

Electronic Supplementary Information

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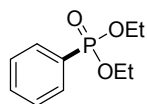
I. General procedures

All reagents and solvents were purchased from commercial sources (Adamas-beta, TCI, Acros, Alfa and Ark) and used without further purification unless otherwise stated. All reactions were monitored by thin-layer chromatography (TLC). All reactions were carried out in argon atmosphere unless otherwise stated. Column chromatography was performed on silica gel (200-300 mesh) and visualized with ultraviolet light. Ethyl acetate and petroleum ether were used as eluents. ^1H , ^{13}C , ^{31}P and ^{19}F spectra were taken on Bruker AV400 and Agilent 600. Chemical shifts of ^1H NMR spectra were reported using the signal of TMS ($\delta = 0.00$ ppm) as internal standard. Chemical shifts of ^{13}C NMR spectra were reported using residual solvent signal of CDCl_3 ($\delta = 77.2$ ppm) as internal standard. Fourier transform infrared spectra (FT-IR) were recorded on Bruker TENSOR 27 instrument. HRMS analyses were made by Lanzhou University by means of ESI. All solvents were purified and dried by standard techniques.

II. General procedures for synthesis of phosphonated products

Aryl triflate **1** (0.2 mmol), K_2CO_3 (0.4 mmol, 55.2 mg) and TBAI (0.1 mmol, 36.9 mg) were added into CH_3CN (1.0 mL) followed by trialkyl phosphite **2** (0.6 mmol) in an airtight quartz tube, which was then evacuated by four freeze-pump-thaw cycles and back-filled with ultra-purified argon prior to use. The reaction mixture was stirred at room temperature (ca 25 °C) while being irradiated by 254 nm light for 24 h and 2 mL H_2O was added into the reaction solution. The resulting mixture was then extracted with 3×10 mL ethyl acetate. The organic layer was washed with saturated NaCl and dried over anhydrous Na_2SO_4 . The resulting solution was concentrated under vacuum, and the residue was purified by preparative TLC on silica gel eluting with petroleum ether/ethyl acetate to provide the desired product **3**.

III. Characterization data of compounds

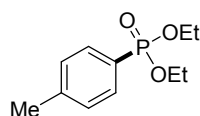


Diethyl phenylphosphonate (3a), colorless oil): 30 mg, 70%.

^1H NMR (400 MHz, CDCl_3) δ 7.86 – 7.79 (m, 2H), 7.59 – 7.54 (m, 1H), 7.51 – 7.44 (m, 2H), 4.20 – 4.03 (m, 4H), 1.33 (t, $J = 7.1$ Hz, 6H);

^{13}C NMR (101 MHz, CDCl_3) δ 132.6 (d, $J = 3.1$ Hz), 131.9 (d, $J = 9.9$ Hz), 128.6 (d, $J = 14.9$ Hz), 128.4 (d, $J = 188.5$ Hz), 62.3 (d, $J = 5.4$ Hz), 16.5 (d, $J = 6.6$ Hz); ^1H and

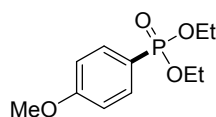
¹³C NMR data agreed with those reported in the literature.^[1]



Diethyl *p*-tolylphosphonate (3b), colorless oil): 31 mg, 68%.

¹H NMR (400 MHz, CDCl₃) δ 7.70 (dd, *J* = 13.1, 8.1 Hz, 2H), 7.28 (dd, *J* = 7.7, 4.0 Hz, 2H), 4.16 – 4.03 (m, 4H), 2.40 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 6H).

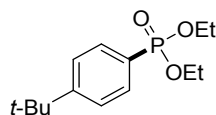
¹³C NMR (101 MHz, CDCl₃) δ 143.1 (d, *J* = 3.1 Hz), 132.0 (d, *J* = 10.3 Hz), 129.4 (d, *J* = 15.4 Hz), 125.1 (d, *J* = 189.9 Hz), 62.1 (d, *J* = 5.3 Hz), 21.8 (d, *J* = 1.2 Hz), 16.5 (d, *J* = 6.6 Hz); ¹H and ¹³C NMR data agreed with those reported in the literature.^[2]



Diethyl (4-methoxyphenyl)phosphonate (3c), colorless oil): 19 mg, 37%.

¹H NMR (400 MHz, CDCl₃) δ 7.75 (dd, *J* = 12.7, 8.8 Hz, 2H), 6.97 (dd, *J* = 8.8, 3.4 Hz, 2H), 4.17 – 4.00 (m, 4H), 3.85 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 6H).

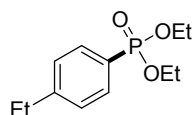
¹³C NMR (101 MHz, CDCl₃) δ 163.0 (d, *J* = 3.4 Hz), 133.9 (d, *J* = 11.4 Hz), 119.6 (d, *J* = 194.7 Hz), 114.1 (d, *J* = 16.0 Hz), 62.1 (d, *J* = 5.2 Hz), 55.5, 16.5 (d, *J* = 6.6 Hz); ¹H and ¹³C NMR data agreed with those reported in the literature.^[1]



Diethyl (4-(*tert*-butyl)phenyl)phosphonate (3d), colorless oil): 37 mg, 68%.

¹H NMR (400 MHz, CDCl₃) δ 7.74 (dd, *J* = 13.0, 8.4 Hz, 2H), 7.48 (dd, *J* = 8.4, 3.9 Hz, 2H), 4.17 – 4.06 (m, 4H), 1.33 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 156.1 (d, *J* = 3.2 Hz), 131.8 (d, *J* = 10.3 Hz), 125.6 (d, *J* = 15.2 Hz), 125.2 (d, *J* = 190.2 Hz), 62.1 (d, *J* = 5.4 Hz), 35.2, 31.2, 16.5 (d, *J* = 6.6 Hz); ¹H and ¹³C NMR data agreed with those reported in the literature.^[3]

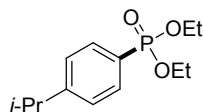


Diethyl (4-ethylphenyl)phosphonate (3e), colorless oil): 32 mg, 67%.

¹H NMR (400 MHz, CDCl₃) δ 7.73 (dd, *J* = 13.1, 8.2 Hz, 2H), 7.30 (dd, *J* = 8.3, 4.0 Hz, 2H), 4.19 – 4.01 (m, 4H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 6H), 1.25 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 149.2 (d, *J* = 3.1 Hz), 132.1 (d, *J* = 10.3 Hz), 128.2 (d,

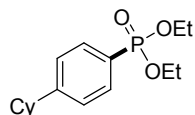
$J = 15.4$ Hz), 125.3 (d, $J = 189.9$ Hz), 62.1 (d, $J = 5.4$ Hz), 29.1, 16.5 (d, $J = 6.6$ Hz), 15.3; ^1H and ^{13}C NMR data agreed with those reported in the literature.^[1]



Diethyl (4-isopropylphenyl)phosphonate (3f), colorless oil): 37 mg, 72%.

^1H NMR (400 MHz, CDCl_3) δ 7.73 (dd, $J = 13.1, 8.2$ Hz, 2H), 7.32 (dd, $J = 8.0, 4.0$ Hz, 2H), 4.15 – 4.05 (m, 4H), 2.98 – 2.90 (m, 1H), 1.32 (t, $J = 7.1$ Hz, 6H), 1.26 (d, $J = 6.9$ Hz, 6H).

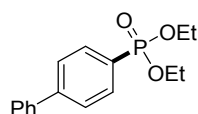
^{13}C NMR (101 MHz, CDCl_3) δ 153.8 (d, $J = 3.1$ Hz), 132.1 (d, $J = 10.3$ Hz), 126.8 (d, $J = 15.3$ Hz), 125.5 (d, $J = 190.0$ Hz), 62.1 (d, $J = 5.3$ Hz), 34.4, 23.8, 16.5 (d, $J = 6.6$ Hz); ^1H and ^{13}C NMR data agreed with those reported in the literature.^[3]



Diethyl (4-cyclohexylphenyl)phosphonate (3g), colorless oil): 39 mg, 66%.

^1H NMR (400 MHz, CDCl_3) δ 7.72 (dd, $J = 13.1, 8.2$ Hz, 2H), 7.30 (dd, $J = 8.2, 4.2$ Hz, 2H), 4.19 – 4.01 (m, 4H), 2.54 (dd, $J = 11.3, 8.5$ Hz, 1H), 1.85 (t, $J = 6.3$ Hz, 4H), 1.76 (d, $J = 12.4$ Hz, 1H), 1.44 – 1.37 (m, 4H), 1.32 (t, $J = 7.1$ Hz, 6H), 1.28 – 1.23 (m, 1H).

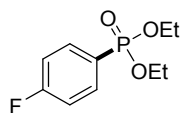
^{13}C NMR (101 MHz, CDCl_3) δ 152.80 (d, $J = 3.1$ Hz), 131.88 (d, $J = 10.3$ Hz), 127.05 (d, $J = 15.3$ Hz), 125.27 (d, $J = 189.9$ Hz), 61.96 (d, $J = 5.3$ Hz), 44.68 (s), 34.10 (s), 26.72 (s), 26.02 (s), 16.34 (d, $J = 6.6$ Hz); ^1H and ^{13}C NMR data agreed with those reported in the literature.^[4]



Diethyl [1,1'-biphenyl]-4-ylphosphonate (3h), colorless oil): 17 mg, 30%.

^1H NMR (400 MHz, CDCl_3) δ 7.88 (dd, $J = 13.0, 8.3$ Hz, 2H), 7.71 – 7.66 (m, 2H), 7.63 – 7.58 (m, 2H), 7.46 (t, $J = 7.5$ Hz, 2H), 7.39 (t, $J = 7.3$ Hz, 1H), 4.23 – 4.06 (m, 4H), 1.35 (t, $J = 7.1$ Hz, 6H);

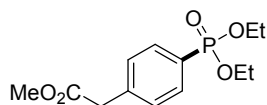
^{13}C NMR (101 MHz, CDCl_3) δ 145.3 (d, $J = 3.2$ Hz), 140.1, 132.4 (d, $J = 10.2$ Hz), 129.1, 128.3, 127.5, 127.4, 127.3, 127.2 (d, $J = 190.5$ Hz), 62.3 (d, $J = 5.4$ Hz), 16.5 (d, $J = 6.5$ Hz); ^1H and ^{13}C NMR data agreed with those reported in the literature.^[5]



Diethyl (4-fluorophenyl)phosphonate (3i), colorless oil): 17 mg, 36%.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.86 – 7.79 (m, 2H), 7.16 (td, $J = 8.8, 3.2$ Hz, 2H), 4.20 – 4.03 (m, 4H), 1.33 (t, $J = 7.1$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 165.5 (dd, $J = 253.5, 4.0$ Hz), 134.5 (dd, $J = 11.3, 8.9$ Hz), 124.6 (dd, $J = 192.7, 3.4$ Hz), 116.0 (dd, $J = 21.4, 16.3$ Hz), 62.3 (d, $J = 5.4$ Hz), 16.4 (d, $J = 6.5$ Hz); ^1H and ^{13}C NMR data agreed with those reported in the literature.^[6]



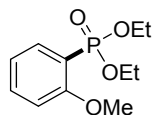
Methyl 2-(4-(diethoxyphosphoryl)phenyl)acetate (3j), colorless oil): 42 mg, 74%.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 (dd, $J = 13.1, 8.0$ Hz, 2H), 7.39 (dd, $J = 8.0, 3.8$ Hz, 2H), 4.19 – 4.02 (m, 4H), 3.71 (s, 3H), 3.68 (s, 2H), 1.32 (t, $J = 7.1$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 171.4, 138.7 (d, $J = 3.3$ Hz), 132.3 (d, $J = 10.3$ Hz), 129.6 (d, $J = 15.3$ Hz), 127.3 (d, $J = 189.4$ Hz), 62.3 (d, $J = 5.4$ Hz), 52.4, 41.3, 16.5 (d, $J = 6.6$ Hz).

$^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 18.7.

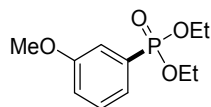
HRMS (ESI): calcd. for $\text{C}_{13}\text{H}_{20}\text{O}_5\text{P}$ ($[\text{M}+\text{H}]^+$): 286.1043, found: 286.1040.



Diethyl (2-methoxyphenyl)phosphonate (3k), colorless oil): 27 mg, 55%.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.82 (dd, $J = 14.8, 7.5$ Hz, 1H), 7.51 (t, $J = 7.8$ Hz, 1H), 7.01 (t, $J = 7.4$ Hz, 1H), 6.95 (t, $J = 7.5$ Hz, 1H), 4.23 – 4.08 (m, 4H), 3.90 (s, 3H), 1.34 (t, $J = 7.0$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 161.4 (d, $J = 2.7$ Hz), 135.2 (d, $J = 7.0$ Hz), 134.4 (d, $J = 2.1$ Hz), 120.5 (d, $J = 14.5$ Hz), 116.7 (d, $J = 187.4$ Hz), 111.3 (d, $J = 9.4$ Hz), 62.2 (d, $J = 5.5$ Hz), 55.9, 16.5 (d, $J = 6.5$ Hz); ^1H and ^{13}C NMR data agreed with those reported in the literature.^[7]

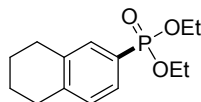


Diethyl (3-methoxyphenyl)phosphonate (3l), colorless oil): 29 mg, 59%.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.40 – 7.32 (m, 3H), 7.10 – 7.07 (m, 1H), 4.20 – 4.03

(m, 4H), 3.85 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 6H).

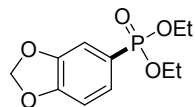
^{13}C NMR (101 MHz, CDCl_3) δ 159.6 (d, $J = 18.8$ Hz), 129.9 (d, $J = 17.6$ Hz), 129.7 (d, $J = 186.7$ Hz), 124.1 (d, $J = 9.2$ Hz), 118.9 (d, $J = 3.2$ Hz), 116.5 (d, $J = 11.4$ Hz), 62.3 (d, $J = 5.4$ Hz), 55.6, 16.5 (d, $J = 6.5$ Hz); ^1H and ^{13}C NMR data agreed with those reported in the literature.^[8]



Diethyl (5,6,7,8-tetrahydronaphthalen-2-yl)phosphonate (3m), colorless oil): 31 mg, 58%.

^1H NMR (400 MHz, CDCl_3) δ 7.64 – 7.55 (m, 2H), 7.15 (dd, $J = 7.7, 4.5$ Hz, 1H), 4.18 – 4.01 (m, 4H), 2.80 (s, 4H), 1.82 – 1.79 (m, 4H), 1.32 (t, $J = 7.1$ Hz, 6H).

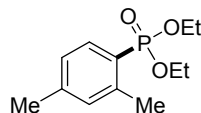
^{13}C NMR (101 MHz, CDCl_3) δ 142.4 (d, $J = 3.3$ Hz), 137.7 (d, $J = 15.0$ Hz), 132.9 (d, $J = 10.4$ Hz), 129.5 (d, $J = 15.5$ Hz), 128.7 (d, $J = 9.9$ Hz), 124.9 (d, $J = 188.8$ Hz), 62.1 (d, $J = 5.3$ Hz), 29.6 (d, $J = 35.8$ Hz), 23.0 (d, $J = 11.4$ Hz), 16.5 (d, $J = 6.6$ Hz); ^1H and ^{13}C NMR data agreed with those reported in the literature.^[9]



Diethyl benzo[d][1,3]dioxol-5-ylphosphonate (3n), colorless oil): 31 mg, 60%.

^1H NMR (400 MHz, CDCl_3) δ 7.38 (ddd, $J = 14.0, 7.9, 1.4$ Hz, 1H), 7.21 (dd, $J = 12.9, 1.3$ Hz, 1H), 6.89 (dd, $J = 7.9, 3.6$ Hz, 1H), 6.03 (s, 2H), 4.18 – 4.01 (m, 4H), 1.32 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 151.3 (d, $J = 3.5$ Hz), 148.0 (d, $J = 22.6$ Hz), 127.6 (d, $J = 11.1$ Hz), 121.4 (d, $J = 193.4$ Hz), 111.4 (d, $J = 12.3$ Hz), 108.7 (d, $J = 18.7$ Hz), 101.7, 62.2 (d, $J = 5.3$ Hz), 16.5 (d, $J = 6.6$ Hz); ^1H and ^{13}C NMR data agreed with those reported in the literature.^[9]

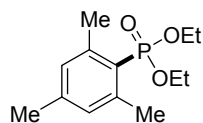


Diethyl (2,4-dimethylphenyl)phosphonate (3o), colorless oil): 30 mg, 62%.

^1H NMR (400 MHz, CDCl_3) δ 7.80 (dd, $J = 14.1, 8.3$ Hz, 1H), 7.08 (d, $J = 5.9$ Hz, 2H), 4.19 – 4.01 (m, 4H), 2.53 (d, $J = 1.2$ Hz, 3H), 2.35 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 143.1 (d, $J = 3.0$ Hz), 141.8 (d, $J = 10.6$ Hz), 134.3 (d, $J = 10.7$ Hz), 132.2 (d, $J = 15.3$ Hz), 126.3 (d, $J = 15.3$ Hz), 123.7 (d, $J = 186.1$ Hz), 61.9 (d, $J = 5.4$ Hz), 21.6 (d, $J = 1.2$ Hz), 21.3 (d, $J = 3.6$ Hz), 16.5 (d, $J = 6.6$ Hz); ^1H

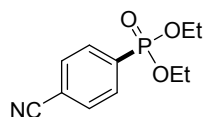
and ^{13}C NMR data agreed with those reported in the literature.^[9]



Diethyl mesitylphosphonate (3p, colorless oil): 16 mg, 32%.

^1H NMR (400 MHz, CDCl_3) δ 6.90 (d, $J = 4.5$ Hz, 2H), 4.39 – 3.89 (m, 4H), 2.60 (d, $J = 1.5$ Hz, 6H), 2.28 (s, 3H), 1.31 (t, $J = 7.1$ Hz, 6H).

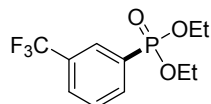
^{13}C NMR (101 MHz, CDCl_3) δ 144.0 (d, $J = 12.0$ Hz), 142.0 (d, $J = 3.1$ Hz), 130.5 (d, $J = 15.8$ Hz), 122.3 (d, $J = 181.9$ Hz), 61.3 (d, $J = 5.3$ Hz), 23.3 (d, $J = 2.8$ Hz), 21.2, 16.46 (d, $J = 6.7$ Hz); ^1H and ^{13}C NMR data agreed with those reported in the literature.^[7]



Diethyl (4-cyanophenyl)phosphonate (3q, colorless oil): 25 mg, 64%.

^1H NMR (400 MHz, CDCl_3) δ 7.93 (dd, $J = 13.1, 8.4$ Hz, 2H), 7.77 (dd, $J = 8.4, 3.6$ Hz, 2H), 4.24 – 4.07 (m, 4H), 1.34 (t, $J = 7.1$ Hz, 6H).

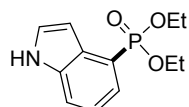
^{13}C NMR (101 MHz, CDCl_3) δ 134.1 (d, $J = 187.7$ Hz), 132.4 (d, $J = 9.8$ Hz), 132.1 (d, $J = 14.9$ Hz), 117.9, 116.1 (d, $J = 3.6$ Hz), 62.8 (d, $J = 5.6$ Hz), 16.5 (d, $J = 6.3$ Hz); ^1H and ^{13}C NMR data agreed with those reported in the literature.^[9]



Diethyl (3-(trifluoromethyl)phenyl)phosphonate (3r, colorless oil): 33 mg, 58%.

^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, $J = 13.7$ Hz, 1H), 8.01 (dd, $J = 13.0, 7.6$ Hz, 1H), 7.81 (d, $J = 7.9$ Hz, 1H), 7.62 (td, $J = 7.7, 3.9$ Hz, 1H), 4.25 – 4.07 (m, 4H), 1.35 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 135.1 (d, $J = 8.6$ Hz), 131.4 – 130.9 (m), 129.28 (s), 129.20 – 129.1 (m), 128.7 (dq, $J = 11.3, 3.8$ Hz), 123.8 (qd, $J = 272.6, 2.6$ Hz), 62.7 (d, $J = 5.6$ Hz), 16.4 (d, $J = 6.4$ Hz); ^1H and ^{13}C NMR data agreed with those reported in the literature.^[6]



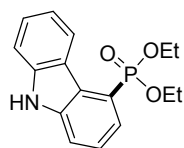
Diethyl (1H-indol-4-yl)phosphonate (3s, colorless oil): 24 mg, 47%.

