

Supporting Information

**KO^tBu and FeCl₃ Sequential Catalyzed Reductive
Phosphonylation of Tertiary Amides for Synthesis of α
Amino Phosphonates or Phosphines**

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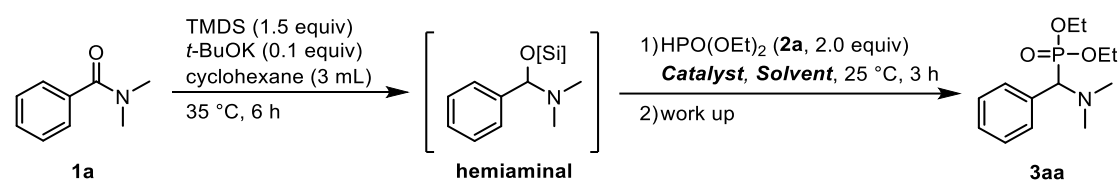
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1. General Information

Unless otherwise noted, all reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Materials were purchased from commercial suppliers and used without further purification. Anhydrous cyclohexane and THF was freshly distilled from sodium. ^1H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR, spectra were recorded on 400, 500, 600 and 700 MHz spectrometer. The chemical shifts for ^1H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard. The chemical shifts for ^{13}C NMR were recorded in ppm downfield using the central peak of deuteriochloroform (77.16 ppm) as the internal standard. Coupling constants (J) are reported in Hz and refer to apparent peak multiplications. HRMS were obtained on an ESI-TOF mass spectrometer. Flash column chromatography was performed on silica gel (300 – 400 mesh) and basic aluminum oxide (200 – 300 mesh).

2. Optimization of the Reductive Phosphonylation of Tertiary Amides

Table S1 Screening of Catalyst and Solvent

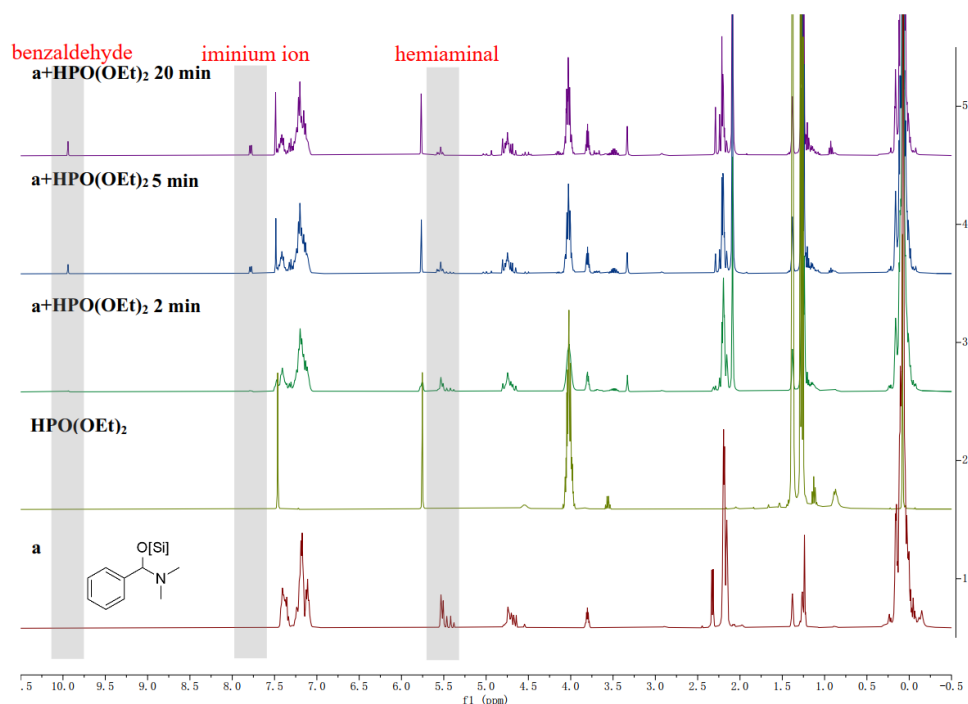


Entry	Catalyst	Solvent (°C)	Conv. (%)	Yield (%)	
				lab	
1	Al(OTf) ₃	Cyclohexane	>99	76	
2	Al(OPri) ₃	Cyclohexane	>99	78	
3	AlBr ₃	Cyclohexane	>99	82	
4	FeCl ₃	THF	>99	74	
5	FeCl ₃	MTBE	>99	84	
6	FeCl ₃	DCM	>99	80	
7	FeCl ₃	Toluene	>99	77	
8	FeCl ₃	DMF	>99	50	

General reaction conditions: **1a** (1.0 mmol, 149.2 mg, 1.0 equiv), *t*-BuOK (0.1 mmol, 11.2 mg, 10 mol%), TMDS (1.5 mmol, 201.5 mg, 1.5 equiv) and cyclohexane (3.0 mL), 35 °C, 6 h. Then added **2a** (2.0 mmol, 220.1 mg, 2.0 equiv), catalyst (20 mol%), solvent (3 mL), 25 °C, 3 h, conversion and yield were determined by GC analysis with 1,2,4,5-tetramethylbenzene as internal standard; reaction was quenched by saturated NaHCO₃ solution.

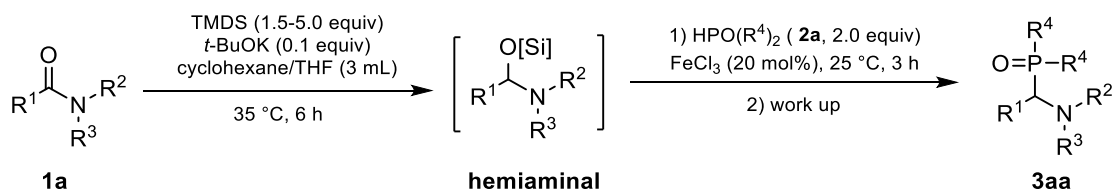
3. Mechanistic Investigations

Figure S1 ^1H NMR Experiments



4. Reductive Phosphonylation of Tertiary Amides

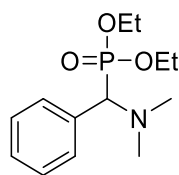
4.1 Experimental Procedures



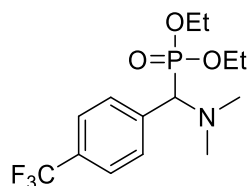
To the mixture of amides **1** (1.0 mmol, 1.0 equiv.) and *t*-BuOK (0.1 mmol, 11.2 mg, 0.1 equiv.) in cyclohexane (3.0 mL) or THF (3.0 mL), was added TMDS (1.5 mmol, 201.5 mg, 0.1 equiv) (the equivalent of TMDS may be adjust on the structure of amides which was shown in Scheme 2) slowly under an atmosphere of nitrogen. The reaction mixture was stirred at 35 °C under an atmosphere of nitrogen. After the amides was consumed completely (detected by TLC), the reaction mixture was cooled to room temperature, and HPOR₂ (**2**, 2.0 mmol, 2.0 equiv) was added and stirred for 15 min at room temperature, and then FeCl₃ (0.2 mmol, 32.4 mg, 0.2 equiv) was added. After the mixture was stirred for 3 h at 25 °C, the reaction mixture was quenched by adding saturated NaHCO₃ solution (2.0 mL). The mixture was filtrated with celite, and the solid was washed with Et₂O (5.0 mL) and water (10.0 mL) in sequence. The aqueous phase of the filtrate was extracted with Et₂O (5.0 mL × 3). The combined organic phase was washed with brine and dried over Na₂SO₄. After removing the solvent under vacuum, the residue was purified by column chromatography (silica gel or basic aluminum oxide) to give the product **3**.

Specially: In the case of HPOR₂ as a solid, HPOR₂ was dissolved in DCM (2.0 mL) and then added into the reaction mixture.

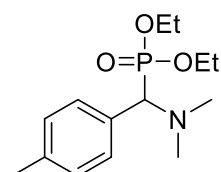
4.2 Characterization of the Products



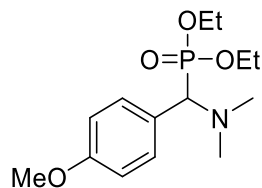
Diethyl ((dimethylamino)(phenyl)methyl)phosphonate (3aa): colorless oil, 187 mg, 78% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 6 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 7.46 – 7.32 (m, 5H), 4.20 – 4.14 (m, 2H), 3.94 – 3.88 (m, 1H), 3.77 (d, *J* = 21.2 Hz, 1H), 3.67 – 3.61 (m, 1H), 2.35 (s, 6H), 1.32 (t, *J* = 6.8 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 132.6 (d, *J* = 1.7 Hz), 130.5 (d, *J* = 8.3 Hz), 128.1, 128.0 (d, *J* = 1.7 Hz), 68.3 (d, *J* = 159.8 Hz), 62.4 (d, *J* = 7.2 Hz), 43.8 (d, *J* = 9.5 Hz), 16.4 (d, *J* = 5.7 Hz), 16.1 (d, *J* = 5.6 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 22.8; HRMS – ESI (*m/z*): [M + H]⁺ called for C₁₃H₂₃NO₃P, 272.1410, found 272.1420.



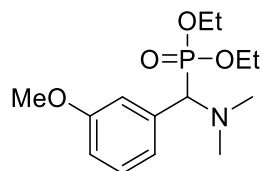
Diethyl ((dimethylamino)(4-(trifluoromethyl)phenyl)methyl)phosphonate (3ba): colorless oil, 253 mg, 75% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 6 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 7.63 – 7.58 (m, 4H), 4.23 – 4.14 (m, 2H), 3.99 – 3.93 (m, 1H), 3.84 (d, *J* = 20.8 Hz, 1H), 3.82 – 3.72 (m, 1H), 2.37 (s, 6H), 1.33 (t, *J* = 6.8 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 137.2, 130.8 (d, ³*J*_{C-P} = 8.1 Hz), 130.3 (q, ²*J*_{C-F} = 32.7 Hz), 125.1 (q, ³*J*_{C-F} = 3.7 Hz), 124.2 (q, ¹*J*_{C-F} = 270.4 Hz), 68.0 (d, ¹*J*_{C-P} = 159.6 Hz), 62.9 (d, ²*J*_{C-P} = 7.0 Hz), 62.5 (d, ²*J*_{C-P} = 7.0 Hz), 43.9 (d, ³*J*_{C-P} = 9.4 Hz), 16.5 (d, ³*J*_{C-P} = 5.7 Hz), 16.2 (d, ³*J*_{C-P} = 5.7 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 21.8; ¹⁹F NMR (376 MHz, CDCl₃): δ -62.6 (d, *J* = 1.9); HRMS – ESI (*m/z*): [M + Na]⁺ called for C₁₄H₂₁F₃NO₃NaP, 362.1103, found 362.1107.



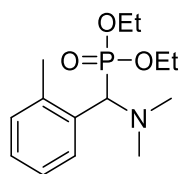
Diethyl ((dimethylamino)(*p*-tolyl)methyl)phosphonate (3ca): colorless oil, 220 mg, 77% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 6 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 7.33 (d, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 4.22 – 4.12 (m, 2H), 3.97 – 3.87 (m, 1H), 3.75 (d, *J* = 21.6 Hz, 2H), 3.70 – 3.62 (m, 2H), 2.33 (s, 9H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 137.8, 130.6 (d, *J* = 8.5 Hz), 129.4, 128.9, 68.0 (d, *J* = 160.0 Hz), 62.5 (d, *J* = 7.1 Hz), 43.9 (d, *J* = 9.6 Hz), 21.3, 16.6 (d, *J* = 5.5 Hz), 16.3 (d, *J* = 5.6 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 23.0; HRMS – ESI (*m/z*): [M + Na]⁺ called for C₁₄H₂₄NO₃NaP, 308.1386, found 308.1389.



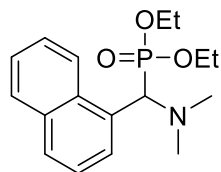
Diethyl ((dimethylamino)(4-methoxyphenyl)methyl)phosphonate (3da): colorless oil, 207 mg, 69% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 6 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 7.39 – 7.36 (m, 2H), 6.89 – 6.87 (m, 2H), 4.20 – 4.14 (m, 2H), 3.95 – 3.89 (m, 1H), 3.77 (s, 3H), 3.74 (d, *J* = 21.6 Hz, 1H), 3.70 – 3.63 (m, 1H), 2.32 (s, 6H), 1.33 (t, *J* = 6.8 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 159.4 (d, *J* = 1.7 Hz), 131.8 (d, *J* = 8.5 Hz), 124.2, 113.5, 67.4 (d, *J* = 160.7 Hz), 62.52 (d, *J* = 6.9 Hz), 62.47 (d, *J* = 7.2 Hz), 55.2, 43.7 (d, *J* = 9.3 Hz), 16.5 (d, *J* = 5.7 Hz), 16.3 (d, *J* = 5.5 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 23.1; HRMS – ESI (*m/z*): [*M* + *H*]⁺ called for C₁₄H₂₅NO₄P, 302.1516, found 302.1516.



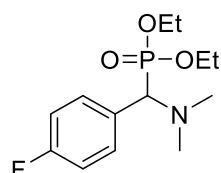
Diethyl ((dimethylamino)(3-methoxyphenyl)methyl)phosphonate (3ea): colorless oil, 214 mg, 71% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 6 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 7.28 – 7.24 (m, 1H), 7.05 – 7.03 (m, 2H), 6.89 – 6.86 (m, 1H), 4.23 – 4.13 (m, 2H), 3.99 – 3.89 (m, 1H), 3.82 (s, 3H), 3.75 (d, *J* = 20.8, 1H), 3.71 – 3.63 (m, 1H), 2.37 (s, 6H), 1.33 (t, *J* = 6.8 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 159.4, 134.3, 129.0, 123.0 (d, *J* = 8.4), 115.8 (d, *J* = 8.3), 113.7 (d, *J* = 1.8), 68.6 (d, *J* = 159.5), 62.6 (d, *J* = 7.0), 62.5 (d, *J* = 7.0), 55.4, 44.1 (d, *J* = 9.4), 16.6 (d, *J* = 5.8), 16.4 (d, *J* = 5.5); ³¹P NMR (162 MHz, CDCl₃): δ 22.8; HRMS – ESI (*m/z*): [*M* + *H*]⁺ called for C₁₄H₂₅NO₄P, 302.1521, found 302.1512.



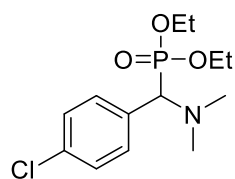
Diethyl ((dimethylamino)(*o*-tolyl)methyl)phosphonate (3fa): colorless oil, 203 mg, 75% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 6 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 7.74 – 7.72 (m, 1H), 7.18 – 7.14 (m, 3H), 4.17 – 4.04 (m, 2H), 3.98 (d, *J* = 19.2 Hz, 1H), 3.84 – 3.77 (m, 1H), 3.45 – 3.38 (m, 2H), 2.37 (s, 6H), 2.34 (s, 3H), 1.30 (t, *J* = 6.8 Hz, 4H), 0.97 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 137.5 (d, *J* = 9.9 Hz), 133.1, 130.5, 130.2 (d, *J* = 4.2 Hz), 127.8 (d, *J* = 2.4 Hz), 126.0 (d, *J* = 2.4 Hz), 63.8 (d, *J* = 155.6 Hz), 62.8 (d, *J* = 7.0 Hz), 62.0 (d, *J* = 7.5 Hz), 44.6 (d, *J* = 9.4 Hz), 20.3, 16.6 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 5.6 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 23.9; HRMS – ESI (*m/z*): [*M* + *Na*]⁺ called for C₁₄H₂₄NO₃NaP, 308.1386, found 308.1385.



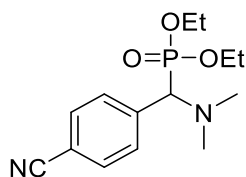
Diethyl ((dimethylamino)(naphthalen-1-yl)methyl)phosphonate (3ga): colorless oil, 199 mg, 62% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 4 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 8.23 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.88 – 7.82 (m, 2H), 7.56 – 7.46 (m, 3H), 4.67 (d, *J* = 20.4 Hz, 1H), 4.22 – 4.11 (m, 2H), 3.81 – 3.75 (m, 1H), 3.41 – 3.34 (m, 1H), 2.45 (s, 6H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.83 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 134.0, 132.9 (d, *J* = 9.7 Hz), 129.7, 129.0, 128.9 (d, *J* = 2.2 Hz), 128.8 (d, *J* = 5.7 Hz), 126.5, 125.7, 125.1 (d, *J* = 2.4 Hz), 123.6, 62.8 (d, *J* = 7.1 Hz), 62.4 (d, *J* = 7.3 Hz), 44.4 (d, *J* = 8.7 Hz), 16.5 (d, *J* = 5.8 Hz), 16.1 (d, *J* = 5.5 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 23.7; HRMS – ESI (*m/z*): [M + Na]⁺ called for C₁₇H₂₄NO₃NaP, 344.1386, found 344.1388.



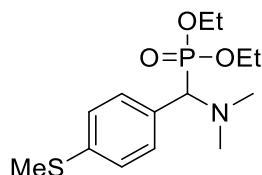
Diethyl ((dimethylamino)(4-fluorophenyl)methyl)phosphonate (3ha): colorless oil, 218 mg, 76% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 5 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 7.47 – 7.43 (m, 2H), 7.07 – 7.03 (m, 2H), 4.23 – 4.14 (m, 2H), 3.96 – 3.90 (m, 1H), 3.78 (d, *J* = 21.6 Hz, 1H), 3.74 – 3.68 (m, 1H), 2.34 (s, 6H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.07 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 162.7 (d, ¹*J*_{C-F} = 247.2 Hz), 132.3 (dd, ³*J*_{C-F} = 8.3 Hz, ³*J*_{C-P} = 8.1 Hz), 128.5 (d, ²*J*_{C-P} = 2.8 Hz), 115.2 (d, ²*J*_{C-F} = 21.1 Hz), 67.4 (d, ¹*J*_{C-P} = 160.5 Hz), 62.7 (d, ²*J*_{C-P} = 7.2 Hz), 62.6 (d, ²*J*_{C-P} = 6.9 Hz), 43.8 (d, ³*J*_{C-P} = 9.4 Hz), 16.6 (d, ³*J*_{C-P} = 5.9 Hz), 16.3 (d, ³*J*_{C-P} = 5.6 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 22.5; ¹⁹F NMR (376 MHz, CDCl₃): δ -114.1; HRMS – ESI (*m/z*): [M + Na]⁺ called for C₁₃H₂₁NO₃NaP, 312.1135, found 312.1137.



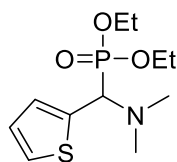
Diethyl ((dimethylamino)(4-methoxyphenyl)methyl)phosphonate (3ia): colorless oil, 223 mg, 73% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 6 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 7.42 – 7.39 (m, 2H), 7.34 – 7.32 (m, 2H), 4.23 – 4.13 (m, 2H), 3.99 – 3.89 (m, 1H), 3.78 – 3.68 (m, 2H), 2.34 (s, 6H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.09 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 134.1 (d, *J* = 1.9 Hz), 131.9 (d, *J* = 8.2 Hz), 131.4, 128.5, 67.7 (d, *J* = 160.5 Hz), 62.8 (d, *J* = 7.0 Hz), 62.6 (d, *J* = 6.9 Hz), 43.9 (d, *J* = 9.3 Hz), 16.6 (d, *J* = 5.5 Hz), 16.4 (d, *J* = 5.5 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 22.2; HRMS – ESI (*m/z*): [M + H]⁺ called for C₁₃H₂₂NO₃PCl, 306.1020, found 306.1019.



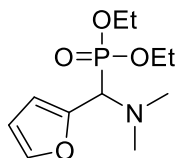
Diethyl ((4-cyanophenyl)(dimethylamino)methyl)phosphonate (3ja): colorless oil, 173 mg, 59% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 6 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 7.66 – 7.64 (m, 2H), 7.60 – 7.58 (m, 2H), 4.21 – 4.14 (m, 2H), 3.98 – 3.91 (m, 1H), 3.83 – 3.73 (m, 2H), 2.35 (s, 6H), 1.32 (t, *J* = 6.8 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 139.1, 132.0, 131.1 (d, *J* = 8.0 Hz), 118.7, 112.0 (d, *J* = 1.8 Hz), 68.2 (d, *J* = 159.1 Hz), 62.9 (d, *J* = 7.1 Hz), 62.4 (d, *J* = 7.0 Hz), 43.9 (d, *J* = 9.2 Hz), 16.4 (d, *J* = 5.8 Hz), 16.2 (d, *J* = 5.5 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 21.3; HRMS – ESI (*m/z*): [M + H]⁺ called for C₁₄H₂₂N₂O₃P, 297.1363, found 297.1359.



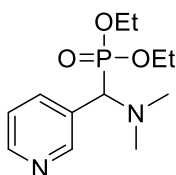
Diethyl ((dimethylamino)(4-(methylthio)phenyl)methyl)phosphonate (3ka): colorless oil, 210 mg, 59% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 8 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 7.37 (d, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.22 – 4.12 (m, 2H), 3.97 – 3.88 (m, 1H), 3.76 – 3.65 (m, 2H), 2.47 (s, 3H), 2.33 (s, 6H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 138.5, 131.1, 131.0, 126.0, 67.8 (d, *J* = 160.2 Hz), 62.6 (t, *J* = 7.2 Hz), 43.9 (d, *J* = 9.3 Hz), 16.6 (d, *J* = 5.6 Hz), 16.4 (d, *J* = 5.6 Hz), 15.7; ³¹P NMR (162 MHz, CDCl₃): δ 22.6; HRMS – ESI (*m/z*): [M + H]⁺ called for C₁₄H₂₅NO₃SP, 318.1287, found 318.1284.



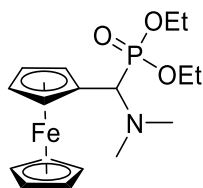
Diethyl ((dimethylamino)(thiophen-2-yl)methyl)phosphonate (3la): colorless oil, 160 mg, 58% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 3.5 : 1 and 1% Et₃N). ¹H NMR (400 MHz, CDCl₃): δ 7.29 (d, *J* = 5.2 Hz, 1H), 7.22 – 7.20 (m, 1H), 7.05 – 7.02 (m, 1H), 4.25 – 4.14 (m, 3H), 4.06 – 3.96 (m, 1H), 3.89 – 3.79 (m, 1H), 2.38 (s, 6H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.12 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 132.9 (d, *J* = 6.6 Hz), 129.2 (d, *J* = 6.8 Hz), 127.0, 125.9 (d, *J* = 2.0 Hz, 1H), 63.1 (d, *J* = 7.6 Hz), 62.7 (d, *J* = 7.1 Hz), 62.3 (d, *J* = 165.1 Hz), 43.3 (d, *J* = 8.7 Hz), 16.6 (d, *J* = 5.5 Hz), 16.4 (d, *J* = 5.5 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 21.2; HRMS – ESI (*m/z*): [M + H]⁺ called for C₁₁H₂₁NO₃PS, 278.0974, found 278.0974.



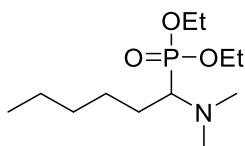
Diethyl ((dimethylamino)(furan-2-yl)methyl)phosphonate (3ma): yellow oil, 144 mg, 55% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 3.5 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 7.42 (s, 1H), 6.49 (s, 1H), 6.37 (s, 1H), 4.23 – 4.16 (m, 2H), 4.08 – 4.01 (m, 2H), 3.98 – 3.89 (m, 1H), 2.35 (s, 6H), 1.33 (t, *J* = 7.6 Hz, 3H), 1.16 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 147.1 (d, *J* = 10.2), 142.8 (d, *J* = 1.9), 111.5 (d, *J* = 4.5), 110.5, 63.0 (d, *J* = 6.9), 62.6 (d, *J* = 6.8), 60.9 (d, *J* = 166.5), 43.6 (d, *J* = 8.9), 16.6 (d, *J* = 5.6), 16.4 (d, *J* = 5.5); ³¹P NMR (162 MHz, CDCl₃): δ 20.5; HRMS – ESI (m/z): [M + Na]⁺ called for C₁₁H₂₀NO₄NaP, 248.1022, found 248.1024.



Diethyl ((dimethylamino)(pyridin-3-yl)methyl)phosphonate (3na): yellow oil, 106 mg, 39% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : CH₃OH = 20 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 8.57 – 8.56 (m, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.30 (m, 1H), 4.25 – 4.15 (m, 2H), 4.01 – 3.91 (m, 1H), 3.86 – 3.75 (m, 2H), 2.36 (s, 6H), 1.33 (t, *J* = 6.8 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (175 MHz, CDCl₃): δ 151.5 (d, *J* = 11.1 Hz), 149.5, 137.8 (d, *J* = 6.0 Hz), 128.8, 123.2, 65.6 (d, *J* = 161.7 Hz), 63.0 (d, *J* = 7.0 Hz), 62.5 (d, *J* = 7.0 Hz), 43.8 (d, *J* = 8.9 Hz), 16.6 (d, *J* = 5.8 Hz), 16.4 (d, *J* = 5.4 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 21.7; HRMS – ESI (m/z): [M + Na]⁺ called for C₁₂H₂₁N₂O₃NaP, 295.1182, found 295.1182.

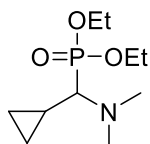


Diethyl ((dimethylamino)(ferrocenyl)methyl)phosphonate (3oa): red oil, 250 mg, 58% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 6 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 4.44 (s, 1H), 4.21 – 4.12 (m, 12H), 3.90 (d, *J* = 22.4 Hz, 1H), 2.27 (s, 6H), 1.40 – 1.32 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 69.6 (d, *J* = 1.8 Hz), 69.3, 68.7 (d, *J* = 16.3 Hz), 67.7, 67.5, 63.0 (d, *J* = 7.3 Hz), 62.8 (d, *J* = 158.5 Hz), 61.4 (d, *J* = 7.5 Hz), 43.1 (d, *J* = 7.0 Hz), 16.7 (d, *J* = 5.7 Hz), 16.6 (d, *J* = 5.8 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 23.2; HRMS – ESI (m/z): [M + Na]⁺ called for C₁₇H₂₆NO₃NaPFe, 402.0892, found 402.0893.

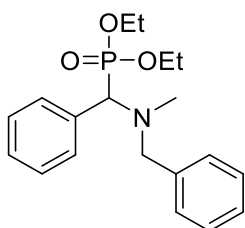


Diethyl (1-(dimethylamino)hexyl)phosphonate (3pa): colorless oil, 204 mg, 77% yield. Purification:

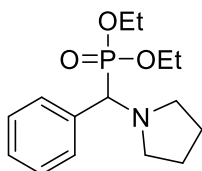
flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 6 : 1 and 1% Et₃N); ¹H NMR (500 MHz, CDCl₃): δ 4.13 – 4.07 (m, 4H), 2.83 – 2.75 (m, 1H), 2.455 (s, 3H), 2.450 (s, 3H), 1.68 – 1.60 (m, 2H), 1.49 – 1.45 (m, 1H), 1.35 – 1.24 (m, 11H), 0.87 (t, *J* = 8.5 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 62.1 (d, *J* = 137.0 Hz), 61.7 (d, *J* = 8.6 Hz), 61.1 (d, *J* = 7.6 Hz), 42.3 (d, *J* = 4.2 Hz), 31.8, 27.3 (d, *J* = 11.8 Hz), 26.9 (d, *J* = 5.7 Hz), 22.6, 16.71, 16.70 (d, *J* = 12.0 Hz), 14.1; ³¹P NMR (202 MHz, CDCl₃): δ 29.8; HRMS – ESI (m/z): [M + Na]⁺ called for C₁₂H₂₈NO₃NaP, 288.1699, found 288.1701.



Diethyl (cyclopropyl(dimethylamino)methyl)phosphonate (3qa): colorless oil, 182 mg, 77% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : CH₃OH = 20 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 4.18 – 4.11 (m, 4H), 2.52 (s, 6H), 2.04 (dd, *J* = 18.8, 10.8 Hz, 1H), 1.32 (t, *J* = 6.8, 6H), 1.16 – 1.05 (m, 1H), 0.69 – 0.60 (m, 2H), 0.36 – 0.34 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 67.6 (d, *J* = 149.9 Hz), 62.0 (d, *J* = 7.2 Hz), 61.3 (d, *J* = 7.2 Hz), 43.1 (d, *J* = 6.8 Hz), 16.6 (d, *J* = 2.3 Hz), 16.5 (d, *J* = 2.4 Hz), 6.9 (d, *J* = 6.9 Hz), 5.5 (d, *J* = 16.2 Hz), 3.4; ³¹P NMR (162 MHz, CDCl₃): δ 26.0; HRMS – ESI (m/z): [M + Na]⁺ called for C₁₀H₂₂NO₃NaP, 258.1230, found 258.1231.

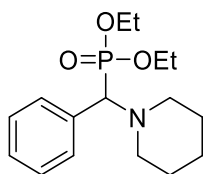


Diethyl ((benzyl(methyl)amino)(phenyl)methyl)phosphonate (3ra)¹: colorless oil, 259 mg, 75% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, PE : DCM : EA = 5 : 1 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 7.50 – 7.48 (m, 2H), 7.39 – 7.23 (m, 8H), 4.30 – 4.16 (m, 2H), 4.05 (d, *J* = 24.0 Hz, 1H), 3.94 – 3.88 (m, 1H), 3.84 (d, *J* = 13.2 Hz, 1H), 3.75 – 3.65 (m, 1H), 3.39 (d, *J* = 13.2 Hz, 1H), 2.41 (s, 3H), 1.37 (t, *J* = 6.8 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 139.1, 132.1 (d, *J* = 4.2 Hz), 130.9 (d, *J* = 8.6 Hz), 129.0, 128.4, 128.2, 128.1 (d, *J* = 1.4 Hz), 127.2, 65.0 (d, *J* = 160.9 Hz), 62.7 (d, *J* = 7.1 Hz), 62.3 (d, *J* = 7.0 Hz), 59.9 (d, *J* = 12.5 Hz), 40.0 (d, *J* = 5.2 Hz), 16.7 (d, *J* = 6.1 Hz), 16.3 (d, *J* = 5.6 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 23.1.

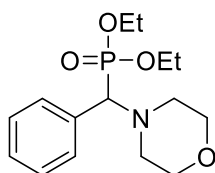


Diethyl (phenyl(pyrrolidin-1-yl)methyl)phosphonate (3sa)²: colorless oil, 166 mg, 56% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 6 : 1 and 1% Et₃N). ¹H NMR (400 MHz, CDCl₃): δ 7.49 – 7.46 (m, 2H), 7.35 – 7.28 (m, 3H), 4.16 – 4.03 (m, 2H), 3.95 – 3.85 (m, 1H), 3.76 (d, *J* = 15.6 Hz, 1H), 3.64 – 3.54 (m, 1H), 2.68 – 2.62 (m, 4H), 1.77– 1.70 (m, 4H), 1.29 (t, *J* = 6.4 Hz, 3H), 1.06 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 135.2, 130.0 (d, *J* = 7.3 Hz), 128.2 (d, *J* = 1.7 Hz), 127.9 (d, *J* = 2.5 Hz), 67.6 (d, *J* = 157.2 Hz), 62.7 (d, *J* = 7.0 Hz), 62.1 (d, *J*

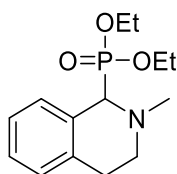
= 7.4 Hz), 53.0 (d, $J = 8.8$ Hz), 23.3, 16.4 (d, $J = 5.8$ Hz), 16.2 (d, $J = 5.7$ Hz); ^{31}P NMR (162 MHz, CDCl_3): δ 22.9.



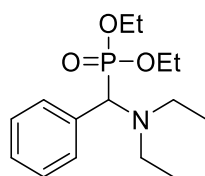
Diethyl (phenyl(piperidin-1-yl)methyl)phosphonate (3ta)¹: colorless oil, 220 mg, 71% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, PE : DCM : EA = 3.5 : 1 : 1 and 1% Et_3N); ^1H NMR (400 MHz, CDCl_3): δ 7.47 – 7.44 (m, 2H), 7.35 – 7.29 (m, 3H), 4.33 – 4.17 (m, 2H), 3.96 – 3.84 (m, 2H), 3.77 – 3.67 (m, 1H), 2.83 – 2.77 (m, 2H), 2.40 – 2.34 (m, 2H), 1.58 – 1.51 (m, 4H), 1.35 (t, $J = 6.8$ Hz, 3H), 1.31 – 1.27 (m, 2H), 1.03 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 132.6 (d, $J = 3.5$ Hz), 130.6 (d, $J = 9.1$ Hz), 128.0, 127.9 (d, $J = 1.4$ Hz), 68.9 (d, $J = 160.8$ Hz), 63.2 (d, $J = 7.0$ Hz), 62.1 (d, $J = 6.9$ Hz), 52.6 (d, $J = 9.1$ Hz), 26.5, 24.1, 16.6 (d, $J = 5.9$ Hz), 16.2 (d, $J = 5.7$ Hz); ^{31}P NMR (162 MHz, CDCl_3): δ 22.4.



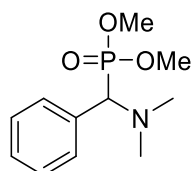
Diethyl (morpholino(phenyl)methyl)phosphonate (3ua)¹: colorless oil, 247 mg, 73% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 5 : 1 and 1% Et_3N). ^1H NMR (400 MHz, CDCl_3): δ 7.46 – 7.43 (m, 2H), 7.36 – 7.28 (m, 3H), 4.26 – 4.14 (m, 2H), 3.93 – 3.87 (m, 1H), 3.80 (d, $J = 21.2$ Hz, 1H), 3.70 – 3.60 (m, 5H), 2.82 – 2.77 (m, 2H), 2.54 – 2.50 (m, 2H), 1.33 (t, $J = 7.2$ Hz, 3H), 1.03 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 132.5, 130.6 (d, $J = 8.4$ Hz), 128.4, 128.3 (d, $J = 1.7$ Hz), 68.7 (d, $J = 159.9$ Hz), 67.3, 63.0 (d, $J = 7.1$ Hz), 62.5 (d, $J = 7.1$ Hz), 52.0 (d, $J = 9.2$ Hz), 16.7 (d, $J = 5.9$ Hz), 16.3 (d, $J = 5.6$ Hz); ^{31}P NMR (162 MHz, CDCl_3): δ 21.8.



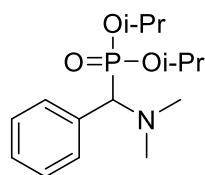
Diethyl (2-methyl-1,2,3,4-tetrahydroisoquinolin-1-yl)phosphonate (3va): pale yellow oil, 220 mg, 78% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, PE : DCM : EA = 1 : 1 : 1 and 1% Et_3N); ^1H NMR (400 MHz, CDCl_3): δ 7.34 – 7.31 (m, 1H), 7.17 – 7.14 (m, 2H), 7.11 – 7.09 (m, 1H), 4.09 – 3.88 (m, 5H), 3.45 – 3.39 (m, 1H), 2.86 – 2.81 (m, 2H), 2.66 – 2.61 (m, 4H), 1.27 (t, $J = 7.2$ Hz, 3H), 1.19 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 136.4 (d, $J = 6.2$ Hz), 129.8 (d, $J = 3.5$ Hz), 129.1 (d, $J = 4.7$ Hz), 128.5 (d, $J = 3.4$ Hz), 126.9 (d, $J = 4.3$ Hz), 125.7 (d, $J = 3.8$ Hz), 62.9 (d, $J = 7.7$ Hz), 62.6 (d, $J = 161.8$ Hz), 62.5 (d, $J = 7.9$ Hz), 49.4 (d, $J = 5.0$ Hz), 45.0 (d, $J = 9.7$ Hz), 26.9, 16.5 (d, $J = 4.1$ Hz), 16.4 (d, $J = 3.9$ Hz); ^{31}P NMR (162 MHz, CDCl_3): δ 23.1; HRMS – ESI (m/z): $[\text{M} + \text{Na}]^+$ called for $\text{C}_{14}\text{H}_{22}\text{NO}_3\text{NaP}$, 306.1230, found 306.1228.



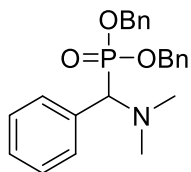
Diethyl ((diethylamino)(phenyl)methyl)phosphonate (3wa)³: colorless oil, 142 mg, 47% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, PE : DCM : EA = 8 : 1 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 7.47 – 7.45 (m, 2H), 7.34 – 7.27 (m, 3H), 4.27 – 4.19 (m, 2H), 4.16 (d, *J* = 24.8 Hz, 1H), 3.97 – 3.87 (m, 1H), 3.79 – 3.69 (m, 1H), 3.03 – 2.94 (m, 2H), 2.34 – 2.26 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 6.8 Hz, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 133.6 (d, *J* = 5.1 Hz), 130.7 (d, *J* = 8.9 Hz), 128.1, 127.8 (d, *J* = 1.4 Hz), 63.2 (d, *J* = 6.9 Hz), 62.2 (d, *J* = 162.1 Hz), 62.0 (d, *J* = 7.2 Hz), 44.9 (d, *J* = 8.4 Hz), 16.6 (d, *J* = 6.0 Hz), 16.3 (d, *J* = 5.7 Hz), 13.4; ³¹P NMR (162 MHz, CDCl₃): δ 23.6.



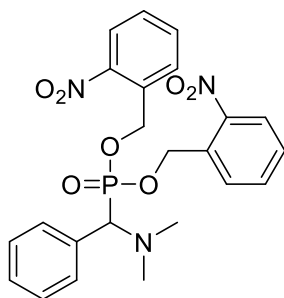
Dimethyl ((dimethylamino)(phenyl)methyl)phosphonate (3ab)⁴: colorless oil, 187 mg, 78% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 3.5 : 1 and 1% Et₃N). ¹H NMR (400 MHz, CDCl₃): δ 7.47 – 7.44 (m, 2H), 7.38 – 7.32 (m, 3H), 3.82 (d, *J* = 22.0 Hz, 1H), 3.81 (d, *J* = 10.8 Hz, 3H), 3.44 (d, *J* = 10.4 Hz, 3H), 2.35 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 132.1, 130.7 (d, *J* = 8.6 Hz), 128.4, 128.3 (d, *J* = 1.6 Hz), 68.0 (d, *J* = 160.6 Hz), 53.3 (d, *J* = 7.2 Hz), 43.8 (d, *J* = 9.7 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 25.0.



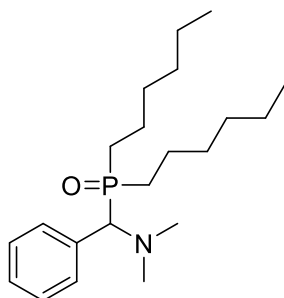
Diisopropyl ((dimethylamino)(phenyl)methyl)phosphonate (3ac): colorless oil, 212 mg, 71% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 6 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 7.44 – 7.41 (m, 2H), 7.33 – 7.27 (m, 3H), 4.79 – 4.71 (m, 1H), 4.46 – 4.38 (m, 1H), 3.70 (d, *J* = 22.0 Hz, 1H), 2.32 (s, 6H), 1.32 – 1.29 (m, 6H), 1.17 (d, *J* = 6.0 Hz, 3H), 0.79 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 132.9 (d, *J* = 2.4 Hz), 130.7 (d, *J* = 8.6 Hz), 128.0, 127.9 (d, *J* = 1.5 Hz), 71.0 (d, *J* = 7.2 Hz), 70.9 (d, *J* = 7.2 Hz), 68.6 (d, *J* = 161.8 Hz), 43.9 (d, *J* = 9.5 Hz), 24.4 (d, *J* = 2.5 Hz), 24.3 (d, *J* = 3.1 Hz), 23.9 (d, *J* = 5.3 Hz), 23.1 (d, *J* = 5.9 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 21.2; HRMS – ESI (m/z): [M + Na]⁺ called for C₁₅H₂₆NO₃NaP, 322.1543, found 322.1540.



Dibenzyl ((dimethylamino)(phenyl)methyl)phosphonate (3ad): pale yellow oil, 289 mg, 73% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, PE : DCM : EA = 4 : 1 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 7.48 – 7.45 (m, 2H), 7.36 – 7.31 (m, 8H), 7.23 – 7.20 (m, 3H), 7.04 – 7.01 (m, 2H), 5.18 – 5.06 (m, 2H), 4.85 – 4.80 (m, 1H), 4.56 – 4.51 (m, 1H), 3.88 (d, *J* = 21.6 Hz, 1H), 2.37 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 136.7 (d, *J* = 6.1 Hz), 136.3 (d, *J* = 6.1 Hz), 132.3 (d, *J* = 1.8 Hz), 130.6 (d, *J* = 8.6 Hz), 128.5, 128.34, 128.26, 128.21, 128.15 (d, *J* = 1.7 Hz), 128.1, 127.9, 127.7, 68.5 (d, *J* = 159.7 Hz), 68.0 (d, *J* = 7.0 Hz), 67.7 (d, *J* = 6.9 Hz), 43.9 (d, *J* = 9.6 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 23.6; HRMS – ESI (*m/z*): [M + H]⁺ called for C₂₃H₂₇NO₃P, 396.1723, found 396.1722.

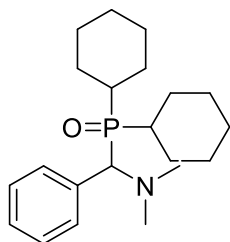


Dis(2-nitrobenzyl) ((dimethylamino)(phenyl)methyl)phosphonate (3ae): yellow oil, 382 mg, 67% yield. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 20 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 8.11 (d, *J* = 8.4, 1H), 8.00 (d, *J* = 8.4, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.66 (t, *J* = 7.6, 1H), 7.50 – 7.34 (m, 8H), 7.20 (d, *J* = 7.6 Hz, 1H), 5.71 – 5.57 (m, 2H), 5.33 – 5.14 (m, 2H), 4.05 (d, *J* = 22.8 Hz, 1H), 2.36 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 146.8, 146.4, 133.9, 133.8, 133.2 (d, *J* = 6.2 Hz), 132.8 (d, *J* = 6.0 Hz), 130.9 (d, *J* = 3.0 Hz), 130.6 (d, *J* = 9.1 Hz), 128.65, 128.60, 128.41, 128.39, 128.3, 128.1, 124.8, 124.7, 68.0 (d, *J* = 162.4 Hz), 65.2 (d, *J* = 6.0 Hz), 64.2 (d, *J* = 6.0 Hz), 43.5 (d, *J* = 9.9 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 23.5; HRMS – ESI (*m/z*): [M + H]⁺ called for C₂₃H₂₅N₃O₇P, 486.1425, found 486.1429.

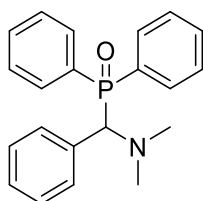


((Dimethylamino)(phenyl)methyl)dihexylphosphine oxide (3ag): colorless oil, 203 mg, 66% yield. Purification: flash column chromatography (200 – 300 mesh basic aluminum oxide, DCM : EA = 5 : 1 and 1% Et₃N); ¹H NMR (500 MHz, CDCl₃): δ 7.47 – 7.46 (m, 2H), 7.38 – 7.32 (m, 3H), 3.42 (d, *J* = 10.5

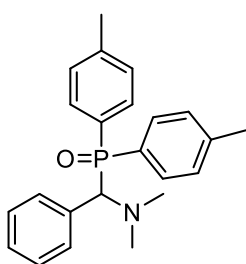
Hz, 1H), 2.33 (s, 6H), 2.02 – 1.79 (m, 2H), 1.63 – 1.11 (m, 18H), 0.89 (t, $J = 6.5$ Hz, 3H), 0.80 (t, $J = 6.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 131.3, 131.2, 128.3, 128.2, 68.3 (d, $J = 78.0$ Hz), 43.9 (d, $J = 6.9$ Hz), 31.4, 31.2, 31.0 (d, $J = 14.0$ Hz), 30.7 (d, $J = 13.4$ Hz), 27.0 (d, $J = 34.1$ Hz), 26.4 (d, $J = 30.1$ Hz), 22.5, 22.4, 22.3 (d, $J = 3.4$ Hz), 21.8 (d, $J = 3.7$ Hz), 14.1, 14.0; ^{31}P NMR (202 MHz, CDCl_3): δ 50.9; HRMS – ESI (m/z): $[\text{M} + \text{H}]^+$ called for $\text{C}_{21}\text{H}_{39}\text{NOP}$, 352.2764, found 352.2765.



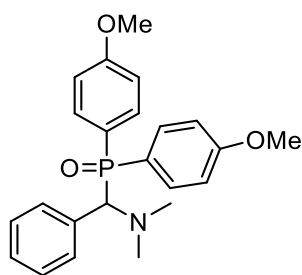
Dicyclohexyl((dimethylamino)(phenyl)methyl)phosphine oxide (3ah): white solid, 203 mg, 58% yield, mp: 177 – 179 °C. Purification: flash column chromatography (100 – 200 mesh silica gel, DCM : EA = 8 : 1 and 1% Et_3N); ^1H NMR (500 MHz, CDCl_3): δ 7.52 – 7.50 (m, 2H), 7.38 – 7.33 (m, 3H), 3.62 (d, $J = 9.5$ Hz, 1H), 2.30 (s, 6H), 2.24 – 2.05 (m, 3H), 1.88 – 1.48 (m, 11H), 1.36 – 1.25 (m, 3H), 1.12 – 0.86 (m, 5H); ^{13}C NMR (126 MHz, CDCl_3): δ 131.8 (d, $J = 6.8$ Hz), 130.8 (d, $J = 2.1$ Hz), 128.02, 127.98, 64.2 (d, $J = 75.0$ Hz), 43.3 (d, $J = 7.1$ Hz), 37.9 (d, $J = 22.7$ Hz), 37.5 (d, $J = 26.7$ Hz), 27.5 (d, $J = 12.0$ Hz), 27.3 (d, $J = 12.0$ Hz), 27.11, 27.05 (d, $J = 9.5$ Hz), 26.93 (d, $J = 4.3$ Hz), 26.87 (d, $J = 4.4$ Hz), 26.7 (d, $J = 2.8$ Hz), 26.5, 26.2 (d, $J = 2.9$ Hz), 26.1; ^{31}P NMR (202 MHz, CDCl_3): δ 50.9; HRMS – ESI (m/z): $[\text{M} + \text{H}]^+$ called for $\text{C}_{21}\text{H}_{35}\text{NOP}$, 348.2451, found 348.2454.



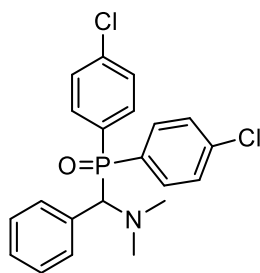
((Dimethylamino)(phenyl)methyl)diphenylphosphine oxide (3aj): white solid, 252 mg, 84% yield, mp: 182 – 183 °C. Purification: flash column chromatography (100 – 200 mesh silica gel, PE : DCM : EA = 1 : 1 : 2, 10% DCM and 1% Et_3N); ^1H NMR (400 MHz, CDCl_3): δ 7.97 – 7.92 (m, 2H), 7.53 – 7.44 (m, 7H), 7.30 – 7.28 (m, 1H), 7.24 – 7.21 (m, 5H), 4.31 (d, $J = 10.6$ Hz, 1H), 2.38 (s, 6H); ^{13}C NMR (126 MHz, CDCl_3): δ 133.4 (d, $J = 65.0$ Hz), 132.7 (d, $J = 61.2$ Hz), 131.6 (d, $J = 8.6$ Hz), 131.52 (d, $J = 2.4$ Hz), 131.50 (d, $J = 7.7$ Hz), 131.3 (d, $J = 8.6$ Hz), 131.1 (d, $J = 2.9$ Hz), 130.8 (d, $J = 2.9$ Hz), 128.4 (d, $J = 11.5$ Hz), 128.1 (d, $J = 11.3$ Hz), 127.94, 127.89, 69.0 (d, $J = 87.6$ Hz), 43.8 (d, $J = 7.6$ Hz); ^{31}P NMR (162 MHz, CDCl_3): δ 30.8; HRMS – ESI (m/z): $[\text{M} + \text{Na}]^+$ called for $\text{C}_{21}\text{H}_{22}\text{NONaP}$, 358.1331, found 358.1332.



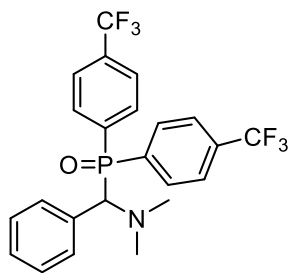
((Dimethylamino)(phenyl)methyl)di-p-tolylphosphine oxide (3ak): white solid, 280 mg, 71 % yield, mp: 150 – 151 °C. Purification: flash column chromatography (100 – 200 mesh silica gel) PE : DCM : EA = 2 : 1 : 1, 10% DCM and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 7.84 – 7.79 (m, 2H), 7.48 – 7.45 (m, 2H), 7.39 – 7.35 (m, 2H), 7.30 – 7.27 (m, 2H), 7.24 – 7.22 (m, 3H), 7.02 – 6.99 (m, 2H), 4.27 (d, *J* = 10.8 Hz, 1H), 2.40 (s, 3H), 2.37 (s, 6H), 2.23 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 141.8, 141.4, 131.6, 131.5 (d, *J* = 2.0 Hz), 131.1 (d, *J* = 8.9 Hz), 131.0, 130.5 (d, *J* = 44.9 Hz), 129.5 (d, *J* = 41.2 Hz), 129.2 (d, *J* = 11.8 Hz), 128.9 (d, *J* = 11.4 Hz), 127.9, 127.8, 69.1 (d, *J* = 86.8 Hz), 43.8 (d, *J* = 7.6 Hz), 21.6 (d, *J* = 19.8 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 31.1; HRMS – ESI (*m/z*): [M + Na]⁺ called for C₂₃H₂₆NONaP, 386.1644, found 386.1653.



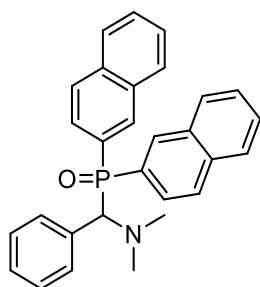
((Dimethylamino)(phenyl)methyl)bis(4-methoxyphenyl)phosphine oxide (3al): white solid, 293 mg, 76% yield, mp: 157 – 159 °C; Purification: flash column chromatography (100 – 200 mesh silica gel) DCM : EA = 4 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 7.86 – 7.81 (m, 2H), 7.44 – 7.36 (m, 4H), 7.23 – 7.21 (m, 3H), 7.0 (d, *J* = 6.4 Hz, 2H), 6.7 (d, *J* = 6.4 Hz, 2H), 4.20 (d, *J* = 10.8 Hz, 1H), 3.83 (s, 3H), 3.69 (s, 3H), 2.36 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 162.1 (d, *J* = 2.8 Hz), 161.7 (d, *J* = 2.8 Hz), 133.4 (d, *J* = 9.6 Hz), 133.0 (d, *J* = 9.8 Hz), 131.5 (d, *J* = 7.3 Hz), 131.1, 127.9, 127.8, 125.0 (d, *J* = 39.9 Hz), 124.0 (d, *J* = 36.5 Hz), 114.0 (d, *J* = 12.3 Hz), 113.7 (d, *J* = 12.1 Hz), 69.5 (d, *J* = 87.0 Hz), 55.3 (d, *J* = 15.4 Hz), 43.7 (d, *J* = 7.5 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 31.0; HRMS – ESI (*m/z*): [M + Na]⁺ called for C₂₃H₂₆NO₃NaP, 418.1543, found 418.1544.



Bis(4-chlorophenyl)((dimethylamino)(phenyl)methyl)phosphine oxide (3am): white solid, 327 mg, 81% yield, mp: 139 – 140 °C. Purification: flash column chromatography (100-200 mesh silica gel, PE : DCM : EA = 5 : 1 : 1, 10% DCM and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 7.88 – 7.83 (m, 2H), 7.49 – 7.39 (m, 6H), 7.27 – 7.20 (m, 5H), 4.25 (d, *J* = 10.8 Hz, 1H), 2.37 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 138.4 (d, *J* = 3.4 Hz), 138.0 (d, *J* = 3.4 Hz), 133.0 (d, *J* = 9.2 Hz), 132.5 (d, *J* = 9.2 Hz), 131.6 (d, *J* = 46.9 Hz), 131.4 (d, *J* = 7.7 Hz), 130.7 (d, *J* = 44.2 Hz), 130.1, 128.9 (d, *J* = 12.0 Hz), 128.7 (d, *J* = 11.7 Hz), 128.3, 128.2, 69.1 (d, *J* = 88.5 Hz), 43.7 (d, *J* = 7.7 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 29.8; HRMS – ESI (*m/z*): [M + Na]⁺ called for C₂₁H₂₀NONaPCl₂, 426.0552, found 426.0560.



