Visible light photocatalytic C(sp^3)–H phosphorylation of xanthenes and 9,10-dihydroacridines with P(O)–H compounds

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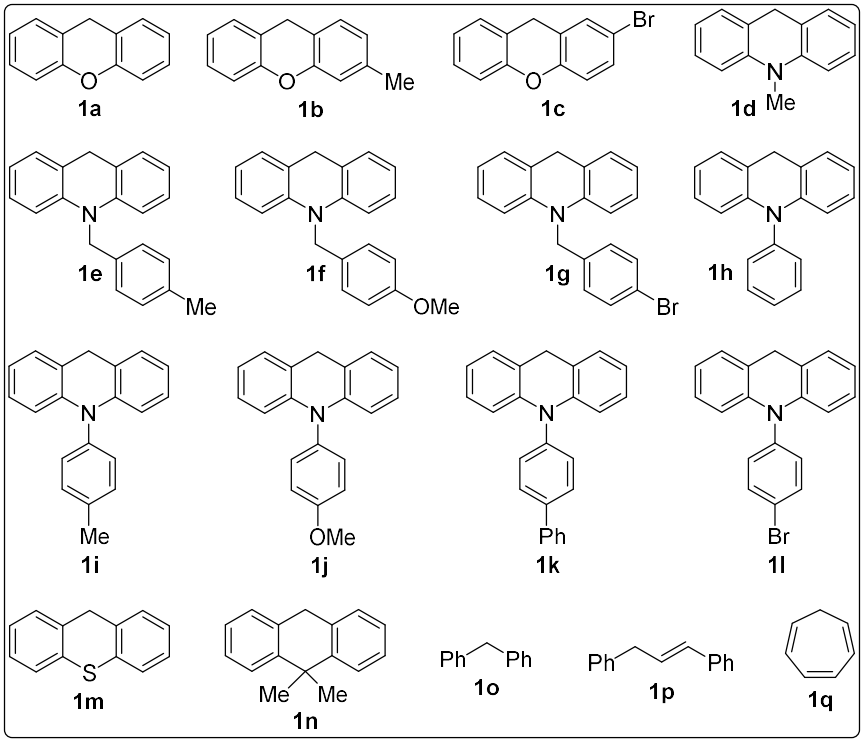
SUPPORTING INFORMATION

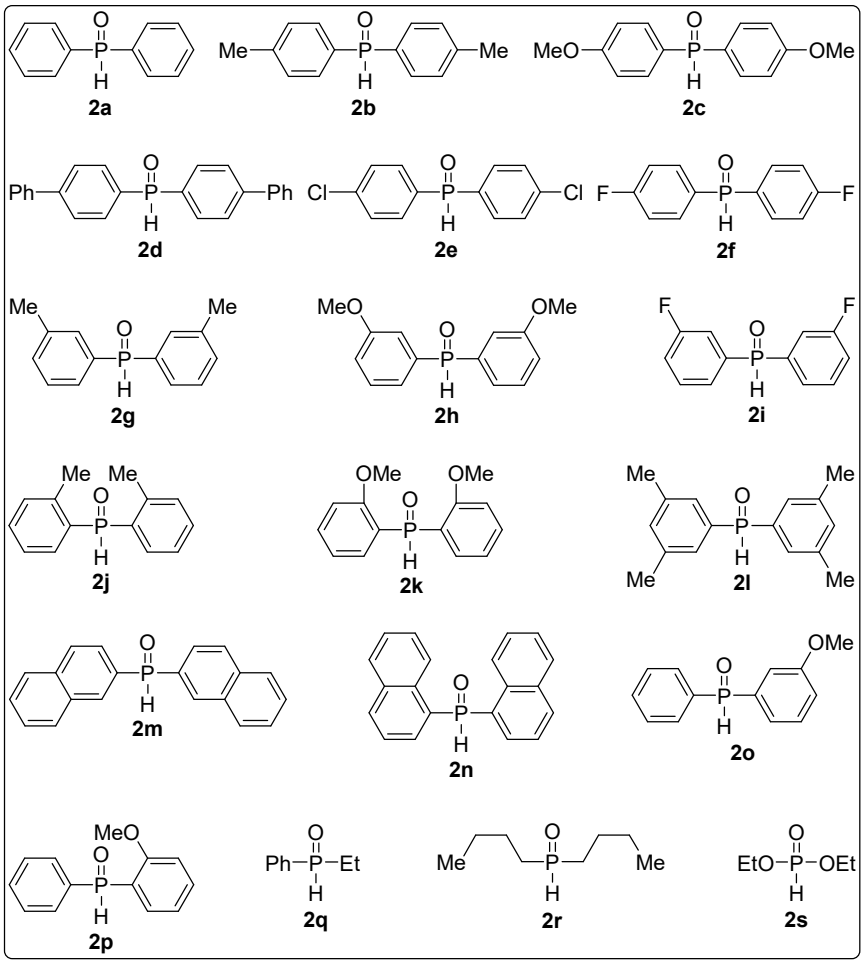
Content:

1. General Information

Unless otherwise stated, commercially available reagents including dry solvents were used without additional purification. Petroleum ether refers to the bp 60–90 °C petroleum fraction. Secondary phosphine oxides which were not commercially available were prepared according to the literature.[1] Xanthenes were prepared according to the literature.[2] 9,10-Dihydroacridines were prepared according to the literature.[3] The instrument for photocatalysis was a PR-PCR2-450 nm instrument with no filters (Shenzhen Purui Material Technology Co., Ltd.). The reaction vessel was a Schlenk borosilicate tube. The distance from the light source to the irradiation Schlenk tube was approximately 20–30 mm. All reactions were studied in oven-dried Schlenk tubes irradiated by 18 W blue light (425–475 nm). Flash chromatography was performed using the indicated solvent system on standard grade silica gel (200–300 mesh). ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker 400 (400 MHz) spectrometer. ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker 400 (100 MHz) spectrometer. ^{31}P NMR spectra were recorded in $CDCl_3$ on a Bruker 400 (162 MHz) spectrometer. ^{19}F NMR spectra were recorded in $CDCl_3$ on a Bruker 400 (376 MHz) spectrometer. Chemical shifts were reported relative to $CDCl_3$ (δ 7.26 ppm) for ^{1}H NMR and $CDCl_3$ (δ 77.00 ppm) for ^{13}C NMR. High-resolution mass spectra (HRMS) were recorded on a Q-Exactive Orbitrap mass spectrometer (Thermo). Melting points (mp) were uncorrected and measured on a micro melting point apparatus. UV-vis absorption spectra were measured on a Shimadzu UV-2700 spectrophotometer. Photoluminescence spectra were recorded on an Edinburgh FLS980 spectrometer. Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet.

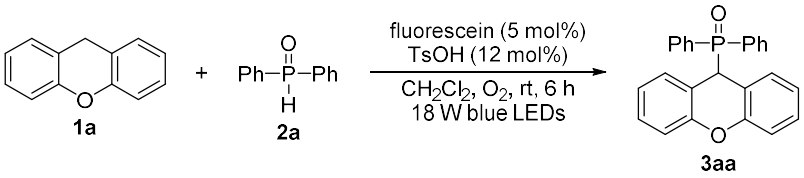
2. Overview of Substrates Numbering





3. Experimental Section

1) General Procedure for the Phosphorylation of Xanthene Derivatives



A mixture of xanthene **1a** (109 mg, 0.6 mmol), diphenylphosphine oxide **2a** (61 mg, 0.3 mmol), fluorescein (5 mg, 0.015 mmol), and TsOH (6 mg, 0.036 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature under a molecular oxygen (O_2) atmosphere (1 atm, in a sealed Schlenk tube) irradiated by 18 W blue-light-emitting diodes (LEDs) with an emitting wavelength range of 425–475 nm for 6 h (Figure S1). After removal of the solvent, the residue was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (3:2) to give diphenyl(9*H*-xanthen-9-yl)phosphine oxide **3aa** (87 mg, 76%) as a white solid.

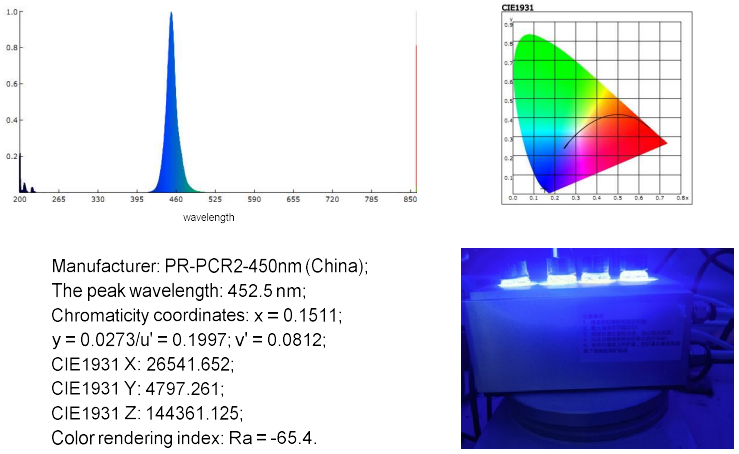


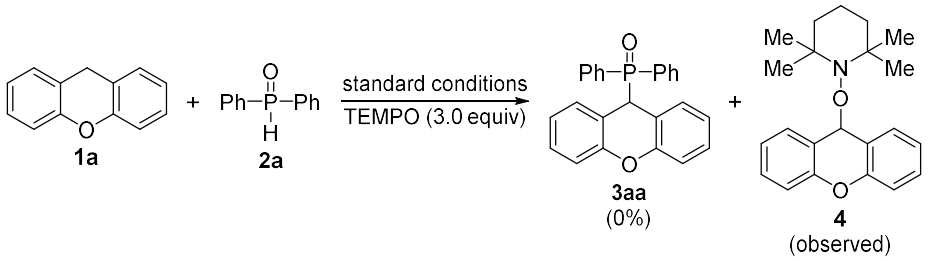
Figure S1. Experimental Apparatus and Pictures

2) General Procedure for the Scale-up Synthesis

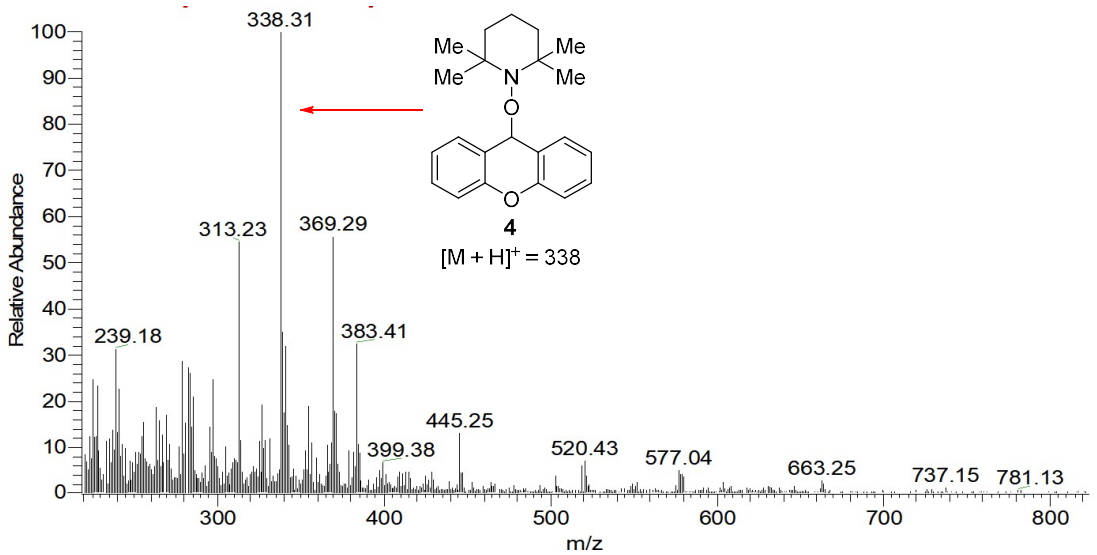
A mixture of **1a** (2.55 g, 14 mmol), **2a** (1.42 g, 7 mmol), fluorescein (132 mg, 0.35 mmol), and TsOH (145 mg, 0.84 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature under an O_2 atmosphere (1 atm, with a balloon) irradiated by 18 W blue LEDs for 12 h. After removal of the solvent, the residue was purified by flash column chromatography on silica gel to give **3aa** (1.07 g, 40%).

4. Mechanistic Studies

1) Radical Trapping Experiments



To a mixture of **1a** (109 mg, 0.6 mmol), **2a** (61 mg, 0.3 mmol), fluorescein (5 mg, 0.015 mmol), and TsOH (6 mg, 0.036 mmol) in CH_2Cl_2 (2 mL) was added a radical scavenger TEMPO (140 mg, 0.9 mmol). The mixture was stirred at room temperature under an O_2 atmosphere (1 atm, in a sealed Schlenk tube) irradiated by 18 W blue LEDs with an emitting wavelength range of 425–475 nm for 6 h. The reaction mixture was then concentrated under reduced pressure. The desired reaction of **1a** with **2a** was completely inhibited, and the adduct xanthene–TEMPO **4** was observed by LC-MS spectra of the crude mixture, suggesting that the reaction might undergo a 9-xanthenyl radical pathway.



2) Stern–Volmer Quenching Experiments

All Stern–Volmer fluorescence quenching studies were recorded on an Ocean Optics QE Pro with temperature controller using a screw-top quartz cuvette (Hellma fluorescence quartz cuvette, 10 x 10 mm, 3.5 mL). Stern–Volmer fluorescence quenching experiments were run with a freshly prepared solution of 5.0 x 10^{-4} M solution of fluorescein in CH_2Cl_2 added the appropriate amount of a quencher in a screw-top quartz cuvette at room temperature. **1a** (1.0 x 10^{-4} M), **2a** (3.0 x 10^{-4} M), or O_2 (1 atm) was used as the quencher. The solutions were irradiated at 450 nm and the fluorescence was measured from 430 nm to 650 nm. Based on the luminescence quenching studies of each component, it was found that the excited photocatalyst (PC*) was effectively quenched by O_2, supporting the notion that the ground-state triplet oxygen ($^3O_2$) could be converted to highly reactive singlet oxygen ($^1O_2$) via the energy transfer (ET) process under photoredox conditions (Figure S2).

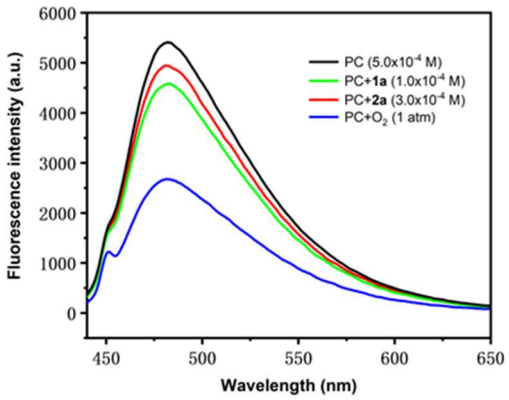


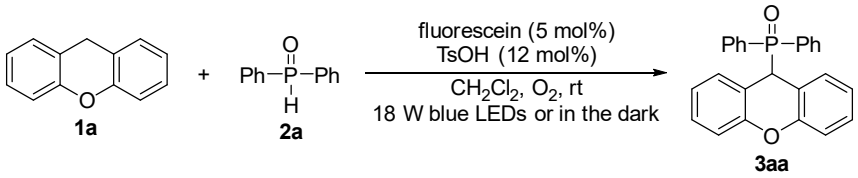
Figure S2. Fluorescence Quenching Experiments

3) Light On–Off Experiments

To study the necessity of continuous irradiation with visible light for the progress of the reaction, we started the light on–off experiments. A mixture of **1a** (109 mg, 0.6 mmol), **2a** (61 mg, 0.3 mmol), fluorescein (5 mg, 0.015 mmol), and TsOH (6 mg, 0.036 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature under an O_2 atmosphere (1 atm, in a sealed Schlenk tube) irradiated by 18 W blue LEDs with an emitting wavelength range of 425–475 nm or in the dark for the corresponding time (Table S1,

Figure S3). Afterwards, the reaction mixture was concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (3:2) to determine the yields of **3aa**. The grey boxes represent the periods in which the reaction vessels were covered (dark period). Light on–off experiments indicated that the yield of **3aa** was still increased in the dark after initiating the reaction with light, suggesting a possible radical chain propagation proceeding in the absence of light.

Table S1. Light On–Off Experiments



entry	time (min)	yield of **3aa** (%)
1	0	0
2	20	22
3	40	36
4	60	42
5	80	51
6	100	65

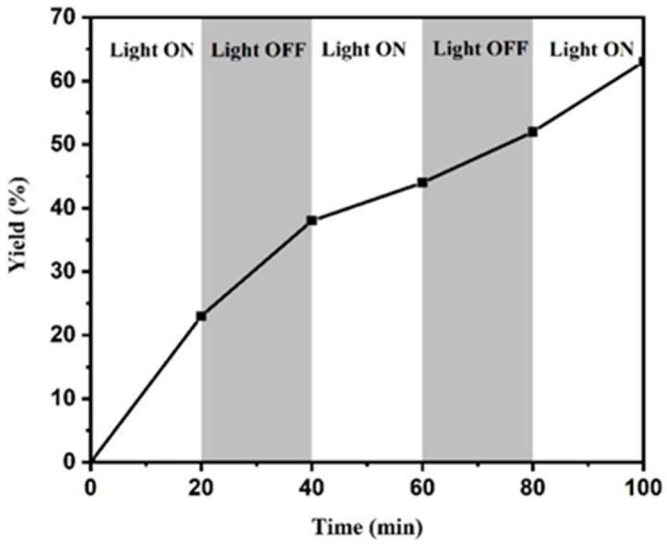
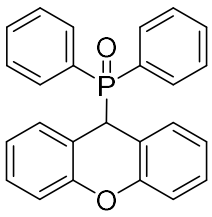


Figure S3. Light On–Off Experiments

5. Analytic Data for Products

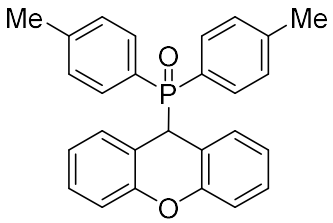
The characterization data of known compounds **3aa**, **3ab**, **3ad**–**3aj**, **3al**, **3an**, **3as**, **3ba**–**3ia**, and **3ka** was in full agreement with previously reported data.[4]

Diphenyl(9*H*-xanthen-9-yl)phosphine oxide (3aa)[4]



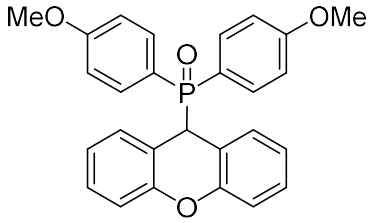
White solid (87 mg, 76%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.46 (m, 6H), 7.38–7.33 (m, 4H), 7.20–7.11 (m, 2H), 6.98–6.84 (m, 6H), 4.91 (d, J = 17.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6 (d, J = 4.7 Hz), 132.2 (d, J = 8.4 Hz), 131.9 (d, J = 2.7 Hz), 130.1 (d, J = 3.5 Hz), 129.6 (d, J = 95.9 Hz), 128.6 (d, J = 3.1 Hz), 128.0 (d, J = 11.4 Hz), 122.8 (d, J = 2.7 Hz), 117.0 (d, J = 4.7 Hz), 116.3 (d, J = 2.7 Hz), 45.5 (d, J = 64.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.8.

Di-*p*-tolyl(9*H*-xanthen-9-yl)phosphine oxide (3ab)[4]



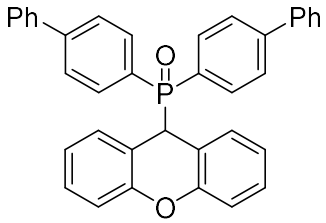
White solid (55 mg, 45%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (dd, J = 10.6, 8.1 Hz, 4H), 7.19–7.14 (m, 6H), 6.98–6.93 (m, 2H), 6.90 (d, J = 7.6 Hz, 4H), 4.87 (d, J = 17.8 Hz, 1H), 2.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6 (d, J = 4.4 Hz), 142.4 (d, J = 2.7 Hz), 132.2 (d, J = 8.8 Hz), 130.2 (d, J = 3.6 Hz), 128.8 (d, J = 11.8 Hz), 128.5 (d, J = 3.1 Hz), 126.3 (d, J = 98.0 Hz), 122.8 (d, J = 2.8 Hz), 117.3 (d, J = 4.7 Hz), 116.3 (d, J = 2.8 Hz), 45.4 (d, J = 64.0 Hz), 21.6 (d, J = 1.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.2.

Bis(4-methoxyphenyl)(9*H*-xanthen-9-yl)phosphine oxide (3ac)



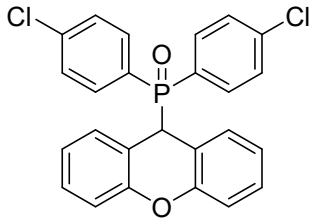
White solid (62 mg, 47%): mp 221–223 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.38 (m, 4H), 7.19–7.12 (m, 2H), 6.96 (d, J = 8.3 Hz, 2H), 6.93–6.82 (m, 8H), 4.83 (d, J = 18.0 Hz, 1H), 3.81 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, J = 2.9 Hz), 152.6 (d, J = 4.3 Hz), 134.1 (d, J = 9.7 Hz), 130.3 (d, J = 3.6 Hz), 128.5 (d, J = 3.2 Hz), 122.9 (d, J = 2.7 Hz), 120.8 (d, J = 101 Hz), 117.5 (d, J = 4.6 Hz), 116.3 (d, J = 2.9 Hz), 113.7 (d, J = 12.3 Hz), 55.3, 45.7 (d, J = 65.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.1; HRMS (ESI-Orbitrap) *m/z* $[M + H]^+$ calcd for $C_{27}H_{24}O_4P$ 443.1407, found 443.1402.

Di([1,1'-biphenyl]-4-yl)(9*H*-xanthen-9-yl)phosphine oxide (3ad)[4]



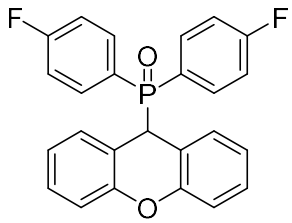
White solid (119 mg, 74%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.60 (m, 12H), 7.50–7.45 (m, 4H), 7.42–7.38 (m, 2H), 7.22–7.17 (m, 2H), 7.05–7.02 (m, 2H), 6.95–6.89 (m, 4H), 4.99 (d, J = 17.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7 (d, J = 4.4 Hz), 144.7 (d, J = 2.8 Hz), 139.8, 132.7 (d, J = 8.8 Hz), 130.3 (d, J = 3.5 Hz), 128.9, 128.8 (d, J = 3.0 Hz), 128.2, 128.0 (d, J = 96.2 Hz), 127.2, 126.8 (d, J = 11.7 Hz), 123.0 (d, J = 2.6 Hz), 117.0 (d, J = 4.7 Hz), 116.5 (d, J = 2.7 Hz), 45.6 (d, J = 64.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.1.

Bis(4-chlorophenyl)(9*H*-xanthen-9-yl)phosphine oxide (3ae)[4]



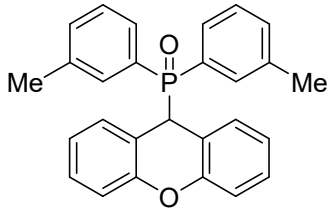
White solid (85 mg, 63%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.38 (m, 4H), 7.37–7.32 (m, 4H), 7.23–7.16 (m, 2H), 6.98–6.89 (m, 6H), 4.88 (d, J = 18.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5 (d, J = 4.4 Hz), 138.9 (d, J = 3.4 Hz), 133.4 (d, J = 9.2 Hz), 130.1 (d, J = 3.6 Hz), 129.0 (d, J = 3.2 Hz), 128.6 (d, J = 12.0 Hz), 127.7 (d, J = 96.7 Hz), 123.1 (d, J = 2.7 Hz), 116.6 (d, J = 2.9 Hz), 116.5 (d, J = 4.8 Hz), 45.5 (d, J = 65.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.5.

Bis(4-fluorophenyl)(9*H*-xanthen-9-yl)phosphine oxide (3af)[4]



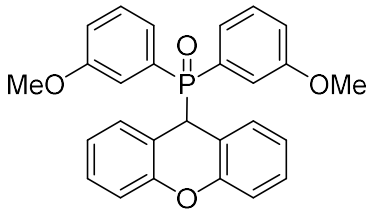
White solid (77 mg, 61%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.44 (m, 4H), 7.21–7.15 (m, 2H), 7.09–7.02 (m, 4H), 6.97–6.88 (m, 6H), 4.86 (d, J = 18.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2 (dd, J = 254, 3.3 Hz), 152.5 (d, J = 4.4 Hz), 134.6 (dd, J = 9.3, 9.3 Hz), 130.1 (d, J = 3.6 Hz), 128.9 (d, J = 3.2 Hz), 125.2 (dd, J = 98.6, 3.4 Hz), 123.0 (d, J = 2.8 Hz), 116.7 (d, J = 4.8 Hz), 116.4 (d, J = 2.9 Hz), 115.6 (dd, J = 21.3, 12.5 Hz), 45.7 (d, J = 65.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.

Di-*m*-tolyl(9*H*-xanthen-9-yl)phosphine oxide (3ag)[4]



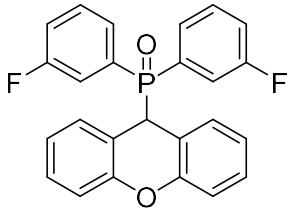
White solid (66 mg, 54%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.21 (m, 5H), 7.20–7.14 (m, 3H), 7.13–7.06 (m, 2H), 6.91–6.78 (m, 6H), 4.81 (d, J = 17.5 Hz, 1H), 2.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7 (d, J = 4.3 Hz), 137.9 (d, J = 11.3 Hz), 132.9 (d, J = 8.2 Hz), 132.7 (d, J = 2.9 Hz), 130.2 (d, J = 3.5 Hz), 129.3 (d, J = 94.6 Hz), 129.2 (d, J = 8.8 Hz), 128.5 (d, J = 3.1 Hz), 127.8 (d, J = 12.2 Hz), 122.8 (d, J = 2.7 Hz), 117.2 (d, J = 4.7 Hz), 116.3 (d, J = 2.8 Hz), 45.5 (d, J = 63.5 Hz), 21.3; ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.2.

Bis(3-methoxyphenyl)(9*H*-xanthen-9-yl)phosphine oxide (3ah)[4]



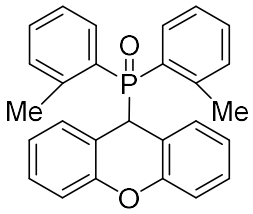
White solid (88 mg, 66%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.27 (m, 2H), 7.20–7.07 (m, 6H), 7.04 (dd, J = 8.2, 2.2 Hz, 2H), 6.97–6.92 (m, 4H), 6.91–6.87 (m, 2H), 4.90 (d, J = 17.0 Hz, 1H), 3.72 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (d, J = 14.3 Hz), 152.7 (d, J = 4.2 Hz), 130.8 (d, J = 95.1 Hz), 130.2 (d, J = 3.5 Hz), 129.3 (d, J = 13.7 Hz), 128.6 (d, J = 3.1 Hz), 124.3 (d, J = 8.6 Hz), 122.9 (d, J = 2.6 Hz), 118.8 (d, J = 2.6 Hz), 117.0 (d, J = 4.8 Hz), 116.6 (d, J = 9.3 Hz), 116.4 (d, J = 2.7 Hz), 55.4, 45.4 (d, J = 62.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.3.

Bis(3-fluorophenyl)(9*H*-xanthen-9-yl)phosphine oxide (3ai)[4]



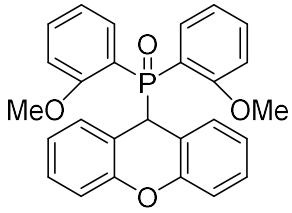
White solid (85 mg, 68%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.21 (m, 4H), 7.18–7.10 (m, 6H), 6.91–6.83 (m, 6H), 4.84 (d, J = 17.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (dd, J = 250, 16.1 Hz), 152.6 (d, J = 4.5 Hz), 130.2 (d, J = 7.3 Hz), 130.1 (d, J = 7.7 Hz), 129.6 (dd, J = 94.8, 3.5 Hz), 127.8 (dd, J = 8.0, 3.3 Hz), 123.1 (d, J = 2.8 Hz), 119.5 (dd, J = 21.1, 2.6 Hz), 119.2 (d, J = 9.3 Hz), 119.0 (d, J = 9.2 Hz), 116.6 (d, J = 2.9 Hz), 116.3 (d, J = 4.8 Hz), 45.5 (d, J = 65.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.

Di-*o*-tolyl(9*H*-xanthen-9-yl)phosphine oxide (3aj)[4]



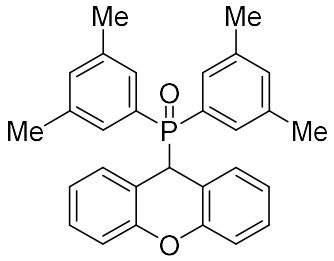
White solid (37 mg, 30%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (dd, J = 12.6, 7.8 Hz, 2H), 7.39–7.31 (m, 2H), 7.21–7.10 (m, 6H), 7.05–6.98 (m, 4H), 6.90–6.83 (m, 2H), 5.17 (d, J = 16.3 Hz, 1H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9 (d, J = 4.1 Hz), 143.9 (d, J = 7.4 Hz), 132.2 (d, J = 10.5 Hz), 132.0 (d, J = 11.4 Hz), 131.7 (d, J = 2.7 Hz), 130.0 (d, J = 3.4 Hz), 129.4 (d, J = 92.5 Hz), 128.5 (d, J = 2.9 Hz), 124.8 (d, J = 12.1 Hz), 123.0 (d, J = 2.6 Hz), 117.8 (d, J = 4.5 Hz), 116.6 (d, J = 2.6 Hz), 44.6 (d, J = 62.6 Hz), 21.4 (d, J = 3.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.0.

Bis(2-methoxyphenyl)(9*H*-xanthen-9-yl)phosphine oxide (3ak)



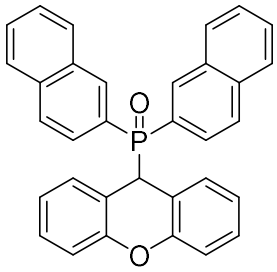
White solid (64 mg, 48%): mp 209–211 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.36 (m, 4H), 7.25–7.21 (m, 2H), 7.13–7.05 (m, 2H), 6.88–7.36 (m, 8H), 5.59 (d, J = 20.4 Hz, 1H), 3.64 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5 (d, J = 3.7 Hz), 152.9 (d, J = 4.7 Hz), 135.6 (d, J = 6.7 Hz), 133.7 (d, J = 2.2 Hz), 129.6 (d, J = 4.0 Hz), 127.9 (d, J = 3.4 Hz), 122.7 (d, J = 3.0 Hz), 120.5 (d, J = 11.3 Hz), 118.8 (d, J = 2.1 Hz), 118.4 (d, J = 96.0 Hz), 115.9 (d, J = 3.0 Hz), 110.3 (d, J = 6.8 Hz), 55.2, 44.7 (d, J = 66.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 37.0; HRMS (ESI-Orbitrap) *m/z* $[M + H]^+$ calcd for $C_{27}H_{24}O_4P$ 443.1407, found 443.1402.

Bis(3,5-dimethylphenyl)(9*H*-xanthen-9-yl)phosphine oxide(3al)[4]



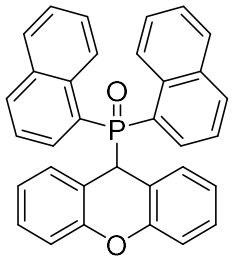
White solid (53 mg, 40%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.14 (m, 2H), 7.14–7.05 (m, 6H), 7.00–6.96 (m, 2H), 6.93–6.88 (m, 4H), 4.92 (d, J = 17.6 Hz, 1H), 2.26 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8 (d, J = 4.3 Hz), 137.6 (d, J = 12.1 Hz), 133.6 (d, J = 2.9 Hz), 130.3 (d, J = 3.5 Hz), 129.9 (d, J = 8.5 Hz), 128.9 (d, J = 94.3 Hz), 128.5 (d, J = 3.1 Hz), 122.8 (d, J = 2.7 Hz), 117.3 (d, J = 4.7 Hz), 116.2 (d, J = 2.8 Hz), 45.3 (d, J = 63.1 Hz), 21.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.3.

Di(naphthalen-2-yl)(9*H*-xanthen-9-yl)phosphine oxide (3am)



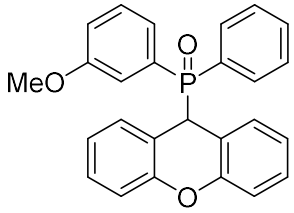
White solid (81 mg, 56%): mp 243–245 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 12.2 Hz, 2H), 7.92–7.75 (m, 6H), 7.61–7.50 (m, 6H), 7.16 (dd, J = 7.7, 7.7 Hz, 2H), 7.01 (d, J = 7.6 Hz, 2H), 6.89–6.83 (m, 4H), 5.12 (d, J = 16.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 134.8 (d, J = 10.7 Hz), 134.7, 132.4 (d, J = 11.8 Hz), 130.2, 129.0, 128.8, 128.3, 127.9, 127.8, 127.3 (d, J = 91.0 Hz), 126.9, 126.8, 123.0, 117.2, 116.5, 45.5 (d, J = 65.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.5; HRMS (ESI-Orbitrap) *m/z* $[M + H]^+$ calcd for $C_{33}H_{24}O_2P$ 483.1508, found 433.1503.

Di(naphthalen-1-yl)(9*H*-xanthen-9-yl)phosphine oxide (3an)[4]



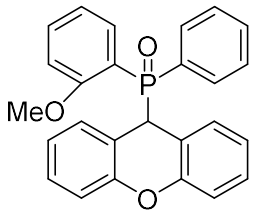
White solid (106 mg, 73%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, J = 8.5 Hz, 2H), 7.87 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.1 Hz, 2H), 7.59 (dd, J = 14.8, 7.1 Hz, 2H), 7.42–7.34 (m, 2H), 7.32–7.28 (m, 2H), 7.25–7.18 (m, 2H), 7.03–6.93 (m, 2H), 6.85–6.83 (m, 2H), 6.73–6.71 (m, 2H), 6.61–6.57 (m, 2H), 5.43 (d, J = 17.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5 (d, J = 4.3 Hz), 134.5, 133.9 (d, J = 9.0 Hz), 133.2 (d, J = 3.0 Hz), 132.7 (d, J = 10.6 Hz), 129.9 (d, J = 3.3 Hz), 128.7 (d, J = 0.5 Hz), 128.5 (d, J = 3.0 Hz), 127.3 (d, J = 3.7 Hz), 127.2, 126.9 (d, J = 91.2 Hz), 126.2, 123.9 (d, J = 13.8 Hz), 122.9 (d, J = 2.6 Hz), 117.7 (d, J = 4.6 Hz), 116.5 (d, J = 2.7 Hz), 45.3 (d, J = 63.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.5.

(3-Methoxyphenyl)(phenyl)(9*H*-xanthen-9-yl)phosphine oxide (3ao)



White solid (74 mg, 60%): mp 211–213 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.47 (m, 3H), 7.39–7.34 (m, 2H), 7.31–7.24 (m, 1H), 7.21–7.00 (m, 5H), 6.99–6.83 (m, 6H), 4.90 (d, J = 17.2 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (d, J = 14.2 Hz), 152.7 (d, J = 4.3 Hz), 132.2 (d, J = 8.0 Hz), 132.1 (d, J = 3.2 Hz), 130.8 (d, J = 94.0 Hz), 130.2 (d, J = 3.0 Hz), 130.1 (d, J = 3.0 Hz), 129.5 (d, J = 95.0 Hz), 129.3 (d, J = 13.2 Hz), 128.7 (d, J = 2.2 Hz), 128.6 (d, J = 2.2 Hz), 128.2 (d, J = 11.4 Hz), 124.3 (d, J = 8.7 Hz), 123.0 (d, J = 3.0 Hz), 122.9 (d, J = 3.0 Hz), 118.8 (d, J = 2.0 Hz), 117.1 (d, J = 5.1 Hz), 117.0 (d, J = 5.1 Hz), 116.7, 116.6, 116.5 (d, J = 2.0 Hz), 116.4 (d, J = 2.0 Hz), 55.4, 45.4 (d, J = 64.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.1; HRMS (ESI-Orbitrap) *m/z* $[M + Na]^+$ calcd for $C_{26}H_{21}O_3PNa$ 413.1301, found 413.1294.

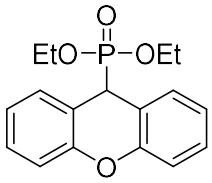
(2-Methoxyphenyl)(phenyl)(9*H*-xanthen-9-yl)phosphine oxide (3ap)



White solid (52 mg, 42%): mp 203–205 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.58 (m, 1H), 7.55–7.47 (m, 3H), 7.44–7.40 (m, 1H), 7.29–7.25 (m, 2H), 7.18–7.08 (m, 2H), 7.05–7.00 (m, 3H), 6.98–6.92 (m, 2H), 6.86–6.79 (m, 1H), 6.76–6.67 (m, 2H), 5.37 (d, J = 13.9 Hz, 1H), 4.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9 (d, J = 4.3 Hz), 153.4 (d, J = 4.5 Hz), 152.9 (d, J = 4.6 Hz), 135.5 (d, J = 5.6 Hz), 134.2 (d, J = 2.2 Hz), 132.4 (d, J = 8.9 Hz), 131.7 (d, J = 2.9 Hz), 130.1 (d, J = 97.0 Hz), 129.4 (d, J = 4.1 Hz), 129.2 (d, J = 4.1 Hz), 128.4 (d, J = 3.3 Hz), 128.3 (d, J = 3.3 Hz), 127.7 (d, J = 11.5 Hz), 122.8 (d, J = 2.9 Hz), 122.5 (d, J = 2.9 Hz), 121.4 (d, J = 10.7 Hz), 119.1 (d,

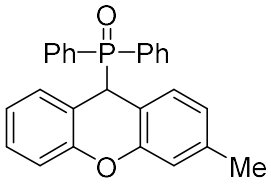
J = 93.0 Hz), 117.5 (d, J = 5.8 Hz), 117.4 (d, J = 5.8 Hz), 116.6 (d, J = 3.1 Hz), 116.4 (d, J = 3.0 Hz), 110.7 (d, J = 6.9 Hz), 55.5, 43.9 (d, J = 65.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.1; HRMS (ESI-Orbitrap) *m/z* $[M + Na]^+$ calcd for $C_{26}H_{21}O_3PNa$ 413.1301, found 413.1295.

Diethyl (9*H*-xanthen-9-yl)phosphonate (3as)[4]



Colorless oil (29 mg, 30%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.26 (m, 2H), 7.22–7.15 (m, 2H), 7.04–6.98 (m, 4H), 4.40 (d, J = 24.7 Hz, 1H), 3.86–3.76 (m, 4H), 1.08 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3 (d, J = 5.3 Hz), 130.1 (d, J = 4.4 Hz), 128.7 (d, J = 3.6 Hz), 123.1 (d, J = 3.2 Hz), 117.2 (d, J = 8.2 Hz), 116.5 (d, J = 3.4 Hz), 63.0 (d, J = 7.5 Hz), 40.4 (d, J = 141 Hz), 16.2 (d, J = 5.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.9.

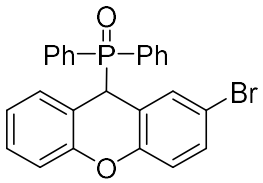
(3-Methyl-9*H*-xanthen-9-yl)diphenylphosphine oxide (3ba)[4]



White solid (59 mg, 50%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.41 (m, 6H), 7.34–7.26 (m, 4H), 7.11–7.05 (m, 1H), 6.90–6.86 (m, 1H), 6.84–6.77 (m, 2H), 6.74 (dd, J = 7.8, 2.0 Hz, 1H), 6.67–6.60 (m, 2H), 4.83 (d, J = 17.4 Hz, 1H), 2.20 (d, J = 1.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8 (d, J = 4.3 Hz), 152.5 (d, J = 4.4 Hz), 138.9 (d, J = 3.3 Hz), 132.3 (d, J = 1.5 Hz), 132.2 (d, J = 1.4 Hz), 132.0 (d, J = 2.6 Hz), 130.2 (d, J = 3.5 Hz), 129.8 (d, J = 3.4 Hz), 129.5 (d, J = 94.9 Hz), 129.4 (d, J = 94.8 Hz), 128.9 (d, J = 13.0 Hz), 128.6 (d, J = 3.1 Hz), 128.2, 128.1, 123.8 (d, J = 2.6 Hz), 122.8 (d, J

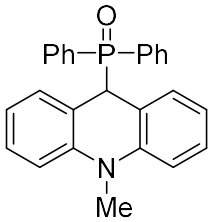
= 2.8 Hz), 117.1 (d, J = 4.6 Hz), 116.8 (d, J = 2.9 Hz), 116.4 (d, J = 2.8 Hz), 113.8 (d, J = 4.7 Hz), 45.0 (d, J = 64.3 Hz), 21.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.2.

(2-Bromo-9*H*-xanthen-9-yl)diphenylphosphine oxide (3ca)[4]



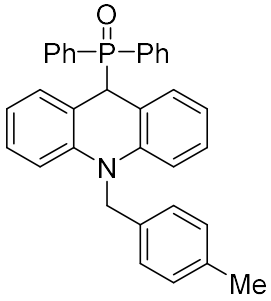
White solid (76 mg, 55%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.51 (m, 6H), 7.46–7.35 (m, 4H), 7.29–7.23 (m, 1H), 7.20–7.13 (m, 1H), 6.95–6.85 (m, 4H), 6.80 (d, J = 8.7 Hz, 1H), 4.81 (d, J = 16.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3 (d, J = 4.3 Hz), 151.8 (d, J = 4.3 Hz), 132.8 (d, J = 3.5 Hz), 132.4 (d, J = 3.0 Hz), 132.3 (d, J = 3.4 Hz), 132.2 (d, J = 8.7 Hz), 132.1 (d, J = 8.8 Hz), 131.6 (d, J = 2.9 Hz), 130.1 (d, J = 3.4 Hz), 129.8 (d, J = 86.8 Hz) 129.7 (d, J = 95.8 Hz), 128.9 (d, J = 3.0 Hz), 128.4 (d, J = 1.4 Hz), 128.3 (d, J = 1.4 Hz), 123.2 (d, J = 2.5 Hz), 119.0 (d, J = 4.7 Hz), 118.0 (d, J = 2.6 Hz), 116.4 (d, J = 2.6 Hz), 116.2 (d, J = 4.9 Hz), 115.0 (d, J = 3.3 Hz), 45.3 (d, J = 63.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.7.

(10-Methyl-9,10-dihydroacridin-9-yl)diphenylphosphine oxide (3da)[4]



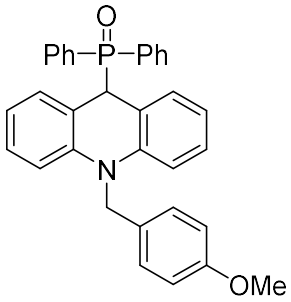
White solid (95 mg, 80%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.42 (m, 6H), 7.35–7.28 (m, 4H), 7.21–7.15 (m, 2H), 7.05–7.01 (m, 2H), 6.88–6.81 (m, 2H), 6.62 (d, J = 8.1 Hz, 2H), 4.95 (d, J = 19.1 Hz, 1H), 2.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9 (d, J = 3.6 Hz), 132.3 (d, J = 8.4 Hz), 131.5 (d, J = 2.3 Hz), 130.3 (d, J = 92.4 Hz), 130.2 (d, J = 4.4 Hz), 128.1 (d, J = 3.0 Hz), 127.6 (d, J = 11.3 Hz), 120.5 (d, J = 2.4 Hz), 118.5 (d, J = 3.8 Hz), 112.2 (d, J = 1.8 Hz), 50.2 (d, J = 63.6 Hz), 32.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.3.

(10-(4-Methylbenzyl)-9,10-dihydroacridin-9-yl)diphenylphosphine oxide (3ea)[4]



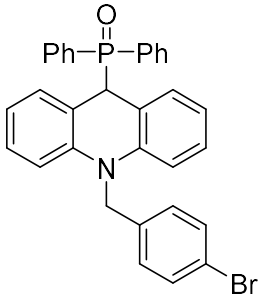
Yellow solid (122 mg, 84%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.44 (m, 6H), 7.39–7.34 (m, 4H), 7.09–6.98 (m, 6H), 6.90–6.88 (m, 2H), 6.83–6.79 (m, 2H), 6.42 (d, J = 8.4 Hz, 2H), 5.01 (d, J = 19.0 Hz, 1H), 4.24 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1 (d, J = 3.5 Hz), 136.4, 133.5, 132.5 (d, J = 8.3 Hz), 131.7 (d, J = 2.7 Hz), 130.3 (d, J = 4.3 Hz), 130.1 (d, J = 92.6 Hz), 129.4, 128.2 (d, J = 3.3 Hz), 127.8 (d, J = 11.2 Hz), 125.8, 120.6 (d, J = 2.8 Hz), 118.0 (d, J = 4.0 Hz), 113.3 (d, J = 2.4 Hz), 50.7, 49.6 (d, J = 63.3 Hz), 21.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.9.

(10-(4-Methoxybenzyl)-9,10-dihydroacridin-9-yl)diphenylphosphine oxide (3fa)[4]



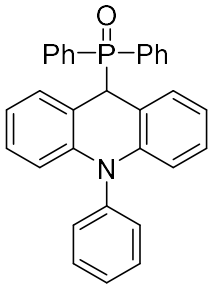
Yellow solid (117 mg, 78%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.44 (m, 6H), 7.40–7.33 (m, 4H), 7.06–6.99 (m, 4H), 6.92–6.90 (m, 2H), 6.84–6.75 (m, 4H), 6.43 (d, J = 8.0 Hz, 2H), 5.00 (d, J = 18.9 Hz, 1H), 4.23 (s, 2H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 142.0 (d, J = 3.6 Hz), 132.5 (d, J = 8.4 Hz), 131.7 (d, J = 2.6 Hz), 130.3 (d, J = 4.4 Hz), 129.5 (d, J = 92.5 Hz), 128.3, 128.2 (d, J = 3.3 Hz), 127.7 (d, J = 11.3 Hz), 126.9, 120.6 (d, J = 2.8 Hz), 118.0 (d, J = 4.0 Hz), 114.1, 113.3 (d, J = 2.4 Hz), 55.2, 50.3, 49.6 (d, J = 63.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.9.

(10-(4-Bromobenzyl)-9,10-dihydroacridin-9-yl)diphenylphosphine oxide (3ga)[4]



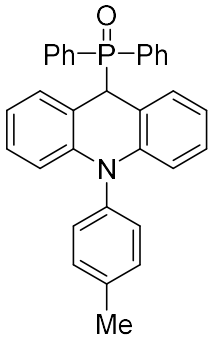
Yellow solid (137 mg, 83%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.46 (m, 6H), 7.40–7.33 (m, 6H), 7.06–6.99 (m, 4H), 6.89 (d, J = 8.4 Hz, 2H), 6.84–6.78 (m, 2H), 6.37 (d, J = 8.1 Hz, 2H), 5.02 (d, J = 18.4 Hz, 1H), 4.24 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8 (d, J = 3.7 Hz), 135.7, 132.5 (d, J = 8.4 Hz), 131.9, 131.8 (d, J = 2.7 Hz), 130.5 (d, J = 4.3 Hz), 129.8 (d, J = 93.4 Hz), 128.3 (d, J = 3.3 Hz), 127.9, 127.8, 120.9 (d, J = 2.7 Hz), 120.7, 118.0 (d, J = 4.1 Hz), 113.1 (d, J = 2.4 Hz), 50.4, 49.4 (d, J = 63.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.5.

