Palladium-Catalyzed $P(O)R_2$ Directed C-H Arylation to Synthesize Electron-rich Polyaromatic Monophosphorus Ligands

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Supporting Information

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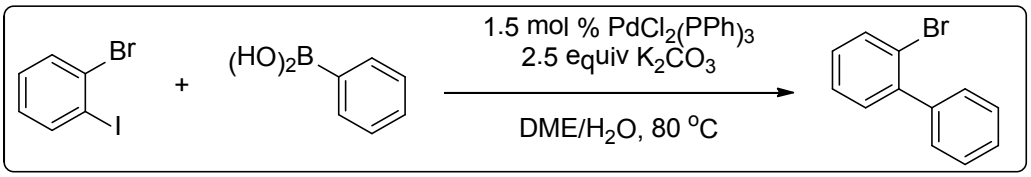
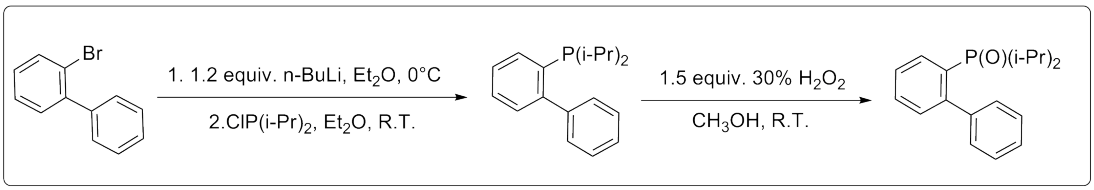
Ⅰ. General Methods and Materials

^{1}H and ^{13}C NMR spectra were recorded on a Bruker advance Ⅲ 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C) in $CDCl_3$ with TMS as internal standard. Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for ^{1}H, or to chloroform δ = 77.0 for ^{13}C as internal standard. ^{31}P NMR spectra and 19F NMR were recorded on the same instrument. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet), Coupling constants, J, are reported in hertz. Mass data were measured with Thermo Scientific DSQ II mass spectrometer. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals Adamas-beta or TCI and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). Substrates were prepared according to literature.

Ⅱ Typical Procedures for the Synthesis of Substrates



Water (4.0 mL) and DME (30.0 mL) were poured into a round-bottomed flask, fitted with a condenser and argon flow, and bubbled through with argon. Potassium carbonate (3.45 g, 25 mmol), 1-bromo-2-iodobenzene (2.8 g, 10.0 mmol), substituted phenylboronic acid (10.5 mmol), and bis(tripheylphosphine)palladium(II) chloride (105 mg, 0.15 mmol) were added to the mixture, which was stirred at 80 °C for 5 h in an oil bath until substrate disappeared as judged by TLC. The reaction mixture was allowed to cool to r.t., DME was evaporated, and water (40.0 mL) and ether (20.0 mL) were added. The layers were separated and the aqueous layer was extracted with diethylether (3 x 20.0 mL). The combined organic layers were washed with brine, dried over magnesium sulfate, filtered, and evaporated in vacuo to obtain a yellow oil, which was purified further using column chromatography on silica gel (eluent: heptane 30% EtOAc in heptane). The title compound was isolated as a white amorphous solid (2.10 g, 90%).

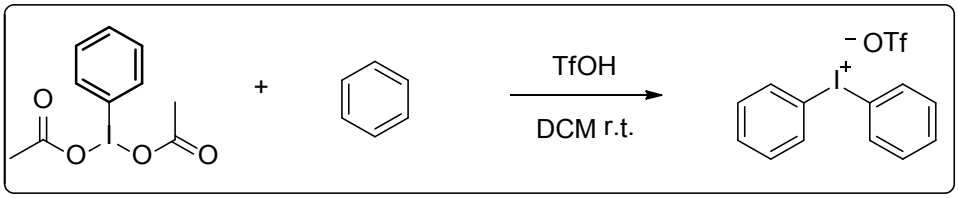


4.0 mL (9.60 mmol) of *n*-BuLi in *n*-hexane (2.40 M) were added dropwise to a suspension of (8.0 mmol) of 2-bromo-1,1'-biphenyl in 24 mL of diethyl ether at 0 °C. The resulting beige-colored suspension was stirred for an additional 2 h at 0 °C. Then, $ClP(i\text{-}Pr)_2$ (1.21 g, 8.0 mmol) was added dropwise in freshly distilled diethyl ether (16.0 ml). The mixture was then stirred at r.t. for 1 h, filtered and solvent was removed in vacuo to yield a residue, which was used without further purification. To

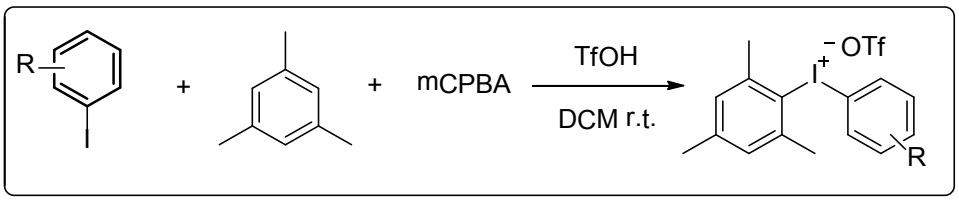
the residue in MeOH (36.0 ml) was added dropwise 30 % aq. H_2O_2, solution (1.63 ml, 16.0 mol). The resulting clear solution was stirred at r.t. for 1 h, treated for 1 h with sat. Na_2SO_3, solution (8.0 ml) and 1N HCl solution (5.0 ml), and the mixture was concentrated at the rotavapor to remove the MeOH. The aqueous layer was extracted with CH_2C1_2 (3 × 20 ml). The extract was washed with brine and dried over $MgSO_4$. The organic layers were dried over Na_2SO_4, filtered and solvent was evaporated under reduced pressure. The desired product was obtained after purification by chromatography on silica gel.

Ⅲ General Procedure for one-pot preparation of diaryliodonium triflates

Method A: Trifluoromethanesulfonic acid (30 mmol,2.0 equiv)was added dropwise to a solution of the iodobenzene diacetate(15 mmol,1.0 equiv) in CH_2Cl_2(30 ml) at 0℃,stirring for 2h at r.t.And then the solution cooled to 0℃, benzene was added dropwise, the reaction allowed to warm to rt over the course of 2h. The solvent was removed in vacuo, the residue was submitted to flash chromatography (CH_2Cl_2–Et_2O=2:1 → CH_2Cl_2 - MeOH = 25:1) to give the diphenyliodonium trifluoromethanesulphonate as a white solid[1].



Method B:mCPBA ((assume 85%) 1.0g, 5 mmol) was added to a solution of the appropriate iodoarene (4.5 mmol) and mesitylene (0.7 ml, 5.0 mmol) in CH_2Cl_2 (20 ml) and the solution cooled to 0℃. Trifluoromethanesulfonic acid (0.66 mL, 7.5 mmol) was added dropwise over mins and the reaction allowed to slowly warm to rt over the course of 2h. The solvent was removed in vacuo and Et_2O added. The solvent was again removed in vacuo and this procedure was repeated several times until crystals started to form.The resulting crystals were filtered and washed on the filter with Et_2O to give the iodonium triflate as a white solid [2].

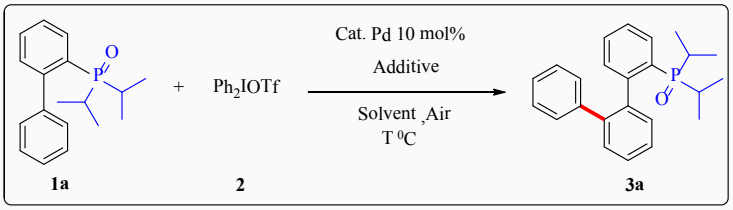


[1] B. J. Wang, R. L. Cerny, S. H. Uppaluri, J. J. Kempinger, St. G. DiMagno, *Journal of Fluorine Chemistry*, 2010, **131**, 1113.

[2] R. J. Phipps and M. J. Gaunt, *Science*, 2009, **323**, 1593.

Ⅳ Detailed optimization studies for the palladium-catalyzed C(sp^2)-H arylation

Table S1 Optimization Studies for the Direct Arylation of **1a**[a]

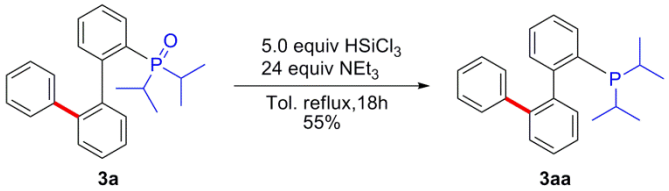


Entry	Cat.(10 mol%)	Additive Ⅰ	Additive Ⅱ	Solvent/T℃	yield(%)[b]
1	$Pd(OAc)_2$	/	/	DMF/100	52
2	$Pd(OAc)_2$	/	/	DCE/100	21
3	$Pd(OAc)_2$	/	/	AcOH/100	25
4	$PdCl_2$	/	/	DMF/100	41
5	$Pd(TFA)_2$	/	/	DMF/100	37
6	$PdCl_2(PPh_3)_2$	/	/	DMF/100	36
7	$Pd(OPiv)_2$	/	/	DMF/100	67
8	$Pd(PPh_3)_4$	/	/	DMF/100	41
9	$Pd(OAc)_2$	K_2CO_3	/	DMF/100	N.R
10	$Pd(OAc)_2$	DABCO	/	DMF/100	N.R
11	$Pd(OAc)_2$	AcOH/3.0 equiv	/	DMF/100	69
12	$Pd(OAc)_2$	TFA/3.0 equiv	/	DMF/100	58
13	$Pd(OAc)_2$	$TsOH.H_2O$/3.0 equiv	/	DMF/100	52
14	$Pd(OAc)_2$	PivOH/3.0 equiv	/	DMF/100	75
15	$Pd(OAc)_2$	Picolinic acid/3.0 equiv	/	DMF/100	N.R
16	$Pd(OAc)_2$	$MgSO_4$/3.0 equiv	/	DMF/100	53
17	$Pd(OAc)_2$	PivOH/2.0 equiv	/	DMF/100	78
18	$Pd(OAc)_2$	PivOH/1.0 equiv	/	DMF/100	72
19	$Pd(OAc)_2$	PivOH/2.0 equiv	Ag_2O/0.5 equiv	DMF/100	75
20	$Pd(OAc)_2$	PivOH/2.0 equiv	AgOAc/0.5 equiv	DMF/100	63
21	$Pd(OAc)_2$	PivOH/2.0 equiv	$AgBF_4$/0.5 equiv	DMF/100	69
22	$Pd(OAc)_2$	PivOH/2.0 equiv	Ag_2CO_3/0.5 equiv	DMF/100	78
23	$PdCl_2$	PivOH/2.0 equiv	Ag_2CO_3/0.5 equiv	DMF/100	78
24	$Pd(TFA)_2$	PivOH/2.0 equiv	Ag_2CO_3/0.5 equiv	DMF/100	61
25	$Pd(PivO)_2$	PivOH/2.0 equiv	Ag_2CO_3/0.5 equiv	DMF/100	35
26	$PdCl_2(PPh_3)_2$	PivOH/2.0 equiv	Ag_2CO_3/0.5 equiv	DMF/100	54
27	$Pd(PPh_3)_4$	PivOH/2.0 equiv	Ag_2CO_3/0.5 equiv	DMF/100	49
28	$PdCl_2$	PivOH/2.0 equiv	Ag_2CO_3/0.5 equiv	DMF/60	N.R
29	$PdCl_2$	PivOH/2.0 equiv	Ag_2CO_3/0.5 equiv	DMF/80	84
30	$PdCl_2$	PivOH/2.0 equiv	Ag_2CO_3/0.5 equiv	DMA/80	31
31	$PdCl_2$	PivOH/2.0 equiv	Ag_2CO_3/0.1 equiv	DMF/80	76
32	$PdCl_2$	PivOH/2.0 equiv	Ag_2CO_3/0.2 equiv	DMF/80	83
33	/	PivOH/2.0 equiv	Ag_2CO_3/0.2 equiv	DMF/80	N.R
34	$PdCl_2$	/	Ag_2CO_3/0.2 equiv	DMF/80	N.R
35	$PdCl_2$	PivOH/2.0 equiv	/	DMF/80	72

[a] All reactions were carried out in the presence of 0.2 mmol of **1** in different solvents under air atmosphere, entry1-22 used 4.0 equiv **2** in 2.0 mL solvent, entry23-35 used 2.5 equiv **2** in 4.0 mL solvent; [b] Isolated yields of products; N.R = no reaction.

Under air atmosphere, (2'-methyl-[1,1'-biphenyl]-2-yl)diphenylphosphine oxide **1a** (57.2mg, 0.2 mmol, 1 equiv), Pd catalyst (0.02 mmol, 10.0 mol%), additive Ⅰ, additive Ⅱ and diphenyliodonium trifluoromethanesulphonate were added to oven-dried reaction tube containing a magnetic stir bar. Solvent was added using a syringe, and then the tube was sealed. The mixture was stirred at 100 or 80℃ in an oil bath for 36h. After cooling to room temperature, the solution was removed by reducing pressure distillation to yield a residue, which was purified by silica gel (eluent CH_2Cl_2/ EtOAc 6:1) to afford **3a**.

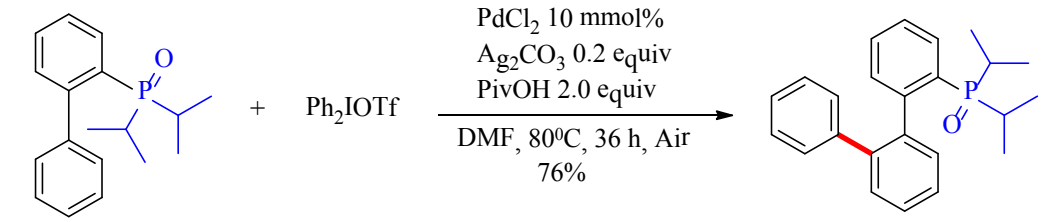
Ⅴ Typical procedure for the reduction of P=O compound



3a **3aa**

At 0℃, $HSiCl_3$(1.0 mmol, 5.0 equiv, 0.1 mL) was carefully added to a mixture of phosphine oxide **3a** (0.2 mmol) and triethylamine (4.8 mmol, 24.0 equiv, 0.21 mL) in toluene (5.0 mL) in a tube under argon atmosphere. The mixture was heated to reflux for 18 h. To the cooled mixture was purified directly by flash column chromatography (SiO_2, EtOAc/Petroleum ether, 1/20) to give the product as colorless oil in yield 55%.

Ⅵ. Large scale reaction under optimized condition

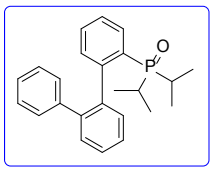


1a 5.0 mmol **2a** 12.5 mmol **3a** 3.8 mmol

Under air atmosphere, (2'-methyl-[1,1'-biphenyl]-2-yl)diphenylphosphine oxide **1a** (1.43 g, 5.0 mmol, 1 equiv), Ph_2IOTf (5.38 g, 12.5 mmol, 2.5 equiv), $PdCl_2$ (88.5 mg, 0.5 mmol, 10.0 mol%), Ag_2CO_3 (276 mg, 1.0 mmol, 0.2 equiv) and PivOH(1.01 g, 10.0 mmol), and were added to oven-dried round flask containing a magnetic stir bar. Solvent was added using a syringe, and then the round flask was sealed. The mixture was stirred at 80℃ in an oil bath for 36h. After cooling to room temperature, the solution was removed by reducing pressure distillation to yield a residue, which was purified by silica gel (eluent CH_2Cl_2/ EtOAc 6:1) to afford **3a** in 76%.

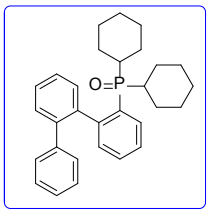
Ⅶ.Characterization of the products

[1,1':2',1''-terphenyl]-2-yldiisopropylphosphine oxide (3a)



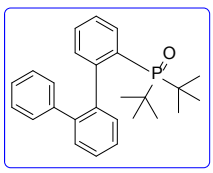
Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.63 (dd, J_1 =7.2 Hz, J_2 =15.3 Hz, 3H), 0.77 (dd, J =7.2 Hz, J_2 =15.4 Hz, 3H), 1.01 (dd ,J_1 =7.1 Hz, J_2 =15.1 Hz, 3H), 1.08 (dd, J_1 =7.0 Hz, J_2 =14.8 Hz, 3H), 1.81-1.96 (m, 2H), 7.05-7.14 (m, 3H), 7.21-7.27 (m, 3H), 7.29-7.36 (m, 3H)，7.38-7.48 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 15.43 (d, J =3.0 Hz), 15.96 (d, J =3.0 Hz), 16.01 (d, J =3.0 Hz), 16.65 (d, J =2.0 Hz), 25.69(d, J =63.0 Hz), 28.31 (d, J =65.0 Hz), 125.78, 126.01, 126.24 (d, J =10.0 Hz), 127.37, 127.68, 129.26(d,J =82 Hz), 129.70, 129.74 (d, J =2.0 Hz), 130.09, 130.28, 131.35 (d, J =9.0 Hz), 133.68 (d, J =9.0 Hz), 139.89 (d, J =2.0 Hz), 140.88, 141.49, 146.45 (d, J =5.0 Hz)； **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 50.83; **MS (ESI):** found $[M+H]^+$ 363.2;

[1,1':2',1''-terphenyl]-2-yldicyclohexylphosphine oxide (3b)



Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.86-1.24 (m, 11H), 1.40-1.73 (m, 11H), 7.08-7.14 (m, 3H), 7.19-7.23 (m, 3H), 7.26-7.34 (m, 3H), 7.36-7.43 (m, 4H);
^{13}C NMR (100 MHz, $CDCl_3$) δ: 24.81, 24.84, 25.19, 25.73, 25.83, 25.86, 26.39, 26.42, 26.55, 26.61, 36.22 (d, J =66.6 Hz), 38.32 (d, J =65.1 Hz), 125.86, 125.92, 126.15 (d, J =10.9 Hz), 127.36, 127.58, 128.91, 129.66, 129.97, 130.41, 1131.05 (d, J =10.2 Hz), 133.66 (d, J =9.2 Hz), 140.03, 140.87, 141.62, 147.03 (d, J =5.1 Hz)； **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 45.78; **MS (ESI):** found $[M+H]^+$443.2;

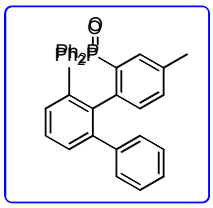
[1,1':2',1''-terphenyl]-2-yldi-tert-butylphosphine oxide (3c)



Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.81 (d, J =13.4 Hz, 9H), 0.77(d, J =13.3 Hz, 9H), 7.01-7.05 (m, 1H), 7.08-7.12 (m, 3H), 7.23-7.27 (m, 3H)，7.28-7.41 (m, 4H),7.48-7.53 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:26.71, 27.88, 36.43 (d, J =58.4 Hz), 36.80 (d, J =58.3Hz), 125.05 (d, J =11.3 Hz), 125.30, 125.72, 127.27, 127.34, 129.03 (d,J =84.4 Hz), 129.37, 129.43, 129.94, 130.75, 131.25 (d, J =11.6

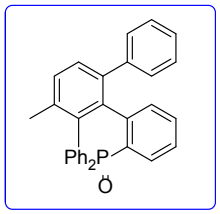
Hz), 134.52 (d, J =9.2 Hz), 140.49 (d, J =2.3 Hz), 141.31, 142.57, 146.45 (d, J =3.7 Hz)； **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 52.63; **MS (ESI):** found $[M+H]^+$391.2;

(4,6'-dimethyl-[1,1':2',1''-terphenyl]-2-yl)diphenylphosphine oxide (3d)



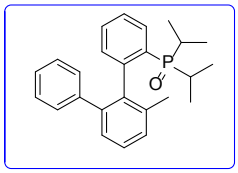
Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.79 (s, 3H), 2.27 (s, 3H), 6.98-7.03 (m, 3H), 7.06-7.10 (m, 4H), 7.15-7.19 (m, 3H), 7.21-7.26 (m, 5H),7.28-7.31 (m, 3H), 7.34-7.42 (m, 3H);**^{13}C NMR** (100 MHz, $CDCl_3$) δ:21.19, 21.9, 125.68, 127.18, 127.36, 127.41, 127.86, 127.98, 128.01, 128.13, 128.43, 129.20, 130.21, 130.24, 131.05, 131.08, 131.10, 131.67, 131.70, 131.73, 131.77, 131.83, 131.86, 132.74, 133.23, 133.45, 133.56, 133.77, 134.26, 134.29, 134.41, 135.74, 135.86, 136.32, 138.61, 138.64, 141.14, 141.98, 142.29, 142.37； **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 28.86; **MS (ESI):** found $[M+H]^+$459.3;

(5',6'-dimethyl-[1,1':2',1''-terphenyl]-2-yl)diphenylphosphine oxide (3e)



Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.58 (s, 3H), 2.15 (s, 3H),7.00-7.06 (m,4 H), 7.07-7.13 (m, 3H), 7.25-7.31 (m, 8H), 7.33-7.45 (m, 6H);**^{13}C NMR** (100 MHz, $CDCl_3$) δ:17.63, 20.36, 125.58, 126.07, 126.20, 126.99, 127.13, 127.18, 127.94, 127.95, 128.07, 129.26, 130.19, 130.31, 130.55, 130.58, 131.09, 131.11, 131.21, 131.72, 131.78, 131.82, 131.87, 132.77, 133.06, 133.60, 133.70, 133.81, 133.95, 134.07, 134.43, 135.10, 138.47, 138.50, 139.16, 142.18, 145.87, 145.95； **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 28.41; **MS (ESI):** found $[M+H]^+$459.3, $[M+Na]^+$481.3;

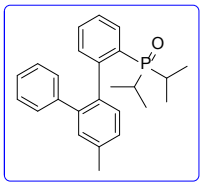
Diisopropyl(6'-methyl-[1,1':2',1''-terphenyl]-2-yl)phosphine oxide (3g)



Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.64 (dd, J_1 =7.3 Hz, J_2 =14.7 Hz, 3H), 0.81 (dd, J_1 =7.6 Hz, J_2 =15.4 Hz, 3H), 0.87 (dd, J_1 =7.1 Hz, J_2 =15.4 Hz, 3H), 1.04 (dd, J_1 =7.0 Hz, J_2 =14.7 Hz, 3H), 1.30-1.41 (m, 1H), 1.97-2.06 (m, 4H), 7.03-7.12 (m, 3H), 7.19-7.24(m, 4H), 7.30-7.37 (m, 3H), 7.45-7.54 (m, 2H); **^{13}C NMR** (100

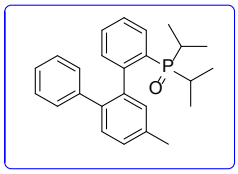
MHz, $CDCl_3$) δ:15.83, 15.85, 16.11 (d, J =3.4 Hz), 16.69 (d, J =3.1 Hz), 21.60，26.84 (d, J =65.6 Hz), 27.16 (d, J =65.2 Hz), 125.86, 126.15 (d, J =10.8 Hz), 127.28, 127.42, 127.62, 128.63, 129.69 (d, J =2.5Hz), 130.56 (d, J =82.5 Hz), 130.65, 131.49 (d, J =10.3 Hz), 134.61 (d, J =9.2 Hz), 136.00, 139.33 (d, J =2.6 Hz), 140.67, 142.29, 145.45 (d, J =5.2 Hz)； **^{31}P NMR** (162 MHz, $CDCl_3$) δ:,49.16; **MS (ESI):** found $[M+H]^+$377.2;

Diisopropyl(4'-methyl-[1,1':2',1''-terphenyl]-2-yl)phosphine oxide (3h)



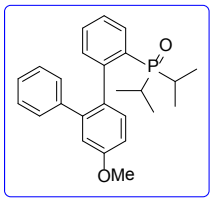
Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.64 (dd, J_1 =7.3 Hz, J_2 =15.2 Hz, 3H), 0.75(dd, J_1 =7.2 Hz, J_2 =16.5 Hz, 3H), 1.02 (dd, J_1=7.1 Hz, J_2 =15.0 Hz, 3H), 1.08(dd, J_1=7.0 Hz, J_2 =14.8 Hz, 3H), 1.82-1.94 (m, 2H), .2.42 (s, 3H), 7.05-7.15 (m, 5H), 7.21-7.26 (m, 3H), 7.29-7.35 (m, 2H), 7.40-7.49 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 15.57 (d, J =3.0 Hz), 15.13 (d, J =3.0 Hz), 16.74 (d, J =2.0 Hz), 21.23, 25.84(d, J =67.0 Hz), 28.39 (d, J =65.0 Hz), 126.02, 126.19 (d, J =10.0 Hz), 126.63, 127.42, 129.61 (d, J =81 Hz),129.77(d, J =2.0 Hz), 130.14, 130.33, 130.65, 131.50 (d, J =9.0 Hz), 133.95 (d, J =10.0 Hz), 137.12, 137.24，140.75, 141.71，146.48； **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 50.64; **MS (ESI):** found $[M+H]^+$377.3;

Diisopropyl(5'-methyl-[1,1':2',1''-terphenyl]-2-yl)phosphine oxide (3i)



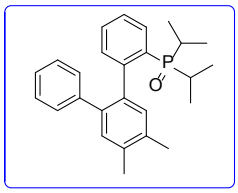
Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.66 (dd, J_1 =7.1 Hz, J_2 =15.3Hz, 3H), 0.72 (dd, J_1 =7.2 Hz, J_2 =15.4 Hz, 3H), 1.02 (dd, J_1 =7.1Hz, J_2 =15.0 Hz, 3H), 1.08 (dd, J_1 =7.0 Hz, J_2 =14.8 Hz, 3H), 1.8-1.89 (m, 2H), 2.38 (s, 3 H), 7.04 (s, 1H), 7.05-7.13 (m, 3H), 7.21-7.25 (m, 3H), 7.30-7.36 (m, 3H), 7.40-7.44(m, 1H), 7.48-7.53 (q, J =8.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 15.59 (d, J =2.9 Hz), 16.09 (d, J =3.3 Hz), 16.17 (d, J =3.5 Hz), 16.70 (d, J =2.5 Hz), 20.93, 25.92 (d, J =66.4 Hz), 28.29 (d, J =65.2 Hz), 125.92, 126.13 (d, J =10.5 Hz), 127.44, 128.52, 129.61 (d, J =81.2 Hz), 129.73, 130.27, 131.06, 131.62, 131.71, 133.55, 133.65, 135.30, 139.75 (d, J =2.4 Hz), 141.45, 146.34 (d, J =5.9 Hz)； **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 50.62; **MS (ESI):** found $[M+H]^+$377.2;

Diisopropyl(4'-methoxy-[1,1':2',1''-terphenyl]-2-yl)phosphine oxide (3j)



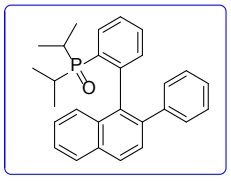
Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.65 (dd, J_1 =7.2 Hz, J_2 =15.3 Hz, 3H), 0.74 (dd, J_1=7.2 Hz, J_2 =15.4 Hz, 3H), 1.02 (dd J_1=7.1 Hz, J_2 =15.0 Hz, 3H), 1.09 (dd, J_1 =6.9 Hz, J_2=14.8 Hz, 3H), 1.82-1.95 (m, 2H), 3.86 (s, 3H), 6.86-6.88 (m, 1H), 6.93 (d, J =4.0 Hz, 1H), 7.07-7.15 (m, 4H), 7.23-7.26 (m, 2H), 7.30-7.34(m, 2H), 7.39-7.41 (d, J =4.0 Hz, 1H), 7.43-7.50 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:15.57 (d, J =3.0 Hz), 16.13 (d, J =3.0 Hz), 16.72 (d, J =2.0 Hz), 25.86 (d, J =66.0 Hz),28.35 (d, J =65.0 Hz), 55.17, 111.56, 115.01, 126.14, 126.24 ,127.49, 129.73 (d, J =82 Hz), 129.81 (d, J =2.0 Hz), 130.25, 131.26, 131.58 (d, J =10.0 Hz), 132.46 (d, J =2.0 Hz), 134.23 (d, J =9.0 Hz), 141.56, 142.17，146.19 (d, J =6.0 Hz), 158.89，; **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 50.98; **MS (ESI):** found $[M+H]^+$393.2;

(4',5'-dimethyl-[1,1':2',1''-terphenyl]-2-yl)diisopropylphosphine oxide (3k)



Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.68 (m, J =7.2 Hz, 6H), 1.02 (dd ,J_1 =7.2 Hz, J_2 =15.0 Hz, 3H), 1.08 (dd ,J_1 =7.2 Hz, J_2 =14.8 Hz, 3H), 1.80-1.87 (m, 2H), 2.29 (s, 3H), 2.33 (s, 3H), 7.00 (s, 1H), 7.04-7.13 (m, 3H), 7.17 (s, 1H), 7.21-7.23 (m, 2H), 7.30-7.35 (m, 2H),7.39-7.43(m, 1H),7.49-7.54 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:15.64 (d, J =2.9 Hz), 16.12 (d, J =3.1 Hz), 16.18 (d, J =3.2 Hz), 16.71 (d, J =2.0 Hz),19.22, 19.52, 25.93 (d, J =66.5 Hz),28.28 (d, J =65.1 Hz), 125.86, 126.10, 126.20, 127.43, 129.71 (d, J =81.7 Hz),129.72(d, J =2.3 Hz), 130.24, 131.23, 131.66, 131.75, 133.82(d, J =9.4 Hz), 134.00, 135.85, 138.28, 141.54, 146.24(d, J =5.9 Hz)； **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 50.72; **MS (ESI):** found $[M+H]^+$413.2;

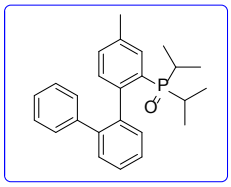
Diisopropyl(2-(2-phenylnaphthalen-1-yl)phenyl)phosphine oxide (3l)



Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.49 (dd ,J_1 =7.3 Hz, J_2 =15.0 Hz, 3H), 0.64 (dd ,J_1 =7.2 Hz, J_2 =15.2 Hz, 3H), 0.81 (dd ,J_1 =7.1Hz, J_2 =15.0 Hz, 3H), 0.87 (dd ,J_1 =7.1Hz, J_2 =15.1 Hz, 3H), 1.53-1.62 (m, 1H), 1.78-1.87 (m, 1H), 7.07-7.11(m, 1H), 7.14-7.17 (m, 2H), 7.22-7.31 (m, 2H), 7.35-7.37 (m, 2H), 7.39-7.51 (m, 3H), 7.54-7.60 (m, 3H), 7.86-7.88 (m, 1H), 7.90-7.92(m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:15.70 (d, J =2.4 Hz), 15.91 (d, J =2.6 Hz), 16.05 (d, J =3.3 Hz), 16.7 (d, J

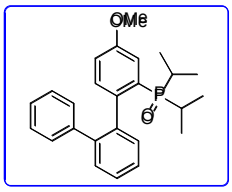
=2.5 Hz), 26.09 (d, J =66.9 Hz), 28.43 (d, J =65.0 Hz), 125.22 (d, J =18.5 Hz), 126.06, 126.56 (d, J =10.6 Hz) 127.15, 127.50, 127.93 (d, J =1.8 Hz),128.44, 129.47 (d, J =2.3 Hz), 131.02, 131.56 (d, J =81.6 Hz), 131.82 (d, J =10.1 Hz), 132.42, 133.17, 135.47(d, J =9.2Hz), 135.98 (d, J =2.5 Hz), 138.16, 142.21, 144.08 (d, J =5.0 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 49.59; **MS (ESI):** found $[M+H]^+$413.2;

Diisopropyl(4-methyl-[1,1':2',1''-terphenyl]-2-yl)phosphine oxide (3m)



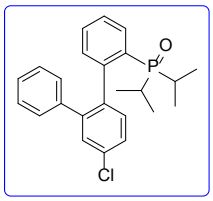
Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.69 (m, 6H), 1.01 (dd, J_1 =7.1 Hz, J_2 =15.2 Hz, 3H), 1.08 (dd, J_1 =7.0 Hz, J_2 =14.7 Hz, 3H), 1.77-1.90 (m, 2H), 2.37 (s, 3H), 7.07-7.16 (m, 3H), 7.20-7.26 (m, 5H), 7.29-7.34 (m, 2H), 7.38-7.43 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:15.65 (d, J =2.9 Hz), 16.13 (d, J =2.9 Hz), 16.32 (d, J =3.3 Hz), 16.73 (d, J =2.5 Hz), 21.19, 26.03 (d, J =66.1 Hz), 28.28 (d, J =65.0 Hz), 125.90, 126.12, 127.51, 127.71, 129.24 (d, J =81.6 Hz),129.93, 130.29, 130.50, 130.68 (d, J =2.5 Hz), 132.10 (d, J =9.2 Hz), 133.63 (d, J =9.7 Hz), 135.97 (d, J =10.6 Hz), 139.96 (d, J =2.3 Hz), 140.97, 141.56, 143.01(d, J =6.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 50.04; **MS (ESI):** found $[M+H]^+$377.2;

Diisopropyl(4-methoxy-[1,1':2',1''-terphenyl]-2-yl)phosphine oxide (3n)



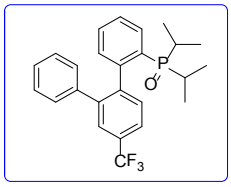
Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.70 (m, 6H), 1.01 (dd ,J_1 =7.1 Hz, J_2 =15.1 Hz, 3H), 1.08 (dd ,J_1 =7.0 Hz, J_2 =14.8 Hz, 3H),1.76-1.87 (m, 2H), 3.84 (s, 3 H), 6.97 (q, 1H), 7.07-7.17 (m, 4H), 7.21-7.28 (m, 4H), 7.29-7.33 (m, 1H), 7.39-7.44(m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:15.69 (d, J =3.0 Hz), 16.13 (d, J =3.0 Hz), 16.37 (d, J =3.4 Hz), 16.7 (d, J =2.5 Hz), 26.10 (d, J =66.1 Hz), 28.22 (d, J =65.0 Hz), 55.33, 115.28 (d, J =2.1 Hz), 117.09 (d, J =10.1 Hz), 126.07 (d, J =20.3 Hz), 127.59, 127.79, 130.01, 130.28, 130.82, 130.85 (d, J =80.5 Hz), 134.87 (d, J =11.0 Hz), 137.86 (d, J =6.2 Hz), 139.62 (d, J =2.1 Hz), 141.23, 141.54, 157.67, 157.80 ; **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 51.33; **MS (ESI)**: found $[M+H]^+$393.1;

(4'-chloro-[1,1':2',1''-terphenyl]-2-yl)diisopropylphosphine oxide (3o)



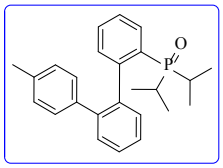
Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.54 (dd, J_1 =7.2, Hz, J_2 =15.4 Hz, 3H), 0.87 (dd, J_1 =7.2 Hz, J_2 =15.4 Hz, 3H), 1.04 (m ,6H), 1.90-2.01 (m, 2H), 7.08-7.16 (m, 4H), 7.21 (d, J =6.8 Hz, 2H), 7.26-7.36 (m, 5H), 7.42-7.46 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:15.21 (d, J =2.6 Hz), 15.57 (d, J =3.4 Hz), 15.94 (d, J =2.9 Hz), 16.71 (d, J =1.8 Hz), 25.36 (d, J =66.9 Hz), 28.47 (d, J =65.1 Hz), 125.71, 126.42, 126.53, 127.45, 128.59, 129.41, 129.96 (d, J =2.5 Hz), 130.28, 130.83 (d, J =10.5 Hz), 131.14, 133.16, 133.76 (d, J =9.2 Hz), 138.59 (d, J =2.7 Hz), 140.56, 142.83, 146.28 (d, J =4.6 Hz)； **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 50.51; **MS (ESI)**: found $[M+H]^+$397.4, $[M+Na]^+$419.4;

Diisopropyl(4'-(trifluoromethyl)-[1,1':2',1''-terphenyl]-2-yl)phosphine oxide (3p)



Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.52 (dd, J_1 =7.2 Hz, J_2 =15.2 Hz, 3H), 0.92 (dd, J =7.2 Hz, J_2 =15.5Hz, 3H), 1.02 (dd ,J =7.1 Hz, J_2 =15.0 Hz, 3H), 1.06 (dd ,J =7.0 Hz, J_2 =14.9 Hz, 3H), 1.94-2.05 (m, 2H), 7.08-7.15 (m, 3H), 7.20-7.28 (m, 3H), 7.31-7.37 (m, 3H), 7.44-7.48 (t, J =8.0 Hz ,1H), 7.54-7.56 (d, J =4.0 Hz ,1H), 7.60 (s, 1H),7.43-7.50 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 15.11 (d, J =2.4 Hz), 15.4(d, J =3.2 Hz), 15.89 (d, J =2.9 Hz), 16.72 (d, J =1.5 Hz), 25.24 (d, J =66.9 Hz),28.2(d, J =65.2 Hz), 120.25, 122.35, 122.39, 122.42, 122.46, 122.95, 125.66, 126.26, 126.30, 126.53, 126.62, 126.73, 127.50, 127.69, 128.37, 129.05, 129.11, 129.37, 129.69, 129.79, 130.04, 130.07, 130.28, 130.40, 130.59, 130.69, 133.50, 133.59, 140.66, 141.98, 143.92, 146.45, 146.49； **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 50.49;**^{19}F NMR**(376 MHz, $CDCl_3$) δ:-62.20; **MS (ESI):** found $[M+H]^+$453.1;

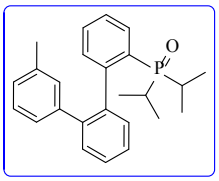
Diisopropyl(4''-methyl-[1,1':2',1''-terphenyl]-2-yl)phosphine oxide (3q)



Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.65-0.76 (m, 6H), 0.99-1.11 (m, 6H)，1.80-1.91 (m, 2H), 2.23 (s, 3H), 6.94 (d, J =7.9 Hz, 2H), 7.11 (d, J =8.1 Hz, 2H), 7.20-7.22 (m, 1H), 7.28-7.36 (m, 3H), 7.38-7.45 (m, 3H), 7.50-7.55(m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:15.63 (d, J =2.9 Hz), 16.12 (d, J =3.1 Hz), 16.19, 16.72 (d, J =2.4 Hz),21.88, 26.00 (d, J =66.4 Hz),28.28 (d, J =65.1 Hz), 125.68, 126.31 (d,

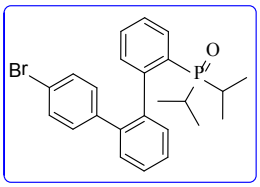
J =10.7 Hz),127.82, 128.21,129.56 (d, *J*=81.3 Hz), 129.80 (d, *J*=2.4 Hz), 129.84, 130.16, 130.23, 131.72 (d,*J*=9.3 Hz), 133.72 (d,*J*=9.4 Hz), 135.75, 138.52, 139.89, 140.48, 146.27 (d, *J* =5.9 Hz)； **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 50.86; **MS (ESI):** found $[M+H]^+$377.2;

Diisopropyl(3''-methyl-[1,1':2',1''-terphenyl]-2-yl)phosphine oxide (3r)



