

Supporting Information

***Csp*³-P versus *Csp*²-P Bond Formation: Catalyst-Controlled Highly Regioselective Tandem Reaction of Ene-Yne-Ketones with *H*-Phosphonates**

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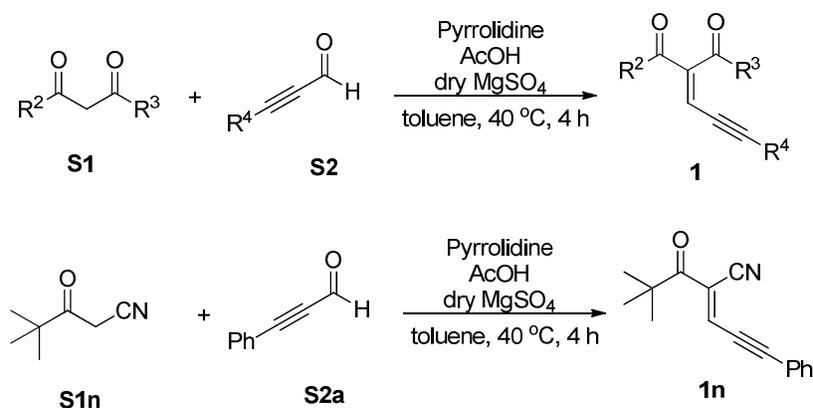
A. General Methods

^1H and ^{13}C NMR spectra were recorded using a Bruker DRX-400 spectrometer using CDCl_3 or $(\text{CD}_3)_2\text{NCDO}$ as solvent. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively. Mass spectra were recorded on a Thermo Scientific ISQ gas chromatograph-mass spectrometer. The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker TENSOR 27 spectrometer. Melting points were determined with a Büchi Melting Point B-545 instrument. Compounds **1a-n** were synthesized according to the literature procedure.^[1] Other compounds were commercially purchased and used without further purification.

B. General Procedure for the Preparation of 1, 3 and 4

General Procedure for the Preparation of 1:

To a 25 mL round bottom flask, the mixture of 1,3-diketones **S1** (0.5 mmol), AcOH (0.2 equiv), piperidine (0.1 equiv) and dry MgSO₄ (1 equiv) was added to a solution of propiolaldehyde **S2** (1.2 equiv) in toluene. The reaction was carried out at 40 °C stirring for 4 h and monitored by TLC. After the completion of the reaction, the reaction mixture was filtered through *celite* and removal of the solvent by rotary evaporation to give the crude product. The ene-yne-ketones **1** was purified by chromatography on silica gel with the appropriate mixture of PE and EA in 60-90% yields (*Z/E* mixture, **1n** was isolated in 48% yield).



General Procedure for Cu-Catalyzed Synthesis of 3:

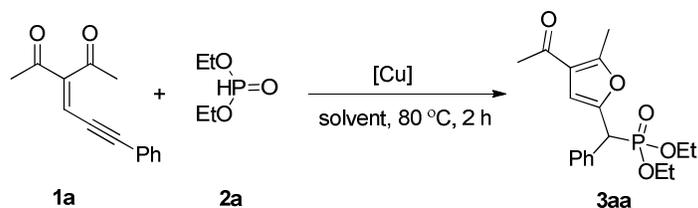
In a Schlenk tube, *H*-phosphonates (0.3 mmol) was added to a mixture of ene-yne-ketones (0.36 mol), CuBr (0.03 mmol), and DIPEA (0.45 mmol) in Et₂O (3 mL). The mixture was allowed to stir at 80 °C for 2 h (monitored by TLC). After the substrate was consumed, the reaction was cooled to room temperature. The solvent was then removed under vacuum and the resulting residue was purified by column chromatography on silica gel to give the product **3**.

General Procedure for Base-Promoted Synthesis of 4:

A mixture of *H*-phosphonates (0.3 mmol), ene-yne-ketones (0.36 mol) and Cs₂CO₃ (0.15 mmol) was stirred in DMF (2 mL) at 100 °C for 1 h. After completion of the reaction (monitored by TLC), water (10 mL) was added to the reaction mixture, and the resulting mixture was extracted with ethyl acetate. The combined organic layers were then dried over MgSO₄, filtered, and then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give **4**.

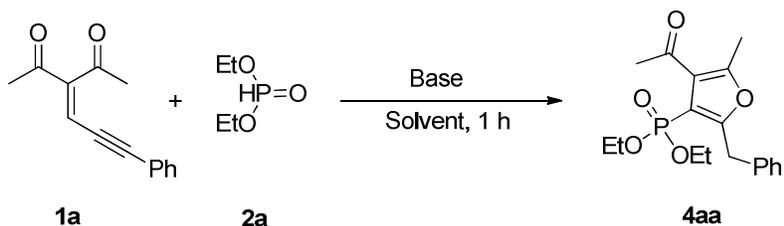
C. Optimization of the Reaction Conditions

Table S1. Optimization of the Reaction Conditions for Synthesis of **3aa**^a



| Entry | [Cu] | Base | Solvent | Yield of 3aa ^b (%) |
|-----------------|----------------------|---------------------------------|------------------------|---|
| 1 | CuBr | - | 1,4-Dioxane | 9 |
| 2 | CuBr | - | CH ₃ CN | 15 |
| 3 | CuBr | - | DMF | 18 |
| 4 | CuBr | - | NMP | 39 |
| 5 | CuBr | - | Et ₂ O | 71 |
| 6 | CuBr | - | THF | 22 |
| 6 | CuI | - | Et ₂ O | 64 |
| 7 | Cu(OAc) ₂ | - | Et ₂ O | 17 |
| 8 | CuBr ₂ | - | Et ₂ O | 38 |
| 9 | CuBr | DIPEA ^c | Et₂O | 89 (87) |
| 10 | CuBr | Et ₃ N | Et ₂ O | 82 |
| 11 | CuBr | K ₂ CO ₃ | Et ₂ O | 39 ^d |
| 12 | CuBr | Cs ₂ CO ₃ | Et ₂ O | trace ^d |
| 13 | CuBr | DABCO | Et ₂ O | trace ^d |
| 14 | CuBr | <i>t</i> -BuOLi | Et ₂ O | 12 ^d |
| 15 ^e | CuBr | DIPEA | Et ₂ O | 63 |
| 16 ^f | CuBr | DIPEA | Et ₂ O | 81 |
| 17 | - | DIPEA | Et ₂ O | n.r. |

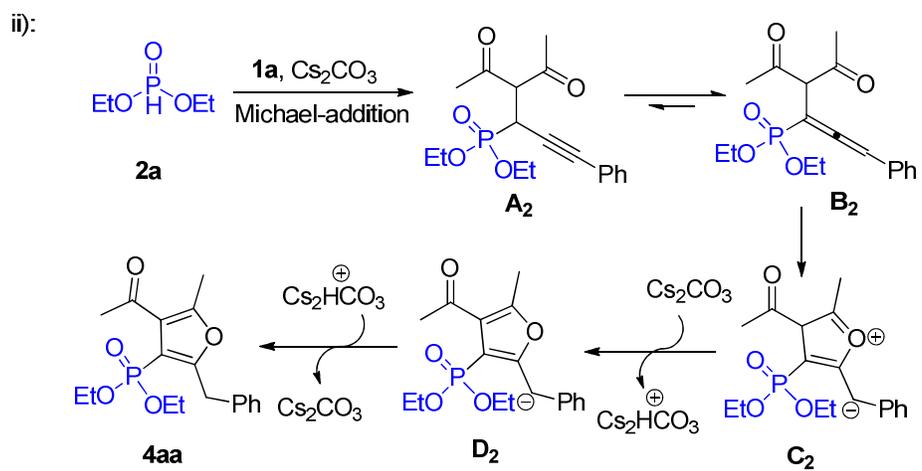
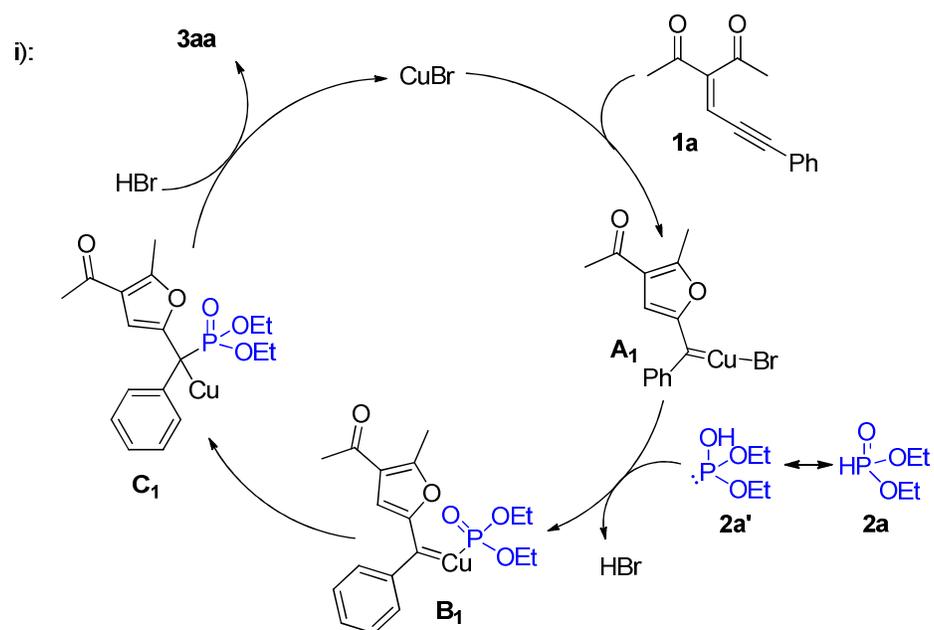
^a Reaction conditions: All reactions were performed with **1a** (0.12 mmol), **2a** (0.1 mmol), [Cu] (10 mol %), base (1.5 equiv) and 1.0 mL solvent at 80 °C for 2 h unless otherwise noted. ^b Yields were analyzed by GC-MS using *n*-dodecane as an internal standard. ^c *N,N*-Diisopropylethylamine. ^d **4aa** was detected. ^e 60 °C. ^f 100 °C.

Table S2. Optimization of the Reaction Conditions for synthesis of **4aa**^a

| Entry | Base (equiv) | Solvent | T (°C) | Yield of 4aa ^b (%) |
|-----------|---|-------------------|------------|--------------------------------------|
| 1 | Cs ₂ CO ₃ (1.5) | Et ₂ O | 80 | 62 |
| 2 | DIPEA ^c (1.5) | Et ₂ O | 80 | n.d. |
| 3 | <i>t</i> -BuOLi (1.5) | Et ₂ O | 80 | 24 |
| 4 | K ₂ CO ₃ (1.5) | Et ₂ O | 80 | 13 |
| 5 | DABCO (1.5) | Et ₂ O | 80 | 40 |
| 6 | Et ₃ N (1.5) | Et ₂ O | 80 | n.d. |
| 7 | Cs ₂ CO ₃ (1.5) | Toluene | 80 | 71 |
| 8 | Cs ₂ CO ₃ (1.5) | Dioxane | 80 | n.d. |
| 9 | Cs ₂ CO ₃ (1.5) | DMSO | 80 | n.d. |
| 10 | Cs ₂ CO ₃ (1.5) | DMF | 80 | 76 |
| 11 | Cs ₂ CO ₃ (1.0) | DMF | 80 | 77 |
| 12 | Cs ₂ CO ₃ (0.5) | DMF | 80 | 80 |
| 13 | Cs ₂ CO ₃ (0.3) | DMF | 80 | 54 |
| 14 | Cs₂CO₃ (0.5) | DMF | 100 | 92 (89) |
| 15 | Cs ₂ CO ₃ (0.5) | DMF | 60 | 72 |

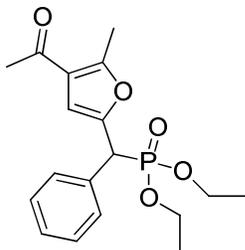
^a Reaction conditions: All reactions were performed with **1a** (0.12 mmol), **2a** (0.1 mmol), base (0.3-1.5 equiv) and 1.0 mL solvent at 80 °C for 1 h unless otherwise noted. ^b Yields were analyzed by GC/MS using *n*-dodecane as an internal standard. ^c *N,N*-Diisopropylethylamine.

D. Proposed catalytic cycle



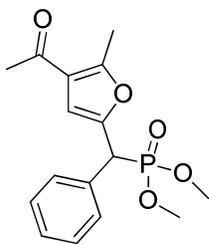
E. Analytical data

Diethyl ((4-Acetyl-5-methylfuran-2-yl)(phenyl)methyl)phosphonate (3aa)



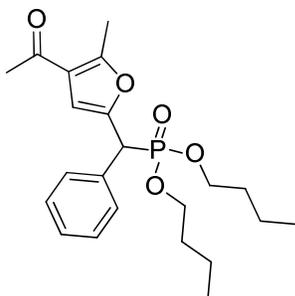
Yellow oil (91.4 mg, 87%); IR (KBr): 2986, 1676, 1239, 1027, 960 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.44 (d, $J = 7.1$ Hz, 2H), 7.31 (dt, $J = 22.8, 7.2$ Hz, 3H), 6.75 (s, 1H), 4.46 (d, $J = 25.9$ Hz, 1H), 4.17-4.00 (m, 2H), 3.99-3.68 (m, 2H), 2.52 (s, 3H), 2.39 (s, 3H), 1.25 (t, $J = 7.0$ Hz, 3H), 1.10 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 194.0, 157.8 ($J = 1.5$ Hz), 147.8 ($J = 0.8$ Hz), 133.8 ($J = 6.4$ Hz), 129.2 ($J = 6.2$ Hz), 128.5 ($J = 2.1$ Hz), 127.6 ($J = 2.8$ Hz), 122.1 ($J = 0.7$ Hz), 109.1 ($J = 4.7$ Hz), 63.0 ($J = 5.1$ Hz), 62.7 ($J = 7.2$ Hz), 44.8 ($J = 139.9$ Hz), 29.0, 16.2 ($J = 5.8$ Hz), 16.0 ($J = 5.7$ Hz), 14.2; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 21.5; MS (EI, 70 eV) m/z : 350.12, 308.15, 213.11, 171.12; HRMS ESI (m/z): calcd for $\text{C}_{18}\text{H}_{23}\text{NaO}_5\text{P}$ [$\text{M} + \text{Na}$] $^+$: 373.1175, found: 373.1170.

Dimethyl ((4-Acetyl-5-methylfuran-2-yl)(phenyl)methyl)phosphonate (3ab)



Yellow oil (81.2 mg, 84%); IR (KBr): 2921, 2358, 1673, 1241, 1037 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.43 (d, $J = 7.4$ Hz, 2H), 7.38-7.29 (m, 3H), 6.74 (s, 1H), 4.49 (d, $J = 26.0$ Hz, 1H), 3.71 (d, $J = 10.9$ Hz, 3H), 3.51 (d, $J = 10.7$ Hz, 3H), 2.53 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 194.1, 158.1 ($J = 1.4$ Hz), 147.6 ($J = 1.0$ Hz), 133.6 ($J = 6.5$ Hz), 129.3 ($J = 6.3$ Hz), 128.8, 127.9 ($J = 2.7$ Hz), 122.3 ($J = 0.9$ Hz), 109.4 ($J = 4.7$ Hz), 53.9 ($J = 6.9$ Hz), 53.5 ($J = 7.0$ Hz), 44.5 ($J = 140.3$ Hz), 29.2, 14.4; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 23.9; MS (EI, 70 eV) m/z : 322.10, 280.11, 213.10, 171.12; HRMS ESI (m/z): calcd for $\text{C}_{16}\text{H}_{19}\text{NaO}_5\text{P}$ [$\text{M} + \text{Na}$] $^+$: 345.0862, found: 345.0866.

Dibutyl ((4-Acetyl-5-methylfuran-2-yl)(phenyl)methyl)phosphonate (3ac)

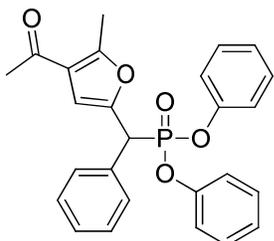


Yellow oil (106.0 mg, 87%); IR (KBr): 2960, 2360, 1764, 1241, 1024 cm^{-1} ;

^1H NMR (400 MHz, CDCl_3) δ ppm 7.43 (d, $J = 7.1$ Hz, 2H), 7.38-7.21 (m, 3H), 6.73 (s, 1H), 4.46 (d, $J = 25.9$ Hz, 1H), 4.09-3.94 (m, 2H), 3.91-3.58 (m, 2H), 2.52 (s, 3H), 2.38 (s, 3H), 1.62-1.51 (m, 2H), 1.48-1.37 (m, 2H), 1.32 (dd,

$J = 14.7, 7.3$ Hz, 2H), 1.21 (dd, $J = 15.3, 7.8$ Hz, 2H), 0.88 (t, $J = 7.4$ Hz, 3H), 0.82 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 194.1, 157.9 ($J = 1.7$ Hz), 148.0 ($J = 1.3$ Hz), 133.9 ($J = 6.6$ Hz), 129.3 ($J = 6.3$ Hz), 128.6 ($J = 2.1$ Hz), 127.6 ($J = 2.8$ Hz), 122.2 ($J = 1.5$ Hz), 109.2 ($J = 4.8$ Hz), 66.8 ($J = 7.1$ Hz), 66.5 ($J = 7.3$ Hz), 44.9 ($J = 140$ Hz), 32.4 ($J = 6.0$ Hz), 32.3 ($J = 8.5$ Hz), 29.1, 18.6, 18.5, 14.3, 13.5, 13.4; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 21.4; MS (EI, 70 eV) m/z : 406.20, 364.18, 213.11, 171.13; HRMS ESI (m/z): calcd for $\text{C}_{22}\text{H}_{31}\text{NaO}_5\text{P}$ [$\text{M} + \text{Na}$] $^+$: 429.1801, found: 429.1806.

Diphenyl ((4-Acetyl-5-methylfuran-2-yl)(phenyl)methyl)phosphonate (3ad)

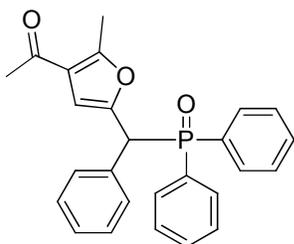


Yellow solid (101.7 mg, 76%), mp 122.8-125.4 $^{\circ}\text{C}$; IR (KBr): 3742, 2923, 2357,

1675, 1199, 940 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.53 (d, $J = 6.8$ Hz, 2H), 7.41-7.32 (m, 3H), 7.27 (t, $J = 7.5$ Hz, 2H), 7.22-7.08 (m, 4H), 7.03 (d, $J = 7.9$ Hz, 2H), 6.83 (d, $J = 8.0$ Hz, 2H), 6.78 (s, 1H), 4.85 (d, $J = 26.4$ Hz, 1H),

2.51 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 194.0, 158.3 ($J = 1.9$ Hz), 150.4 ($J = 9.8$ Hz), 150.3 ($J = 9.6$ Hz), 146.5 ($J = 1.5$ Hz), 132.8, 132.7, 129.6 ($J = 1.6$ Hz), 129.5, 128.9 ($J = 2.2$ Hz), 128.1 ($J = 2.9$ Hz), 125.2, 125.1, 122.3 ($J = 1.6$ Hz), 120.4 ($J = 4.3$ Hz), 120.3 ($J = 4.4$ Hz), 110.2 ($J = 5.4$ Hz), 45.1 ($J = 141.7$ Hz), 29.1, 14.3; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 13.9; MS (EI, 70 eV) m/z : 446.12, 326.08, 213.07, 171.12; HRMS ESI (m/z): calcd for $\text{C}_{26}\text{H}_{23}\text{NaO}_5\text{P}$ [$\text{M} + \text{Na}$] $^+$: 469.1175, found: 469.1176.

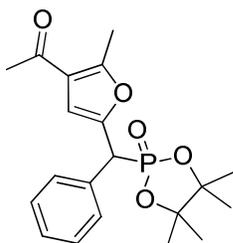
1-(5-((Diphenylphosphoryl)(phenyl)methyl)-2-methylfuran-3-yl)ethanone (3ae)



Yellow solid (78.2 mg, 63%), mp 200.5-202.8 °C; IR (KBr): 3741, 2920, 2357, 1673, 1239 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.88-7.70 (m, 2H), 7.48 (dd, $J = 18.9, 7.9$ Hz, 5H), 7.38 (t, $J = 6.9$ Hz, 1H), 7.29 (d, $J = 10.2$ Hz, 4H), 7.18 (s, 3H), 6.81 (s, 1H), 4.90 (d, $J = 10.9$ Hz, 1H), 2.39 (s, 3H), 2.31 (s, 3H);

^{13}C NMR (100 MHz, CDCl_3) δ ppm 194.3, 157.6, 147.8 ($J = 1.0$ Hz), 133.4 ($J = 5.2$ Hz), 131.9 ($J = 33.2$ Hz), 131.9 ($J = 2.7$ Hz), 131.6 ($J = 2.6$ Hz), 131.2 ($J = 8.7$ Hz), 131.2 ($J = 8.9$ Hz), 130.8, 129.7 ($J = 5.2$ Hz), 128.5 ($J = 11.7$ Hz), 128.4 ($J = 1.2$ Hz), 128.1 ($J = 11.8$ Hz), 127.4 ($J = 2.0$ Hz), 122.2, 110.1 ($J = 3.8$ Hz), 47.3 ($J = 65.0$ Hz), 29.1, 14.0. ^{31}P NMR (162 MHz, CDCl_3) δ ppm 29.4; HRMS ESI (m/z): calcd for $\text{C}_{26}\text{H}_{23}\text{NaO}_3\text{P} [\text{M} + \text{Na}]^+$: 437.1280, found: 437.1279.

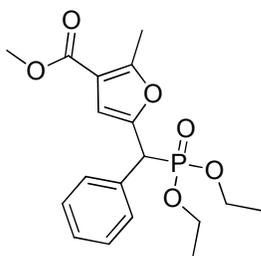
1-(2-Methyl-5-(phenyl(4,4,5,5-tetramethyl-2-oxido-1,3,2-dioxaphospholan-2-yl)methyl)fur an-3-yl)ethanone (3af)



Brown oil (72.2 mg, 64%); IR (KBr): 2987, 2357, 1673, 1237, 952 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.40 (d, $J = 7.5$ Hz, 2H), 7.36-7.27 (m, 3H), 6.83 (s, 1H), 4.45 (d, $J = 24.5$ Hz, 1H), 2.51 (s, 3H), 2.39 (s, 3H), 1.49 (s, 3H), 1.46 (s, 3H), 1.27 (s, 3H), 1.25 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 194.2, 158.3, 147.2, 133.5 ($J = 7.2$ Hz), 129.3 ($J = 6.3$ Hz), 128.7 ($J = 2.2$ Hz), 127.9 ($J = 2.8$ Hz), 122.2 ($J =$

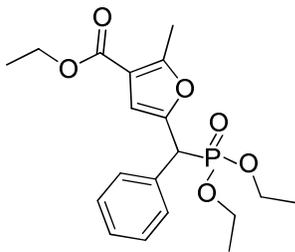
1.4 Hz), 109.9 ($J = 4.0$ Hz), 89.0 ($J = 1.6$ Hz), 88.9, 46.8 ($J = 132.4$ Hz), 29.1, 24.9 ($J = 3.5$ Hz), 24.8 ($J = 3.7$ Hz), 24.0 ($J = 5.4$ Hz), 23.8 ($J = 5.5$ Hz), 14.3; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 32.6; MS (EI, 70 eV) m/z : 376.14, 334.14, 213.09, 171.12; HRMS ESI (m/z): calcd for $\text{C}_{20}\text{H}_{25}\text{NaO}_5\text{P} [\text{M} + \text{Na}]^+$: 399.1332, found: 399.1335.

Methyl 5-((Diethoxyphosphoryl)(phenyl)methyl)-2-methylfuran-3-carboxylate (3ba)



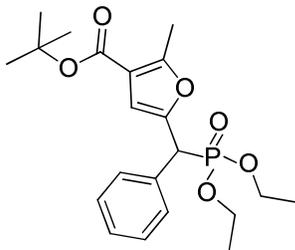
Yellow oil (95.6 mg, 87%); IR (KBr): 2985, 1719, 1240, 1032, 961 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.43 (d, $J = 7.5$ Hz, 2H), 7.30 (dt, $J = 13.4, 8.0$ Hz, 3H), 6.75 (s, 1H), 4.46 (d, $J = 25.9$ Hz, 1H), 4.17-3.68 (m, 7H), 2.52 (s, 3H), 1.24 (t, $J = 7.0$ Hz, 3H), 1.12 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 164.3, 158.8 ($J = 1.5$ Hz), 147.8 ($J = 1.7$ Hz), 133.8 ($J = 6.5$ Hz), 129.3 ($J = 6.3$ Hz), 128.5 ($J = 2.2$ Hz), 127.6 ($J = 2.8$ Hz), 114.1 ($J = 1.5$ Hz), 109.4 ($J = 4.8$ Hz), 63.0 ($J = 7.0$ Hz), 62.9 ($J = 7.2$ Hz), 51.2, 44.9 ($J = 140.7$ Hz), 16.2 ($J = 5.9$ Hz), 16.1 ($J = 5.8$ Hz), 13.6; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 21.5; MS (EI, 70 eV) m/z : 366.12, 335.09, 229.10, 197.06; HRMS ESI (m/z): calcd for $\text{C}_{18}\text{H}_{23}\text{NaO}_6\text{P}$ [$\text{M} + \text{Na}$] $^+$: 389.1124, found: 389.1126.

Ethyl 5-((Diethoxyphosphoryl)(phenyl)methyl)-2-methylfuran-3-carboxylate (3ca)



Light yellow oil (103.8 mg, 91%); IR (KBr): 2984, 1714, 1239, 1031, 961 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.44 (d, $J = 7.3$ Hz, 2H), 7.36-7.23 (m, 3H), 6.77 (s, 1H), 4.46 (d, $J = 25.9$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 4.12-3.71 (m, 4H), 2.52 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 3H), 1.25 (t, $J = 7.0$ Hz, 3H), 1.12 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.9, 158.6 ($J = 1.5$ Hz), 147.7 ($J = 1.7$ Hz), 133.9 ($J = 6.5$ Hz), 129.3 ($J = 6.3$ Hz), 128.5 ($J = 2.1$ Hz), 127.5 ($J = 2.7$ Hz), 114.4 ($J = 1.4$ Hz), 109.4 ($J = 4.9$ Hz), 63.0 ($J = 6.9$ Hz), 62.8 ($J = 7.0$ Hz), 60.0, 44.9 ($J = 140$ Hz), 16.2 ($J = 5.8$ Hz), 16.1 ($J = 5.7$ Hz), 14.3, 13.6; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 21.3; MS (EI, 70 eV) m/z : 380.14, 335.12, 243.12, 215.10; HRMS ESI (m/z): calcd for $\text{C}_{19}\text{H}_{25}\text{NaO}_6\text{P}$ [$\text{M} + \text{Na}$] $^+$: 403.1281, found: 403.1283.

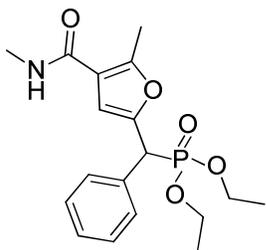
tert-Butyl 5-((Diethoxyphosphoryl)(phenyl)methyl)-2-methylfuran-3-carboxylate (3da)



Yellow oil (100.4 mg, 82%); IR (KBr): 2980, 1709, 1246, 1032, 960 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.42 (d, $J = 7.5$ Hz, 2H), 7.31 (dd, $J = 14.9, 7.4$ Hz, 3H), 6.68 (s, 1H), 4.45 (d, $J = 26.0$ Hz, 1H), 4.10-3.74 (m, 4H), 2.49 (s, 3H), 1.53 (s, 9H), 1.24 (t, $J = 7.0$ Hz, 3H), 1.12 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.4, 158.0 ($J = 1.4$ Hz), 147.4 ($J = 2.2$ Hz), 134.0 ($J = 6.5$ Hz), 129.3 ($J = 6.3$ Hz), 128.5 ($J = 2.2$ Hz), 127.6 ($J = 2.6$ Hz), 116.0 ($J = 1.2$ Hz), 109.8 ($J = 5.0$ Hz), 80.5, 63.1 ($J = 7.1$ Hz), 62.9 ($J = 7.2$ Hz), 45.0 ($J = 140.8$ Hz), 28.3, 16.3 ($J = 5.8$ Hz), 16.2 ($J = 5.0$ Hz), 80.5, 63.1 ($J = 7.1$ Hz), 62.9 ($J = 7.2$ Hz), 45.0 ($J = 140.8$ Hz), 28.3, 16.3 ($J = 5.8$ Hz), 16.2 ($J = 5.0$ Hz).

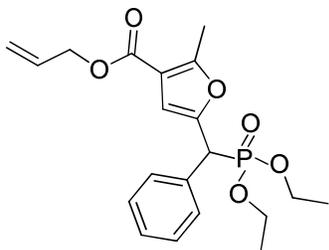
= 5.7 Hz), 13.8; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 21.6; MS (EI, 70 eV) m/z : 408.18, 335.11, 271.14, 215.05; HRMS ESI (m/z): calcd for $\text{C}_{21}\text{H}_{29}\text{NaO}_6\text{P}$ [$\text{M} + \text{Na}$] $^+$: 431.1594, found: 431.1595.

Diethyl ((4-Benzoyl-5-methylfuran-2-yl)(phenyl)methyl)phosphonate (3ea)



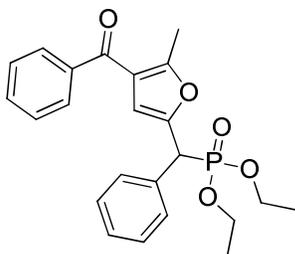
Brown oil (92.0 mg, 84%); IR (KBr): 3321, 2983, 2358, 1645, 1240, 1031, 963 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.42 (d, $J = 7.2$ Hz, 2H), 7.32 (dd, $J = 14.5, 6.9$ Hz, 3H), 6.67 (s, 1H), 6.12 (s, 1H), 4.46 (d, $J = 25.8$ Hz, 1H), 4.06 (td, $J = 15.8, 8.1$ Hz, 2H), 3.96-3.69 (m, 2H), 2.88 (d, $J = 4.5$ Hz, 3H), 2.54 (s, 3H), 1.24 (t, $J = 6.9$ Hz, 3H), 1.10 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 164.3, 156.3 ($J = 1.5$ Hz), 147.5, 133.9 ($J = 6.5$ Hz), 129.2 ($J = 6.3$ Hz), 128.5 ($J = 2.1$ Hz), 127.6 ($J = 2.6$ Hz), 116.3, 107.3 ($J = 4.2$ Hz), 63.2 ($J = 7.1$ Hz), 62.9 ($J = 7.0$ Hz), 44.8 ($J = 140.7$ Hz), 26.0, 16.3 ($J = 5.8$ Hz), 16.1 ($J = 5.8$ Hz), 13.4; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 21.7; MS (EI, 70 eV) m/z : 365.14, 308.14, 228.13, 197.04; HRMS ESI (m/z): calcd for $\text{C}_{18}\text{H}_{24}\text{NNaO}_5\text{P}$ [$\text{M} + \text{Na}$] $^+$: 388.1284, found: 388.1283.

Allyl 5-((Diethoxyphosphoryl)(phenyl)methyl)-2-methylfuran-3-carboxylate (3fa)



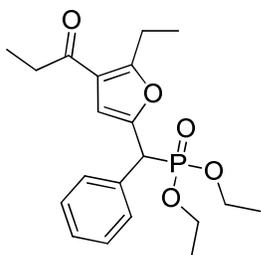
Light yellow oil (105.9 mg, 90%); IR (KBr): 2985, 2359, 1718, 1238, 1031, 961 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.44 (d, $J = 7.4$ Hz, 2H), 7.30 (dt, $J = 11.4, 8.3$ Hz, 3H), 6.78 (s, 1H), 5.99 (qd, $J = 10.8, 5.6$ Hz, 1H), 5.36 (d, $J = 17.2$ Hz, 1H), 5.25 (d, $J = 10.4$ Hz, 1H), 4.72 (d, $J = 5.4$ Hz, 2H), 4.46 (d, $J = 25.9$ Hz, 1H), 4.12-3.71 (m, 4H), 2.53 (s, 3H), 1.24 (t, $J = 7.0$ Hz, 3H), 1.12 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.5, 158.9 ($J = 1.4$ Hz), 147.9 ($J = 1.7$ Hz), 133.8 ($J = 6.4$ Hz), 132.3, 129.3 ($J = 6.3$ Hz), 128.5 ($J = 2.1$ Hz), 127.5 ($J = 2.8$ Hz), 117.9, 114.1 ($J = 1.2$ Hz), 109.4 ($J = 4.8$ Hz), 64.7, 63.0 (d, $J = 6.9$ Hz), 62.8 ($J = 7.0$ Hz), 44.9 ($J = 140.7$ Hz), 16.2 ($J = 5.8$ Hz), 16.1 ($J = 5.8$ Hz), 13.7; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 21.6; MS (EI, 70 eV) m/z : 392.15, 335.12, 255.13, 214.08; HRMS ESI (m/z): calcd for $\text{C}_{20}\text{H}_{25}\text{NaO}_6\text{P}$ [$\text{M} + \text{Na}$] $^+$: 415.1281, found: 415.1280.

Diethyl ((4-Benzoyl-5-methylfuran-2-yl)(phenyl)methyl)phosphonate (3ga)



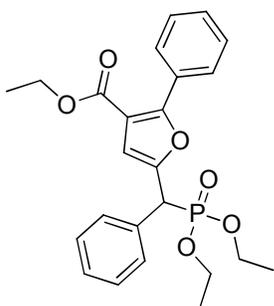
Brown oil (84.1 mg, 68%); IR (KBr): 2984, 2356, 1671, 1242, 1034, 696 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.79 (d, $J = 7.0$ Hz, 2H), 7.58-7.49 (m, 1H), 7.46 (t, $J = 7.1$ Hz, 4H), 7.40-7.27 (m, 3H), 6.72 (s, 1H), 4.50 (d, $J = 25.9$ Hz, 1H), 4.13-3.75 (m, 4H), 2.49 (s, 3H), 1.25 (t, $J = 6.7$ Hz, 3H), 1.12 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 191.1, 159.1 ($J = 1.3$ Hz), 147.8 ($J = 1.5$ Hz), 139.0, 133.9 ($J = 6.4$ Hz), 132.2, 129.4 ($J = 6.2$ Hz), 128.9, 128.6 ($J = 2.2$ Hz), 128.3, 127.7 ($J = 2.8$ Hz), 121.4 ($J = 1.3$ Hz), 110.6 ($J = 4.8$ Hz), 63.1 ($J = 7.0$ Hz), 62.9 ($J = 7.2$ Hz), 45.0 ($J = 140.7$ Hz), 16.3 ($J = 5.8$ Hz), 16.2 ($J = 5.9$ Hz), 14.2; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 21.5; MS (EI, 70 eV) m/z : 412.19, 275.14, 105.08, 77.07; HRMS ESI (m/z): calcd for $\text{C}_{23}\text{H}_{25}\text{NaO}_5\text{P}$ [$\text{M} + \text{Na}$] $^+$: 435.1332, found: 435.1336.

Diethyl ((5-Ethyl-4-propionylfuran-2-yl)(phenyl)methyl)phosphonate (3ha)



Yellow oil (102.1mg, 90%); IR (KBr): 2981, 1678, 1246, 1031, 962 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.44 (d, $J = 7.4$ Hz, 2H), 7.32 (dd, $J = 17.2, 9.7$ Hz, 3H), 6.73 (s, 1H), 4.48 (d, $J = 25.9$ Hz, 1H), 4.14-3.69 (m, 4H), 2.96 (ddq, $J = 22.7, 15.1, 7.5$ Hz, 2H), 2.74 (q, $J = 7.2$ Hz, 2H), 1.17 (ddt, $J = 33.2, 11.2, 7.1$ Hz, 12H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 197.0, 162.6 ($J = 1.5$ Hz), 147.6 ($J = 1.9$ Hz), 133.8 ($J = 6.3$ Hz), 129.2 ($J = 6.3$ Hz), 128.5 ($J = 2.1$ Hz), 127.5 ($J = 2.7$ Hz), 120.7 ($J = 1.3$ Hz), 108.7 ($J = 4.9$ Hz), 63.0 ($J = 7.0$ Hz), 62.7 ($J = 7.0$ Hz), 44.9 ($J = 139.6$ Hz), 34.3, 21.5, 16.2 ($J = 5.8$ Hz), 16.1 ($J = 5.8$ Hz), 11.9, 7.7; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 21.5; MS (EI, 70 eV) m/z : 378.19, 241.16, 183.12; HRMS ESI (m/z): calcd for $\text{C}_{20}\text{H}_{27}\text{NaO}_5\text{P}$ [$\text{M} + \text{Na}$] $^+$: 401.1488, found: 401.1490.

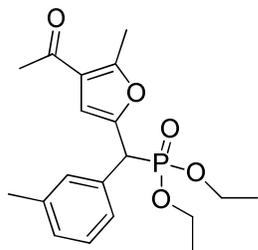
Ethyl 5-((Diethoxyphosphoryl)(phenyl)methyl)-2-phenylfuran-3-carboxylate (3ia)



Light yellow oil (103.5 mg, 78%); IR (KBr): 2983, 1716, 1245, 1033, 962 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.96 (d, $J = 7.0$ Hz, 2H), 7.50 (d, $J = 7.4$ Hz, 2H), 7.37 (dt, $J = 15.3, 7.1$ Hz, 5H), 7.31-7.26 (m, 1H), 6.95 (s, 1H), 4.58 (d, $J = 25.8$ Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 4.15-3.72 (m, 4H), 1.32 (t, $J = 7.1$ Hz, 3H), 1.25 (t, $J = 7.0$ Hz, 3H), 1.12 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.3, 156.7 ($J = 1.9$ Hz), 148.7 ($J = 2.6$ Hz), 133.6 ($J = 6.3$ Hz), 129.4, 129.2, 129.1, 128.5 ($J = 2$ Hz), 128.1 ($J = 4.9$ Hz), 127.9, 127.6 ($J = 2.7$ Hz), 114.7 ($J = 1.5$ Hz),

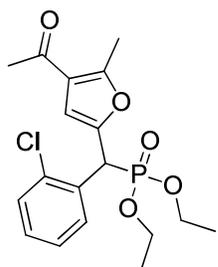
111.7 ($J = 5.1$ Hz), 63.1 ($J = 7.1$ Hz), 62.8 ($J = 7.2$ Hz), 60.4, 45.0 ($J = 139.5$ Hz), 16.2 ($J = 5.8$ Hz), 16.1 ($J = 5.8$ Hz), 14.1; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 21.3; MS (EI, 70 eV) m/z : 442.19, 305.15, 277.14, 105.05; HRMS ESI (m/z): calcd for $\text{C}_{24}\text{H}_{27}\text{NaO}_6\text{P}$ $[\text{M} + \text{Na}]^+$: 465.1437, found: 465.1443.

