Supporting Information

HFIP-promoted phosphorylation of indol-3-yl methanols to access (indol-3-yl)methyl phosphonates

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1. General information

All reactions were carried out under air, in oven dried glassware with magnetic stirring, unless otherwise noted. All commercially available compounds were purchased from Energy® Scientific Ltd or Shanghai Macklin Biochemical Co., Ltd and used without further purification. Dry CH_2Cl_2 was distilled from CaH_2. Anhydrous THF was distilled from sodium sand. Flash column chromatography was performed on silica gel (particle size 200-300 mesh, purchased from Qingdao Puke Co., China) and eluted with petroleum ether /ethyl acetate. ^{1}H, ^{13}C and ^{31}P NMR spectra were collected on a Bruker AV 400 MHz NMR spectrometer using residue solvent peaks as an internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm, ^{13}C NMR: $CDCl_3$ at 77.0 ppm, DMSO-d_6 at 39.5 ppm). NMR data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), dd (doublet of doublets), dt (doublet of triplets). Melting point was measured on the melting point meter without calibration prior use. LC-MS data were collected on Agilent 1260-6125B (Column: Unisil 5-120 C18 Ultra, Dimensions: 4.6 × 150 nm, 5 μm, Eluent: water and acetonitrile with 0.1% TFA, ESI). High-resolution mass spectra (HRMS) were recorded on Thermo Scientific Orbitrap Exploris 120 mass spectrometer using electrospray ionization (ESI) technique and a TOF analyzer.

2. Substrate preparation

All the alcohol substrates used in this work are shown below. **1a** and **2a-2f** were purchased. **1b**[1], **1c**[2], **1h**[3], **1l**[4], **1o**[5], **1q**[6], **1r**[7], **1t**[8] are known in literature, their NMR spectra are in full accordance with those reported in literature. **1d-g**, **1i-k**, **1m-n**, **1p**, **1s**, **1u** were new compounds.

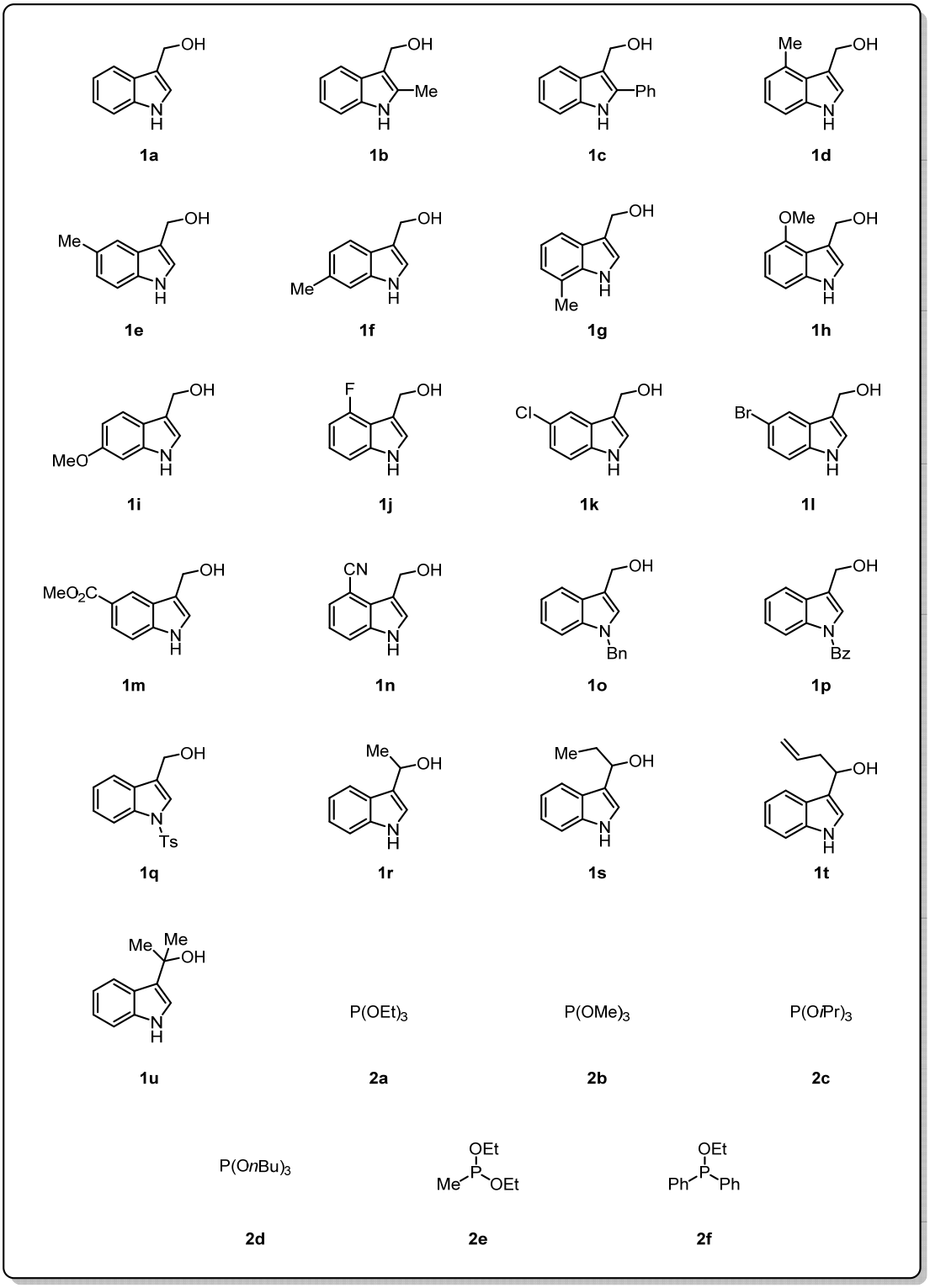
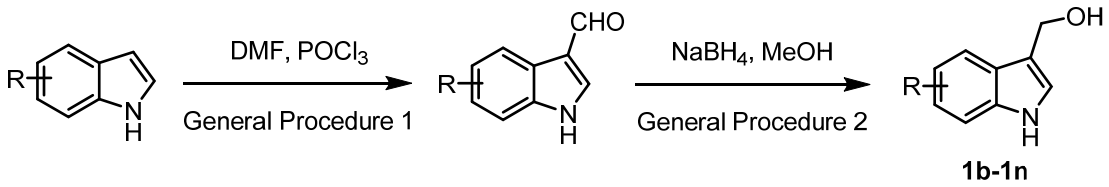


Figure S1: Substrates used in the study.

General Procedure (GP) 1 and 2 for the synthesis of 1b-1n



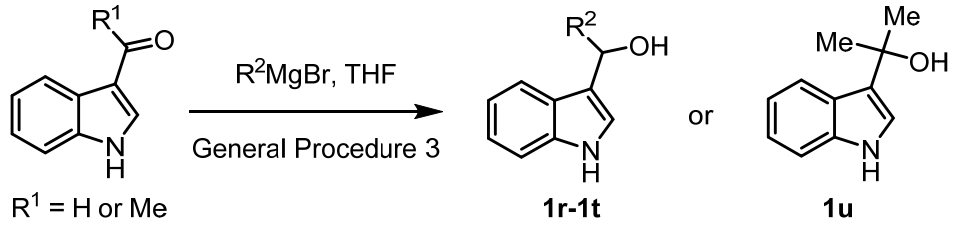
GP 1[9]:

In a round-bottomed flask, to a solution DMF (8.8 equiv.) in DCM was added dropwise $POCl_3$ (1.3 equiv.) at 0 ºC. After stirring for 30 min, indole substrate was added dropwise to the reaction mixture at 0 ºC. After stirring for 1 h at 35 ºC, H_2O (0.03 equiv.) and 30% NaOH (0.08 equiv.) was added sequentially dropwise to the reaction mixture at 0 ºC, and then heated to reflux at 130 ºC for 30 min. The crude product was filtered and washed with water, then was purified by silica gel column chromatography to give 3-formyl indole.

GP 2[10]:

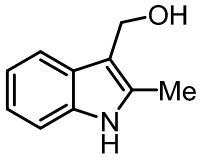
To a solution of the above-mentioned 3-formyl indole (1 equiv.) in MeOH (0.3 M) was added $NaBH_4$ (1.1 equiv.) at 0 ºC for 30 min. The mixture was quenched by NH_4Cl and extracted with EtOAc. After concentration in vacuo and the combined organic layer and dried over Na_2SO_4 and removed under reduced pressure then was purified by silica gel column chromatography to give **1b-1n**.

General procedure (GP) 3 for the synthesis of 1r-1t



GP 3[11]:

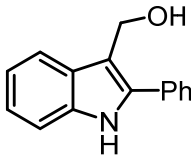
Under an argon atmosphere, to a solution of 1H-indole-3-carbaldehyde in dry THF (0.3 M) was added dropwise a solution of R^2MgBr (3 equiv.) at 0 ºC. After stirring for 1 h, the mixture was quenched by H_2O and extracted with EtOAc, and the organic layer was dried over Na_2SO_4 and removed under reduced pressure then was purified by silica gel column chromatography to give **1r-1u**.



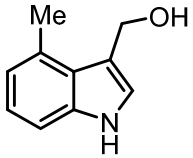
(2-Methyl-1H-indol-3-yl)methanol (1b) was prepared according to the GP 1 and 2 as yellow solid in 74% yield (476.6 mg) from 2-methyl-1H-indole substrate (424.0 mg, 4.0 mmol). Melting Point: 112–114 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.82 (s, 1H), 7.18 (dd, J = 13.3, 5.2 Hz, 2H), 6.93 (dd, J = 14.0, 6.1 Hz, 1H), 6.73 (d, J = 7.1 Hz, 1H), 4.69 (s, 2H), 2.65 (s, 3H).

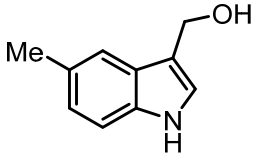
The **^{1}H NMR** spectrum is identical to ref. 1.



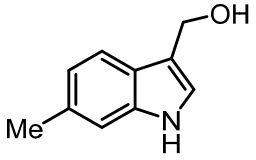
(2-Phenyl-1H-indol-3-yl)methanol (1c) was prepared according to the GP 1 and 2 as white solid in 34% yield (591.4 mg) from 2-phenyl-1H-indole substrate (1.5 g, 7.8 mmol).
Melting Point: 223–225 °C.
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.25 (s, 1H), 7.74 – 7.69 (m, 2H), 7.59 (d, J = 7.8 Hz, 1H), 7.41 (t, J = 7.7 Hz, 2H), 7.30 (t, J = 7.3 Hz, 2H), 7.06 – 6.99 (m, 1H), 6.98 – 6.89 (m, 1H), 4.89 (s, 1H), 4.61 (s, 2H).
The **^{1}H NMR** spectrum is identical to ref. 2.



(4-Methyl-1H-indol-3-yl)methanol (1d) was prepared according to the GP 1 and 2 as brown solid in 60% yield (966.0 mg) from 4-methyl-1H-indole substrate (1.34 g, 10.0 mmol). Melting Point: 96–99 °C.
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.81 (s, 1H), 7.19 (d, J = 2.4 Hz, 1H), 7.15 (d, J = 8.1 Hz, 1H), 6.96 – 6.89 (m, 1H), 6.72 (d, J = 7.1 Hz, 1H), 4.68 (s, 3H) (hydroxyl group is included), 2.64 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 136.9, 130.0, 125.5, 124.1, 121.1, 120.0, 116.5, 109.1, 56.4, 19.6.
HRMS (ESI–TOF) m/z: calcd. for $C_{10}H_{11}NO$ $[M+H]^+$: 162.0913, found: 162.0915.

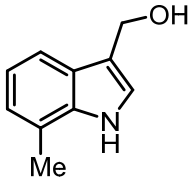


(5-Methyl-1H-indol-3-yl)methanol (1e) was prepared according to the GP 1 and 2 as yellow solid in 34% yield (547.4 mg) from 5-methyl-1H-indole substrate (1.34 g, 10.0 mmol).
Melting Point: 97–100 °C.
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.71 (s, 1H), 7.38 (d, J = 0.6 Hz, 1H), 7.23 (d, J = 8.2 Hz, 1H), 7.17 (d, J = 2.3 Hz, 1H), 6.90 (dd, J = 8.3, 1.5 Hz, 1H), 4.68 (s, 1H), 4.62 (s, 2H), 2.38 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 134.8, 126.9, 126.7, 123.3, 122.6, 118.5, 115.4, 111.0, 55.5, 21.3.
HRMS (ESI–TOF) m/z: calcd. for $C_{10}H_{11}NO$ $[M+H]^+$: 162.0913, found: 162.0915.

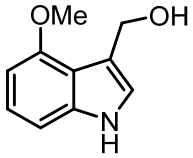


(6-Methyl-1H-indol-3-yl)methanol (1f) was prepared according to the GP 1 and 2 as yellow solid in 55% yield (673.0 mg) from 6-methyl-1H-indole substrate (1.0 g, 7.6 mmol).
Melting Point: 85–88 °C.

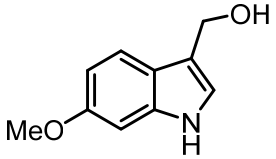
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.69 (s, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.15 (s, 2H), 6.83 (dd, J = 8.0, 0.9 Hz, 1H), 4.75 – 4.69 (m, 1H), 4.63 (d, J = 5.4 Hz, 2H), 2.39 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 136.9, 129.9, 124.6, 122.6, 120.1, 118.6, 115.8, 111.2, 55.6, 21.4.
HRMS (ESI–TOF) m/z: calcd. for $C_{10}H_{11}NO$ $[M+Na]^+$: 184.0733, found: 184.0739.



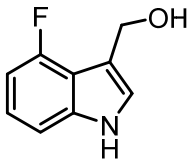
(7-Methyl-1H-indol-3-yl)methanol (1g) was prepared according to the GP 1 and 2 as green solid in 97% yield (1.2 g) from 7-methyl-1H-indole substrate (1.0 g, 7.6 mmol).
Melting Point: 100–102 °C.
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.84 (s, 1H), 7.46 (d, J = 7.3 Hz, 1H), 7.24 (d, J = 2.3 Hz, 1H), 6.96 – 6.84 (m, 2H), 4.78 – 4.72 (m, 1H), 4.67 (d, J = 5.4 Hz, 2H), 2.74 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 136.0, 126.4, 123.0, 121.5, 120.4, 118.6, 116.6, 116.4, 55.6, 16.8.
HRMS (ESI–TOF) m/z: calcd. for $C_{10}H_{11}NO$ $[M+Na]^+$: 184.0733, found: 184.0740.



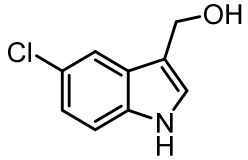
(4-Methoxy-1H-indol-3-yl)methanol (1h) was prepared according to the GP 1 and 2 as green liquid in 50% yield (778.8 mg) from 4-methoxy-1H-indole substrate (1.3 g, 8.8 mmol).
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.84 (s, 1H), 7.12 – 7.06 (m, 1H), 7.01 – 6.91 (m, 2H), 6.44 (dt, J = 9.5, 4.7 Hz, 1H), 4.76 (d, J = 5.6 Hz, 2H), 4.46 (t, J = 5.6 Hz, 1H), 3.83 (s, 3H).
The **^{1}H NMR** spectrum is identical to ref. 3.



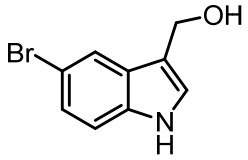
(6-Methoxy-1H-indol-3-yl)methanol (1i) was prepared according to the GP 1 and 2 as yellow solid in 48% yield (645.7 mg) from 6-methoxy-1H-indole substrate (1.1 g, 7.6 mmol).
Melting Point: 140–142 °C.
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.67 (s, 1H), 7.49 (d, J = 8.6 Hz, 1H), 7.11 (d, J = 2.1 Hz, 1H), 6.88 (d, J = 2.2 Hz, 1H), 6.67 (dd, J = 8.6, 2.3 Hz, 1H), 4.75 (s, 1H), 4.63 (s, 2H), 3.76 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 155.6, 137.2, 121.9, 121.1, 119.5, 116.0, 108.6, 94.4, 55.6, 55.1.
HRMS (ESI–TOF) m/z: calcd. for $C_{10}H_{11}NO_2$ $[M+Na]^+$: 200.0682, found: 200.0690.



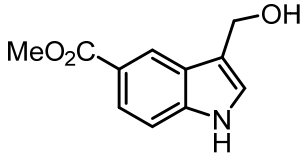
(4-Fluoro-1H-indol-3-yl)methanol (1j) was prepared according to the GP 1 and 2 as green solid in 60% yield (732.6 mg) from 4-fluoro-1H-indole substrate (1.0 g, 7.4 mmol).
Melting Point: 94–97 °C.
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.18 (s, 1H), 7.26 (d, J = 1.1 Hz, 1H), 7.18 (d, J = 8.1 Hz, 1H), 7.03 (td, J = 7.9, 5.3 Hz, 1H), 6.72 (dd, J = 11.1, 7.8 Hz, 1H), 4.79 (s, 1H), 4.70 (s, 2H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 156.4 (d, $J_{C\text{-}F}$ = 224.4 Hz), 139.3 (d, $J_{C\text{-}F}$ = 12.4 Hz), 123.9, 121.5 (d, $J_{C\text{-}F}$ = 7.6 Hz), 114.8 (d, $J_{C\text{-}F}$ = 21.2 Hz), 114.5, 107.9 (d, $J_{C\text{-}F}$ = 3.3 Hz), 103.5 (d, $J_{C\text{-}F}$ = 19.2 Hz), 56.0.
^{19}F NMR (376 MHz, DMSO-d_6) δ –124.0.
HRMS (ESI–TOF) m/z: calcd. for C_9H_8FNO $[M+Na]^+$: 188.0482, found: 188.0487.



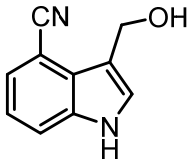
(5-Chloro-1H-indol-3-yl)methanol (1k) was prepared according to the GP 1 and 2 as green solid in 74% yield (1.0 g) from 5-chloro-1H-indole substrate (1.1 g, 7.5 mmol).
Melting Point: 102–103 °C.
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.07 (s, 1H), 7.64 (d, J = 1.9 Hz, 1H), 7.37 (d, J = 8.6 Hz, 1H), 7.32 (d, J = 2.2 Hz, 1H), 7.08 (dd, J = 8.6, 2.0 Hz, 1H), 4.83 (s, 1H), 4.62 (s, 2H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 134.9, 127.8, 125.1, 123.1, 120.9, 118.3, 115.9, 112.9, 55.2.
HRMS (ESI–TOF) m/z: calcd. for C_9H_8ClNO $[M+H]^+$: 182.0367, found: 182.0370.



(5-Bromo-1H-indol-3-yl)methanol (1l) was prepared according to the GP 1 and 2 as brown solid in 65% yield (263.3 mg) from 5-bromo-1H-indole substrate (352.8 mg, 1.8 mmol).
Melting Point: 124–125 °C.
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.08 (s, 1H), 7.79 (s, 1H), 7.40 – 7.25 (m, 2H), 7.19 (d, J = 8.0 Hz, 1H), 4.84 (s, 1H), 4.62 (s, 2H).
The **^{1}H NMR** spectrum is identical to ref. 4.



Methyl 3-(hydroxymethyl)-1H-indole-5-carboxylate (1m) was prepared according to the GP 1 and 2 as white solid in 25% yield (143.5 mg) from methyl 1H-indole-5-carboxylate substrate (500.0 mg, 2.8 mmol).
Melting Point: 160–161 °C.
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.29 (s, 1H), 8.36 (s, 1H), 7.74 (d, J = 8.5 Hz, 1H), 7.44 (d, J = 8.6 Hz, 1H), 7.37 (s, 1H), 4.92 (s, 1H), 4.68 (s, 2H), 3.85 (s, 3H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 167.4, 139.1, 126.3, 125.1, 122.1, 121.8, 119.9, 117.5, 111.3, 55.3, 51.6.
HRMS (ESI–TOF) m/z: calcd for $C_{11}H_{11}NO_3$ $[M+H]^+$: 206.0812, found: 206.0817



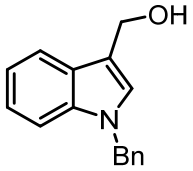
3-(Hydroxymethyl)-1H-indole-4-carbonitrile (1n) was prepared according to the GP 1 and 2 as green solid in 22% yield (181.6 mg) from 1H-indole-4-carbonitrile substrate (680.0 mg, 4.8 mmol).

Melting Point: 150–151 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.55 (s, 1H), 7.72 (d, J = 8.2 Hz, 1H), 7.55 (s, 1H), 7.48 (d, J = 7.3 Hz, 1H), 7.21 (t, J = 7.8 Hz, 1H), 4.85 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 136.6, 127.5, 125.5, 125.3, 120.9, 119.3, 116.9, 115.6, 100.6, 54.7.

HRMS (ESI–TOF) m/z: calcd for $C_{10}H_8N_2O$ $[M+H]^+$: 173.0709, found: 173.0710.

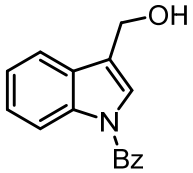


(1-Benzyl-1H-indol-3-yl)methanol (1o) was prepared according to the GP 1 and 2 as brown solid in 38% yield (432.3 mg) from 1-benzyl-1H-indole substrate (1.0 g, 4.8 mmol).

Melting Point: 92–94 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.70 (m, 1H), 7.36 – 7.27 (m, 3H), 7.25 – 7.05 (m, 6H), 5.28 (d, J = 16.2 Hz, 2H), 4.90 (d, J = 10.7 Hz, 2H).

The **^{1}H NMR** spectrum is identical to ref. 5.

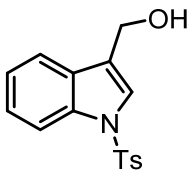


(3-(Hydroxymethyl)-1H-indol-1-yl)(phenyl)methanone (1p) was prepared according to the GP 2 as yellow oil in 81% yield (1.4 g) from 1-benzoyl-1H-indole-3-carbaldehyde[12] substrate (1.0 g, 7.0 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 7.9 Hz, 1H), 7.62 – 7.45 (m, 4H), 7.38 (t, J = 6.8 Hz, 2H), 7.25 (dt, J = 14.0, 6.8 Hz, 2H), 7.14 (d, J = 7.1 Hz, 1H), 4.68 (s, 2H), 2.11 (s, 1H).

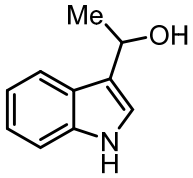
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 136.5, 134.3, 131.9, 129.4, 129.0, 128.5, 125.3, 125.0, 123.9, 121.8, 119.2, 116.5, 57.0.

HRMS (ESI–TOF) m/z: calcd for $C_{16}H_{13}NO_2$ $[M+Na]^+$: 274.0838, found: 274.0846.

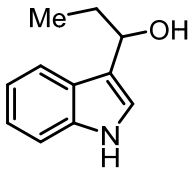


(1-Tosyl-1H-indol-3-yl)methanol (1q) was prepared according to the GP 2 as pink solid in 44%

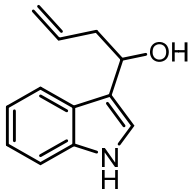
yield (927.1 mg) from 1-tosyl-1H-indole-3-carbaldehyde[13] substrate (1.0 g, 7.0 mmol).
Melting Point: 112–114 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.74 – 7.69 (m, 2H), 7.55 – 7.46 (m, 2H), 7.32 (dd, *J* = 11.4, 4.1 Hz, 1H), 7.18 (dd, *J* = 9.5, 5.2 Hz, 1H), 7.07 (d, *J* = 2.1 Hz, 2H), 4.68 (s, 2H), 2.19 (s, 3H).
The **^{1}H NMR** spectrum is identical to ref. 6.



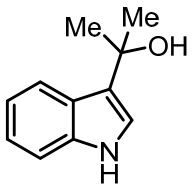
1-(1H-indol-3-yl)ethan-1-ol (1r) was prepared according to the GP 3 as green liquid in 65% yield (366.3 mg) from 1H-indole-3-carbaldehyde substrate (507.0 mg, 3.5 mmol) with MeMgBr.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.13 (dd, *J* = 13.0, 5.2 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.99 (s, 1H), 5.15 (q, *J* = 6.4 Hz, 1H), 1.88 (s, 1H), 1.58 (d, *J* = 6.5 Hz, 3H).
The **^{1}H NMR** spectrum is identical to ref. 7.



1-(1H-Indol-3-yl)propan-1-ol (1s) was prepared according to the GP 3 as green oil in 94% yield (329.0 mg) from 1H-indole-3-carbaldehyde substrate (300.0 mg, 2.0 mmol) with EtMgBr.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.97 (s, 1H), 4.83 (t, *J* = 6.7 Hz, 1H), 1.94 – 1.89 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 125.7, 122.2, 121.4, 119.6, 119.5, 119.4, 111.3, 69.9, 30.4, 10.5.
HRMS (ESI–TOF) m/z: calcd for $C_{11}H_{13}NO$ $[M+Na]^+$: 198.0889, found: 198.0892.



1-(1H-indol-3-yl)but-3-en-1-ol (1t) was prepared according to the GP 3 as brown liquid in 37% yield (138.4 mg) from 1H-indole-3-carbaldehyde substrate substrate (300.0 mg, 2.0 mmol) with allylMgBr.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.19 – 7.10 (m, 1H), 7.10 – 7.03 (m, 2H), 5.90 – 5.75 (m, 1H), 5.12 – 4.99 (m, 2H), 2.67 (dd, *J* = 9.0, 4.3 Hz, 2H), 1.92 (s, 1H).
The **^{1}H NMR** spectrum is identical to ref. 8.



2-(1H-Indol-3-yl)propan-2-ol (1u) was prepared according to the GP 3 as gray oil in 83% yield (290.5 mg) from 1-(1H-indol-3-yl)ethan-1-one substrate (318.0 mg, 2.0 mmol) with MeMgBr.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.19 (dt, *J* = 15.0, 7.2 Hz, 2H), 7.06 (d, *J* = 2.3 Hz, 1H), 2.03 (s, 1H), 1.76 (s, 6H).

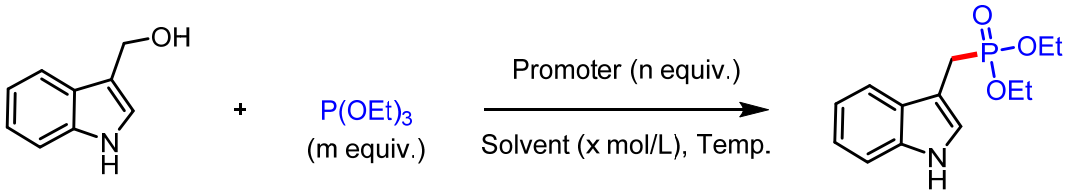
^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 125.1, 124.5, 121.9, 121.0, 119.8, 119.4, 111.3, 70.4, 30.9.

HRMS (ESI–TOF) m/z: calcd for $C_{11}H_{13}NO$ $[M+Na]^+$: 198.0889, found: 198.0893.

3. Scope and generality studies

3.1 Optimization of the reaction conditions[a]

Table S1:



1a **2a** **3aa**

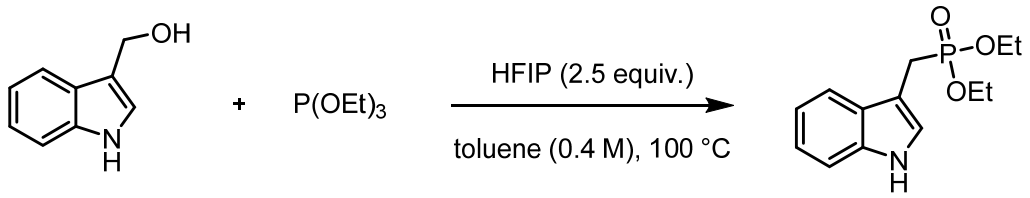
Entry	Promoter	n	Solvent	x	m	Temp. (°C)	Yield(%)[b]
Screening solvent							
1	HFIP	2.5	DMF	0.2	2.0	100	N.R.
2	HFIP	2.5	THF	0.2	2.0	100	62
3	HFIP	2.5	EtOAc	0.2	2.0	100	77
4	HFIP	2.5	o-xylene	0.2	2.0	100	74
5	HFIP	2.5	DME	0.2	2.0	100	N.R.
6	HFIP	2.5	o-DCB	0.2	2.0	100	75
7	HFIP	2.5	DMSO	0.2	2.0	100	49
8	HFIP	2.5	toluene	0.2	2.0	100	85
Screening concentration (x mol/L)							
9	HFIP	2.5	toluene	0.1	2.0	100	80
10	HFIP	2.5	toluene	0.3	2.0	100	88
11	HFIP	2.5	toluene	0.4	2.0	100	91
12	HFIP	2.5	toluene	0.5	2.0	100	89
Screening temperature							
13	HFIP	2.5	toluene	0.4	2.0	130 (reflux)	73
14	HFIP	2.5	toluene	0.4	2.0	90	66
Screening other acid promoters							
15	TFA	2.5	toluene	0.4	2.0	100	Trace
16	AcOH	2.5	toluene	0.4	2.0	100	22

17	$PhCO_2H$	2.5	toluene	0.4	2.0	100	40
18	MsOH	2.5	toluene	0.4	2.0	100	Trace
19	TfOH	2.5	toluene	0.4	2.0	100	Trace
20	TsOH	2.5	toluene	0.4	2.0	100	Trace
21	CSA	2.5	toluene	0.4	2.0	100	Trace
22	HCl	2.5	toluene	0.4	2.0	100	N.R.
23	HI	2.5	toluene	0.4	2.0	100	Trace
Screening HFIP equivalence (n)							
24	HFIP	1.0	toluene	0.4	2.0	100	78
25	HFIP	2.5	toluene	0.4	2.0	100	89
26	HFIP	3.0	toluene	0.4	2.0	100	69
Screening **2a** stoichiometry (m)							
27	HFIP	2.5	toluene	0.4	1.0	100	50
28	HFIP	2.5	toluene	0.4	1.5	100	66
29	HFIP	2.5	toluene	0.4	2.5	100	88
30	HFIP	2.5	toluene	0.4	3.0	100	85

[a]Reaction conditions: **1a** (0.2 mmol) and **2a** (m equiv.) were dissolved in solvent, promoter (n equiv.) was added, and the mixture was heated and monitored by TLC until full consumption of **1a**. [b]Isolated yield. N.R. = no reaction.

3.2 Scope study

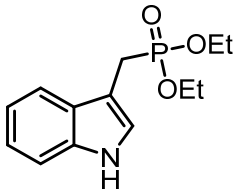
Standard conditions of the HFIP-promoted phosphorylation reaction using **3aa** as an example from substrates **1a** and **2a**



1a **2a** **3aa**

To a solution of HFIP (84 mg, 2.5 equiv.) in toluene (0.5 mL, 0.4 M) was added **1a** (29.4 mg, 0.2 mmol) and **2a** (69.6 mg, 2 equiv.). Then the mixture was stirred at 100 ºC about 20 h, and monitored by TLC. The crude mixture was purified by column chromatography on silica gel (PE/EtOAc = 1:1-1:5) to get product **3aa**.

All the phosphonate products are prepared according to the above-mentioned standard conditions. The reactions were monitored by thin-layer chromatography (TLC) to reach the full consumption of indole substrates.



Diethyl ((1H-indol-3-yl)methyl)phosphonate (3aa) was prepared according to the standard conditions as brown solid in 91% yield (51.1 mg) from substrate **1a** (29.4 mg, 0.2 mmol) for 17 h.

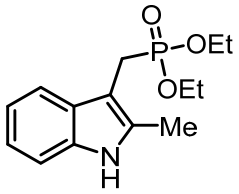
Melting Point: 54–56 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.19 – 7.08 (m, 2H), 7.00 (s, 1H), 4.12 – 3.91 (m, 4H), 3.31 (d, *J* = 20.0 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 127.3 (d, $J_{C\text{-}P}$ = 5.8 Hz), 124.1 (d, $J_{C\text{-}P}$ = 7.6 Hz), 121.6, 119.1, 118.6, 111.4, 104.0, 62.1 (d, $J_{C\text{-}P}$ = 6.9 Hz), 23.0 (d, $J_{C\text{-}P}$ = 143.6 Hz), 16.3 (d, $J_{C\text{-}P}$ = 6.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.1.

The NMR spectra of **3aa** are identical to ref. 14



Diethyl ((2-methyl-1H-indol-3-yl)methyl)phosphonate (3ba) was prepared according to the standard conditions as yellow solid in 82% yield (46.0 mg) from substrate **1b** (32.3 mg, 0.2 mmol) for 15 h.

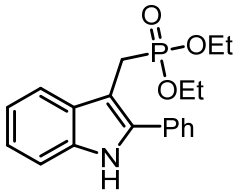
Melting Point: 115–116 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 21.9 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.24 – 7.18 (m, 1H), 7.11 – 7.02 (m, 2H), 4.10 – 3.86 (m, 4H), 3.23 (d, *J* = 19.5 Hz, 2H), 2.27 (t, *J* = 3.7 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.2, 133.3, 128.4, 120.8, 118.6 (d, $J_{C\text{-}P}$ = 99.6 Hz), 118.1, 110.3, 100.0, 61.9 (d, $J_{C\text{-}P}$ = 6.9 Hz), 22.7 (d, $J_{C\text{-}P}$ = 144.8 Hz), 16.4 (d, $J_{C\text{-}P}$ = 6.0 Hz), 11.6.

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.7.

HRMS (ESI–TOF) m/z: calcd for $C_{14}H_{20}NO_3P$ $[M+H]^+$: 282.1254, found: 282.1260.



Diethyl ((2-phenyl-1H-indol-3-yl)methyl)phosphonate (3ca) was prepared according to the standard conditions as green solid in 77% yield (52.5 mg) from substrate **1c** (44.6 mg, 0.2 mmol) for 22 h.

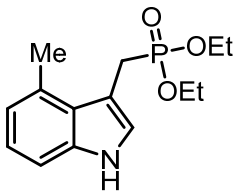
Melting Point: 126–127 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 29.2 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 3H), 7.43 (t, *J* = 6.8 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.16 (dt, *J* = 18.9, 7.1 Hz, 2H), 4.09 – 3.82 (m, 4H), 3.41 (d, *J* = 20.3 Hz, 2H), 1.19 (t, *J* = 7.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 135.8, 132.5, 128.8, 128.3, 127.8, 122.3, 120.0, 119.6, 110.8, 102.4, 99.9, 62.0 (d, $J_{C\text{-}P}$ = 6.8 Hz), 23.6 (d, $J_{C\text{-}P}$ = 145.4 Hz), 16.3 (d, $J_{C\text{-}P}$ = 6.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.5.

HRMS (ESI–TOF) m/z: calcd for $C_{19}H_{22}NO_3P$ $[M+H]^+$: 344.1410, found: 344.1419.



Diethyl ((4-methyl-1H-indol-3-yl)methyl)phosphonate (3da) was prepared according to the standard conditions as brown solid in 80% yield (44.9 mg) from substrate **1d** (32.3 mg, 0.2 mmol) for 24 h.

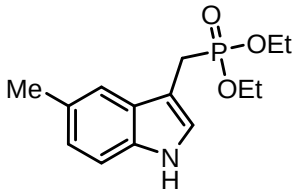
Melting Point: 148–150 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 7.19 (d, J = 8.1 Hz, 1H), 7.10 (s, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.81 (d, J = 7.0 Hz, 1H), 4.10 – 3.91 (m, 4H), 3.53 (d, J = 20.4 Hz, 2H), 2.75 (s, 3H), 1.21 (t, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 130.2, 125.6 (d, $J_{C\text{-}P}$ = 6.0 Hz), 124.5 (d, $J_{C\text{-}P}$ = 7.2 Hz), 121.7, 121.1, 109.6, 104.2, 62.1 (d, $J_{C\text{-}P}$ = 7.0 Hz), 24.7 (d, $J_{C\text{-}P}$ = 142.4 Hz), 20.2, 16.3 (d, $J_{C\text{-}P}$ = 5.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9.

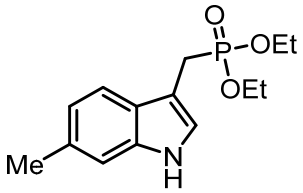
HRMS (ESI–TOF) m/z: calcd for $C_{14}H_{20}NO_3P$ $[M+H]^+$: 282.1254, found: 282.1260.



Diethyl ((5-methyl-1H-indol-3-yl)methyl)phosphonate (3ea) was prepared according to the standard conditions as brown oil in 76% yield (42.7 mg) from substrate **1e** (32.3 mg, 0.2 mmol) for 14 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.40 (s, 1H), 7.22 (d, J = 8.3 Hz, 1H), 7.00 (dd, J = 9.5, 5.6 Hz, 2H), 4.12 – 3.93 (m, 4H), 3.28 (d, J = 20.0 Hz, 2H), 2.45 (s, 3H), 1.23 (t, J = 7.1 Hz, 6H).

The **^{1}H NMR** spectrum is identical to ref. 15.



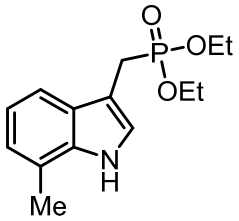
Diethyl ((6-methyl-1H-indol-3-yl)methyl)phosphonate (3fa) was prepared according to the standard conditions as yellow oil in 80% yield (44.8 mg) from substrate **1f** (32.3 mg, 0.2 mmol) for 29 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.12 (s, 1H), 7.00 (s, 1H), 6.94 (d, J = 8.1 Hz, 1H), 4.10 – 3.93 (m, 4H), 3.28 (d, J = 20.1 Hz, 2H), 2.43 (s, 3H), 1.23 (t, J = 7.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 131.5, 125.3, 123.2 (d, $J_{C\text{-}P}$ = 7.5 Hz), 121.1, 118.3, 111.2, 104.1, 62.0 (d, $J_{C\text{-}P}$ = 6.8 Hz), 23.1 (d, $J_{C\text{-}P}$ = 143.4 Hz), 21.6, 16.4 (d, $J_{C\text{-}P}$ = 6.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.9.

HRMS (ESI–TOF) m/z: calcd for $C_{14}H_{20}NO_3P$ $[M+H]^+$: 282.1254, found: 282.1261.



Diethyl ((7-methyl-1H-indol-3-yl)methyl)phosphonate (3ga) was prepared according to the standard conditions as yellow solid in 81% yield (45.8 mg) from substrate **1g** (32.3 mg, 0.2 mmol) for 29 h.

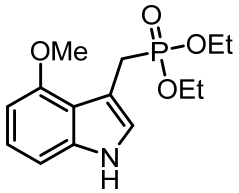
Melting Point: 111–113 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.10 – 7.02 (m, 2H), 6.97 (d, J = 7.0 Hz, 1H), 4.11 – 3.93 (m, 4H), 3.31 (d, J = 20.1 Hz, 2H), 2.48 (s, 3H), 1.24 (t, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.7, 126.9 (d, J_{C-P} = 6.1 Hz), 123.9 (d, J_{C-P} = 7.5 Hz), 122.2, 120.7, 119.4, 116.2, 104.4 (d, J_{C-P} = 9.3 Hz), 62.0 (d, J_{C-P} = 6.9 Hz), 23.0 (d, J_{C-P} = 144.4 Hz), 16.5, 16.3 (d, J_{C-P} = 5.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0.

HRMS (ESI–TOF) m/z: calcd for $C_{14}H_{20}NO_3P$ $[M+H]^+$: 282.1254, found: 282.1260.



Diethyl ((4-methoxy-1H-indol-3-yl)methyl)phosphonate (3ha) was prepared according to the standard conditions as brown solid in 99% yield (60.4 mg) from substrate **1h** (35.4 mg, 0.2 mmol) for 28 h.

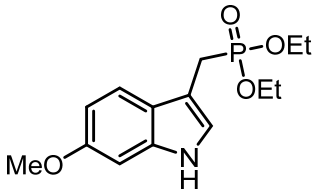
Melting Point: 131–132 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.07 (s, 1H), 7.03 (d, J = 7.9 Hz, 1H), 6.95 (d, J = 7.8 Hz, 1H), 6.46 (d, J = 7.7 Hz, 1H), 4.10 – 3.97 (m, 4H), 3.90 (s, 3H), 3.66 (d, J = 20.4 Hz, 2H), 1.21 (t, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 137.4, 122.6 (d, J_{C-P} = 6.5 Hz), 122.3, 117.1 (d, J_{C-P} = 7.1 Hz), 104.8, 104.1, 99.1, 61.7 (d, J_{C-P} = 6.7 Hz), 54.8, 23.5 (d, J_{C-P} = 140.4 Hz), 16.2 (d, J_{C-P} = 6.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.0.

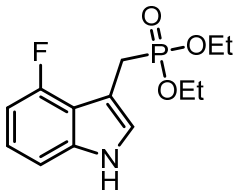
HRMS (ESI–TOF) m/z: calcd for $C_{14}H_{20}NO_4P$ $[M+H]^+$: 298.1203, found: 298.1211.



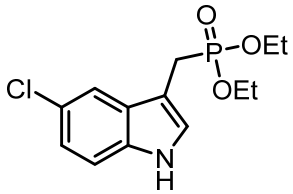
Diethyl ((6-methoxy-1H-indol-3-yl)methyl)phosphonate (3ia) was prepared according to the standard conditions as black solid in 99% yield (61.2 mg) from substrate **1i** (35.4 mg, 0.2 mmol) for 28 h.

Melting Point: 120–122 °C.

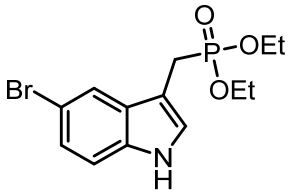
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 6.91 (s, 1H), 6.83 – 6.74 (m, 2H), 4.09 – 3.93 (m, 4H), 3.79 (s, 3H), 3.26 (d, *J* = 20.1 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 136.8, 122.7 (d, J_{C-P} = 8.2 Hz), 121.8 (d, J_{C-P} = 5.6 Hz), 119.3, 109.4, 104.0, 94.6, 62.1 (d, J_{C-P} = 6.8 Hz), 55.5, 23.1 (d, J_{C-P} = 144.4 Hz), 16.4 (d, J_{C-P} = 5.9 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 28.1.
HRMS (ESI–TOF) m/z: calcd for $C_{14}H_{20}NO_4P$ $[M+H]^+$: 298.1203, found: 298.1209.



Diethyl ((4-fluoro-1H-indol-3-yl)methyl)phosphonate (3ja) was prepared according to the standard conditions as brown oil in 98% yield (55.9 mg) from substrate **1j** (33 mg, 0.2 mmol) for 26 h.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 7.01 (q, *J* = 8.2 Hz, 2H), 6.70 (dd, *J* = 11.2, 7.9 Hz, 1H), 4.11 – 3.97 (m, 4H), 3.47 (d, *J* = 20.3 Hz, 2H), 1.23 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 155.8, 138.8 (d, J_{C-F} = 11.1 Hz), 124.4 (d, J_{C-F} = 7.1 Hz), 122.0 (d, J_{C-F} = 7.9 Hz), 107.7 (d, J_{C-F} = 3.5 Hz), 104.2 (d, J_{C-F} = 19.4 Hz), 102.1 (d, J_{C-P} = 9.8 Hz), 62.1 (d, J_{C-P} = 6.9 Hz), 23.5 (d, J_{C-P} = 140.4 Hz), 16.3 (d, J_{C-P} = 6.0 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 28.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ -125.7.
HRMS (ESI–TOF) m/z: calcd for $C_{13}H_{17}FNO_3P$ $[M+H]^+$: 286.1003, found: 286.1007.



Diethyl ((5-chloro-1H-indol-3-yl)methyl)phosphonate (3ka) was prepared according to the standard conditions as yellow solid in 99% yield (63.2 mg) from substrate **1k** (36.2 mg, 0.2 mmol) for 26 h.
Melting Point: 71–73 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 7.57 (s, 1H), 7.19 (d, *J* = 8.6 Hz, 1H), 7.06 (d, *J* = 8.6 Hz, 1H), 6.89 (s, 1H), 4.13 – 3.94 (m, 4H), 3.23 (d, *J* = 19.9 Hz, 2H), 1.26 (t, *J* = 7.0 Hz, 6H).
The **^{1}H NMR** spectrum is identical to ref. 15.



Diethyl ((5-bromo-1H-indol-3-yl)methyl)phosphonate (3la) was prepared according to the standard conditions as yellow oil in 74% yield (51.1 mg) from substrate **1l** (45.0 mg, 0.2 mmol)

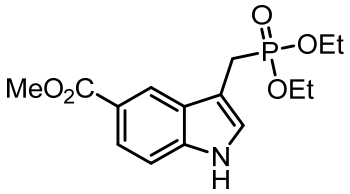
for 20 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 7.74 (s, 1H), 7.19 (dt, *J* = 15.3, 5.1 Hz, 2H), 6.92 (s, 1H), 4.12 – 3.96 (m, 4H), 3.23 (d, *J* = 20.0 Hz, 2H), 1.27 – 1.24 (t, 8H) (grease peak is included).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.8, 129.0, 125.3, 124.6, 121.4, 112.9, 112.5, 103.9, 62.2 (d, $J_{C\text{-}P}$ = 7.0 Hz), 23.1 (d, $J_{C\text{-}P}$ = 145.4 Hz), 16.4 (d, $J_{C\text{-}P}$ = 6.1 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.6.

HRMS (ESI–TOF) m/z: calcd for $C_{13}H_{17}BrNO_3P$ $[M+Na]^+$: 368.0022, found: 368.0031.



Methyl 3-((diethoxyphosphoryl)methyl)-1H-indole-5-carboxylate (3ma) was prepared according to the standard conditions as yellow solid in 99% yield (64.7 mg) from substrate **1m** (41.0 mg, 0.2 mmol) for 24 h.

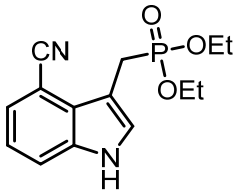
Melting Point: 102–104 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.32 (s, 1H), 7.74 (dd, *J* = 8.6, 1.4 Hz, 1H), 7.21 (s, 1H), 6.88 (d, *J* = 2.5 Hz, 1H), 4.03 – 3.90 (m, 4H), 3.84 (s, 3H), 3.23 (d, *J* = 20.1 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 138.7, 126.9, 125.5, 123.1, 121.9, 121.3, 111.1, 105.7, 62.2 (d, $J_{C\text{-}P}$ = 6.7 Hz), 51.8, 23.0 (d, $J_{C\text{-}P}$ = 144.4 Hz), 16.3 (d, $J_{C\text{-}P}$ = 6.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.7.

HRMS (ESI–TOF) m/z: calcd for $C_{15}H_{20}NO_5P$ $[M+Na]^+$: 348.0971, found:348.0978.



Diethyl ((4-cyano-1H-indol-3-yl)methyl)phosphonate (3na) was prepared according to the standard conditions as green solid in 64% yield (37.3 mg) from substrate **1n** (34.4 mg, 0.2 mmol) for 26 h.

