

Supporting Information

Novel Lanthanide Amides Incorporating Neutral Pyrrole Ligand in a Constrained Geometry Architecture: Synthesis, Characterization, Reaction and Catalytic Activity

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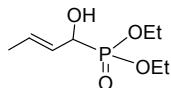
EXPERIMENTAL SECTION

1. General Considerations

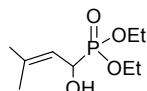
All syntheses and manipulations of air- and moisture-sensitive materials were performed under dry argon and oxygen-free atmosphere using standard Schlenk techniques or in a glovebox. All solvents were refluxed and distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}^{\text{III}}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ ($\text{Ln} = \text{Nd}, \text{Sm}, \text{La}$ and Y),¹ 2-[$(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{NCH}$]C₄H₃NH and 2-($t\text{BuNCH}_2$)C₄H₃NH were prepared according to literature methods.² Acetonylacetone and N-Phenylethylenediamine were purchased and used without purification. Solid α, β -unsaturated carbonyl derivatives were used directly, and liquid derivatives were distilled before use. Elemental analyses were obtained on a Perkin-Elmer 2400 Series II elemental analyzer. ¹H NMR, ¹³C NMR and ³¹P NMR spectra were recorded on a Bruker AV-300 NMR spectrometer (300 MHz for ¹H; 75.0 MHz for ¹³C; 121 MHz for ³¹P NMR) in C₆D₆ for lanthanide complexes and in CDCl₃ for organic compounds. Chemical shifts (δ) were reported in ppm. J values are reported in Hz. IR spectra were recorded on a Shimadzu FTIR-8400s spectrometer (KBr pellet). Mass spectra were performed on a Micromass GCT-MS spectrometer. Melting points were determined in capillaries and were uncorrected.

General procedure for hydrophosphonylation of α, β -unsaturated carbonyl derivatives. (9c as an example). A 30.0 mL Schlenk tube was charged with the complex **3** (13.5 mg, 0.02 mmol), diethyl phosphite (1.657 g, 2.4 mmol) and solvent-free or solvent (2.0 mL), then cinnamaldehyde (1.061 g, 2.0 mmol) was added to the mixture. The mixture was stirred at room temperature for 20 min. After the reaction was completed, the reaction mixture was hydrolyzed by water, extracted with ethyl ether, dried over anhydrous sodium sulfate and then filtered. After the solvent was removed under the reduced pressure, the final products were further purified by recrystallization from ethyl acetate. Compound **9c** was isolated as white crystals (0.530 g, 98 %).

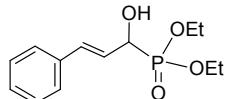
II ^1H and ^{13}C NMR, HRMS Data of Phosphonates



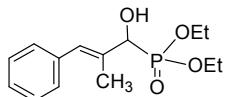
Diethyl 1-hydroxybut-2-enylphosphonate (9a) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 5.82-5.78 (m, 1H), 5.57-5.52 (m, 1H), 4.35-4.40 (m, 1H), 4.15-4.06 (m, 4H), 2.79 (br, 1H), 1.70 (s, 3H), 1.29-1.24 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 129.2 (d, $J = 13.5$ Hz), 125.5 (d, $J = 3.0$ Hz), 68.8 (d, $J = 153.7$ Hz), 62.6 (d, $J = 2.2$ Hz), 62.5 (d, $J = 7.1$ Hz), 17.5 (d, $J = 7.1$ Hz), 16.1 (d, $J = 5.2$ Hz). ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 23.2. HRMS (ESI) calcd. for $\text{C}_8\text{H}_{18}\text{O}_4\text{P}$ [$\text{M}+\text{H}^+$]: 209.0943, found: 209.0935.



Diethyl 1-hydroxy-3-methylbut-2-enylphosphonate (9b) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 5.31 (s, 1H), 4.62 (s, 1H), 4.17-4.12 (m, 4H), 3.29 (s, 1H), 1.74 (d, 6H, $J = 22.5$ Hz), 1.32-1.31 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 138.0 (d, $J = 14.1$ Hz), 119.8 (d, $J = 2.55$ Hz), 65.3 (d, $J = 163.5$ Hz), 62.5 (d, $J = 7.0$ Hz), 62.4 (d, $J = 7.2$ Hz), 25.6 (d, $J = 1.8$ Hz), 18.3, 16.2 (d, $J = 6.0$ Hz). ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 24.0. HRMS (ESI) calcd. for $\text{C}_9\text{H}_{20}\text{O}_4\text{P}$ [$\text{M}+\text{H}^+$]: 223.1099, found: 223.1091.

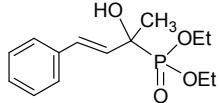


Diethyl 1-hydroxy-3-phenylallylphosphonate (9c) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.35-7.20 (m, 5H), 6.72 (d, H, $J = 15.9$ Hz), 6.30-6.22 (m, 1H), 4.63-4.59 (m, H), 4.15-4.03 (m, 4H), 1.26 (d, $J = 6.4$ Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 136.3 (d, $J = 3.0$ Hz), 131.8 (d, $J = 13.5$ Hz), 128.3, 127.5, 126.3 (d, $J = 1.3$ Hz), 124.1 (d, $J = 3.7$ Hz), 69.1 (d, $J = 161.2$ Hz), 63.1 (d, $J = 7.5$ Hz), 62.8 (d, $J = 7.2$ Hz), 16.2 (d, $J = 6.0$ Hz).

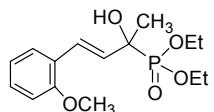


Diethyl 1-hydroxy-2-methyl-3-phenylallylphosphonate (9d) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.28-7.19 (m, 5H), 6.62 (s, 1H), 4.46 (d, $J = 12.3$ Hz, 1H), 4.11-4.16 (m, 4H), 2.80 (s, br, 1H), 1.96 (s, 3H), 1.27-1.31 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 137.2 (d, $J = 3.0$ Hz), 133.6 (d, $J = 4.5$ Hz), 128.9 (d, $J = 2.5$ Hz), 128.0, 127.8 (d, $J = 12.0$ Hz), 126.5,

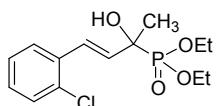
73.7 (d, $J = 156.0$ Hz), 63.2 (d, $J = 6.7$ Hz), 62.8 (d, $J = 7.5$ Hz), 16.4 (d, $J = 5.2$ Hz), 15.3 (d, $J = 1.5$ Hz). ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 24.1. HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{22}\text{O}_4\text{P}$ [$\text{M}+\text{H}^+$]: 285.1255, found: 285.1246.



Diethyl 2-hydroxy-4-phenylbut-3-en-2-ylphosphonate (9e)^[4] ^1H NMR (300 MHz, CDCl_3 , ppm): δ = 7.35-7.20 (m, 5H), 6.70 (d, $J = 15.6$ Hz, 1H), 6.30 (d, $J = 15.9$ Hz, 1H), 4.56 (m, H), 4.12 (t, $J = 5.7$ Hz, 4H), 3.21 (s, br, 1H), 1.55 (d, $J = 15.6$ Hz, 3H), 1.28-1.23 (m, 6H). $^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3 , ppm): δ 136.6, 129.6 (d, $J = 10.5$ Hz), 129.4, 128.4, 127.5, 126.5 (d, $J = 0.7$ Hz), 72.7 (d, $J = 157.5$ Hz), 63.3 (d, $J = 7.5$ Hz), 63.0 (d, $J = 7.5$ Hz), 23.9, 16.4 (d, $J = 3.7$ Hz).

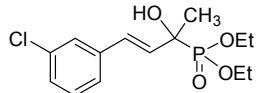


Diethyl 2-hydroxy-4-(2-methoxyphenyl)but-3-en-2-ylphosphonate (9f) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.37 (d, $J = 5.4$ Hz, 1H), 7.19 (s, 1H), 7.02 (d, $J = 16.2$ Hz, 1H), 6.81-6.78 (m, 2H), 6.33 (d, $J = 15.9$ Hz, 1H), 4.12-4.10 (m, 4H), 3.76 (s, 3H), 1.55 (d, $J = 15.6$ Hz, 3H), 1.25-1.24 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 156.5, 129.9, 128.3, 126.6, 125.5 (d, $J = 3.1$ Hz), 124.5 (d, $J = 10.5$ Hz), 120.2, 110.5, 72.5 (d, $J = 160.6$ Hz), 63.1 (d, $J = 7.3$ Hz), 62.7 (d, $J = 7.3$ Hz), 55.0, 23.4, 16.2 (d, $J = 3.7$ Hz), 16.1 (d, $J = 3.7$ Hz). ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 24.5. HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{24}\text{O}_5\text{P}$ [$\text{M}+\text{H}^+$]: 315.1361, found: 315.1355.

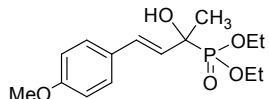


Diethyl 4-(2-chlorophenyl)-2-hydroxybut-3-en-2-ylphosphonate (9g) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.55-7.52 (m, 1H), 7.37-7.34 (m, 1H), 7.22-7.13 (m, 3H), 6.36 (d of d, $J = 4.2$ Hz, 1H), 4.26-4.14 (m, 4H), 1.88 (br, 1H), 1.64 (d, $J = 15.6$ Hz, 3H), 1.33 (t, $J = 6.9$ Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 134.8 (d, $J = 3.1$ Hz), 133.1 (d, $J = 2.3$ Hz), 132.6, 129.5, 128.5, 126.9 (d, $J = 1.7$ Hz), 126.6, 126.1 (d, $J = 10.4$ Hz), 72.7 (d, $J = 160.8$ Hz), 63.4 (d, $J = 7.5$ Hz), 63.0 (d, $J = 7.6$ Hz), 23.6, 16.4 (d, $J = 1.7$ Hz), 16.3 (d, $J = 1.7$ Hz). ^{31}P NMR

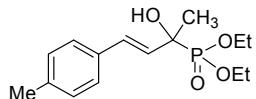
(121 MHz, CDCl₃, ppm): δ 27.5. HRMS (ESI) calcd. for C₁₄H₂₁O₄PCl [M+H⁺]: 319.0866, found: 319.0857.



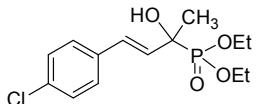
Diethyl 4-(3-chlorophenyl)-2-hydroxybut-3-en-2-ylphosphonate (9h) ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.39 (s, 1H), 7.24-7.22 (m, 3H), 6.73 (d of d, J = 11.1 Hz, 1H), 6.37 (d of d, J = 4.8 Hz, 1H), 4.22-4.15 (m, 4H), 3.61 (br, 1H), 1.61 (d, J = 15.6 Hz, 3H), 1.36-1.31 (m, 6H). ¹³C NMR (75 MHz, CDCl₃, ppm): 138.5 (d, J = 3.1 Hz), 134.2, 131.1, 129.5, 128.2 (d, J = 3.1 Hz), 127.2, 126.1, 124.6, 72.3 (d, J = 161.4 Hz), 63.2 (d, J = 7.5 Hz), 62.9 (d, J = 7.6 Hz), 23.6, 16.3 (d, J = 2.3 Hz), 16.2 (d, J = 2.4 Hz). ³¹P NMR (121 MHz, CDCl₃, ppm): δ 24.1. HRMS (ESI) calcd. for C₁₄H₂₁O₄PCl [M+H⁺]: 319.0866, found: 319.0859.



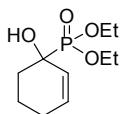
Diethyl 2-hydroxy-4-(4-methoxyphenyl)but-3-en-2-ylphosphonate (9i) ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.47-7.45 (m, 1H), 7.30-7.27 (m, 1H), 7.17-7.05 (m, 3H), 6.28 (d of d, J = 4.5 Hz, 1H), 4.16-4.09 (m, 4H), 3.68-3.61 (m, 3H), 2.00 (br, 1H), 1.56 (d, J = 15.9 Hz, 3H), 1.27-1.14 (m, 6H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 159.2, 129.3, 129.2, 127.7, 126.9, 113.8, 72.6 (d, J = 161.2 Hz), 63.24 (d, J = 7.5 Hz), 55.2, 23.9, 16.4. ³¹P NMR (121 MHz, CDCl₃, ppm): δ 24.7. HRMS (ESI) calcd. for C₁₅H₂₄O₅P [M+H⁺]: 315.1361, found: 315.1354.



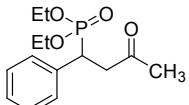
Diethyl 2-hydroxy-4-p-tolylbut-3-en-2-ylphosphonate (9j) ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.29 (d, J = 7.5 Hz, 1H), 7.12 (d, J = 7.5 Hz, 1H), 6.74 (d of d, J = 4.8 Hz, 1H), 6.31 (d of d, J = 4.8 Hz, 1H), 4.21-4.15 (m, 4H), 3.50 (br, 1H), 2.33 (s, 3H), 1.61 (d, J = 15.6 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ 137.2, 133.7 (d, J = 3.2 Hz), 129.5 (d, J = 10.4 Hz), 129.0, 128.3, 126.3 (d, J = 10.4 Hz), 72.4 (d, J = 161.3 Hz), 63.1 (d, J = 7.5 Hz), 63.0 (d, J = 7.5 Hz), 23.7 (d, J = 1.4 Hz), 21.0, 16.3 (d, J = 1.9 Hz), 16.2 (d, J = 1.9 Hz). ³¹P NMR (121 MHz, CDCl₃, ppm): δ 24.5. HRMS (ESI) calcd. for C₁₅H₂₄O₄P [M+H⁺]: 299.1412, found: 299.1405.



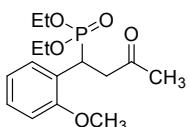
Diethyl 4-(4-chlorophenyl)-2-hydroxybut-3-en-2-ylphosphonate (9k) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.24-7.19 (m, 4H), 6.65 (d, $J = 16.2$ Hz, 2H), 6.26 (d, $J = 15.6$ Hz, 2H), 4.11 (m, 4H), 3.14 (br, 1H), 1.54 (d, $J = 15.6$ Hz, 3H), 1.26 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 135.1 (d, $J = 3.1$ Hz), 133.1, 130.1, 128.5, 128.4, 127.7 (d, $J = 1.3$ Hz), 72.5 (d, $J = 161.1$ Hz), 63.3 (d, $J = 7.5$ Hz), 63.2 (d, $J = 7.5$ Hz), 23.8, 16.4 (d, $J = 3.7$ Hz) ppm. ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 24.2. HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{21}\text{O}_4\text{PCl} [\text{M}+\text{H}^+]$: 319.0866, found: 319.0858.



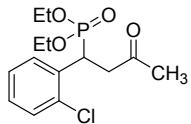
Diethyl 1-hydroxycyclohex-2-enylphosphonate (9l) ^5H NMR (300 MHz, CDCl_3 , ppm): δ 6.08 (s, 1H), 5.84 (s, 1H), 4.19 (d, $J = 6.9$ Hz, 4H), 3.17 (br, 1H), 2.01-1.89 (m, 4H), 1.77 (s, 3H), 1.33 (d, $J = 5.4$ Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 133.5 (d, $J = 13.1$ Hz), 125.3, 68.8 (d, $J = 166.1$ Hz), 62.8 (d, $J = 7.2$ Hz), 30.5 (d, $J = 3.1$ Hz), 24.6, 17.2 (d, $J = 7.4$ Hz), 16.2 (d, $J = 2.4$ Hz), 16.2 (d, $J = 2.6$ Hz).



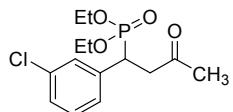
Diethyl 3-oxo-1-phenylbutylphosphonate (10a) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.29-7.15 (m, 5H), 3.96-3.59 (m, 5H), 3.09-3.03 (m, 2H), 2.01 (s, 3H), 1.20 (t, $J = 6.9$ Hz, 3H), 1.00 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 204.6 (d, $J = 14.4$ Hz), 135.5 (d, $J = 6.9$ Hz), 128.9 (d, $J = 6.5$ Hz), 128.2 (d, $J = 2.6$ Hz), 127.0 (d, $J = 3.2$ Hz), 62.6 (d, $J = 6.9$ Hz), 61.8 (d, $J = 7.3$ Hz), 43.4 (d, $J = 1.9$ Hz), 38.6 (d, $J = 139.2$ Hz), 30.1, 16.1 (d, $J = 5.9$ Hz), 15.9 (d, $J = 5.8$ Hz). ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 28.6. HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{22}\text{O}_4\text{P} [\text{M}+\text{H}^+]$: 285.1255, found: 285.1248.



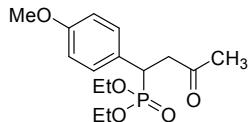
Diethyl 1-(2-methoxyphenyl)-3-oxobutylphosphonate (10b) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.34 (d, $J = 7.2$ Hz, 1H), 7.21 (t, $J = 7.2$ Hz, 1H), 4.46-4.33 (m, 1H), 4.11-4.02 (m, 2H), 3.95-3.70 (m, 5H), 3.23-3.01 (m, 2H), 2.08 (s, 3H), 1.27 (t, $J = 7.2$ Hz, 3H), 1.09 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 204.7 (d, $J = 14.3$ Hz), 158.6 (d, $J = 7.1$ Hz), 128.3 (d, $J = 4.9$ Hz), 127.9 (d, $J = 3.1$ Hz), 124.0 (d, $J = 7.0$ Hz), 120.3 (d, $J = 3.0$ Hz), 110.6 (d, $J = 2.3$ Hz), 62.1 (d, $J = 7.0$ Hz), 61.6 (d, $J = 6.8$ Hz), 55.4, 43.3, 30.1 (d, $J = 140.0$ Hz), 29.5, 15.9 (d, $J = 6.1$ Hz), 15.7 (d, $J = 5.9$ Hz). ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 29.0. HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{24}\text{O}_5\text{P} [\text{M}+\text{H}^+]$: 315.1361, found: 315.1353.



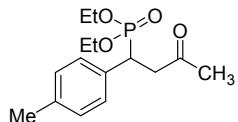
Diethyl 1-(2-chlorophenyl)-3-oxobutylphosphonate (10c) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.46-7.38 (m, 2H), 7.30-7.14 (m, 2H), 4.27-4.11 (m, 4H), 3.89-3.74 (m, 1H), 3.22-3.09 (m, 2H), 2.10 (s, 3H), 1.31 (t, $J = 6.0$ Hz, 3H), 1.09 (t, $J = 6.3$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 204.2 (d, $J = 14.4$ Hz), 134.8 (d, $J = 8.7$ Hz), 133.7 (d, $J = 6.5$ Hz), 129.5 (d, $J = 2.3$ Hz), 129.0 (d, $J = 4.5$ Hz), 128.1 (d, $J = 3.1$ Hz), 126.8 (d, $J = 3.1$ Hz), 62.7 (d, $J = 7.0$ Hz), 62.1 (d, $J = 7.0$ Hz), 43.7, 34.3 (d, $J = 139.8$ Hz), 29.7, 16.1 (d, $J = 6.1$ Hz), 15.9 (d, $J = 5.7$ Hz). ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 27.6. HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{21}\text{O}_4\text{PCl} [\text{M}+\text{H}^+]$: 319.0866, found: 319.0858.



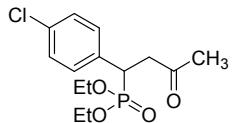
Diethyl 1-(3-chlorophenyl)-3-oxobutylphosphonate (10d) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.34 (s, 1H), 7.27-7.24 (m, 3H), 4.11-3.65 (m, 5H), 3.17-3.054 (m, 2H), 2.11 (s, 3H), 1.29 (t, $J = 7.2$ Hz, 3H), 1.14 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): 204.1 (d, $J = 14.2$ Hz), 137.8 (d, $J = 6.9$ Hz), 134.0, 129.4 (d, $J = 2.3$ Hz), 128.9 (d, $J = 6.5$ Hz), 127.2 (d, $J = 3.0$ Hz), 127.1, 62.6 (d, $J = 6.9$ Hz), 61.9 (d, $J = 7.1$ Hz), 43.3, 38.3 (d, $J = 139.4$ Hz), 30.0, 16.1 (d, $J = 5.9$ Hz), 15.9 (d, $J = 5.8$ Hz). ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 27.7. HRMS (ESI) calcd. for $\text{C}_{14}\text{H}_{21}\text{O}_4\text{PCl} [\text{M}+\text{H}^+]$: 319.0866, found: 319.0859.



Diethyl 1-(4-methoxyphenyl)-3-oxobutylphosphonate (10e) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.19 (s, 2H), 6.76 (d, $J = 7.8$ Hz, 2H), 3.98-3.78 (m, 4H), 3.71 (s, 3H), 3.67-3.54 (m, 1H), 3.06-3.02 (m, 2H), 2.01 (s, 3H), 1.21 (t, $J = 6.9$ Hz, 3H), 1.04 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 204.7 (d, $J = 14.7$ Hz), 158.5 (d, $J = 2.9$ Hz), 129.8 (d, $J = 6.5$ Hz), 127.3 (d, $J = 7.1$ Hz), 113.7 (d, $J = 2.3$ Hz), 62.5 (d, $J = 6.9$ Hz), 61.7 (d, $J = 7.2$ Hz), 54.9, 43.6, 37.8 (d, $J = 140.2$ Hz), 30.1, 16.1 (d, $J = 5.9$ Hz), 16.0 (d, $J = 5.7$ Hz). ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 28.7. HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{24}\text{O}_5\text{P}$ [$\text{M}+\text{H}^+$]: 315.1361, found: 315.1352.

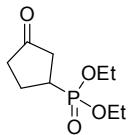


Diethyl 3-oxo-1-p-tolylbutylphosphonate (10f) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.23 (d, $J = 7.8$ Hz, 2H), 7.10 (d, $J = 7.5$ Hz, 2H), 4.06-3.63 (m, 5H), 3.14-3.08 (m, 2H), 2.30 (s, 3H), 2.08 (s, 3H), 1.28 (t, $J = 6.9$ Hz, 3H), 1.11 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 204.8 (d, $J = 14.6$ Hz), 136.7 (d, $J = 3.3$ Hz), 132.3 (d, $J = 7.1$ Hz), 129.0 (d, $J = 2.5$ Hz), 128.7 (d, $J = 6.5$ Hz), 62.6 (d, $J = 7.0$ Hz), 61.8 (d, $J = 7.2$ Hz), 43.6 (d, $J = 1.7$ Hz), 38.3 (d, $J = 139.5$ Hz), 30.2, 20.8, 16.1 (d, $J = 6.0$ Hz), 16.0 (d, $J = 5.8$ Hz). ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 28.7. HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{24}\text{O}_4\text{P}$ [$\text{M}+\text{H}^+$]: 299.1412, found: 299.1406.

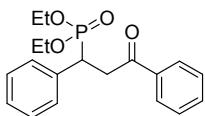


Diethyl 1-(4-chlorophenyl)-3-oxobutylphosphonate (10g) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.20-7.15 (m, 2H), 7.11-6.99 (m, 2H), 3.97-3.76 (m, 4H), 3.70-3.45 (m, 1H), 3.06-2.82 (m, 2H), 1.98 (s, 3H), 1.22-1.12 (m, 3H), 1.05-0.98 (m, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 203.1 (d, $J = 51.7$ Hz), 133.9, 133.6, 132.9, 130.3 (d, $J = 6.2$ Hz), 129.8 (d, $J = 6.2$ Hz), 128.3 (d, $J = 7.9$ Hz), 62.6 (d, $J = 6.6$ Hz), 61.9 (d, $J = 7.2$ Hz), 43.1 (d,

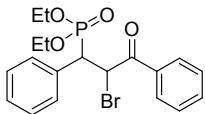
$J = 20.8$ Hz), 38.9 (d, $J = 24.3$ Hz), 37.1 (d, $J = 24.0$ Hz), 15.9. ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 29.3. HRMS (ESI) Calcd. for $\text{C}_{14}\text{H}_{21}\text{O}_4\text{PCl} [\text{M}+\text{H}^+]$: 319.0866, found: 319.0861.



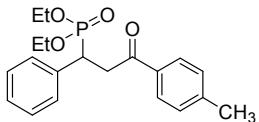
Diethyl 3-oxocyclopentylphosphonate (10h)⁵ ^1H NMR (300 MHz, CDCl_3 , ppm): δ 4.15-4.10 (m, 4H), 2.45-1.90 (m, 7H), 1.31 (t, $J = 6.9$ Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 216.3 (d, $J = 15.6$ Hz), 61.9 (t, $J = 6.9$ Hz), 38.5 (d, $J = 4.6$ Hz), 37.4 (d, $J = 7.7$ Hz), 32.6 (d, $J = 152.5$ Hz), 23.3 (d, $J = 3.6$ Hz), 16.3 (d, $J = 5.7$ Hz).



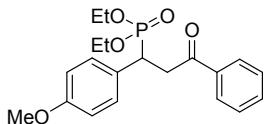
Diethyl 3-oxo-1,3-diphenylpropylphosphonate (10i)⁶ ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.89-7.86 (m, 2H), 7.48-7.26 (m, 1H), 7.37 (m, 3H), 7.25-7.15 (m, 4H), 4.02-3.92 (m, 4H), 3.87-3.82 (m, 1H), 3.76-3.55 (m, 2H), 1.22 (t, $J = 6.9$ Hz, 3H), 1.00 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 196.1 (d, $J = 14.9$ Hz), 136.3, 135.7 (d, $J = 6.7$ Hz), 133.0, 129.0 (d, $J = 6.6$ Hz), 128.4, 128.2 (d, $J = 2.3$ Hz), 127.8, 127.0 (d, $J = 3.0$ Hz), 62.7 (d, $J = 6.9$ Hz), 61.7 (d, $J = 7.2$ Hz), 38.9, 38.7 (d, $J = 139.4$ Hz), 16.2 (d, $J = 6.0$ Hz), 16.0 (d, $J = 5.8$ Hz).



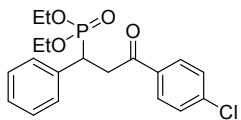
Diethyl 2-bromo-3-oxo-1,3-diphenylpropylphosphonate (10j) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.56 (d, $J = 6.6$ Hz, 4H), 7.70 (d, $J = 6.6$ Hz, 4H), 7.19 (s, 3H), 4.66 (d, $J = 9.3$ Hz, 1H), 4.20-4.13 (m, 4H), 3.48 (s, 1H), 1.23-1.25 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 134.9 (d, $J = 2.5$ Hz), 130.9, 130.7, 129.0 (d, $J = 1.9$ Hz), 128.2, 128.0, 120.3 (d, $J = 2.5$ Hz), 74.3 (d, $J = 161.8$ Hz), 63.8 (d, $J = 7.1$ Hz), 63.3 (d, $J = 7.1$ Hz), 16.4 (d, $J = 2.4$ Hz), 16.3 (d, $J = 2.6$ Hz). ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 20.1. HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{22}\text{BrO}_4\text{P} [\text{M}+\text{H}^+]$: 425.0517, found: 425.0511.



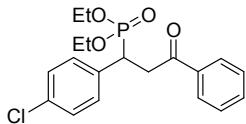
Diethyl 3-oxo-1-phenyl-3-p-tolylpropylphosphonate (10k) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.77 (d, $J = 1.8$ Hz, 2H), 7.36 (d, $J = 6.0$ Hz, 4H), 7.22-7.16 (m, 5H), 4.03-3.56 (m, 7H), 2.31 (s, 3H), 1.21 (t, $J = 6.9$ Hz, 3H), 1.01 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 195.9 (d, $J = 7.1$ Hz), 144.0, 136.0 (d, $J = 6.8$ Hz), 134.0, 129.1, 128.4 (d, $J = 2.4$ Hz), 128.1, 127.1 (d, $J = 3.0$ Hz), 62.8 (d, $J = 7.1$ Hz), 61.9 (d, $J = 7.3$ Hz), 38.8 (d, $J = 139.4$ Hz), 38.8, 21.5, 16.3 (d, $J = 5.9$ Hz), 16.2 (d, $J = 5.8$ Hz). ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 29.1. HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{26}\text{O}_4\text{P}$ [$\text{M}+\text{H}^+$]: 361.1569, found: 361.1560.



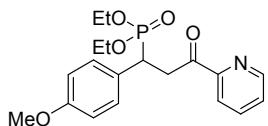
Diethyl 1-(4-methoxyphenyl)-3-oxo-3-phenylpropylphosphonate (10l)⁶ ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.93 (d, $J = 2.3$ Hz, 2H), 7.43 (d, $J = 5.7$ Hz, 2H), 7.28-7.20 (m, 3H), 6.91 (d, $J = 8.7$ Hz, 2H), 4.09-4.04 (m, 4H), 3.85 (s, 3H), 3.71-3.65 (m, 3H), 1.28 (t, $J = 6.9$ Hz, 3H), 1.07 (m, $J = 6.6$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 196.4 (d, $J = 15.3$ Hz), 158.6, 136.5, 133.2, 130.1 (d, $J = 6.5$ Hz), 128.5, 128.0, 127.6 (d, $J = 6.7$ Hz), 113.9, 62.8 (d, $J = 7.0$ Hz), 61.8 (d, $J = 7.2$ Hz), 55.1, 39.1, 38.0 (d, $J = 140.3$ Hz), 16.3 (d, $J = 5.9$ Hz), 16.2 (d, $J = 5.6$ Hz).



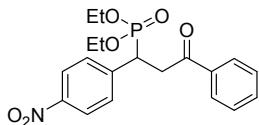
Diethyl 3-(4-chlorophenyl)-3-oxo-1-phenylpropylphosphonate (10m)⁶ ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.80 (d, $J = 8.1$ Hz, 2H), 7.35-7.33 (m, 3H), 7.24-7.14 (m, 4H), 4.02-3.97 (m, 4H), 3.89-3.79 (m, 1H), 3.69-3.58 (m, 2H), 1.21 (t, $J = 13.5$ Hz, 3H), 1.00 (m, $J = 6.6$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): 195.1 (d, $J = 14.8$ Hz), 139.6, 135.7 (d, $J = 6.6$ Hz), 134.7, 129.4, 129.1, 128.8, 128.4, 127.2, 62.9 (d, $J = 6.0$ Hz), 61.9 (d, $J = 7.1$ Hz), 39.0, 38.9 (d, $J = 139.4$ Hz), 16.2 (d, $J = 5.8$ Hz), 16.1 (d, $J = 5.8$ Hz).



Diethyl 1-(4-chlorophenyl)-3-oxo-3-phenylpropylphosphonate (10n) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.86 (d, $J = 7.2$ Hz, 2H), 7.52-7.47 (m, 1H), 7.40-7.29 (m, 4H), 7.20 (d, $J = 4.2$ Hz, 2H), 4.11-3.83 (m, 4H), 3.75-3.67 (m, 1H), 3.64-3.59 (m, 2H), 1.22 (t, $J = 13.8$ Hz, 3H), 1.05 (t, $J = 13.8$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 196.2 (d, $J = 15.2$ Hz), 136.3, 134.6 (d, $J = 7.0$ Hz), 133.4, 133.1 (d, $J = 3.6$ Hz), 130.5 (d, $J = 6.6$ Hz), 128.6, 128.0, 63.0 (d, $J = 6.9$ Hz), 62.2 (d, $J = 7.1$ Hz), 39.0, 38.4 (d, $J = 140.1$ Hz), 16.3 (d, $J = 5.9$ Hz), 16.2 (d, $J = 5.7$ Hz).

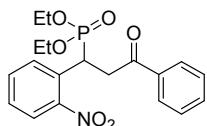


diethyl 1-(4-methoxyphenyl)-3-oxo-3-(pyridin-2-yl)propylphosphonate (10o) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 8.50 (d, $J = 7.2$ Hz, 1H), 7.82-7.69 (m, 1H), 7.31-7.20 (m, 2H), 6.97-6.90 (m, 1H), 6.77 (d, $J = 8.1$ Hz, 1H), 6.57-6.46 (m, 2H), 4.21-4.08 (m, 4H), 3.99-3.80 (m, 3H), 3.72 (s, 3H), 1.24 (t, $J = 6.9$ Hz, 3H), 1.05 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 159.4, 156.1, 147.1, 137.2 (d, $J = 2.0$ Hz), 130.2 (d, $J = 10.1$ Hz), 129.2, 128.0, 124.9, 123.0 (d, $J = 2.0$ Hz), 122.2 (d, $J = 2.2$ Hz), 113.9, 64.1 (d, $J = 7.6$ Hz), 63.7 (d, $J = 7.6$ Hz), 55.2, 38.3, 38.2 (d, $J = 139.7$ Hz), 16.5 (d, $J = 5.3$ Hz), 16.2 (d, $J = 5.4$ Hz) ppm. ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 19.4. HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{25}\text{NO}_5\text{P}$ [M+H $^+$]: 378.1470, found: 378.1472.

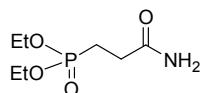


Diethyl 1-(4-nitrophenyl)-3-oxo-3-phenylpropylphosphonate (10p) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 8.10 (d, $J = 8.1$ Hz, 2H), 7.86 (d, $J = 7.5$ Hz, 2H), 7.56-7.49 (m, 2H), 7.42-7.37 (m, 2H), 7.19 (s, 1H), 4.07-3.87 (m, 4H), 3.84-3.77 (m, 1H), 3.73-3.67 (m, 2H), 1.24 (t, $J = 6.9$ Hz, 3H), 1.08 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 195.5 (d, $J = 15.3$ Hz), 146.8 (d, $J = 3.4$ Hz), 144.0 (d, $J = 4.8$ Hz), 135.9, 133.5, 130.0 (d, $J = 6.3$ Hz), 128.6, 127.9, 123.4 (d, $J = 2.1$ Hz), 62.9 (d, $J = 7.0$ Hz), 62.3 (d, $J = 7.1$ Hz), 39.0 (d, J

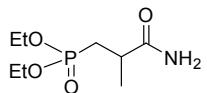
= 139.0 Hz), 38.6, 16.2 (d, J = 5.9 Hz), 16.1 (d, J = 5.7 Hz) ppm. ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 27.0. HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{23}\text{NO}_6\text{P} [\text{M}+\text{H}^+]$: 392.1263, found: 392.1253.



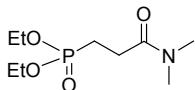
Diethyl 1-(2-nitrophenyl)-3-oxo-3-phenylpropylphosphonate (10q) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 8.20 (d, J = 7.5 Hz, 1H), 7.75-7.66 (m, 2H), 7.52-7.39 (m, 5H), 7.15 (d, J = 6.9 Hz, 1H), 4.30-4.17 (m, 2H), 4.08-3.94 (m, 2H), 3.90-3.82 (m, 1H), 3.79-3.60 (m, 2H), 1.44 (t, J = 6.9 Hz, 3H), 1.22 (t, J = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 199.1 (d, J = 16.9 Hz), 145.3, 137.4, 135.2 (d, J = 7.0 Hz), 134.0, 130.5, 128.3, 129.2 (d, J = 6.5 Hz), 128.5 (d, J = 2.4 Hz), 127.4 (d, J = 3.0 Hz), 127.2, 124.2, 62.9 (d, J = 6.9 Hz), 62.1 (d, J = 7.3 Hz), 43.1, 39.3 (d, J = 139.4 Hz), 16.3 (d, J = 5.9 Hz), 16.1 (d, J = 5.7 Hz). ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 27.8. HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{23}\text{NO}_6\text{P} [\text{M}+\text{H}^+]$: 392.1263, found: 392.1258.