Diphenyl(10-phenyl-9,10-dihydroacridin-9-yl)phosphine oxide (3ha)[4]



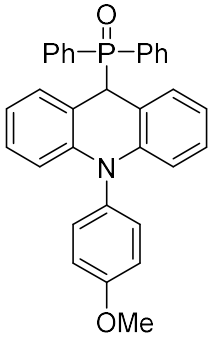
White solid (91 mg, 66%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.45 (m, 8H), 7.43–7.33 (m, 5H), 7.00–6.90 (m, 4H), 6.78–6.70 (m, 4H), 6.06 (d, J = 8.2 Hz, 2H), 5.14 (d, J = 18.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7 (d, J = 3.5 Hz), 140.0, 132.6 (d, J = 8.4 Hz), 131.6 (d, J = 2.7 Hz), 130.8, 130.4, 130.3 (d, J = 4.0 Hz), 130.0 (d, J = 92.3 Hz), 128.1, 128.0 (d, J = 11.1 Hz), 127.7 (d, J = 3.1 Hz), 120.4 (d, J = 2.7 Hz), 115.4 (d, J = 4.6 Hz), 113.9 (d, J = 2.5 Hz), 49.1 (d, J = 63.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.8.

Diphenyl(10-(*p*-tolyl)-9,10-dihydroacridin-9-yl)phosphine oxide (3ia)[4]



White solid (102 mg, 72%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.48 (m, 6H), 7.38–7.33 (m, 4H), 7.28–7.26 (m, 2H), 7.00–6.90 (m, 4H), 6.77–6.71 (m, 2H), 6.58 (d, J = 8.1 Hz, 2H), 6.09 (d, J = 8.2 Hz, 2H), 5.15 (d, J = 18.4 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8 (d, J = 3.6 Hz), 137.9, 137.2, 132.6 (d, J = 8.4 Hz), 131.6 (d, J = 2.7 Hz), 131.1, 130.4, 130.3 (d, J = 4.0 Hz), 130.0 (d, J = 92.3 Hz), 128.0 (d, J = 11.1 Hz), 127.7 (d, J = 3.2 Hz), 120.3 (d, J = 2.7 Hz), 115.3 (d, J = 4.5 Hz), 113.9 (d, J = 2.5 Hz), 49.1 (d, J = 63.9 Hz), 21.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9.

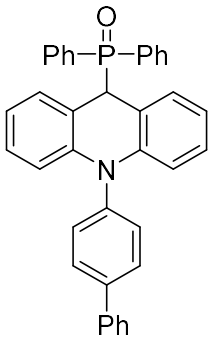
(10-(4-Methoxyphenyl)-9,10-dihydroacridin-9-yl)diphenylphosphine oxide (3ja)



White solid (86 mg, 59%): mp 202–204 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.44 (m, 6H), 7.39–7.35 (m, 4H), 6.98–6.92 (m, 6H), 6.74 (dd, J = 7.4, 7.4 Hz, 2H), 6.62 (d, J = 8.5 Hz, 2H), 6.09 (d, J = 8.2 Hz, 2H), 5.13 (d, J = 18.0 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 143.1 (d, J = 3.6 Hz), 132.7 (d, J = 8.1 Hz), 132.6, 131.8, 131.7 (d, J = 3.0 Hz), 130.4 (d, J = 4.0 Hz), 130.2 (d, J = 92.0 Hz), 128.1 (d, J = 11.0 Hz), 127.8 (d, J = 3.0 Hz), 120.4 (d, J = 2.7 Hz), 115.6, 115.4 (d, J = 4.6 Hz), 114.0

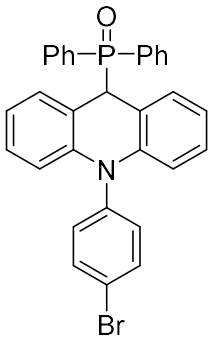
(d, J = 2.4 Hz), 55.5, 49.2 (d, J = 64.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9; HRMS (ESI-Orbitrap) *m/z* $[M + Na]^+$ calcd for $C_{32}H_{26}NO_2PNa$ 510.1593, found 510.1587.

(10-([1,1'-Biphenyl]-4-yl)-9,10-dihydroacridin-9-yl)diphenylphosphine oxide (3ka)[4]



Yellow solid (101 mg, 63%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 7.2 Hz, 2H), 7.57–7.46 (m, 8H), 7.42–7.35 (m, 5H), 7.02–6.95 (m, 4H), 6.82–6.74 (m, 4H), 6.17 (d, J = 8.1 Hz, 2H), 5.18 (d, J = 18.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8 (d, J = 3.6 Hz), 141.0, 140.2, 139.2, 132.7 (d, J = 8.4 Hz), 131.8 (d, J = 2.7 Hz), 131.1, 130.5 (d, J = 4.0 Hz), 129.9 (d, J = 93.1 Hz), 129.2, 128.9, 128.1 (d, J = 11.2 Hz), 127.9 (d, J = 3.1 Hz), 127.7, 127.1, 120.6 (d, J = 2.7 Hz), 115.4 (d, J = 4.6 Hz), 114.1 (d, J = 2.4 Hz), 49.1 (d, J = 63.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0.

(10-(4-Bromophenyl)-9,10-dihydroacridin-9-yl)diphenylphosphine oxide (3la)



White solid (97 mg, 60%): mp 189–191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.59 (m, 2H), 7.56–7.46 (m, 6H), 7.40–7.34 (m, 4H), 6.99–6.91 (m, 4H), 6.75 (dd, J = 6.9,

6.9 Hz, 2H), 6.66–6.62 (m, 2H), 6.07 (d, J = 8.2 Hz, 2H), 5.11 (d, J = 17.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4 (d, J = 3.6 Hz), 139.1, 133.9, 132.8, 132.6 (d, J = 9.0 Hz), 131.7 (d, J = 2.7 Hz), 130.4 (d, J = 4.1 Hz), 130.1 (d, J = 93.0 Hz), 128.1 (d, J = 11.0 Hz), 127.9 (d, J = 3.0 Hz), 122.1, 120.8 (d, J = 2.8 Hz), 115.7 (d, J = 4.7 Hz), 113.8 (d, J = 2.5 Hz), 49.0 (d, J = 64.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9; HRMS (ESI-Orbitrap) *m/z* $[M + Na]^+$ calcd for $C_{31}H_{23}BrNOPNa$ 558.0593, found 558.0588.

References:

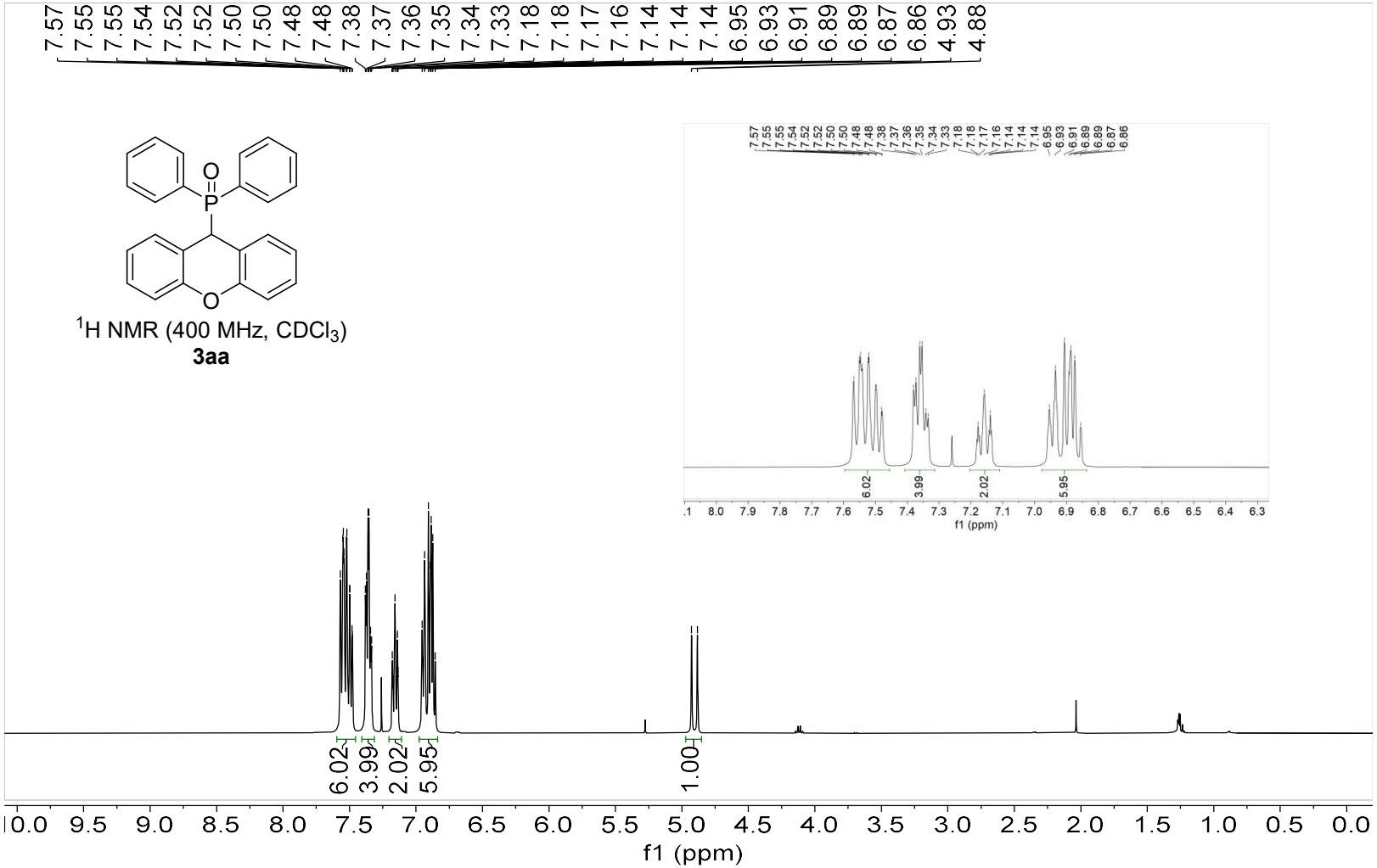
(1) (*a*) H. R. Hays, *J. Org. Chem.*, 1968, **33**, 3690; (*b*) M. J. P. Harger and S. Westlake, *Tetrahedron*, 1982, **38**, 1511.

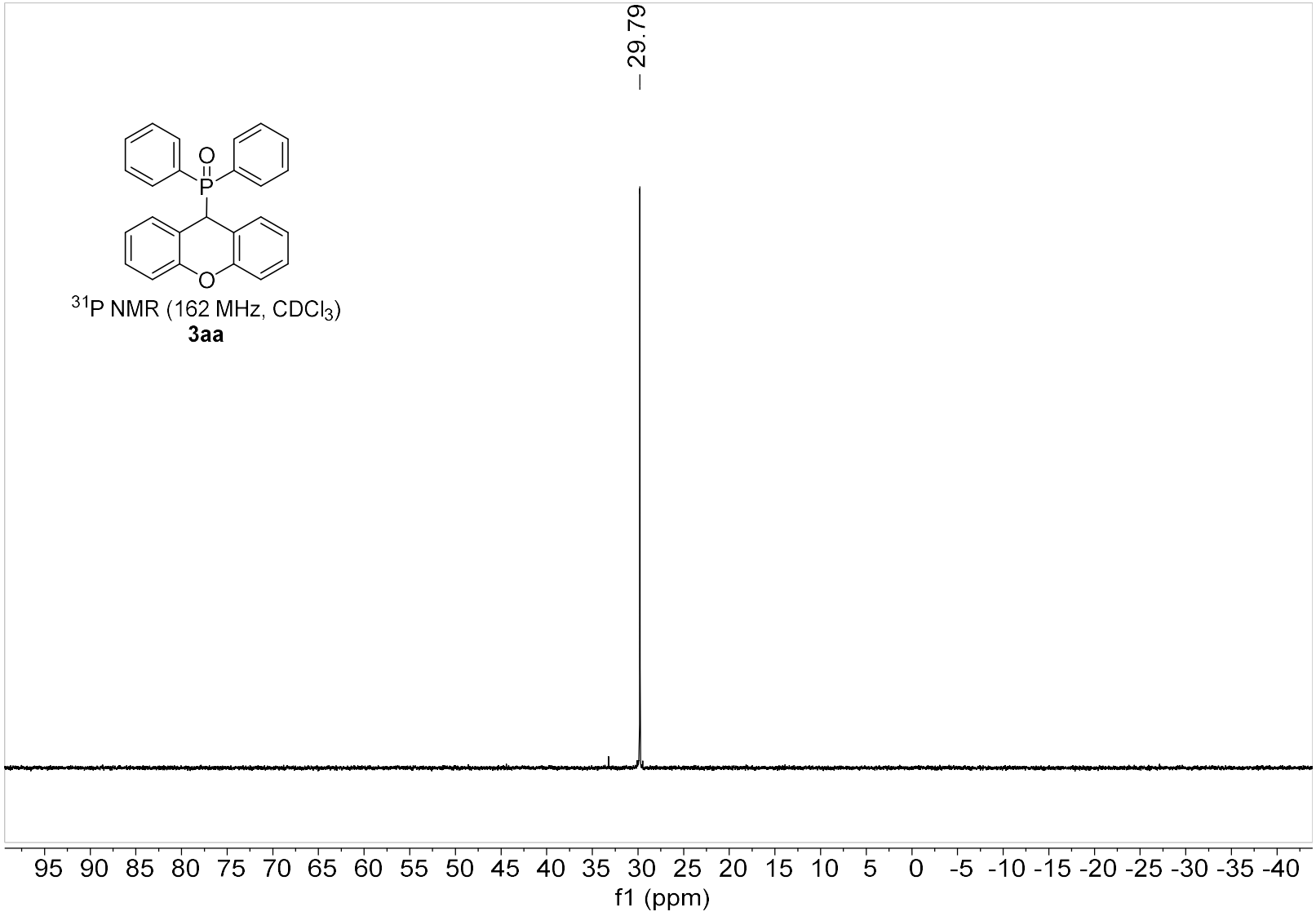
(2) C. A. Menéndez, F. Nador, G. Radivoy and D. C. Gerbino, *Org. Lett.*, 2014, **16**, 2846.

(3) Á. Pintér, A. Sud, D. Sureshkumar and M. Klussmann, *Angew. Chem., Int. Ed.*, 2010, **49**, 5004.

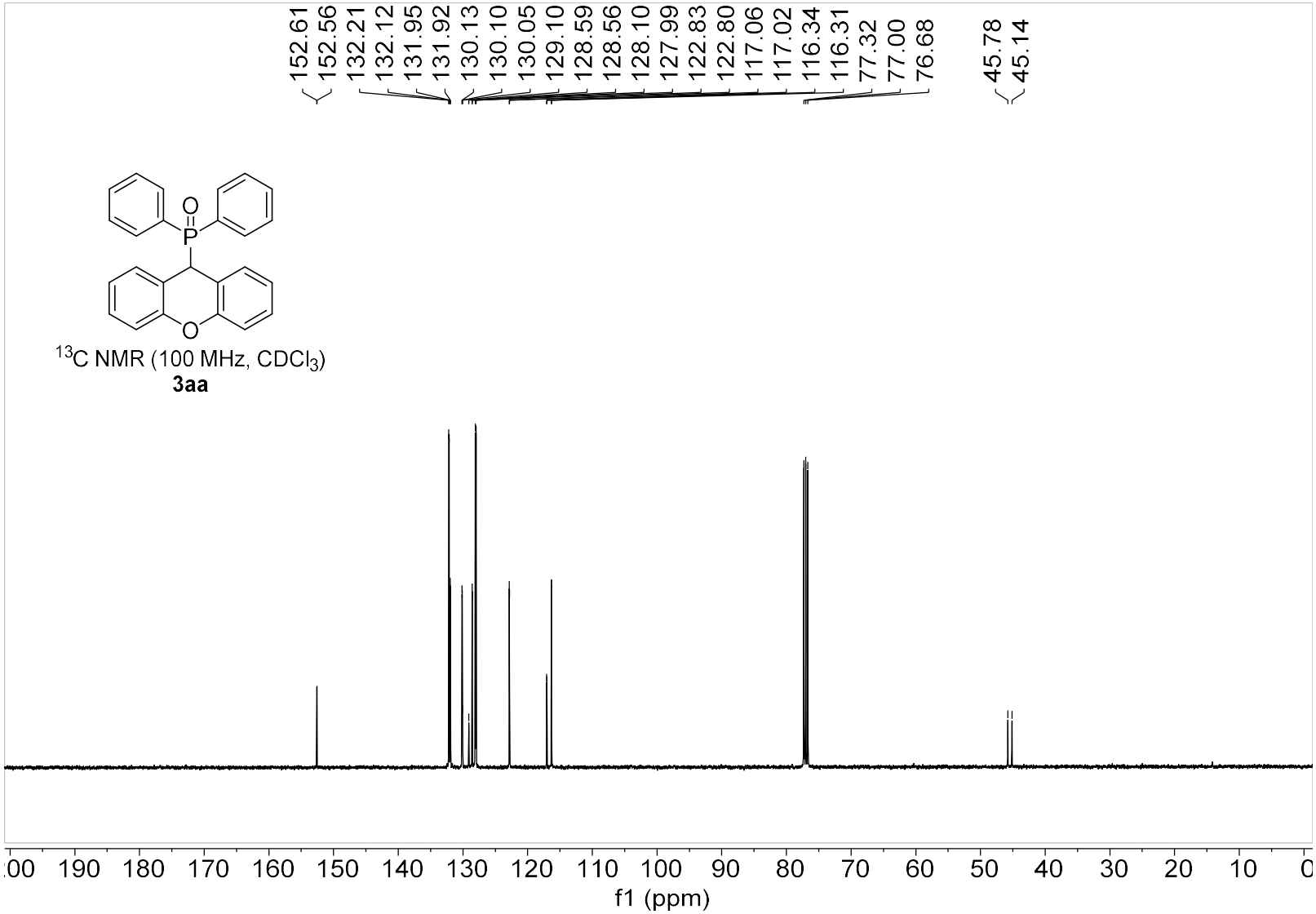
(4) Q. Chen, X. Wang, G. Yu, C. Wen and Y. Huo, *Org. Chem. Front.*, 2018, **5**, 2652.

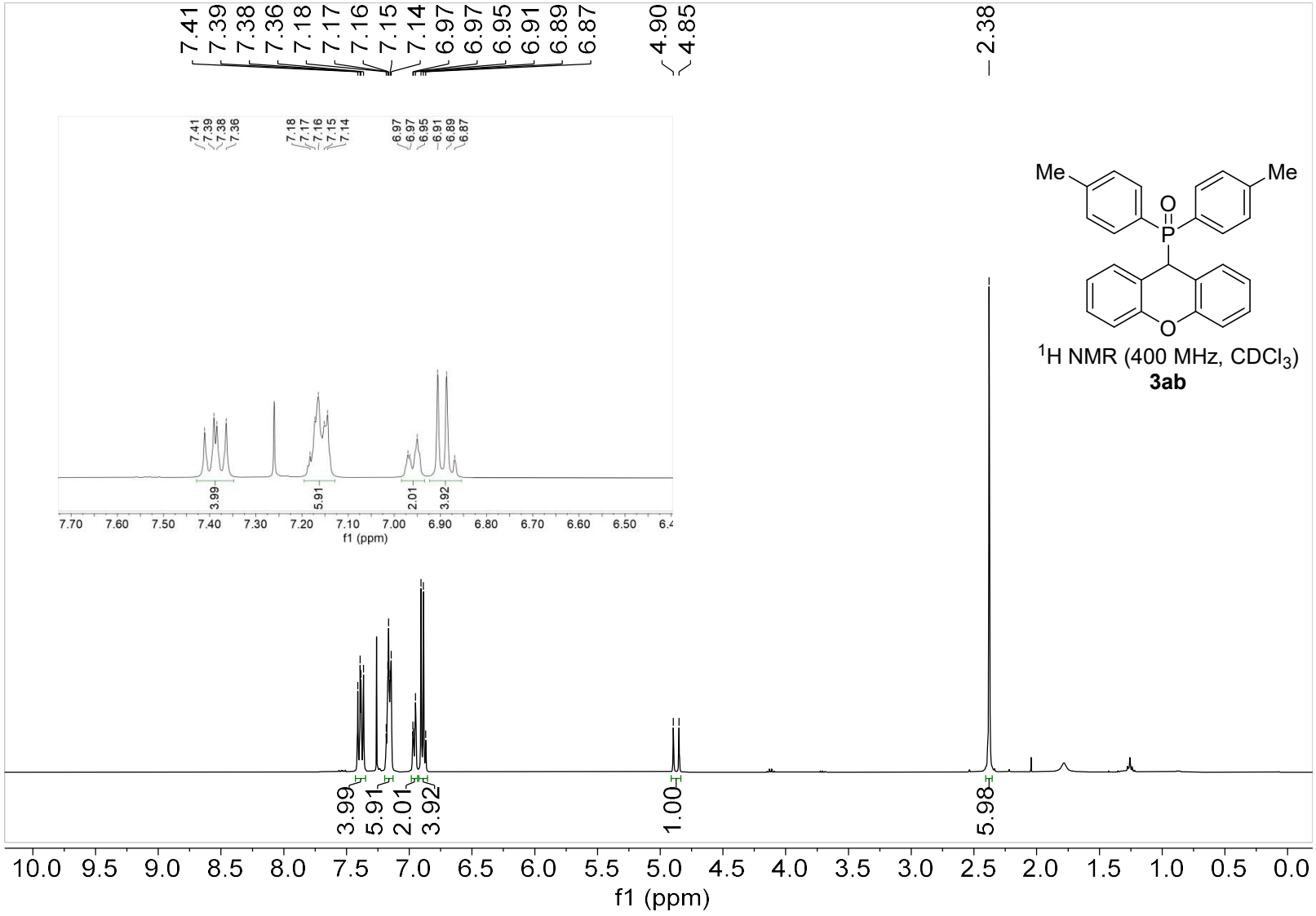
6. NMR Spectra for Products



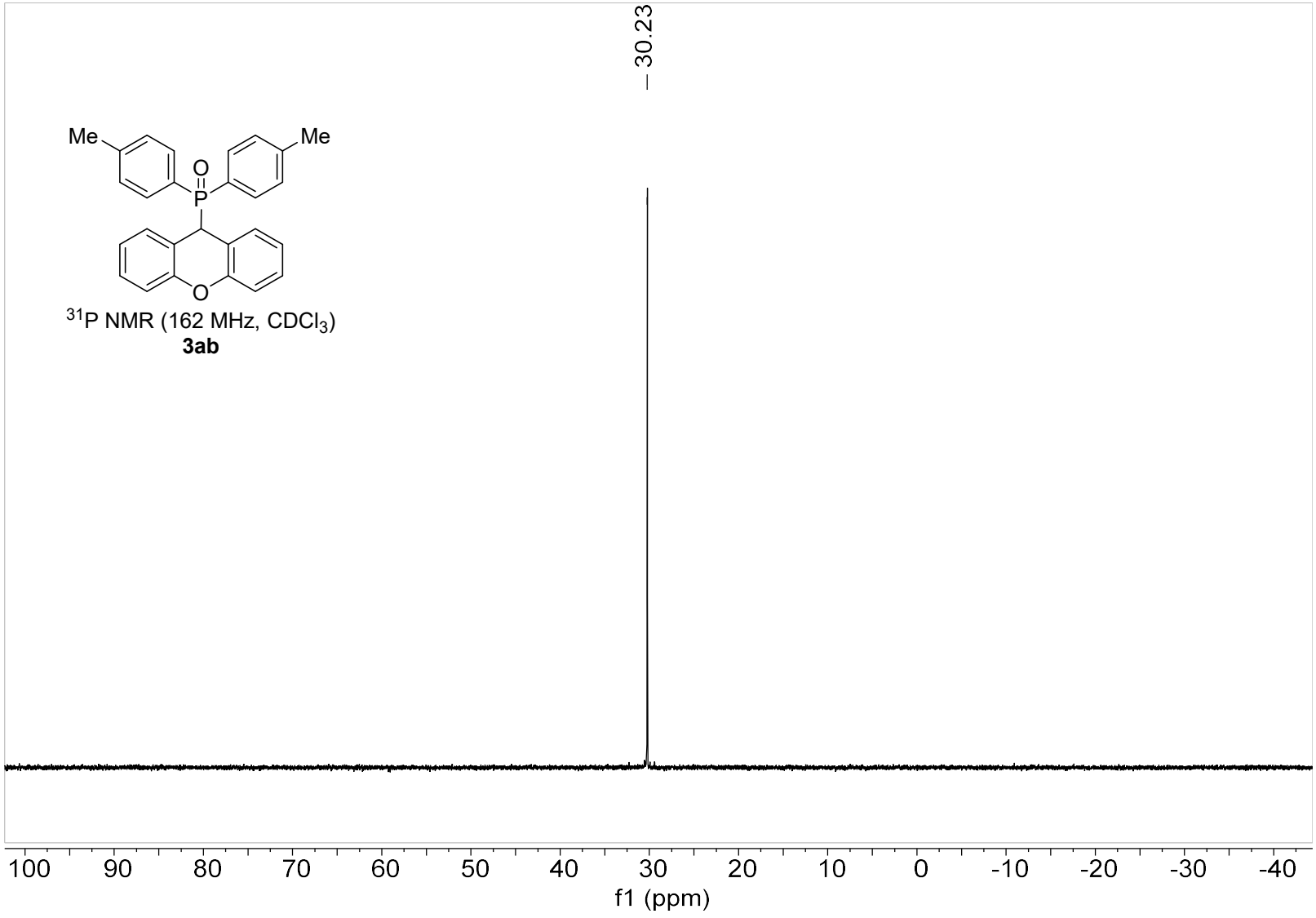


^{31}P NMR (162 MHz, $CDCl_3$)
3aa

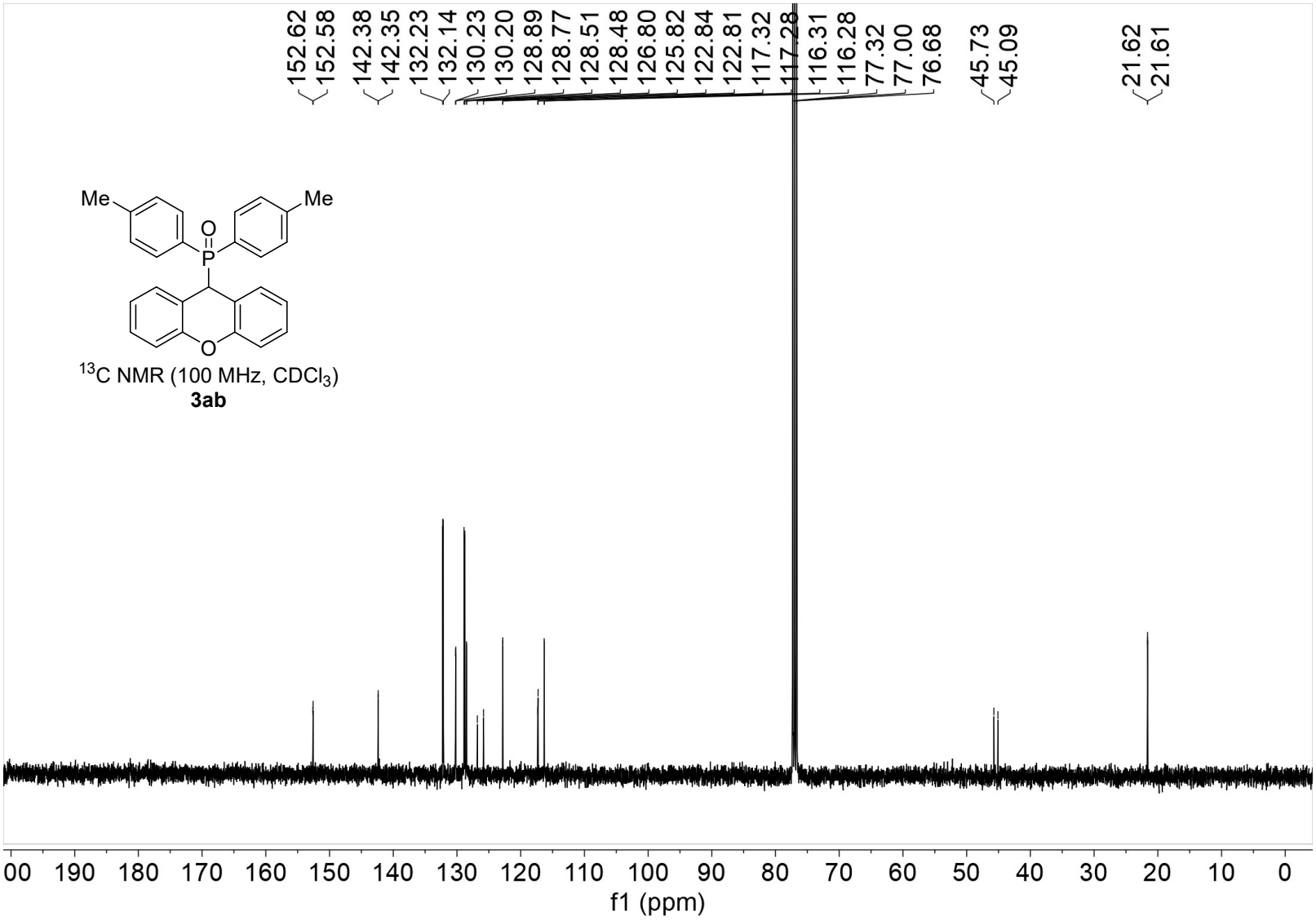

152.61
152.56
132.21
132.12
131.95
131.92
130.13
130.10
130.05
129.10
128.59
128.56
128.10
127.99
122.83
122.80
117.06
117.02
116.34
116.31
77.32
77.00
76.68
45.78
45.14
O
P
O
^{13}C NMR (100 MHz, $CDCl_3$)
3aa
f1 (ppm)



^{1}H NMR (400 MHz, $CDCl_3$)
3ab

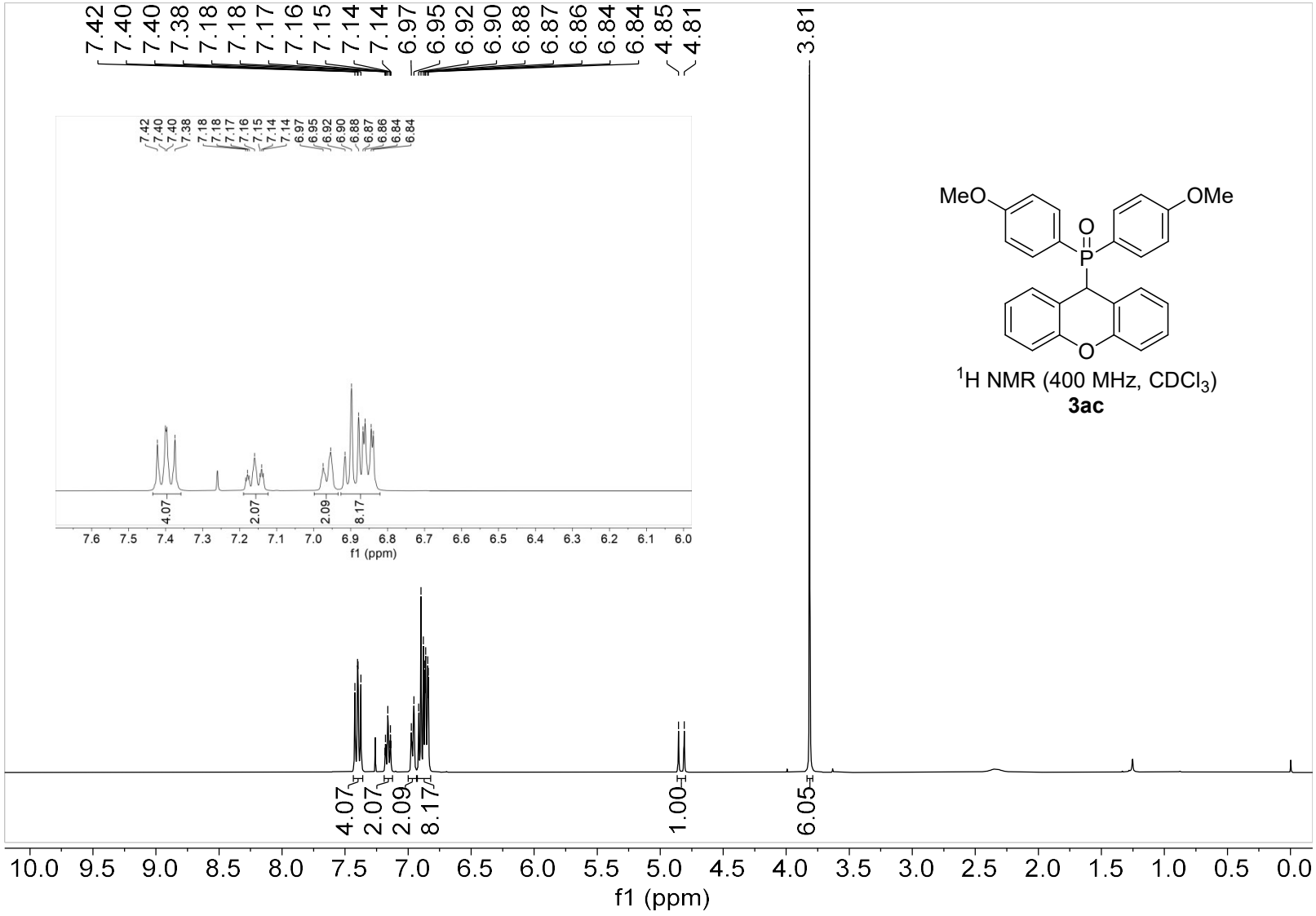


^{31}P NMR (162 MHz, $CDCl_3$)
3ab



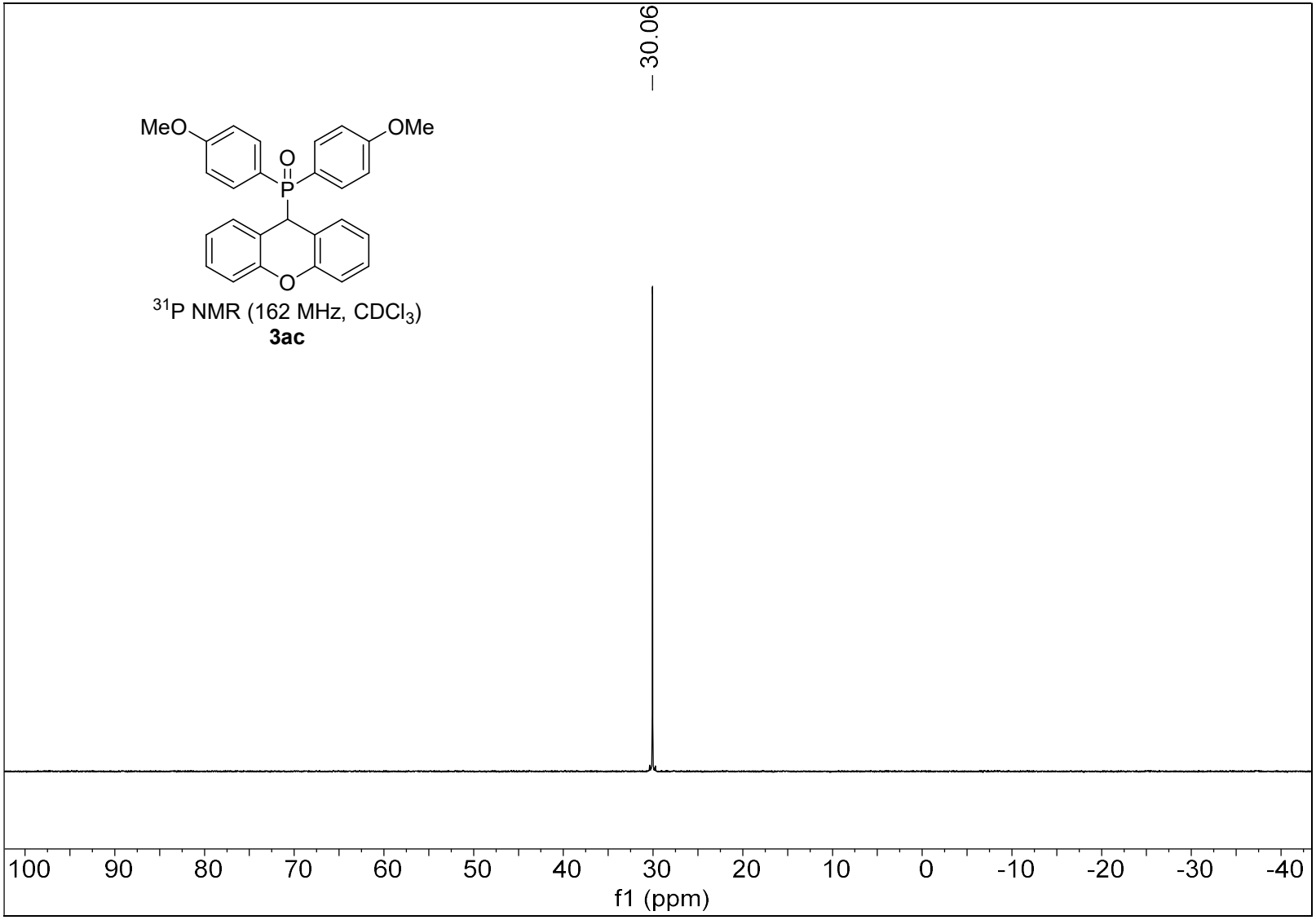
^{13}C NMR (100 MHz, $CDCl_3$)

3ab



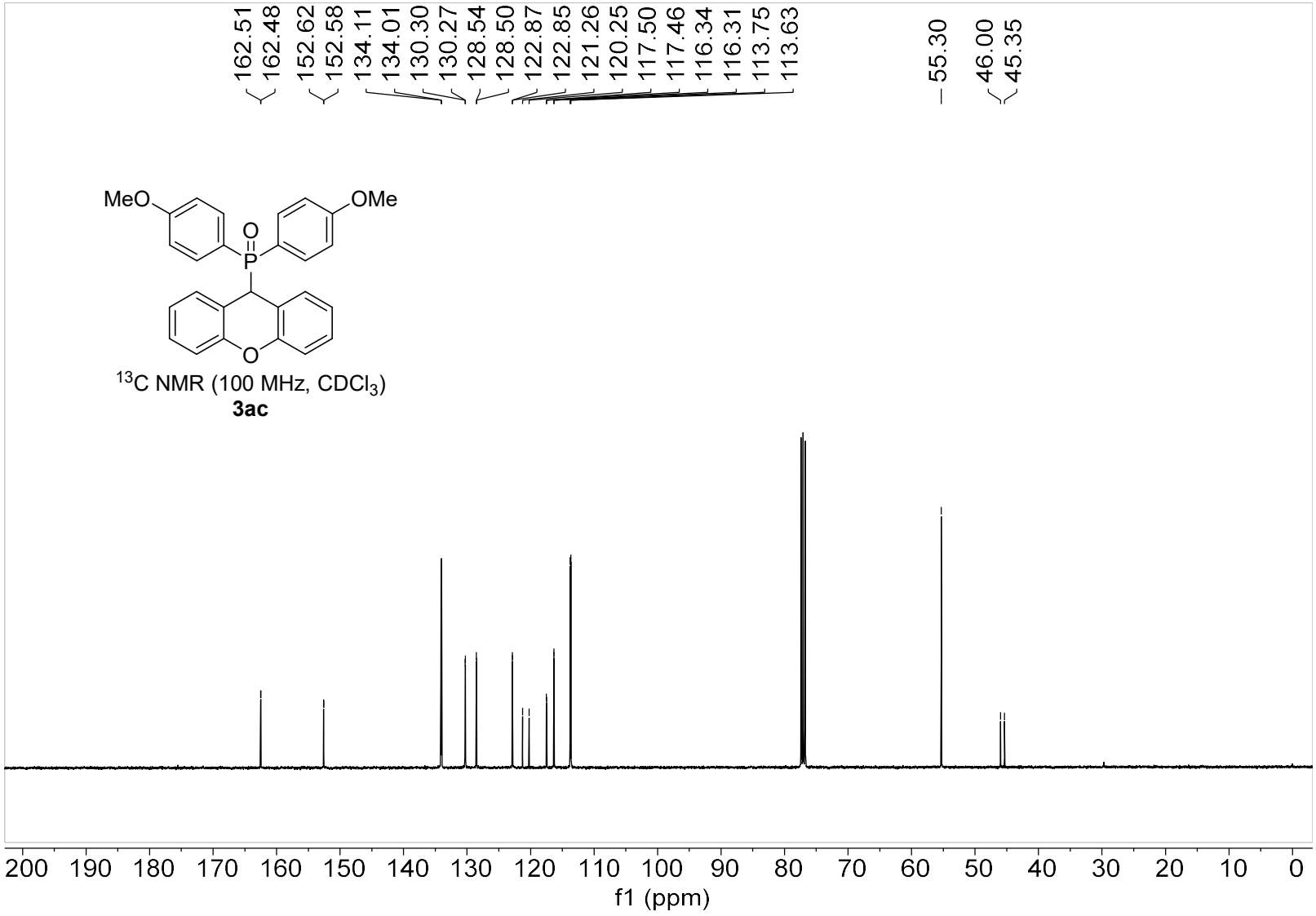
^{1}H NMR (400 MHz, $CDCl_3$)

3ac



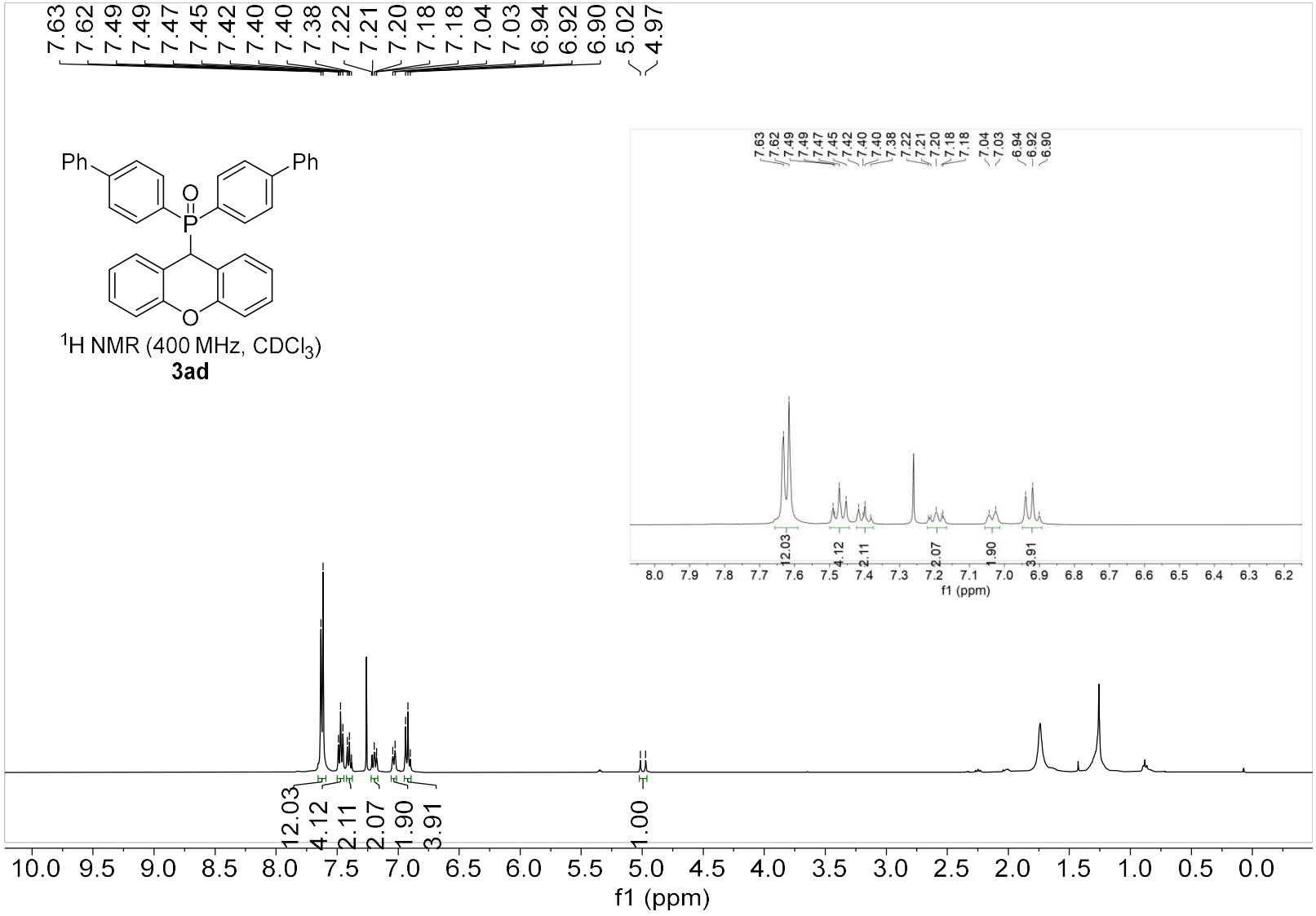
^{31}P NMR (162 MHz, $CDCl_3$)

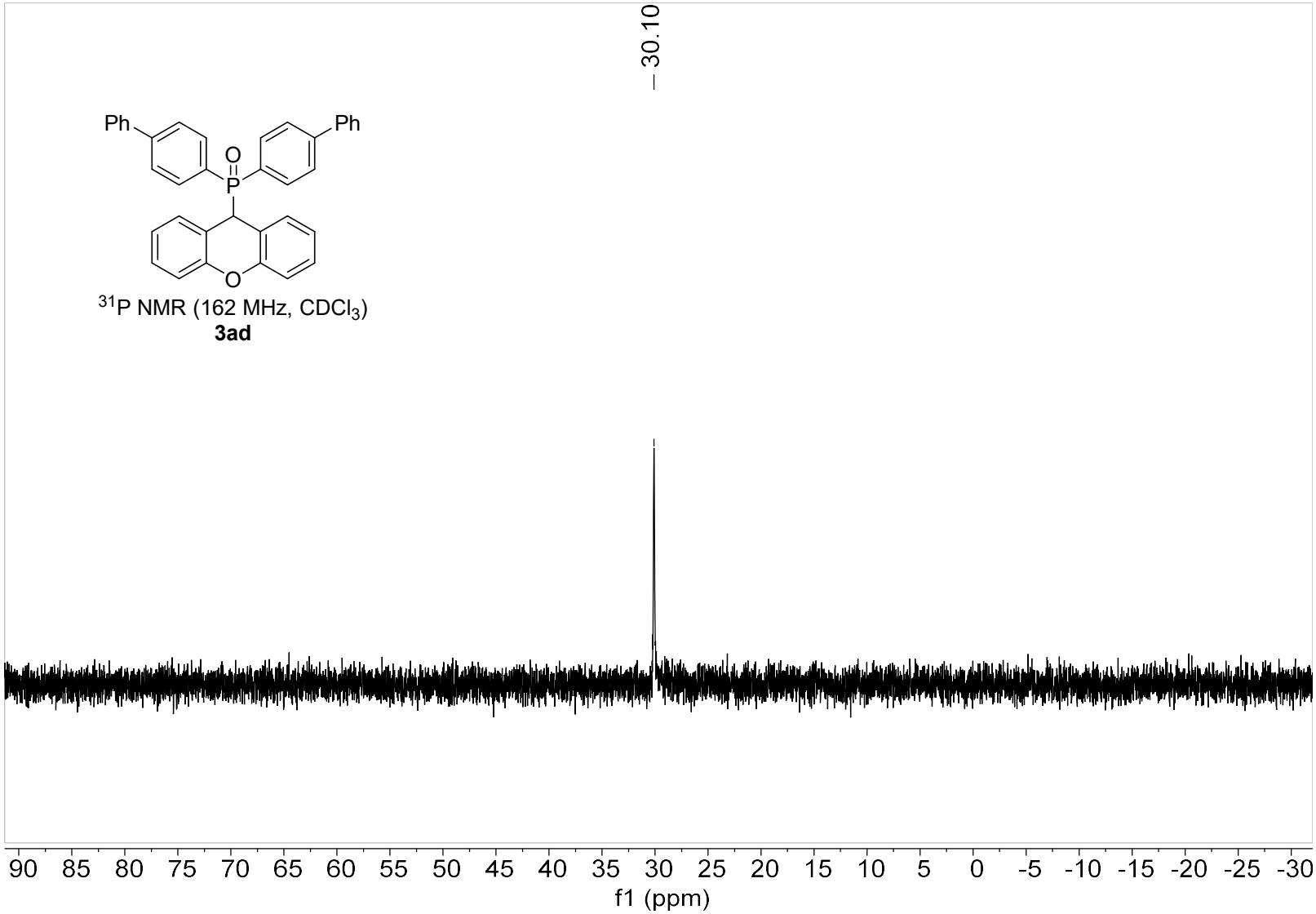
3ac



^{13}C NMR (100 MHz, $CDCl_3$)

