

*RSC Advances*

SUPPORTING INFORMATION

Supporting Information

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## **Supporting Information**

### **Inorganic base catalyzed synthesis of (2-amino-3-cyano-4H-chromen-4-yl) phosphonate derivatives via multi-component reaction under mild and efficient conditions**

Peng Dai, Gaofeng Zha, Xiaoyan Lai, Wei Liu, Qianwen Gan, Yongcun

Shen\*

E-mail: sycmichael@163.com.

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### General Experimental Methods

All reactions were carried out in reaction tubes with magnetic stirring and no special precautions were taken to exclude air from the reaction vessels. NMR spectra were recorded with a Bruker Avance HD III 500NMR spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from TMS with the solvent resonance as the internal standard. Coupling constants (J) are reported in Hz and refer to apparent peak multiplicity. ESI-MS was recorded on a Thermo-LTQ XL mass spectrometer. Melting points were determined on a WRS-2A(Shanghai Jingke) instrument and uncorrected, All other reagents were purchased from commercial sources and used without further purification.

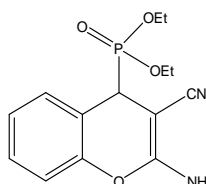
### General Experimental Methods for Compounds 4a

LiOH (0.2 mmol) was added to a mixture of Salicylaldehyde (1 mmol), Malononitrile (1 mmol) and Diethyl phosphite (Triethyl phosphate) (1 mmol) in neat condition. The resulting mixture was stirred for the appropriate time at room temperature. Then the appropriate amount of ethanol (3mL) was added to reaction mixture. After completion of the reaction (monitored by TLC), distilled water (15mL) was added to the reaction mixture and stirring continued till a free flowing solid was obtained. It was filtered and then washed successively with water (5mLx3), anhydrous ether (2mLx3). The crude product was further purified by recrystallization from anhydrous ethanol solution.

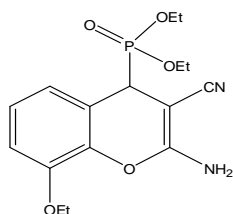
### General Experimental Methods for Compounds 7a

LiOH (0.2 mmol) was added to a mixture of Salicylaldehyde (1 mmol), Malononitrile (1 mmol) and Diphenyl phosphate (1 mmol) in neat condition. The resulting mixture was stirred at room temperature for 20min. Then added 3ml of anhydrous ethanol. After completion of the reaction (monitored by TLC), the reaction mixture was evaporated under reduced pressure, then distilled water (10 mL) was added to the reaction mixture and stirring 30min. Some desired product precipitated directly and some product was purified by silica column chromatography using Ethylacetate/petroleum ether=1/2. Finally the crude product was purified by recrystallization from ethyl acetate and ethanol solution.

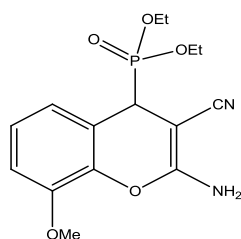
## Spectroscopic Data for Compounds 4

**4a. diethyl 2-amino-3-cyano-4H-chromen-4-ylphosphonate**

Yield: 94%; white solid; mp 178.8-180.5 °C. IR (neat): 3311, 3166, 2986, 2189, 1646, 1419, 1228, 1013, 971  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$ (ppm) 7.34 (t,  $J = 8.0$  Hz, 1H, Ar-H), 7.28 (d,  $J = 8.3$  Hz, 1H, Ar-H), 7.16 (d,  $J = 7.7$  Hz, 1H, Ar-H), 6.99 (d,  $J = 7.3$  Hz, 1H, Ar-H), 5.12 (s, 2H,  $-\text{NH}_2$ ), 4.06 – 3.98 (m, 4H,  $-\text{OCH}_2$ ), 3.96 (d,  $J = 17.6$  Hz, 1H, P-CH), 1.35 (t,  $J = 7.0$  Hz, 3H,  $-\text{CH}_3$ ), 1.30 (t,  $J = 7.0$  Hz, 3H,  $-\text{CH}_3$ ).  $^{13}\text{C-NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 162.01, 149.93, 129.58, 129.02, 124.95, 119.54, 116.51, 77.31, 77.06, 76.80, 63.32, 62.98, 51.42, 36.05, 34.87, 16.38.  $^{31}\text{P-NMR}$  (202 MHz,  $\text{CDCl}_3$ )  $\delta$ : 22.25 – 21.16. MS (ESI):  $m/z$  639.32 ( $2\text{M}+\text{Na}$ ), 635.32 ( $2\text{M}+\text{NH}_4^+$ ).

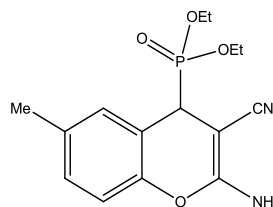
**4b. diethyl 2-amino-3-cyano-8-ethoxy-4H-chromen-4-ylphosphonate**

Yield: 96%; yellow solid, mp 180.1-180.6 °C. IR (neat): 3445, 3177, 2986, 2188, 1640, 1401, 1201, 1017, 964  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$ (ppm) 7.13 (s, 2H,  $-\text{NH}_2$ ), 7.06 (t,  $J = 7.9$  Hz, 1H, Ar-H), 7.00 (d,  $J = 8.3$  Hz, 1H, Ar-H), 6.81 (d,  $J = 7.7$  Hz, 1H, Ar-H), 4.10 (tt,  $J = 7.0, 3.5$  Hz, 2H,  $-\text{OCH}_2$ ), 4.05 (d,  $J = 17.6$  Hz, 1H, P-CH), 3.99 – 3.87 (m, 4H,  $-\text{OCH}_2$ ), 1.34 (dd,  $J = 8.7, 5.2$  Hz, 3H,  $-\text{CH}_3$ ), 1.20 (t,  $J = 7.0$  Hz, 3H,  $-\text{CH}_3$ ), 1.15 (t,  $J = 7.0$  Hz, 3H,  $-\text{CH}_3$ ).  $^{13}\text{C-NMR}$  (126 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 163.08, 146.77, 140.16, 124.50, 121.25, 120.55, 119.26, 113.59, 64.78, 62.69, 47.95, 40.00, 39.83, 39.66, 39.50, 35.88, 34.72, 16.67, 15.07.  $^{31}\text{P-NMR}$  (202 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 23.00–21.99. MS (ESI):  $m/z$  375.45 ( $\text{M}+\text{Na}$ ).



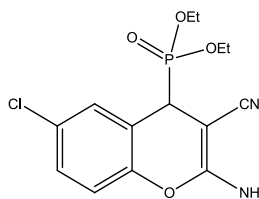
**4c. diethyl 2-amino-3-cyano-8-methoxy-4H-chromen-4-ylphosphonate**

Yield: 96%; yellow solid; mp 184.5-184.8 °C. IR (neat): 3421, 3170, 2982, 2188, 1641, 1408, 1261, 1018, 965  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$ (ppm) 7.17 (d,  $J = 16.6$  Hz, 2H,  $-\text{NH}_2$ ), 7.09 (t,  $J = 8.0$  Hz, 1H, Ar-H), 7.01 (d,  $J = 8.3$  Hz, 1H, Ar-H), 6.82 (d,  $J = 7.7$  Hz, 1H, Ar-H), 4.05 (d,  $J = 17.6$  Hz, 1H, P-CH), 3.99 – 3.88 (m, 4H,  $-\text{OCH}_2$ ), 3.82 (s, 3H,  $-\text{OCH}_3$ ), 1.20 (t,  $J = 7.0$  Hz, 3H,  $-\text{CH}_3$ ), 1.15 (t,  $J = 7.0$  Hz, 3H,  $-\text{CH}_3$ ).  $^{13}\text{C-NMR}$  (126 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 163.10, 147.62, 139.81, 124.48, 121.15, 120.52, 119.15, 112.14, 79.67, 79.41, 79.15, 62.70, 56.52, 56.20, 47.88, 40.01, 39.84, 39.67, 39.50, 35.87, 34.72, 18.98, 16.67.  $^{31}\text{P-NMR}$  (202 MHz,  $\text{DMSO}$ )  $\delta$ : 23.01 – 21.99. MS (ESI):  $m/z$  361.76 ( $\text{M}+\text{Na}$ ).



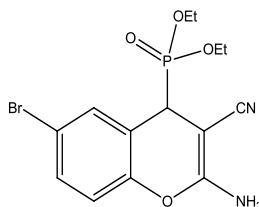
**4d. diethyl 2-amino-3-cyano-6-methyl-4H-chromen-4-ylphosphonate**

Yield: 97%; yellow solid; mp 177.4-179.6 °C. IR (neat): 3353, 3164, 2984, 2185, 1648, 1418, 1230, 1016, 968  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$ (ppm) 7.10 (s, 2H,  $-\text{NH}_2$ ), 7.10 – 7.08 (m, 1H, Ar-H), 7.06 (s, 1H, Ar-H), 6.91 (d,  $J = 8.2$  Hz, 1H, Ar-H), 4.03 (d,  $J = 17.6$  Hz, 1H, P-CH), 3.99 – 3.88 (m, 4H,  $-\text{OCH}_2$ ), 2.27 (s, 3H,  $-\text{CH}_3$ ), 1.20 (t,  $J = 7.0$  Hz, 3H,  $-\text{CH}_3$ ), 1.15 (t,  $J = 7.0$  Hz, 3H,  $-\text{CH}_3$ ).  $^{13}\text{C-NMR}$  (126 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 163.22, 148.40, 133.69, 130.14, 129.63, 120.65, 117.82, 116.12, 62.67, 47.84, 40.48, 39.98, 39.82, 39.68, 39.57, 35.60, 34.44, 20.72, 16.66.  $^{31}\text{P-NMR}$  (202 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 23.03 – 22.08. MS (ESI):  $m/z$  345.68 ( $\text{M} + \text{Na}$ ).



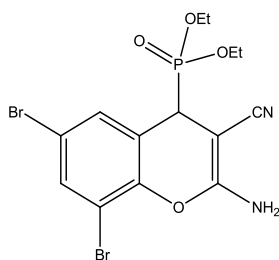
**4e. diethyl 2-amino-6-chloro-3-cyano-4H-chromen-4-ylphosphonate**

Yield: 90%; pink solid; mp 175.7-177.6°C. IR (neat): 3354, 3152, 2988, 2188, 1655, 1418, 1242, 1041, 969  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$ (ppm) 7.37 (dt,  $J = 8.7, 2.3$  Hz, 1H, Ar-H), 7.31 (t,  $J = 2.3$  Hz, 1H, Ar-H), 7.26 (s, 2H,  $-\text{NH}_2$ ), 7.06 (d,  $J = 8.7$  Hz, 1H, Ar-H), 4.20 (d,  $J = 18.3$  Hz, 1H, P-CH), 3.97 (dddd,  $J = 12.2, 8.3, 5.8, 2.2$  Hz, 4H,  $-\text{OCH}_2$ ), 1.21 (t,  $J = 7.0$  Hz, 3H,  $-\text{CH}_3$ ), 1.15 (t,  $J = 7.0$  Hz, 3H,  $-\text{CH}_3$ ).  $^{13}\text{C-NMR}$  (126 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 162.87, 149.26, 129.47, 129.05, 128.27, 120.53, 120.24, 118.24, 62.86, 47.61, 40.42, 40.00, 39.83, 39.67, 39.50, 35.39, 34.23, 16.63.  $^{31}\text{P-NMR}$  (202 MHz,  $\text{DMSO}$ )  $\delta$ : 22.39–21.37. MS (ESI):  $m/z$  365.86 (M+Na).



**4f. diethyl 2-amino-6-bromo-3-cyano-4H-chromen-4-ylphosphonate**

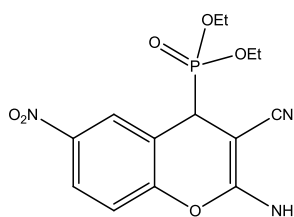
Yield: 91%; white solid; mp 178.1-179.2°C. IR (neat): 3353, 3155, 2986, 2189, 1654, 1416, 1238, 1043, 969  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$ (ppm) 7.48 (d,  $J = 8.7$  Hz, 1H, Ar-H), 7.44 (t,  $J = 2.2$  Hz, 1H, Ar-H), 7.24 (s, 2H,  $-\text{NH}_2$ ), 7.01 (d,  $J = 8.7$  Hz, 1H, Ar-H), 4.20 (d,  $J = 18.3$  Hz, 1H, P-CH), 4.07 – 3.86 (m, 4H,  $-\text{OCH}_2$ ), 1.21 (t,  $J = 7.0$  Hz, 3H,  $-\text{CH}_3$ ), 1.16 (t,  $J = 7.0$  Hz, 3H,  $-\text{CH}_3$ ).  $^{13}\text{C-NMR}$  (126 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 162.83, 149.73, 132.37, 131.92, 120.94, 120.23, 118.62, 116.13, 62.86, 39.99, 39.83, 39.66, 39.49, 35.25, 34.10, 16.63.  $^{31}\text{P-NMR}$  (202 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 22.41–21.39. MS (ESI):  $m/z$  411.80 (M+Na).



**4g. diethyl 2-amino-6,8-dibromo-3-cyano-4H-chromen-4-yl**

**phosphonate**

Yield: 89%; white solid; mp 183.2-185.1 °C. IR (neat): 3354, 3155, 2985, 2197, 1662, 1414, 1238, 1045, 967  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$ (ppm) 7.87 (t,  $J = 2.1$  Hz, 1H, Ar-H), 7.45 (t,  $J = 2.1$  Hz, 1H, Ar-H), 7.40 (s, 2H,  $-\text{NH}_2$ ), 4.28 (d,  $J = 18.5$  Hz, 1H, P-CH), 4.06 – 3.88 (m, 4H,  $-\text{OCH}_2$ ), 1.20 (t,  $J = 7.0$  Hz, 3H,  $-\text{CH}_3$ ), 1.16 (t,  $J = 7.0$  Hz, 3H,  $-\text{CH}_3$ ).  $^{13}\text{C-NMR}$  (126 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 162.50, 146.88, 134.43, 131.86, 122.52, 119.77, 116.32, 110.98, 63.02, 48.03, 40.00, 39.83, 39.67, 39.50, 35.73, 34.58, 16.60.  $^{31}\text{P-NMR}$  (202 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 22.01– 21.07. MS (ESI):  $m/z$  489.63 (M+Na).