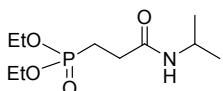
Diethyl 3-amino-3-oxopropylphosphonate (10r) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 6.27 (s, br, 1H), 5.54 (s, br, 1H), 4.05-4.01 (m, 4H), 2.52-2.42 (m, 2H), 2.08-1.97 (m, 2H), 1.26 (t, J = 6.6 Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 173.8 (d, J = 16.4 Hz), 61.7 (d, J = 6.5 Hz), 28.0 (d, J = 3.4 Hz), 20.6 (d, J = 142.7 Hz), 16.2 (d, J = 5.9 Hz). ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 31.6. HRMS (ESI) calcd. for $\text{C}_7\text{H}_{17}\text{NO}_4\text{P} [\text{M}+\text{H}^+]$: 210.0895, found: 210.0889.



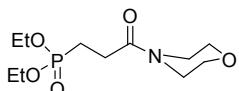
Diethyl 3-amino-2-methyl-3-oxopropylphosphonate (10s) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 6.16 (s, br, 1H), 5.33 (s, br, 1H), 4.04-3.99 (m, 4H), 2.73-2.62 (m, 1H), 2.24-2.11 (m, 1H), 1.79-1.71 (m, 1H), 1.28-1.22 (m, 9H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 177.6 (d, J = 10.6 Hz), 61.3 (d, J = 6.4 Hz), 61.1 (d, J = 6.5 Hz), 34.2, 28.5 (d, J = 139.9 Hz), 19.1 (d, J = 11.0 Hz), 15.8 (d, J = 6.0 Hz). ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 30.7. HRMS (ESI) Calcd. for $\text{C}_7\text{H}_{17}\text{NO}_4\text{P} [\text{M}+\text{H}^+]$: 224.1051, found: 224.1045.



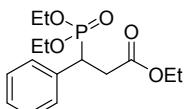
Diethyl 3-(dimethylamino)-3-oxopropylphosphonate (10t) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 4.11-4.07 (m, 4H), 2.98 (d, $J = 17.1$ Hz, 6H), 2.63-2.55 (m, 2H), 2.15-2.04 (m, 2H), 1.32 (t, $J = 6.9$ Hz, 6H). $^{13}\text{C}\{\text{H}\}$ NMR (75 MHz, CDCl_3 , ppm): δ 170.5 (d, $J = 17.8$ Hz), 61.4 (d, $J = 6.5$ Hz), 36.7, 35.4, 26.1 (d, $J = 2.1$ Hz), 20.6 (d, $J = 142.5$ Hz), 16.1 (d, $J = 6.0$ Hz) ppm. ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 32.4. HRMS (ESI) calcd. for $\text{C}_9\text{H}_{21}\text{NO}_4\text{P}$ $[\text{M}+\text{H}^+]$: 238.1208, found: 238.1199.



Diethyl 3-(isopropylamino)-3-oxopropylphosphonate (10u) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 5.91 (s, br, 1H), 4.10-4.03 (m, 5H), 2.47-2.37 (m, 2H), 2.13-2.02 (m, 2H), 1.31 (t, $J = 7.2$ Hz, 6H), 1.13 (d, $J = 6.6$ Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 169.7 (d, $J = 17.5$ Hz), 61.2 (d, $J = 6.4$ Hz), 40.7, 28.2, 22.0 (d, $J = 2.0$ Hz), 20.5 (d, $J = 142.3$ Hz), 15.9 (d, $J = 5.8$ Hz). ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 31.9. HRMS (ESI) calcd. for $\text{C}_{10}\text{H}_{23}\text{NO}_4\text{P}$ $[\text{M}+\text{H}^+]$: 252.1364, found: 252.1357.

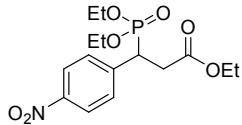


Diethyl 3-morpholino-3-oxopropylphosphonate (10v) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 4.10-4.06 (m, 4H), 3.65-3.45 (m, 8H), 2.62-2.53 (m, 2H), 2.14-1.98 (m, 2H), 1.30 (t, $J = 1.8$ Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 168.5 (d, $J = 17.6$ Hz), 65.6 (d, $J = 18.2$ Hz), 60.7 (d, $J = 6.4$ Hz), 44.8, 41.2, 25.1 (d, $J = 2.1$ Hz), 19.9 (d, $J = 142.6$ Hz), 15.5 (d, $J = 5.9$ Hz). ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 32.1. HRMS (ESI) calcd. for $\text{C}_{11}\text{H}_{23}\text{NO}_5\text{P}$ $[\text{M}+\text{H}^+]$: 280.1313, found: 280.1318.

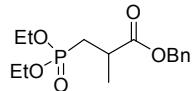


Ethyl 3-(diethoxyphosphoryl)-3-phenylpropanoate (10w) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.28-7.20 (m, 5H), 3.99-3.69 (m, 6H), 3.65-3.51 (m, 1H), 3.06-2.96 (m, 2H), 1.21 (t, $J = 1.5$ Hz, 3H), 1.07-1.02 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 170.7 (d, $J = 19.3$ Hz), 144.8 (d, $J = 12.5$ Hz), 128.5, 127.5, 125.5, 124.5, 123.5, 122.5, 121.5, 120.5, 119.5, 118.5, 117.5, 116.5, 115.5, 114.5, 113.5, 112.5, 111.5, 110.5, 109.5, 108.5, 107.5, 106.5, 105.5, 104.5, 103.5, 102.5, 101.5, 100.5, 99.5, 98.5, 97.5, 96.5, 95.5, 94.5, 93.5, 92.5, 91.5, 90.5, 89.5, 88.5, 87.5, 86.5, 85.5, 84.5, 83.5, 82.5, 81.5, 80.5, 79.5, 78.5, 77.5, 76.5, 75.5, 74.5, 73.5, 72.5, 71.5, 70.5, 69.5, 68.5, 67.5, 66.5, 65.5, 64.5, 63.5, 62.5, 61.5, 60.5, 59.5, 58.5, 57.5, 56.5, 55.5, 54.5, 53.5, 52.5, 51.5, 50.5, 49.5, 48.5, 47.5, 46.5, 45.5, 44.5, 43.5, 42.5, 41.5, 40.5, 39.5, 38.5, 37.5, 36.5, 35.5, 34.5, 33.5, 32.5, 31.5, 30.5, 29.5, 28.5, 27.5, 26.5, 25.5, 24.5, 23.5, 22.5, 21.5, 20.5, 19.5, 18.5, 17.5, 16.5, 15.5, 14.5, 13.5, 12.5, 11.5, 10.5, 9.5, 8.5, 7.5, 6.5, 5.5, 4.5, 3.5, 2.5, 1.5, 0.5 ppm. HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{34}\text{NO}_5\text{P}$ $[\text{M}+\text{H}^+]$: 400.2080, found: 400.2070.

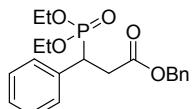
Hz), 134.9 (d, J = 6.9 Hz), 128.8 (d, J = 6.4 Hz), 128.2, 127.2 (d, J = 6.4 Hz), 62.6 (d, J = 6.9 Hz), 61.9 (d, J = 7.1 Hz), 60.4, 40.1 (d, J = 139.3 Hz), 34.9, 16.1 (d, J = 5.9 Hz), 16.0 (d, J = 5.8 Hz), 13.7. ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 27.7. HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{24}\text{O}_5\text{P}$ [$\text{M}+\text{H}^+$]: 315.1361, found: 315.1356.



Ethyl 3-(diethoxyphosphoryl)-3-(4-nitrophenyl)propanoate (10x) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 8.12 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 7.8 Hz, 2H), 4.06-3.63 (m, 7H), 3.11-2.85 (m, 2H), 1.23 (t, J = 6.9 Hz, 3H), 1.13-1.04 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 170.1 (d, J = 19.4 Hz), 146.9 (d, J = 3.5 Hz), 143.2 (d, J = 7.0 Hz), 129.8 (d, J = 6.2 Hz), 123.4 (d, J = 2.5 Hz), 62.8 (d, J = 7.0 Hz), 62.4 (d, J = 7.1 Hz), 60.8, 40.8 (d, J = 138.8 Hz), 34.5 (d, J = 1.9 Hz), 16.1 (d, J = 6.0 Hz), 16.0 (d, J = 1.6 Hz), 13.8. ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 25.7. HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{23}\text{NO}_7\text{P}$ [$\text{M}+\text{H}^+$]: 360.1212, found: 360.1205.



Benzyl 3-(diethoxyphosphoryl)-2-methylpropanoate (10y) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.27-7.20 (m, 5H), 4.93 (d, J = 3.6 Hz, 2H), 4.02-3.81 (m, 4H), 3.74-3.51 (m, 1H), 3.06-2.86 (m, 2H), 1.21 (t, J = 6.9 Hz, 3H), 1.07-1.02 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 174.8 (d, J = 17.6 Hz), 135.6, 128.4, 128.1, 127.9, 66.4, 66.1 (d, J = 6.2 Hz), 60.6, 34.4 (t, J = 4.4 Hz), 28.9 (d, J = 141.4 Hz), 18.5 (d, J = 9.8 Hz), 16.2 (d, J = 6.0 Hz), 13.9. ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 29.7. HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{24}\text{O}_5\text{P}$ [$\text{M}+\text{H}^+$]: 315.1361, found: 315.1356.



Benzyl 3-(diethoxyphosphoryl)-3-phenylpropanoate (10z) ^1H NMR (300 MHz, CDCl_3 , ppm): δ 7.27-7.09 (m, 10H), 4.93 (s, 2H), 3.99-3.81 (m, 4H), 3.74-3.52 (m, 1H), 3.01-2.85 (m, 2H), 1.21 (t, J = 6.9 Hz, 3H), 1.04 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 170.8 (d, J =

19.3 Hz), 135.1 (d, J = 7.1 Hz), 129.0 (d, J = 6.3 Hz), 128.4 (d, J = 2.3 Hz), 128.1, 128.0, 127.3 (d, J = 3.1 Hz), 66.5, 62.8 (d, J = 7.0 Hz), 62.1 (d, J = 7.2 Hz), 40.4 (d, J = 139.4 Hz), 35.1, 16.3 (d, J = 5.9 Hz), 16.1 (d, J = 5.9 Hz). ^{31}P NMR (121 MHz, CDCl_3 , ppm): δ 27.3. HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{26}\text{O}_5\text{P}$ [M+H $^+$]: 377.1518, found: 377.1508.

III Crystallographic Data of Complexes

Table 1 Crystallographic data and structure refinement for complexes **2, 3**

Crustal date	2	3
Empirica formula	$\text{C}_{26}\text{H}_{53}\text{LaN}_4\text{Si}_4$	$\text{C}_{26}\text{H}_{53}\text{NdN}_4\text{Si}_4$
Crystal system, Space group	Monoclinic, C2/c	Monoclinic, C2/c
a (Å)	20.6220(12)	20.5269(14)
b (Å)	15.6675(9)	15.6748(11)
c (Å)	21.8991(13)	21.8103(15)
α (°)	90	90
β (°)	92.9010(10)	92.9220(10)
γ (°)	90	90
V (Å 3)	7066.4(7)	7008.5(8)
T (K)	293(2)	293(2)
D _{calc} (g cm $^{-3}$)	1.265	1.286
Z	8	8
F(0 0 0)	2800	2824
Reflections collected / unique	8163 / 8163	29990 / 8079
Completeness to theta	27.58° , 99.7 %	27.59° , 99.5 %
λ (Mo K α radiation) (Å)	0.71073	0.71073
μ (mm $^{-1}$)	1.364	1.638
θ Range (°)	1.63 to 27.58	1.64 to 27.59
Goodness-of-fit (GOF)	1.030	1.018
Final R indices [I > 2 σ (I)]; R ₁ , wR ₂	0.0263, 0.0546	0.0298, 0.0715
R indices (all data); R ₁ , wR ₂	0.0408, 0.0576	0.0458, 0.0798
Largest difference in peak and hole (e Å $^{-3}$)	0.487 and -0.389	1.190 and -0.563

Table 2 Crystallographic data and structure refinement for complexes **4, 5**

Crustal date	4	5
Empirica formula	$\text{C}_{34}\text{H}_{52}\text{N}_5\text{Si}_2\text{Sm}$	$\text{C}_{42}\text{H}_{51}\text{N}_6\text{Nd}$
Crystal system, Space group	Triclinic, P1	Triclinic, P-1
a (Å)	10.6399(7)	10.4579(18)
b (Å)	13.2558(8)	11.2161(19)
c (Å)	15.8529(10)	17.663(3)
α (°)	81.5240(10)	79.498(2)

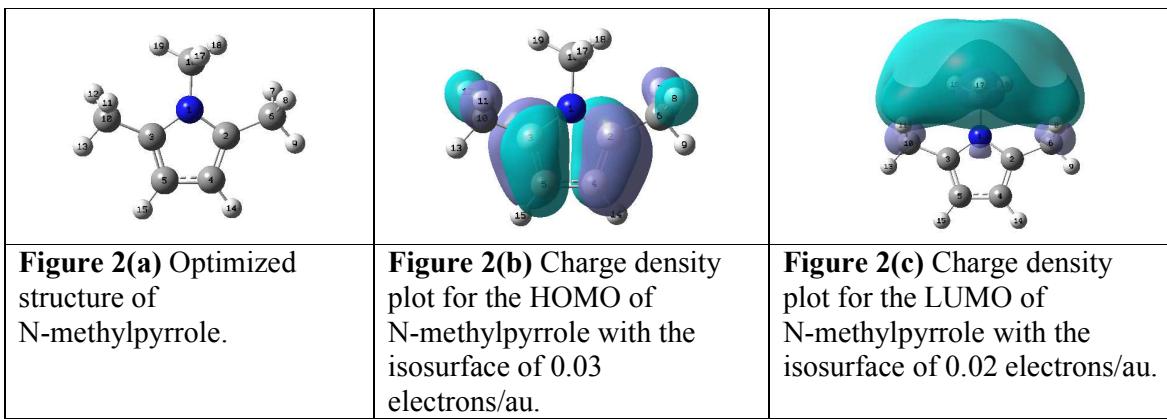
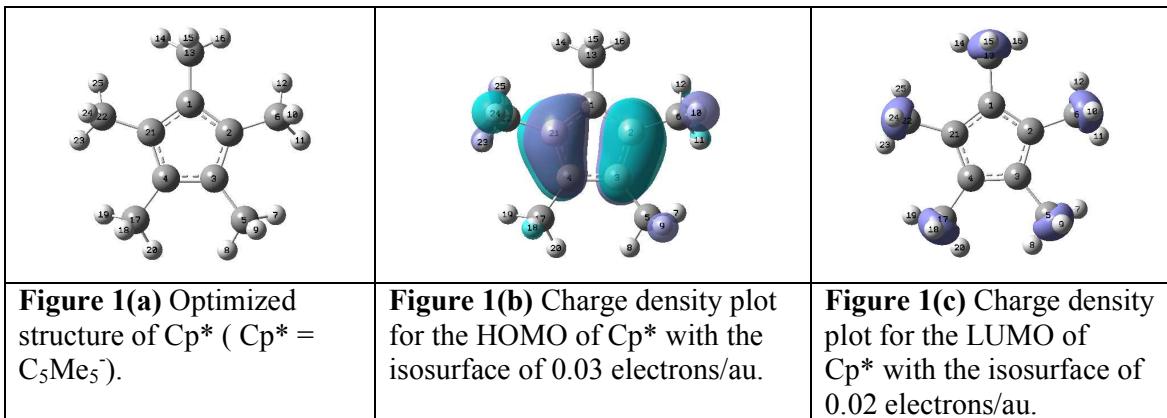
β (°)	82.0510(10)	89.236(2)
γ (°)	67.1210(10)	67.474(2)
V (Å ³)	2029.4(2)	1878.0(6)
T (K)	293(2)	293(2)
D _{calc} (g cm ⁻³)	1.277	1.387
Z	2	2
F(0 0 0)	2800	810
Reflections collected / unique	17638 / 9173 [R(int) = 0.0187]	15803 / 8413 [R(int) = 0.0323]
Completeness to theta	27.63°, 97.2 %	27.61°, 99.7 %
λ (Mo K α radiation) (Å)	0.71073	0.71073
μ (mm ⁻¹)	1.535	1.420
θ Range (°)	1.30 to 27.63	1.63 to 27.58
Goodness-of-fit (GOF)	1.056	1.033
Final R indices [I > 2 σ (I)]; R ₁ , wR ₂	0.0242, 0.0680	0.0561, 0.1471
R indices (all data); R ₁ , wR ₂	0.0279, 0.0709	0.0733, 0.1617
Largest difference in peak and hole (e Å ⁻³)	0.293 and -0.697	3.558 and -1.475

Table 3 Crystallographic data and structure refinement for complexes **6**, **7**, and **8**

Crustal date	6	7	8
Empirica formula	C ₃₇ H ₅₆ LaN ₅ Si ₂	C ₃₂ H ₄₃ LaN ₆	C ₃₂ H ₄₃ NdN ₆
Crystal system, Space group	Triclinic, P-1	Triclinic, P-1	Triclinic, P-1
a (Å)	8.949(4)	10.143(2)	10.1491(18)
b (Å)	14.039(5)	10.307(2)	10.3206(18)
c (Å)	17.128(7)	16.905(4)	16.842(3)
α (°)	90.736(5)	85.596(3)	85.741(2)
β (°)	95.994(5)	81.225(3)	81.455(2)
γ (°)	107.657(5)	66.324(3)	66.256(2)
V (Å ³)	2037.0(14)	1599.4(6)	1596.7(5)
T (K)	293(2)	293(2)	293(2)
D _{calc} (g cm ⁻³)	1.249	1.351	1.364
Z	2	2	2
F(0 0 0)	796	668	674
Reflections collected / unique	13916 / 7016 [R(int) = 0.0416]	13174 / 6986 [R(int) = 0.0394]	13329 / 7119 [R(int) = 0.0327]
Completeness to theta	25.00°, 97.8 %	27.36°, 96.4 %	27.56°, 96.4 %
λ (Mo K α radiation) (Å)	0.71073	0.71073	0.71073
μ (mm ⁻¹)	1.137	1.365	1.655
θ Range (°)	1.52 to 25.00	2.21 to 27.36	2.16 to 27.56
Goodness-of-fit (GOF)	1.098	0.990	1.025
Final R indices [I > 2 σ (I)]; R ₁ , wR ₂	0.1254, 0.3641	0.0514, 0.1161	0.0422, 0.1026
R indices (all data); R ₁ , wR ₂	0.1407, 0.3732	0.0822, 0.1328	0.0649, 0.1158

Largest difference in peak and hole ($e \text{ \AA}^{-3}$)	5.725 and -2.791	1.643 and -1.393	1.617 and -1.232
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IV Theoretical calculation of energy differences between HOMO and LUMO of Cp* and N-methyl-2,5-dimethylpyrrole



Using DFT with the B3LYP/6-311++g (d,p) method, we calculated the atomic and electronic structures of Cp* and N-methylpyrrole. Our calculations predict that the energy differences between HOMO and LUMO are 2.310 eV for Cp* and 4.910 eV for N-methyl-2,5-dimethylpyrrole. The charge density distributions of HOMO and LUMO are plotted in Figures 1(b) and 1(c) for Cp*, and in Figures 2(b) and 2(c) for N-methylpyrrole, respectively. The decompositions of HOMO and LUMO into atomic orbitals are given in the following.

Table 4 Relative contributions from atomic orbitals to the molecular orbitals.

	HOMO	LUMO
Cp*	C21-p = 0.33	C22-s = -2.05 C6-s = -2.04 C5-s = -2.03 C17-s = -2.02
	C2-p = 0.29	C13-s = -2.01 C21-s = 1.14 C1-s = 1.13 C2-s = 1.12
	C3-p = 0.16	C3-s = 1.06 C4-s = 1.06 H8-s = 0.34 H12-s = 0.34 H25-s = 0.34 H23-s = 0.33 H20-s = 0.33 H11-s = 0.32

		H16-s=0.31 H7-s = 0.30 H14-s = 0.30 H19-s = 0.30
		H18-s = 0.24 H15-s = 0.23 H9-s = 0.23 H10-s = 0.21
		H24-s = 0.20 C21-p = 0.14 C2-p = 0.13 C17-p = 0.13
		C13-p = 0.13 C5-p = 0.13 C6-p = 0.13 C22-p = 0.13
		C3-p = 0.13 C1-p = 0.12 C4-p = 0.12
	C2-p = 0.31	C6-s = -1.87 C10-s = -1.87 C16-s = -1.68 H17-s = 0.70
N-methyl-2,5-	C3-p = 0.31	H19-s = 0.67 H18-s = 0.67 C3-s = 0.62 C2-s = 0.62
dimethylpyrrol	C5-p = 0.13	H11-s = 0.37 H8-s = 0.37 H12-s = 0.37 H7-s = 0.37
e	C4-p = 0.13	N1-s = 0.29 C2-p = 0.19 C3-p = 0.19 C4-s = 0.16
		C5-s = 0.16 H13-s = 0.15 H9-s = 0.15

Cartesian coordinate (in Å) of atoms in the optimized structures of Cp* and N-methylpyrrole.

Pentamethylcyclopentadienyl anion (Cp*)

C	1.949513622303	1.232996734591	0.103945380265
C	3.365929041284	1.269708238150	0.020904721803
C	3.831412972668	-0.063169935259	-0.124883163375
C	2.703159002703	-0.923386127467	-0.134016805269
C	5.272746793145	-0.481214021227	-0.231920280518
C	4.230821601807	2.498034896724	0.095157009011
H	5.869550436165	0.241163796042	-0.806336474673
H	5.378352787334	-1.449685917422	-0.738895379303
H	5.781271641091	-0.587938056920	0.743383676849
H	4.590052281081	2.730750015706	1.114087722854
H	5.130726438994	2.405850918827	-0.529444832890
H	3.698424501920	3.394017314337	-0.249297030452
C	1.040616867638	2.417729871390	0.285749968460
H	0.069884809731	2.269790302936	-0.207469454842
H	0.813187420365	2.648464310653	1.342466389182
H	1.472381855048	3.333483252277	-0.139358163567
C	2.726081614603	-2.422994858953	-0.251159953818
H	2.709721593440	-2.948031914702	0.721835649649
H	1.865938002822	-2.805223497489	-0.818385080632
H	3.624153931656	-2.776534339601	-0.773026594772
C	1.540303879944	-0.122028167209	0.008255989447
C	0.124938288009	-0.627128294787	0.070817060097
H	-0.014103233016	-1.533414054695	-0.534125580019
H	-0.212335477624	-0.886755718217	1.090737715082
H	-0.590848493065	0.116178232252	-0.304852497859

N-methyl-2,5-dimethylpyrrole

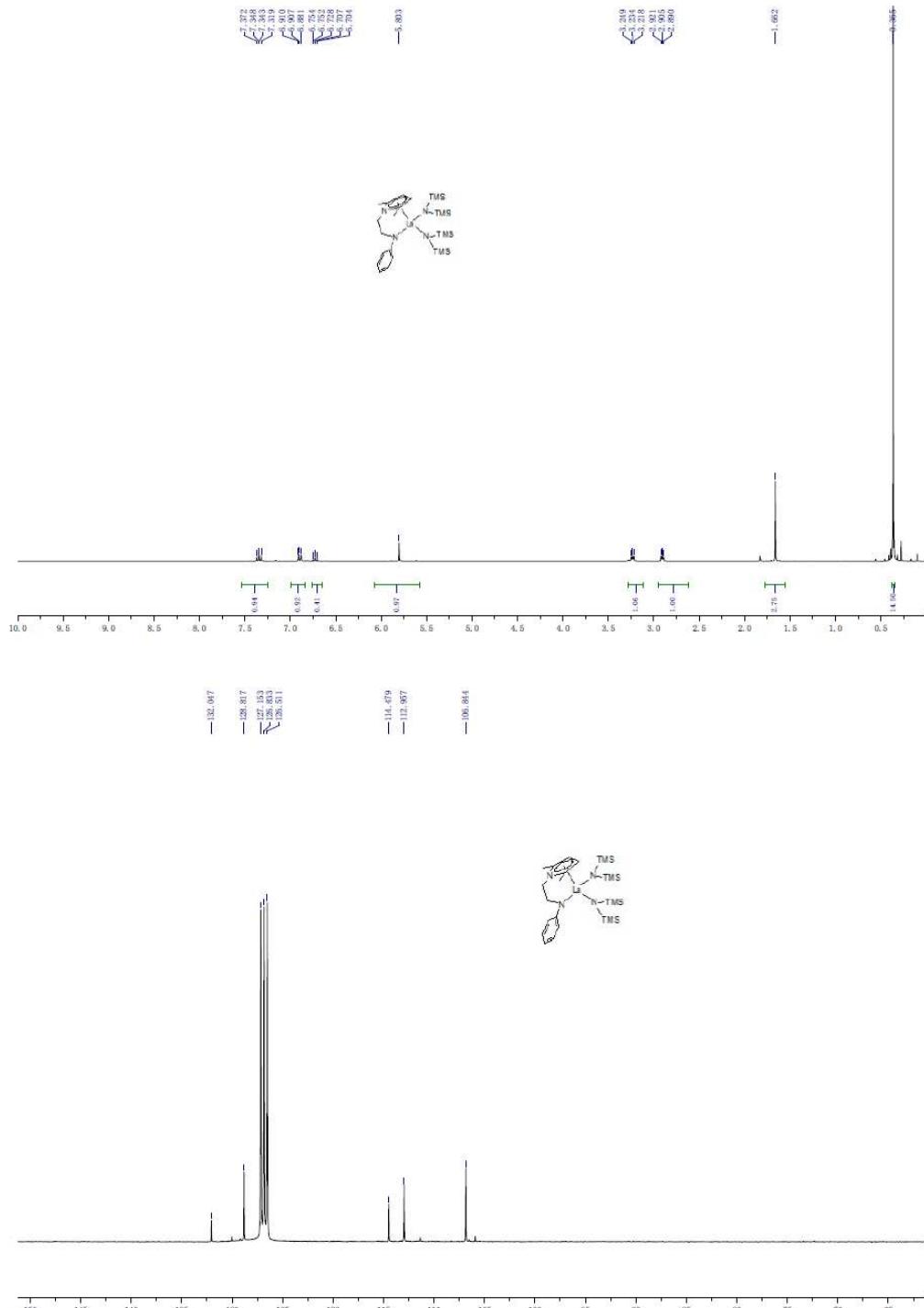
N	2.407518624002	0.000350539779	-0.342884688806
C	3.078526970118	1.136190901569	0.085417553133
C	3.087651122135	-1.129983906698	0.085558321252
C	4.195823562428	0.719393854136	0.774436727055
C	4.201756029148	-0.704112483048	0.774178221968

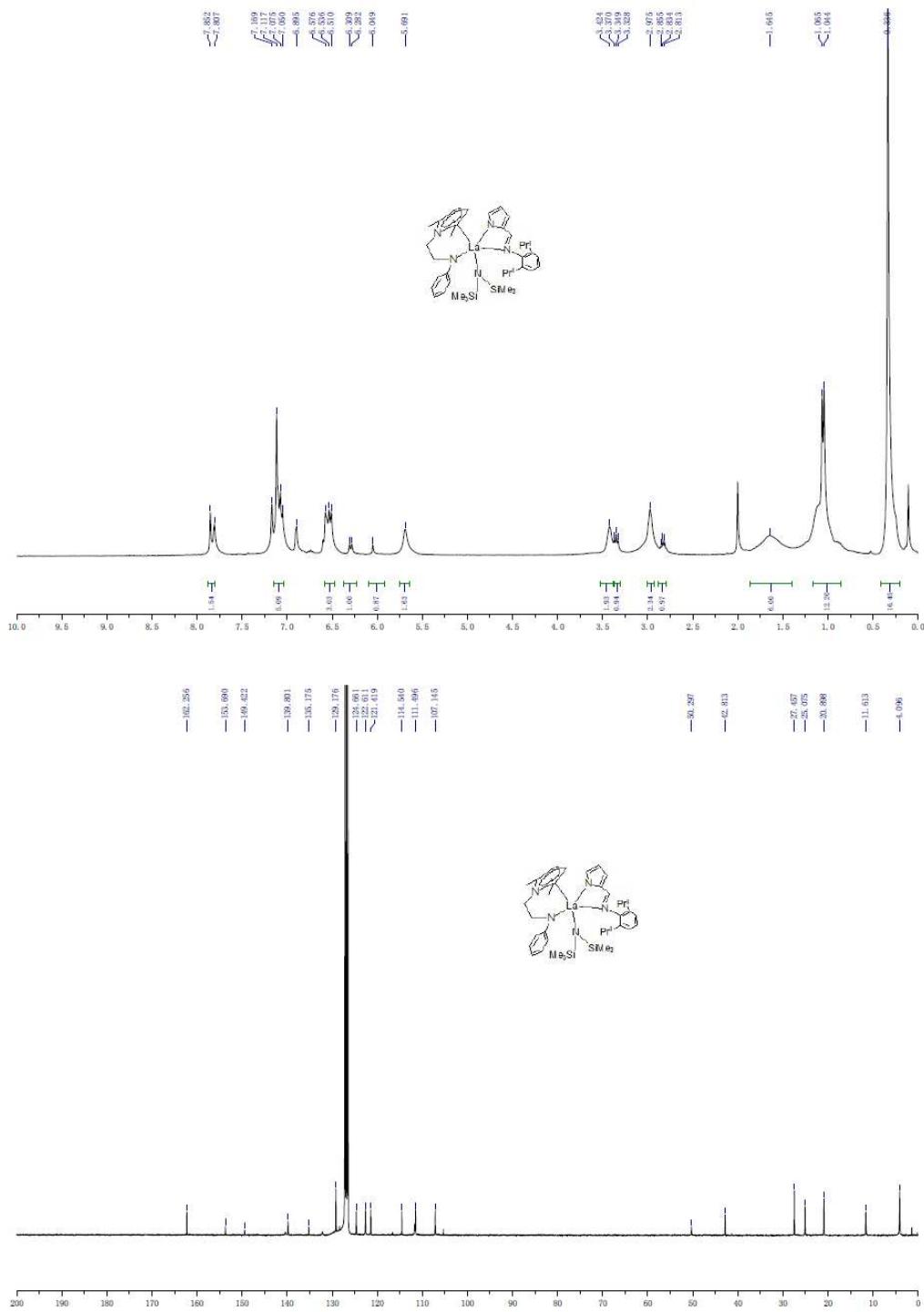
C	2.592154765059	2.518922541938	-0.206928247015
H	2.544045555404	2.729760123253	-1.282001577913
H	1.596706233051	2.712458672189	0.209537230561
H	3.278708615812	3.242014833181	0.235986425141
C	2.612388342202	-2.516634974449	-0.206503172733
H	1.618289107358	-2.717943664529	0.209533012463
H	2.566512343981	-2.728214052818	-1.281531643124
H	3.304447457206	-3.234092537442	0.237023707264
H	4.930212090103	1.371548916051	1.222777462745
H	4.941625231015	-1.350279895579	1.222163445276
C	1.127075327279	-0.004855728020	-1.027238088926
H	0.288302647759	-0.008724573312	-0.321745814725
H	1.040464196235	0.877045169153	-1.662085840223
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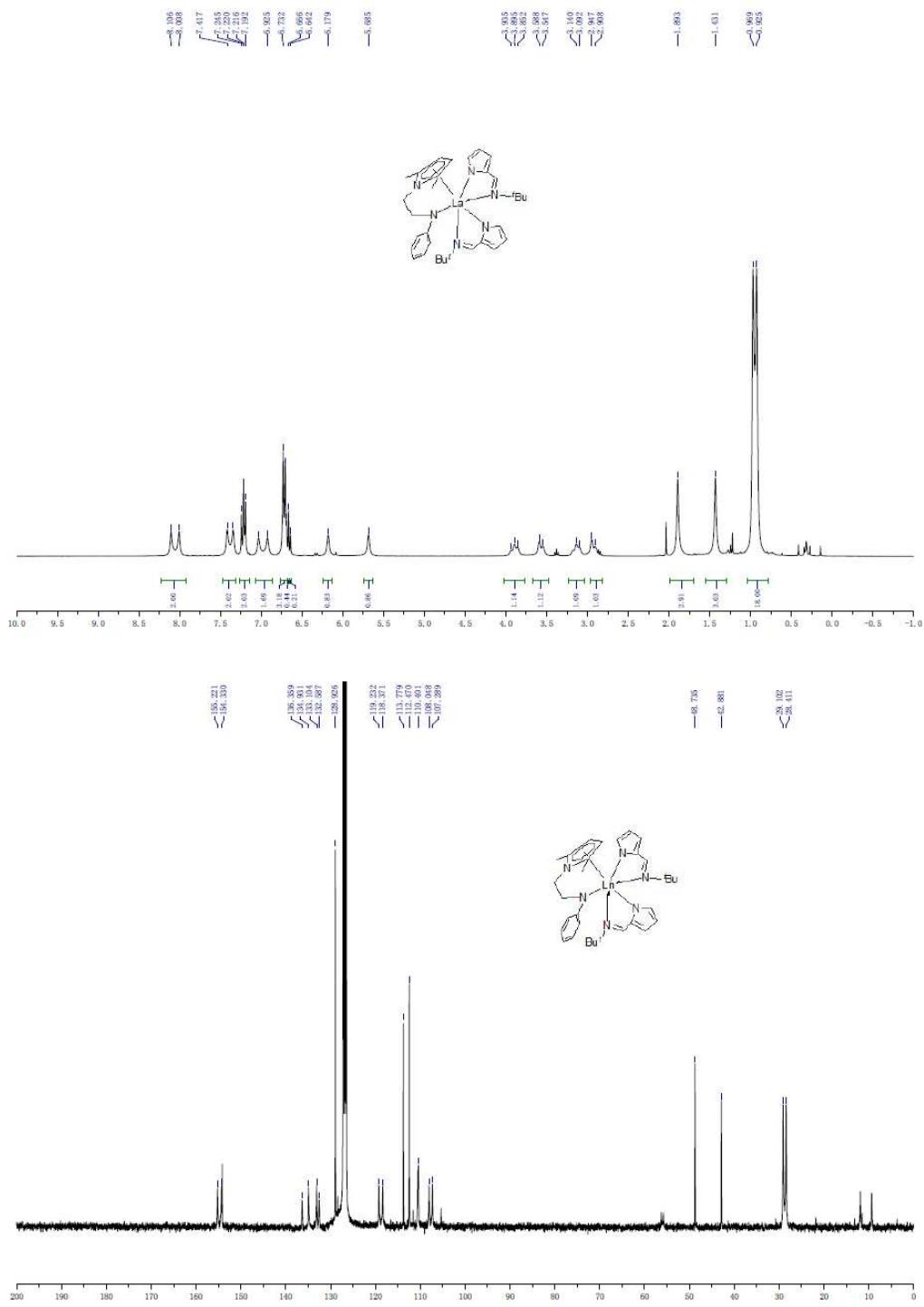
V References:

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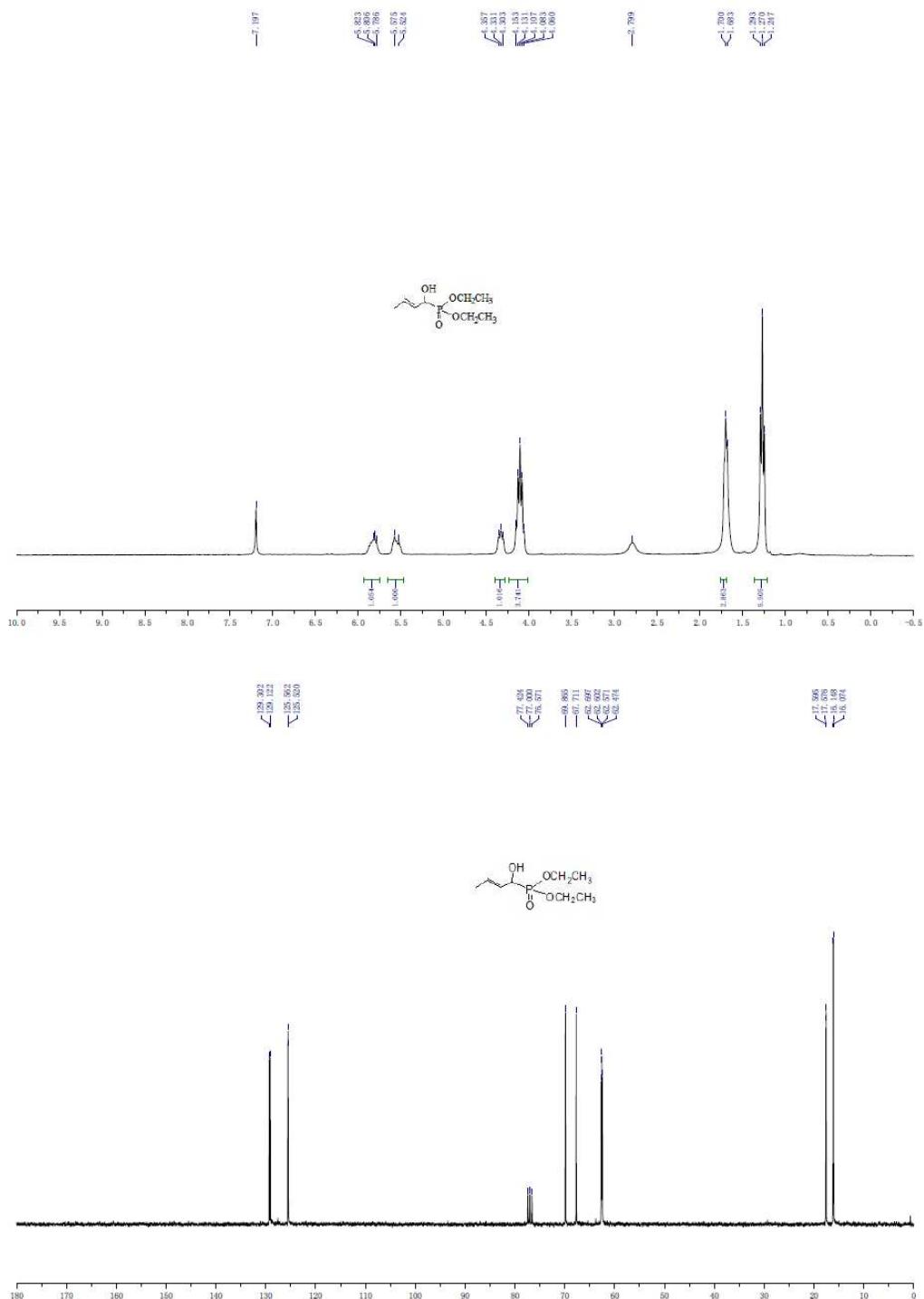
VI Copies of ^1H NMR, ^{13}C NMR Spectra of complexes.