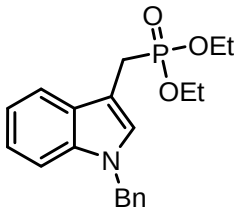
Melting Point: 159–161 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.40 (s, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.40 (d, *J* = 7.3 Hz, 1H), 7.14 (s, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 4.18 – 4.04 (m, 4H), 3.63 (d, *J* = 20.0 Hz, 2H), 1.26 (t, 8H) (grease peak is included).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 127.7 (d, $J_{C\text{-}P}$ = 6.4 Hz), 126.3, 126.2, 121.0, 119.4, 116.7, 103.8, 101.3, 62.5 (d, $J_{C\text{-}P}$ = 7.0 Hz), 21.9 (d, $J_{C\text{-}P}$ = 142.4 Hz), 16.3 (d, $J_{C\text{-}P}$ = 6.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 27.5.

HRMS (ESI–TOF) m/z: calcd for $C_{14}H_{17}N_2O_3P$ $[M+H]^+$: 293.1050, found: 293.1054.

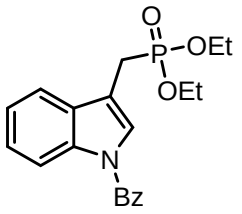


Diethyl ((1-benzyl-1H-indol-3-yl)methyl)phosphonate (3oa) was prepared according to the standard conditions as brown solid in 68% yield (48.6 mg) from substrate **1o** (47.4 mg, 0.2 mmol) for 22 h.

Melting Point: 66–68 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.09 (ddd, *J* = 22.5, 20.6, 6.2 Hz, 9H), 5.20 (s, 2H), 4.00 – 3.82 (m, 4H), 3.22 (d, *J* = 20.3 Hz, 2H), 1.12 (t, *J* = 7.0 Hz, 6H).

The **^{1}H NMR** spectrum is identical to ref. 15.



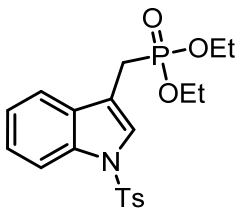
Diethyl ((1-benzoyl-1H-indol-3-yl)methyl)phosphonate (3pa) was prepared according to the standard conditions as yellow oil in 52% yield (38.4 mg) from substrate **1p** (50.4 mg, 0.2 mmol) for 17 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 2H), 7.61 (dd, *J* = 13.2, 7.4 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.43 – 7.32 (m, 3H), 4.09 – 3.96 (m, 4H), 3.20 (d, *J* = 21.1 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 136.0, 134.5, 131.9, 130.6, 129.1, 128.6, 126.3 (d, $J_{C\text{-}P}$ = 9.0 Hz), 125.3, 123.8, 119.1, 116.4, 111.9 (d, $J_{C\text{-}P}$ = 9.9 Hz), 62.2 (d, $J_{C\text{-}P}$ = 6.8 Hz), 22.9 (d, $J_{C\text{-}P}$ = 144.4 Hz), 16.3 (d, $J_{C\text{-}P}$ = 5.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 26.0.

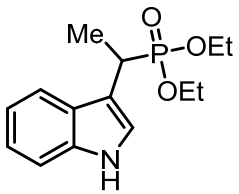
HRMS (ESI–TOF) m/z: calcd for $C_{20}H_{22}NO_4P$ $[M+H]^+$: 372.1359, found: 372.1364.



Diethyl ((1-tosyl-1H-indol-3-yl)methyl)phosphonate (3qa) was prepared according to the standard conditions as yellow oil in 58% yield (48.8 mg) from substrate **1q** (60.2 mg, 0.2 mmol) for 17 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.45 (m, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.21 – 7.14 (m, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 3.99 – 3.80 (m, 4H), 3.12 (d, *J* = 20.9 Hz, 2H), 2.24 (s, 3H), 1.10 (t, *J* = 7.0 Hz, 6H).

The **^{1}H NMR** spectrum is identical to ref. 16.



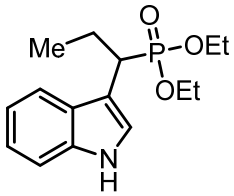
Diethyl (1-(1H-indol-3-yl)ethyl)phosphonate (3ra) was prepared according to the standard conditions as brown oil in 77% yield (43.1 mg) from substrate **1r** (32.2 mg, 0.2 mmol) for 17 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 – 8.94 (m, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.19 – 7.08 (m, 2H), 7.05 (s, 1H), 4.18 – 4.05 (m, 2H), 3.93 – 3.84 (m, 1H), 3.71 – 3.61 (m, 1H), 3.58 – 3.47 (m, 1H), 1.63 (dd, *J* = 18.2, 7.4 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.0, 126.9, 126.8, 123.2, 121.8, 119.1, 119.0, 111.4, 62.5 (d, $J_{C\text{-}P}$ = 7.0 Hz), 61.8 (d, $J_{C\text{-}P}$ = 7.5 Hz), 29.1 (d, $J_{C\text{-}P}$ = 143.4 Hz), 16.5 (d, $J_{C\text{-}P}$ = 5.9 Hz), 16.3 (d, $J_{C\text{-}P}$ = 5.6 Hz), 15.8 (d, $J_{C\text{-}P}$ = 3.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 31.3.

HRMS (ESI–TOF) m/z: calcd for $C_{14}H_{20}NO_3P$ $[M+H]^+$: 282.1254, found: 282.1261.



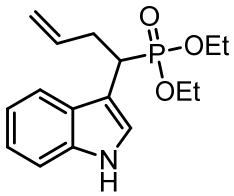
Diethyl (1-(1H-indol-3-yl)propyl)phosphonate (3sa) was prepared according to the standard conditions as green oil in 78% yield (46.1 mg) from substrate **1s** (35.0 mg, 0.2 mmol) for 22 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.14 – 7.07 (m, 2H), 4.18 – 4.04 (m, 2H), 3.91 – 3.80 (m, 1H), 3.66 – 3.55 (m, 1H), 3.32 – 3.23 (m, 1H), 2.26 – 2.17 (m, 1H), 2.05 – 1.94 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.99 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 127.7 (d, $J_{C\text{-}P}$ = 6.2 Hz), 123.5 (d, $J_{C\text{-}P}$ = 7.1 Hz), 121.7, 119.1, 118.9, 111.3, 109.5, 62.4 (d, $J_{C\text{-}P}$ = 7.1 Hz), 61.6 (d, $J_{C\text{-}P}$ = 7.5 Hz), 36.6 (d, $J_{C\text{-}P}$ = 141.4 Hz), 23.5, 16.4 (d, $J_{C\text{-}P}$ = 6.0 Hz), 16.2 (d, $J_{C\text{-}P}$ = 5.7 Hz), 12.6 (d, $J_{C\text{-}P}$ = 15.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 30.3.

HRMS (ESI–TOF) m/z: calcd for $C_{15}H_{22}NO_3P$ $[M+H]^+$: 296.1410, found: 296.1415.



Diethyl (1-(1H-indol-3-yl)but-3-en-1-yl)phosphonate (3ta) was prepared according to the standard conditions as brown solid in 99% yield (64.5 mg) from substrate **1t** (37.4 mg, 0.2 mmol) for 36 h.

Melting Point: 78–80 °C.

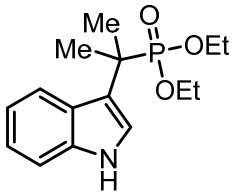
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.19 – 7.07 (m, 3H), 5.71 (m, 1H), 5.00 (dd, *J* = 17.0, 1.3 Hz, 1H), 4.87 (d, *J* = 10.1 Hz, 1H),

4.20 – 4.03 (m, 2H), 3.88 – 3.78 (m, 1H), 3.65 – 3.55 (m, 1H), 3.51 – 3.42 (m, 1H), 2.95 – 2.83 (m, 1H), 2.77 (dt, J = 10.5, 8.4 Hz, 1H), 1.32 (t, J = 7.1 Hz, 3H), 0.99 (t, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.0 (d, $J_{C\text{-}P}$ = 6.8 Hz), 135.8, 127.4 (d, $J_{C\text{-}P}$ = 5.8 Hz), 123.8 (d, $J_{C\text{-}P}$ = 6.9 Hz), 121.8, 119.2, 118.9, 116.4, 111.4, 109.2, 62.6 (d, $J_{C\text{-}P}$ = 7.1 Hz), 61.8 (d, $J_{C\text{-}P}$ = 7.4 Hz), 35.6, 34.3 (d, $J_{C\text{-}P}$ = 22.2 Hz), 16.4 (d, $J_{C\text{-}P}$ = 5.9 Hz), 16.2 (d, $J_{C\text{-}P}$ = 5.6 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 29.4.

HRMS (ESI–TOF) m/z: calcd for $C_{16}H_{22}NO_3P$ $[M+H]^+$: 308.1410, found: 308.1416.



Diethyl (2-(1H-indol-3-yl)propan-2-yl)phosphonate (3ua) was prepared according to the standard conditions as white solid in 77% yield (45.7 mg) from substrate **1u** (35.0 mg, 0.2 mmol) for 22 h.

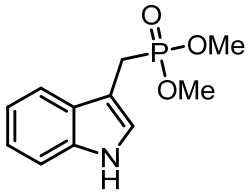
Melting Point: 135–137 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.99 (d, J = 7.9 Hz, 1H), 7.31 (d, J = 7.9 Hz, 1H), 7.10 (dt, J = 14.6, 7.0 Hz, 2H), 6.80 (s, 1H), 4.03 – 3.83 (m, 4H), 1.73 (d, J = 16.5 Hz, 6H), 1.23 (t, J = 7.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 126.1, 123.6 (d, $J_{C\text{-}P}$ = 8.2 Hz), 122.2, 121.2, 118.7, 115.8, 111.5, 62.2 (d, $J_{C\text{-}P}$ = 7.7 Hz), 36.2 (d, $J_{C\text{-}P}$ = 142.4 Hz), 24.2 (d, $J_{C\text{-}P}$ = 3.2 Hz), 16.4 (d, $J_{C\text{-}P}$ = 5.6 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 33.4.

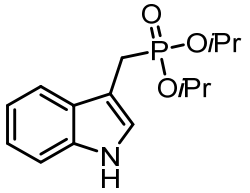
HRMS (ESI–TOF) m/z: calcd for $C_{15}H_{22}NO_3P$ $[M+H]^+$: 296.1410, found: 296.1415.



Dimethyl ((1H-indol-3-yl)methyl)phosphonate (3ab) was prepared according to the standard conditions as yellow solid in 86% yield (41.0 mg) from substrate **1a** (29.4 mg, 0.2 mmol) for 11 h.

Melting Point: 100–102 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 7.61 (d, J = 7.5 Hz, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.22 – 7.08 (m, 2H), 7.05 – 6.98 (m, 1H), 3.66 (d, J = 10.7 Hz, 6H), 3.33 (d, J = 20.1 Hz, 2H). The **^{1}H NMR** spectrum is identical to ref. 17.

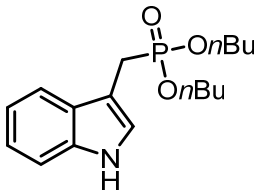


Diisopropyl ((1H-indol-3-yl)methyl)phosphonate (3ac) was prepared according to the standard conditions as yellow solid in 49% yield (28.9 mg) from substrate **1a** (29.4 mg, 0.2 mmol) for 11 h.

Melting Point: 107–109 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.22 – 7.07 (m, 3H), 4.80 – 4.48 (m, 2H), 3.26 (d, *J* = 20.2 Hz, 2H), 1.29 (d, *J* = 6.2 Hz, 6H), 1.11 (d, *J* = 6.2 Hz, 6H).

The **^{1}H NMR** spectrum is identical to ref. 17.

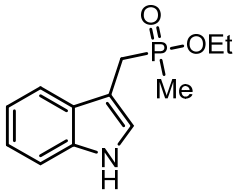


Dibutyl ((1H-indol-3-yl)methyl)phosphonate (3ad) was prepared according to the standard conditions as brown solid in 50% yield (32.0 mg) from substrate **1a** (29.4 mg, 0.2 mmol) for 18 h.

Melting Point: 70–72 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.20 – 7.06 (m, 2H), 7.03 (s, 1H), 4.04 – 3.86 (m, 4H), 3.31 (d, *J* = 20.1 Hz, 2H), 1.60 – 1.49 (m, 4H), 1.31 (td, *J* = 14.9, 7.4 Hz, 4H), 0.86 (t, *J* = 7.4 Hz, 6H).

The **^{1}H NMR** spectrum is identical to ref. 17.



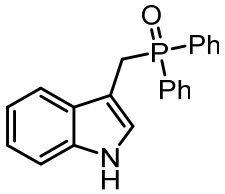
Ethyl ((1H-indol-3-yl)methyl)(methyl)phosphinate (3ae) was prepared according to the standard conditions as yellow liquid in 86% yield (40.8 mg) from substrate **1a** (29.4 mg, 0.2 mmol) for 13 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.15 (ddd, *J* = 14.0, 12.9, 7.1 Hz, 3H), 4.16 – 3.98 (m, 2H), 3.29 (dq, *J* = 15.6, 17.2 Hz, 2H), 1.38 (d, *J* = 13.6 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 127.2, 123.8 (d, $J_{C\text{-}P}$ = 6.7 Hz), 122.0, 119.5, 118.4, 111.4, 104.9, 60.4 (d, $J_{C\text{-}P}$ = 6.7 Hz), 26.9 (d, $J_{C\text{-}P}$ = 93.6 Hz), 16.7 (d, $J_{C\text{-}P}$ = 6.0 Hz), 13.3 (d, $J_{C\text{-}P}$ = 93.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$) δ 53.25.

HRMS (ESI–TOF) m/z: calcd for $C_{12}H_{16}NO_2P$ $[M+H]^+$: 238.0991, found: 238.0996.



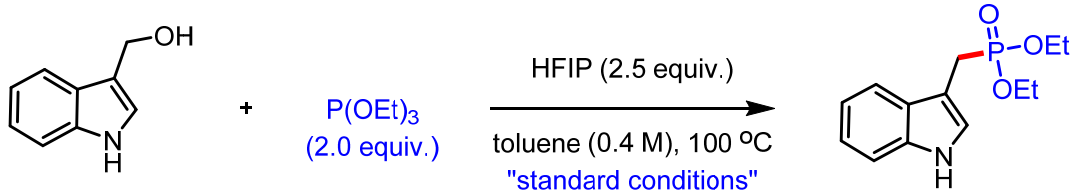
((1H-indol-3-yl)methyl)diphenylphosphine oxide (3af) was prepared according to the standard conditions as white solid in 75% yield (49.8 mg) from substrate **1a** (29.4 mg, 0.2 mmol) for 13 h.

Melting Point: 194–195 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.86 (s, 1H), 7.95 – 7.79 (m, 4H), 7.67 (t, J = 14.3 Hz, 1H), 7.54 – 7.39 (m, 6H), 7.27 (d, J = 8.0 Hz, 1H), 7.03 (dd, J = 16.3, 9.0 Hz, 2H), 6.92 (t, J = 7.4 Hz, 1H), 3.96 (d, J = 12.8 Hz, 2H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 135.6, 134.7, 133.7, 131.4, 130.8, 130.7, 128.5, 128.4, 128.0, 124.4 (d, $J_{C\text{-}P}$ = 6.4 Hz), 120.9, 119.2, 118.3, 111.2, 104.1, 104.0, 26.1 (d, $J_{C\text{-}P}$ = 70.7 Hz).
^{31}P NMR (162 MHz, DMSO-d_6) δ 27.50.
HRMS (ESI–TOF) m/z: calcd for $C_{21}H_{18}NOP$ $[M+H]^+$: 332.1199, found: 332.1207.

3.3 Generality and utilization studies

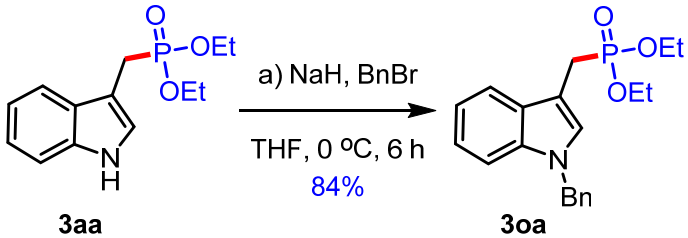
Gram-scale reaction:



1a 1.00 g | **2a** 2.90 g | **3aa** 1.67 g

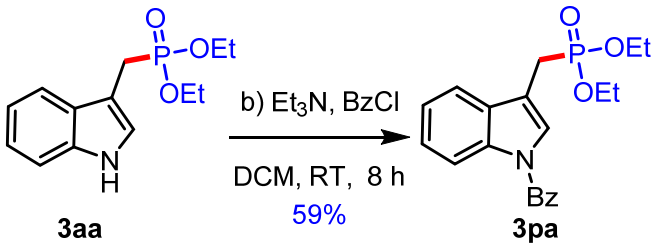
The reaction of **1a** (1.00 g) and **2a** (2.90 g) was conducted under standard conditions, and finally, **3aa** (1.67 g) was obtained in 89% yield.

Product derivatizations:



3aa **3oa**

In a 10 ml round-bottomed flask, to a solution of **3aa** (53.4 mg) in dry THF (1 ml) was added NaH (12 mg, 1.5 equiv.) at 0 °C. After stirring at room temperature for 30 min. BnBr (51.3 mg, 1.5 equiv.) was added at 0 °C. After stirring at room temperature overnight, the mixture was quenched by saturated NH_4Cl solution and extracted with EtOAc. The organic layer was dried over Na_2SO_4, removed under reduced pressure and purified by silica gel column chromatography (petroleum ester/ethyl acetate = 1:1) to give the desired product **3oa** (60.0 mg, 84%). The spectra were in accordance with the above-mentioned data.

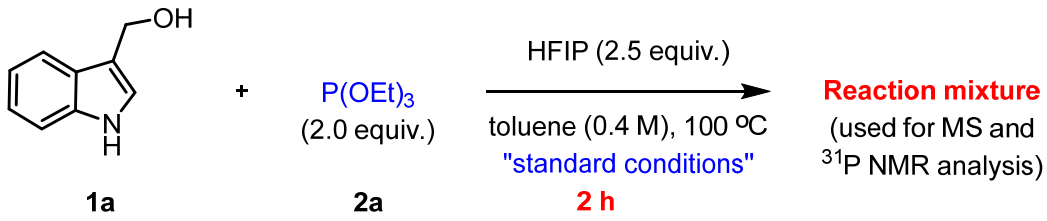


3aa **3pa**

In a 10 ml round-bottomed flask, to a solution of **3aa** (53.4 mg) in DCM (2 ml) was added Et_3N (40.4 mg, 2 equiv.) and BzCl (33.6 mg, 1.2 equiv.) under an argon atmosphere. After stirring at room temperature overnight, the mixture was quenched by saturated NH_4Cl solution and extracted with

EtOAc. The organic layer was dried over Na_2SO_4, removed under reduced pressure and purified by silica gel column chromatography (petroleum ester/ethyl acetate = 1:1) to give the desired product **3pa** (43.8 mg, 59%). The spectra were in accordance with the above-mentioned data.

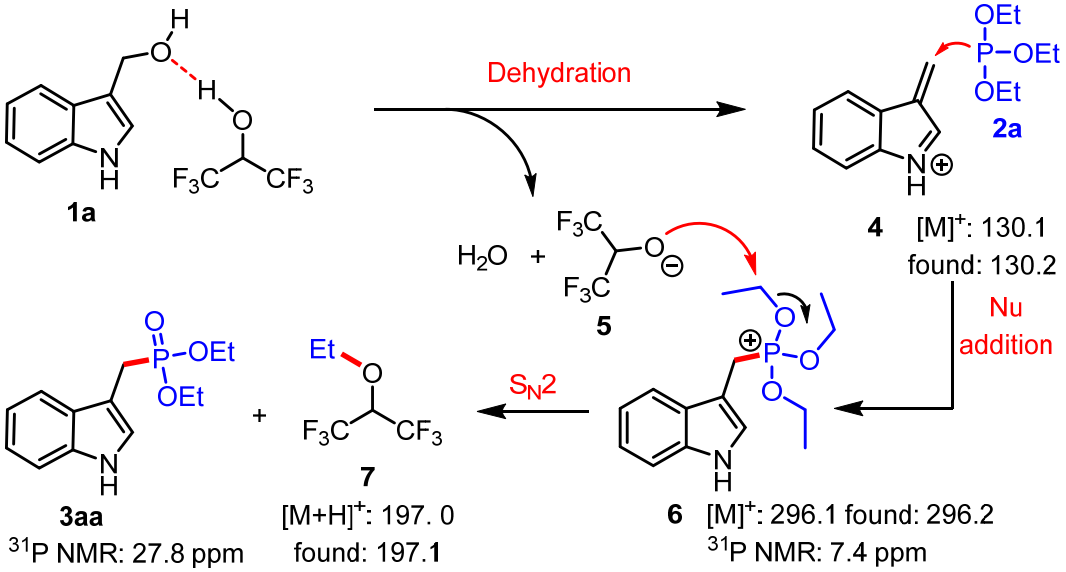
4. Mechanism study

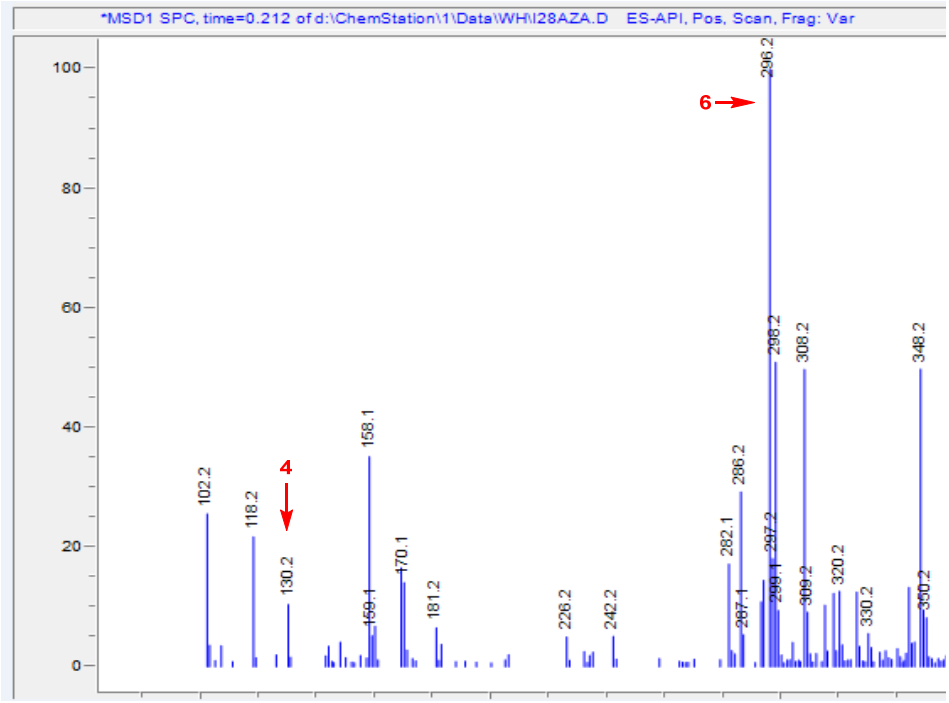


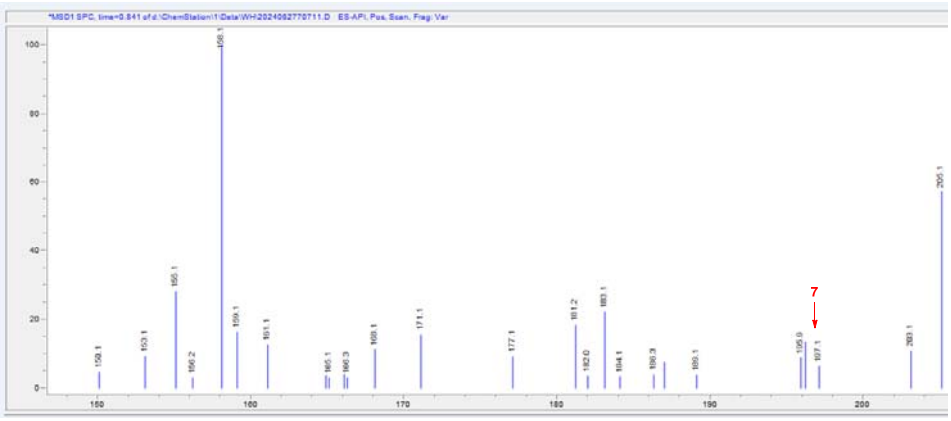
The standard reaction of **1a** and **2a** were reacted for 2 h and cooled to room temperature to stop the reaction. The starting materials were not fully consumed. The reaction mixture was used for Mass Spectroscopic analysis. The active intermediates (**4** and **6**) and by-product (**7**) in the proposed mechanism were detected in the Mass Spectrum.

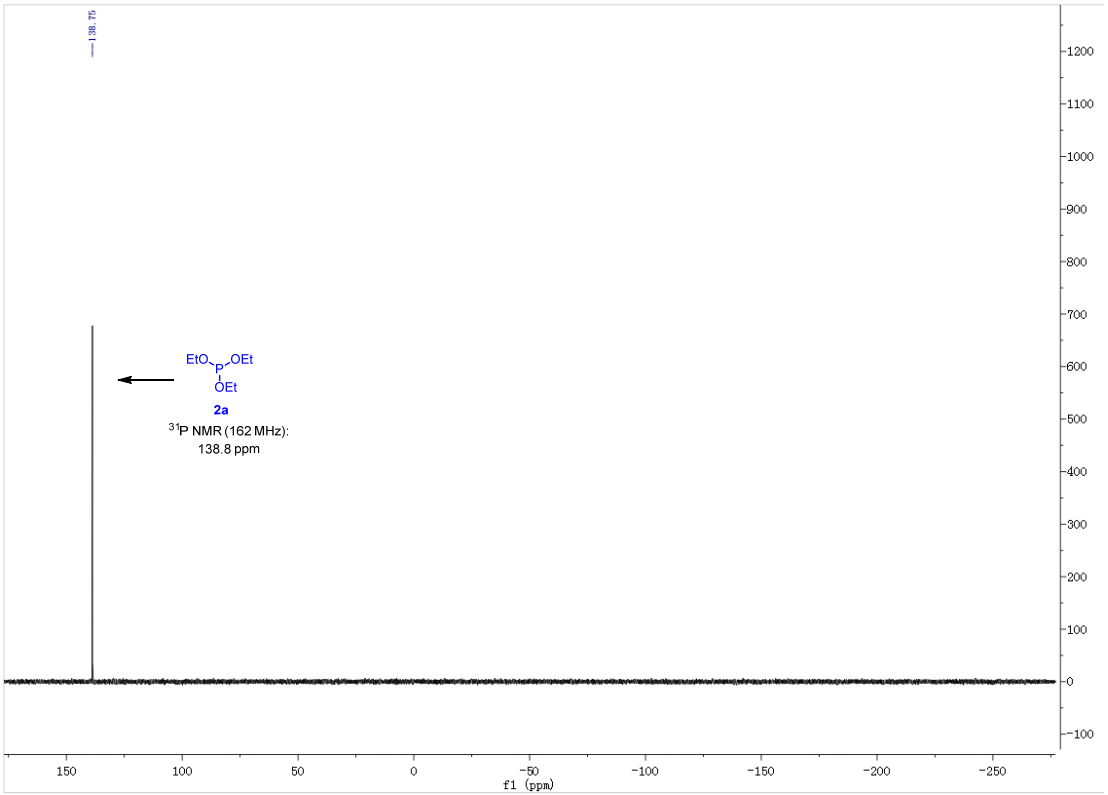
The ^{31}P NMR spectrum of **2a** showed 138.8 ppm peak, and that of **3aa** showed 27.8 ppm peak. The reaction mixture was evaporated and used for ^{31}P NMR analysis. The ^{31}P NMR spectrum of this mixture only showed the **3aa** and intermediate **6** peaks. Therefore, intermediate **6** was observed to be 7.4 ppm. Notably, the ^{31}P NMR spectrum of the reaction mixture did not show the **2a** peak as compound **2a** was removed out from the mixture when evaporated on oil pump.

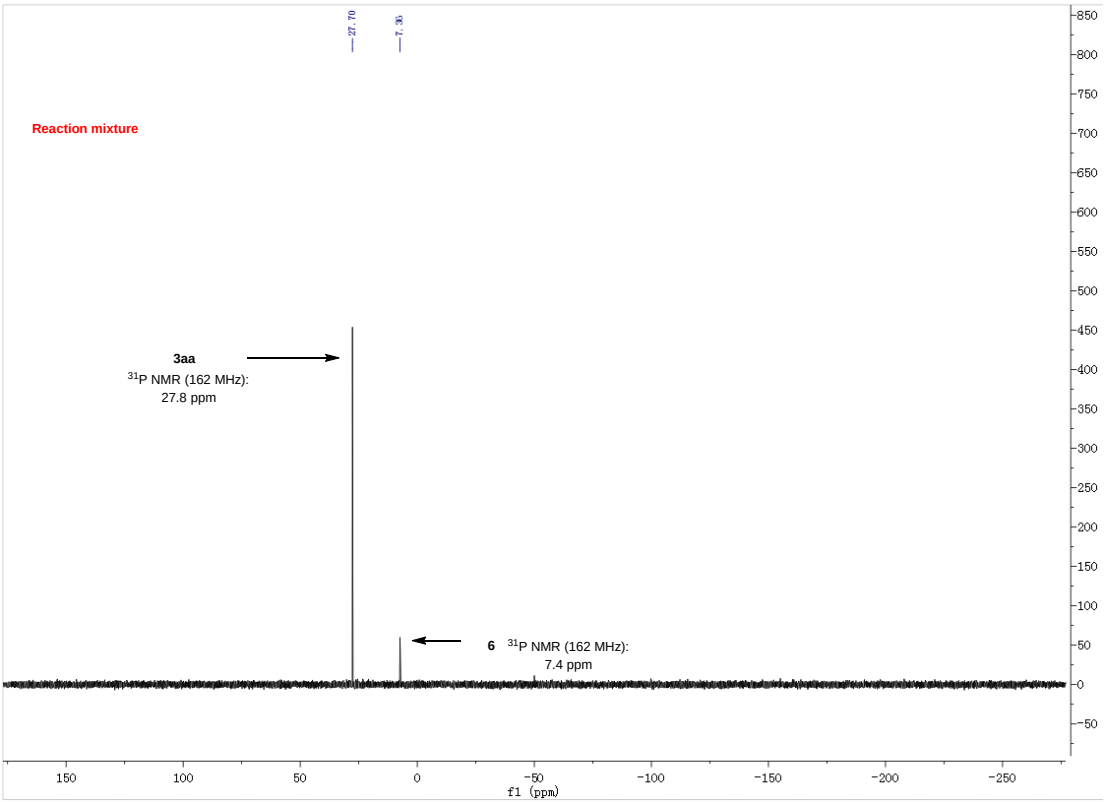
The key signal peaks in the Mass spectrum and ^{31}P NMR spectra are given below.




*MSD1 SPC, time=0.212 of d:\ChemStation\1\Data\WH\I28AZA.D ES-API, Pos, Scan, Frag: Var
100
80
60
40
20
0
296.2
6
298.2
308.2
348.2
158.1
4
102.2
118.2
130.2
286.2
282.1
297.2
299.1
287.1
309.2
320.2
330.2
350.2
470.1
181.2
226.2
242.2


7


138.75
EtO
P
OEt
OEt
2a
31P NMR (162 MHz):
138.8 ppm
f1 (ppm)


27.70
7.30
Reaction mixture
3aa
31P NMR (162 MHz):
27.8 ppm
6
31P NMR (162 MHz):
7.4 ppm
f1 (ppm)

5. References

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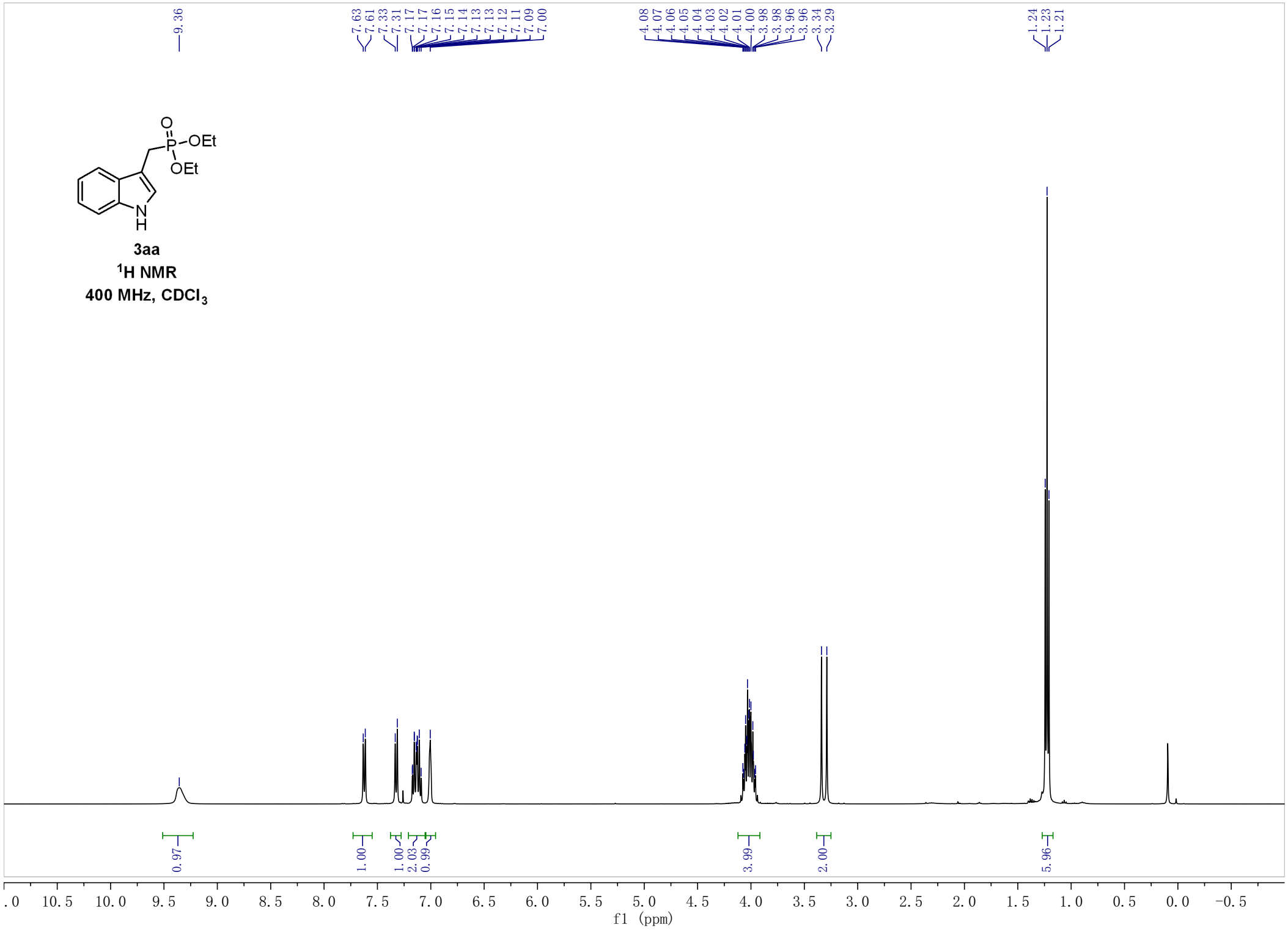
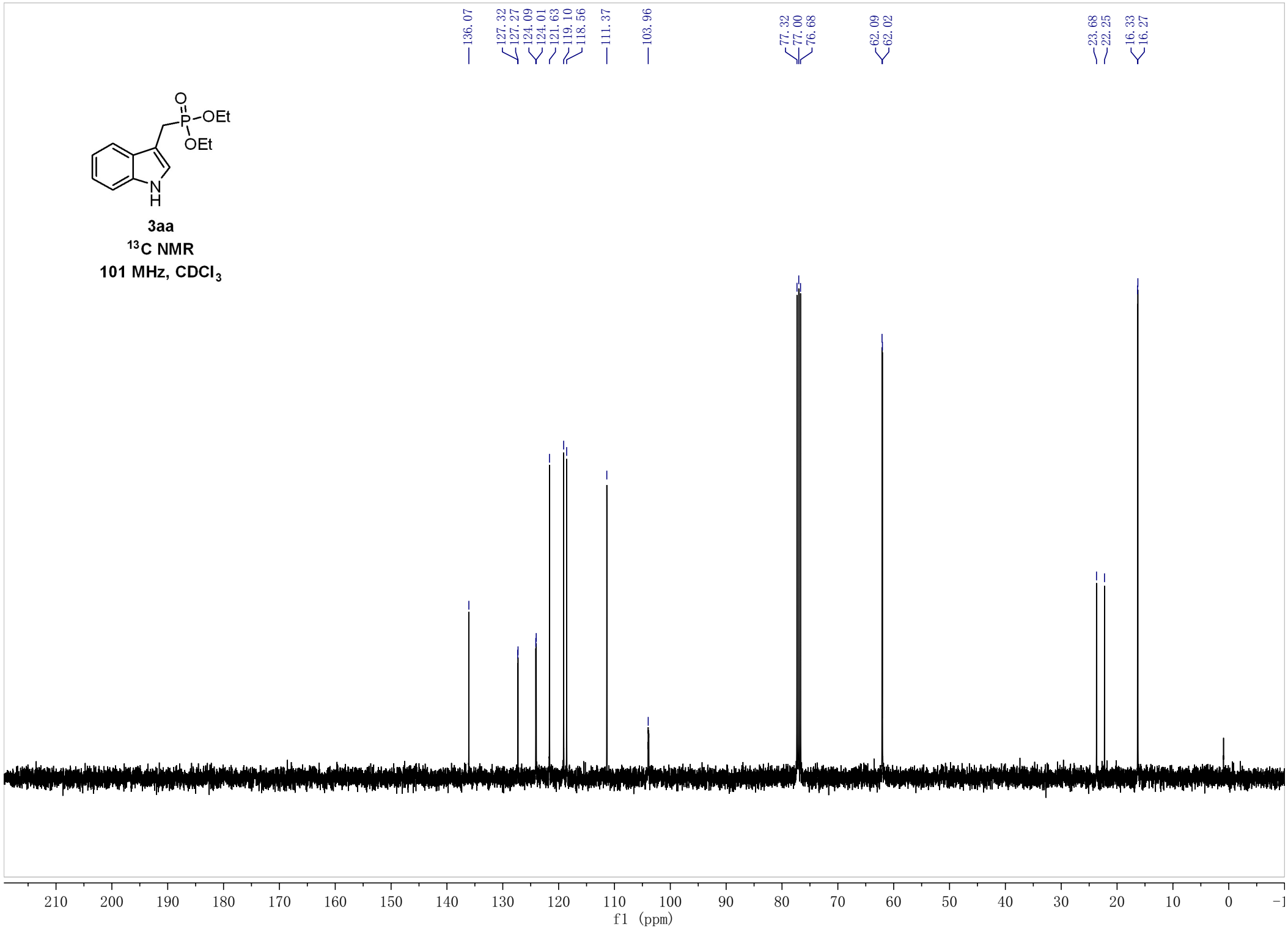
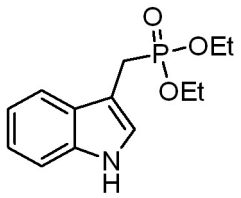
6. NMR spectra copies


9.36
7.63
7.61
7.33
7.31
7.17
7.16
7.15
7.14
7.13
7.12
7.11
7.09
7.00
4.08
4.07
4.06
4.05
4.04
4.03
4.02
4.01
4.00
3.98
3.98
3.96
3.96
3.34
3.29
1.24
1.23
1.21
O
P
OEt
OEt
N
H
3aa
1H NMR
400 MHz, CDCl3
0.97
1.00
1.00
2.03
0.99
3.99
2.00
5.96
f1 (ppm)


136.07
127.32
127.27
124.09
124.01
121.63
119.10
118.56
111.37
103.96
77.32
77.00
76.68
62.09
62.02
23.68
22.25
16.33
16.27
O
P
OEt
OEt
N
H
3aa
13C NMR
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)



3aa

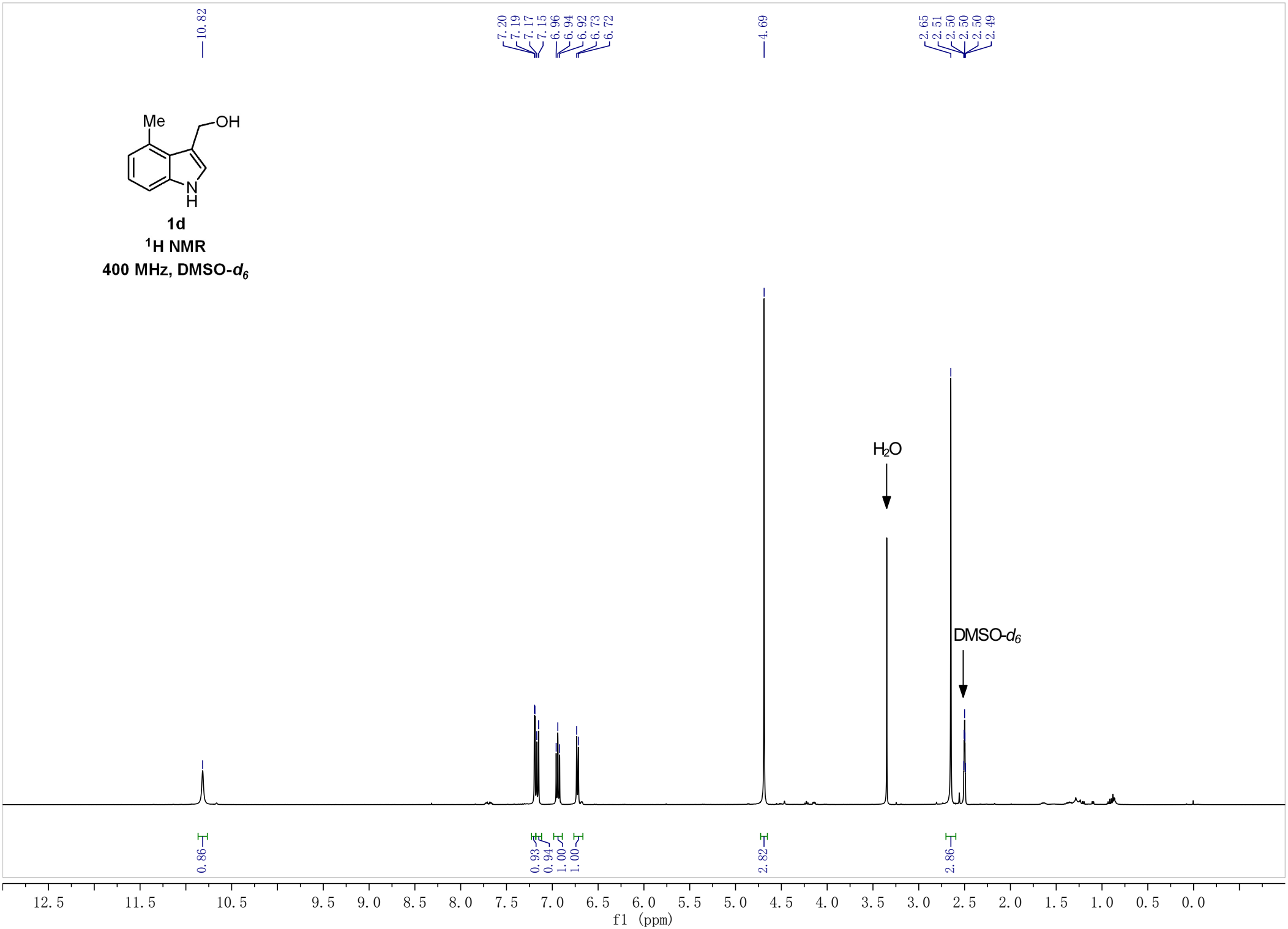
^{31}P NMR

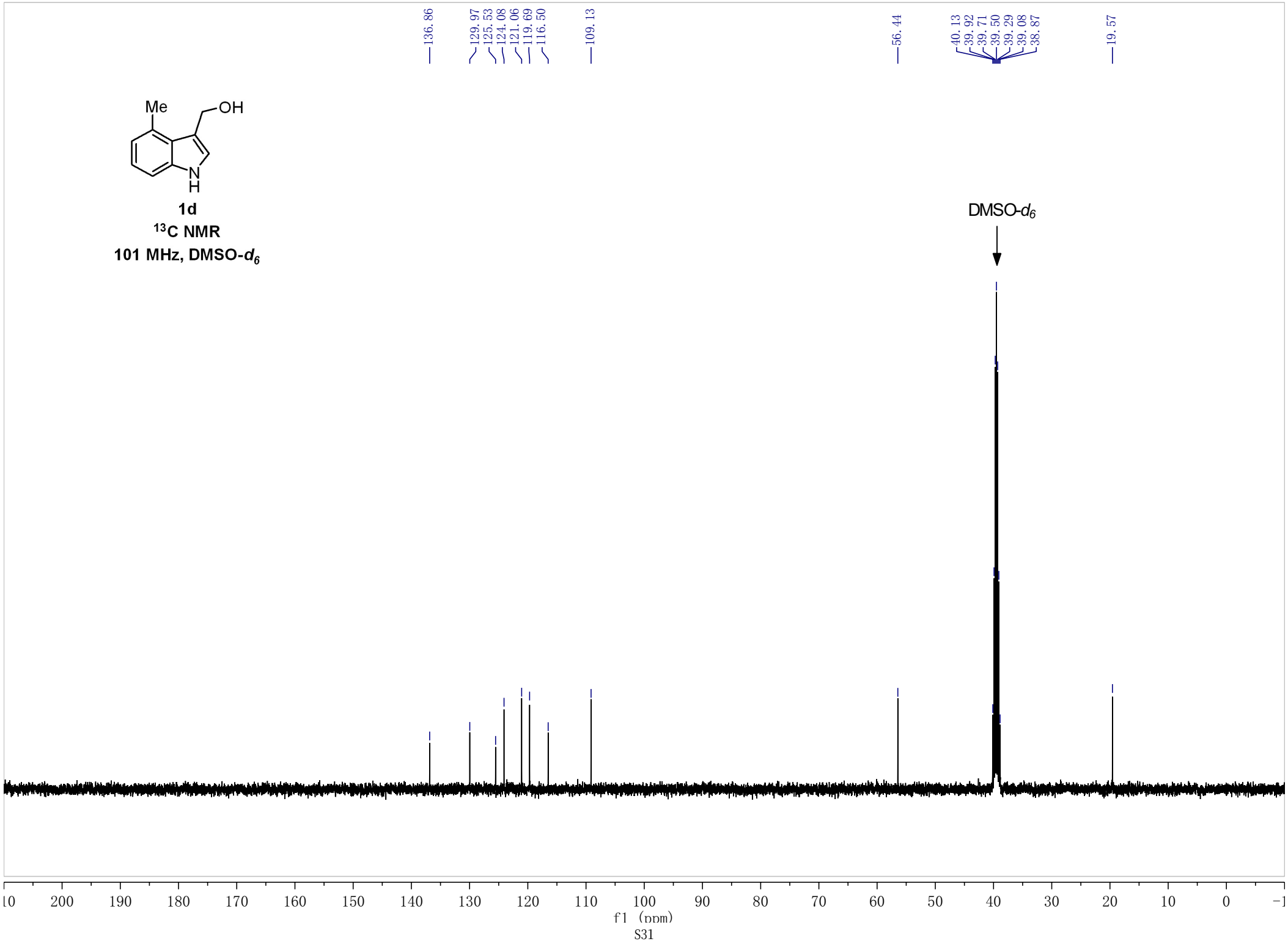
162 MHz, $CDCl_3$

28.10

130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230

f1 (ppm)


