Electronic Supplementary Information

Photocatalytic and straightforward olefination of alkyl aldehydes with alkynylphosphonates enabled by Cu(I)-photosensitizers

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1. General Information

Unless otherwise noted, all reactions were carried out in flame-dried reaction vessels with Teflon screw caps under nitrogen. Solvents were purified and dried according to standard methods prior to use. Unless otherwise stated, all reagents were purchased from commercial suppliers and used as received. Flash column chromatography was performed on silica gel (100-200 mesh) with the indicated eluent solvents. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualize with UV light or phosphomolybdic acid indicator.

^{1}H NMR spectra were recorded on a spectrometer at 25 °C in $CDCl_3$ at 400 MHz, with TMS as internal standard. ^{13}C NMR and ^{31}P NMR spectra were recorded on a spectrometer at 25 °C in $CDCl_3$ at 101 MHz and 162 MHz, respectively. Chemical shifts (δ) are expressed in ppm and coupling constants J are given in Hz. The following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, br = broad and all combinations thereof can be explained by their integral parts. High resolution mass spectra (HRMS) were obtained on a TOF-MS instrument with EI or ESI source.

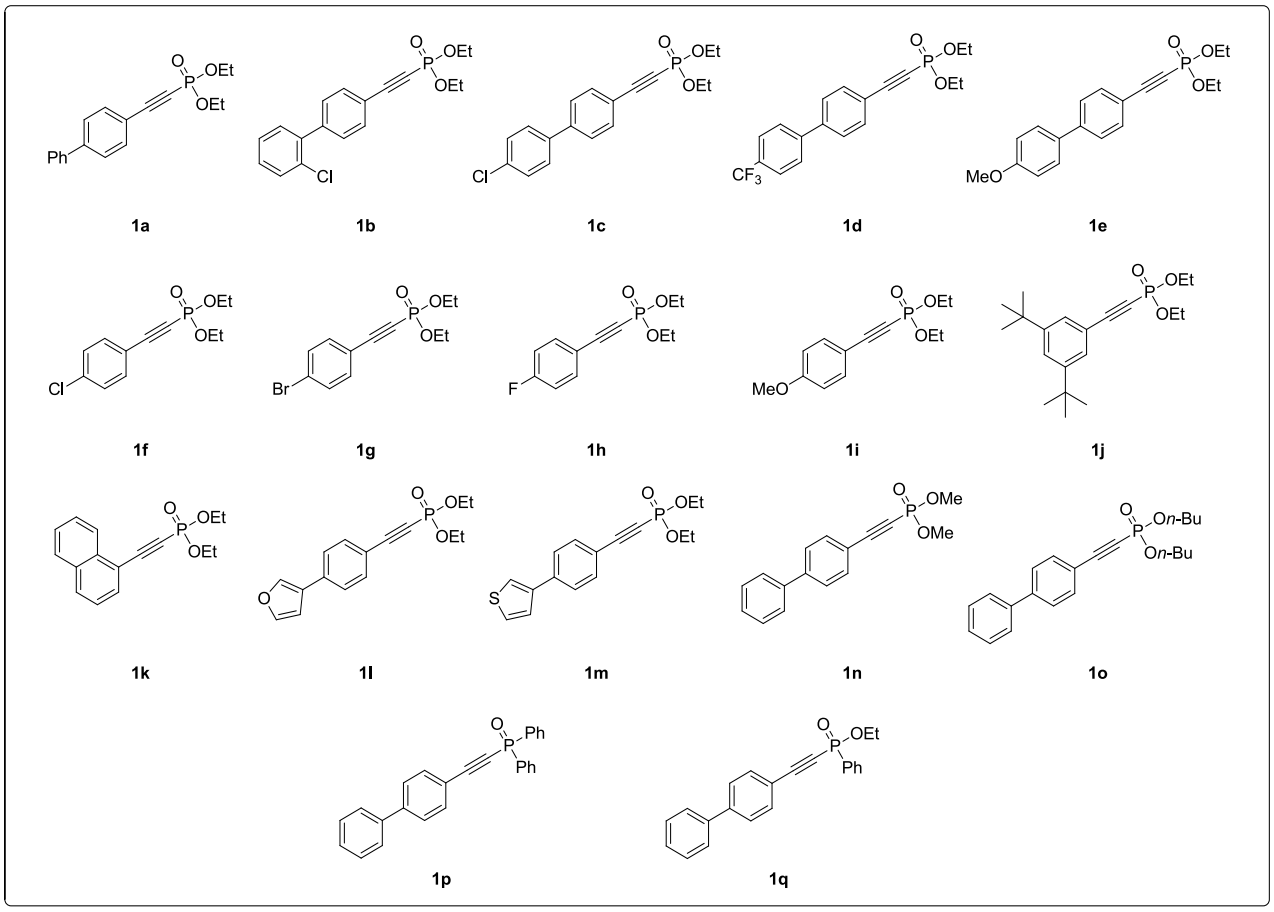
UV-vis absorption spectra were recorded on a UV-1800 UV spectrophotometer (Shimadzu, Japan).

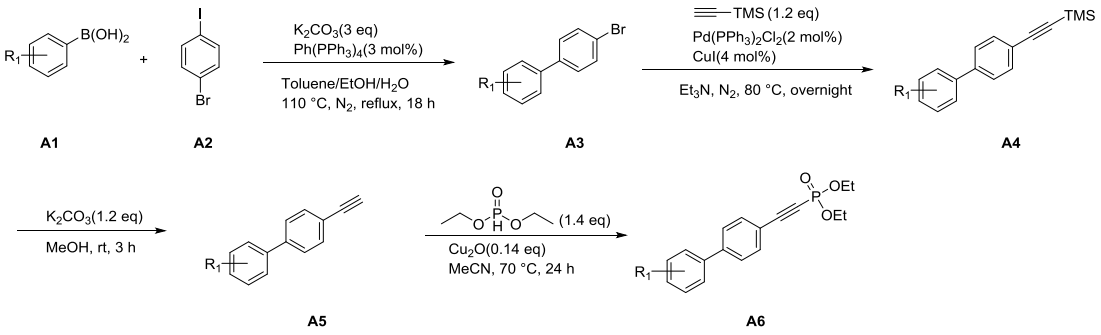
The emission spectra were investigated by a HORIBA fluorolog-3 luminescene spectrophotometer (the common intergration time were set to be 0.1 s in order to shorten the measurement time to be less than 40 s).

2. Preparation of Substrates and Catalyst

2.1 General procedure for the preparation of alkynes 1.

All alkynylphosphonates **1** are prepared according to the reported procedures.[1-6]



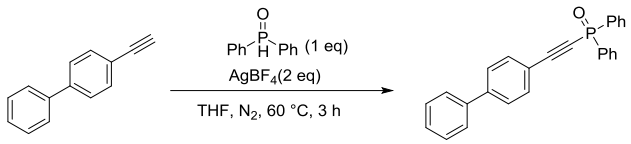


General procedure for the synthesis of **A3**: To a solution of boronic acid **A2** (10 mmol) in toluene/EtOH/H_2O (v/v/v = 18/14/6 mL) was added 1-bromo-4-iodobenzene **A1** (12 mmol), $Pd(PPh_3)_4$ (0.3 mmol) and K_2CO_3 (30 mmol), the mixture was stirred at 110 ℃ in a sealed tube under N_2 for 18 h. The reaction mixture was cooled and poured into an ice-water mixture solution, filtering to get solid material. The residue was purified by column chromatography on silica gel (petroleum ether) to yield the product **A3**.

General procedure for the synthesis of **A4**: To a mixture of 4-bromobiphenyl **A3** (10 mmol), $Pd(PPh_3)_2Cl_2$ (0.2 mmol) and CuI (0.4 mmol) in dry Et_3N (40 mL) was added trimethylsilylacetylene (12 mmol). The reaction mixture was stirred at 80 ℃ overnight under N_2 and monitored by TLC. After solvent removal, the residue was purified by column chromatography on silica gel (petroleum ether) to afford **A4**.

General procedure for the synthesis of **A5**: **A4** (8 mmol) and K_2CO_3 (9.6 mmol) were suspended in methanol (20 mL) and stirred at r.t. for 3 h. After solvent removal, the reaction mixture was taken up in water and CH_2Cl_2, the phases separated, and the aqueous layer was extracted trice with CH_2Cl_2. Removal of the solvent yielded **A5** as crude products.

General procedure for the synthesis of **A6**: To a mixture of 4-ethynyl-1,1′-biphenyl **A5** (8 mmol) and Cu_2O (1.1 mmol) in MeCN (30 mL) was added diethyl phosphite (11.2 mmol). The reaction mixture was stirred at 70 ℃ for 24 h in the atmosphere of the air and monitored by TLC. After solvent removal, the residue was purified by column chromatography on silica gel (petroleum ether : ethyl acetate) to afford the product **A6**.

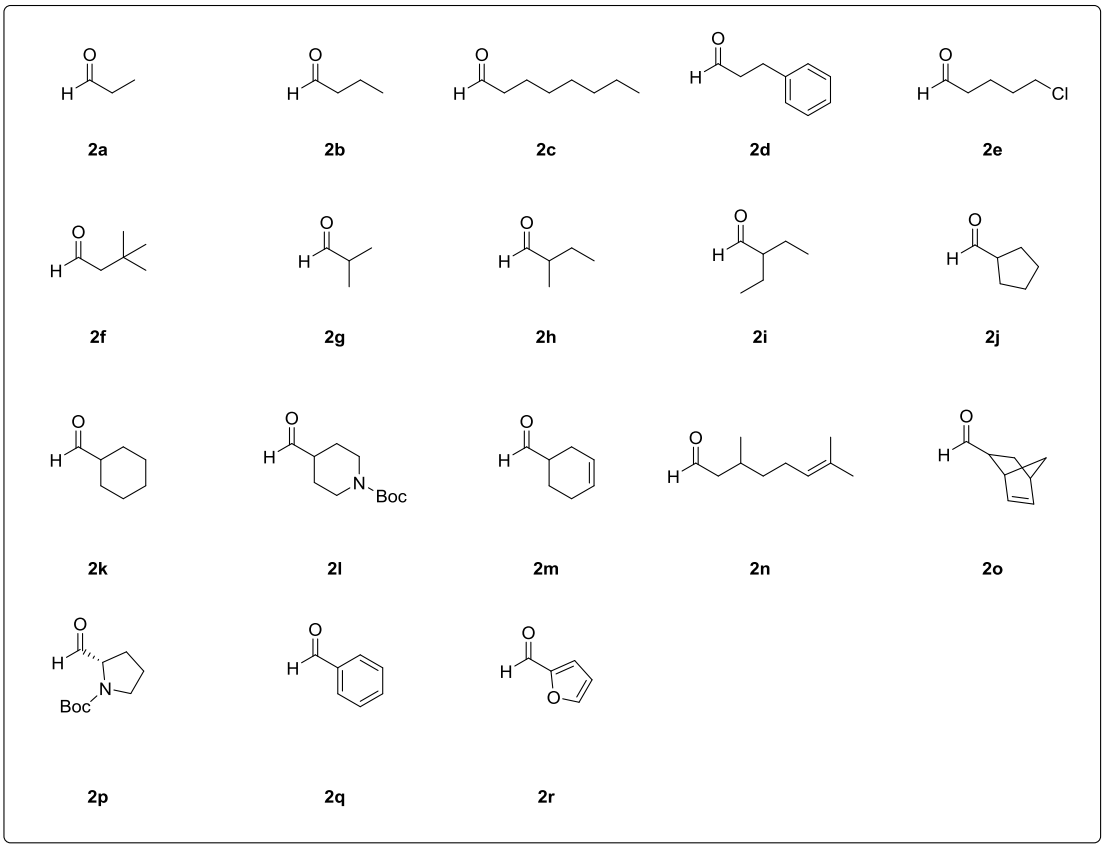


A5 **A7**

Procedure for the synthesis of **A7**: A mixture of diphenylphosphine oxide (1 mmol), $AgBF_4$ (2 mmol) and 4-ethynyl-1,1′-biphenyl **A5** (1 mmol) in THF (3 mL) was stirred under N_2 at 60 ℃ for 3 h and monitored by TLC. After solvent removal, the residue was purified by column chromatography on silica gel (petroleum ether : ethyl acetate) to afford the product **A7**.

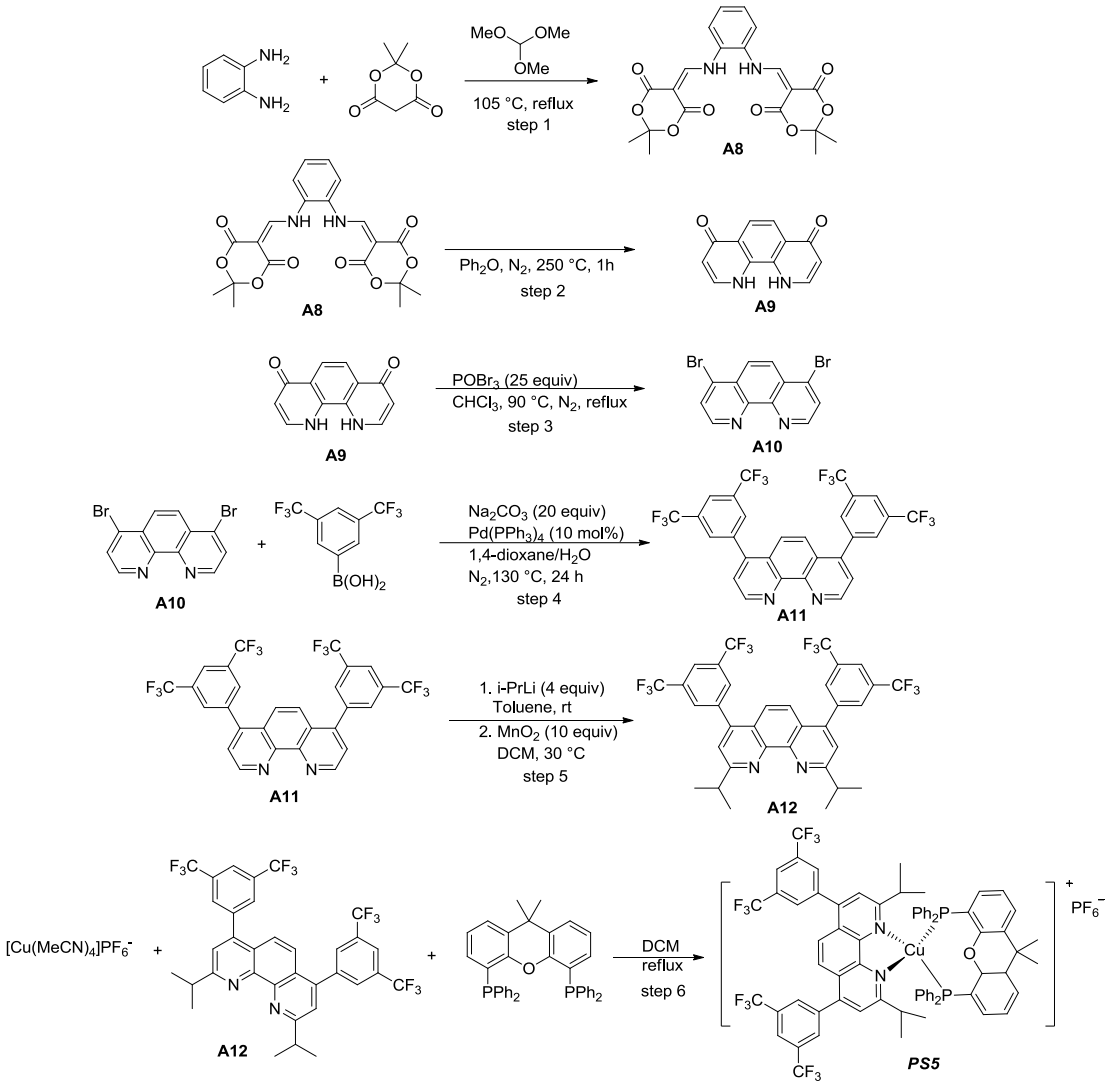
1a-1e, **1l**, **1m**, **1p** are prepared according to the above procedures. **1f-1k**, **1n** are prepared according to the procedure for the synthesis of **A6**. **1o**, **1q** are prepared according to the procedure for the synthesis of **A7**.

2.2 General procedure for the preparation of aldehydes 2.



Aldehydes **2a**-**2r** are commercial available and distilled prior to use.

2.3 Synthesis and characterization of *PS5*



2,9-diisopropyl-4,7-di(3,5-bis(trifluoromethyl-phenyl))-1,10-phenanthroline (***PS5***) was synthesized according to the reported procedure.[7-9]

Step 1: A mixture of 2,2-dimethyl-1,3-dioxane-4,6-dione (10.09 g, 70.00 mmol) and $HC(OMe)_3$ (124.73 mL, 0.98 mol) was refluxed in an oil bath for 1 h under nitrogen atmosphere. After cooling to 80 ℃, *o*-phenylenediamine (3.24 g, 30.00 mmol) was added and the reaction mixture was refluxed in an oil bath for 4 h under nitrogen atmosphere. After stirring at room temperature for 24 h, the precipitate was filtered and washed with Et_2O (3 × 100 mL) to give pure product **A8** as a white solid in 82% yield (10.2 g).

Step 2: **A8** (8.2 g, 19.80 mmol) was added slowly to Ph_2O (250 mL) and then heated to 240 ^oC in a sand bath. The reaction mixture was stirred for 1 h under nitrogen atmosphere. After cooling to 70 ^oC, the precipitate was filtered and washed with acetone (3 × 30 mL), *n*-hexane (3 × 30 mL) and Et_2O (3 × 30 mL) to give **A9** as a brown solid in 80% yield (4.2 g).

Step 3: The product from the previous step (4 mmol) and tribromophosphate oxide (100 mmol) were added to the three-port flask, nitrogen was pumped three times, and 30 mL anhydrous chloroform was added. The reaction was heated to 90 ℃ and stirred for 4 hours until the reaction was completed. The reaction mixture was cooled to 60 ℃. Slowly pour the reaction solution into 150 mL ice water and stir for another hour at room temperature, then add 50 mL chloroform and adjust pH to 13-14 with 50% sodium hydroxide solution, continue stirring for 1 hour, and finally extract with dichloromethane (3×50 mL), collect the organic phase, dry with anhydrous magnesium sulfate, filter, and remove the solvent under vacuum conditions. Crude product was separated by column chromatography (CH_2Cl_2:CH_3OH = 50:1) to obtain pure white solid in 40% yield. A mixture of **A9** (0.85 g, 4 mmol) and $POBr_3$ (28.6 g, 0.125 mol) were heated to 90 ^oC in an oil bath and stirred for 4 h under nitrogen atmosphere. After cooling to room temperature, iced H_2O (150 mL) was added slowly and the resultant mixture was stirred at room temperature for 1 h. $CHCl_3$ (50 mL) was added and the pH of the resultant mixture was adjusted to 13-14 by adding 50% NaOH solution. The reaction mixture was extracted with $CHCl_3$ (3 × 50 mL). The combined organic layer was washed with 50% NaOH solution and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to give **A10** as a white solid in 40% yield (0.54 g).

Step 4: **A10** (0.34 g, 1 mmol), Na_2CO_3 (2.12 g, 20 mmol), $Pd(PPh_3)_4$ (115 mg, 0.1 mmol) and (3,5-bis(trifluoromethyl)phenyl)boronic acid (1.0 g, 4 mmol) were added to 250 mL three-necked bottom in a mixture solvent of 50 mL 1,4-dioxane and

20 mL H_2O. Then the mixture was heated to 130 °C in an oil bath and stirred for 24 h under nitrogen atmosphere. The mixture was extracted with dichlormethane (3 × 30 mL), then dried over MgSO4. Filtration, concentration, and purification of the orange residue by flash column chromatography (1:100 MeOH/DCM) to give **A11** as a white solid in 50% yield (0.3 g).

Step 5: **A11** (0.604 g, 1 mmol) and 20 mL of dry toluene was stirred in a sealed tube under an argon atmosphere, and isopropyl lithium (4 mL,.4 mmol) was added at 0 ℃. The resulting suspension was stirred at 0 ℃ for 2 h, then stirred at room temperature for 16 h. The reaction was quenched with water (10 mL), and the mixture was extracted with dichloromethane (3 ×20 mL), then dried over $MgSO_4$. The organic solvent was removed under vacuum conditions. Then the active manganese dioxide (1.74 g, 20 mmol) and 20 mL dichloromethane were added and the reaction mixture was stirred at 30 ℃ for another 2 hours until the reaction was completed (TLC detection). The reaction mixture was cooled to room temperature, filtered and washed with dichloromethane. The organic solvents were removed under vacuum and the crude product was purified by column chromatography (PE:EA = 20:1) to give pure product **A12** in 59% yield (0.41 g).

Step 6: In an over-dried Schlenk tube, $[Cu(MeCN)_4]PF_6^-$ (373.0 mg, 1.0 mmol) and Xantphos (579.0 mg, 1.0 mmol) were dissolved in dry DCM (20 mL) at room temperature. The resulting solution was stirred at reflux in an oil bath overnight. The reaction mixture was then allowed to cool to room temperature and the 2,9-diisopropyl-4,7-di(3,5-bis(trifluoromethyl-phenyl))-1,10-phenanthroline **A 12** (604 mg, 1.0 mmol) was added at room temperature dissolved in a minimal amount of DCM. The resulting mixture was then heated to reflux in an oil bath for 3 hours until no further color change was observed (at this point red to yellow solution was obtained). The reaction mixture was then allowed to cool to room temperature and n-hexane was added to precipitate the product. It was filtered and washed with

n-hexane. The resulting solid was further purified by recrystallization in a DCM/n-hexane mixture at 4 ℃ to give pure ***PS5***.

Other Cu(I)-photosensitizers (***PS1***-***PS4, PS6, PS7***) were synthesized according to the previously reported literature.[10,11]

2.4 The photoelectric physical properties of *PS5*

Analysis of UV-Vis absorption spectra of *PS5*

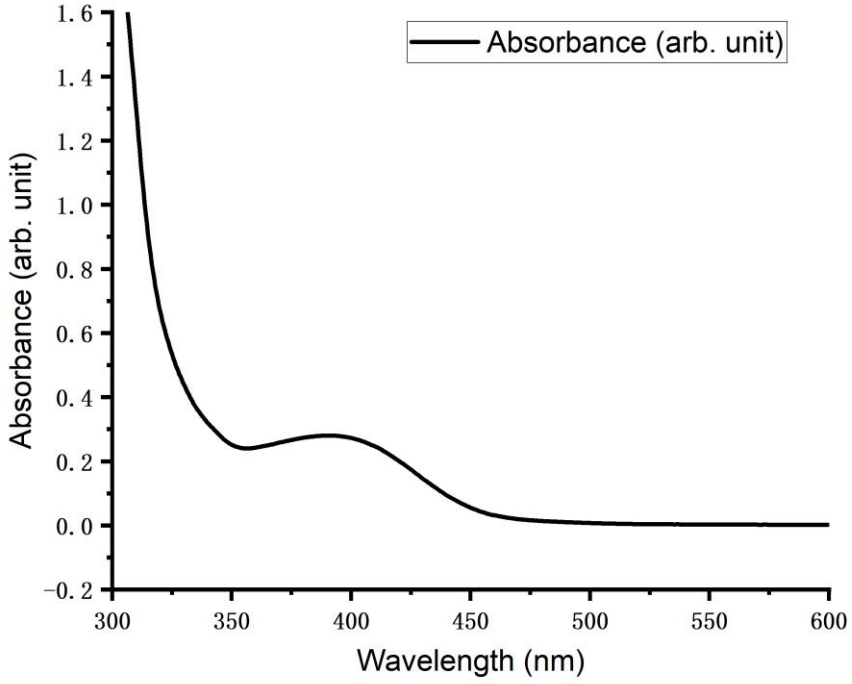


Figure *S1*: UV-visible absorption spectrum of [Cu(2,9-diisopropyl-4,7-di(3,5-bis(trifluoromethyl)-phenyl)-1,10-phenanthroline)(xantphos)]PF^{6-} (***PS5***) recorded at ambient temperature in MeCN (1×10^{-4} M).

Note: the maximum absorption (λ_{abs}) was observed at 390.5 nm.

Emission spectra of *PS5*

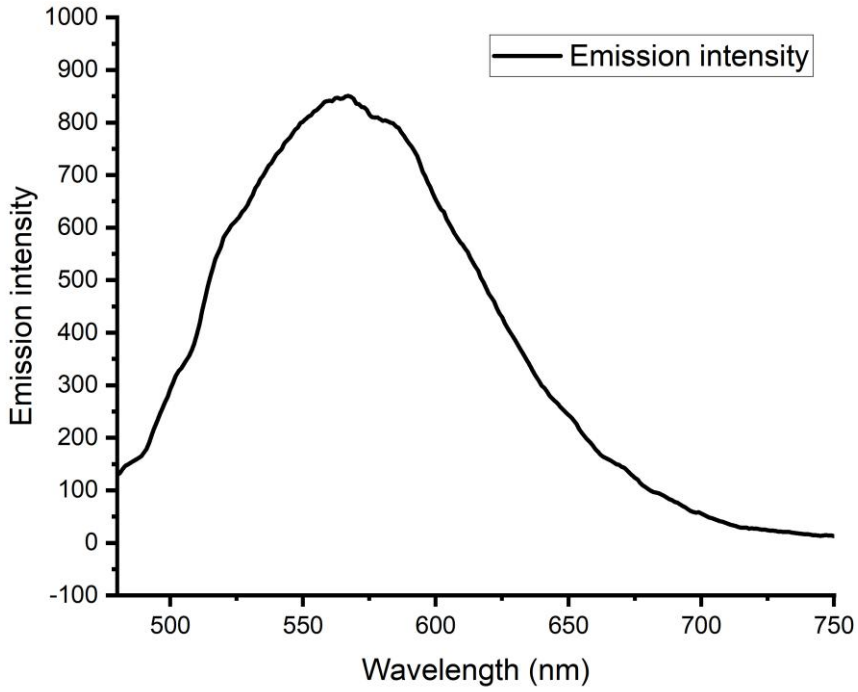


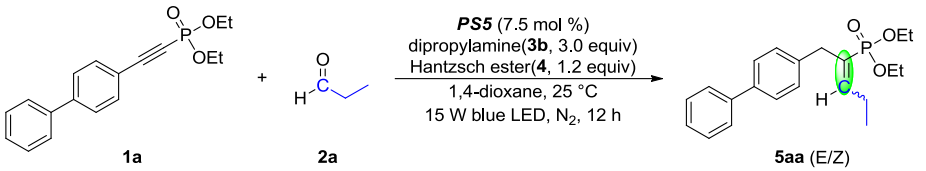
Figure *S2*: Visible emission spectrum of [Cu(2,9-diisopropyl-4,7-di(3,5-bis(trifluoromethyl)-phenyl)-1,10-phenanthroline)(xantphos)]PF^{6-} (***PS5***) obtained by excitation at 380 nm and recorded at ambient temperature in MeCN (1×10^{-4} M).

Note: the maximum emission was observed at 562 nm.

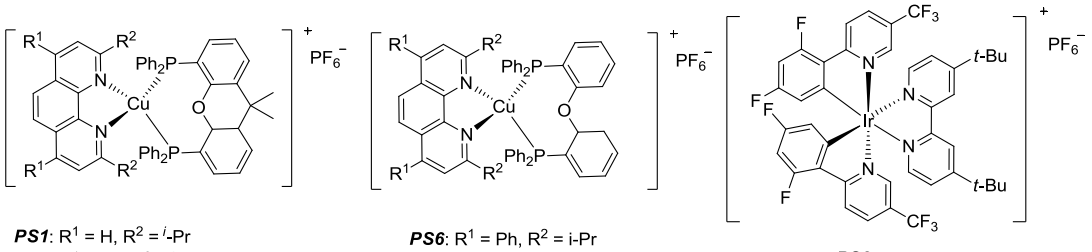
3. General Procedures for Synthesis of Vinylphosphonates 5

3.1 Optimization of reaction conditions

Table *S1*. Summary of screening of reaction parameters



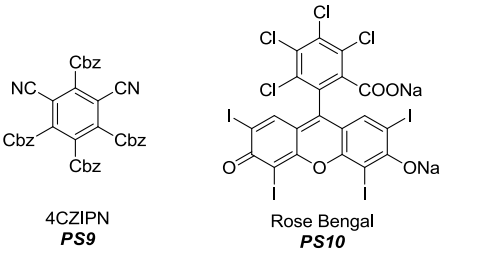
1a **2a** **5aa** (E/Z)



PS1: R^1 = H, R^2 = ^{i}-Pr
PS2: R^1 = Ph, R^2 = ^{i}-Pr
PS3: R^1 = Ph, R^2 = Me
PS4: R^1 = Ph, R^2 = *s*-Bu
PS5: R^1 = 3,5-bis(trifluoromethyl)-phenyl, R_2 = ^{i}-Pr

PS6: R^1 = Ph, R^2 = i-Pr
PS7: R^1 = Ph, R^2 = Me

PS8



4CZIPN
PS9

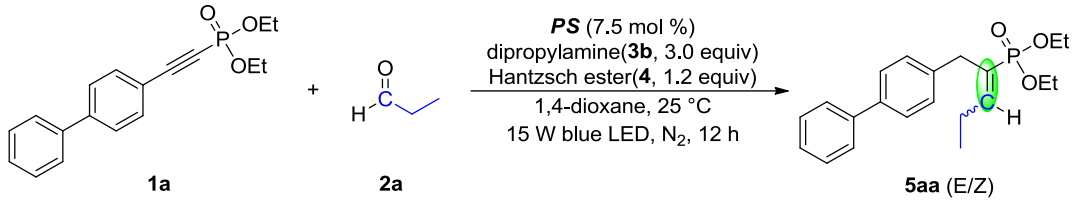
Rose Bengal
PS10

Entry	***PS***	Solvent	Amine [b]	Yield(%)[c] (E/Z)[d]
1	***PS2***	1,4-dioxane	**3b**	55 (>99:1)
2	***PS1***	1,4-dioxane	**3b**	trace
3	***PS3***	1,4-dioxane	**3b**	53 (>99:1)
4	***PS4***	1,4-dioxane	**3b**	41 (>99:1)
5	***PS5***	1,4-dioxane	**3b**	66 (>99:1)
6	***PS6***	1,4-dioxane	**3b**	55 (>99:1)
7	***PS7***	1,4-dioxane	**3b**	56 (>99:1)
8	***PS8***	1,4-dioxane	**3b**	28 (>99:1)
9	***PS9***	1,4-dioxane	**3b**	45 (>99:1)
10	***PS10***	1,4-dioxane	**3b**	0
11	***PS5***	**MeCN**	**3b**	**74 (**>99:1**)**
12	***PS5***	THF	**3b**	45 (>99:1)
13	***PS5***	*t*-BuOH	**3b**	65 (>99:1)
14	***PS5***	MeCN	**3a**	39 (>99:1)
15	***PS5***	MeCN	**3c**	trace
16	***PS5***	MeCN	**3d**	47 (>99:1)
17[g]	***PS5***	MeCN	**3b**	74 (>99:1)
18	without ***PS***	MeCN	**3b**	0
19	in the dark	MeCN	**3b**	0

[a]Standard conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), **3** (0.6 mmol), ***PS*** (7.5 mol %), Hantzsch ester **4** (0.24 mmol), solvent (4 mL), irradiation with 15 W blue LED under nitrogen atmosphere

at 25 ℃ for 12 h. [b]Amines: diethylamine (**3a**), dipropylamine (**3b**), pirrolidine (**3c**), piperidine (**3d**). [c]Isolated yield. [d]E/Z ratios were determined by GC analysis.

Table *S2.* Screening of the different photosensitizers[a]

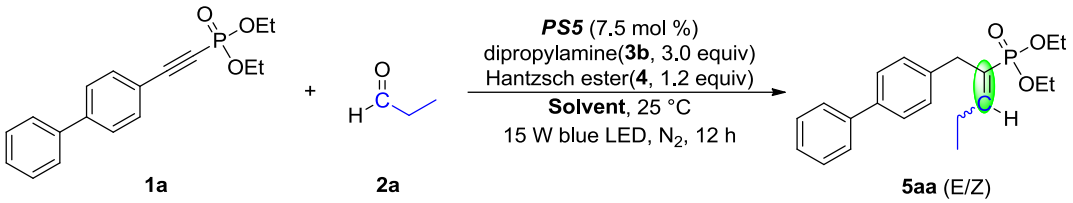


1a **2a** **5aa** (E/Z)

Entry	Photosensitizer	Yield of **5aa** (%)[b] (E/Z)[c]
1	***PS1***	trace
2	***PS2***	55 (> 99/1)
3	***PS3***	53 (> 99/1)
4	***PS4***	41 (> 99/1)
5	***PS5***	**66 (> 99/1)**
6	***PS6***	55 (> 99/1)
7	***PS7***	56 (> 99/1)
8	***PS8***	28 (> 99/1)
9	***PS9*** (Rose Bengal)	0
10	***PS10*** (4CzIPN)	45 (> 99/1)

[a]Standard conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), dipropylamine **3b** (0.6 mmol), ***PS*** (7.5 mol %), Hantzsch ester **4** (0.24 mmol), 1,4-dioxane (4 mL), irradiation with 15 W blue LED under nitrogen atmosphere at 25 ℃ for 12 h. [b]Isolated yield. [c]E/Z ratios were determined by GC analysis.

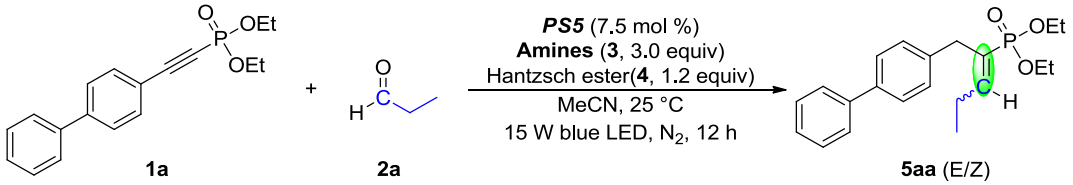
Table *S3*. Screening of the solvents[a]



Entry	Solvent	Yield of **5aa** (%)[b] (E/Z)[c]
1	1,4-dioxane	66 (> 99/1)
2	**MeCN**	**74 (> 99/1)**
3	1,4-dioxane/H_2O (4 mL/0.2 mL)	60 (> 99/1)
4	THF	45 (> 99/1)
5	tBuOH	65 (> 99/1)
6	CH_3OH	57 (> 99/1)
7	DMF	39 (> 99/1)

[a]Standard conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), dipropylamine **3b** (0.6 mmol), ***PS5*** (7.5 mol %), Hantzsch ester **4** (0.24 mmol), solvent (4 mL), irradiation with 15 W blue LED under nitrogen atmosphere at 25 ℃ for 12 h. [b]Isolated yield. [c]E/Z ratios were determined by GC analysis.

Table *S4*. Screening of the amines[a]



Entry	Amine(**3**)	Yield of **5aa** (%)[b] (E/Z)[c]
1	Diethyl amine (**3a**)	39 (> 99/1)
2	**Dipropylamine (3b)**	**74 (> 99/1)**
3	Pyrrolidine (**3c**)	trace
4	Piperidine (**3d**)	47 (> 99/1)

[a]Standard conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), Amine **3** (0.6 mmol), ***PS5*** (7.5 mol %), Hantzsch ester **4** (0.24 mmol), MeCN (4 mL), irradiation with 15 W blue LED under nitrogen

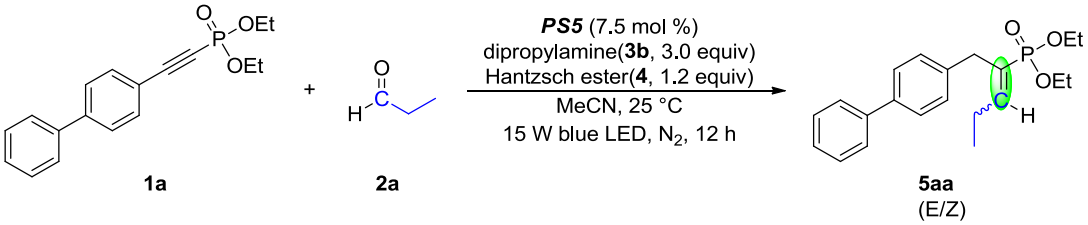
atmosphere at 25 ℃ for 12 h. [b]Isolated yield. [c]E/Z ratios were determined by GC analysis.

Table *S5*. Screening of the light source[a]

Entry	Light source	Yield of **5aa** (%)[b] (E/Z)[c]
1	**15 W blue lighht**	**74 (> 99/1)**
2	30 W blue light	74 (> 99/1)

[a]Standard conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), dipropylamine **3b** (0.6 mmol), ***PS5*** (7.5 mol %), Hantzsch ester **4** (0.24 mmol), MeCN (4 mL), irradiation with blue LED under nitrogen atmosphere at 25 ℃ for 12 h. [b]Isolated yield. [c]E/Z ratios were determined by GC analysis.

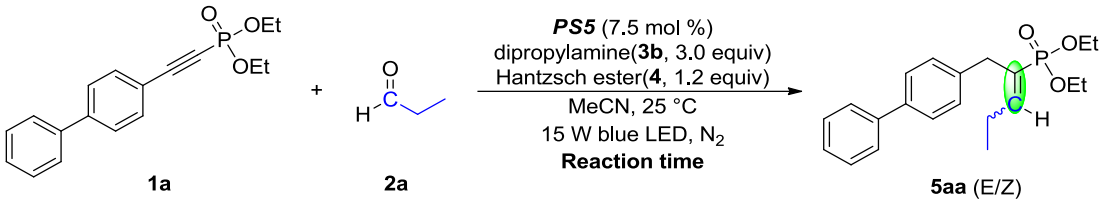
Table *S6*. Screening the amount of **1a**, **2a** and **3b**[a]



Entry	**1a**/**2a**/**3b** (equiv./equiv.)	Yield of **5aa** (%)[b] (E/Z)[c]
1	1/2/2	36 (> 99/1)
2	**1/3/3**	**74 (> 99/1)**
3	1/4/4	45 (> 99/1)

[a]Standard conditions: **1a** (0.2 mmol), **2a** (x mmol), dipropylamine **3b** (y mmol), ***PS5*** (7.5 mol %), Hantzsch ester **4** (0.24 mmol), MeCN (4 mL), irradiation with 15 W blue LED under nitrogen atmosphere at 25 ℃ for 12 h. [b]Isolated yield. [c]E/Z ratios were determined by GC analysis.

Table *S7*. Screening of reaction time[a]



Entry	Time (h)	Yield of **5aa** (%)[b] (E/Z)[c]
1	6	51 (> 99/1)
2	**12**	**74 (> 99/1)**

[a]Standard conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), dipropylamine **3b** (0.6 mmol), ***PS5*** (7.5 mol %), Hantzsch ester **4** (0.24 mmol), MeCN (4 mL), irradiation with 15 W blue LED under nitrogen atmosphere at 25 ℃. [b]Isolated yield. [c]E/Z ratios were determined by GC analysis.

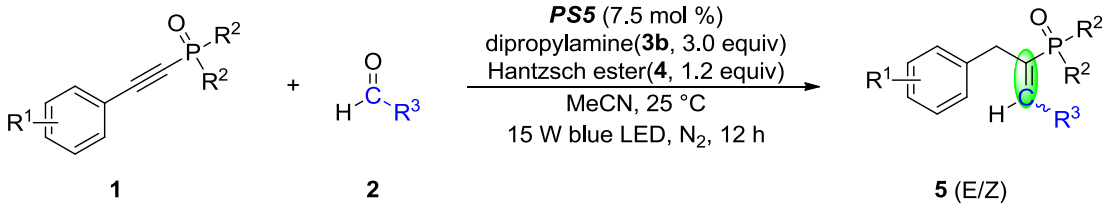
Table *S8*. Controlled experiments[a]

Entry	Varied from the standard condition	Yield of **5aa** (%)[b] (E/Z)[c]
1	Without photosensitizer	0
2	In the dark condition	0
3	Without light and photosensitizer	0

[a]Standard conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), dipropylamine **3b** (0.6 mmol), ***PS5*** (7.5 mol %), Hantzsch ester **4** (0.24 mmol), MeCN (4 mL), irradiation with 15 W blue LED under nitrogen atmosphere at 25 ℃ for 12 h. [b]Isolated yield. [c]E/Z ratios were determined by GC analysis.

3.2 Experimental details and characterization of products

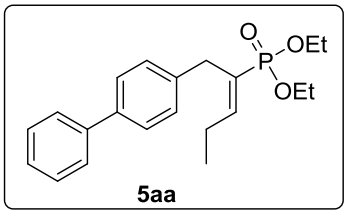
General procedure for the synthesis of vinylphosphonates 5.



To a 25 mL flame-dried Schlenk tube was added ***PS5*** (20 mg, 0.015 mmol) and Hantzsch ester **4** (61 mg, 0.24 mmol). The tube was evacuated and refilled with N_2 for

three times. A solution of **1** (0.2 mmol), aldehyde **2** (0.6 mmol), dipropylamine **3b** (0.6 mmol) and MeCN (4 mL) was added under nitrogen atmosphere. The reaction mixture was irradiated at a distance of 3 cm from blue LED and stirred at 25 °C for 12 h. Upon completion, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography on silica gel (100-200 mesh), eluting with the indicated mixture of ethyl acetate (EA)/petroleum ether (PE) to give pure alkene **5**.

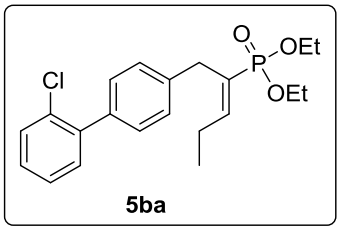
diethyl (1-([1,1'-biphenyl]-4-yl)pent-2-en-2-yl)phosphonate (5aa)



5aa

Yellow liquid. Yield: 74%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.1 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 7.1 Hz, 2H), 6.78 (dt, *J* = 23.2, 7.2 Hz, 1H)., 0.5H), 3.99 (m, 2H), 3.85 (m, 2H), 3.65 (d, *J* = 18.3 Hz, 2H), 2.36–2.25 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 6H), 1.08 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.6 (d, *J* = 10.0 Hz), 141.0, 139.1, 138.1 (d, *J* = 2.2 Hz), 128.9, 128.8, 127.2 (d, *J* = 180.0 Hz), 127.1, 127.0, 61.5 (d, *J* = 5.6 Hz), 32.5 (d, *J* = 11.0 Hz), 22.6 (d, *J* = 19.3 Hz), 16.2 (d, *J* = 6.8 Hz), 13.1 (d, *J* = 1.9 Hz). **HR-MS** (ESI) for $C_{21}H_{27}O_3NaP$ $([M+Na])^+$: calcd. 381.1596, found. 381.1598.

diethyl (1-(2'-chloro-[1,1'-biphenyl]-4-yl)pent-2-en-2-yl)phosphonate (5ba)

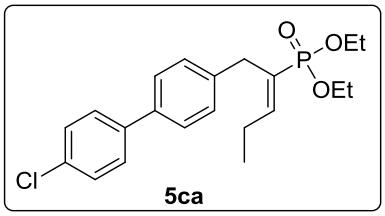


5ba

Yellow liquid. Yield: 52%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 6.9 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.24–7.17 (m, 5H), 6.72 (dt, *J* = 23.2, 7.2 Hz, 1H), 4.01–3.85 (m, 2H), 3.81–3.69 (m, 2H), 3.59 (d, *J* = 18.5 Hz, 2H), 2.32–2.20 (m, 2H), 1.09 (t, *J* = 7.1 Hz, 6H), 1.02 (t, *J* = 7.5 Hz, 3H). **^{13}C** NMR (101 MHz, $CDCl_3$): δ 150.5 (d, *J* = 10.1 Hz), 140.3, 138.4 (d, *J* = 2.0 Hz), 137.3, 132.5, 131.3, 129.9, 129.3, 128.4, 128.2, 127.2 (d, *J* = 179.8 Hz), 126.8, 61.5 (d, *J* = 5.5 Hz), 32.6 (d, *J* = 11.0 Hz), 22.6 (d, *J* = 19.2 Hz), 16.2 (d, *J* = 6.7 Hz), 13.1

(d, *J* = 1.9 Hz). **HR-MS** (ESI) for $C_{21}H_{26}O_3NaPCl$ ($[M+Na]^+$): calcd. 415.1206, found. 415.1212.

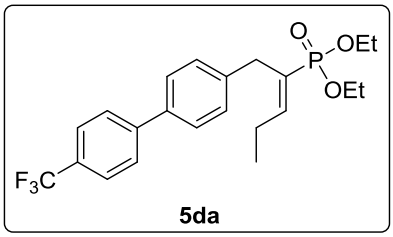
diethyl (1-(4'-chloro-[1,1'-biphenyl]-4-yl)pent-2-en-2-yl)phosphonate (5ca)



5ca

Yellow liquid. Yield: 53%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.50–7.45 (m, 3H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.12 (m, 1H), 6.78 (dt, *J* = 23.2, 7.1 Hz, 1H), 4.05–3.93 (m, 2H), 3.93–3.80 (m, 2H), 3.65 (d, *J* = 18.4 Hz, 2H), 2.32–2.27 (m, 2H), 1.18 (t, *J* = 8.0 Hz, 6H), 1.08 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.6 (d, *J* = 9.9 Hz), 139.4, 138.5 (d, *J* = 2.1 Hz), 137.8, 133.2, 132.0, 131.3, 130.2, 129.0, 128.9, 128.4, 128.2, 127.1 (d, *J* = 179.8 Hz), 126.8, 61.6 (d, *J* = 5.6 Hz), 32.5 (d, *J* = 11.2 Hz), 22.6 (d, *J* = 19.3 Hz), 16.2 (d, *J* =6.7 Hz), 13.1 (d, *J* = 1.6 Hz). **HR-MS** (ESI+) for $C_{21}H_{26}O_3NaPCl$ ($[M+Na]^+$): calcd. 415.1206, found. 415.1210.