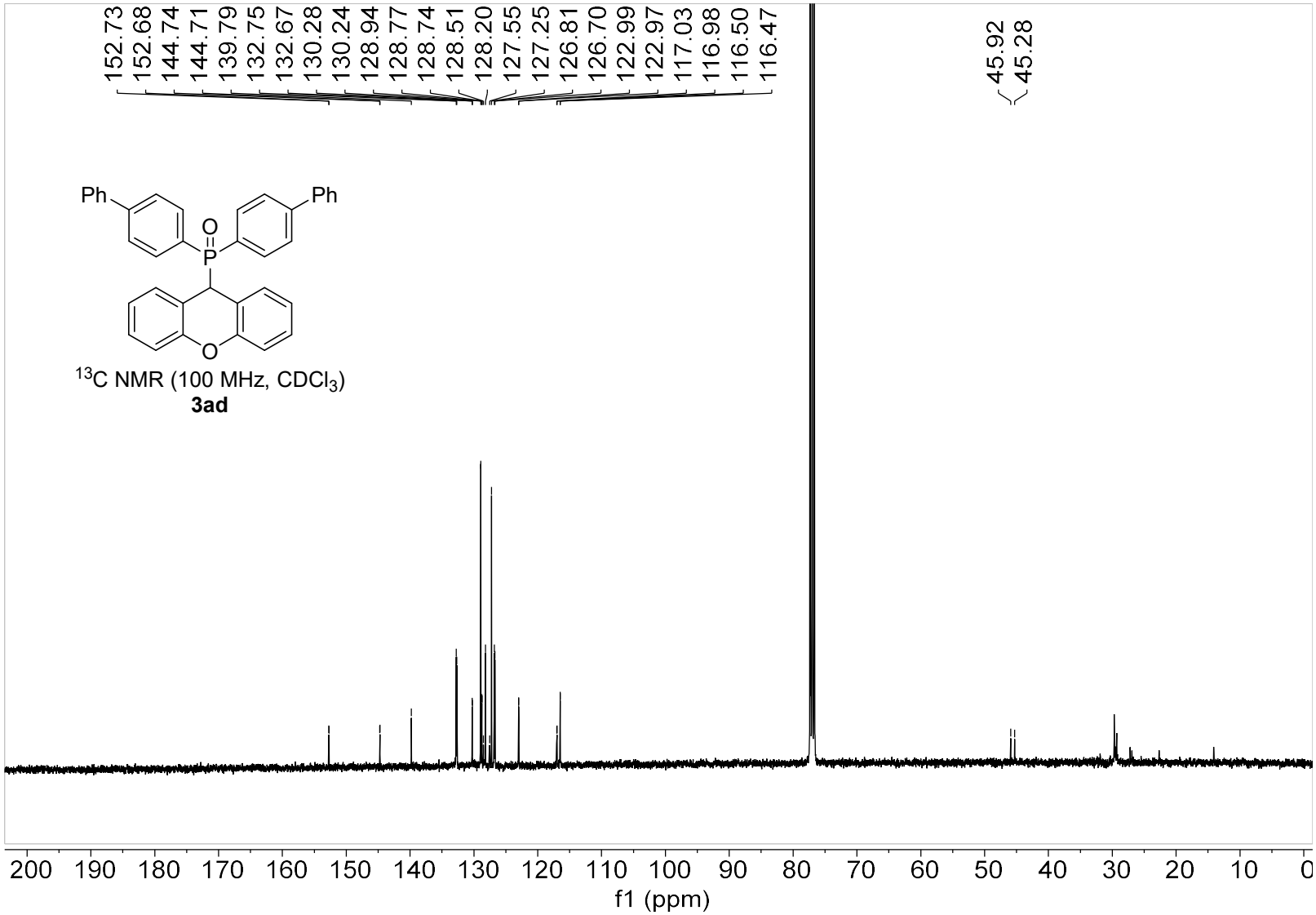
3ac


7.63
7.62
7.49
7.49
7.47
7.45
7.42
7.40
7.40
7.38
7.22
7.21
7.20
7.18
7.18
7.04
7.03
6.94
6.92
6.90
5.02
4.97
Ph
Ph
O
P
O
1H NMR (400 MHz, CDCl3)
3ad
12.03
4.12
2.11
2.07
1.90
3.91
1.00
f1 (ppm)



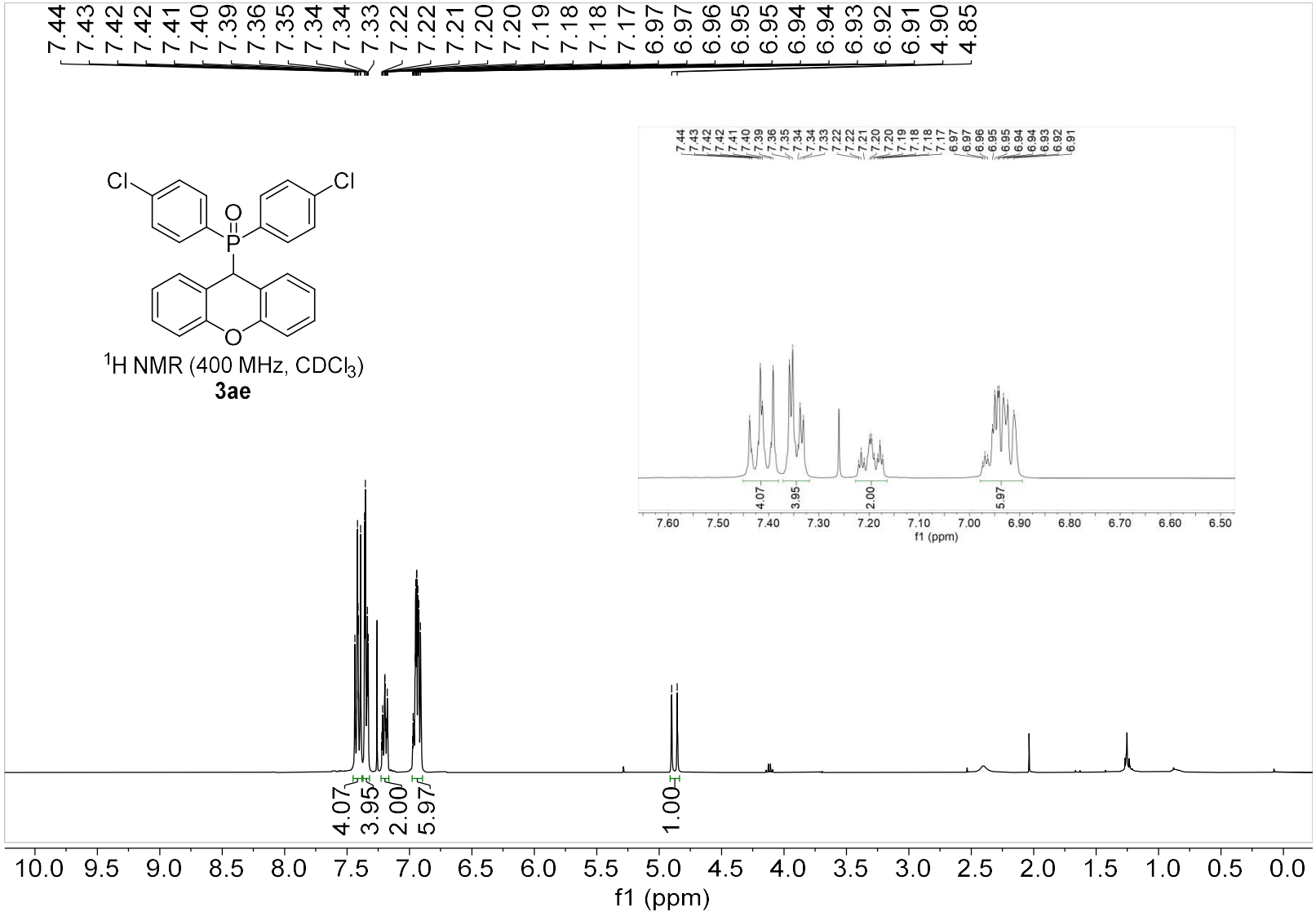
^{31}P NMR (162 MHz, $CDCl_3$)

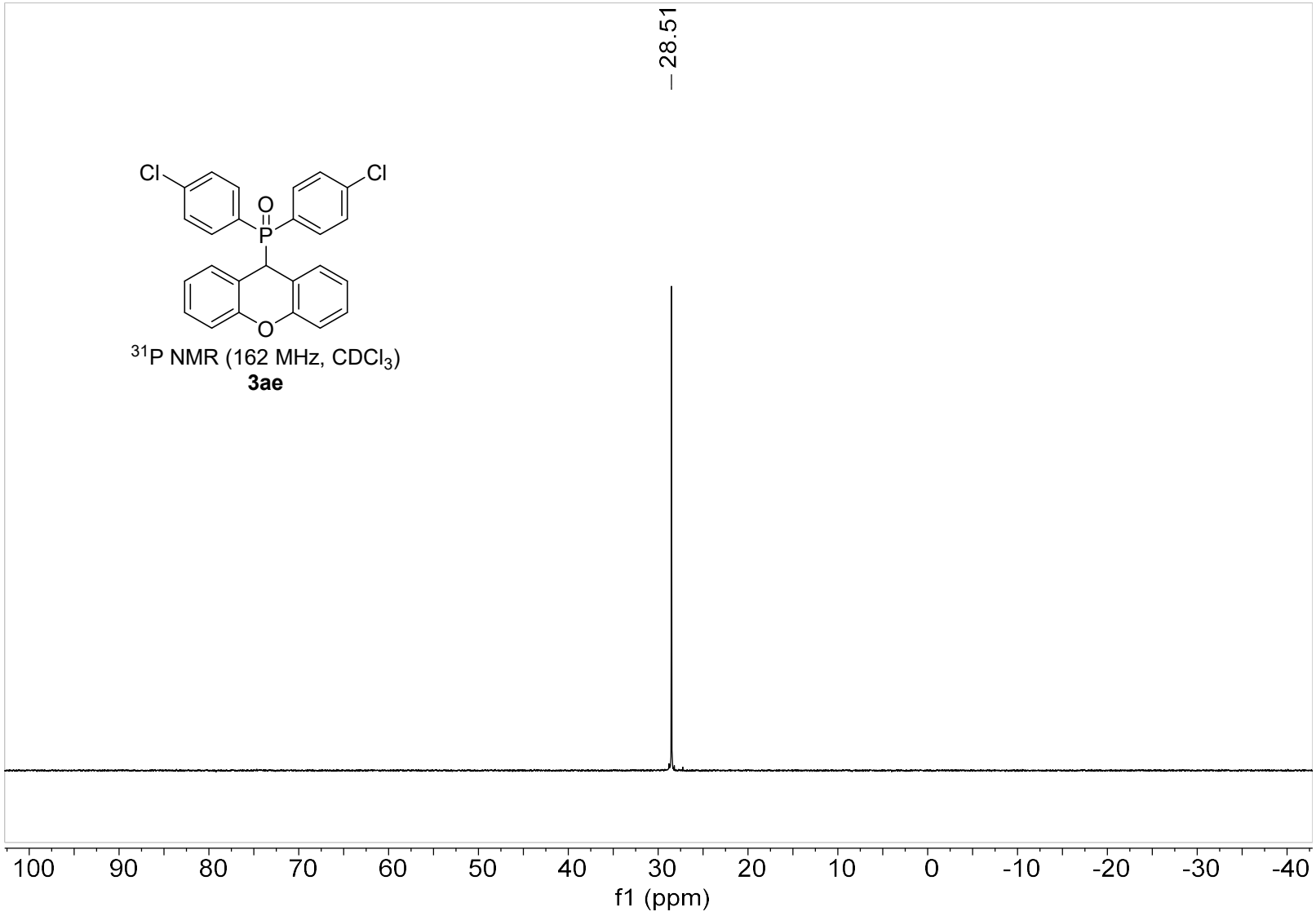
3ad



^{13}C NMR (100 MHz, $CDCl_3$)

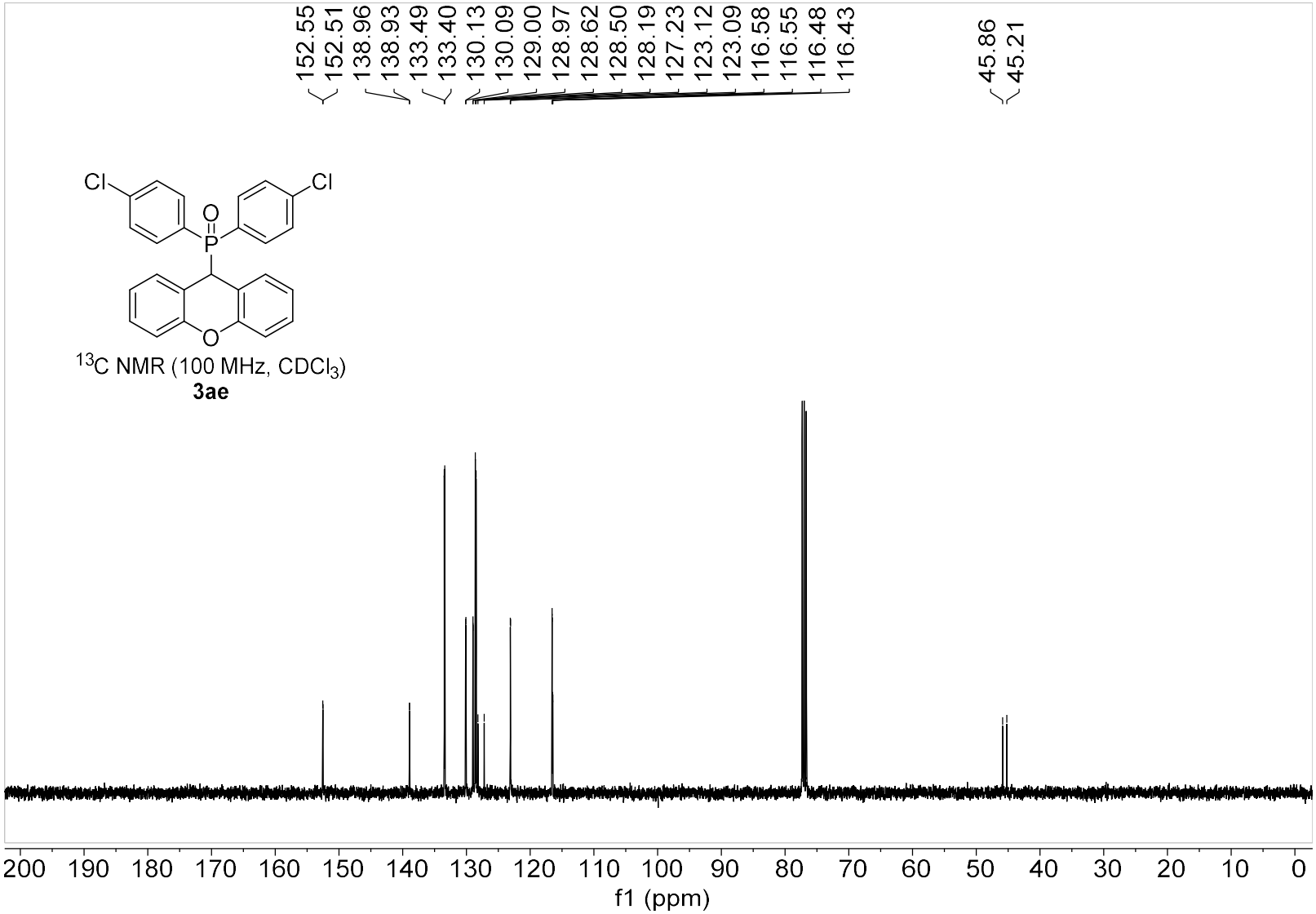
3ad

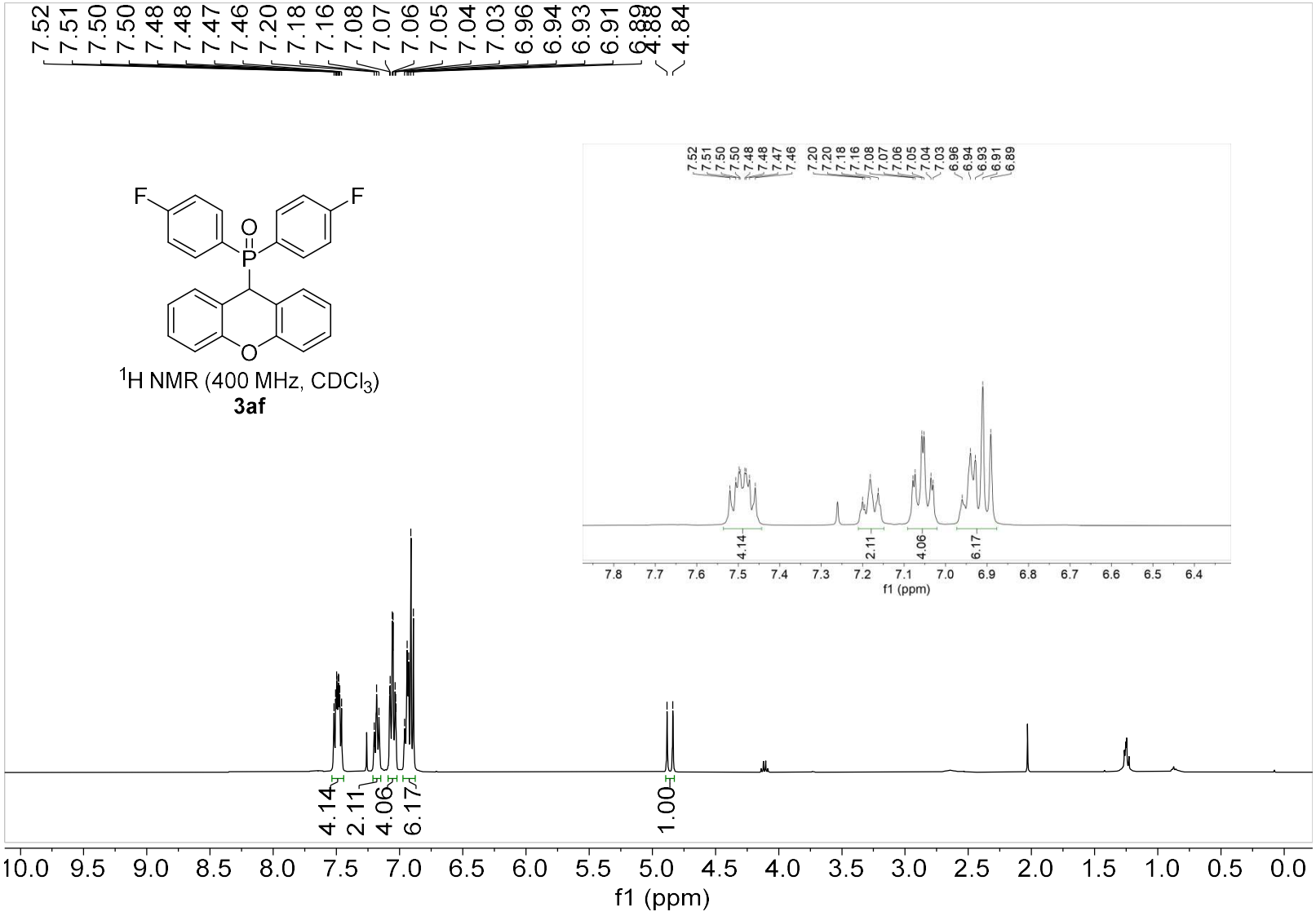

7.44 7.43 7.42 7.42 7.41 7.40 7.39 7.36 7.35 7.34 7.34 7.33 7.22 7.22 7.21 7.20 7.20 7.19 7.18 7.18 7.17 6.97 6.97 6.96 6.95 6.95 6.94 6.94 6.93 6.92 6.91 4.90 4.85
Cl
Cl
O
P
O
1H NMR (400 MHz, CDCl3)
3ae
4.07
3.95
2.00
5.97
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
7.60 7.50 7.40 7.30 7.20 7.10 7.00 6.90 6.80 6.70 6.60 6.50
f1 (ppm)

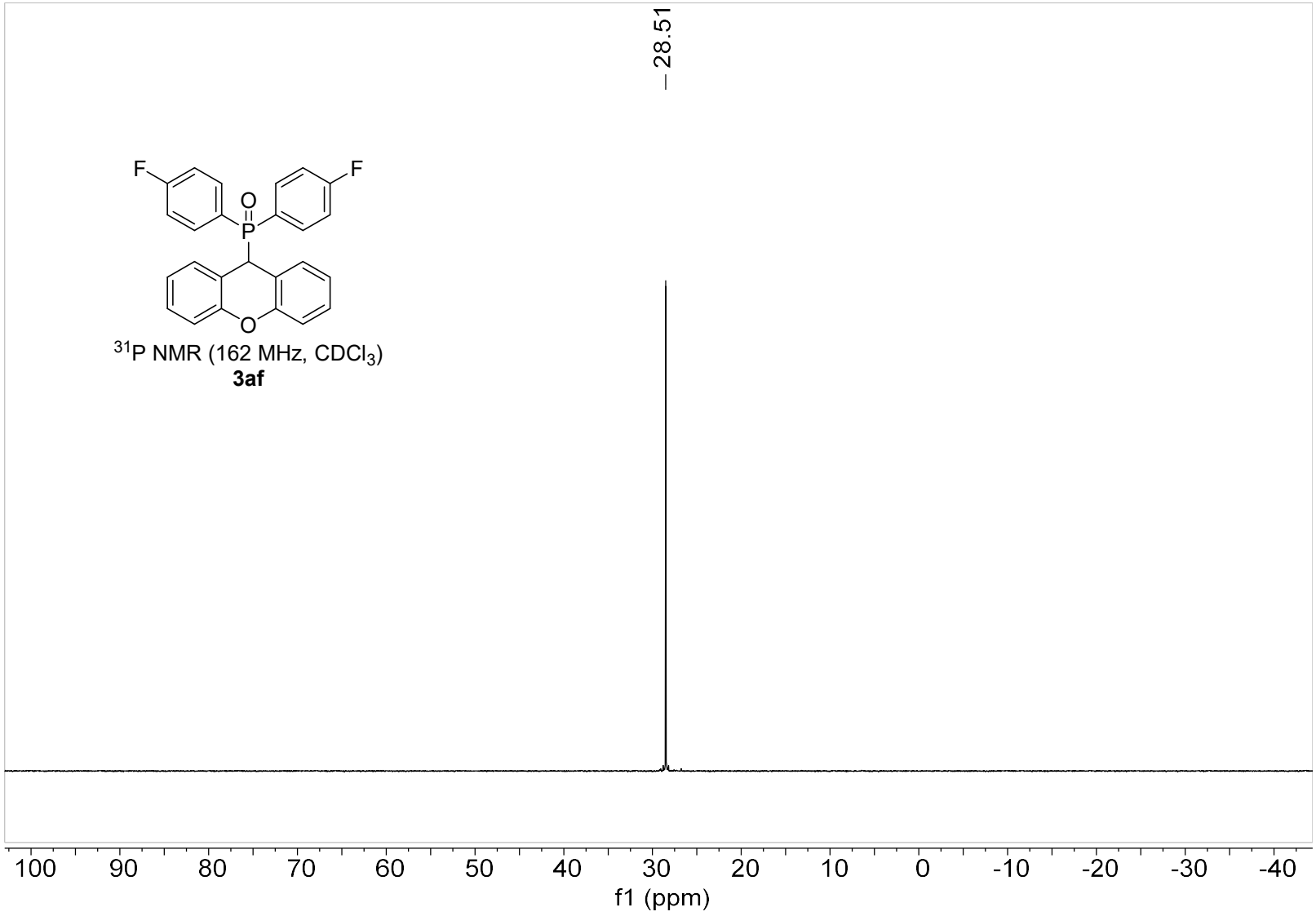


^{31}P NMR (162 MHz, $CDCl_3$)

3ae

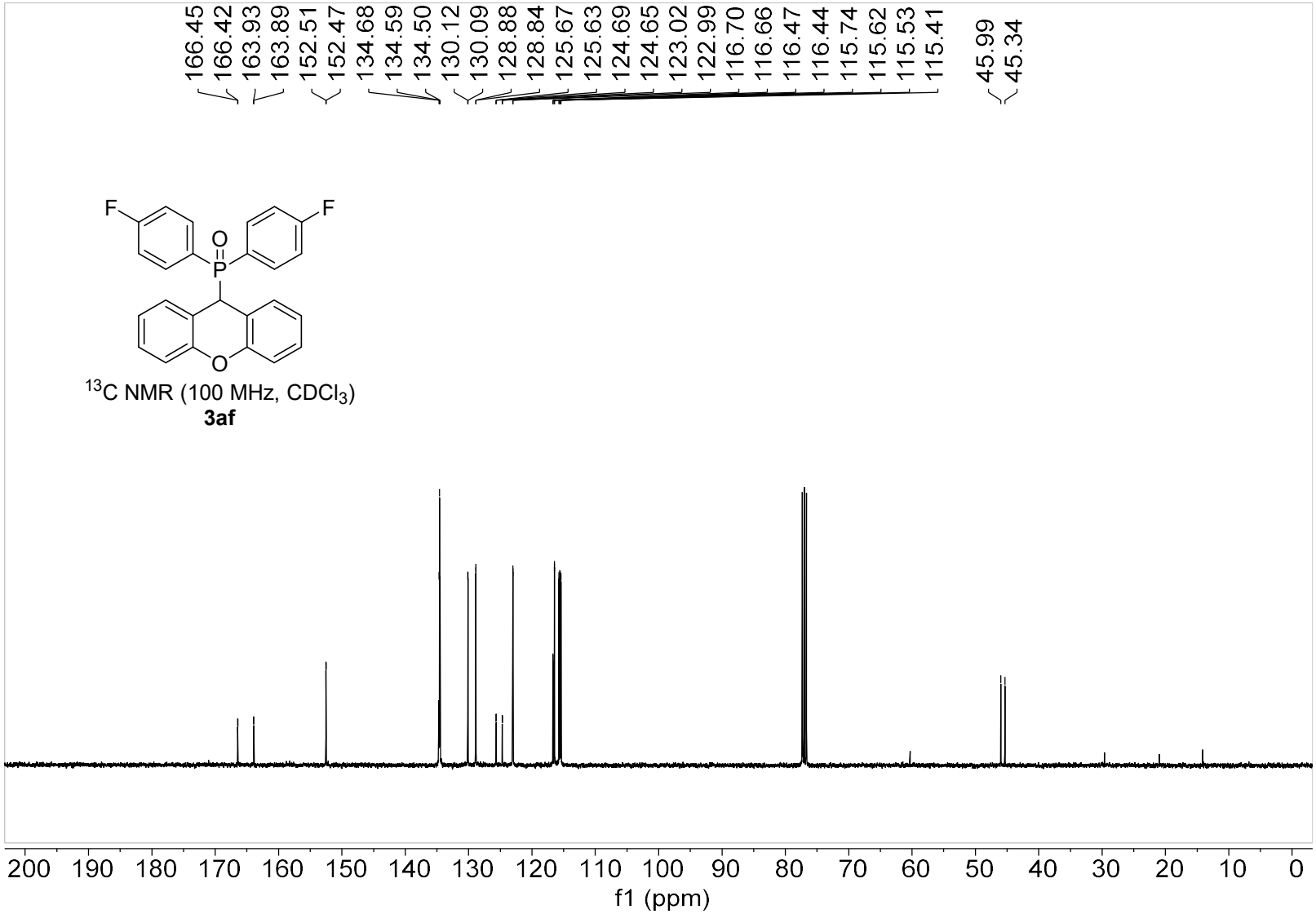

152.55
152.51
138.96
138.93
133.49
133.40
130.13
130.09
129.00
128.97
128.62
128.50
128.19
127.23
123.12
123.09
116.58
116.55
116.48
116.43
45.86
45.21
Cl
Cl
O
P
O
13C NMR (100 MHz, CDCl3)
3ae
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.52
7.51
7.50
7.50
7.48
7.48
7.47
7.46
7.20
7.18
7.16
7.08
7.07
7.06
7.05
7.04
7.03
6.96
6.94
6.93
6.91
6.89
4.88
4.84
F
F
O
P
O
1H NMR (400 MHz, CDCl3)
3af
4.14
2.11
4.06
6.17
1.00
f1 (ppm)



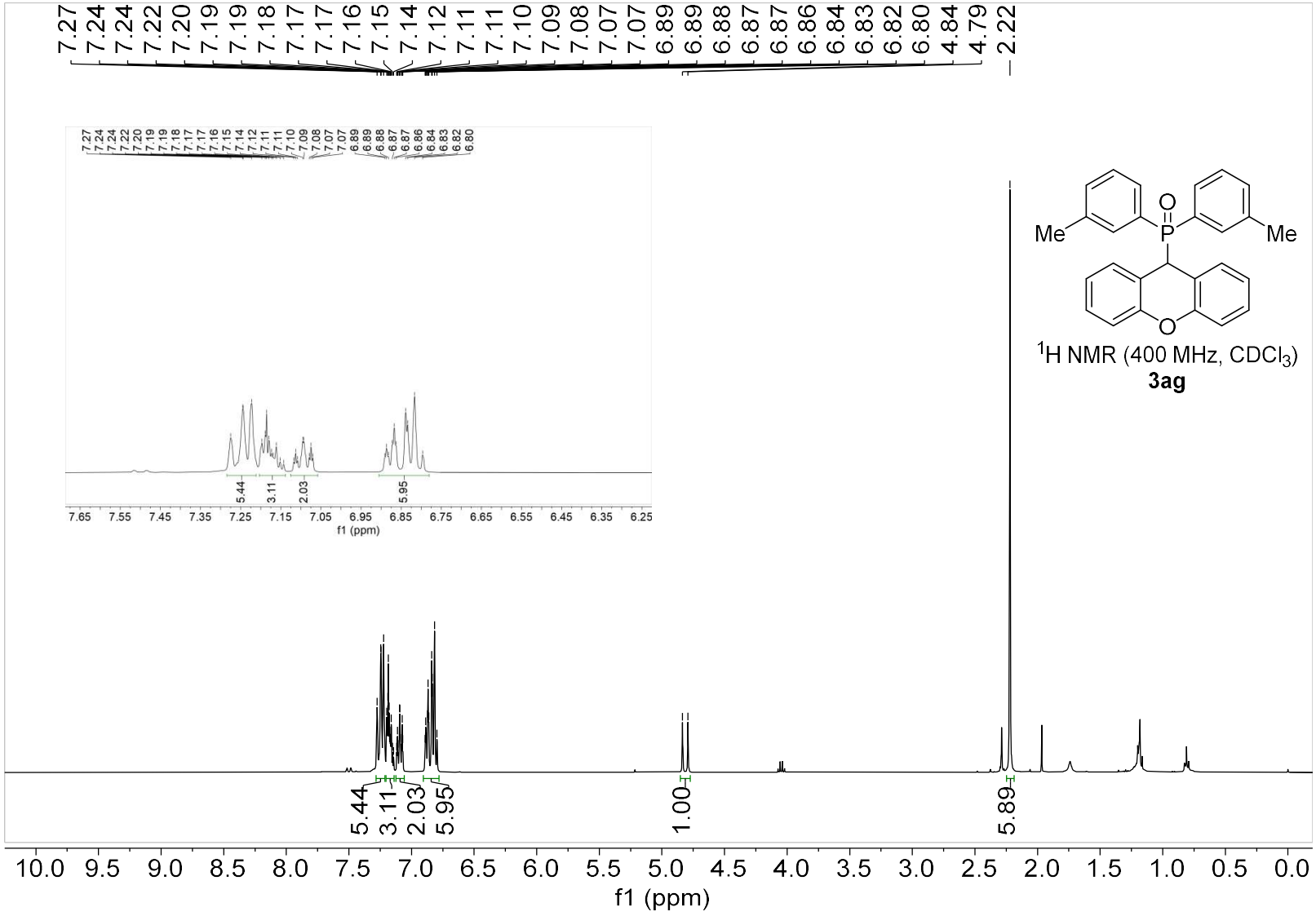
^{31}P NMR (162 MHz, $CDCl_3$)

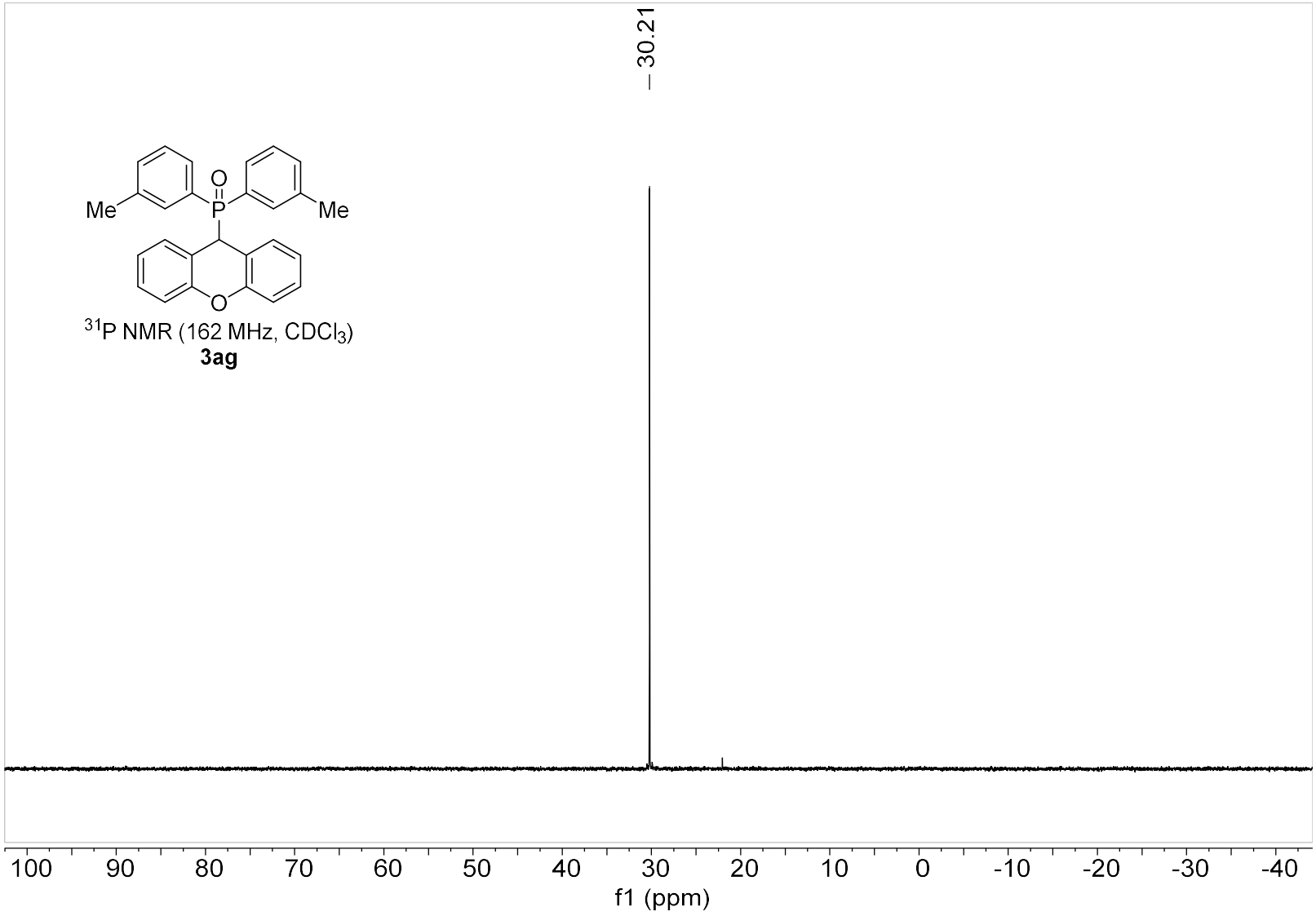
3af



^{13}C NMR (100 MHz, $CDCl_3$)

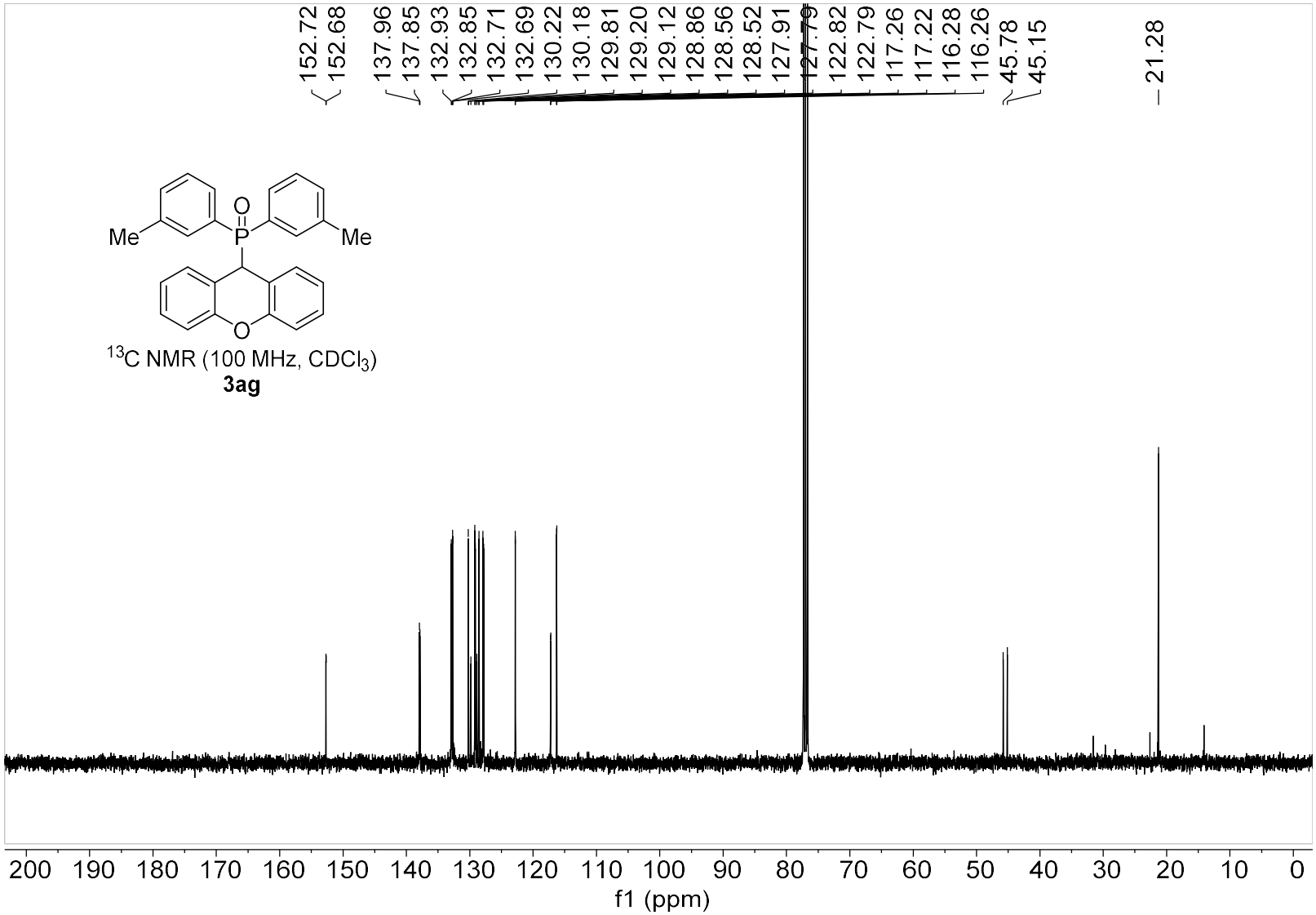
3af

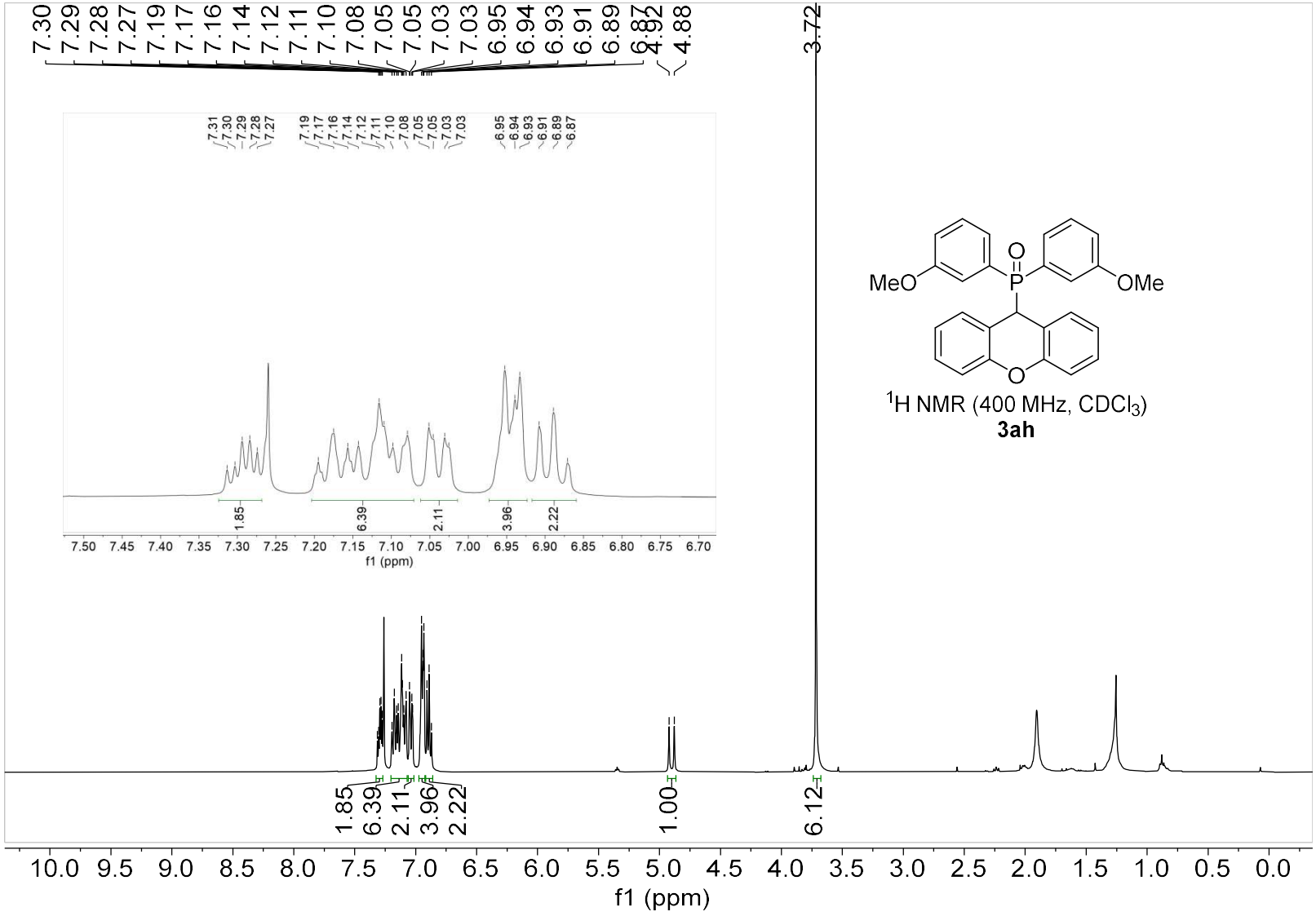

7.27 7.24 7.24 7.22 7.20 7.19 7.19 7.18 7.17 7.17 7.16 7.15 7.14 7.12 7.11 7.11 7.10 7.09 7.08 7.07 7.07 6.89 6.89 6.88 6.87 6.87 6.86 6.84 6.83 6.82 6.80 4.84 4.79 2.22
Me
O
P
Me
O
1H NMR (400 MHz, CDCl3)
3ag
5.44 3.11 2.03 5.95 1.00 5.89
f1 (ppm)

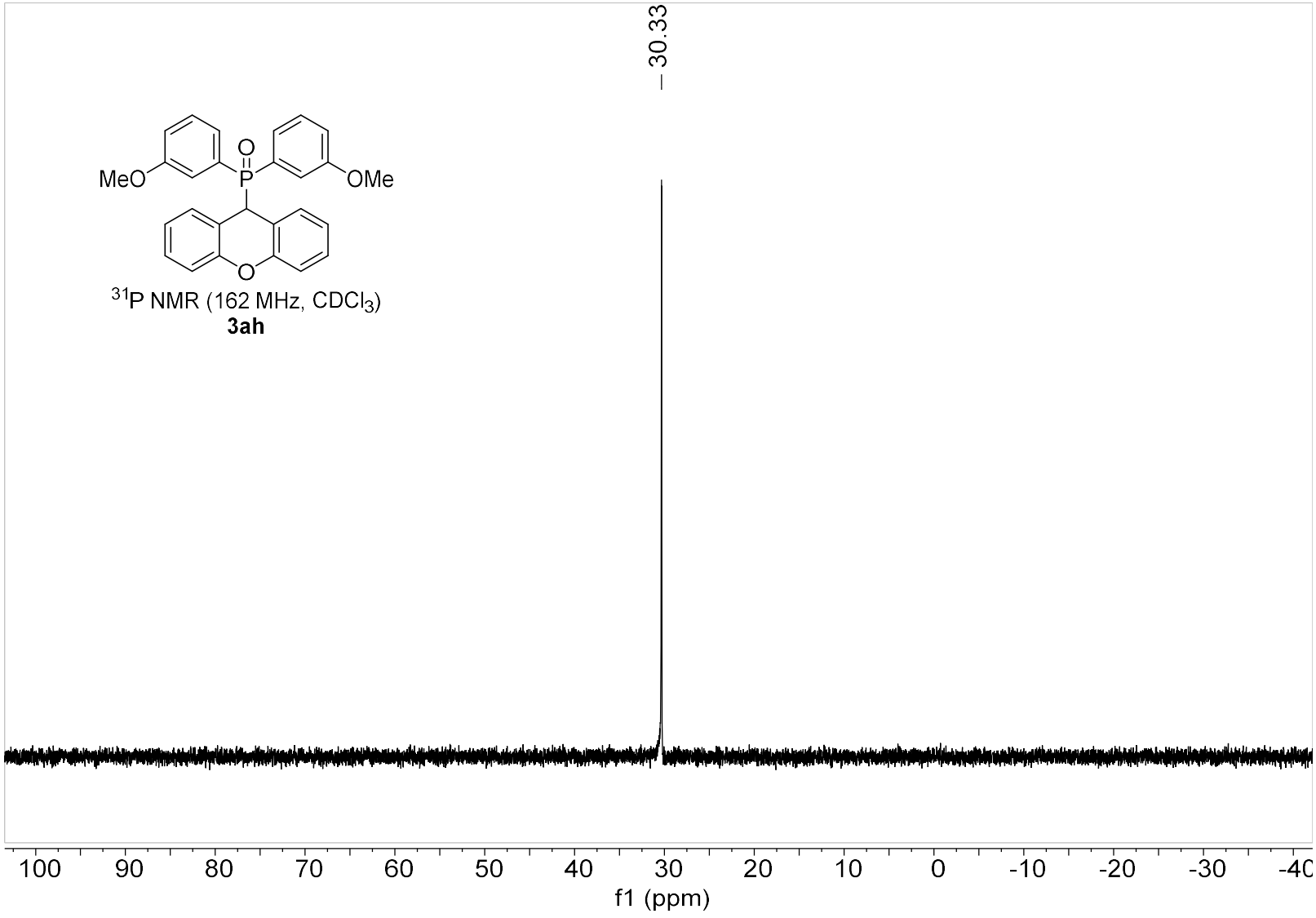


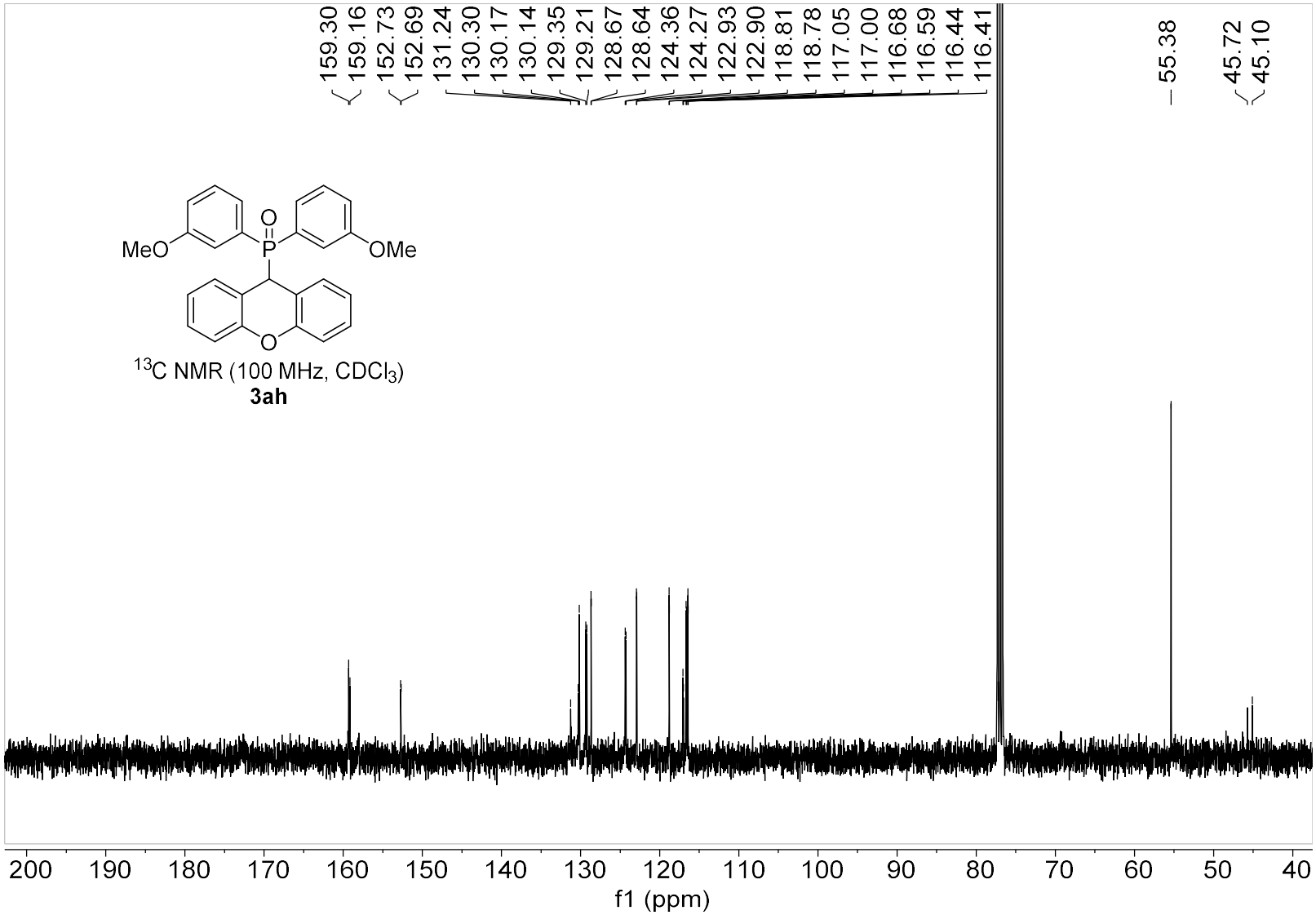
^{31}P NMR (162 MHz, $CDCl_3$)