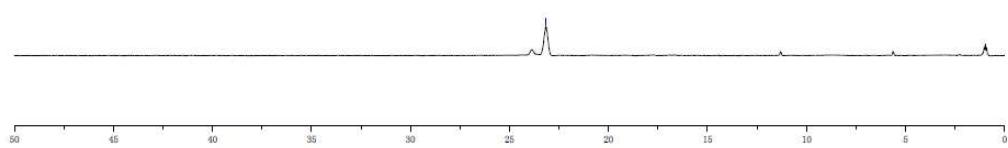




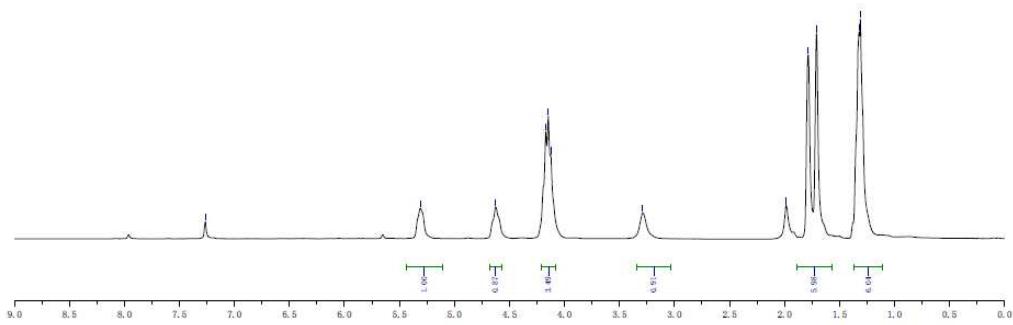
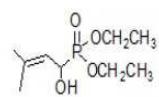
VII Copies of ^1H NMR, ^{13}C NMR Spectra and ^{31}P NMR of phosphonates

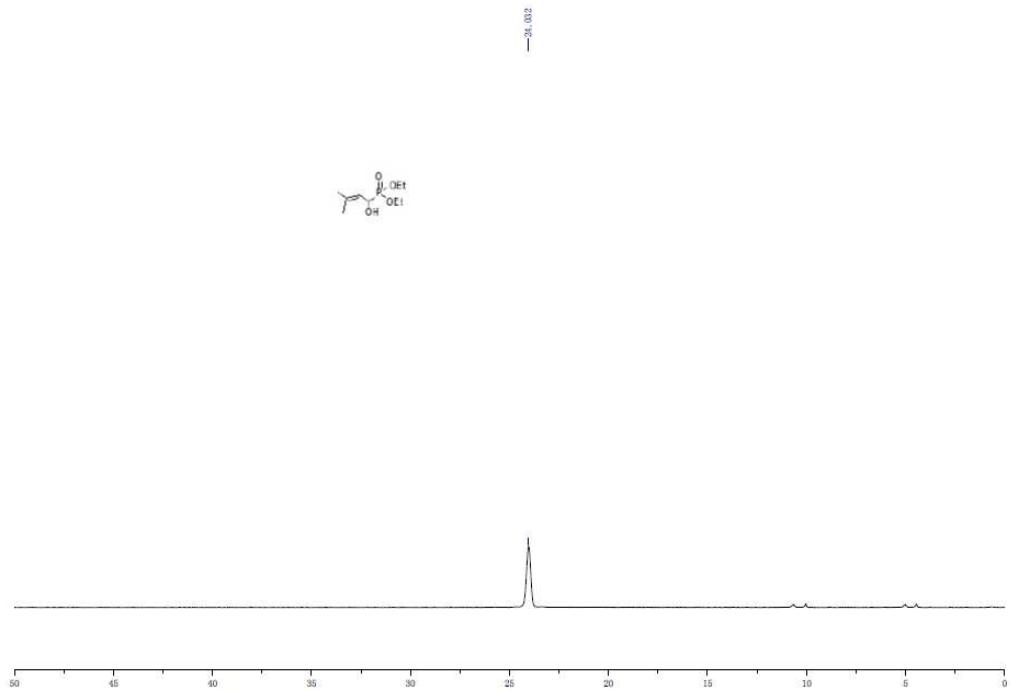
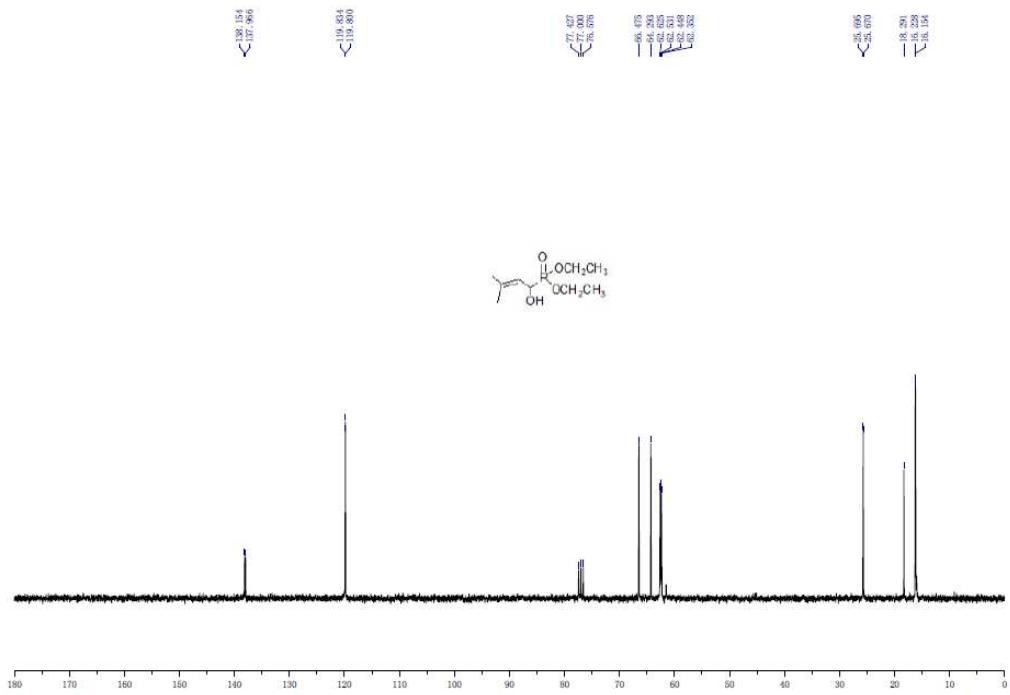


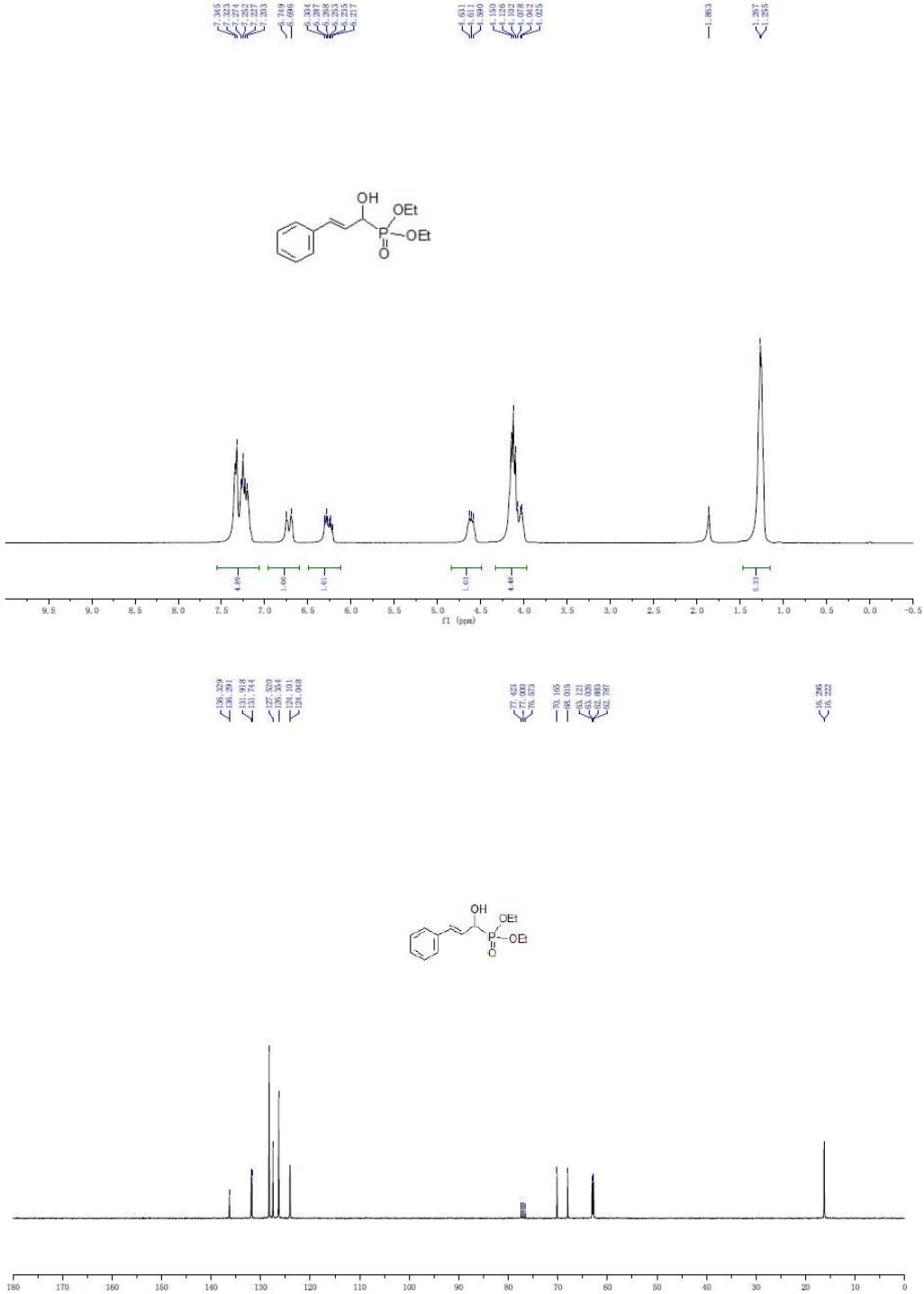
-25.173

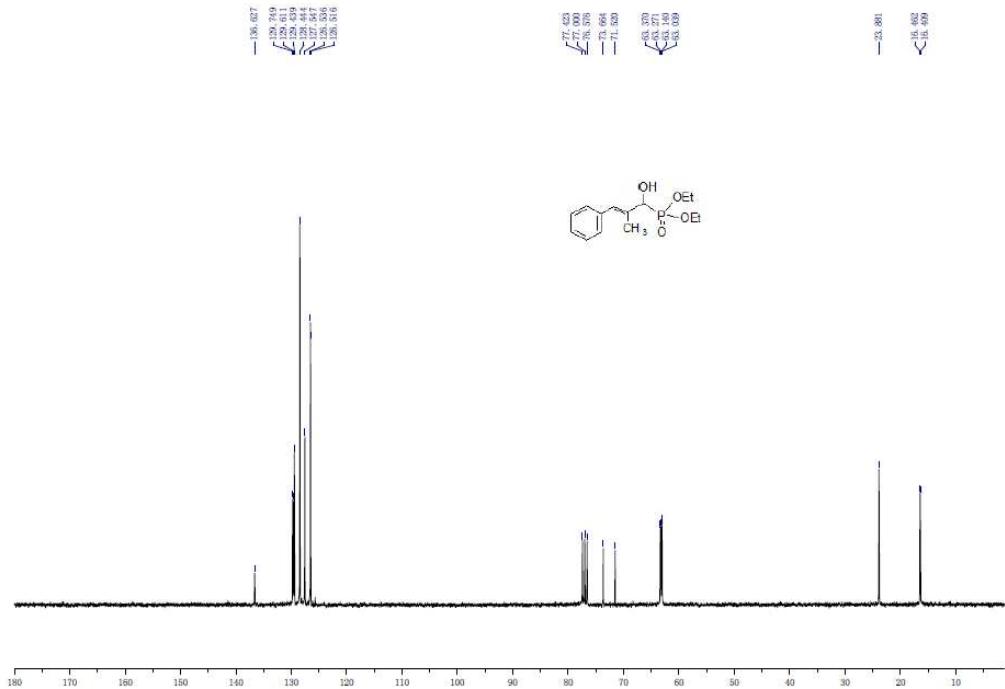
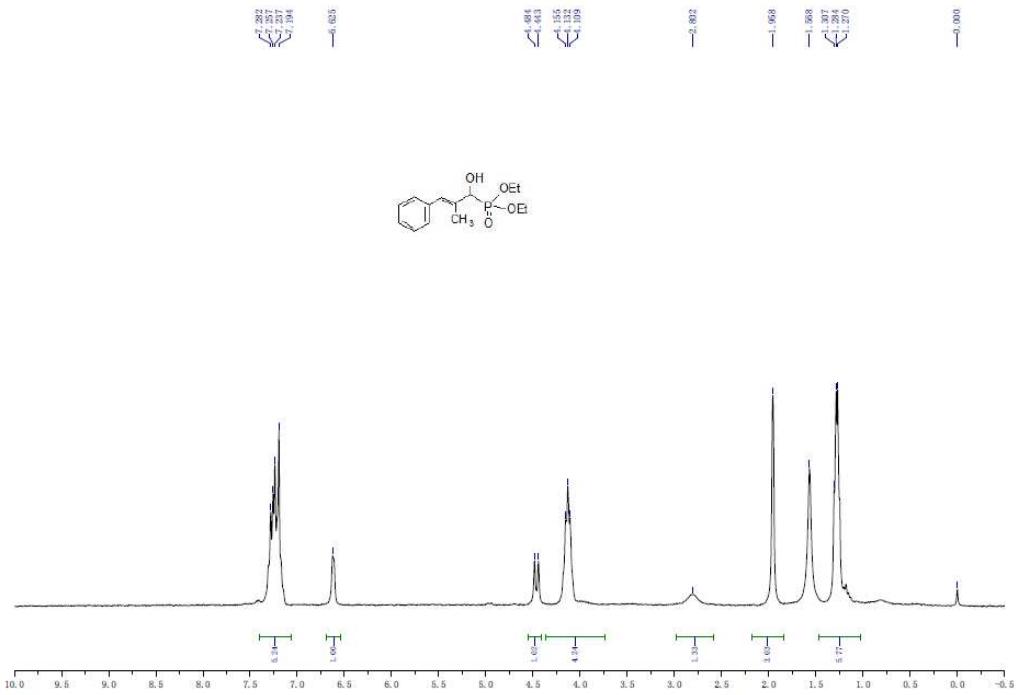


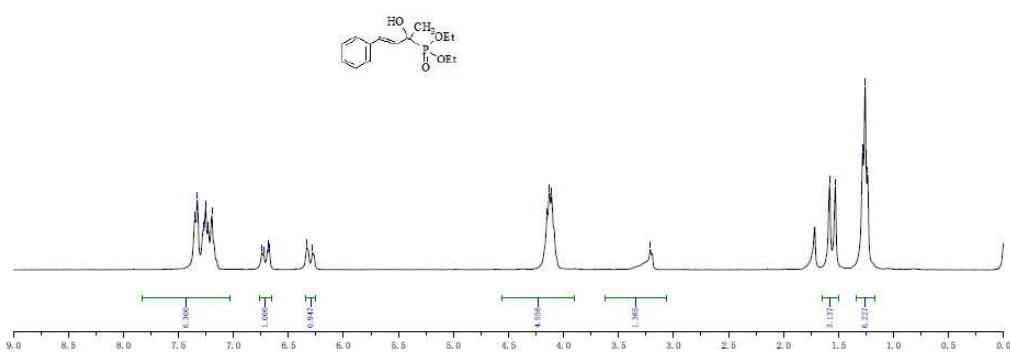
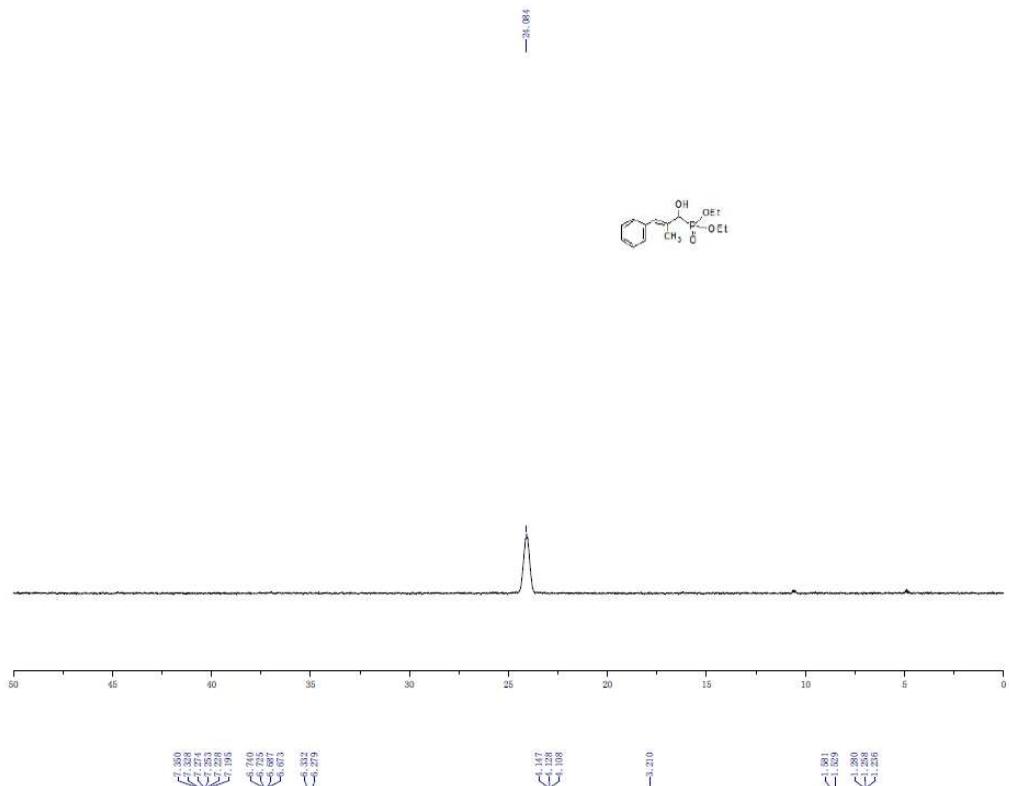
7.264
5.309
4.624
3.179
3.147
3.125
3.089
1.984
1.785
1.710
1.324
1.301

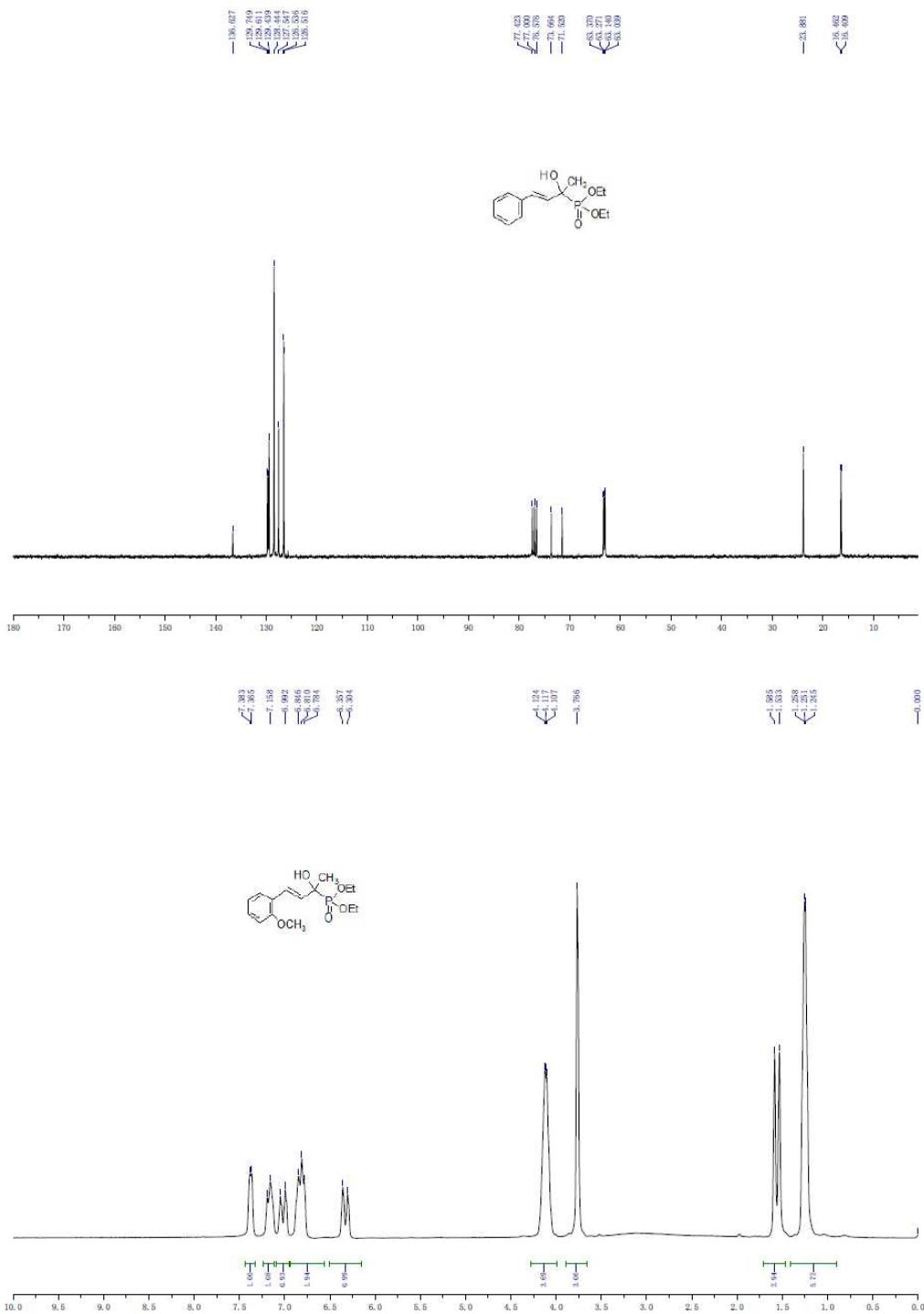


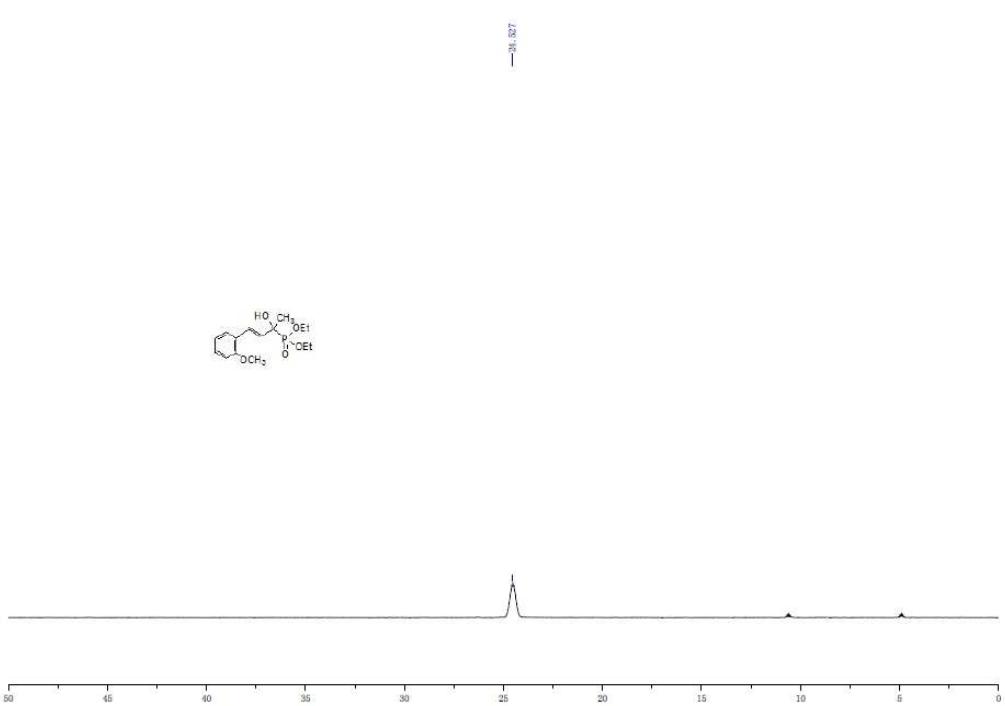
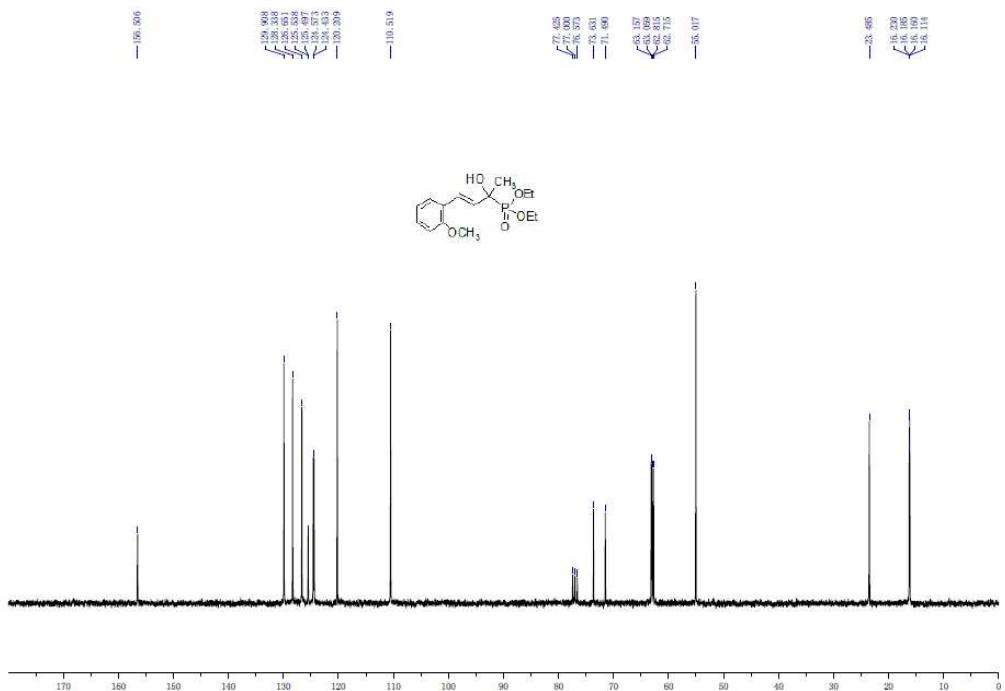