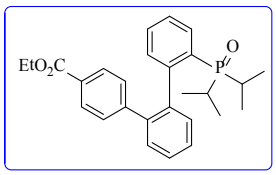
Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.67 (dd, J_1 =7.2 Hz, J_2 =15.3 Hz, 3H), 0.75 (dd, J_1 =7.2 Hz, J_2 =15.4 Hz, 3H), 1.02 (dd, J_1 =7.1 Hz, J_2 =15.0 Hz, 3H), 1.09 (dd, J_1 =7.0 Hz, J_2 =14.8 Hz, 3H)，1.81-1.90 (m, 2H), 2.19 (s, 3H), 6.89-6.91 (m, 1H), 6.98-7.01 (m, 2H), 7.08 (s, 1H), 7.21-7.23 (m, 1H), 7.29-7.36 (m, 3H), 7.38-7.44 (m, 3H), 7.417-7.52(m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:15.64 (d, *J* =2.8 Hz), 16.12 (d, *J* =3.0 Hz), 16.20 (d, *J* =3.3 Hz), 16.73 (d, *J* =2.4 Hz), 21.17, 25.96 (d, *J* =66.0 Hz),28.34 (d, *J* =65.2 Hz), 125.78, 126.28 (d, *J* =10.7 Hz), 126.84, 127.26, 127.36, 127.76, 129.50 (d, *J* =81.7 Hz), 129.69 (d, *J* =2.4 Hz), 129.79, 130.16, 131.19, 131.58 (d, *J* =9.3 Hz), 133.77 (d, *J* =9.3 Hz), 136.96, 139.91 (d, *J* =2.2 Hz), 140.98, 141.37, 146.34 (d, *J* =5.6 Hz),； **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 50.79; **MS (ESI):** found $[M+H]^+$377.3;

(4''-bromo-[1,1':2',1''-terphenyl]-2-yl)diisopropylphosphine oxide (3s)



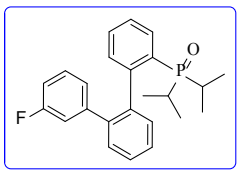
Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.60 (dd, J_1 =7.2 Hz, J_2 =15.2 Hz, 3H), 0.87 (dd, J_1 =7.2 Hz, J_2 =15.5 Hz, 3H), 0.99 (dd, J_1 =7.1 Hz, J_2 =15.1 Hz, 3H), 1.09 (dd, J_1 =7.0 Hz, J_2 =14.8 Hz, 3H), 1.90-1.98 (m, 1H), 1.99-2.09 (m, 1H), 7.11 (d, *J* =8.5Hz 2H), 7.20-7.26 (m, 3H), 7.31-7.37 (m, 5H), 7.38-7.46 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 15.24 (d, *J* =2.5 Hz), 15.57 (d, *J* =3.2 Hz), 15.98 (d, *J* =2.9 Hz), 16.75 (d, *J* =1.6 Hz), 25.29 (d, *J* =66.8 Hz), 28.58 (d, *J* =65.1 Hz), 120.29, 126.17, 126.39 (d, *J* =10.7 Hz), 127.76, 128.49, 129.29, 130.03 (d, *J* =2.5 Hz), 130.08, 131.05 (d, *J* =10.3 Hz), 132.17, 132.07, 133.69 (d, *J* =9.1 Hz), 139.97 (d, *J* =2.8 Hz), 140.03, 140.81, 146.98 (d, *J* =5.0 Hz)； **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 50.69; **MS (ESI):** found $[M+H]^+$441.3;

Ethyl 2''-(diisopropylphosphoryl)-[1,1':2',1''-terphenyl]-4-carboxylate (3t)



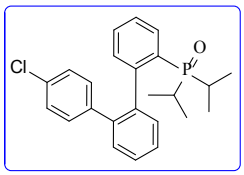
Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.57 (dd, J_1 =7.2 Hz, J_2 =15.2 Hz, 3H), 0.87 (dd, J_1 =7.2 Hz, J_2 =15.7 Hz, 3H), 1.01 (dd, J_1 =7.1 Hz, J_2 =15.1 Hz, 3H), 1.08 (dd, J_1 =7.0 Hz, J_2 =14.8 Hz, 3H), 1.35 (t, J =7.1 Hz, 3H),1.91-2.07 (m, 2H), 4.31 (q, J =7.1 Hz, 2H), 7.23 (d, J =7.5 Hz, 1H), 7.31-7.38(m, 7H), 7.40-7.44 (m, 2H), 7.80 (d, J =8.3 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:14.25, 15.24 (d, J =2.5 Hz), 15.63 (d, J =3.3 Hz), 15.97 (d, J =2.9 Hz), 16.74 (d, J =1.7 Hz), 25.33 (d, J =66.9 Hz), 28.58 (d, J =65.2 Hz), 60.73, 126.40 (d, J =10.8 Hz), 126.41, 127.73, 127.92, 128.61, 129.37, 129.99 (d, J =2.2 Hz), 130.15, 130.43, 131.13 (d, J =10.1 Hz), 133.68 (d, J =9.2 Hz), 140.02 (d,J =2.4 Hz), 140.25, 146.61, 146.88 (d, J =4.9 Hz), 166.63； **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 50.67; **MS (ESI):** found $[M+H]^+$435.5;

(3''-fluoro-[1,1':2',1''-terphenyl]-2-yl)diisopropylphosphine oxide (3u)



Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.64 (dd, J_1 =7.2 Hz, J_2 =15.2 Hz, 3H), 0.87 (dd, J_1 =7.2 Hz, J_2 =15.4 Hz, 3H), 1.02 (dd, J_1 =7.1 Hz, J_2 =15.1 Hz, 3H), 1.10 (dd, J_1 =7.0 Hz, J_2 =14.8 Hz, 3H)， 1.88-2.08 (m, 2H), 6.75-6.80 (m, 1H),6.97-7.10(m, 3H), 7.22 (d, J =7.6Hz 1H), 7.32-7.46 (m, 7H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:15.32 (d, J =2.7 Hz), 15.73 (d, J =3.4 Hz), 16.02 (d, J =2.9 Hz), 16.75 (d, J =2.0 Hz), 25.40 (d, J =66.8 Hz), 28.61 (d, J =65.2 Hz), 112.81 (d, J =21.0 Hz), 117.42 (d, J =21.8 Hz), 126.16 (d, J =2.7 Hz), 126.25, 126.41 (d, J =12.6 Hz), 127.71, 128.65 (d, J =8.4 Hz), 129.07(d, J =81.1 Hz), 129.41, 129.97 (d, J =2.3 Hz), 130.08, 131.09 (d, J =10.8 Hz), 133.63 (d, J =9.2 Hz), 139.96, 140.06 (d, J =2.5 Hz), 144.09 (d, J =8.0 Hz), 146.82 (d, J =5.1 Hz), 162.14 (d, J =242.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 50.54; **^{19}F NMR** (376 MHz, $CDCl_3$) δ:(t, -114.86); **MS (ESI):** found $[M+H]^+$381.3;

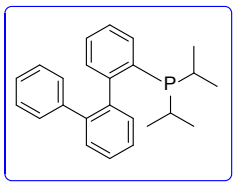
(4''-chloro-[1,1':2',1''-terphenyl]-2-yl)diisopropylphosphine oxide (3v)



Yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.61 (dd, J_1 =7.2 Hz, J_2 =15.2 Hz, 3H), 0.87 (dd, J_1 =7.2 Hz, J_2 =15.4 Hz, 3H), 1.00 (dd, J_1 =7.1 Hz, J_2 =15.1 Hz, 3H), 1.09 (dd, J_1 =7.0 Hz, J_2 =14.8 Hz, 3H), 1.89-1.98 (m, 1H), 1.99-2.08 (m, 1H), 7.09 (d, J

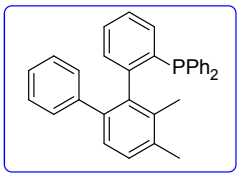
=8.5Hz, 2H), 7.17 (d, *J* =8.5Hz, 2H), 7.20-7.22 (m, 1H), 7.31-7.35 (m, 5H), 7.37-7.46 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:15.27 (d, *J* =2.7 Hz), 15.62 (d, *J* =3.4 Hz), 16.00 (d, *J* =2.9 Hz), 16.76 (d, *J* =1.8 Hz), 25.33 (d, *J* =66.9 Hz), 28.60 (d, *J* =65.1 Hz), 126.13, 126.36 (d, *J* =10.8 Hz), 127.47, 127.74, 128.99 (d, *J* =81.4 Hz), 129.35, 130.00 (d, *J* =2.5 Hz), 130.07, 131.07 (d, *J* =10.2 Hz), 131.79, 132.07, 133.67 (d, *J* =9.0 Hz), 140.03, 140.35, 146.99 (d, *J* =5.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ: 50.56; **MS (ESI):** found $[M+Na]^+$419.1;

[1,1':2',1''-terphenyl]-2-yldiisopropylphosphine (3aa)



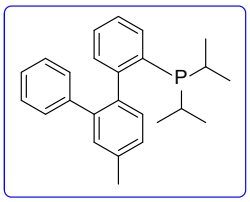
White oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.18 (dd, J_1 =7.0 Hz, J_2 =13.7 Hz, 3H), 0.82 (m, 6H), 0.95 (dd, J_1 =6.8 Hz, J_2 =14.9 Hz, 3H),1.71-1.73 (m, 1H), 1.88-1.96 (m, 1H), 7.04-7.16 (m, 5H), 7.22-7.28 (m, 2H), 7.32-7.44 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:18.49 (d, *J* =5.1 Hz), 18.90 (d, *J* =15.1 Hz), 19.80 (d, *J* =22.2Hz), 20.48 (d, *J* =14.9 Hz), 22.37 (d, *J* =12.3 Hz),26.22 (d, *J* =15.4 Hz), 126.10, 126.17, 126.38, 127.58, 127.63, 127.98, 129.86, 130.30, 131.48 (d, *J* =5.8 Hz), 132.07 (d, *J* =1.3 Hz), 132.46 (d, *J* =3.2 Hz), 134.58 (d, *J* =21.8 Hz), 140.94 (d, *J* =2.7 Hz), 141.77, 149.20, 149.49; **^{31}P NMR** (162 MHz, $CDCl_3$) δ: -4.36;

(5',6'-dimethyl-[1,1':2',1''-terphenyl]-2-yl)diphenylphosphine (3ee)



White oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 1.46 (s, 3H), 2.22 (s, 3H), 6.60-6.64 (m, 2H), 6.97-7.00 (m, 1H), 7.06-7.17 (m, 12H), 7.19-7.25 (m, 4H), 7.29-7.30 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:17.05, 120.55, 125.73, 126.94, 127.04, 127.12, 127.35, 127.90, 127.95, 128.03, 128.11, 128.56, 129.10, 130.36, 130.38, 131.58, 131.64, 132.36, 132.54, 134.11, 134.13, 134.45, 134.67, 135.53, 135.55, 135.61, 136.65, 136.79, 137.19, 137.31, 138.12, 138.25, 139.39, 139.46, 142.28, 146.75, 147.08; **^{31}P NMR** (162 MHz, $CDCl_3$) δ: -14.76;

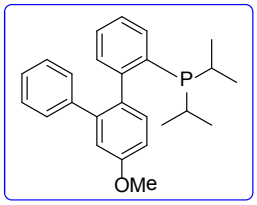
Diisopropyl(4'-methyl-[1,1':2',1''-terphenyl]-2-yl)phosphine(3hh)



White oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.17 (dd, J_1 =7.0 Hz, J_2 =14.7 Hz 3H),

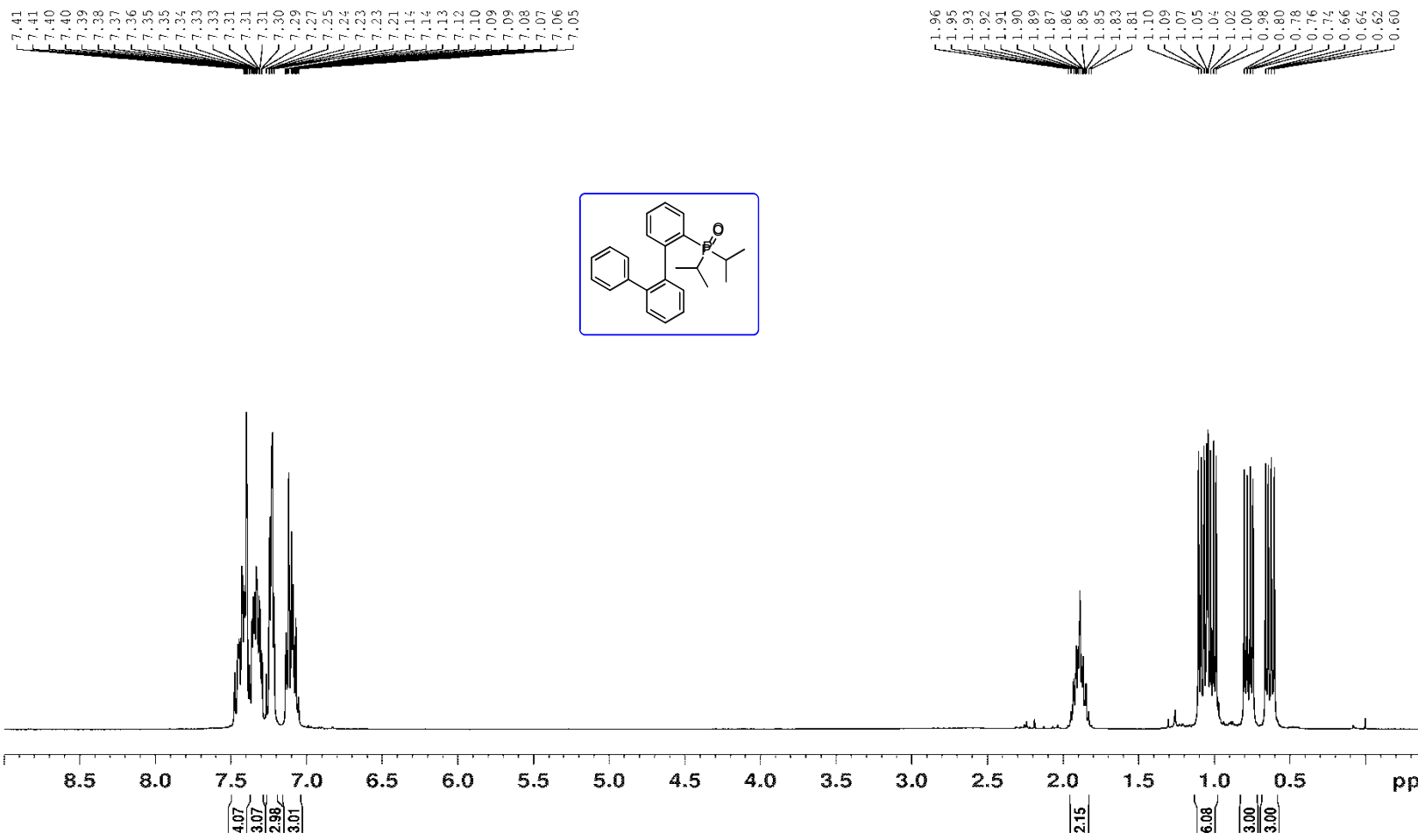
0.79-0.86 (m, 6H), 0.95 (dd, J_1 =6.8 Hz, J_2 =15.0 Hz 3H), 1.72-1.76 (m, 1H), 1.89-1.97 (m, 1H), 2.43 (s, 3H), 7.05-7.17 (m, 7H), 7.22 (s, 1H), 7.25-7.27 (m, 1H), 7.32-7.33 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ:18.29 (d, J =2.1 Hz), 18.81 (d, J =15.1 Hz), 19.77 (d, J =22.1Hz), 20.52 (d, J =14.8 Hz), 21.31, 22.35 (d, J =11.7 Hz), 26.12 (d, J =15.5 Hz), 126.02, 126.23, 126.38, 127.02, 127.55, 127.97, 130.21, 130.72, 131.60 (d, J =5.6 Hz), 131.96, 132.45, 134.49 (d, J =20.3 Hz), 137.16, 138.17, 140.66, 141.89, 149.41 (d, J =29.9 Hz)； **^{31}P NMR** (162 MHz, $CDCl_3$) δ: -4.85;

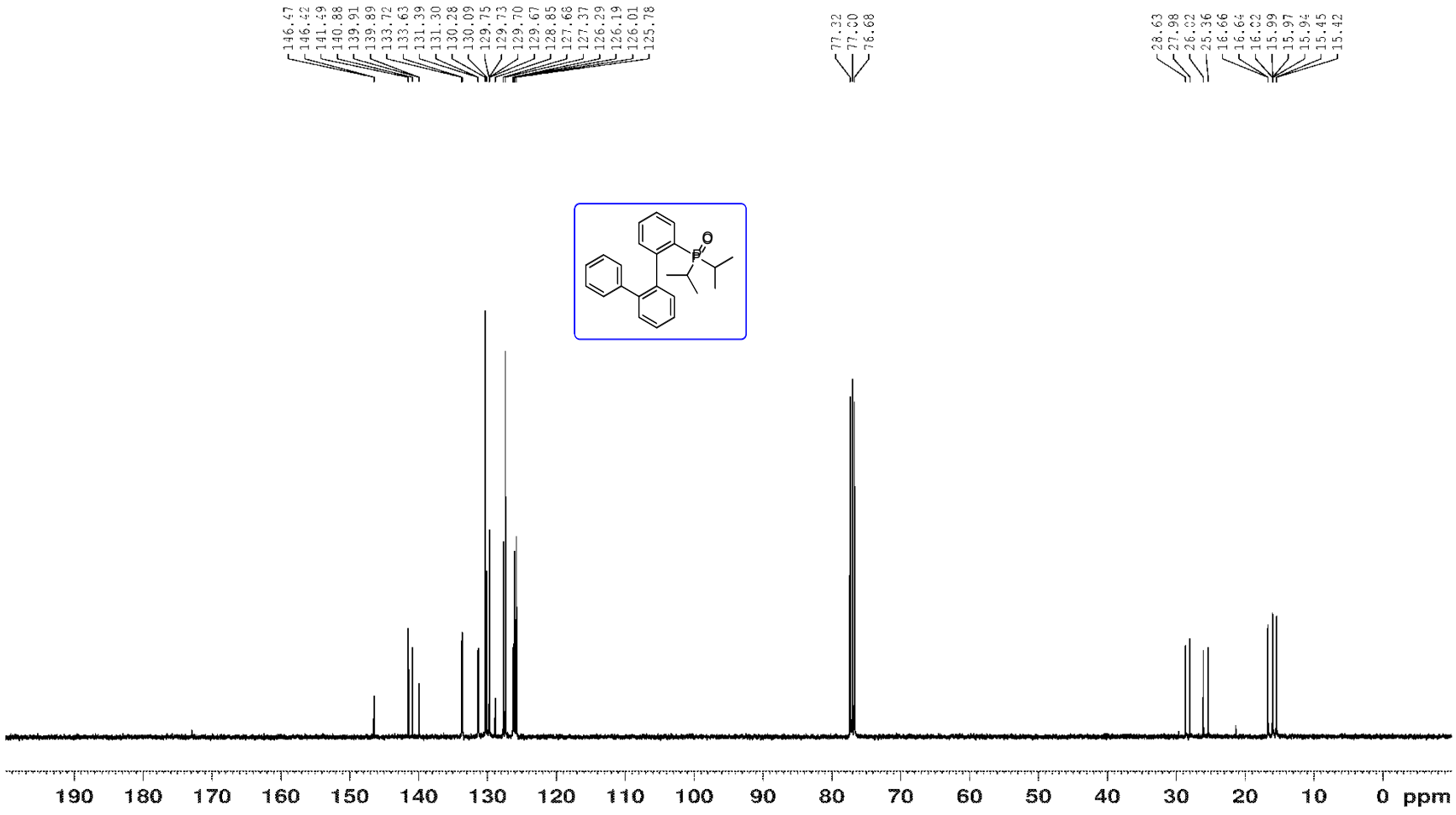
Diisopropyl(4'-methoxy-[1,1':2',1''-terphenyl]-2-yl)phosphine(3jj)



White oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.19 (dd, J_1 =7.0 Hz, J_2 =13.8 Hz 3H), 0.80-0.87 (m, 6H), 0.97 (dd, J_1 =6.2 Hz, J_2 =14.5 Hz 3H), 1.74 (m, 1H), 1.93 (m, 1H), 3.87 (s, 3H), 6.88-6.91 (m, 1H), 6.94-6.95 (m, 1H), 7.07-7.17 (m, 6H), 7.26-7.32 (br, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 18.29, 18.93, 19.65, 19.89, 20.43, 55.18, 111.87, 114.97, 126.25, 127.61, 127.98, 130.17, 131.86, 132.48, 133.06, 141.71, 141.96, 148.87, 149.18, 158.80； **^{31}P NMR** (162 MHz, $CDCl_3$) δ: -4.65;

Ⅷ. NMR charts

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129.70
129.67
128.85
127.68
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126.29
126.19
126.01
125.78
77.32
77.00
76.68
28.63
27.98
26.02
25.36
16.66
16.64
16.62
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15.94
15.45
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P
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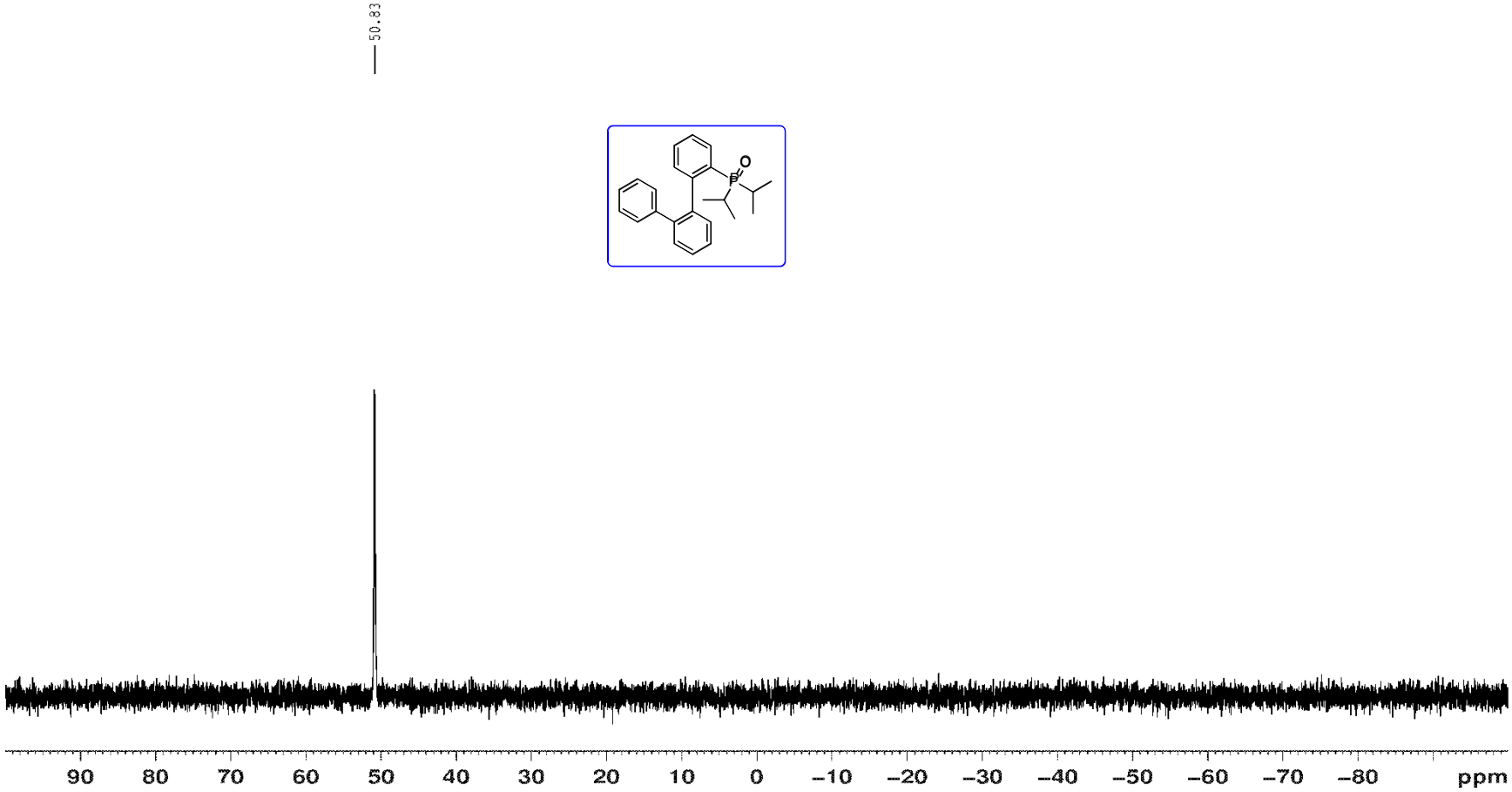

