(9)	-1.3(9)	-0.2(8)
C006	34.7(10)	23.5(9)	33.1(12)	0.9(8)	-0.1(9)	4.2(7)
C007	40.6(11)	22.3(9)	33.8(12)	1.7(8)	-2.5(9)	1.6(8)
C008	37.4(11)	26.9(10)	30.5(12)	1.1(8)	-1.8(9)	4.6(8)
C009	35.8(10)	23.7(9)	33.8(12)	-0.4(8)	1.5(9)	4.1(7)
C00A	41.0(12)	29.4(10)	34.8(12)	1.2(9)	-6.8(9)	-3.0(8)
C00B	39.3(12)	32.8(11)	42.5(14)	2.9(10)	-5.7(10)	-0.8(8)
C00C	40.9(11)	31.8(10)	29.9(12)	-0.9(9)	-6.8(9)	3.9(8)
C00D	34.8(11)	23.6(9)	35.9(12)	5.8(8)	-2.3(9)	3.1(7)
C00E	38.6(11)	34.7(11)	40.8(13)	1.0(10)	-3.4(10)	9.8(8)
C00F	43.1(12)	34.2(11)	39.1(13)	7.5(10)	4.6(10)	0.7(9)
C00G	48.2(12)	27.7(10)	37.8(13)	-2.2(9)	-2.2(10)	8.7(9)
C00H	45.5(12)	30.0(11)	35.8(13)	-4.8(9)	-2.2(10)	2.1(9)

C00I	35.6(11)	29.1(11)	59.9(16)	0.8(10)	7.2(11)	3.5(8)
C00J	41.7(12)	40.1(12)	41.0(14)	-3.1(10)	-8.7(10)	7.5(9)
C00K	60.1(15)	23.0(10)	53.0(16)	1.2(10)	-3.0(12)	9.7(9)
C00L	35.0(11)	33.1(11)	51.7(15)	1.8(10)	3.0(10)	1.2(8)
C00M	44.6(13)	33.7(12)	60.9(17)	1.6(11)	7.9(11)	13.7(9)
C00N	46.5(13)	29.7(11)	62.6(18)	0.9(11)	-0.5(12)	-5.1(9)
C00O	42.2(13)	41.1(13)	64.7(19)	0.1(12)	-10.2(12)	5.6(10)
C00P	44.0(13)	51.7(15)	50.8(16)	-8.4(12)	-0.3(12)	1.4(10)
C00Q	50.1(14)	36.7(12)	51.0(16)	-3.6(11)	1.6(12)	-2.3(10)
C00R	68.6(17)	53.9(16)	40.4(15)	6.4(12)	-2.3(13)	16.2(12)
C00S	70.3(18)	44.1(14)	64(2)	9.6(13)	-20.8(15)	12.8(12)
C00T	74.0(18)	33.4(13)	60.9(19)	-5.6(12)	-0.7(15)	-4.1(12)
C00U	82(2)	43.0(14)	51.2(17)	-10.6(12)	-10.7(15)	22.2(13)
C00V	58.4(16)	64.6(18)	58.0(18)	-12.3(14)	-0.2(14)	21.9(13)
C00W	54.8(16)	101(2)	47.9(17)	9.6(16)	-1.3(13)	33.1(15)
C00X	90(2)	66.2(19)	45.0(17)	-0.7(14)	4.9(15)	28.0(16)
C00Y	98(2)	61.5(18)	41.4(16)	14.3(14)	-8.7(16)	21.1(16)
C00Z	76(2)	53.2(17)	72(2)	-20.5(15)	-27.5(17)	3.4(14)
C010	78(2)	139(4)	43.4(19)	12(2)	-9.5(17)	15(2)
C011	112(3)	112(3)	43.2(19)	-8.8(19)	6.8(19)	30(2)
C012	73(2)	167(4)	56(2)	23(2)	-9.0(18)	51(2)
P001	32.5(3)	24.7(3)	38.0(4)	2.9(2)	3.2(2)	5.89(19)
O002	50.4(9)	25.6(7)	38.4(9)	-4.6(6)	-13.9(7)	9.4(6)
O003	35.5(8)	39.5(9)	59.7(11)	2.2(8)	7.1(7)	13.6(6)
O004	63.7(11)	36.2(9)	58.7(12)	-17.0(8)	-15.9(9)	6.5(7)
C005	37.2(11)	29.2(10)	34.2(12)	2.8(9)	-1.3(9)	-0.2(8)
C006	34.7(10)	23.5(9)	33.1(12)	0.9(8)	-0.1(9)	4.2(7)
C007	40.6(11)	22.3(9)	33.8(12)	1.7(8)	-2.5(9)	1.6(8)
C008	37.4(11)	26.9(10)	30.5(12)	1.1(8)	-1.8(9)	4.6(8)

Table S6. Bond Lengths for mo_CL_ZH_65_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P001	O003	1.4872(15)	C00D	C00L	
P001	C009	1.859(2)	C00E	C00J	
P001	C00D	1.802(2)	C00F	C00W	
P001	C00F	1.797(2)	C00F	C00X	
O002	C007	1.403(2)	C00G	C00H	
O002	C008	1.378(2)	C00H	C00J	
O004	C00H	1.369(3)	C00I	C00M	
O004	C00Z	1.415(3)	C00K	C00M	

C005	C007	1.324(3)	C00K	C00N
C005	C00A	1.485(3)	C00L	C00N
C005	C00C	1.502(3)	C00O	C00S
C006	C008	1.381(3)	C00P	C00V
C006	C009	1.510(3)	C00Q	C00T
C006	C00E	1.372(3)	C00R	C00Y
C007	C009	1.519(3)	C00S	C00Y
C008	C00G	1.371(3)	C00T	C00U
C00A	C00B	1.390(3)	C00U	C00V
C00A	C00R	1.386(3)	C00W	C012
C00B	C00O	1.383(3)	C00X	C011
C00C	C00P	1.374(3)	C010	C011
C00C	C00Q	1.387(3)	C010	C012
C00D	C00I	1.382(3)		

Table S7. Bond Angles for mo_CL_ZH_65_0m.

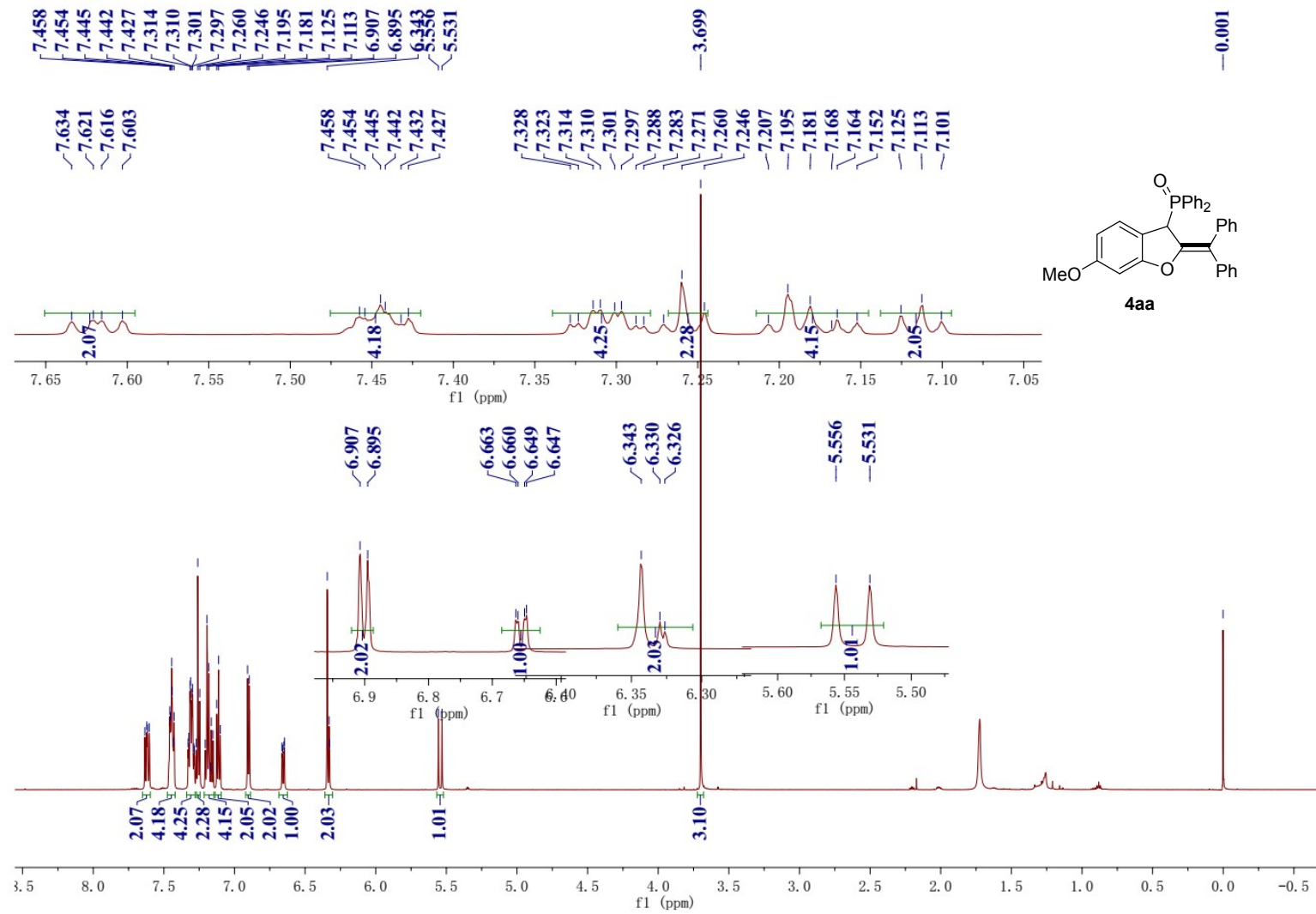
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O003	P001	C009	111.77(9)	C00I	C00D	C00L	
O003	P001	C00D	112.70(9)	C00L	C00D	P001	
O003	P001	C00F	111.02(11)	C006	C00E	C00J	
C00D	P001	C009	106.94(10)	C00W	C00F	P001	
C00F	P001	C009	108.18(10)	C00X	C00F	P001	
C00F	P001	C00D	105.92(10)	C00X	C00F	C00W	
C008	O002	C007	107.47(15)	C008	C00G	C00H	
C00H	O004	C00Z	117.96(19)	O004	C00H	C00G	
C007	C005	C00A	121.91(19)	O004	C00H	C00J	
C007	C005	C00C	121.23(19)	C00J	C00H	C00G	
C00A	C005	C00C	116.85(18)	C00D	C00I	C00M	
C008	C006	C009	107.65(17)	C00E	C00J	C00H	
C00E	C006	C008	118.95(19)	C00N	C00K	C00M	
C00E	C006	C009	133.29(18)	C00N	C00L	C00D	
O002	C007	C009	108.35(16)	C00K	C00M	C00I	
C005	C007	O002	119.52(18)	C00K	C00N	C00L	
C005	C007	C009	132.09(19)	C00S	C00O	C00B	
O002	C008	C006	112.36(17)	C00C	C00P	C00V	
C00G	C008	O002	123.71(18)	C00C	C00Q	C00T	
C00G	C008	C006	123.79(19)	C00A	C00R	C00Y	
C006	C009	P001	114.03(15)	C00O	C00S	C00Y	
C006	C009	C007	100.93(15)	C00U	C00T	C00Q	
C007	C009	P001	109.23(13)	C00T	C00U	C00V	

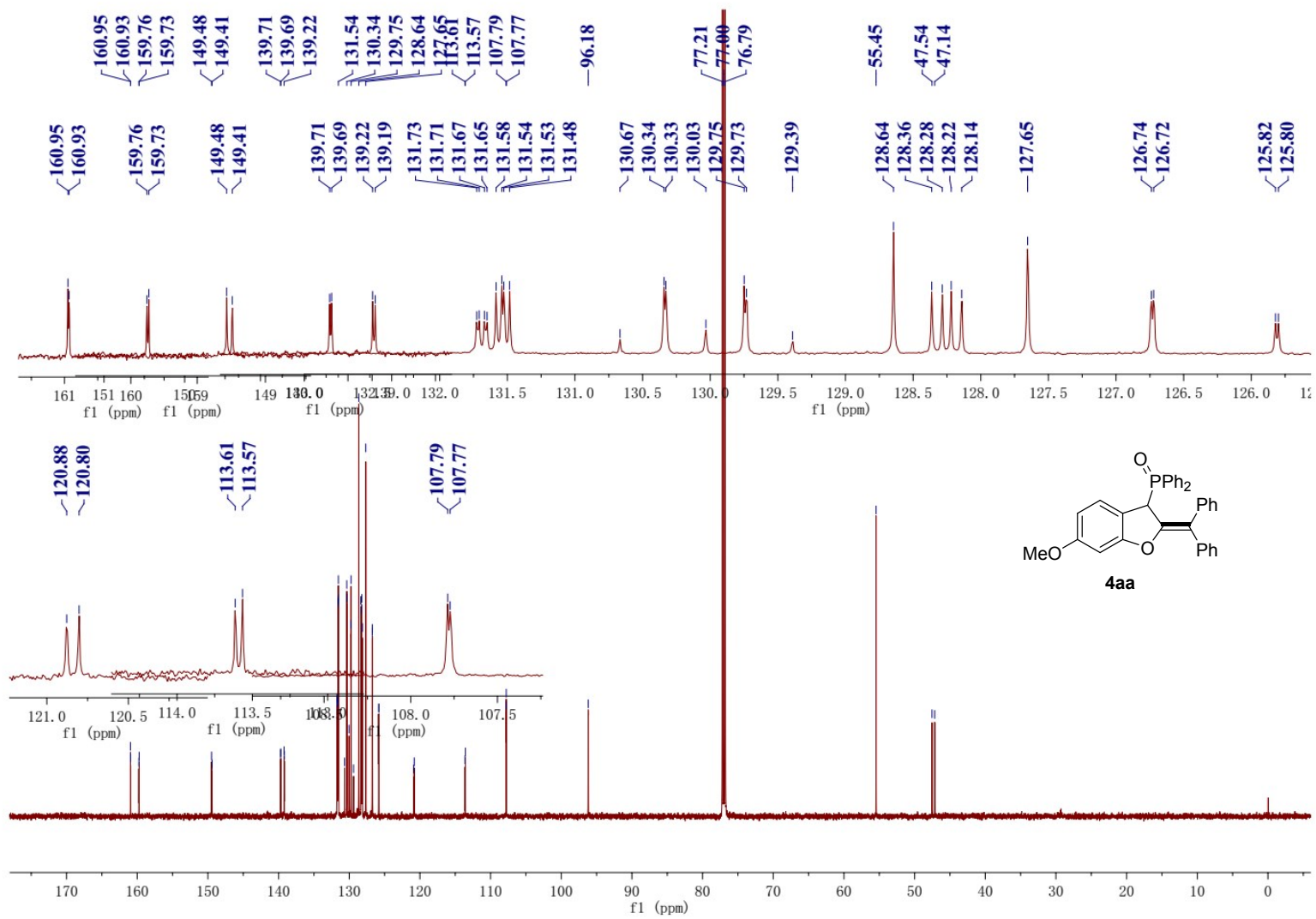
C00B	C00A	C005	121.2(2)	C00U	C00V	C00P
C00R	C00A	C005	121.4(2)	C012	C00W	C00F
C00R	C00A	C00B	117.4(2)	C00F	C00X	C011
C00O	C00B	C00A	121.2(2)	C00S	C00Y	C00R
C00P	C00C	C005	122.20(19)	C012	C010	C011
C00P	C00C	C00Q	118.3(2)	C010	C011	C00X
C00Q	C00C	C005	119.5(2)	C010	C012	C00W
O003	P001	C009	111.77(9)	C00I	C00D	C00L
O003	P001	C00D	112.70(9)	C00L	C00D	P001
O003	P001	C00F	111.02(11)	C006	C00E	C00J
C00D	P001	C009	106.94(10)	C00W	C00F	P001
C00F	P001	C009	108.18(10)	C00X	C00F	P001
C00F	P001	C00D	105.92(10)	C00X	C00F	C00W
C008	O002	C007	107.47(15)	C008	C00G	C00H
C00I	C00D	P001	124.37(15)			

Table S8. Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for mo_CL_ZH_65_0m.

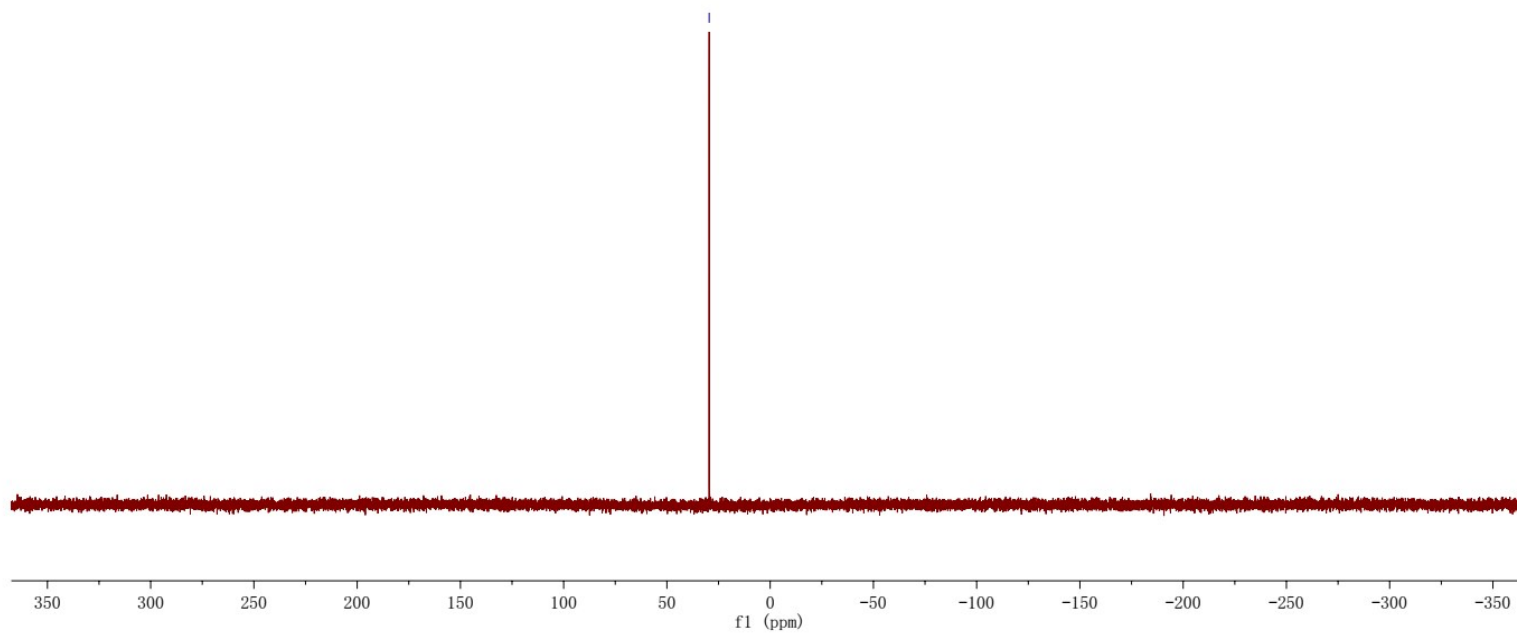
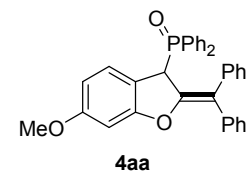
Atom	x	y	z	U(eq)
H009	5809	3868	2342	38
H00B	-1182	5784	2051	47
H00E	8558	4804	3440	45
H00G	4623	8216	3159	45
H00I	6296	1836	2308	50
H00J	9893	6804	3938	50
H00K	2973	-1785	1797	54
H00L	-355	462	2804	49
H00M	6282	-122	1799	55
H00N	-283	-1514	2328	58
H00O	-3394	7060	1575	60
H00P	5698	3994	1012	60
H00Q	-855	2368	1473	57
H00R	2258	5442	535	64
H00S	-2717	7583	595	71
H00T	-581	489	931	70
H00U	2755	368	422	69
H00V	5930	2111	468	71
H00W	6237	1723	3557	78
H00X	1625	3870	4083	78
H00Y	136	6799	81	79

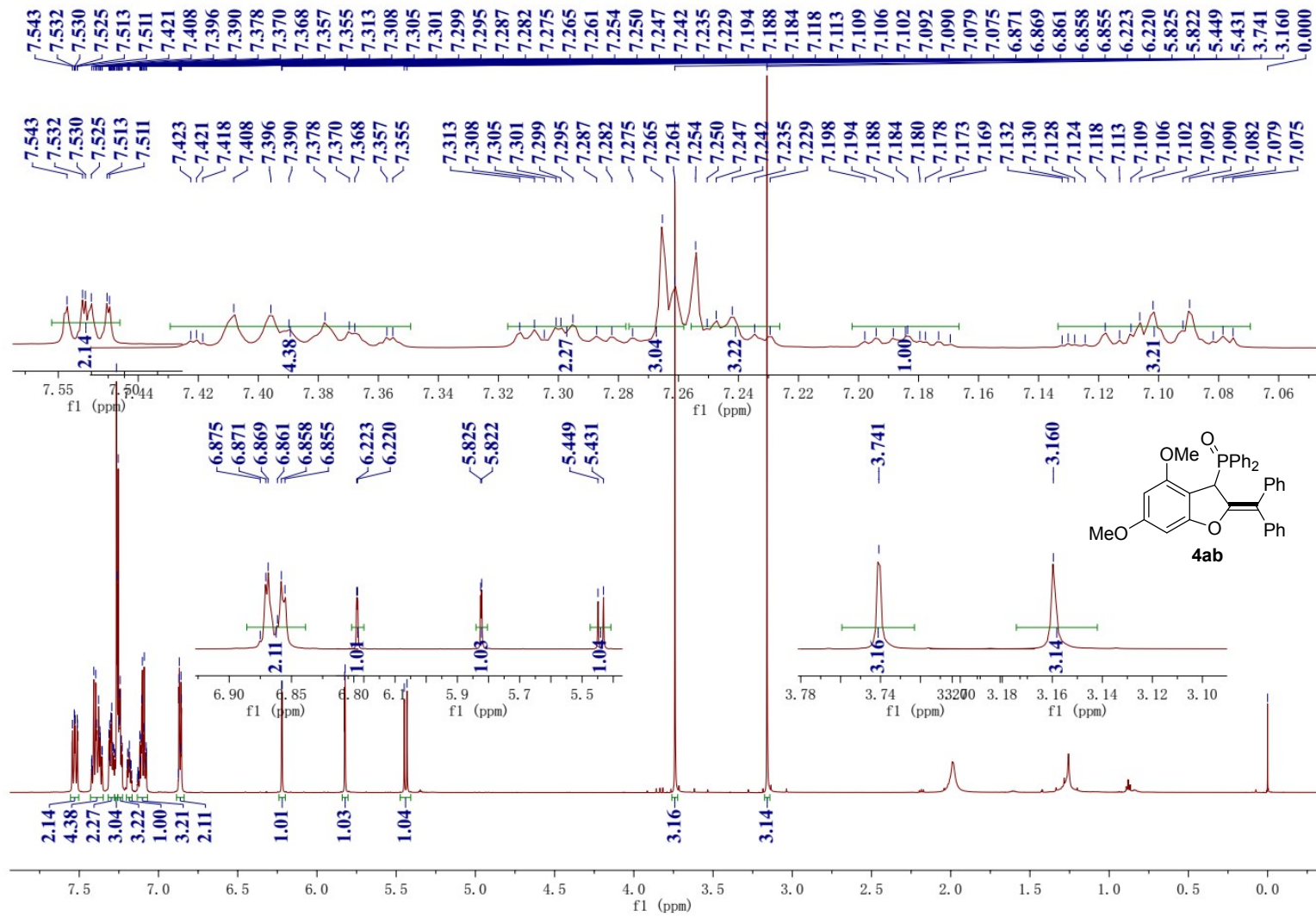
H00A	11494	9028	3921	104
H00C	10218	8734	4530	104
H00D	10650	10146	4286	104
H010	5702	2610	5290	105
H011	2899	3801	5064	106
H012	7385	1619	4544	114

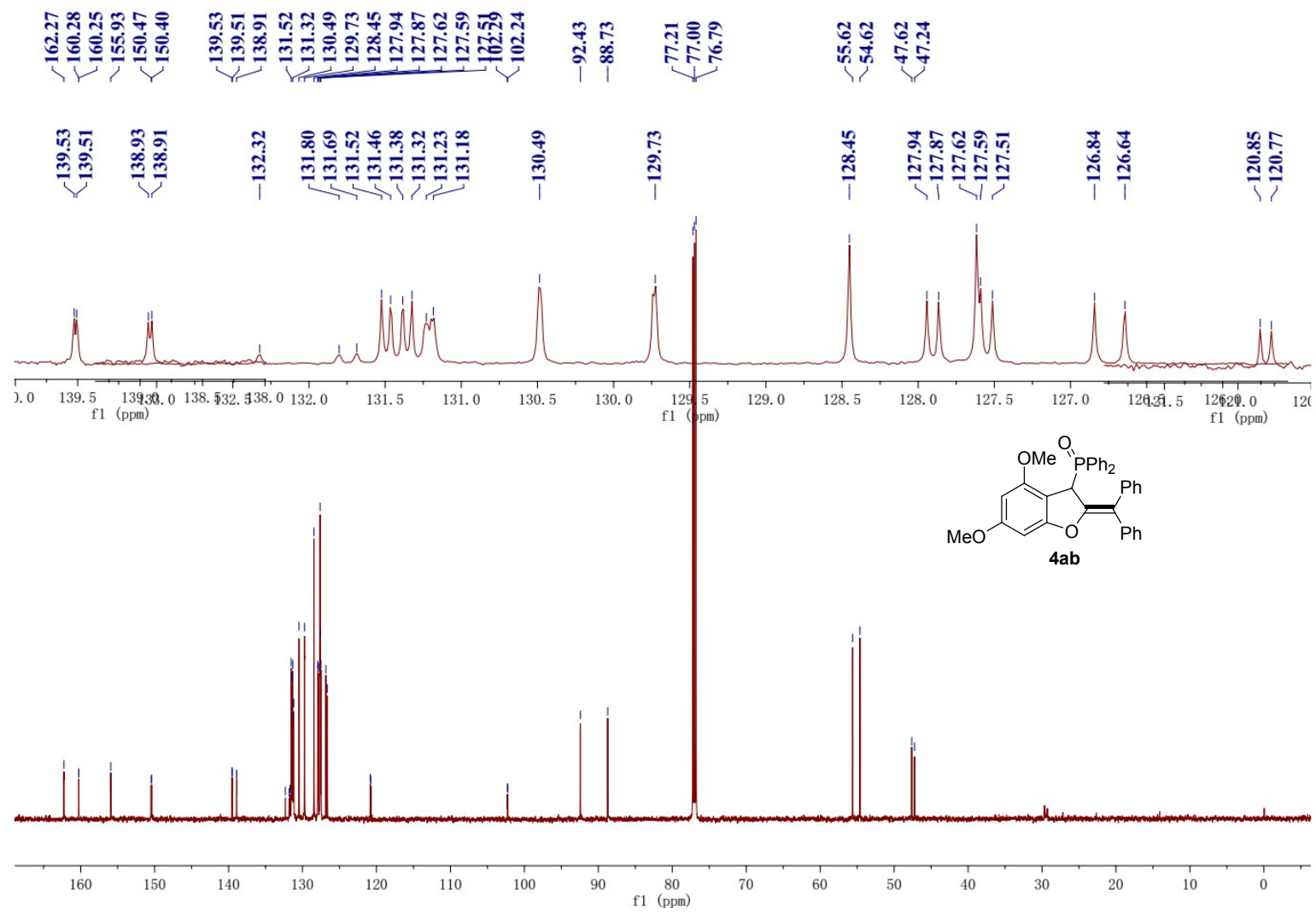


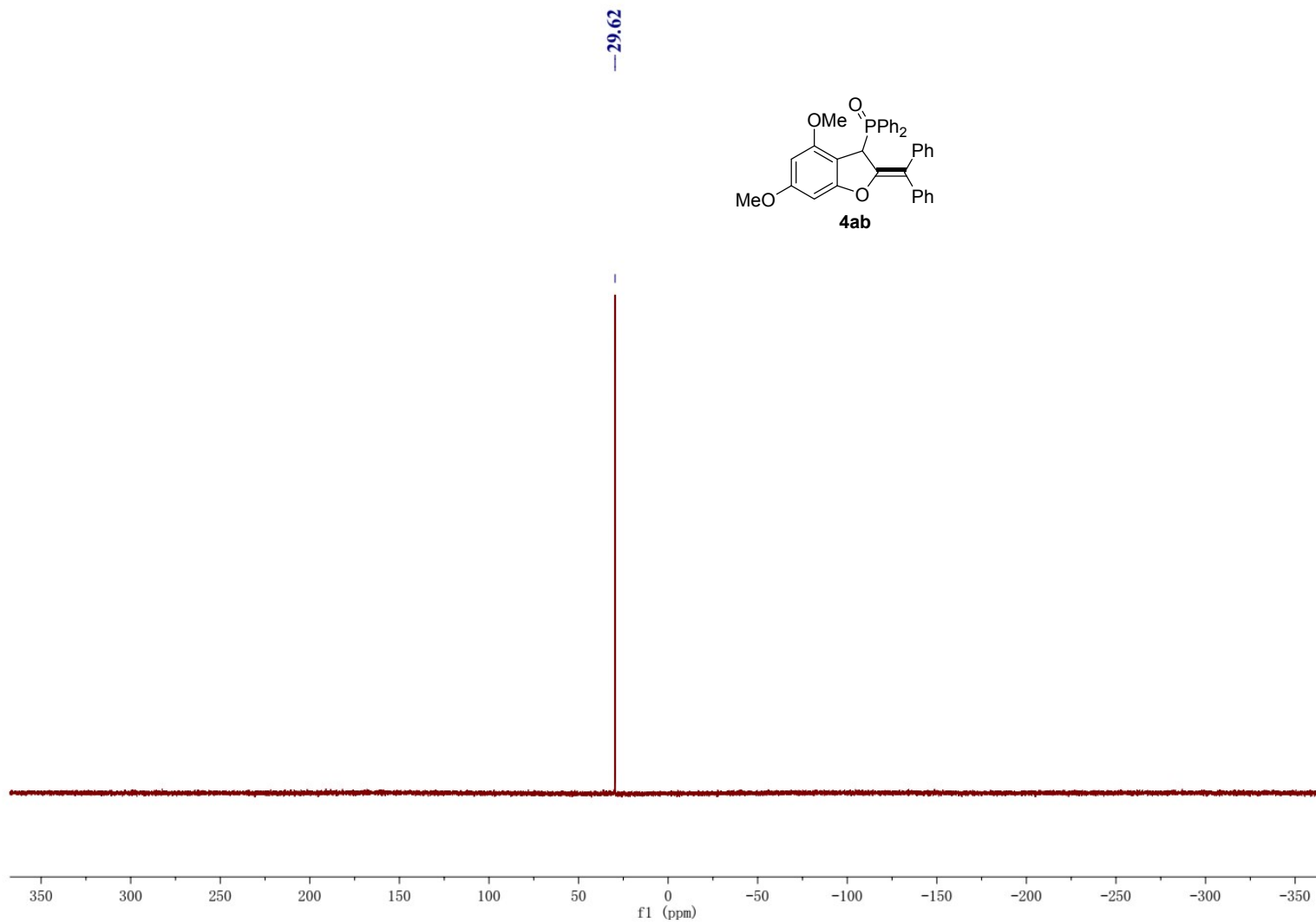


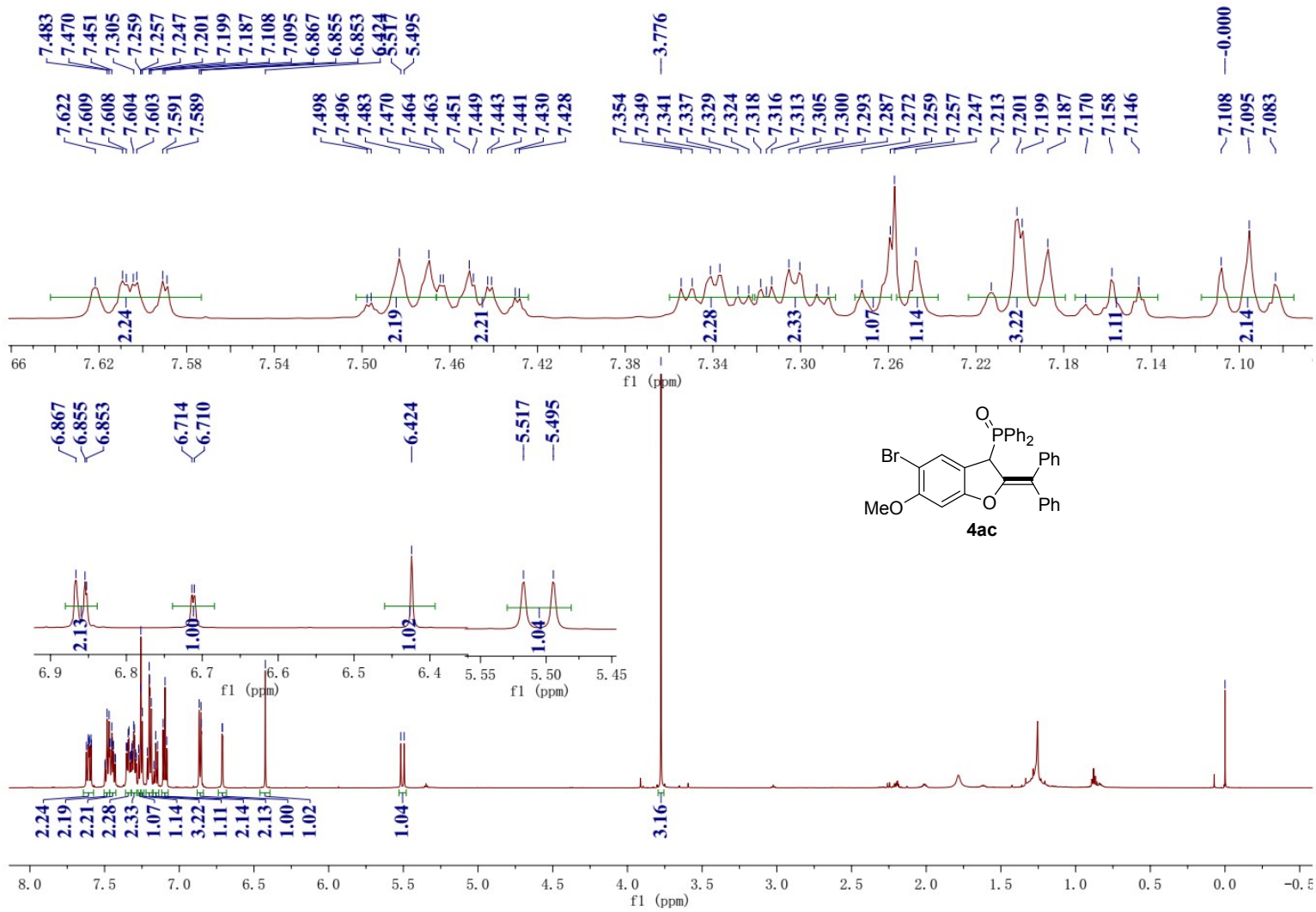
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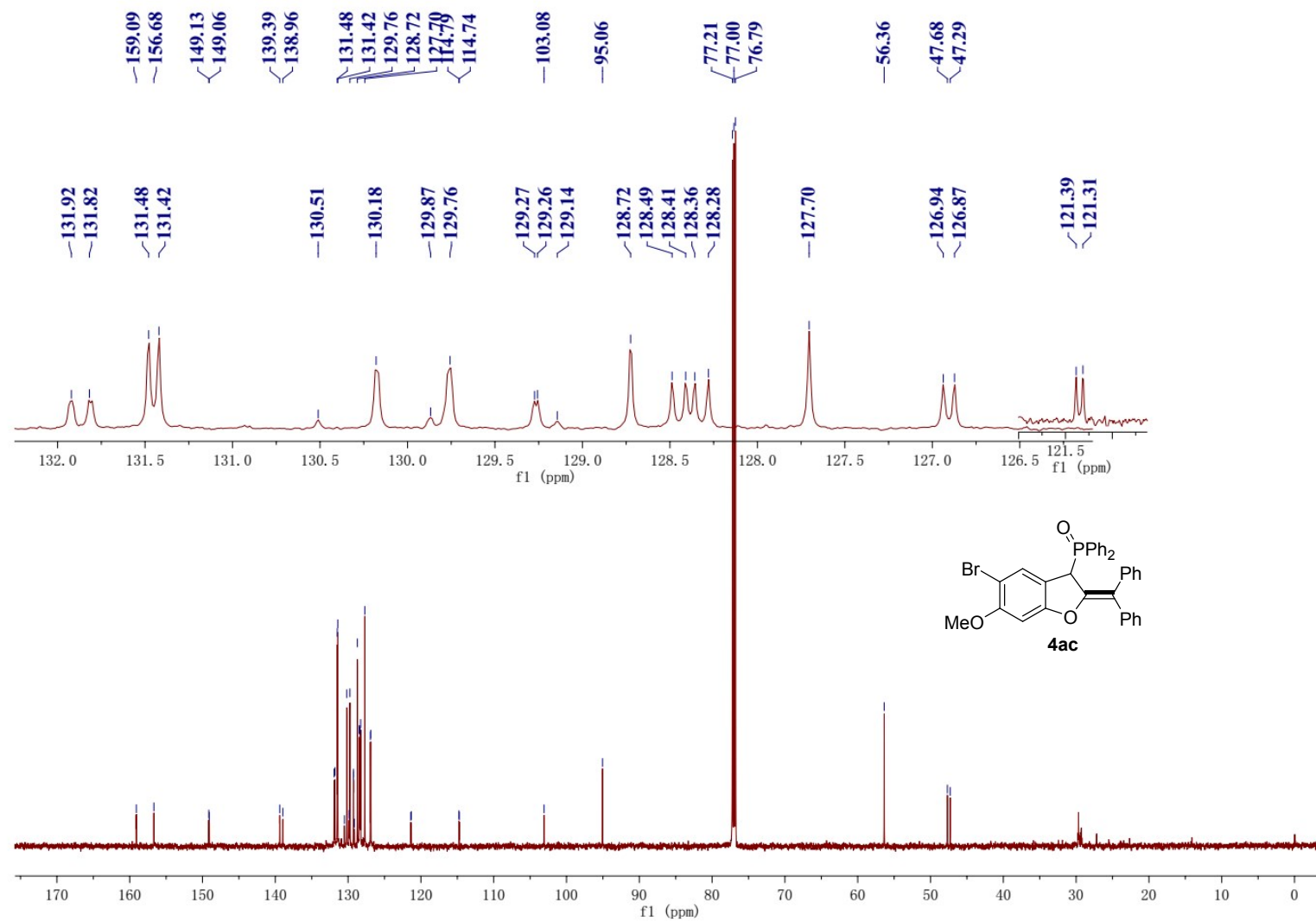


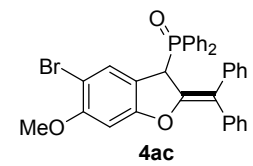




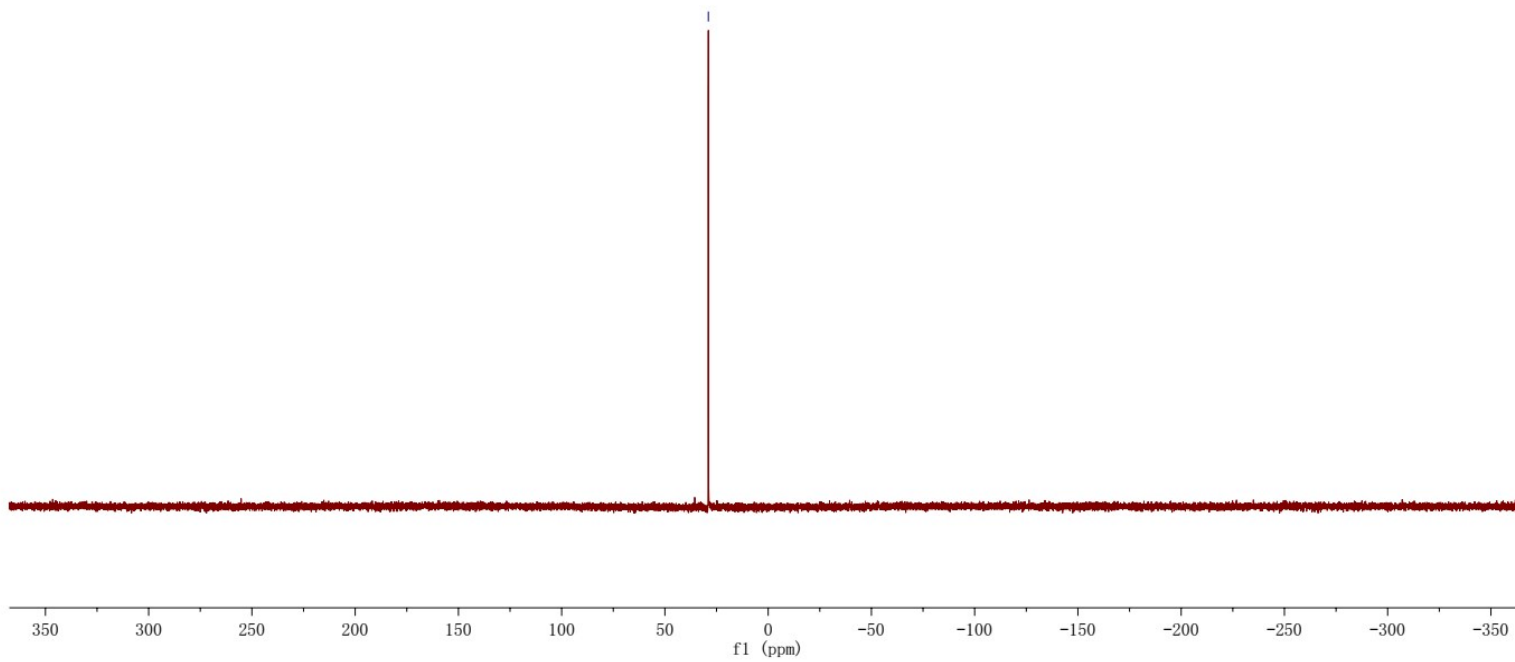


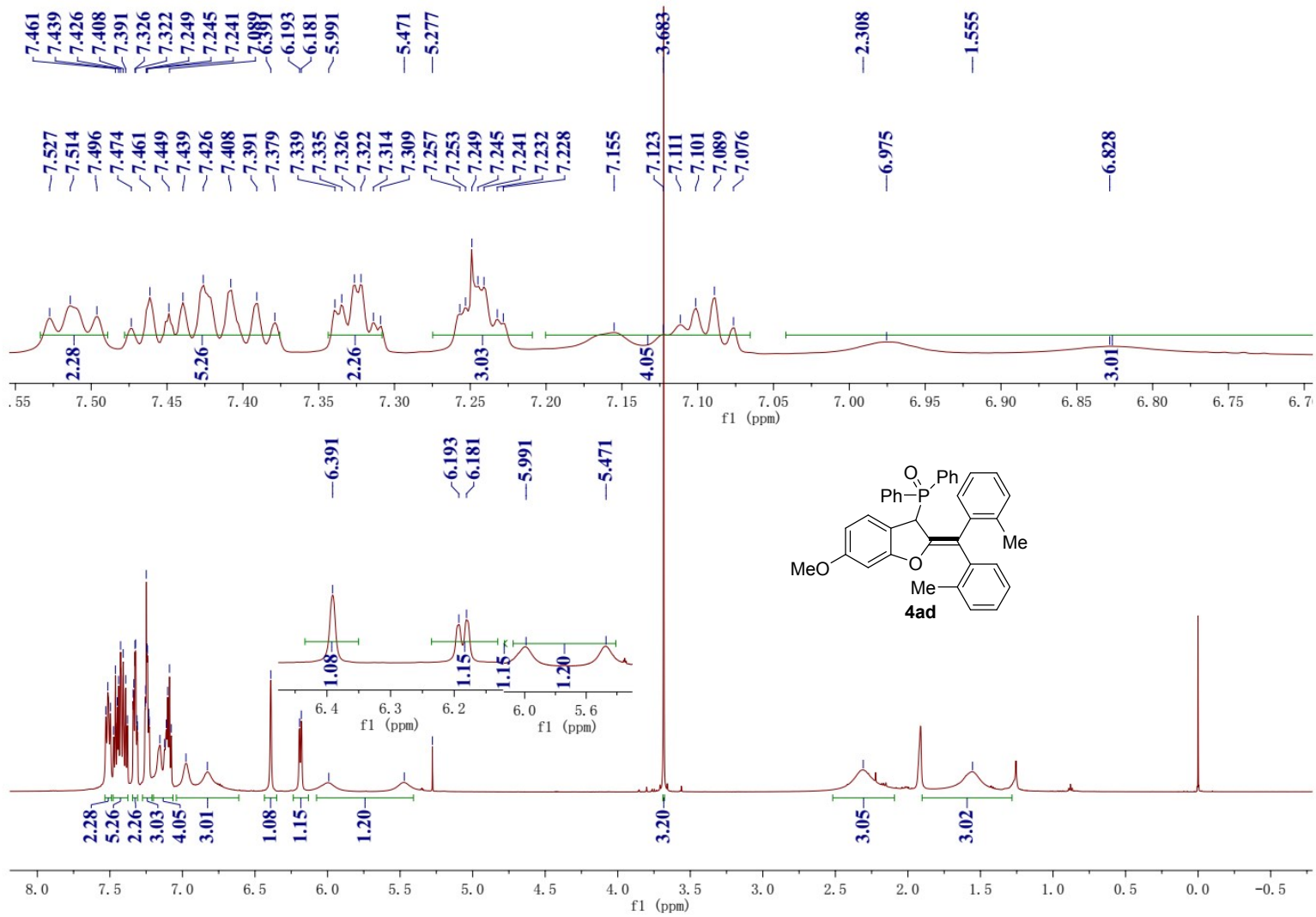


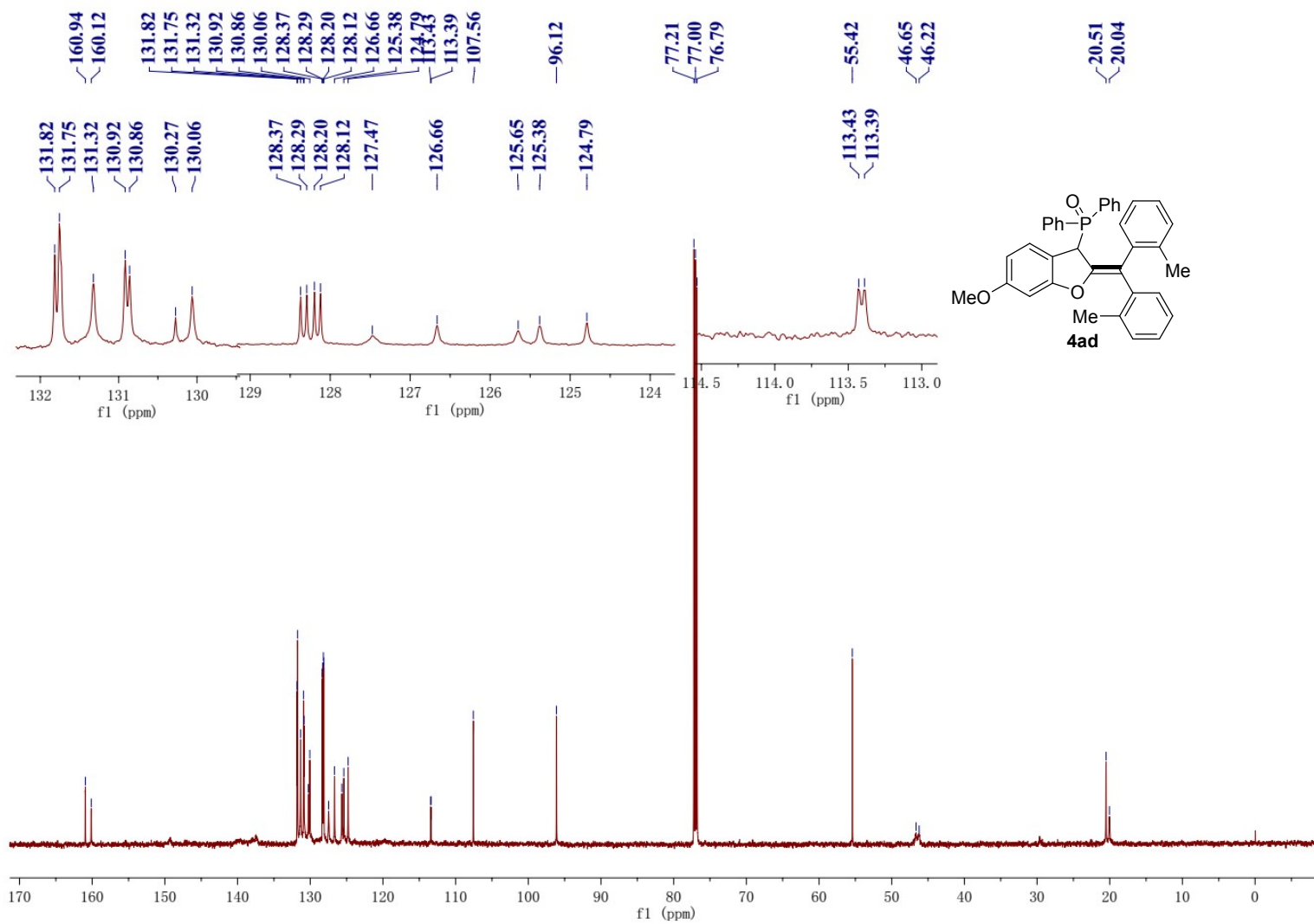


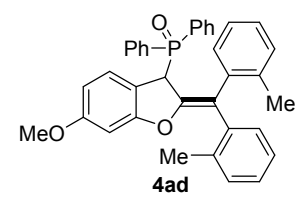


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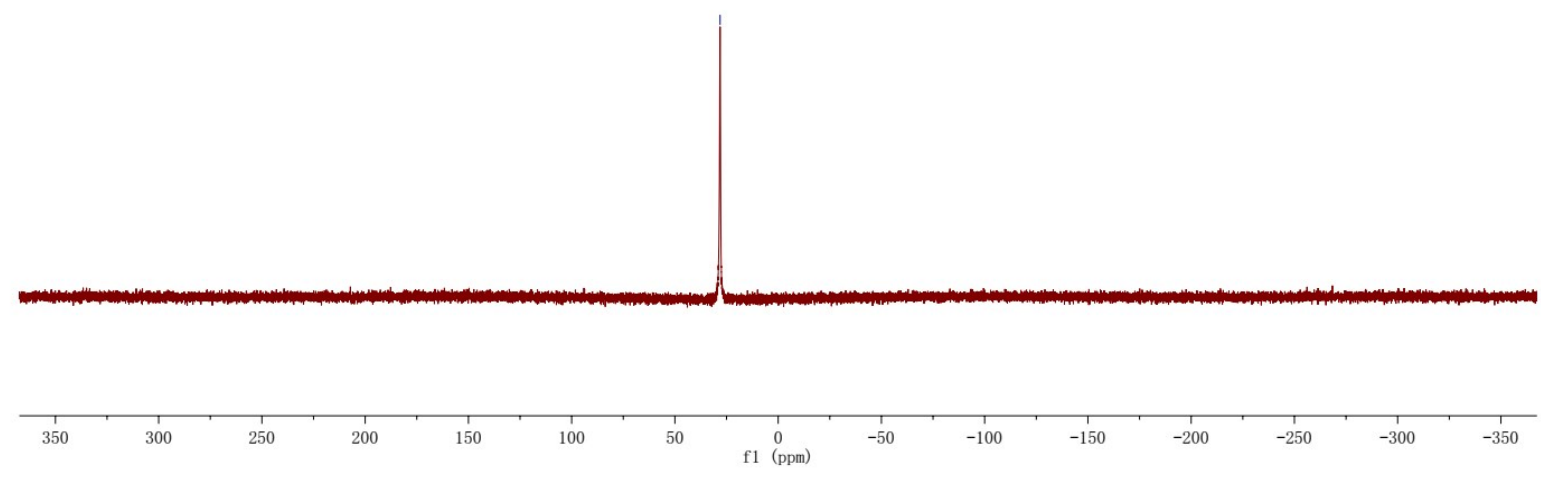


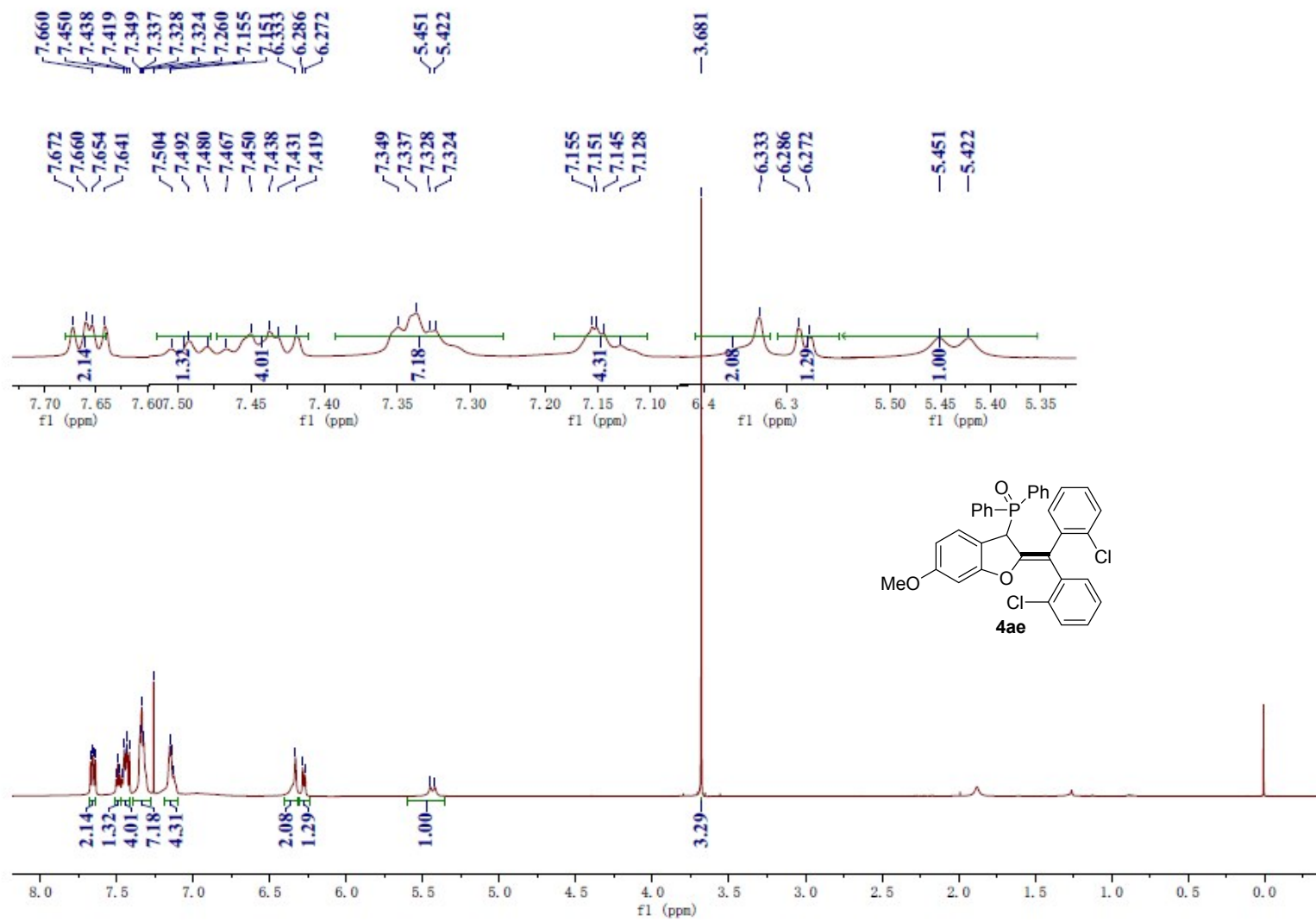


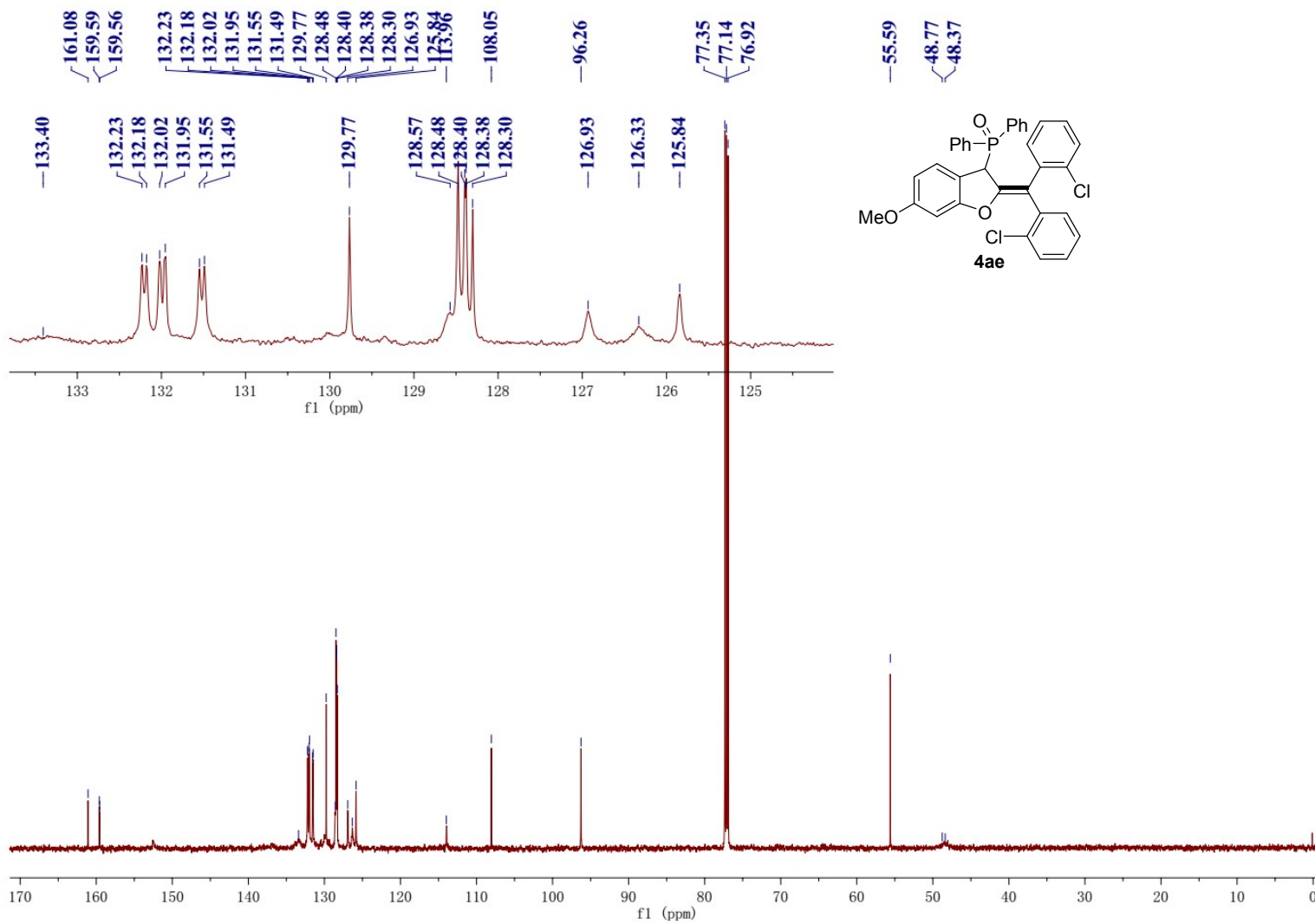




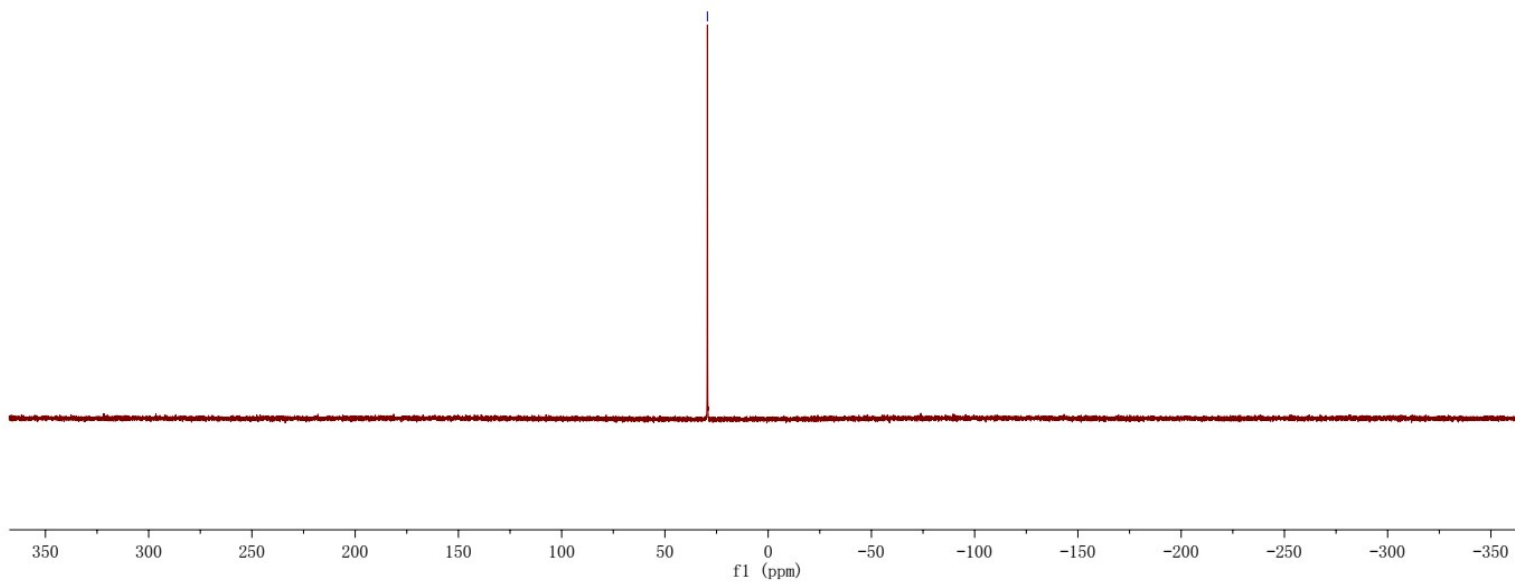
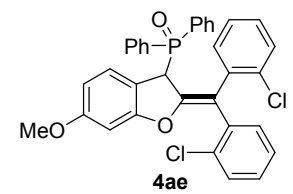
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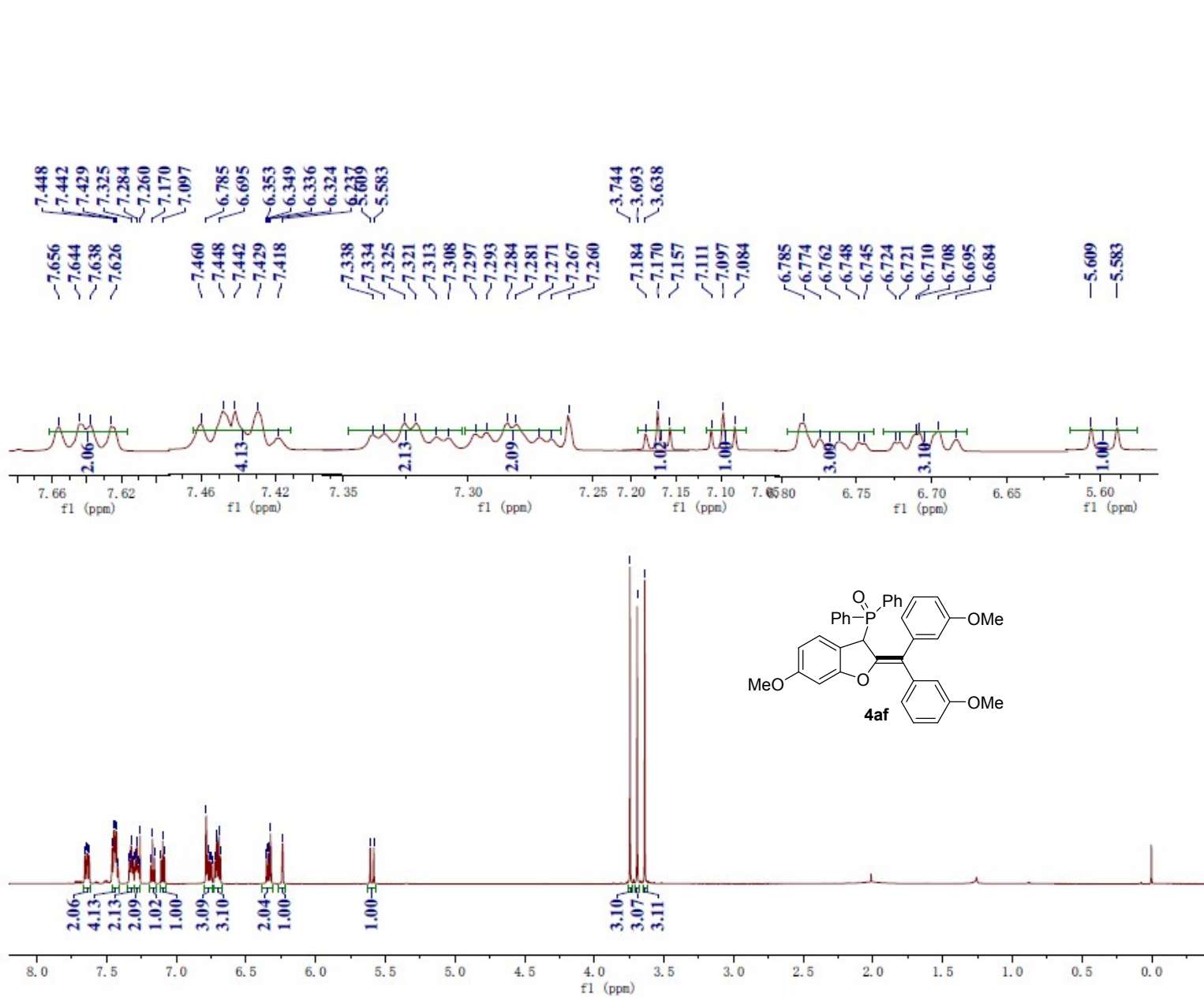