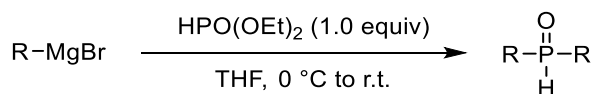
((Dimethylamino)(phenyl)methyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3an): white solid, 314 mg, 67% yield, mp: 46 – 47 °C. Purification: flash column chromatography (200 – 300 mesh basic aluminum oxide, PE : DCM : EA = 6 : 1 : 1 and 1% Et₃N); ¹H NMR (500 MHz, CDCl₃): δ 8.08 – 8.05 (m, 2H), 7.78 – 7.76 (m, 2H), 7.65 – 7.62 (m, 2H), 7.51 – 7.46 (m, 4H), 7.28 – 7.27 (m, 3H), 4.35 (d, *J* = 11.0 Hz, 1H), 2.38 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 136.8 (q, ²*J*_{C-F} = 43.8 Hz), 133.9 – 133.2 (m, 1C), 132.0 (d, *J*_{C-P} = 8.7 Hz), 131.6 (d, *J*_{C-P} = 8.8 Hz), 131.4 (d, *J*_{C-P} = 7.9 Hz), 129.6 (d, *J*_{C-P} = 3.2 Hz), 128.5, 128.4, 125.6 – 125.1 (m, 3C), 125.0 (dq, ¹*J*_{C-F} = 248.5 Hz, ⁵*J*_{C-P} = 22.5), 68.8 (d, ¹*J*_{C-P} = 88.9 Hz), 43.7 (d, ³*J*_{C-P} = 7.7 Hz); ³¹P NMR (202 MHz, CDCl₃): δ 28.9; ¹⁹F NMR (376 MHz, CDCl₃): δ -63.2, -63.3; HRMS – ESI (m/z): [M + H]⁺ called for C₂₃H₂₁NOF₆P, 472.1259, found 472.1265.



((Dimethylamino)(phenyl)methyl)di(naphthalen-2-yl)phosphine oxide (3ao): white solid, 261 mg, 55% yield, mp: 192 – 193 °C. Purification: flash column chromatography (100 – 200 mesh silica gel, PE : DCM : EA = 3 : 1 : 1, 10% DCM and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 8.62 (d, *J* = 12.8 Hz, 1H), 8.20 (d, *J* = 12.4 Hz, 1H), 7.96 – 7.87 (m, 4H), 7.76 – 7.65 (m, 3H), 7.60 – 7.42 (m, 7H), 7.25 – 7.18 (m, 3H), 4.56 (d, *J* = 10.8 Hz, 1H), 2.44 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 134.7 (d, *J* = 2.5 Hz), 134.3 (d, *J* = 2.4 Hz), 133.6 (d, *J* = 7.8 Hz), 133.3 (d, *J* = 7.7 Hz), 132.8 (d, *J* = 12.6 Hz), 132.4 (d, *J* = 12.1 Hz), 131.6, 131.5, 130.8 (d, *J* = 49.5 Hz), 130.7 (d, *J* = 2.9 Hz), 129.9 (d, *J* = 45.2 Hz), 129.08, 128.87, 128.1, 128.04, 128.02, 127.98, 127.94, 127.86, 127.84, 127.7, 126.7 (d, *J* = 12.0 Hz), 126.6 (d, *J* = 9.4 Hz), 125.9 (d, *J* = 9.6 Hz), 68.9 (d, *J* = 87.3 Hz), 43.8 (d, *J* = 7.6 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 31.2; HRMS – ESI (m/z): [M + Na]⁺ called for C₂₉H₂₆NONaP, 458.1644, found 458.1643.

5. Synthesis and Characterization of Reactants

5.1 General Synthesis Procedure for phosphine oxide

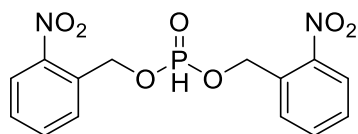


Method A: To a solution of Grignard reagent (0.5 M, 40 mmol, 4.0 equiv) in THF (80.0 mL), under nitrogen and cooled in an ice-bath, was added a solution of HPO(OEt)₂ (10 mmol, 1.0 equiv) in

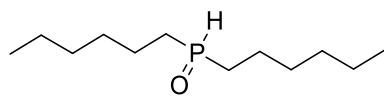
THF (8.0 mL) dropwise at a rate to maintain temperature between 0 ~ 10 °C. The reaction was allowed to stir at room temperature for 12 h. The reaction mixture was quenched with 1 M HCl and extracted with EA. The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄, filtered, concentrated and purified with silica gel column chromatography (PE/DCM/EtOAc).

Method B⁵: A dry 500 mL 3-neck round containing a magnetic stir bar was charged with Phosphorus trichloride (2.75 g, 20 mmol) and toluene (120 mL). The addition funnel was charged with 2-nitrobenzyl alcohol (6.126 g, 40 mmol), toluene (40 mL), and *N,N*-dimethylaniline (4.85 g, 40 mmol). The mixture in the addition funnel was heated via a heat gun until homogeneous. This solution was added to the pot in small portions over 30 min, re-heating as necessary. After 1 h, 2-nitrobenzyl alcohol (3.06 g, 20 mmol) in warm toluene (40 mL) was added to the reaction over 15 min via the addition funnel. The reaction vessel was wrapped with aluminum foil to exclude light. After 12 h, the reaction mixture was washed with deionized water (3 × 50 mL), an aqueous solution of ammonia (5 M, 2 × 50 mL), deionized water (2 × 50 mL), and brine (50 mL). The organic solution was dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. Products were prepared by recrystallization with toluene.

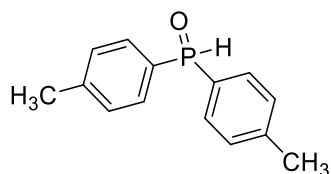
5.2 Characterization of the Compounds



Bis(2-nitrobenzyl) phosphonate (2e)⁵: prepared by method B, white solid, 3.12 g, 44% yield, mp: 91 – 93 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.15 (d, *J* = 8.4 Hz, 2H), 7.77 – 7.68 (m, 4H), 7.55 – 7.51 (m, 2H), 7.17 (d, *J* = 716.0 Hz, 1H), 5.64 – 5.51 (m, 4H); ¹³C NMR (150 MHz, CDCl₃): δ 146.8, 134.3, 131.9 (d, *J* = 7.6 Hz), 129.2, 128.7, 125.2, 64.2 (d, *J* = 4.3 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 8.1.

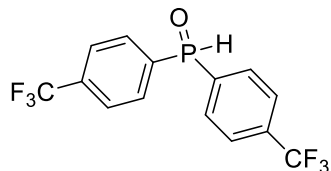


Dihexylphosphine oxide (2g)⁶: prepared by method A, white solid, 1.92 g, 59% yield, mp: 69 – 70 °C. Purification: flash column chromatography (100 – 200 mesh silica gel, EA: DCM: PE = 2 : 1 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 6.83 (d, *J* = 445.2 Hz, 1H), 1.82 – 1.56 (m, 8H), 1.42 – 1.38 (m, 4H), 1.30 – 1.27 (m, 8H), 0.87 (t, *J* = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 30.9, 30.0 (d, *J* = 13.2 Hz), 27.9 (d, *J* = 64.6 Hz), 22.0, 21.4 (d, *J* = 3.7 Hz), 13.6; ³¹P NMR (162 MHz, CDCl₃): δ 34.6.

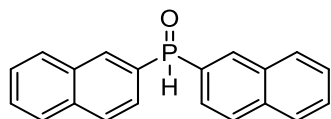


Di-p-tolylphosphine oxide (2k)⁷: prepared by method A, yellow solid, 2.42 g, 70% yield, mp: 96 –

97 °C. Purification: flash column chromatography (100 – 200 mesh silica gel, PE : EA = 1 : 1, 10% DCM and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 8.02 (d, *J* = 478.4 Hz, 1H), δ 7.59 – 7.54 (m, 4H), 7.30–7.27 (m, 4H), 2.39 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 143.2 (d, *J* = 2.8 Hz), 130.8 (d, *J* = 11.8 Hz), 129.7 (d, *J* = 13.2 Hz), 128.4 (d, *J* = 103.2 Hz), 21.7 (d, *J* = 1.3 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 21.7.



Bis(4-(trifluoromethyl)phenyl)phosphine oxide (2n)⁷: prepared by method A, yellow solid, 1.78 g, 50% yield, mp: 58 – 59 °C. Purification: flash column chromatography (100 – 200 mesh silica gel, PE : EA : DCM = 2.5 : 1 : 1 and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): δ 8.20 (d, *J* = 491.2 Hz, 1H), 7.89 – 7.78 (m, 8H); ¹³C NMR (100 MHz, CDCl₃): δ 134.9 (q, *J*²_{C-F} = 32.5 Hz), 131.3 (d, *J*²_{C-P} = 11.9 Hz), 126.1 (dq, *J*³_{C-P} = 13.0 Hz, *J*³_{C-F} = 3.7 Hz), 123.4 (q, *J*¹_{C-F} = 271.0 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 17.9; ¹⁹F NMR (376 MHz, CDCl₃): δ -63.3.

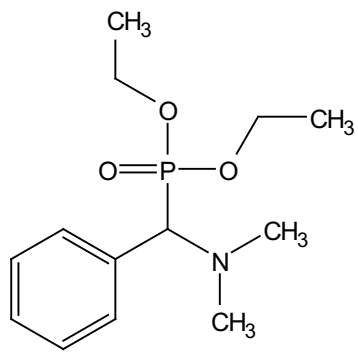


Di(naphthalen-2-yl)phosphine oxide (2o)⁸: prepared by method A, yellow solid, 0.81g, 25% yield, mp: 98 – 99 °C; Purification: flash column chromatography (100 – 200 mesh silica gel, PE : EA = 1.5 : 1, 10% DCM and 1% Et₃N); ¹H NMR (400 MHz, CDCl₃): 8.39 (d, *J* = 15.6 Hz, 2H), δ 8.35 (d, *J* = 481.2 Hz, 1H), 7.94 – 7.86 (m, 6H), 7.66 – 7.55 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 135.2 (d, *J* = 2.5 Hz), 133.0 (d, *J* = 10.9 Hz), 132.6 (d, *J* = 14.1 Hz), 129.1, 129.0, 128.9, 128.6, 128.1, 127.3, 125.3 (d, *J* = 12.4 Hz); ³¹P NMR (162 MHz, CDCl₃): δ 21.7.

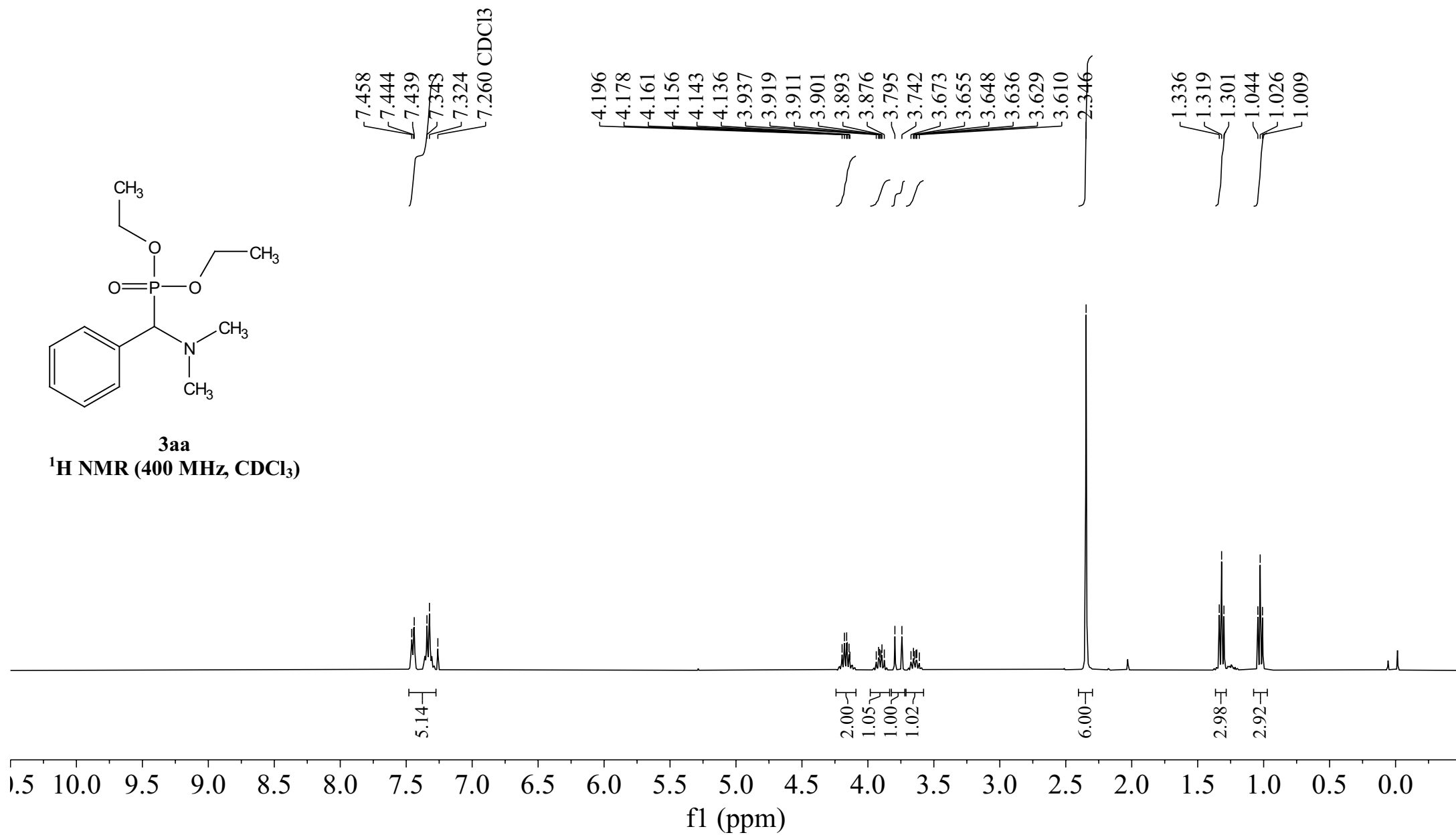
6. References

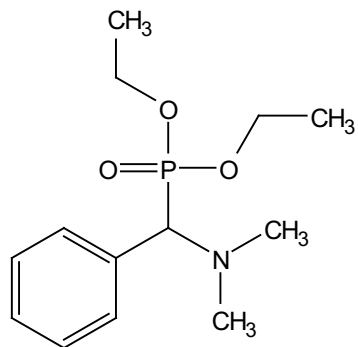
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2. Y. Gao, Z. Huang, R. Zhuang, J. Xu, P. Zhang, G. Tang and Y. Zhao, *Org. Lett.*, 2013, **15**, 4214-4217.
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7. NMR Spectra Copies



3aa
 $^1\text{H NMR}$ (400 MHz, CDCl_3)





3aa

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

132.561
132.544
130.536
130.453
128.068
127.970
127.953

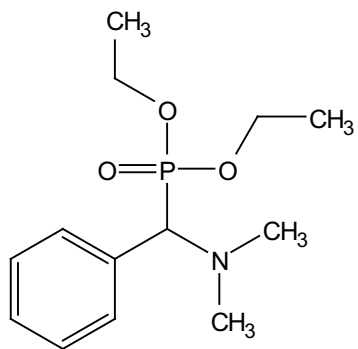
77.479
77.160 CDCl_3
77.160
76.842
69.067
67.469
62.388
62.316

43.866
43.771

16.459
16.402
16.161
16.105

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

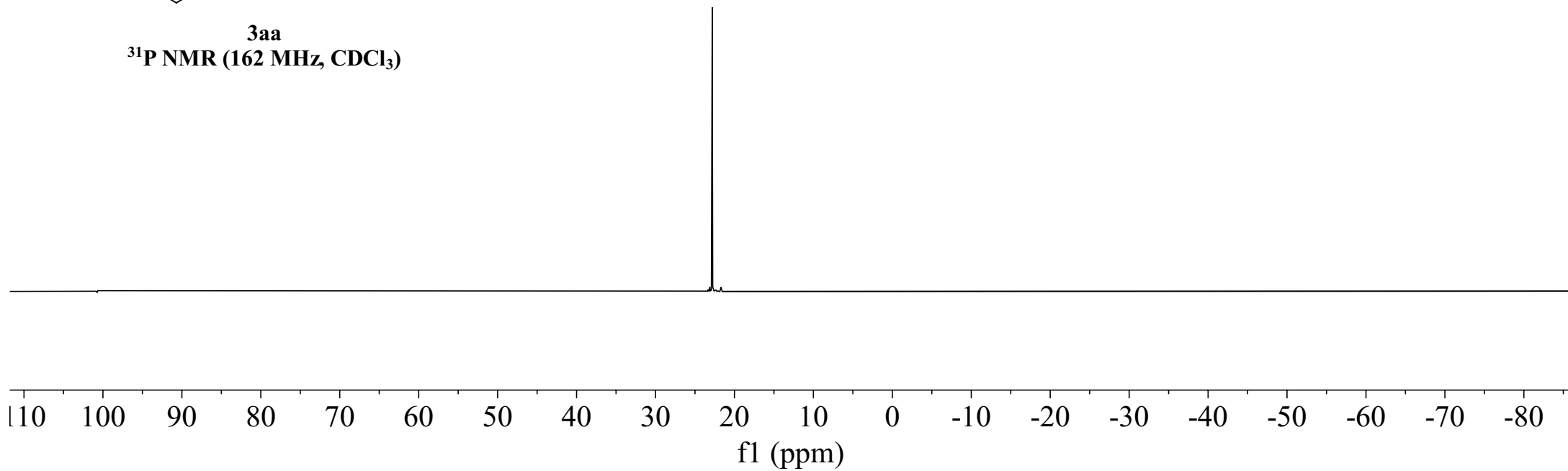
f1 (ppm)

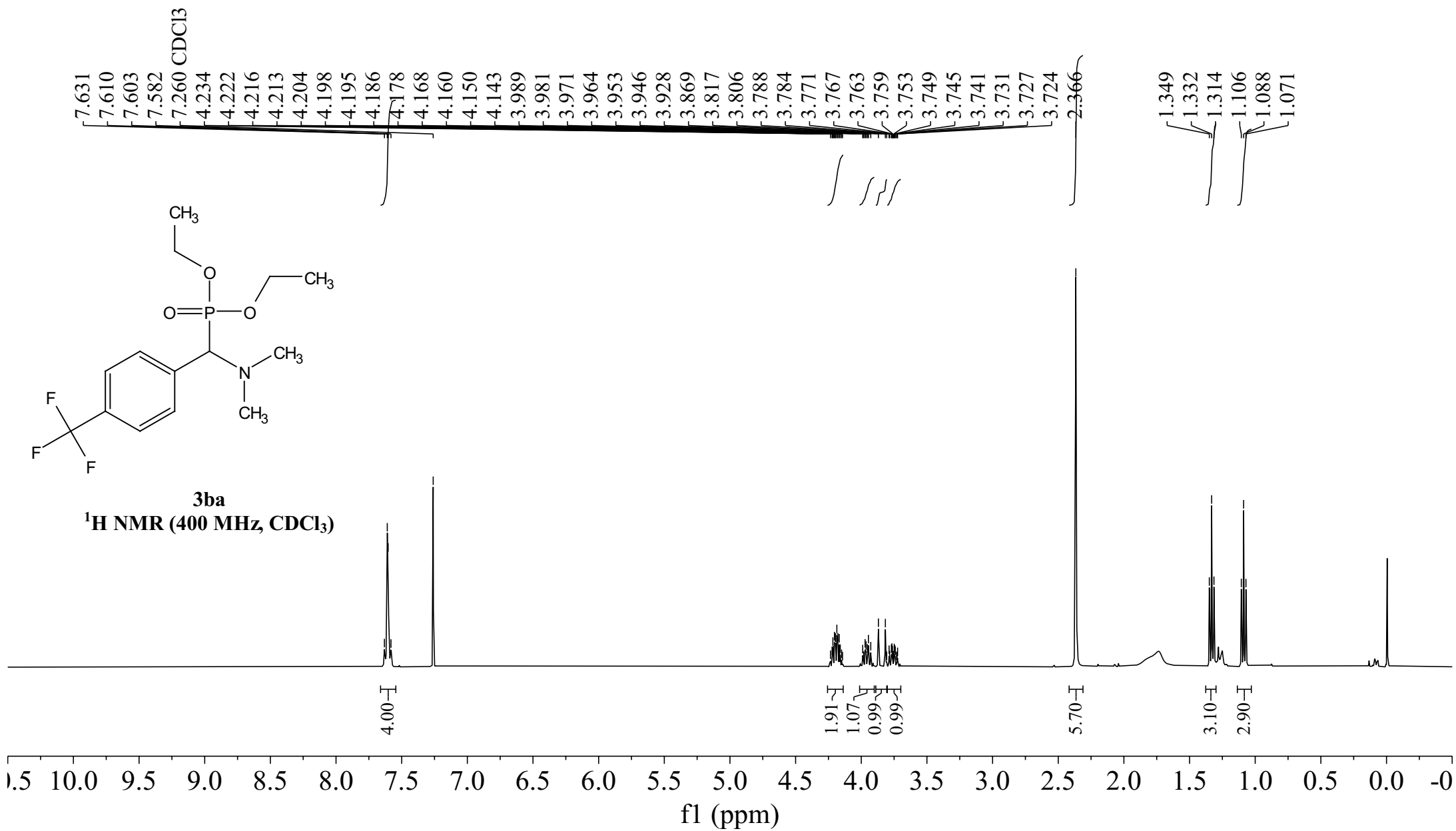


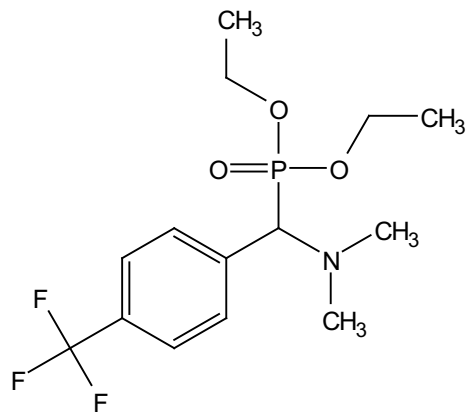
3aa

³¹P NMR (162 MHz, CDCl₃)

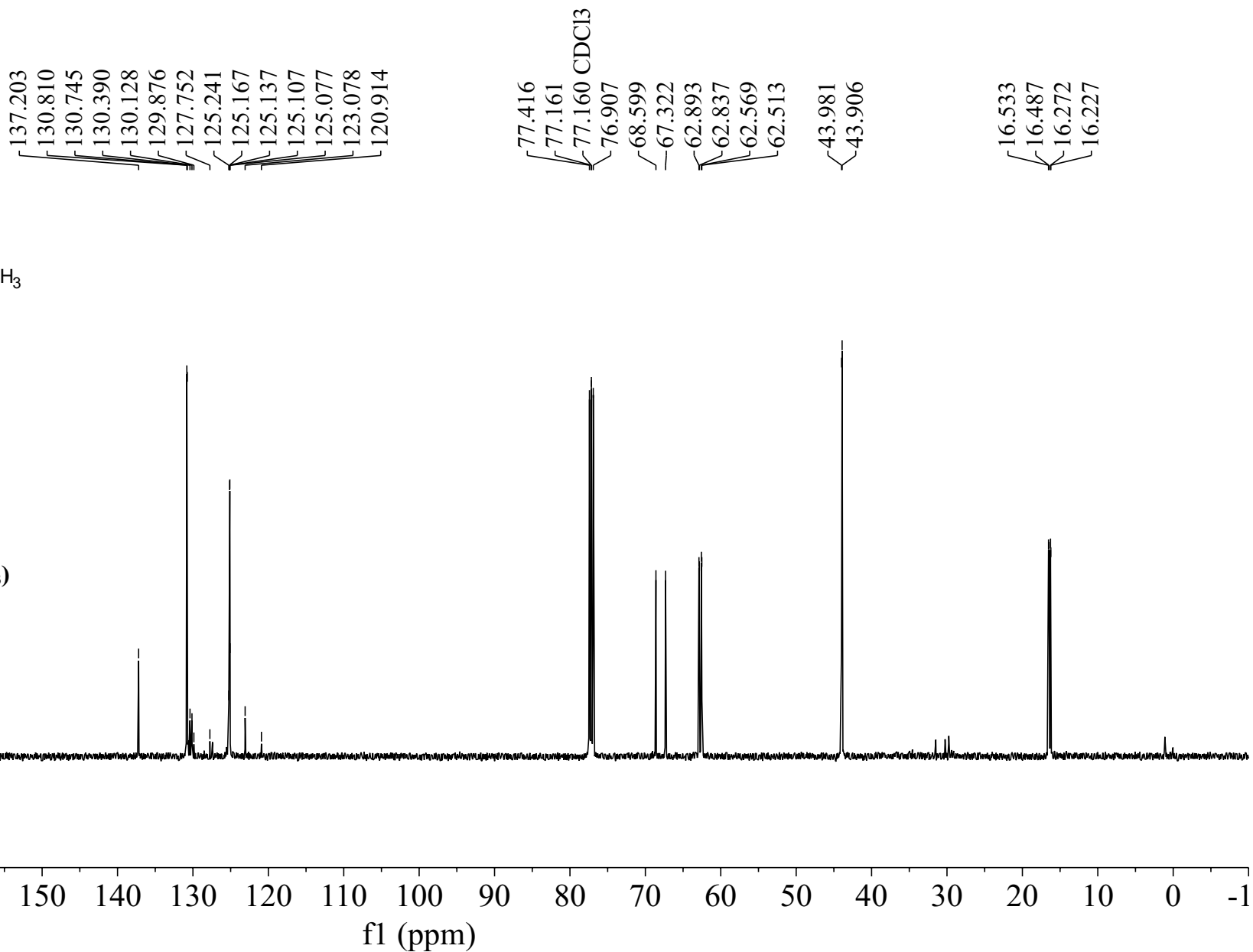
—22.810



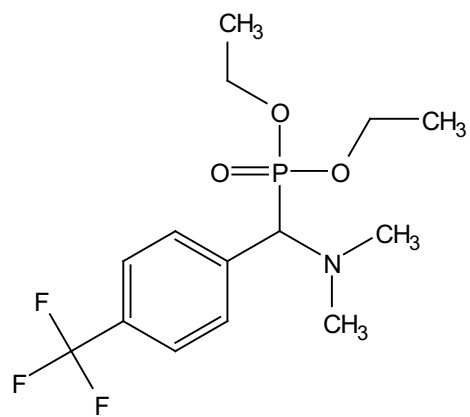




3ba
¹³C NMR (125 MHz, CDCl₃)

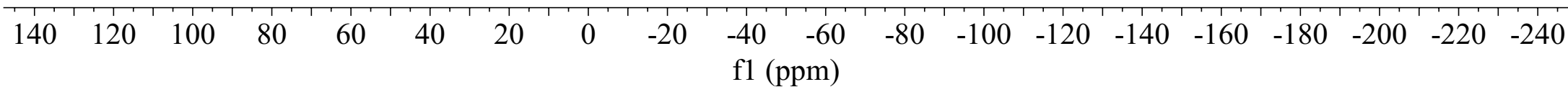


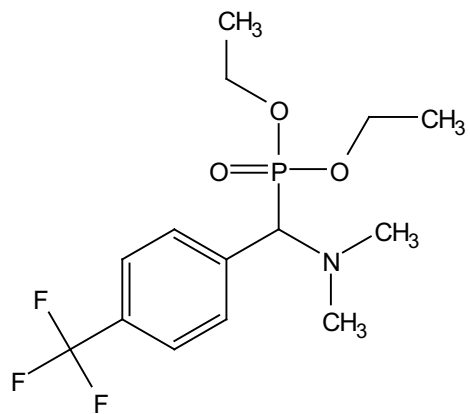
-21.783



3ba

³¹P NMR (162 MHz, CDCl₃)





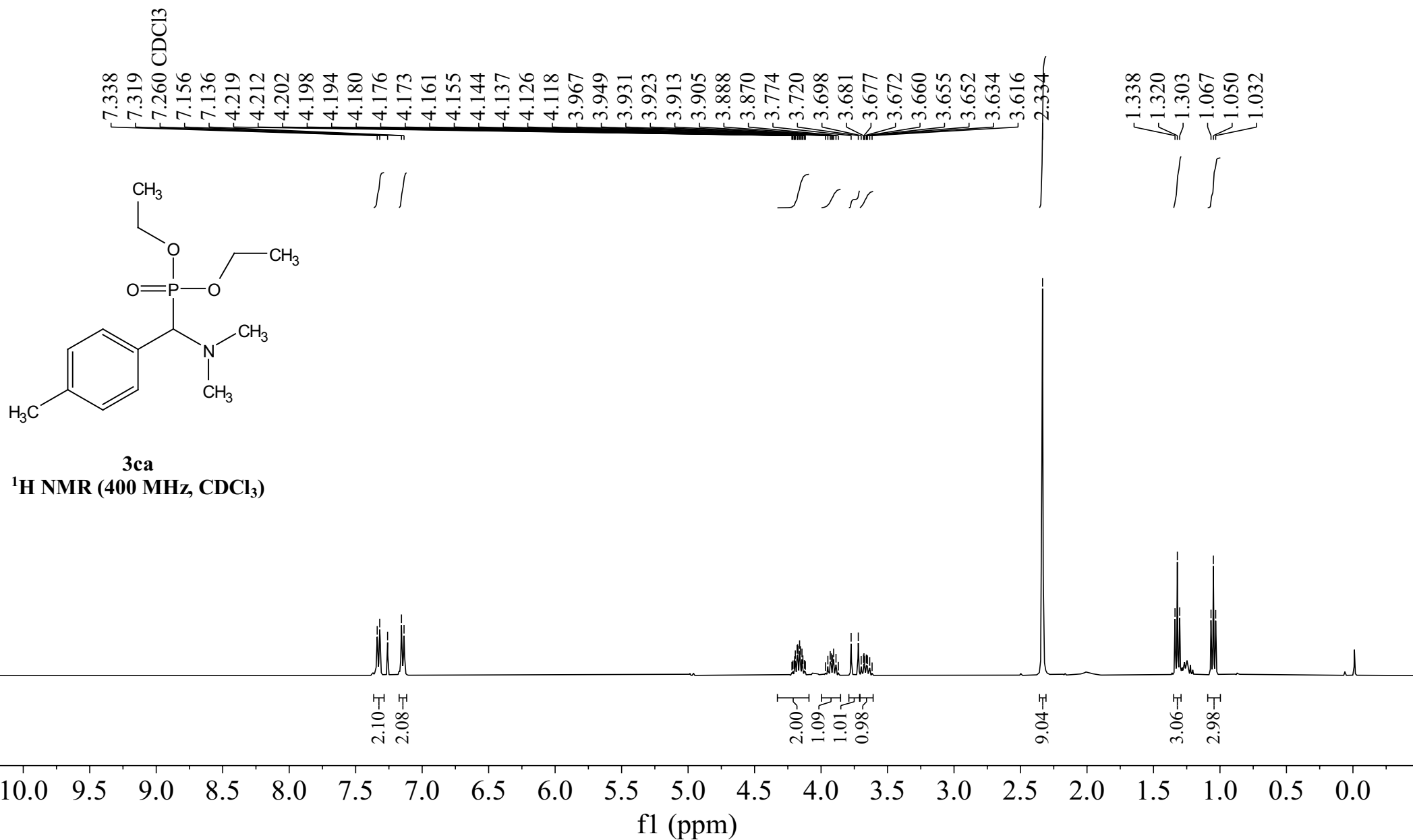
3ba
¹⁹F NMR (376 MHz, CDCl₃)

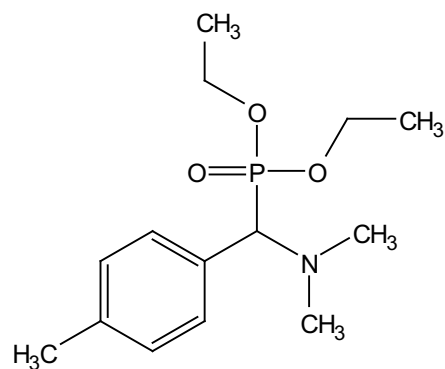
-62.579
-62.584



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

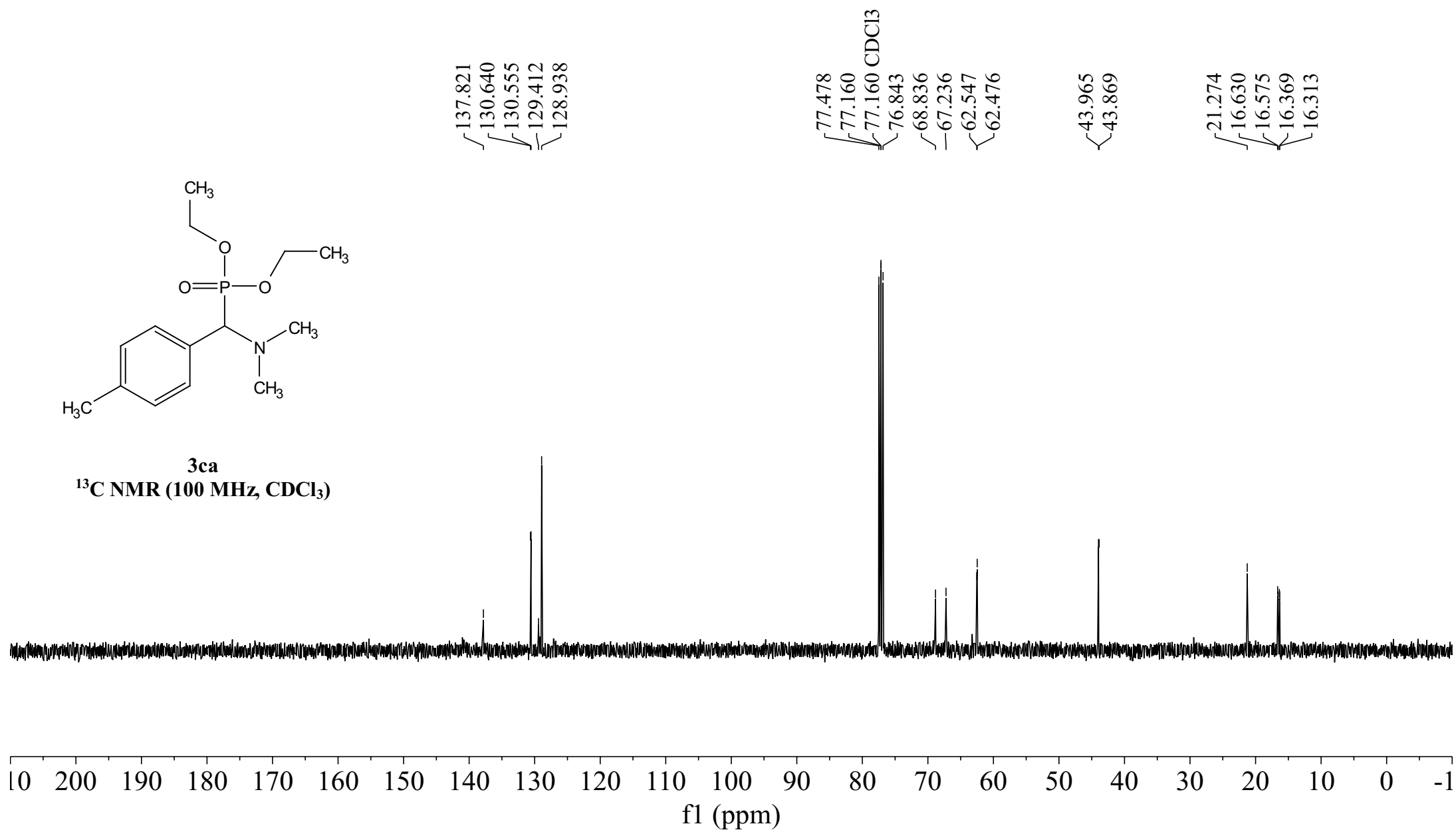
f1 (ppm)

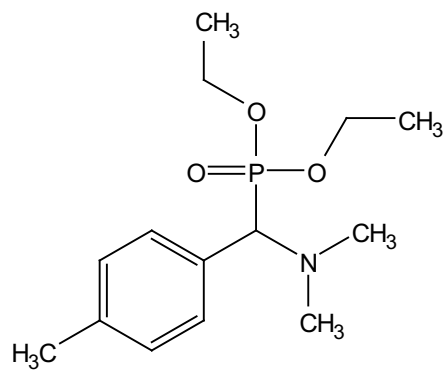




3ca

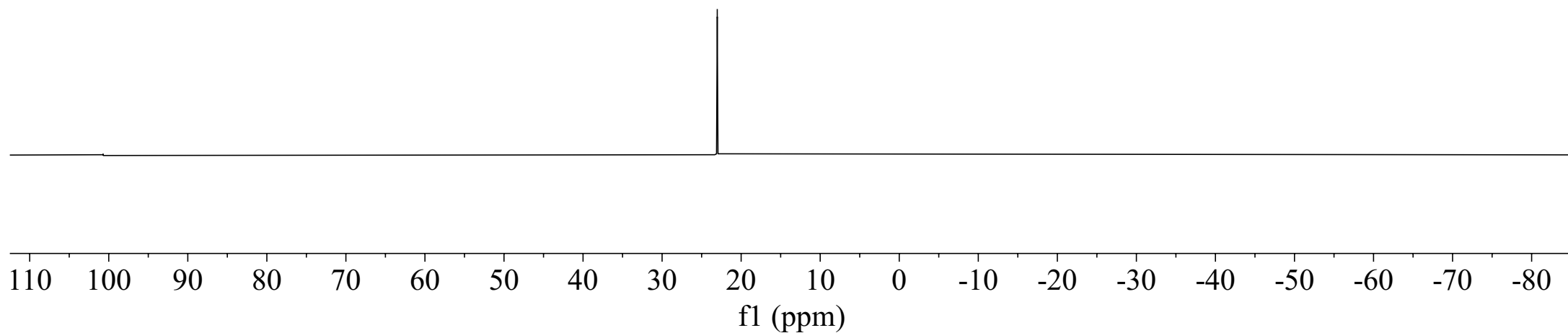
¹³C NMR (100 MHz, CDCl₃)

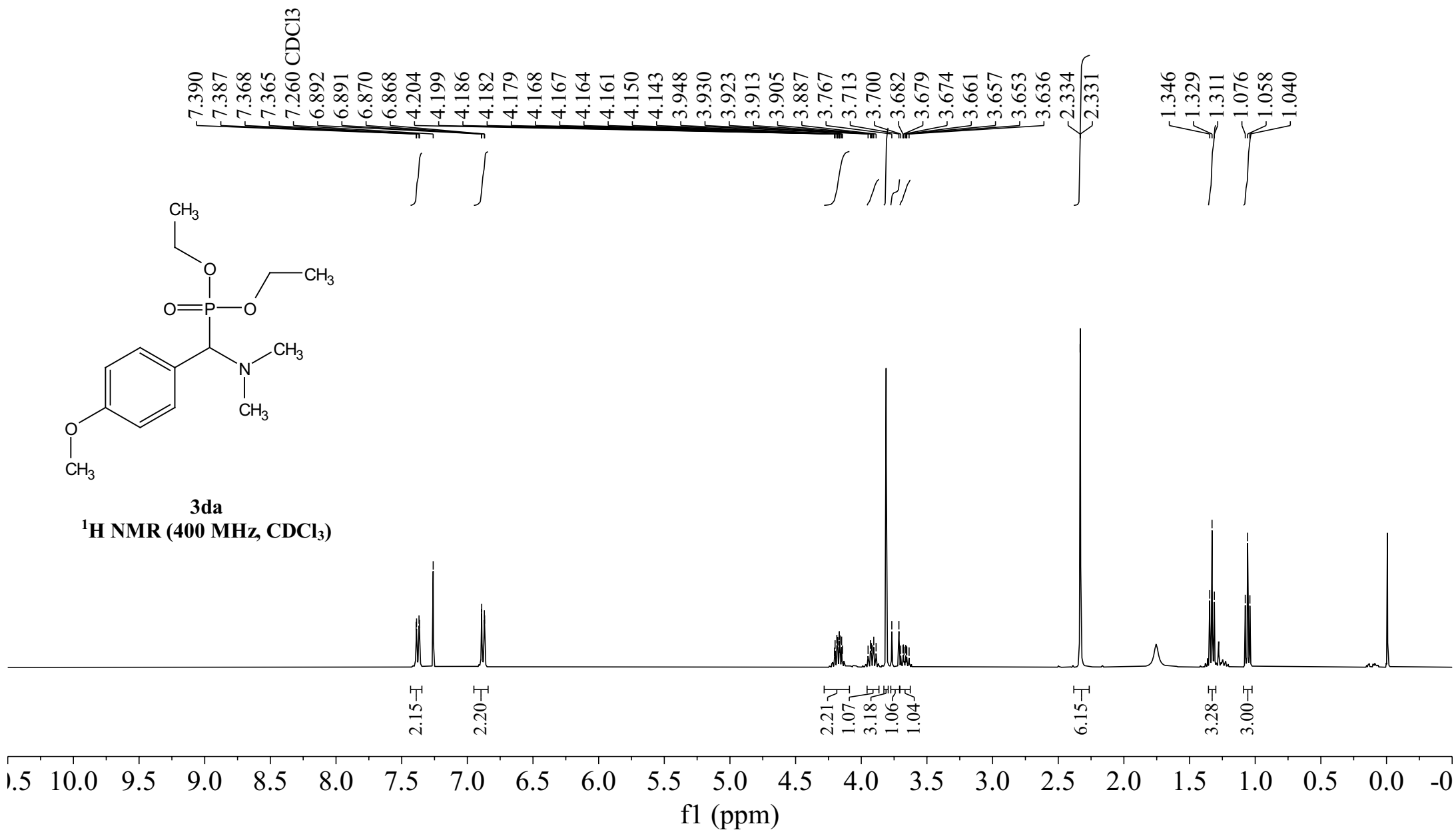


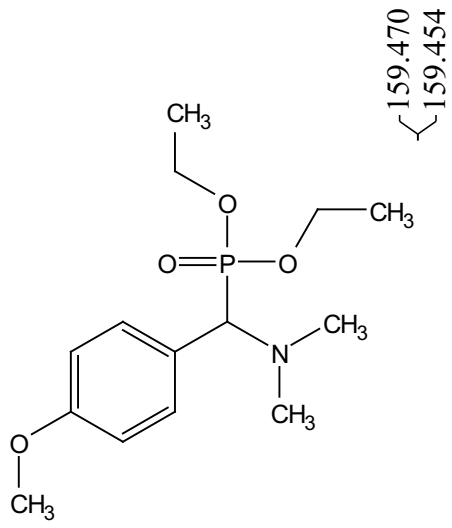


3ca

³¹P NMR (162 MHz, CDCl₃)

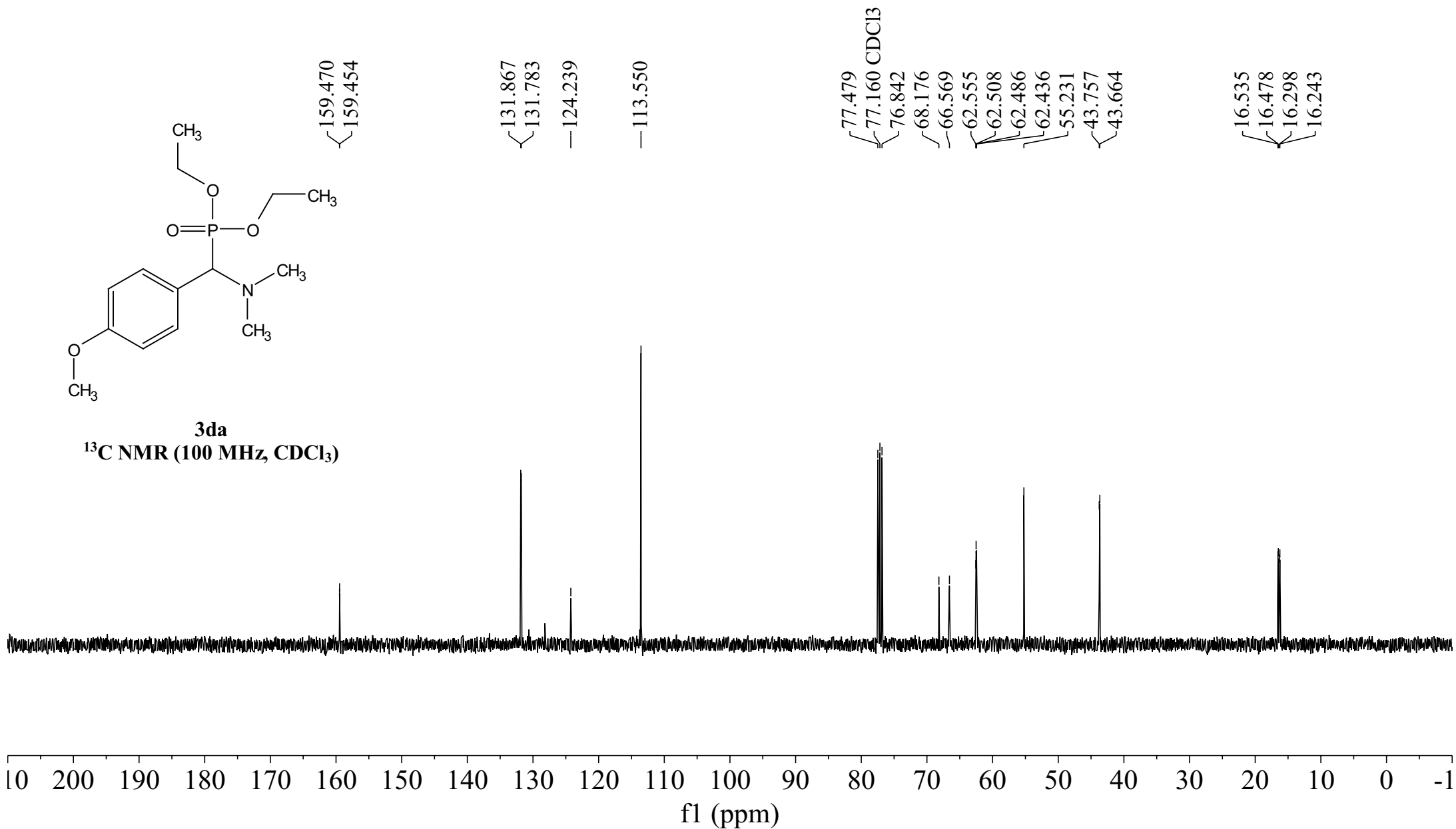


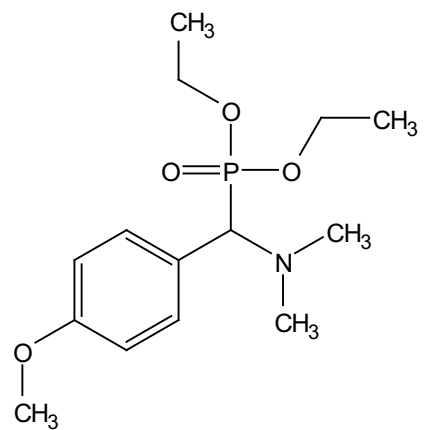




3da

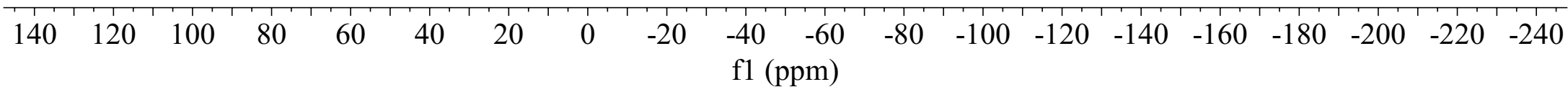
¹³C NMR (100 MHz, CDCl₃)

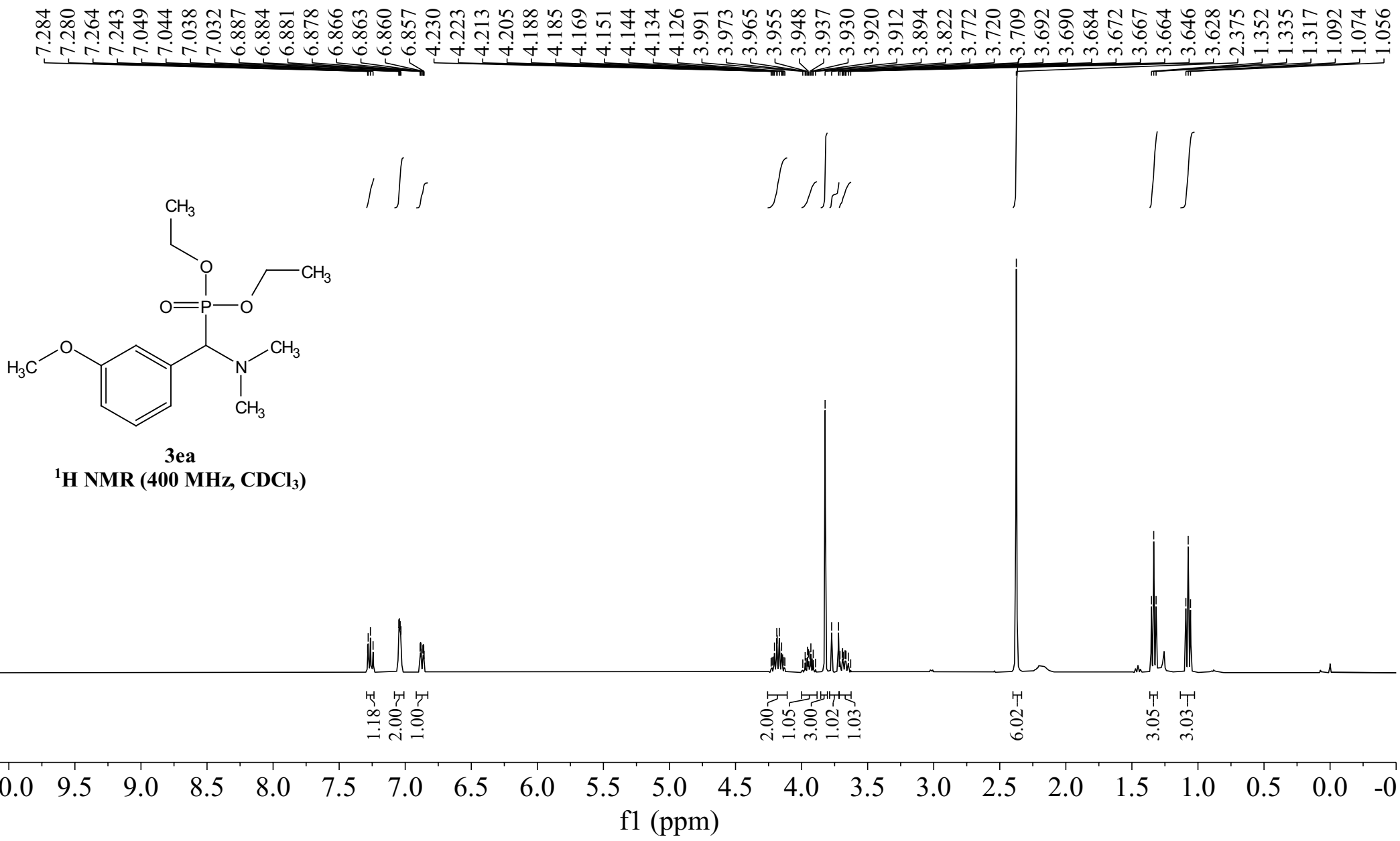


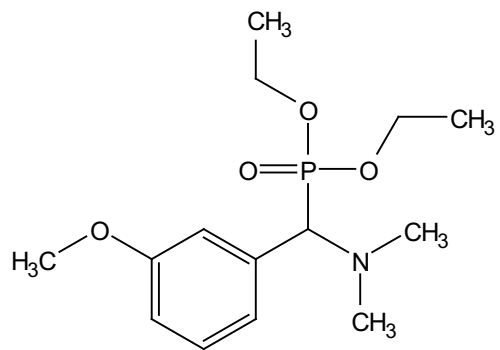


3da
³¹P NMR (162 MHz, CDCl₃)

—23.148

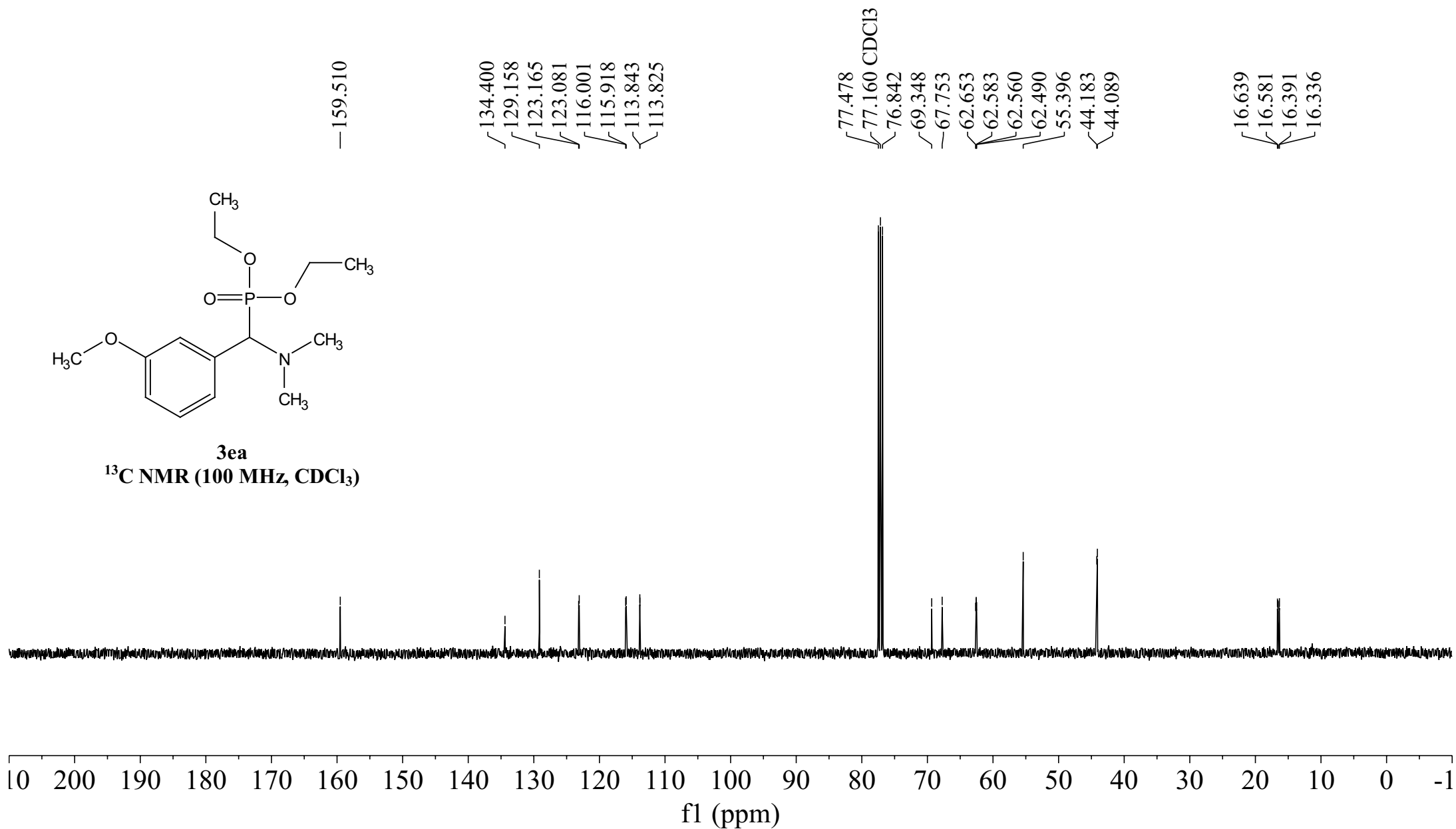


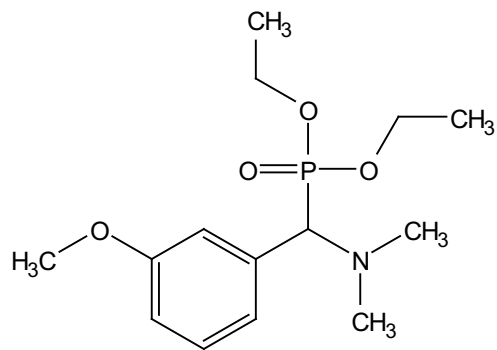




3ea

¹³C NMR (100 MHz, CDCl₃)