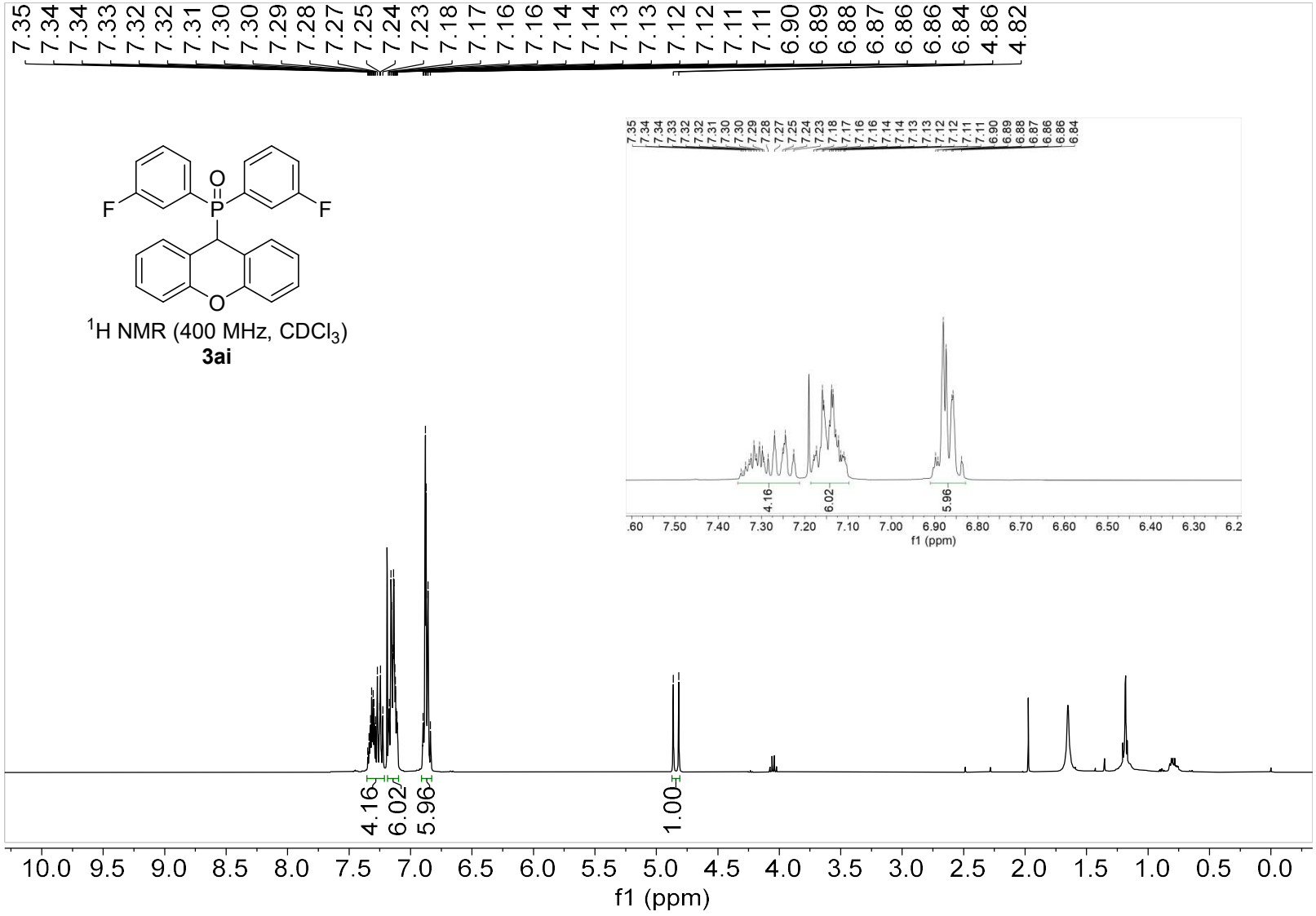
3ag

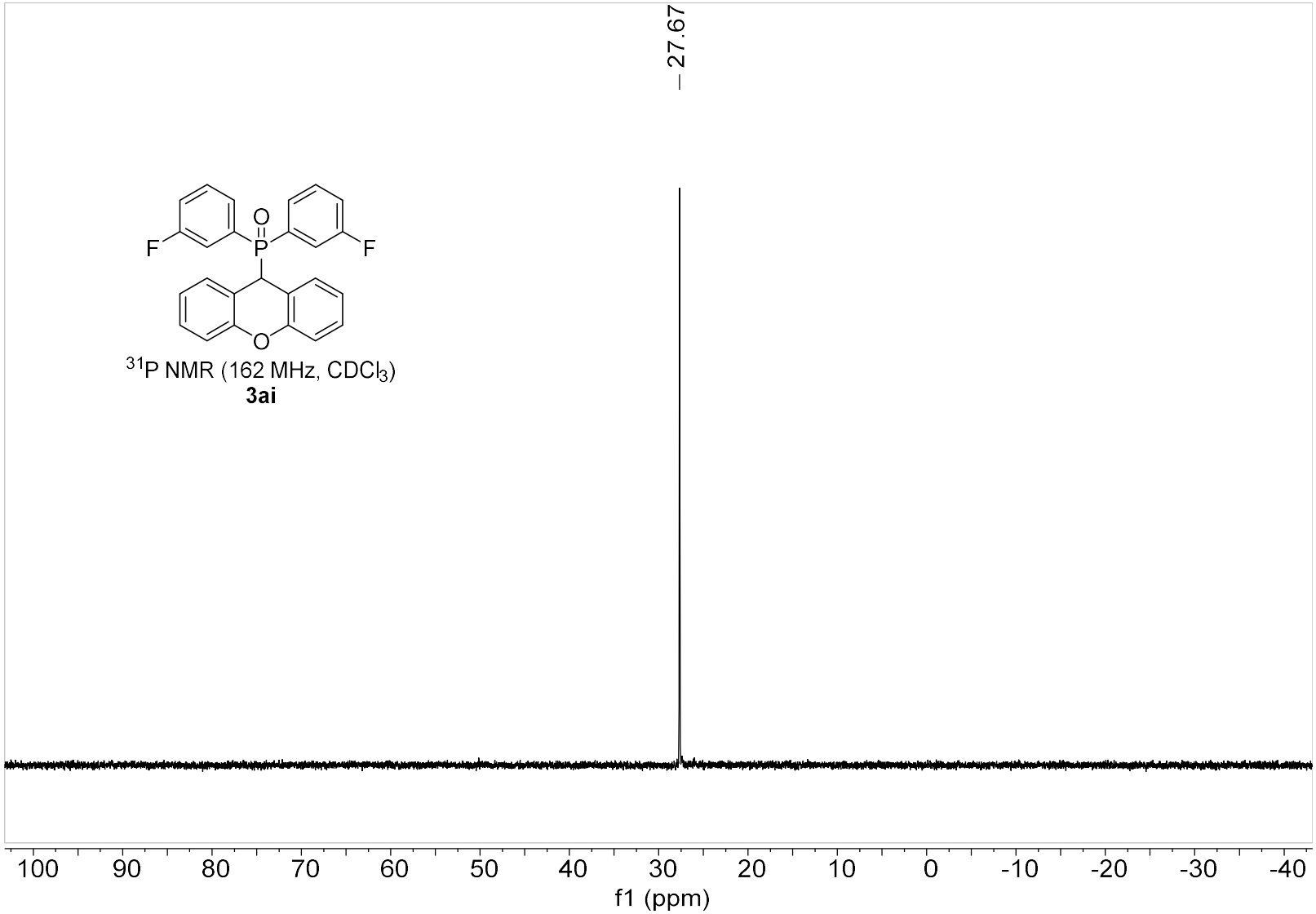

152.72
152.68
137.96
137.85
132.93
132.85
132.71
132.69
130.22
130.18
129.81
129.20
129.12
128.86
128.56
128.52
127.91
127.79
122.82
122.79
117.26
117.22
116.28
116.26
45.78
45.15
21.28
Me
P
O
Me
O
13C NMR (100 MHz, CDCl3)
3ag
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.30
7.29
7.28
7.27
7.19
7.17
7.16
7.14
7.12
7.11
7.10
7.08
7.05
7.05
7.03
7.03
6.95
6.94
6.93
6.91
6.89
6.87
4.92
4.88
3.72
1.85
6.39
2.11
3.96
2.22
1.00
6.12
f1 (ppm)
MeO
OMe
O
P
O
1H NMR (400 MHz, CDCl3)
3ah

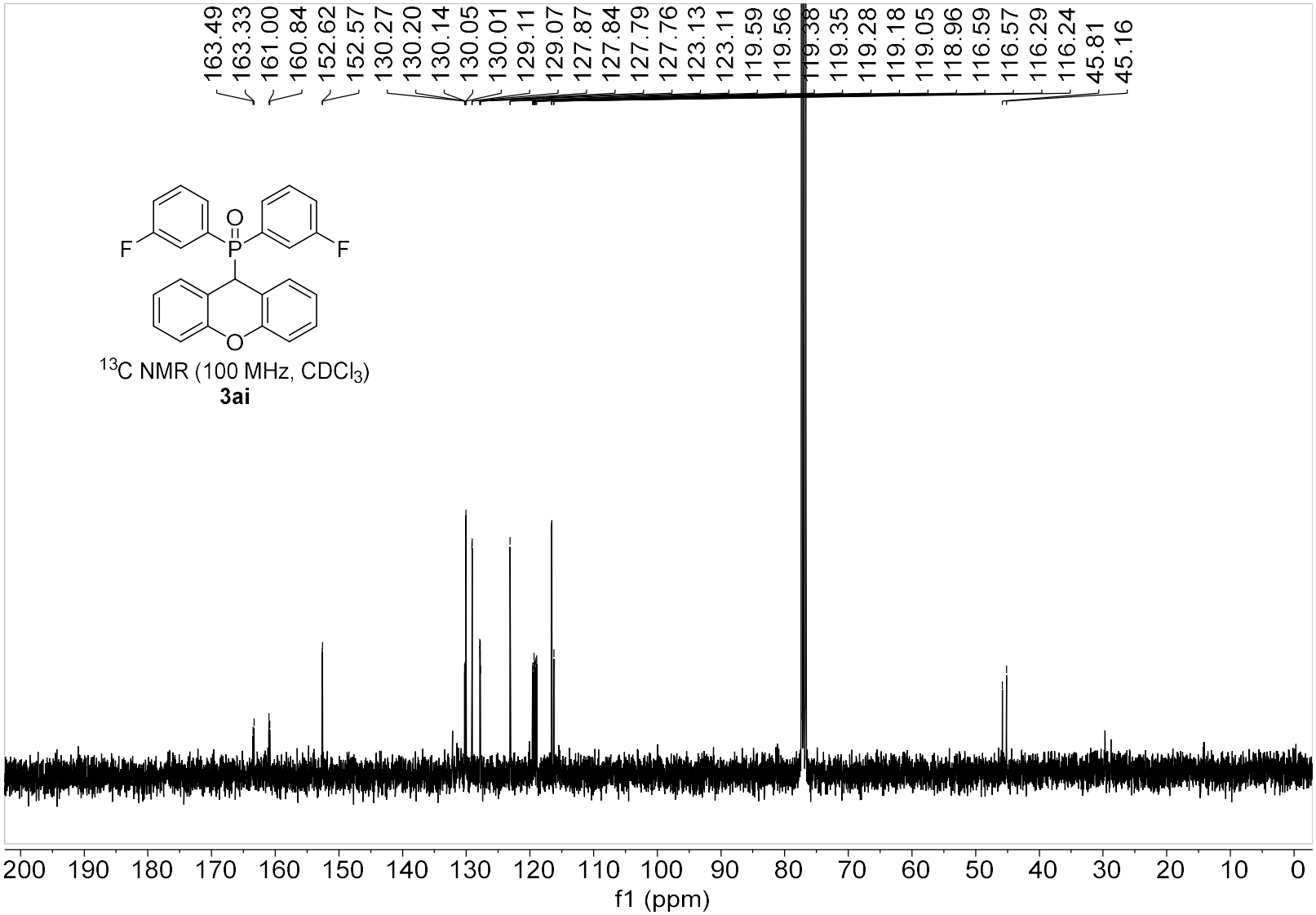

30.33
MeO
O
P
OMe
O
31P NMR (162 MHz, CDCl3)
3ah
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)

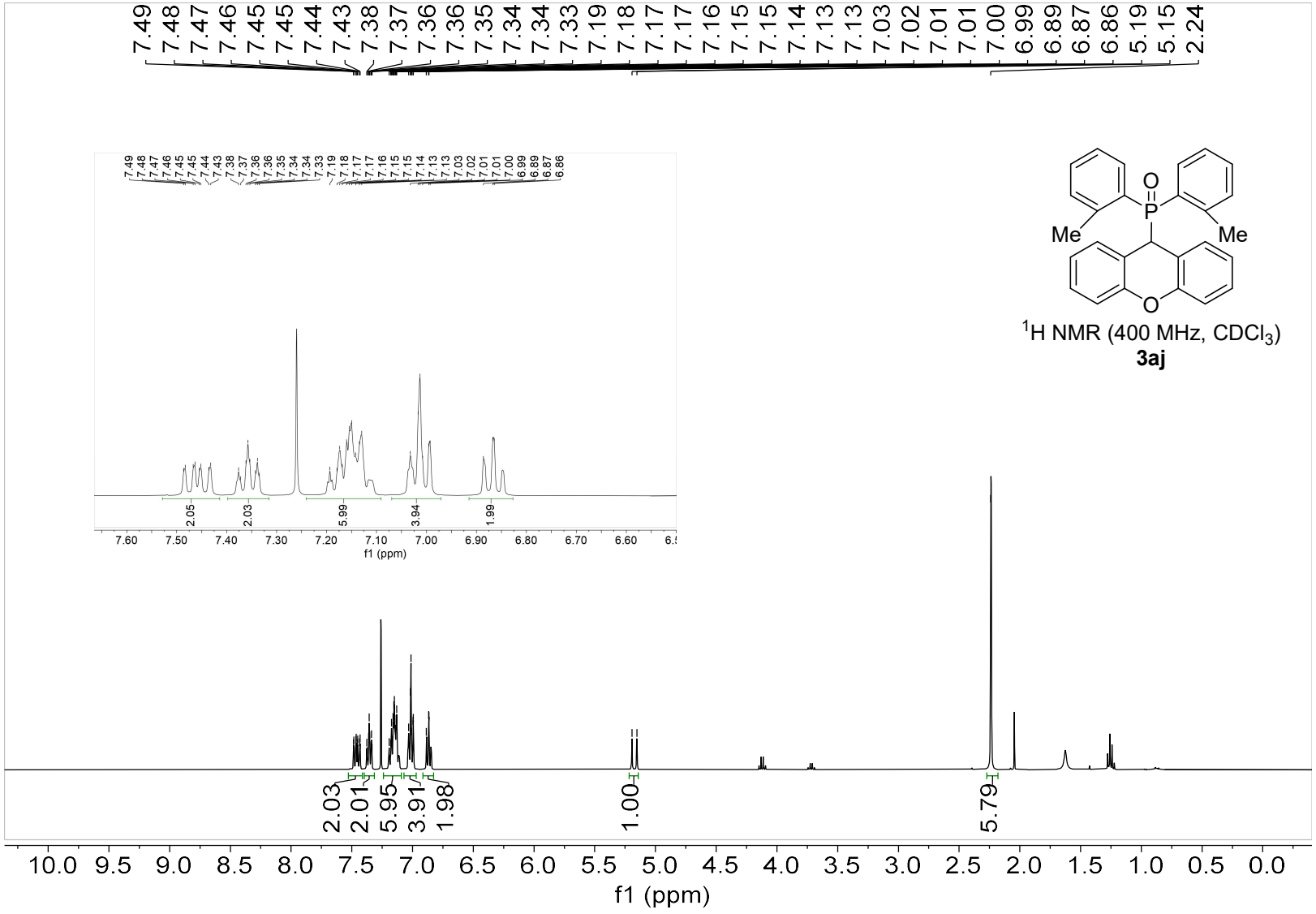

159.30
159.16
152.73
152.69
131.24
130.30
130.17
130.14
129.35
129.21
128.67
128.64
124.36
124.27
122.93
122.90
118.81
118.78
117.05
117.00
116.68
116.59
116.44
116.41
55.38
45.72
45.10
MeO
OMe
O
P
O
13C NMR (100 MHz, CDCl3)
3ah
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
f1 (ppm)


7.35 7.34 7.34 7.33 7.32 7.32 7.31 7.30 7.30 7.29 7.28 7.27 7.25 7.24 7.23 7.18 7.17 7.16 7.16 7.14 7.14 7.13 7.13 7.12 7.12 7.11 7.11 6.90 6.89 6.88 6.87 6.86 6.86 6.84 4.86 4.82
F
O
P
F
O
1H NMR (400 MHz, CDCl3)
3ai
4.16
6.02
5.96
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

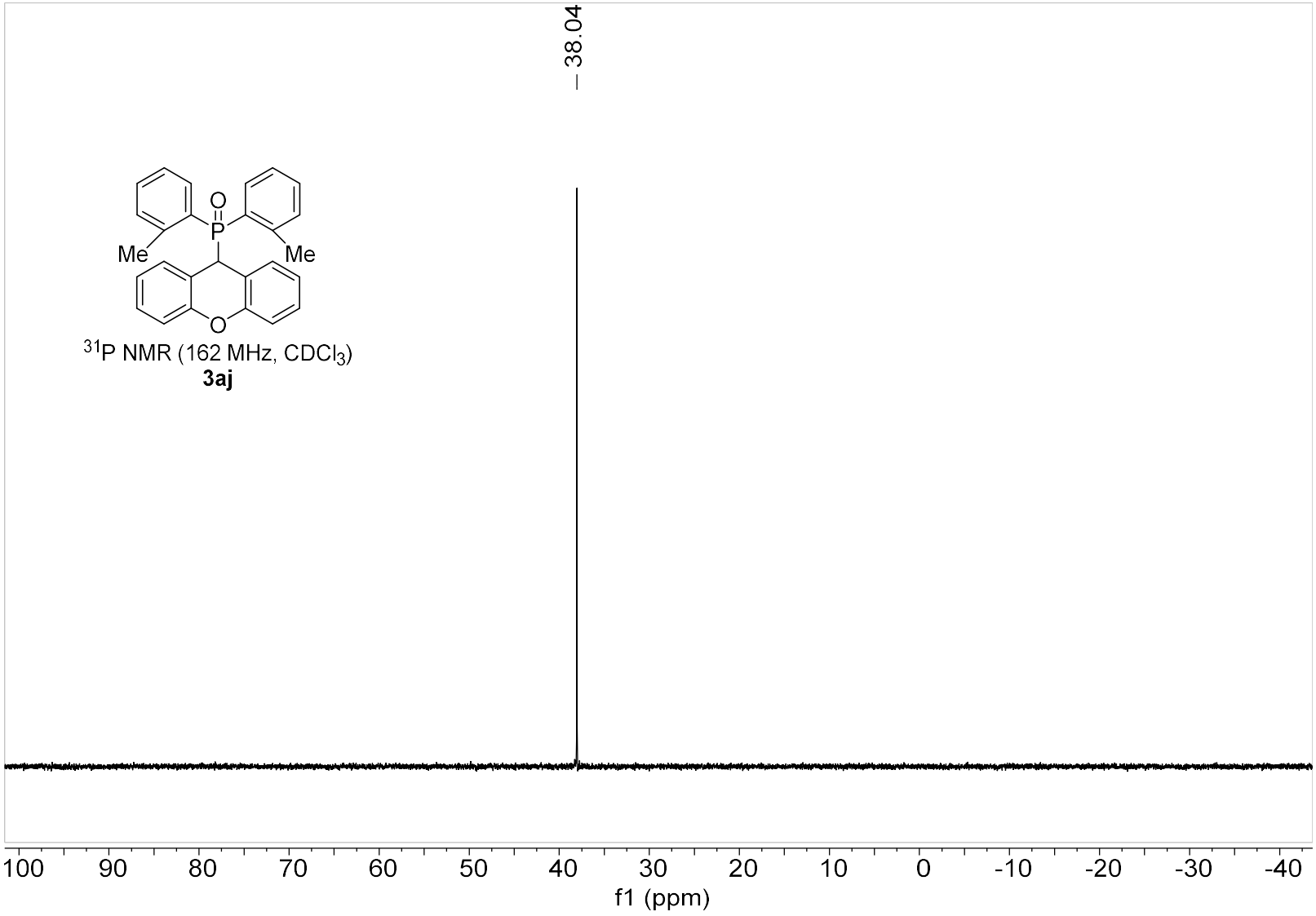


^{31}P NMR (162 MHz, $CDCl_3$)
3ai

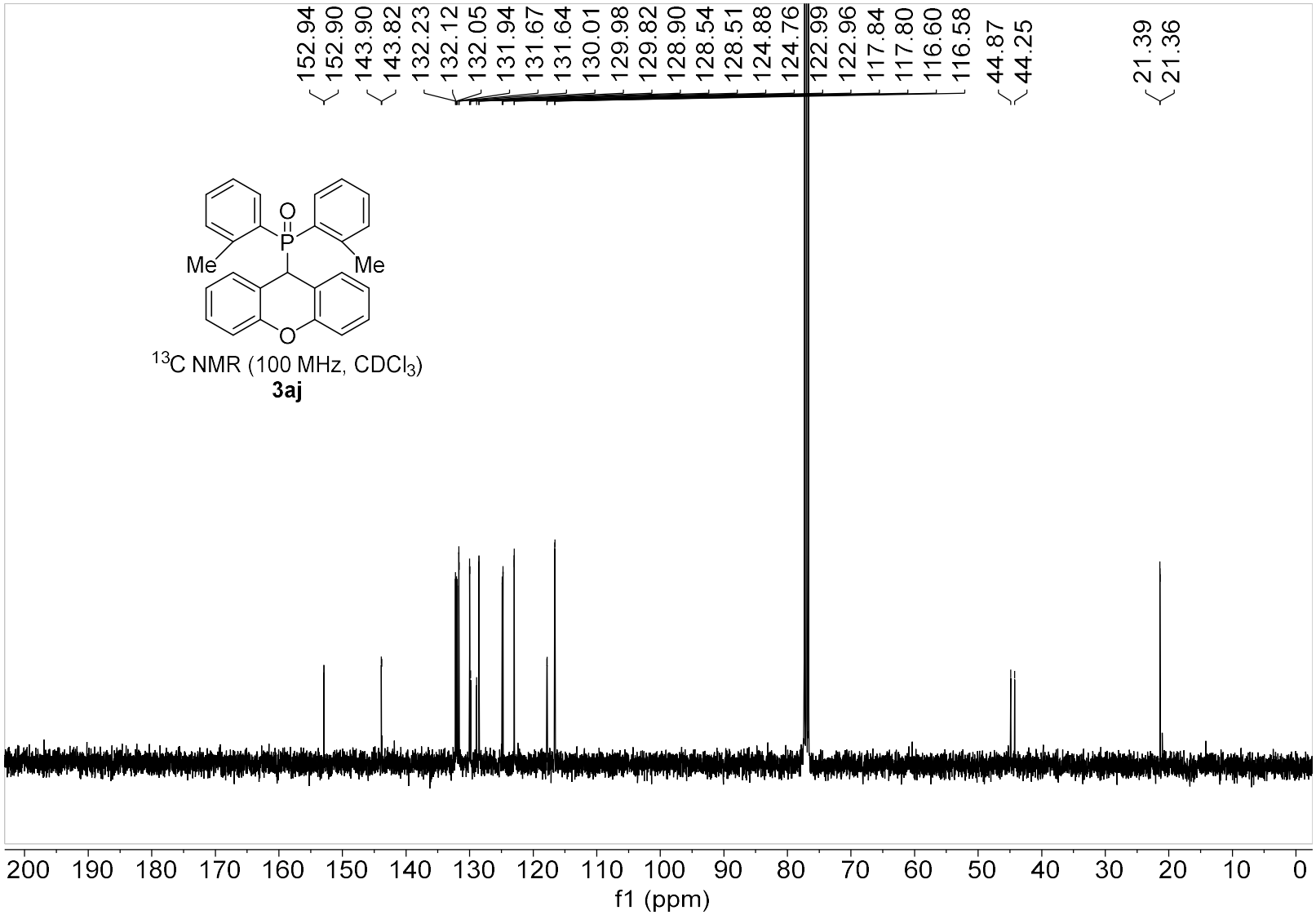

163.49
163.33
161.00
160.84
152.62
152.57
130.27
130.20
130.14
130.05
130.01
129.11
129.07
127.87
127.84
127.79
127.76
123.13
123.11
119.59
119.56
119.38
119.35
119.28
119.18
119.05
118.96
116.59
116.57
116.29
116.24
45.81
45.16
O
P
F
F
O
13C NMR (100 MHz, CDCl3)
3ai
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

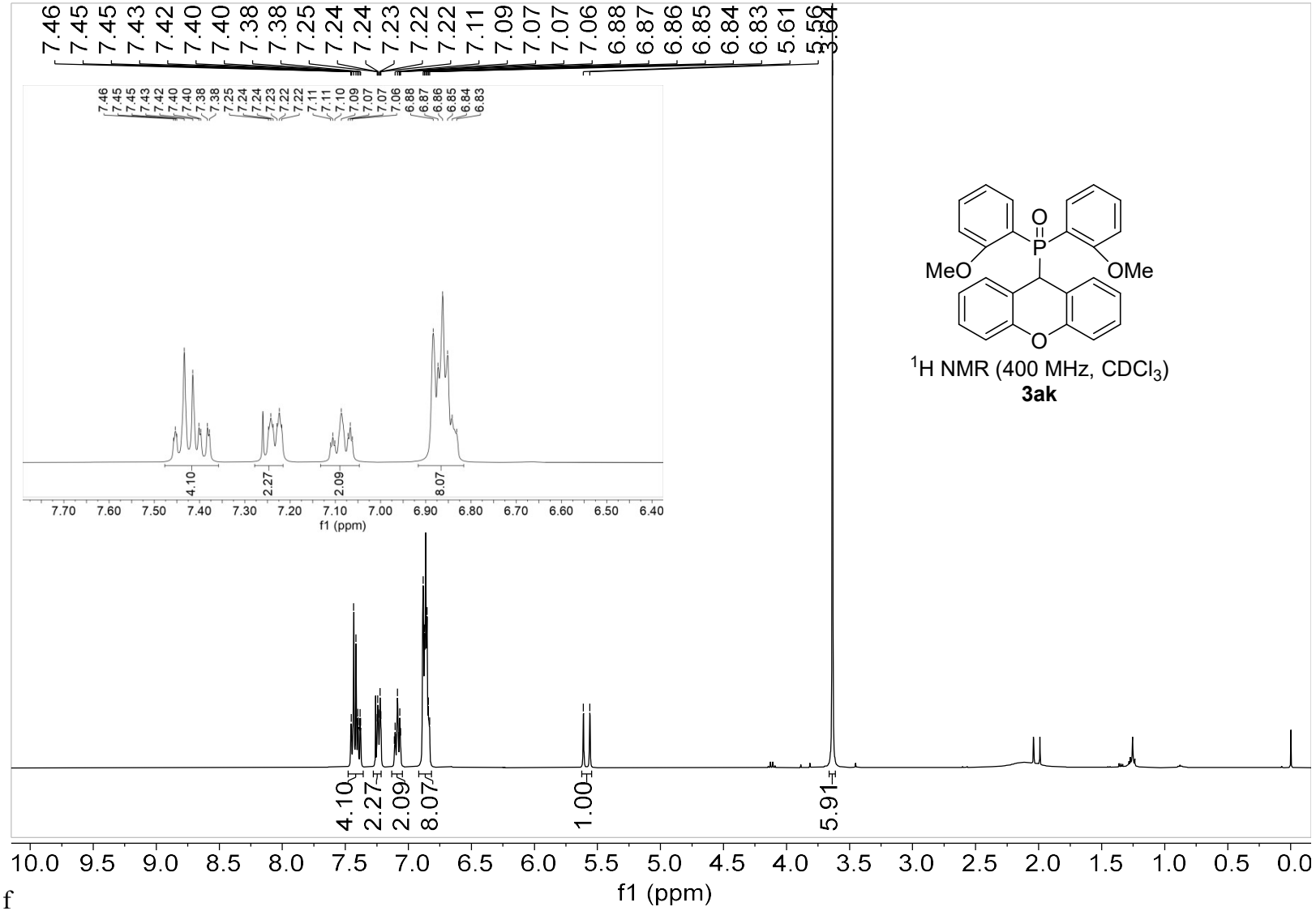


^{1}H NMR (400 MHz, $CDCl_3$)
3aj

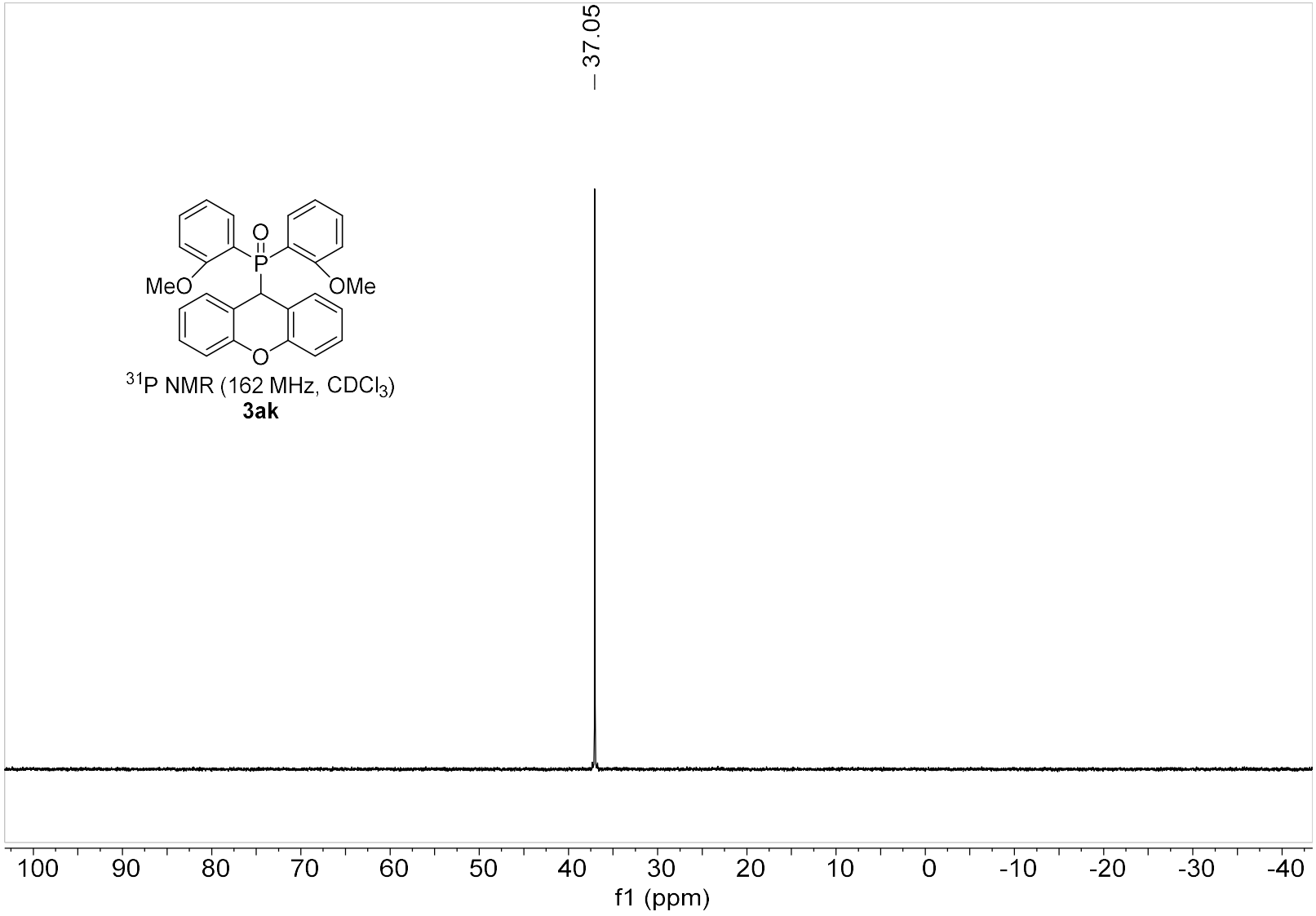


^{31}P NMR (162 MHz, $CDCl_3$)
3aj

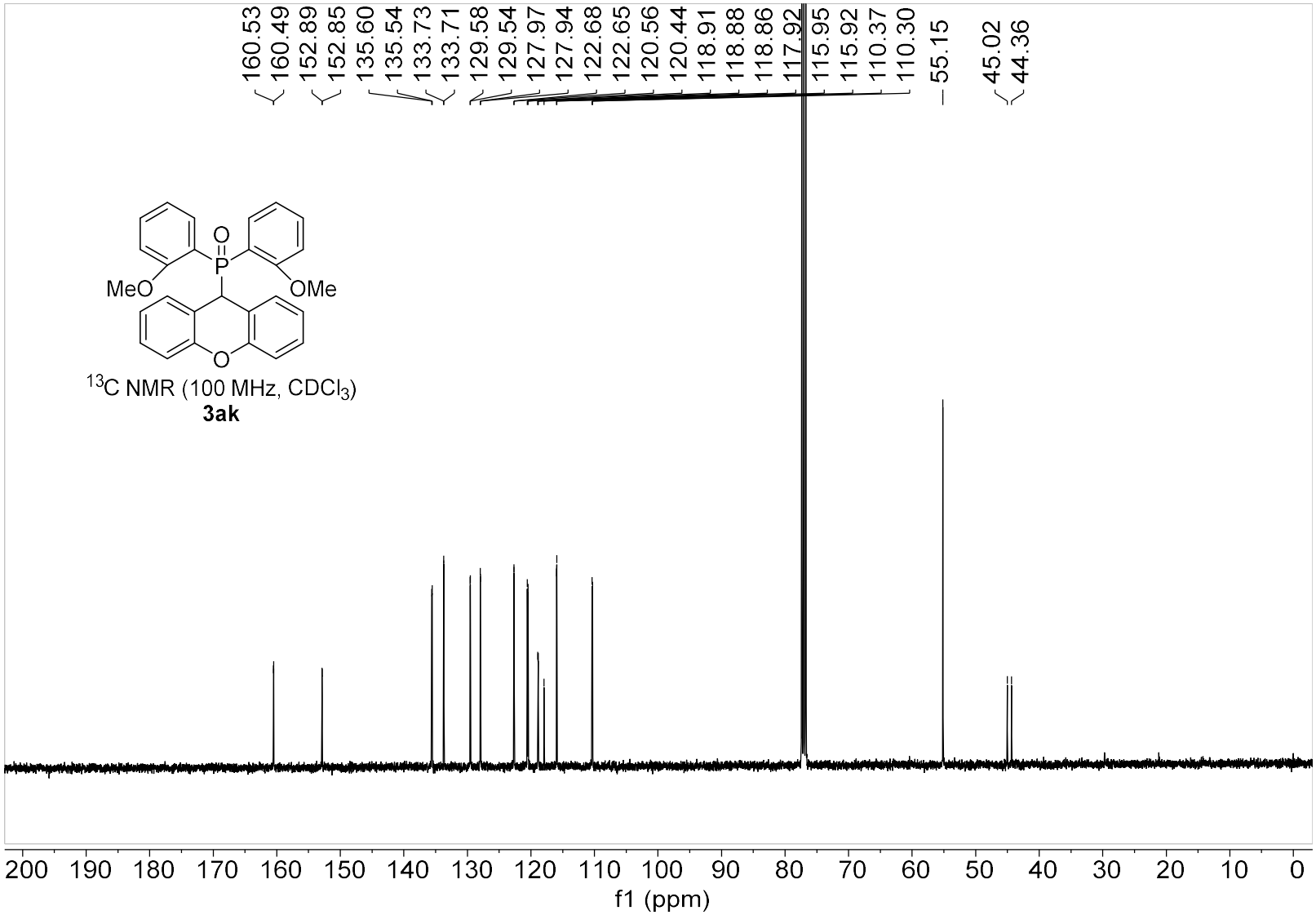

152.94
152.90
143.90
143.82
132.23
132.12
132.05
131.94
131.67
131.64
130.01
129.98
129.82
128.90
128.54
128.51
124.88
124.76
122.99
122.96
117.84
117.80
116.60
116.58
44.87
44.25
21.39
21.36
O
P
Me
Me
O
13C NMR (100 MHz, CDCl3)
3aj
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.46 7.45 7.45 7.43 7.42 7.40 7.40 7.38 7.38 7.25 7.24 7.24 7.23 7.22 7.22 7.11 7.09 7.07 7.07 7.06 6.88 6.87 6.86 6.85 6.84 6.83 5.61 5.56 3.64
4.10 2.27 2.09 8.07 1.00 5.91
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
MeO
OMe
O
P
O
^{1}H NMR (400 MHz, $CDCl_3$)
3ak

f

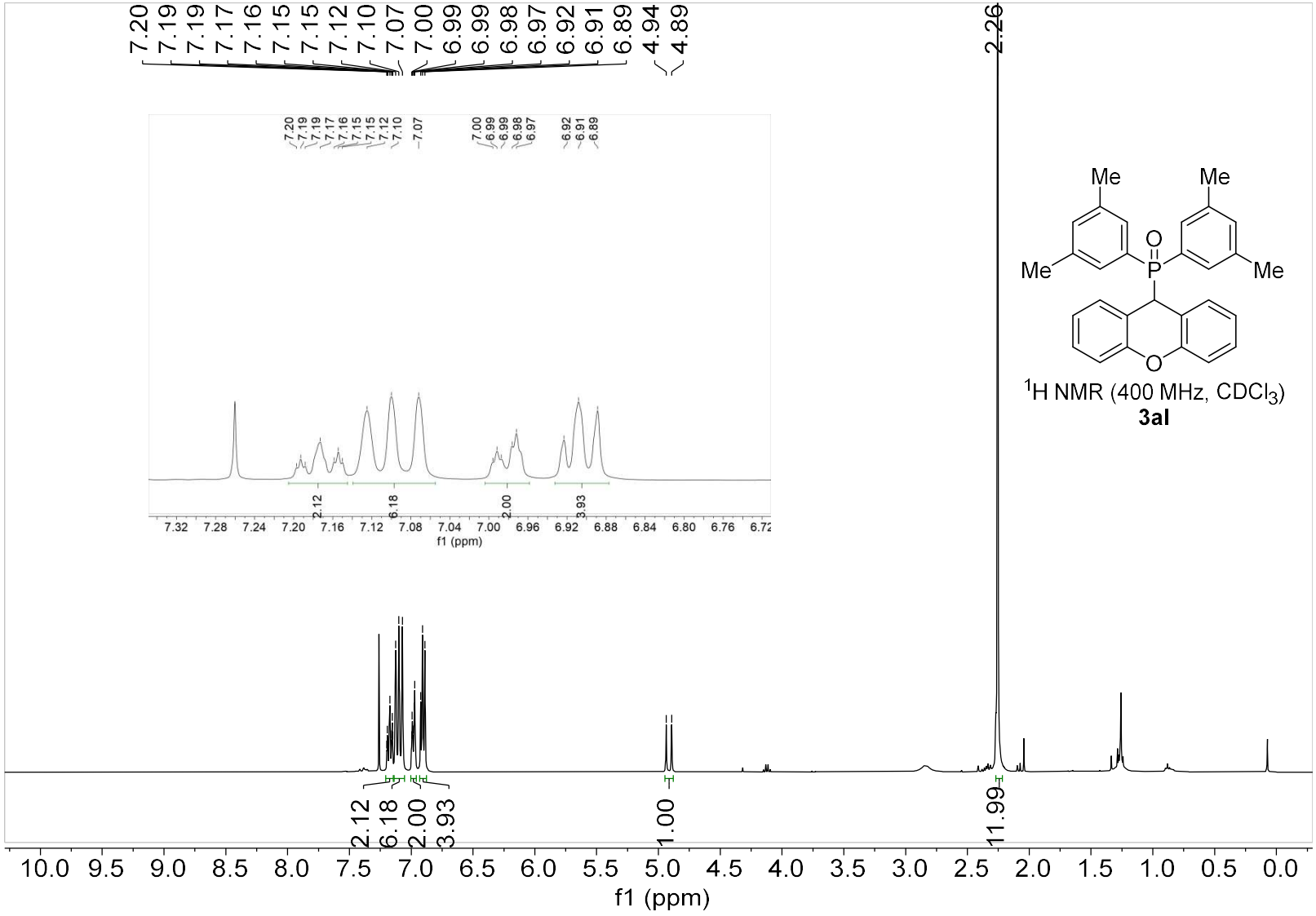


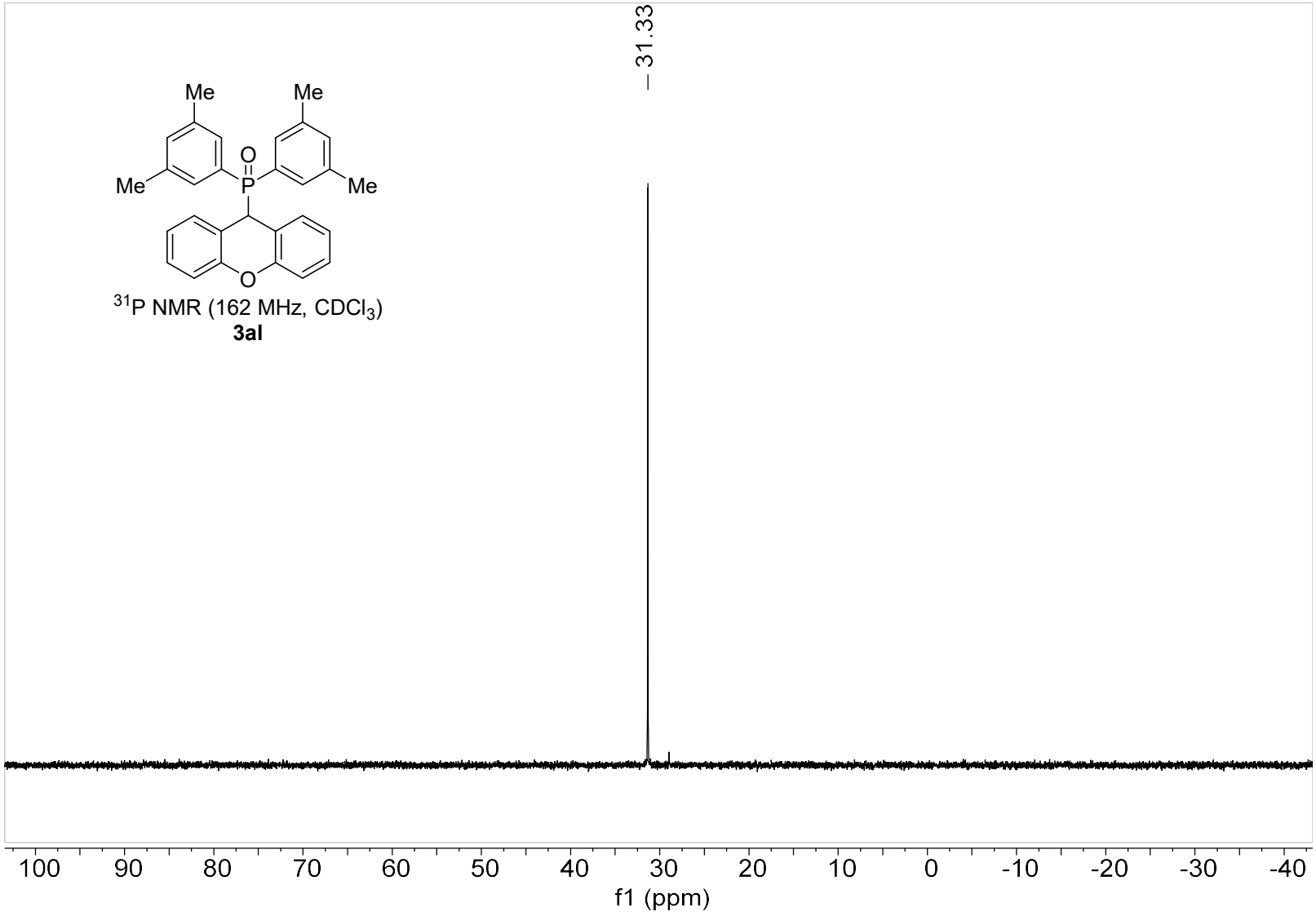
^{31}P NMR (162 MHz, $CDCl_3$)
3ak



^{13}C NMR (100 MHz, $CDCl_3$)