Diethyl ((4-Acetyl-5-methylfuran-2-yl)(*m*-tolyl)methyl)phosphonate (3ja)



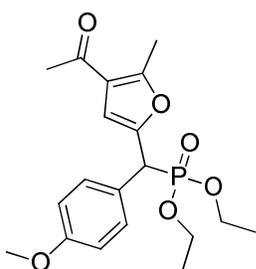
Yellow oil (79.8 mg, 73%); IR (KBr): 2983, 1677, 1236, 1031, 961 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.25 (d, $J = 19.7$ Hz, 3H), 7.10 (s, 1H), 6.75 (s, 1H), 4.42 (d, $J = 25.9$ Hz, 1H), 4.15-3.97 (m, 2H), 3.95-3.69 (m, 2H), 2.53 (s, 3H), 2.40 (s, 3H), 2.35 (s, 3H), 1.26 (t, $J = 7.0$ Hz, 3H), 1.12 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 194.2, 157.9 ($J = 1.6$ Hz), 148.0, 138.3 ($J = 2.2$ Hz), 133.6 ($J = 6.5$ Hz), 129.9 ($J = 6.5$ Hz), 128.5, 128.5, 126.3 ($J = 6.3$ Hz), 122.2 ($J = 1.3$ Hz), 109.2 ($J = 4.6$ Hz), 63.2 ($J = 6.9$ Hz), 62.8 ($J = 7.1$ Hz), 44.8 ($J = 140.8$ Hz), 29.1, 21.4, 16.3 ($J = 5.8$ Hz), 16.1 ($J = 5.8$ Hz), 14.3; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 21.6; MS (EI, 70 eV) m/z : 364.16, 322.17, 227.15, 185.17; HRMS ESI (m/z): calcd for $\text{C}_{19}\text{H}_{25}\text{NaO}_5\text{P}$ $[\text{M} + \text{Na}]^+$: 387.1332, found: 387.1330.

Diethyl ((4-Acetyl-5-methylfuran-2-yl)(2-chlorophenyl)methyl)phosphonate (3ka)



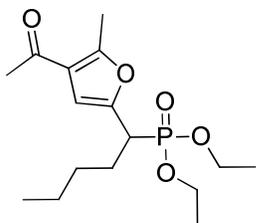
Yellow oil (73.8 mg, 64%); IR (KBr): 2986, 1678, 1238, 1033, 960, 753 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.77 (d, $J = 7.6$ Hz, 1H), 7.41 (d, $J = 7.7$ Hz, 1H), 7.27 (dd, $J = 17.8, 9.9$ Hz, 2H), 6.76 (s, 1H), 5.22 (d, $J = 26.0$ Hz, 1H), 4.12 (dq, $J = 16.7, 8.3$ Hz, 2H), 3.99-3.74 (m, 2H), 2.53 (s, 3H), 2.39 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.12 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 194.0, 158.1 ($J = 1.4$ Hz), 147.2 ($J = 1.8$ Hz), 133.9 ($J = 9.3$ Hz), 131.8 ($J = 5.2$ Hz), 130.9 ($J = 4.5$ Hz), 129.5 ($J = 1.5$ Hz), 128.9 ($J = 2.5$ Hz), 127.0 ($J = 2.5$ Hz), 122.1 ($J = 1.4$ Hz), 109.5 ($J = 4.9$ Hz), 63.1 ($J = 7.1$ Hz), 63.0 ($J = 7.0$ Hz), 40.1 ($J = 142.8$ Hz), 29.1, 16.1 ($J = 19.4, 5.8$ Hz), 14.2; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 20.9; MS (EI, 70 eV) m/z : 384.14, 342.14, 247.09, 141.10; HRMS ESI (m/z): calcd for $\text{C}_{18}\text{H}_{22}\text{ClNaO}_5\text{P}$ $[\text{M} + \text{Na}]^+$: 407.0786, found: 407.0784.

Diethyl ((4-Acetyl-5-methylfuran-2-yl)(4-methoxyphenyl)methyl)phosphonate (3la)



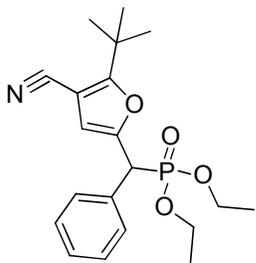
Yellow oil (100.0mg, 88%); IR (KBr): 2985, 1676, 1511, 1247, 1030, 959 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.55-7.09 (m, 2H), 6.85 (d, $J = 8.4$ Hz, 2H), 6.69 (s, 1H), 4.38 (d, $J = 25.8$ Hz, 1H), 4.11-3.68 (m, 7H), 2.51 (s, 3H), 2.37 (s, 3H), 1.23 (t, $J = 7.0$ Hz, 3H), 1.11 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 194.1, 159.1 ($J = 2.5$ Hz), 157.8 ($J = 1.6$ Hz), 148.2, 130.3 ($J = 6.3$ Hz), 125.7 ($J = 6.6$ Hz), 122.2 ($J = 1.4$ Hz), 114.0 ($J = 2.0$ Hz), 108.9 ($J = 4.7$ Hz), 63.1 ($J = 6.9$ Hz), 62.7 ($J = 7.1$ Hz), 55.2, 44.0 ($J = 141.6$ Hz), 29.1, 16.3 ($J = 5.8$ Hz), 16.2 ($J = 5.9$ Hz), 14.3; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 21.8; MS (EI, 70 eV) m/z : 380.15, 243.12, 228.12; HRMS ESI (m/z): calcd for $\text{C}_{19}\text{H}_{25}\text{NaO}_6\text{P}$ $[\text{M} + \text{Na}]^+$: 403.1281, found: 403.1284.

Diethyl (1-(4-Acetyl-5-methylfuran-2-yl)pentyl)phosphonate (3ma)



Yellow oil (61.4 mg, 62%); IR (KBr): 2953, 2357, 1678, 1240, 1035, 957 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 6.44 (d, $J = 3.3$ Hz, 1H), 4.30-3.71 (m, 4H), 3.09 (ddd, $J = 22.9, 11.0, 3.4$ Hz, 1H), 2.55 (s, 3H), 2.37 (s, 3H), 1.92 (ddd, $J = 23.4, 22.0, 16.2$ Hz, 2H), 1.26 (dt, $J = 24.8, 7.0$ Hz, 10H), 0.86 (t, $J = 6.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 194.1, 157.6 ($J = 2.3$ Hz), 148.4 ($J = 8.6$ Hz), 122.3 ($J = 2.5$ Hz), 108.3 ($J = 7.7$ Hz), 62.4 ($J = 6.9$ Hz), 62.2 ($J = 6.8$ Hz), 38.2 ($J = 141.7$ Hz), 29.9, 29.8, 29.1, 28.0 ($J = 2.8$ Hz), 22.2, 16.6, 14.4, 13.7; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 25.8; MS (EI, 70 eV) m/z : 330.15, 274.13, 193.16, 137.08; HRMS ESI (m/z): calcd for $\text{C}_{16}\text{H}_{27}\text{NaO}_5\text{P}$ $[\text{M} + \text{Na}]^+$: 353.1488, found: 353.1489.

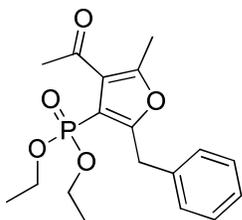
Diethyl ((5-(tert-Butyl)-4-cyanofuran-2-yl)(phenyl)methyl)phosphonate (3na)



Brown oil (41.6 mg, 37%); IR (KBr): 2977, 2359, 1251, 1028, 965 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.45-7.30 (m, 5H), 6.54 (s, 1H), 4.45 (d, $J = 25.9$ Hz, 1H), 3.95 (dddd, $J = 68.9, 24.2, 16.1, 7.9$ Hz, 4H), 1.39 (s, 9H), 1.24 (t, $J = 7.0$ Hz, 3H), 1.12 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 170.6 ($J = 1.6$ Hz), 148.7 ($J = 3.2$ Hz), 133.2 ($J = 6.5$ Hz), 129.3 ($J = 6.2$ Hz), 128.7 ($J = 2.1$ Hz), 127.9 ($J = 2.7$ Hz), 114.8,

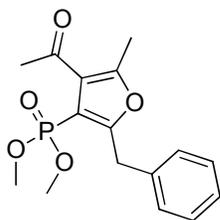
110.8 ($J = 5.4$ Hz), 95.7 ($J = 857.4$ Hz), 63.2 ($J = 6.9$ Hz), 62.9 ($J = 7.1$ Hz), 44.9 ($J = 140.4$ Hz), 34.7, 28.7, 16.3 ($J = 5.9$ Hz), 16.2 ($J = 5.5$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ ppm 20.8; MS (EI, 70 eV) m/z : 375.20, 238.17, 208.12, 91.10; HRMS ESI (m/z): calcd for $\text{C}_{20}\text{H}_{26}\text{NNaO}_4\text{P}$ [$\text{M} + \text{Na}$] $^+$: 398.1492, found: 398.1492.

Diethyl (4-Acetyl-2-benzyl-5-methylfuran-3-yl)phosphonate (4aa)



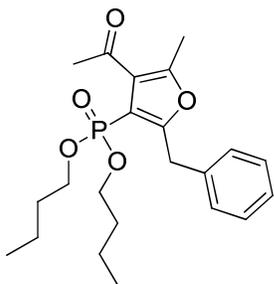
Yellow oil (93.5 mg, 89%); IR (KBr): 2984, 1680, 1252, 1028, 963 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.30 (dd, $J = 16.9, 6.7$ Hz, 4H), 7.21 (t, $J = 6.7$ Hz, 1H), 4.35 (s, 2H), 4.20-4.02 (m, 4H), 2.51 (s, 3H), 2.42 (s, 3H), 1.30 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 195.6, 161.9 ($J = 26.1$ Hz), 156.6 ($J = 13.8$ Hz), 137.5, 128.7, 128.4, 126.6, 123.9 ($J = 11.7$ Hz), 106.3 ($J = 210.8$ Hz), 62.1 ($J = 5.2$ Hz), 33.3, 30.7, 16.2 ($J = 6.6$ Hz), 13.9; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 13.1; MS (EI, 70 eV) m/z : 350.13, 276.07, 258.05, 211.10; HRMS ESI (m/z): calcd for $\text{C}_{18}\text{H}_{23}\text{NaO}_5\text{P}$ [$\text{M} + \text{Na}$] $^+$: 373.1175, found: 373.1180.

Dimethyl (4-Acetyl-2-benzyl-5-methylfuran-3-yl)phosphonate (4ab)



Yellow oil (80.2 mg, 83%); IR (KBr): 2943, 2357, 1680, 1252, 1032, 832 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.29 (dd, $J = 15.3, 8.0$ Hz, 4H), 7.21 (t, $J = 6.6$ Hz, 1H), 4.33 (s, 2H), 3.75 (s, 3H), 3.72 (s, 3H), 2.47 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 194.9, 162.4 ($J = 26.4$ Hz), 156.8 ($J = 13.9$ Hz), 137.5 ($J = 1.2$ Hz), 128.8, 128.5, 126.6, 123.9 ($J = 11.4$ Hz), 105.3 ($J = 212.8$ Hz), 52.6 ($J = 5.4$ Hz), 33.4, 30.5, 14.1; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 15.8; MS (EI, 70 eV) m/z : 322.09, 290.08, 258.05, 211.10; HRMS ESI (m/z): calcd for $\text{C}_{16}\text{H}_{19}\text{NaO}_5\text{P}$ [$\text{M} + \text{Na}$] $^+$: 345.0862, found: 345.0869.

Dibutyl (4-Acetyl-2-benzyl-5-methylfuran-3-yl)phosphonate (4ac)



Yellow oil (109.7 mg, 90%); IR (KBr): 2958, 1683, 1251, 1022, 579 cm^{-1} ; ^1H

NMR (400 MHz, CDCl_3) δ ppm 7.34-7.26 (m, 4H), 7.21 (t, $J = 7.0$ Hz, 1H), 4.36

(s, 2H), 4.13-3.92 (m, 4H), 2.51 (s, 3H), 2.42 (s, 3H), 1.68-1.57 (m, 4H),

1.42-1.31 (m, 4H), 0.90 (t, $J = 7.4$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm

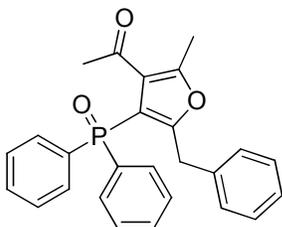
195.6, 161.9 ($J = 26.4$ Hz), 156.6 ($J = 13.9$ Hz), 137.6 ($J = 1.1$ Hz), 128.7, 128.4, 126.5, 123.8 ($J = 11.6$

Hz), 106.2 ($J = 210.8$ Hz), 65.8 ($J = 5.5$ Hz), 33.3, 32.3 ($J = 6.6$ Hz), 30.65, 18.7, 13.8, 13.5; ^{31}P NMR (162

MHz, CDCl_3) δ ppm 13.2; MS (EI, 70 eV) m/z : 406.19, 350.14, 294.06, 276.06; HRMS ESI (m/z): calcd for

$\text{C}_{22}\text{H}_{31}\text{NaO}_5\text{P}$ [$\text{M} + \text{Na}$] $^+$: 429.1801, found: 429.1803.

1-(5-Benzyl-4-(diphenylphosphoryl)-2-methylfuran-3-yl)ethanone (4ae)



Brown oil (57.1 mg, 46%); IR (KBr): 2925, 1675, 1556, 1031, 701, 554 cm^{-1} ;

^1H NMR (400 MHz, CDCl_3) δ ppm 7.73 (dd, $J = 12.2, 7.9$ Hz, 4H), 7.51-7.45

(m, 2H), 7.41 (d, $J = 7.0$ Hz, 4H), 7.29-7.18 (m, 5H), 4.24 (s, 2H), 2.51 (s, 3H),

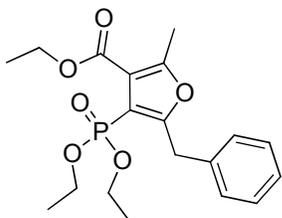
2.13 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 192.7, 162.5 ($J = 16.5$ Hz),

156.2 ($J = 9.9$ Hz), 137.6, 134.2, 133.1, 131.7 ($J = 10.3$ Hz), 131.5 ($J = 2.7$ Hz), 128.6 ($J = 56.3$ Hz), 128.1 (J

= 12.7 Hz), 126.4, 125.4 ($J = 8.0$ Hz), 110.3 ($J = 115.3$ Hz), 33.4, 30.1, 14.7; ^{31}P NMR (162 MHz, CDCl_3) δ

ppm 25.1; HRMS ESI (m/z): calcd for $\text{C}_{26}\text{H}_{23}\text{NaO}_3\text{P}$ [$\text{M} + \text{Na}$] $^+$: 437.1277, found: 437.1279.

Ethyl 5-Benzyl-4-(diethoxyphosphoryl)-2-methylfuran-3-carboxylate (4ca)

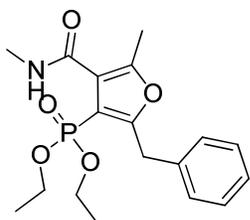


Yellow oil (92.4 mg, 81%); IR (KBr): 2984, 2358, 1717, 1248, 1030, 586 cm^{-1} ;

^1H NMR (400 MHz, CDCl_3) δ ppm 7.35-7.26 (m, 4H), 7.23-7.18 (m, 1H), 4.39

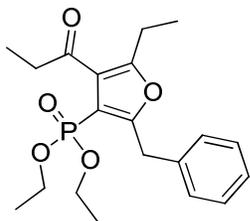
(s, 2H), 4.29 (q, $J = 7.1$ Hz, 2H), 4.16-4.02 (m, 4H), 2.49 (s, 3H), 1.35 (t, $J = 7.1$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.1, 162.3 ($J = 26.1$ Hz), 158.7 ($J = 13.0$ Hz), 137.7 ($J = 1.1$ Hz), 128.8, 128.4, 126.5, 114.6 ($J = 10.0$ Hz), 106.8 ($J = 211.4$ Hz), 61.8 ($J = 5.2$ Hz), 60.4, 33.3, 16.3 ($J = 6.8$ Hz), 14.1, 13.7; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 12.5; MS (EI, 70 eV) m/z : 380.13, 334.10, 277.03, 139.05; HRMS ESI (m/z): calcd for $\text{C}_{19}\text{H}_{25}\text{NaO}_6\text{P}$ [$\text{M} + \text{Na}$] $^+$: 403.1281, found: 403.1281.

Diethyl (2-Benzyl-5-methyl-4-(methylcarbamoyl)furan-3-yl)phosphonate (4ea)



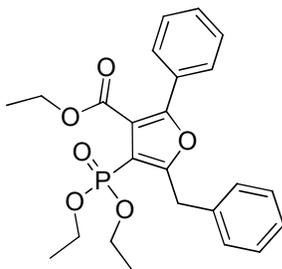
Brown oil (81.1 mg, 74%); IR (KBr): 2956, 2357, 1653, 1236, 1025, 584 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 8.68 (s, 1H), 7.45-7.05 (m, 5H), 4.20 (s, 2H), 4.16 m-3.96 (m, 4H), 2.89 (d, $J = 4.5$ Hz, 3H), 2.56 (s, 3H), 1.27 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 163.7, 159.9 ($J = 22.8$ Hz), 158.4 ($J = 14.9$ Hz), 137.2, 128.5, 128.4, 126.7, 117.0 ($J = 14.3$ Hz), 105.1 ($J = 207.2$ Hz), 62.6 ($J = 5.3$ Hz), 33.6, 26.1, 16.1 ($J = 6.7$ Hz), 14.0; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 16.0; MS (EI, 70 eV) m/z : 365.17, 334.12, 306.10, 278.07; HRMS ESI (m/z): calcd for $\text{C}_{18}\text{H}_{24}\text{NNaO}_5\text{P}$ [$\text{M} + \text{Na}$] $^+$: 388.1284, found: 388.1288.

Diethyl (2-Benzyl-5-ethyl-4-propionylfuran-3-yl)phosphonate (4ha)



Yellow oil (69.2 mg, 61%); IR (KBr): 2981, 1685, 1251, 1025, 965 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.29 (dd, $J = 14.9, 6.9$ Hz, 4H), 7.21 (t, $J = 6.7$ Hz, 1H), 4.34 (s, 2H), 4.08 (qd, $J = 16.5, 8.6$ Hz, 4H), 2.85 (q, $J = 7.2$ Hz, 2H), 2.74 (q, $J = 7.5$ Hz, 2H), 1.28 (t, $J = 7.1$ Hz, 6H), 1.20 (t, $J = 7.5$ Hz, 3H), 1.12 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 199.7, 161.6 ($J = 26.5$ Hz), 159.6 ($J = 13.6$ Hz), 137.6, 128.7, 128.4, 126.5, 123.07 ($J = 11.8$ Hz), 106.1 ($J = 209.6$ Hz), 62.1 ($J = 5.4$ Hz), 36.1, 33.4, 21.0, 16.2 ($J = 6.7$ Hz), 12.5, 8.2; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 13.3; MS (EI, 70 eV) m/z : 378.19, 349.14, 321.14, 303.13; HRMS ESI (m/z): calcd for $\text{C}_{20}\text{H}_{27}\text{NaO}_5\text{P}$ [$\text{M} + \text{Na}$] $^+$: 401.1488, found: 401.1489.

Ethyl 5-Benzyl-4-(diethoxyphosphoryl)-2-phenylfuran-3-carboxylate (4ia)

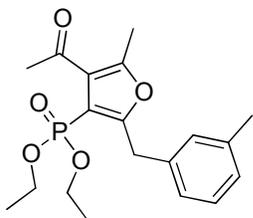


Yellow oil (95.5 mg, 76%); IR (KBr): 2984, 2358, 1728, 1240, 1027, 967 cm^{-1} ;

^1H NMR (400 MHz, CDCl_3) δ ppm 7.66 (d, $J = 7.0$ Hz, 2H), 7.37 (dd, $J = 11.9$, 6.6 Hz, 5H), 7.28 (dd, $J = 13.9$, 6.4 Hz, 2H), 7.21 (t, $J = 7.2$ Hz, 1H), 4.43 (s, 2H), 4.31 (q, $J = 7.1$ Hz, 2H), 4.18-4.01 (m, 4H), 1.31 (t, $J = 7.1$ Hz, 9H); ^{13}C

NMR (100 MHz, CDCl_3) δ ppm 164.0, 162.4 ($J = 25.4$ Hz), 153.8 ($J = 13.0$ Hz), 137.3, 137.2, 129.2, 128.8, 128.5, 128.3, 127.1, 126.6, 115.6 ($J = 10.8$ Hz), 108.6 ($J = 211.0$ Hz), 62.0 ($J = 5.1$ Hz), 61.3, 33.4, 16.2 ($J = 6.9$ Hz), 13.8; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 11.8; MS (EI): m/z (%) = 442.19, 396.14, 339.08, 105.06; HRMS ESI (m/z): calcd for $\text{C}_{24}\text{H}_{27}\text{NaO}_6\text{P}$ [$\text{M} + \text{Na}$] $^+$: 465.1437, found: 465.1443.

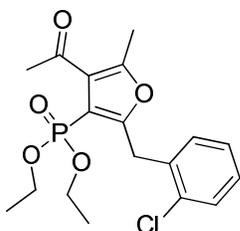
Diethyl (4-Acetyl-5-methyl-2-(3-methylbenzyl)furan-3-yl)phosphonate (4ja)



Yellow oil (85.2 mg, 78%); IR (KBr): 2984, 1681, 1249, 964 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.14 (dt, $J = 15.9$, 7.4 Hz, 3H), 7.02 (d, $J = 7.2$ Hz, 1H), 4.31 (s, 2H), 4.23-4.02 (m, 4H), 2.51 (s, 3H), 2.42 (s, 3H), 2.31 (s, 3H), 1.30 (t, $J = 7.0$

Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 195.6, 162.0 ($J = 26.3$ Hz), 156.6 ($J = 13.8$ Hz), 138.1, 137.4, 129.5, 128.3, 127.3, 125.8, 123.9 ($J = 11.4$ Hz), 106.2 ($J = 213.5$ Hz), 62.1 ($J = 5.2$ Hz), 33.2, 30.8, 21.3, 16.2 ($J = 6.6$ Hz), 13.9; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 13.2; MS (EI, 70 eV) m/z : 364.17, 335.15, 272.11, 225.14; HRMS ESI (m/z): calcd for $\text{C}_{19}\text{H}_{25}\text{NaO}_5\text{P}$ [$\text{M} + \text{Na}$] $^+$: 387.1332, found: 387.1328.

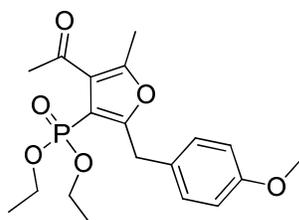
Diethyl (4-Acetyl-2-(2-chlorobenzyl)-5-methylfuran-3-yl)phosphonate (4ka)



Yellow oil (74.9 mg, 65%); IR (KBr): 2985, 1682, 1247, 1030, 964, 755 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.45-7.28 (m, 1H), 7.23-7.08 (m, 3H), 4.48 (s, 2H),

4.26-4.00 (m, 4H), 2.53 (s, 3H), 2.41 (s, 3H), 1.29 (t, $J = 7.1$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 195.4, 160.2 ($J = 25.8$ Hz), 156.9 ($J = 13.8$ Hz), 135.3, 134.0, 130.3, 129.5, 128.1, 126.8, 124.0 ($J = 11.8$ Hz), 107.6 ($J = 211.5$ Hz), 62.3 ($J = 5.5$ Hz), 31.2, 30.8, 16.2 ($J = 6.7$ Hz), 14.0; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 12.7; MS (EI, 70 eV) m/z : 384.13, 321.15, 272.11, 225.14; HRMS ESI (m/z): calcd for $\text{C}_{18}\text{H}_{22}\text{ClNaO}_5\text{P} [\text{M} + \text{Na}]^+$: 407.0786, found: 407.0780.

Diethyl (4-Acetyl-2-(4-methoxybenzyl)-5-methylfuran-3-yl)phosphonate (4la)

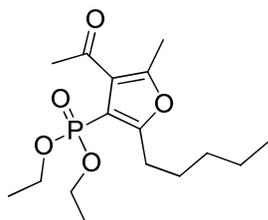


Yellow oil (70.7 mg, 62%); IR (KBr): 2984, 1679, 1249, 1030, 963, 808 cm^{-1} ;

^1H NMR (400 MHz, CDCl_3) δ ppm 7.25 (d, $J = 8.4$ Hz, 2H), 6.82 (d, $J = 8.4$ Hz, 2H), 4.28 (s, 2H), 4.11 (qd, $J = 17.0, 9.6$ Hz, 4H), 3.78 (s, 3H), 2.51 (s,

3H), 2.42 (s, 3H), 1.30 (t, $J = 7.0$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ ppm 195.6, 162.4 ($J = 26.5$ Hz), 158.3, 156.6 ($J = 13.8$ Hz), 129.8, 129.6 ($J = 1.3$ Hz), 123.9 ($J = 10.4$ Hz), 113.9, 105.9 ($J = 211.1$ Hz), 62.1 ($J = 5.3$ Hz), 55.2, 32.5, 30.8, 16.2 ($J = 6.6$ Hz), 13.9; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 13.2; MS (EI, 70 eV) m/z : 380.15, 351.13, 305.08, 153.11; HRMS ESI (m/z): calcd for $\text{C}_{19}\text{H}_{25}\text{NaO}_6\text{P} [\text{M} + \text{Na}]^+$: 403.1281, found: 403.1273.

Diethyl (4-Acetyl-5-methyl-2-pentylfuran-3-yl)phosphonate (4ma)

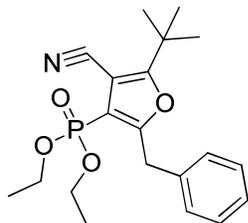


Yellow oil (53.5 mg, 54%); IR (KBr): 2984, 1762, 1551, 1244, 1048 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 4.12 (tt, $J = 16.1, 8.2$ Hz, 4H), 2.94 (t, $J = 7.6$ Hz, 2H), 2.51 (s, 3H), 2.43 (s, 3H), 1.71-1.52 (m, 2H), 1.31 (t, $J = 6.9$ Hz, 10H), 0.87 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 195.9, 164.4 ($J =$

26.8 Hz), 155.8 ($J = 14.0$ Hz), 123.9 ($J = 12.1$ Hz), 105.3 ($J = 213.6$ Hz), 62.0 ($J = 5.3$ Hz), 31.4, 30.8, 28.4, 27.5, 22.3, 16.2 ($J = 6.7$ Hz), 13.9, 13.8; ^{31}P NMR (162 MHz, CDCl_3) δ ppm 13.6; MS (EI, 70 eV) m/z : 330.14, 287.15, 245.14, 189.08; HRMS ESI (m/z): calcd for $\text{C}_{16}\text{H}_{27}\text{NaO}_5\text{P} [\text{M} + \text{Na}]^+$: 353.1488, found:

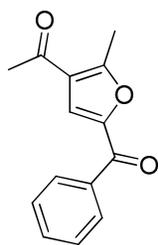
353.1492.

Diethyl (2-Benzyl-5-(*tert*-butyl)-4-cyanofuran-3-yl)phosphonate (4na)



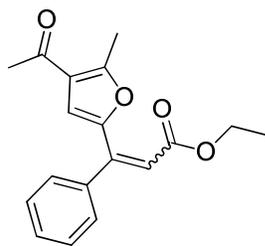
Brown oil (32.6 mg, 29%); IR (KBr): 2924, 1763, 1558, 1247, 1028, 963 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.28 (d, $J = 13.8$ Hz, 5H), 4.30 (s, 2H), 4.24-4.05 (m, 4H), 1.39 (s, 9H), 1.35 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 171.3 ($J = 10.8$ Hz), 161.2 ($J = 24.9$ Hz), 136.8, 128.7, 128.6, 126.8, 113.3, 109.1 ($J = 212.8$ Hz), 92.2 ($J = 8.2$ Hz), 62.6 ($J = 5.6$ Hz), 33.9 ($J = 169.7$ Hz), 29.7, 28.7, 16.2 ($J = 6.5$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ ppm 8.9; MS (EI, 70 eV) m/z : 375.19, 319.13, 304.09, 152.05; HRMS ESI (m/z): calcd for $\text{C}_{20}\text{H}_{26}\text{NNaO}_4\text{P}$ [$\text{M} + \text{Na}$] $^+$: 398.1492, found: 398.1494.

1-(5-Benzoyl-2-methylfuran-3-yl)ethanone (5aa)



Brown oil (30.1 mg, 44%); IR (KBr): 2361, 1678, 1646, 1573, 1243, 722 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.93 (d, $J = 7.6$ Hz, 2H), 7.61 (t, $J = 7.3$ Hz, 1H), 7.51 (t, $J = 7.5$ Hz, 2H), 7.39 (s, 1H), 2.73 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 193.2, 182.1, 163.1, 149.6, 136.9, 132.8, 129.1, 128.6, 123.3, 120.6, 29.0, 14.9; MS (EI, 70 eV) m/z : 228.10, 213.07, 171.08, 105.06.

Ethyl 3-(4-Acetyl-5-methylfuran-2-yl)-3-phenylacrylate (7aa)



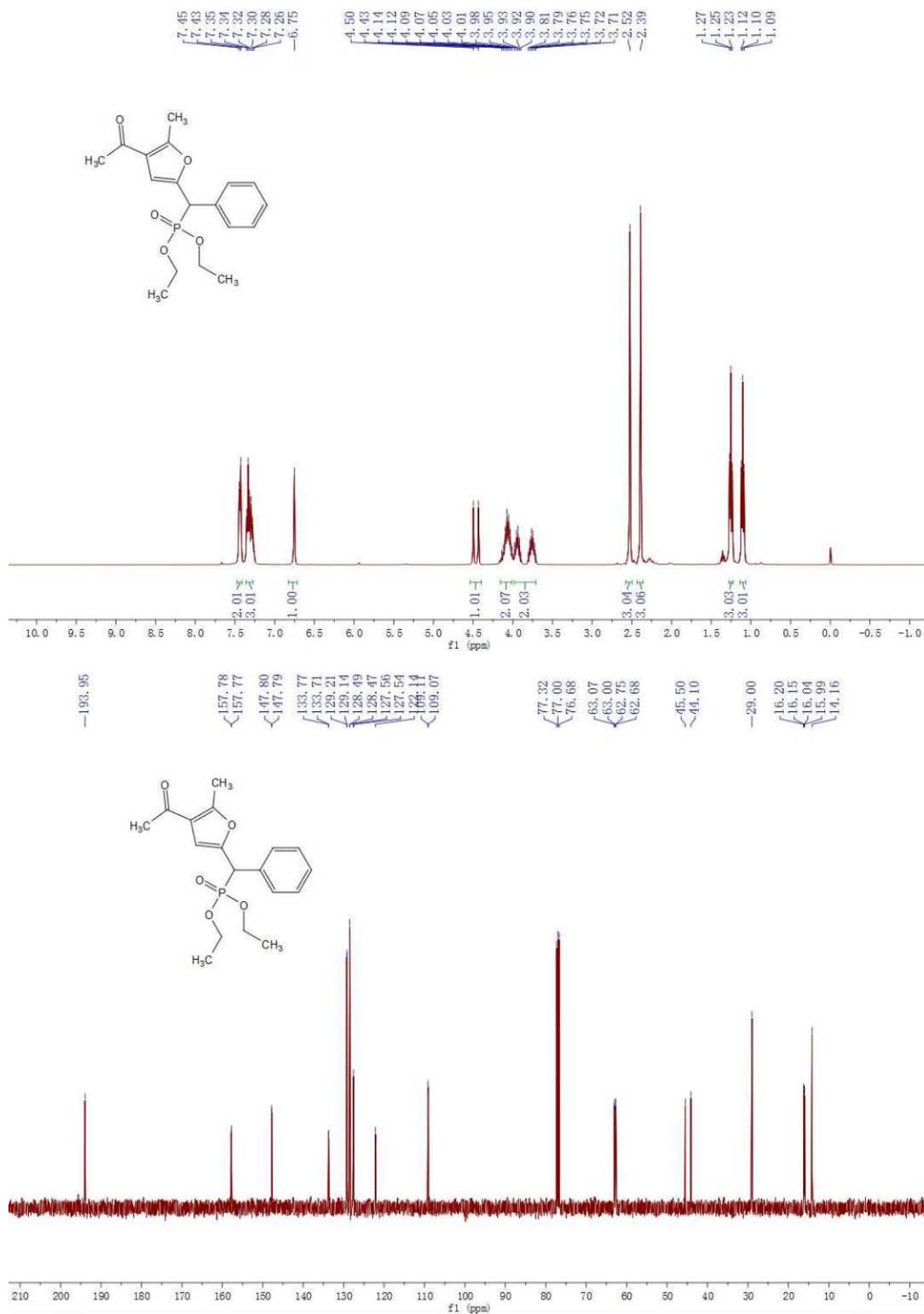
Brown oil (42.0 mg, 47%); IR (KBr): 2984, 1719, 1598, 1239, 1173, 699 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.32 (d, $J = 47.1$ Hz, 5H), 6.87 (s, 1H), 6.03 (s, 1H), 4.22 (dd, $J = 13.8, 6.8$ Hz, 2H), 2.59 (s, 3H), 2.39 (s, 3H), 1.29 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ ppm 193.8, 165.9, 159.4, 157.8, 152.4, 148.5, 141.5, 140.0, 138.9, 130.0, 129.4, 128.6, 128.4, 128.1, 127.6, 122.8, 122.6, 118.2, 114.9, 112.8, 60.5, 59.9, 29.0, 28.8, 14.5, 14.2, 14.0, 13.9; MS (EI, 70 eV) m/z : 298.18, 253.14, 226.16, 139.11; HRMS ESI (m/z): calcd for $\text{C}_{18}\text{H}_{18}\text{NaO}_4$ [$\text{M} + \text{Na}$] $^+$: 321.1097, found: 321.1101.

References

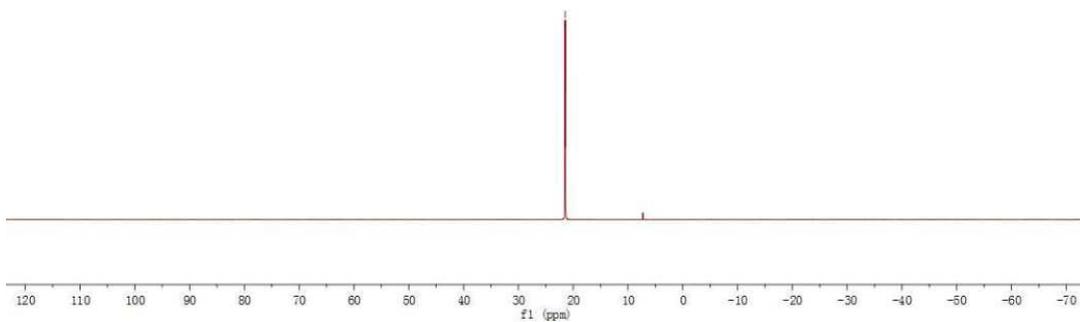
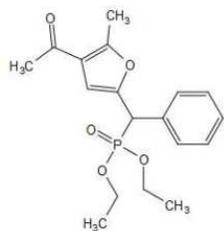
- [1] J. Ma, H. Jiang, S. Zhu, *Org. Lett.* **2014**, *16*, 4472.