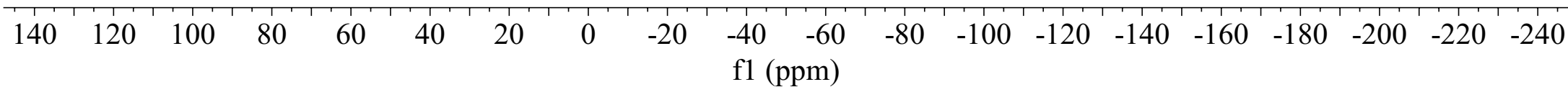


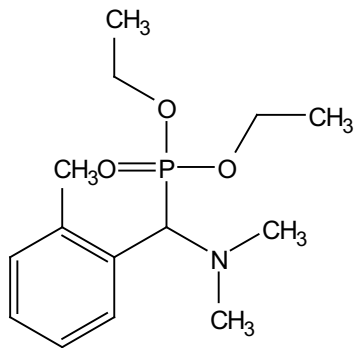


3ea

³¹P NMR (162 MHz, CDCl₃)

—22.799

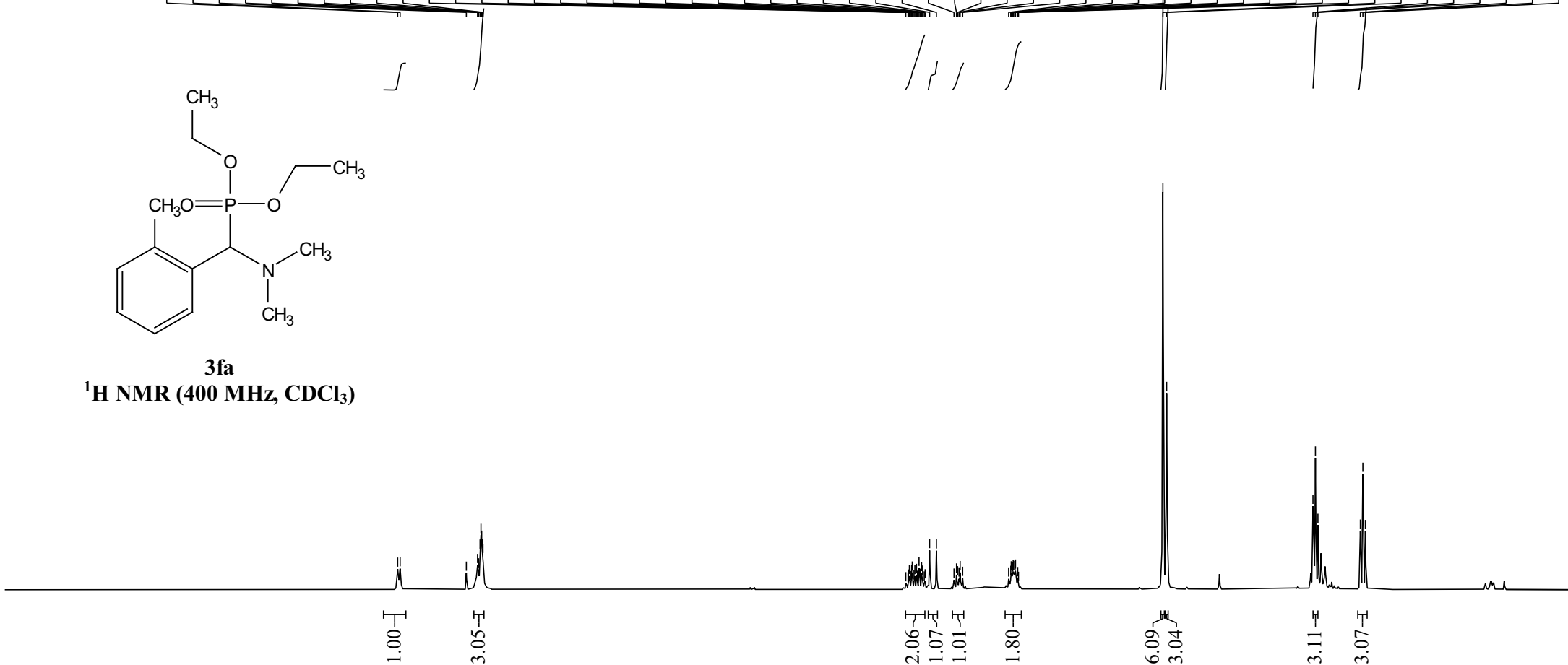




3fa

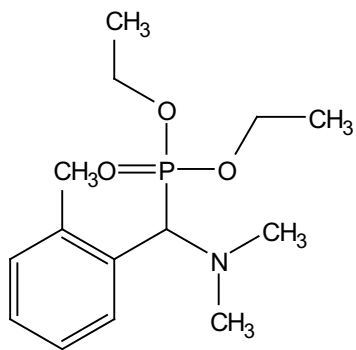
¹H NMR (400 MHz, CDCl₃)

7.742
7.725
7.260 CDCl₃
7.181
7.174
7.164
7.158
7.152
7.147
7.143
4.175
4.159
4.156
4.150
4.138
4.134
4.130
4.118
4.111
4.100
4.093
4.082
4.075
4.064
4.057
4.046
4.039
4.008
3.960
3.837
3.819
3.811
3.802
3.794
3.776
3.453
3.438
3.435
3.428
3.424
3.421
3.418
3.408
3.405
3.390
3.384
2.370
2.344
1.317
1.300
1.282
0.984
0.967
0.949



10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

f1 (ppm)



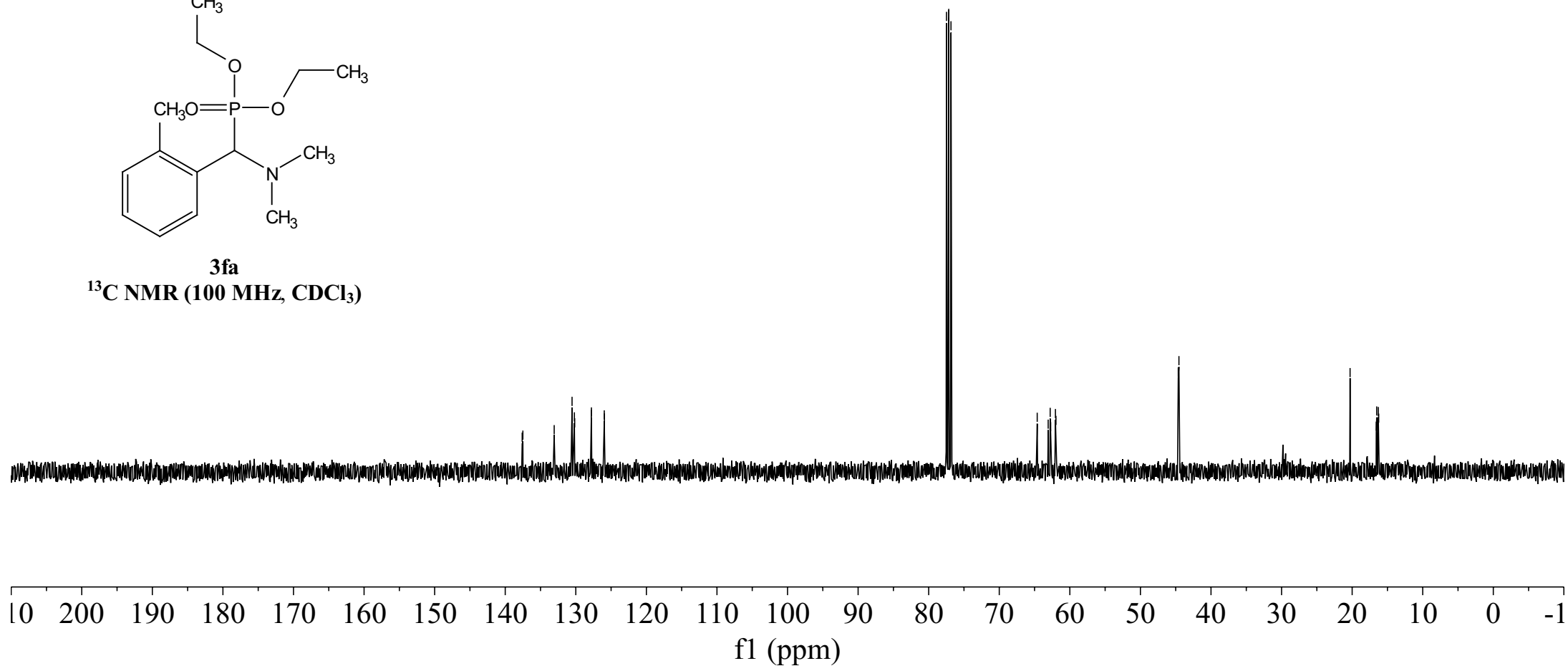
3fa

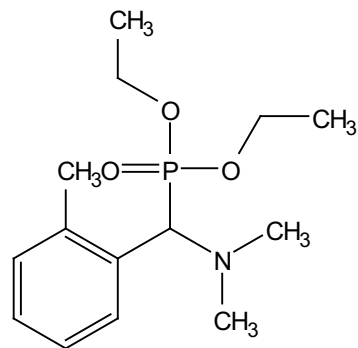
¹³C NMR (100 MHz, CDCl₃)

137.599
137.500
133.062
130.531
130.201
130.159
127.811
127.787
125.967
125.943

77.478
77.160 CDCl₃
77.160
76.843
64.624
63.068
62.787
62.717
62.043
61.968
44.638
44.544

20.294
16.586
16.526
16.294
16.238

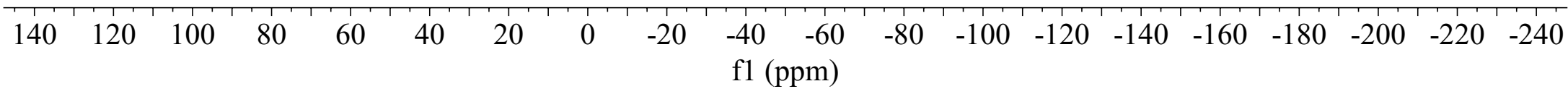


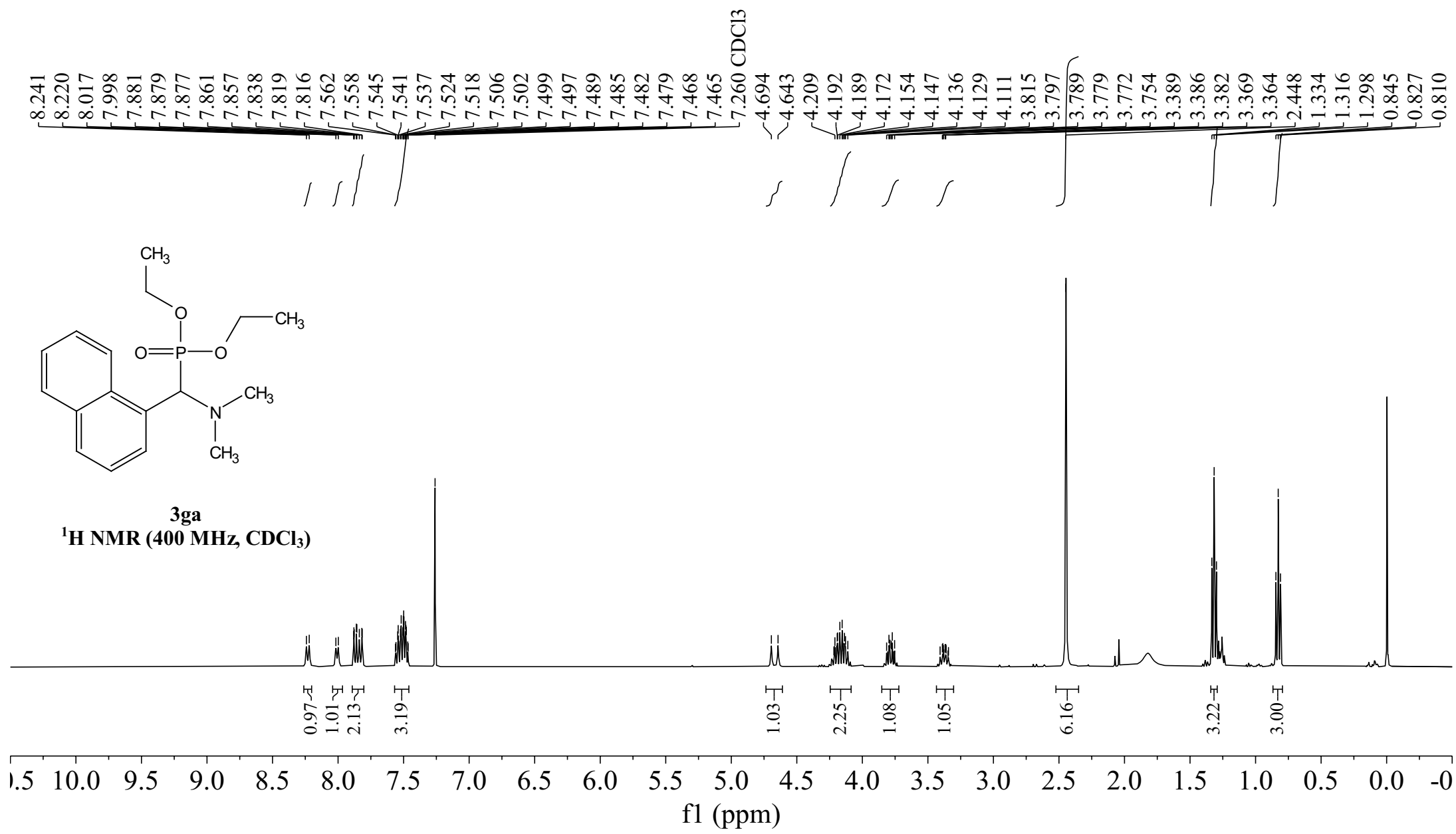


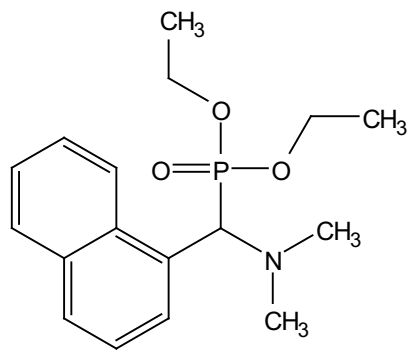
3fa

³¹P NMR (162 MHz, CDCl₃)

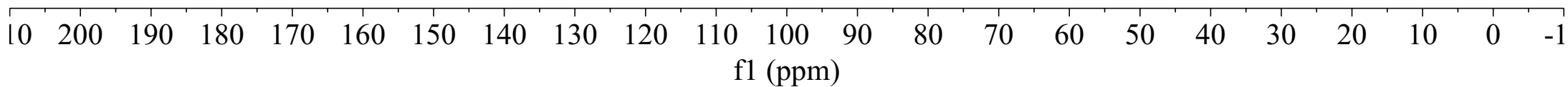
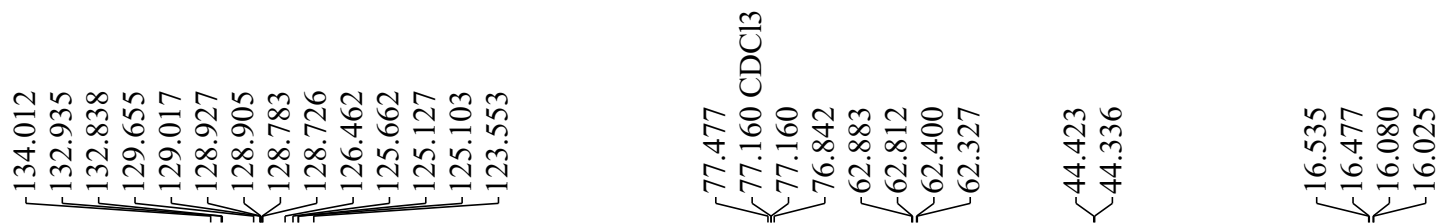
—23.883

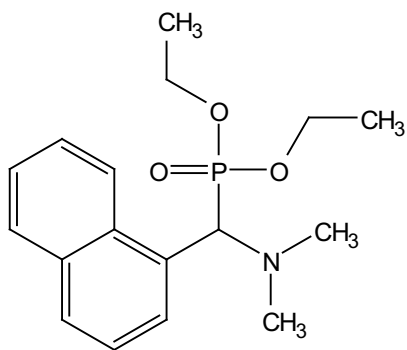




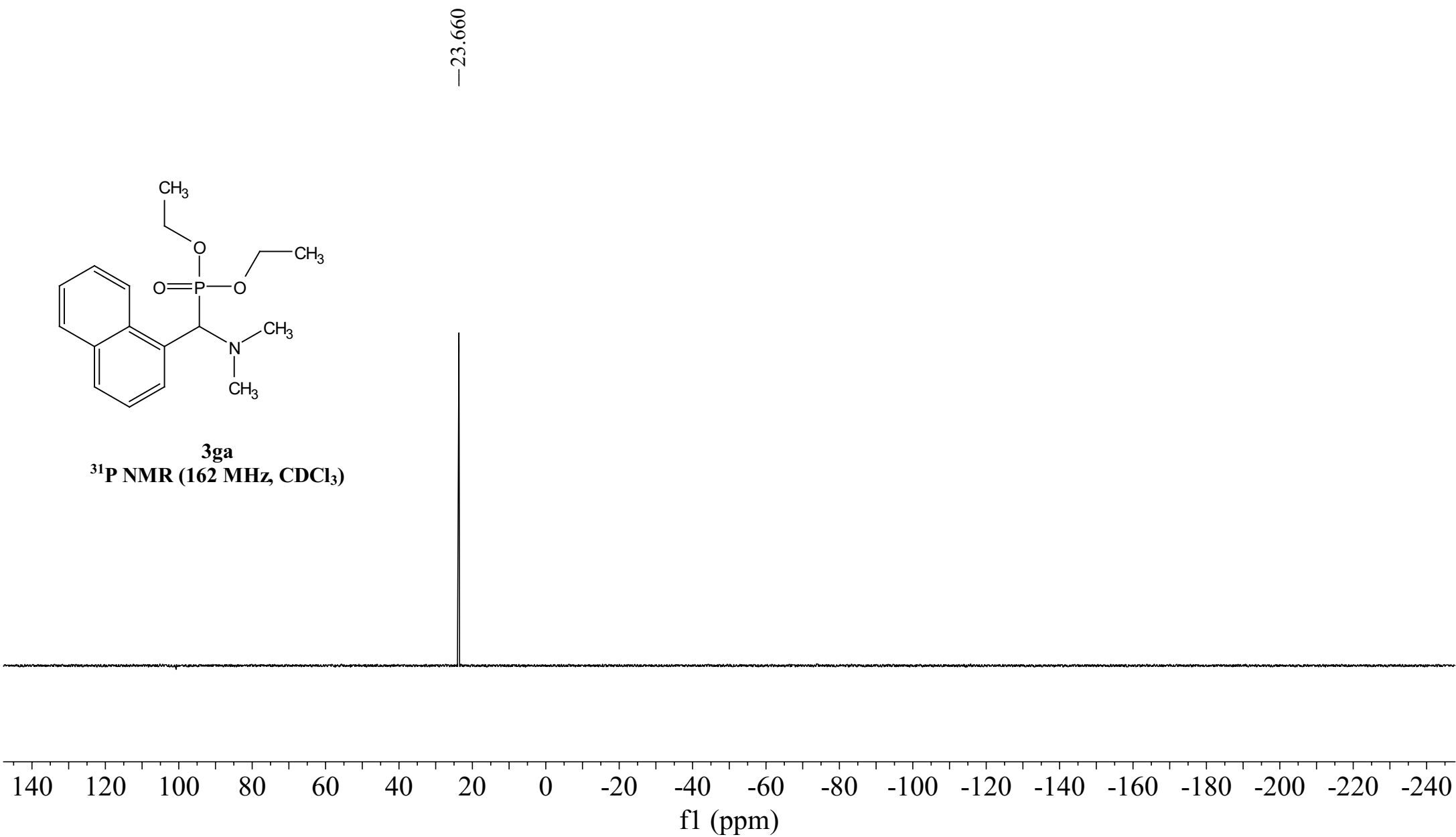


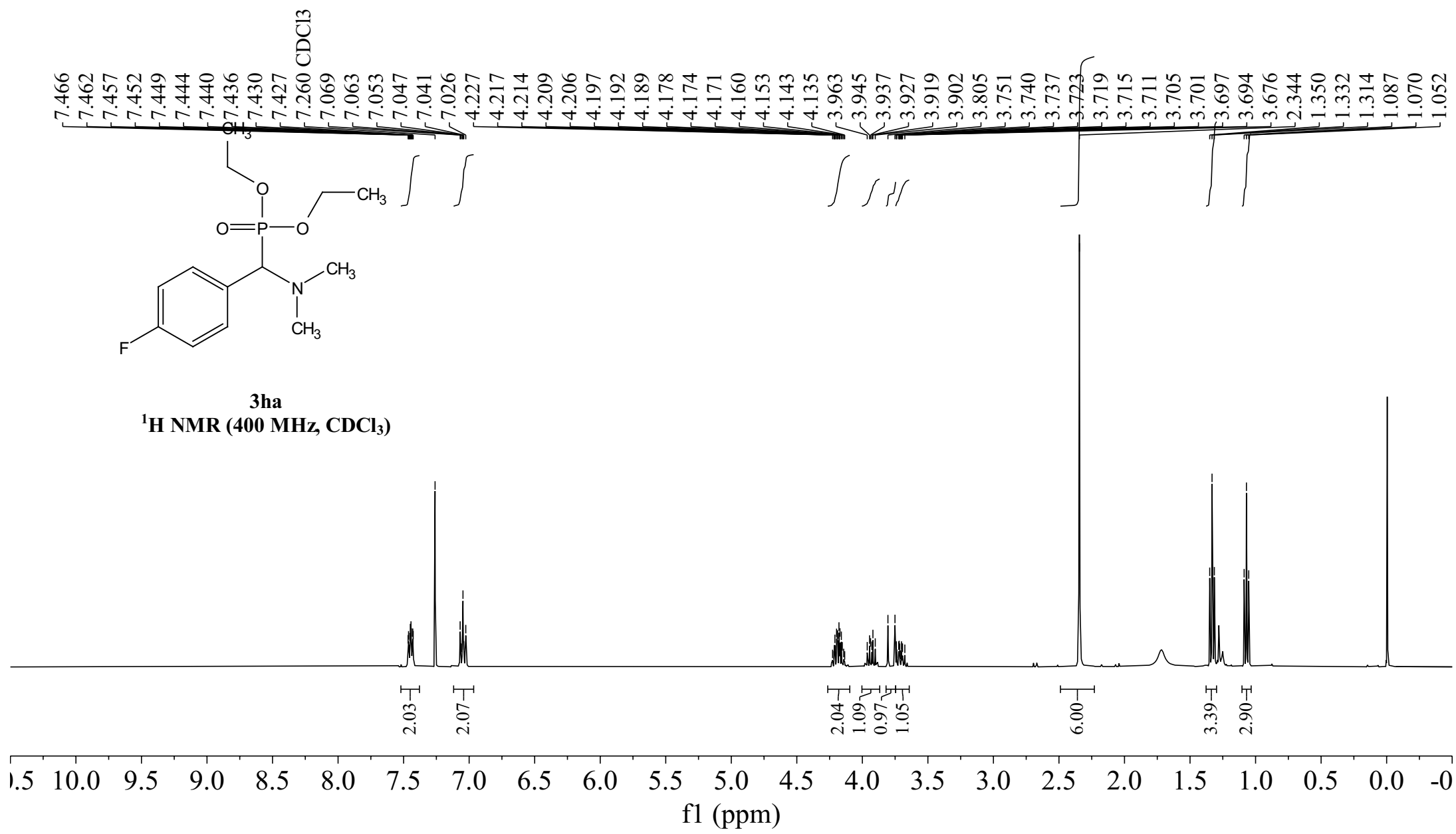
3ga
¹³C NMR (100 MHz, CDCl₃)

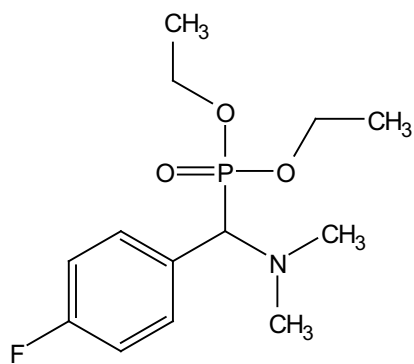




3ga
³¹P NMR (162 MHz, CDCl₃)

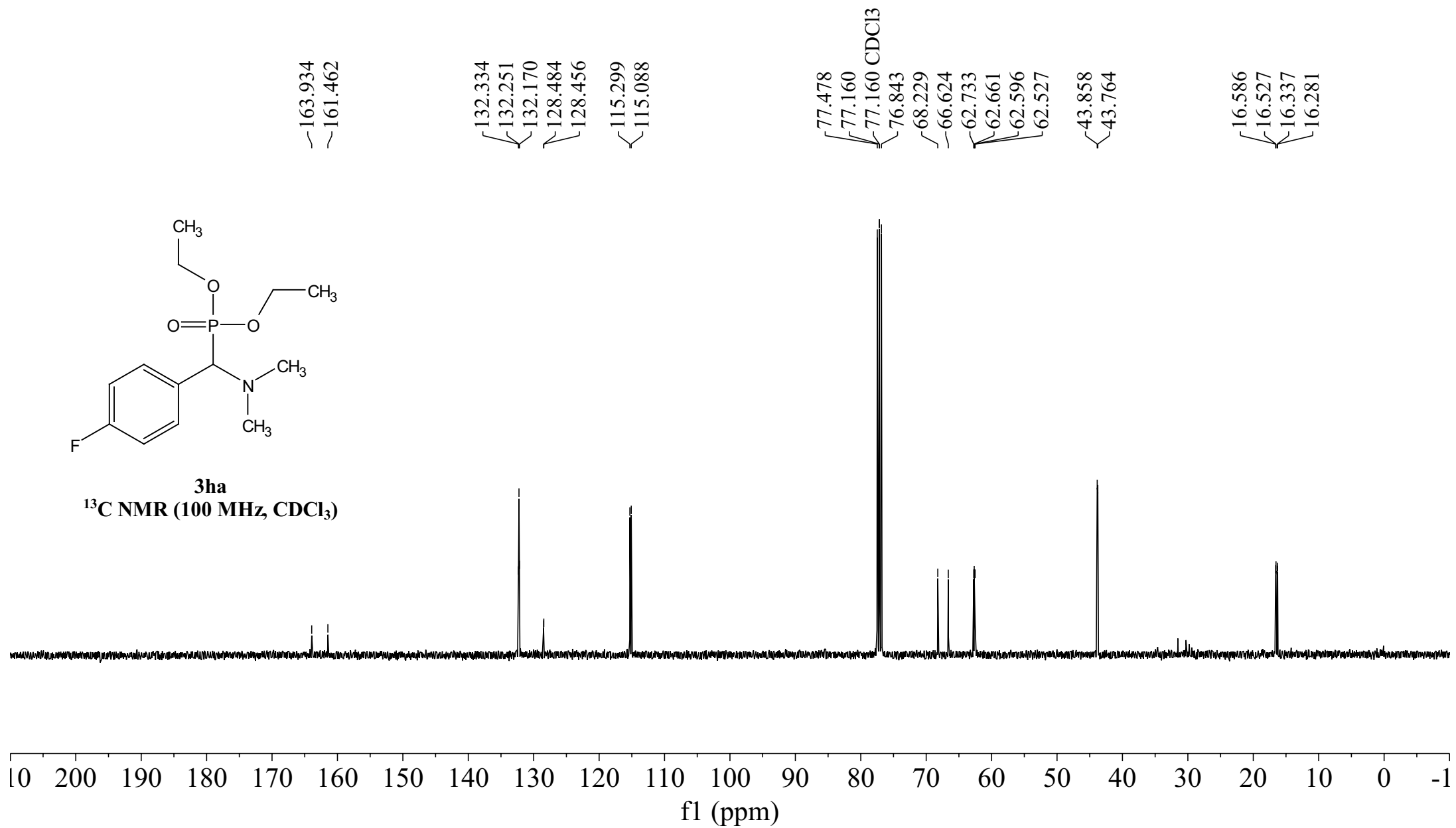


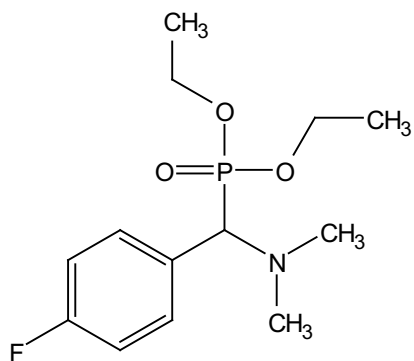




3ha

¹³C NMR (100 MHz, CDCl₃)

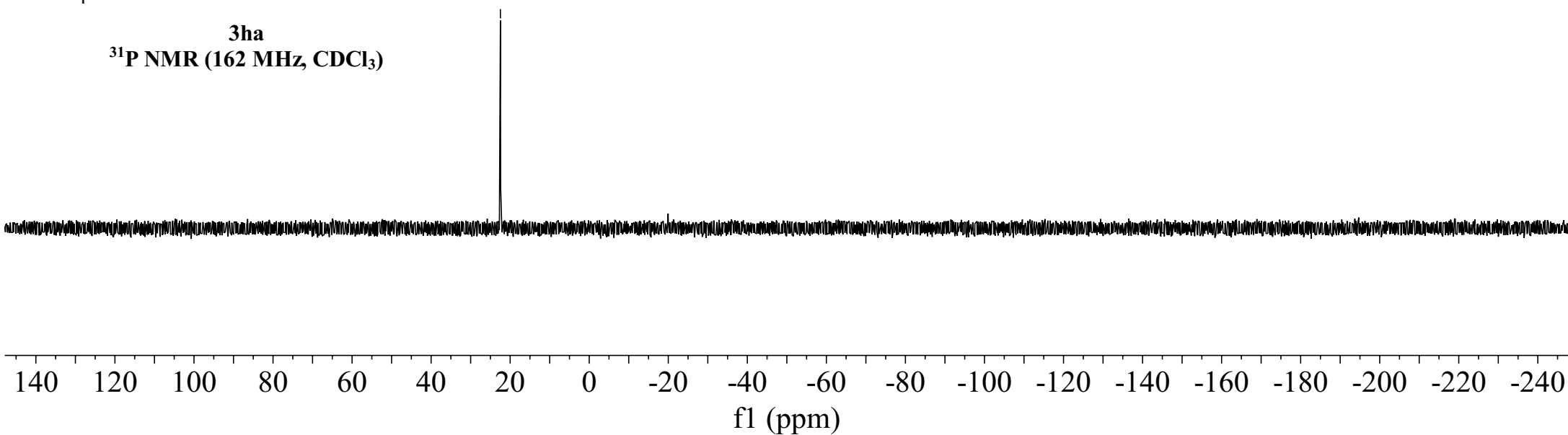


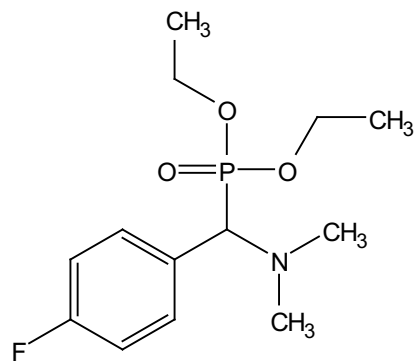


3ha

³¹P NMR (162 MHz, CDCl₃)

—22.470





3ha

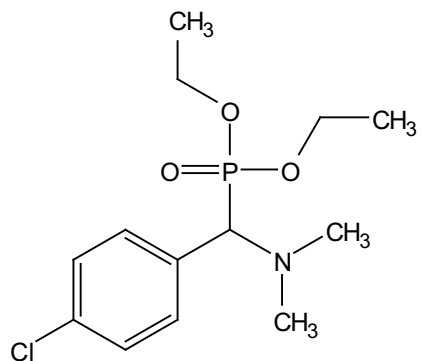
¹⁹F NMR (376 MHz, CDCl₃)

--114.115

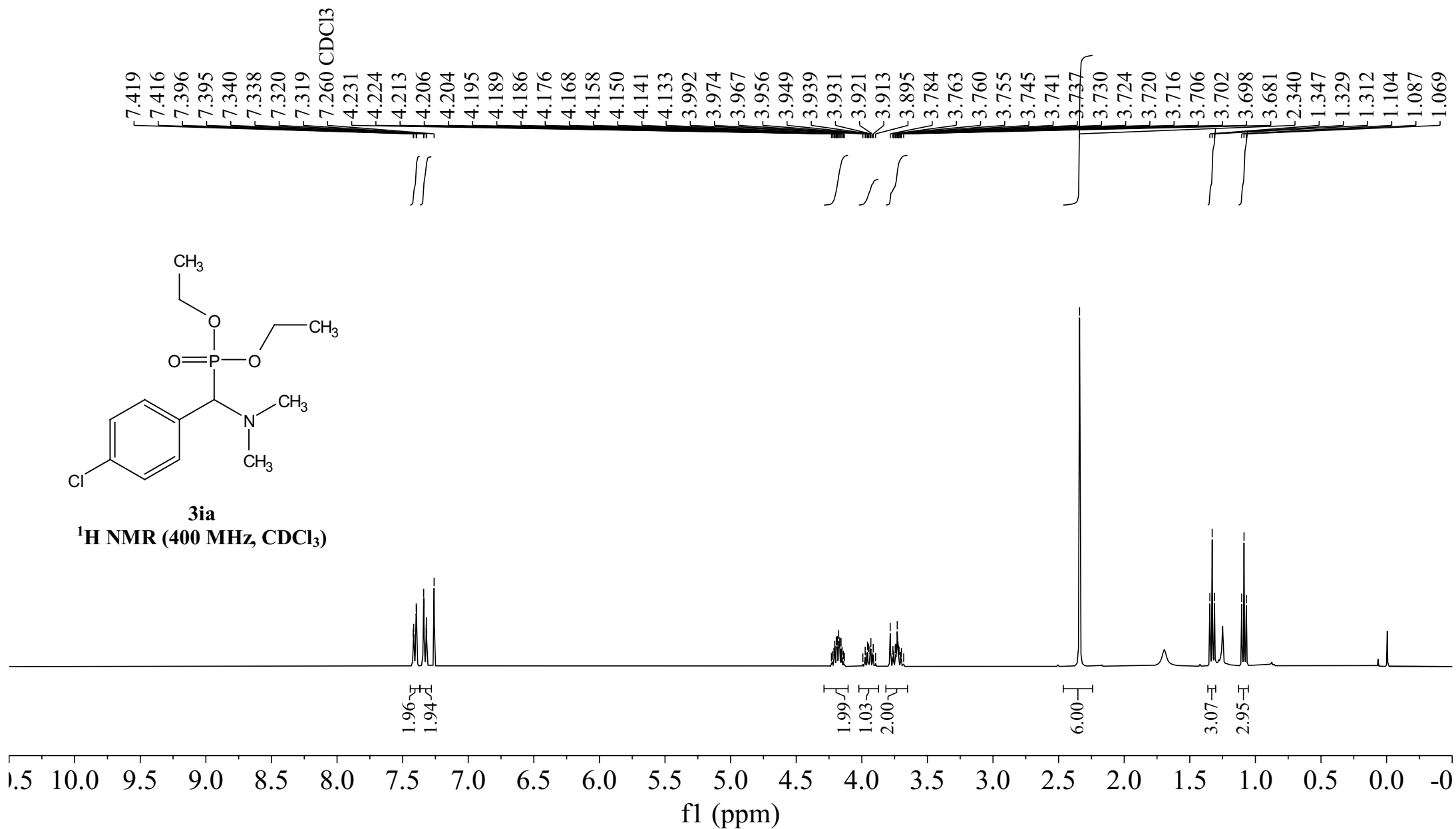


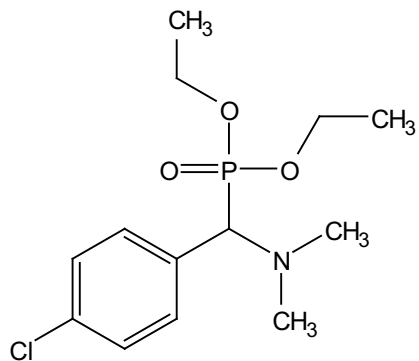
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

f1 (ppm)



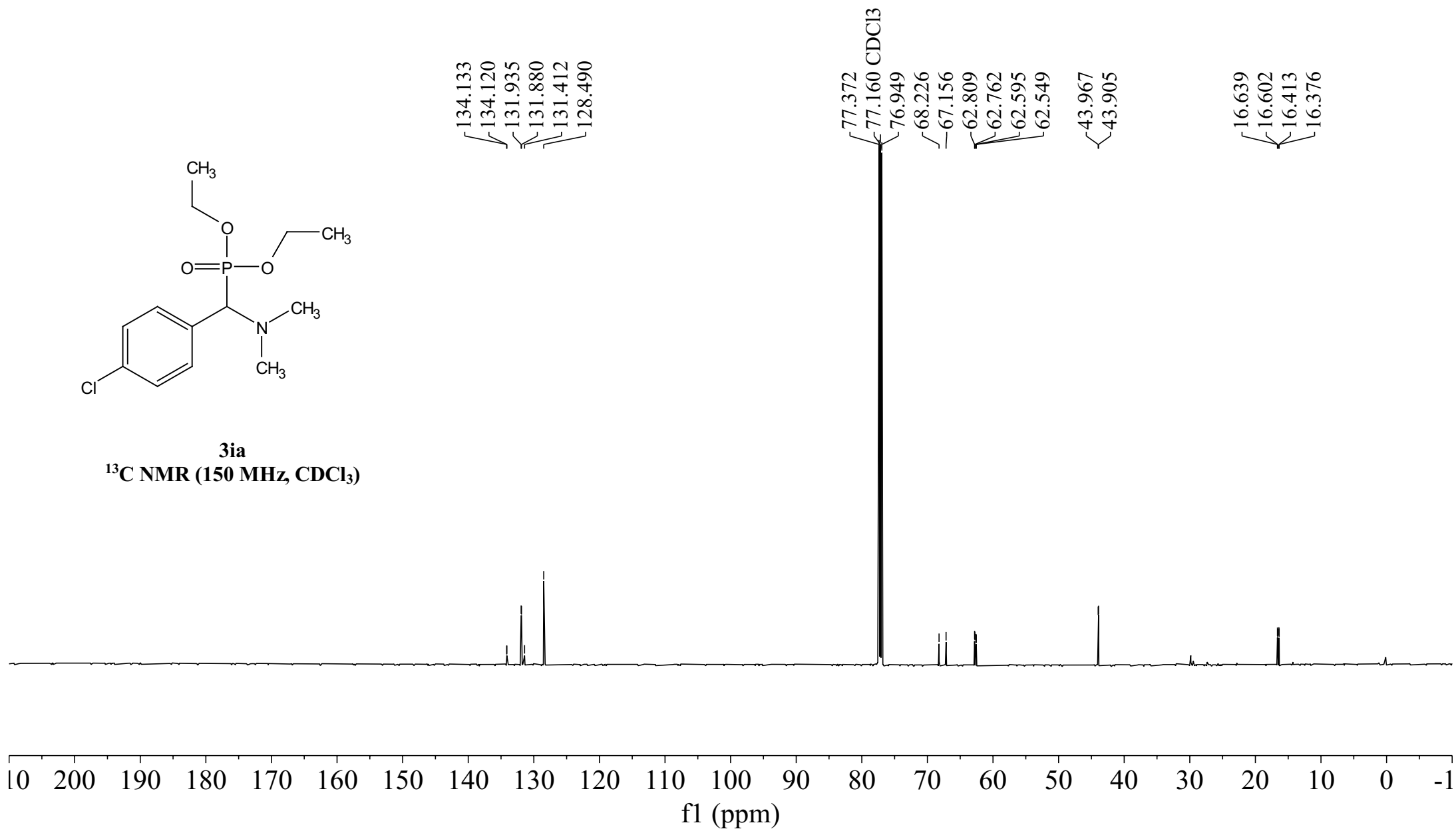
3ia
 $^1\text{H NMR}$ (400 MHz, CDCl_3)

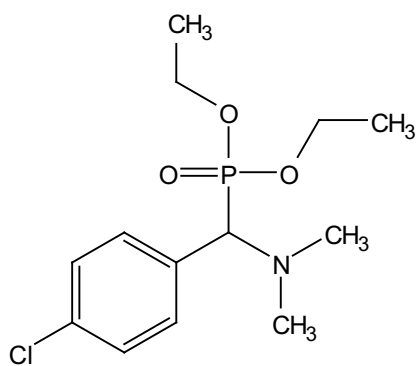




3ia

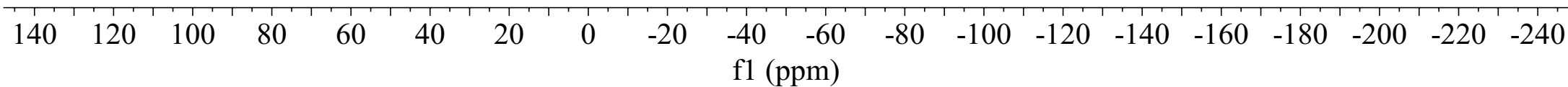
^{13}C NMR (150 MHz, CDCl_3)

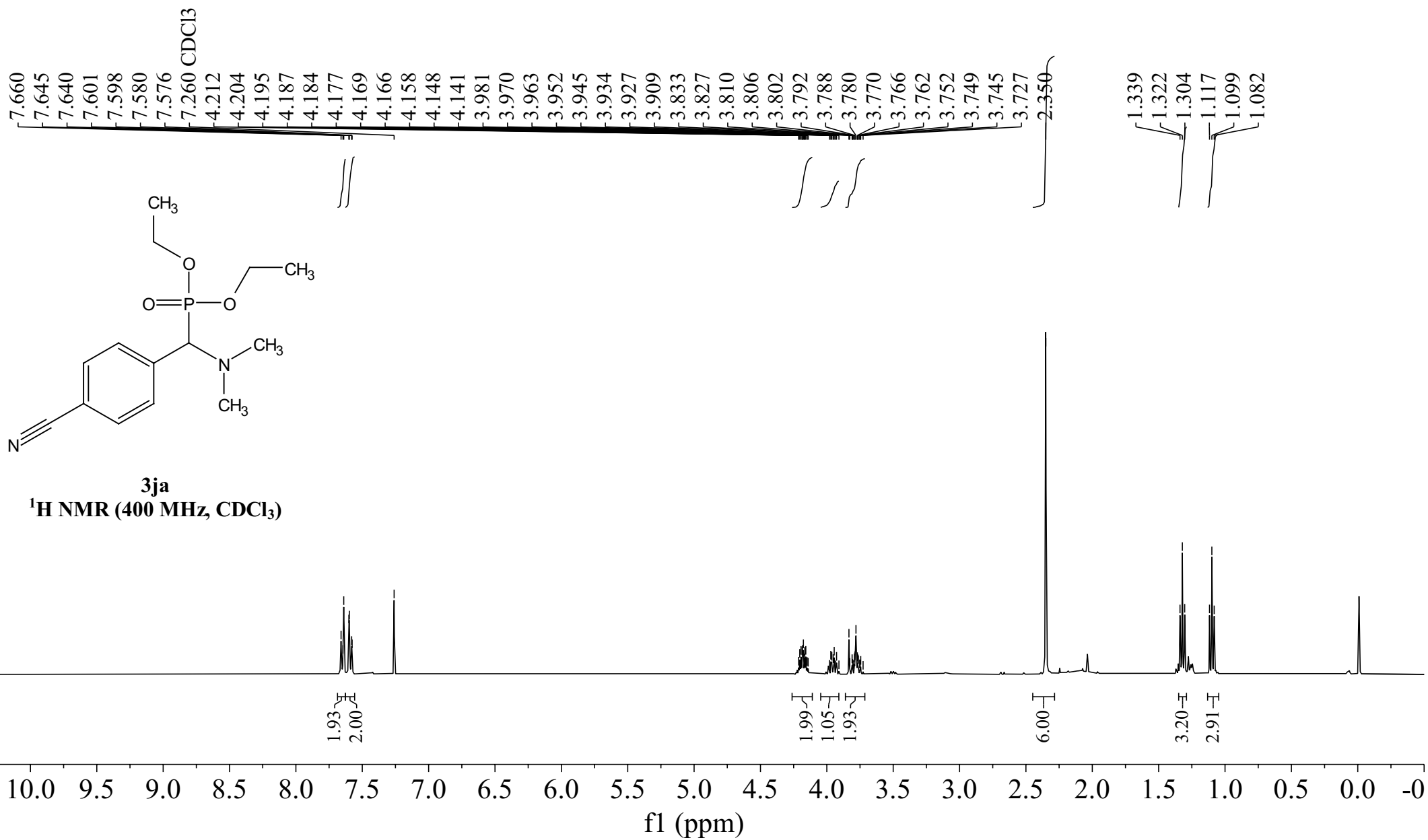


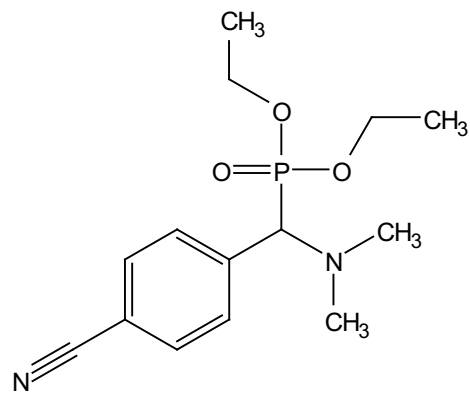


3ia
³¹P NMR (162 MHz, CDCl₃)

—22.213

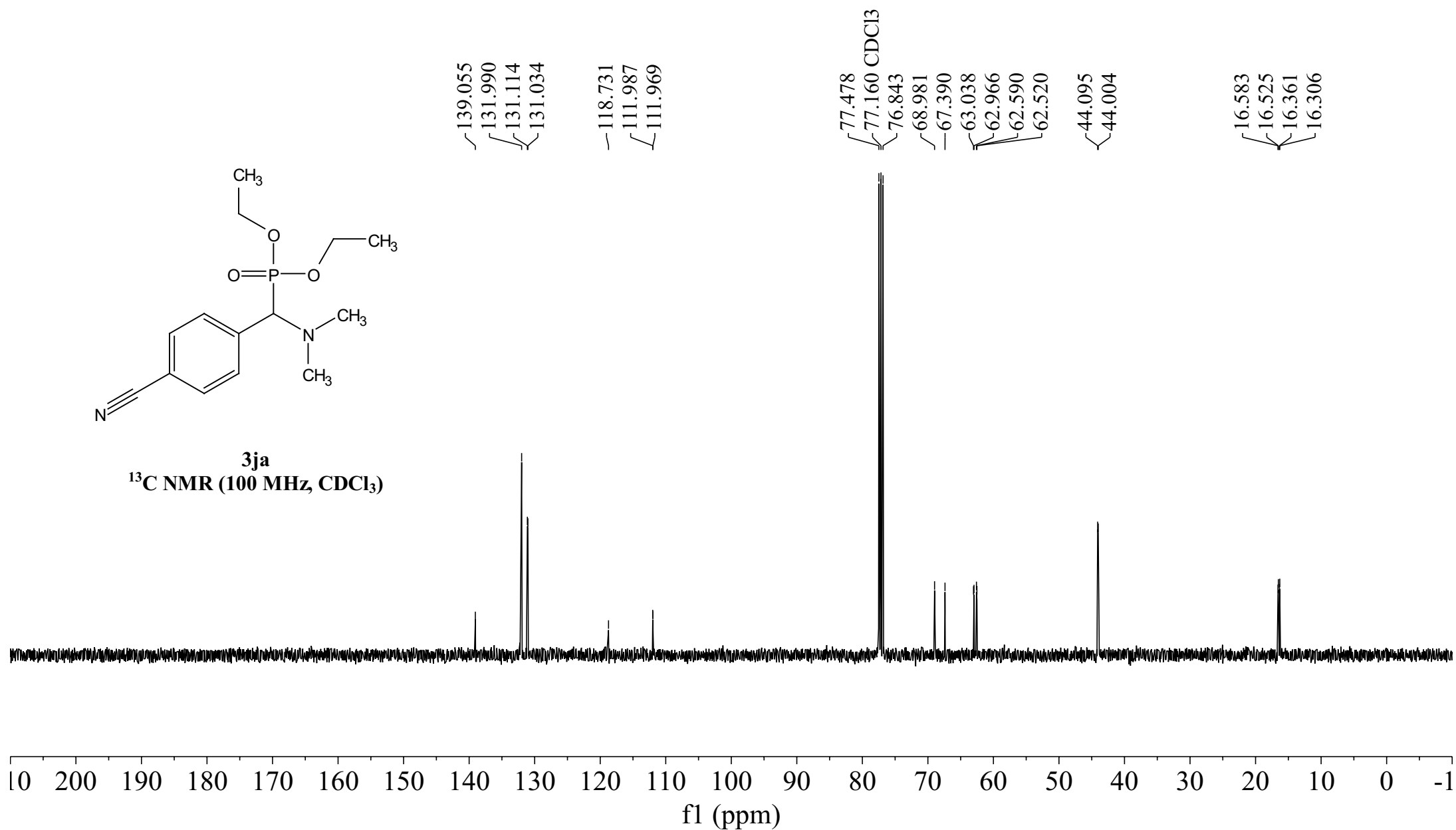




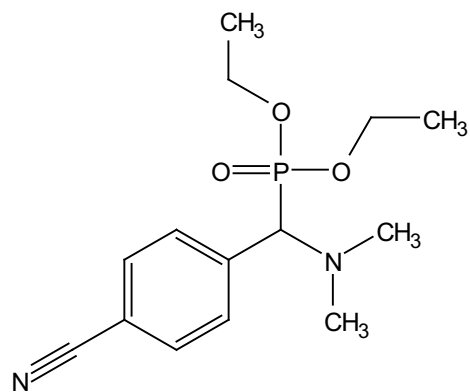


3ja

¹³C NMR (100 MHz, CDCl₃)