10.82
7.20
7.19
7.17
7.15
6.96
6.94
6.92
6.73
6.72
4.69
2.65
2.51
2.50
2.50
2.50
2.49
Me
OH
N
H
1d
1H NMR
400 MHz, DMSO-d6
H2O
DMSO-d6
0.86
0.93
0.94
1.00
1.00
2.82
2.86
12.5
11.5
10.5
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)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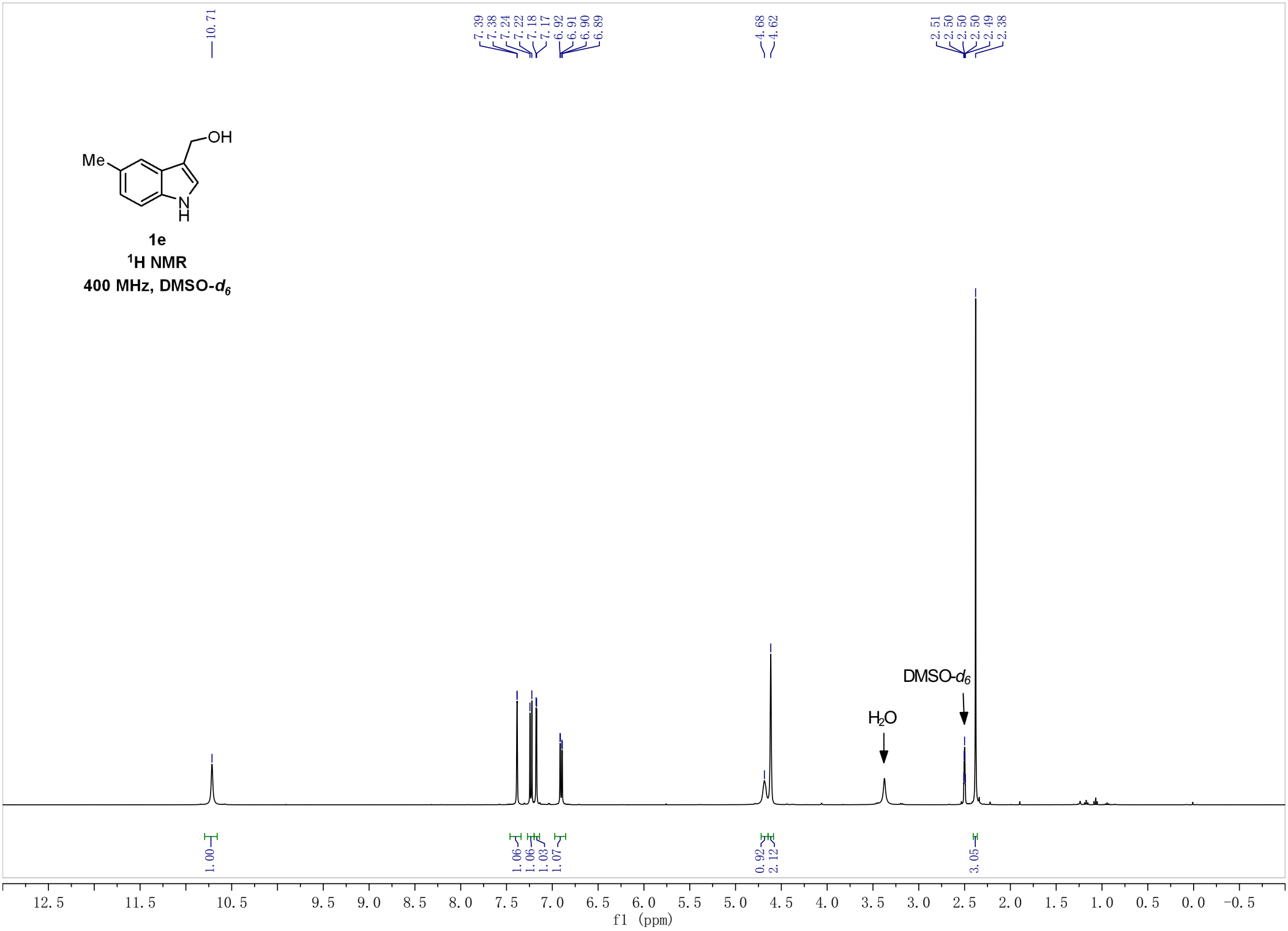
125.53
124.08
121.06
119.69
116.50
109.13
56.44
40.13
39.92
39.71
39.50
39.29
39.08
38.87
19.57
Me
OH
N
H
1d
13C NMR
101 MHz, DMSO-d6
DMSO-d6
f1 (ppm)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7.22
7.18
7.17
6.92
6.91
6.90
6.89
4.68
4.62
2.51
2.50
2.50
2.50
2.49
2.38
OH
Me
N
H
1e
1H NMR
400 MHz, DMSO-d6
H2O
DMSO-d6
1.00
1.06
1.06
1.03
1.07
0.92
2.12
3.05
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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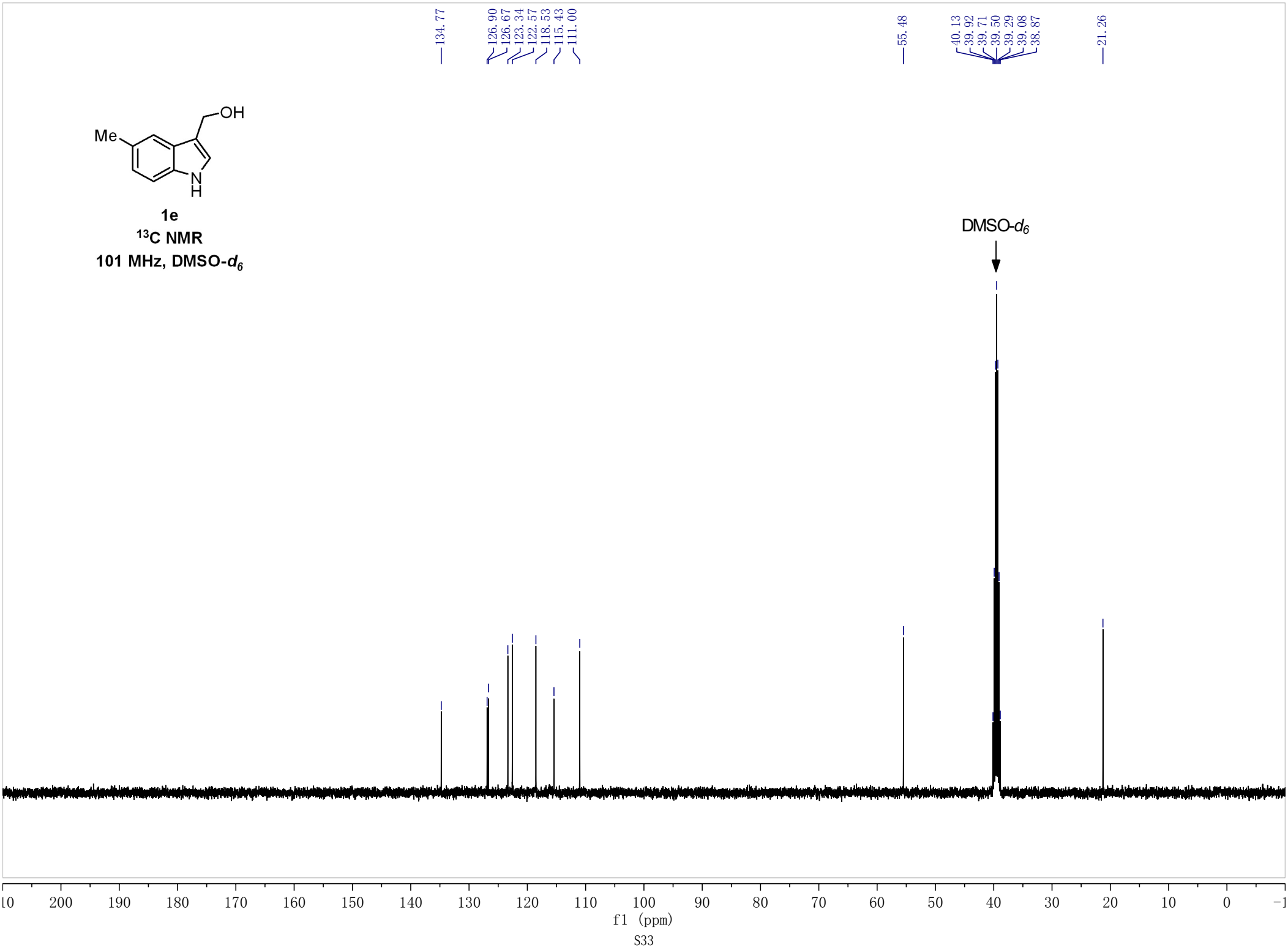
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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126.90
126.67
123.34
122.57
118.53
115.43
111.00
55.48
40.13
39.92
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39.50
39.29
39.08
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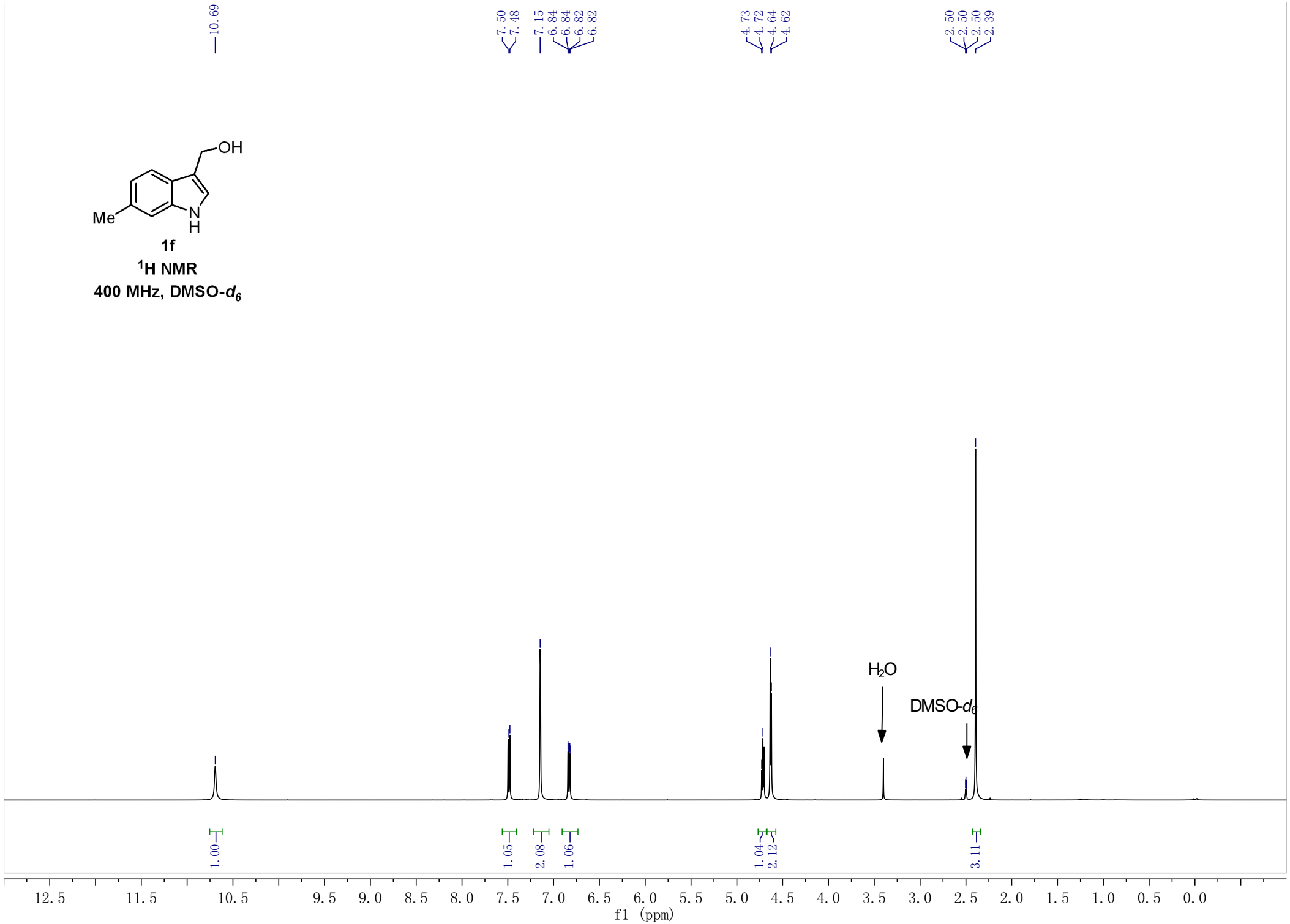
21.26
OH
Me
N
H
1e
13C NMR
101 MHz, DMSO-d6
DMSO-d6
f1 (ppm)


10.69
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7.48
7.15
6.84
6.84
6.82
6.82
4.73
4.72
4.64
4.62
2.50
2.50
2.50
2.39
OH
Me
N
H
1f
1H NMR
400 MHz, DMSO-d6
H2O
DMSO-d6
1.00
1.05
2.08
1.06
1.04
2.12
3.11
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
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2.5
2.0
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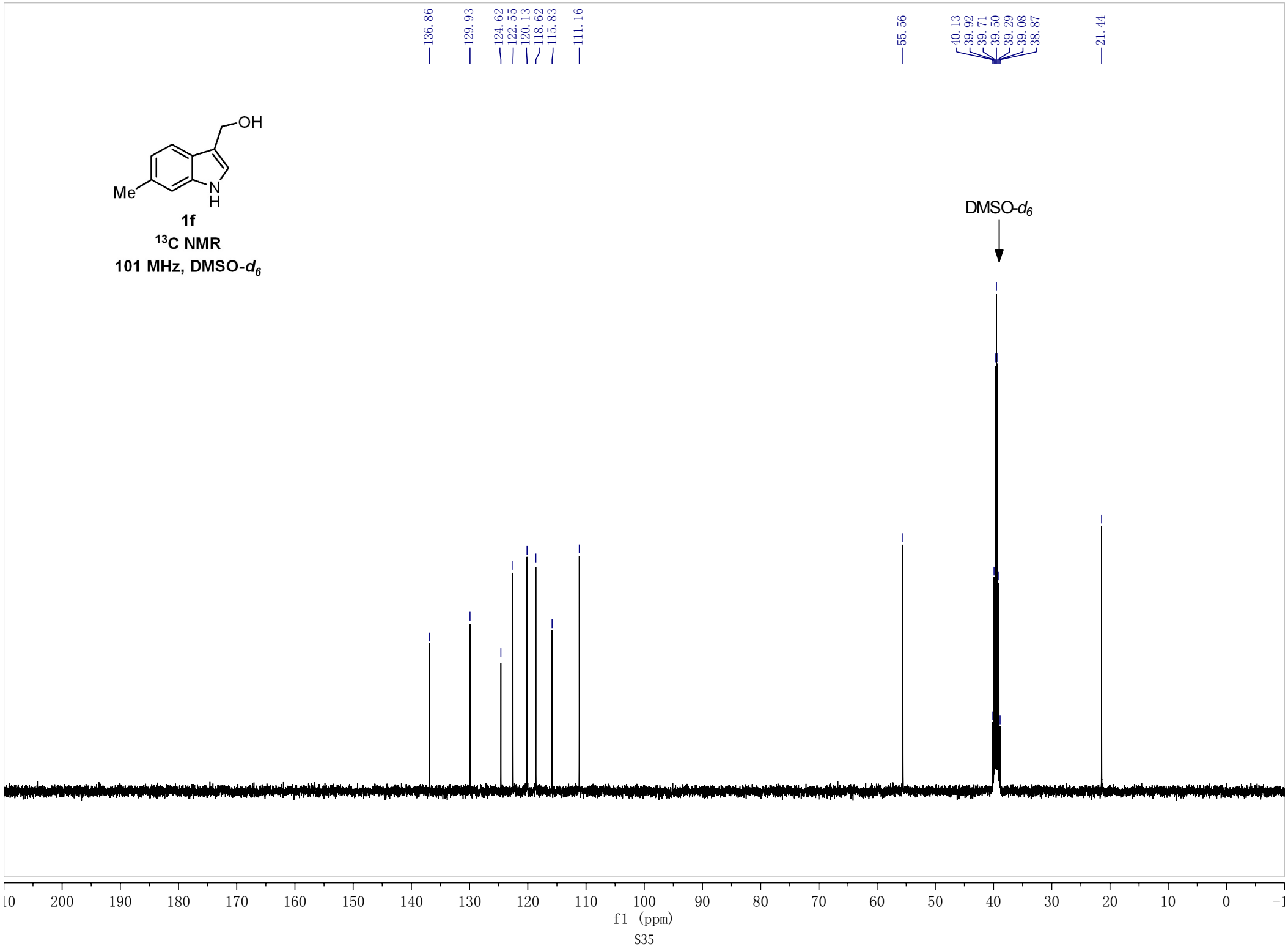
1.0
0.5
0.0
f1 (ppm)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40.13
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39.50
39.29
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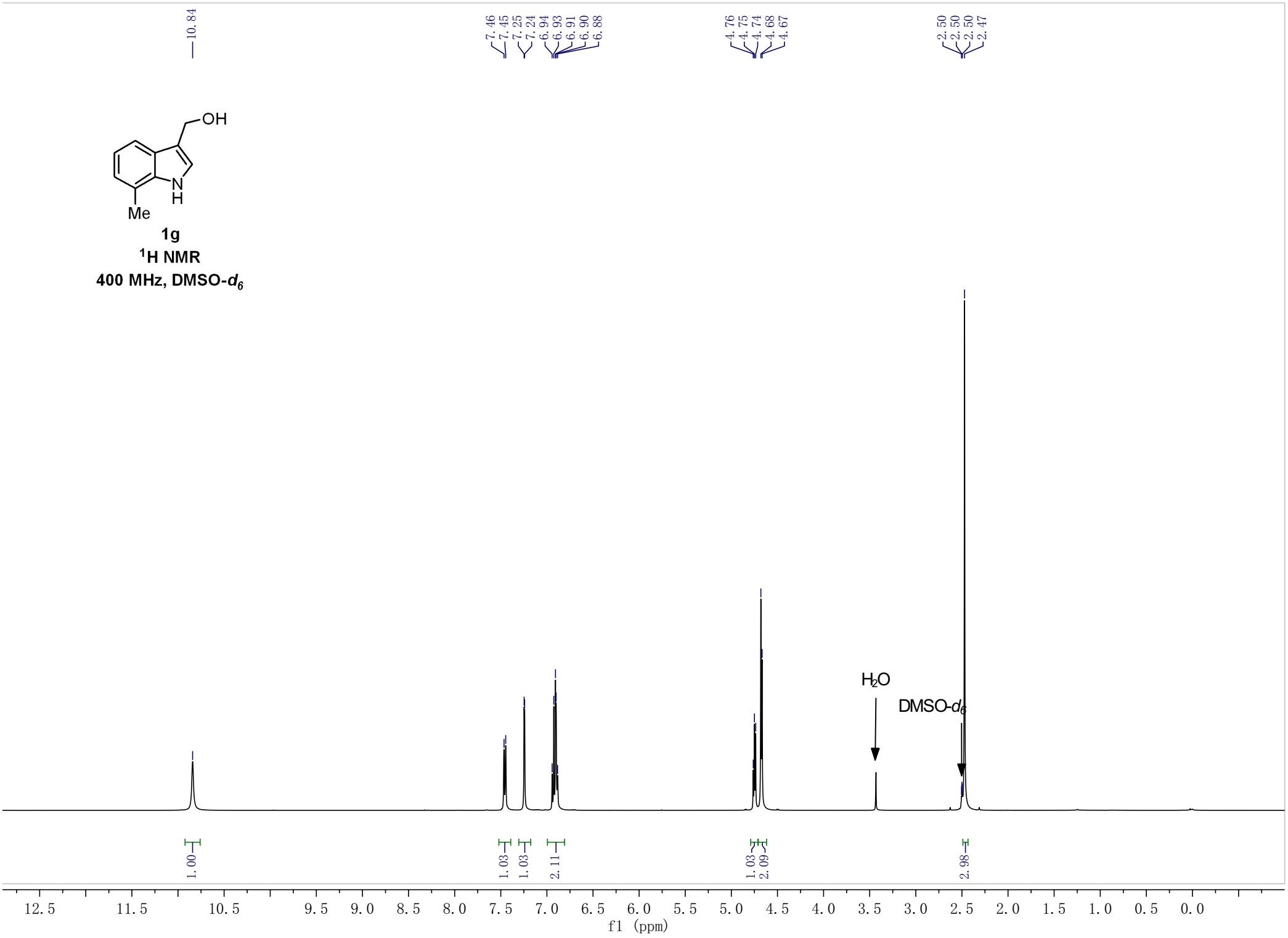
N
H
1f
13C NMR
101 MHz, DMSO-d6
DMSO-d6
f1 (ppm)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6.91
6.90
6.88
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4.74
4.68
4.67
2.50
2.50
2.50
2.47
OH
N
H
Me
1g
1H NMR
400 MHz, DMSO-d6
H2O
DMSO-d6
1.00
1.03
1.03
2.11
1.03
2.09
2.98
12.5
11.5
10.5
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
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2.5
2.0
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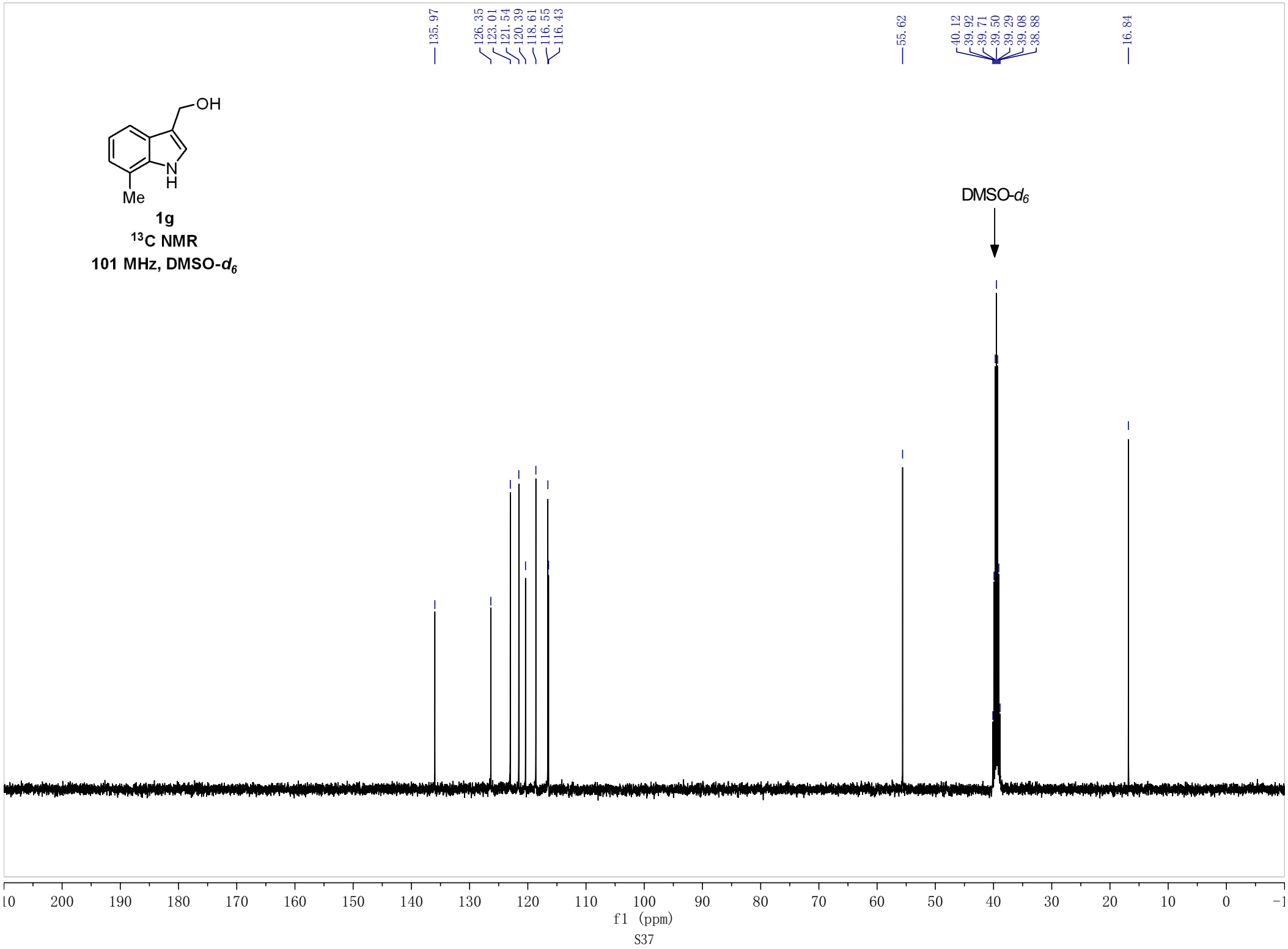
1.0
0.5
0.0
f1 (ppm)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123.01
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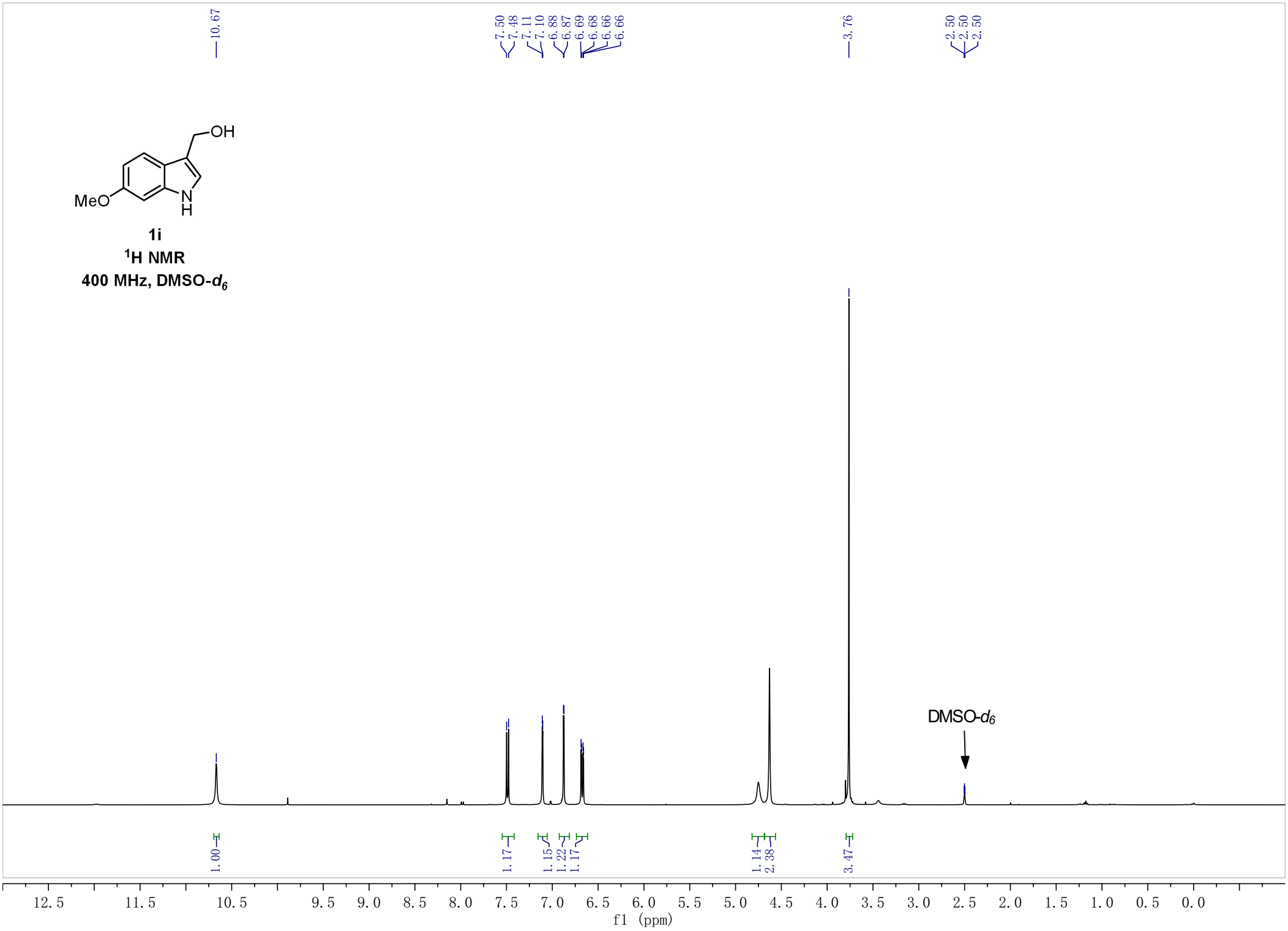
120.39
118.61
116.55
116.43
55.62
40.12
39.92
39.71
39.50
39.29
39.08
38.88
16.84
OH
N
H
Me
1g
13C NMR
101 MHz, DMSO-d6
DMSO-d6
f1 (ppm)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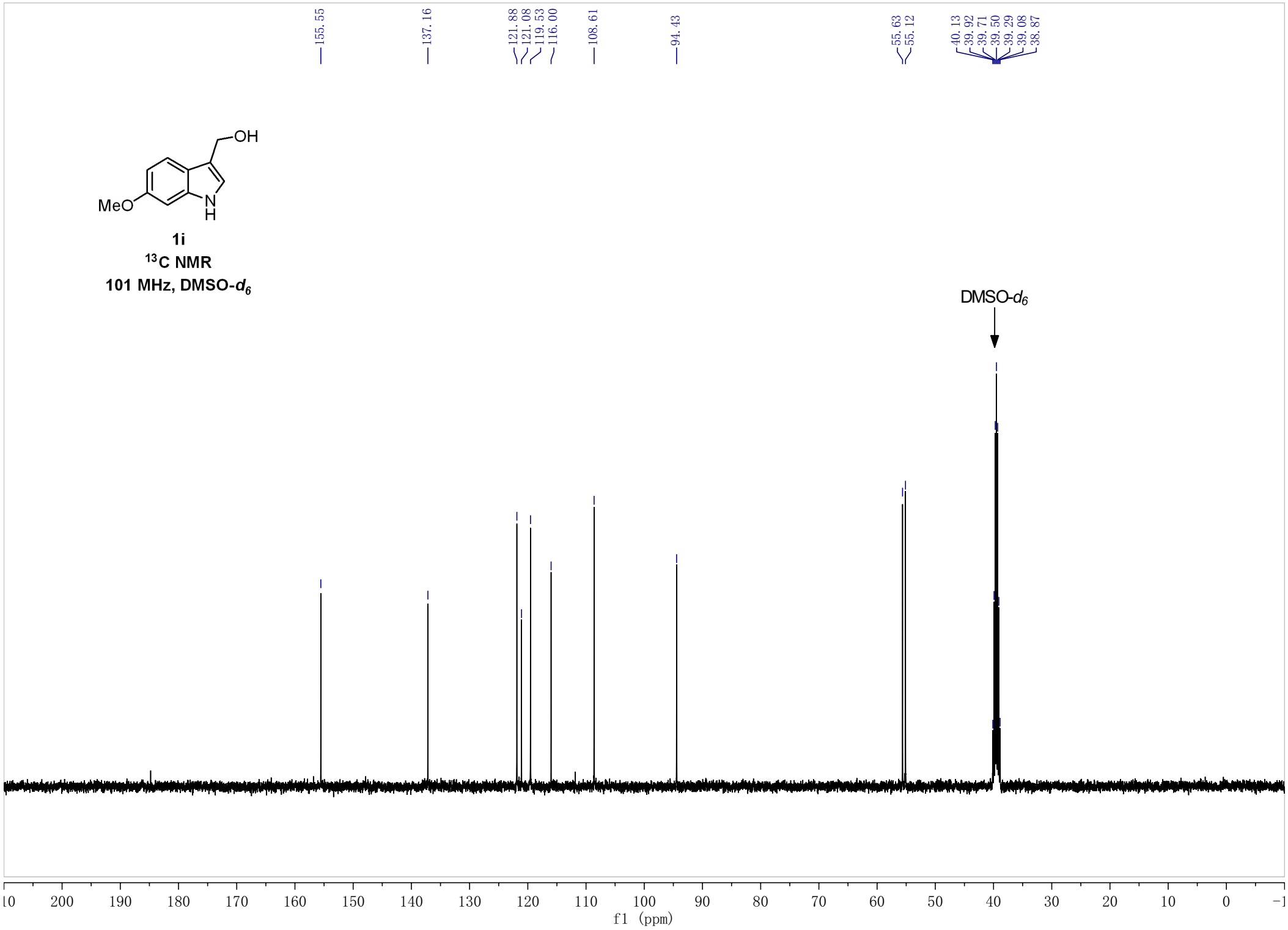
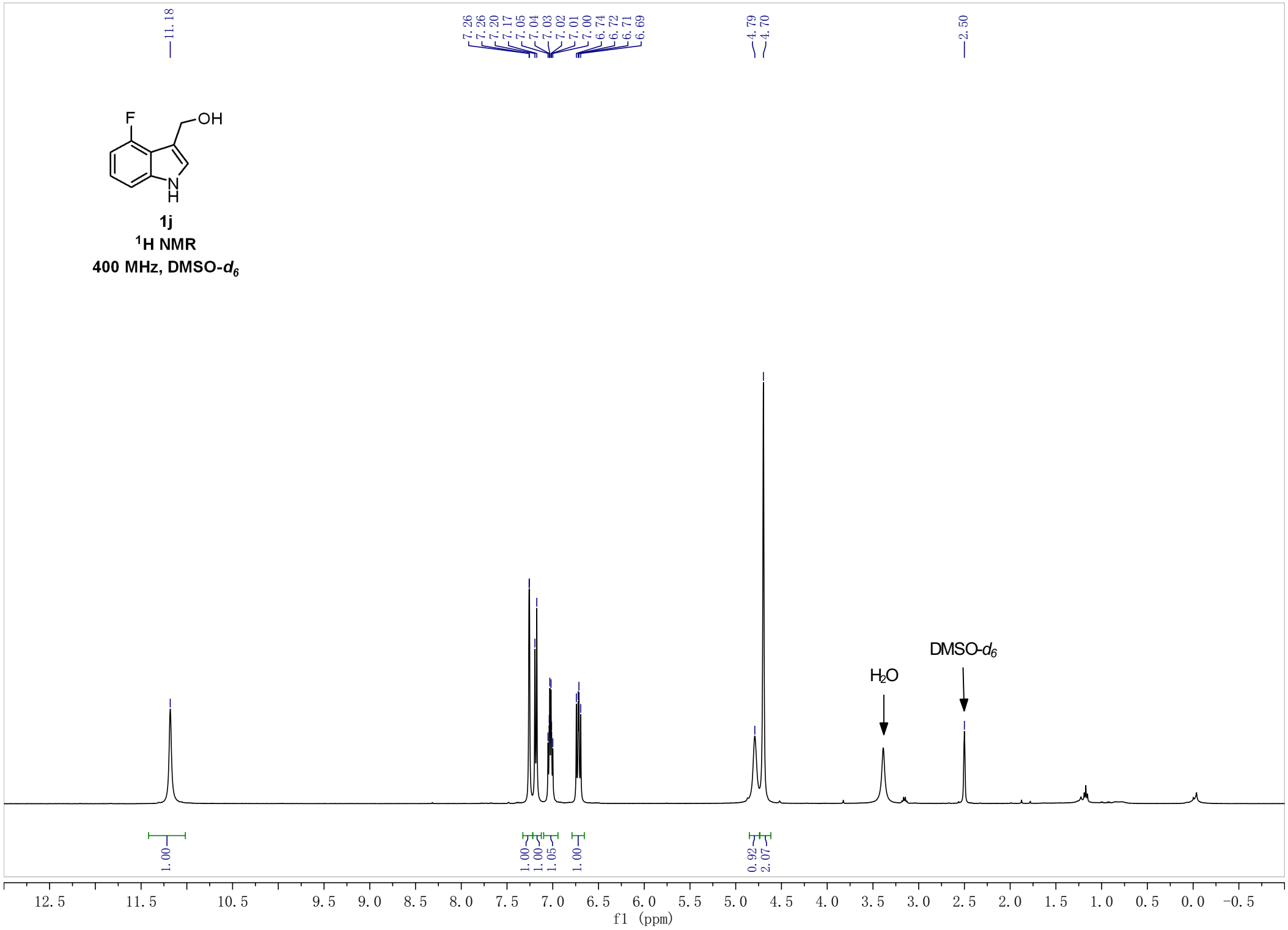
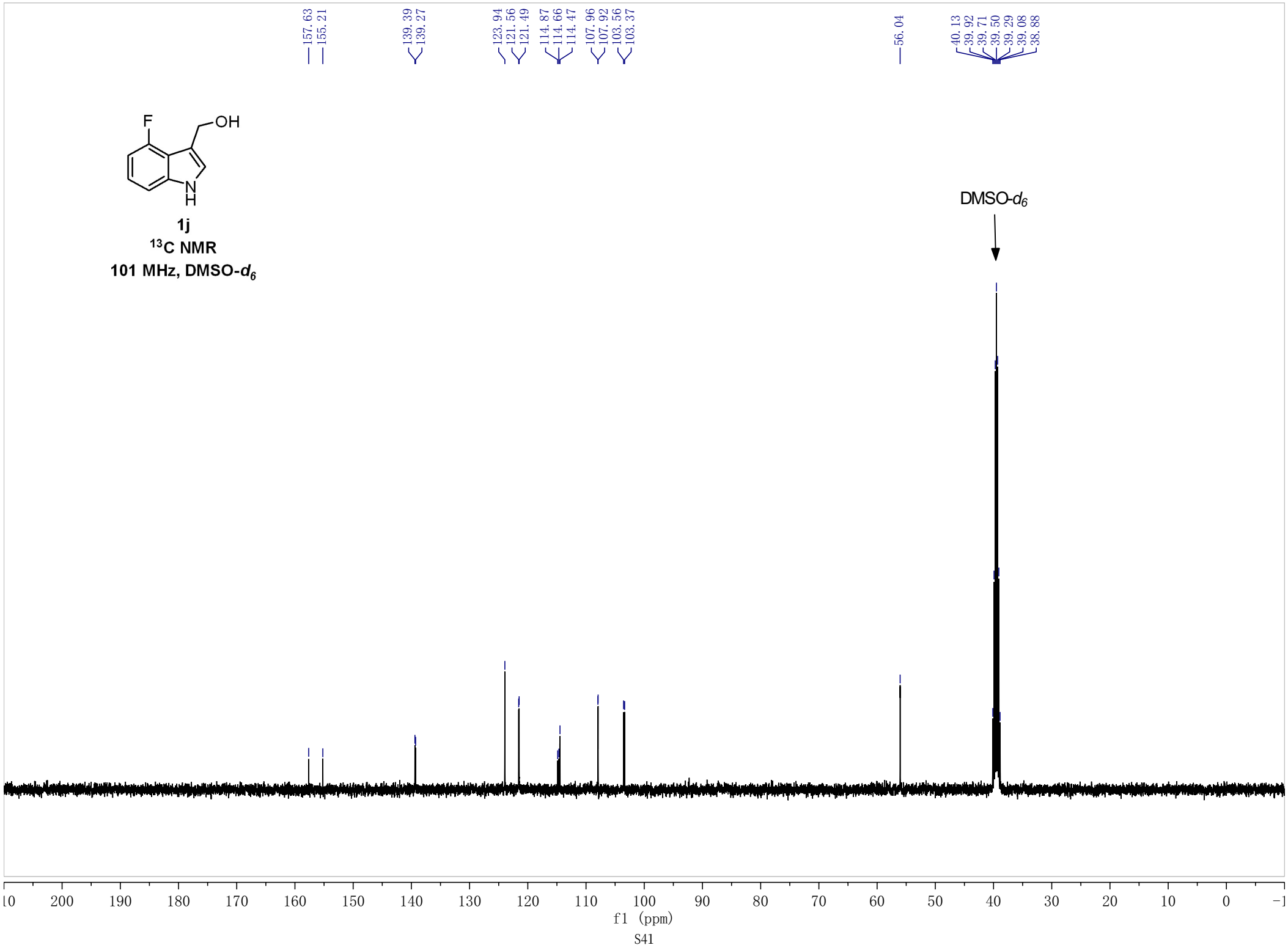
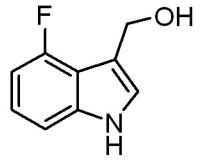
2.50
2.50
OH
MeO
N
H
1i
1H NMR
400 MHz, DMSO-d6
DMSO-d6
1.00
1.17
1.15
1.22
1.17
1.14
2.38
3.47
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


155.55
137.16
121.88
121.08
119.53
116.00
108.61
94.43
55.63
55.12
40.13
39.92
39.71
39.50
39.29
39.08
38.87
OH
MeO
N
H
1i
13C NMR
101 MHz, DMSO-d6
DMSO-d6
f1 (ppm)


11.18
7.26
7.26
7.20
7.17
7.05
7.04
7.03
7.02
7.01
7.00
6.74
6.72
6.71
6.69
4.79
4.70
2.50
F
OH
N
H
1j
1H NMR
400 MHz, DMSO-d6
H2O
DMSO-d6
1.00
1.00
1.00
1.05
1.00
0.92
2.07
12.5
11.5
10.5
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
-0.5
f1 (ppm)

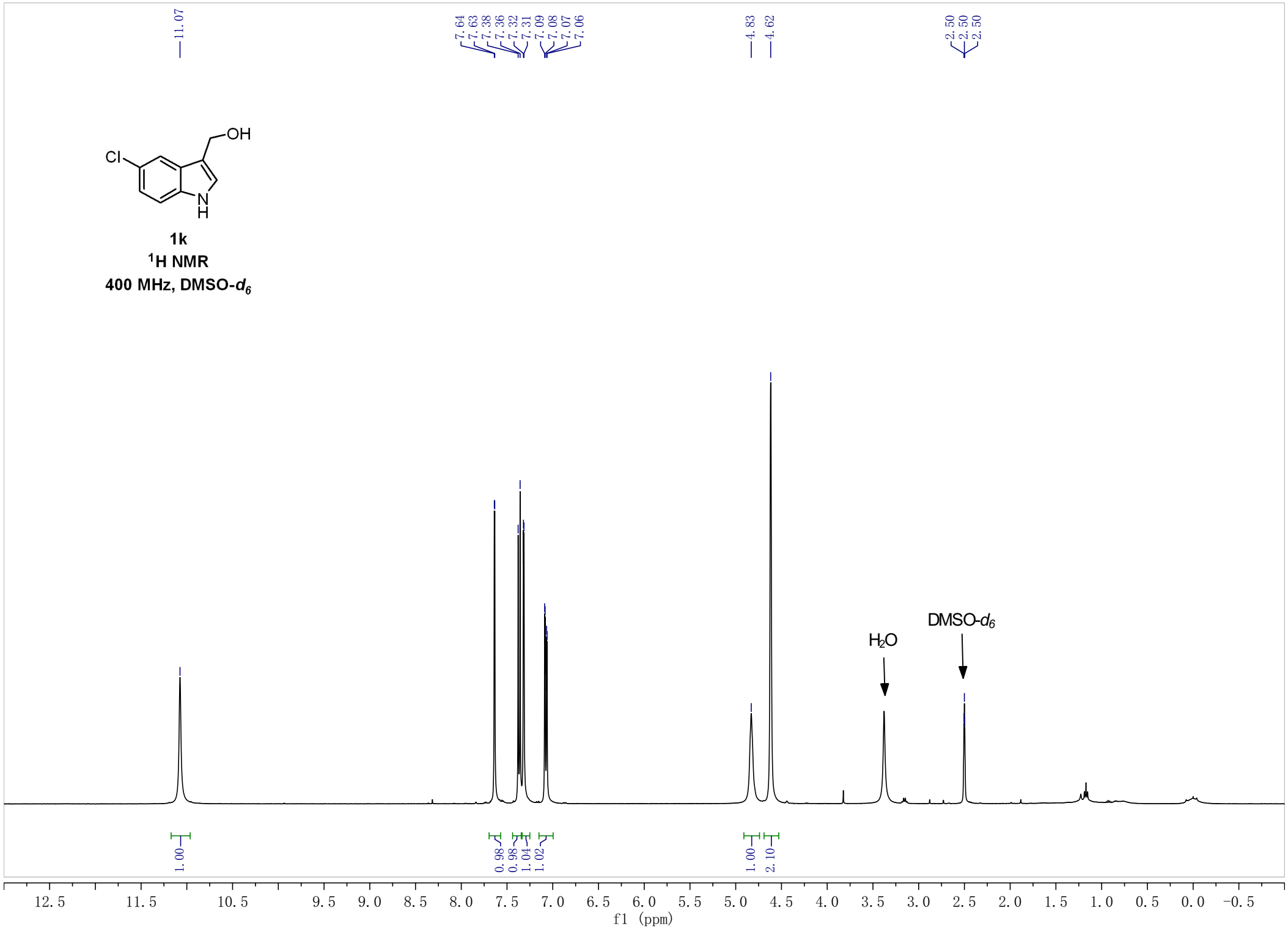

157.63
155.21
139.39
139.27
123.94
121.56
121.49
114.87
114.66
114.47
107.96
107.92
103.56
103.37
56.04
40.13
39.92
39.71
39.50
39.29
39.08
38.88
F
OH
N
H
1j
13C NMR
101 MHz, DMSO-d6
DMSO-d6
f1 (ppm)