F. NMR Spectra

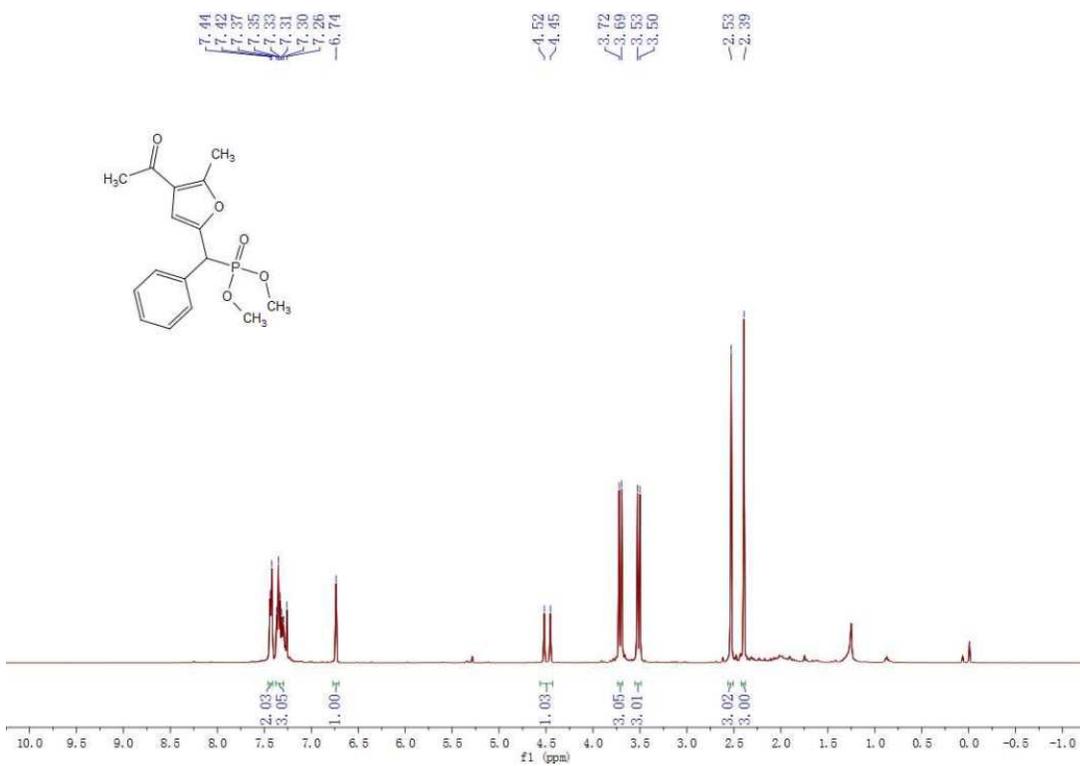
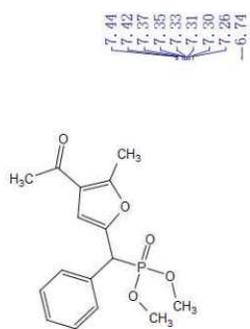
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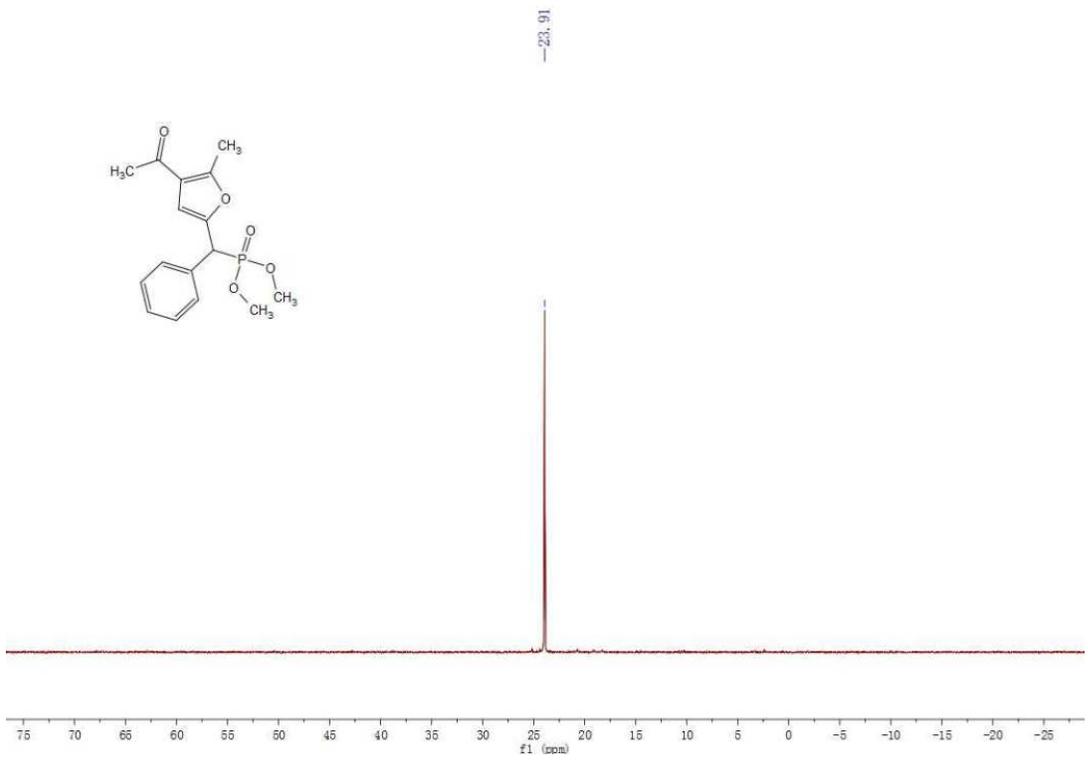
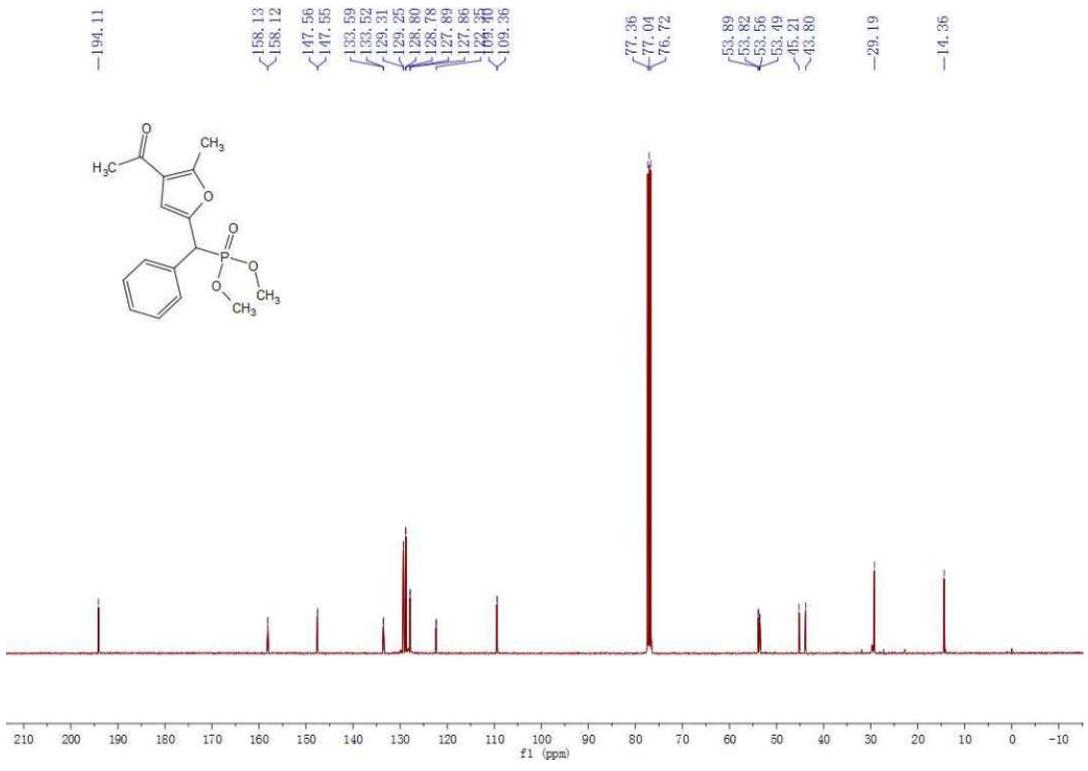


-21.45

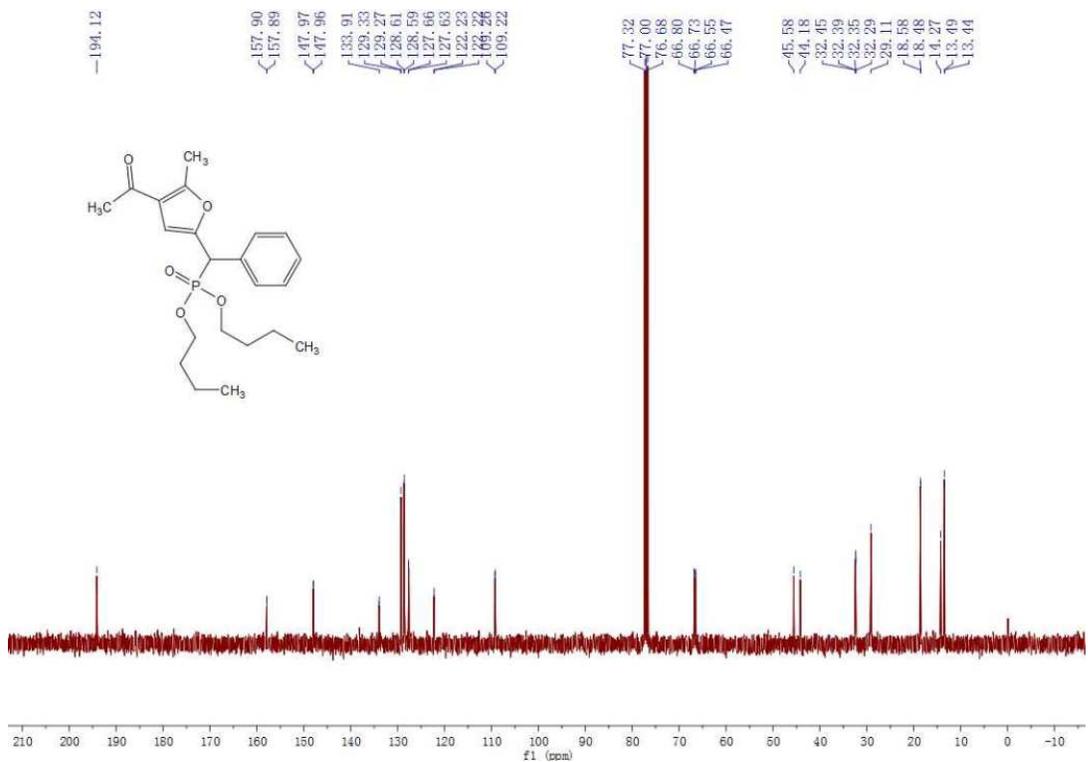
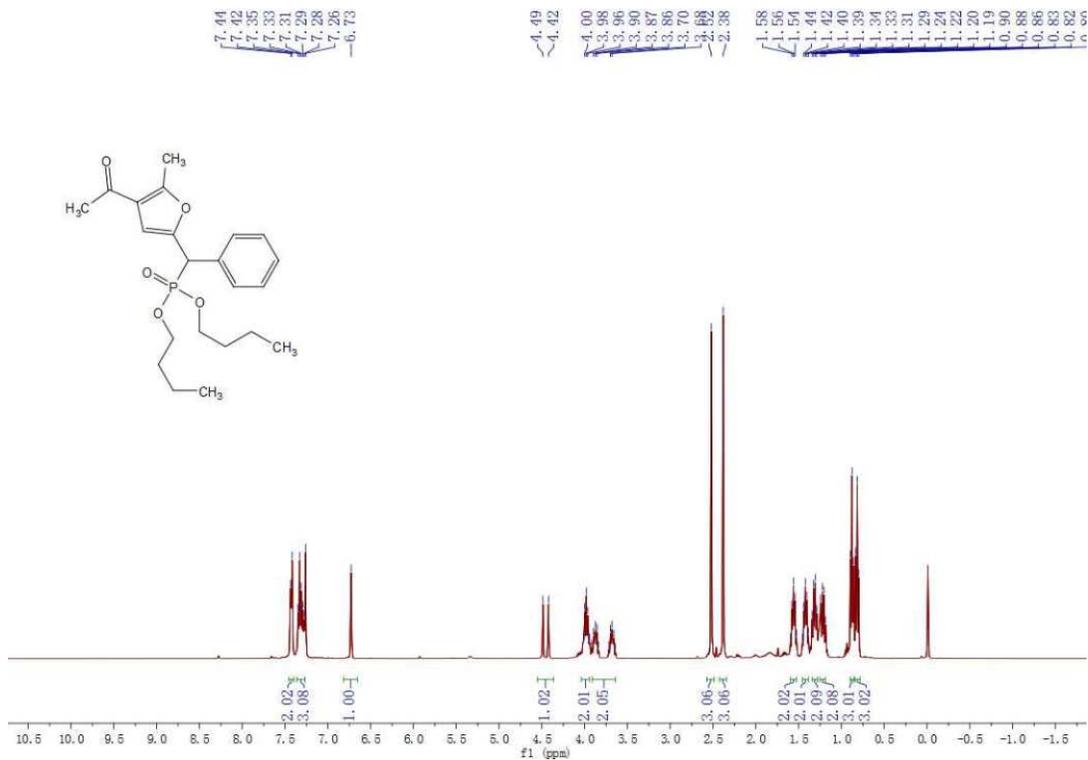


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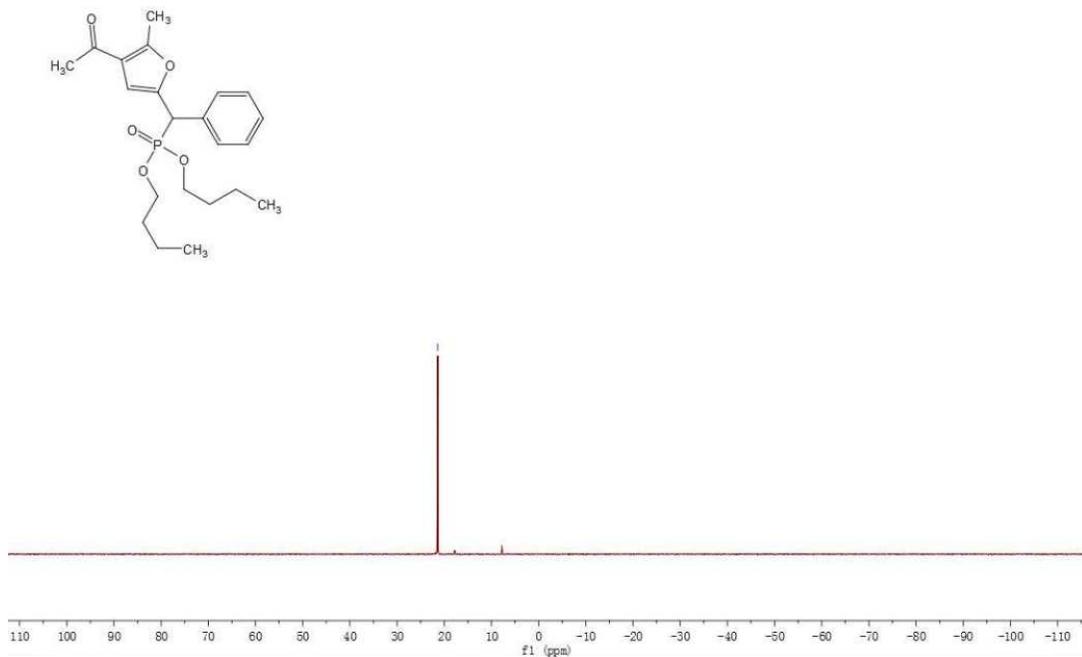




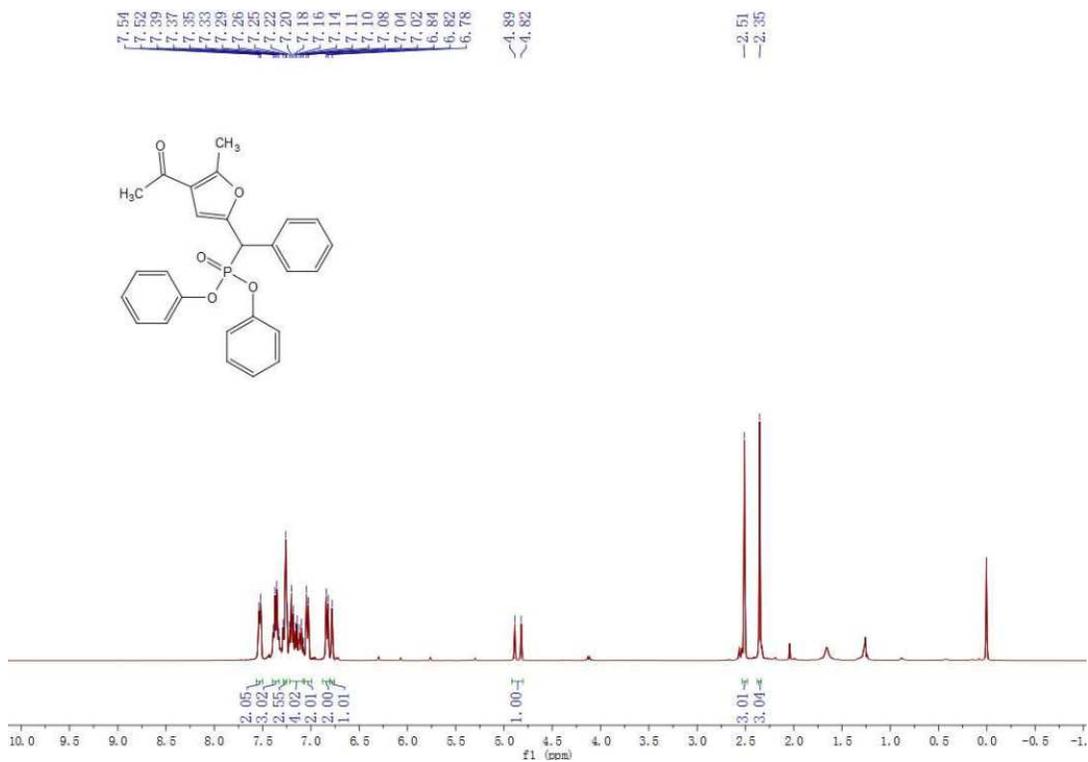
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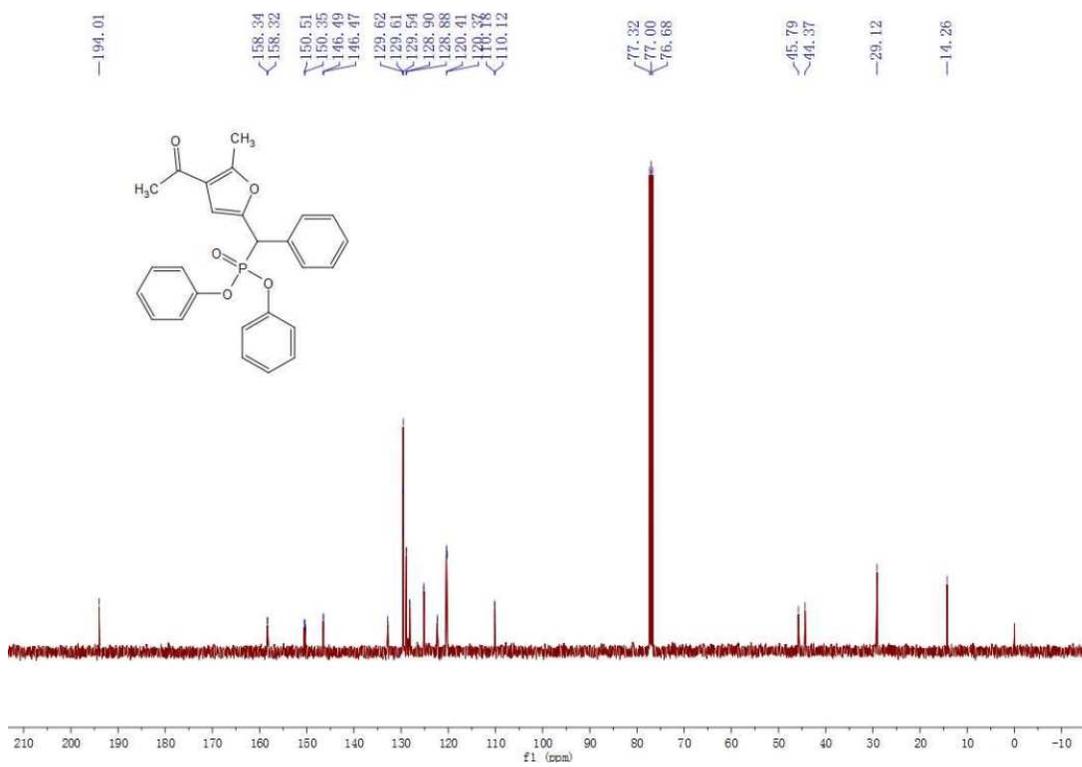


-21.39

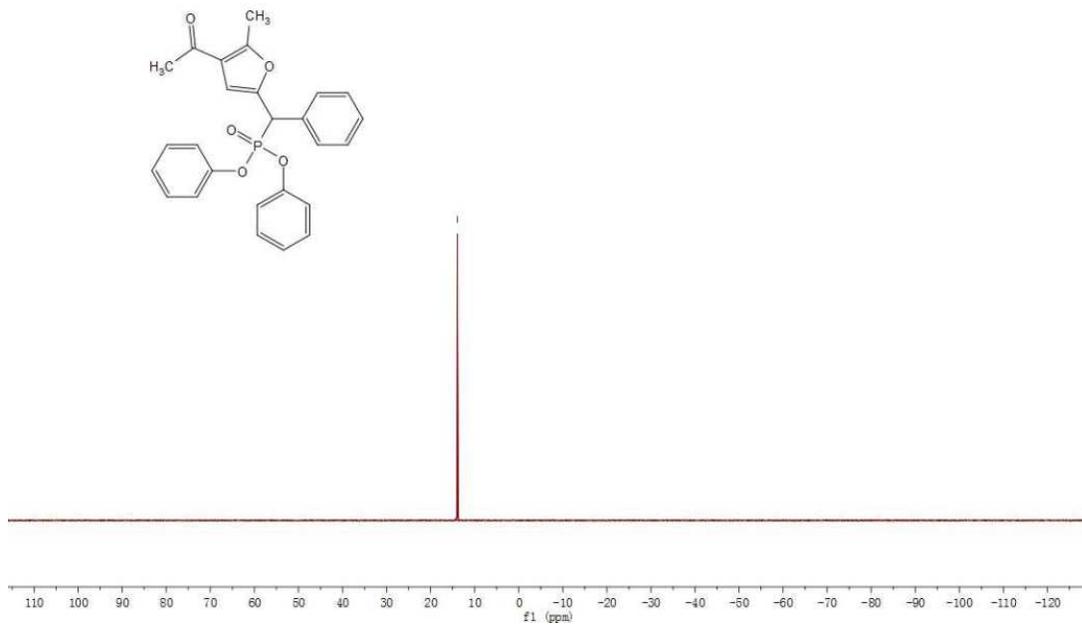


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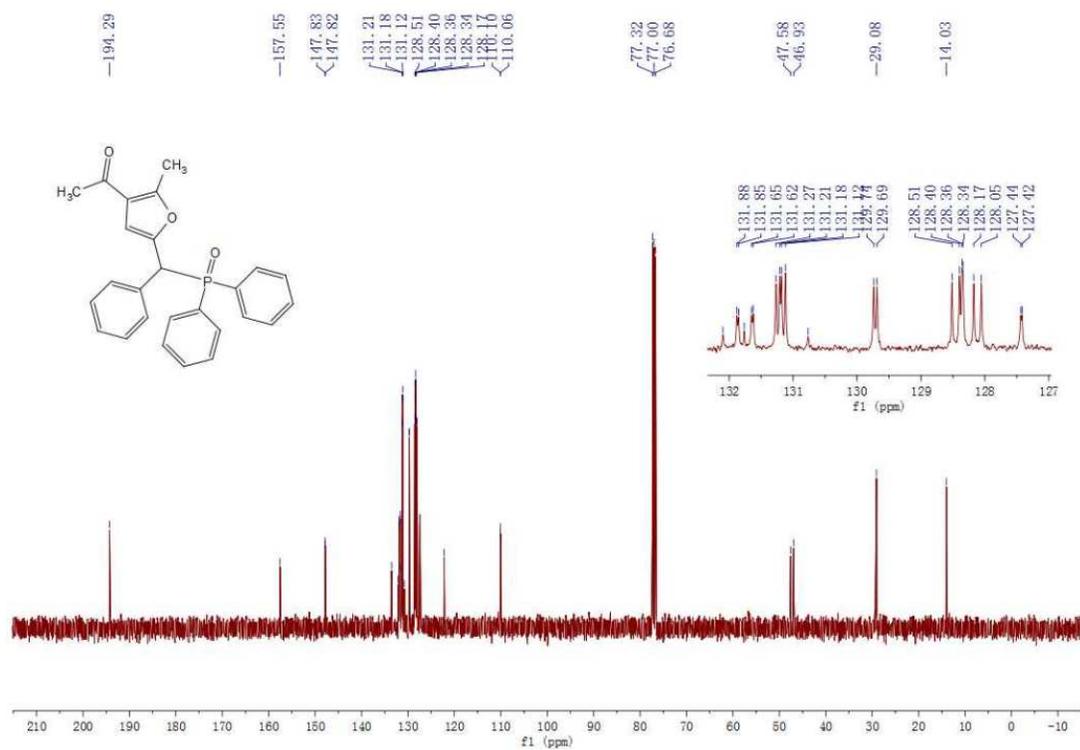
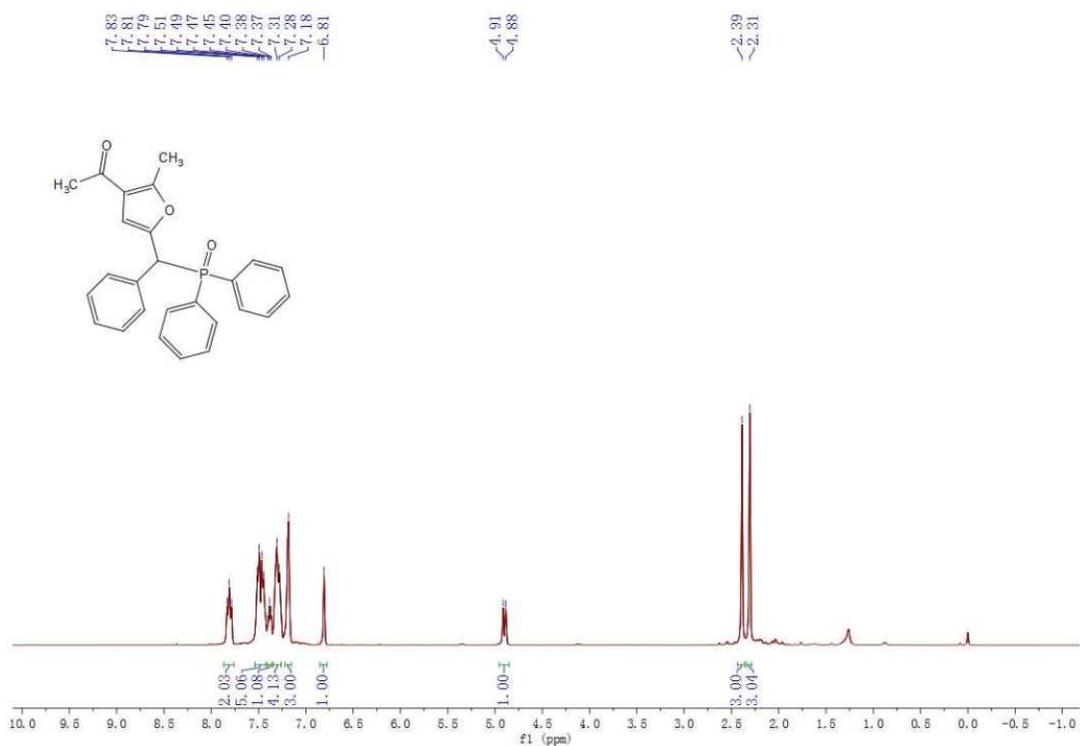


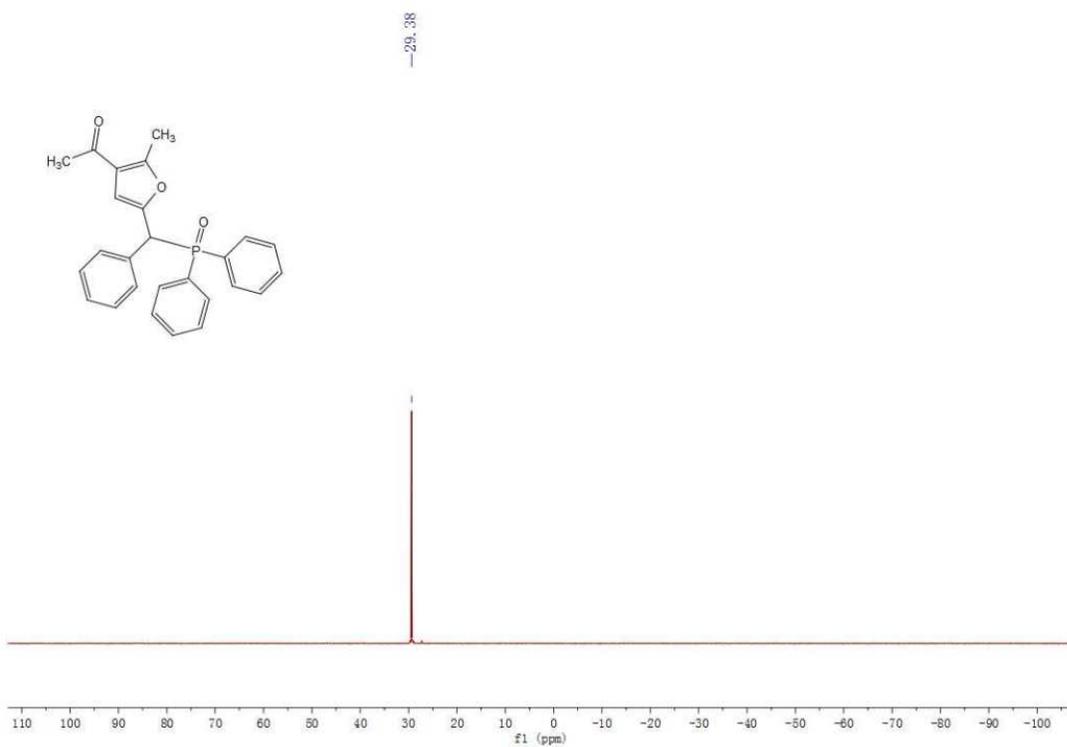


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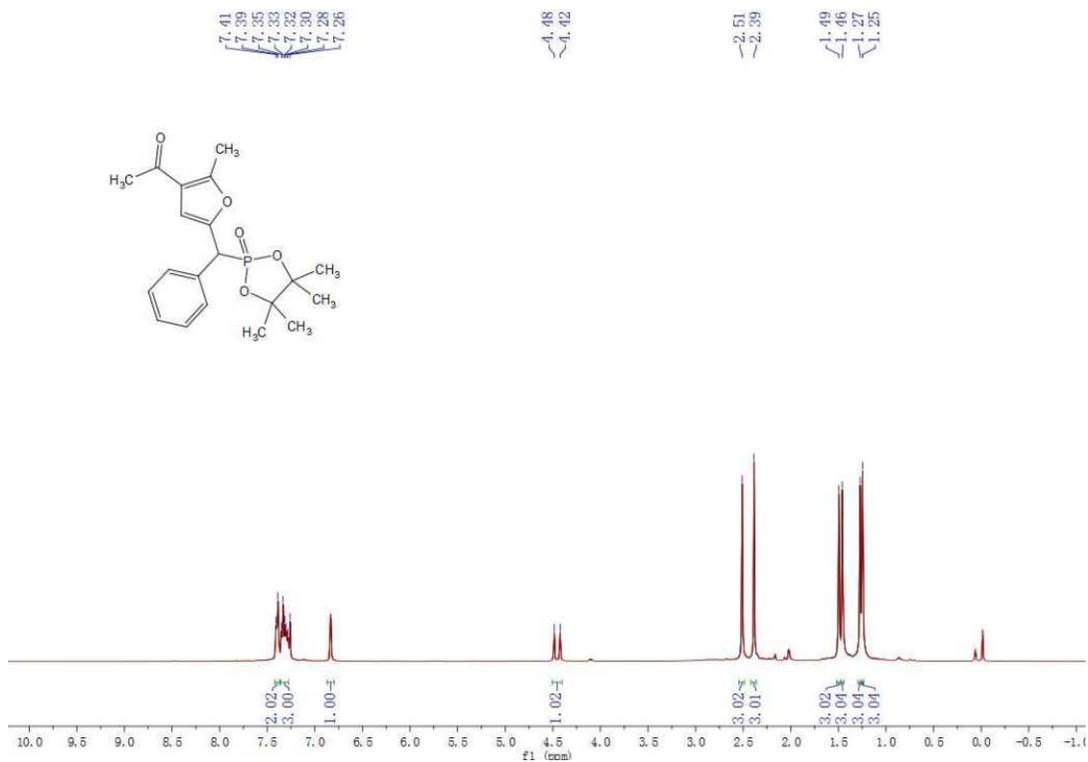


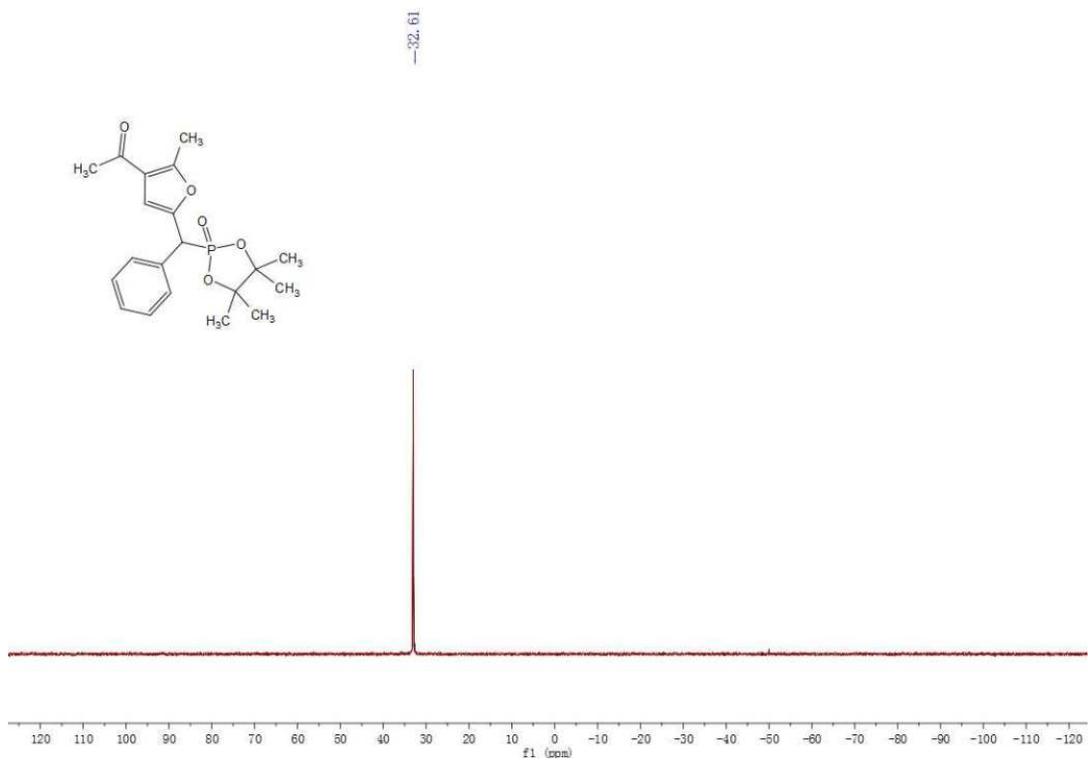
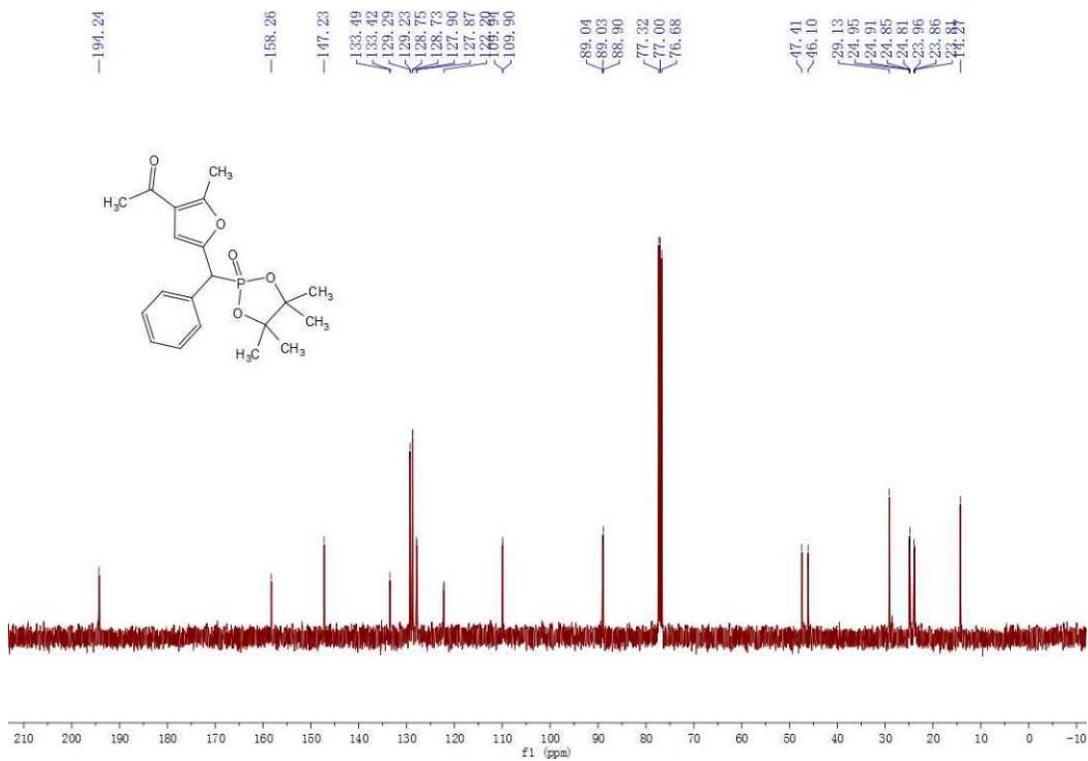
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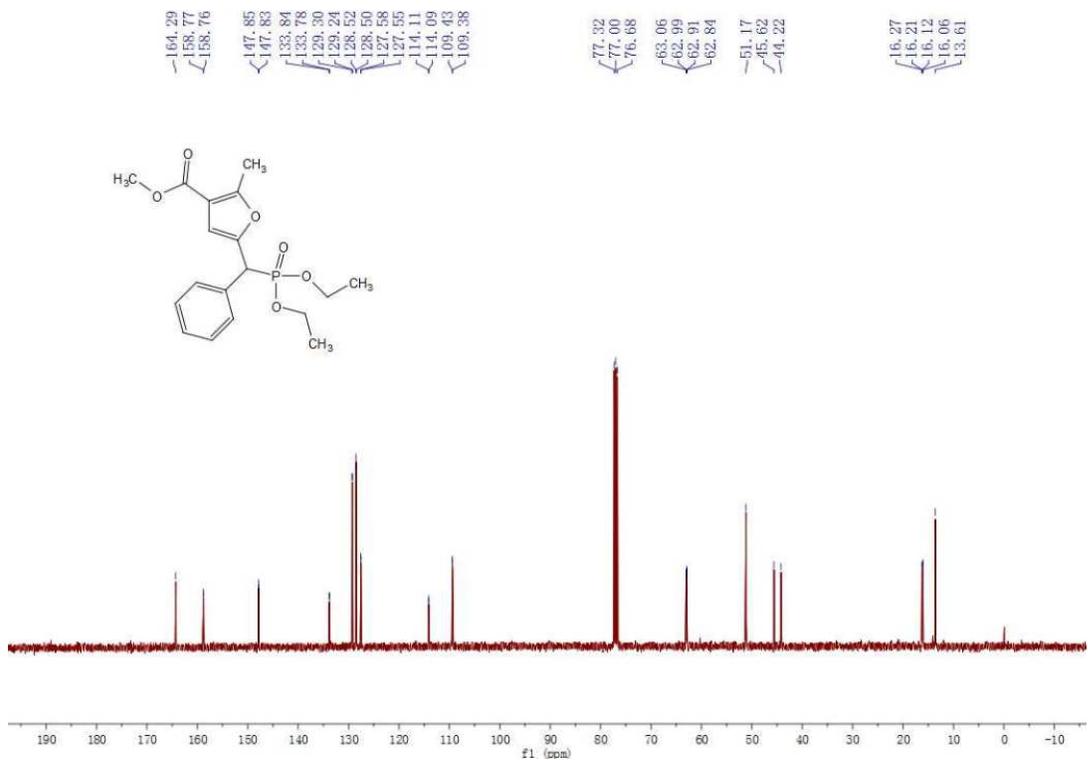
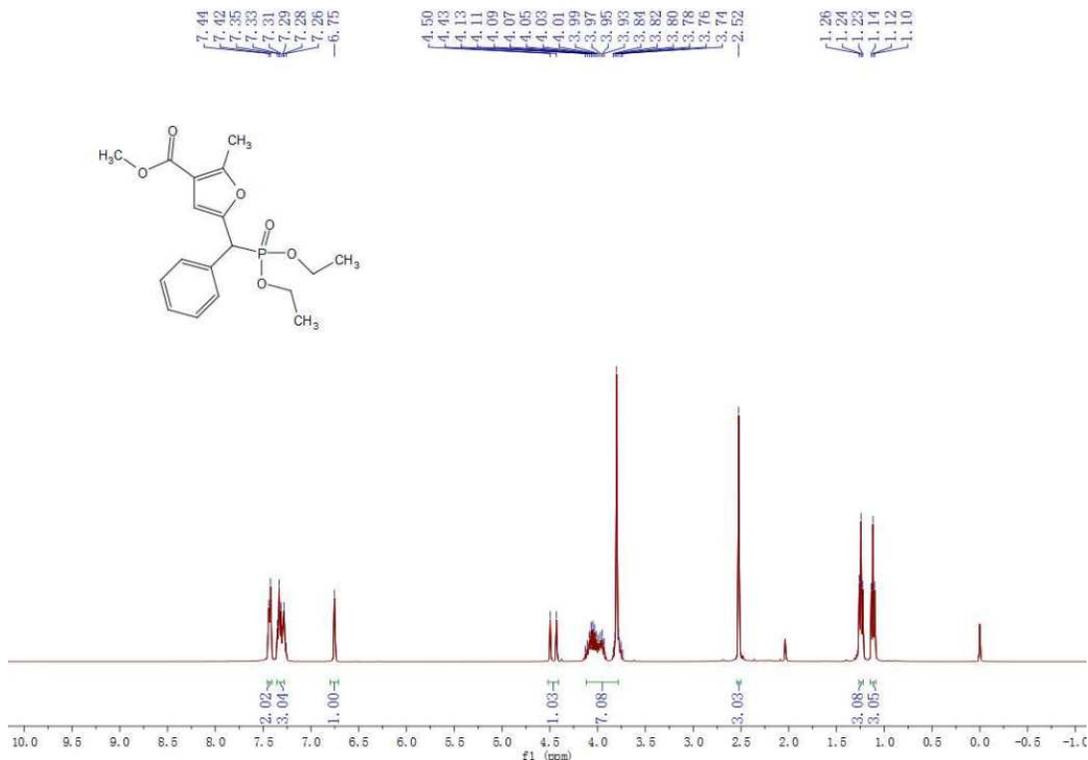