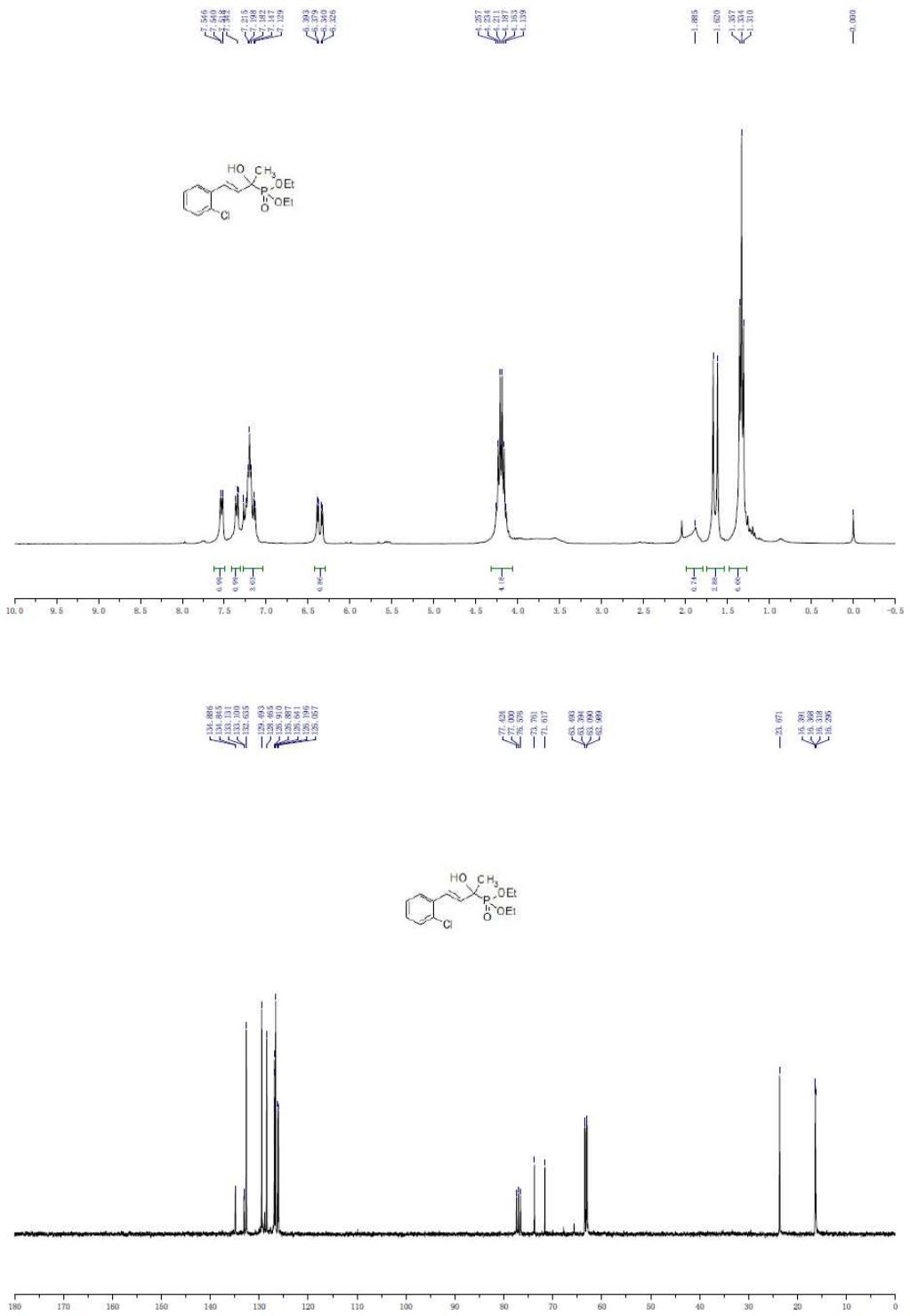


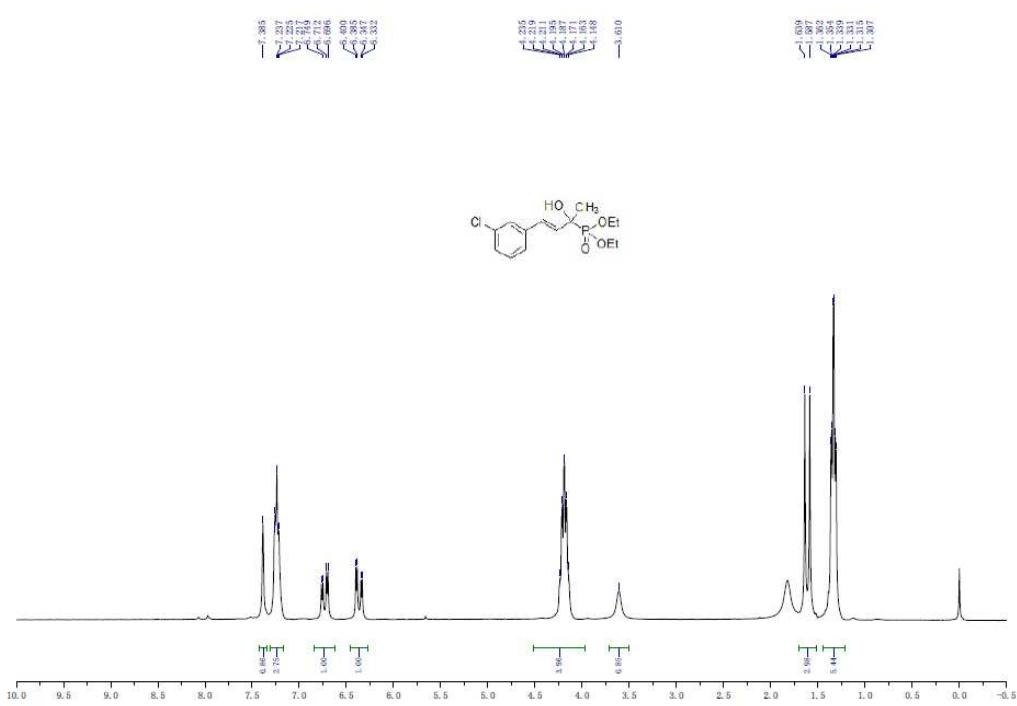
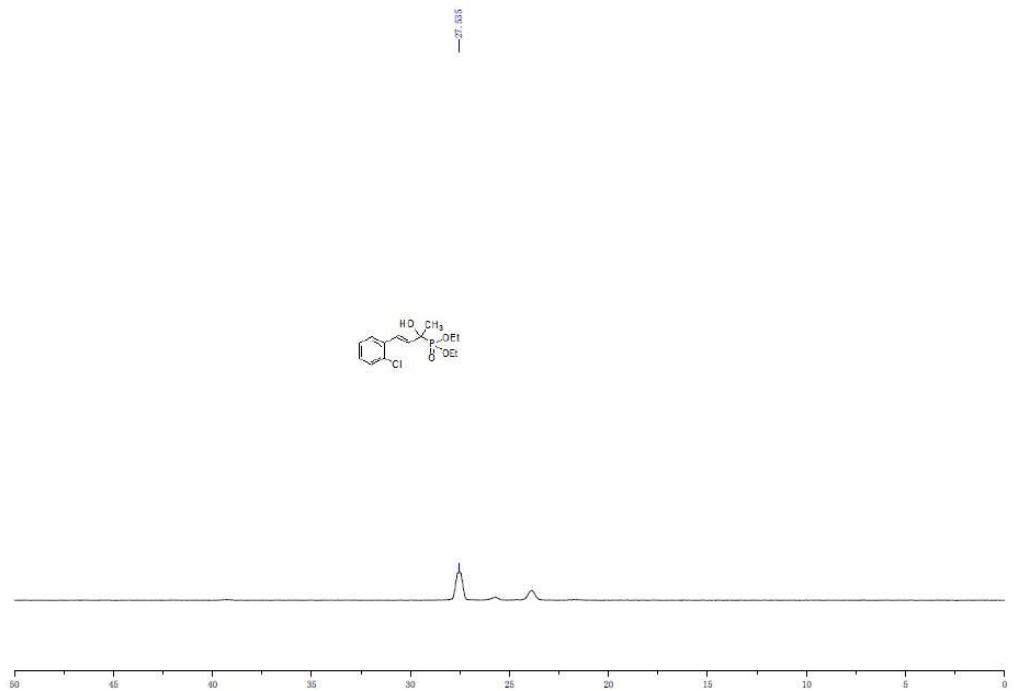


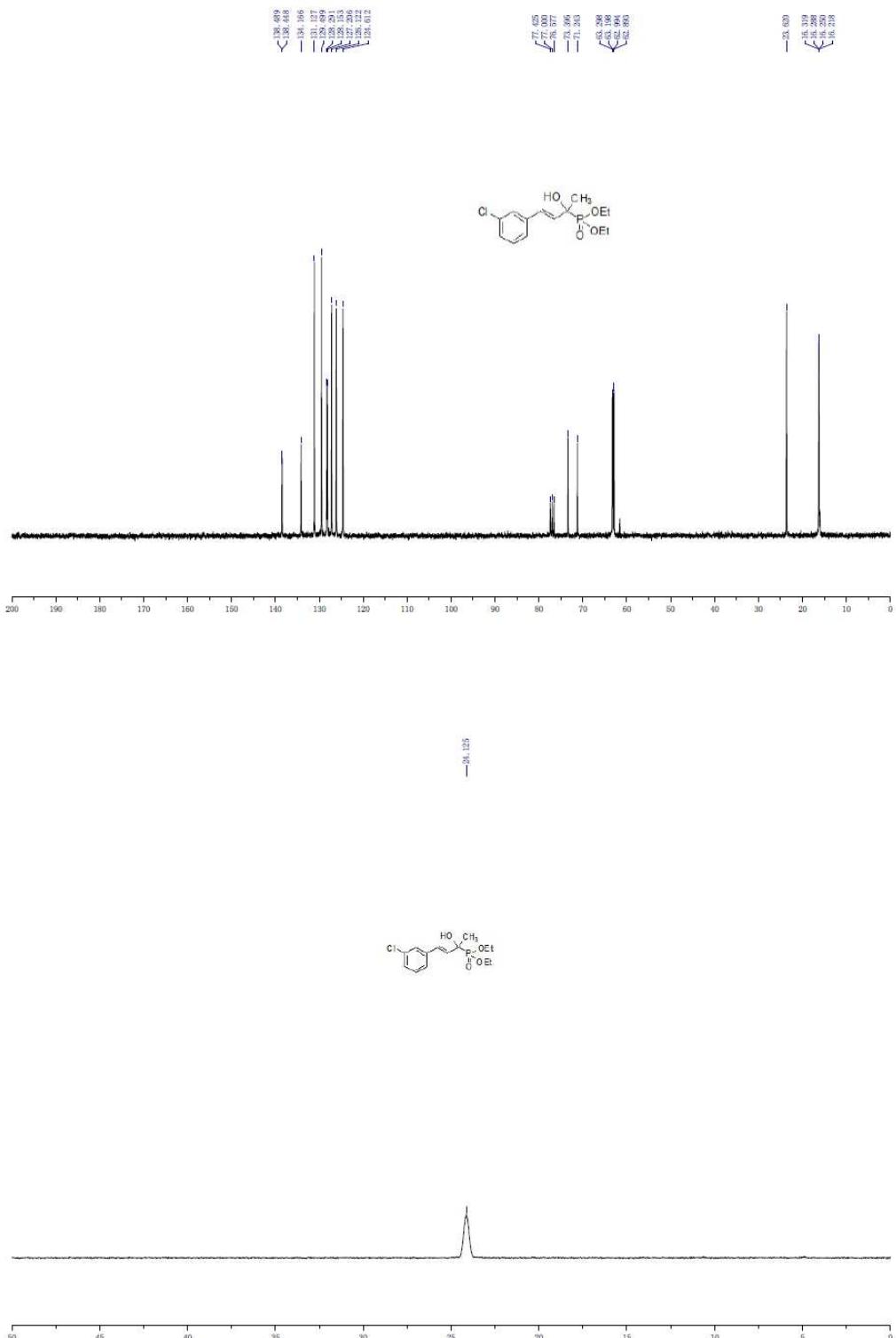


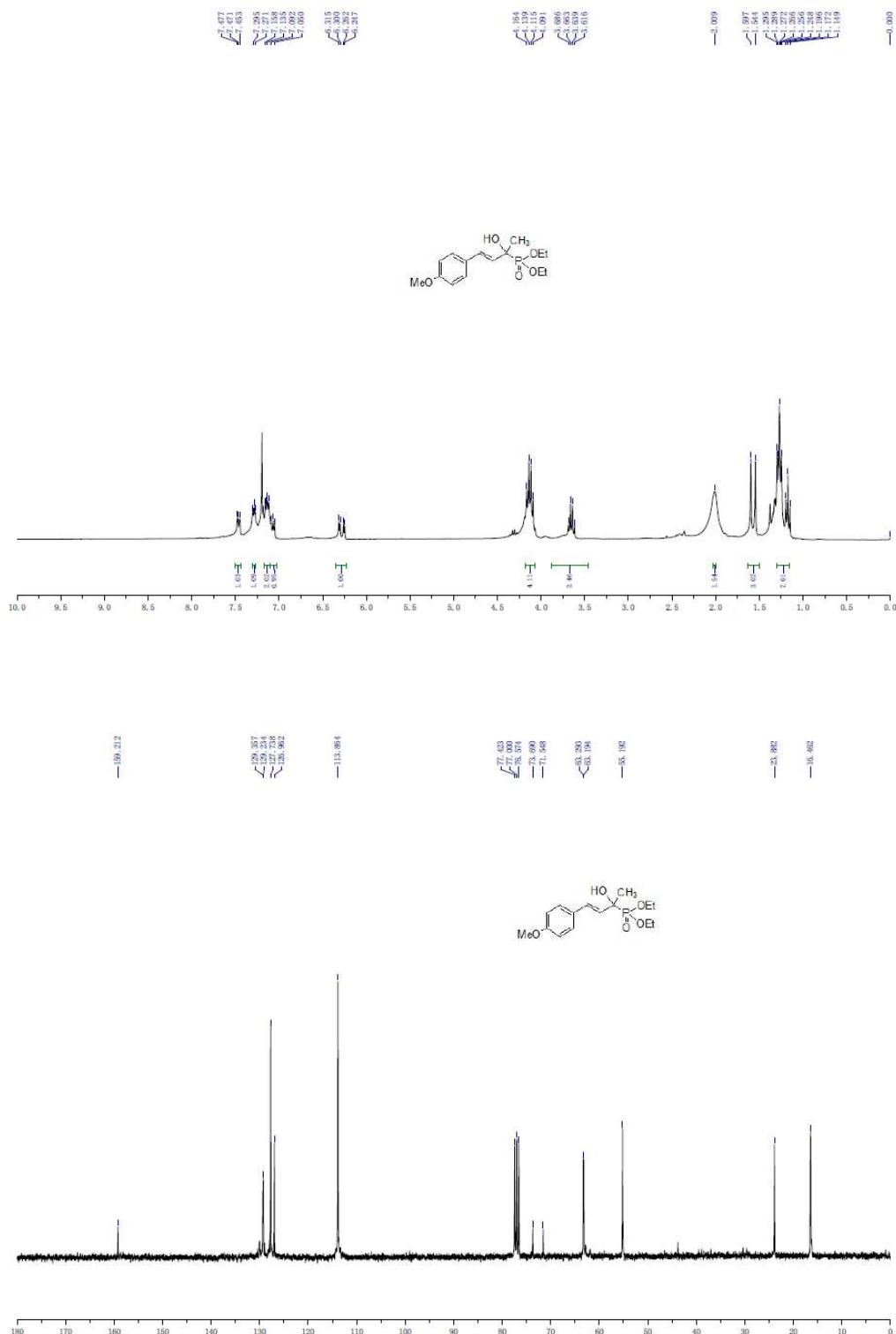


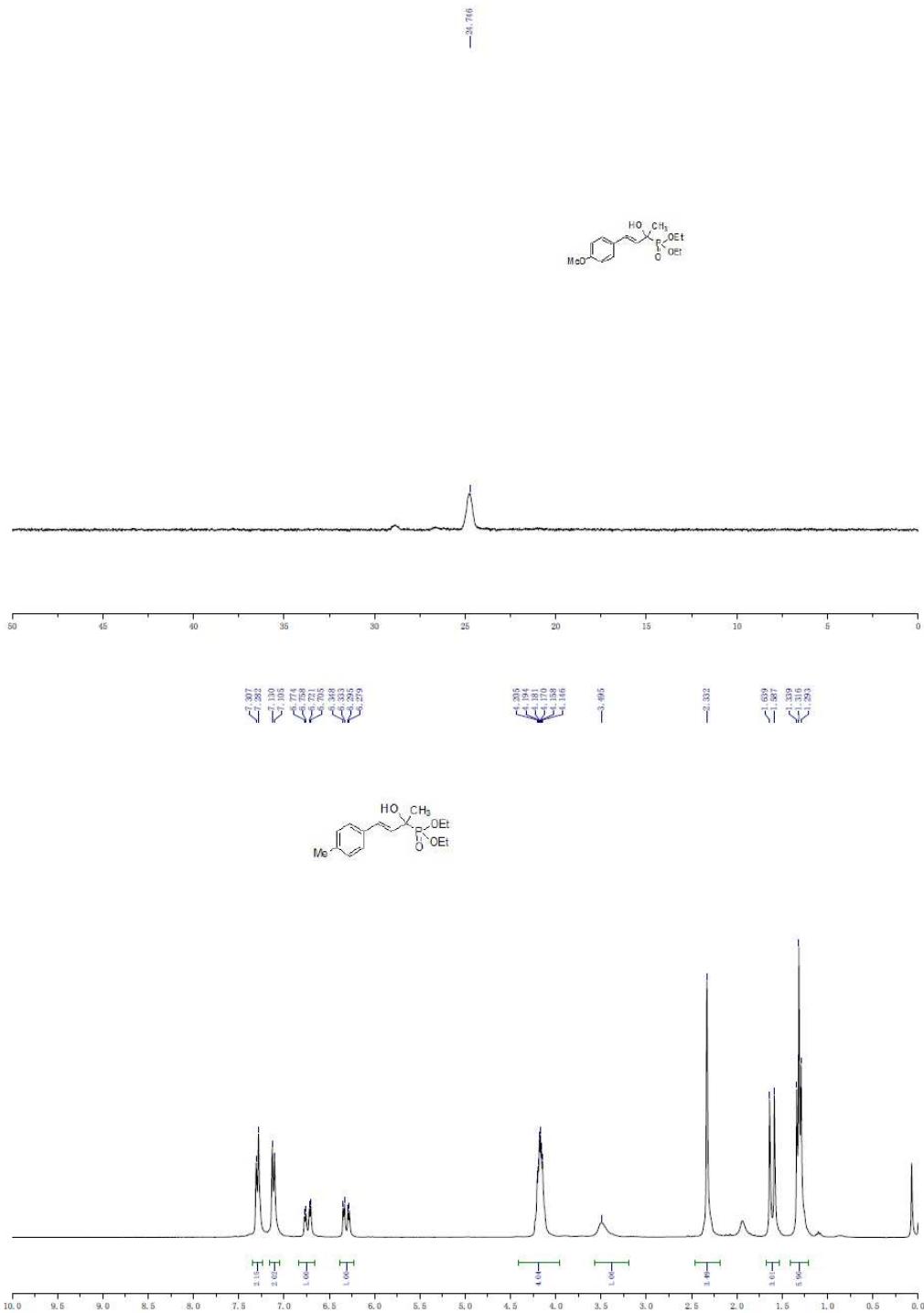


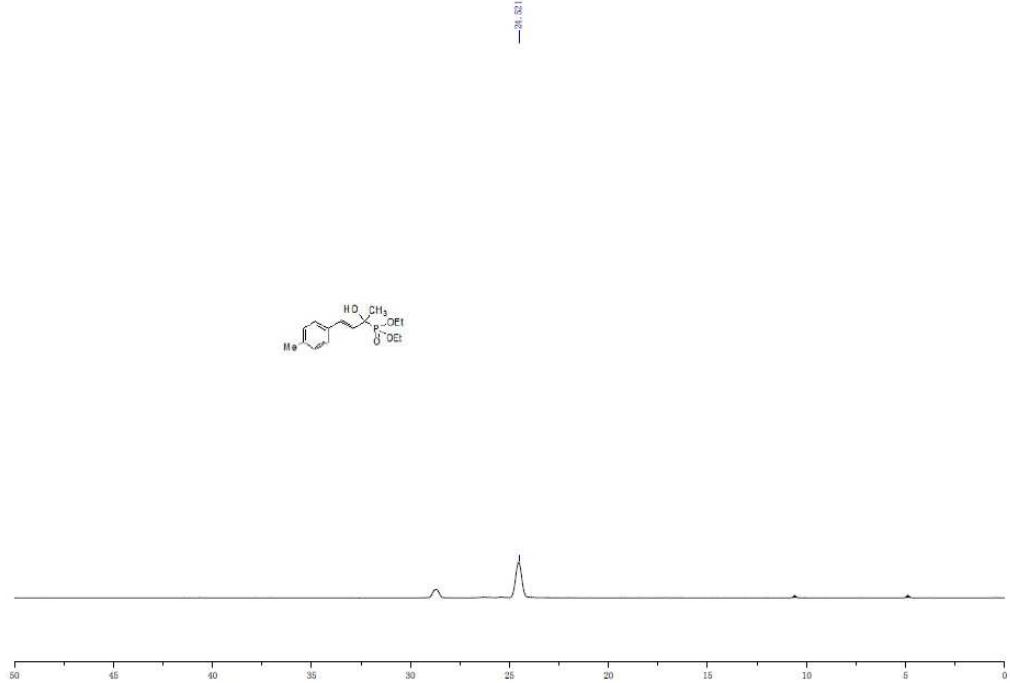
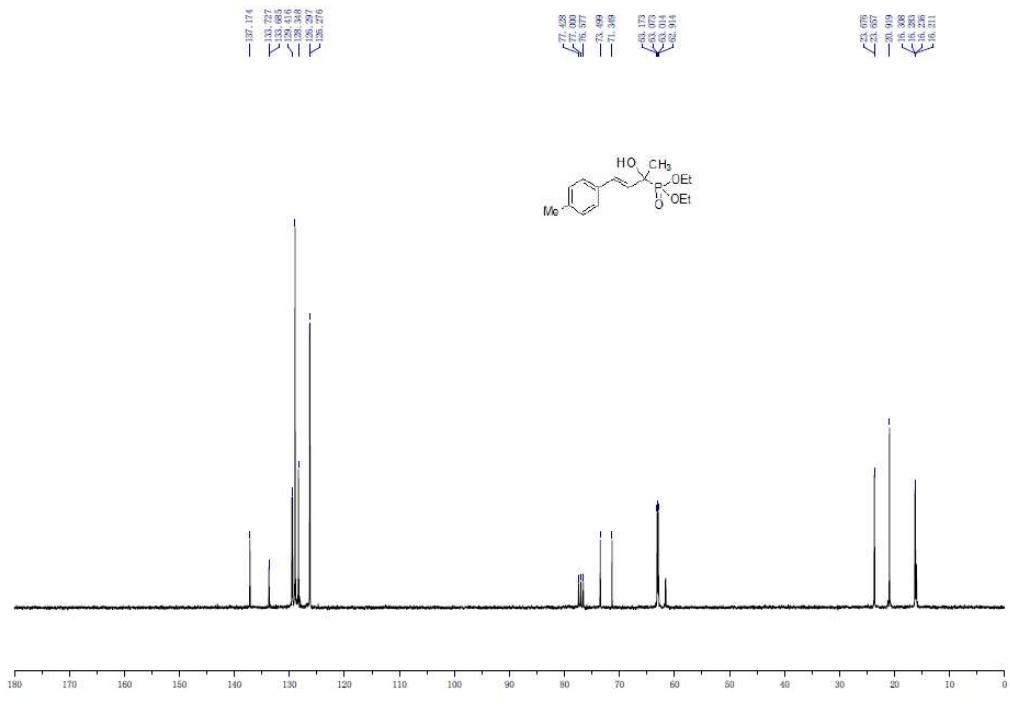


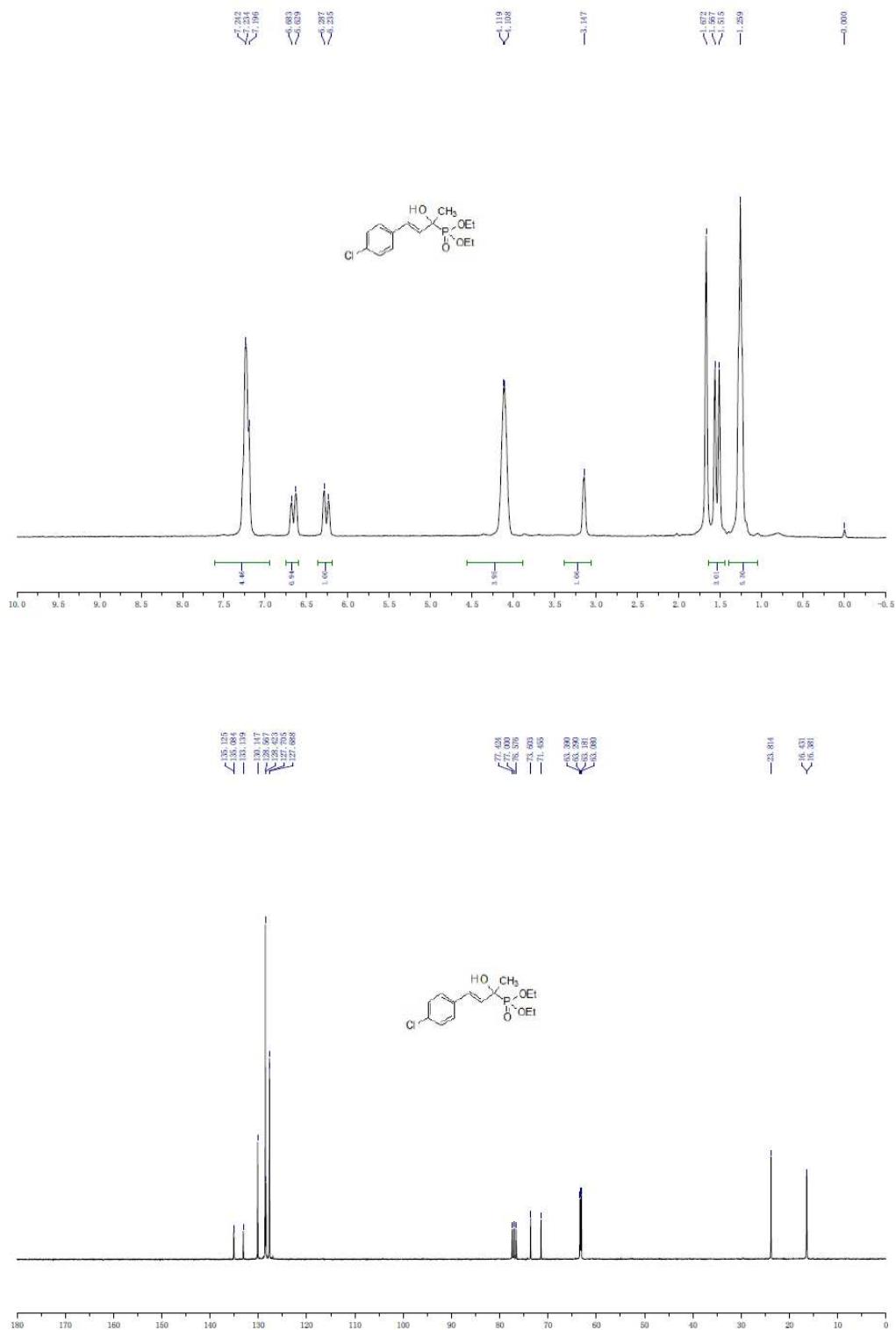


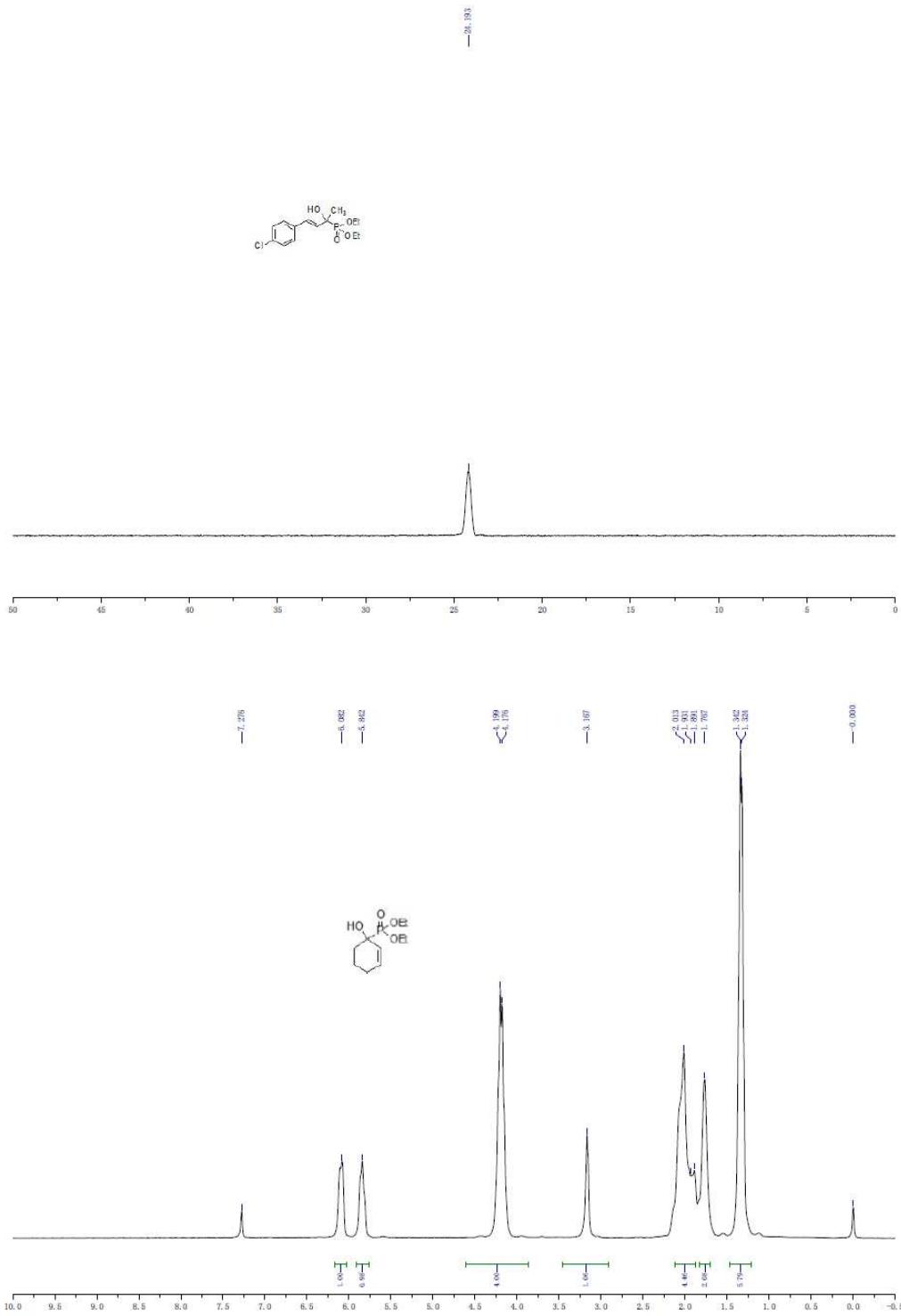


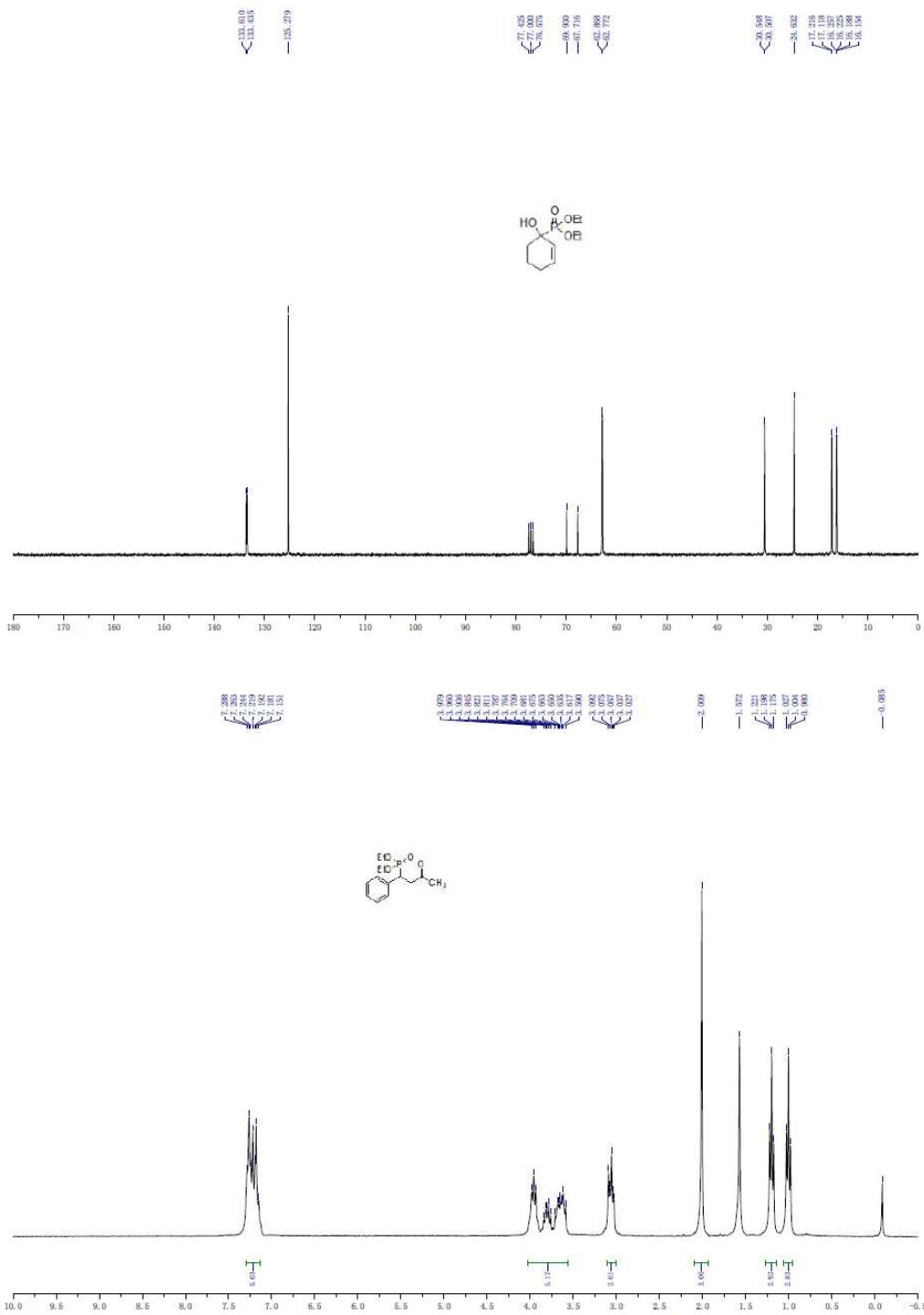


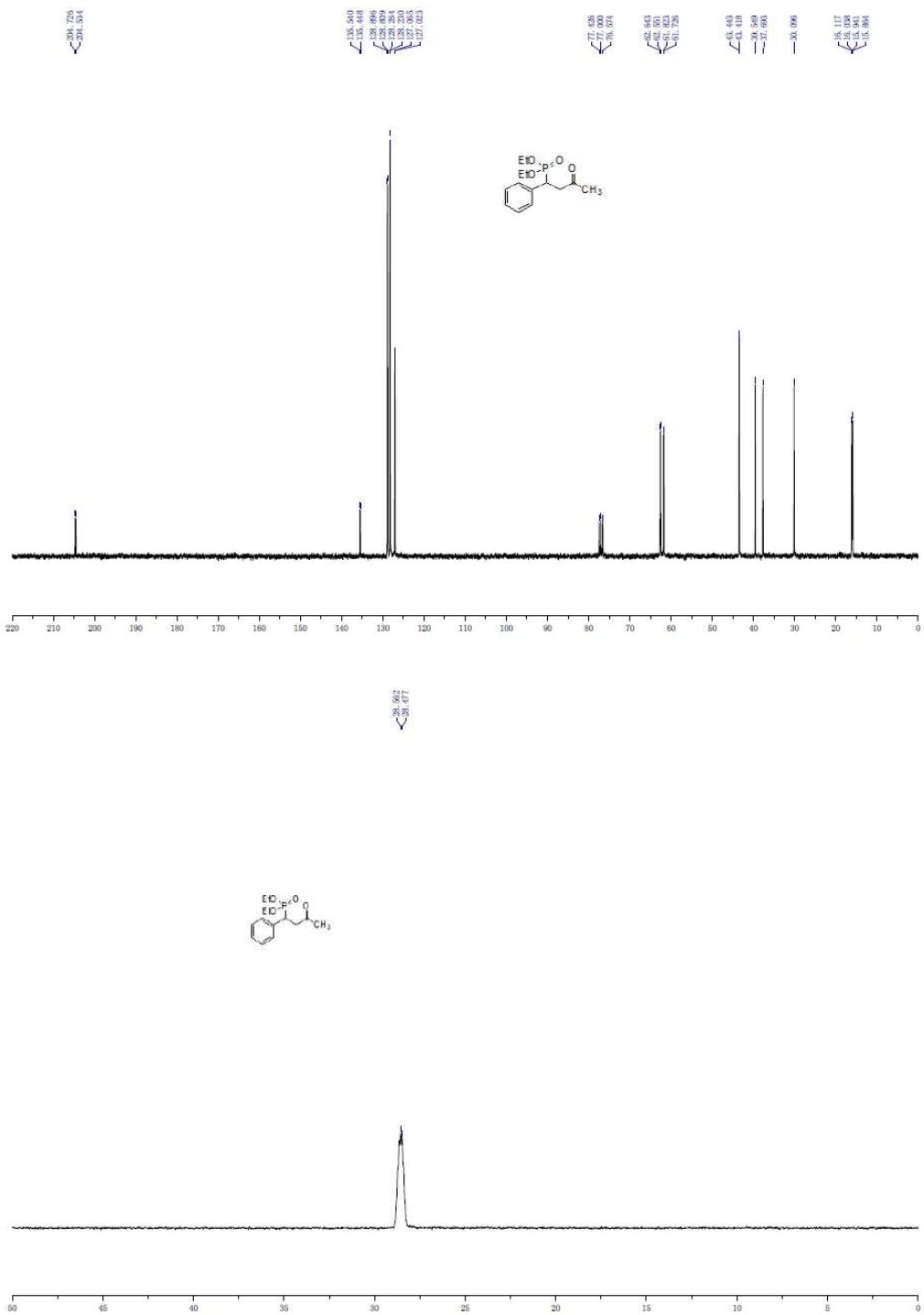


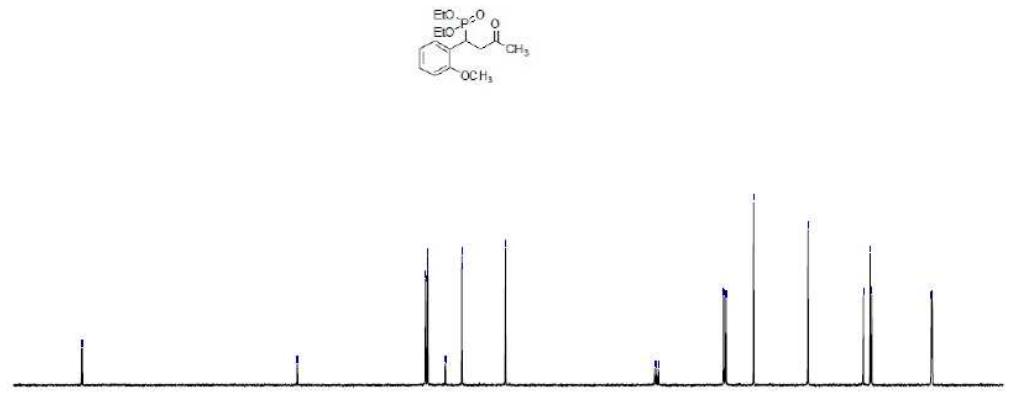
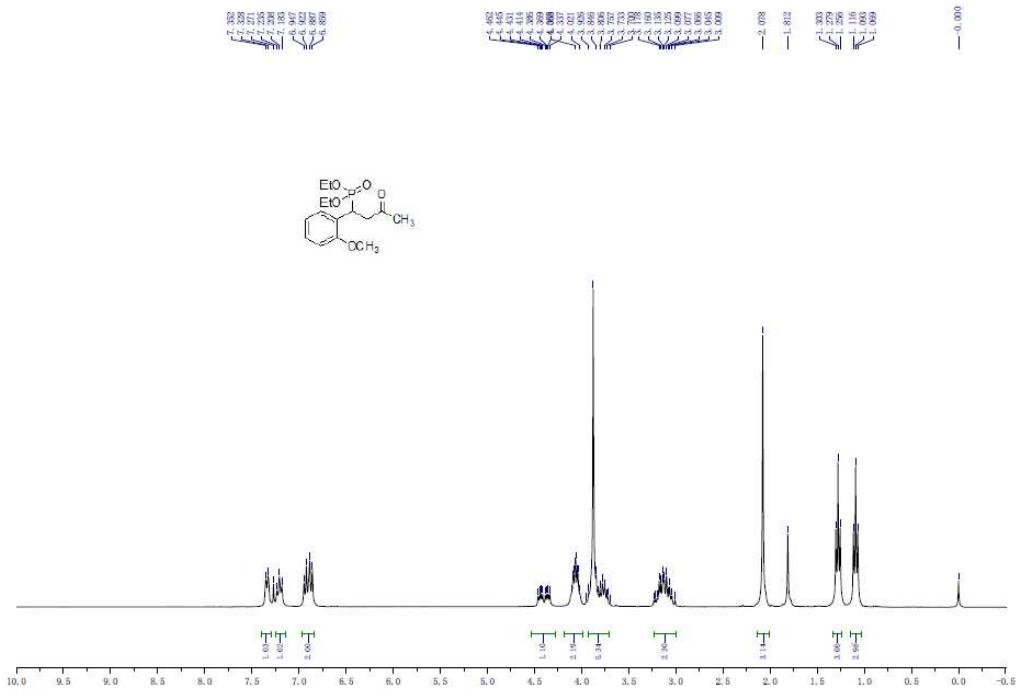