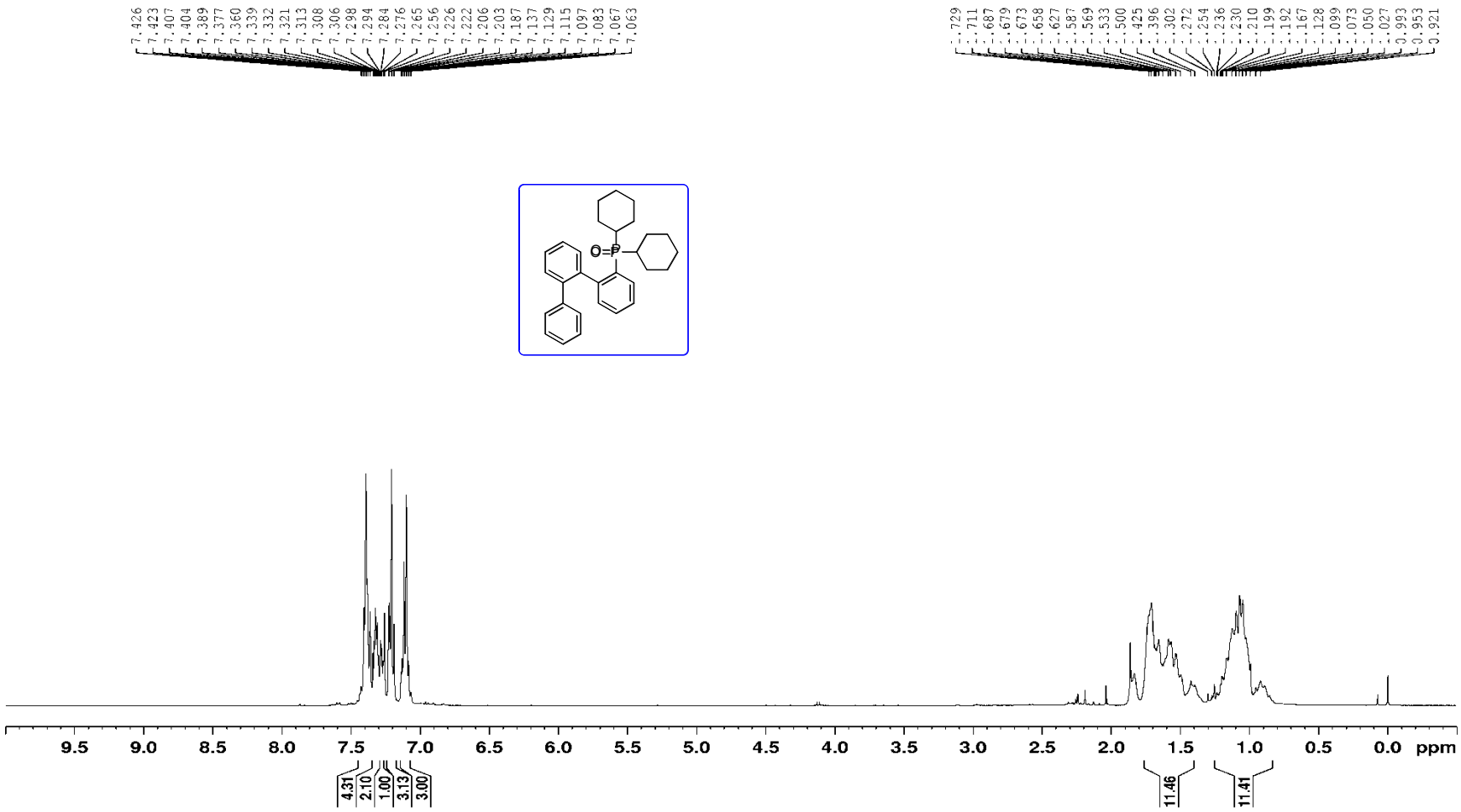

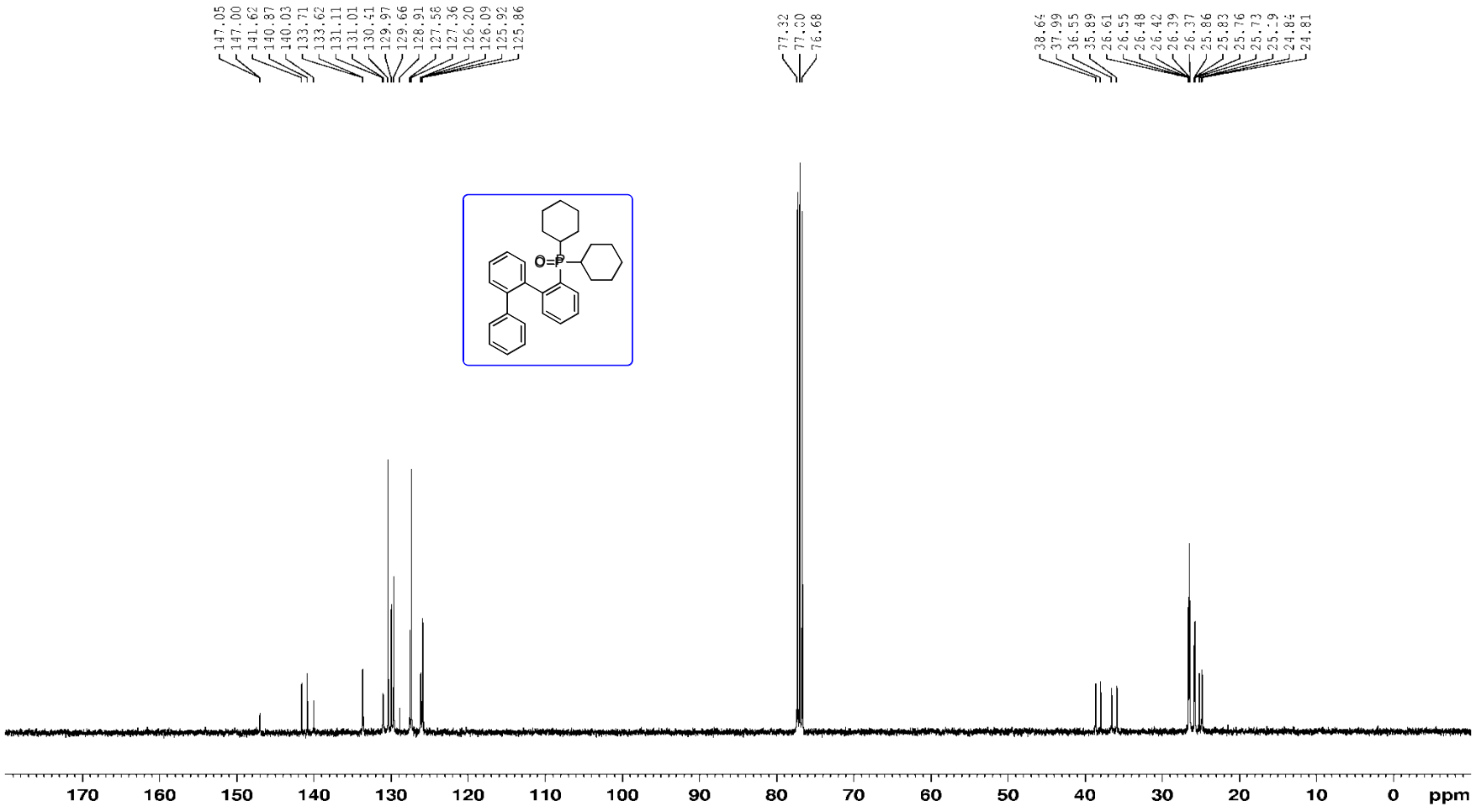

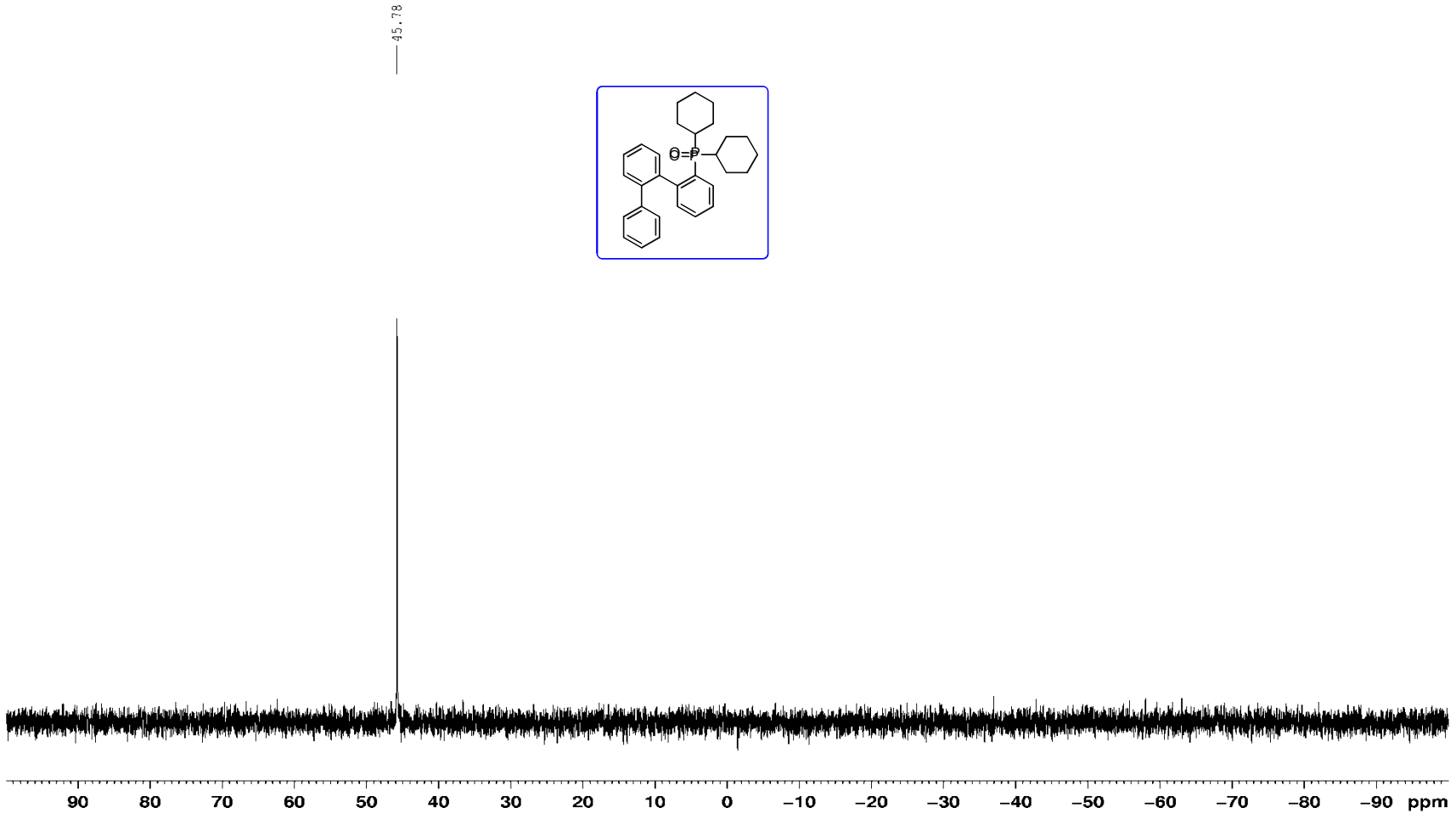

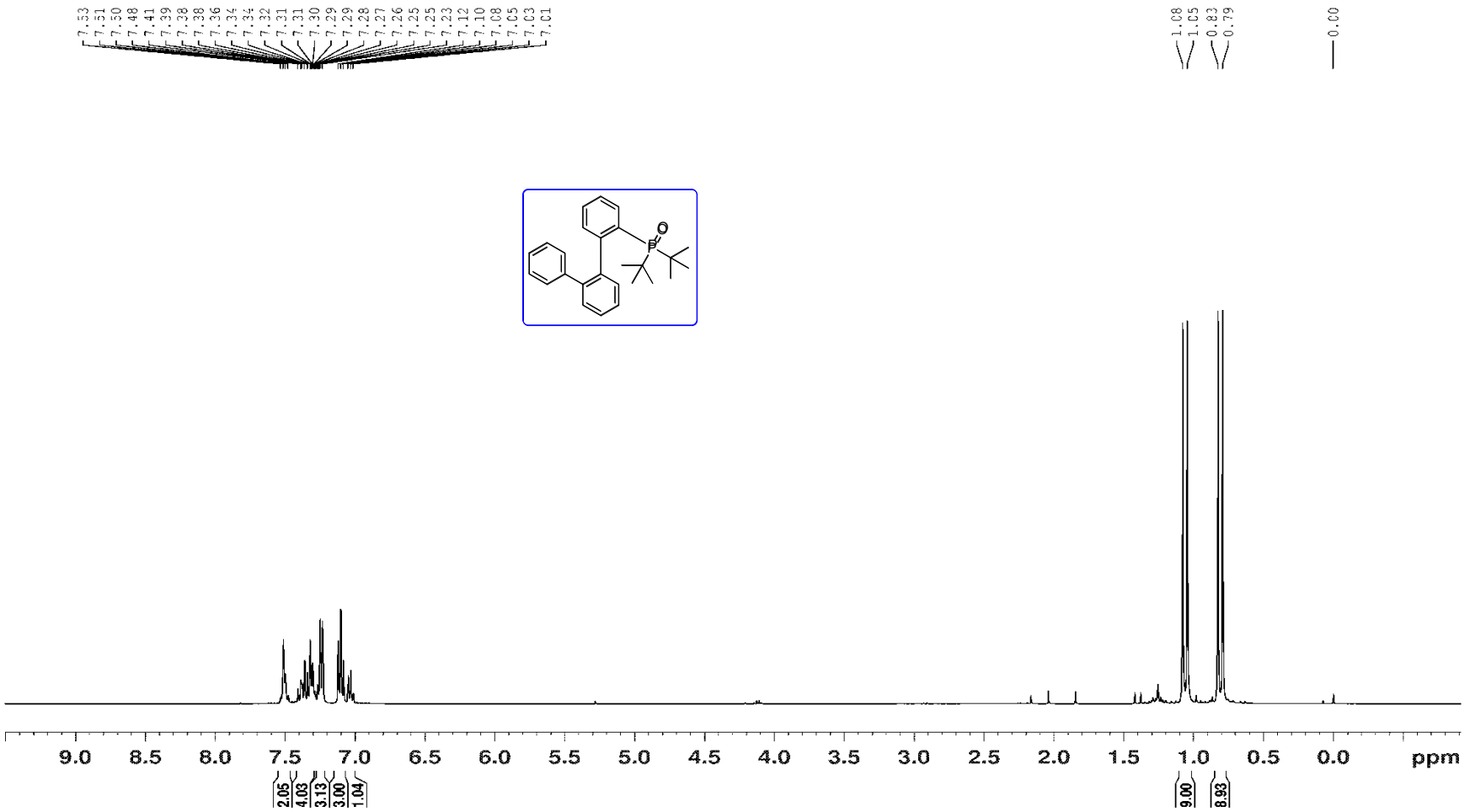

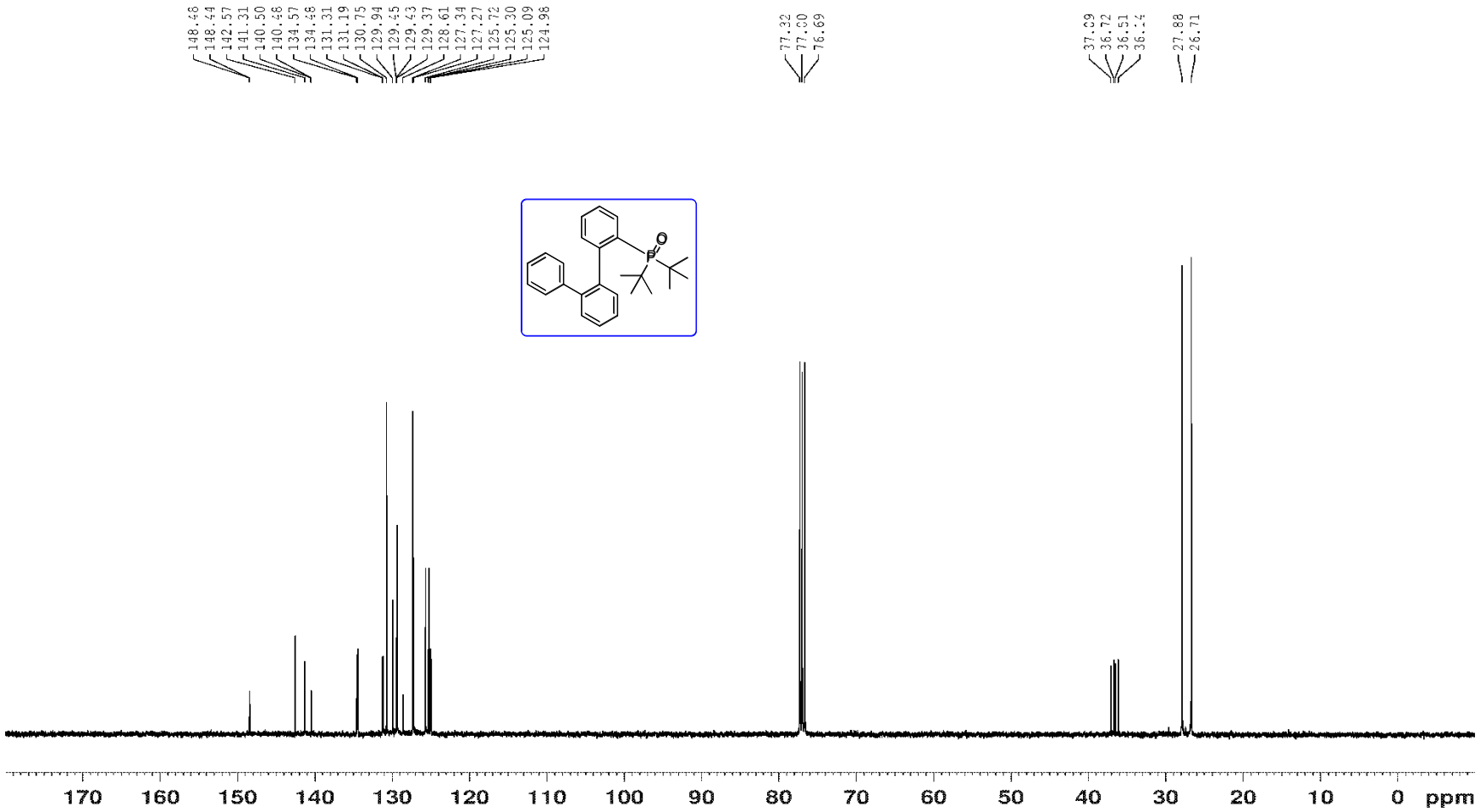

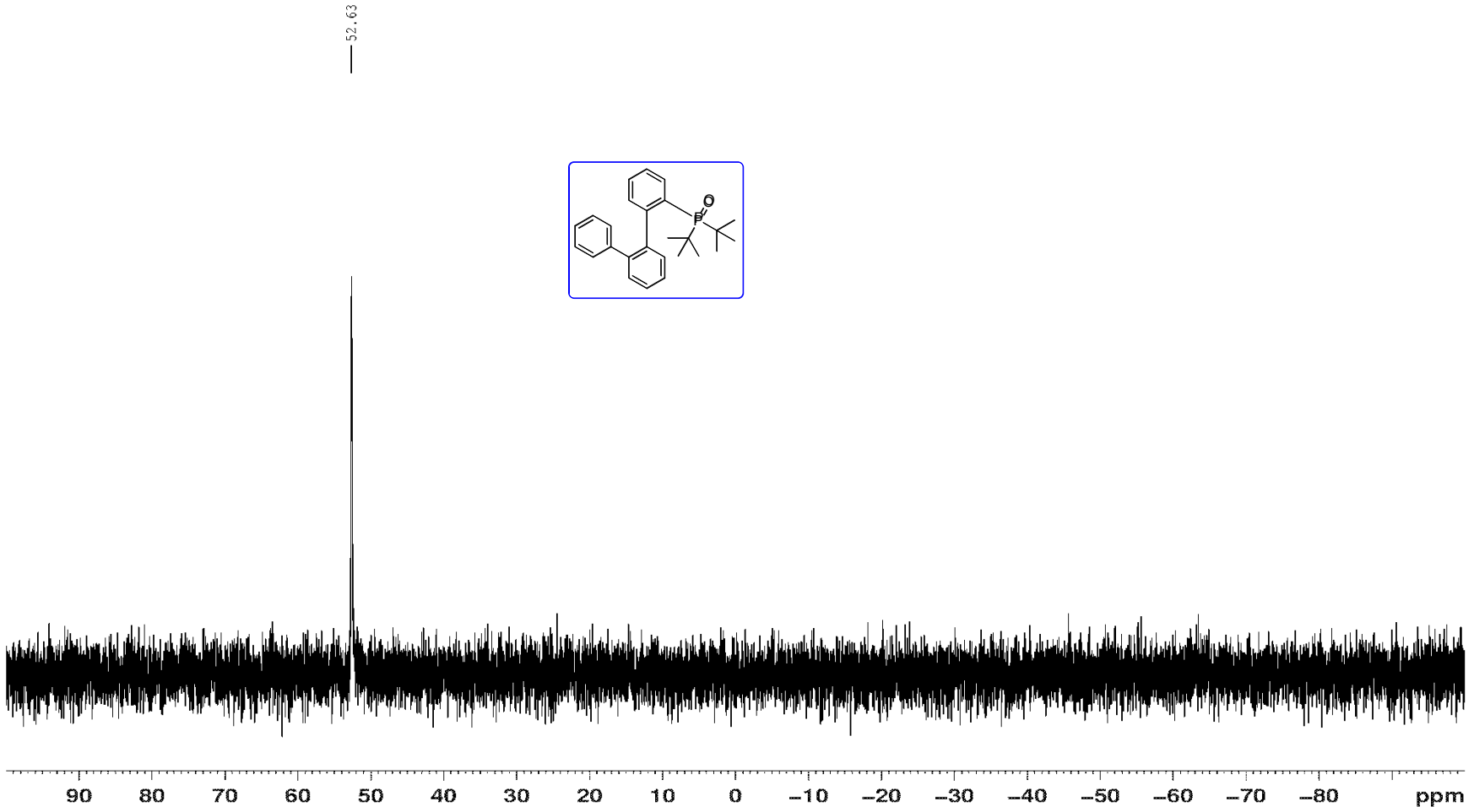

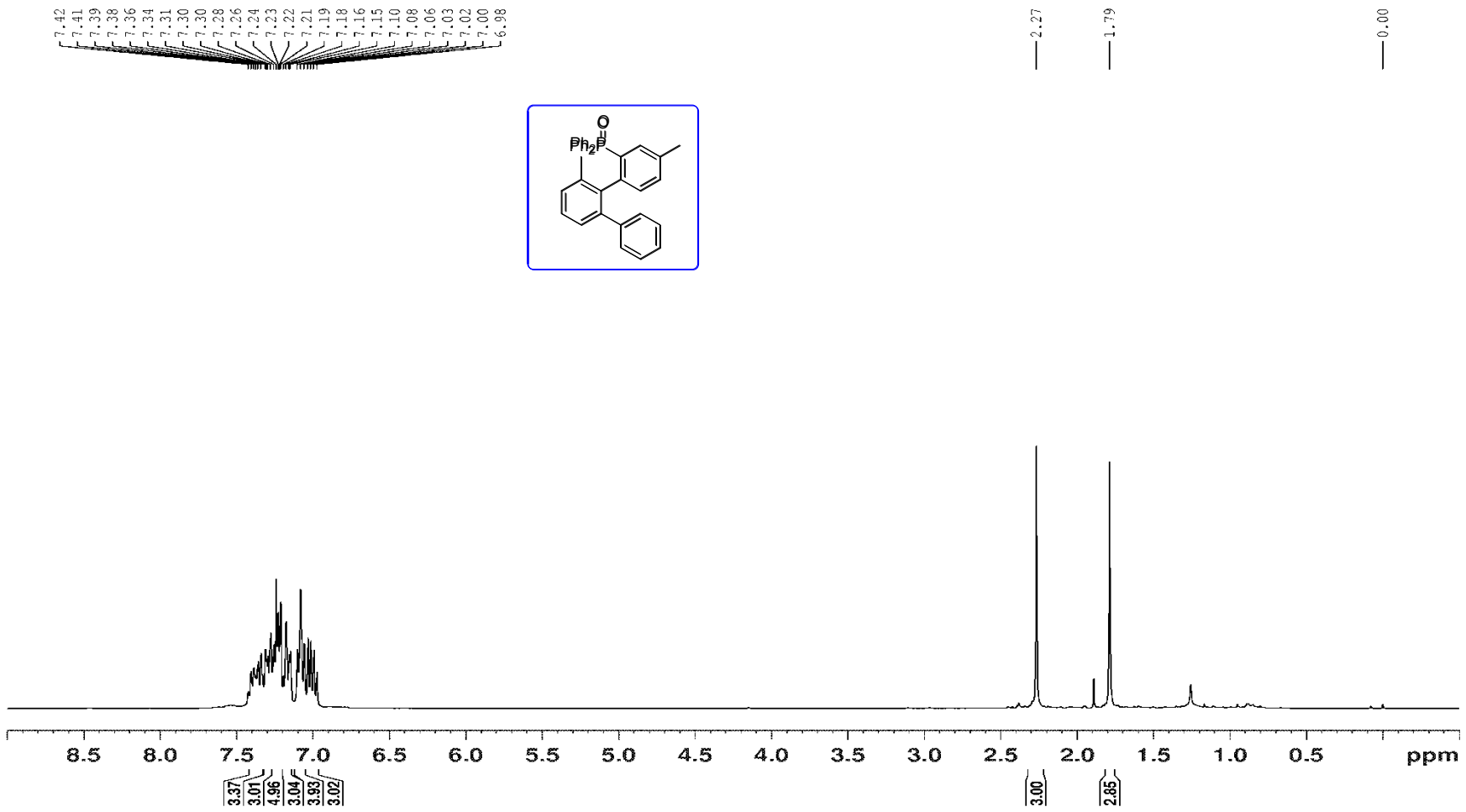

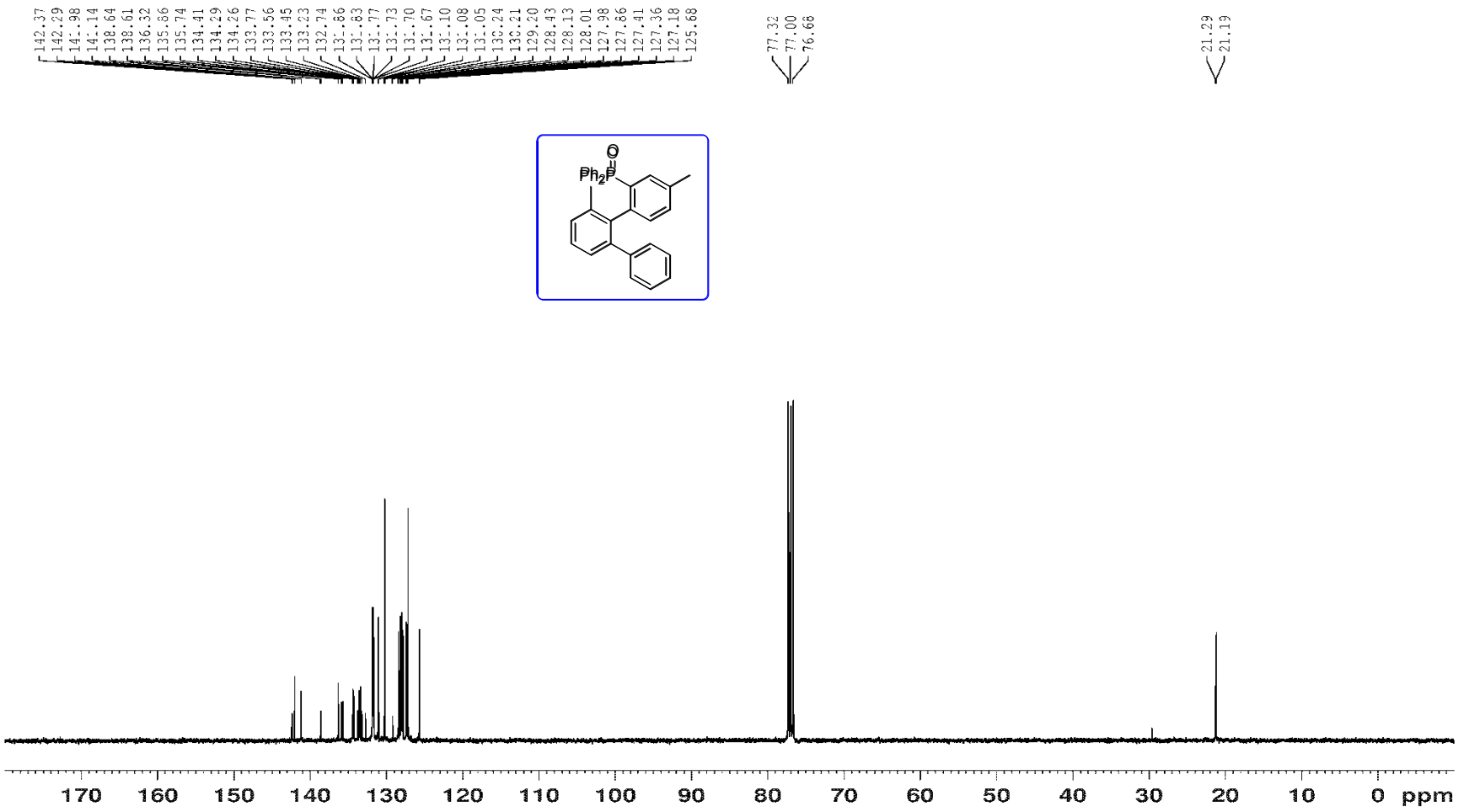
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131.83
131.77
131.73
131.70
131.67
131.10
131.08
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130.24
130.21
129.20
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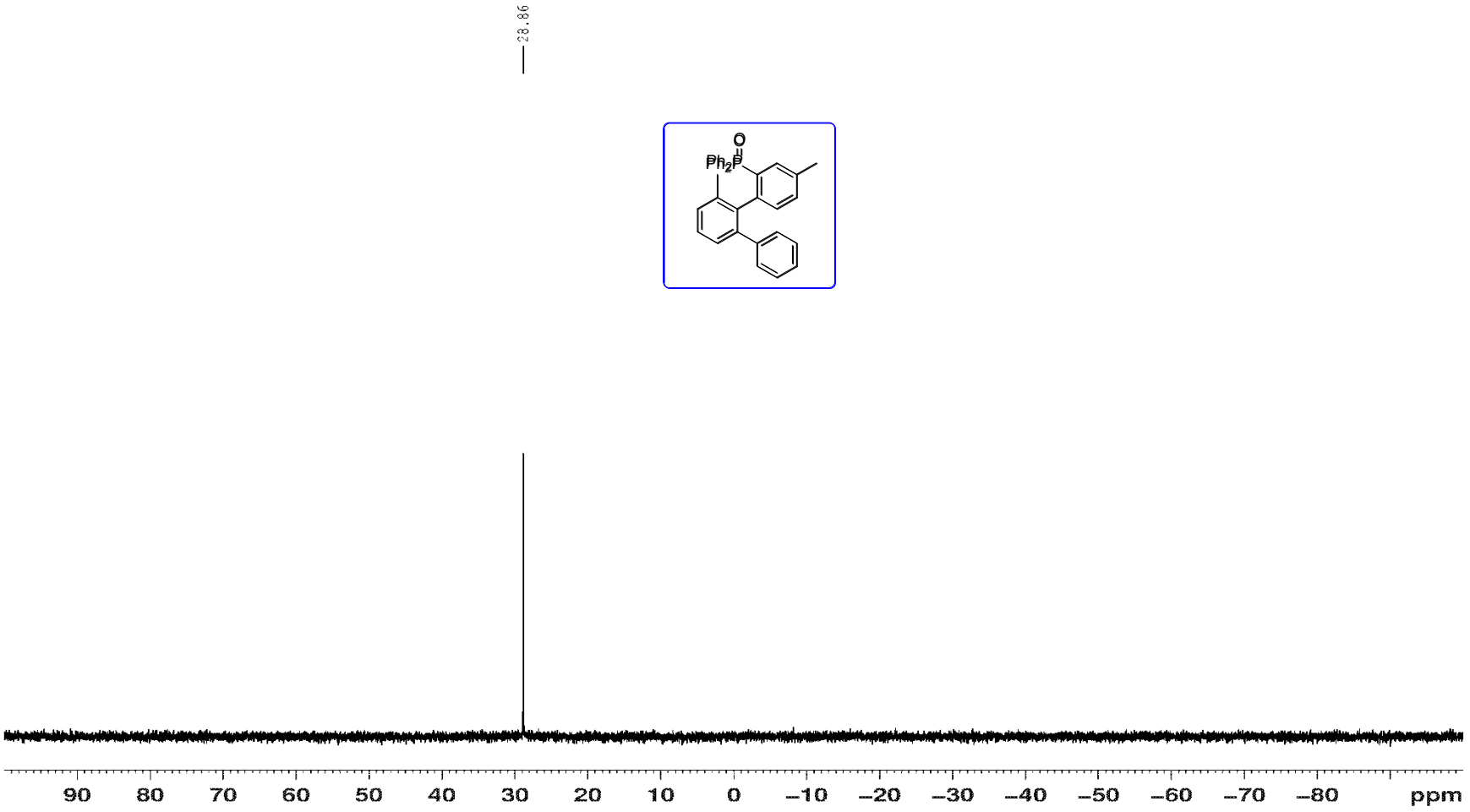

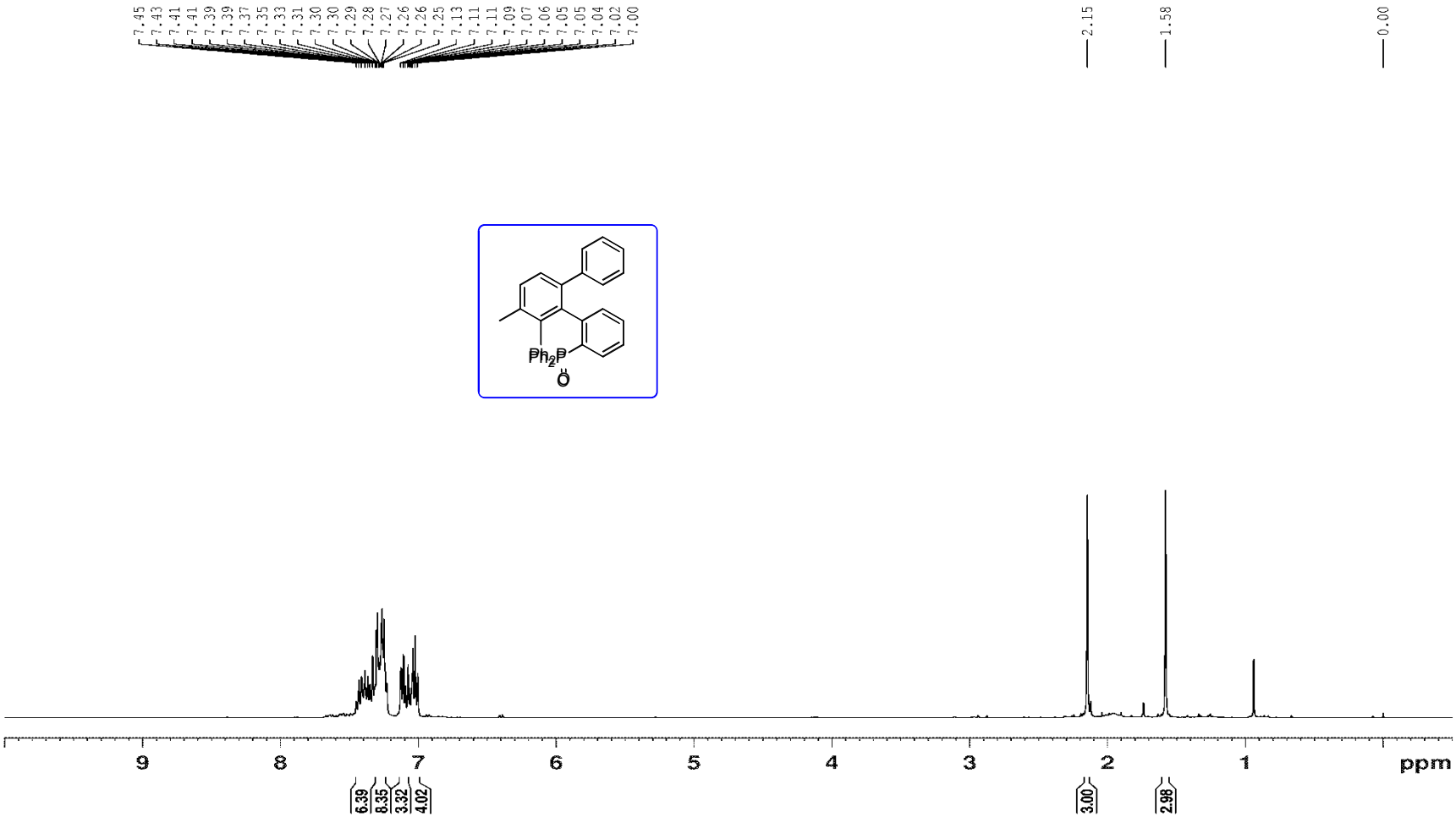

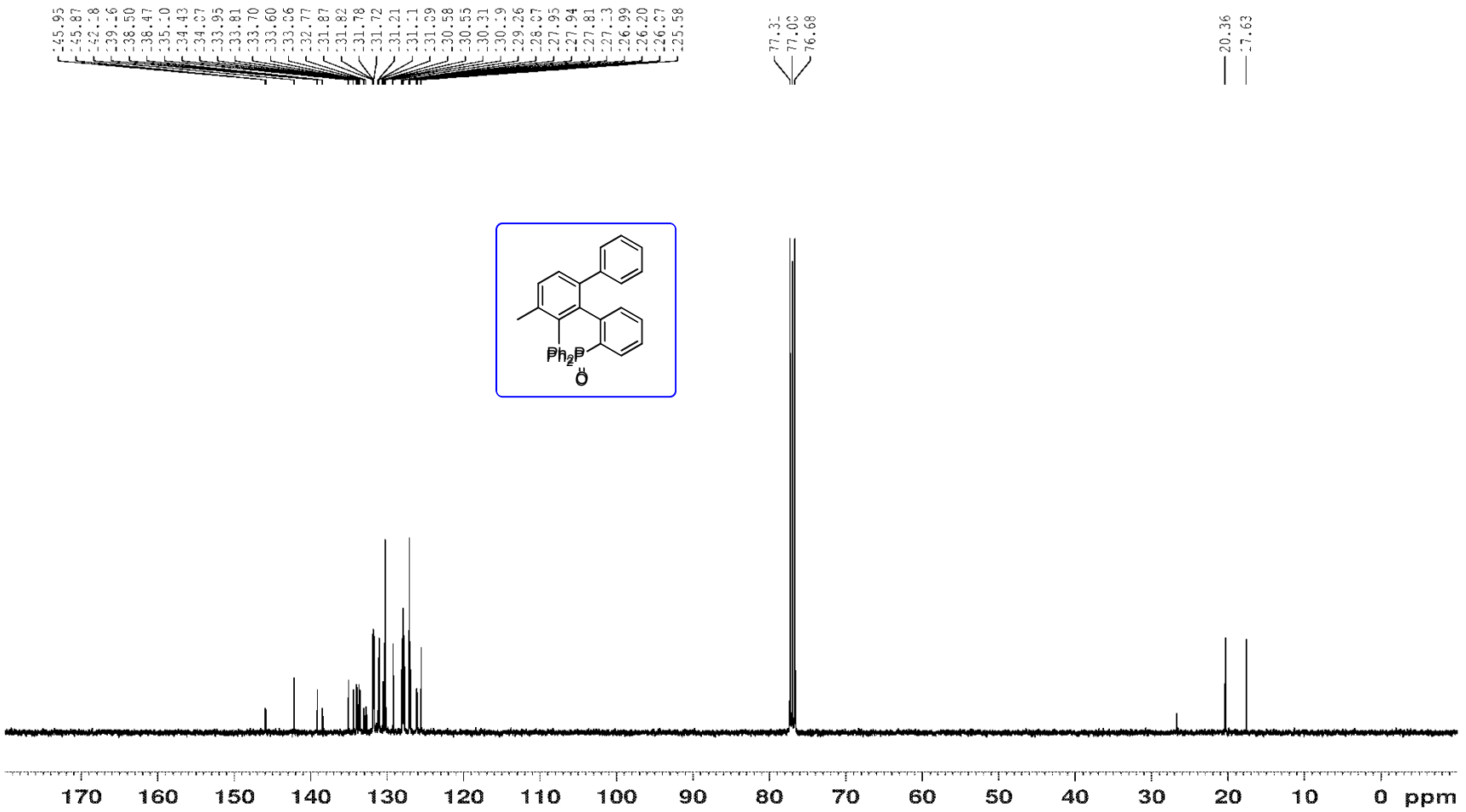
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131.87
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130.19
129.26
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127.95
127.94
127.81
127.13
126.99
126.20
126.07
125.58
77.31
77.00
76.68
20.36
17.63
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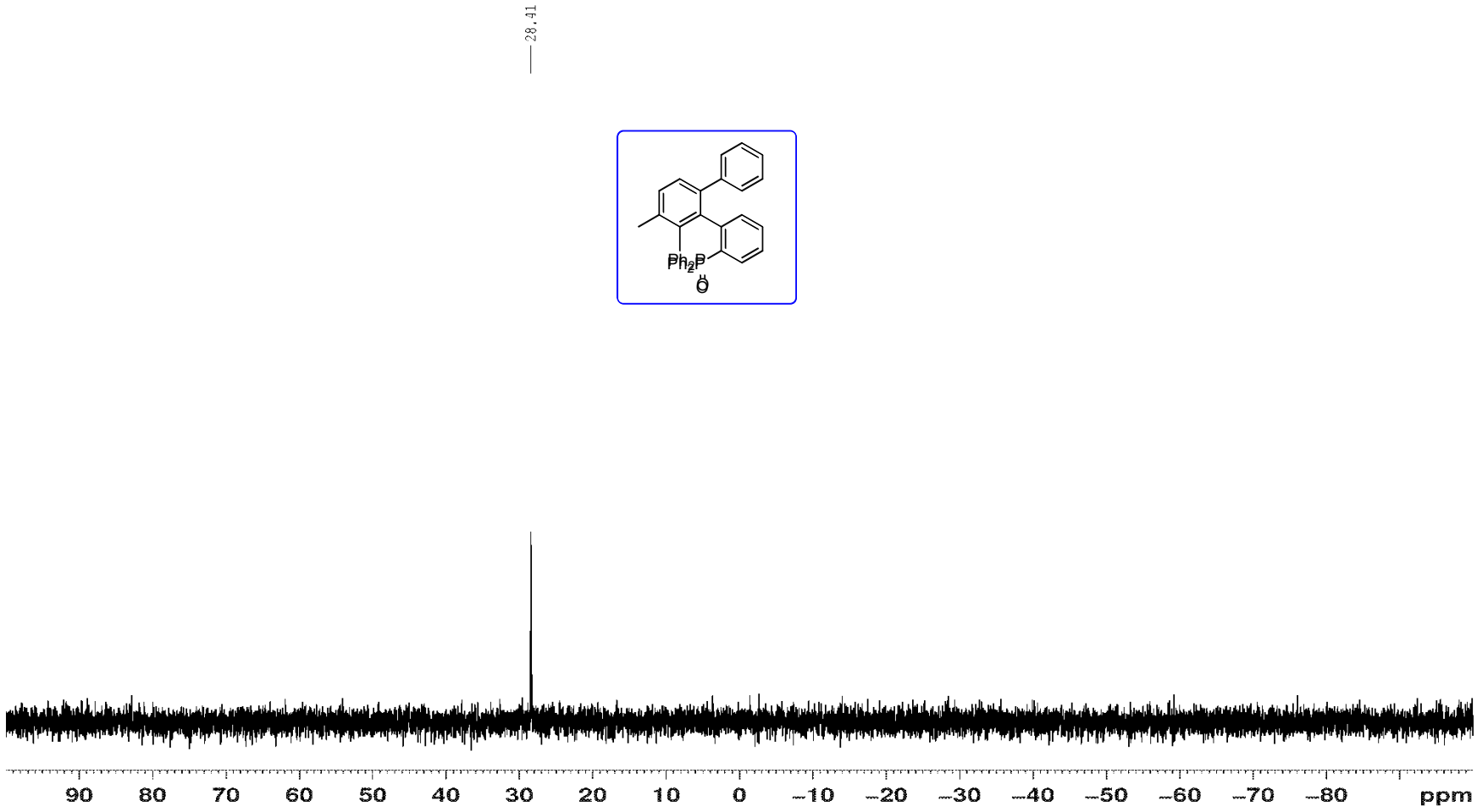

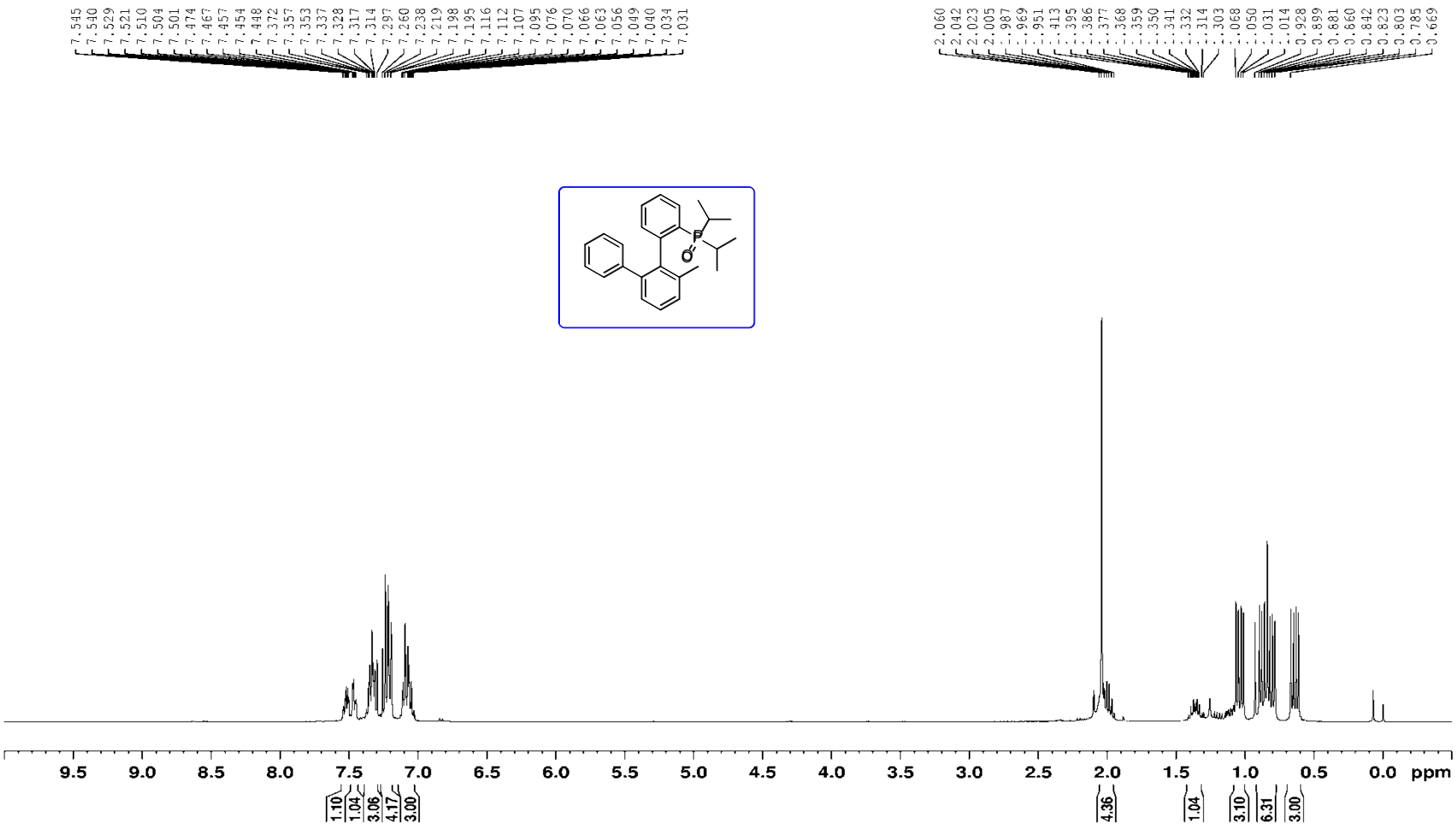
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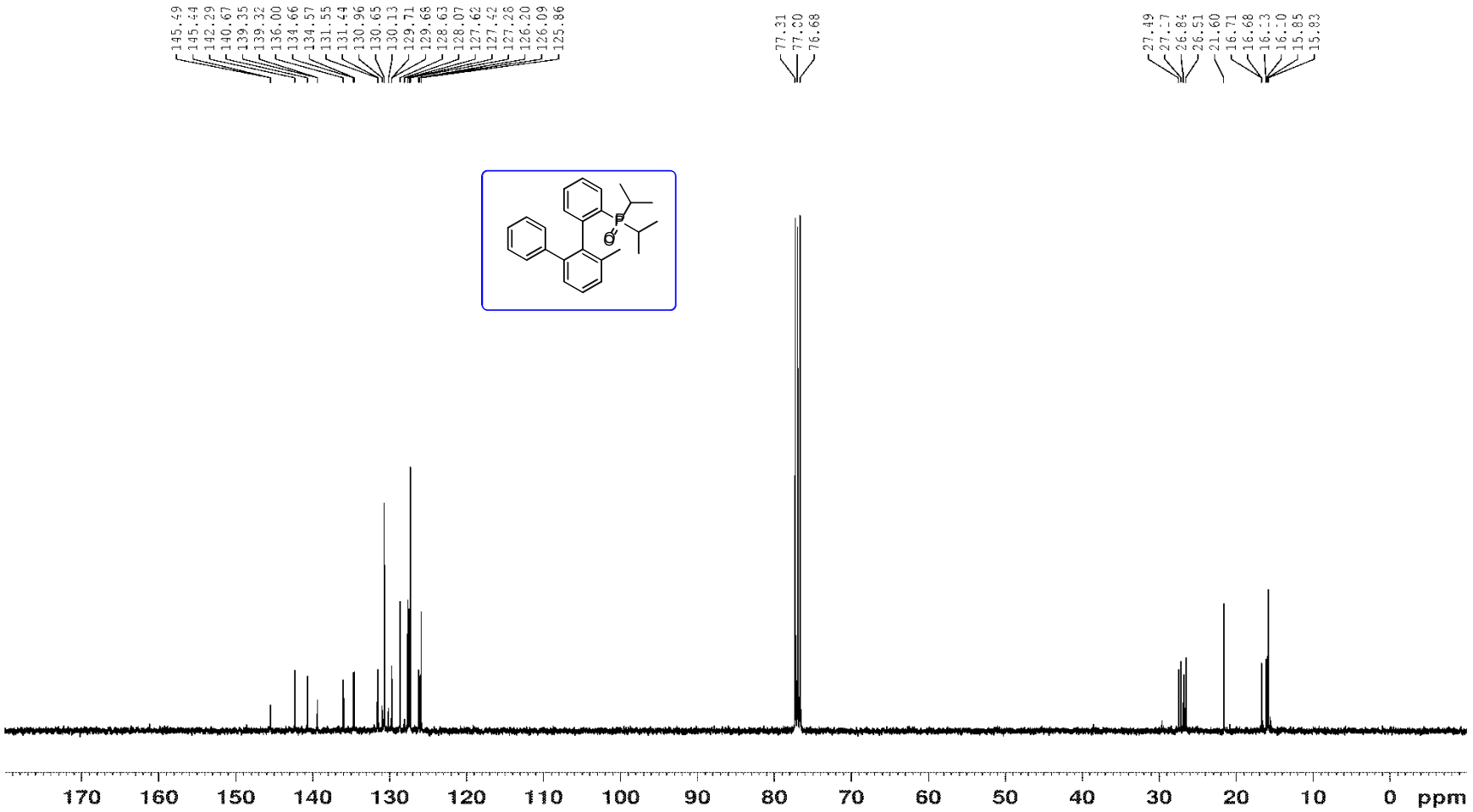

