

Supplementary Material

S-to-O phosphoryl migration in the rhodium-catalyzed reaction of phosphorothioates with α -diazocarbonyl compounds: An access to tetrasubstituted enol phosphates

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I- General information

Chemicals :

Unless otherwise stated, reagents and solvents were used without any further purification and obtained from commercially available sources. TLC (Thin Layer Chromatography) were performed on Merck silica gel 60 F254 plates and visualized with UV light and/or chemical stain. Crude products were purified by column chromatography using VWR silica gel (40-63 μm) or reverse phased chromatography using an Interchim PF-30C18HP-F0025 column on a Combiflash system.

NMR analysis :

^1H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR spectra were recorded on 400 or 500 MHz instruments Bruker spectrometer. Chemical shifts are reported in parts per million (ppm) and the residual non deuterated solvent was used as c reference. Coupling constants values (J) are reported in Hertz (Hz). Signals are described as br (broad), s (singlet), d (doublet), t (triplet), p (pentuplet), hept (heptuplet) and m (multiplet). Spectra were processed with the software MestreNova (Version 14.2.3-29241). Assignments were determined either based on unambiguous chemical shifts or coupling patterns, and COSY, HSQC, HMBC, NOESY experiments were sometimes needed to fully interpret spectra for related compounds.

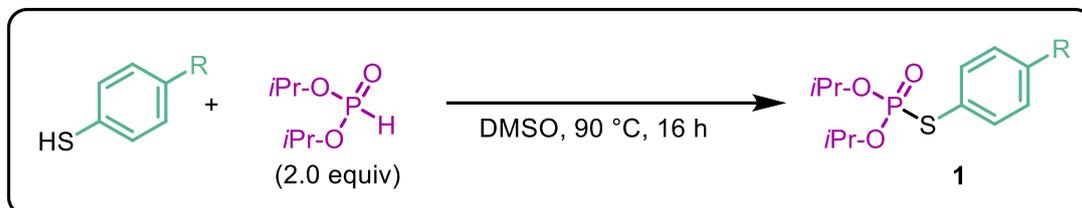
Mass analysis :

High Resolution Mass Spectroscopy (HRMS) were performed by the "Plateforme d'analyse chimique de Strasbourg Illkirch" (PACSI) and were obtained on an Agilent Technologies 6520 Accurate-Mass Q-TOF LC/MS apparatus equipped with a Zorbax SB C18 column (1.8 μm , 2.1 \times 50 mm) using electrospray ionization mode and a time-of-flight analyzer (ESI-TOF). The parent ions $[\text{M} + \text{H}]^+$, $[\text{M} + \text{Na}]^+$ are quoted.

II- Synthesis of starting materials

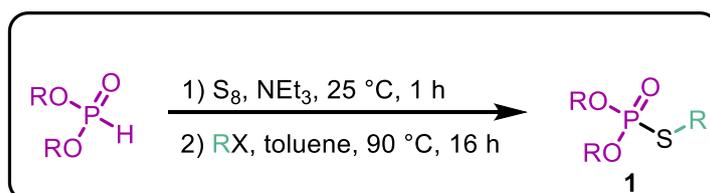
1. Synthesis of phosphorothioates

General procedure A:¹



To a solution of dialkyl phosphite (2.0 equiv) was added benzenethiol (1.0 equiv) in DMSO (0.5 M). The reaction mixture was stirred at 90 °C for 16 h. Solvent was concentrated. Reaction mixture was quenched with NaOH (15% w/w) and extracted with EtOAc. Organic layers were combined, washed with brine, dried over MgSO₄, filtered and concentrated under vacuum. Crude product was purified by column chromatography on silica gel to afford the desired compound **1**.

General procedure B:²



Step 1:

To a round-bottom flask dialkyl phosphite (1.0 equiv) and sulfur (1.0 equiv) was added. Then triethylamine (1.7 equiv) was added dropwise. After 1 hour, the reaction was stopped and the excess triethylamine was concentrated under vacuum. The intermediate product was obtained and was used without further purification for the next step.

Step 2:

To a round-bottom flask equipped with a condenser was added the crude from the first step and haloalkane (1.5 eq) in toluene (0.33 M). The mixture was heated overnight at 70 °C, then allowed to reach room temperature. The reaction mixture was then quenched with water and extracted with EtOAc. Organic layers were combined, dried over MgSO₄, filtered and concentrated under vacuum. The crude was purified by column chromatography on a small pad of silica gel to afford the desired compound **1**.

O,O-diisopropyl *S*-phenyl phosphorothioate (1a)

¹ Kaboudin, B.; Daliri, P.; Esfandiari, H.; Kazemi, F. *Synlett* **2023**, 34 (03), 249–252.

² Tual, L.; Rognan, C.; Maujean, T.; Pertschi, R.; Girard, N.; Blond, G.; Gulea, M. *Synthesis* **2025**, 57 (08), 1490–1498.



Was obtained according to **General procedure A**, from diisopropyl phosphite (2.0 equiv, 1.51 mL, 9.08 mmol) and thiophenol (1.0 equiv, 0.46 mL, 4.54 mmol). Purification by column chromatography on silica gel (eluent: 70/30 to 60/40 *n*-pentane/Et₂O) led to **1a** (1187 mg, 4.33 mmol, **95%**, colorless oil).

¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.57 (m, 2H), 7.36 – 7.31 (m, 3H), 4.77 (dp, ³J_{H-P} = 8.8 Hz, J = 6.2 Hz, 2H), 1.33 (d, J = 6.2 Hz, 6H), 1.25 (d, J = 6.2 Hz, 6H).

³¹P NMR (162 MHz, CDCl₃) δ 20.43.

Chemical shifts were in accordance with literature.³

R_f = 0.37 (70/30 *n*-heptane/EtOAc).

***O,O*-diethyl S-phenyl phosphorothioate (1b)**



From the literature⁴: To a solution of copper(I) iodide (5 mol%, 48 mg, 0.25 mmol) and triethylamine (2.5 equiv, 1.74 mL, 13 mmol) in DMF (5 mL) was added diethyl phosphite (1.0 equiv, 0.64 mL, 5.0 mmol). Benzenethiol (1.2 equiv, 0.61 mL, 6.0 mmol) was added to the reaction mixture and the mixture was stirred at 25 °C for 16 h under O₂ atmosphere. Solvent was concentrated and the resulting solution was quenched with water and extracted with dichloromethane. The organic layers were combined, washed with brine, dried over MgSO₄, filtered and concentrated under vacuum. Crude product was purified by column chromatography on silica gel (eluent: 70/30 *n*-pentane/Et₂O) to afford **1b** (585 mg, 2.38 mmol, **48%**, colorless oil).

¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.53 (m, 2H), 7.39 – 7.31 (m, 3H), 4.28 – 4.11 (m, 4H), 1.31 (td, J = 7.1 Hz, ⁴J_{H-P} = 0.9 Hz, 6H).

³¹P NMR (202 MHz, CDCl₃) δ 22.90.

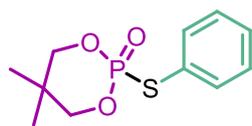
Chemical shifts were in accordance with literature.³

R_f = 0.29 (70/30 *n*-pentane/Et₂O).

5,5-dimethyl-2-(phenylthio)-1,3,2-dioxaphosphinane 2-oxide (1c)

³ Xu, J.; Zhang, L.; Li, X.; Gao, Y.; Tang, G.; Zhao, Y. *Org. Lett.* **2016**, *18* (6), 1266–1269.

⁴ Kaboudin, B.; Abedi, Y.; Kato, J.; Yokomatsu, T. *Synthesis* **2013**, *45* (16), 2323–2327.



CAS : 60519-65-3

Under N₂ atmosphere, thiophenol (1.0 equiv) was deprotonated by sodium hydride (1.3 equiv, 60% in oil) in THF at 0 °C. The reaction mixture was stirred at 25 °C for 16 h. The reaction mixture was quenched with saturated aqueous solution of ammonium chloride and extracted with Et₂O. Organic layers were combined, washed with aqueous solution of KOH (1 M), dried over MgSO₄, filtered and concentrated under vacuum. Crude product was purified by column chromatography on silica gel (eluent: 80/20 *n*-pentane/EtOAc) to afford the phosphorothioate **1c**.

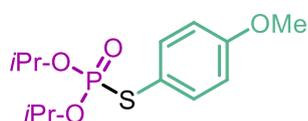
¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.61 (m, 2H), 7.39 – 7.32 (m, 3H), 4.25 – 4.17 (m, 2H), 3.97 (dt, *J* = 11.4, 1.6 Hz, 1H), 3.91 (dt, *J* = 11.4, 1.6 Hz, 1H), 1.28 (s, 3H), 0.87 (s, 3H).

³¹P NMR (162 MHz, CDCl₃) δ 14.87.

¹³C NMR (101 MHz, CDCl₃) δ 134.8 (d, ³J_{C-P} = 5.2 Hz, 2C), 129.6 (d, ⁴J_{C-P} = 2.2 Hz, 2C), 129.2 (d, *J* = 2.8 Hz), 124.9 (d, ²J_{C-P} = 6.6 Hz), 78.3 (d, ²J_{C-P} = 7.3 Hz, 2C), 32.5 (d, ³J_{C-P} = 6.9 Hz), 22.0, 20.4 (d, ⁴J_{C-P} = 1.2 Hz).

R_f = 0.16 (70/30 *n*-heptane/EtOAc).

O,O-diisopropyl *S*-(4-methoxyphenyl) phosphorothioate (**1d**)



CAS : 2370016-81-0

Was obtained according to **General procedure A**, from diisopropyl phosphite (2.0 equiv, 0.59 mL, 3.57 mmol) and thiophenol (1.0 equiv, 0.22 mL, 1.78 mmol). Purification by column chromatography on silica gel (eluent: 95/5 to 70/30 *n*-heptane/EtOAc) led to **1d** (342 mg, 1.12 mmol, **63%**, colorless oil).

¹H NMR (500 MHz, CDCl₃) δ 7.55 – 7.44 (m, 2H), 6.91 – 6.80 (m, 2H), 4.74 (dp, ³J_{H-P} = 8.7 Hz, *J* = 6.2 Hz, 2H), 3.79 (s, 3H), 1.32 (d, *J* = 6.2 Hz, 6H), 1.26 (d, *J* = 6.2 Hz, 6H).

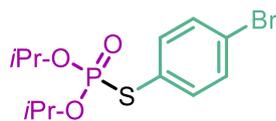
³¹P NMR (202 MHz, CDCl₃) δ 21.16.

Chemical shifts were in accordance with literature.⁵

R_f = 0.29 (70/30 *n*-heptane/EtOAc).

S-(4-bromophenyl) *O,O*-diisopropyl phosphorothioate (**1e**)

⁵ Mondal, M.; Saha, A. *Tetrahedron Lett.* **2019**, *60* (34), 150965.



CAS : 1466450-16-7

Was obtained according to **General procedure A**, from diisopropyl phosphite (2.0 equiv, 0.44 mL, 2.64 mmol) and 4-bromothiophenol (1.0 equiv, 263 mg, 1.32 mmol). Purification by column chromatography on silica gel (eluent: 90/10 to 80/20 *n*-heptane/EtOAc) led to **1e** (303 mg, 0.86 mmol, **65%**, colorless oil).

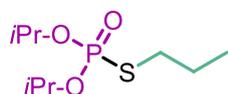
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.47 (d, $J = 0.6$ Hz, 4H), 4.76 (dhept, $^3J_{\text{H-P}} = 8.7$, $J = 6.2$ Hz, 2H), 1.34 (d, $J = 6.2$ Hz, 6H), 1.28 (d, $J = 6.2$ Hz, 6H).

$^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 19.50.

Chemical shifts were in accordance with literature.⁴

$R_f = 0.42$ (80/20 *n*-heptane/EtOAc).

O,O-diisopropyl S-propyl phosphorothioate (1f)



CAS : 1900702-72-8

Was obtained according to **General procedure B**, from bis(propan-2-yl) phosphonate (1.0 equiv, 0.30 mL, 1.81 mmol) and iodopropane (1.5 equiv, 0.26 mL, 2.71 mmol). Purification by column chromatography on silica gel (eluent: 70/30 *n*-pentane/Et₂O) led to **1f** (315 mg, 1.31 mmol, **73%**, colorless oil).

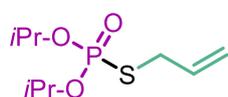
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.73 (dhept, $^3J_{\text{H-P}} = 9.0$ Hz, $J = 6.2$ Hz, 2H), 2.81 (dt, $^3J_{\text{H-P}} = 13.6$, $J = 7.3$ Hz, 2H), 1.82 – 1.63 (m, 2H), 1.36 (d, $J = 6.2$ Hz, 6H), 1.34 (d, $J = 6.2$ Hz, 6H), 1.00 (t, $J = 7.3$ Hz, 3H).

$^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 25.77.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 72.4 (d, $J = 6.4$ Hz), 33.0 (d, $^2J_{\text{C-P}} = 4.0$ Hz), 24.1 (d, $J = 6.4$ Hz), 23.9 (d, $J = 4.1$ Hz, 2C), 23.6 (d, $J = 5.5$ Hz, 2C), 13.2.

$R_f = 0.22$ (70/30 *n*-pentane/Et₂O).

O,O-diisopropyl S-(prop-2-yn-1-yl) phosphorothioate (1g)



CAS : 10428-97-4

Was obtained according to the **General procedure B**, from diisopropyl phosphite (1.0 equiv, 10 mmol, 1.66 g) and allyl bromide (1.5 equiv, 15 mmol, 1.31 mL). Purification by column chromatography on a small pad of silica gel (eluent: 70/30 *n*-heptane/EtOAc) led to **1g** (9.61 mmol, 2.29 g, **96%**, colorless oil).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.91 (ddt, $J = 17.0, 9.8, 7.1$ Hz, 1H, H), 5.26 (d, $J = 16.9$ Hz, 1H, H), 5.13 (d, $J = 10.0$ Hz, 1H, H), 4.74 (dhept, $J = 8.9, 6.1$ Hz, 2H, H), 3.48 (ddt, $J = 13.9, 7.2, 1.2$ Hz,

2H, H), 1.37 (d, $J = 6.1$ Hz, 6H, H), 1.34 (d, $J = 6.2$ Hz, 6H, H).
 ^{31}P NMR (162 MHz, CDCl_3) δ 24.59.
Chemical shifts were in accordance with literature.²
 $R_f = 0.35$ (70/30 *n*-heptane/EtOAc).

***O,O*-diethyl *S*-(prop-2-yn-1-yl) phosphorothioate (1h)**



Was obtained according to the **General procedure B**, from diisopropyl phosphite (1.0 equiv, 10 mmol, 1.66 g) and propargyl bromide (1.5 equiv, 15 mmol, 1.62 mL). Purification by column chromatography on a small pad of silica gel (eluent: 70/30 *n*-heptane/EtOAc) led to **1h** (9.73 mmol, 2.30 g, **98%**, colorless oil).

^1H NMR (400 MHz, CDCl_3) δ 4.30 – 4.09 (m, 4H, H), 3.55 (ddd, $J = 14.3, 2.6, 1.3$ Hz, 2H, H), 2.30 (t, $J = 2.7$ Hz, 1H, H), 1.38 (td, $J = 7.1, 1.3$ Hz, 6H, H).
 ^{31}P NMR (162 MHz, CDCl_3) δ 25.31.
Chemical shifts were in accordance with literature.²
 $R_f = 0.37$ (70/30 *n*-heptane/EtOAc).

***S*-benzyl *O,O*-diisopropyl phosphorothioate (1i)**



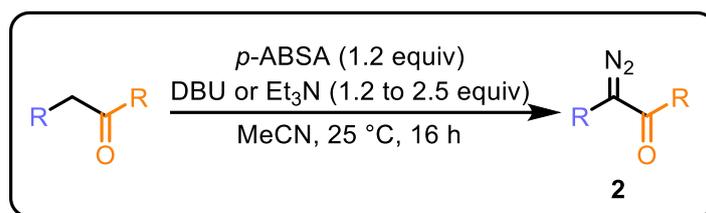
Was obtained according to **General procedure B**, from bis(propan-2-yl) phosphonate (1.0 equiv, 0.30 mL, 1.81 mmol) and benzyl bromide (1.5 equiv, 0.32 mL, 2.71 mmol). Purification by column chromatography on a small pad of silica gel (eluent: 70/30 *n*-heptane/EtOAc) led to **1i** (500 mg, 1.73 mmol, **96%**, colorless oil).

^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.21 (m, 5H), 4.78 – 4.61 (m, 2H), 4.06 (dd, $J = 13.0, 3.7$ Hz, 2H), 1.34 (d, $J = 6.0$ Hz, 6H), 1.29 (d, $J = 6.0$ Hz, 6H).
 ^{31}P NMR (162 MHz, CDCl_3) δ 24.14.
Chemical shifts were in accordance with literature.⁶
 $R_f = 0.37$ (70/30 *n*-heptane/EtOAc).

2. Synthesis of diazo compounds

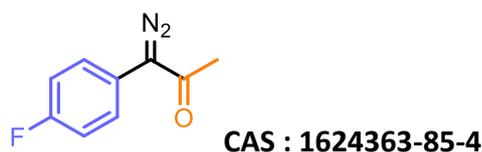
General procedure C for Regitz transfer:

⁶ Philippitsch, V.; Hammerschmidt, F. *Org. Biomol. Chem.* **2011**, *9* (14), 5220.



To a solution of 4-acetamidobenzene-1-sulfonyl azide (*p*-ABSA) (1.2 equiv) in acetonitrile (0.5 M) was added dropwise the substrate (1.0 equiv). The solution was then cooled to 0°C and base (1.2 to 2.5 equiv) was added dropwise. Reaction mixture was stirred at 25 °C for 16 h. Solvent was concentrated. Crude product was quenched with water and extracted with Et₂O. Organic layers were combined, washed with brine, dried over MgSO₄, filtered and concentrated under vacuum. The crude product was purified by column chromatography on silica gel to afford the diazo compound **2**.

1-diazo-1-(4-fluorophenyl)propan-2-one (**2A**)



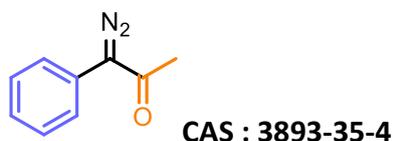
Was obtained according to **General procedure C**, from 1-(4-fluorophenyl)propan-2-one (1.0 equiv, 2008 mg, 13.2 mmol) and DBU (1.2 equiv, 2.37 mL, 15.8 mmol). Purification by column chromatography on silica gel (eluent: 100/0 to 80/20 *n*-heptane/EtOAc) led to **2A** (550 mg, 7.86 mmol, **60%**, red crystals).

¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.40 (m, 2H), 7.18 – 7.05 (m, 2H), 2.36 (s, 3H).

R_f = 0.53 (70/30 *n*-heptane/EtOAc).

Chemical shifts were in accordance with literature.⁷

1-diazo-1-phenylpropan-2-one (**2B**)



Was obtained according to **General procedure C**, from phenyl-2-propanone (1.0 equiv, 580 mg, 4.32 mmol) and DBU (1.2 equiv, 0.77 mL, 5.2 mmol). Purification by column chromatography on silica gel (eluent: 90/10 *n*-heptane/EtOAc) led to **2B** (313 mg, 1.95 mmol, **45%**, red crystals).

¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, *J* = 7.5 Hz, 2H), 7.44 – 7.39 (m, 2H), 7.28 (s, 1H), 2.37 (s, 3H).

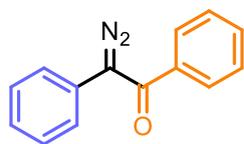
Chemical shifts were in accordance with literature.⁸

⁷ Xu, B.; Zhu, S.; Zuo, X.; Zhang, Z.; Zhou, Q. *Angew. Chem. Int. Ed.* **2014**, 53 (15), 3913–3916.

⁸ Denton, J. R.; Davies, H. M. L. *Org. Lett.* **2009**, 11 (4), 787–790.

$R_f = 0.32$ (90/10 *n*-heptane/EtOAc).

2-diazo-1,2-diphenylethan-1-one (2C)



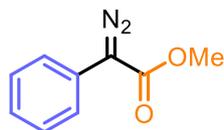
CAS : 3469-17-8

Was obtained according to **General procedure C**, from 1,2-diphenylethan-1-one (1.0 equiv, 1500 mg, 7.64 mmol) and DBU (1.2 equiv, 1.37 mL, 9.17 mmol). Purification by column chromatography on silica gel (eluent: 100/0 to 80/20 *n*-heptane/EtOAc) led to **2C** (550 mg, 2.47 mmol, **32%**, red crystals).

$R_f = 0.45$ (90/10 *n*-heptane/EtOAc).

Chemical shifts were in accordance with literature.⁸

Methyl 2-diazo-2-phenylacetate (2D)



CAS : 22979-35-7

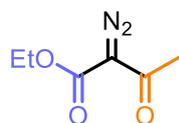
Was obtained according to **General procedure C** from methyl phenylacetate (1.0 equiv, 10 g, 66.6 mmol) and DBU (1.2 equiv, 2.98 mL, 20.0 mmol). Purification by column chromatography on silica gel (95/5 *n*-heptane/EtOAc) led to **2D** (11 g, 62.4 mmol, **94%**, red oil).

¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.45 (m, 2H), 7.39 (dd, $J = 8.4, 7.6$ Hz, 2H), 7.19 (ddt, $J = 7.7, 7.1, 1.2$ Hz, 1H), 3.87 (s, 3H).

Chemical shifts were in accordance with literature.⁹

$R_f = 0.40$ (95/5 *n*-heptane/EtOAc).

Ethyl 2-diazo-3-oxobutanoate (2E)



CAS : 2009-97-4

Was obtained according to **General procedure C** from ethyl acetoacetate (1.0 equiv, 6.0 g, 46.1 mmol) and triethylamine (2.5 equiv, 16.0 mL, 115.3 mmol). Purification by column chromatography on silica gel (80/20 to 70/30 *n*-heptane/EtOAc) led to **2E** (5.6 g, 35.7 mmol, **78%**, yellow oil).

¹H NMR (500 MHz, CDCl₃) δ 4.30 (t, $J = 7.7$ Hz, 2H), 2.48 (q, $J = 2.9$ Hz, 3H), 1.36 – 1.30 (m, 3H). Chemical shifts were in accordance with literature.¹⁰

$R_f = 0.44$ (80/20 *n*-heptane/EtOAc).

⁹ Rognan, C.; Locquet, P.; Pertschi, R.; Girard, N.; Gulea, M. *Adv. Synth. Catal.* **2024**, *366* (19), 4078–4083.

¹⁰ Green, G. M.; Peet, N. P.; Metz, W. A. *J. Org. Chem.* **2001**, *66* (7), 2509–2511.

III- Computational studies

All calculations were carried out using Gaussian 16 software at the DFT level of theory and the obtained structures were visualized using CYL view.^{11, 12} The optimization and single point energy calculations of the structures were performed using the hybrid functional M06-2X all atoms were described by the Pople 6-311++G**.¹³ To account for the solvation energy the SMD model was used (dichloromethane, $\epsilon = 8.93$).¹⁴ All reported data are *Gibbs* free energies given in kcal.mol⁻¹ at 298 K and 1 atm. All optimized structures were characterized by frequency analysis either as energy minima without imaginary frequencies or with only one imaginary frequencies for transition states.

¹¹ Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

¹² CYLview20; Legault, C. Y., Université de Sherbrooke, 2020 (<http://www.cylview.org>).

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XYZ Coordinates of the Computed Structures

A_{keto}

Gibbs Free Energy = -1742.120476 a.u.

Number of imaginary frequencies: 0

C	4.4563400	12.2568770	5.0071850
C	3.8516790	11.9389550	3.8665900
H	4.2104550	13.1809920	5.5241230
H	3.0930120	12.5842830	3.4372610
S	7.1390230	12.2360730	5.4579550
P	7.5335410	11.6184010	3.3610580
O	6.6417740	10.5676220	2.8501880
O	7.3266750	13.0091450	2.6336310
O	9.0913770	11.3985040	3.3624570
C	5.5007320	11.3952710	5.6394050
H	5.5872240	10.4101460	5.1862980
H	5.3839110	11.3148230	6.7215370
H	4.1019770	11.0269910	3.3342420
C	8.1805730	14.1764450	2.8772520
H	8.7389940	14.0084430	3.8040660
C	9.7312780	10.0892060	3.1463580
H	9.0479000	9.3326710	3.5329010
C	9.1390150	14.3037670	1.7125200
H	8.5815660	14.4388650	0.7825640
H	9.7834720	15.1725370	1.8641900
H	9.7656000	13.4143640	1.6279680
C	7.2526920	15.3602740	3.0342300
H	6.5644000	15.2061040	3.8677400
H	7.8379620	16.2622230	3.2251440
H	6.6728850	15.5052690	2.1195400
C	9.9572070	9.9204090	1.6592930
H	10.6134920	10.7076900	1.2799930
H	10.4302090	8.9531430	1.4737010
H	9.0110590	9.9498590	1.1145610
C	11.0057720	10.1174670	3.9562460
H	11.5101110	9.1518960	3.8765910
H	11.6772240	10.8955230	3.5838450
H	10.7857510	10.3139760	5.0066460
C	8.3005430	11.5104780	6.5136270
C	9.0746310	12.4454270	7.3505870
C	8.4683680	13.5405040	7.9887190
C	10.4580000	12.2761870	7.5269490
C	9.2092140	14.4252110	8.7638220
H	7.3983850	13.6926060	7.8879730
C	11.1935460	13.1453870	8.3256170
H	10.9630450	11.4616300	7.0203660
C	10.5762770	14.2291130	8.9449280
H	8.7118130	15.2614830	9.2425810
H	12.2592100	12.9848830	8.4471740
H	11.1524190	14.9123970	9.5579230
C	8.4439260	10.1048510	6.3954170
O	7.8546280	9.4592930	5.5056190
C	9.2960920	9.3441590	7.3921900
H	10.2544480	9.0832020	6.9336150
H	9.4867460	9.8981480	8.3106170
H	8.7775920	8.4126430	7.6257570

B_{keto}

Gibbs Free Energy = -1742.172415 a.u.

Number of imaginary frequencies: 0

C	3.5830610	10.9715970	5.7095140
C	2.6553740	10.9354150	4.7575380
H	3.2924580	11.0113010	6.7566930
H	1.5979640	10.9301430	4.9986560
S	5.7145080	12.6310060	5.8898160
P	8.1367520	11.4650330	3.0719130
O	7.2114730	10.8818810	2.0890910
O	8.1251820	13.0379030	3.1219310
O	9.6838170	11.1332350	2.9076800
C	5.0506350	10.9774510	5.4233410
H	5.2532390	10.7847060	4.3713610
H	5.5797480	10.2453260	6.0354990
H	2.9294480	10.9051820	3.7067630
C	9.1780980	13.9006700	3.6593900
H	9.7380350	13.3321950	4.4066730
C	10.1526660	9.7512640	2.7913380
H	9.5392970	9.1368010	3.4587460
C	10.0888180	14.3104420	2.5203120
H	9.5146810	14.8445040	1.7591390
H	10.8693370	14.9750250	2.8981330
H	10.5610280	13.4382870	2.0662170
C	8.4753690	15.0717530	4.3100470
H	7.8012680	14.7323410	5.0980660
H	9.2146880	15.7476270	4.7460800
H	7.8969460	15.6218750	3.5636320
C	10.0026040	9.2897230	1.3546570
H	10.5996480	9.9260550	0.6962940
H	10.3614210	8.2618450	1.2652690
H	8.9603980	9.3263460	1.0361120
C	11.5929130	9.7515280	3.2555420
H	11.9984330	8.7402210	3.1814220
H	12.1891120	10.4114410	2.6201410
H	11.6768230	10.0846740	4.2906080
C	7.3812510	12.2882440	6.4158460
C	7.8225850	12.9966610	7.6449440
C	7.0396820	12.9892610	8.8044260
C	9.0298030	13.7041100	7.6493960
C	7.4697590	13.6498380	9.9495370
H	6.0946480	12.4580950	8.8052550
C	9.4561540	14.3709630	8.7935850
H	9.6299860	13.7363190	6.7455660
C	8.6782650	14.3430240	9.9476880
H	6.8584500	13.6265750	10.8444510
H	10.3914220	14.9189140	8.7803300
H	9.0077720	14.8644160	10.8391010
C	8.1995550	11.4730960	5.7320310
O	7.7382580	10.9212710	4.5401660
C	9.5419180	10.9622330	6.1511320
H	10.3444170	11.4216870	5.5663950
H	9.7282050	11.1509110	7.2067740
H	9.5770030	9.8841080	5.9697590

C_{keto}

Gibbs Free Energy = -1742.174274 a.u.

Number of imaginary frequencies: 0

C	4.6290610	9.8440800	7.0670760
C	5.4269060	11.0911230	7.3270880
H	5.0355320	8.9087580	7.4483300
H	5.6573950	11.1697360	8.3939140
S	6.3751820	11.1534680	4.7783750
P	8.0686160	11.9330560	3.8173160

O	8.3536330	13.3744580	3.9817450
O	9.2253430	10.9309310	4.2452550
O	7.7535000	11.5083790	2.3104050
C	3.4664100	9.8355790	6.4229920
H	3.0298780	10.7522700	6.0359160
H	2.9138630	8.9155880	6.2654710
H	4.8381300	11.9614620	7.0385620
C	10.5699080	11.0932710	3.6792710
H	10.4666380	11.5935110	2.7108580
C	7.2155670	12.4644140	1.3437310
H	6.6660020	13.2317820	1.8957590
C	11.4026120	11.9367330	4.6213460
H	11.5077460	11.4328540	5.5855460
H	12.3980490	12.0810790	4.1943500
H	10.9411110	12.9133910	4.7764840
C	11.1098190	9.6939370	3.4834920
H	10.4653290	9.1206730	2.8147420
H	12.1110440	9.7434990	3.0498330
H	11.1735380	9.1781640	4.4451990
C	8.3733120	13.0898160	0.5935940
H	8.9500450	12.3147340	0.0816720
H	7.9940170	13.7916560	-0.1528840
H	9.0283650	13.6320870	1.2781060
C	6.2730540	11.6830360	0.4546310
H	5.8261710	12.3511570	-0.2847850
H	6.8162390	10.8940210	-0.0713930
H	5.4739010	11.2296170	1.0440560
C	6.8032310	11.1333630	6.5968400
C	7.5988210	12.3750460	6.9841910
C	8.9768980	12.3134680	7.1983360
C	6.9633460	13.6165120	7.0786980
C	9.6985620	13.4593300	7.5207270
H	9.5040160	11.3714380	7.1129200
C	7.6829550	14.7603240	7.4020860
H	5.9020020	13.7074390	6.8818820
C	9.0547010	14.6864450	7.6283950
H	10.7682870	13.3877730	7.6831760
H	7.1697580	15.7126590	7.4717690
H	9.6158030	15.5788090	7.8813050
C	7.5251130	9.8256190	7.0287020
O	7.8567560	9.7430420	8.1879100
C	7.7160150	8.6894390	6.0682610
H	6.7577550	8.3968790	5.6315910
H	8.3603670	9.0039620	5.2441500
H	8.1587000	7.8501050	6.6025160

TS A_{keto}-B_{keto}

Gibbs Free Energy = -1742.110535 a.u.