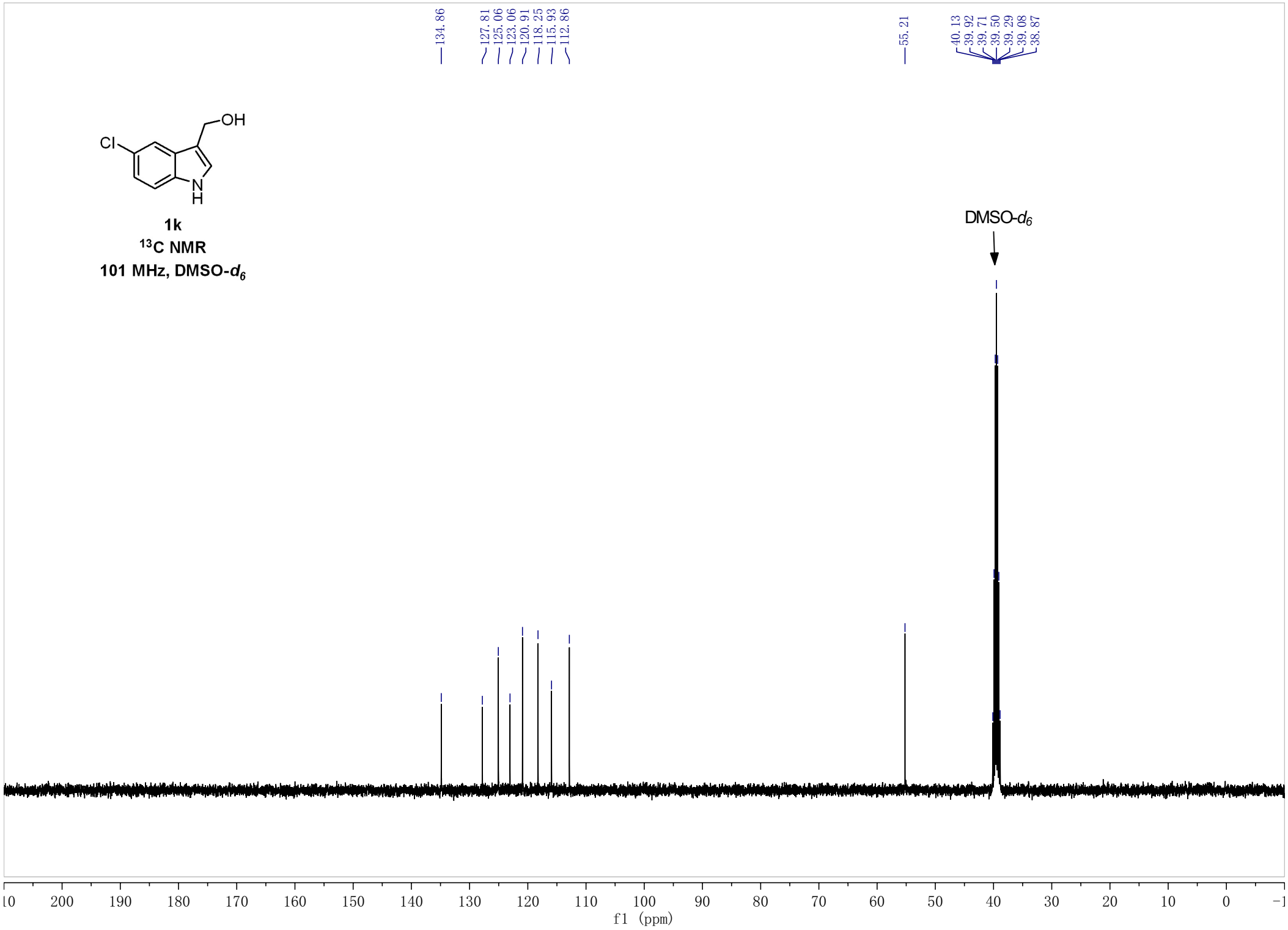


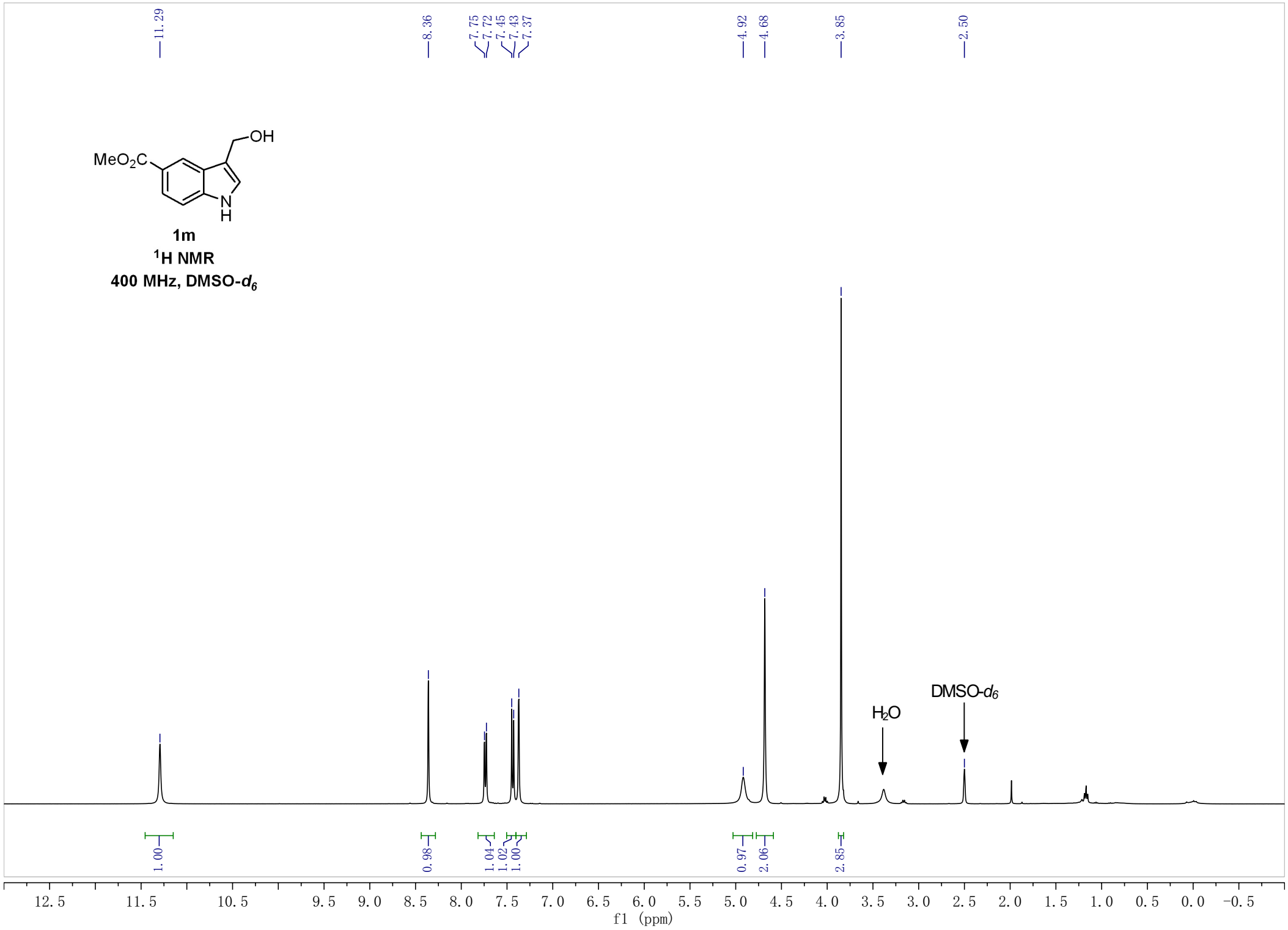
1j

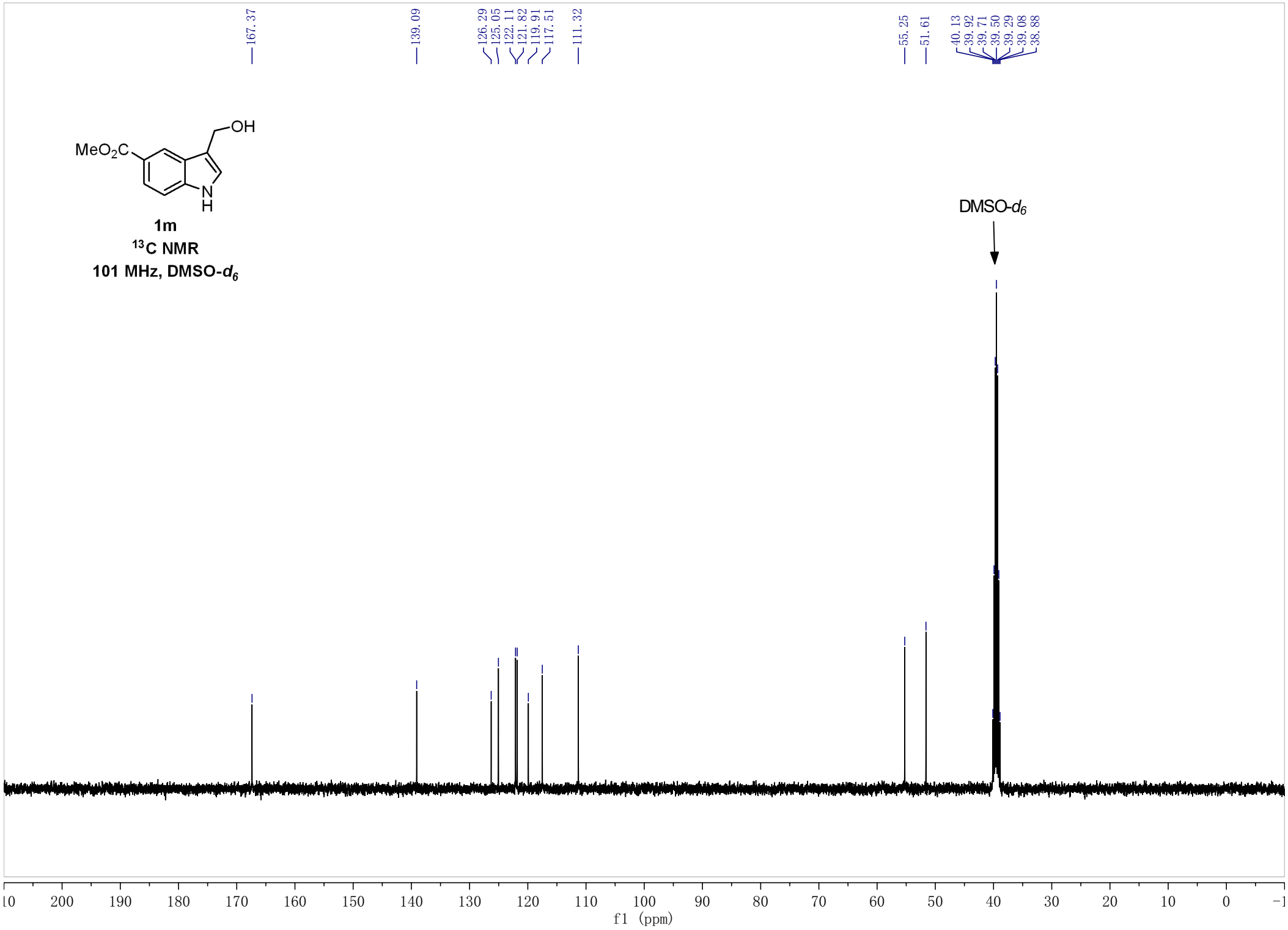
^{19}F NMR

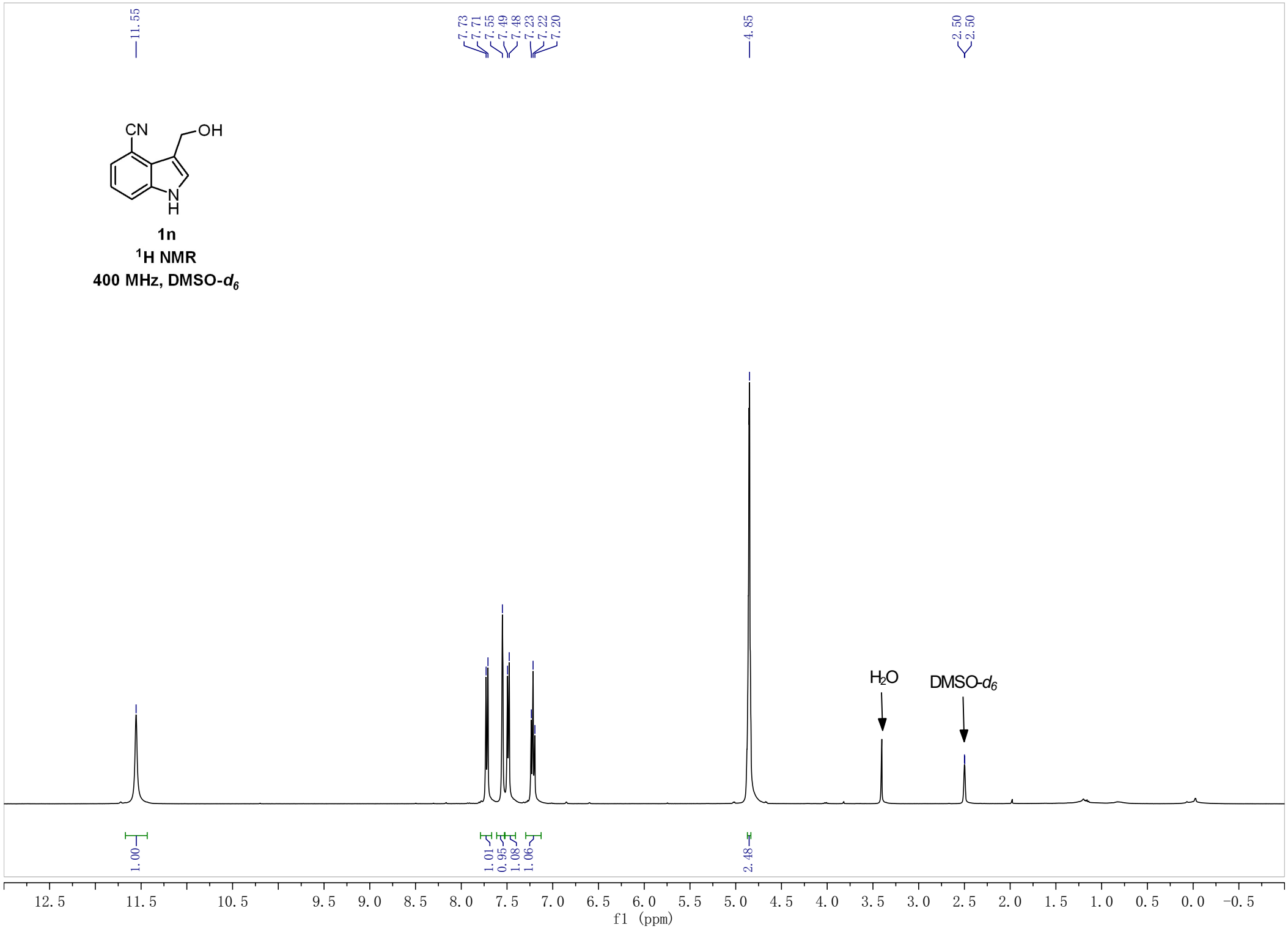
376 MHz, DMSO-d_6

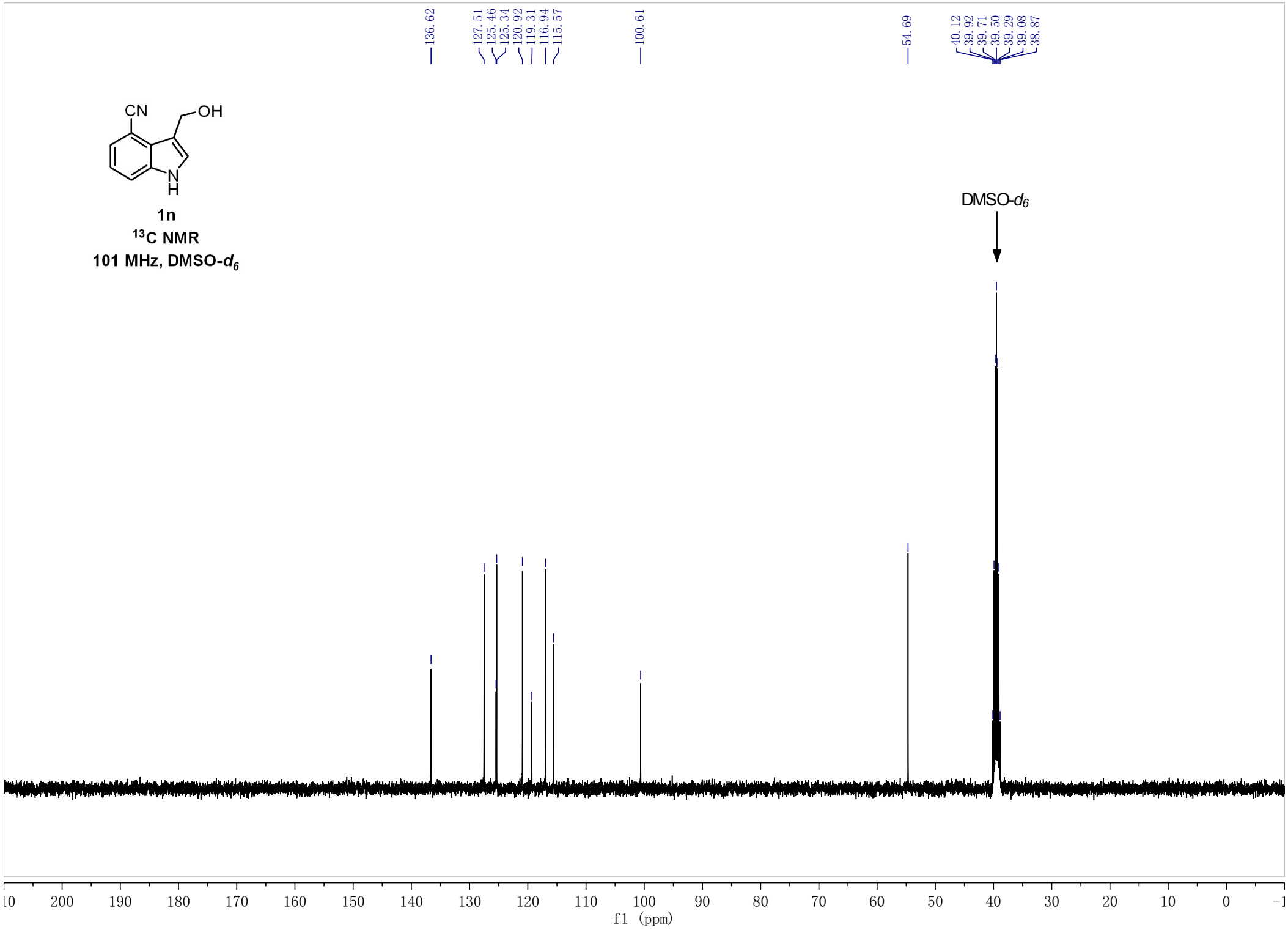

11.07
7.64
7.63
7.38
7.36
7.32
7.31
7.09
7.08
7.07
7.06
4.83
4.62
2.50
2.50
2.50
OH
Cl
N
H
1k
1H NMR
400 MHz, DMSO-d6
H2O
DMSO-d6
1.00
0.98
0.98
1.04
1.02
1.00
2.10
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

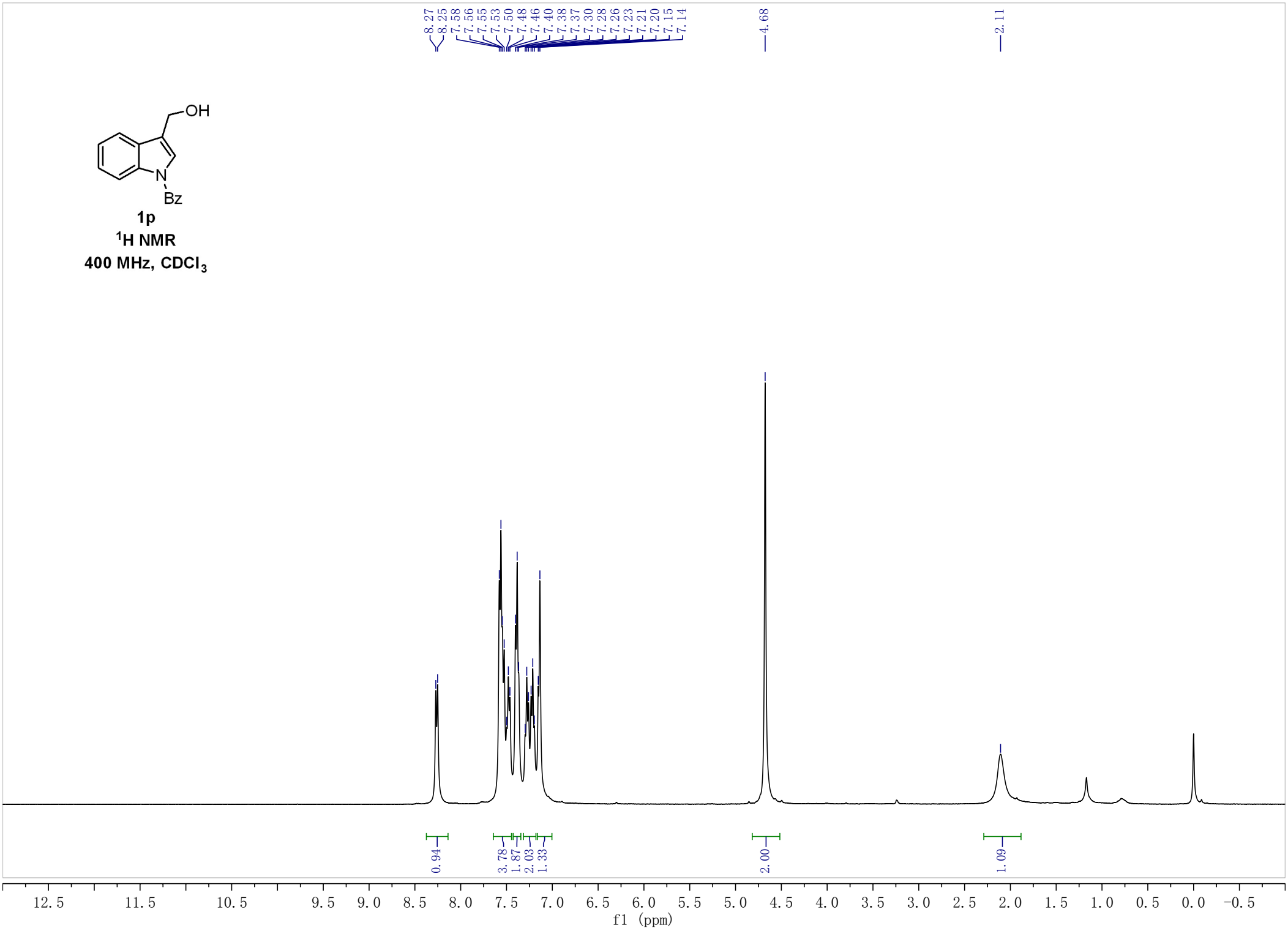

134.86
127.81
125.06
123.06
120.91
118.25
115.93
112.86
55.21
40.13
39.92
39.71
39.50
39.29
39.08
38.87
OH
Cl
N
H
1k
13C NMR
101 MHz, DMSO-d6
DMSO-d6
f1 (ppm)

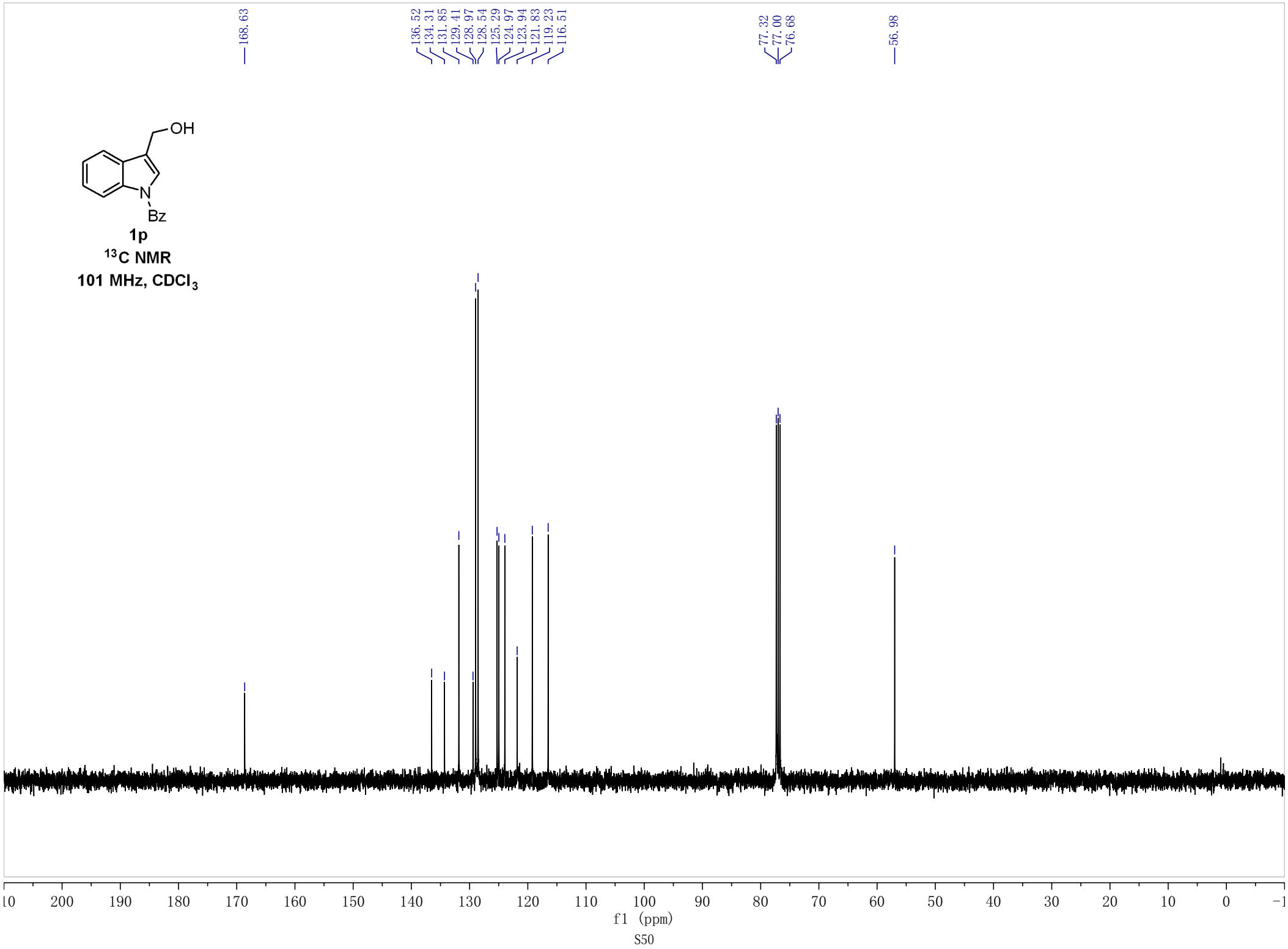

11.29
8.36
7.75
7.72
7.45
7.43
7.37
4.92
4.68
3.85
2.50
MeO2C
OH
N
H
1m
1H NMR
400 MHz, DMSO-d6
H2O
DMSO-d6
1.00
0.98
1.04
1.02
1.00
0.97
2.06
2.85
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

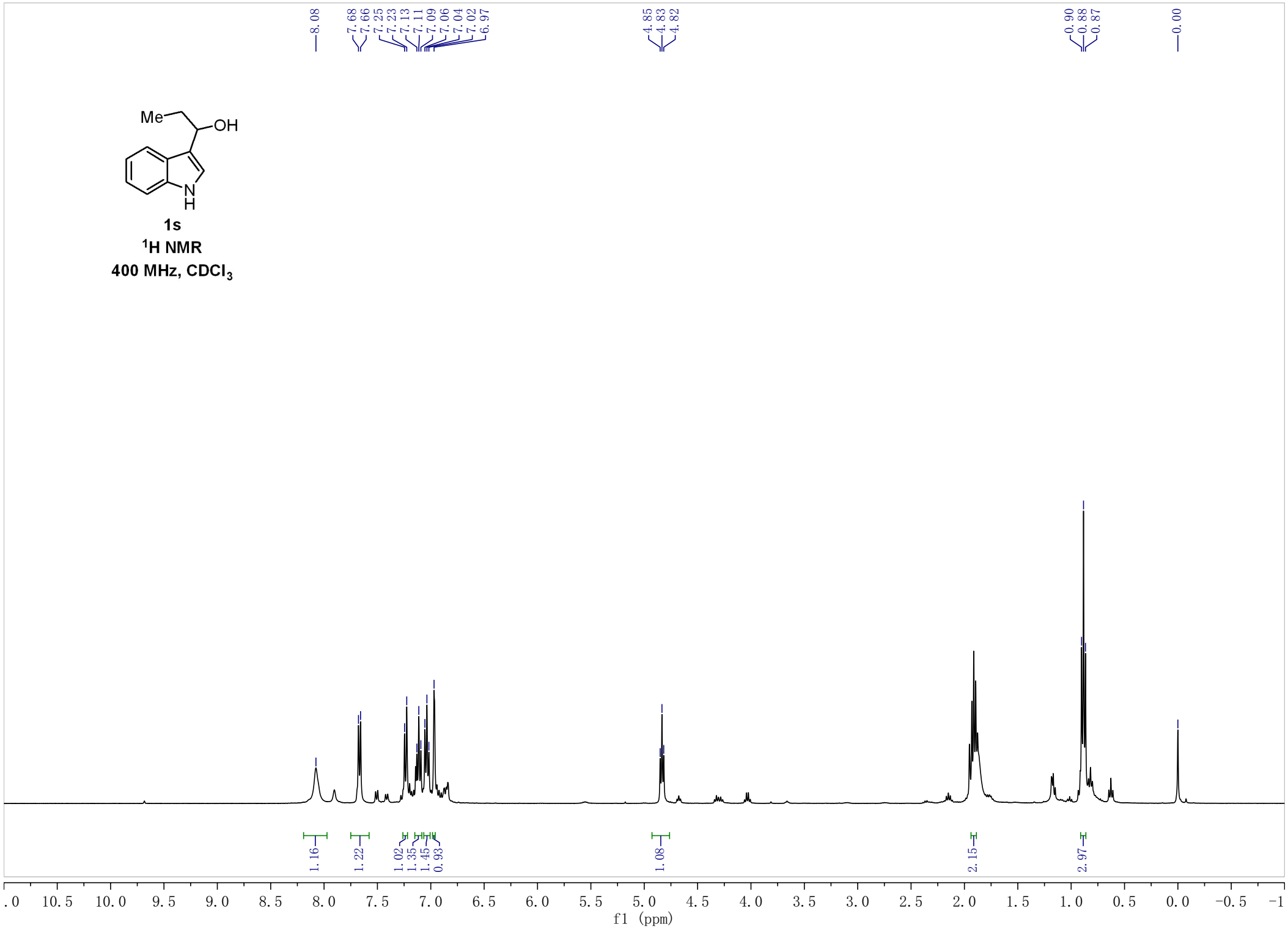

167.37
139.09
126.29
125.05
122.11
121.82
119.91
117.51
111.32
55.25
51.61
40.13
39.92
39.71
39.50
39.29
39.08
38.88
OH
MeO2C
N
H
1m
13C NMR
101 MHz, DMSO-d6
DMSO-d6
f1 (ppm)

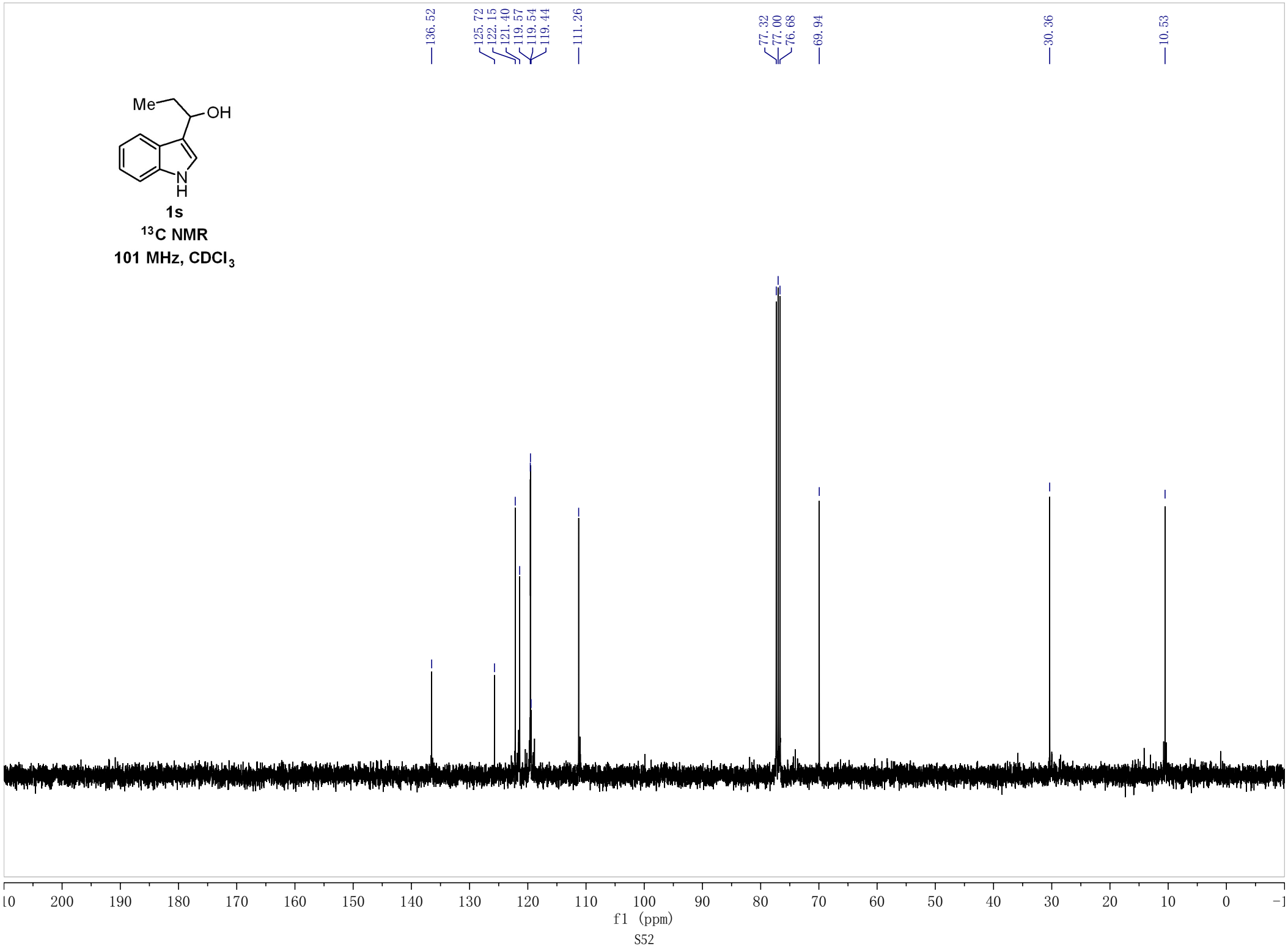

11.55
7.73
7.71
7.55
7.49
7.48
7.23
7.22
7.20
4.85
2.50
2.50
CN
OH
N
H
1n
1H NMR
400 MHz, DMSO-d6
H2O
DMSO-d6
1.00
1.01
0.95
1.08
1.06
2.48
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

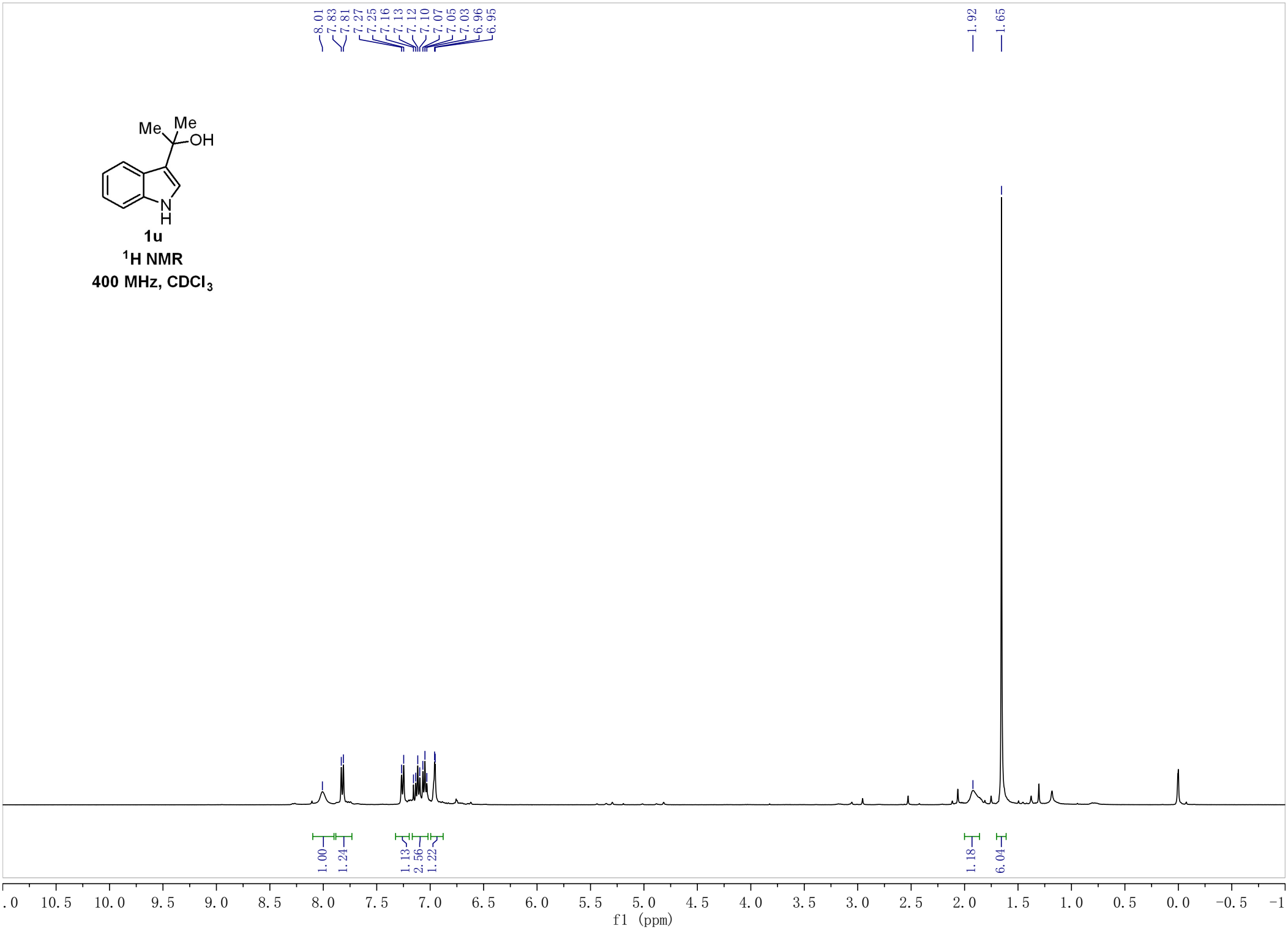

136.62
127.51
125.46
125.34
120.92
119.31
116.94
115.57
100.61
54.69
40.12
39.92
39.71
39.50
39.29
39.08
38.87
CN
OH
N
H
1n
13C NMR
101 MHz, DMSO-d6
DMSO-d6
f1 (ppm)

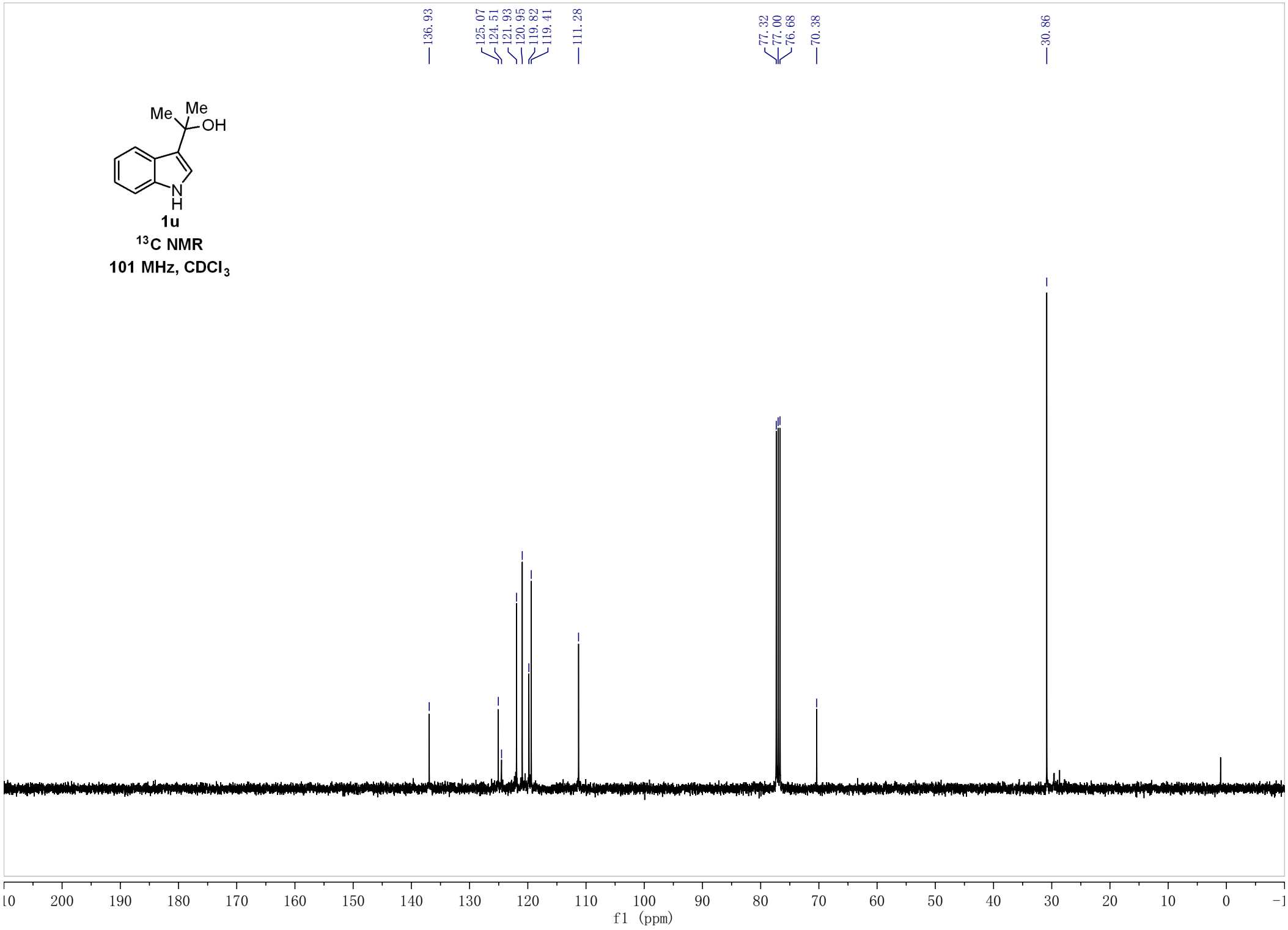

8.27
8.25
7.58
7.56
7.55
7.53
7.50
7.48
7.46
7.40
7.38
7.37
7.30
7.28
7.26
7.23
7.21
7.20
7.15
7.14
4.68
2.11
OH
N
Bz
1p
1H NMR
400 MHz, CDCl3
0.94
3.78
1.87
2.03
1.33
2.00
1.09
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

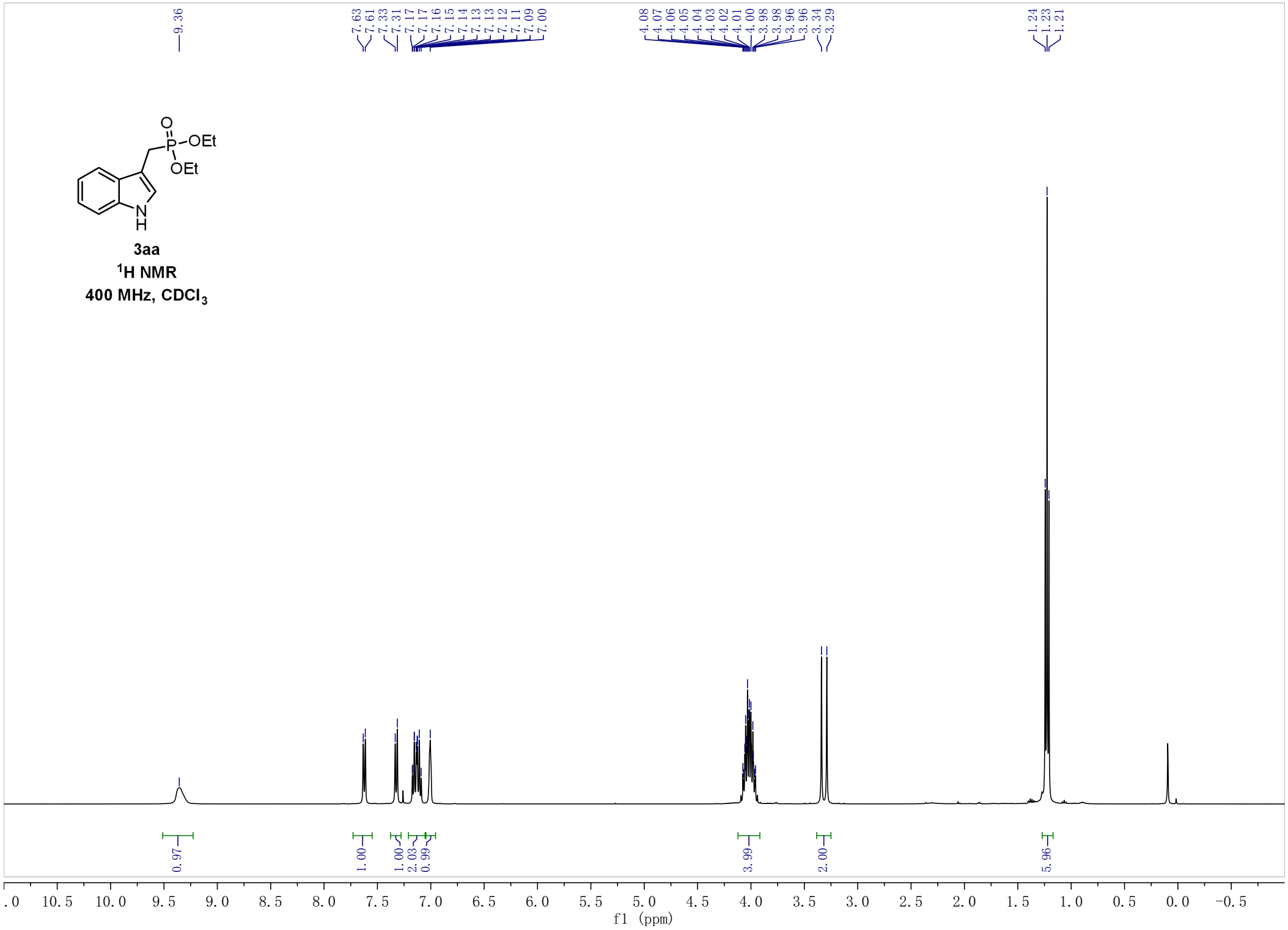

168.63
136.52
134.31
131.85
129.41
128.97
128.54
125.29
124.97
123.94
121.83
119.23
116.51
77.32
77.00
76.68
56.98
OH
N
Bz
1p
13C NMR
101 MHz, CDCl3
f1 (ppm)