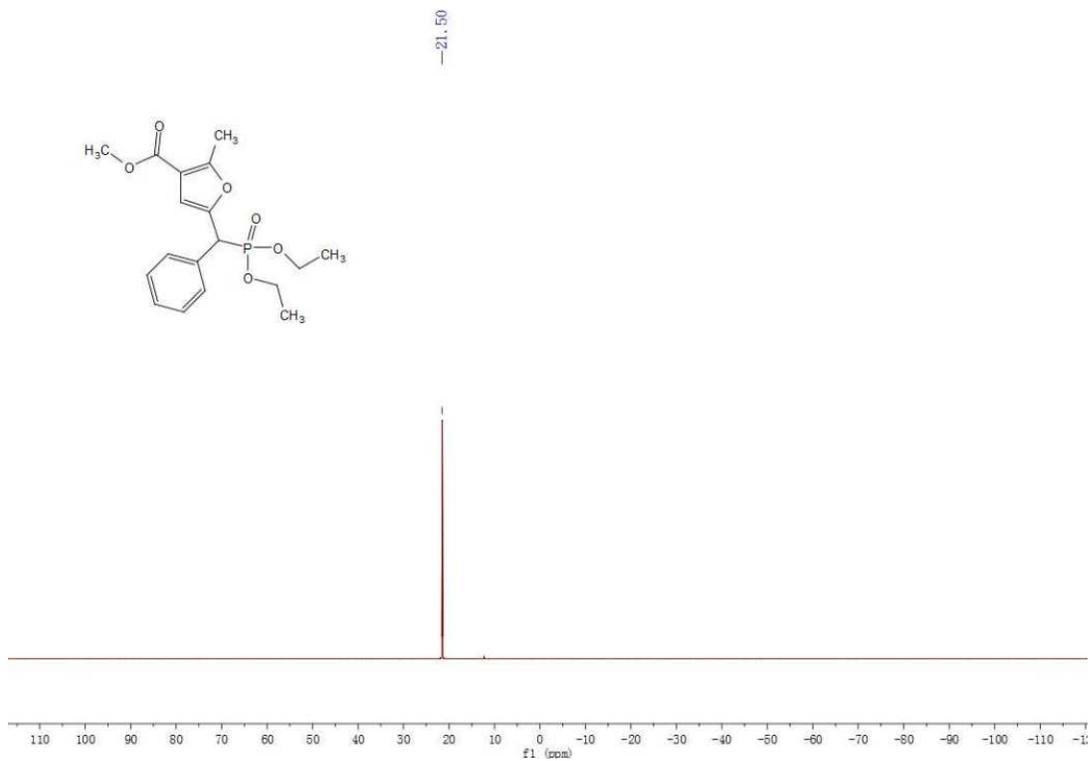
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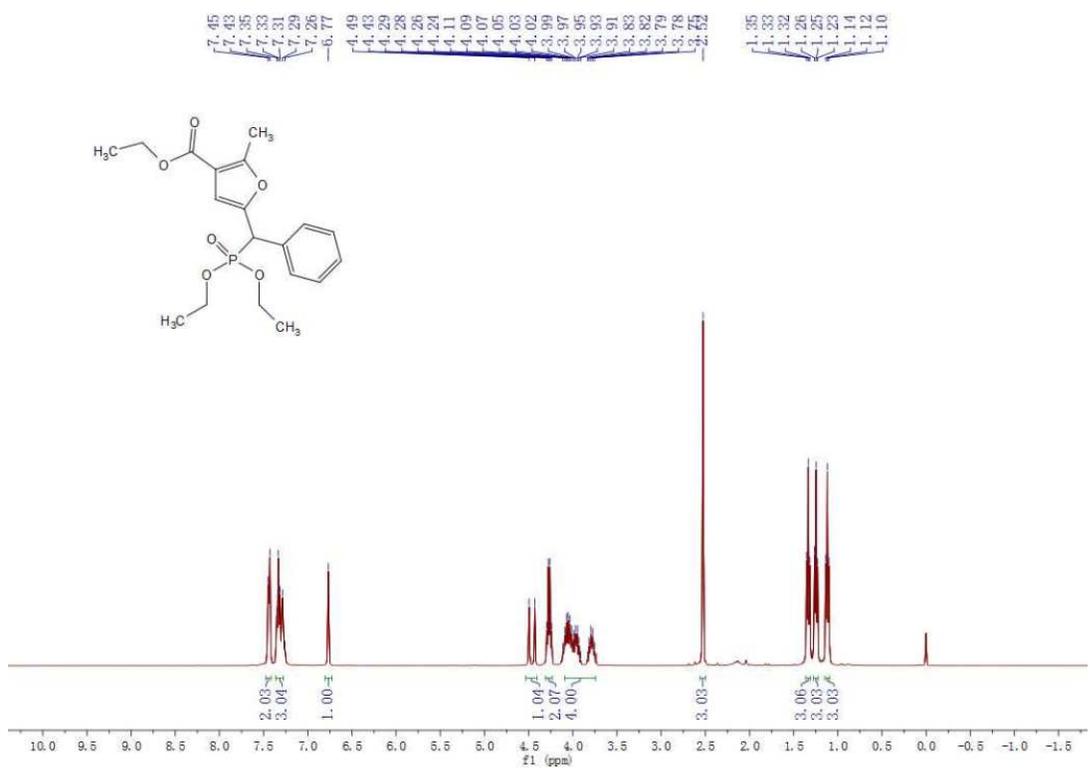


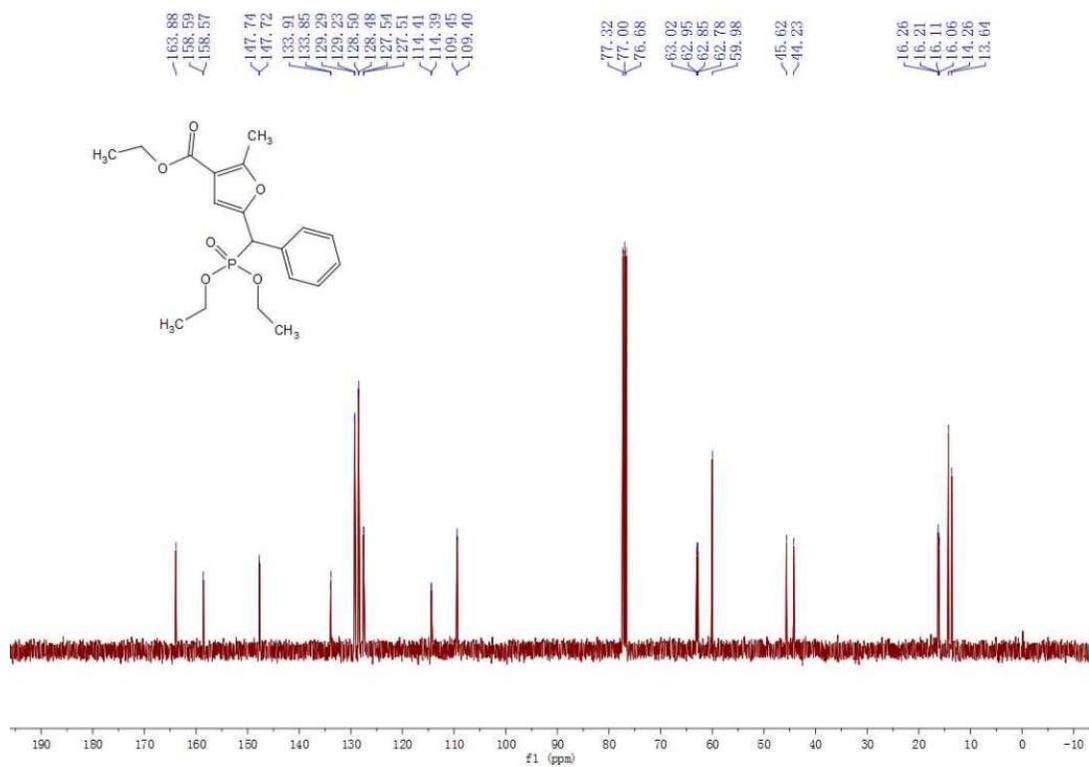
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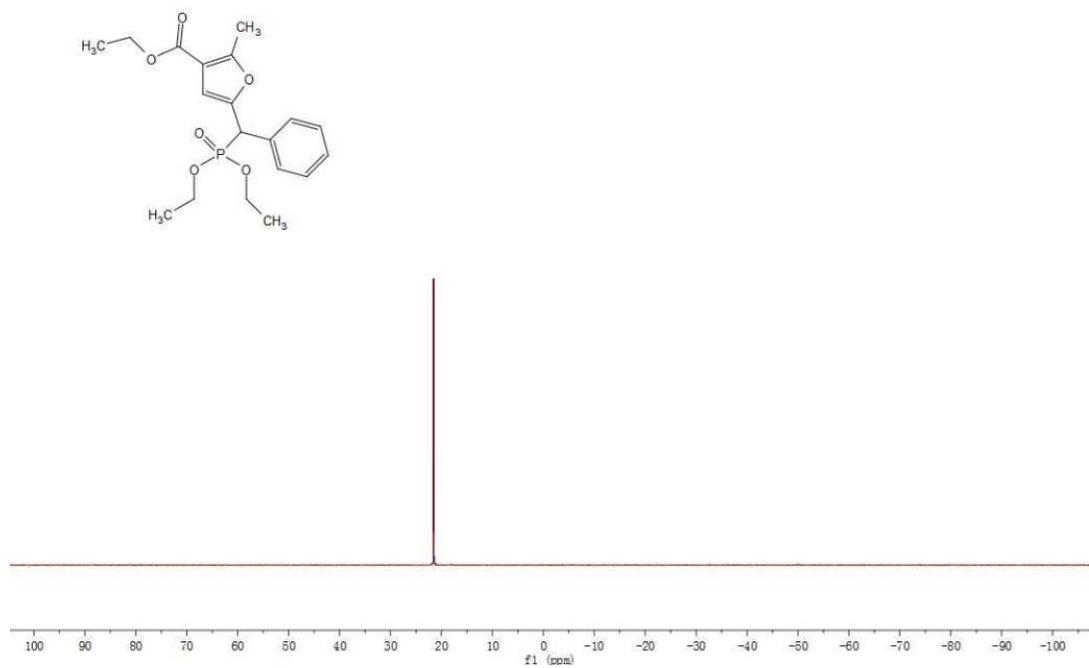


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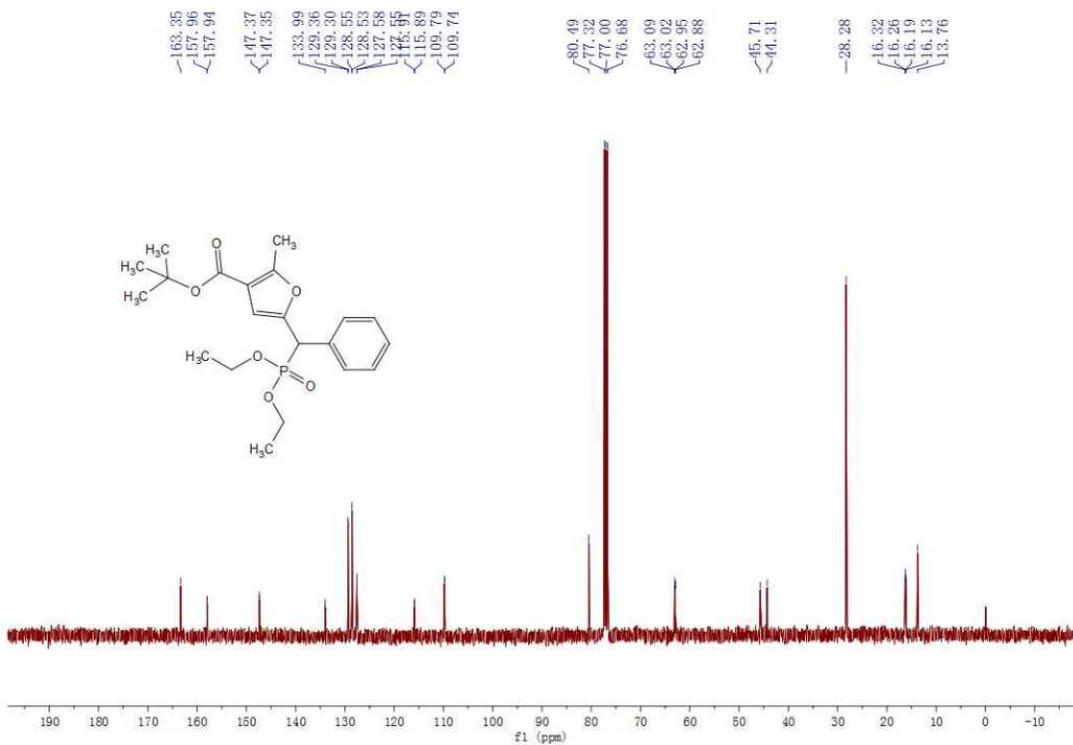
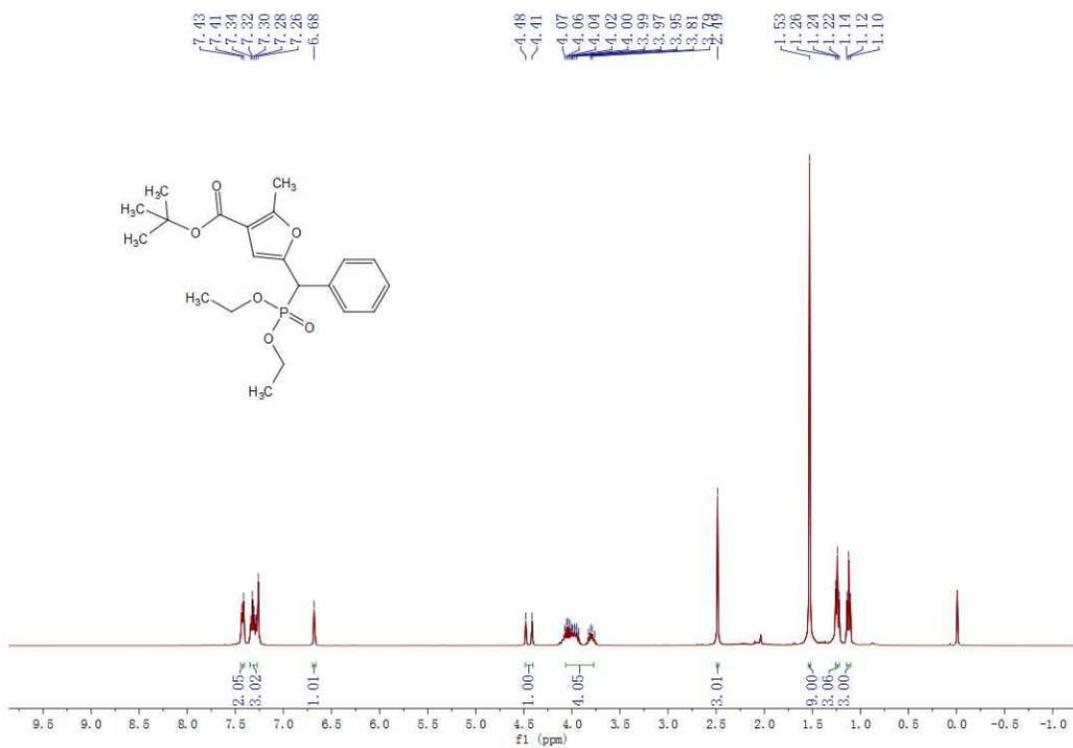


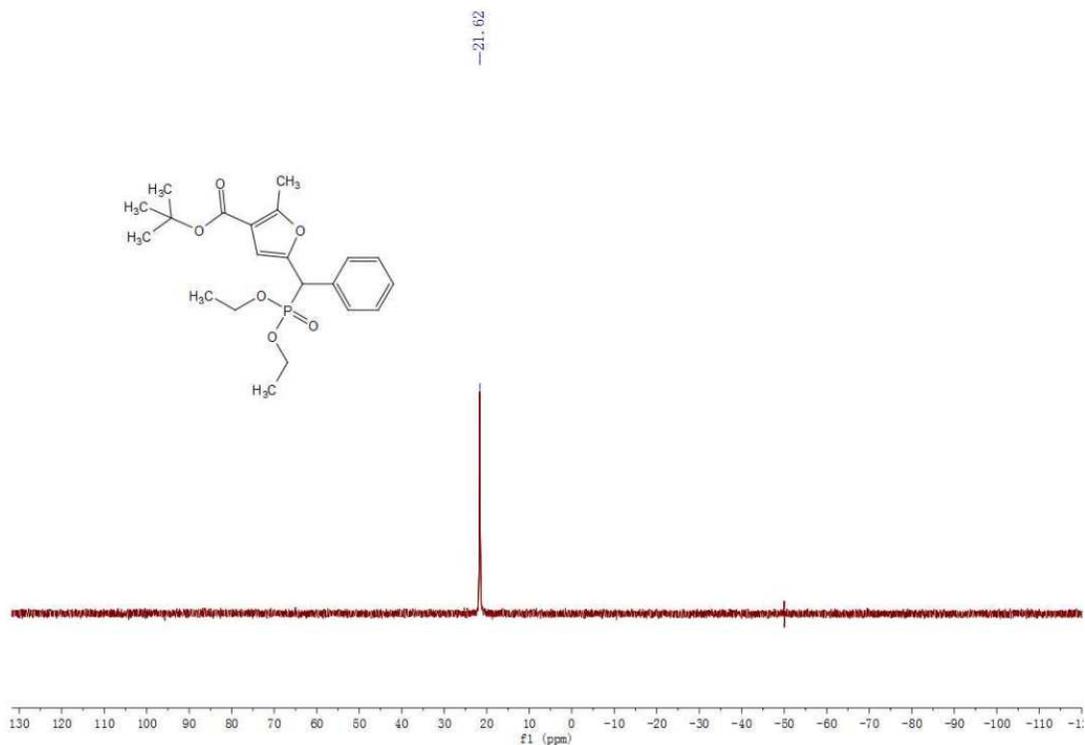


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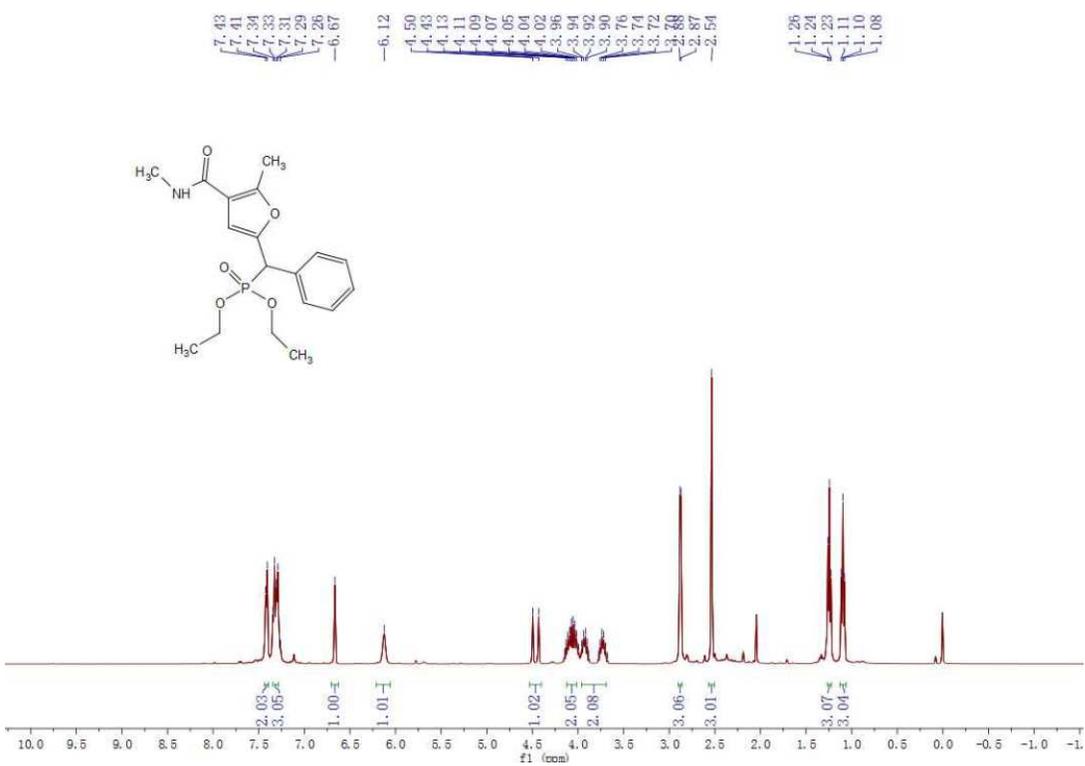


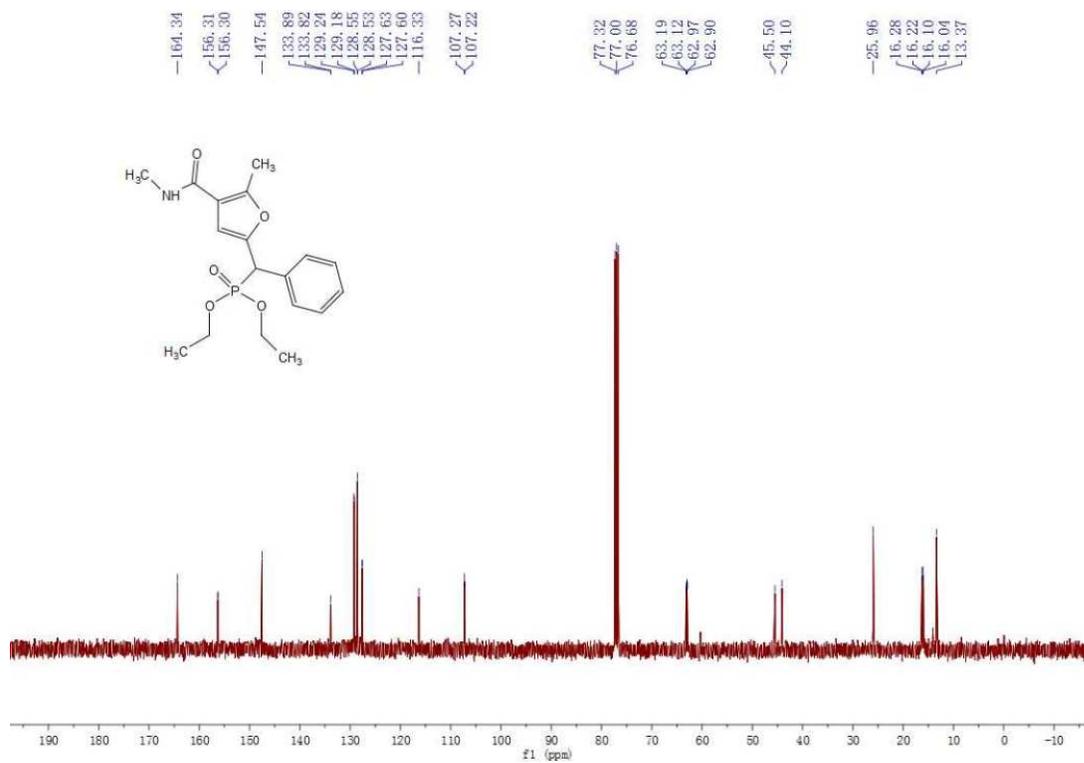
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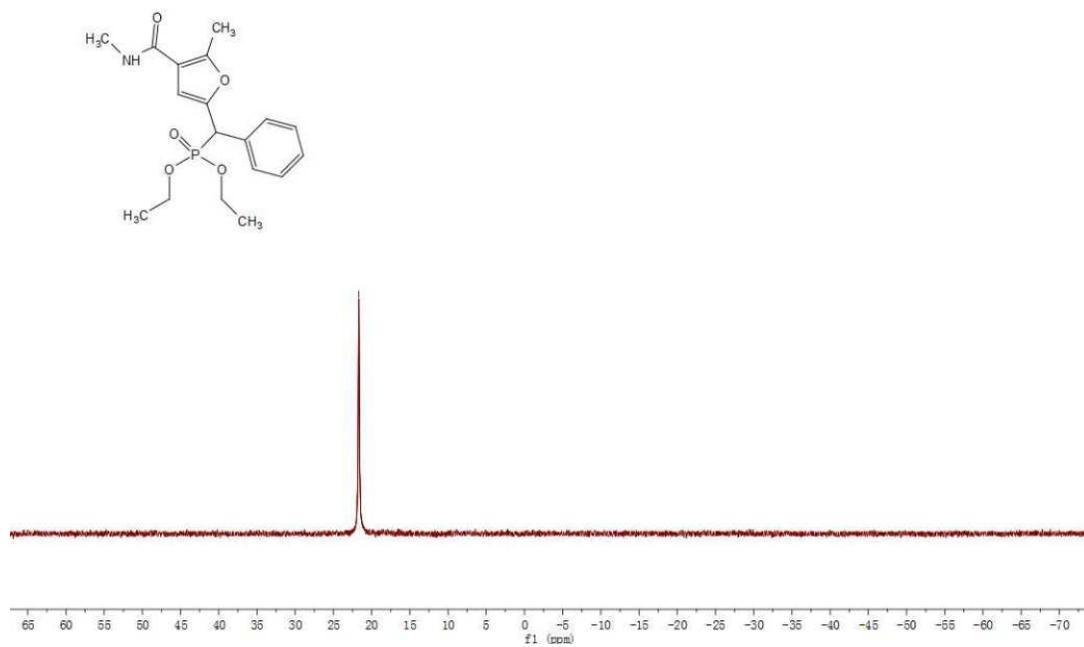


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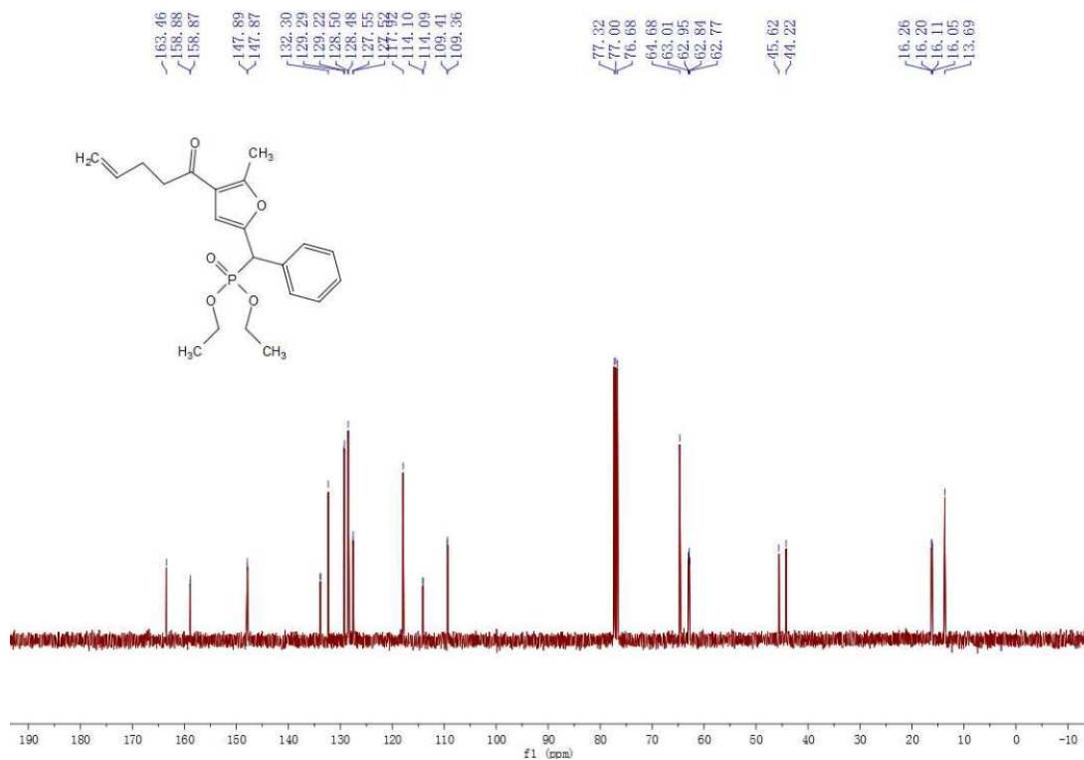
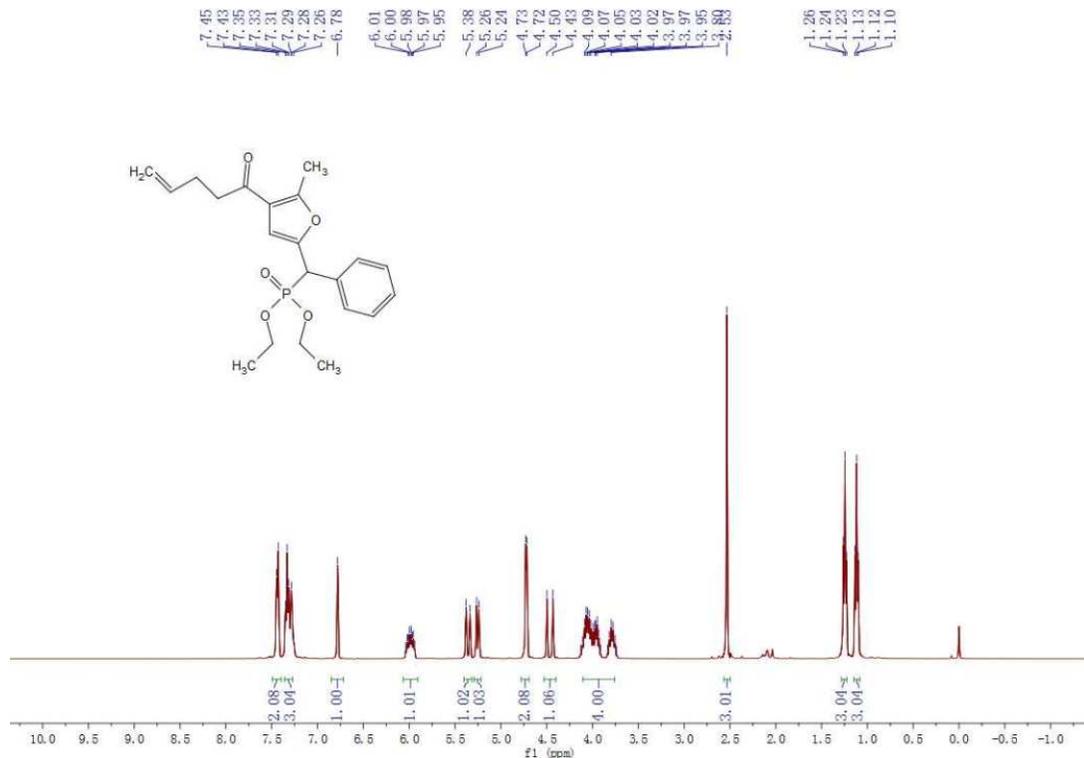




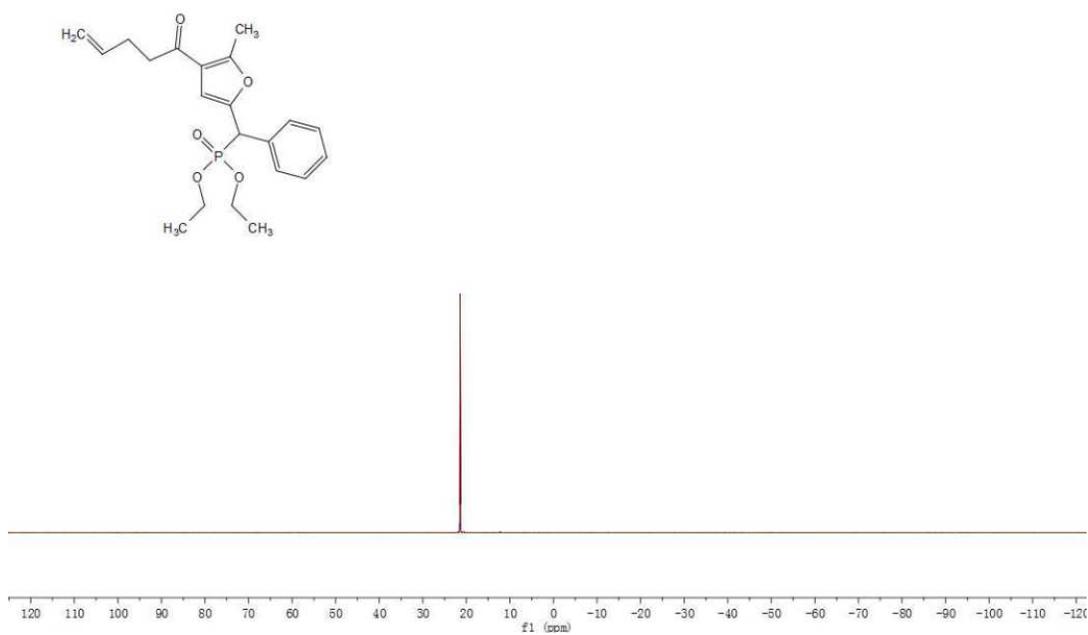
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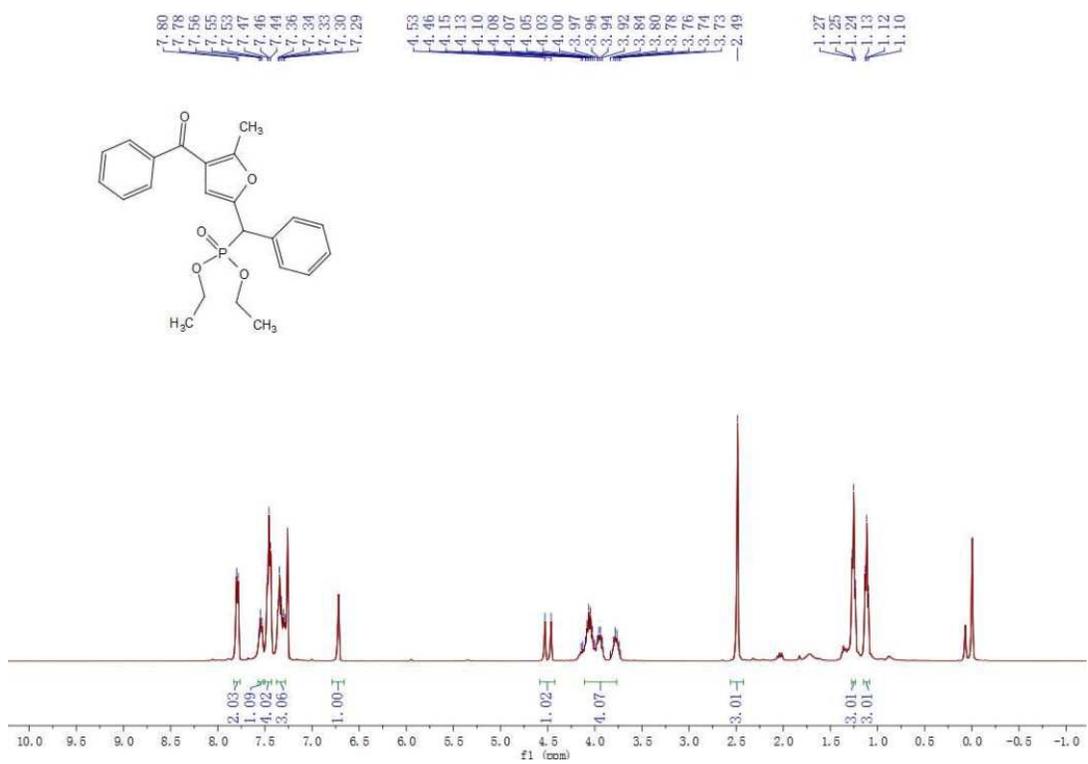
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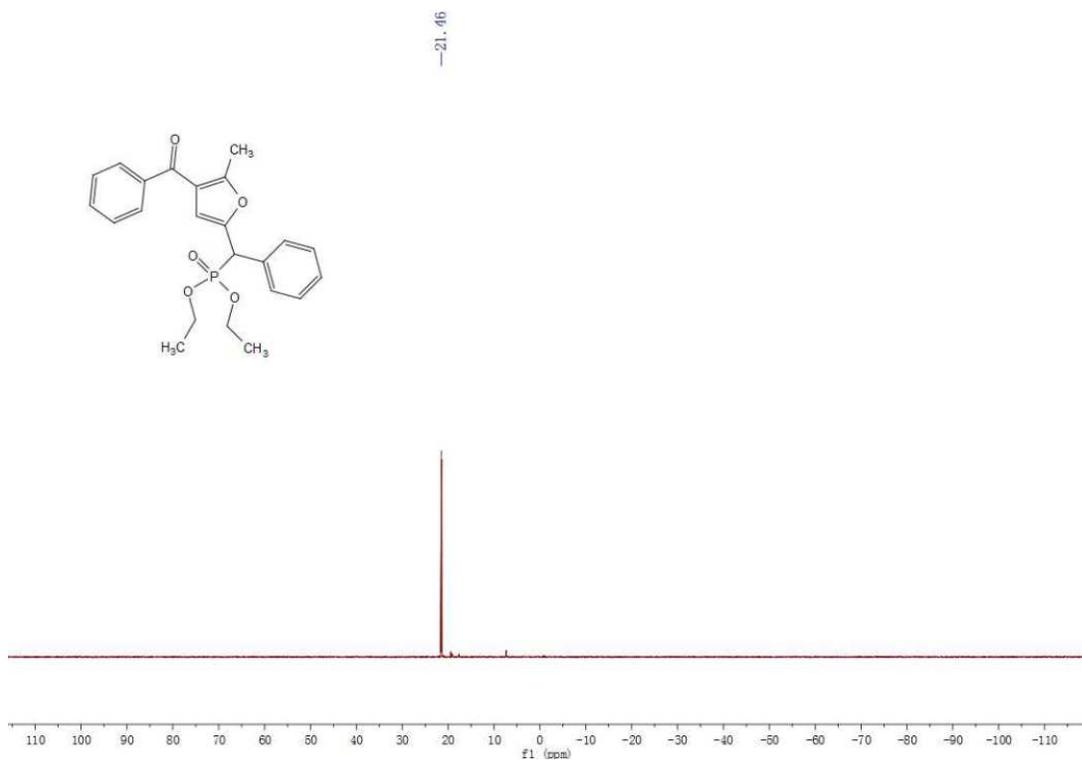
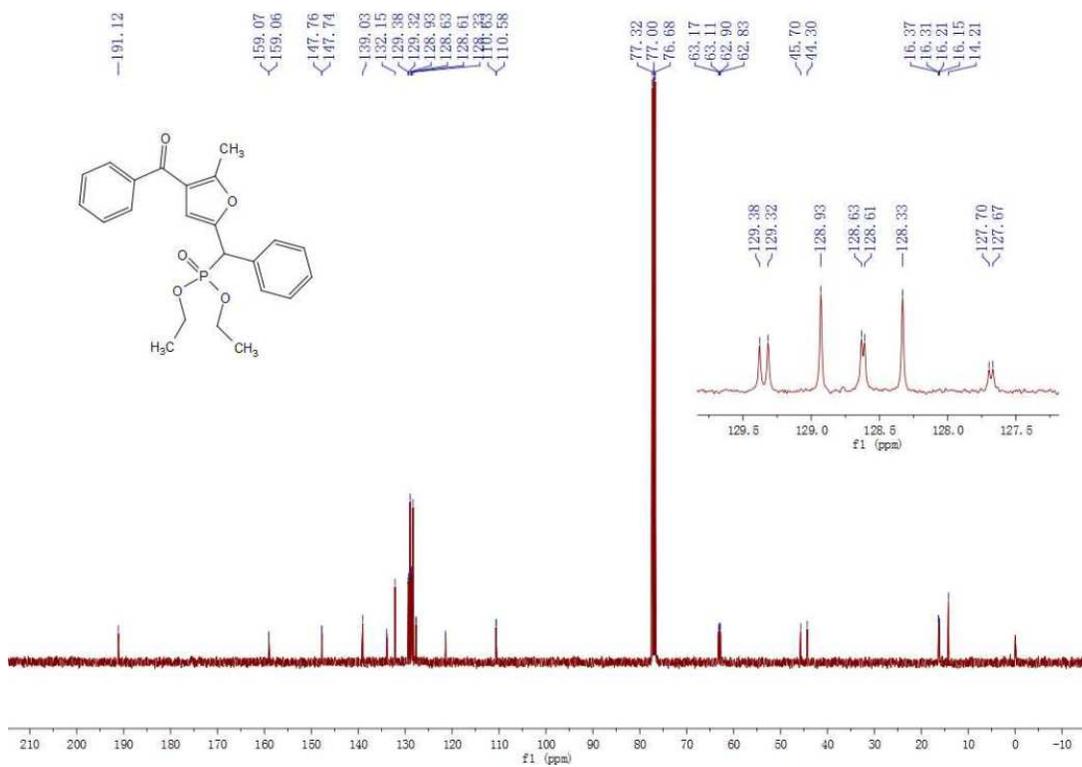