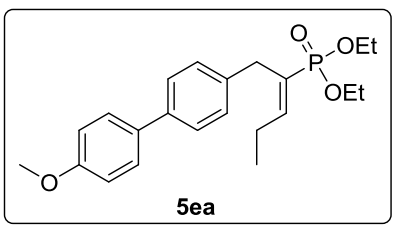
diethyl (1-(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)pent-2-en-2-yl)phosphonate (5da)



5da

Yellow liquid. Yield: 34%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.67 (s, 4H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.78 (dt, *J* = 23.2, 7.2 Hz, 1H), 4.01–3.97 (m, 2H), 3.89–3.86 (m, 2H), 3.67 (d, *J* = 18.3 Hz, 2H), 2.31–2.28 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 6H), 1.08 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.7 (d, *J* = 10.0 Hz), 144.4, 139.2 (d, *J* = 2.1 Hz), 137.6, 129.2 (q, *J* = 32.3 Hz), 129.1, 127.2, 127.1, 127.0 (d, *J* = 179.8 Hz), 125.7 (q, *J* = 3.0 Hz), 124.3 (q, *J* = 272.7 Hz), 61.6 (d, *J* = 5.4 Hz), 32.5 (d, *J* = 11.1 Hz), 22.6 (d, *J* = 19.0 Hz), 16.2 (d, *J* = 6.6 Hz), 13.1 (d, *J* = 1.9 Hz). **HR-MS** (ESI+) for $C_{22}H_{26}O_3F_3NaP$ ($[M+Na]^+$): calcd. 449.1469, found. 449.1463.

diethyl (1-(4'-methoxy-[1,1'-biphenyl]-4-yl)pent-2-en-2-yl)phosphonate (5ea)

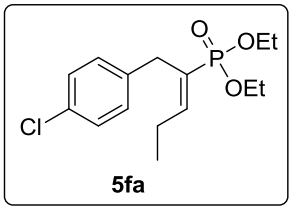


5ea

Yellow liquid. Yield: 50%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.18 (m, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.70 (dt, *J* = 23.2, 7.2 Hz, 1H), 3.92–3.90 (m, 2H), 3.83–3.71 (m, 5H), 3.56 (d, *J* = 18.4 Hz, 2H), 2.25–2.21 (m, 2H), 1.09 (t, *J* = 7.1

Hz, 6H), 1.00 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 159.0, 150.6 (d, *J* = 10.0 Hz), 138.7, 137.4, 133.5, 128.8, 128.0, 127.2 (d, *J* = 178.8 Hz), 126.5, 114.2, 61.5 (d, *J* = 5.5 Hz), 55.4, 32.4 (d, *J* = 11.0 Hz), 22.6 (d, *J* = 19.2 Hz), 16.2 (d, *J* = 6.7 Hz), 13.1 (d, *J* = 1.5 Hz). **HR-MS** (ESI+) for $C_{22}H_{29}O_4NaP$ $([M+Na])^+$: calcd. 411.1701, found. 411.1705.

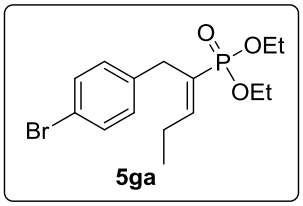
diethyl (1-(4-chlorophenyl)pent-2-en-2-yl)phosphonate (5fa)



5fa

Yellow liquid. Yield: 68%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.75 (dt, *J* = 23.1, 7.2 Hz, 1H), 4.00–3.97 (m, 2H), 3.87–3.85 (m, 2H), 3.57 (d, *J* = 18.2 Hz, 2H), 2.26–2.23 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 6H), 1.05 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.6 (d, *J* = 10.0 Hz), 137 (d, *J* = 2.1 Hz), 131.8, 129.8, 128.3, 126.9 (d, *J* = 179.9 Hz), 61.5 (d, *J* = 5.6 Hz), 32.1 (d, *J* = 11.2 Hz), 22.5 (d, *J* = 19.2 Hz), 16.1 (d, *J* = 6.6 Hz), 13.0 (d, *J* = 1.6 Hz). **HR-MS** (ESI+) for $C_{15}H_{22}O_3NaPCl$ $([M+Na])^+$: calcd. 339.0892, found. 339.0893.

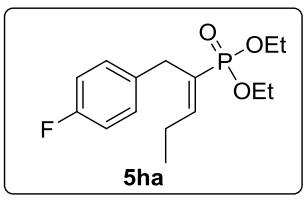
diethyl (1-(4-bromophenyl)pent-2-en-2-yl)phosphonate (5ga)



5ga

Yellow liquid. Yield: 53%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.74 (dt, *J* = 23.1, 7.2 Hz, 1H), 4.00–3.97 (m, 2H), 3.95–3.86 (m, 2H), 3.55 (d, *J* = 18.2 Hz, 2H), 2.26–2.22 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 6H), 1.05 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.6 (d, *J* = 9.9 Hz), 138.0 (d, *J* = 2.2 Hz), 131.3, 130.2, 126.9 (d, *J* = 180.0 Hz), 119.9, 61.6 (d, *J* = 5.6 Hz), 32.2 (d, *J* = 11.0 Hz), 22.5 (d, *J* = 19.0 Hz), 16.2 (d, *J* = 6.5 Hz), 13.0 (d, *J* = 1.6 Hz). **HR-MS** (ESI+) for $C_{15}H_{22}O_3NaPBr$ $([M+Na])^+$: calcd. 383.0388, found. 383.0388.

diethyl (1-(4-fluorophenyl)pent-2-en-2-yl)phosphonate (5ha)

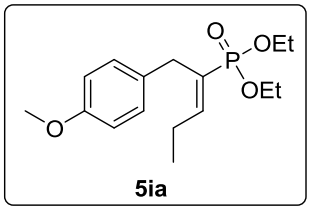


5ha

Yellow liquid. Yield: 45%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.16 (m, 2H), 6.95 (m, 2H), 6.74 (dt, *J* = 23.2, 7.2 Hz, 1H), 4.01–3.95 (m, 2H), 3.88–3.81 (m, 2H), 3.57 (d, *J* = 18.4 Hz, 2H), 2.28–2.23 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 6H), 1.05 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 161.4 (d, *J* = 241.4 Hz), 150.4 (d, *J* = 10.0 Hz), 134.6, 129.8 (d, *J* = 7.7 Hz), 127.3 (d, *J* = 179.3 Hz), 115.0 (d, *J* = 21.2 Hz), 61.5 (d, *J*

= 5.5 Hz), 32.0 (d, *J* = 11.1 Hz), 22.5 (d, *J* = 19.2 Hz), 16.2 (d, *J* = 6.6 Hz), 13.0 (d, *J* = 1.0 Hz). **HR-MS** (ESI+) for $C_{15}H_{22}O_3NaPF$ $([M+Na])^+$: calcd. 383.0388, found. 383.0388.

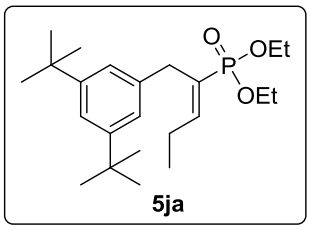
diethyl (1-(4-methoxyphenyl)pent-2-en-2-yl)phosphonate (5ia)



5ia

Yellow liquid. Yield: 50%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.11 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.73 (dt, *J* = 23.3, 7.2 Hz, 1H), 3.98–3.96 (m, 2H), 3.87–3.81 (m, 2H), 3.78 (s, 3H), 3.54 (d, *J* = 18.5 Hz, 2H), 2.29–2.26 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 6H), 1.05 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ158.0, 150.2 (d, *J* = 10.1 Hz), 131.0 (d, *J* = 2.2 Hz), 129.4, 127.6 (d, *J* = 178.1 Hz), 113.6, 61.4 (d, *J* = 5.4 Hz), 55.3, 31.9 (d, *J* = 11.0 Hz), 22.5 (d, *J* = 19.3 Hz), 16.2 (d, *J* = 6.6 Hz), 13.1 (d, *J* = 1.8 Hz). **HR-MS** (ESI+) for $C_{16}H_{25}O_4NaP$ $([M+Na])^+$: calcd. 335.1388, found. 335.1388.

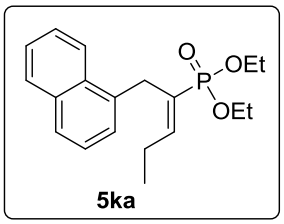
diethyl (1-(3,5-di-tert-butylphenyl)pent-2-en-2-yl)phosphonate (5ja)



5ja

Yellow liquid. Yield: 46%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.16 (s, 1H), 6.95 (s, 2H), 6.71 (dt, *J* = 23.4, 7.3 Hz, 1H), 3.89–3.83 (m, 2H), 3.72–3.66 (m, 2H), 3.52 (d, *J* = 18.7 Hz, 2H), 2.26–2.22 (m, 2H), 1.22 (s, 18H), 1.01 (m, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.6 (d, *J* = 9.1 Hz), 150.5, 137.6 (d, *J* = 2.0 Hz), 127.4 (d, *J* = 177.0 Hz), 122.6, 120.0, 61.4 (d, *J* = 5.3 Hz), 34.8, 33.2 (d, *J* = 10.9 Hz), 31.5, 22.6 (d, *J* = 19.2 Hz), 16.0 (d, *J* = 6.9 Hz), 13.1 (d, *J* = 1.9 Hz). **HR-MS** (ESI+) for $C_{23}H_{39}O_3NaP$ $([M+Na])^+$: calcd. 417.2535, found. 417.2534.

diethyl (1-(naphthalen-1-yl)pent-2-en-2-yl)phosphonate (5ka)

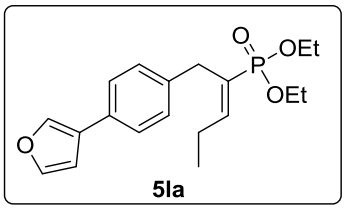


5ka

Yellow liquid. Yield: 55%, E/Z > 99/1. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.56–7.49 (m, 2H), 7.44–7.35 (m, 1H), 7.31 (d, *J* = 6.8 Hz, 1H), 6.93 (dt, *J* = 23.3, 7.2 Hz, 1H), 4.07 (d, *J* = 17.4 Hz, 2H), 3.99–3.96 (m, 2H), 3.91–3.87 (m, 2H), 2.21–2.18 (m, 2H), 1.12 (t, *J* = 7.1 Hz, 6H), 1.06 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 151.5 (d, *J* = 9.8 Hz), 133.9 (d, *J* = 2.7 Hz), 133.7, 132.1, 128.8, 126.9, 126.4 (d, *J* = 183.8 Hz), 125.9, 125.5, 125.4, 125.0, 123.3, 61.61 (d, *J* = 5.8 Hz), 29.6 (d, *J* = 11.0

Hz), 22.6 (d, *J* = 19.6 Hz), 16.1 (d, *J* = 6.6 Hz), 13.0 (d, *J* = 1.9 Hz). **HR-MS** (ESI+) for $C_{19}H_{25}O_3NaP$ $([M+Na])^+$: calcd. 355.1439, found. 355.1441.

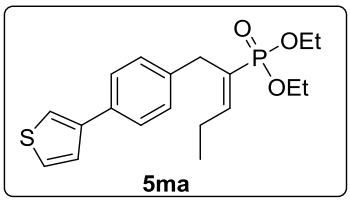
diethyl (1-(4-(furan-3-yl)phenyl)pent-2-en-2-yl)phosphonate (5la)



5la

Yellow liquid. Yield: 52%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 1.2 Hz, 1H), 7.14 (d, *J* = 8.3 Hz, 2H), 6.70 (dt, *J* = 23.2, 7.2 Hz, 1H), 6.53 (d, *J* = 3.3 Hz, 1H), 6.39 (m, 1H), 3.94–3.88 (m, 2H), 3.81–3.76 (m, 2H), 3.54 (d, *J* = 18.3 Hz, 2H), 2.23–2.18 (m, 2H), 1.10 (t, *J* = 7.1 Hz, 6H), 0.99 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 154.0, 150.7 (d, *J* = 10.1 Hz), 141.8, 138.1 (d, *J* = 2.1 Hz), 128.9, 128.8, 127.0 (d, *J* = 179.2 Hz), 123.7, 111.6, 104.5, 61.6 (d, *J* = 5.4 Hz), 32.6 (d, *J* = 11.0 Hz), 22.6 (d, *J* = 19.2 Hz), 16.2 (d, *J* = 6.6 Hz), 13.1 (d, *J* = 1.5 Hz). **HR-MS** (ESI+) for $C_{19}H_{25}O_4PNa$ $([M+Na])^+$: calcd. 371.1388, found. 371.1393.

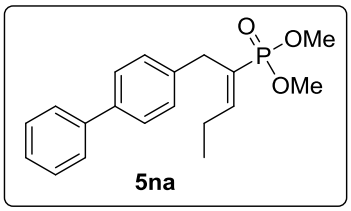
diethyl (1-(4-(thiophen-3-yl)phenyl)pent-2-en-2-yl)phosphonate (5ma)



5ma

Yellow liquid. Yield: 63%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 4.2 Hz, 1H), 7.16 (d, *J* = 5.1 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.99–6.97 (m, 1H), 6.69 (dt, *J* = 23.2, 7.2 Hz, 1H), 3.92–3.88 (m, 2H), 3.81–3.76 (m, 2H), 3.53 (d, *J* = 18.3 Hz, 2H), 2.22–2.17 (m, 2H), 1.09 (t, *J* = 7.1 Hz, 6H), 0.98 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ150.6 (d, *J* = 10.1 Hz), 144.3, 138.3 (d, *J* = 2.1 Hz), 132.4, 129.0, 128.0, 125.8, 125.3 (d, *J* = 173.7 Hz), 124.5, 122.7, 61.5 (d, *J* = 5.5 Hz), 32.5 (d, *J* = 11.0 Hz), 22.6 (d, *J* = 19.1 Hz), 16.2 (d, *J* = 6.6 Hz), 13.1 (d, *J* = 1.8 Hz). **HR-MS** (ESI+) for $C_{19}H_{25}O_3PNaS$ $([M+Na])^+$: calcd. 387.1160, found. 387.1160.

dimethyl (1-([1,1'-biphenyl]-4-yl)pent-2-en-2-yl)phosphonate (5na)

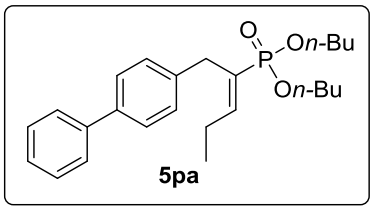


5na

Yellow liquid. Yield: 77%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 7.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.35 (m, 2H), 7.25 (m, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.72 (dt, *J* = 23.3, 7.2 Hz, 1H), 3.56 (d, *J* = 18.5 Hz, 2H), 3.48 (d, *J* = 10.9 Hz, 6H), 2.26–2.22 (m, 2H), 1.01 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 151.5 (d, *J* = 10.0 Hz), 140.8, 139.1, 137.8 (d, *J* = 2.1 Hz), 128.82, 128.77, 127.2, 127.0, 126.9, 126.2 (d, *J* = 179.8 Hz), 52.2 (d, *J* = 5.7

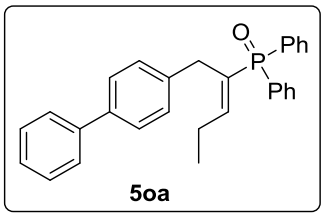
Hz), 32.4 (d, *J* = 11.0 Hz), 22.7 (d, *J* = 19.2 Hz), 13.1 (d, *J* = 1.9 Hz). **HR-MS** (ESI+) for $C_{19}H_{23}O_3NaP$ $([M]+Na)^+$: calcd. 353.1283, found. 353.1279.

dibutyl (1-([1,1'-biphenyl]-4-yl)pent-2-en-2-yl)phosphonate (5oa)



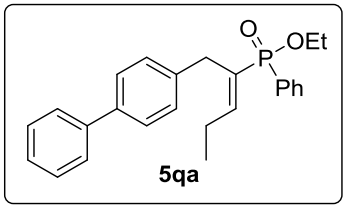
Yellow liquid. Yield: 64%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 6.80 (dt, *J* = 23.2, 7.2 Hz, 1H), 3.94 (dq, *J* = 9.9, 6.6 Hz, 2H), 3.81 (dq, *J* = 9.9, 6.7 Hz, 2H), 3.66 (d, *J* = 18.4 Hz, 2H), 2.32 (dq, *J* = 7.5, 3.5 Hz, 2H), 1.57–1.45 (m, 4H), 1.32–1.26 (m, 4H), 1.10 (t, *J* = 7.5 Hz, 3H), 0.86 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.5 (d, *J* = 10.0 Hz), 141.0, 139.1, 138.0 (d, *J* = 2.1 Hz), 128.8, 128.7, 128.1, 127.1, 127.0, 126.3, 65.2 (d, *J* = 5.8 Hz), 32.5 (d, *J* = 10.9 Hz), 32.4 (d, *J* = 6.6 Hz), 22.6 (d, *J* = 19.3 Hz), 18.7, 13.1 (d, *J* = 1.5 Hz). **HR-MS** (ESI+) for $C_{25}H_{35}O_3NaP$ $([M+Na])^+$: calcd. 437.2222, found. 437.2220.

(1-([1,1'-biphenyl]-4-yl)pent-2-en-2-yl)diphenylphosphine oxide (5pa)



Yellow solid. Yield: 45%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.67–7.62 (m, 4H), 7.51–7.46 (m, 4H), 7.44 (d, *J* = 8.0 Hz), 7.41–7.36 (m, 6H), 7.32–7.30 (m, 3H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.40 (dt, *J* = 20.8, 7.1 Hz, 1H), 3.74 (d, *J* = 15.7 Hz, 2H), 2.32–2.28 (m, 2H), 1.00 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.4 (d, *J* = 9.4 Hz), 141.0, 138.7, 137.7 (d, *J* = 1.6 Hz), 132.1 (d, *J* = 9.5 Hz), 131.8 (d, *J* = 102.0 Hz), 131.61, 131.59, 130.2 (d, *J* = 164.6 Hz), 128.8 (d, *J* = 18.4 Hz), 128.3 (d, *J* = 11.8 Hz), 127.0, 126.9, 126.8, 32.9 (d, *J* = 11.7 Hz), 23.1 (d, *J* = 15.3 Hz), 13.1 (d, *J* = 1.3 Hz). **HR-MS** (ESI+) for $C_{29}H_{27}ONaP([M+Na])^+$: calcd. 445.1697, found. 445.1691.

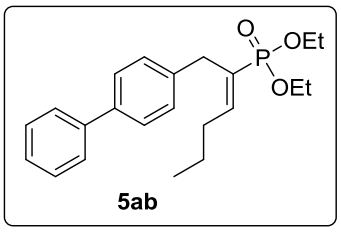
ethyl (1-([1,1'-biphenyl]-4-yl)pent-2-en-2-yl)(phenyl)phosphinate (5qa)



Yellow liquid. Yield: 58%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77–7.66 (m, 2H), 7.56 (dd, *J* = 8.1, 1.0 Hz, 2H), 7.47–7.34 (m, 8H), 7.14 (d, *J* = 8.3 Hz, 2H), 6.81 (dt, *J* = 21.1, 7.2 Hz, 1H), 4.04–3.85 (m, 2H), 3.64 (m, 2H), 2.29 (dq, *J* = 7.5, 2.8 Hz, 2H), 1.23 (t, *J* = 7.0 Hz, 3H), 1.07 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 149.9 (d, *J* = 9.3 Hz), 141.0, 138.9, 137.8 (d, *J*

= 2.1 Hz), 131.8, 131.7 (d, *J* = 10.1 Hz), 131.2 (d, *J* = 133.3 Hz), 130.5 (d, *J* = 131.3 Hz), 128.8, 128.7, 128.30 (d, *J* = 12.7 Hz), 127.1, 126.94, 126.87, 60.6 (d, *J* = 5.9 Hz), 32.3 (d, *J* = 12.4 Hz), 22.8 (d, *J* = 16.4 Hz), 16.3 (d, *J* = 6.7 Hz), 13.1 (d, *J* = 1.3 Hz). **HR-MS** (ESI+) for $C_{25}H_{27}O_2PNa$ $([M+Na])^+$: calcd. 413.1641, found. 413.1647.

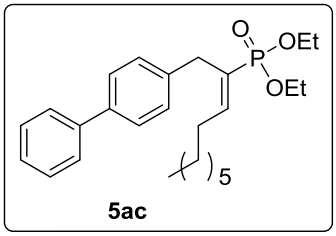
diethyl (1-([1,1'-biphenyl]-4-yl)hex-2-en-2-yl)phosphonate (5ab)



5ab

Yellow liquid. Yield: 54%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.80 (dt, *J* = 23.3, 7.2 Hz, 1H), 4.01–3.95 (m, 2H), 3.86–3.82 (m, 2H), 3.65 (d, *J* = 18.4 Hz, 2H), 2.31–2.24 (m, 2H), 1.51 (m, 2H), 1.16 (t, *J* = 7.1 Hz, 6H), 0.94 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 149.1 (d, *J* = 10.2 Hz), 141.0, 139.1 138.1 (d, *J* = 2.1 Hz), 128.91, 128.89, 128.8, 127.9 (d, *J* = 178.8 Hz), 127.1, 127.0, 61.5 (d, *J* = 5.6 Hz), 32.6 (d, *J* = 11.2 Hz), 31.2 (d, *J* = 18.6 Hz), 21.9 (d, *J* = 1.4 Hz), 16.2 (d, *J* = 6.8 Hz), 14.0. **HR-MS** (ESI+) for $C_{22}H_{29}O_3NaP$ $([M+Na])^+$: calcd. 395.1752, found. 395.1756.

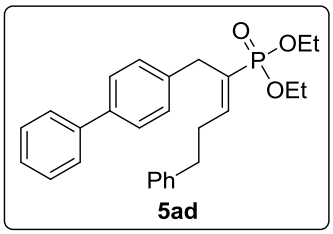
diethyl (1-([1,1'-biphenyl]-4-yl)dec-2-en-2-yl)phosphonate (5ac)



5ac

Yellow liquid. Yield: 64%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 7.2 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.21 (m, 2H), 6.72 (dt, *J* = 23.3, 7.2 Hz, 1H), 3.94–3.88 (m, 2H), 3.81–3.75 (m, 2H), 3.58 (d, *J* = 18.3 Hz, 2H), 2.23–2.20 (m, 2H), 1.21–1.08 (m, 10H), 1.09 (t, *J* = 7.1 Hz, 6H), 0.80 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): 149.4 (d, *J* = 10.2 Hz), 141.0, 139.1, 138.1 (d, *J* = 2.1 Hz), 128.9, 128.8, 127.6 (d, *J* = 178.8 Hz), 127.1, 127.0, 61.5 (d, *J* = 5.6 Hz), 32.6 (d, *J* = 11.1 Hz), 31.8, 29.4, 29.2, 29.1, 28.6 (d, *J* = 1.2 Hz), 22.6, 16.2 (d, *J* = 6.7 Hz), 14.1. **HR-MS** (ESI+) for $C_{26}H_{37}O_3NaP$ $([M+Na])^+$: calcd. 451.2378, found. 451.2383.

diethyl (1-([1,1'-biphenyl]-4-yl)-5-phenylpent-2-en-2-yl)phosphonate (5ad)

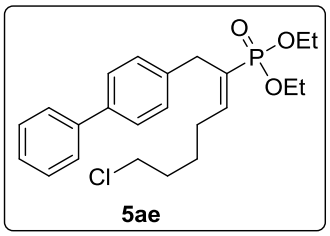


5ad

Yellow liquid. Yield: 52%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58–7.54 (m, 2H), 7.48–7.39 (m, 4H), 7.34 (m, 1H), 7.27–7.25 (m, 2H), 7.20–7.14 (m, 5H), 6.82 (dt, *J* = 23.2, 7.3 Hz, 1H), 3.98–3.92 (m, 2H), 3.83–3.76 (m, 2H), 3.56 (d, *J* = 18.2 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 2.62–2.59 (m, 2H), 1.14 (t, *J* = 8.4 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ

147.8 (d, *J* = 10.4 Hz), 141.0, 140.9, 139.1, 137.9 (d, *J* = 2.2 Hz), 128.9, 128.8, 128.6 (d, *J* = 177.8 Hz), 128.50, 128.48, 127.2, 126.99, 126.97, 126.2, 61.6 (d, *J* = 5.5 Hz), 34.7, 32.5 (d, *J* = 11.0 Hz), 31.2 (d, *J* = 19.0 Hz), 16.1 (d, *J* = 6.7 Hz). **HR-MS** (ESI+) for $C_{27}H_{31}O_3NaP$ $([M+Na])^+$: calcd. 457.1909, found. 457.1902.

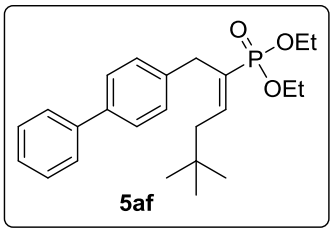
diethyl (1-([1,1'-biphenyl]-4-yl)-7-chlorohept-2-en-2-yl)phosphonate (5ae)



5ae

Yellow liquid. Yield: 66%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.1 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 6.6 Hz, 2H), (dt, *J* = 23.2, 7.2 Hz, 1H), 4.01–3.97 (m, 2H), 3.90–3.86 (m, 2H), 3.65 (d, *J* = 18.2 Hz, 2H), 3.50 (t, *J* = 6.5 Hz, 2H), 2.33–2.30 (m, 2H), 1.80–1.77 (m, 2H), 1.66–1.62 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 148.1 (d, *J* = 10.4 Hz), 140.9, 139.2 (d, J = 2.3 Hz), 137.9, 128.9, 128.8, 128.6 (d, *J* = 178.8 Hz), 127.2, 127.02, 126.97, 61.6 (d, *J* = 5.6 Hz), 44.6, 32.6 (d, *J* = 10.8 Hz), 32.1, 28.4 (d, *J* = 19.1 Hz), 25.8, 16.2 (d, *J* = 6.6 Hz). **HR-MS** (ESI+) for $C_{23}H_{30}O_3PNaCl$ $([M+Na])^+$: calcd. 443.1519, found. 443.1520.

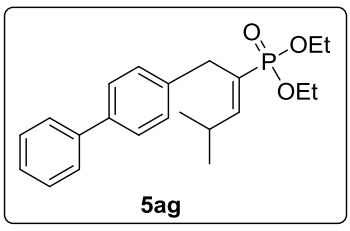
diethyl (1-([1,1'-biphenyl]-4-yl)-5,5-dimethylhex-2-en-2-yl)phosphonate (5af)



5af

Yellow liquid. Yield: 64%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 3H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.89 (dt, *J* = 23.8, 7.5 Hz, 1H), 4.00–3.95 (m, 2H), 3.88–3.83 (m, 2H), 3.66 (d, *J* = 18.5 Hz, 2H), 2.22 (dd, *J* = 7.5, 3.5 Hz, 2H), 1.16 (t, *J* = 7.1 Hz, 6H), 0.97 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 146.3 (d, *J* = 10.6 Hz), 141.0, 139.1, 138.0 (d, *J* = 2.0 Hz), 129.0 (d, *J* = 178.8 Hz), 128.9, 128.8, 127.1, 127.0, 126.9, 61.5 (d, *J* = 5.3 Hz), 42.9 (d, *J* = 18.1 Hz), 32.5 (d, *J* = 11.4 Hz), 31.4, 29.5, 16.2 (d, *J* = 6.6 Hz). **HR-MS** (ESI+) for $C_{24}H_{33}O_3NaP$ $([M+Na])^+$: calcd. 423.2065, found. 423.2060.

diethyl (1-([1,1'-biphenyl]-4-yl)-4-methylpent-2-en-2-yl)phosphonate (5ag)

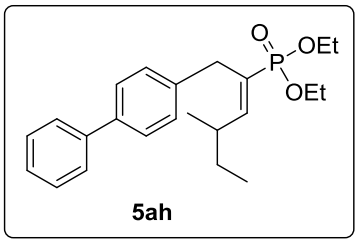


5ag

Yellow liquid. Yield: 62%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 2H), 6.59 (dd, *J* = 23.4, 10.1 Hz, 1H), 4.00–3.95 (m, 2H), 3.88–3.84 (m, 2H), 3.65 (d, *J* = 18.5 Hz, 2H), 2.85–2.78

(m, 1H), 1.16 (t, *J* = 7.1 Hz, 6H), 1.04 (d, *J* = 6.6 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 155.3 (d, *J* = 8.9 Hz), 141.0, 139.1, 138.2, 128.9, 128.8, 127.1, 127.0, 126.9, 125.1 (d, *J* = 178.0 Hz), 61.5 (d, *J* = 5.5 Hz), 32.5 (d, *J* = 10.9 Hz), 28.4 (d, *J* = 18.4 Hz), 22.0, 16.1 (d, *J* = 6.6 Hz). **HR-MS** (ESI+) for $C_{22}H_{29}O_3NaP$ $([M+Na])^+$: calcd. 395.1752, found. 395.1754.

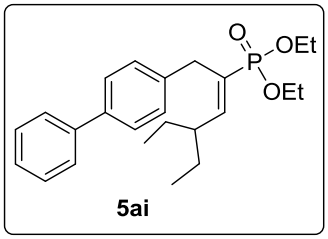
diethyl (1-([1,1'-biphenyl]-4-yl)-4-methylhex-2-en-2-yl)phosphonate (5ah)



5ah

Yellow liquid. Yield: 54%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.1 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.34 (d, *J* = 7.3 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.56 (dd, *J* = 23.5, 10.3 Hz, 1H), 4.01–3.98 (m, 2H), 3.97–3.84 (m, 2H), 3.69–3.61 (m, 2H), 2.57–2.55 (m, 1H), 1.41–1.38 (m, 2H), 1.17 (dt, *J* = 20.6, 7.0 Hz, 1H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 154.6 (d, *J* = 9.3 Hz), 141.0, 139.1, 138.3, 129.0, 128.8, 127.1, 127.0, 126.9, 126.3 (d, *J* = 176.8 Hz), 61.5 (d, *J* = 5.1 Hz), 35.3 (d, *J* = 18.0 Hz), 32.7 (d, *J* = 11.1 Hz), 29.5, 19.7, 16.2 (d, *J* = 7.9 Hz), 12.0. **HR-MS** (ESI+) for $C_{23}H_{31}O_3NaP$ $([M+Na])^+$: calcd. 409.1909, found. 409.1908.

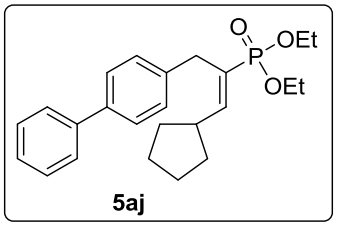
diethyl (1-([1,1'-biphenyl]-4-yl)-4-ethylhex-2-en-2-yl)phosphonate (5ai)



5ai

Yellow liquid. Yield: 46%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.1 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 4.2 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 2H), 6.78 (dt, *J* = 23.2, 7.2 Hz, 1H), 4.02–3.96 (m, 2H), 3.88–3.82 (m, 2H), 3.65 (d, *J* = 18.4 Hz, 2H), 2.33–2.29 (m, 2H), 1.97 (m, 1H), 1.34–1.26 (m, 5H), 1.16 (t, *J* = 7.1 Hz, 6H), 1.08 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.5 (d, *J* = 10.1 Hz), 141.0, 139.1, 138.1 (d, *J* = 2.1 Hz), 128.9, 128.8, 127.3 (d, *J* = 179.8 Hz), 127.1, 127.0, 61.5 (d, *J* = 5.5 Hz), 32.5 (d, *J* = 11.1 Hz), 29.7, 22.6 (d, *J* = 19.3 Hz), 16.2 (d, *J* = 6.6 Hz), 13.1 (d, *J* = 1.9 Hz). **HR-MS** (ESI+) for $C_{24}H_{33}O_3NaP$ $([M+Na])^+$: calcd. 423.2065, found. 423.2055.

diethyl (3-([1,1'-biphenyl]-4-yl)-1-cyclopentylprop-1-en-2-yl)phosphonate (5aj)

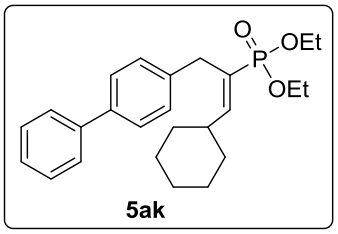


5aj

Yellow liquid. Yield: 59%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.1 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H),

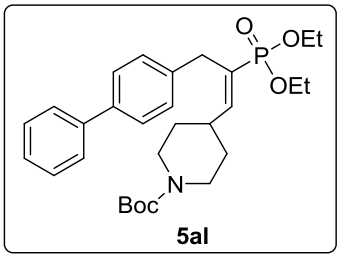
7.27 (d, *J* = 8.3 Hz, 2H), 6.71 (dd, *J* = 23.1, 10.1 Hz, 1H), 4.00–3.95 (m, 2H), 3.86–3.81 (m, 2H), 3.66 (d, *J* = 18.5 Hz, 2H), 2.90–2.85 (m, 1H), 1.83–1.80 (m, 2H), 1.73–1.71 (m, 2H), 1.60–1.58 (m, 2H), 1.44–1.37 (m, 3H), 1.15 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 154.1 (d, *J* = 9.7 Hz), 141.0, 139.0, 138.3 (d, *J* = 2.1 Hz), 128.9, 128.8, 127.1, 127.0, 126.9, 125.5 (d, *J* = 178.2 Hz), 61.5 (d, *J* = 5.4 Hz), 39.6 (d, *J* = 18.5 Hz), 33.1, 32.6 (d, *J* = 11.0 Hz), 25.7, 16.1 (d, *J* = 6.8 Hz). **HR-MS** (ESI+) for $C_{24}H_{31}O_3NaP$ $([M+Na])^+$: calcd. 421.1909, found. 421.1907.

diethyl (3-([1,1'-biphenyl]-4-yl)-1-cyclohexylprop-1-en-2-yl)phosphonate (5ak)



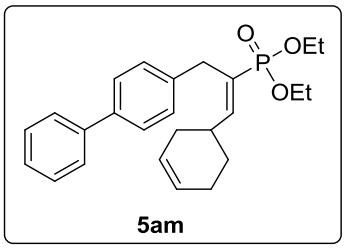
Yellow liquid. Yield: 61%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.1, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.60 (dd, *J* = 23.5, 10.0 Hz, 1H), 3.98–3.95 (m, 2H), 3.86–3.83 (m, 2H), 3.65 (d, *J* = 18.5 Hz, 2H), 2.48 (m, 1H), 1.73 (m, 2H), 1.67–1.62 (m, 2H), 1.25–1.23 (m, 6H), 1.15 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 154.0 (d, *J* = 9.3 Hz), 141.0, 139.1, 138.2 (d, *J* = 2.0 Hz), 128.9, 128.8, 127.1, 127.0, 126.9, 125.4 (d, *J* = 177.8 Hz), 61.6 (d, *J* = 5.5 Hz), 38.3 (d, *J* = 18.1 Hz), 32.6 (d, *J* = 11.1 Hz), 32.0 (d, *J* = 1.8 Hz), 25.8, 25.5, 16.1 (d, *J* = 6.6 Hz). **HR-MS** (ESI+) for $C_{25}H_{33}O_3NaP$ $([M+Na])^+$: calcd. 435.2065, found. 435.2068.

tert-butyl 4-(3-([1,1'-biphenyl]-4-yl)-2-(diethoxyphosphoryl)prop-1-en-1-yl) piperidine-1-carboxylate (5al)



Yellow liquid. Yield: 51%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.7 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 6.56 (dd, *J* = 23.3, 9.9 Hz, 1H), 4.10–4.05 (m, 2H), 4.03–3.97 (m, 2H), 3.91–3.87(m, 2H), 3.68 (d, *J* = 18.2 Hz, 2H), 2.68–2.65 (m, 2H), 2.61 (m, 1H), 1.52 (m, 2H), 1.45 (s, 9H), 1.41–1.33 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 154.8, 151.3 (d, *J* = 9.6 Hz), 140.8, 139.2, 138.0 (d, *J* = 2.2 Hz), 128.9, 128.8, 127.4 (d, *J* = 178.8 Hz), 127.2, 127.0, 126.9, 79.6, 61.7 (d, *J* = 5.6 Hz), 36.4 (d, *J* = 18.8 Hz), 32.7 (d, *J* = 10.8 Hz), 30.8, 28.4, 16.2 (d, *J* = 6.6 Hz). **HR-MS** (ESI+) for $C_{29}H_{40}NO_5NaP$ $([M+Na])^+$: calcd. 536.2542, found. 536.2548.

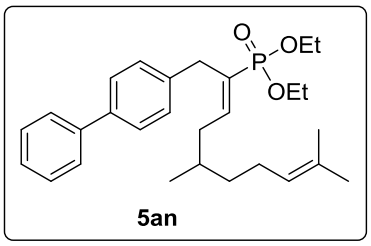
diethyl (3-([1,1'-biphenyl]-4-yl)-1-(cyclohex-3-en-1-yl)prop-1-en-2-yl) phosphonate (5am)



5am

Yellow liquid. Yield: 45%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.2 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 2H), 6.67 (dd, *J* = 23.4, 10.1 Hz, 1H), 5.68 (m, 2H), 4.02–3.96 (m, 2H), 3.89–3.65 (m, 2H), 3.68 (d, *J* = 18.1 Hz, 2H), 2.77 (m, 1H), 2.07–2.04 (m, 2H), 1.99–1.96 (m, 1H), 1.89–1.85 (m, 1H), 1.70–1.66 (m, 1H), 1.53–1.50 (m, 1H), 1.16 (td, *J* = 7.1, 3.3 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 153.0 (d, *J* = 9.4 Hz), 140.9, 139.1, 138.2 (d, *J* = 2.0 Hz), 128.9, 128.8, 127.1, 127.0, 126.4 (d, *J* = 178.8 Hz), 125.3, 61.6 (d, *J* = 5.5 Hz), 34.1 (d, *J* = 18.6 Hz), 32.6 (d, *J* = 10.9 Hz), 30.4, 27.9 (d, *J* = 1.6 Hz), 24.2, 16.2 (d, *J* = 6.5 Hz). **HR-MS** (ESI+) for $C_{25}H_{31}O_3NaP$ $([M+Na])^+$: calcd. 433.1909, found. 433.1911.

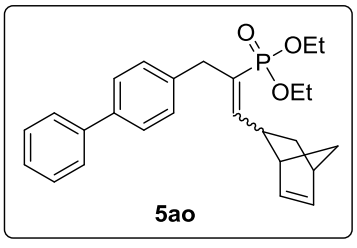
diethyl (1-([1,1'-biphenyl]-4-yl)-5,9-dimethyldeca-2,8-dien-2-yl)phosphonate (5an)



5an

Yellow liquid. Yield: 68%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.82 (dt, *J* = 23.5, 7.2 Hz, 1H), 5.09–5.05 (m, 1H), 4.02–3.97 (m, 2H), 3.95–3.81 (m, 2H), 3.65 (d, *J* = 18.4 Hz, 2H), 2.29 (m, 1H), 2.17–2.12 (m, 1H), 2.02–1.93 (m, 3H), 1.67 (d, *J* = 0.8 Hz, 4H), 1.59 (s, 3H), 1.41–1.34 (m, 1H), 1.16 (td, *J* = 7.0, 4.0 Hz, 6H), 0.93 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 148.2 (d, *J* = 10.4 Hz), 141.0, 139.1, 138.1 (d, *J* = 2.0 Hz), 131.5, 128.9, 128.8, 128.4 (d, *J* = 178.8 Hz), 127.1, 127.0, 126.9, 124.4, 61.5 (d, *J* = 5.4 Hz), 36.9, 36.4 (d, *J* = 18.3 Hz), 32.7 (d, *J* = 11.2 Hz), 32.5, 25.7 (d, *J* = 18.6 Hz), 19.7, 17.7, 16.2 (d, *J* = 7.5 Hz). **HR-MS** (ESI+) for $C_{28}H_{39}O_3NaP$ $([M+Na])^+$: calcd. 477.2535, found. 477.2541.

diethyl (3-([1,1'-biphenyl]-4-yl)-1-(bicyclo[2.2.1]hept-5-en-2-yl)prop-1-en-2-yl) phosphonate (5ao)

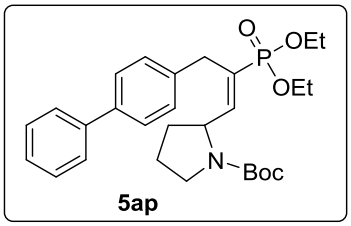


5ao

Yellow liquid. Yield: 53%, E/Z = 1:1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (m, 2H), 7.53–7.50 (m, 2H), 7.45–7.41 (m, 2H), 7.35–7.28 (m, 3H), 6.75 (dd, *J* =

23.1, 10.5 Hz, 0.5H), 6.33 (dd, *J* = 23.3, 10.4 Hz, 1H), 6.24 (m, 0.5H), 6.08 (m, 0.5H), 6.08 (m, 1H), 3.97 (m, 2H), 3.85 (m, 2H), 3.74–3.67 (m, 2H), 3.09 (m, 0.5H), 2.91 (m, 1H), 2.84 (m, 0.5H), 2.61 (m, 0.5H), 2.43 (m, 0.5H), 1.97 (m, 0.5H), 1.44–1.37 (m, 2H), 1.27 (m, 1H), 1.17 (m, 6H), 0.90–0.86 (m, 0.5H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 154.1 (d, *J* = 10.5 Hz), 154.0 (d, *J* = 9.9 Hz), 141.0, 139.1, 138.31, 138.29, 138.27, 138.2, 137.5, 136.0,132.6, 129.0, 128.9, 128.8, 127.1, 127.0, 126.9, 126.3 (d, *J* = 177.8 Hz), 61.5 (d, *J* = 5.5 Hz), 49.7, 48.0, 47.6, 45.7, 42.9, 42.3, 38.5 (d, *J* = 19.1Hz), 38.1 (d, *J* = 18.5 Hz), 33.4 (d, *J* = 13.2 Hz), 32.8 (d, *J* = 12.6 Hz), 16.2 (d, *J* = 6.7 Hz). **HR-MS** (ESI+) for $C_{26}H_{31}O_3NaP$ $([M+Na])^+$: calcd. 445.1909, found. 445.1908.

tert-butyl 2-(3-([1,1'-biphenyl]-4-yl)-2-(diethoxyphosphoryl)prop-1-en-1-yl) pyrrolidine-1-carboxylate (5ap)



5ap

Yellow liquid. Yield: 48%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.32 (m, 3H), 6.59 (dd, *J* = 23.1, 9.3 Hz, 1H), 4.63–4.56 (m, 1H), 4.00–3.82 (m, 5H), 3.66–3.62 (m, 1H), 3.49–3.40 (m, 2H), 1.95–1.65 (m, 6H), 1.46 (s, 9H), 1.26 (t, *J* = 6.8 Hz, 3H), 1.13 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 154.3, 148.8 (d, *J* = 10.9 Hz), 140.9, 139.4, 138.2, 129.0, 128.8, 127.9 (d, *J* = 122.2 Hz), 127.2, 127.0, 126.9, 79.9, 61.6 (d, *J* = 6.5 Hz), 46.6, 32.6, 28.5, 28.3 (d, *J* = 16.8 Hz), 26.9, 23.7, 16.5 (d, *J* = 6.1 Hz). **HR-MS** (ESI+) for $C_{28}H_{38}NO_5NaP$ $([M+Na])^+$: calcd. 522.2385, found. 522.2390.

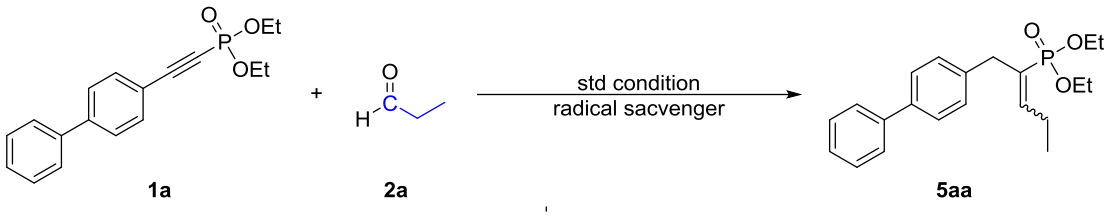
3.3 1 mmol-scale synthesis of 5aa

To a 50 mL flame-dried Schlenk tube was added ***PS5*** (100 mg, 0.075 mmol) and Hantzsch ester **4** (304 mg, 1.2 mmol). The tube was evacuated and refilled with N_2 for three times. A solution of **1a** (1.0 mmol), aldehyde **2a** (3.0 mmol), dipropylamine **3b** (3.0 mmol) and MeCN (20 mL) was added under nitrogen atmosphere. The reaction mixture was irradiated at a distance of 3 cm from blue LED and stirred at 25 °C for 12 h. Upon completion, the reaction mixture was concentrated under vacuum and the residue was purified by column chromatography on silica gel (100-200 mesh), eluting

with the indicated mixture of ethyl acetate (EA)/petroleum ether (PE) to give pure product **5aa** (229 mg, yield: 64%).