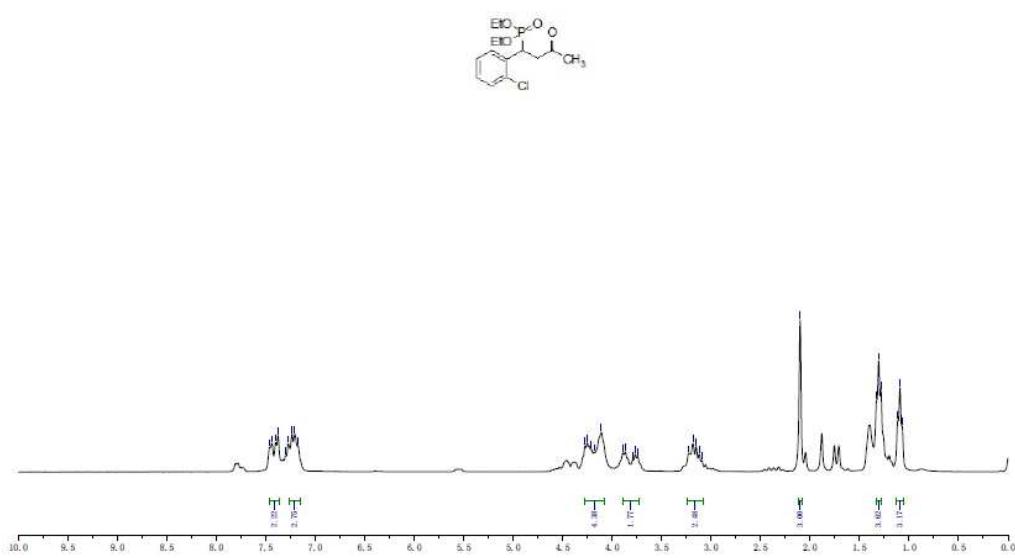
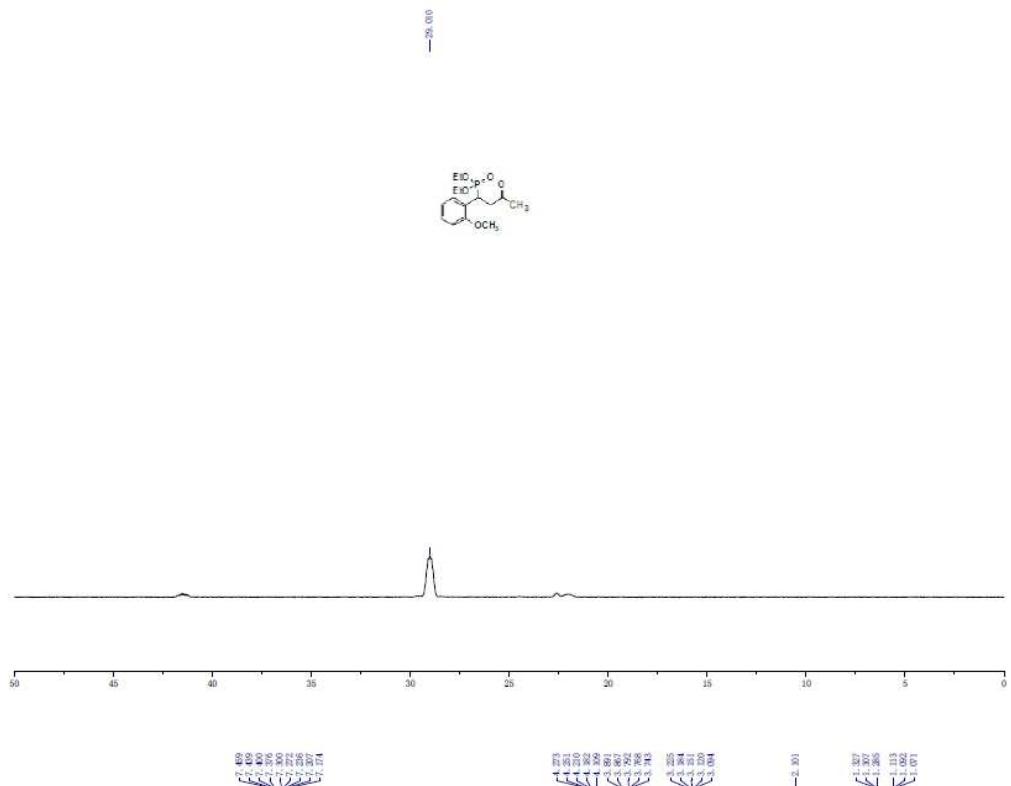


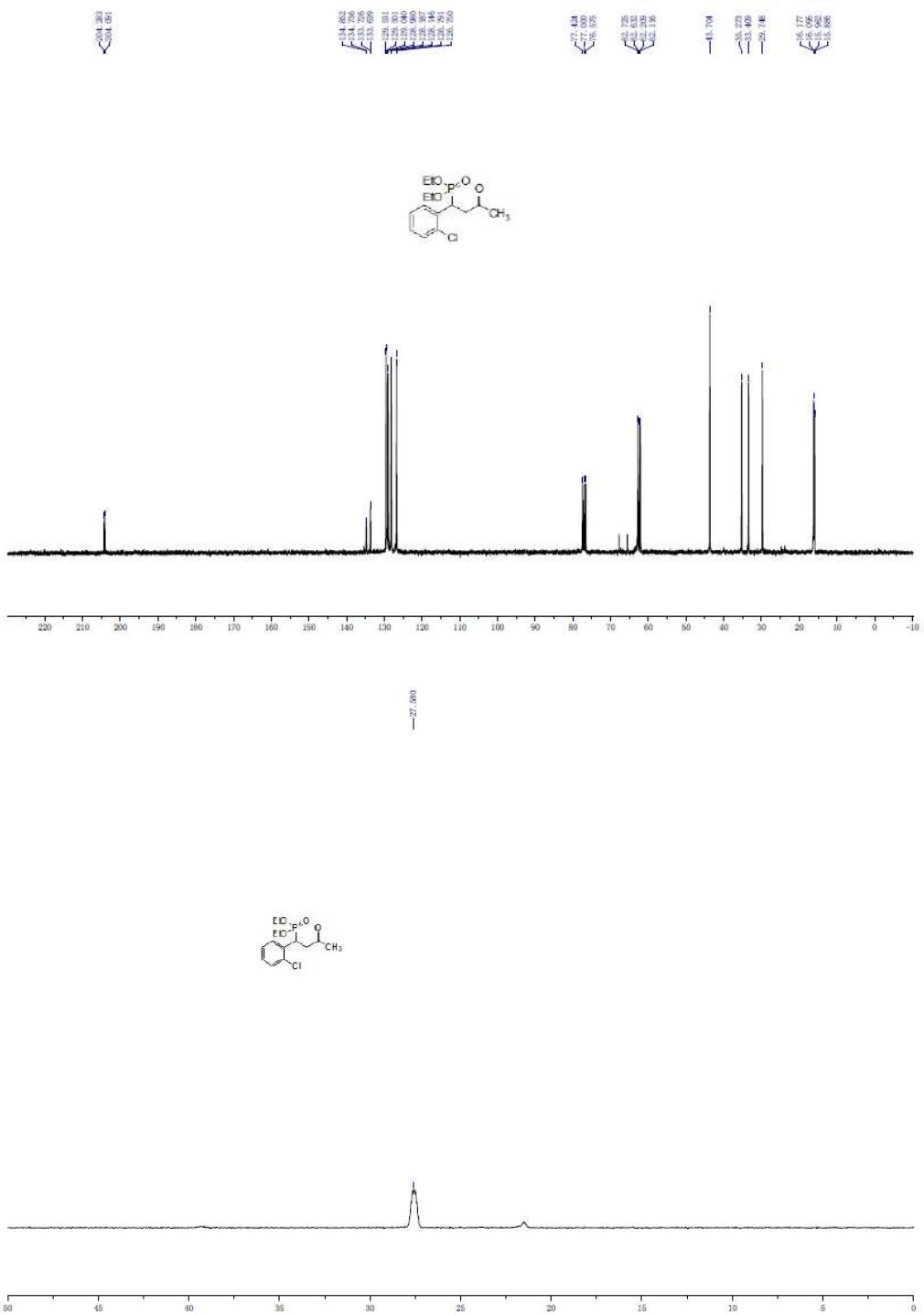


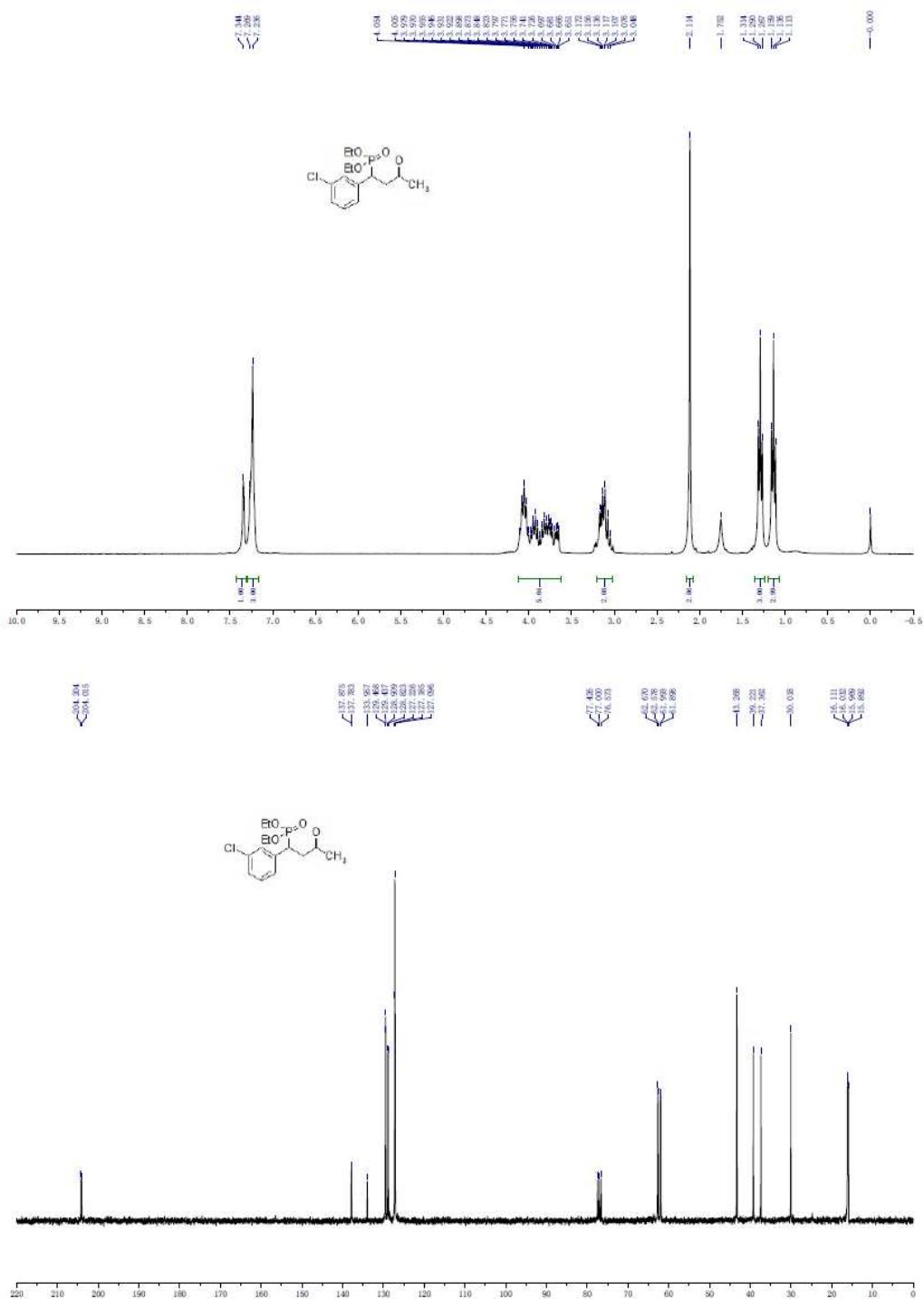


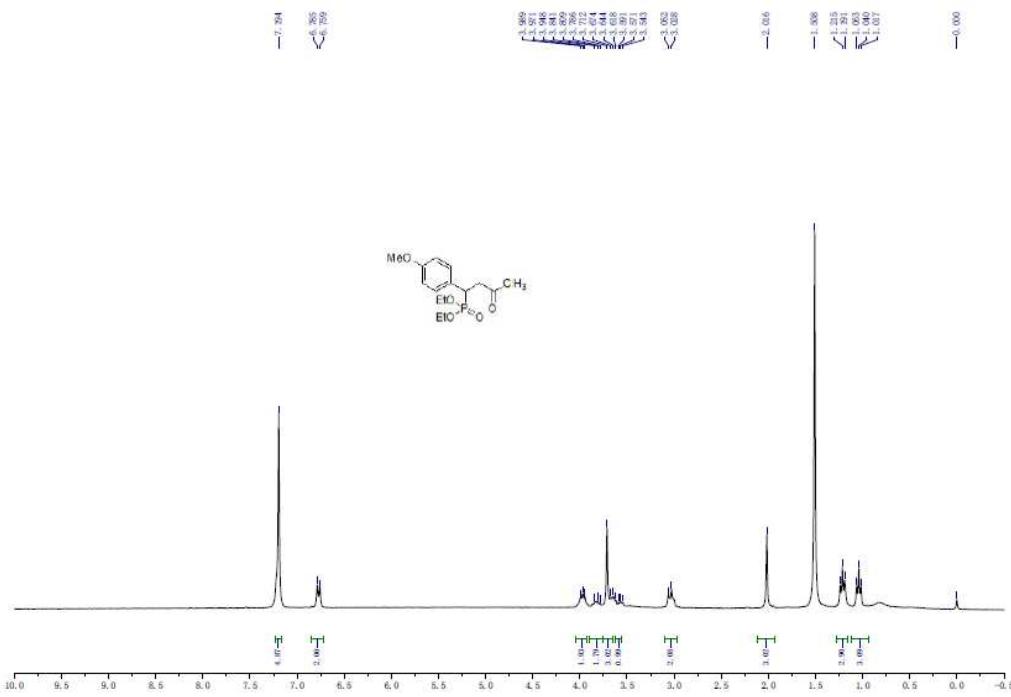
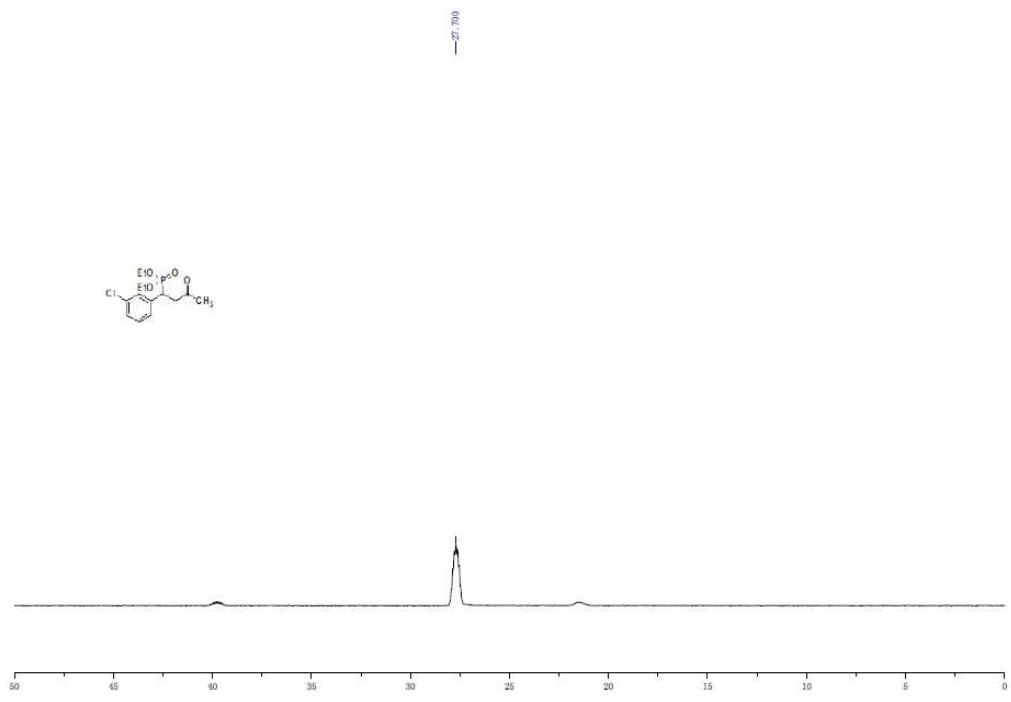


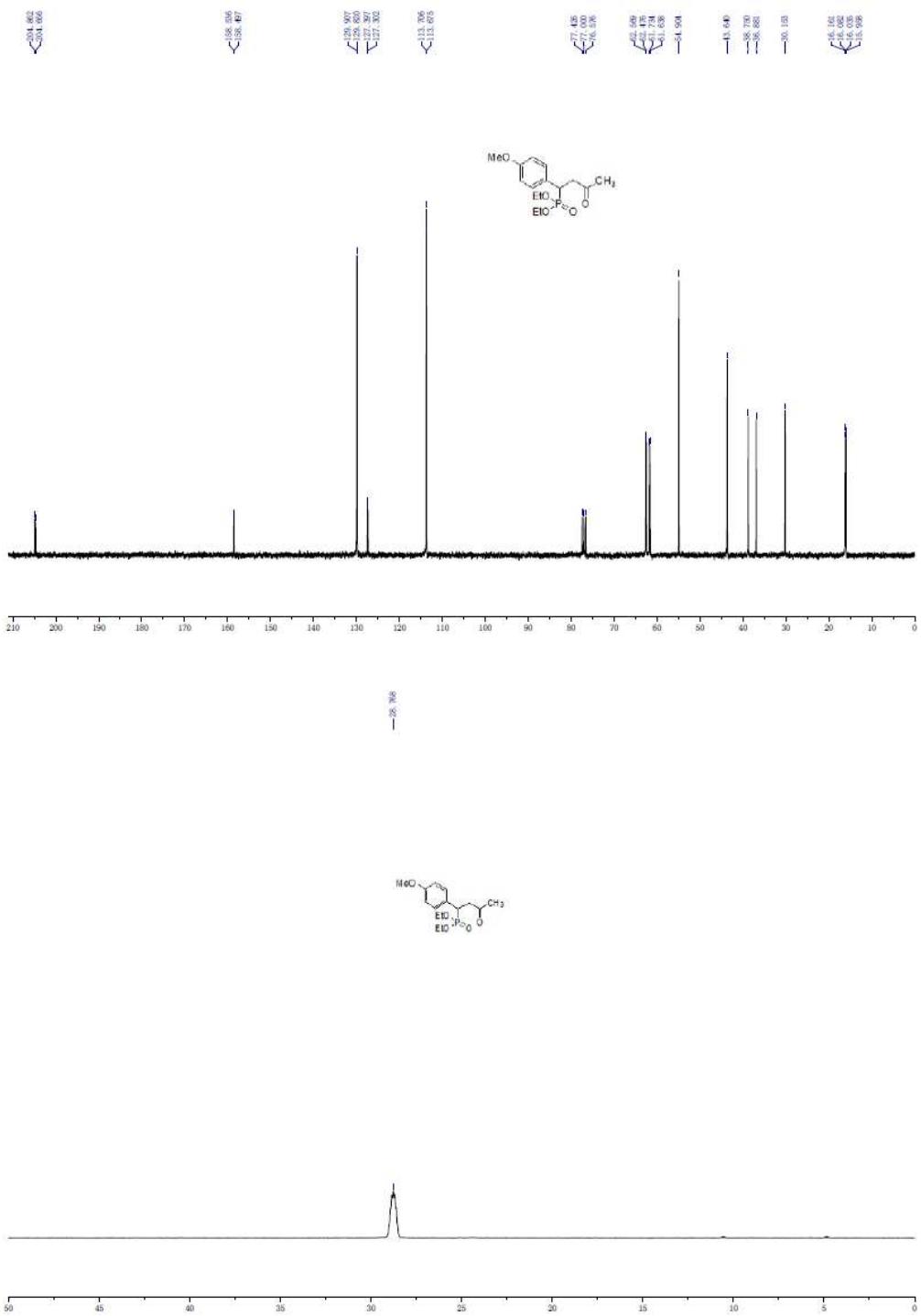


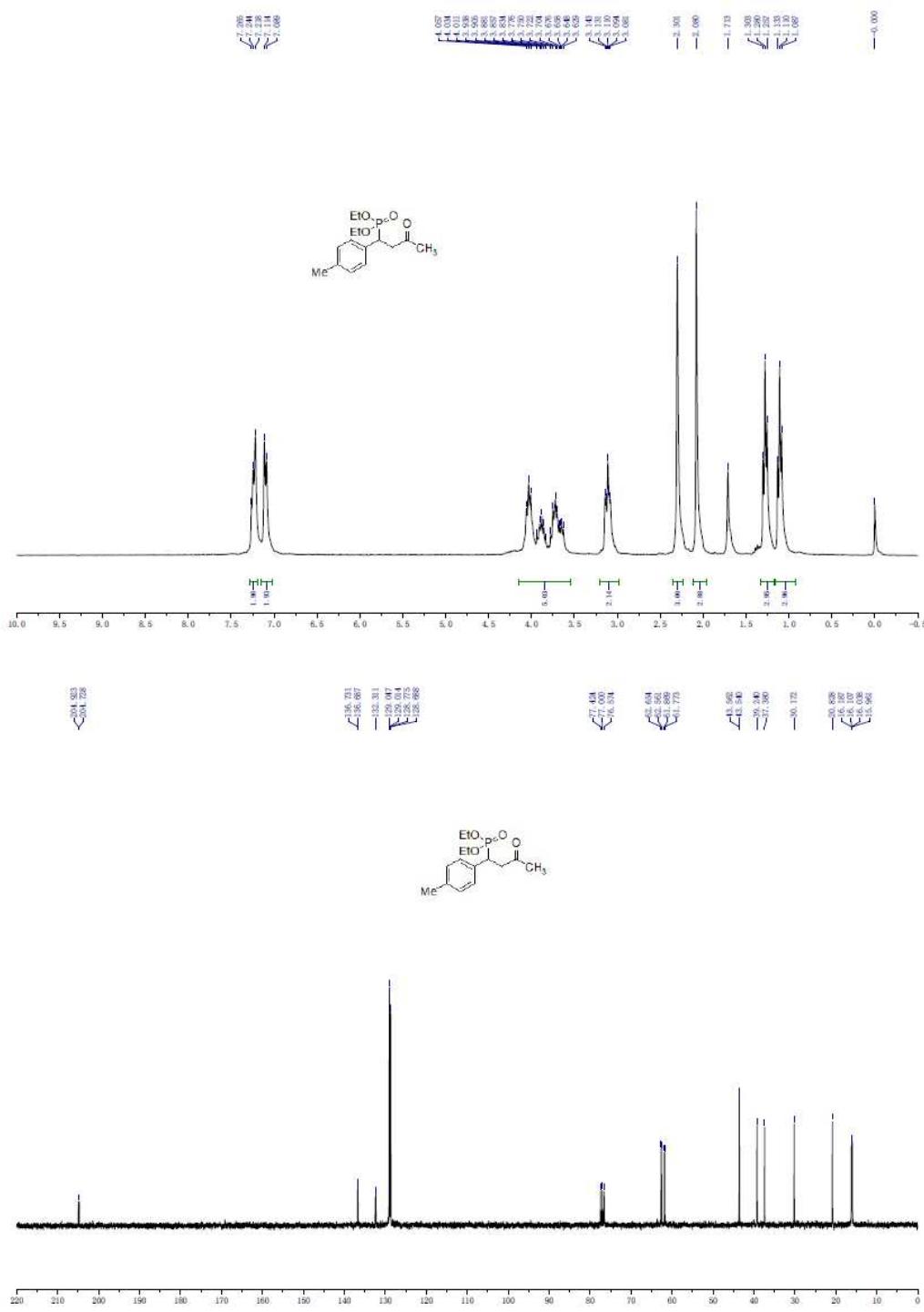


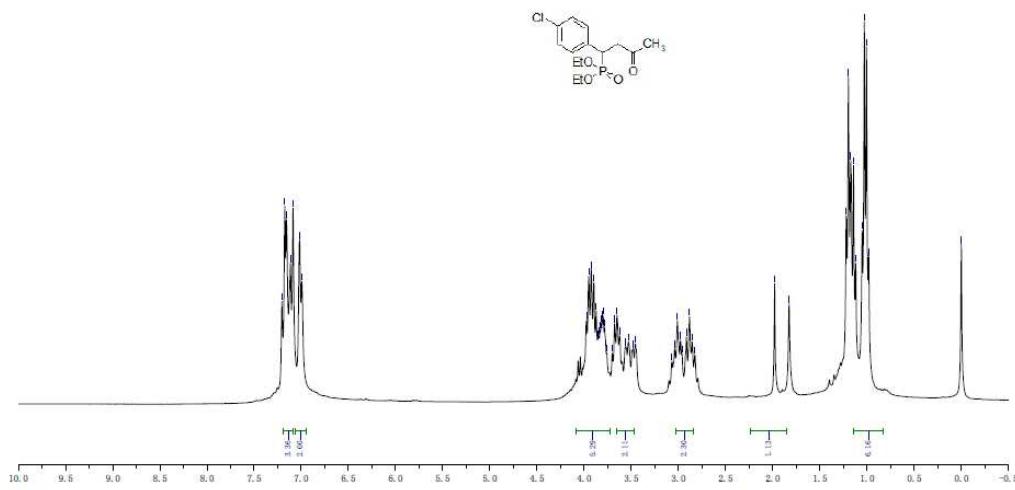
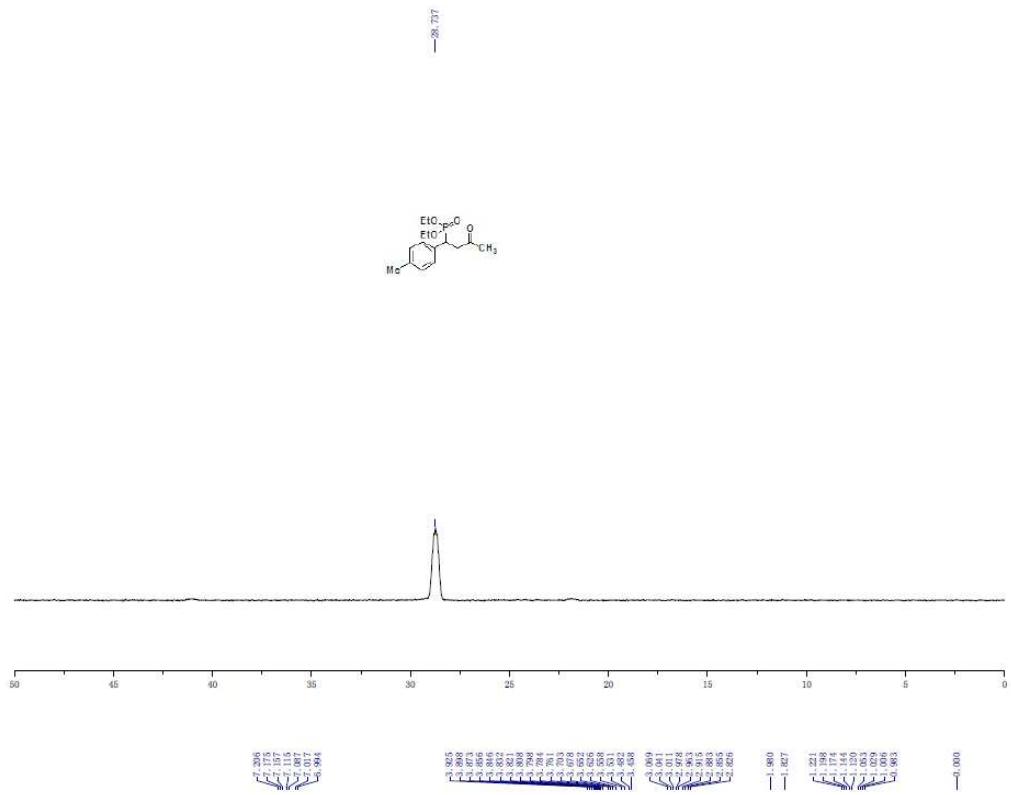