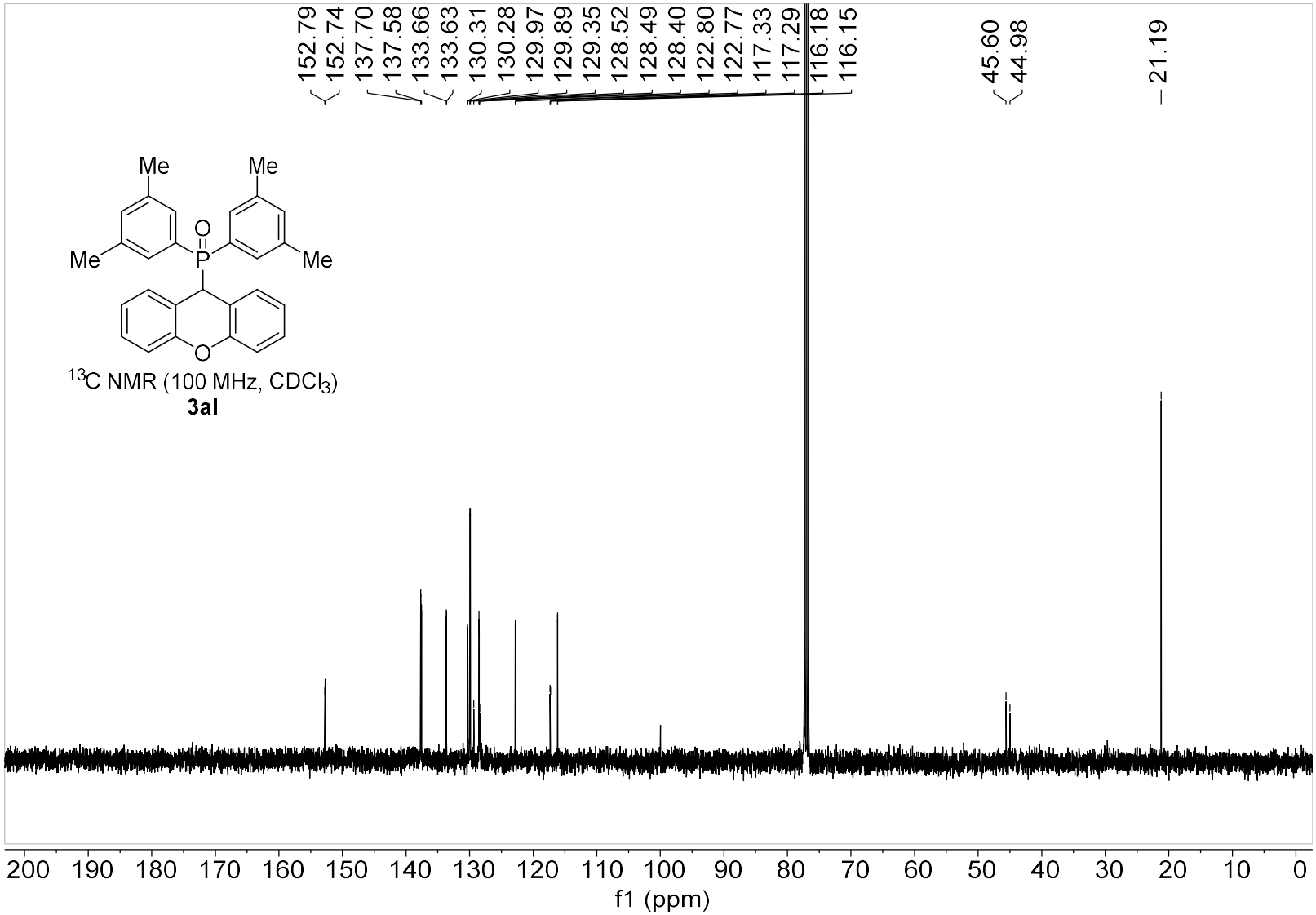
3ak


7.20 7.19 7.19 7.17 7.16 7.15 7.15 7.12 7.10 7.07 7.00 6.99 6.99 6.98 6.97 6.92 6.91 6.89 4.94 4.89
2.26
Me
Me
Me
Me
O
P
O
1H NMR (400 MHz, CDCl3)
3al
2.12 6.18 2.00 3.93
1.00
11.99
f1 (ppm)



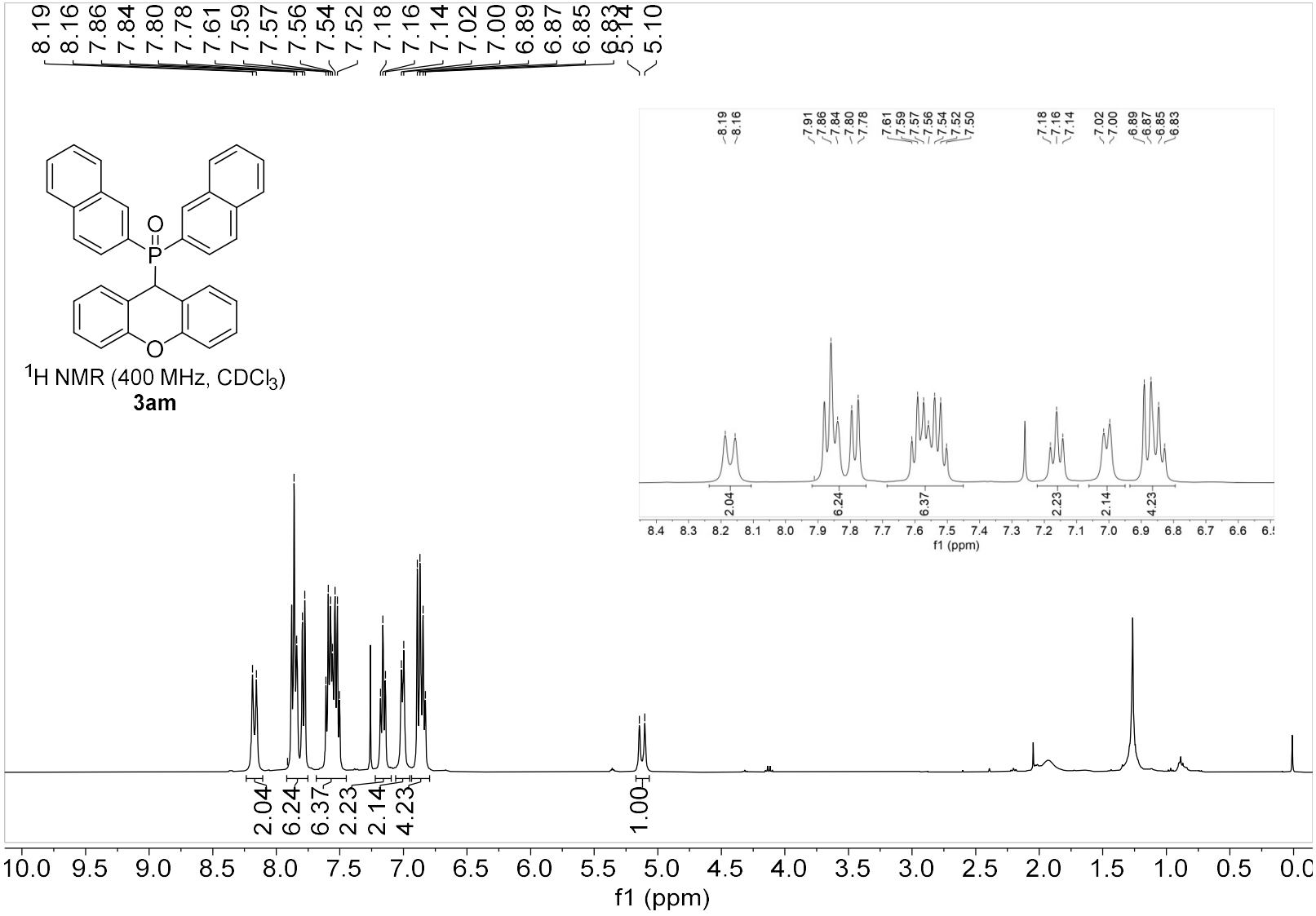
^{31}P NMR (162 MHz, $CDCl_3$)

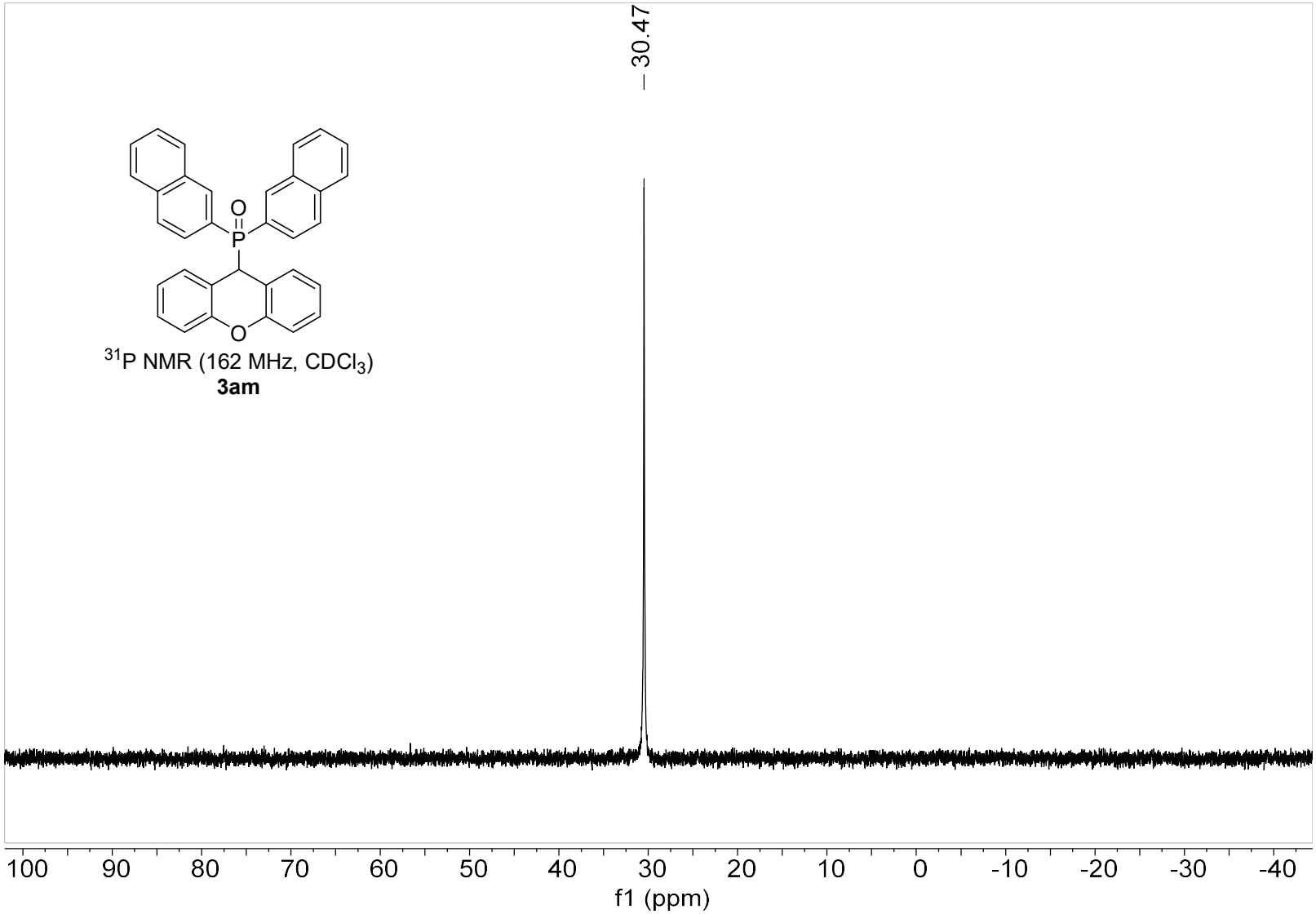
3al



^{13}C NMR (100 MHz, $CDCl_3$)

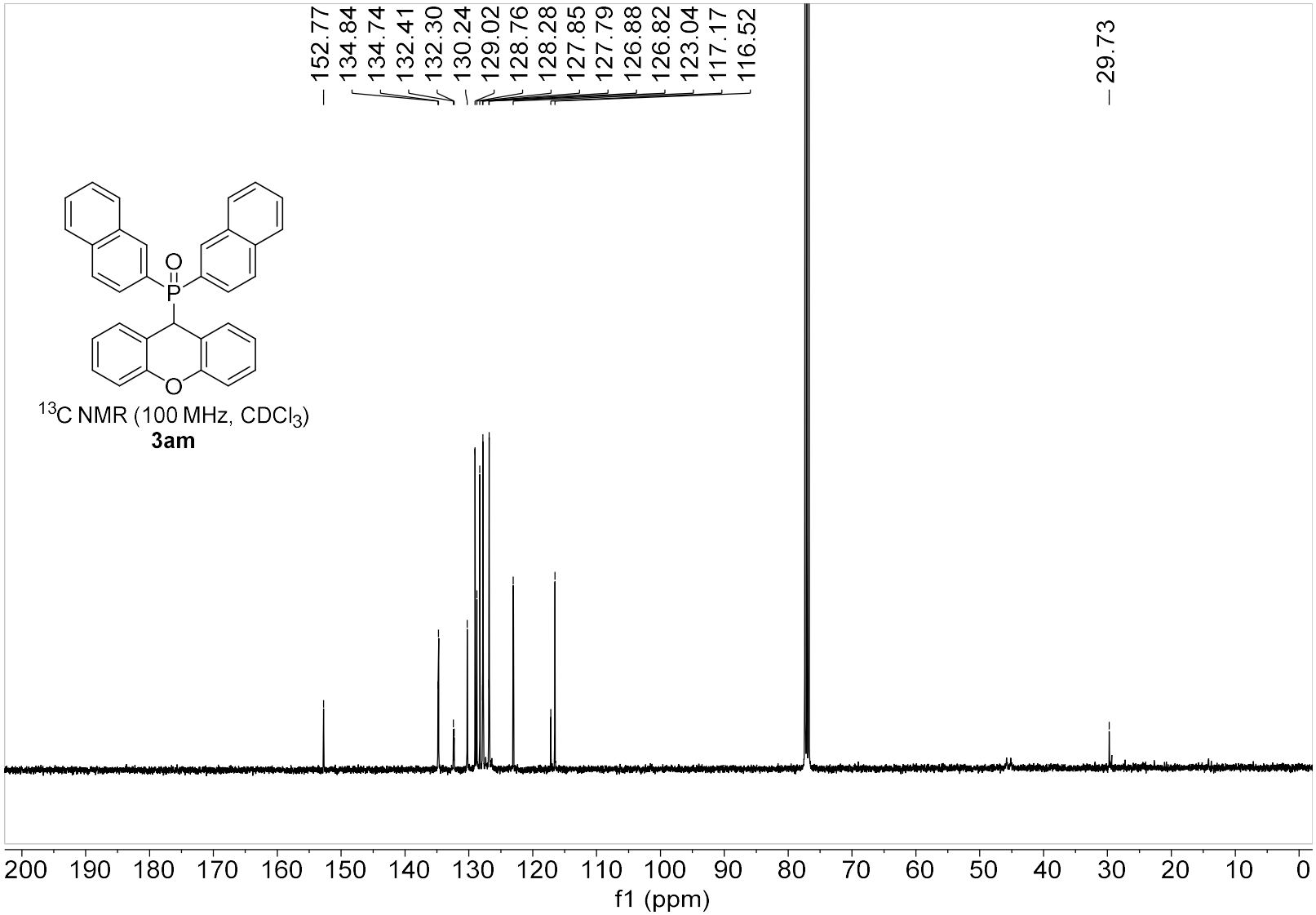
3al

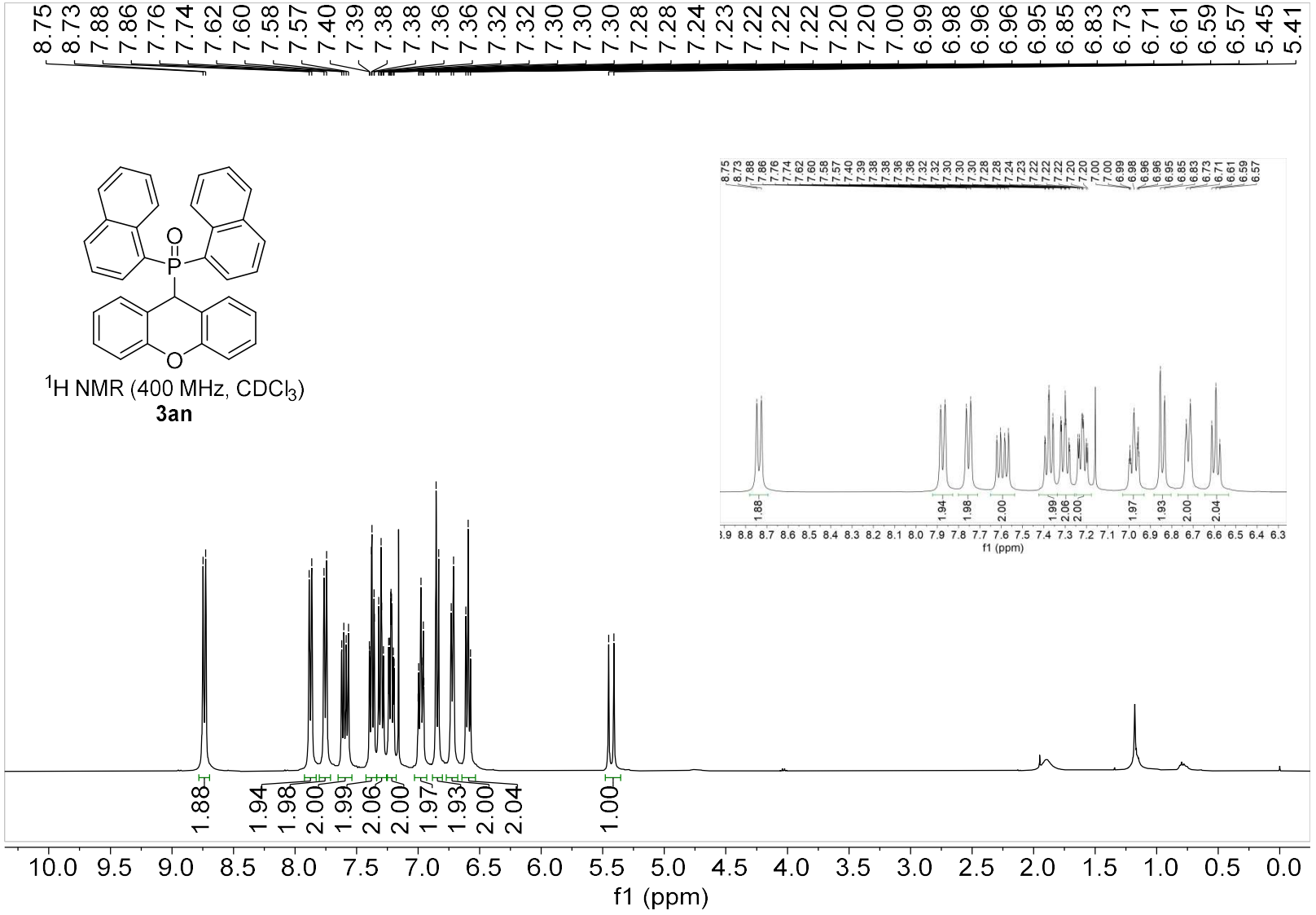

8.19
8.16
7.86
7.84
7.80
7.78
7.61
7.59
7.57
7.56
7.54
7.52
7.18
7.16
7.14
7.02
7.00
6.89
6.87
6.85
6.83
5.14
5.10
O
P
O
1H NMR (400 MHz, CDCl3)
3am
2.04
6.24
6.37
2.23
2.14
4.23
1.00
f1 (ppm)

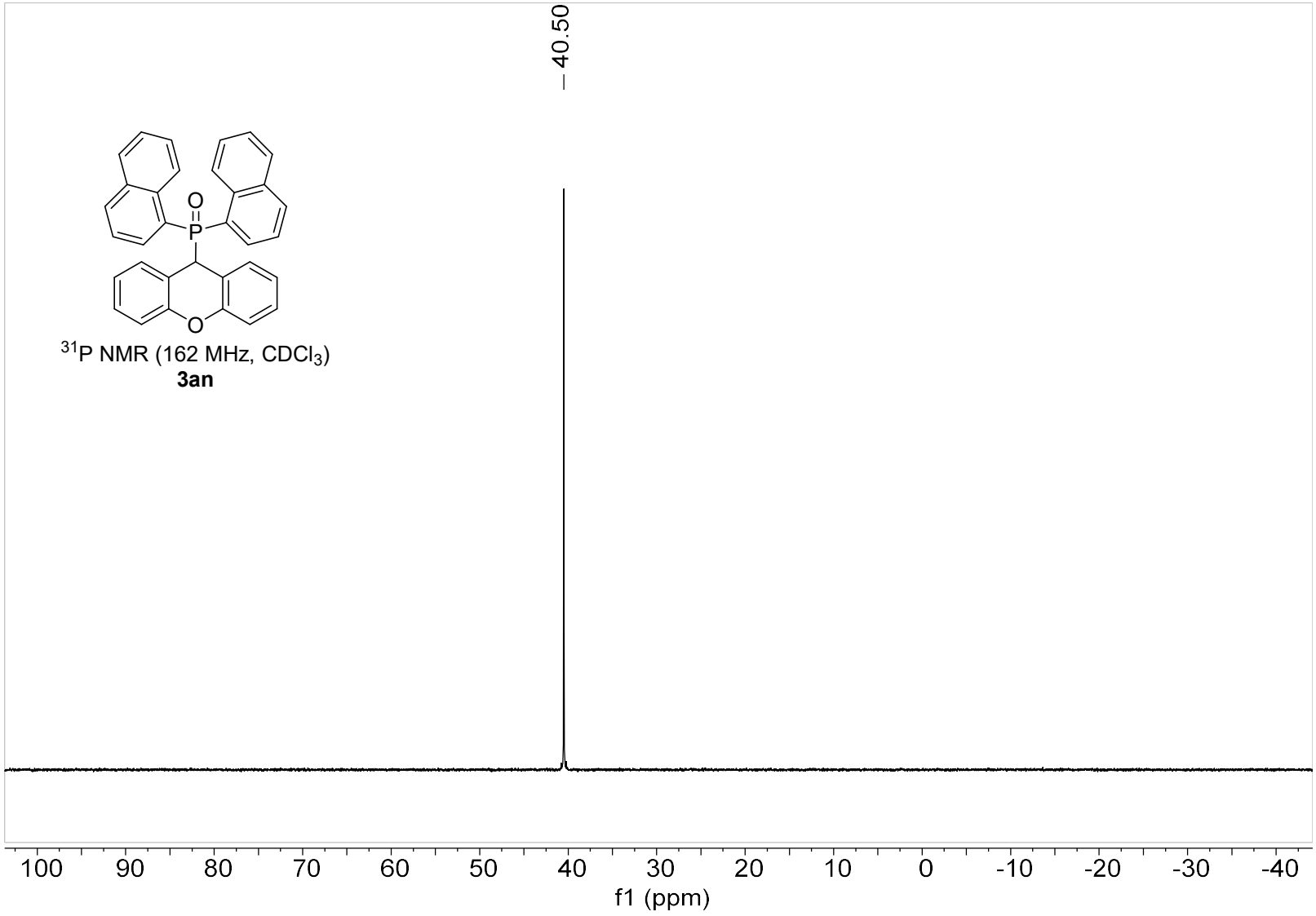


^{31}P NMR (162 MHz, $CDCl_3$)

3am

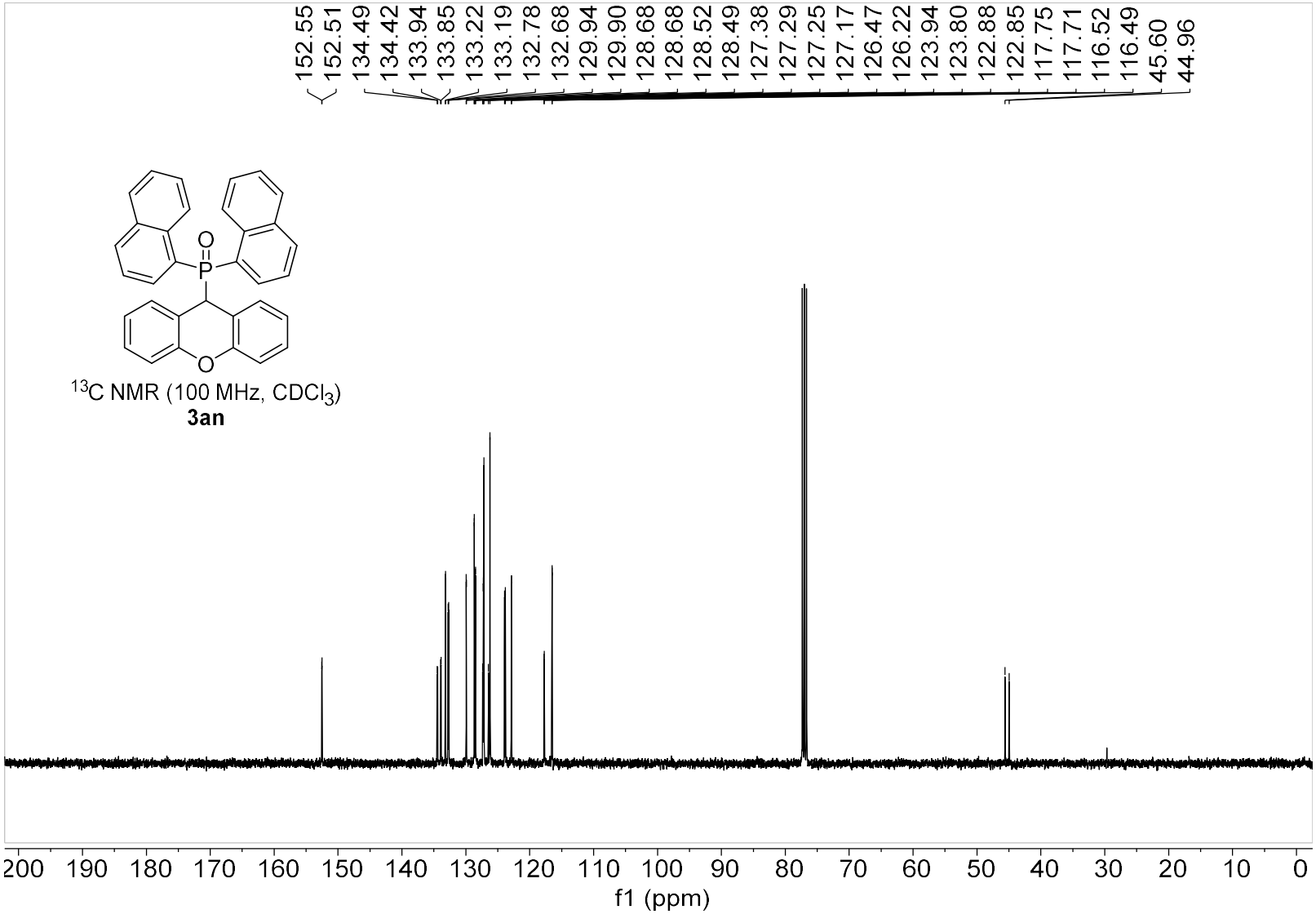

152.77
134.84
134.74
132.41
132.30
130.24
129.02
128.76
128.28
127.85
127.79
126.88
126.82
123.04
117.17
116.52
29.73
O
P
O
13C NMR (100 MHz, CDCl3)
3am
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.75 8.73 7.88 7.86 7.76 7.74 7.62 7.60 7.58 7.57 7.40 7.39 7.38 7.38 7.36 7.36 7.32 7.32 7.30 7.30 7.30 7.28 7.28 7.24 7.23 7.22 7.22 7.22 7.20 7.20 7.00 6.99 6.98 6.96 6.96 6.95 6.85 6.83 6.73 6.71 6.61 6.59 6.57 5.45 5.41
O
P
O
1H NMR (400 MHz, CDCl3)
3an
1.88 1.94 1.98 2.00 1.99 2.06 2.00 1.97 1.93 2.00 2.04 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



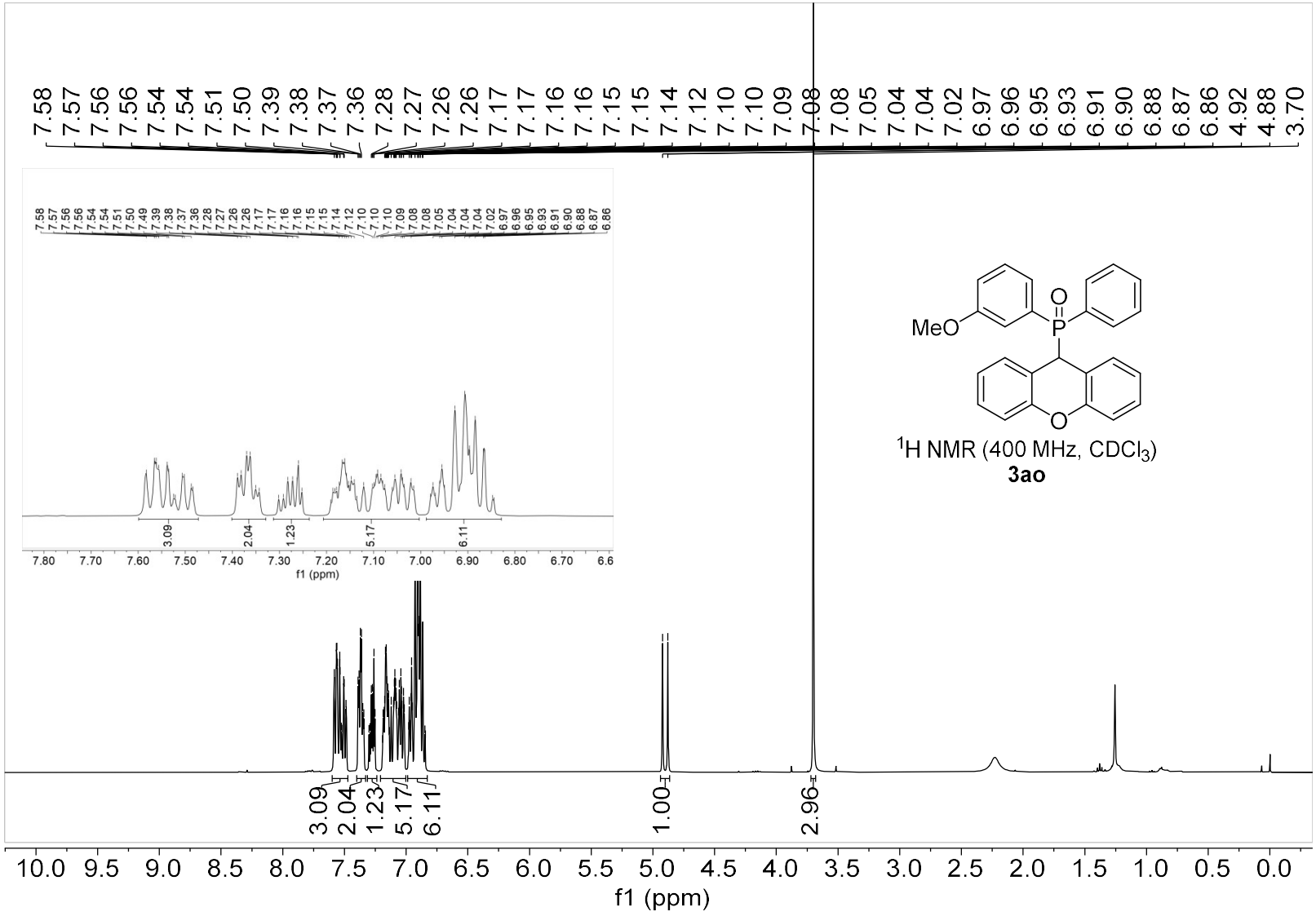
^{31}P NMR (162 MHz, $CDCl_3$)

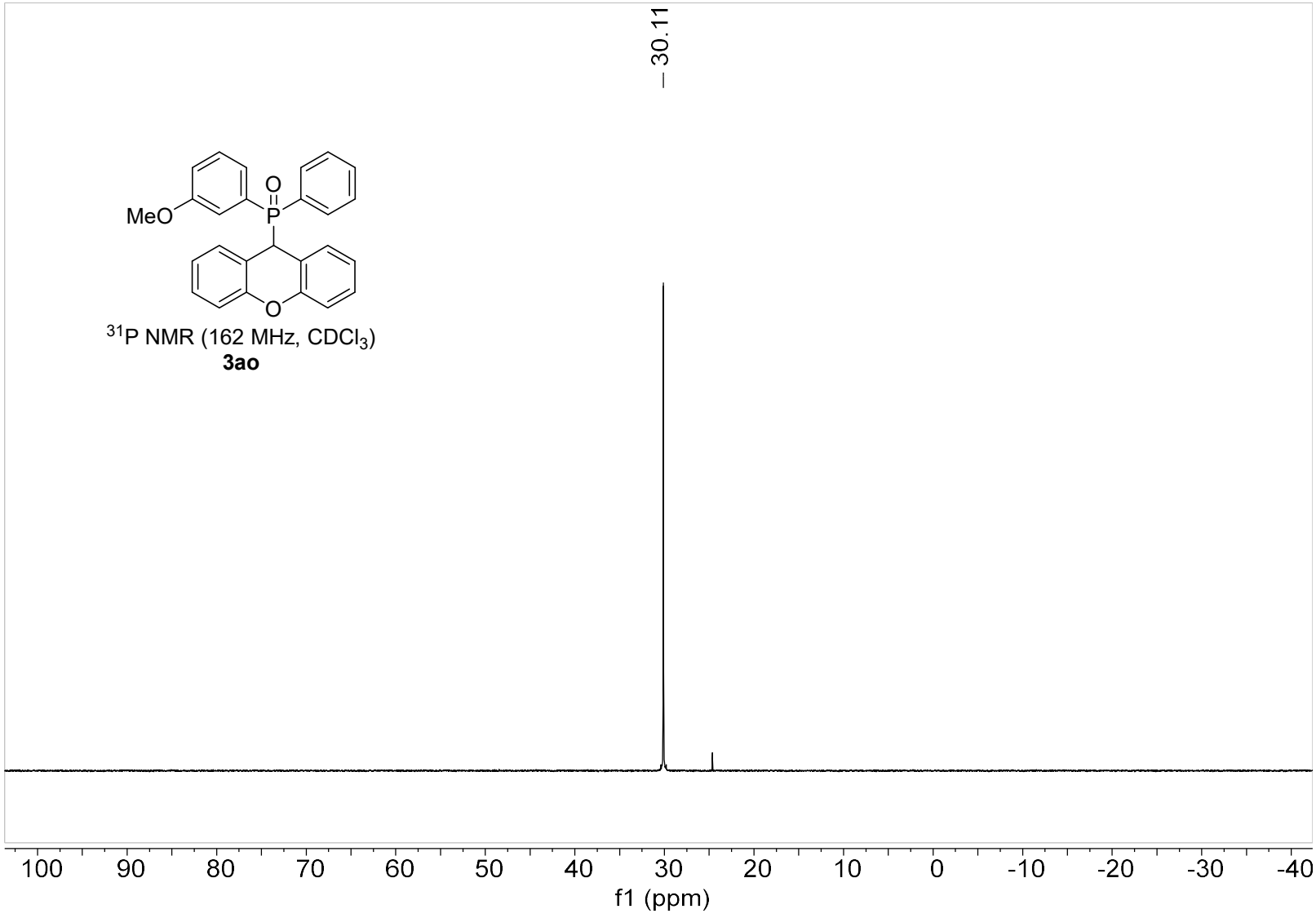
3an



^{13}C NMR (100 MHz, $CDCl_3$)

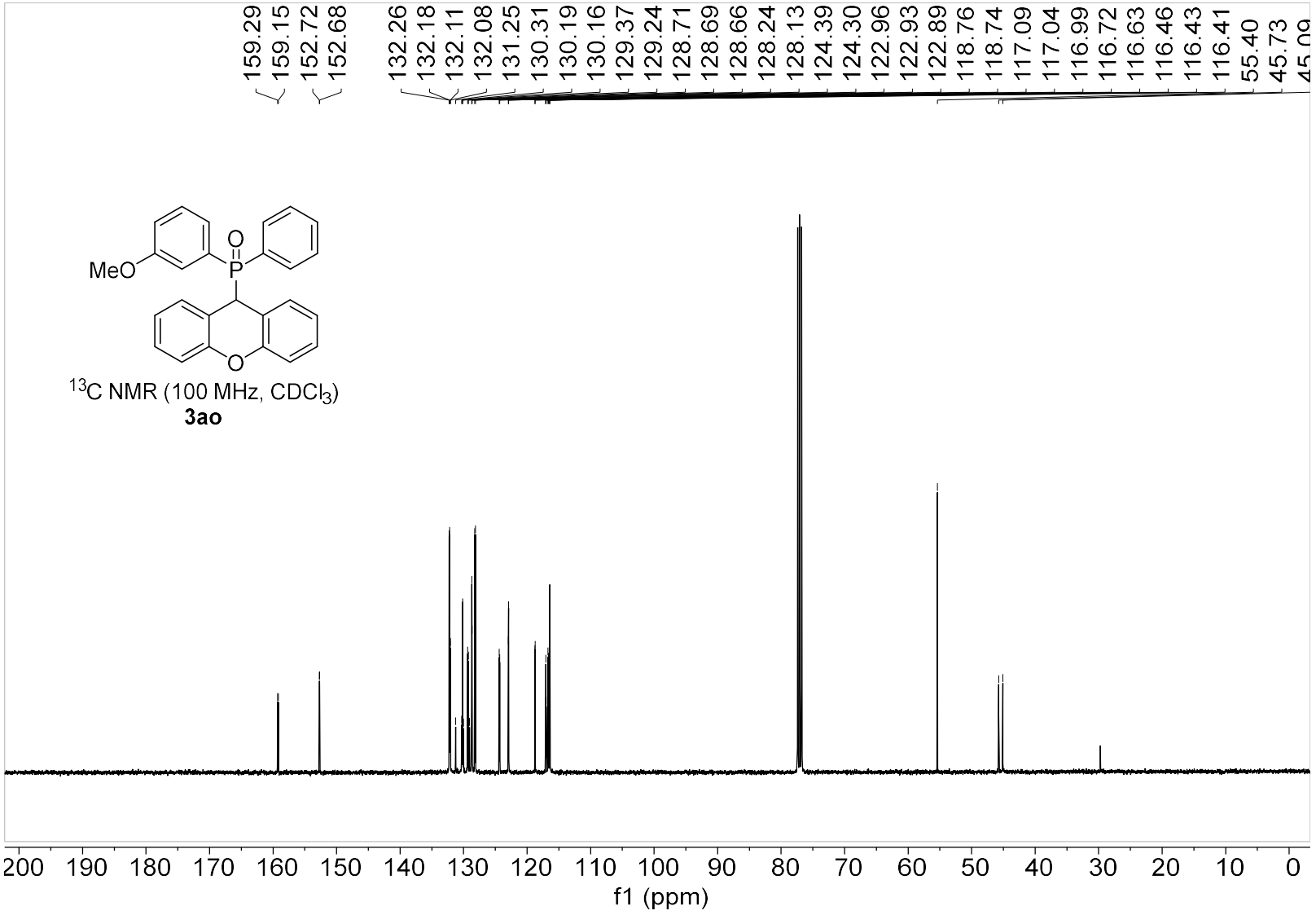
3an


7.58 7.57 7.56 7.56 7.54 7.54 7.51 7.50 7.39 7.38 7.37 7.36 7.28 7.27 7.26 7.26 7.17 7.17 7.16 7.16 7.15 7.15 7.14 7.12 7.10 7.10 7.09 7.08 7.08 7.05 7.04 7.04 7.02 6.97 6.96 6.95 6.93 6.91 6.90 6.88 6.87 6.86 4.92 4.88 3.70
MeO
O
P
O
1H NMR (400 MHz, CDCl3)
3ao
3.09 2.04 1.23 5.17 6.11 1.00 2.96
f1 (ppm)



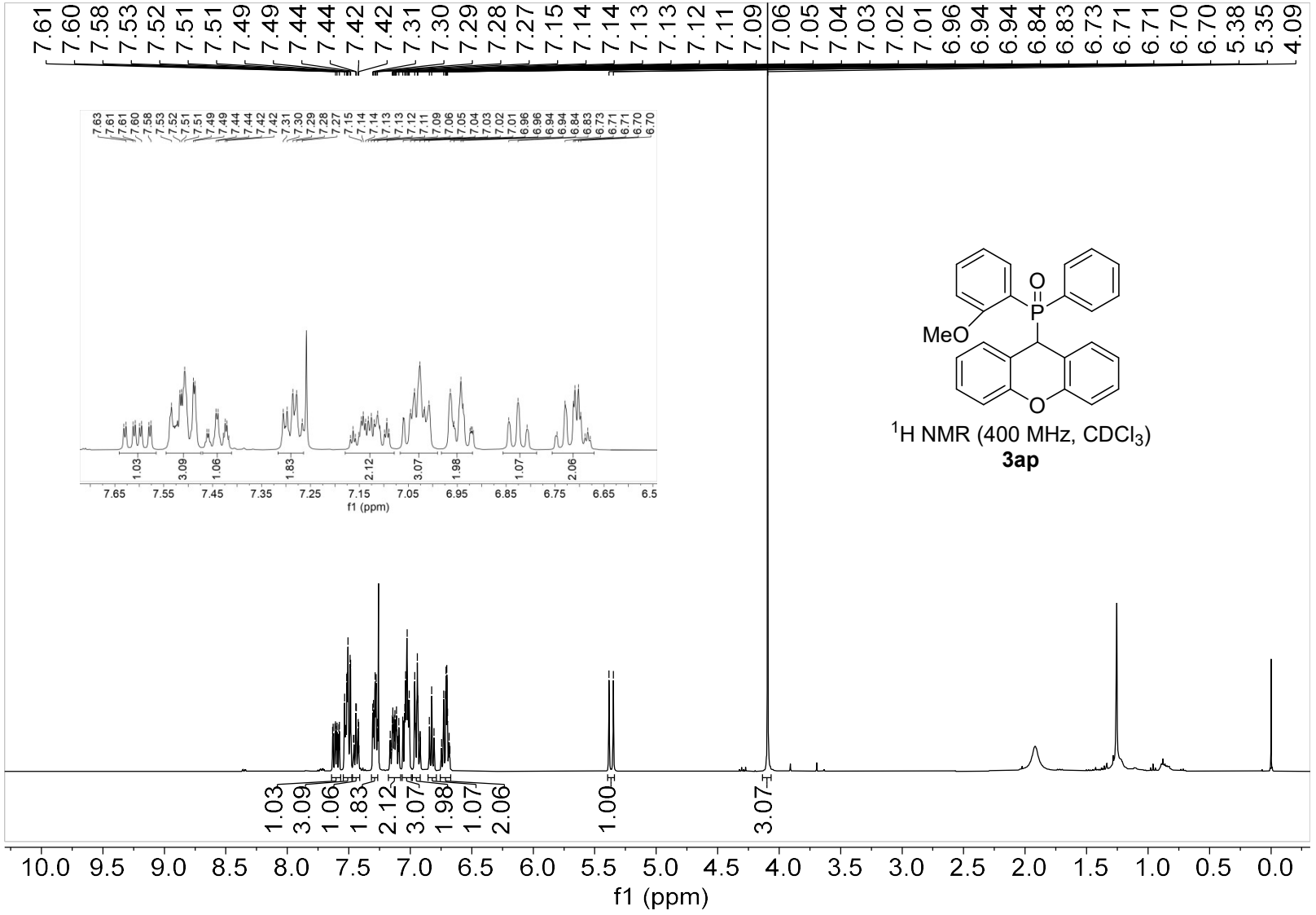
^{31}P NMR (162 MHz, $CDCl_3$)

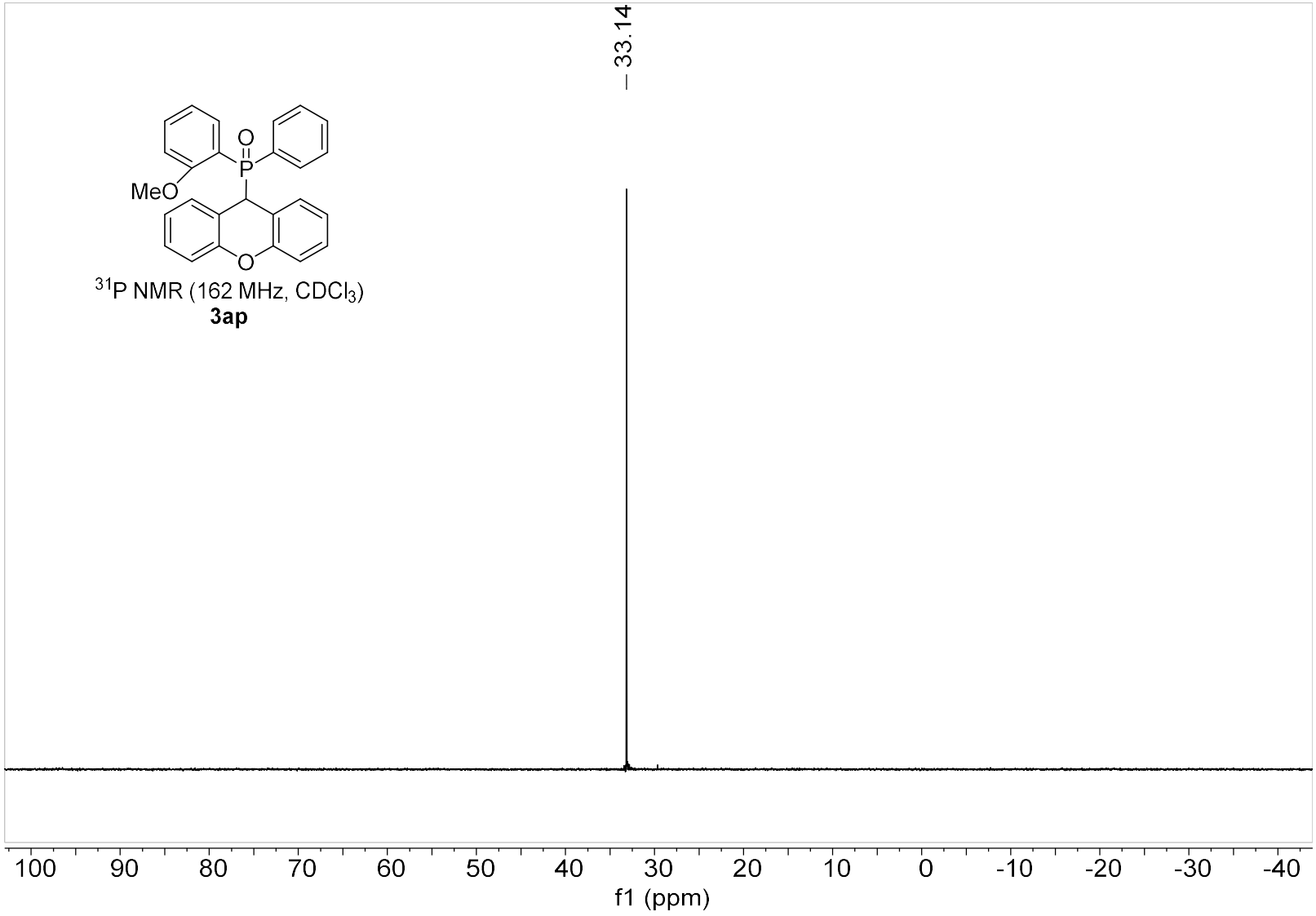
3ao



^{13}C NMR (100 MHz, $CDCl_3$)