¹H NMR (600 MHz, CDCl₃) δ 8.74 (d, *J* = 8.2 Hz, 1H), 8.67 (s, 1H), 7.93 (dd, *J* = 14.9, 7.3 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.50 – 7.43 (m, 3H), 7.32 – 7.23 (m, 2H), 4.32 – 4.19 (m, 2H), 4.16 – 4.06 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (151 MHz, CDCl₃) δ 135.94 (d, *J* = 16.7 Hz), 128.73 (d, *J* = 11.9 Hz), 126.27 (d, *J* = 10.2 Hz), 126.09, 121.30 (d, *J* = 16.2 Hz), 118.47 (d, *J* = 187.6 Hz), 115.96 (d, *J* = 3.4 Hz), 103.36 (d, *J* = 2.3 Hz), 62.09 (d, *J* = 4.9 Hz), 16.55 (d, *J* = 6.7 Hz).

³¹P NMR (121 MHz, CDCl₃) δ 21.12.

HRMS (ESI): calcd. for C₁₂H₁₇NO₃P ([M+H]⁺): 254.0941, found: 254.0938.



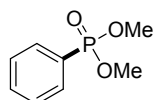
Diethyl (9H-carbazol-4-yl)phosphonate (3t, colorless oil): 24 mg, 39%.

¹H NMR (600 MHz, CDCl₃) δ 8.74 (d, *J* = 8.2 Hz, 1H), 8.67 (s, 1H), 7.93 (dd, *J* = 14.9, 7.3 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.43 (m, 3H), 7.34 – 7.22 (m, 2H), 4.28 – 4.19 (m, 2H), 4.16 – 4.07 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 6H).

¹³C NMR (151 MHz, CDCl₃) δ 140.17, 139.92 (d, *J* = 16.9 Hz), 126.87, 126.81, 124.87, 124.86 (d, *J* = 15.8 Hz), 123.34 (d, *J* = 11.6 Hz), 121.85 (d, *J* = 3.1 Hz), 120.31 (d, *J* = 185.2 Hz), 119.86, 115.71 (d, *J* = 3.4 Hz), 110.69, 62.43 (d, *J* = 5.0 Hz), 16.47 (d, *J* = 6.8 Hz).

³¹P NMR (121 MHz, CDCl₃) δ 20.52.

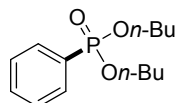
HRMS (ESI): calcd. for C₁₆H₁₉NO₃P ([M+H]⁺): 304.1097, found: 304.1094.



Dimethyl phenylphosphonate (3u, colorless oil): 23 mg, 61%.

¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.75 (m, 2H), 7.59 (td, *J* = 7.5, 1.4 Hz, 1H), 7.49 (td, *J* = 7.5, 4.3 Hz, 2H), 3.79 (s, 3H), 3.76 (s, 3H);

¹³C NMR (101 MHz, CDCl₃) δ 132.8 (d, *J* = 3.0 Hz), 132.1 (d, *J* = 9.9 Hz), 128.7 (d, *J* = 15.0 Hz), 127.0 (d, *J* = 188.5 Hz), 52.9 (d, *J* = 5.5 Hz); ¹H and ¹³C NMR data agreed with those reported in the literature.^[10]

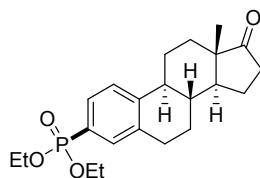


Dibutyl phenylphosphonate (3v, colorless oil): 39 mg, 73%.

¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.78 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.47 (dt,

$J = 11.4, 5.7$ Hz, 2H), 4.12 – 3.79 (m, 4H), 1.69 – 1.62 (m, 4H), 1.39 (dq, $J = 14.6, 7.3$ Hz, 4H), 0.90 (t, $J = 7.4$ Hz, 6H).

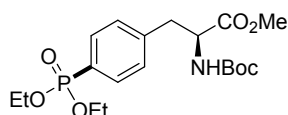
^{13}C NMR (101 MHz, CDCl_3) δ 132.4 (d, $J = 3.0$ Hz), 131.9 (d, $J = 9.7$ Hz), 128.5 (d, $J = 15.0$ Hz), 128.5 (d, $J = 188.1$ Hz), 65.8 (d, $J = 5.7$ Hz), 32.5 (d, $J = 6.5$ Hz), 18.8, 13.7; ^1H and ^{13}C NMR data agreed with those reported in the literature.^[7]



Diethyl ((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)phosphonate (3w, white solid): 35 mg, 45%.

^1H NMR (400 MHz, CDCl_3): δ 7.60 – 7.51 (m, 2H), 7.39 (dd, $J = 7.8, 4.1$ Hz, 1H), 4.19 – 4.00 (m, 4H), 2.96 (dd, $J = 9.7, 6.2$ Hz, 2H), 2.52 (dd, $J = 18.7, 8.7$ Hz, 1H), 2.46 – 2.42 (m, 1H), 2.34 (d, $J = 7.7$ Hz, 1H), 2.22 – 2.13 (m, 1H), 2.12 – 2.03 (m, 2H), 2.02 – 1.95 (m, 1H), 1.69 – 1.40 (m, 6H), 1.33 (t, $J = 6.7$ Hz, 6H), 0.92 (s, 3H).

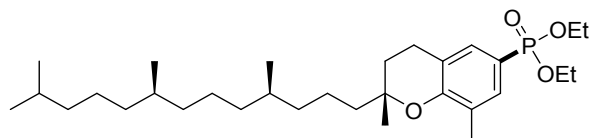
^{13}C NMR (151 MHz, CDCl_3): δ 220.4, 144.7 (d, $J = 2.5$ Hz), 137.1 (d, $J = 14.6$ Hz), 132.7 (d, $J = 10.4$ Hz), 129.1 (d, $J = 9.8$ Hz), 125.7 (d, $J = 188.4$ Hz), 125.6 (d, $J = 15.2$ Hz), 62.2 (d, $J = 4.9$ Hz), 48.0, 44.8, 38.0, 35.9, 31.8, 29.3, 26.4, 25.7, 21.8, 16.5 (d, $J = 6.3$ Hz), 14.0; ^1H and ^{13}C NMR data agreed with those reported in the literature.^[8]



Methyl (S)-2-((tert-butoxycarbonyl)amino)-3-(4-(diethoxyphosphoryl)-phenyl)propanoate (3x, white solid): 33 mg, 40%.

^1H NMR (400 MHz, CDCl_3): δ 7.74 (dd, $J = 13.1, 7.9$ Hz, 2H), 7.25 (dd, $J = 7.6, 3.7$ Hz, 2H), 5.05 (d, $J = 7.7$ Hz, 1H), 4.62 (dd, $J = 12.6, 5.7$ Hz, 1H), 4.23 – 3.98 (m, 4H), 3.72 (s, 3H), 3.19 (dd, $J = 13.8, 5.5$ Hz, 1H), 3.07 (dd, $J = 13.6, 6.2$ Hz, 1H), 1.41 (s, 9H), 1.32 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (101 MHz, CDCl_3): δ 172.1, 155.1, 141.0 (d, $J = 3.0$ Hz), 132.0 (d, $J = 10.2$ Hz), 129.6 (d, $J = 15.3$ Hz), 127.1 (d, $J = 189.7$ Hz), 80.2, 62.2 (d, $J = 5.5$ Hz), 54.3, 52.5, 38.5, 28.4, 16.4 (d, $J = 6.5$ Hz); ^1H and ^{13}C NMR data agreed with those reported in the literature.^[11]



Diethyl ((*R*)-2,8-dimethyl-2-((*4R,8R*)-4,8,12-trimethyltridecyl)chroman-6-yl)phosphonate (3w, colorless oil): 16 mg, 14%.

¹H NMR (600 MHz, CDCl₃): δ 7.37 (t, $J = 14.4$ Hz, 3H), 4.15 – 4.01 (m, 4H), 2.82 – 2.70 (m, 2H), 2.17 (s, 3H), 1.80 (ddt, $J = 40.8, 13.2, 6.5$ Hz, 2H), 1.62 – 1.55 (m, 3H), 1.55 – 1.43 (m, 2H), 1.32 (t, $J = 7.0$ Hz, 6H), 1.29 – 1.11 (m, 19H), 0.85 (dd, $J = 13.5, 6.6$ Hz, 12H).

¹³C NMR (151 MHz, CDCl₃): δ 156.2 (d, $J = 3.3$ Hz), 131.7 (t, $J = 10.5$ Hz), 126.9 (d, $J = 15.8$ Hz), 120.8 (d, $J = 16.5$ Hz), 117.1 (d, $J = 193.7$ Hz), 61.9 (d, $J = 5.3$ Hz), 40.5, 39.6, 37.6, 37.6, 37.6, 37.5, 32.9, 32.8, 31.0, 29.9, 28.2, 25.0, 24.6, 24.5, 22.9, 22.8, 22.3, 21.1, 19.9, 19.8, 16.6 (d, $J = 6.6$ Hz), 16.2.

³¹P NMR (121 MHz, CDCl₃): δ 22.3.

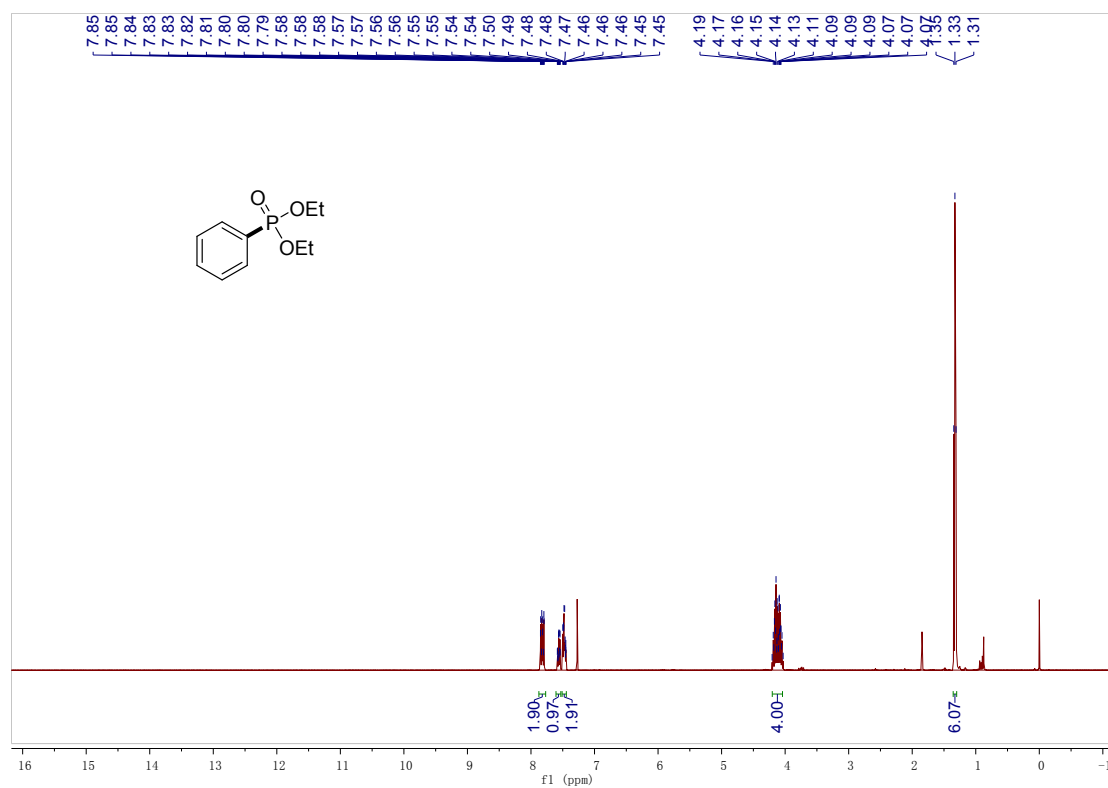
HRMS (ESI): calcd. for C₃₁H₅₆O₄P ([M+H]⁺): 523.3911, found: 523.3912.

IV. References

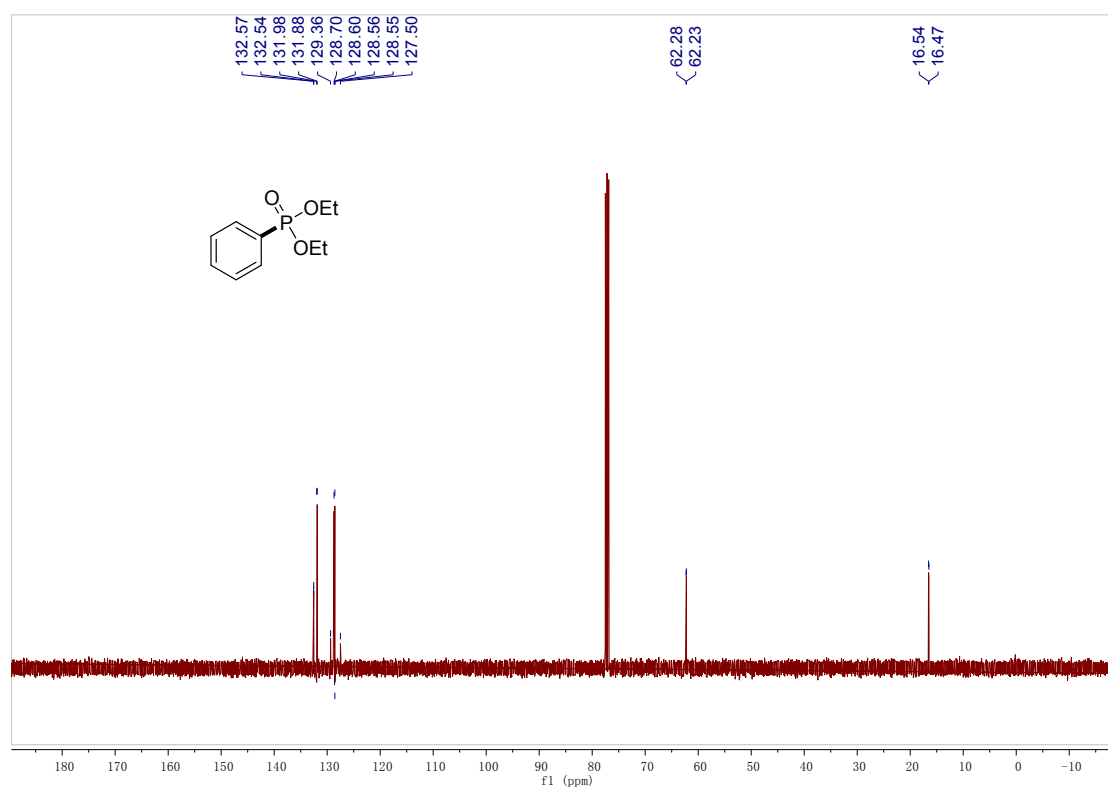
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V. Copies of the ^1H , ^{13}C NMR and ^{31}P NMR spectra