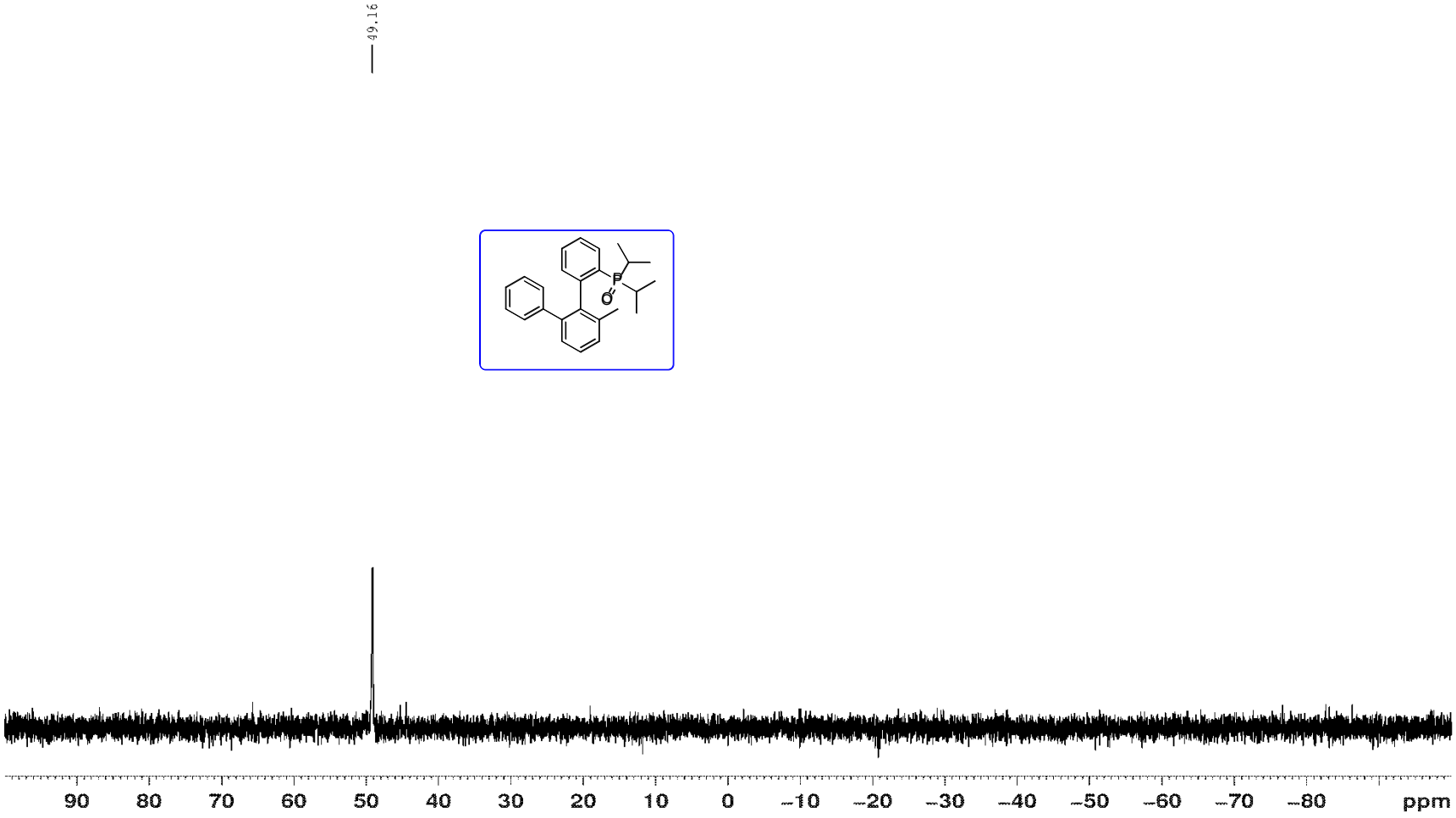

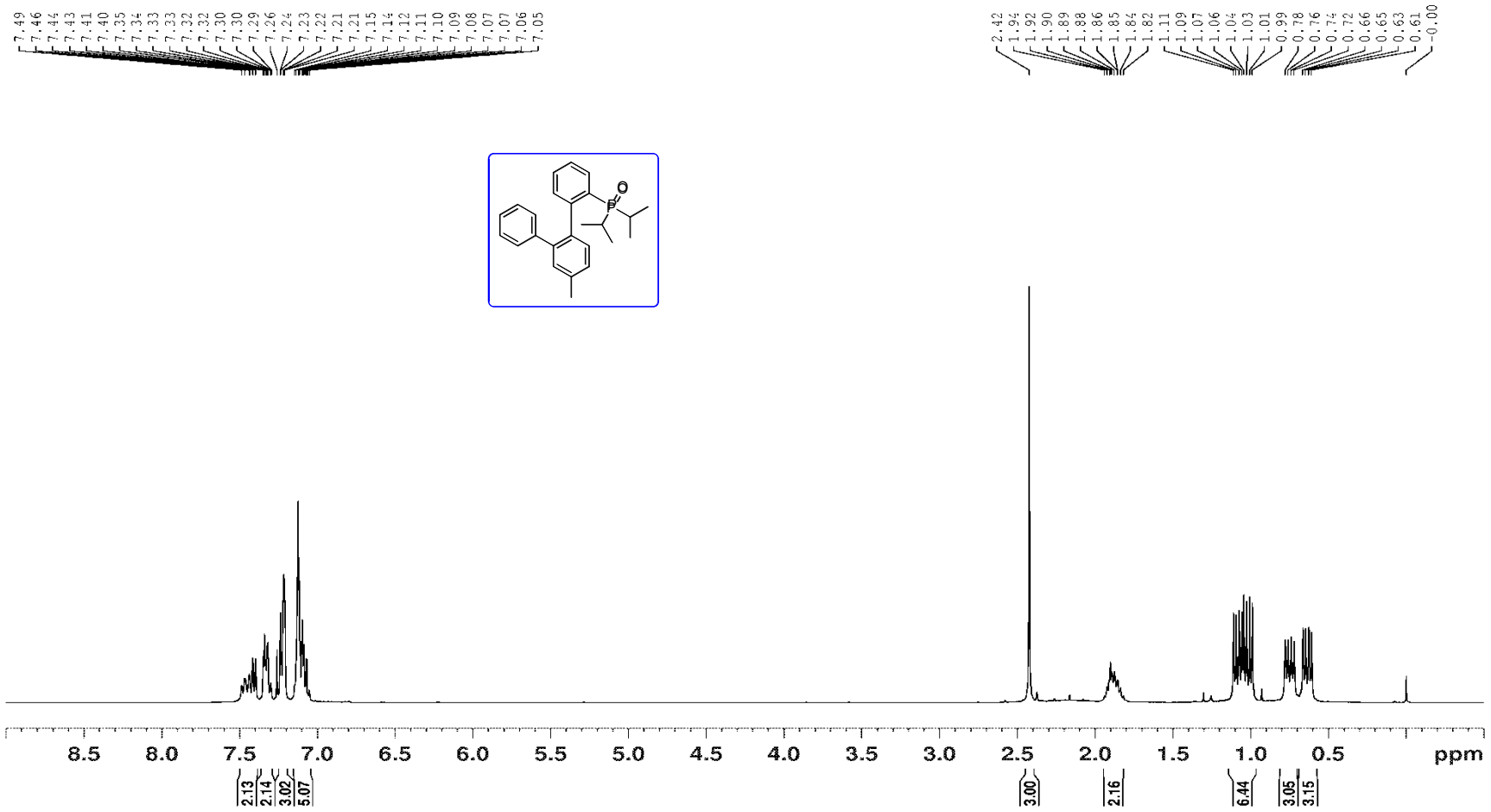

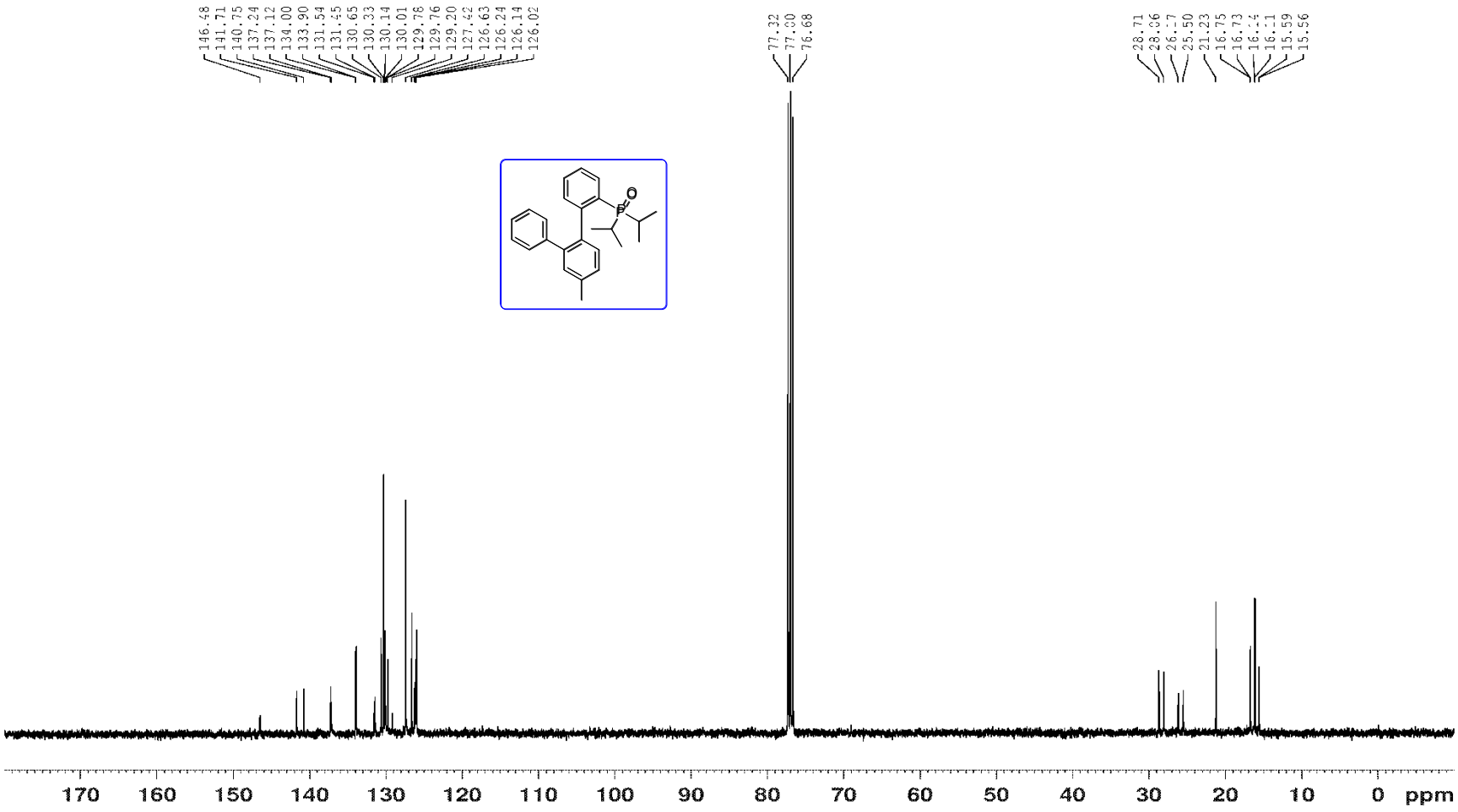

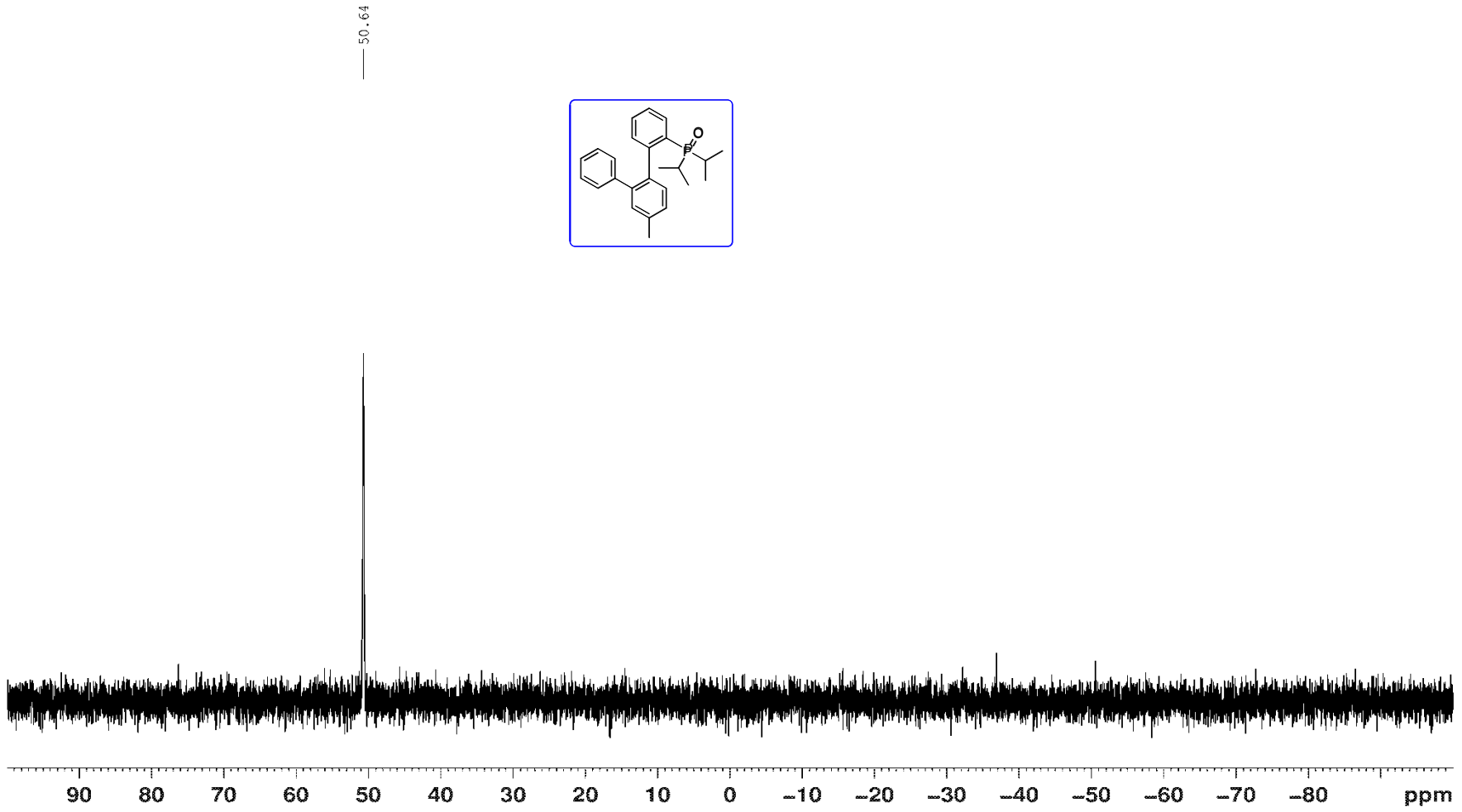

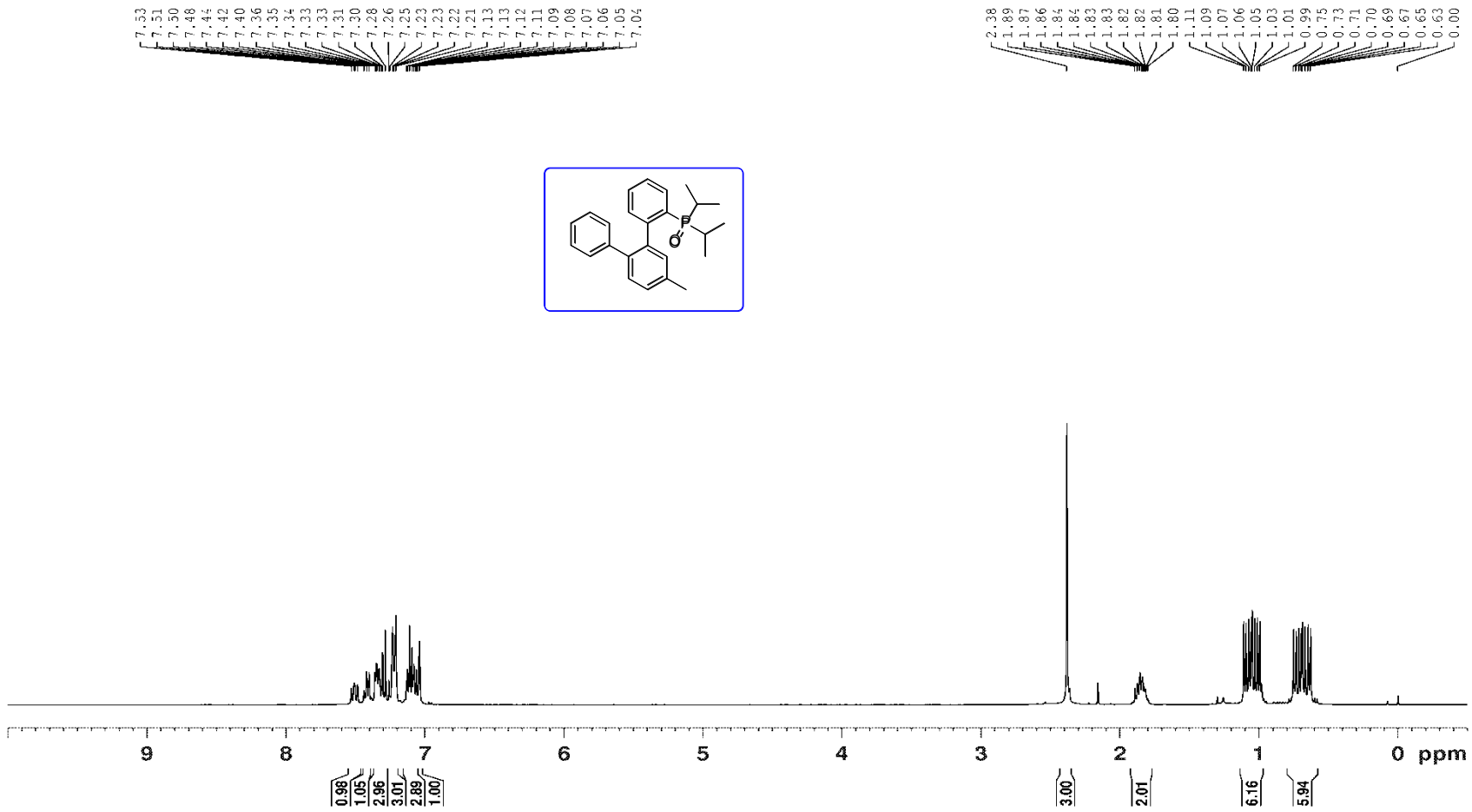
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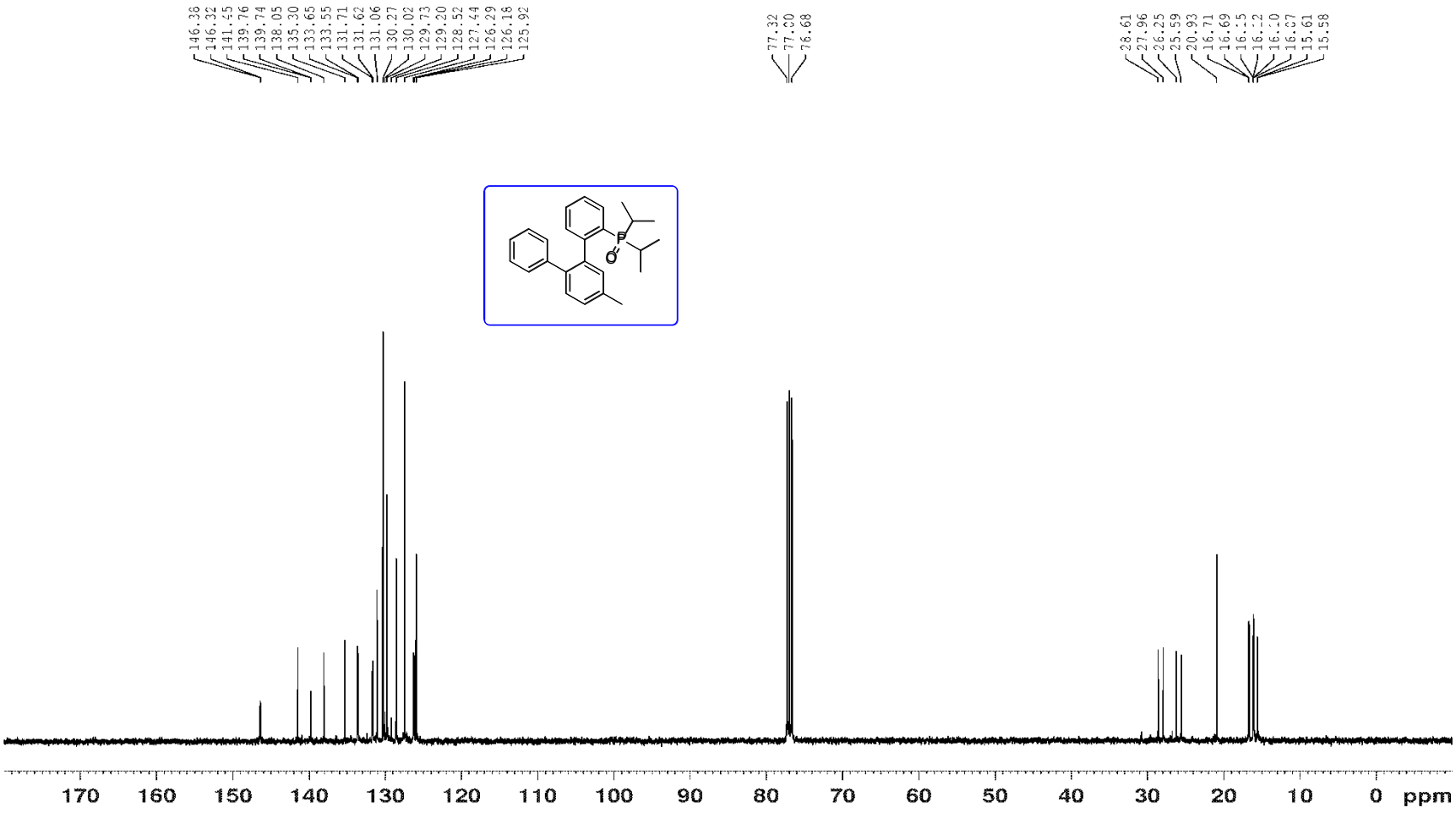

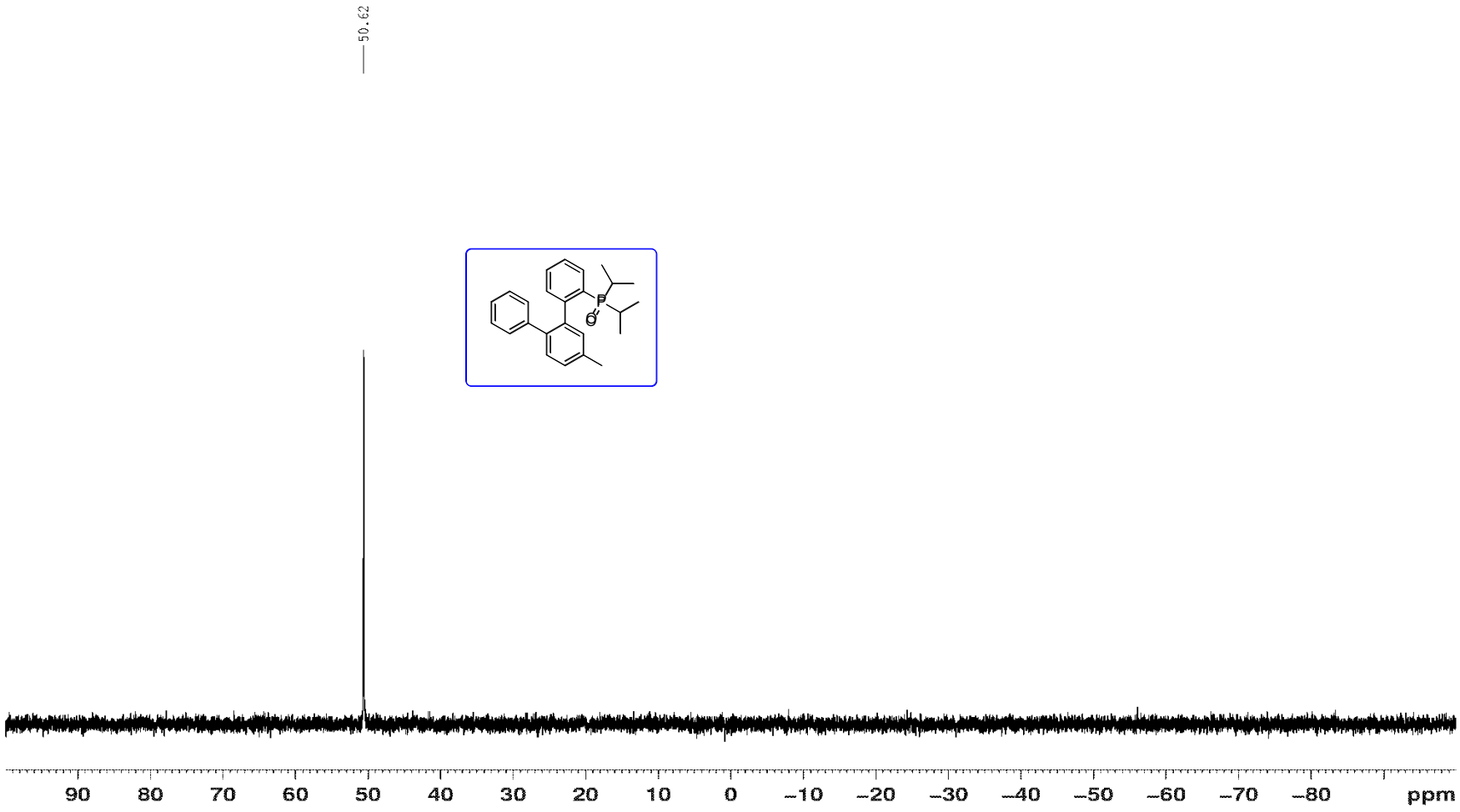

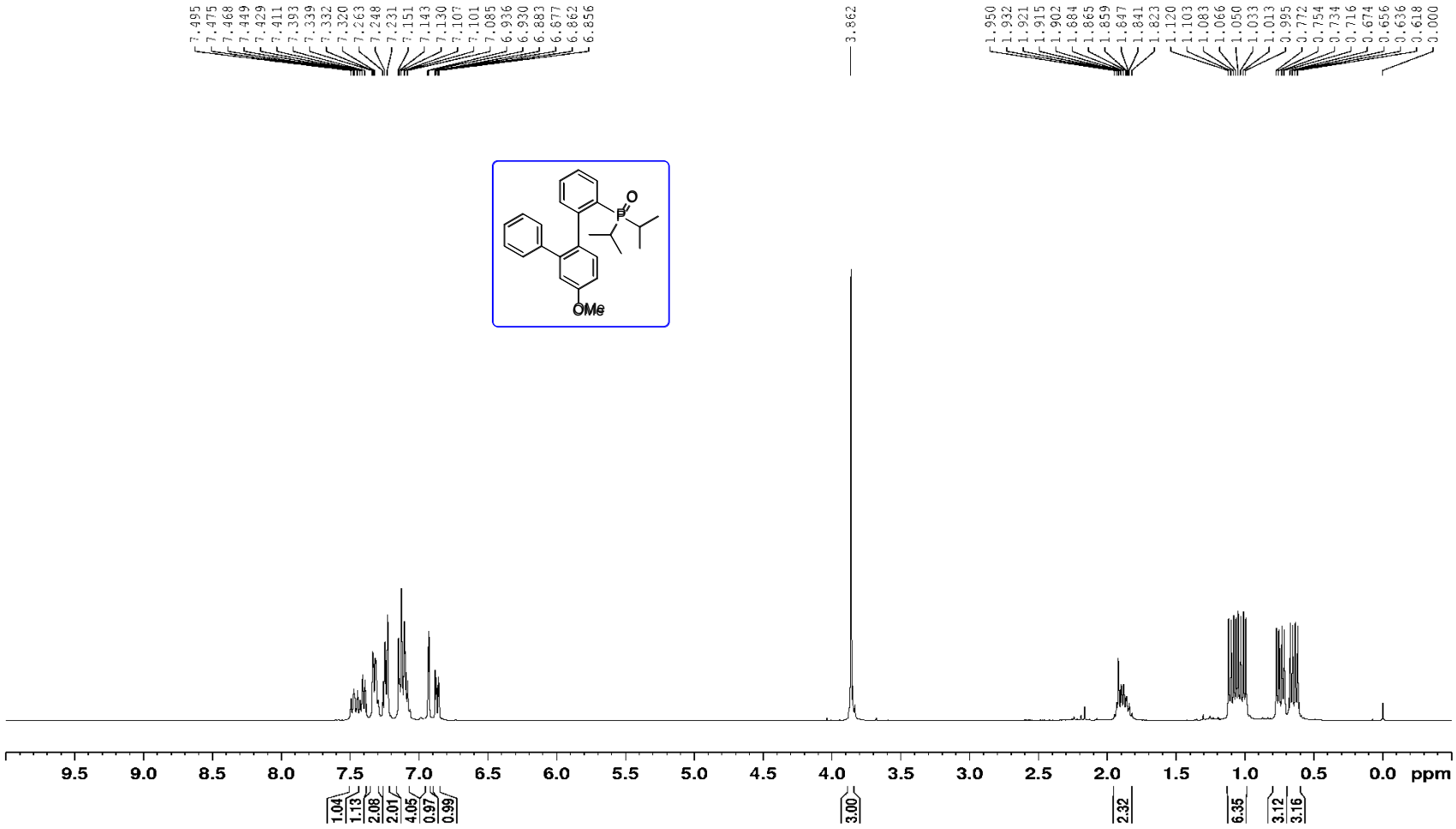

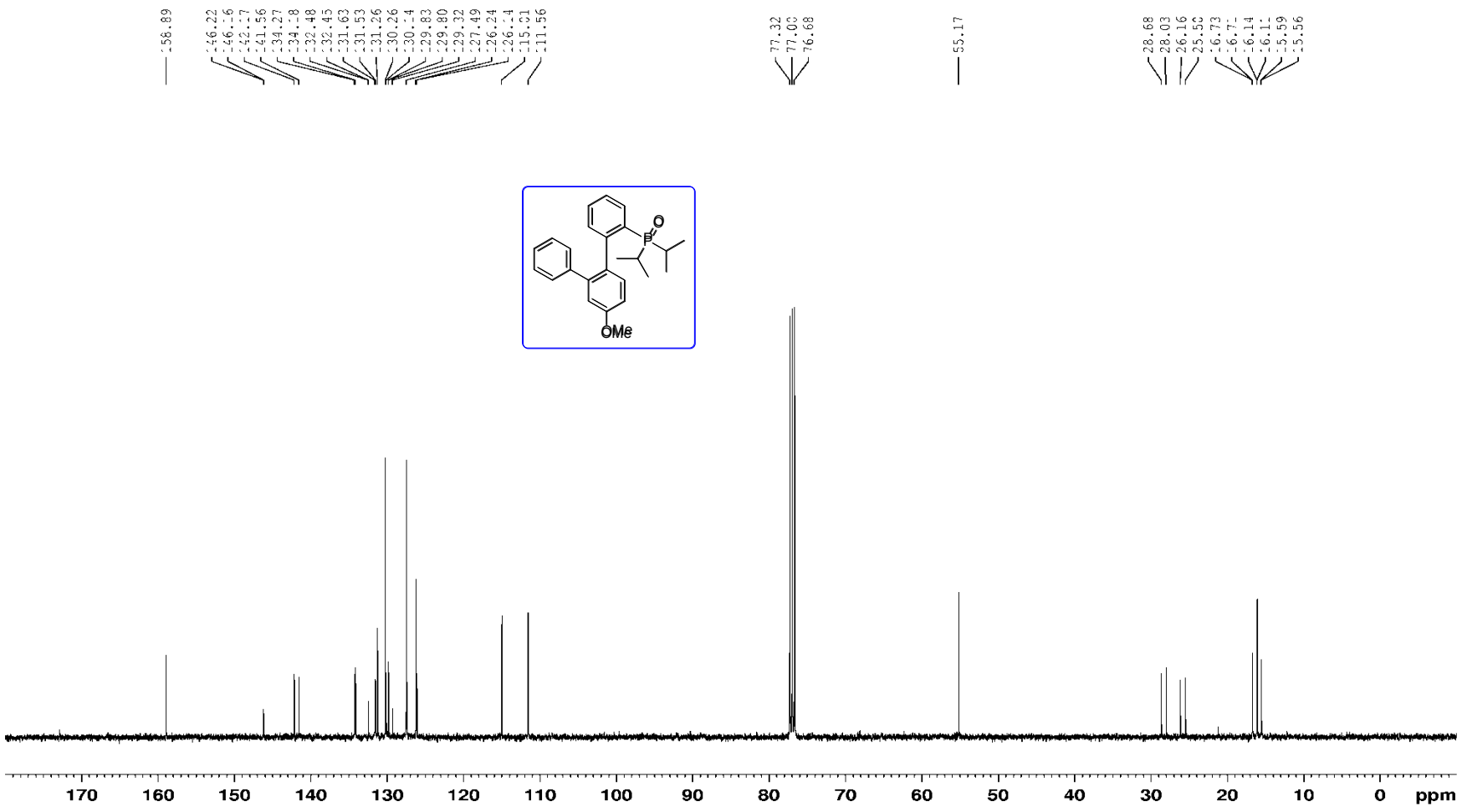

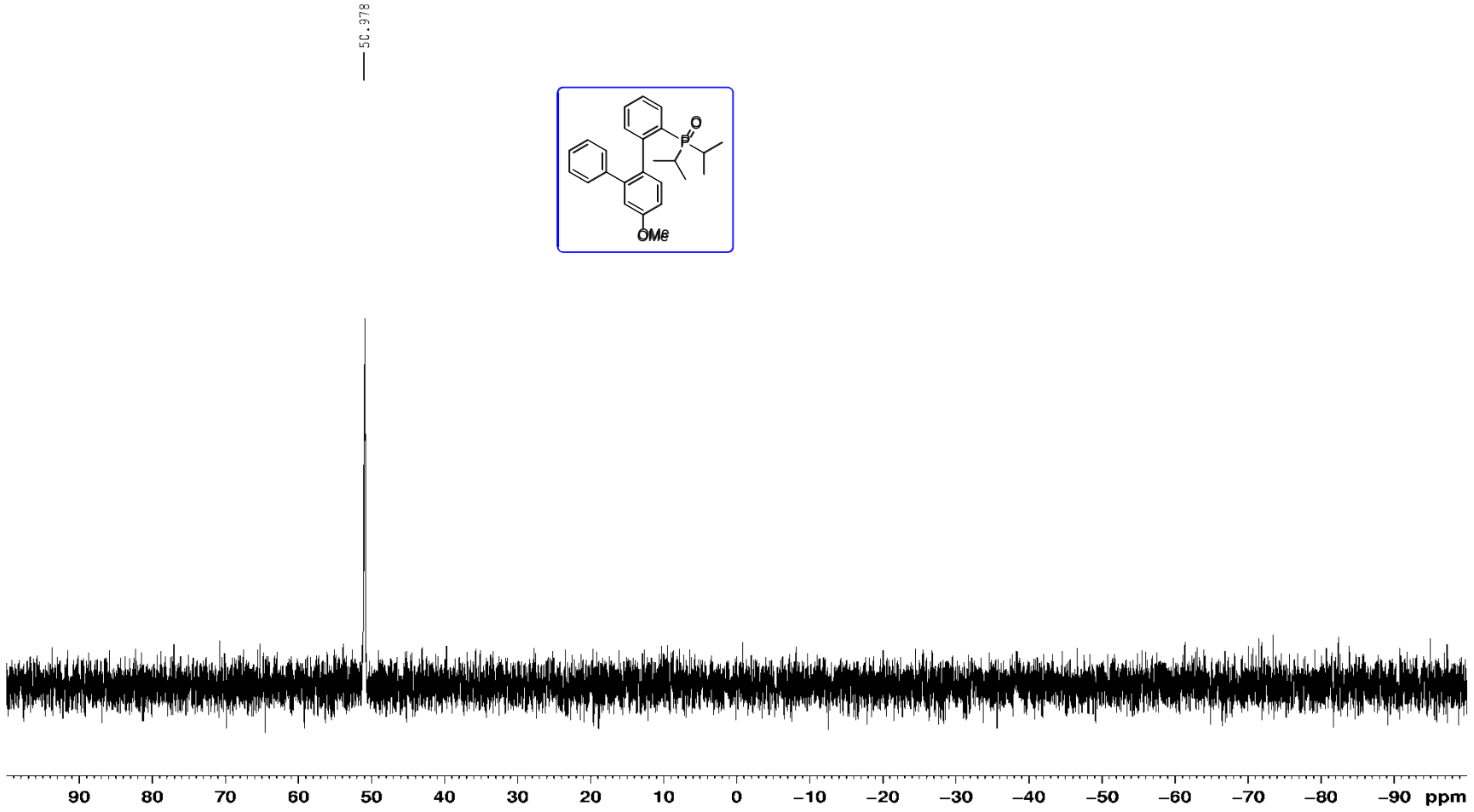

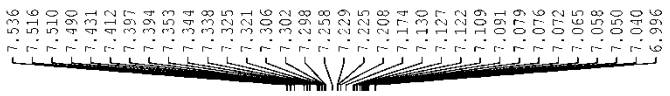
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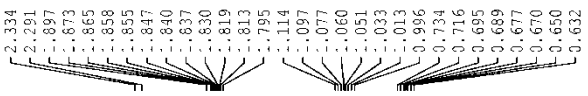
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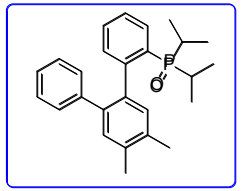
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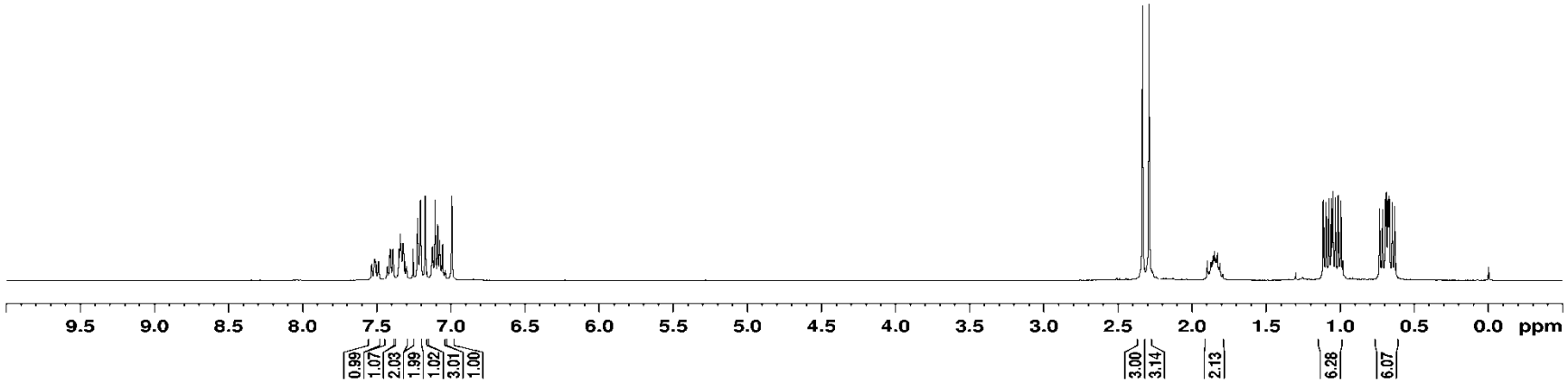
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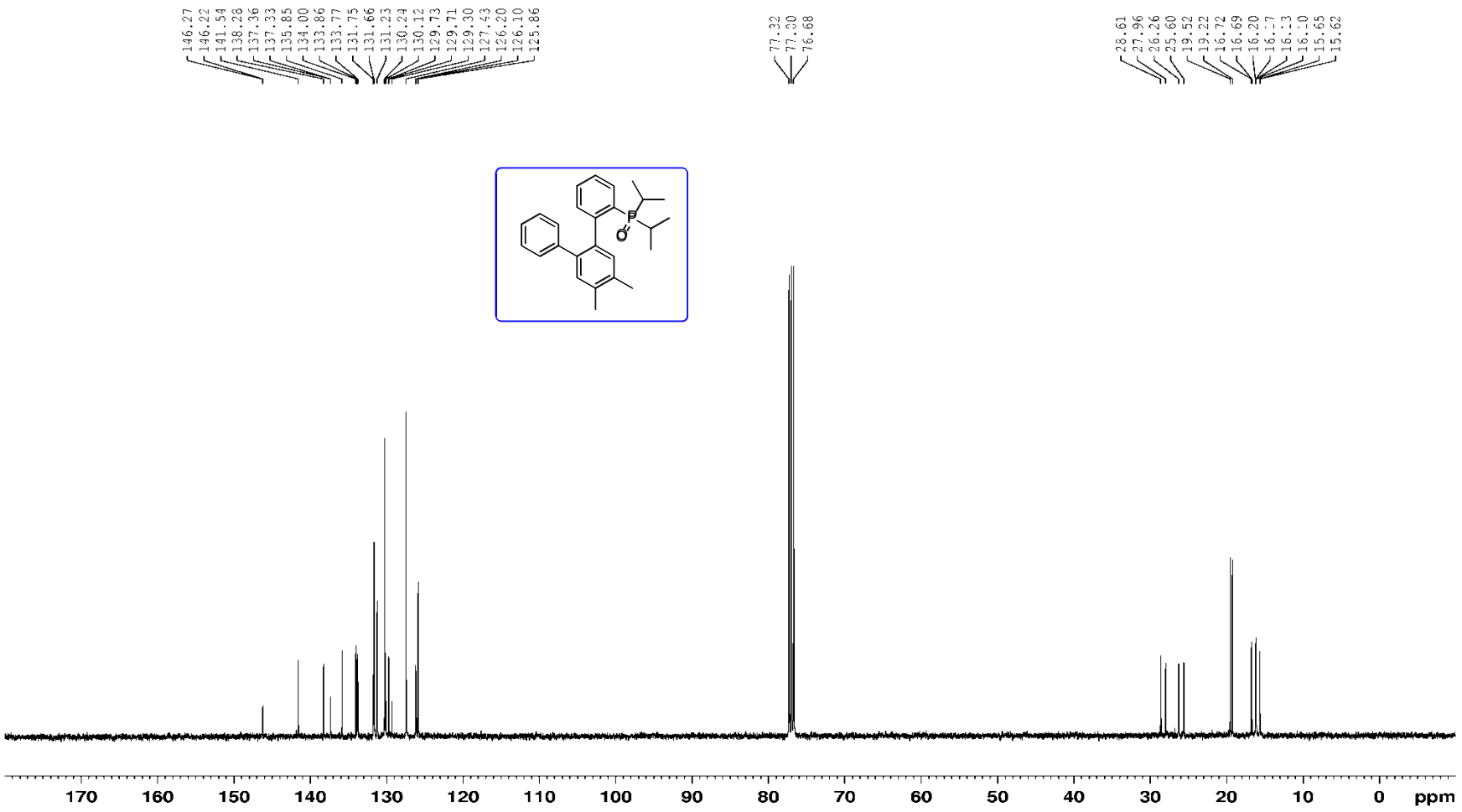
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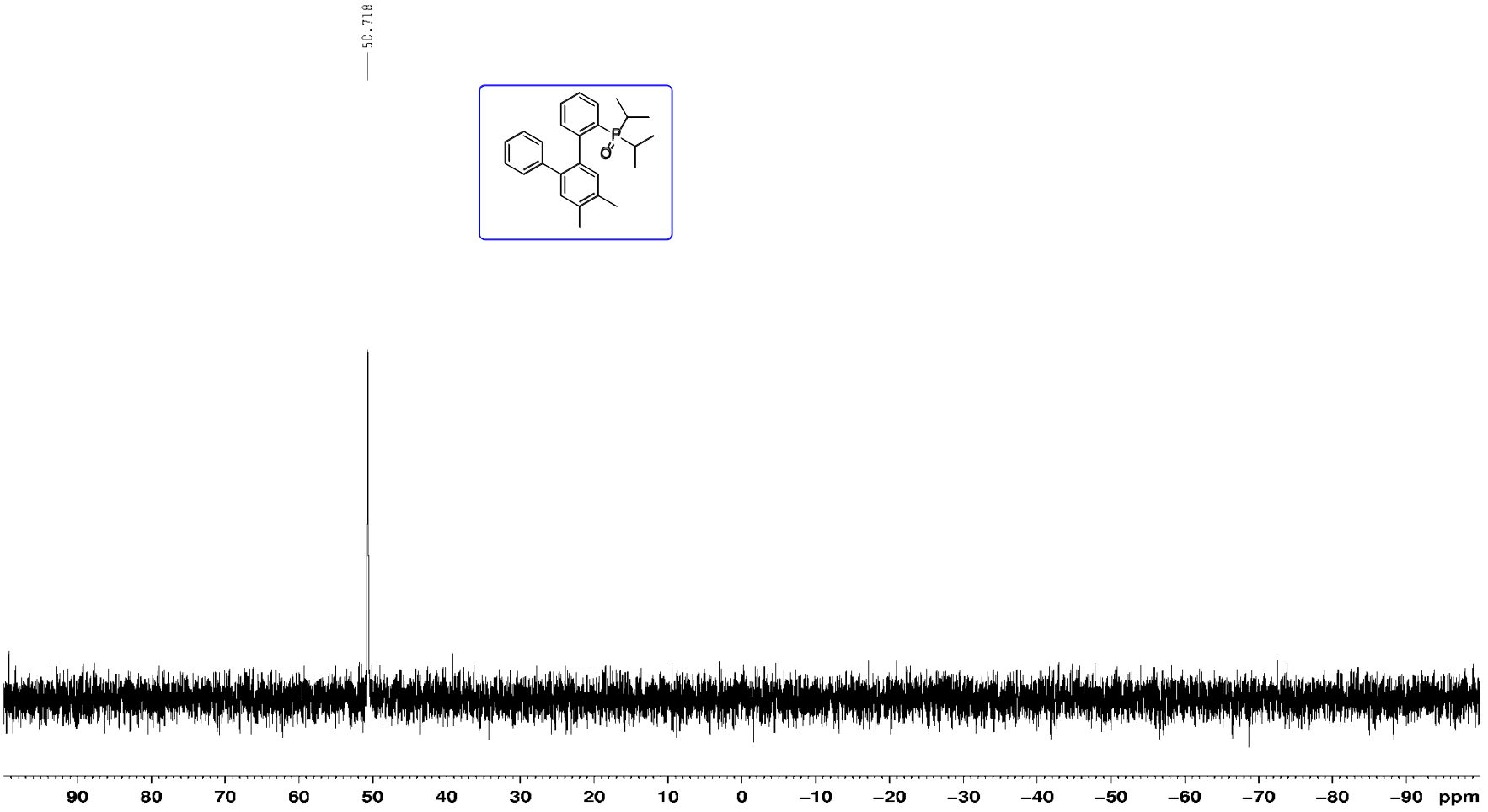