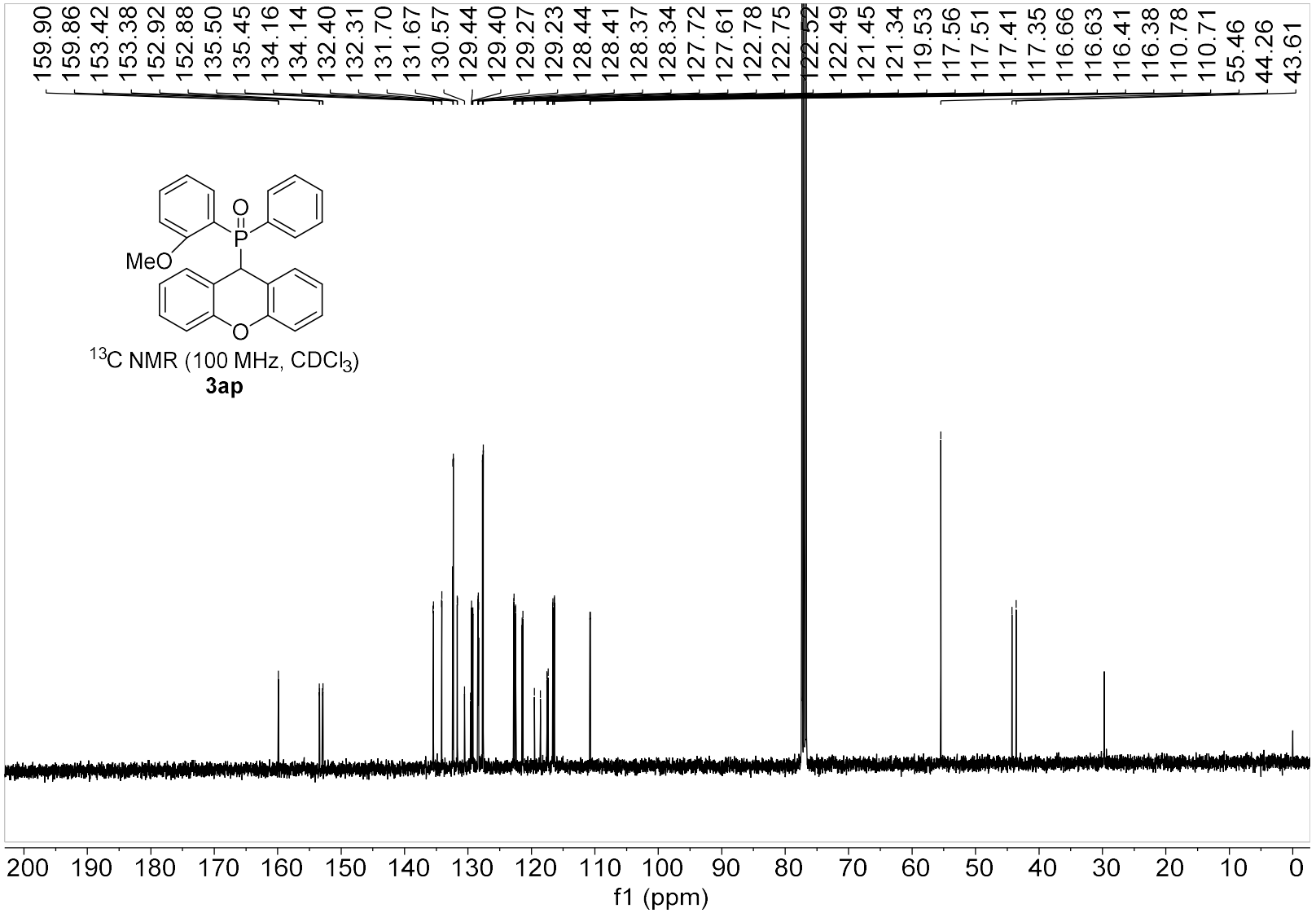
3ao


MeO
O
P
O
^{1}H NMR (400 MHz, $CDCl_3$)
3ap
f1 (ppm)



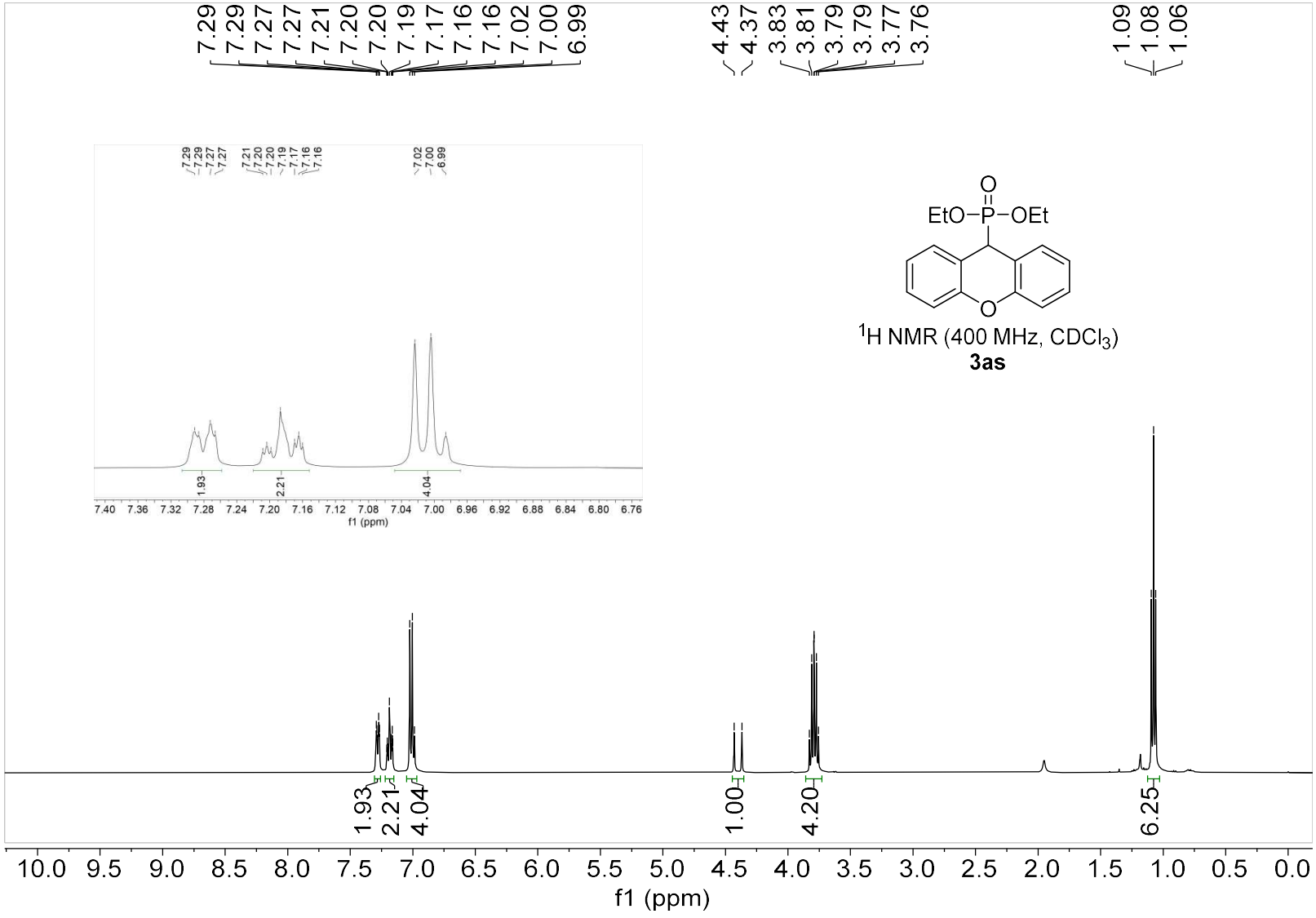
^{31}P NMR (162 MHz, $CDCl_3$)

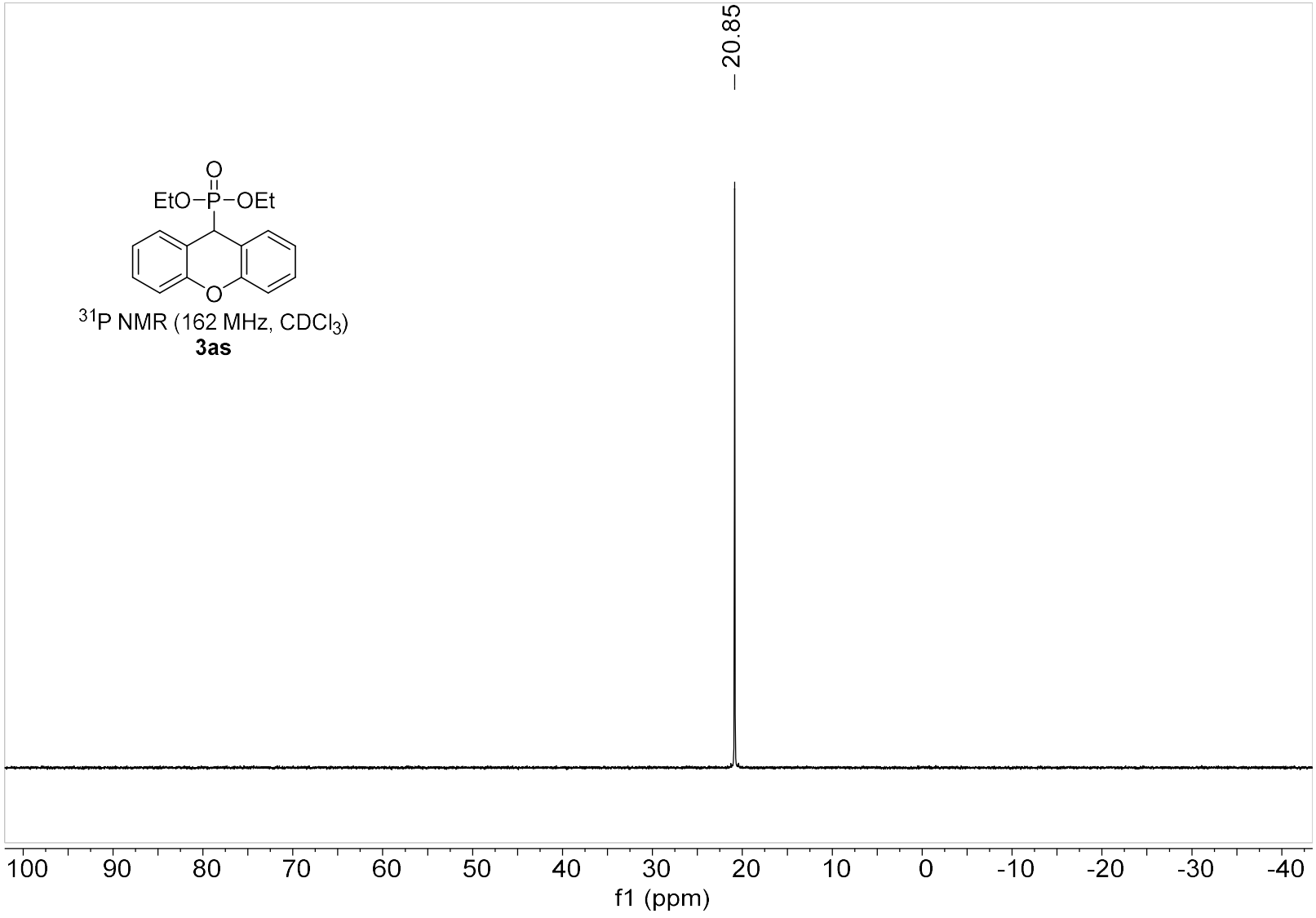
3ap



^{13}C NMR (100 MHz, $CDCl_3$)

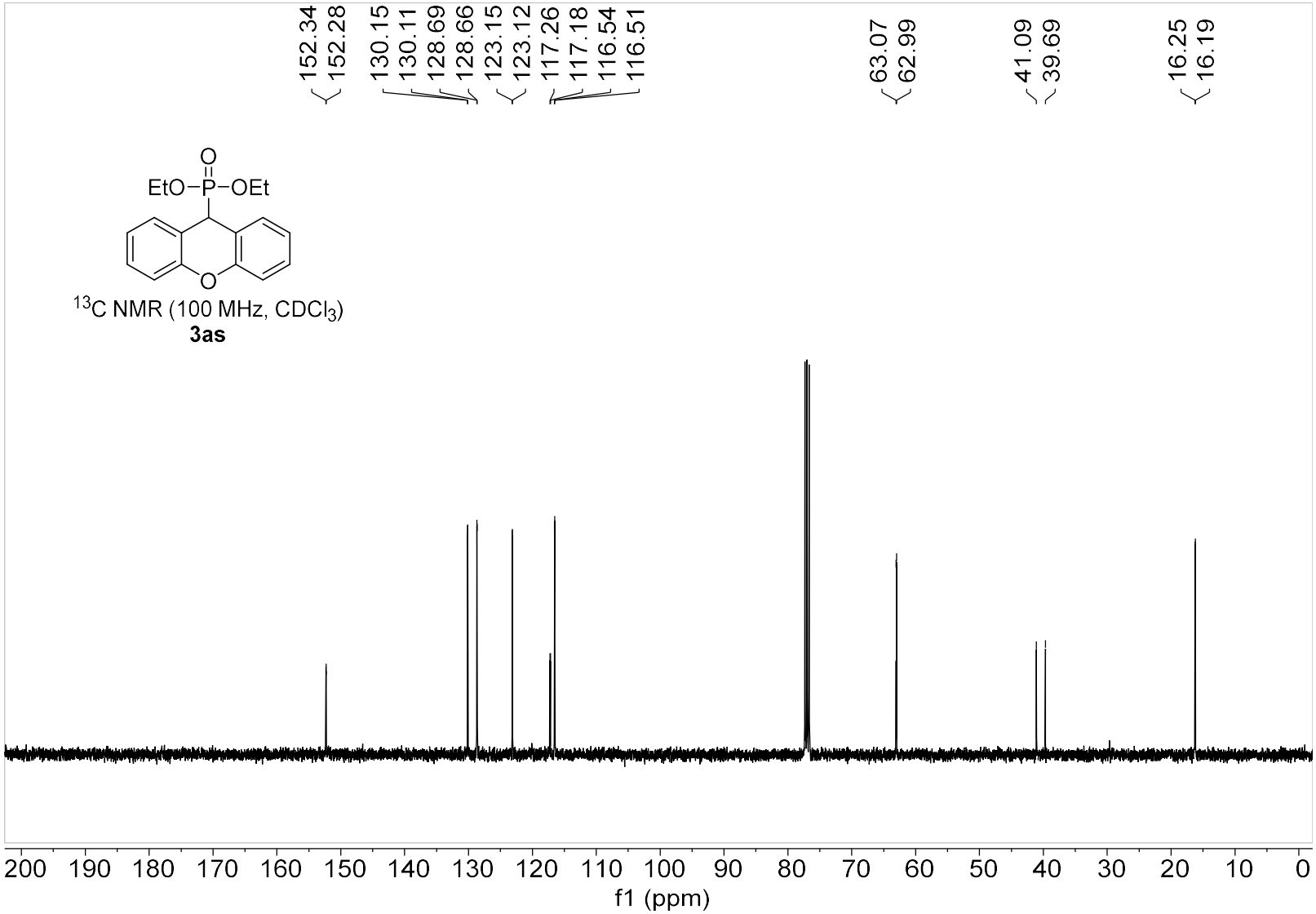
3ap

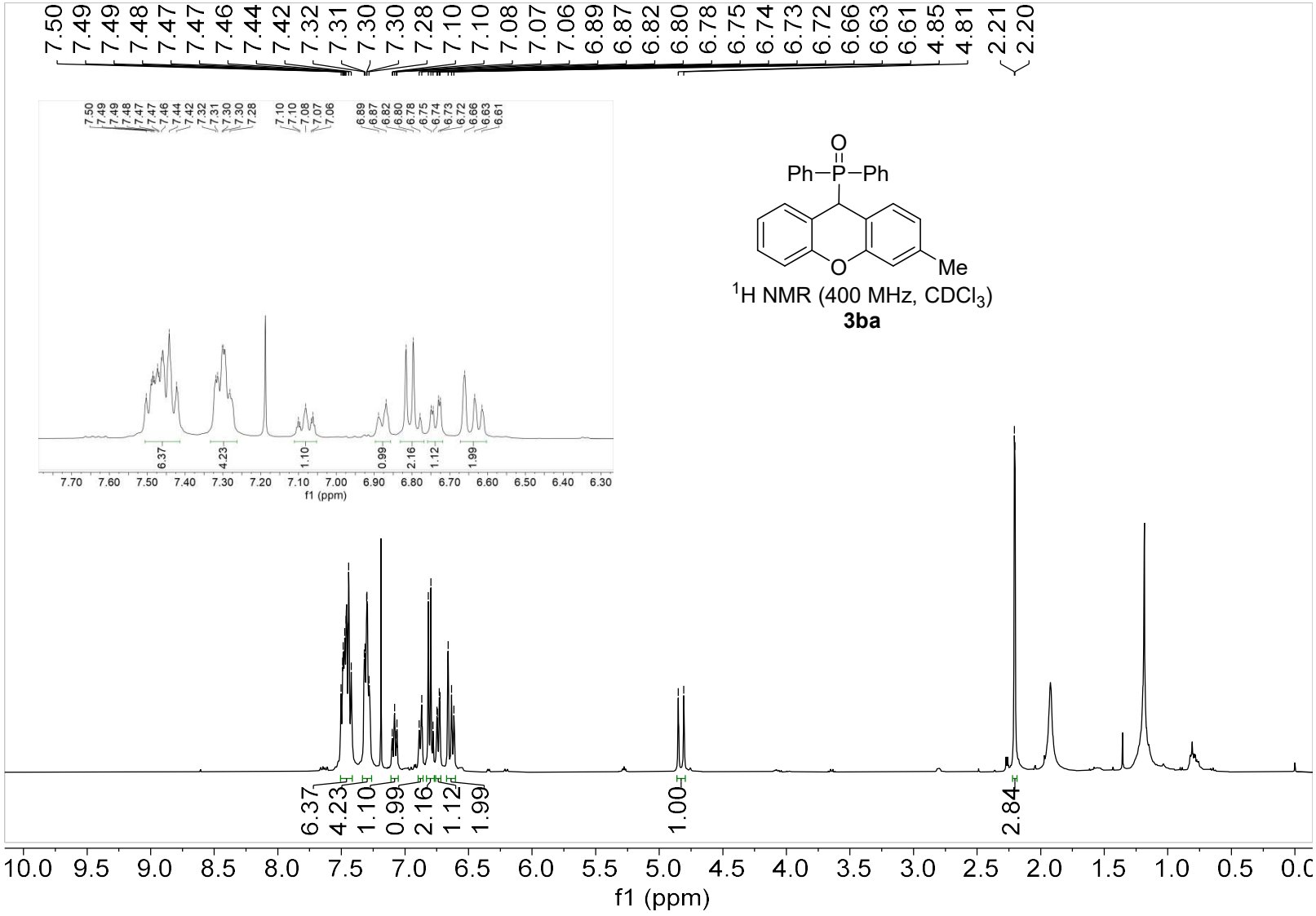

7.29
7.29
7.27
7.27
7.21
7.20
7.20
7.19
7.17
7.16
7.16
7.02
7.00
6.99
4.43
4.37
3.83
3.81
3.79
3.79
3.77
3.76
1.09
1.08
1.06
EtO−P−OEt
O
O
1H NMR (400 MHz, CDCl3)
3as
1.93
2.21
4.04
1.00
4.20
6.25
f1 (ppm)

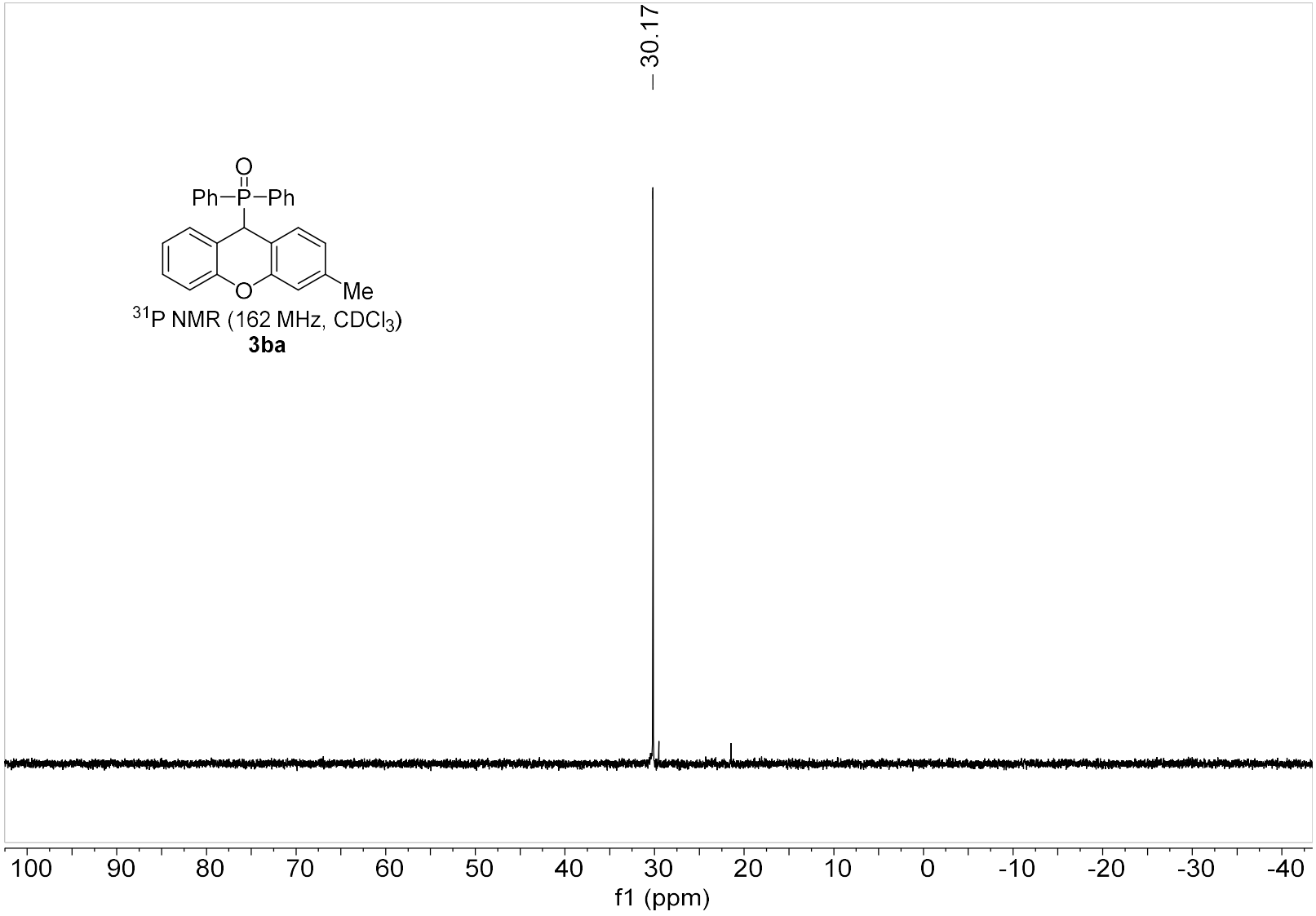


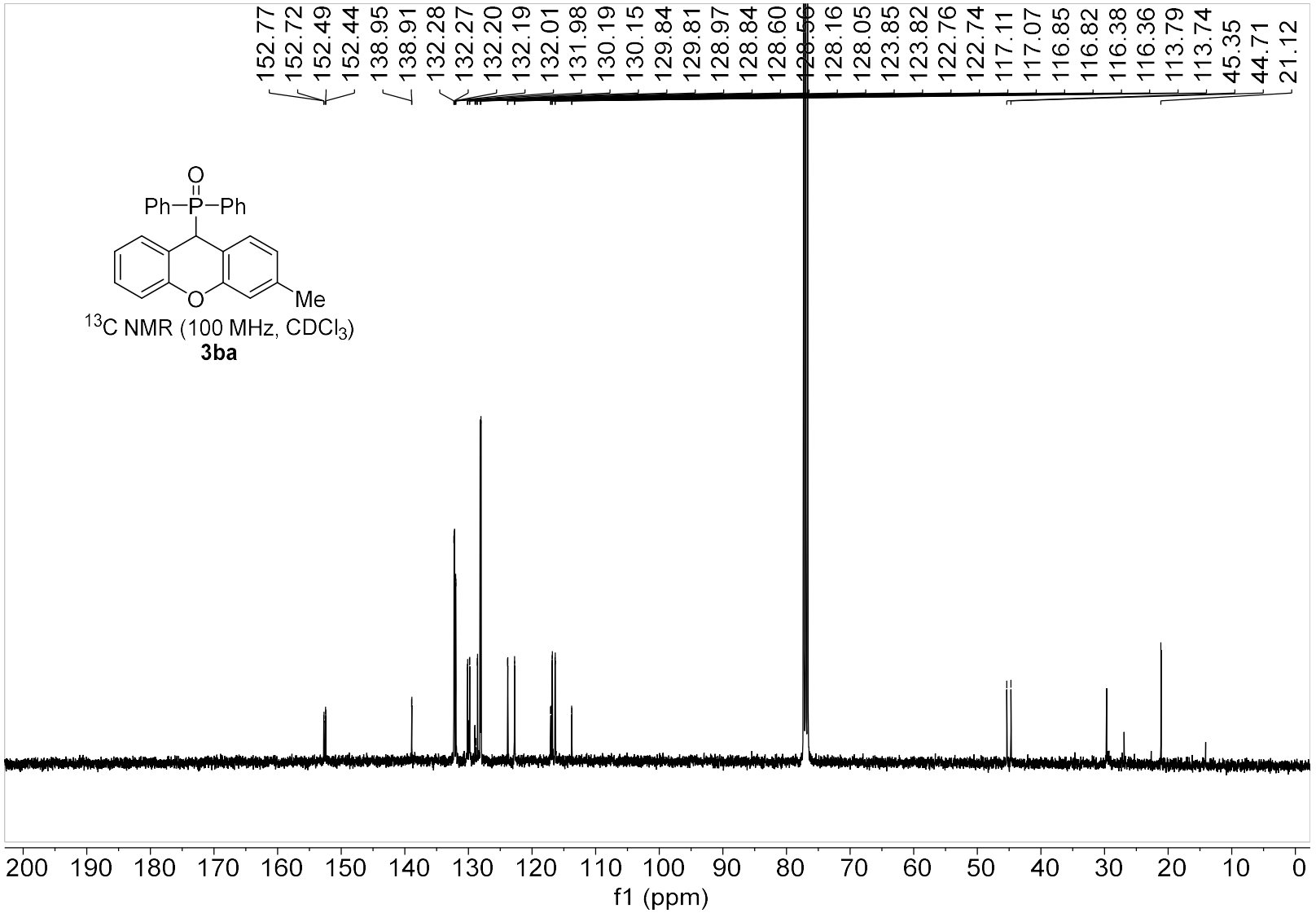
^{31}P NMR (162 MHz, $CDCl_3$)

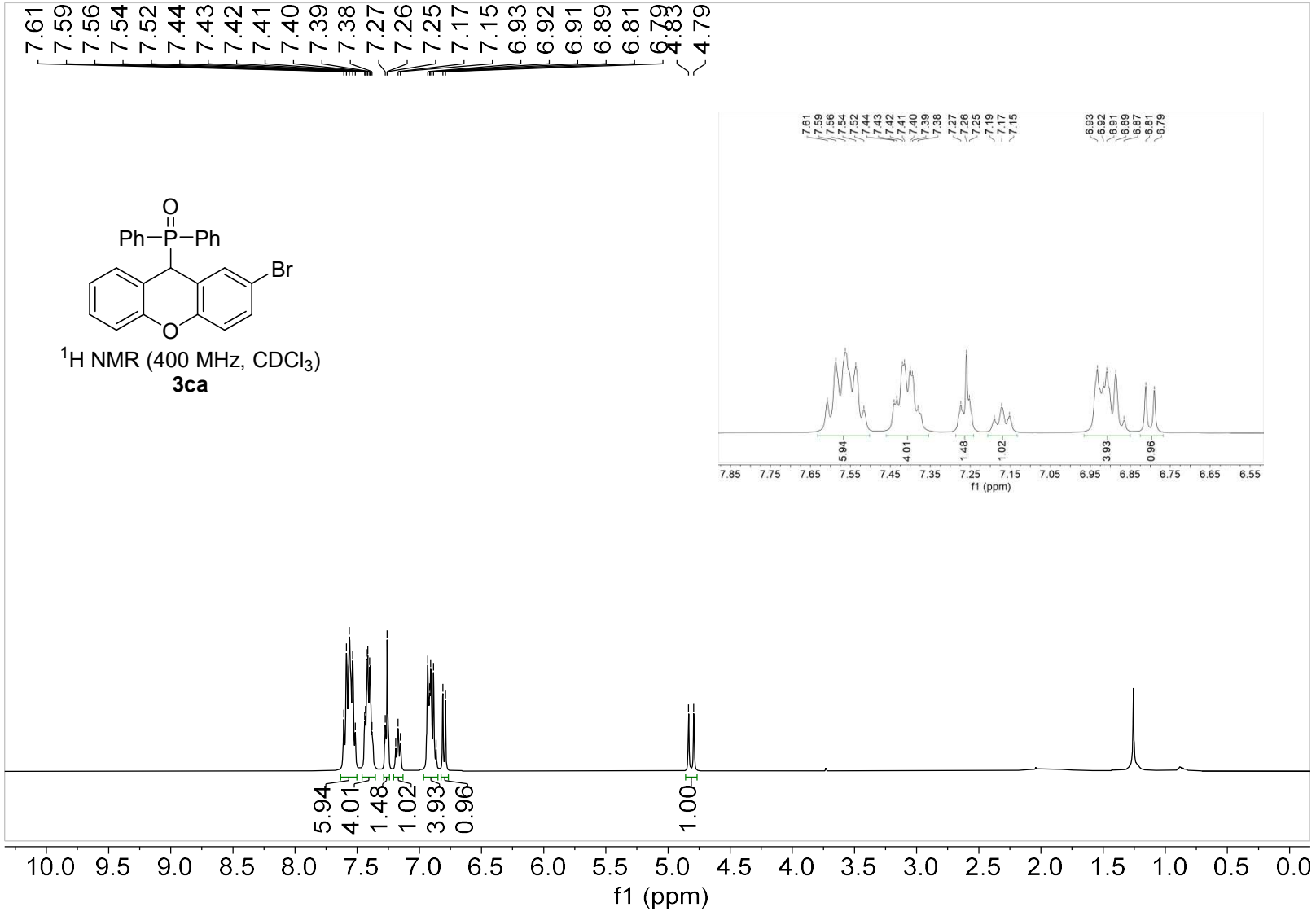
3as

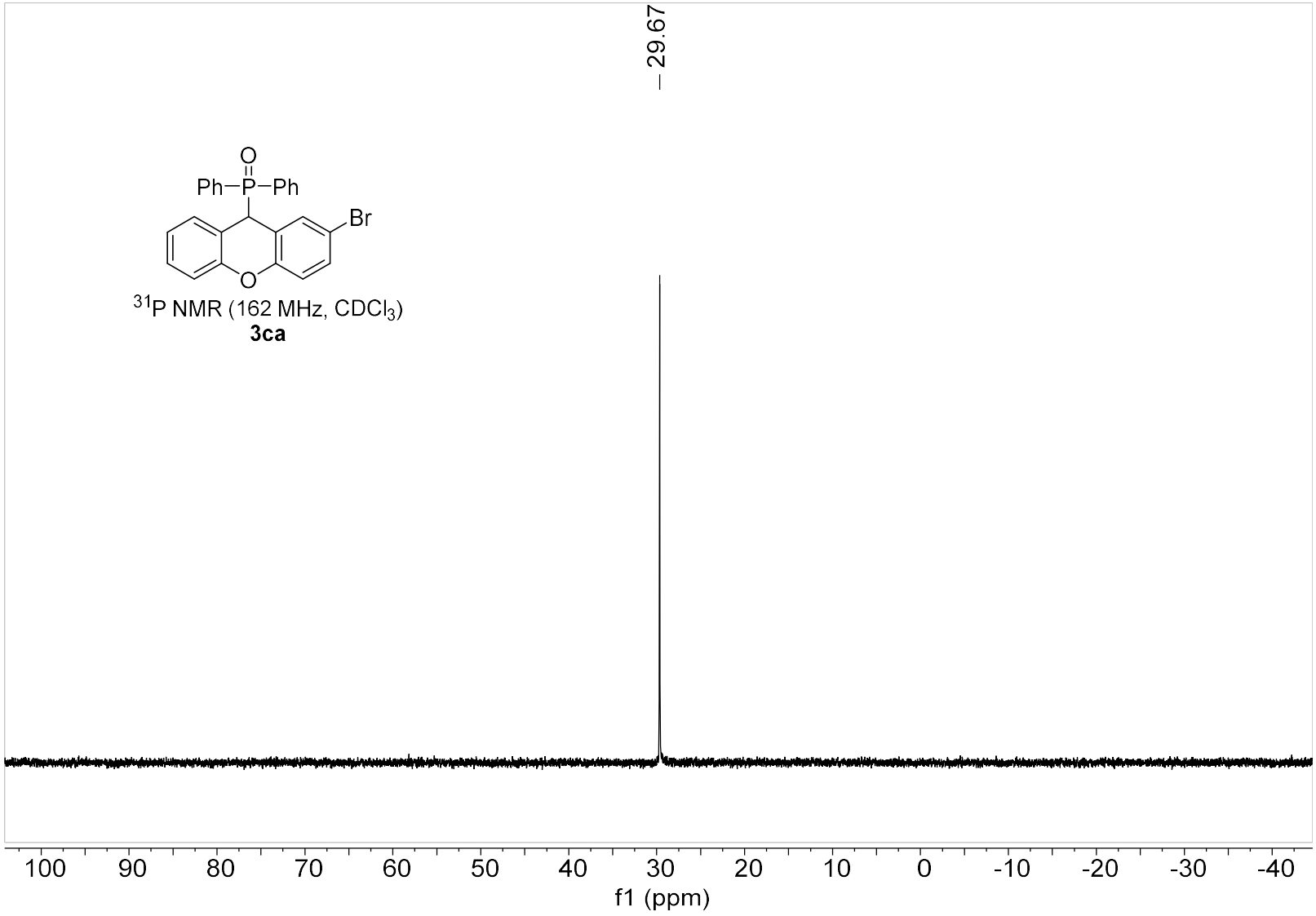

152.34
152.28
130.15
130.11
128.69
128.66
123.15
123.12
117.26
117.18
116.54
116.51
63.07
62.99
41.09
39.69
16.25
16.19
EtO−P−OEt
O
O
^{13}C NMR (100 MHz, $CDCl_3$)
3as
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

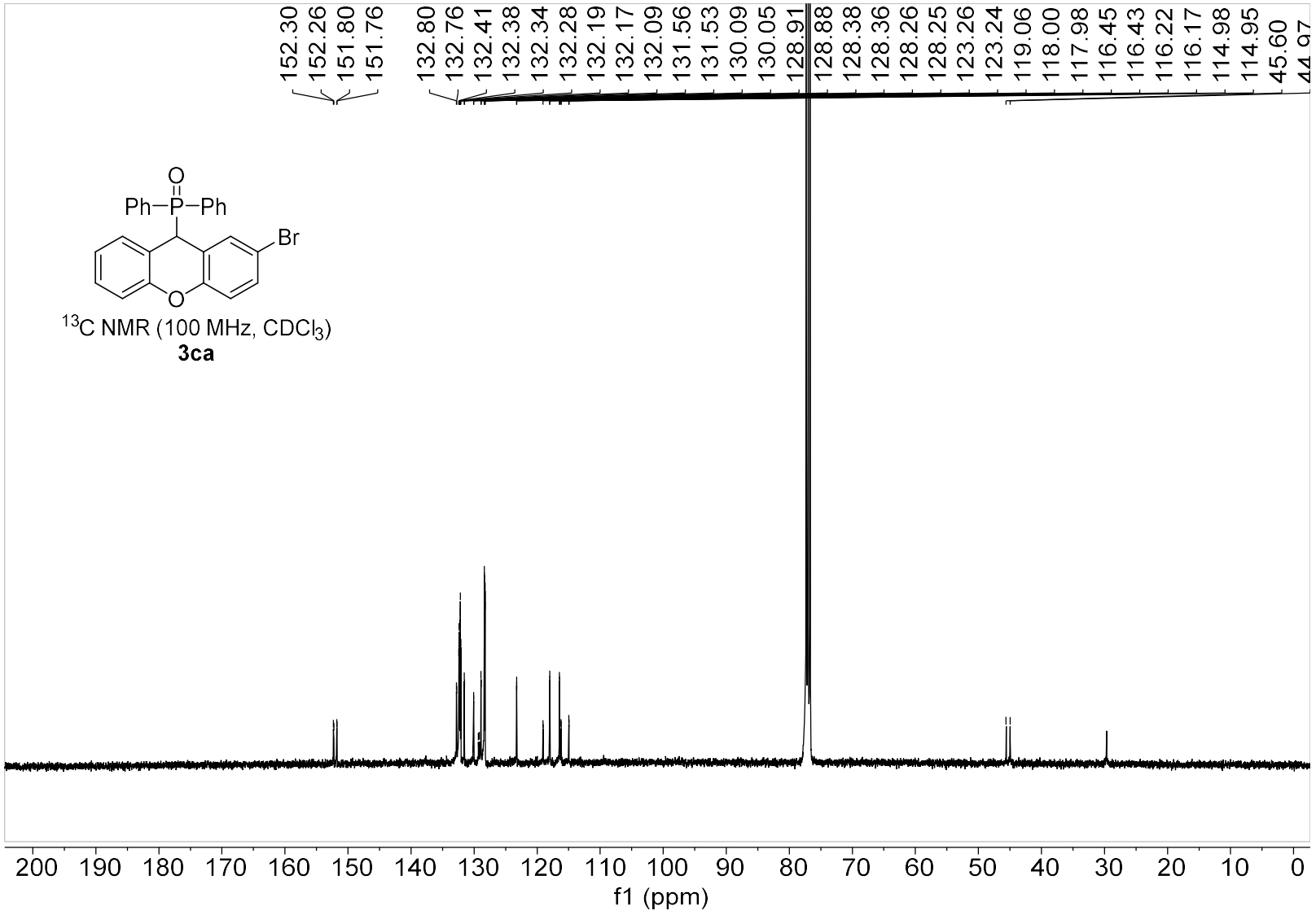

7.50 7.49 7.49 7.48 7.47 7.47 7.46 7.44 7.42 7.32 7.31 7.30 7.30 7.28 7.10 7.10 7.08 7.07 7.06 6.89 6.87 6.82 6.80 6.78 6.75 6.74 6.73 6.72 6.66 6.63 6.61 4.85 4.81 2.21 2.20
O
Ph—P—Ph
O
Me
1H NMR (400 MHz, CDCl3)
3ba
6.37 4.23 1.10 0.99 2.16 1.12 1.99 1.00 2.84
f1 (ppm)


30.17
O
Ph–P–Ph
O
Me
31P NMR (162 MHz, CDCl3)
3ba
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)


152.77
152.72
152.49
152.44
138.95
138.91
132.28
132.27
132.20
132.19
132.01
131.98
130.19
130.15
129.84
129.81
128.97
128.84
128.60
128.56
128.16
128.05
123.85
123.82
122.76
122.74
117.11
117.07
116.85
116.82
116.38
116.36
113.79
113.74
45.35
44.71
21.12
O
Ph–P–Ph
O
Me
13C NMR (100 MHz, CDCl3)
3ba
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

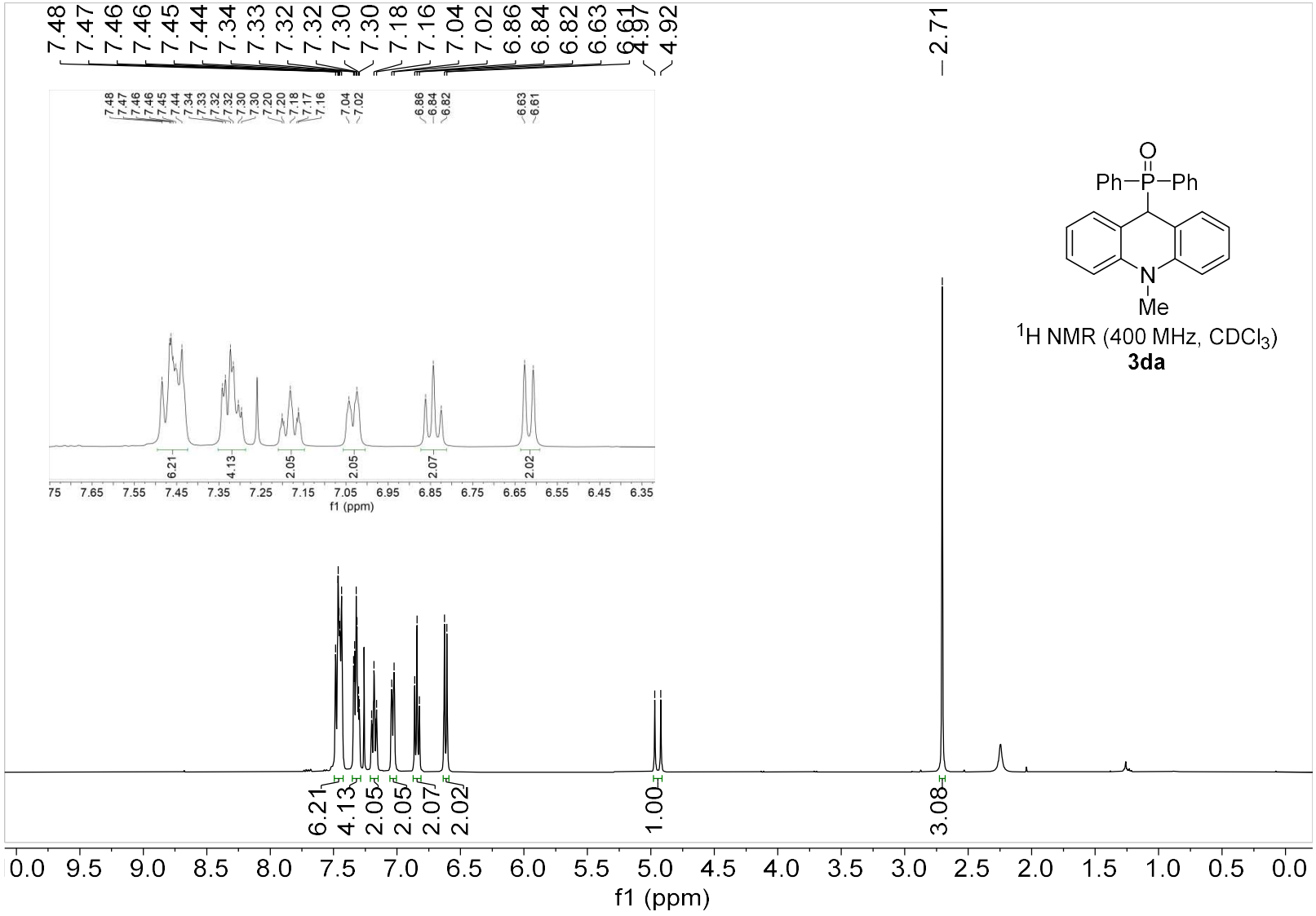

7.61
7.59
7.56
7.54
7.52
7.44
7.43
7.42
7.41
7.40
7.39
7.38
7.27
7.26
7.25
7.17
7.15
6.93
6.92
6.91
6.89
6.81
6.79
4.83
4.79
O
Ph—P—Ph
Br
O
1H NMR (400 MHz, CDCl3)
3ca
5.94
4.01
1.48
1.02
3.93
0.96
1.00
f1 (ppm)

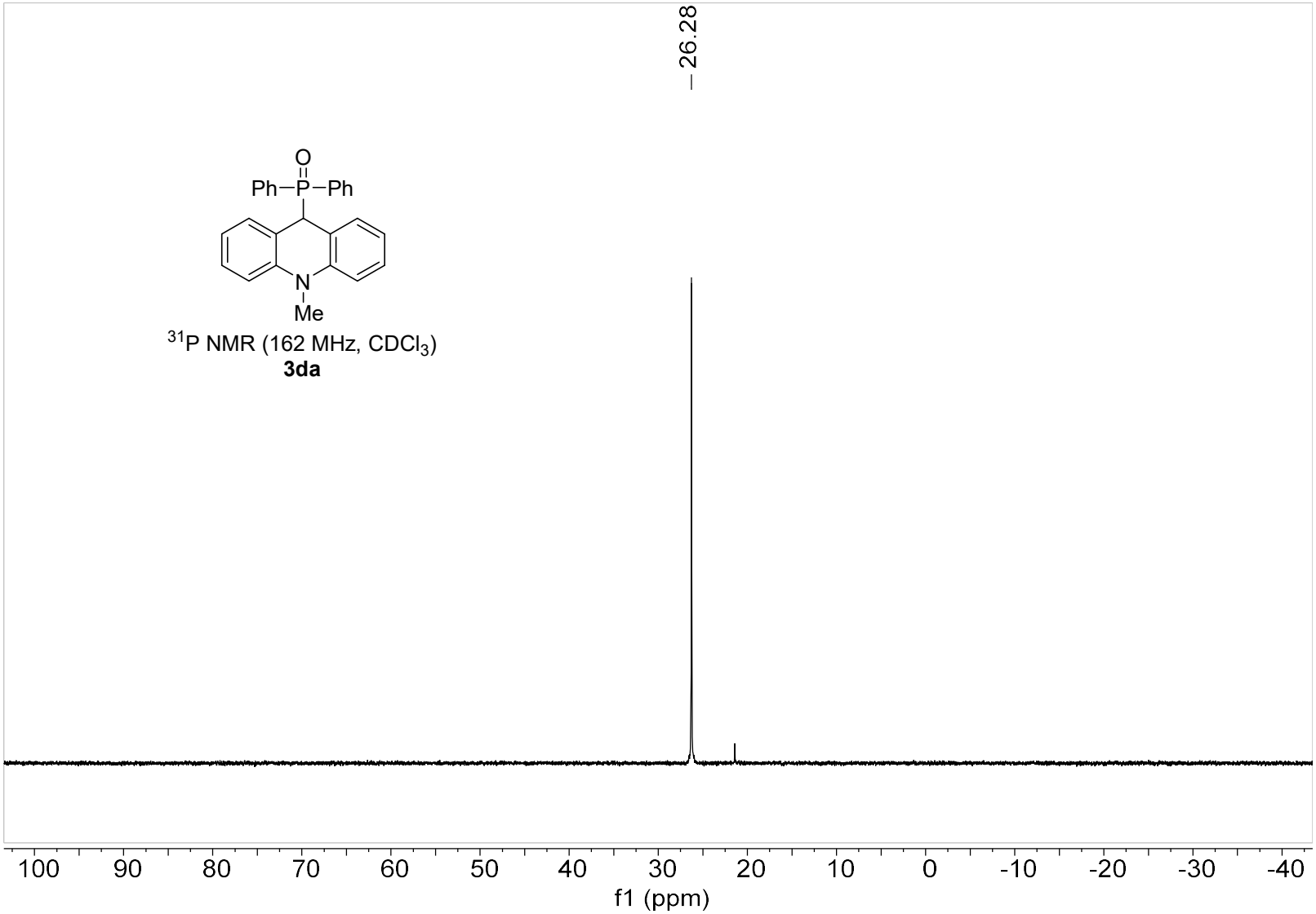

29.67
Ph–P–Ph
O
Br
O
31P NMR (162 MHz, CDCl3)
3ca
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
f1 (ppm)



^{13}C NMR (100 MHz, $CDCl_3$)

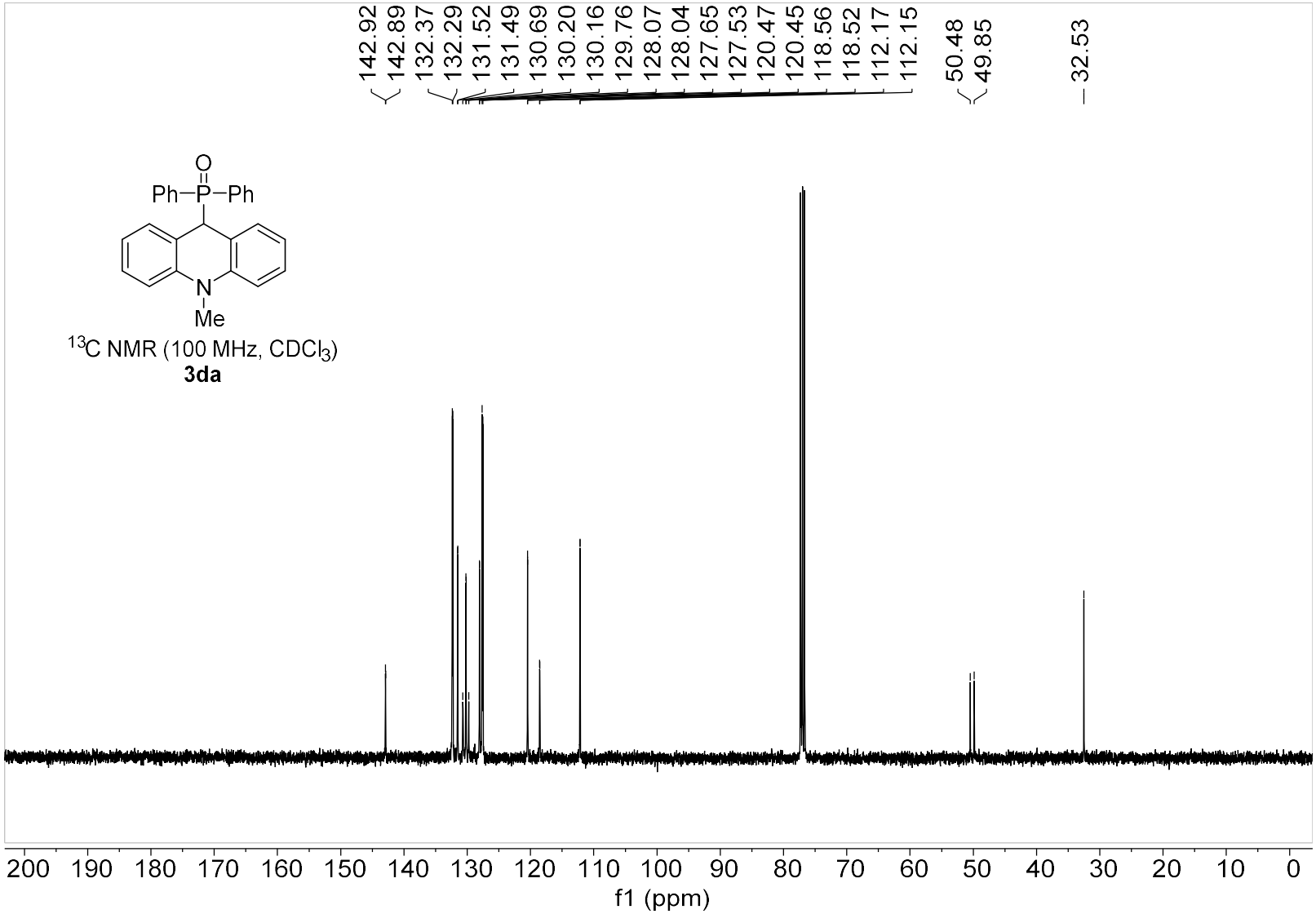
3ca


7.48
7.47
7.46
7.46
7.45
7.44
7.34
7.33
7.32
7.32
7.30
7.30
7.18
7.16
7.04
7.02
6.86
6.84
6.82
6.63
6.61
4.97
4.92
2.71
Ph—P—Ph
O
N
Me
1H NMR (400 MHz, CDCl3)
3da
6.21
4.13
2.05
2.05
2.07
2.02
1.00
3.08
f1 (ppm)