4. Mechanistic Studies

4.1 Radical capture experiment.

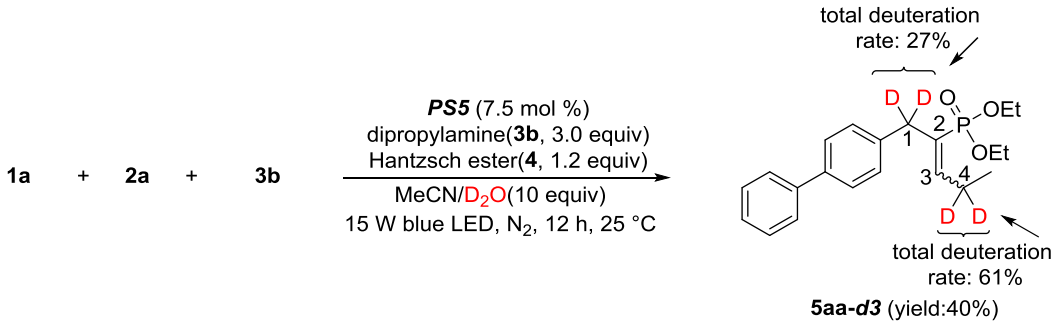


1a **2a** **5aa**

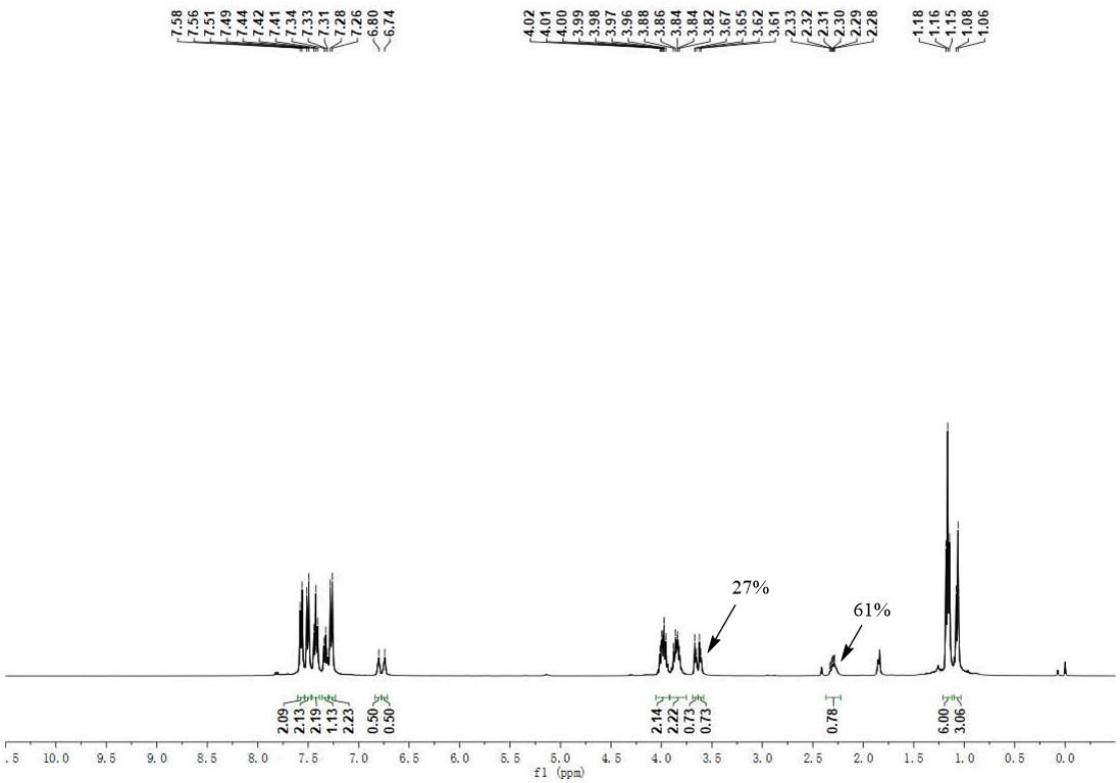
TEMPO	Yield of 5aa
2.0 equivalents	18%
5.0 equivalents	0%

To a 25 ml flame-dried Schlenk tube was added **1a** (62.9 mg, 0.2 mmol), **2a** (34.8 mg, 0.6 mmol), **3b** (60.7 mg, 0.6 mmol), **4** (60.8 mg,0.24 mmol), ***PS5*** (20.1 mg, 0.015 mmol), TEMPO (0.4 mmol/1 mmol) and mixture solvent of MeCN (4 mL) under nitrogen atmosphere. The reaction mixture was irradiated at a distance of 3 cm from 15 W blue light and stirred at 25 °C for 12 h. Upon completion, the reaction mixture was analyzed by TLC and **5aa** was not detected when TEMPO was added to 5 equivalents.

4.2 Deuterium-labeling experiments



The procedure is identical as the standard reaction conditions except using D_2O (10 equiv, D-enrichment of D_2O> 99.8%) medium. A **5aa-*d3*** was obtained in 40% yield. The ^1H NMR spectra of **5aa-*d3*** and the calculated D-incorporated rates are listed as below:



4.3 Stern-Volmer experiments

Stern-Volmer quenching experiment were carried out with freshly prepared solution of 1×10^{-4} M ***PS5*** and different concentrations quenchers in MeCN at room temperature under Ar atmosphere. Although the maximum UV absorption of ***PS5*** was observed at 385 nm, the solutions should be irradiated at 450 nm to avoid direct excitation of Hantzsch ester when the quencher was Hantzsch ester.

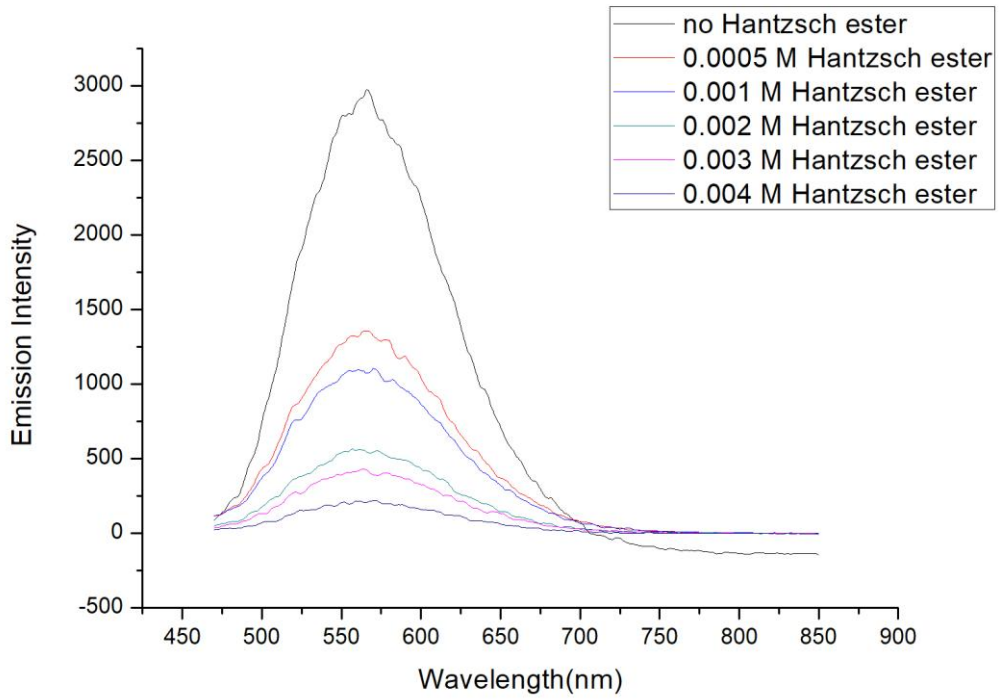
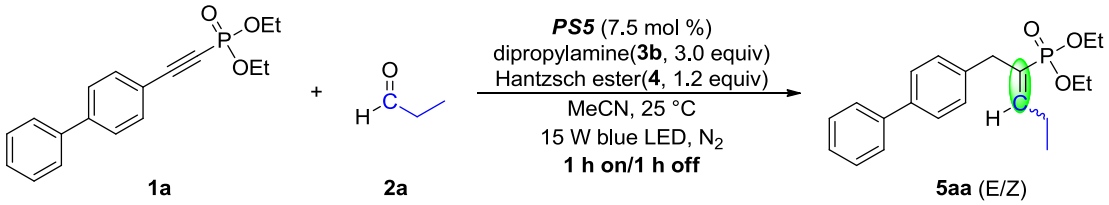


Figure *S3*. Stern Volmer quenching experiments with varying concentration of Hantzsch ester.

Studies have shown that dipropylamine can also quench copper-based photosensitizers so it is an effective quencher, as evidenced by its Stern-Vormer experiments.[12]

4.4 Light on/off interval experiment



To a 25 mL flame-dried Schlenk tube was added ***PS5*** (20 mg, 0.015 mmol) and Hantzsch ester **4** (60.7 mg, 0.24 mmol). The tube was evacuated and refilled with N_2 for three times. A solution of **1a** (0.2 mmol), aldehyde **2a** (0.6 mmol), amine **3b** (0.6 mmol) and MeCN (4 mL) was added under nitrogen atmosphere. The reaction mixture was irradiated at a distance of 3 cm from 30 W blue LED and stirred at 25 ℃

for 6 h. The light was turned on or off every 1 h, and the yield was determined by LC analysis.

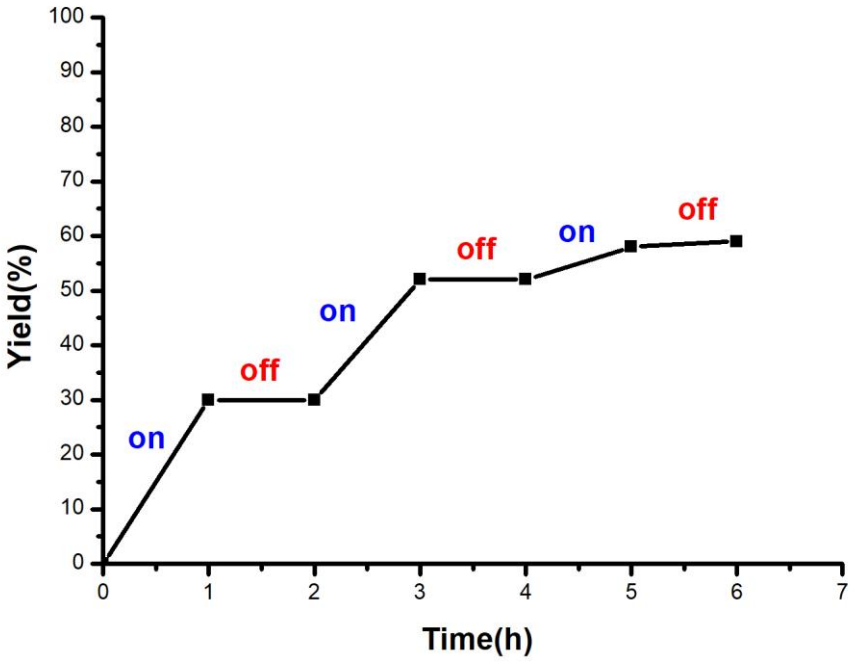
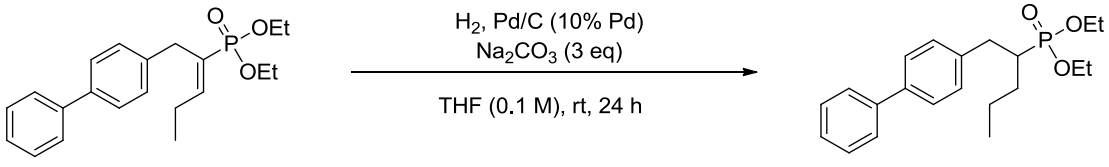


Figure *S4*. Yields of **5aa** during on/off experiments.

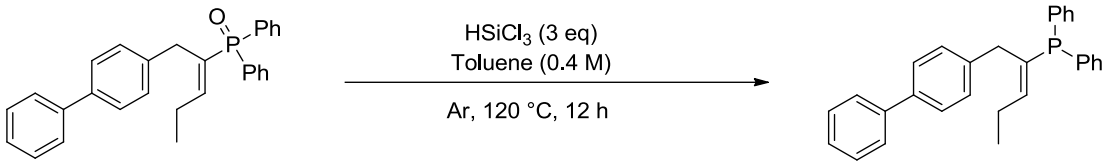
5. Practical application of the product 5aa and 5pa



5aa **6aa** (yield: 82%)

To a solution of vinyl phosphate **5aa** (0.2 mmol) was added dry THF (2 mL), anhydrous Na_2CO_3 (0.6 mmol) and Palladium on carbon (Pd/C, 50 mg, 10% Pd). The reaction was placed under H_2 (at 1 atmosphere) and was stirred for 24 hours at room temperature. The mixture was filtered over a celite pad and the pad was washed with portions of CH_2Cl_2. The filtrate was evaporated under reduced pressure and the

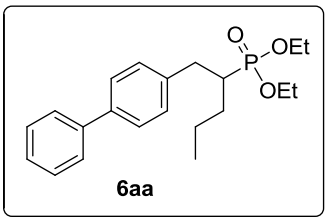
yellow oil was purified by column chromatography using a mixture of acetate (EA)/petroleum ether (PE) to give the product **6aa** in 82% yield.



5pa **6pa** (yield: 60%)

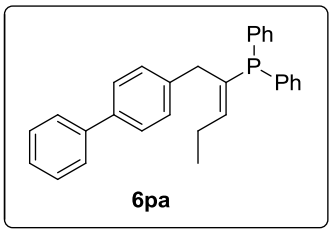
To a 25 mL flame-dried Schlenk tube was added **5pa** (0.4 mmol). The tube was evacuated and refilled with Ar for three times. A solution of trichlorosilane (1.2 mmol) and toluene (1 mL) was added under argon atmosphere. The mixture was stirred at 120 °C overnight. After cooling to room temperature, a saturated $NaHCO_3$ aqueous solution (1 mL) was added, and further stirred for 5 min. The aqueous phase was extracted with CH_2Cl_2, the organic phase was combined, dried with anhydrous sodium sulfate, filtered, and distilled under reduced pressure. The yellow oil was purified by column chromatography using a mixture of acetate (EA)/petroleum ether (PE) to give the product **6pa** in 60% yield.

diethyl (1-([1,1'-biphenyl]-4-yl)pentan-2-yl)phosphonate (6aa)


6aa

Yellow liquid. Yield: 82%. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.3 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 4.18–4.05 (m, 4H), 4.04–3.80 (m, 1H), 3.65 (d, *J* = 18.4 Hz, 1H), 2.97 (td, *J* = 9.8, 5.3 Hz, 2H), 2.19–2.02 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 6H), 1.16 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 140.9, 140.2, 140.0, 139.4, 128.8, 128.5, 127.3, 127.0, 61.7 (d, *J* = 6.5 Hz), 29.7, 28.29, 28.28, 27.6 (d, *J* = 136.7 Hz), 22.7, 16.5 (d, *J* = 6.0 Hz). **HR-MS** (ESI+) for $C_{21}H_{29}O_3NaP$ $([M+Na])^+$: calcd. 383.1747, found. 383.1750.

(1-([1,1'-biphenyl]-4-yl)pent-2-en-2-yl)diphenylphosphane (6pa)


6pa

Yellow liquid. Yield: 60%, E/Z > 99/1. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.1 Hz, 2H), 7.52–7.43 (m,

8H), 7.42–7.35 (m, 7H), 7.21 (d, *J* = 8.2 Hz, 2H), 5.79 (dt, *J* = 11.5, 7.2 Hz, 1H), 3.68 (d, *J* = 12.7 Hz, 2H), 2.32 (m, 2H), 1.05 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 144.3 (d, *J* = 16.1 Hz), 141.3, 138.9, 138.7, 136.2 (d, *J* = 11.5 Hz), 134.9 (d, *J* = 13.8 Hz), 134.1, 134.0, 129.1 (d, *J* = 148.5 Hz), 128.9, 128.7 (d, *J* = 4.8 Hz), 128.4 (d, *J* = 6.9 Hz), 127.9 (d, *J* = 183.0 Hz), 127.1. **^{31}P NMR** (162 MHz, $CDCl_3$): δ 0.87. **HR-MS** (ESI+) for $C_{29}H_{27}NaP$ $([M+Na])^+$: calcd. 429.1743, found. 429.1741.

6. References

1. S. Zhao, X. Wang, P. Wang, G. Wang, W. Zhao, X. Tang and M. Guo, *Org. Lett.*, 2019, **21**, 3990–3993.

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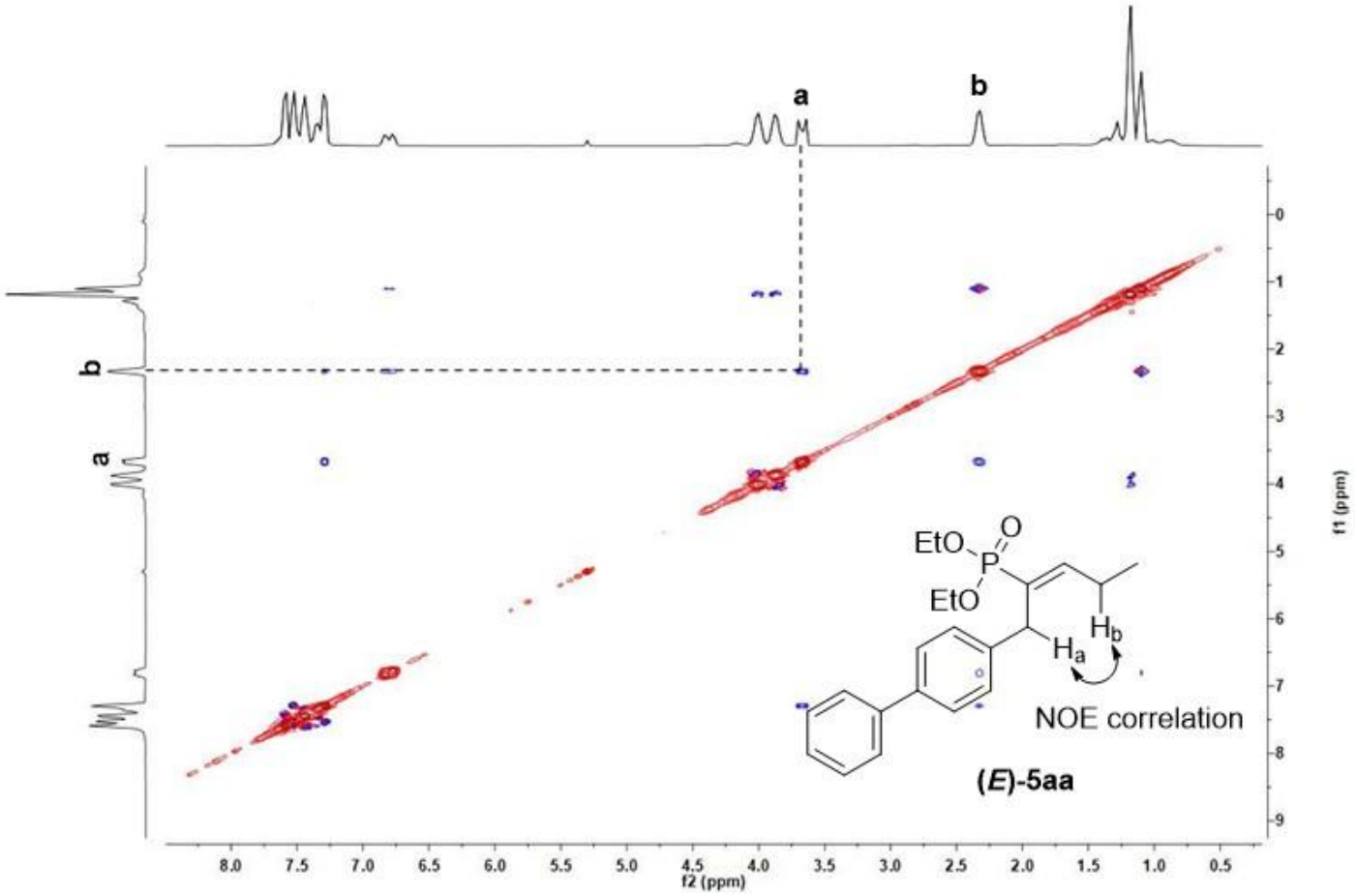
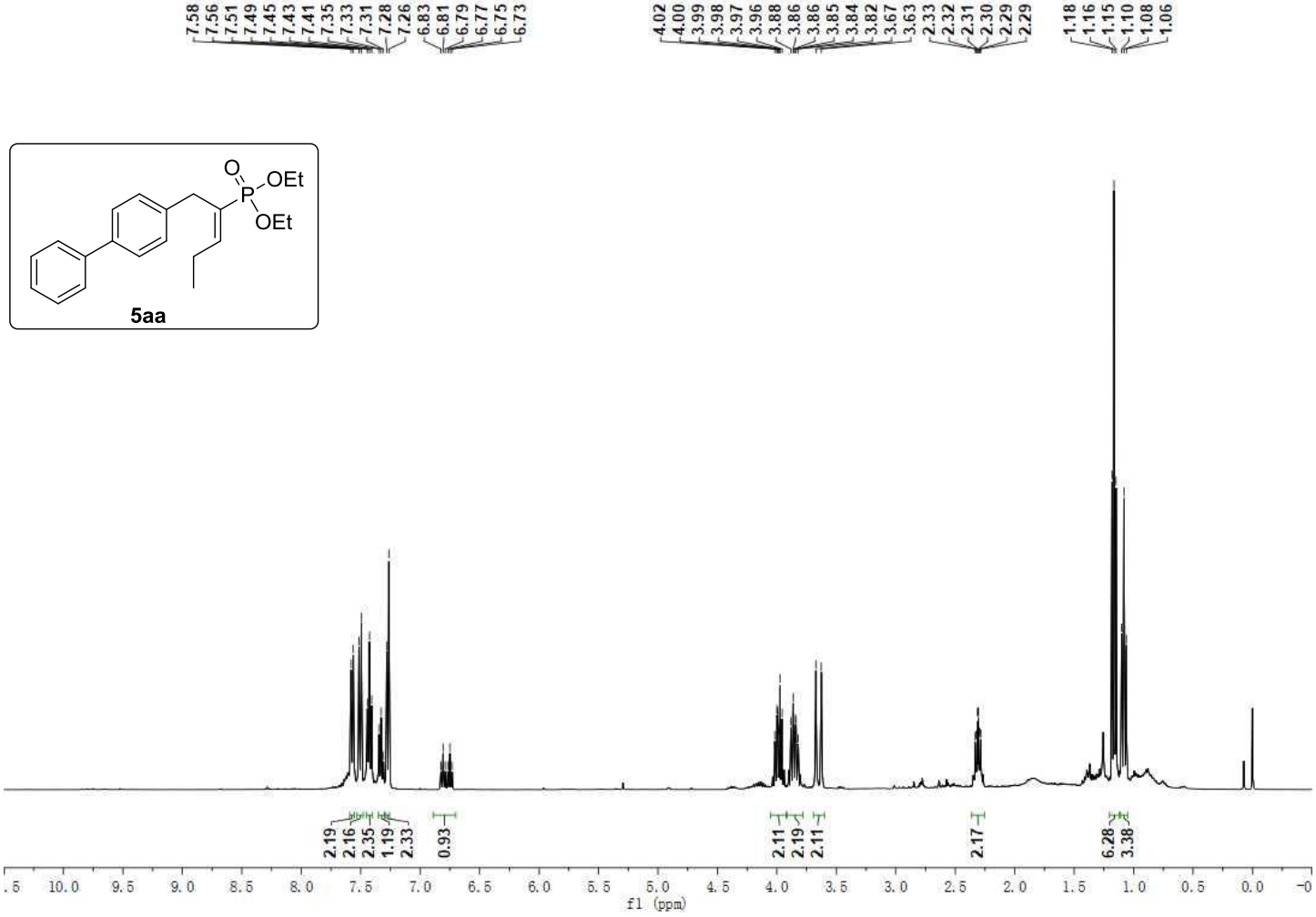
7. ^{1}H NOESY spectra of (*E*)-5aa in $CDCl_3$ at 298 K (400 MHz)

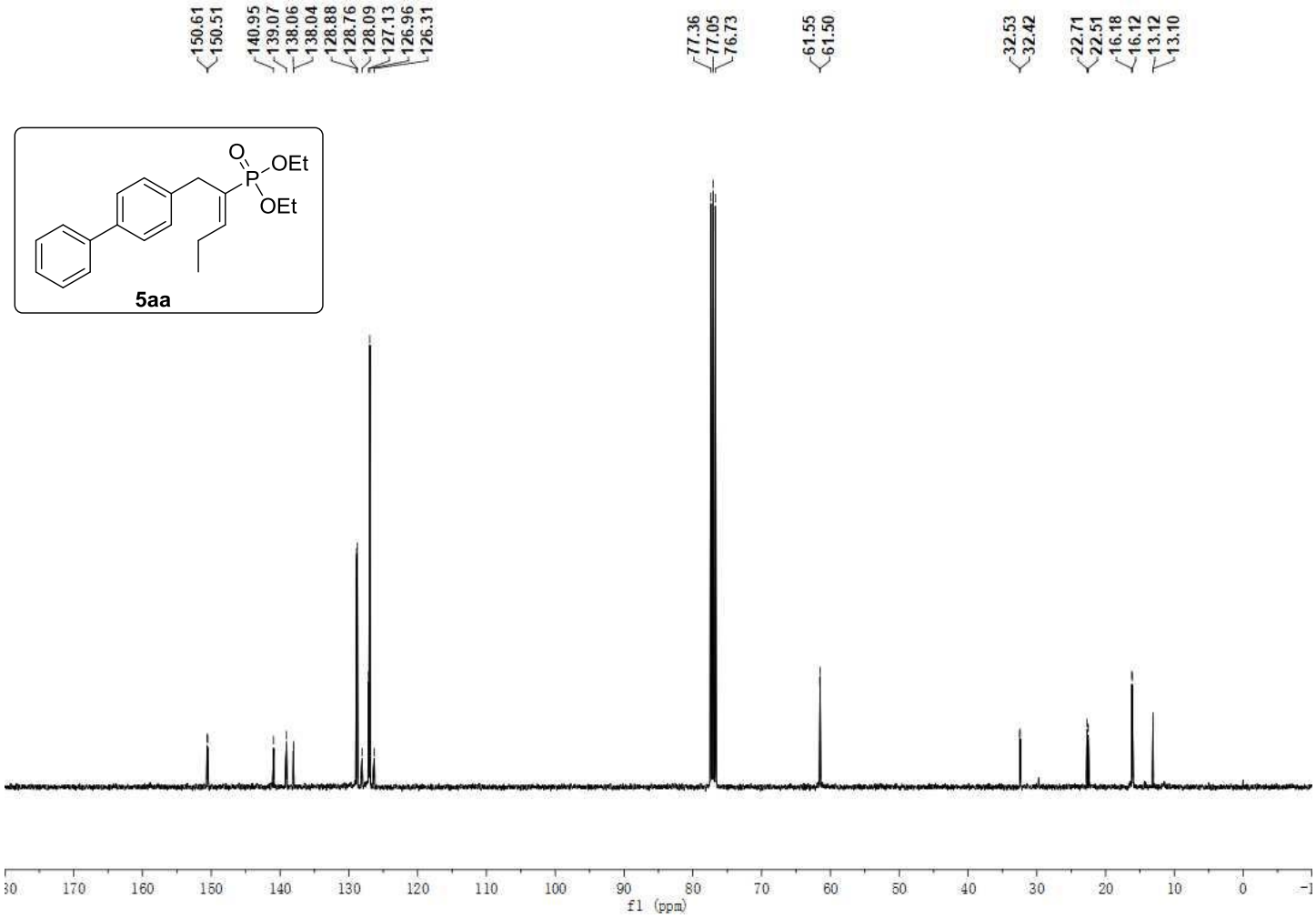


8. Copies of ^{1}H and ^{13}C NMR Spectra

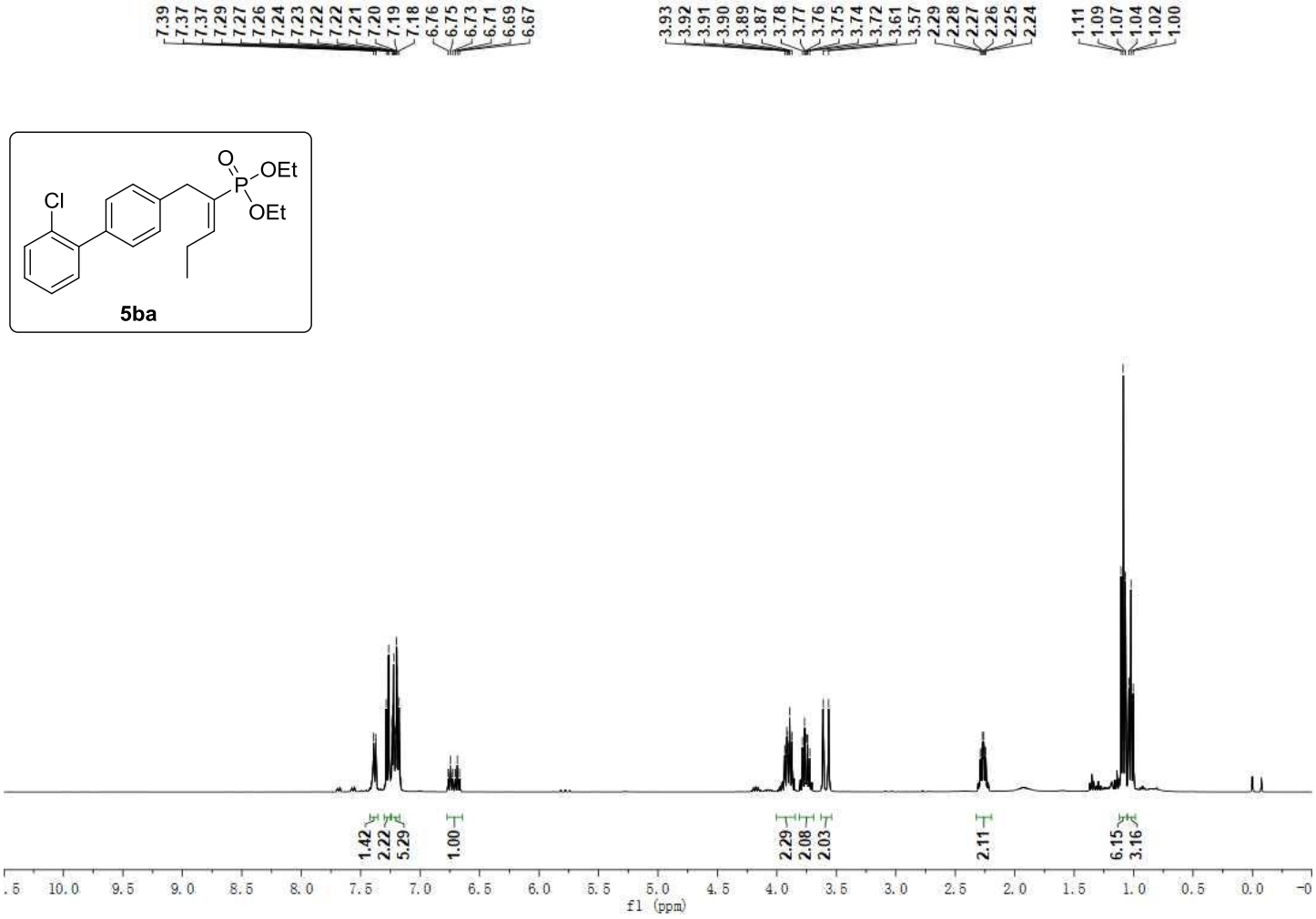
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5aa



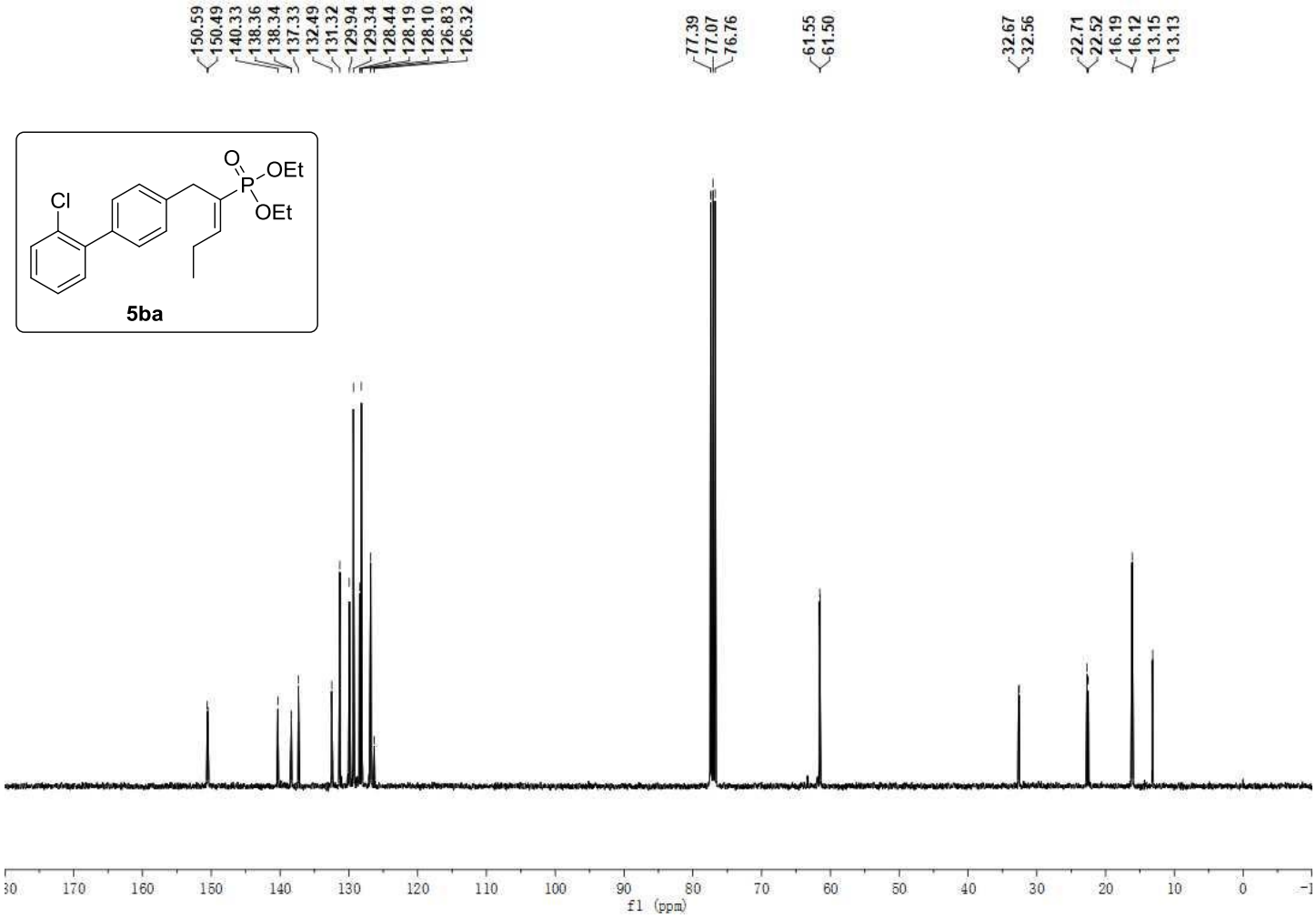
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5aa



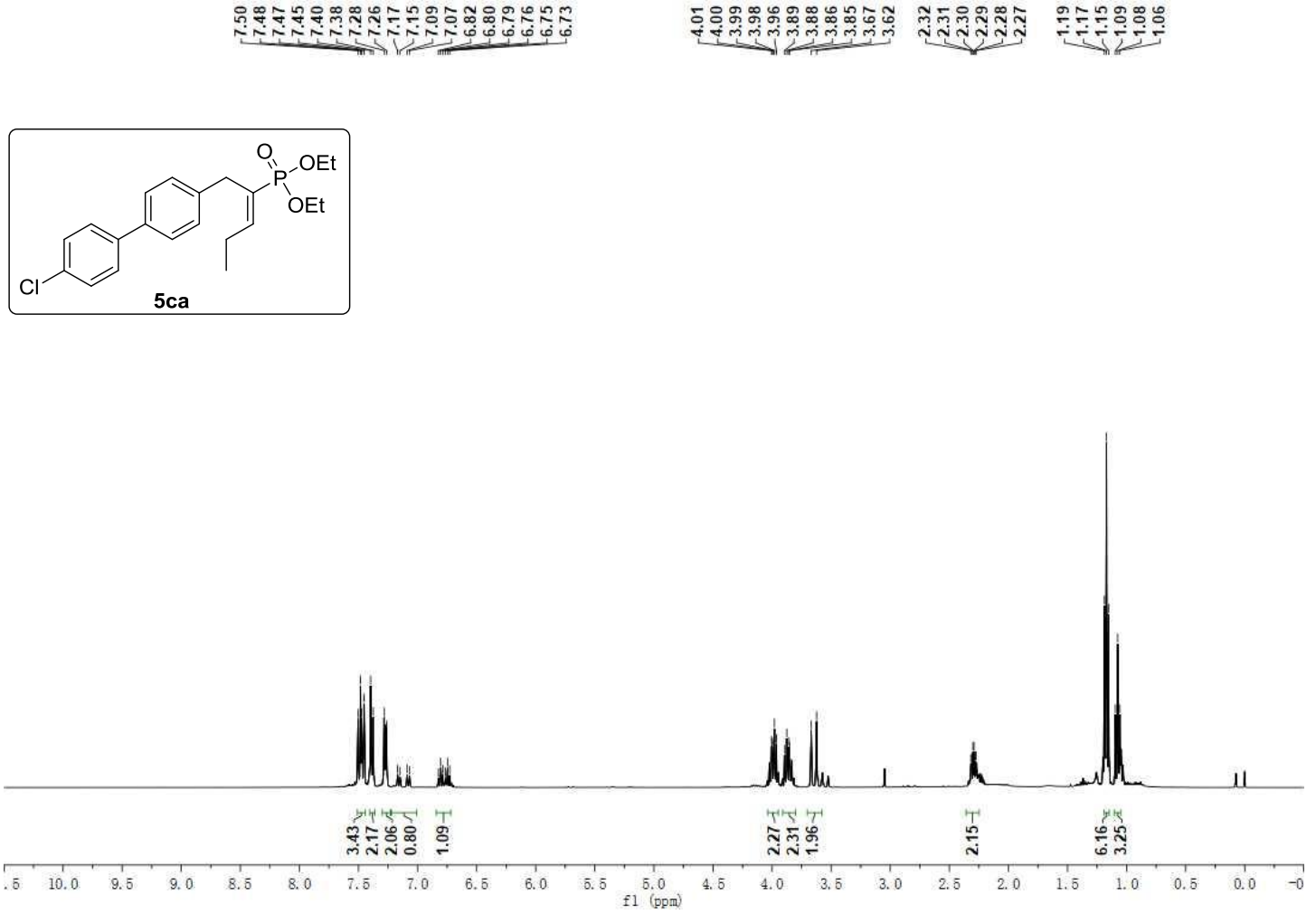
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5ba



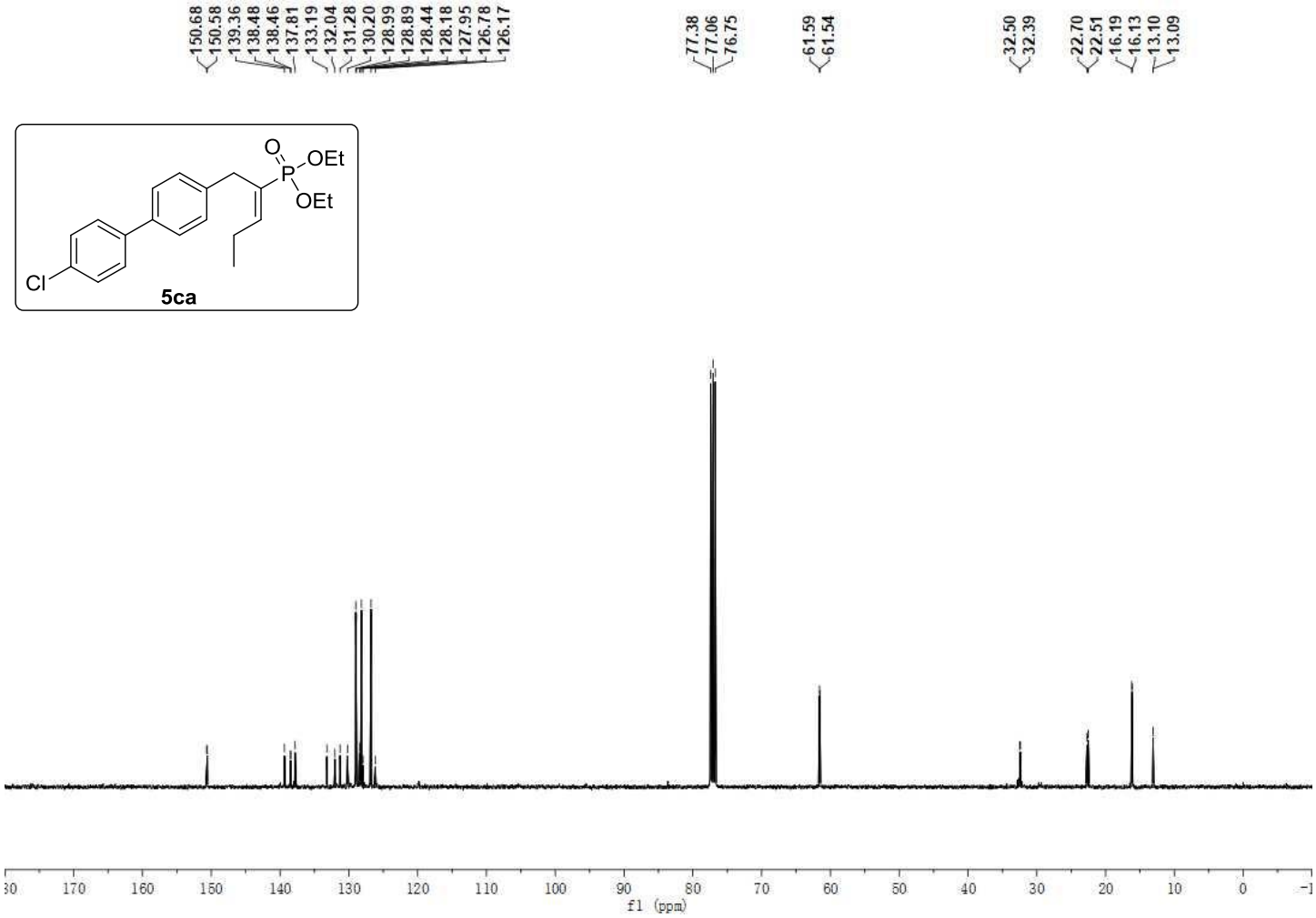
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5ba



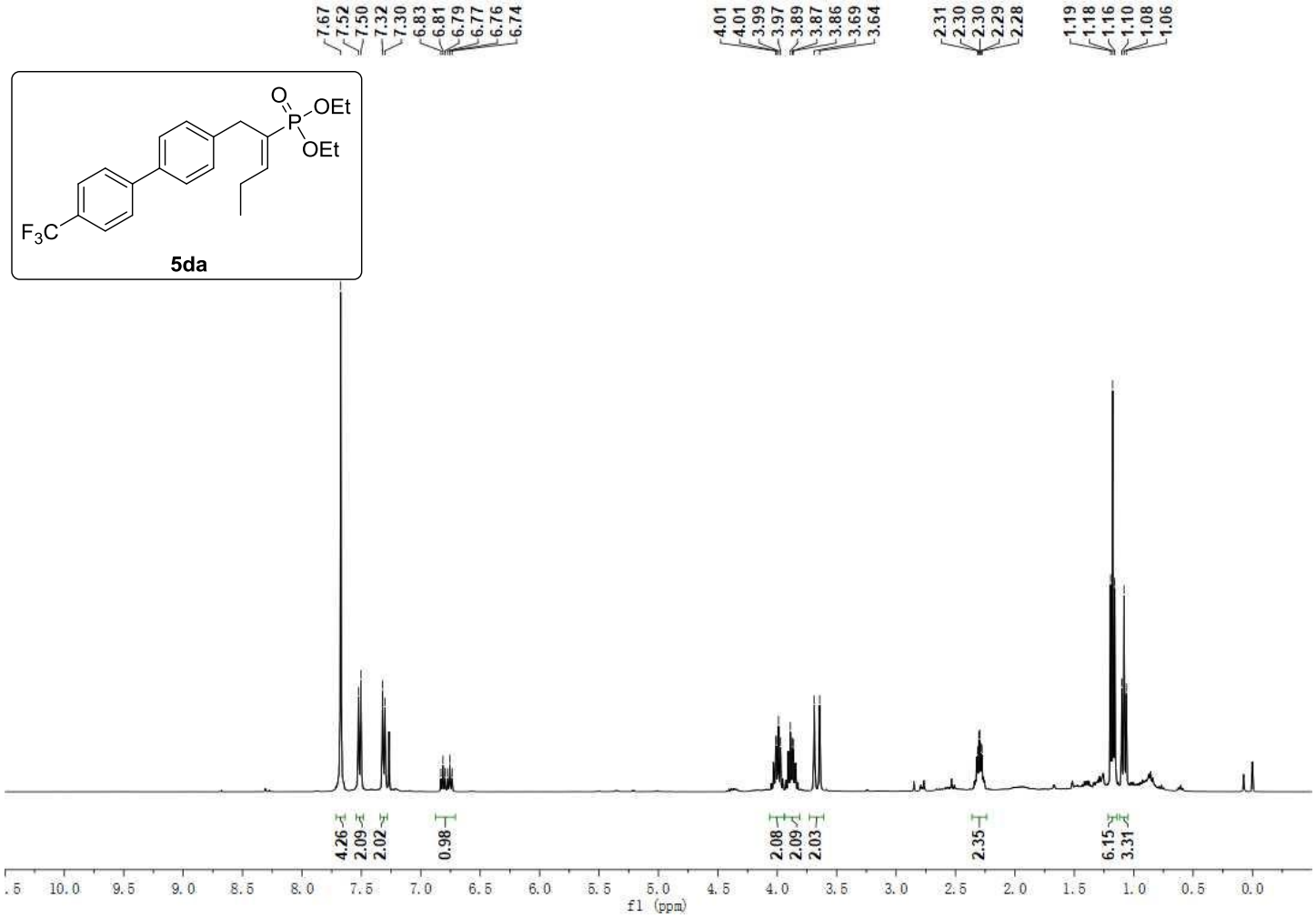
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5ca