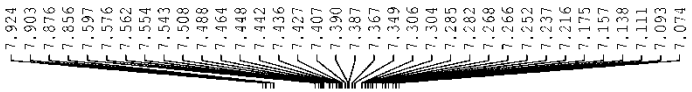
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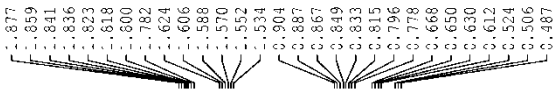
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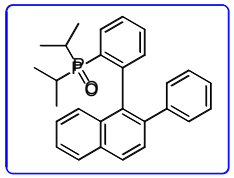
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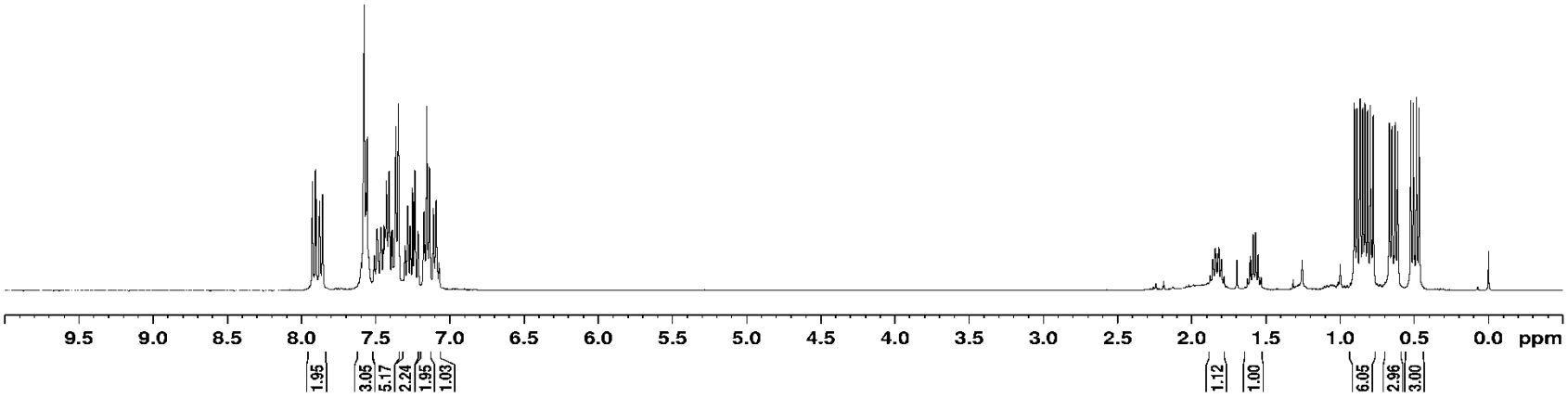
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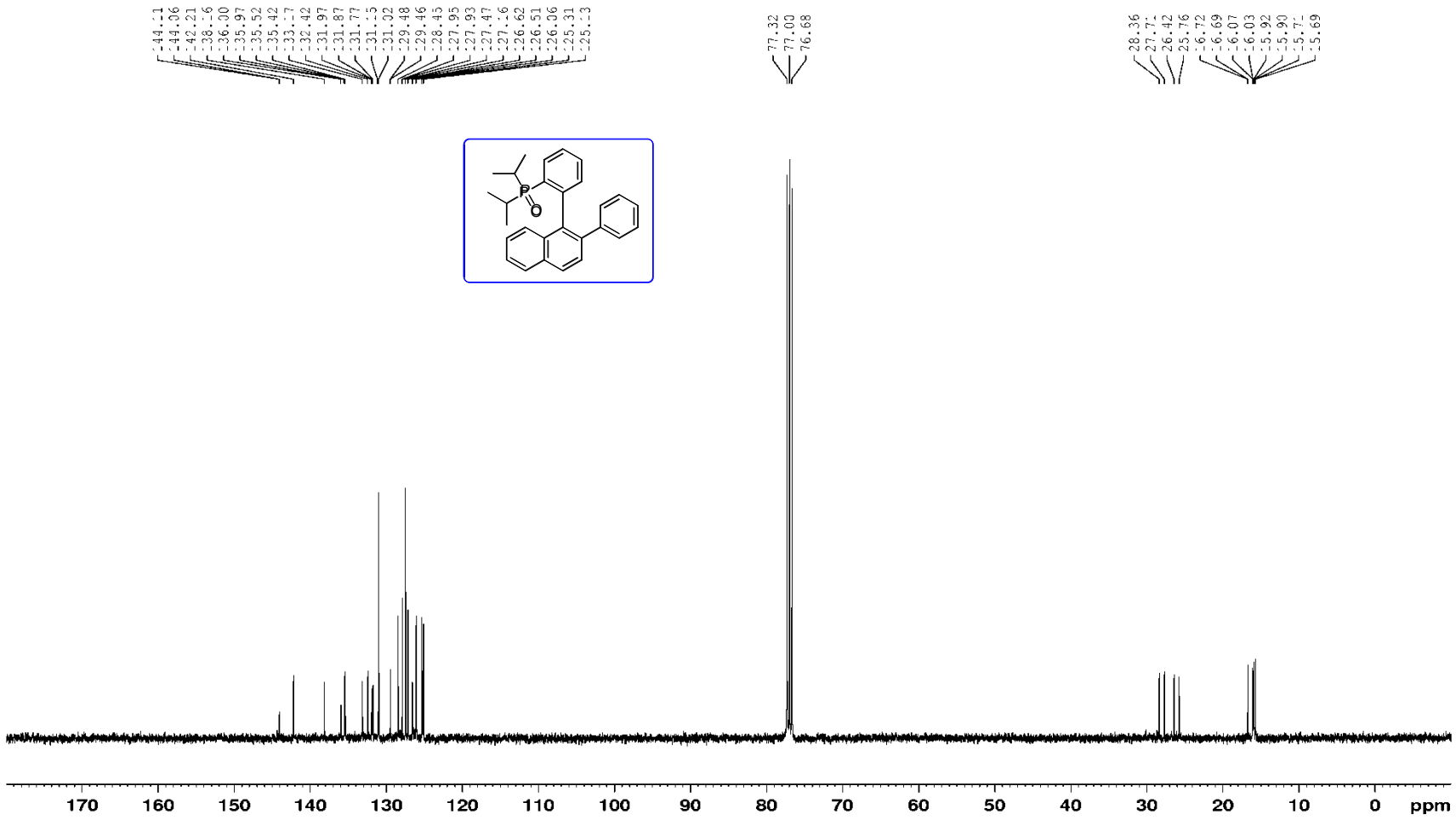

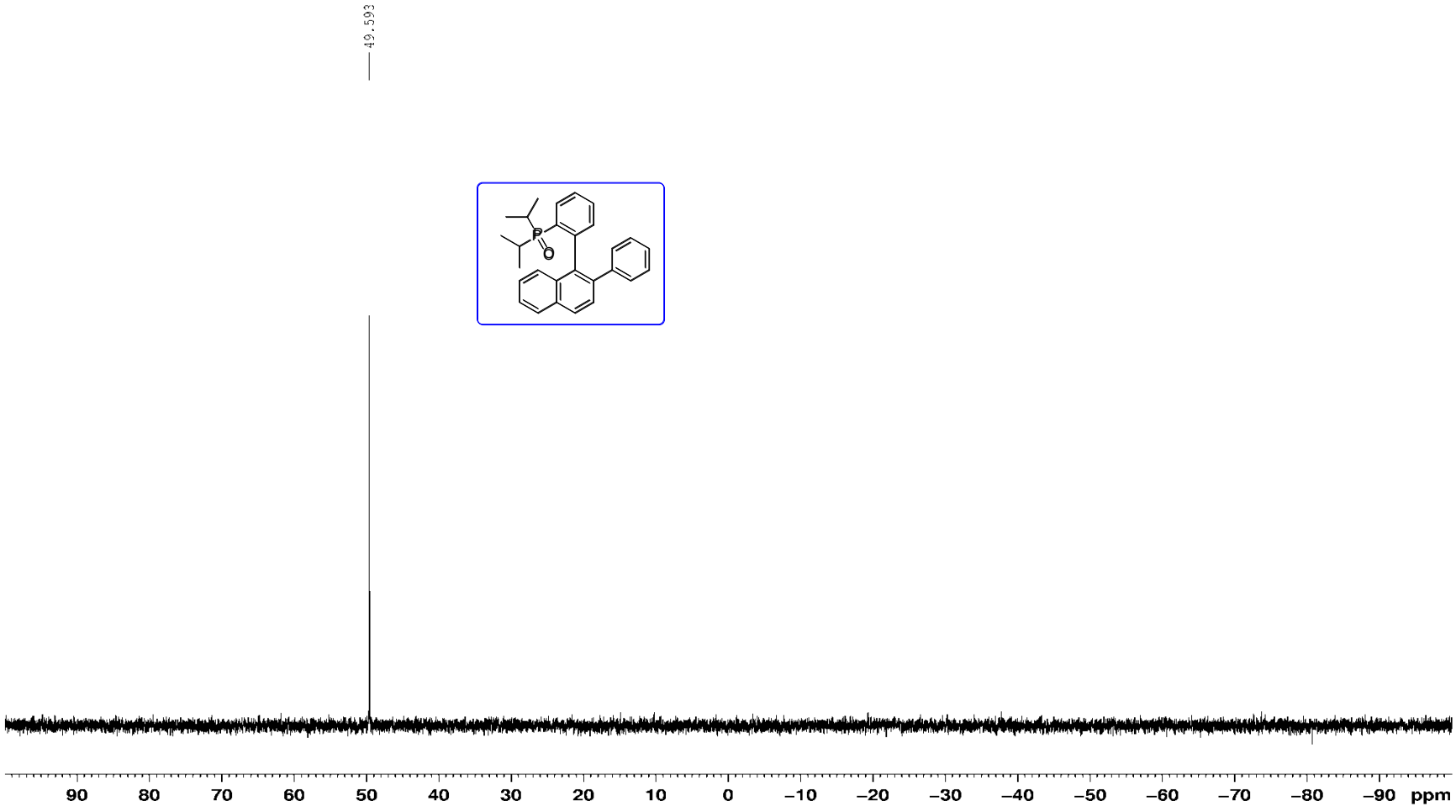

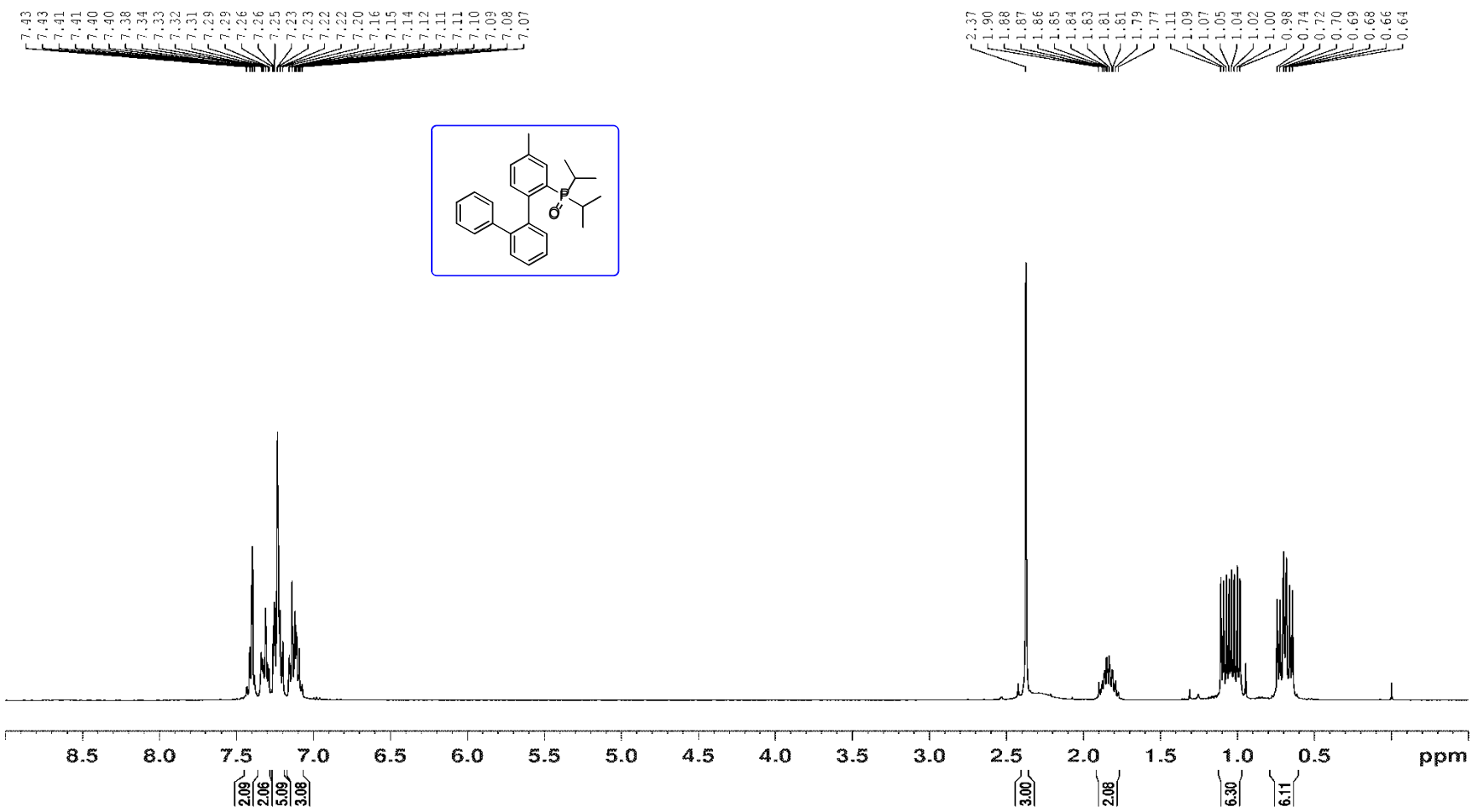

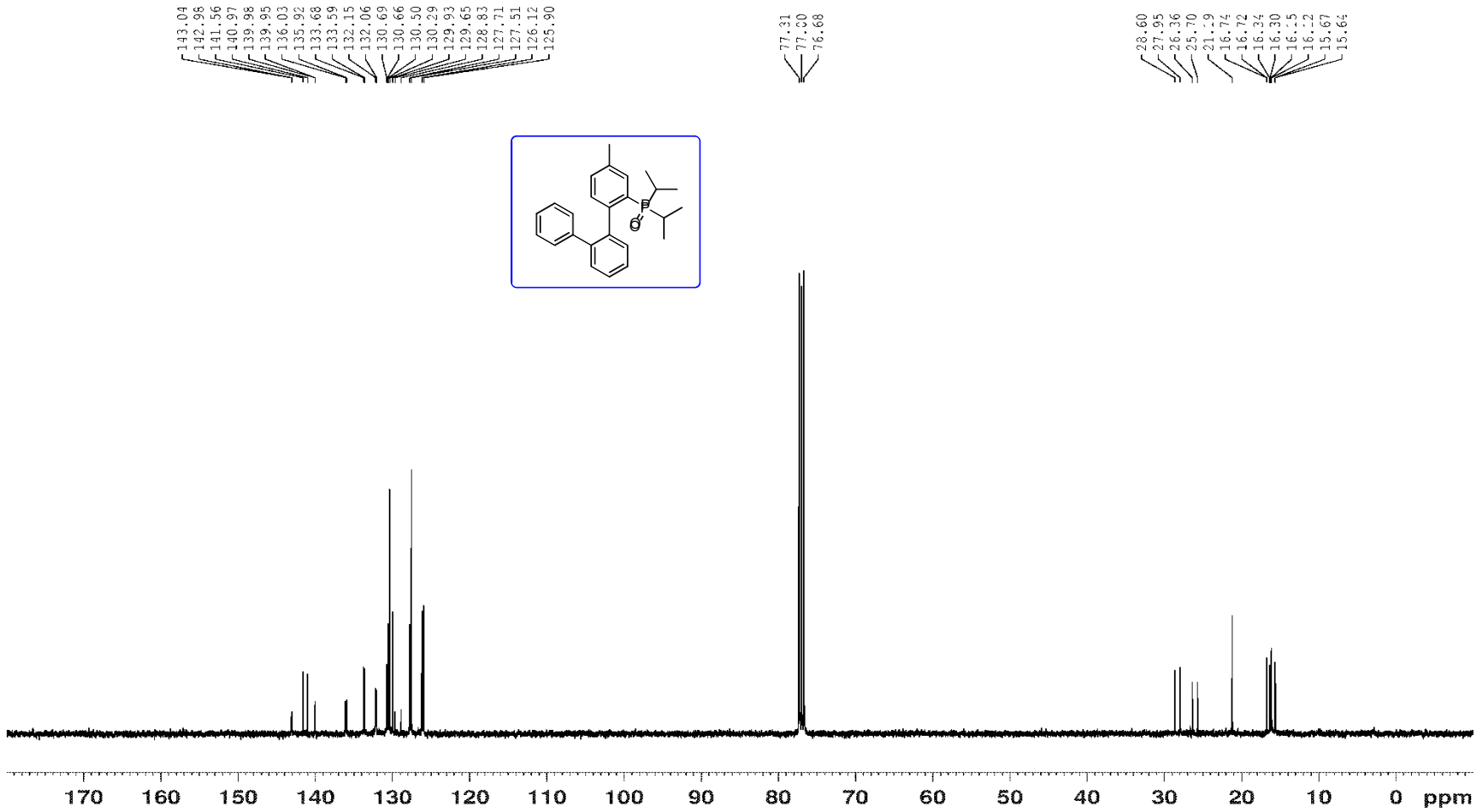

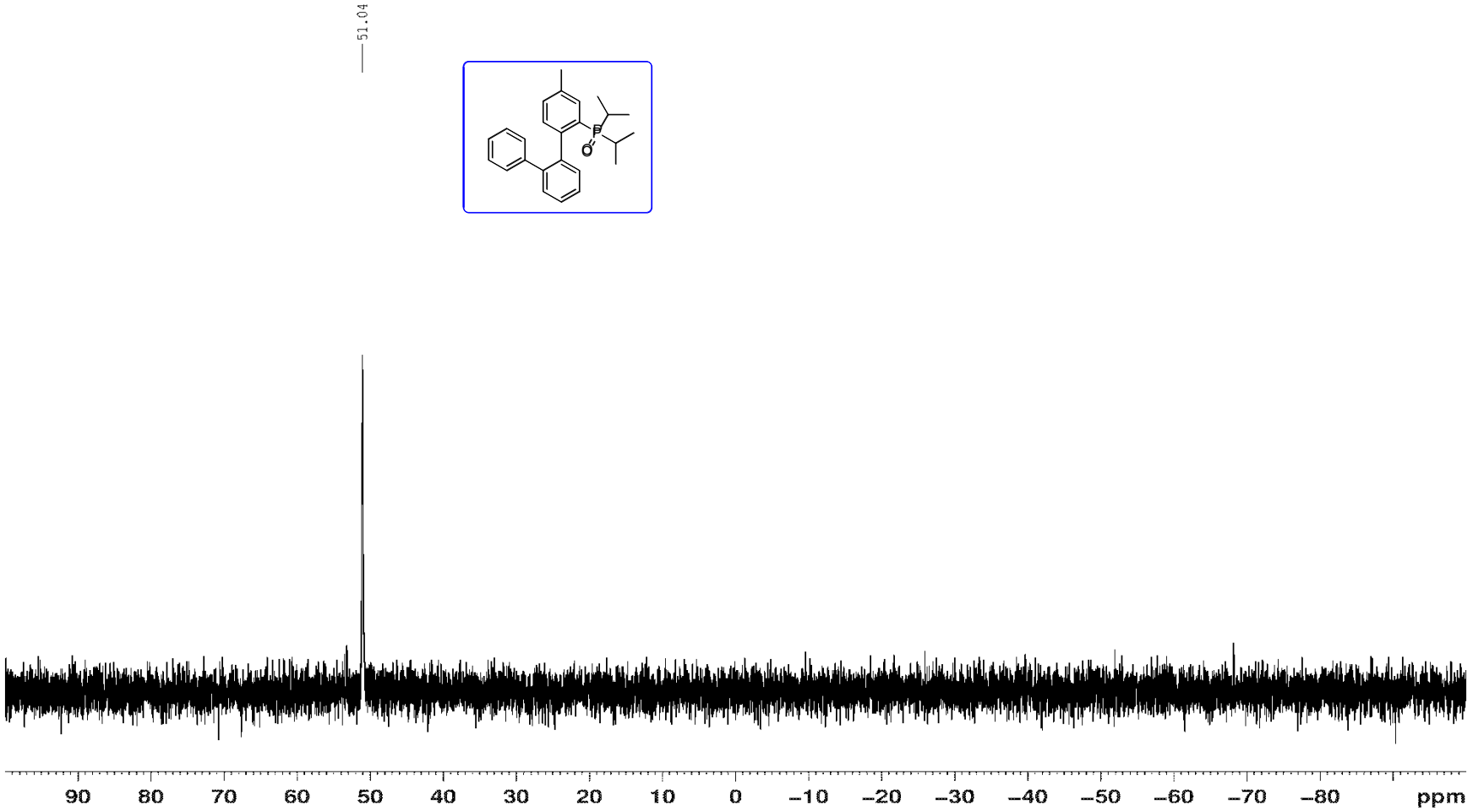

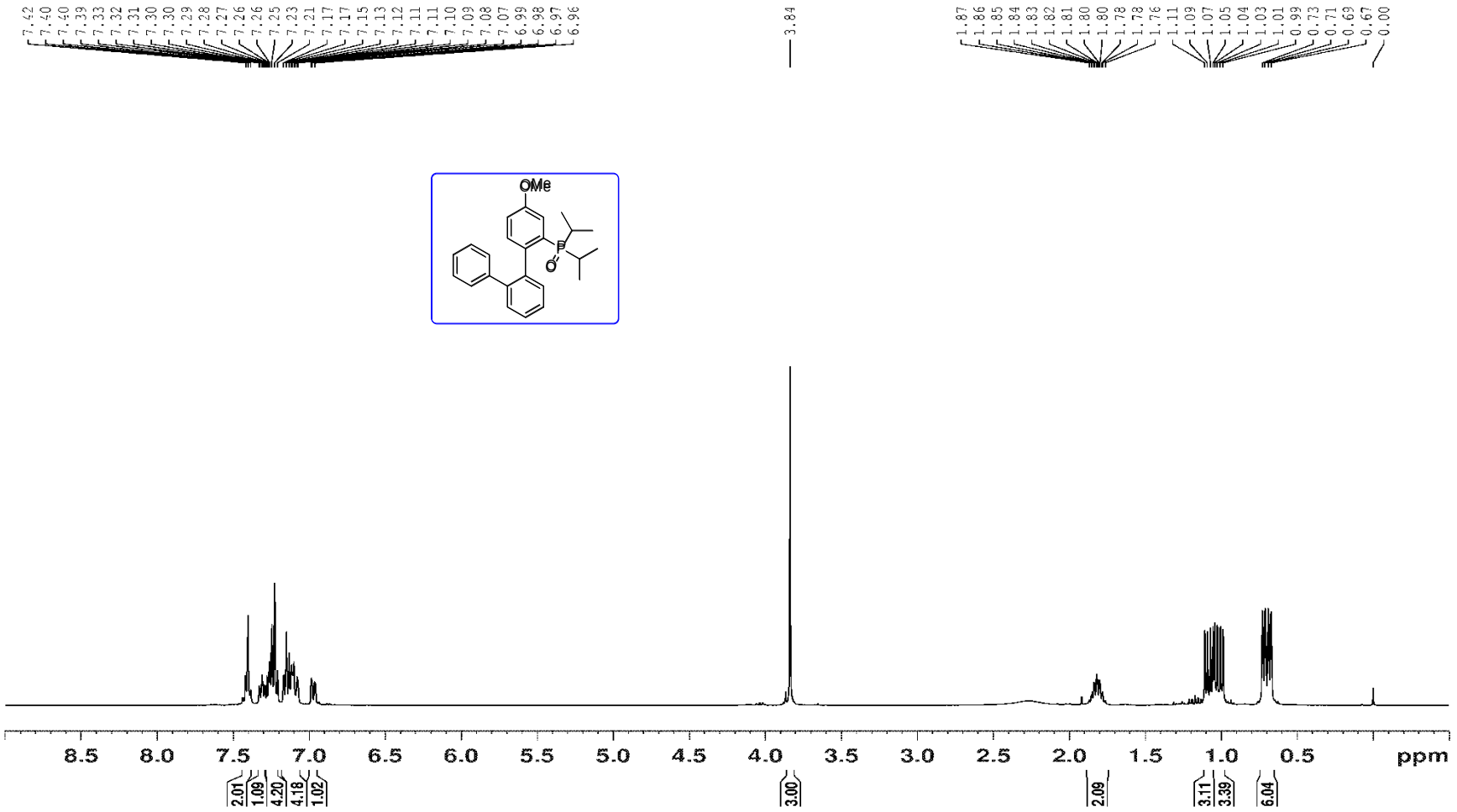
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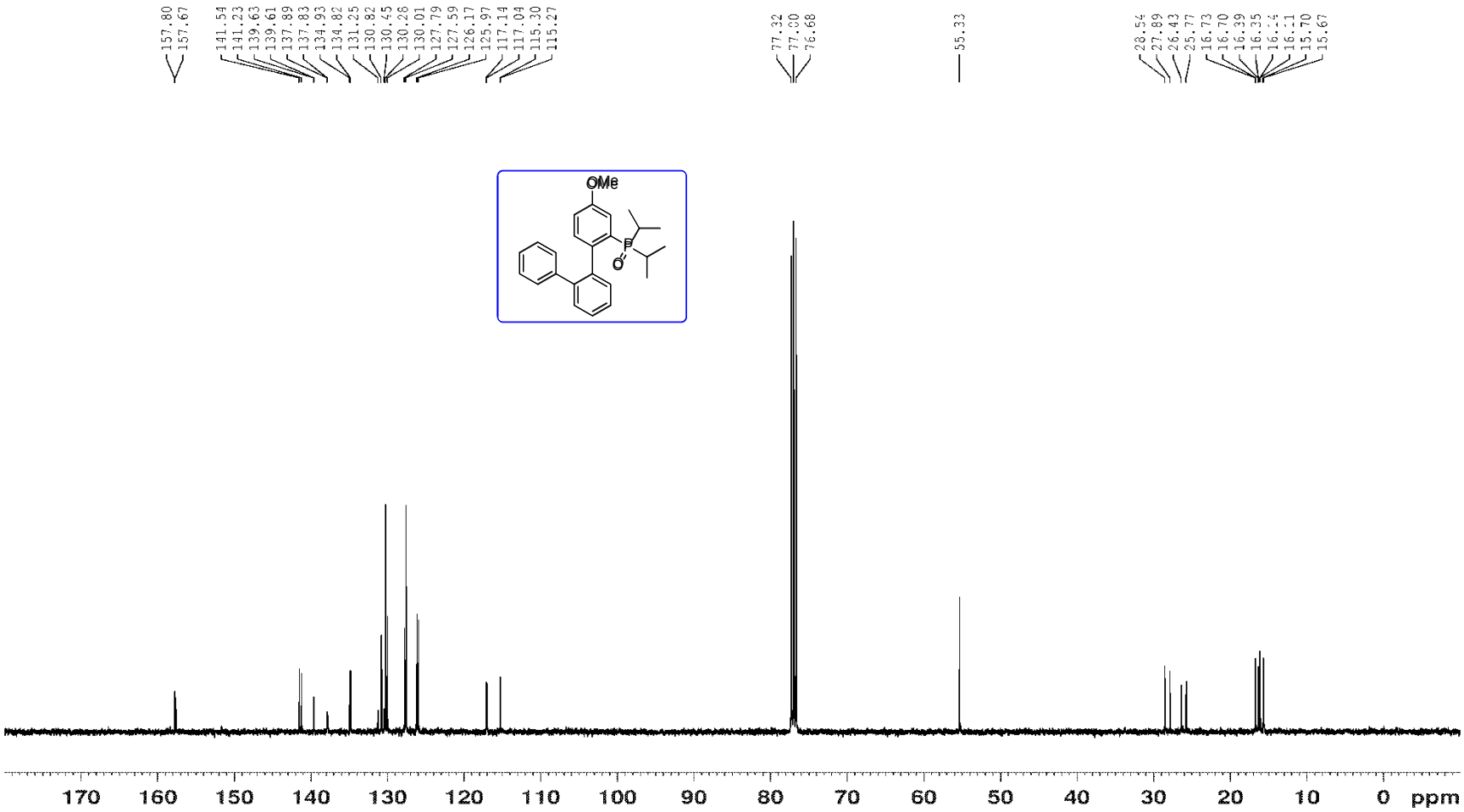