Number of imaginary frequencies: 1 (-110.3)

C	4.3437590	12.2378380	4.8607960
C	3.8504280	11.7886770	3.7114130
H	4.0082430	13.1850700	5.2750480
H	3.0957520	12.3488500	3.1700040
S	7.0106810	12.3675690	5.5088140
P	7.5843160	11.4226780	3.5091200
O	6.7291890	10.4054050	2.8637010
O	7.1968860	12.8102850	2.7553740
O	9.1588980	11.5442870	3.3705340
C	5.3758980	11.4955270	5.6443490
H	5.5307150	10.4746590	5.2955970
H	5.1749630	11.5061300	6.7165400
H	4.1976850	10.8556180	3.2794900
C	7.9198080	14.0515180	2.9196770
H	8.5359480	13.9929890	3.8239050
C	10.1620660	10.4847250	3.3083300
H	9.7010700	9.5628400	3.6577970
C	8.8172120	14.2542320	1.7125520

H	8.2119090	14.3007860	0.8035410
H	9.3697260	15.1917900	1.8116280
H	9.5300790	13.4336110	1.6220240
C	6.8855410	15.1495520	3.0721410
H	6.2523730	14.9694800	3.9437550
H	7.3791750	16.1166260	3.1920870
H	6.2507310	15.1886760	2.1832040
C	10.5878210	10.3532830	1.8600580
H	11.0281460	11.2874250	1.5028490
H	11.3344160	9.5603190	1.7714890
H	9.7345560	10.0974120	1.2283300
C	11.2865110	10.9082220	4.2286470
H	12.0557360	10.1329990	4.2554160
H	11.7381970	11.8364940	3.8684800
H	10.9156780	11.0723370	5.2426720
C	8.0769300	11.5332480	6.6128880
C	8.5683650	12.2591720	7.7939060
C	7.7147030	13.0856620	8.5398080
C	9.9087860	12.1607530	8.1973600
C	8.1797320	13.7801130	9.6508100
H	6.6707650	13.1760260	8.2553720
C	10.3669570	12.8385270	9.3216720
H	10.5993930	11.5629820	7.6130980
C	9.5067360	13.6537380	10.0532610
H	7.4995030	14.4128070	10.2098280
H	11.4065240	12.7442100	9.6152040
H	9.8681000	14.1894400	10.9233070
C	8.4038070	10.2681410	6.1527970
O	7.9810230	9.8797420	5.0092590
C	9.2252230	9.2872190	6.9444620
H	10.2333020	9.2225410	6.5239330
H	9.2953220	9.5524830	7.9982030
H	8.7615870	8.3041310	6.8443990

TS A_{keto}-C_{keto}

Gibbs Free Energy = -1742.095811 a.u.

Number of imaginary frequencies: 1 (-282.8)

C	4.3628250	10.9557060	6.2276530
C	5.0613930	11.2762940	7.3605570
H	3.7254520	10.0760640	6.2264180
H	4.8939120	10.7413440	8.2898110
S	6.7817750	10.3674200	4.8709100
P	7.8566720	11.6718680	3.5553340
O	7.4743670	13.0956380	3.6123720
O	9.3395570	11.2571550	3.8670270
O	7.5280840	10.9608570	2.1752630
C	4.7415790	11.5036750	4.9903850
H	5.1964190	12.4891680	4.9556440
H	4.2418760	11.1868960	4.0801110
H	5.6180760	12.2017920	7.4329080
C	10.4710600	11.9952550	3.2724160
H	10.1486810	12.3626930	2.2931320
C	6.4353380	11.4251880	1.3109640
H	5.7212440	11.9695780	1.9350530
C	10.8249040	13.1437300	4.1913090
H	11.0827490	12.7608480	5.1820130
H	11.6856870	13.6805540	3.7853290
H	9.9902790	13.8400390	4.2860730
C	11.5789330	10.9802890	3.1134110
H	11.2621060	10.1571470	2.4712190
H	12.4499060	11.4618800	2.6637720
H	11.8647390	10.5820480	4.0900040
C	7.0245830	12.3468230	0.2653650
H	7.7734810	11.8127830	-0.3250210
H	6.2349650	12.6952230	-0.4042310
H	7.4906210	13.2154960	0.7343770
C	5.7940280	10.1822130	0.7363120

H	4.9618300	10.4662340	0.0886940
H	6.5211930	9.6211500	0.1444970
H	5.4136360	9.5385970	1.5320460
C	7.3463600	10.5493310	6.4869910
C	8.2237540	11.6716010	6.9026070
C	9.4265620	11.4063230	7.5782580
C	7.9019740	13.0091420	6.6405730
C	10.2560840	12.4402720	7.9931120
H	9.7059880	10.3810820	7.7808450
C	8.7369450	14.0445850	7.0526100
H	6.9961390	13.2553610	6.1014210
C	9.9133530	13.7675320	7.7391690
H	11.1780240	12.2070850	8.5145110
H	8.4597670	15.0701840	6.8351680
H	10.5604620	14.5733870	8.0665390
C	7.1987130	9.3602300	7.3273020
O	7.6376030	9.3250930	8.4737730
C	6.4676920	8.1480880	6.7782570
H	5.4898770	8.4040350	6.3642140
H	7.0538340	7.6793420	5.9830690
H	6.3370450	7.4352890	7.5910840

A_{ester}

Gibbs Free Energy = -1817.343607 a.u.

Number of imaginary frequencies: 0

C	4.4102630	12.2673700	4.9774840
C	3.8273990	11.9680200	3.8206020
H	4.1597150	13.1865830	5.5007880
H	3.0820060	12.6240870	3.3843770
S	7.0858190	12.2214800	5.4631340
P	7.4995730	11.6302090	3.3599950
O	6.6103630	10.5874470	2.8275910
O	7.3260890	13.0266000	2.6371740
O	9.0534580	11.3816890	3.4045530
C	5.4381690	11.3936160	5.6201040
H	5.5214060	10.4092580	5.1636730
H	5.3072290	11.3101020	6.7003990
H	4.0821860	11.0611840	3.2817190
C	8.1966600	14.1775130	2.9061150
H	8.7315300	13.9933370	3.8437620
C	9.6784110	10.0790320	3.1175150
H	8.9632550	9.3098980	3.4108260
C	9.1817890	14.2922120	1.7628680
H	8.6472590	14.4447940	0.8222200
H	9.8408650	15.1462160	1.9342240
H	9.7915130	13.3904000	1.6856130
C	7.2869280	15.3765680	3.0509820
H	6.5781450	15.2290300	3.8683980
H	7.8842670	16.2662240	3.2611770
H	6.7300410	15.5383820	2.1249600
C	9.9666010	10.0199680	1.6327140
H	10.6590530	10.8151680	1.3457830
H	10.4218450	9.0568680	1.3902070
H	9.0462720	10.1203640	1.0530370
C	10.9178070	10.0126850	3.9791990
H	11.4170420	9.0537220	3.8229680
H	11.6104400	10.8143150	3.7100930
H	10.6651780	10.1080630	5.0366740
C	8.2438820	11.4928850	6.4963330
C	9.0373190	12.4003180	7.3429490
C	8.4577110	13.5355990	7.9348480
C	10.4070340	12.1801430	7.5713510
C	9.2103580	14.4165070	8.7036690
H	7.3974960	13.7257570	7.8027930
C	11.1517750	13.0500290	8.3593520
H	10.8889200	11.3209630	7.1230340
C	10.5633450	14.1779430	8.9273070

H	8.7301200	15.2835030	9.1439900
H	12.2060520	12.8507270	8.5184420
H	11.1491610	14.8572830	9.5354700
C	8.4027920	10.0873860	6.3277460
O	7.8025920	9.4107960	5.4940300
O	9.2804680	9.5183760	7.1890200
C	9.4669830	8.1110200	7.0393910
H	10.2186780	7.8341690	7.7760860
H	8.5377400	7.5734310	7.2338510
H	9.8198900	7.8699900	6.0349700

B_{ester}

Gibbs Free Energy = -1817.375707 a.u.

Number of imaginary frequencies: 0

C	3.5167790	11.0044450	5.7775440
C	2.6079620	10.9064740	4.8118950
H	3.2059790	11.1183690	6.8134060
H	1.5460190	10.9227230	5.0316290
S	5.6516340	12.6712480	5.8660150
P	8.1059940	11.4782500	3.0531210
O	7.1648160	10.8958710	2.0871030
O	8.1135640	13.0489170	3.1160530
O	9.6412830	11.1277560	2.8855920
C	4.9895940	10.9868060	5.5205800
H	5.2110620	10.7136330	4.4903740
H	5.5059500	10.3049490	6.1989310
H	2.9024430	10.8028550	3.7713550
C	9.1911920	13.8759090	3.6731280
H	9.7295270	13.2767230	4.4134670
C	10.1066190	9.7417420	2.8530840
H	9.4035160	9.1372950	3.4349890
C	10.1191060	14.2741890	2.5442600
H	9.5646970	14.8341260	1.7870900
H	10.9146880	14.9120570	2.9363690
H	10.5711040	13.3959490	2.0819310
C	8.5180080	15.0591850	4.3321220
H	7.8275410	14.7334840	5.1113890
H	9.2747670	15.7062650	4.7815690
H	7.9637640	15.6356670	3.5873230
C	10.1350760	9.2712770	1.4133300
H	10.8136370	9.8979200	0.8292620
H	10.4904830	8.2390970	1.3729340
H	9.1389860	9.3157190	0.9699390
C	11.4677260	9.7409600	3.5128870
H	11.8501980	8.7194490	3.5689790
H	12.1668470	10.3434730	2.9272370
H	11.4078060	10.1533620	4.5212430
C	7.3163220	12.3521300	6.4042250
C	7.7717100	13.0278400	7.6456360
C	6.9634610	13.0435580	8.7870320
C	9.0092560	13.6803110	7.6837880
C	7.3954080	13.6736640	9.9491010
H	5.9953260	12.5563630	8.7610540
C	9.4359970	14.3170100	8.8439590
H	9.6325940	13.6896910	6.7967960
C	8.6321780	14.3127350	9.9814150
H	6.7624660	13.6689900	10.8291810
H	10.3946830	14.8229720	8.8573740
H	8.9646330	14.8105000	10.8851690
C	8.1312650	11.5567810	5.6968080
O	7.7062560	10.9442930	4.5414620
O	9.3880150	11.2405790	6.0646170
C	9.5255290	9.8860410	6.5292930
H	9.2685620	9.1775750	5.7393030
H	10.5674810	9.7627010	6.8165270
H	8.8792800	9.7314150	7.3973180

C_{ester}

Gibbs Free Energy = -1817.397648 a.u.

Number of imaginary frequencies: 0

C	4.6093250	9.9002810	7.1635960
C	5.4106200	11.1420010	7.4338320
H	5.0709260	8.9485140	7.4227700
H	5.7054800	11.1756010	8.4872950
S	6.2134560	11.3107930	4.8363140
P	7.9565650	11.9369900	3.8516590
O	8.3049010	13.3730650	3.9307640
O	9.0497940	10.9155450	4.3808520
O	7.6483240	11.4409100	2.3647260
C	3.3835060	9.9131510	6.6508450
H	2.8933740	10.8458920	6.3855190
H	2.8318190	8.9947600	6.4819520
H	4.8025840	12.0215290	7.2228890
C	10.3992920	10.9351960	3.8119800
H	10.3284220	11.3284210	2.7923680
C	7.3206760	12.3772830	1.2918530
H	6.8424470	13.2510760	1.7413180
C	11.2851830	11.8264070	4.6578660
H	11.3670230	11.4255940	5.6713090
H	12.2847890	11.8660540	4.2181170
H	10.8821470	12.8395370	4.7073060
C	10.8525900	9.4923110	3.7783900
H	10.1739430	8.8885910	3.1733480
H	11.8561840	9.4297210	3.3517210
H	10.8800220	9.0867810	4.7930320
C	8.6041130	12.7853900	0.5984100
H	9.1065680	11.9042660	0.1901140
H	8.3783890	13.4690270	-0.2234660
H	9.2753810	13.2917260	1.2949850
C	6.3496840	11.6556030	0.3829230
H	6.0539480	12.3142490	-0.4365800
H	6.8183550	10.7629130	-0.0387070
H	5.4549370	11.3586030	0.9331430
C	6.7363940	11.2282470	6.6194560
C	7.5428550	12.4635020	7.0098650
C	8.9213720	12.4054470	7.2155180
C	6.9031220	13.7029130	7.1101250
C	9.6415030	13.5552250	7.5296720
H	9.4496380	11.4650300	7.1274140
C	7.6209250	14.8494060	7.4260970
H	5.8402190	13.7884580	6.9183120
C	8.9953480	14.7803820	7.6401000
H	10.7128060	13.4871470	7.6830240
H	7.1050080	15.7999830	7.4984560
H	9.5559810	15.6752240	7.8850350
C	7.4901750	9.9296500	6.9560950
O	7.9398530	9.7379700	8.0594250
O	7.5155600	9.0330840	5.9875750
C	8.1742370	7.7974960	6.2956490
H	8.1694090	7.2254010	5.3714110
H	9.1960760	7.9854480	6.6248760
H	7.6293630	7.2650510	7.0764560

TS A_{ester}-B_{ester}

Gibbs Free Energy = -1817.320182 a.u.

Number of imaginary frequencies: 1 (-19.3)

C	10.4642640	11.6389450	6.1673360
C	9.8191870	12.0961880	7.2825370

H	10.7552660	12.3386550	5.3911150
H	9.7452060	13.1574300	7.4983730
S	8.1136760	10.1274520	5.5332590
P	8.0889260	10.3384720	3.3873030
O	8.1064910	8.9403590	2.9040640
O	6.8259360	11.2122070	3.0324310
O	9.3029340	11.2300470	2.9255700
C	10.3802560	10.2720220	5.8442710
H	10.3498540	9.5450700	6.6499230
H	10.7931070	9.8999960	4.9102150
H	9.5514790	11.4174250	8.0862330
C	5.4690660	10.6698170	3.1901570
H	5.5327430	9.7550790	3.7877720
C	10.3768460	10.6831540	2.0857460
H	10.5262900	9.6403080	2.3743680
C	4.6626330	11.7189680	3.9219030
H	4.6561050	12.6526010	3.3539390
H	3.6327290	11.3725420	4.0337250
H	5.0730720	11.9088820	4.9158130
C	4.9452590	10.3502460	1.8066830
H	5.5810190	9.6122600	1.3138720
H	3.9337970	9.9451820	1.8826640
H	4.9143610	11.2578460	1.1988150
C	9.9454680	10.7733760	0.6369450
H	9.7566910	11.8150210	0.3652000
H	10.7370130	10.3816600	-0.0059140
H	9.0392760	10.1891700	0.4620790
C	11.6055480	11.5056370	2.4020250
H	12.4455900	11.1463750	1.8035170
H	11.4303960	12.5569500	2.1605520
H	11.8699460	11.4228910	3.4578660
C	7.5470500	11.4967540	6.3892300
C	6.7480070	11.2132140	7.6065590
C	6.7943870	12.1027990	8.6919590
C	5.9378650	10.0755410	7.7248640
C	6.0568670	11.8626910	9.8443520
H	7.4156900	12.9875540	8.6257720
C	5.2126940	9.8283760	8.8869880
H	5.8621620	9.3803350	6.8963670
C	5.2648430	10.7209110	9.9523460
H	6.1087060	12.5674070	10.6669460
H	4.5947480	8.9396260	8.9500620
H	4.6950010	10.5321060	10.8548050
C	7.4961800	12.8255800	5.7943350
O	6.8441190	13.7643280	6.2134070
O	8.2560860	12.9137690	4.6924170
C	8.1505300	14.1095030	3.9276050
H	7.1124030	14.2971210	3.6488880
H	8.5372650	14.9616510	4.4892630
H	8.7532270	13.9389440	3.0377170

TS A_{ester}-C_{ester}

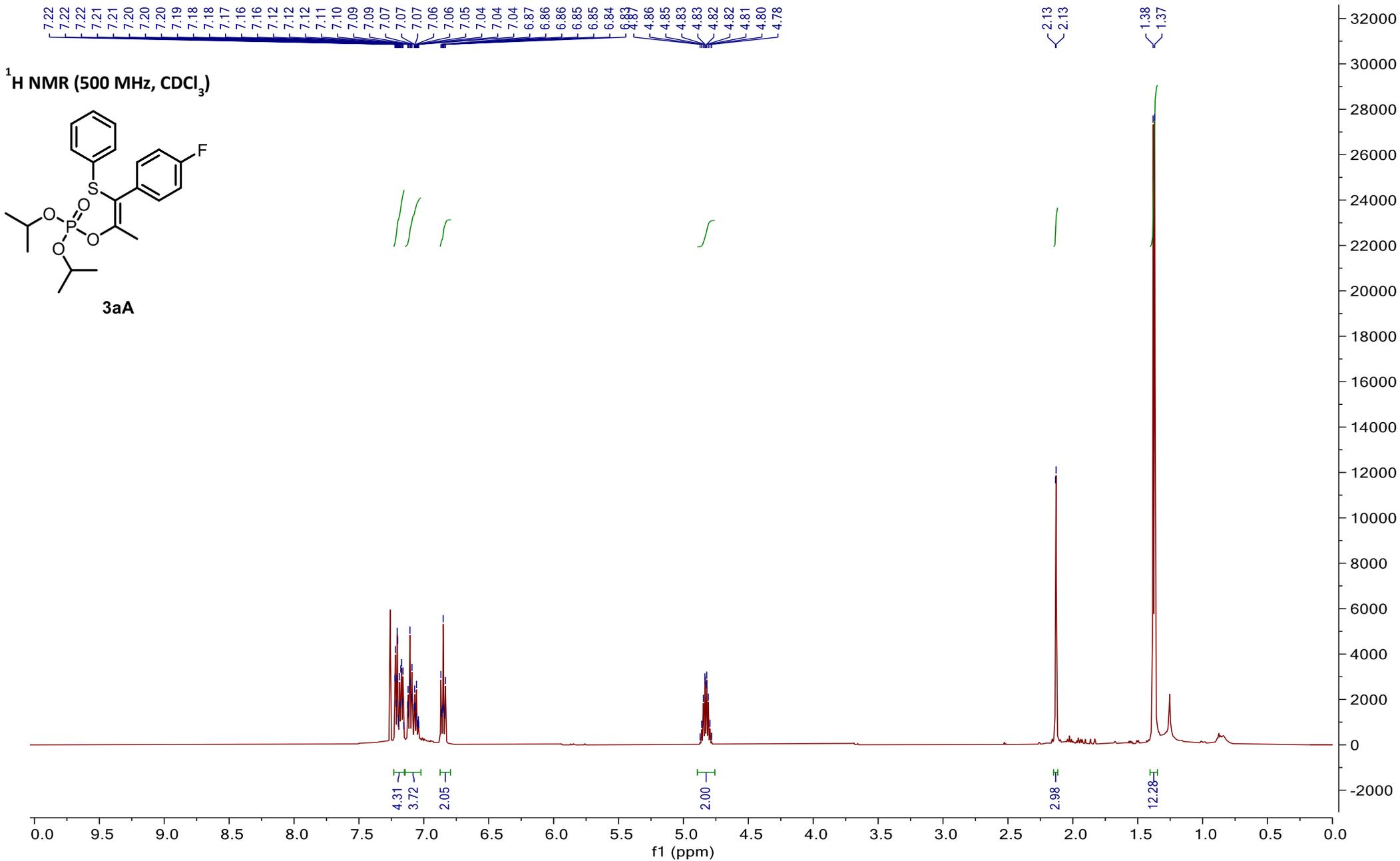
Gibbs Free Energy = -1817.325097 a.u.

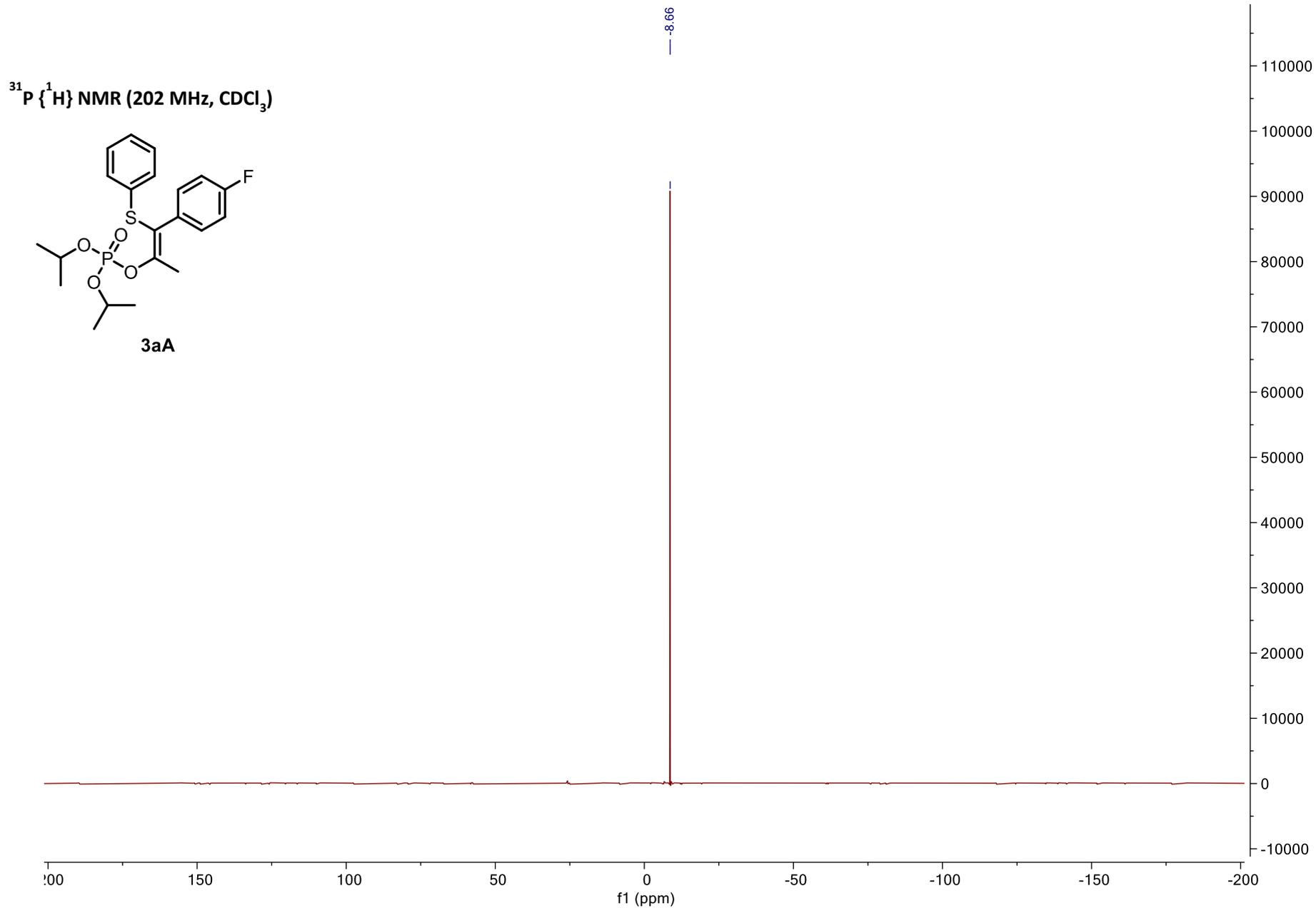
Number of imaginary frequencies: 1 (-282.5)

C	4.8452030	13.1572830	5.3123440
C	4.0038850	12.8823580	4.3220580
H	4.8795520	14.1522750	5.7495480
H	3.3259920	13.6348710	3.9339540
S	7.5507120	12.5576410	5.5469700
P	7.7982540	11.1520380	3.6776600
O	6.7858940	10.0724330	3.5877690
O	7.0557380	12.4027700	2.9077560
O	9.1185050	11.2704930	2.7917720
C	5.7684220	12.1412160	5.8927860
H	5.5952830	11.1369530	5.5047390
H	5.7319110	12.1345470	6.9845310
H	3.9699210	11.8953490	3.8707010

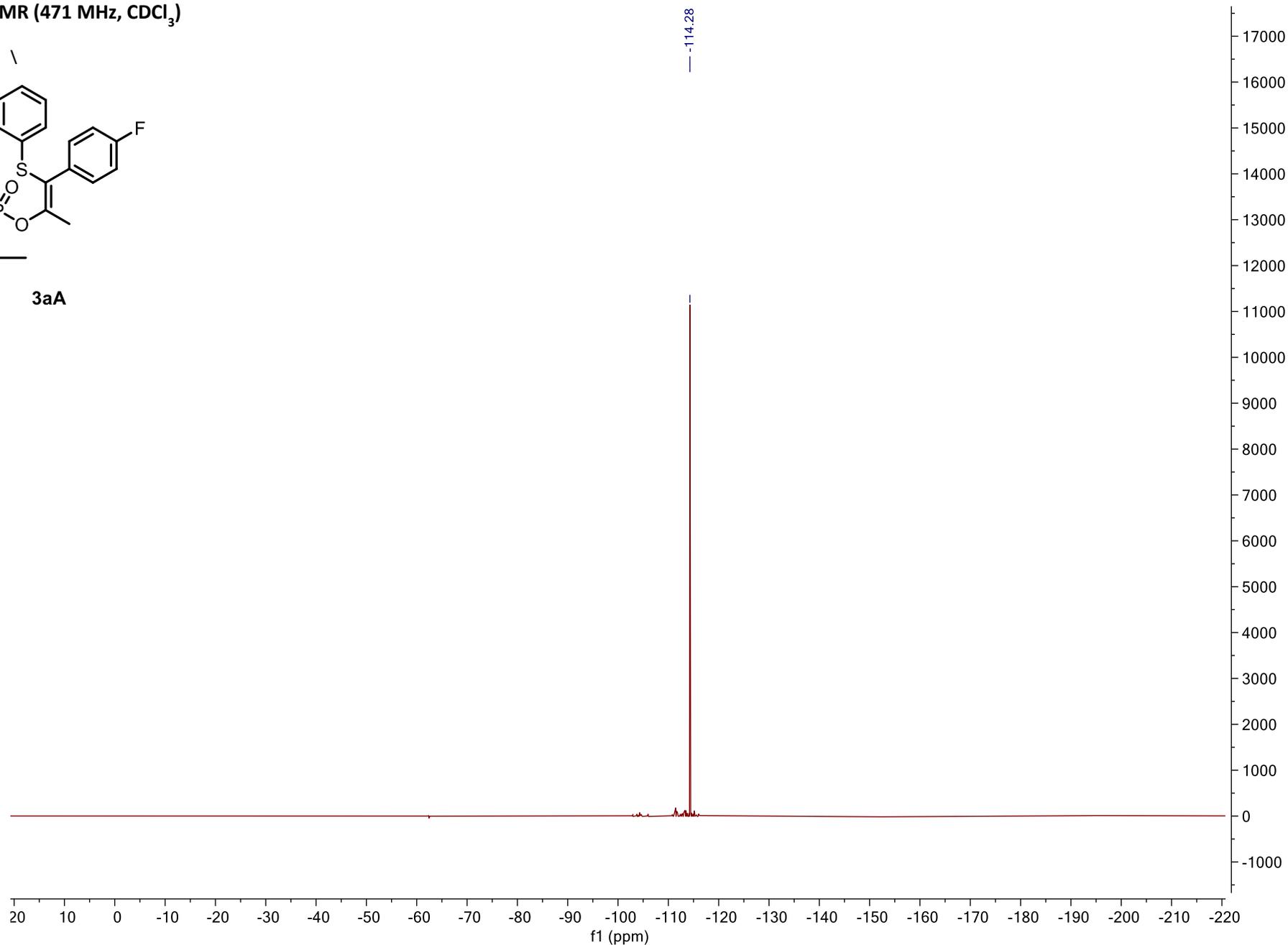
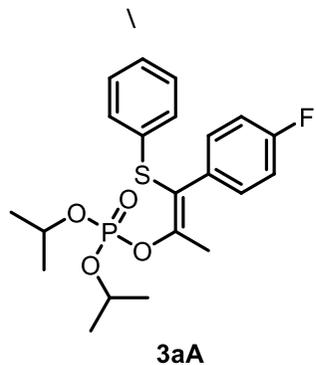
C	7.7259520	13.5983760	2.4542740
H	8.6754740	13.7028050	2.9906870
C	10.3389130	10.4782570	2.7704260
H	10.1257580	9.4981160	3.1947850
C	7.9924930	13.4777880	0.9633320
H	7.0447270	13.3857560	0.4258840
H	8.5096690	14.3703930	0.6021970
H	8.6067970	12.6031270	0.7496560
C	6.8266030	14.7783710	2.7738330
H	6.6709080	14.8793820	3.8496030
H	7.2804870	15.6997940	2.4008990
H	5.8531590	14.6488210	2.2936420
C	10.7110440	10.3438400	1.3067830
H	10.9052220	11.3262530	0.8693750
H	11.6161220	9.7386950	1.2163540
H	9.9091960	9.8579810	0.7479670
C	11.3995900	11.2032740	3.5750350
H	12.3301770	10.6305880	3.5612690
H	11.5920110	12.1852910	3.1340310
H	11.0915790	11.3409370	4.6133910
C	8.4099490	11.6264290	6.7550770
C	8.4677520	12.1012150	8.1414540
C	7.9881100	13.3829850	8.4707810
C	8.9673290	11.3118130	9.1957490
C	8.0194170	13.8577110	9.7766830
H	7.5882290	14.0313070	7.6986720
C	8.9964400	11.7947060	10.4987160
H	9.3314030	10.3149140	8.9976430
C	8.5263110	13.0689760	10.8042050
H	7.6430400	14.8526790	9.9869300
H	9.3888560	11.1591480	11.2850820
H	8.5500260	13.4373310	11.8229320
C	8.9741580	10.5050000	6.1881990
O	8.8509080	10.2016160	4.9414990
O	9.7173210	9.6807550	6.9230870
C	10.3378610	8.5739330	6.2494860
H	10.8833080	8.0418490	7.0253290
H	9.5843320	7.9254810	5.8037920
H	11.0264910	8.9319900	5.4834400