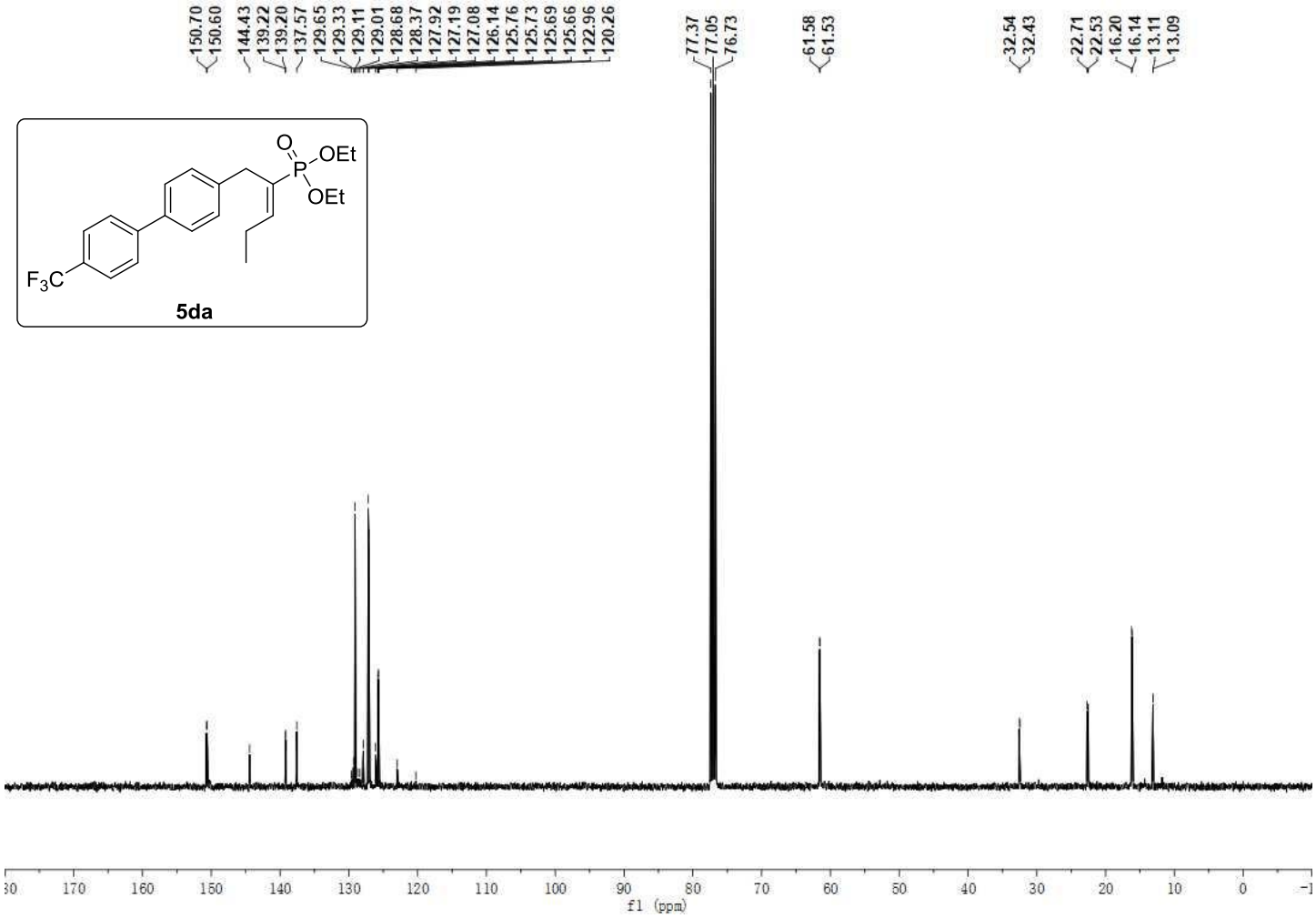
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5ca



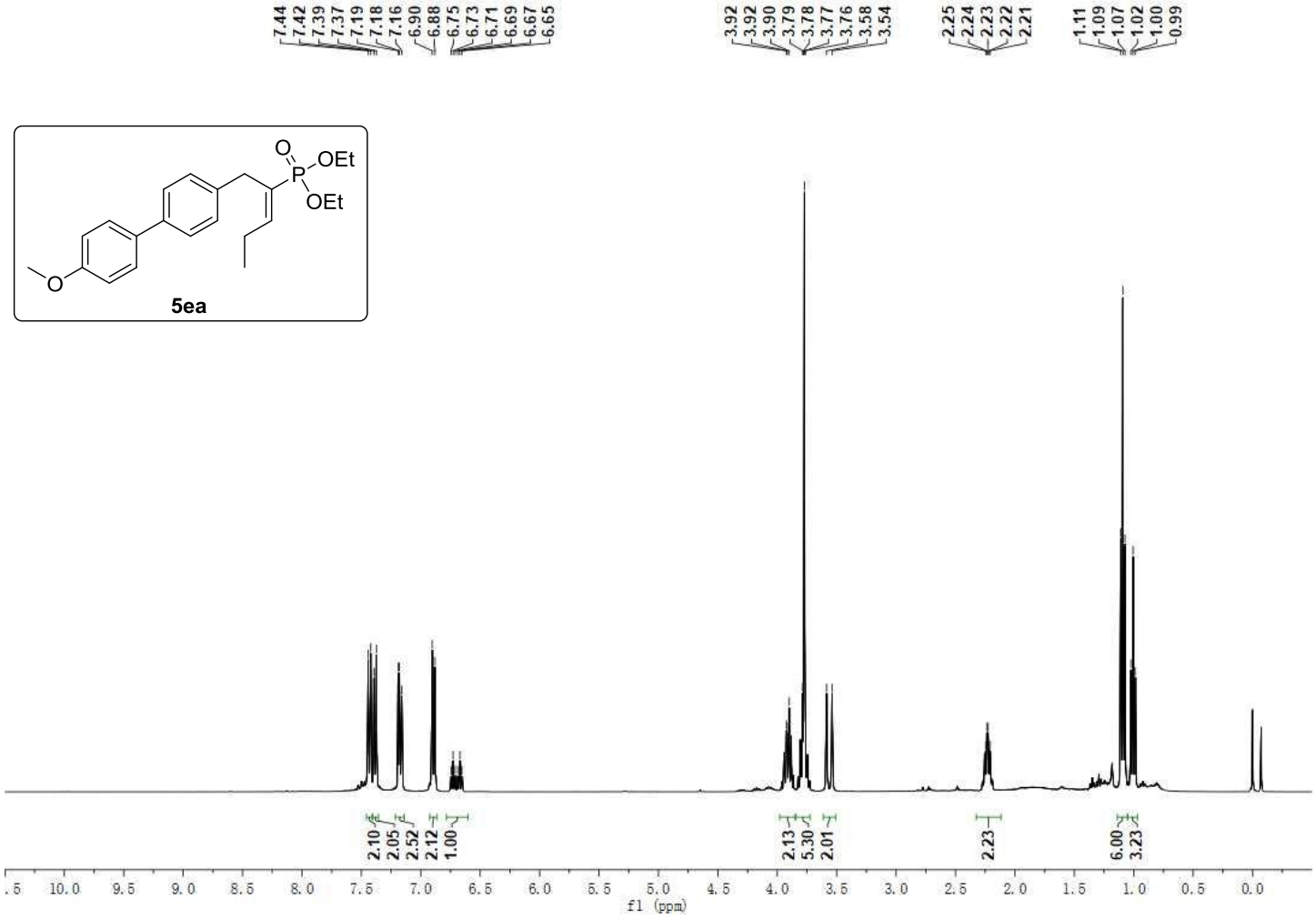
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5da



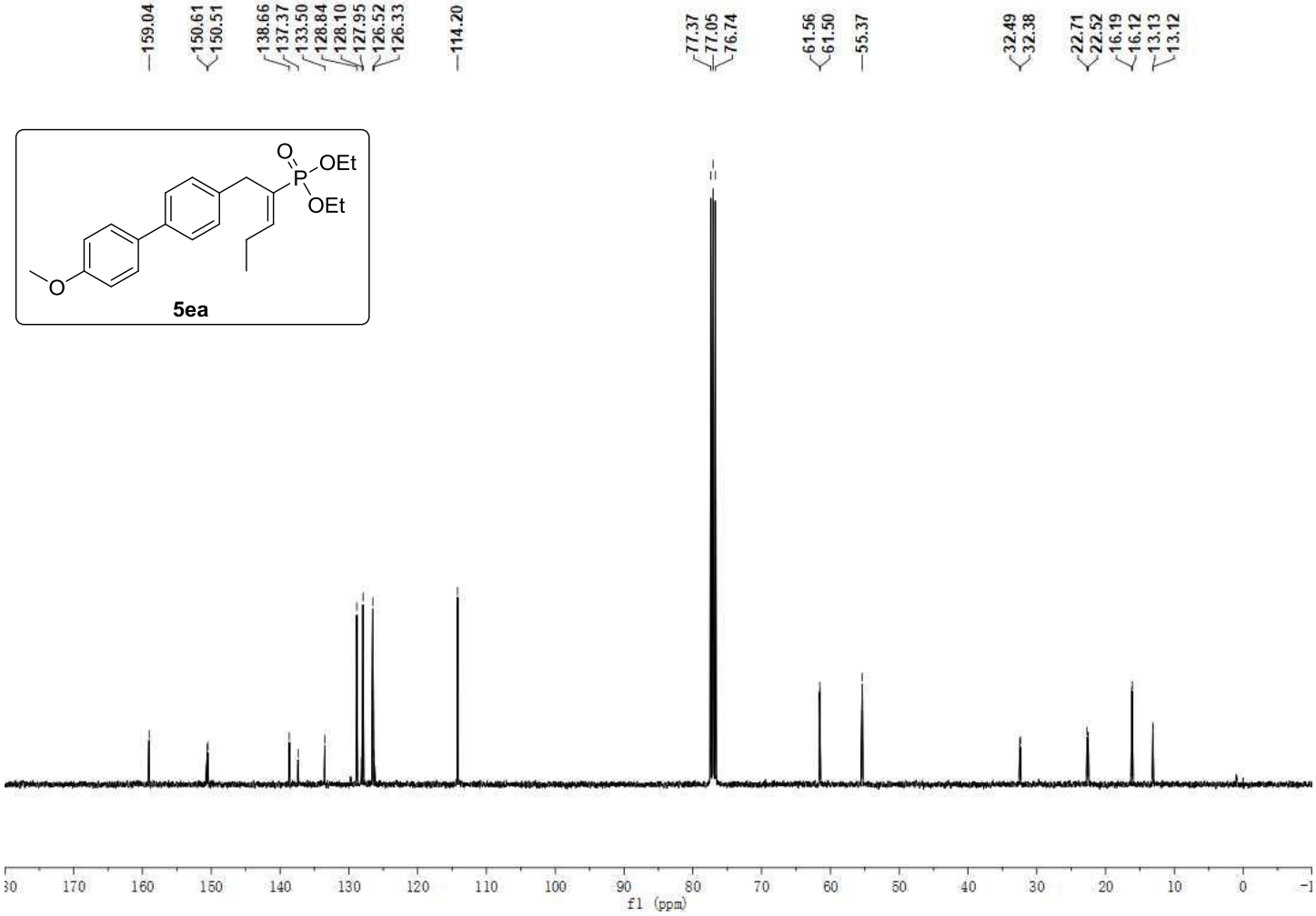
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5da



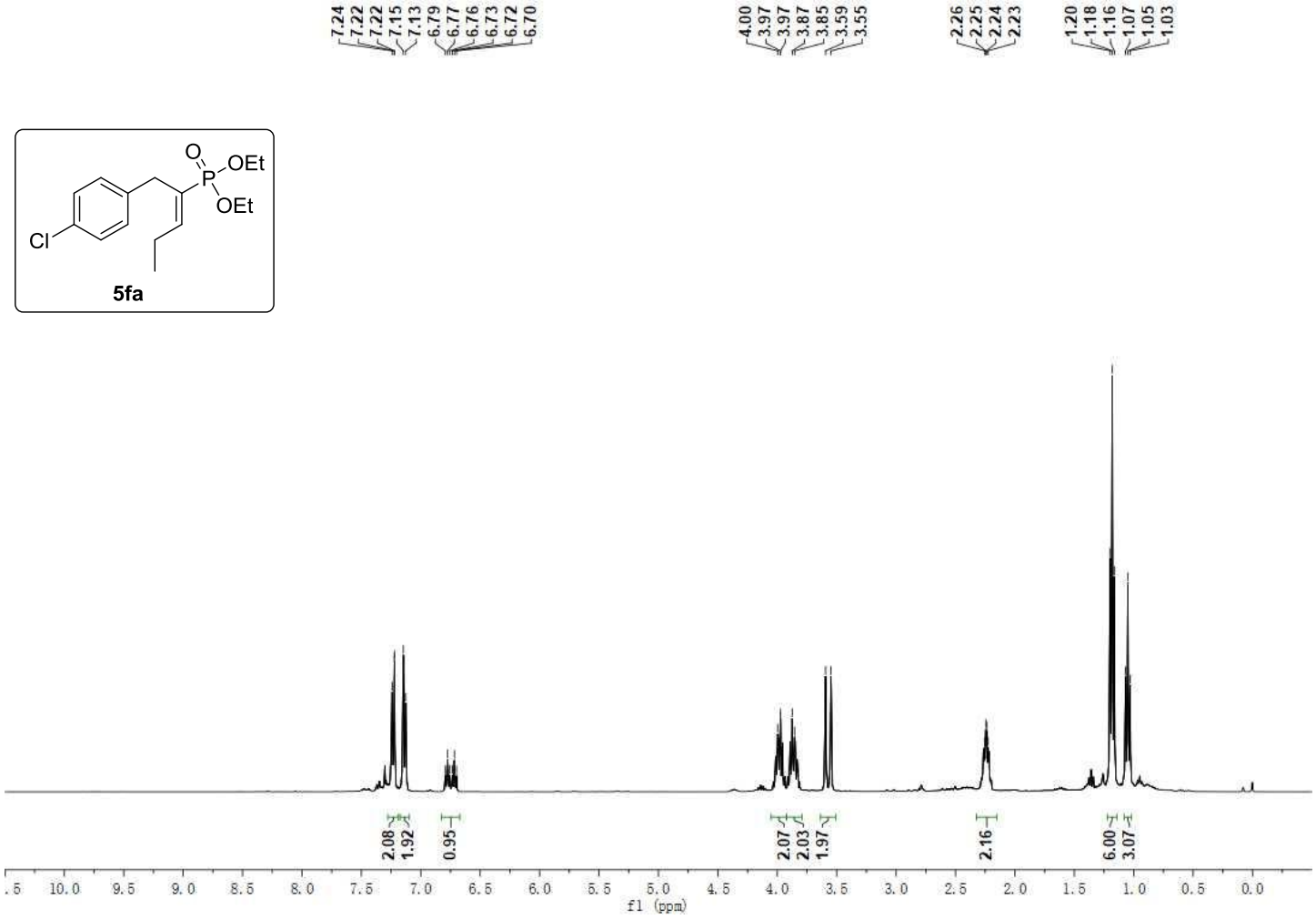
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5ea



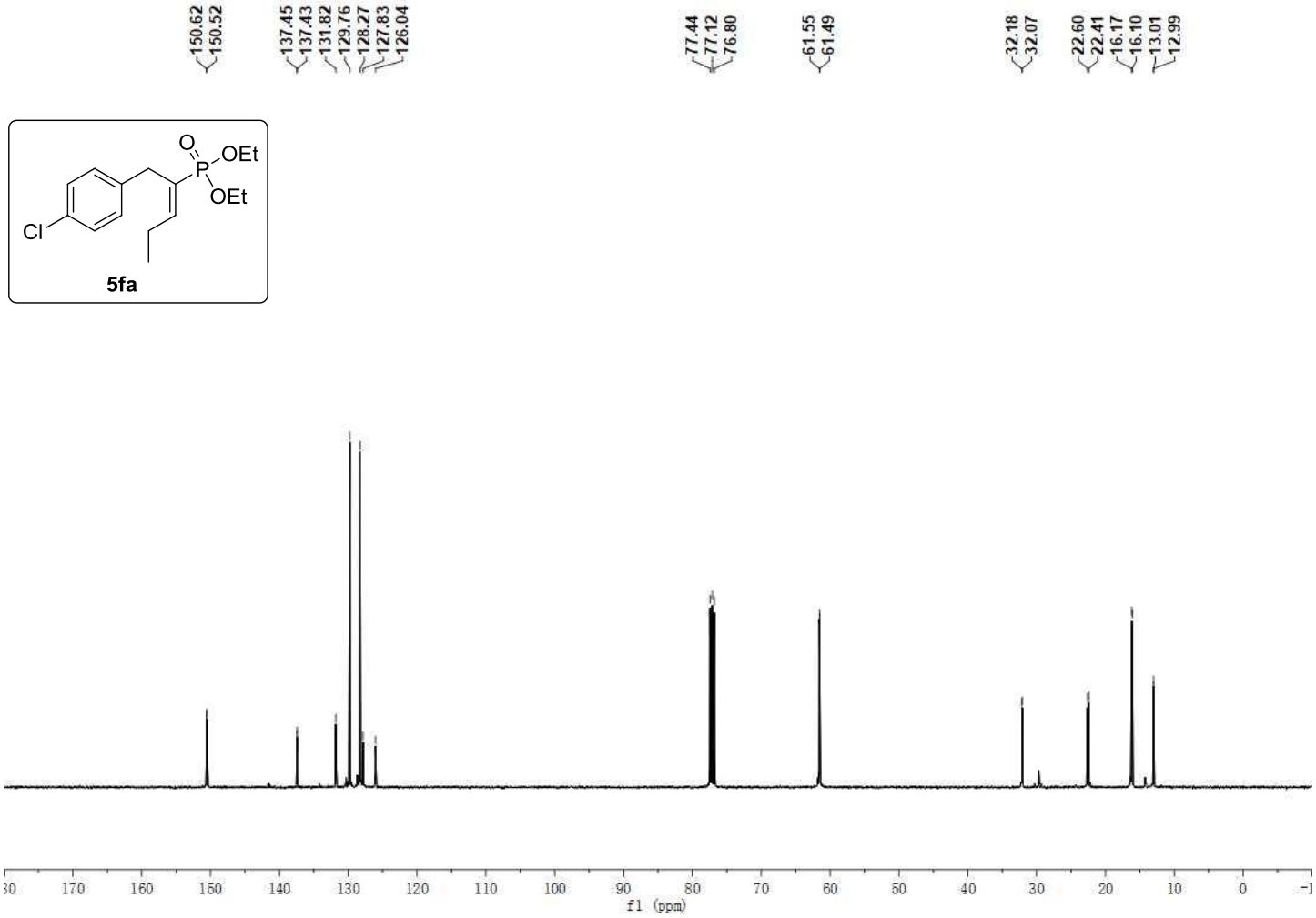
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5ea



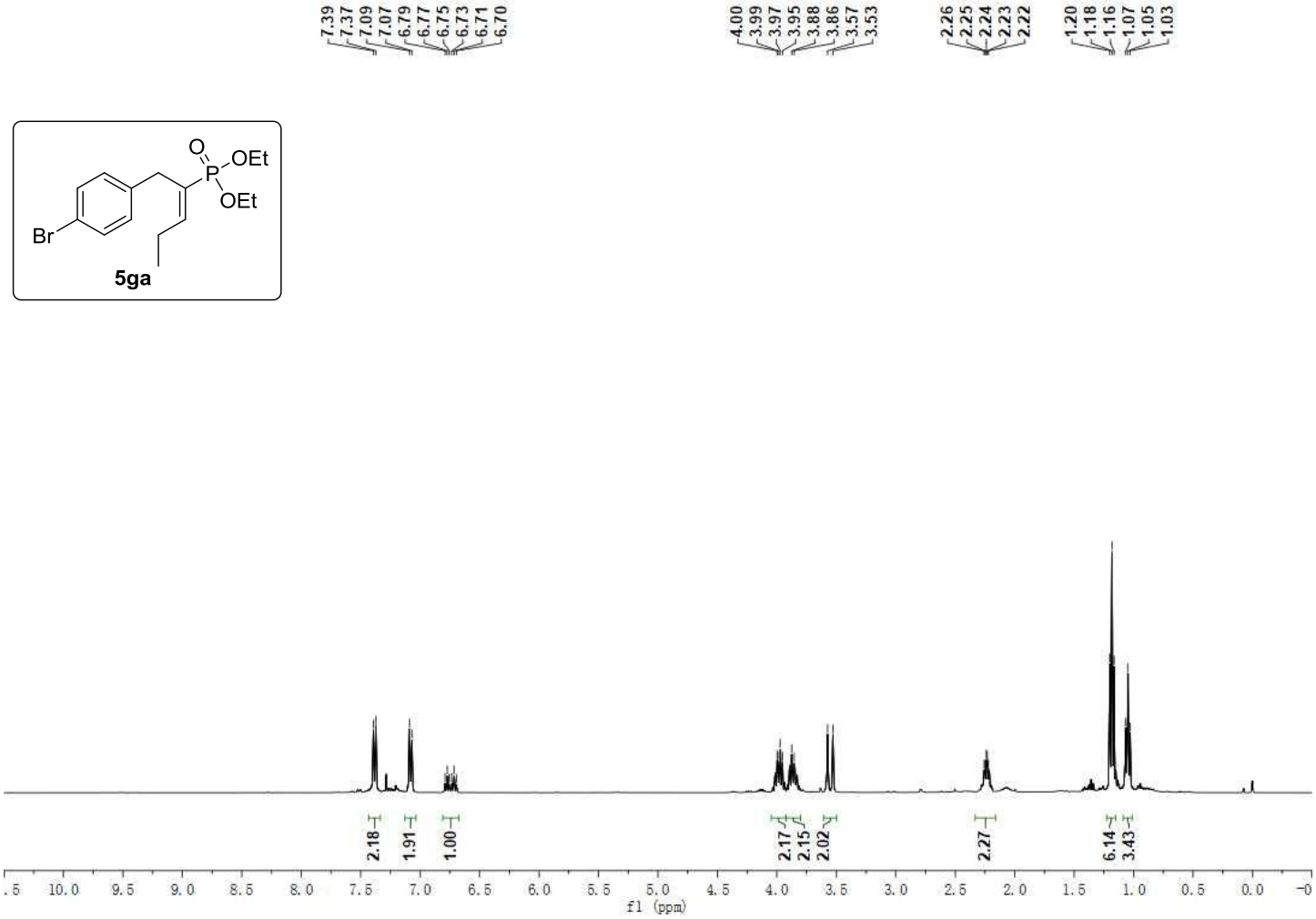
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5fa



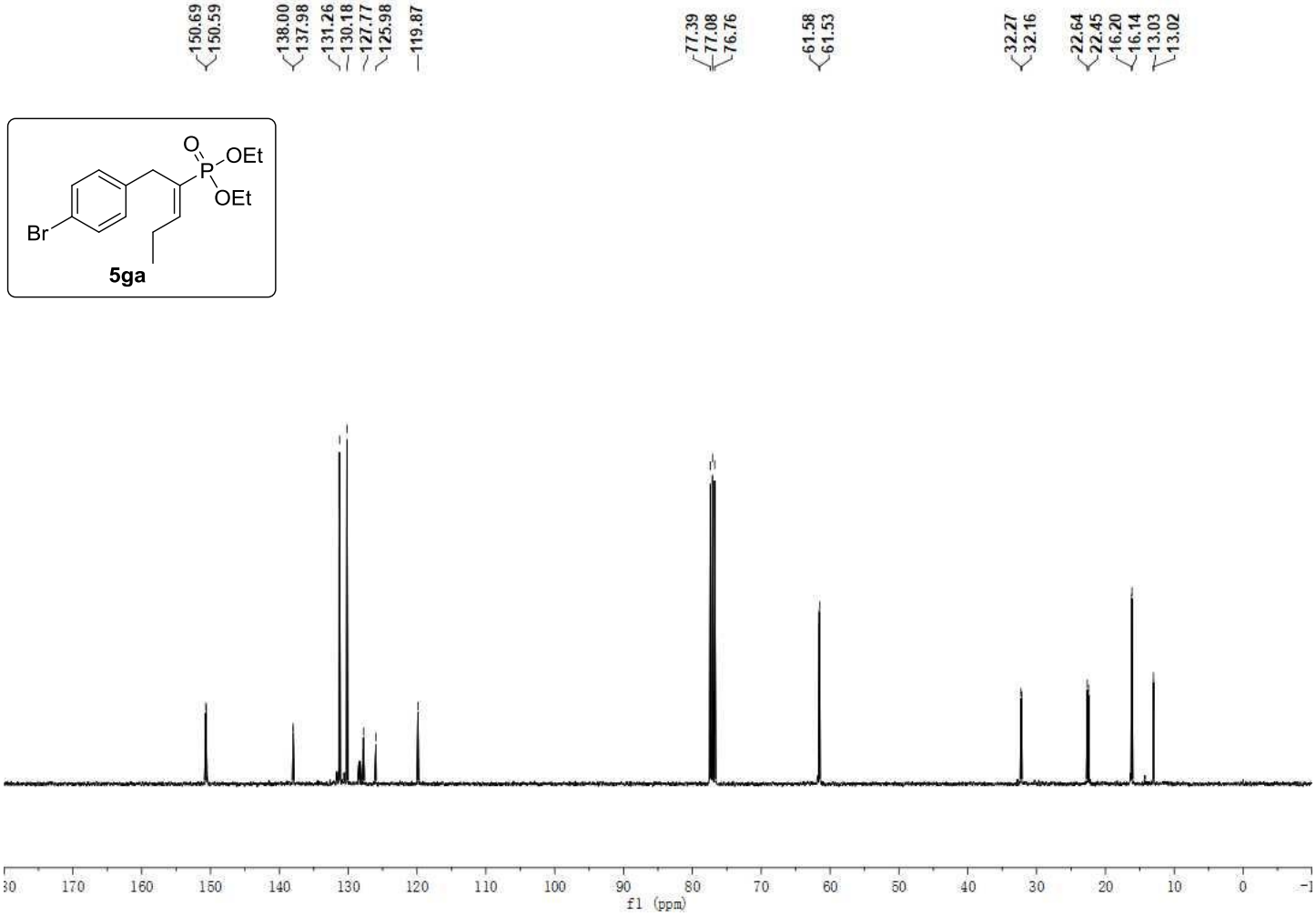
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5fa



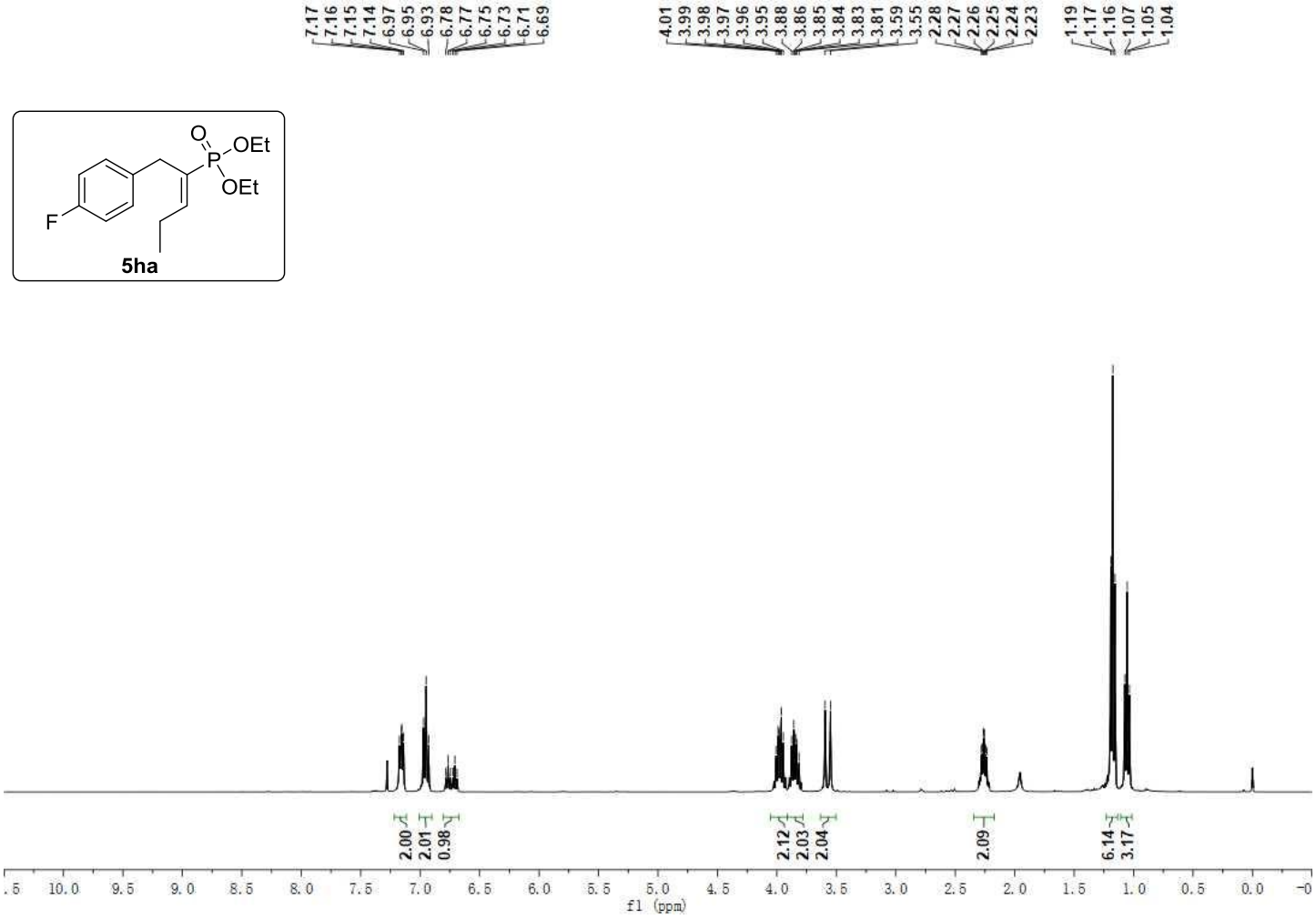
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5ga



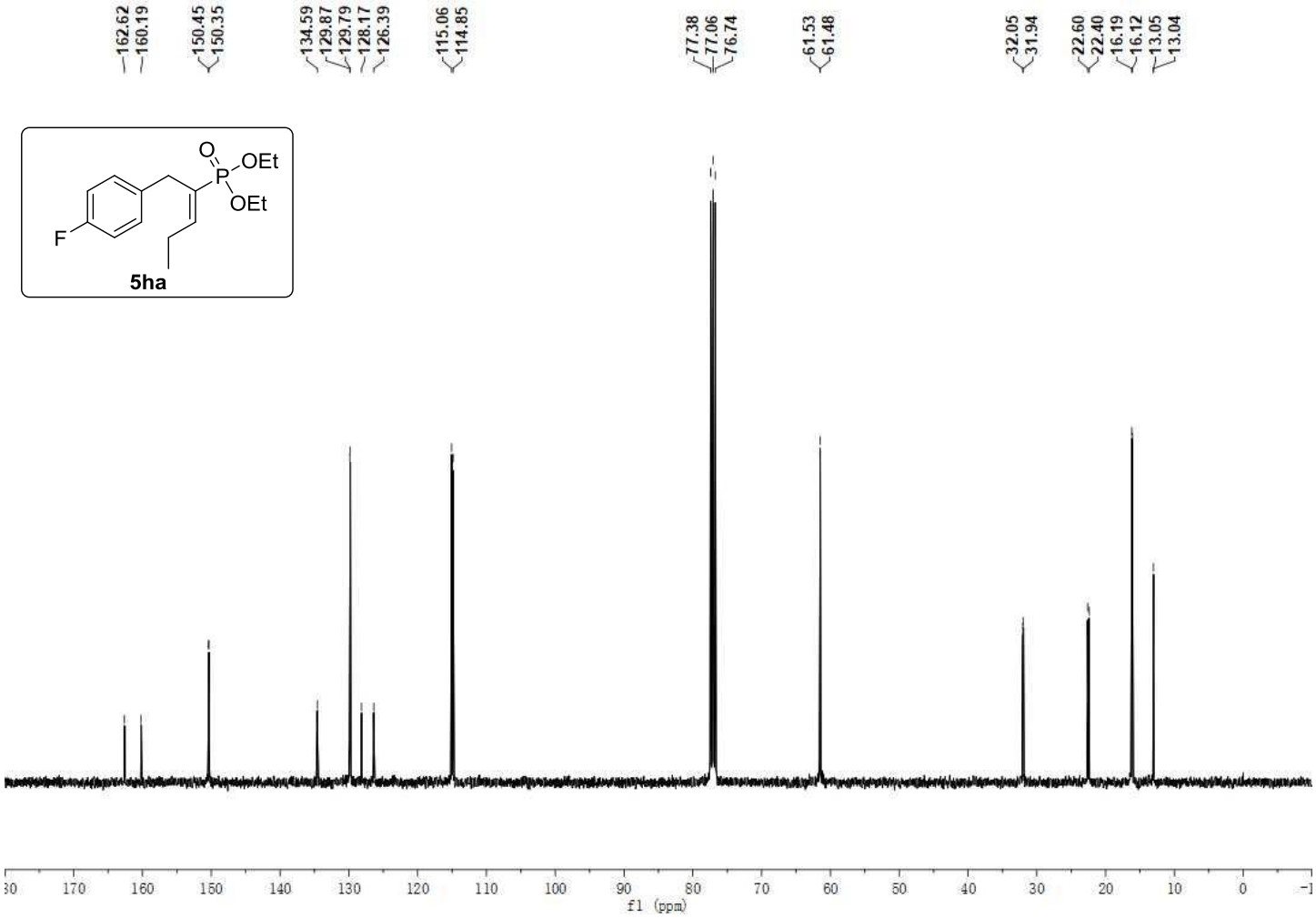
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5ga



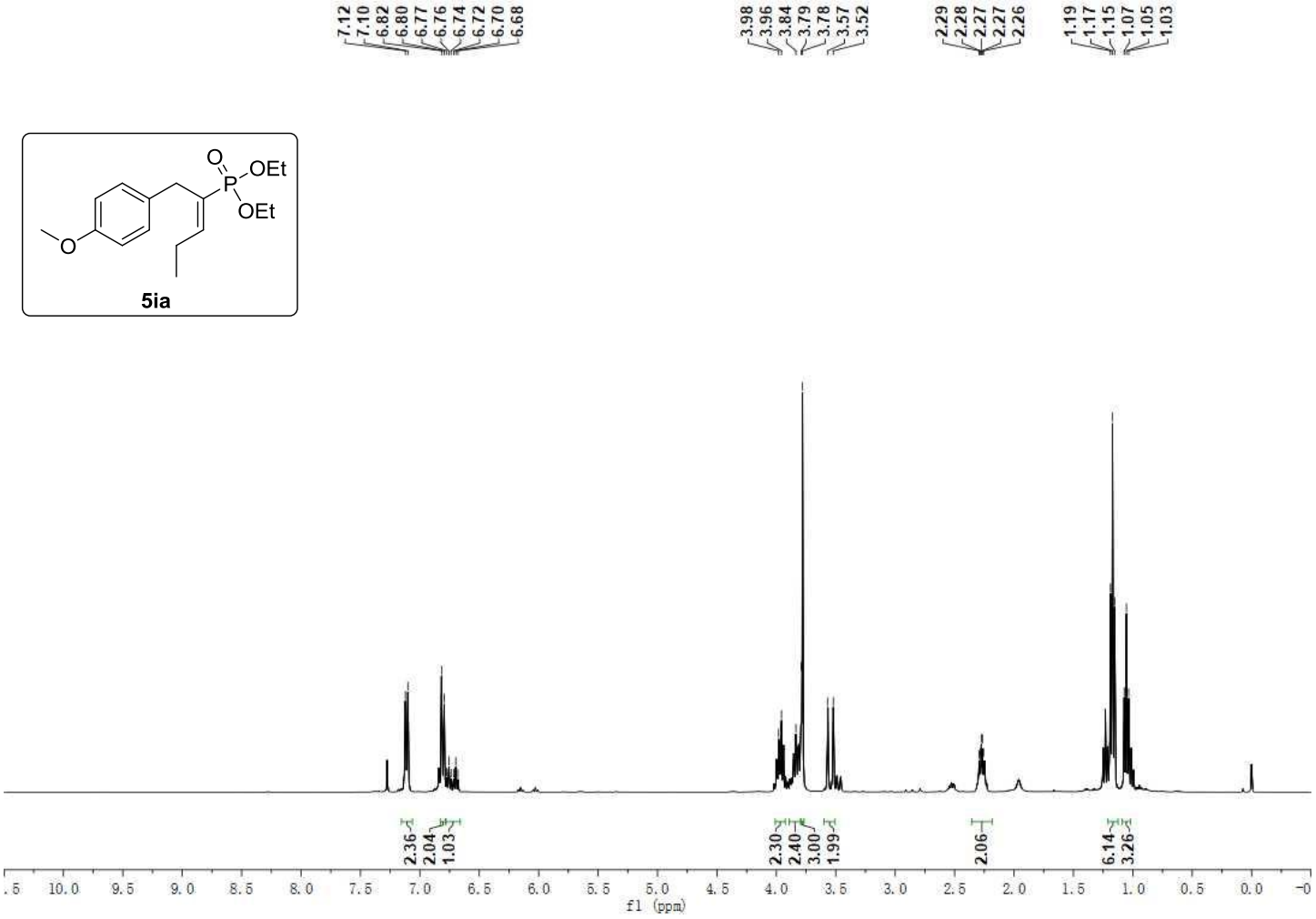
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5ha



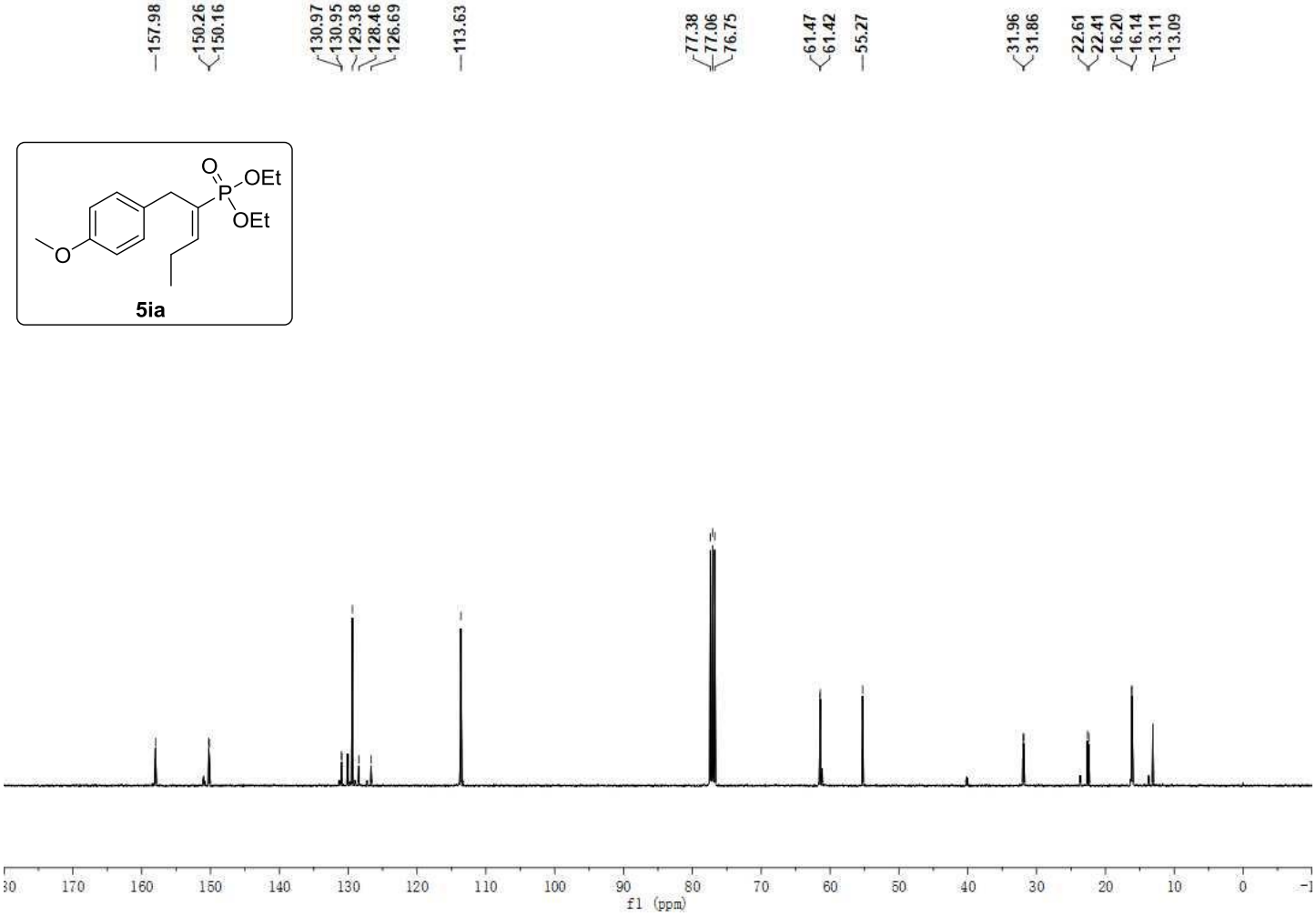
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5ha



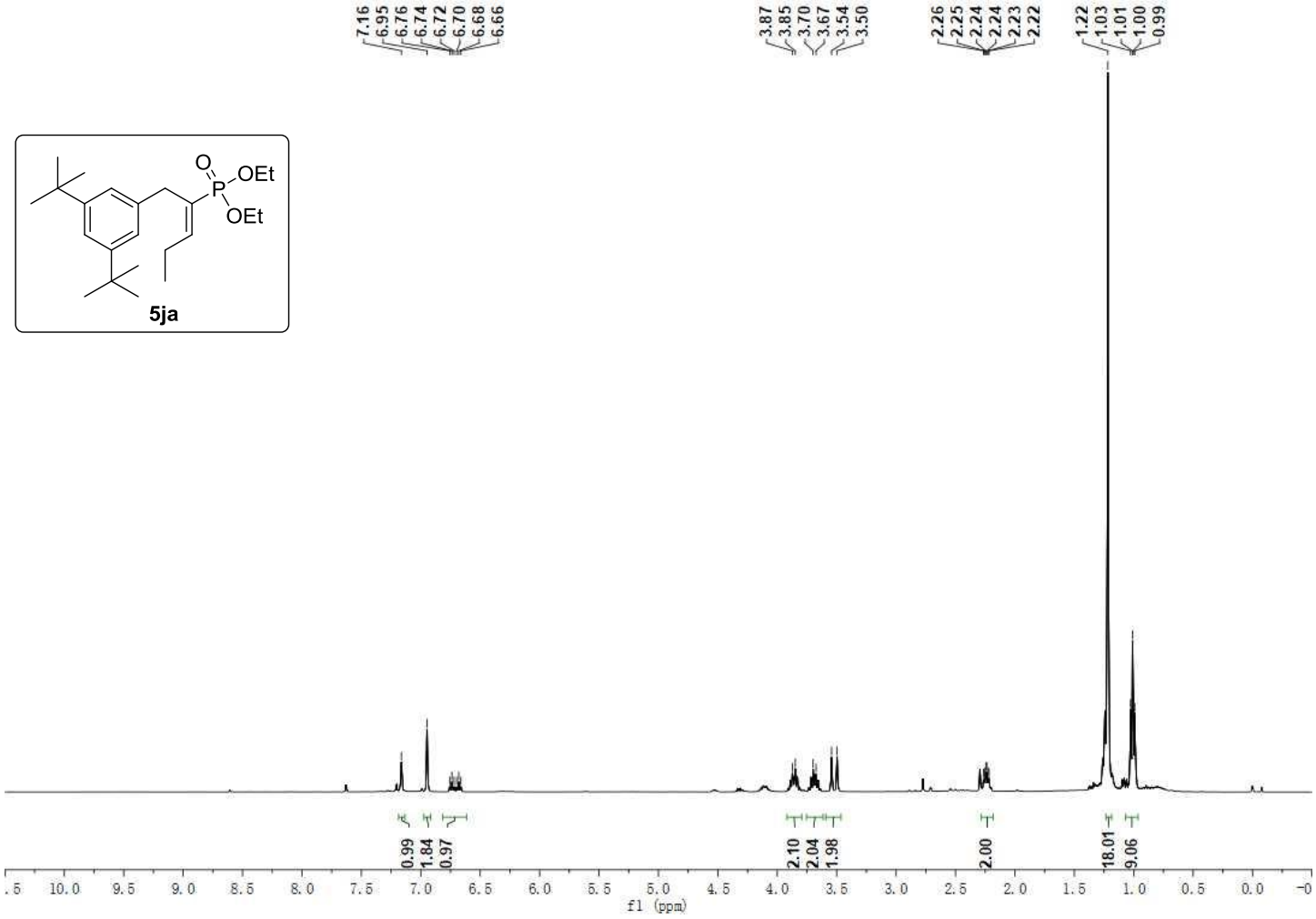
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5ia