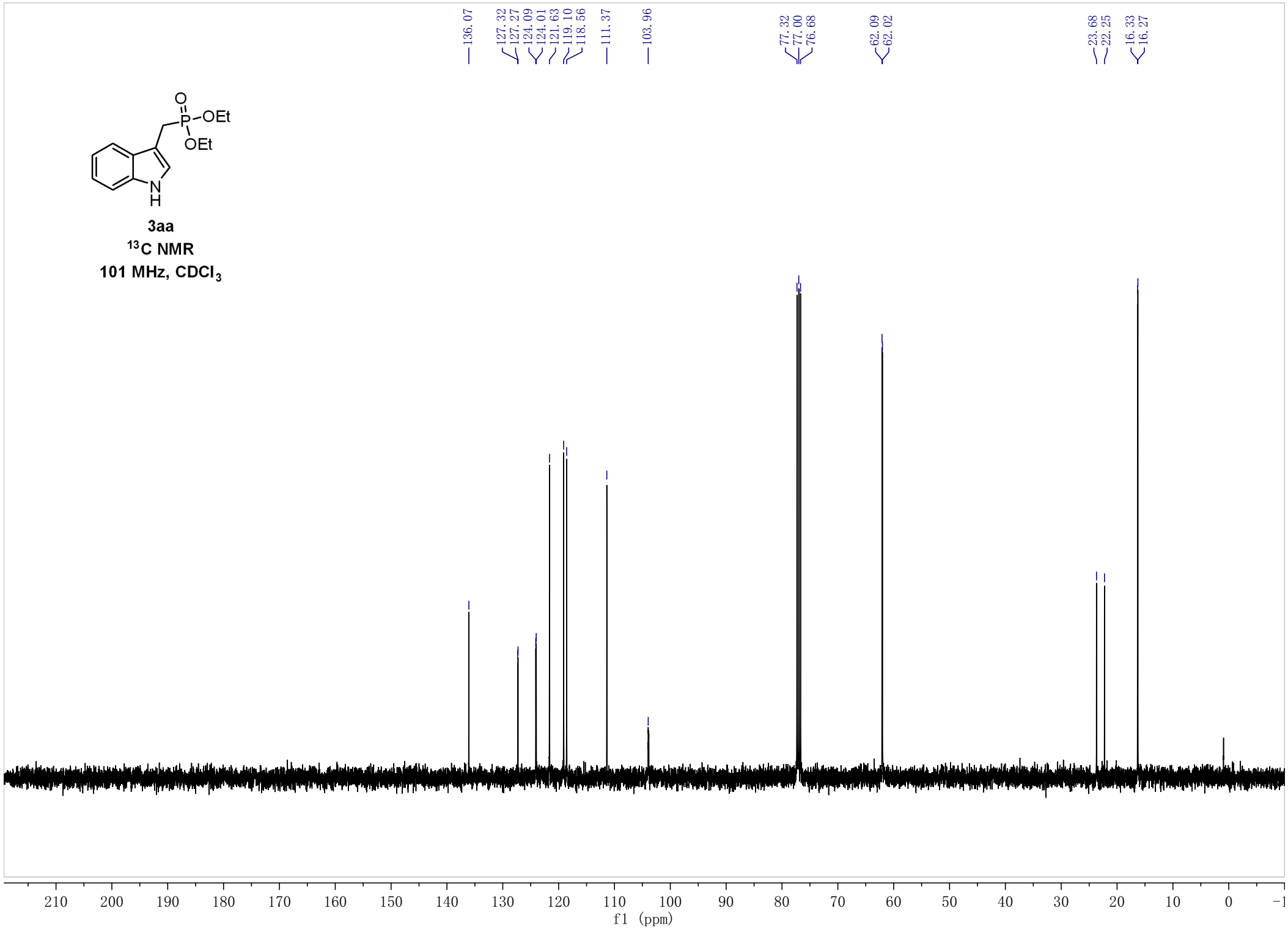

8.08
7.68
7.66
7.25
7.23
7.13
7.11
7.09
7.06
7.04
7.02
6.97
4.85
4.83
4.82
0.90
0.88
0.87
0.00
Me
OH
N
H
1s
1H NMR
400 MHz, CDCl3
1.16
1.22
1.02
1.35
1.45
0.93
1.08
2.15
2.97
f1 (ppm)

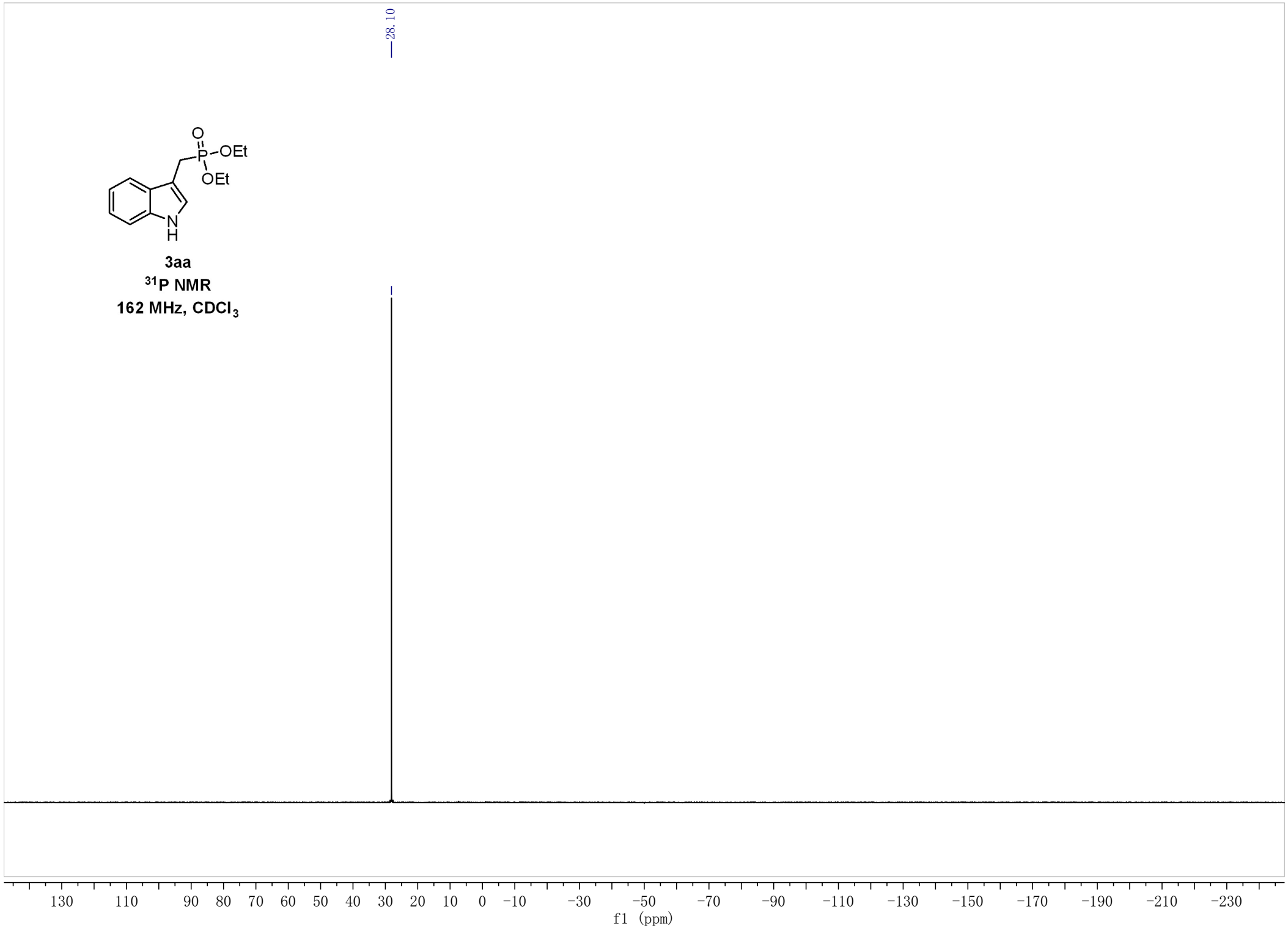

136.52
125.72
122.15
121.40
119.57
119.54
119.44
111.26
77.32
77.00
76.68
69.94
30.36
10.53
Me
OH
N
H
1s
13C NMR
101 MHz, CDCl3
f1 (ppm)

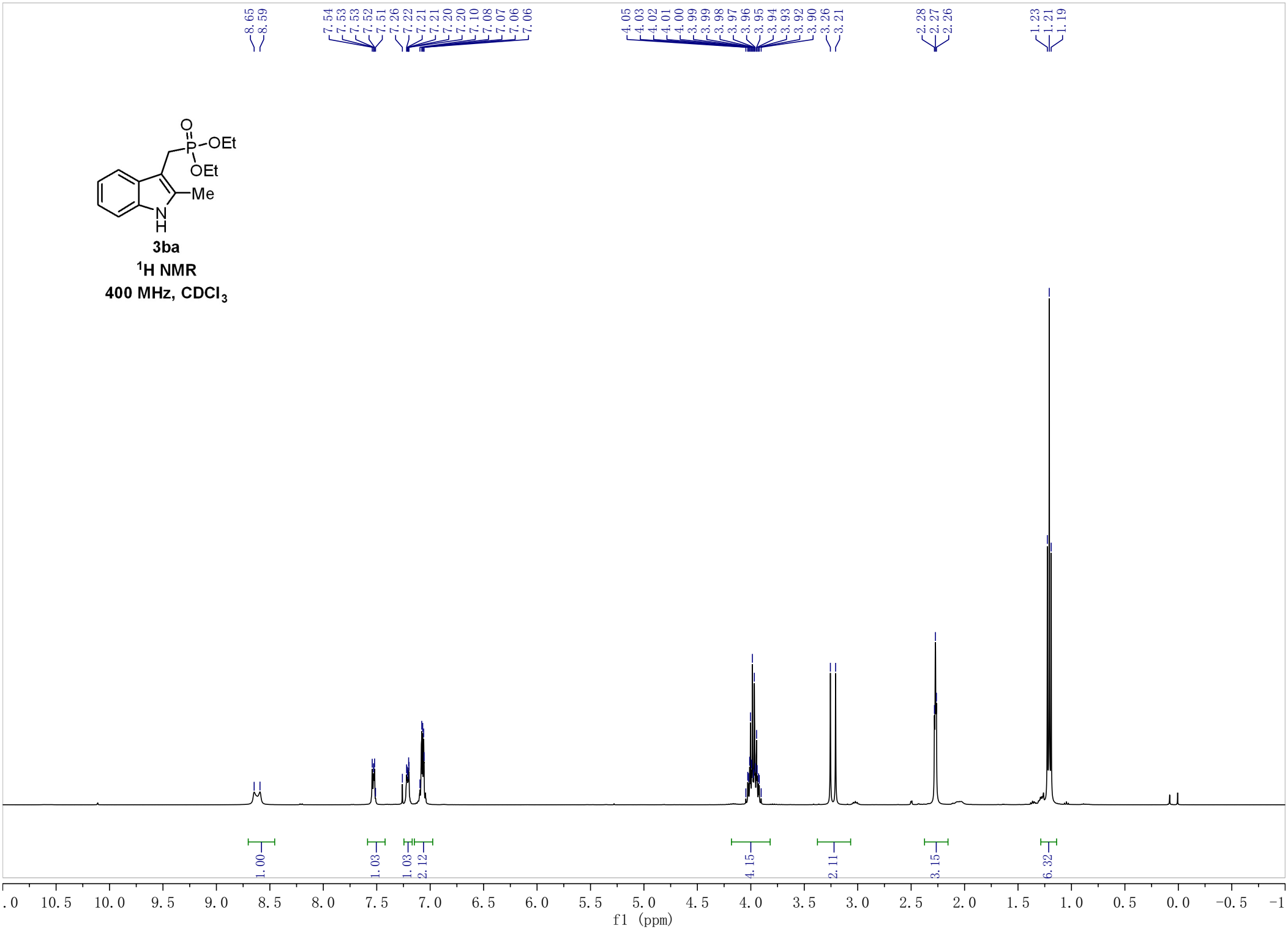

8.01
7.83
7.81
7.27
7.25
7.16
7.13
7.12
7.10
7.07
7.05
7.03
6.96
6.95
1.92
1.65
Me
Me
OH
N
H
1u
1H NMR
400 MHz, CDCl3
1.00
1.24
1.13
2.56
1.22
1.18
6.04
f1 (ppm)

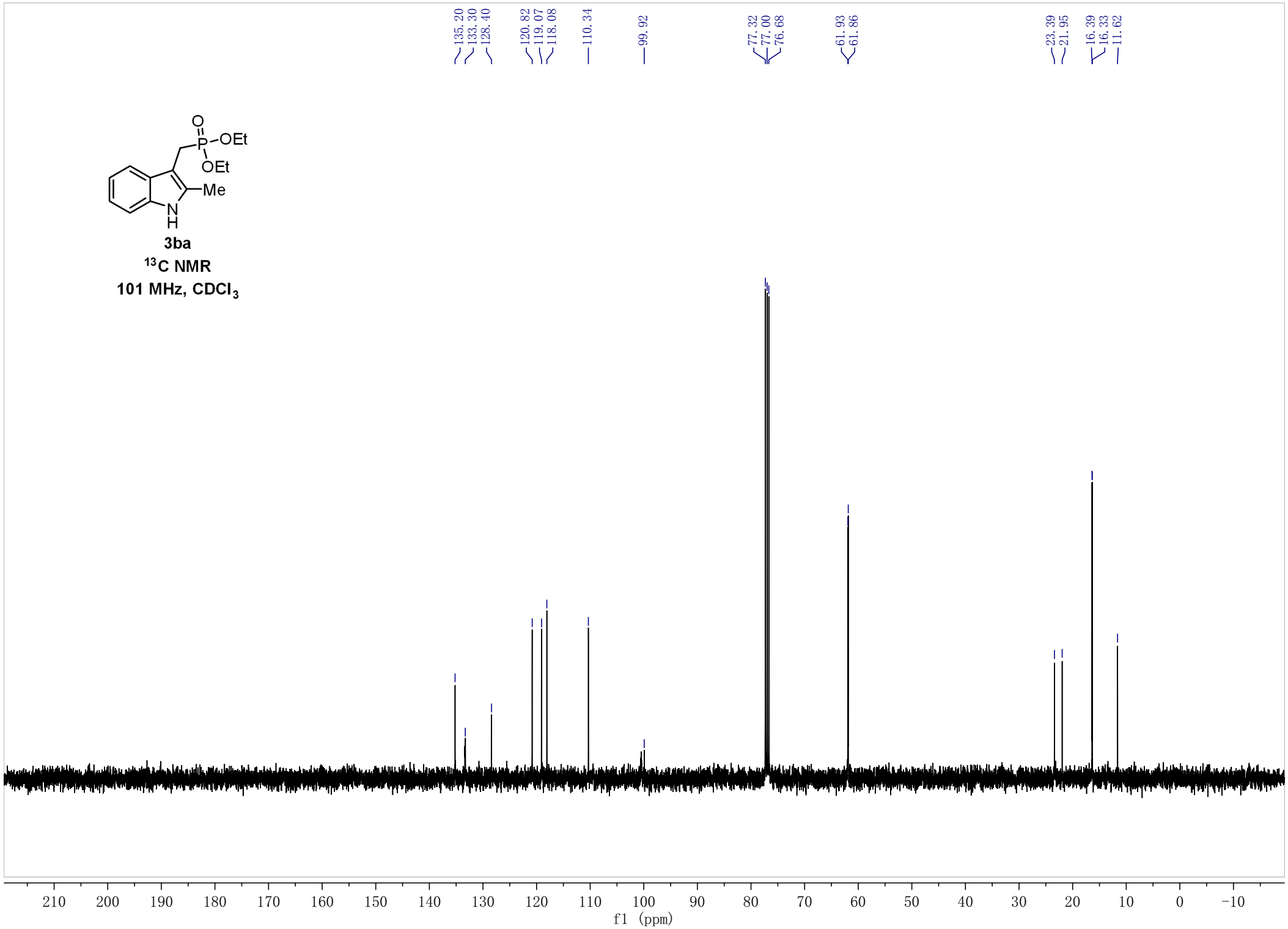

136.93
125.07
124.51
121.93
120.95
119.82
119.41
111.28
77.32
77.00
76.68
70.38
30.86
Me
Me
OH
N
H
1u
13C NMR
101 MHz, CDCl3
f1 (ppm)

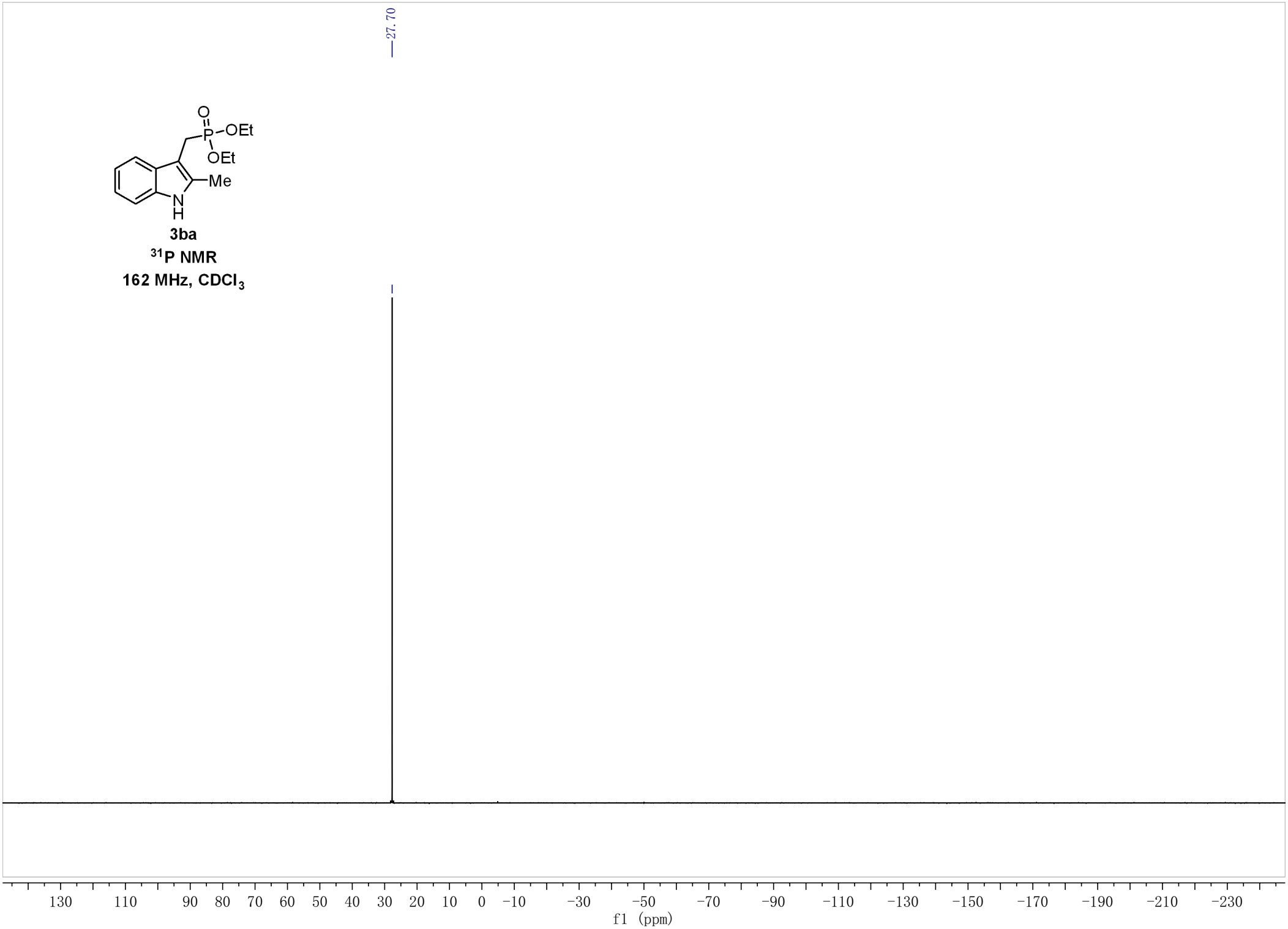

9.36
7.63
7.61
7.33
7.31
7.17
7.16
7.15
7.14
7.13
7.12
7.11
7.09
7.00
4.08
4.07
4.06
4.05
4.04
4.03
4.02
4.01
4.00
3.98
3.98
3.96
3.96
3.34
3.29
1.24
1.23
1.21
O
P
OEt
OEt
N
H
3aa
1H NMR
400 MHz, CDCl3
0.97
1.00
1.00
2.03
0.99
3.99
2.00
5.96
f1 (ppm)

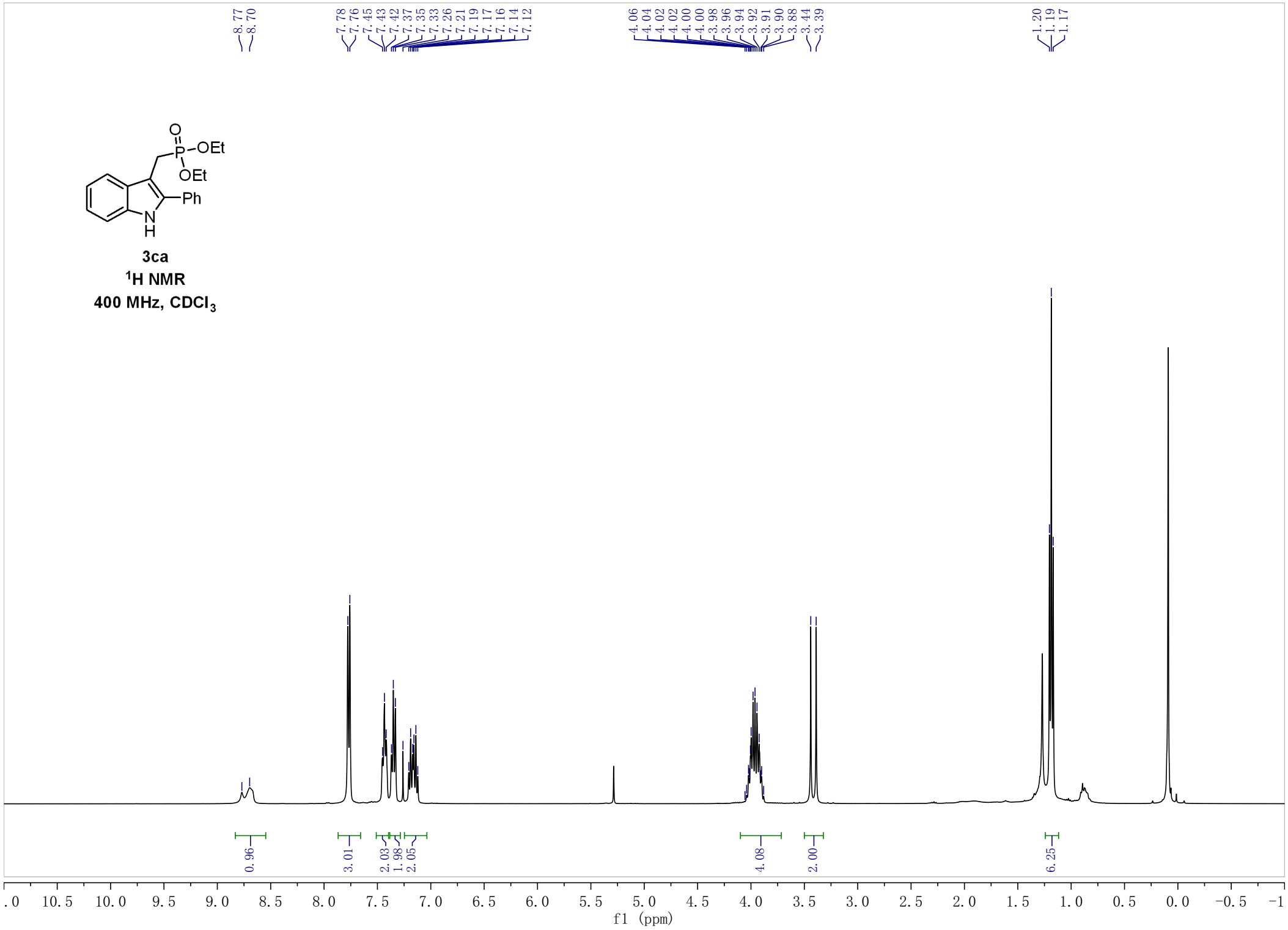

136.07
127.32
127.27
124.09
124.01
121.63
119.10
118.56
111.37
103.96
77.32
77.00
76.68
62.09
62.02
23.68
22.25
16.33
16.27
O
P
OEt
OEt
N
H
3aa
13C NMR
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

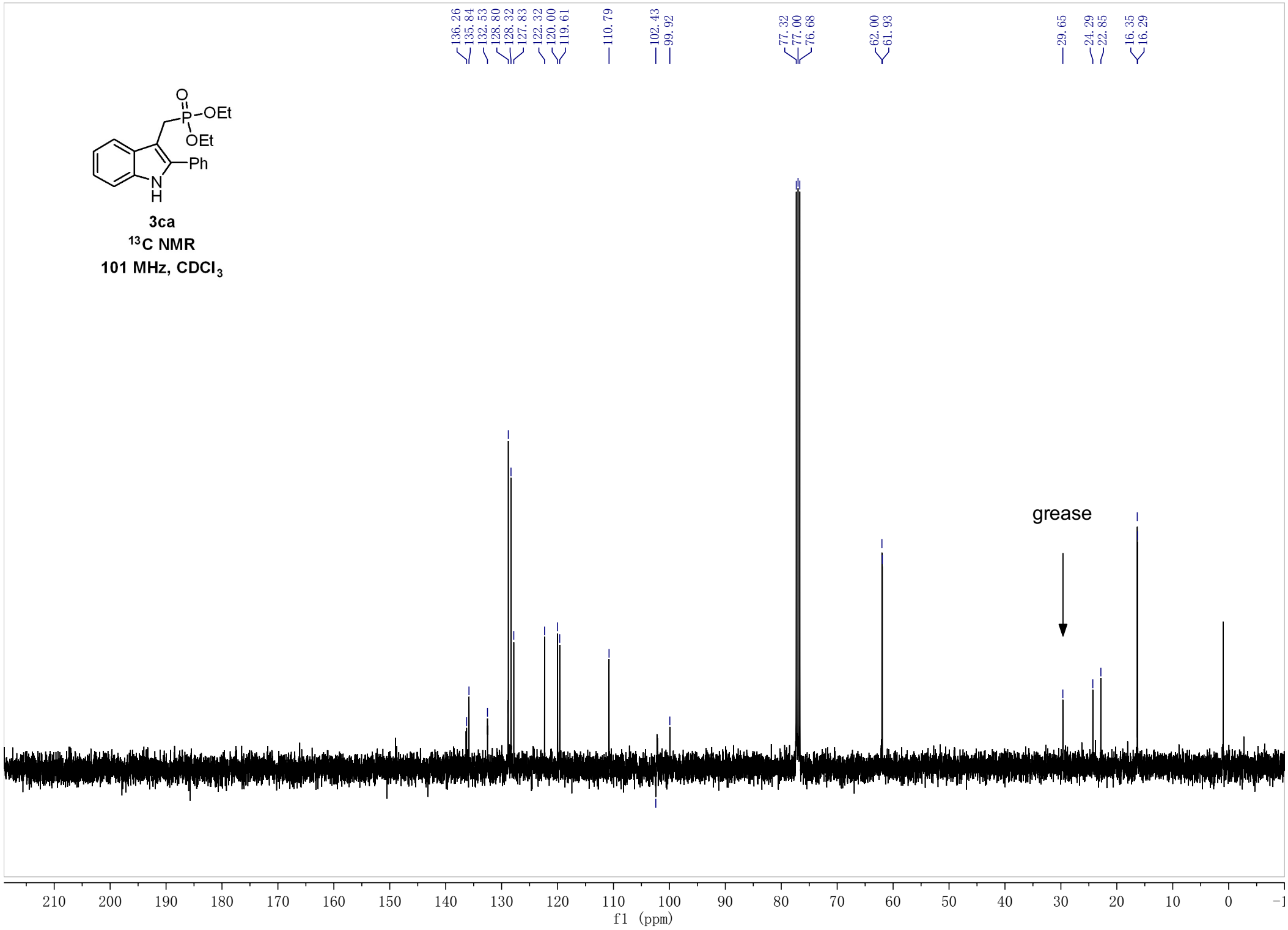

28.10
O
P
OEt
OEt
N
H
3aa
31P NMR
162 MHz, CDCl3
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

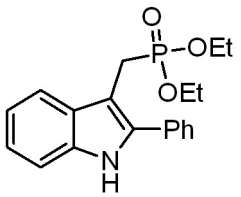

8.65
8.59
7.54
7.53
7.53
7.52
7.51
7.26
7.22
7.21
7.21
7.20
7.20
7.10
7.08
7.07
7.06
7.06
4.05
4.03
4.02
4.01
4.00
3.99
3.99
3.98
3.97
3.96
3.95
3.94
3.93
3.92
3.90
3.26
3.21
2.28
2.27
2.26
1.23
1.21
1.19
O
P
OEt
OEt
Me
N
H
3ba
1H NMR
400 MHz, CDCl3
1.00
1.03
1.03
2.12
4.15
2.11
3.15
6.32
f1 (ppm)


135.20
133.30
128.40
120.82
119.07
118.08
110.34
99.92
77.32
77.00
76.68
61.93
61.86
23.39
21.95
16.39
16.33
11.62
O
P
OEt
OEt
Me
N
H
3ba
13C NMR
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


27.70
O
P
OEt
OEt
Me
N
H
3ba
31P NMR
162 MHz, CDCl3
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)


8.77
8.70
7.78
7.76
7.45
7.43
7.42
7.37
7.35
7.33
7.26
7.21
7.19
7.17
7.16
7.14
7.12
4.06
4.04
4.02
4.02
4.00
4.00
3.98
3.96
3.94
3.92
3.91
3.90
3.88
3.44
3.39
1.20
1.19
1.17
O
P
OEt
OEt
Ph
N
H
3ca
1H NMR
400 MHz, CDCl3
0.96
3.01
2.03
1.98
2.05
4.08
2.00
6.25
f1 (ppm)


136.26
135.84
132.53
128.80
128.32
127.83
122.32
120.00
119.61
110.79
102.43
99.92
77.32
77.00
76.68
62.00
61.93
29.65
24.29
22.85
16.35
16.29
O
P
OEt
OEt
Ph
N
H
3ca
13C NMR
101 MHz, CDCl3
grease
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)



3ca

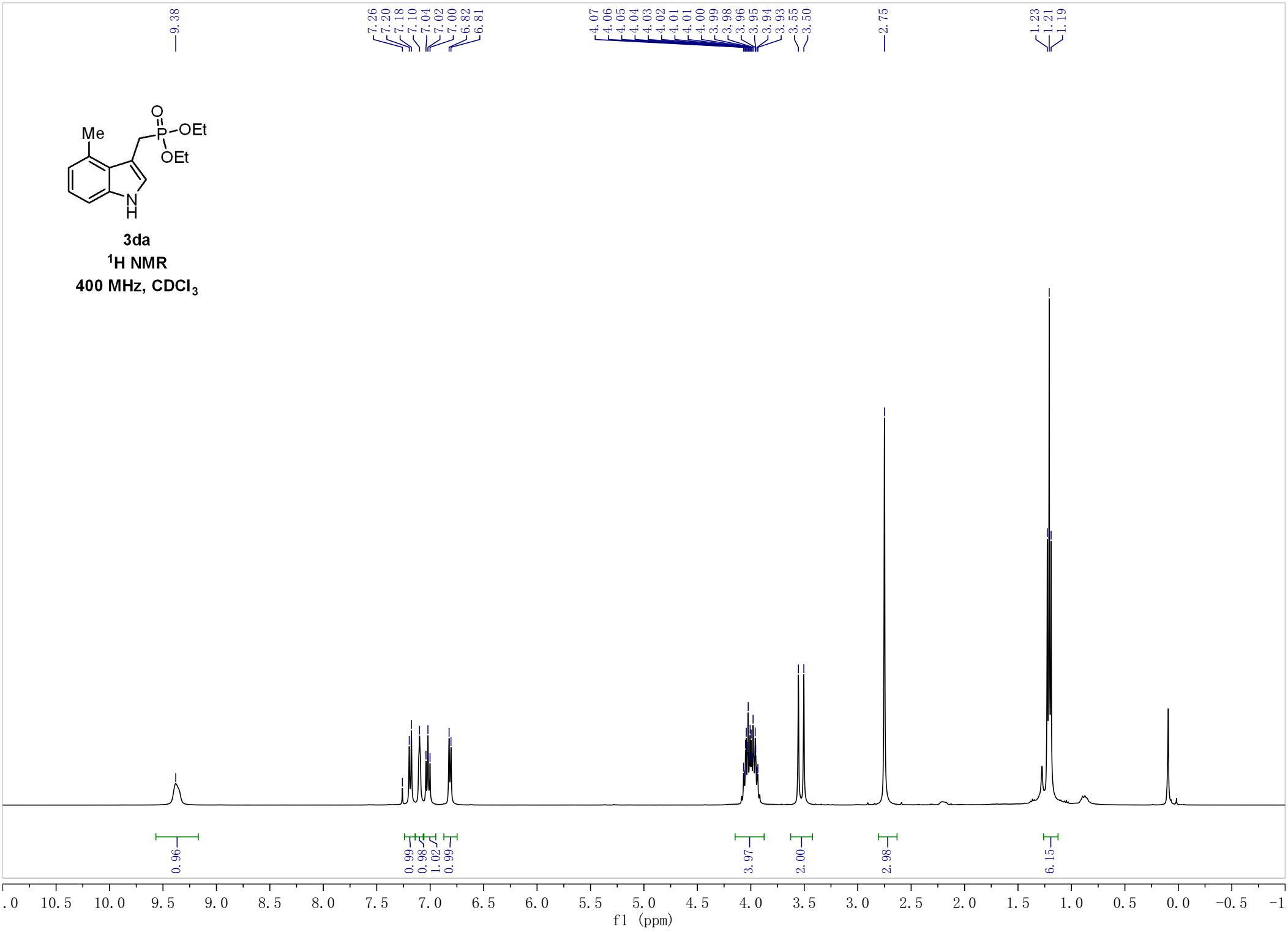
^{31}P NMR

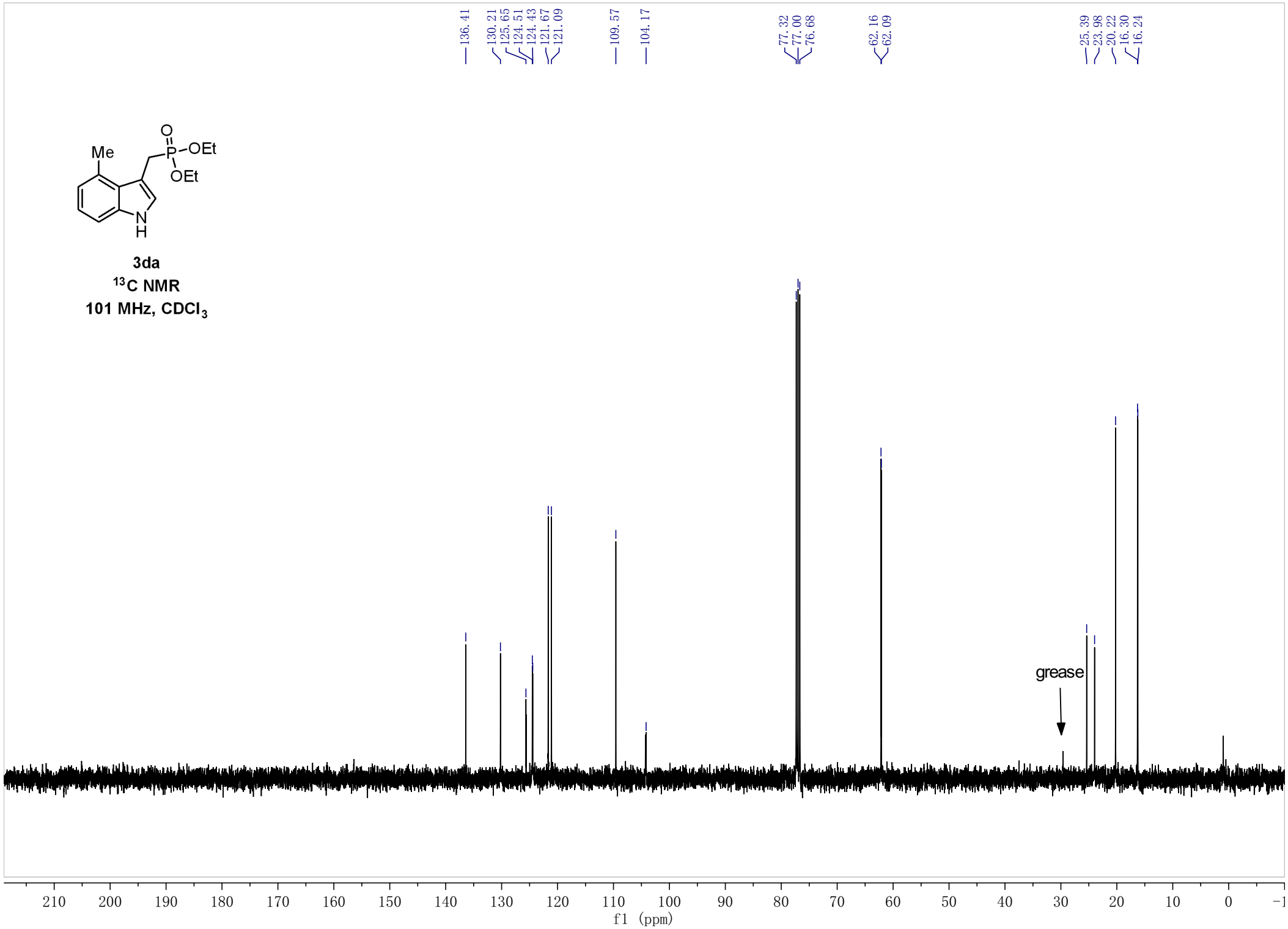
162 MHz, $CDCl_3$

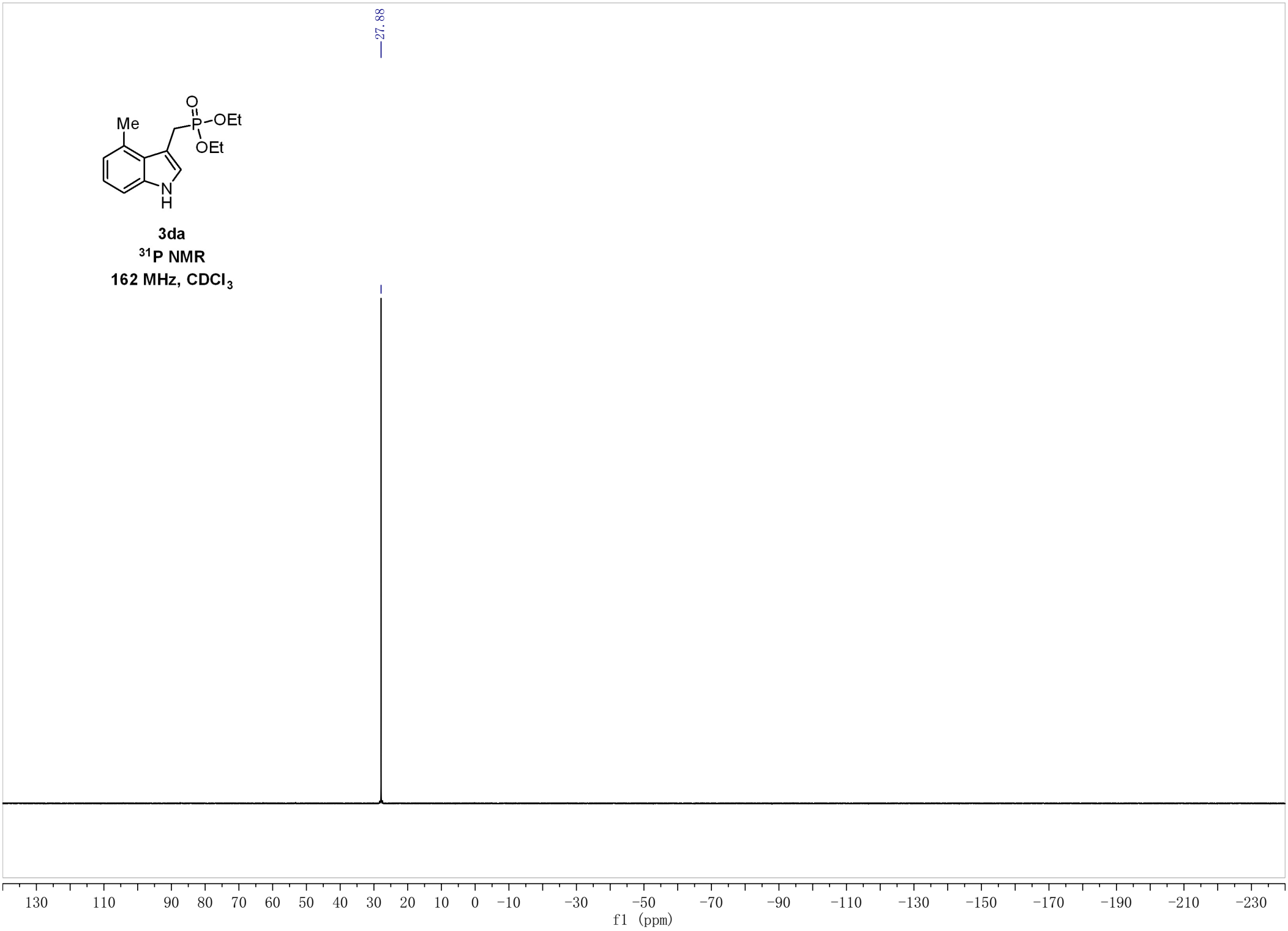
27.48

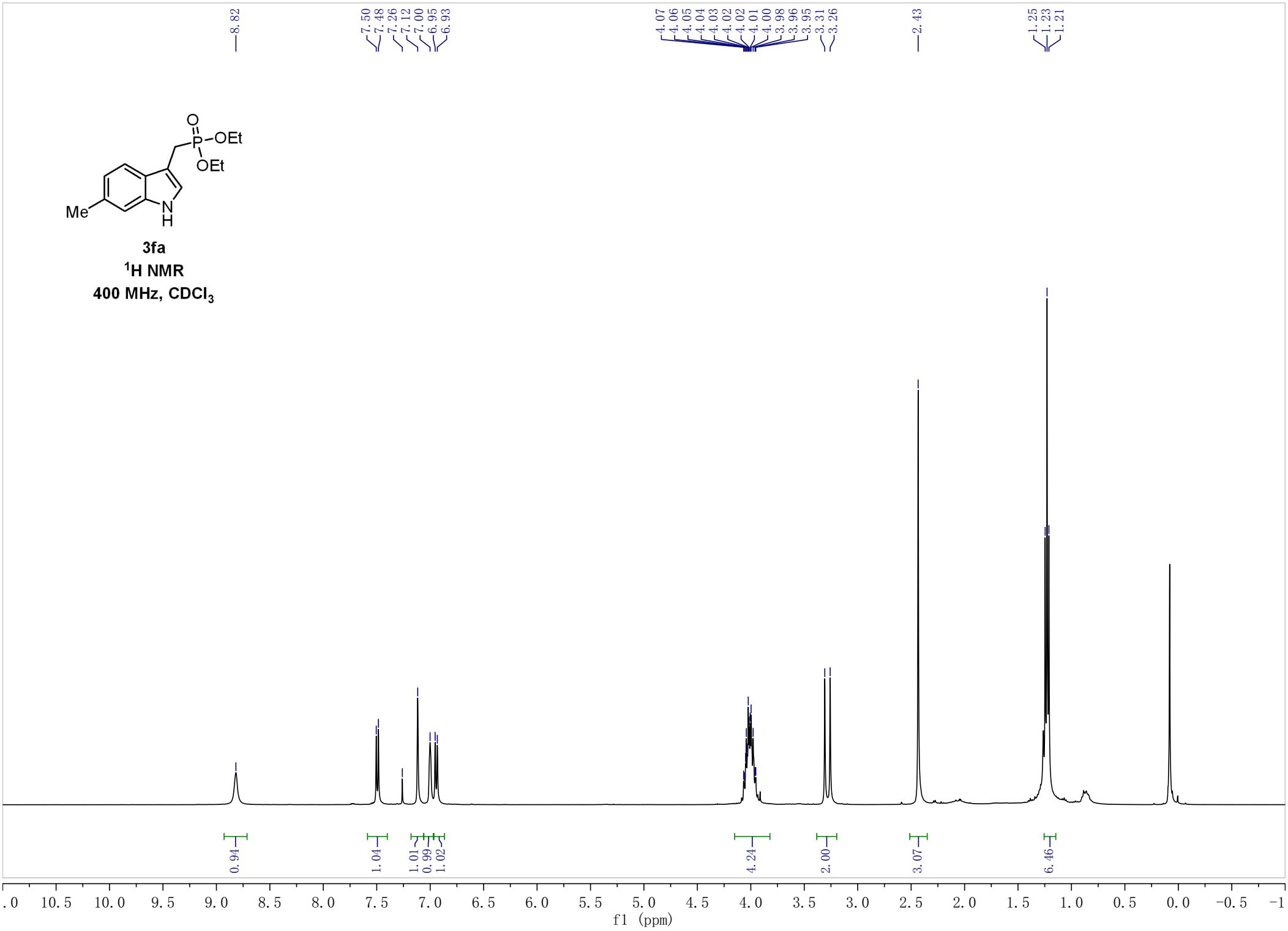
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230