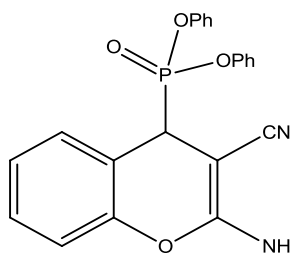
**4h. diethyl 2-amino-3-cyano-6-nitro-4H-chromen-4-yl**

**phosphonate**

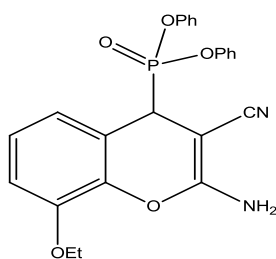
Yield: 86%; yellow solid, mp 182.5-183.8 °C. IR (neat): 3340, 3151, 2986, 2192, 1658, 1417, 1237, 1033, 972  $\text{cm}^{-1}$ .  $^{13}\text{C-NMR}$  (126 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 162.21, 154.85, 143.89, 125.74, 125.15, 120.06, 119.83, 117.85, 63.04, 47.67, 39.99, 39.83, 39.66, 39.49, 35.16, 34.01, 16.60.  $^{31}\text{P-NMR}$  (202 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 21.97– 20.95. MS (ESI):  $m/z$  376.59 (M+Na).



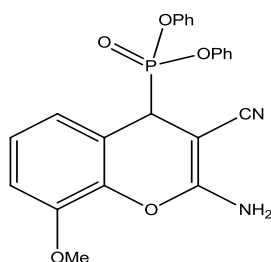
## Spectroscopic Data for Compounds 7

**7a. diphenyl 2-amino-3-cyano-4H-chromen-4-ylphosphonate**

Yield: 91%; white solid; mp 179.1-180.2°C. IR (neat): 3385, 3308, 3187, 2182, 1655, 1585, 1488, 1267, 1052, 929  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  (ppm) 7.45 (s, 2H,  $-\text{NH}_2$ ), 7.45 – 6.63 (m, 14H, Ar-H), 4.77 (d,  $J = 16.8$  Hz, 1H, P-CH).  $^{13}\text{C-NMR}$  (126 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 163.62, 150.59, 130.33, 129.92, 125.62, 125.14, 120.70, 120.44, 117.00, 116.71, 47.05, 40.00, 39.84, 39.67, 39.58, 36.71, 35.53.  $^{31}\text{P-NMR}$  (202 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 16.05. MS (ESI):  $m/z$  427.70 (M+Na).

**7b. diphenyl 2-amino-3-cyano-8-ethoxy-4H-chromen-4-yl****phosphonate**

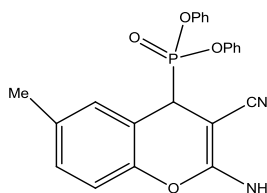
Yield: 92%; yellow solid; mp 178.8-179.7°C. IR (neat): 3385, 3308, 3196, 2189, 1643, 1583, 1484, 1267, 1076, 933  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  (ppm) 7.39 (s, 2H,  $-\text{NH}_2$ ), 7.37 – 6.87 (m, 13H, Ar-H), 4.71 (d,  $J = 16.9$  Hz, 1H, P-CH), 4.12 (q,  $J = 7.0$  Hz, 2H,  $-\text{OCH}_2$ ), 1.34 (t,  $J = 7.0$  Hz, 3H,  $-\text{CH}_3$ ).  $^{13}\text{C-NMR}$  (126 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 163.59, 150.62, 146.94, 140.31, 130.27, 125.59, 124.94, 121.51, 120.72, 120.46, 117.98, 114.18, 64.85, 47.04, 40.00, 39.83, 39.58, 36.95, 35.78, 15.04.  $^{31}\text{P-NMR}$  (202 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 16.06. MS (ESI):  $m/z$  467.04 (M+ $\text{NH}_4^+$ ), 471.93(M+Na).



**7c. diphenyl 2-amino-3-cyano-8-methoxy-4H-chromen-4-yl**

**phosphonate**

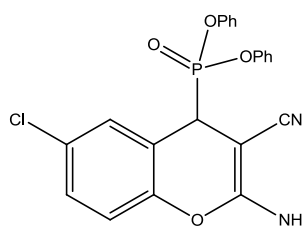
Yield: 92%; yellow solid; mp 177.5-178.7°C. IR (neat): 3441, 3318, 3198, 2189, 1646, 1583, 1486, 1272, 1080, 935  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  (ppm) 7.44 (s, 2H,  $-\text{NH}_2$ ), 7.38 – 6.92 (m, 13H, Ar-H), 4.72 (d,  $J = 16.9$  Hz, 1H, P-CH), 3.83 (s, 3H,  $-\text{OCH}_3$ ).  $^{13}\text{C-NMR}$  (126 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 163.61, 150.61, 147.78, 139.96, 130.28, 125.60, 124.97, 121.42, 120.73, 120.47, 117.91, 112.79, 56.28, 46.92, 39.99, 39.82, 39.66, 39.49, 36.88, 35.70.  $^{31}\text{P-NMR}$  (202 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 16.04. MS (ESI):  $m/z$  457.58 (M+Na).



**7d. diphenyl 2-amino-3-cyano-6-methyl-4H-chromen-4-yl**

**phosphonate**

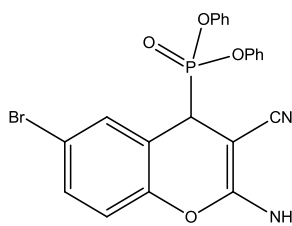
Yield: 93%; white solid; mp 188.6-188.9°C. IR (neat): 3361, 3302, 3186, 2187, 1647, 1588, 1490, 1199, 1060, 933  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  (ppm) 7.38 (d,  $J = 3.3$  Hz, 2H,  $-\text{NH}_2$ ), 7.38 – 6.89 (m, 13H, Ar-H), 4.69 (d,  $J = 16.8$  Hz, 1H, P-CH), 2.27 (s, 3H,  $-\text{CH}_3$ ).  $^{13}\text{C-NMR}$  (126 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 163.77, 150.65, 148.58, 134.16, 130.34, 125.59, 123.20 – 118.88, 117.24 – 113.96, 46.98, 39.84, 39.67, 39.50, 38.14, 36.16, 35.53 – 31.88, 20.72.  $^{31}\text{P-NMR}$  (202 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 16.07. MS (ESI):  $m/z$  441.58 (M+Na).



**7e. diphenyl 2-amino-6-chloro-3-cyano-4H-chromen-4-yl**

**phosphonate**

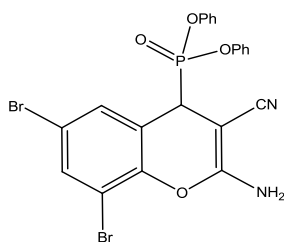
Yield: 90%; white solid; mp 181.1-181.5°C. IR (neat)  $\nu$ : 3352 3302 3181 2189 1648 1590 1485 1258 1053 937  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  (ppm) 7.50 (s,  $J = 2.1$  Hz, 2H, -NH<sub>2</sub>), 7.50 – 6.81 (m, 13H, Ar-H), 4.84 (d,  $J = 17.7$  Hz, 1H, P-CH).  $^{13}\text{C-NMR}$  (126 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 163.41, 150.50, 149.42, 130.39, 129.73, 128.66, 125.76, 120.60, 120.17, 119.21, 118.62, 46.66, 40.46, 39.96, 39.79, 39.65, 39.54, 36.48, 35.31.  $^{31}\text{P-NMR}$  (202 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 15.38. MS (ESI):  $m/z$  462.06 (M+Na).



**7f. diphenyl 2-amino-6-bromo-3-cyano-4H-chromen-4-yl**

**phosphonate**

Yield: 89%; white solid; mp 175.5-176.1°C. IR (neat): 3346, 3300, 3182, 2190, 1646, 1601, 1485, 1260, 1191, 937  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  (ppm) 7.59 (ddd,  $J = 8.7, 5.5, 2.3$  Hz, 2H, Ar-H), 7.53 (s, 2H, -NH<sub>2</sub>), 7.47 – 6.85 (m, 11H, Ar-H), 4.85 (d,  $J = 17.7$  Hz, 1H, P-CH).  $^{13}\text{C-NMR}$  (126 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 163.37, 154.48 – 145.91, 132.65, 130.39, 125.75, 120.60, 120.16, 118.97, 116.50, 46.68, 39.99, 39.82, 39.66, 39.49, 36.36, 35.16 – 31.88.  $^{31}\text{P-NMR}$  (202 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 15.42. MS (ESI):  $m/z$  507.49 (M+Na).

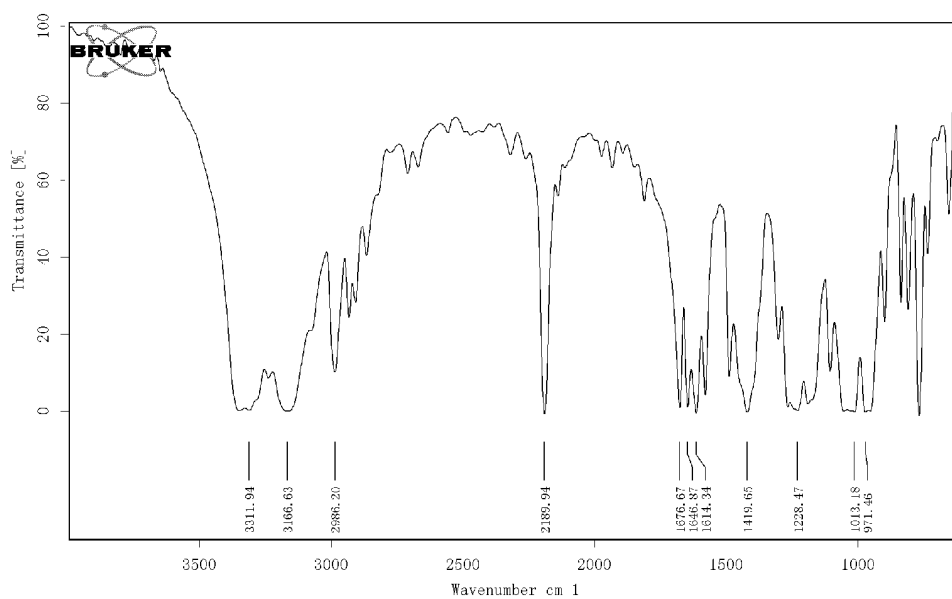


**7g. diphenyl 2-amino-6,8-dibromo-3-cyano-4H-chromen-4-**

**ylphosphonate**

Yield: 85%; yellow solid; mp 175.3-176.5 °C. IR (neat): 3439, 3337, 3072, 2194, 1735, 1648, 1419, 1244, 1034, 937  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  (ppm) 7.94 (t,  $J = 2.2$  Hz, 1H, Ar-H), 7.67 (s, 2H,  $-\text{NH}_2$ ), 7.65 – 6.95 (m, 11H, Ar-H), 4.92 (d,  $J = 18.1$  Hz, 1H, P-CH).  $^{13}\text{C-NMR}$  (126 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 163.40, 146.73, 135.91, 131.47, 130.43, 122.18, 119.17, 117.06, 113.14, 111.33, 49.30, 39.98, 39.81, 39.65, 39.48, 37.54, 32.75.  $^{31}\text{P-NMR}$  (202 MHz,  $\text{DMSO-d}_6$ )  $\delta$ : 14.90. MS (ESI):  $m/z$  585.62 ( $\text{M}+\text{Na}$ ).

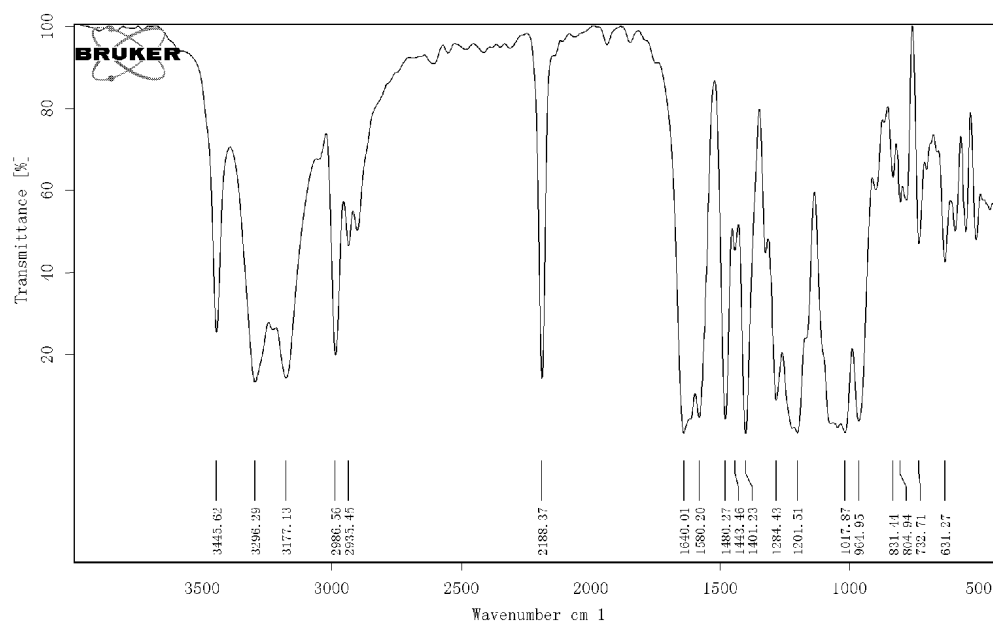
## Copies of IR Spectra for Compounds 4



C:\OPUS 7.0.129\WFAS\Sample description.238	Sample description	Instrument type and / or accessory	2014-3-5
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Page 1 of 1