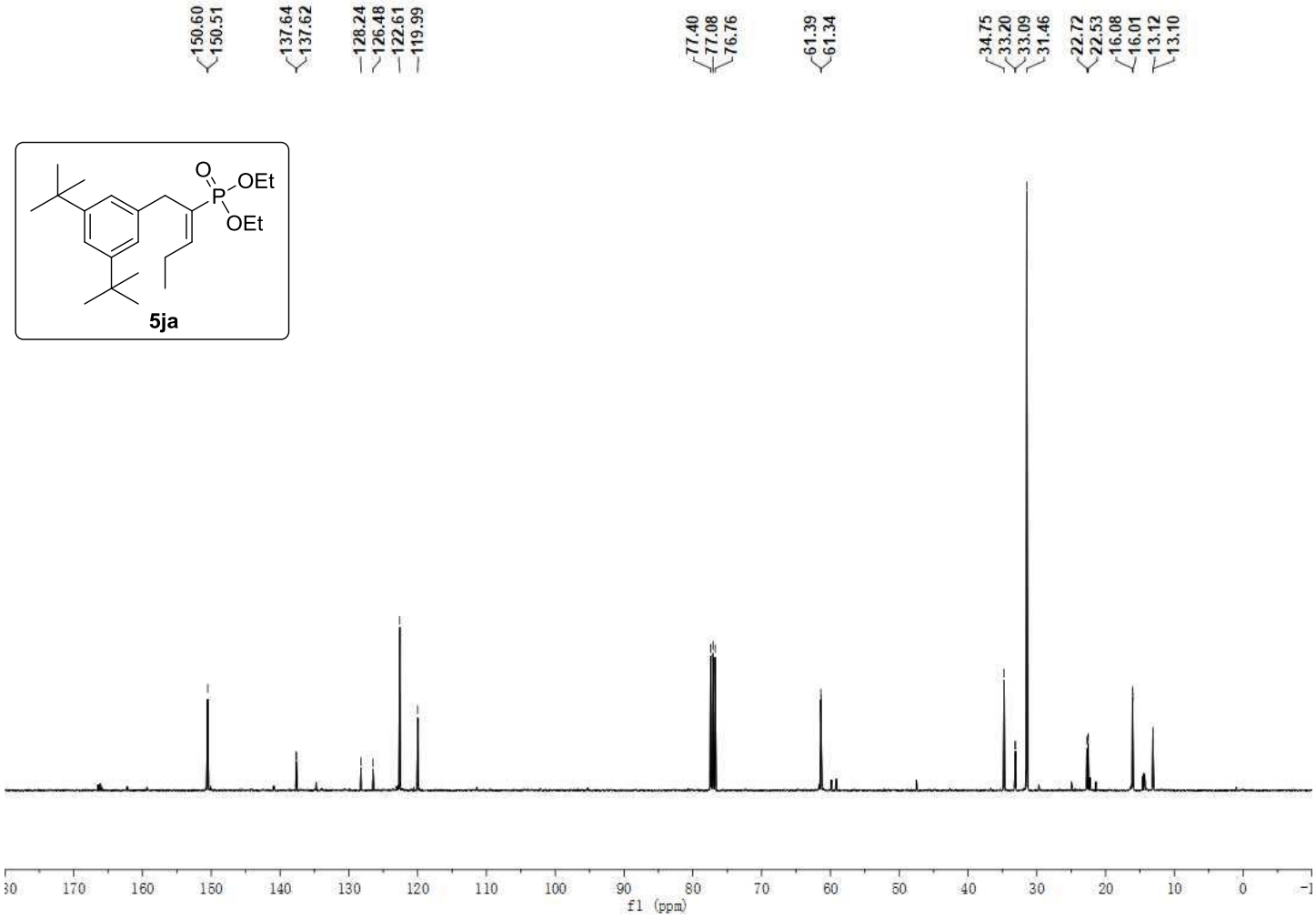
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5ia



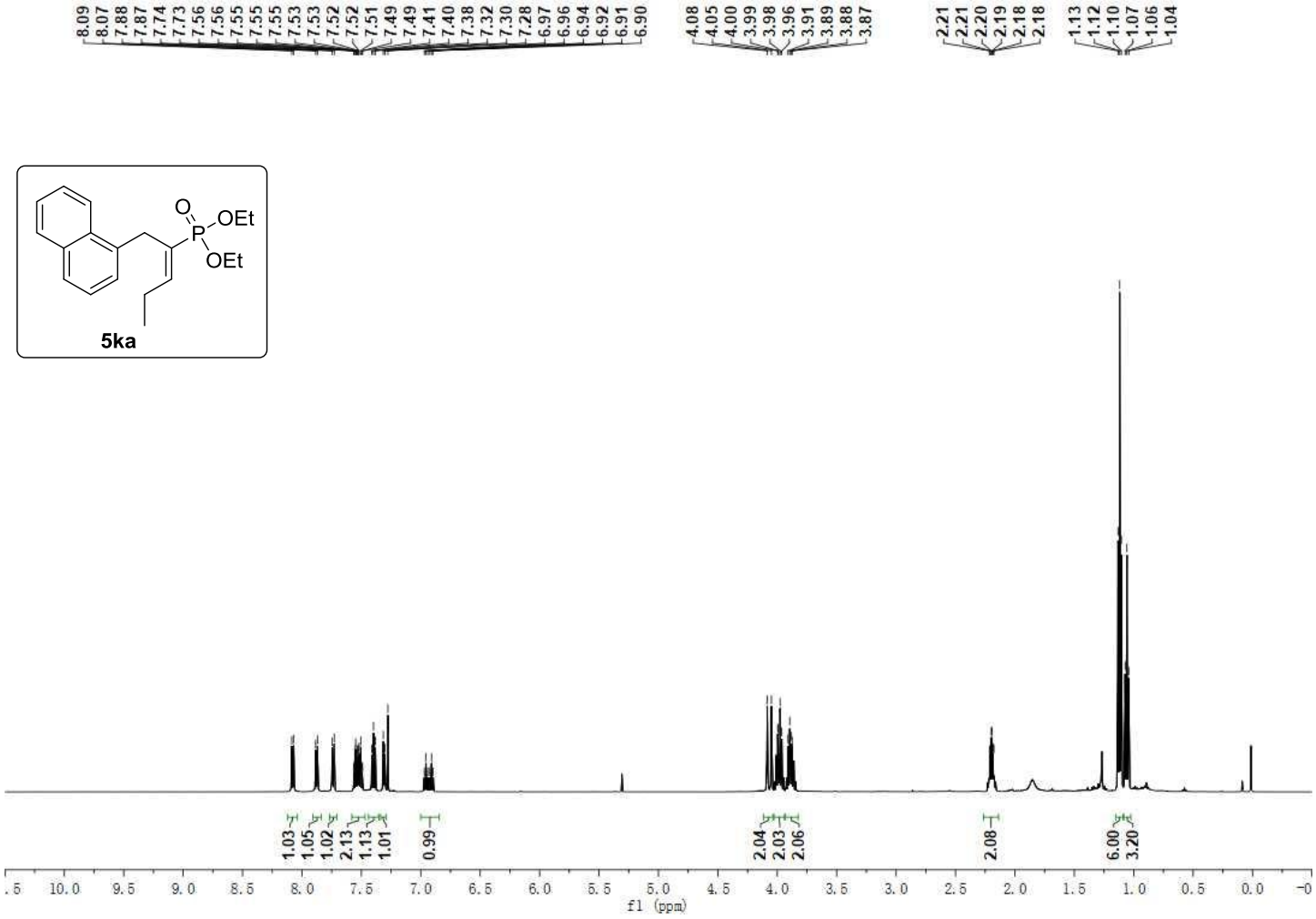
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5ja



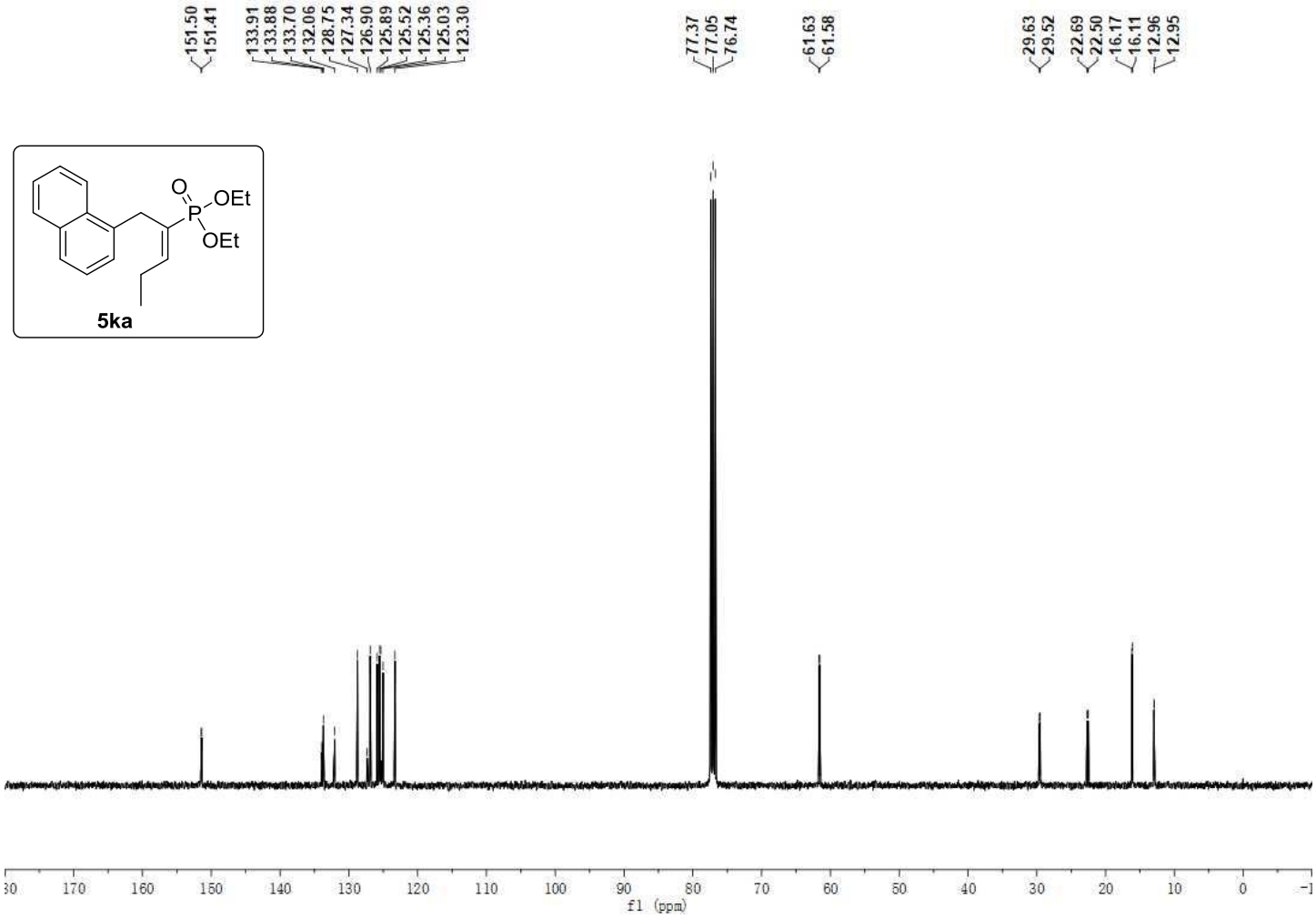
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5ja



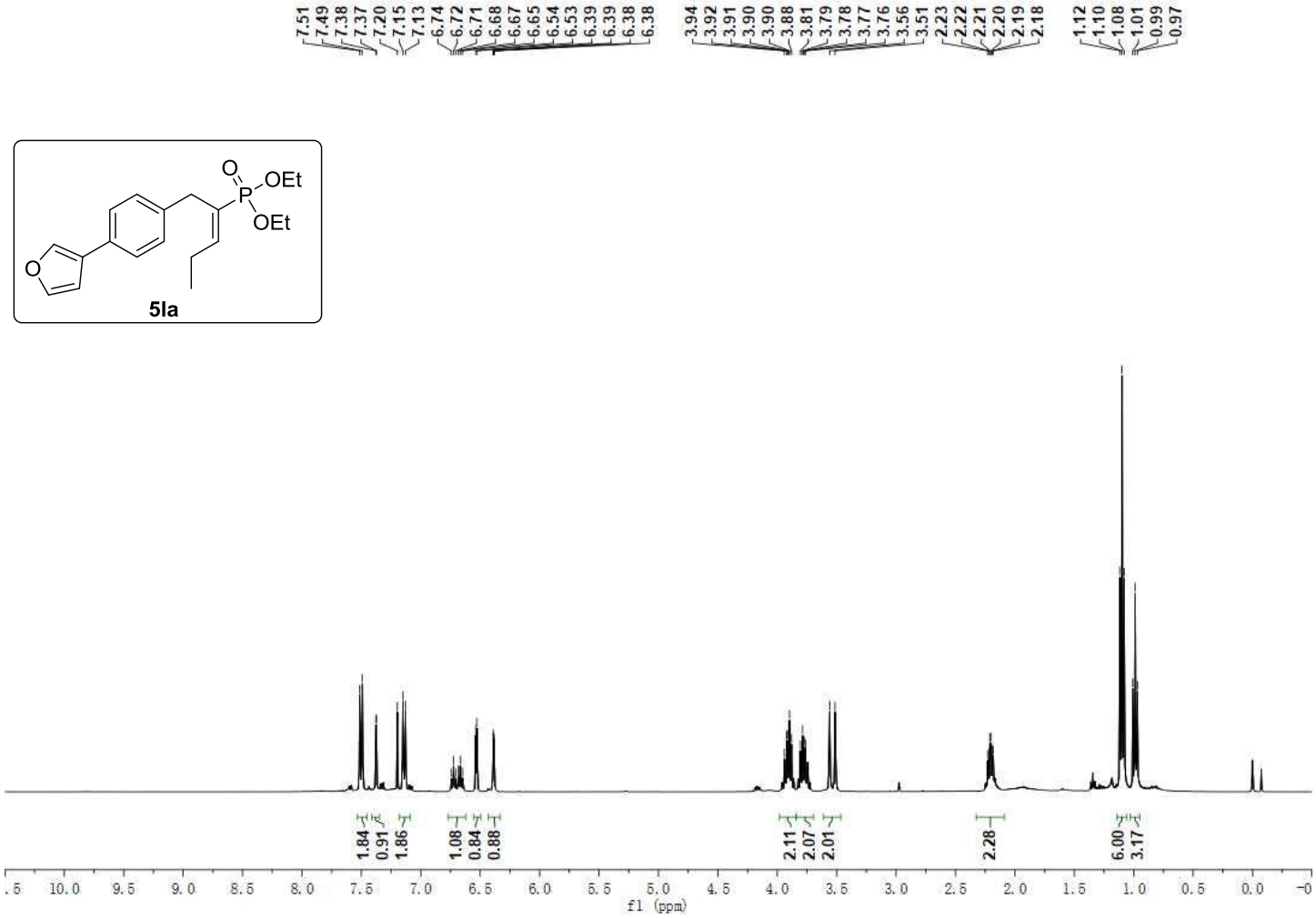
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5ka



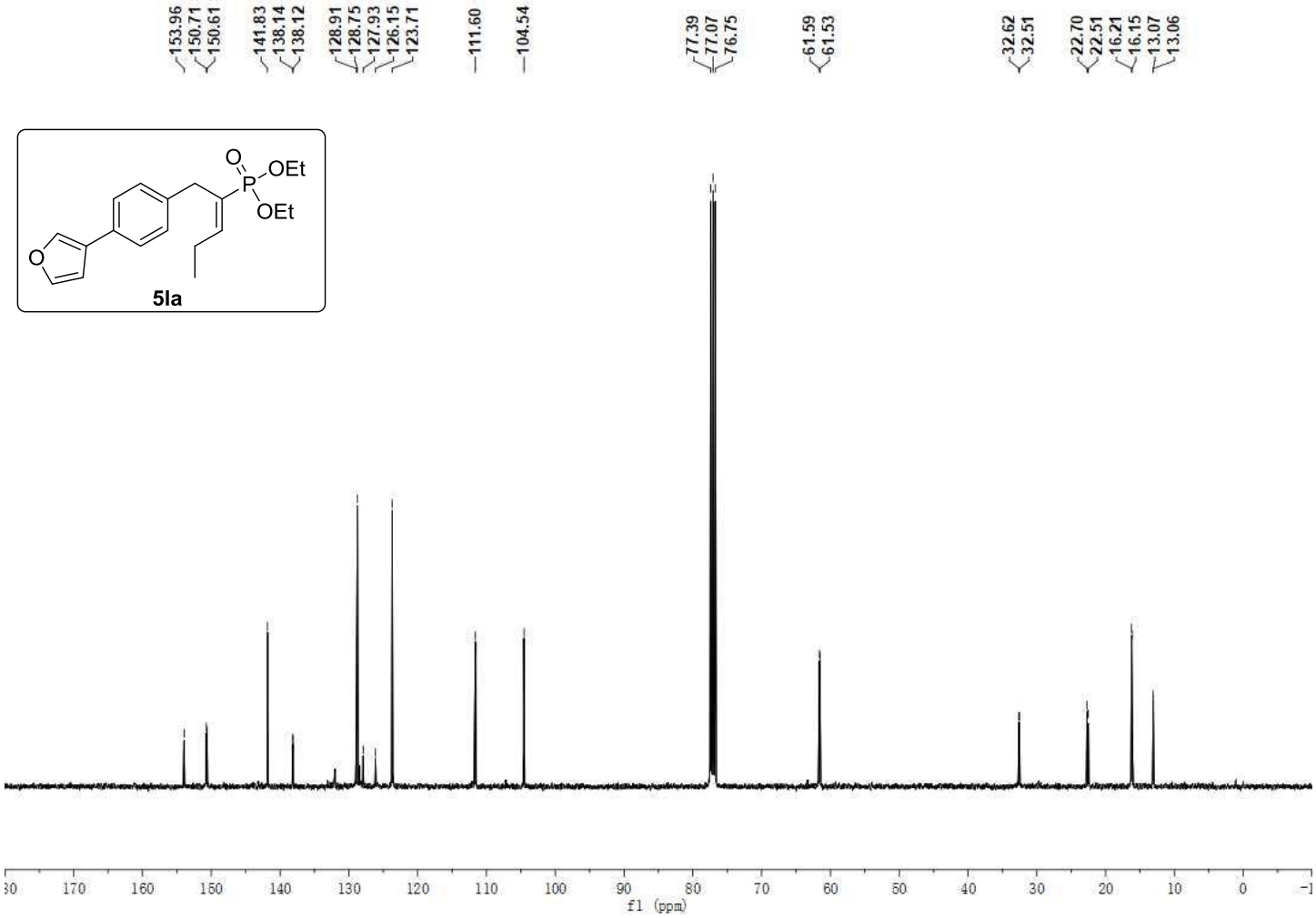
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5ka



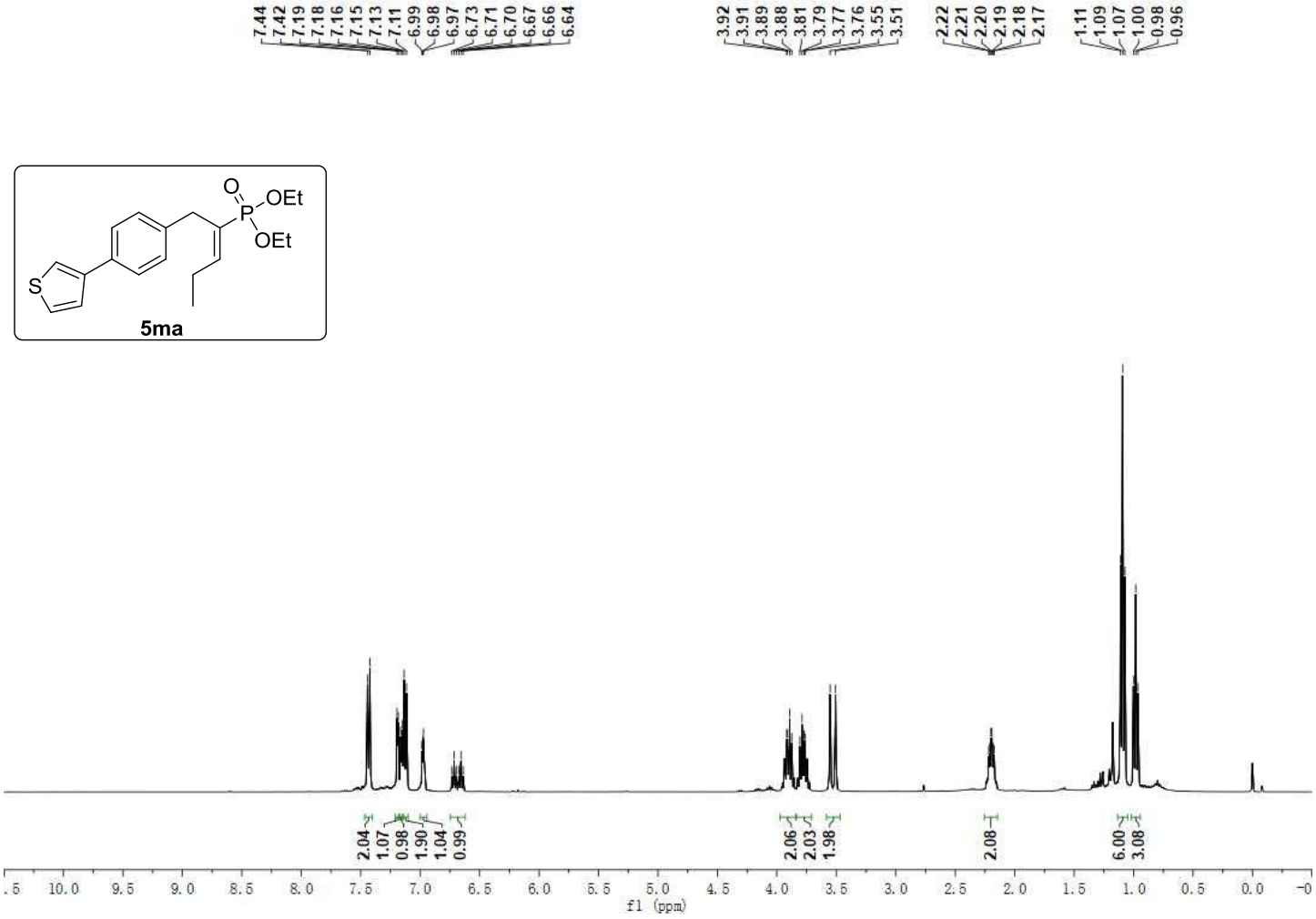
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5la



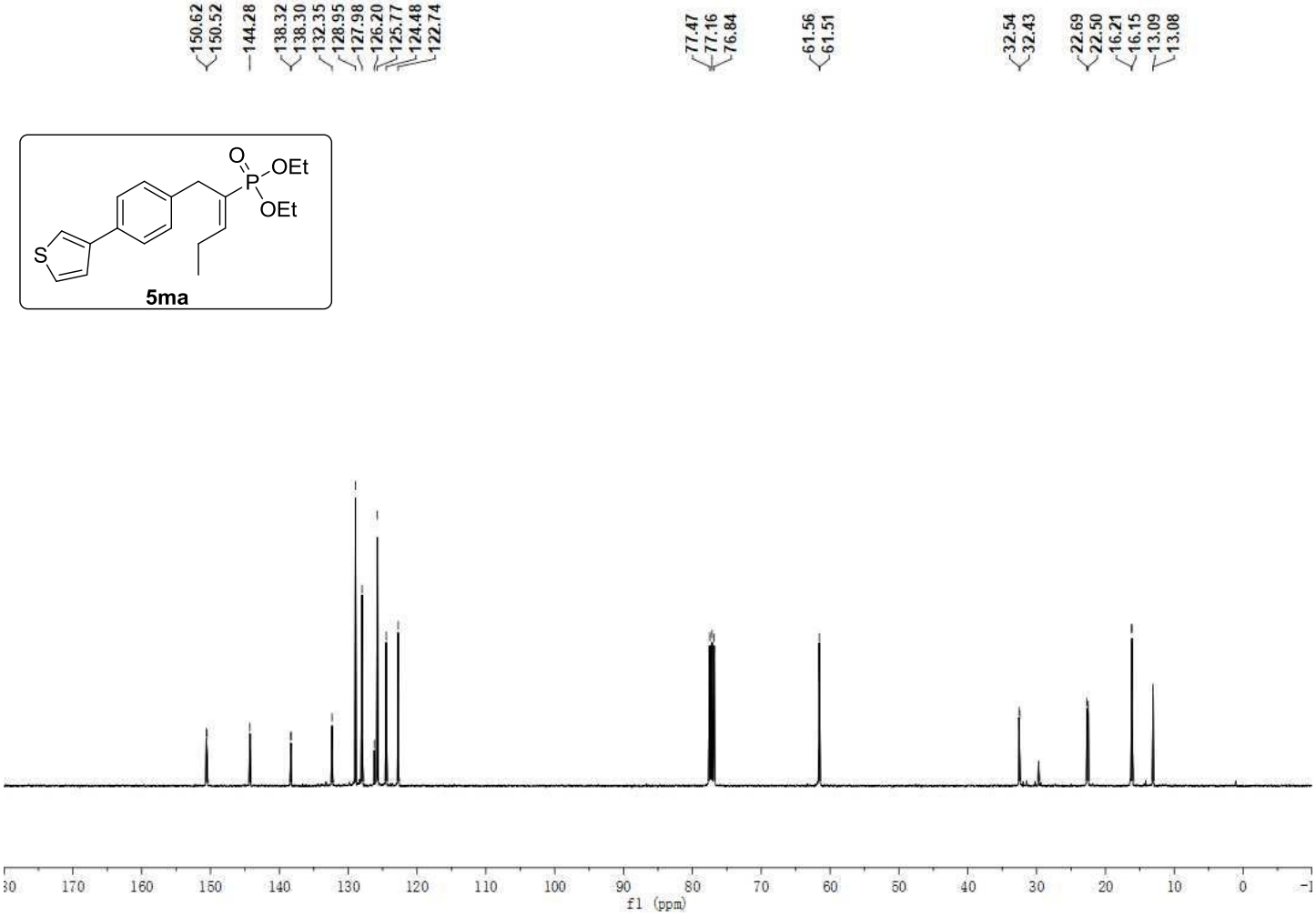
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5la



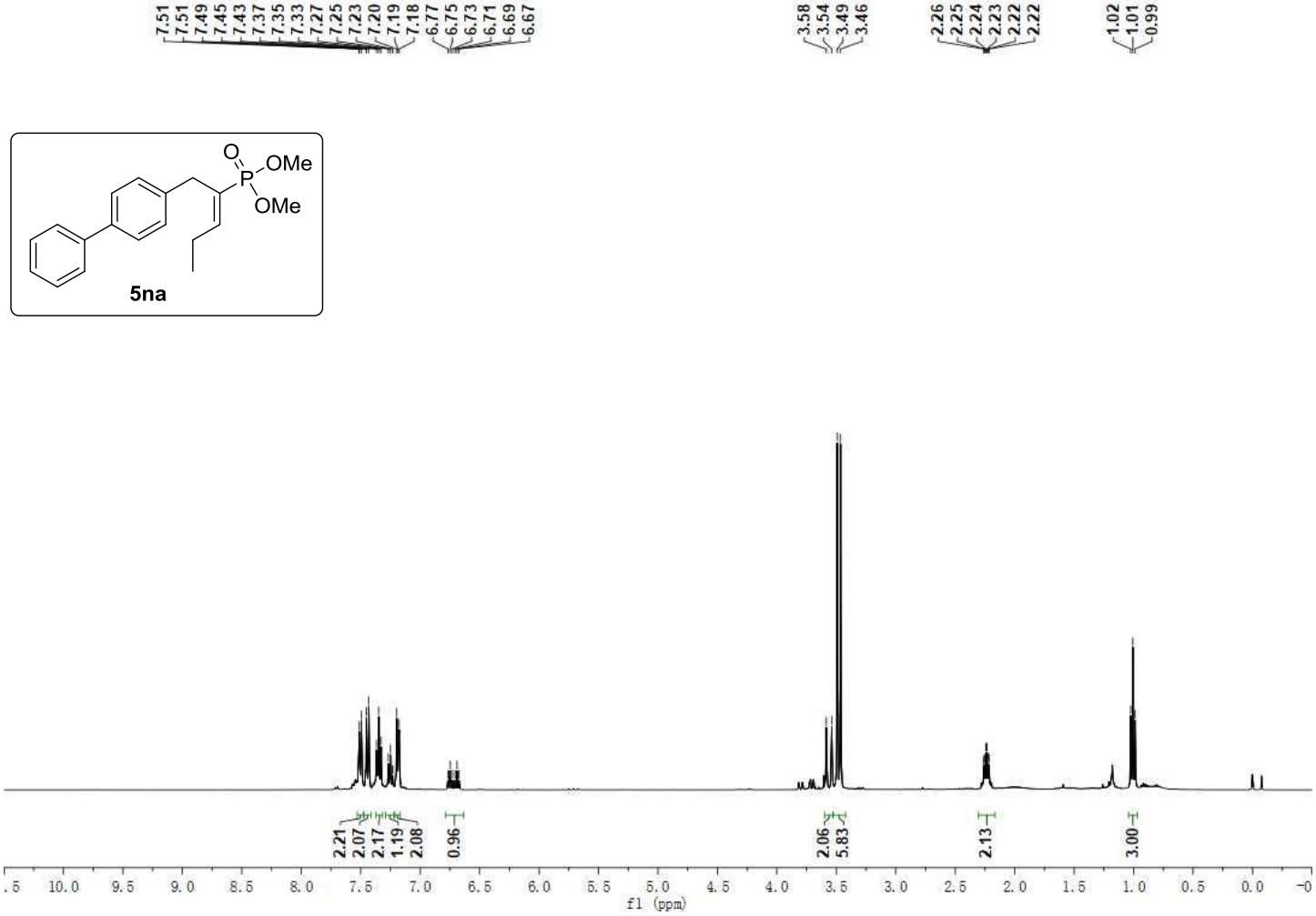
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5ma



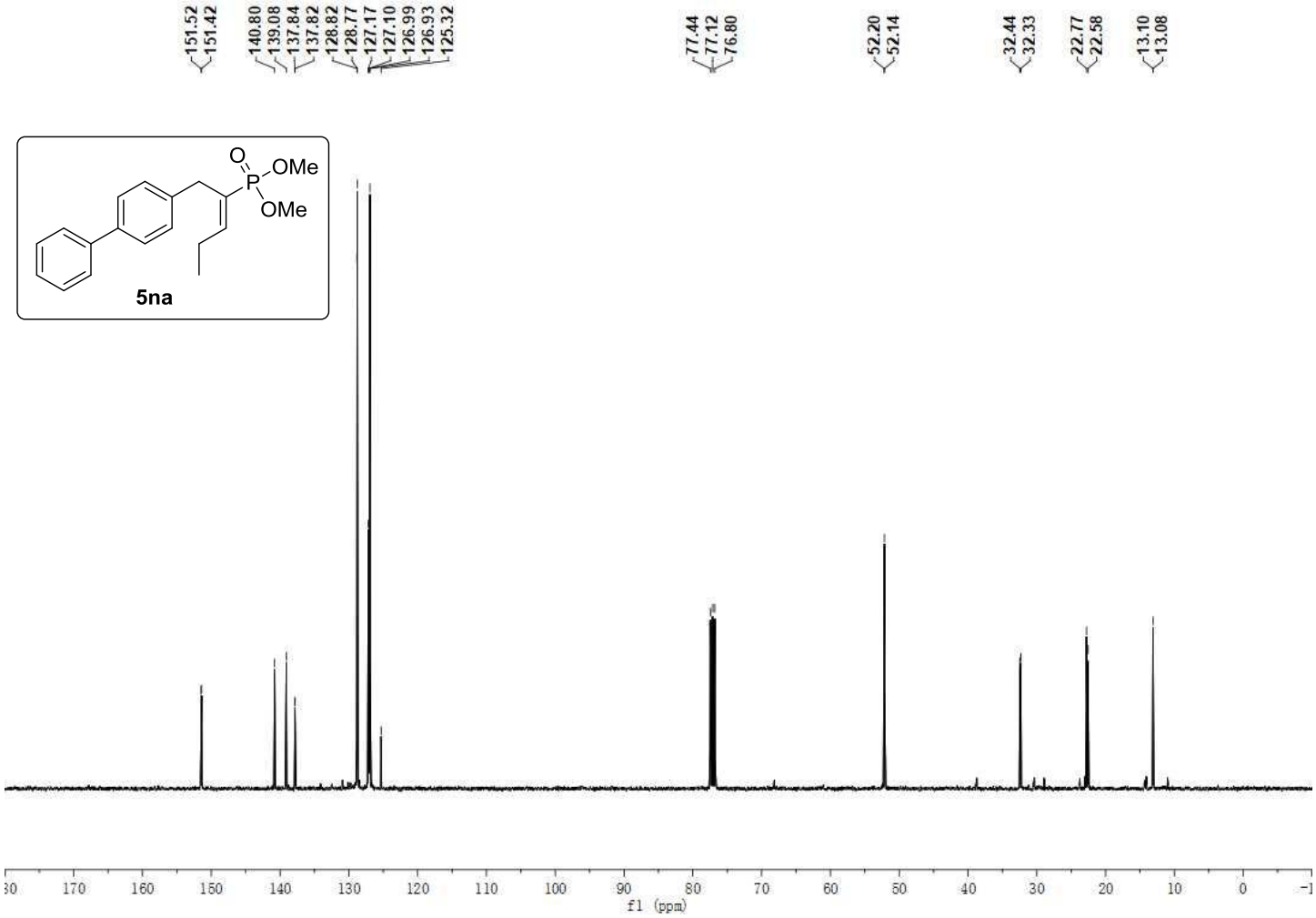
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5ma



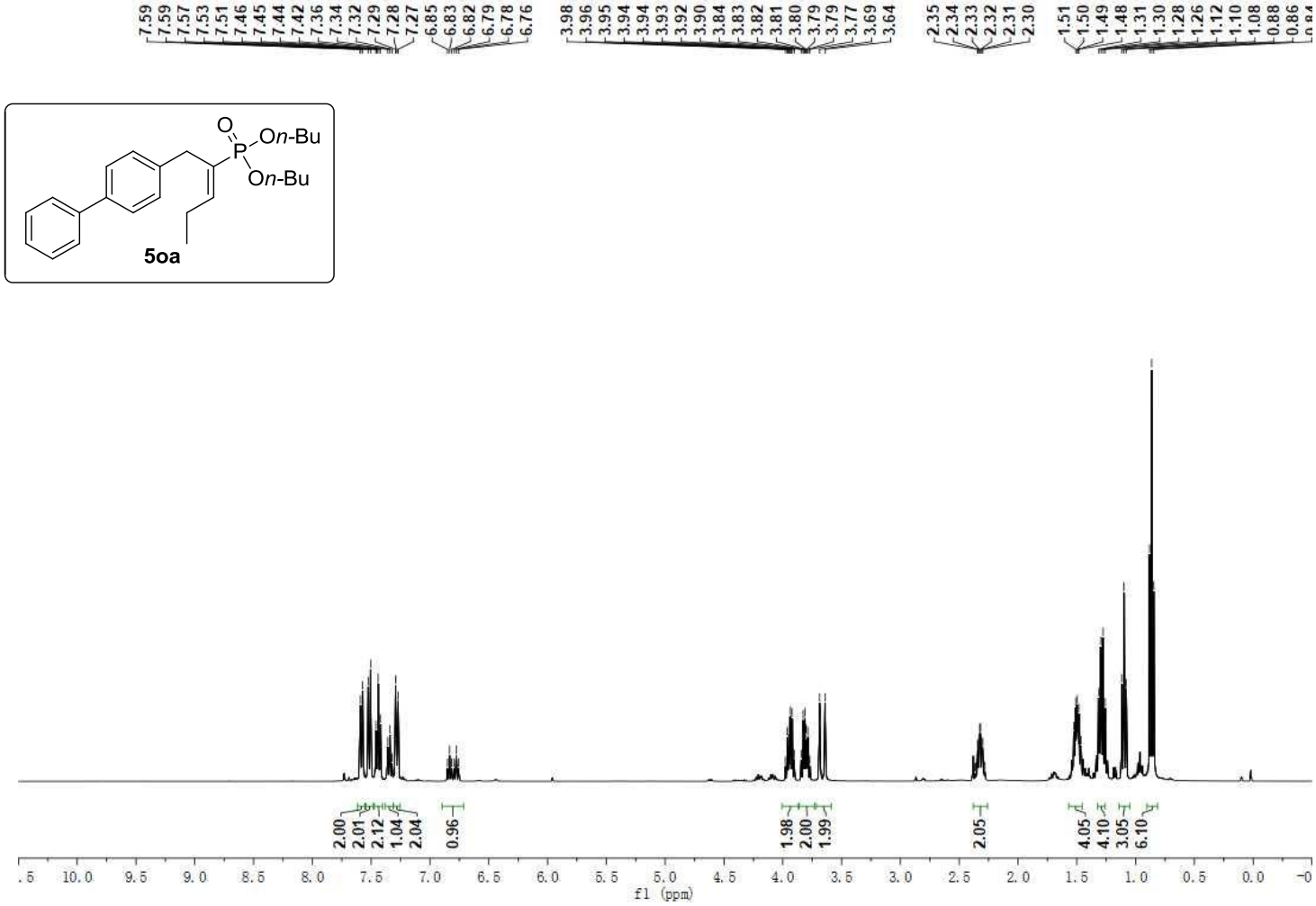
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5na



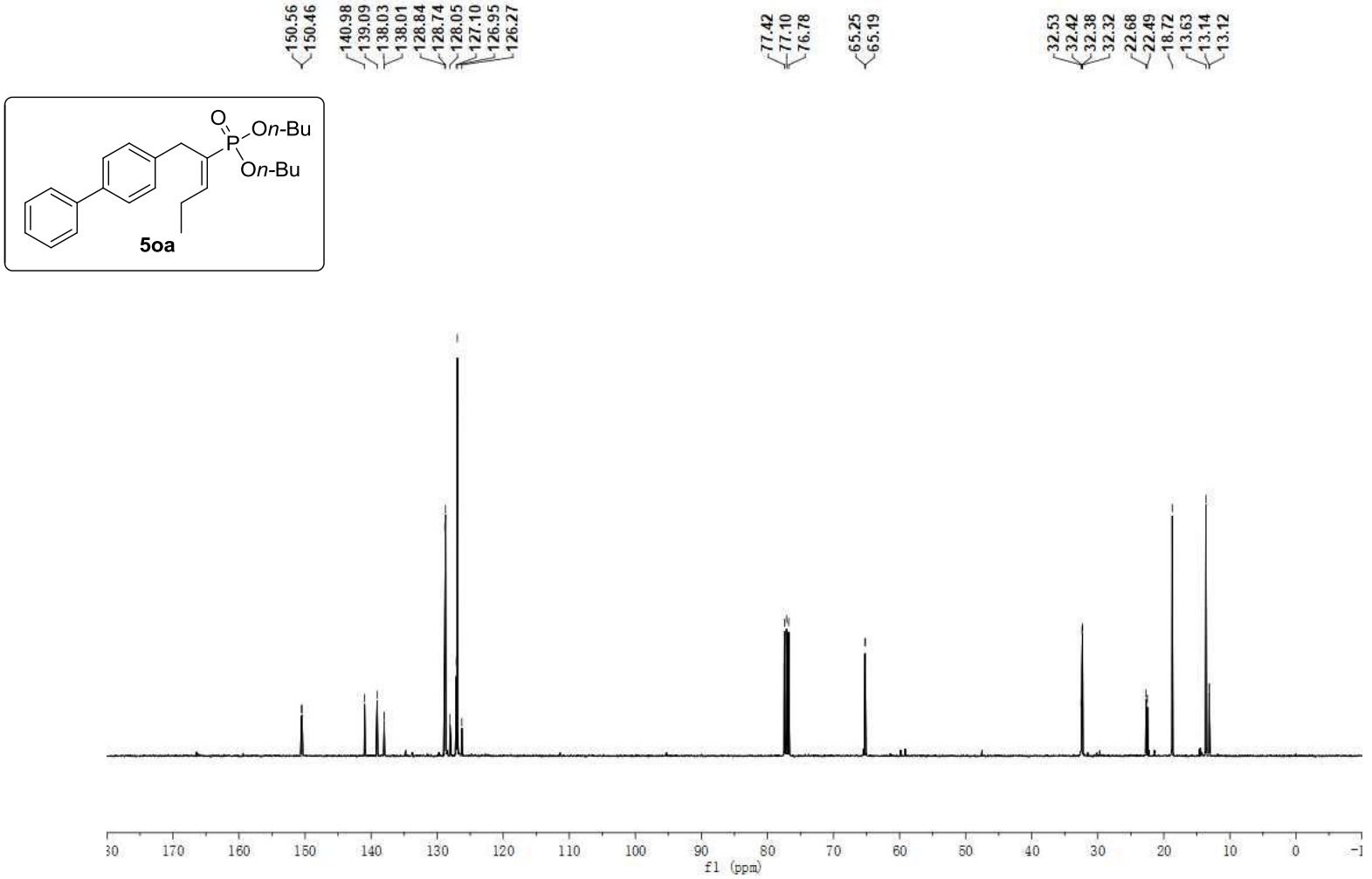
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5na



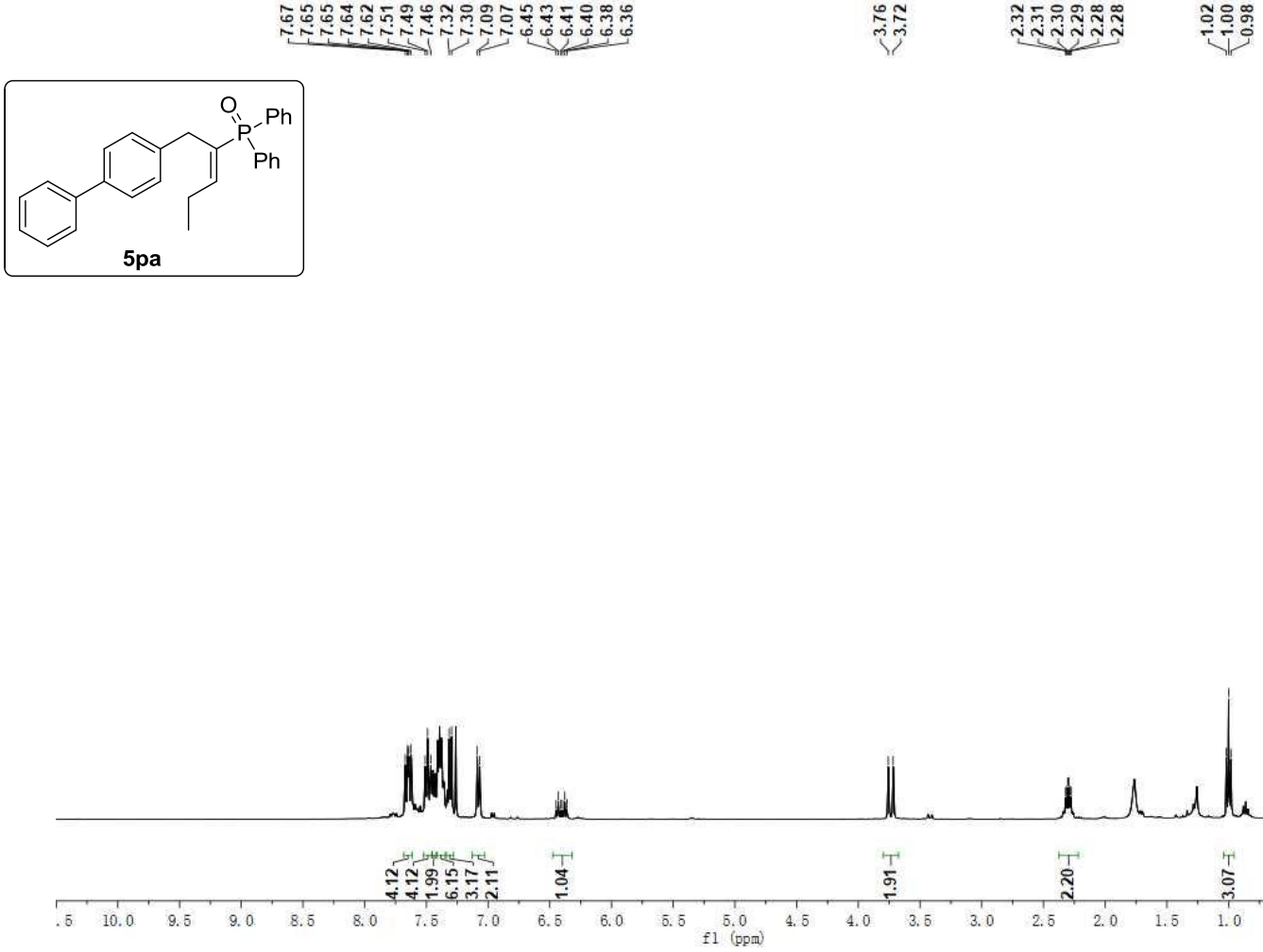
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5oa