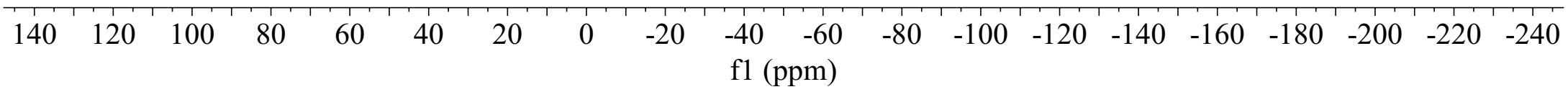


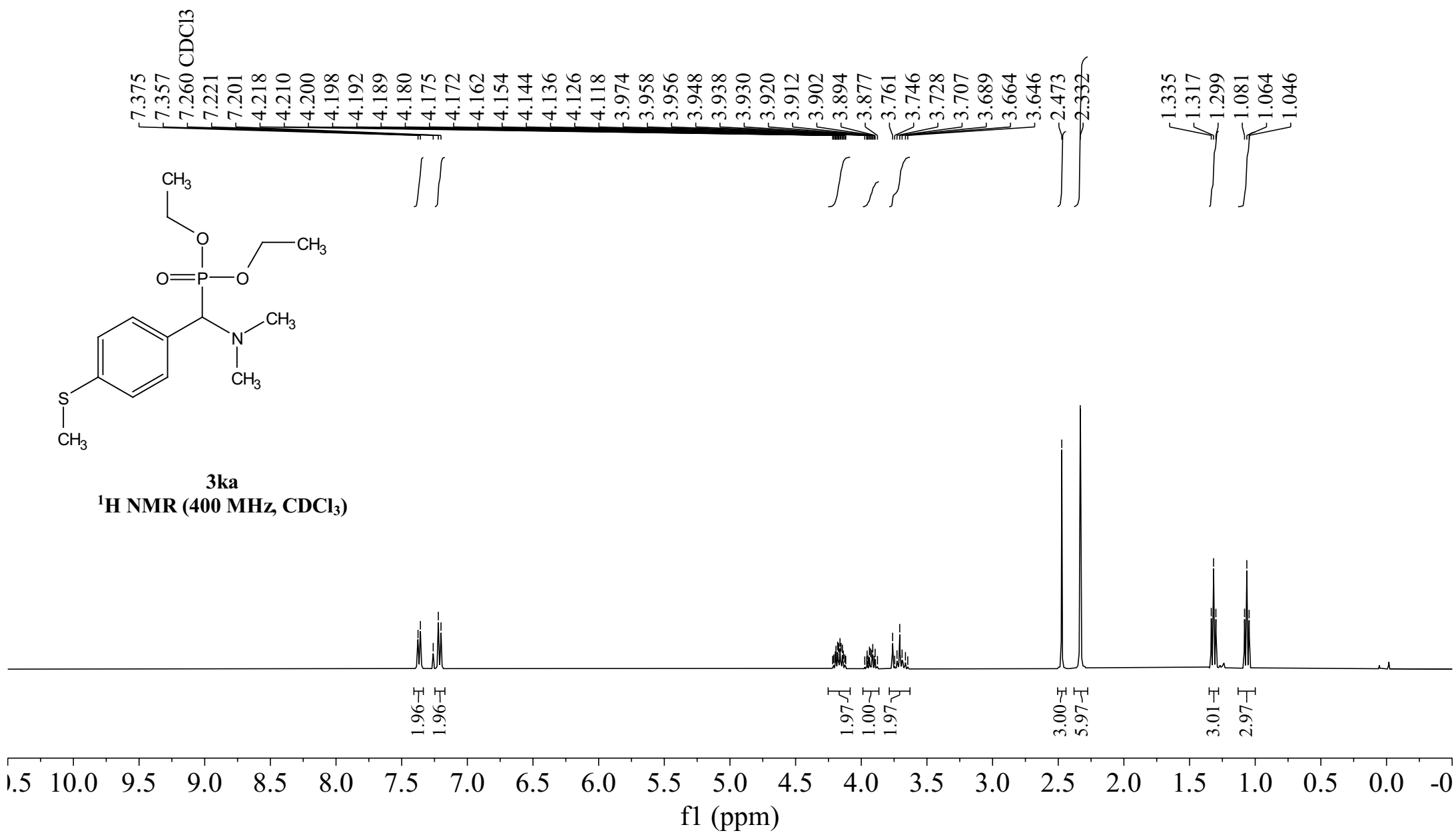
-21.330

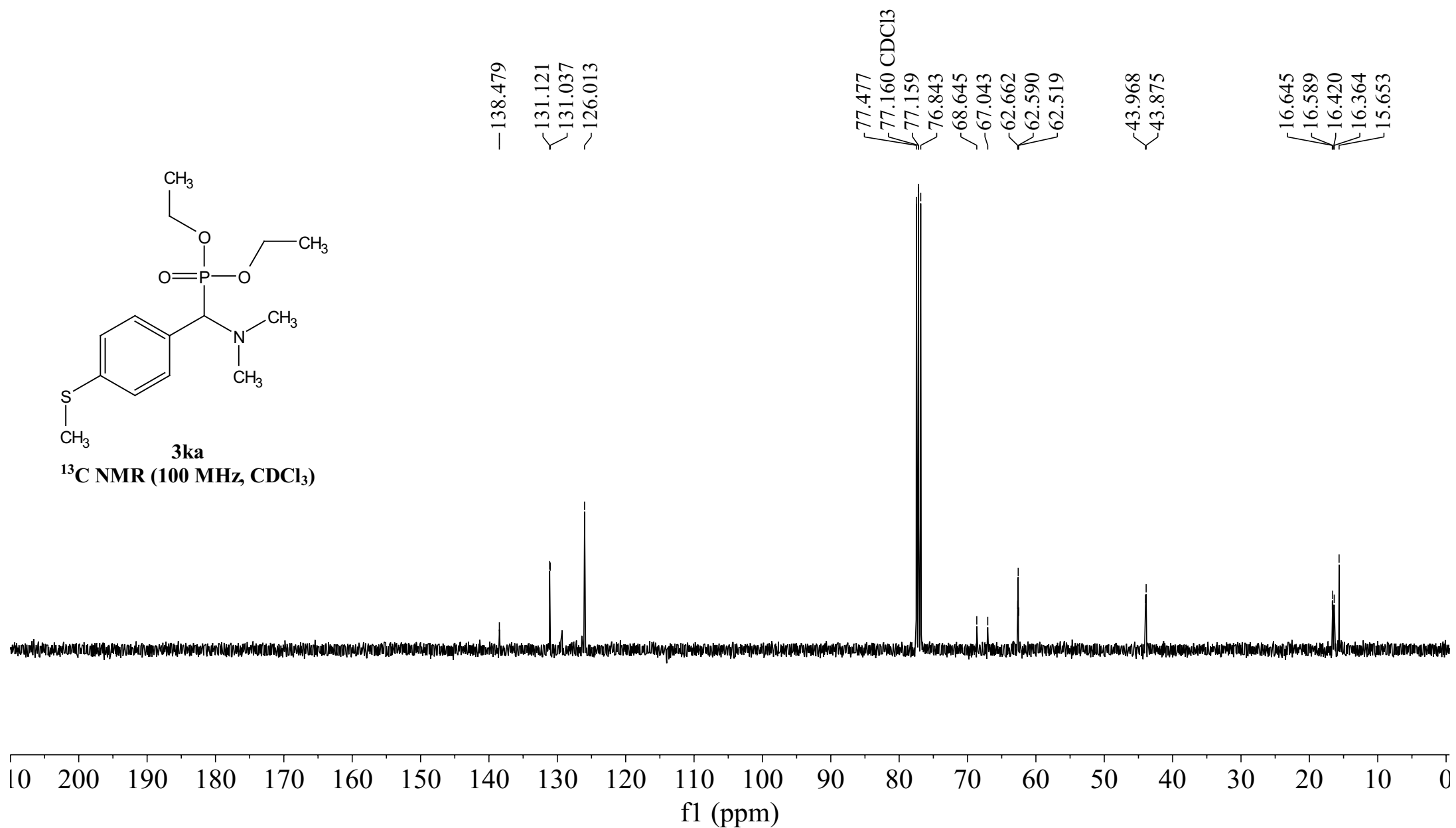
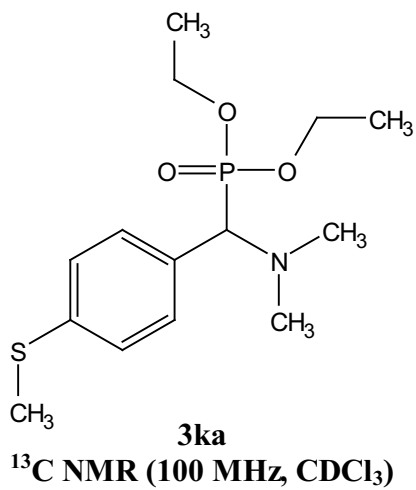


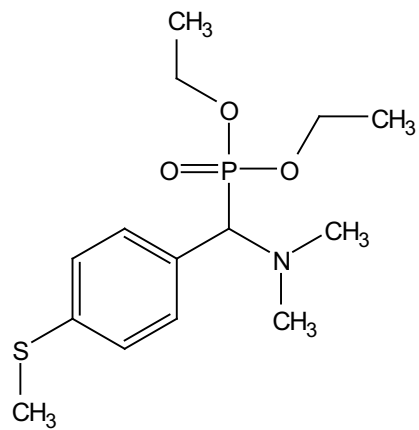
3ja

³¹P NMR (162 MHz, CDCl₃)





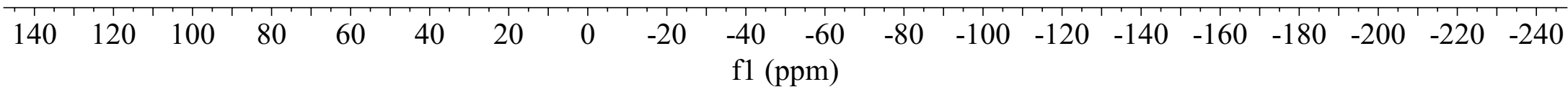


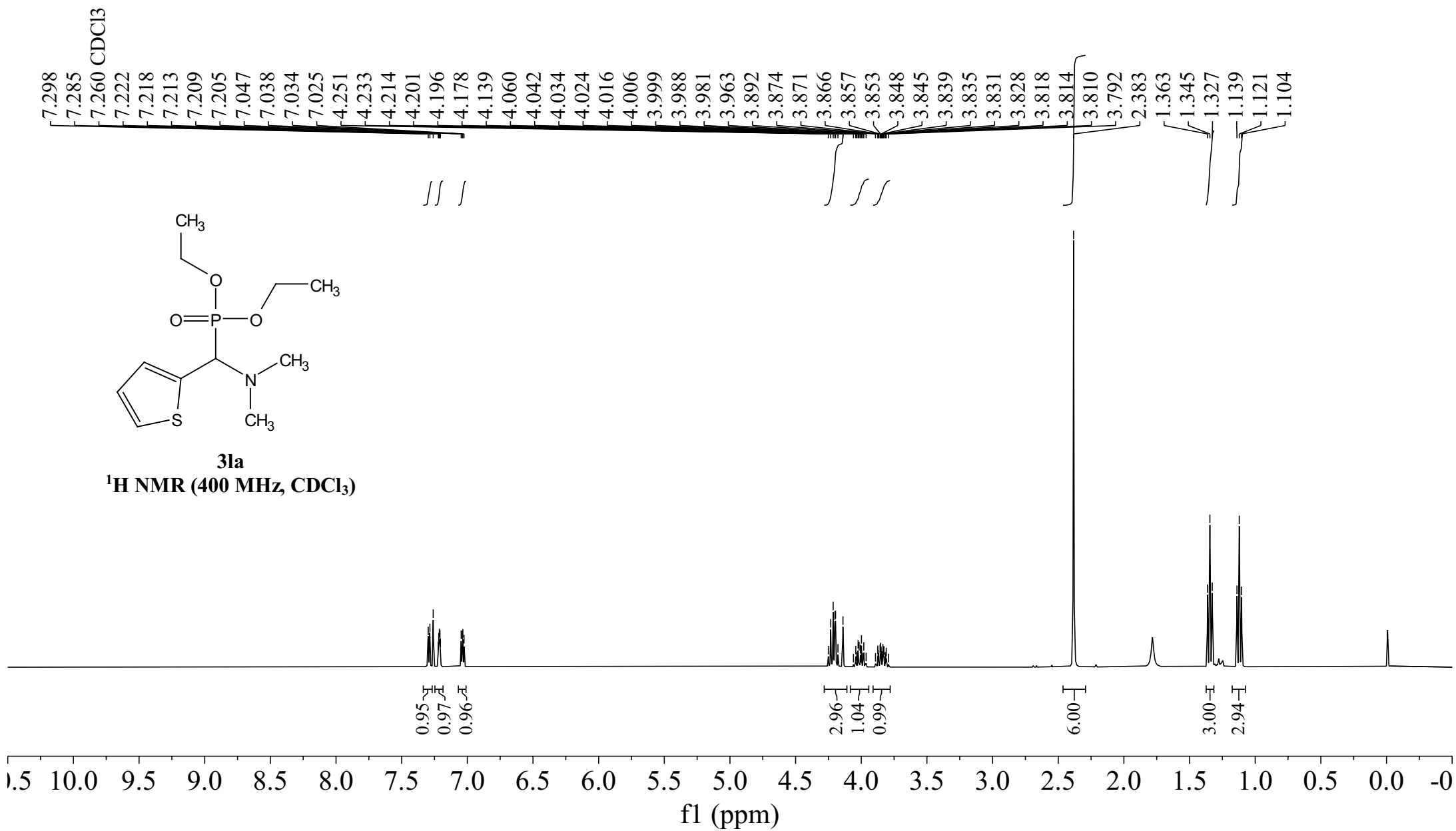


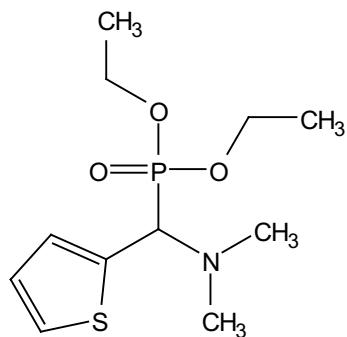
3ka

³¹P NMR (162 MHz, CDCl₃)

—22.616







3la

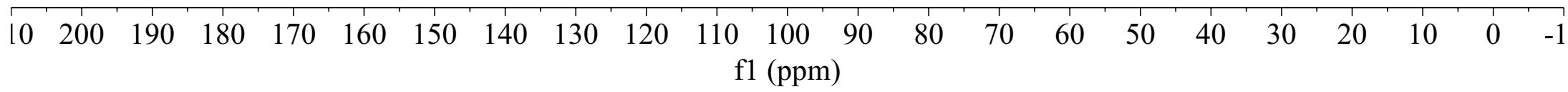
¹³C NMR (100 MHz, CDCl₃)

132.931
132.865
129.226
129.158
126.967
125.900
125.880

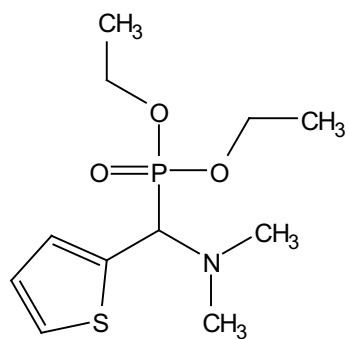
77.477
77.160 CDCl₃
76.843
63.129
63.053
62.773
62.702
61.478

43.327
43.240

16.669
16.614
16.413
16.358

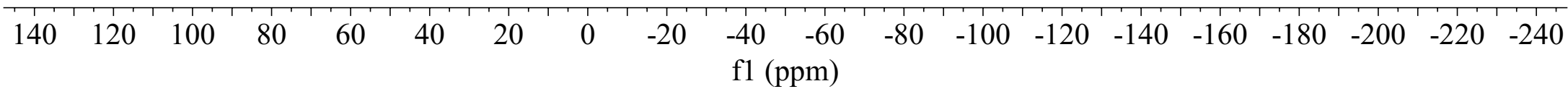


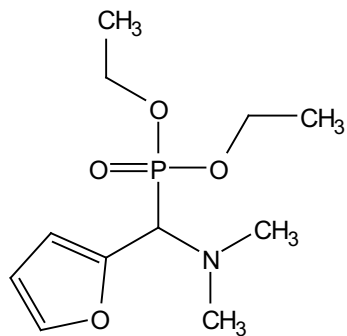
—21.238



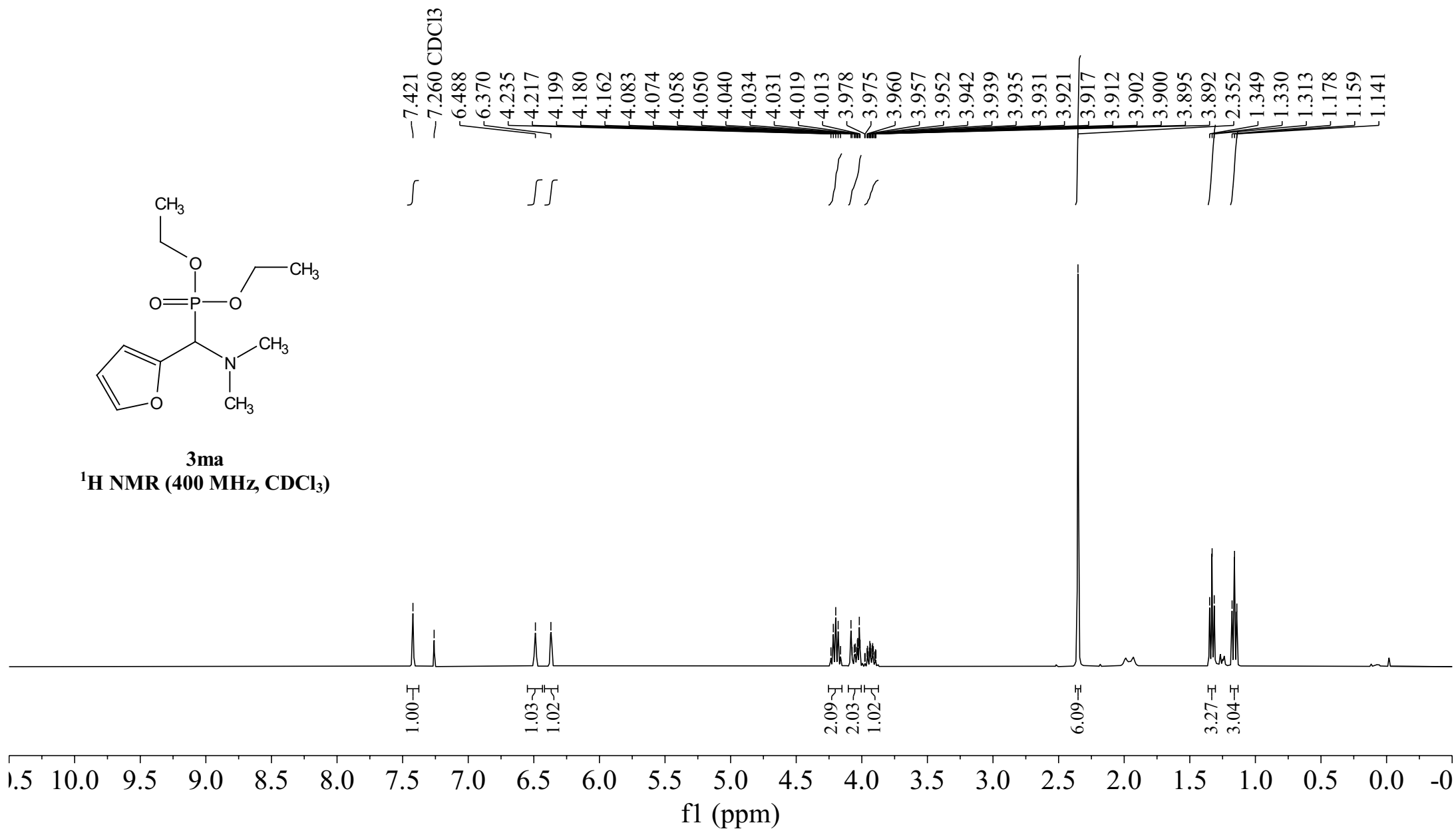
3la

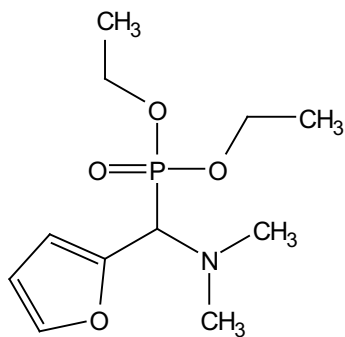
³¹P NMR (162 MHz, CDCl₃)





3ma
¹H NMR (400 MHz, CDCl₃)





3ma

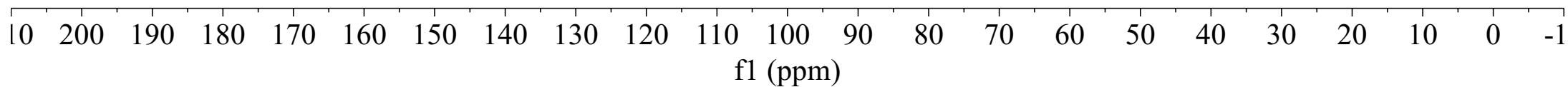
^{13}C NMR (100 MHz, CDCl_3)

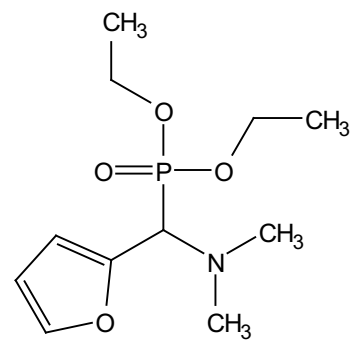
147.188
147.086
142.791
142.772

111.483
111.438
110.467

77.478
77.160 CDCl_3
76.843
63.077
63.008
62.682
62.614
61.688
60.023
43.676
43.587

16.626
16.570
16.444
16.389

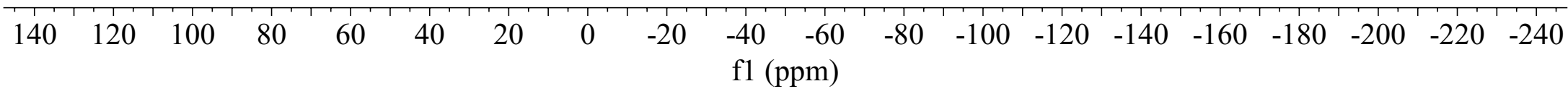


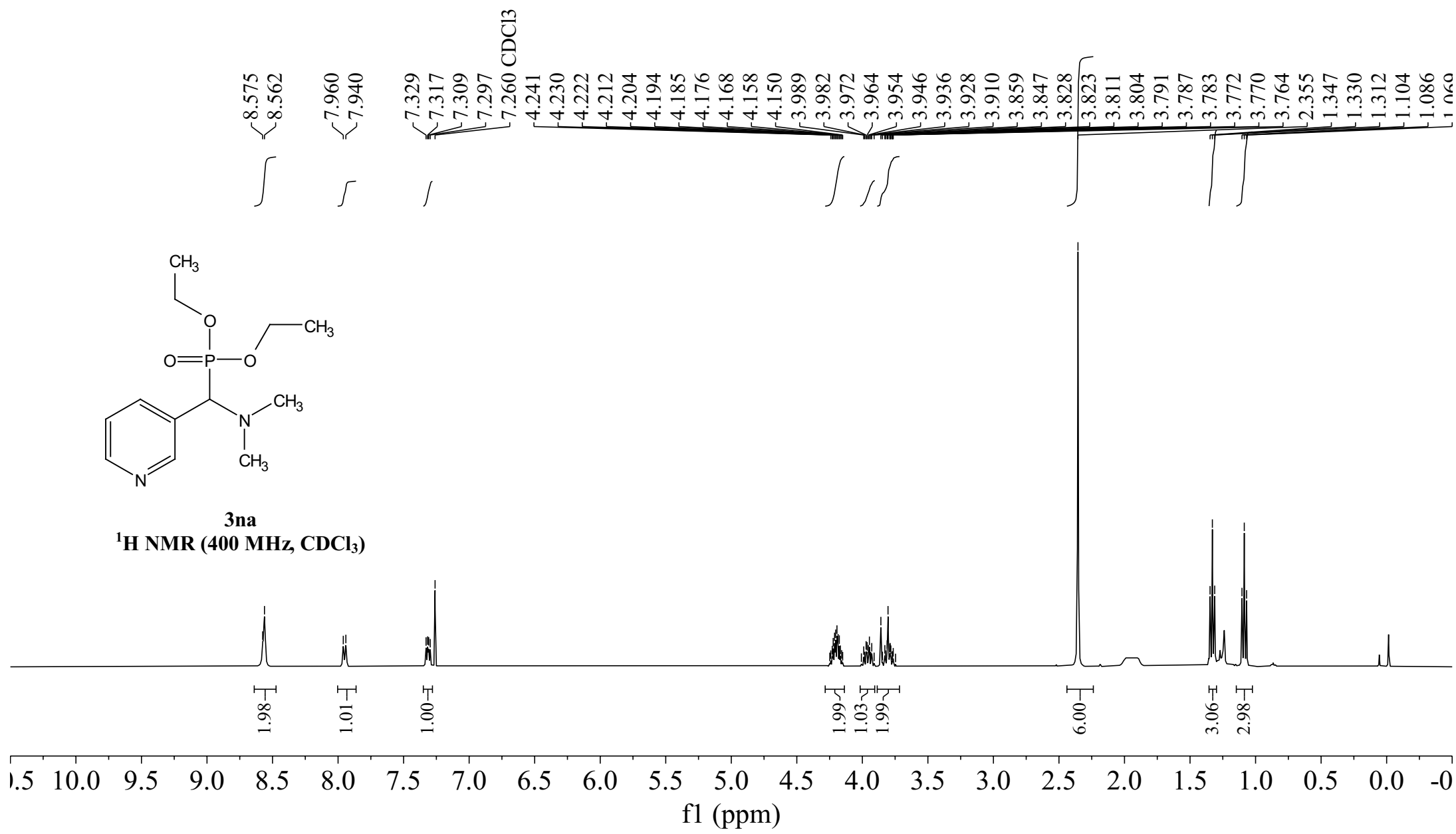


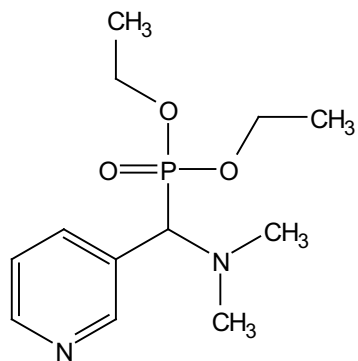
3ma

³¹P NMR (162 MHz, CDCl₃)

—20.545







3na

¹³C NMR (175 MHz, CDCl₃)

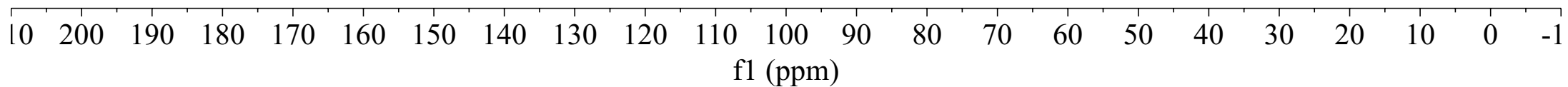
151.491
151.428
149.468

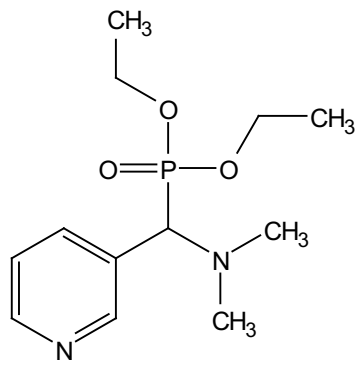
137.841
137.807

128.773
123.248

77.342
77.160 CDCl₃
76.978
66.108
65.184
63.046
63.006
62.530
62.490
43.847
43.796

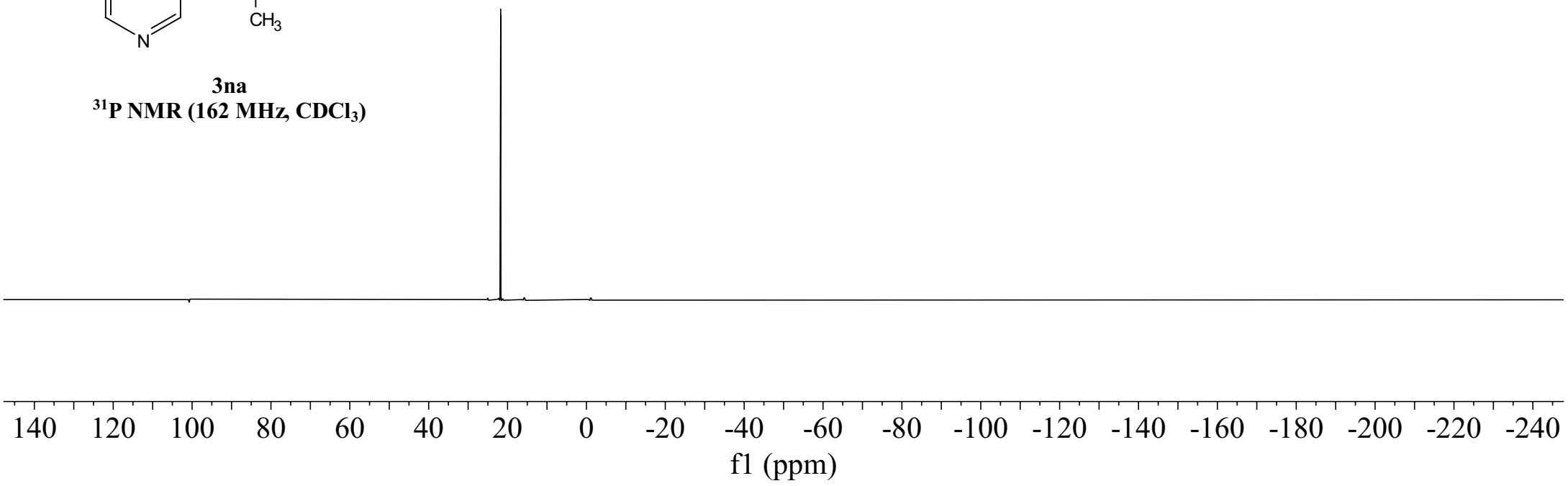
16.614
16.581
16.367
16.336

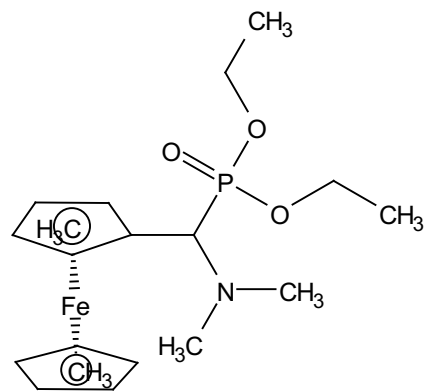




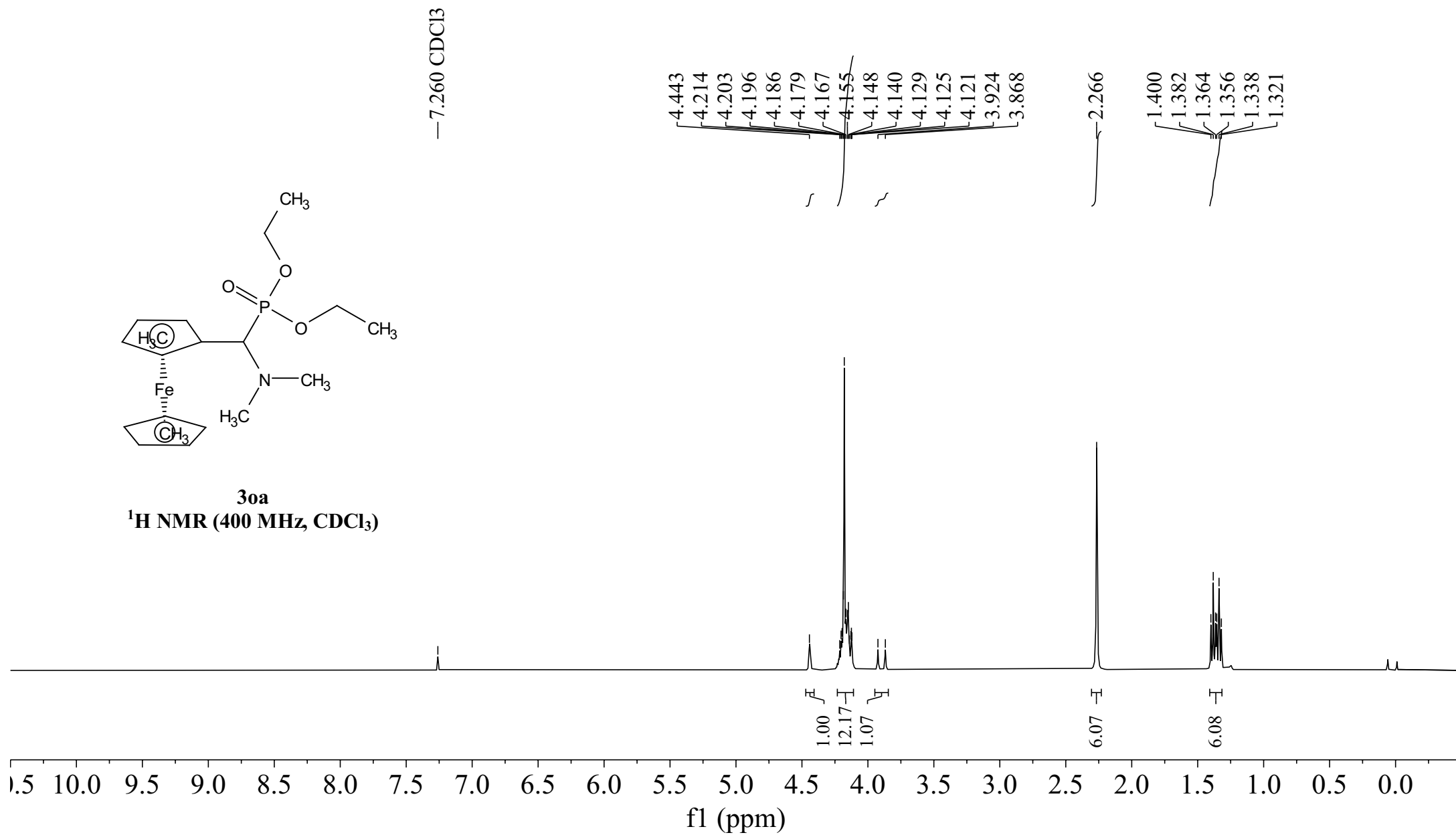
3na
³¹P NMR (162 MHz, CDCl₃)

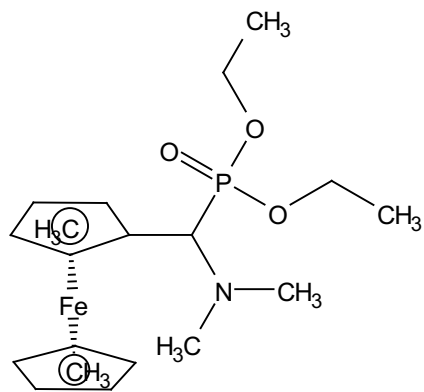
—21.740





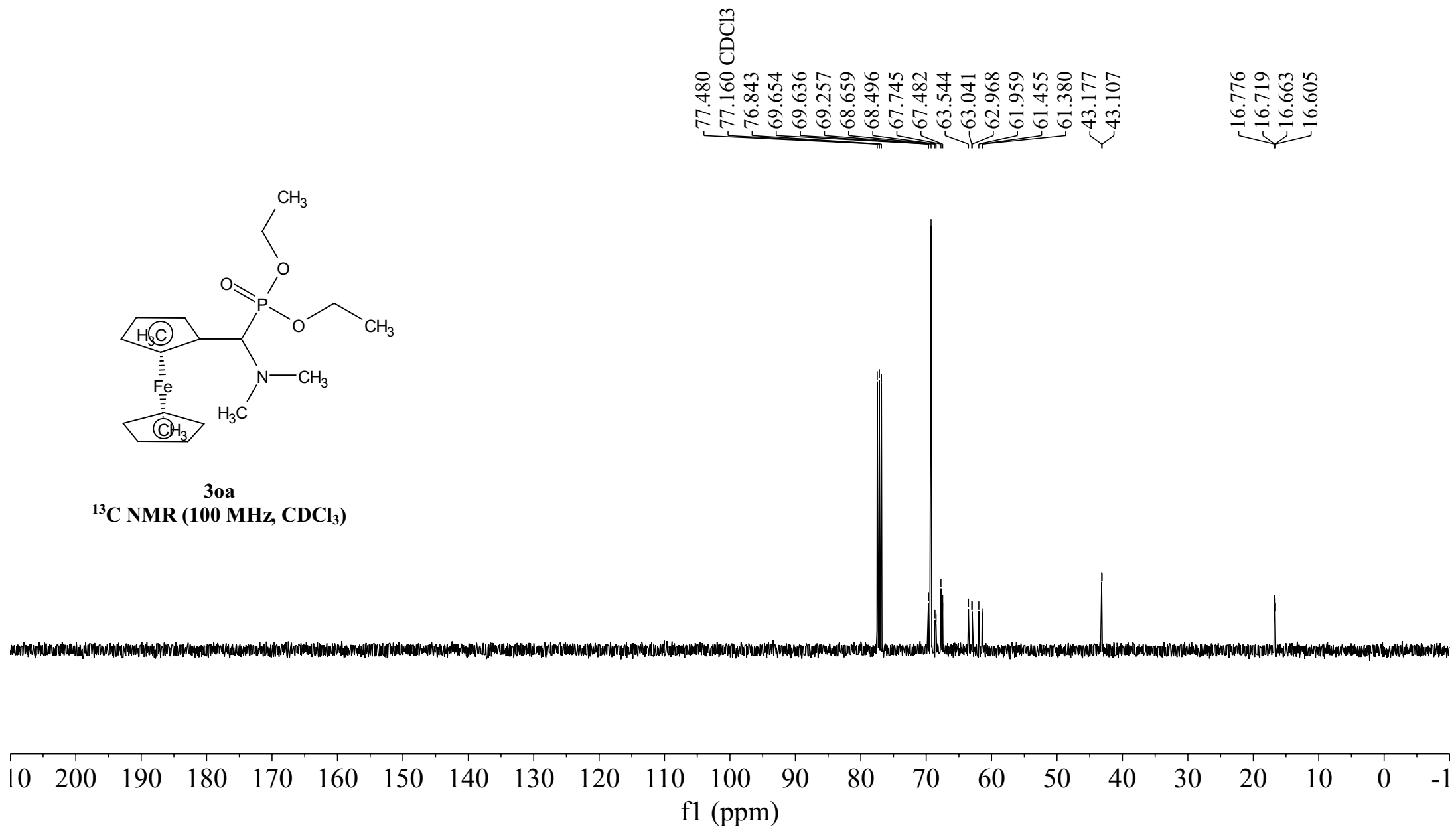
3a
¹H NMR (400 MHz, CDCl₃)

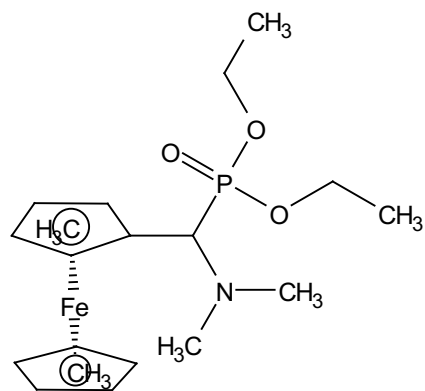




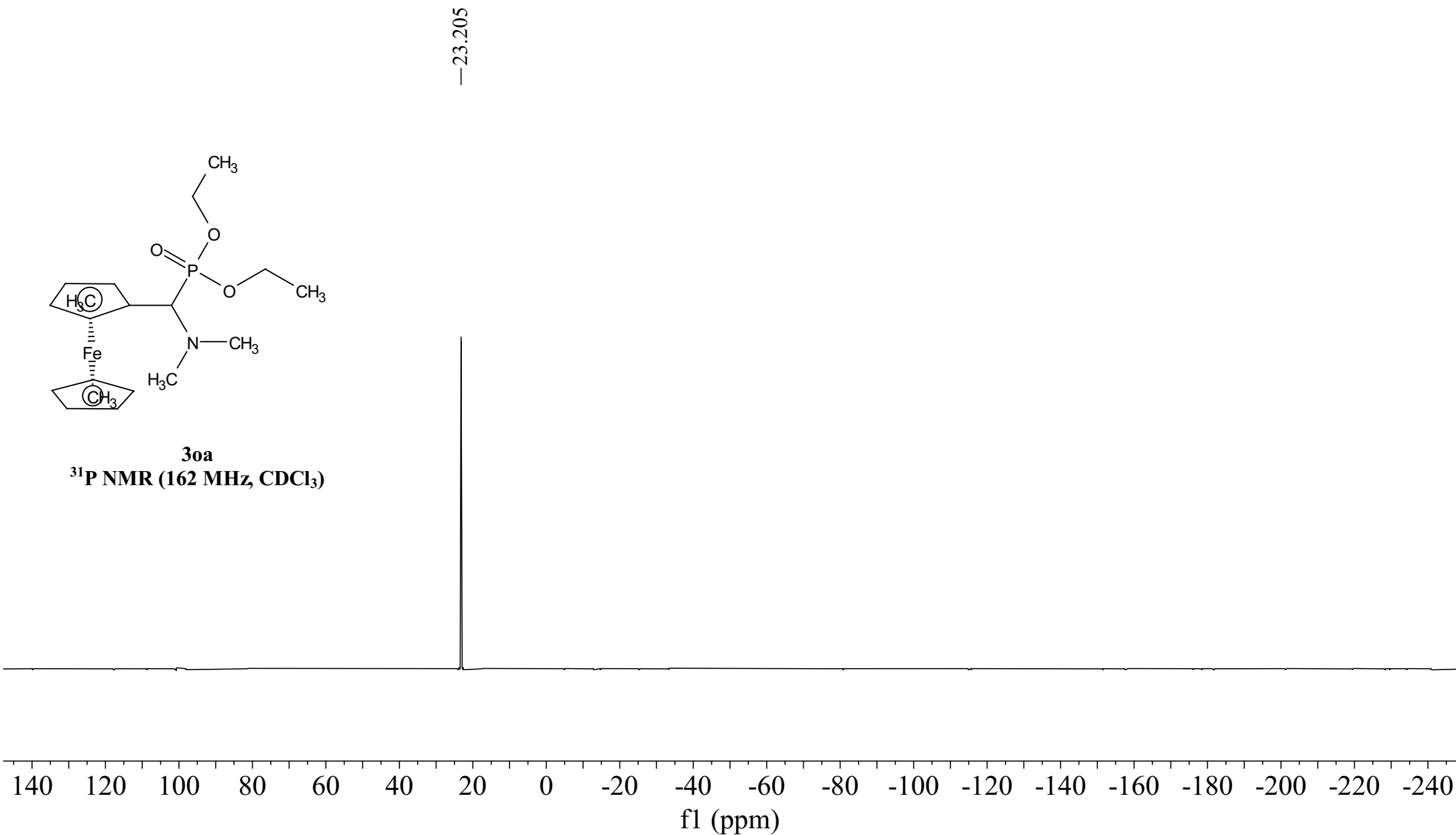
30a

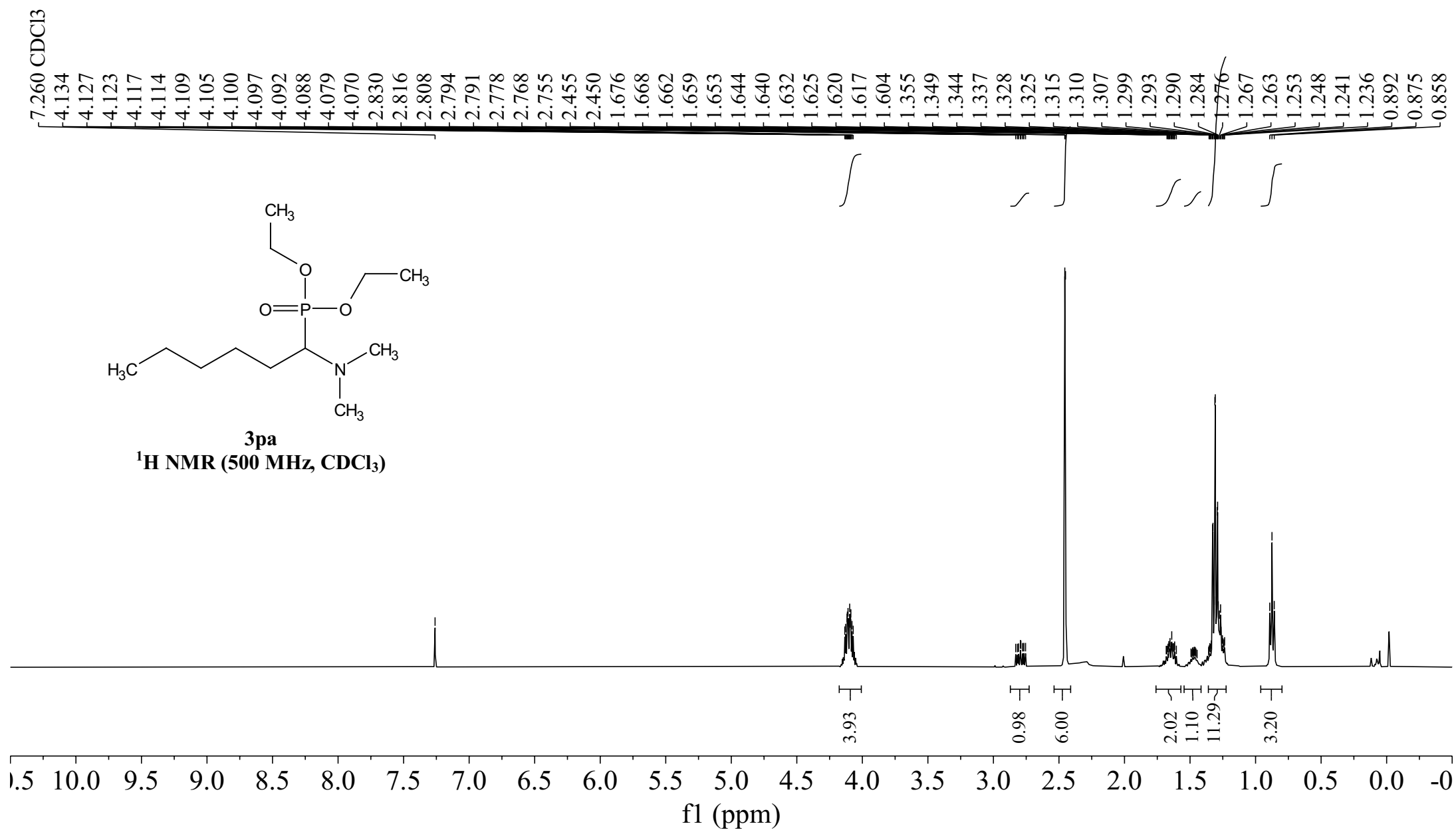
¹³C NMR (100 MHz, CDCl₃)

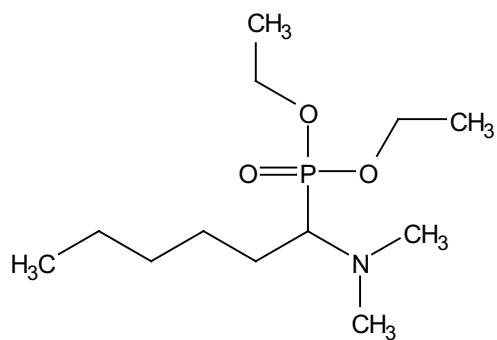




30a
³¹P NMR (162 MHz, CDCl₃)

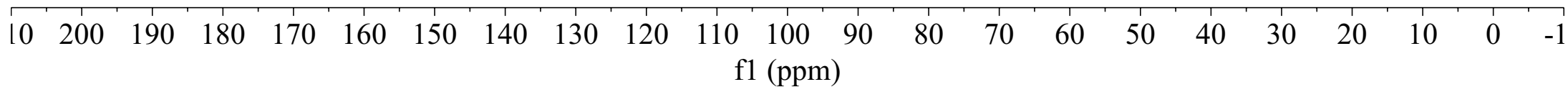


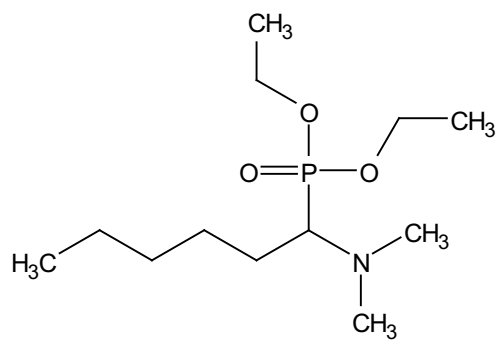




3pa
¹³C NMR (126 MHz, CDCl₃)

77.414
 77.160
 77.160 CDCl₃
 76.906
 62.646
 61.709
 61.651
 61.559
 61.173
 61.113
 42.346
 42.313
 31.775
 27.321
 27.227
 26.888
 26.843
 22.637
 16.752
 16.705
 16.657
 14.153





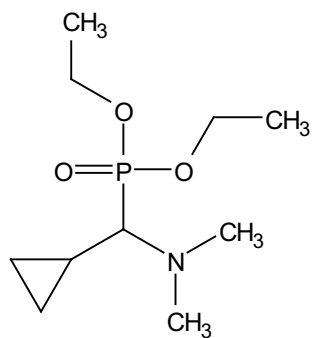
3pa
³¹P NMR (202 MHz, CDCl₃)

—29.782

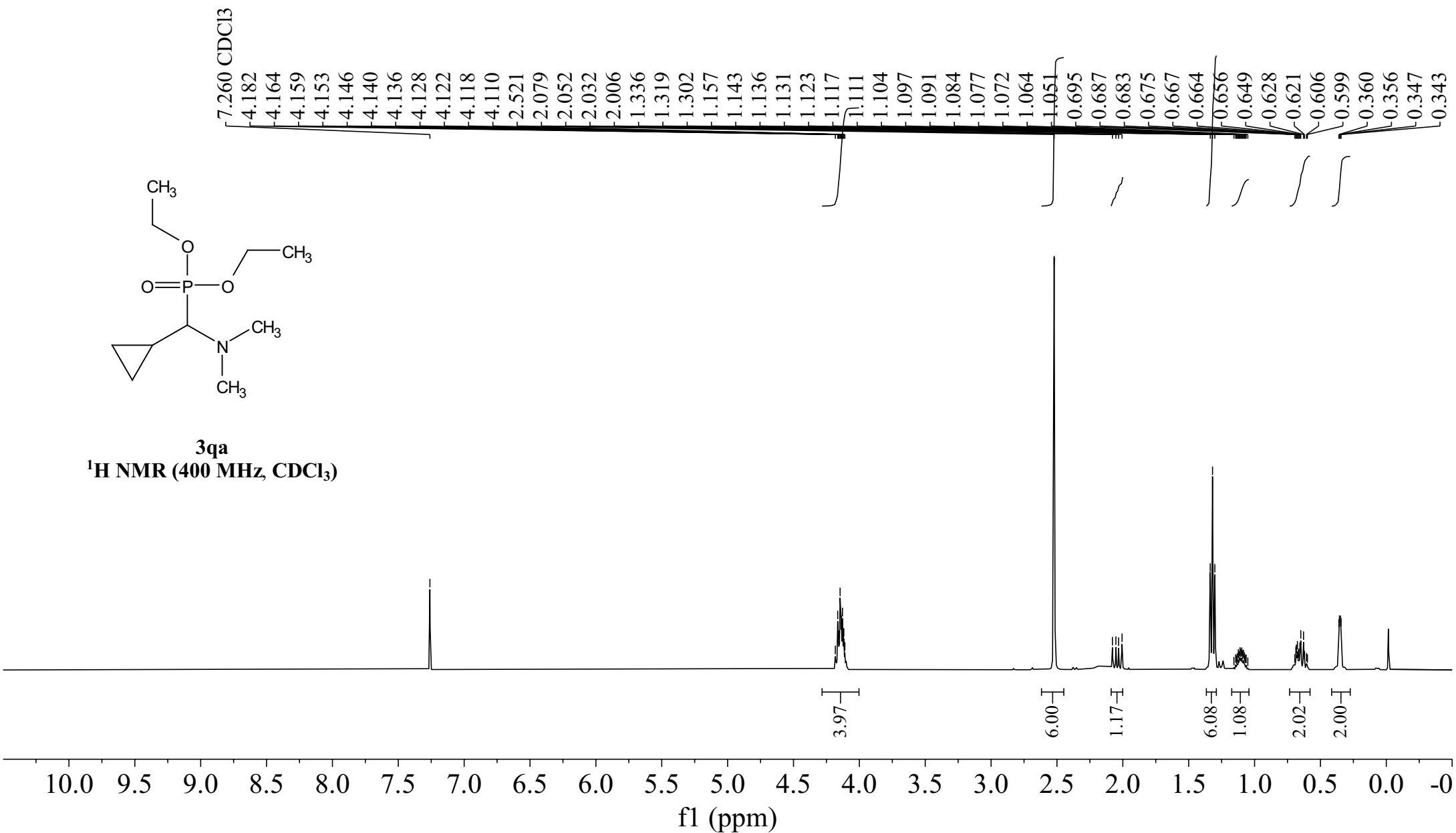


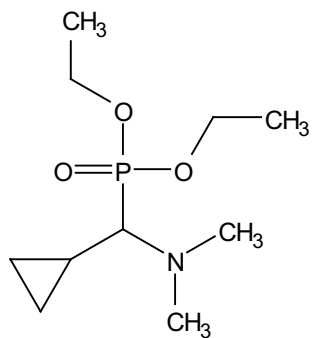
60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55

f1 (ppm)



3qa
¹H NMR (400 MHz, CDCl₃)

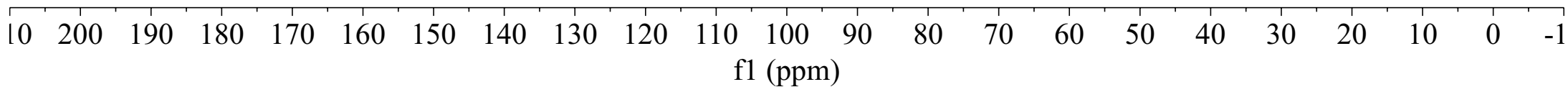


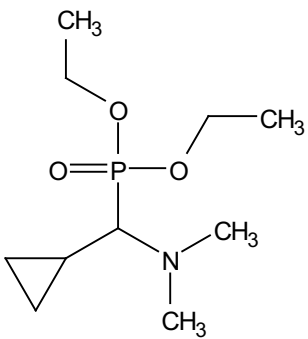


3qa

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

77.481
77.161
77.160 CDCl_3
76.843
68.378
66.879
62.047
61.975
61.386
61.314
43.165
43.097
16.590
16.567
16.533
16.509
6.979
6.910
5.564
5.402
3.361