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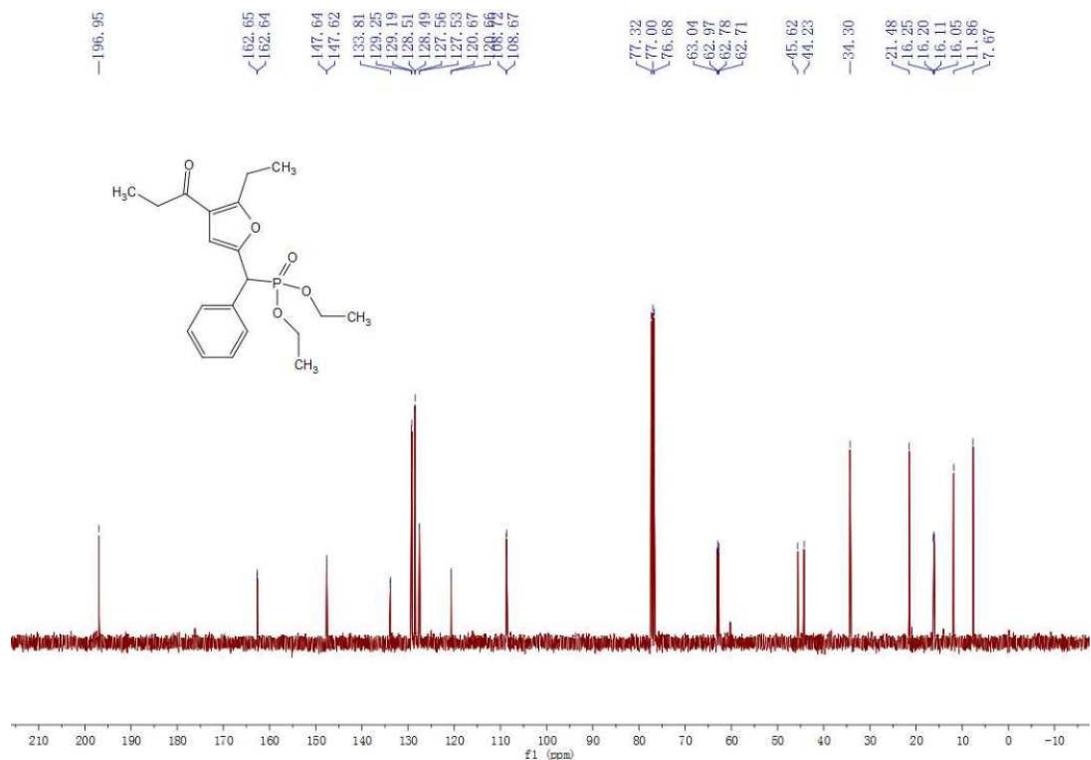
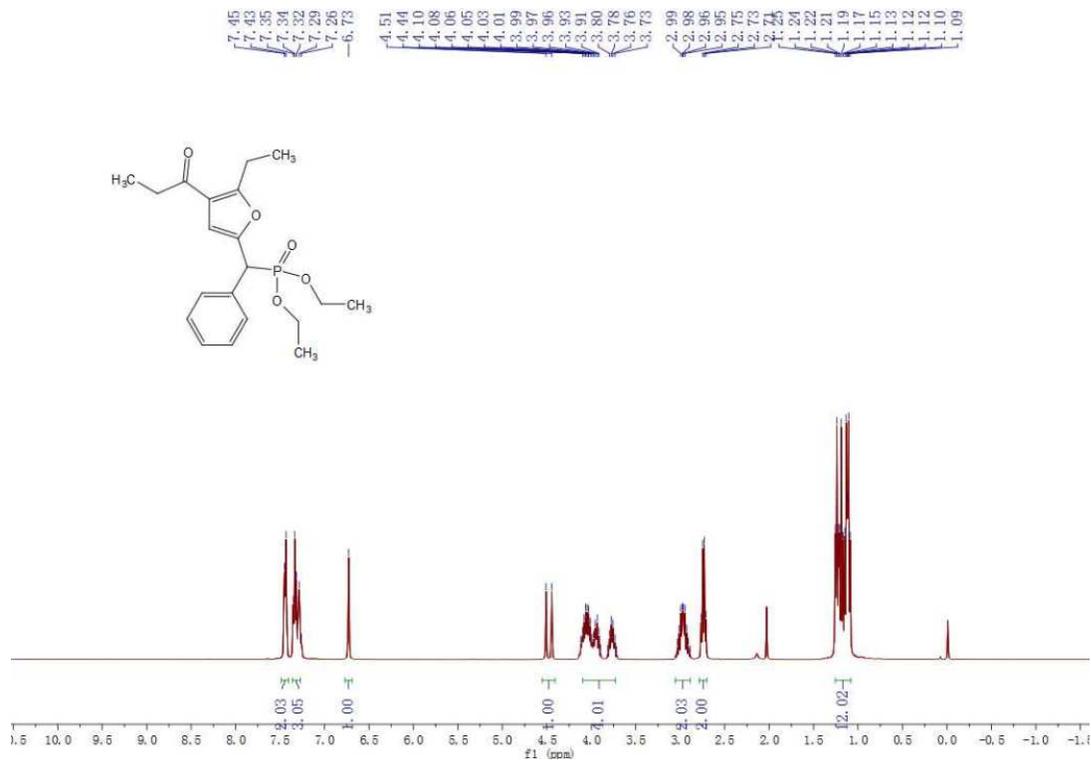


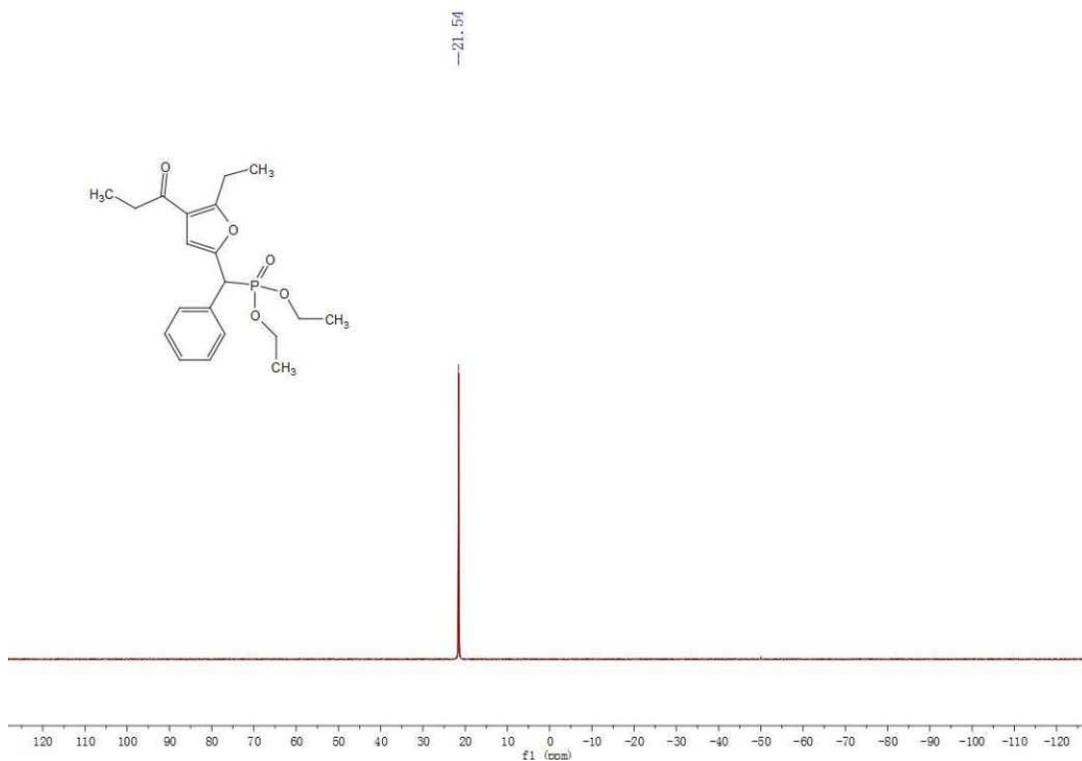
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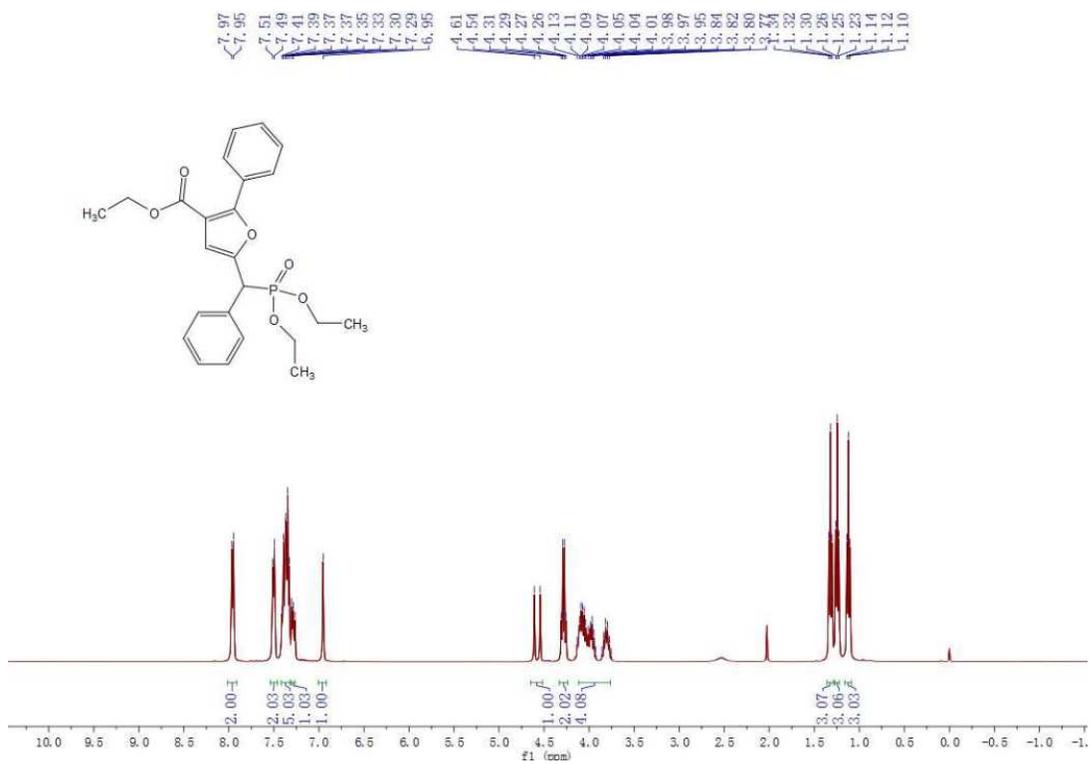


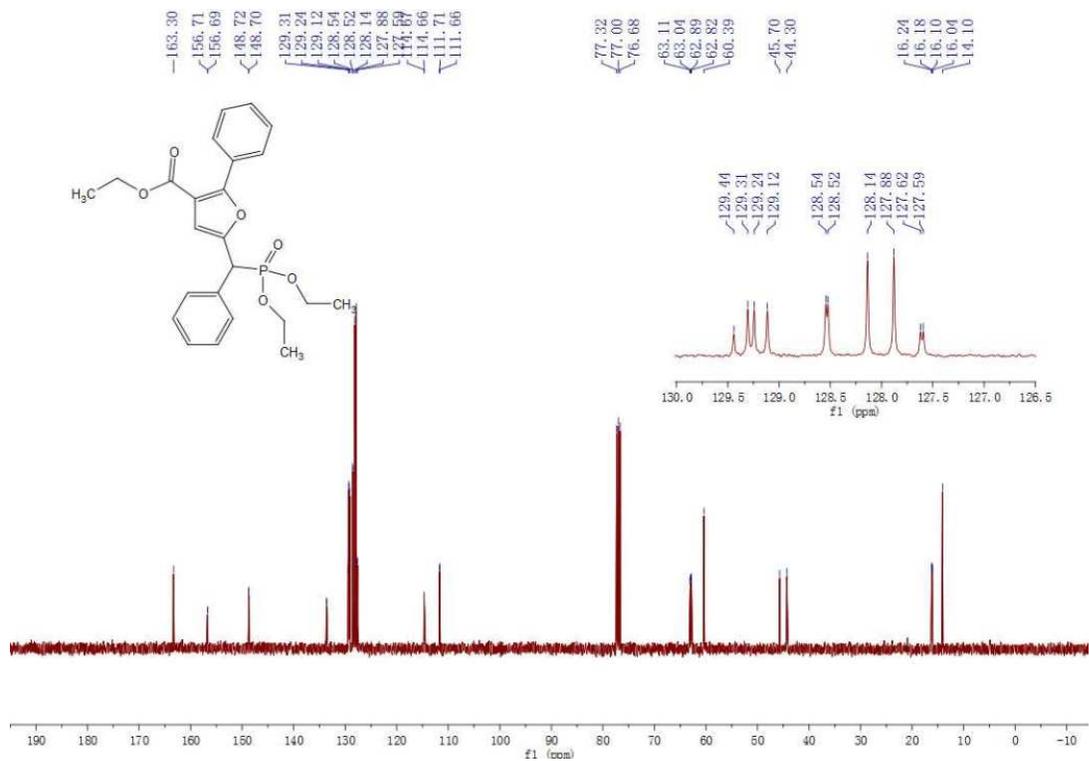
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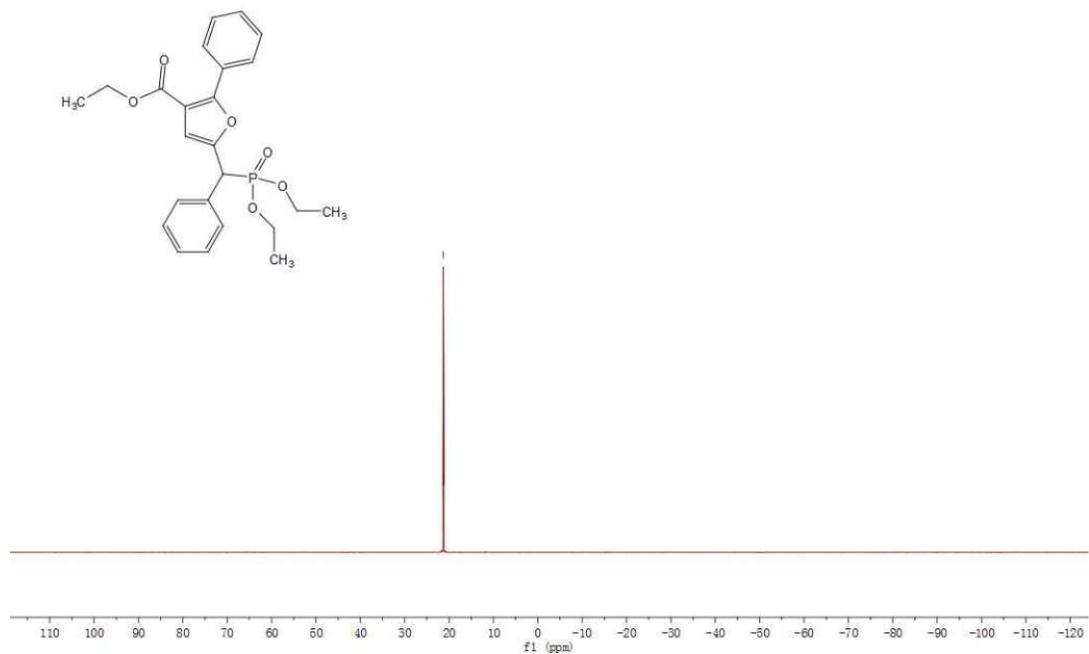


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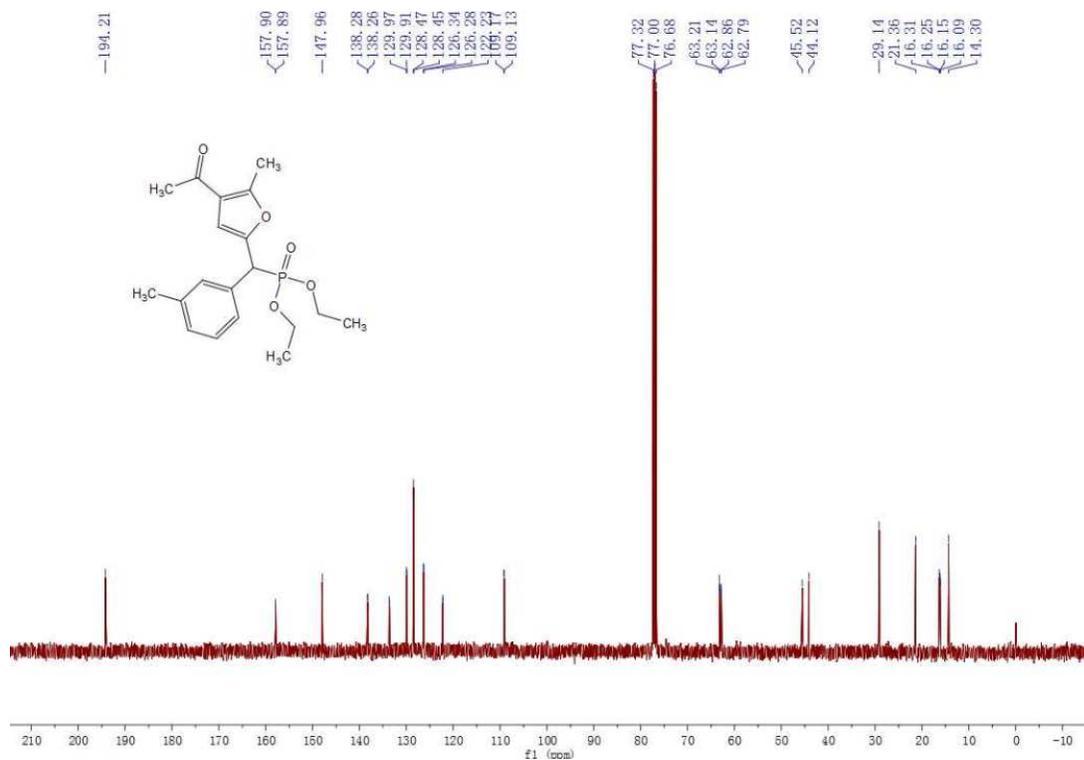
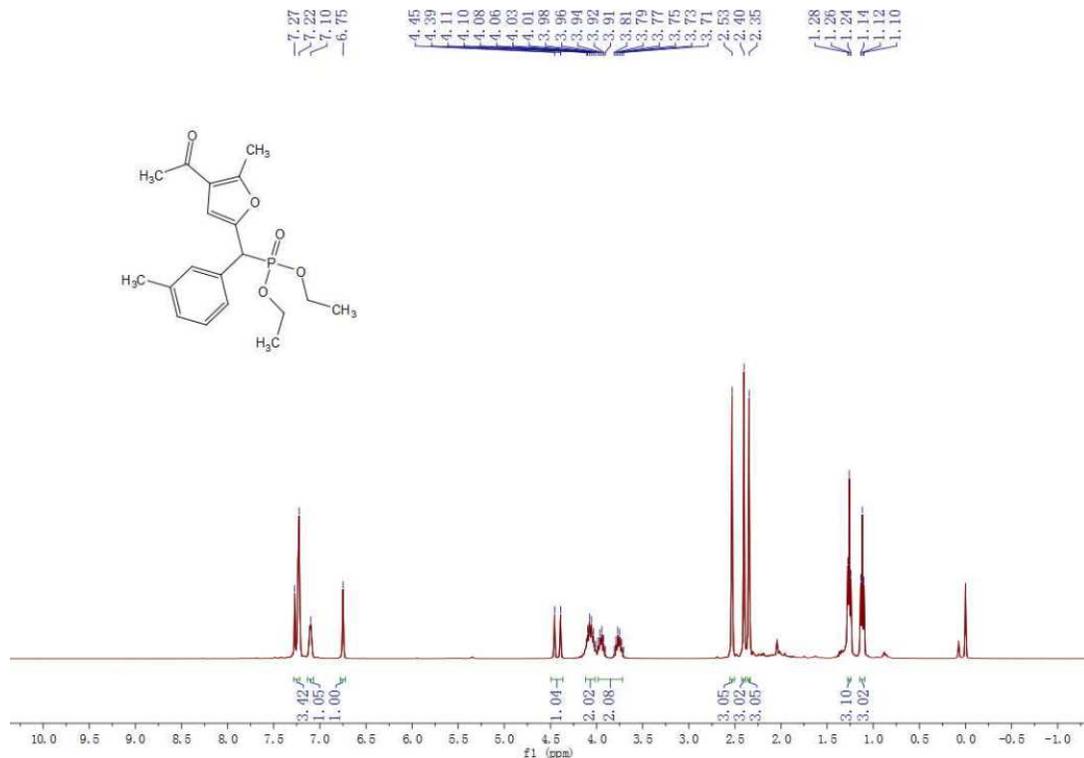


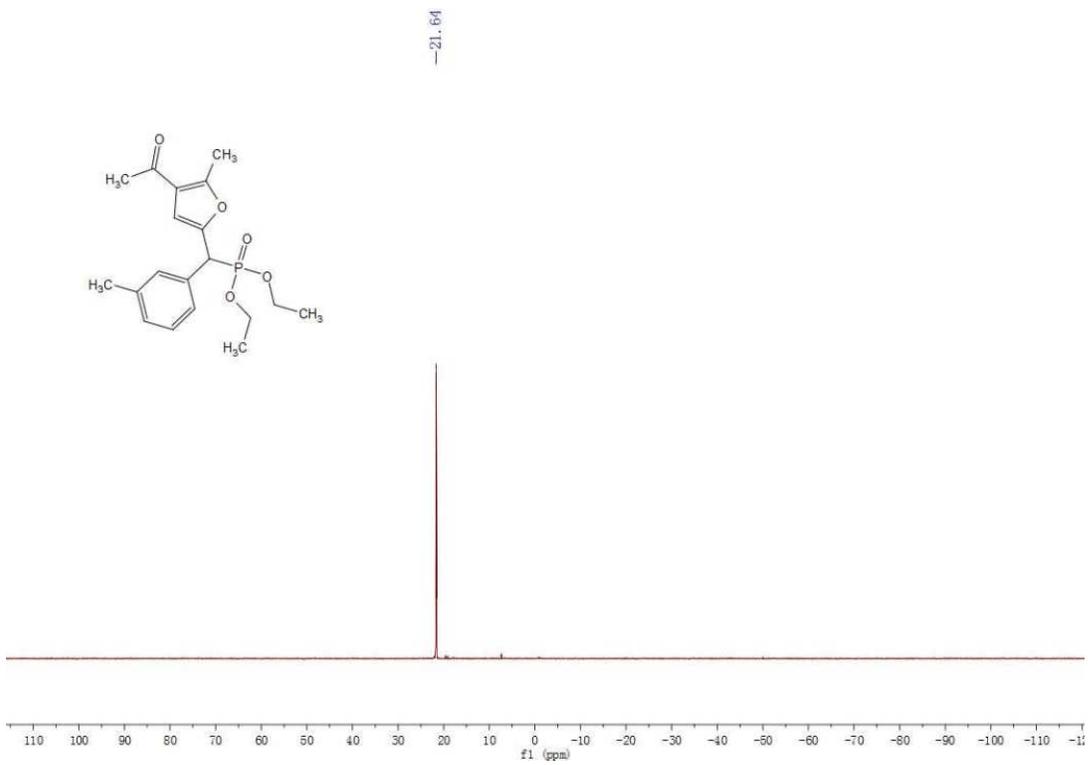


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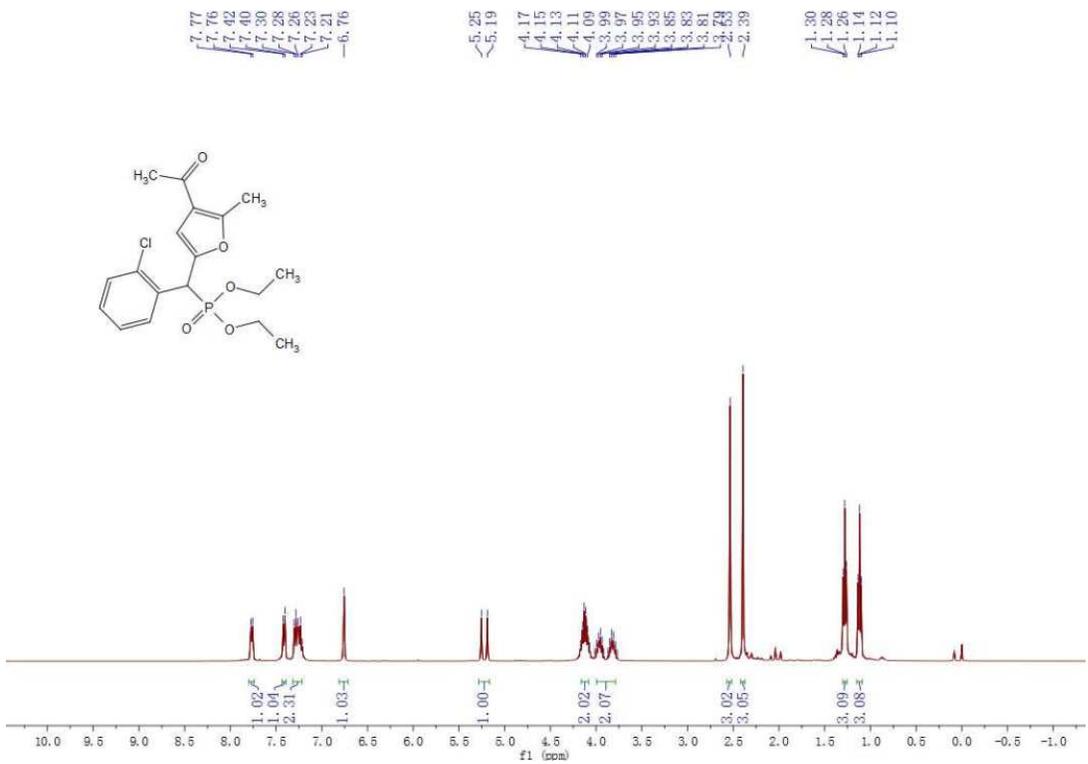


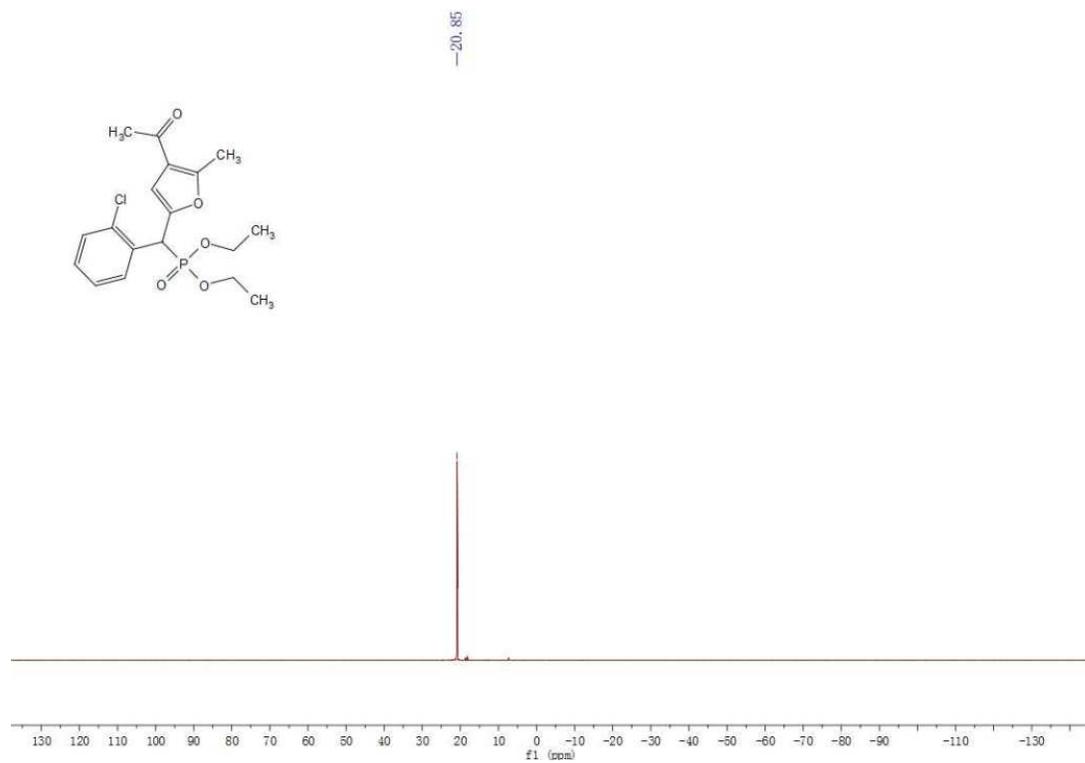
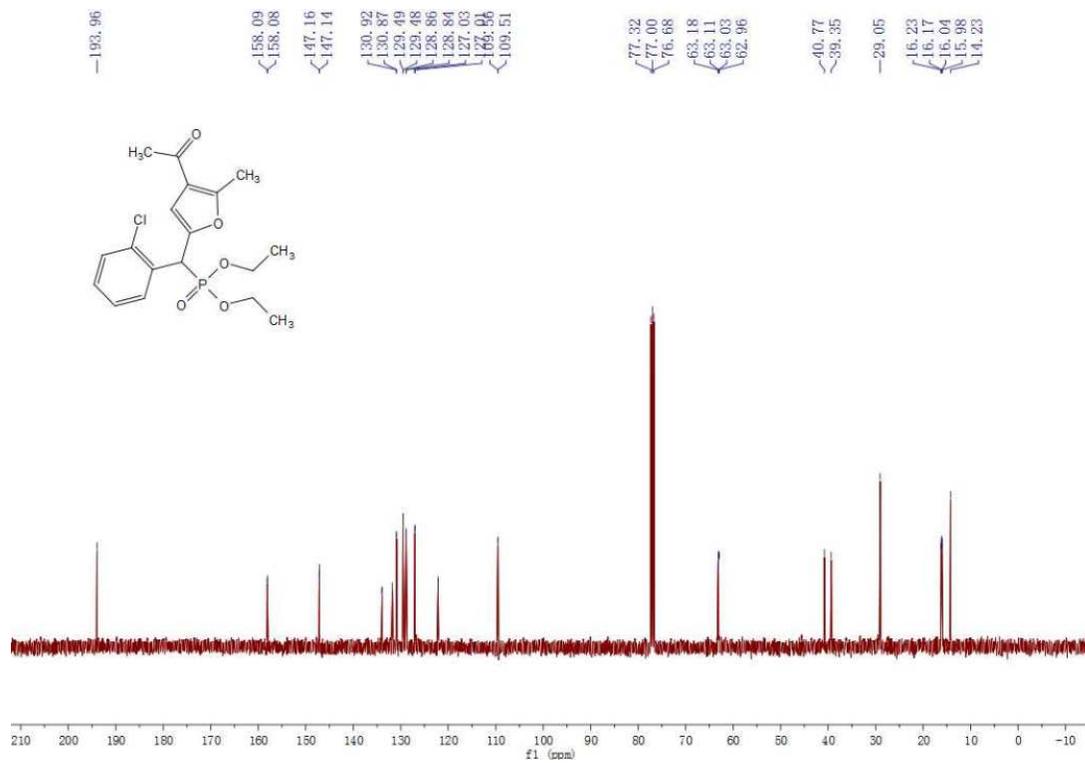
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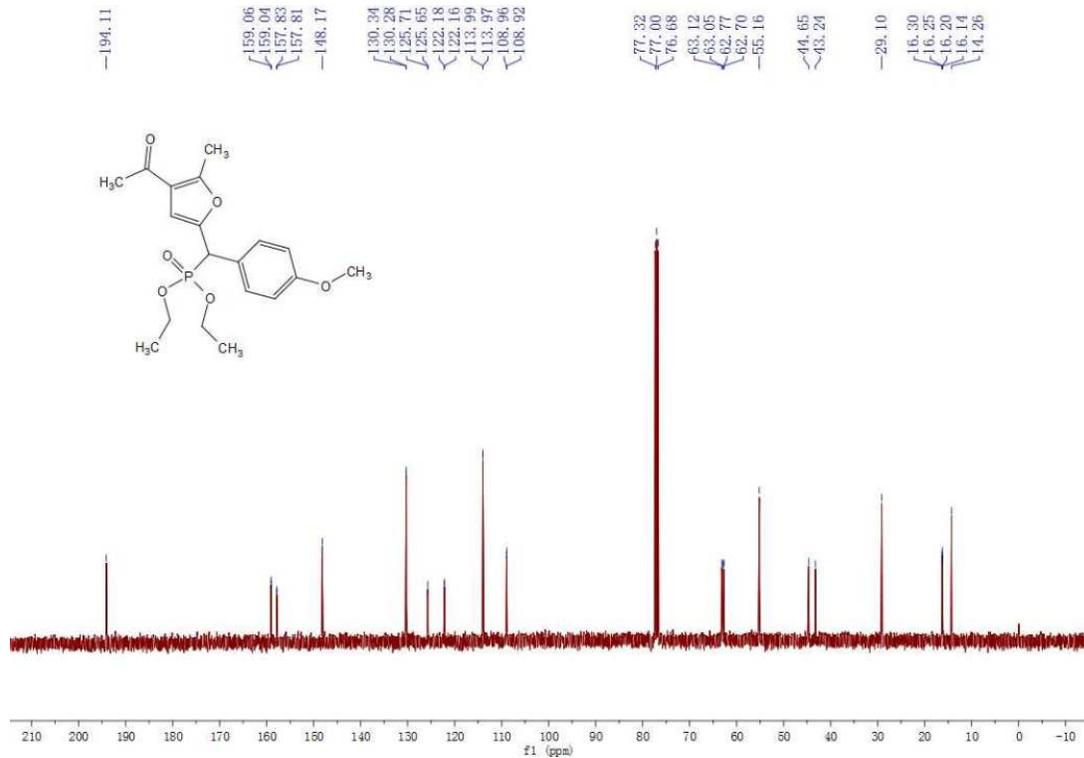
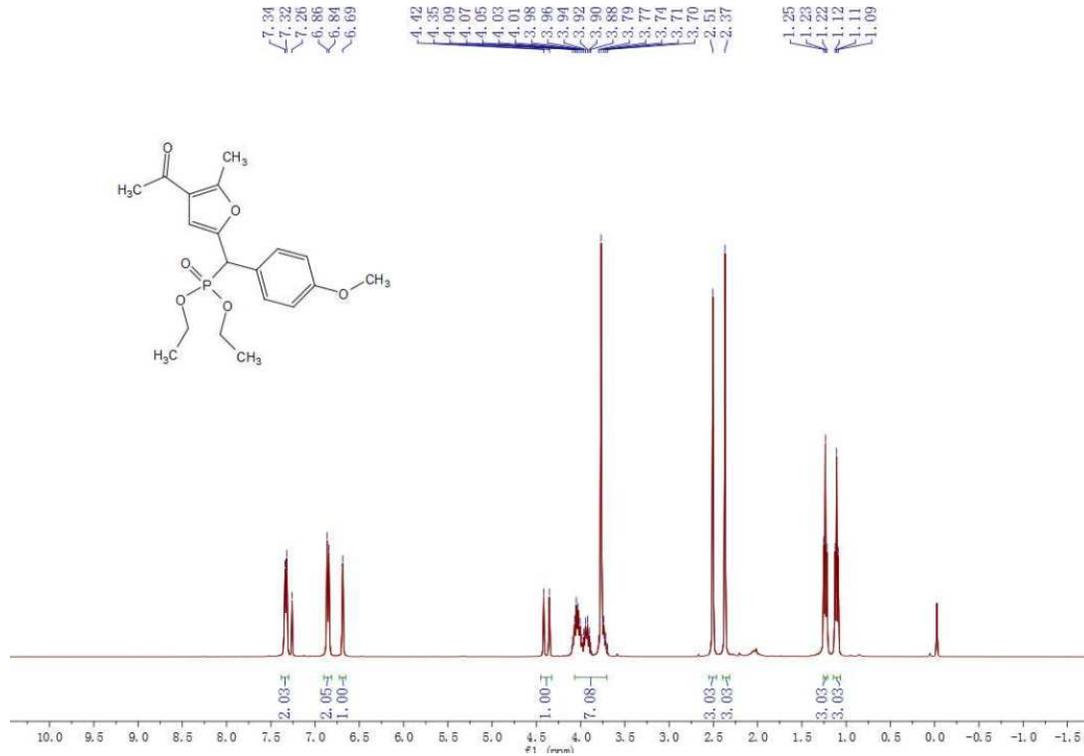