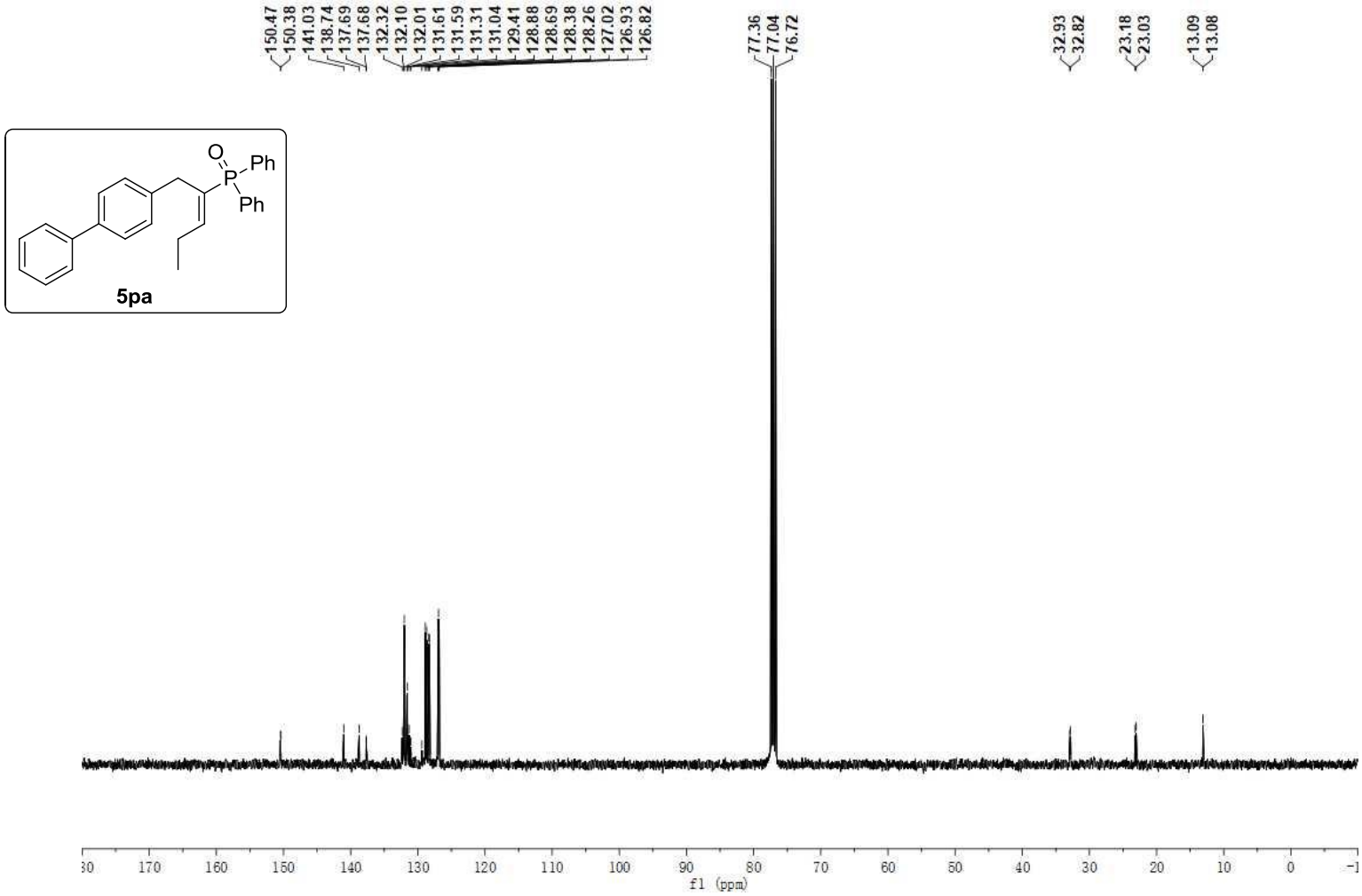
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5oa



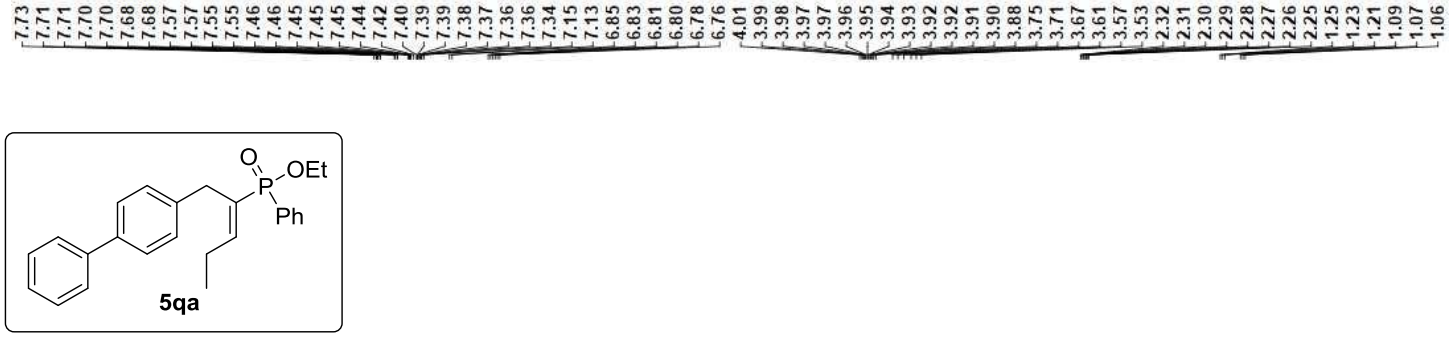
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5pa

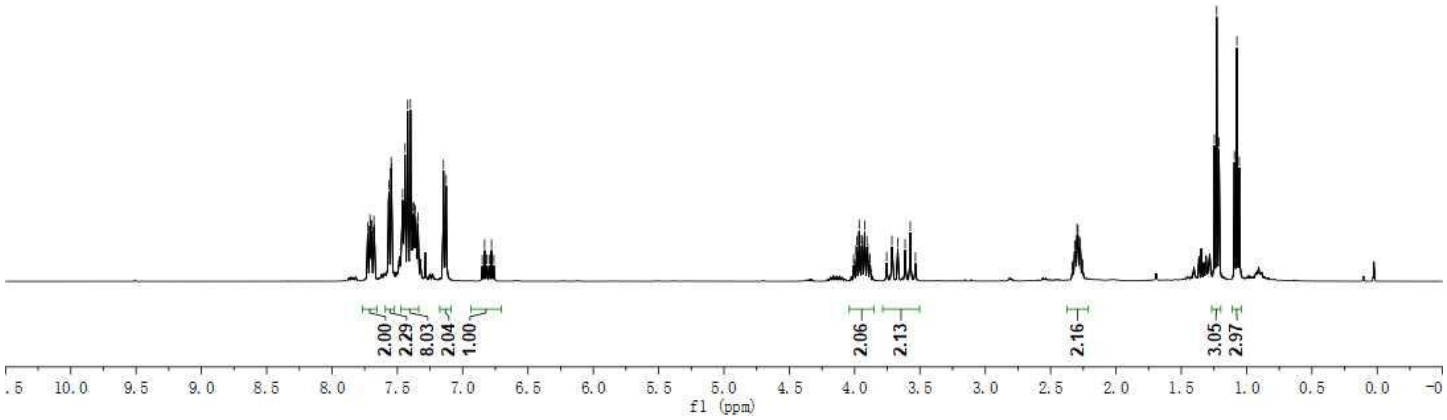


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5pa

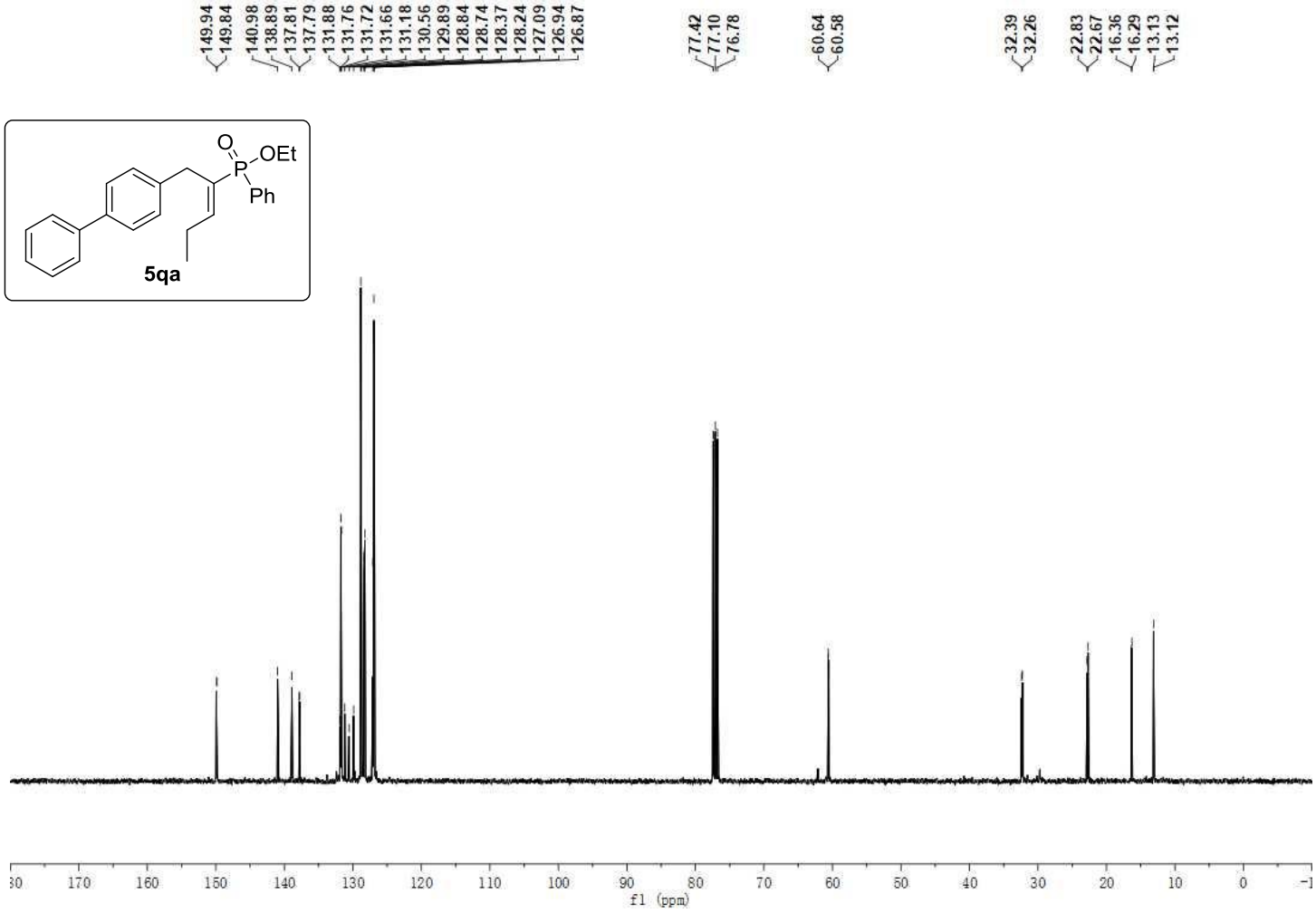


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5qa

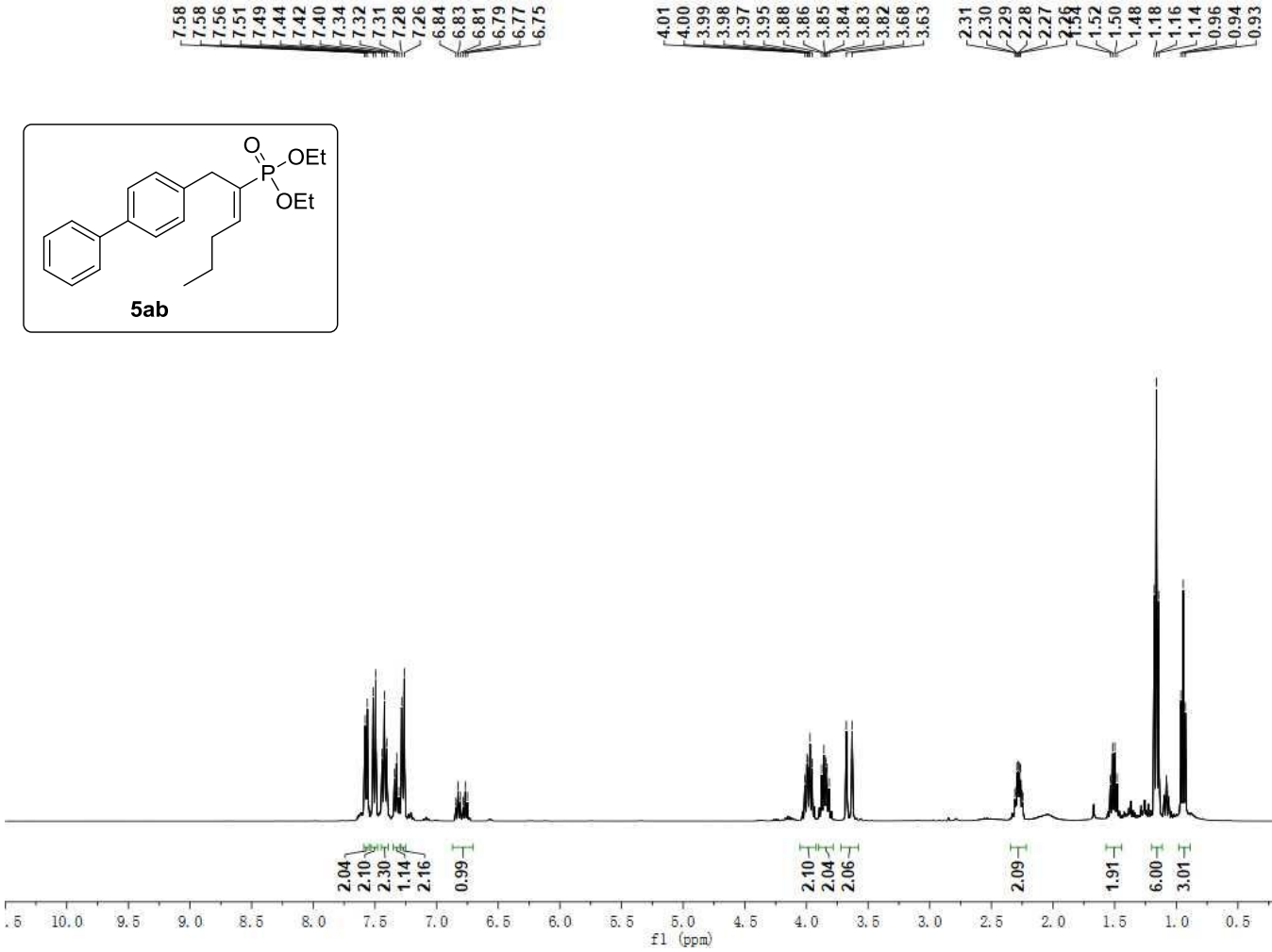




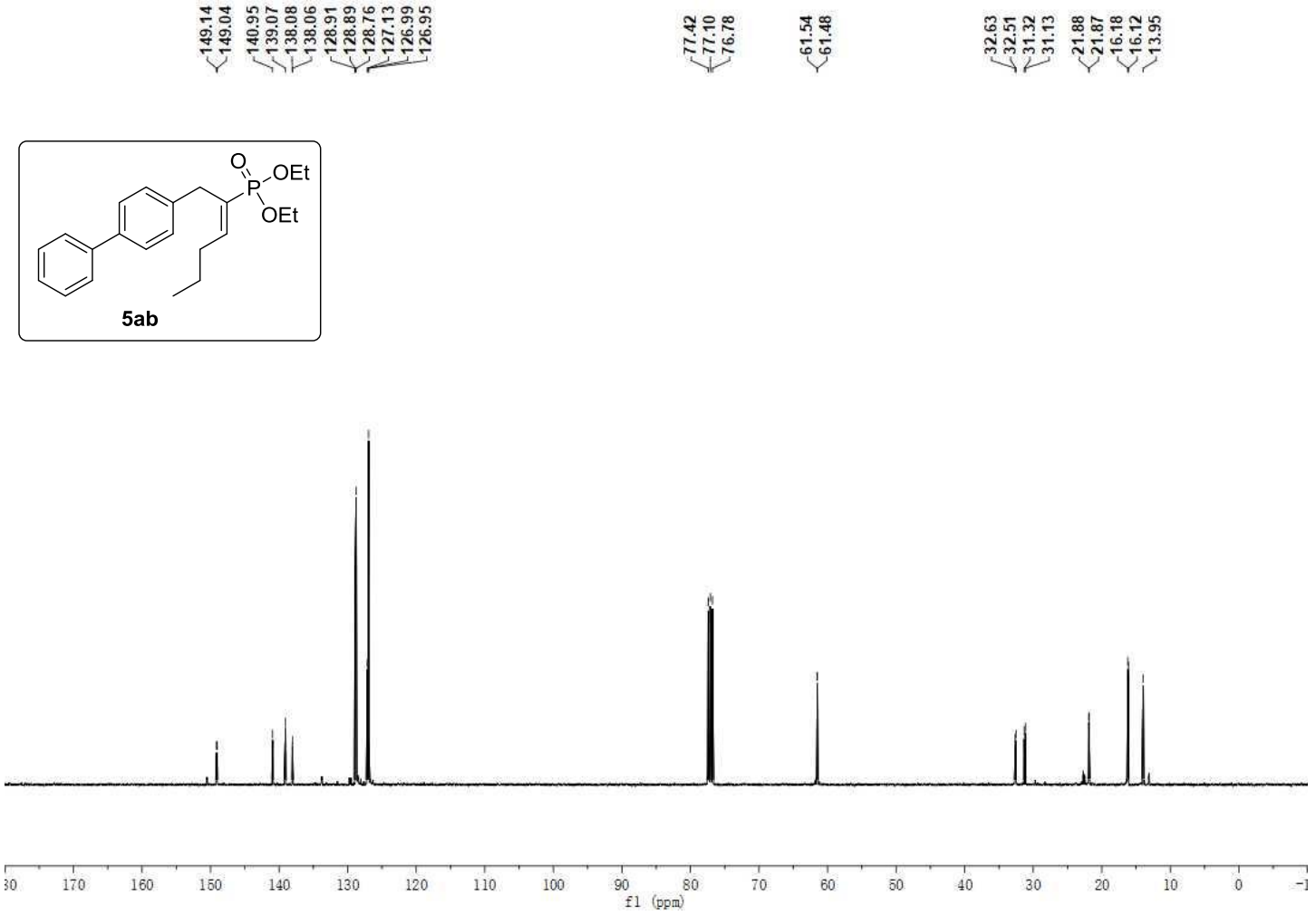
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5qa



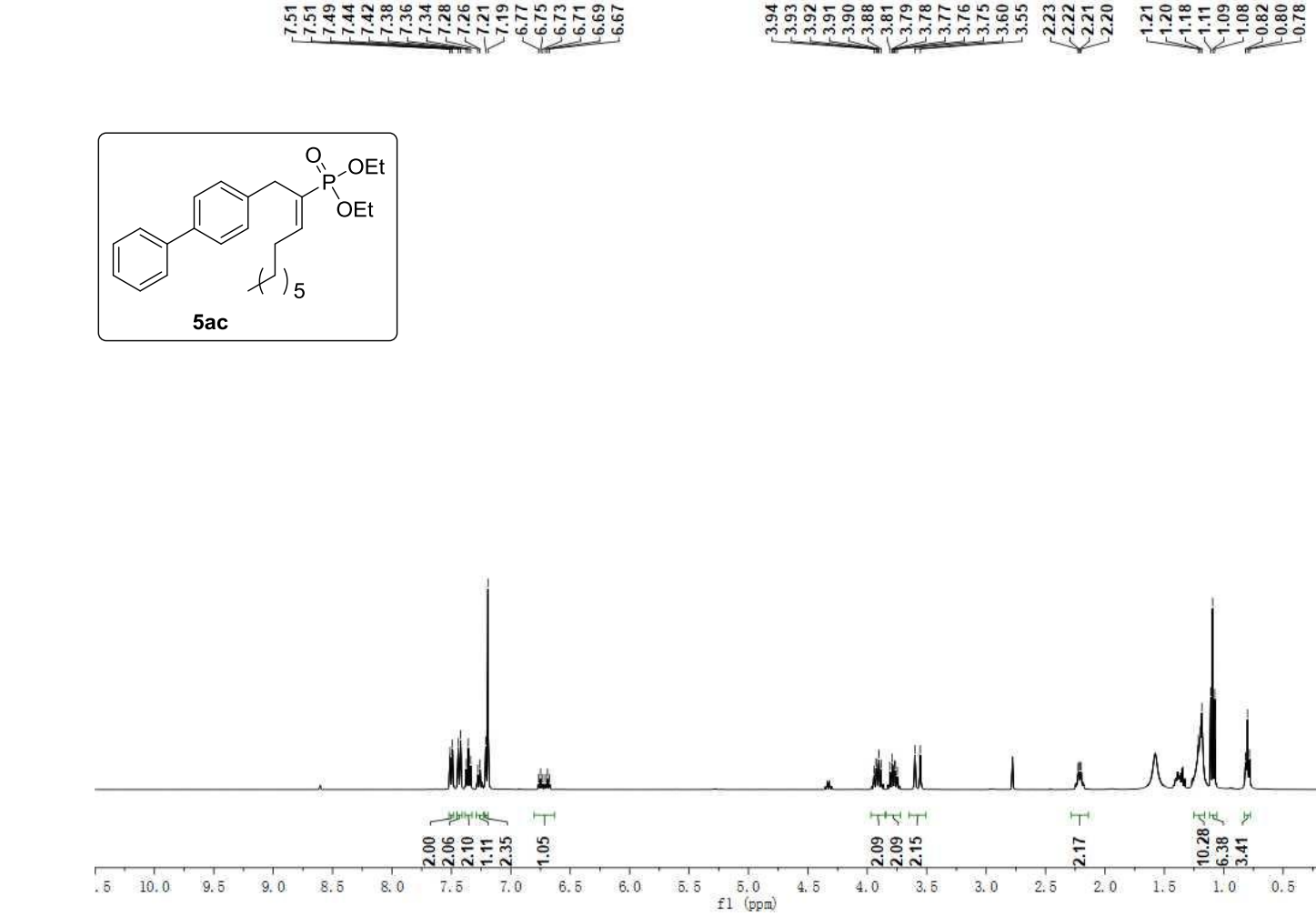
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5ab



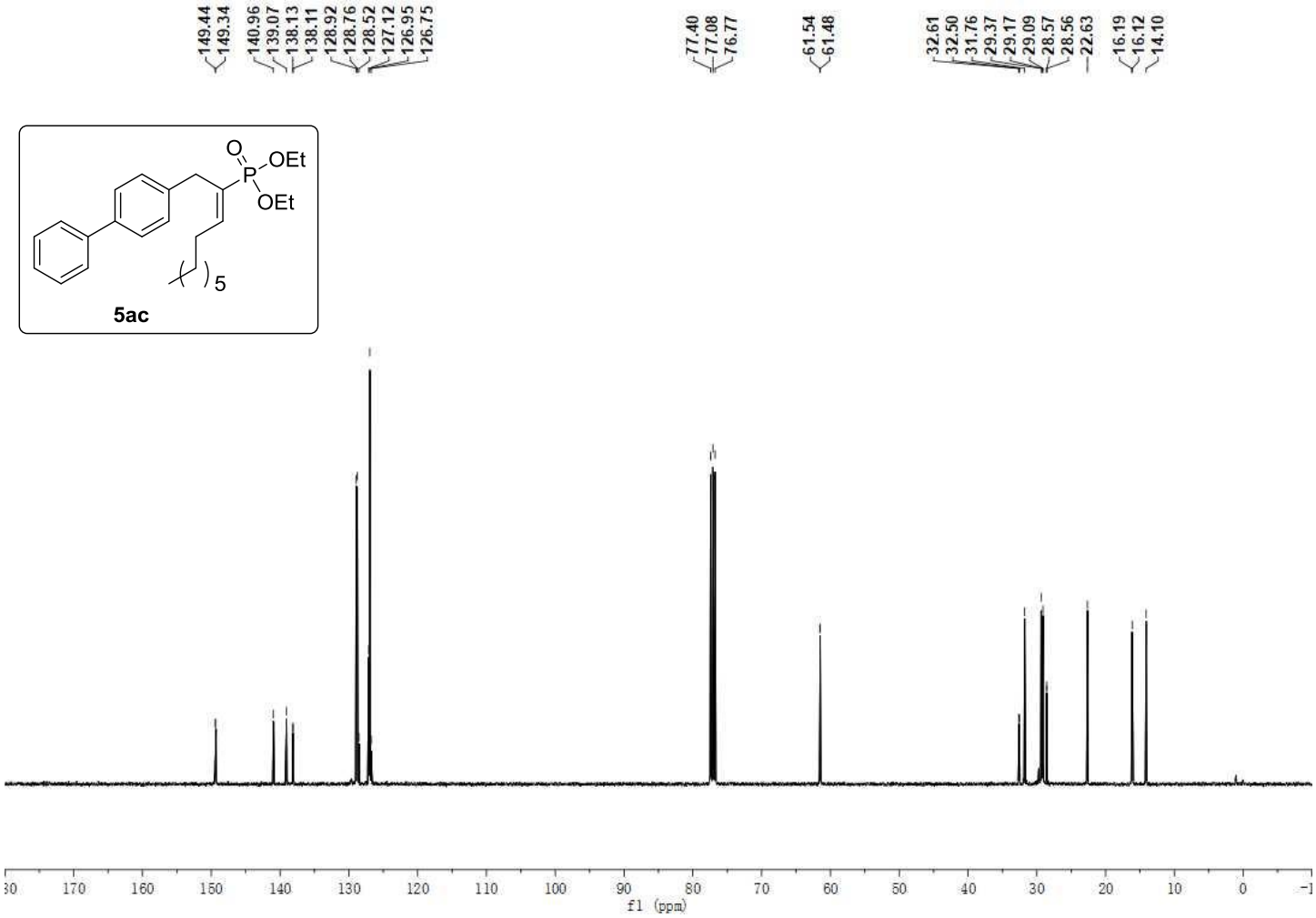
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5ab



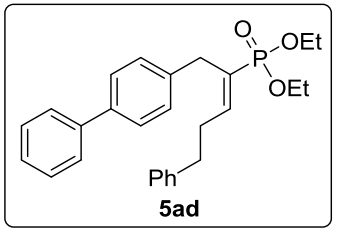
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5ac



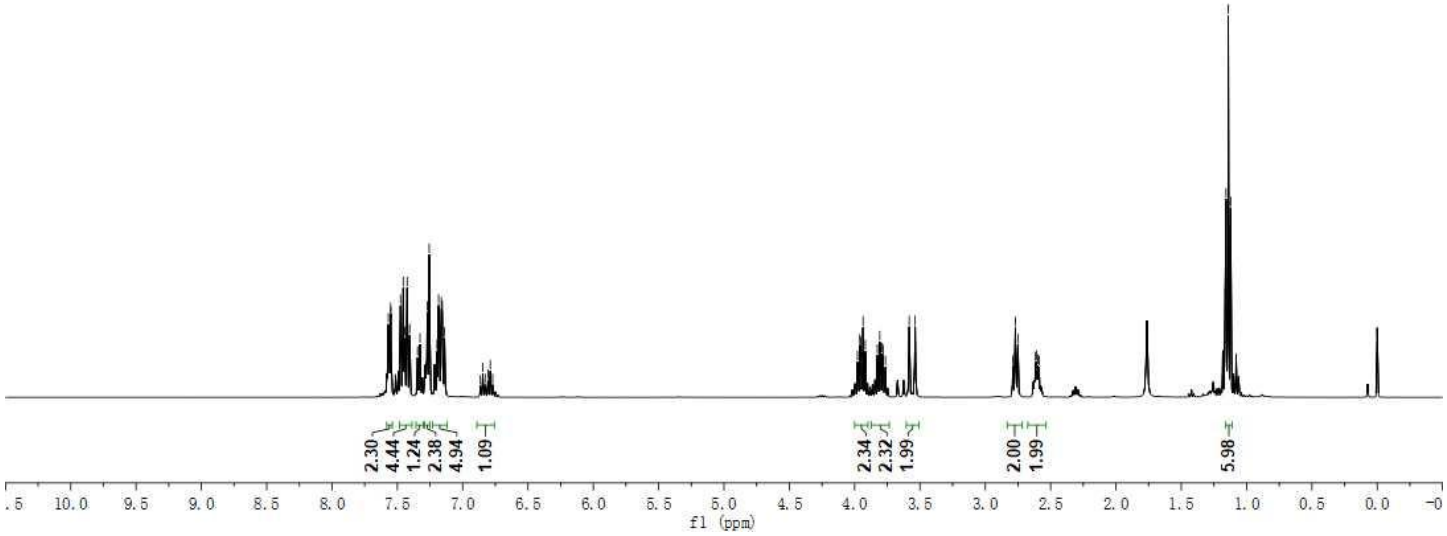
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5ac



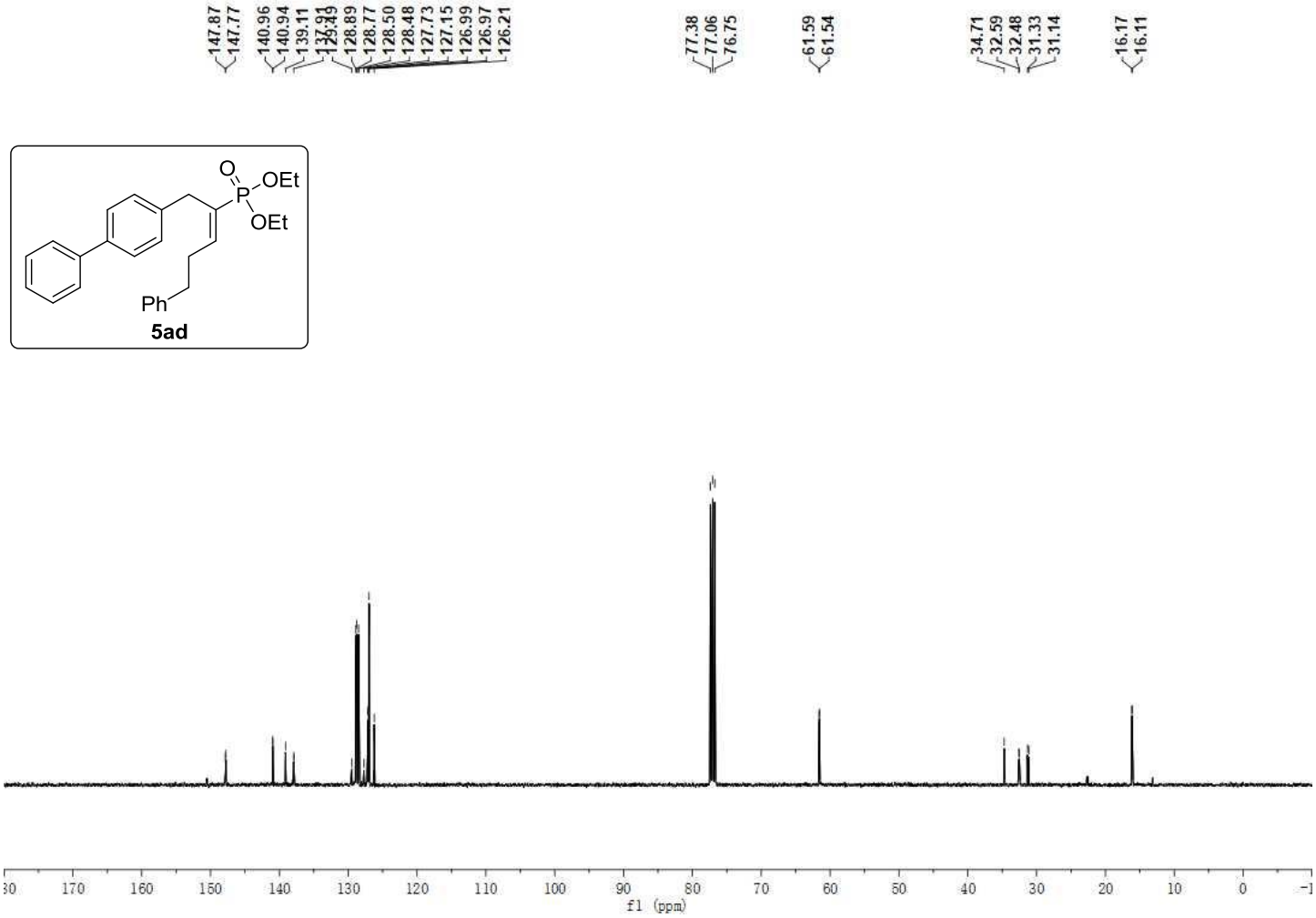
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5ad



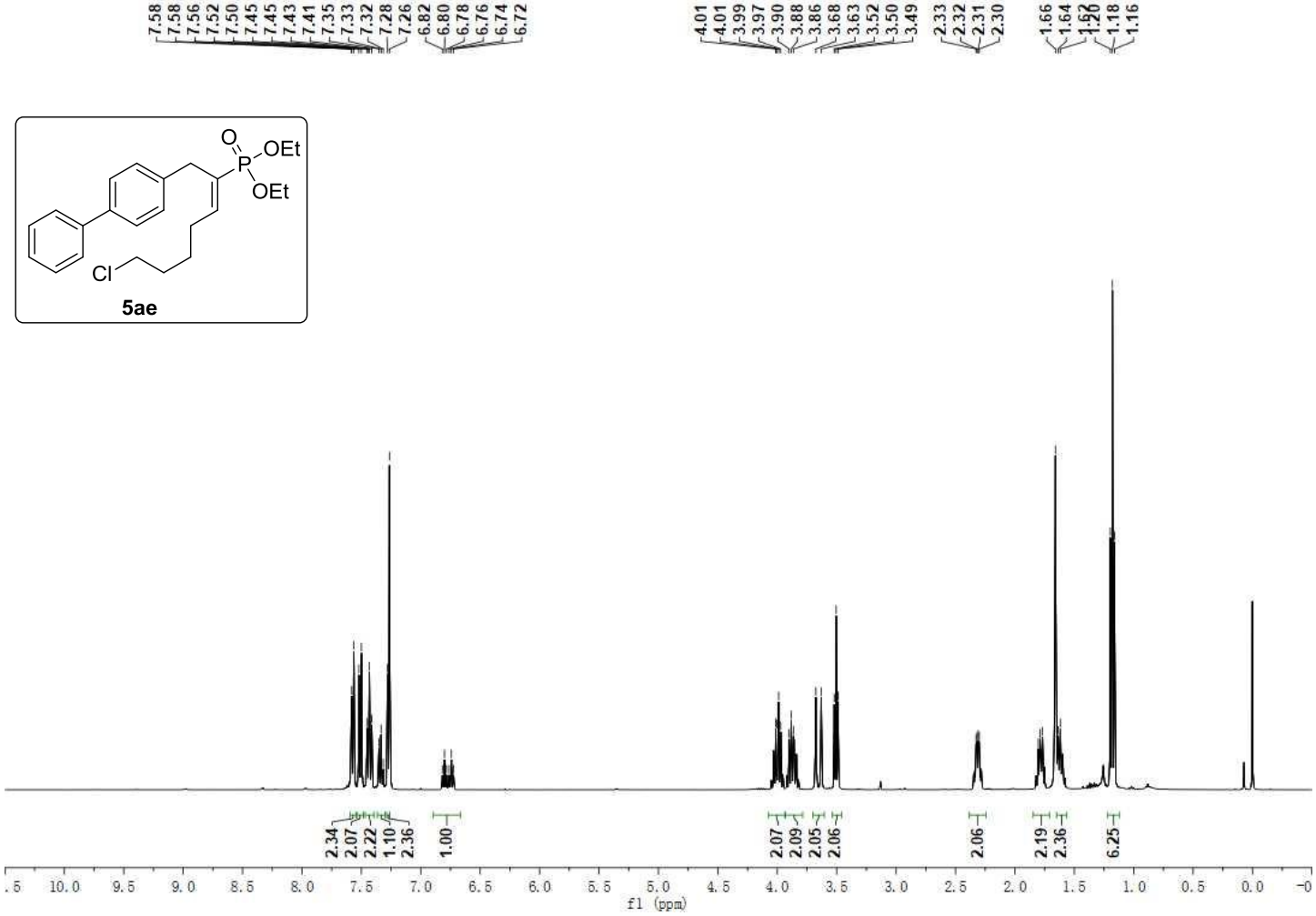
5ad



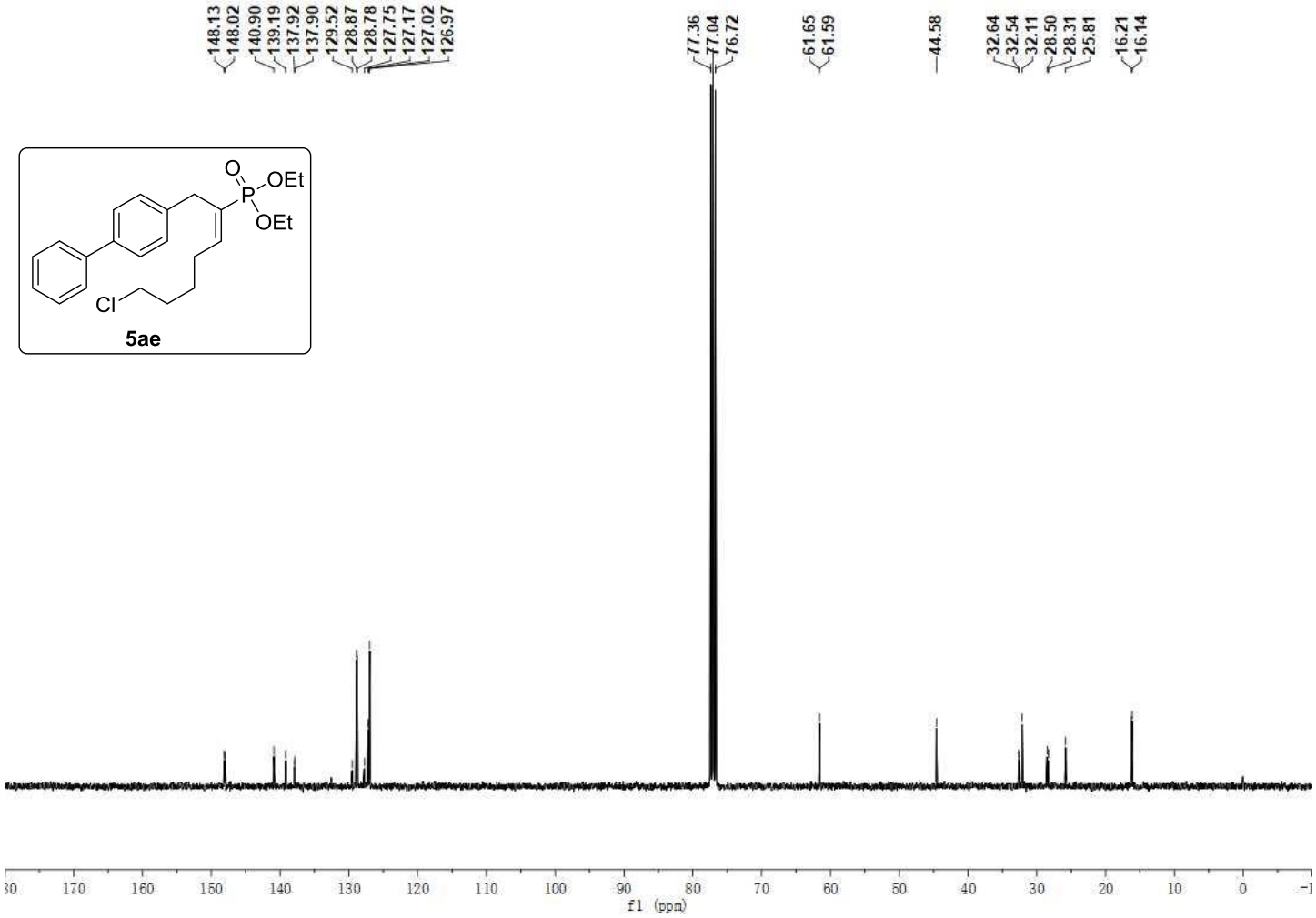
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5ad



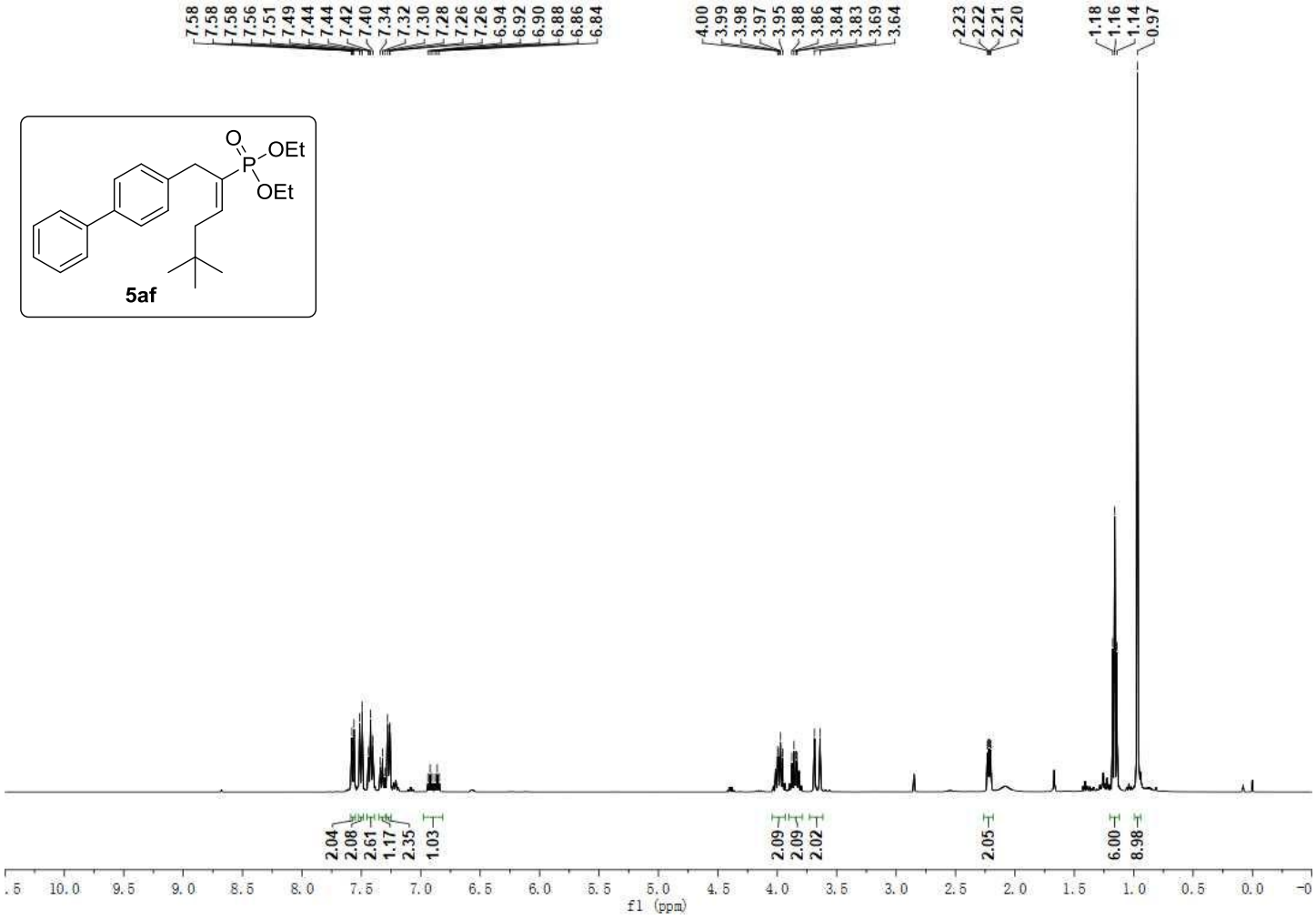
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5ae