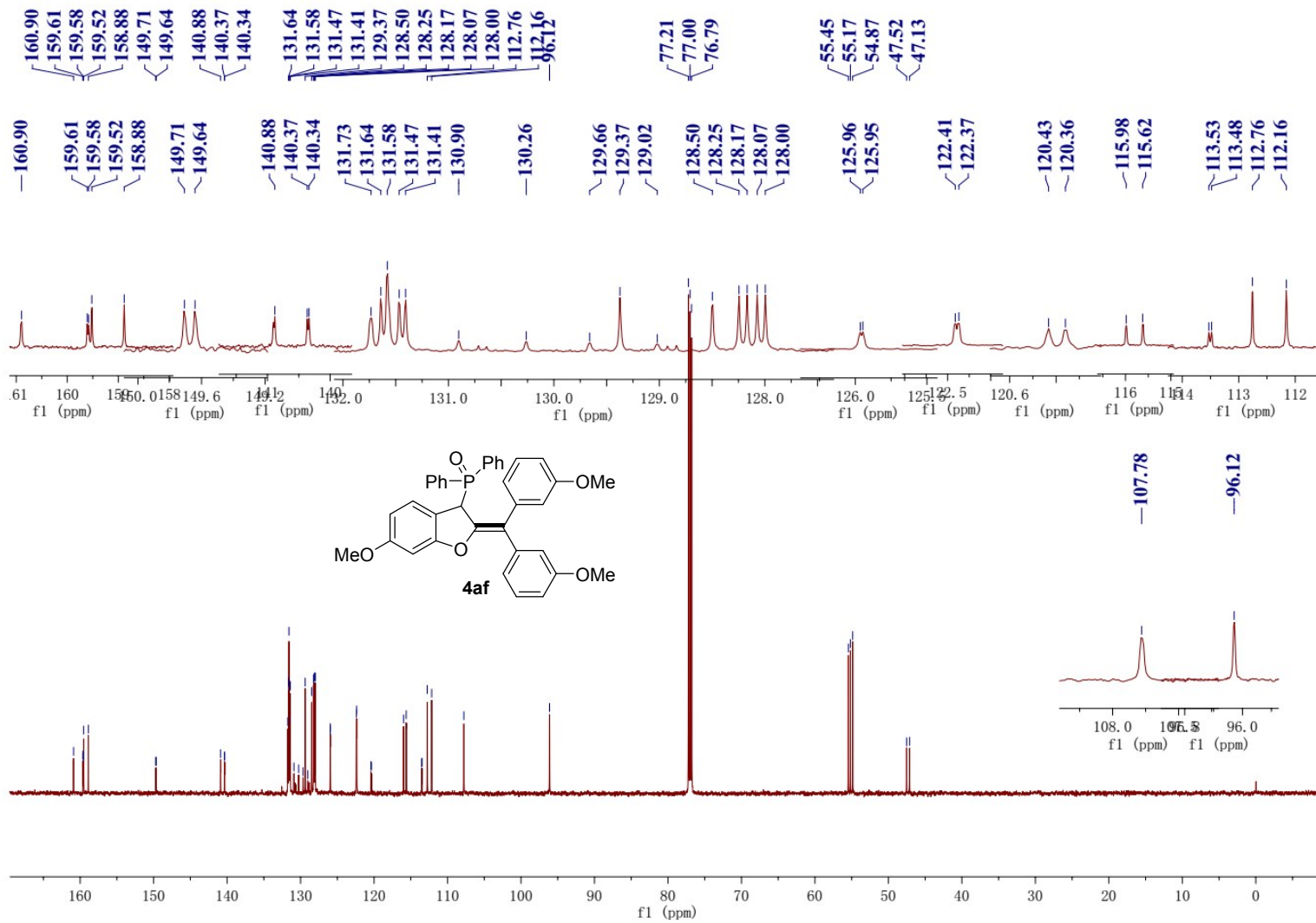


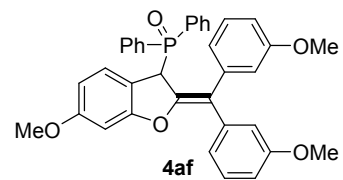


— 29.42

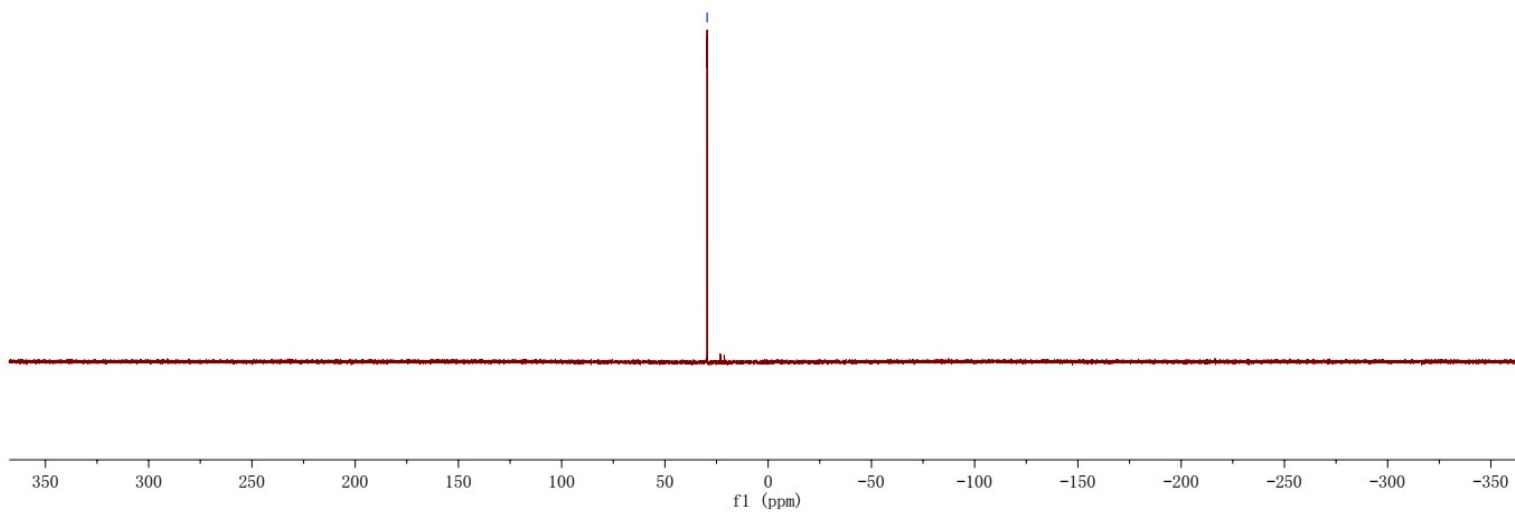


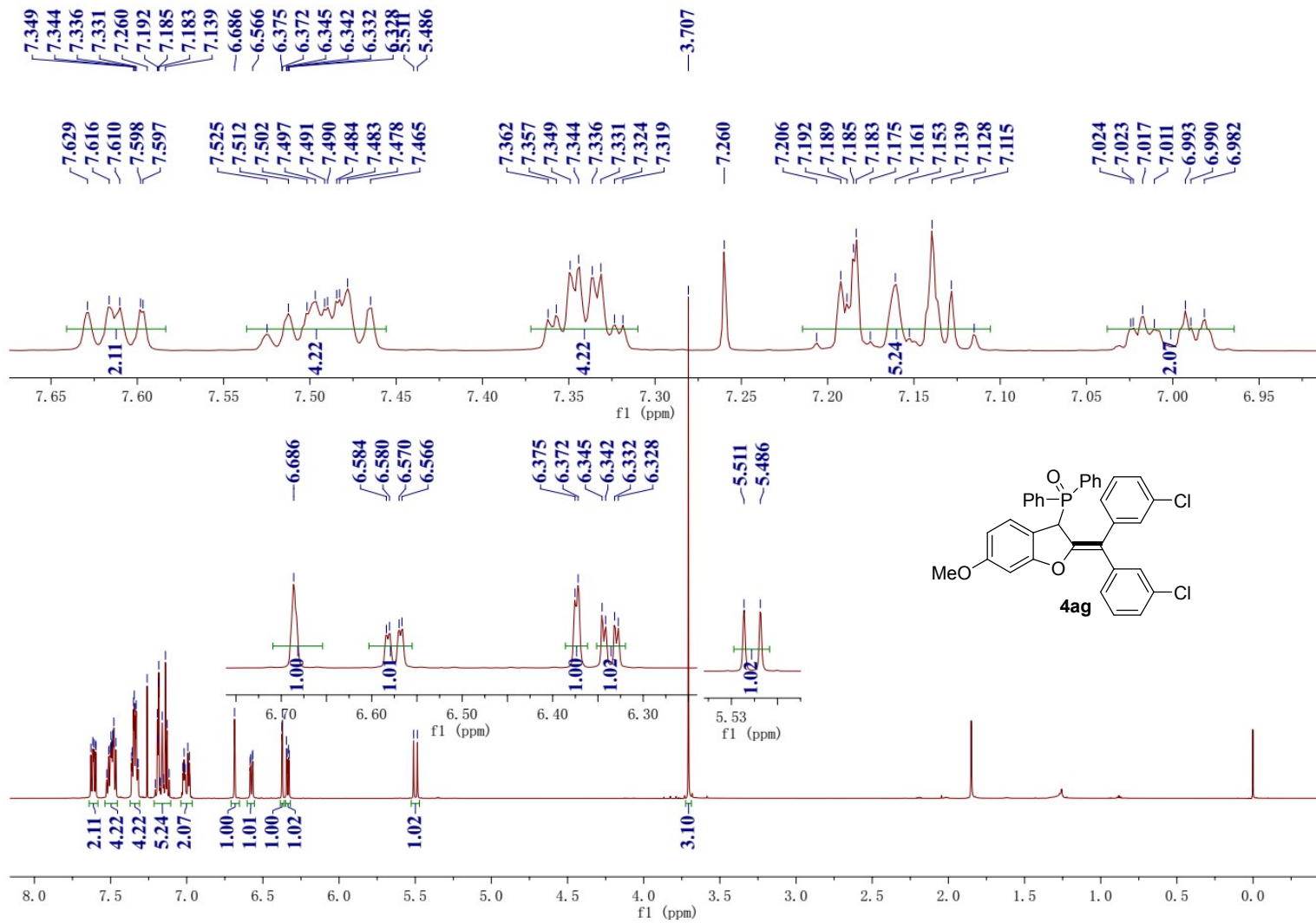


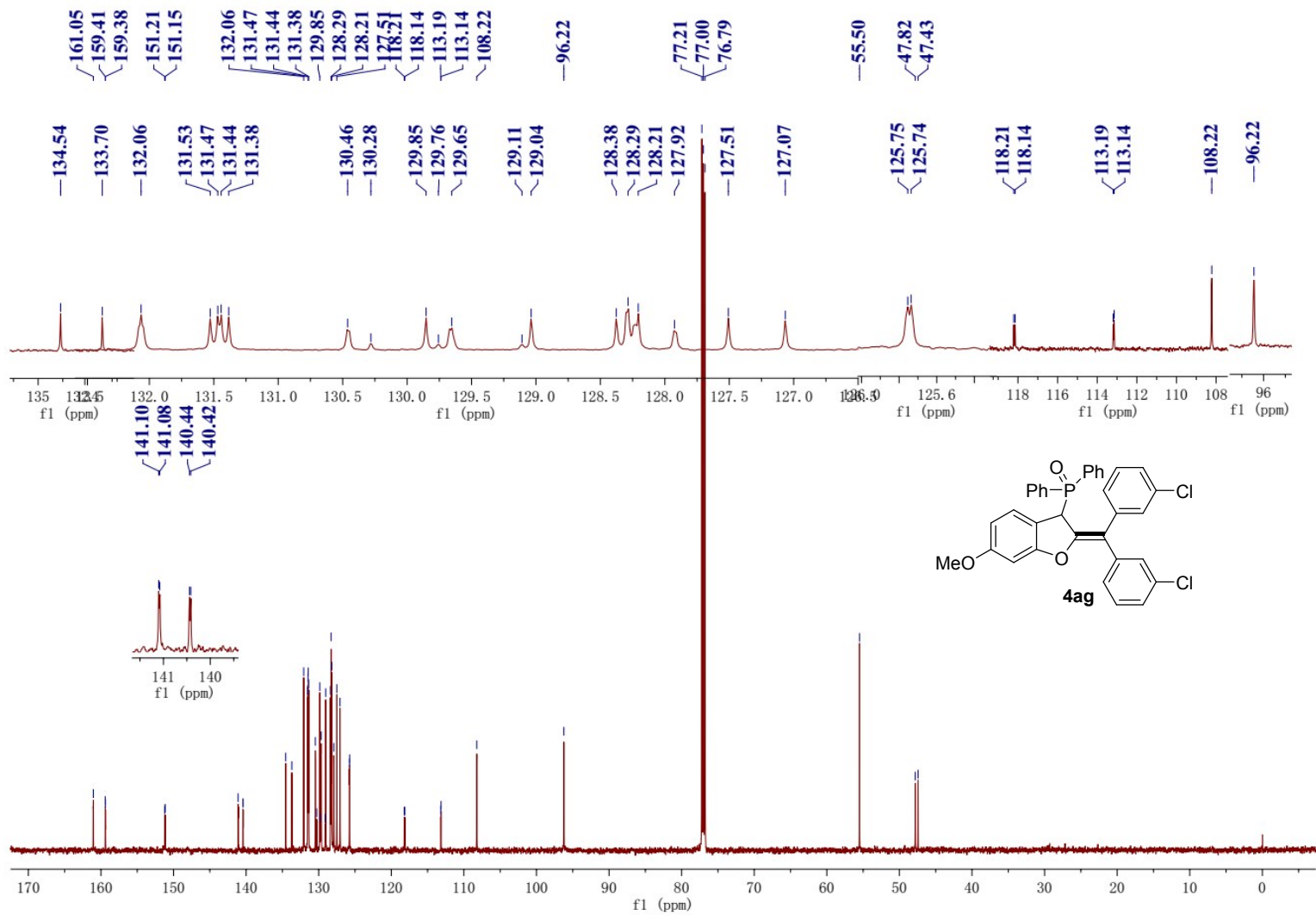




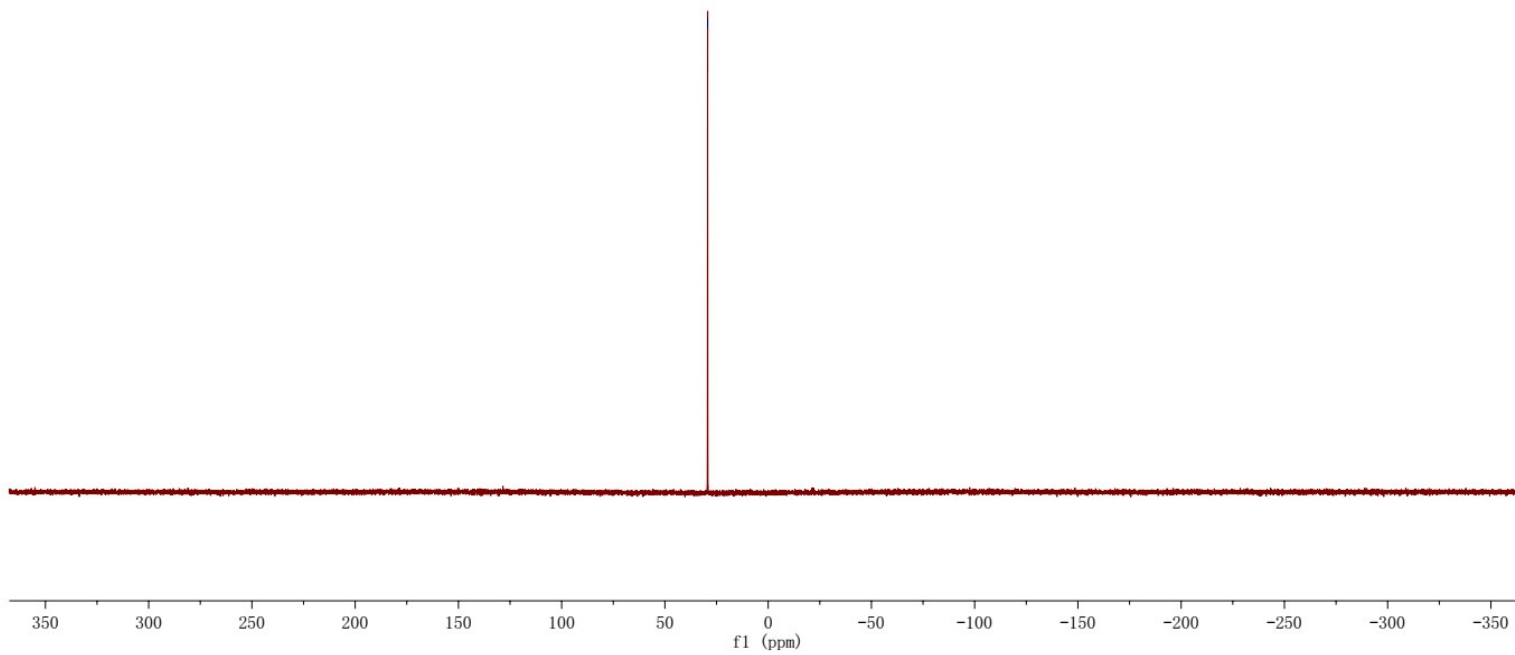
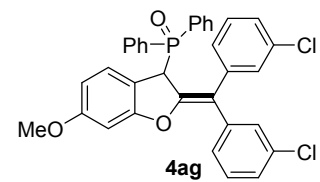
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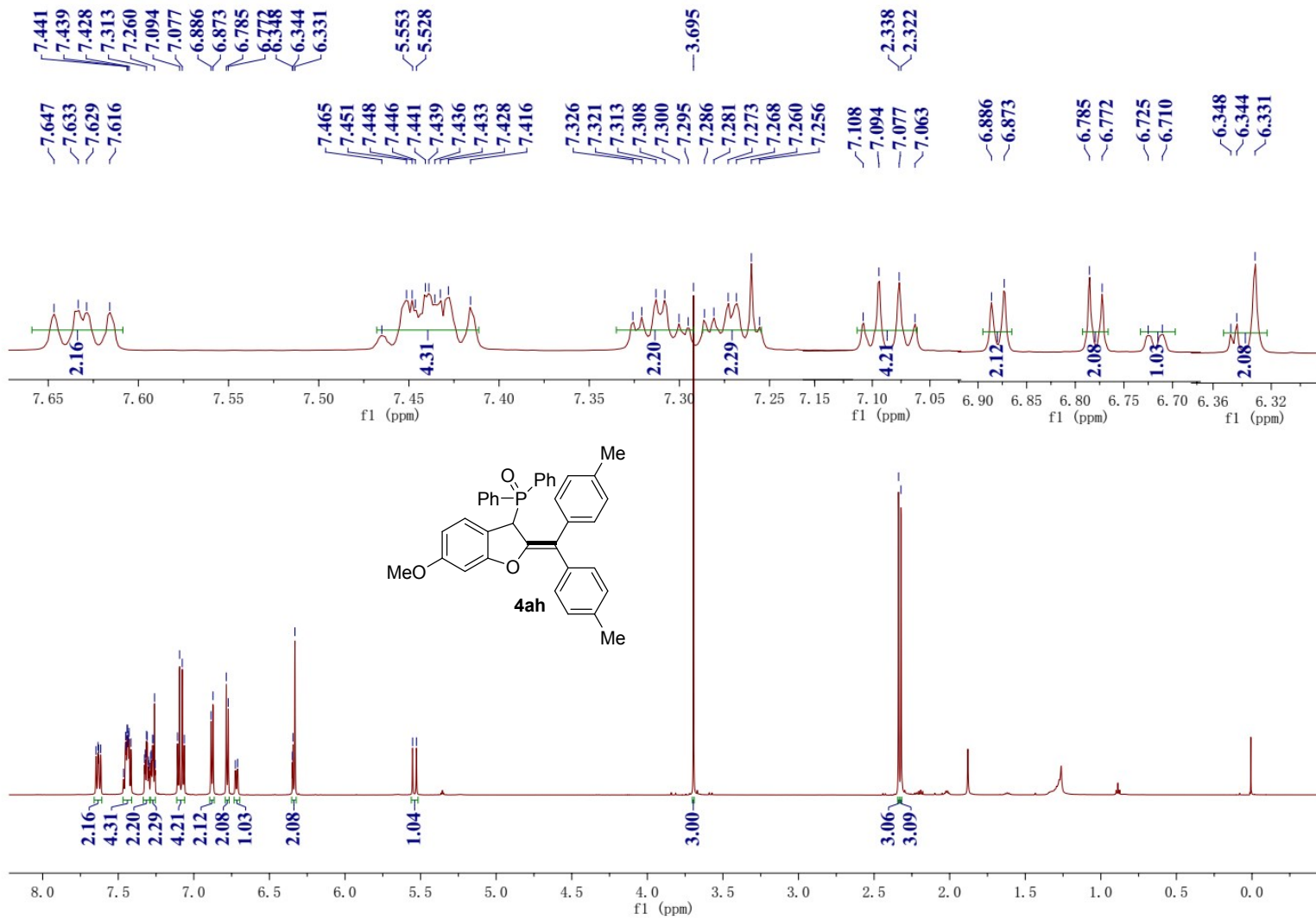


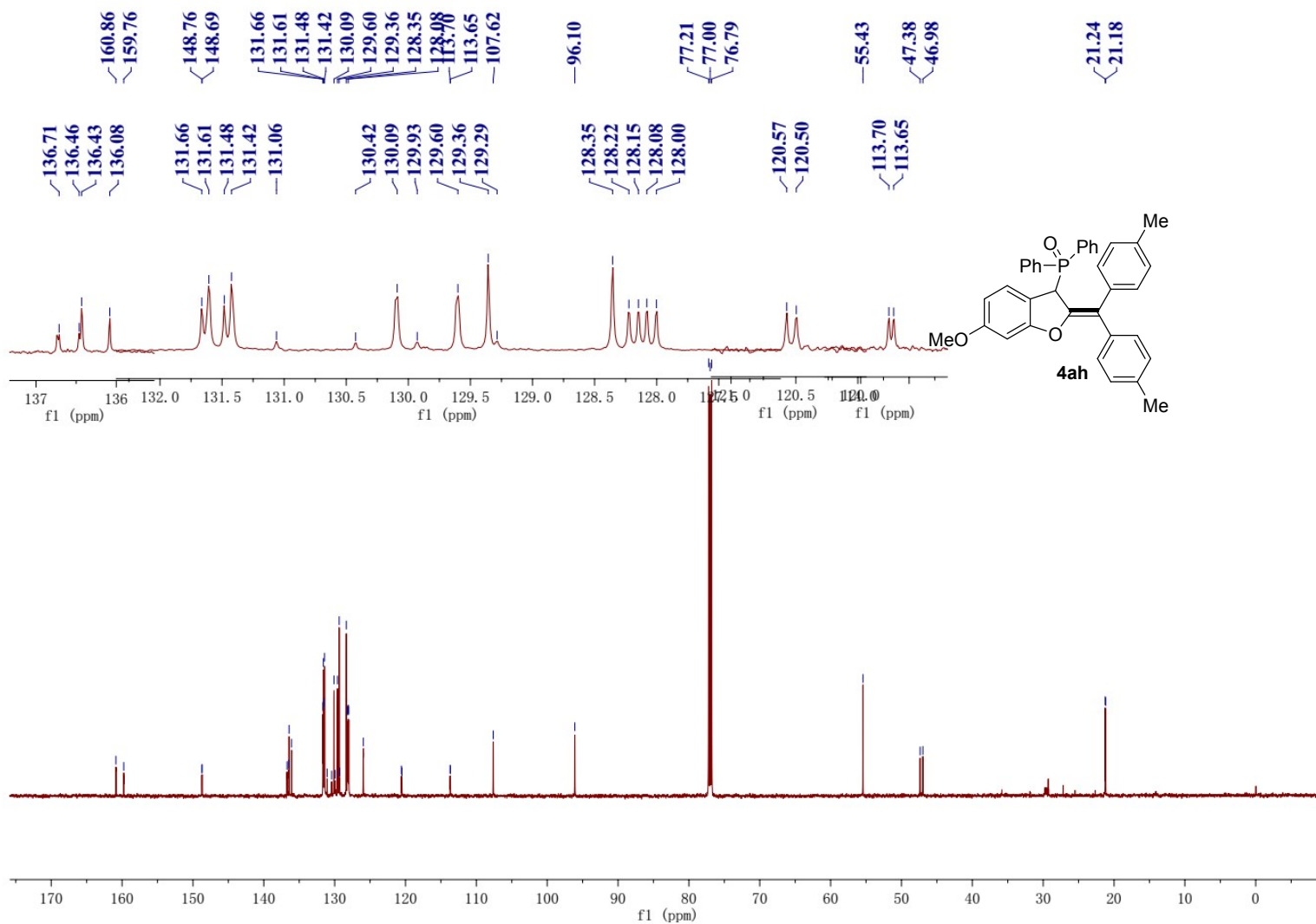




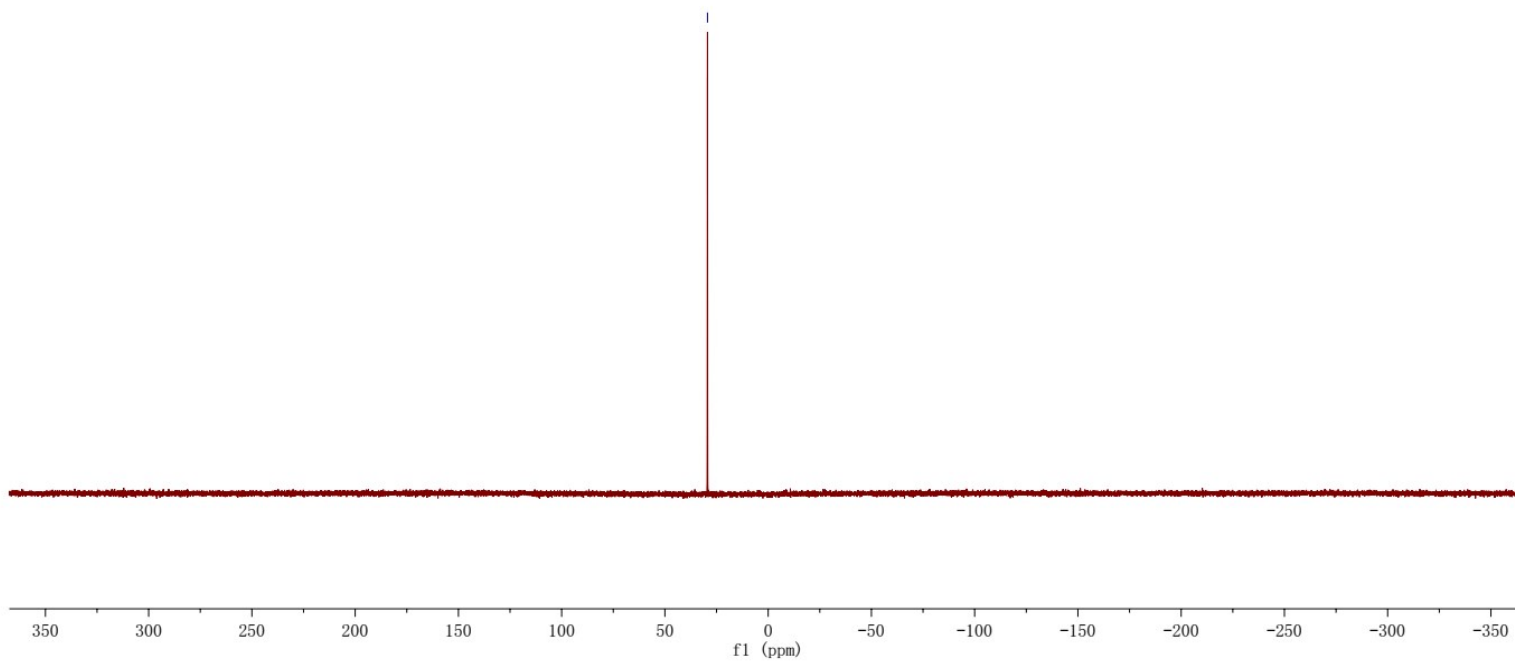
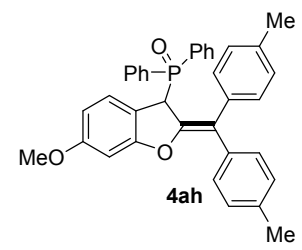
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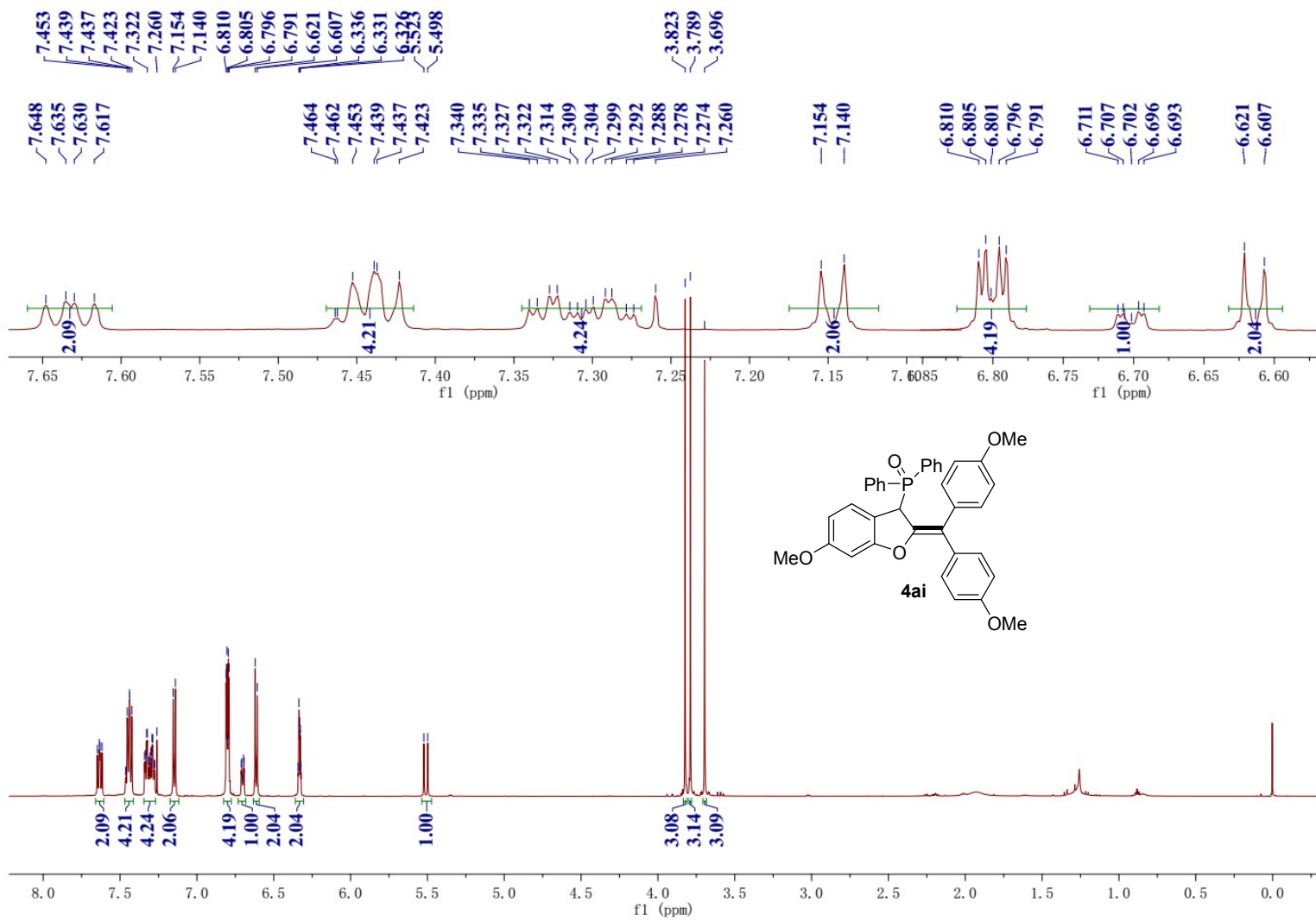


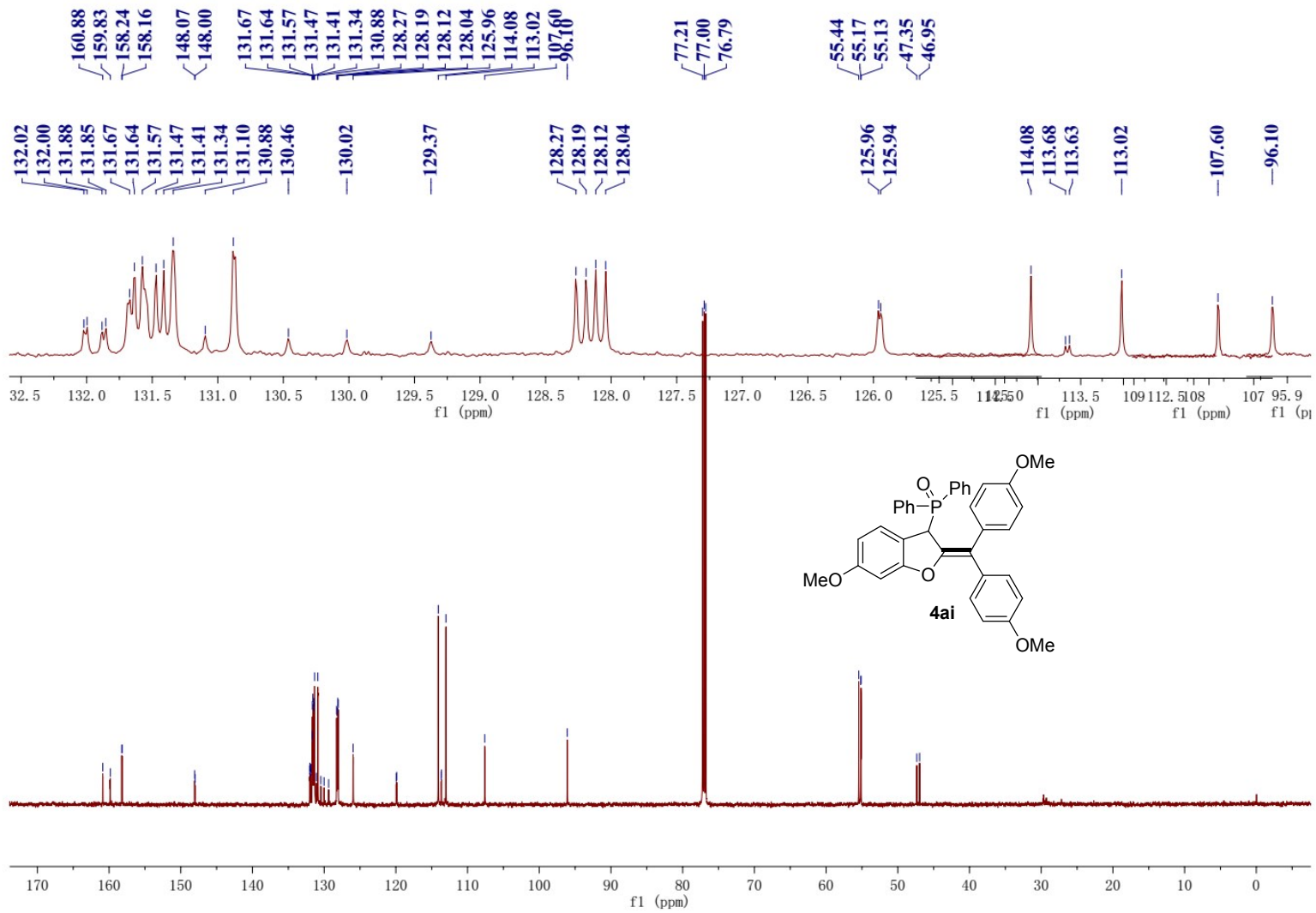




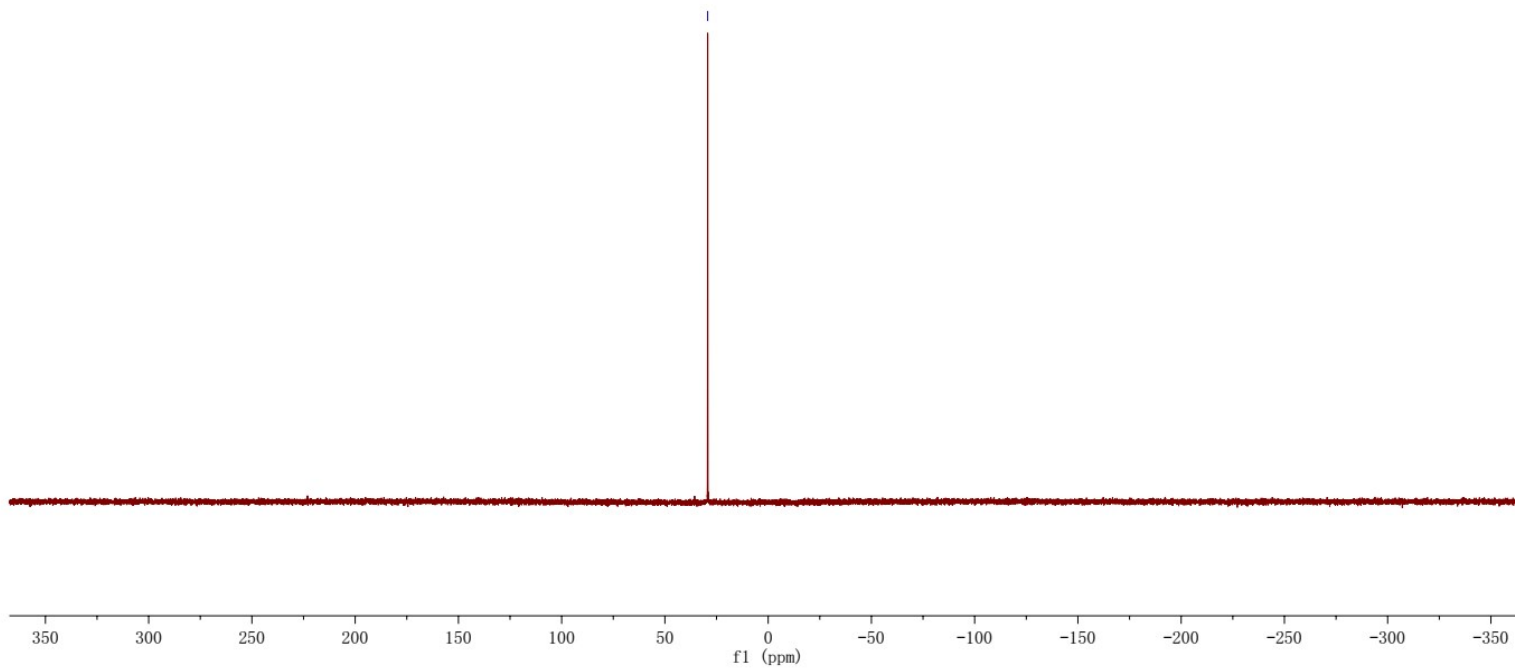
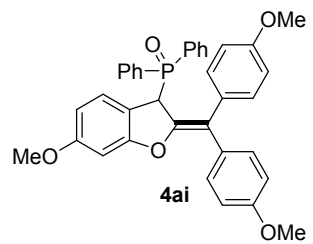
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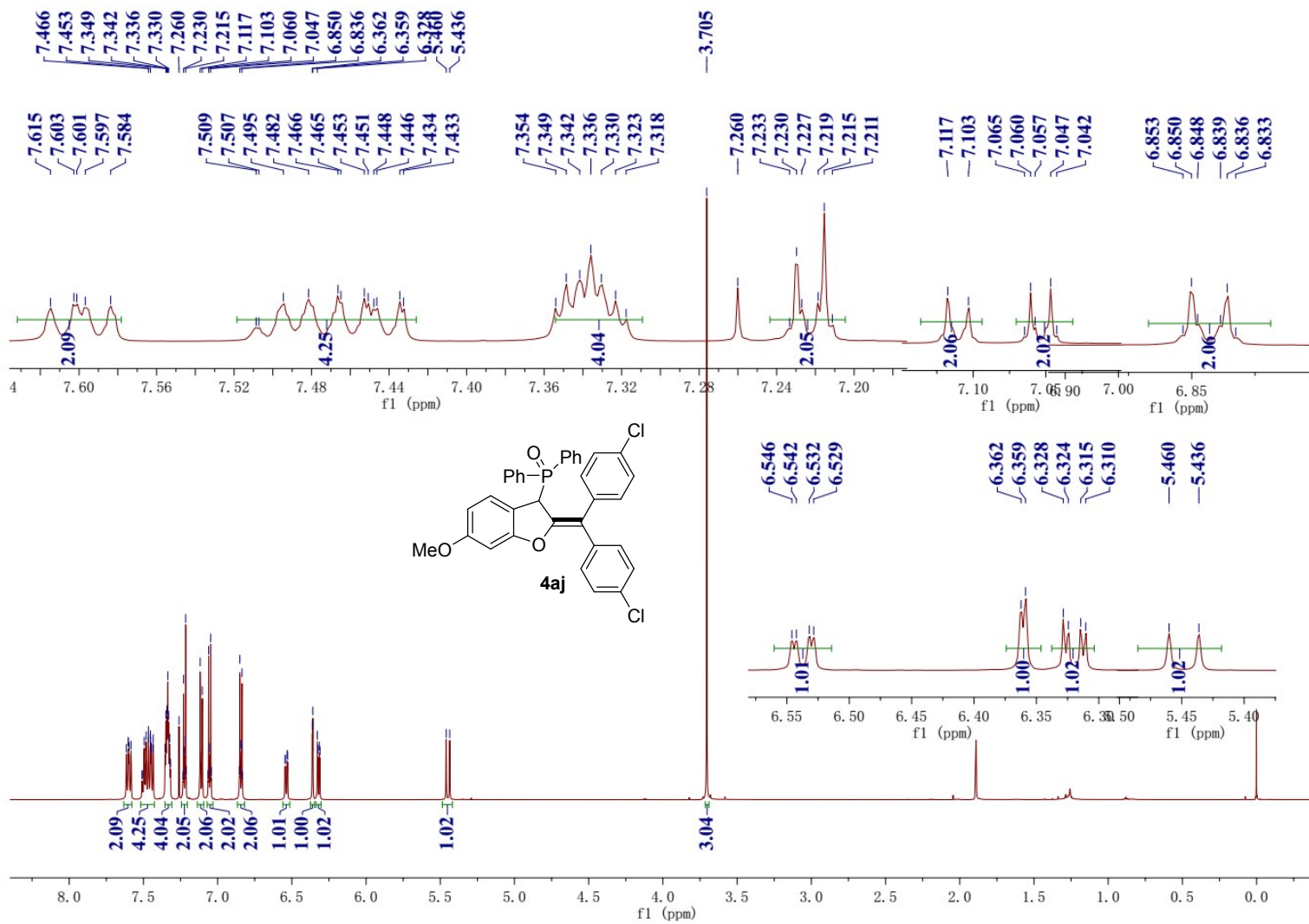


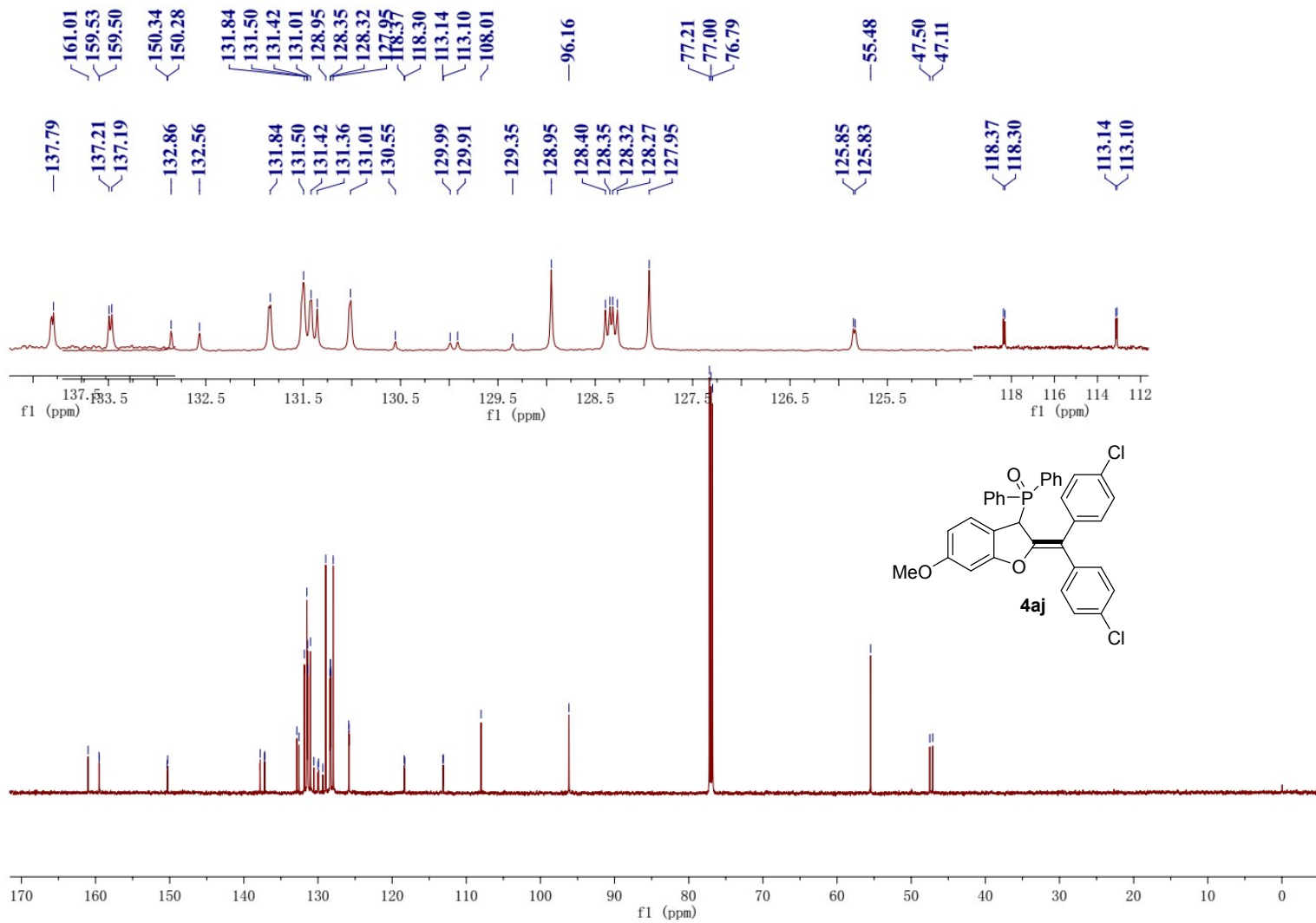


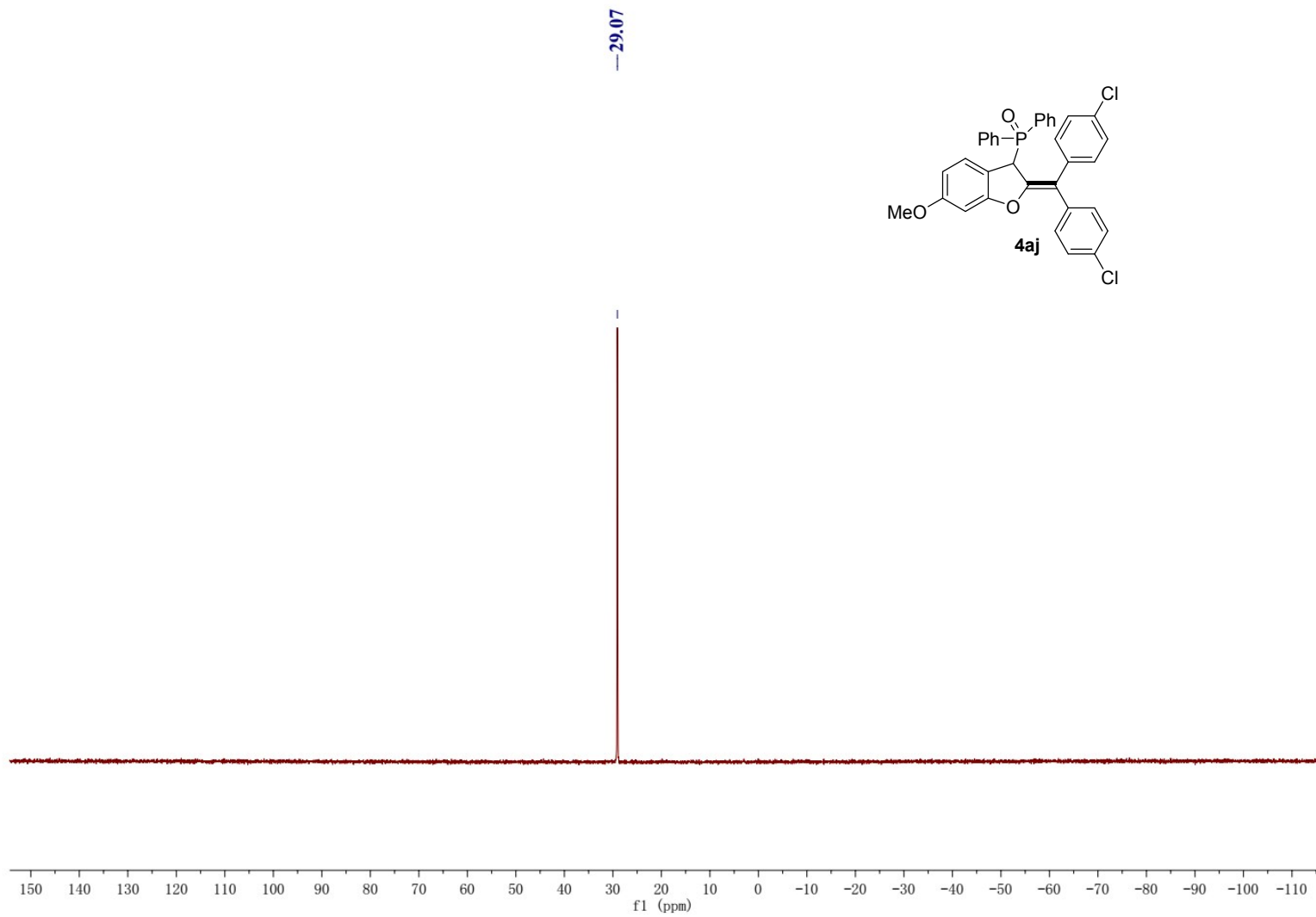


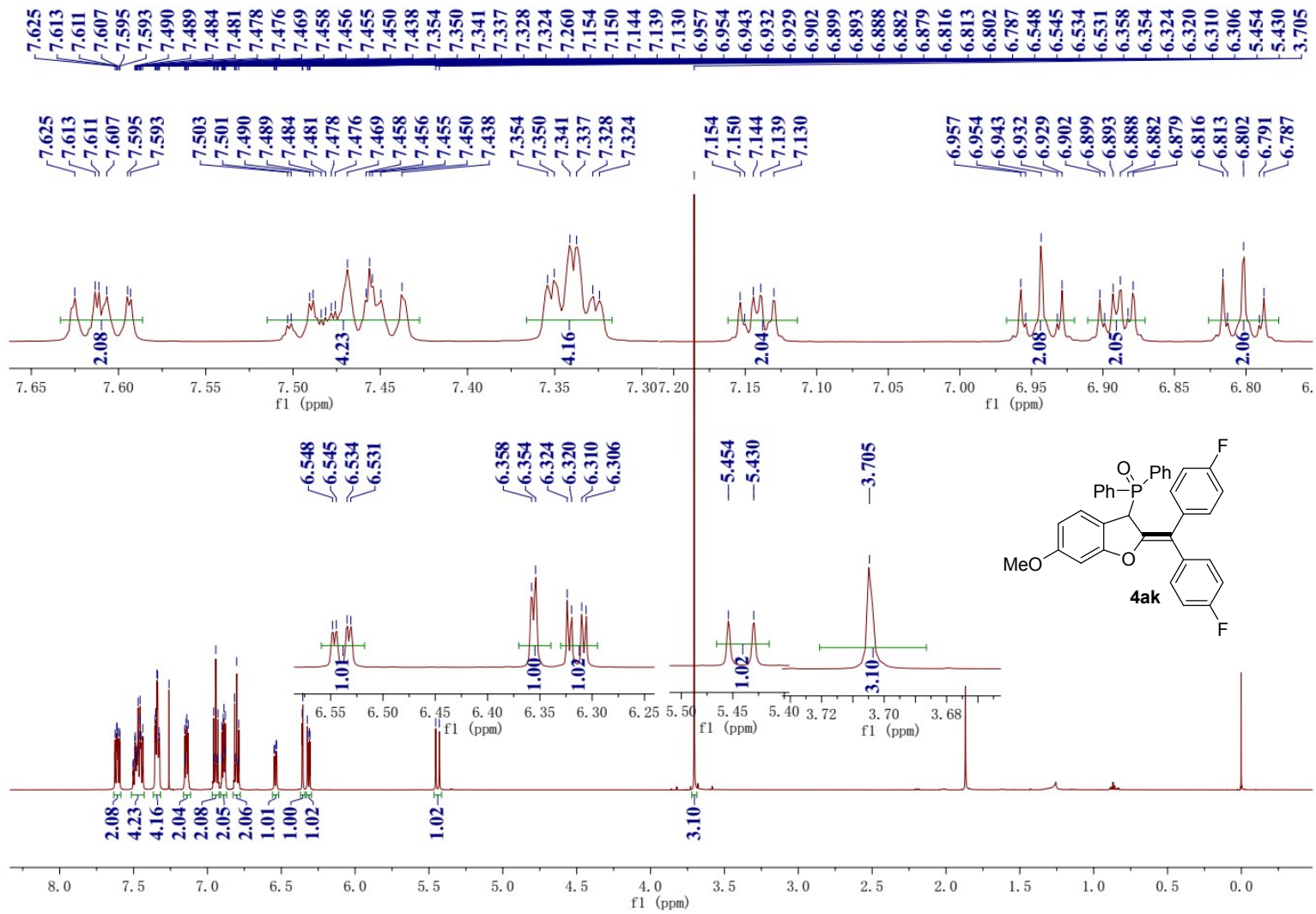
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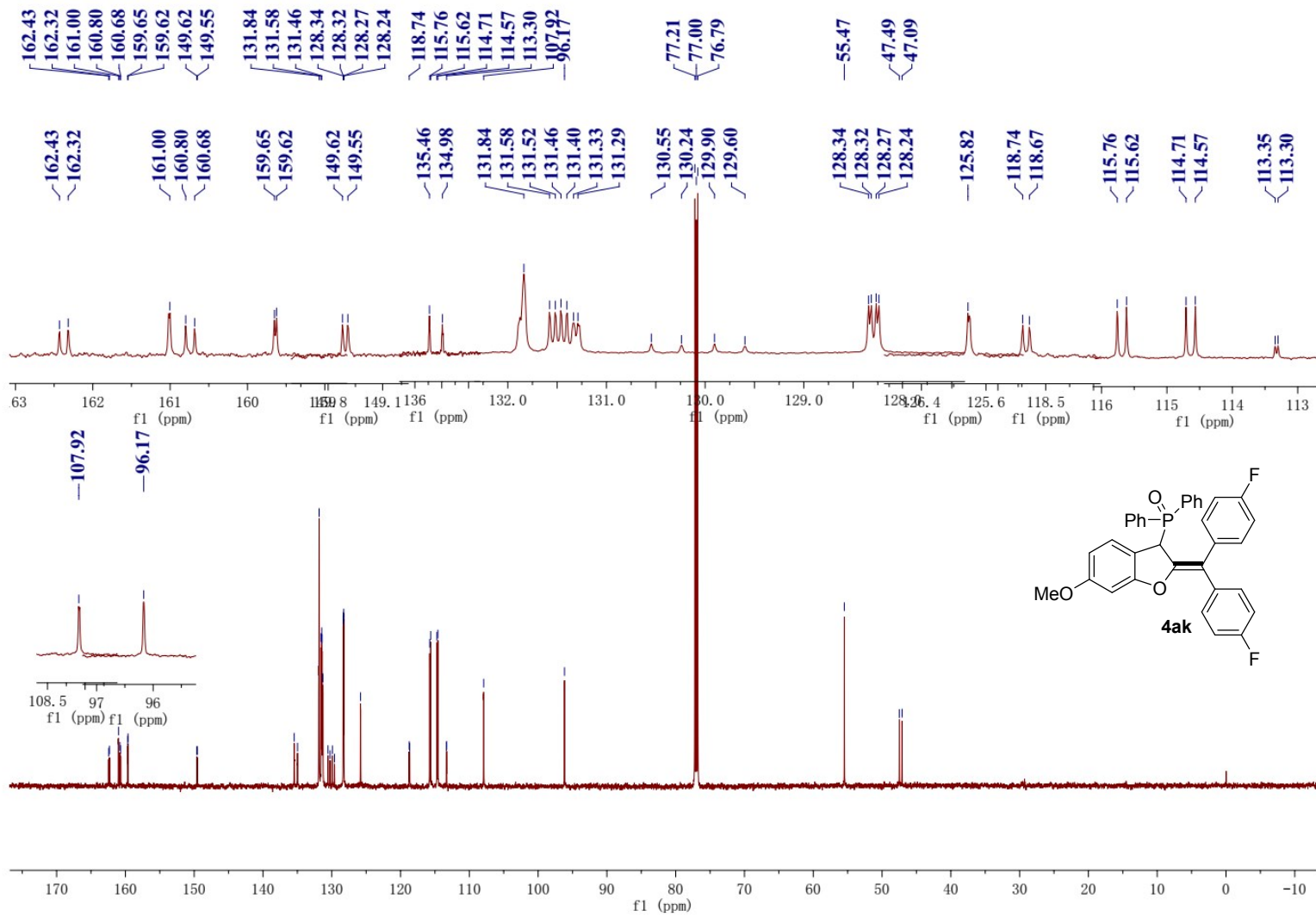