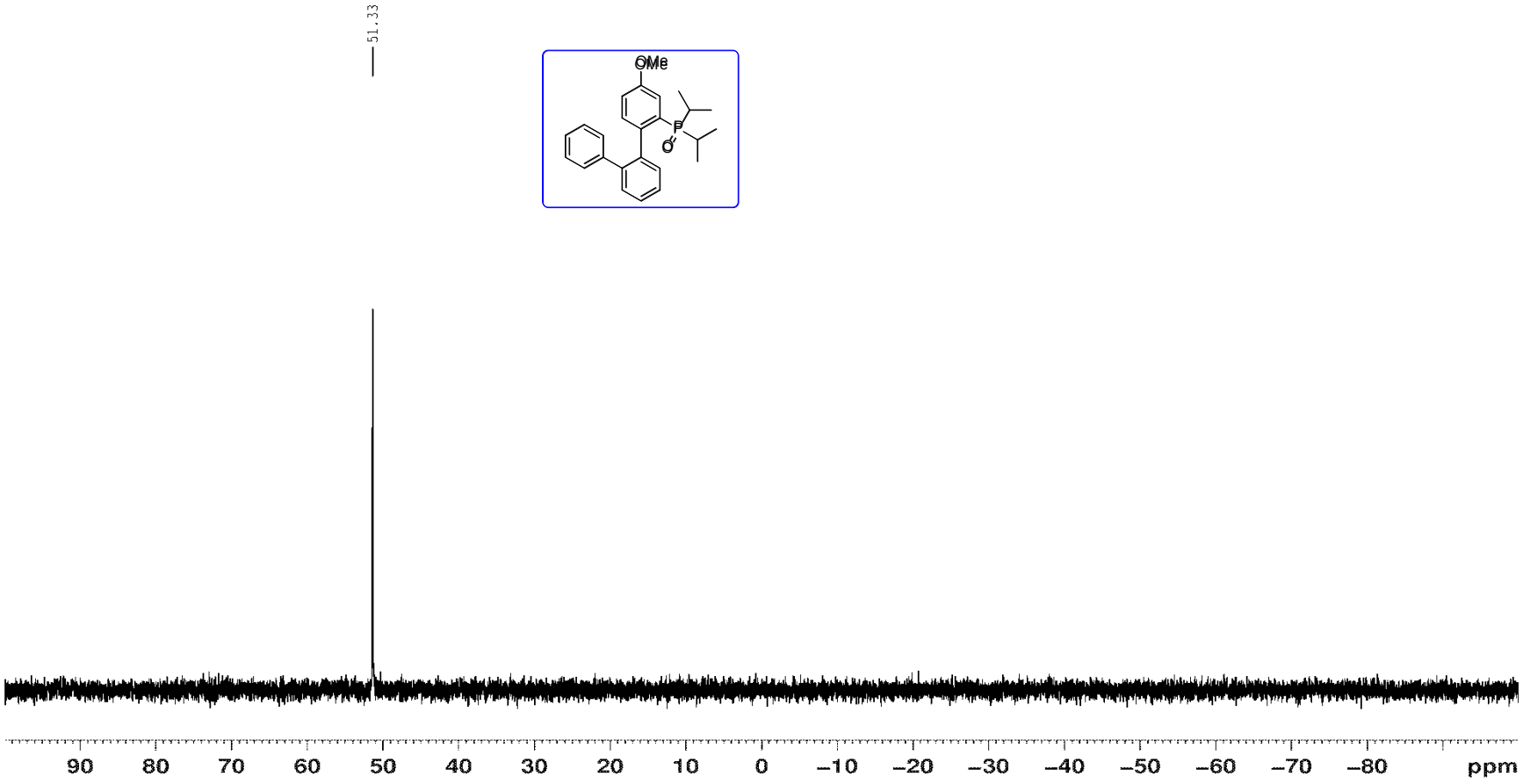

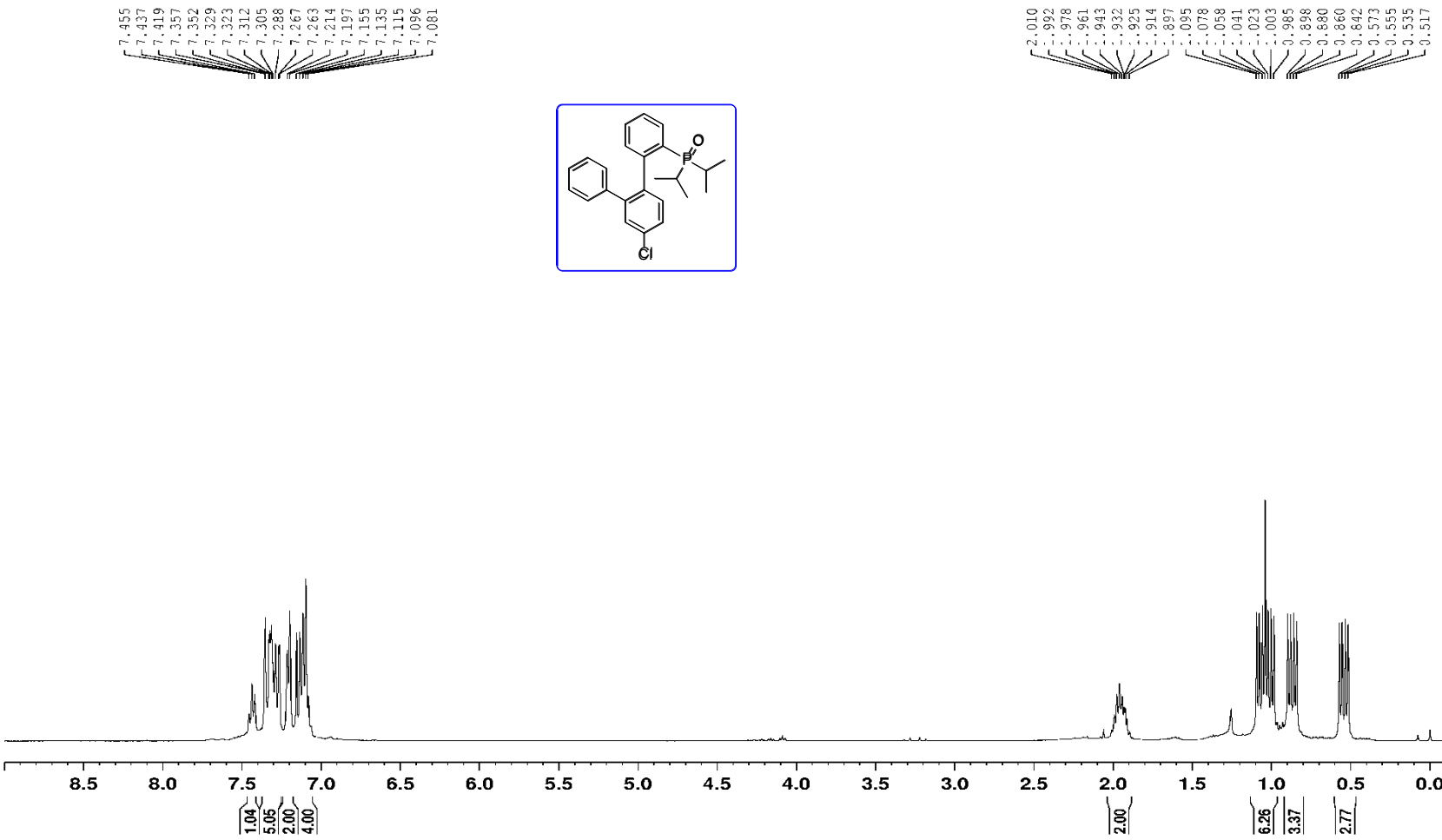

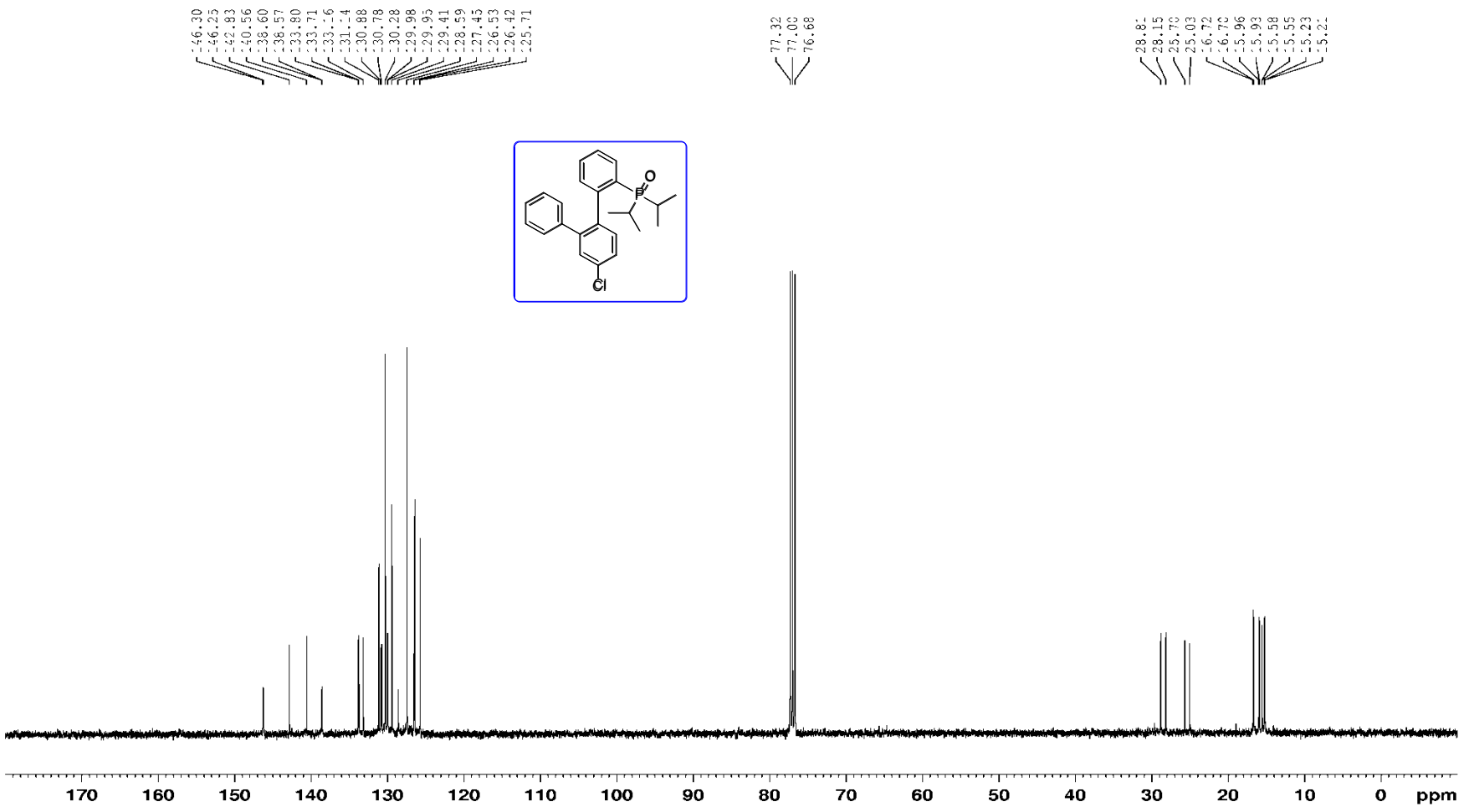

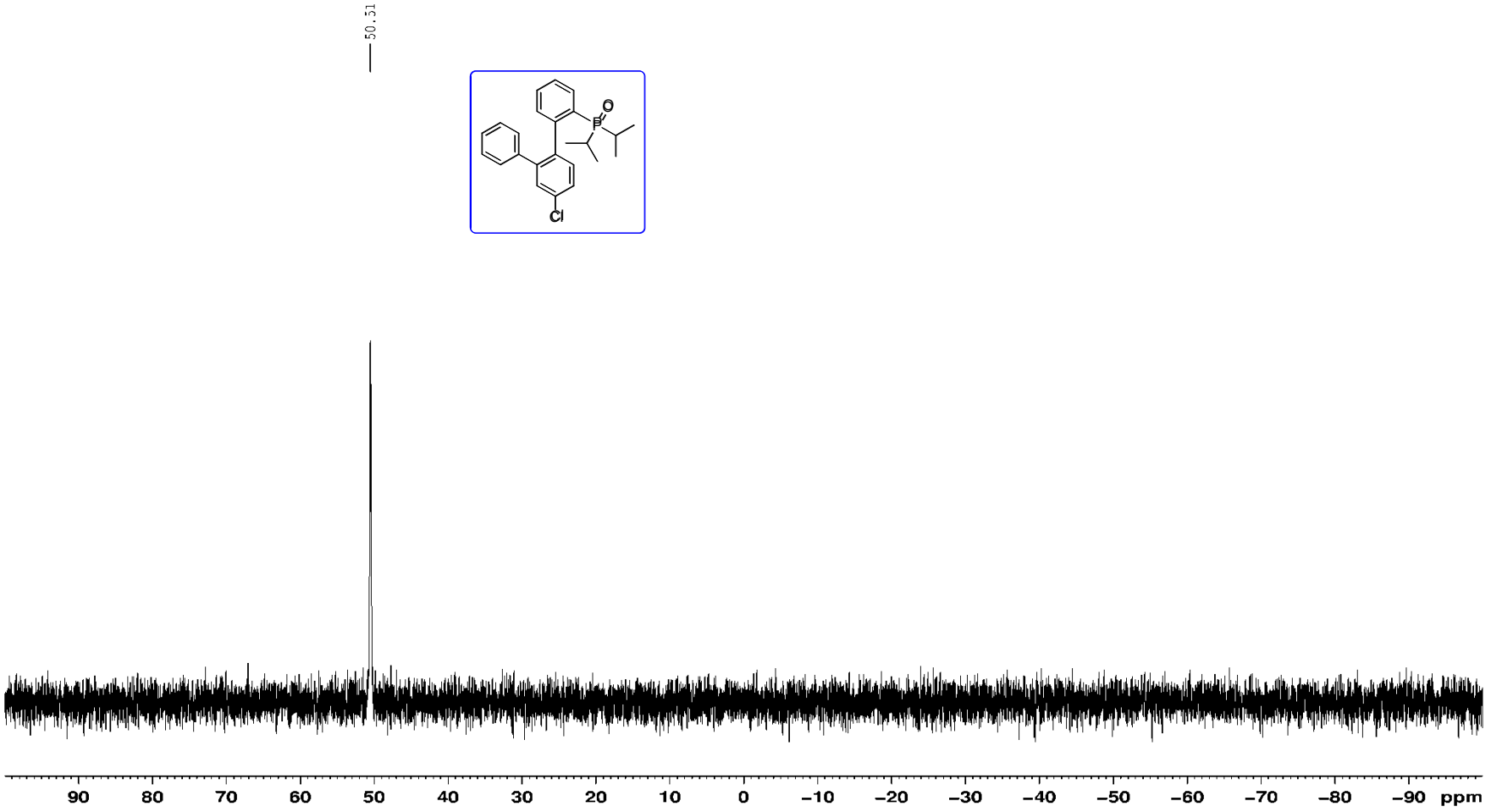

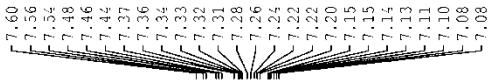
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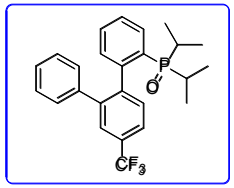
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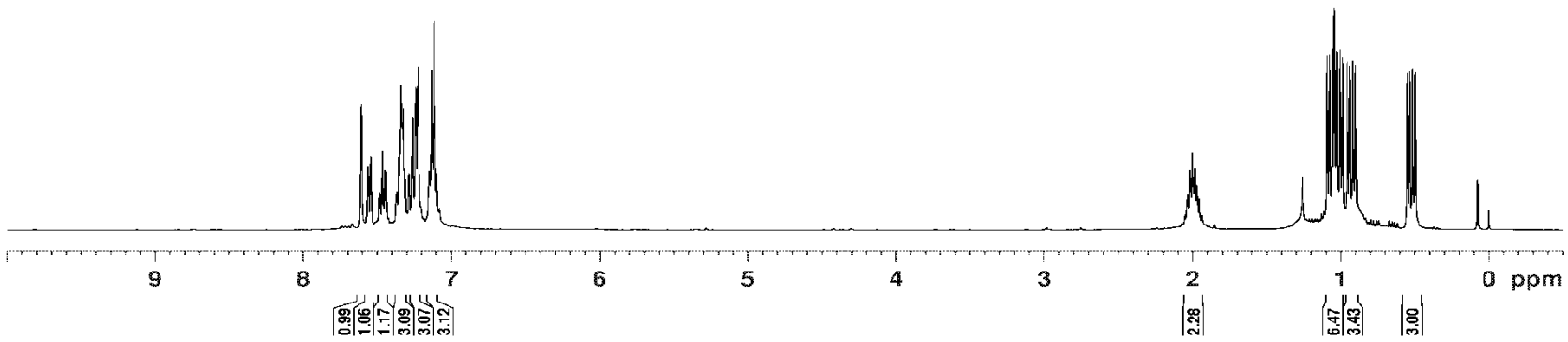
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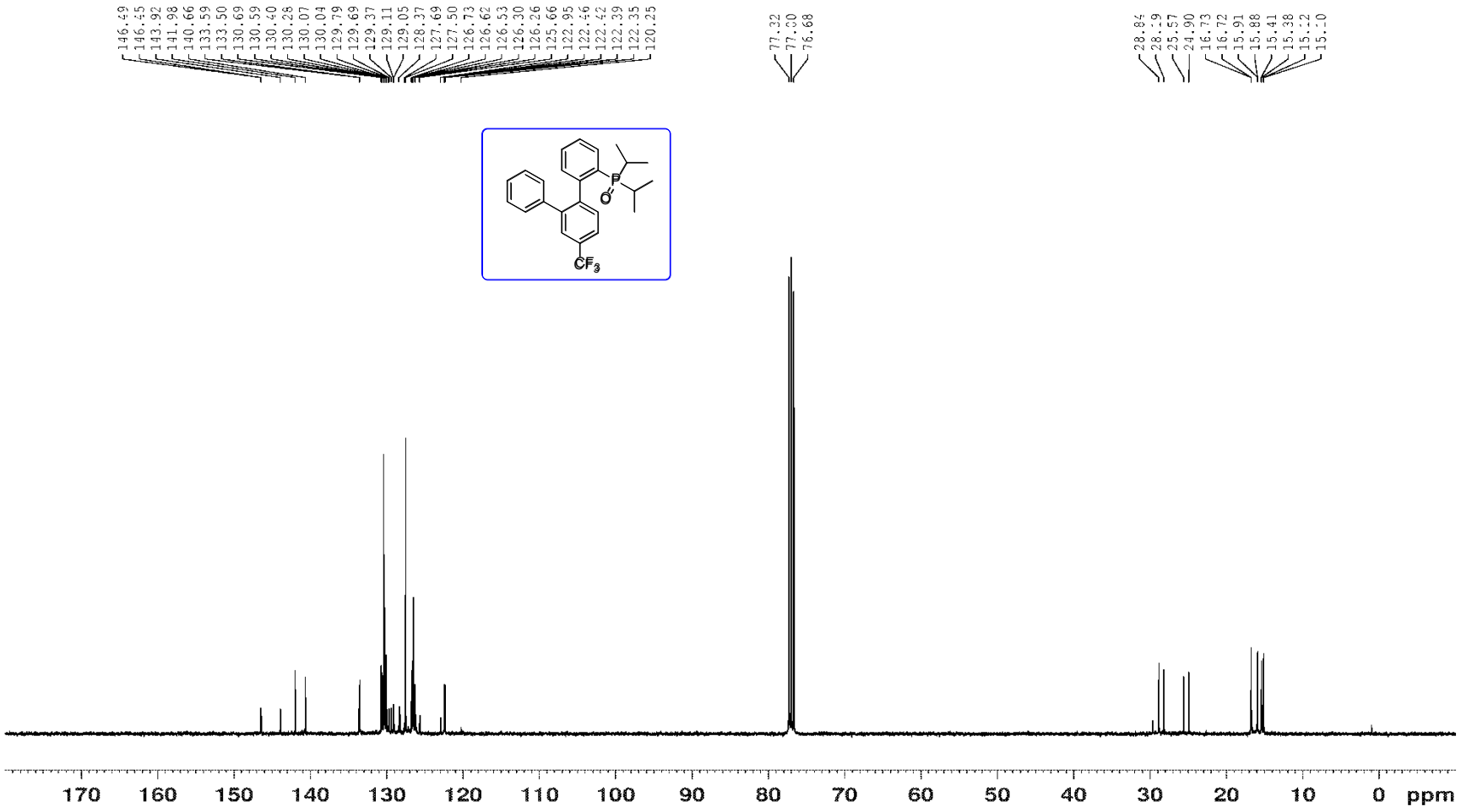

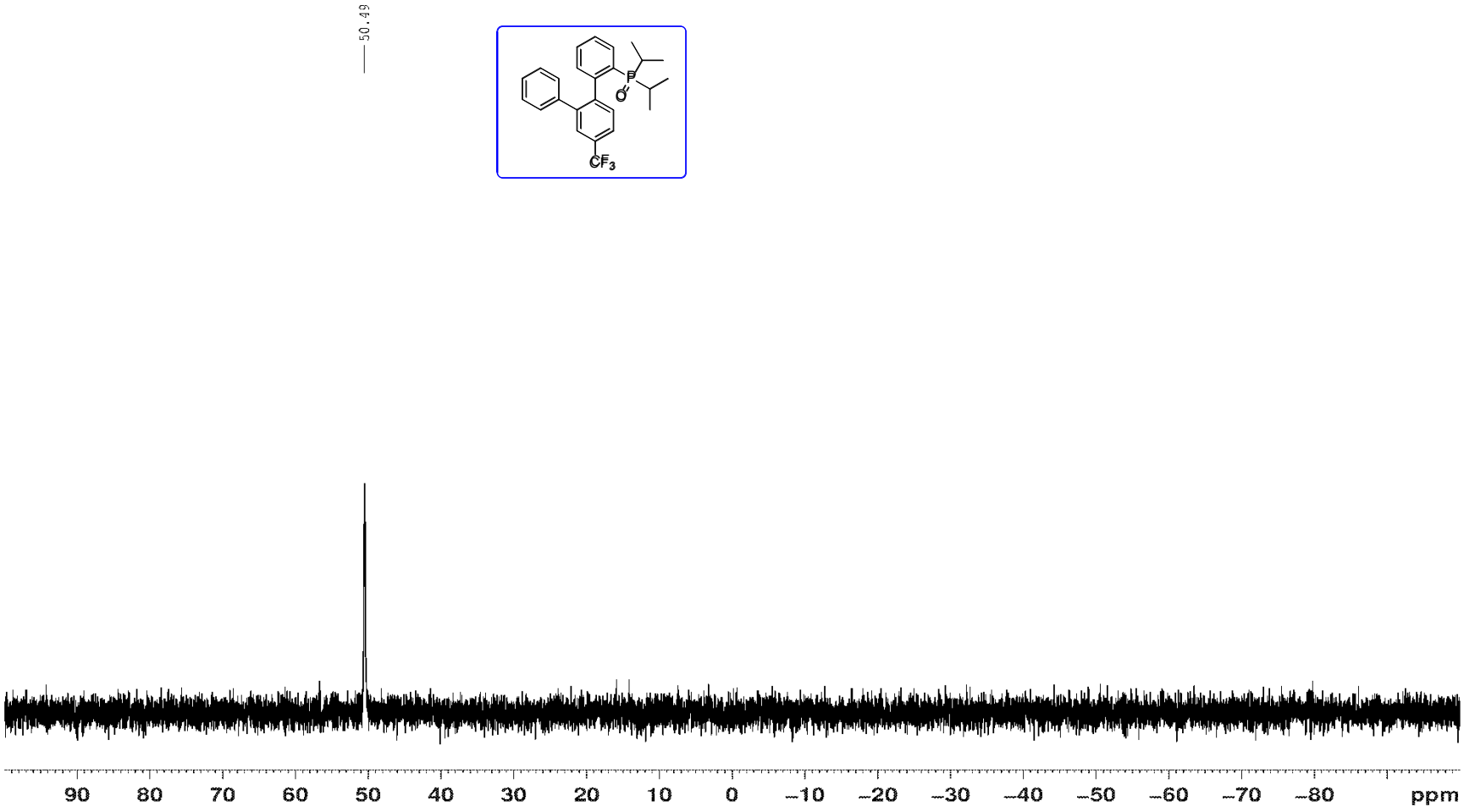

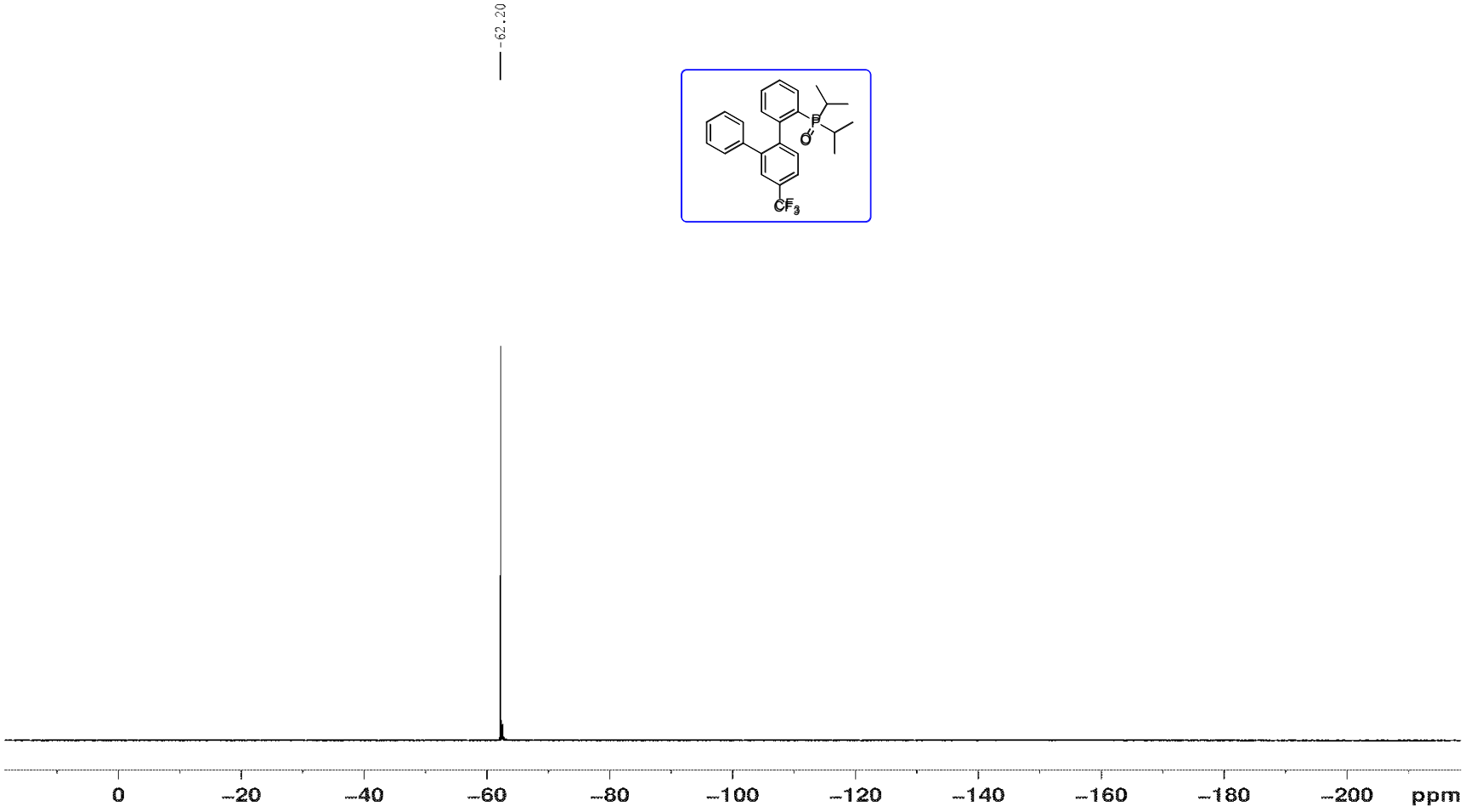

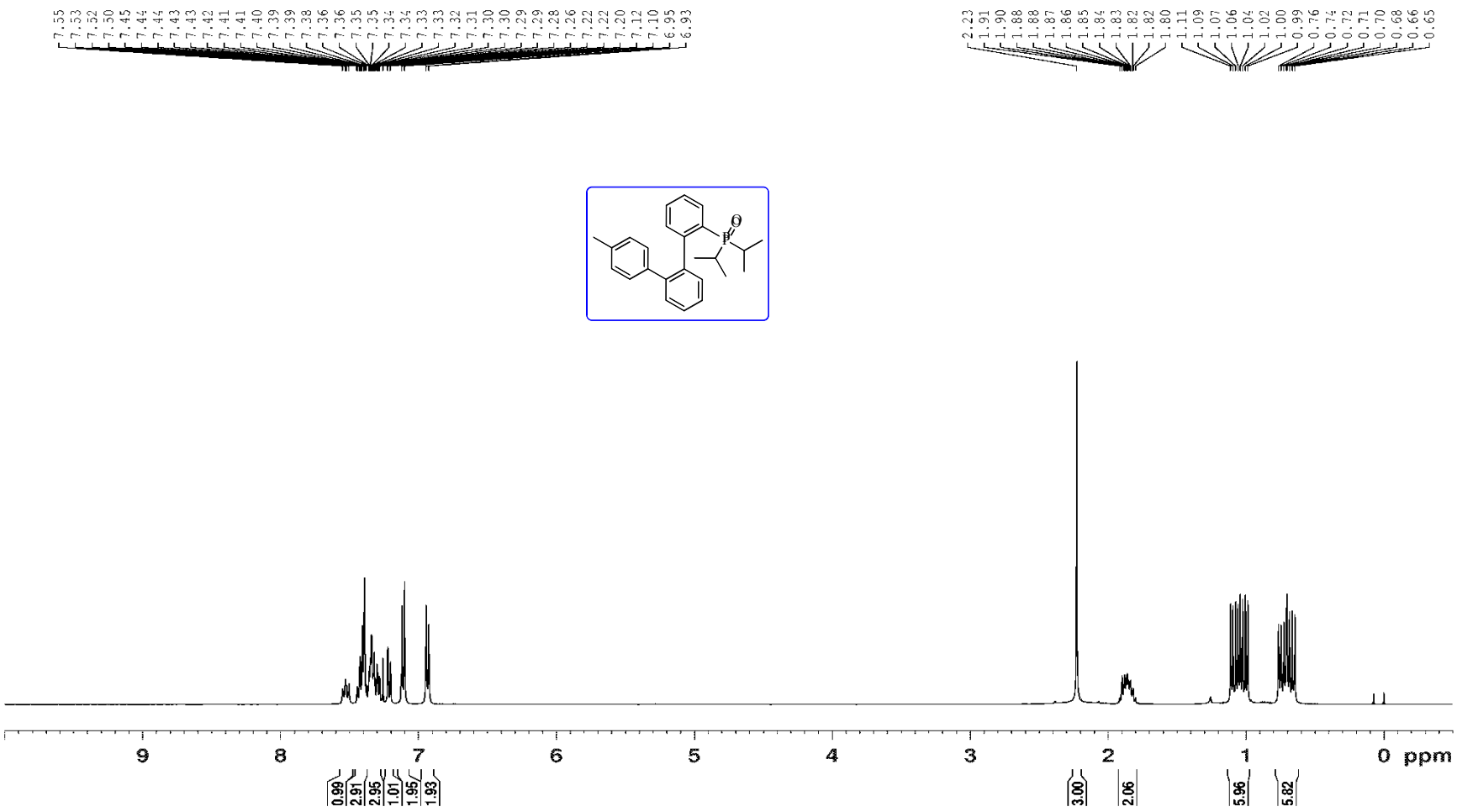
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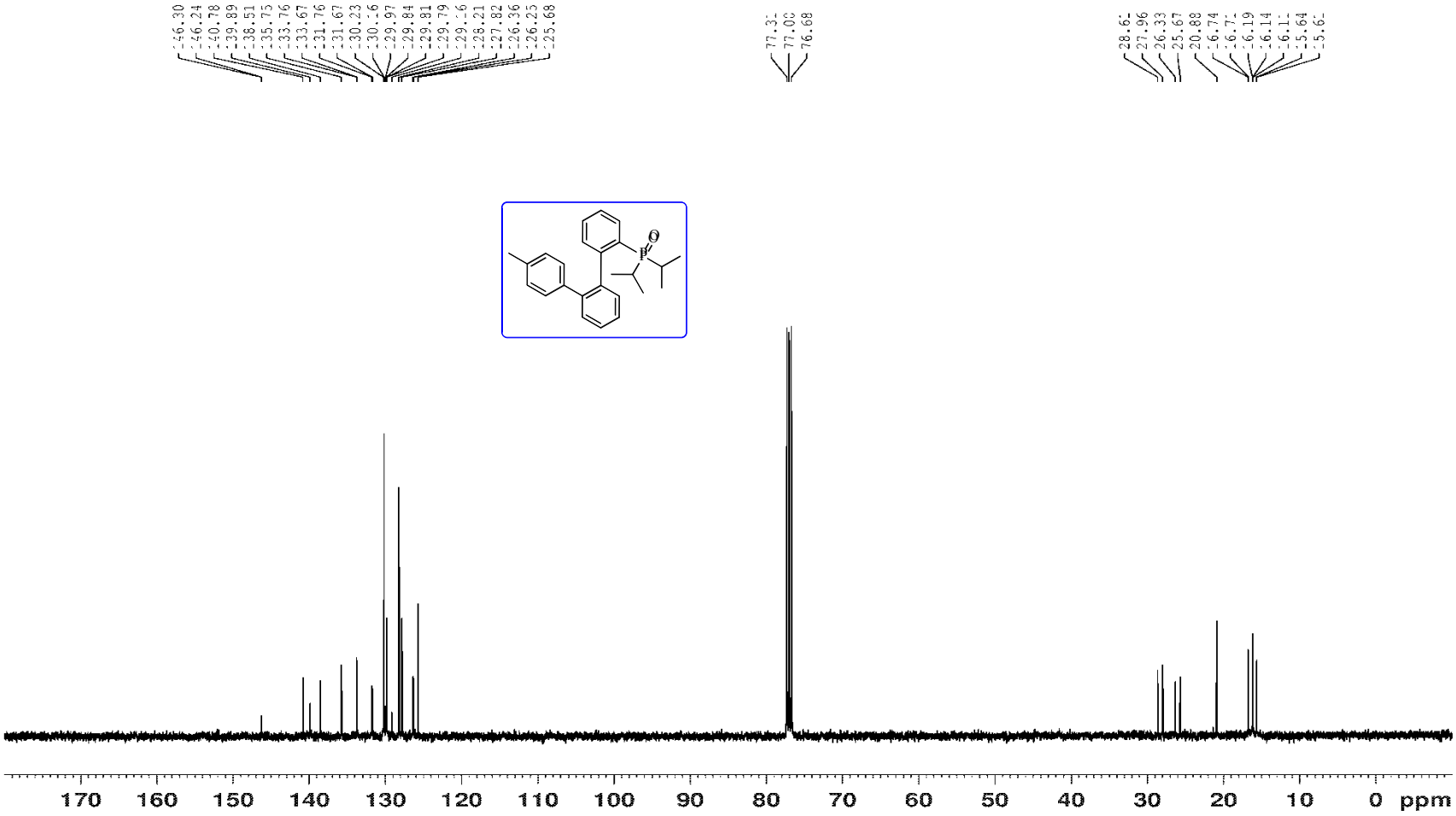

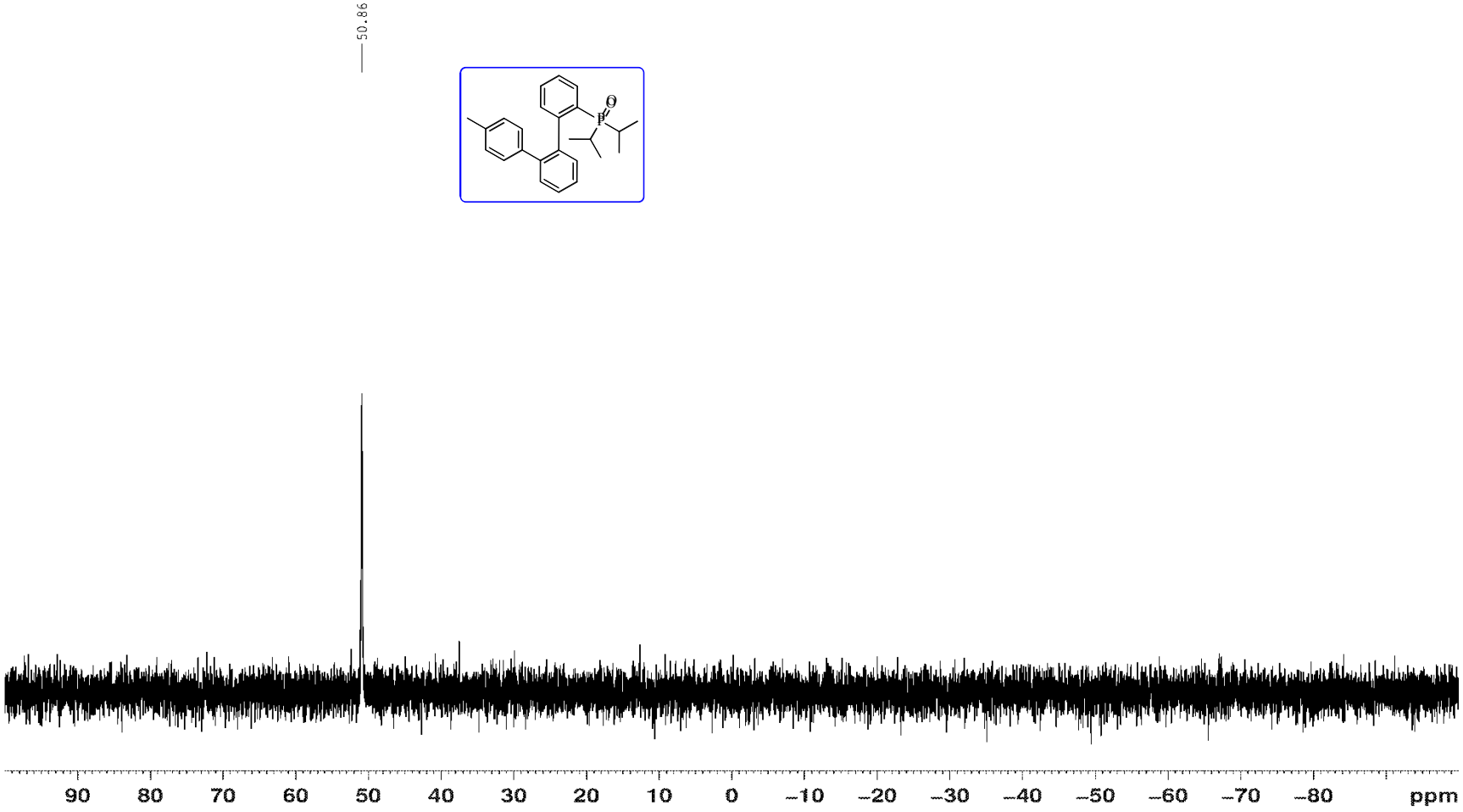

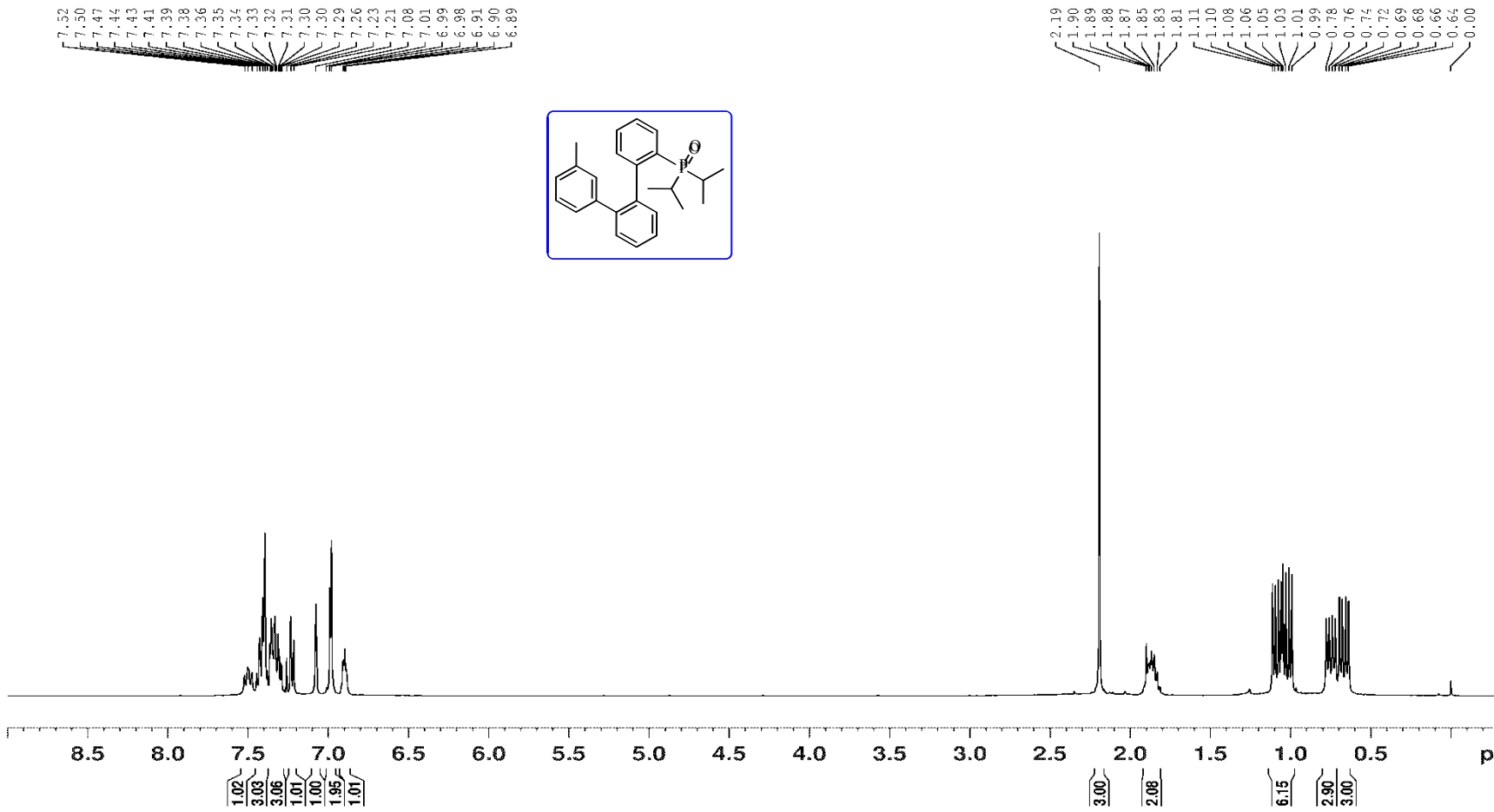

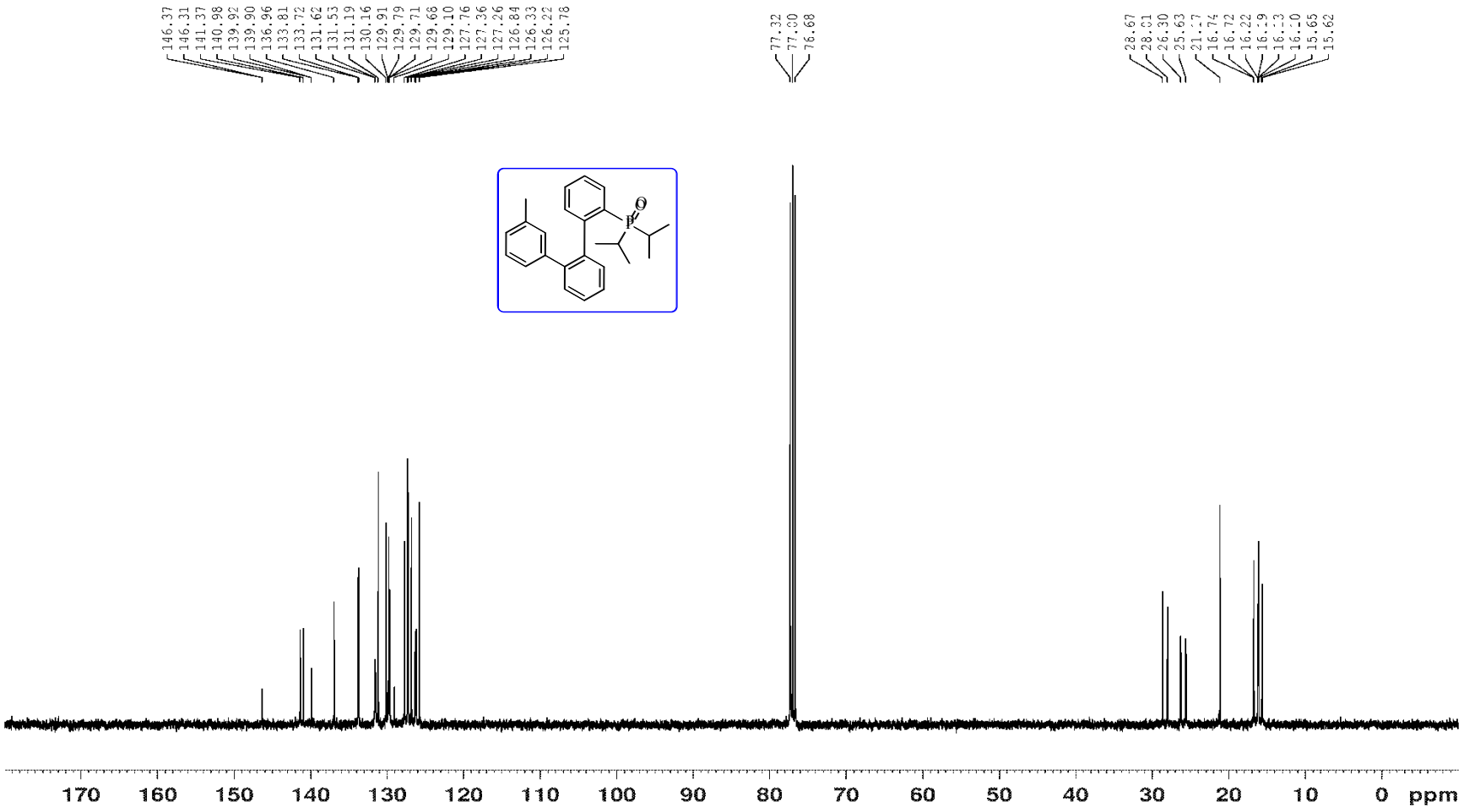
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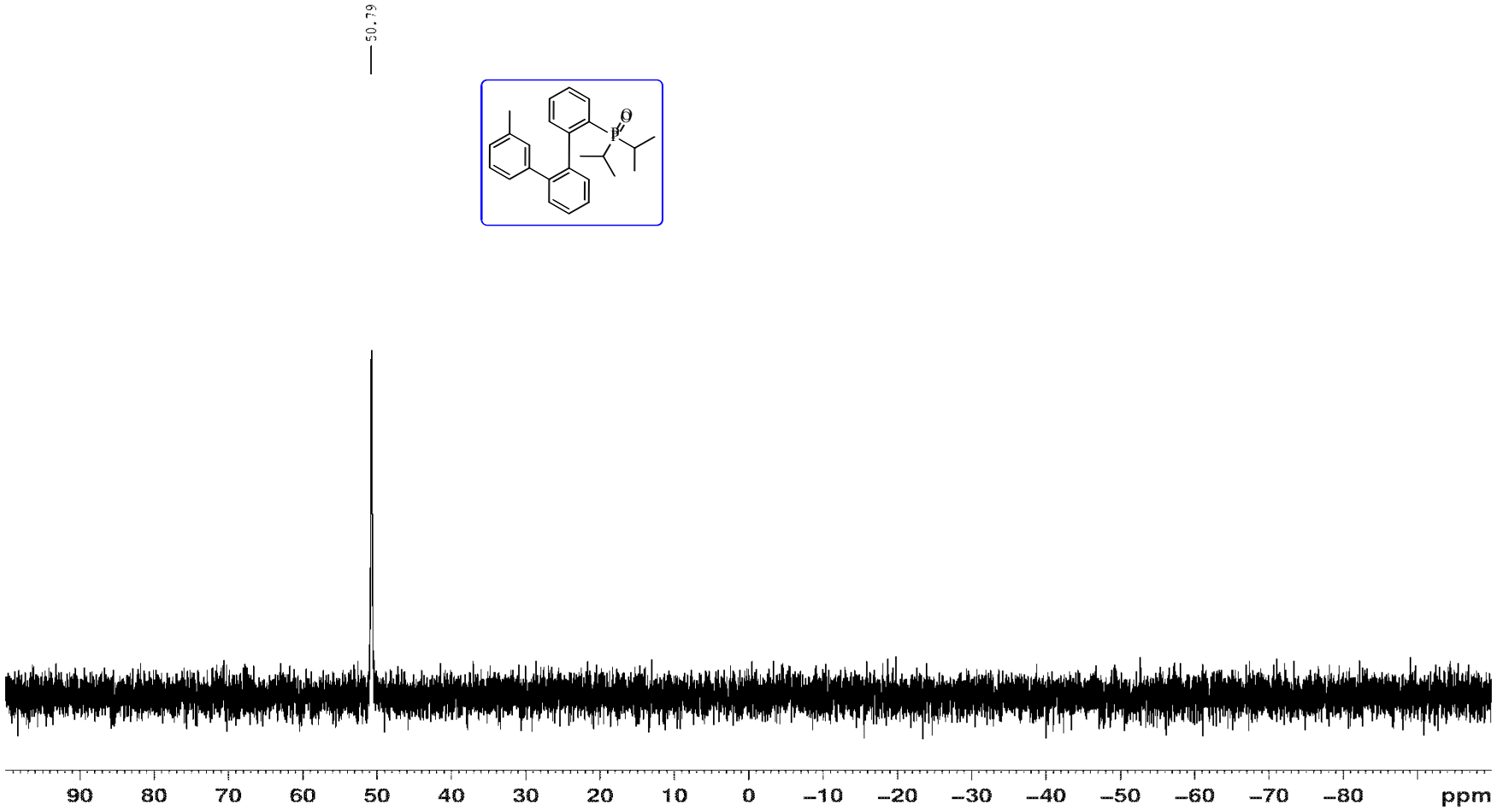