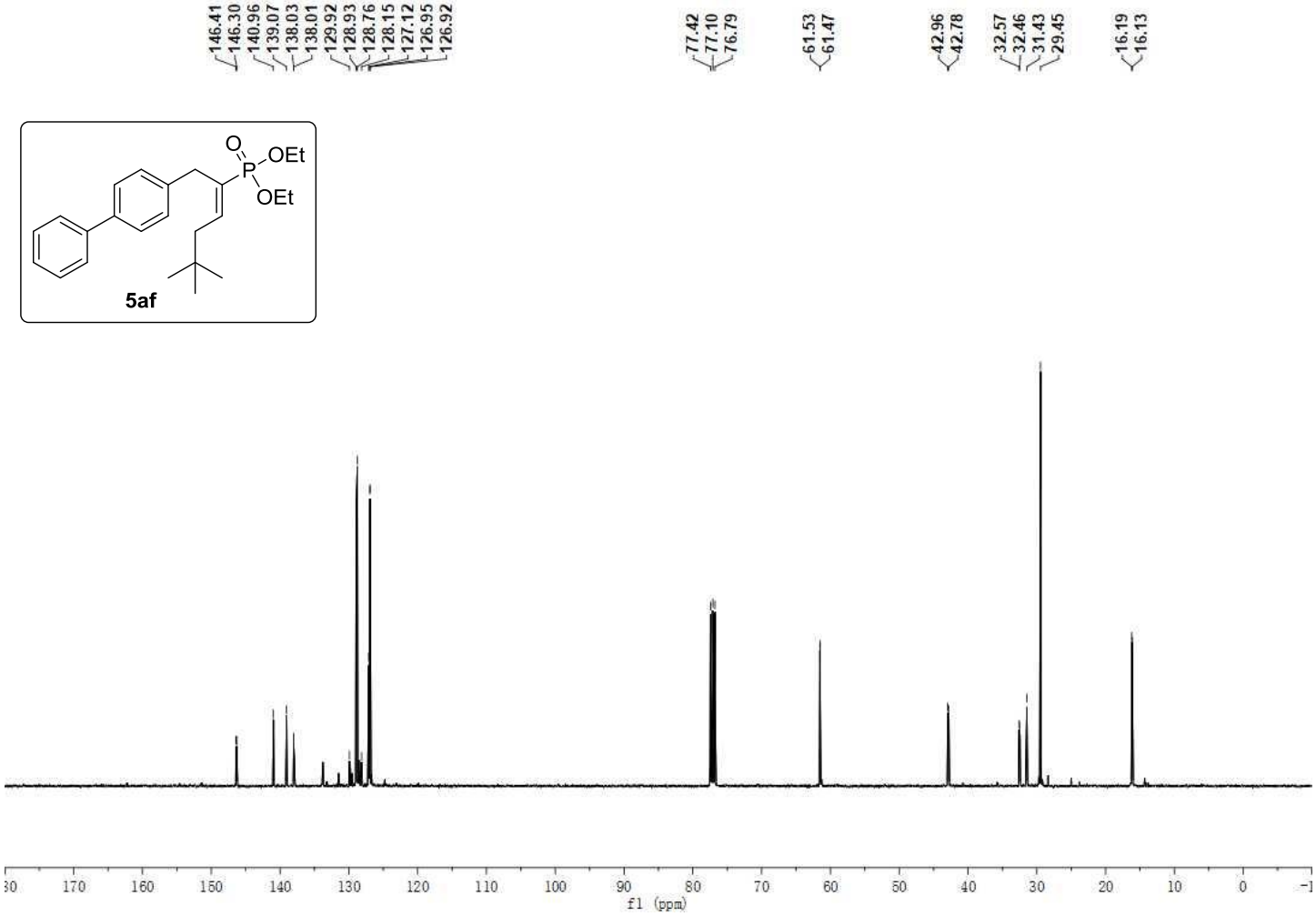
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5ae



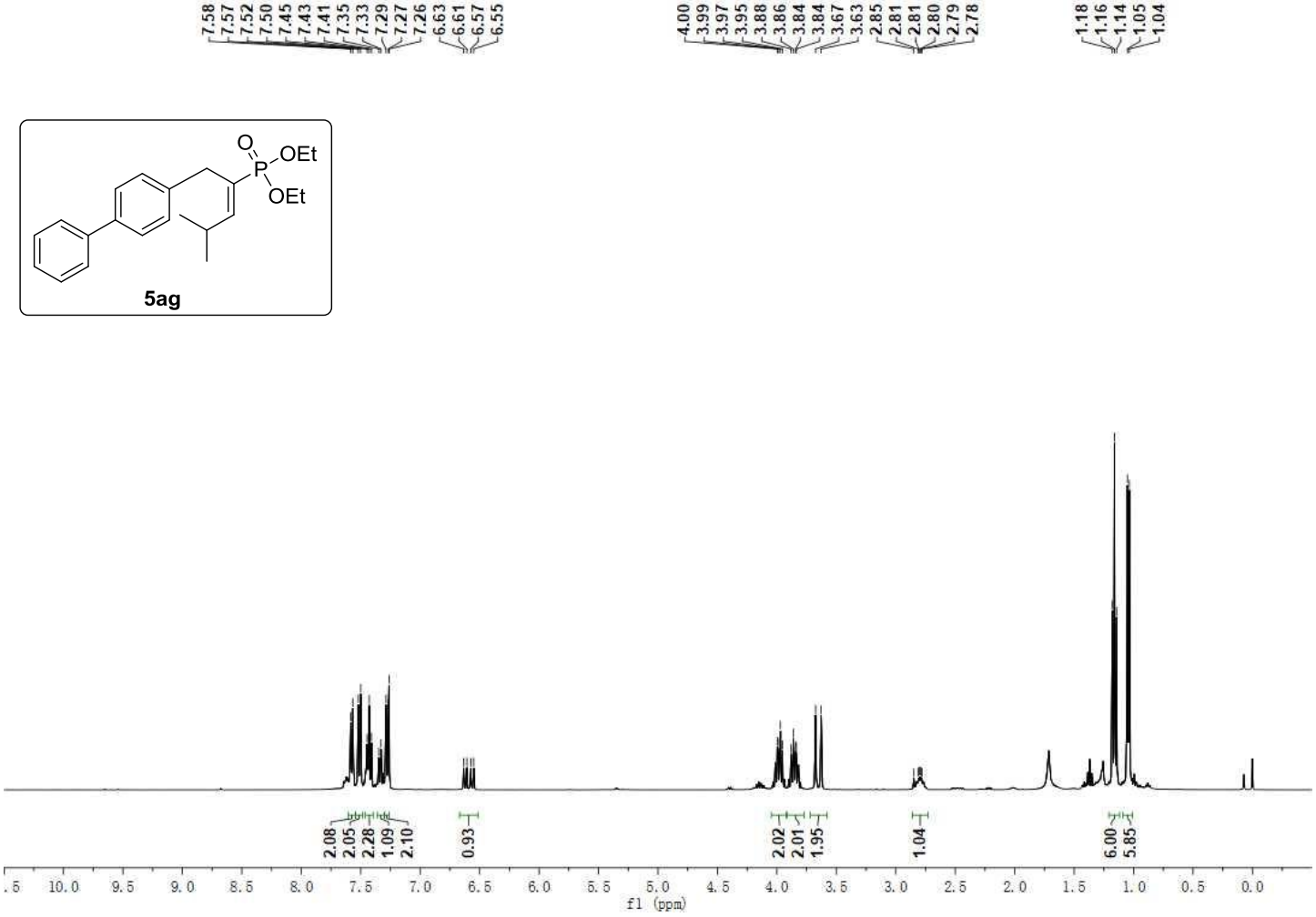
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5af



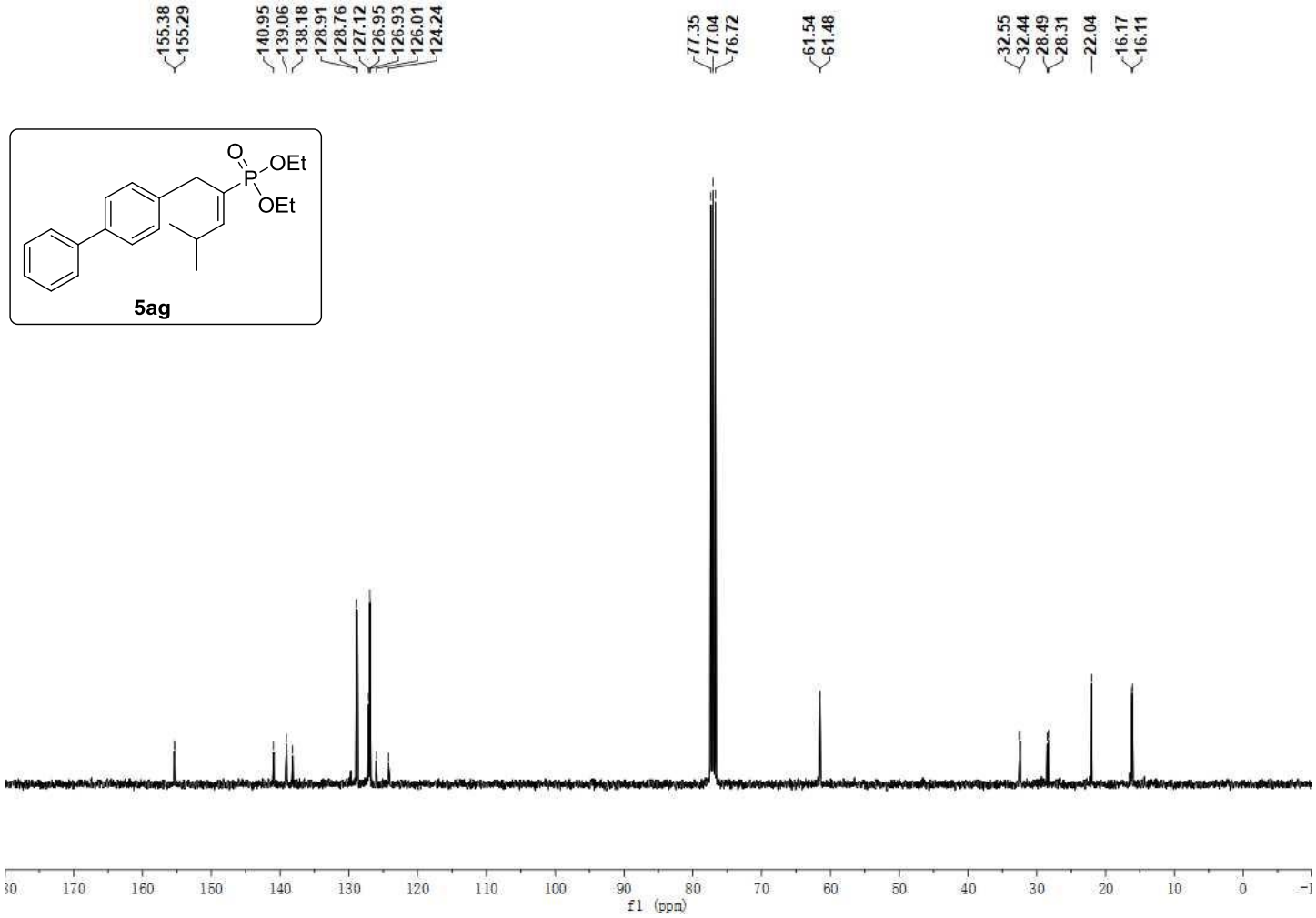
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5af



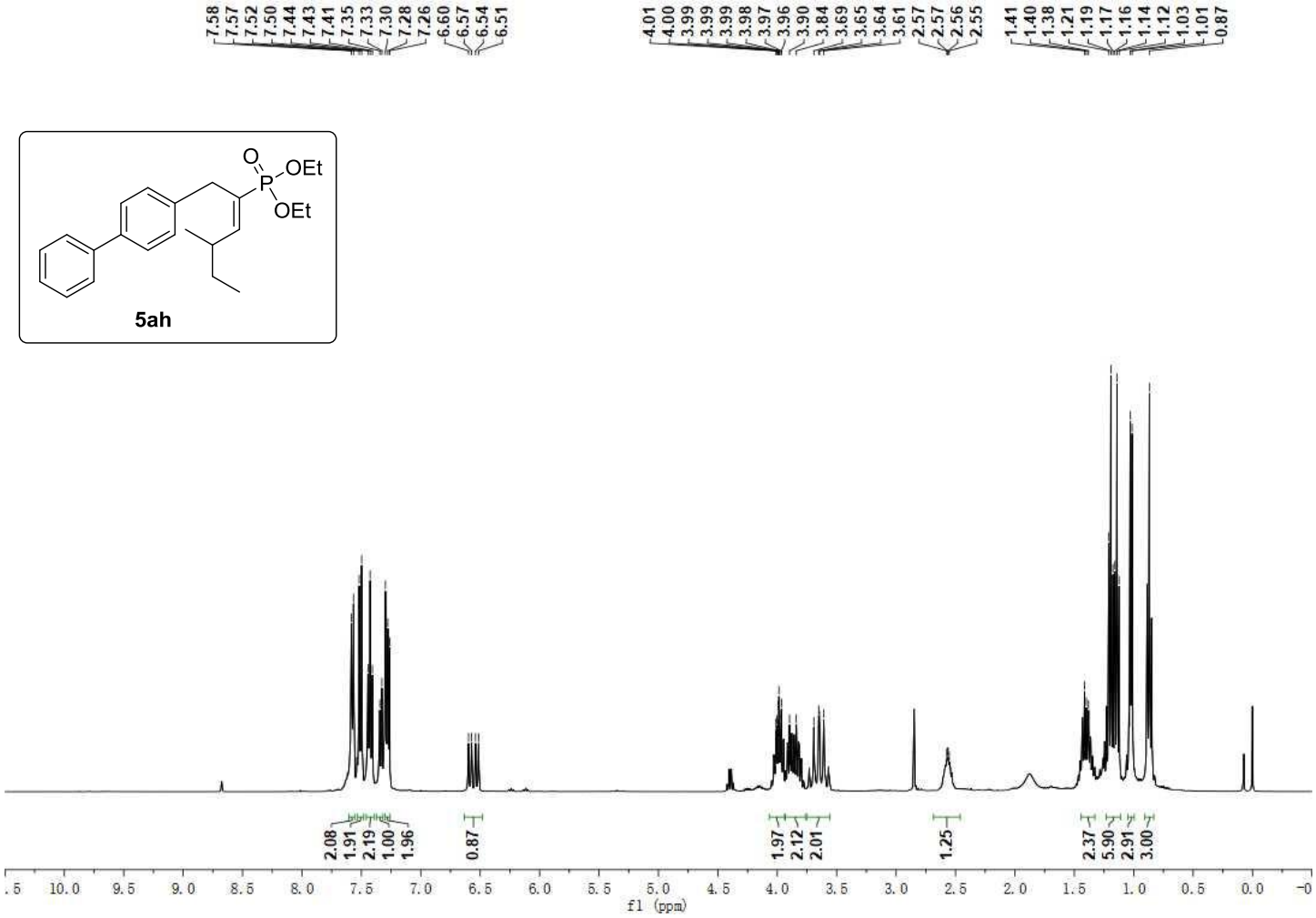
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5ag



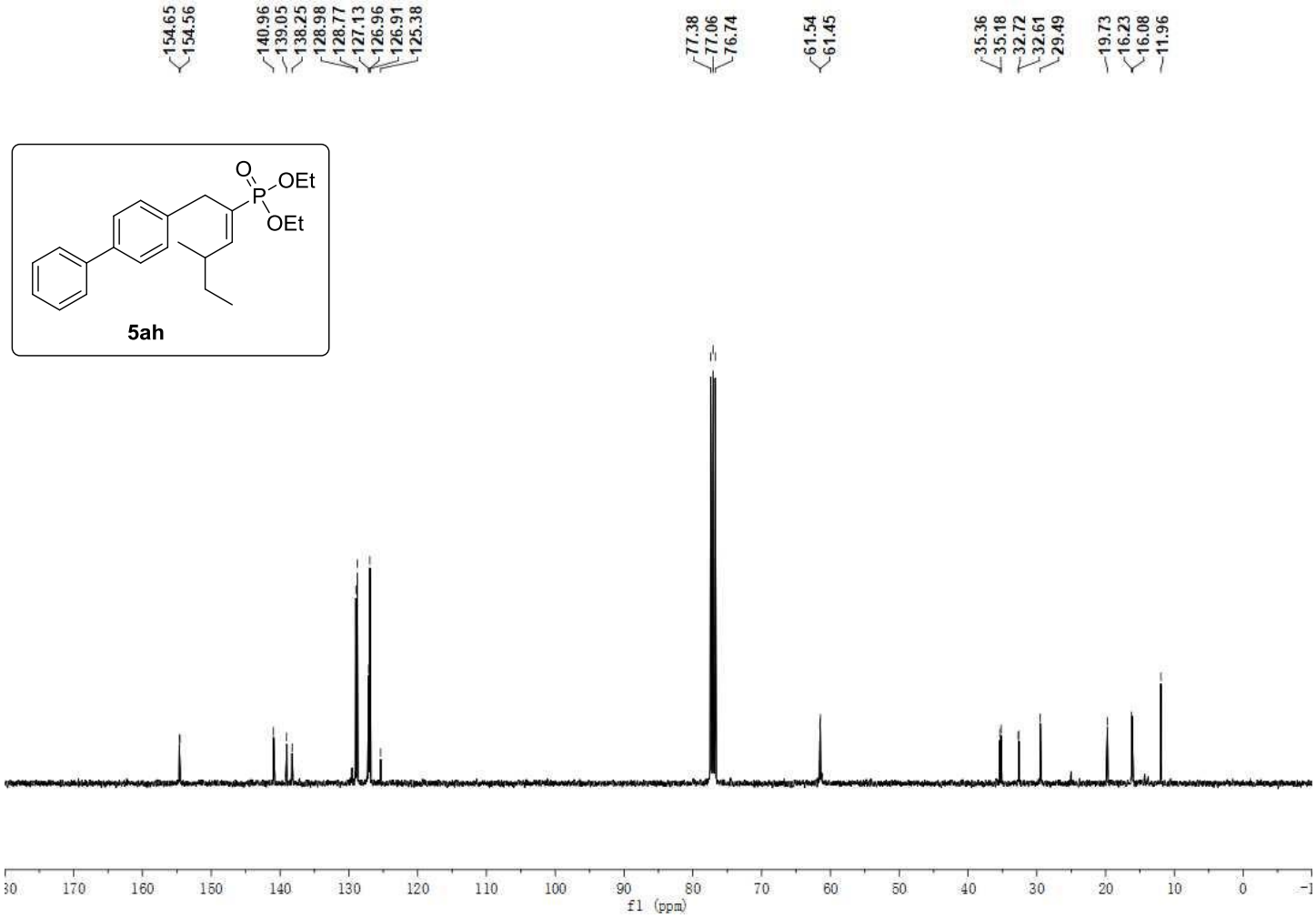
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5ag



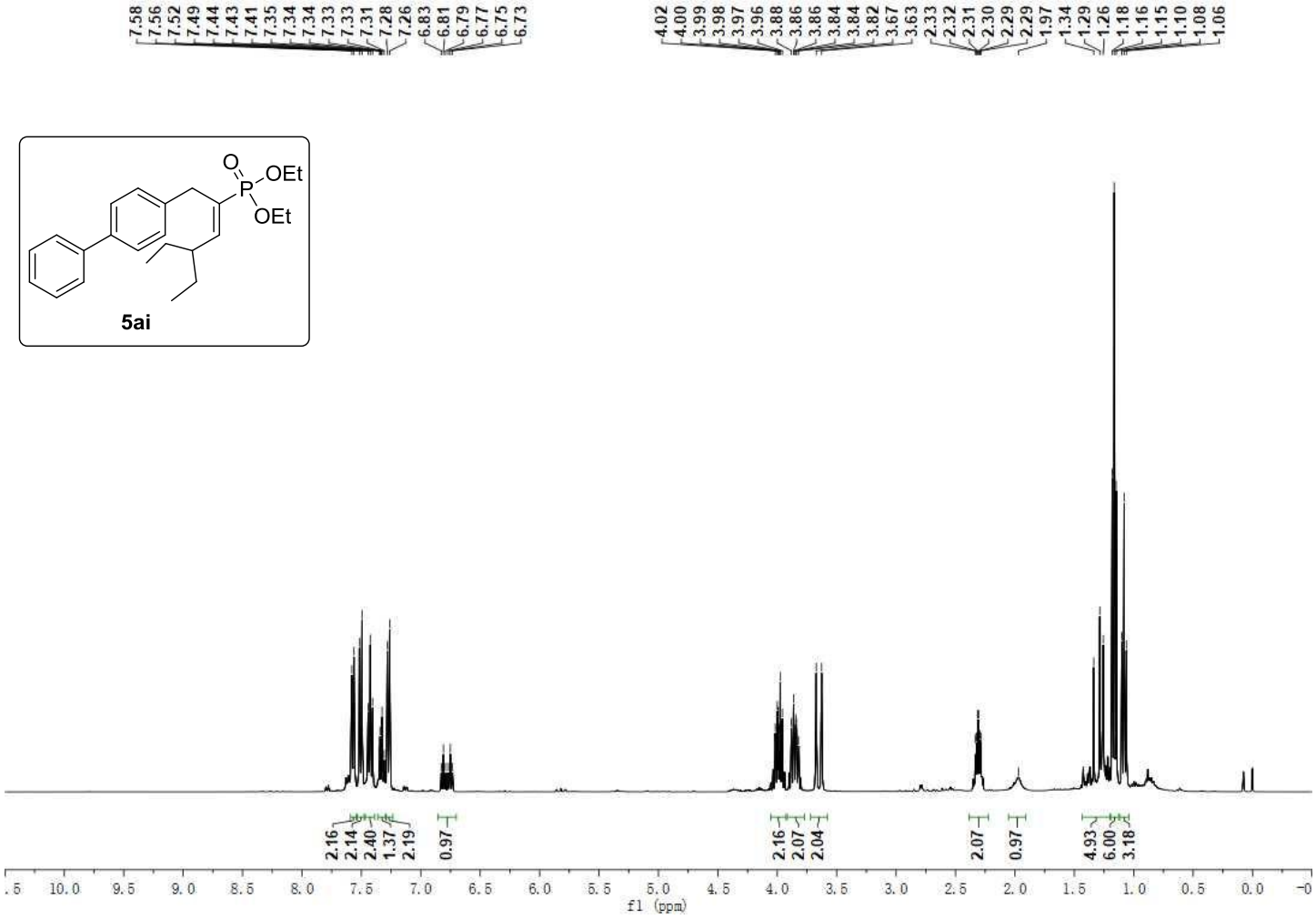
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5ah



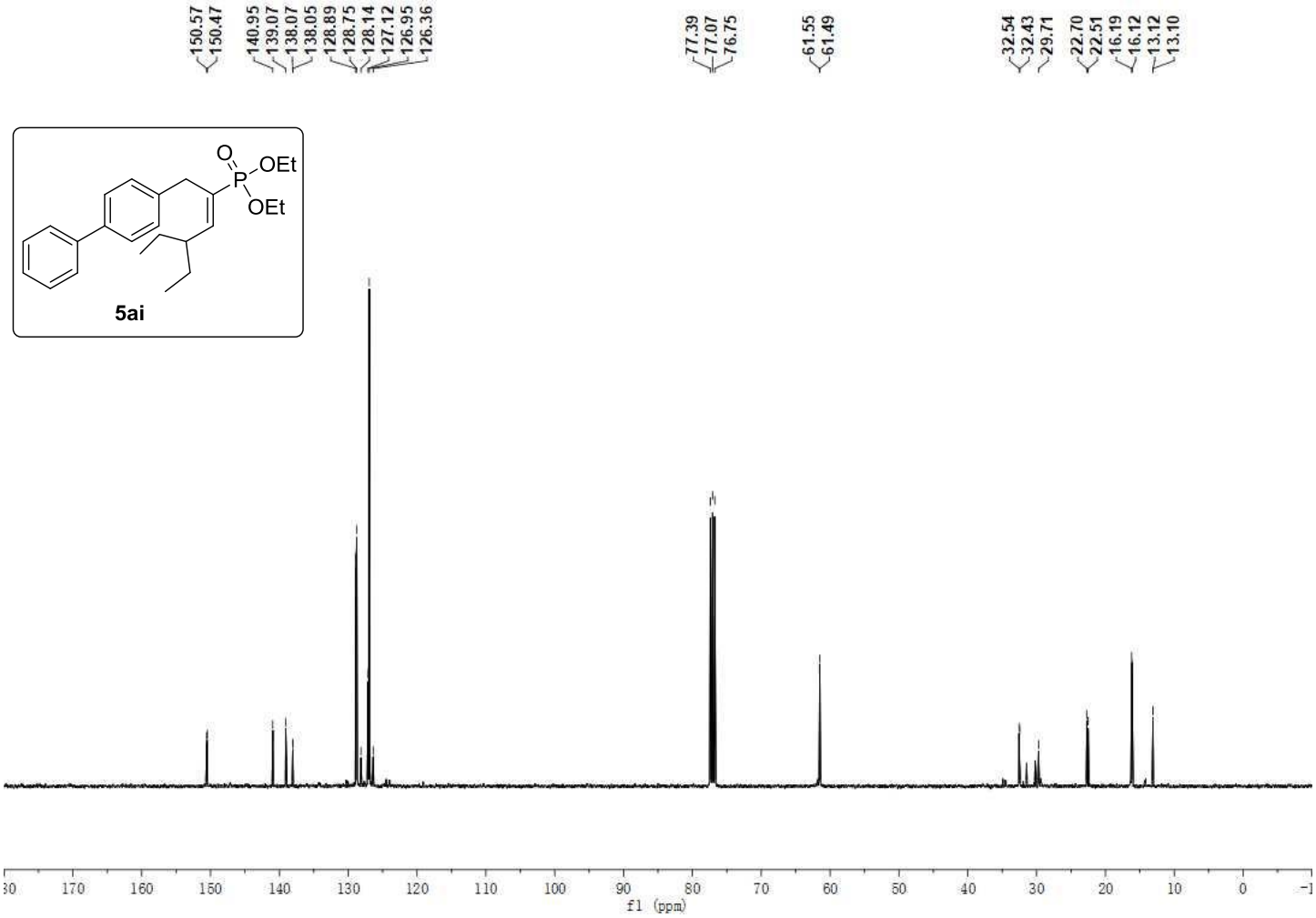
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5ah



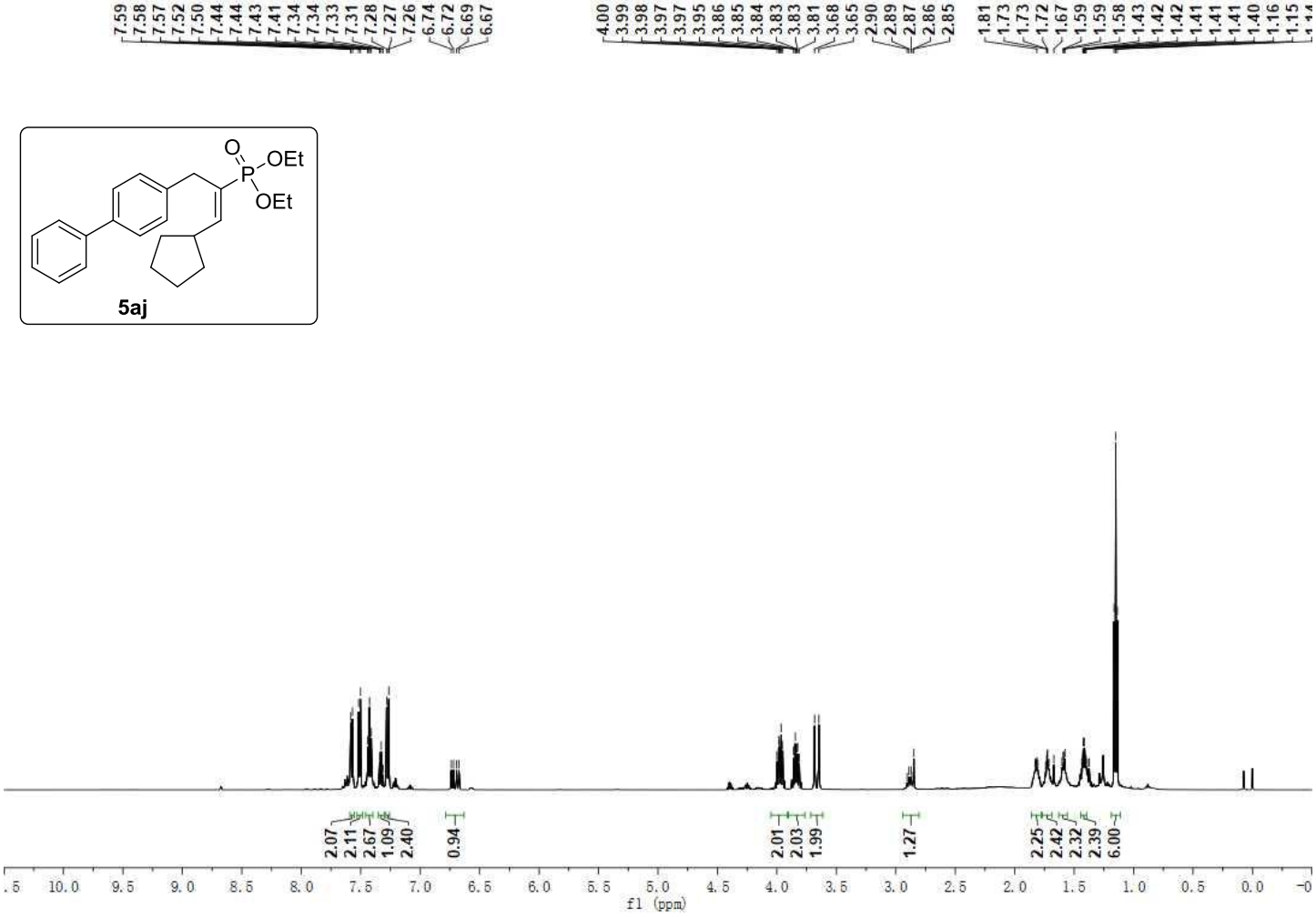
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5ai



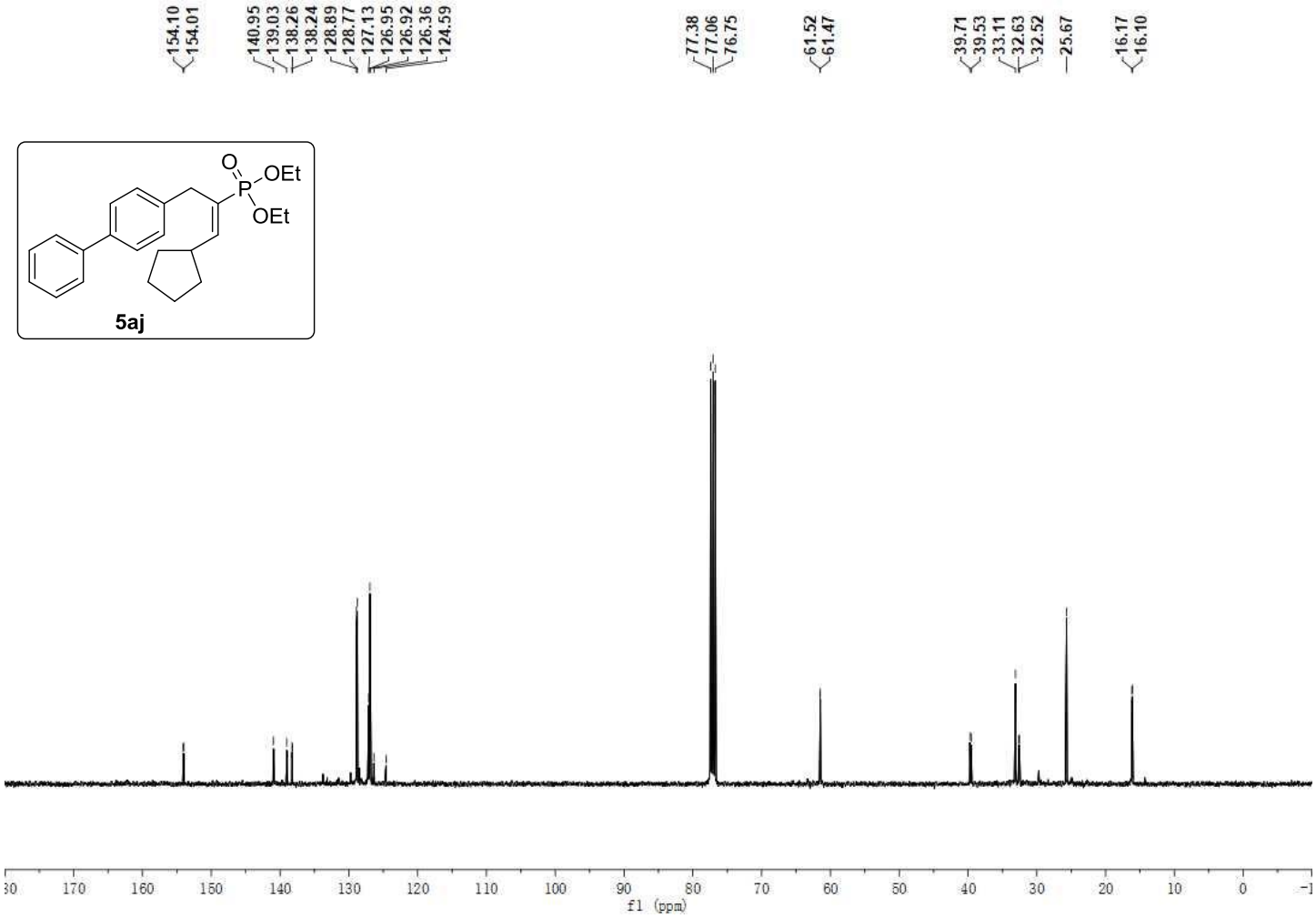
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5ai



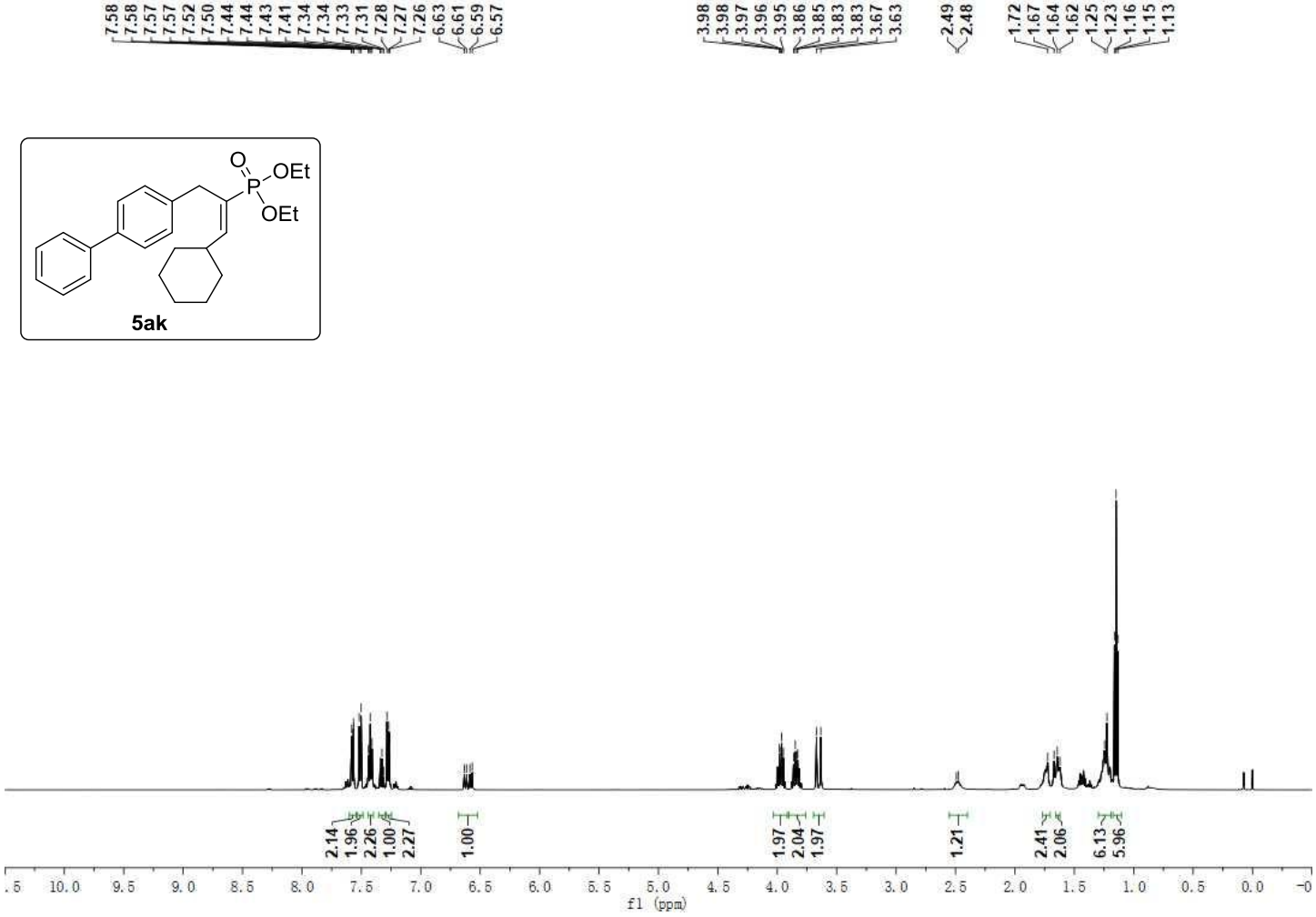
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5aj



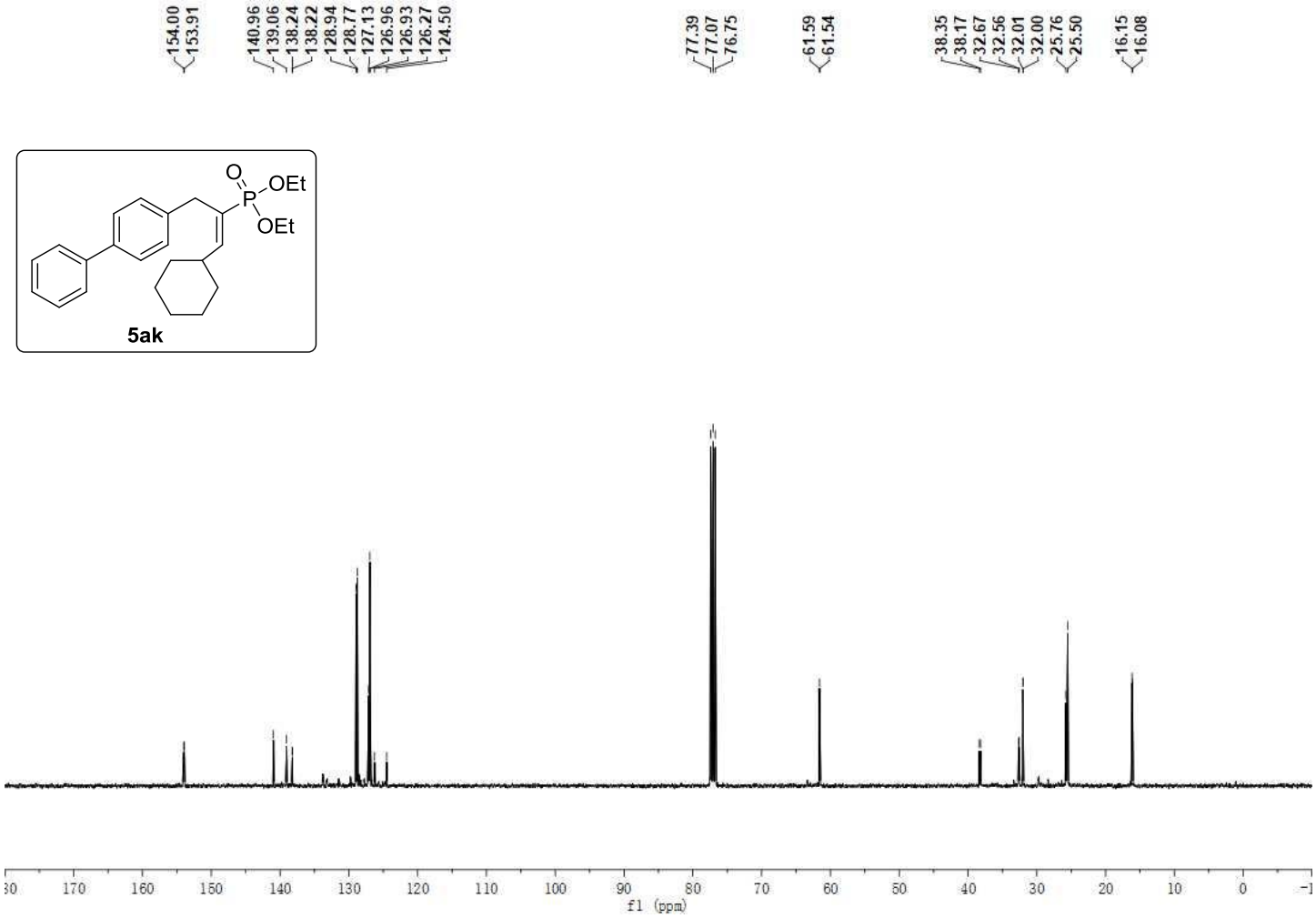
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5aj



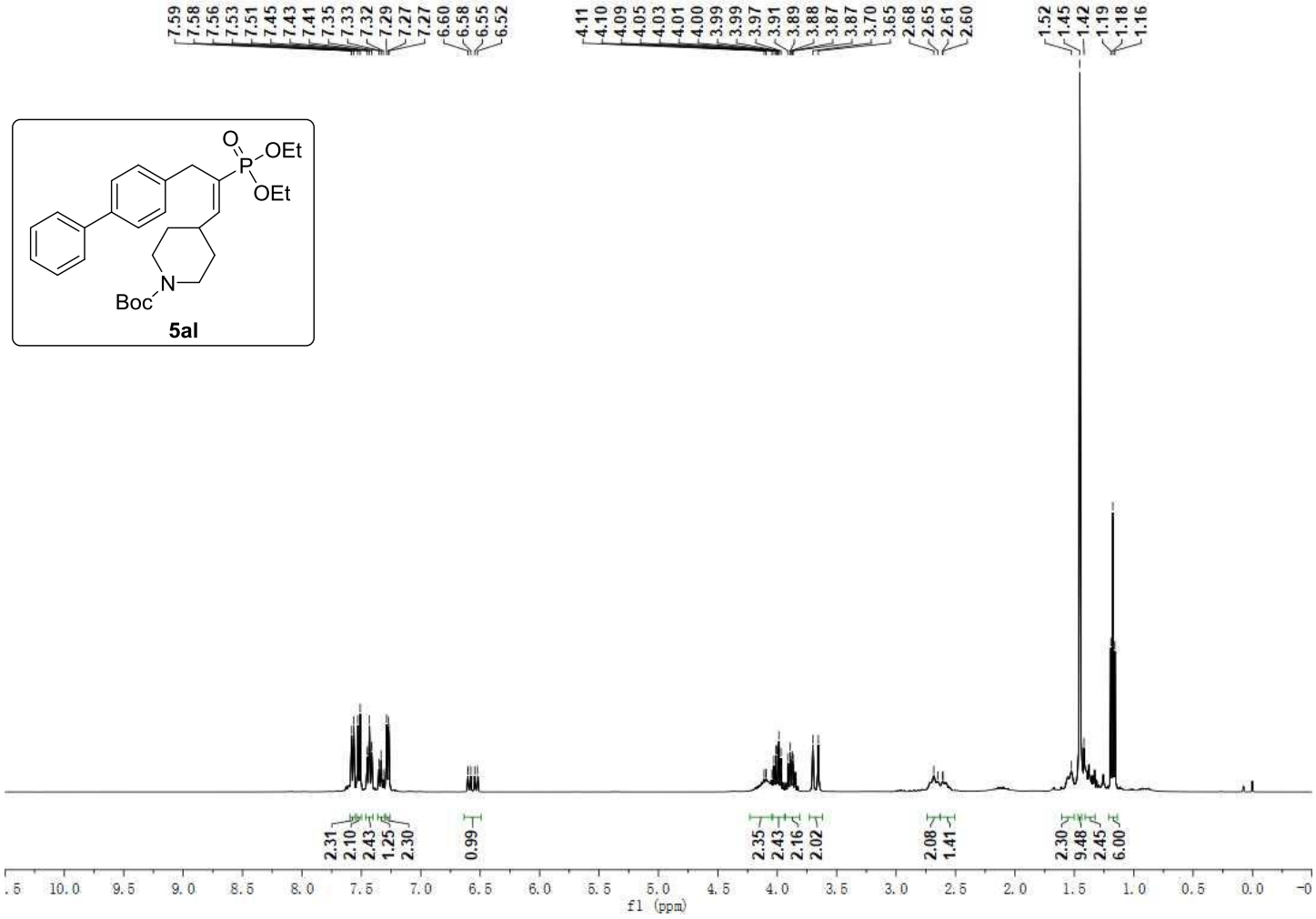
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5ak