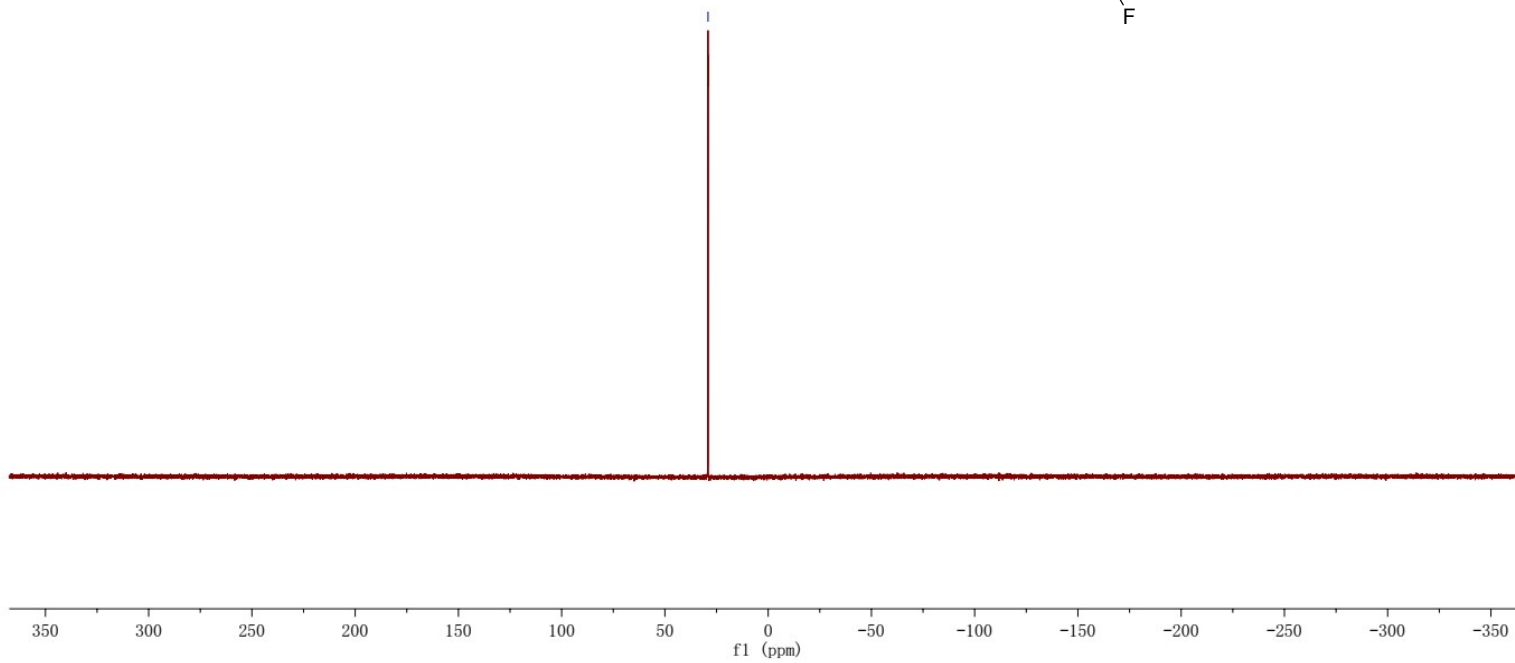
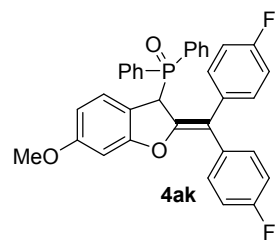


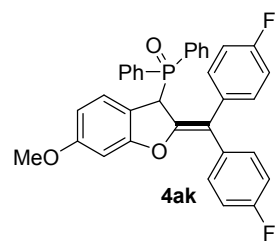




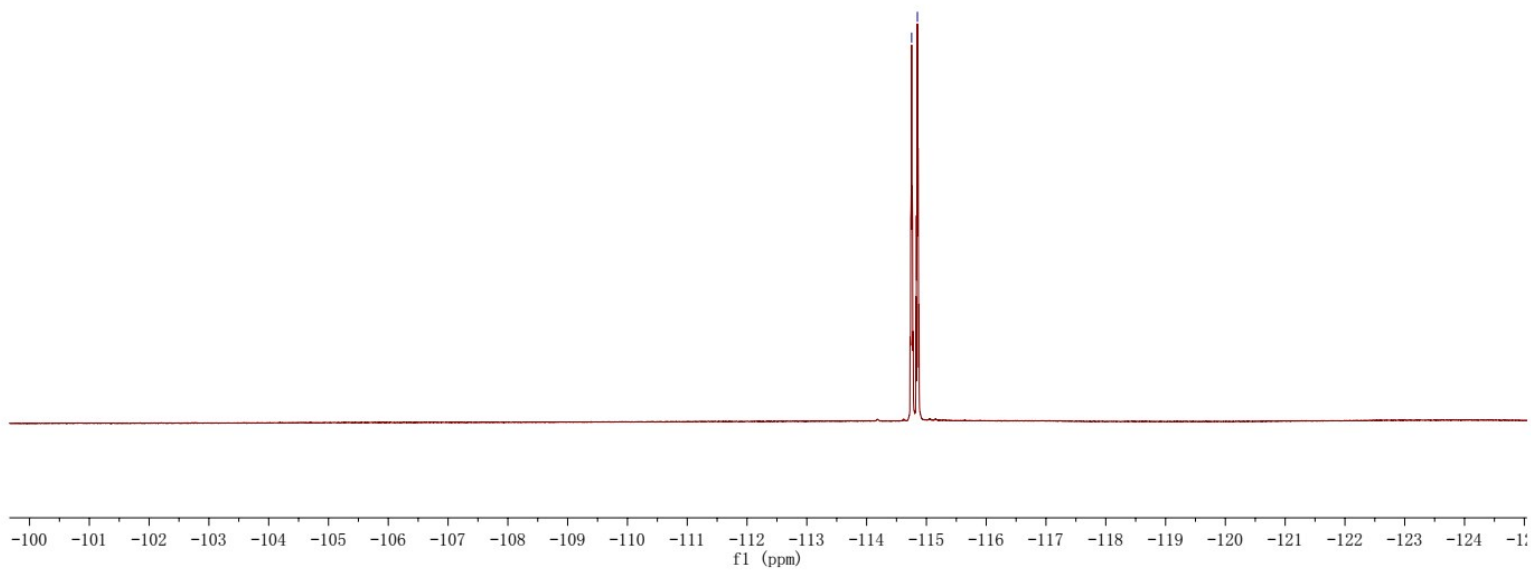


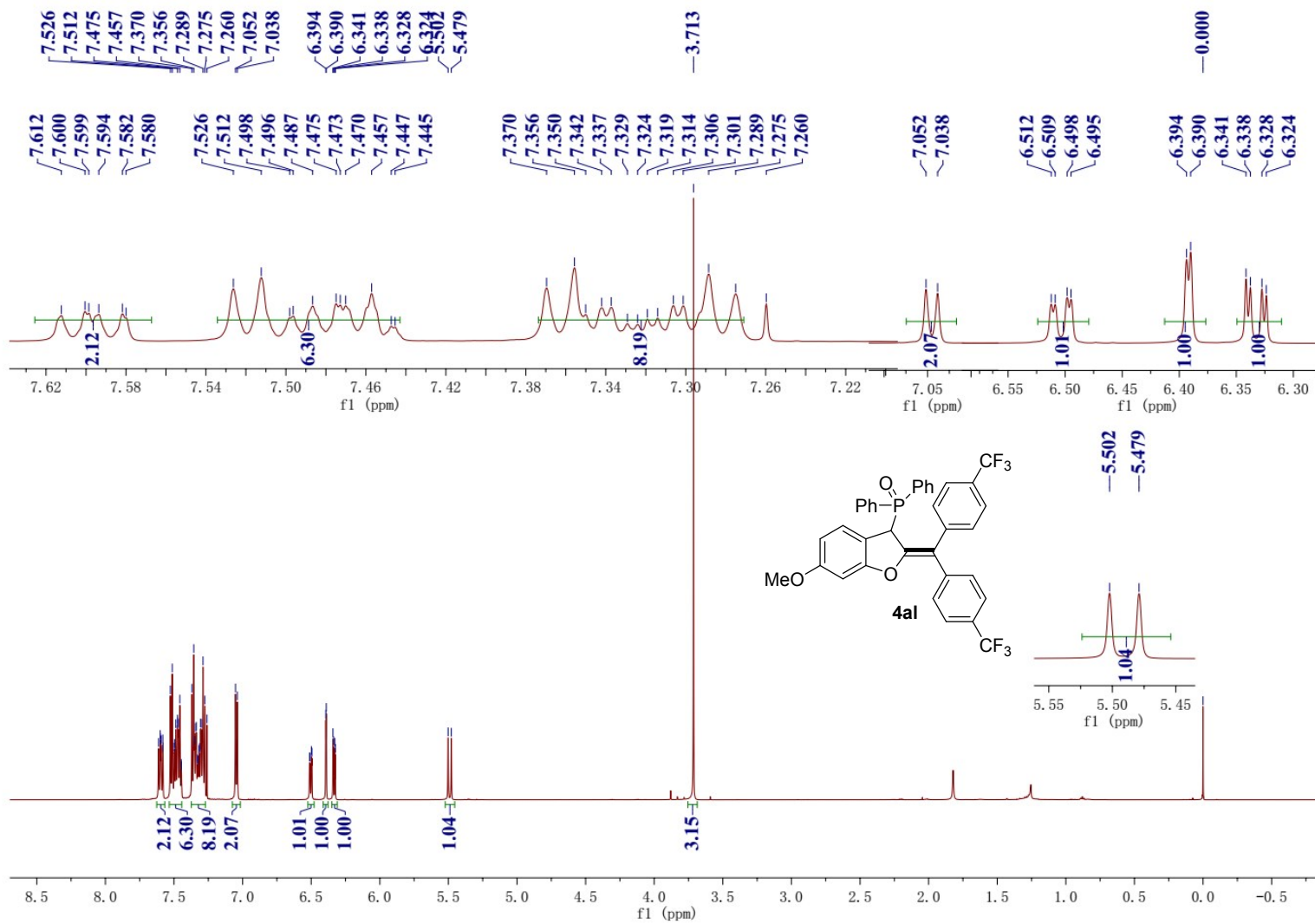
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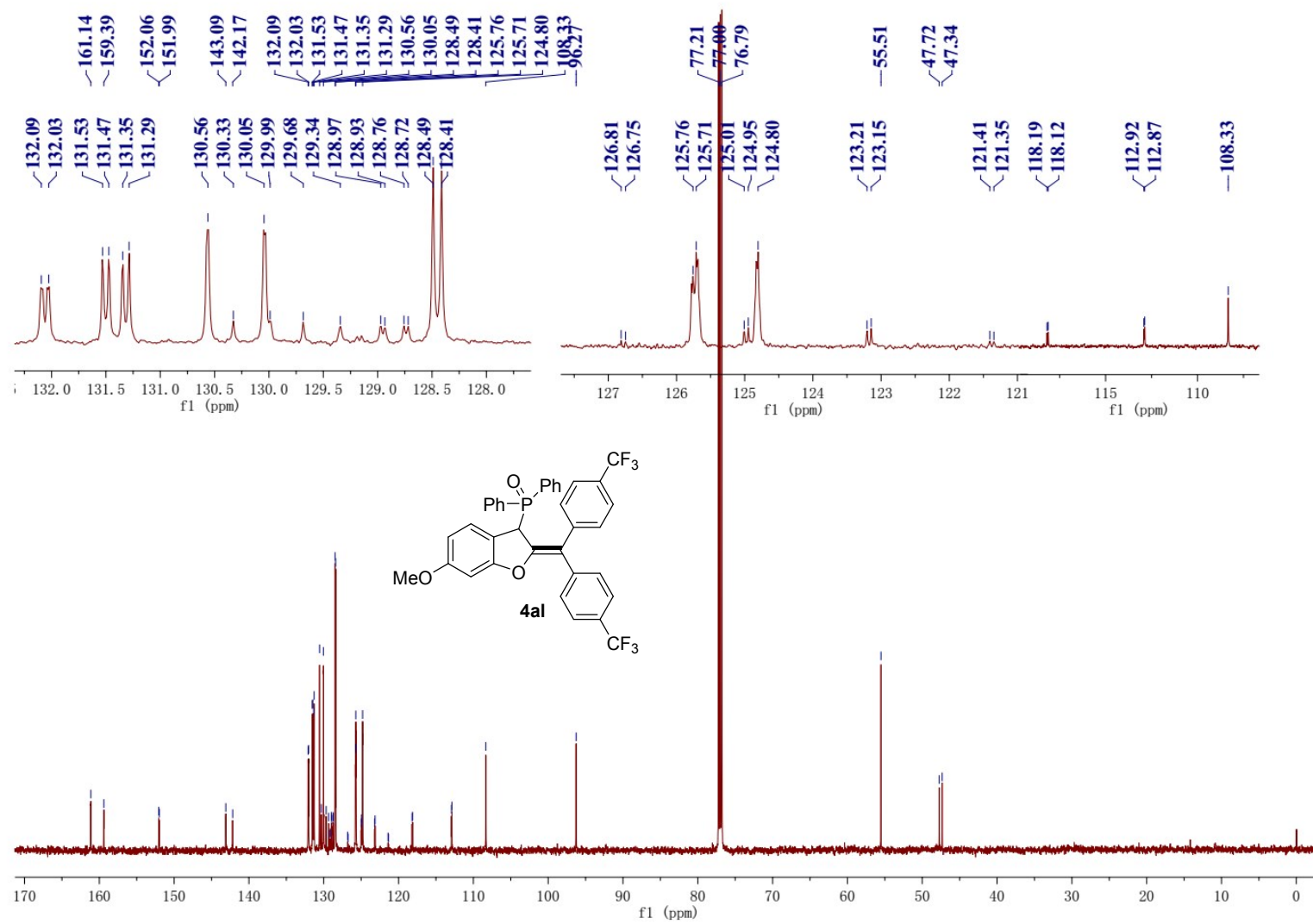


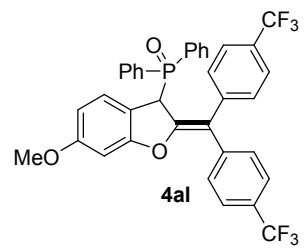


-114.75
-114.85

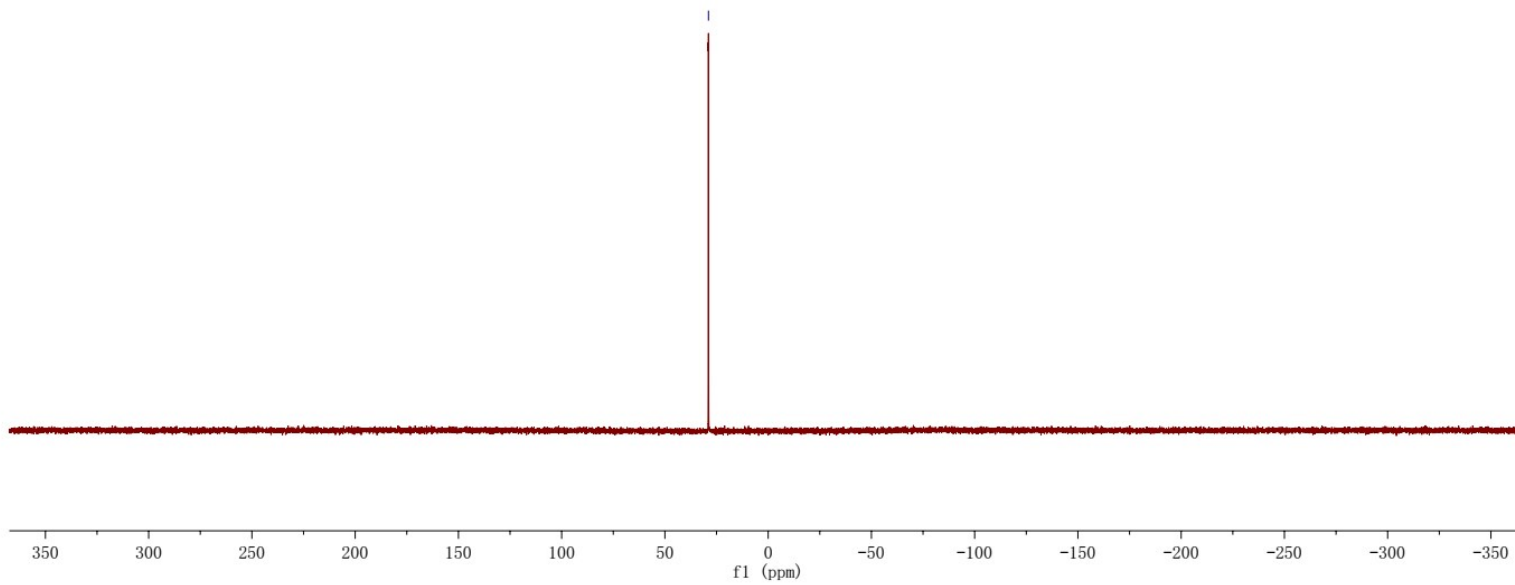


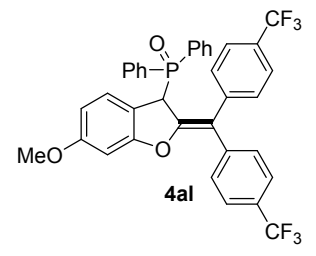




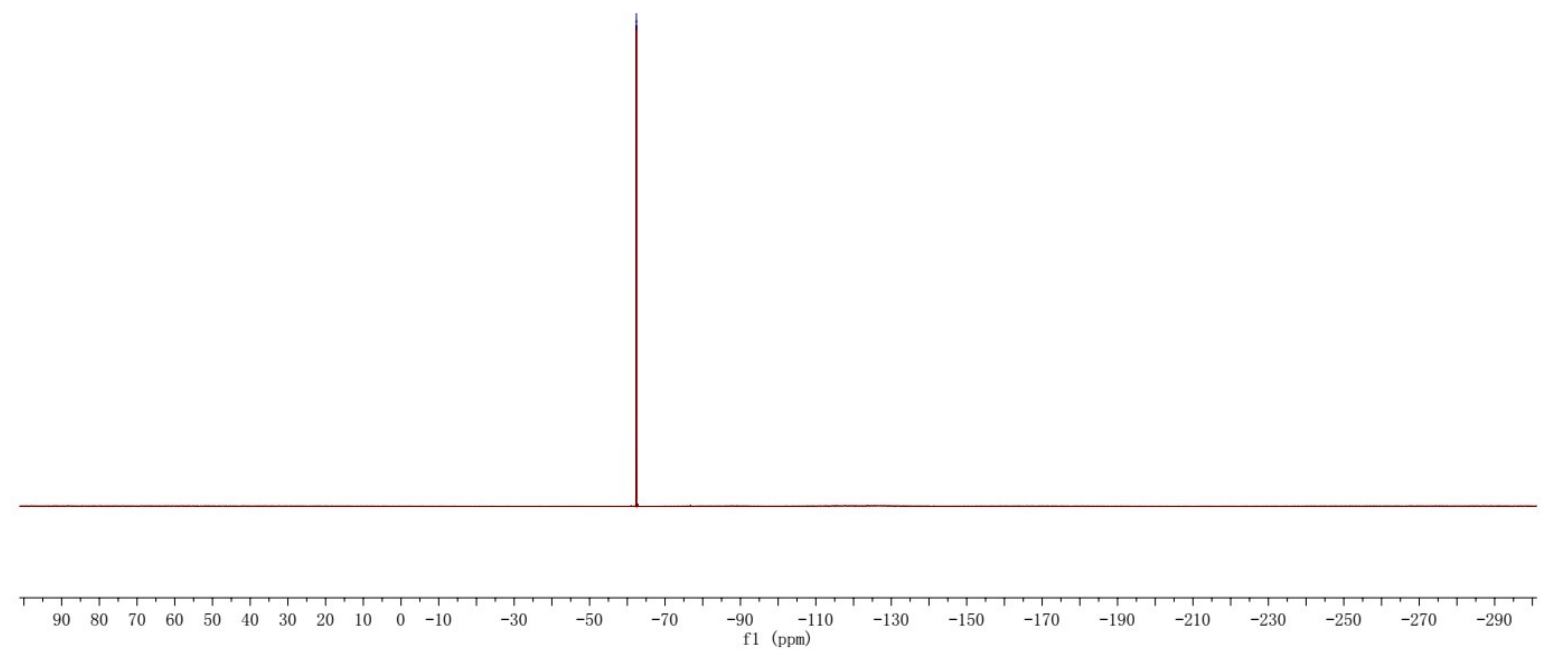


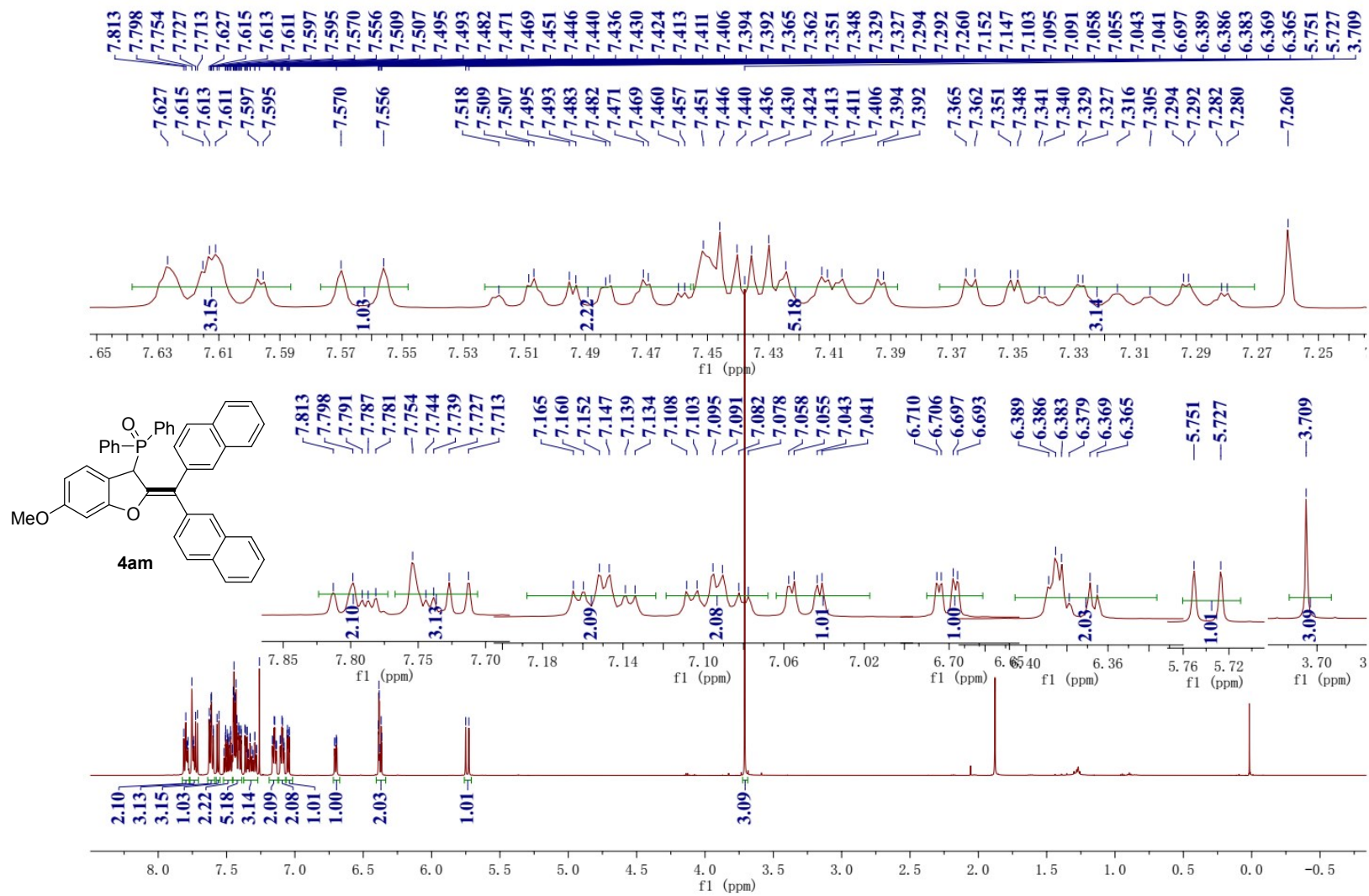
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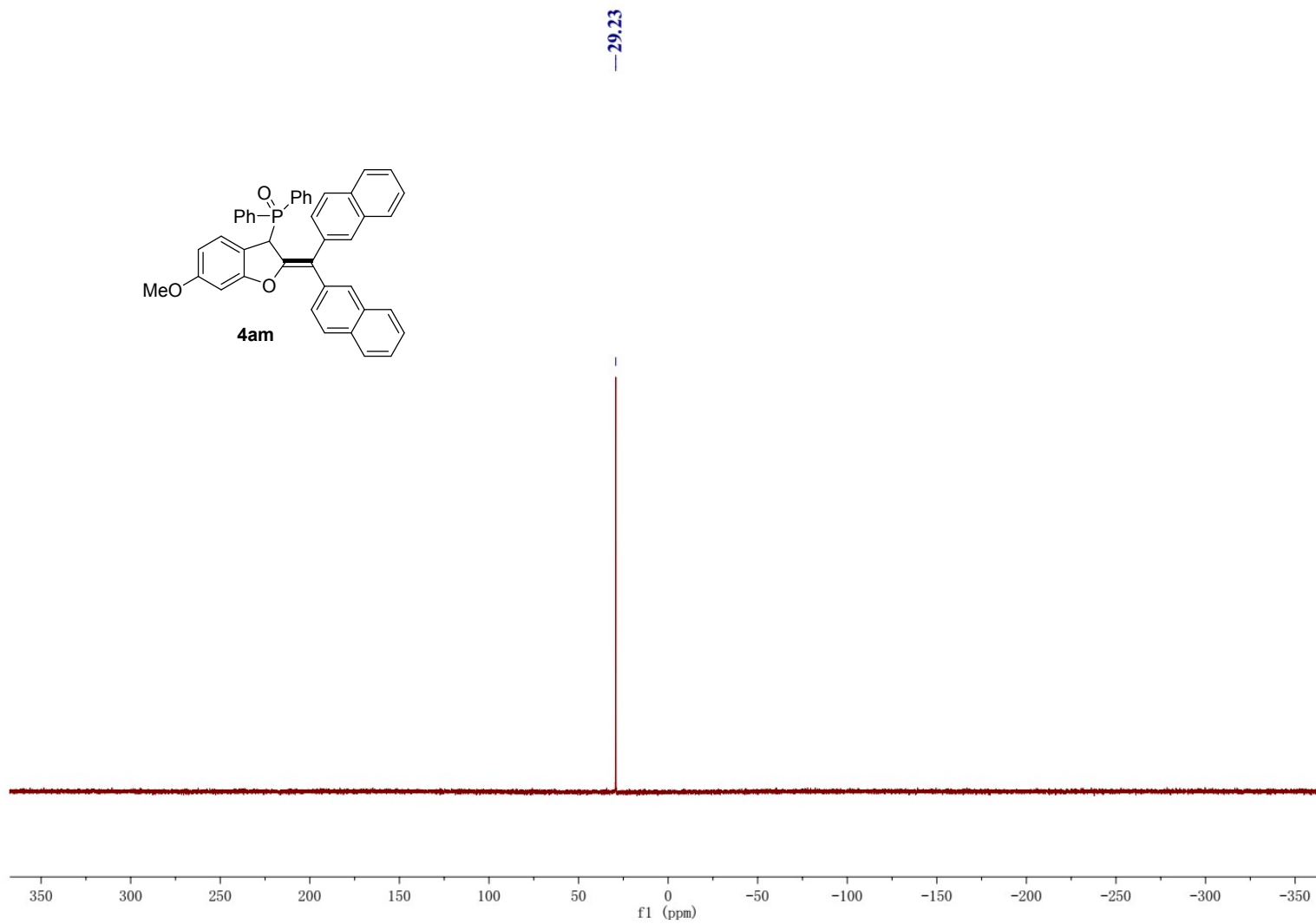
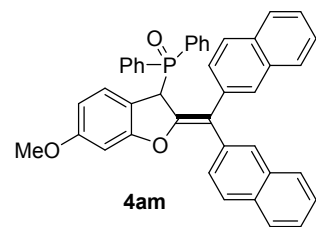


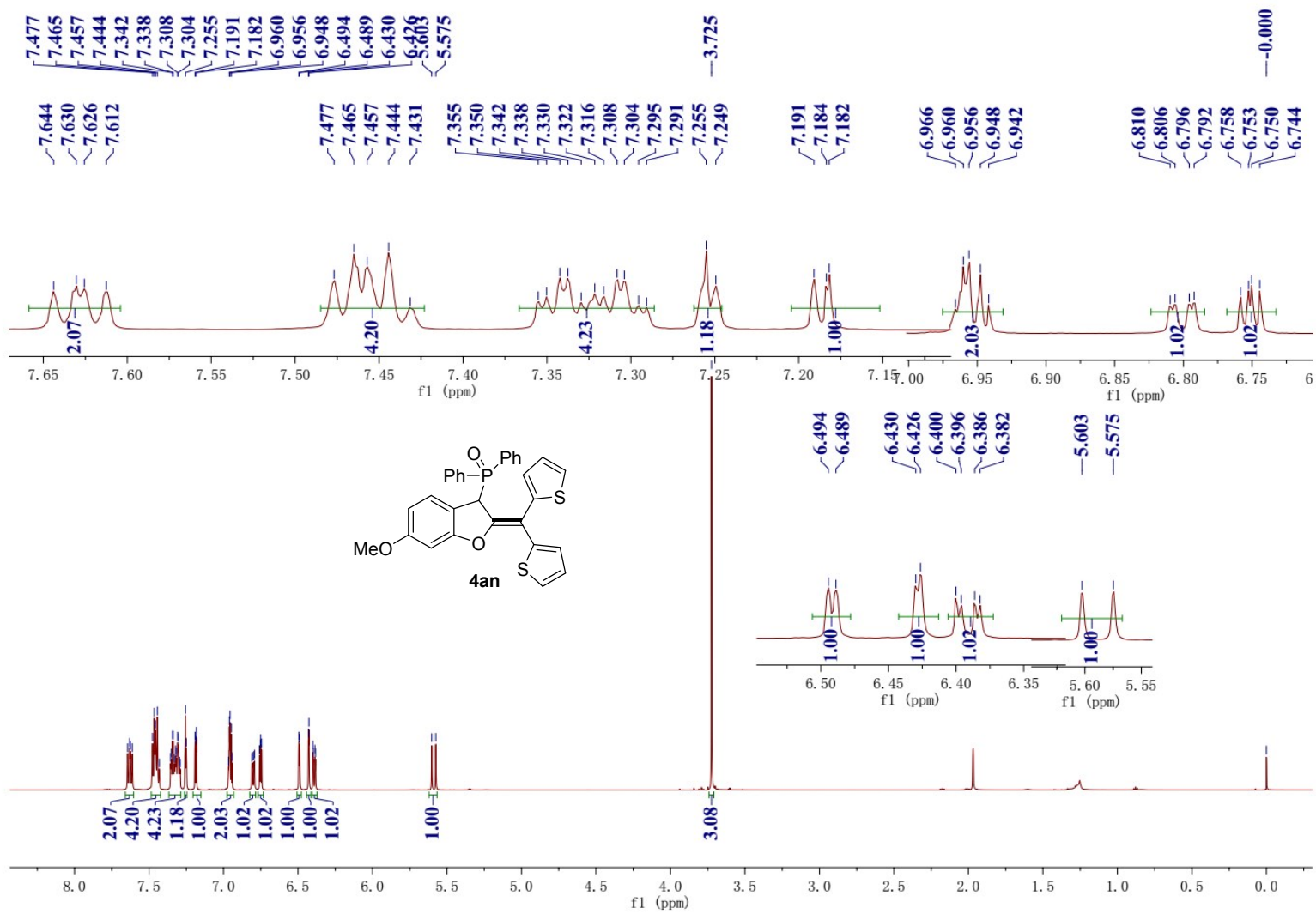


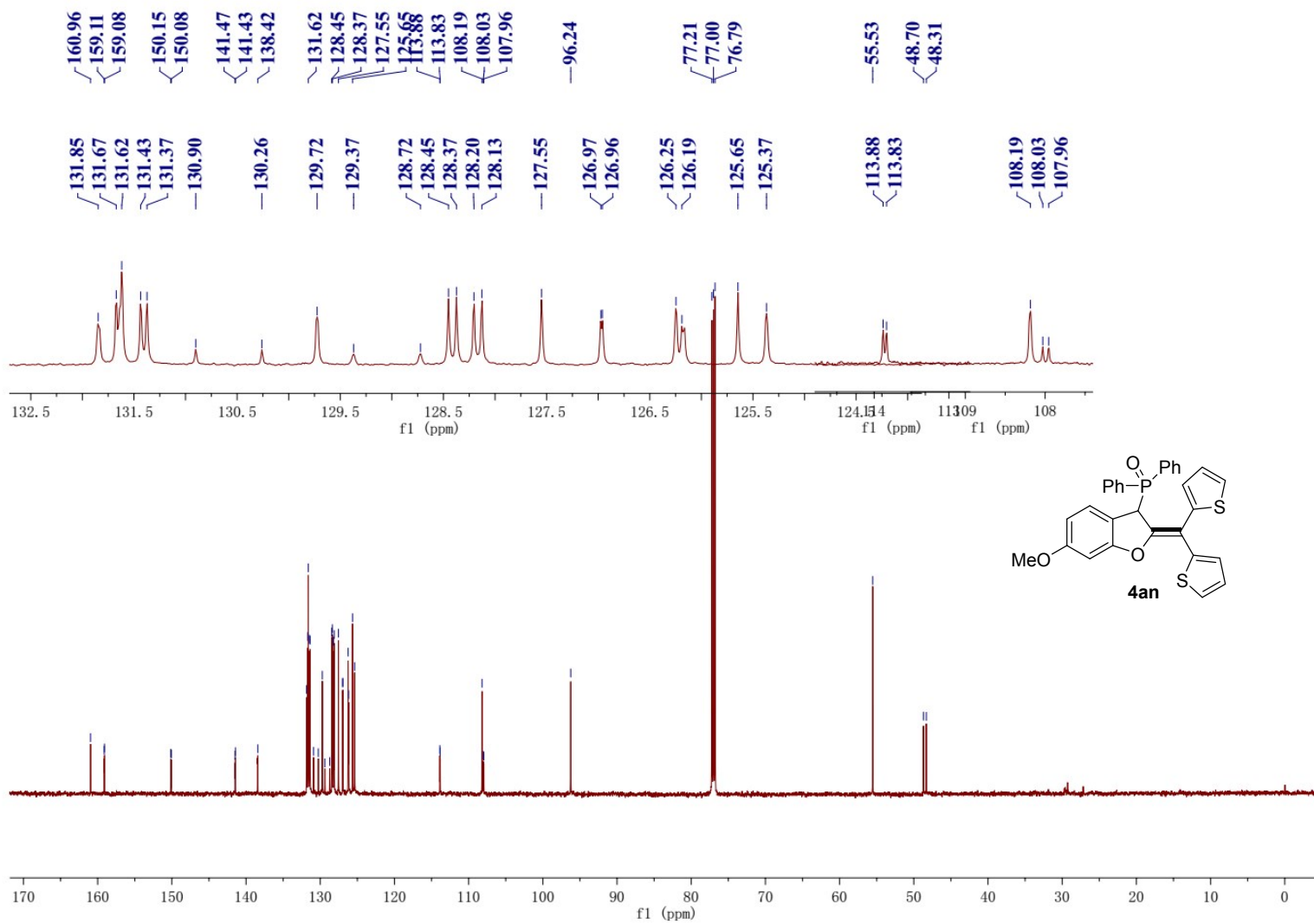
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-62.42

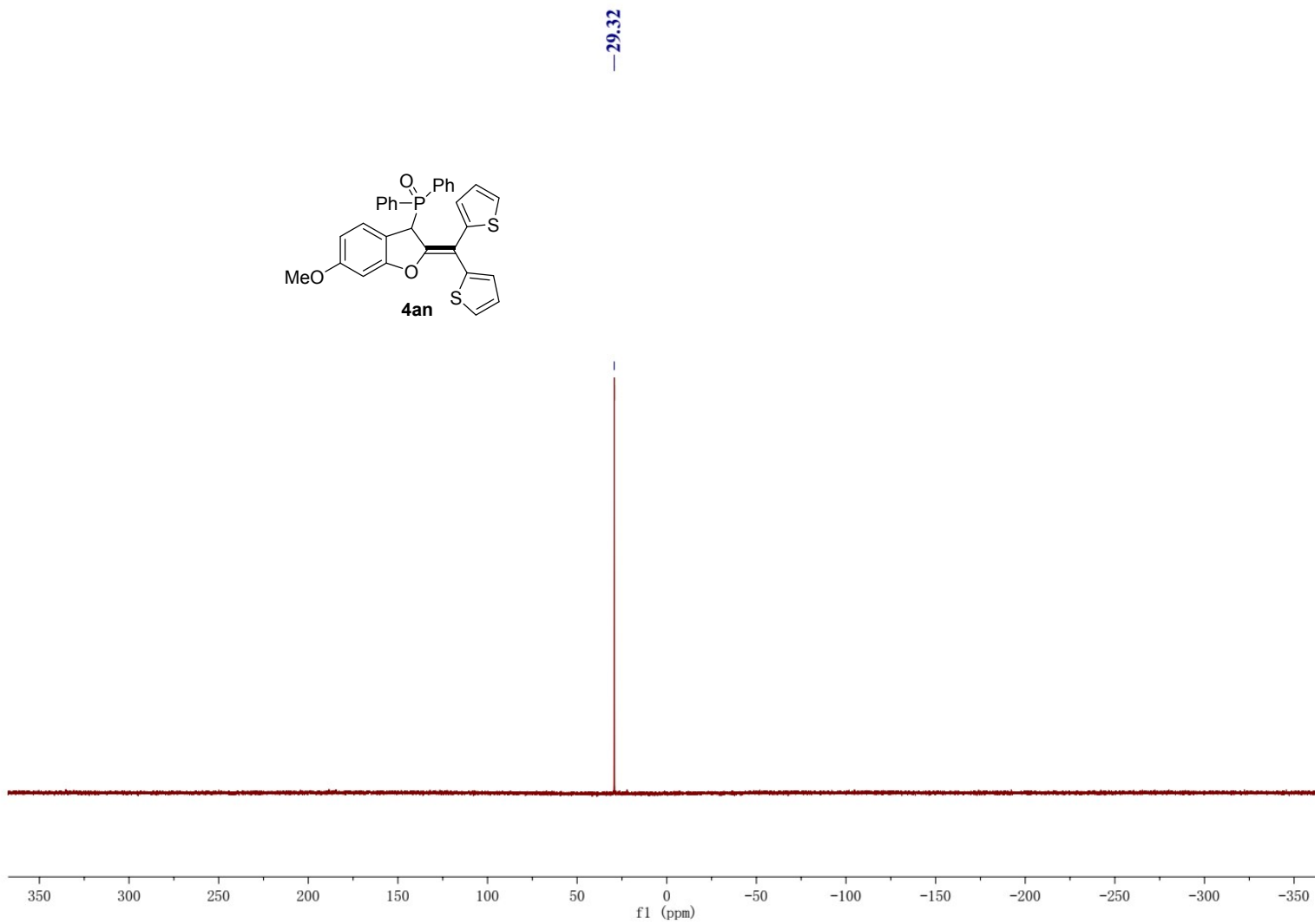
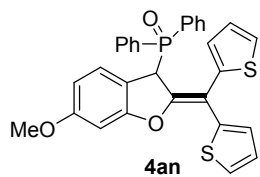


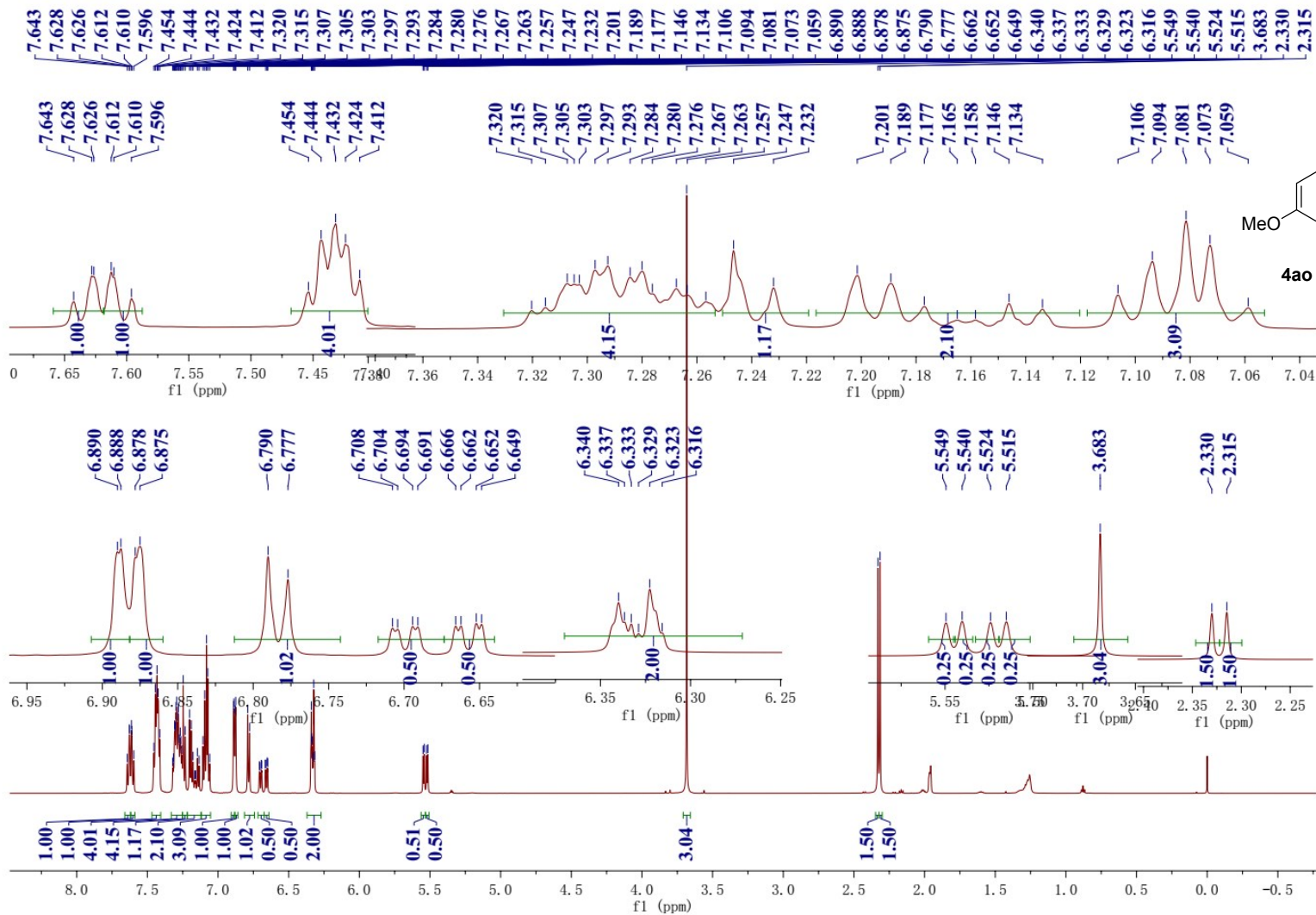


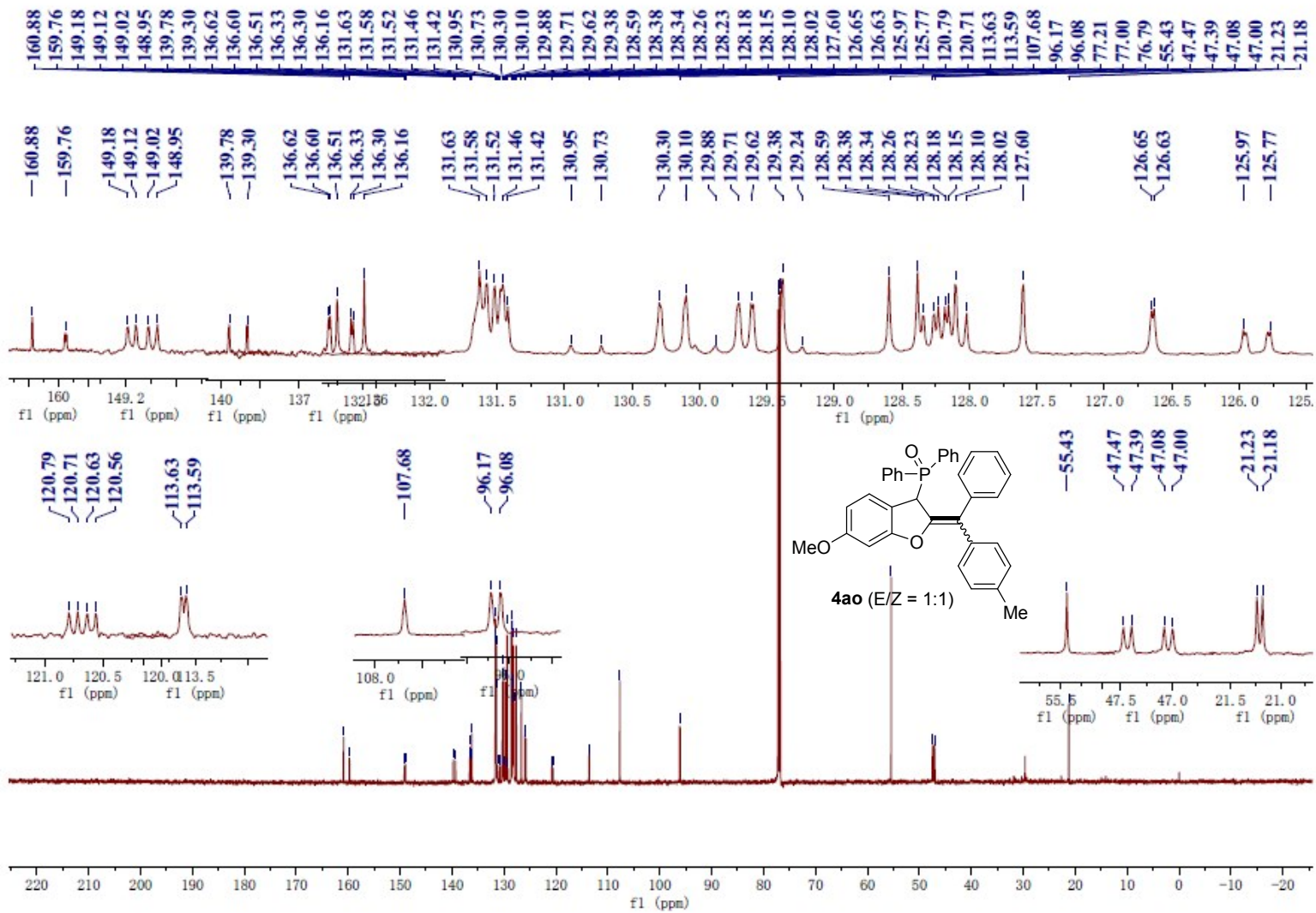




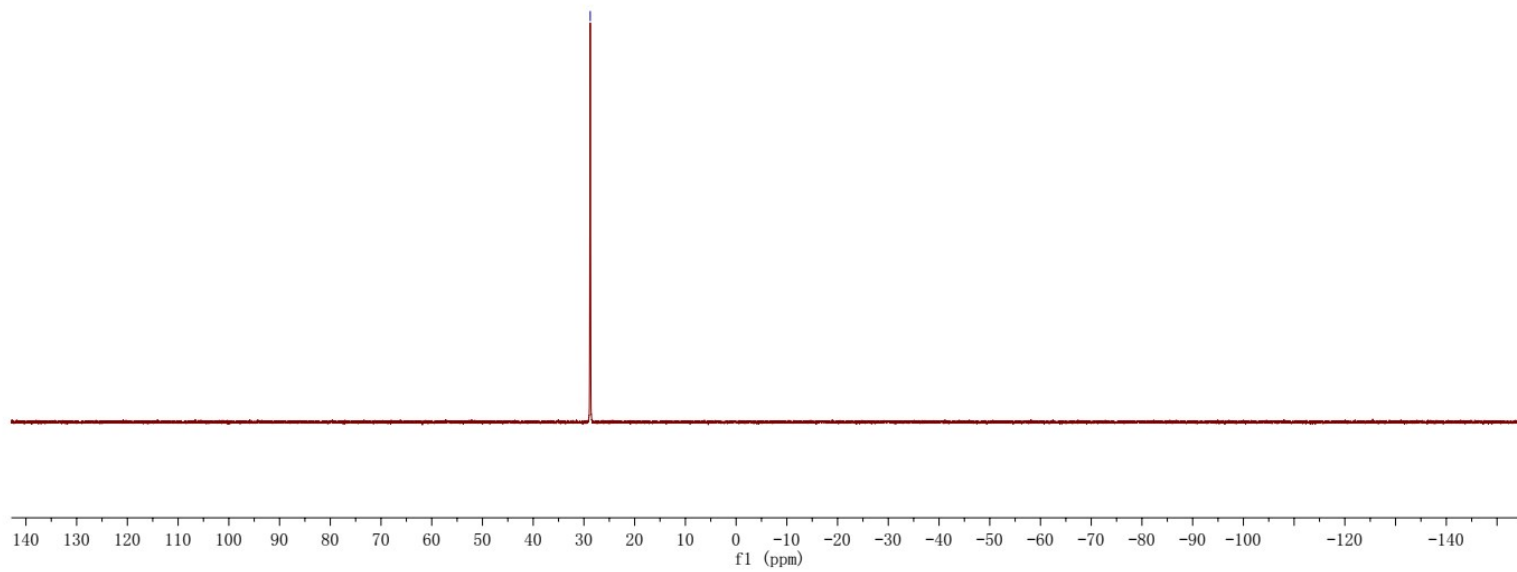
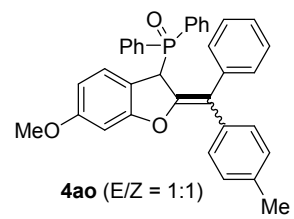


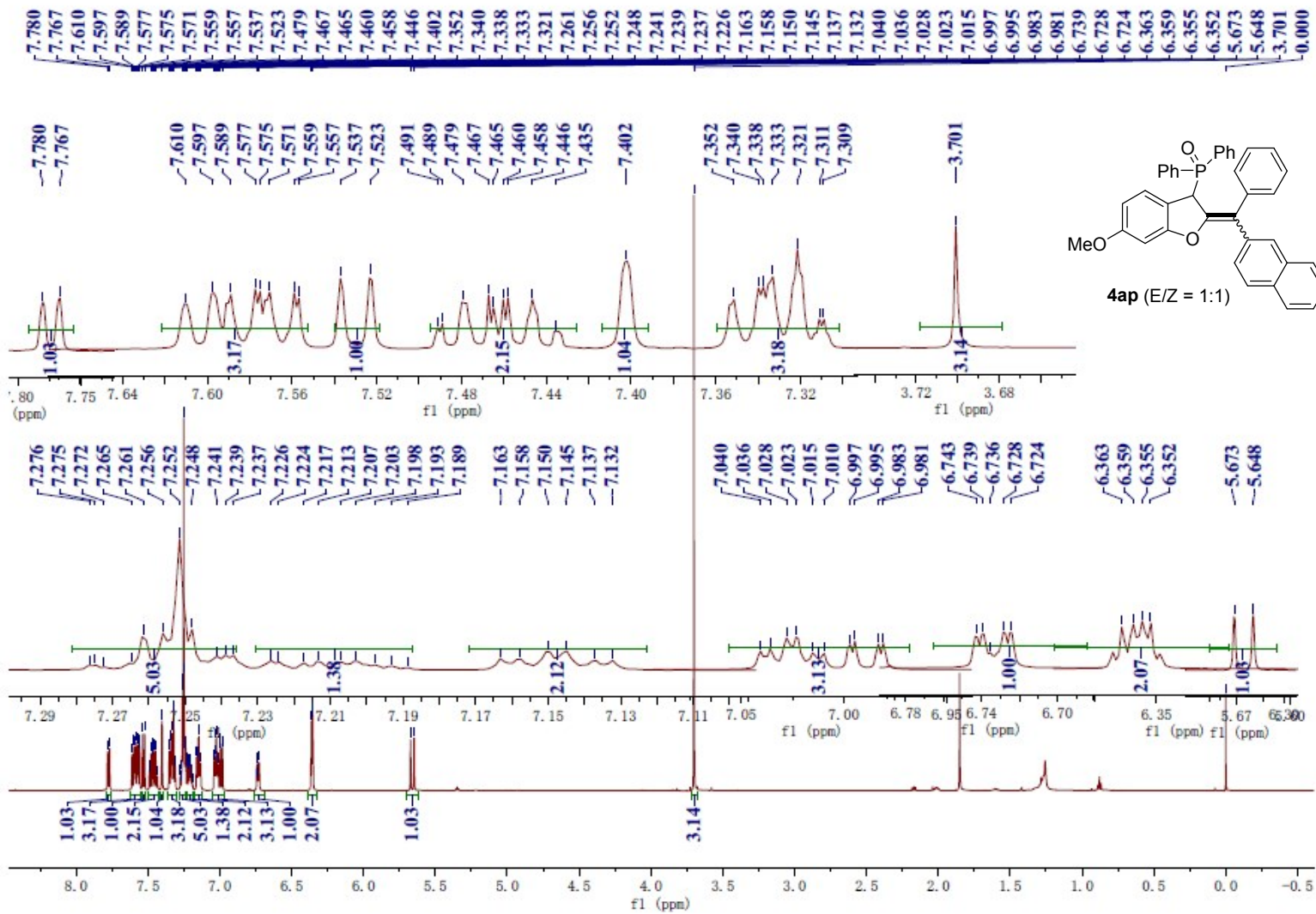


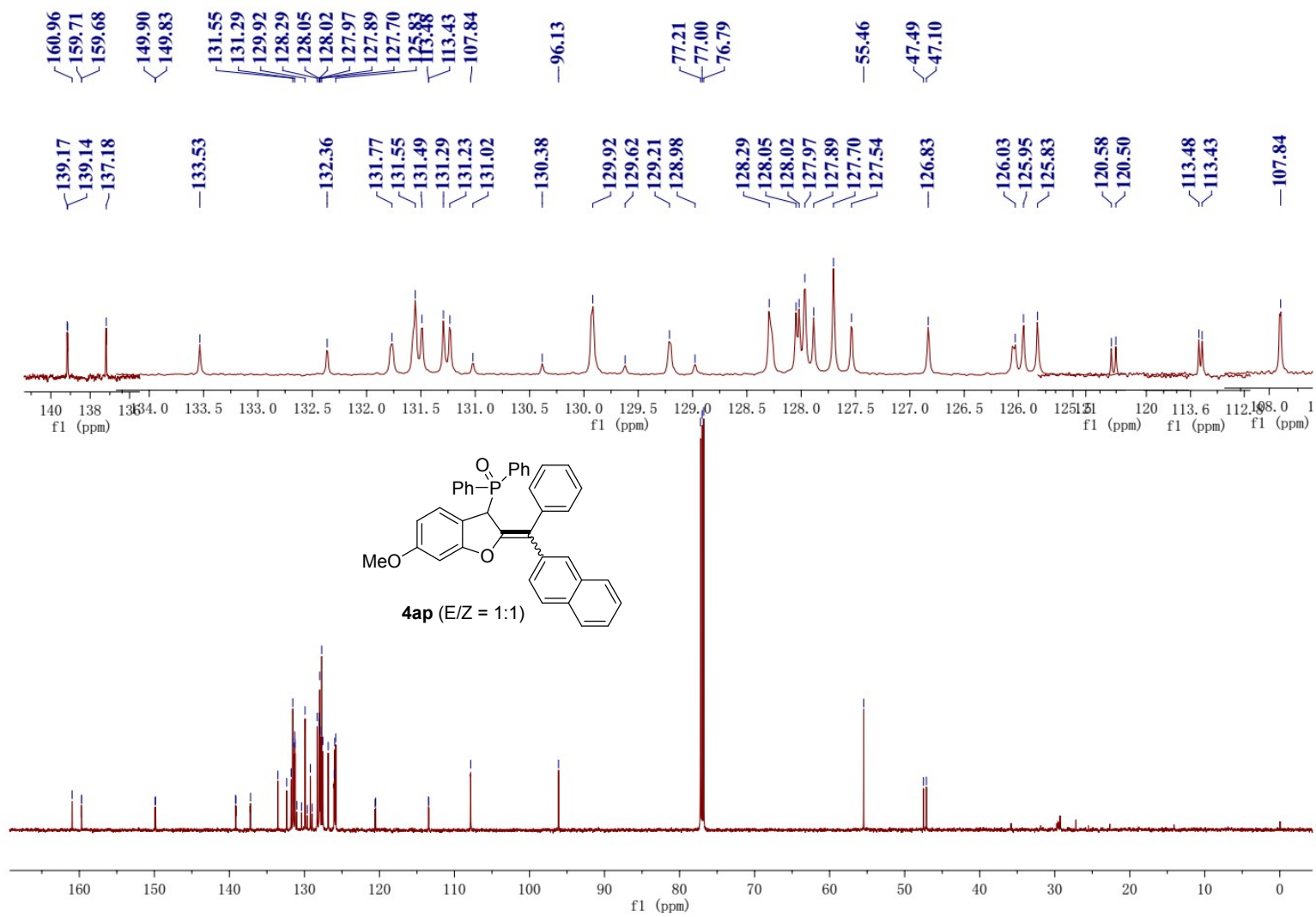


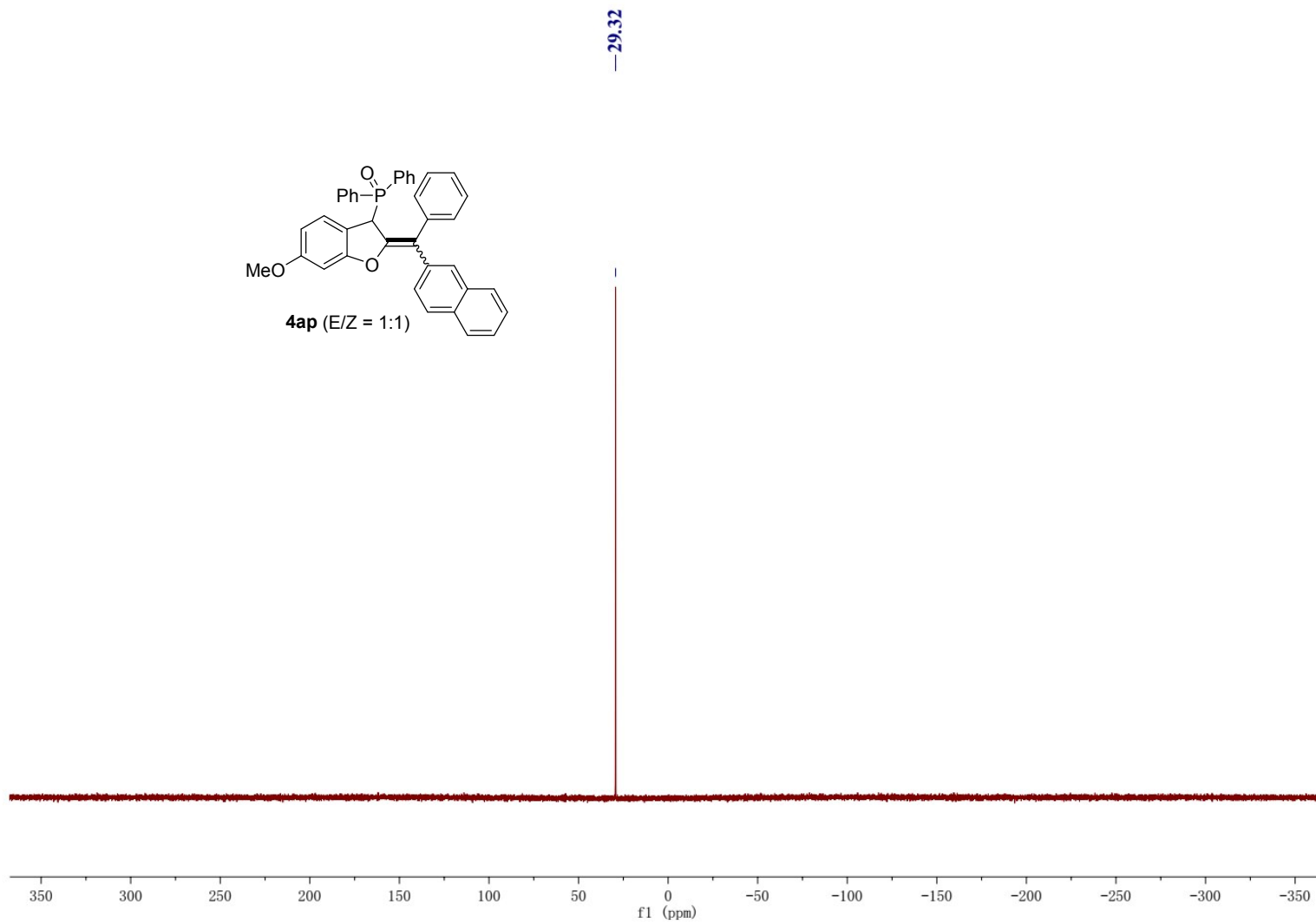
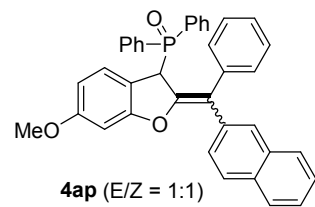