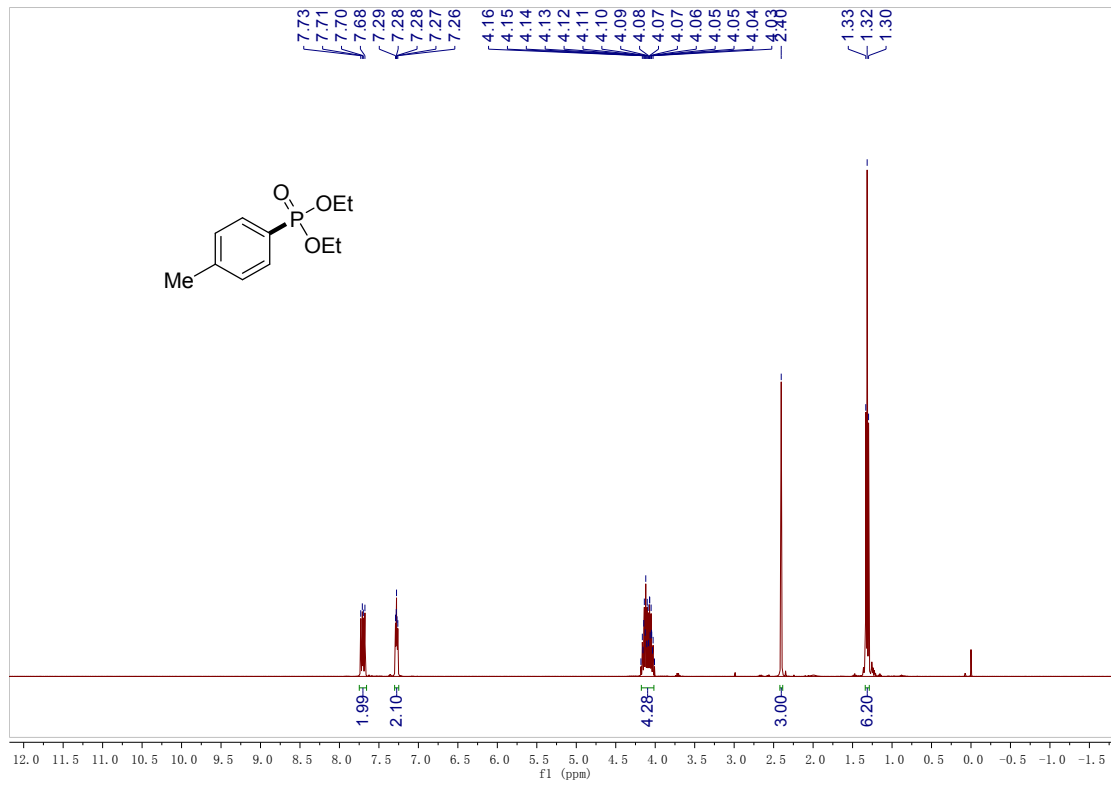
^1H NMR spectrum of compound **3a**



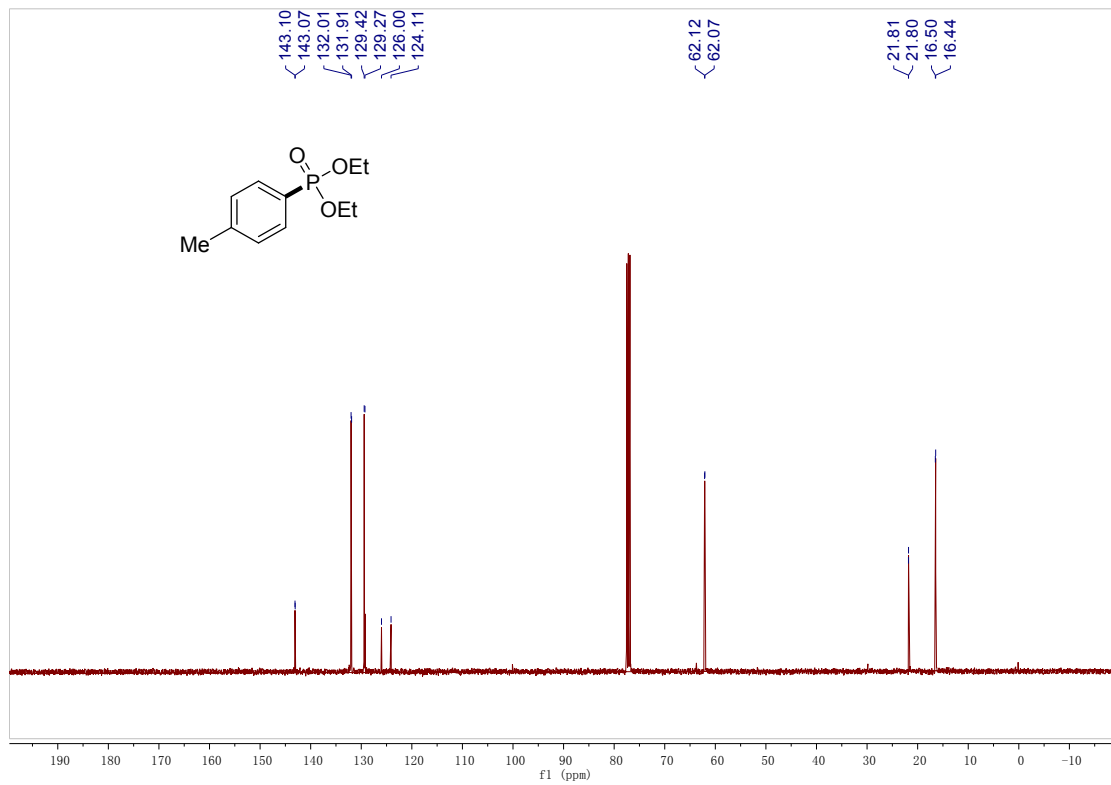
^{13}C NMR spectrum of compound **3a**



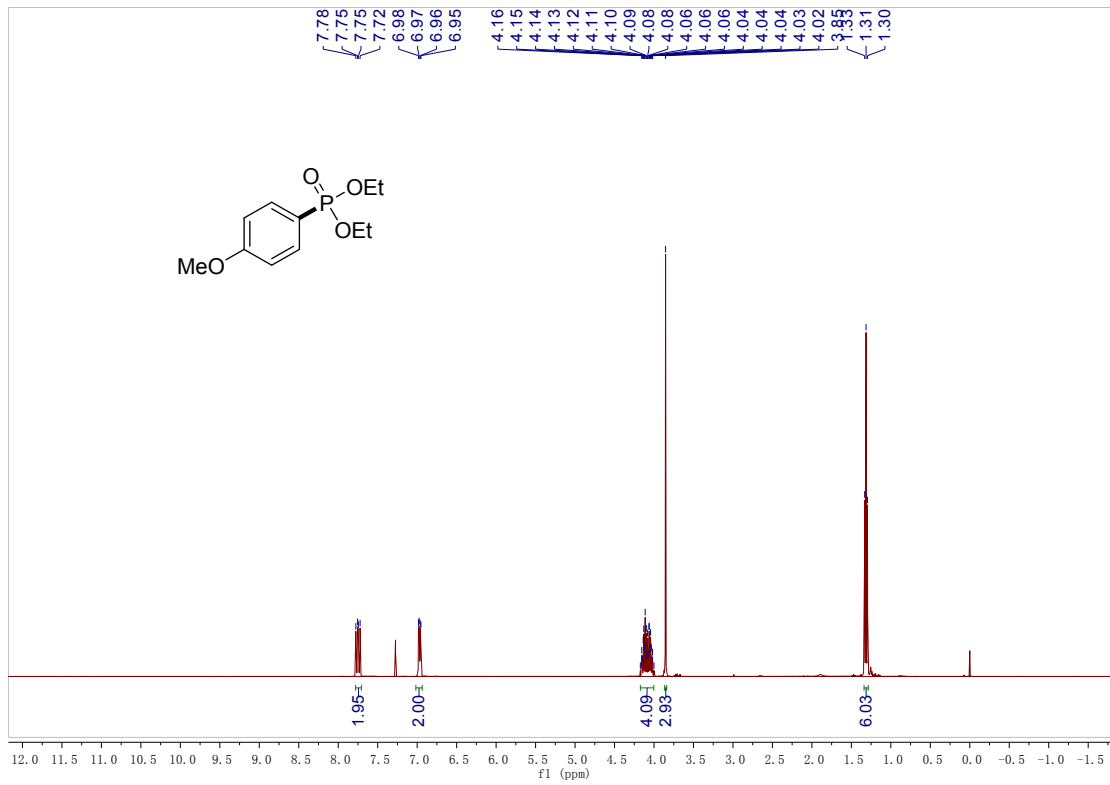
¹H NMR spectrum of compound **3b**



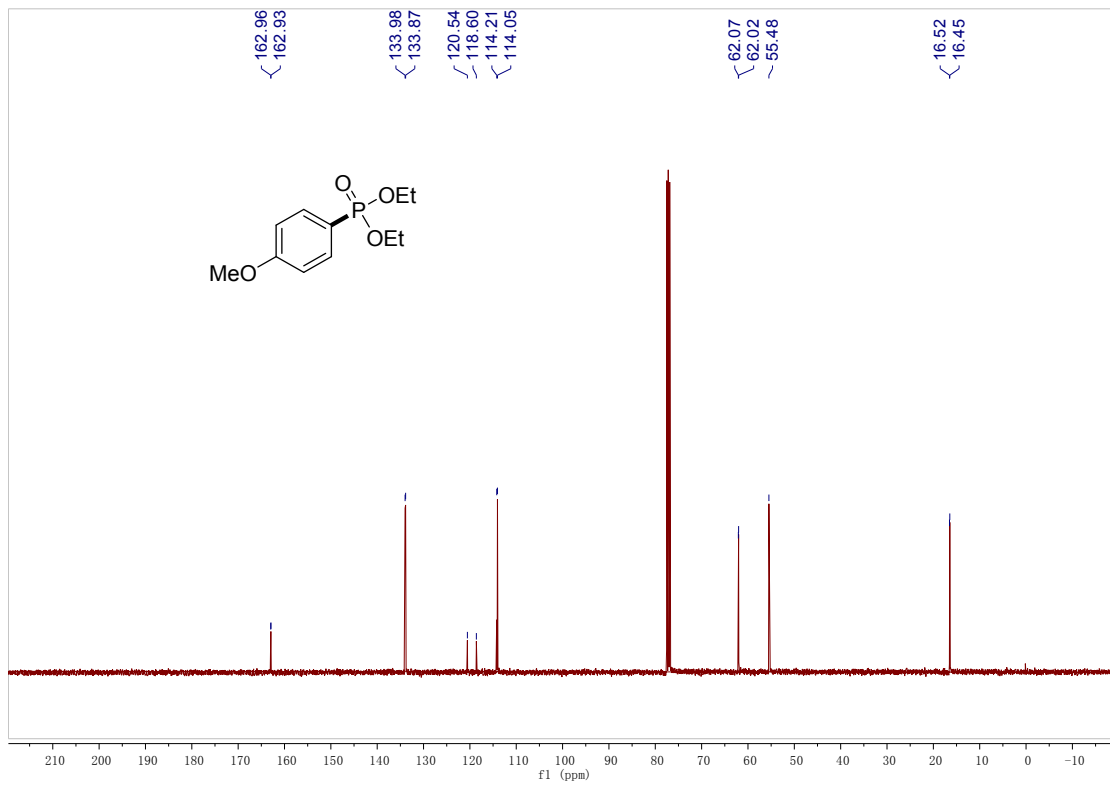
¹³C NMR spectrum of compound **3b**



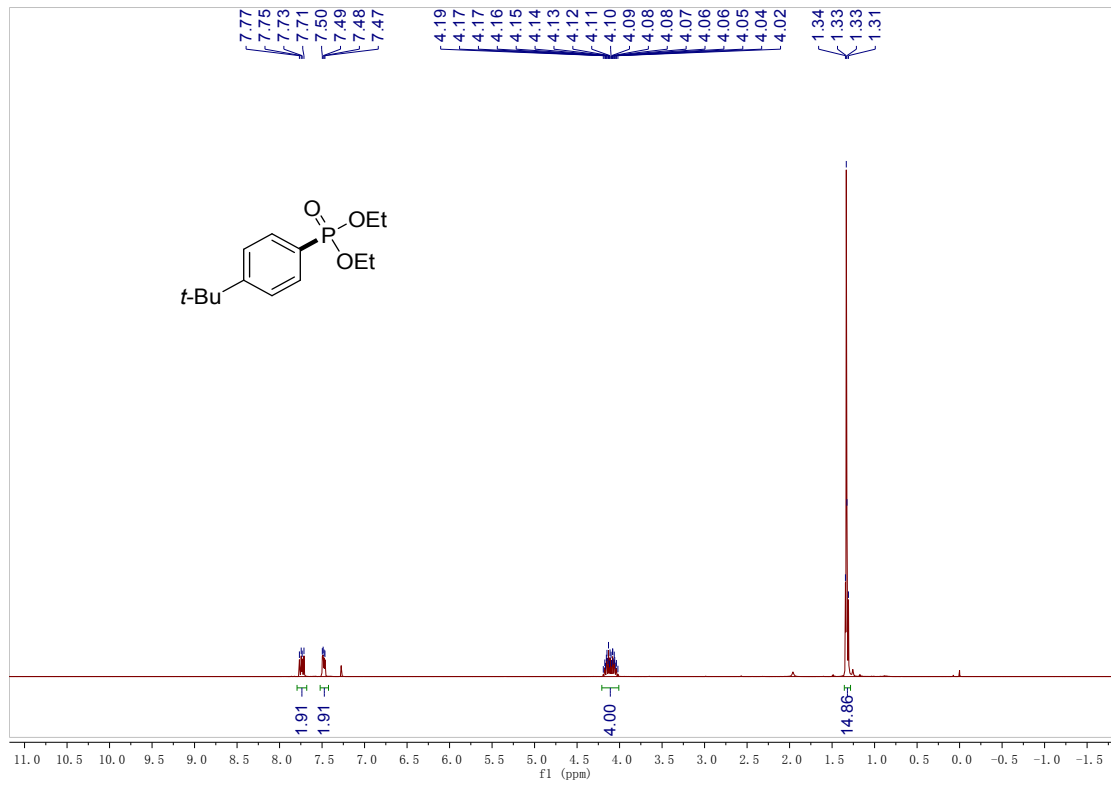
¹H NMR spectrum of compound **3c**



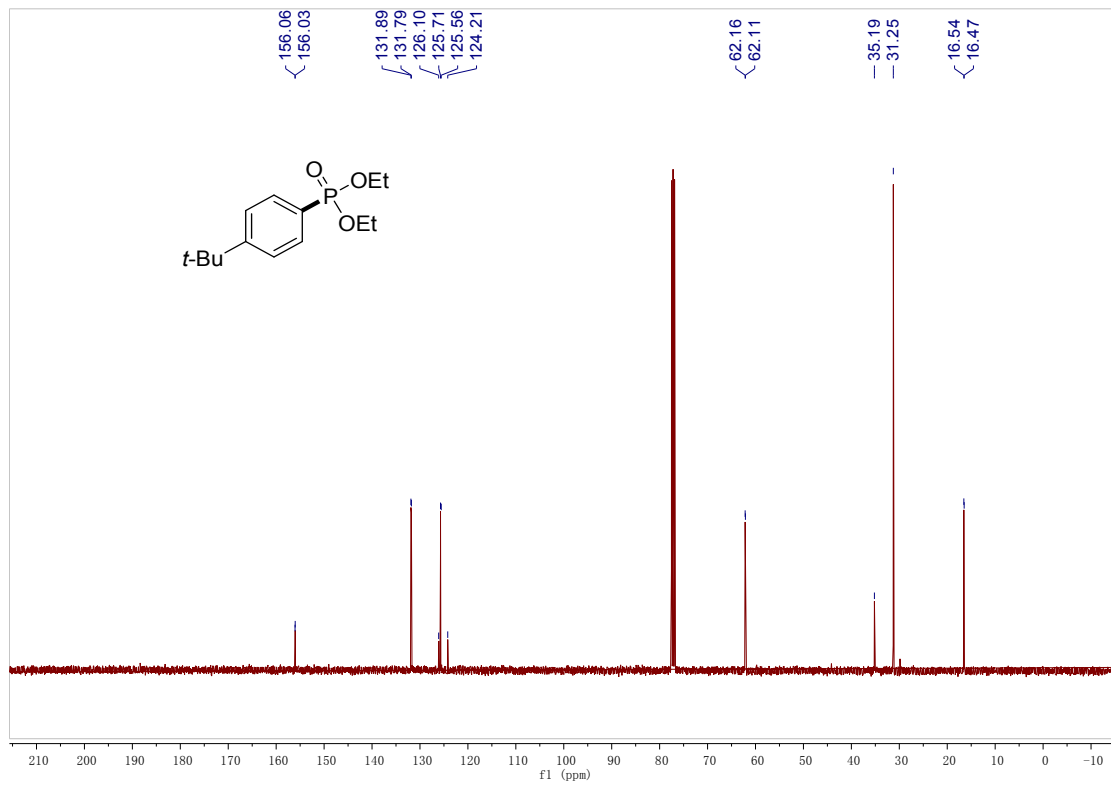
¹³C NMR spectrum of compound **3c**



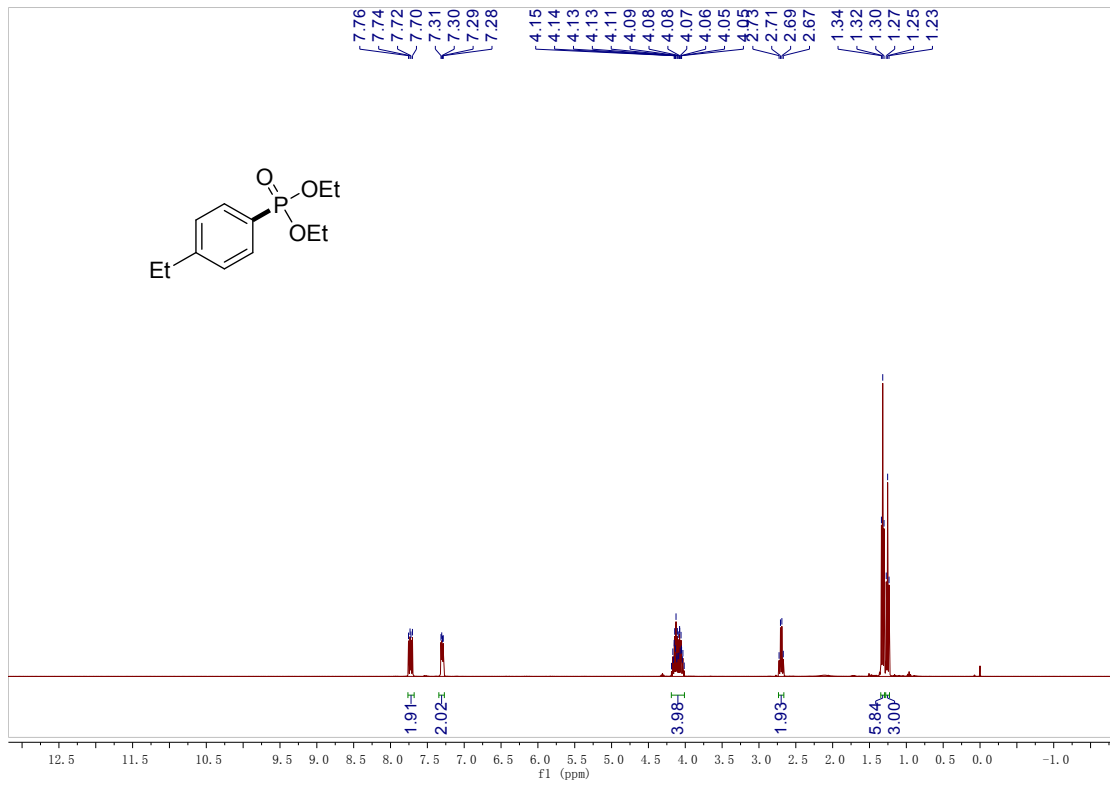
¹H NMR spectrum of compound **3d**



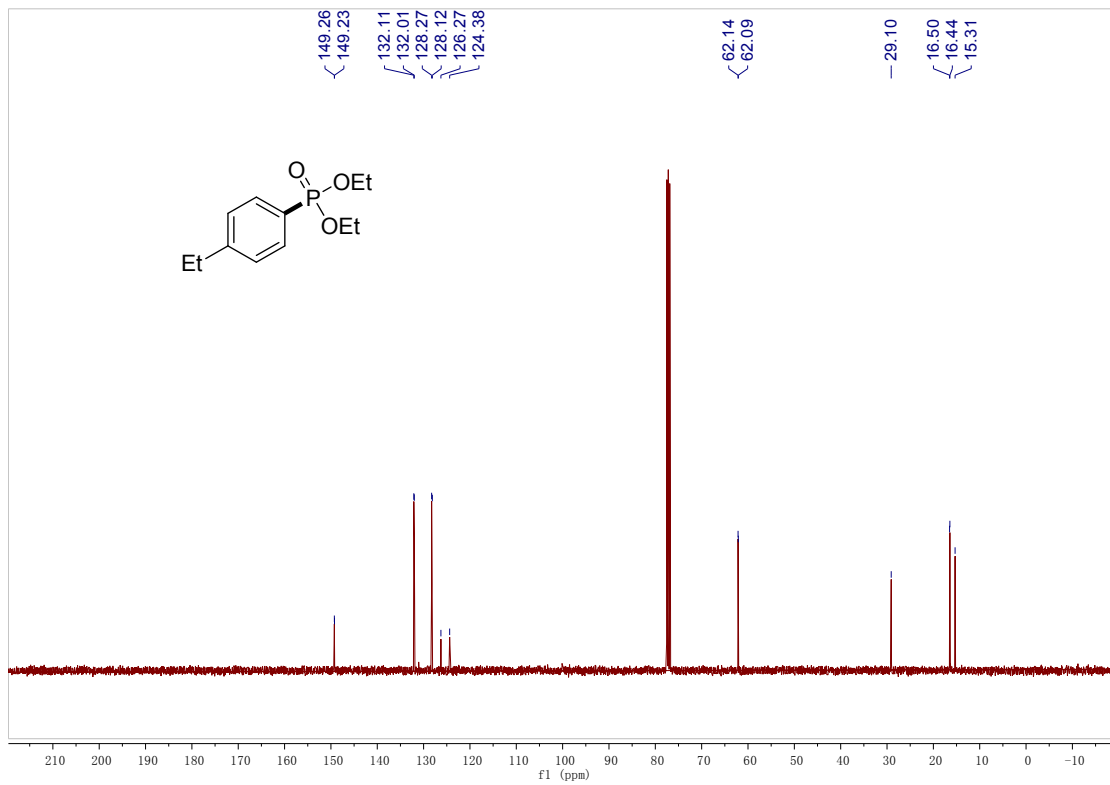
¹³C NMR spectrum of compound **3d**