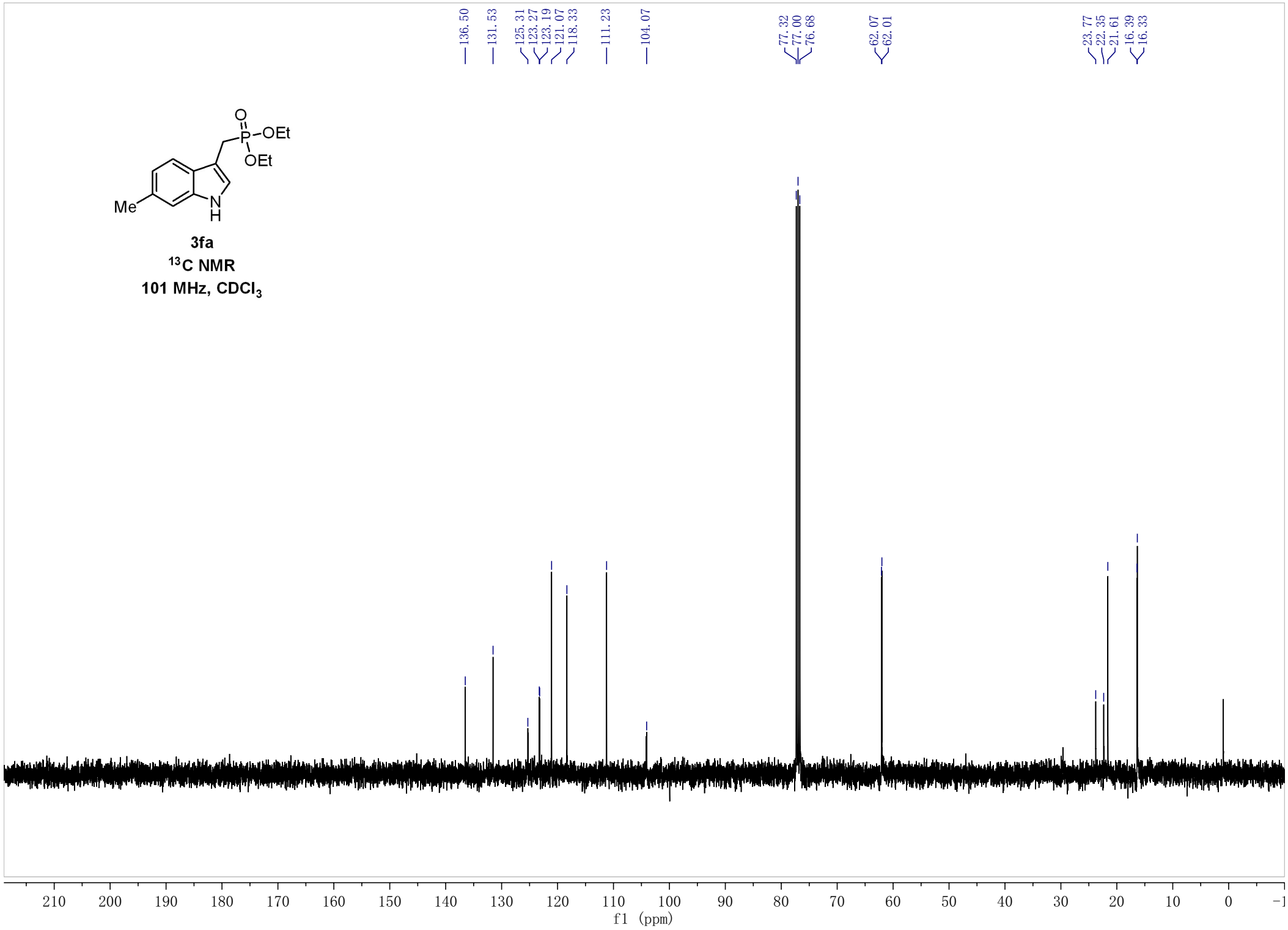
f1 (ppm)

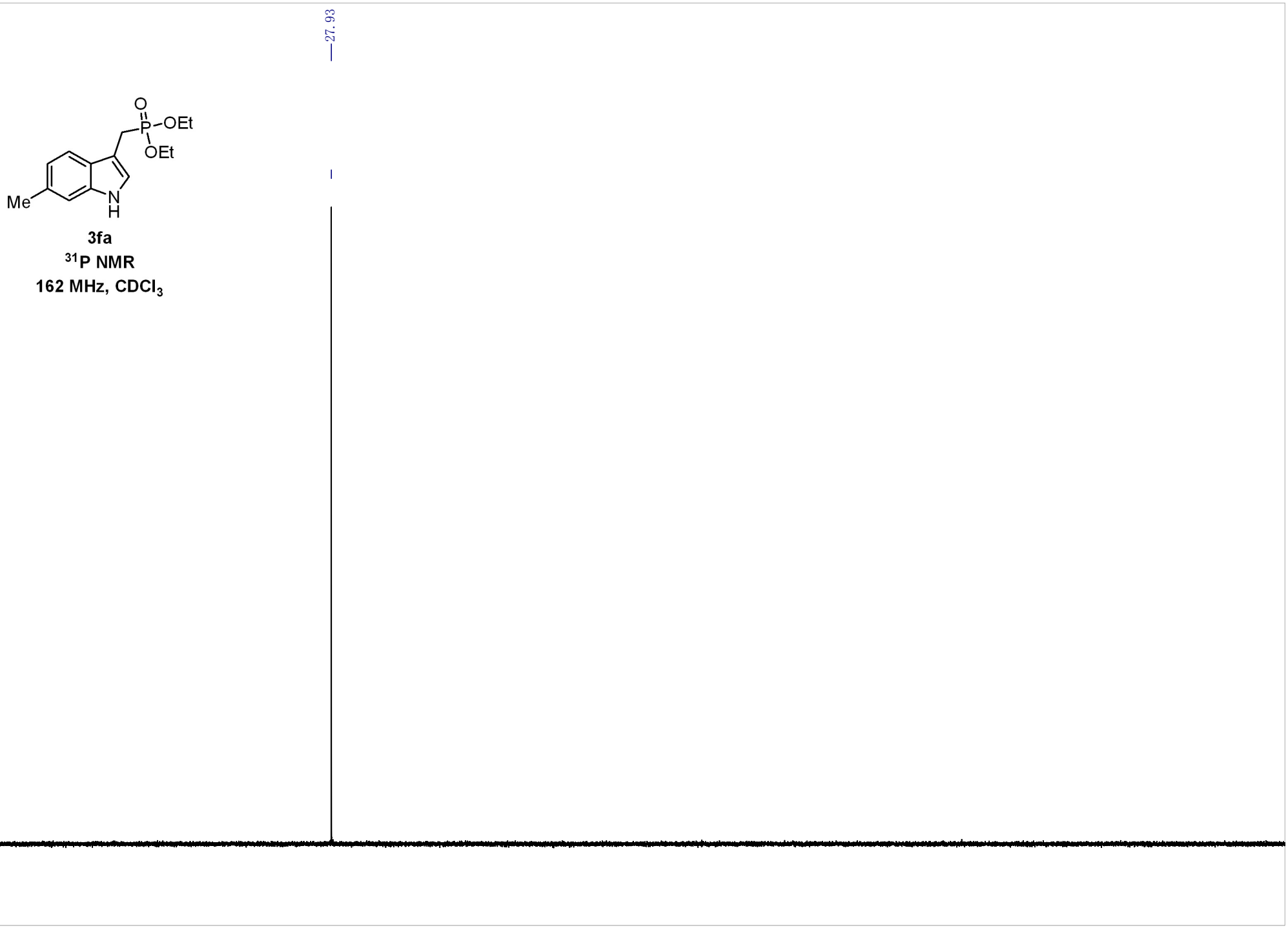

9.38
7.26
7.20
7.18
7.10
7.04
7.02
7.00
6.82
6.81
4.07
4.06
4.05
4.04
4.03
4.02
4.01
4.01
4.00
3.99
3.98
3.96
3.95
3.94
3.93
3.55
3.50
2.75
1.23
1.21
1.19
Me
O
P
OEt
OEt
N
H
3da
1H NMR
400 MHz, CDCl3
0.96
0.99
0.98
1.02
0.99
3.97
2.00
2.98
6.15
f1 (ppm)

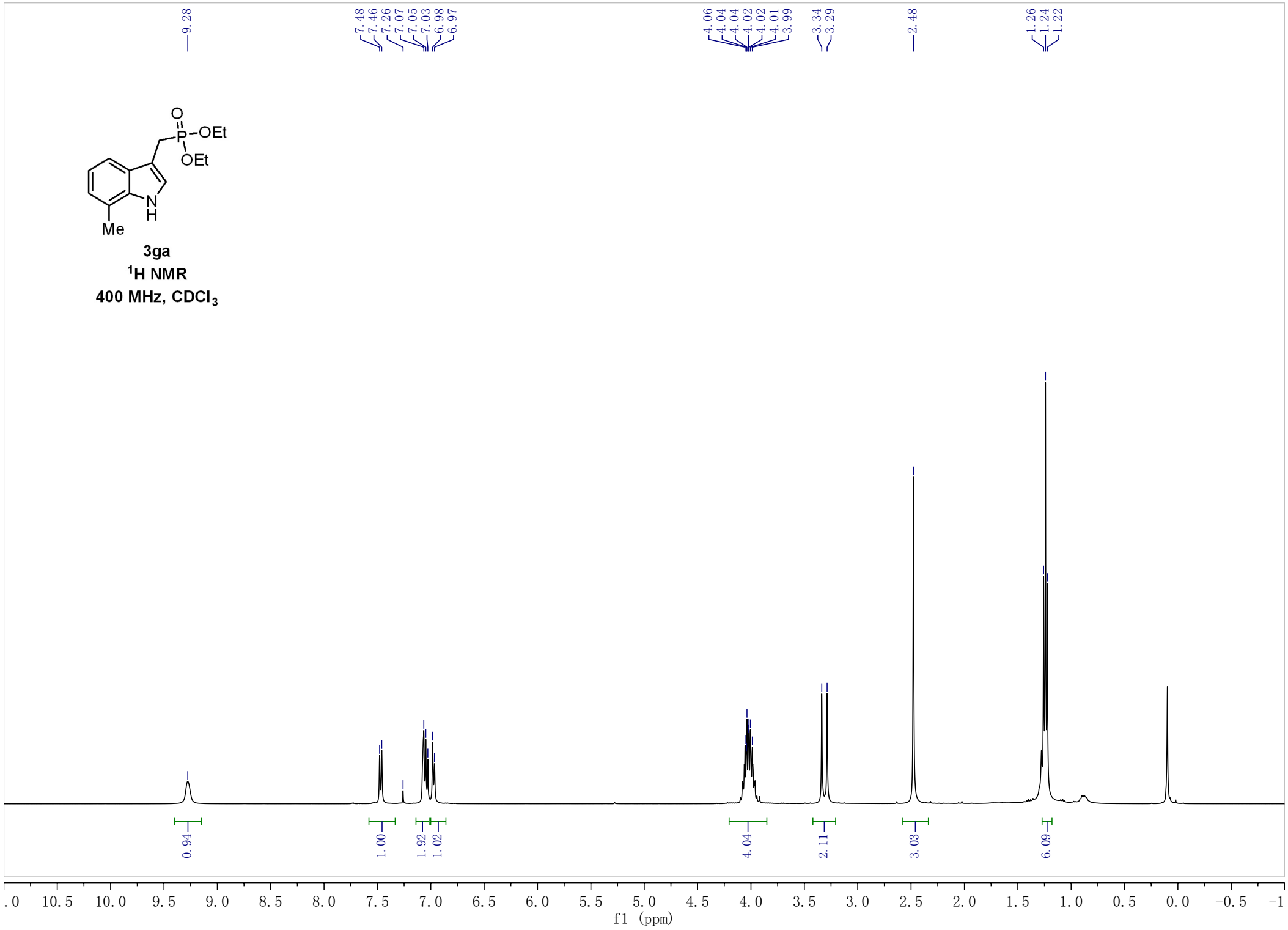

136.41
130.21
125.65
124.51
124.43
121.67
121.09
109.57
104.17
77.32
77.00
76.68
62.16
62.09
25.39
23.98
20.22
16.30
16.24
Me
O
P
OEt
OEt
N
H
3da
13C NMR
101 MHz, CDCl3
grease
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

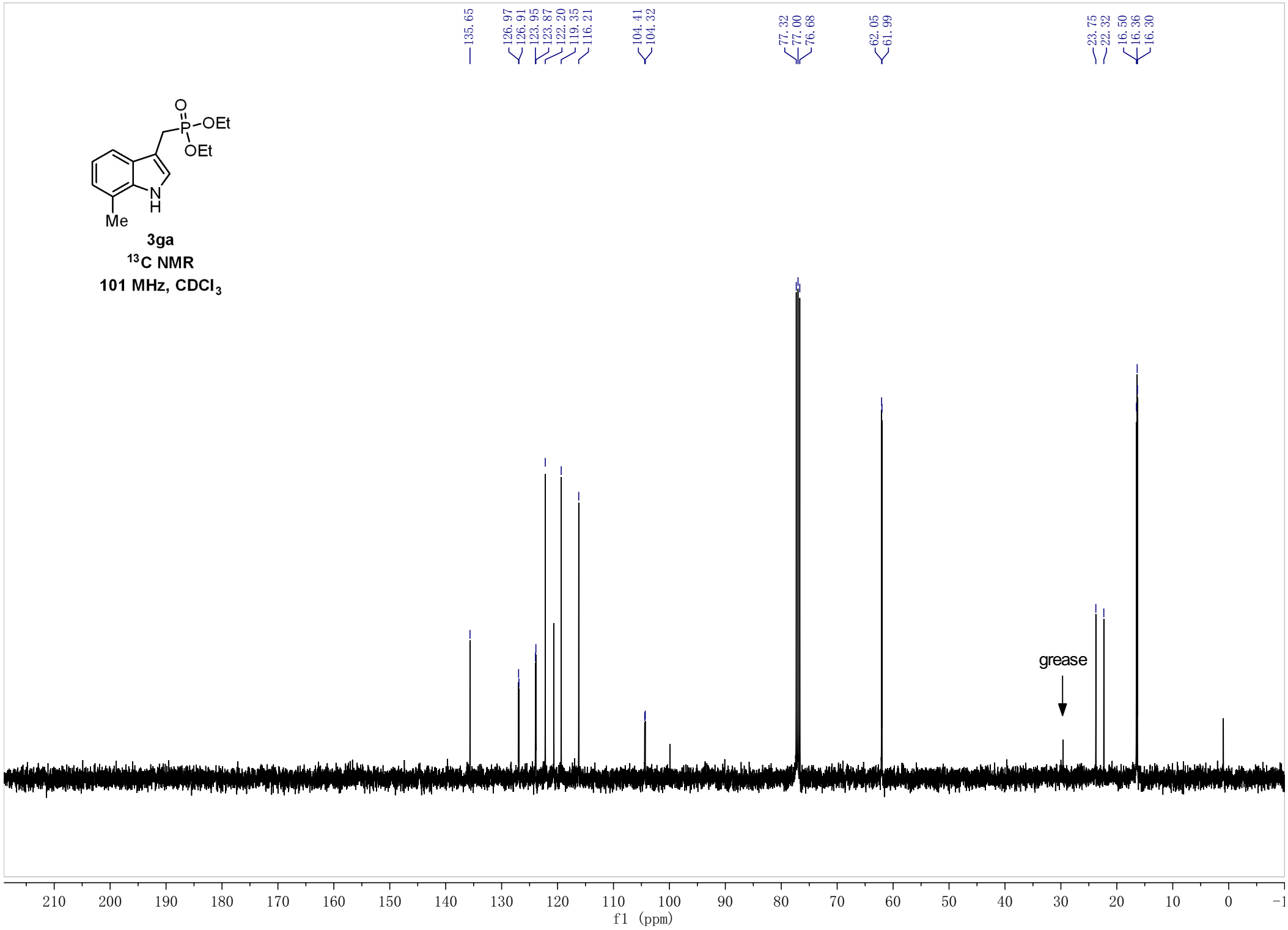

27.88
Me
O
P
OEt
OEt
N
H
3da
31P NMR
162 MHz, CDCl3
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

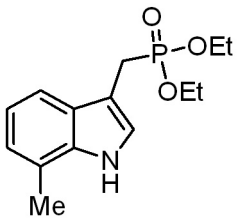

8.82
7.50
7.48
7.26
7.12
7.00
6.95
6.93
4.07
4.06
4.05
4.04
4.03
4.02
4.02
4.01
4.00
3.98
3.96
3.95
3.31
3.26
2.43
1.25
1.23
1.21
O
P
OEt
OEt
Me
N
H
3fa
1H NMR
400 MHz, CDCl3
0.94
1.04
1.01
0.99
1.02
4.24
2.00
3.07
6.46
f1 (ppm)


136.50
131.53
125.31
123.27
123.19
121.07
118.33
111.23
104.07
77.32
77.00
76.68
62.07
62.01
23.77
22.35
21.61
16.39
16.33
O
P
OEt
OEt
Me
N
H
3fa
13C NMR
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


27.93
O
P
OEt
OEt
Me
N
H
3fa
31P NMR
162 MHz, CDCl3
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)


9.28
7.48
7.46
7.26
7.07
7.05
7.03
6.98
6.97
4.06
4.04
4.04
4.02
4.02
4.01
3.99
3.34
3.29
2.48
1.26
1.24
1.22
O
P
OEt
OEt
N
H
Me
3ga
1H NMR
400 MHz, CDCl3
0.94
1.00
1.92
1.02
4.04
2.11
3.03
6.09
f1 (ppm)


135.65
126.97
126.91
123.95
123.87
122.20
119.35
116.21
104.41
104.32
77.32
77.00
76.68
62.05
61.99
23.75
22.32
16.50
16.36
16.30
O
P
OEt
OEt
N
H
Me
3ga
13C NMR
101 MHz, CDCl3
grease
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)



3ga

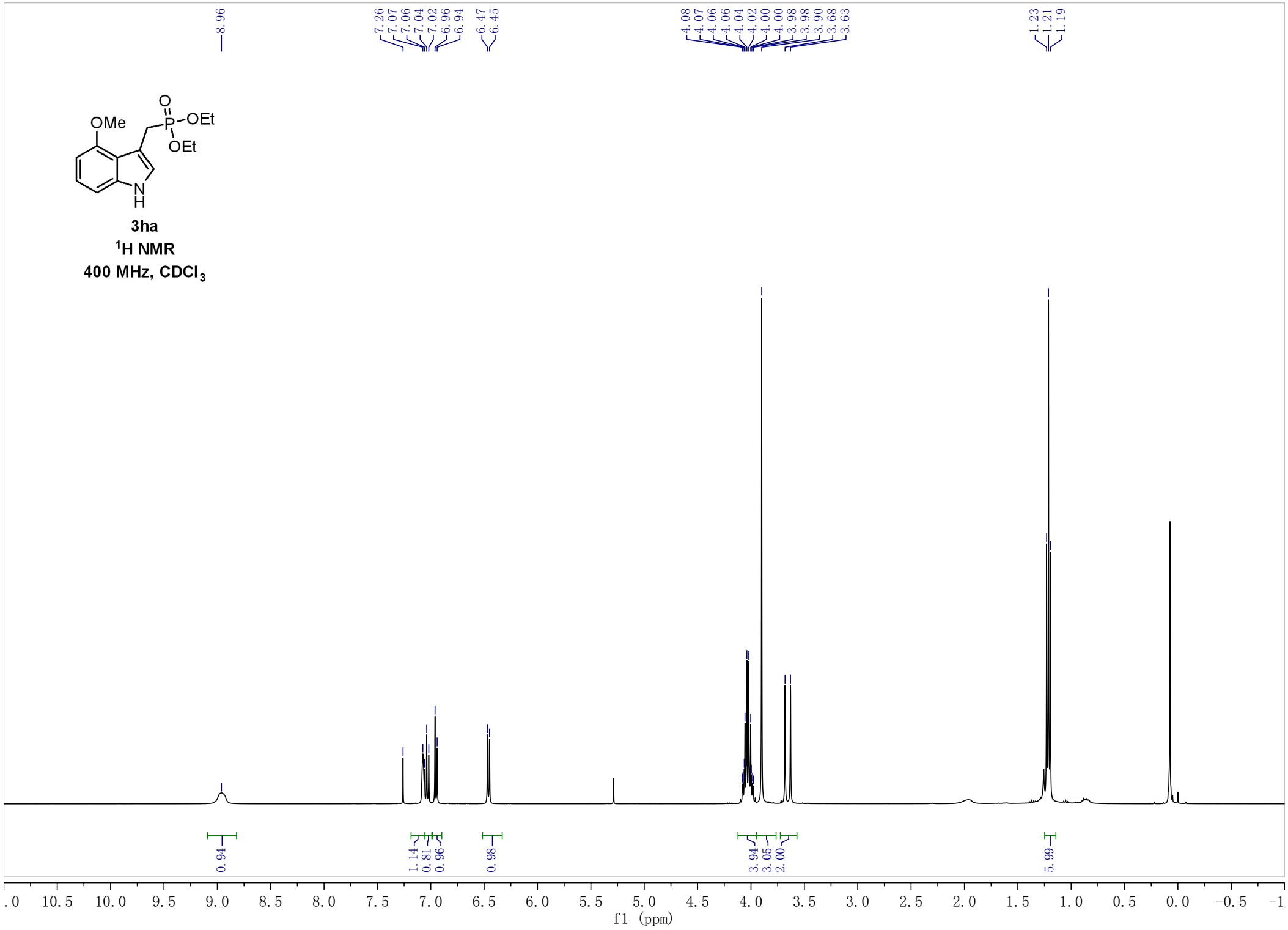
^{31}P NMR

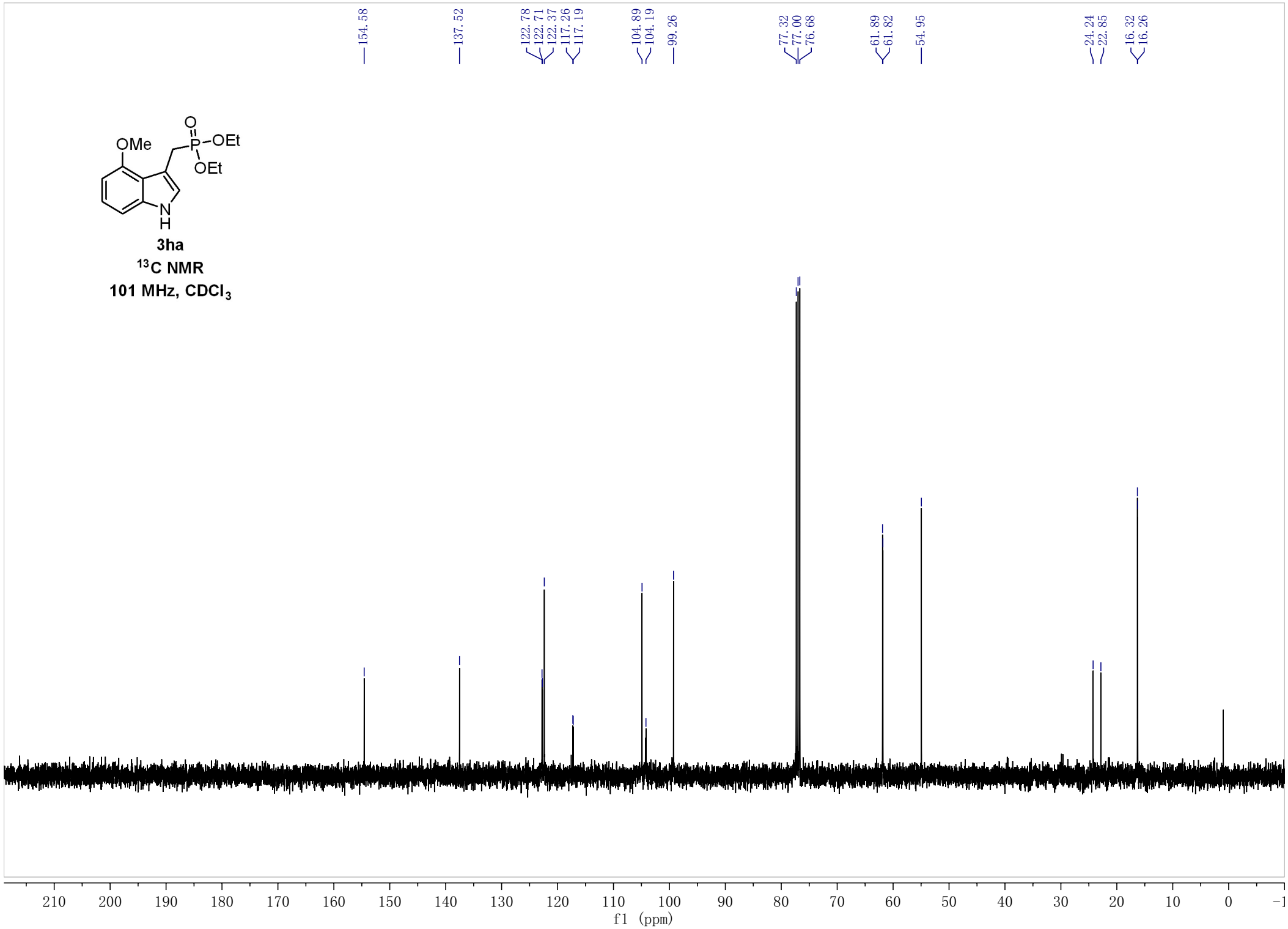
162 MHz, $CDCl_3$

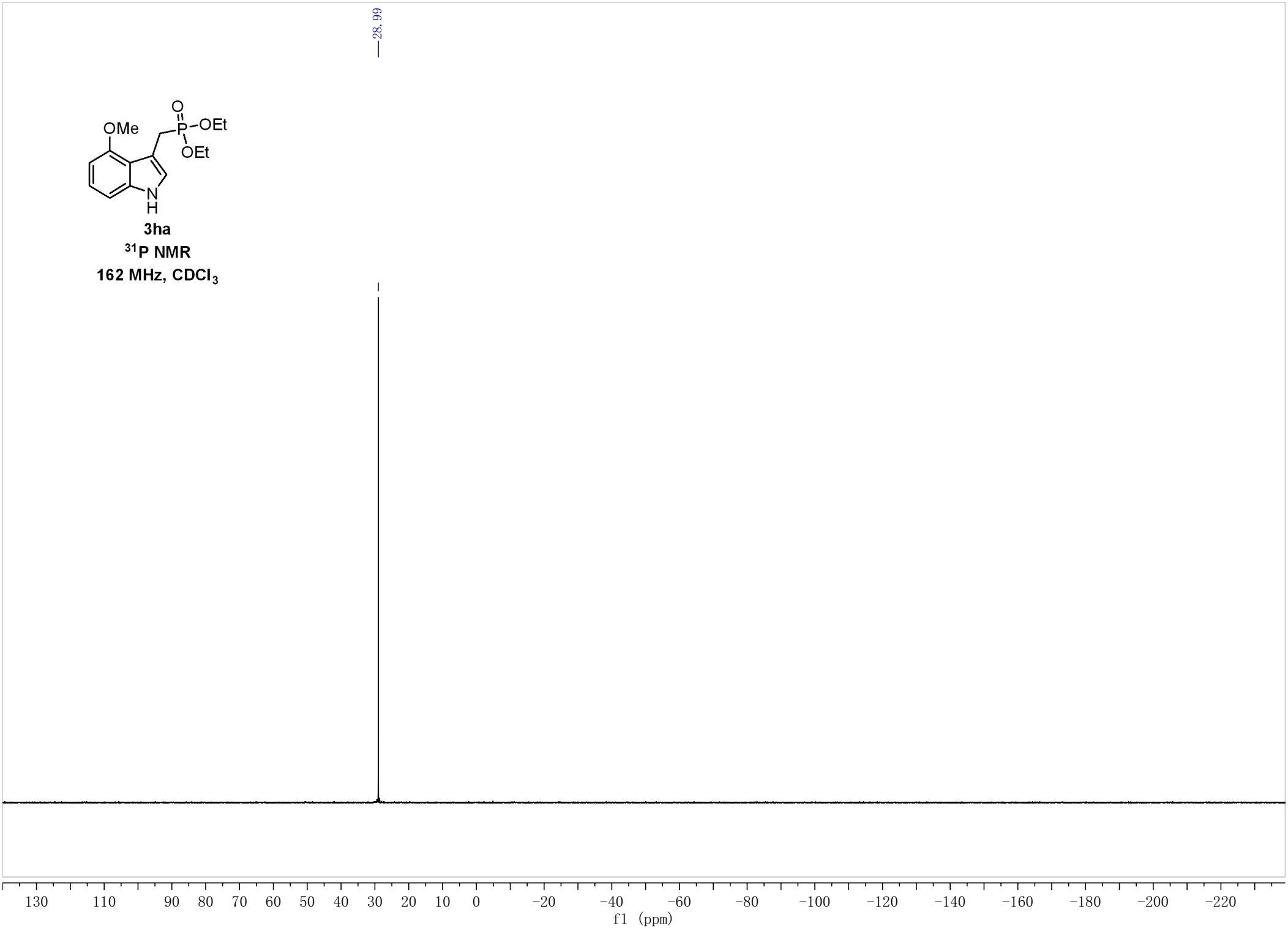
28.01

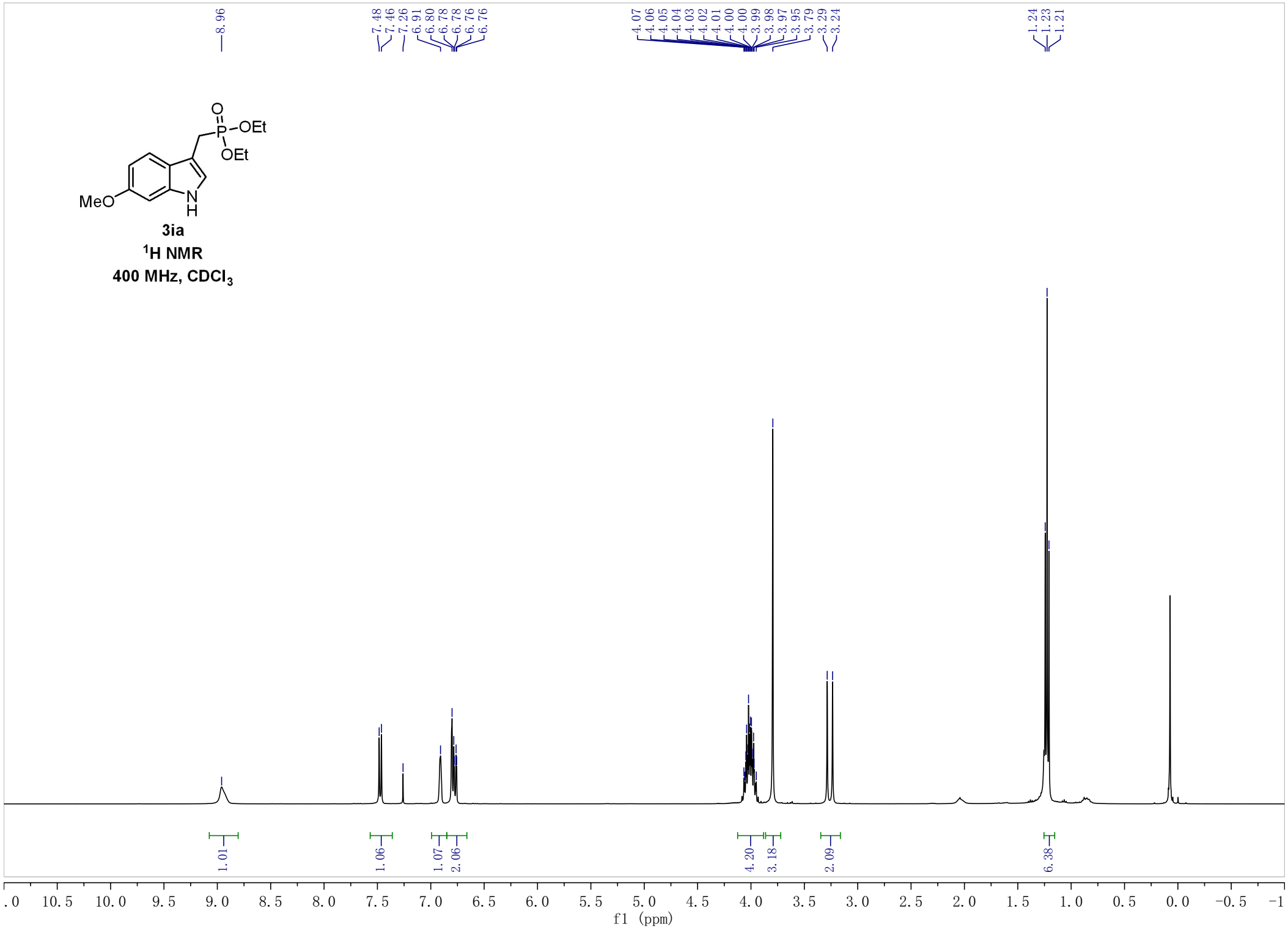
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230

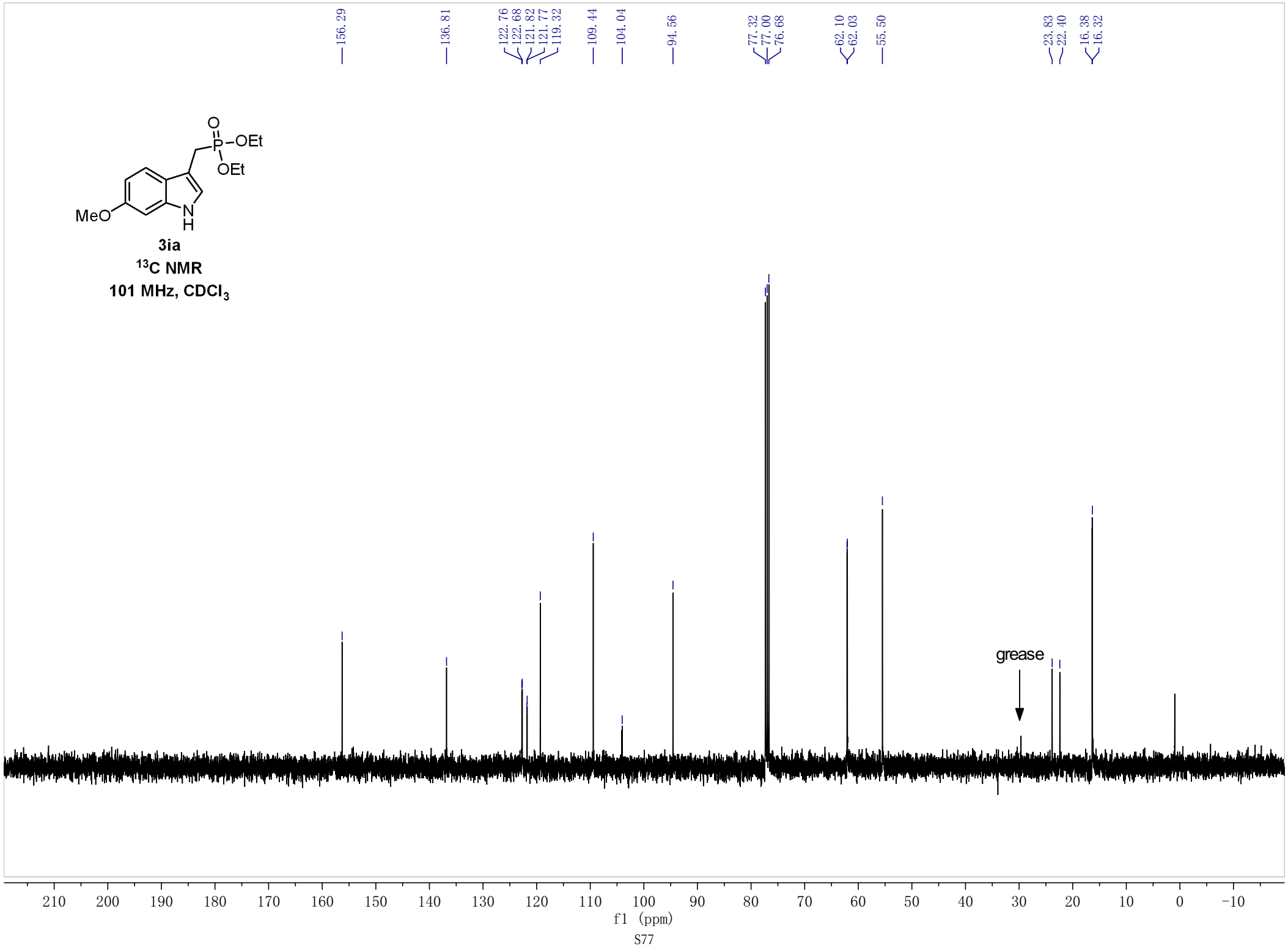
f1 (ppm)

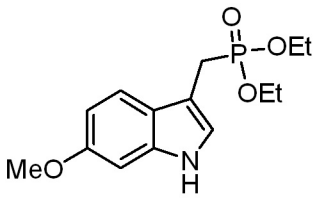

8.96
7.26
7.07
7.06
7.04
7.02
6.96
6.94
6.47
6.45
4.08
4.07
4.06
4.06
4.04
4.02
4.00
4.00
3.98
3.98
3.90
3.68
3.63
1.23
1.21
1.19
OMe
O
P
OEt
OEt
N
H
3ha
1H NMR
400 MHz, CDCl3
0.94
1.14
0.81
0.96
0.98
3.94
3.05
2.00
5.99
f1 (ppm)


154.58
137.52
122.78
122.71
122.37
117.26
117.19
104.89
104.19
99.26
77.32
77.00
76.68
61.89
61.82
54.95
24.24
22.85
16.32
16.26
OMe
O
P
OEt
OEt
N
H
3ha
13C NMR
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


28.99
OMe
O
P
OEt
OEt
N
H
3ha
31P NMR
162 MHz, CDCl3
130
110
90
80
70
60
50
40
30
20
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
f1 (ppm)


8.96
7.48
7.46
7.26
6.91
6.80
6.78
6.78
6.76
6.76
4.07
4.06
4.05
4.04
4.03
4.02
4.01
4.00
4.00
3.99
3.98
3.97
3.95
3.79
3.29
3.24
1.24
1.23
1.21
O
P
OEt
OEt
MeO
N
H
3ia
1H NMR
400 MHz, CDCl3
1.01
1.06
1.07
2.06
4.20
3.18
2.09
6.38
f1 (ppm)


156.29
136.81
122.76
122.68
121.82
121.77
119.32
109.44
104.04
94.56
77.32
77.00
76.68
62.10
62.03
55.50
23.83
22.40
16.38
16.32
O
P
OEt
OEt
MeO
N
H
3ia
13C NMR
101 MHz, CDCl3
grease
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



3ia

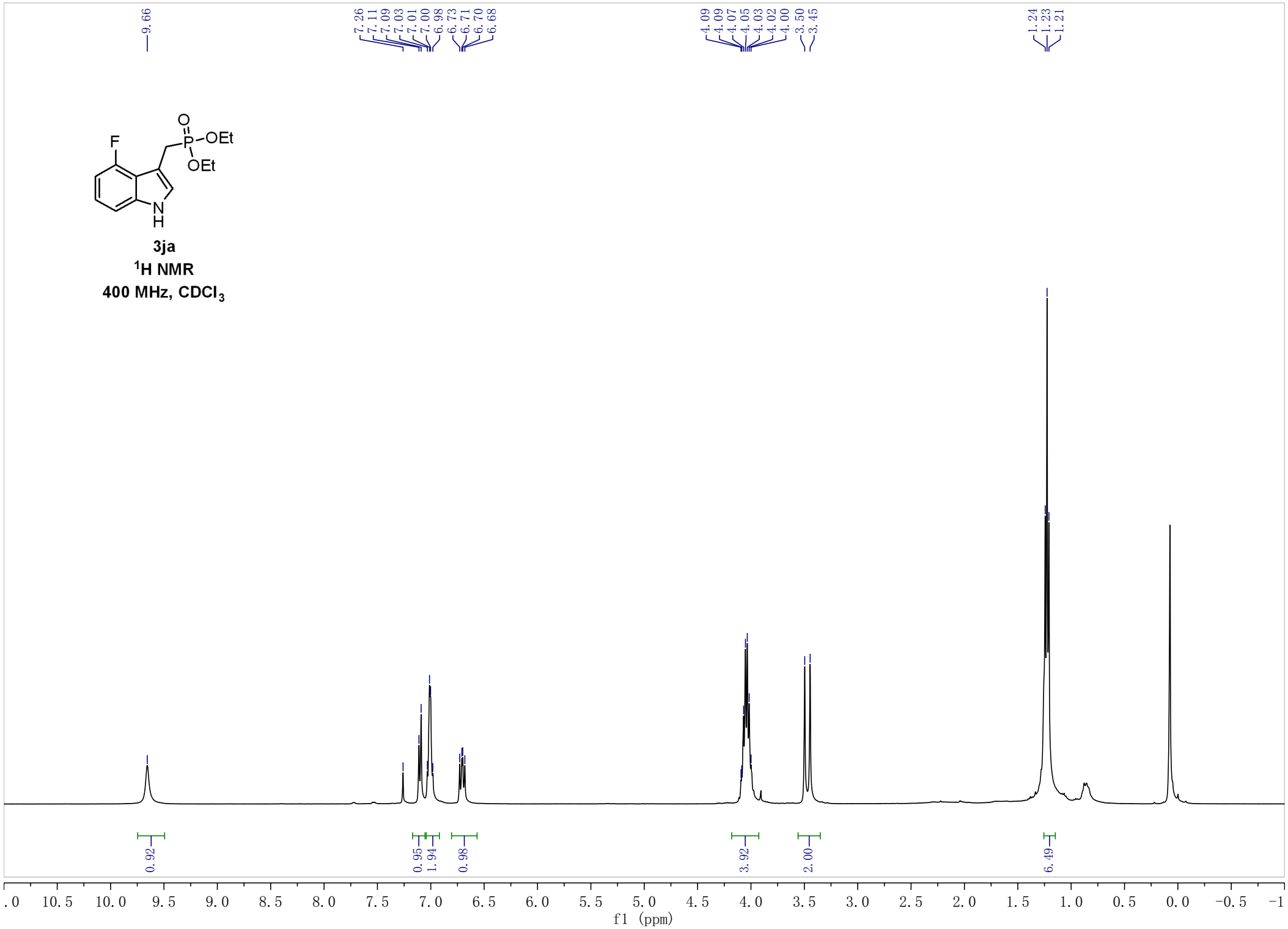
^{31}P NMR

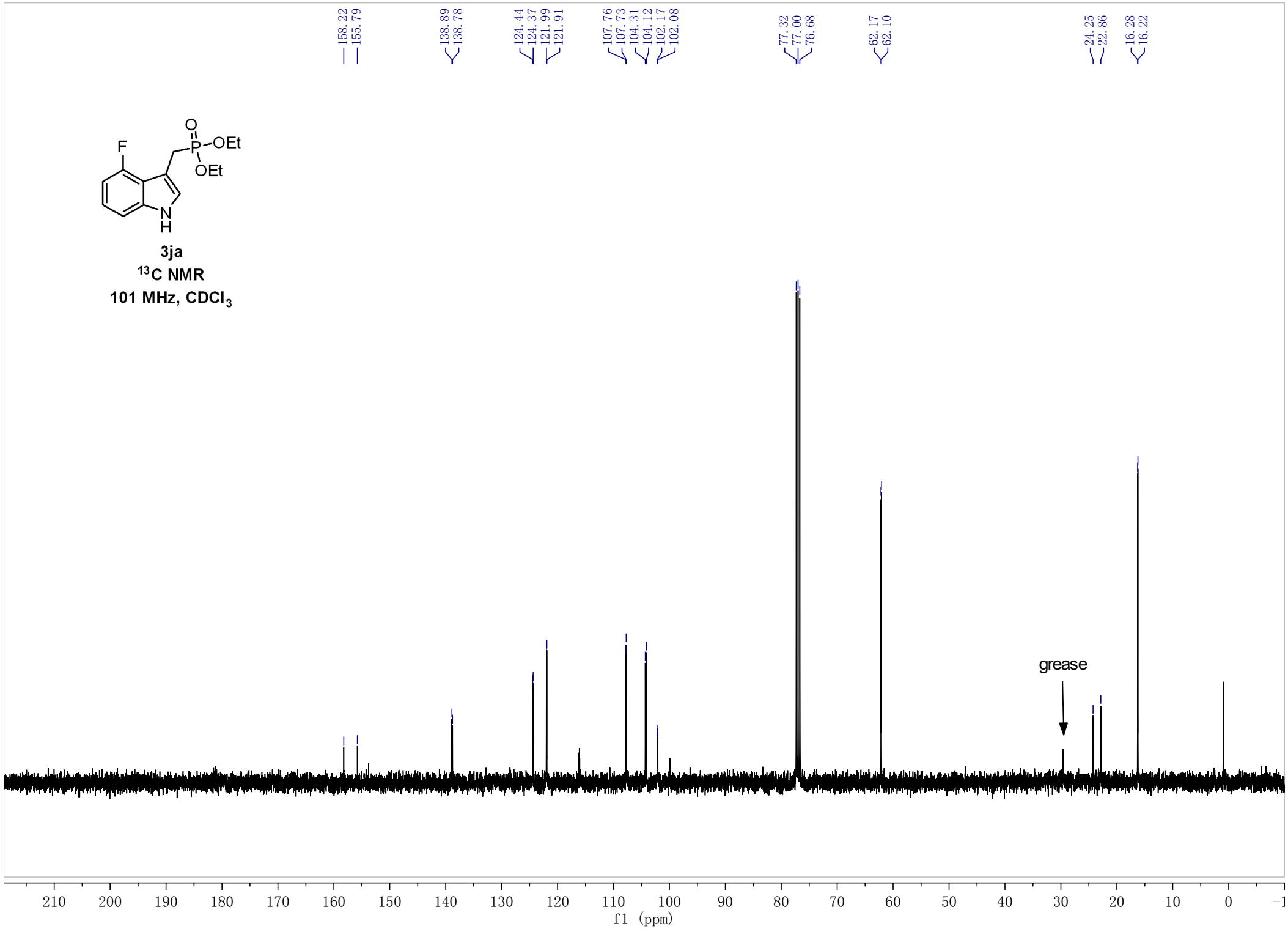
162 MHz, $CDCl_3$

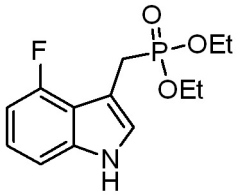
28.14

130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230

f1 (ppm)


9.66
7.26
7.11
7.09
7.03
7.01
7.00
6.98
6.73
6.71
6.70
6.68
4.09
4.09
4.07
4.05
4.03
4.02
4.00
3.50
3.45
1.24
1.23
1.21
F
O
P
OEt
OEt
N
H
3ja
1H NMR
400 MHz, CDCl3
0.92
0.95
1.94
0.98
3.92
2.00
6.49
f1 (ppm)