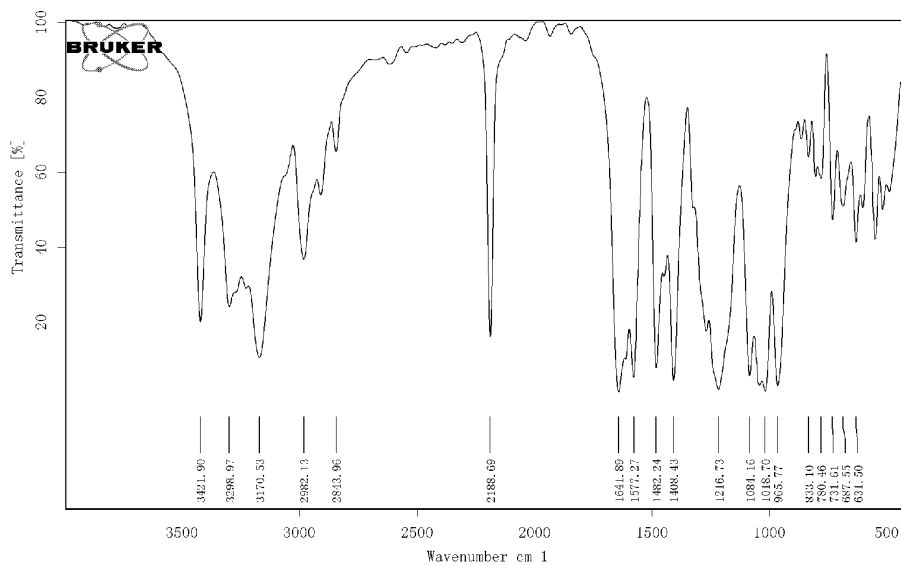
## 4a.diethyl 2-amino-3-cyano-4H-chromen-4-ylphosphonate



C:\OPUS 7.0.129\WFAS\Sample description.646	Sample description	Instrument type and / or accessory	2014-5-6
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Page 1 of 1

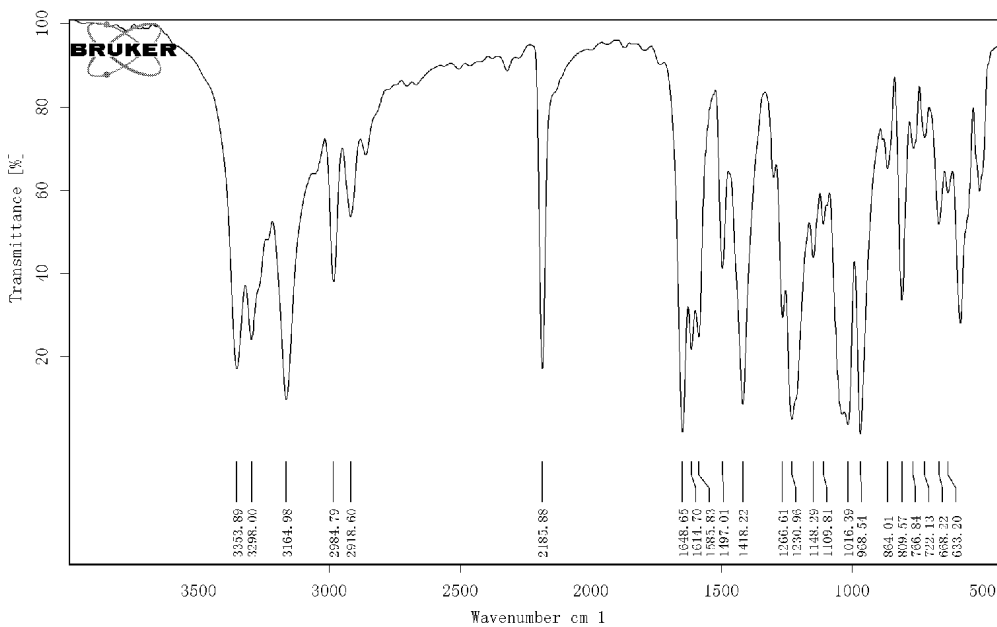
## 4b.diethyl 2-amino-3-cyano-8-ethoxy-4H-chromen-4-ylphosphonate



C:\OPUS 7.0.129\WFAS\Sample description.647	Sample description	Instrument type and / or accessory	2014-5-6
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Page 1 of 1

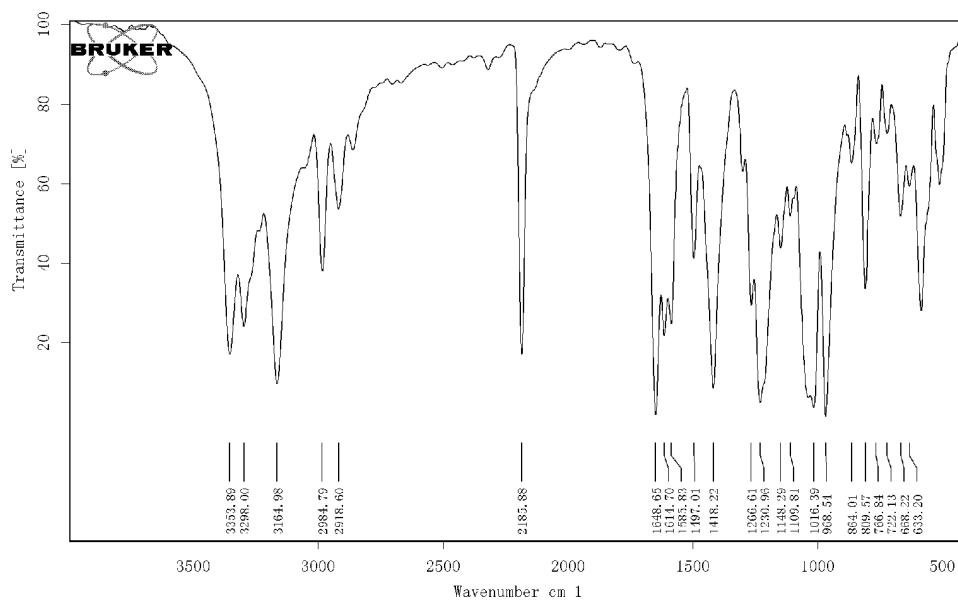
**4c. diethyl 2-amino-3-cyano-8-methoxy-4H-chromen-4-ylphosphonate**



C:\OPUS 7.0.129\WFAS\Sample description.645	Sample description	Instrument type and / or accessory	2014-3-6
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Page 1 of 1

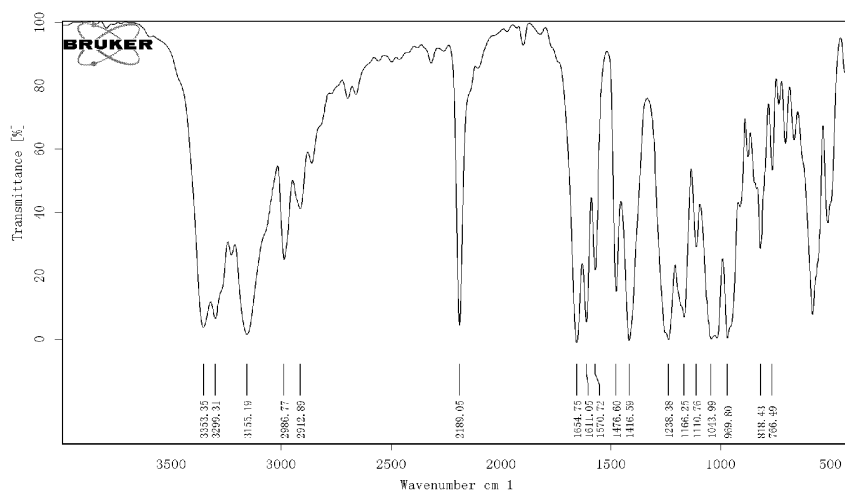
**4d. diethyl 2-amino-3-cyano-6-methyl-4H-chromen-4-ylphosphonate**



C:\VOPUS 7.0.129\MEAS\Sample description.645	Sample description	Instrument type and / or accessory	2014-5-6
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Page 1 of 1

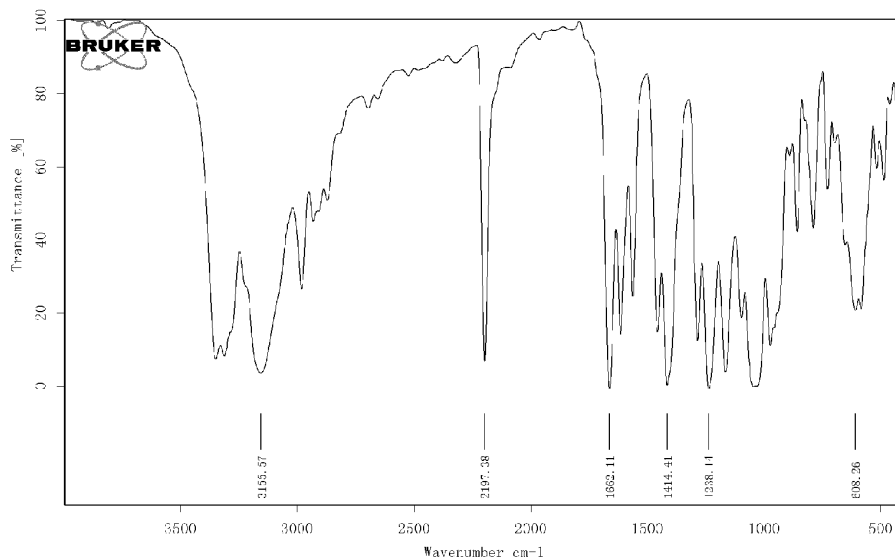
**4e. diethyl 2-amino-6-chloro-3-cyano-4H-chromen-4-ylphosphonate**



C:\VOPUS 7.0.129\MEAS\Sample description.648	Sample description	Instrument type and / or accessory	2014-5-6
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Page 1 of 1

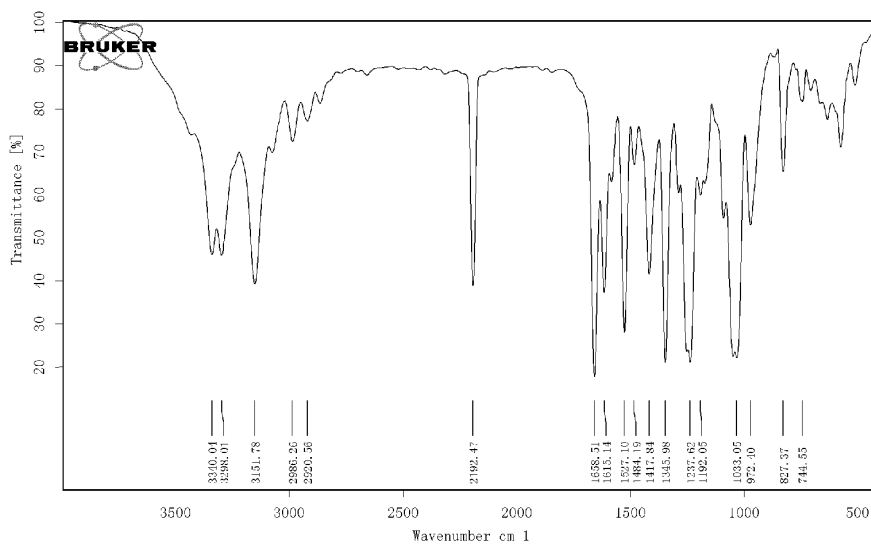
**4f. diethyl 2-amino-6-bromo-3-cyano-4H-chromen-4-ylphosphonate**



C:\OPUS 7.0.129\MEAS\Sample description.643	Sample description	Instrument type and / or accessory	2014 5 6
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**4g. diethyl 2-amino-6, 8-dibromo-3-cyano-4H-chromen-4-ylphosphonate**

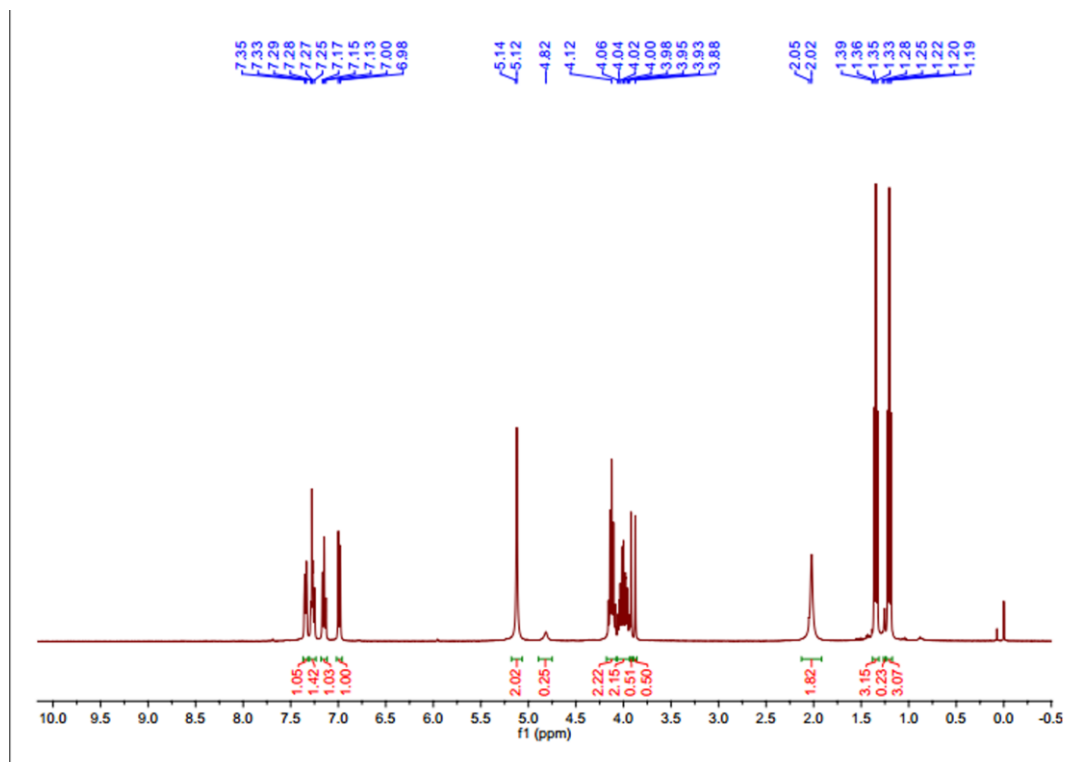


C:\OPUS 7.0.129\MEAS\Sample description.644	Sample description	Instrument type and / or accessory	2014-5-6
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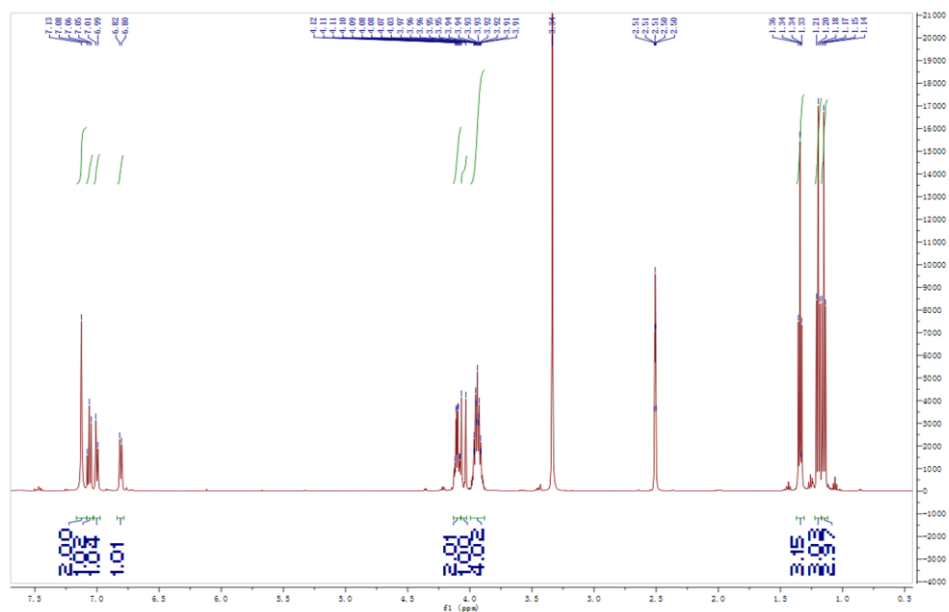
Page 1 of 1