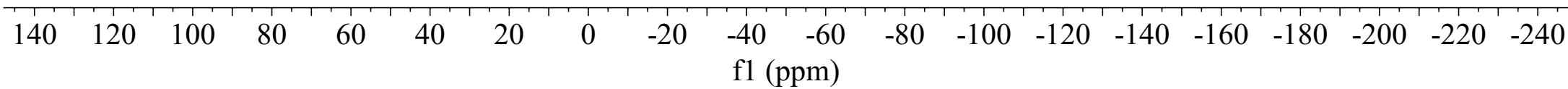


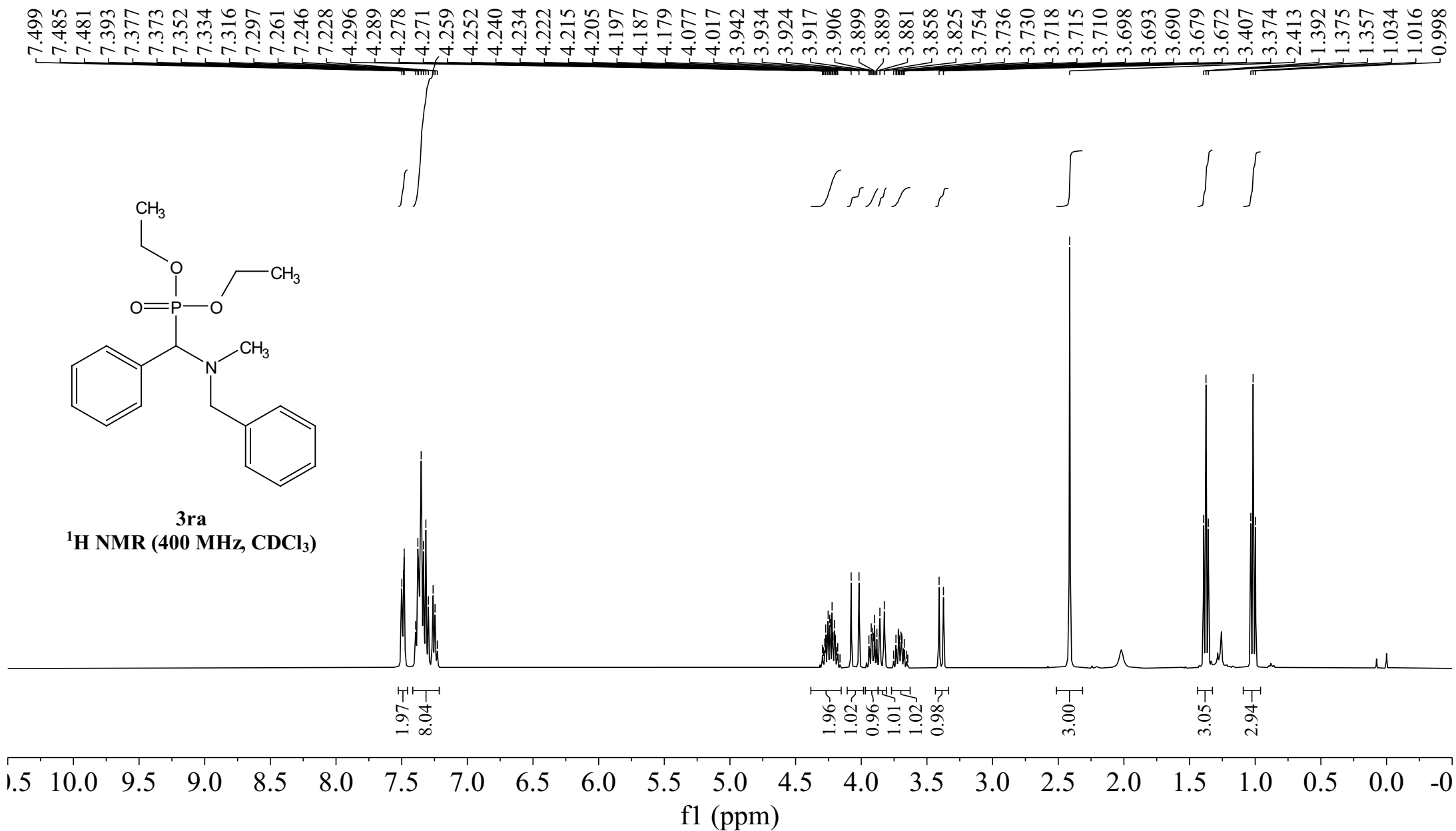


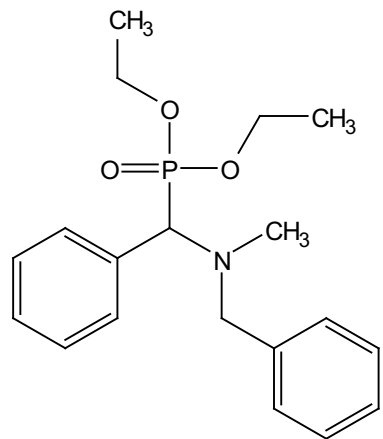
3qa

³¹P NMR (162 MHz, CDCl₃)

—25.955







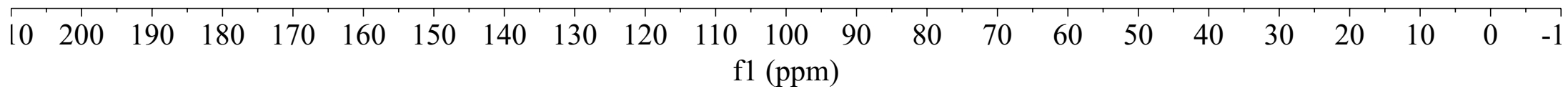
3ra

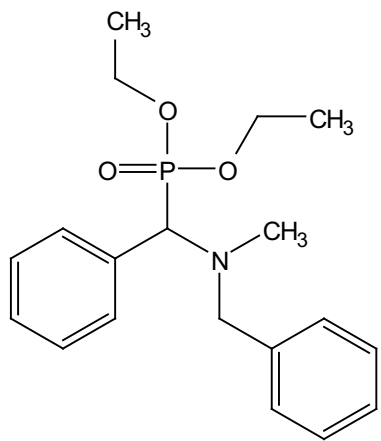
¹³C NMR (100 MHz, CDCl₃)

139.145
132.124
132.082
130.975
130.889
129.046
128.358
128.228
128.113
128.099
127.173

77.477
77.160 CDCl₃
76.842
65.778
64.169
62.703
62.632
62.355
62.285
60.003
59.878
39.991
39.939

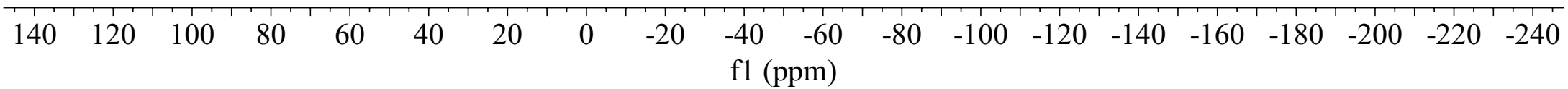
16.708
16.647
16.283
16.227

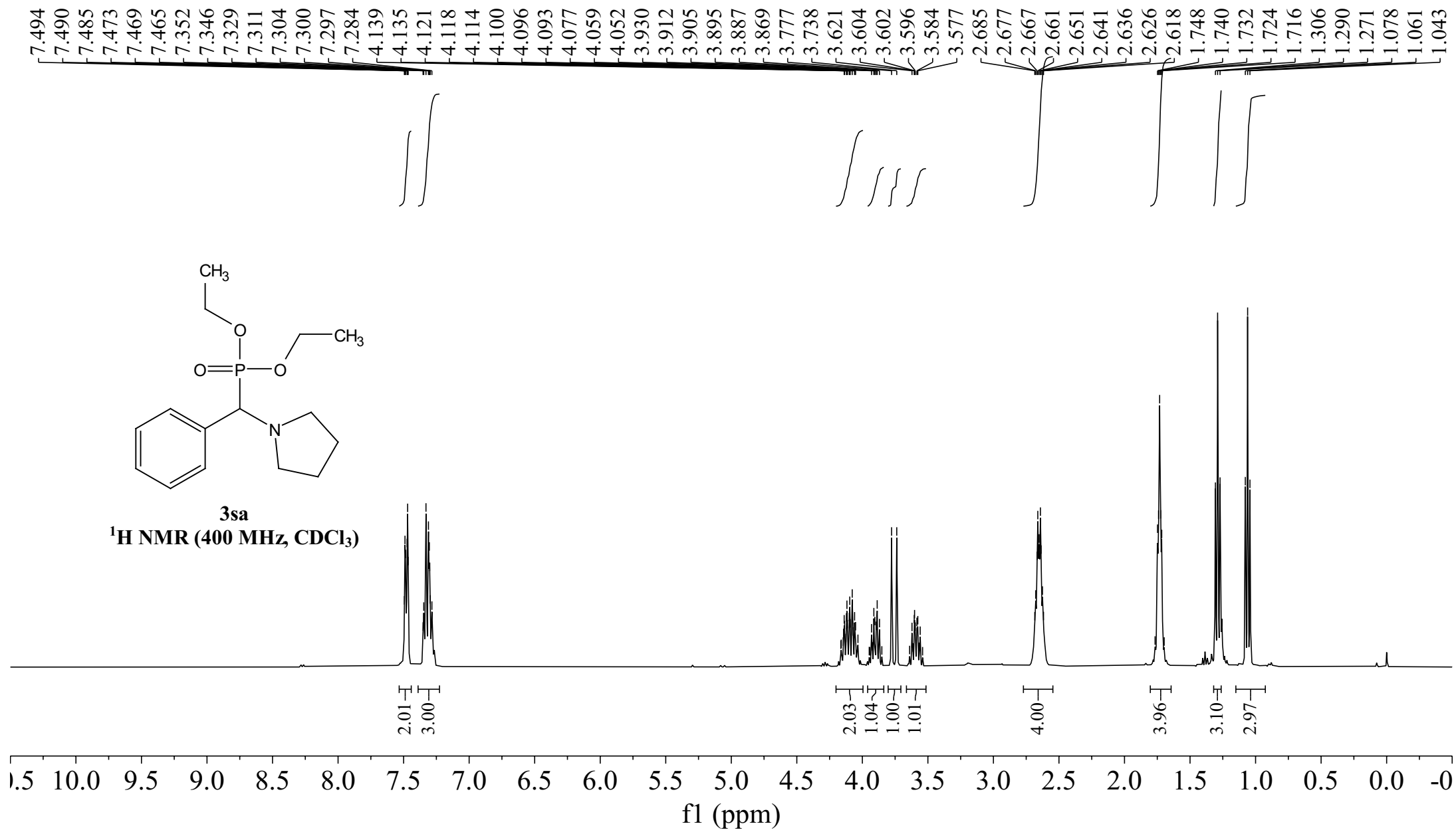


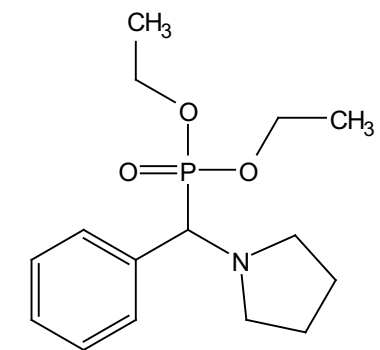


3ra
³¹P NMR (162 MHz, CDCl₃)

-23.123







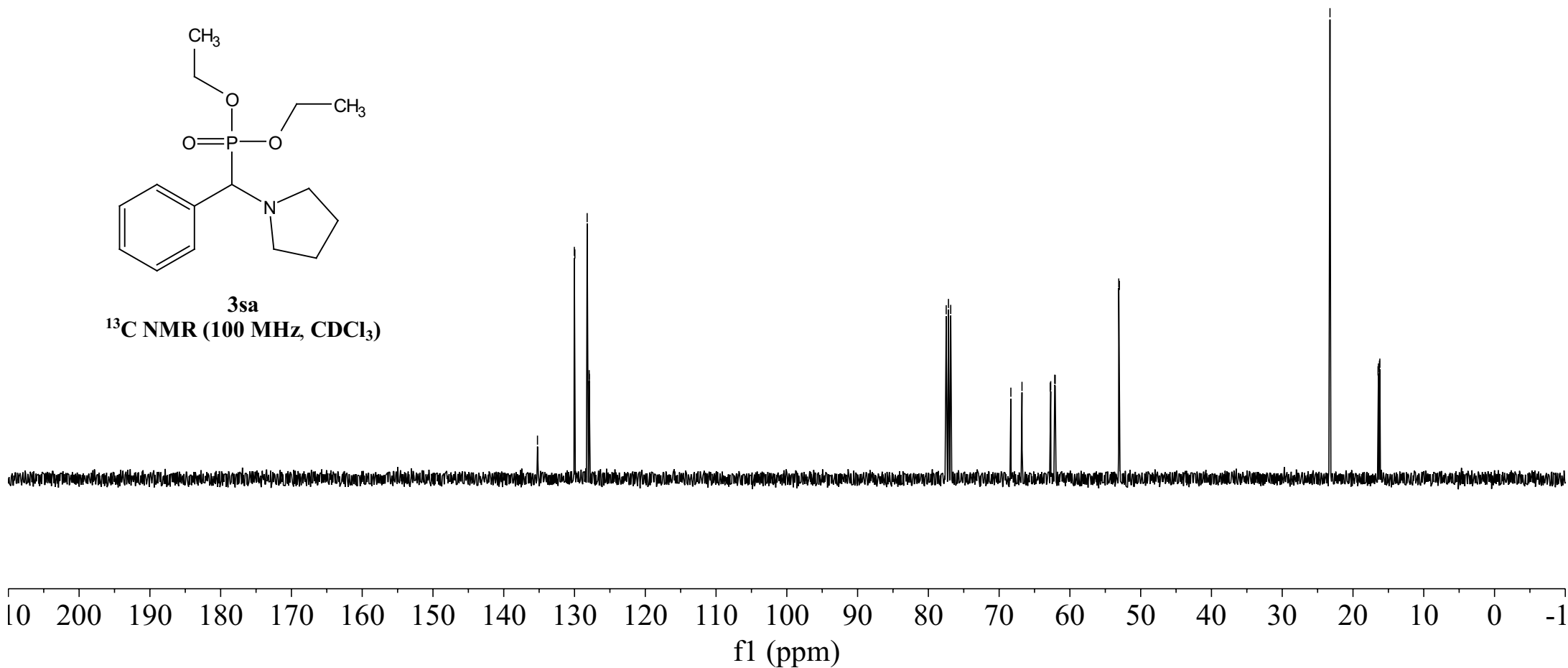
3sa

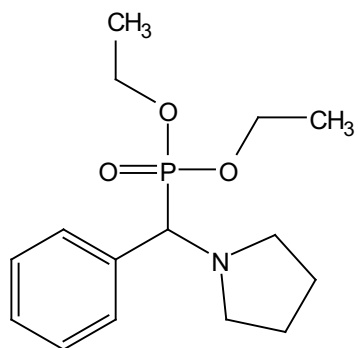
^{13}C NMR (100 MHz, CDCl_3)

135.233
130.025
129.952
128.213
128.196
127.929
127.904

77.478
77.160 CDCl_3
76.842
68.343
66.771
62.782
62.712
62.150
62.076
53.098
53.010

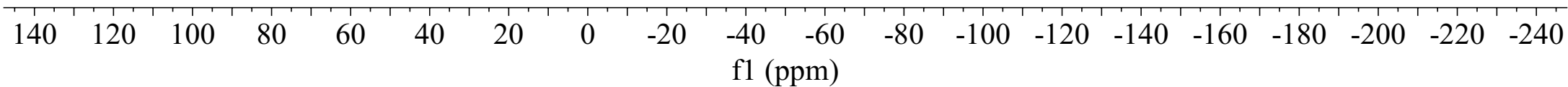
23.252
16.463
16.405
16.263
16.206

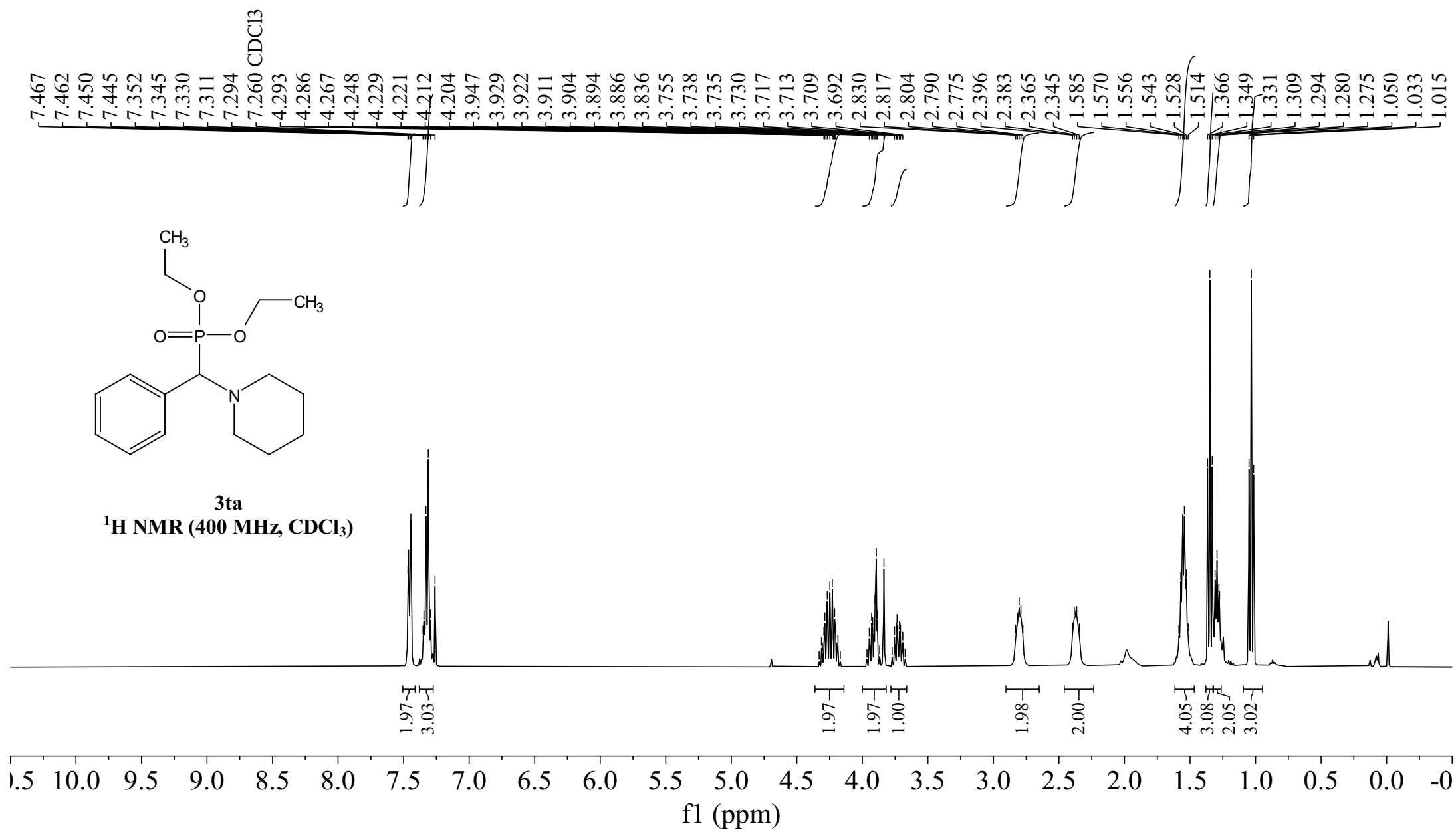


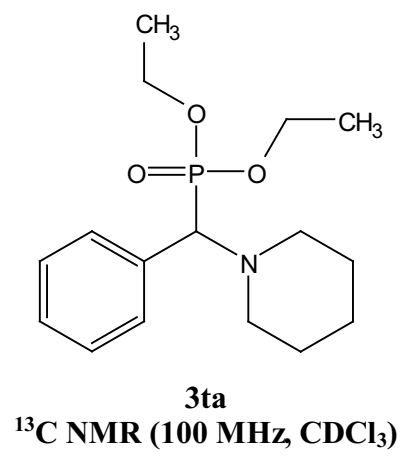


3sa
³¹P NMR (162 MHz, CDCl₃)

—22.859



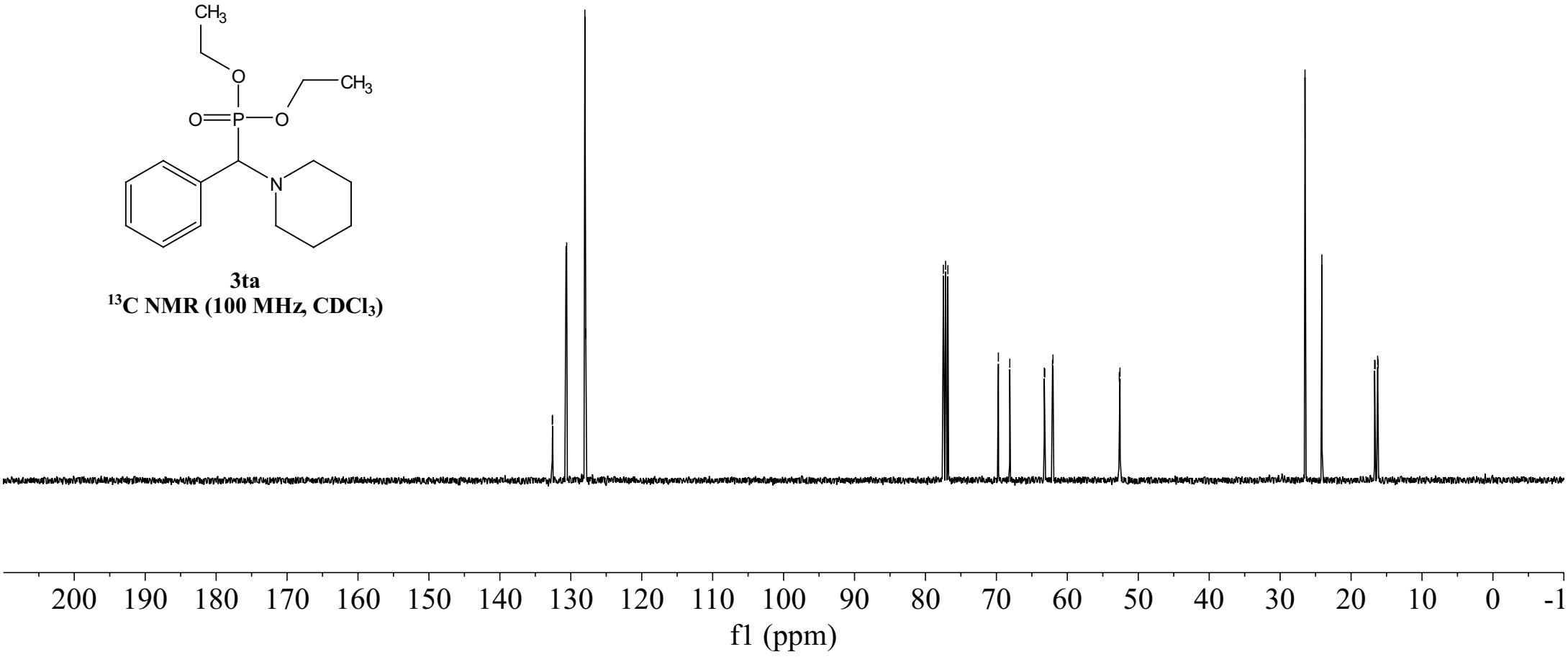


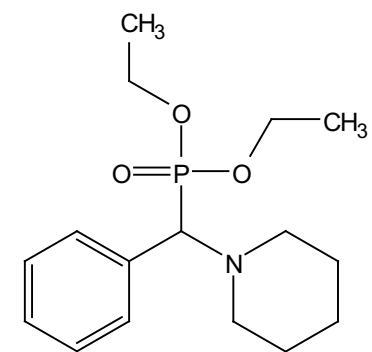


132.611
 132.576
 130.672
 130.581
 128.018
 127.880
 127.866

77.477
 77.160 CDCl₃
 76.842
 69.719
 68.111
 63.248
 63.178
 62.093
 62.024
 52.670
 52.579

26.495
 24.115
 16.676
 16.617
 16.250
 16.193

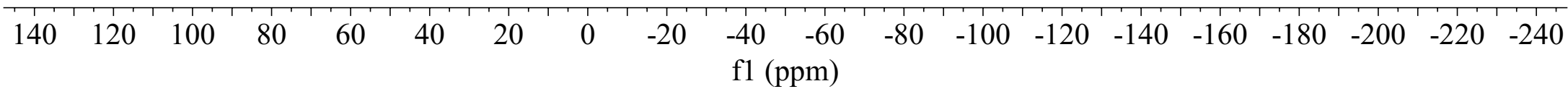


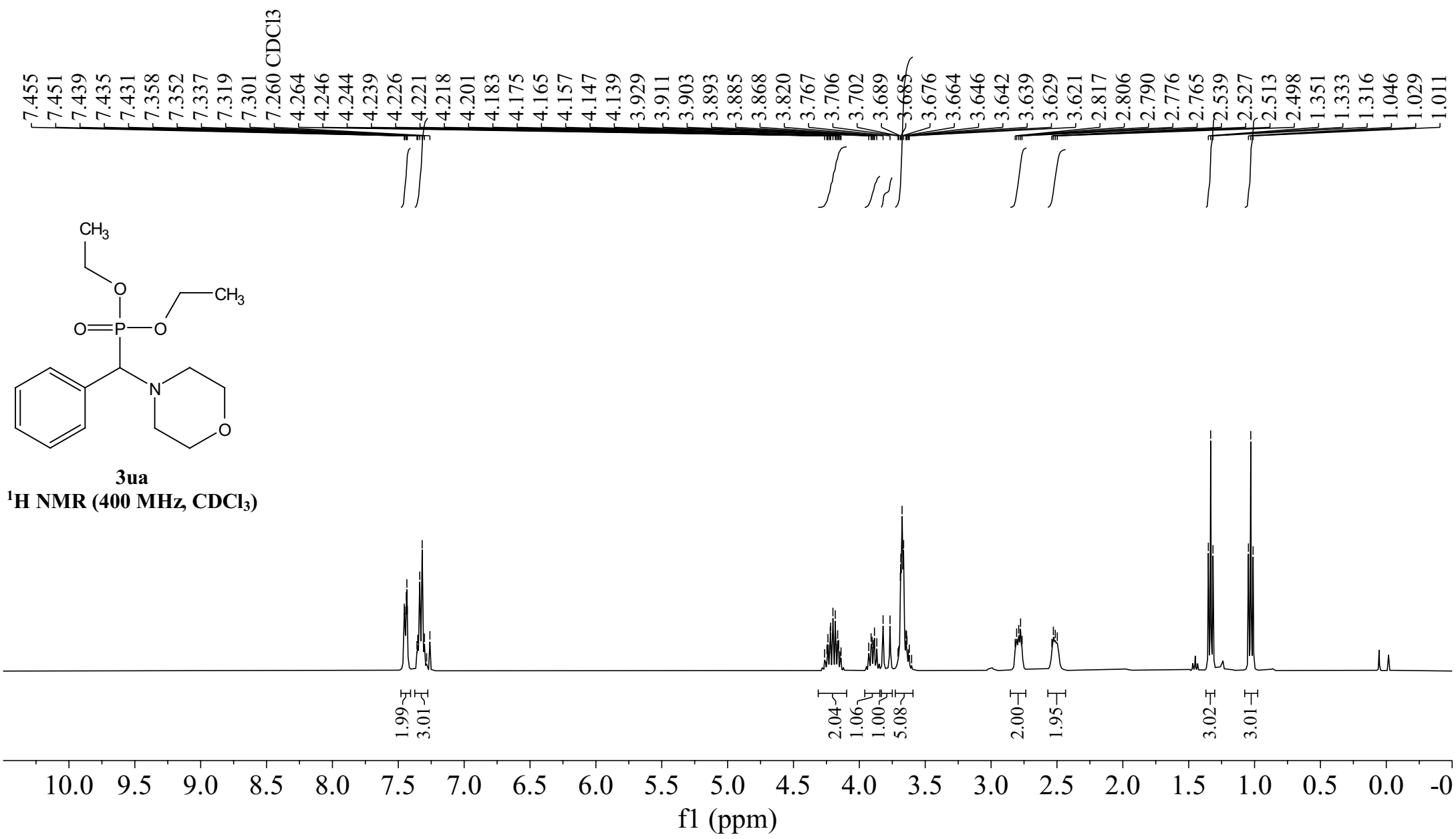


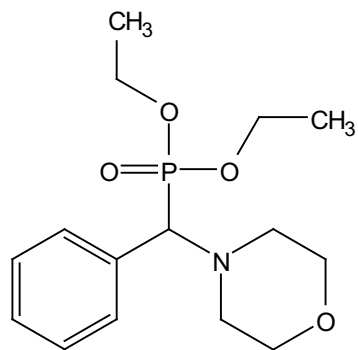
3ta

³¹P NMR (162 MHz, CDCl₃)

—22.433





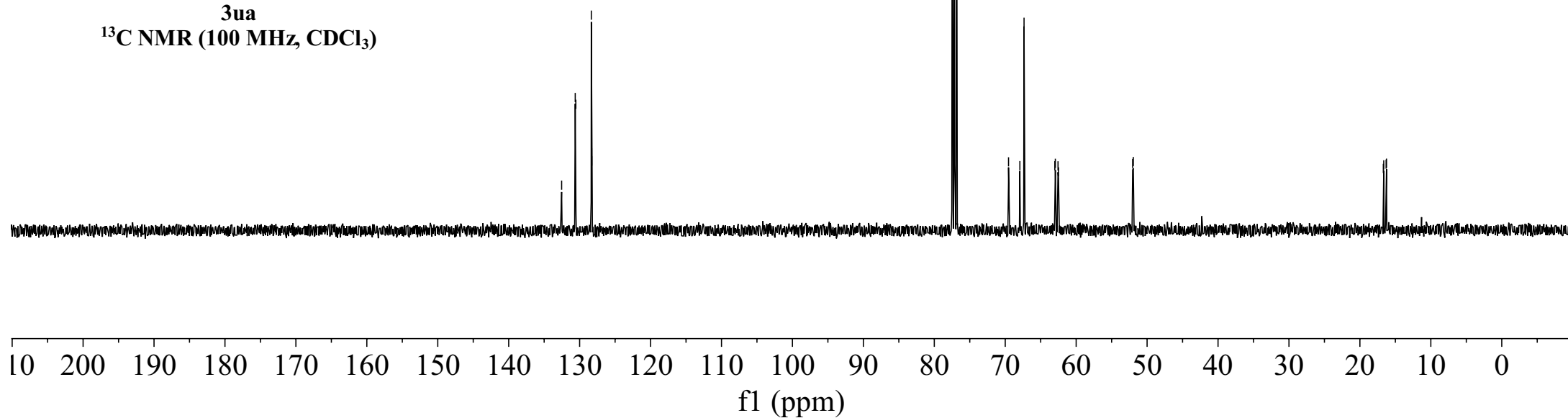


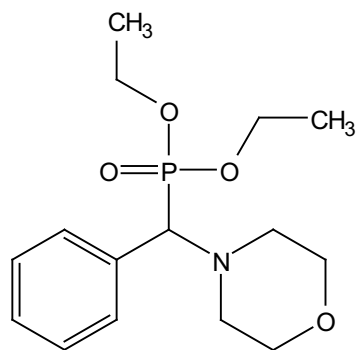
3ua
¹³C NMR (100 MHz, CDCl₃)

132.537
130.619
130.535
128.352
128.297
128.280

77.478
77.160 CDCl₃
76.842
69.535
67.936
67.347
63.008
62.937
62.557
62.486
52.037
51.945

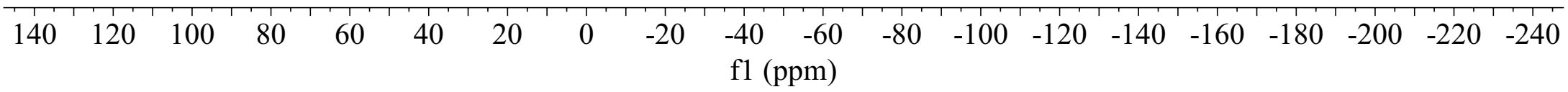
16.697
16.638
16.304
16.248



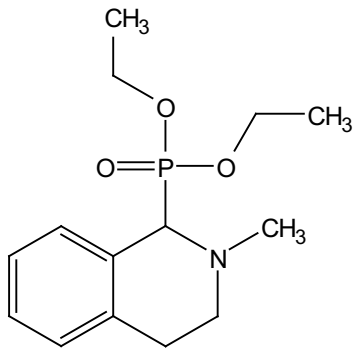


-21.819

3ua
³¹P NMR (162 MHz, CDCl₃)

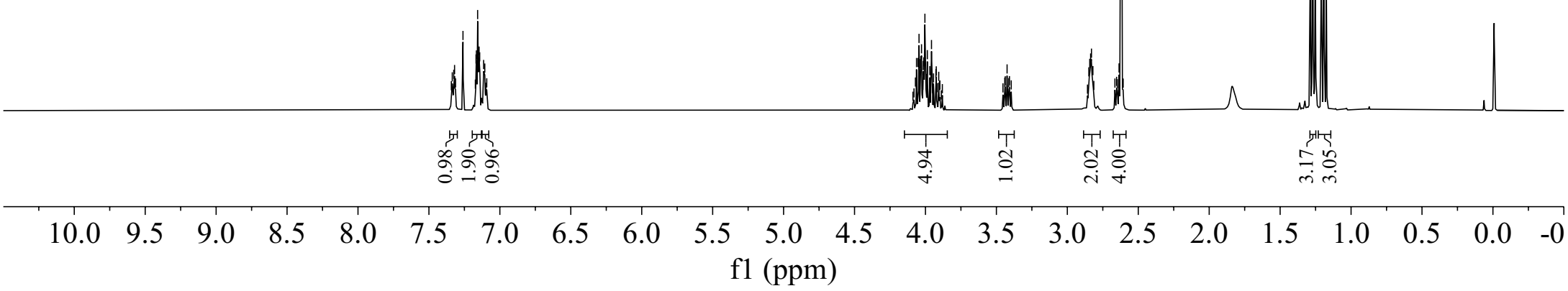


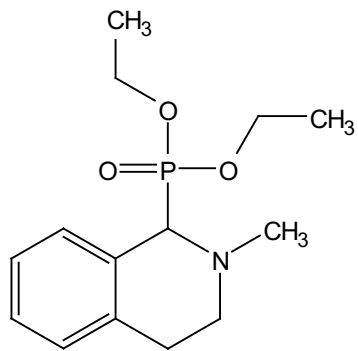
7.336
7.325
7.319
7.312
7.260 CDCl₃
7.173
7.168
7.165
7.157
7.150
7.146
7.142
7.115
7.106
7.092
4.071
4.063
4.053
4.045
4.036
4.033
4.028
4.019
4.015
4.012
4.004
3.994
3.987
3.969
3.957
3.943
3.926
3.924
3.906
3.901
3.899
3.441
3.438
3.425
3.412
3.408
3.395
2.849
2.842
2.836
2.830
2.820
2.665
2.653
2.648
2.636
2.620
2.606
1.288
1.270
1.253
1.210
1.192
1.174



3va

¹H NMR (400 MHz, CDCl₃)





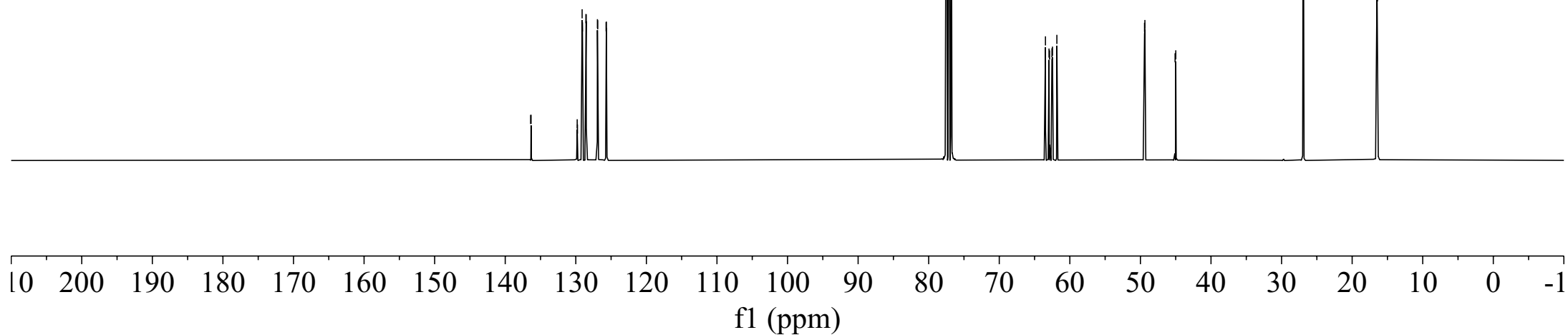
3va

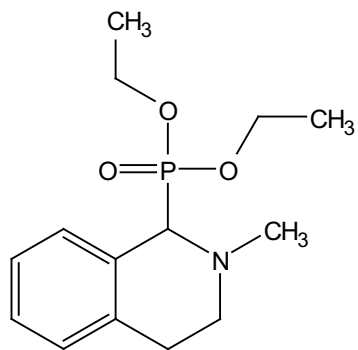
¹³C NMR (100 MHz, CDCl₃)

136.401
136.339
129.803
129.768
129.104
129.057
128.565
128.531
126.939
126.896
125.711
125.673

77.481
77.160 CDCl₃
76.840
63.456
62.953
62.876
62.537
62.458
61.838
49.417
49.367
45.089
44.992

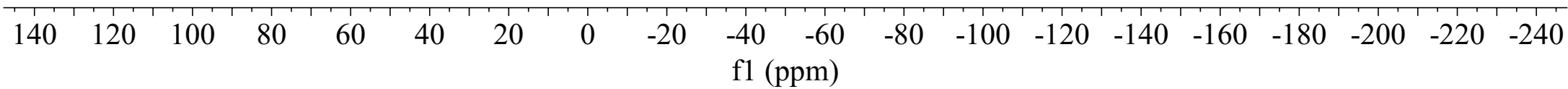
26.927
16.515
16.474
16.453
16.414

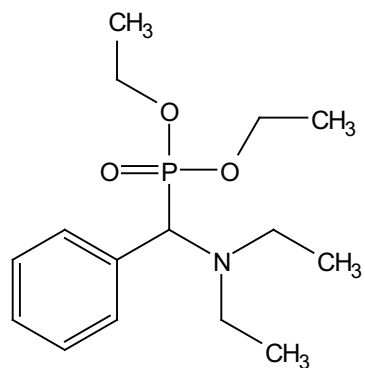




3va
³¹P NMR (162 MHz, CDCl₃)

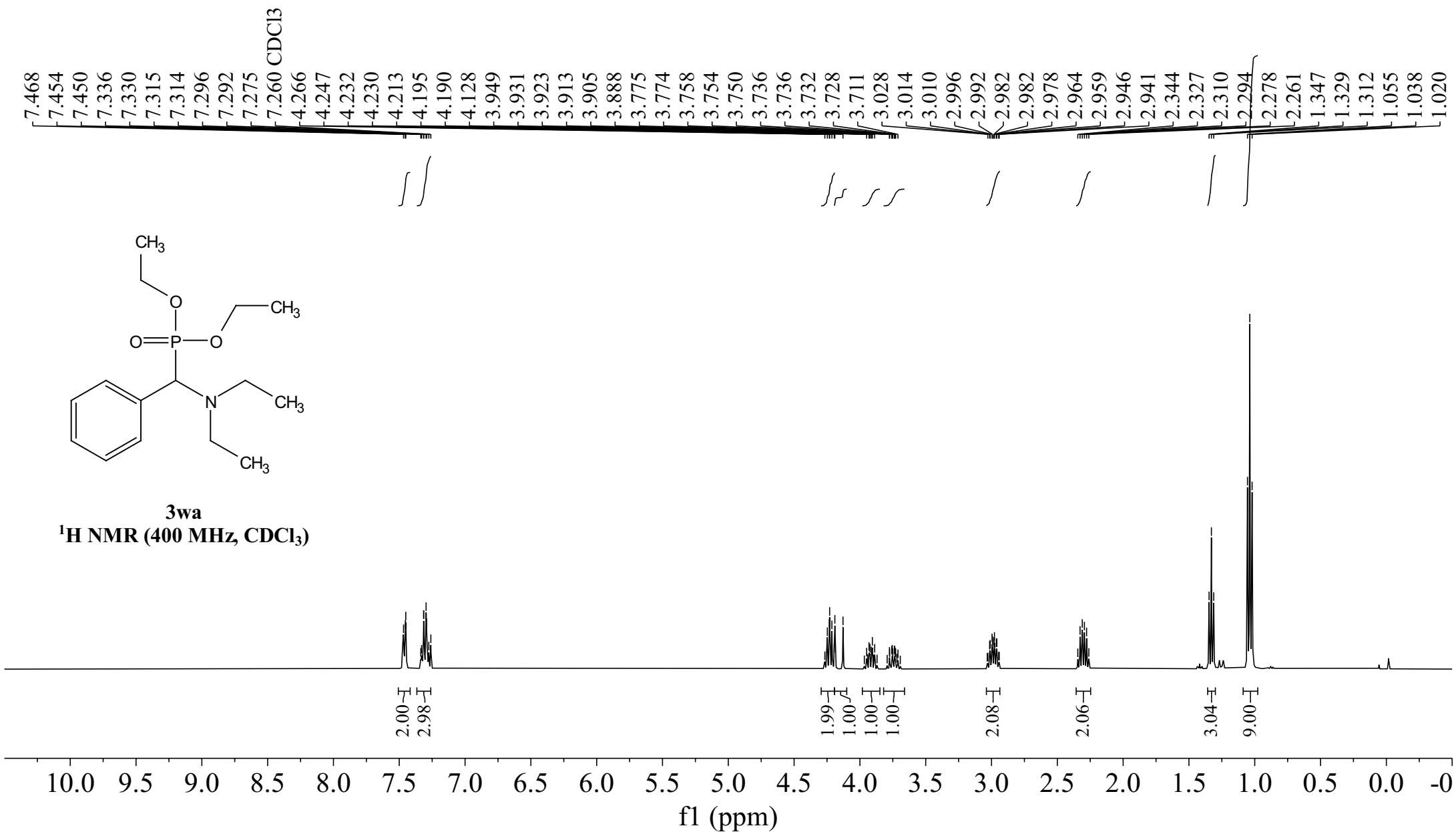
—23.057

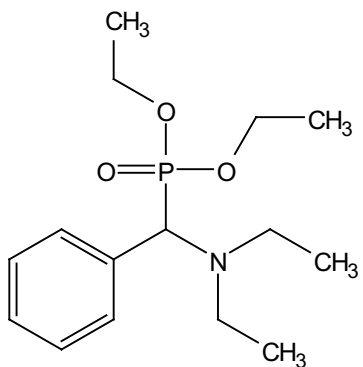




3wa

¹H NMR (400 MHz, CDCl₃)



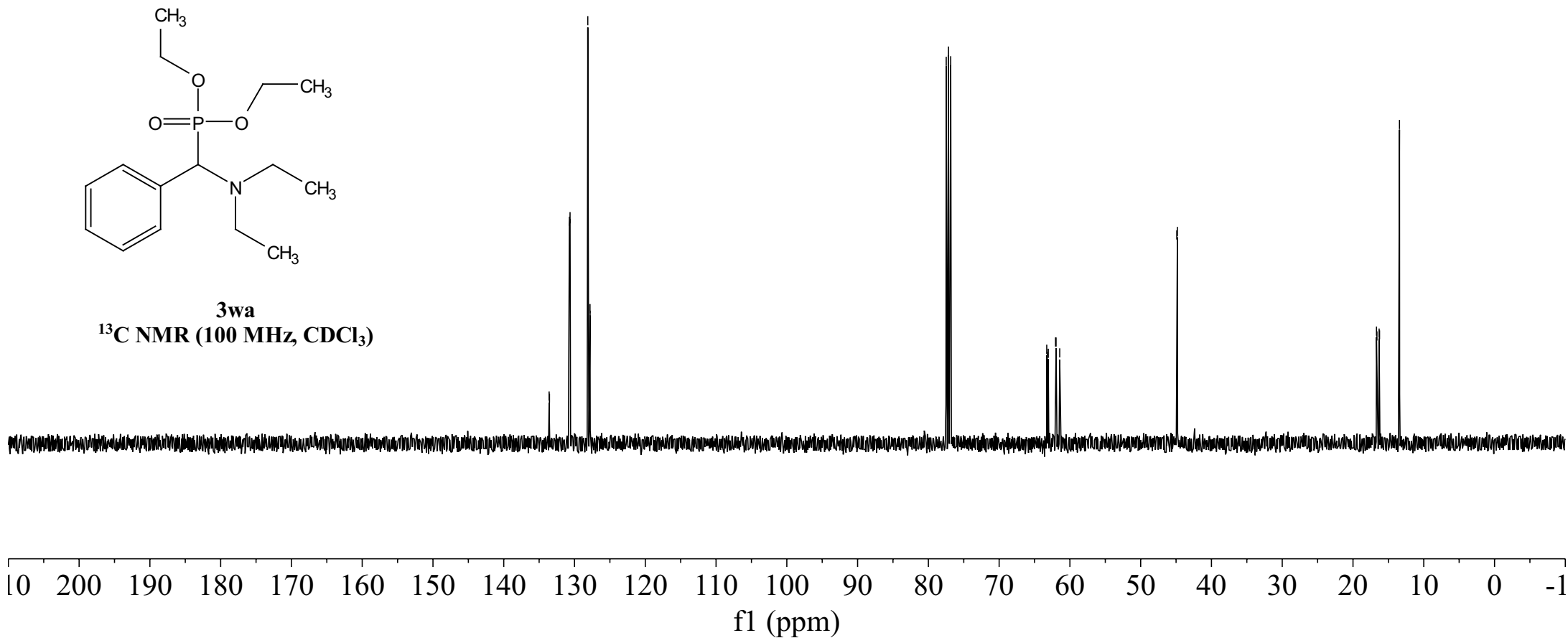


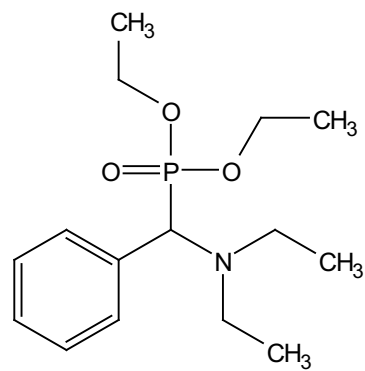
3wa
¹³C NMR (100 MHz, CDCl₃)

133.589
 133.538
 130.721
 130.632
 128.125
 127.813
 127.799

77.478
 77.160 CDCl₃
 76.842
 63.272
 63.203
 63.060
 62.030
 61.958
 61.439
 44.900
 44.816

16.678
 16.618
 16.307
 16.250
 13.431

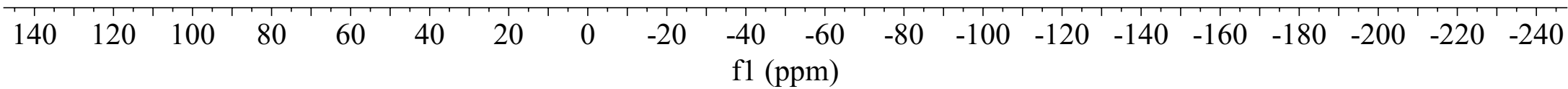


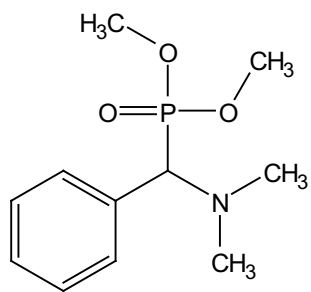


3wa

³¹P NMR (162 MHz, CDCl₃)

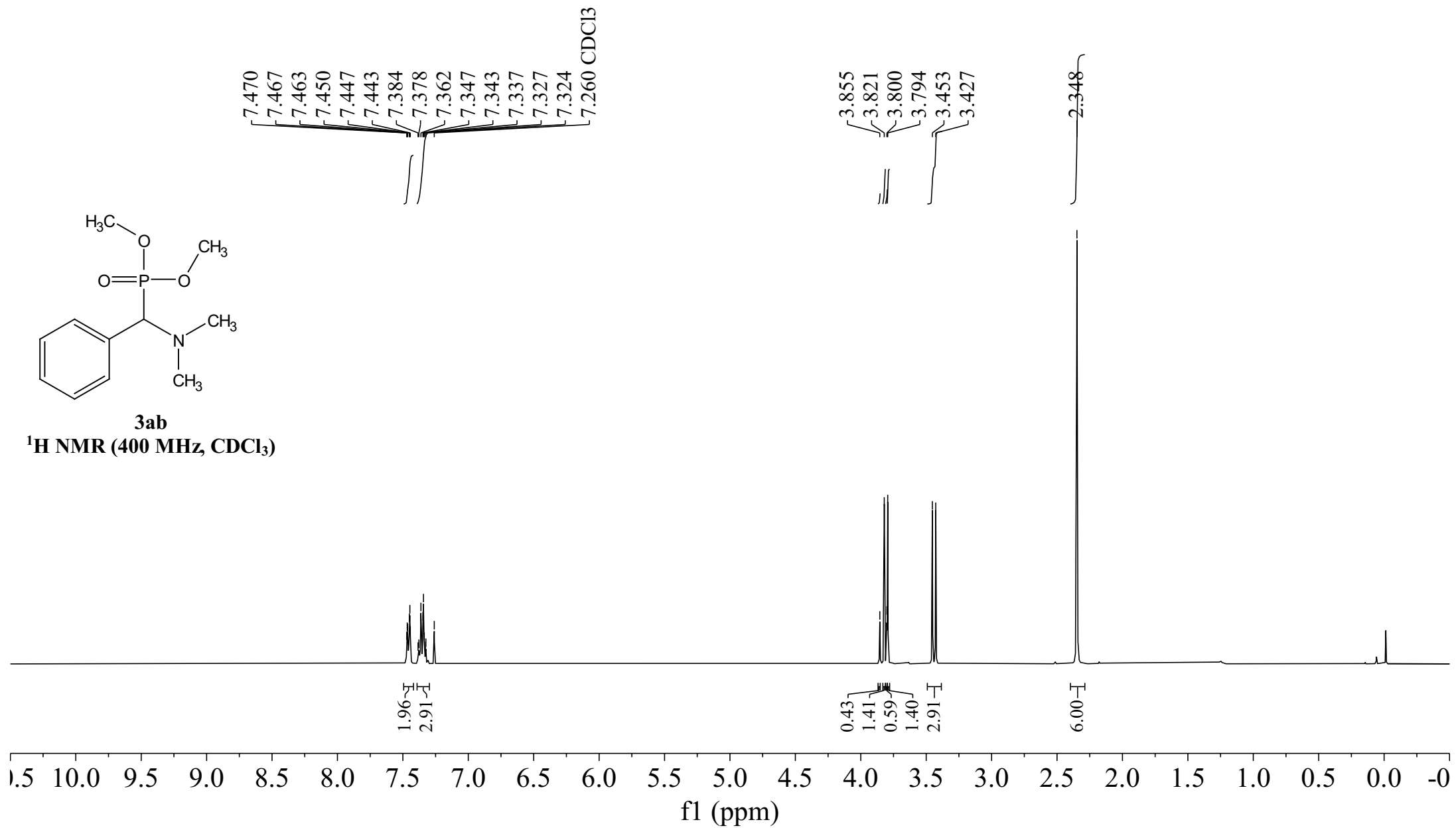
—23.629

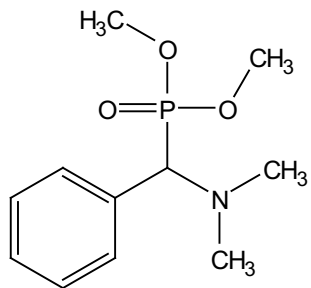




3ab

¹H NMR (400 MHz, CDCl₃)





3ab

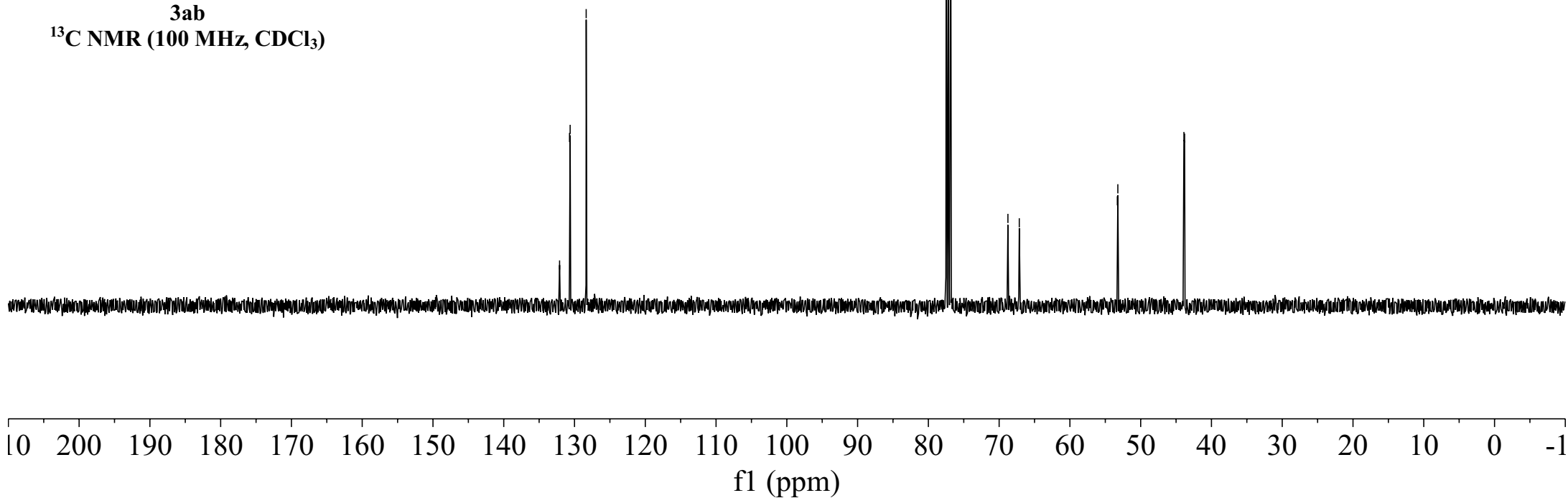
^{13}C NMR (100 MHz, CDCl_3)