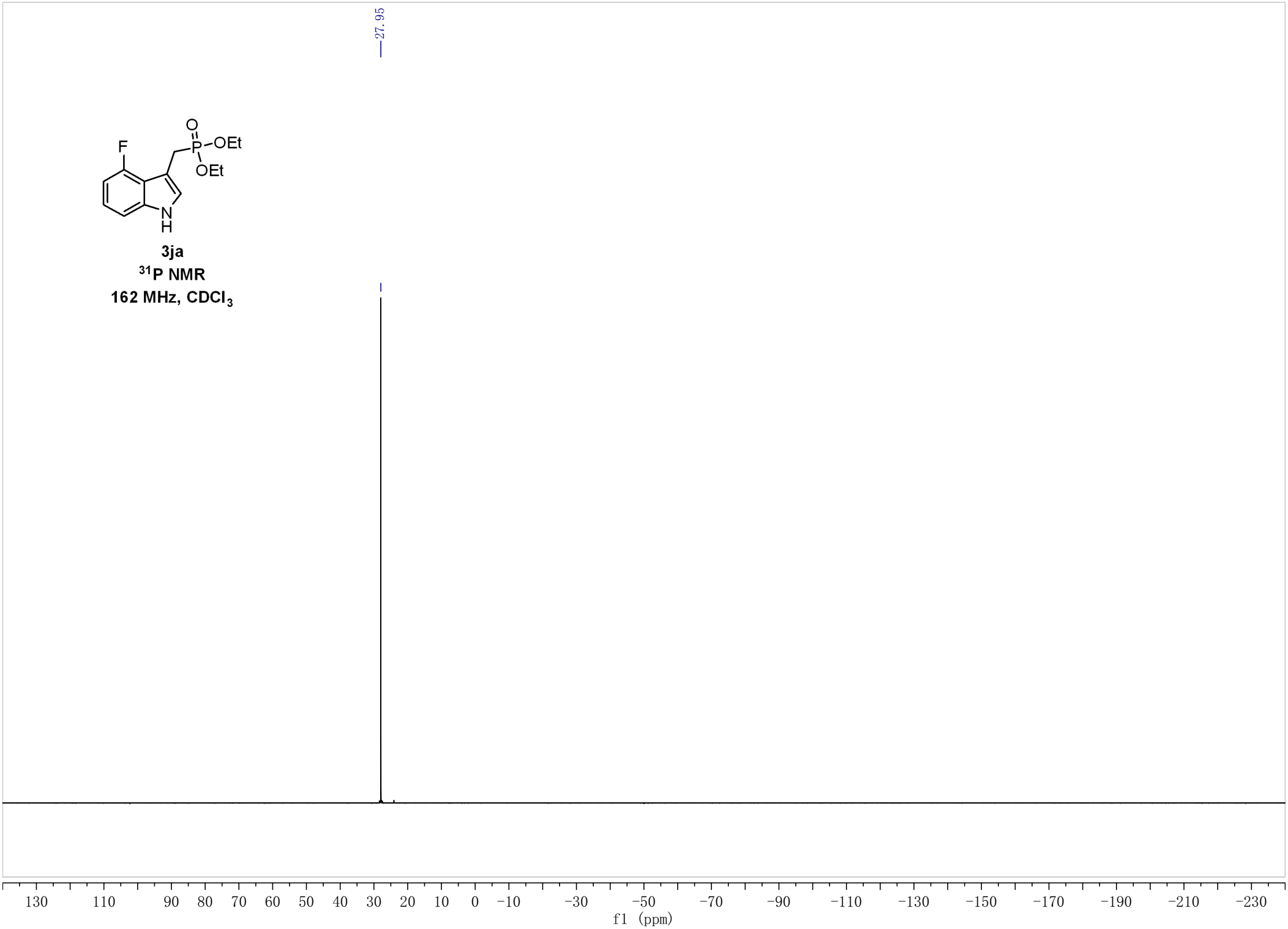

158.22
155.79
138.89
138.78
124.44
124.37
121.99
121.91
107.76
107.73
104.31
104.12
102.17
102.08
77.32
77.00
76.68
62.17
62.10
24.25
22.86
16.28
16.22
F
O
P
OEt
OEt
N
H
3ja
13C NMR
101 MHz, CDCl3
grease
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

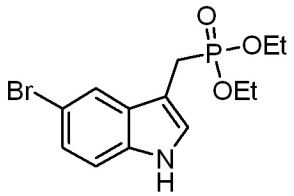


3ja

^{19}F NMR

376 MHz, $CDCl_3$

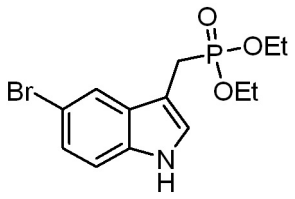

27.95
F
O
P
OEt
OEt
N
H
3ja
31P NMR
162 MHz, CDCl3
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)



3la

^{1}H NMR

400 MHz, $CDCl_3$



3Ia

^{13}C NMR

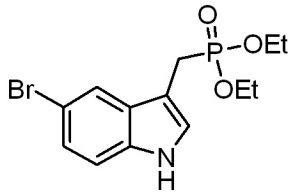
101 MHz, $CDCl_3$

134.76
128.96
125.27
124.59
121.44
112.88
112.54
103.91
77.32
77.00
76.68
62.24
62.17
29.67
23.77
22.33
16.41
16.35

grease

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

f1 (ppm)



3Ia

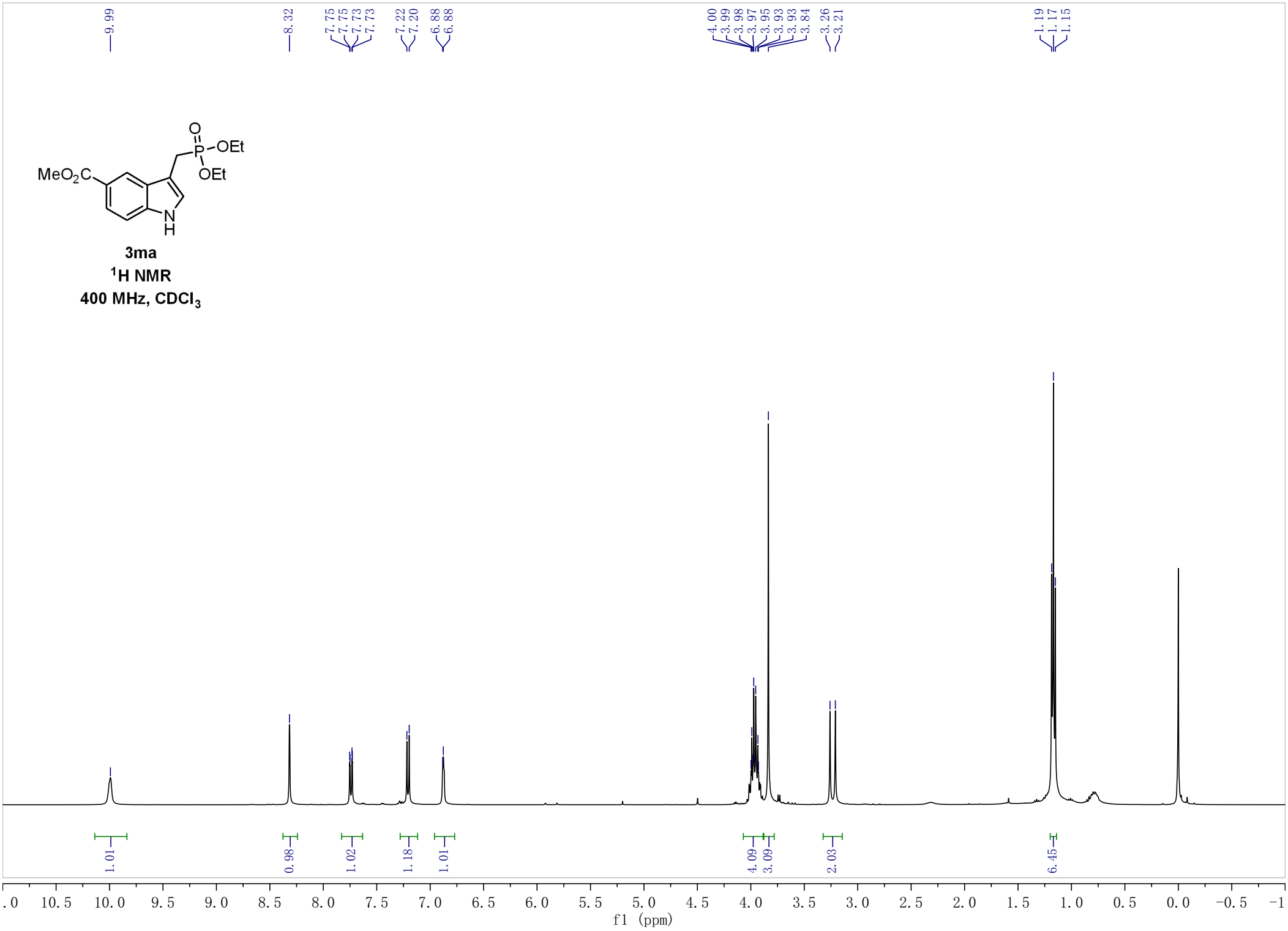
^{31}P NMR

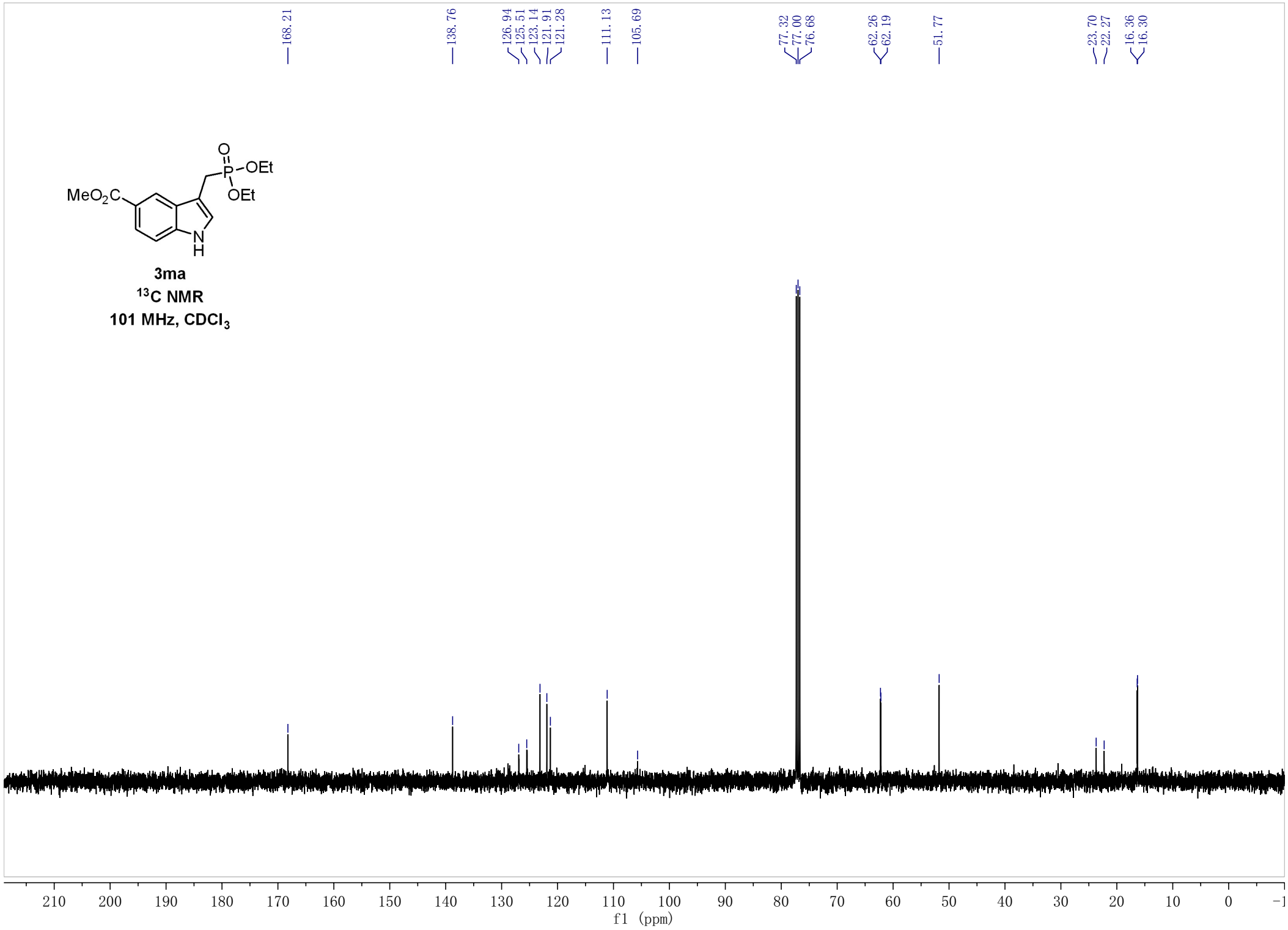
162 MHz, $CDCl_3$

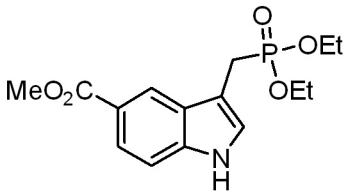
27.63

130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230

f1 (ppm)


9.99
8.32
7.75
7.75
7.73
7.73
7.22
7.20
6.88
6.88
4.00
3.99
3.98
3.97
3.95
3.93
3.93
3.84
3.26
3.21
1.19
1.17
1.15
MeO2C
O
P
OEt
OEt
N
H
3ma
1H NMR
400 MHz, CDCl3
1.01
0.98
1.02
1.18
1.01
4.09
3.09
2.03
6.45
f1 (ppm)


168.21
138.76
126.94
125.51
123.14
121.91
121.28
111.13
105.69
77.32
77.00
76.68
62.26
62.19
51.77
23.70
22.27
16.36
16.30
O
P
OEt
OEt
MeO2C
N
H
3ma
13C NMR
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)



3ma

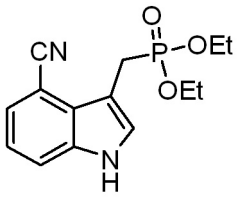
^{31}P NMR

162 MHz, $CDCl_3$

27.69

130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230

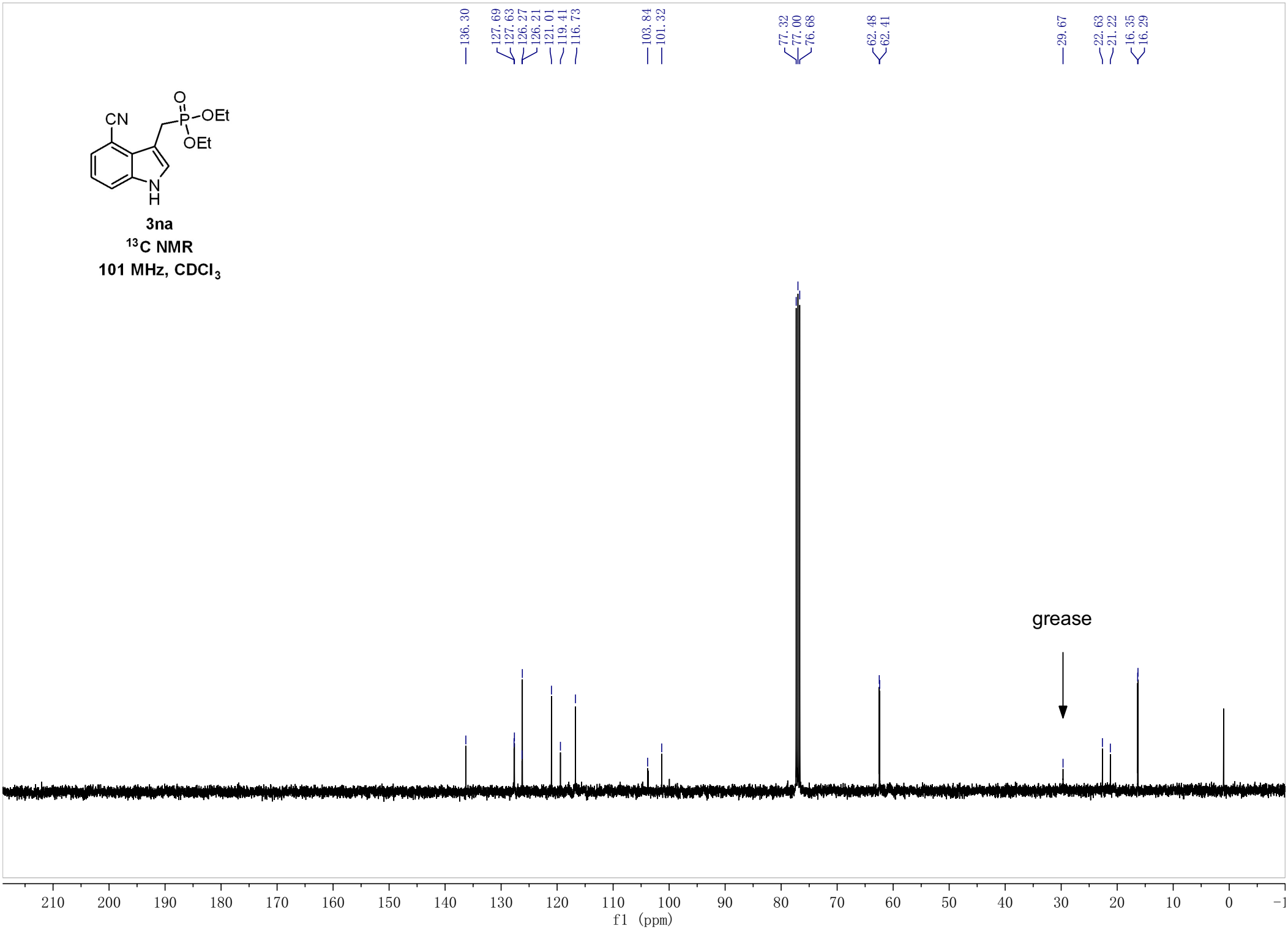
f1 (ppm)

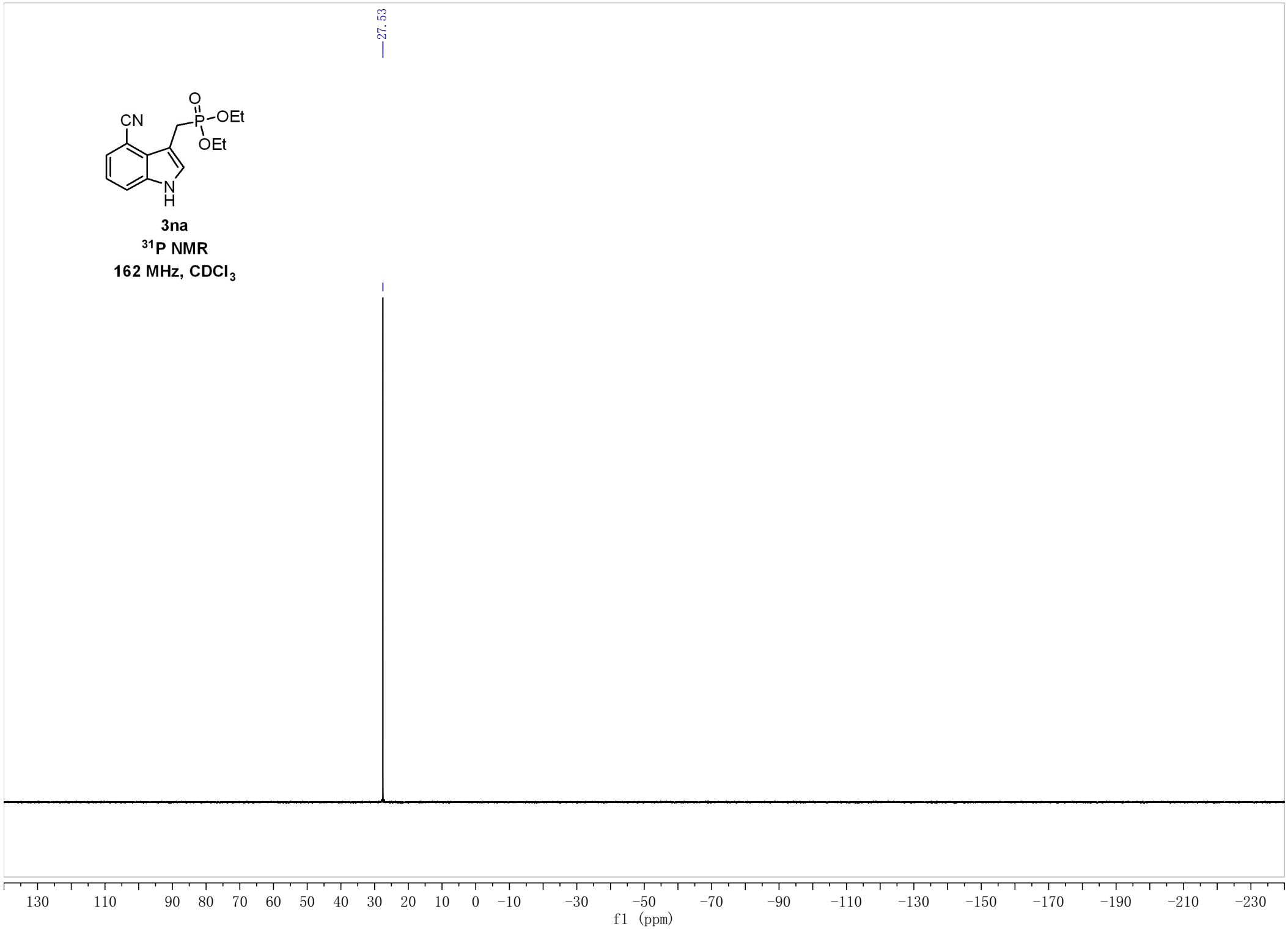


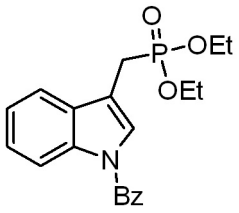
3na

^{1}H NMR

400 MHz, $CDCl_3$


136.30
127.69
127.63
126.27
126.21
121.01
119.41
116.73
103.84
101.32
77.32
77.00
76.68
62.48
62.41
29.67
22.63
21.22
16.35
16.29
CN
O
P
OEt
OEt
N
H
3na
13C NMR
101 MHz, CDCl3
grease
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

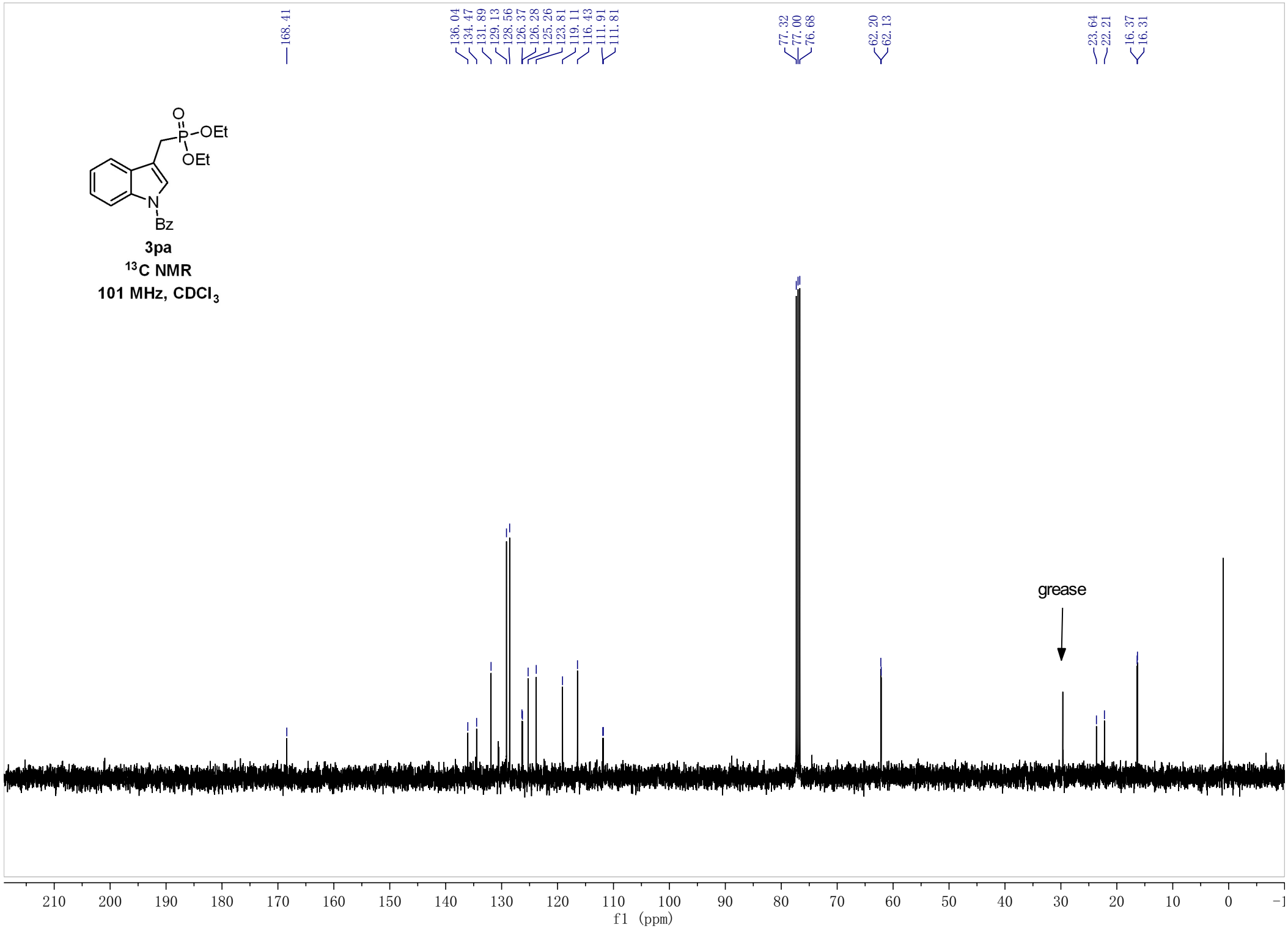

27.53
CN
O
P
OEt
OEt
N
H
3na
31P NMR
162 MHz, CDCl3
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

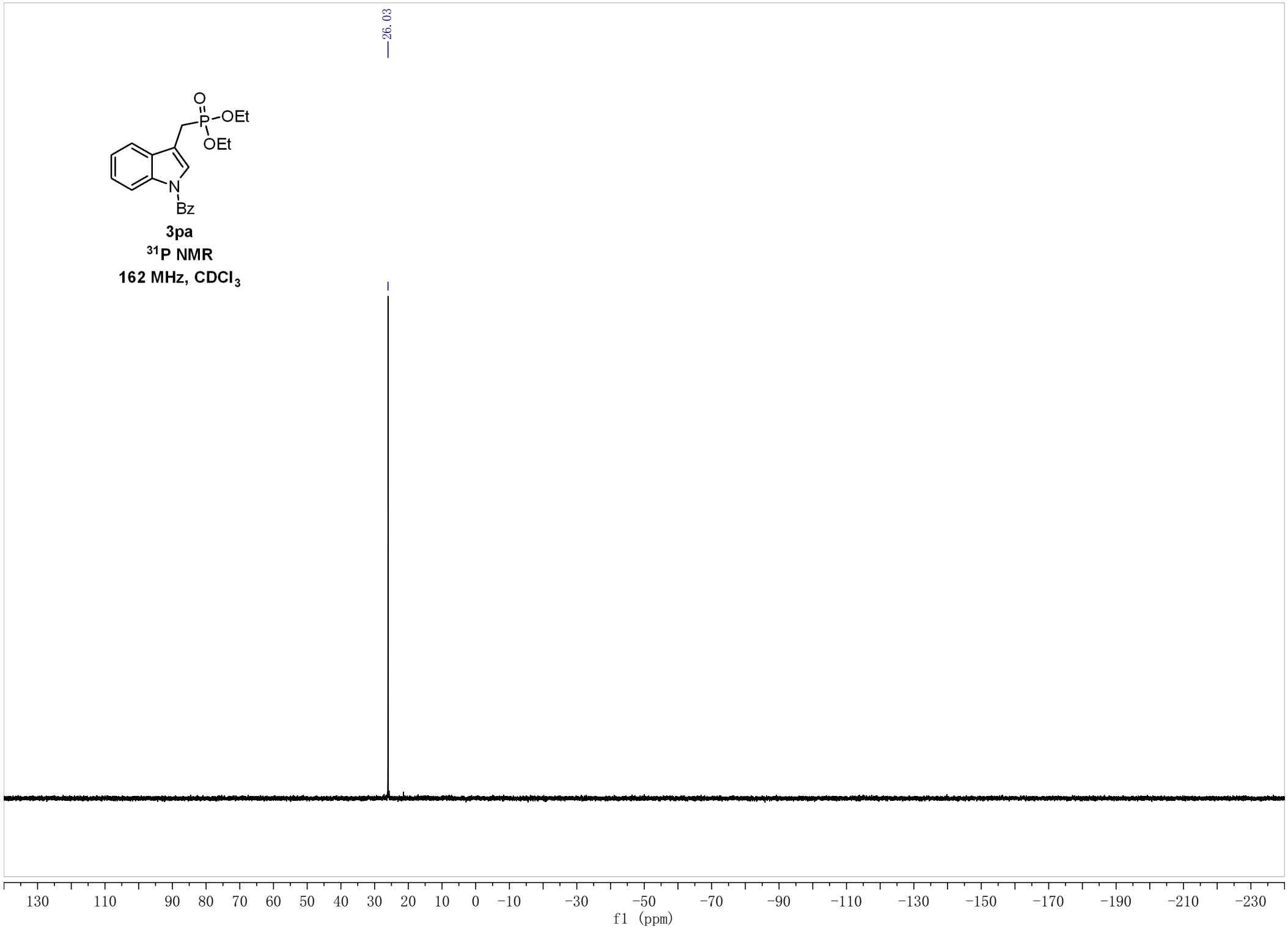


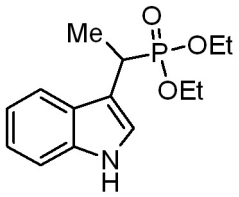
3pa

^{1}H NMR

400 MHz, $CDCl_3$


168.41
136.04
134.47
131.89
129.13
128.56
126.37
126.28
125.26
123.81
119.11
116.43
111.91
111.81
77.32
77.00
76.68
62.20
62.13
23.64
22.21
16.37
16.31
O
P
OEt
OEt
N
Bz
3pa
13C NMR
101 MHz, CDCl3
grease
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

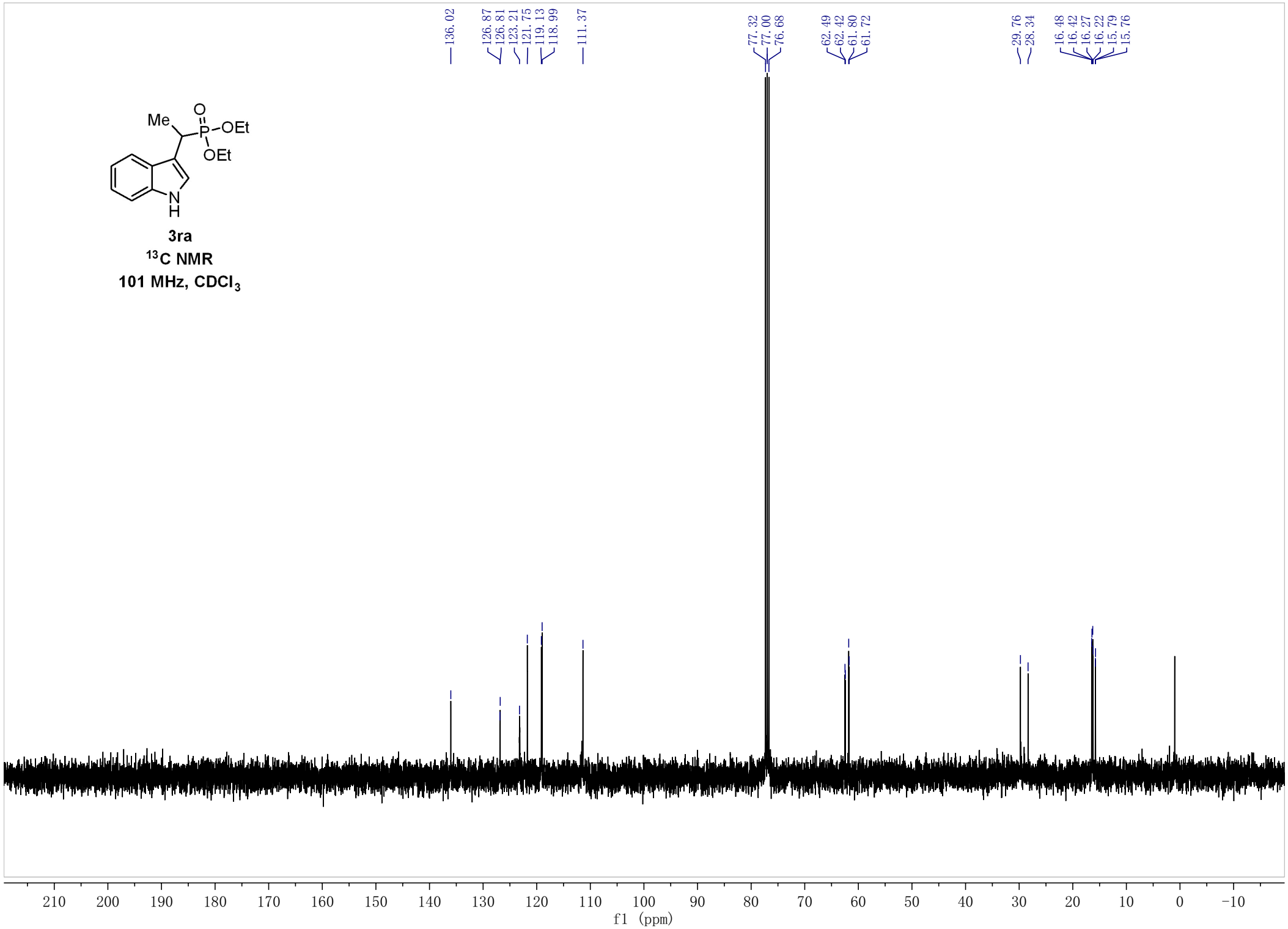

26.03
O
P
OEt
OEt
N
Bz
3pa
31P NMR
162 MHz, CDCl3
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

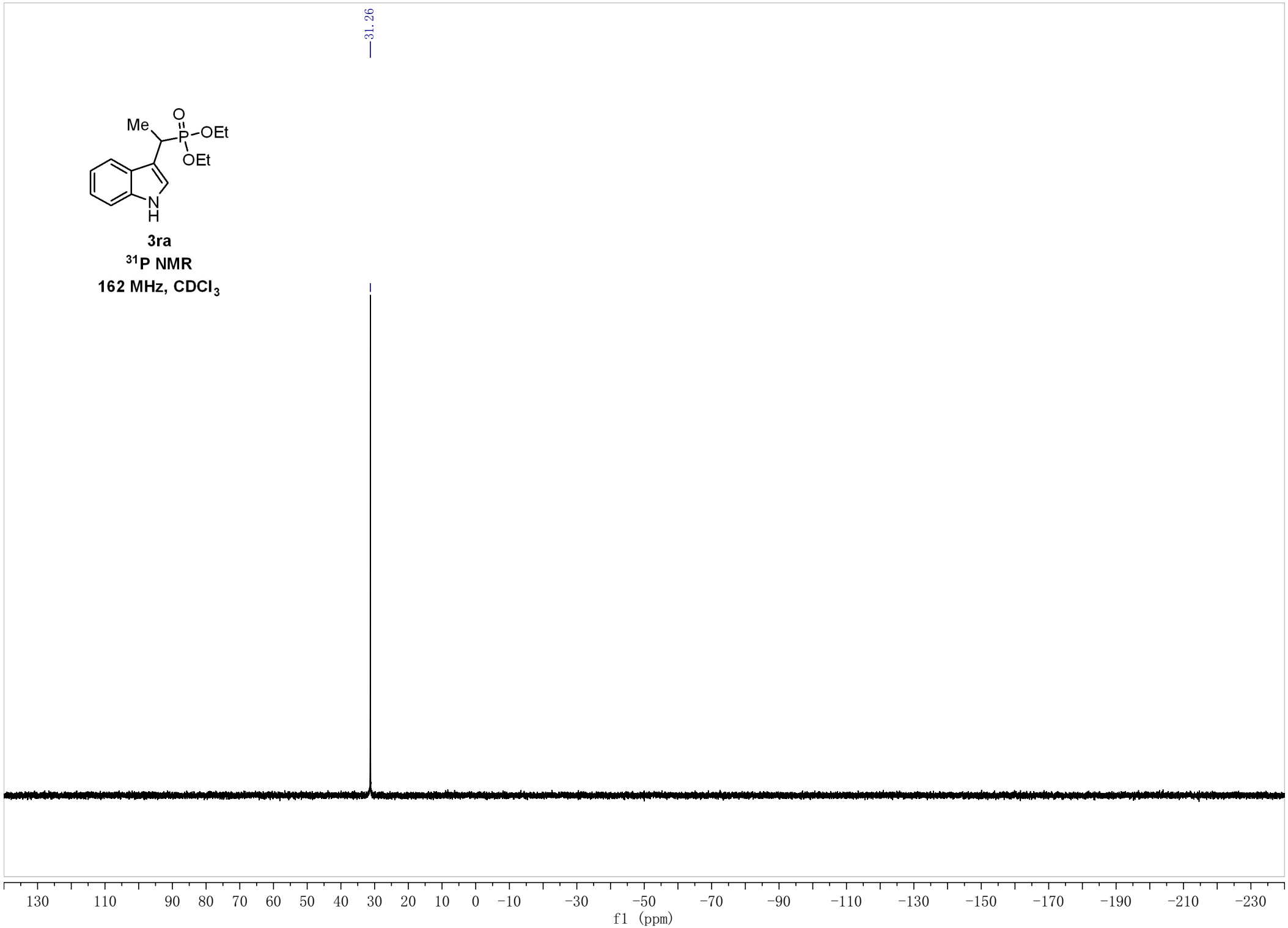


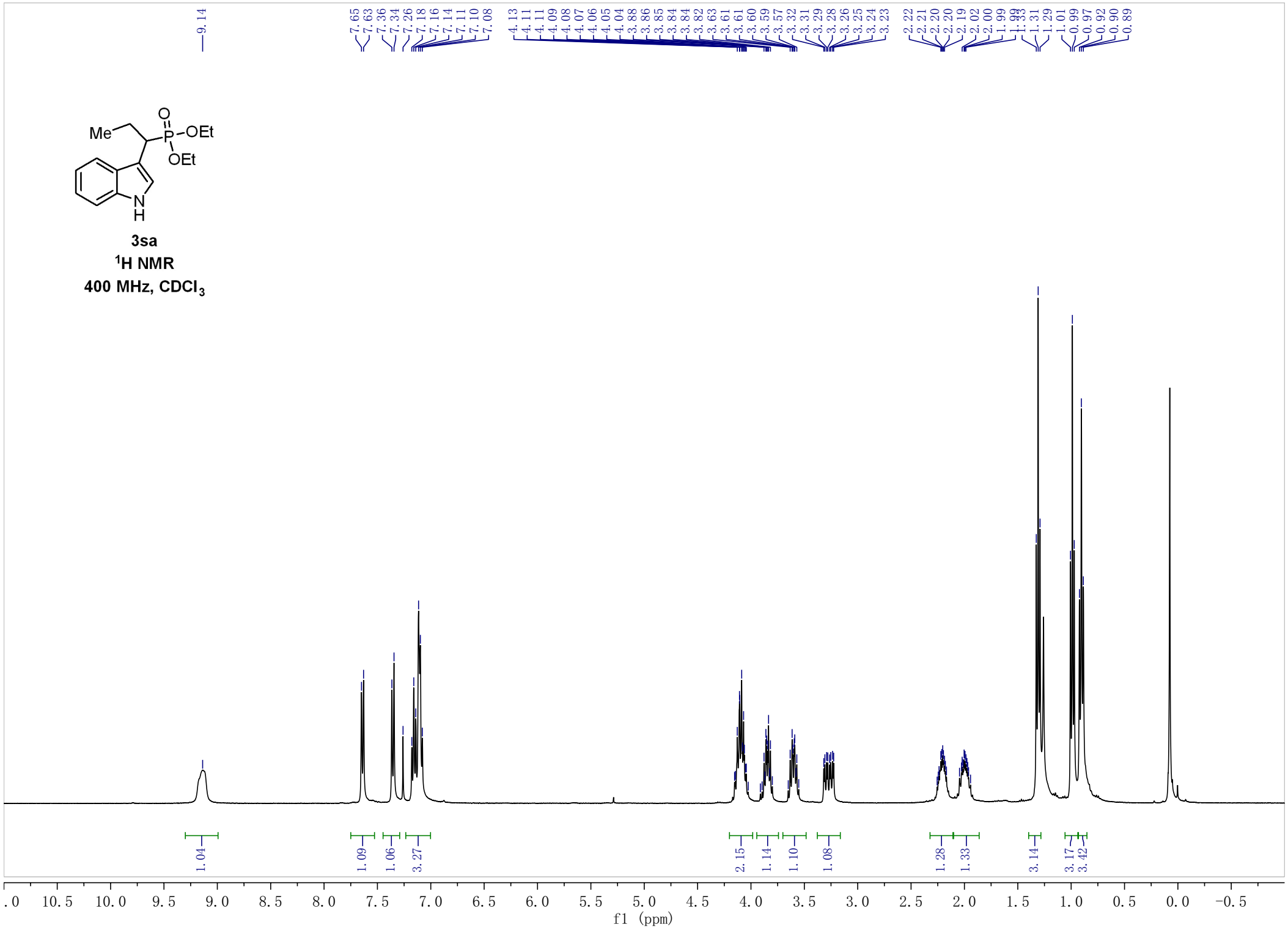
3ra

^{1}H NMR

400 MHz, $CDCl_3$


136.02
126.87
126.81
123.21
121.75
119.13
118.99
111.37
77.32
77.00
76.68
62.49
62.42
61.80
61.72
29.76
28.34
16.48
16.42
16.27
16.22
15.79
15.76
Me
O
P
OEt
OEt
N
H
3ra
13C NMR
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