**4h. diethyl 2-amino-3-cyano-6-nitro-4H-chromen-4-ylphosphonate**

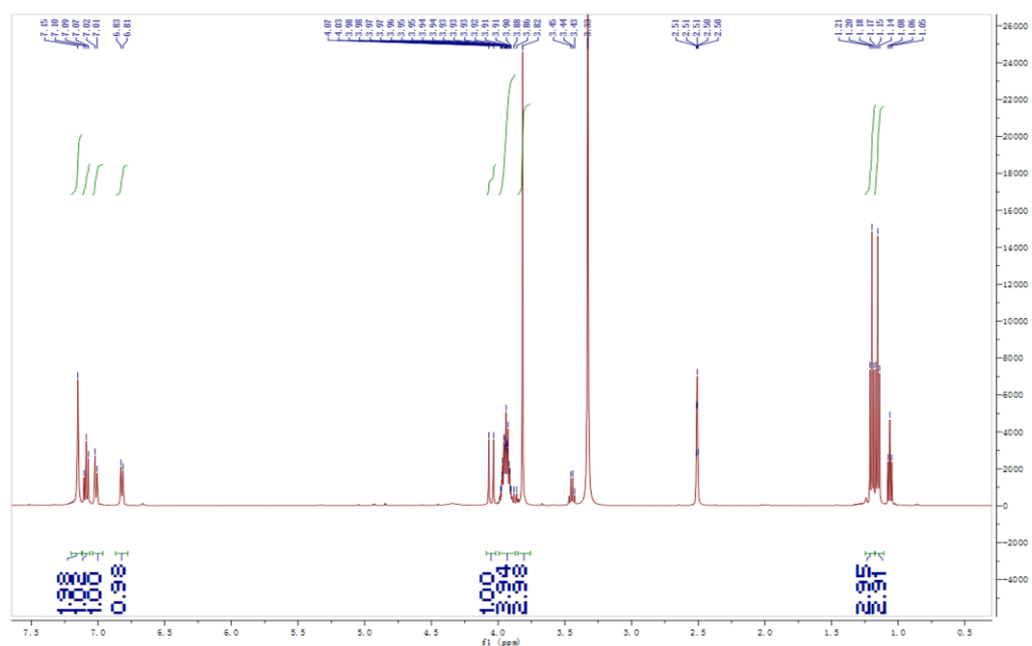


Copies of  $^1\text{H-NMR}$  Spectra for Compounds 4

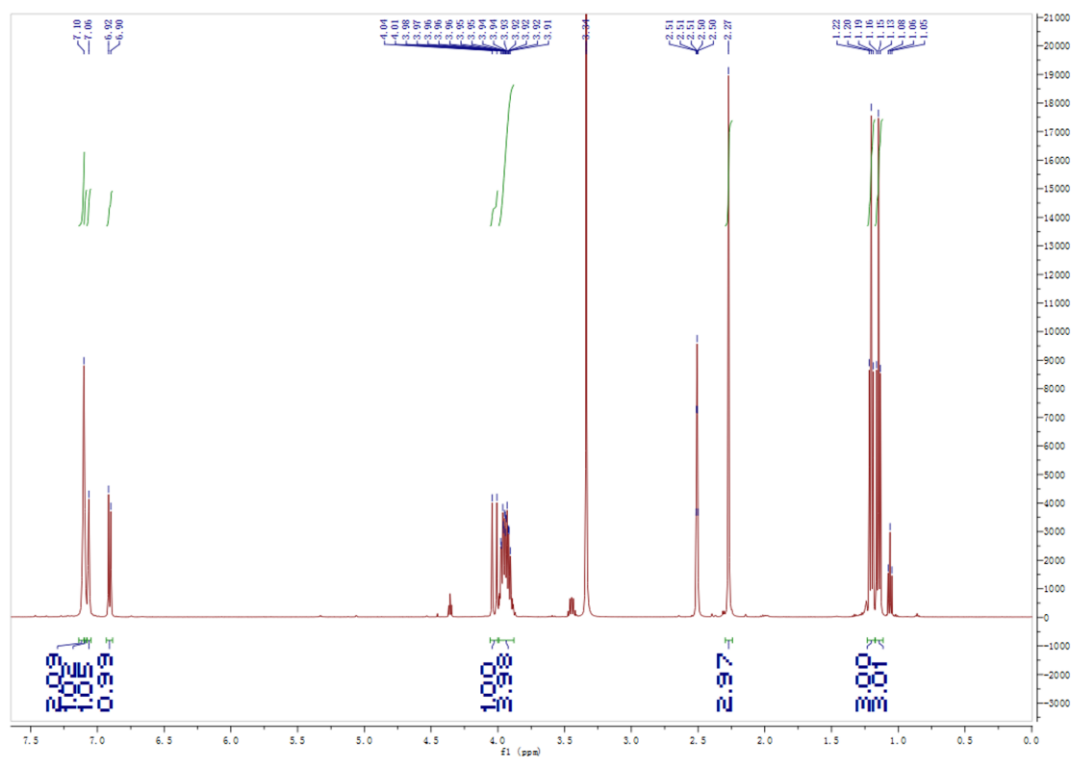
4a. diethyl 2-amino-3-cyano-4H-chromen-4-ylphosphonate



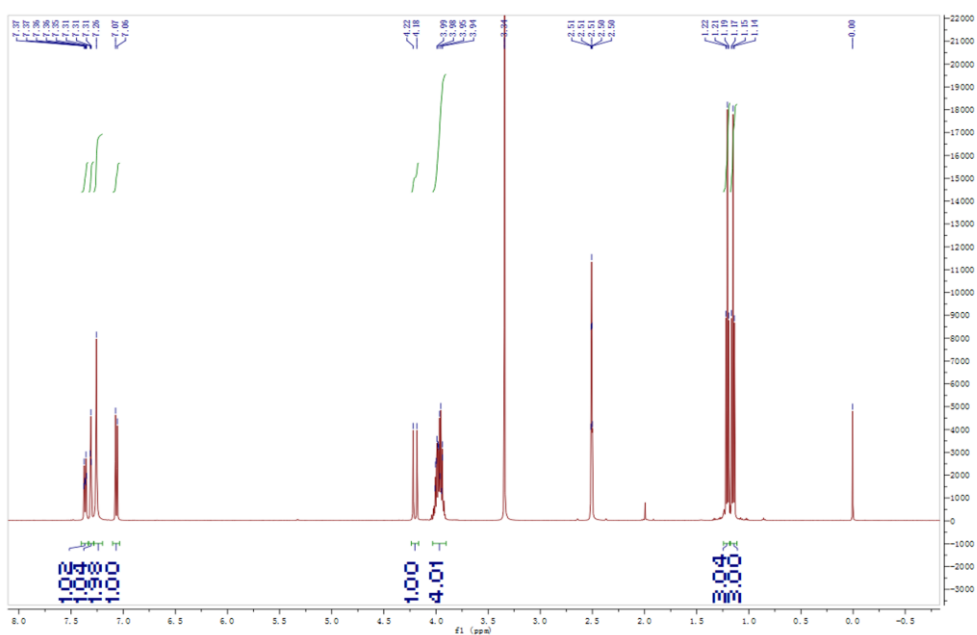
4b. diethyl 2-amino-3-cyano-8-ethoxy-4H-chromen-4-ylphosphonate



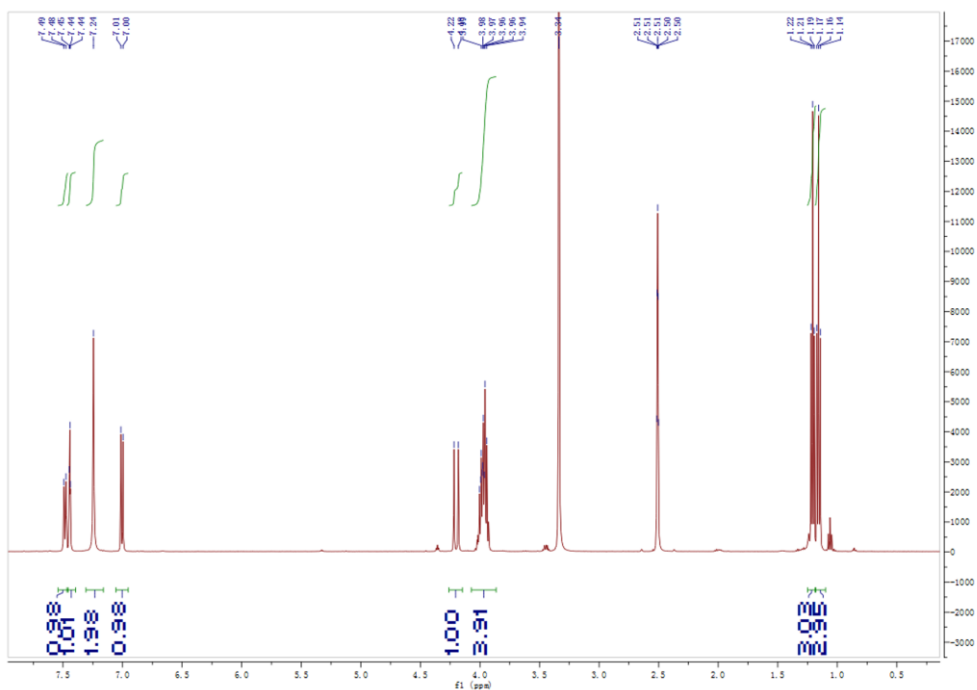
4c. diethyl 2-amino-3-cyano-8-methoxy-4H-chromen-4-ylphosphonate



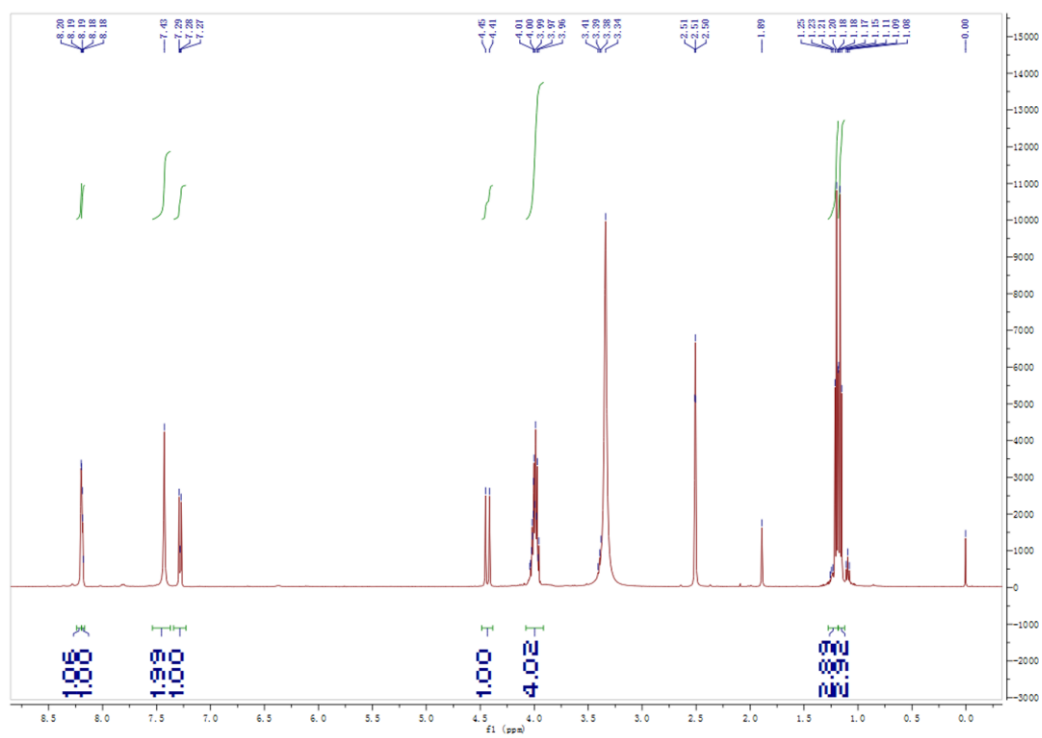
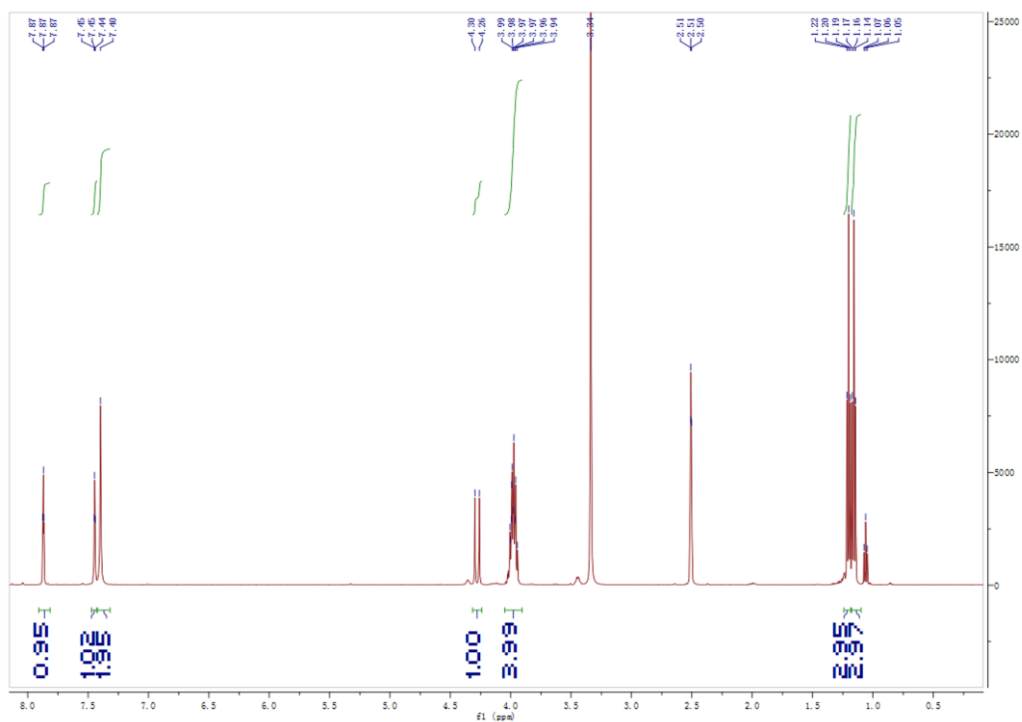
4d. diethyl 2-amino-3-cyano-6-methyl-4H-chromen-4-ylphosphonate