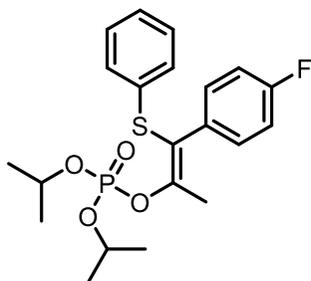
IV- NMR spectra



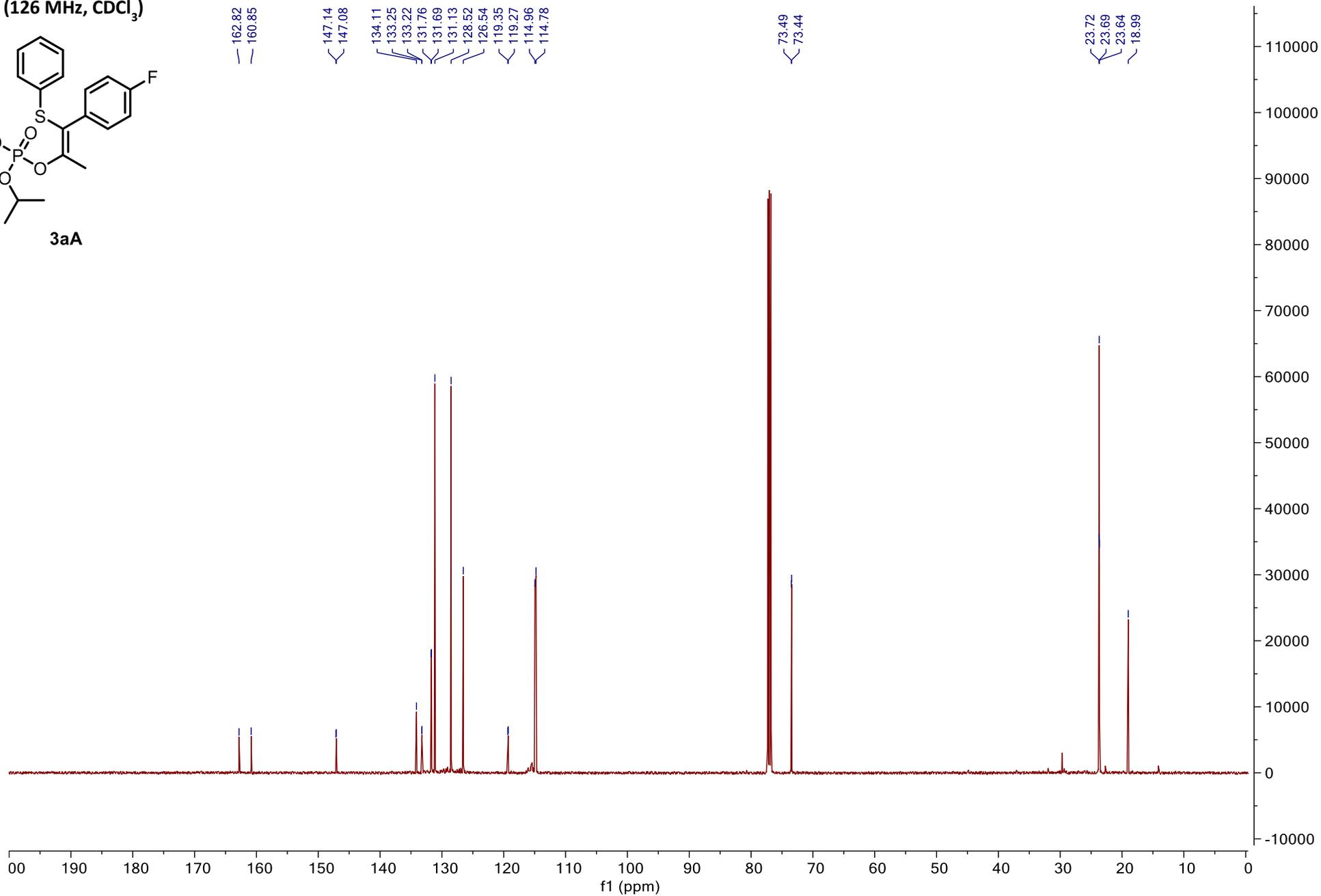


¹⁹F {¹H} NMR (471 MHz, CDCl₃)

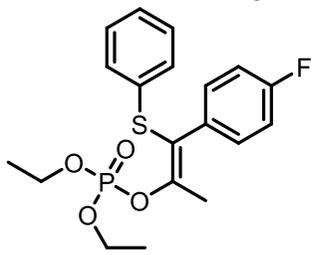


^{13}C NMR (126 MHz, CDCl_3)

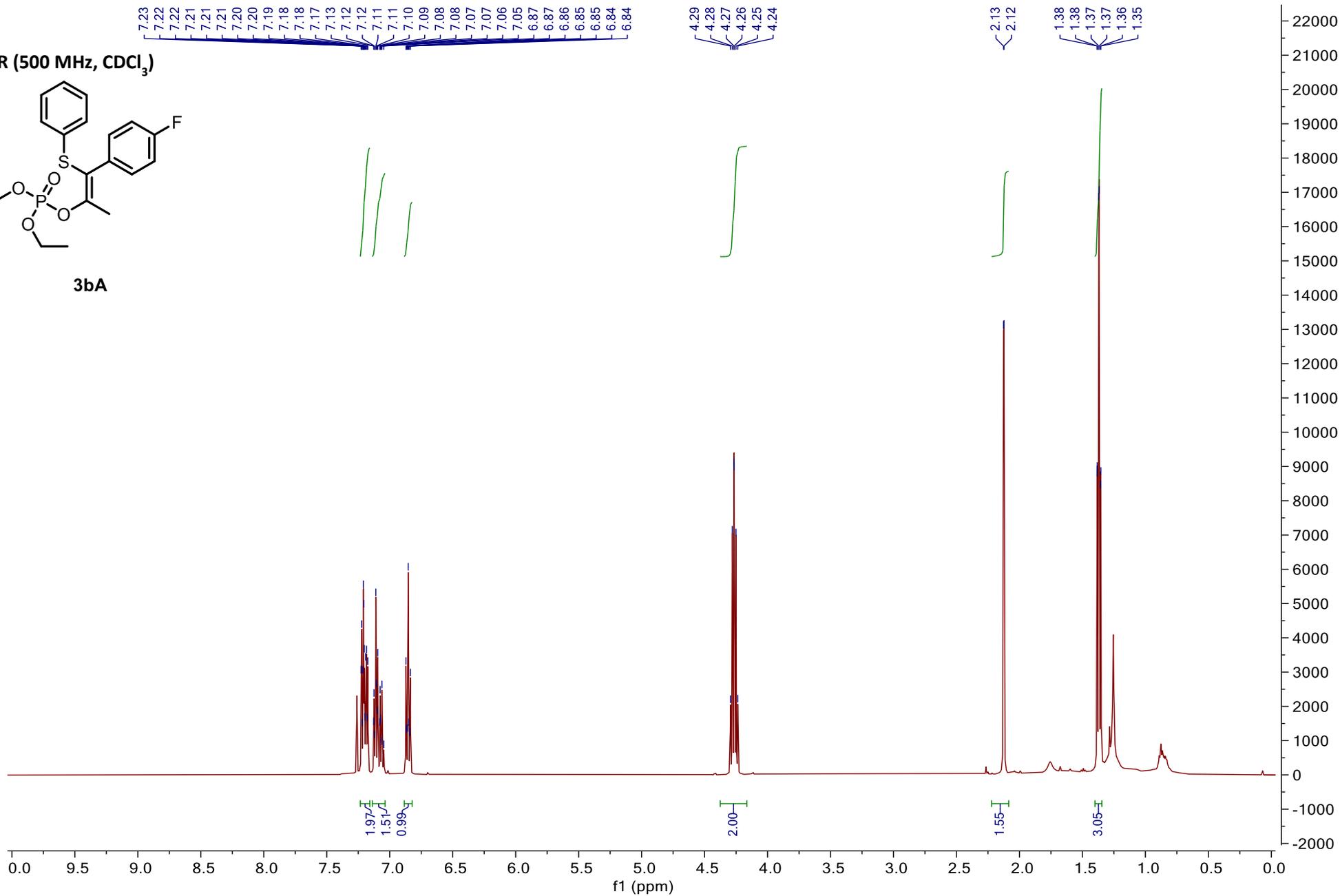
3aA



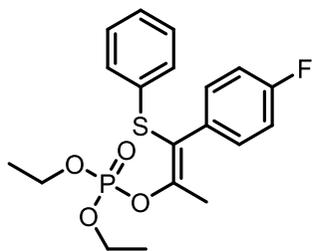
¹H NMR (500 MHz, CDCl₃)



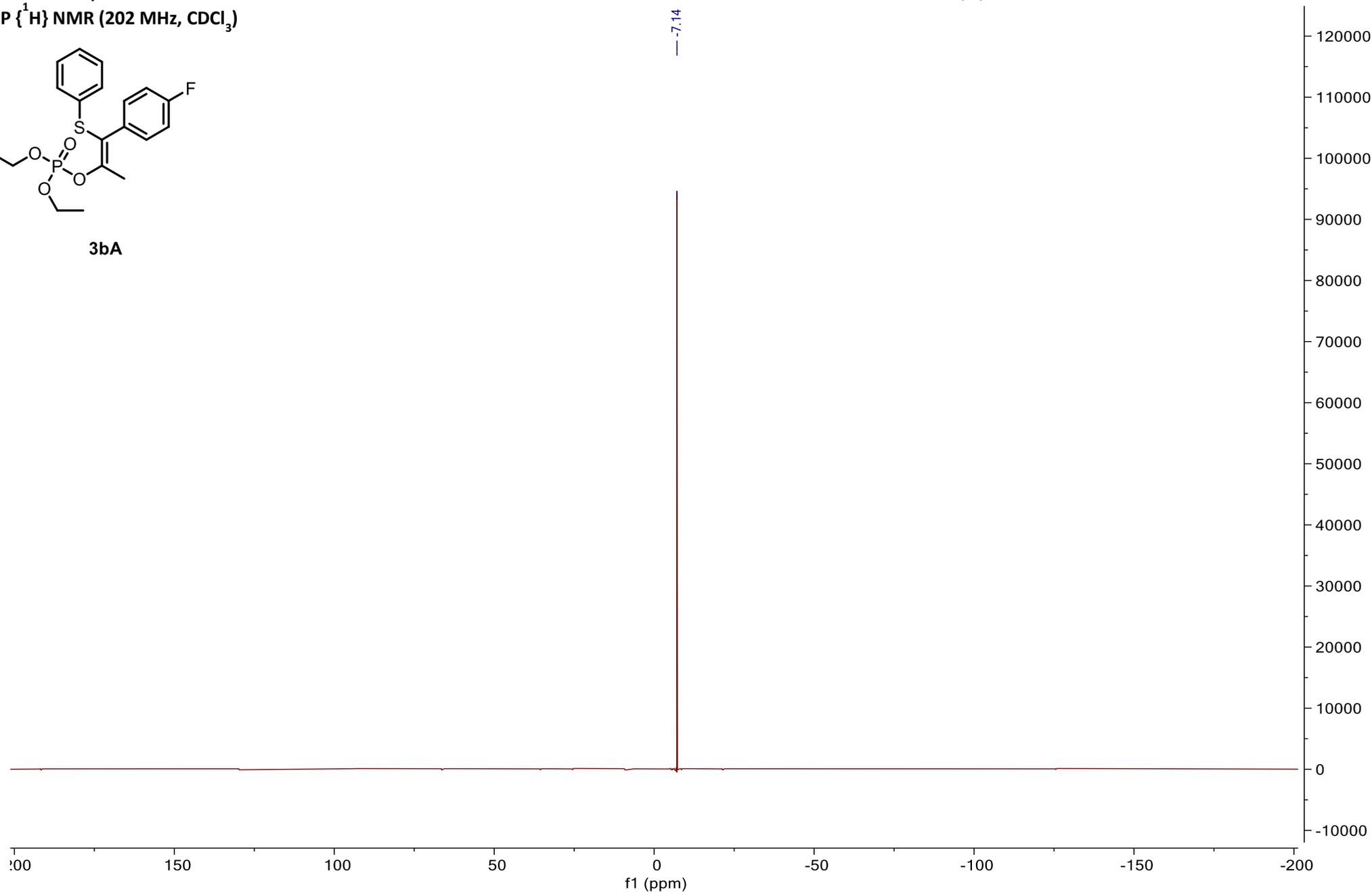
3bA



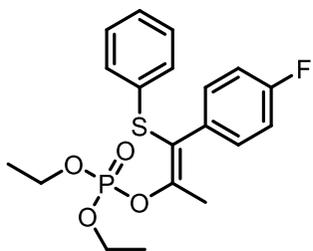
³¹P { ¹H } NMR (202 MHz, CDCl₃)



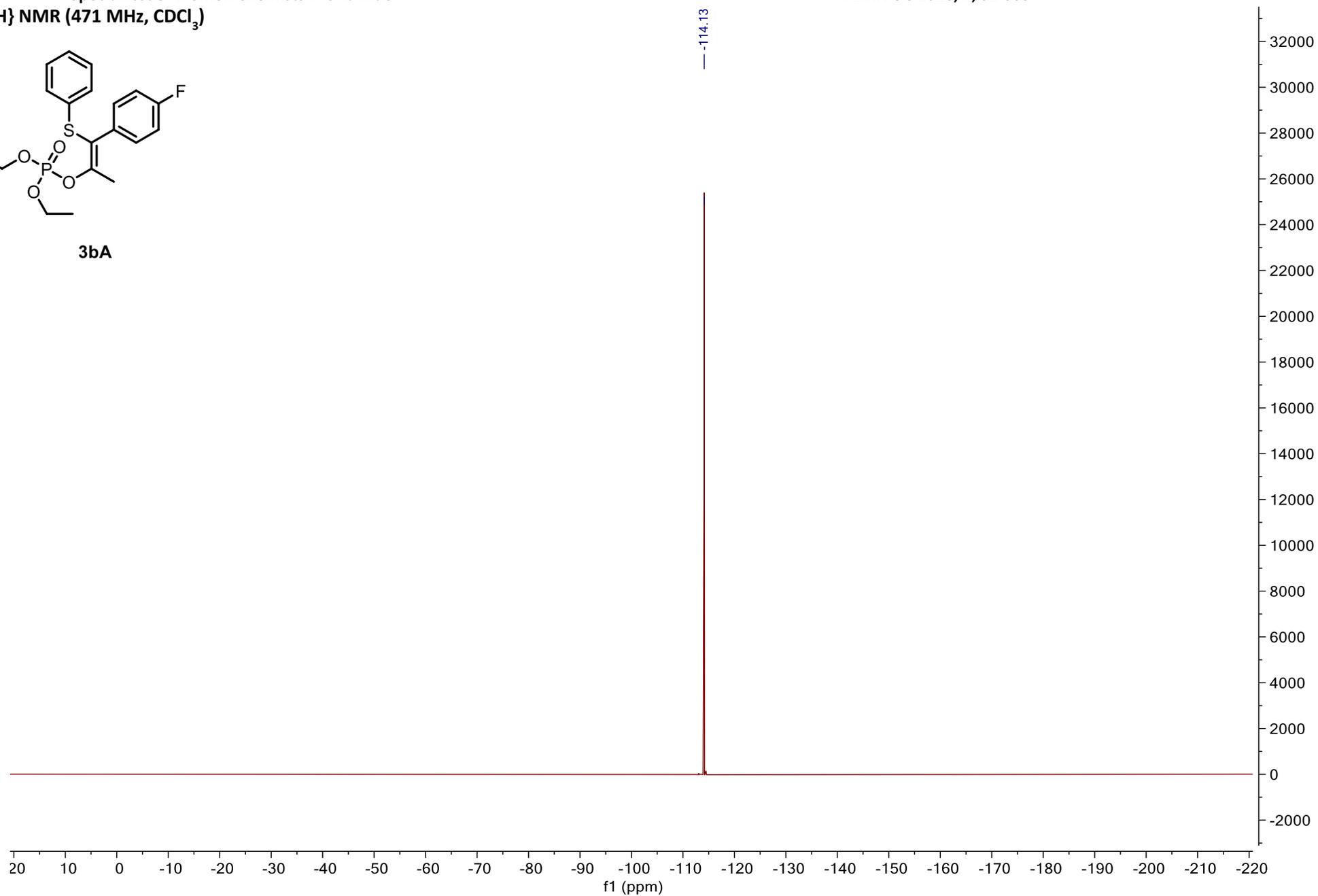
3bA



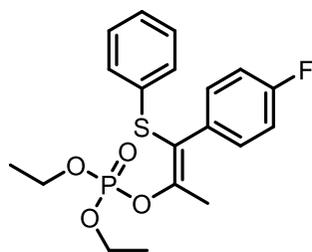
¹⁹F {¹H} NMR (471 MHz, CDCl₃)



3bA



¹³C NMR (126 MHz, CDCl₃)

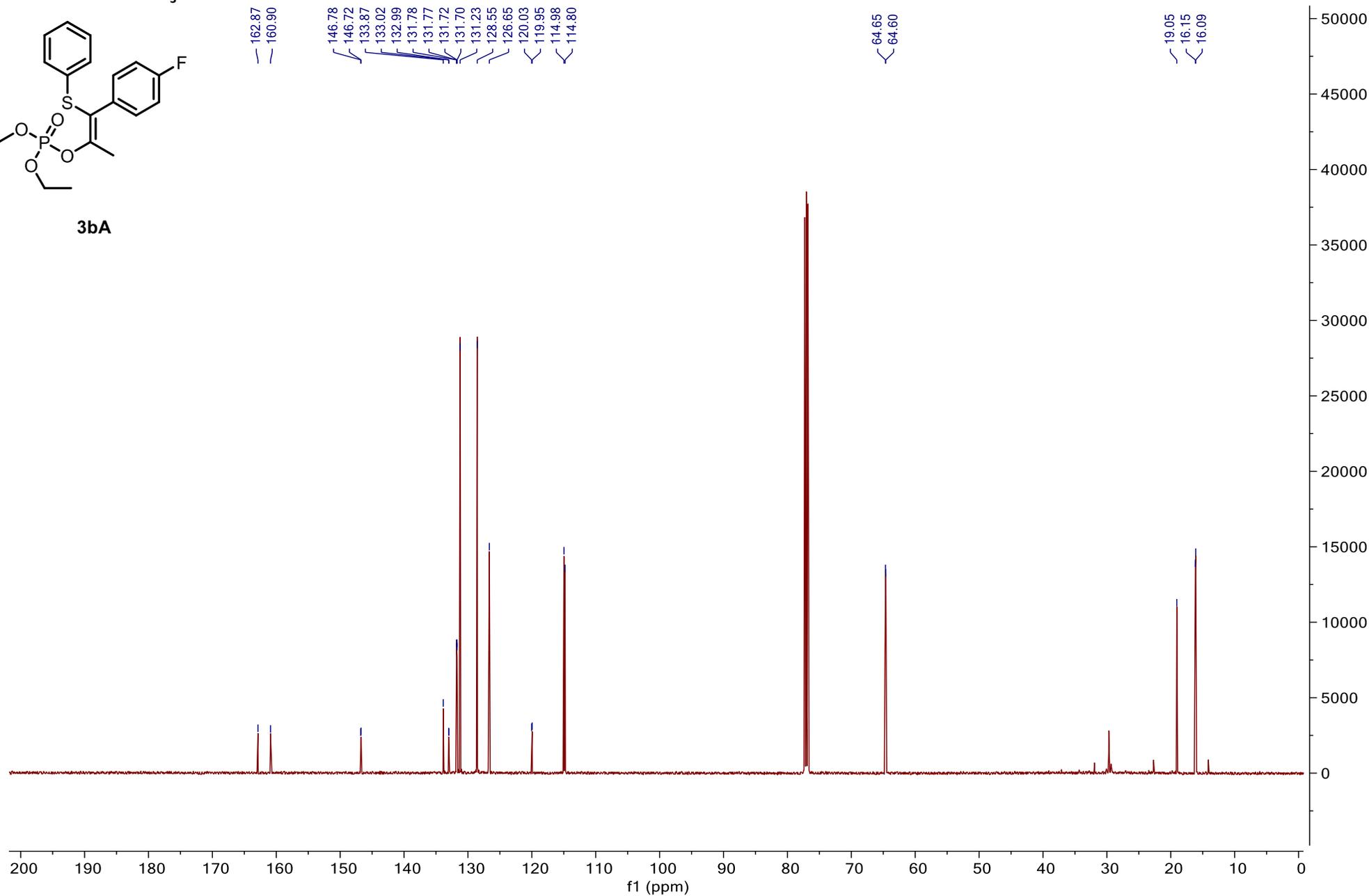


3bA

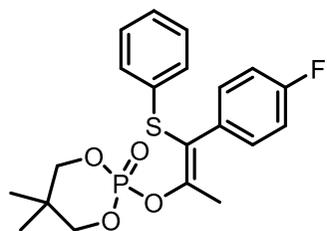
162.87
160.90
146.78
146.72
133.87
133.02
132.99
131.78
131.77
131.72
131.70
131.23
128.55
126.65
120.03
119.95
114.98
114.80

64.65
64.60

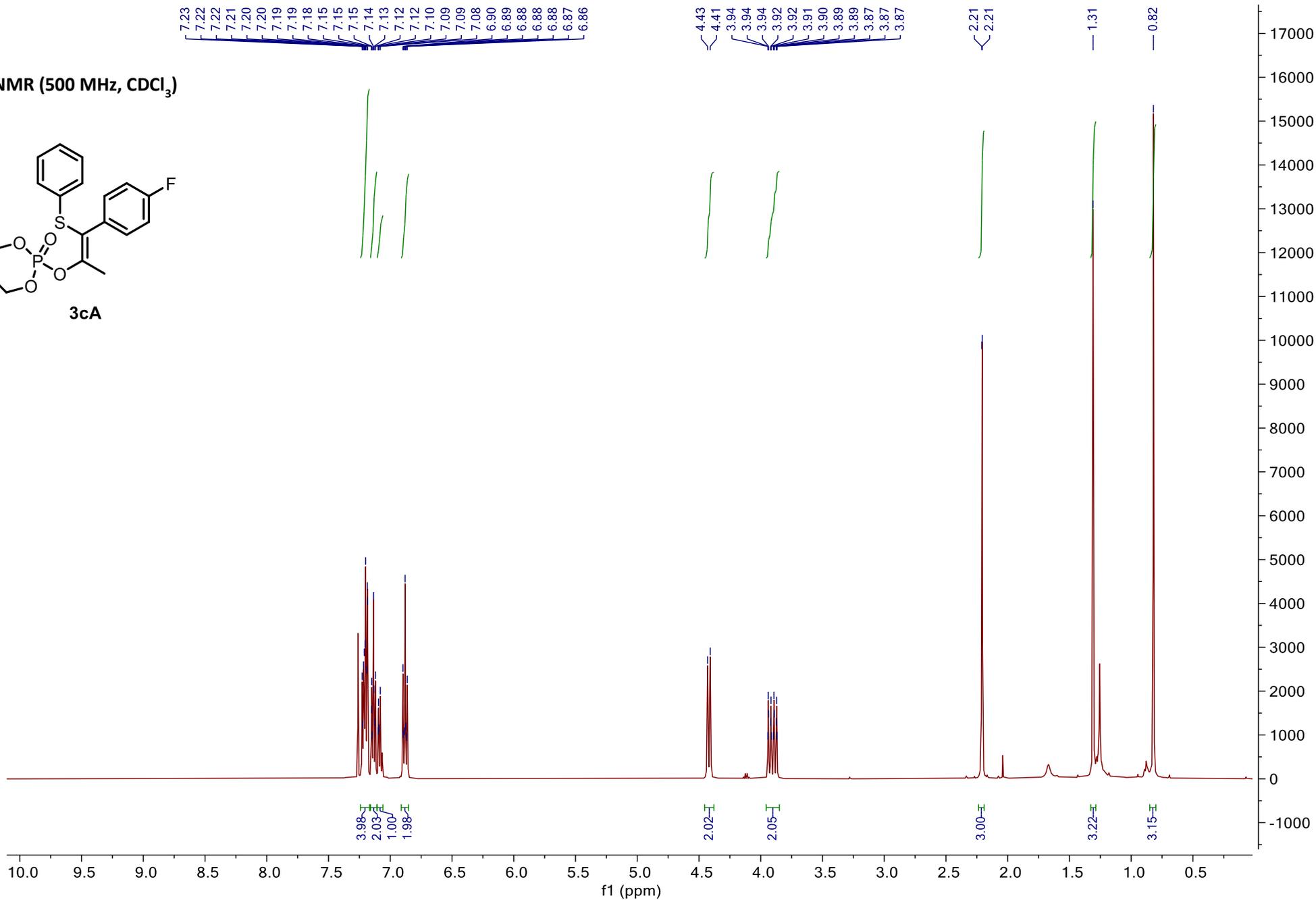
19.05
16.15
16.09



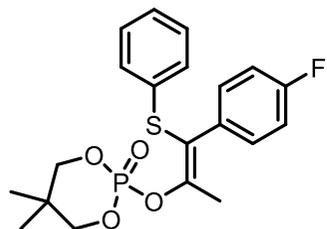
¹H NMR (500 MHz, CDCl₃)



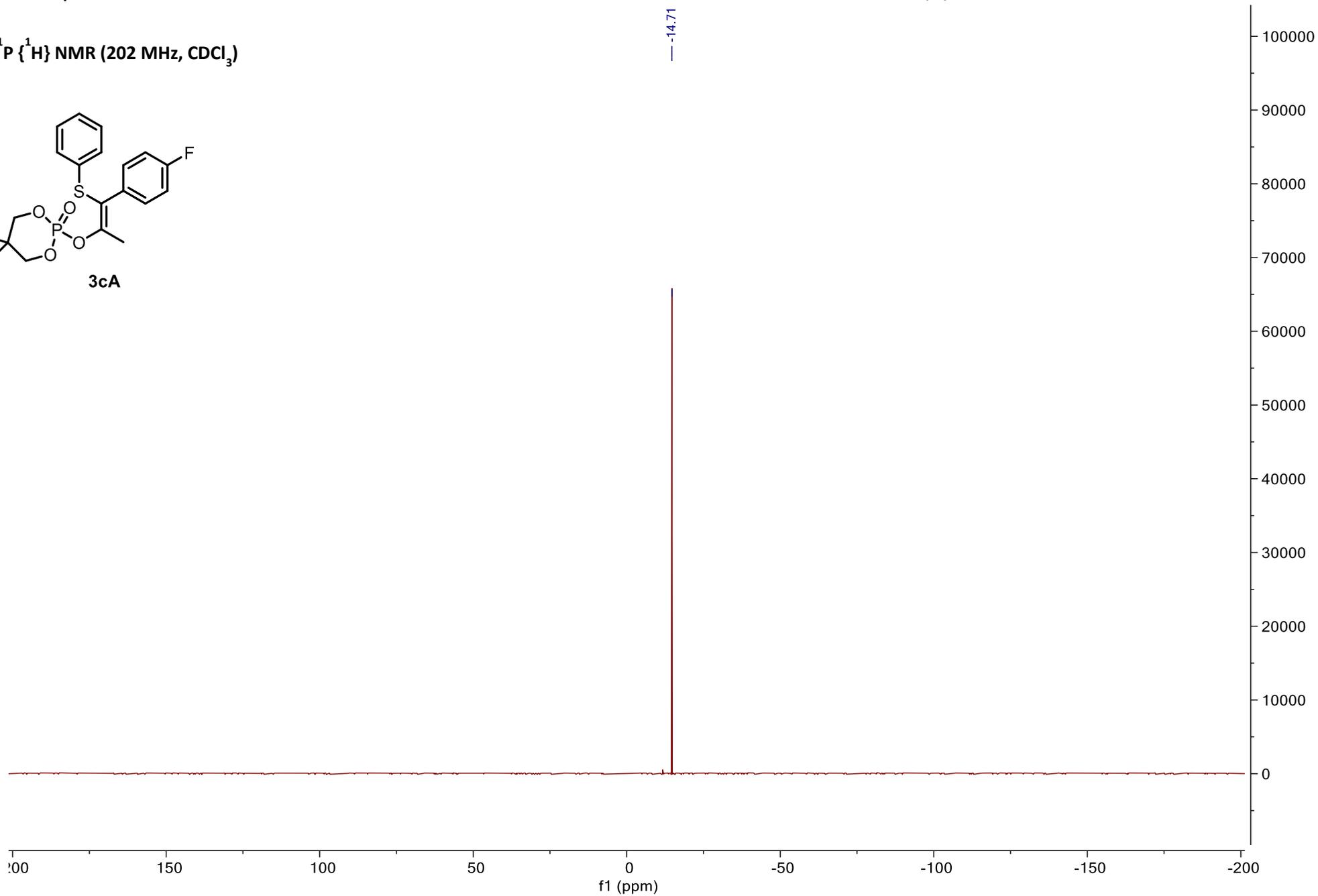
3cA



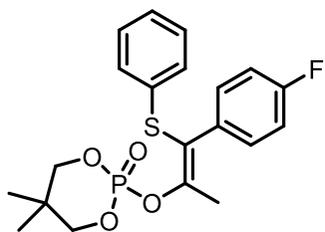
$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3)