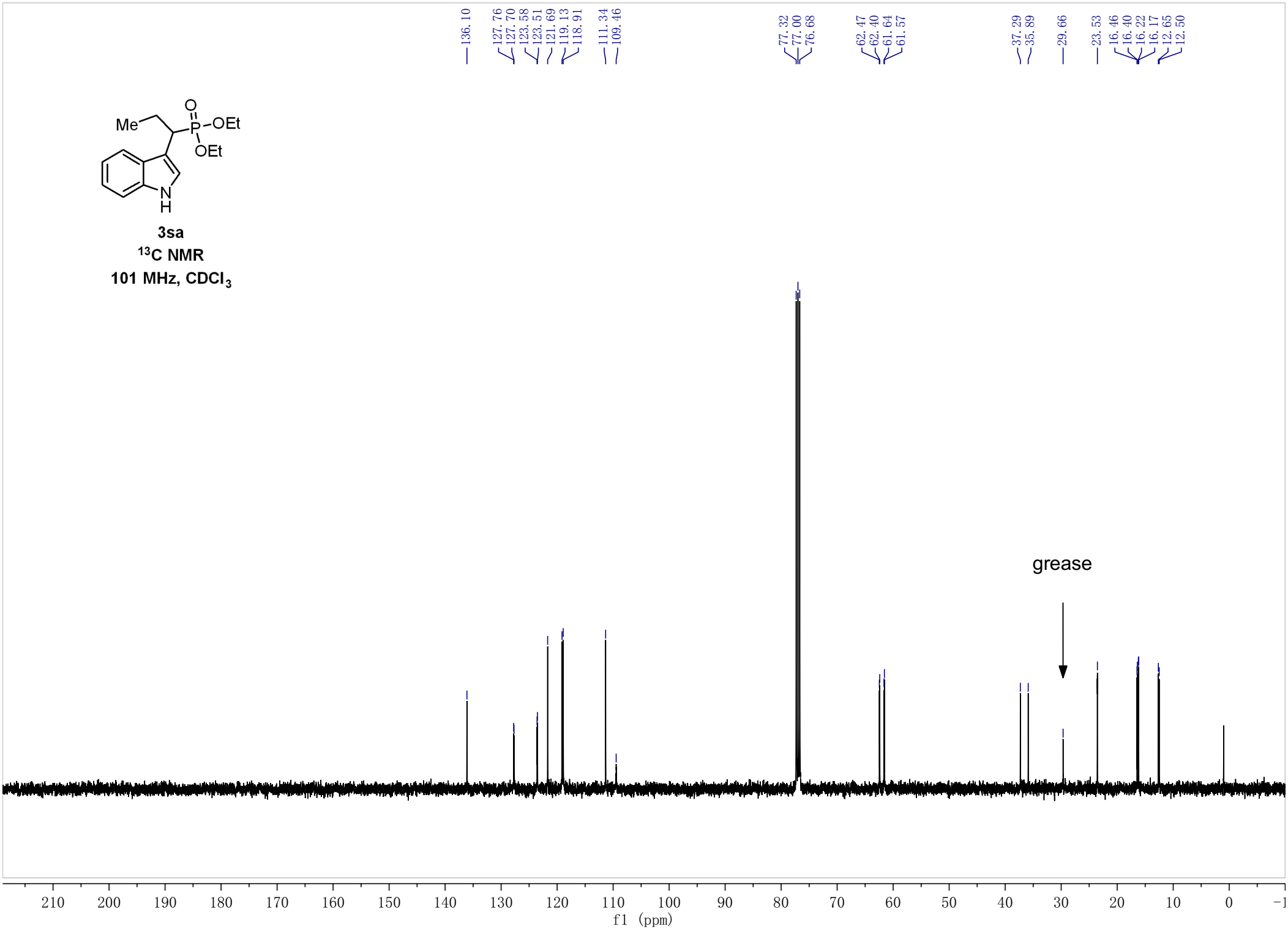

31.26
Me
O
P
OEt
OEt
N
H
3ra
31P NMR
162 MHz, CDCl3
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

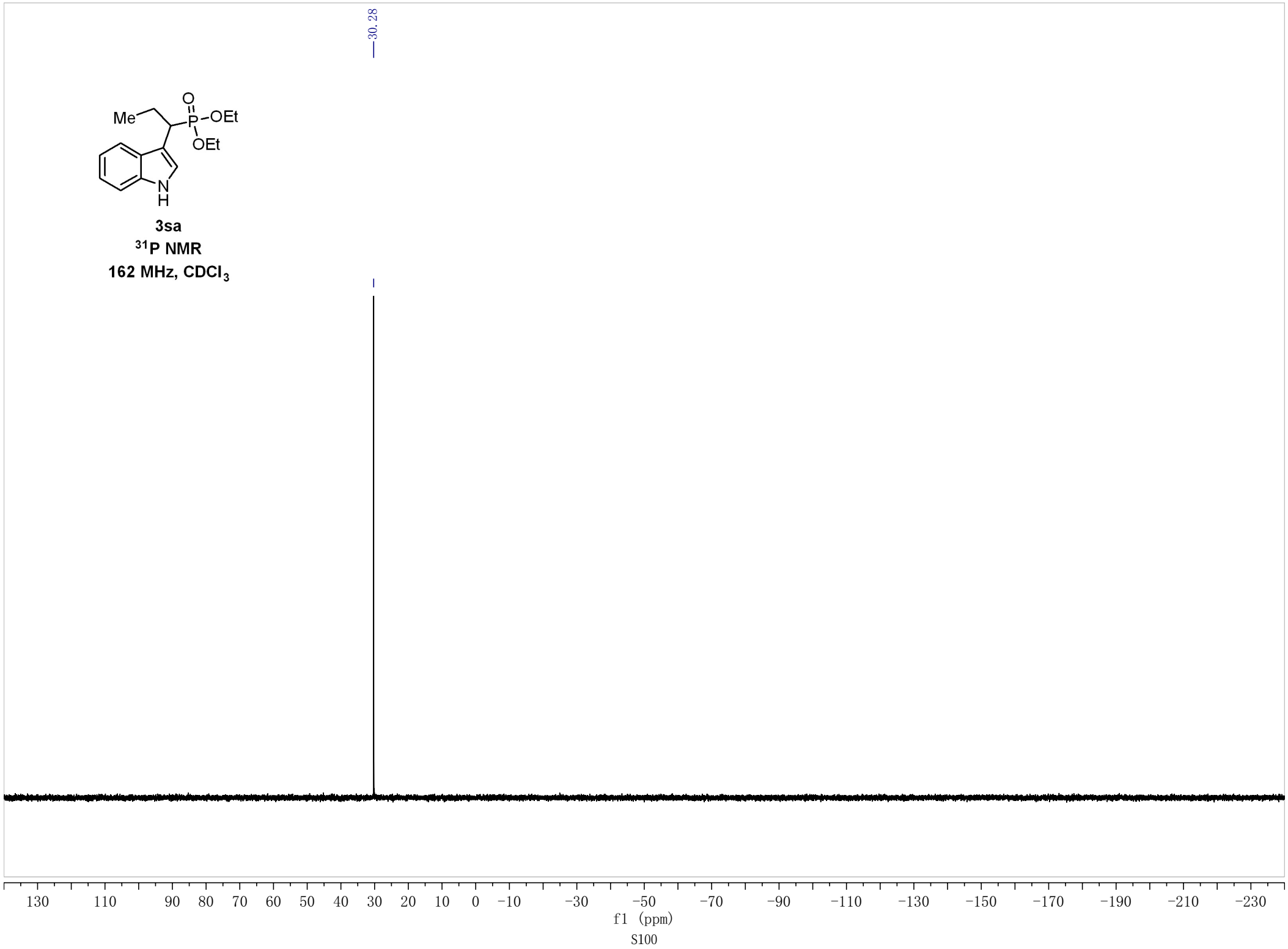


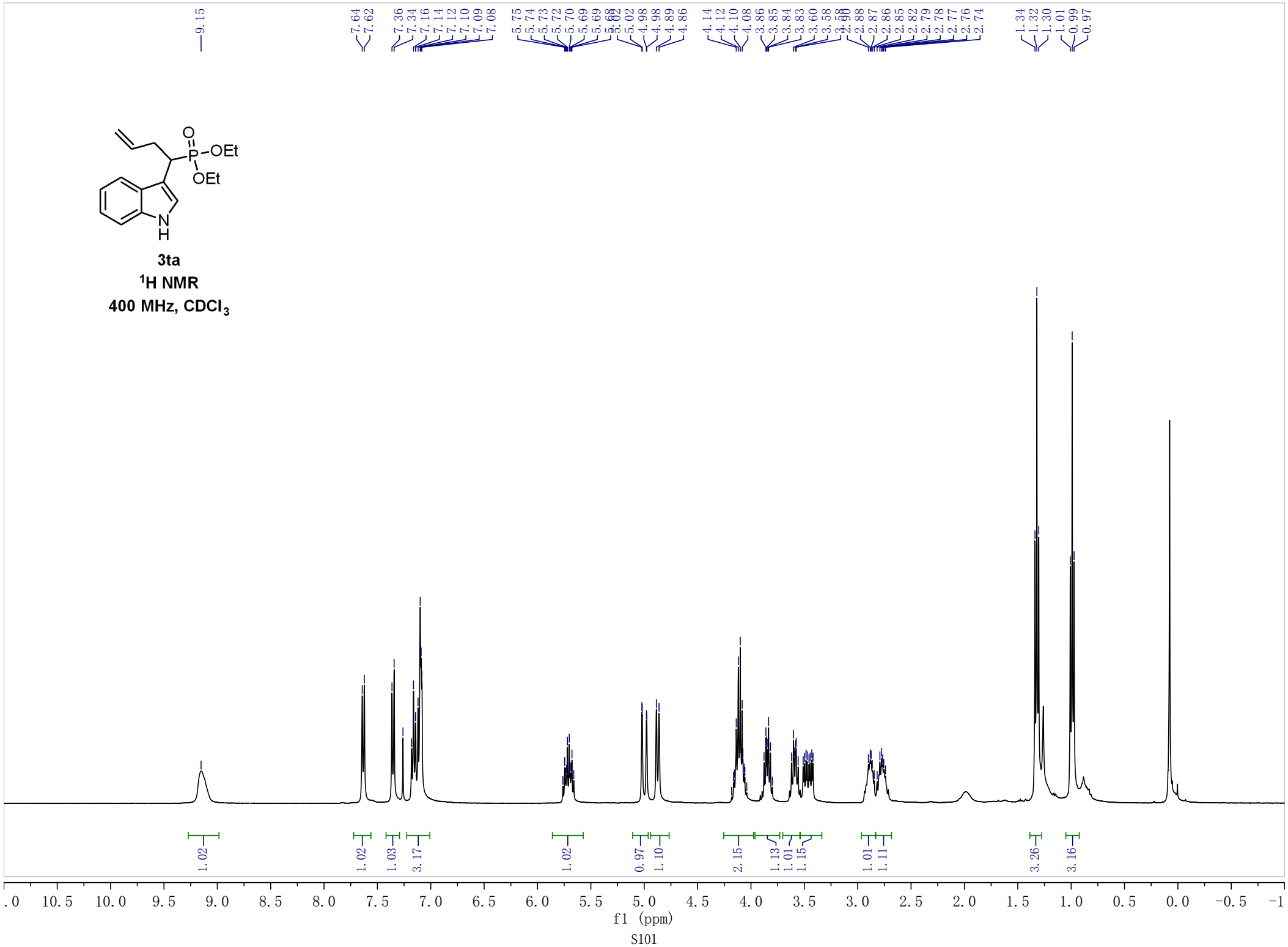
3sa

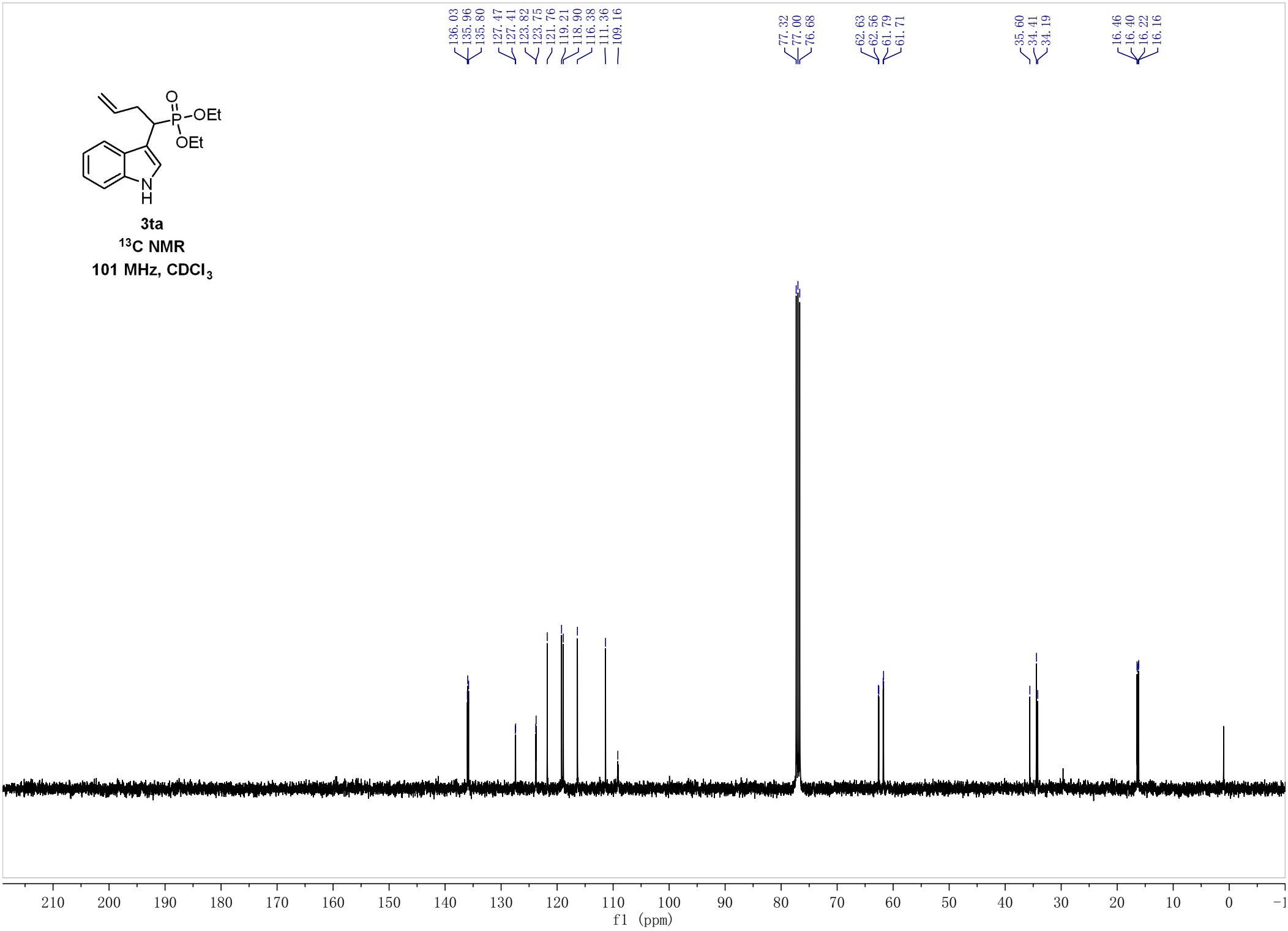
^{1}H NMR

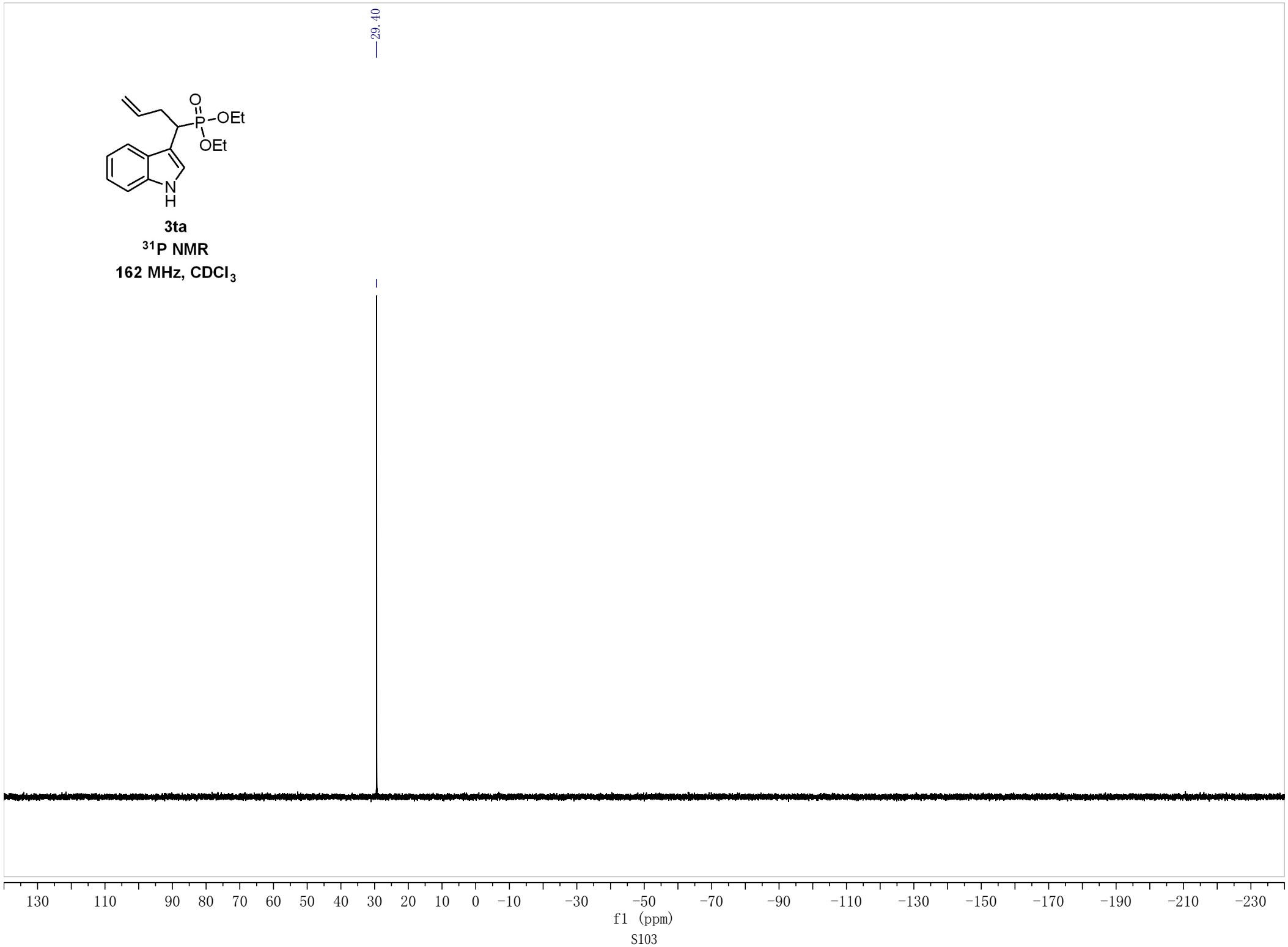
400 MHz, $CDCl_3$

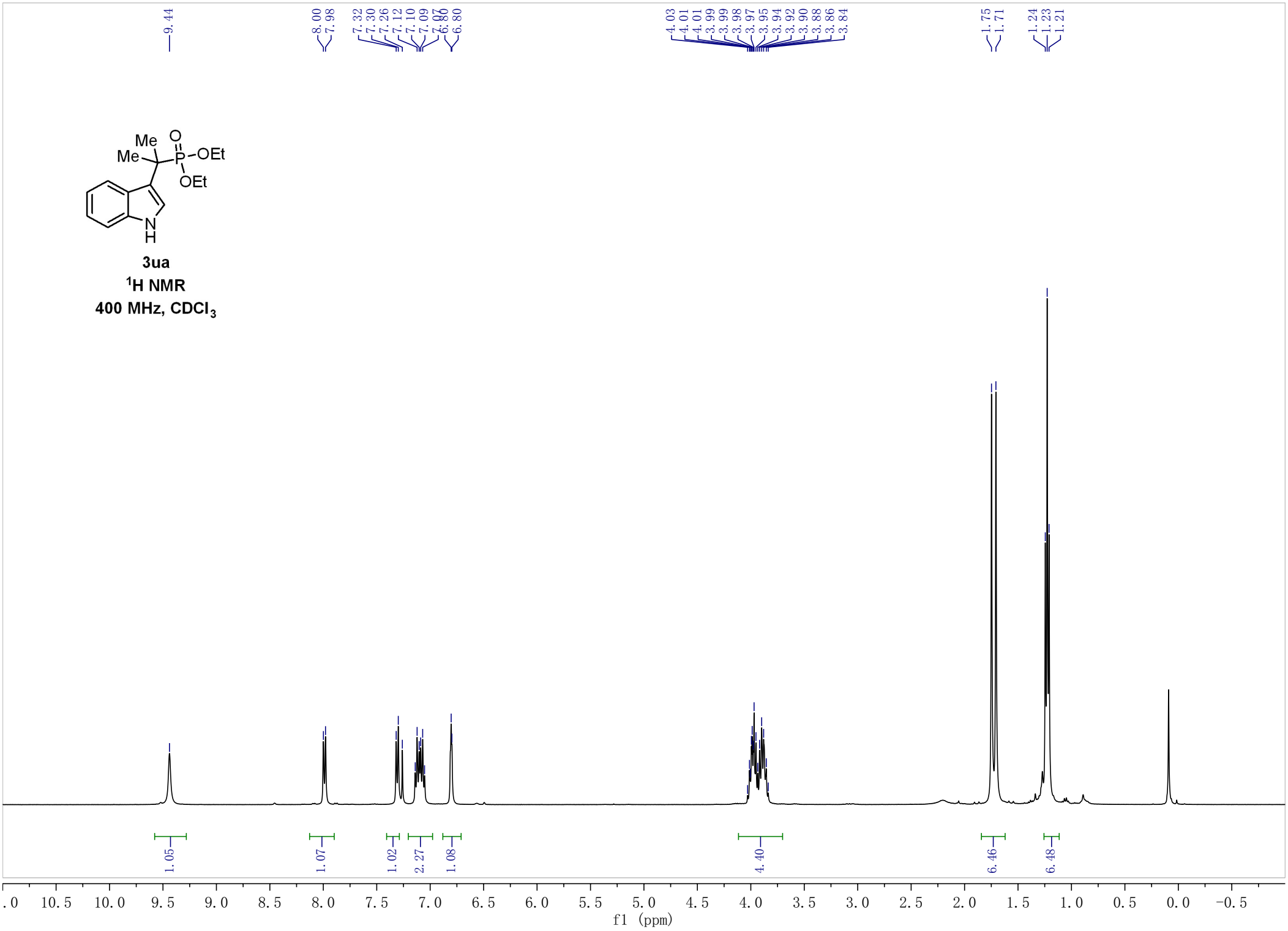

136.10
127.76
127.70
123.58
123.51
121.69
119.13
118.91
111.34
109.46
77.32
77.00
76.68
62.47
62.40
61.64
61.57
37.29
35.89
29.66
23.53
16.46
16.40
16.22
16.17
12.65
12.50
Me
O
P
OEt
OEt
N
H
3sa
13C NMR
101 MHz, CDCl3
grease
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

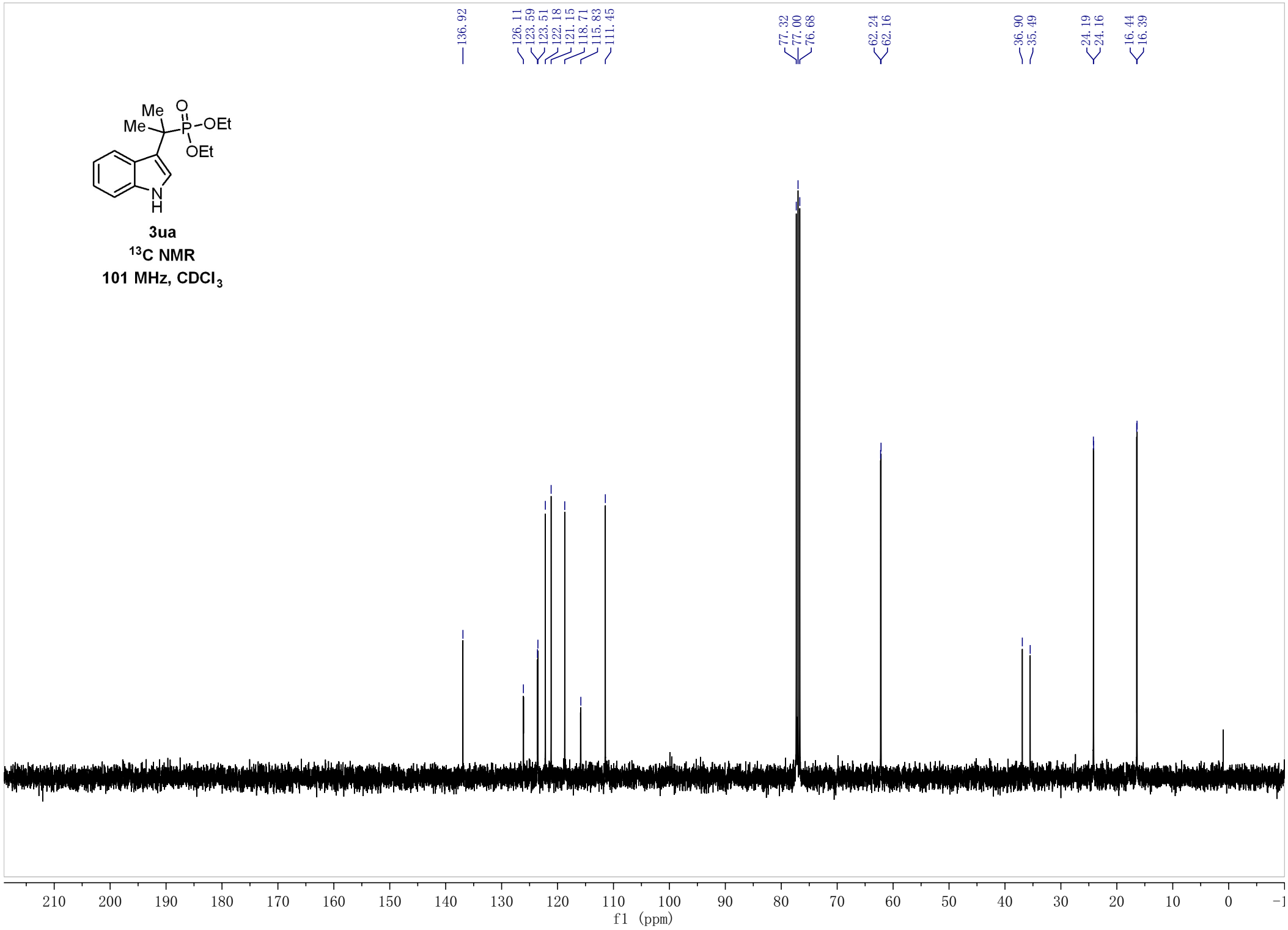

30.28
Me
O
P
OEt
OEt
N
H
3sa
31P NMR
162 MHz, CDCl3
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

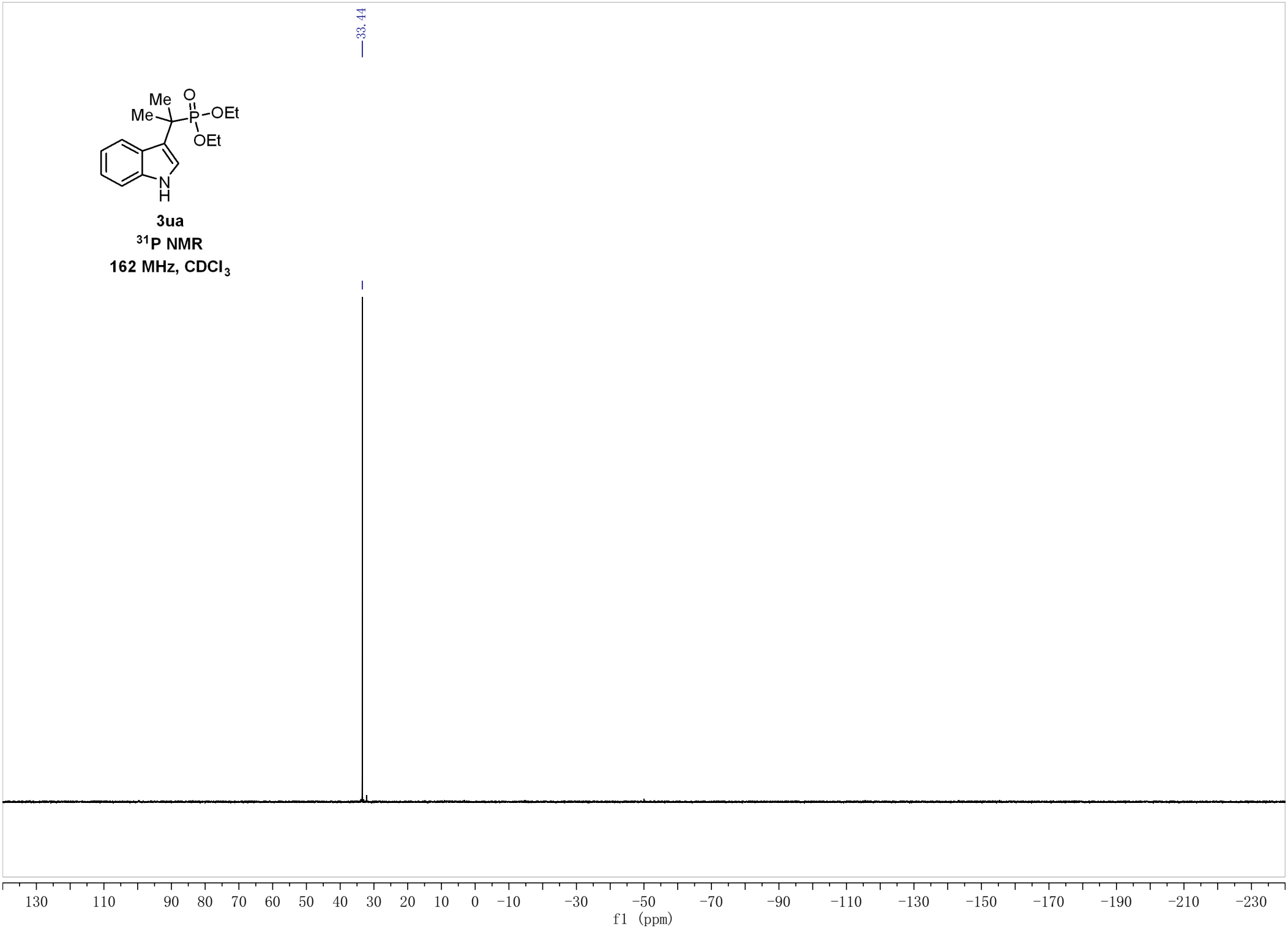

9.15
7.64
7.62
7.36
7.34
7.16
7.14
7.12
7.10
7.09
7.08
5.75
5.74
5.73
5.72
5.70
5.69
5.68
5.02
4.98
4.98
4.89
4.86
4.14
4.12
4.10
4.08
3.86
3.85
3.84
3.83
3.60
3.58
2.88
2.87
2.86
2.85
2.82
2.79
2.78
2.77
2.76
2.74
1.34
1.32
1.30
1.01
0.99
0.97
O
P
OEt
OEt
N
H
3ta
1H NMR
400 MHz, CDCl3
1.02
1.02
1.03
3.17
1.02
0.97
1.10
2.15
1.13
1.01
1.15
1.01
1.11
3.26
3.16
f1 (ppm)

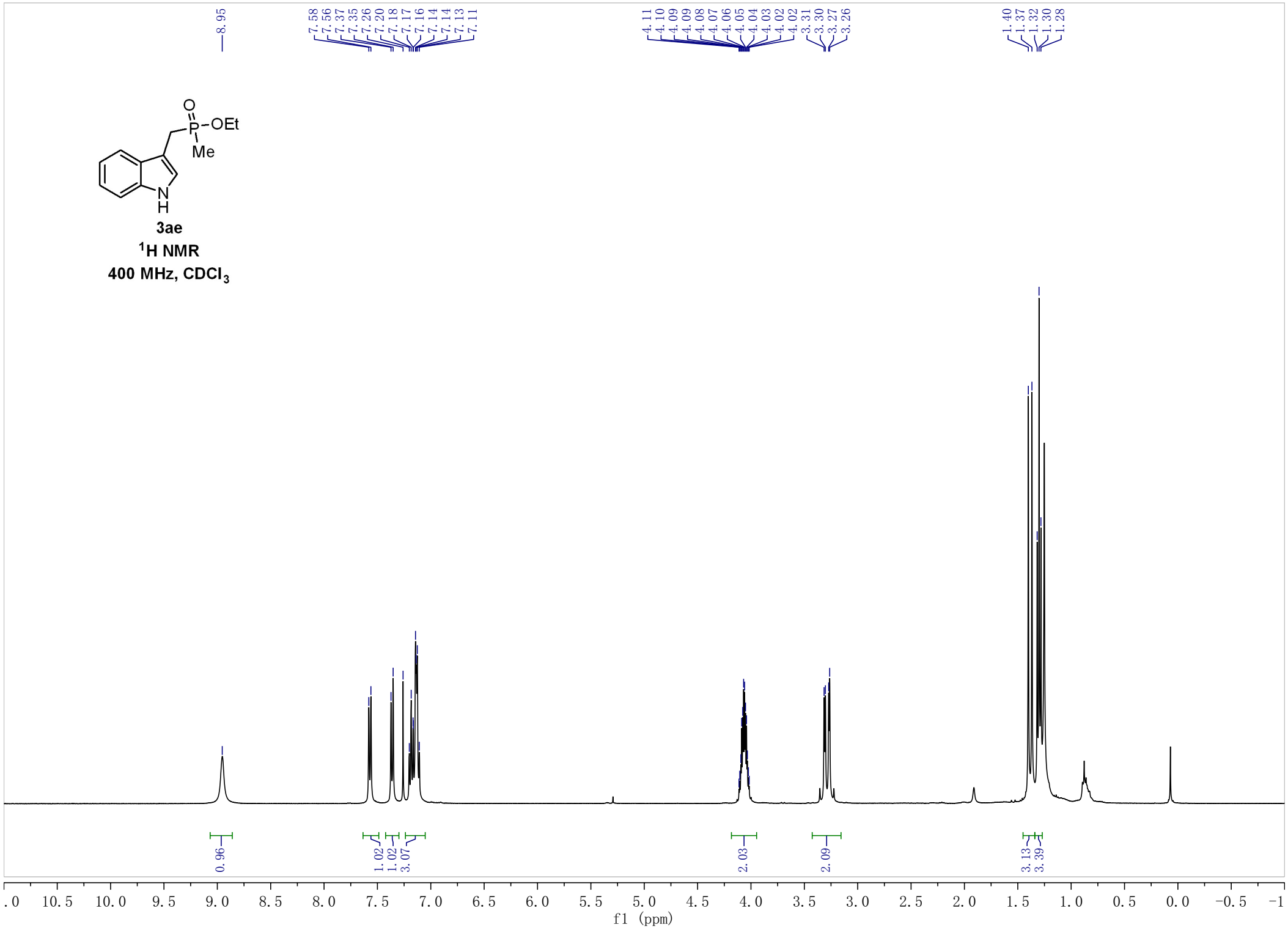

136.03
135.96
135.80
127.47
127.41
123.82
123.75
121.76
119.21
118.90
116.38
111.36
109.16
77.32
77.00
76.68
62.63
62.56
61.79
61.71
35.60
34.41
34.19
16.46
16.40
16.22
16.16
O
P
OEt
OEt
N
H
3ta
13C NMR
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

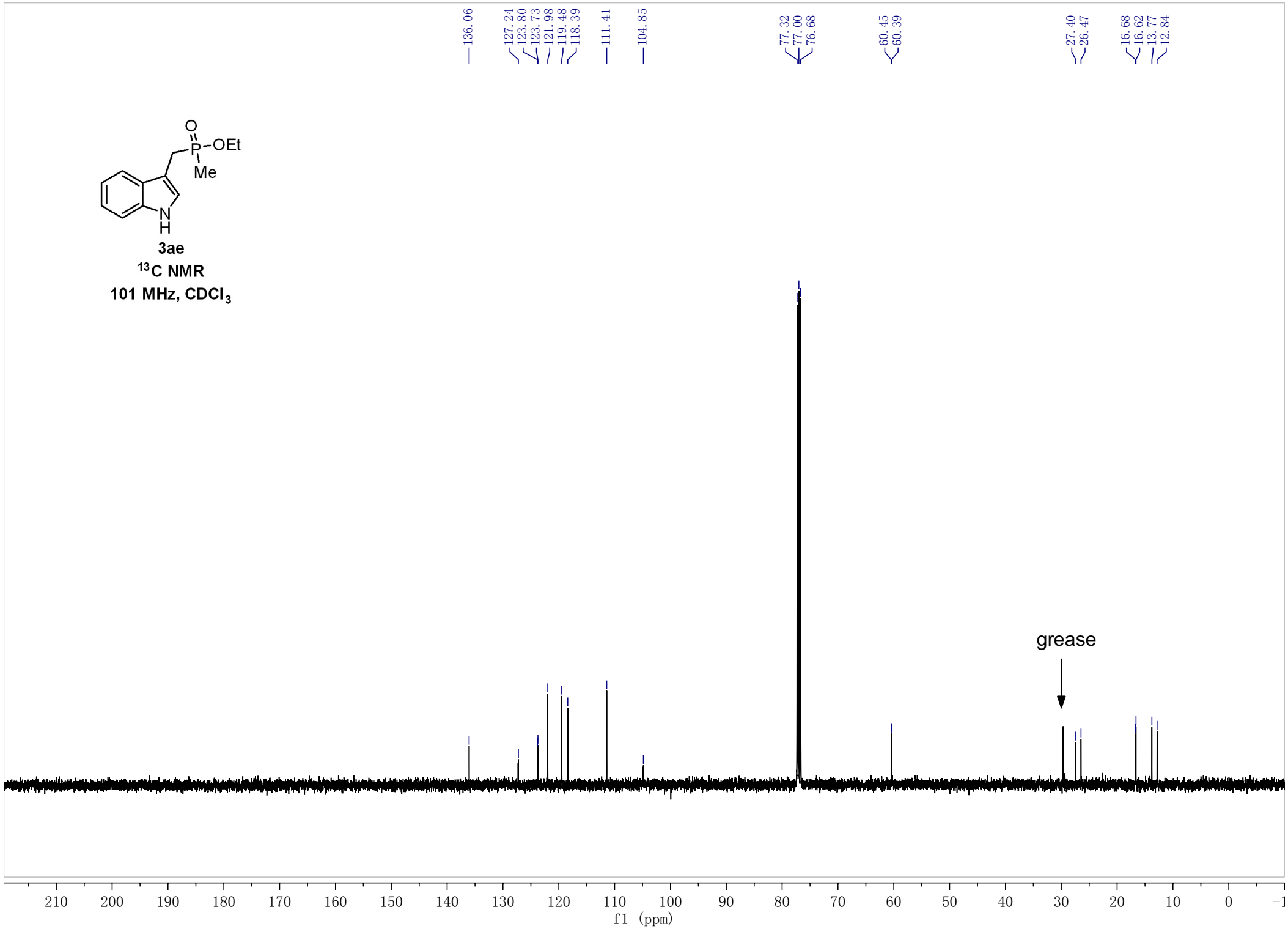

29.40
O
P
OEt
OEt
N
H
3ta
31P NMR
162 MHz, CDCl3
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

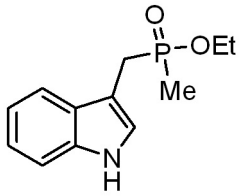

9.44
8.00
7.98
7.32
7.30
7.26
7.12
7.10
7.09
7.07
6.80
6.80
4.03
4.01
4.01
3.99
3.99
3.98
3.97
3.95
3.94
3.92
3.90
3.88
3.86
3.84
1.75
1.71
1.24
1.23
1.21
Me
Me
O
P
OEt
OEt
N
H
3ua
1H NMR
400 MHz, CDCl3
1.05
1.07
1.02
2.27
1.08
4.40
6.46
6.48
f1 (ppm)


136.92
126.11
123.59
123.51
122.18
121.15
118.71
115.83
111.45
77.32
77.00
76.68
62.24
62.16
36.90
35.49
24.19
24.16
16.44
16.39
Me
Me
O
P
OEt
OEt
N
H
3ua
13C NMR
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


33.44
Me
Me
O
P
OEt
OEt
N
H
3ua
31P NMR
162 MHz, CDCl3
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)


8.95
7.58
7.56
7.37
7.35
7.26
7.20
7.18
7.17
7.16
7.14
7.14
7.13
7.11
4.11
4.10
4.09
4.09
4.08
4.07
4.06
4.05
4.04
4.03
4.02
4.02
3.31
3.30
3.27
3.26
1.40
1.37
1.32
1.30
1.28
O
P
OEt
Me
N
H
3ae
1H NMR
400 MHz, CDCl3
0.96
1.02
1.02
3.07
2.03
2.09
3.13
3.39
f1 (ppm)


136.06
127.24
123.80
123.73
121.98
119.48
118.39
111.41
104.85
77.32
77.00
76.68
60.45
60.39
27.40
26.47
16.68
16.62
13.77
12.84
O
P
OEt
Me
N
H
3ae
13C NMR
101 MHz, CDCl3
grease
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)



3ae

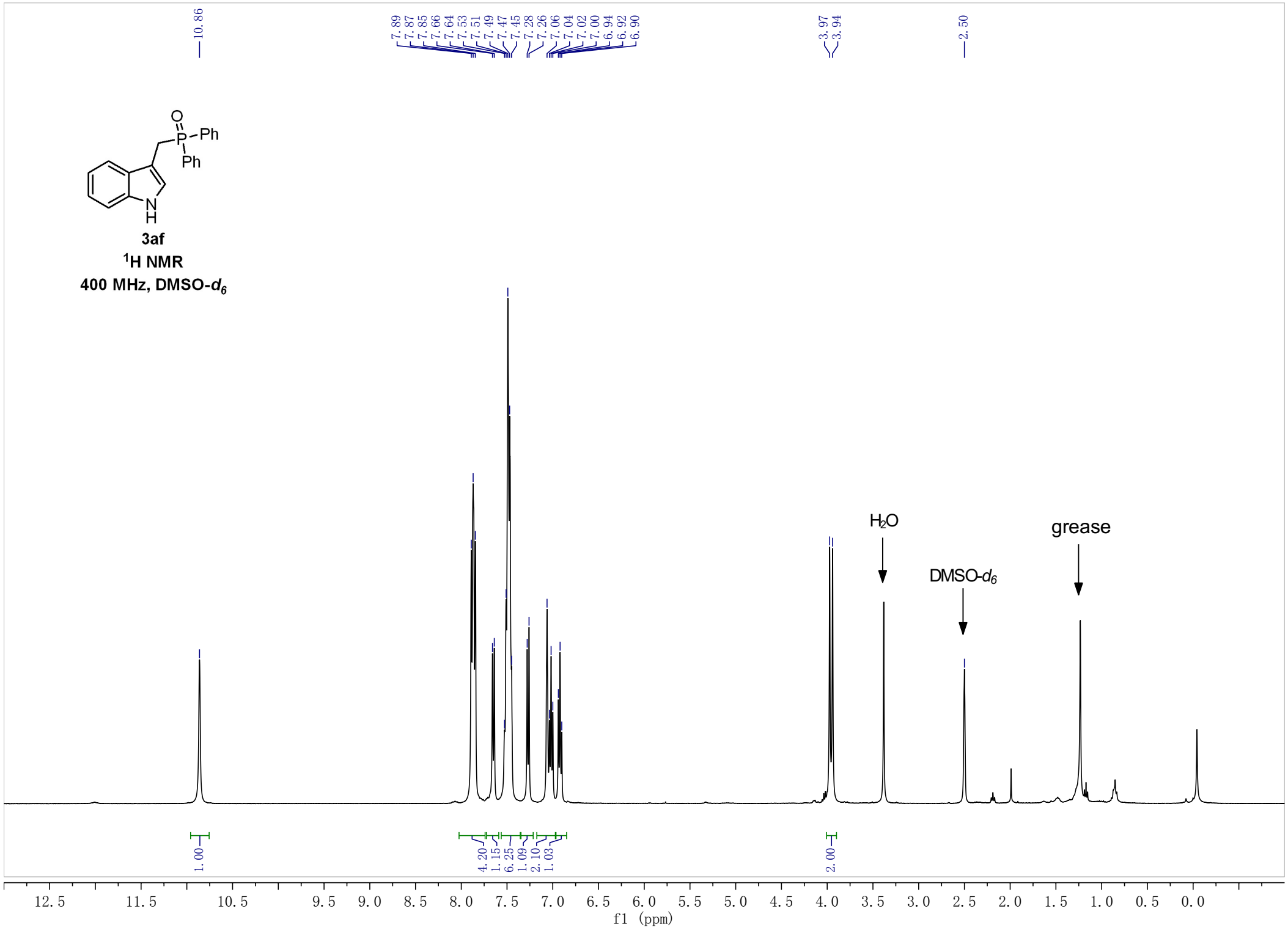
^{31}P NMR

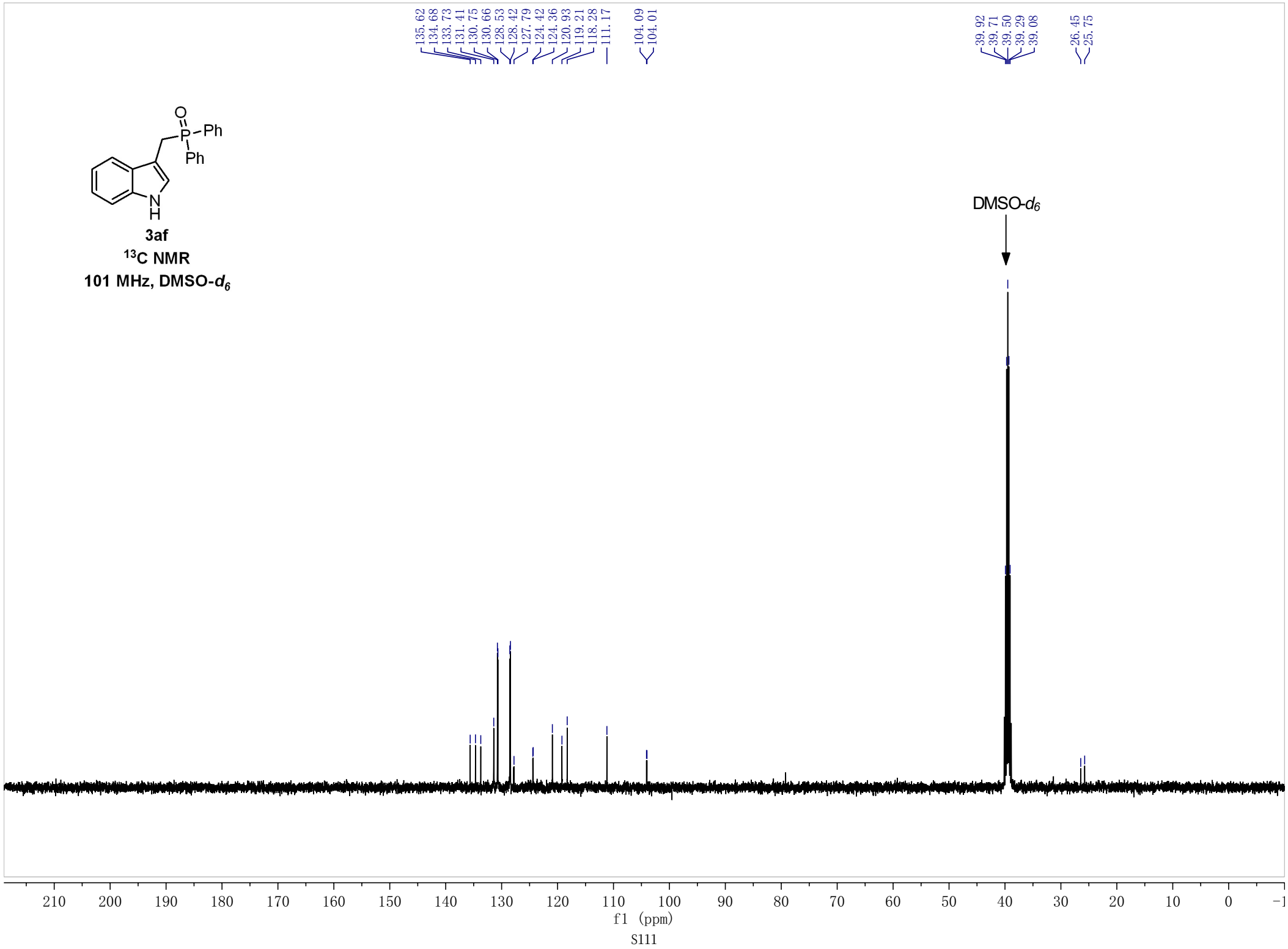
162 MHz, $CDCl_3$

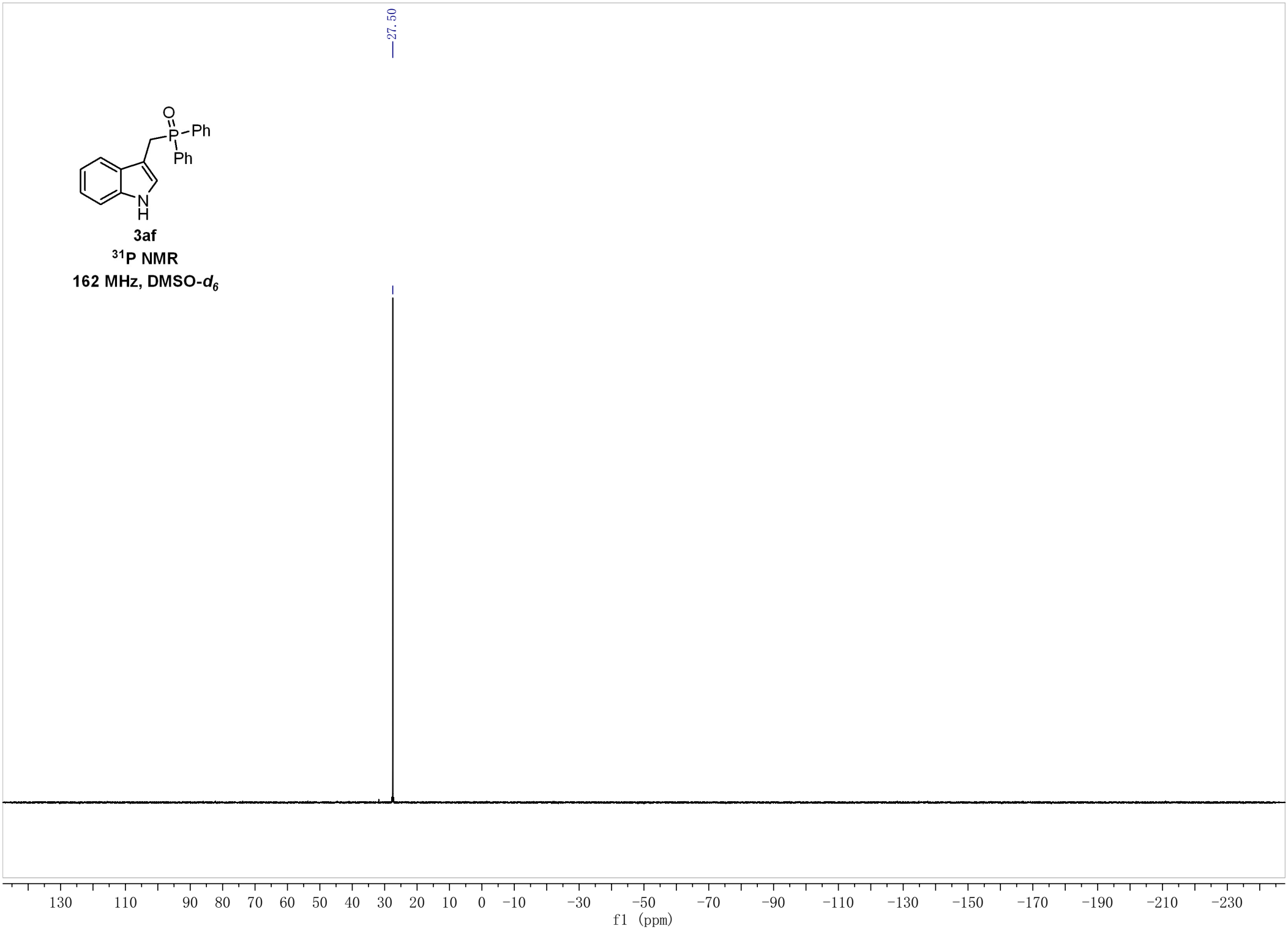
53.25

130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230

f1 (ppm)


10.86
7.89
7.87
7.85
7.66
7.64
7.53
7.51
7.49
7.47
7.45
7.28
7.26
7.06
7.04
7.02
7.00
6.94
6.92
6.90
3.97
3.94
2.50
O
P
Ph
Ph
N
H
3af
1H NMR
400 MHz, DMSO-d6
H2O
DMSO-d6
grease
1.00
4.20
1.15
6.25
1.09
2.10
1.03
2.00
12.5
11.5
10.5
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)


135.62
134.68
133.73
131.41
130.75
130.66
128.53
128.42
127.79
124.42
124.36
120.93
119.21
118.28
111.17
104.09
104.01
39.92
39.71
39.50
39.29
39.08
26.45
25.75
DMSO-d6
O
P
Ph
Ph
N
H
3af
13C NMR
101 MHz, DMSO-d6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


27.50
O
P
Ph
Ph
N
H
3af
31P NMR
162 MHz, DMSO-d6
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)