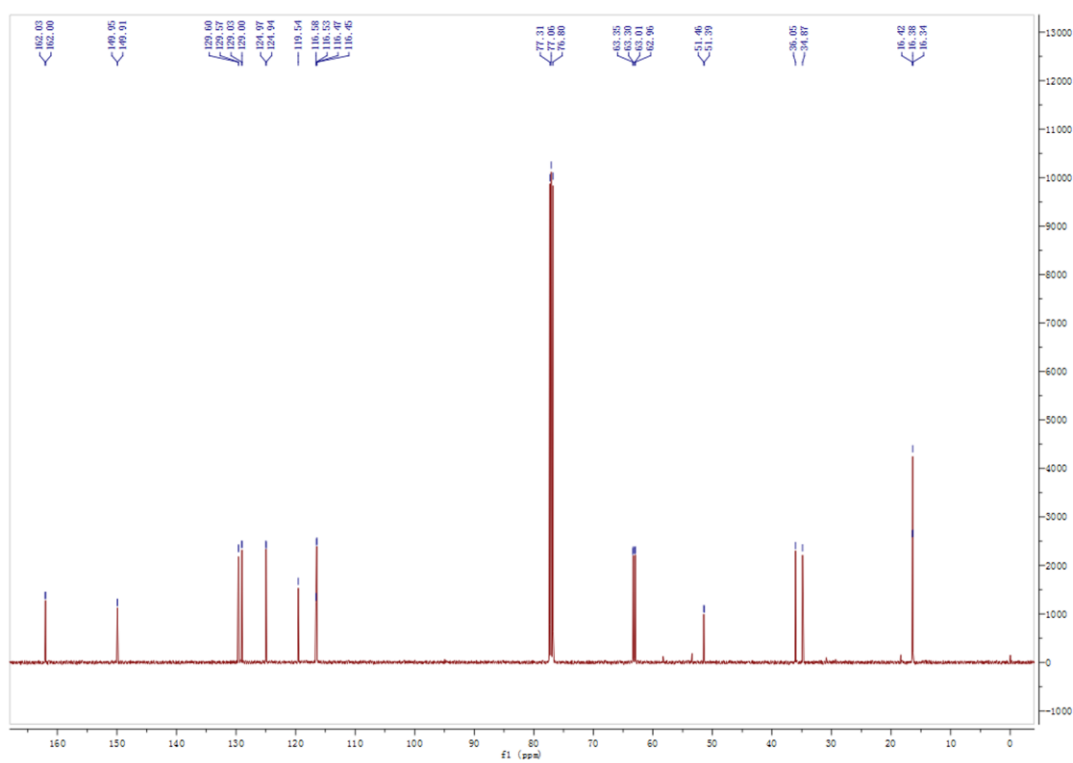


4e. diethyl 2-amino-6-chloro-3-cyano-4H-chromen-4-ylphosphonate

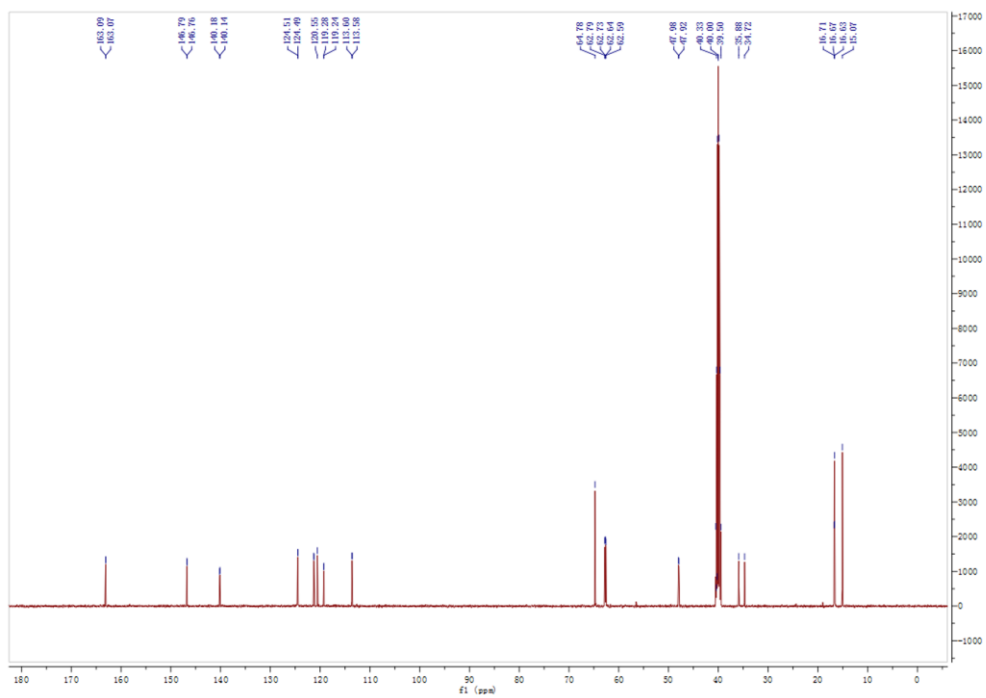


4f. diethyl 2-amino-6-bromo-3-cyano-4H-chromen-4-ylphosphonate

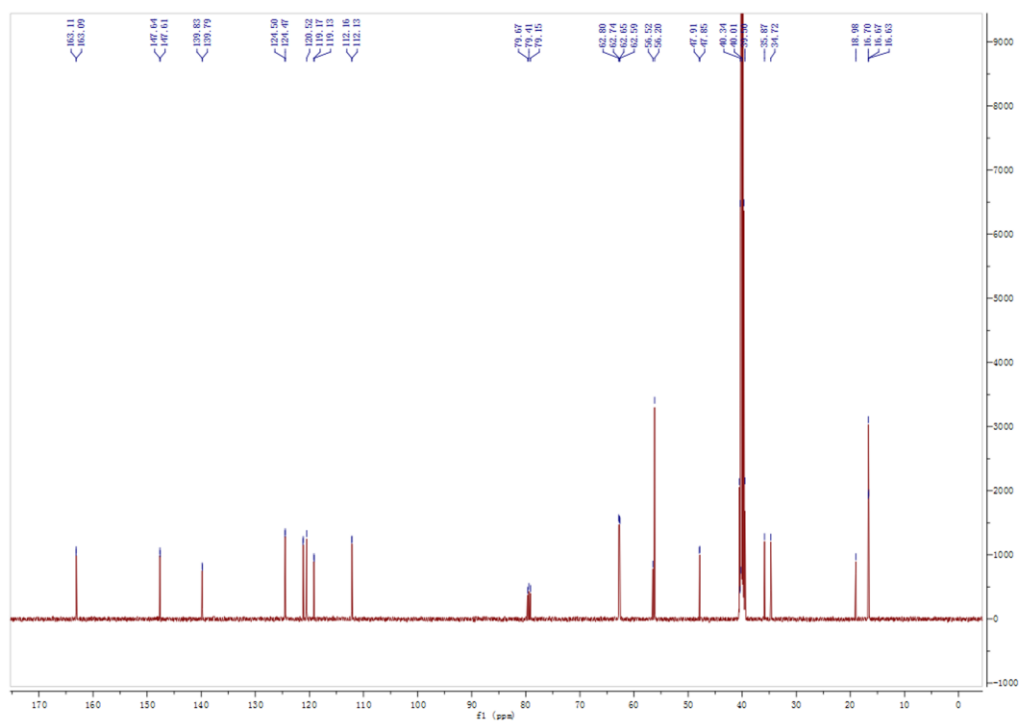


Copies of  $^{13}\text{C}$ -NMR Spectra for Compounds 4

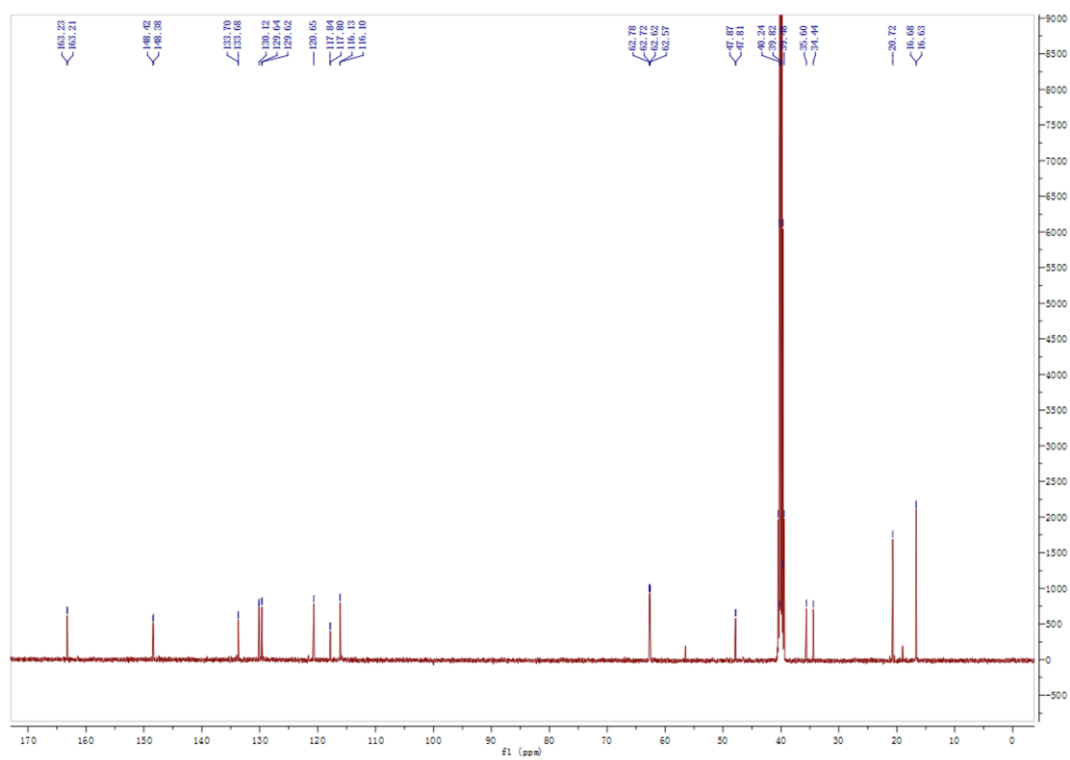
4a, diethyl 2-amino-3-cyano-4H-chromen-4-ylphosphonate



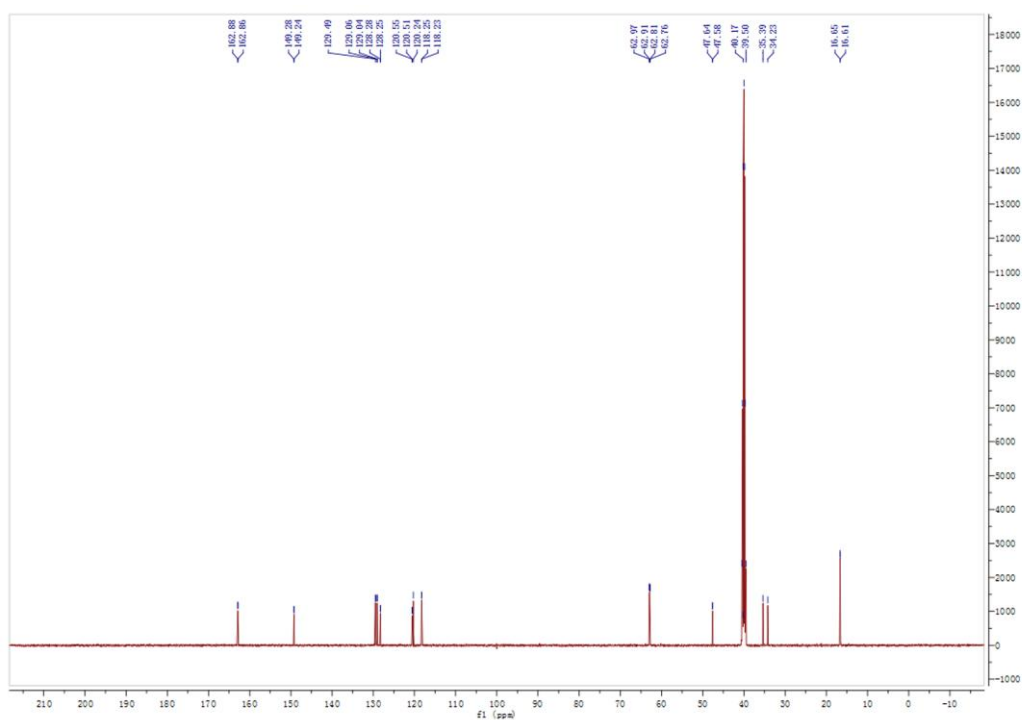
4b, diethyl 2-amino-3-cyano-8-ethoxy-4H-chromen-4-ylphosphonate