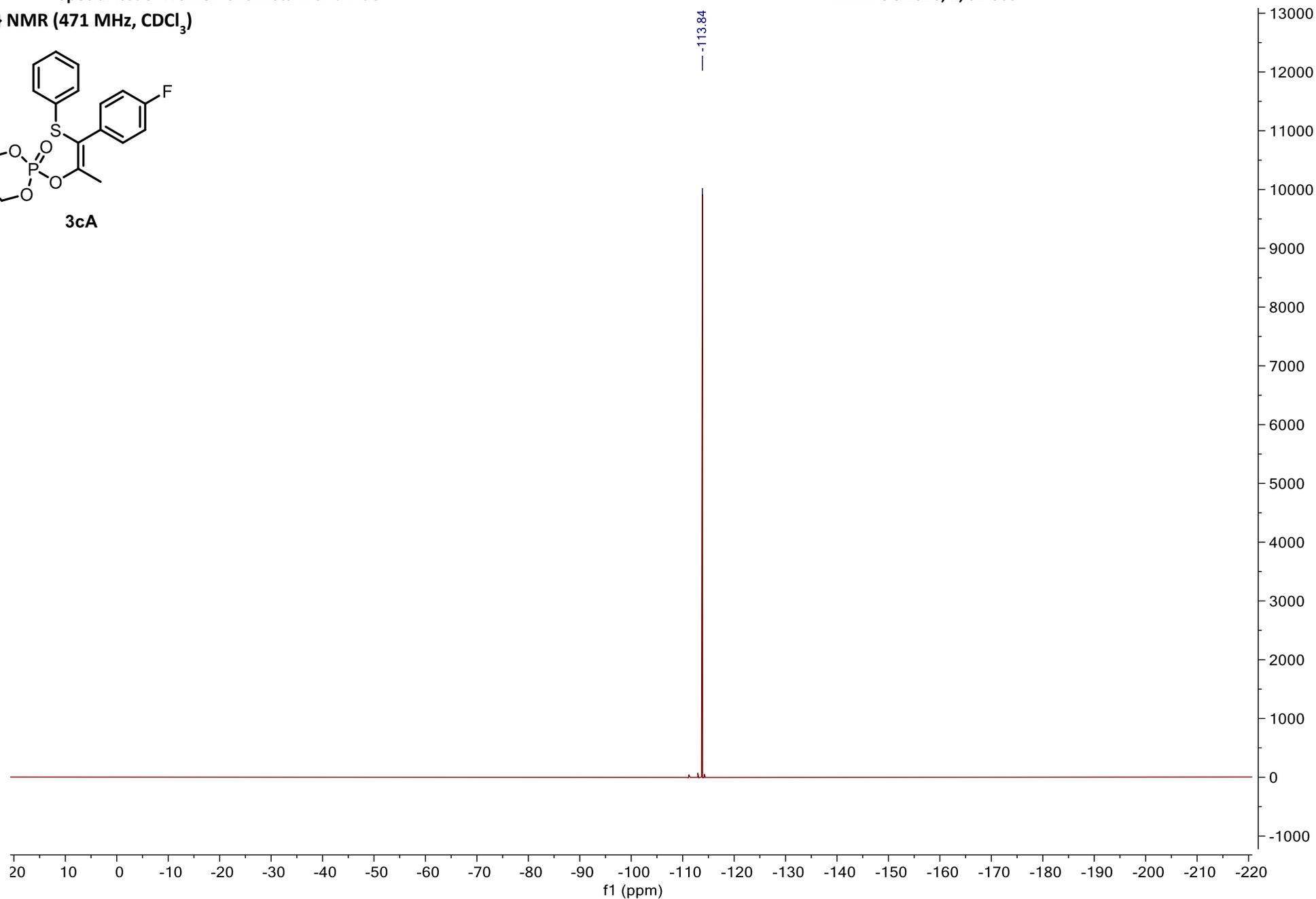
3cA

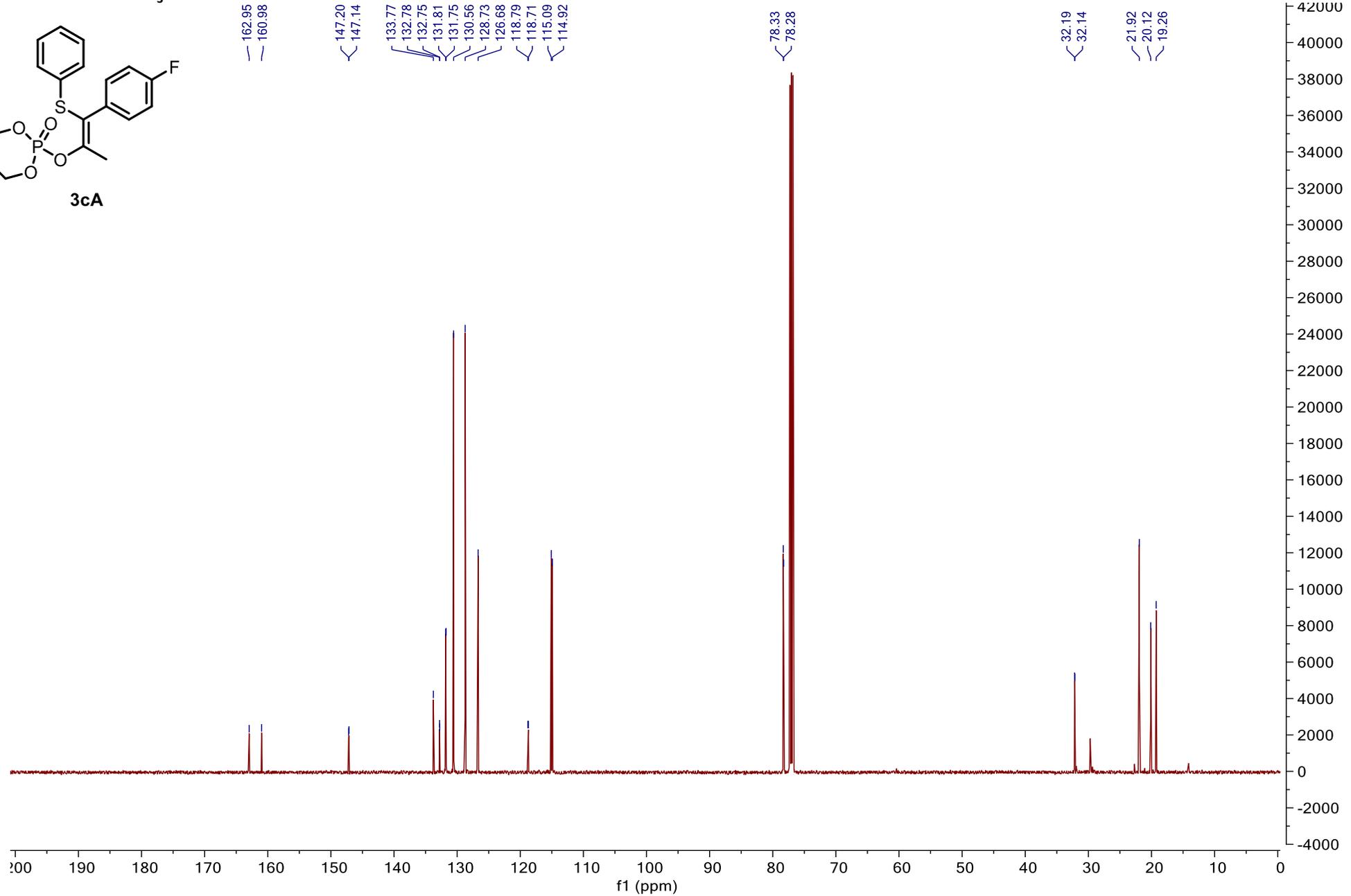
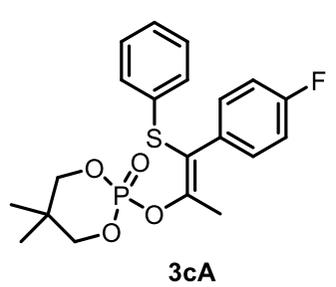


¹⁹F {¹H} NMR (471 MHz, CDCl₃)

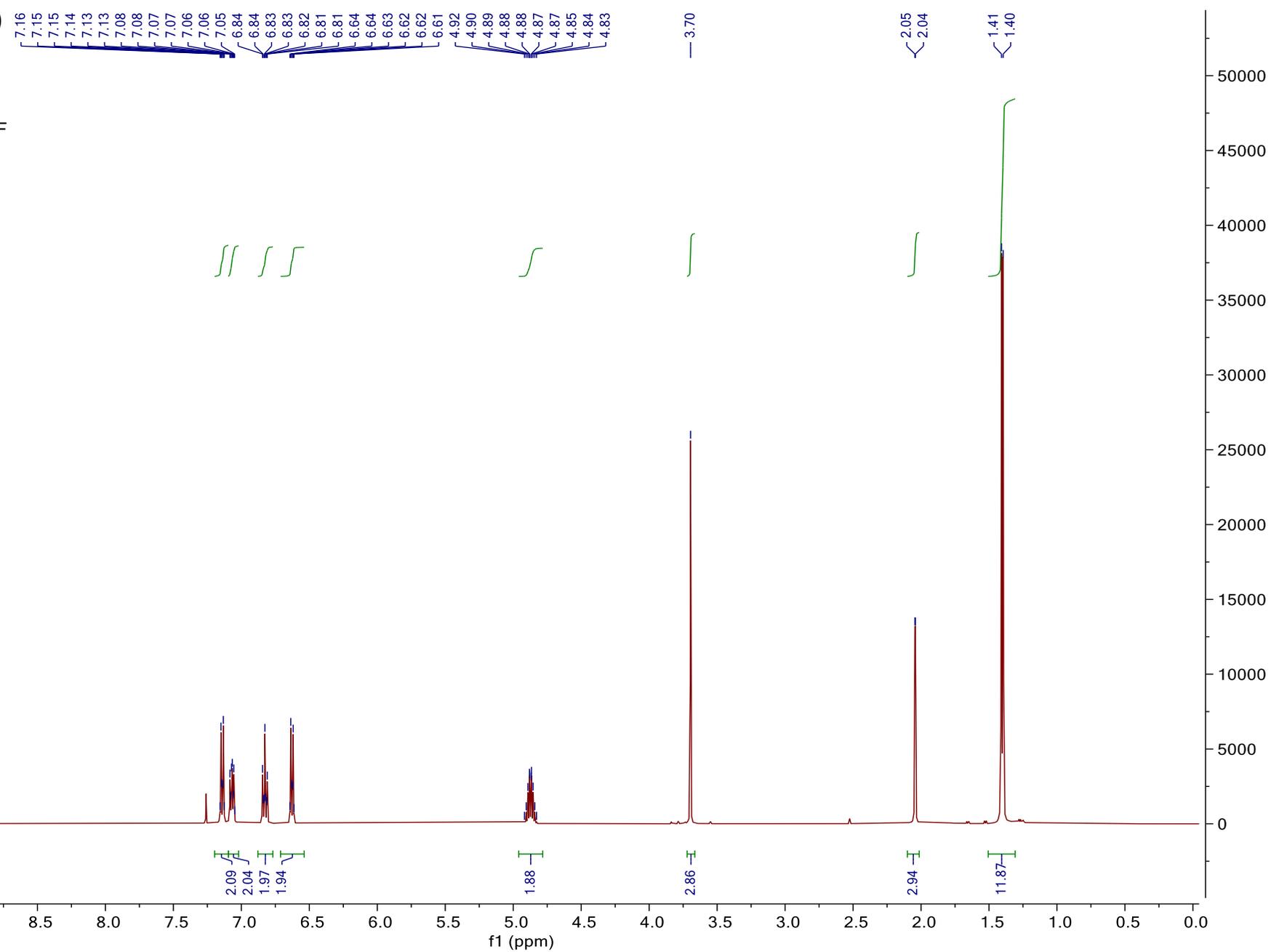
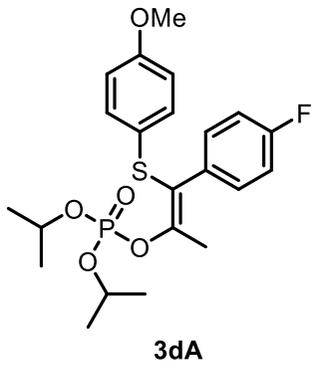


3cA

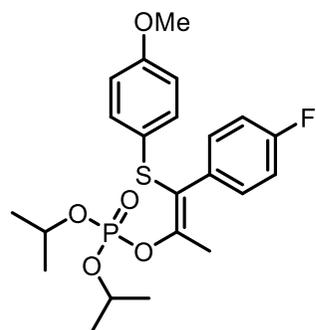




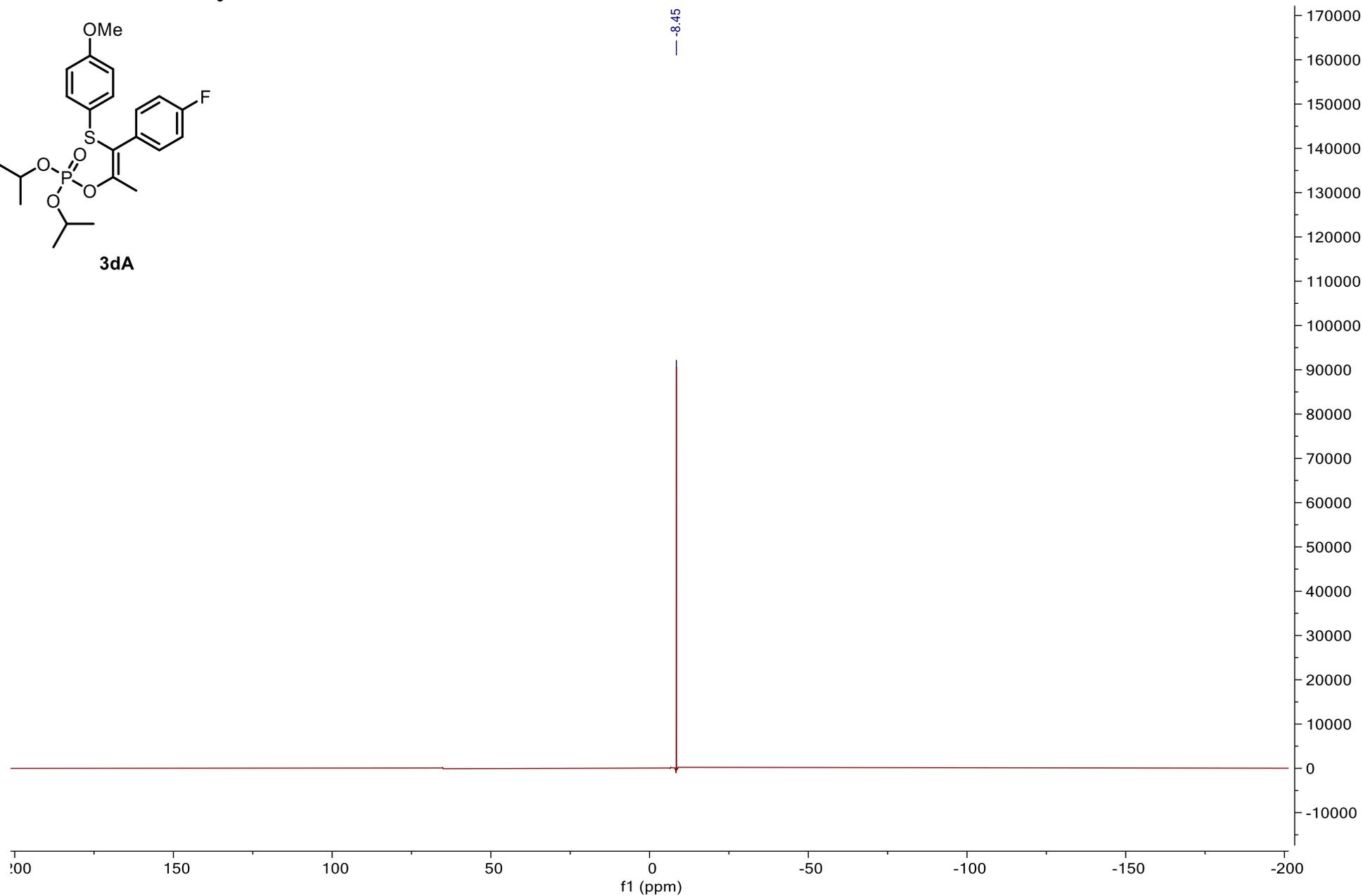
¹H NMR (500 MHz, CDCl₃)

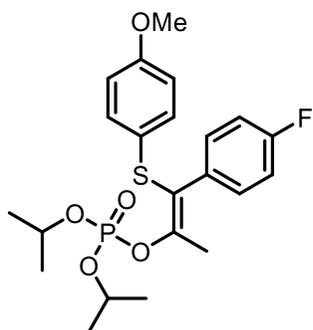


³¹P {¹H} NMR (202 MHz, CDCl₃)

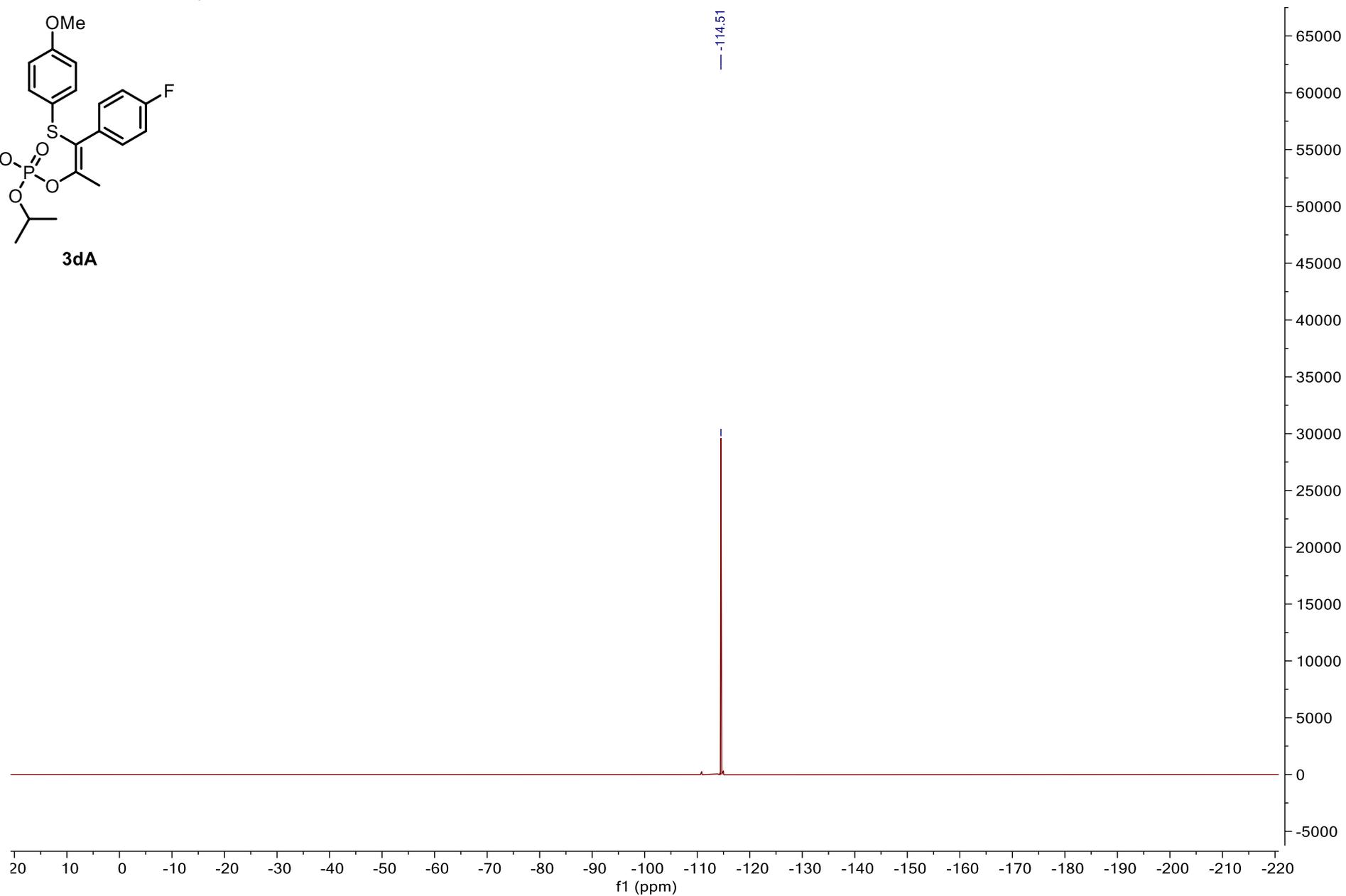


3dA

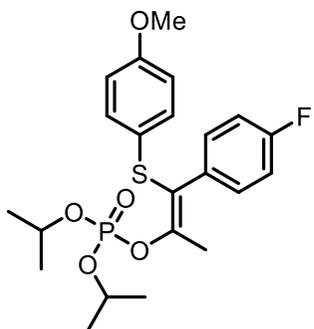


¹⁹F {¹H} NMR (471 MHz, CDCl₃)

3dA



¹³C NMR (126 MHz, CDCl₃)



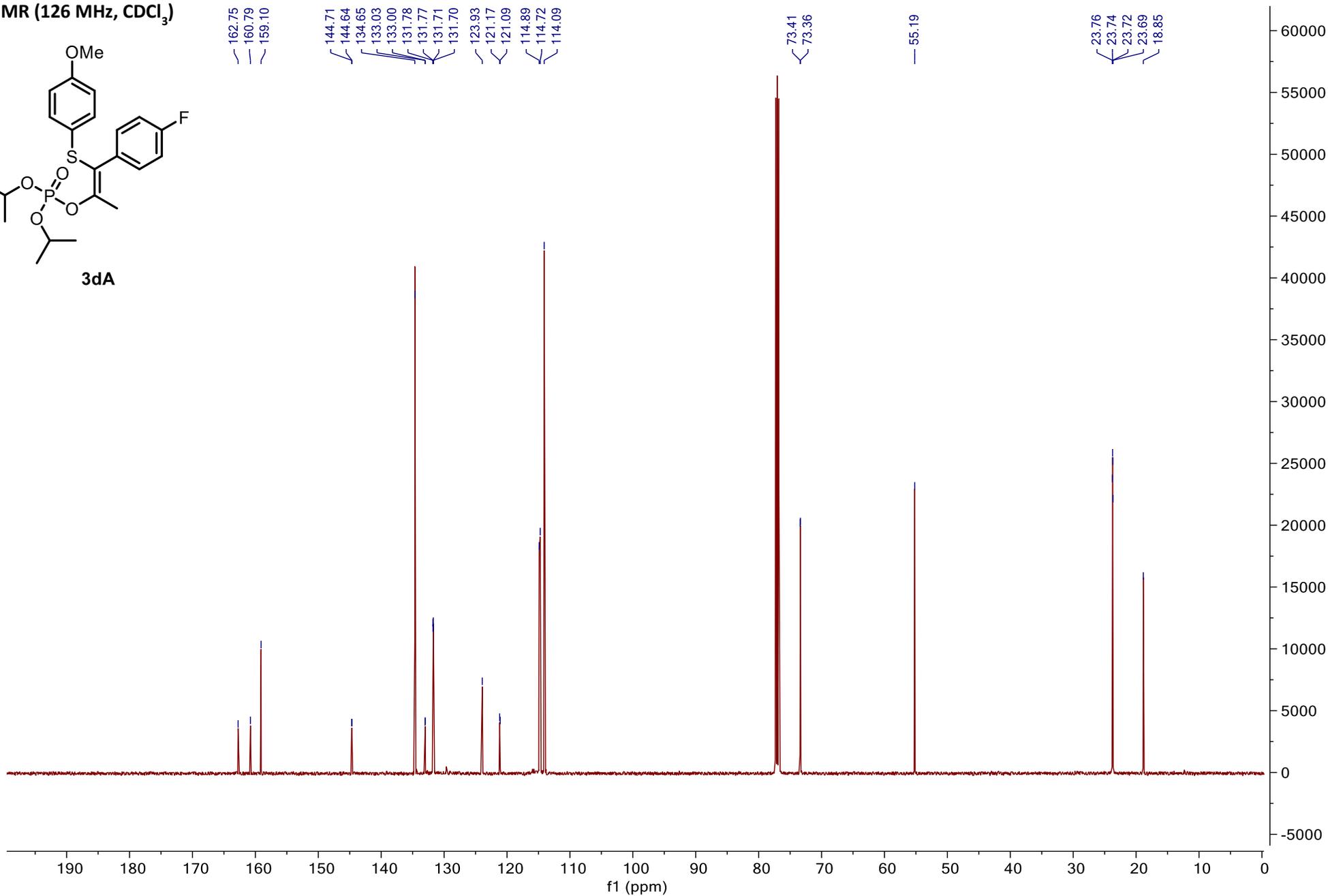
3dA

162.75
160.79
159.10
144.71
144.64
134.65
133.03
133.00
131.78
131.77
131.71
131.70
123.93
121.17
121.09
114.89
114.72
114.09

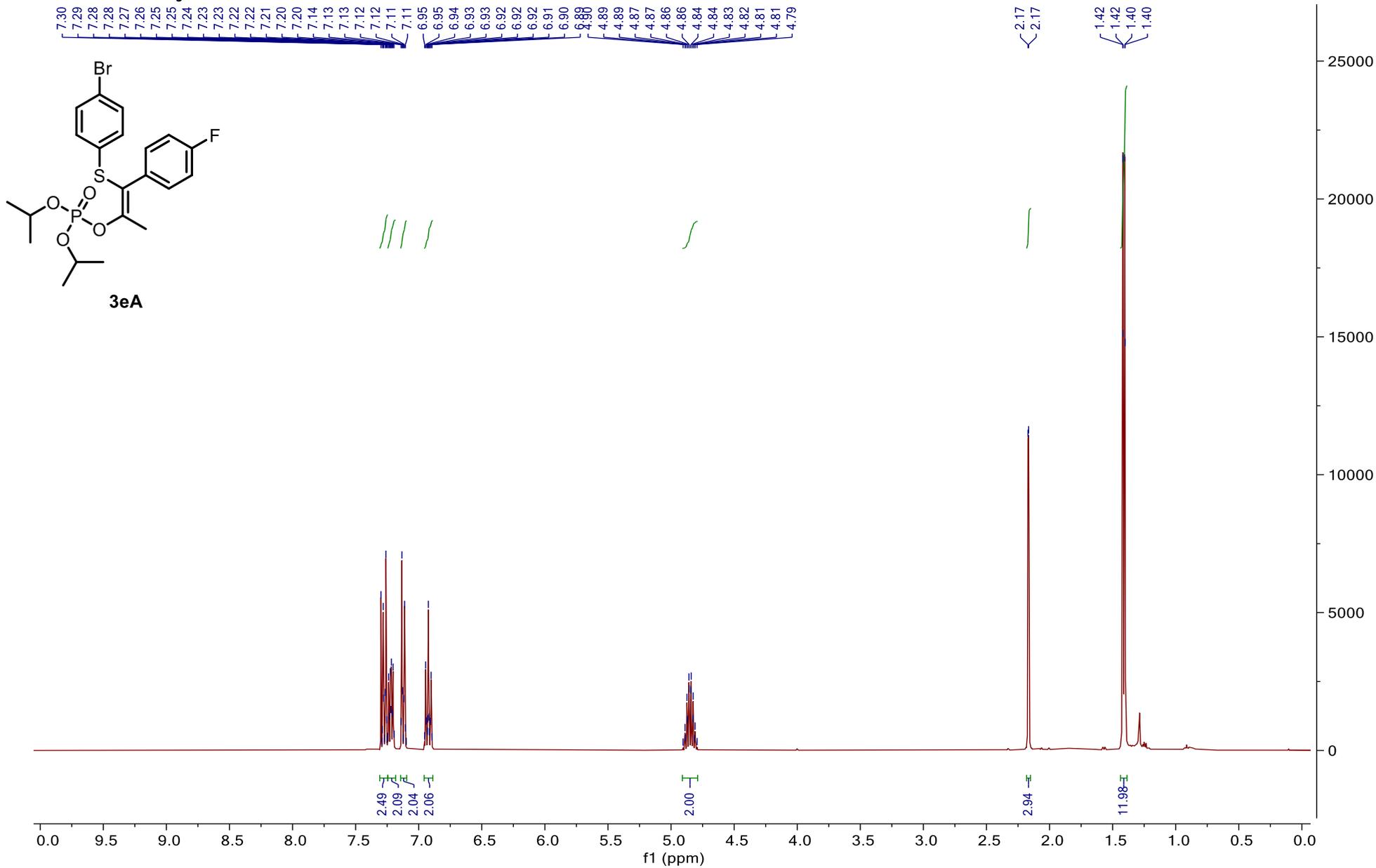
73.41
73.36

55.19

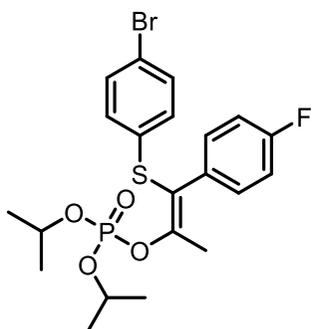
23.76
23.74
23.72
23.69
18.85



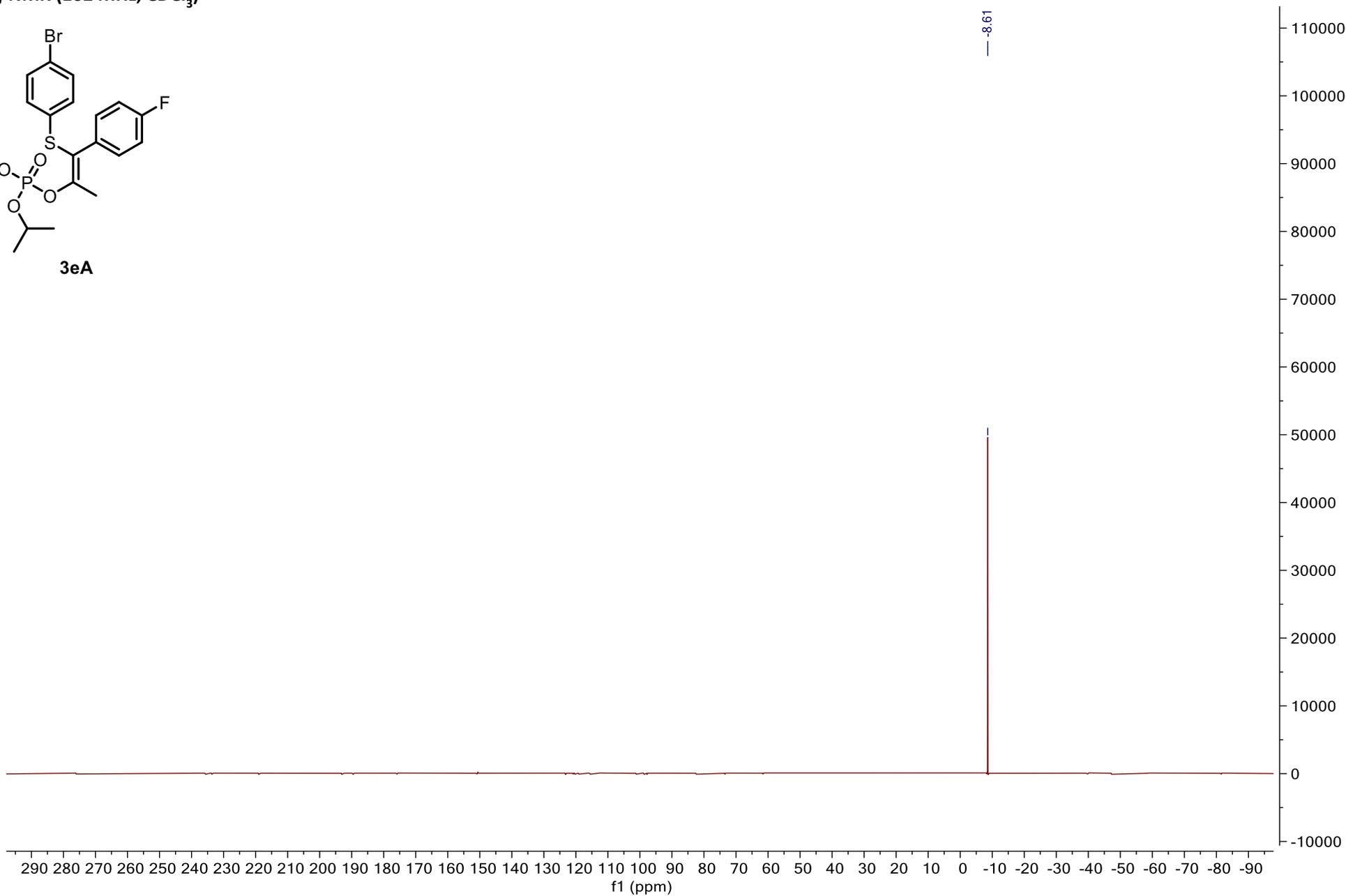
¹H NMR (400 MHz, CDCl₃)