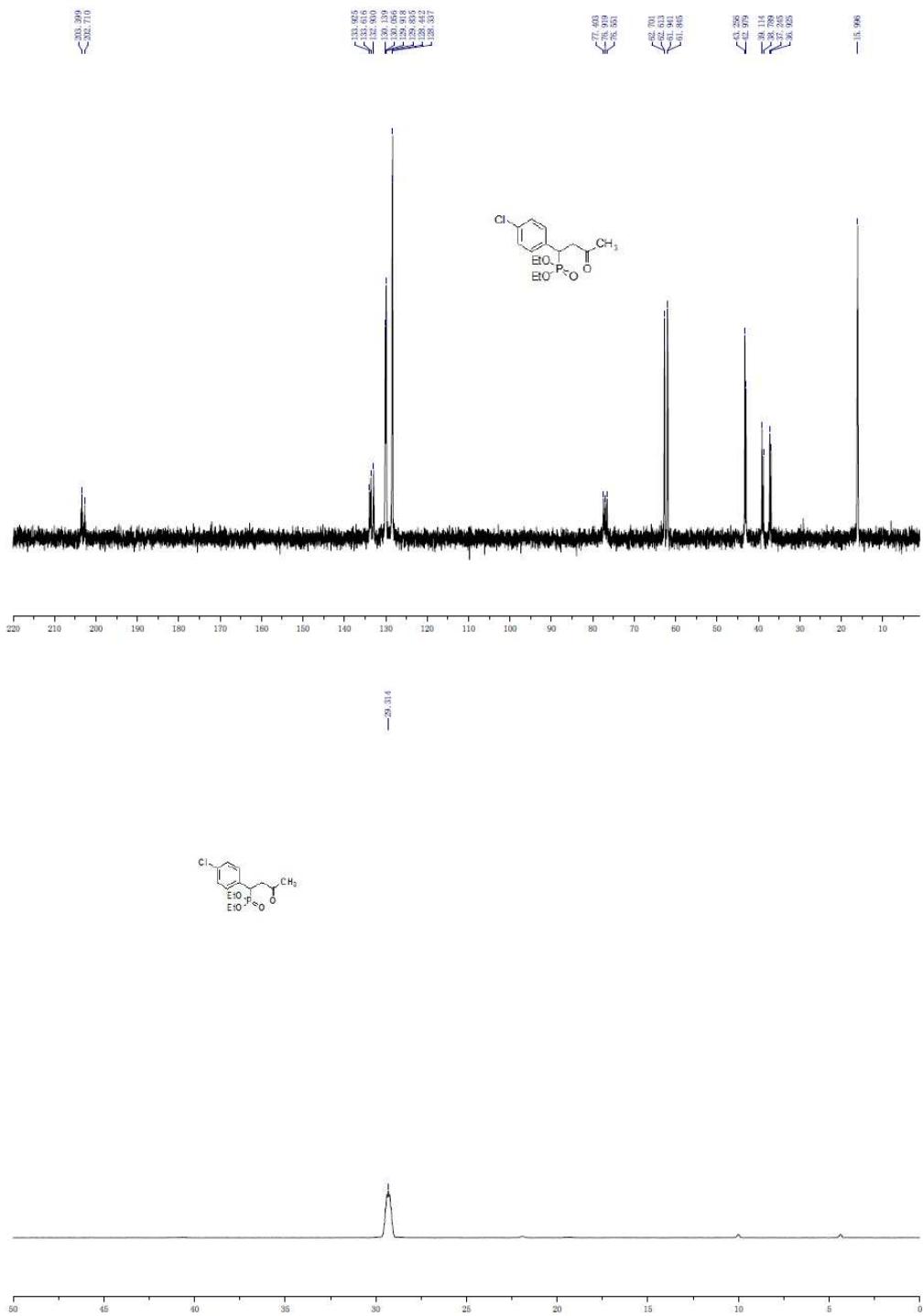


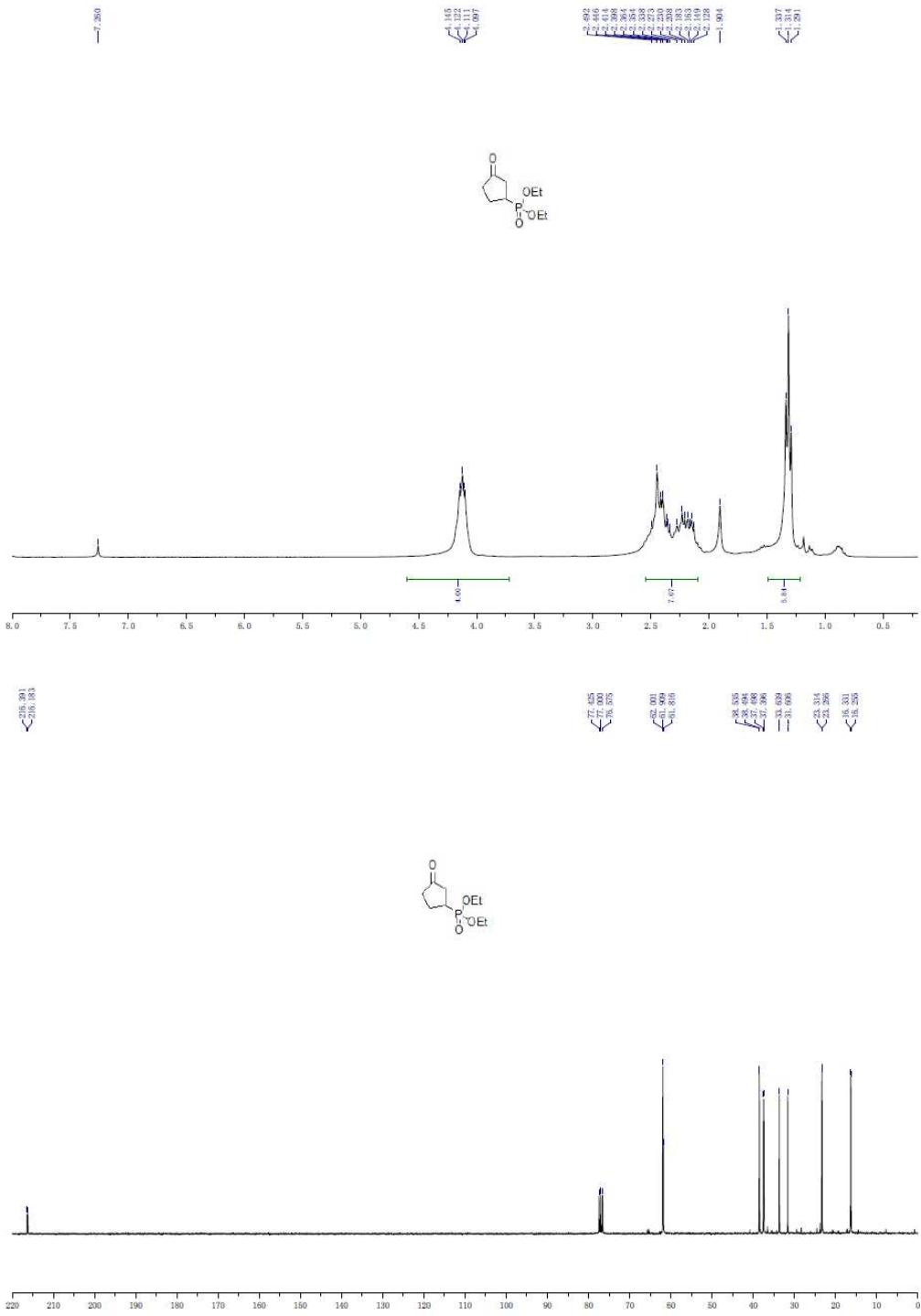


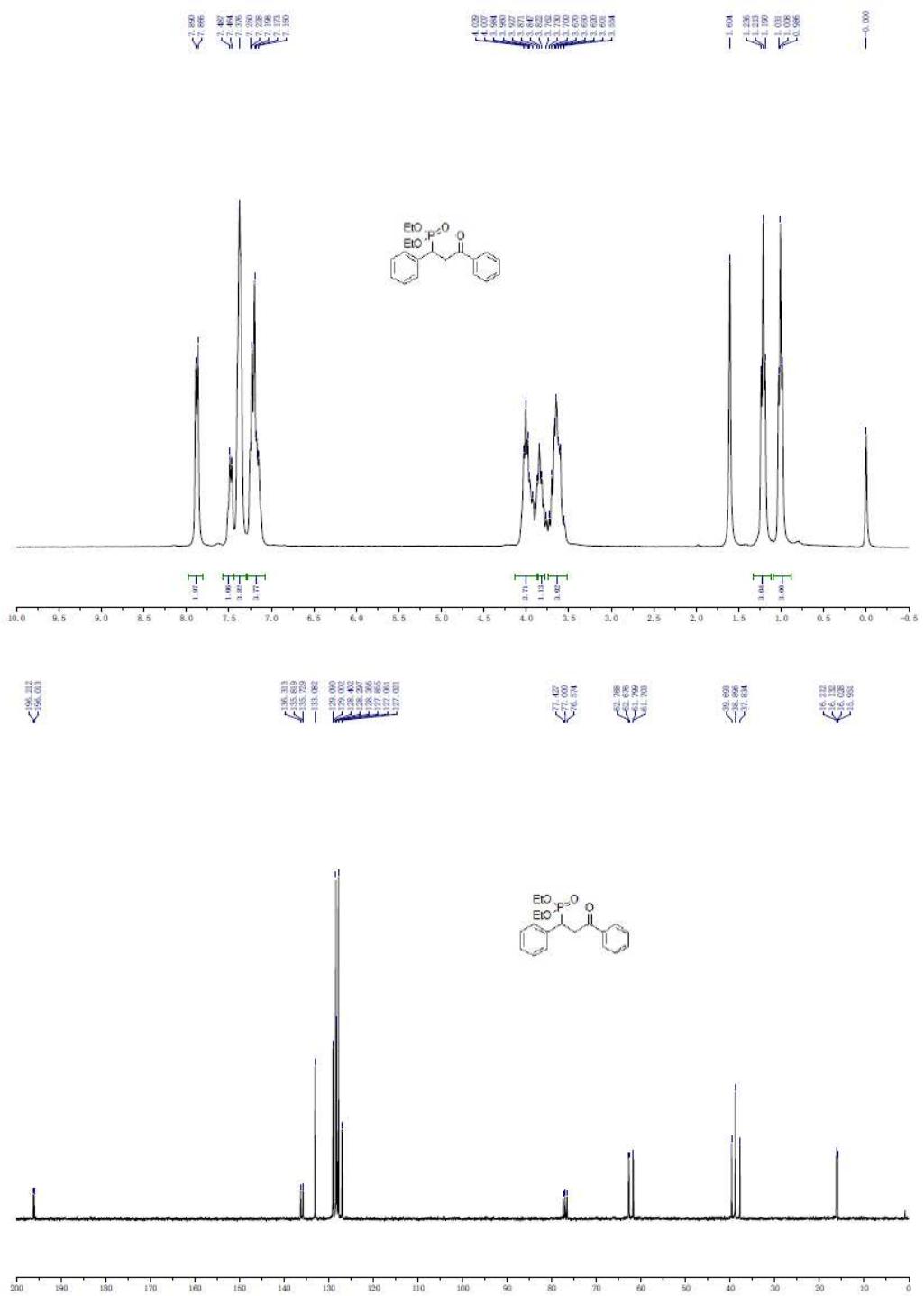


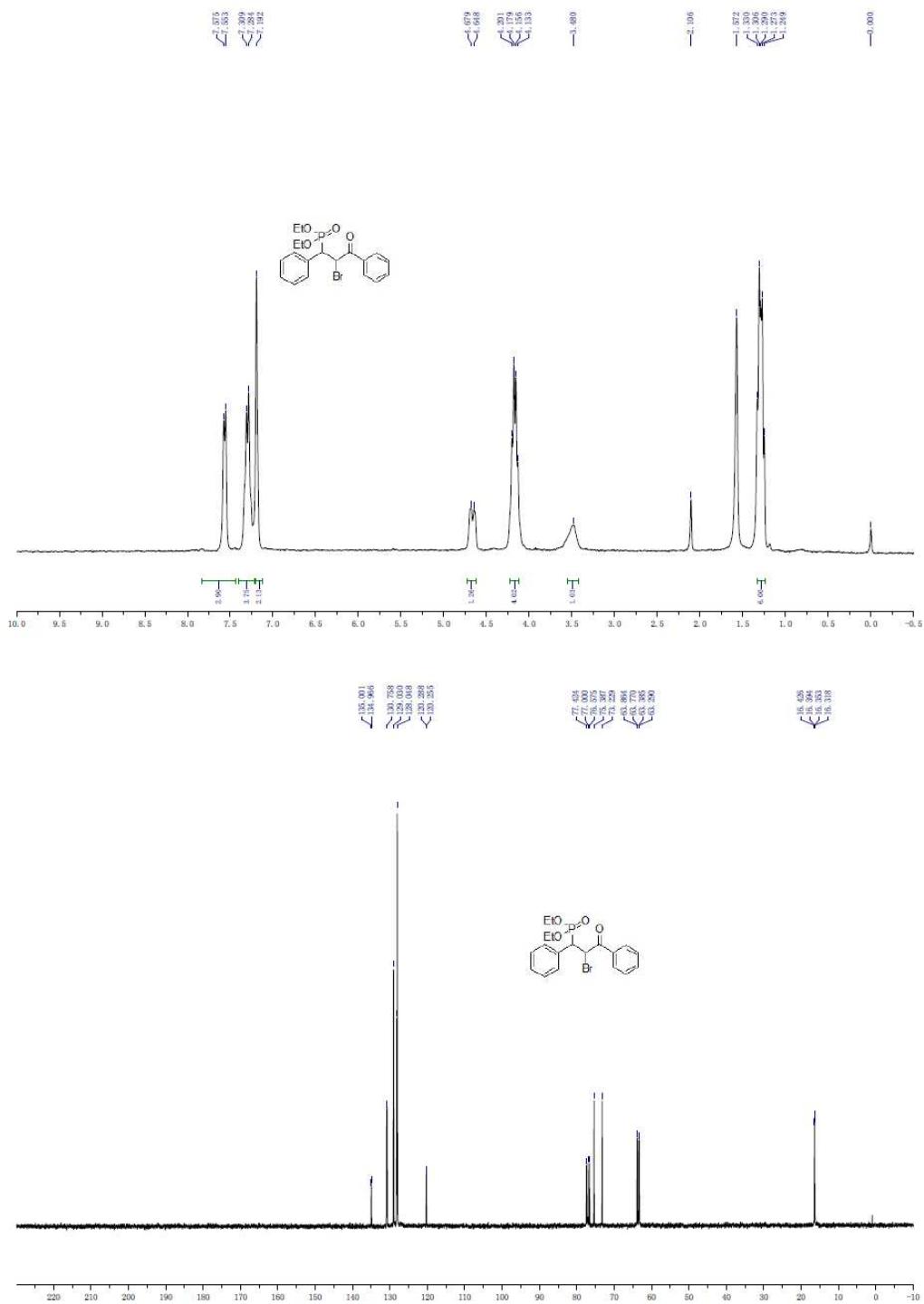


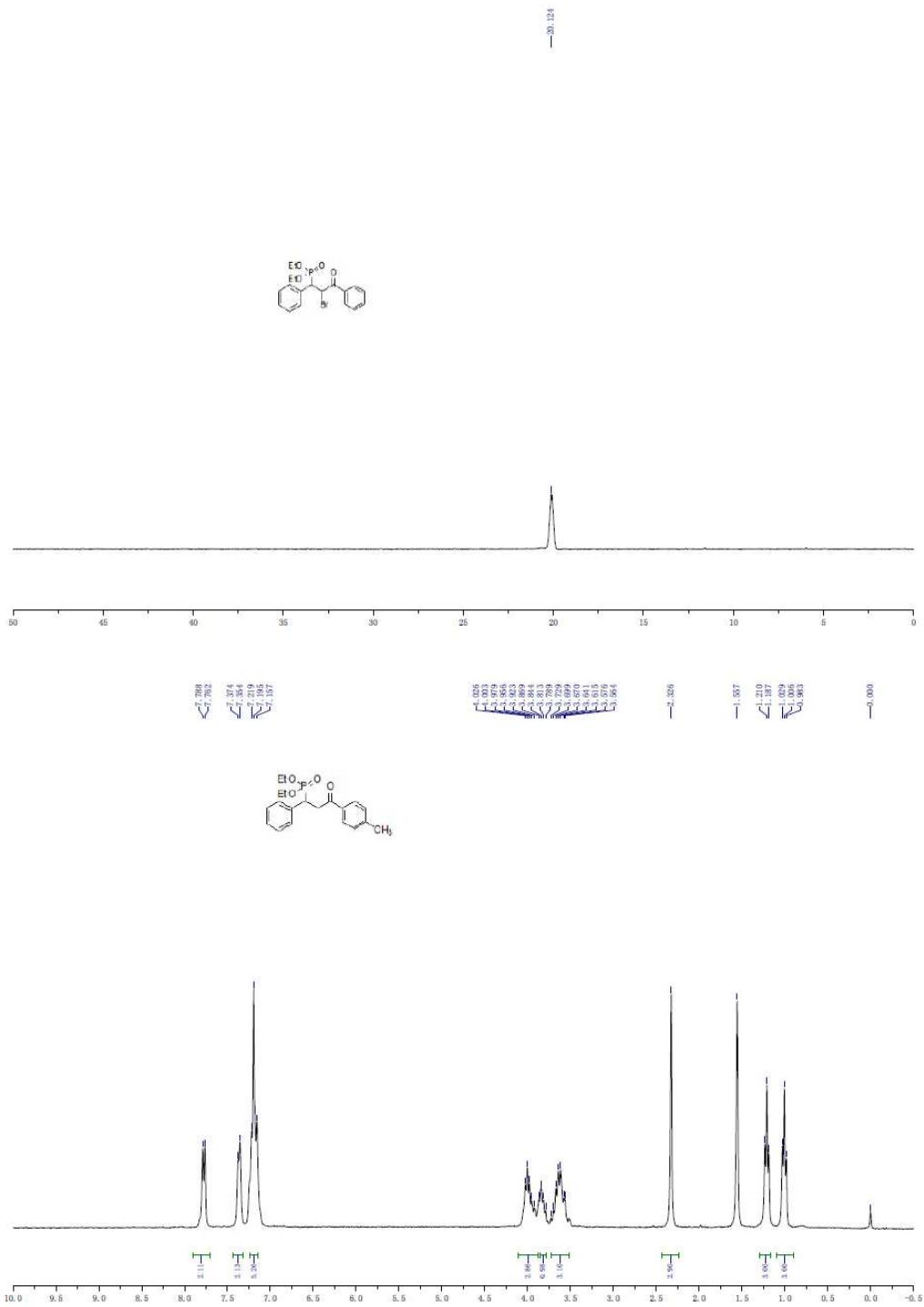


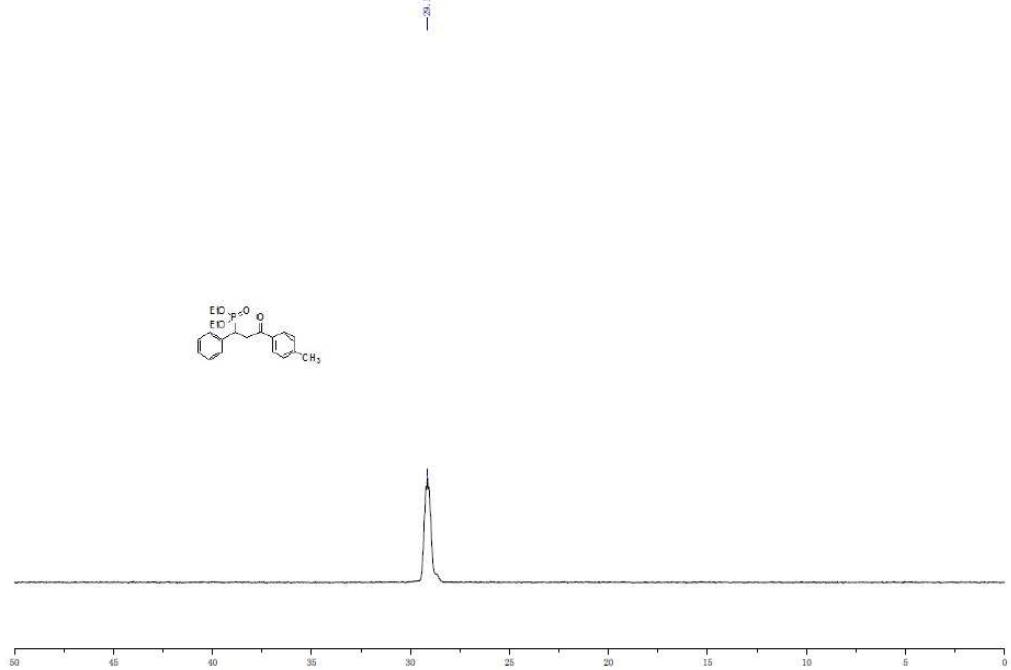
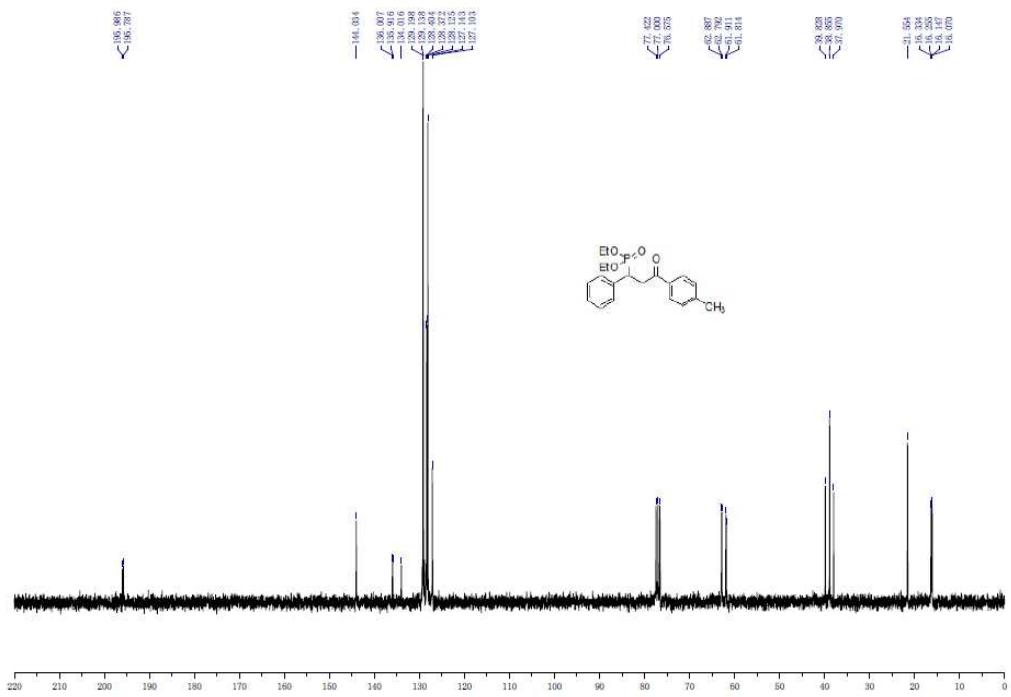


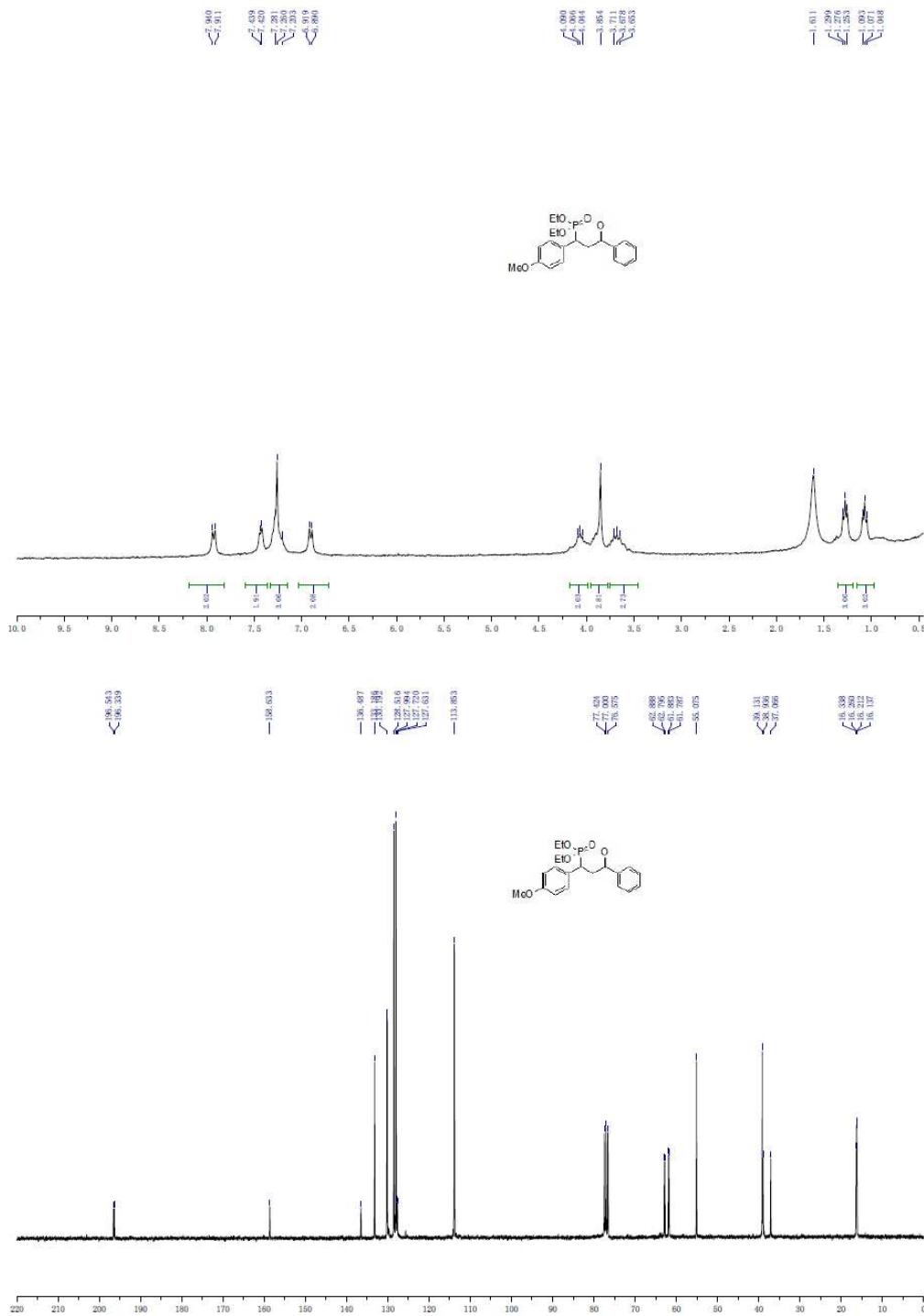


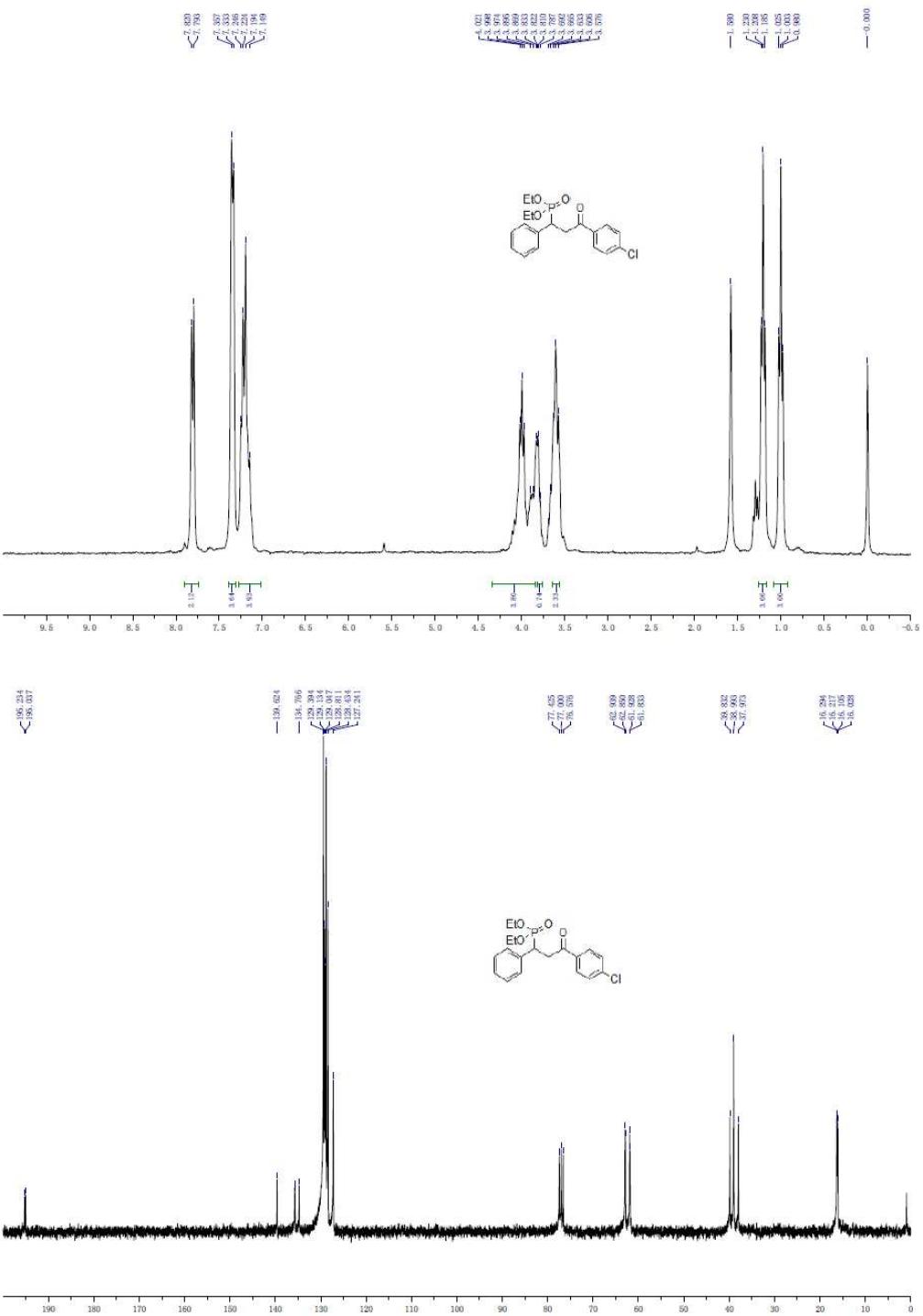


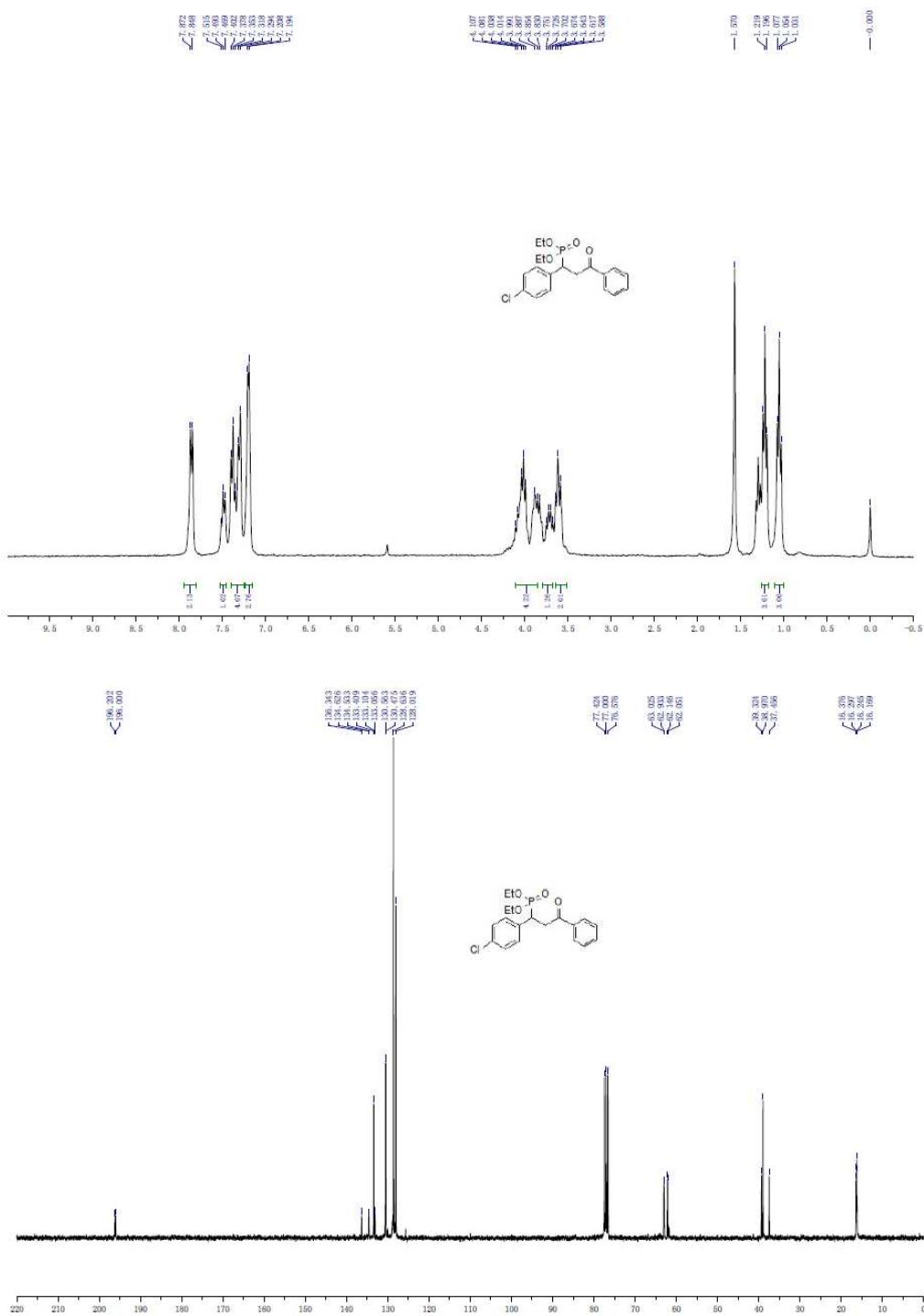


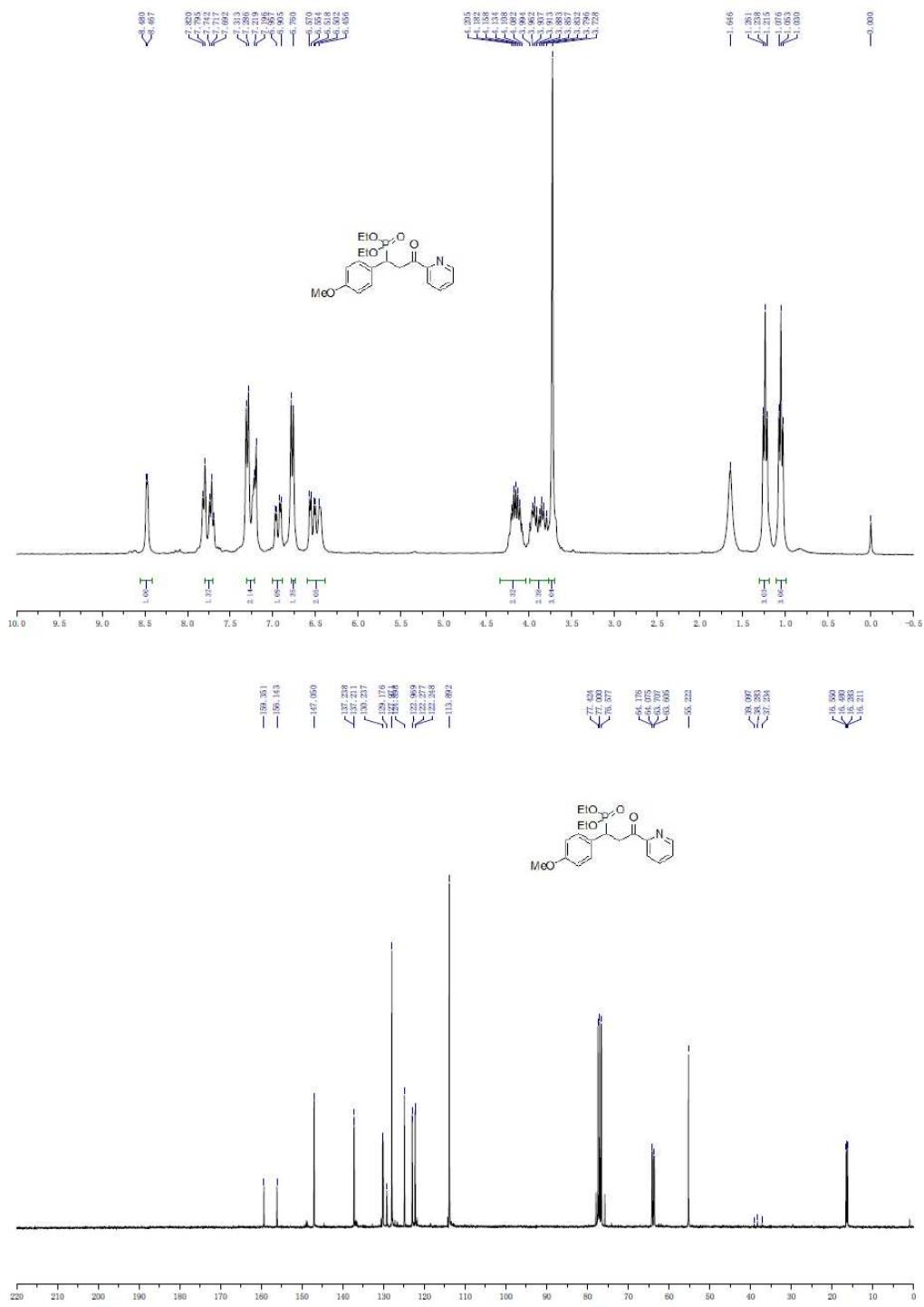


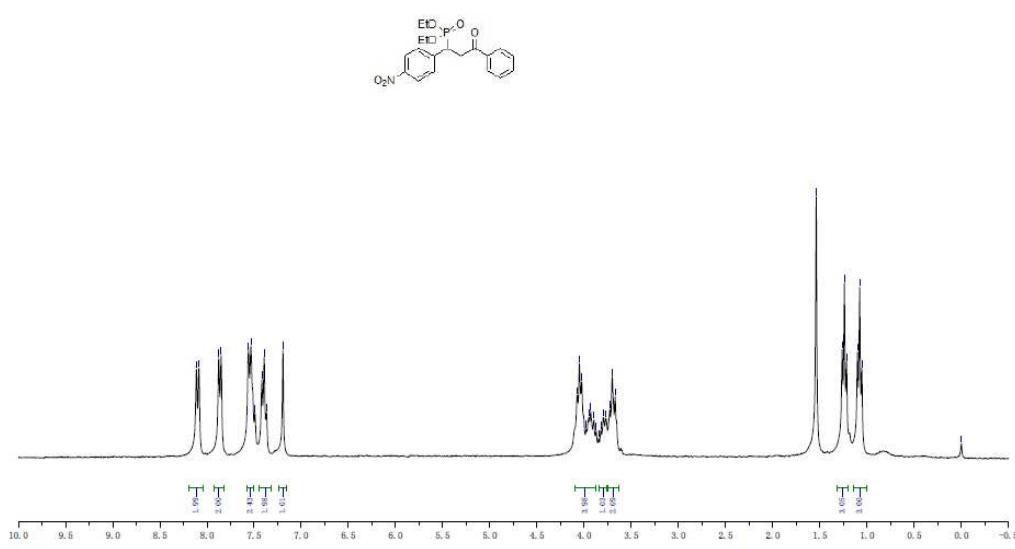
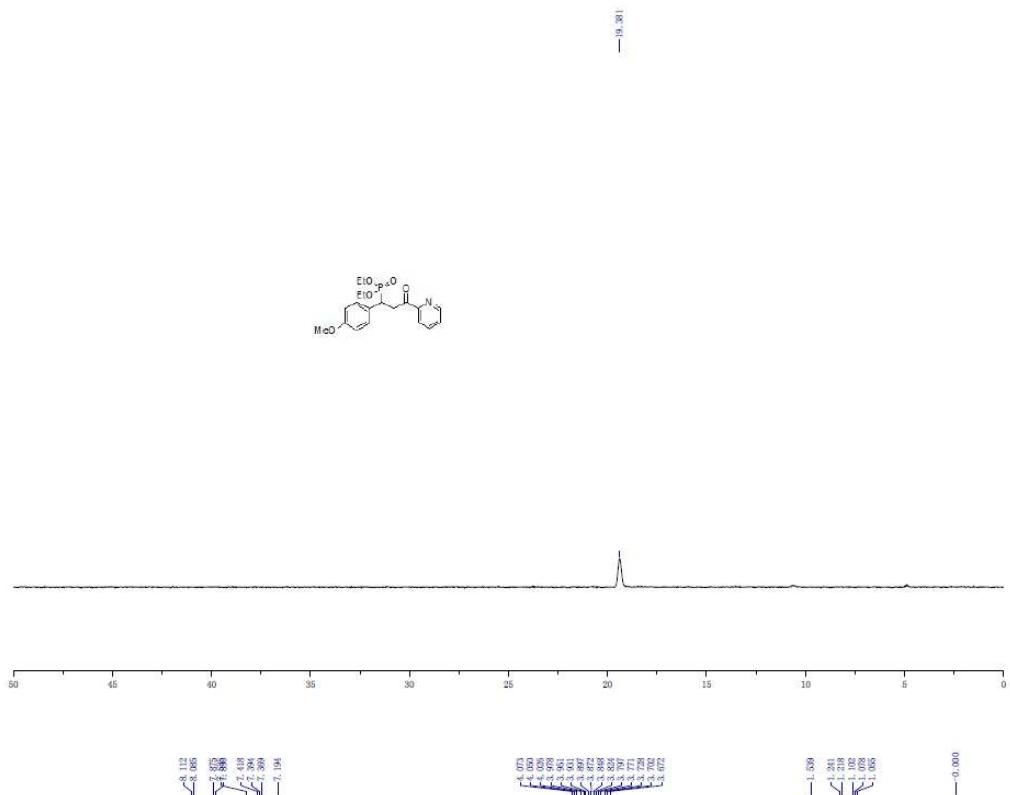