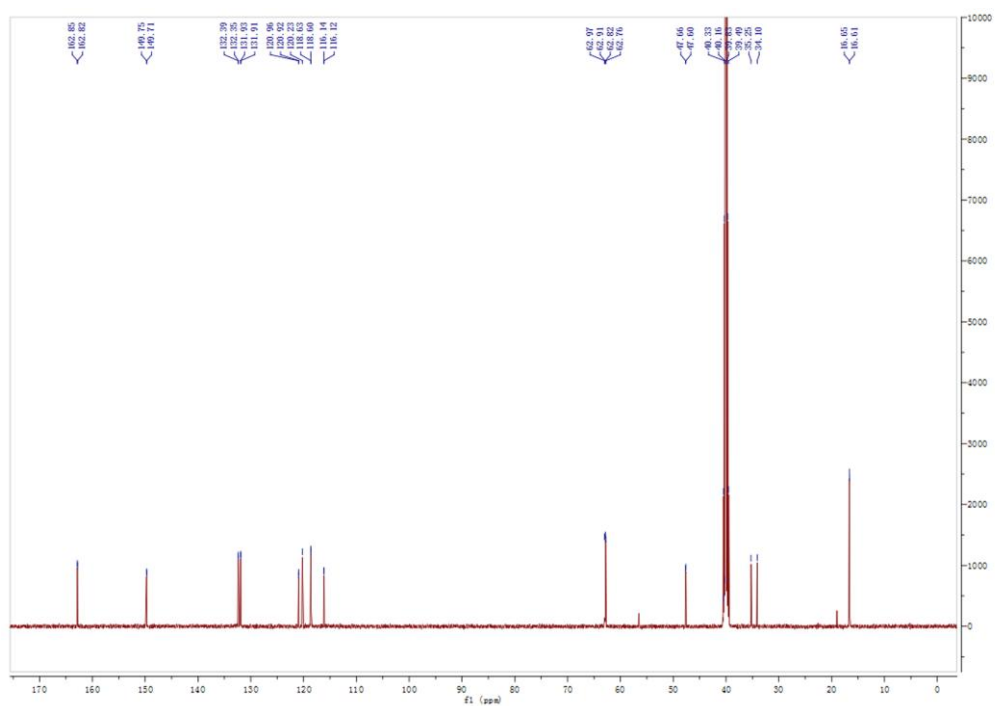
4c. diethyl 2-amino-3-cyano-8-methoxy-4H-chromen-4-ylphosphonate



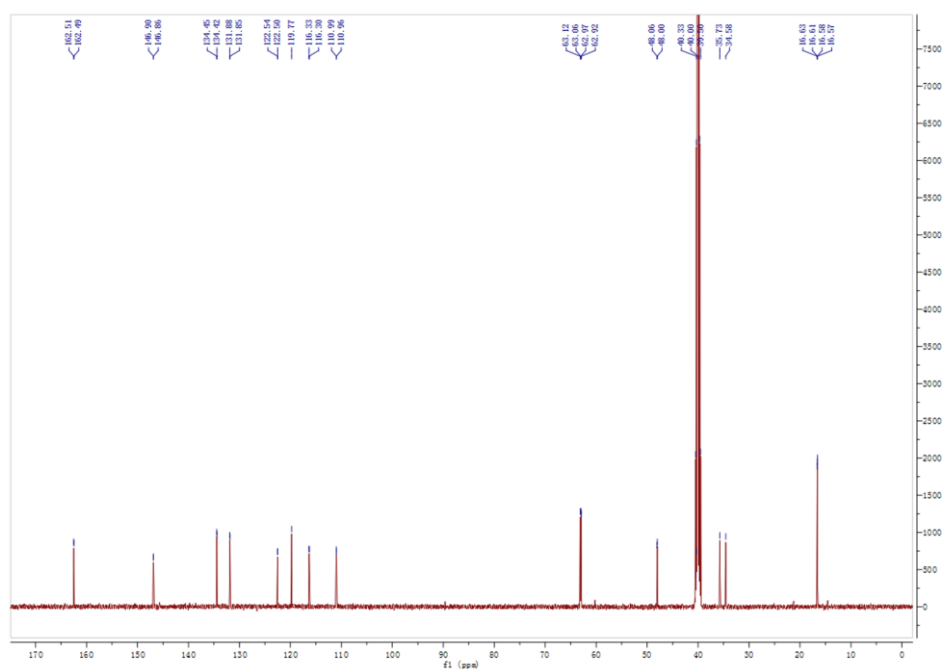
4d. diethyl 2-amino-3-cyano-6-methyl-4H-chromen-4-ylphosphonate



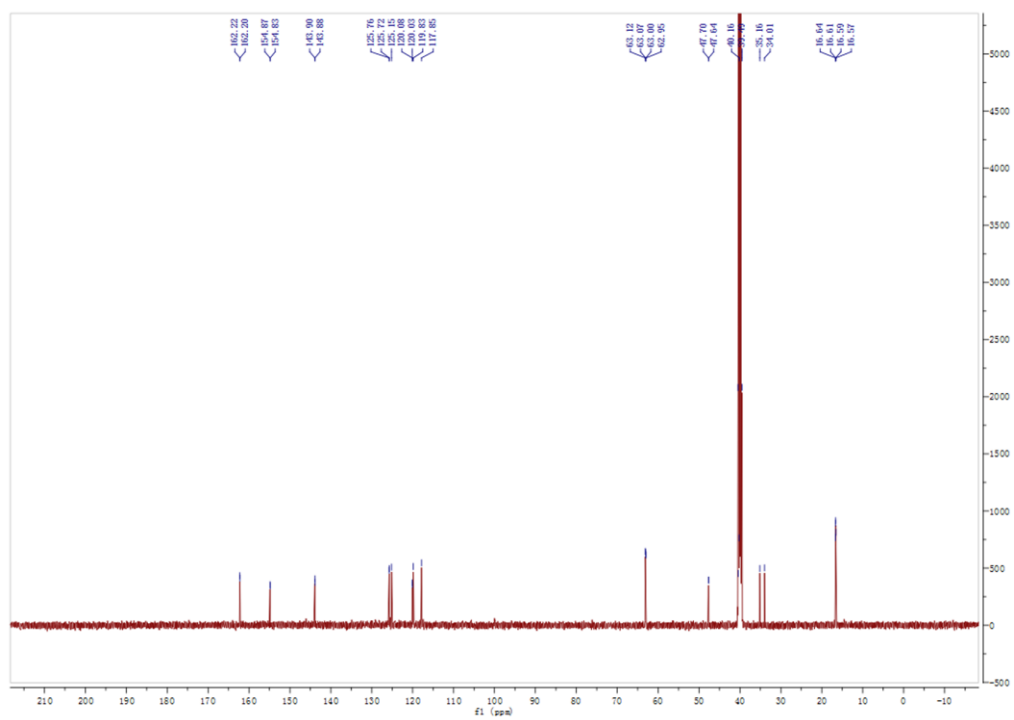
4e. diethyl 2-amino-6-chloro-3-cyano-4H-chromen-4-ylphosphonate



4f. diethyl 2-amino-6-bromo-3-cyano-4H-chromen-4-ylphosphonate

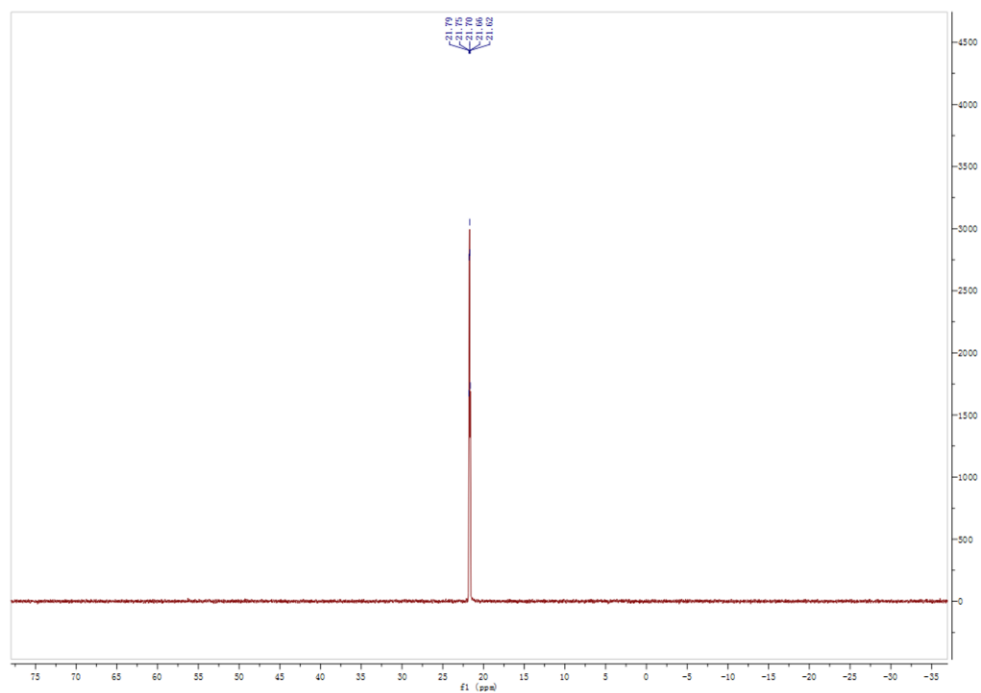
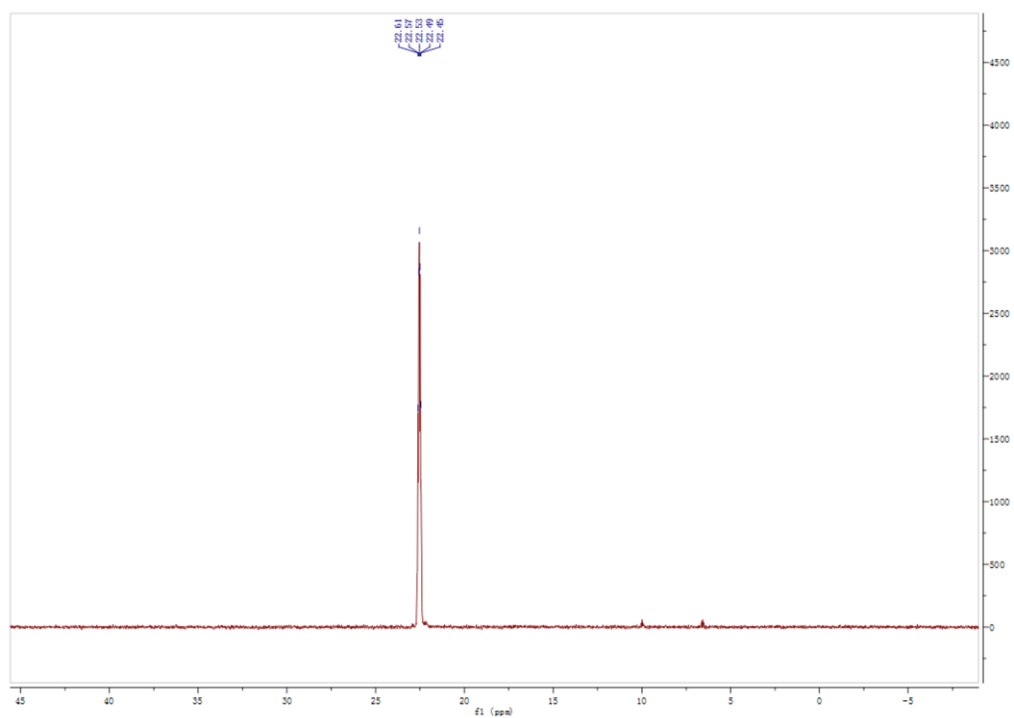


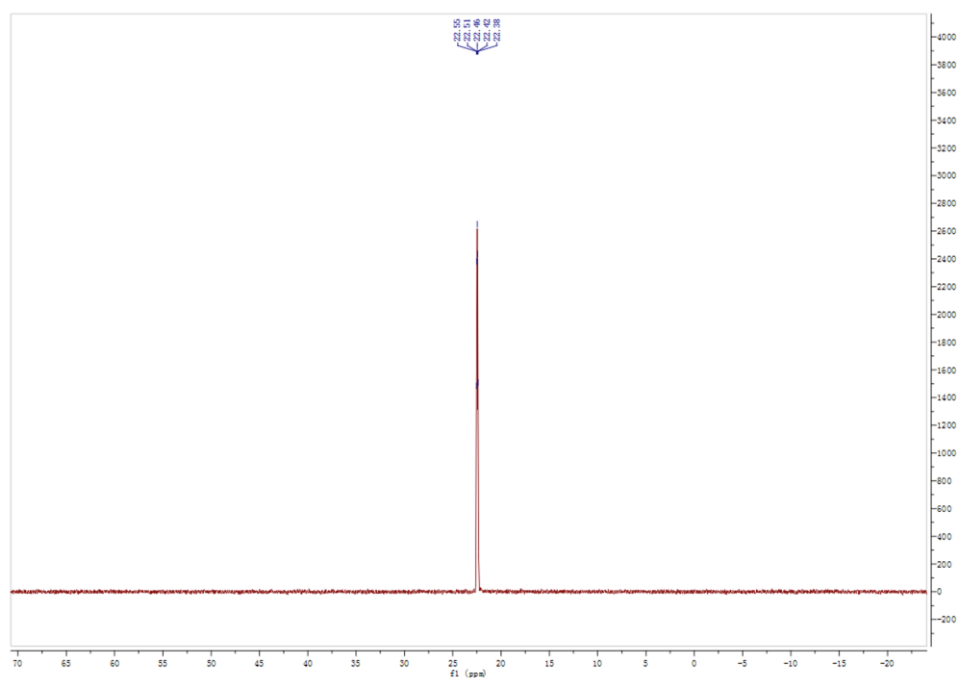
**4g. diethyl 2-amino-6, 8-dibromo-3-cyano-4H-chromen-4-ylphosphonate**