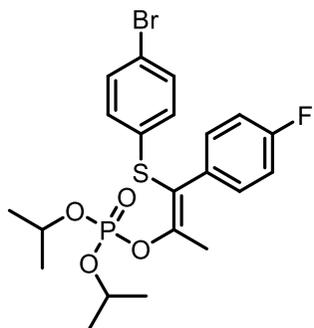
³¹P { ¹H } NMR (162 MHz, CDCl₃)



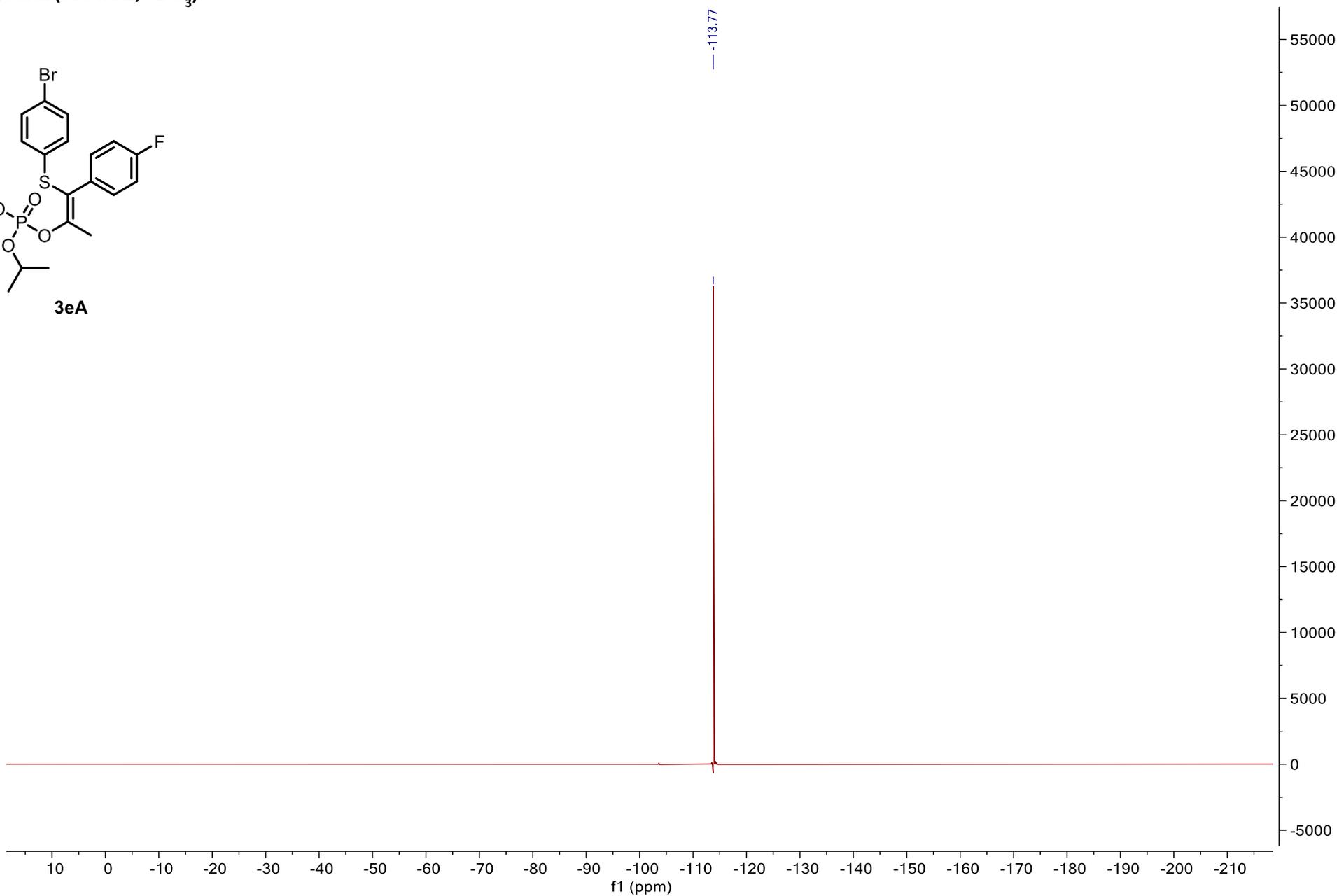
3eA



¹⁹F {¹H} NMR (376 MHz, CDCl₃)



3eA



¹³C NMR (101 MHz, CDCl₃)

163.17
160.71

148.00
147.92

133.53
133.53

132.97
132.94

132.40
131.73

131.72
131.65

131.63

120.55
118.80

118.71
115.18

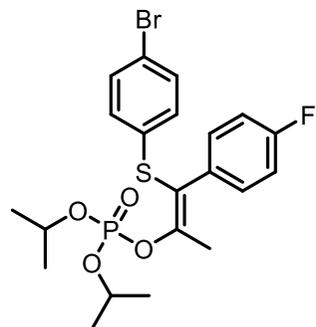
114.97

73.55
73.49

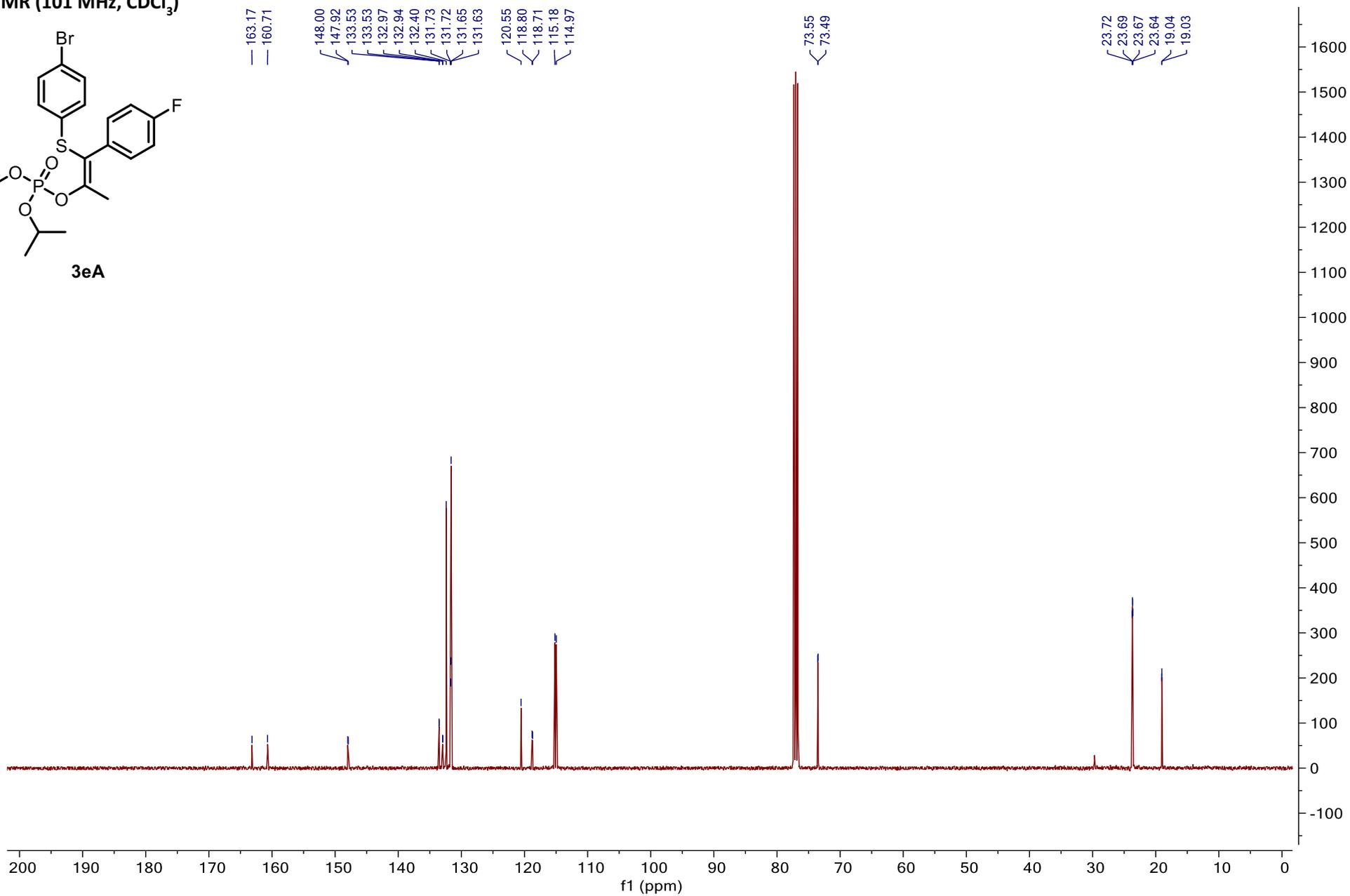
23.72
23.69

23.67
23.64

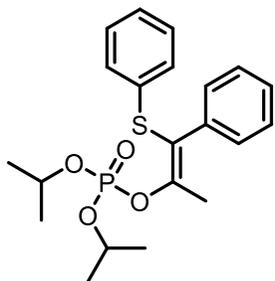
19.04
19.03



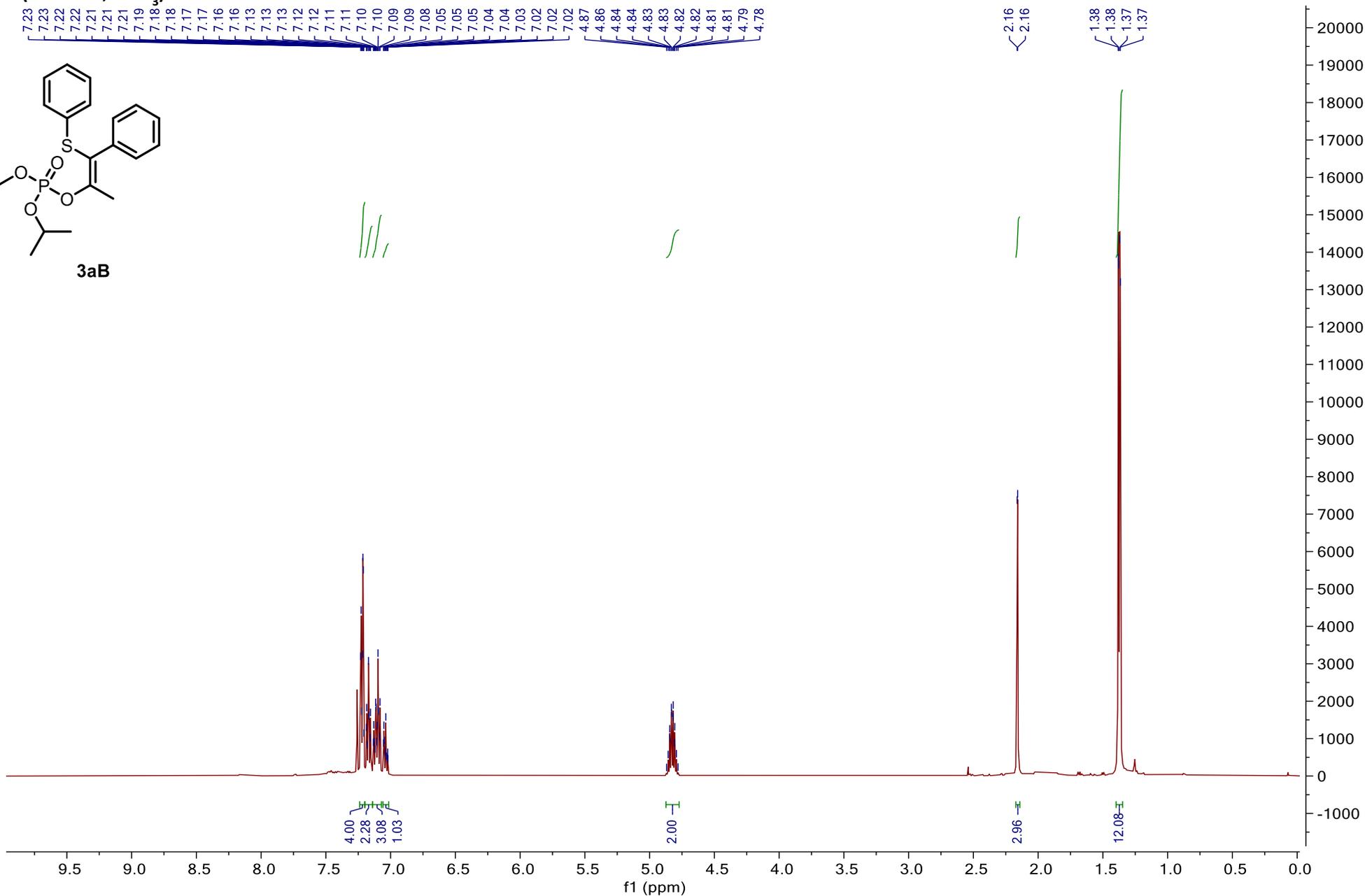
3eA



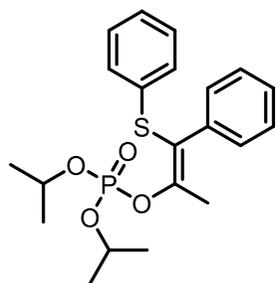
¹H NMR (500 MHz, CDCl₃)



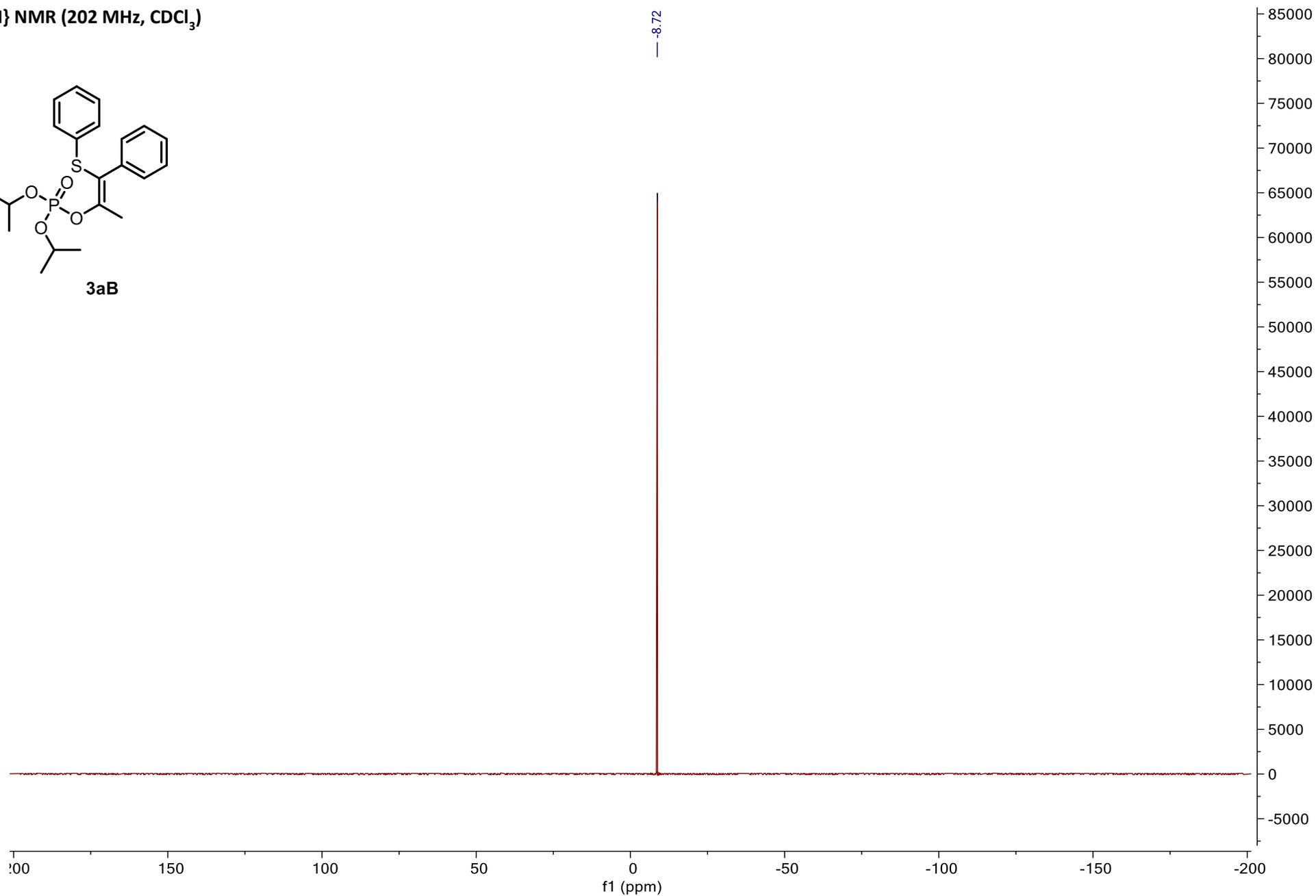
3aB



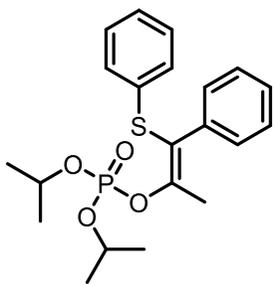
³¹P { ¹H } NMR (202 MHz, CDCl₃)



3aB



¹³C NMR (126 MHz, CDCl₃)

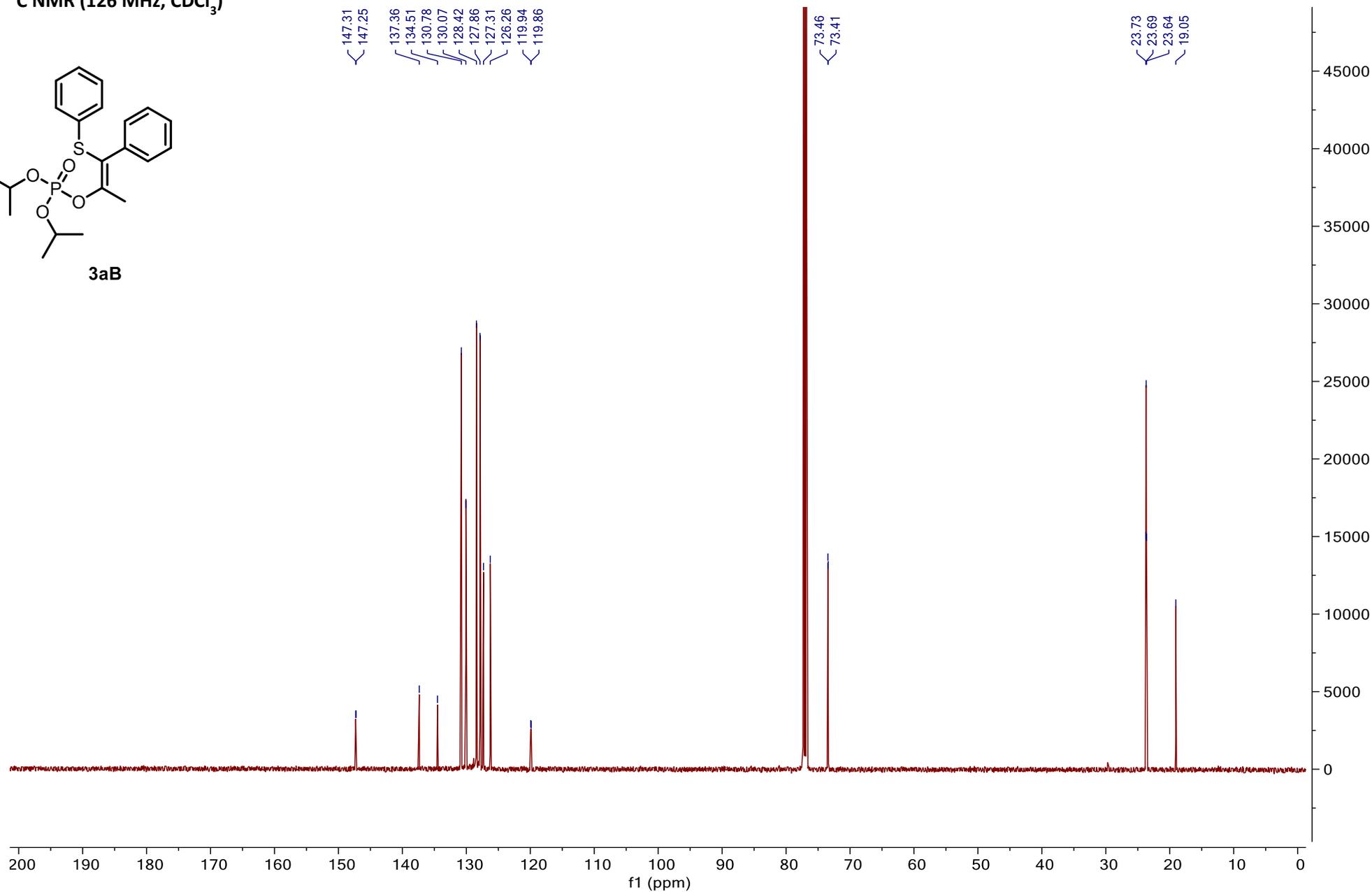


3aB

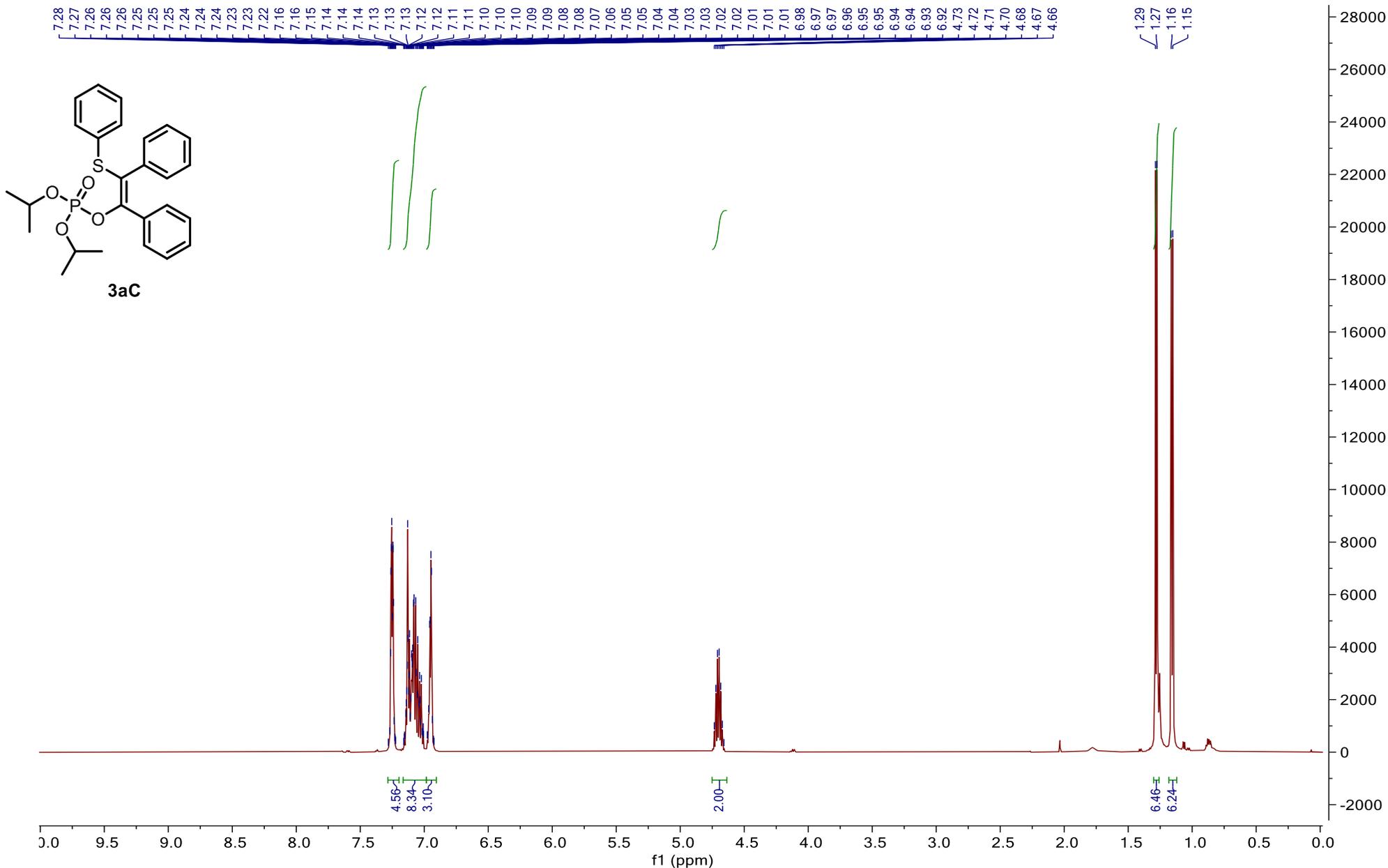
147.31
147.25
137.36
134.51
130.78
130.07
128.42
127.86
127.31
126.26
119.94
119.86