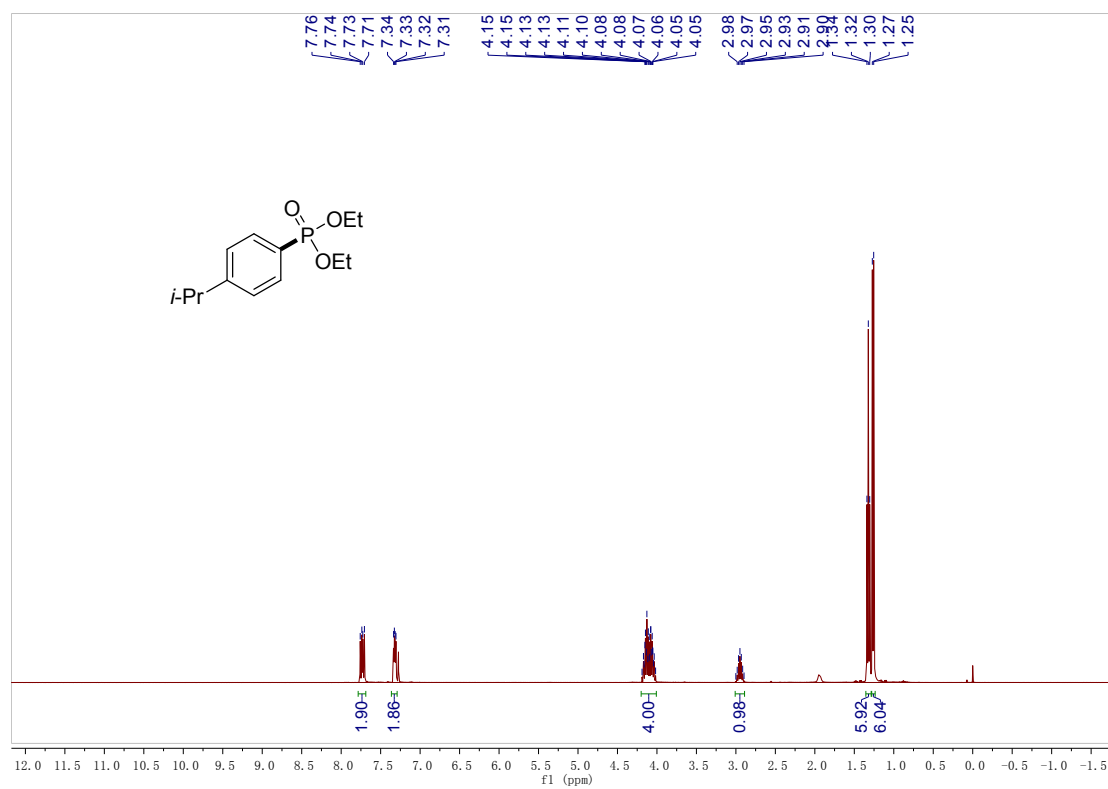
¹H NMR spectrum of compound **3e**



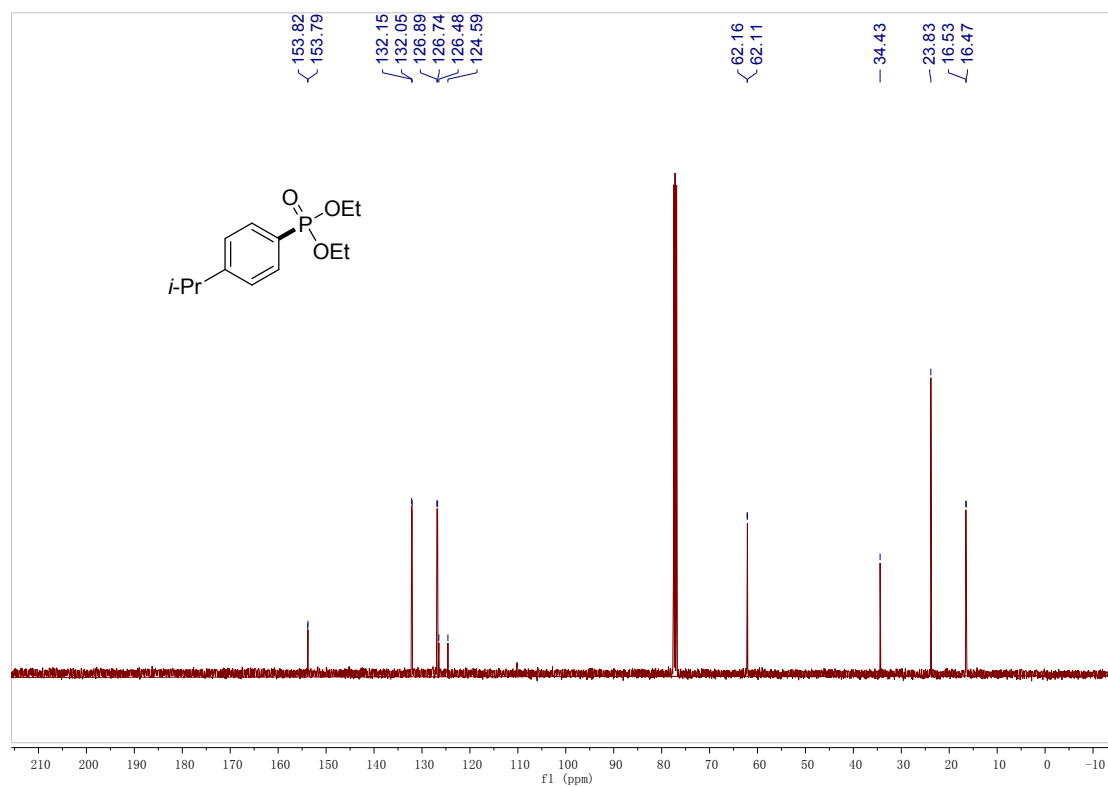
¹³C NMR spectrum of compound **3e**



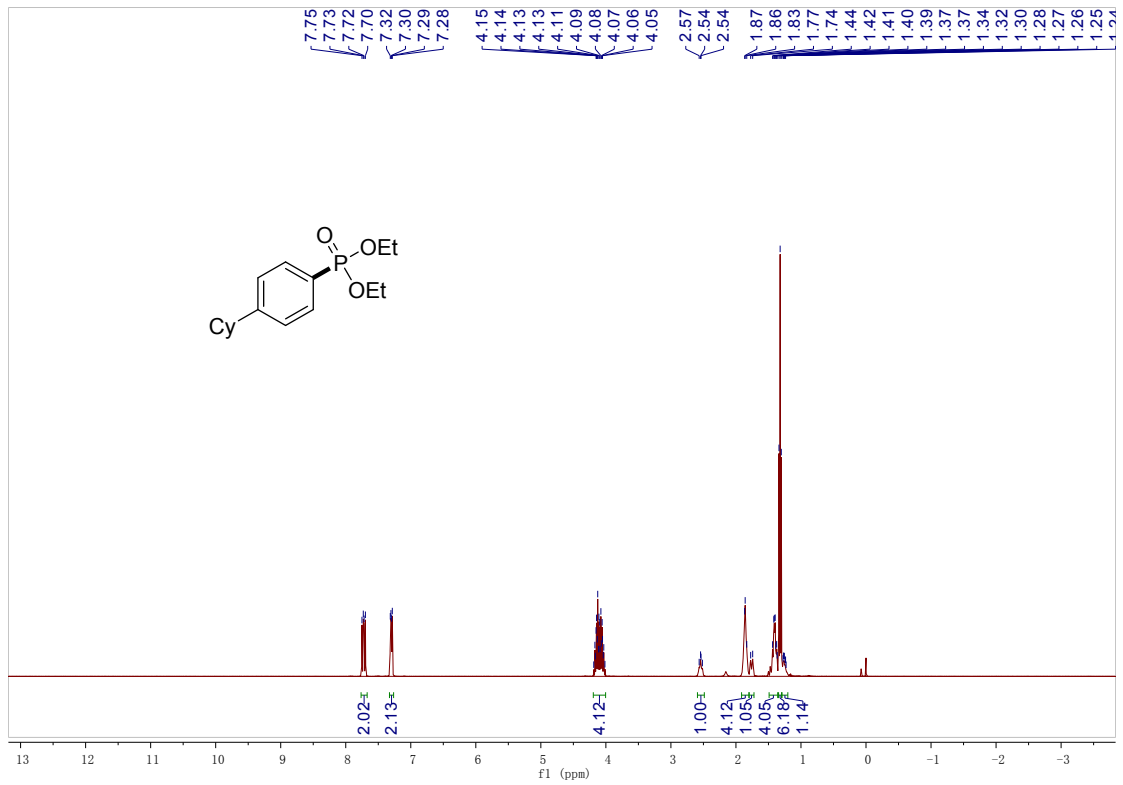
¹H NMR spectrum of compound **3f**



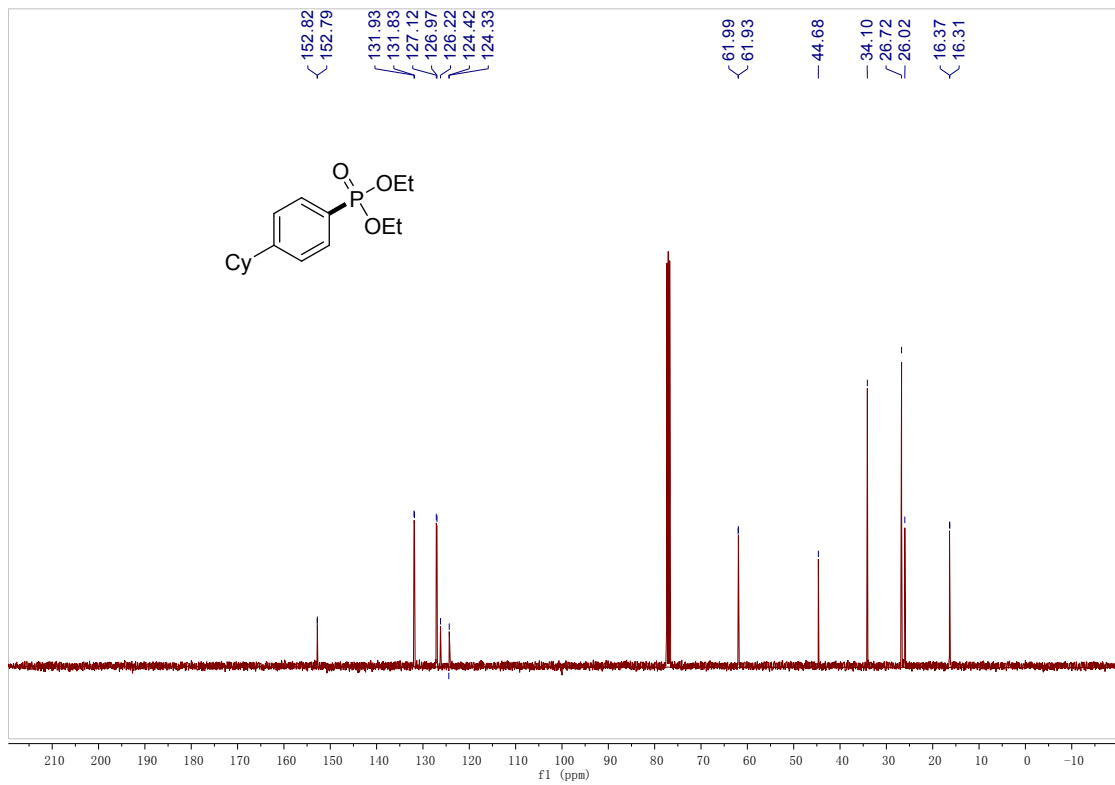
¹³C NMR spectrum of compound **3f**



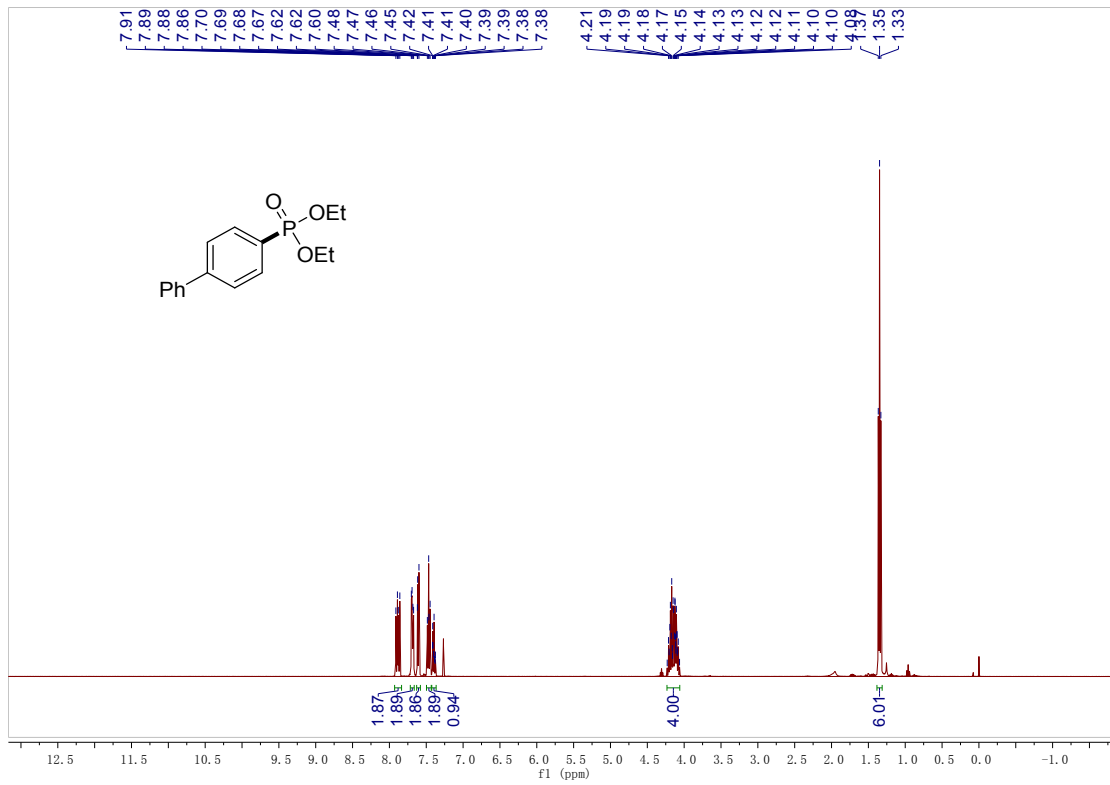
¹H NMR spectrum of compound **3g**



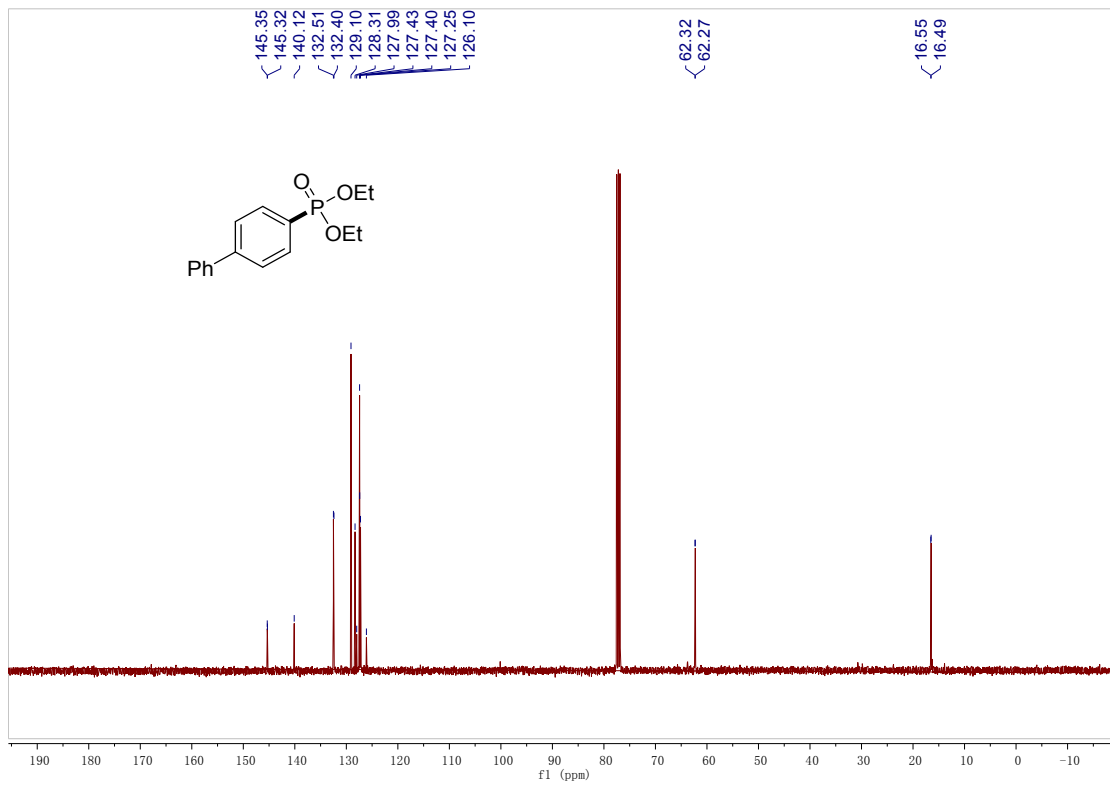
¹³C NMR spectrum of compound **3g**



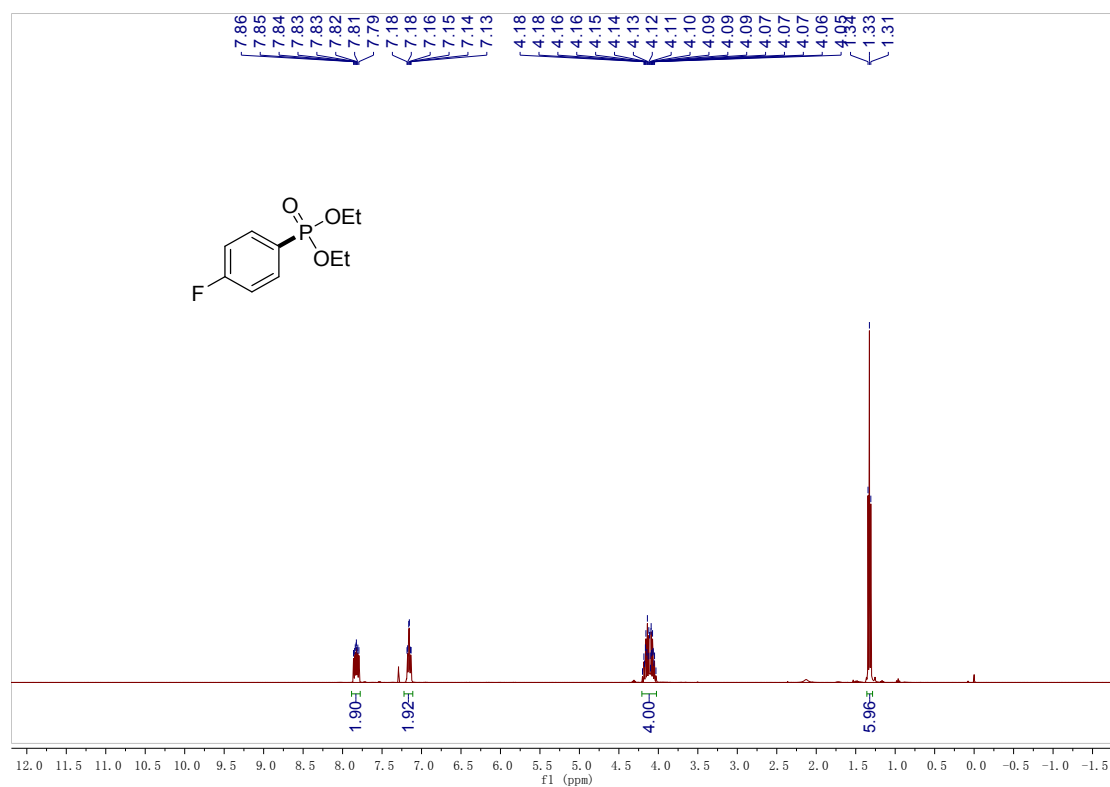
¹H NMR spectrum of compound 3h



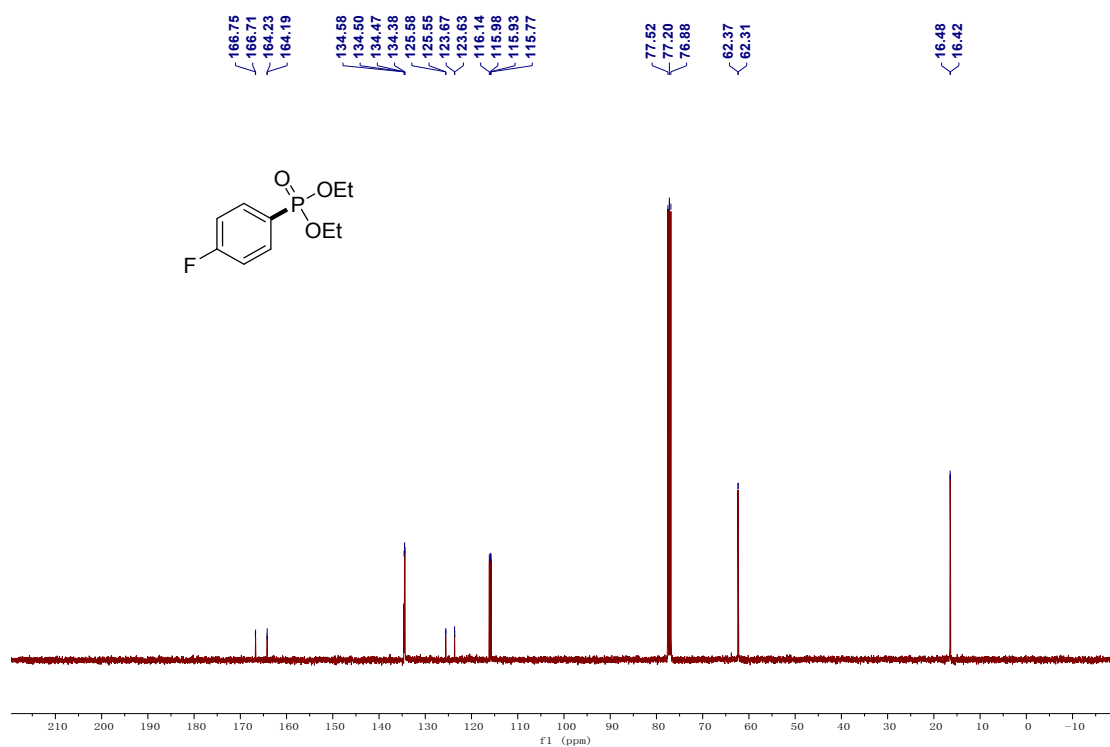
¹³C NMR spectrum of compound 3h