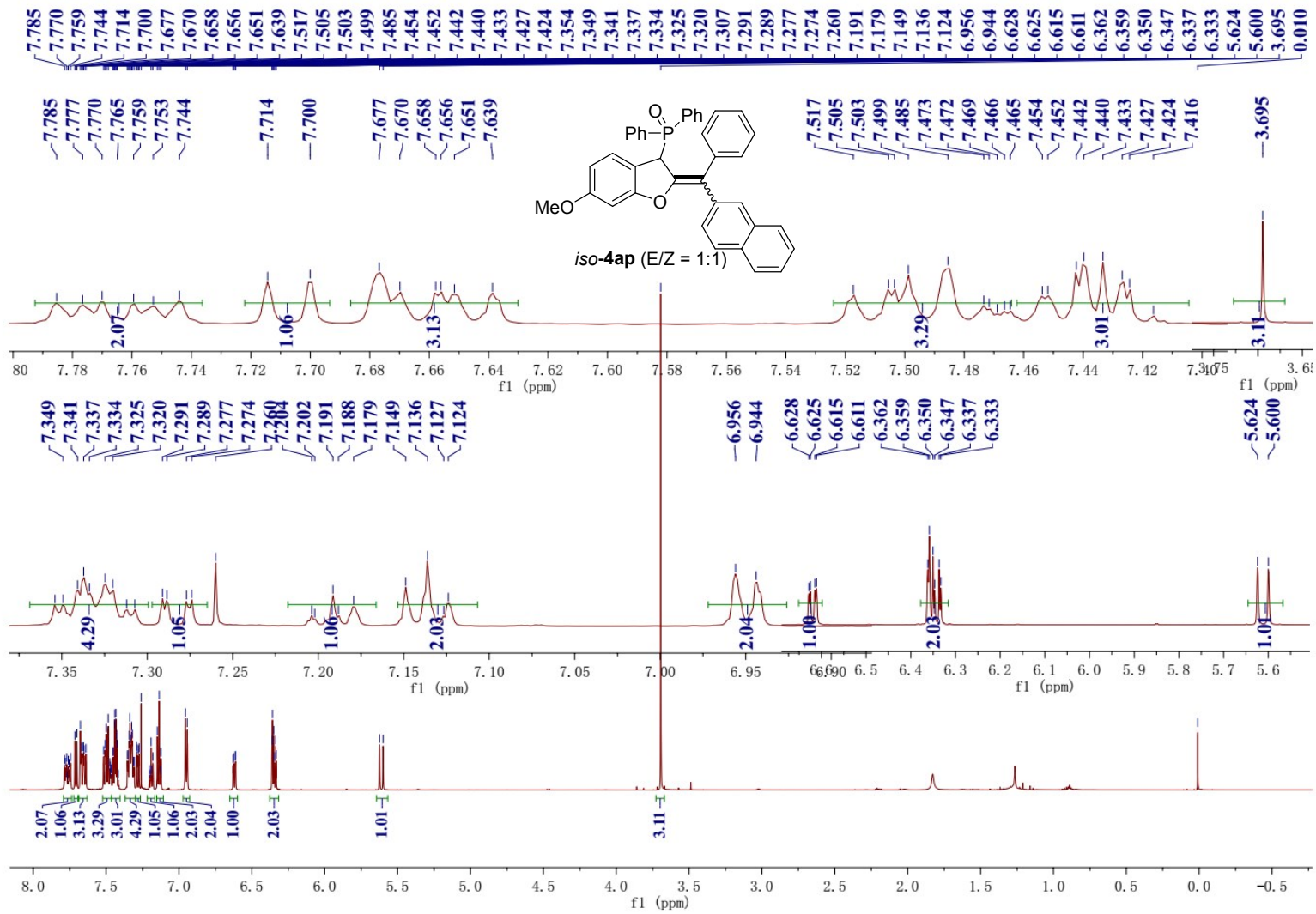
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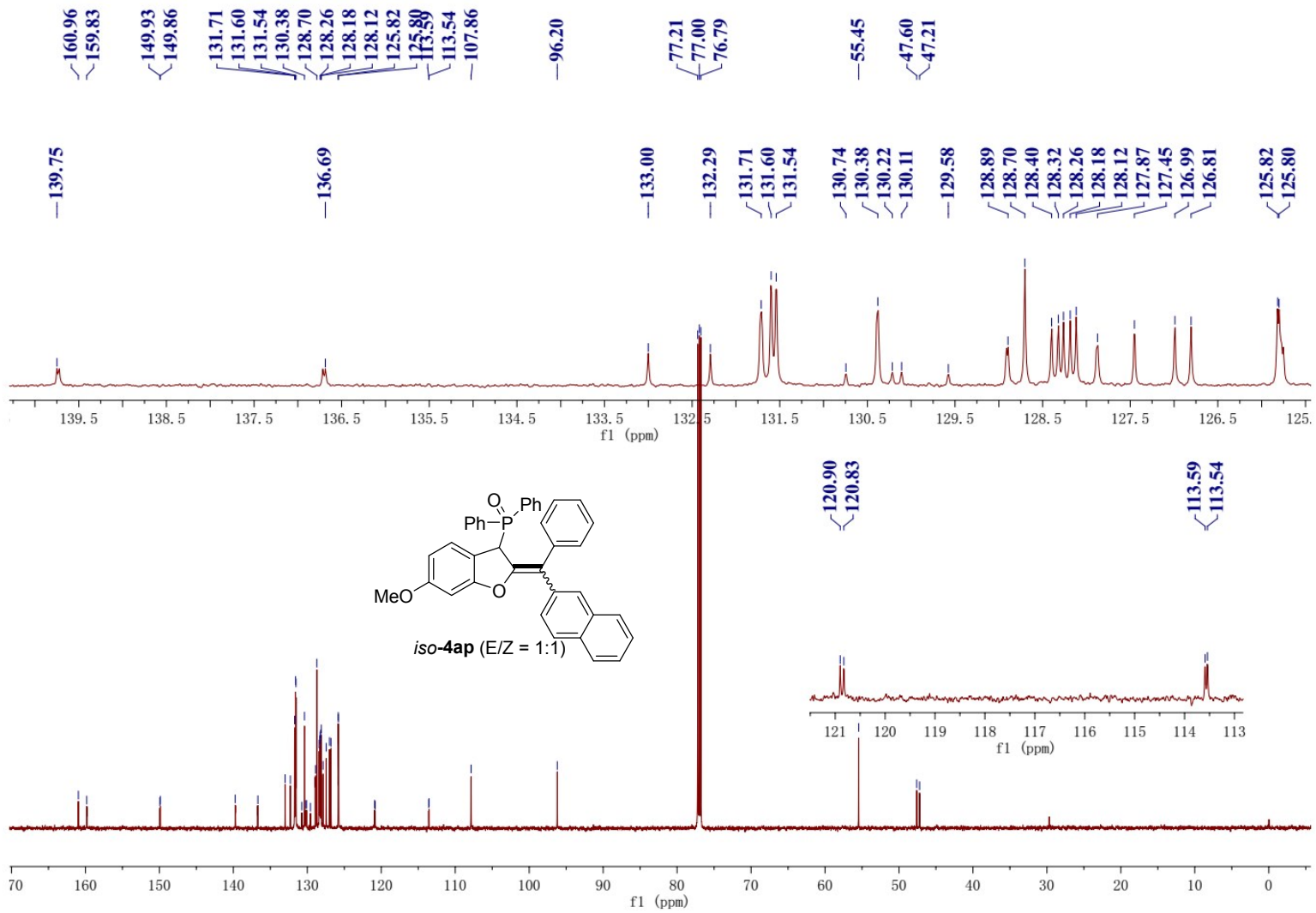


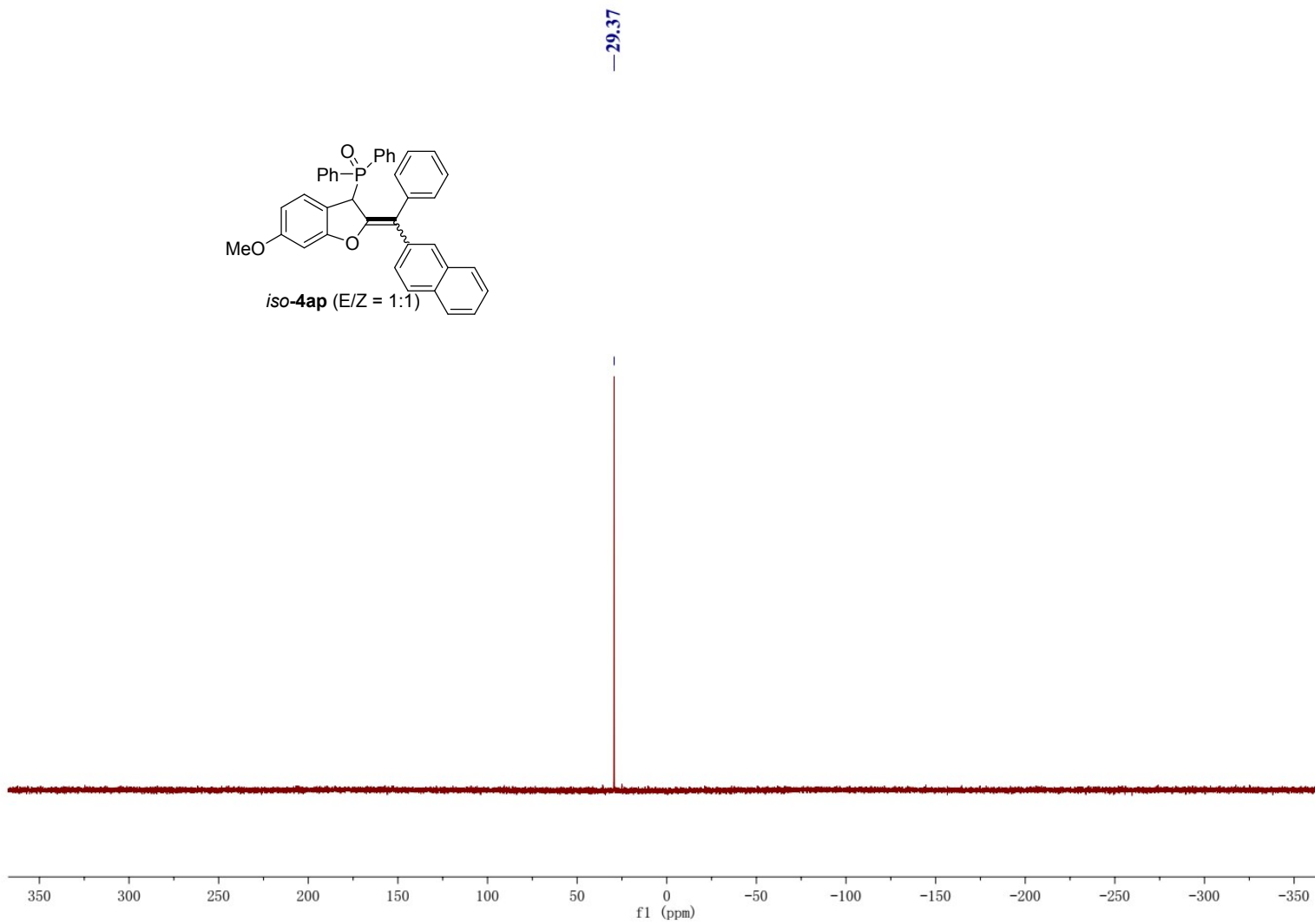
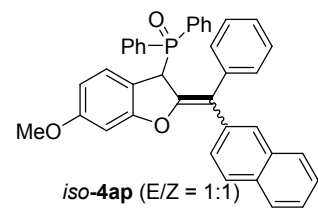


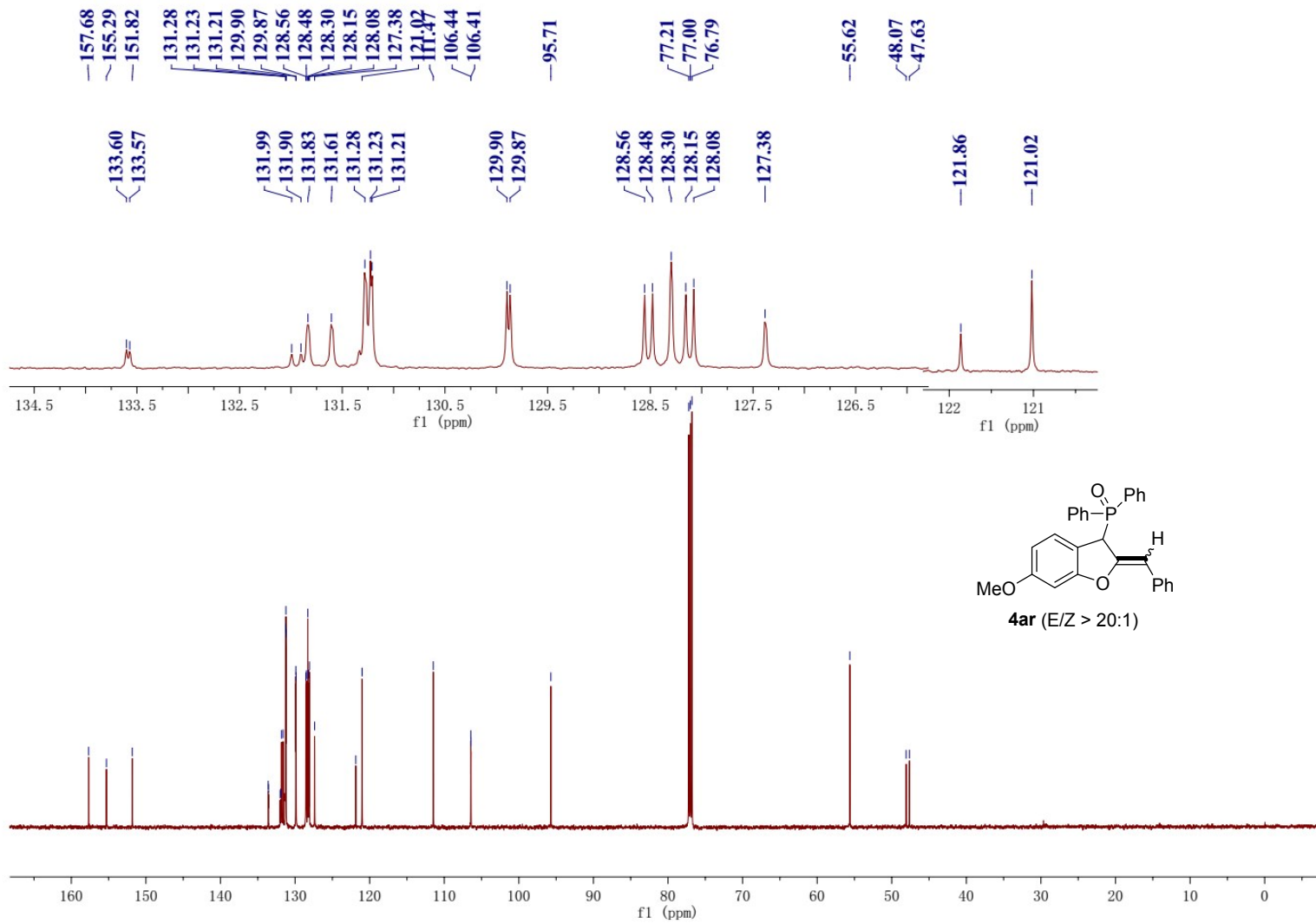




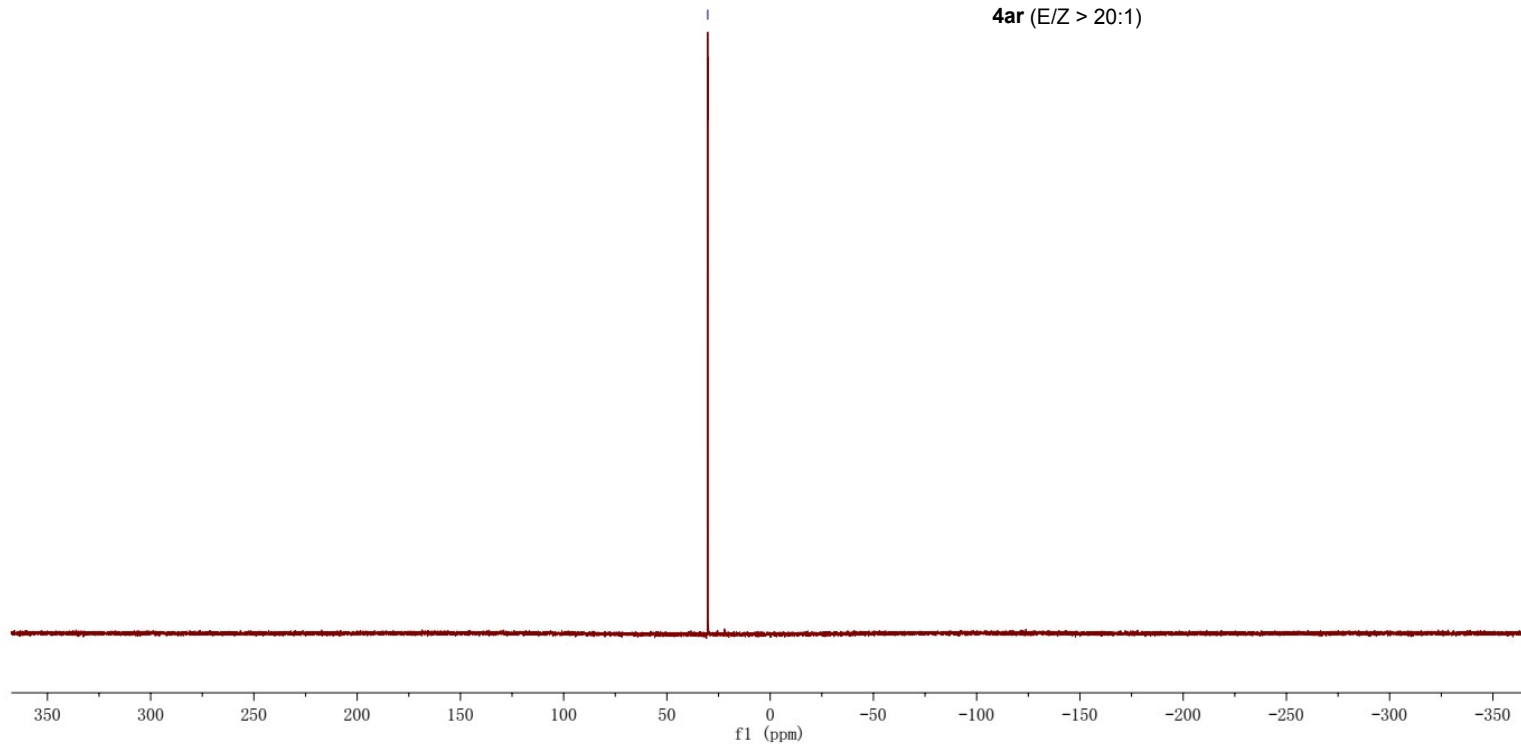
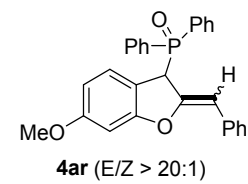


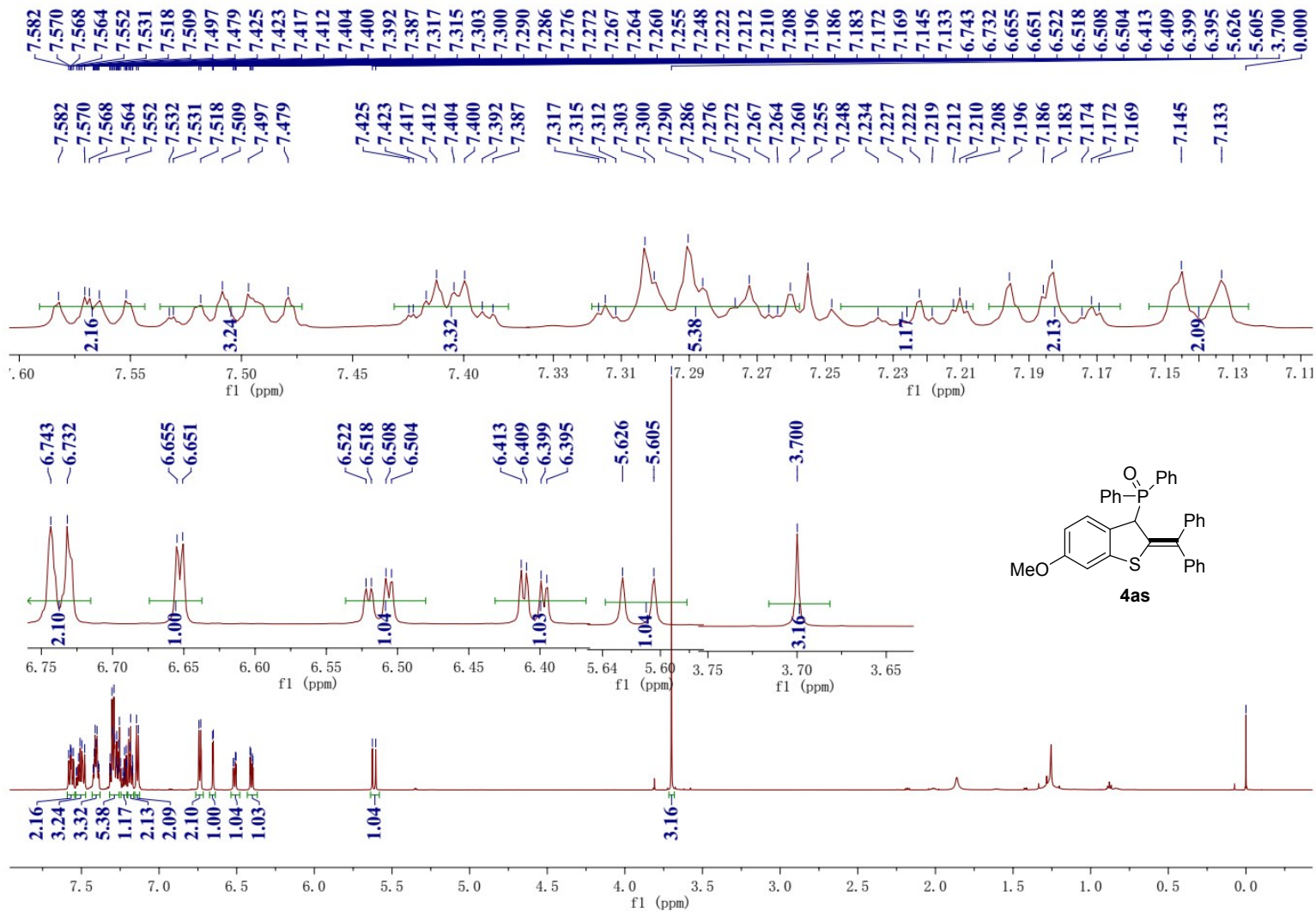


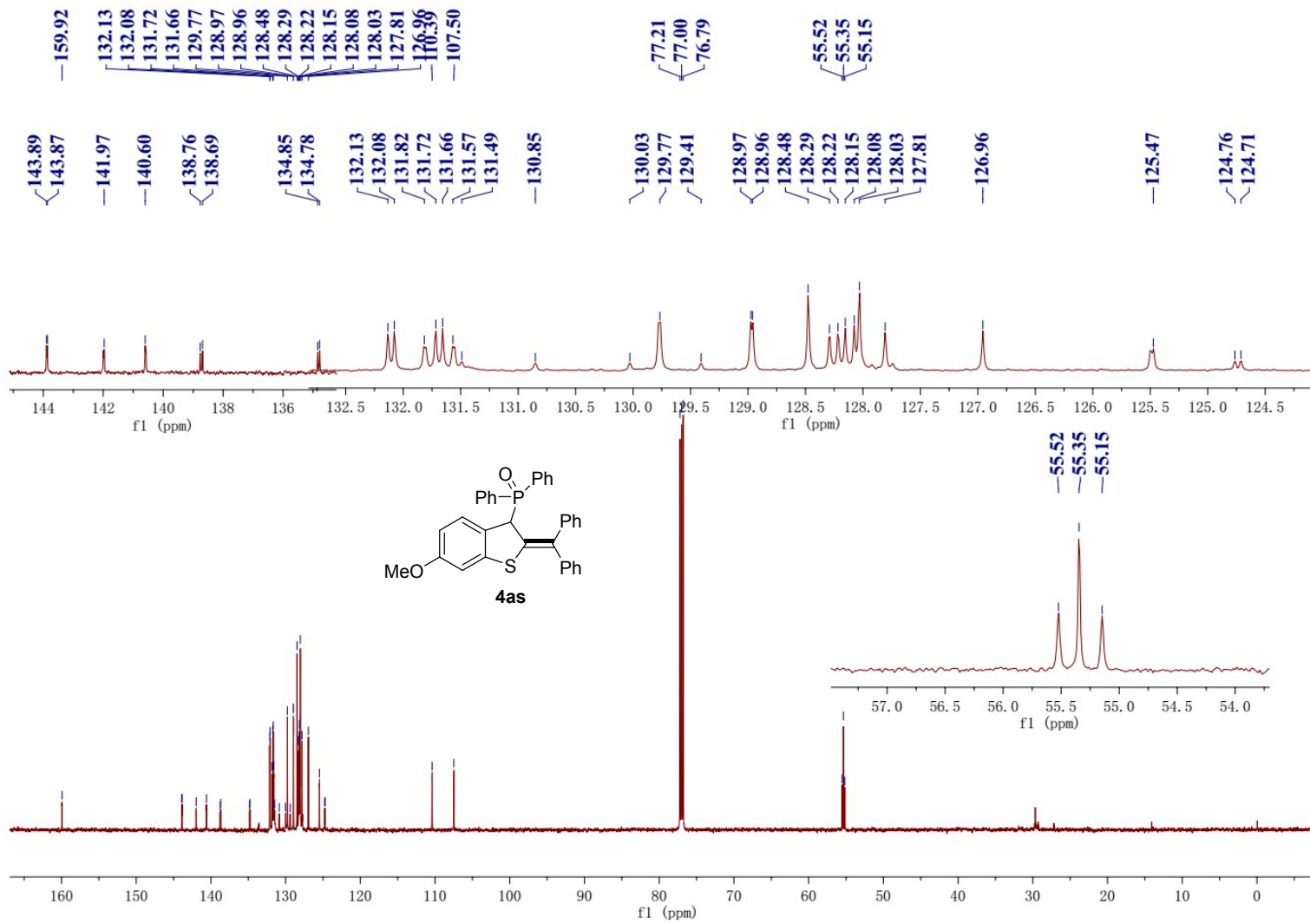




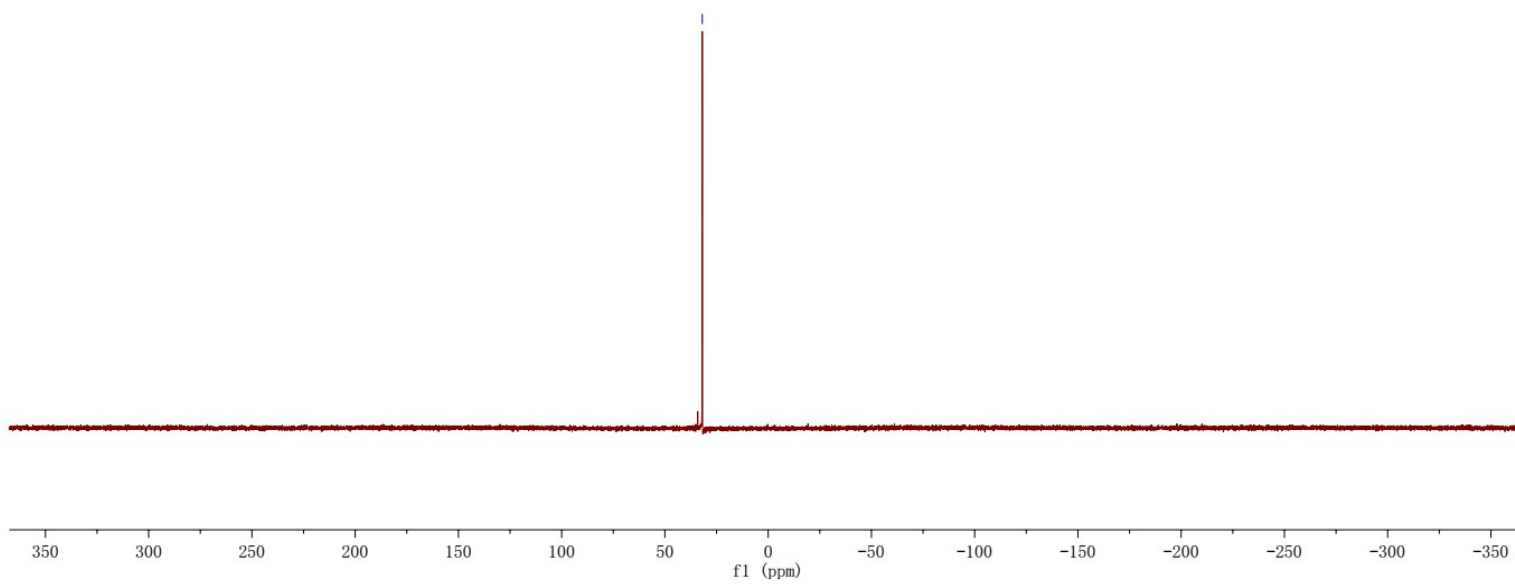
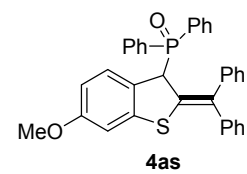
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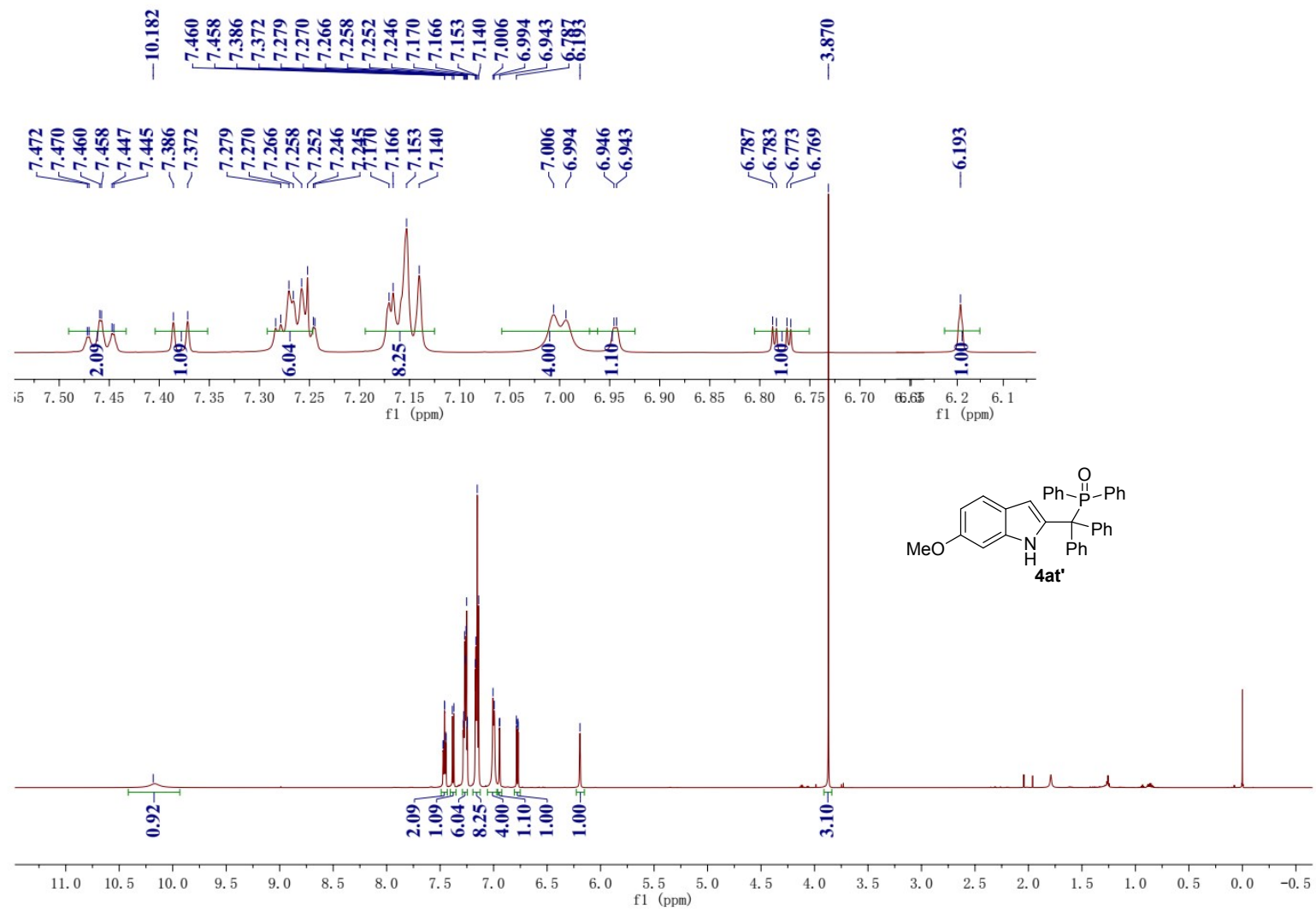


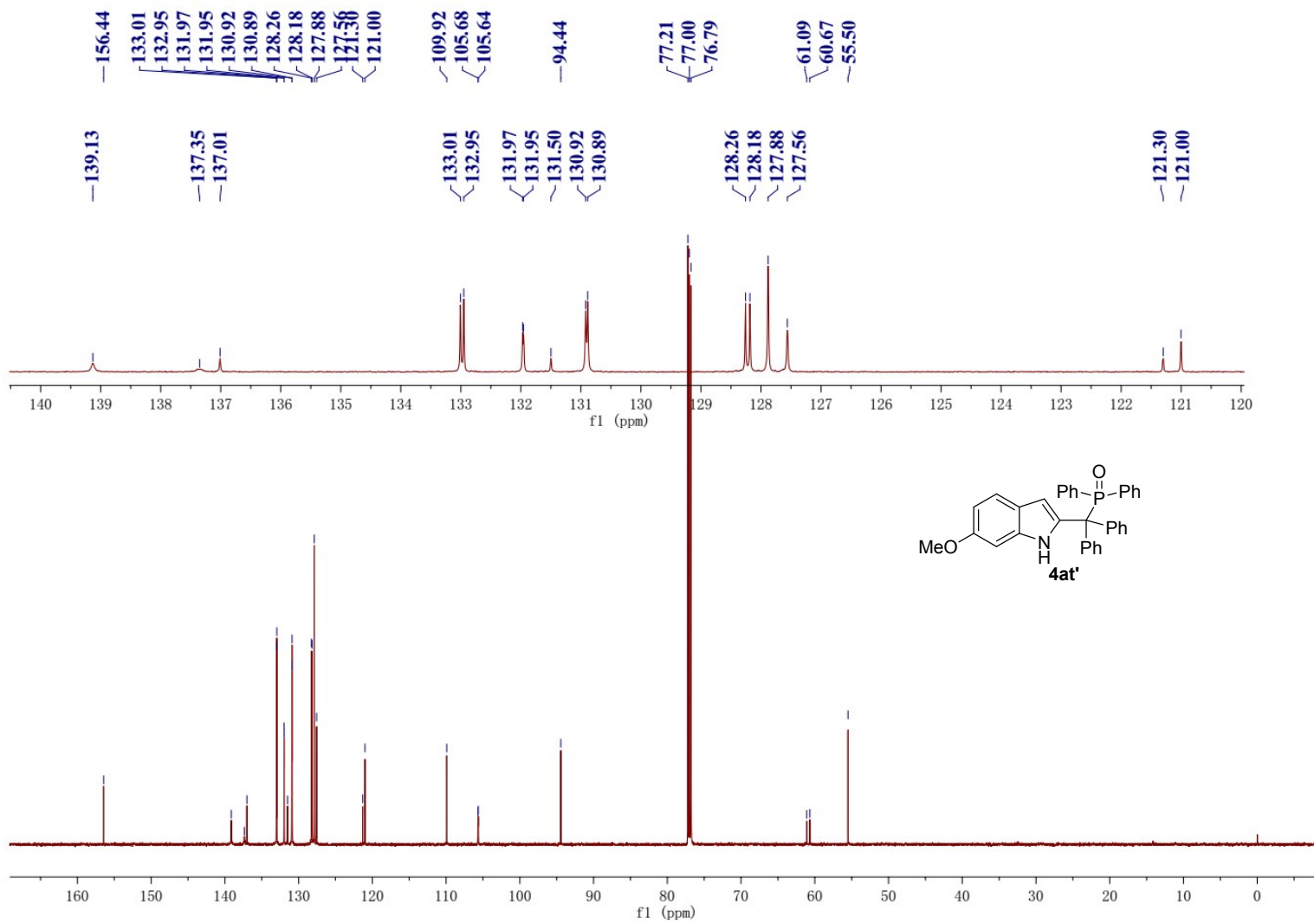


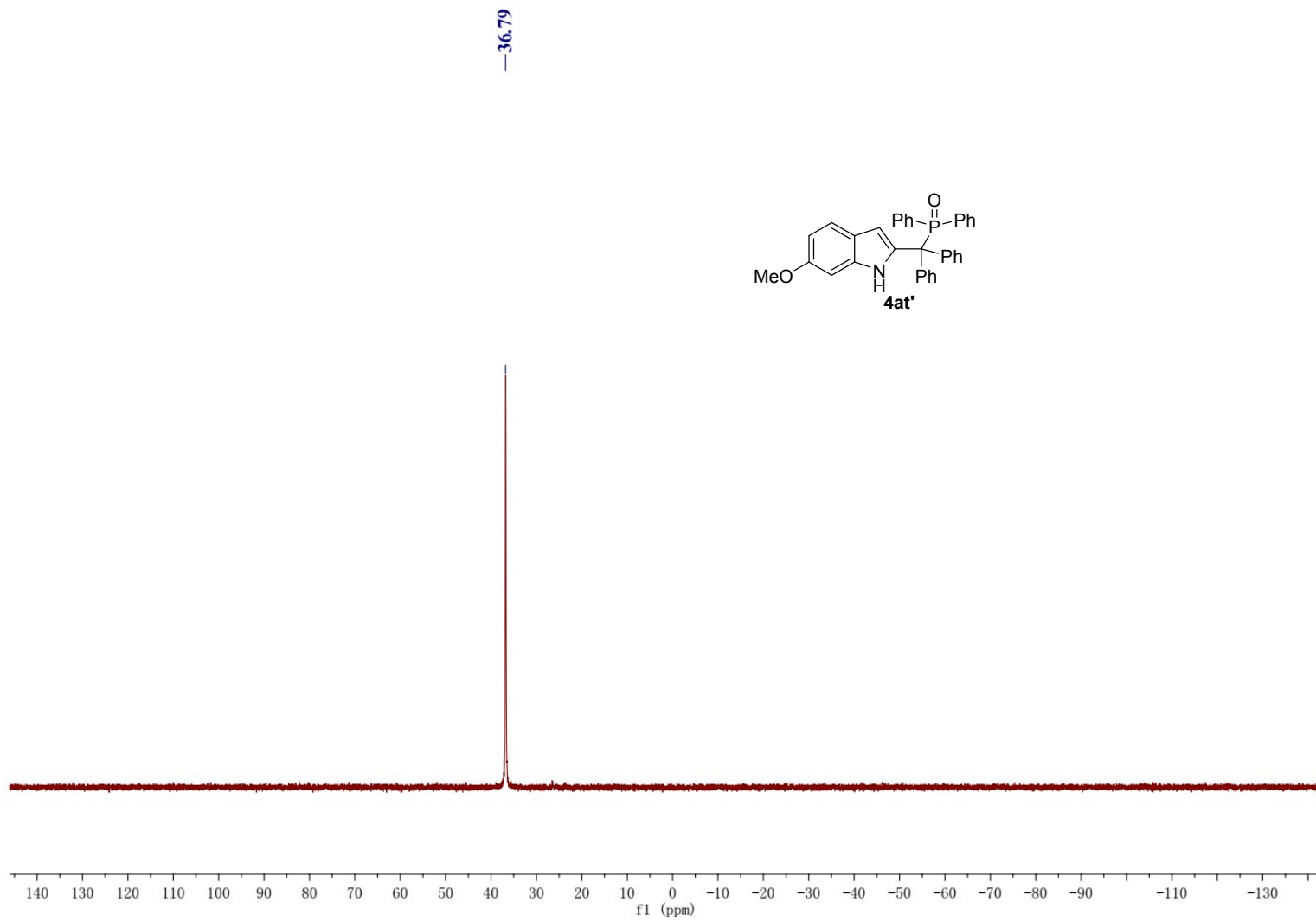
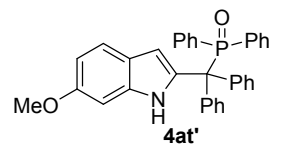


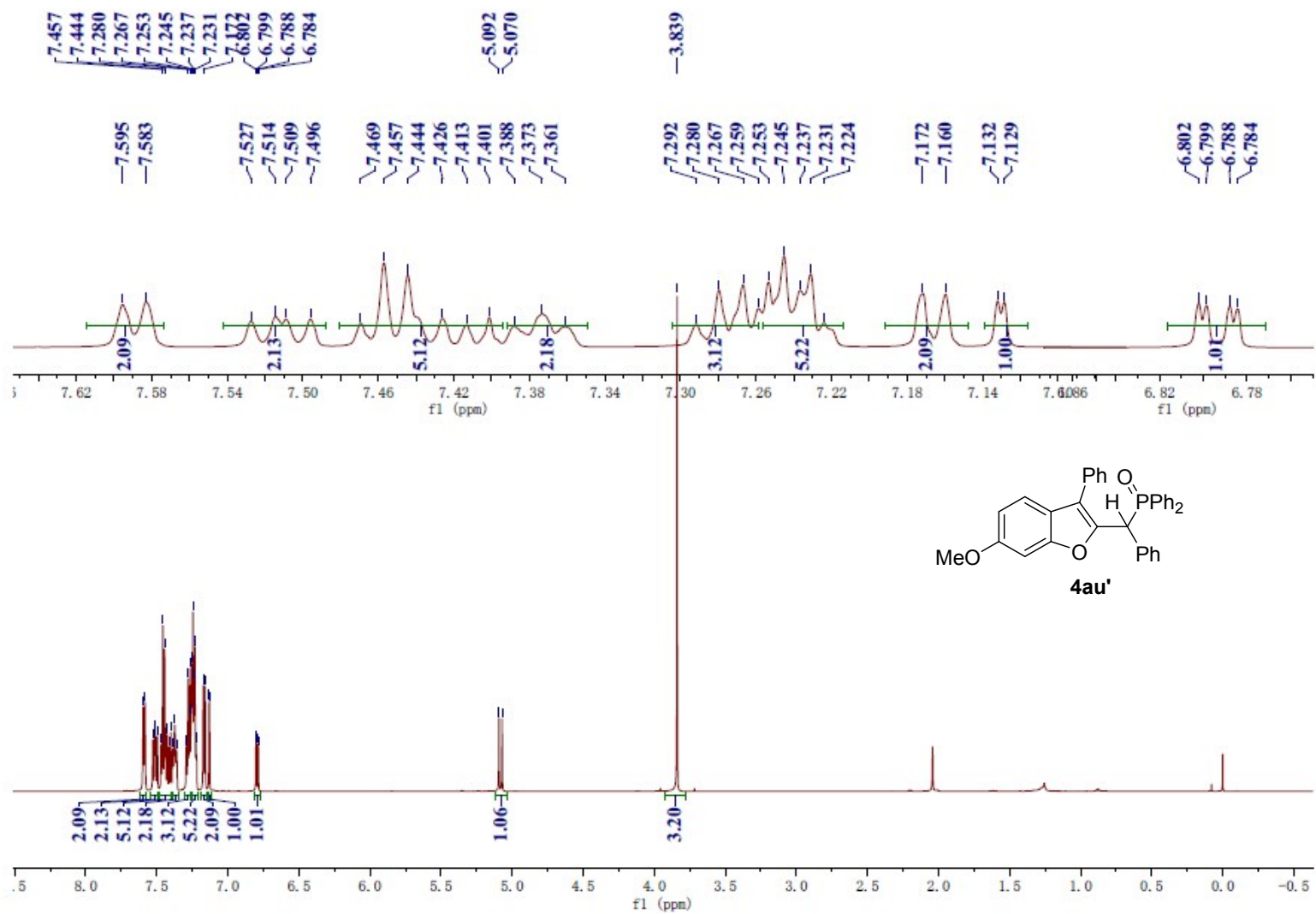
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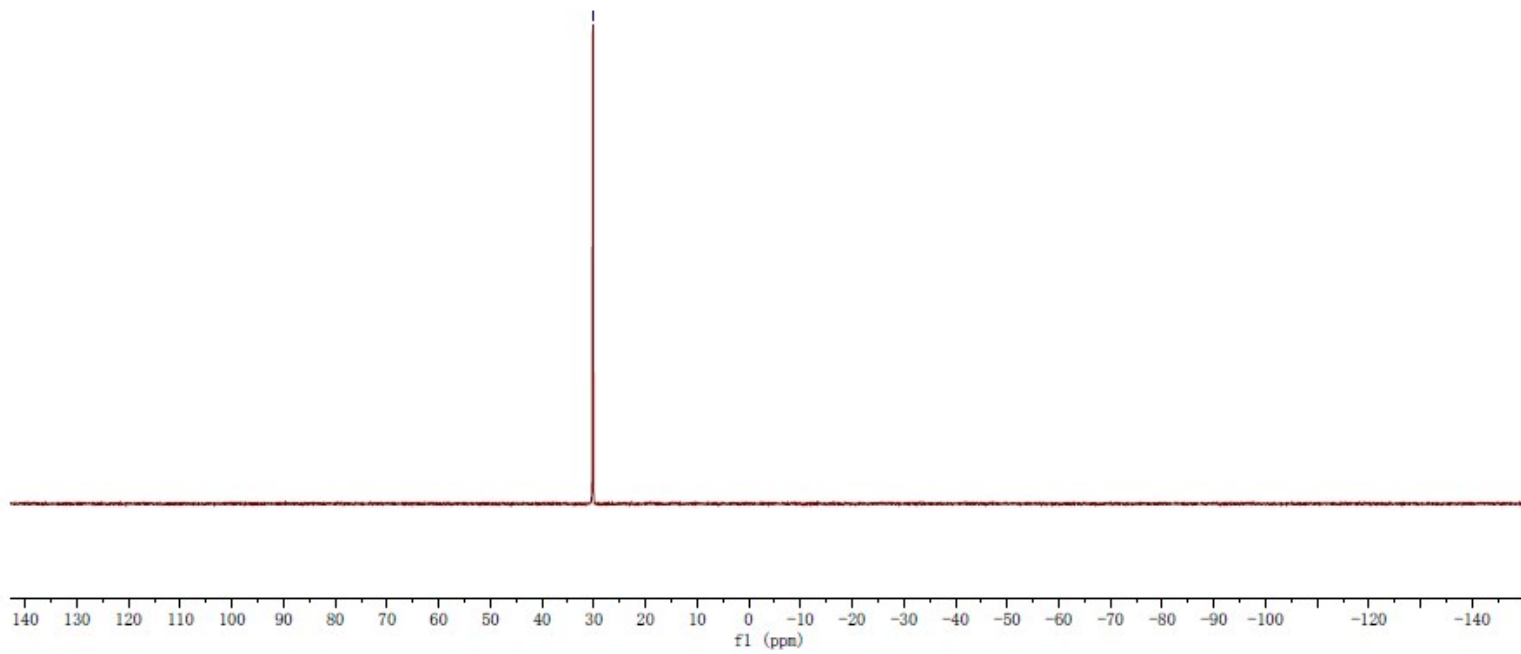
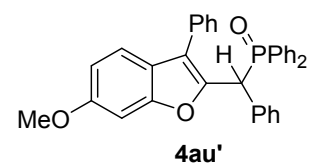


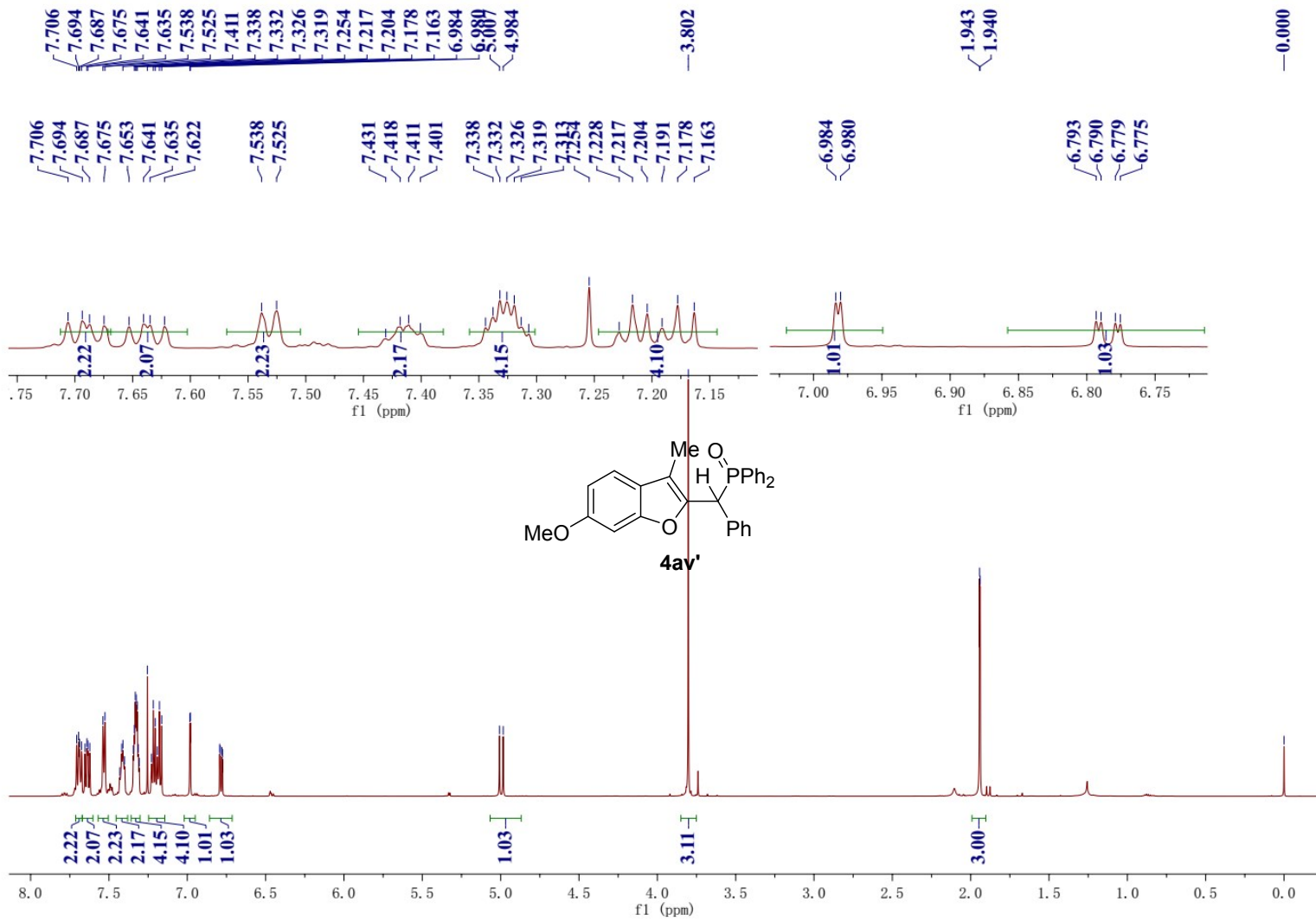


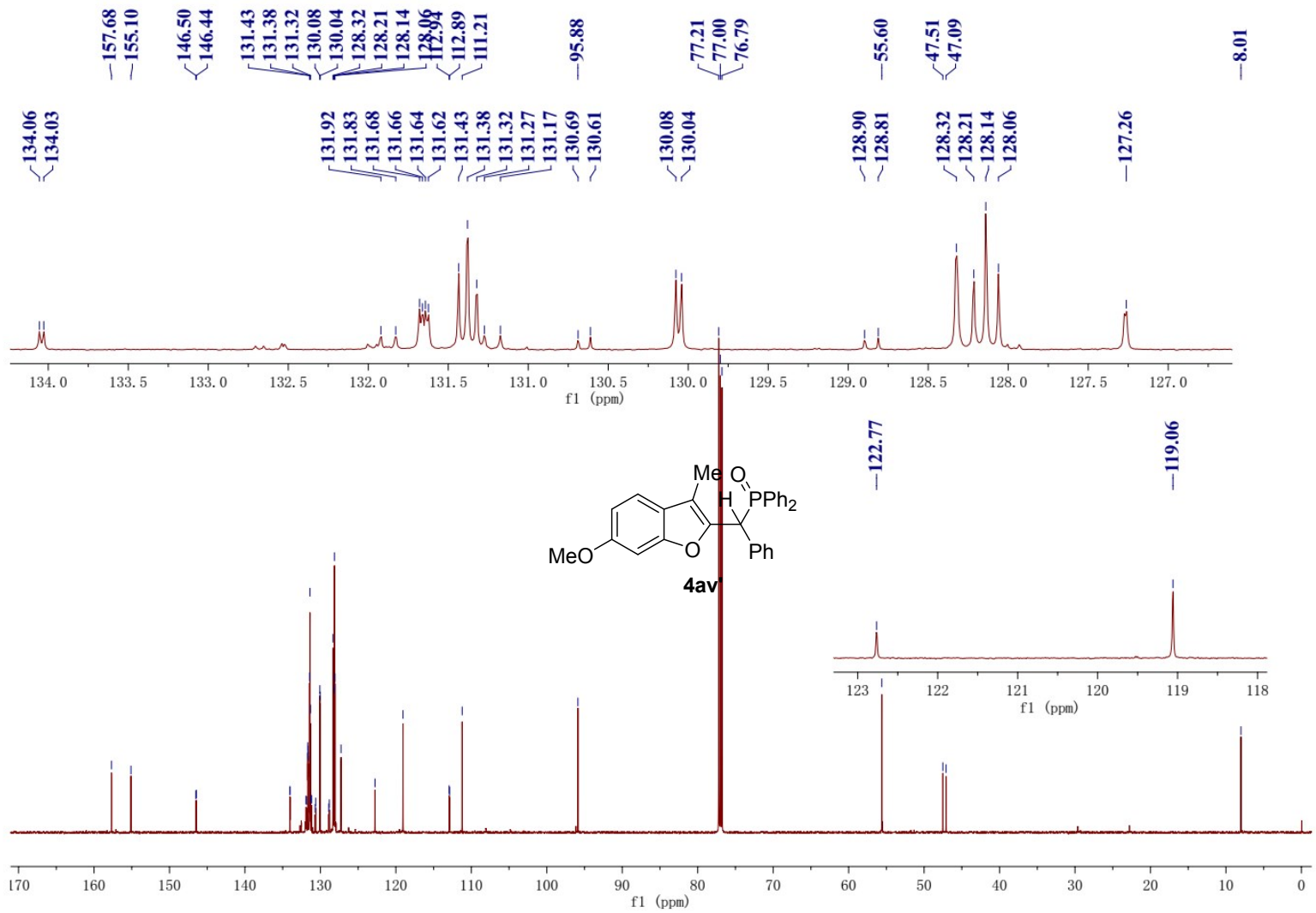




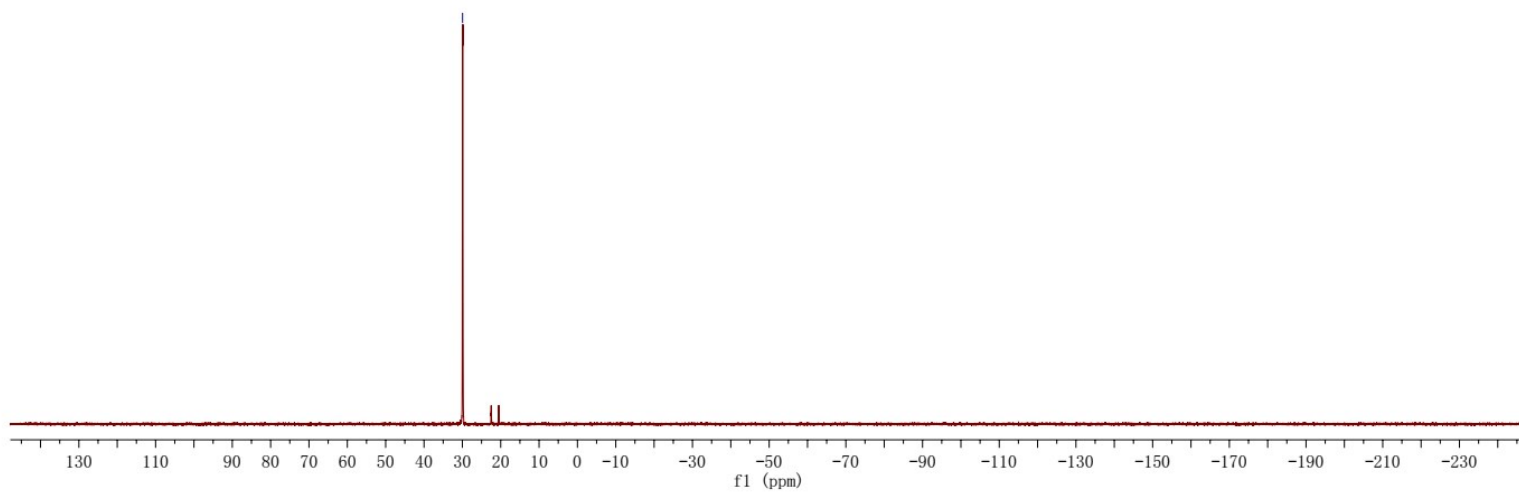
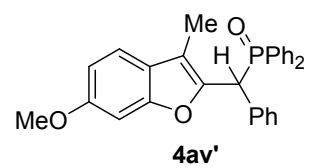
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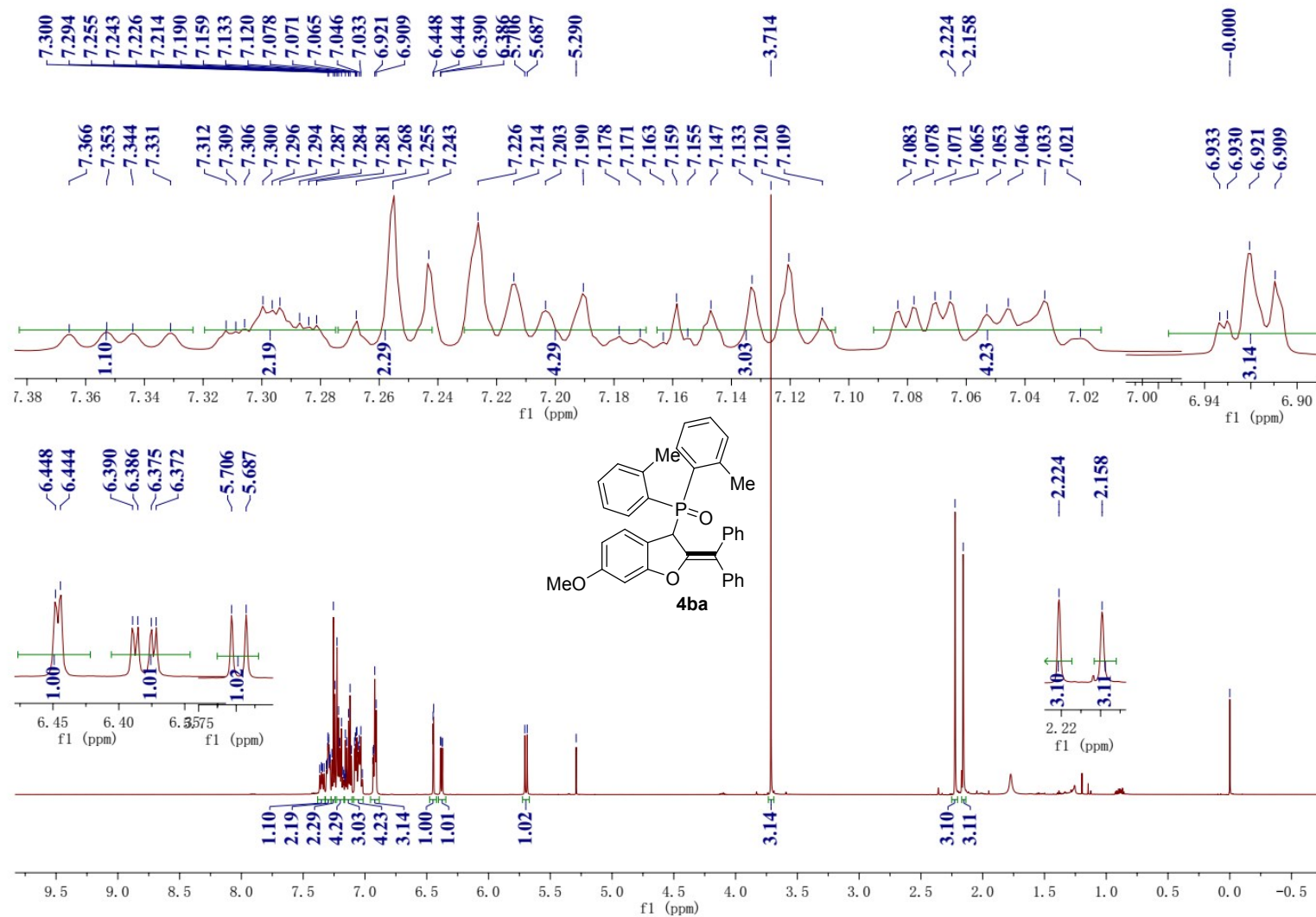