73.46
73.41

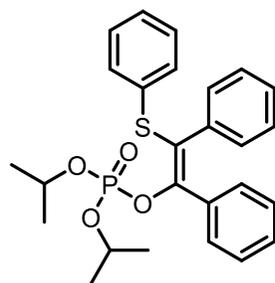
23.73
23.69
23.64
19.05



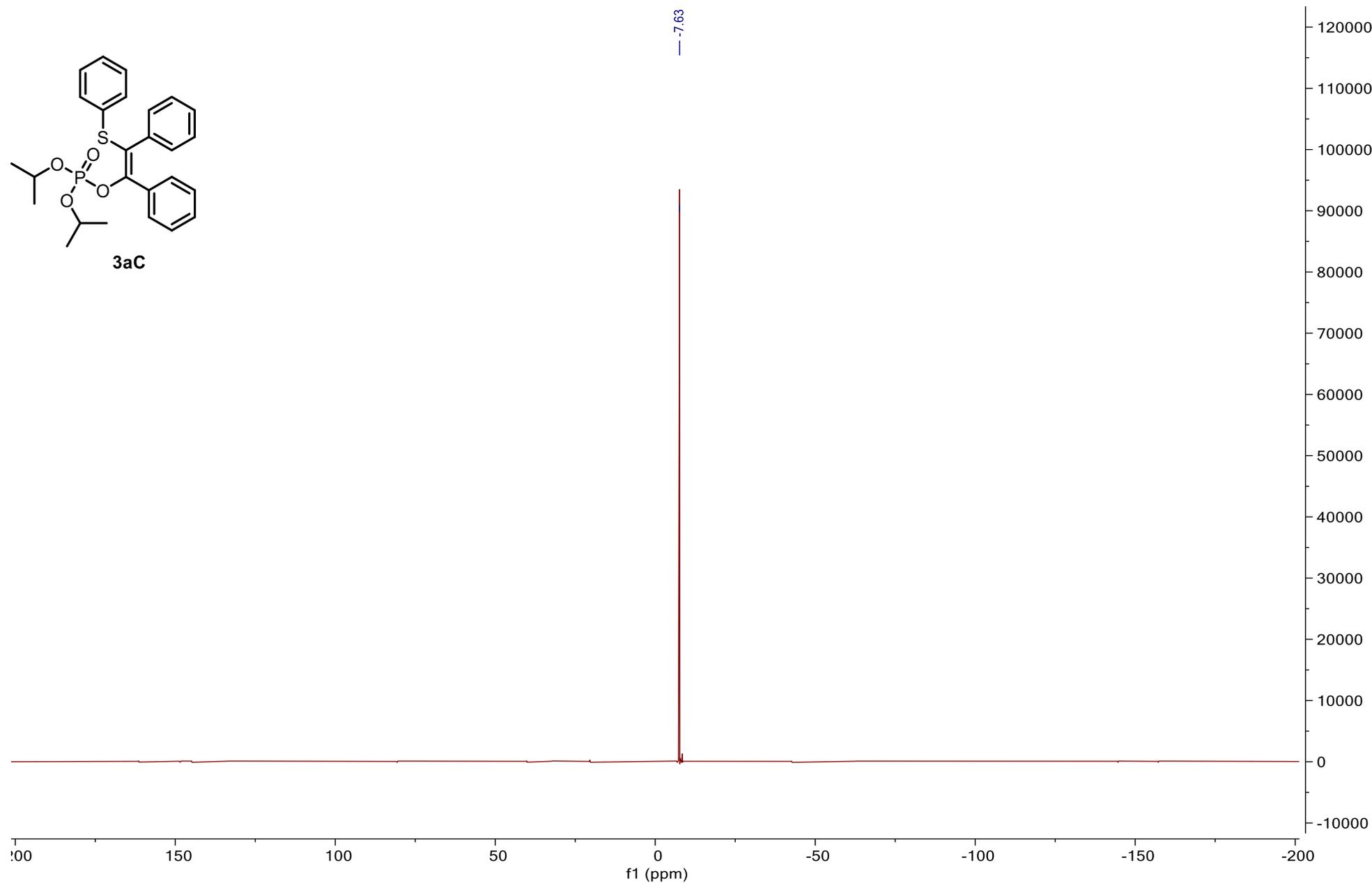
¹H NMR (500 MHz, CDCl₃)

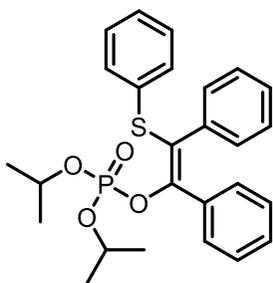


$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3)

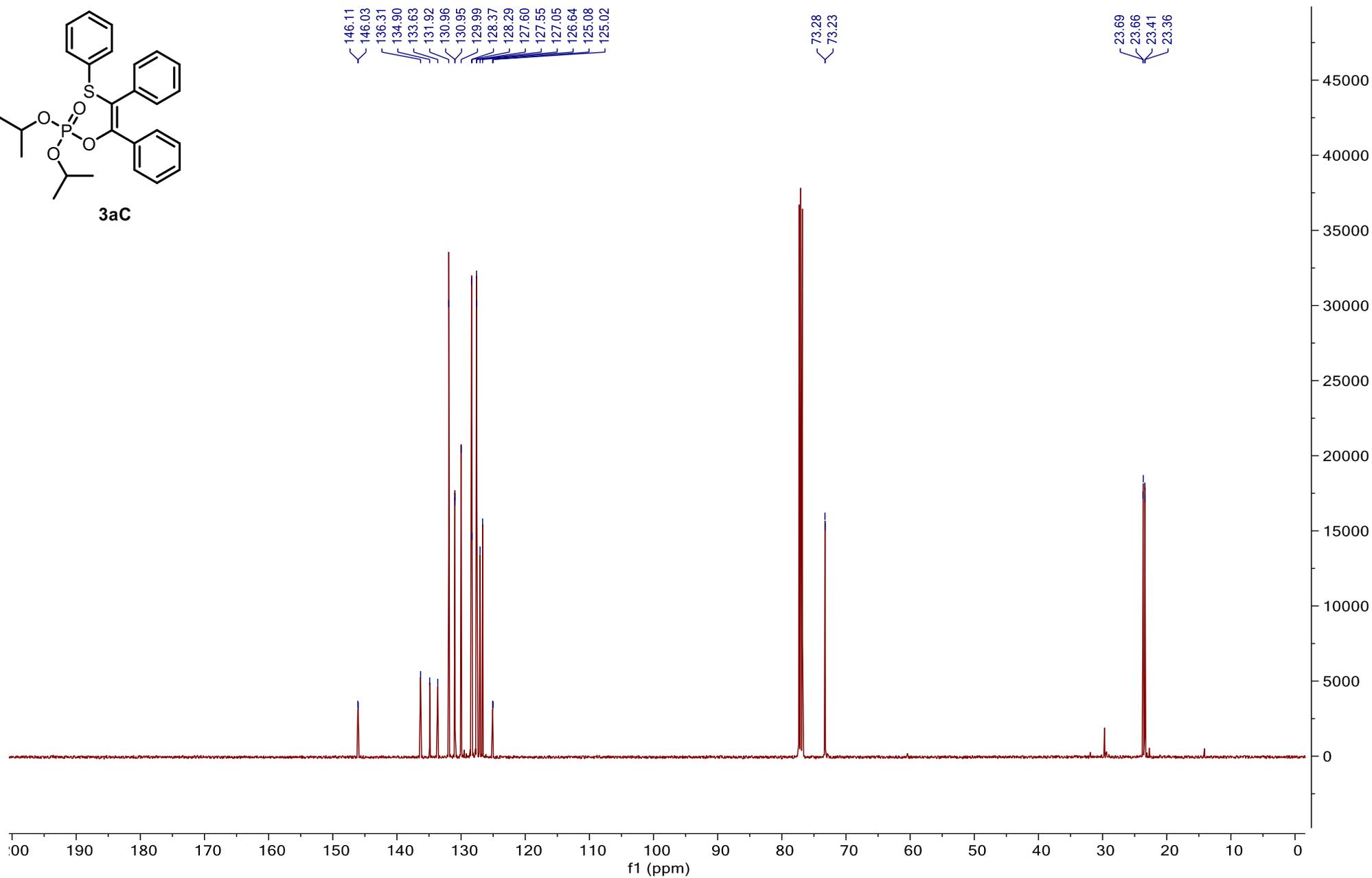


3aC

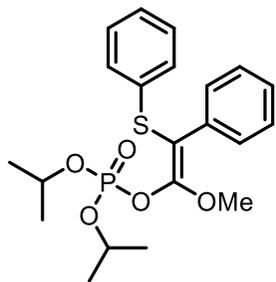


^{13}C NMR (126 MHz, CDCl_3)

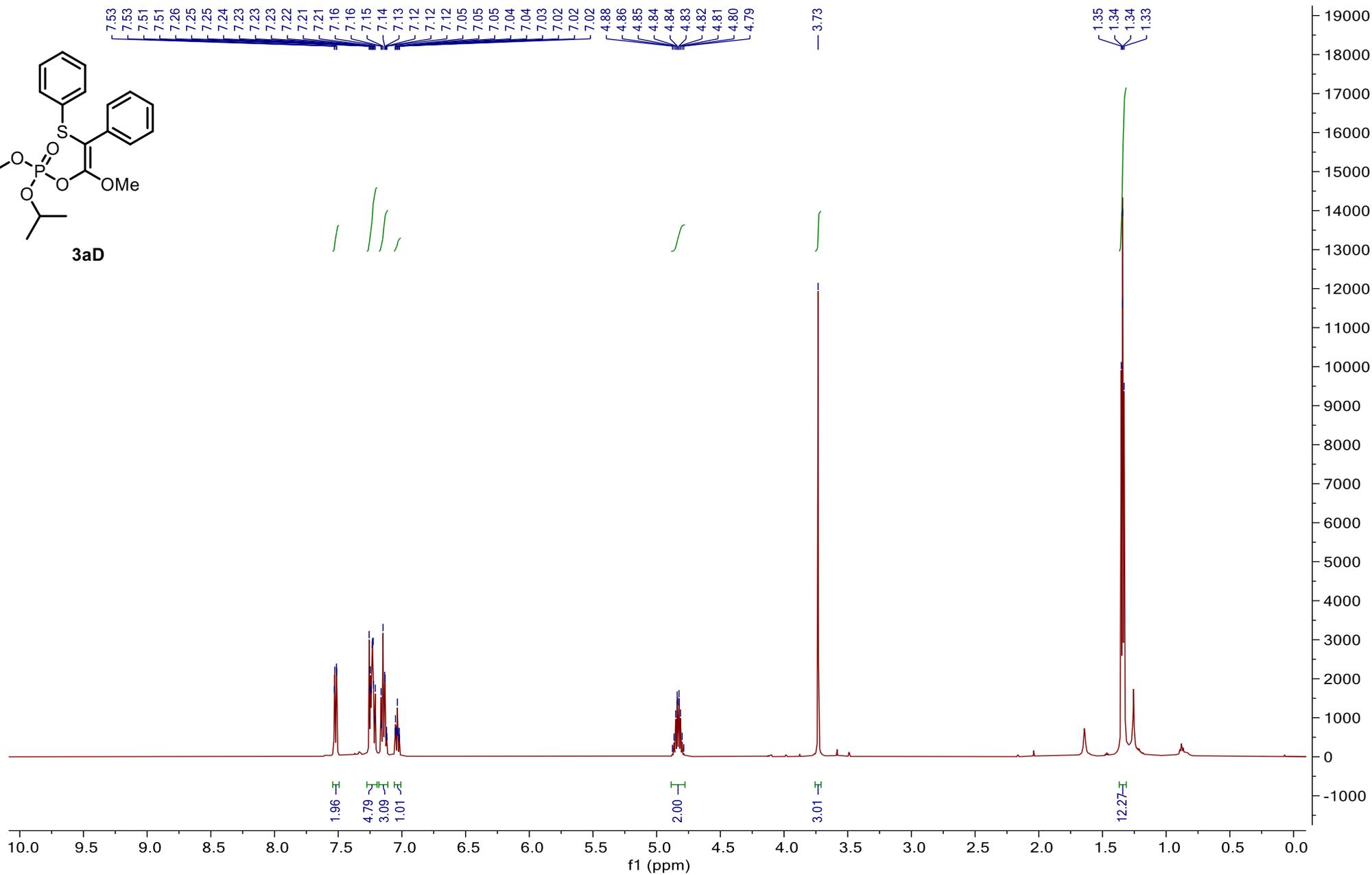
3aC



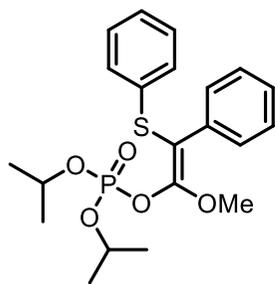
¹H NMR (500 MHz, CDCl₃)



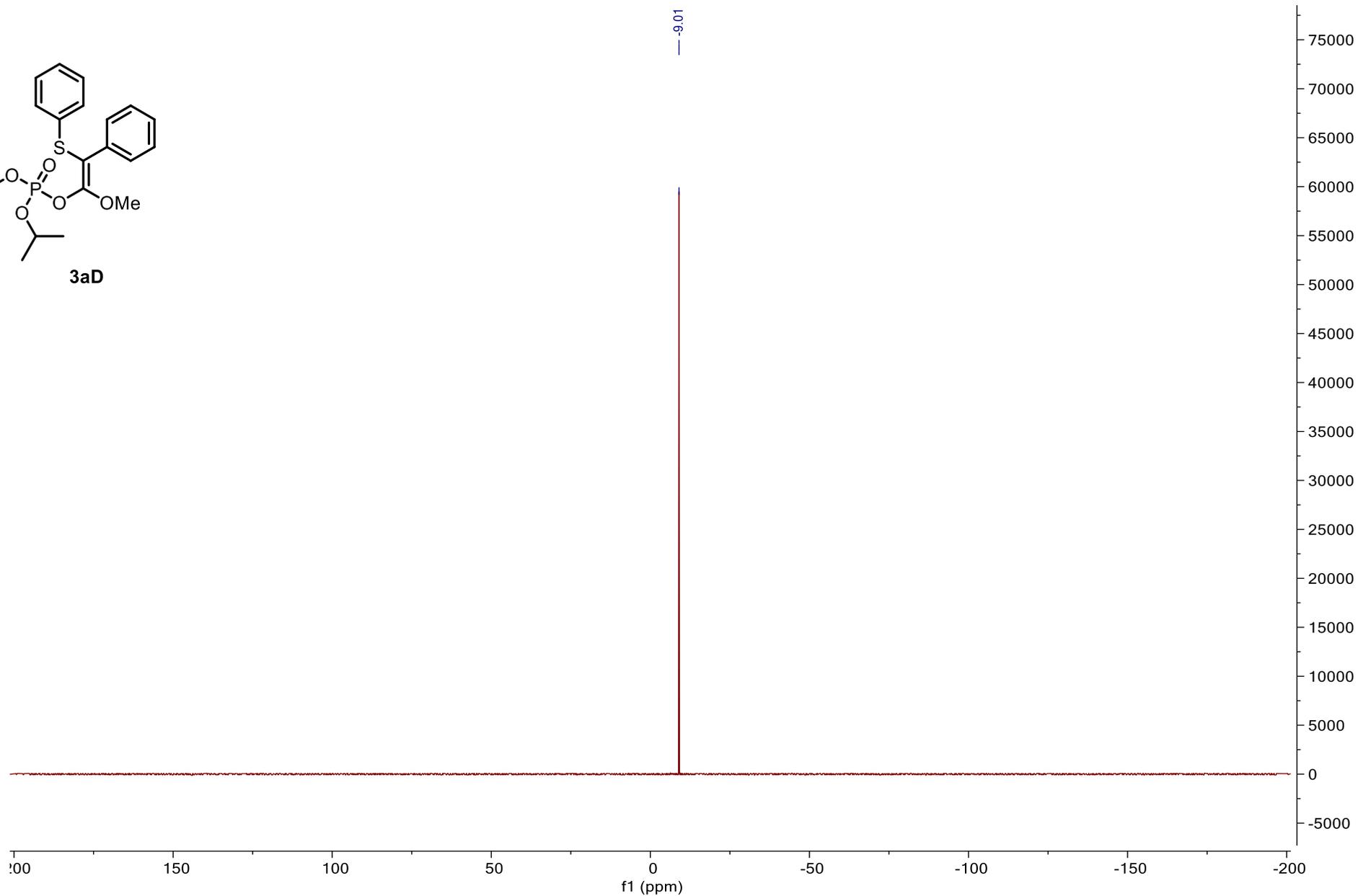
3aD



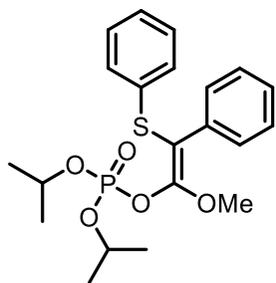
$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3)



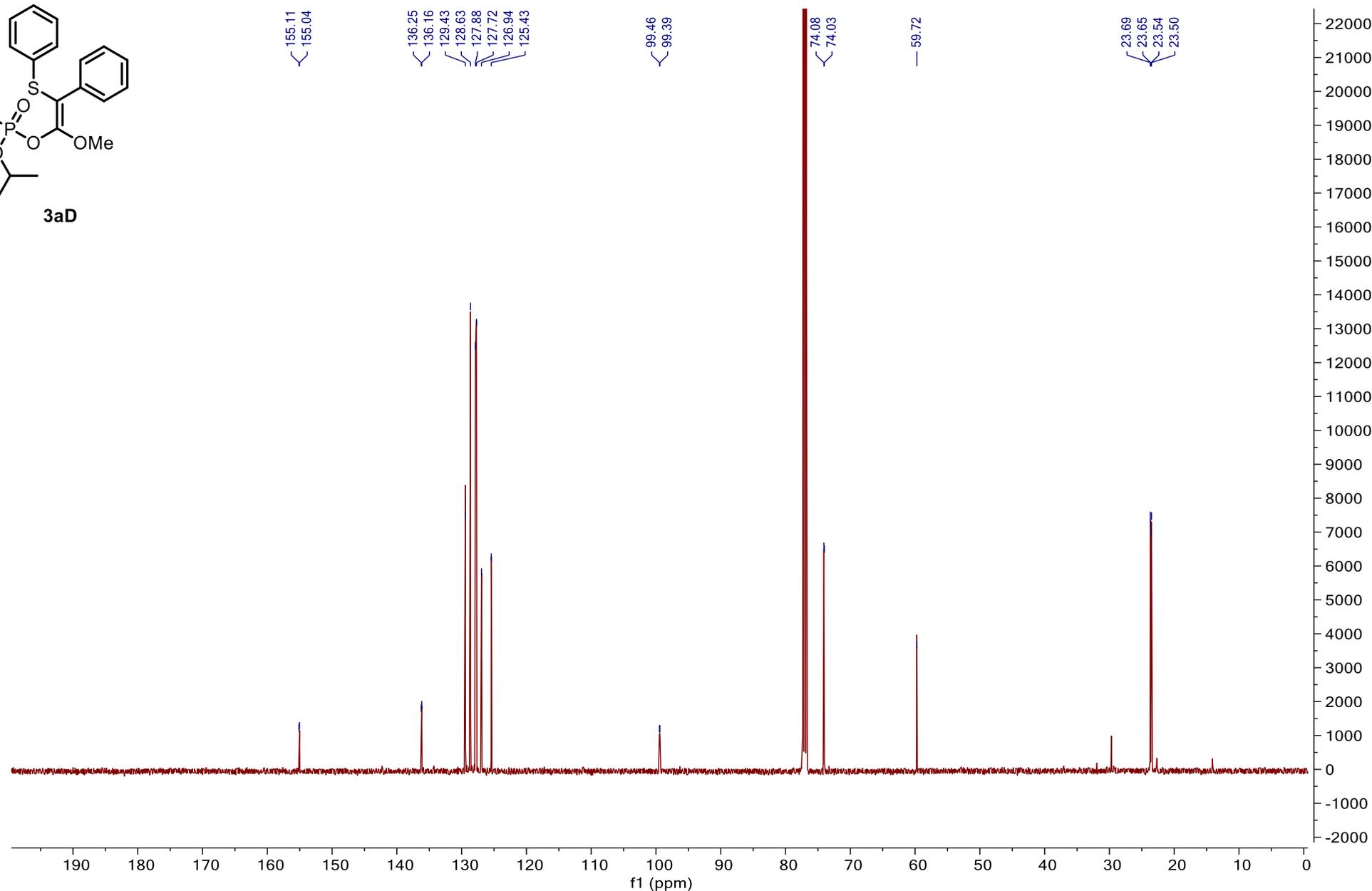
3aD



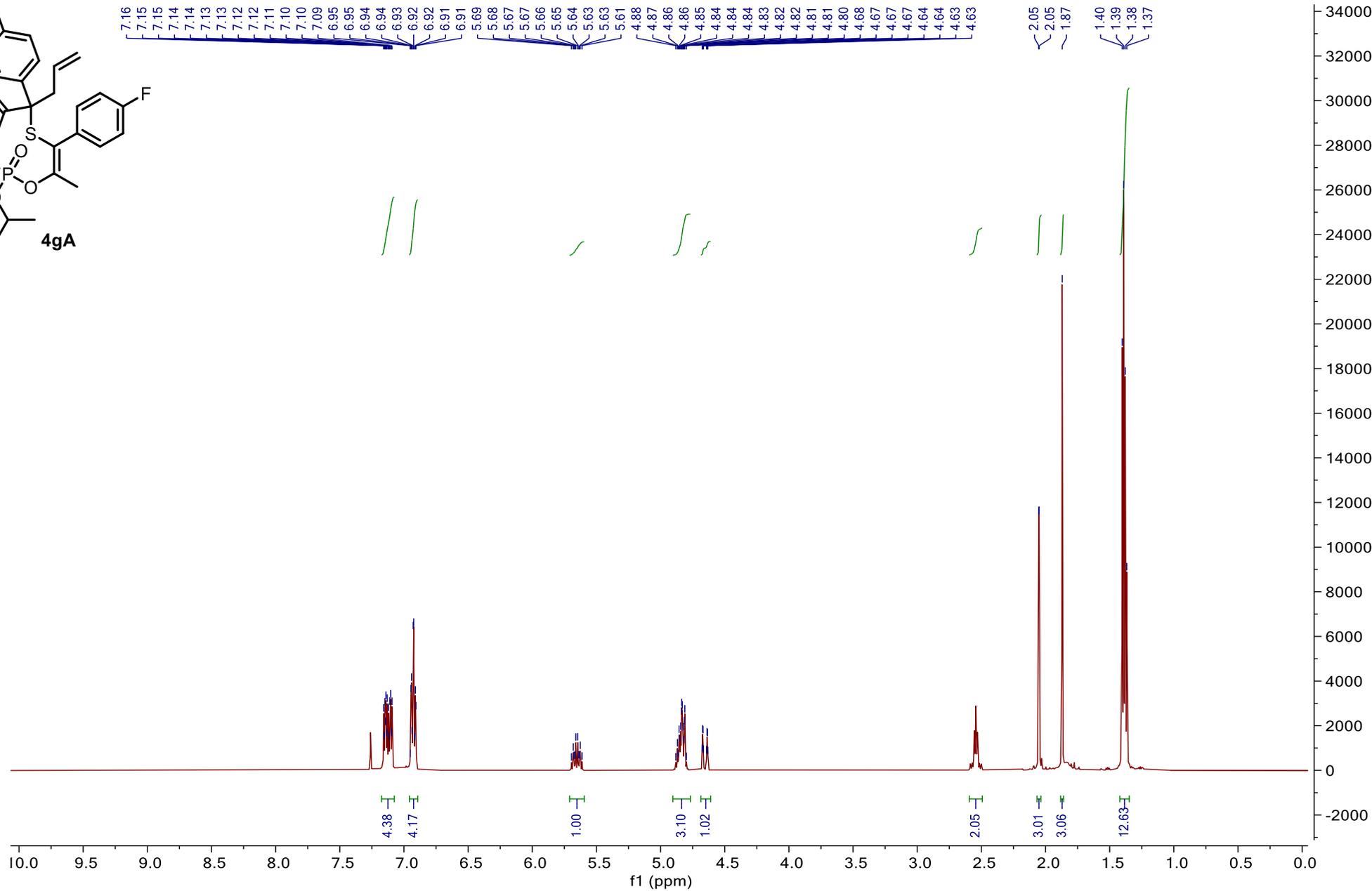
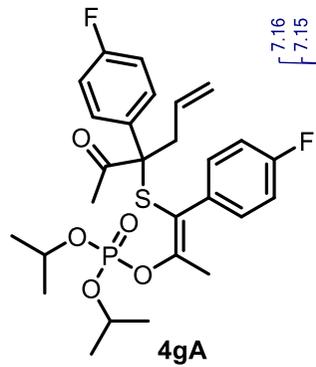
¹³C NMR (126 MHz, CDCl₃)



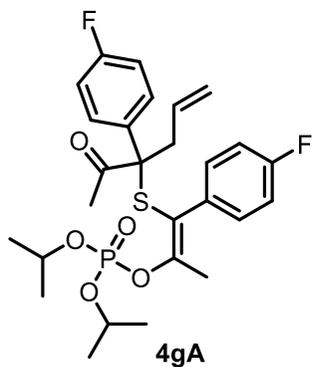
3aD



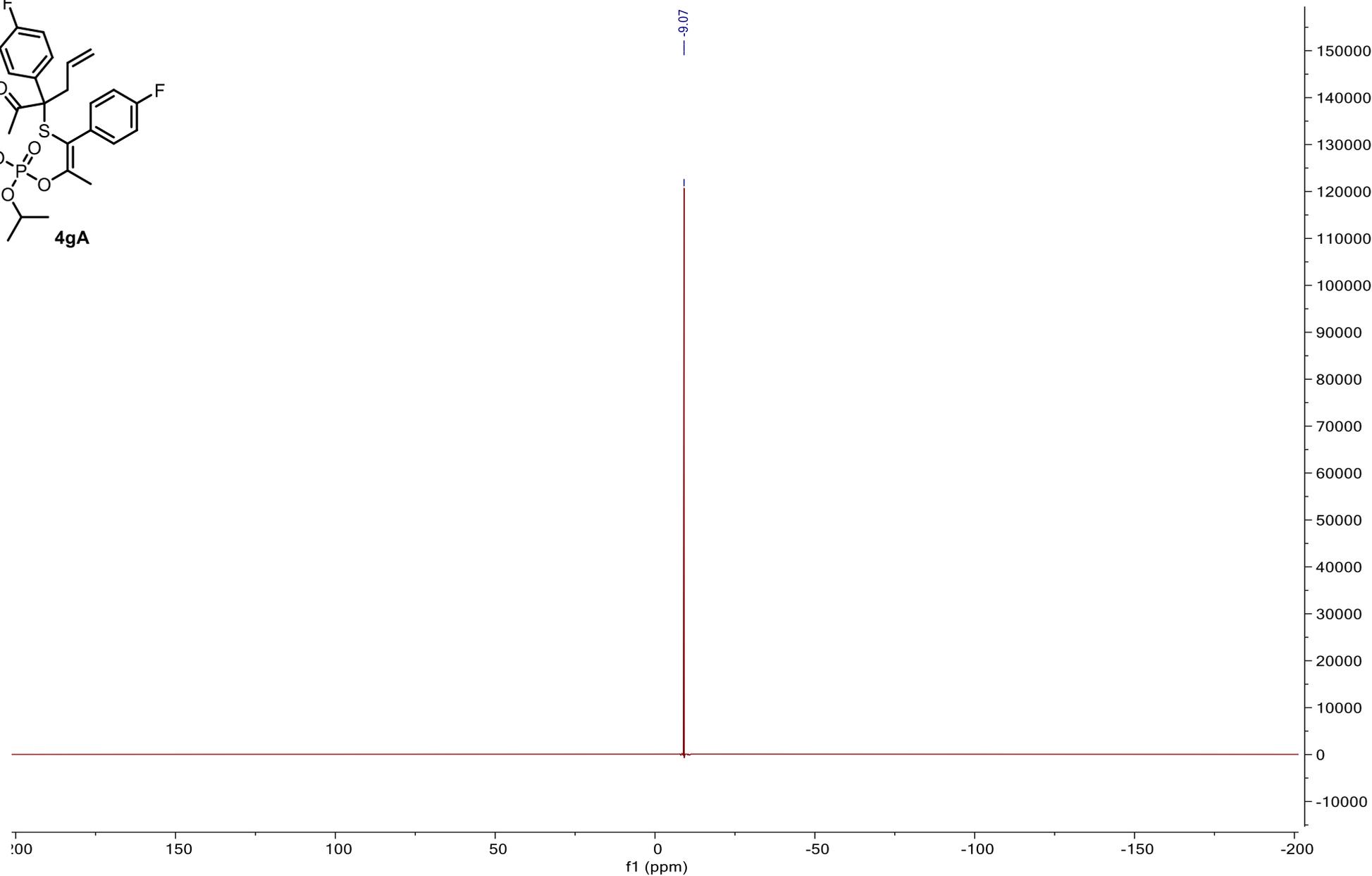
¹H NMR (500 MHz, CDCl₃)



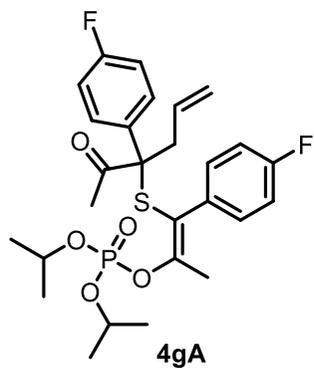
$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3)