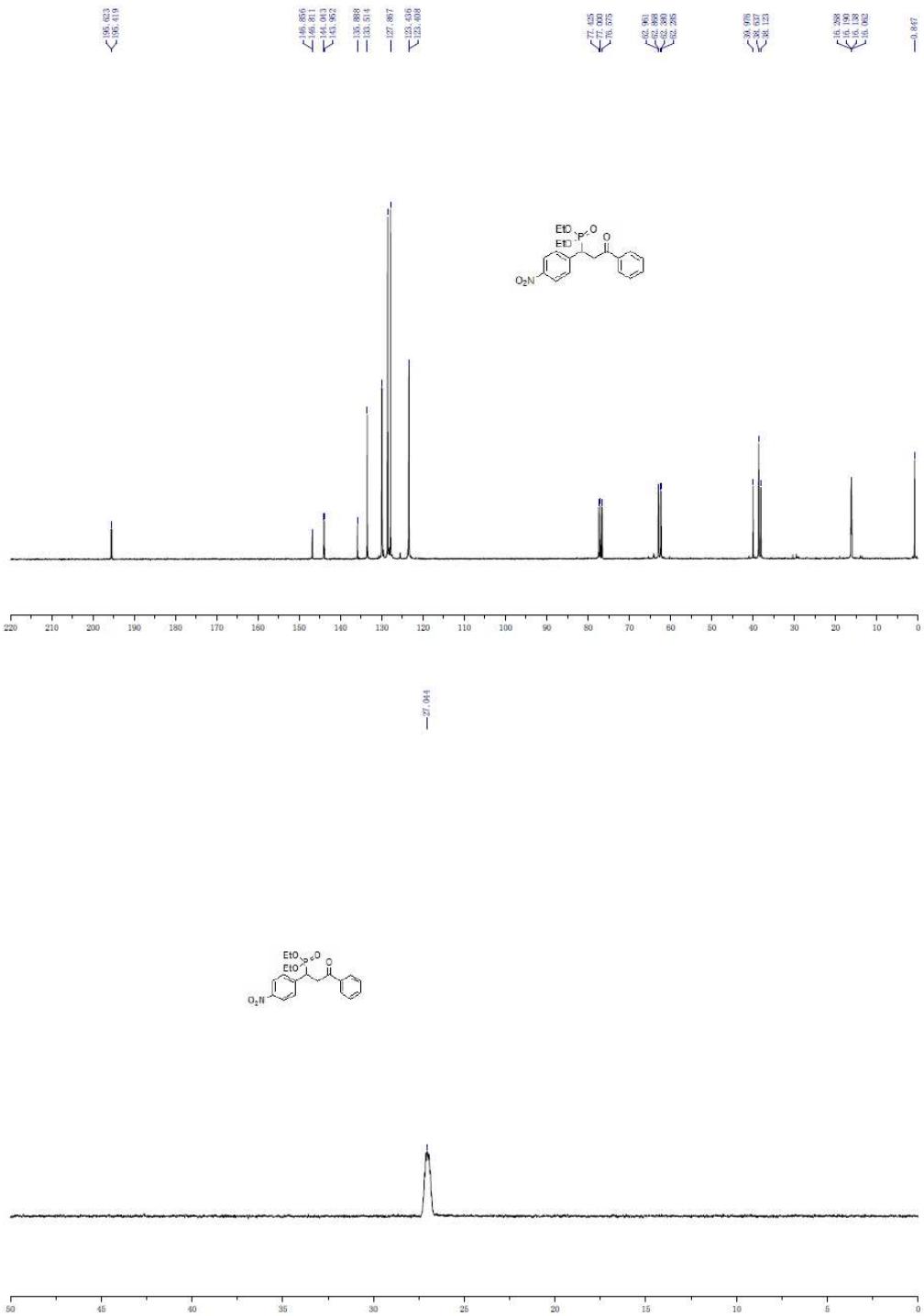


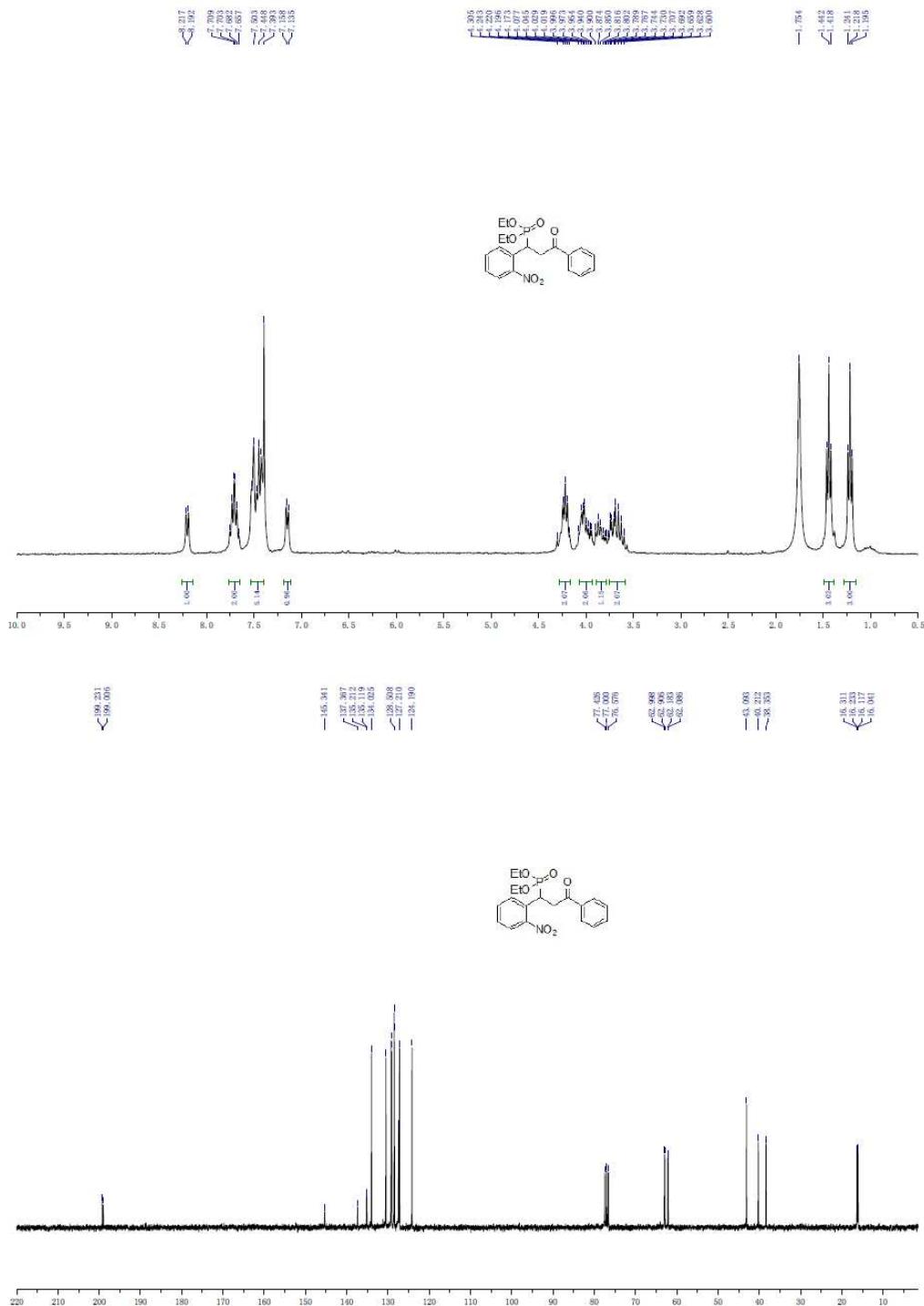


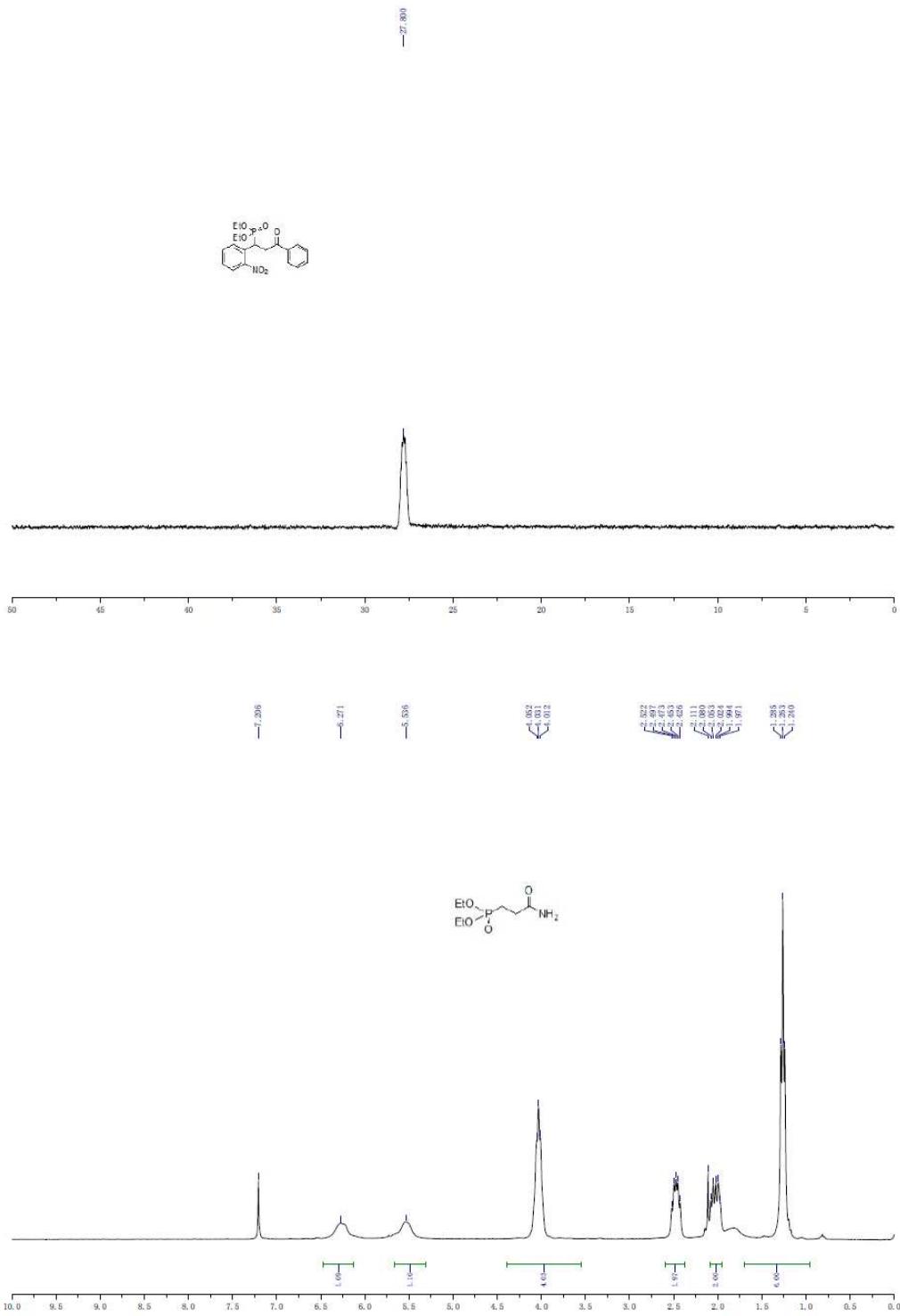


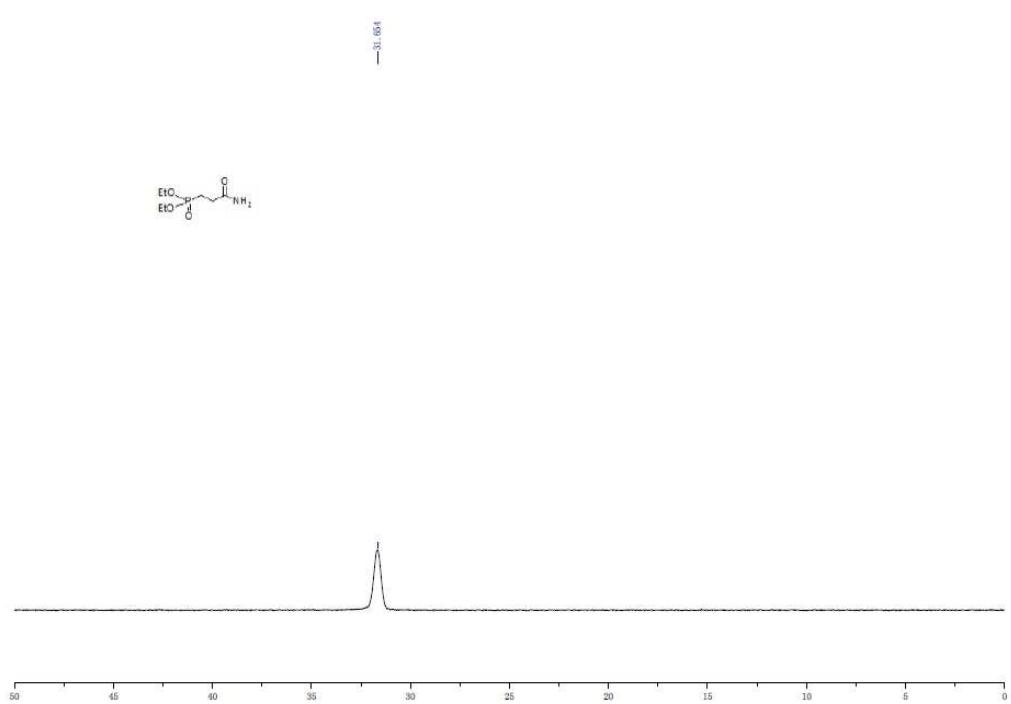
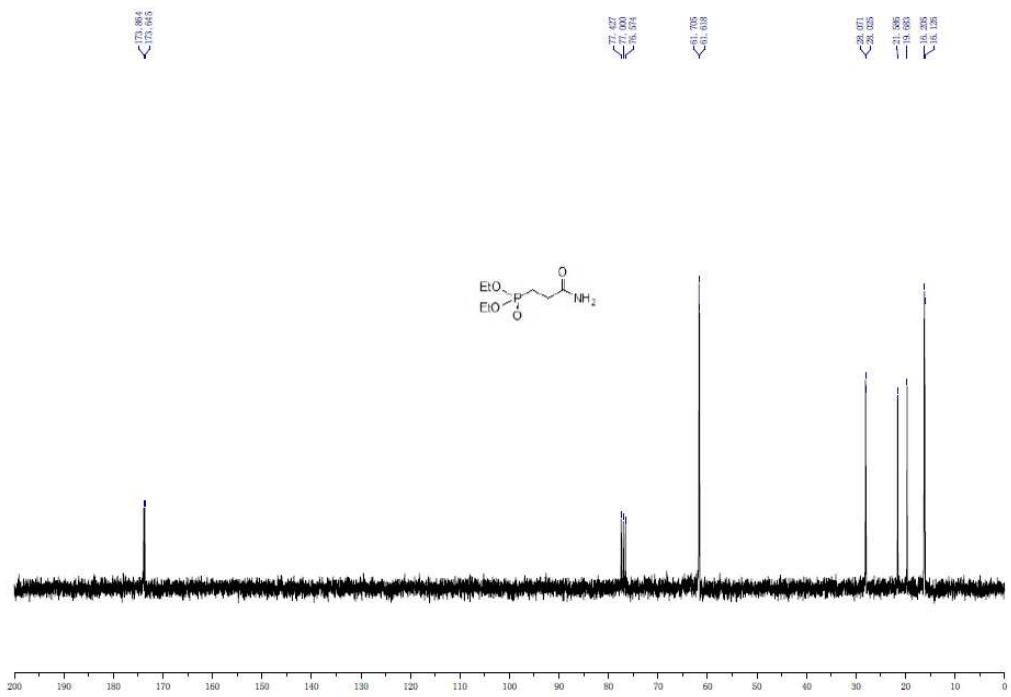


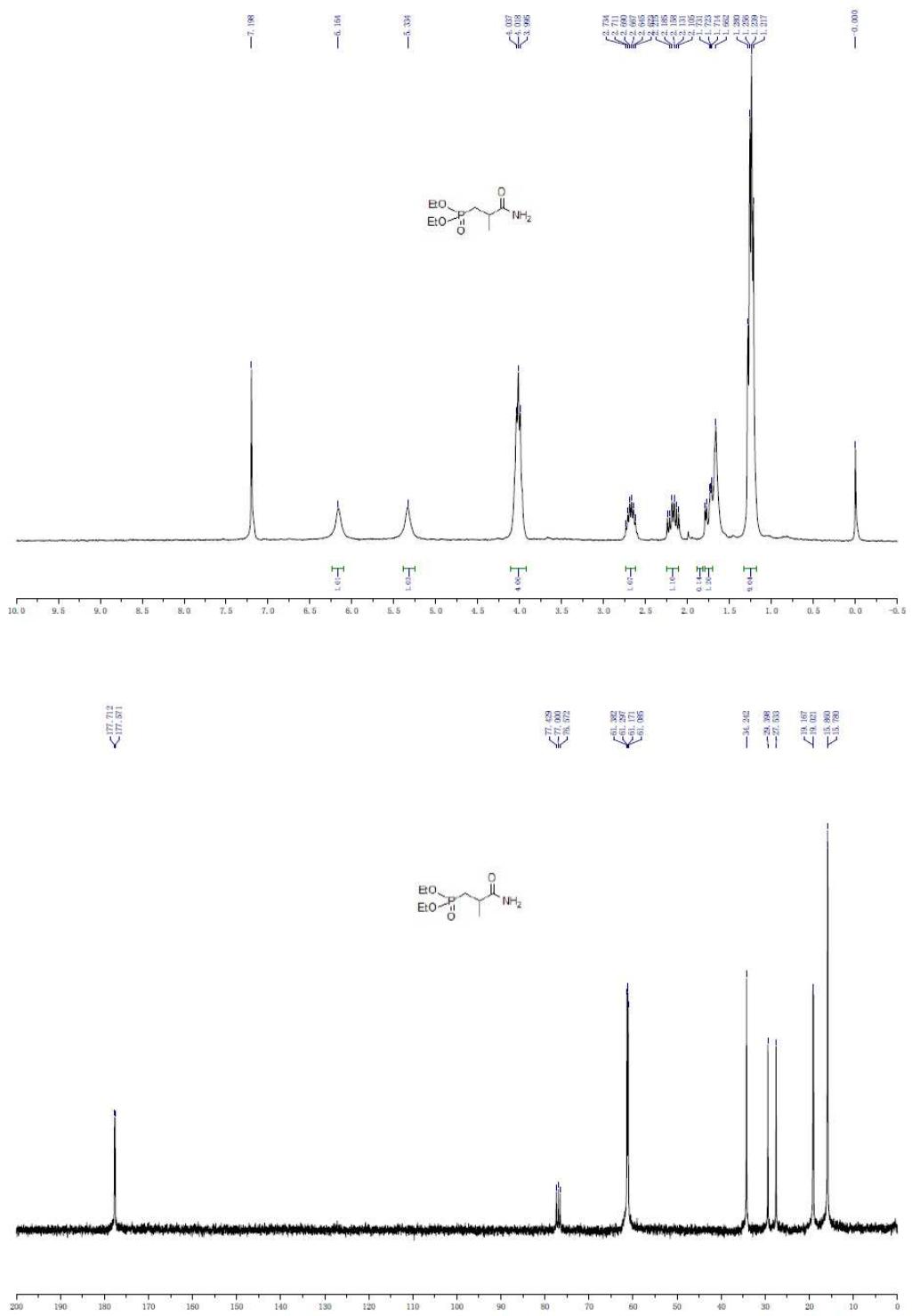


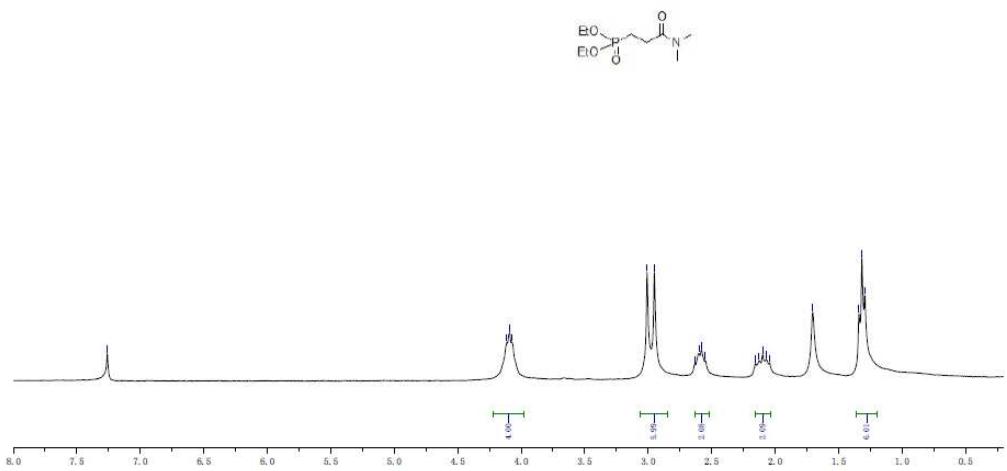
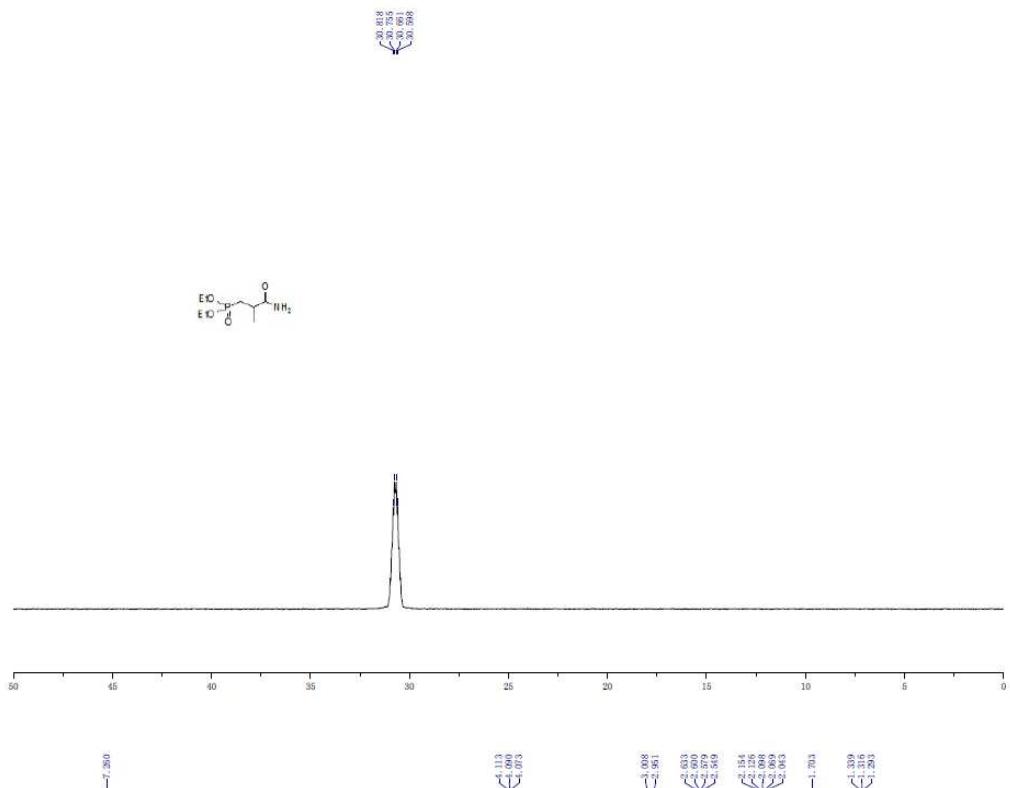


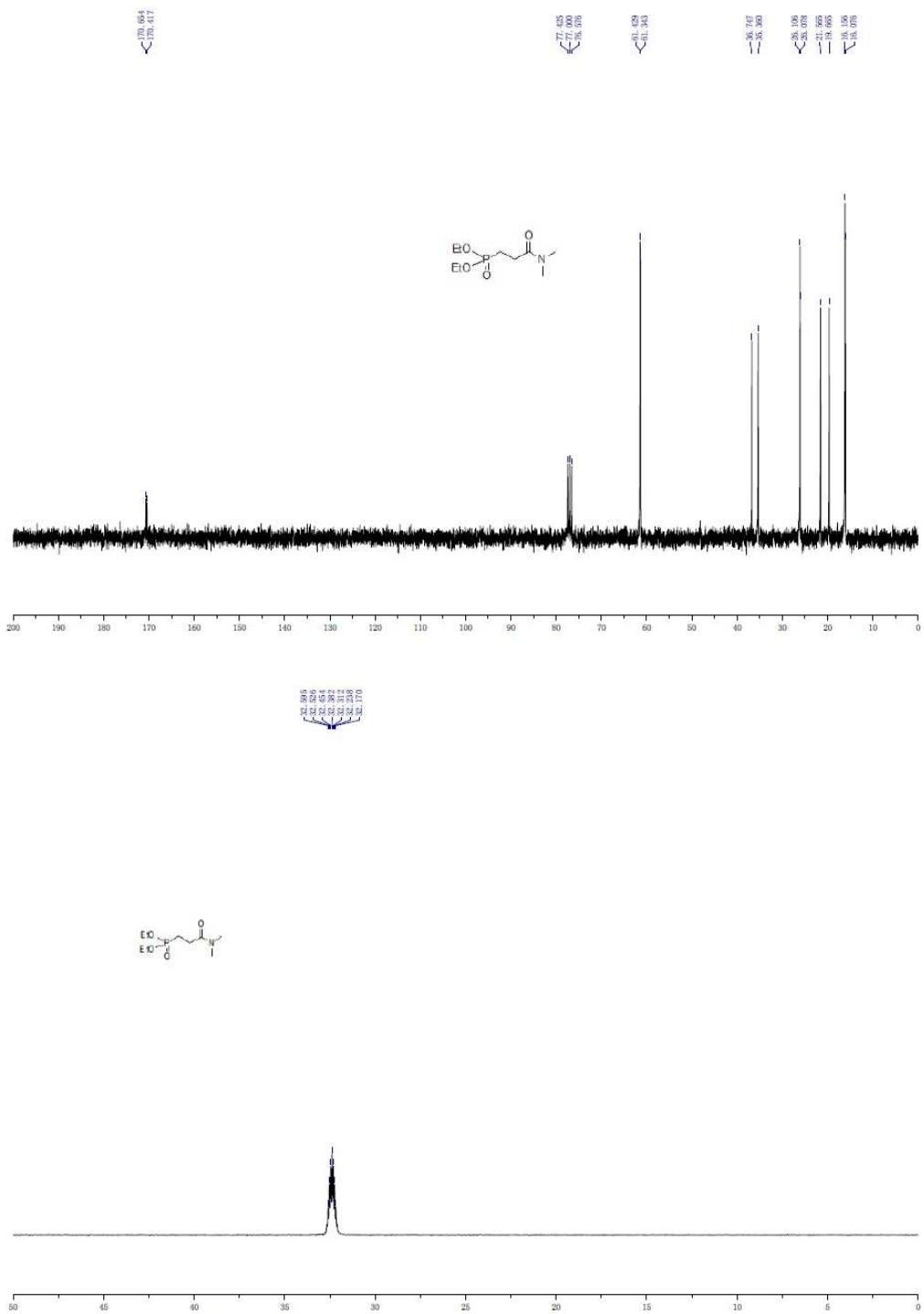


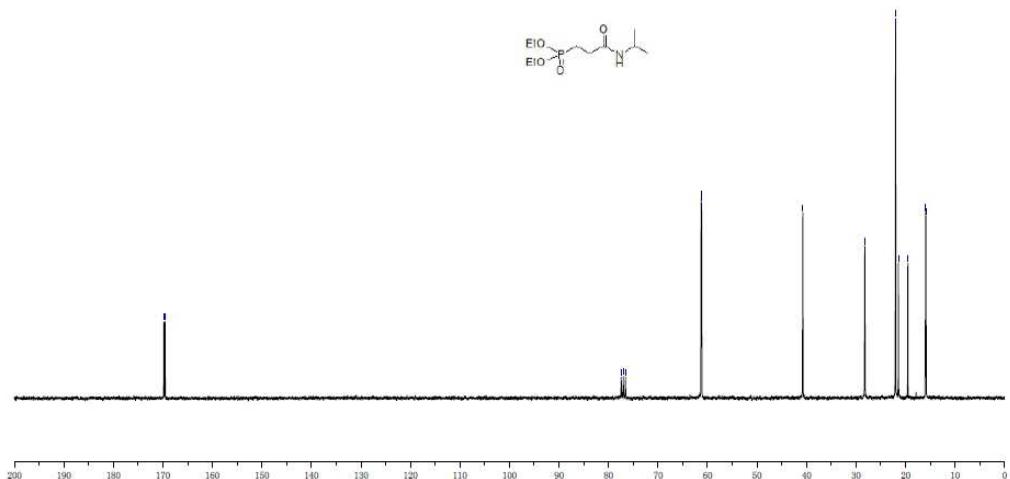
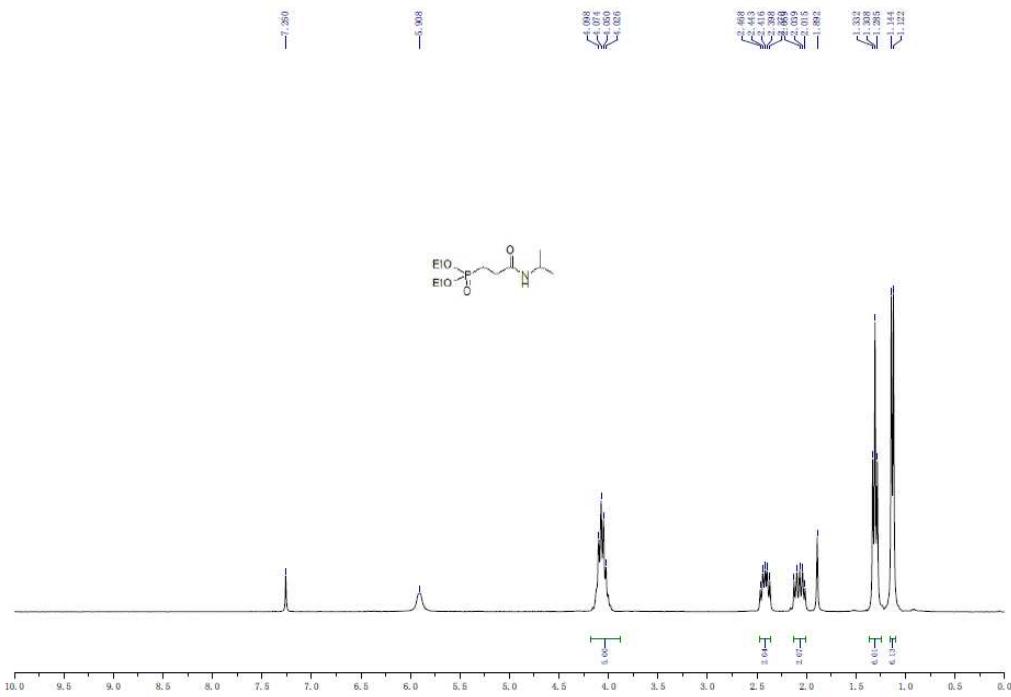