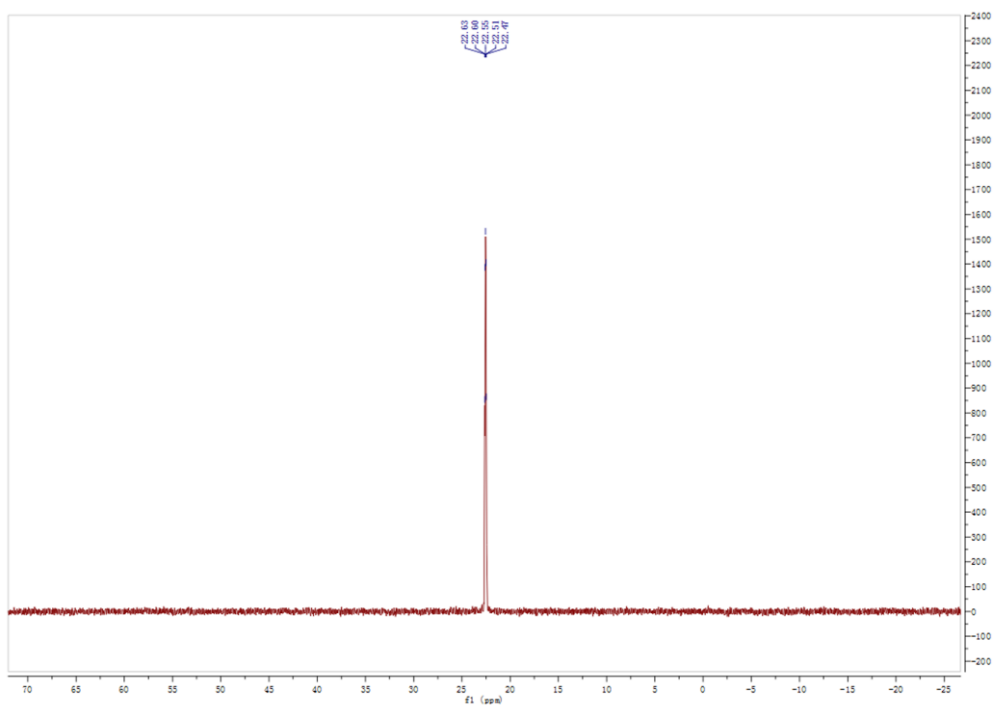
**4h. diethyl 2-amino-3-cyano-6-nitro-4H-chromen-4-ylphosphonate**



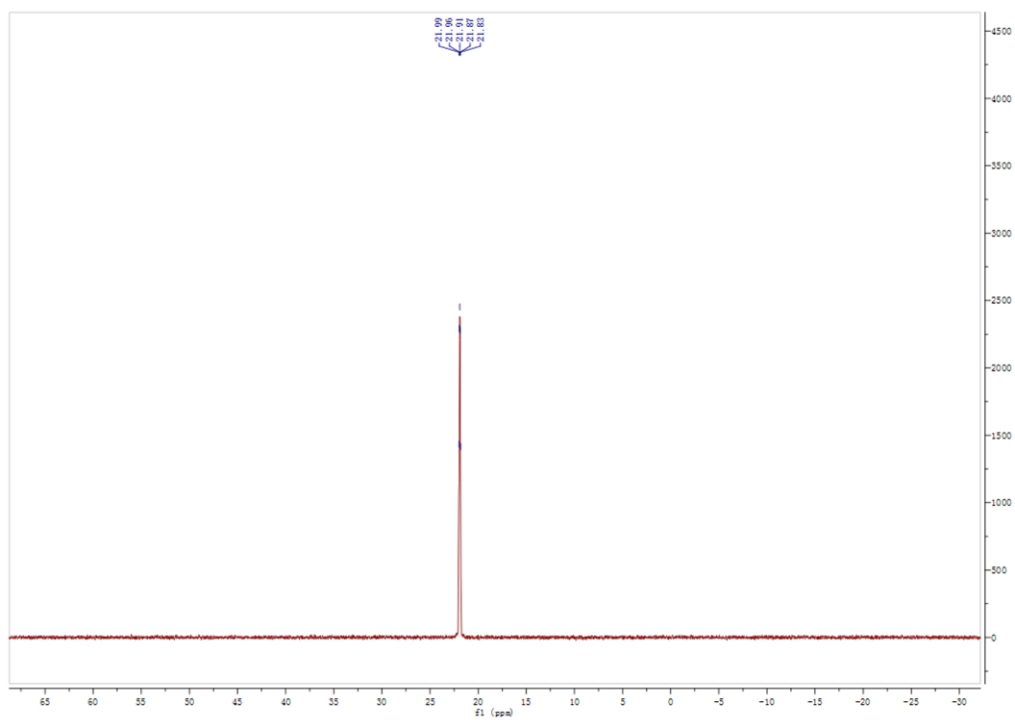
Copies of  $^{31}\text{P}$ -NMR Spectra for Compounds 4**4a. diethyl 2-amino-3-cyano-4H-chromen-4-ylphosphonate****4b. diethyl 2-amino-3-cyano-8-ethoxy-4H-chromen-4-ylphosphonate**



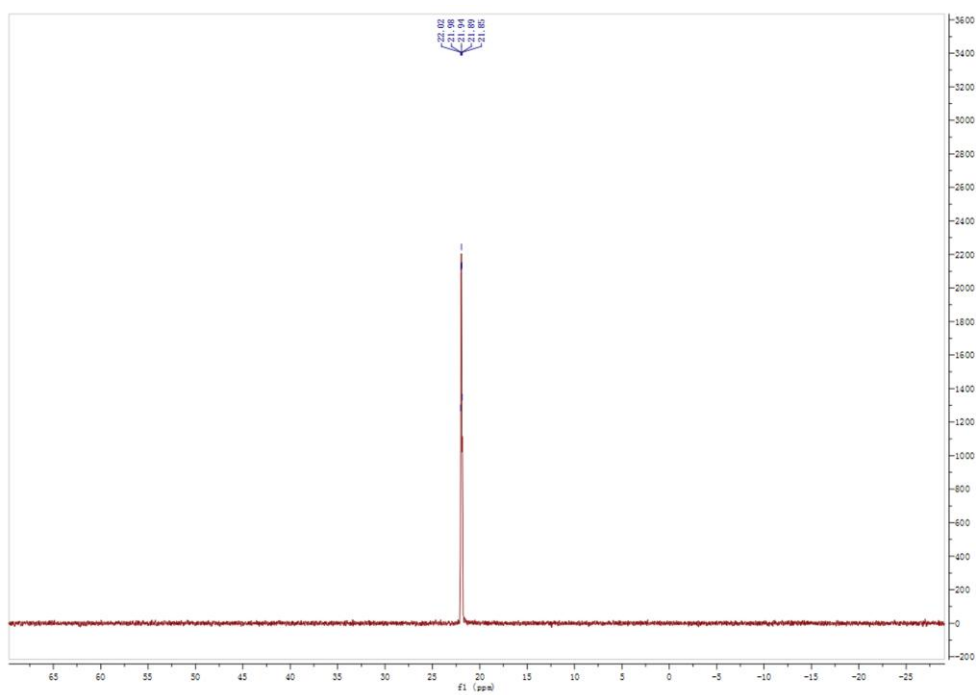
**4c. diethyl 2-amino-3-cyano-8-methoxy-4H-chromen-4-ylphosphonate**



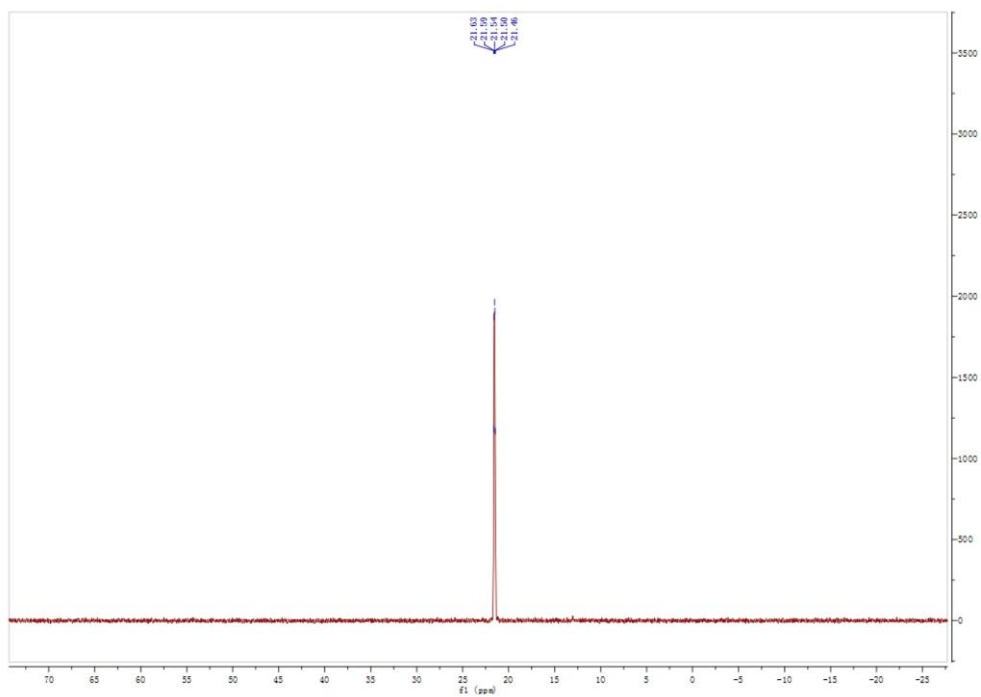
**4d. diethyl 2-amino-3-cyano-6-methyl-4H-chromen-4-ylphosphonate**



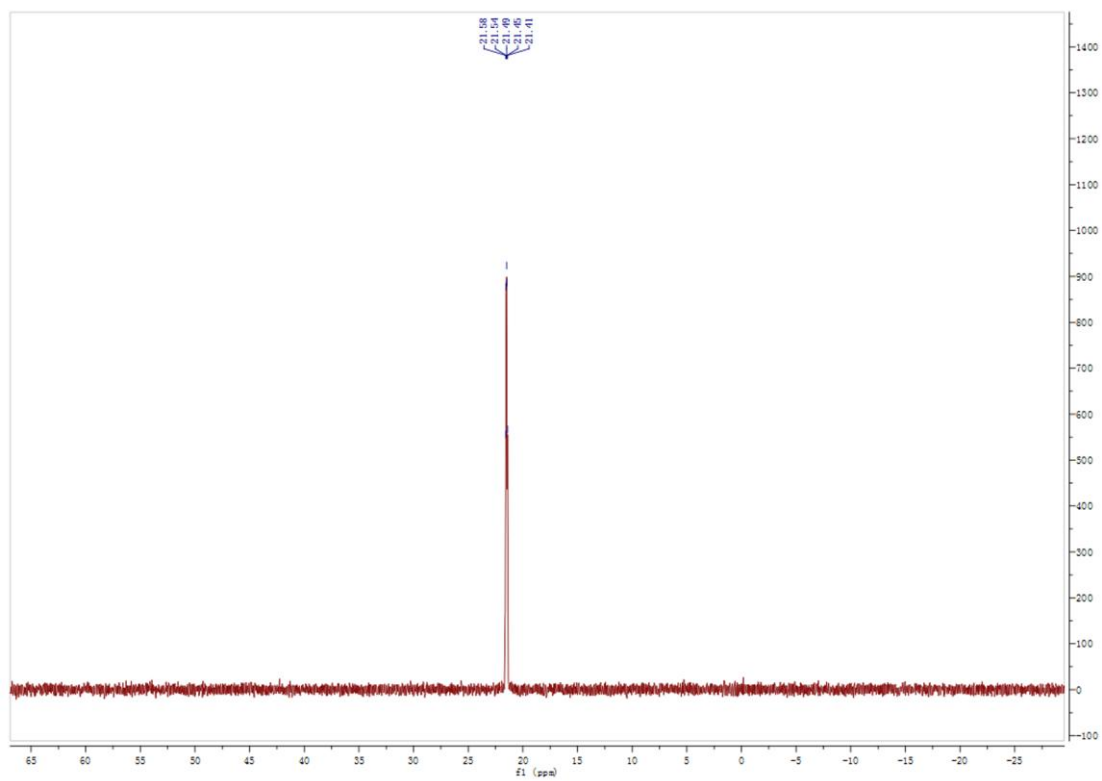
**4e.** diethyl 2-amino-6-chloro-3-cyano-4H-chromen-4-ylphosphonate



**4f.** diethyl 2-amino-6-bromo-3-cyano-4H-chromen-4-ylphosphonate



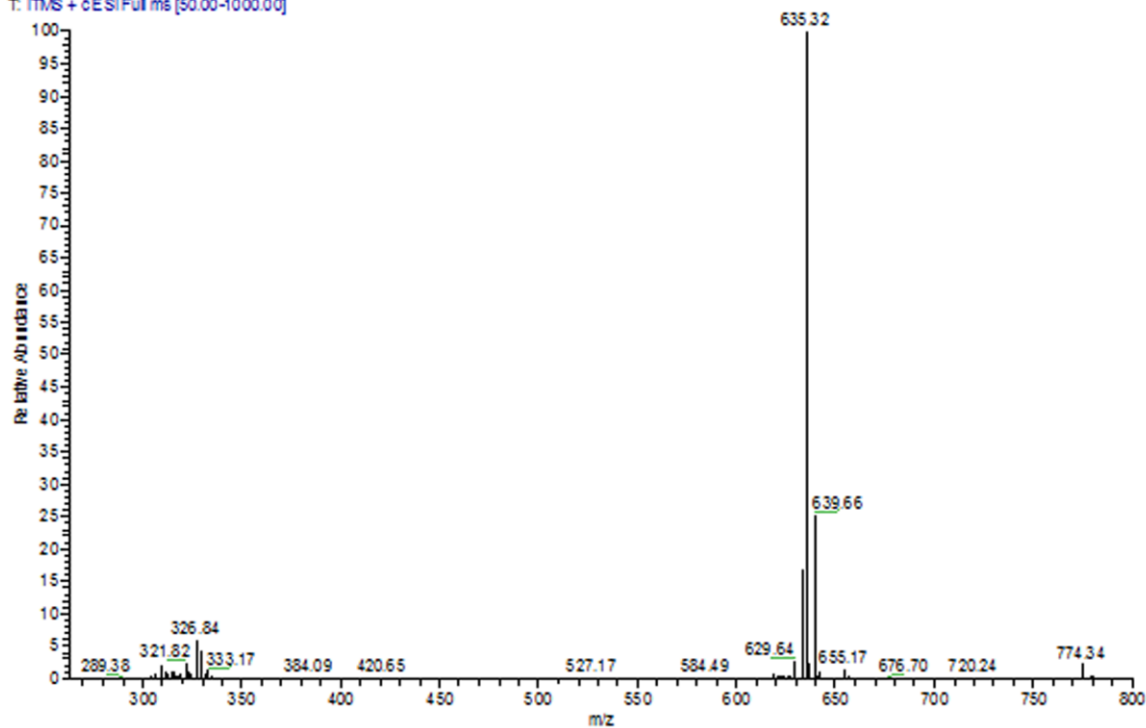
**4g. diethyl 2-amino-6, 8-dibromo-3-cyano-4H-chromen-4-ylphosphonate**