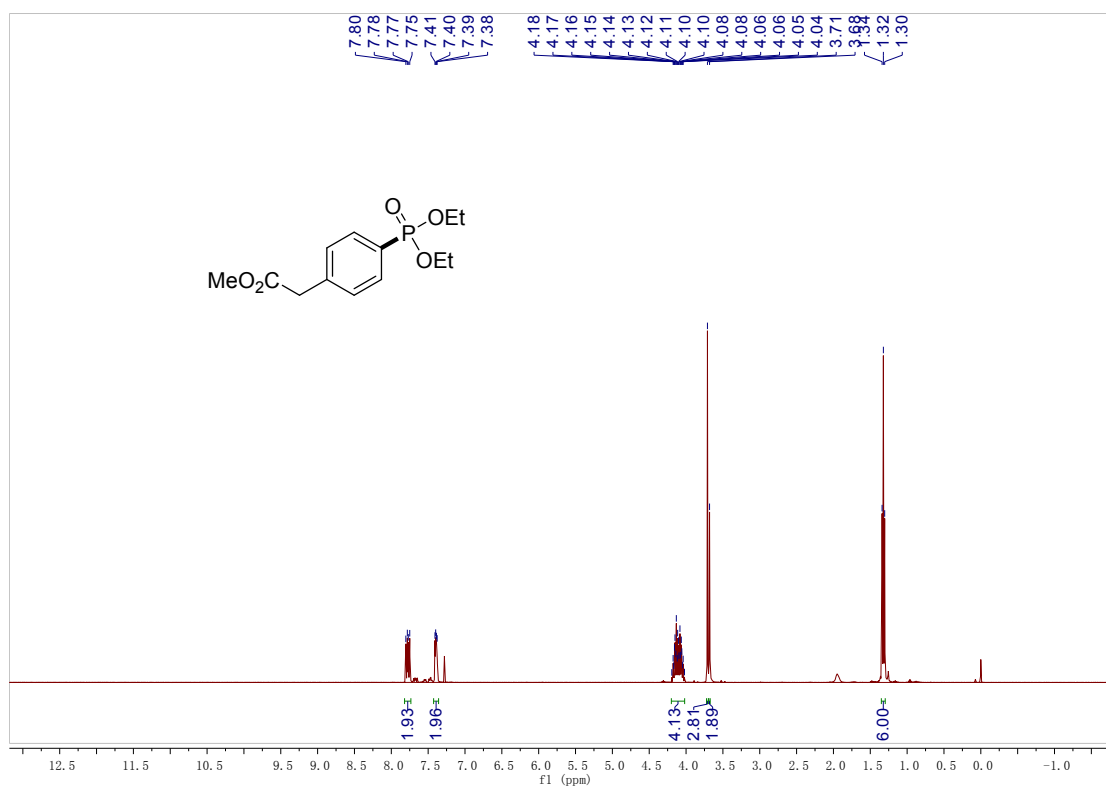
¹H NMR spectrum of compound **3i**



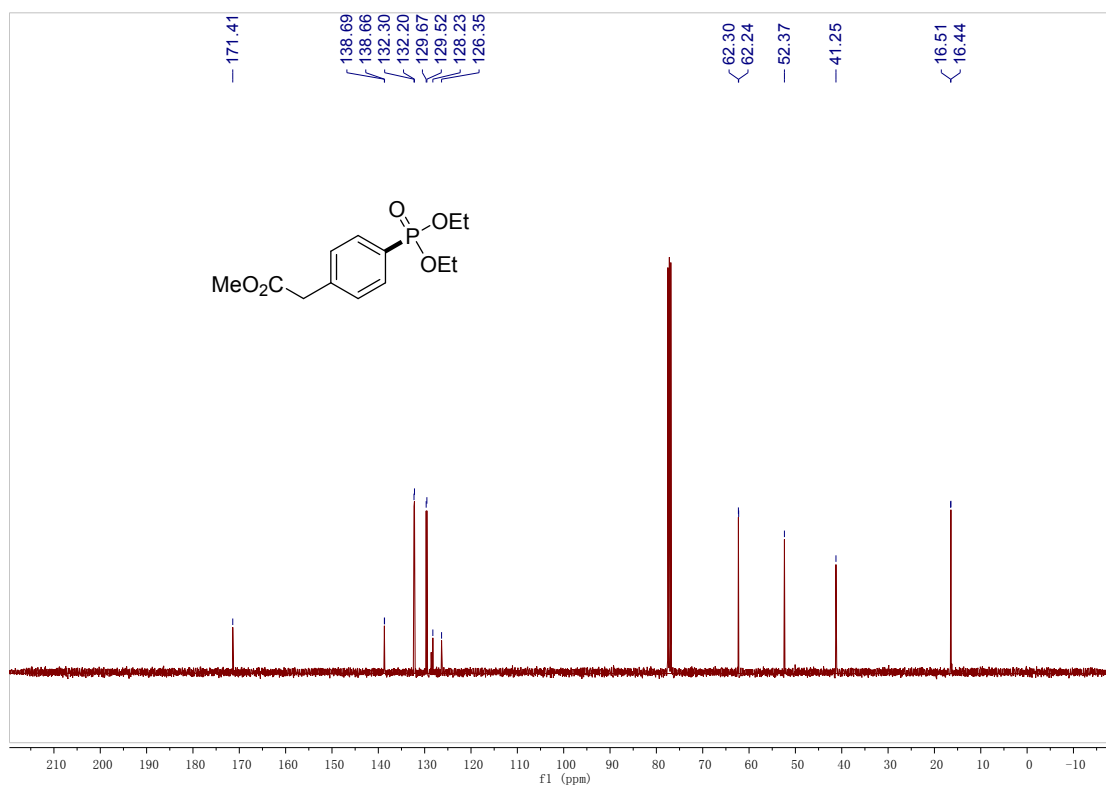
¹³C NMR spectrum of compound **3i**



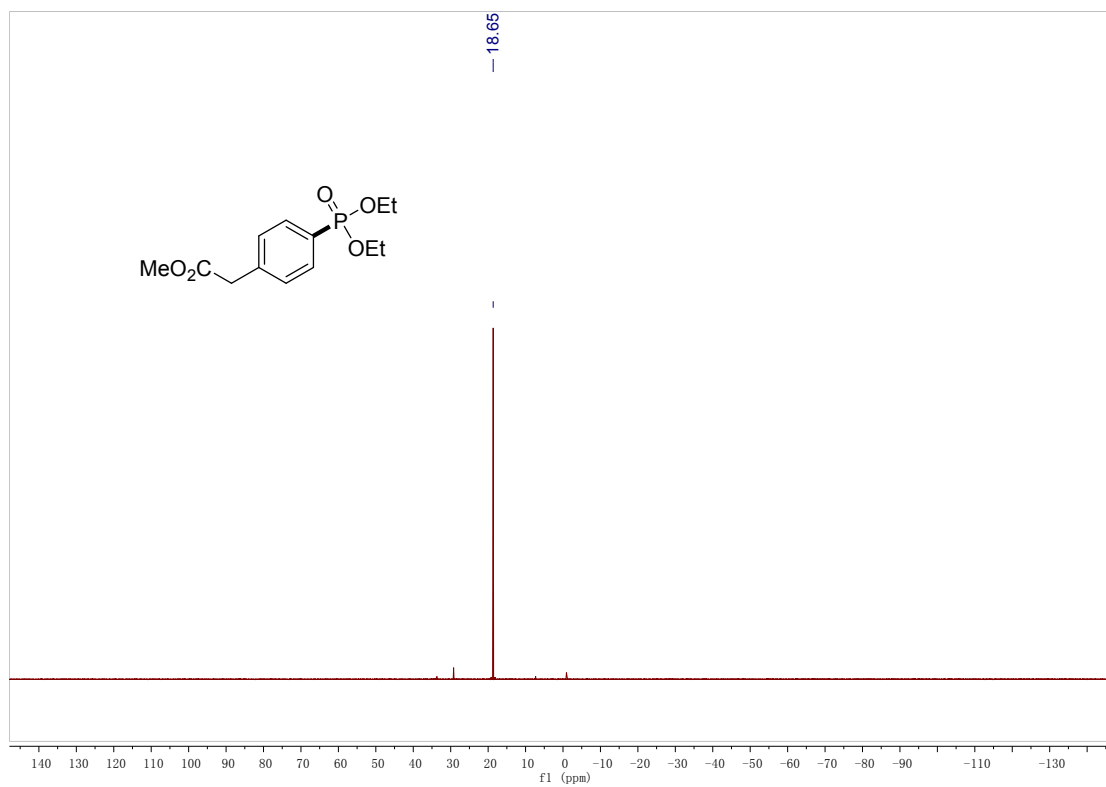
¹H NMR spectrum of compound **3j**



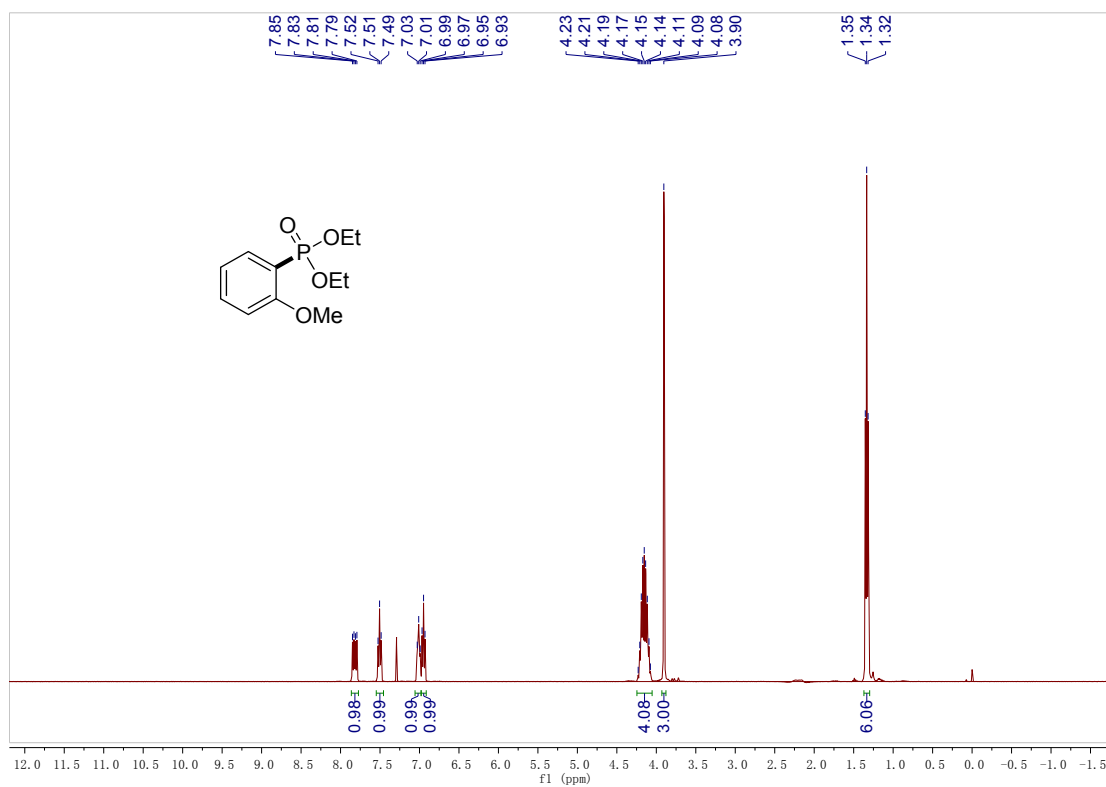
¹³C NMR spectrum of compound **3j**



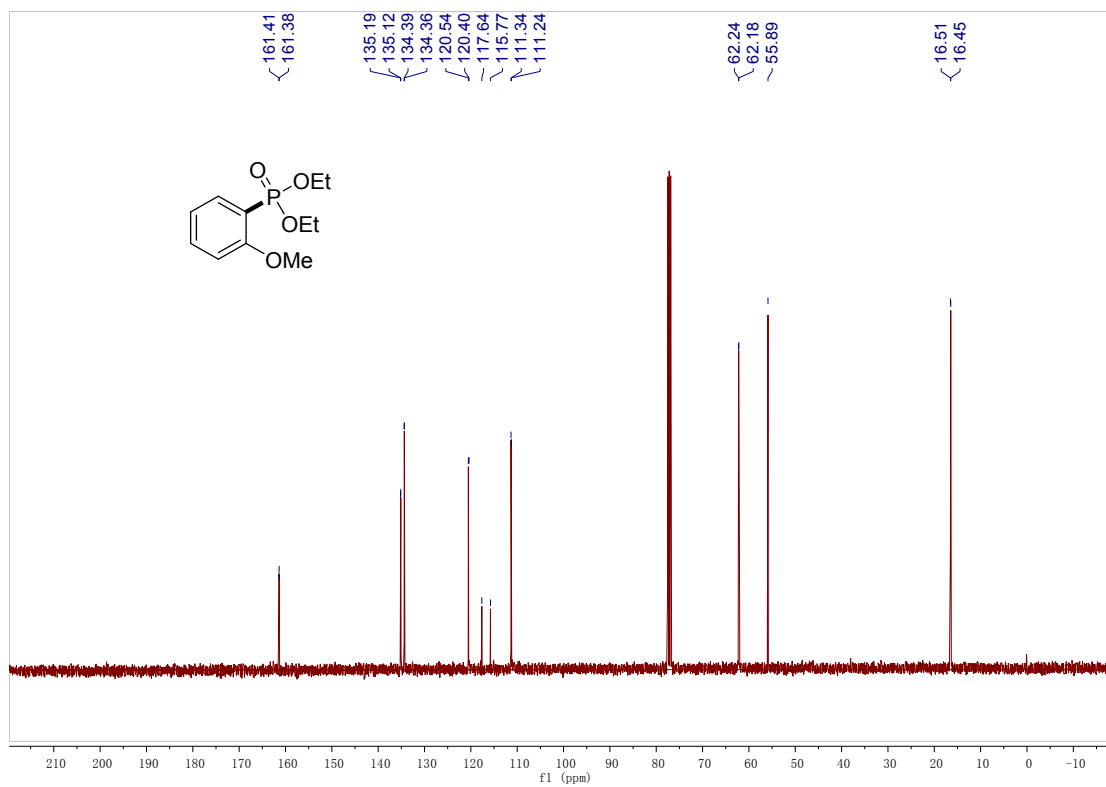
³¹P NMR spectrum of compound **3j**



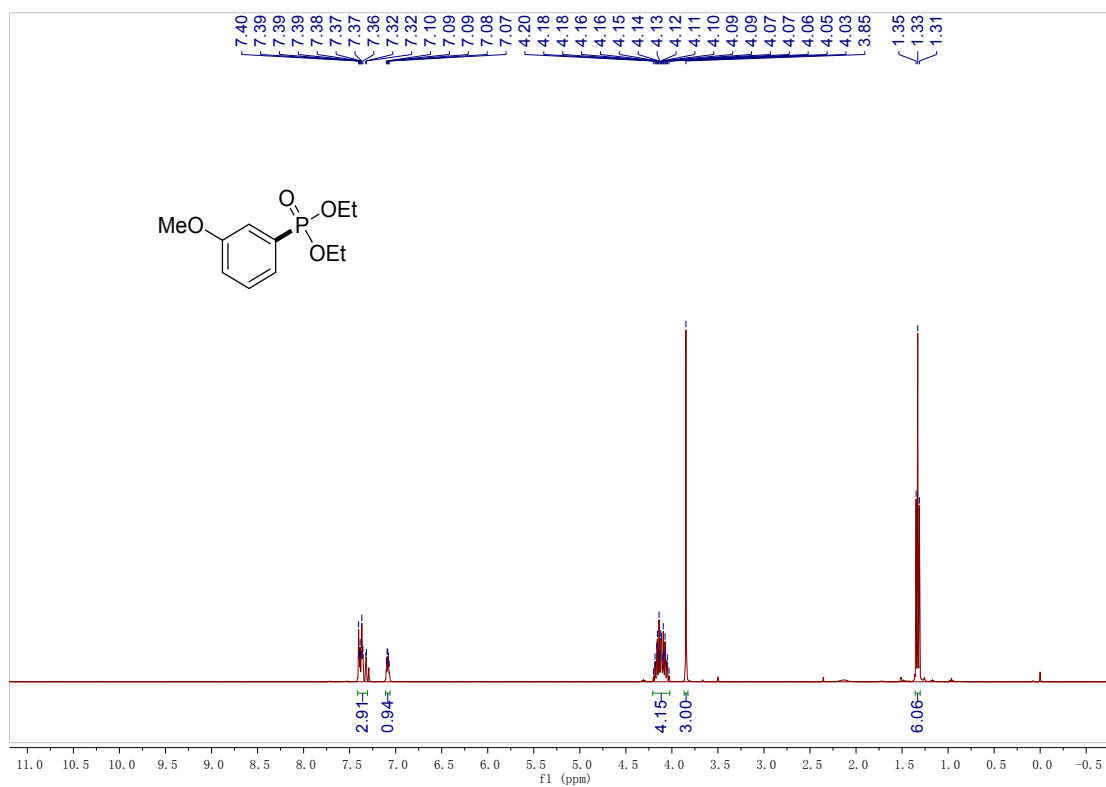
¹H NMR spectrum of compound **3k**



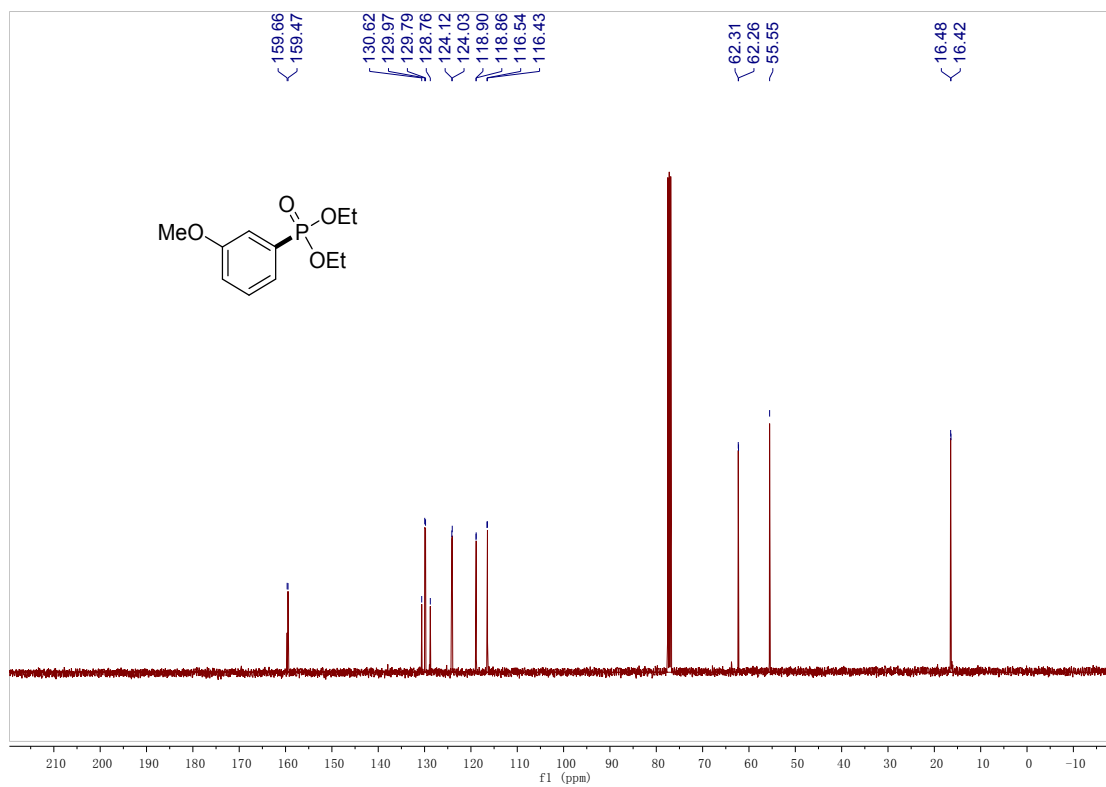
^{13}C NMR spectrum of compound **3k**



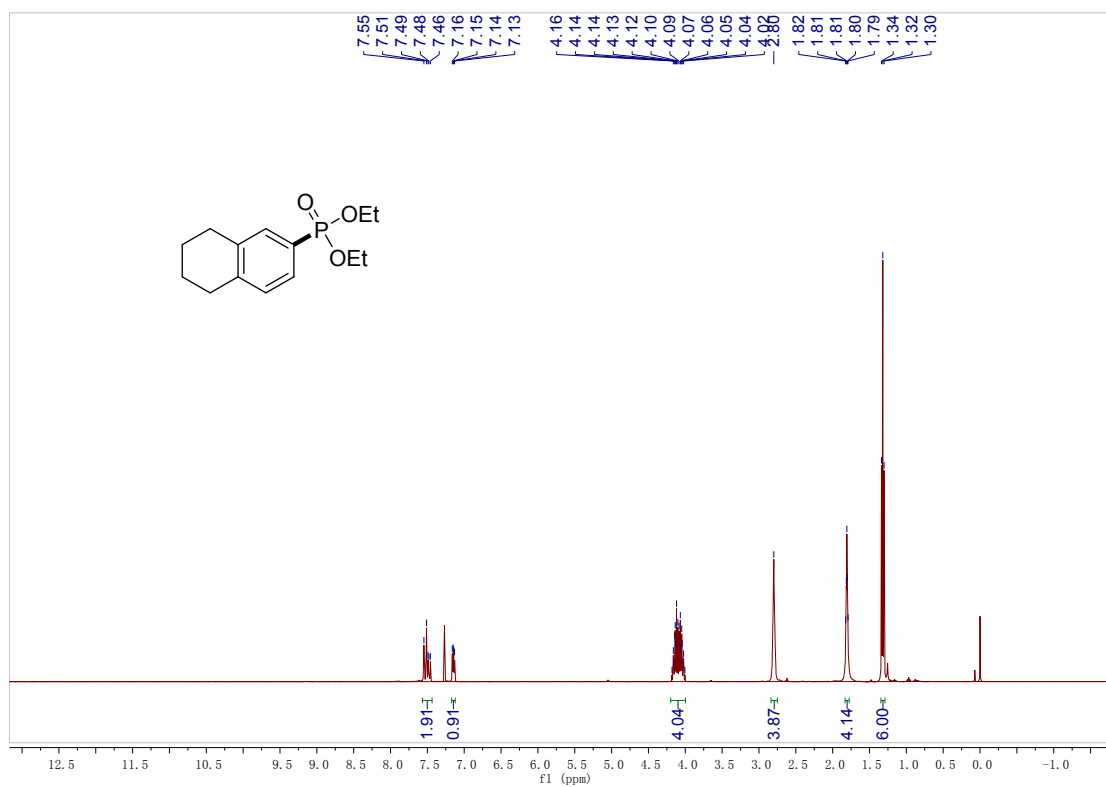