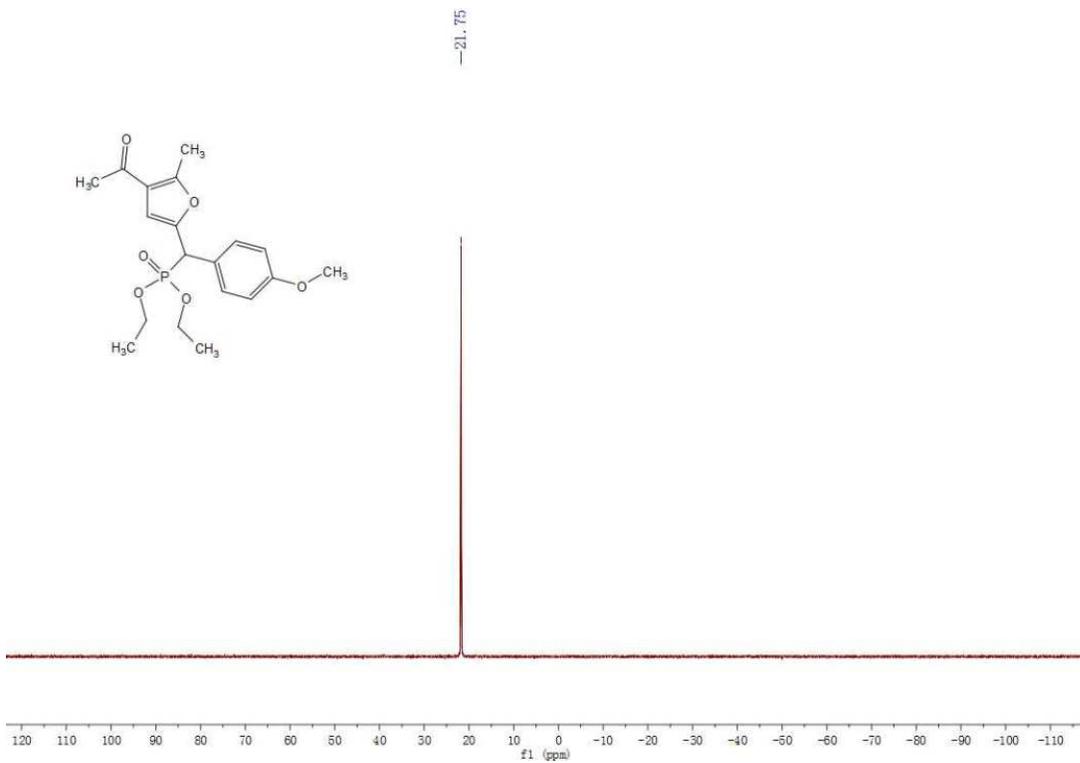
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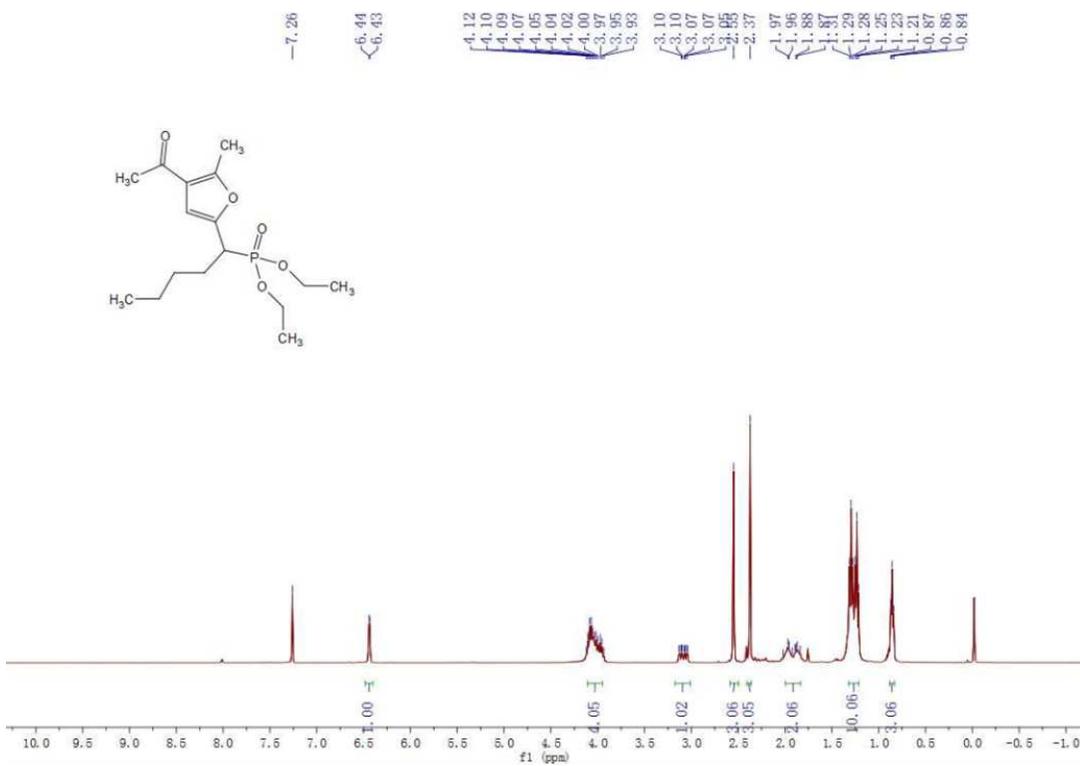


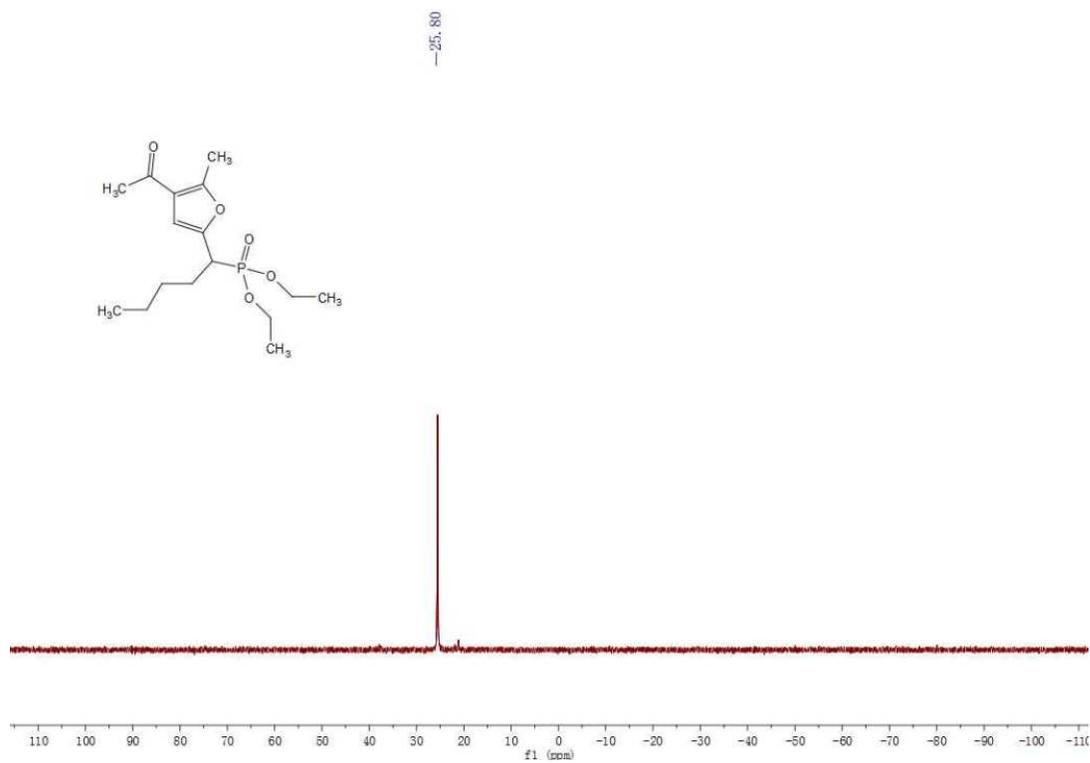
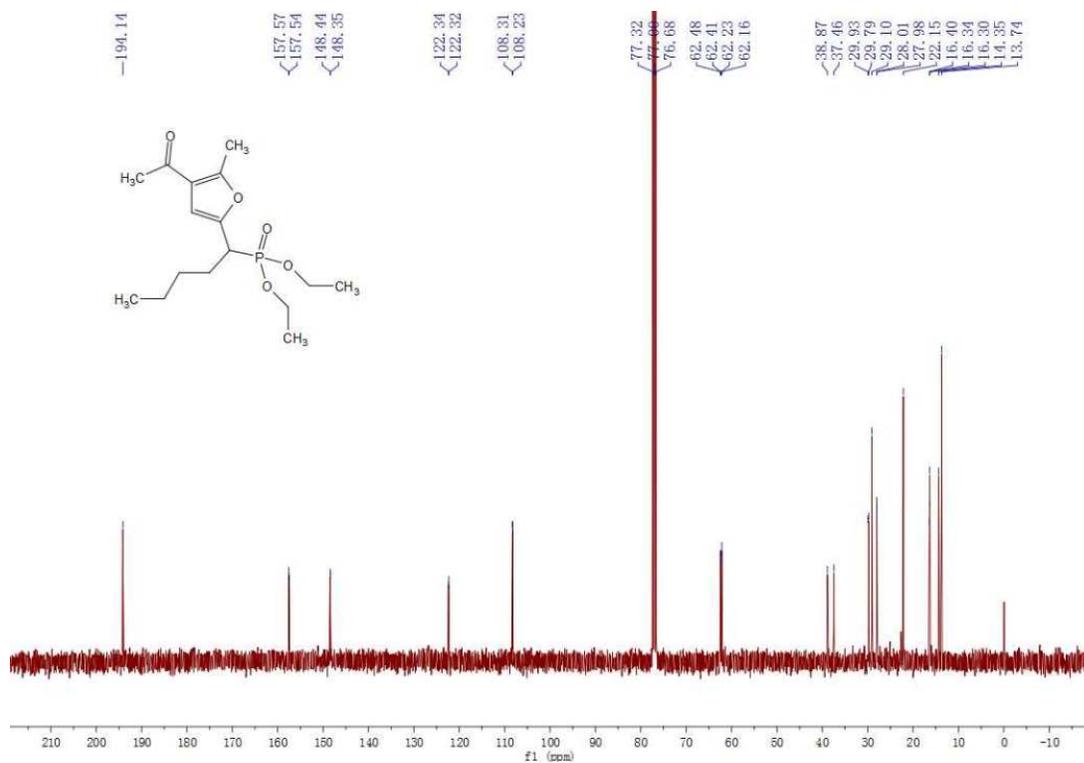
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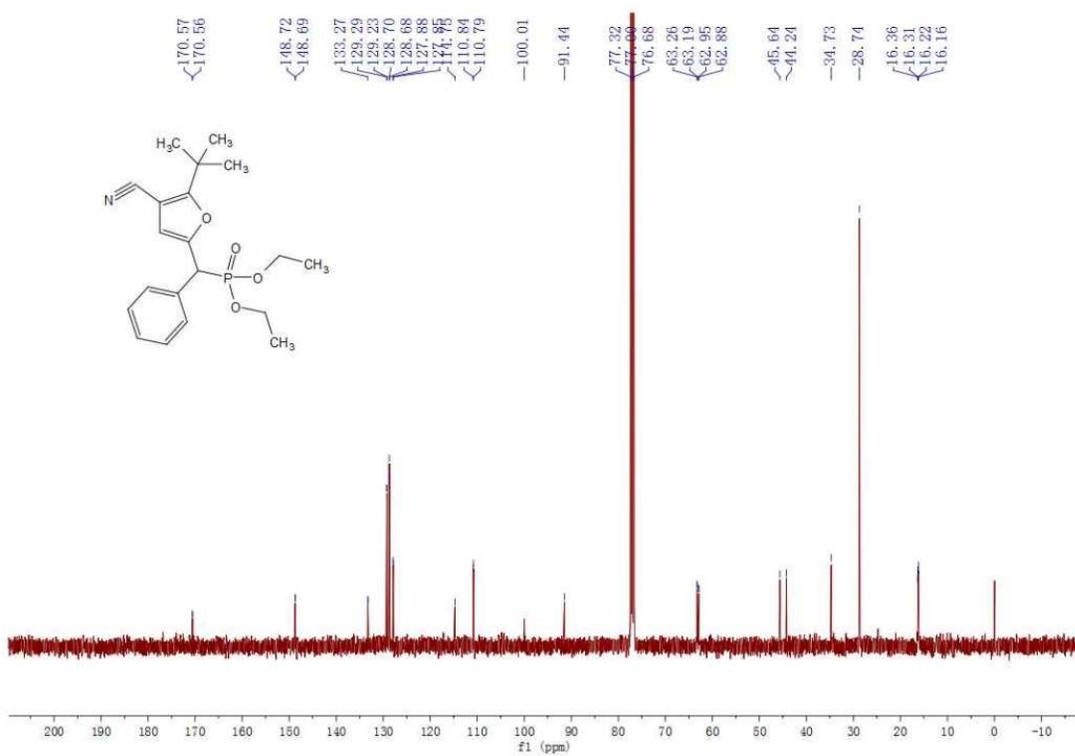
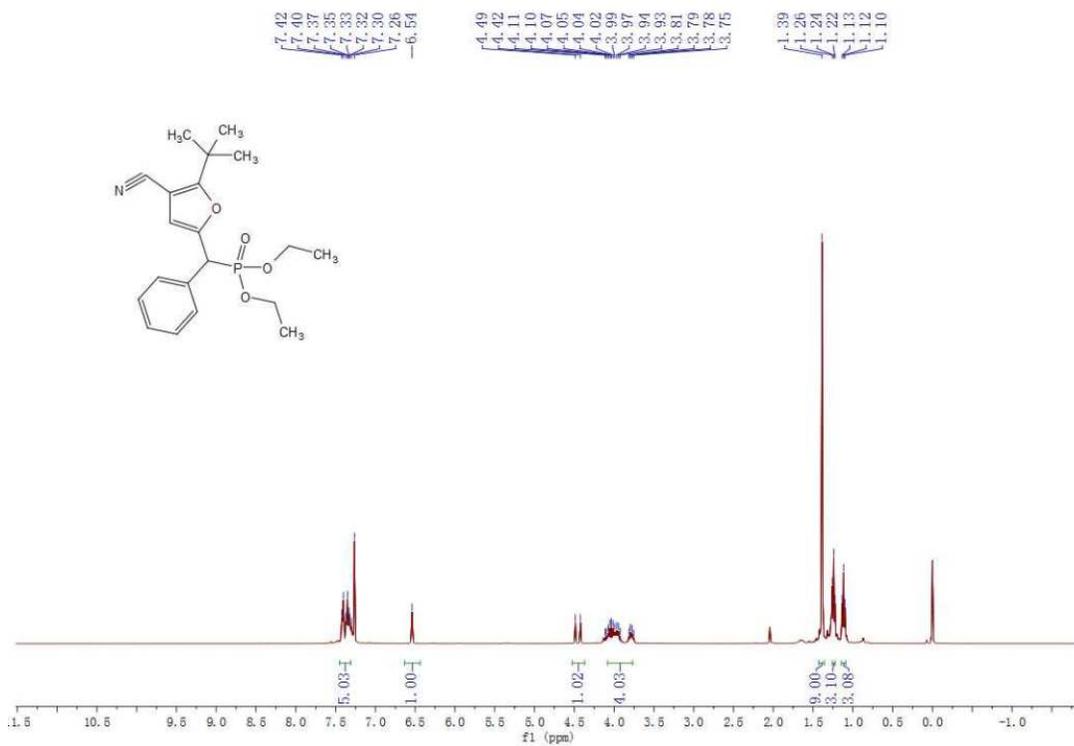


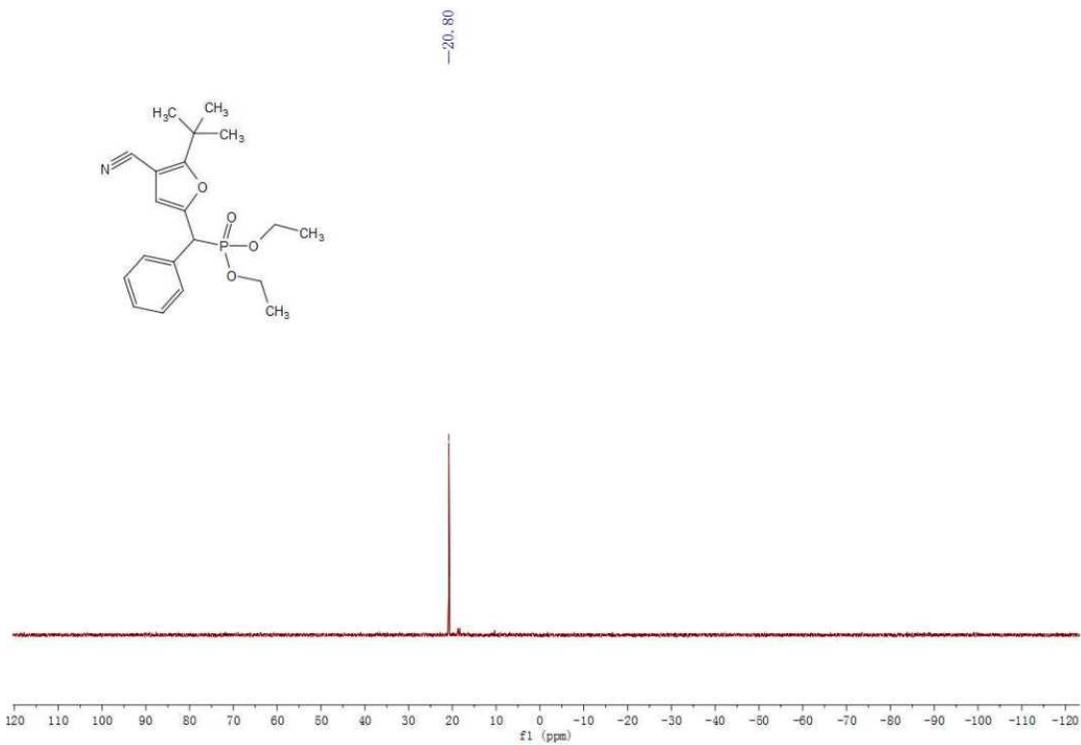
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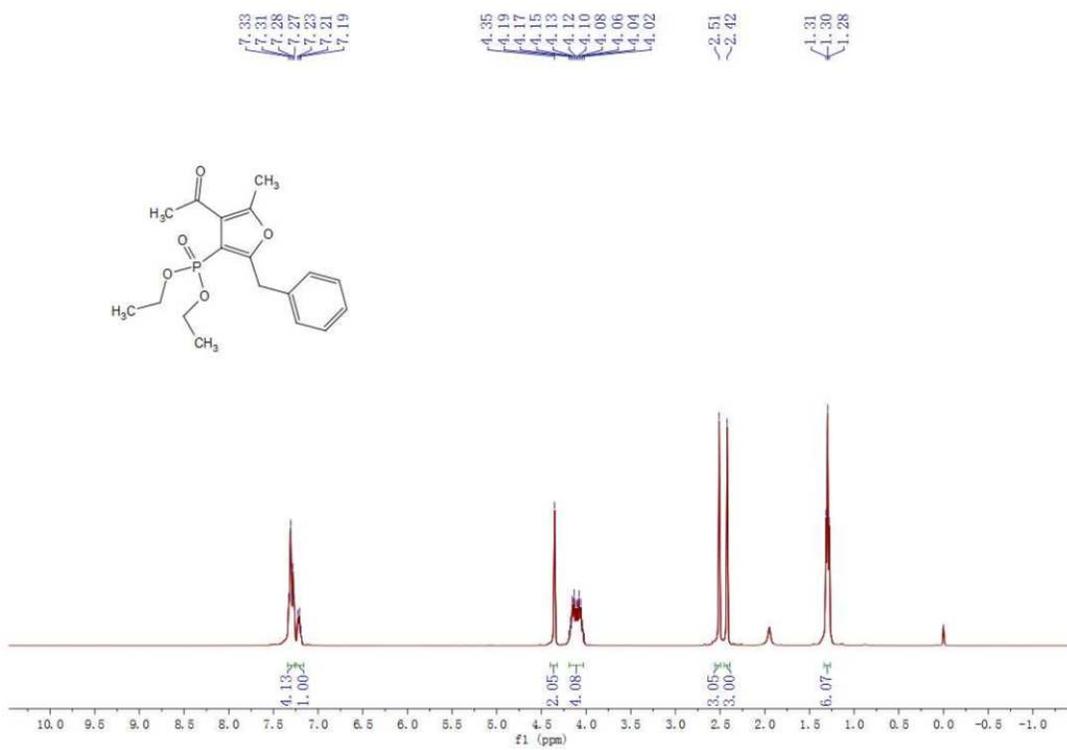


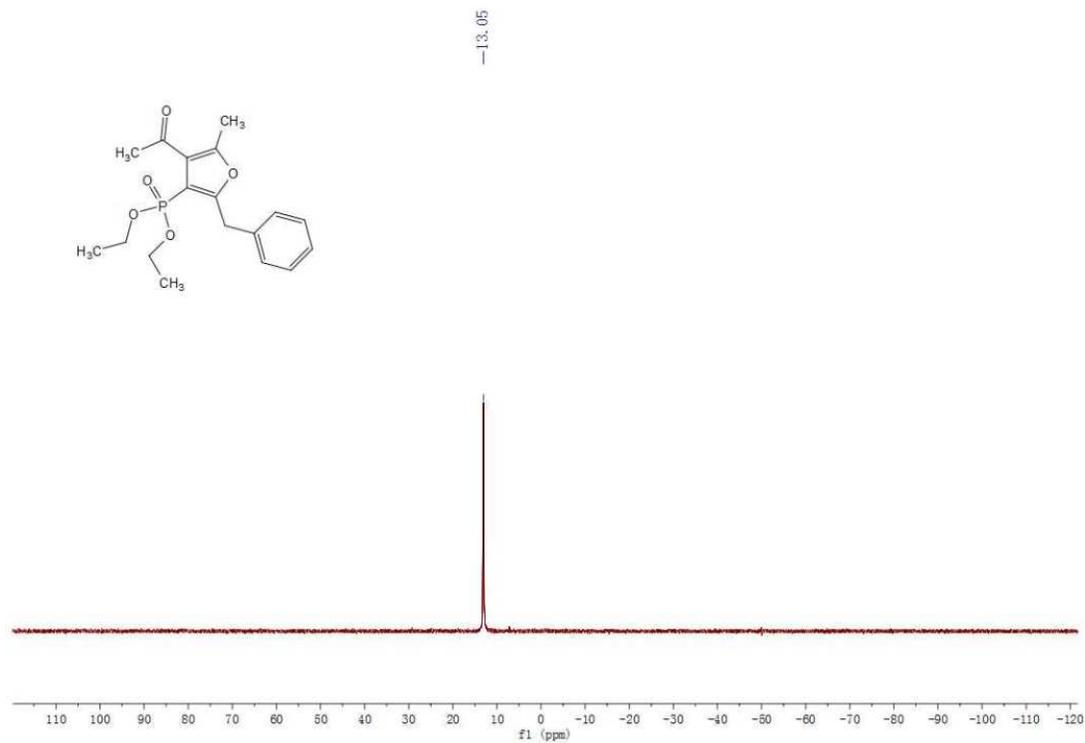
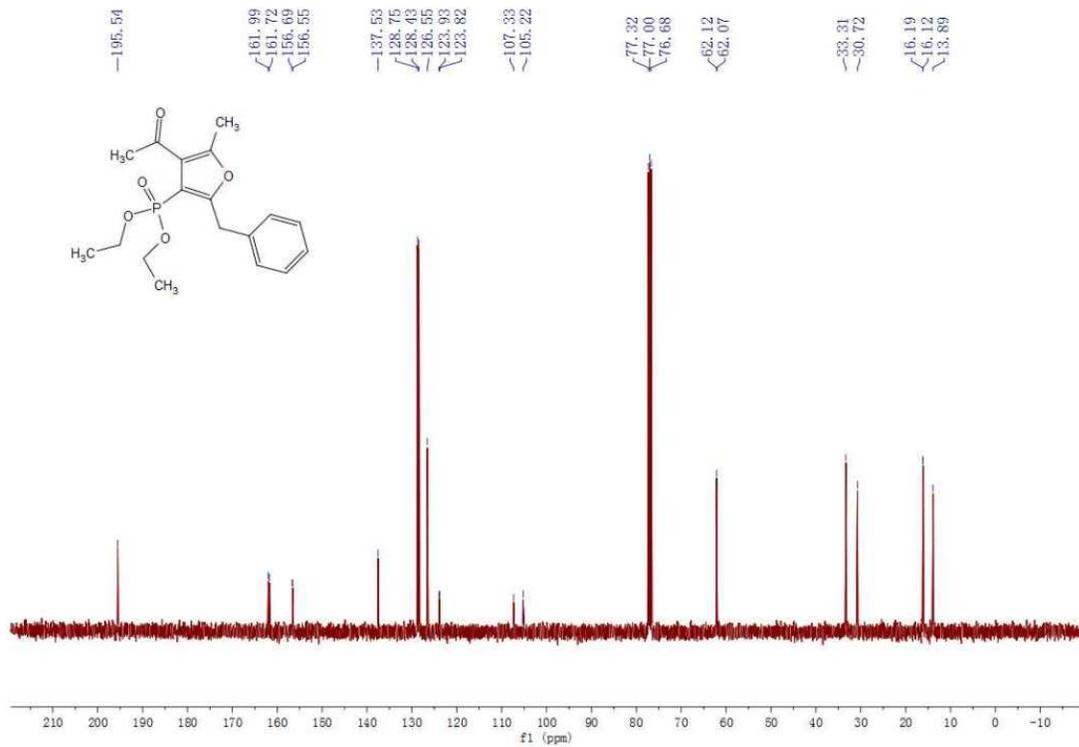
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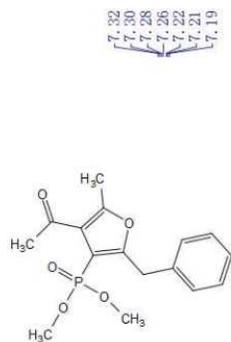


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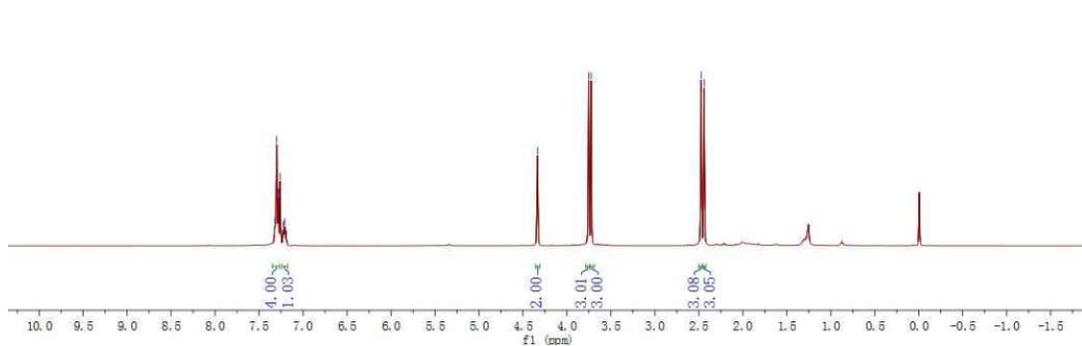


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2.44



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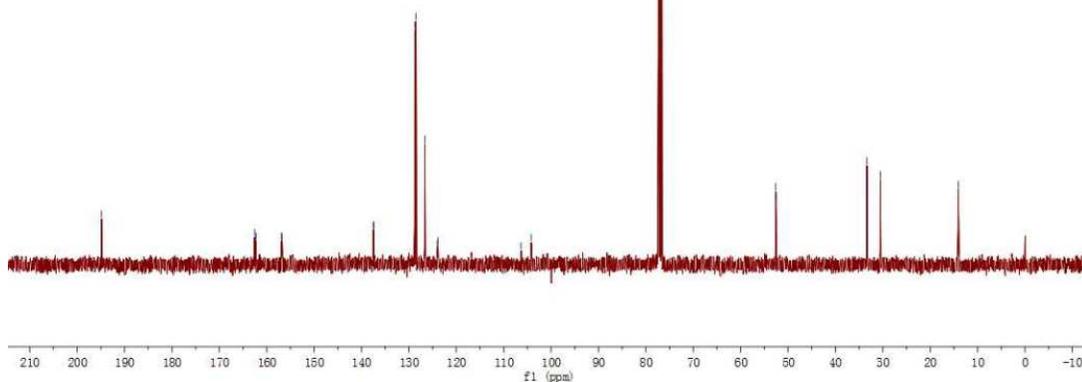
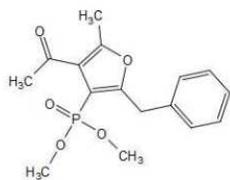
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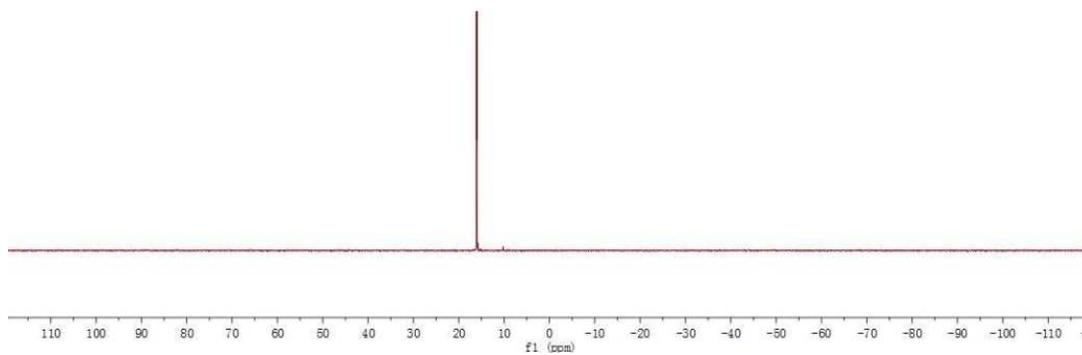
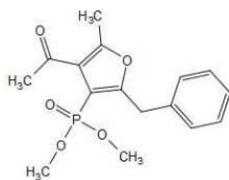
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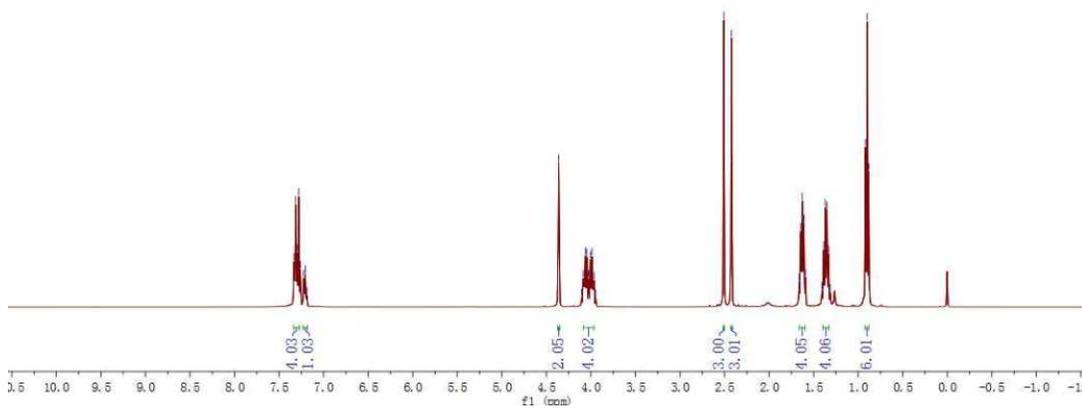
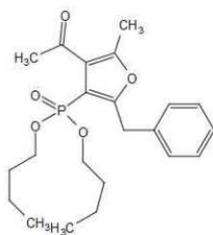