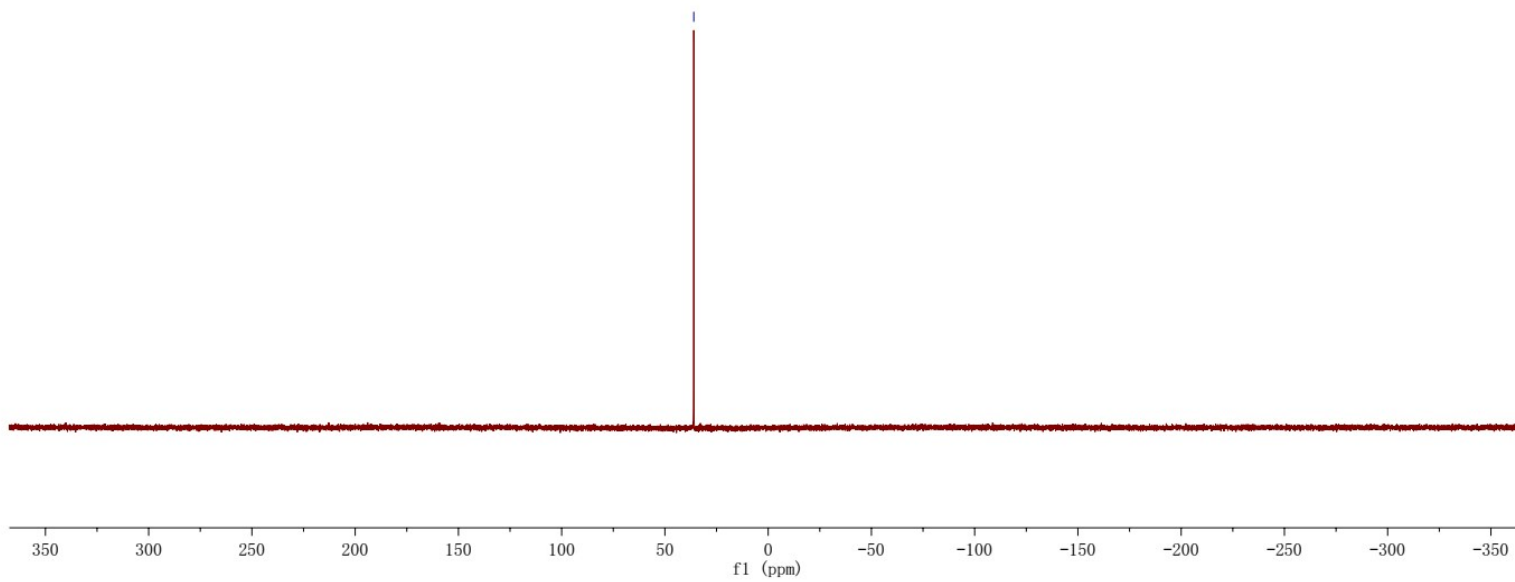
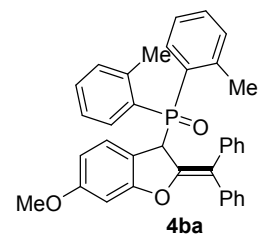


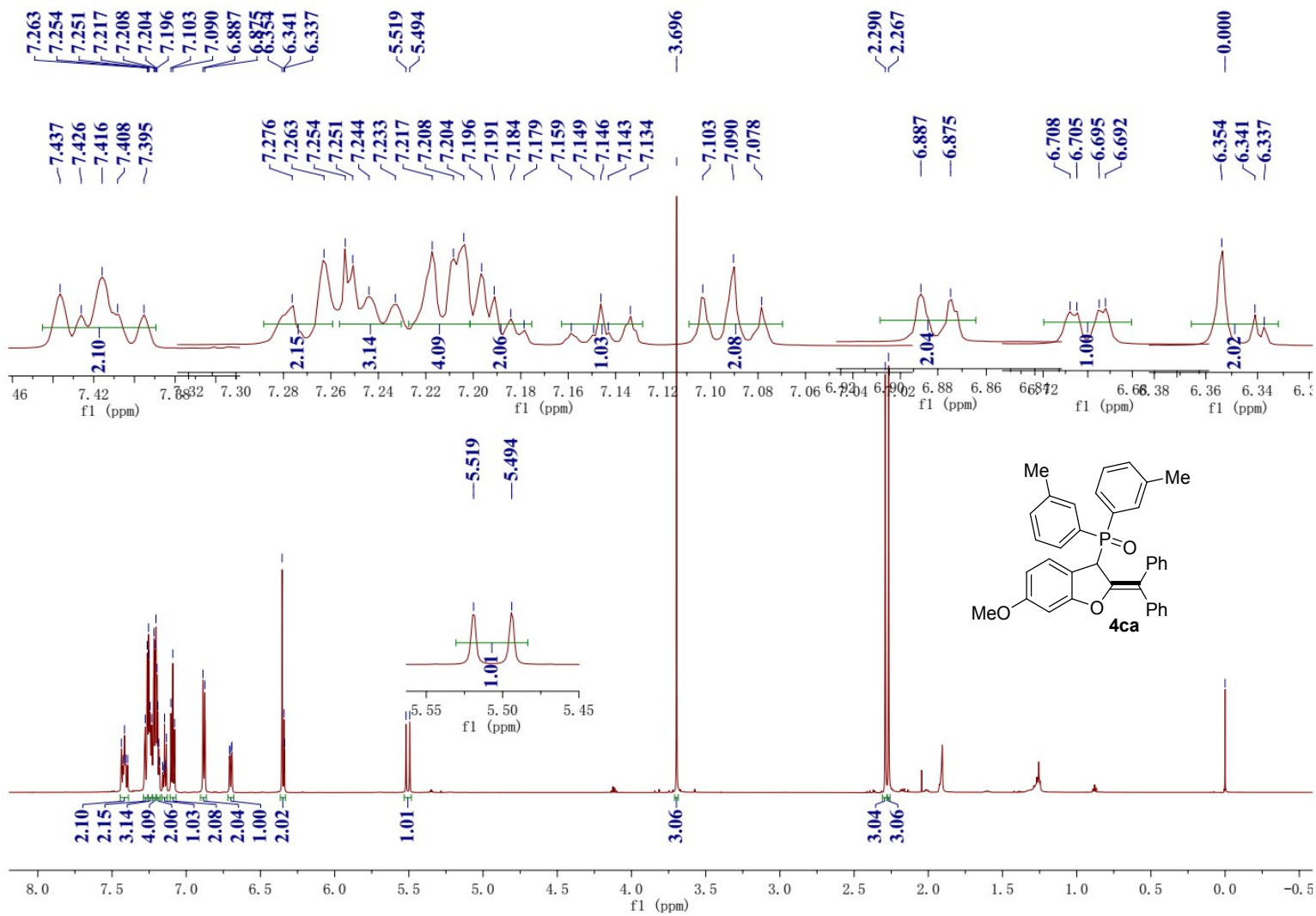
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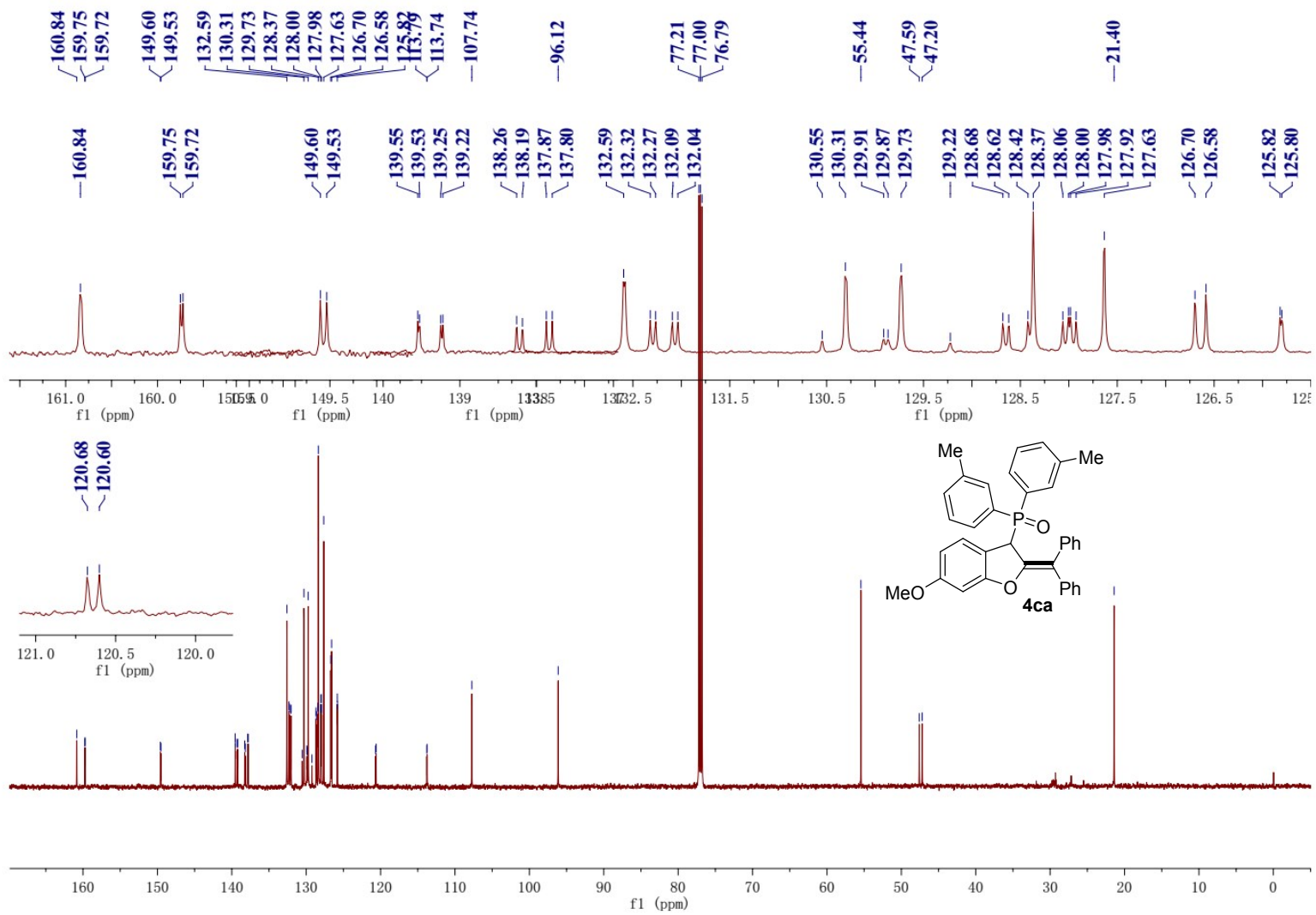


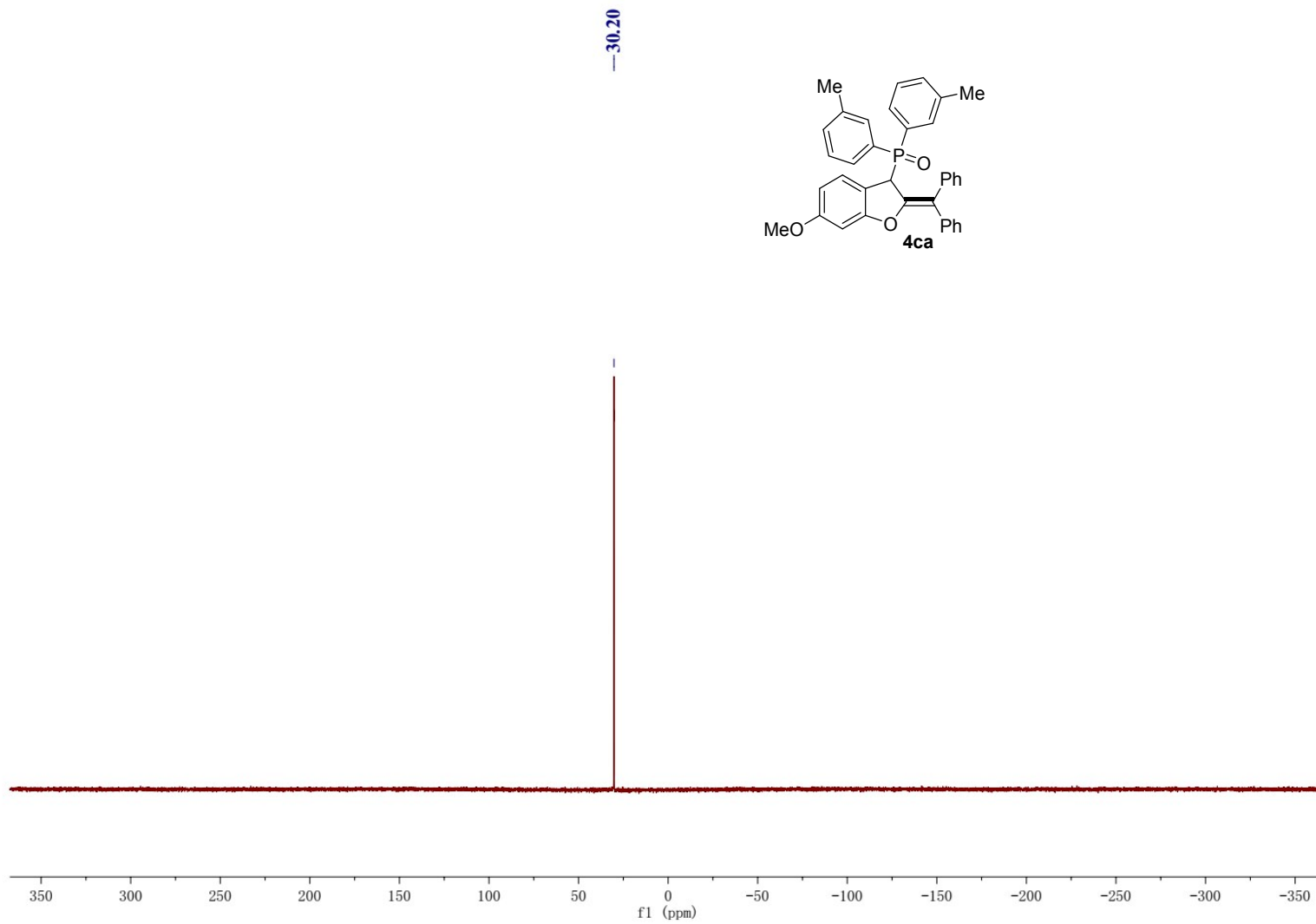


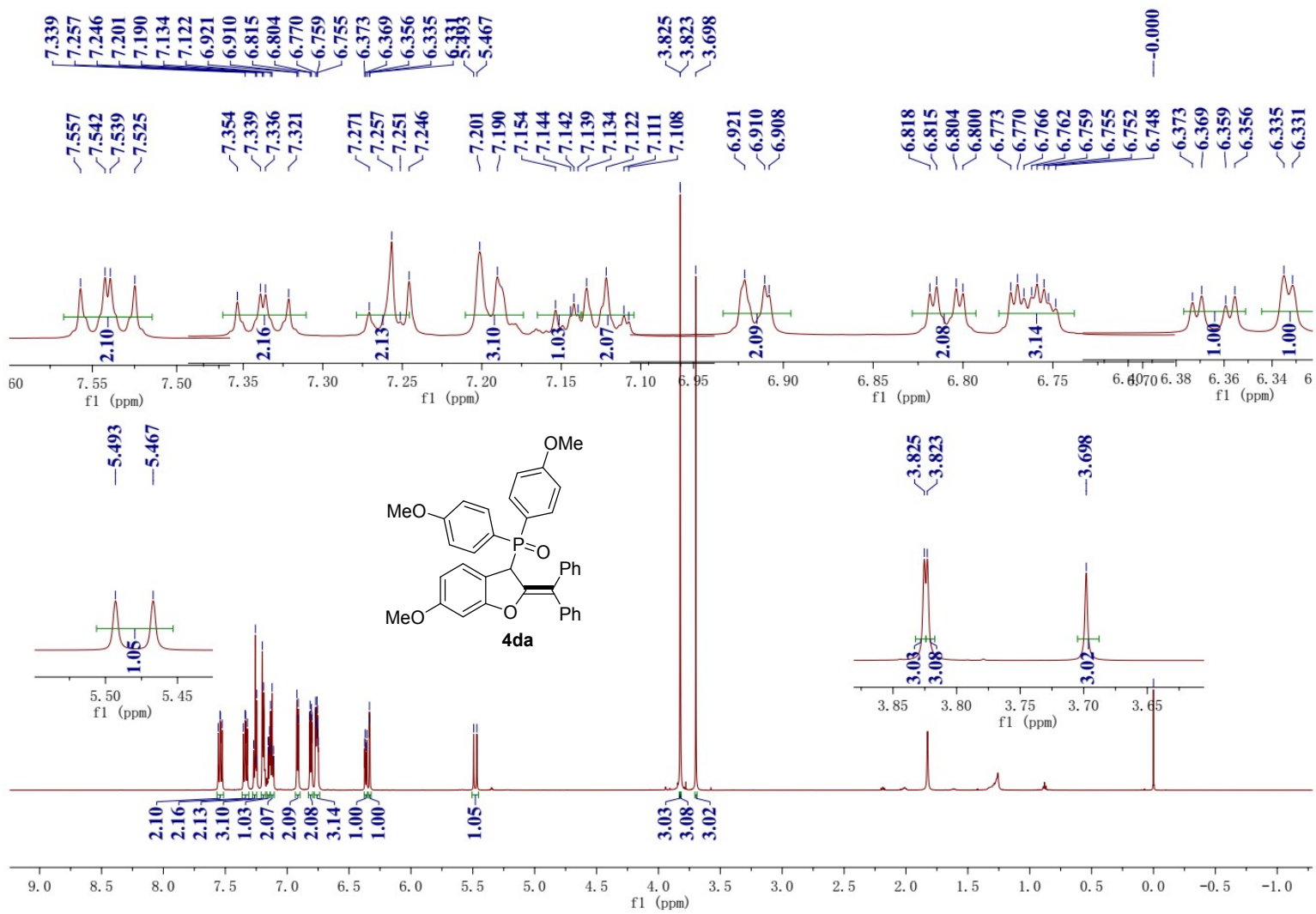
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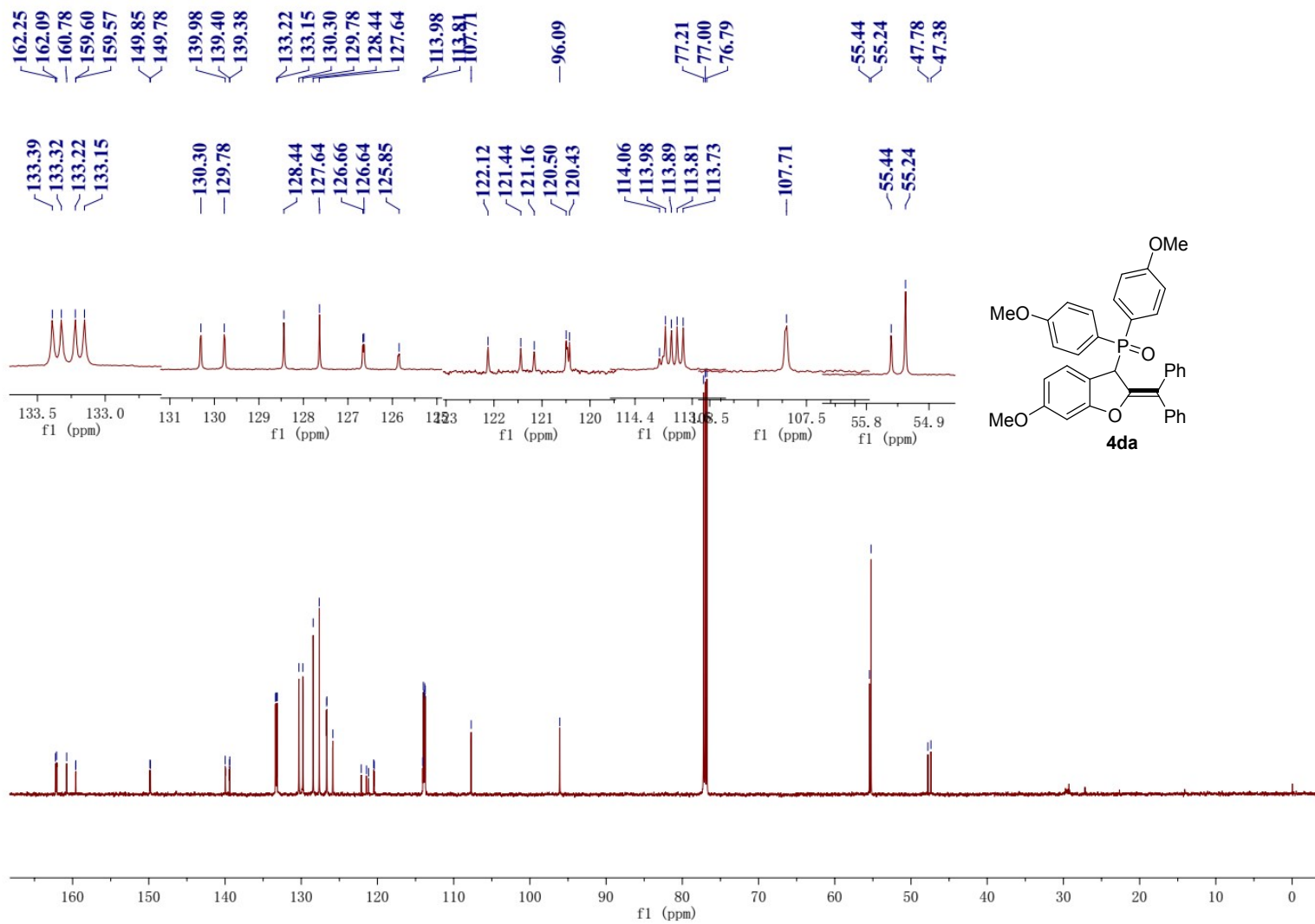




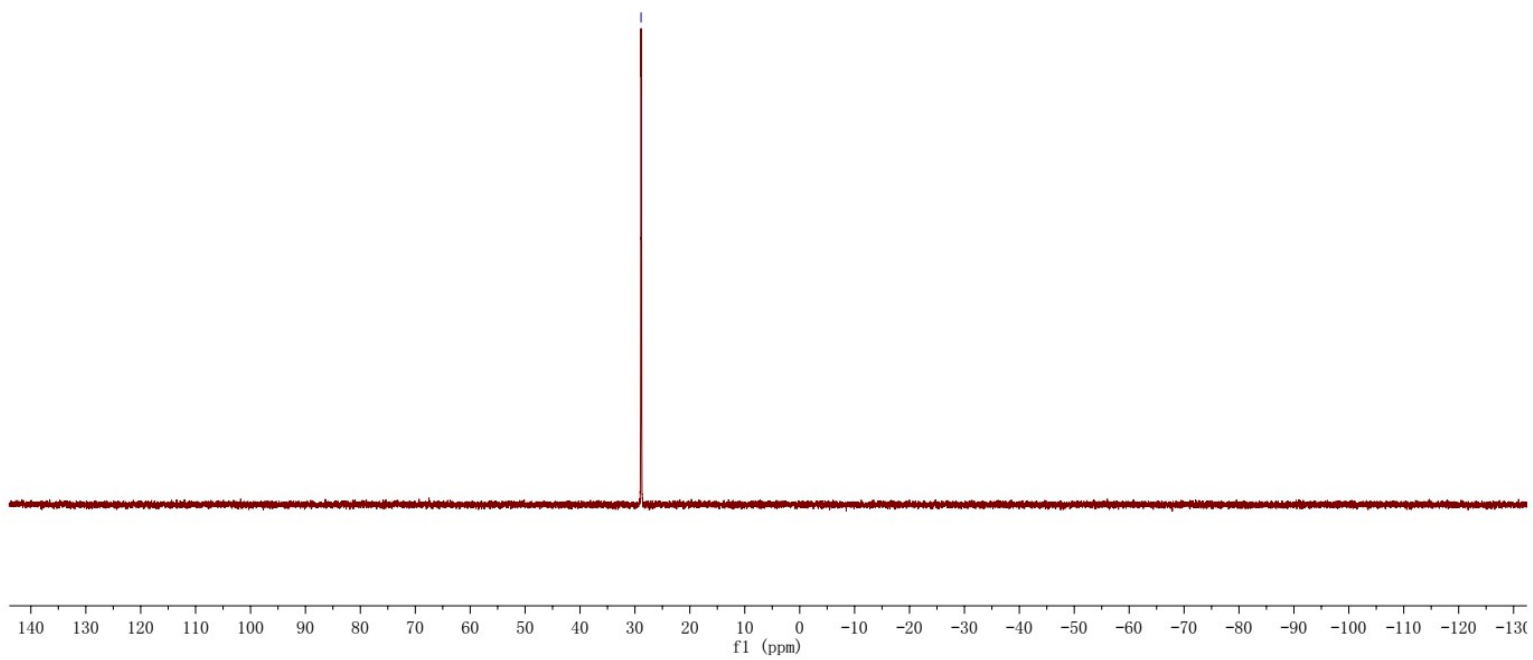
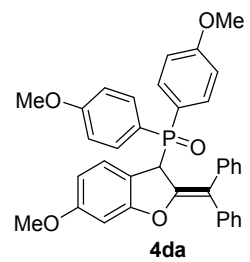


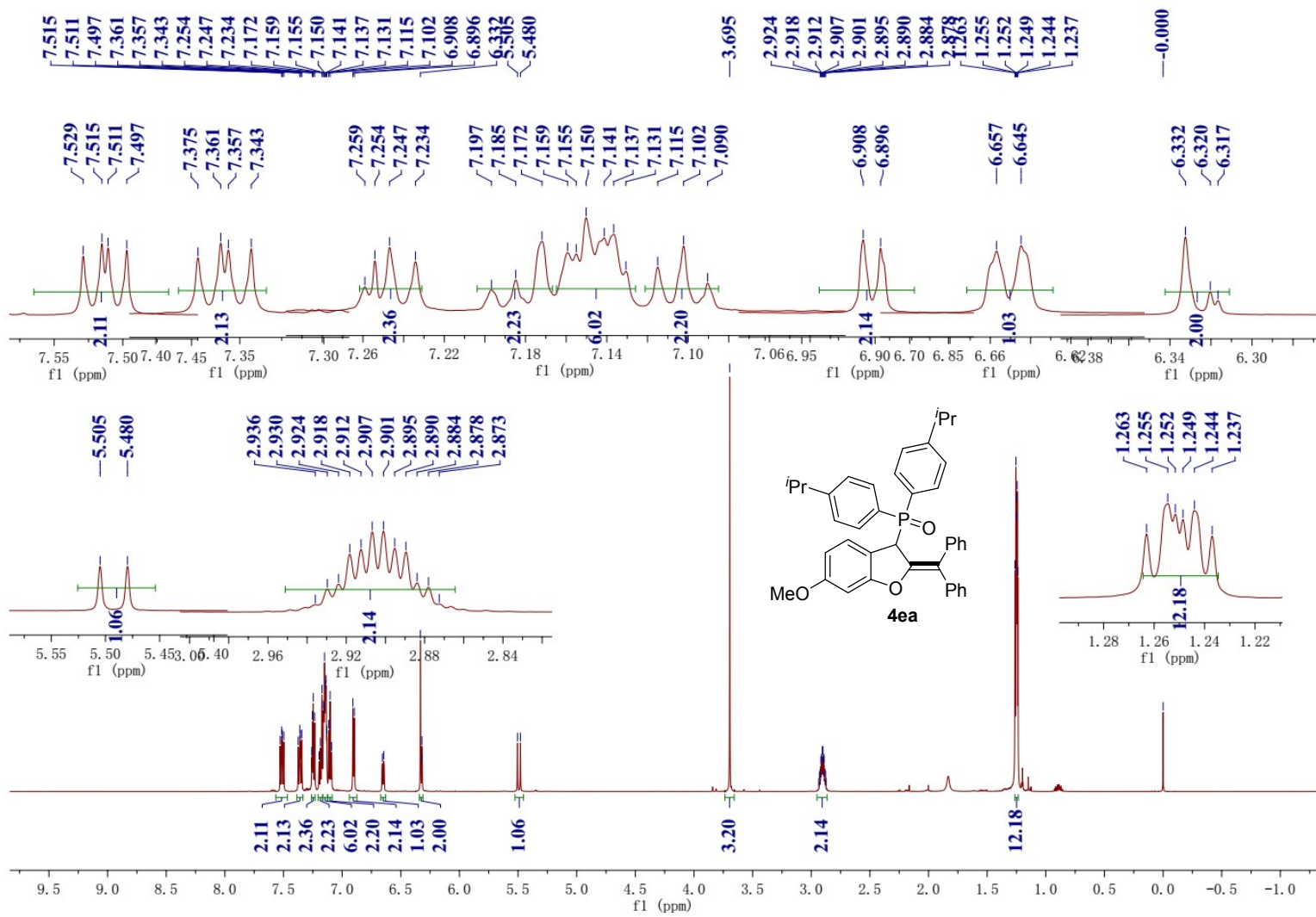


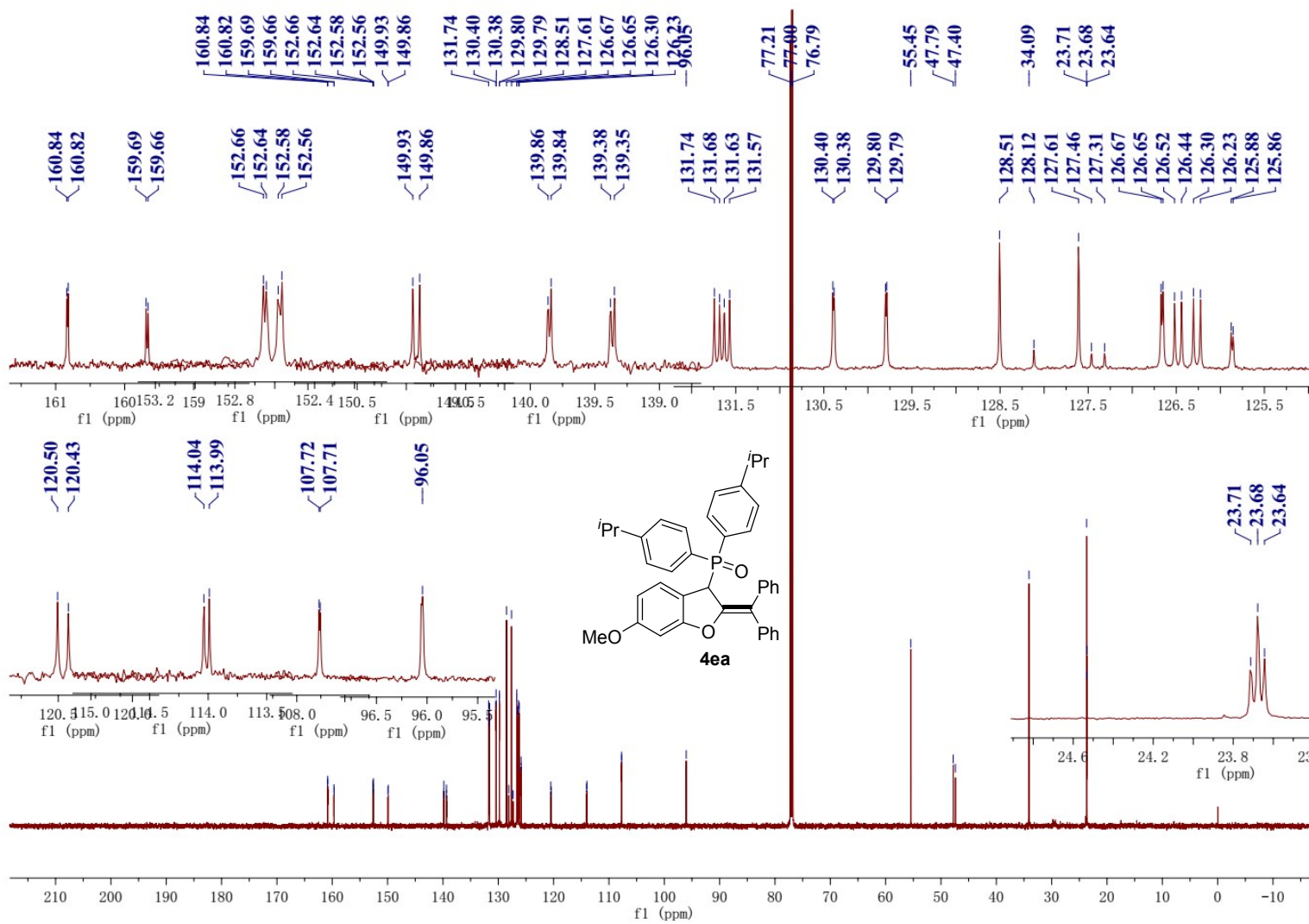




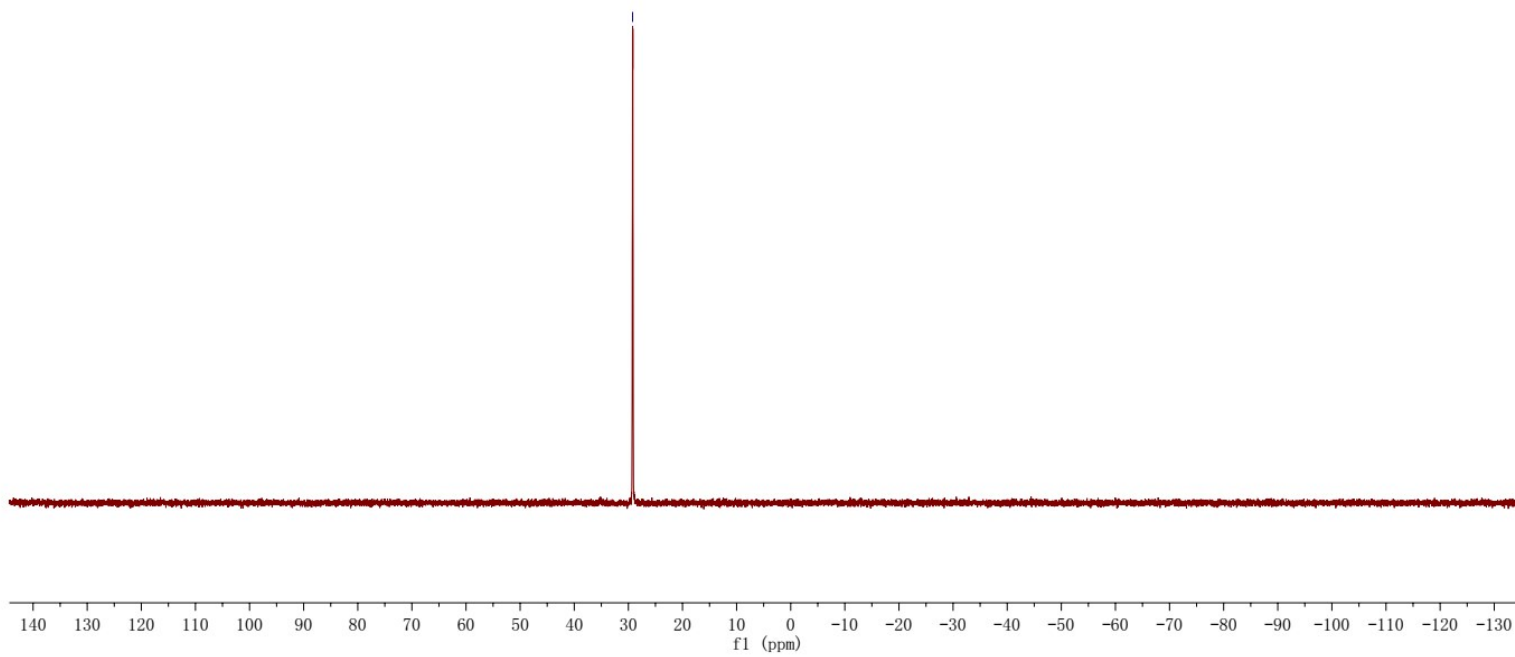
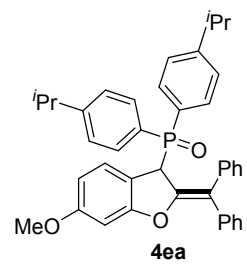
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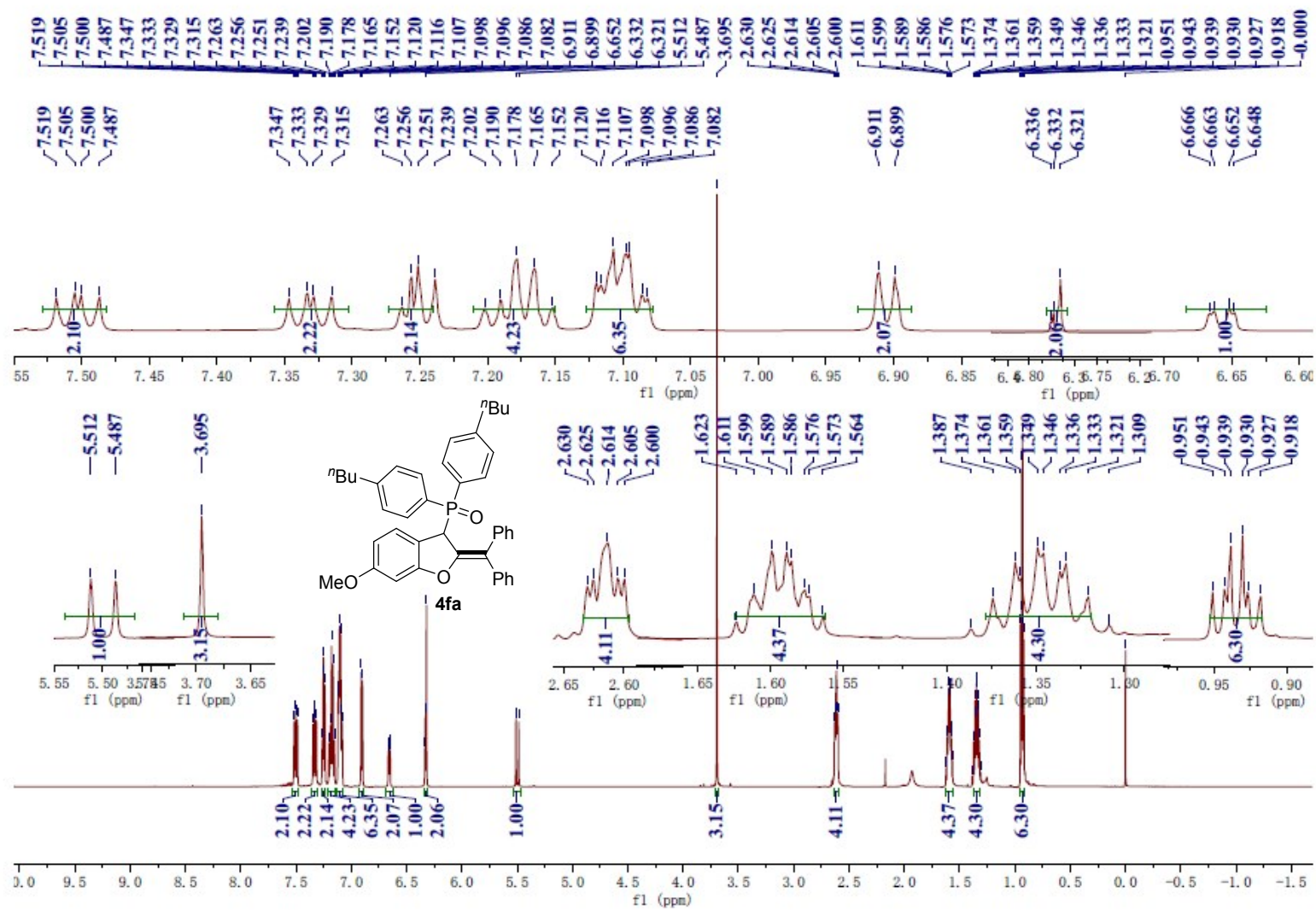


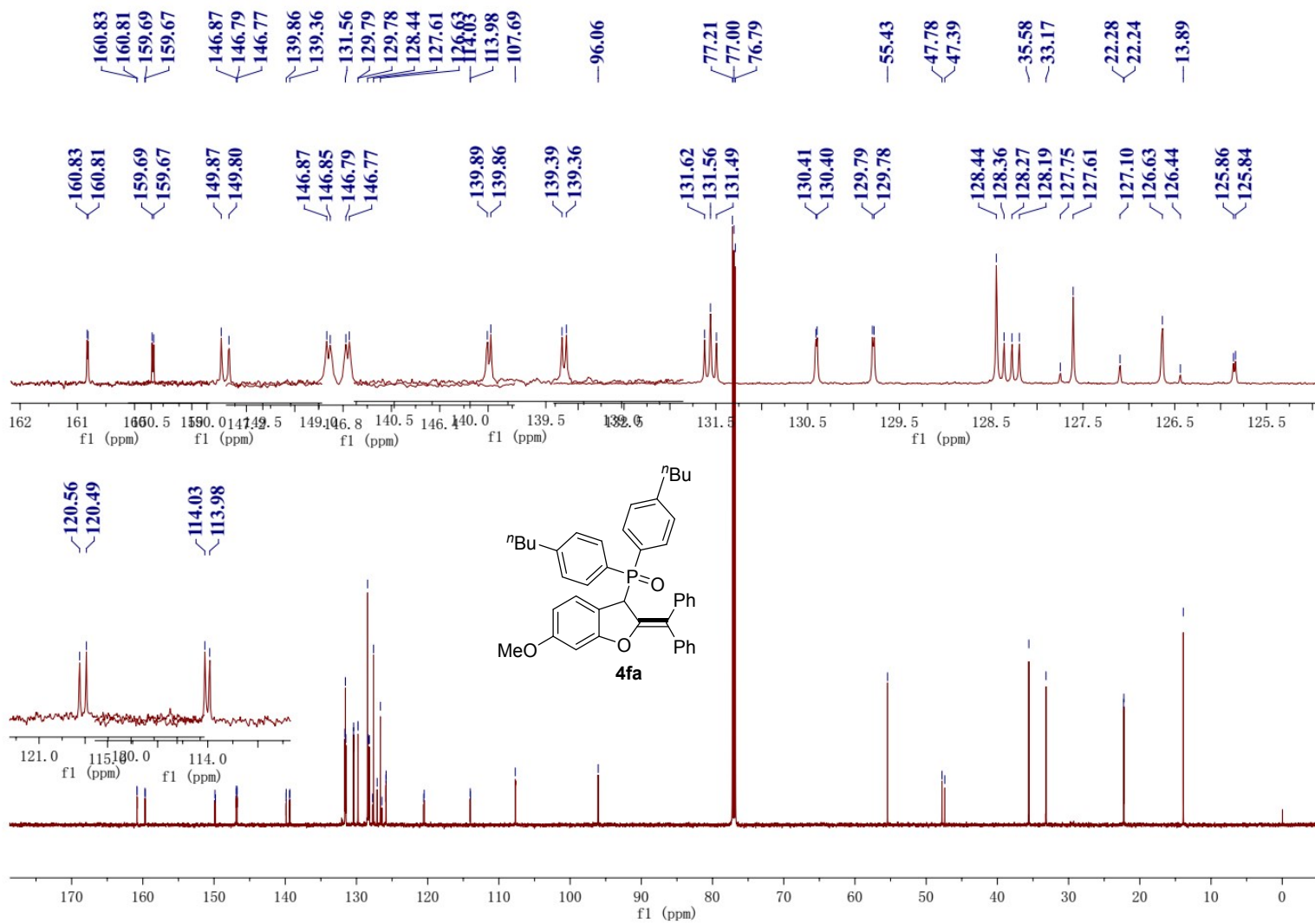


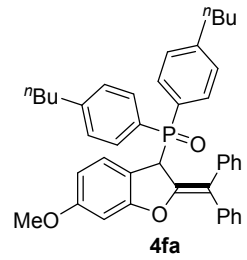


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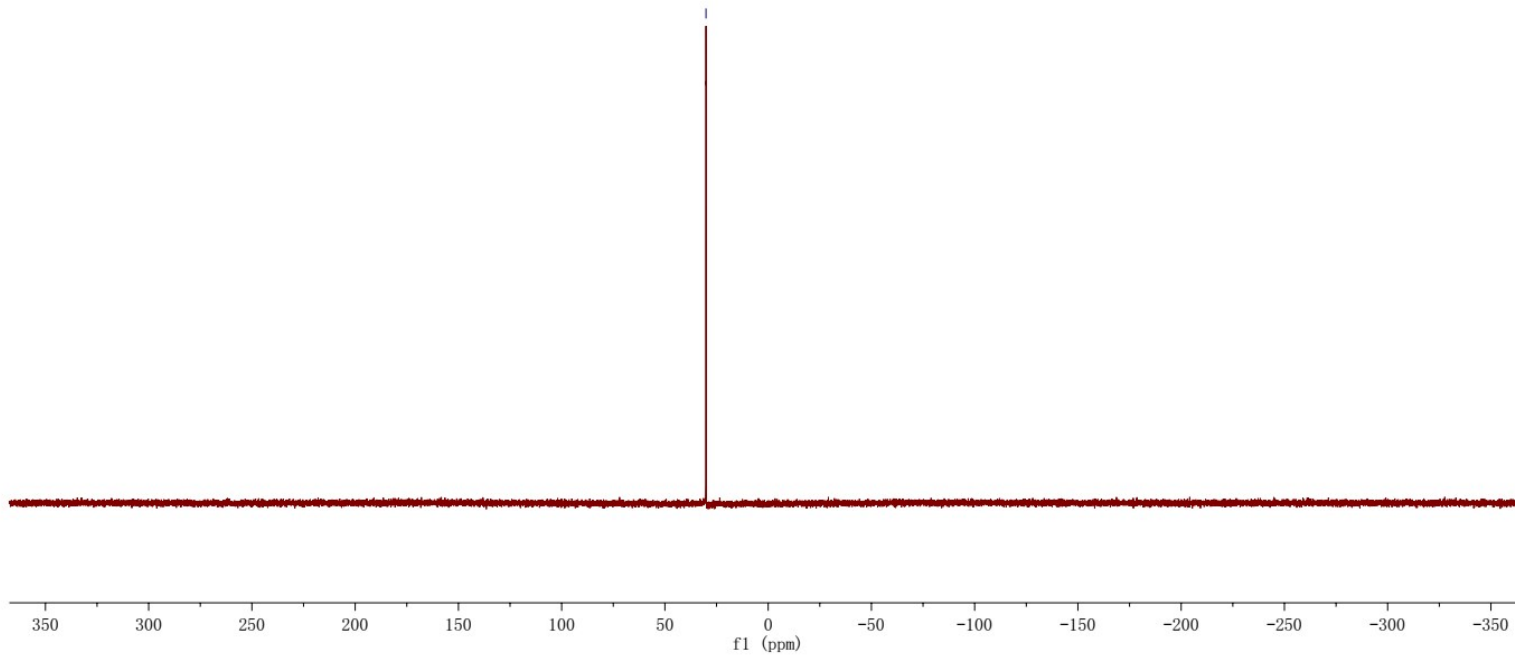


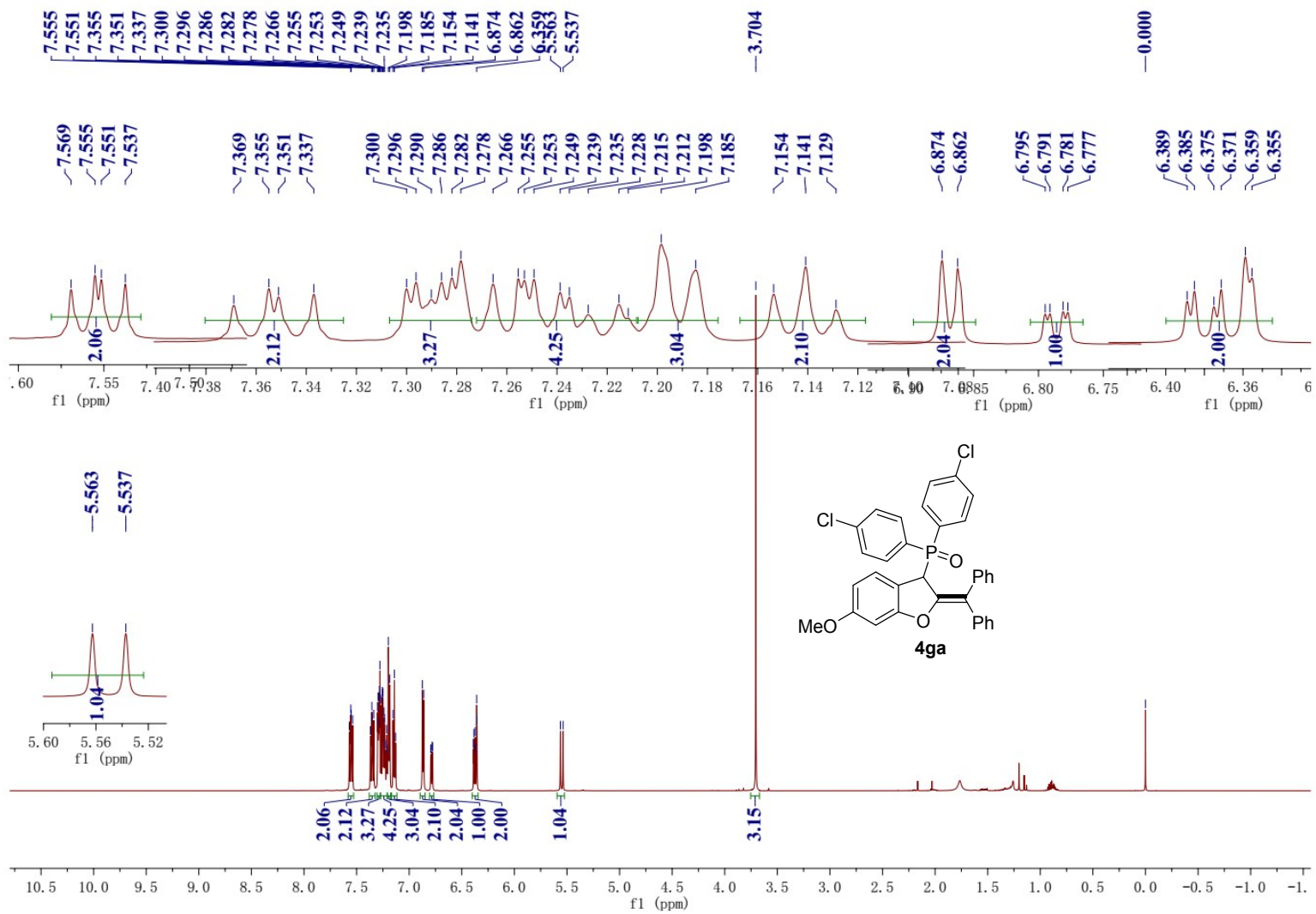


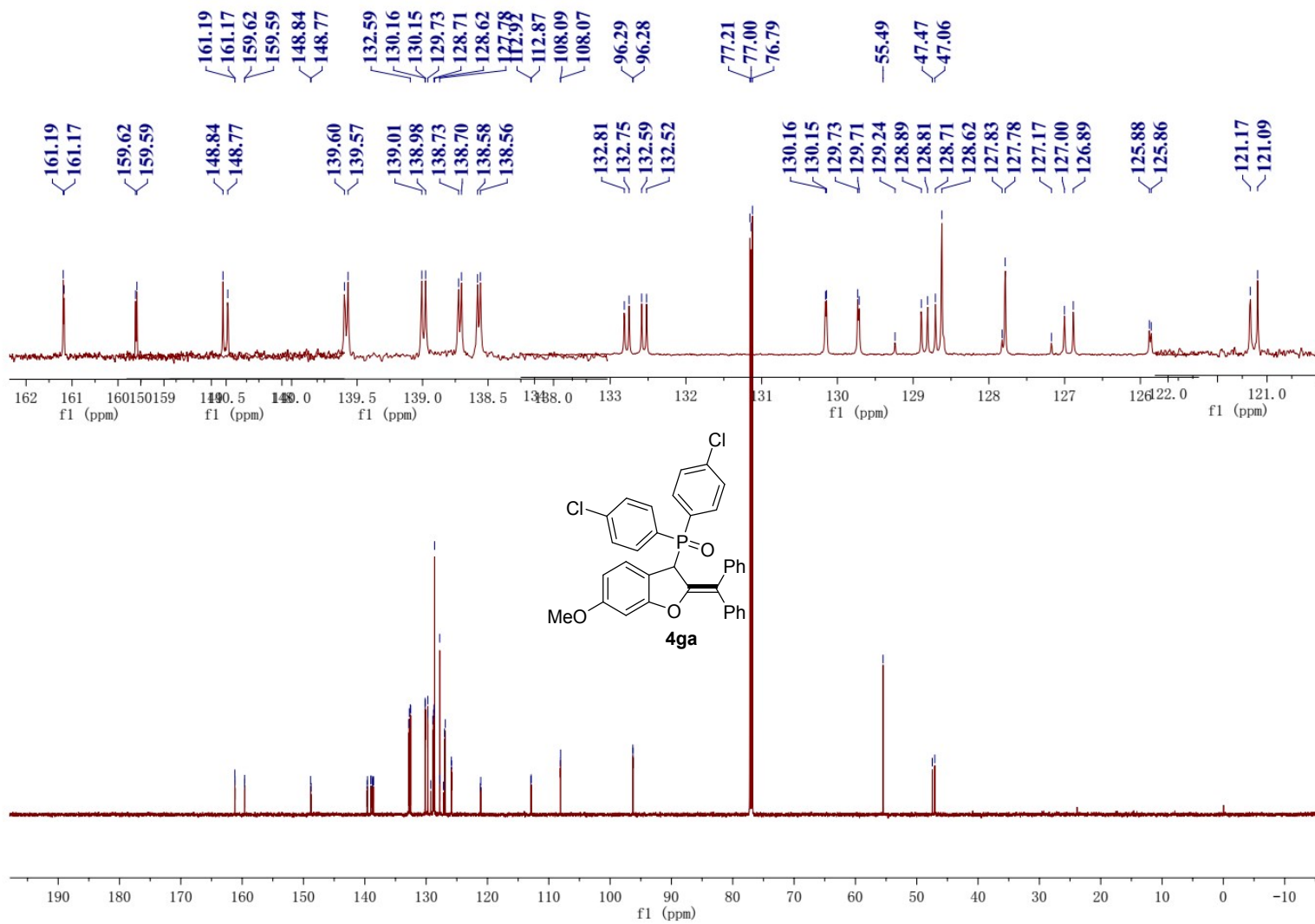


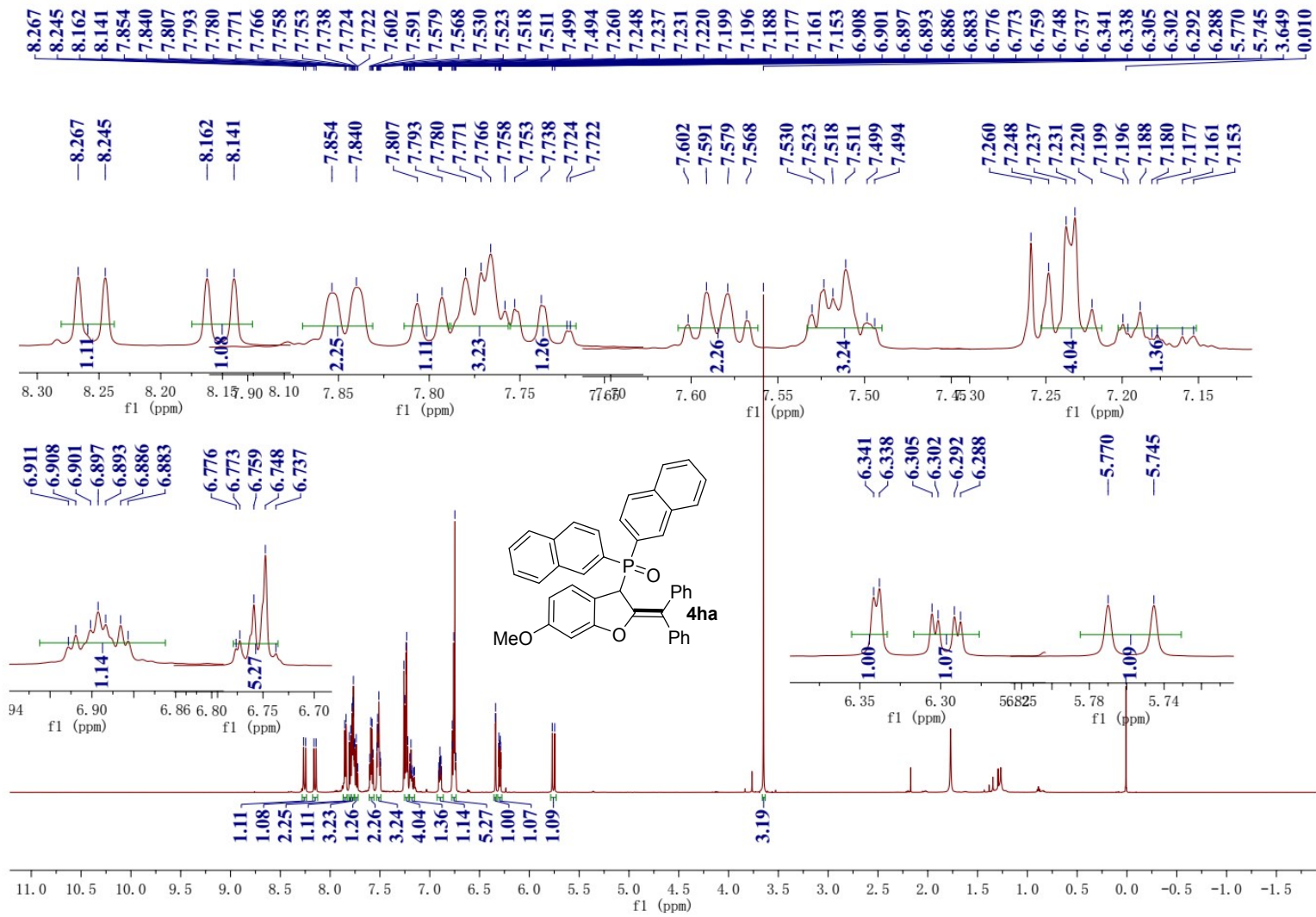


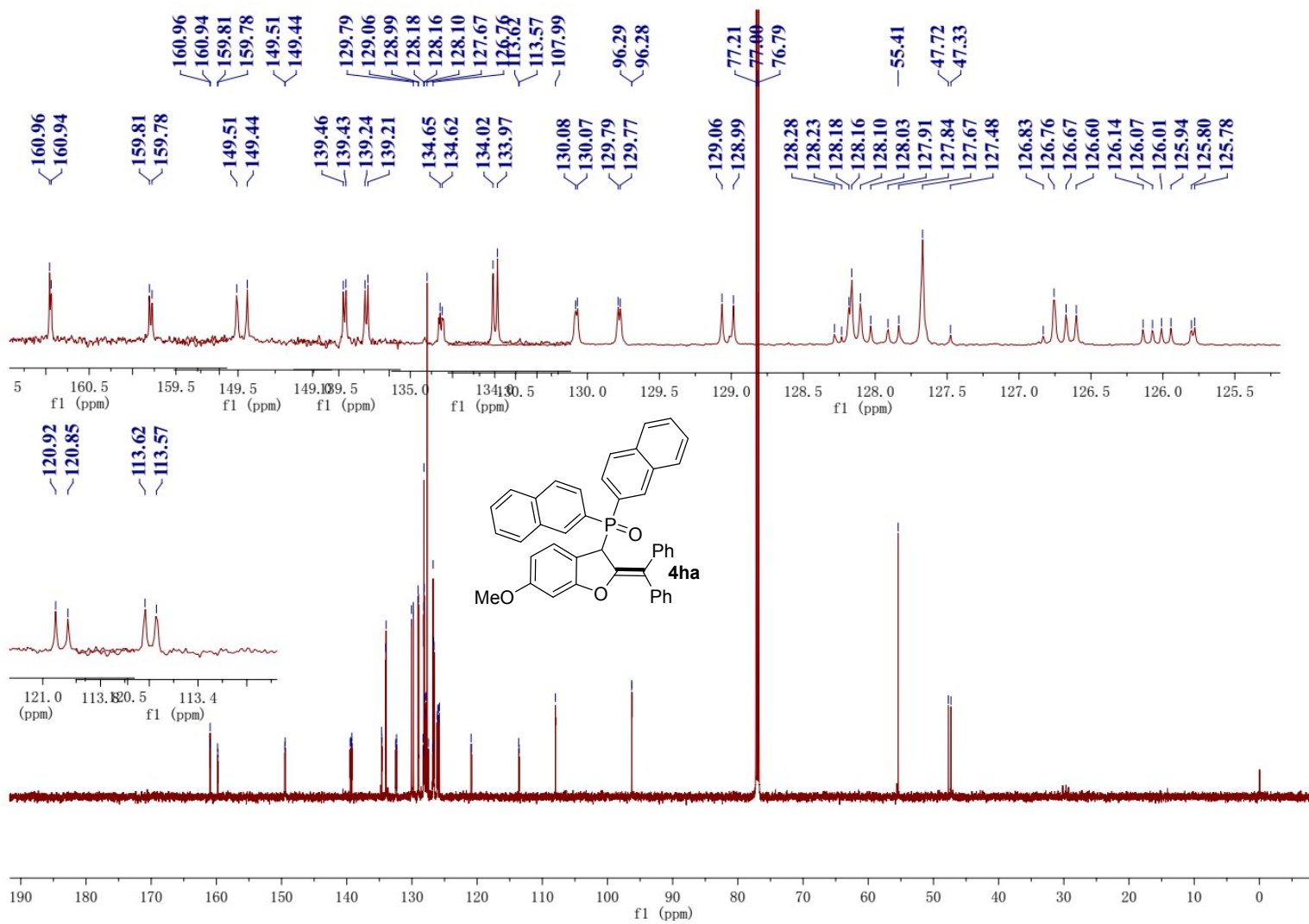
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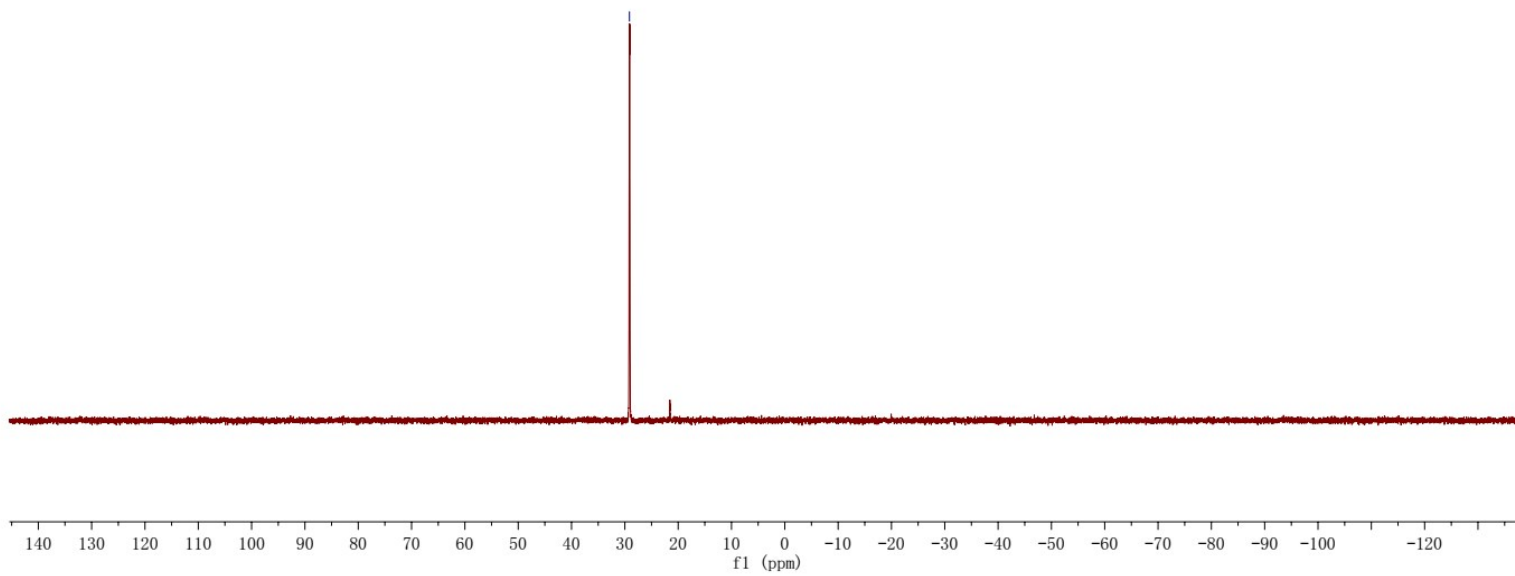
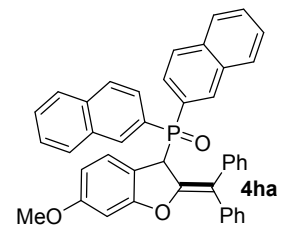