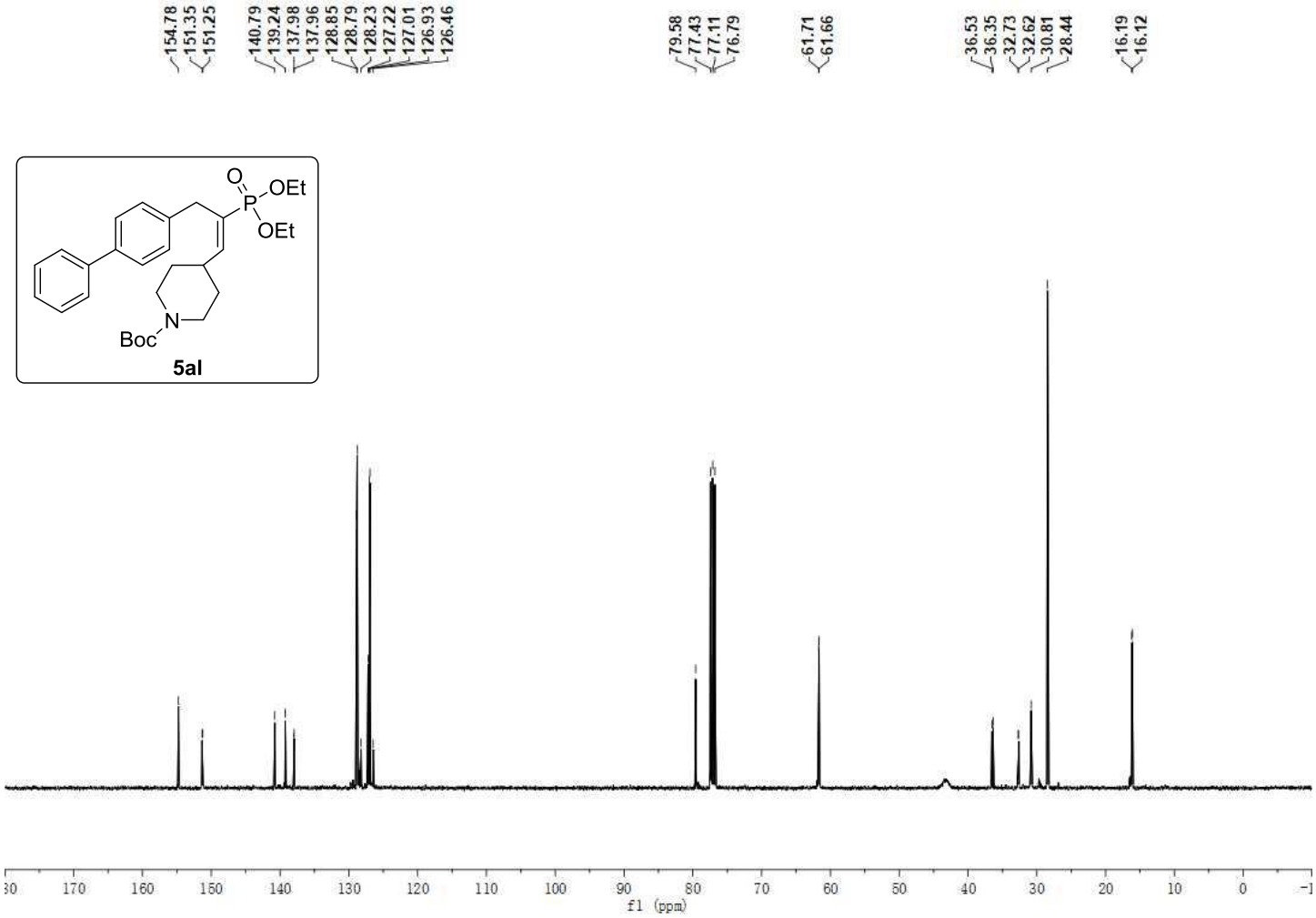
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5ak



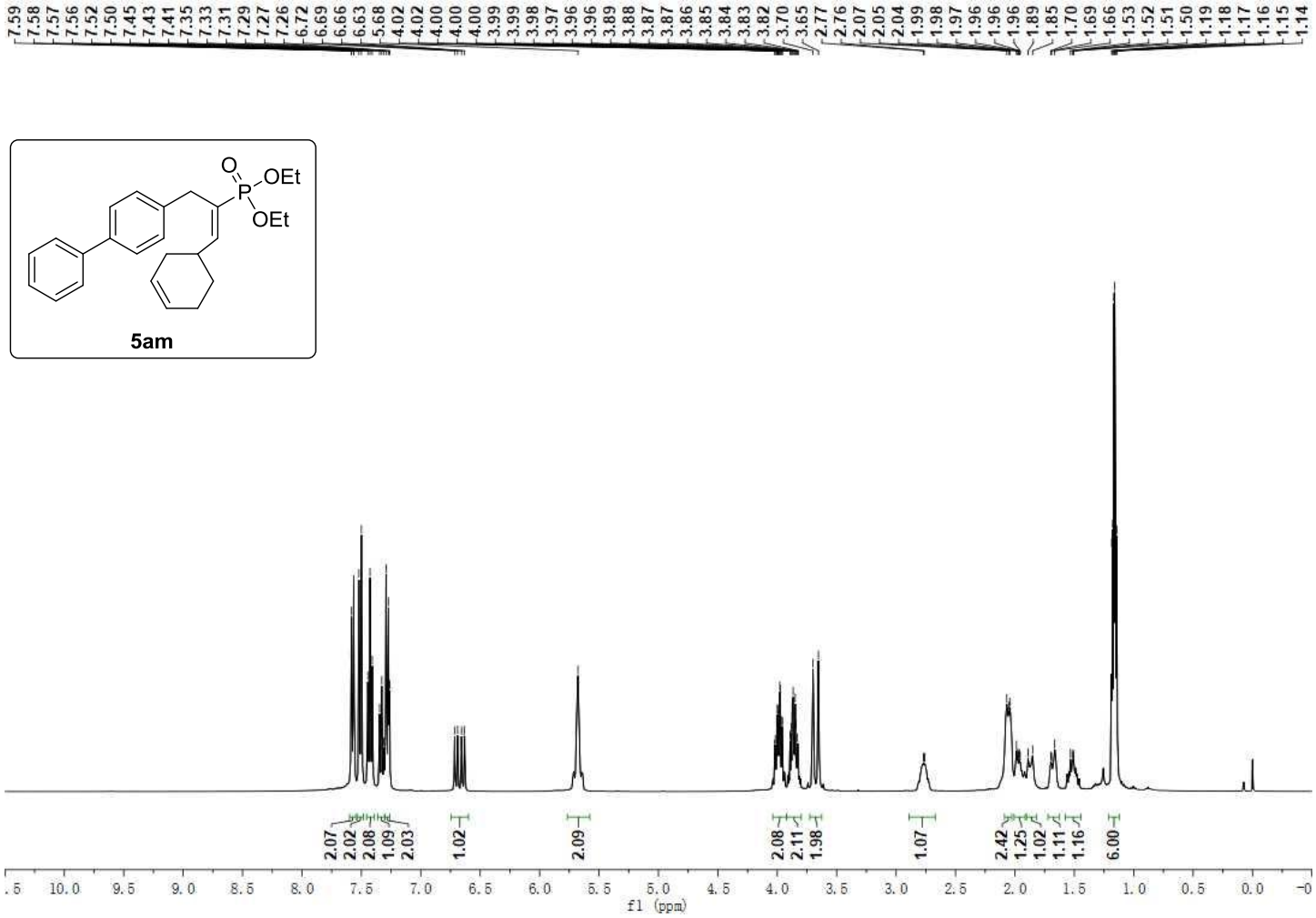
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5al



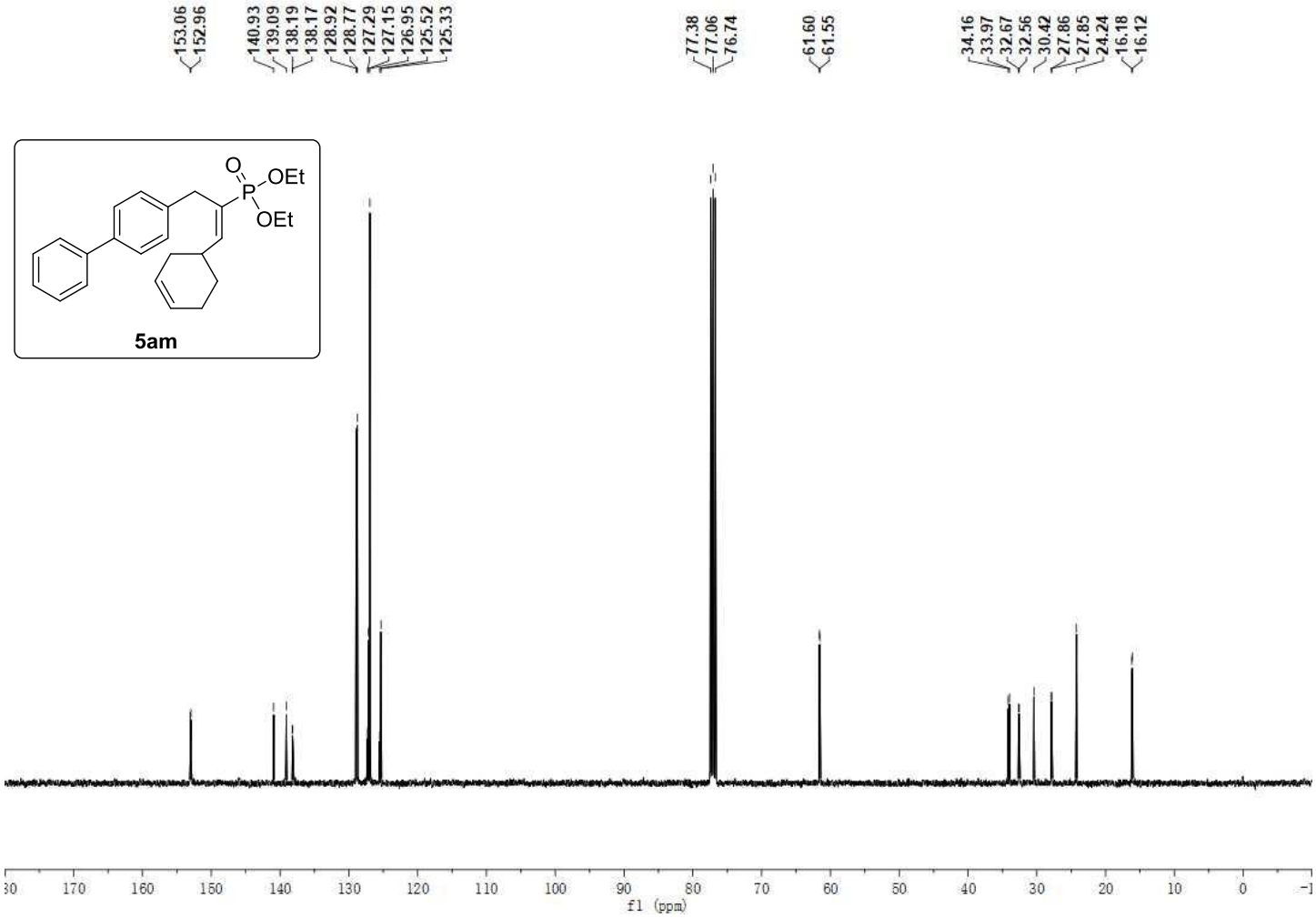
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5al



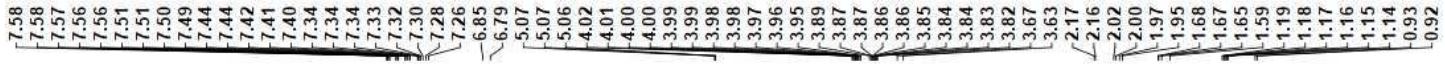
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5am

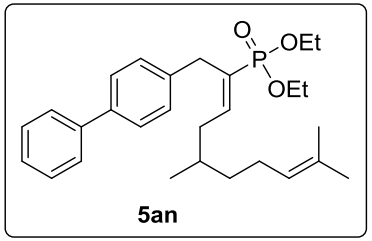


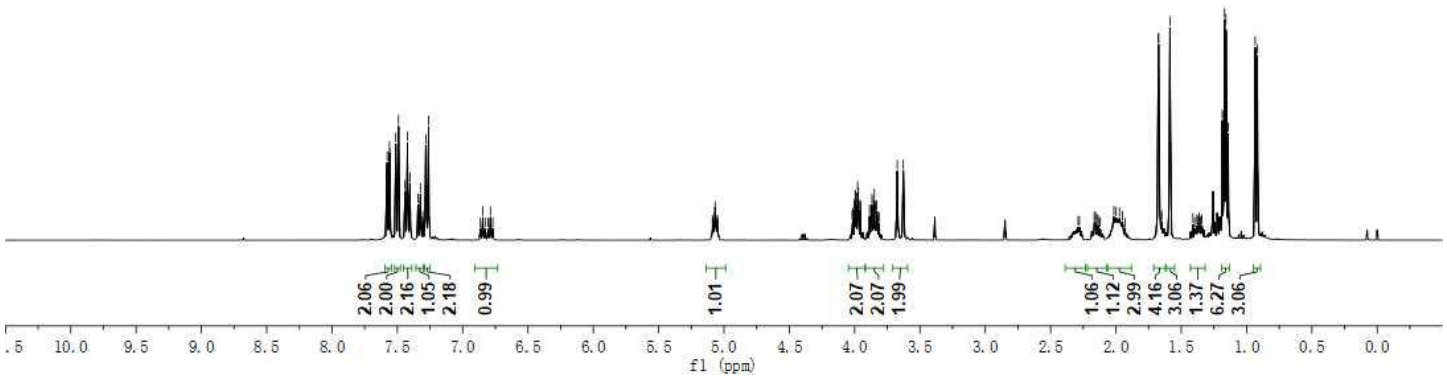
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5am



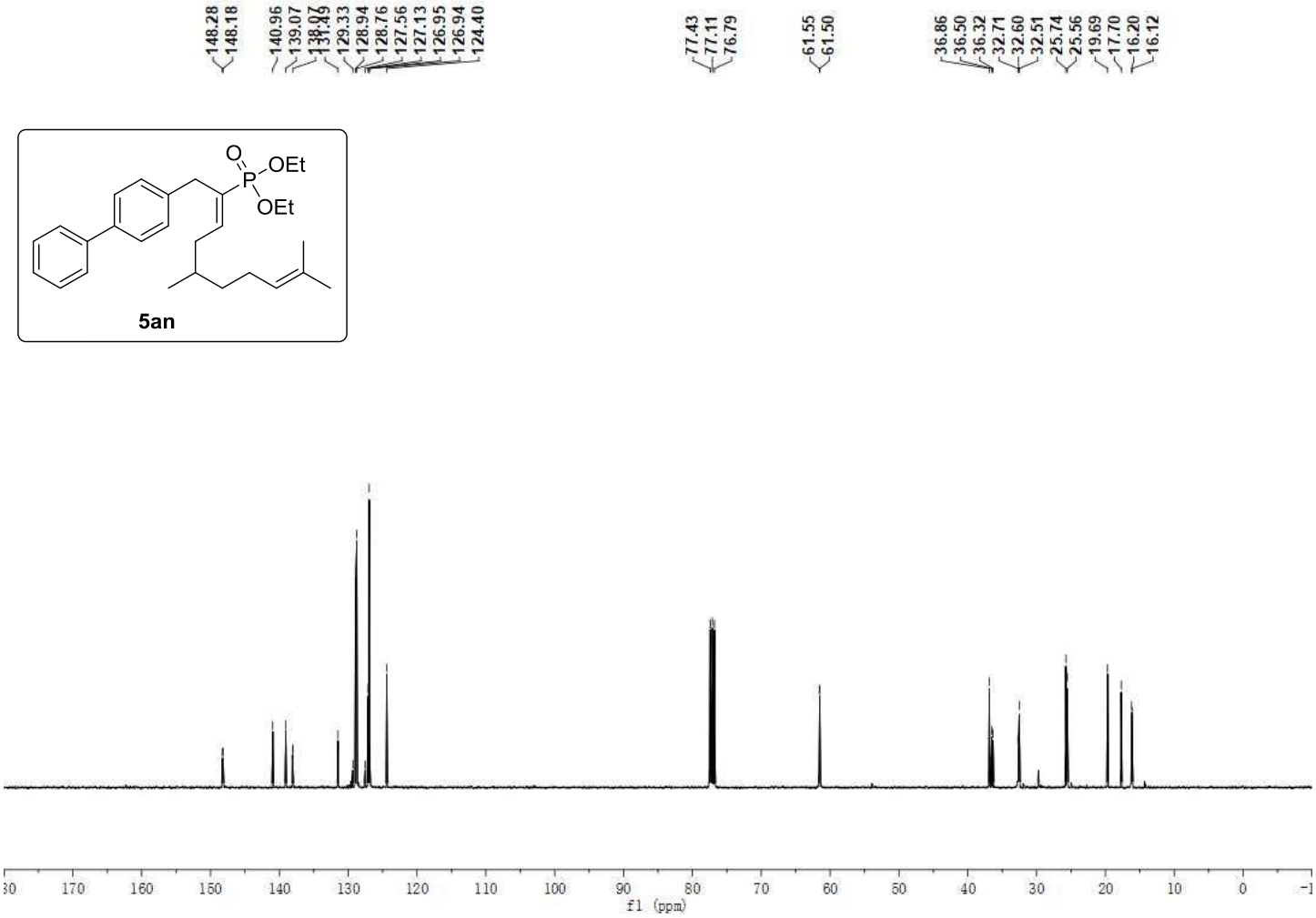
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5an



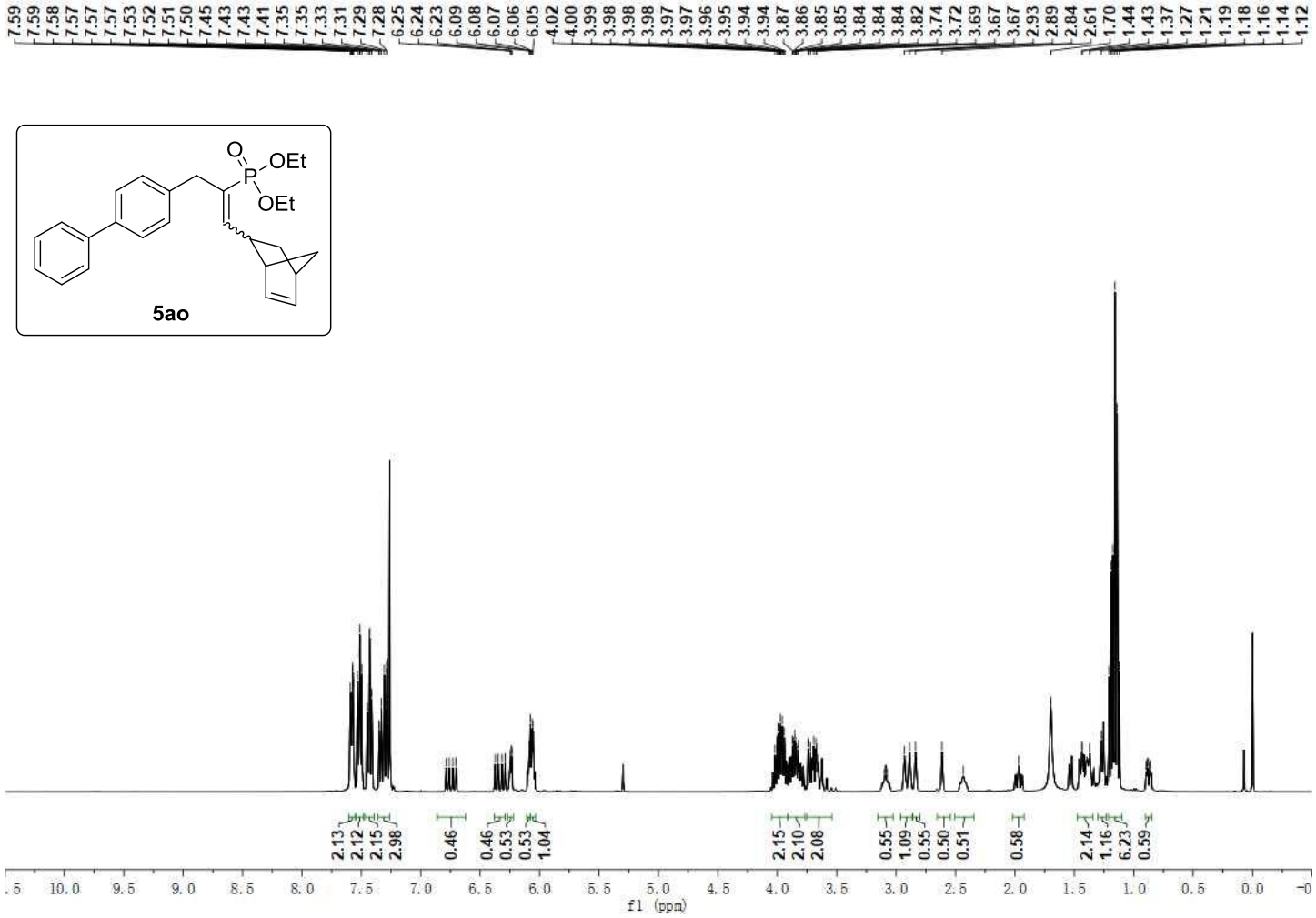




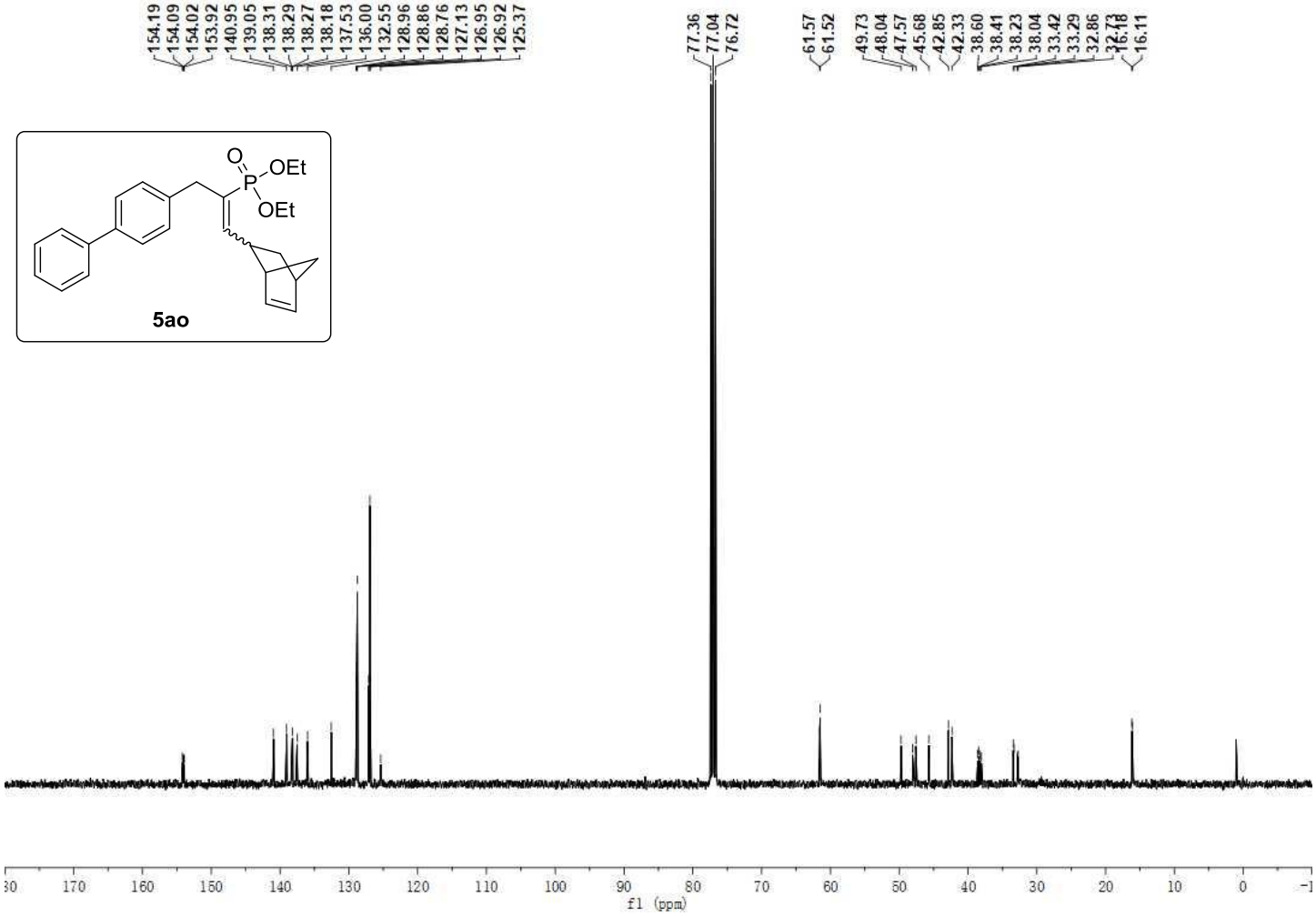
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5an



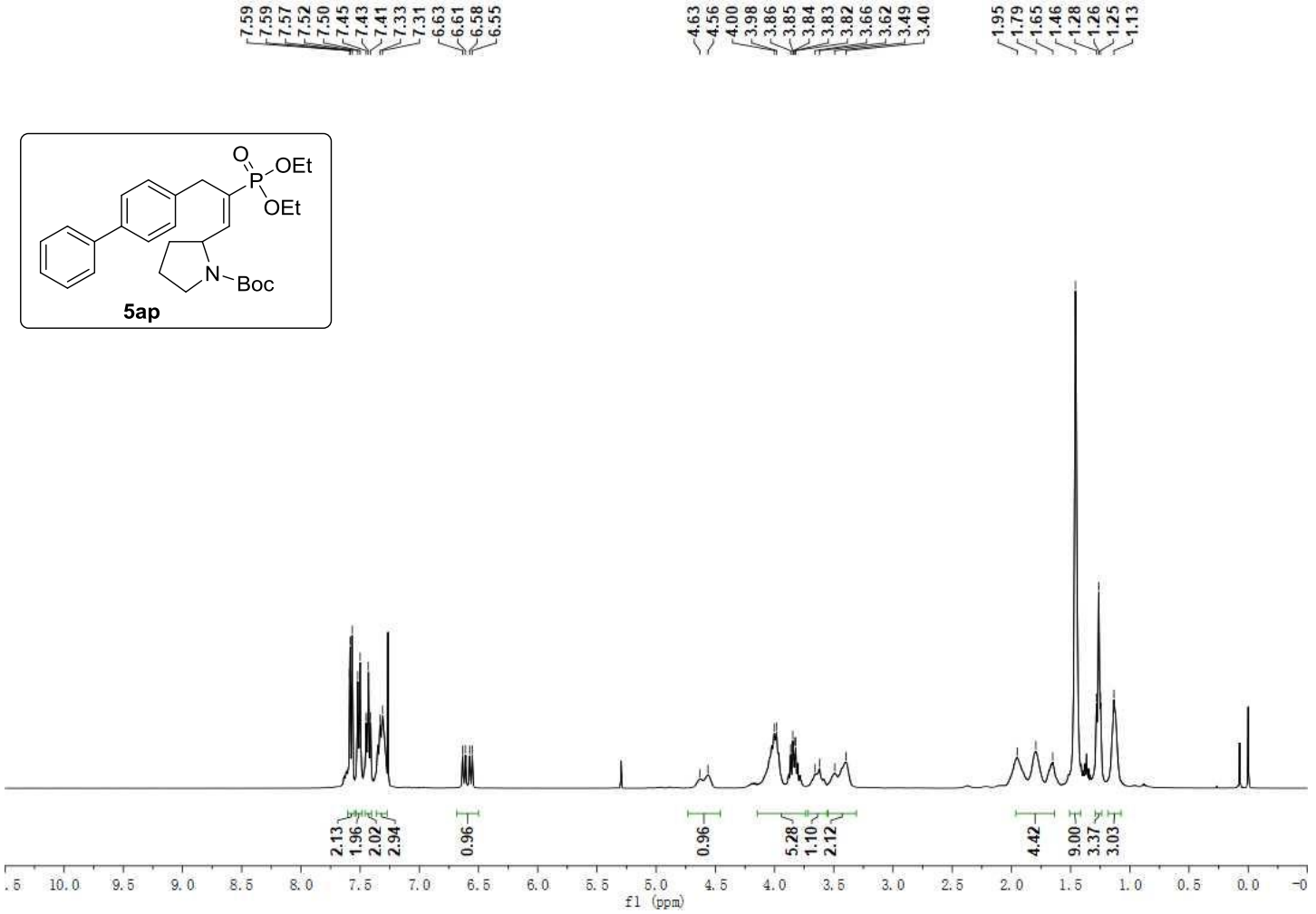
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5ao



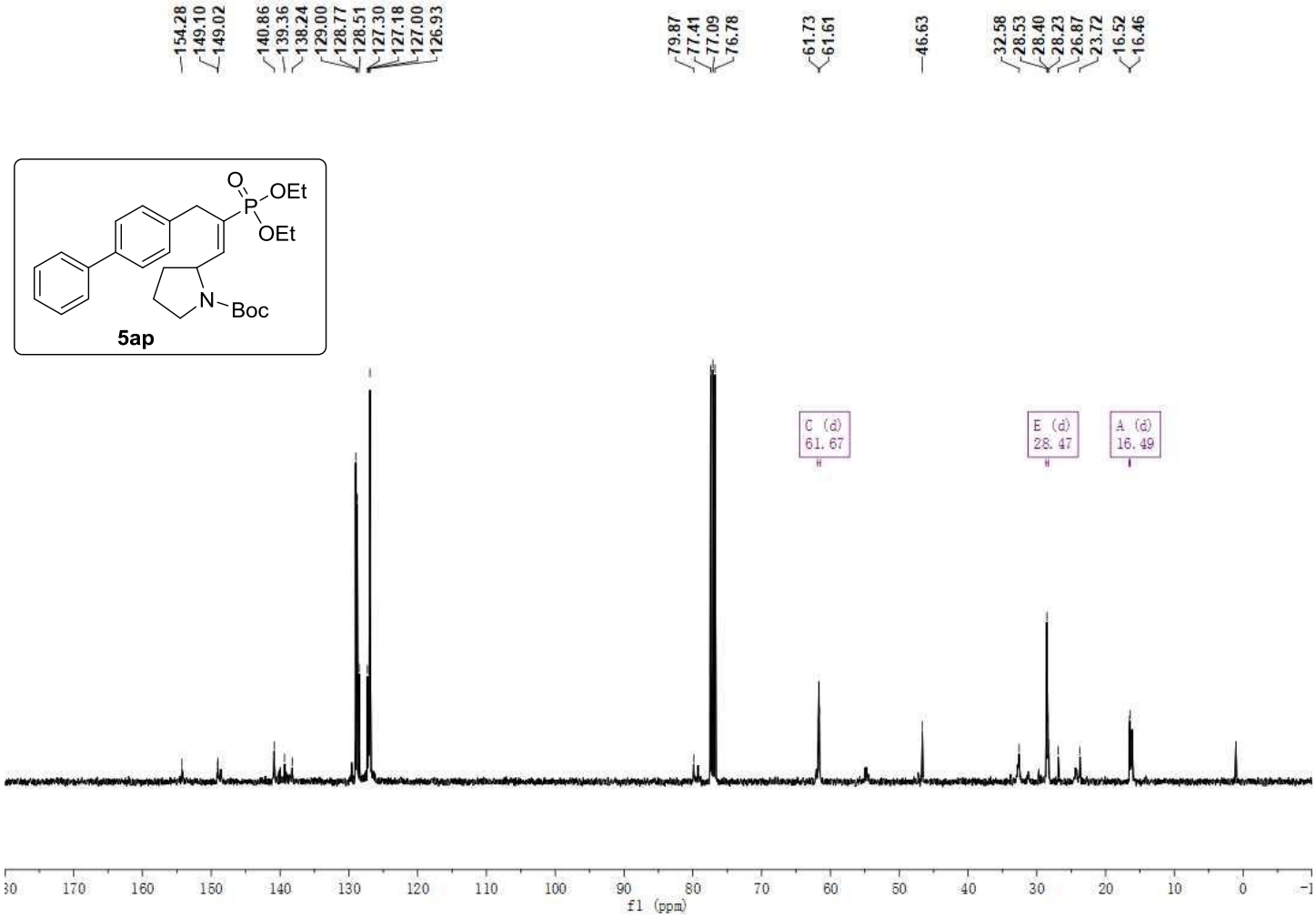
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5ao



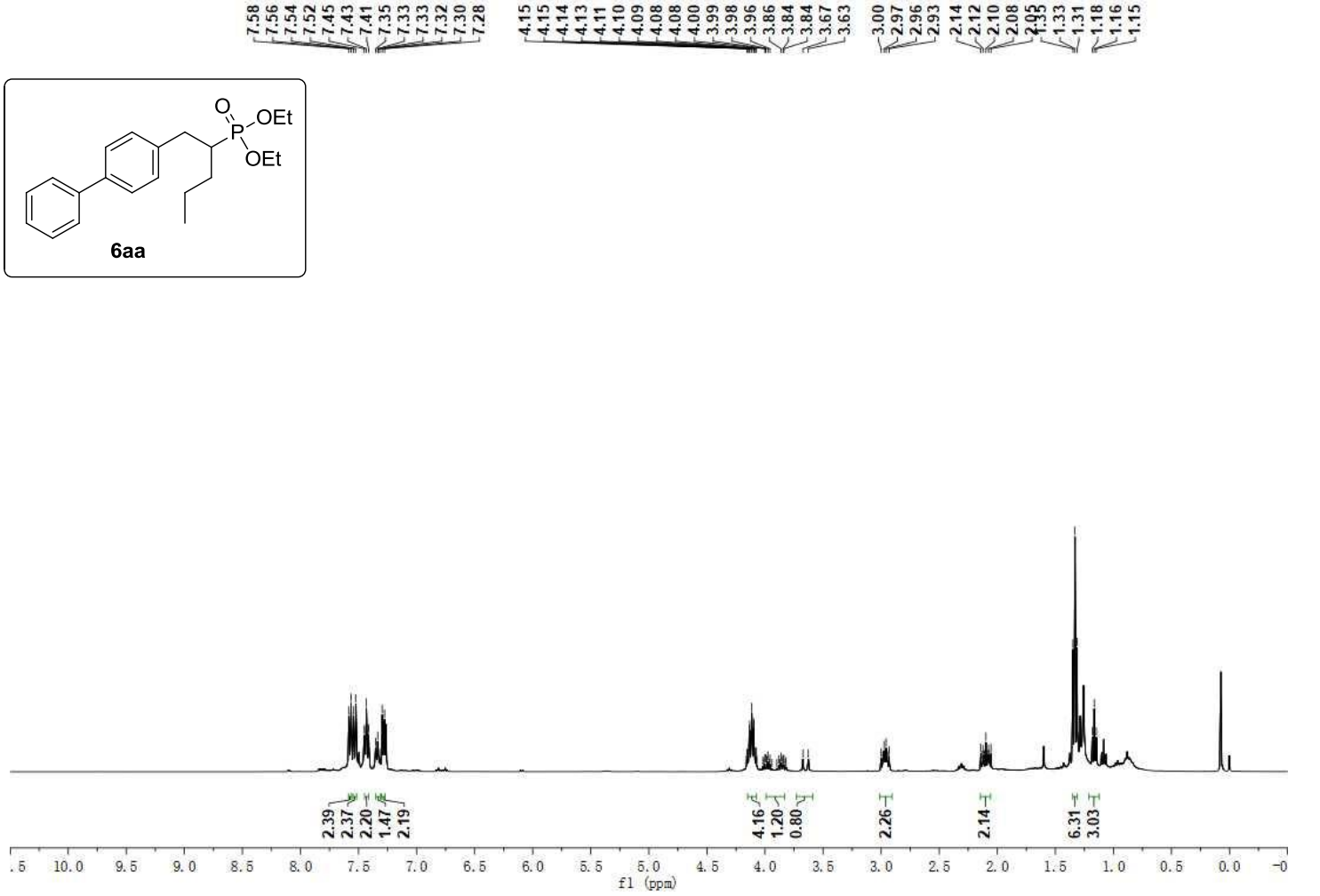
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5ap



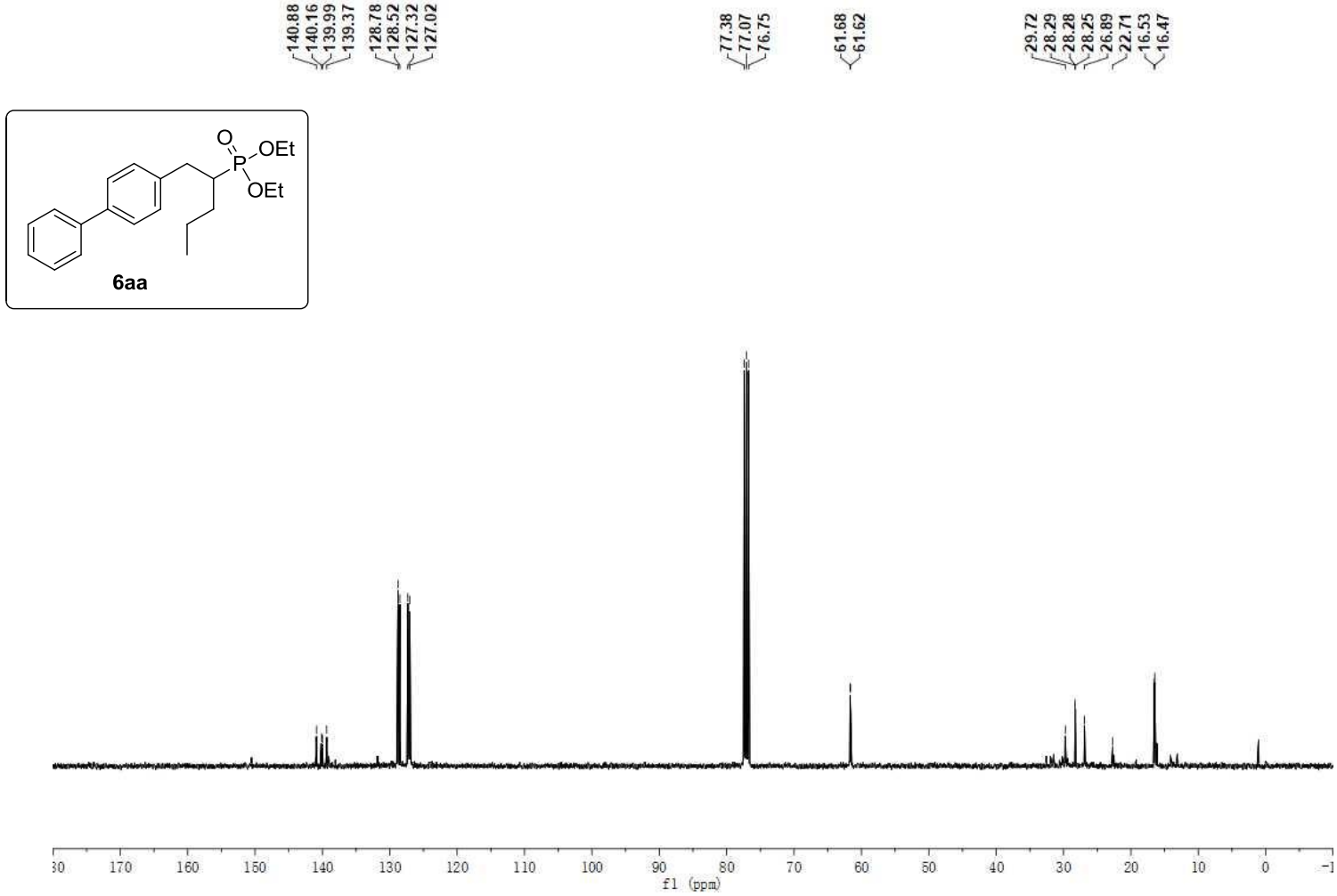
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 5ap



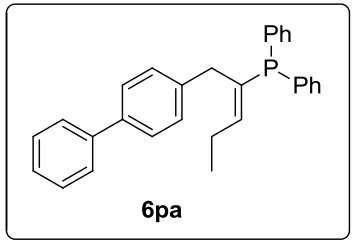
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 6aa

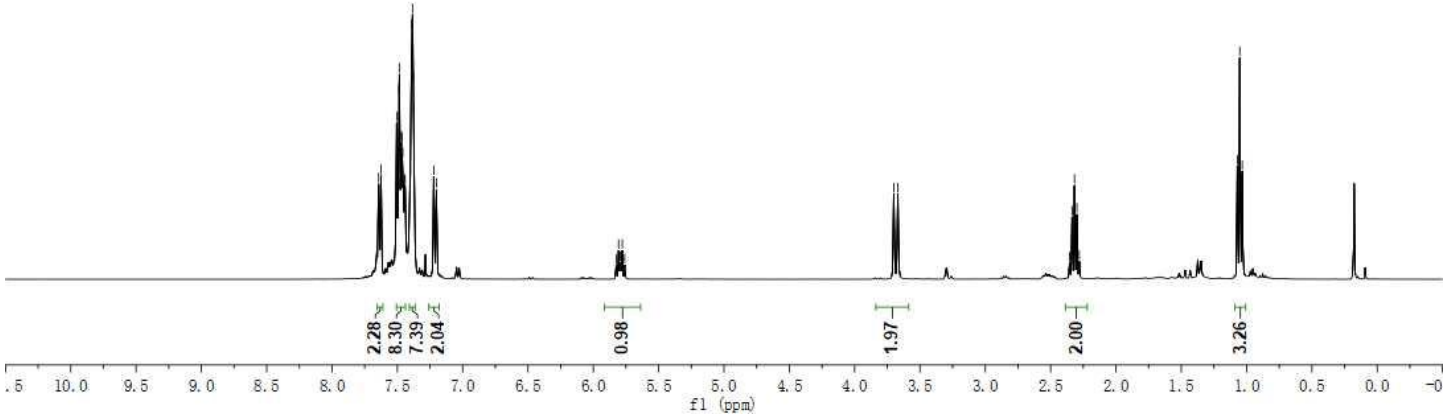


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 6aa

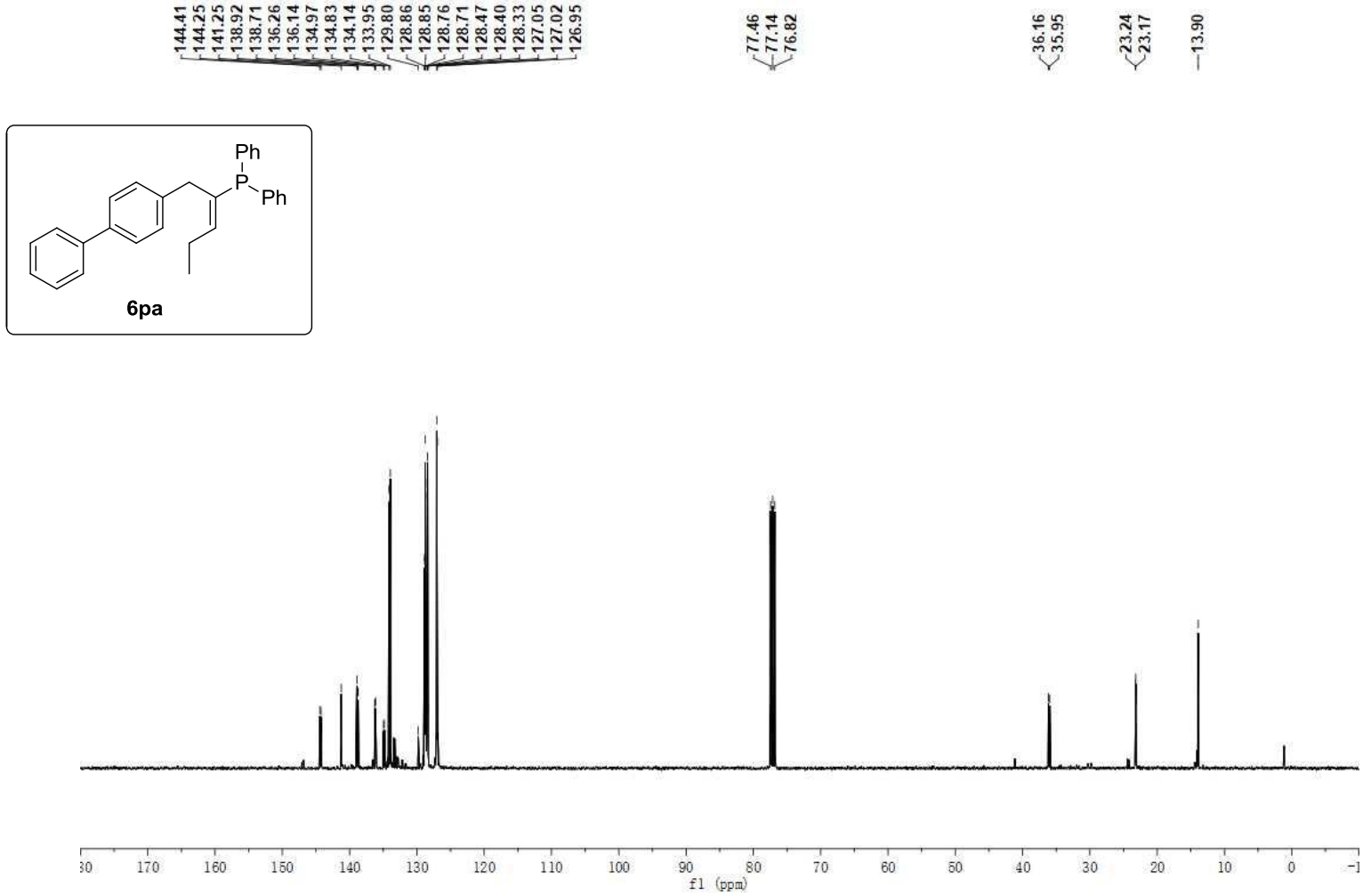


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 6pa

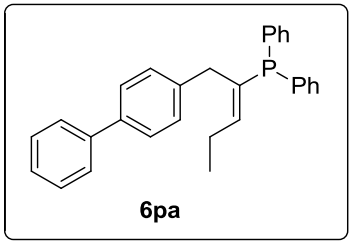




^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 6pa



^{31}P NMR (162 MHz, $CDCl_3$) spectrum of compound 6pa



6pa