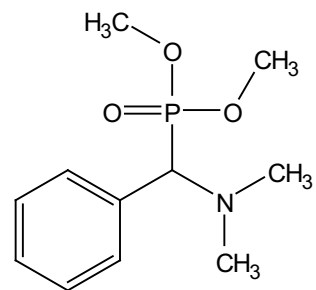
132.111
130.704
130.618
128.352
128.314
128.298

77.479
77.160 CDCl_3
76.843
68.760
67.154

53.299
53.227

43.890
43.793

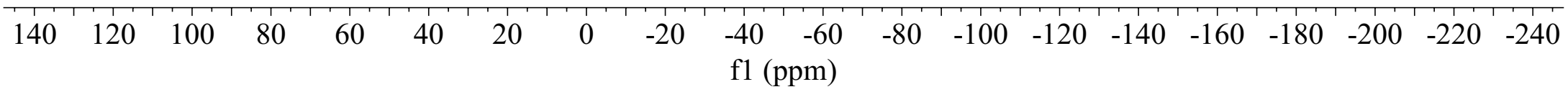


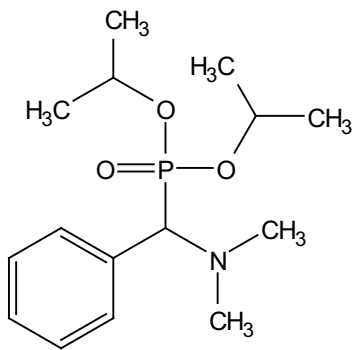


3ab

³¹P NMR (162 MHz, CDCl₃)

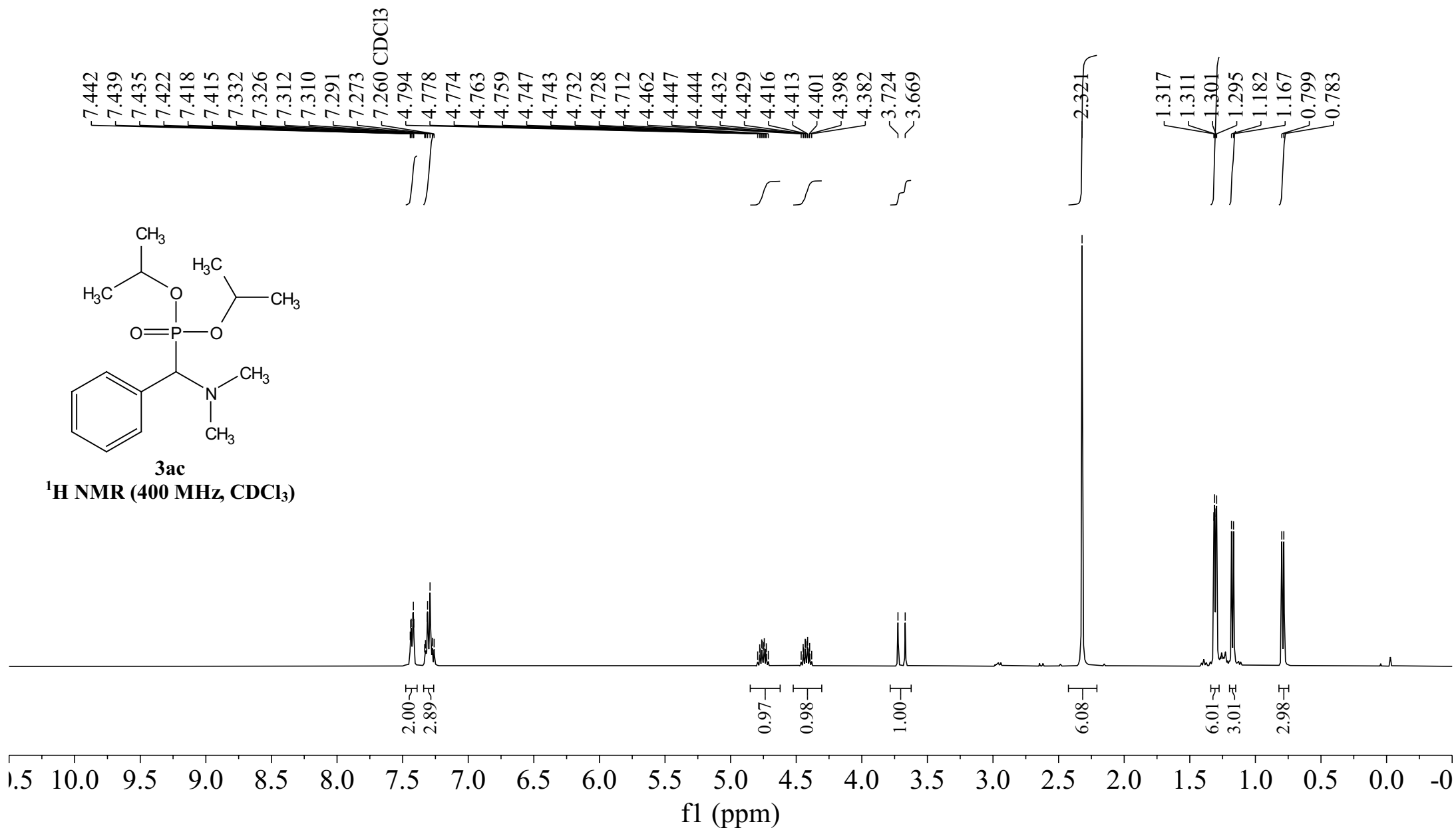
-24.984

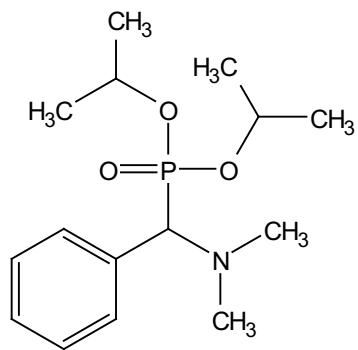




3ac

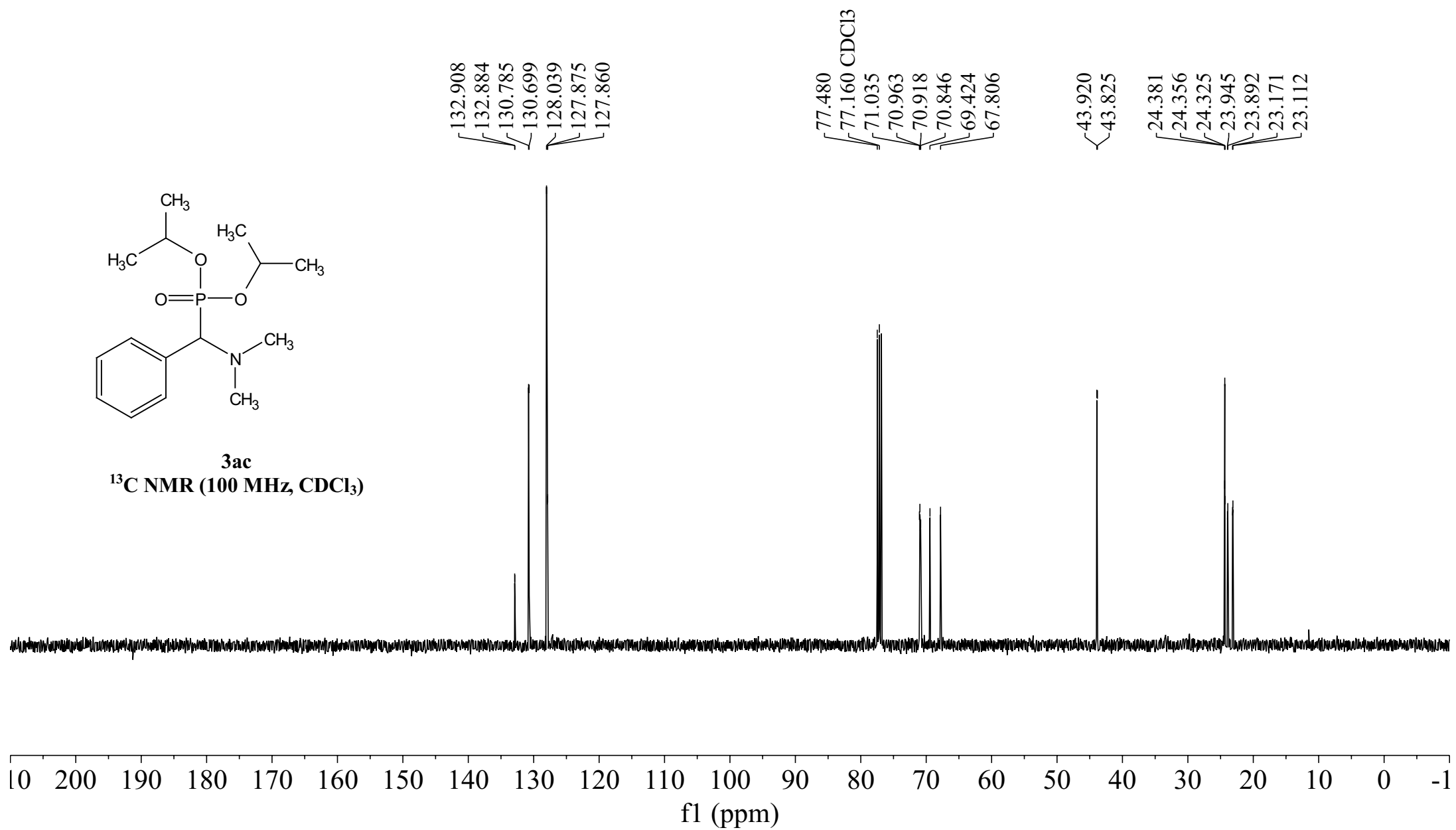
¹H NMR (400 MHz, CDCl₃)

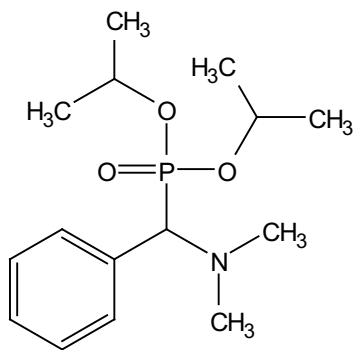




3ac

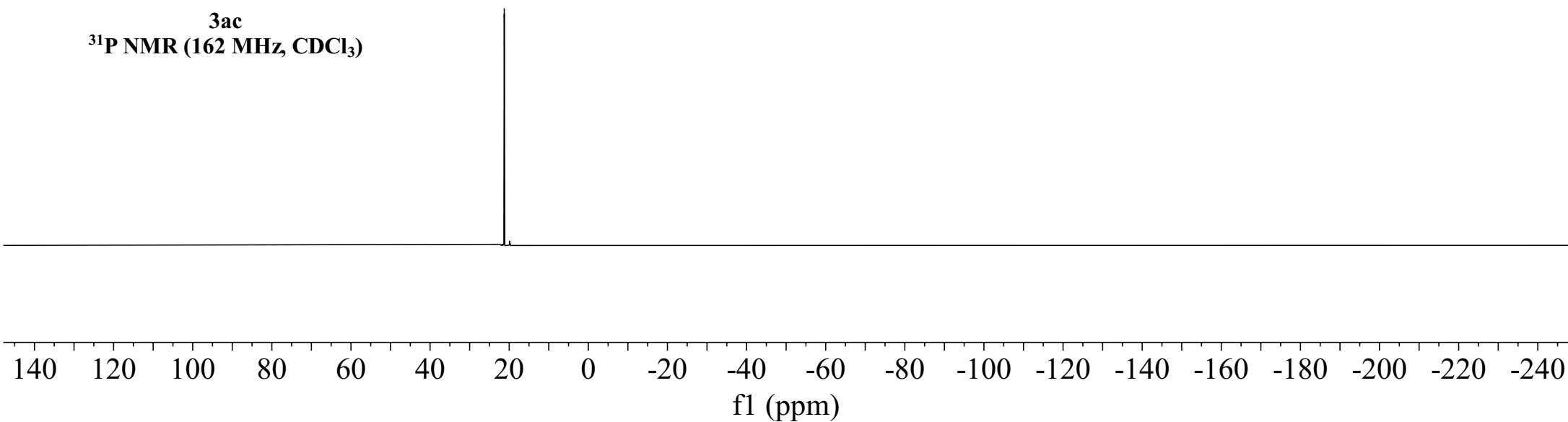
¹³C NMR (100 MHz, CDCl₃)

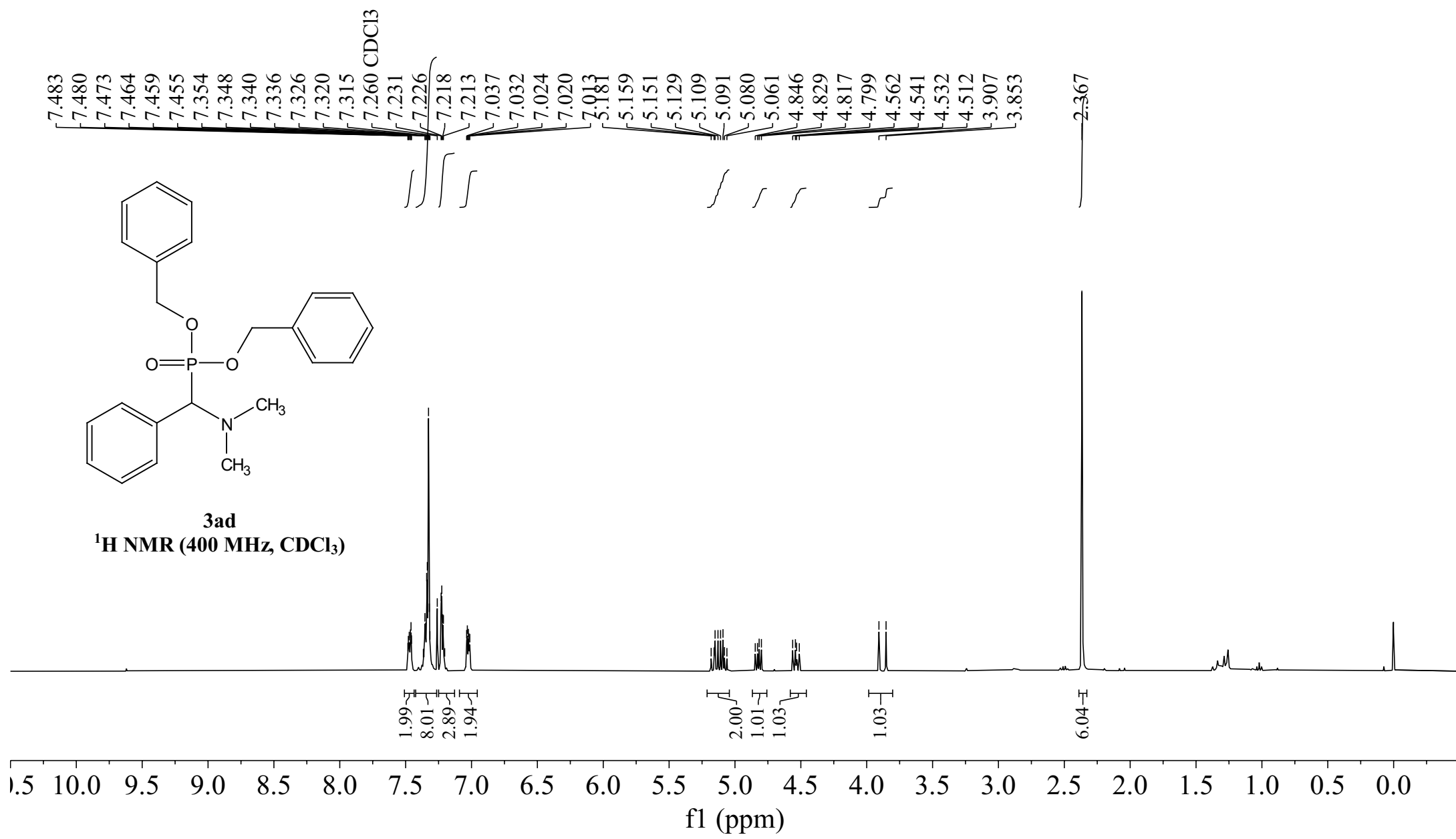


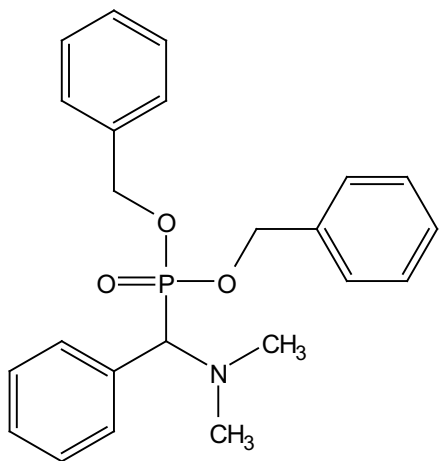


3ac
³¹P NMR (162 MHz, CDCl₃)

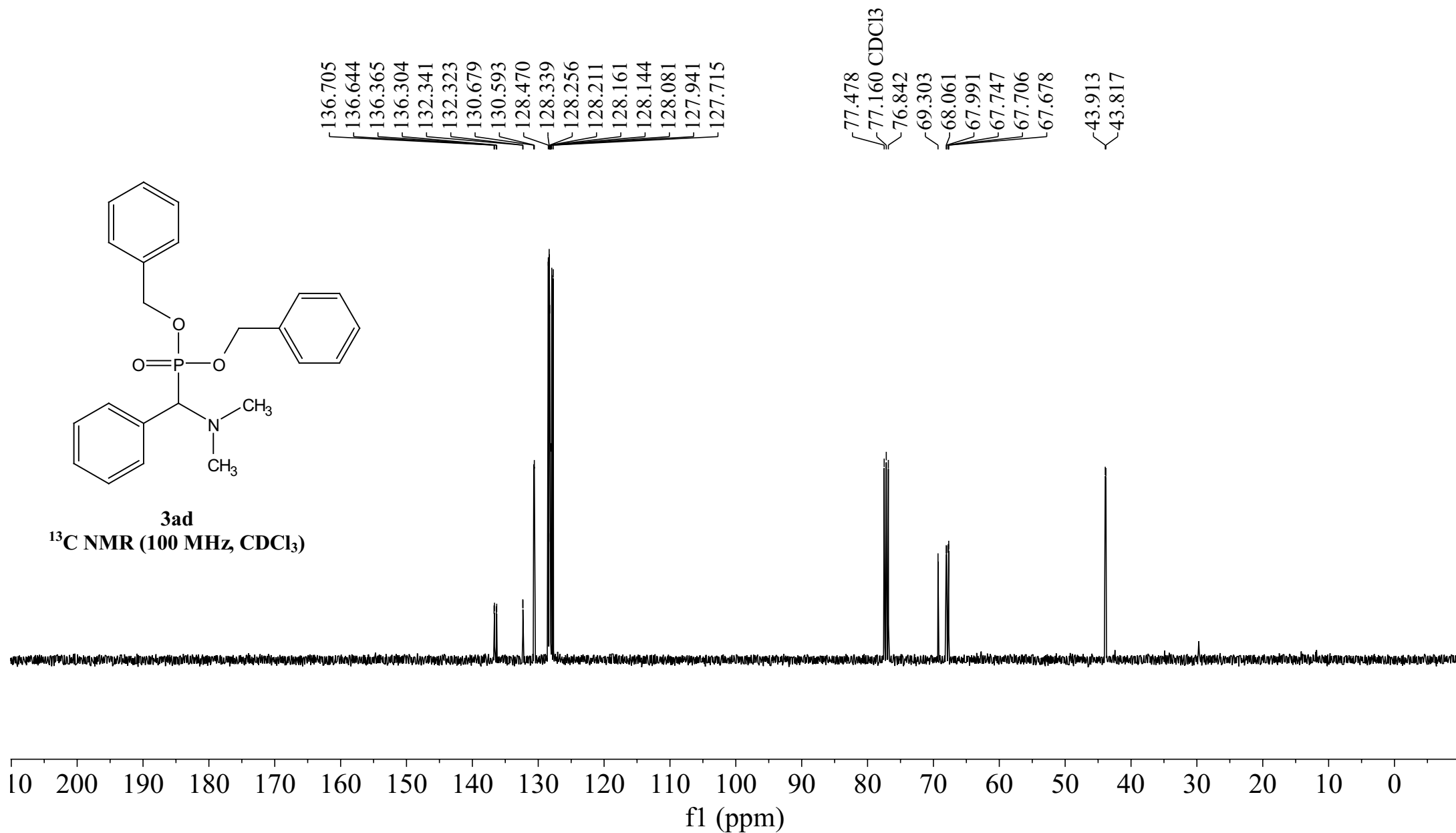
—21.246

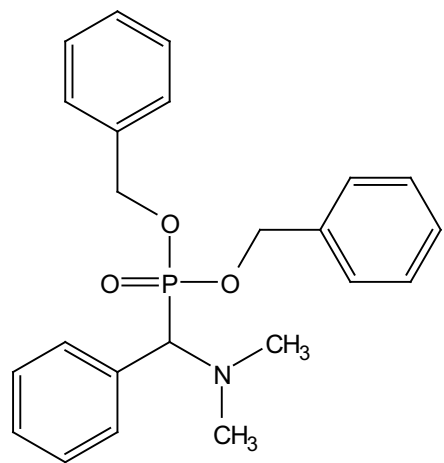






3ad
¹³C NMR (100 MHz, CDCl₃)

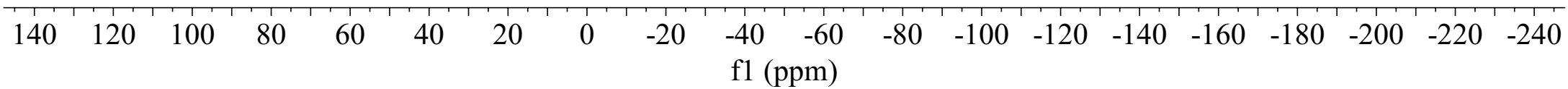


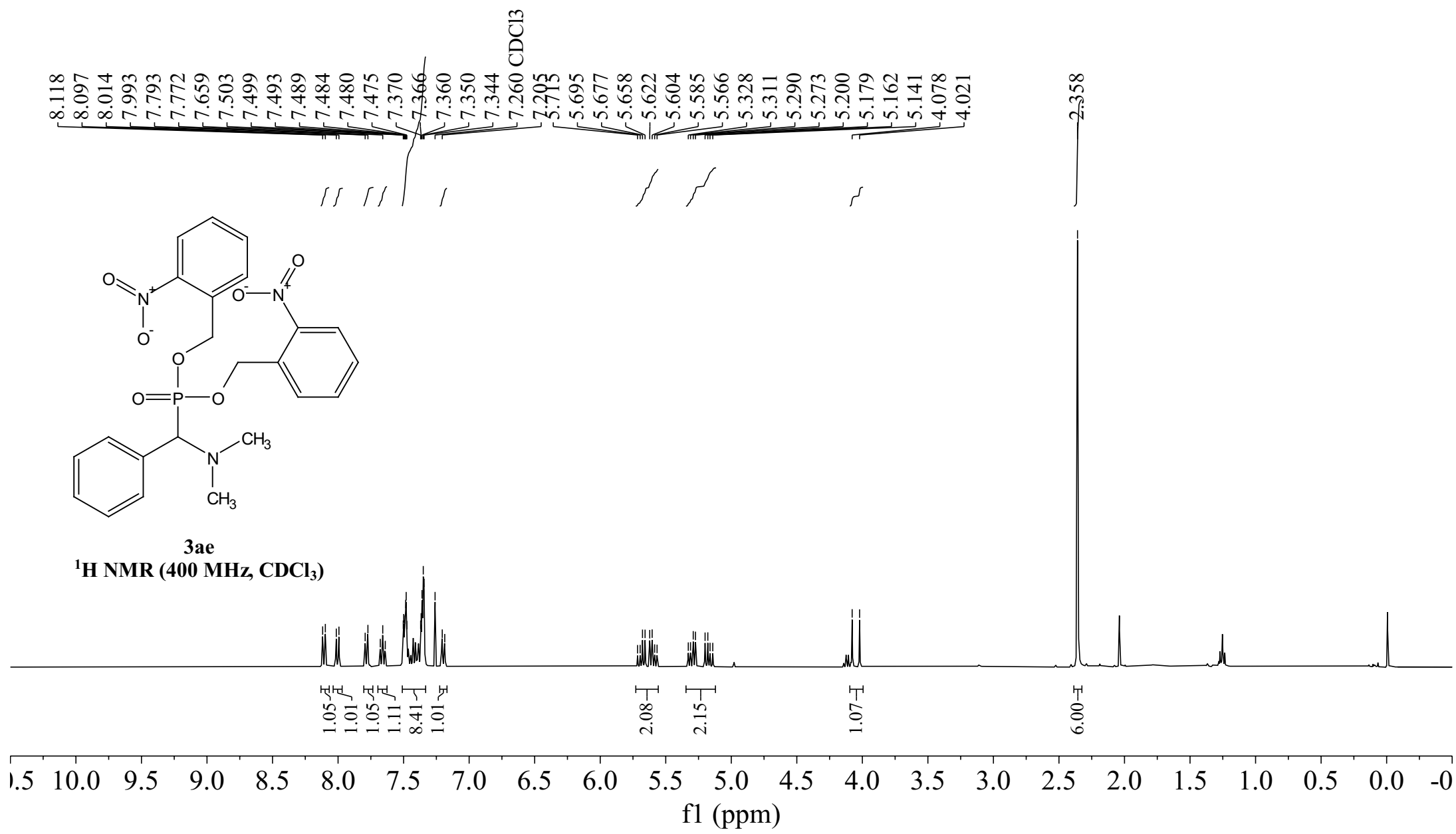


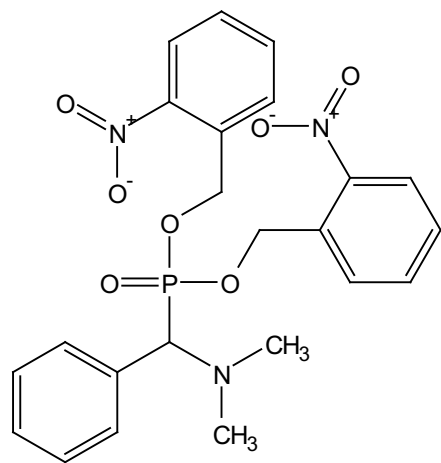
3ad

³¹P NMR (162 MHz, CDCl₃)

—23.559

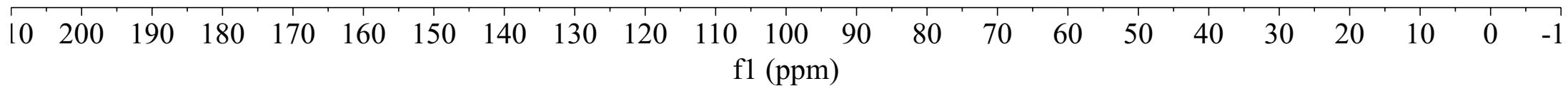
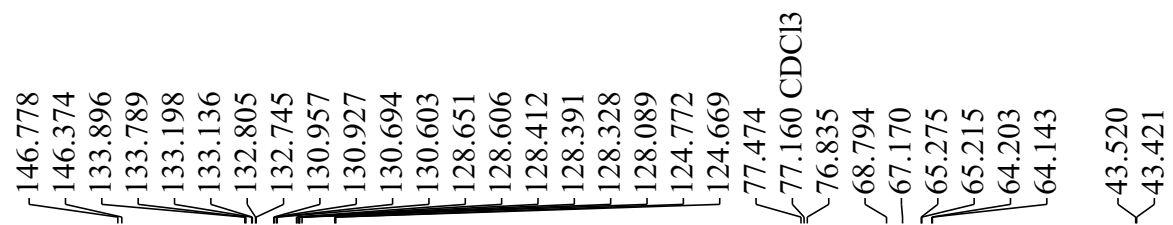


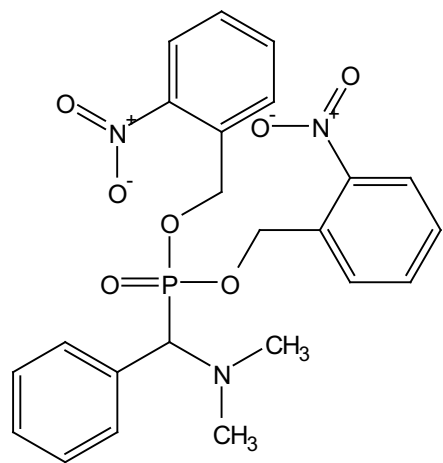




3ae

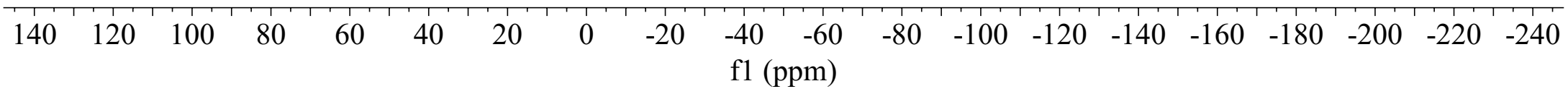
¹³C NMR (100 MHz, CDCl₃)

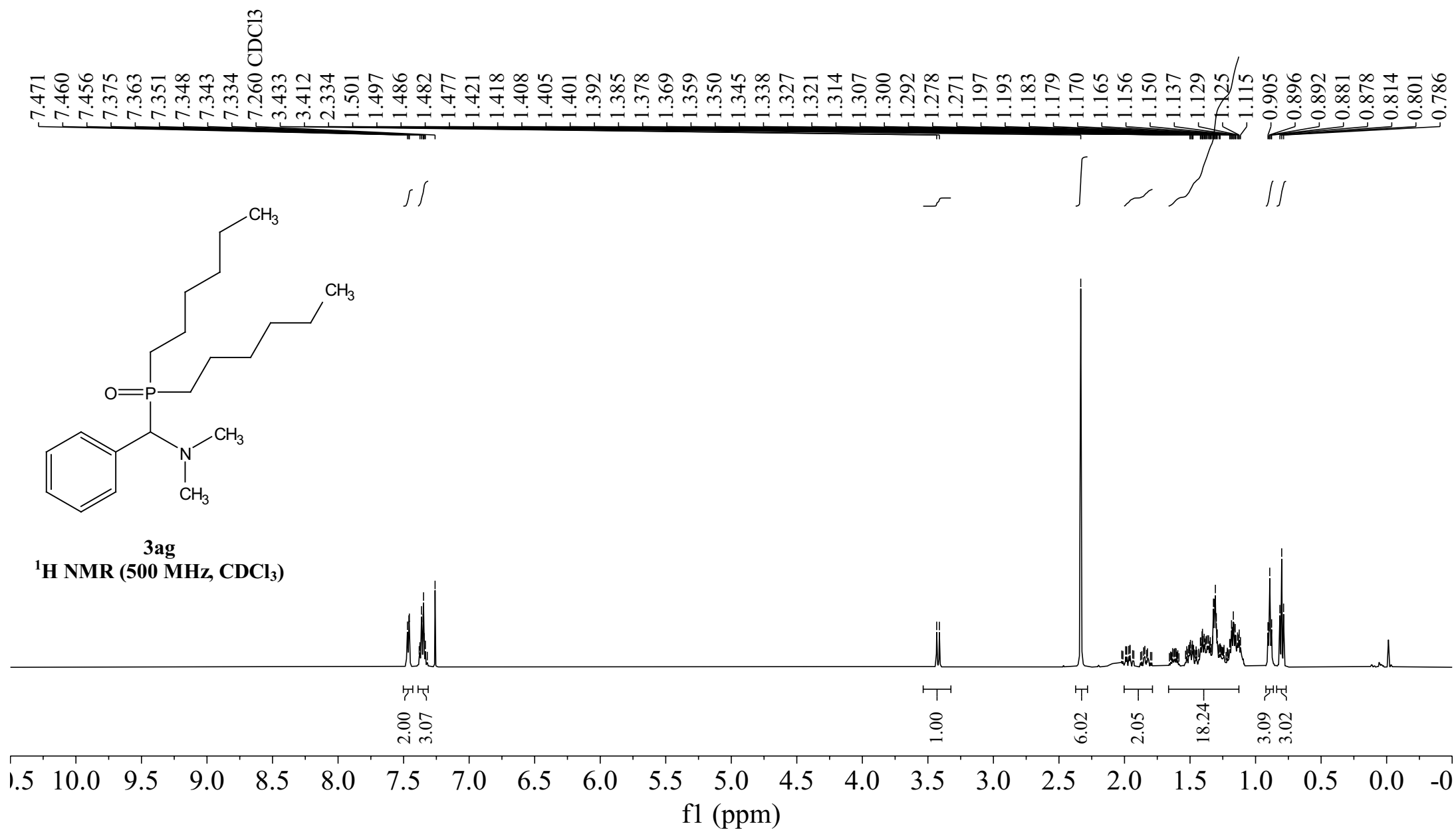


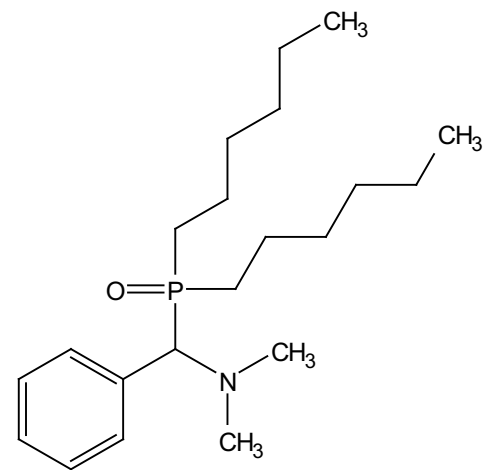


3ae
³¹P NMR (162 MHz, CDCl₃)

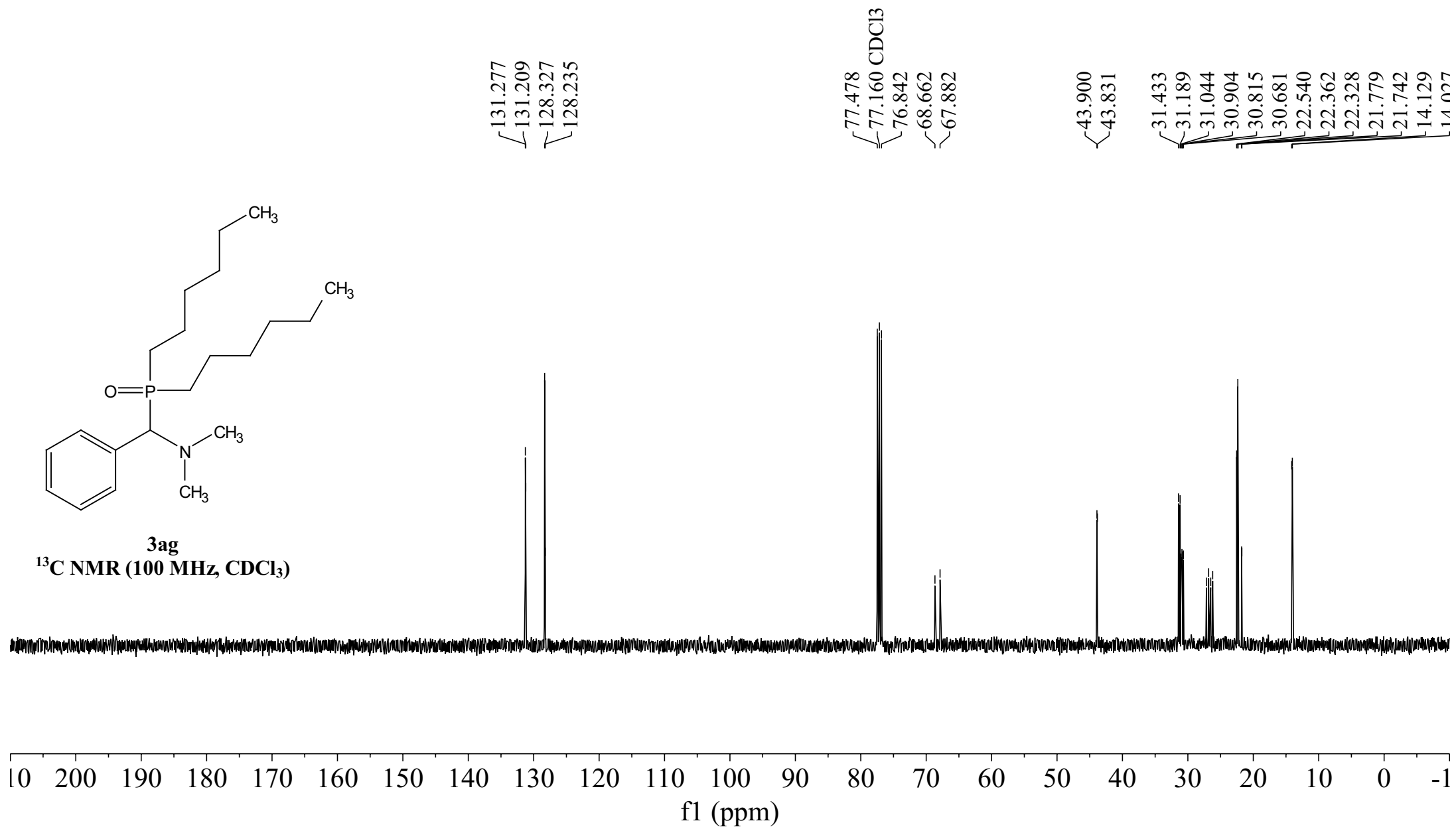
—23.492

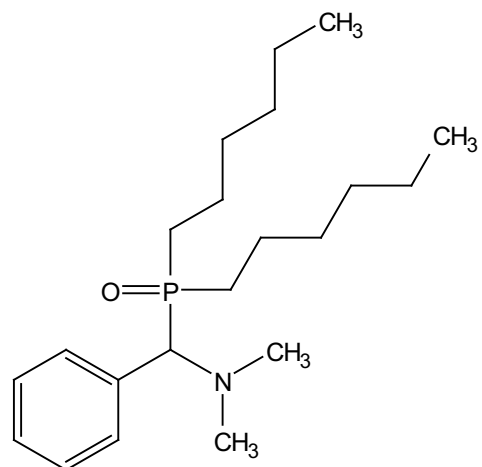






3ag
¹³C NMR (100 MHz, CDCl₃)

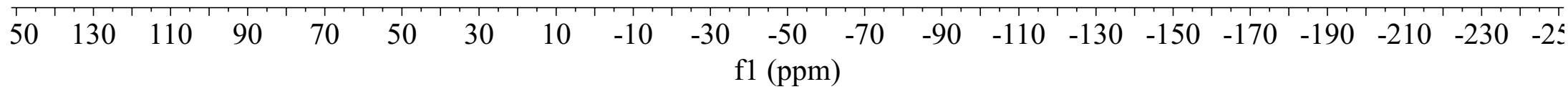


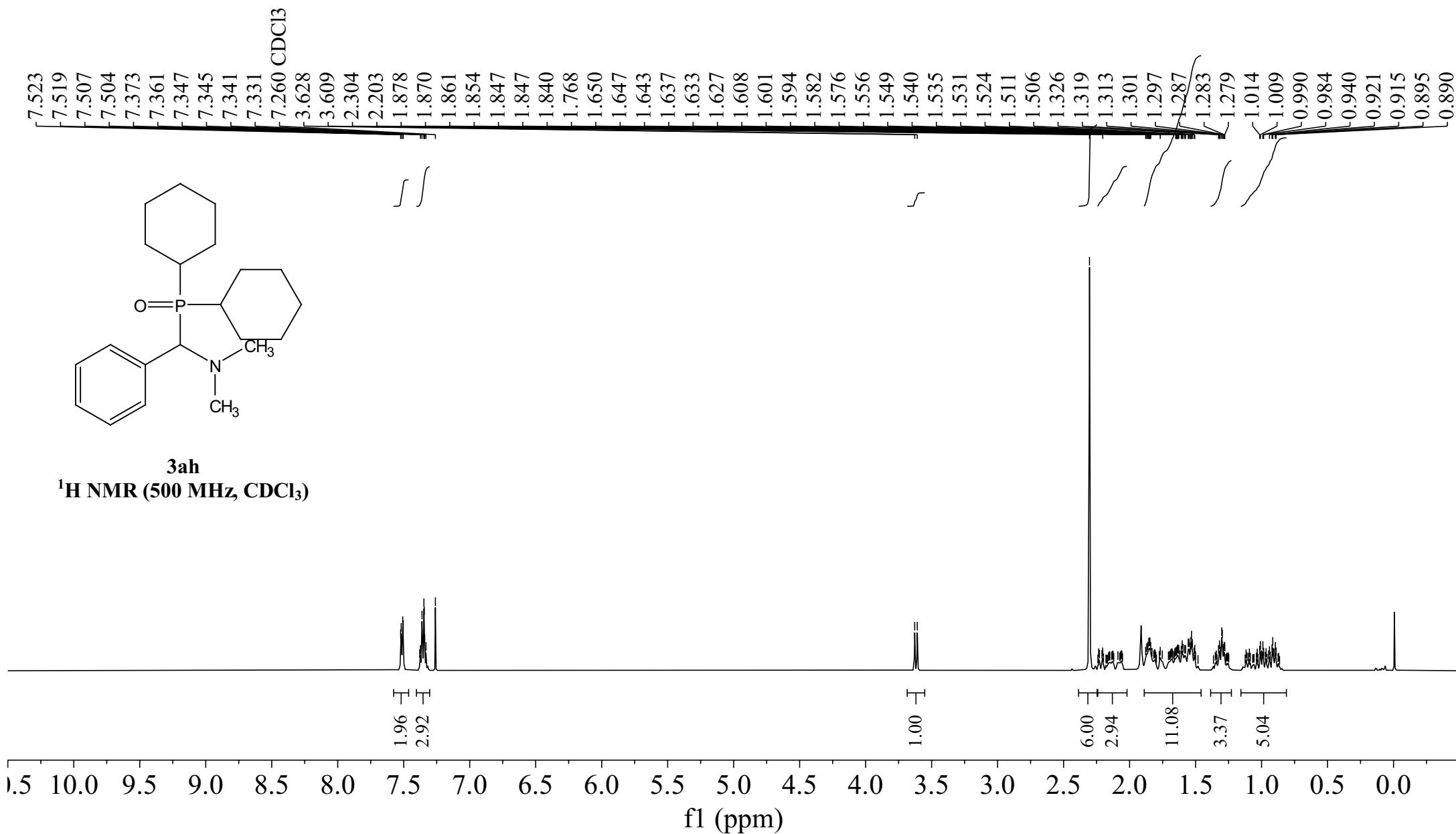


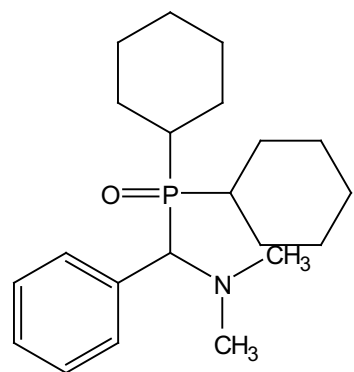
3ag

³¹P NMR (202 MHz, CDCl₃)

—50.896







3ah

¹³C NMR (126 MHz, CDCl₃)

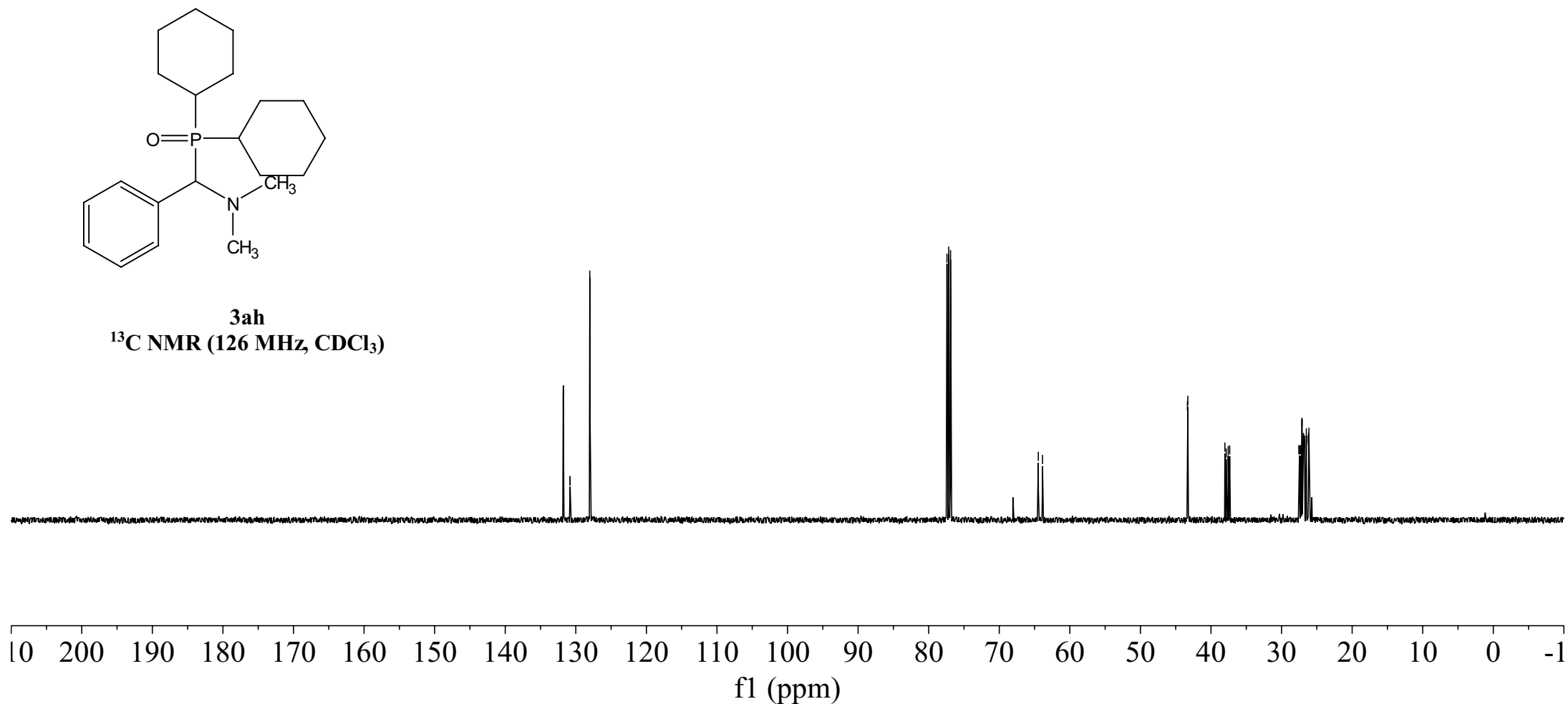
131.784
131.731
130.824
130.807
128.017
127.979

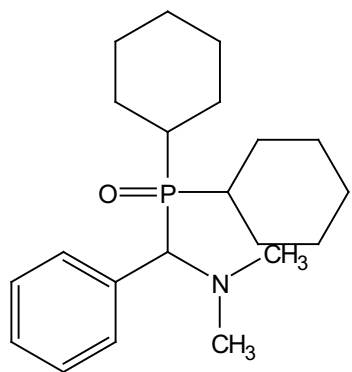
77.414
77.160 CDCl₃
76.906

64.468
63.873

43.339
43.283
38.032
37.852
37.561
37.349

27.112
26.948
26.914
26.892
26.857
26.744
26.722
26.492
26.202
26.179
26.155

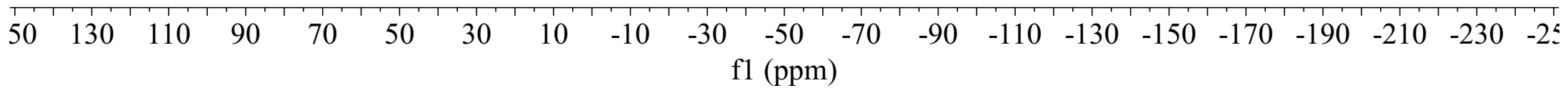


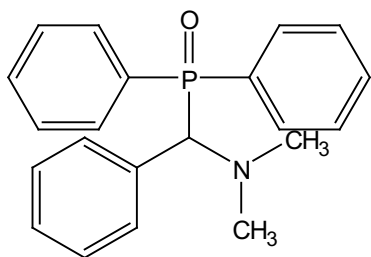


3ah

³¹P NMR (202 MHz, CDCl₃)

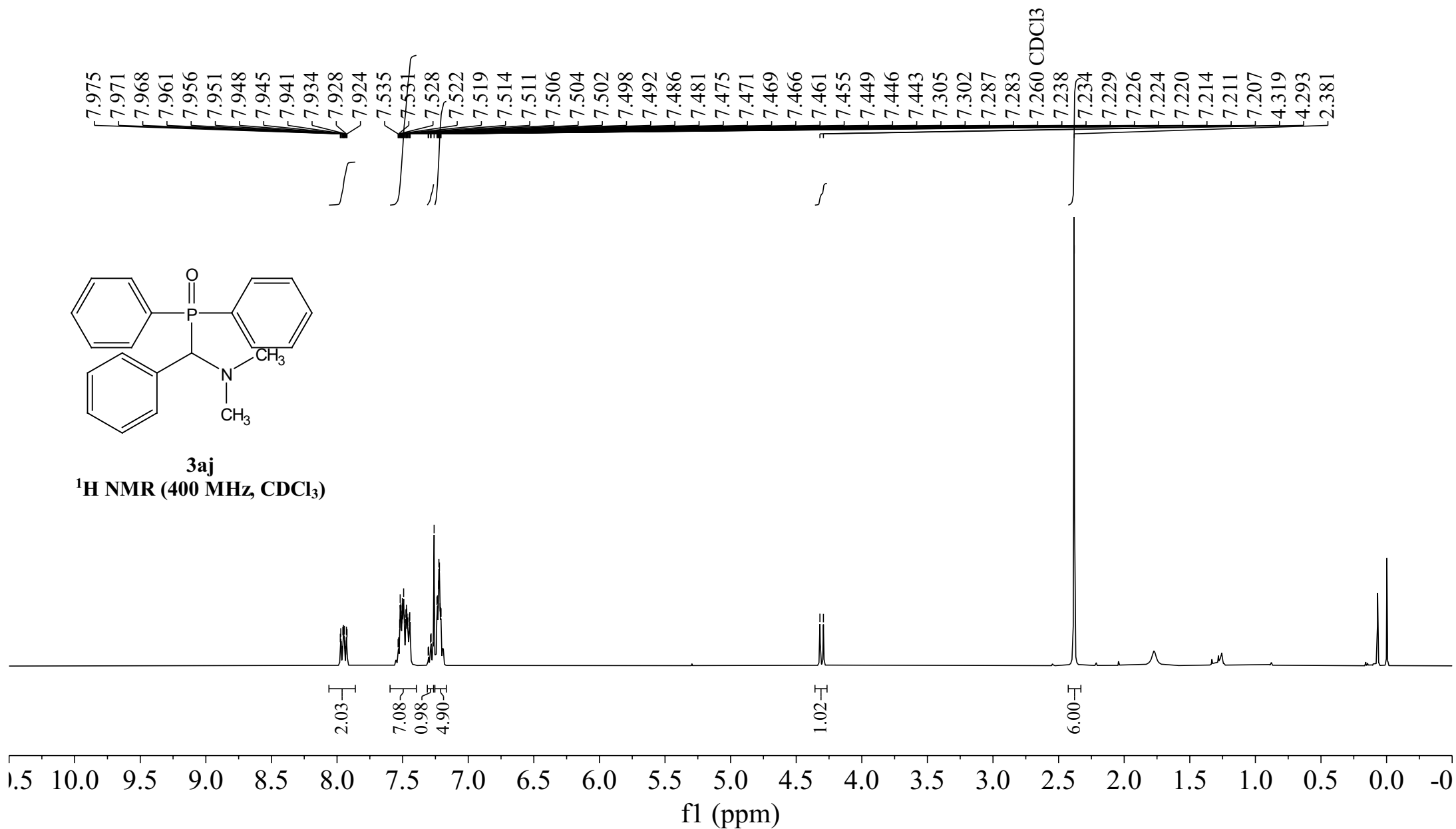
—50.881

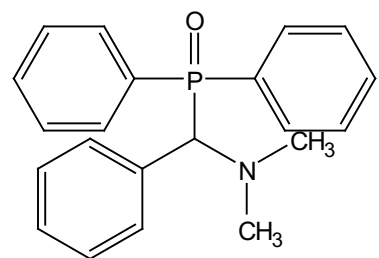




3aj

¹H NMR (400 MHz, CDCl₃)