^1H NMR spectrum of compound **3l**



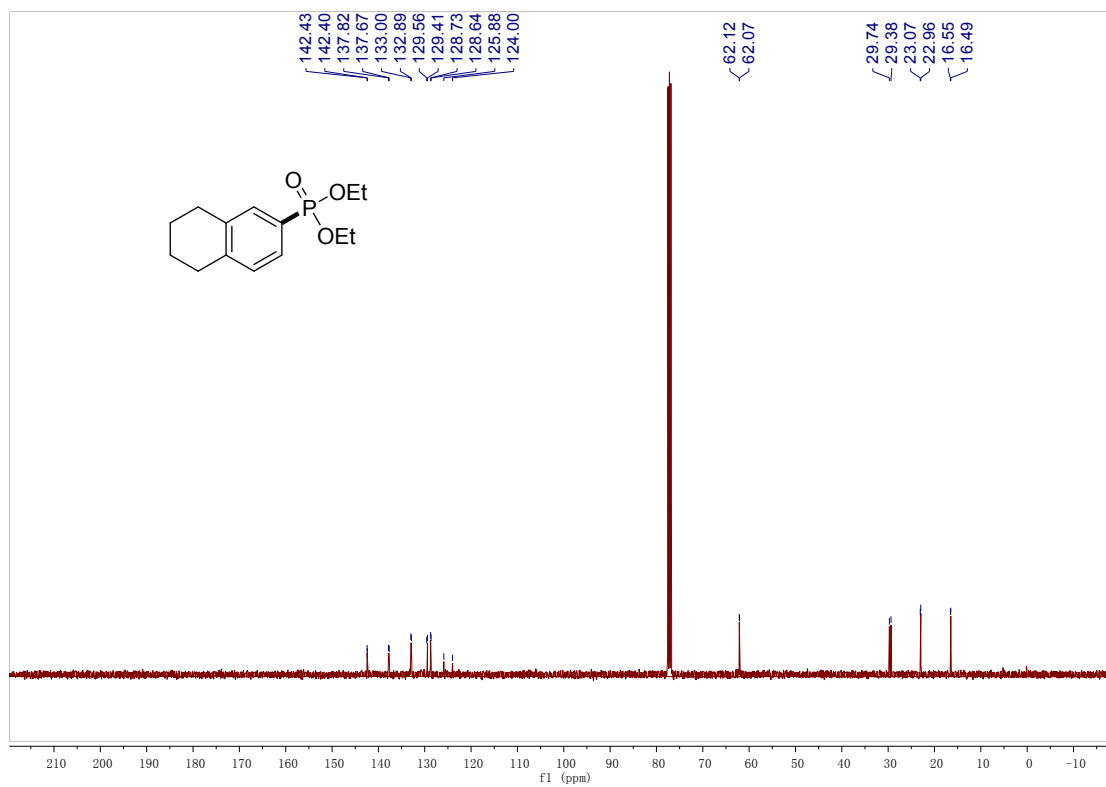
^{13}C NMR spectrum of compound **3l**



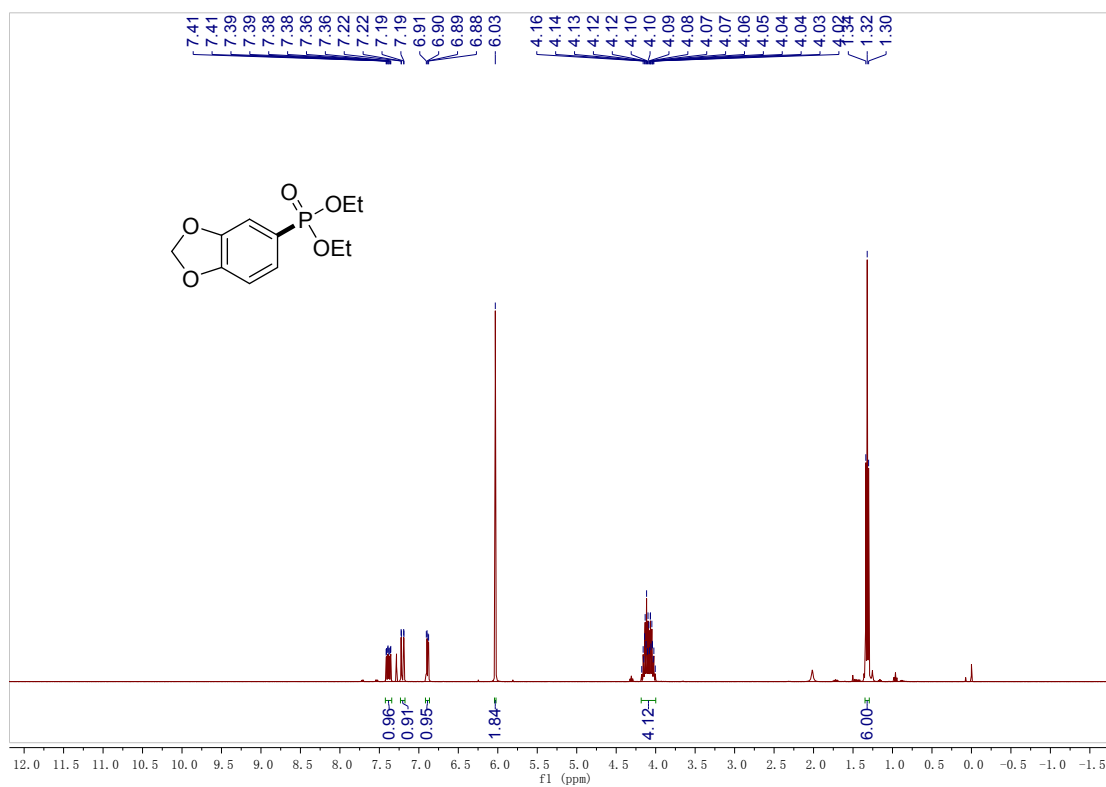
^1H NMR spectrum of compound **3m**



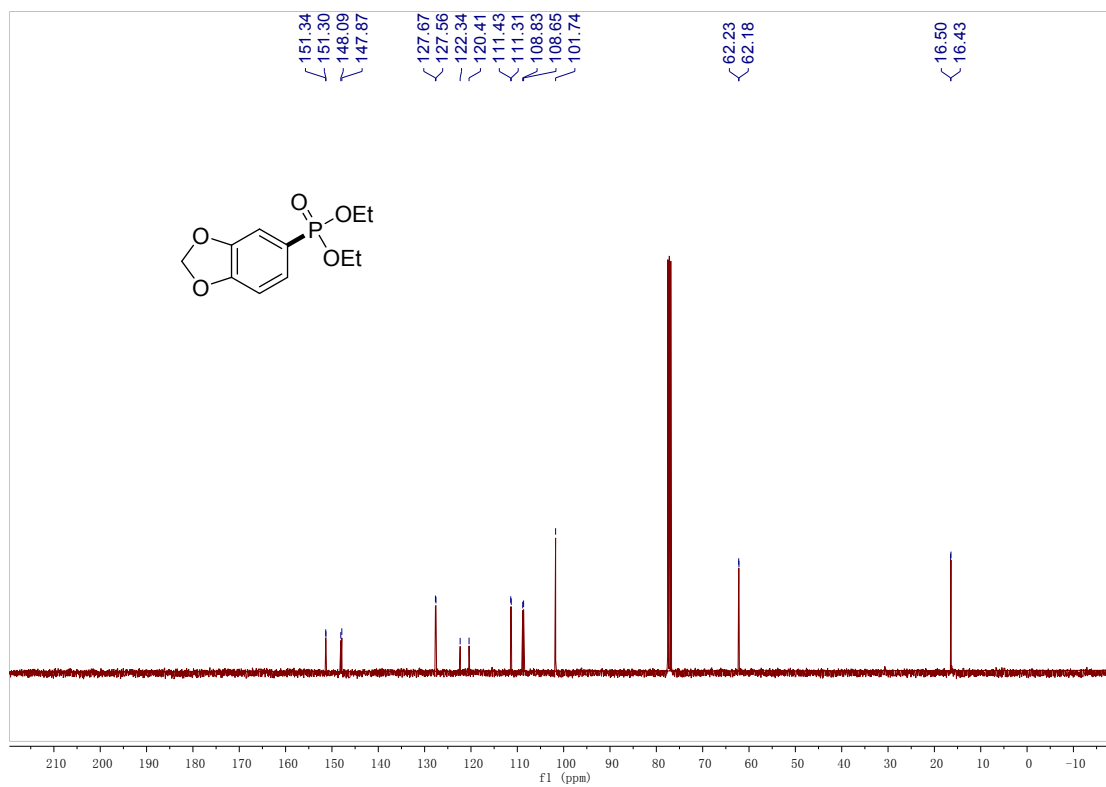
^{13}C NMR spectrum of compound **3m**



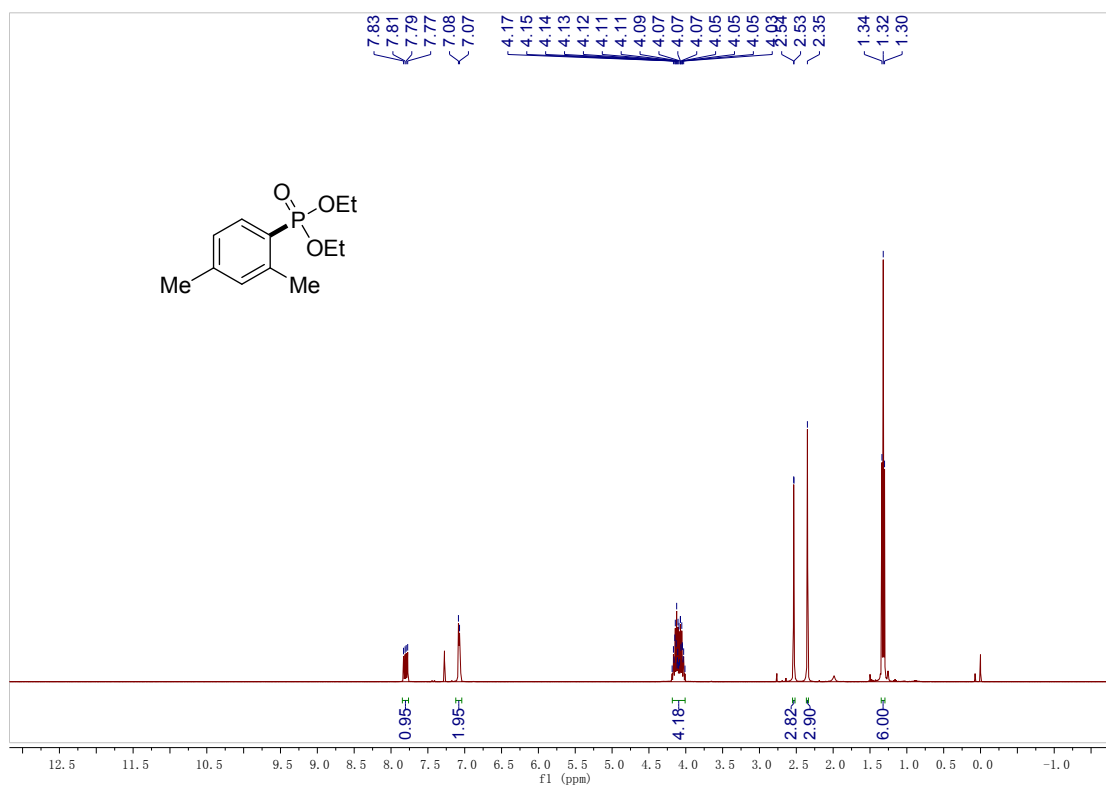
^1H NMR spectrum of compound **3n**



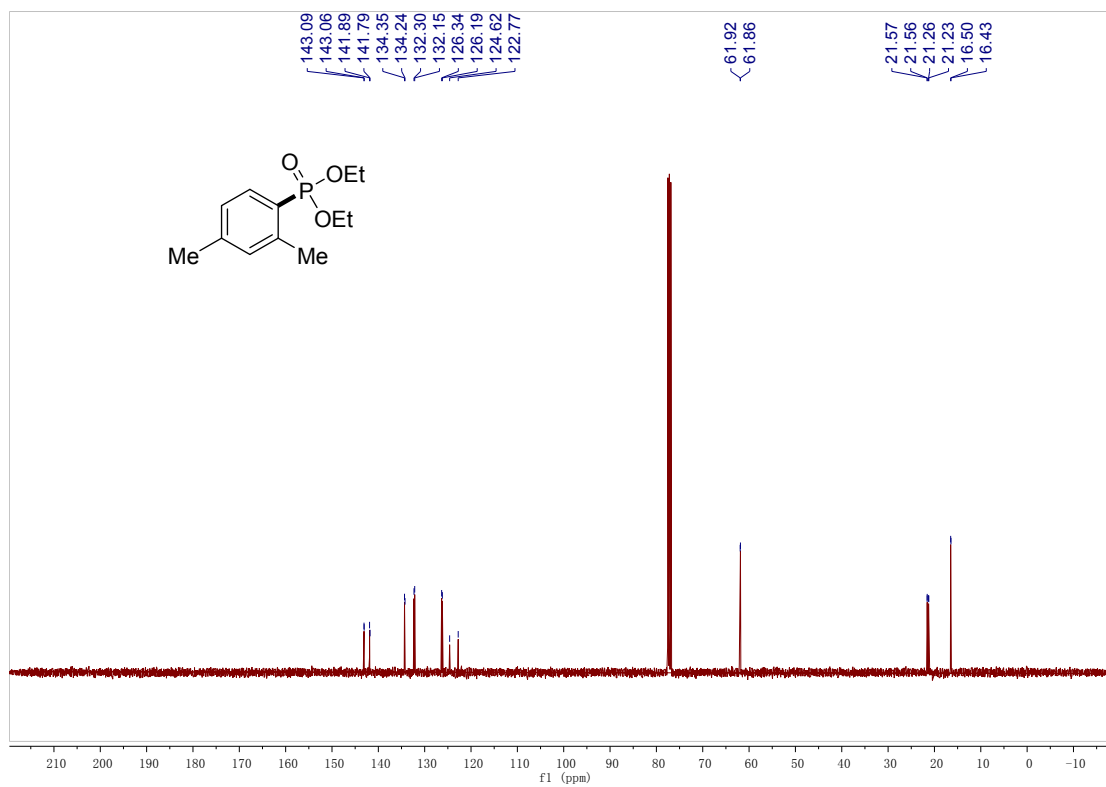
¹³C NMR spectrum of compound **3n**



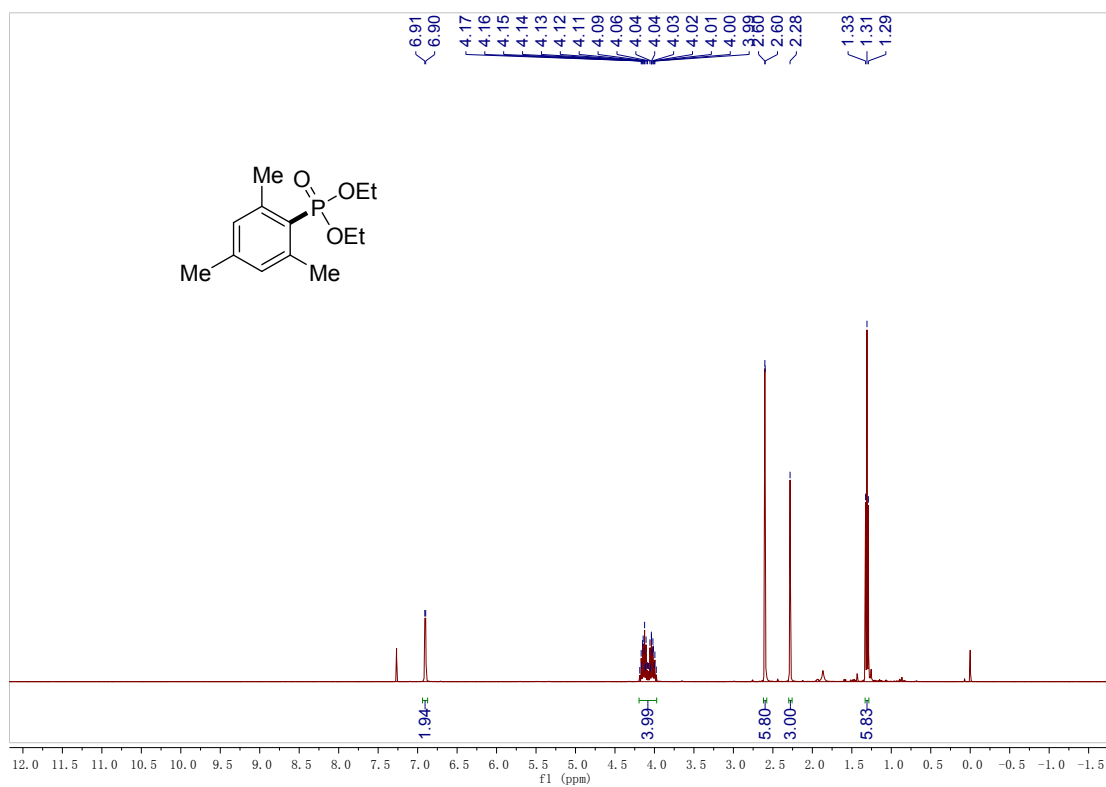
¹H NMR spectrum of compound **3o**



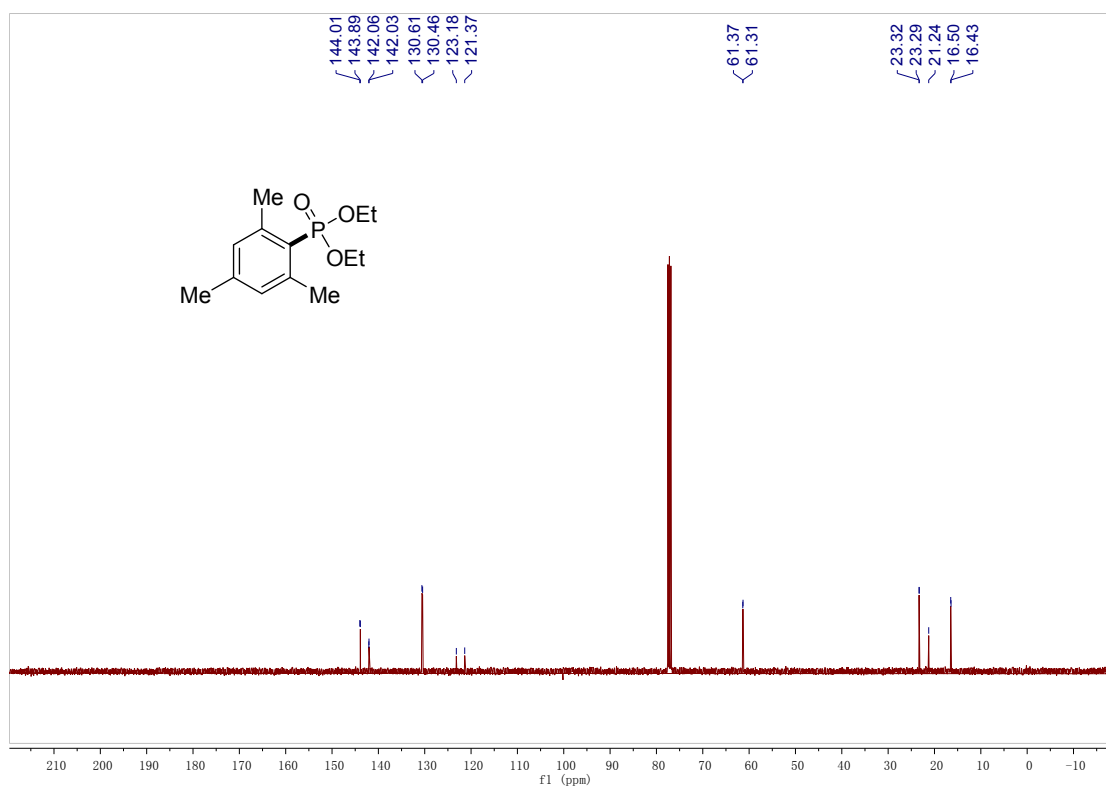
¹³C NMR spectrum of compound **3o**



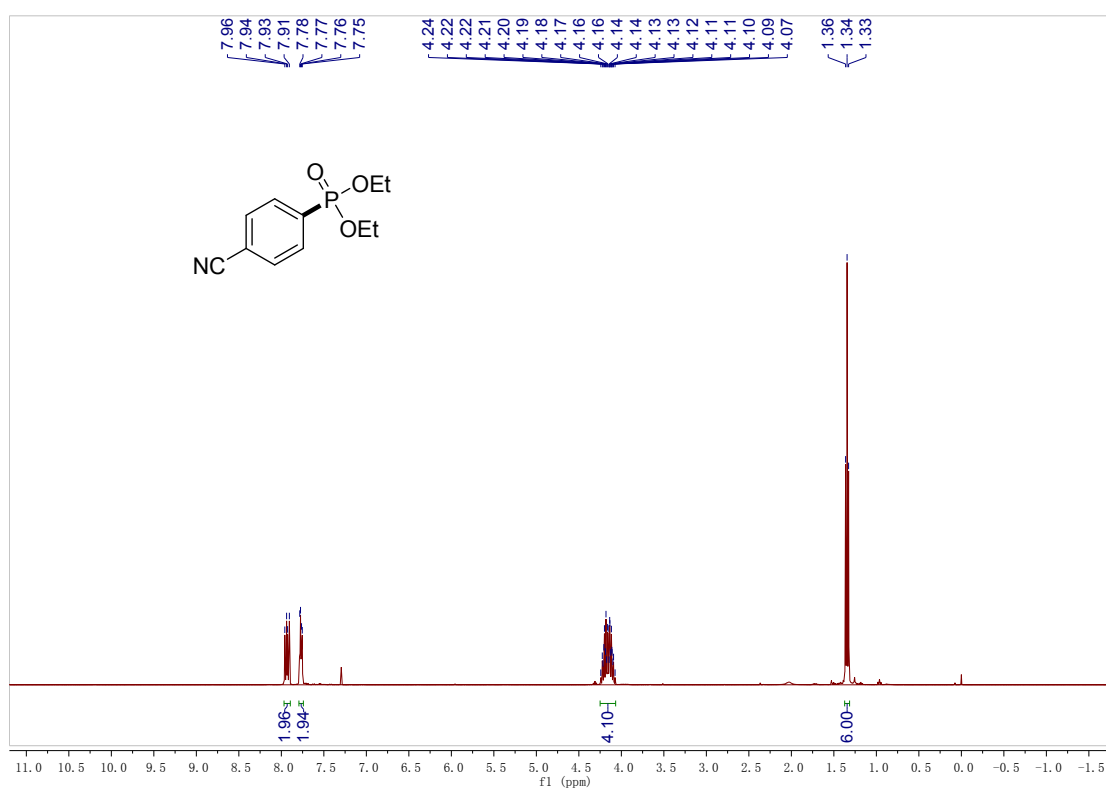