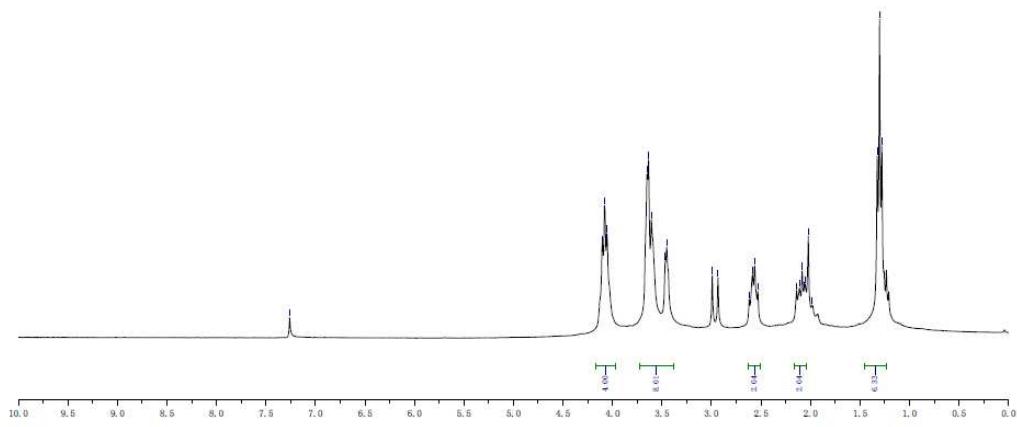
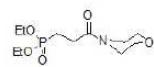
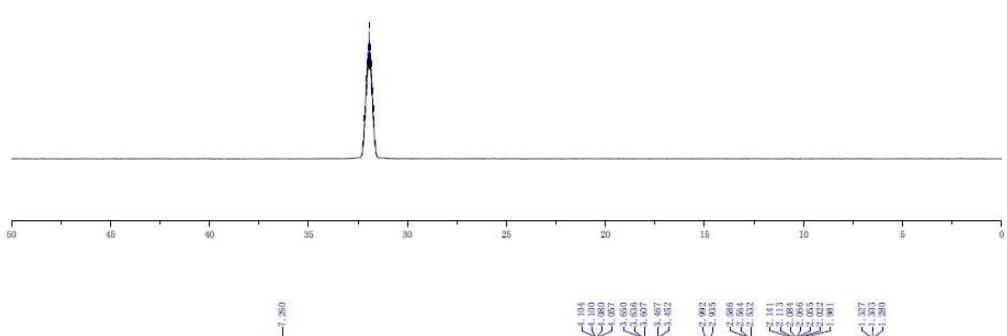


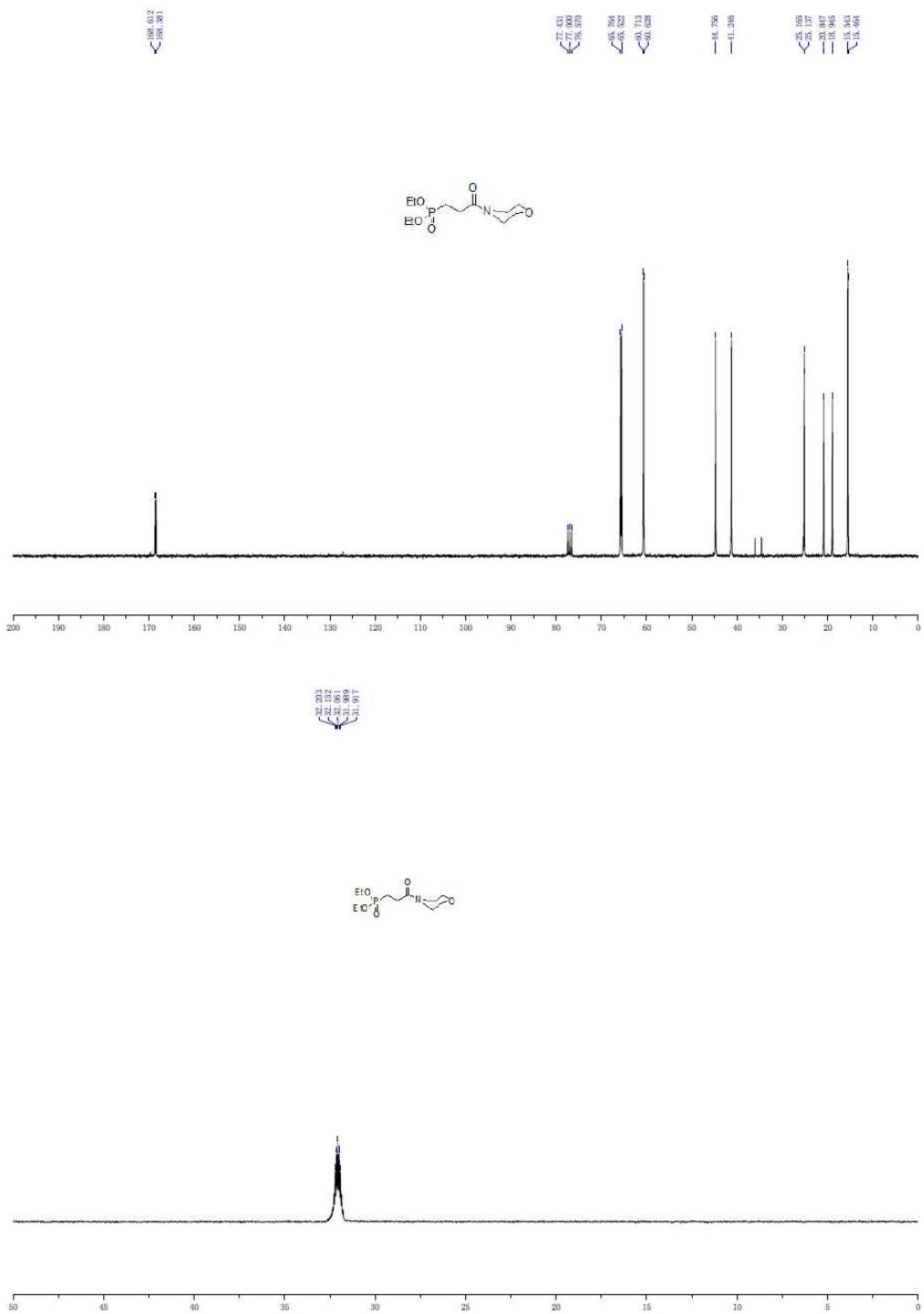


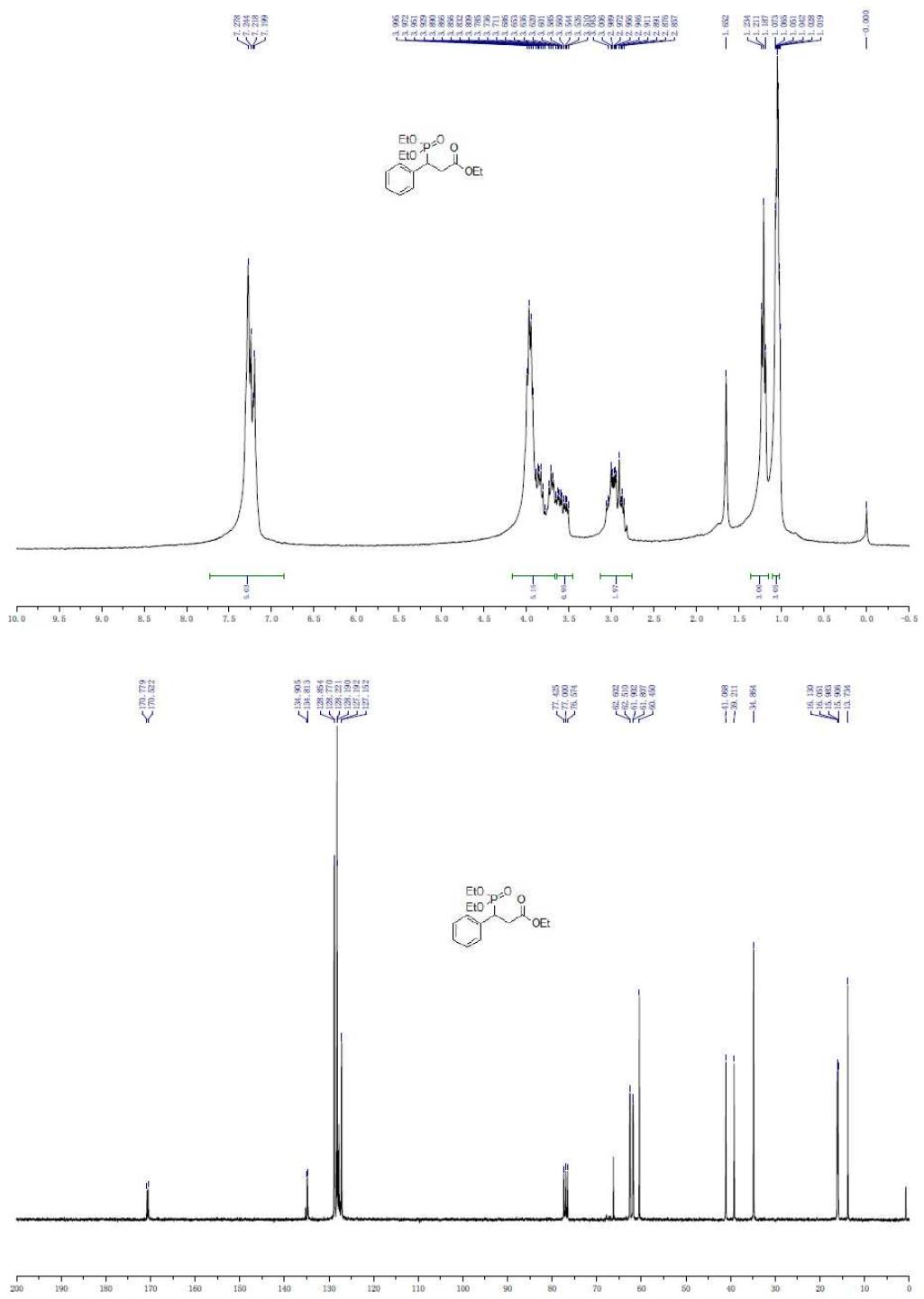




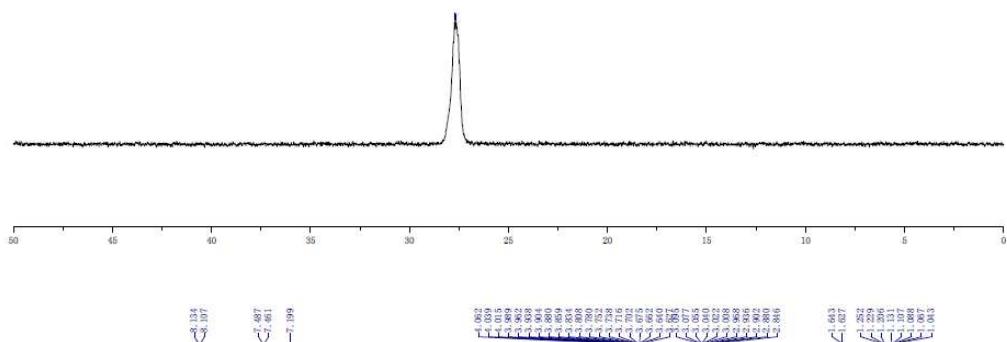




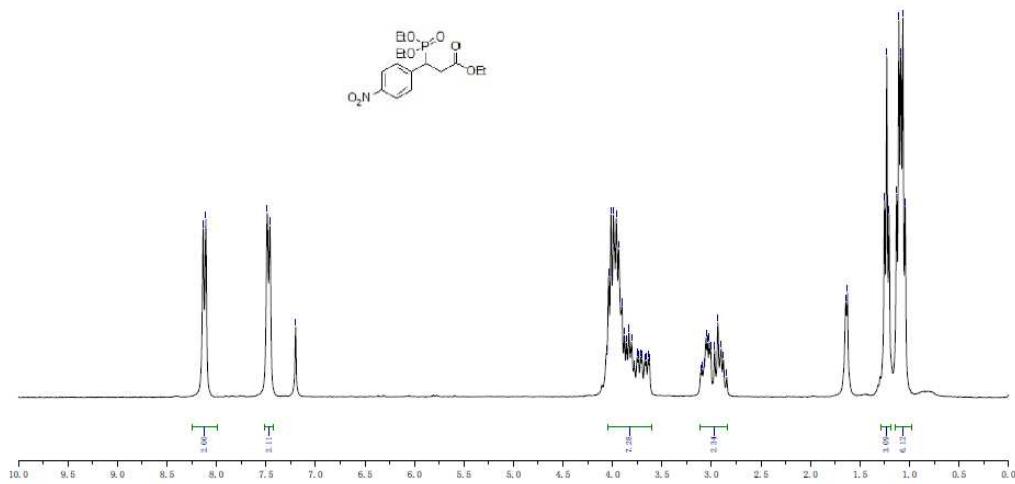
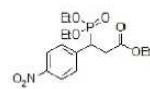


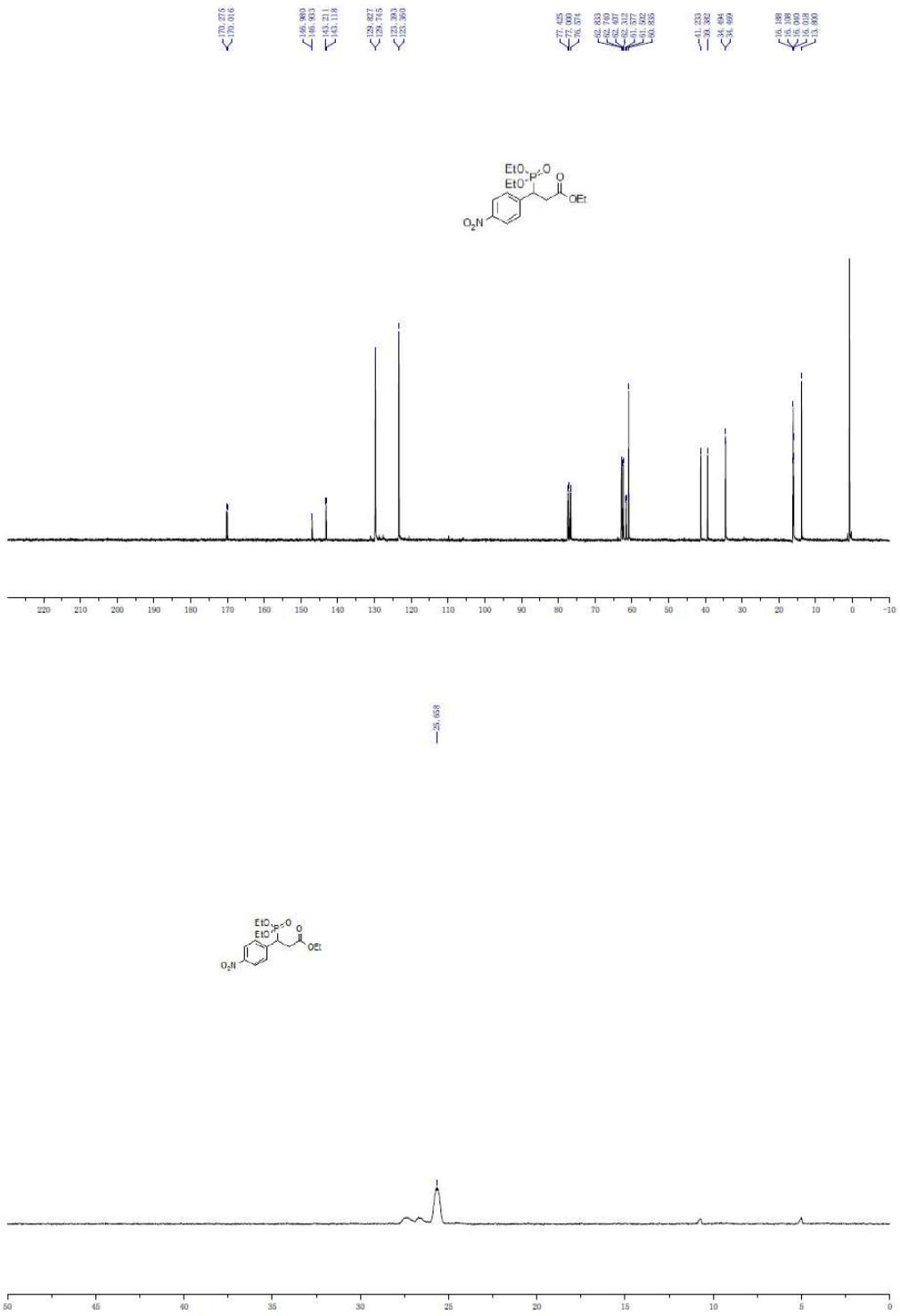


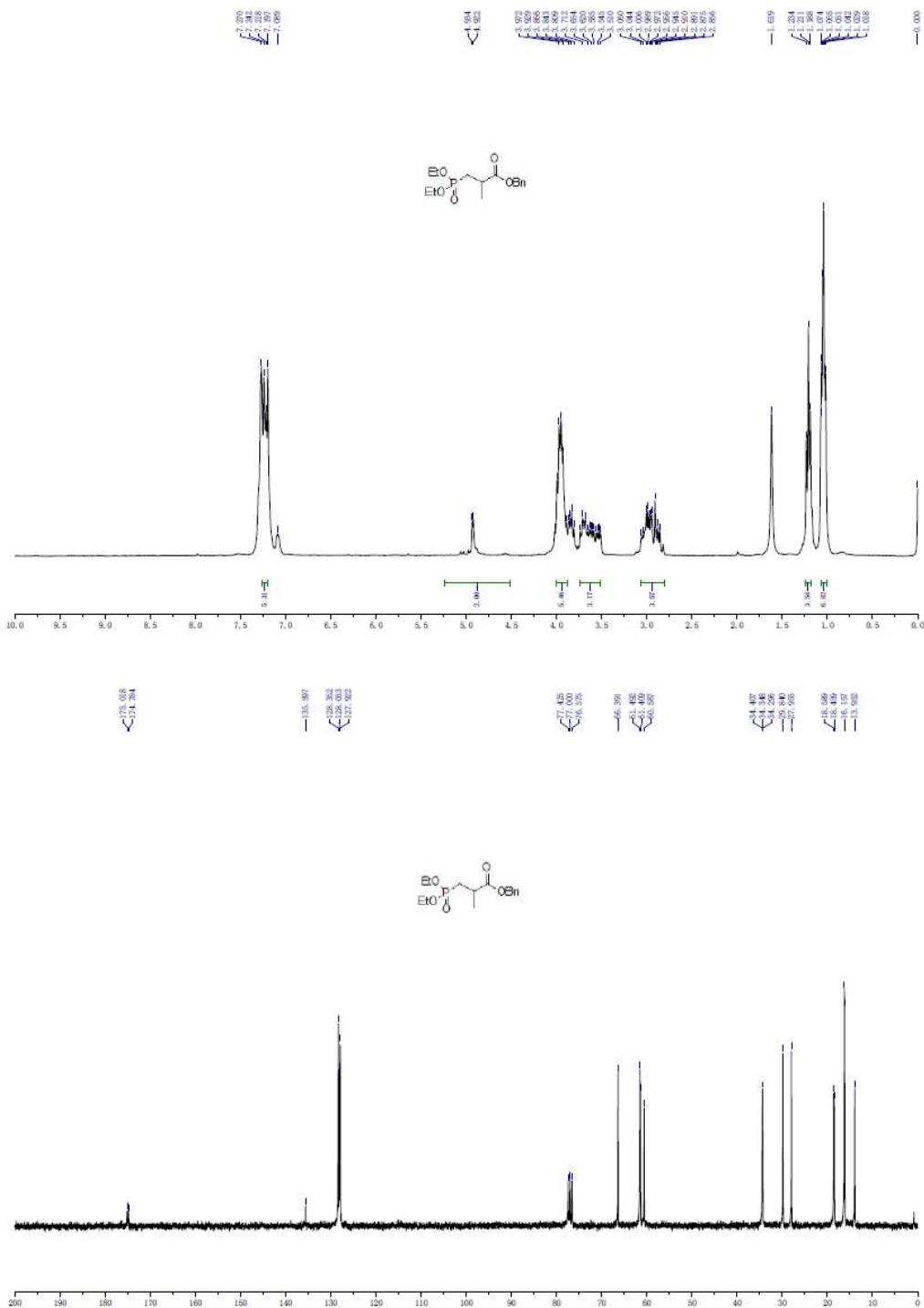
δ 27.711
27.692

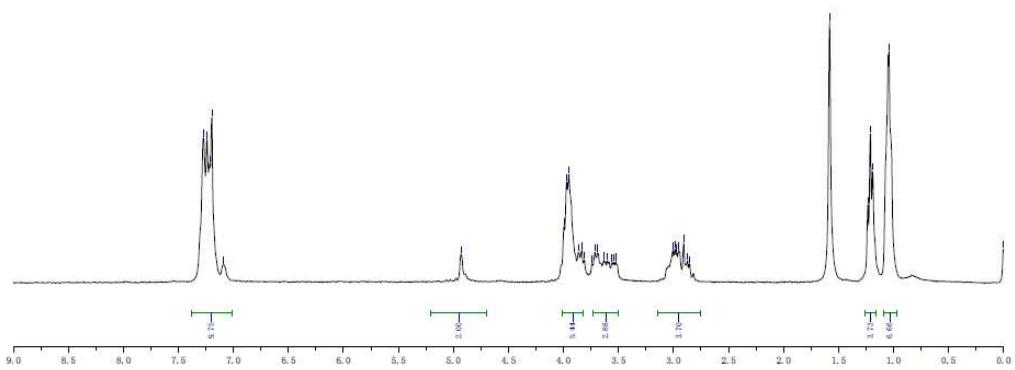
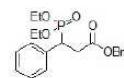
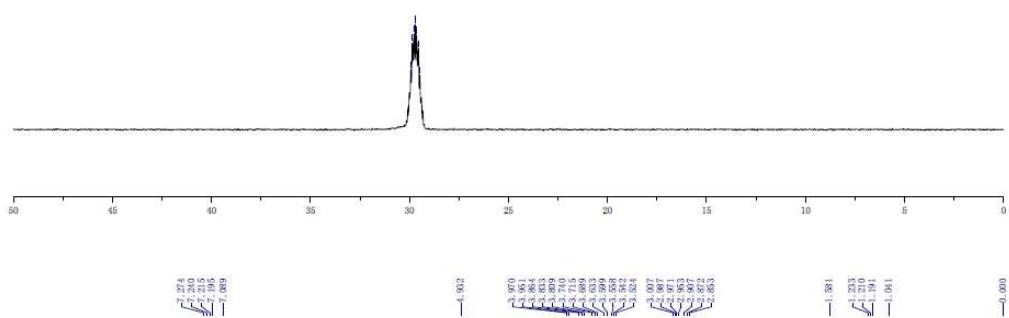


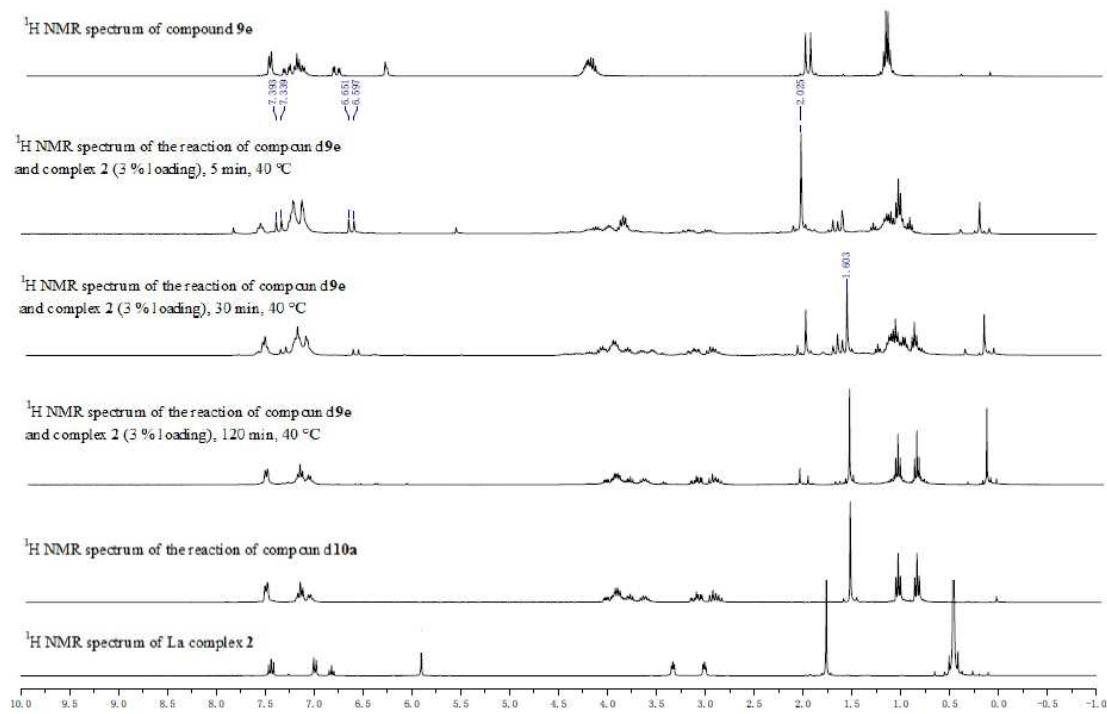
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3.880
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3.865
3.860
3.859
3.858
3.752
3.750
3.749
3.748
3.747
3.660
3.655
3.654
3.077
3.076
3.040
3.022
3.008
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2.932
2.930
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1.220
1.101
1.107
1.088
1.087
1.085





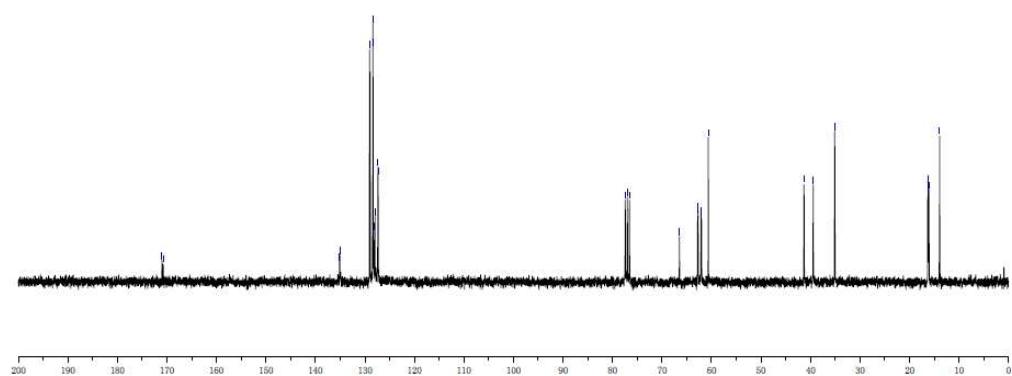
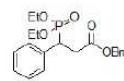


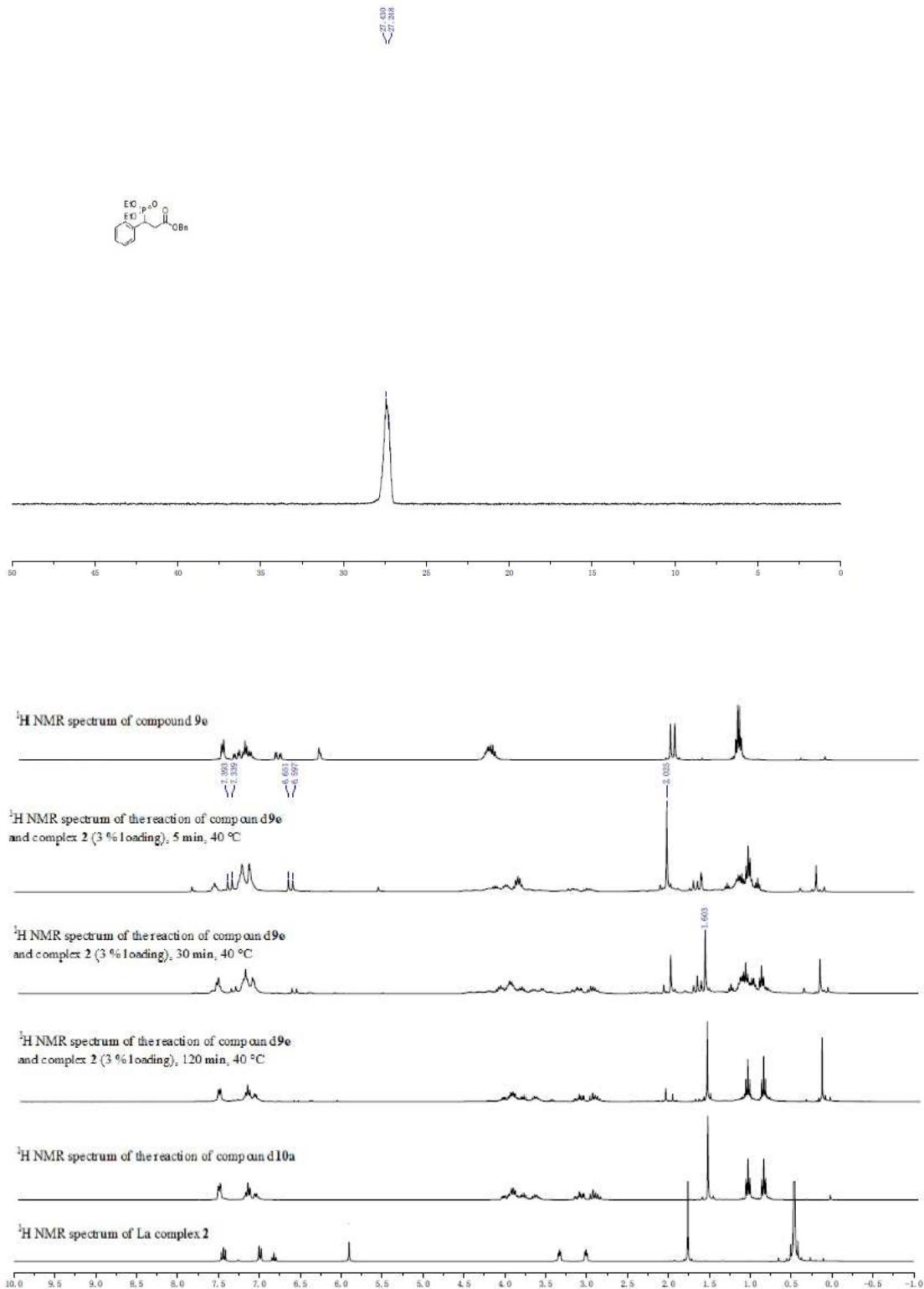




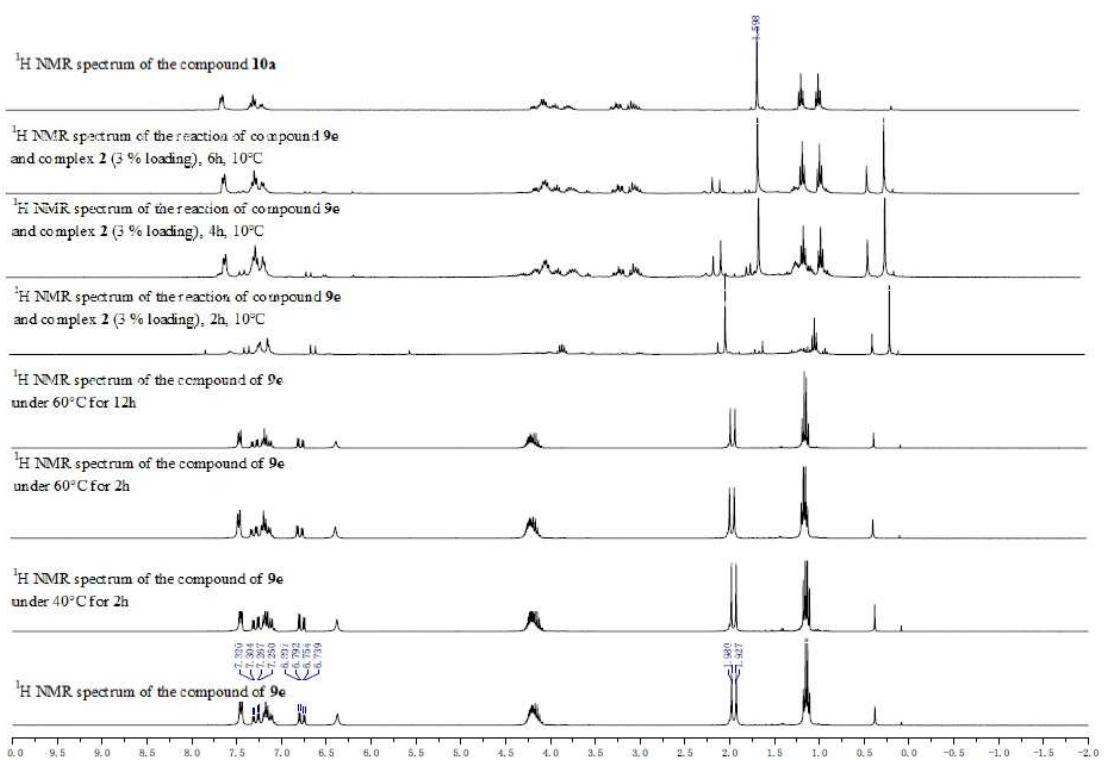
171.002
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128.052
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127.367
127.366

77.425
77.000
76.976
76.975
66.698
62.785
62.692
62.688
62.682
60.675
—41.399
—38.693
—35.109
—16.322
—16.203
—16.177
—16.088
—13.899





¹H NMR probing the transformation of 1,4-addition product (**9e**) to 1,2-addition (**10a**) product in the presence of catalysts **2** (3 mol% loading) at 40 °C.



¹H NMR probing the transformation of 1,4-addition product (**9e**) to 1,2-addition (**10a**) product without catalysts, and ¹H NMR probing the transformation of 1,4-addition product (**9e**) to 1,2-addition (**10a**) product in the presence of catalysts **2** (3 mol% loading) at 10 °C.