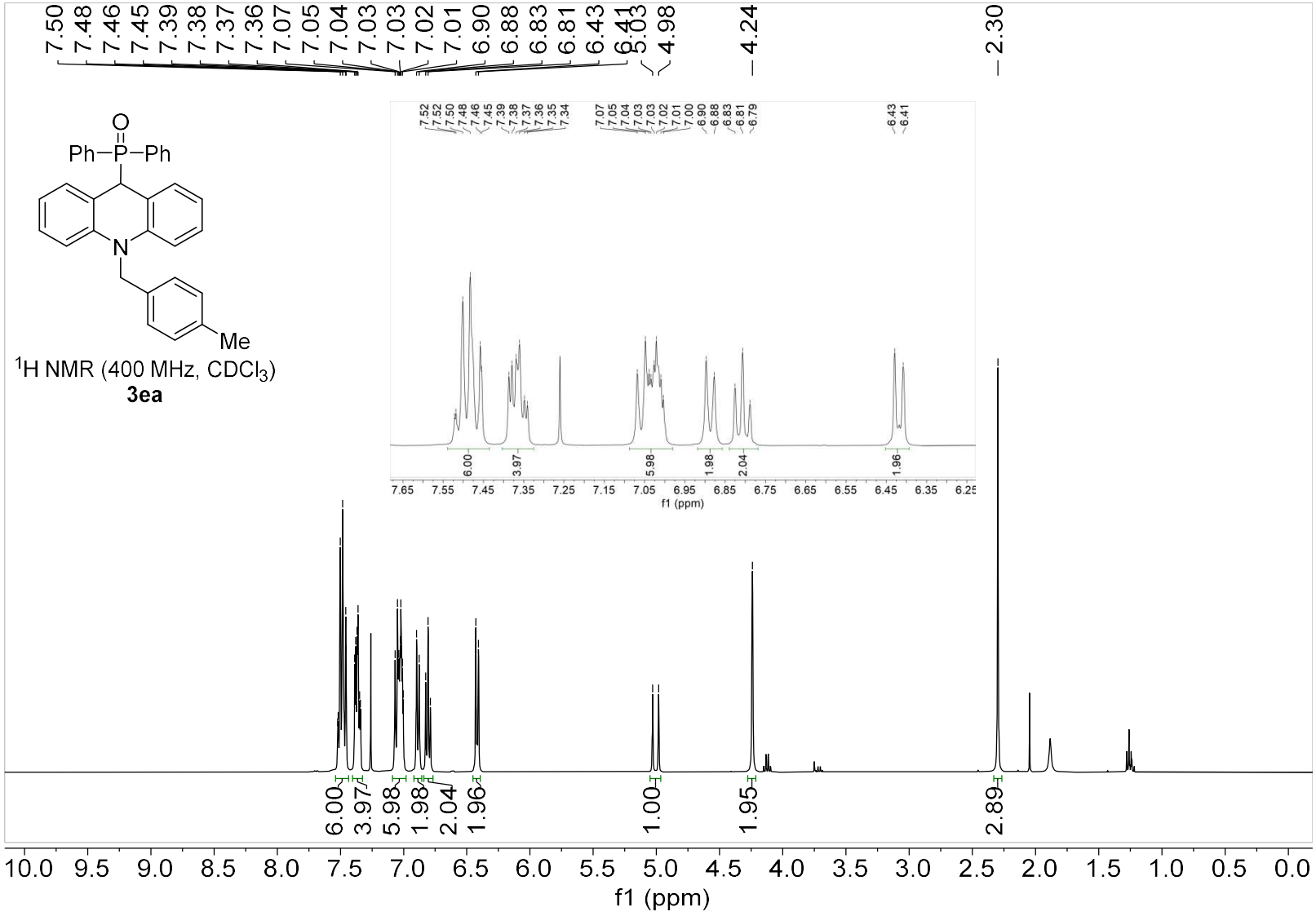
^{31}P NMR (162 MHz, $CDCl_3$)

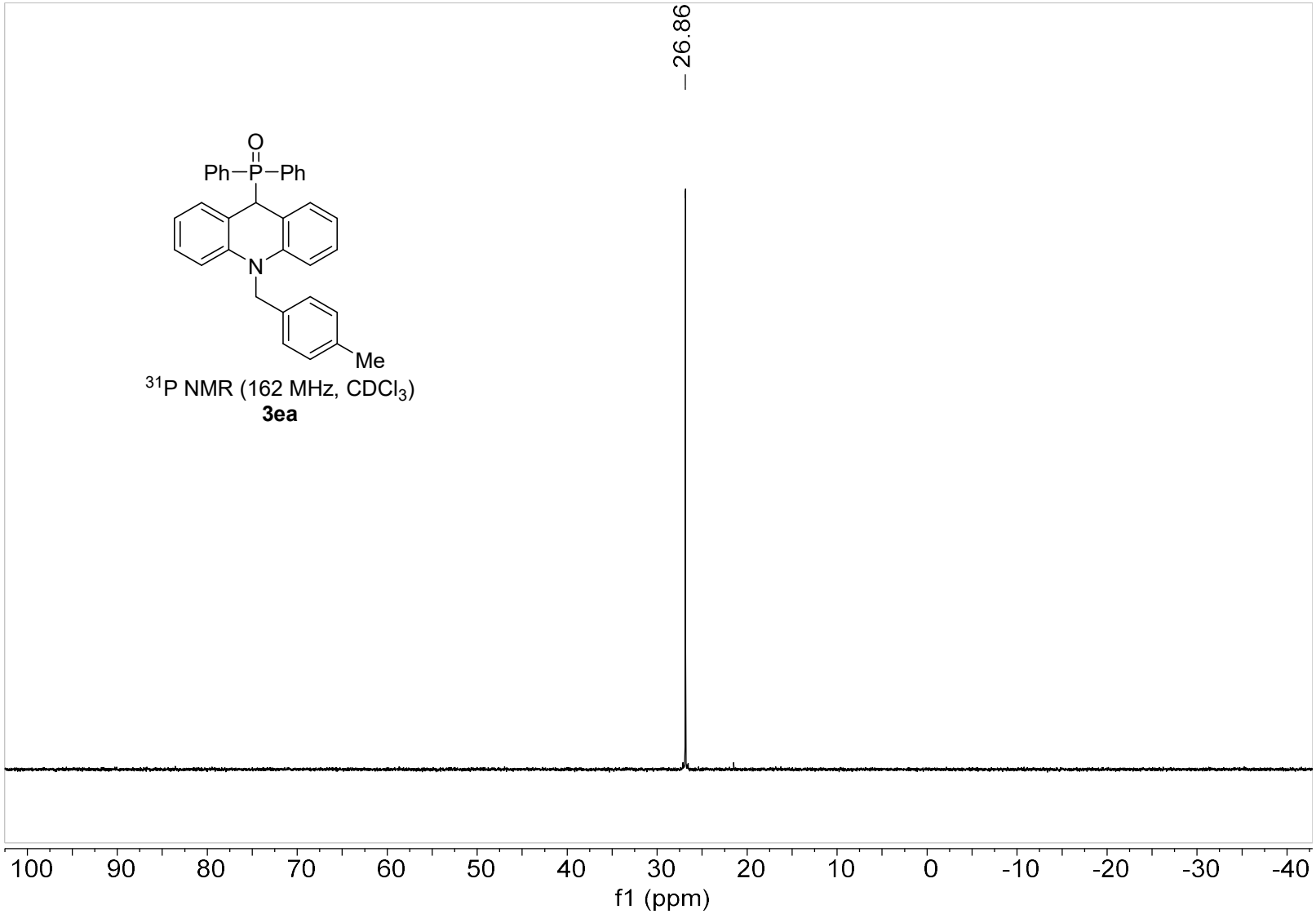
3da



^{13}C NMR (100 MHz, $CDCl_3$)

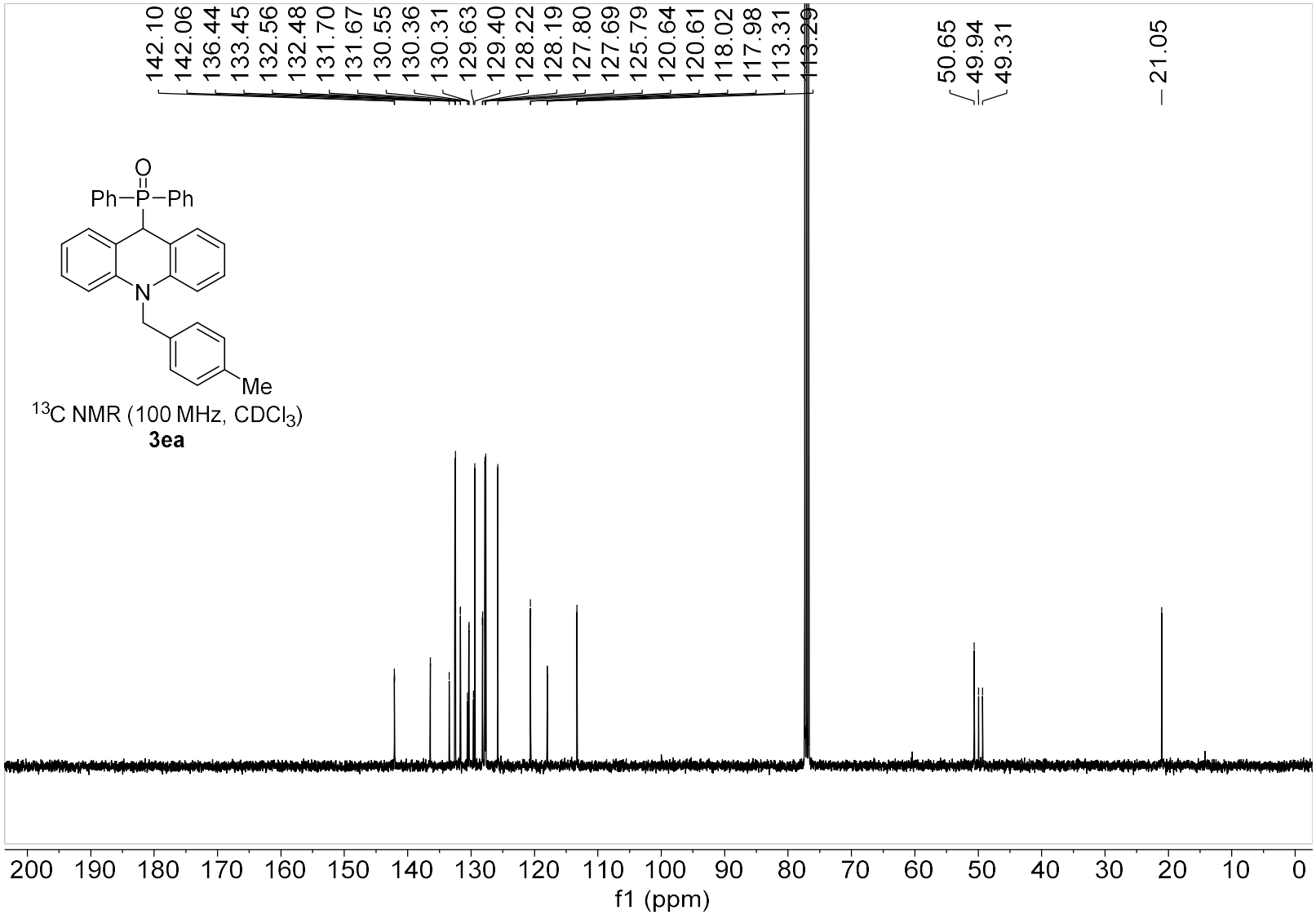
3da


7.50
7.48
7.46
7.45
7.39
7.38
7.37
7.36
7.07
7.05
7.04
7.03
7.03
7.02
7.01
6.90
6.88
6.83
6.81
6.43
6.41
5.03
4.98
4.24
2.30
O
Ph—P—Ph
N
Me
1H NMR (400 MHz, CDCl3)
3ea
6.00
3.97
5.98
1.98
2.04
1.96
1.00
1.95
2.89
f1 (ppm)



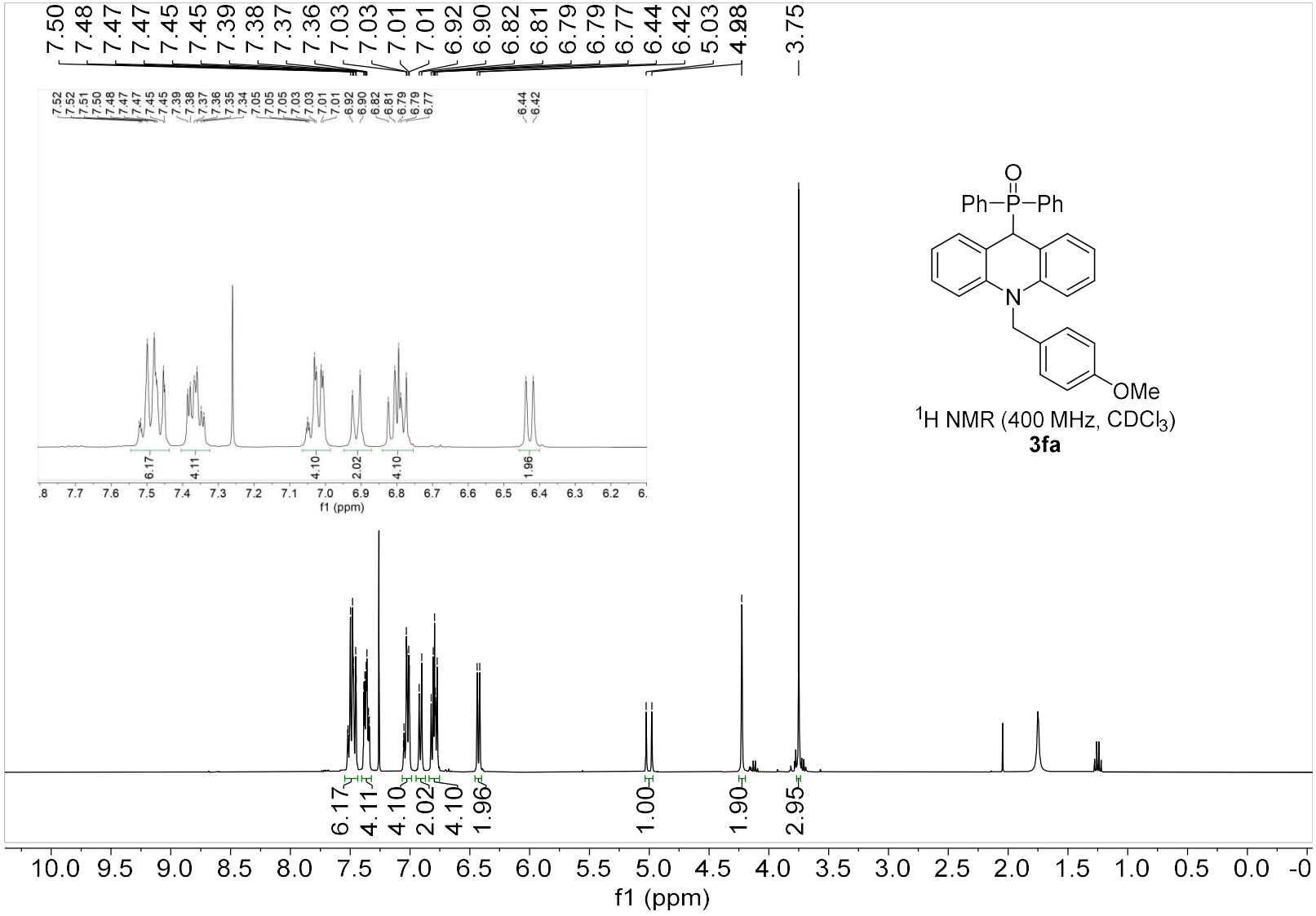
^{31}P NMR (162 MHz, $CDCl_3$)

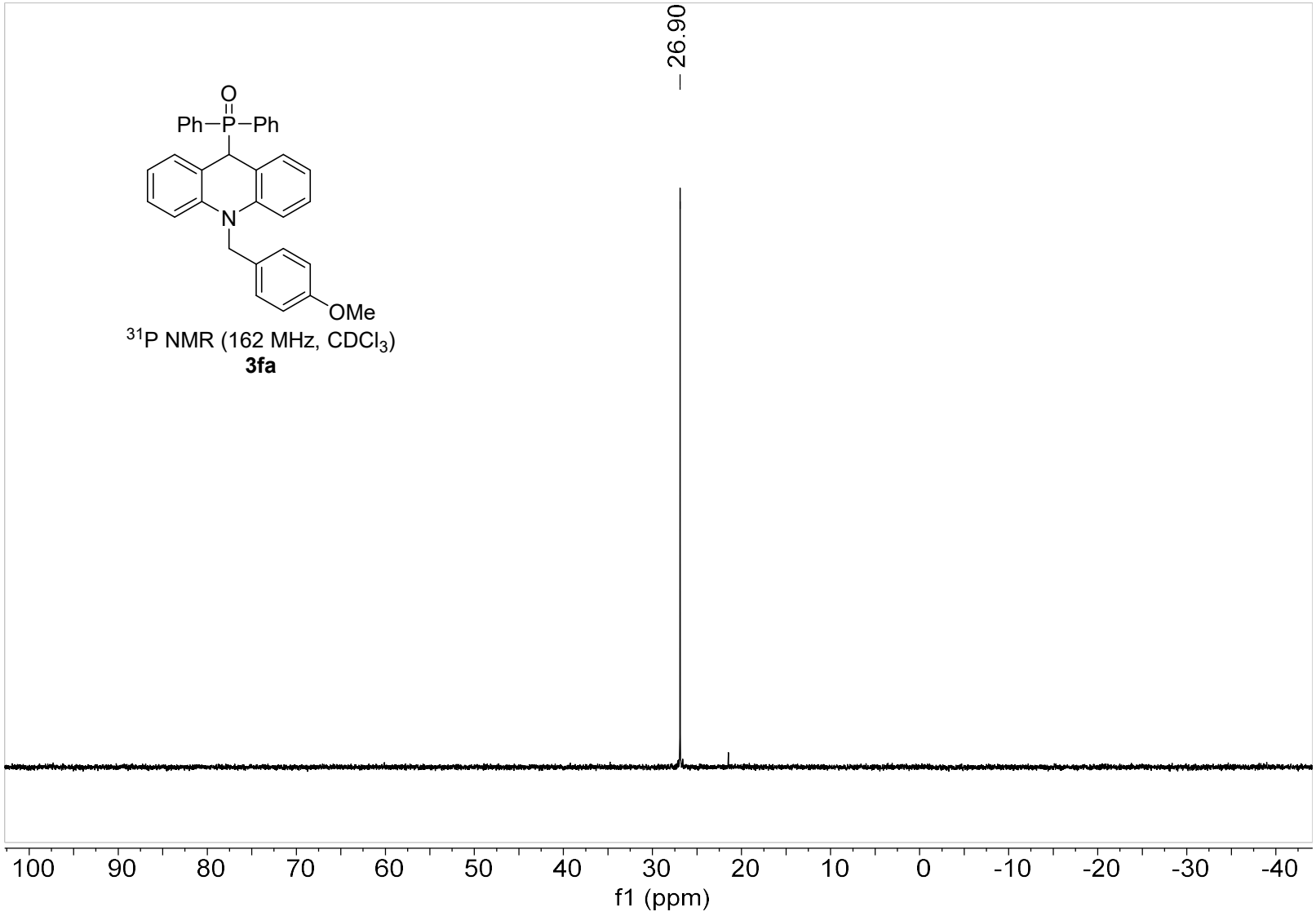
3ea



^{13}C NMR (100 MHz, $CDCl_3$)

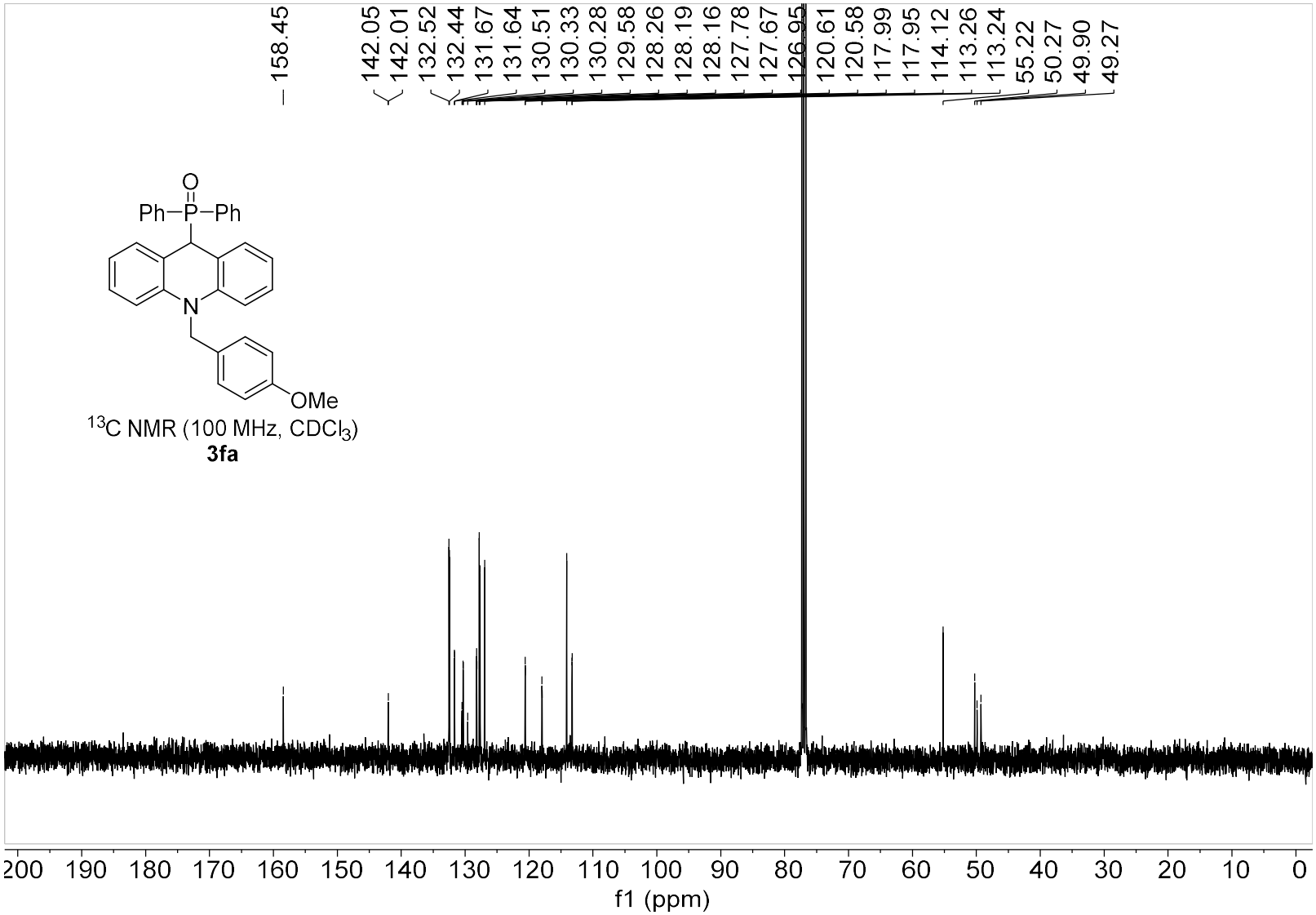
3ea


7.50 7.48 7.47 7.47 7.45 7.45 7.39 7.38 7.37 7.36 7.03 7.03 7.01 7.01 6.92 6.90 6.82 6.81 6.79 6.79 6.77 6.44 6.42 5.03 4.98 3.75
6.17 4.11 4.10 2.02 4.10 1.96 1.00 1.90 2.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)
6.17 4.11 4.10 2.02 4.10 1.96
f1 (ppm)
O
Ph–P–Ph
N
OMe
1H NMR (400 MHz, CDCl3)
3fa



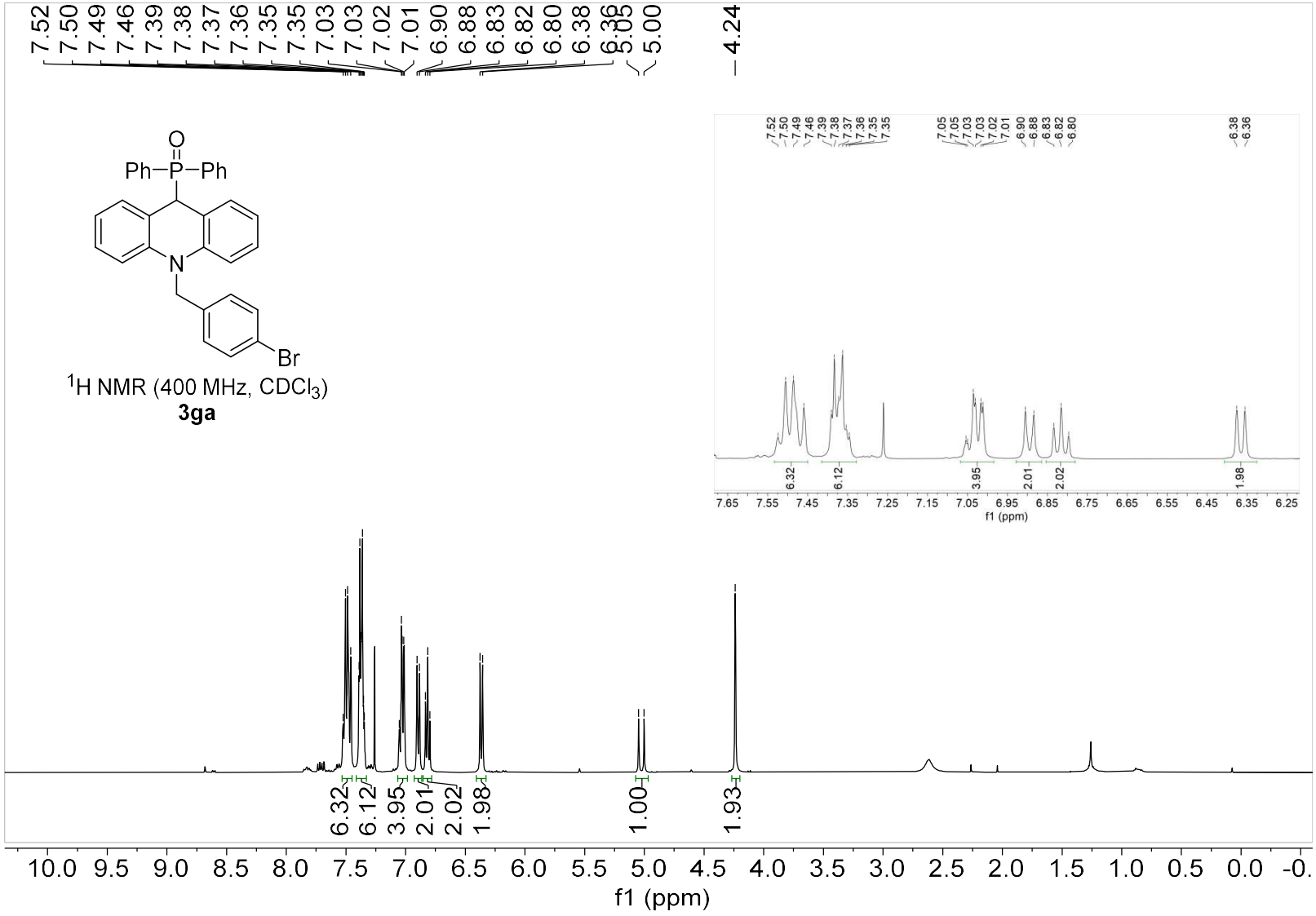
^{31}P NMR (162 MHz, $CDCl_3$)

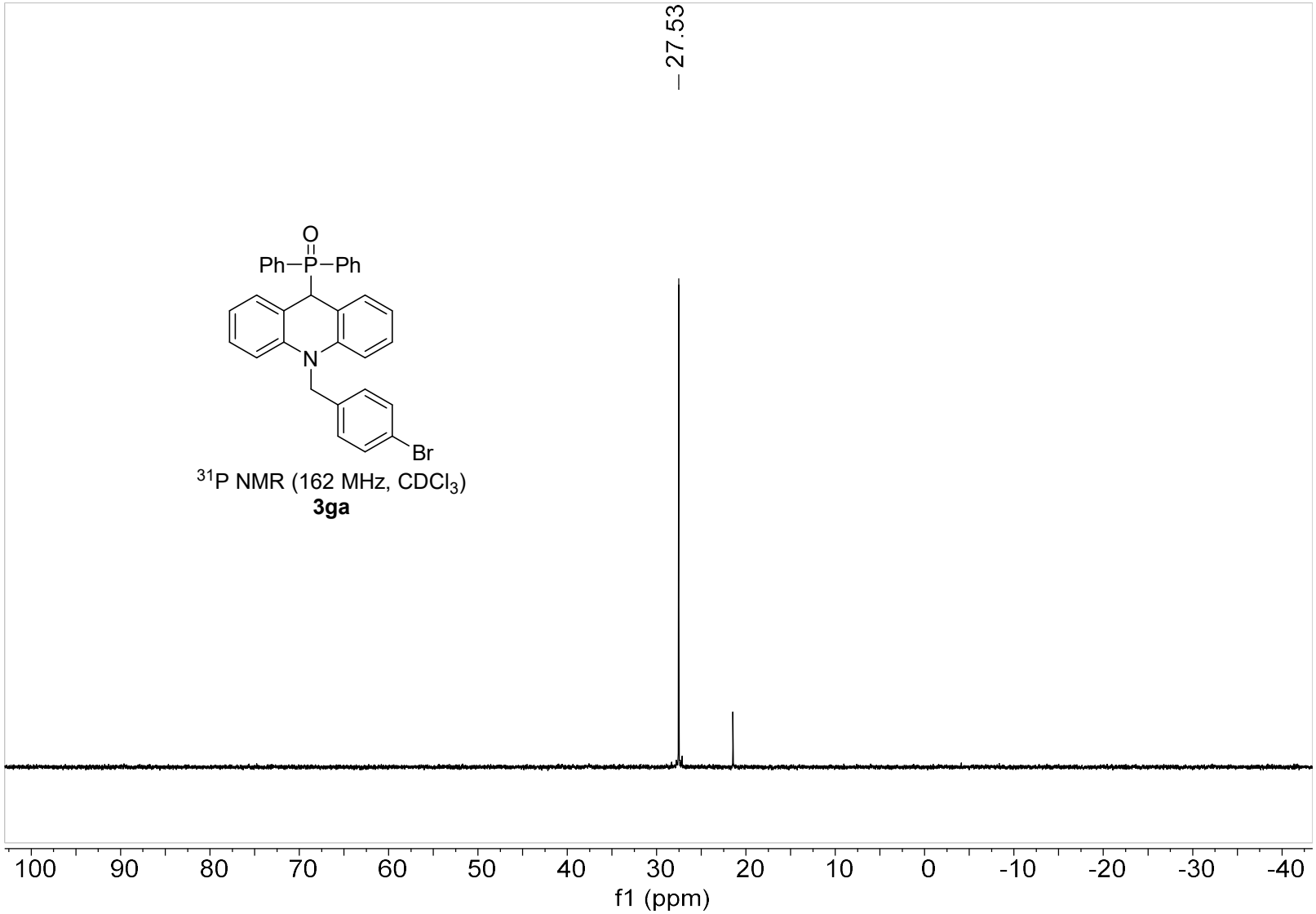
3fa



^{13}C NMR (100 MHz, $CDCl_3$)

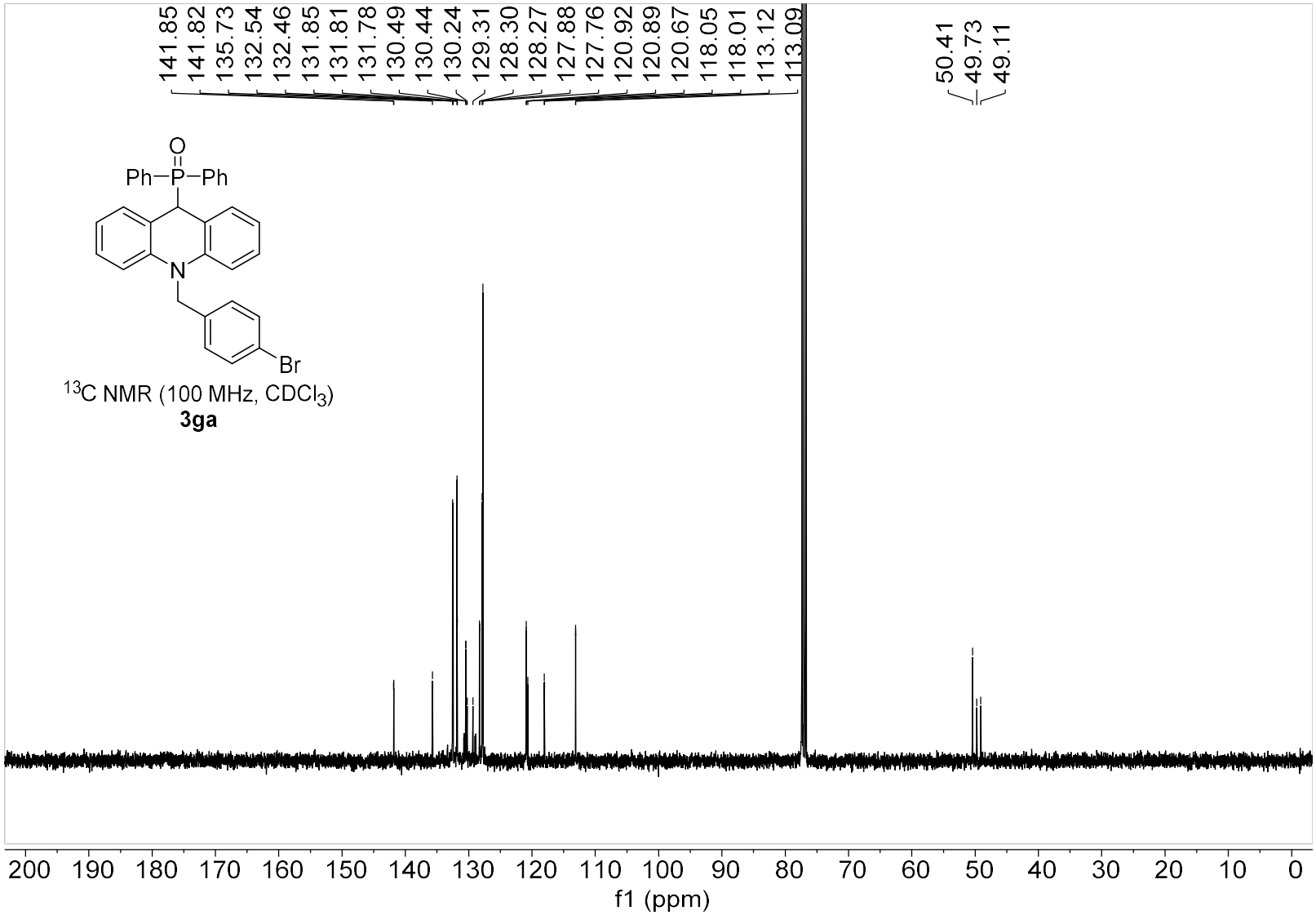
3fa


7.52
7.50
7.49
7.46
7.39
7.38
7.37
7.36
7.35
7.35
7.03
7.03
7.02
7.01
6.90
6.88
6.83
6.82
6.80
6.38
6.36
5.05
5.00
4.24
O
Ph–P–Ph
N
Br
1H NMR (400 MHz, CDCl3)
3ga
6.32
6.12
3.95
2.01
2.02
1.98
1.00
1.93
f1 (ppm)



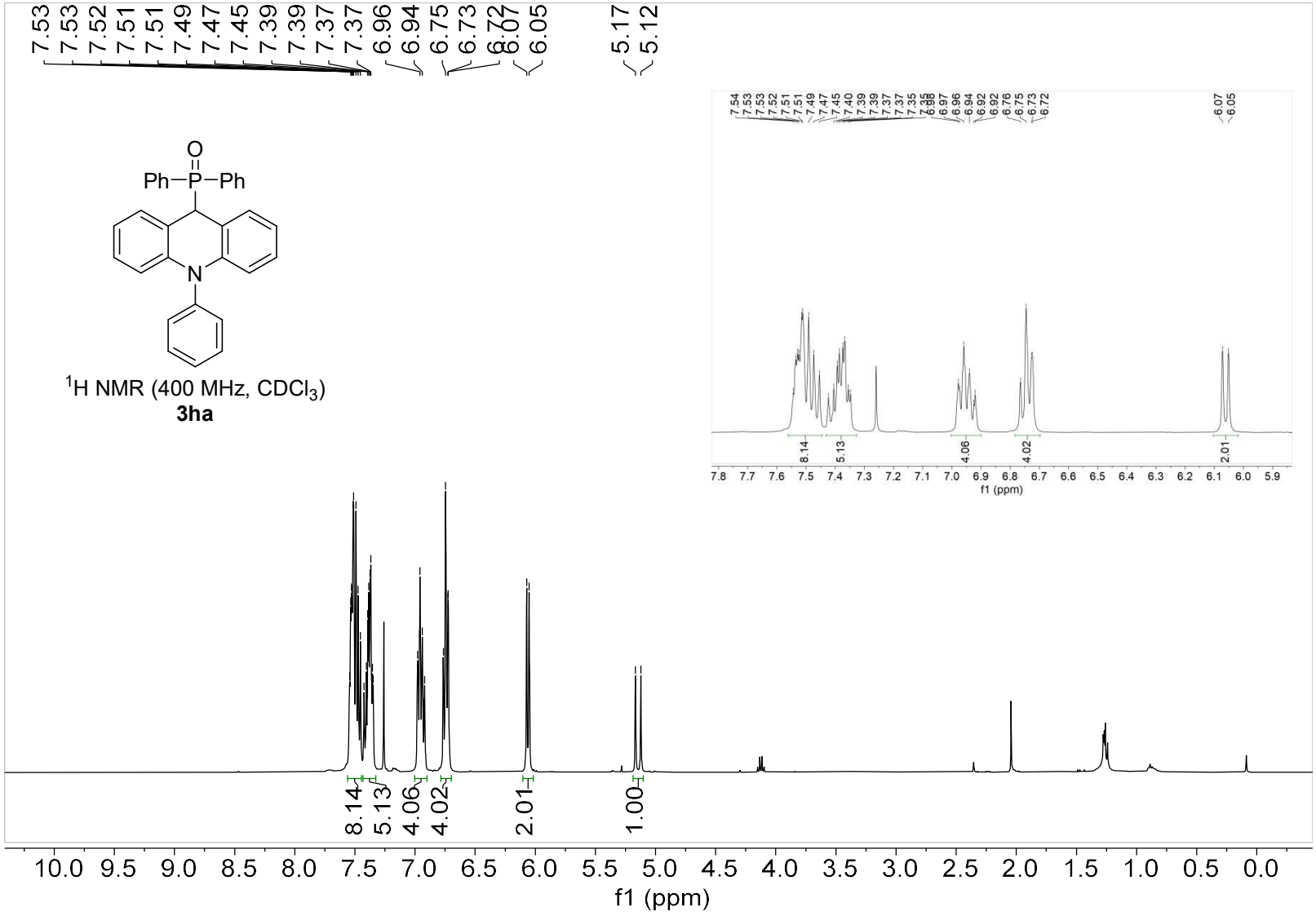
^{31}P NMR (162 MHz, $CDCl_3$)

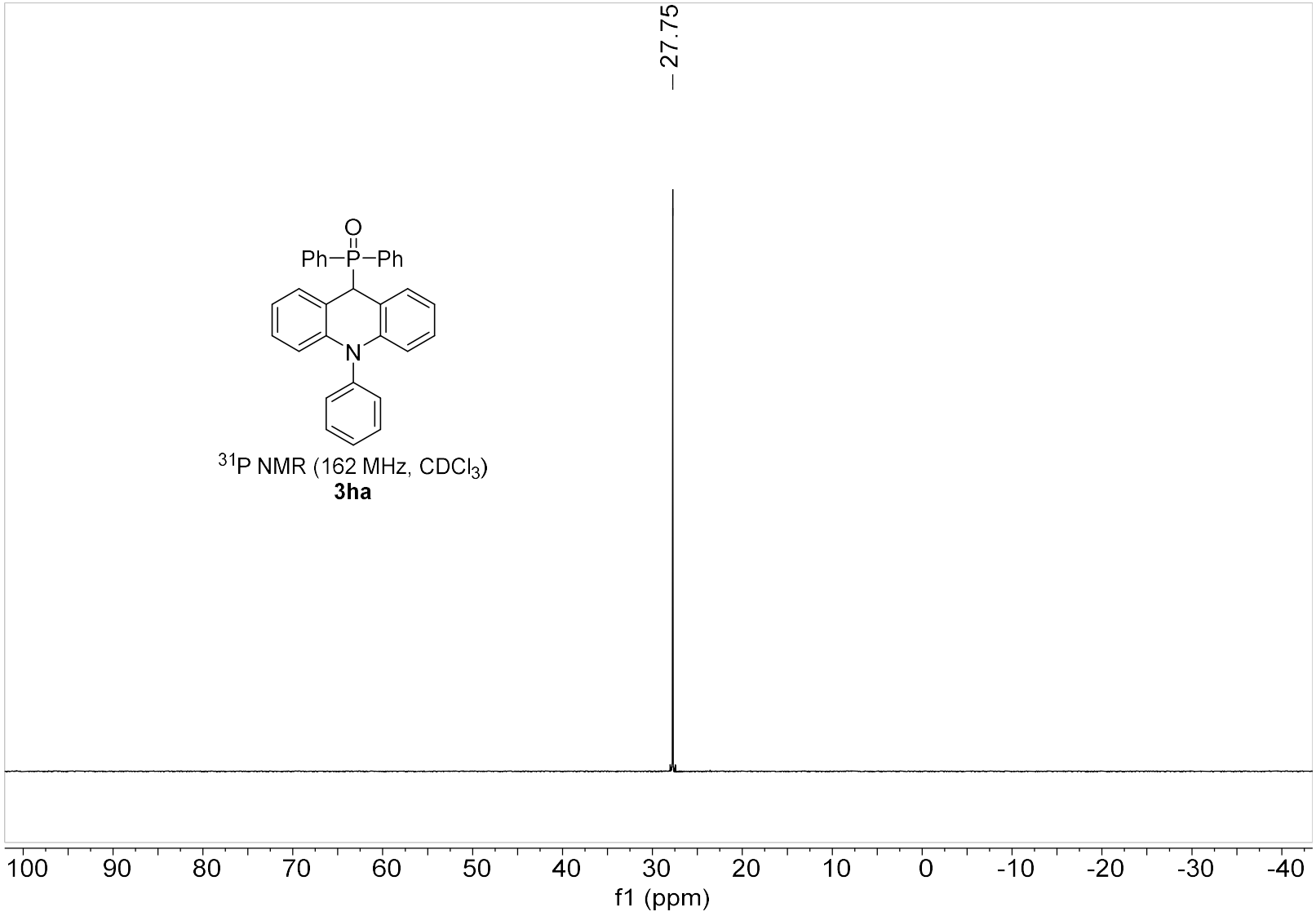
3ga



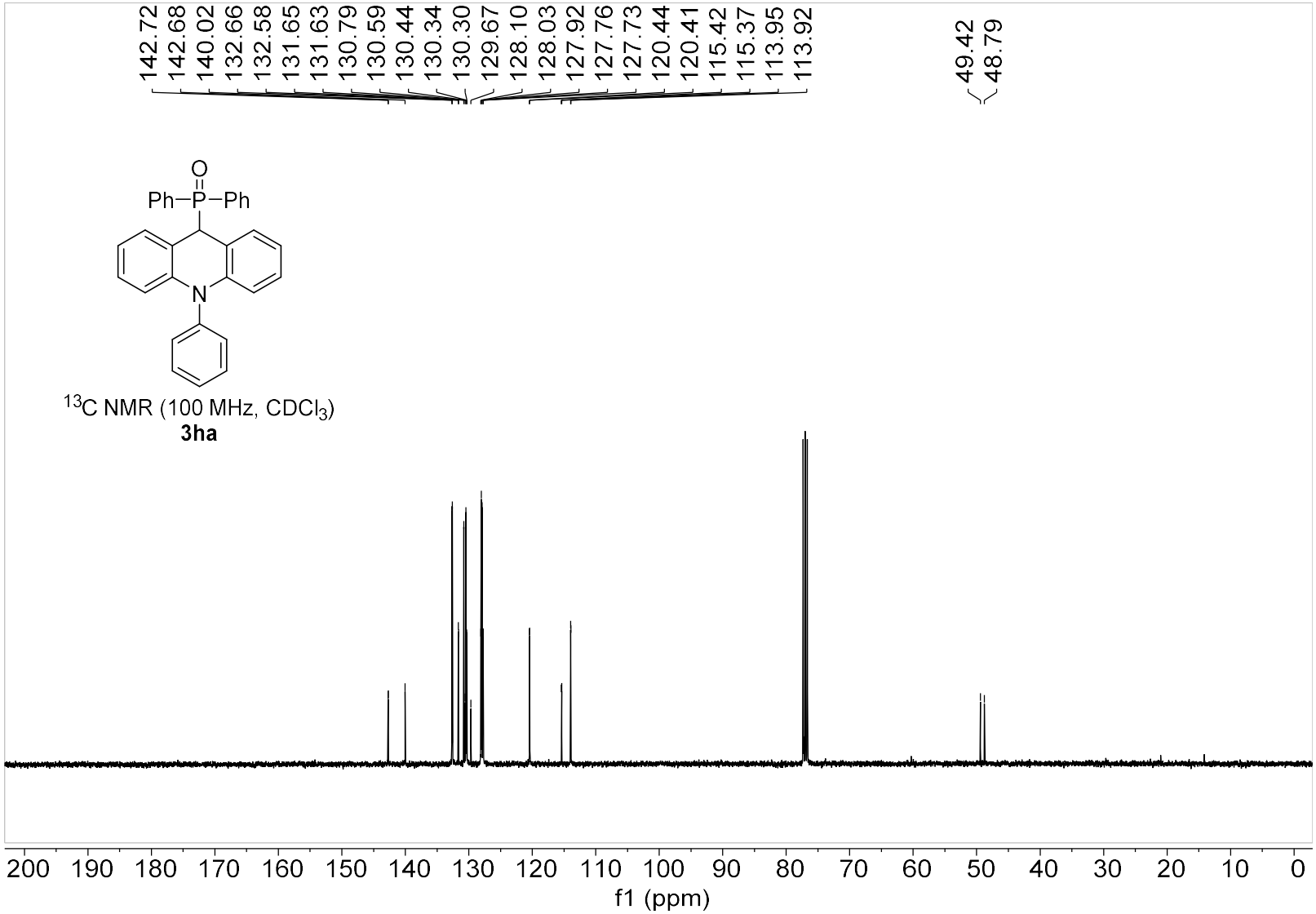
^{13}C NMR (100 MHz, $CDCl_3$)