¹H NMR spectrum of compound **3p**



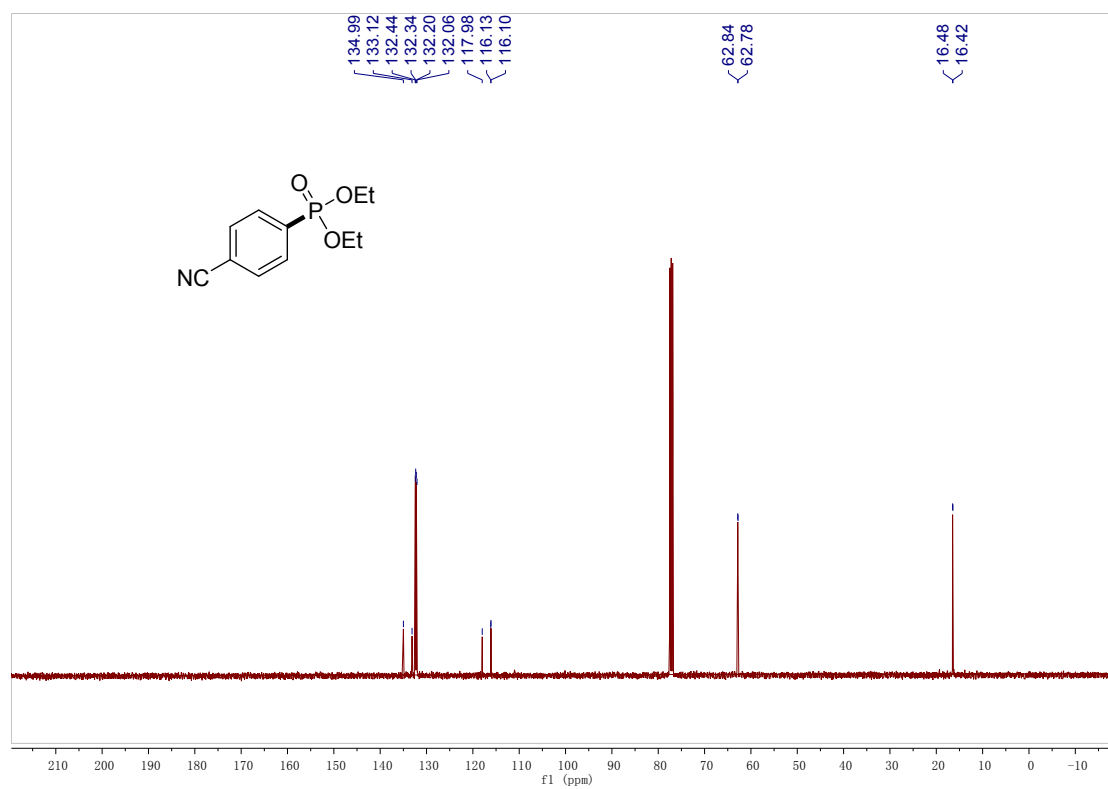
¹³C NMR spectrum of compound **3p**



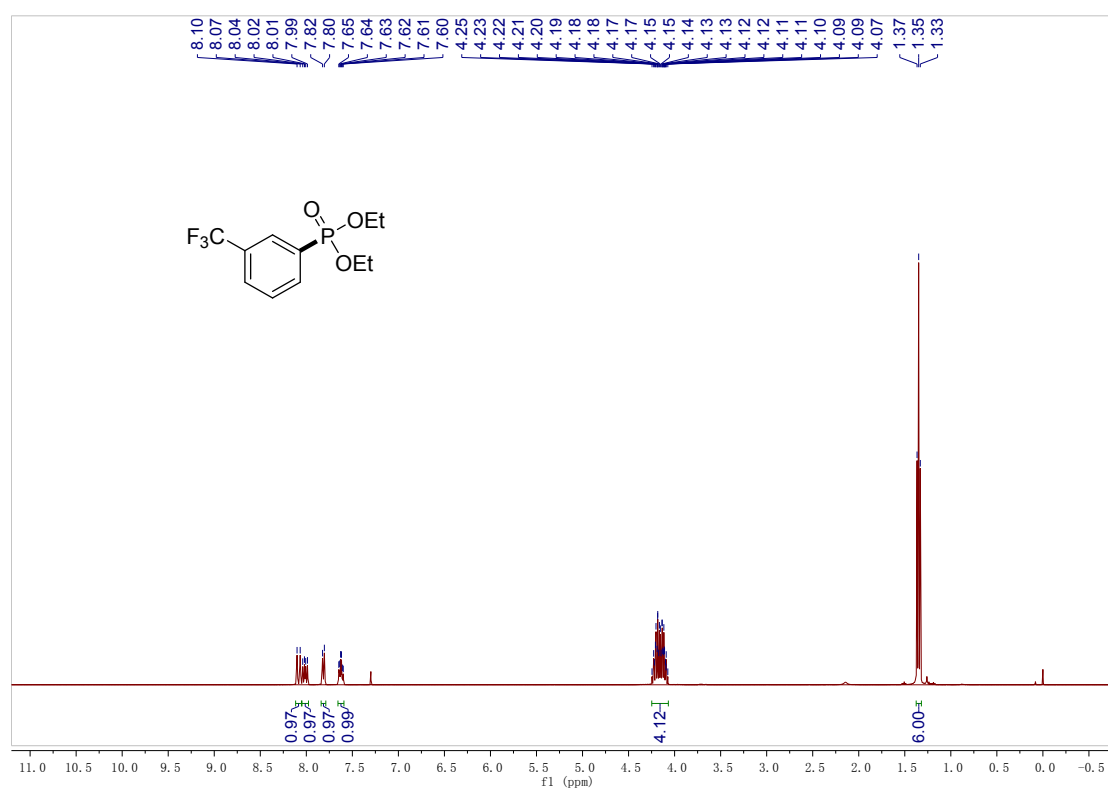
¹H NMR spectrum of compound **3q**



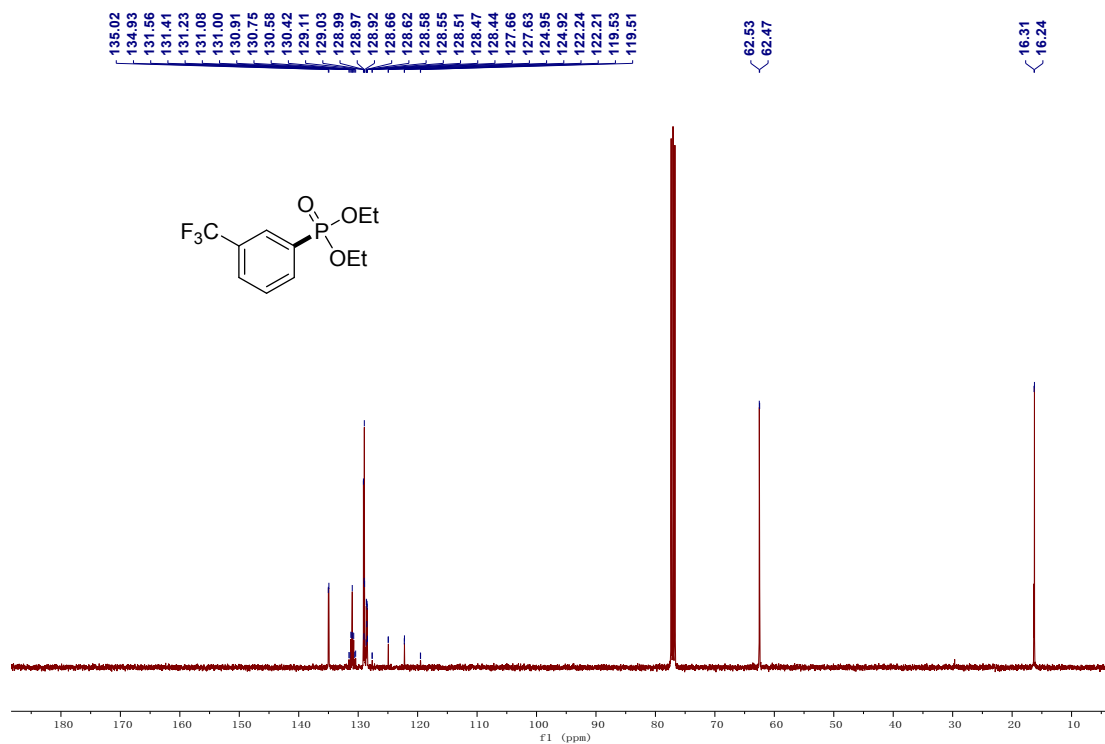
¹³C NMR spectrum of compound **3q**



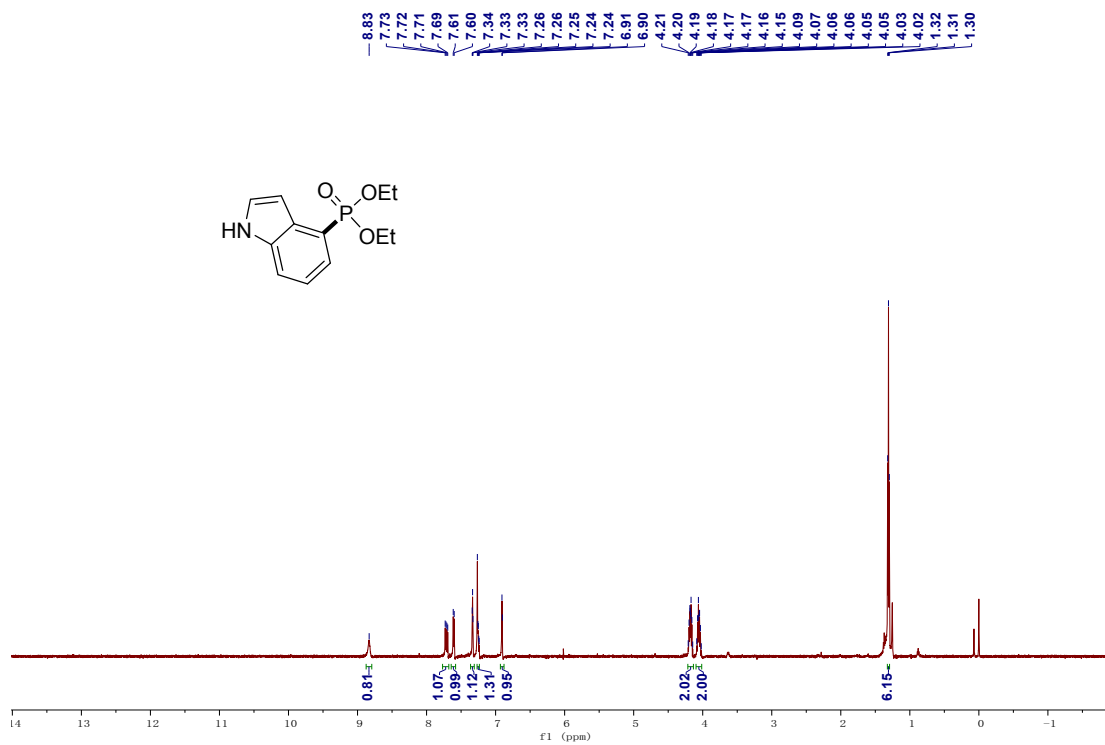
¹H NMR spectrum of compound **3r**



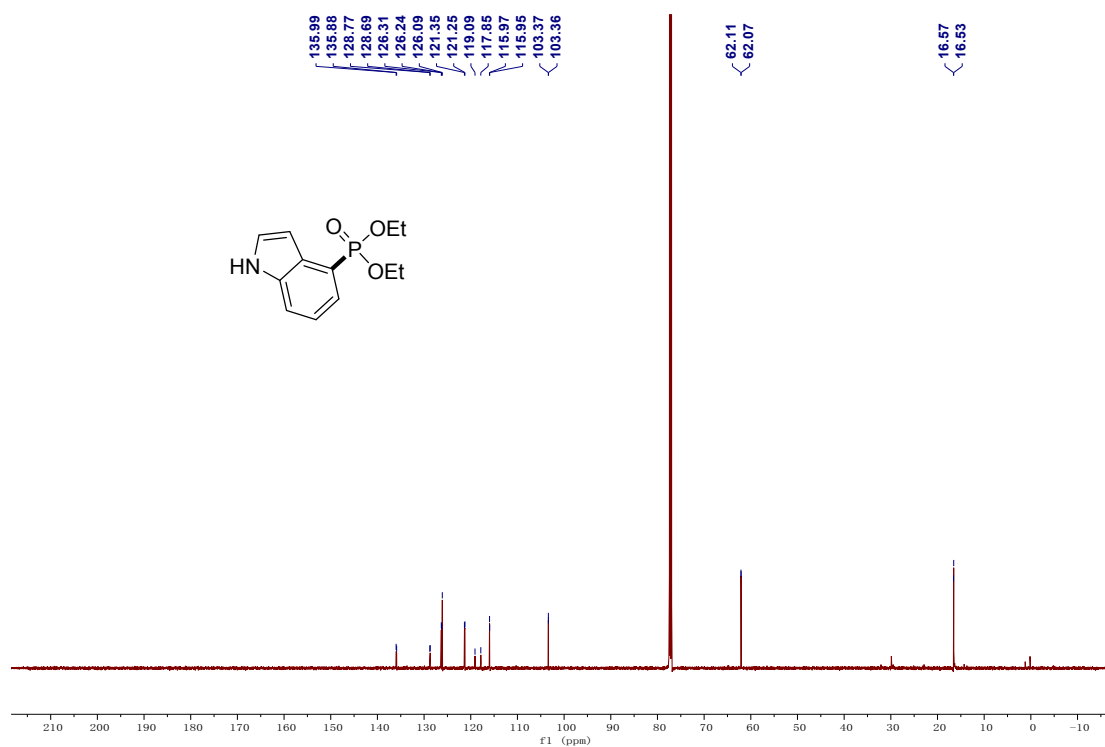
¹³C NMR spectrum of compound **3r**



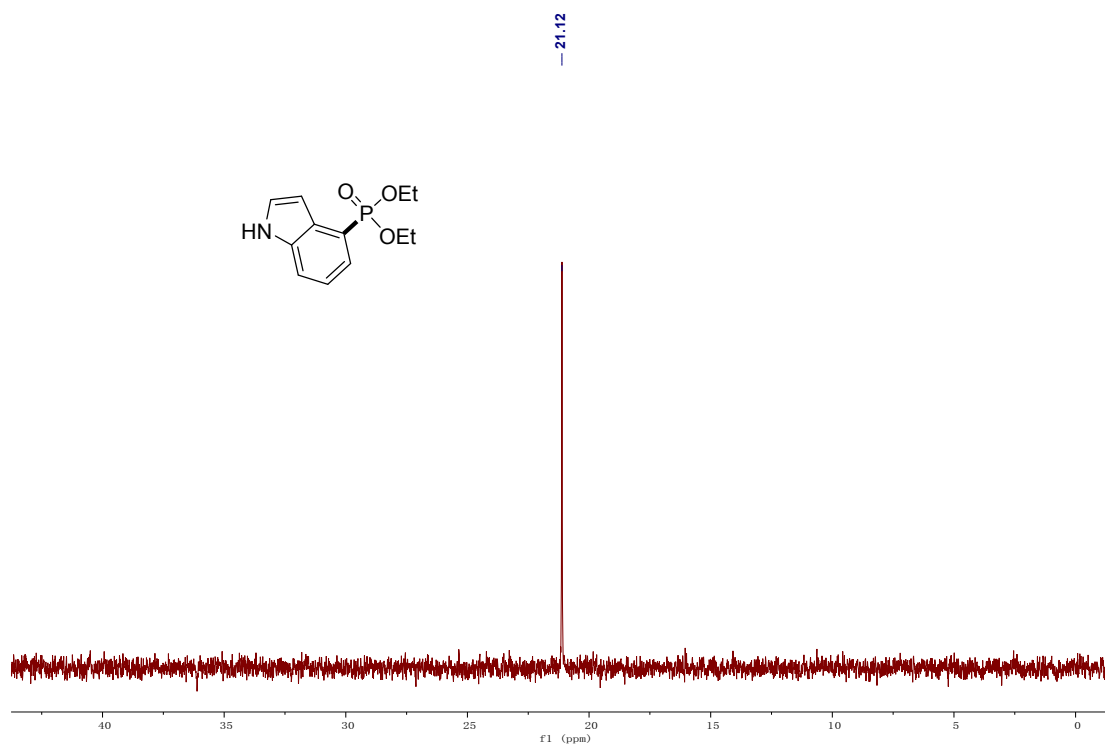
¹H NMR spectrum of compound **3s**



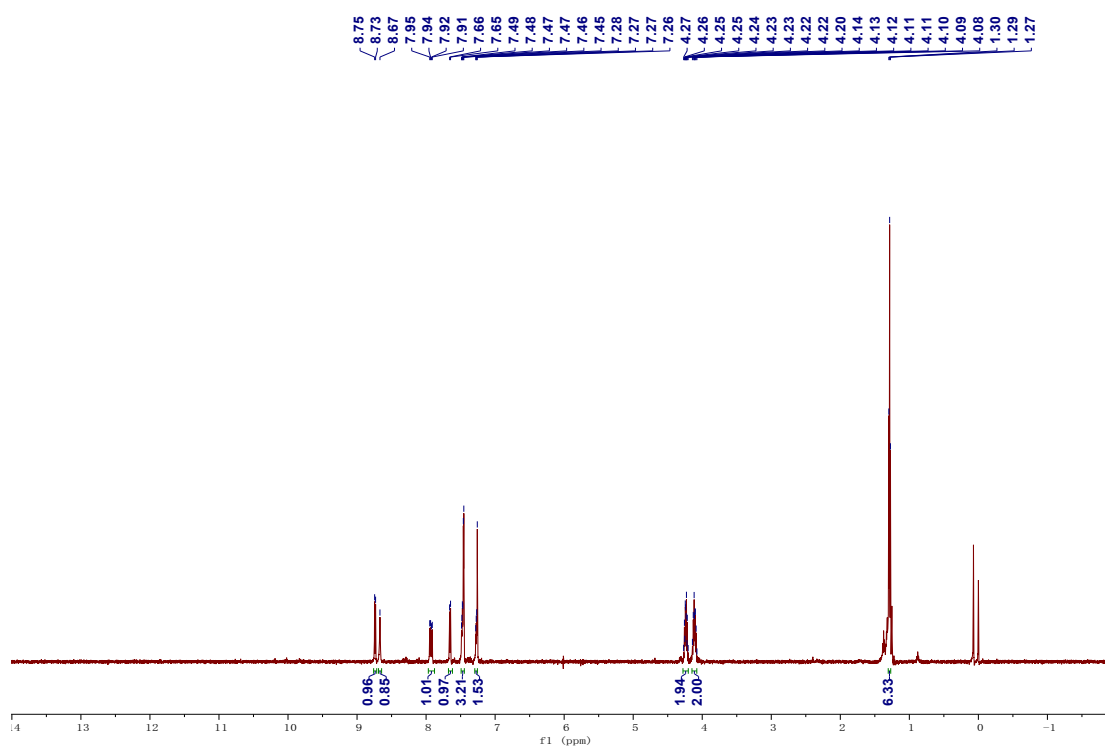
¹³C NMR spectrum of compound 3s



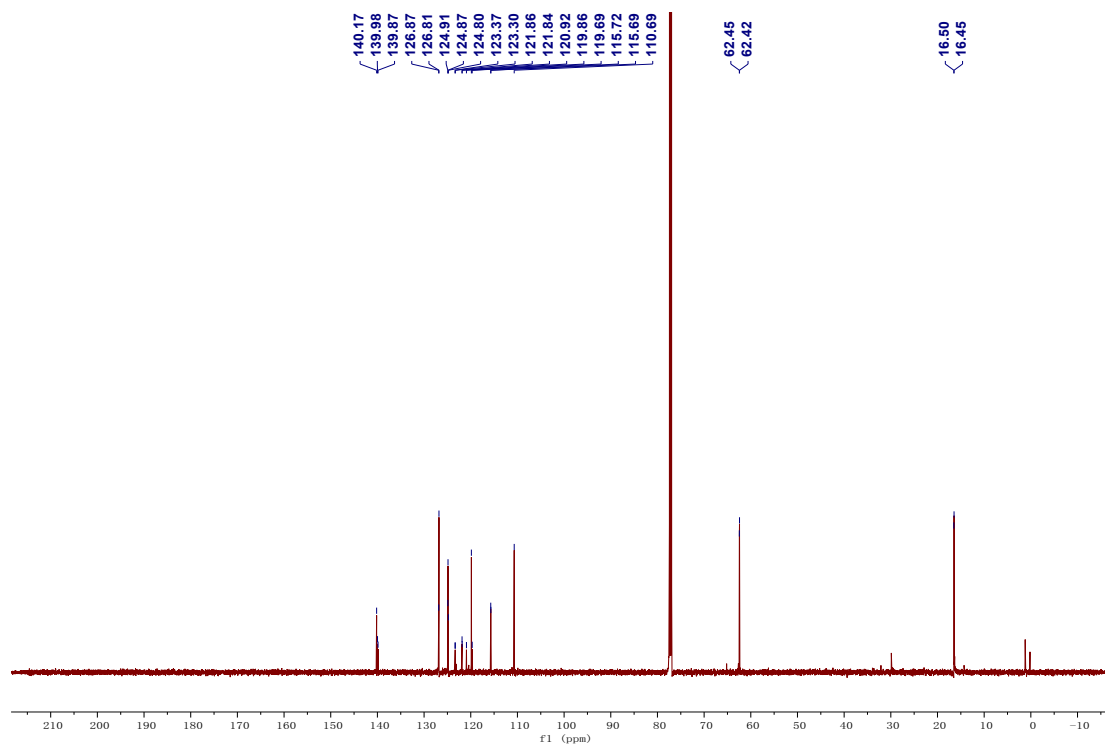