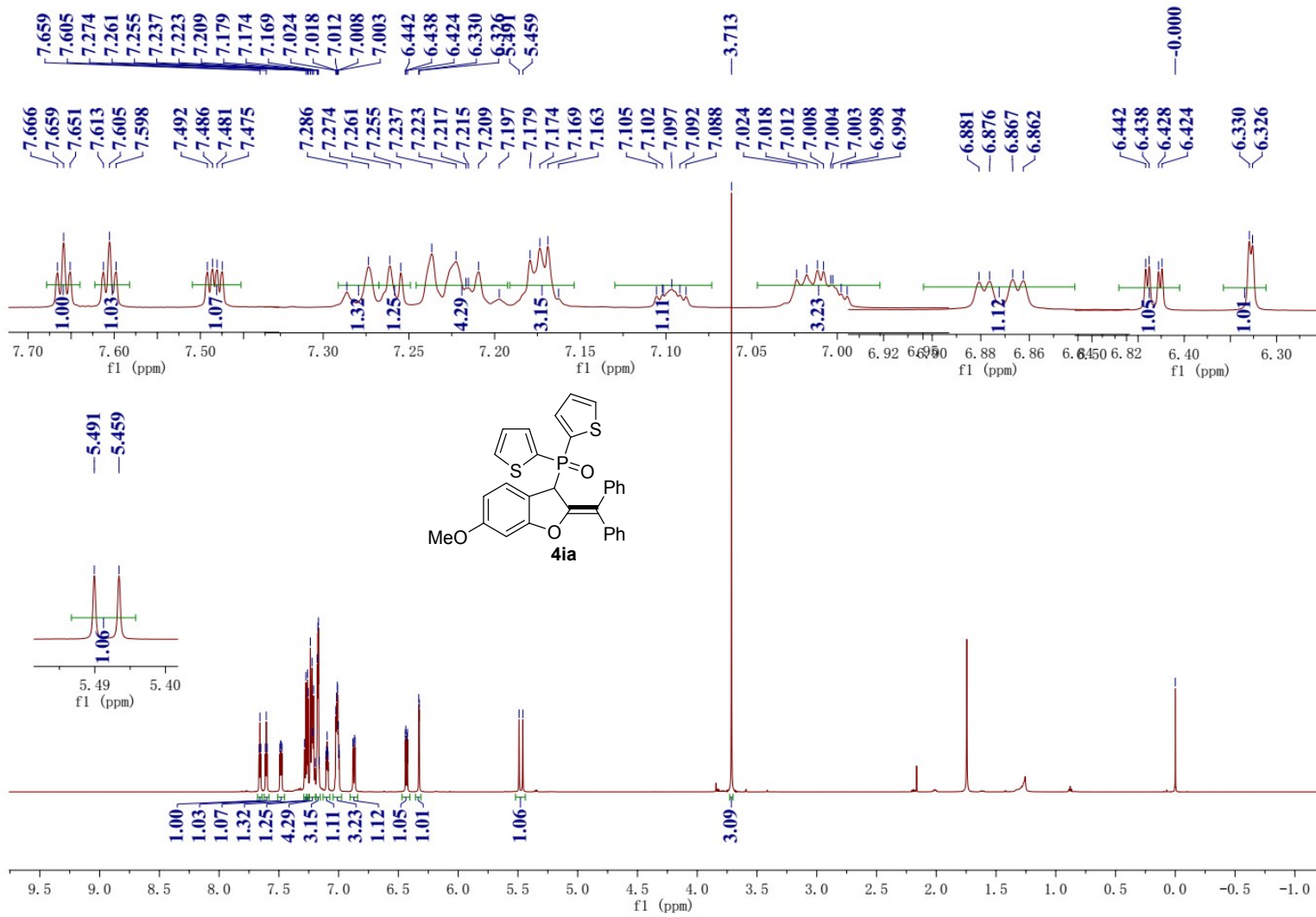


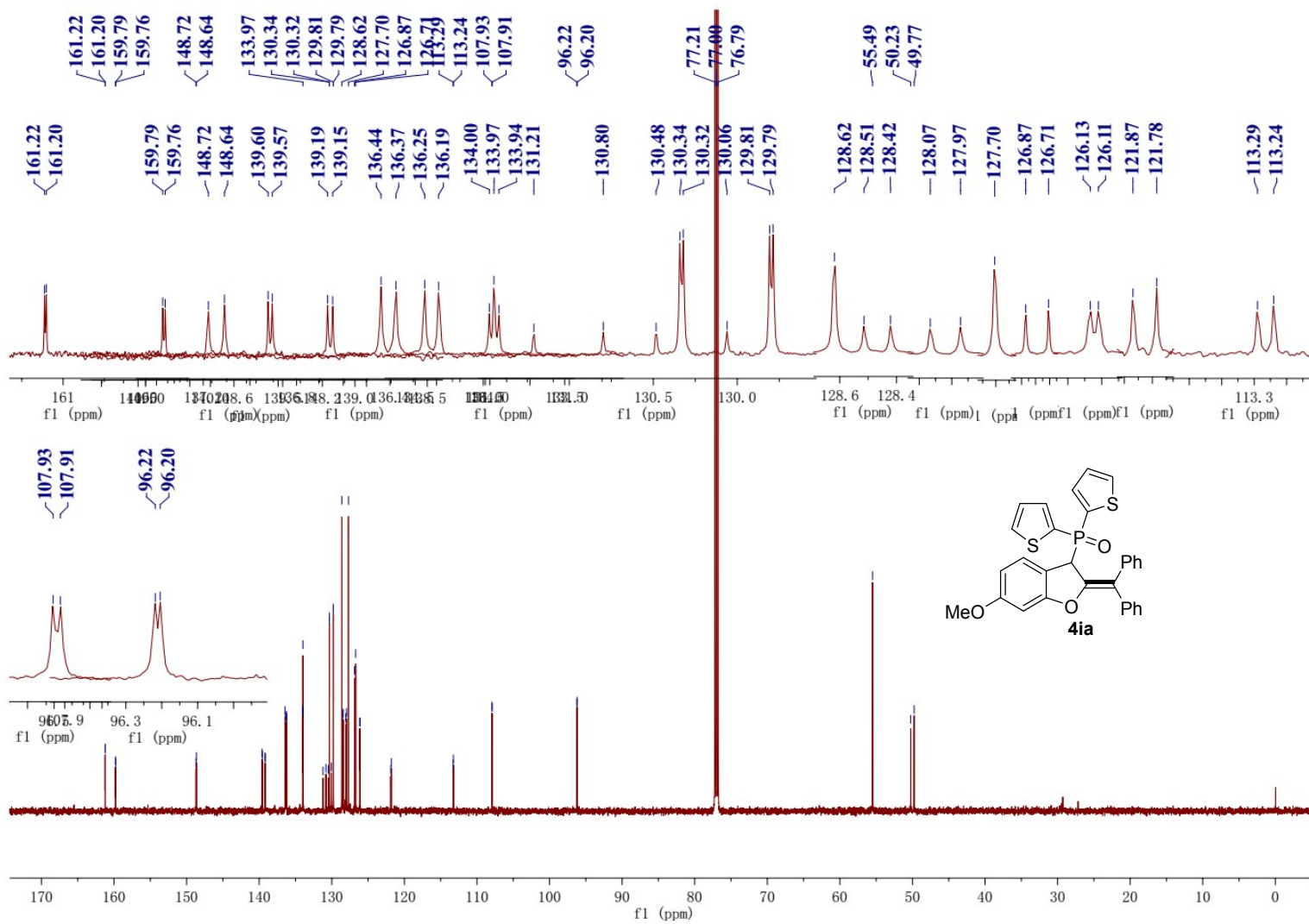




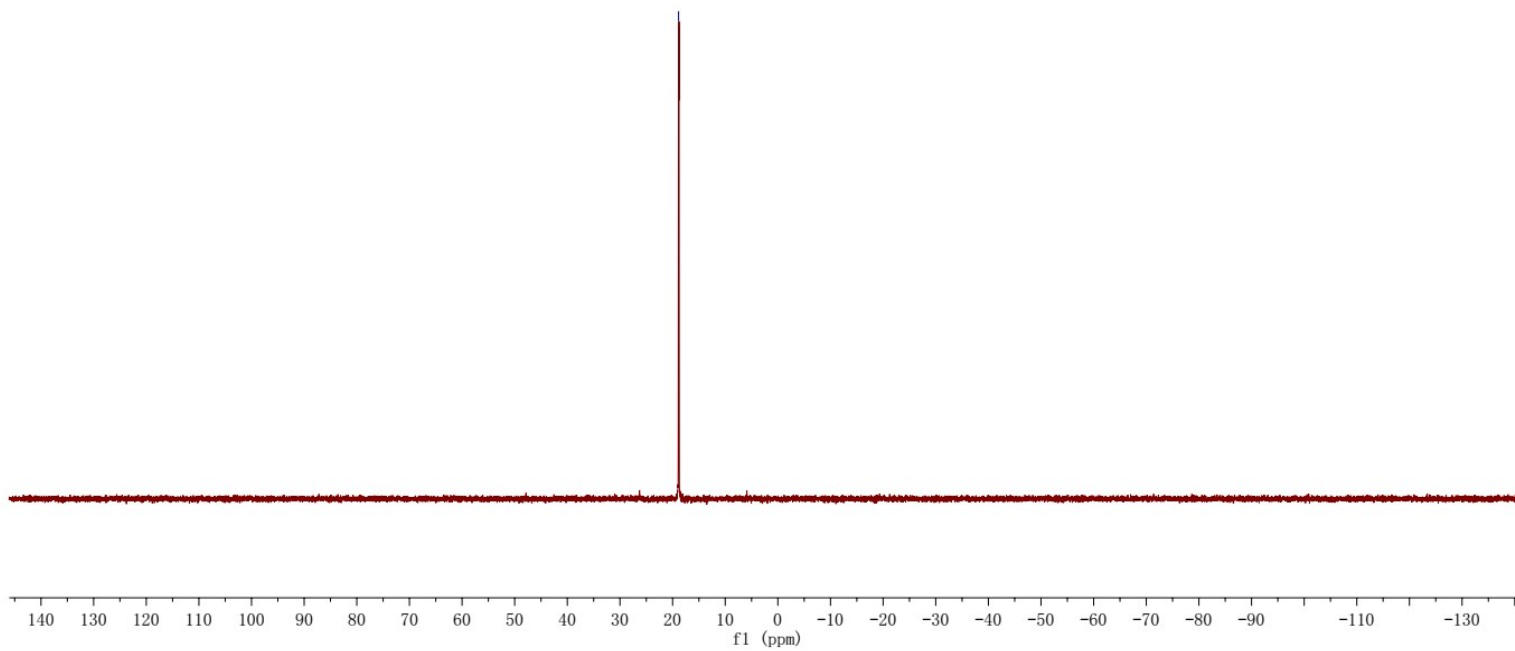
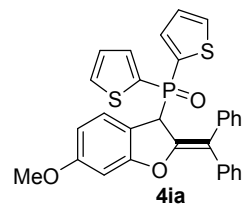
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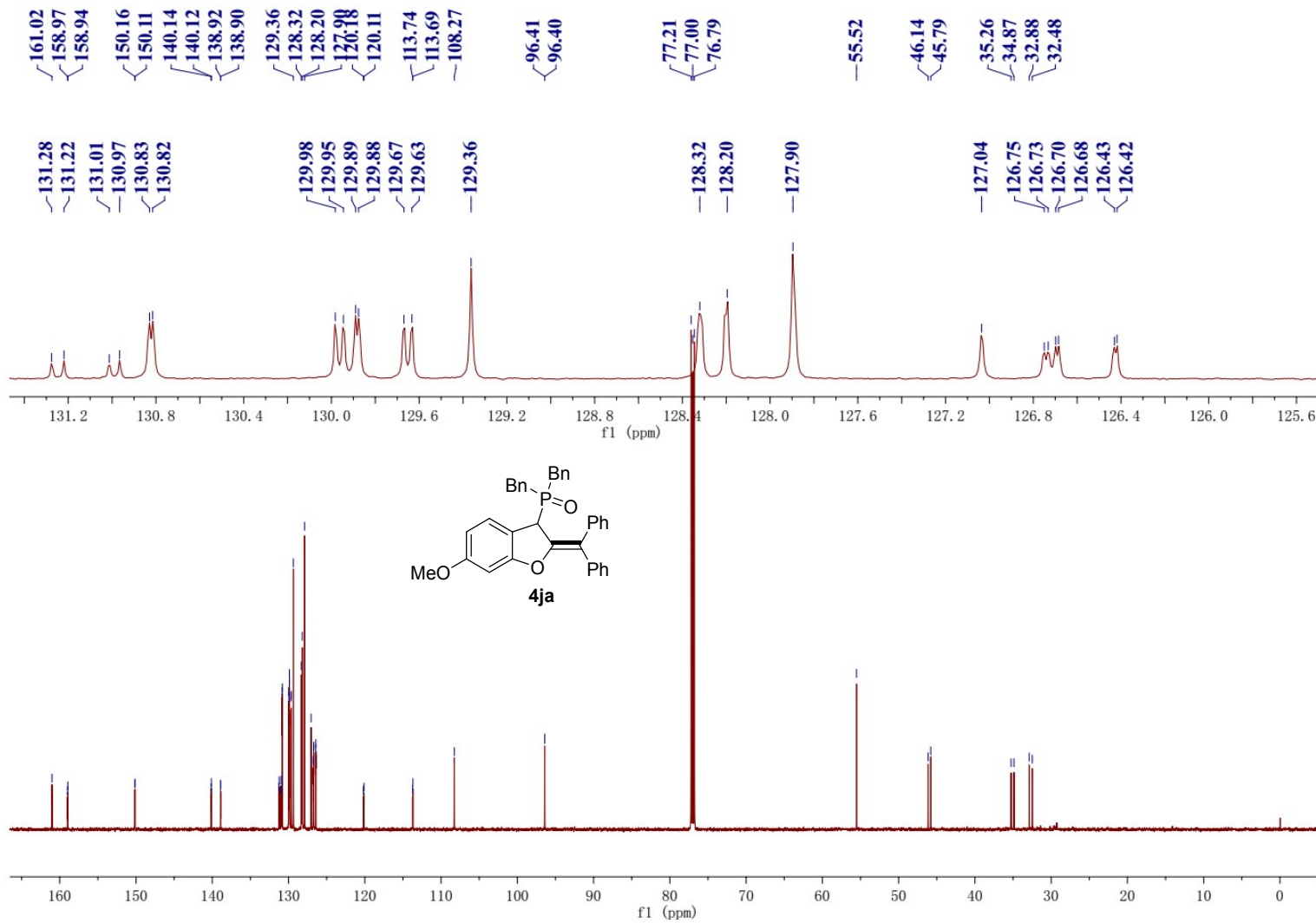




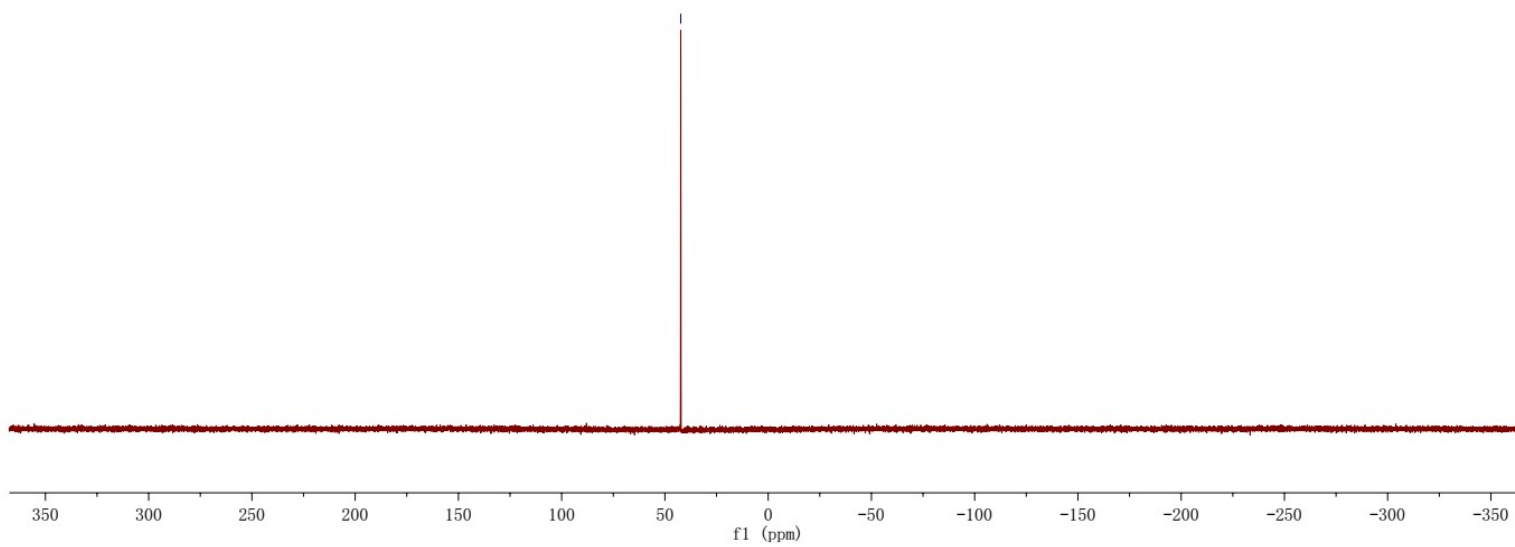
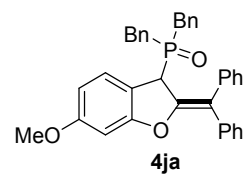


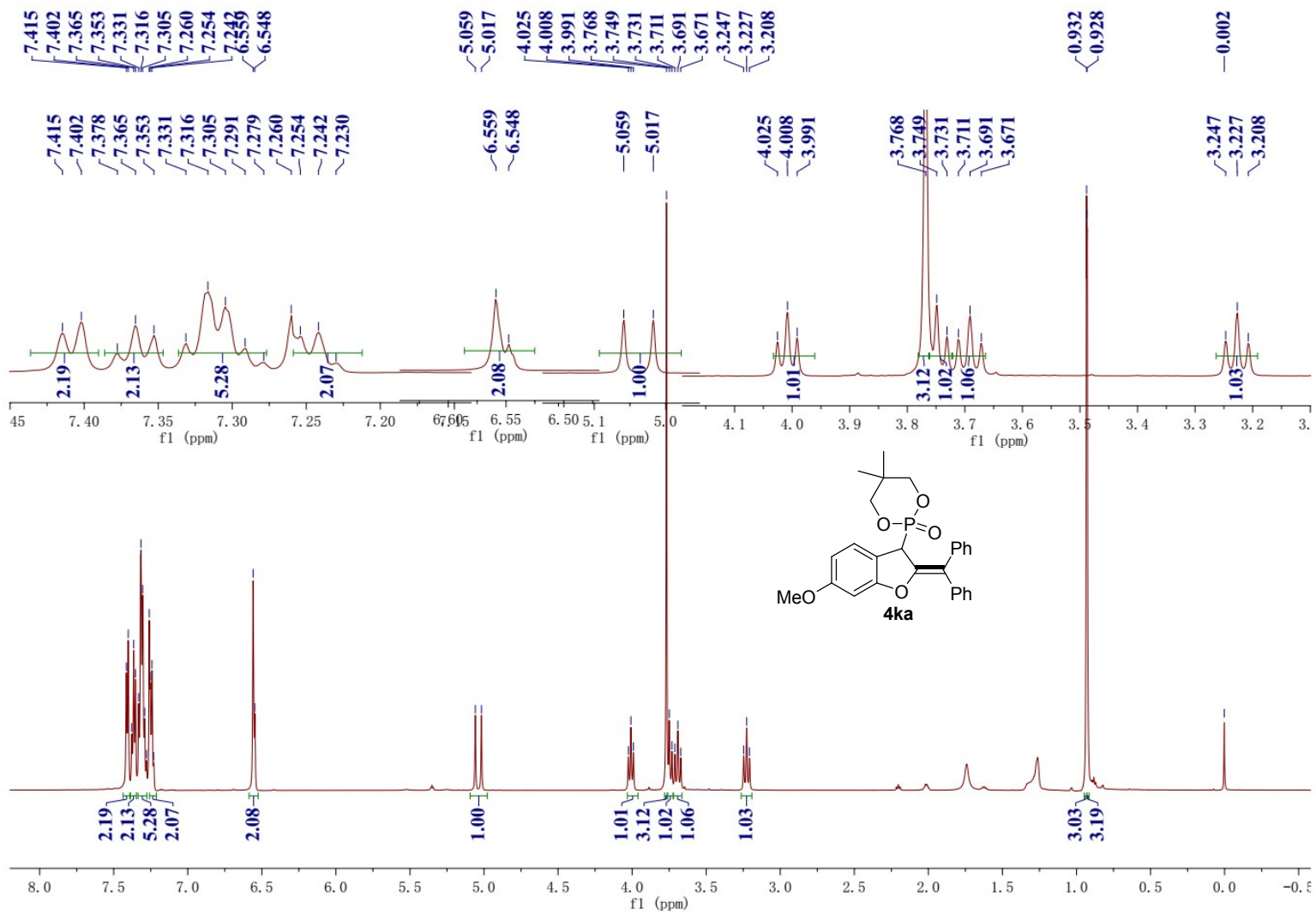
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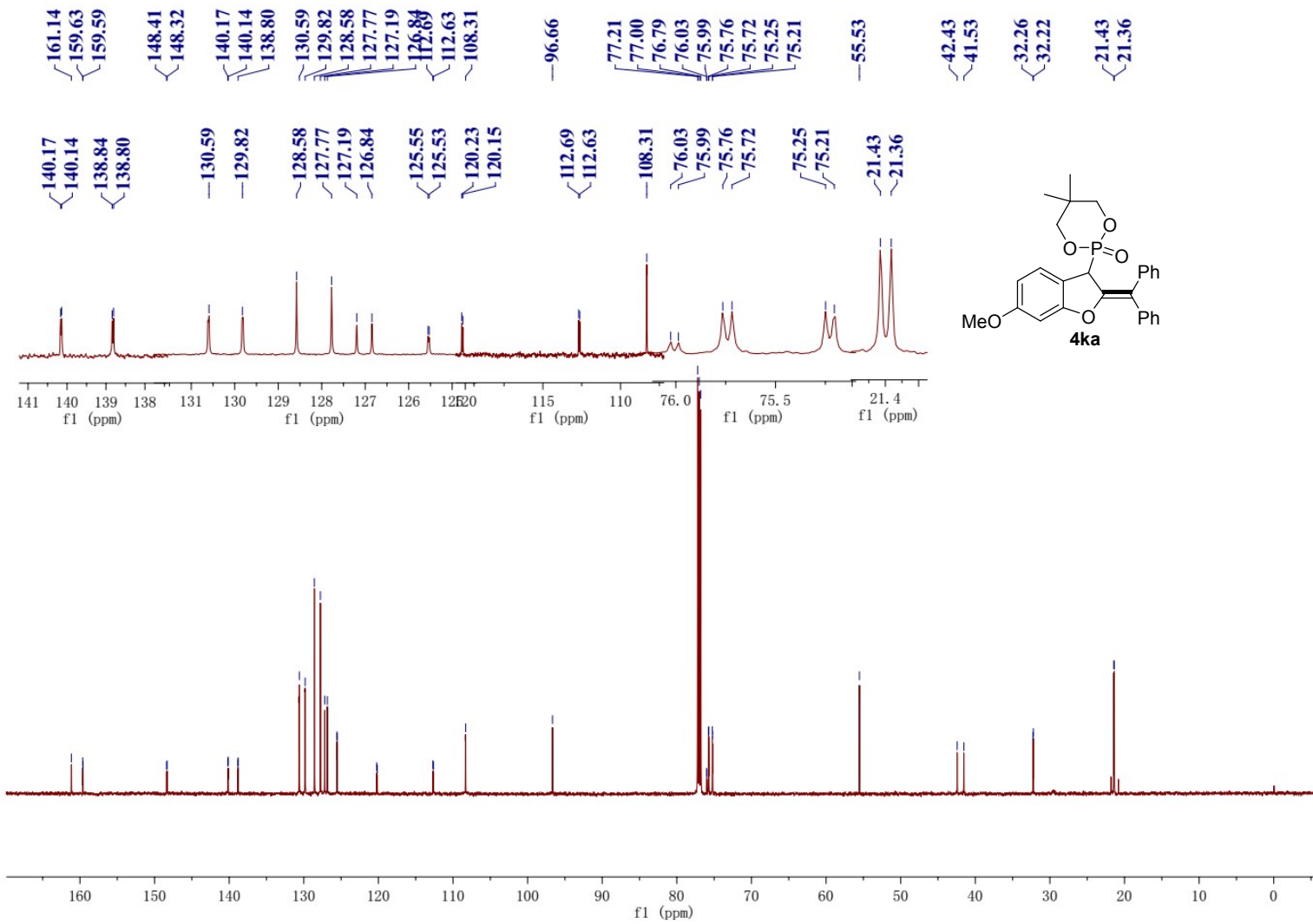




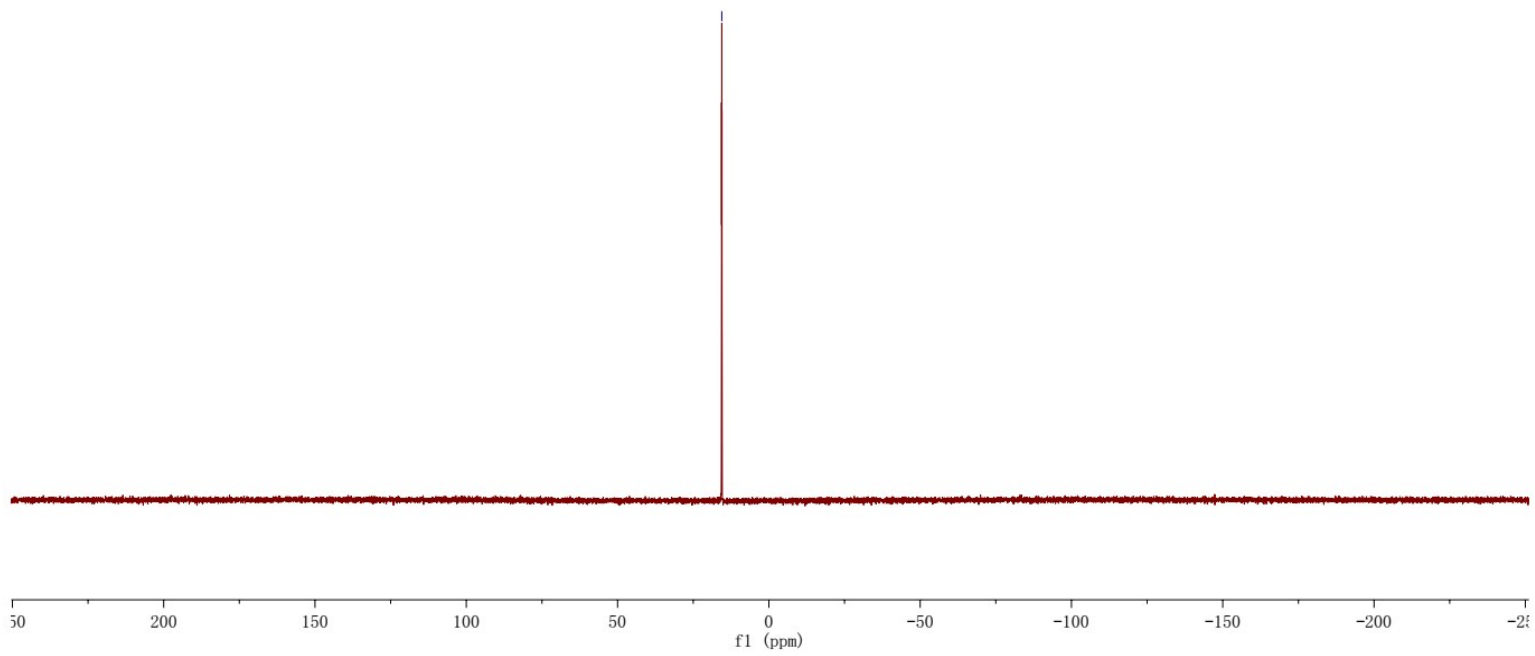
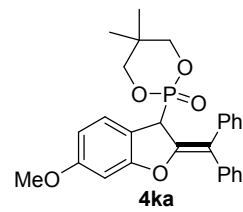
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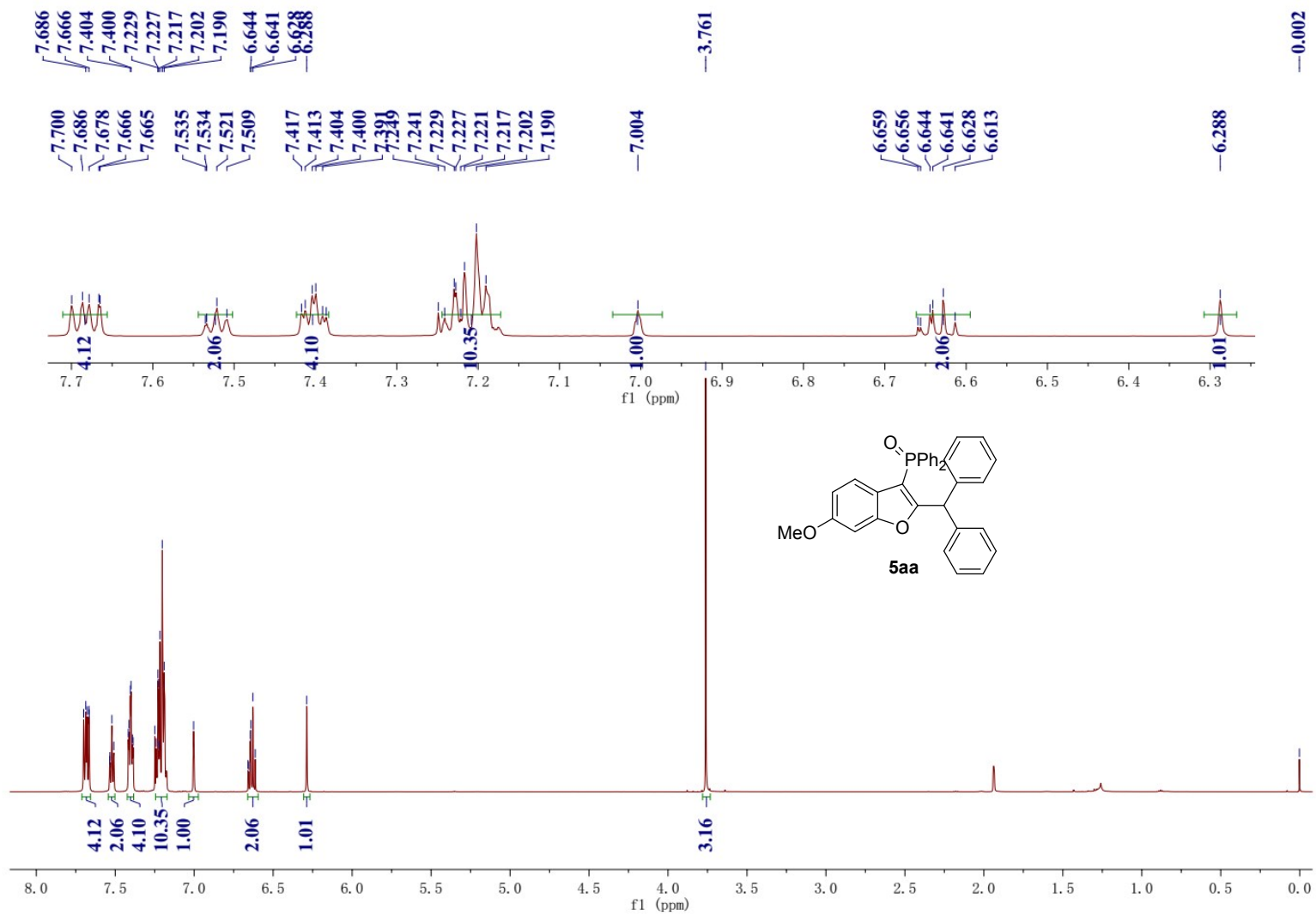




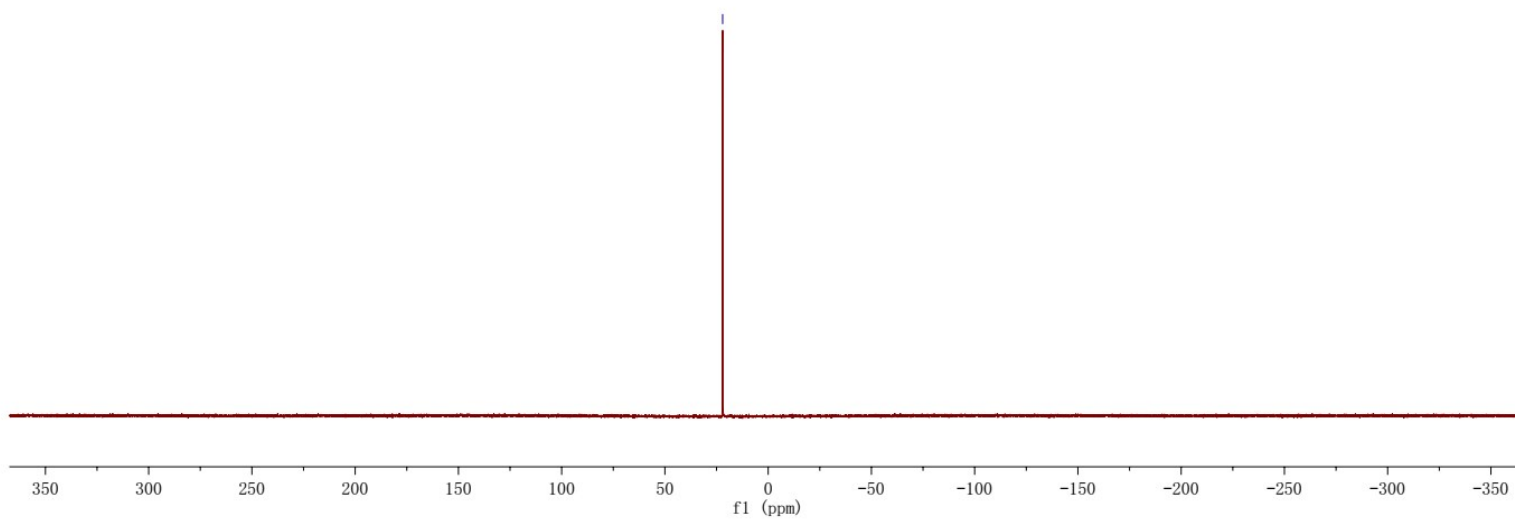
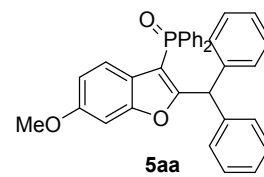


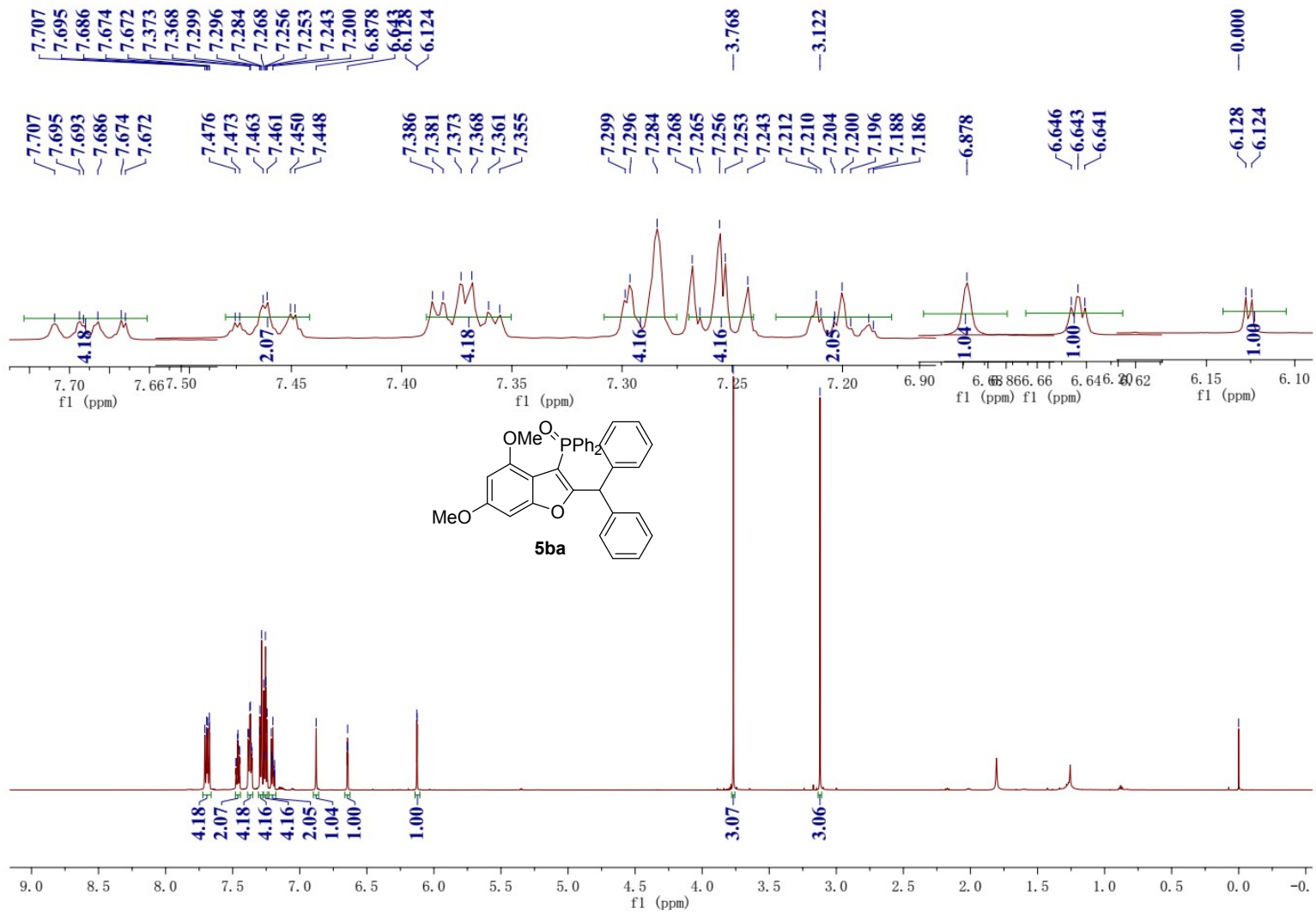
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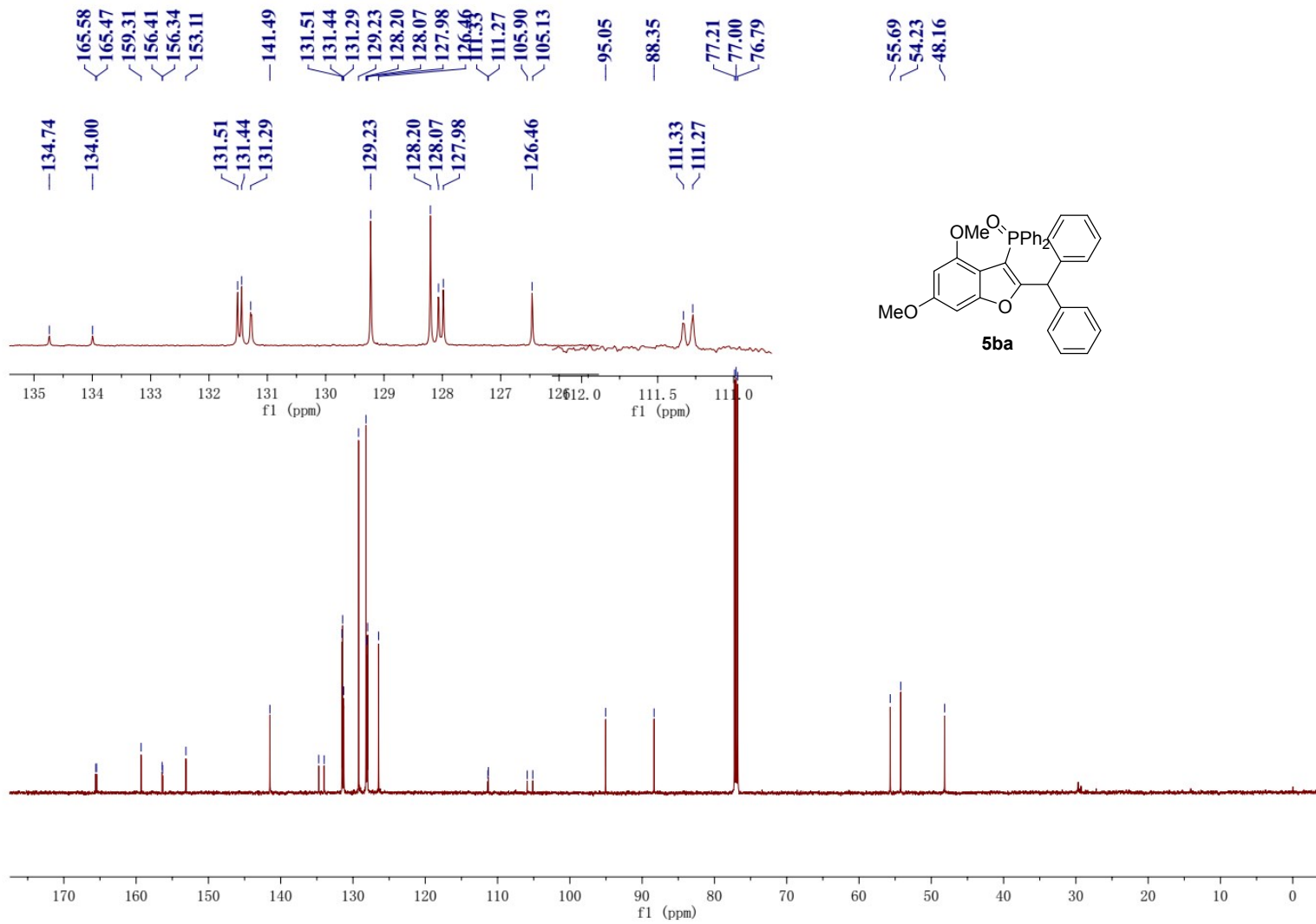


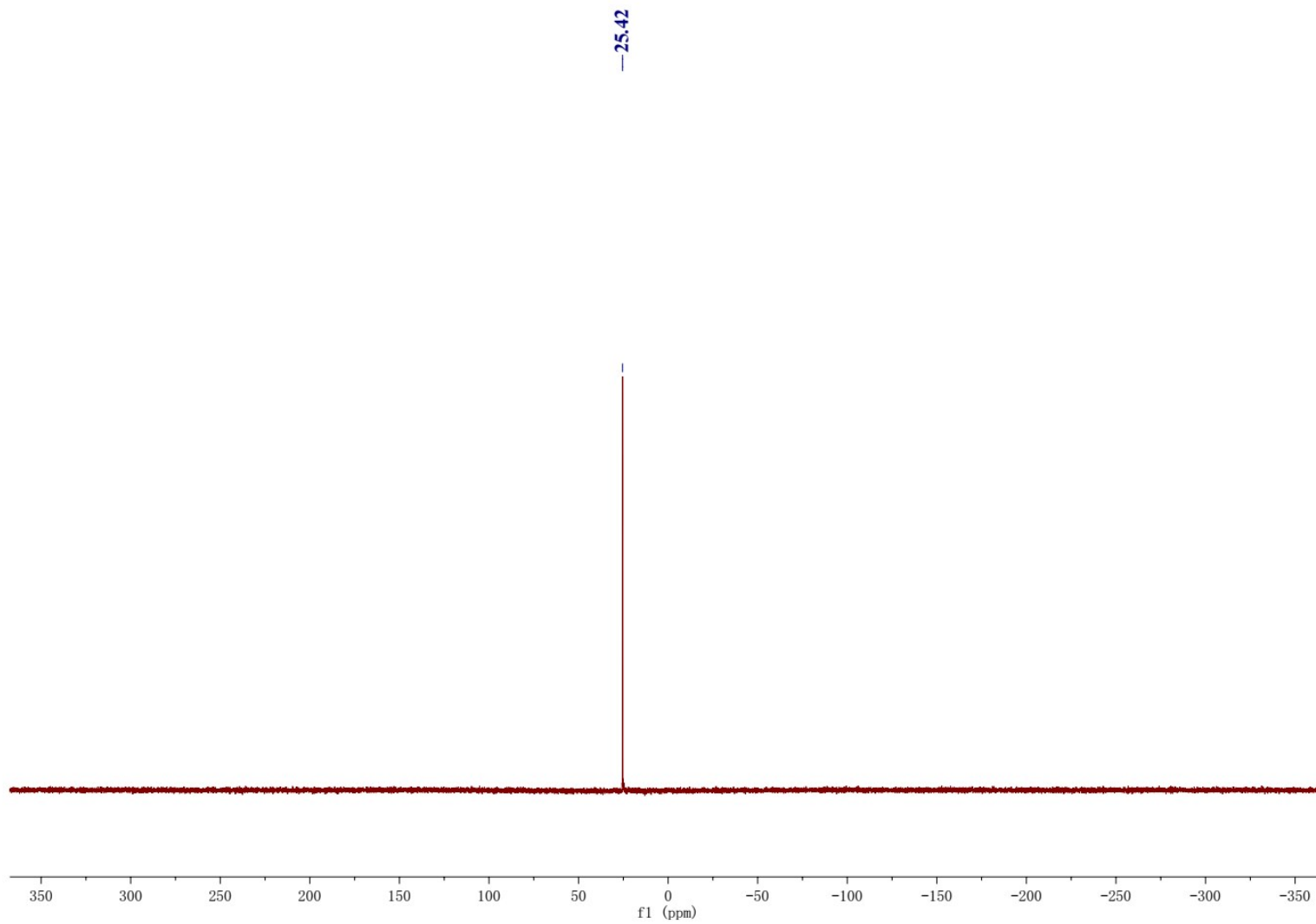


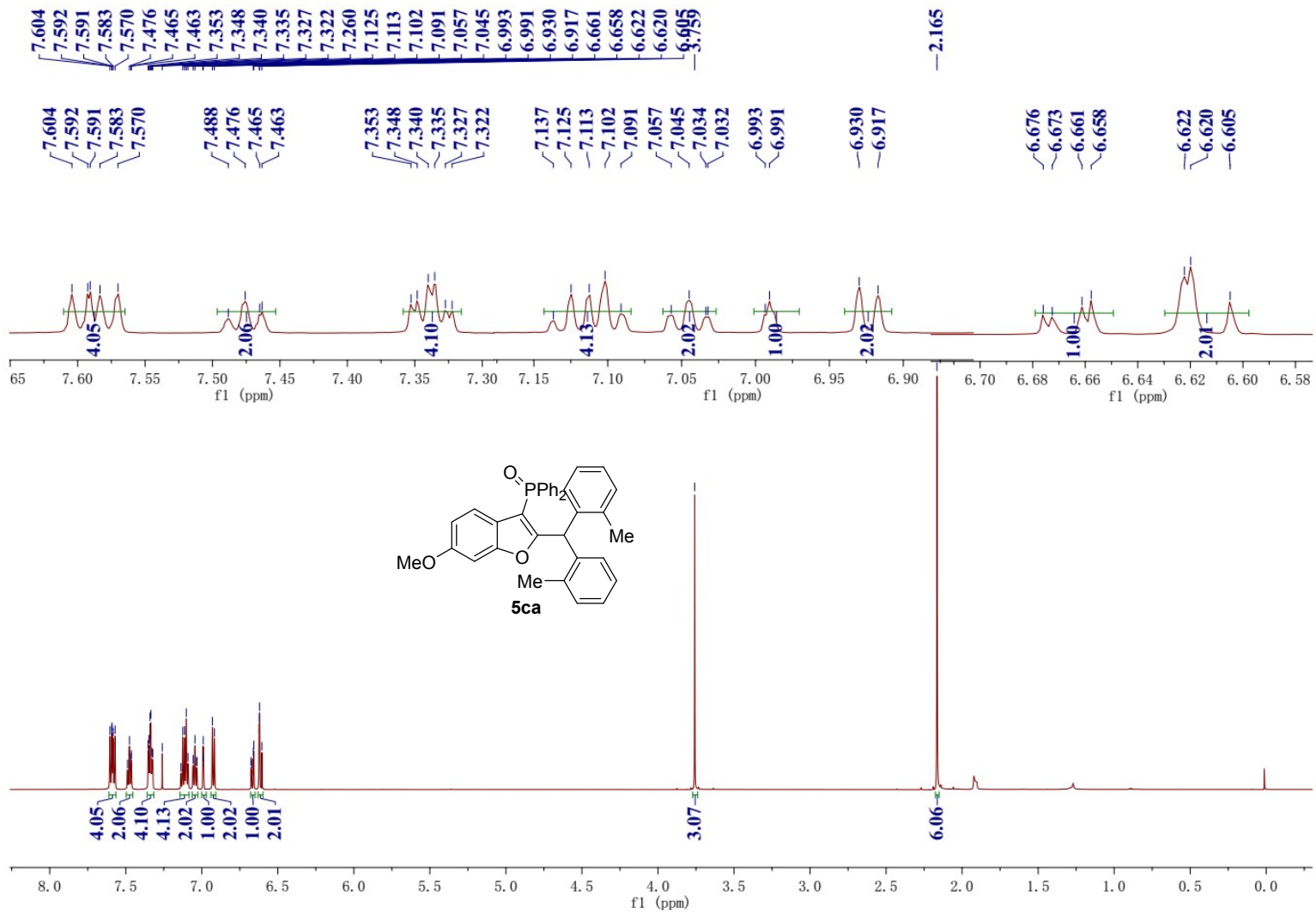
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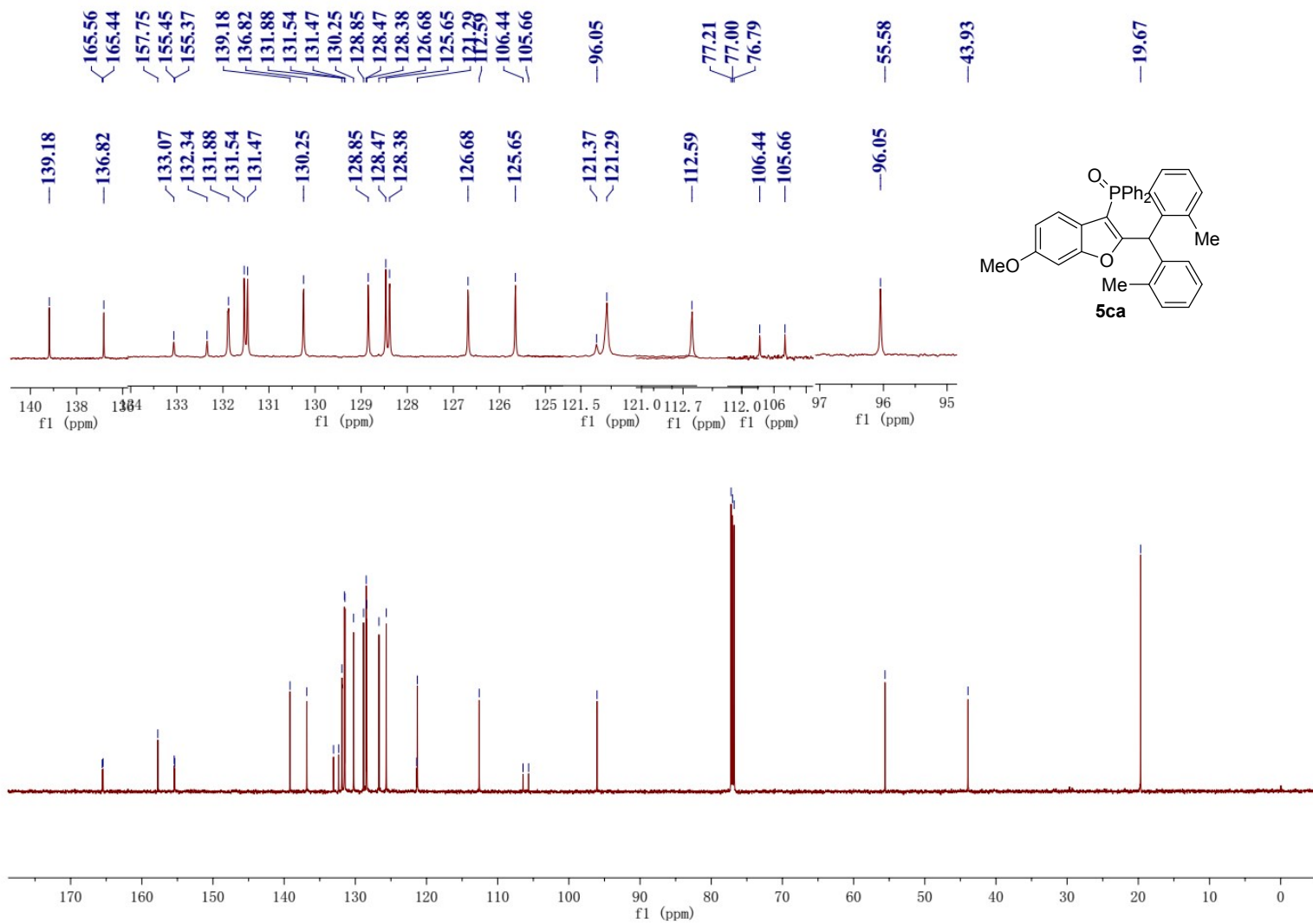




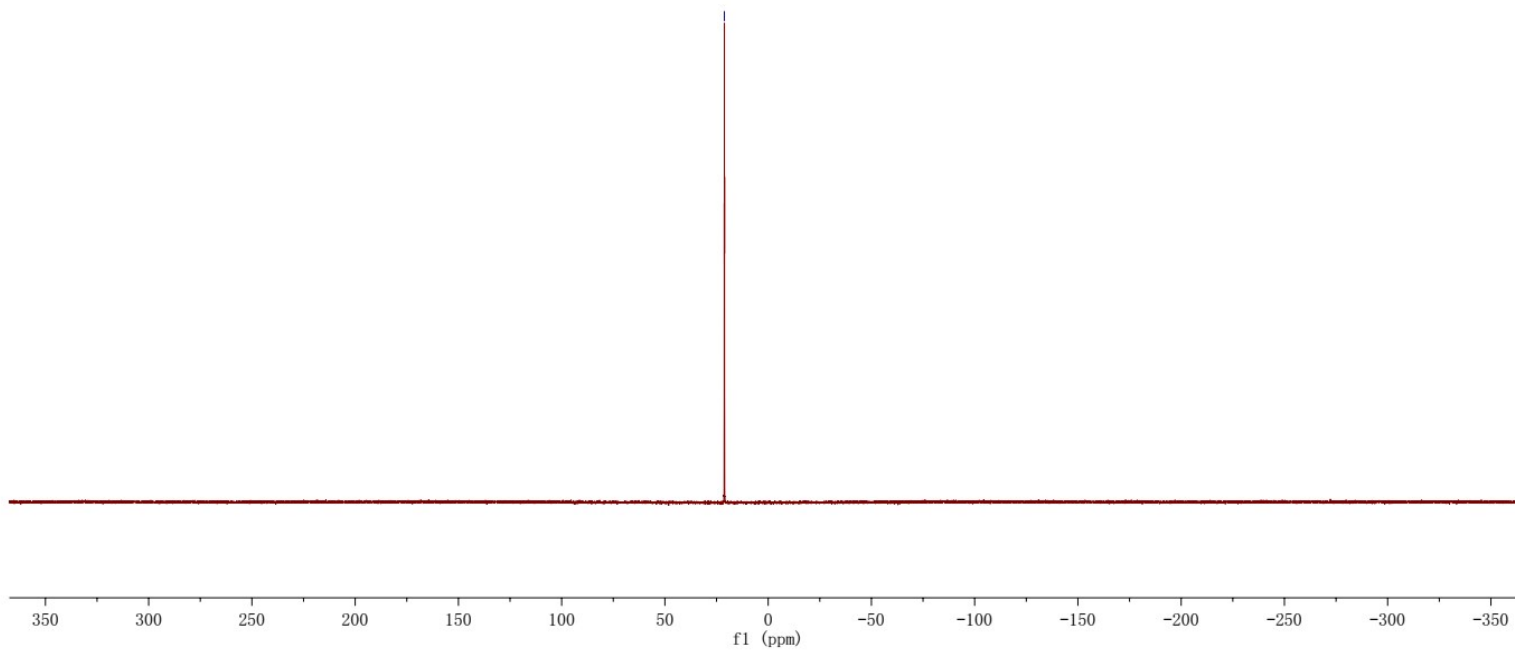
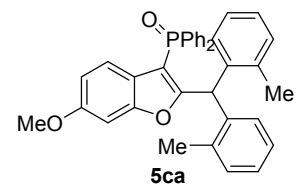