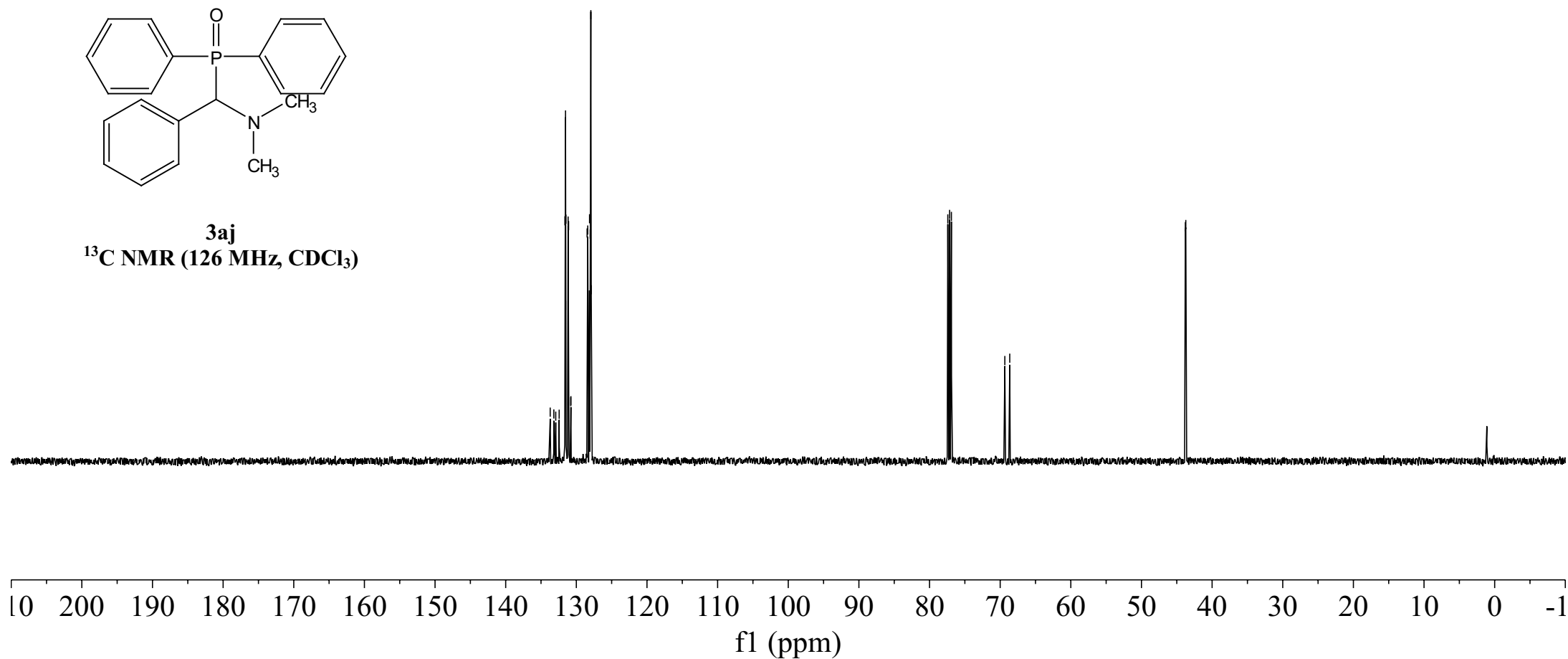


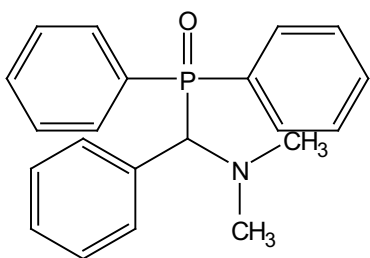
3aj
¹³C NMR (126 MHz, CDCl₃)

133.700
133.184
132.915
132.429
131.619
131.551
131.531
131.512
131.470
131.163
131.145
131.122
131.095
130.792
130.769
128.475
128.384
128.130
128.040
127.945
127.889

77.414
77.160 CDCl₃
76.906
69.341
68.646

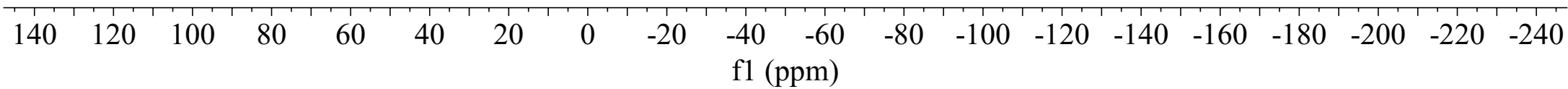
43.785
43.725

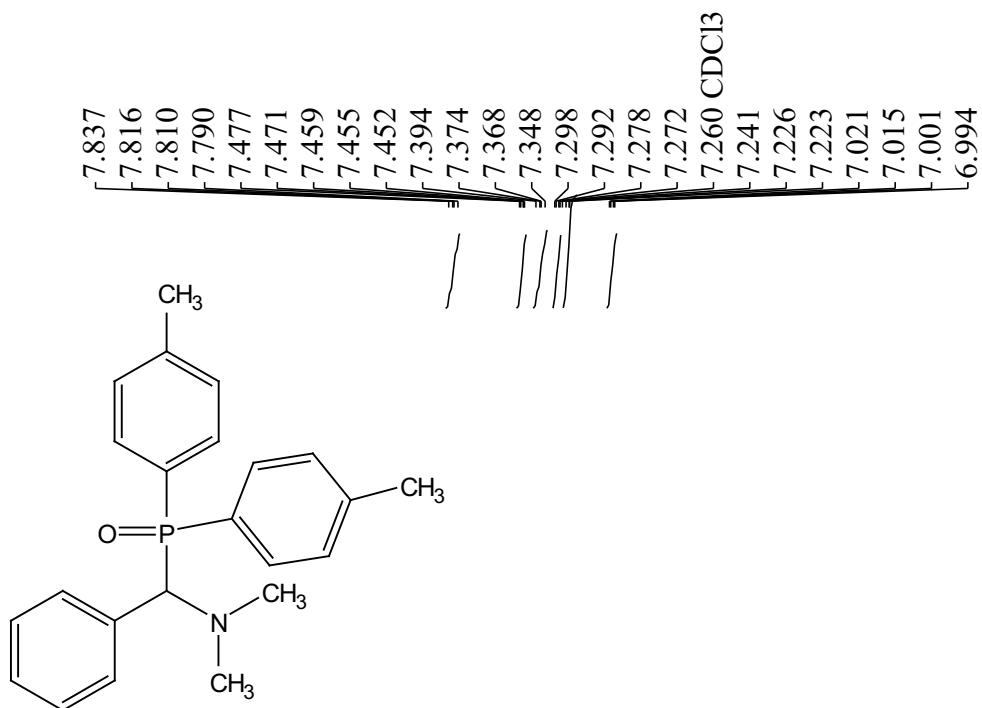




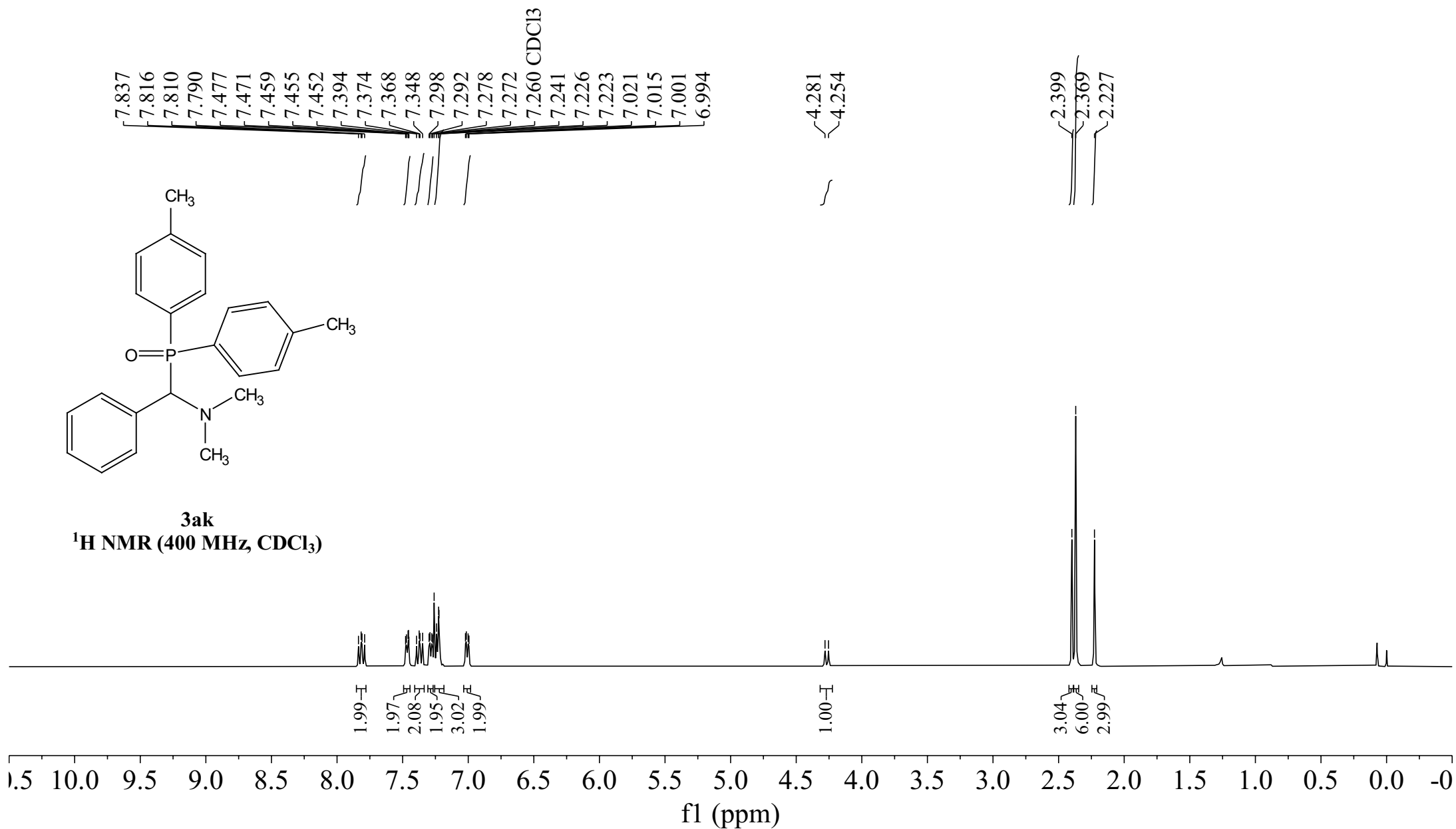
3aj
³¹P NMR (162 MHz, CDCl₃)

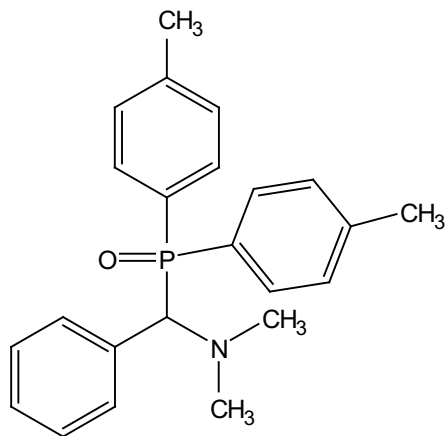
—30.761





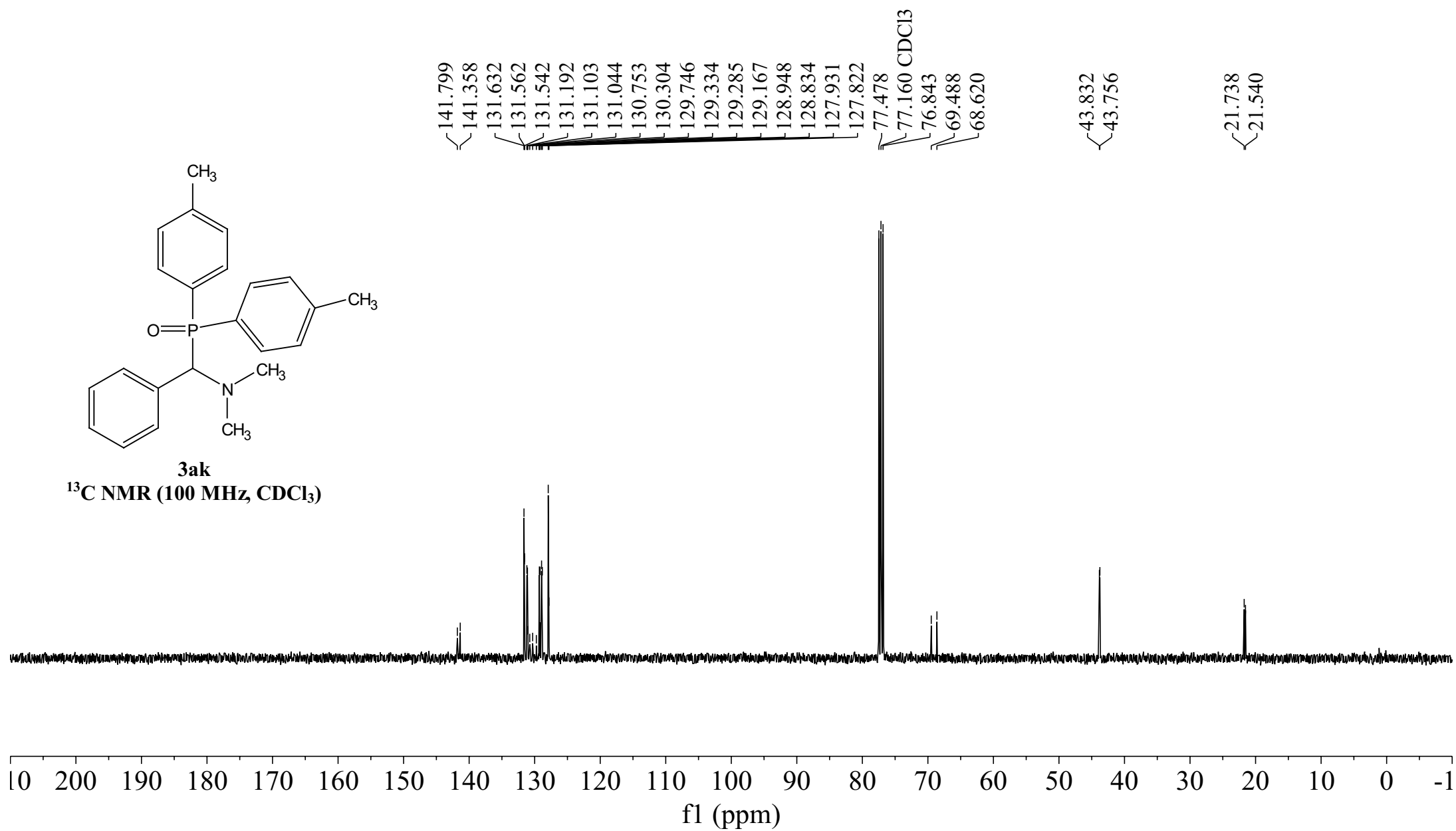
3ak
¹H NMR (400 MHz, CDCl₃)

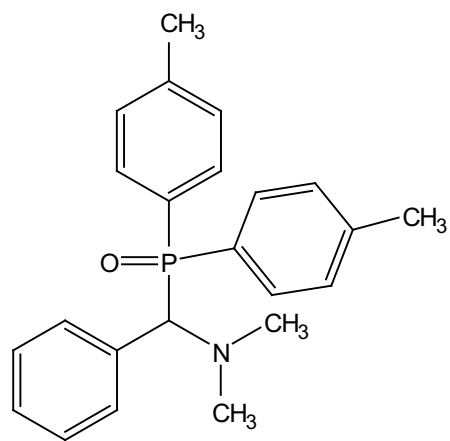




3ak

¹³C NMR (100 MHz, CDCl₃)

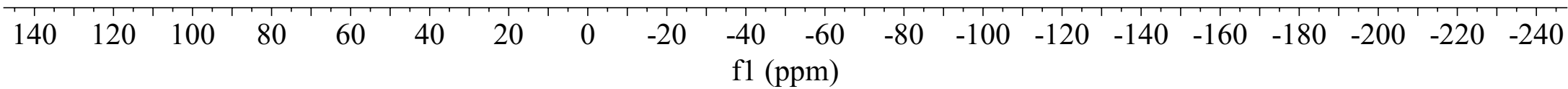


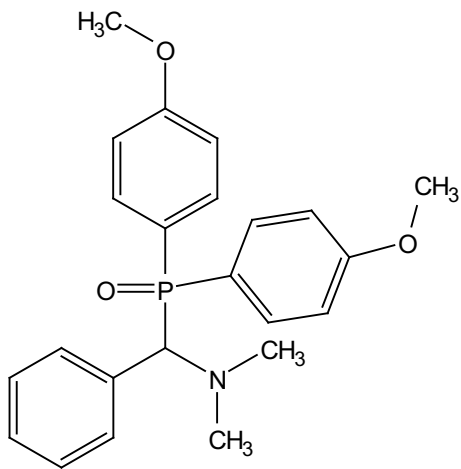


3ak

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

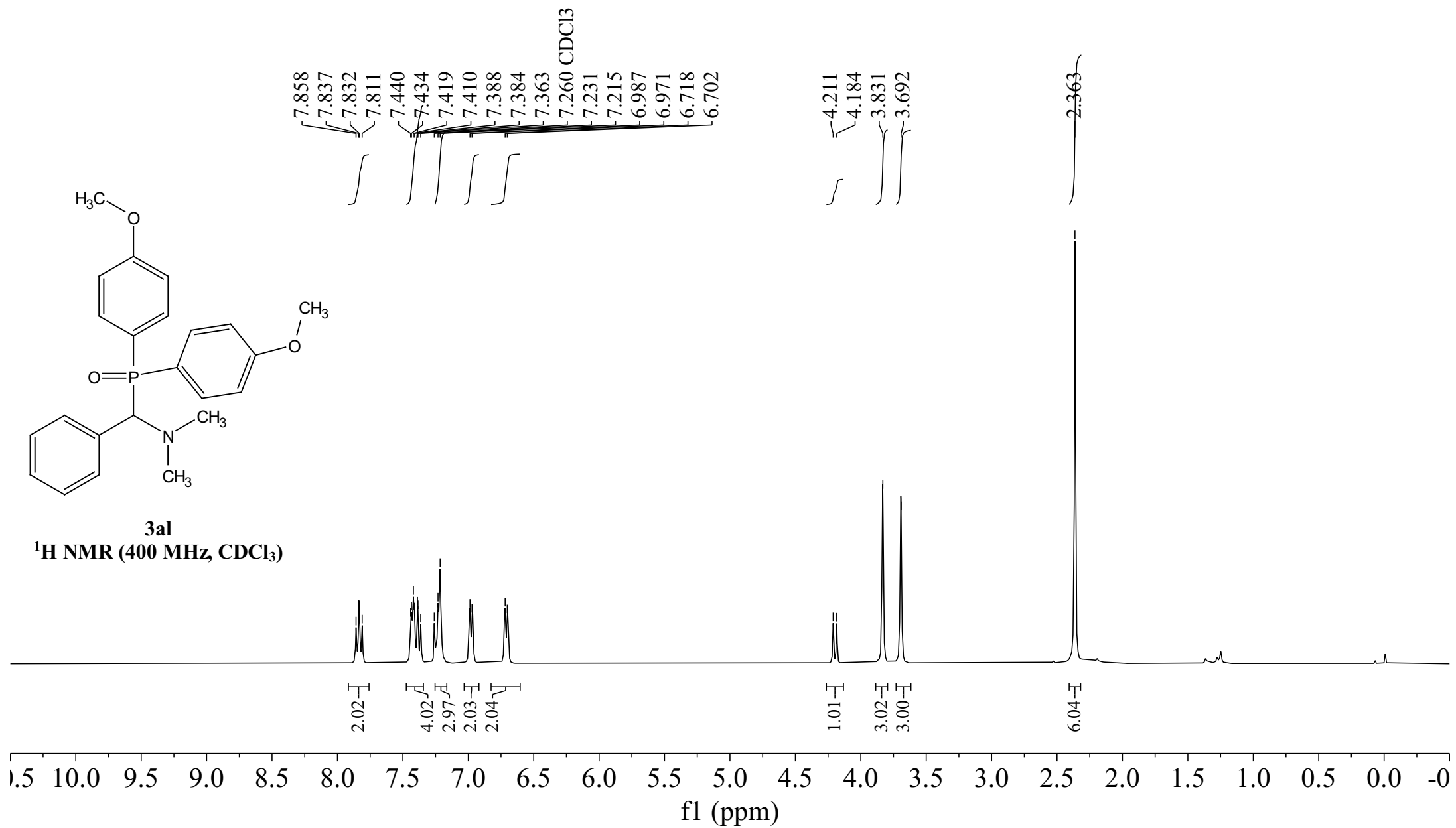
—31.134

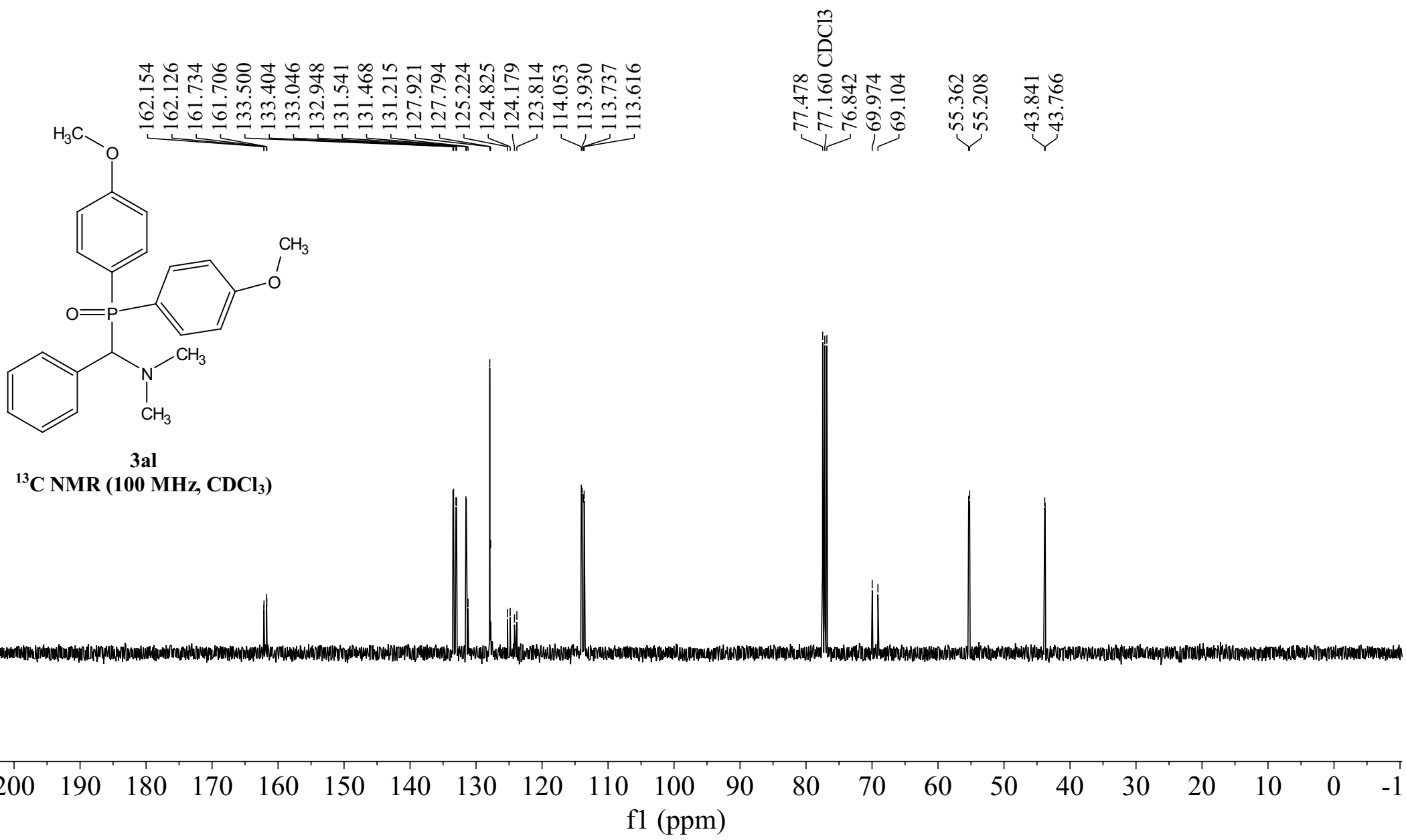


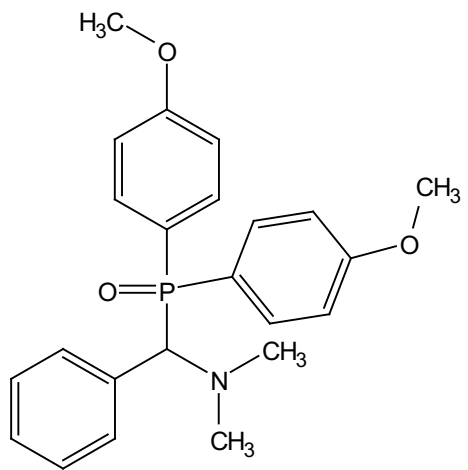


3al

¹H NMR (400 MHz, CDCl₃)



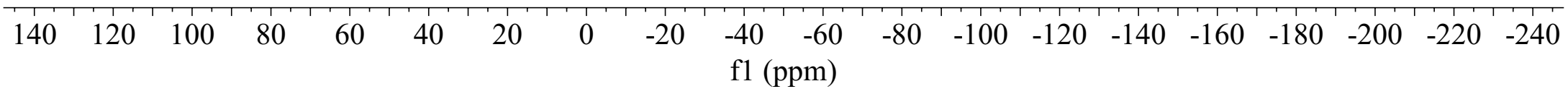


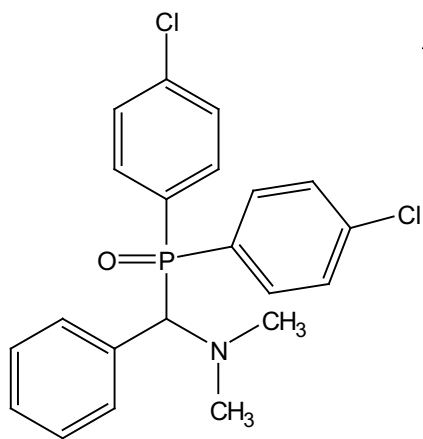


3al

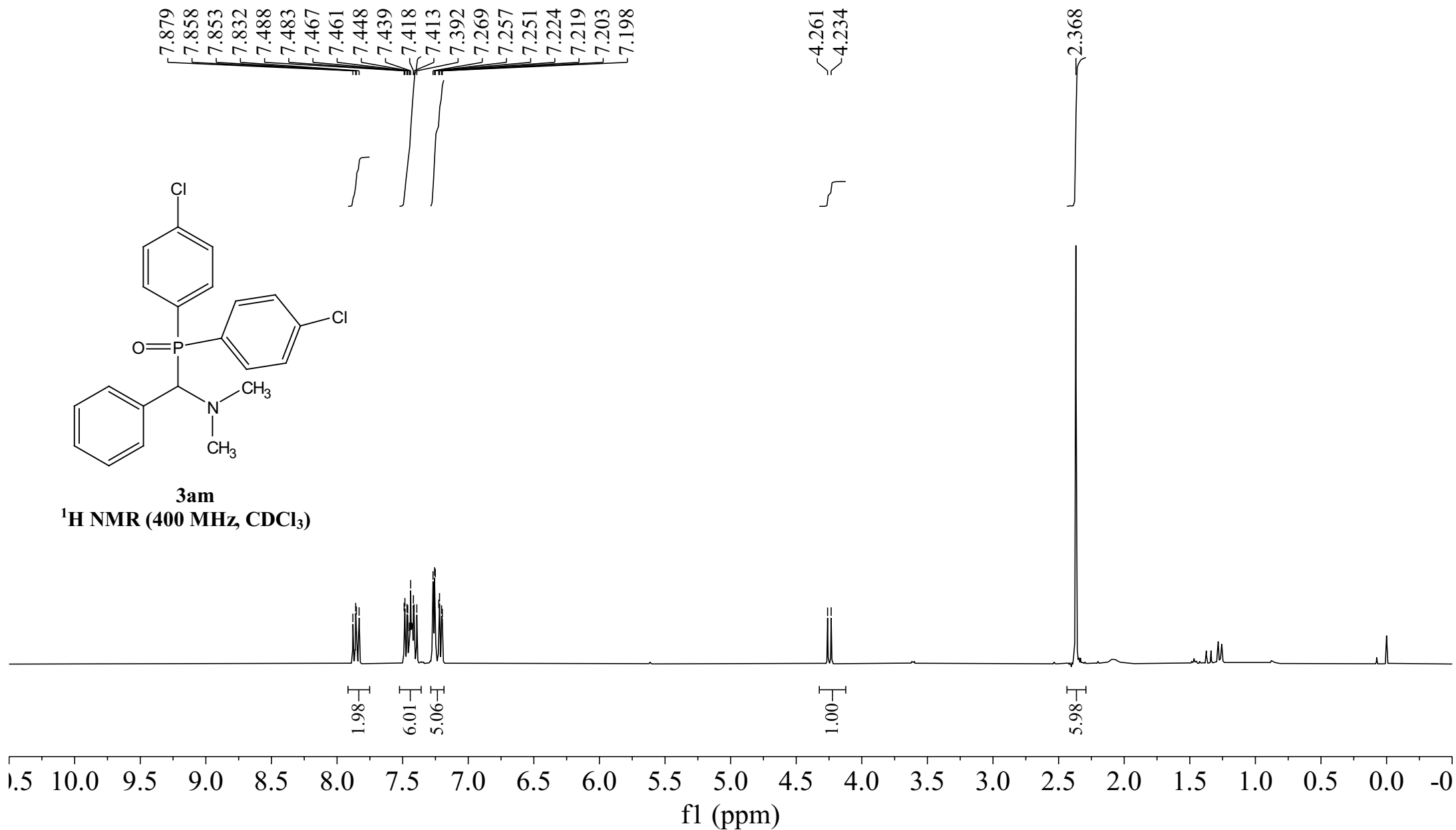
³¹P NMR (162 MHz, CDCl₃)

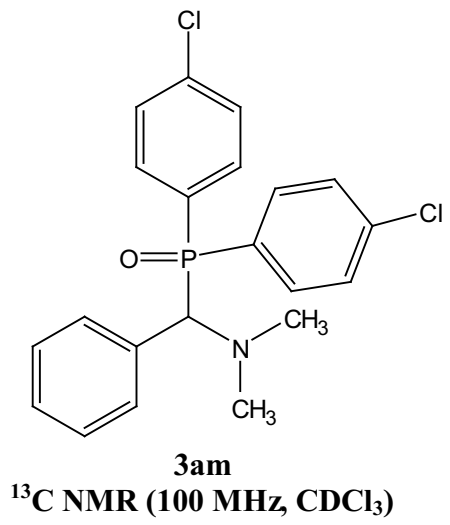
—30.991





3am
¹H NMR (400 MHz, CDCl₃)

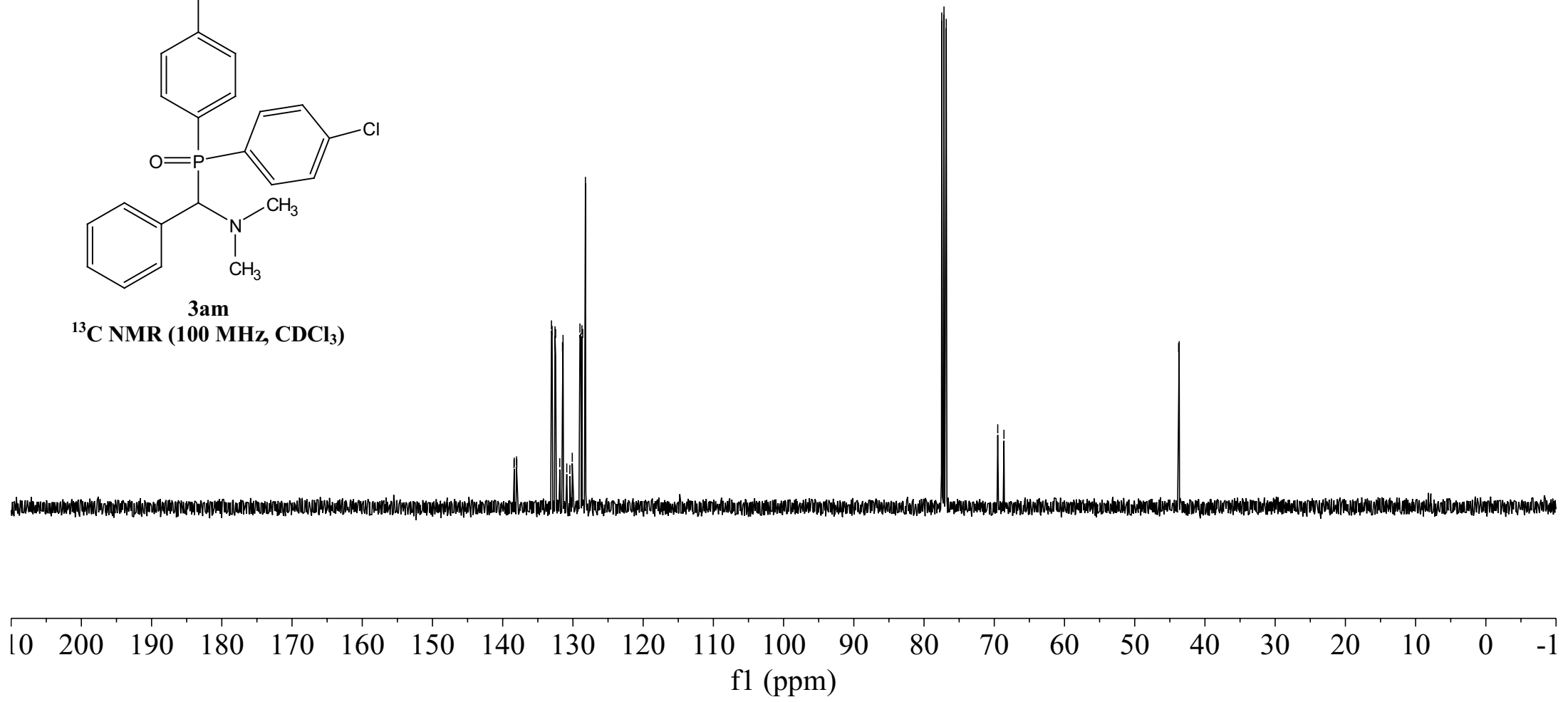


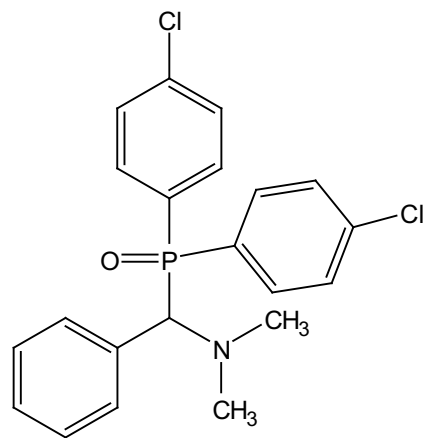


138.389
 138.355
 138.029
 137.995
 133.058
 132.966
 132.555
 132.463
 131.877
 131.485
 131.408
 130.877
 130.435
 130.094
 129.001
 128.881
 128.724
 128.607
 128.298
 128.221

77.478
 77.160 CDCl₃
 76.842
 69.506
 68.621

43.748
 43.671

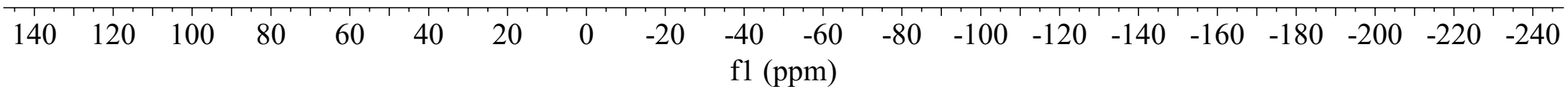


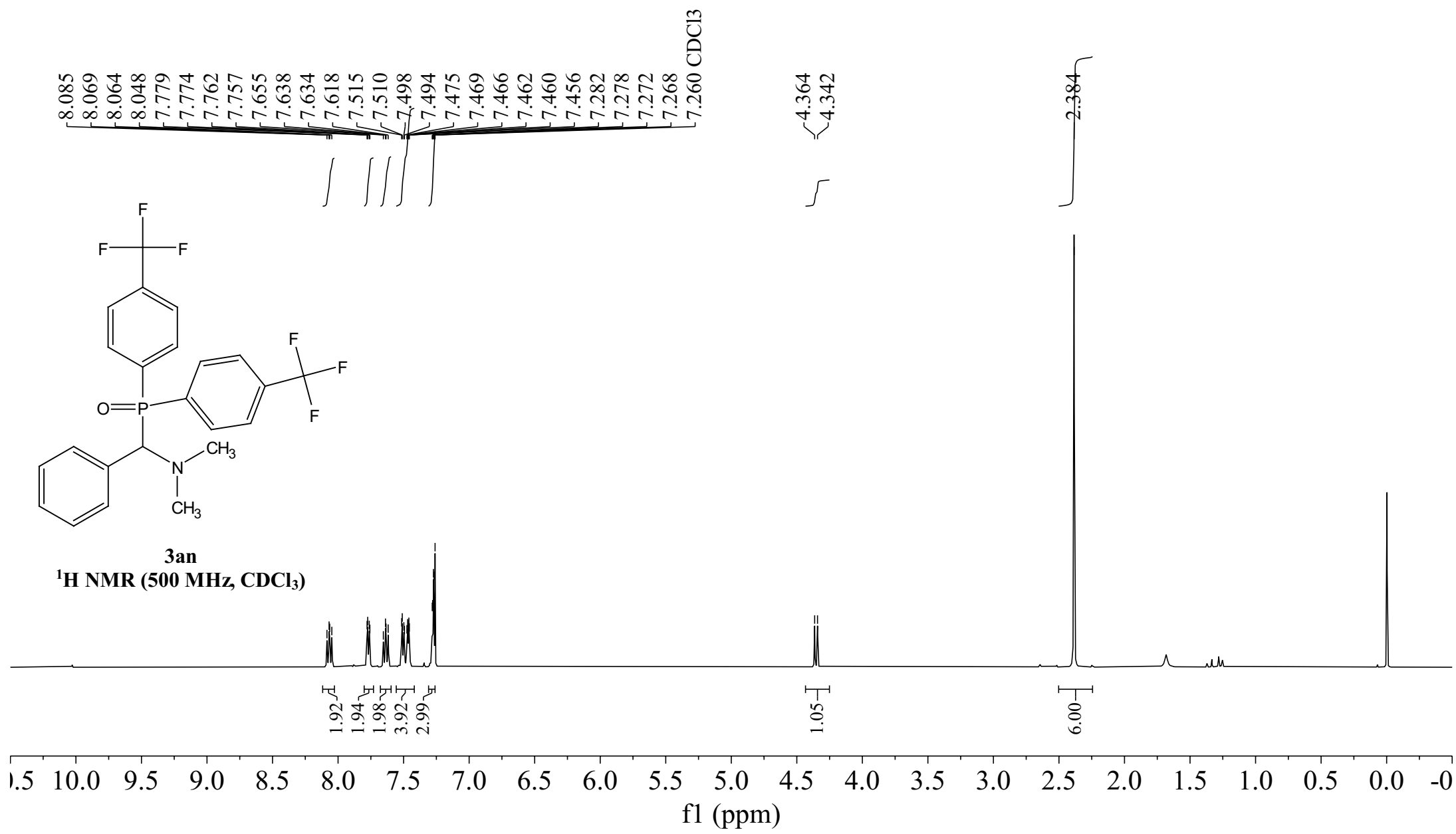


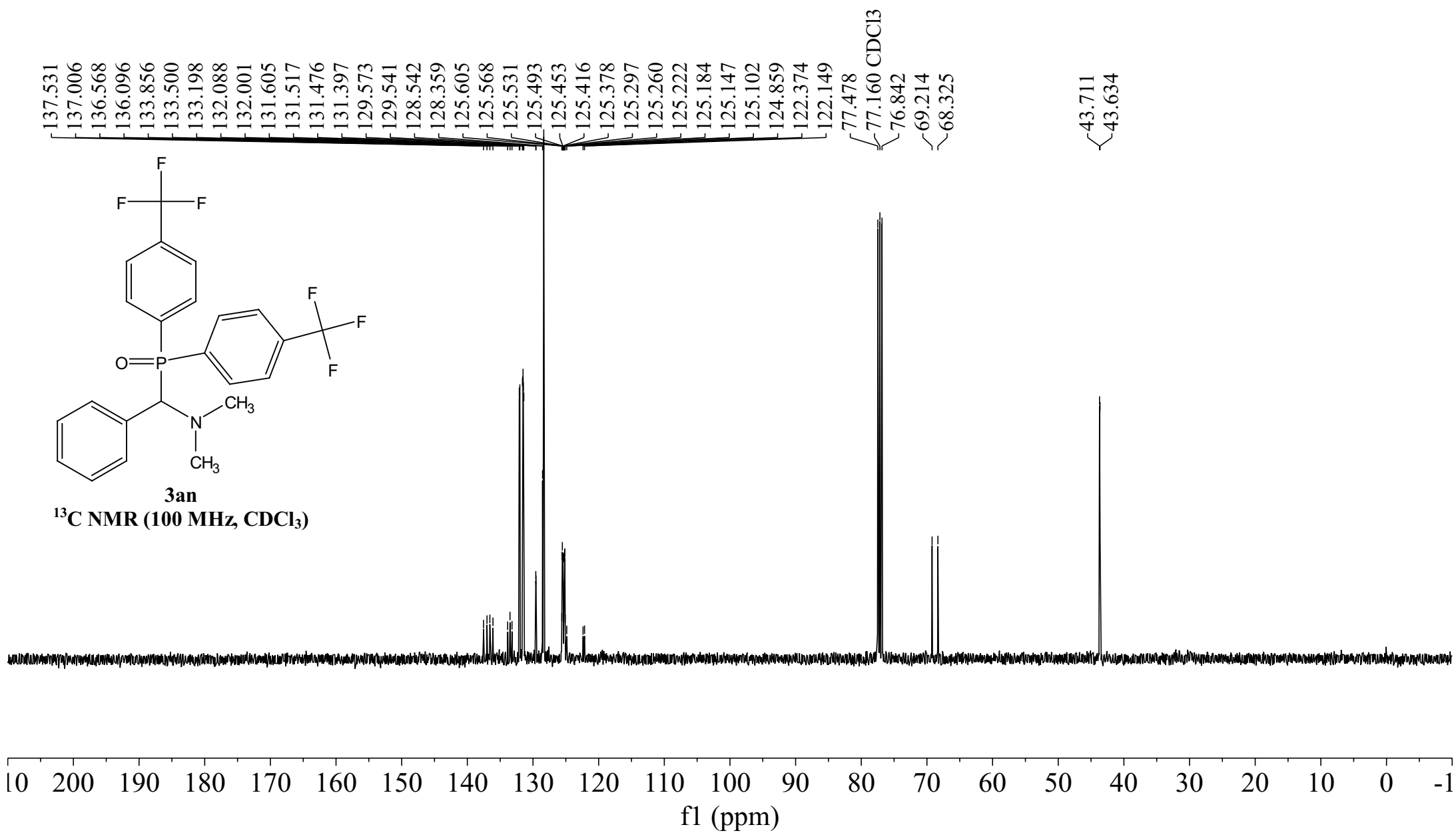
3am

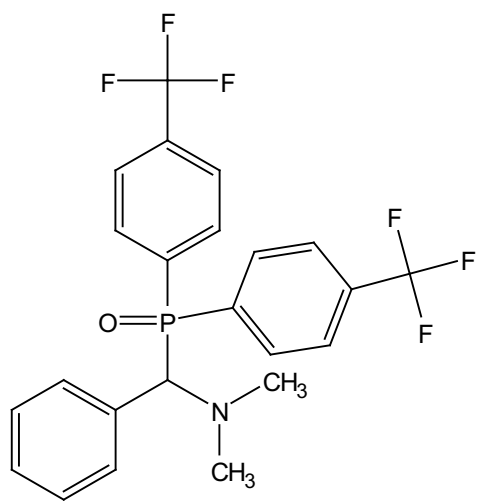
³¹P NMR (162 MHz, CDCl₃)

—29.821



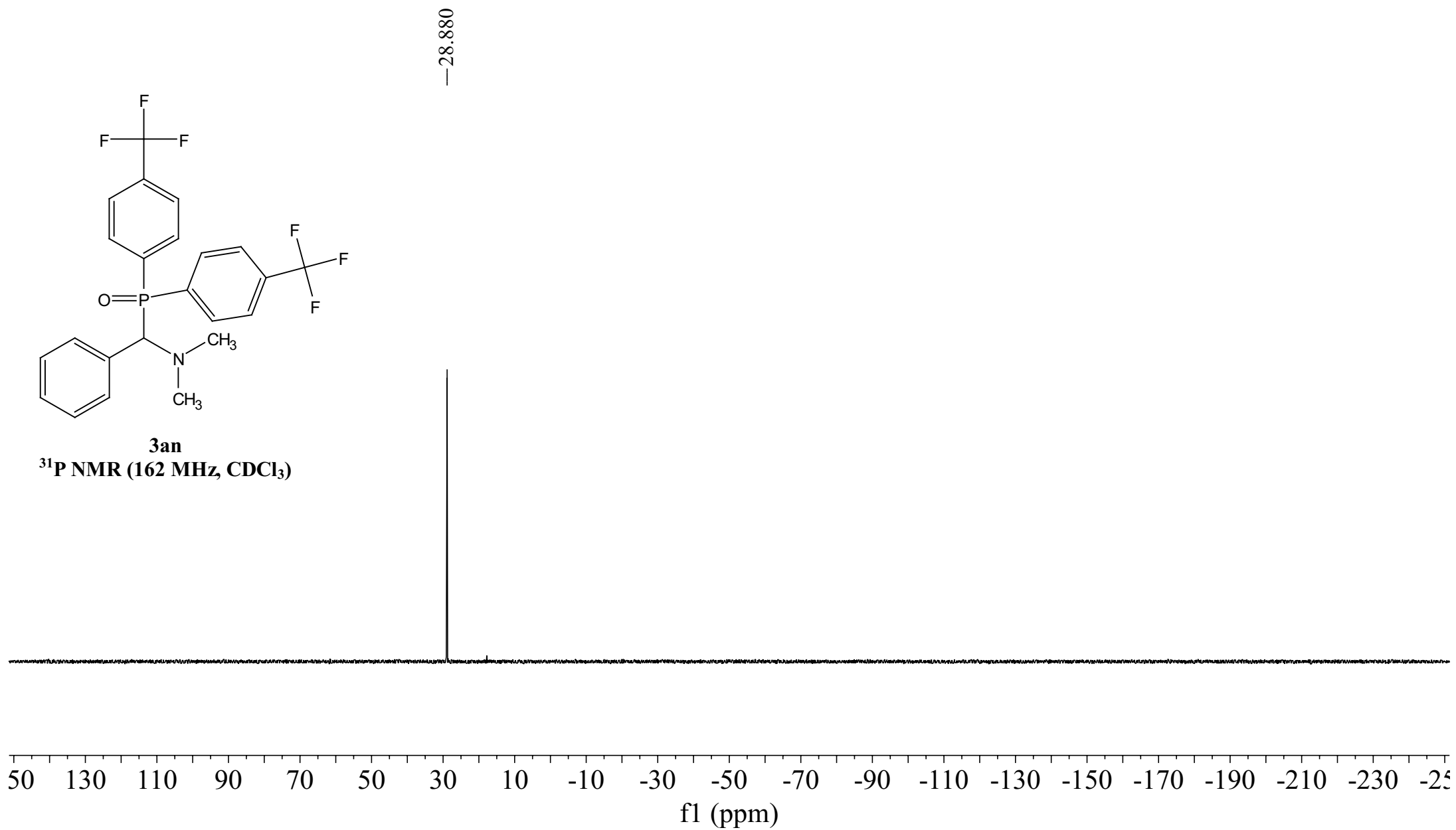


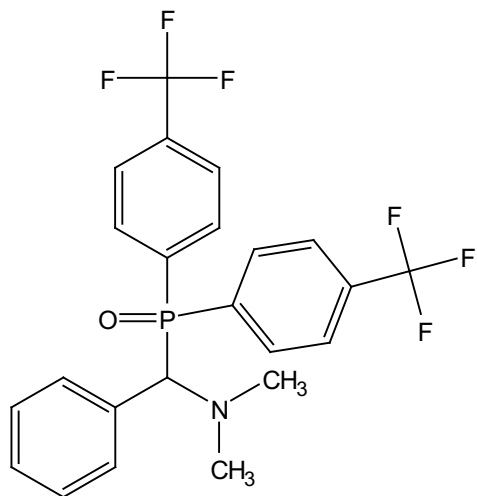




3an

³¹P NMR (162 MHz, CDCl₃)





3an

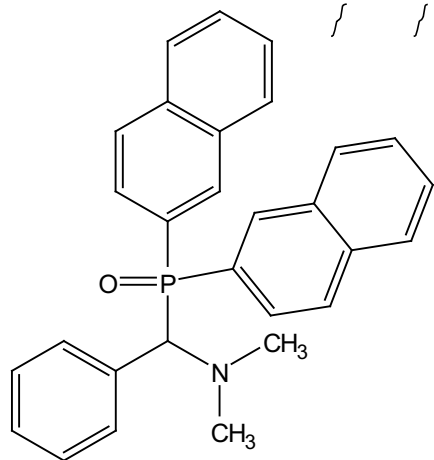
^{19}F NMR (376 MHz, CDCl_3)

-63.163
-63.293



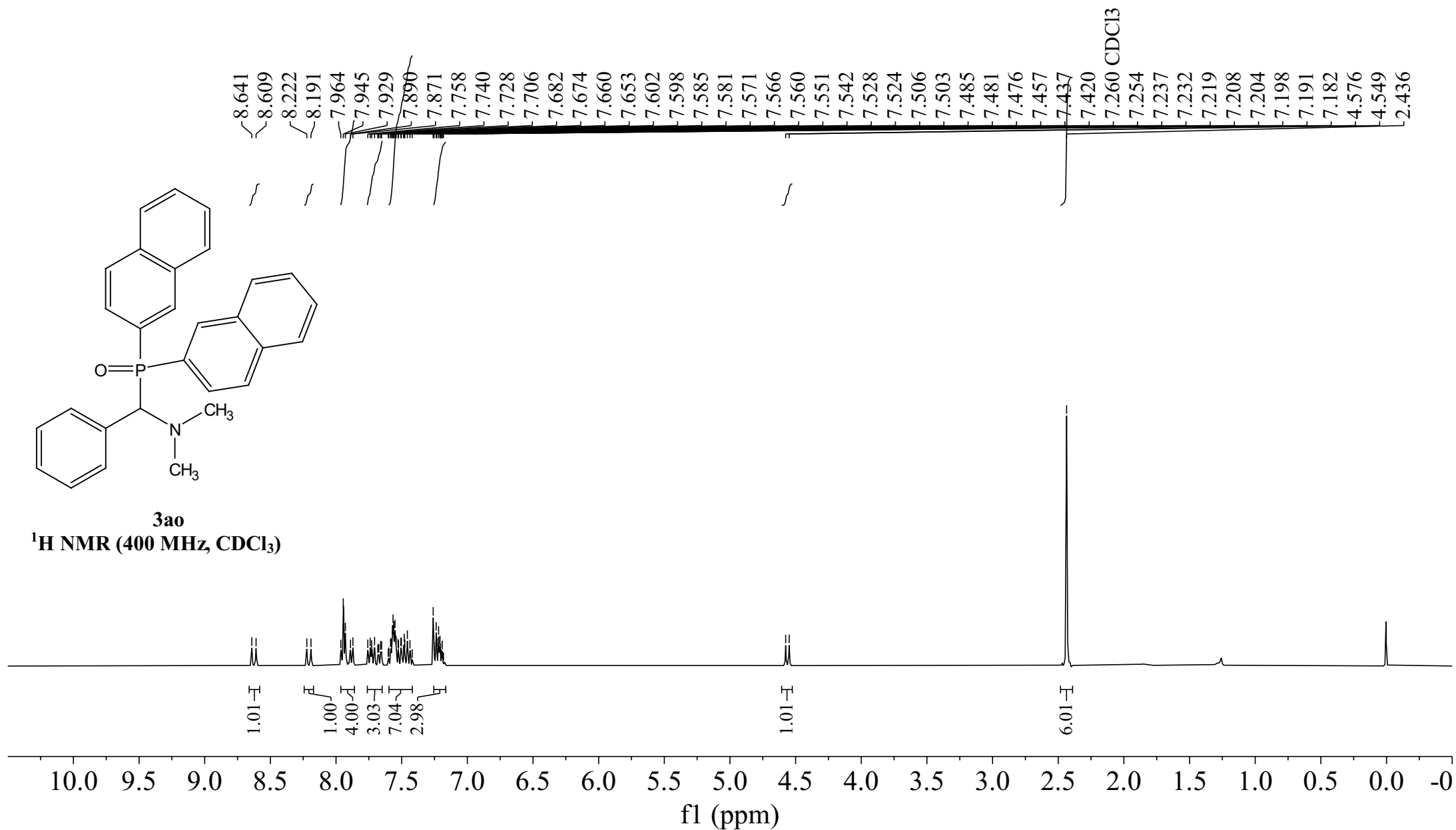
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

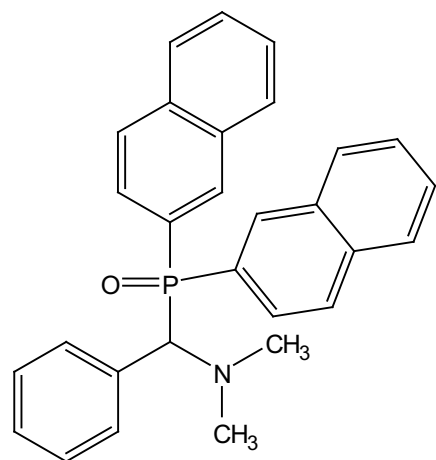
f1 (ppm)