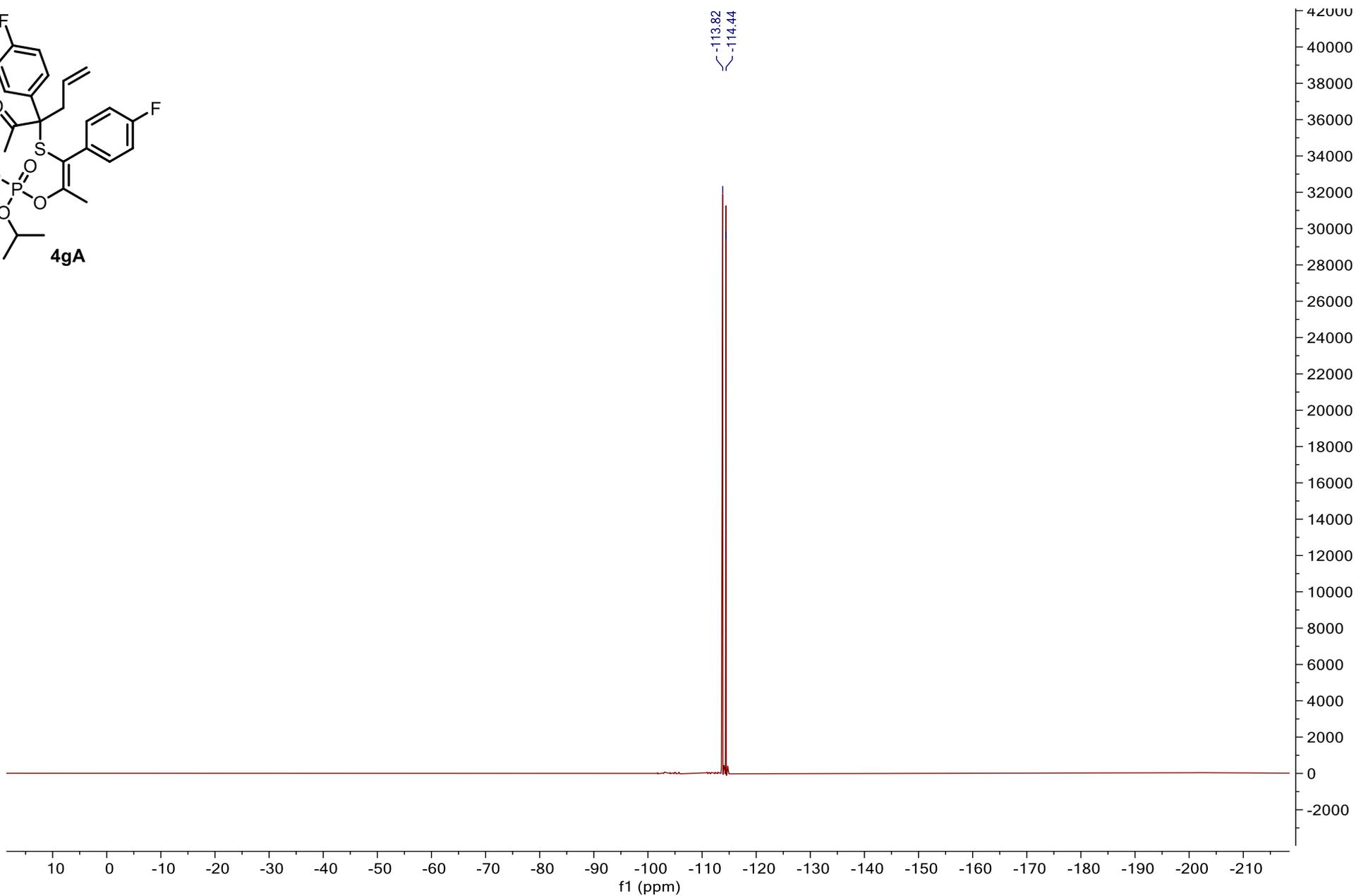
4gA



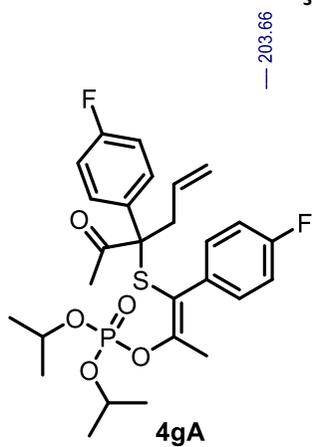
¹⁹F {¹H} NMR (376 MHz, CDCl₃)



-113.82
-114.44



¹³C NMR (126 MHz, CDCl₃)



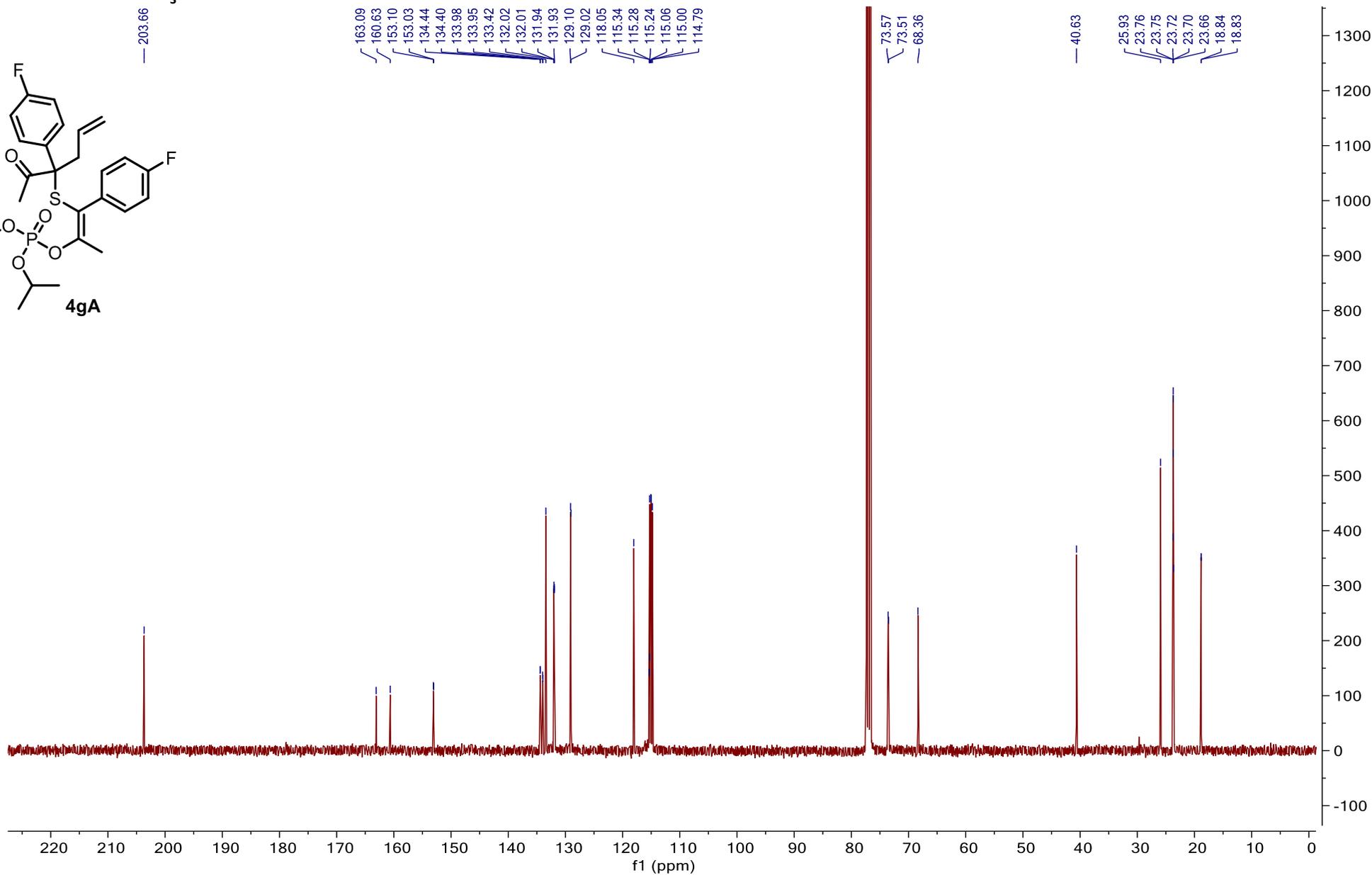
— 203.66

163.09
160.63
153.10
153.03
134.44
134.40
133.98
133.95
133.42
132.02
132.01
131.94
131.93
129.10
129.02
118.05
115.34
115.28
115.24
115.06
115.00
114.79

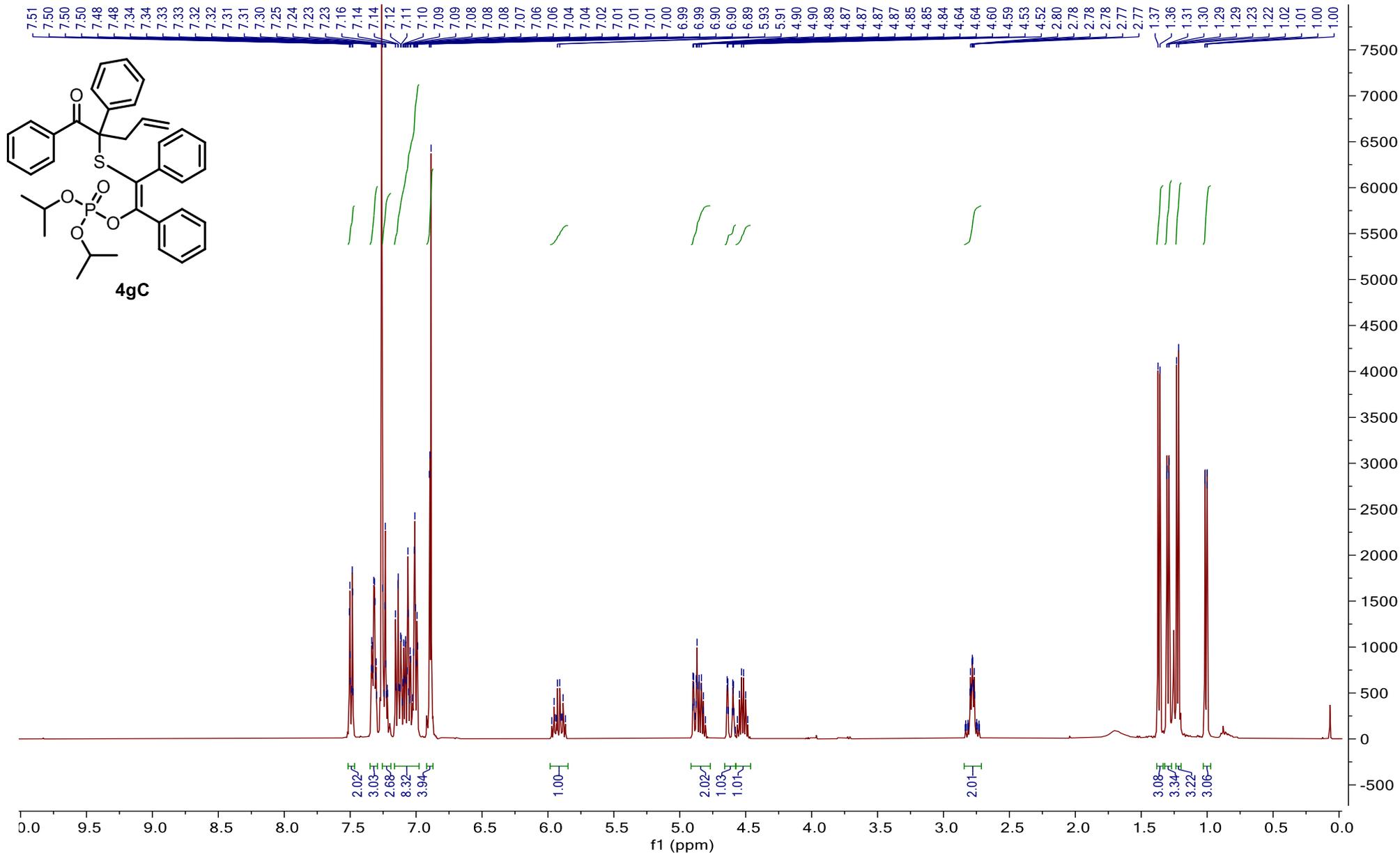
73.57
73.51
68.36

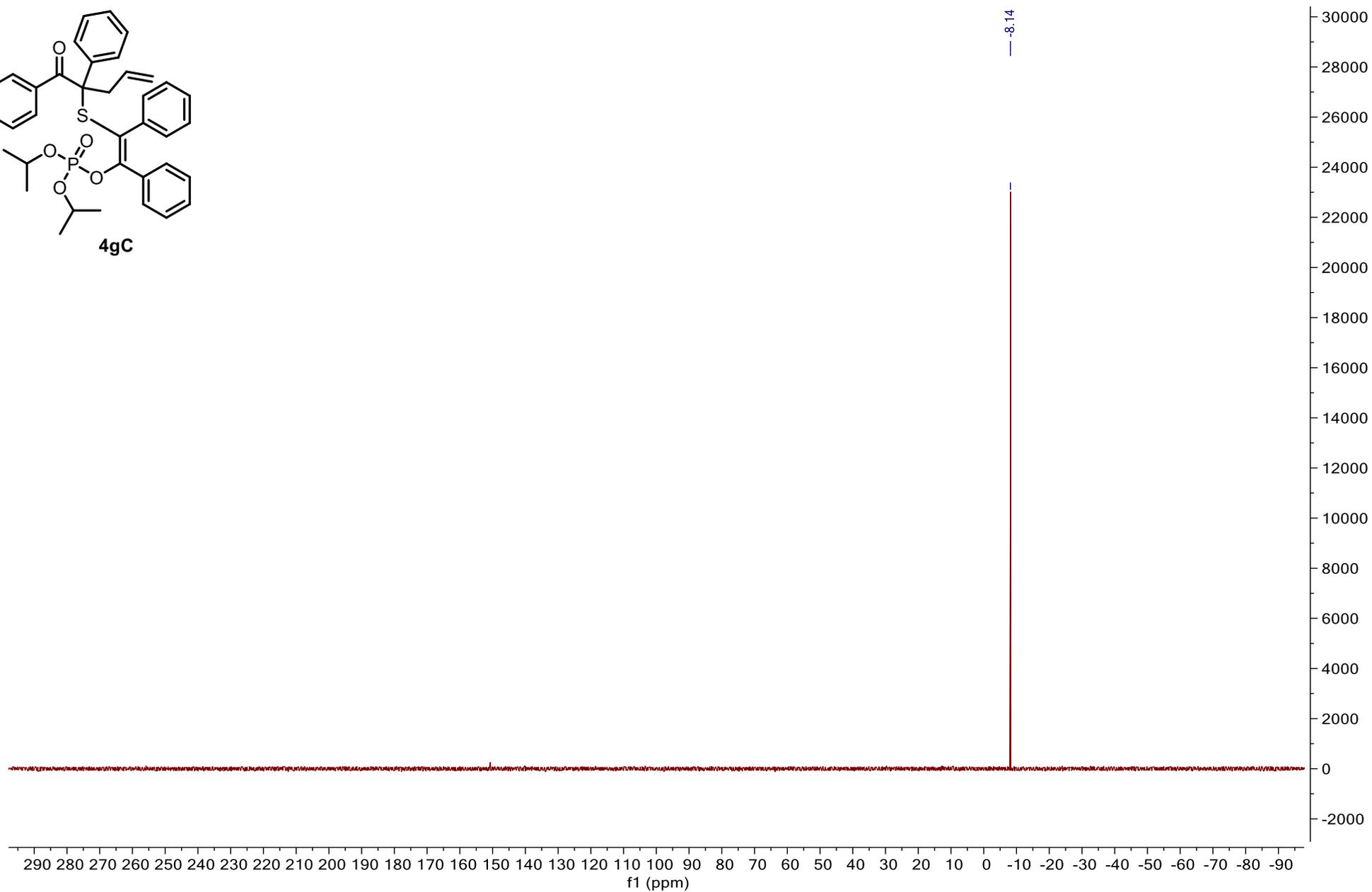
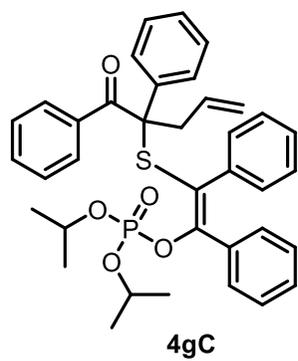
— 40.63

25.93
23.76
23.75
23.72
23.70
23.66
18.84
18.83

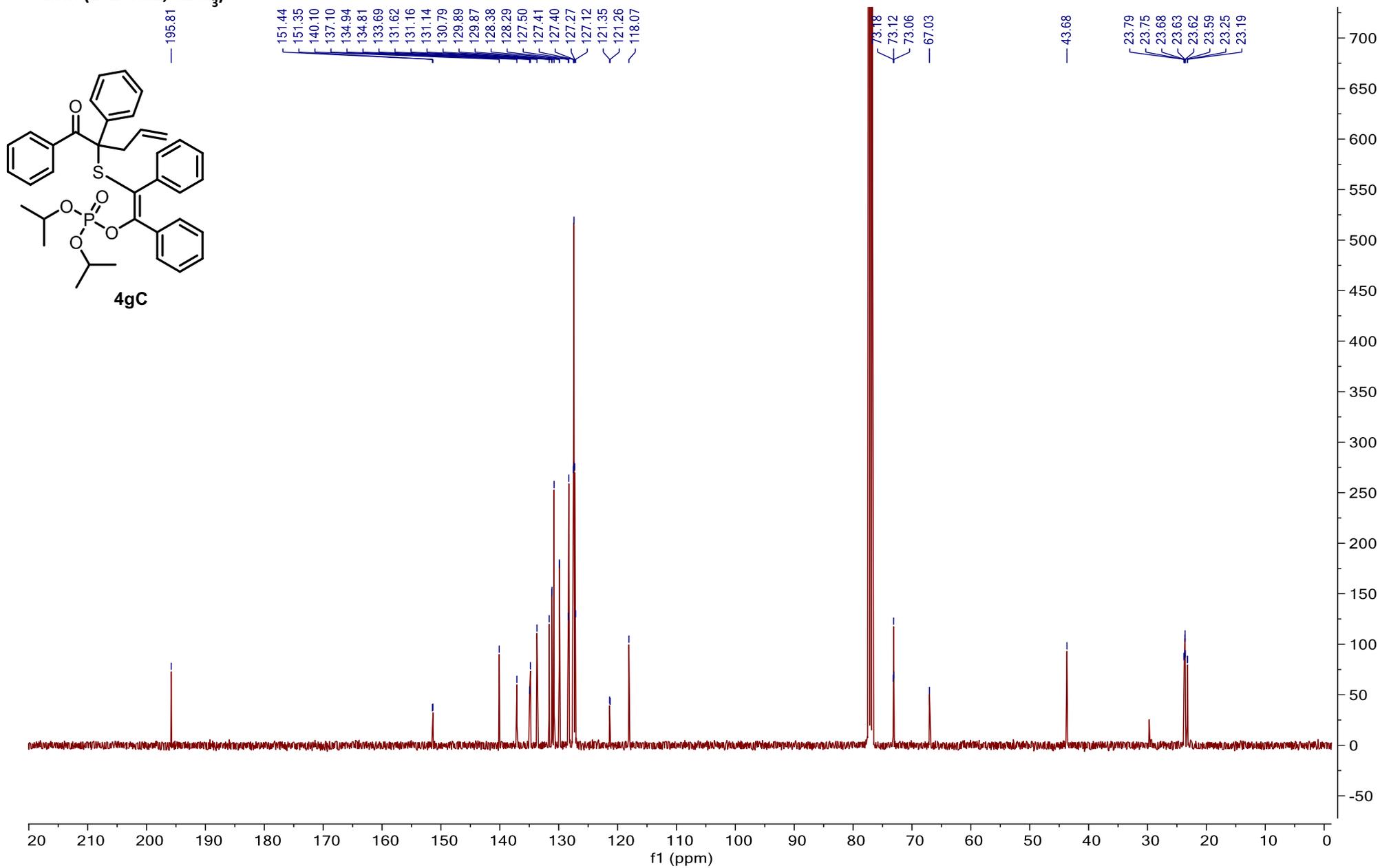


¹H NMR (400 MHz, CDCl₃)

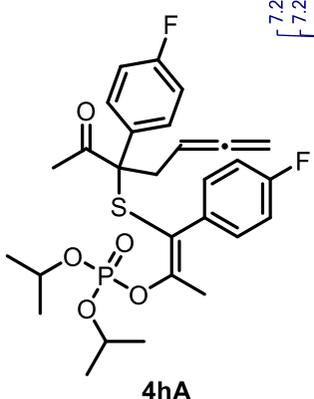


$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3)

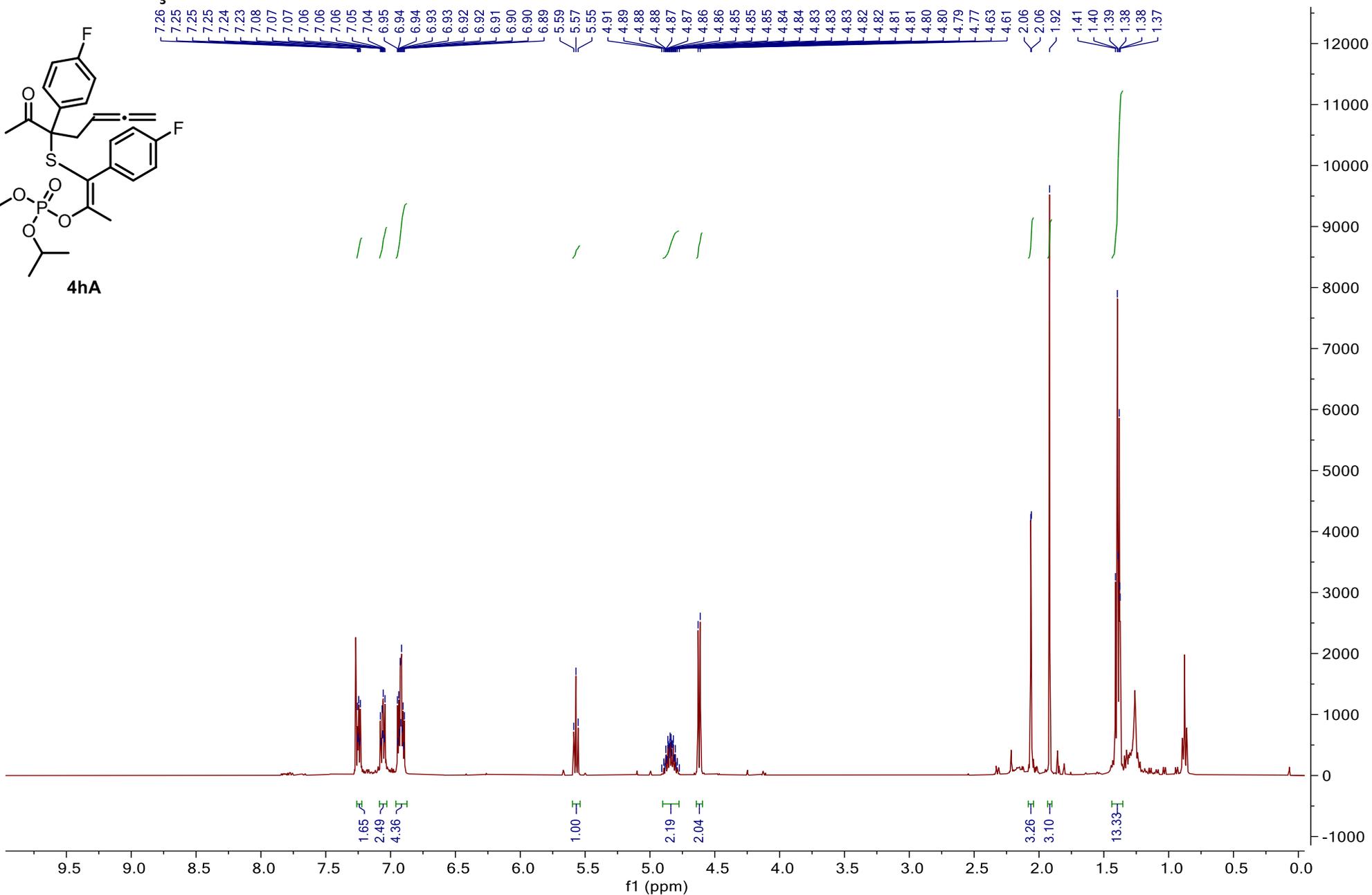
¹³C NMR (101 MHz, CDCl₃)

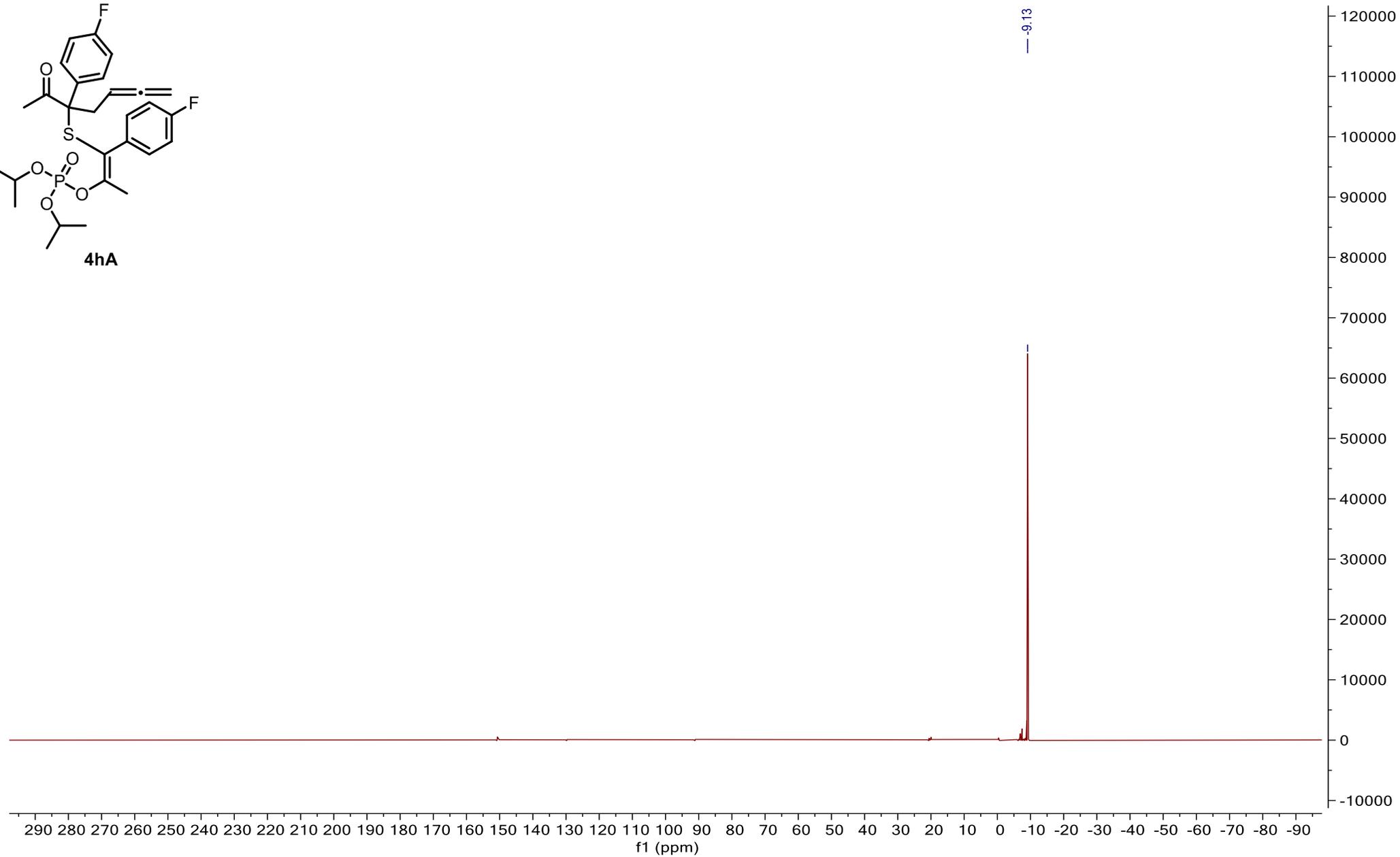
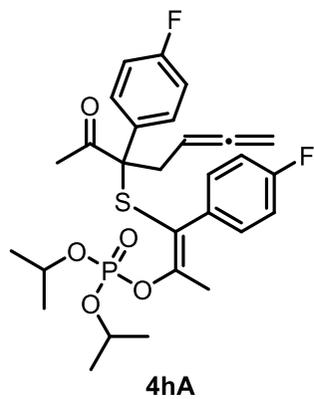


¹H NMR (400 MHz, CDCl₃)

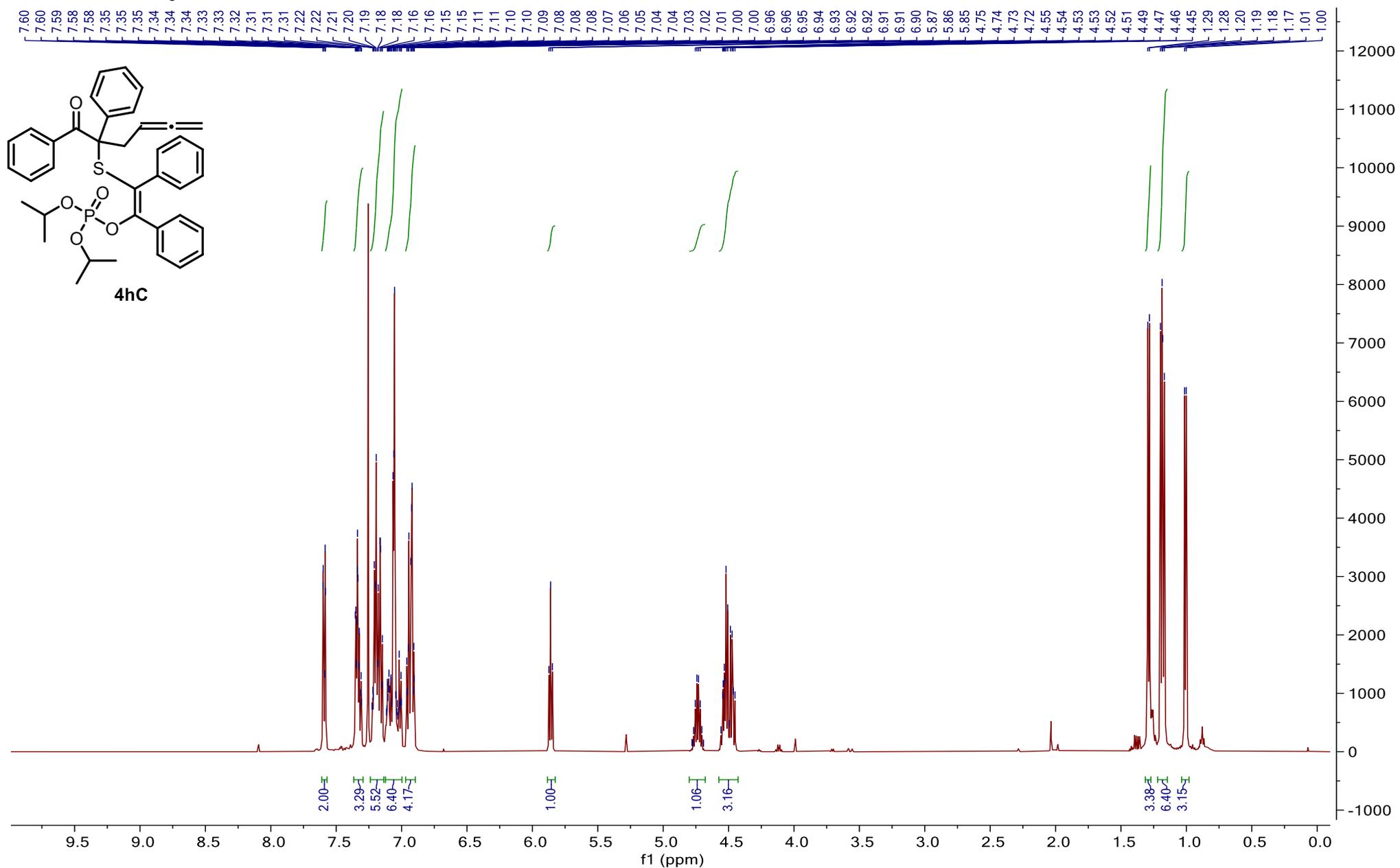


7.26
7.25
7.25
7.24
7.23
7.08
7.07
7.07
7.06
7.06
7.05
7.04
6.95
6.94
6.94
6.93
6.93
6.92
6.92
6.91
6.90
6.90
6.89
5.59
5.57
5.55
4.91
4.89
4.88
4.88
4.87
4.87
4.86
4.86
4.85
4.85
4.85
4.84
4.84
4.83
4.83
4.82
4.82
4.81
4.81
4.80
4.80
4.79
4.77
4.63
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2.06
2.06
1.92
1.41
1.40
1.39
1.38
1.38
1.37