3ga


7.53
7.53
7.52
7.51
7.51
7.49
7.47
7.45
7.39
7.39
7.37
7.37
6.96
6.94
6.75
6.73
6.72
6.07
6.05
5.17
5.12
O
Ph—P—Ph
N
1H NMR (400 MHz, CDCl3)
3ha
8.14
5.13
4.06
4.02
2.01
1.00
f1 (ppm)

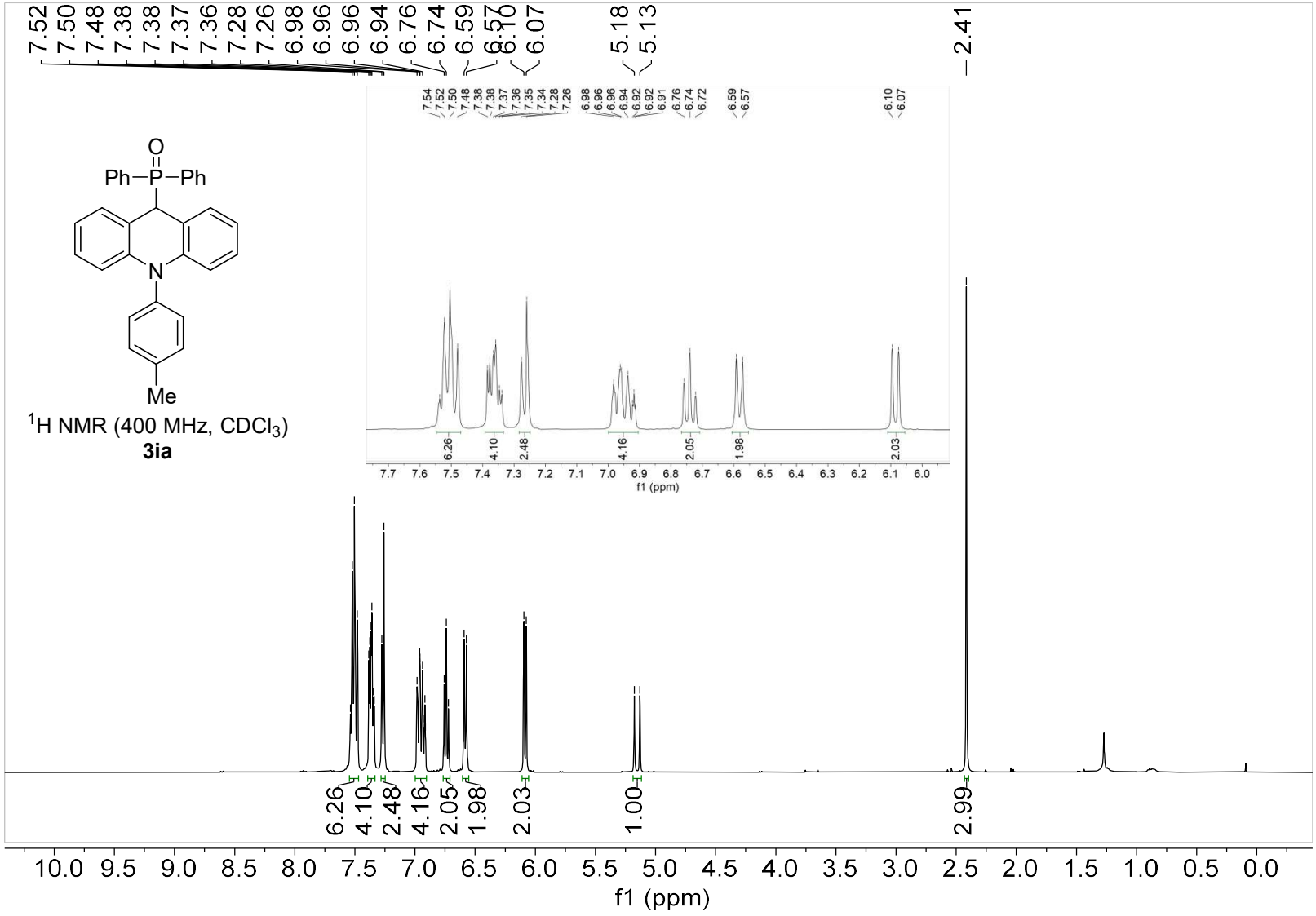


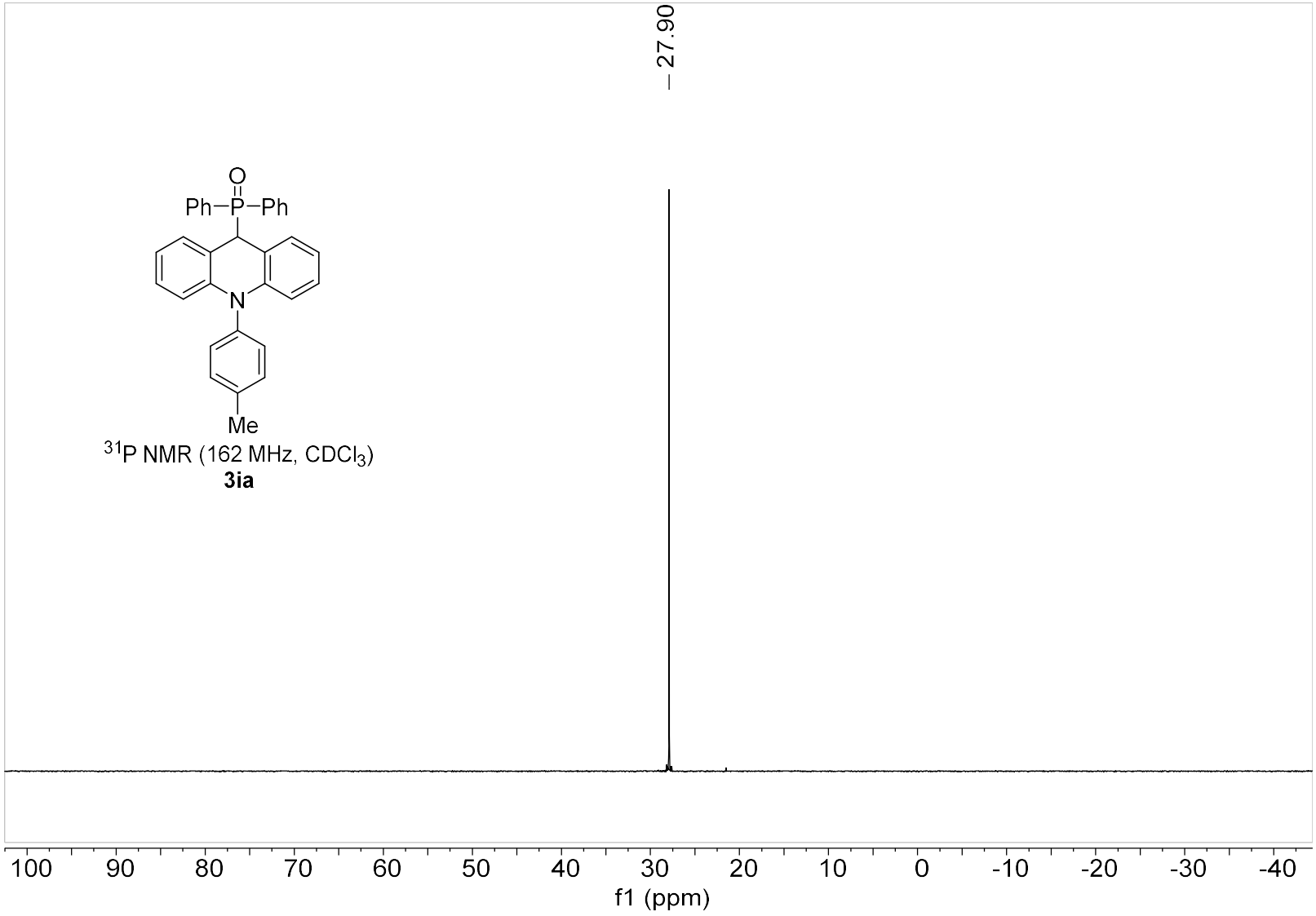
^{31}P NMR (162 MHz, $CDCl_3$)
3ha



^{13}C NMR (100 MHz, $CDCl_3$)

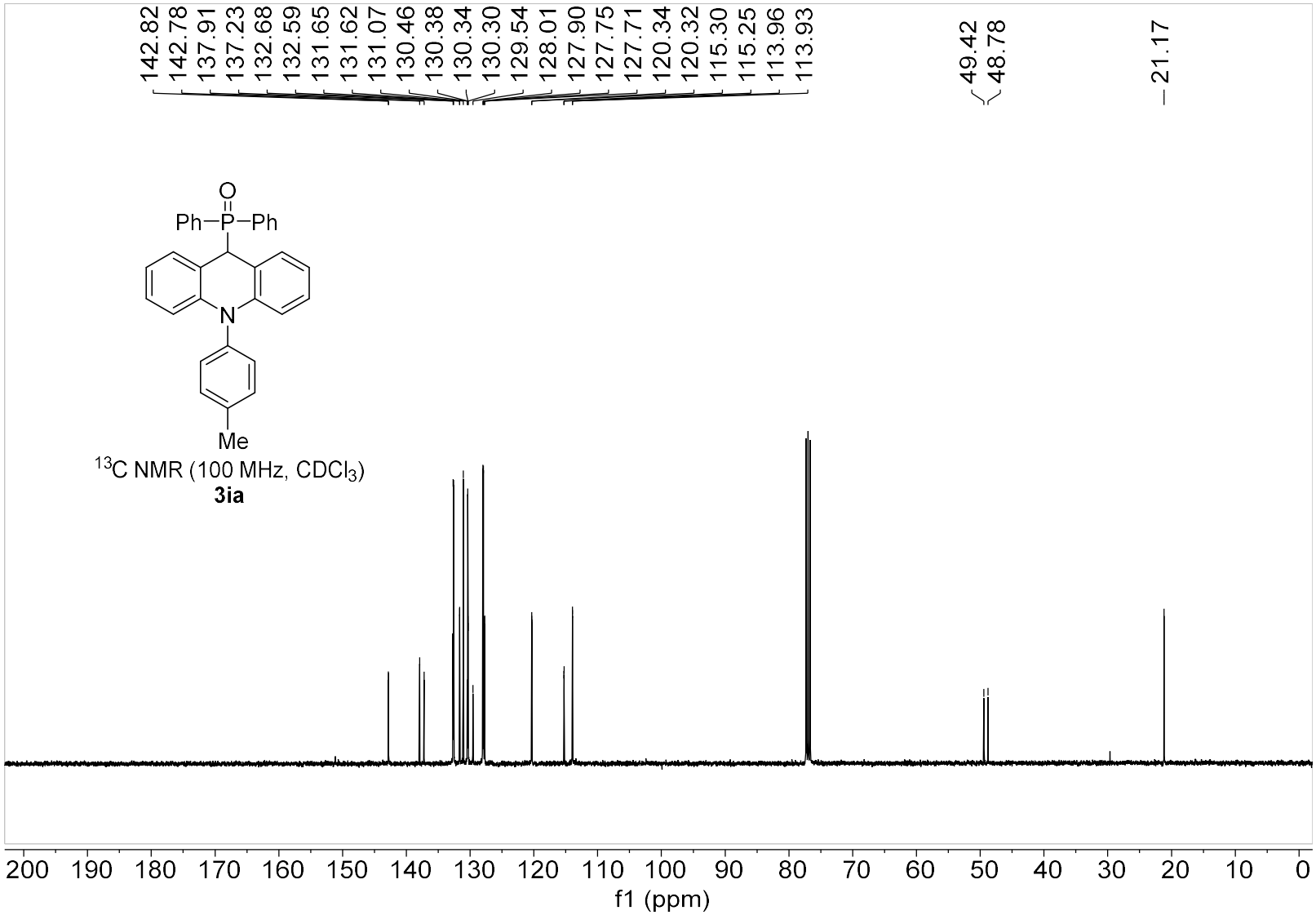
3ha


7.52
7.50
7.48
7.38
7.38
7.37
7.36
7.28
7.26
6.98
6.96
6.96
6.94
6.76
6.74
6.59
6.57
6.10
6.07
5.18
5.13
2.41
O
Ph—P—Ph
N
Me
1H NMR (400 MHz, CDCl3)
3ia
6.26
4.10
2.48
4.16
2.05
1.98
2.03
1.00
2.99
f1 (ppm)



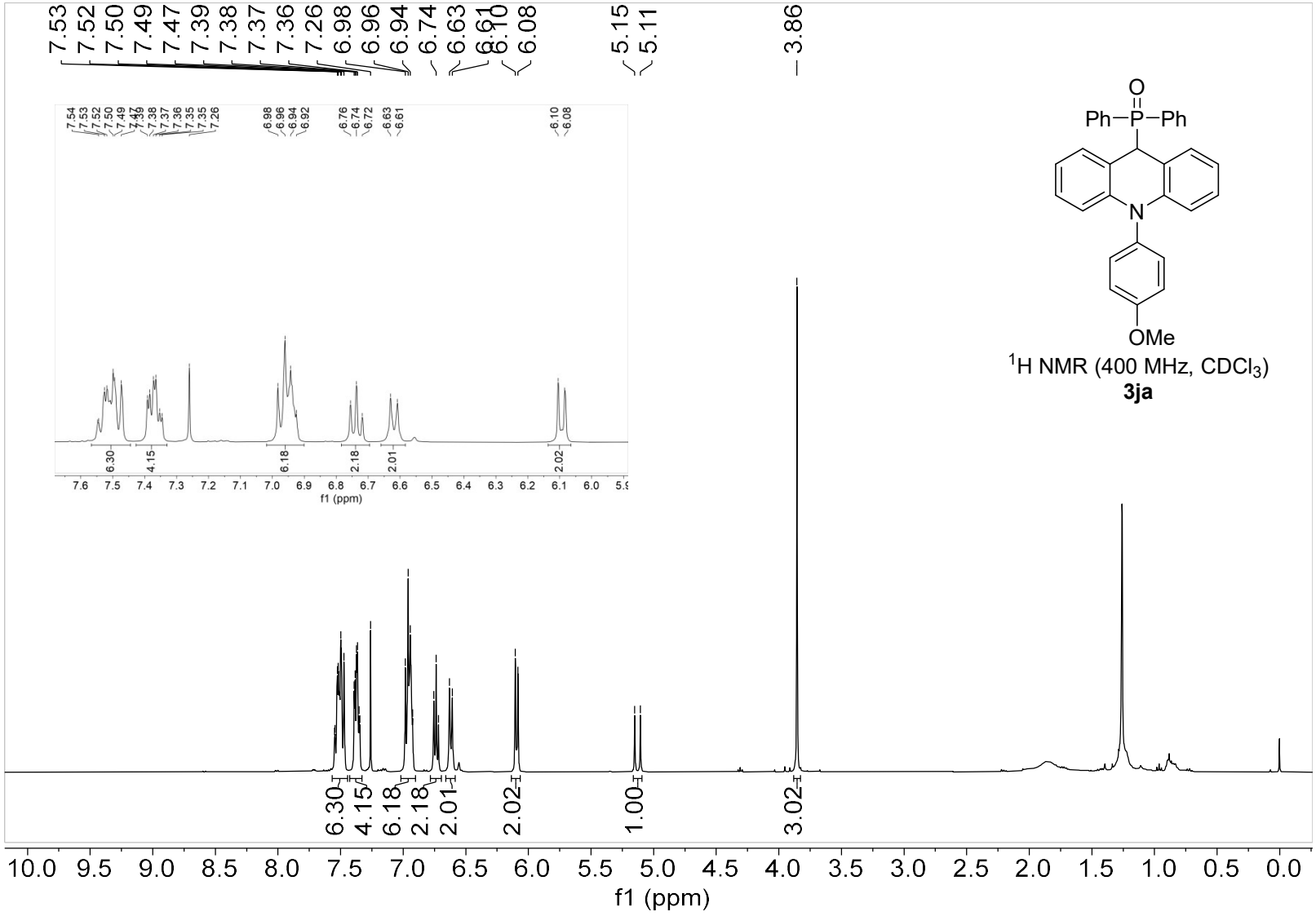
^{31}P NMR (162 MHz, $CDCl_3$)

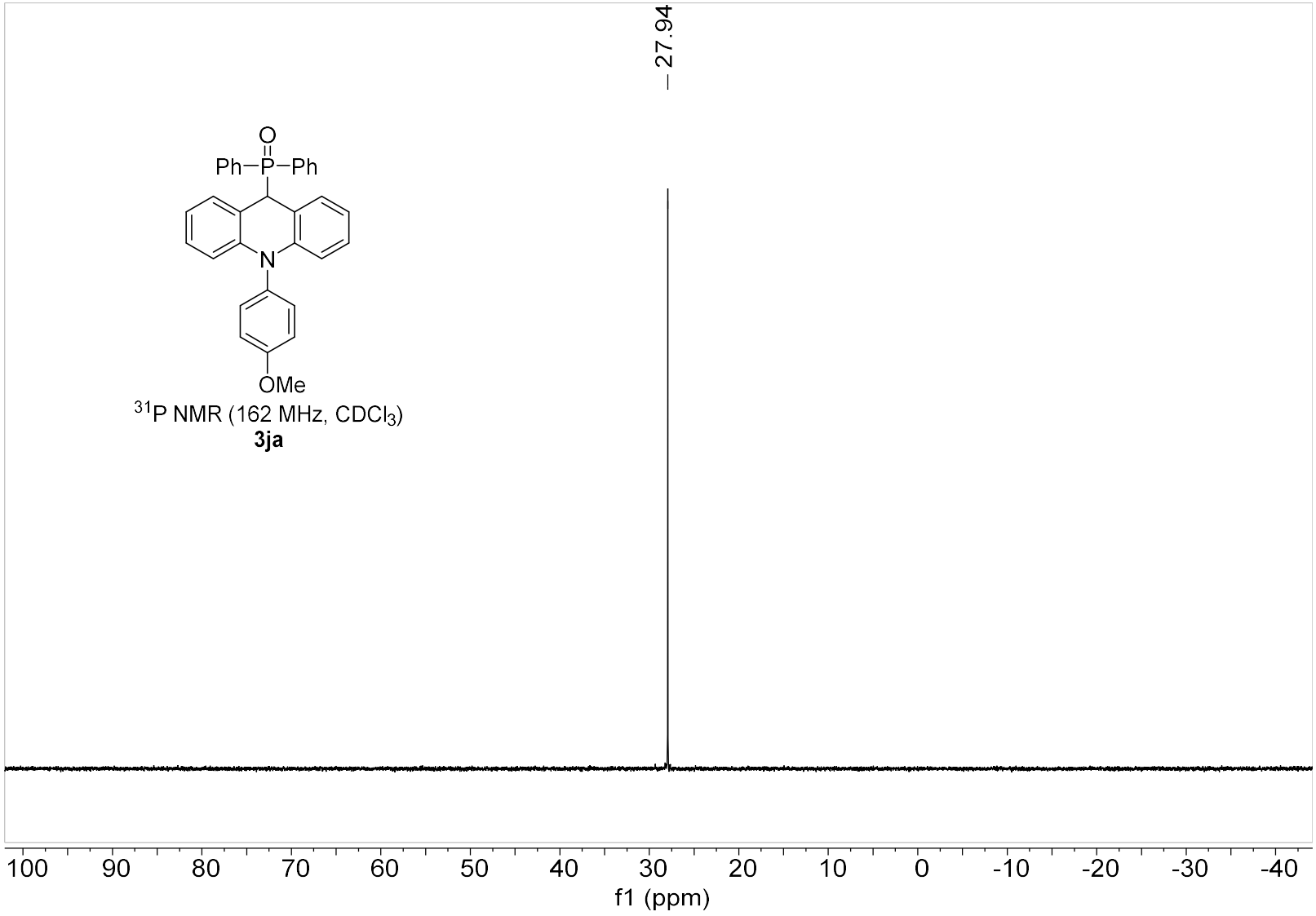
3ia



^{13}C NMR (100 MHz, $CDCl_3$)

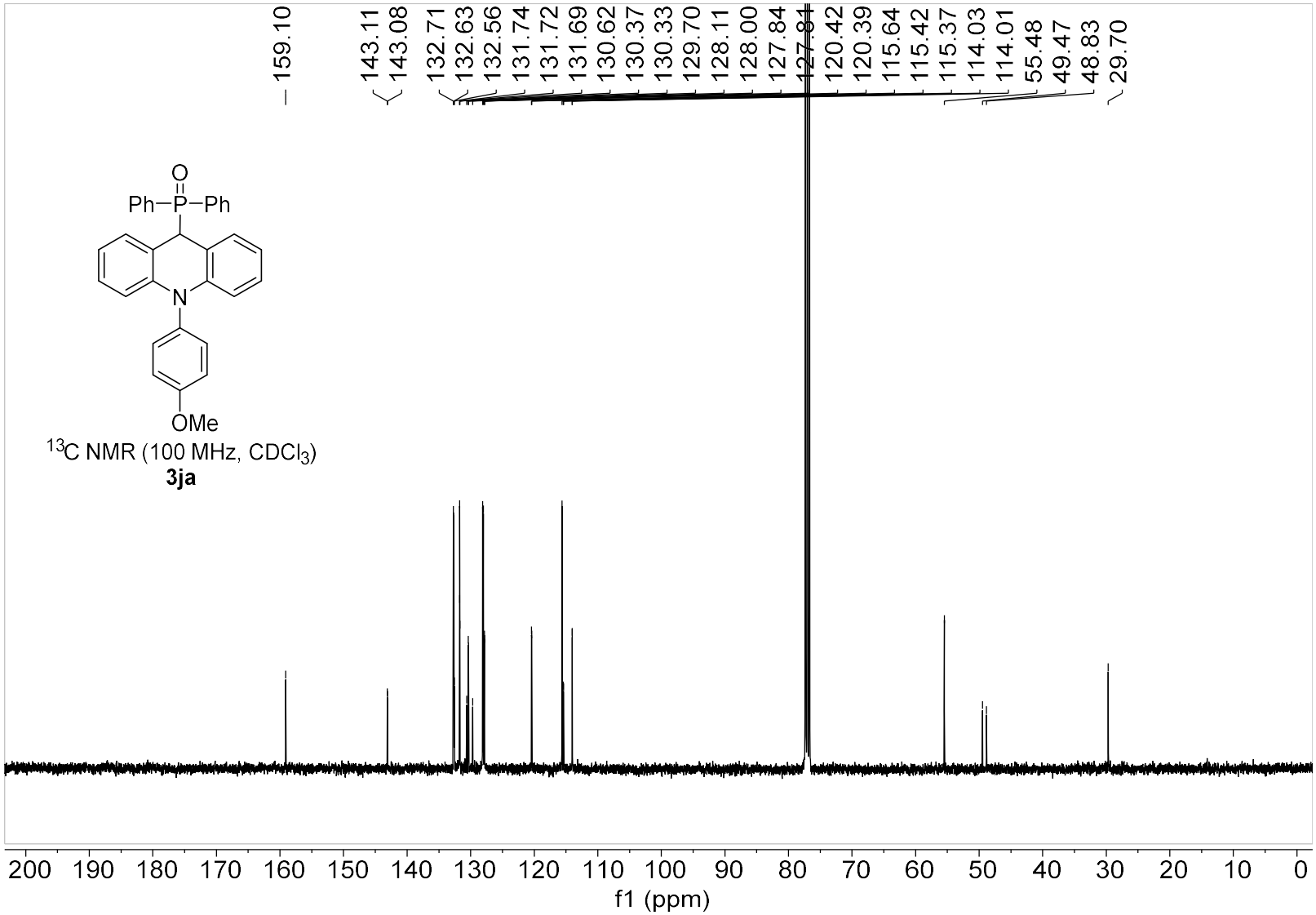
3ia


7.53
7.52
7.50
7.49
7.47
7.39
7.38
7.37
7.36
7.26
6.98
6.96
6.94
6.74
6.63
6.61
6.10
6.08
5.15
5.11
3.86
6.30
4.15
6.18
2.18
2.01
2.02
1.00
3.02
f1 (ppm)
O
Ph—P—Ph
N
OMe
1H NMR (400 MHz, CDCl3)
3ja



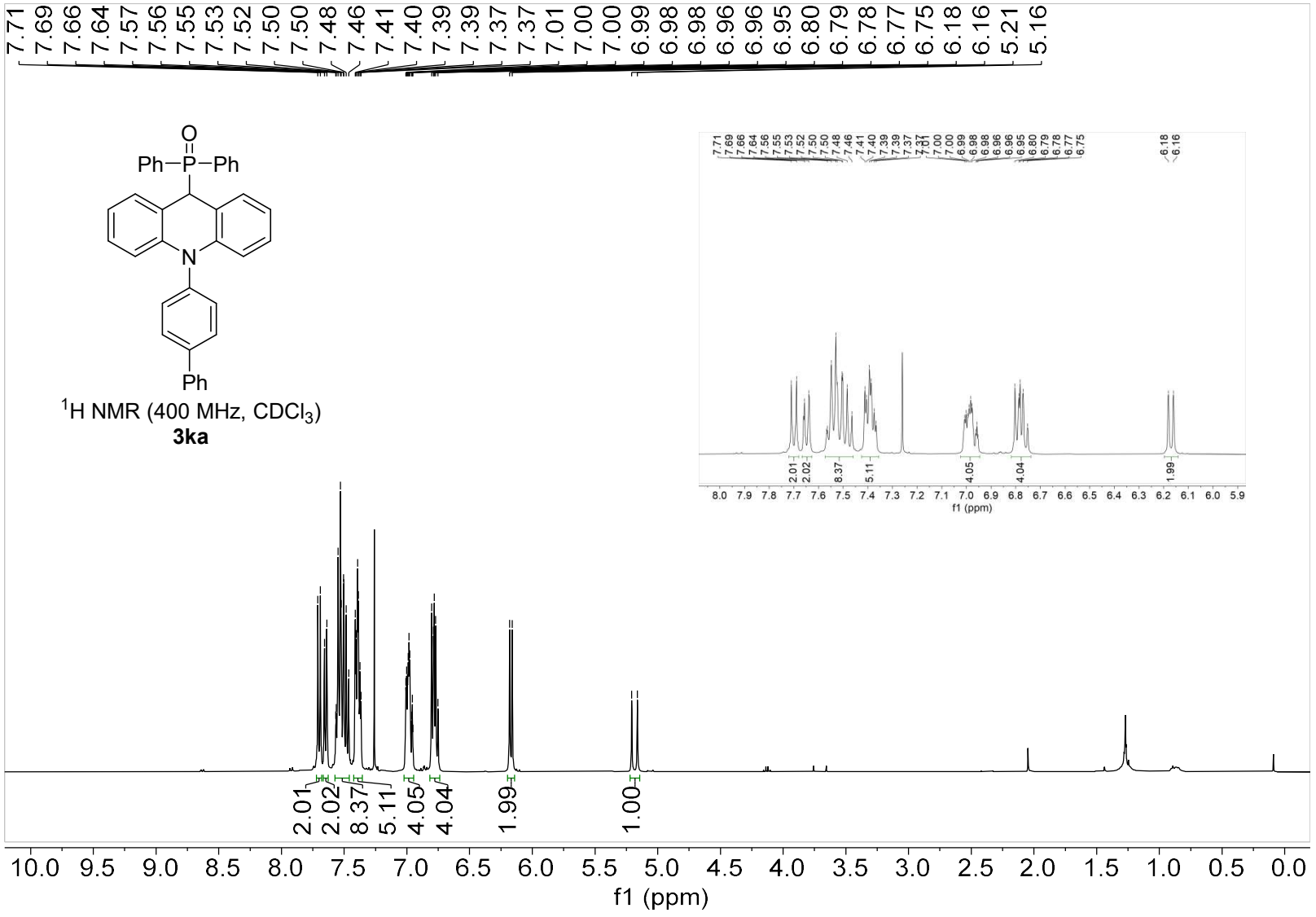
^{31}P NMR (162 MHz, $CDCl_3$)

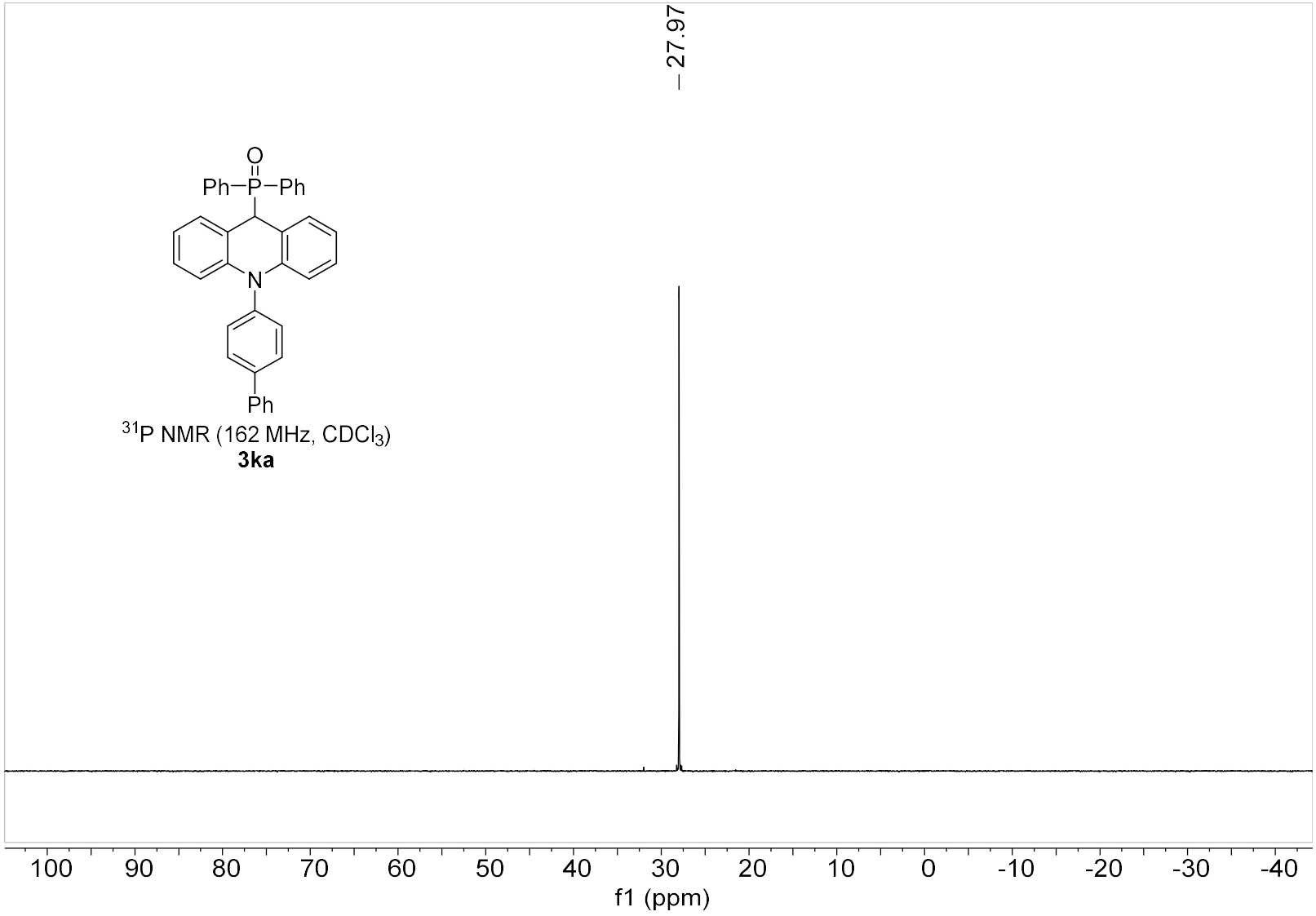
3ja



^{13}C NMR (100 MHz, $CDCl_3$)

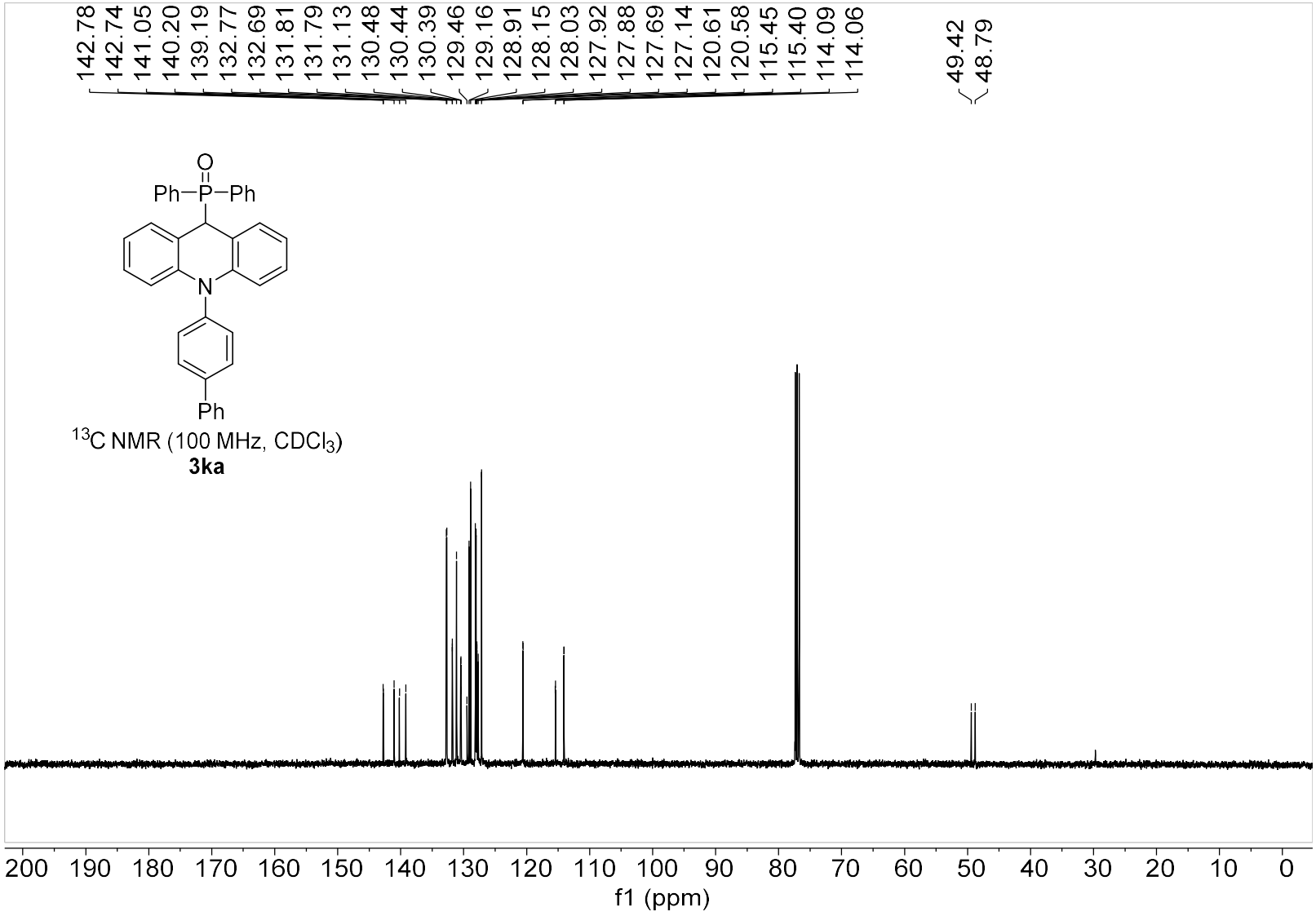
3ja


7.71 7.69 7.66 7.64 7.57 7.56 7.55 7.53 7.52 7.50 7.50 7.48 7.46 7.41 7.40 7.39 7.39 7.37 7.37 7.01 7.00 7.00 6.99 6.98 6.98 6.96 6.96 6.95 6.80 6.79 6.78 6.77 6.75 6.18 6.16 5.21 5.16
O
Ph–P–Ph
N
Ph
1H NMR (400 MHz, CDCl3)
3ka
2.01 2.02 8.37 5.11 4.05 4.04 1.99 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



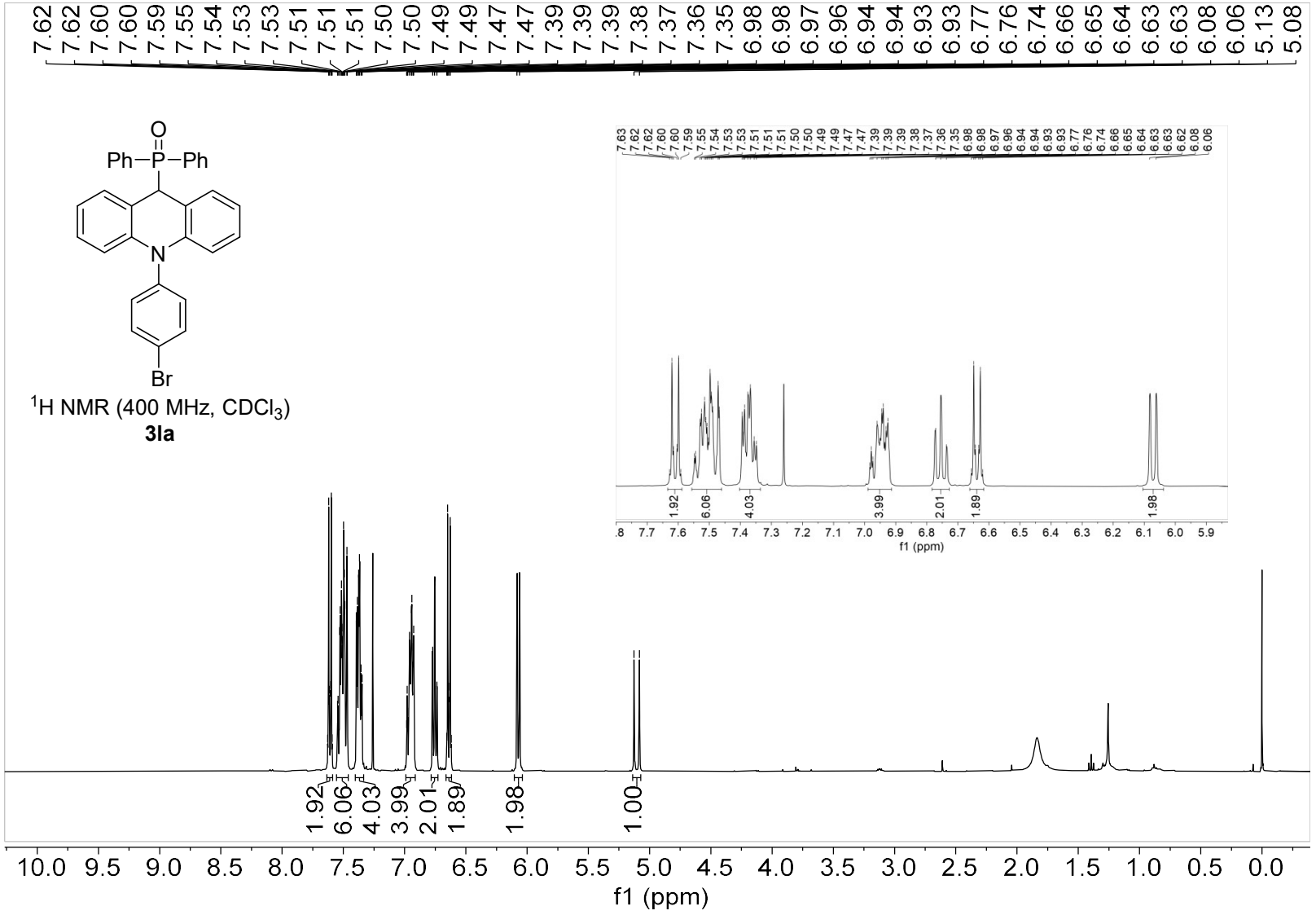
^{31}P NMR (162 MHz, $CDCl_3$)

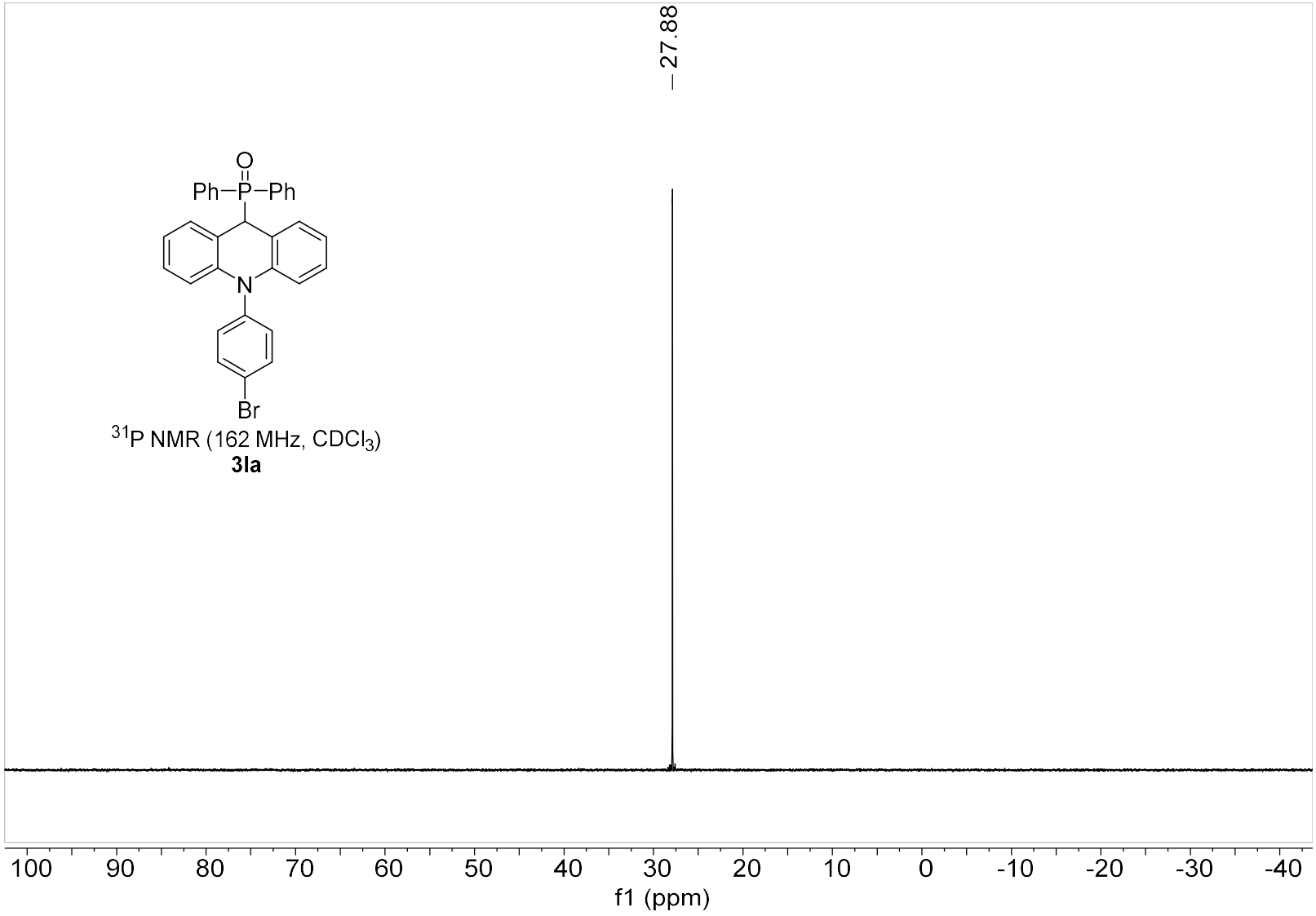
3ka



^{13}C NMR (100 MHz, $CDCl_3$)

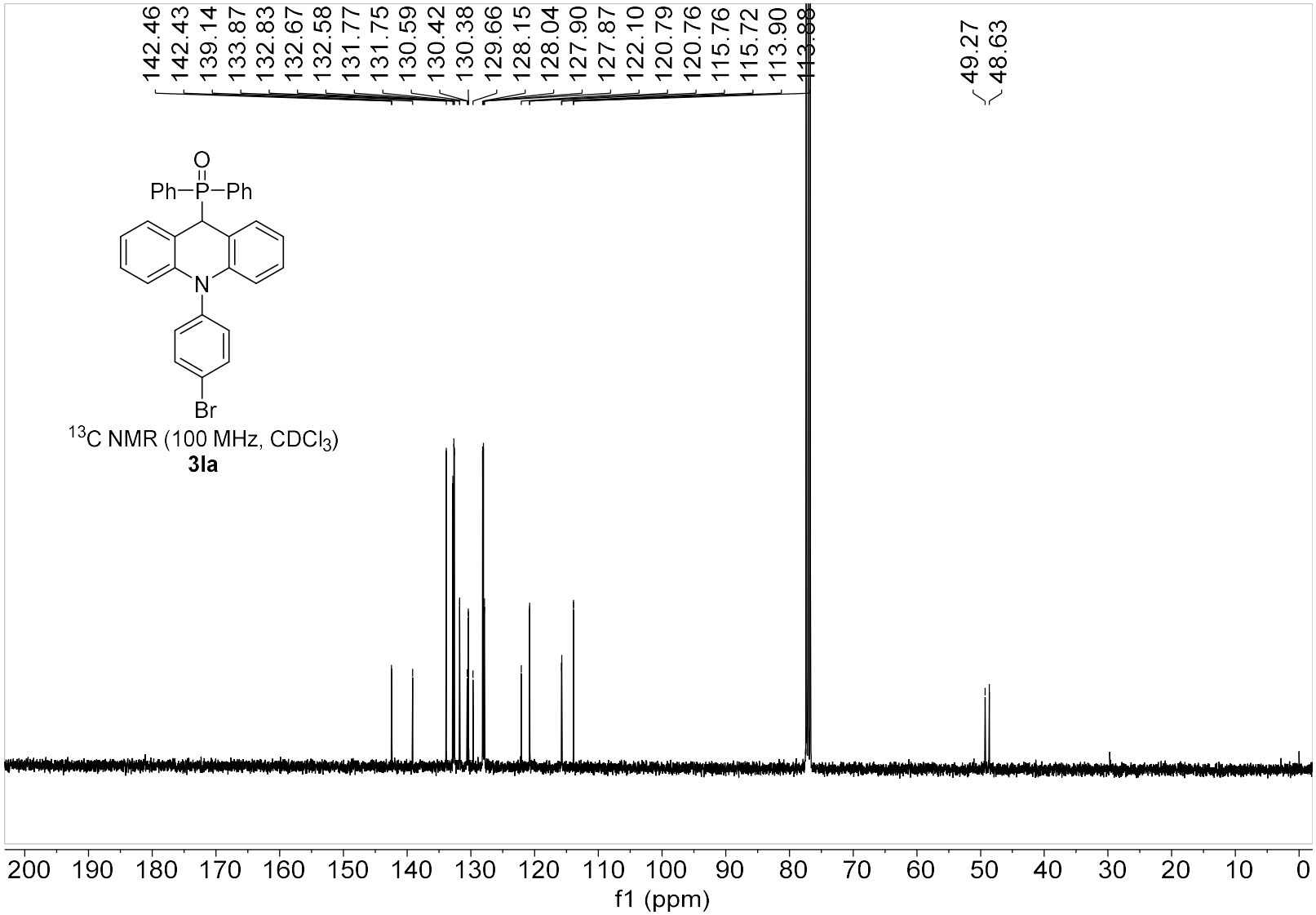
3ka


7.62 7.62 7.60 7.60 7.59 7.55 7.54 7.53 7.53 7.51 7.51 7.51 7.50 7.50 7.49 7.49 7.47 7.47 7.39 7.39 7.39 7.38 7.37 7.36 7.35 6.98 6.98 6.97 6.96 6.94 6.94 6.93 6.93 6.77 6.76 6.74 6.66 6.65 6.64 6.63 6.63 6.08 6.06 5.13 5.08
O
Ph—P—Ph
N
Br
1H NMR (400 MHz, CDCl3)
3la
1.92 6.06 4.03 3.99 2.01 1.89 1.98 1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



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

3la



^{13}C NMR (100 MHz, $CDCl_3$)

3la