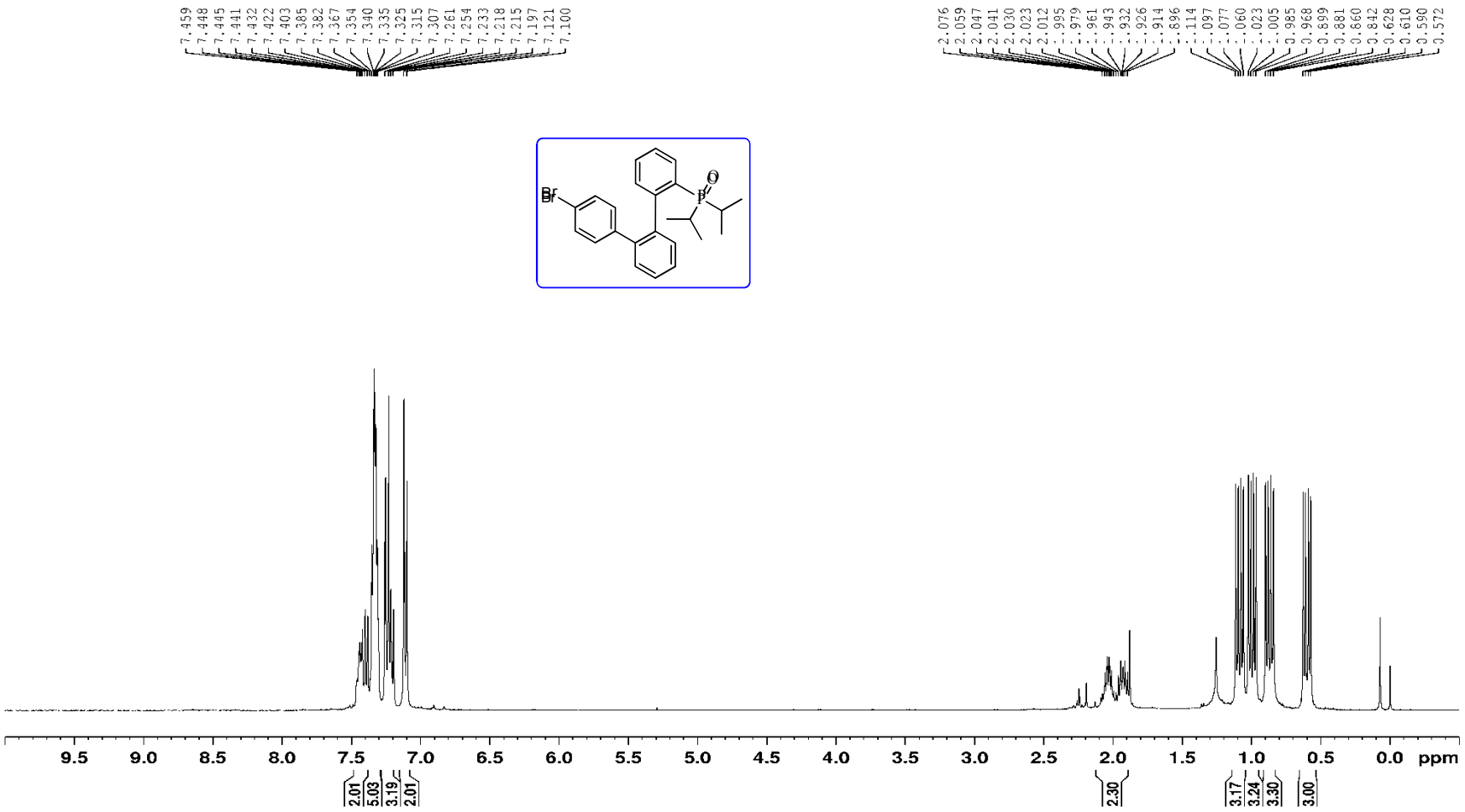

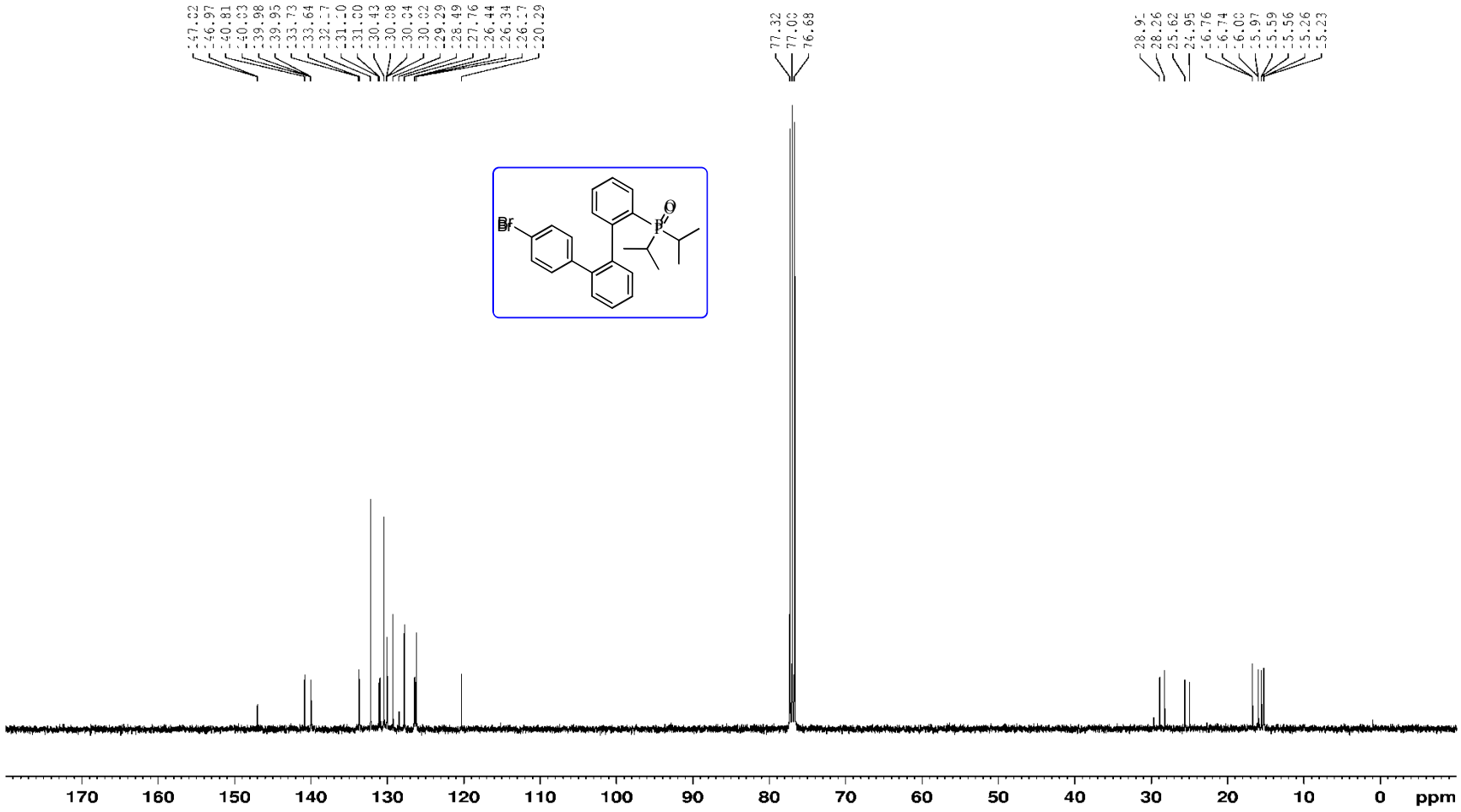
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24.95
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16.00
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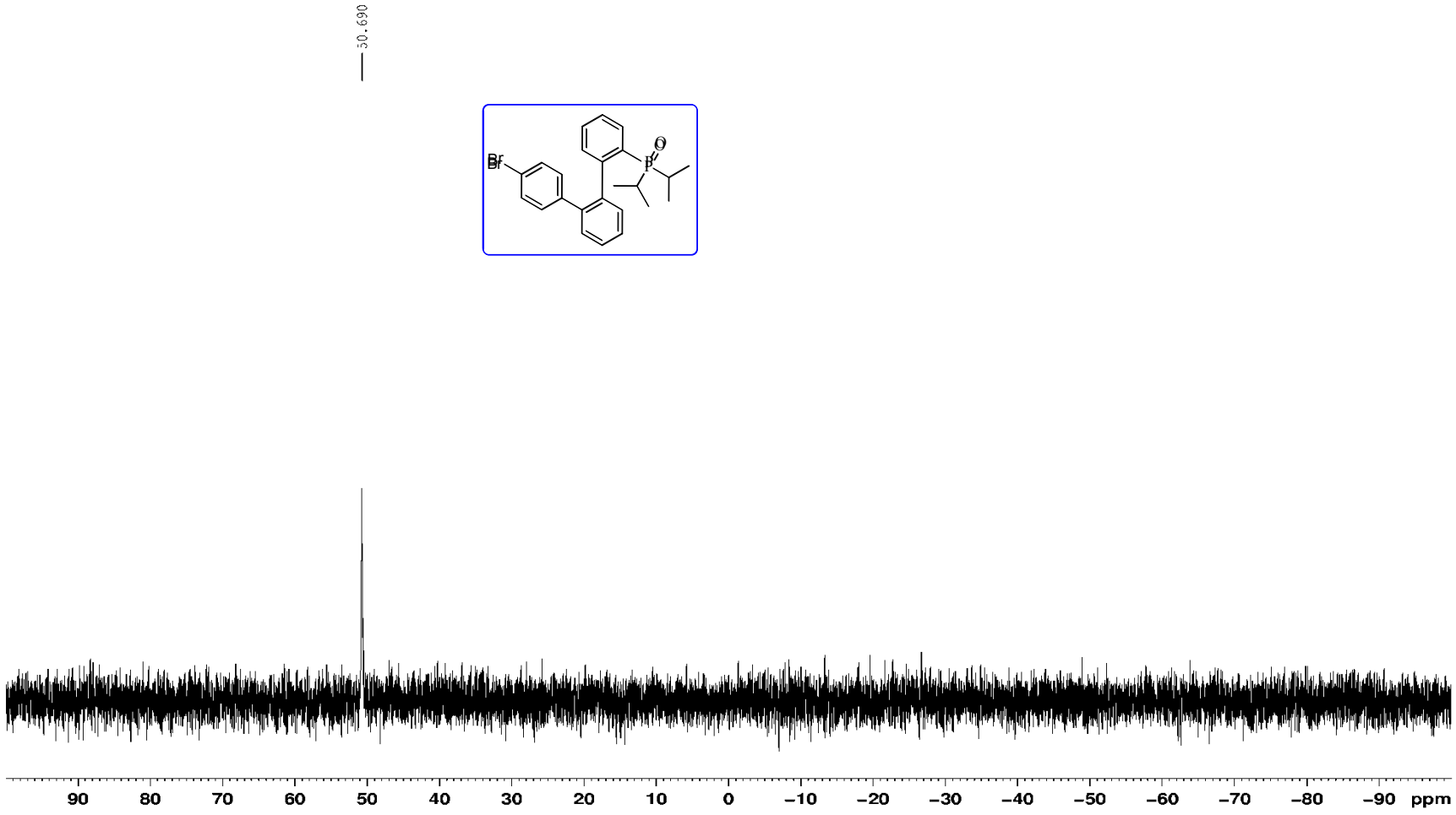
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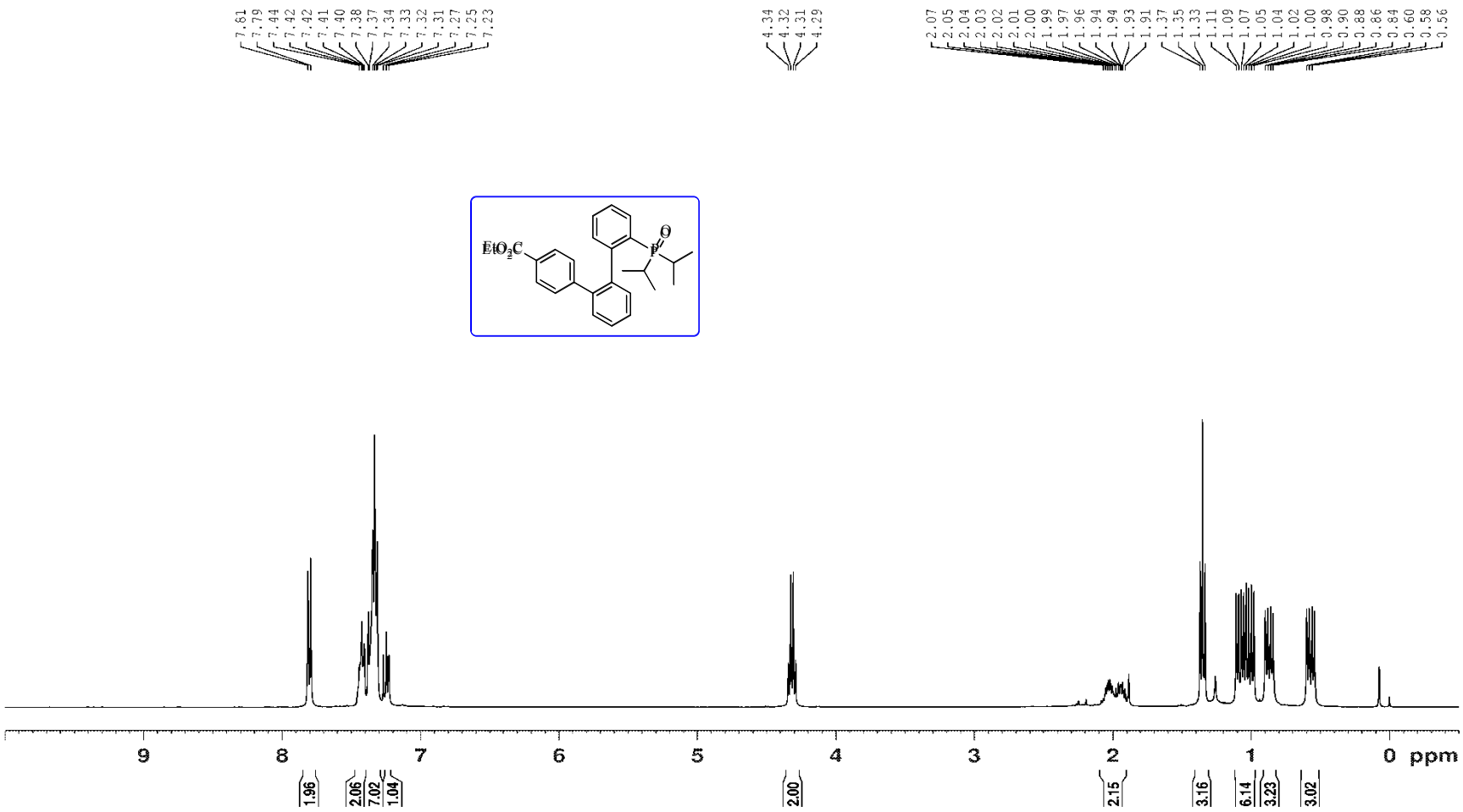
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2.04
2.03
2.02
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O
P
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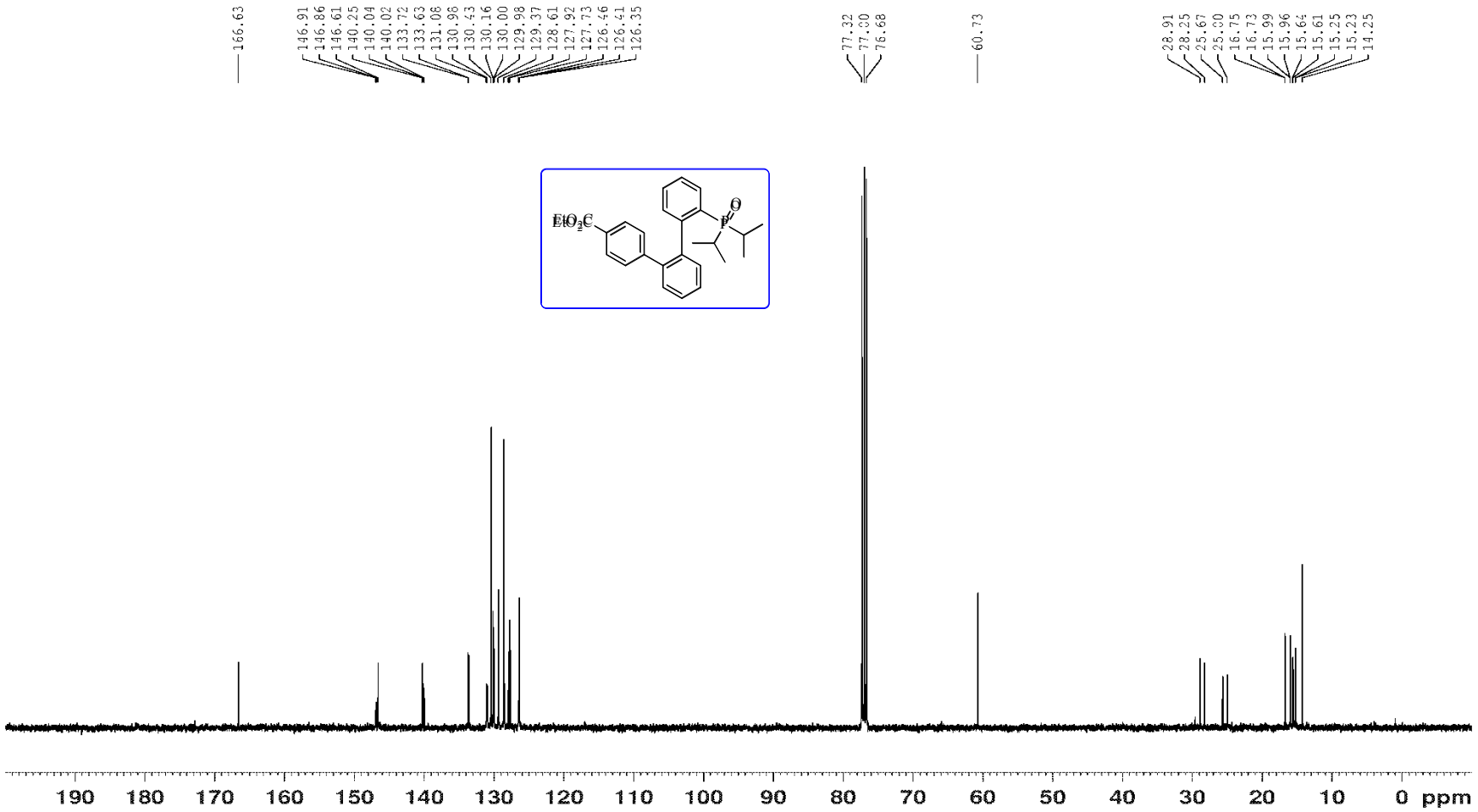

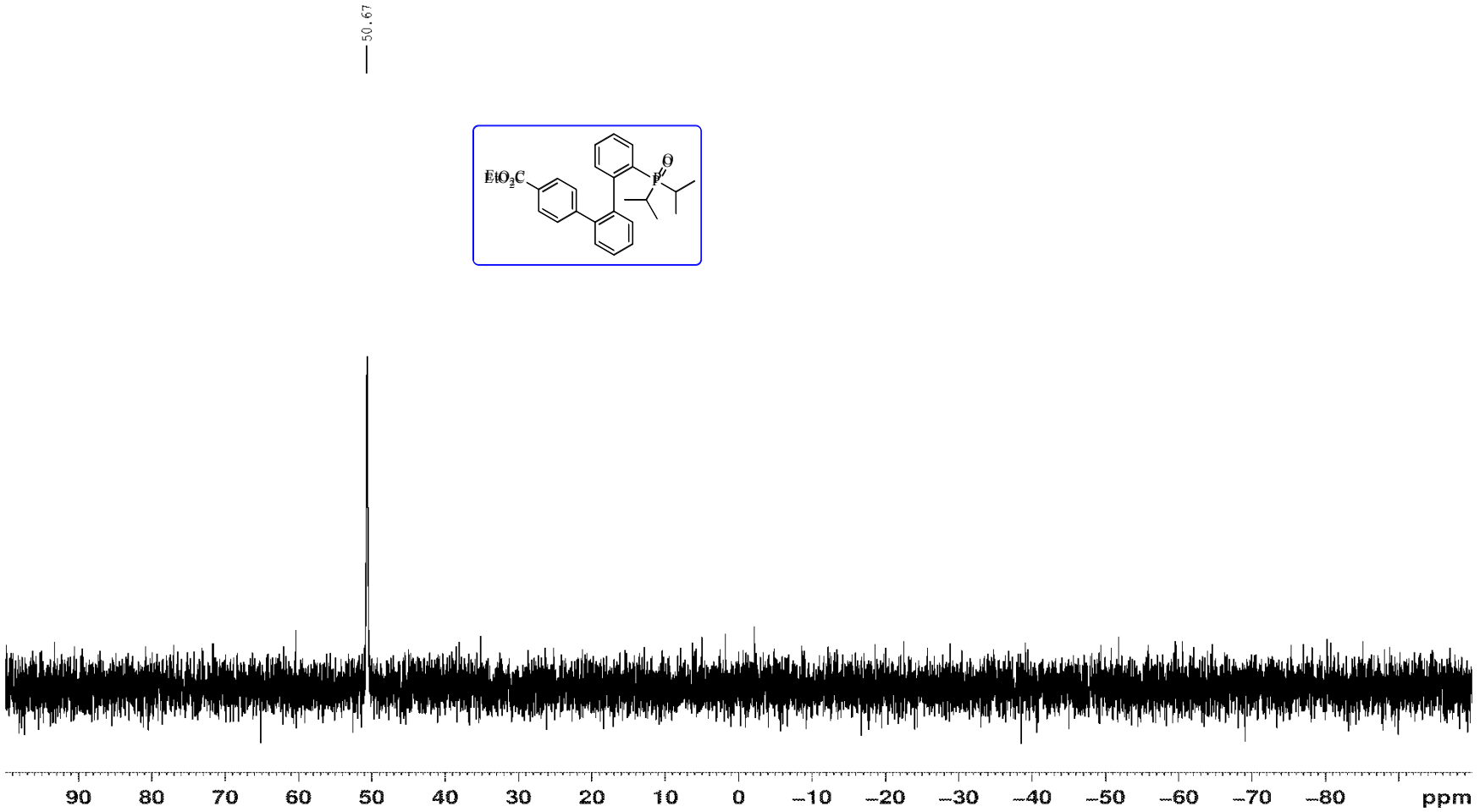

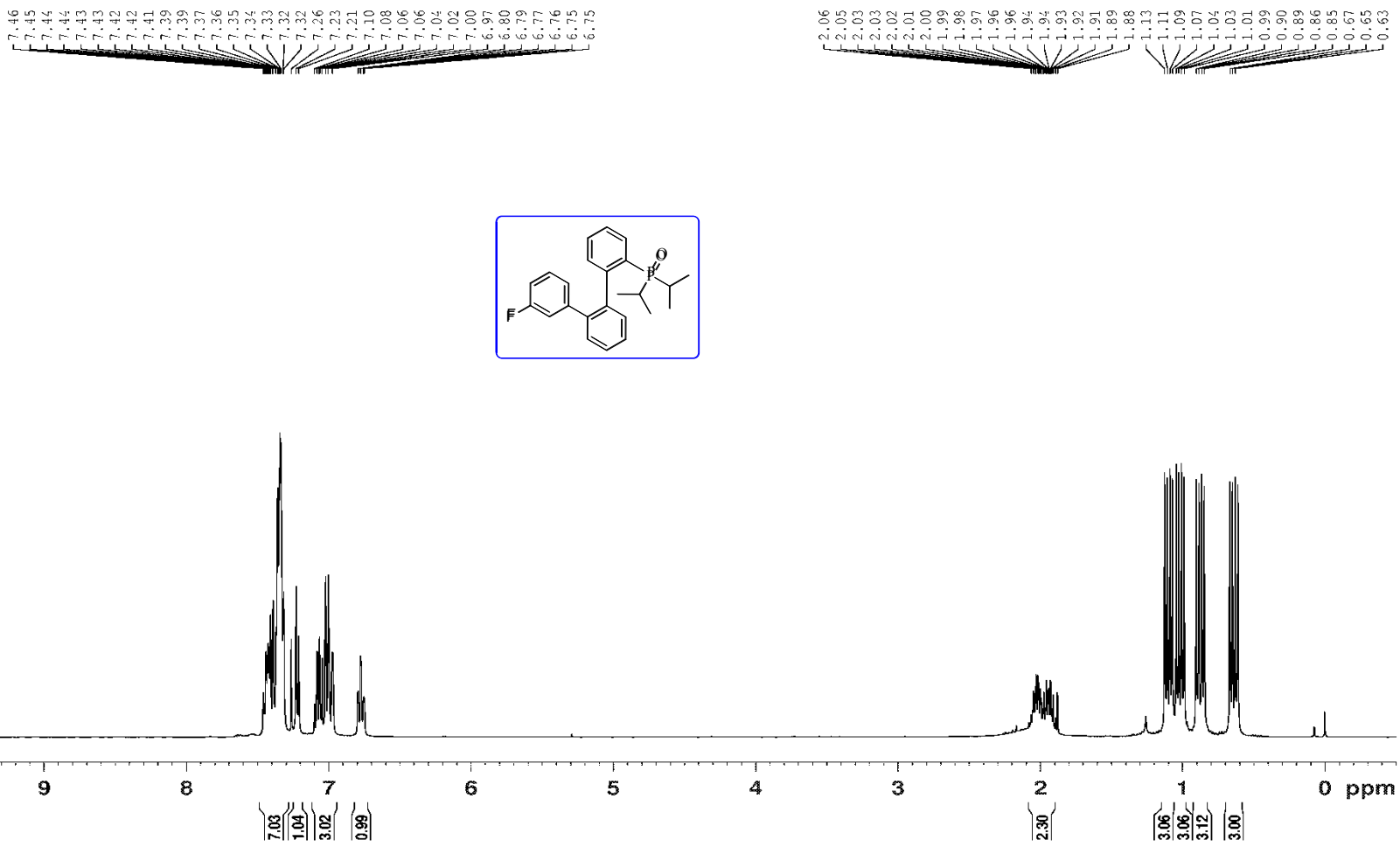
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P
F
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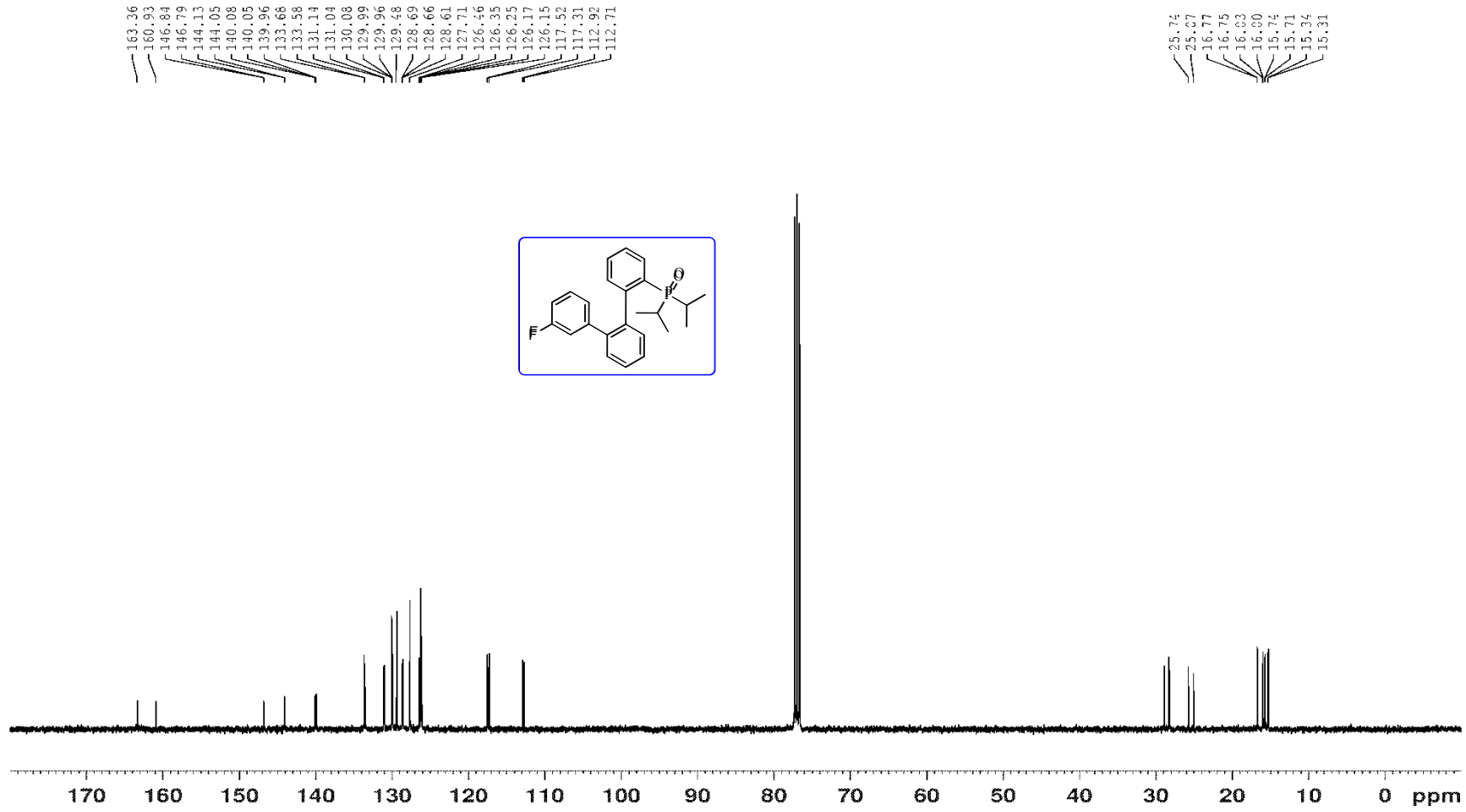