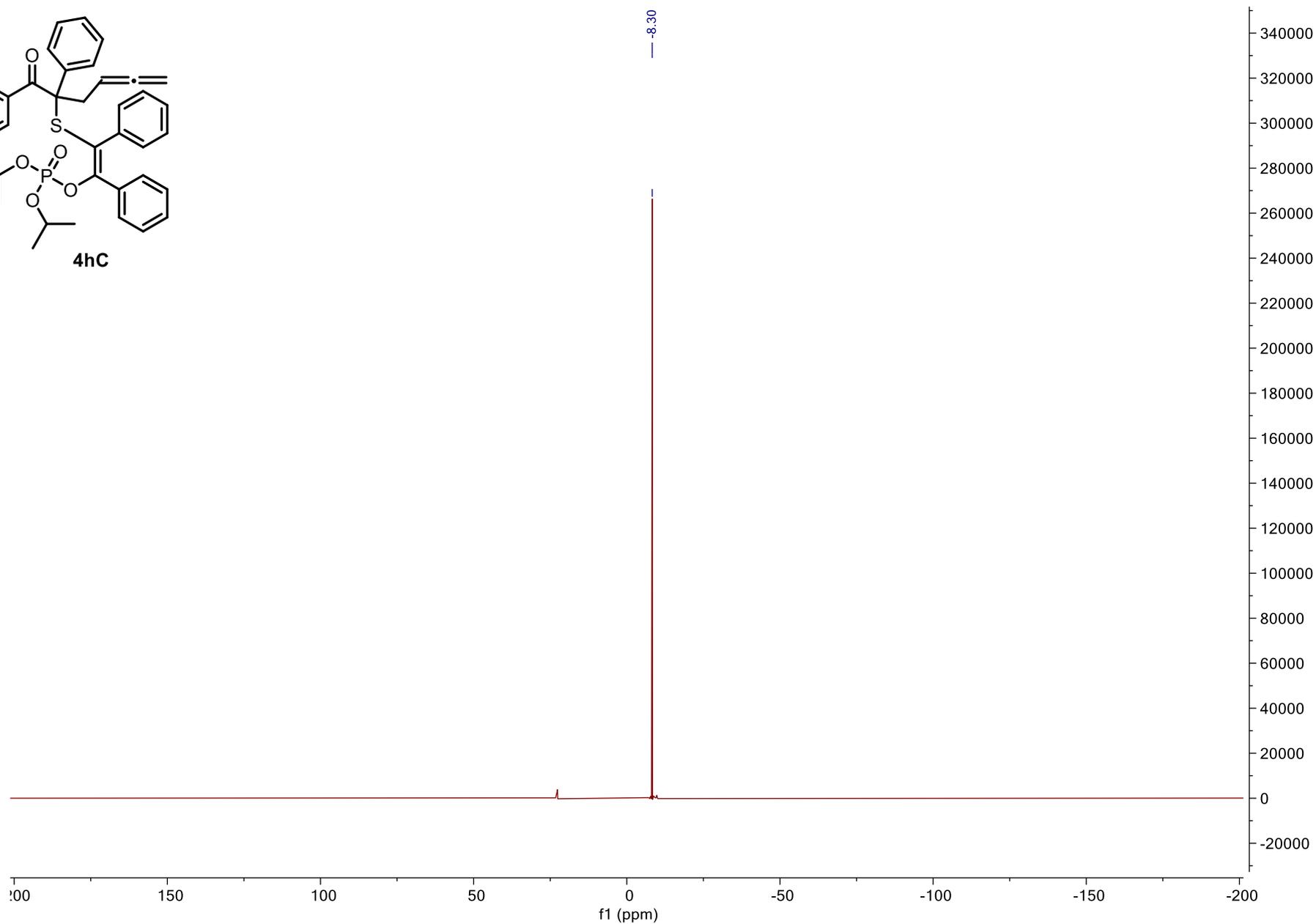
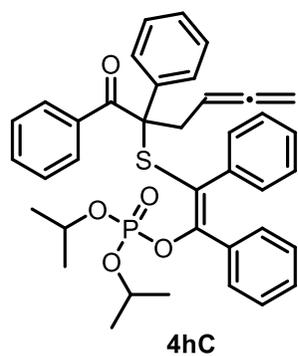


³¹P {¹H} NMR (162 MHz, CDCl₃)

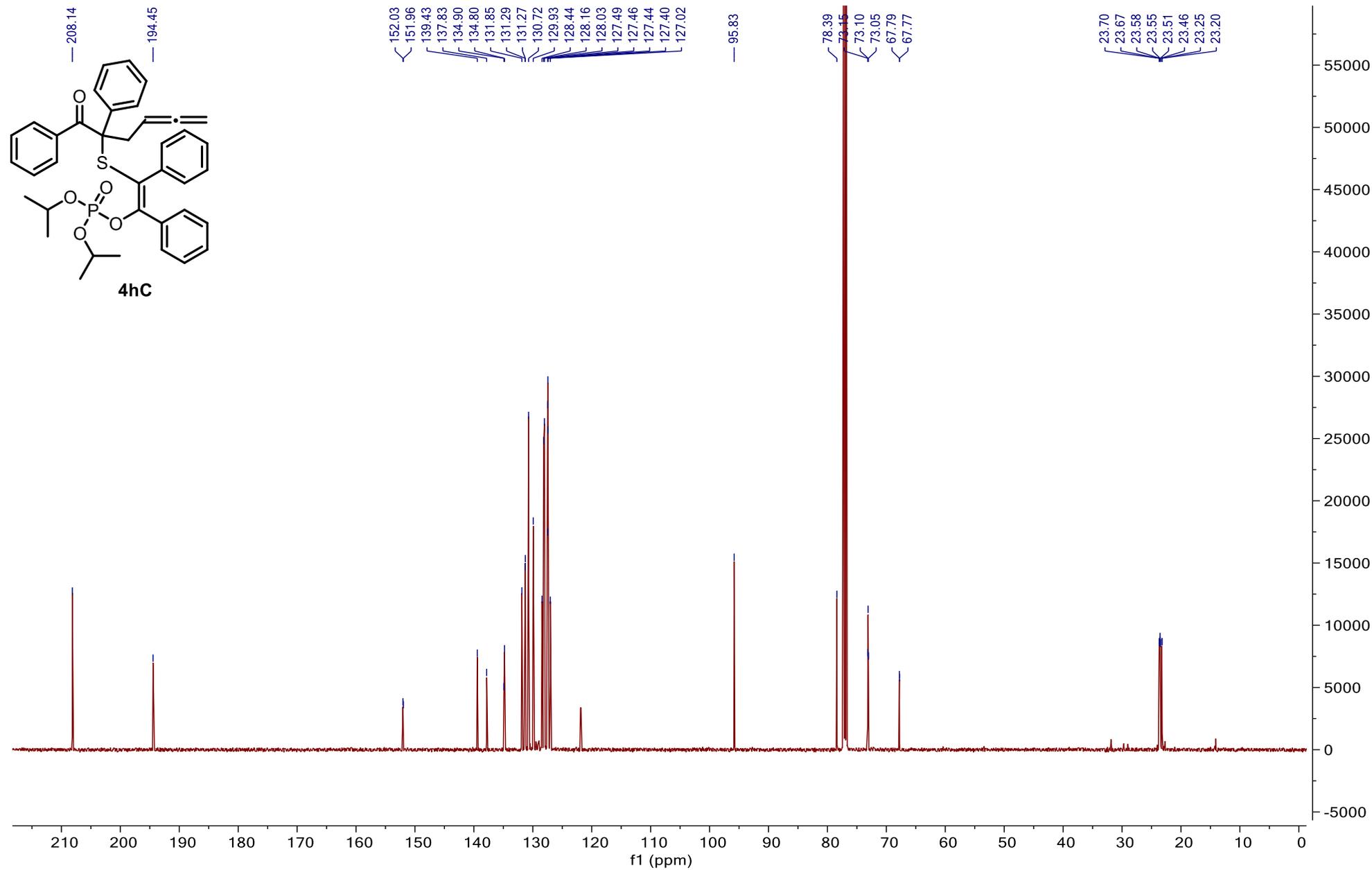
¹H NMR (500 MHz, CDCl₃)



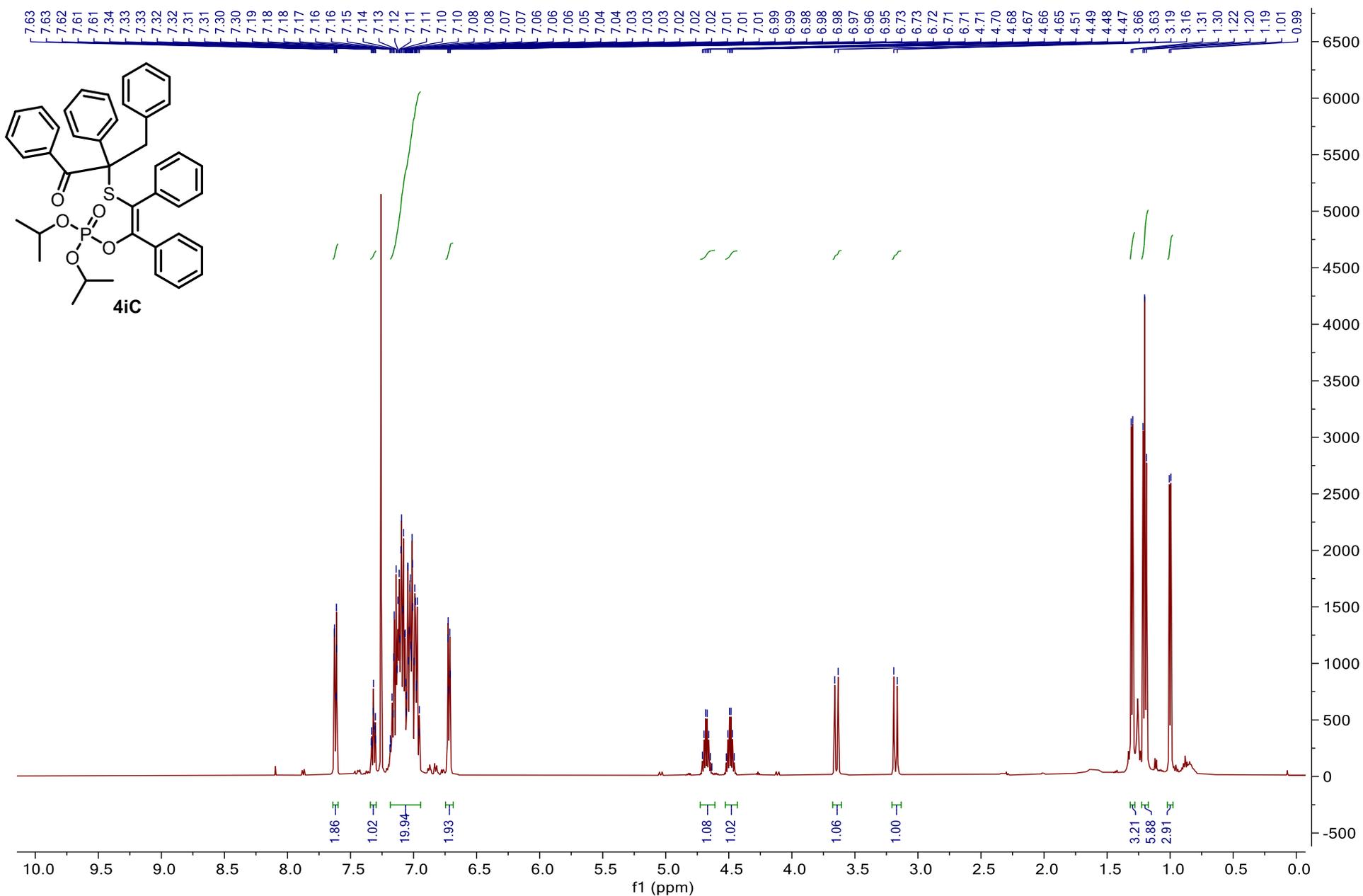
$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3)



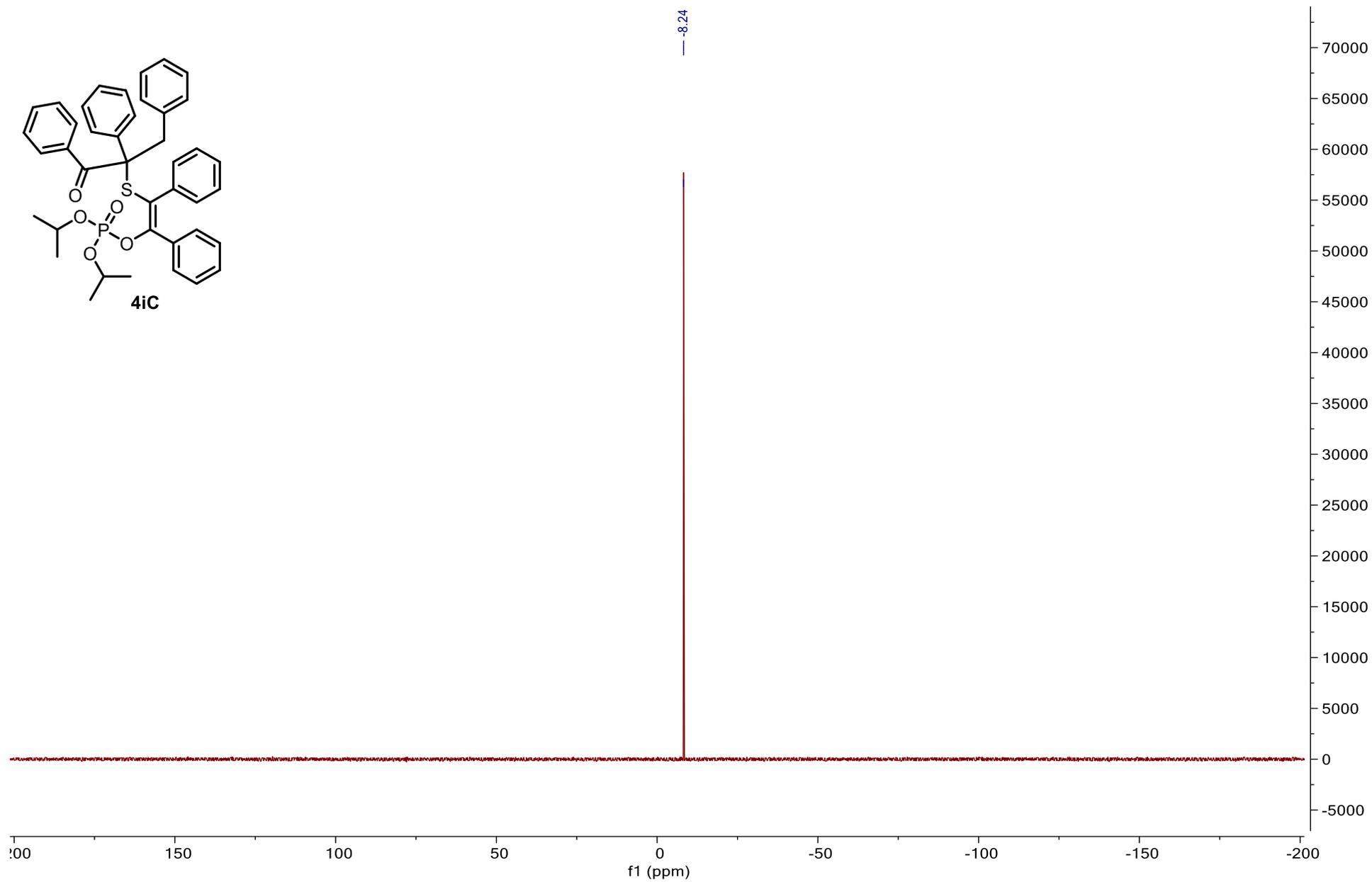
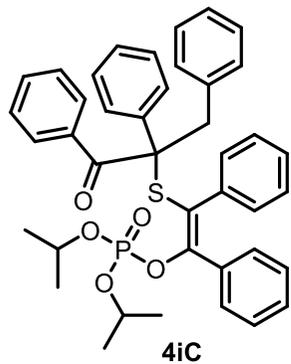
¹³C NMR (126 MHz, CDCl₃)



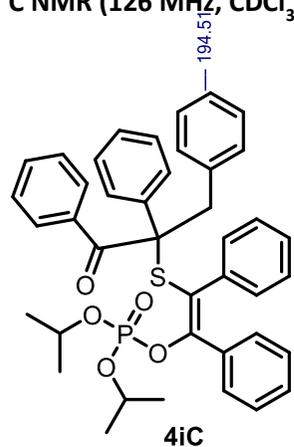
¹H NMR (500 MHz, CDCl₃)



$^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3)



¹³C NMR (126 MHz, CDCl₃)

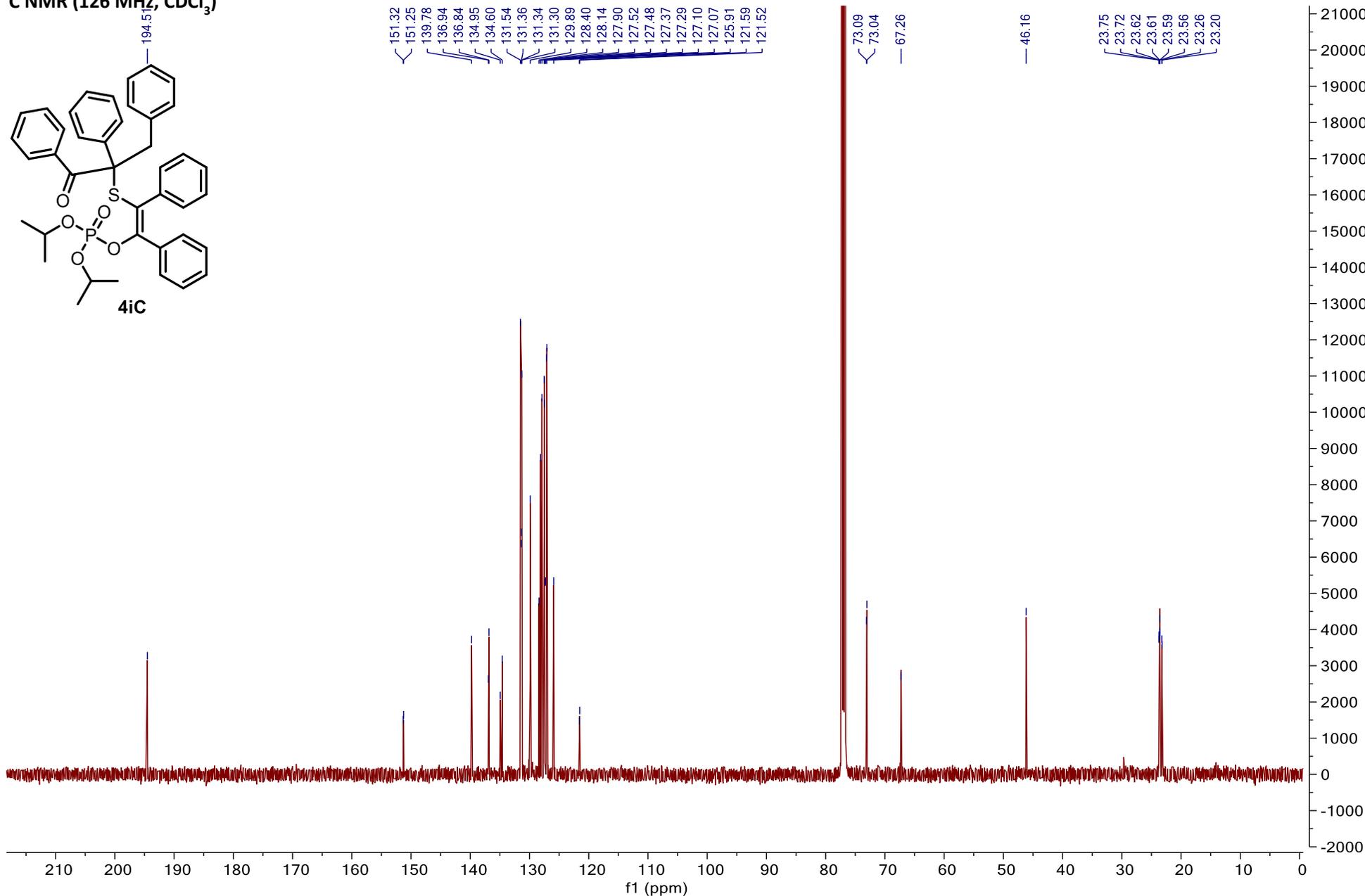


151.32
151.25
139.78
136.94
136.84
134.95
134.60
131.54
131.36
131.34
131.30
129.89
128.40
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127.37
127.29
127.10
127.07
125.91
121.59
121.52

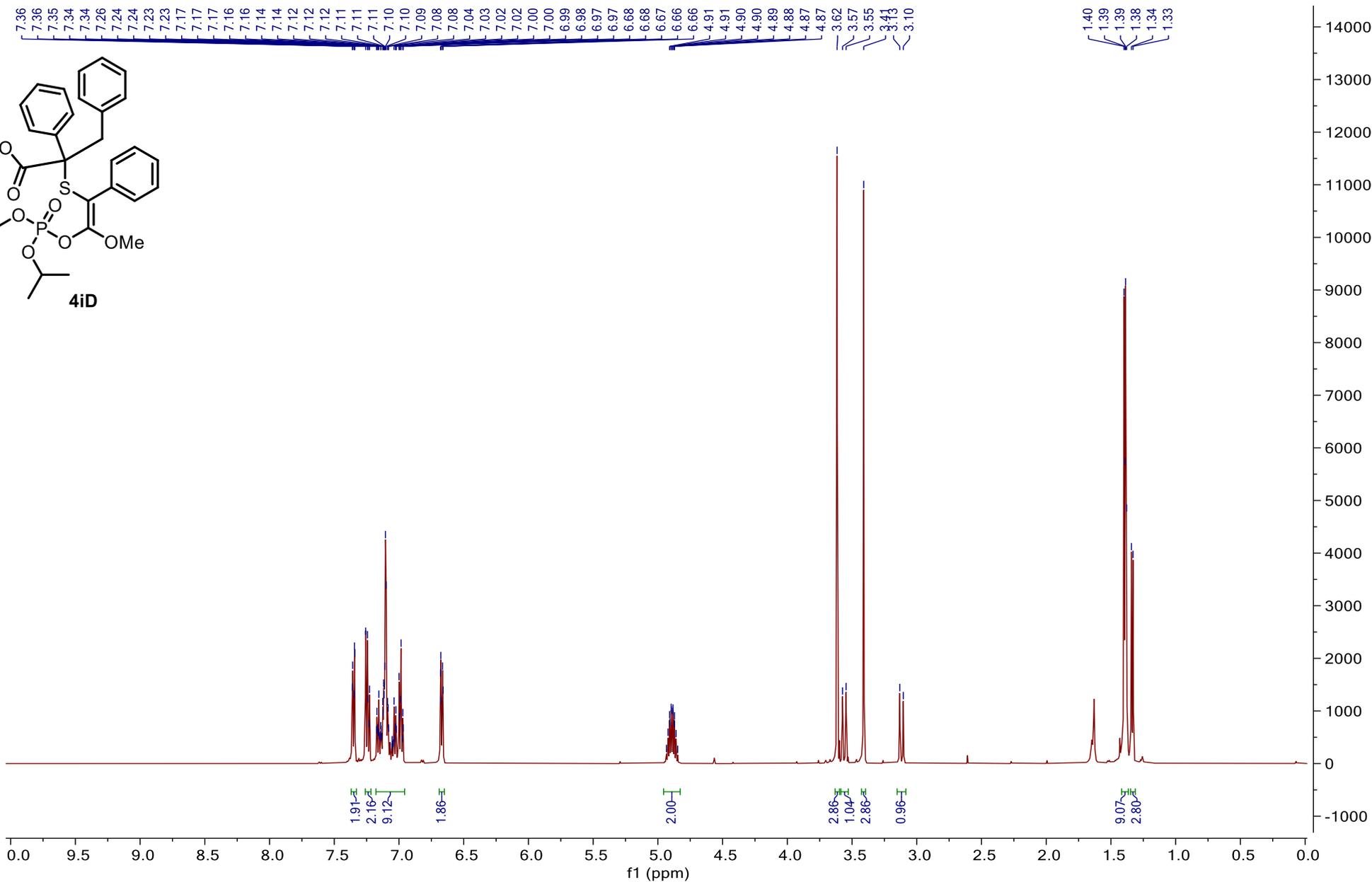
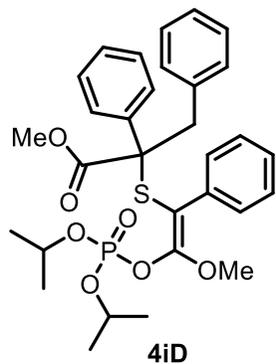
73.09
73.04
67.26

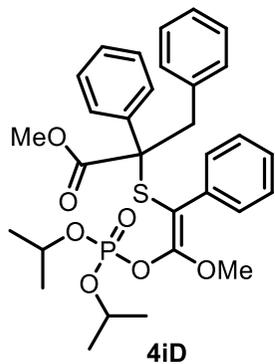
46.16

23.75
23.72
23.62
23.61
23.59
23.56
23.26
23.20

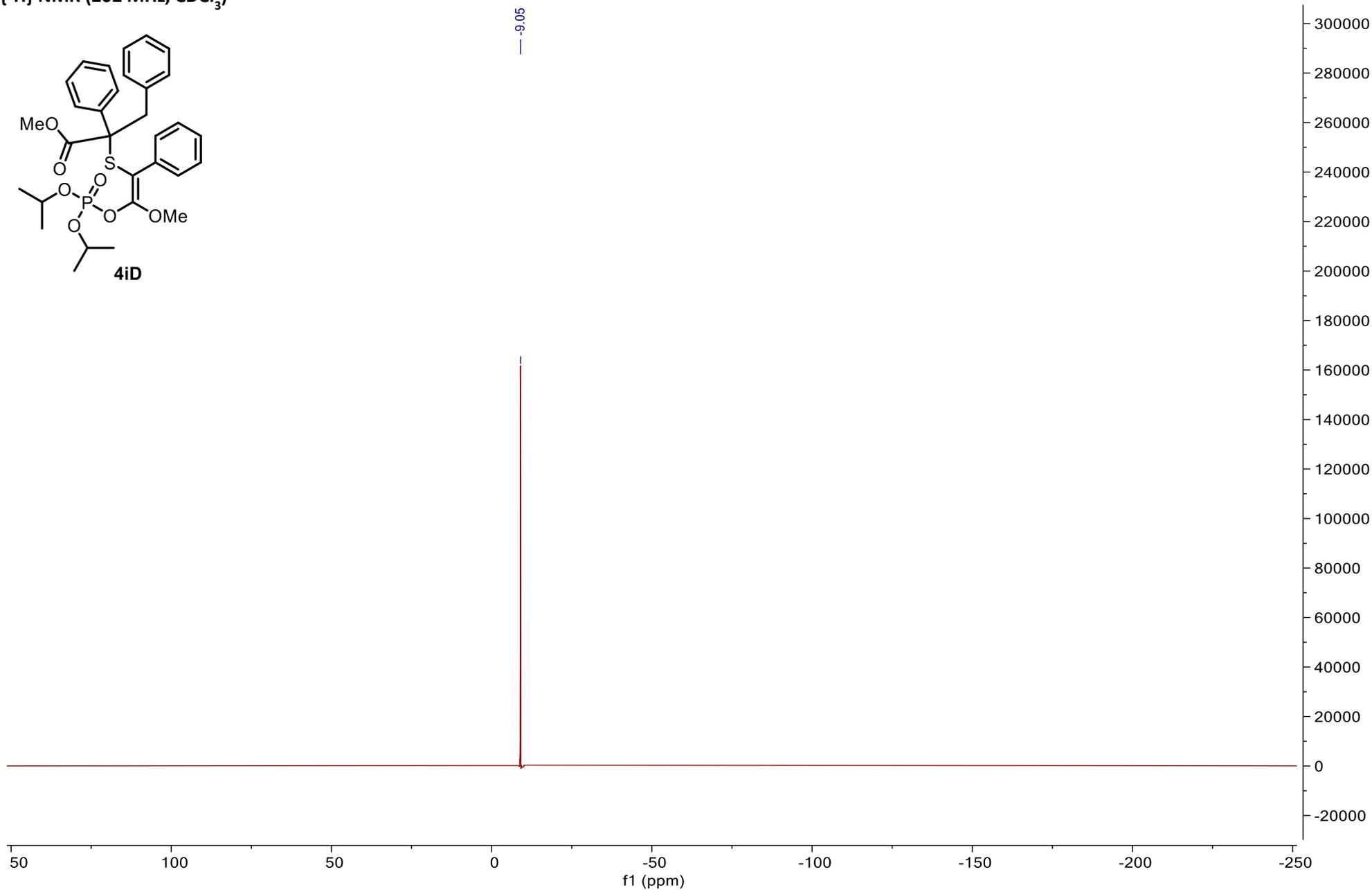


¹H NMR (500 MHz, CDCl₃)





-9.05



¹³C NMR (126 MHz, CDCl₃)