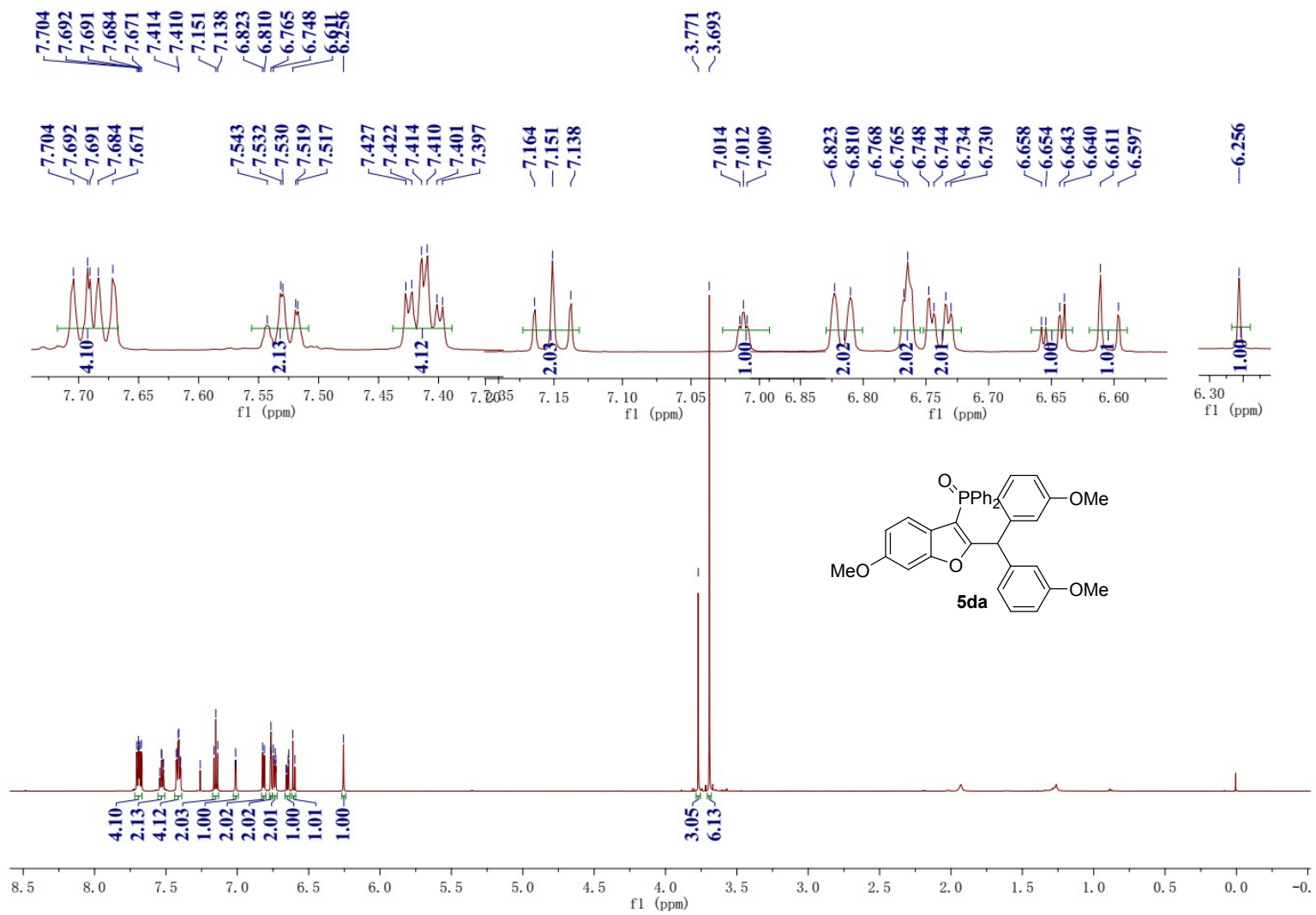


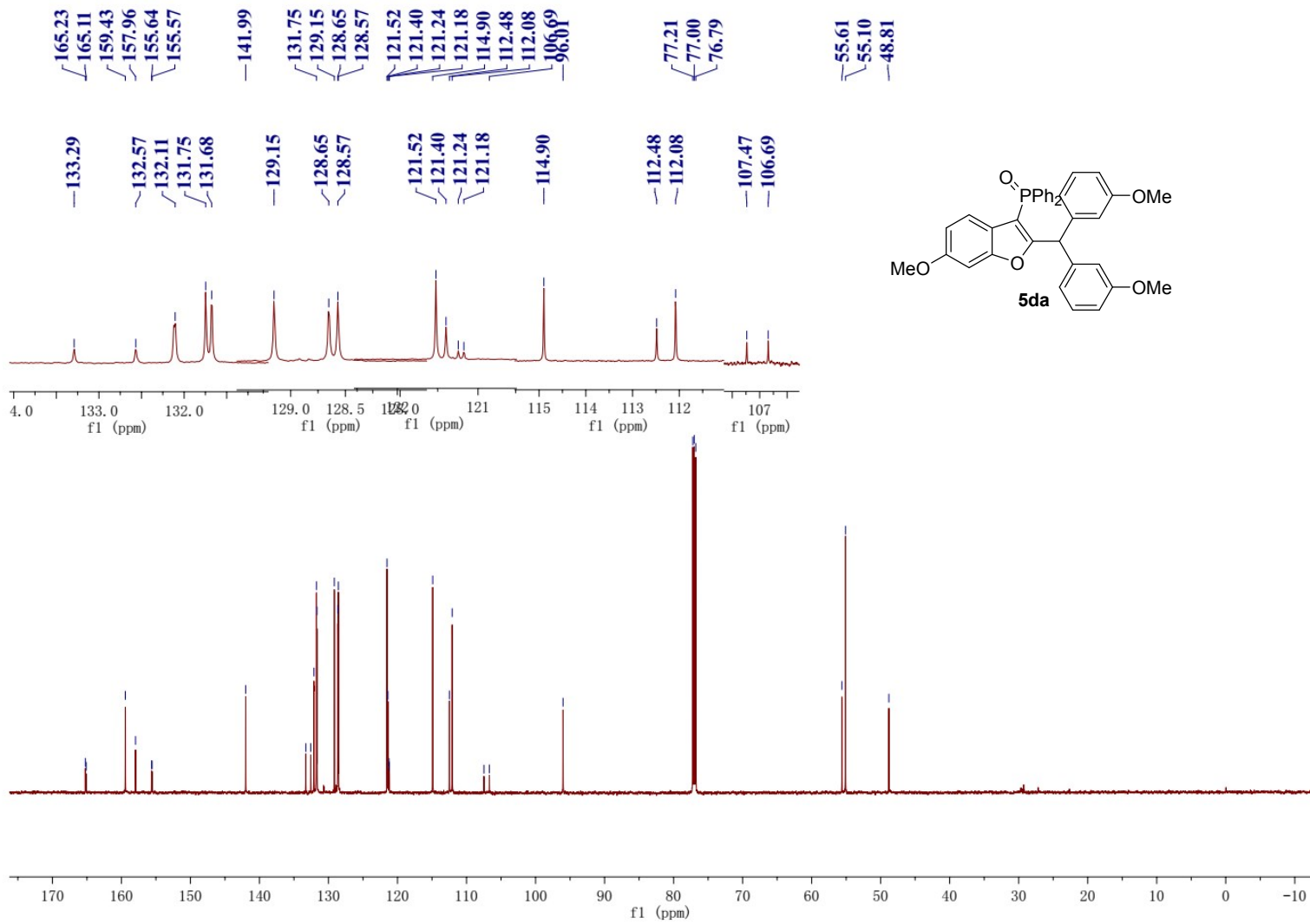




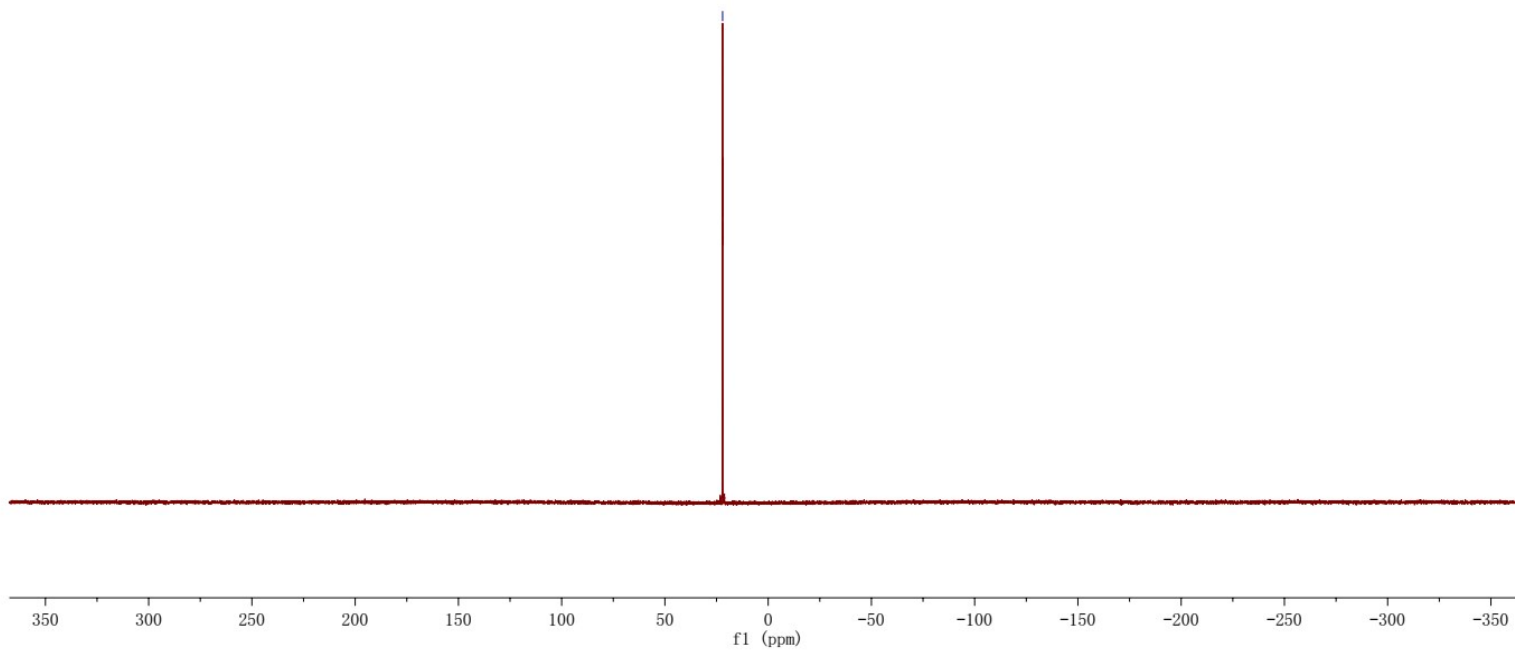
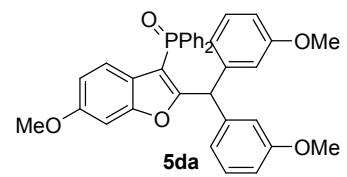
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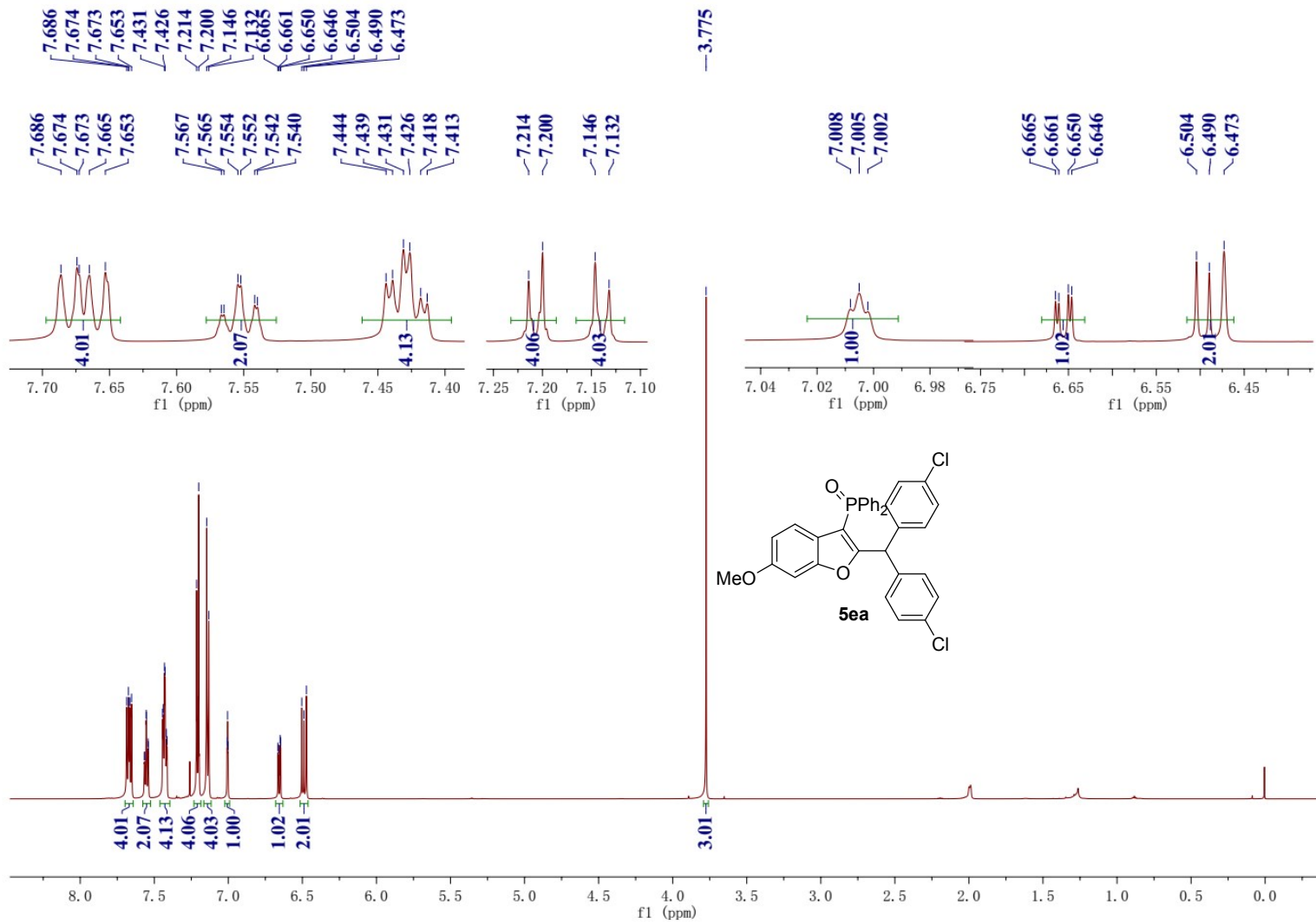


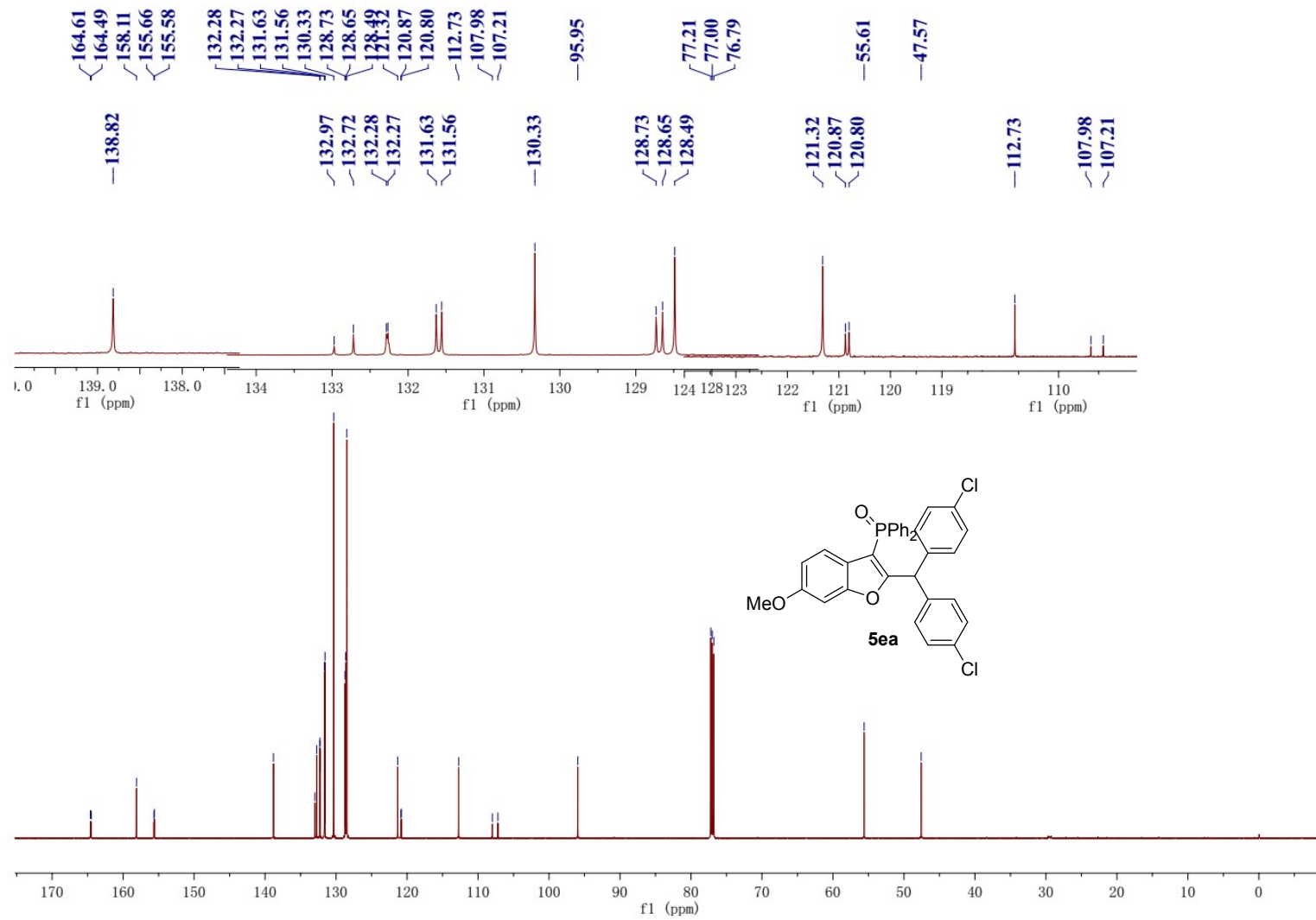




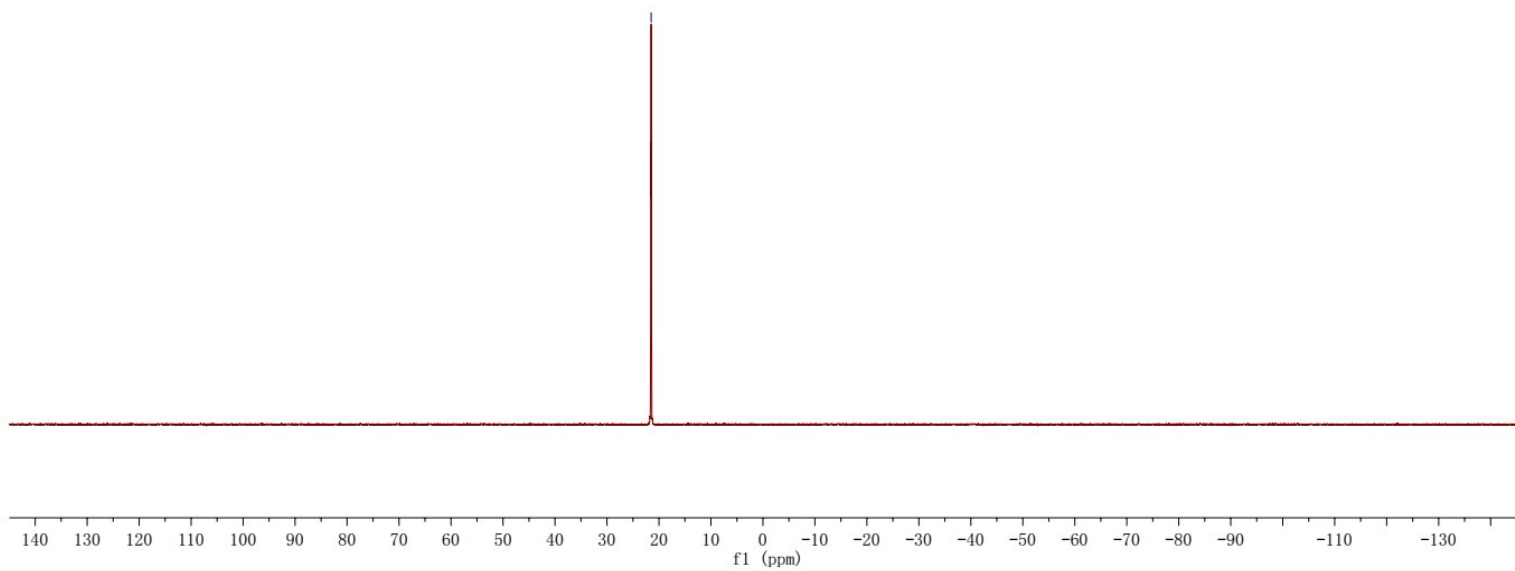
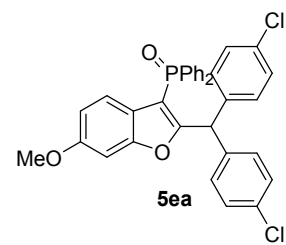
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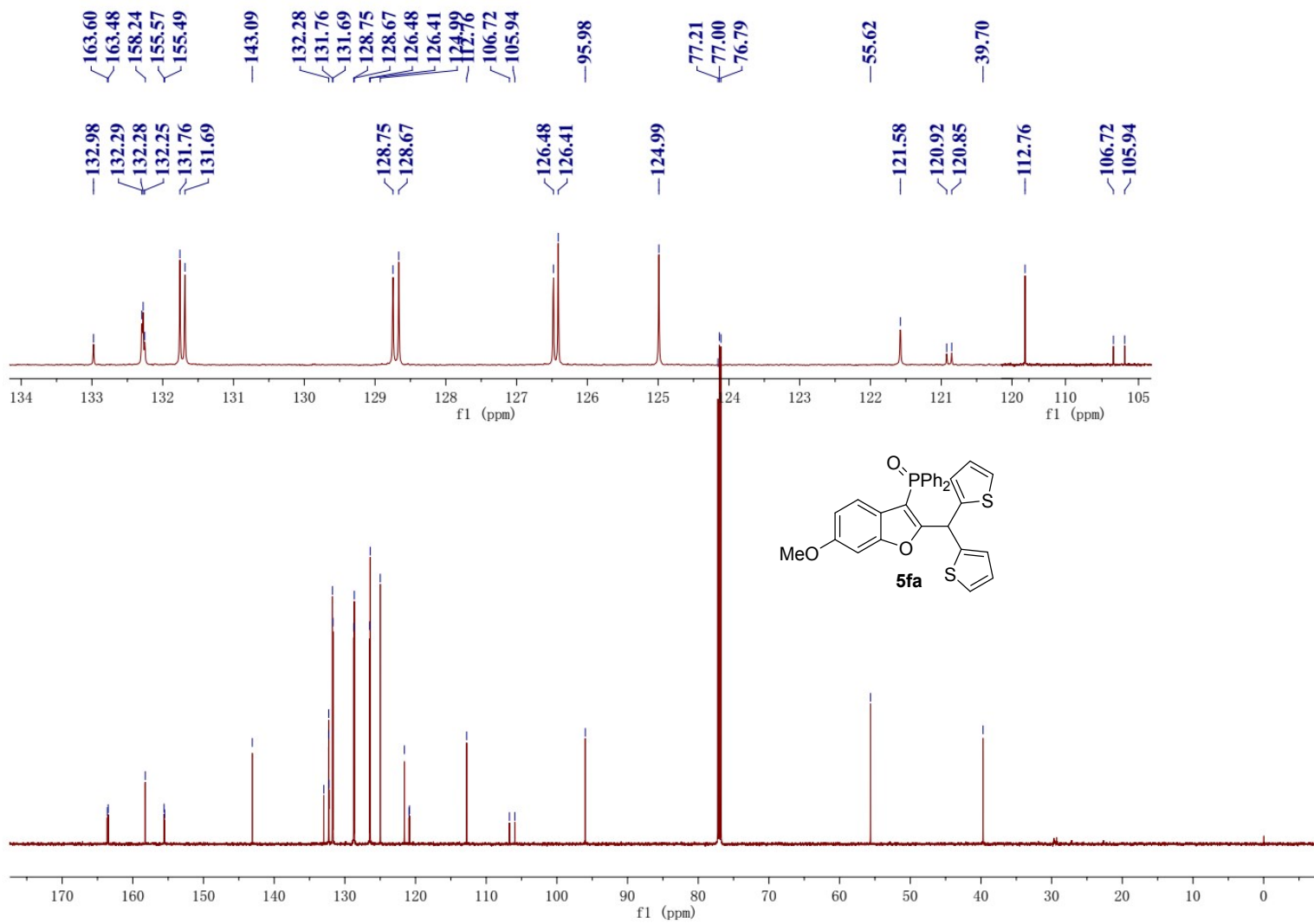




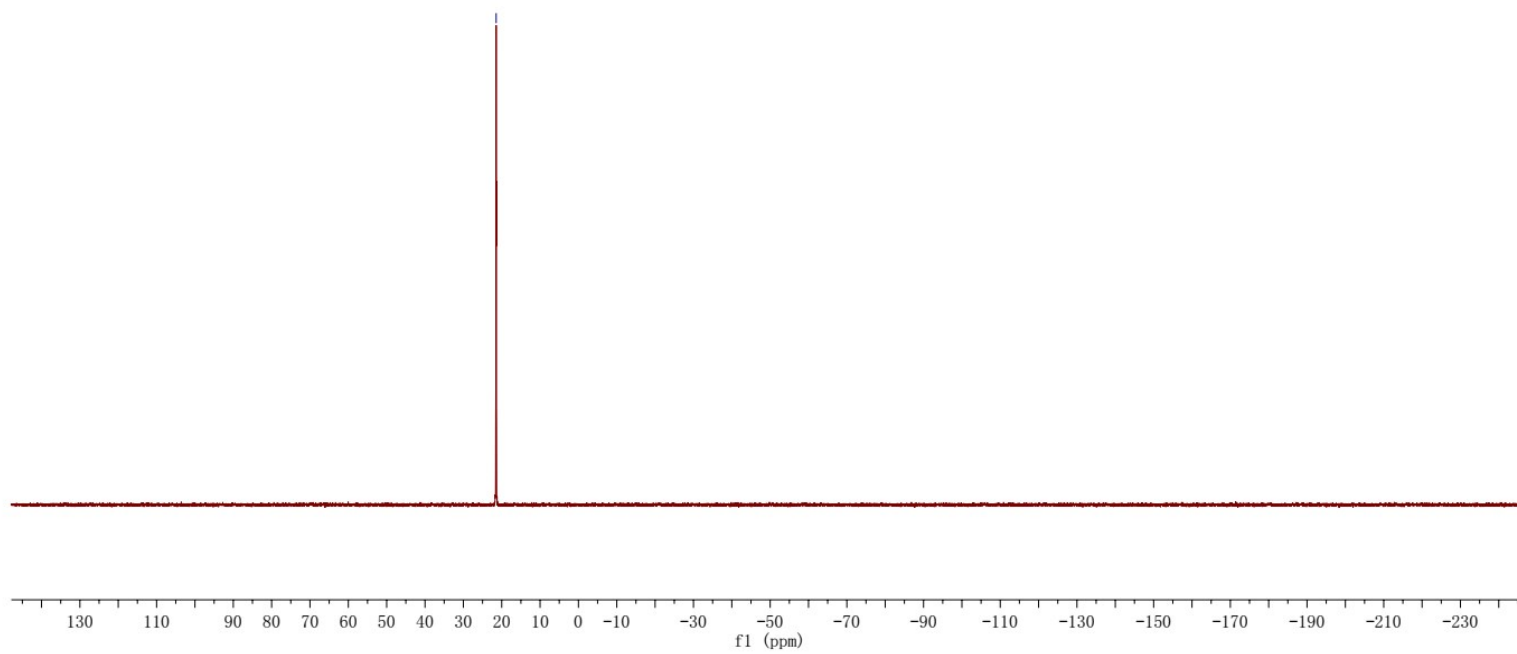
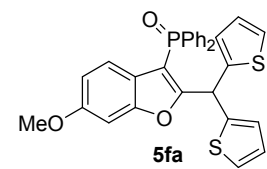


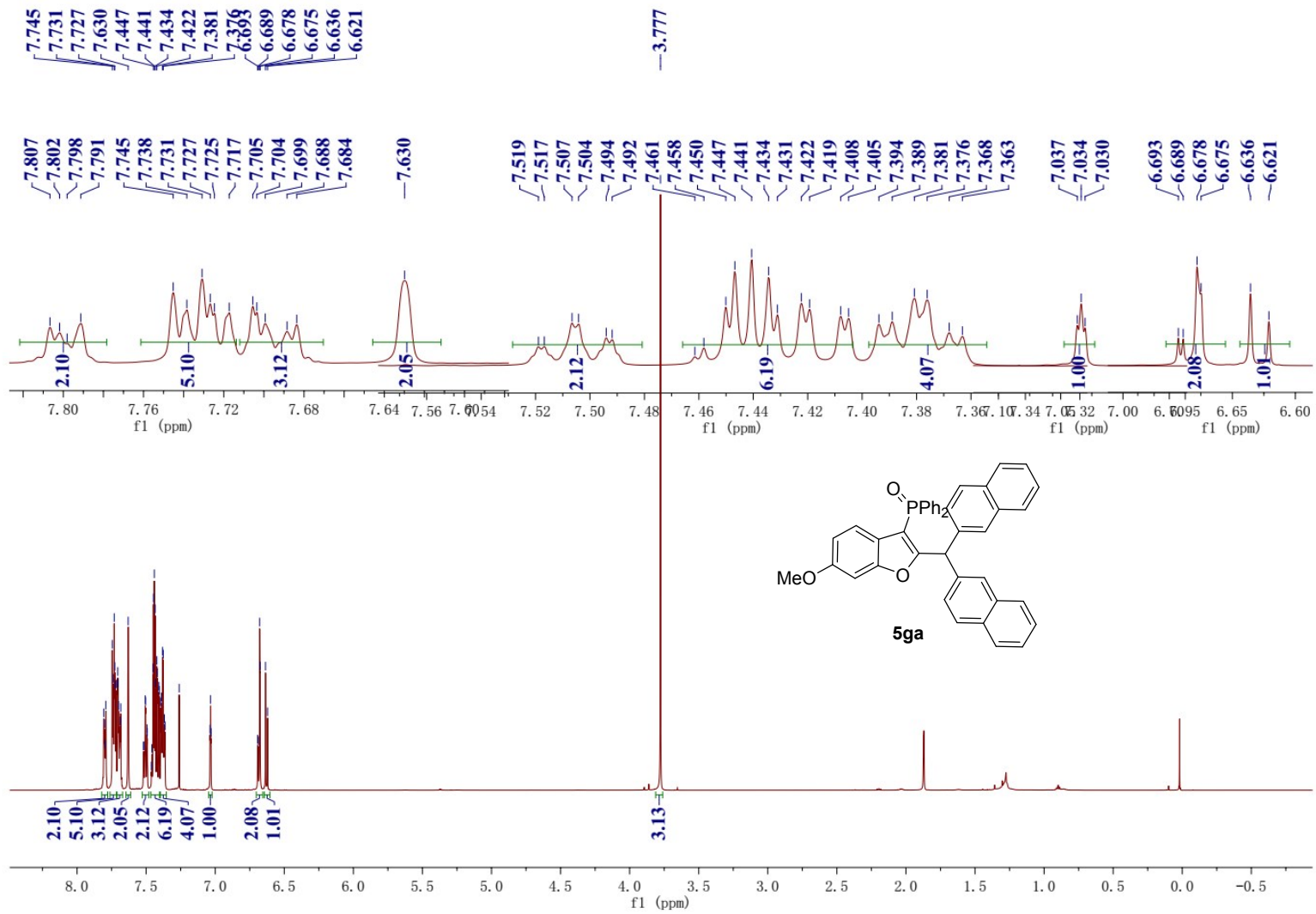
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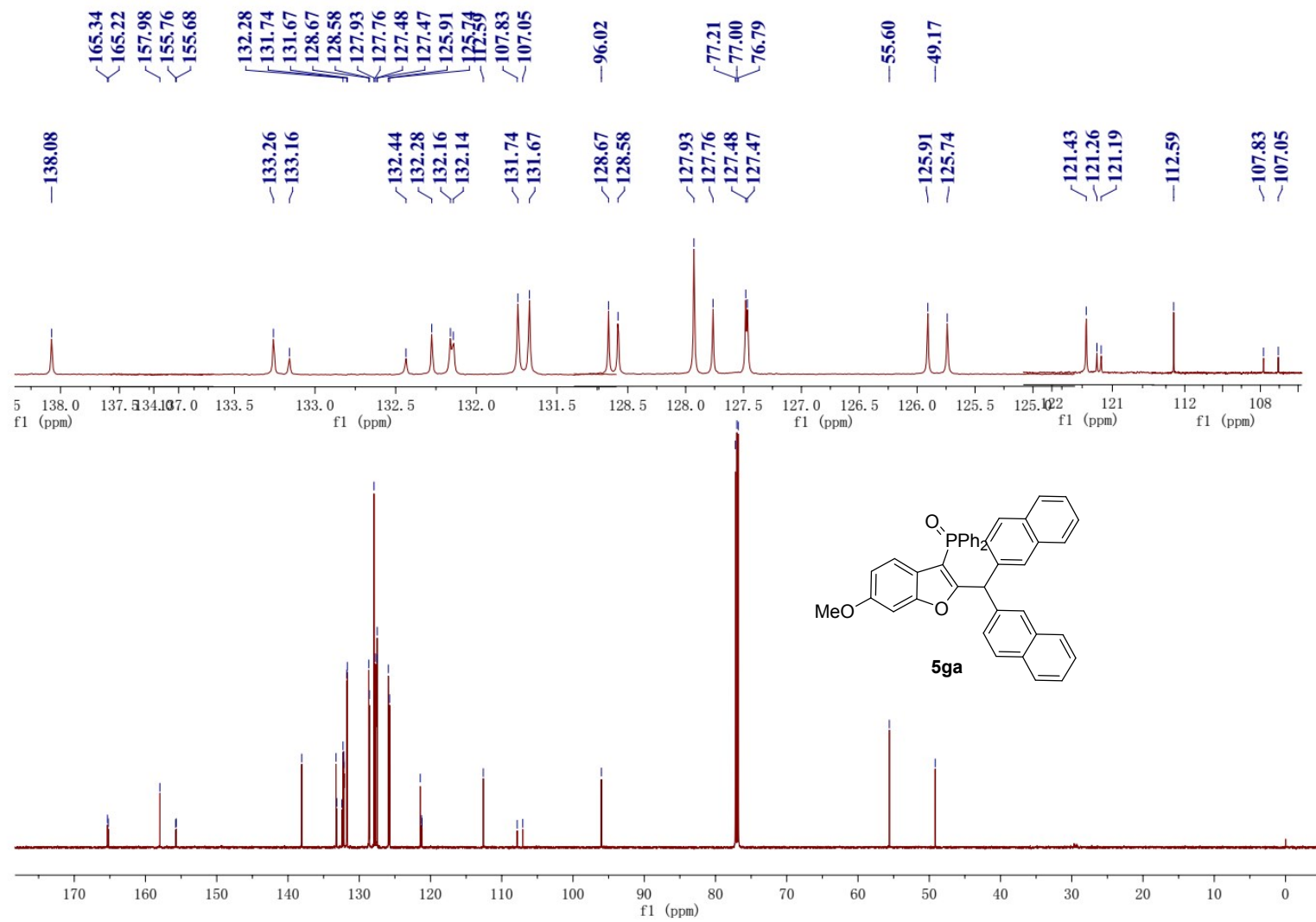




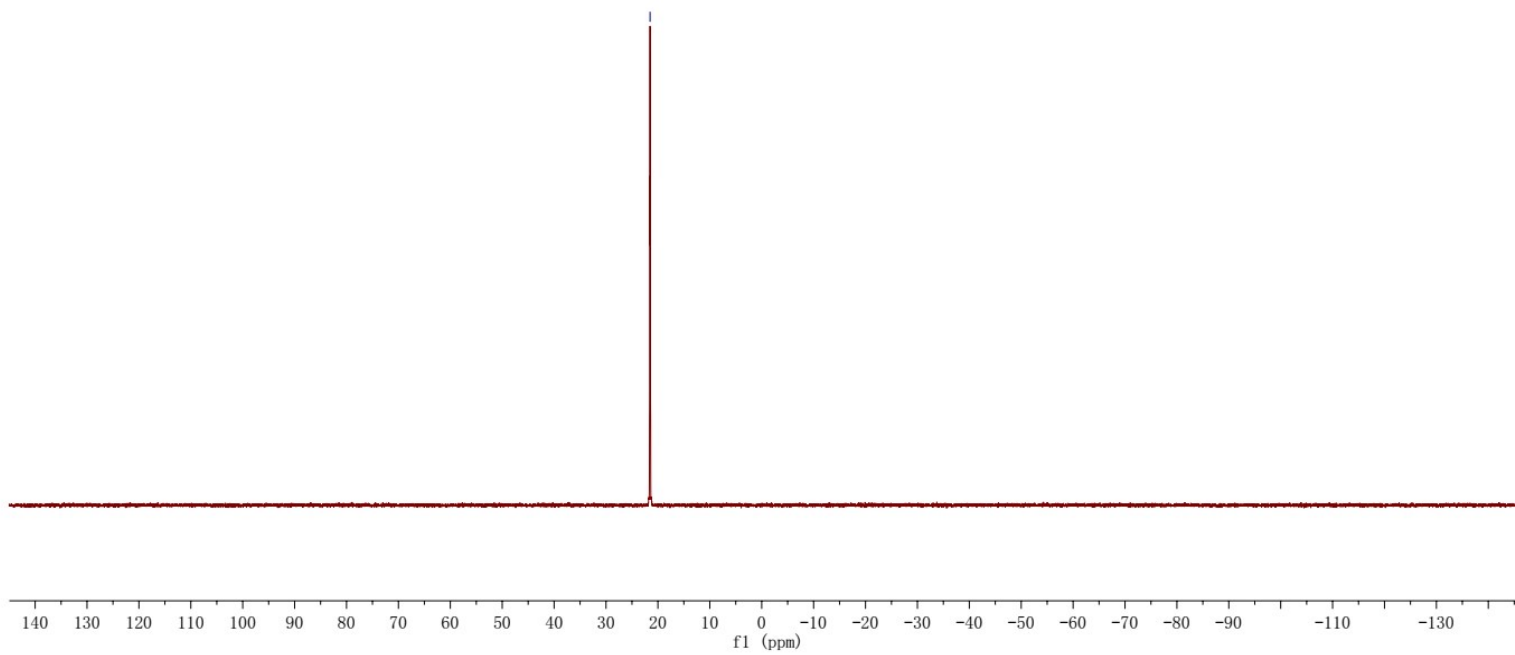
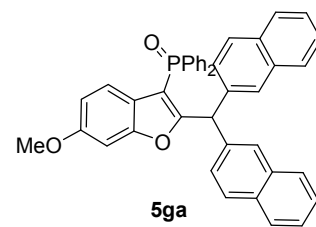
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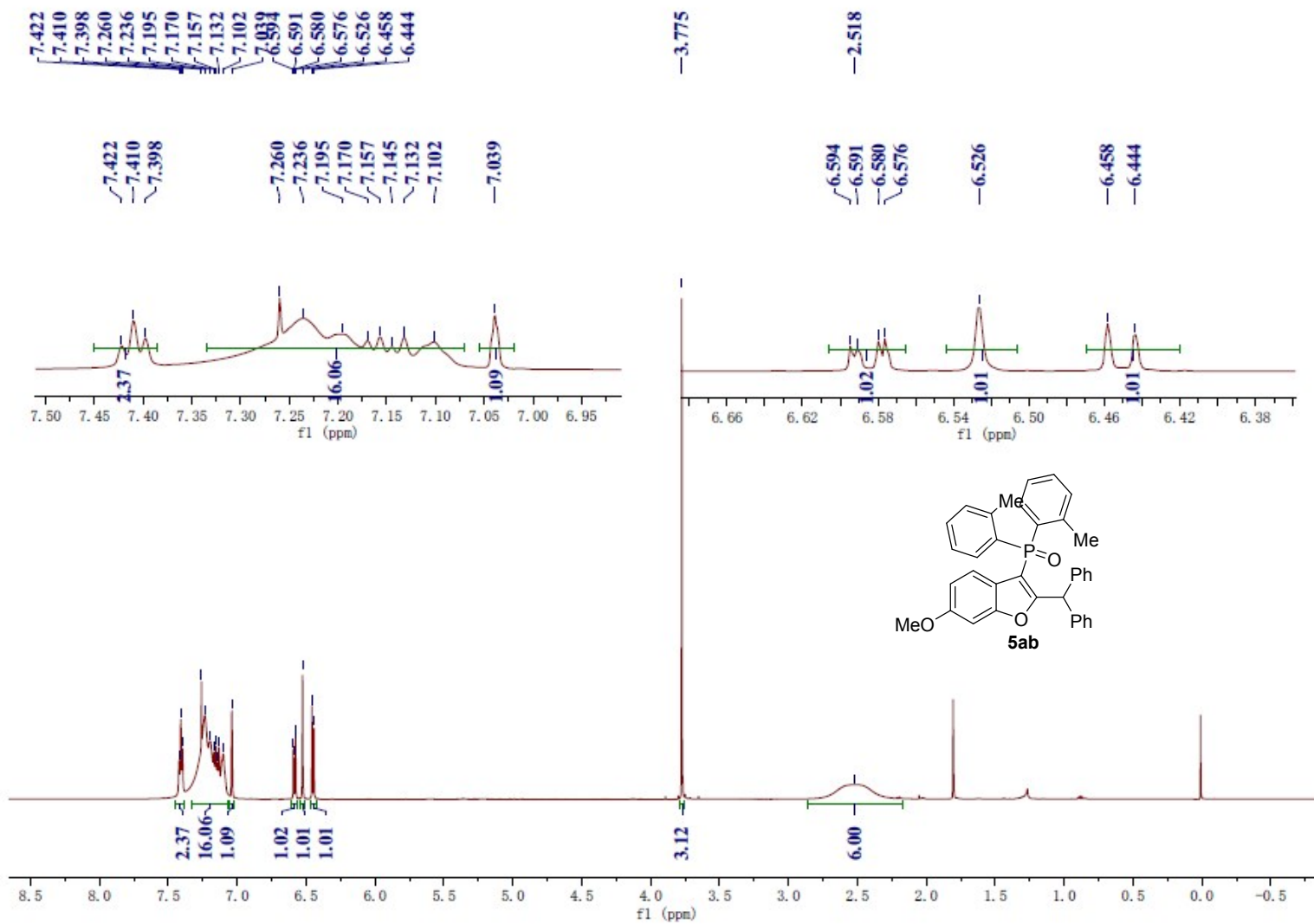


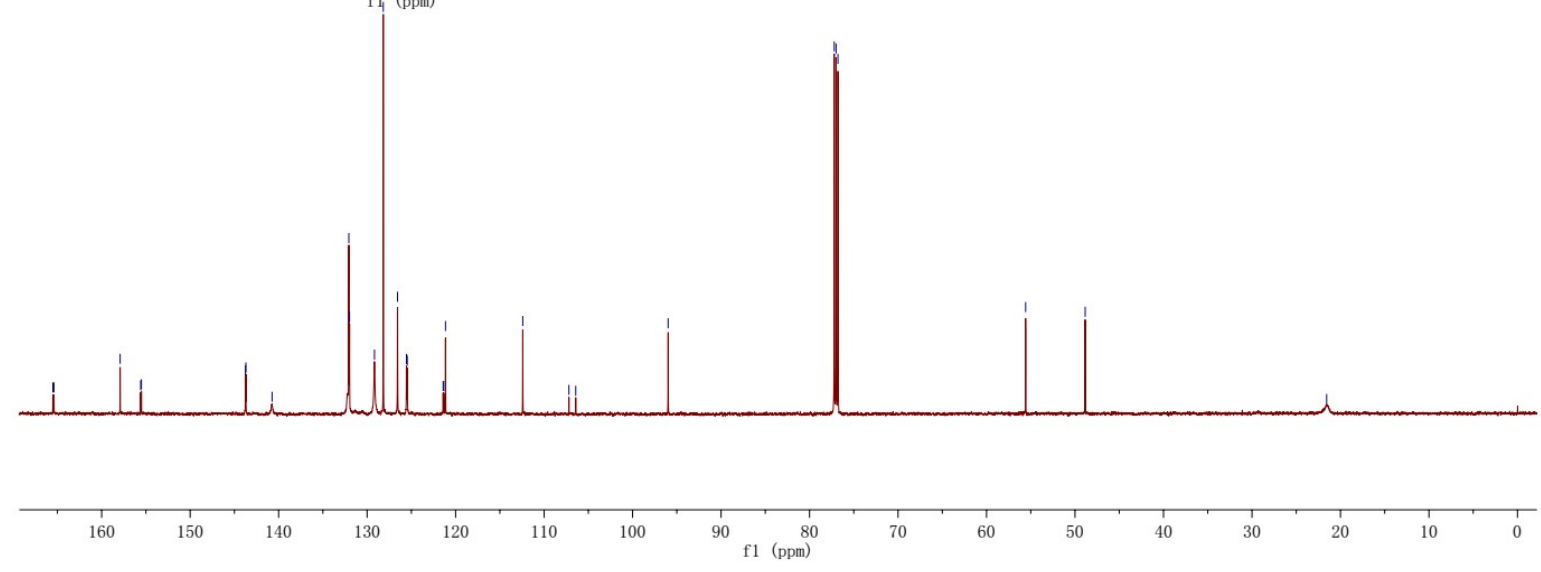
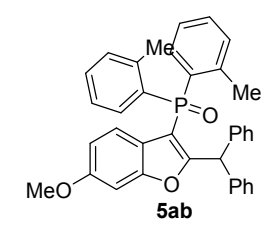
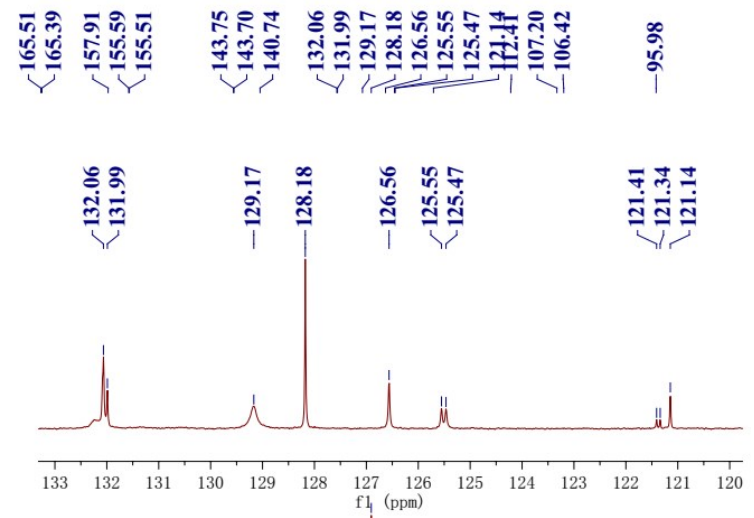


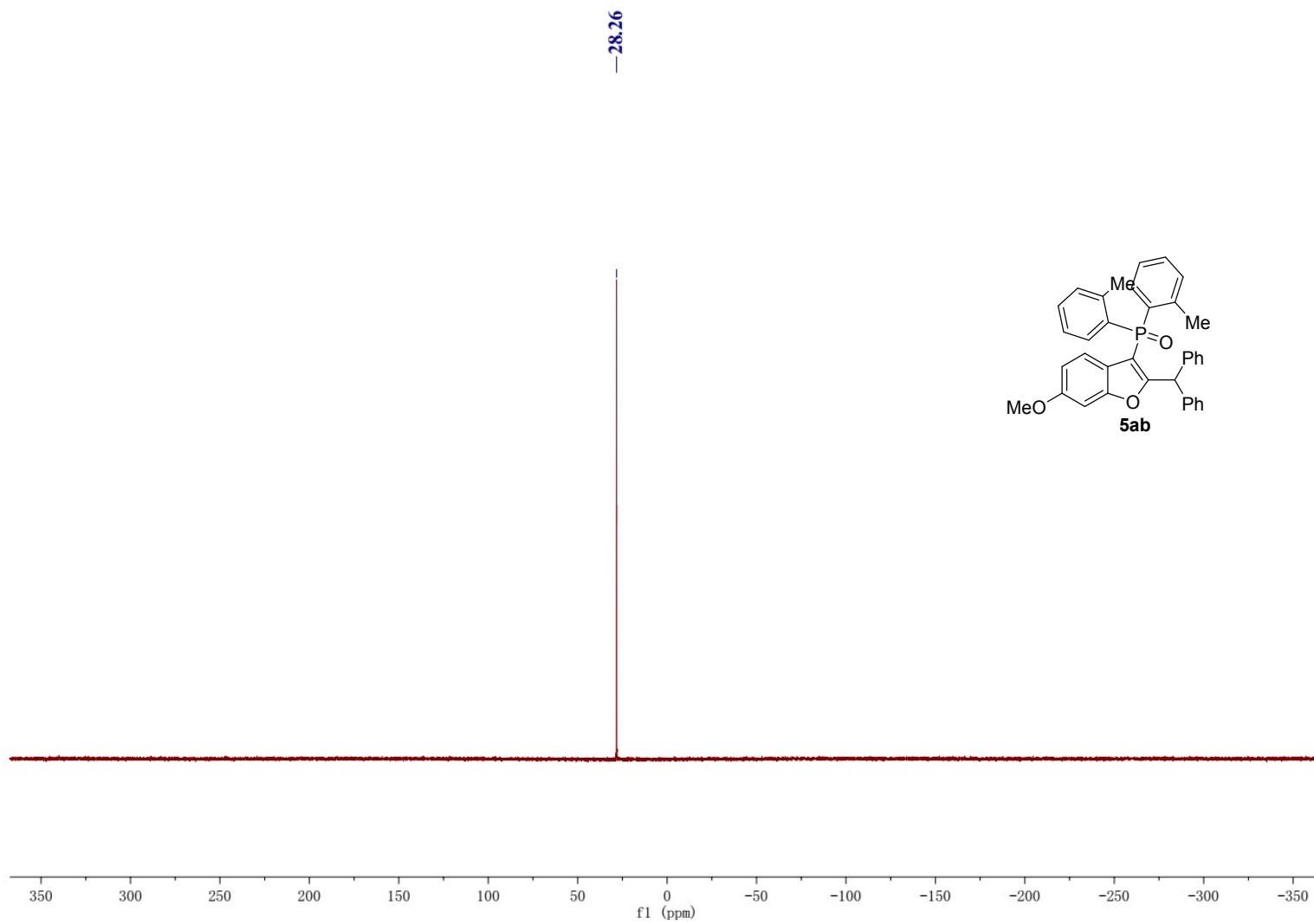


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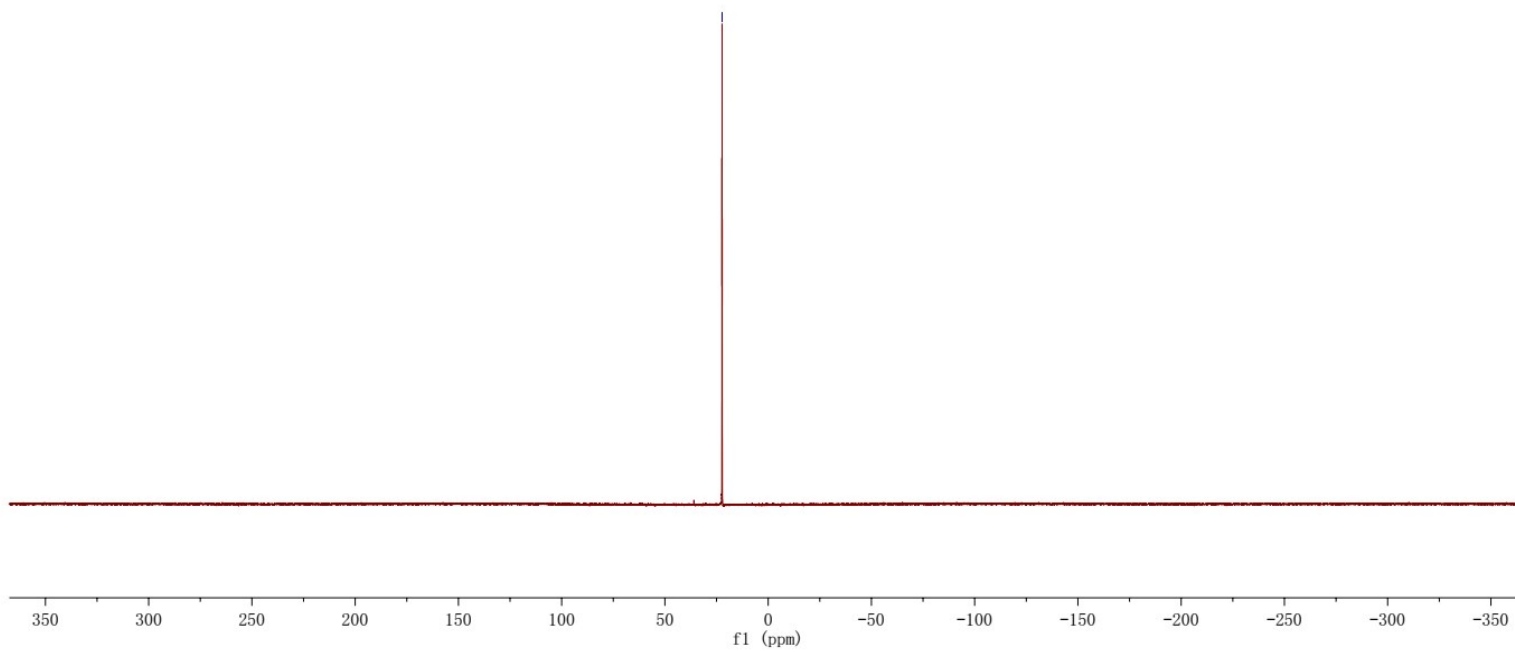
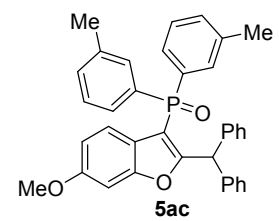