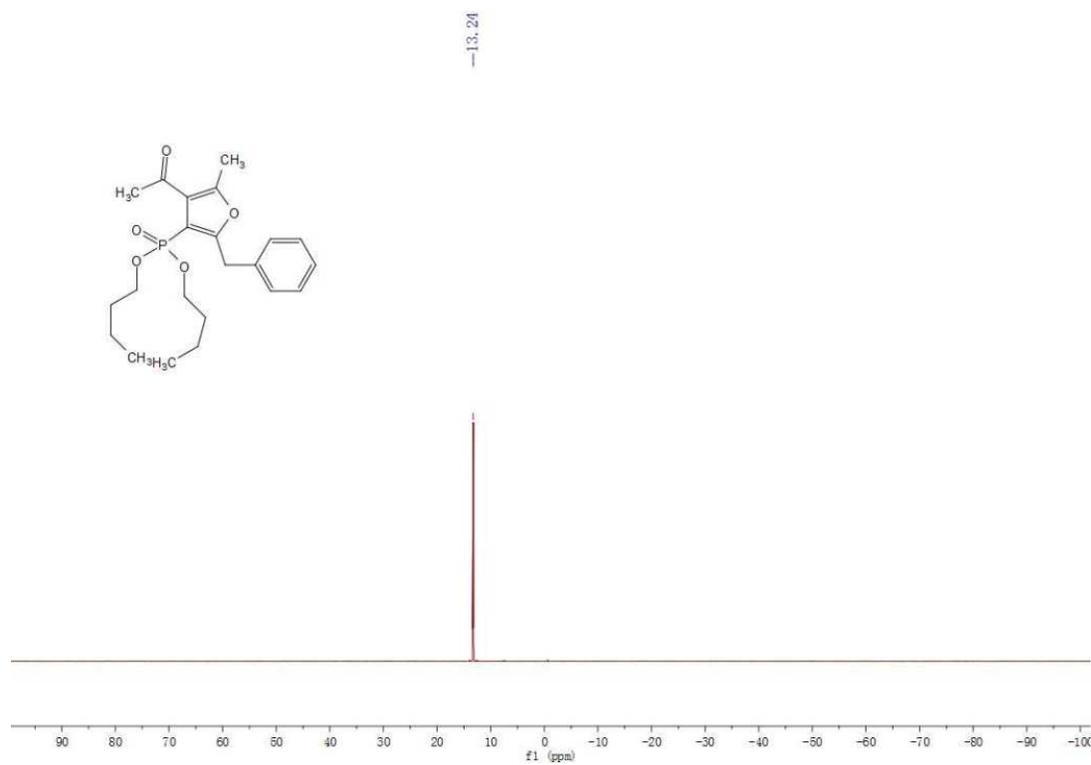
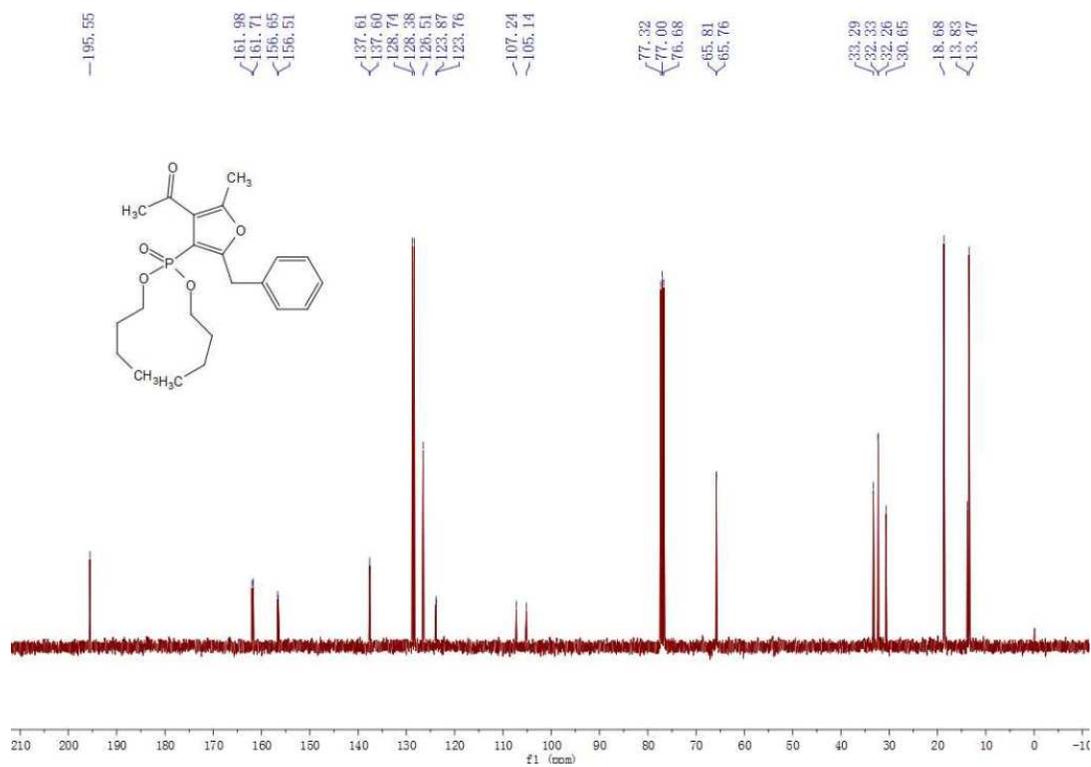
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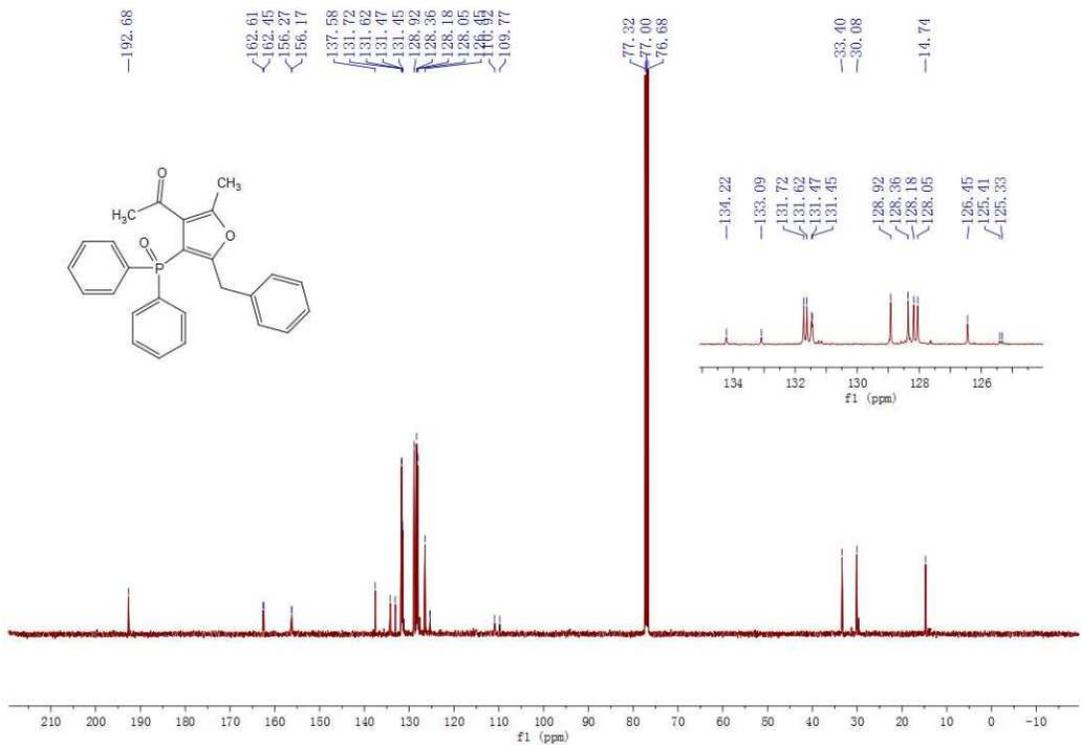
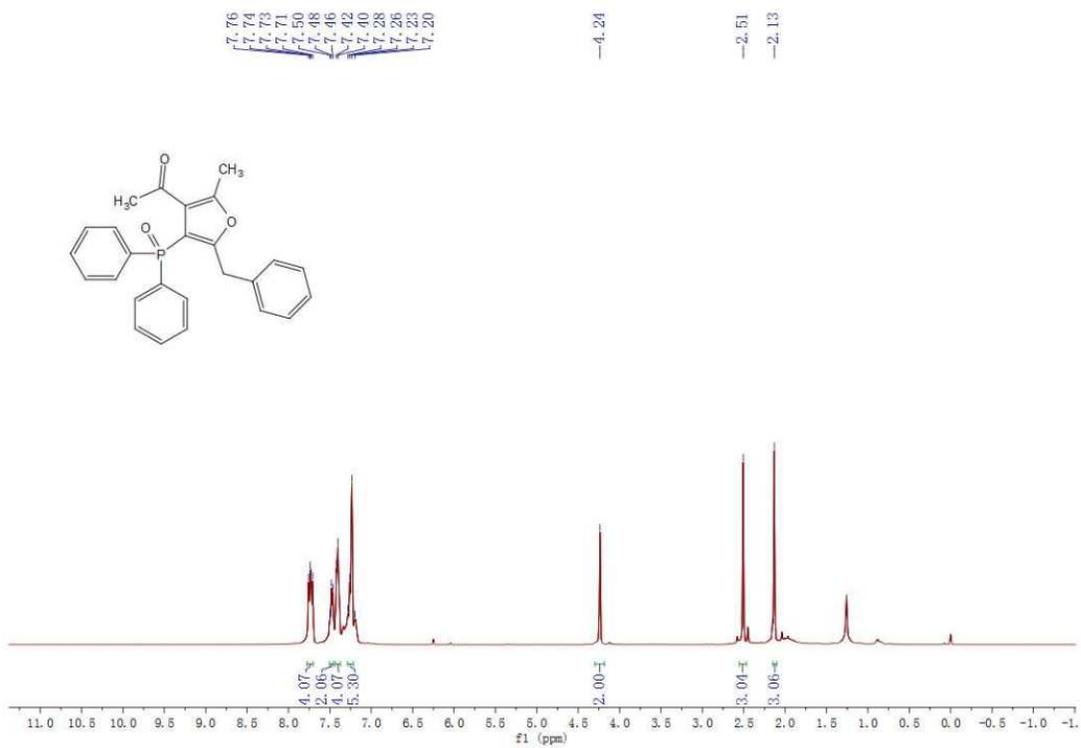
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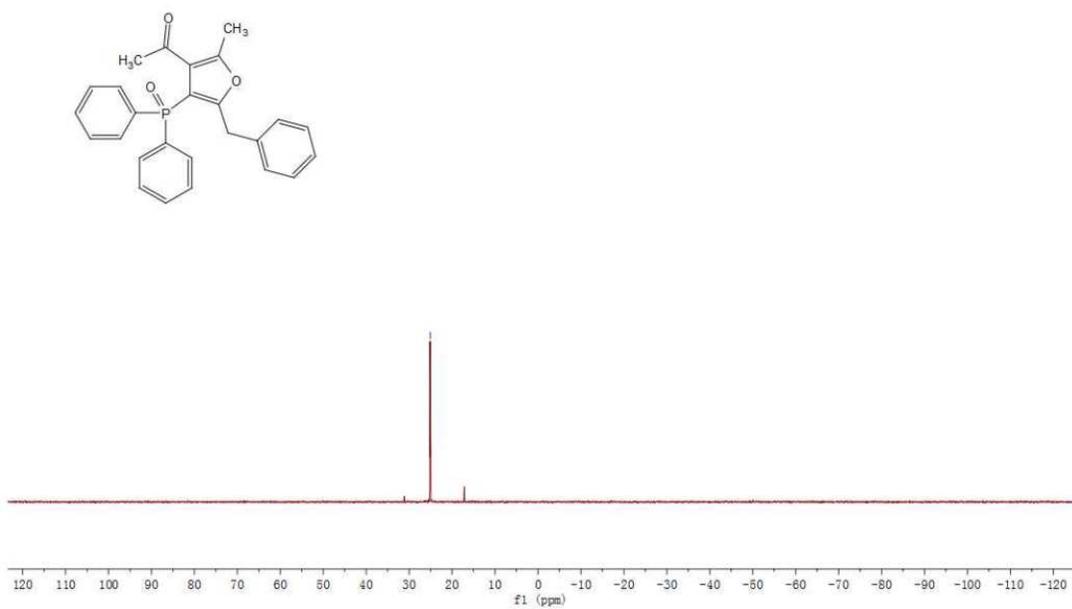




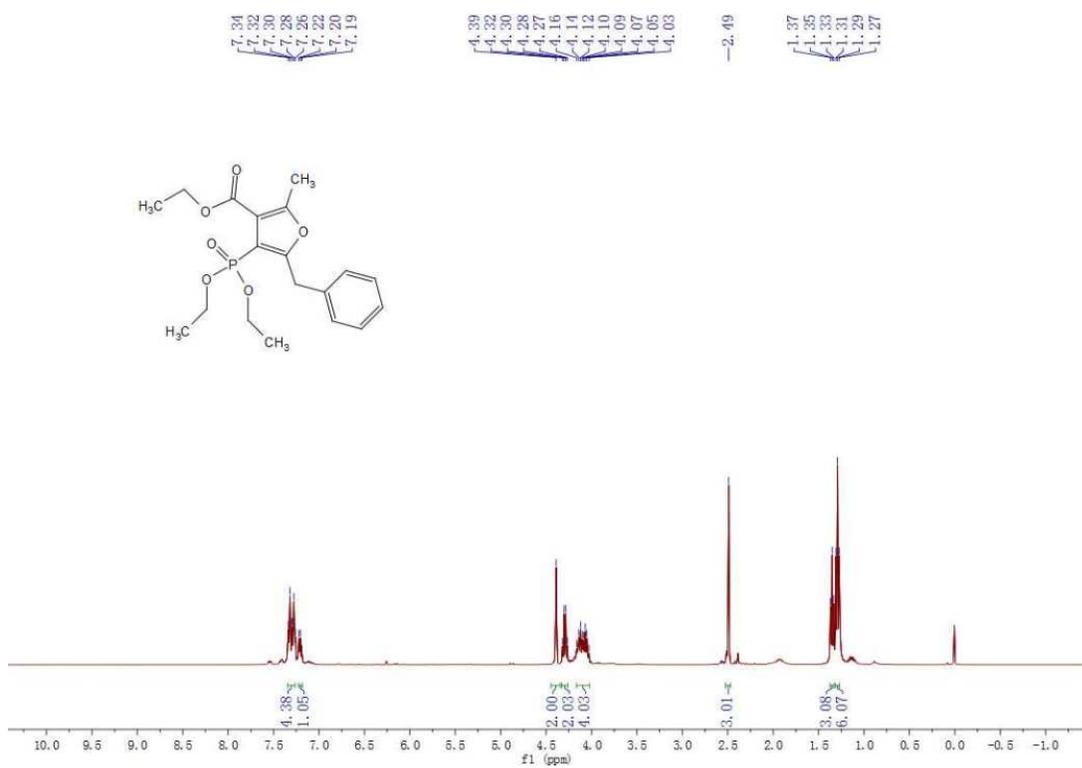
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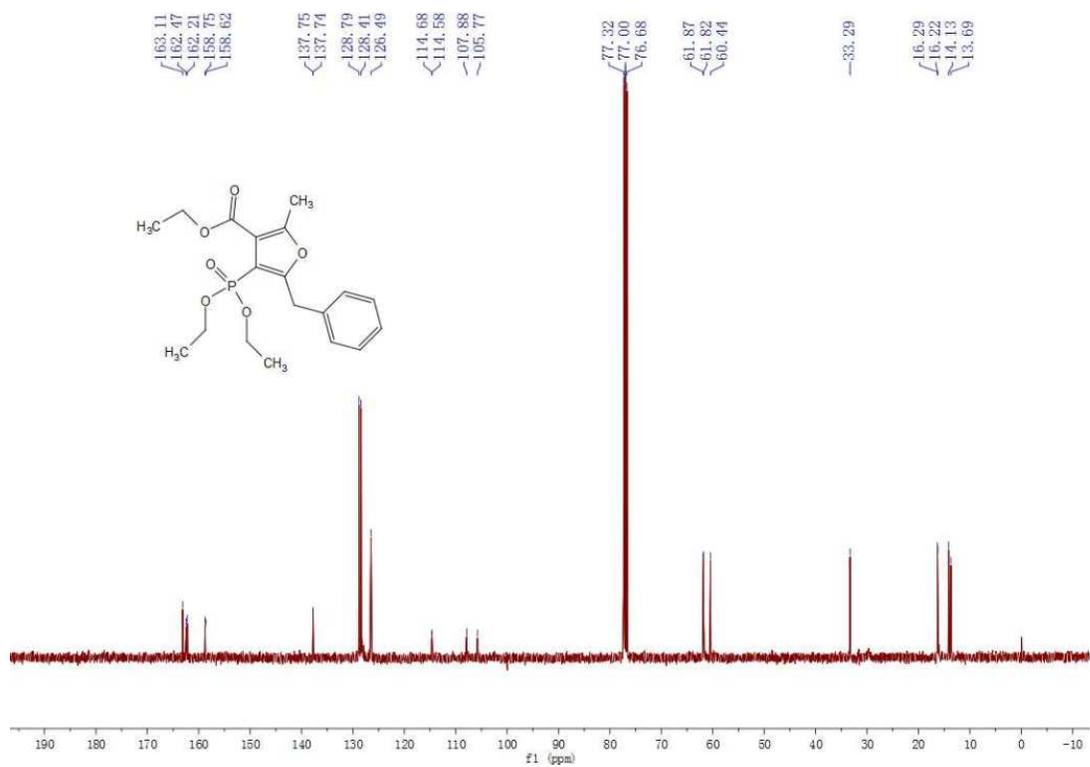


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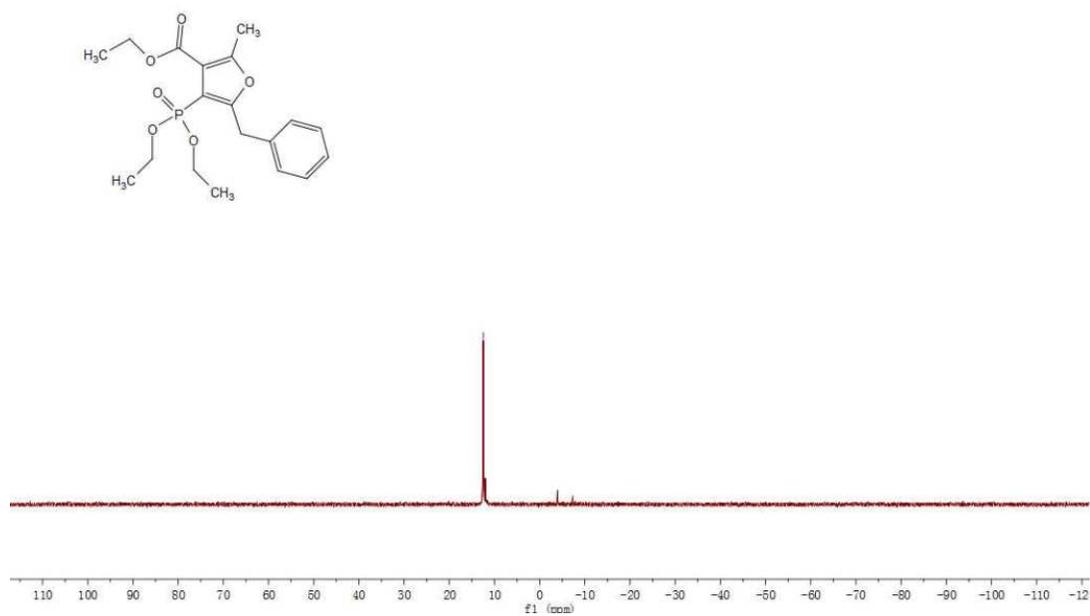


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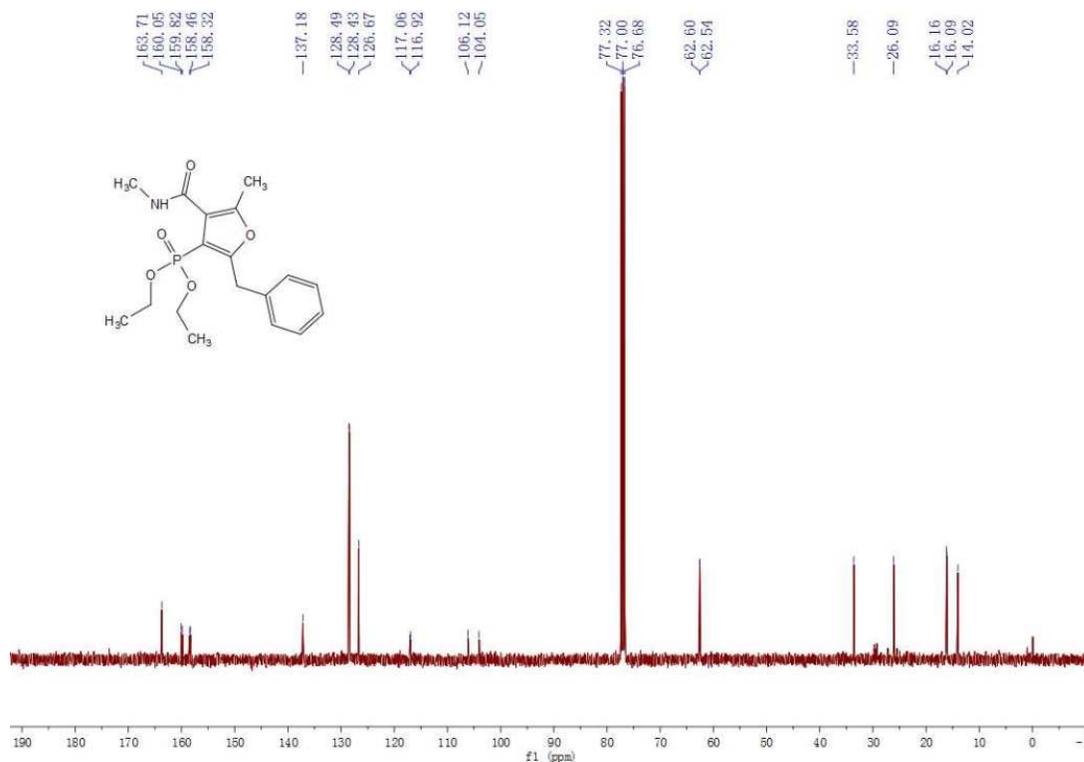
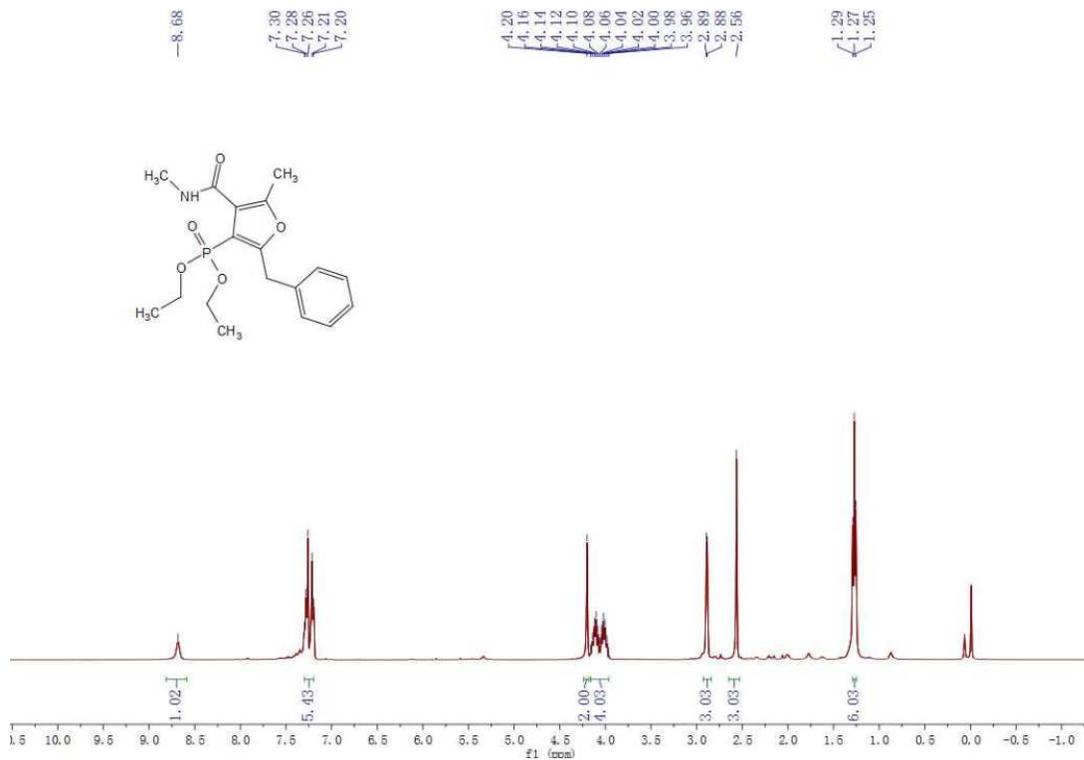
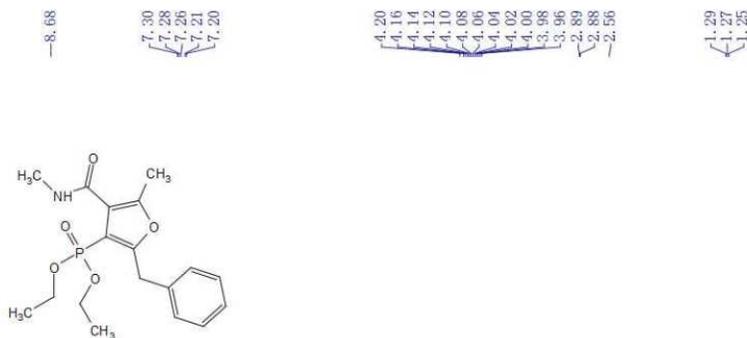




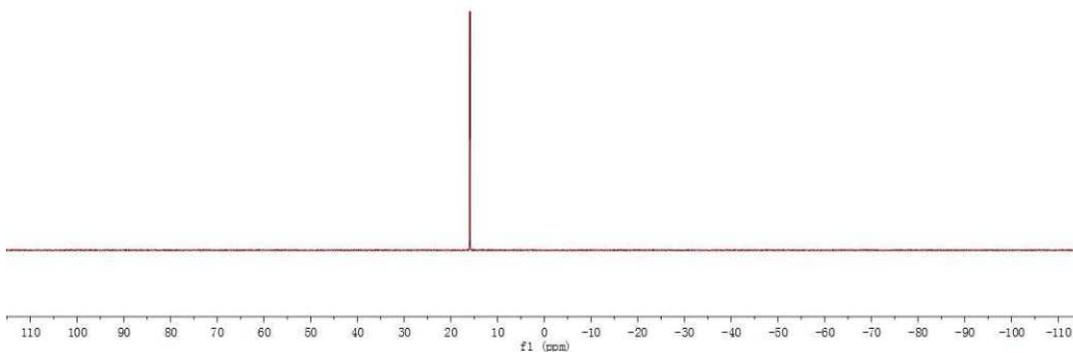
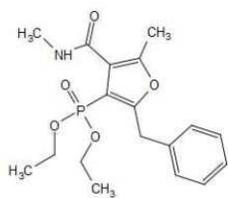
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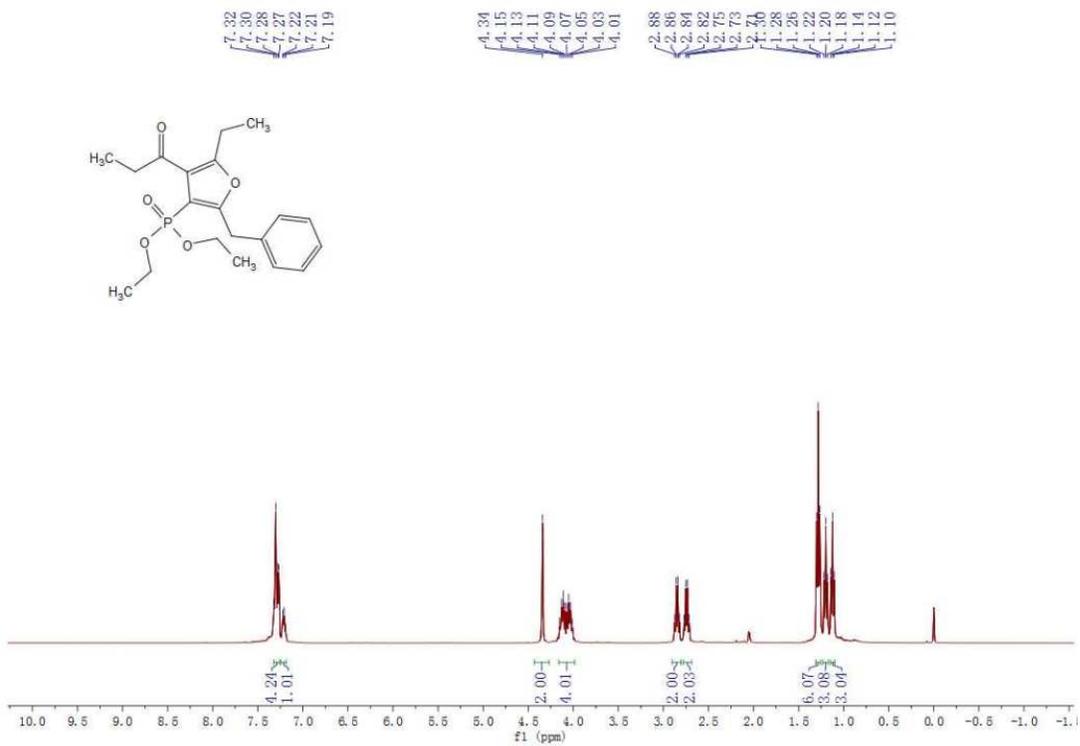
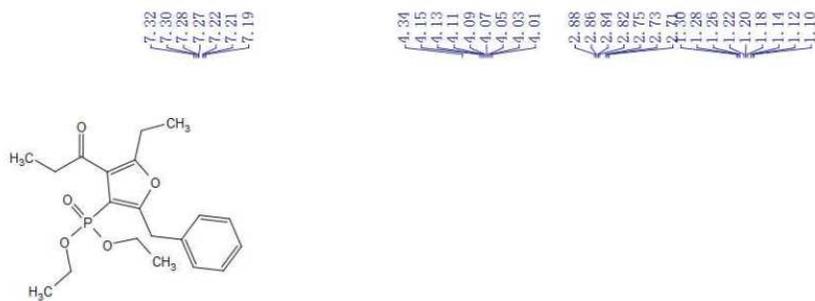
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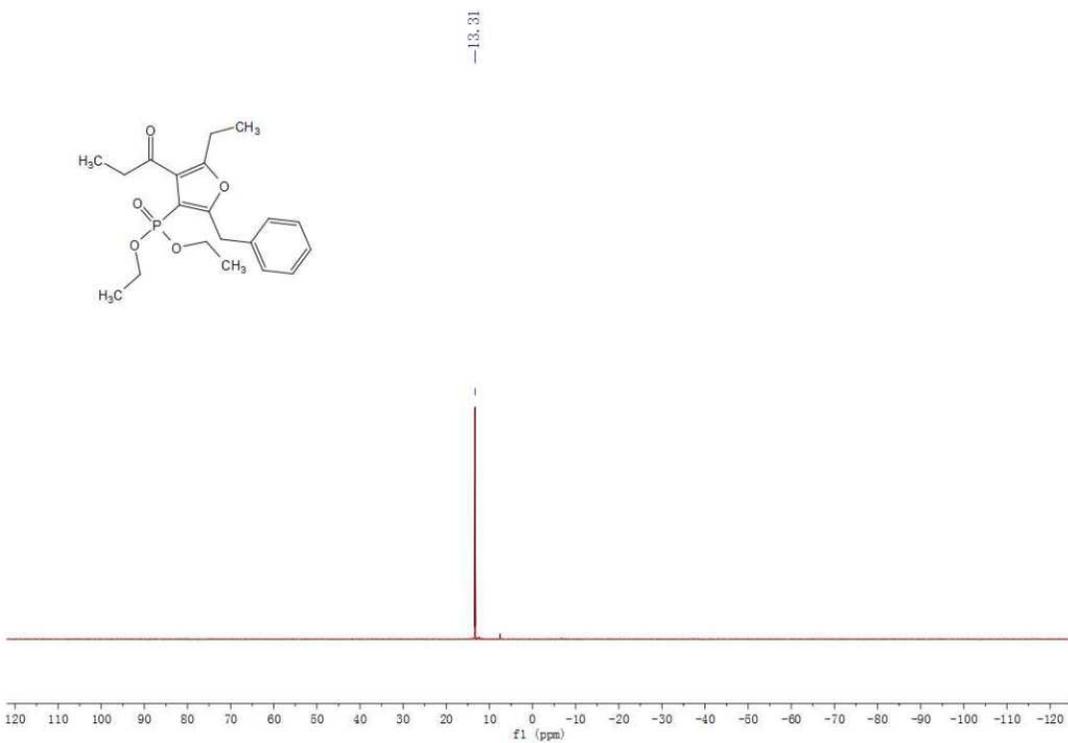
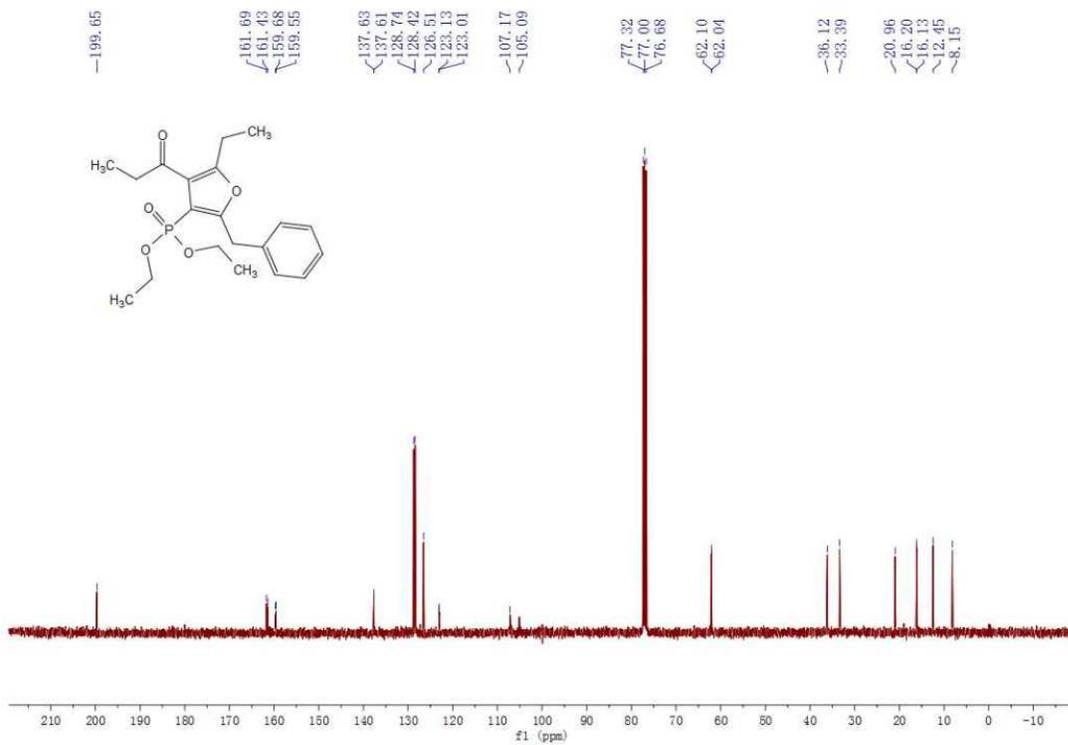


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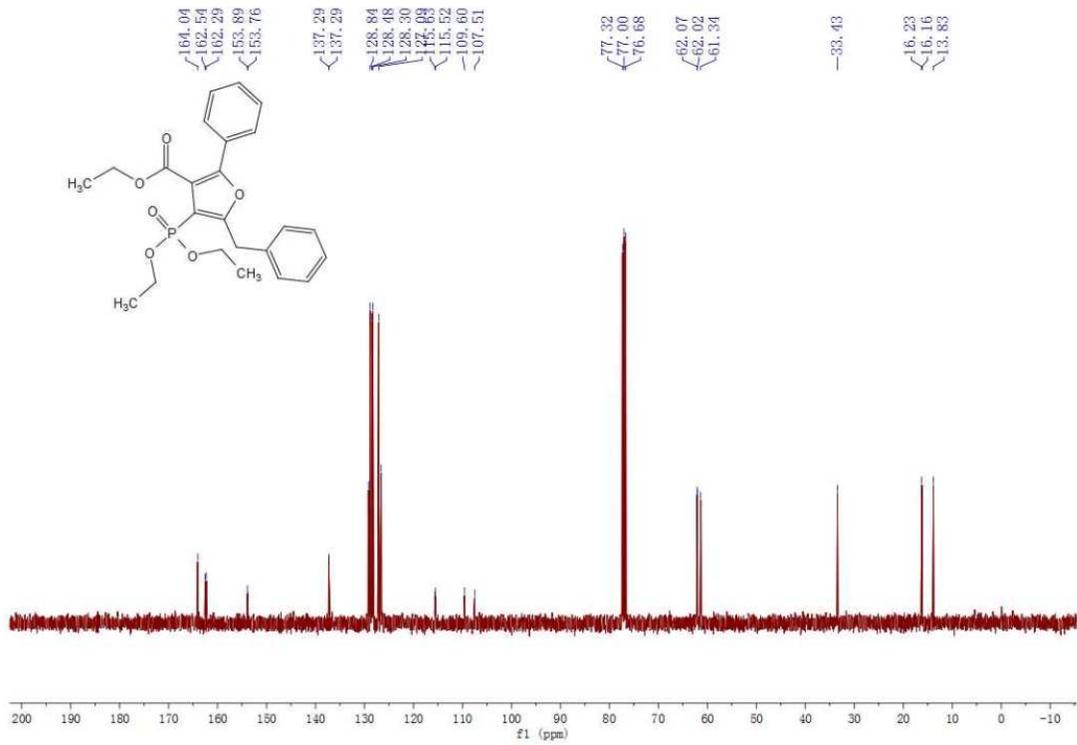
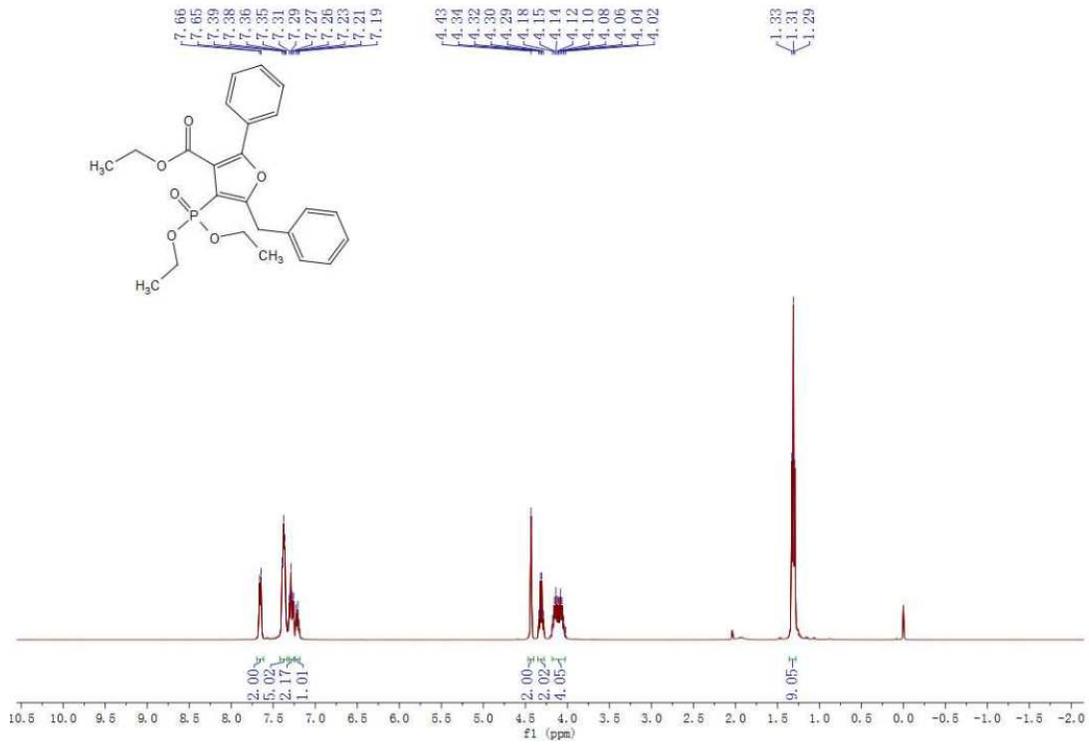


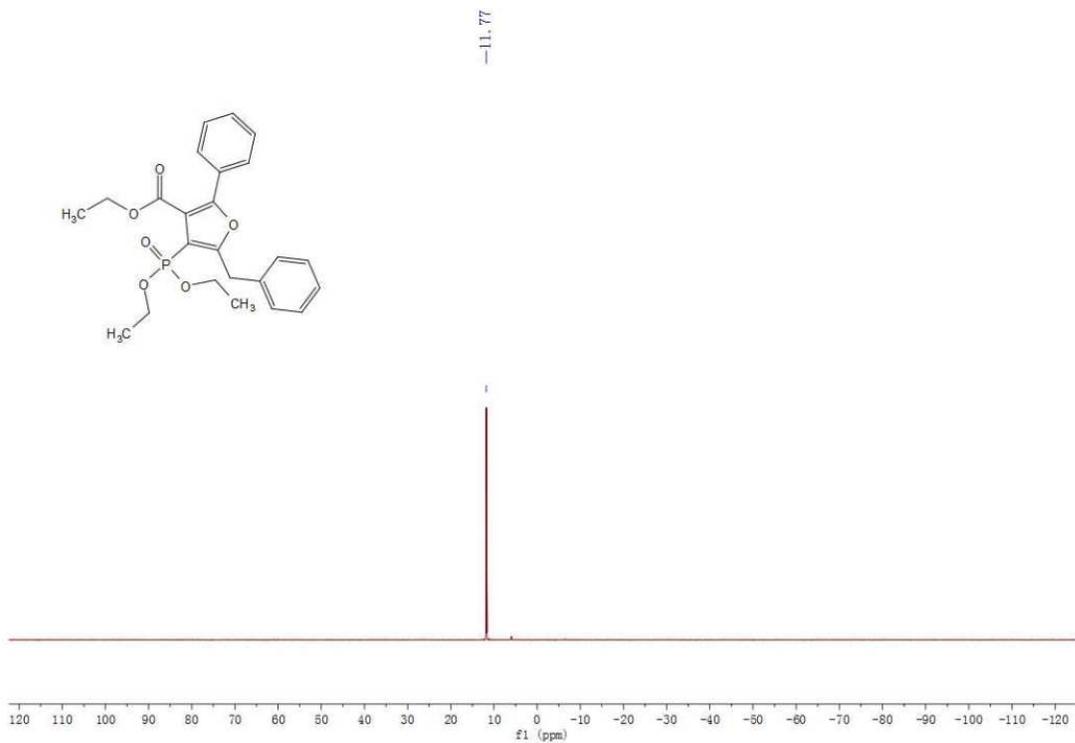
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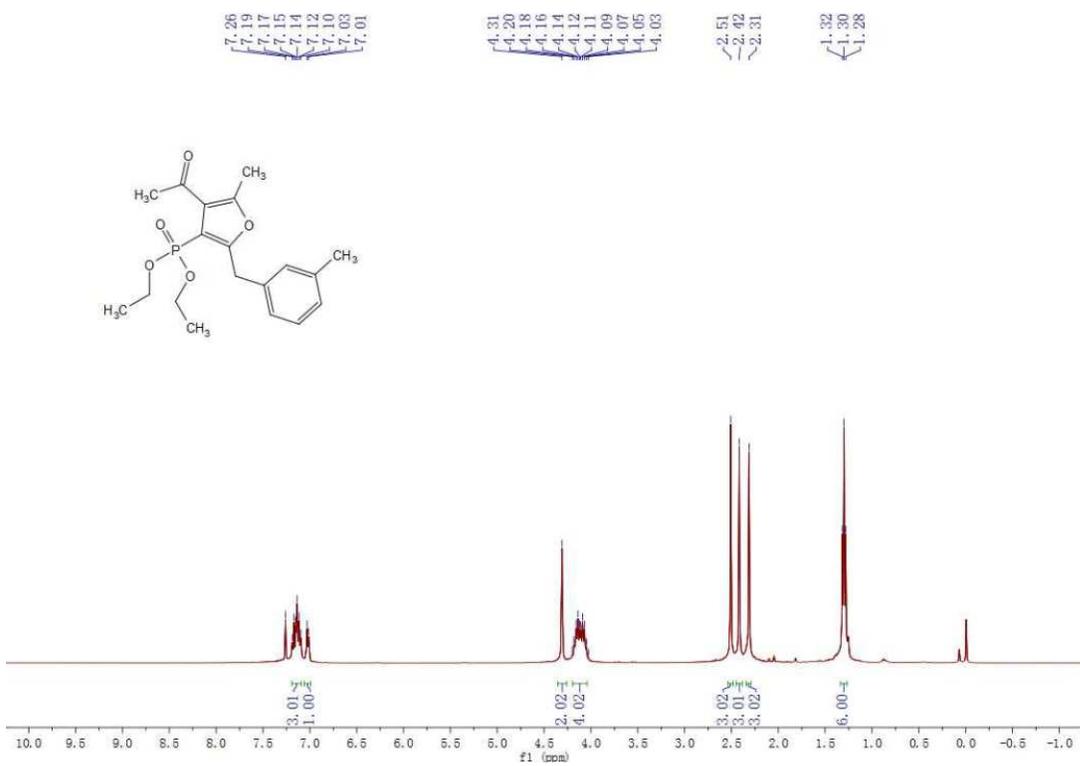