3ao

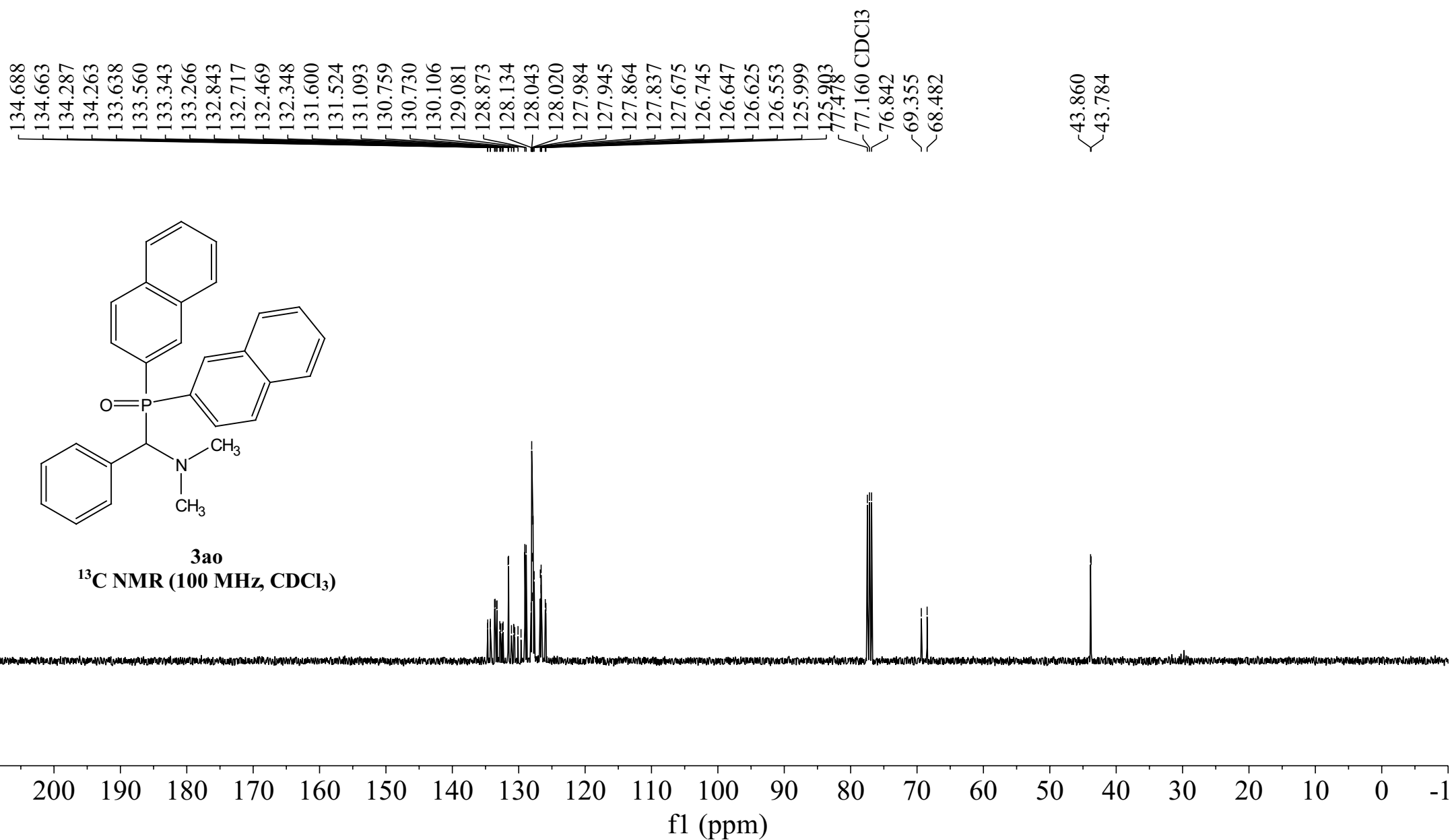
¹H NMR (400 MHz, CDCl₃)

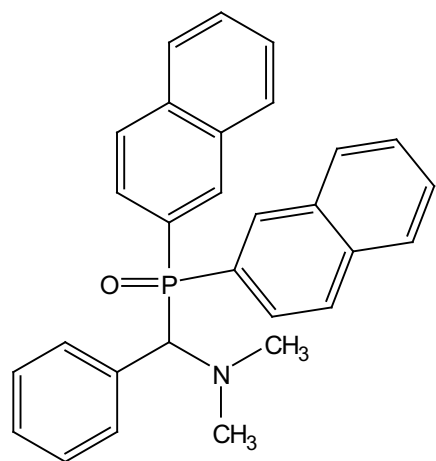




3ao

¹³C NMR (100 MHz, CDCl₃)

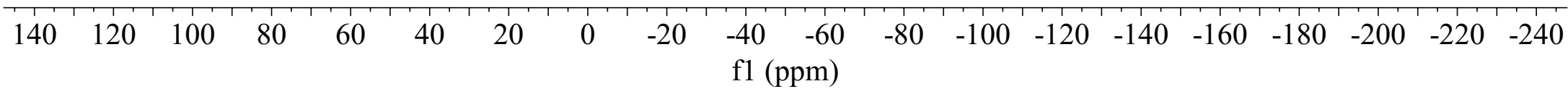


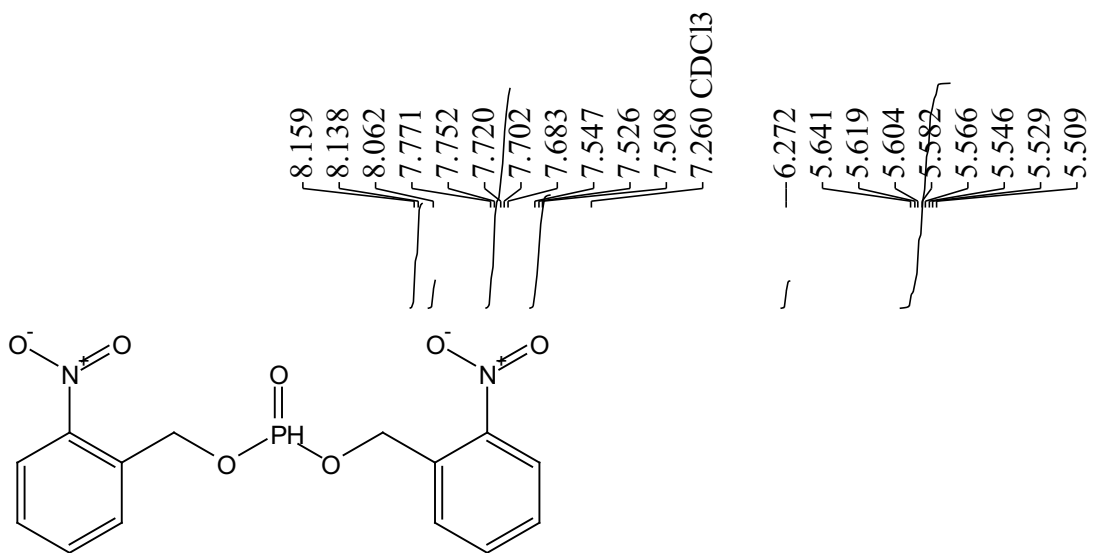


3ao

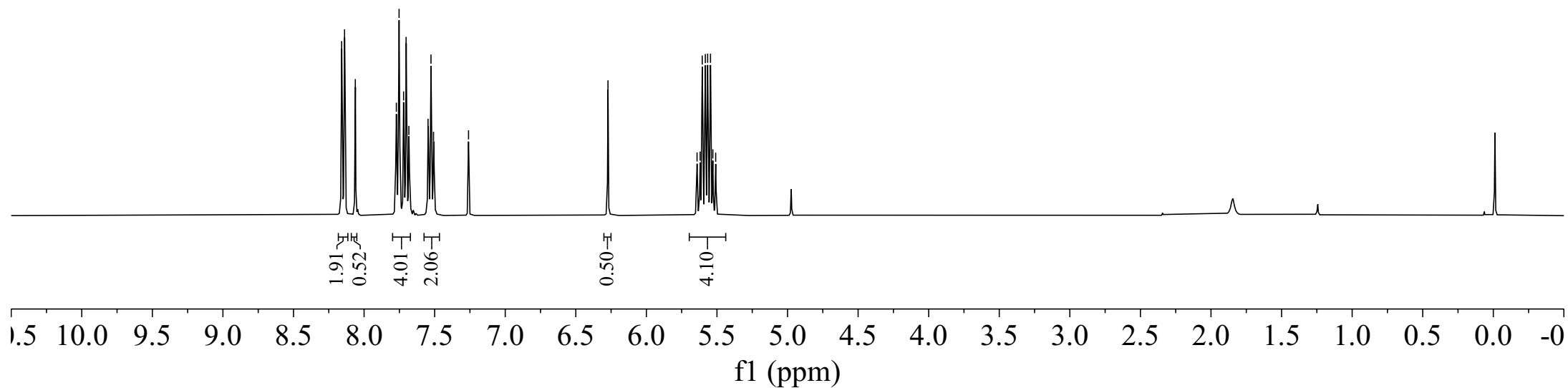
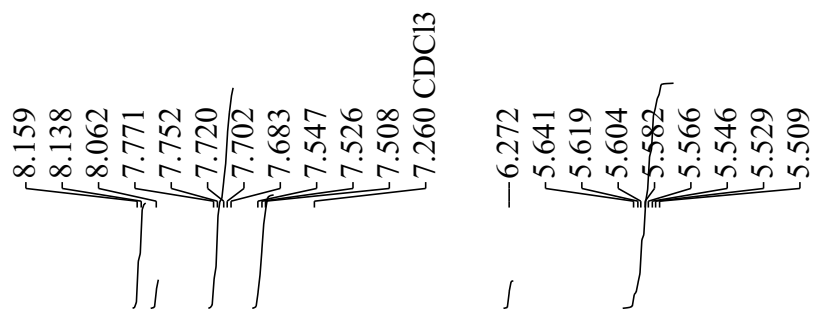
³¹P NMR (162 MHz, CDCl₃)

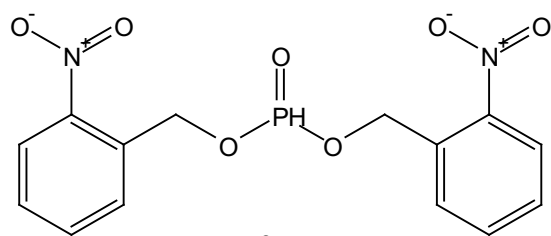
—31.172





2e
¹H NMR (400 MHz, CDCl₃)



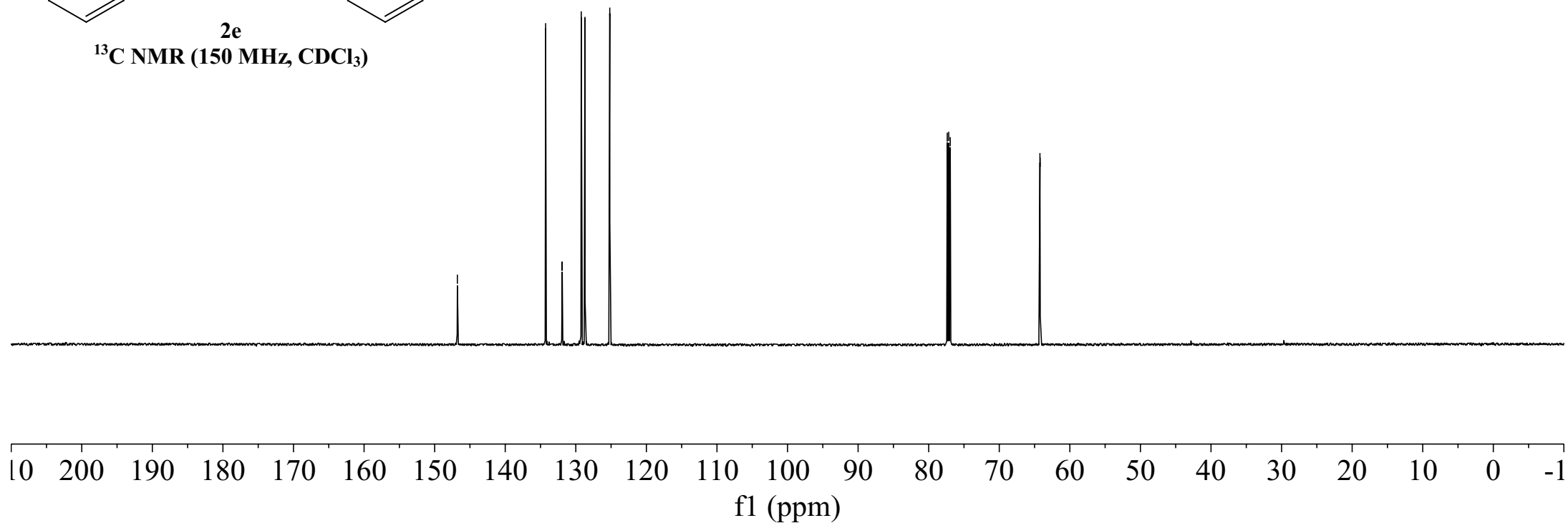


2e

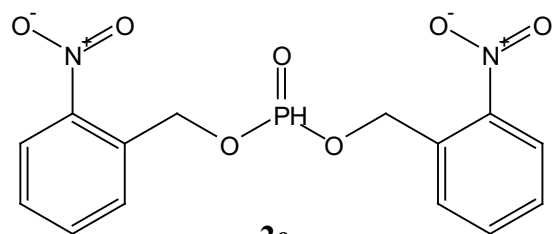
¹³C NMR (150 MHz, CDCl₃)

146.780
134.277
131.975
131.924
129.230
128.702
125.187

77.371
77.160 CDCl₃
76.946
64.239
64.210

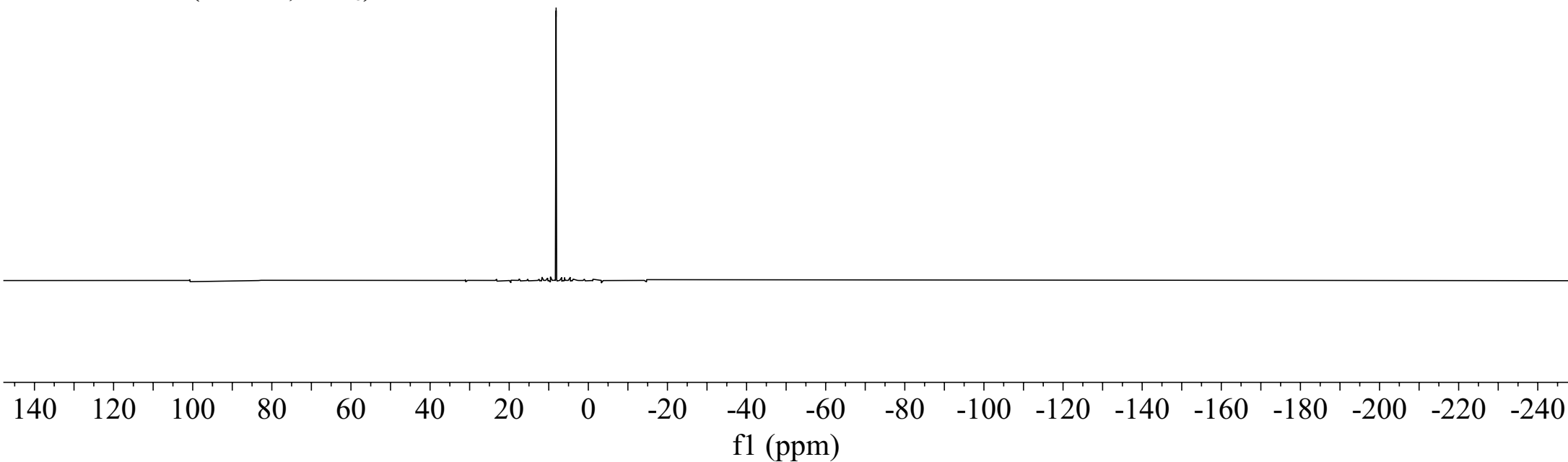


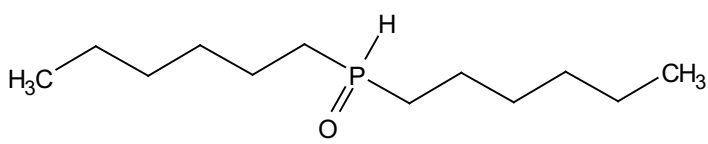
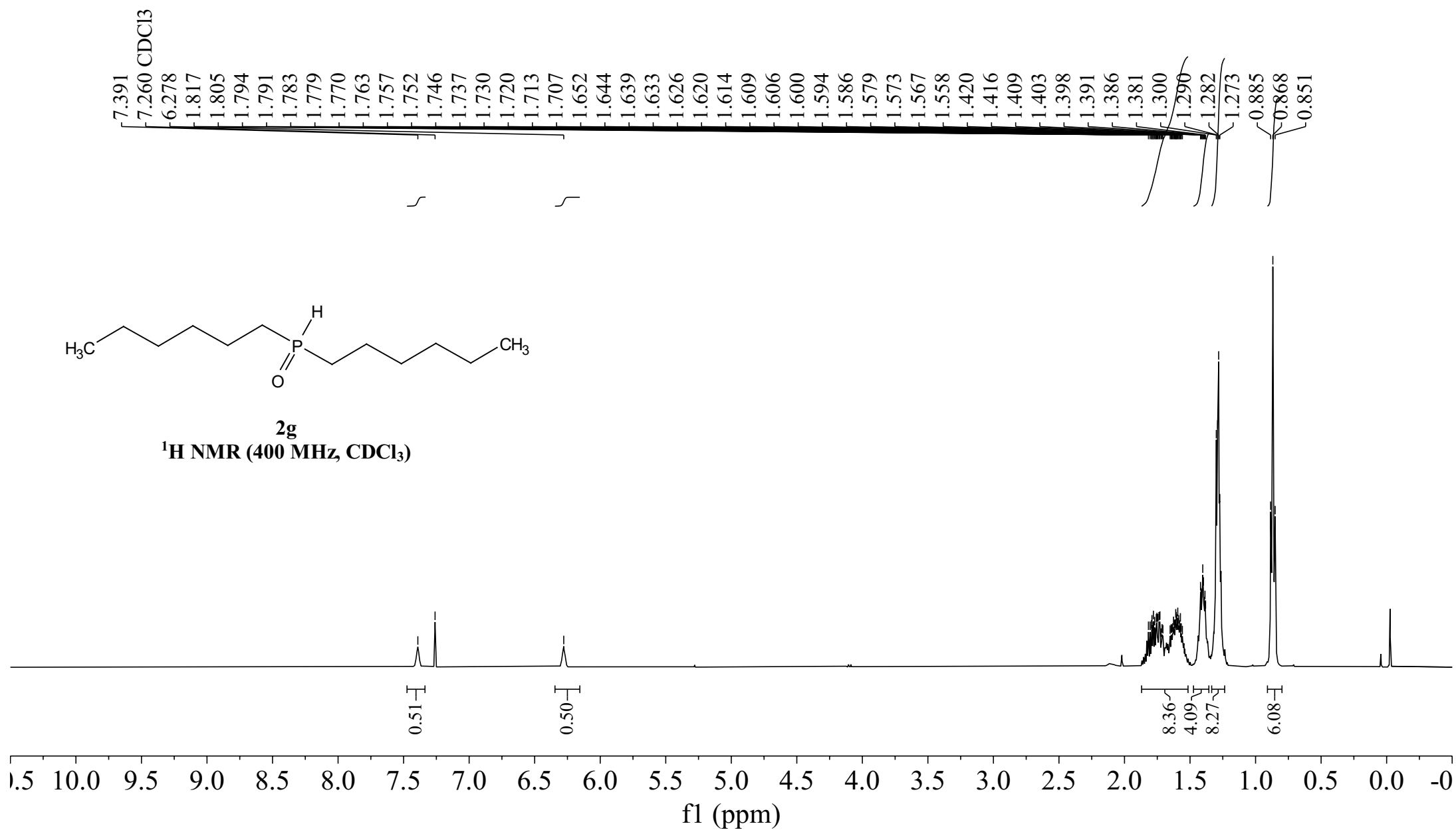
—8.141



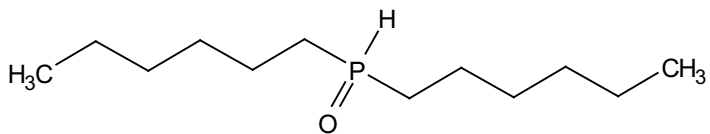
2e

³¹P NMR (162 MHz, CDCl₃)

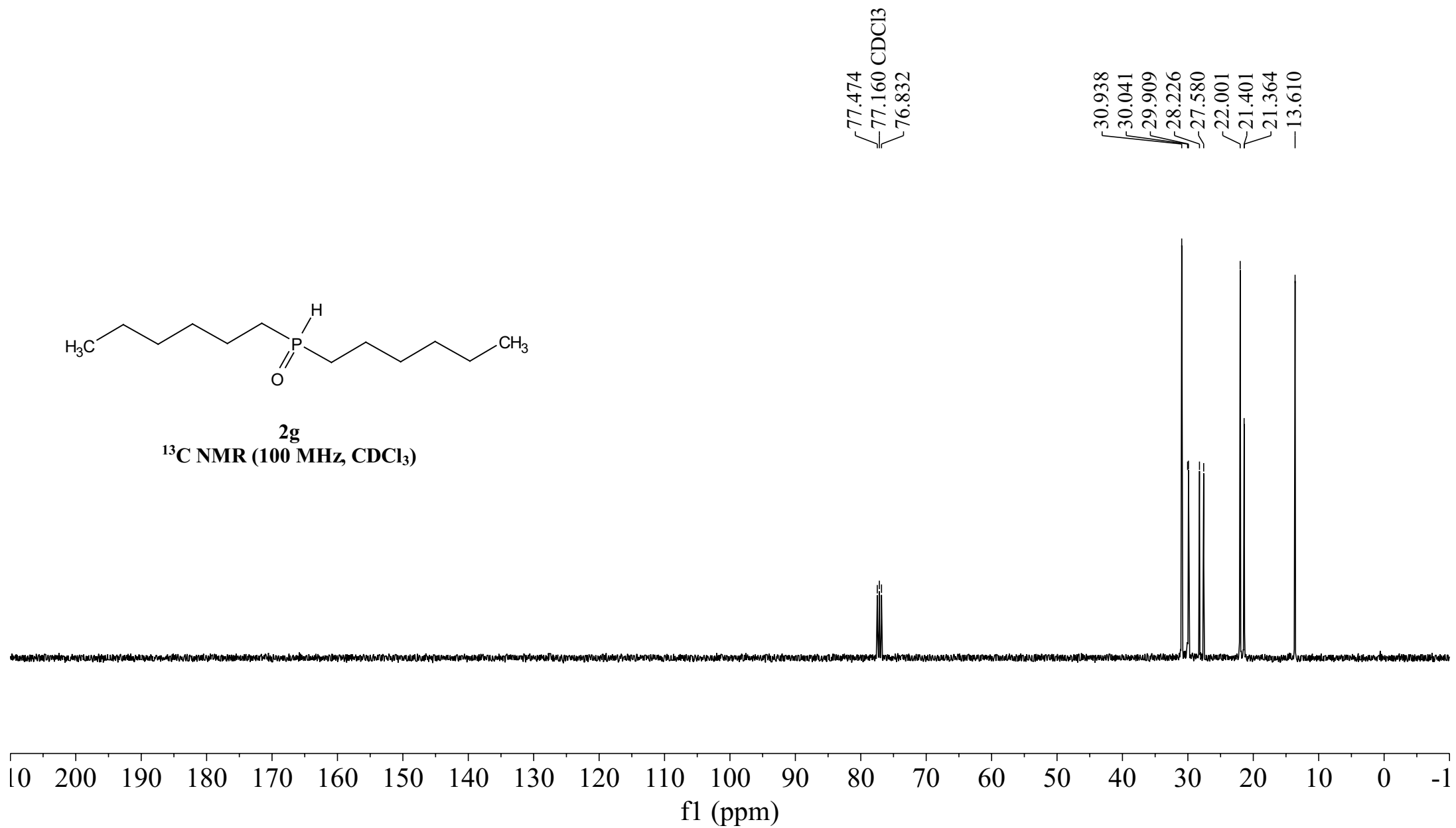


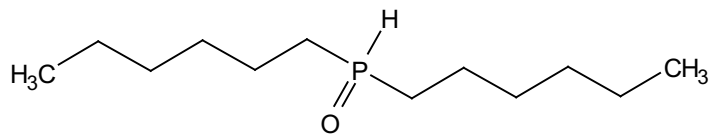


2g
¹H NMR (400 MHz, CDCl₃)



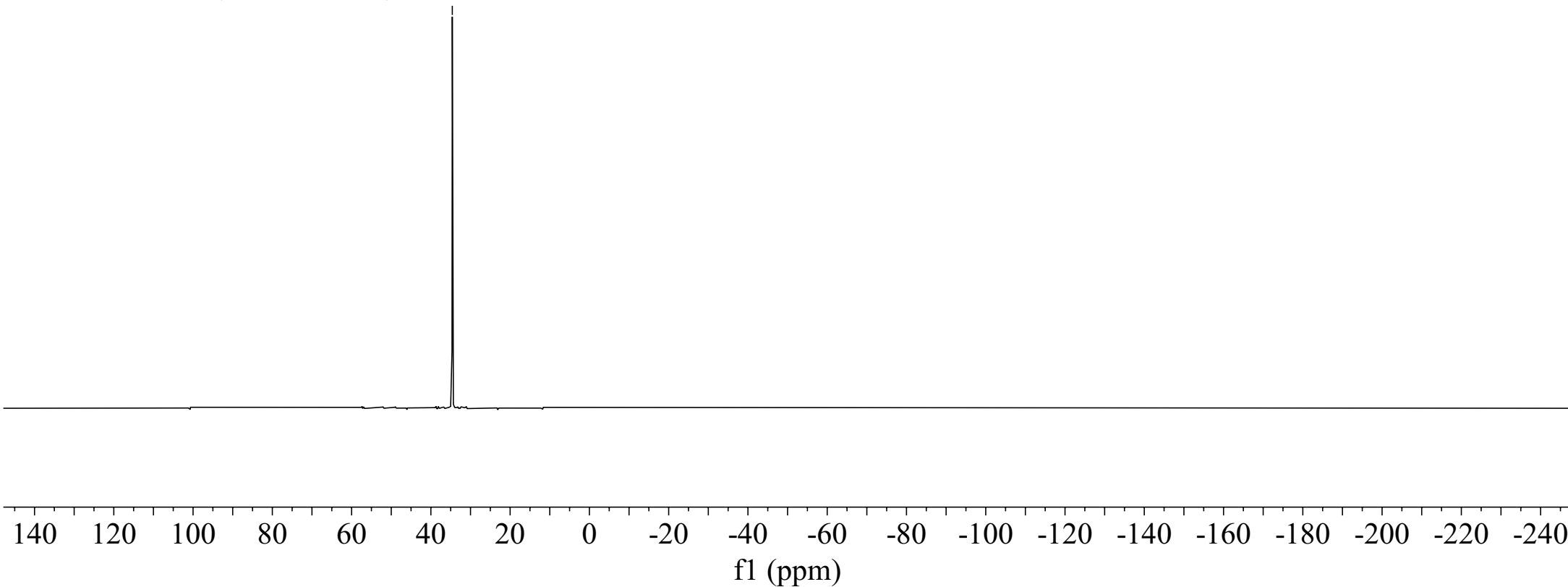
2g
¹³C NMR (100 MHz, CDCl₃)

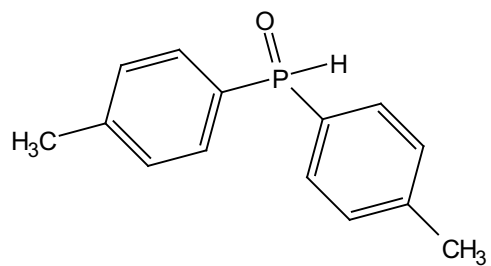




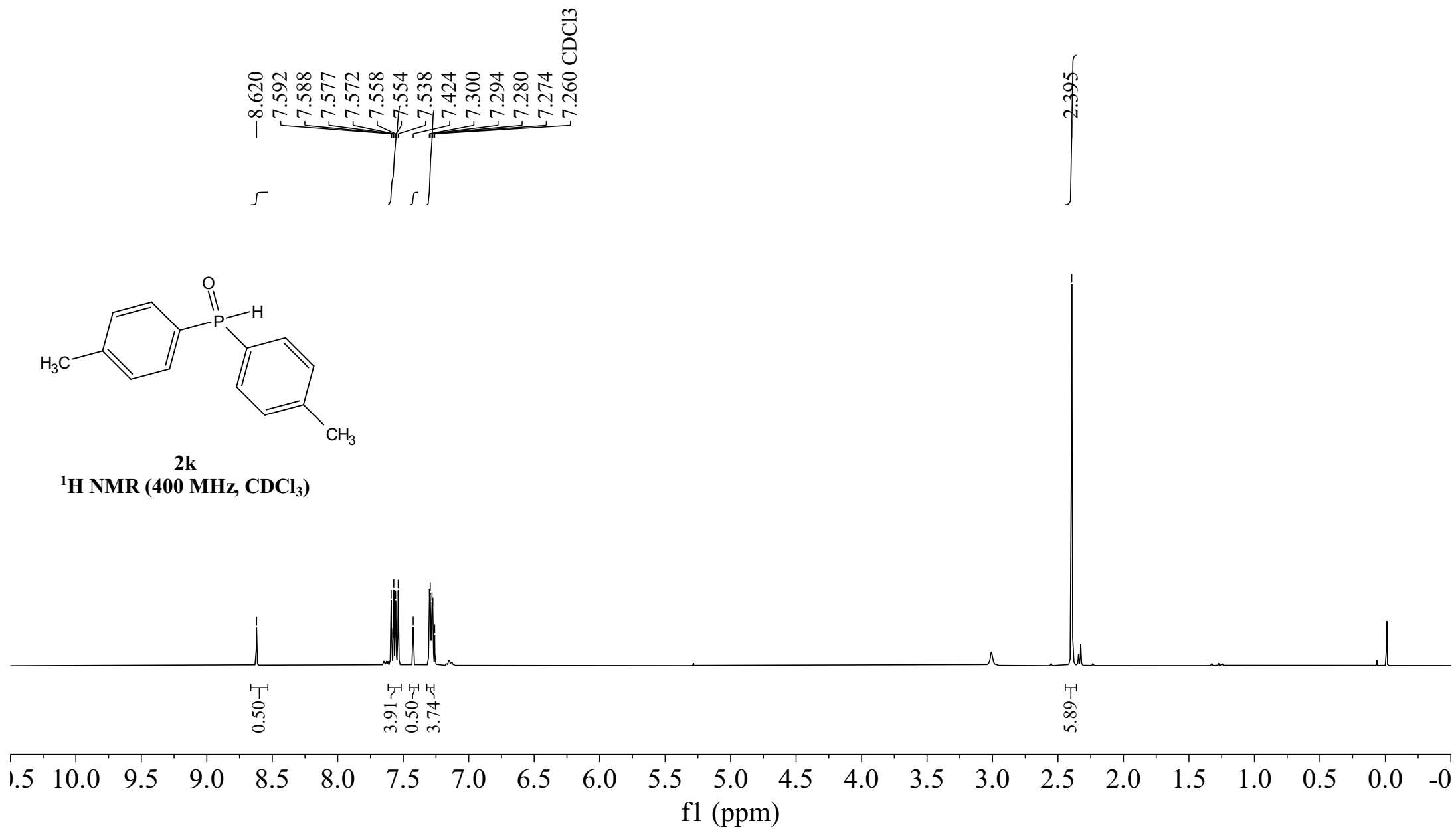
2g
³¹P NMR (162 MHz, CDCl₃)

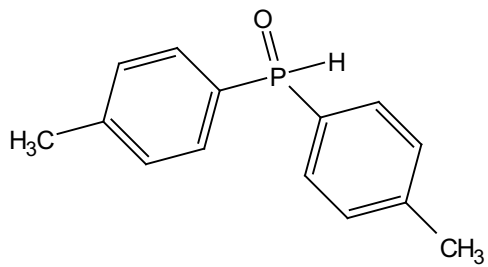
—34.592



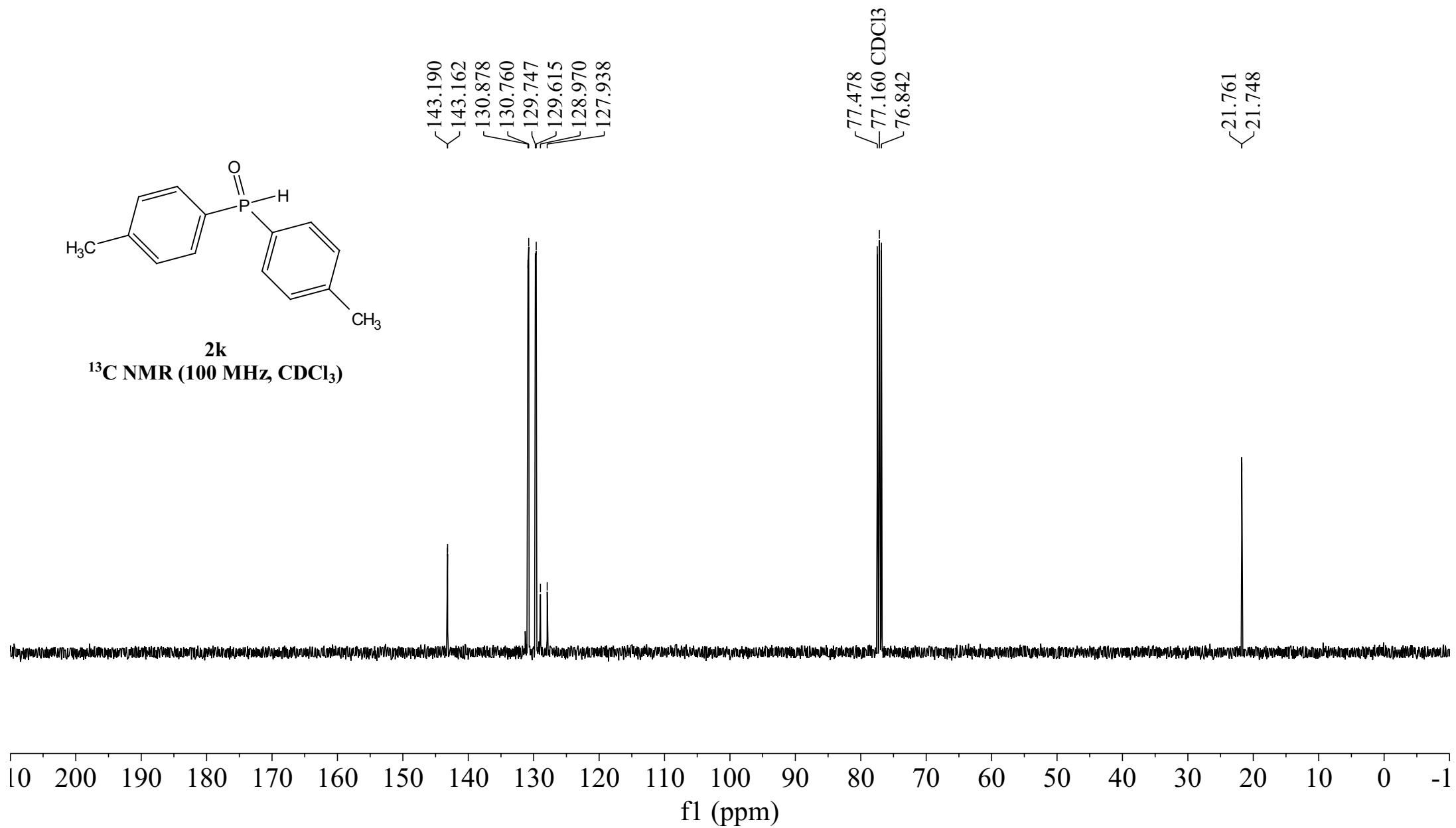


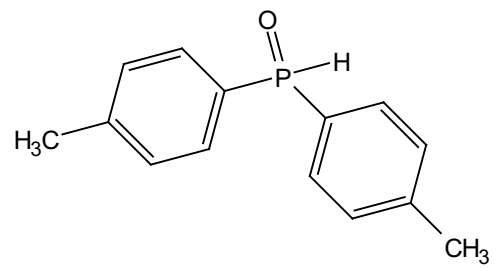
2k
¹H NMR (400 MHz, CDCl₃)





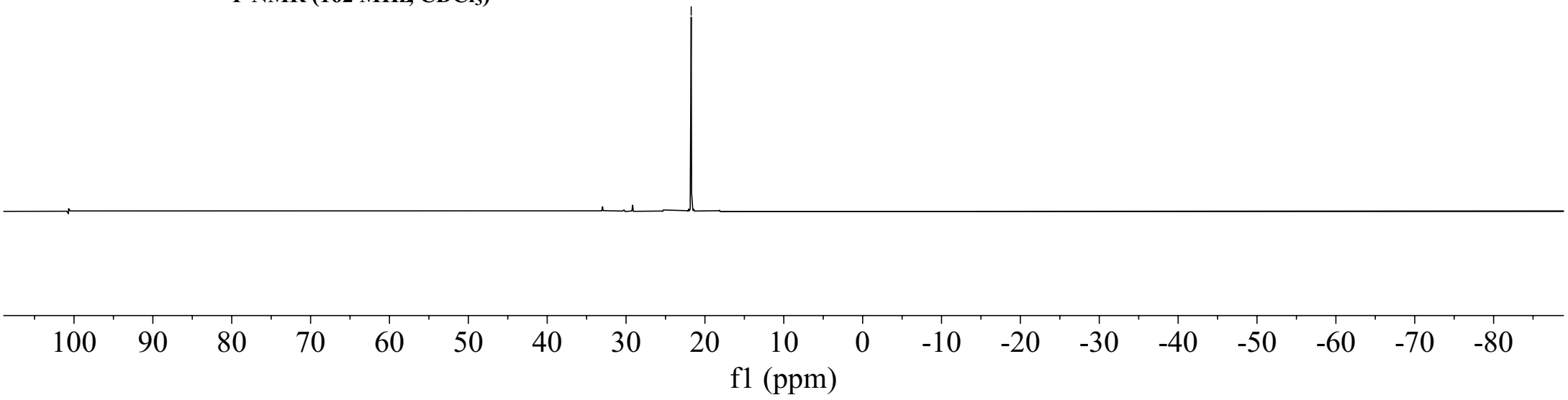
2k
¹³C NMR (100 MHz, CDCl₃)

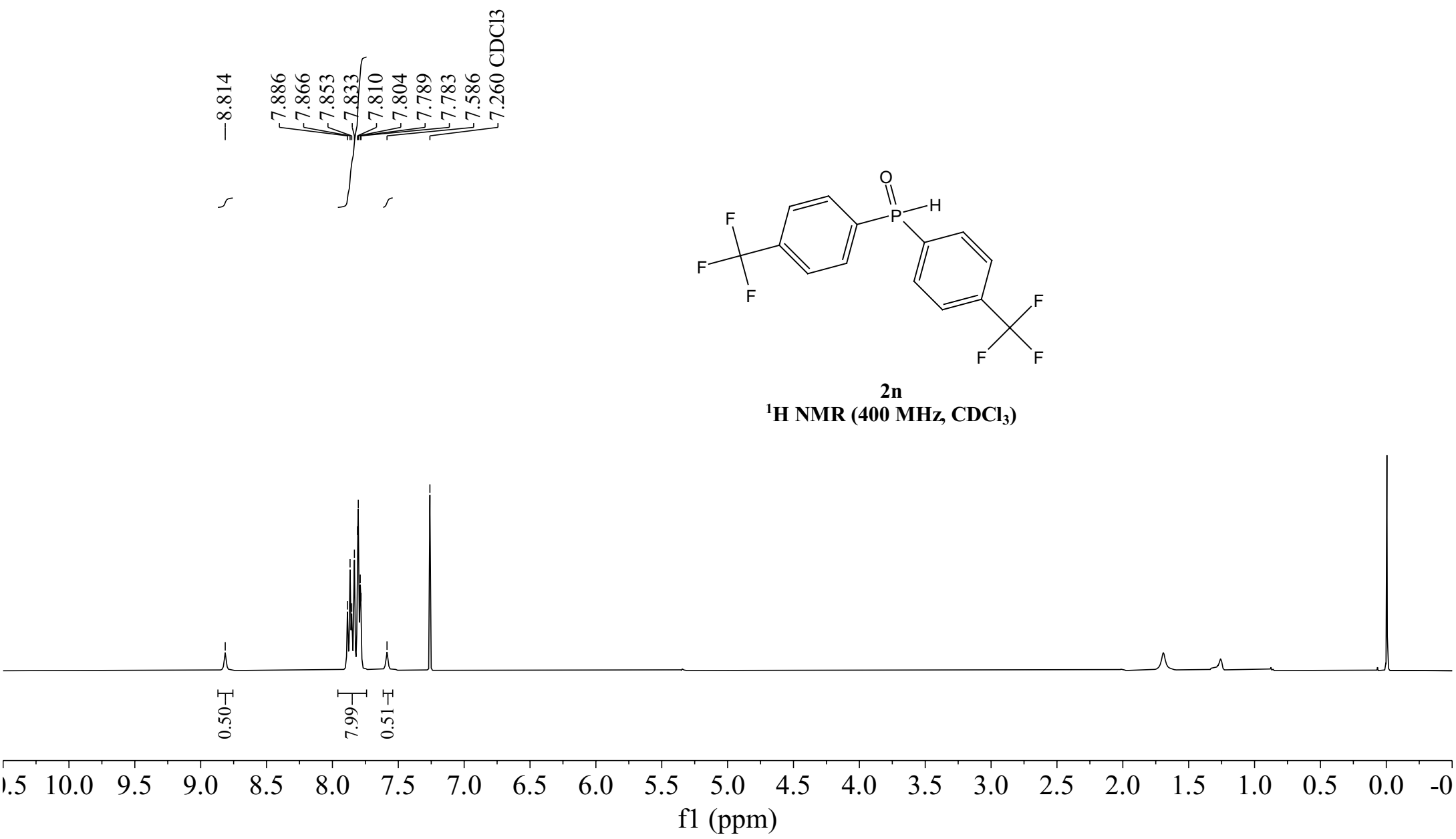


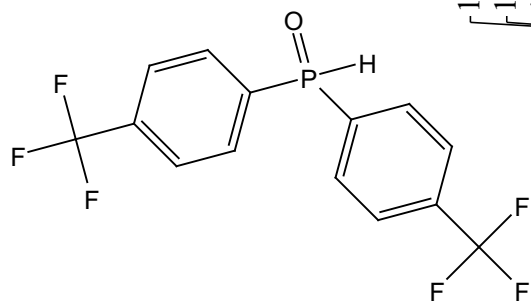


2k
³¹P NMR (162 MHz, CDCl₃)

—21.741





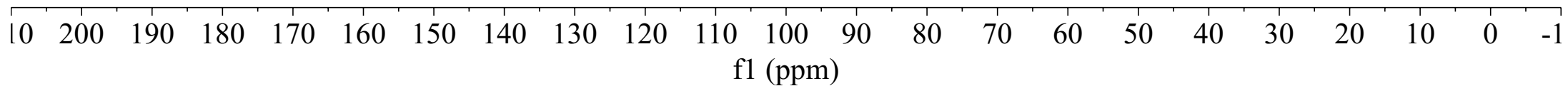


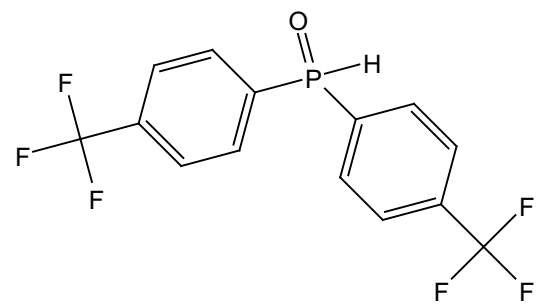
2n

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

135.412
135.029
134.704
134.420
131.325
131.206
127.457
126.212
126.181
126.144
126.095
126.051
126.014
125.977
124.743
122.033
119.320

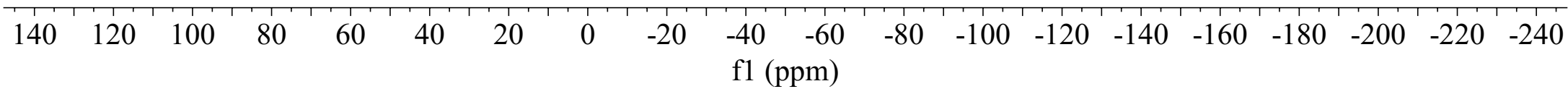
77.477
77.160 CDCl_3
76.841

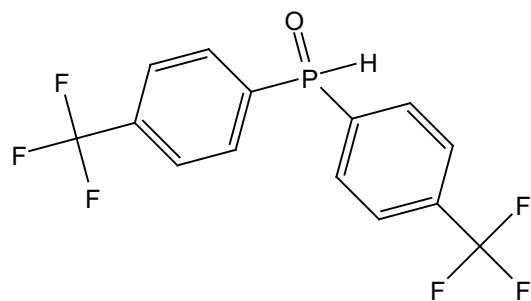




2n
³¹P NMR (162 MHz, CDCl₃)

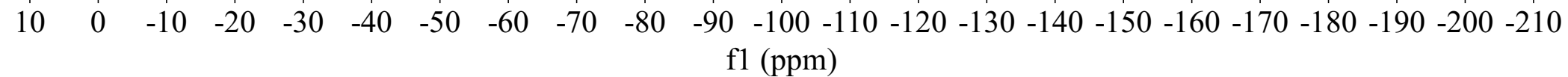
—17.876

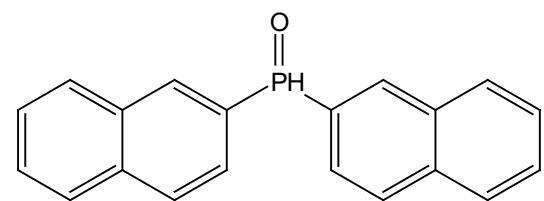




2n
¹⁹F NMR (376 MHz, CDCl₃)

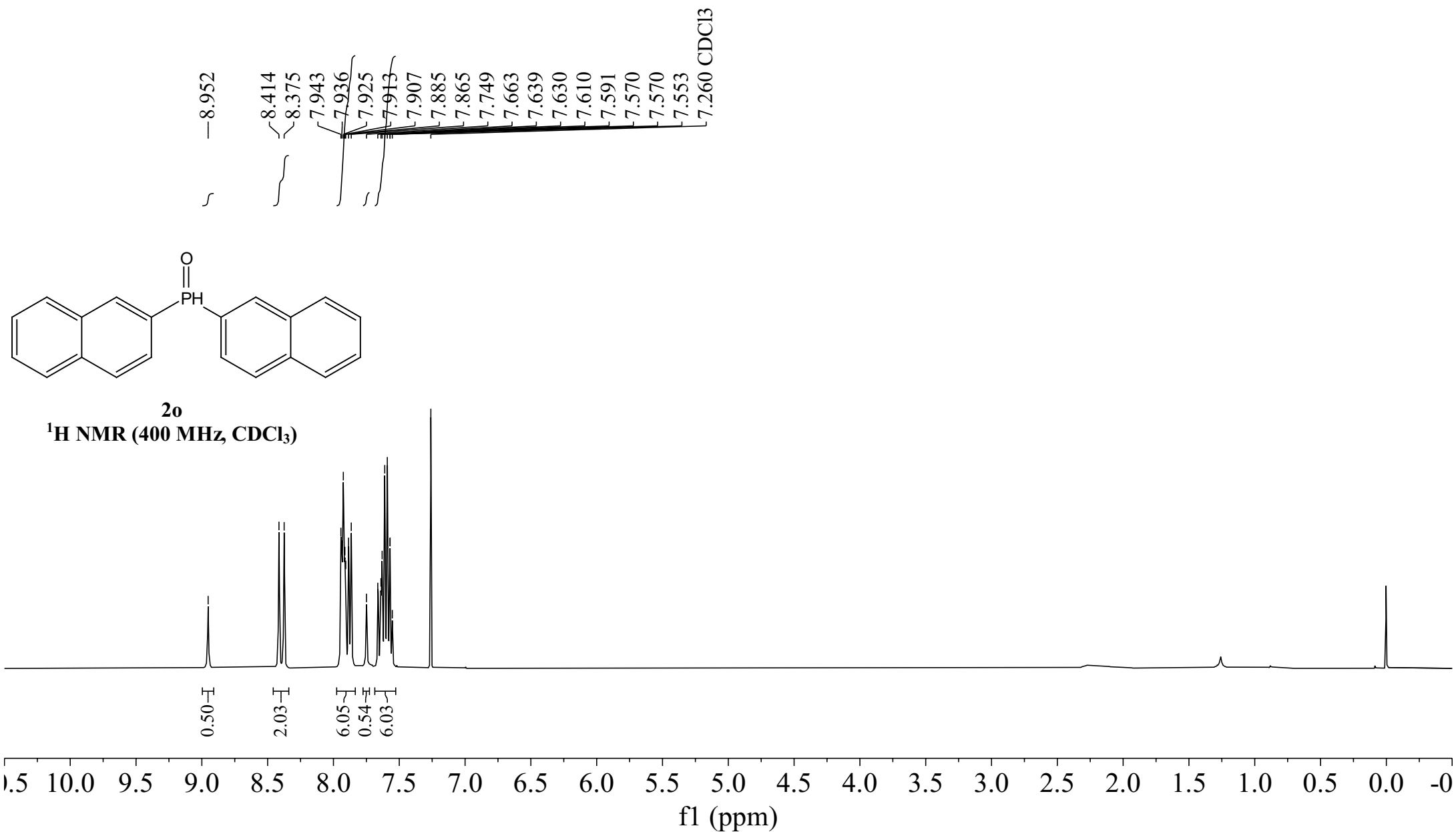
— -63.344

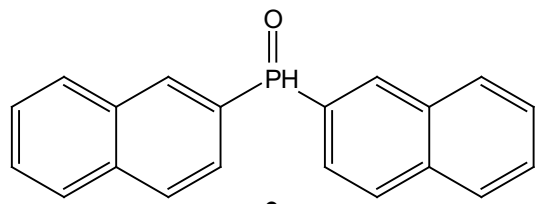




20

¹H NMR (400 MHz, CDCl₃)



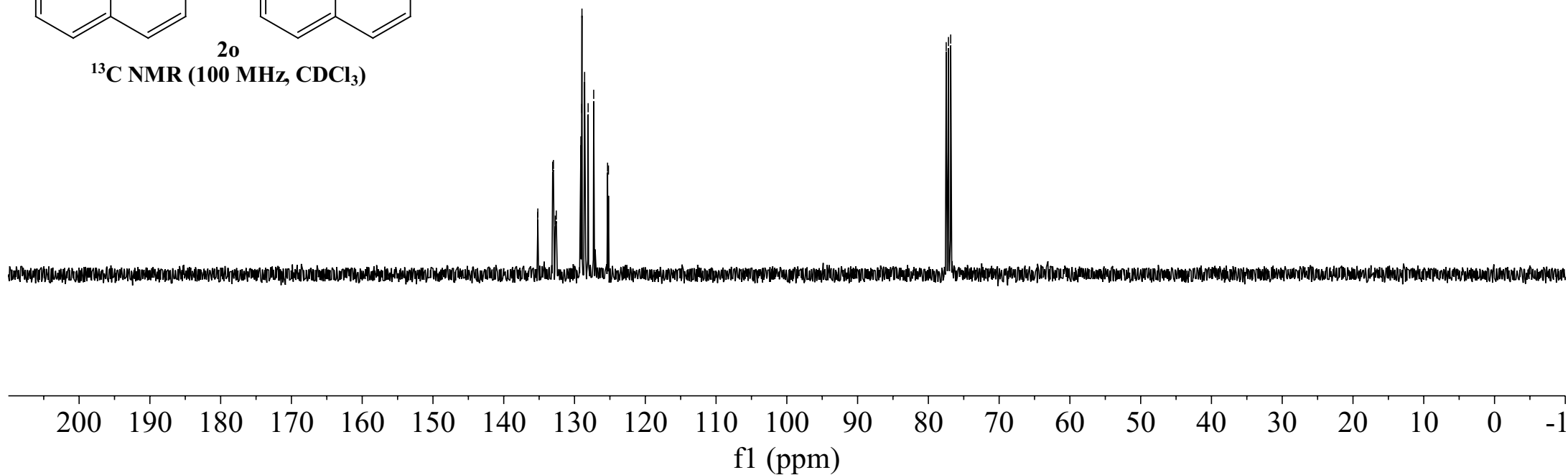


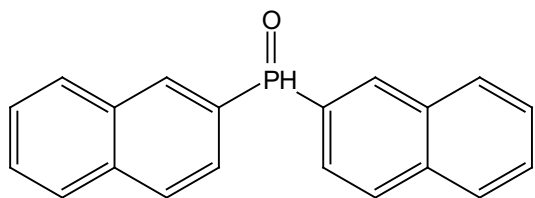
2o

¹³C NMR (100 MHz, CDCl₃)

135.211
135.186
133.089
132.980
132.714
132.573
129.103
128.977
128.948
128.573
128.076
127.289
125.330
125.206

77.479
77.160 CDCl₃
76.843





2o

³¹P NMR (162 MHz, CDCl₃)

-21.737