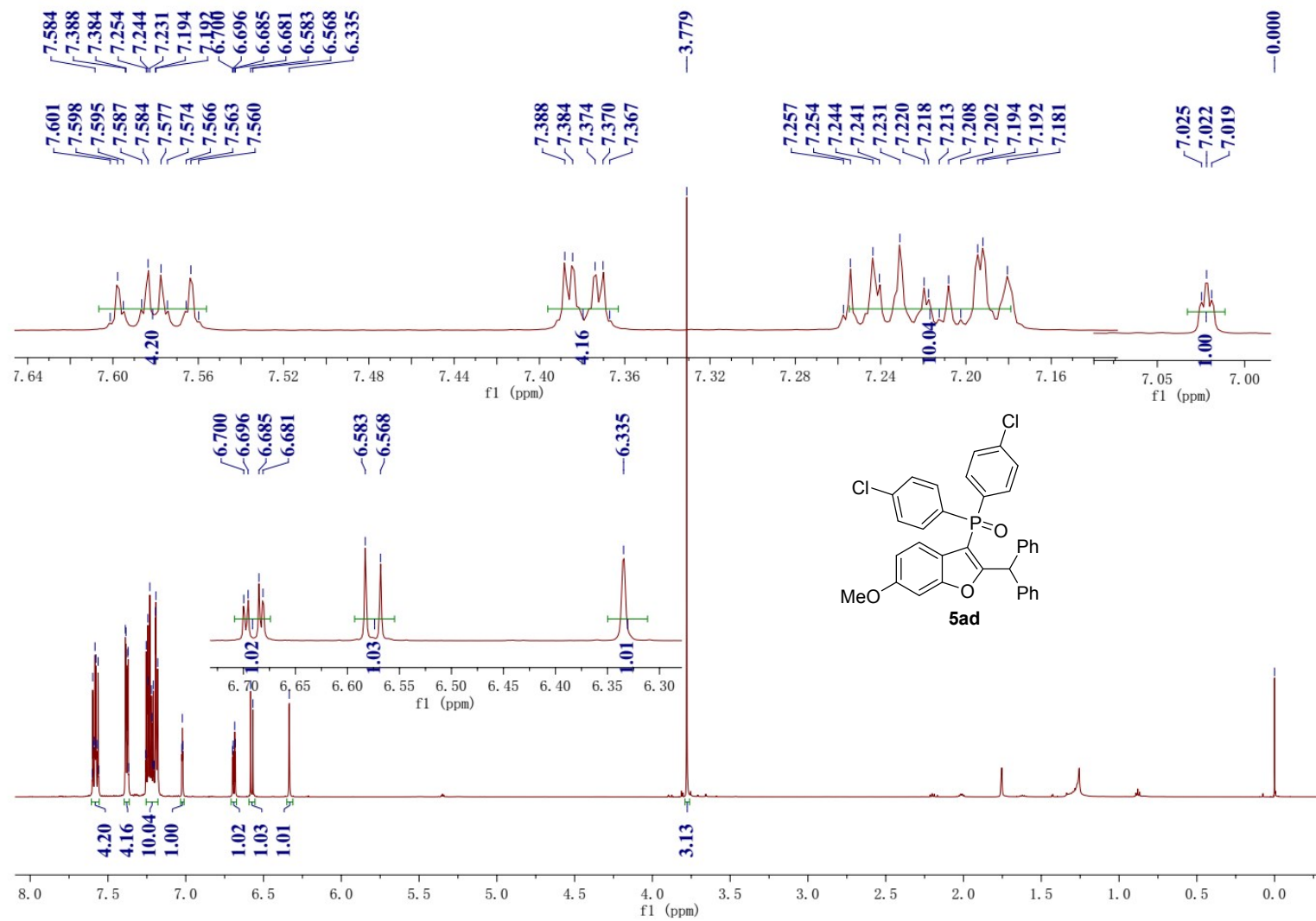


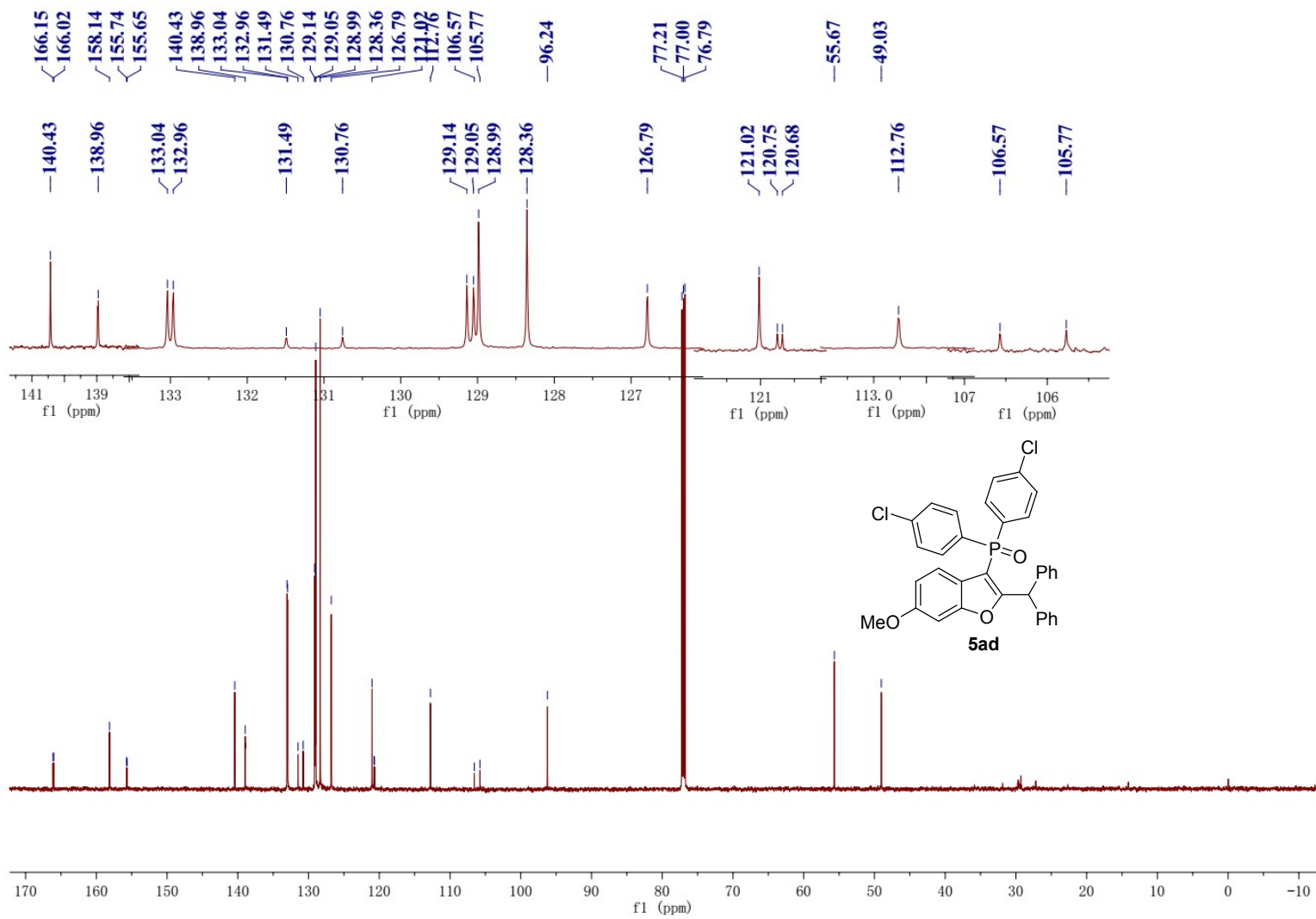




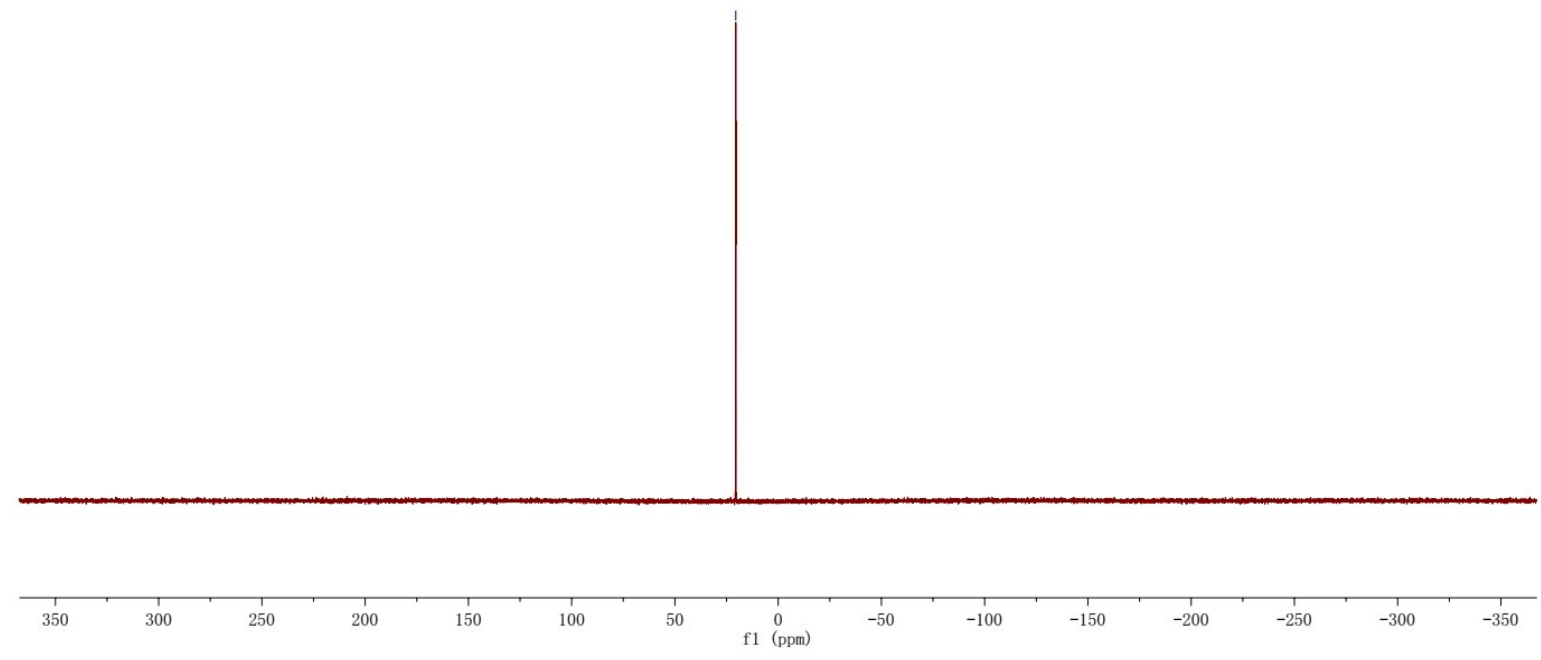
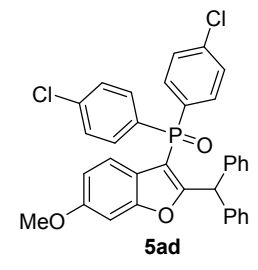
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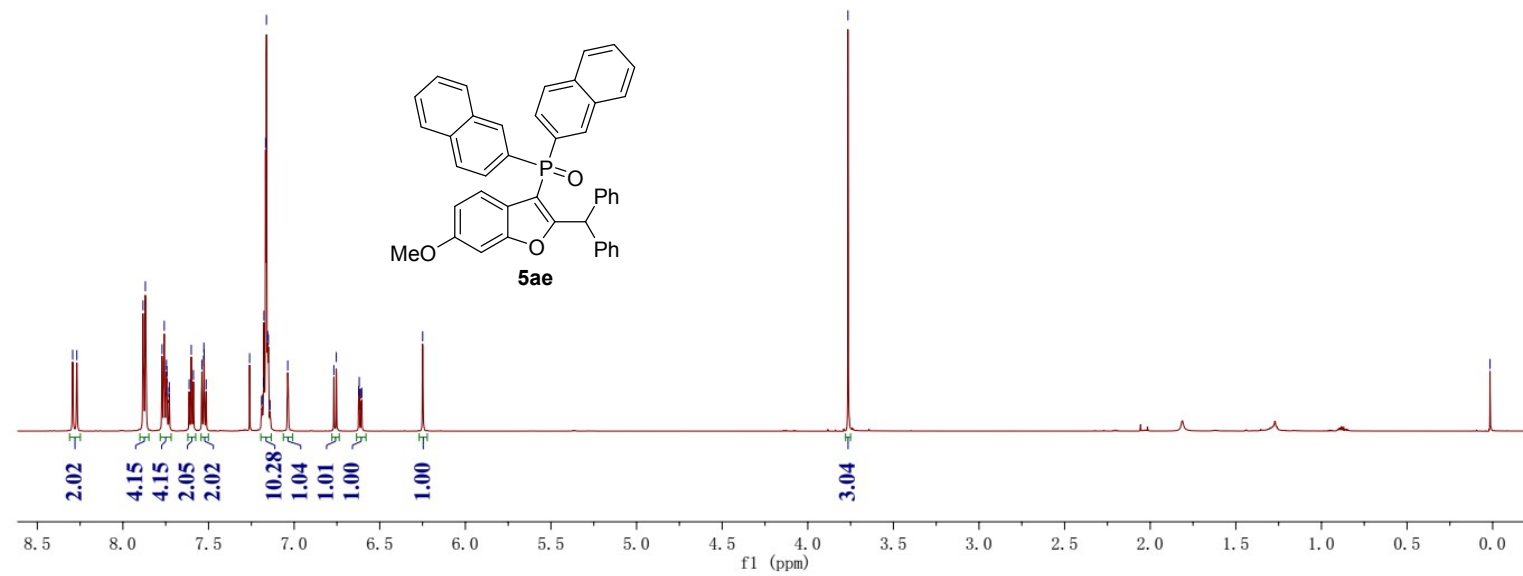
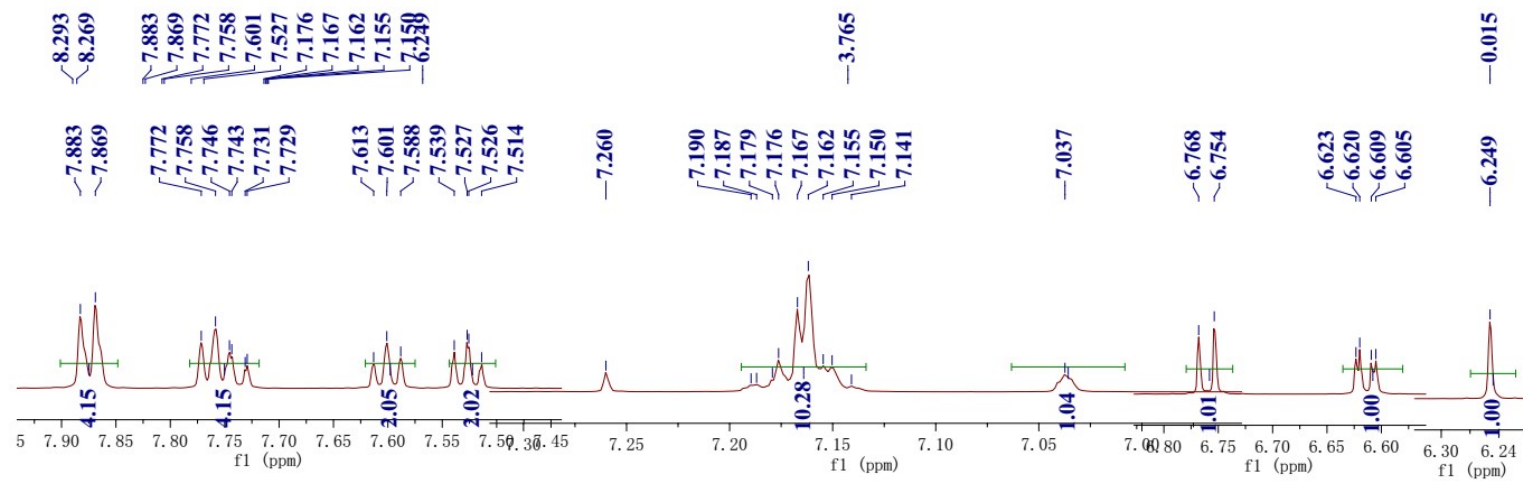


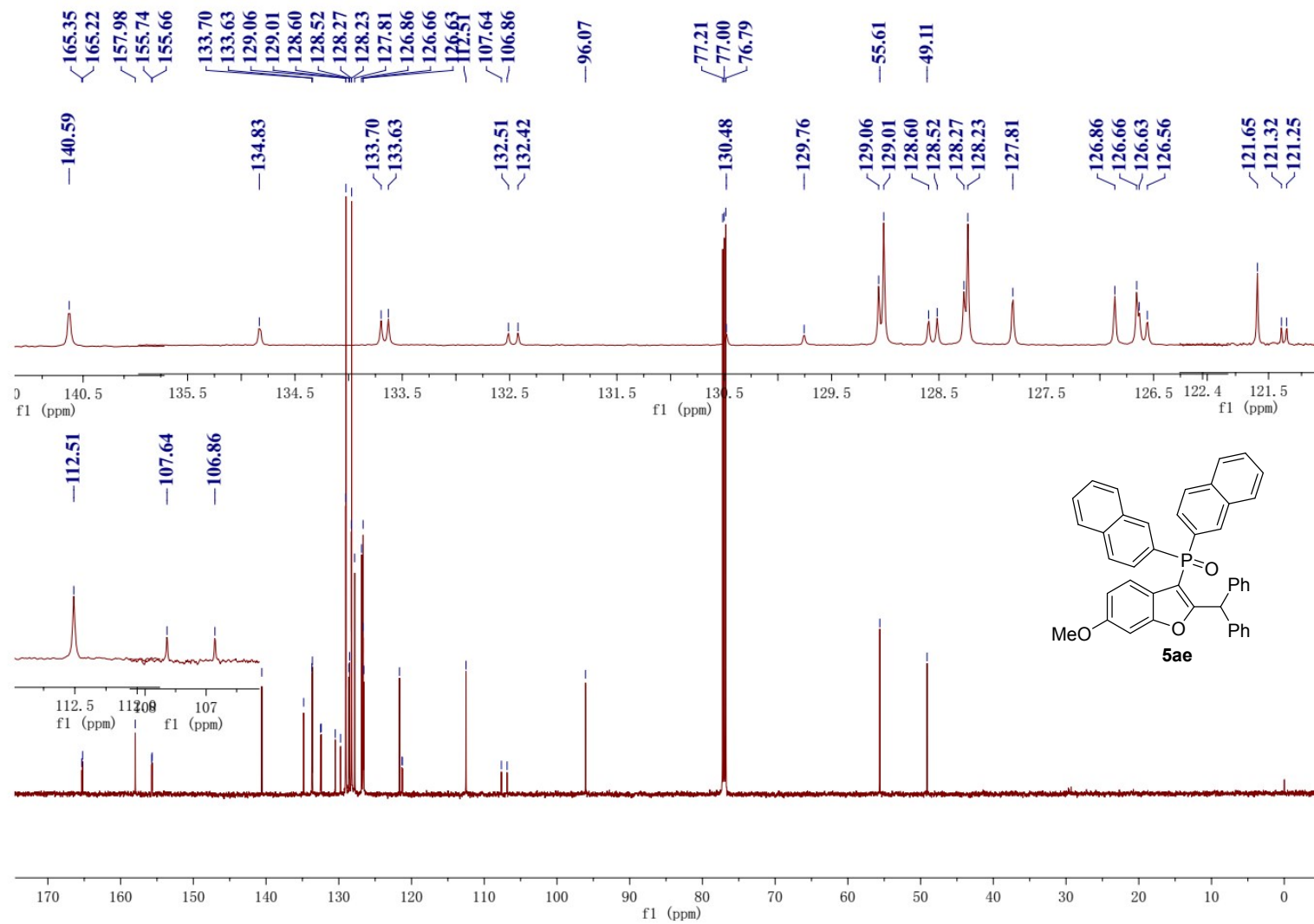


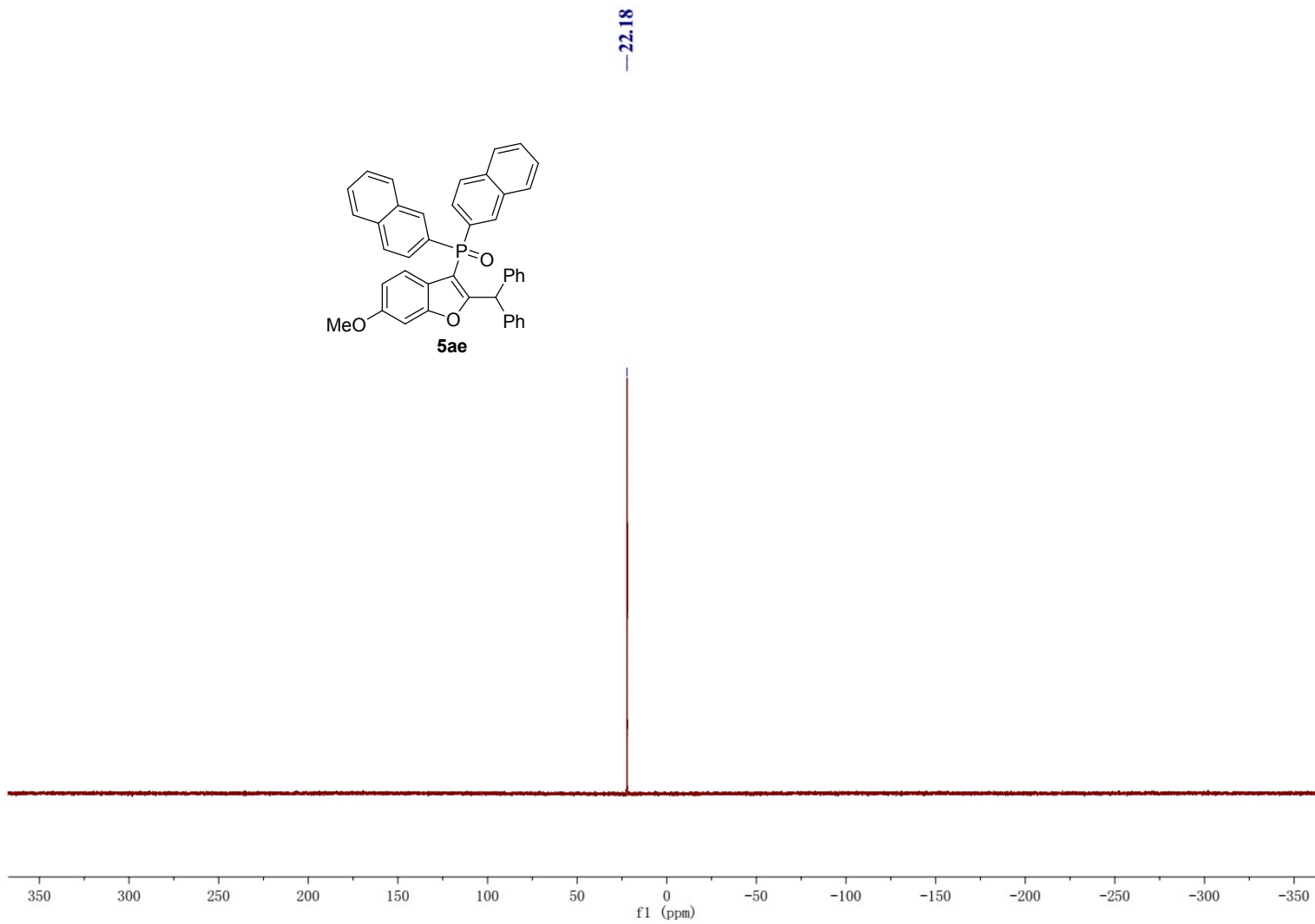
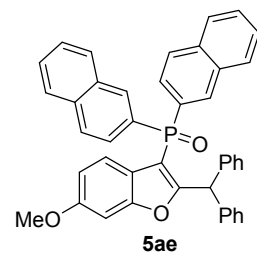


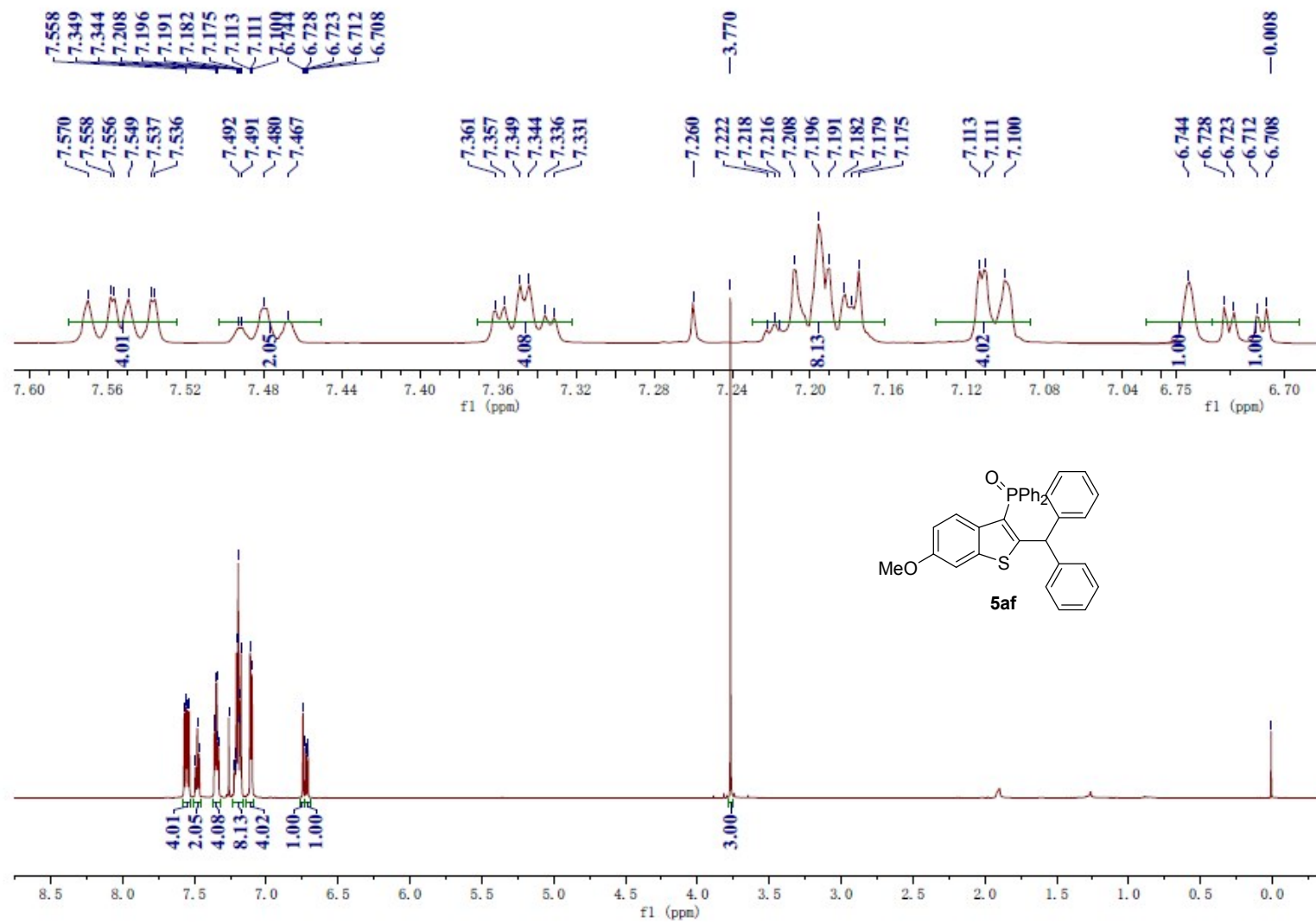
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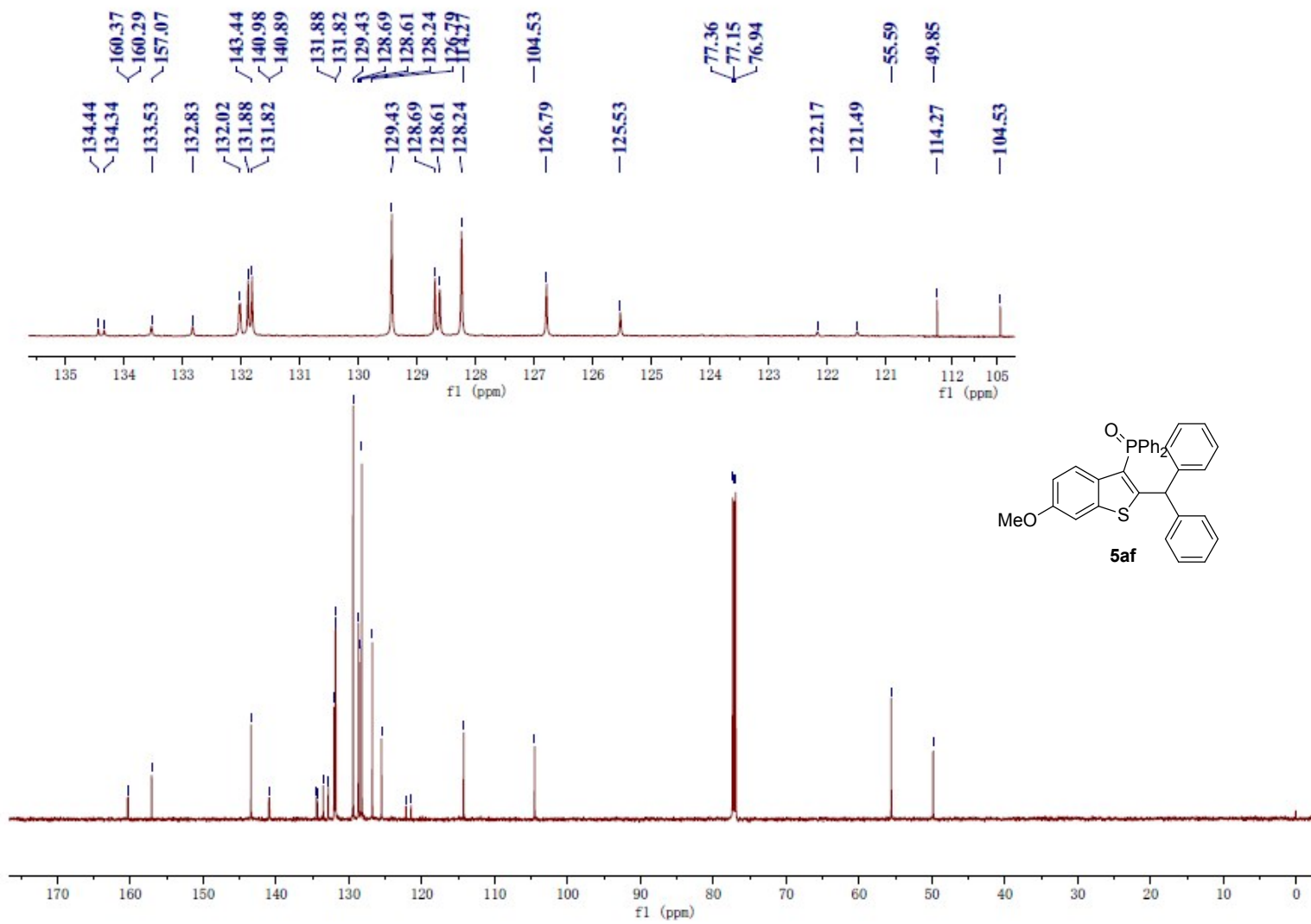


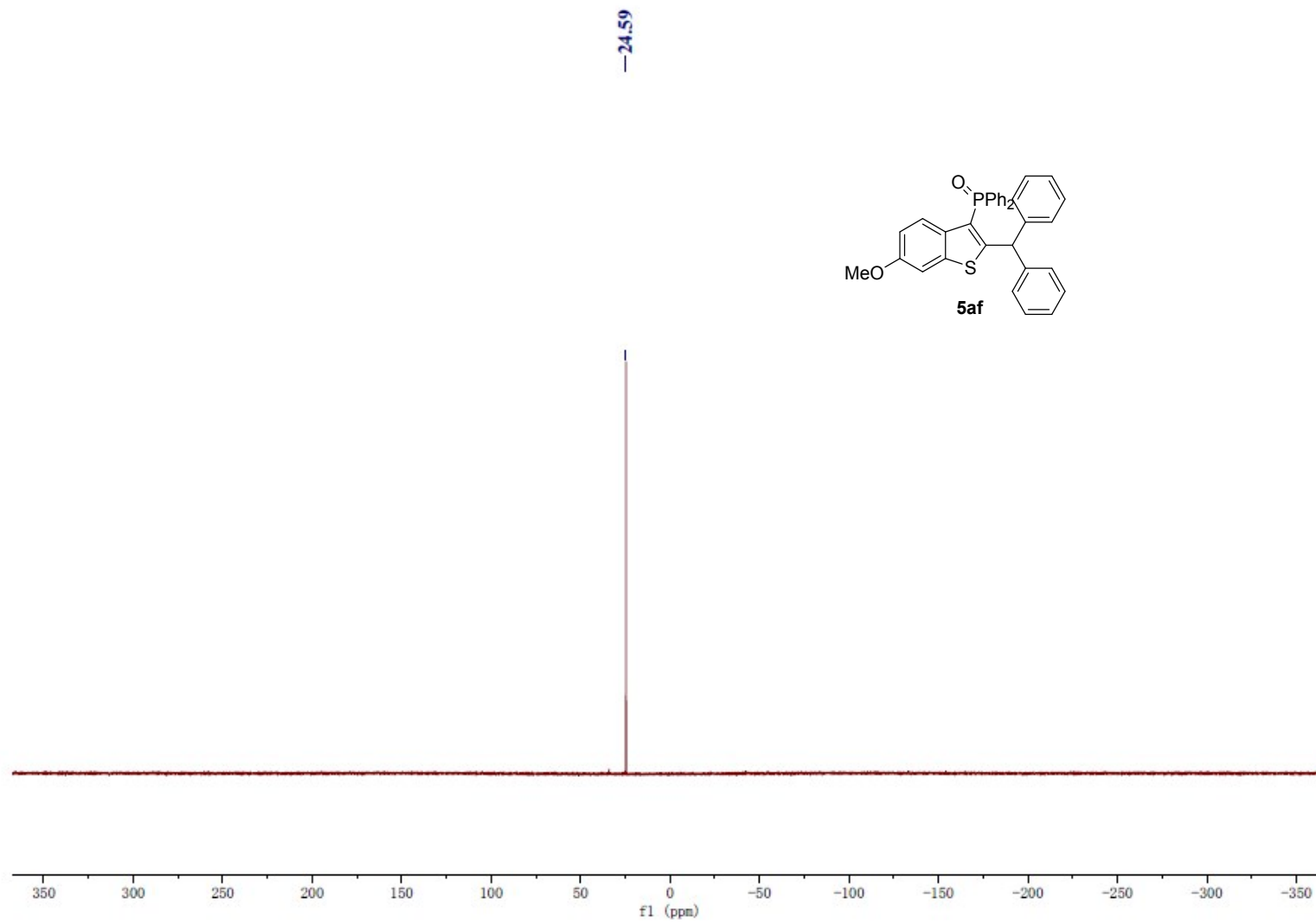


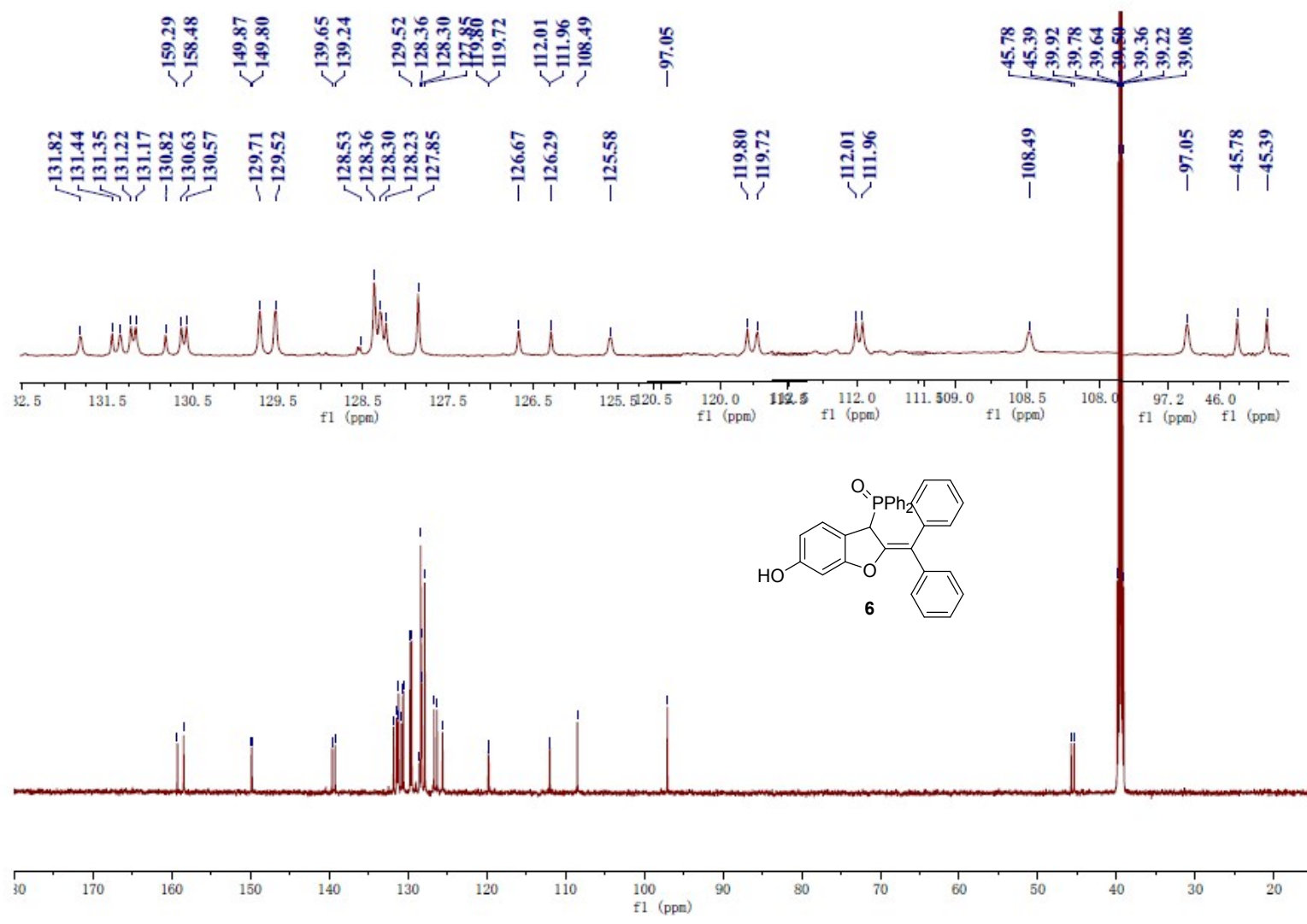




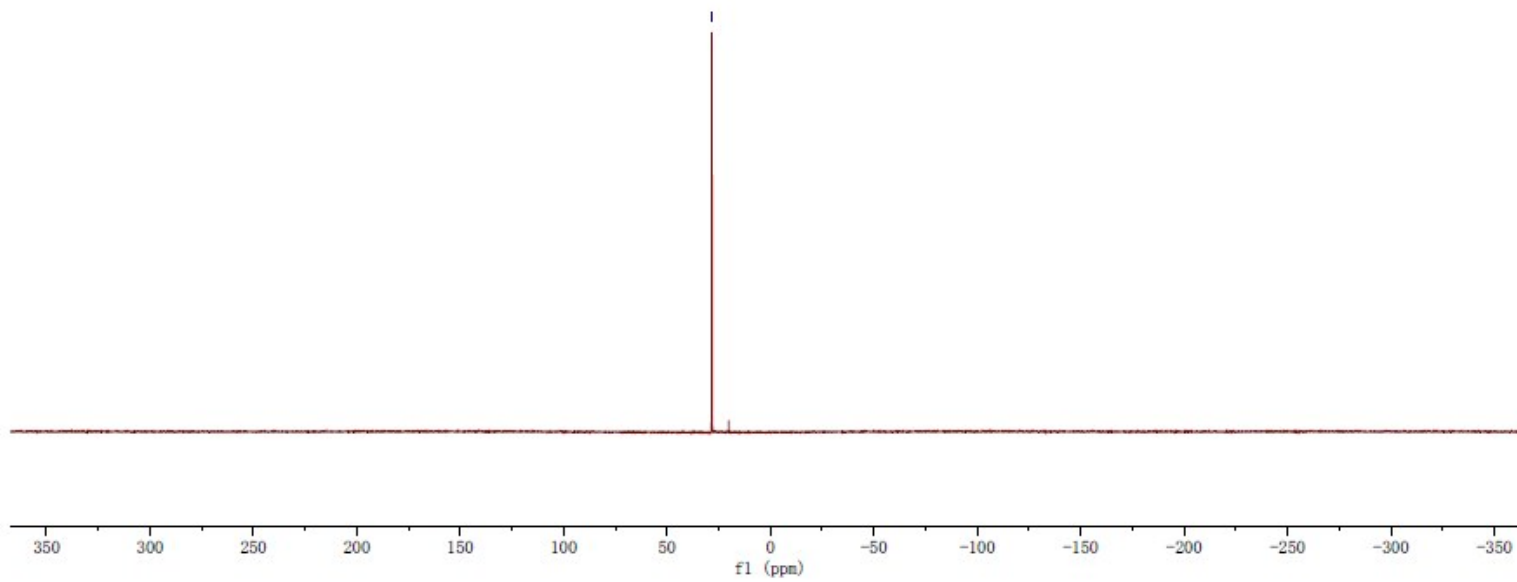
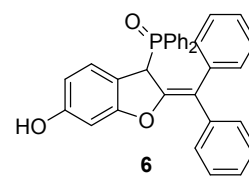


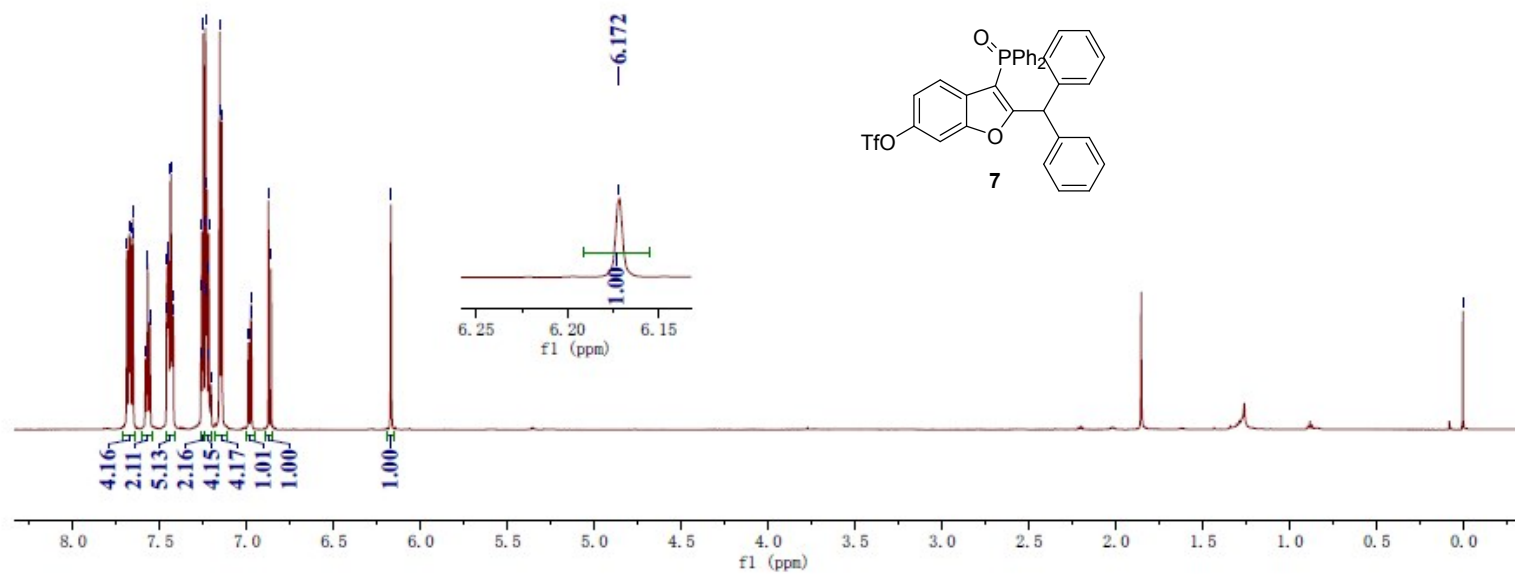
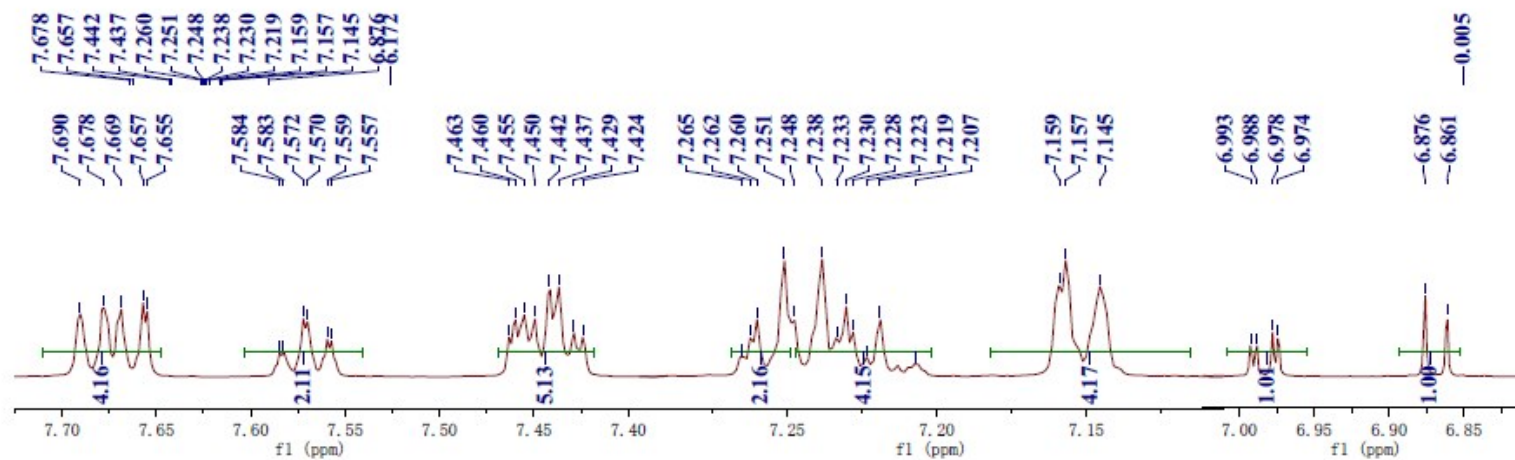


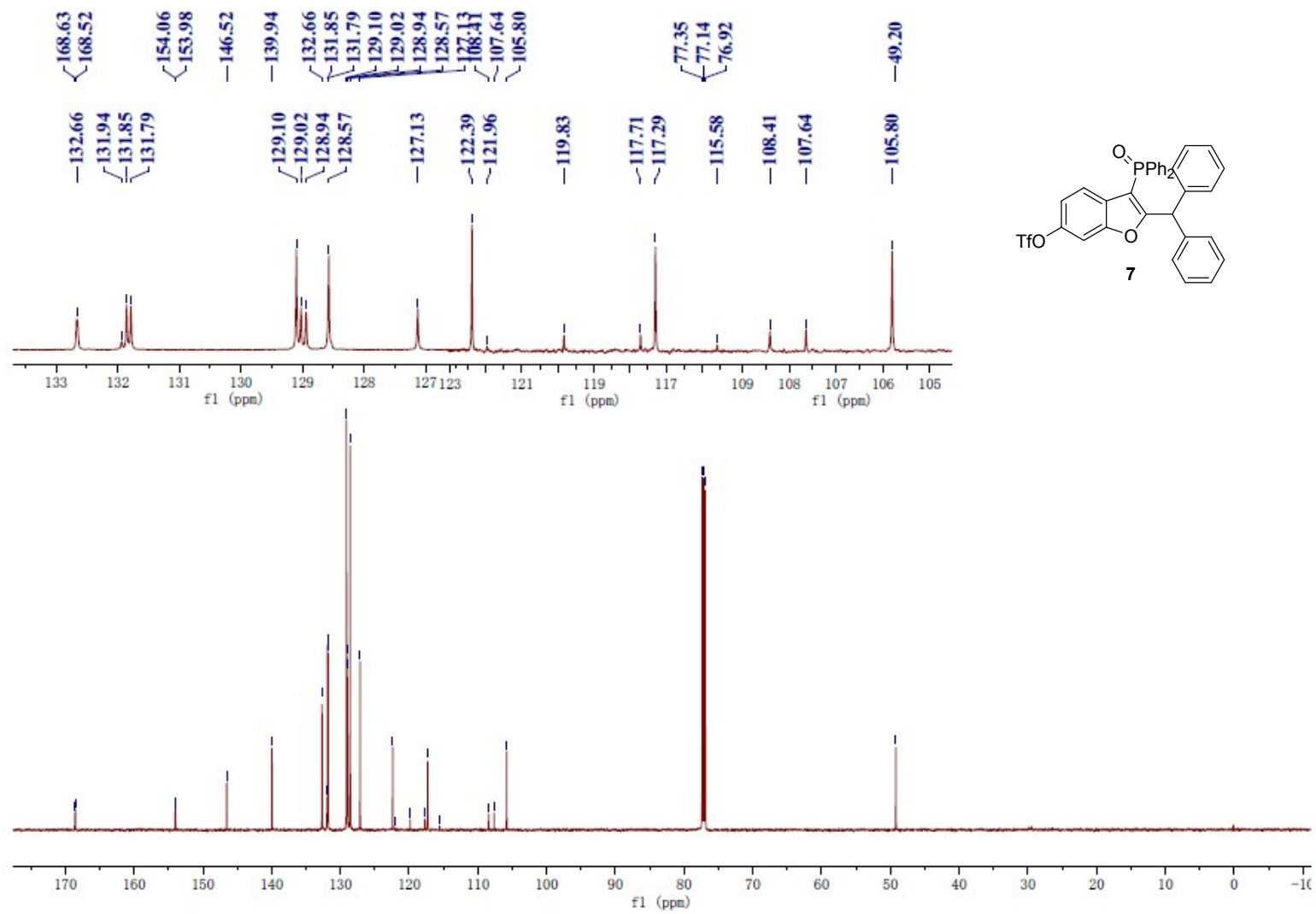




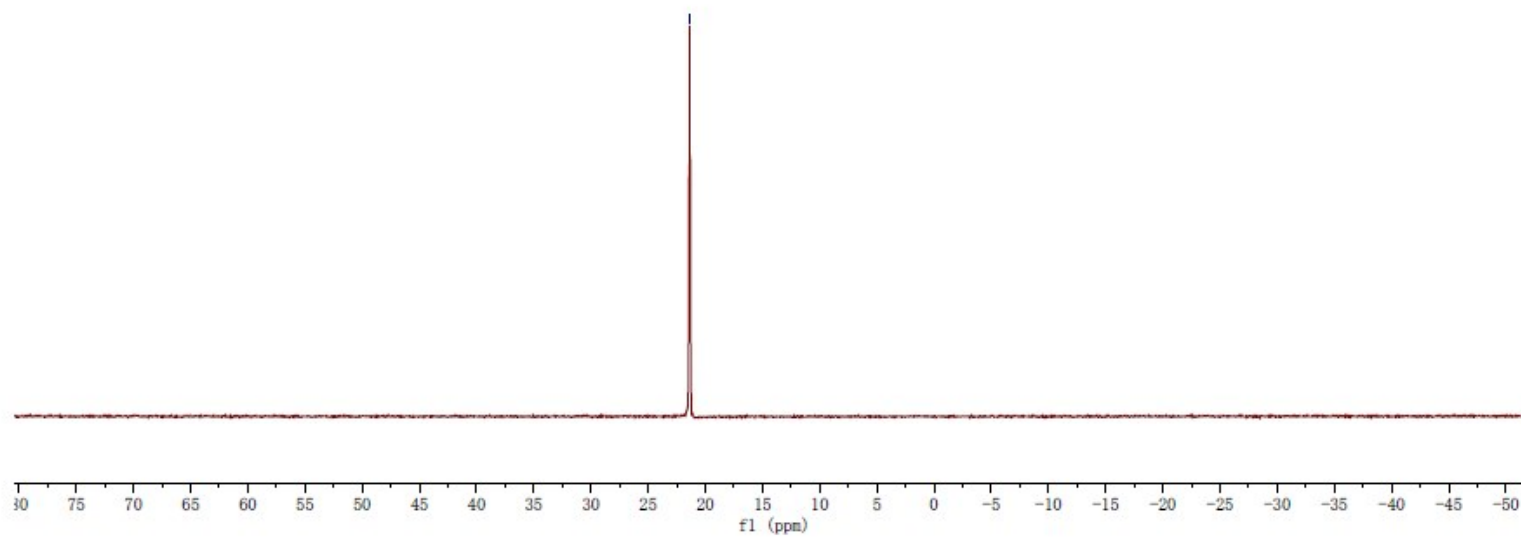
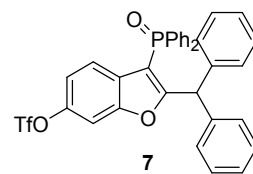
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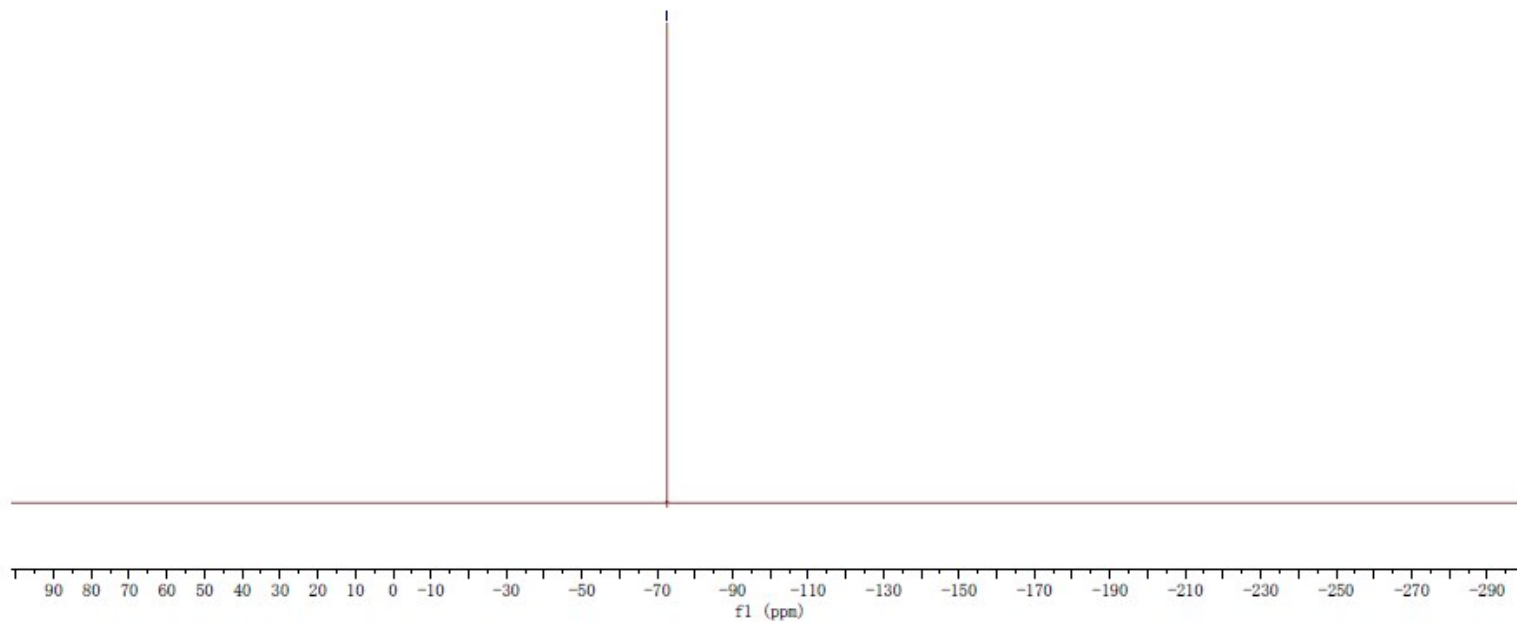
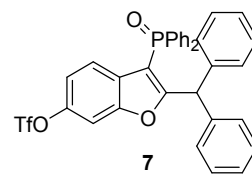


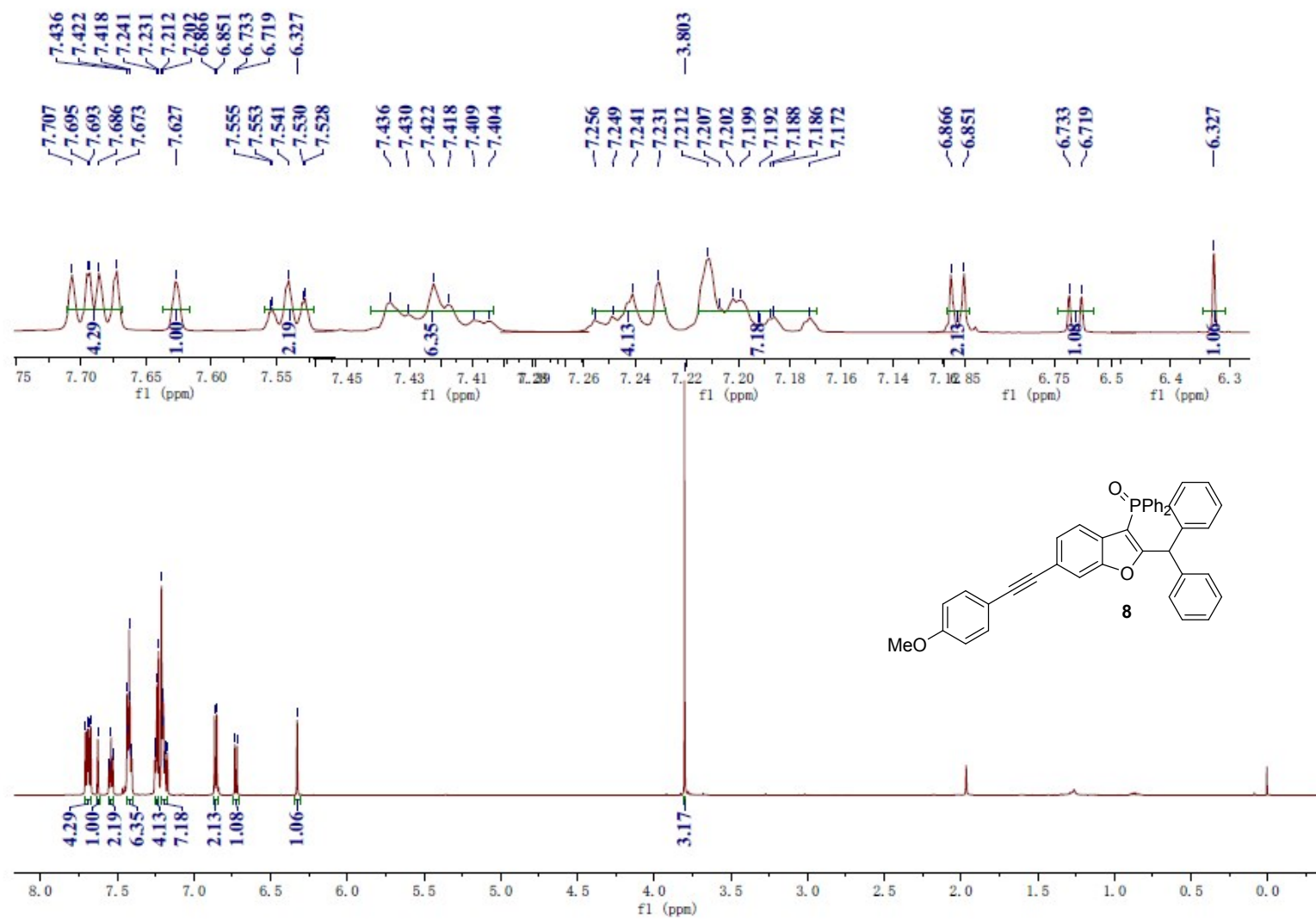


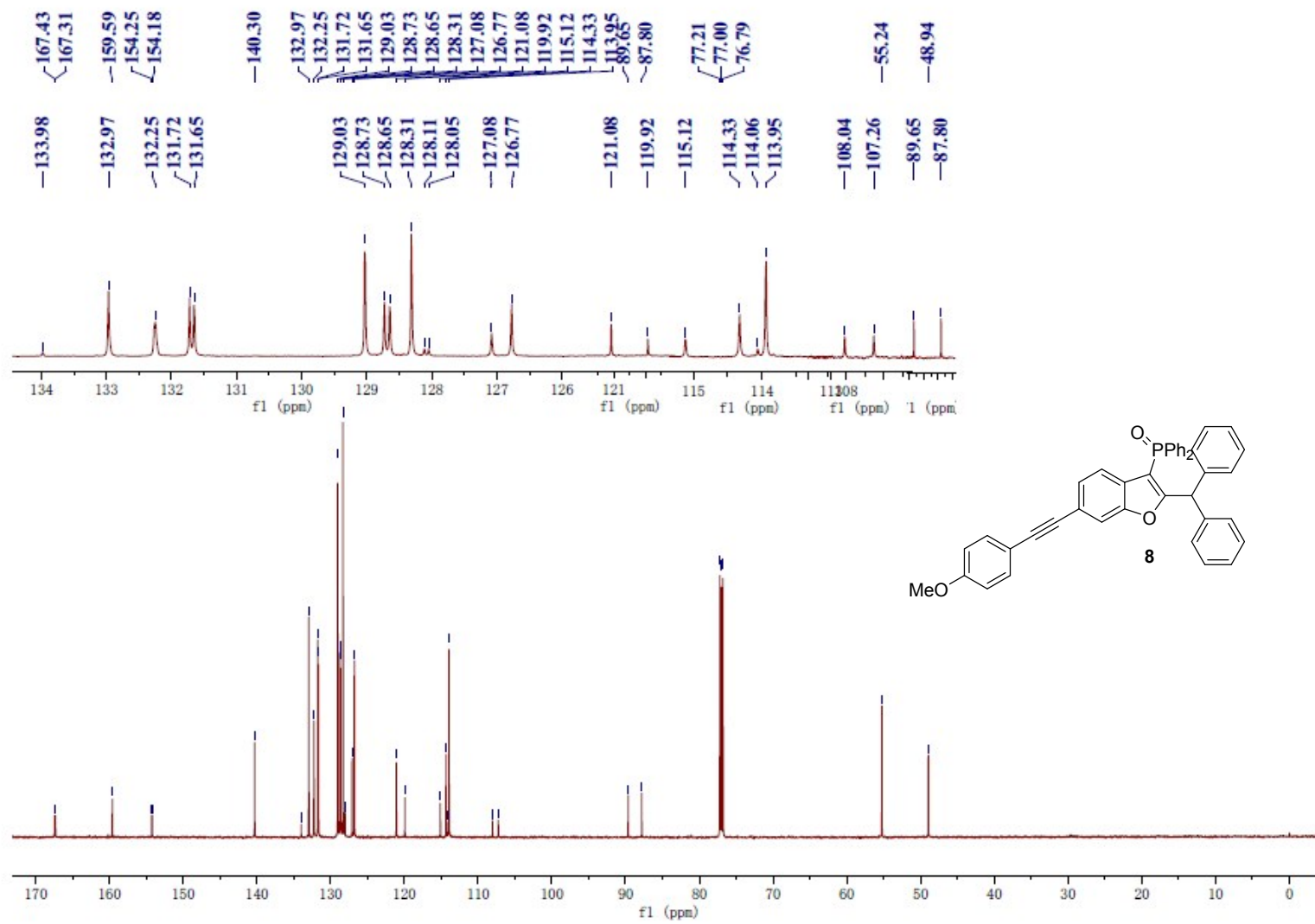
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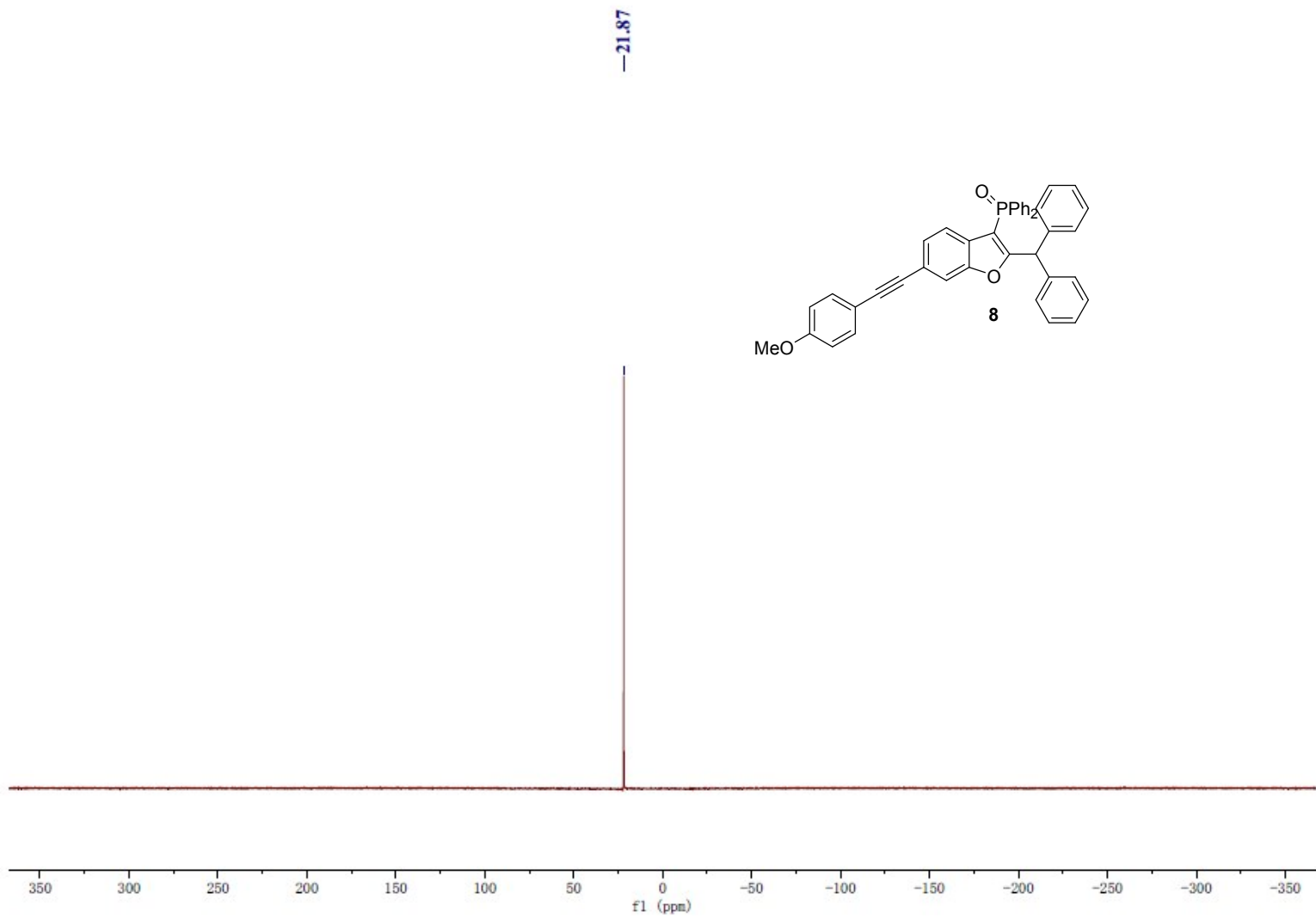


-72.60









-21.87