³¹P NMR spectrum of compound 3s



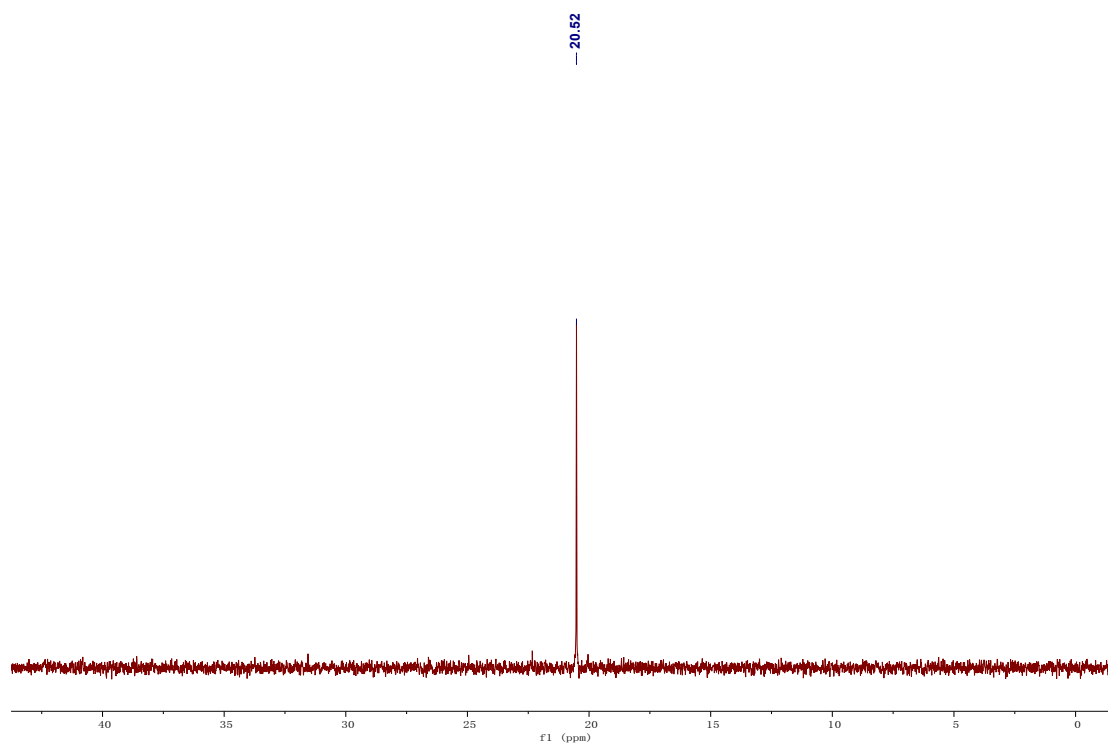
¹H NMR spectrum of compound 3t



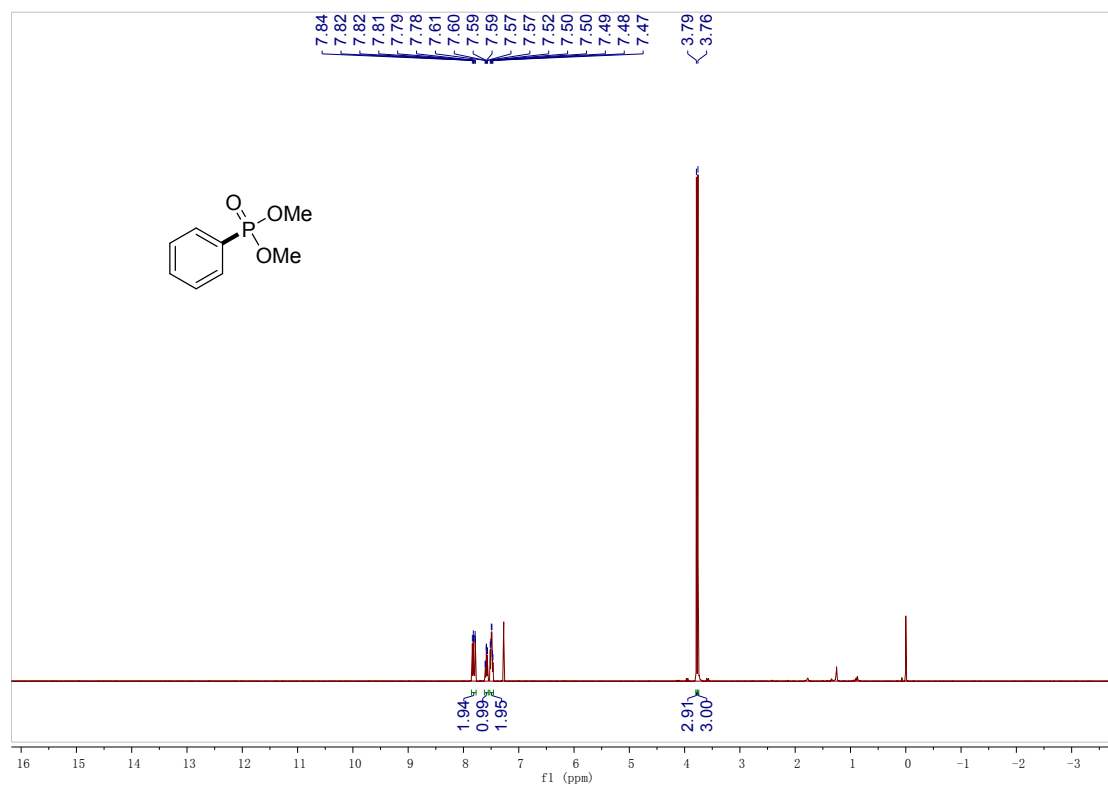
¹³C NMR spectrum of compound 3t



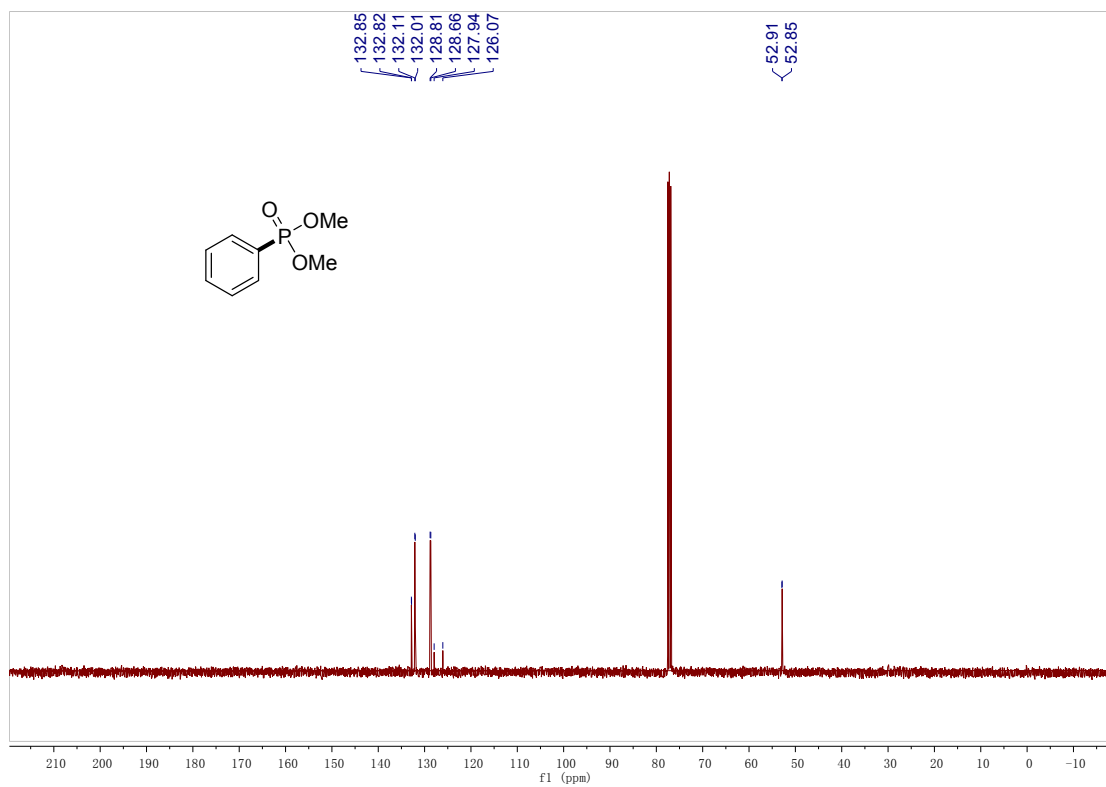
^{31}P NMR spectrum of compound **3t**



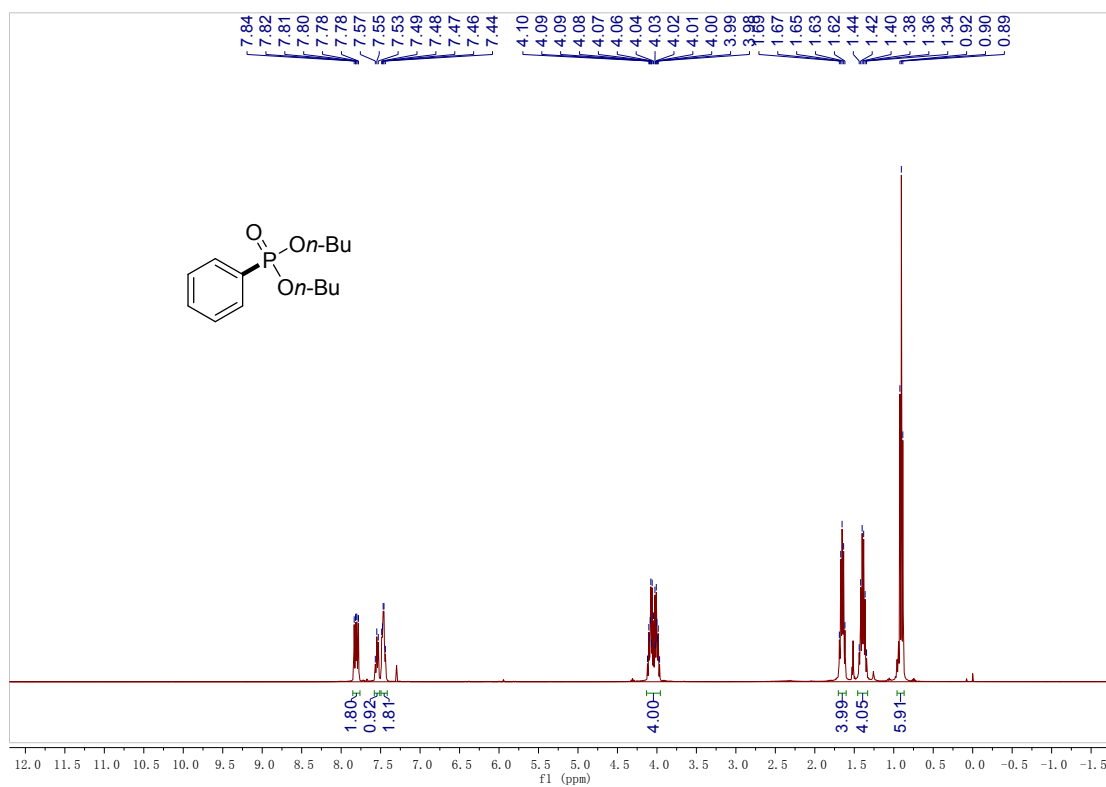
^1H NMR spectrum of compound **3u**



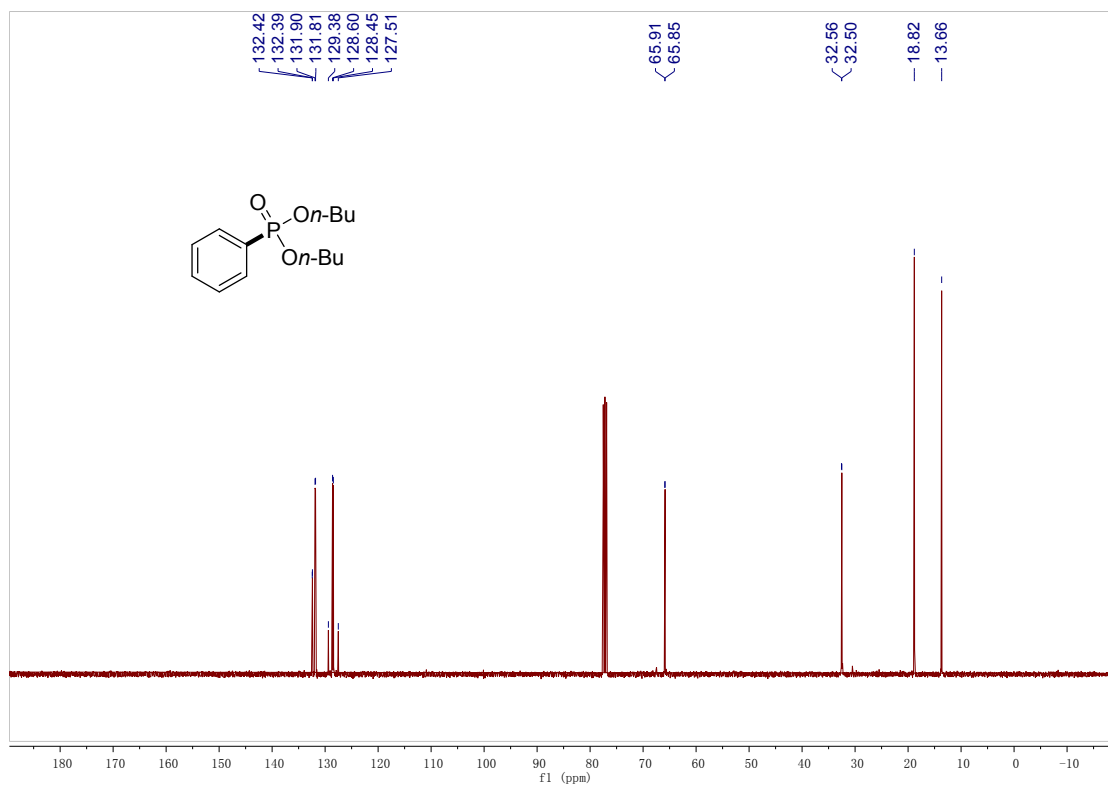
¹³C NMR spectrum of compound **3u**



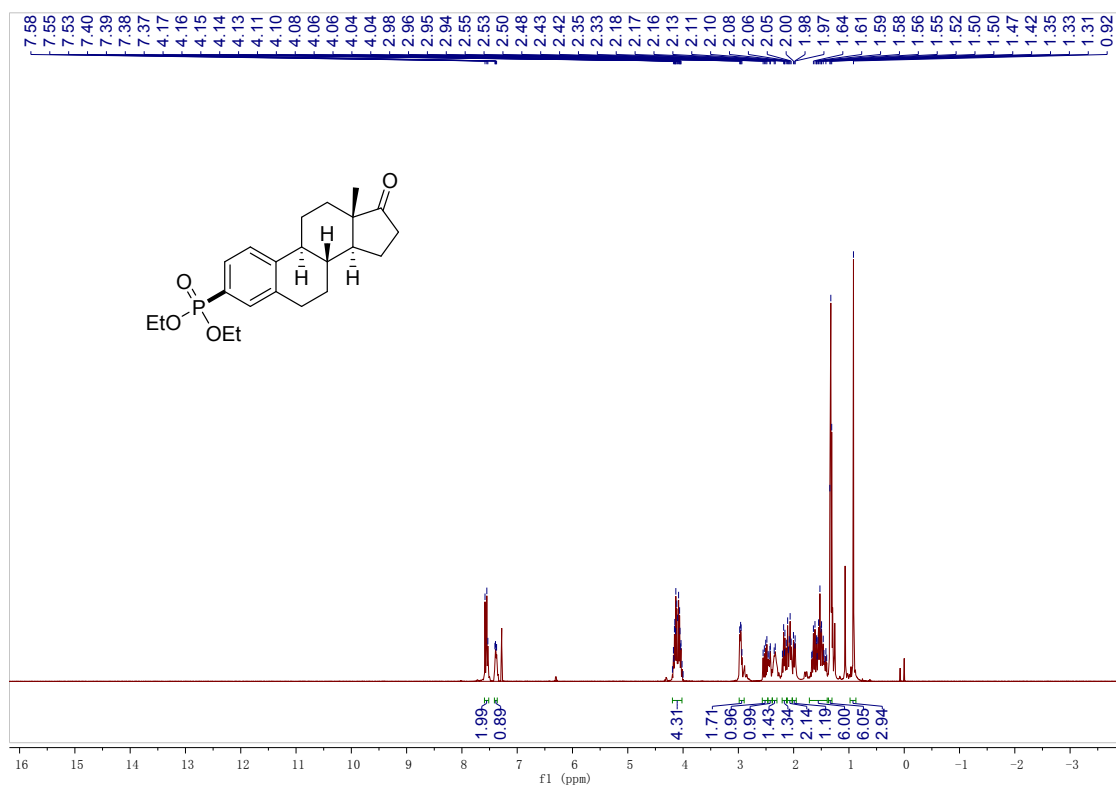
¹H NMR spectrum of compound **3v**



¹³C NMR spectrum of compound **3v**



¹H NMR spectrum of compound **3w**



¹³C NMR spectrum of compound **3x**