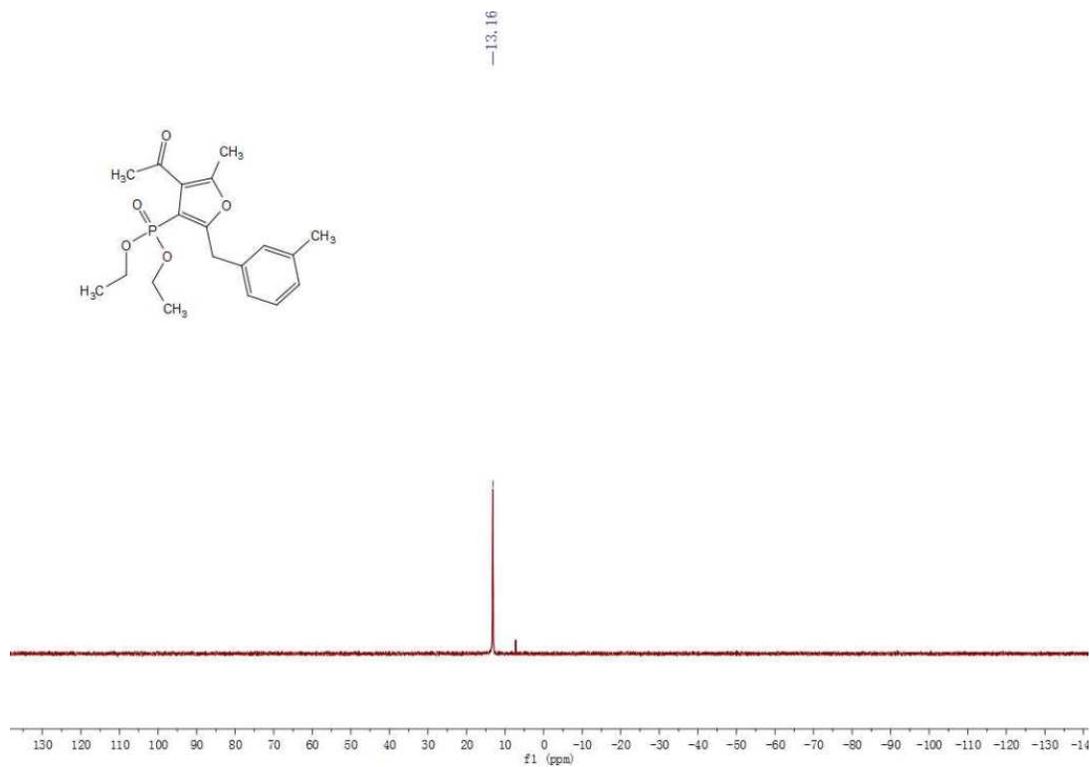
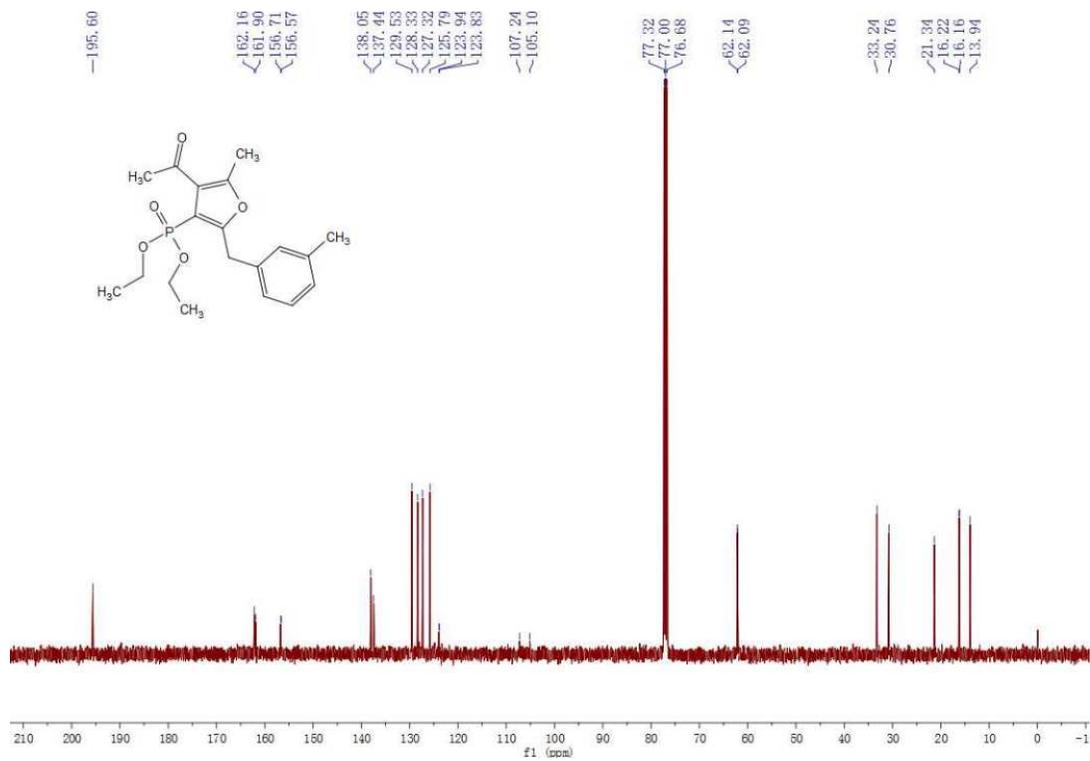
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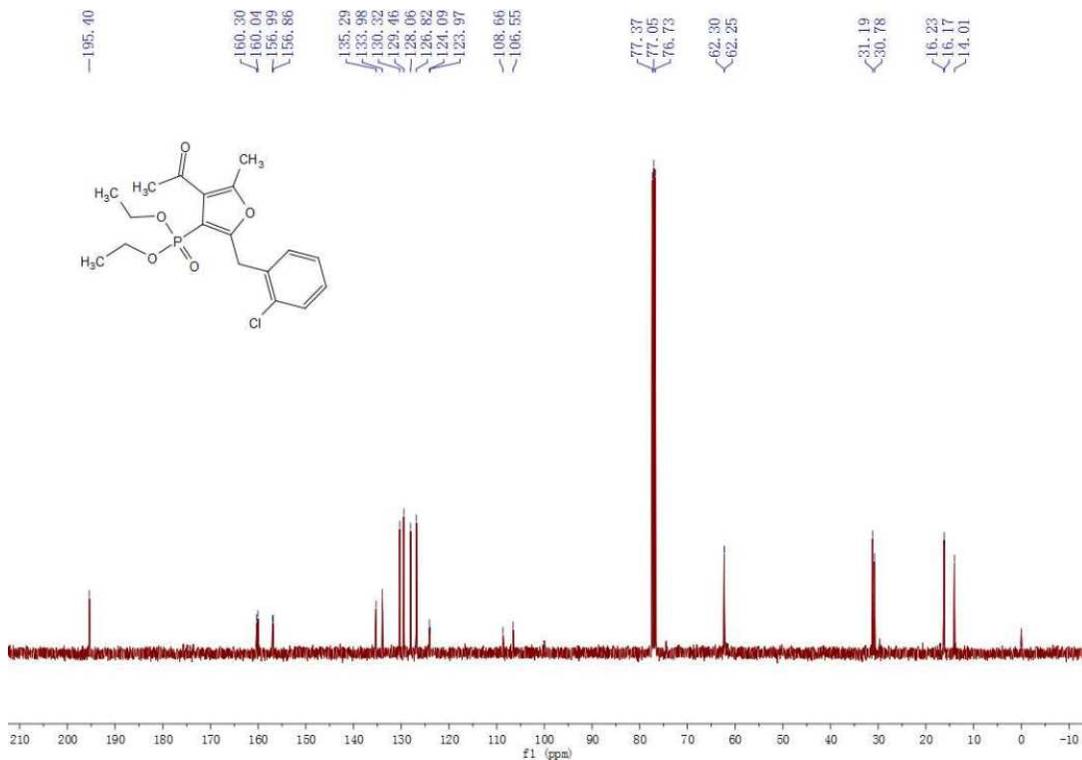
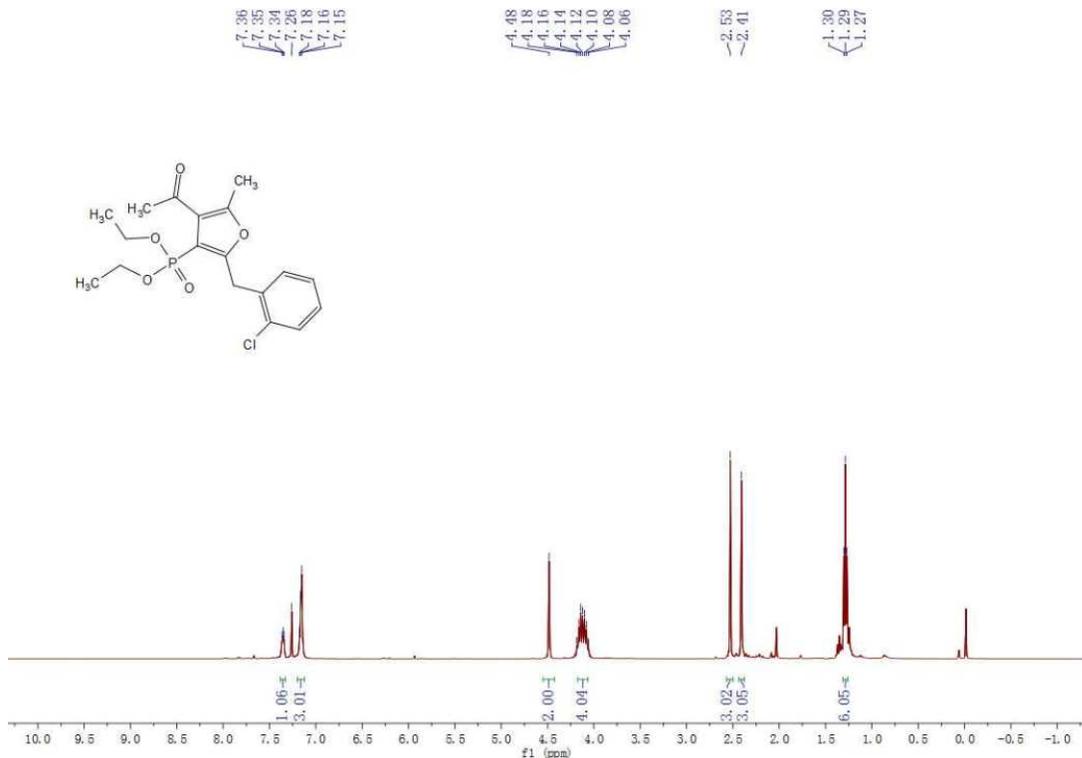


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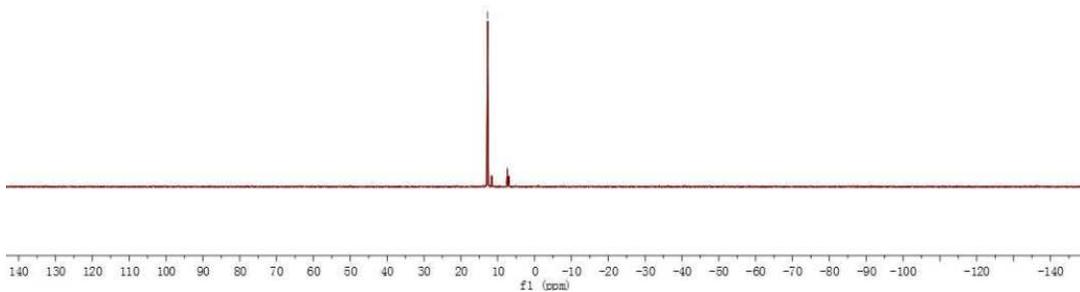
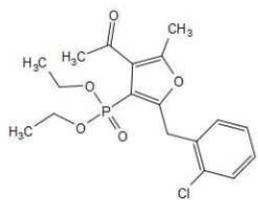




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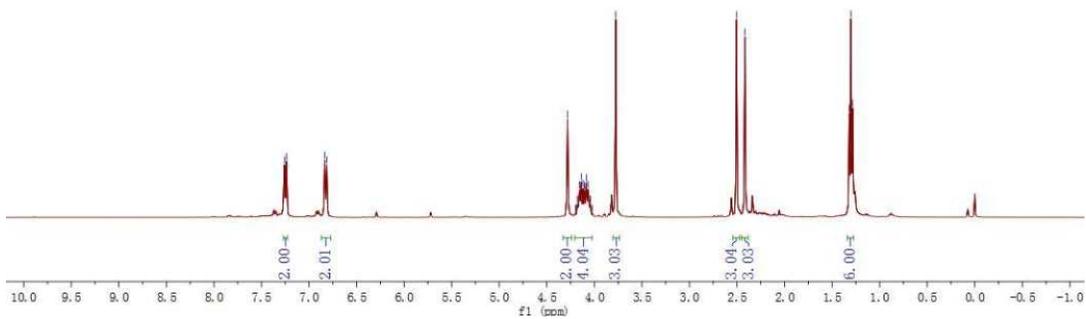
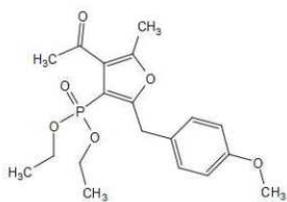


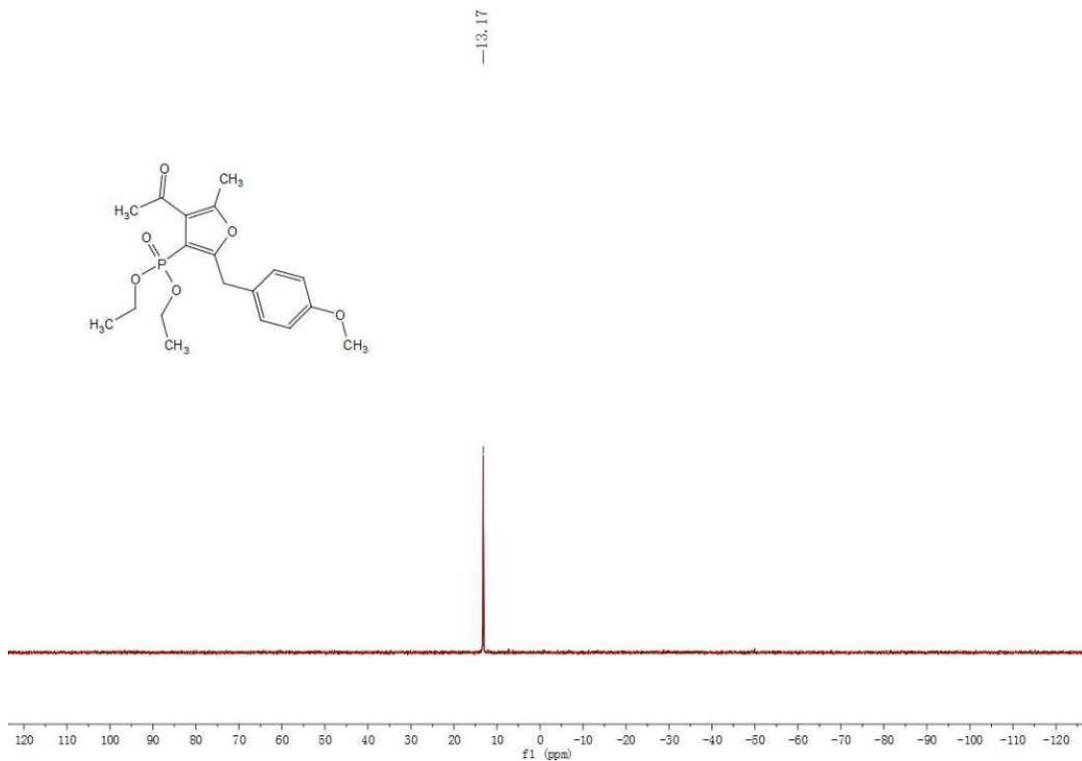
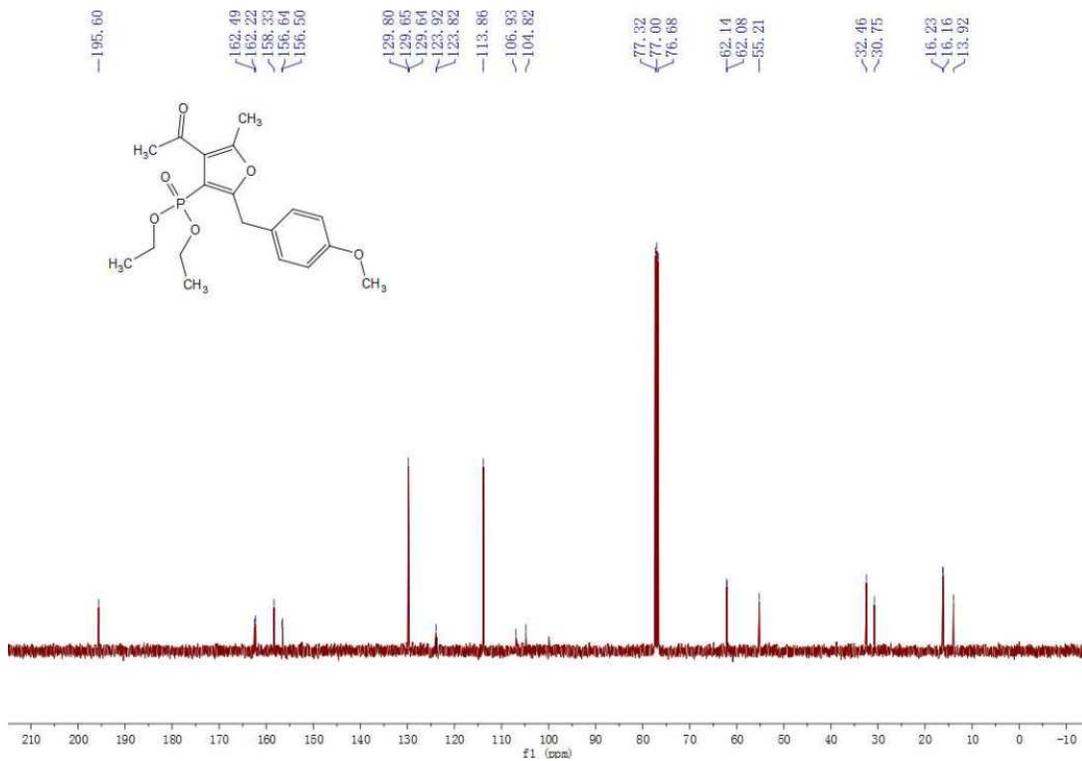
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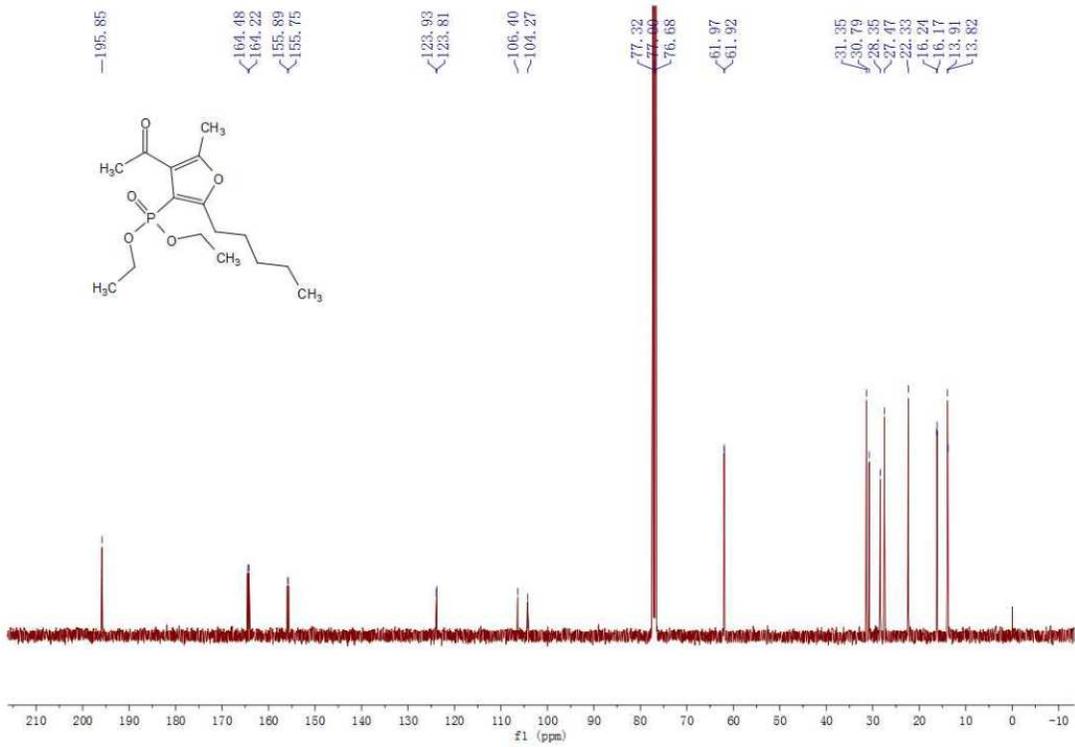
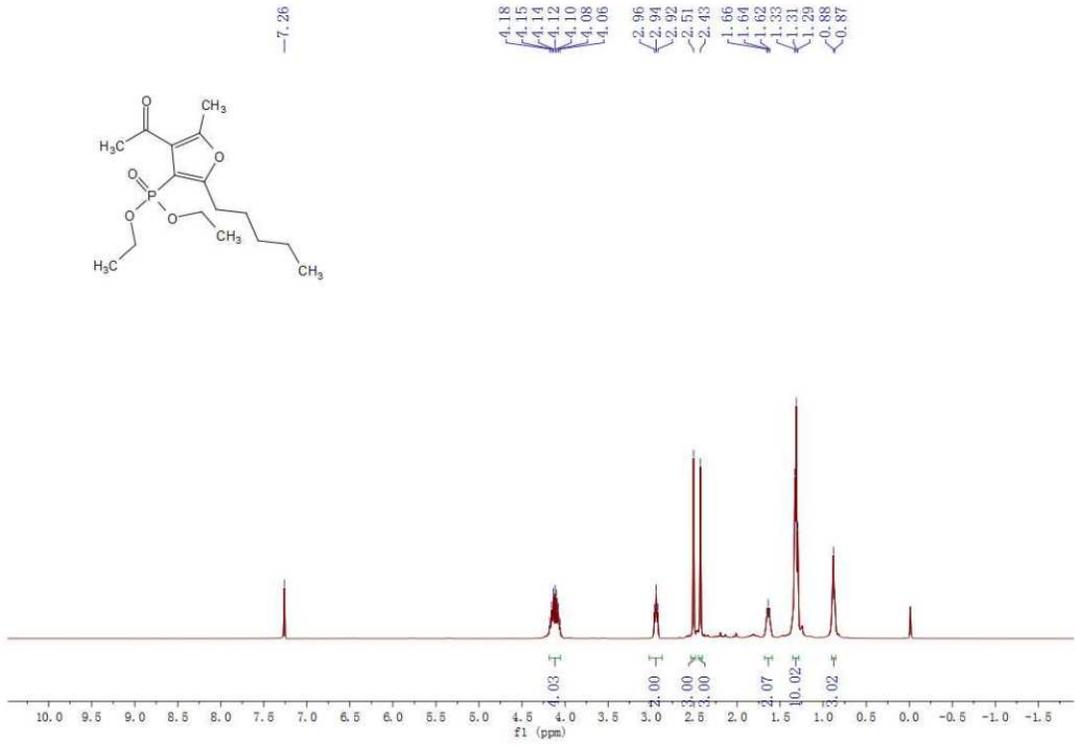
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7.24
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6.81
4.28
4.20
4.18
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4.14
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4.07
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4.02
3.78
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2.42
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1.30
1.28

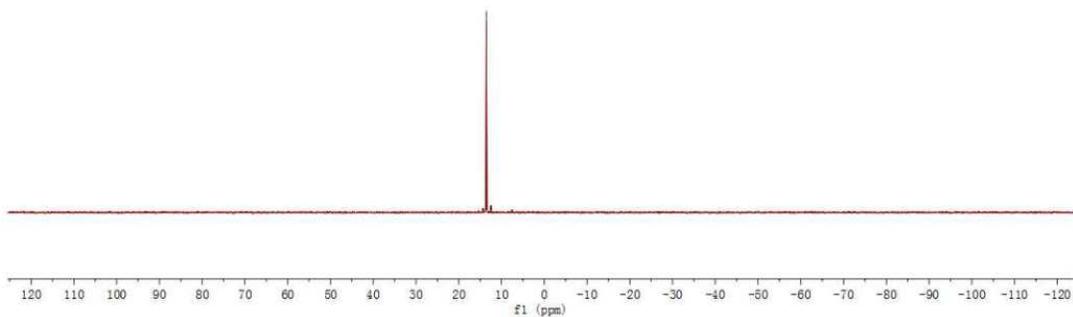
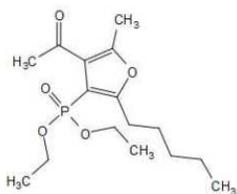




4ma



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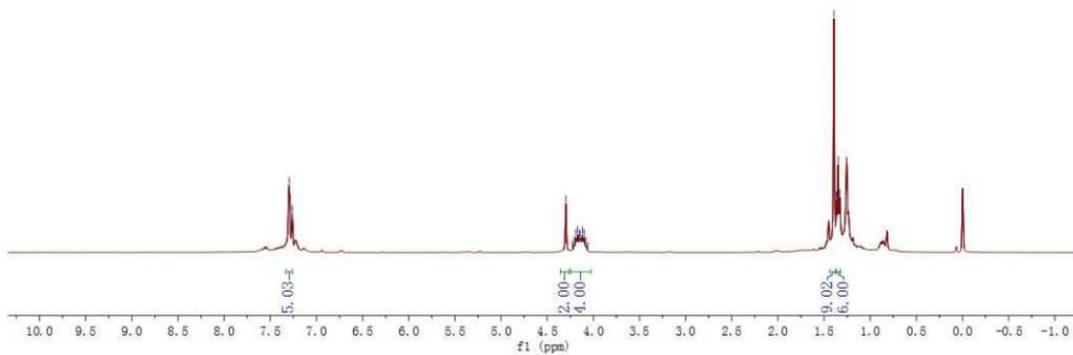
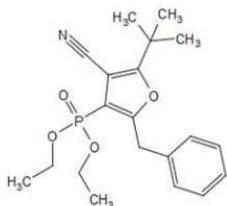


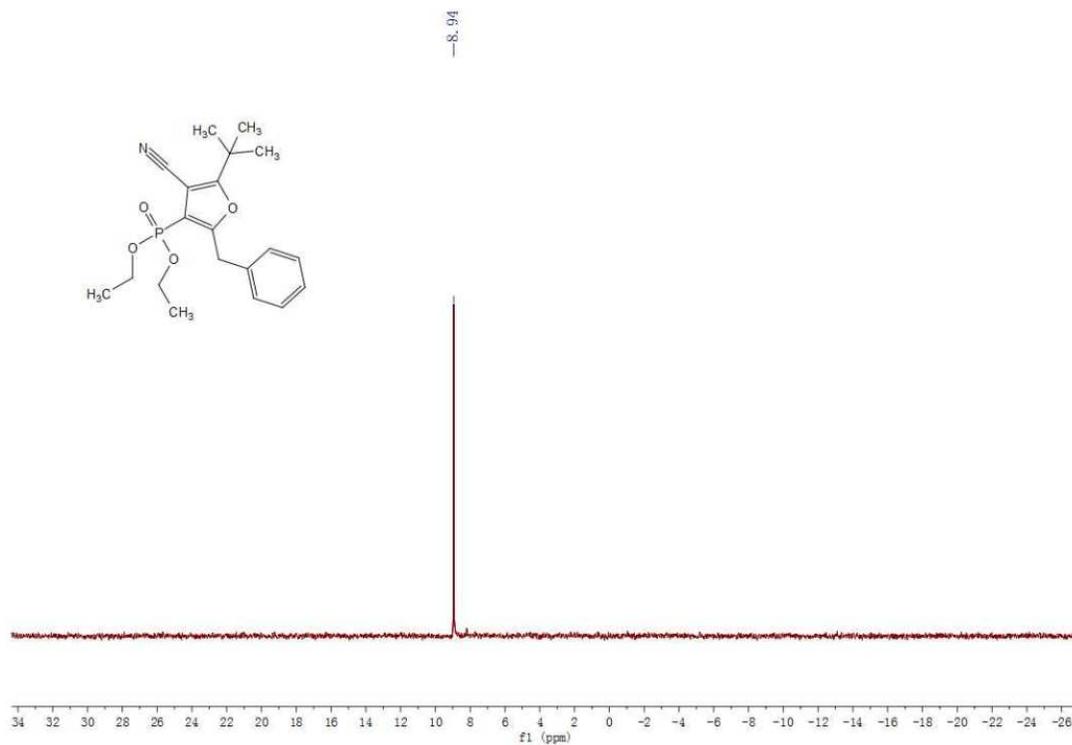
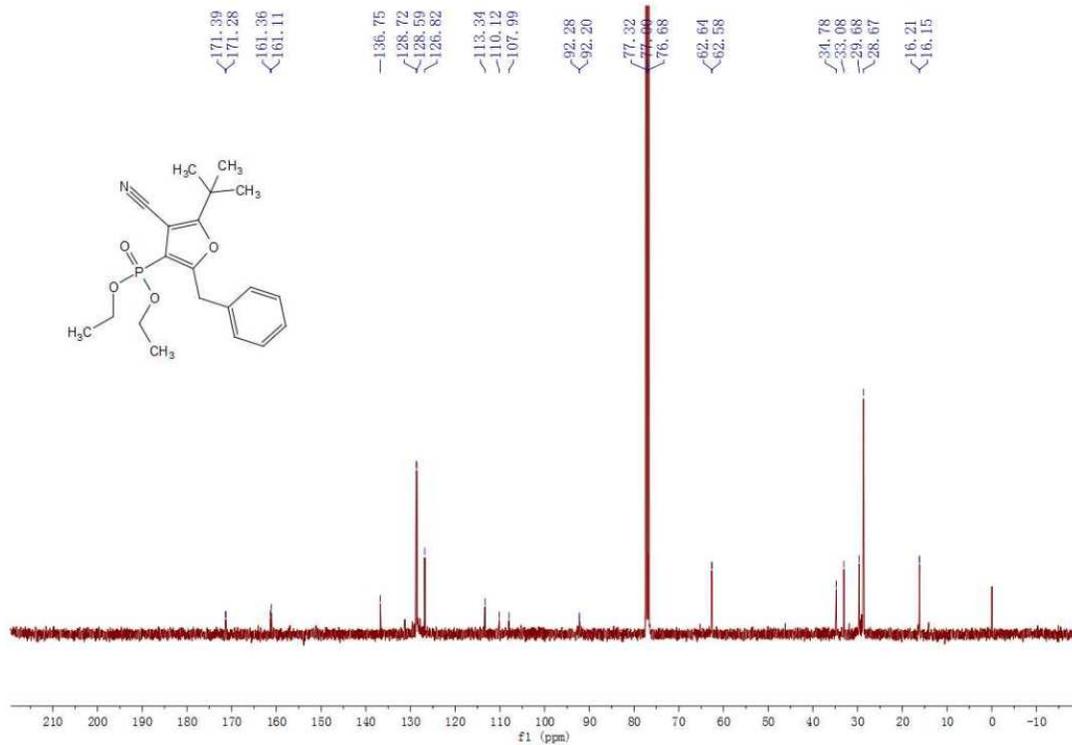
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7.29
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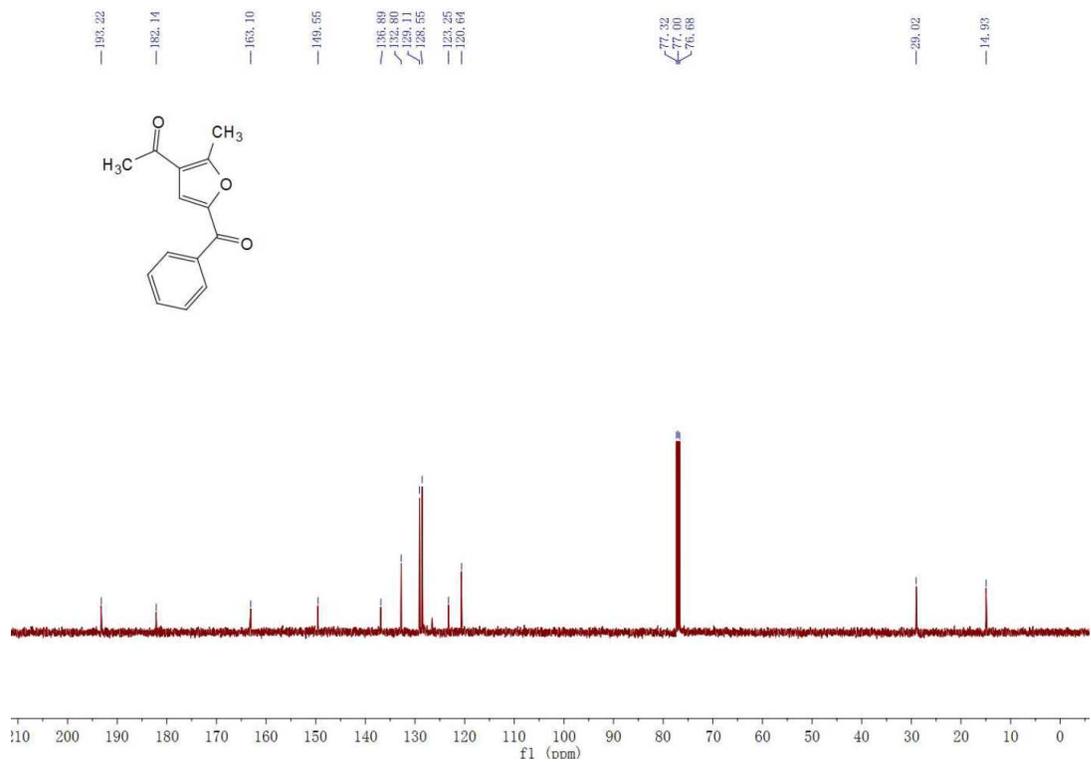
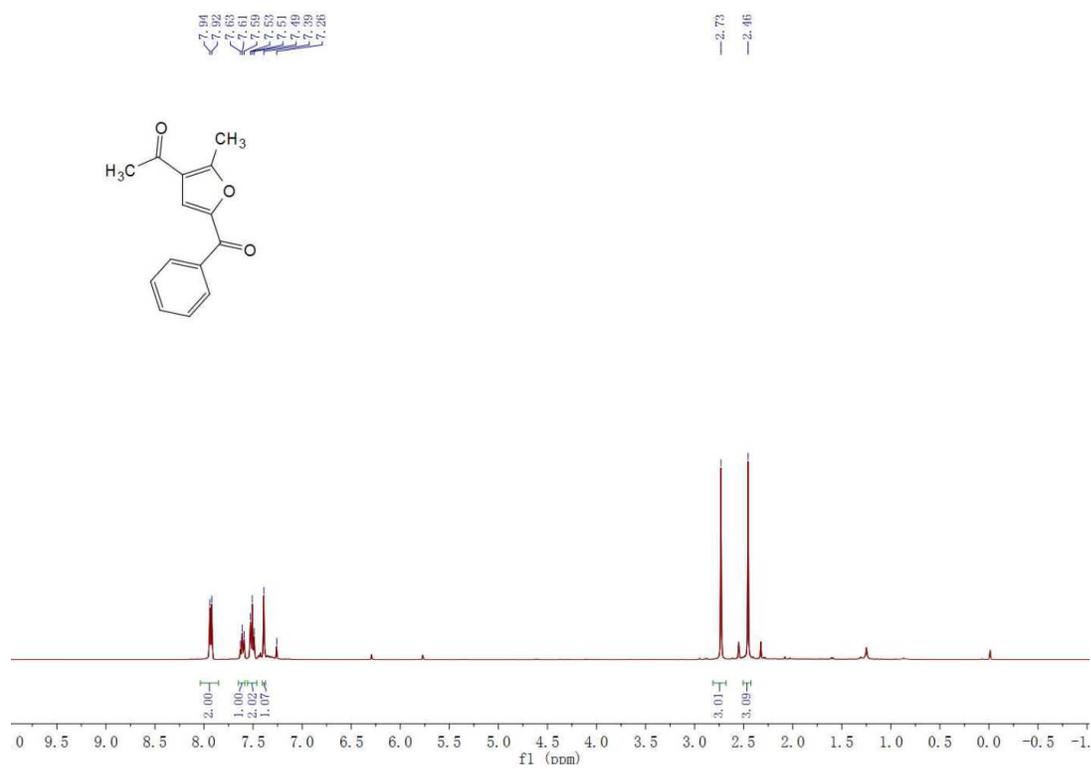
4.30
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4.17
4.15
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4.12
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4.08
4.06

1.39
1.36
1.35
1.33





5aa



7aa