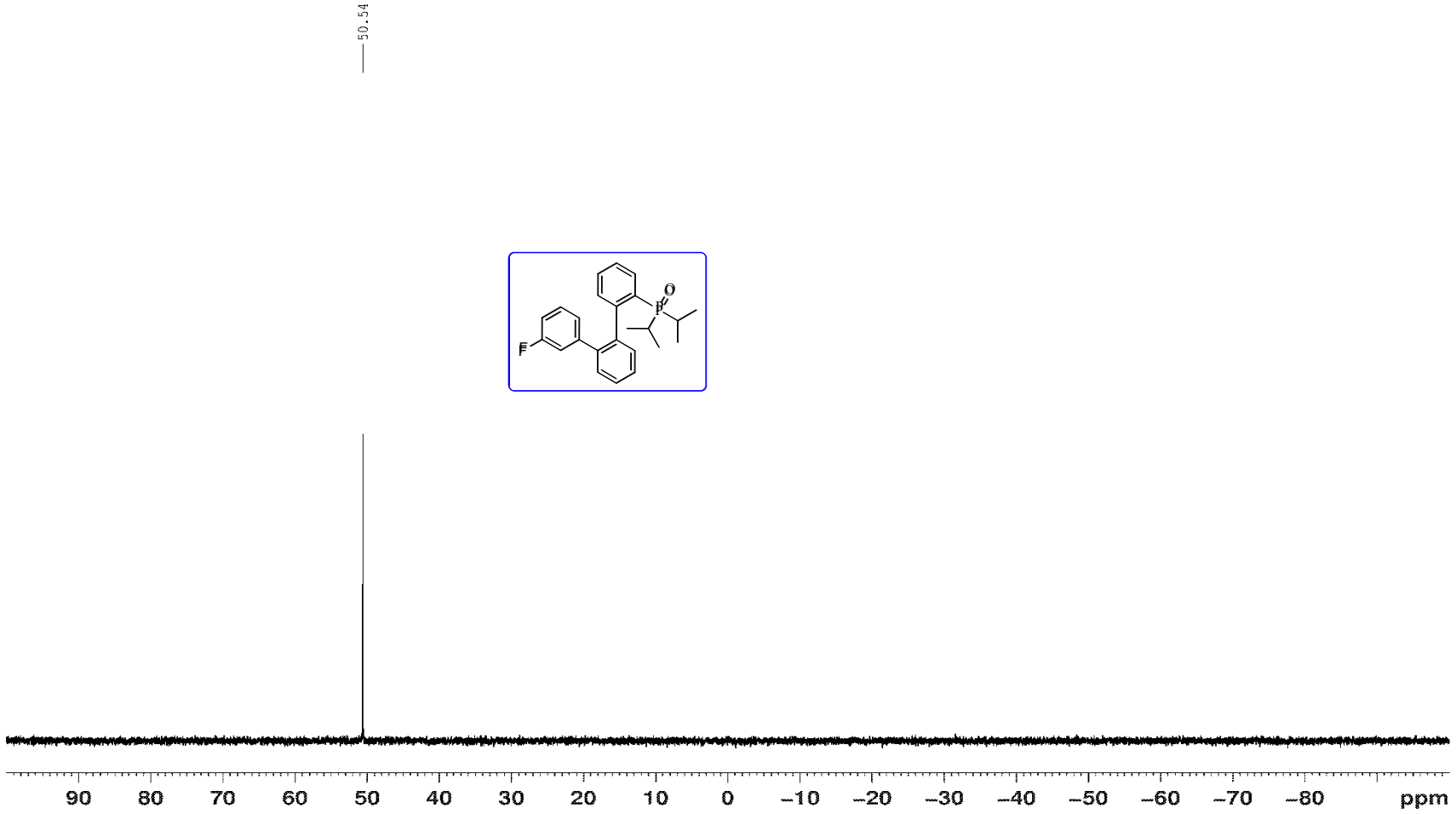

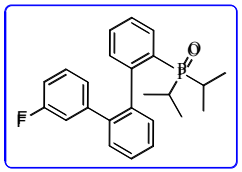

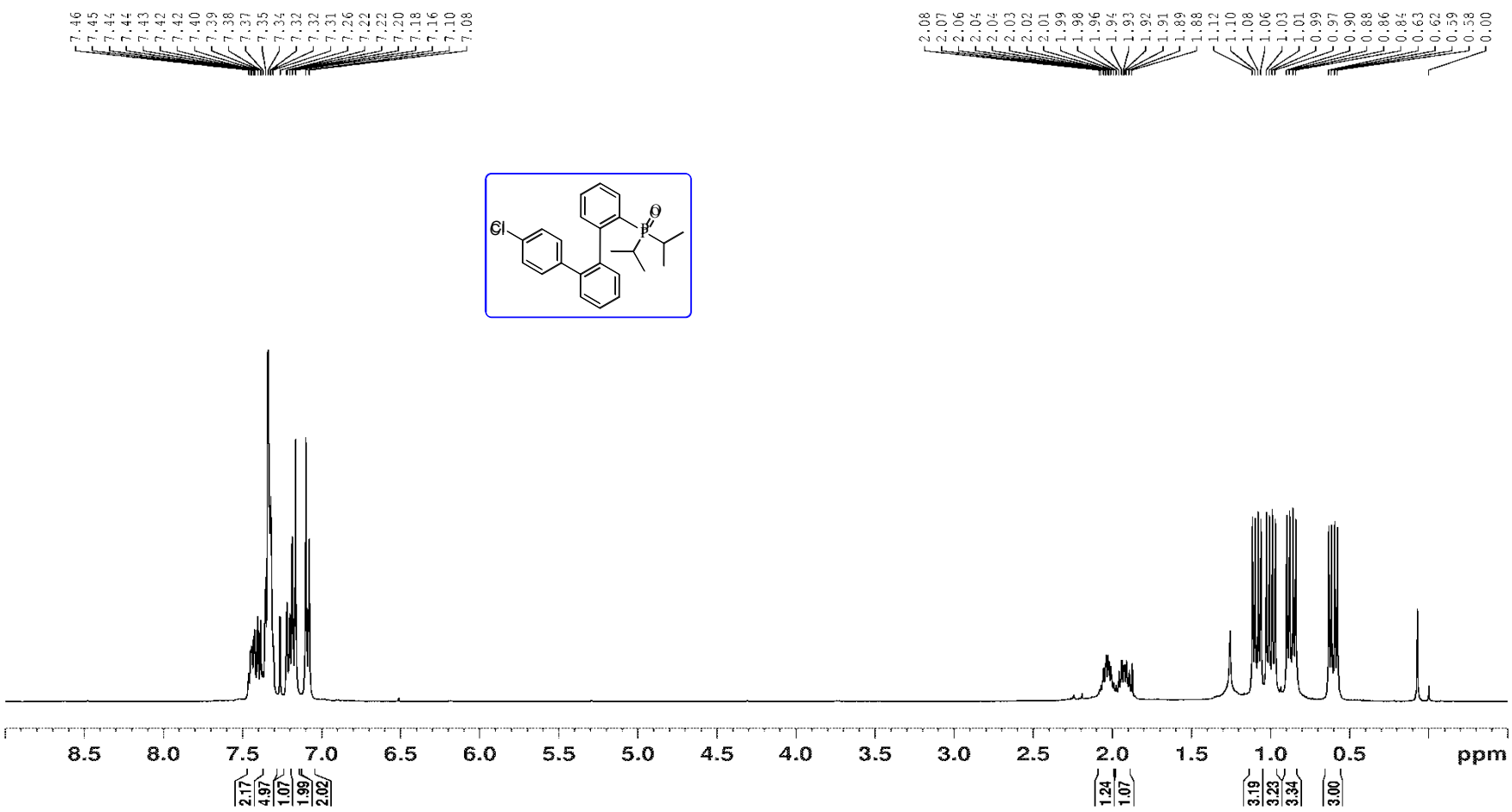

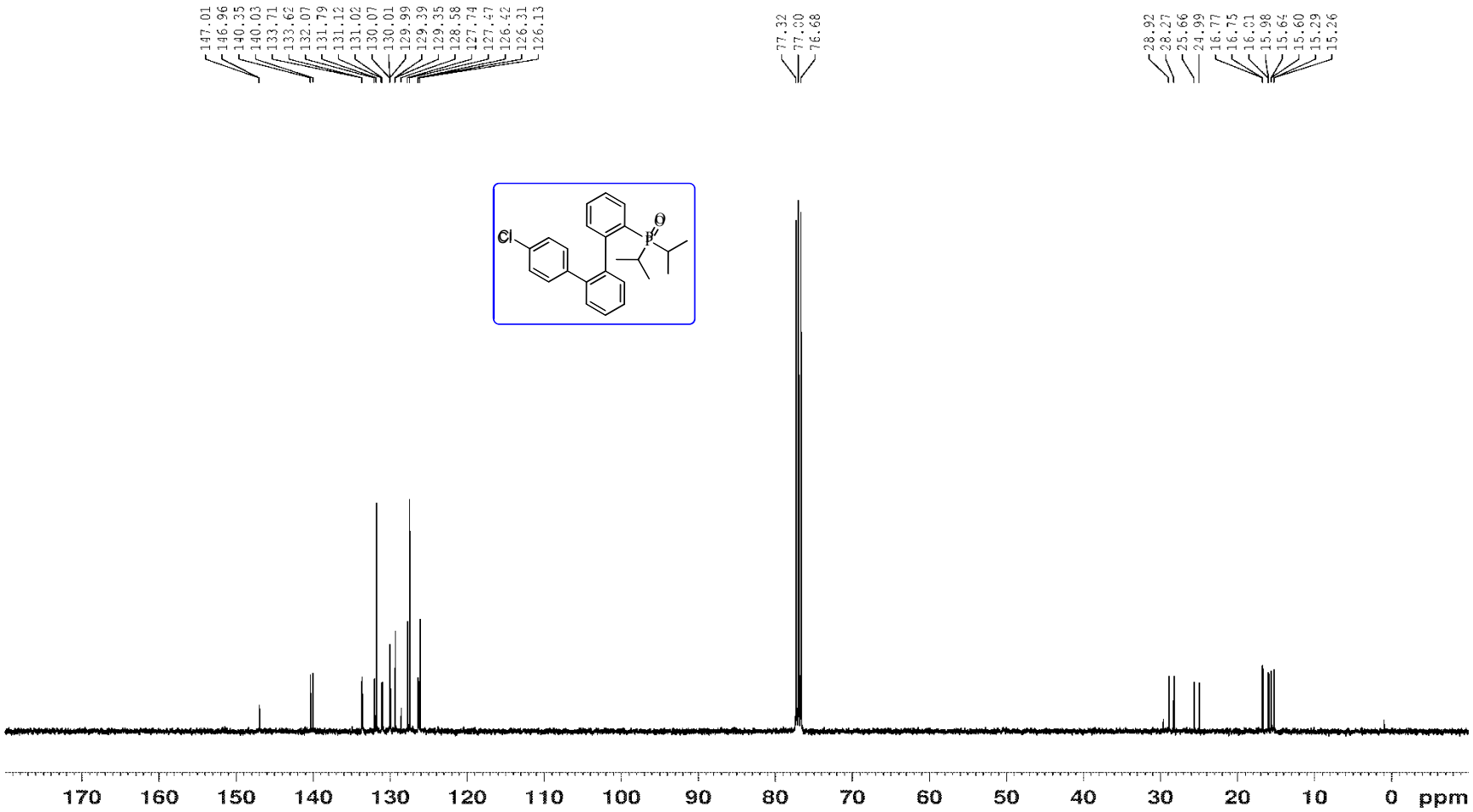

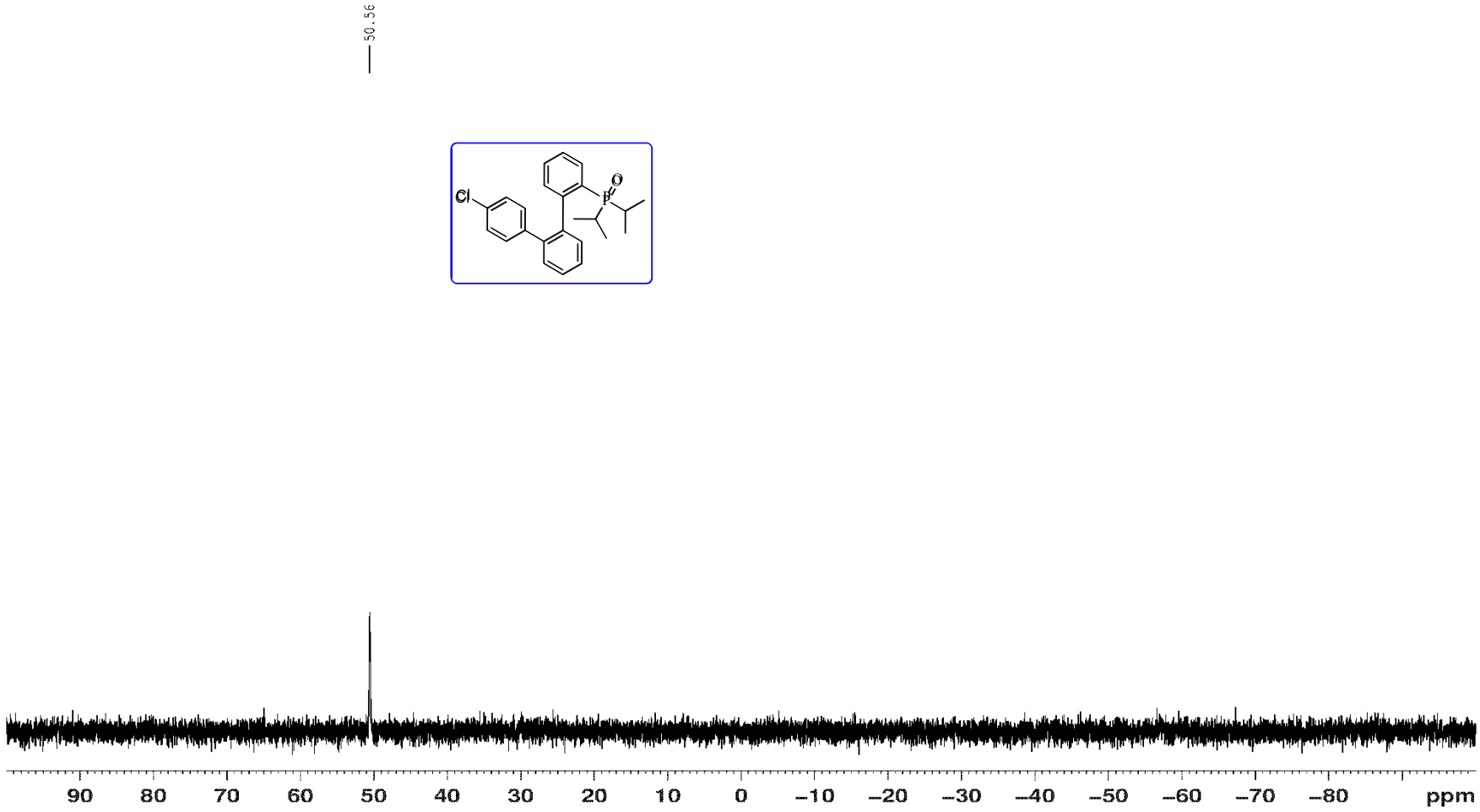

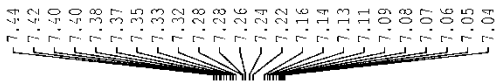

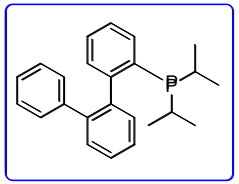

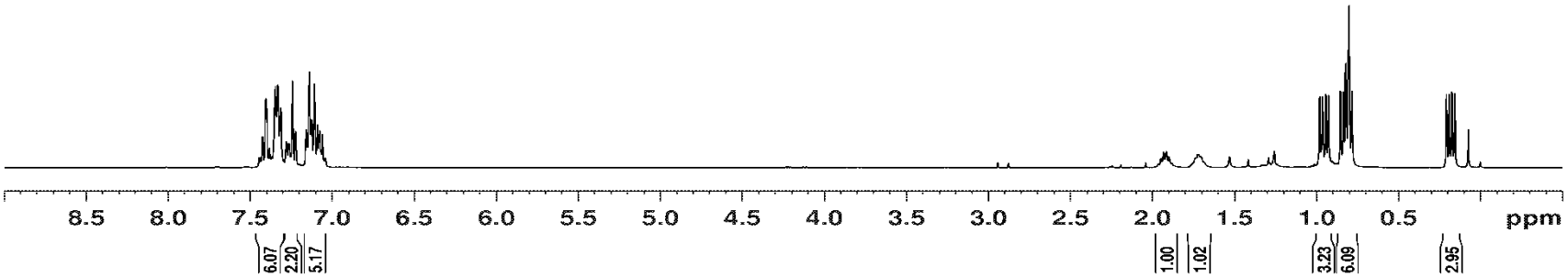

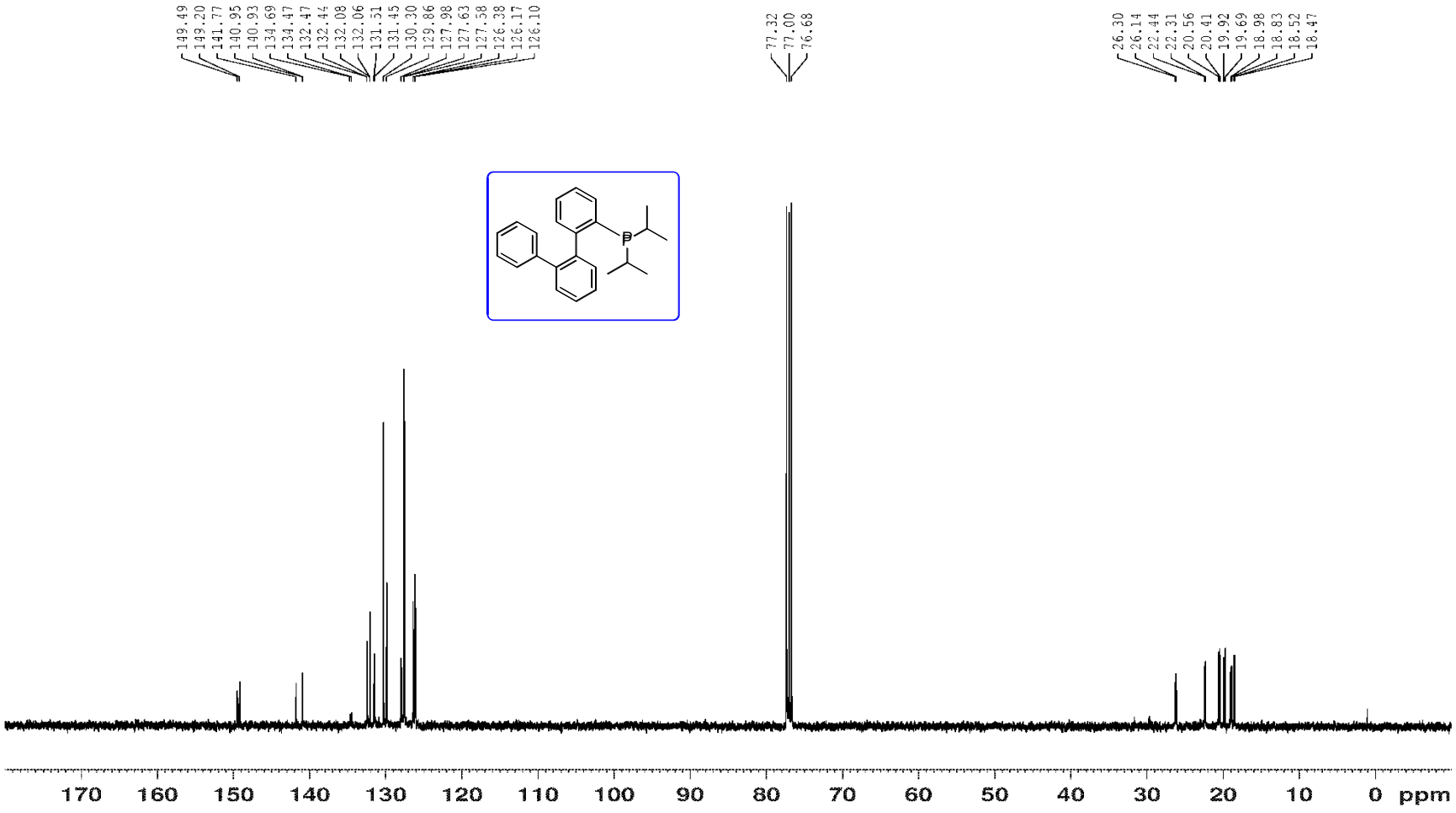

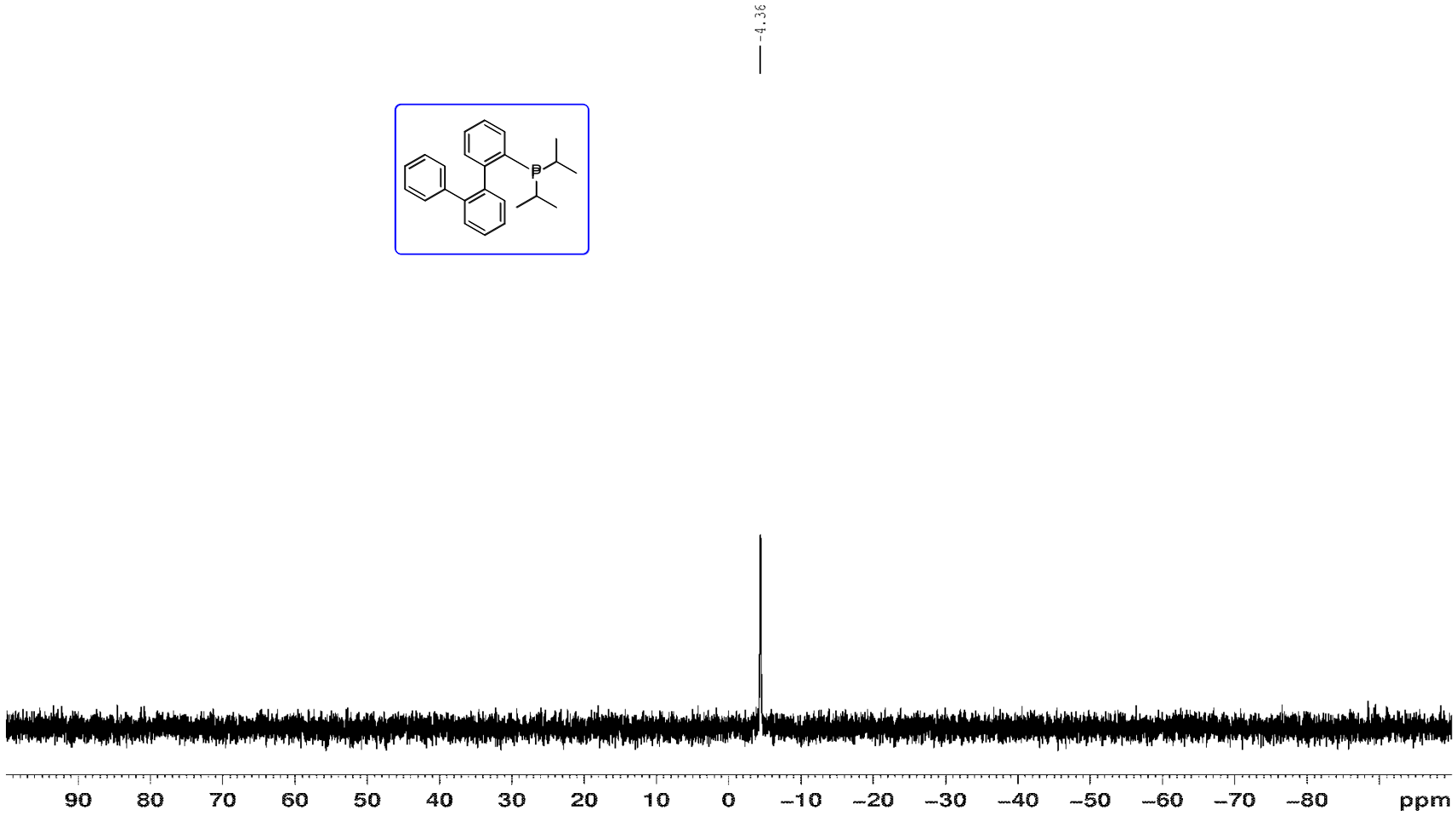

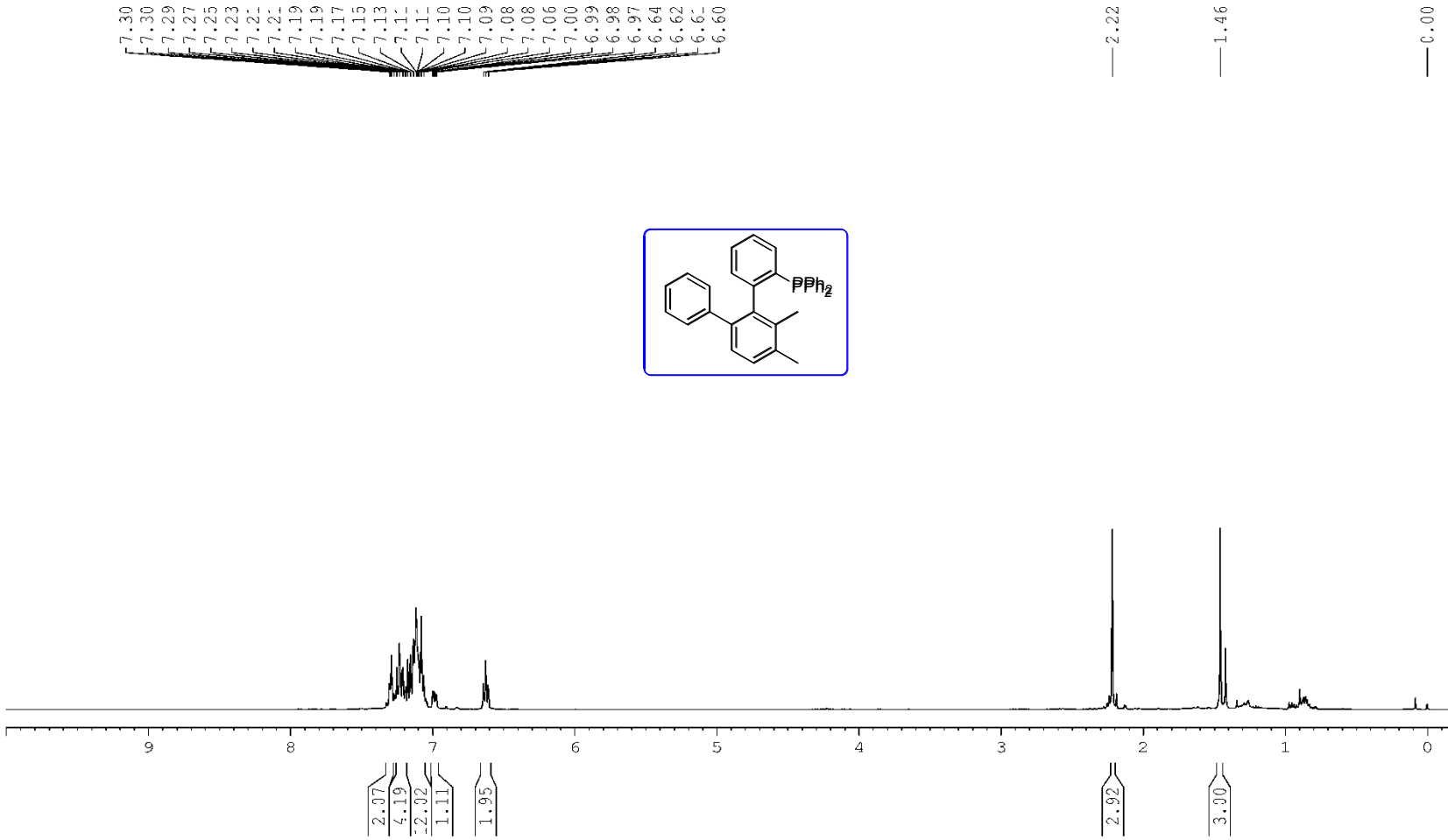
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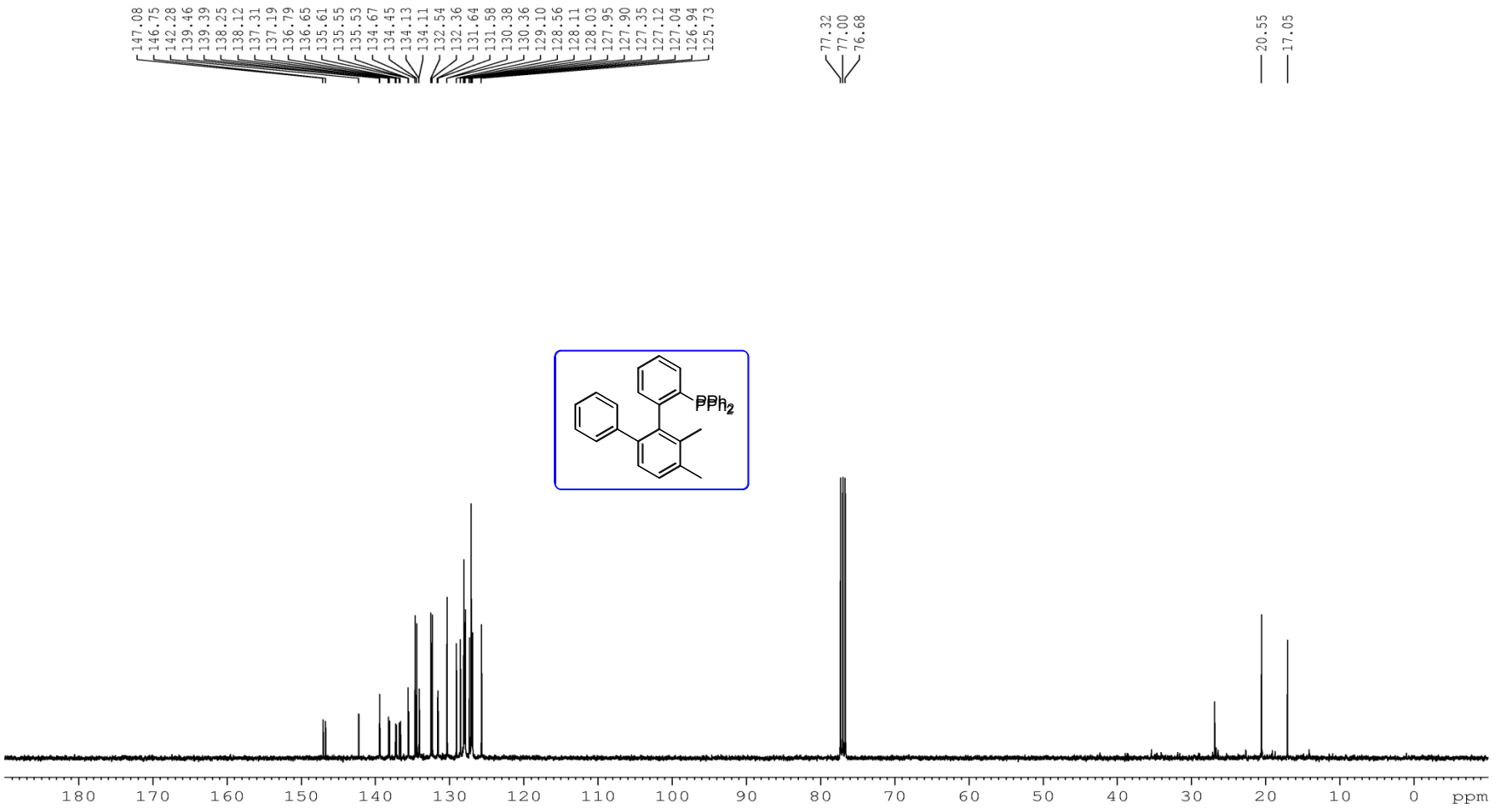
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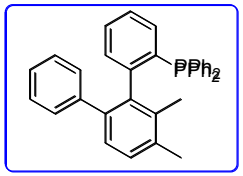

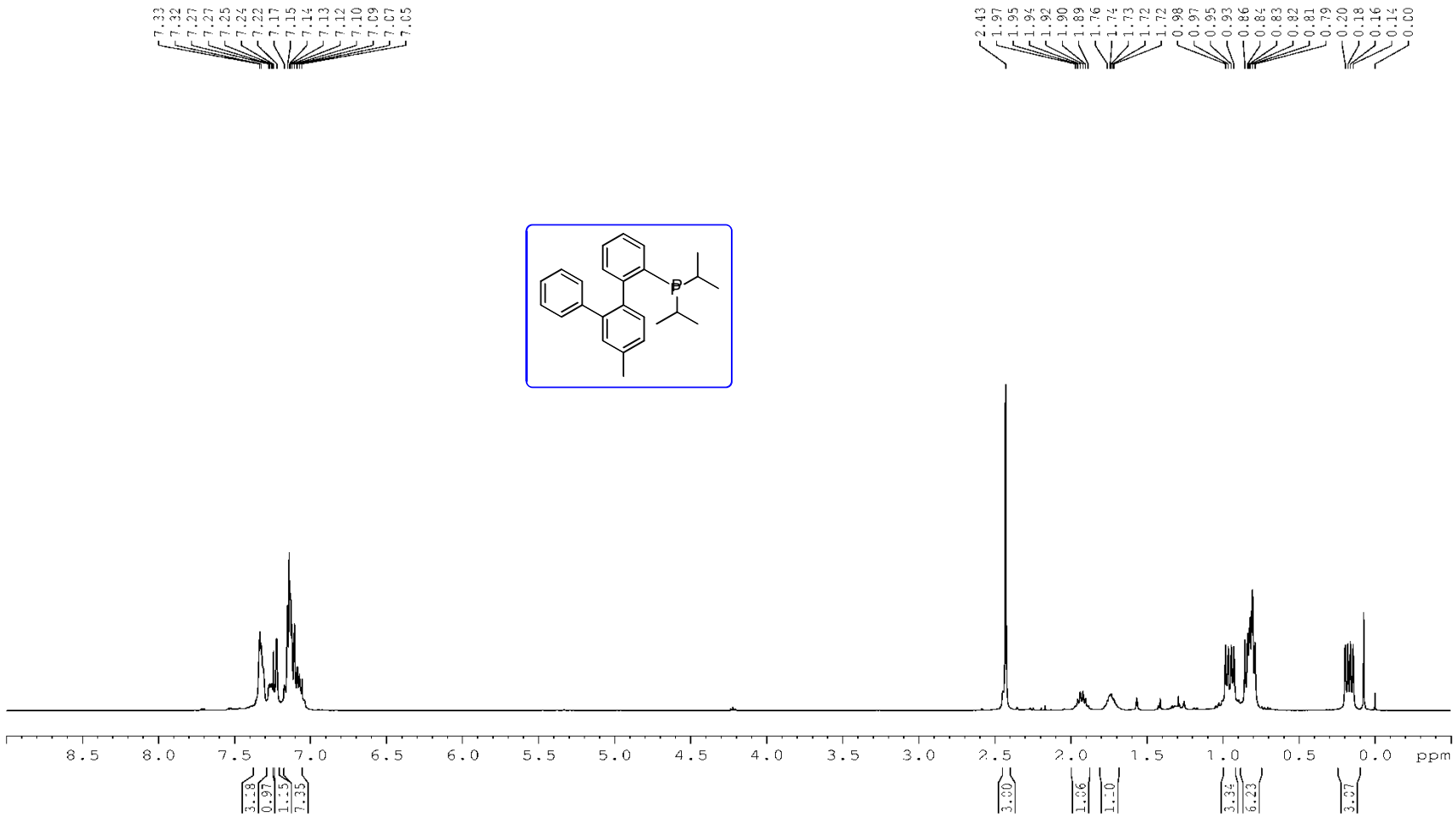

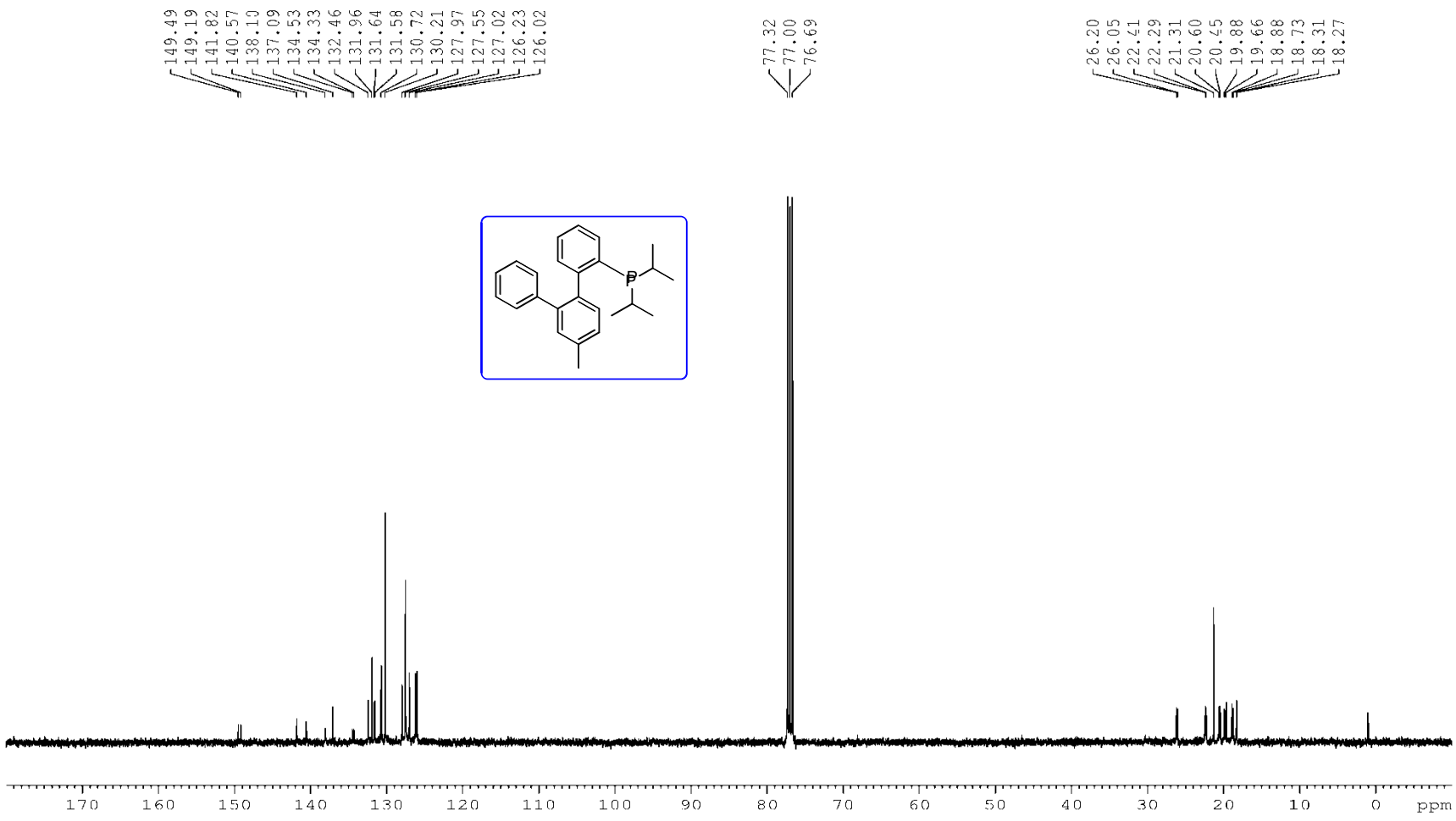

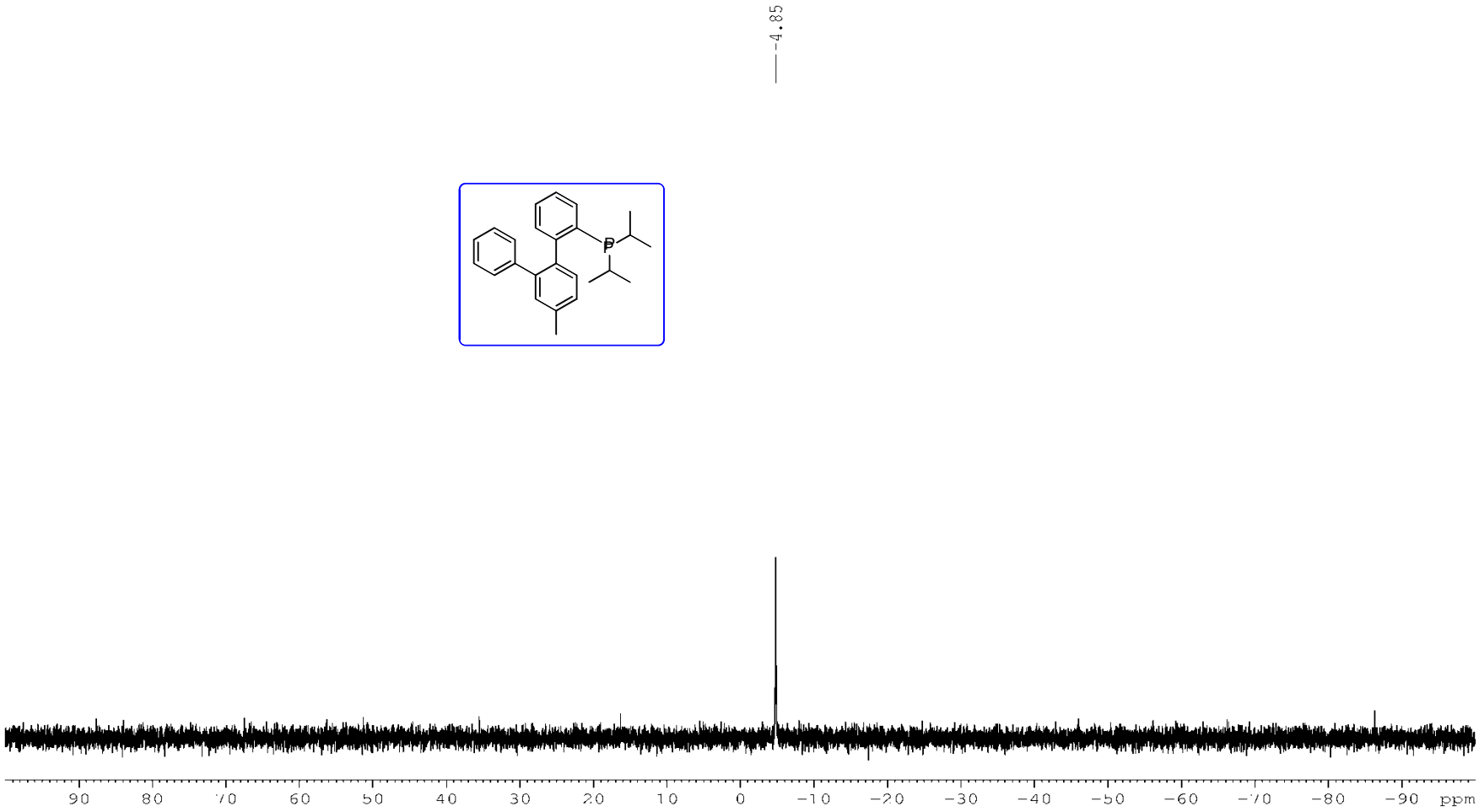

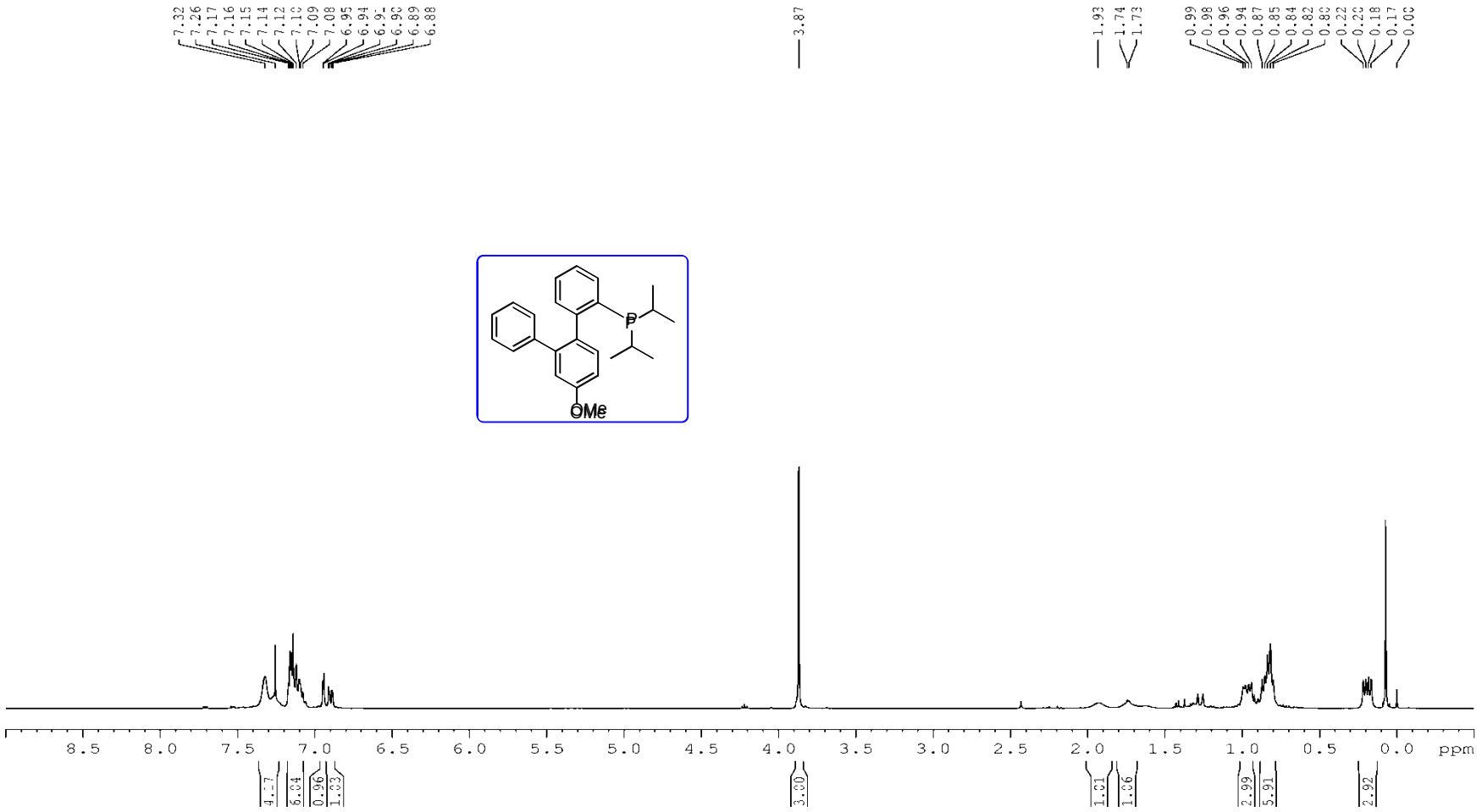
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OMe
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