**4h. diethyl 2-amino-3-cyano-6-nitro-4H-chromen-4-ylphosphonate**

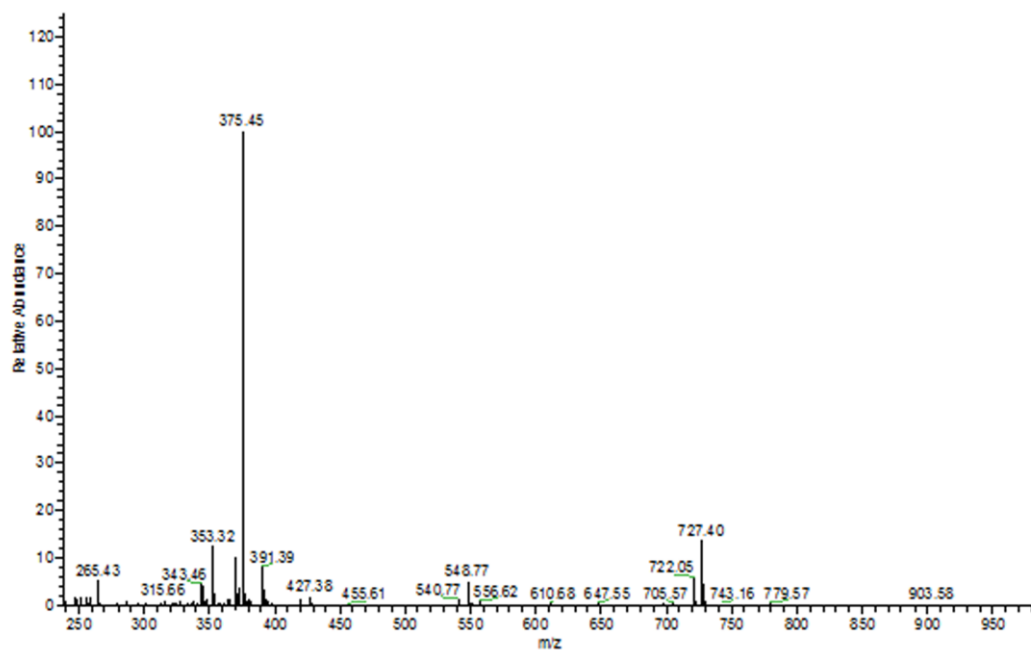
## Copies of MS Spectra for Compounds 4

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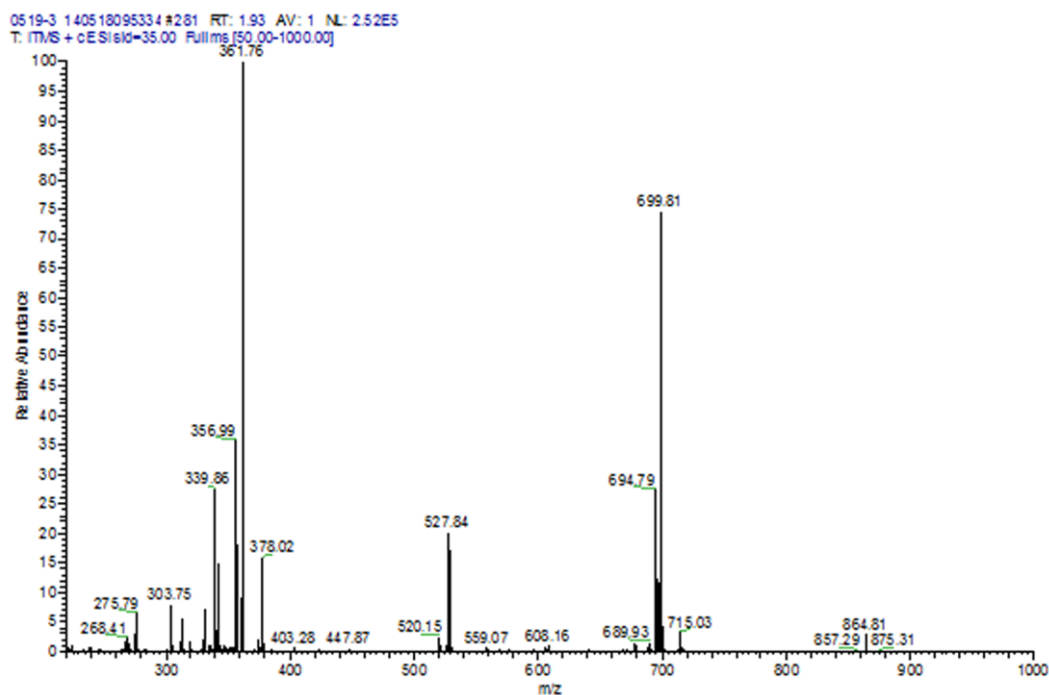


4a, diethyl 2-amino-3-cyano-4H-chromen-4-ylphosphonate

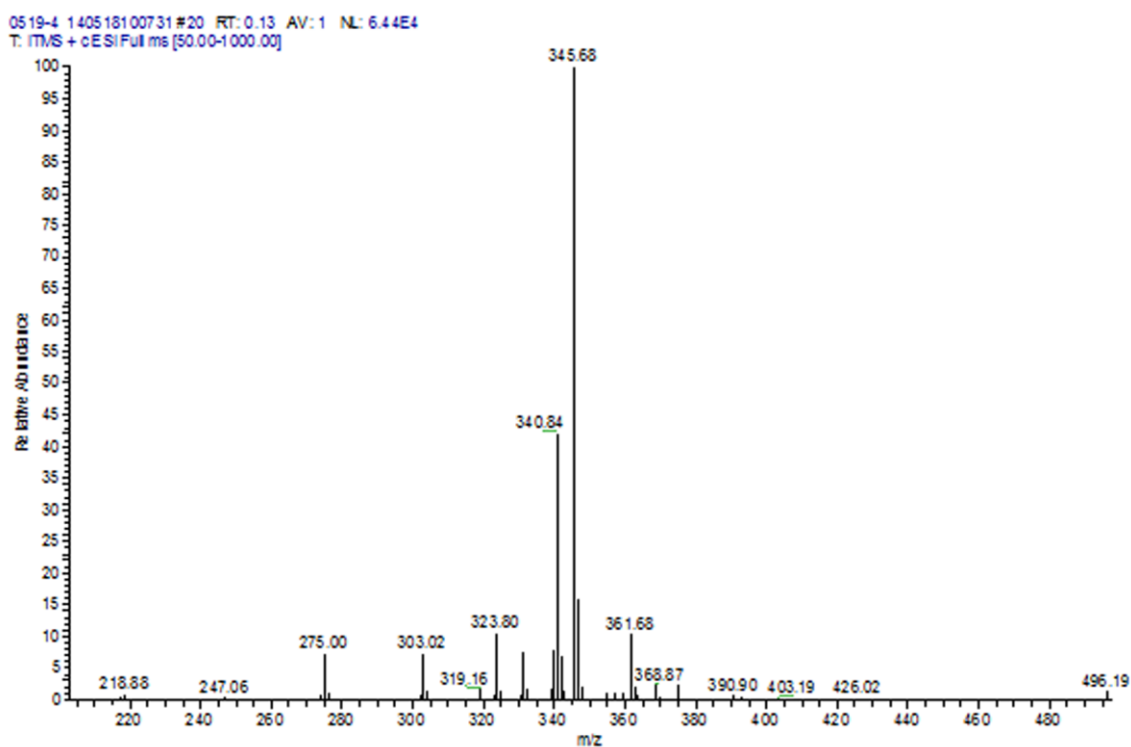
0519-2 140518095334 #270 RT: 1.81 AV: 1 NL: 1.14E5  
T: ITMS + cESI 6id=35.00 Full ms [50.00-1000.00]



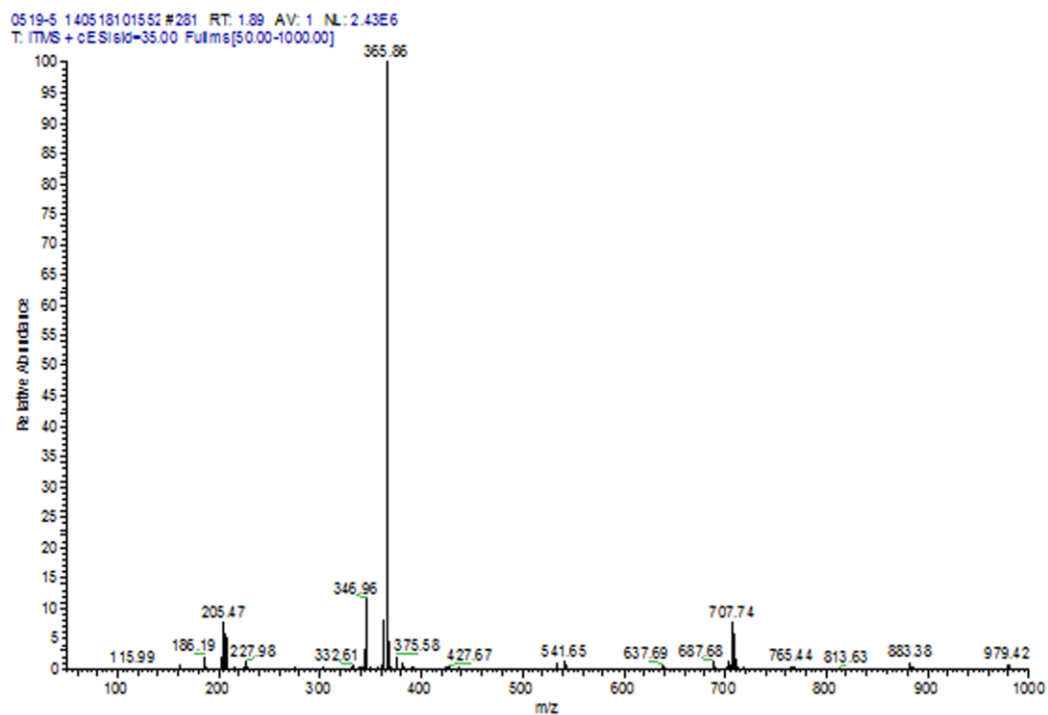
4b, diethyl 2-amino-3-cyano-8-ethoxy-4H-chromen-4-ylphosphonate



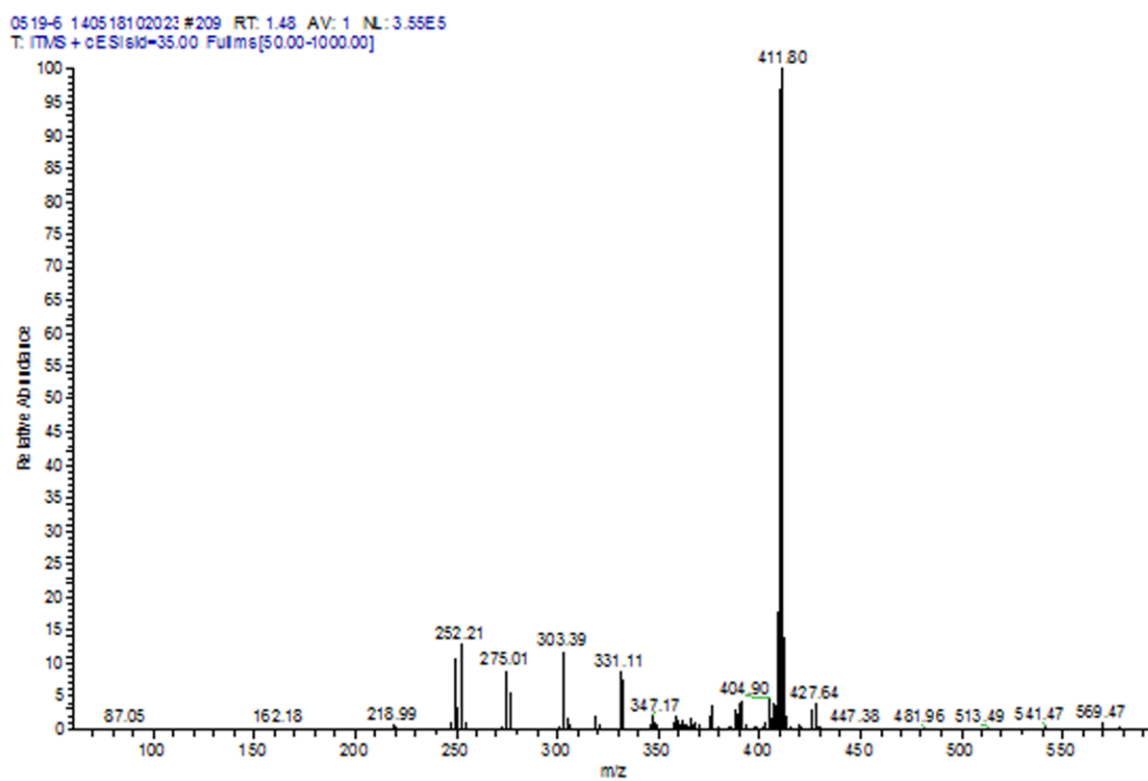
4c. diethyl 2-amino-3-cyano-8-methoxy-4H-chromen-4-ylphosphonate



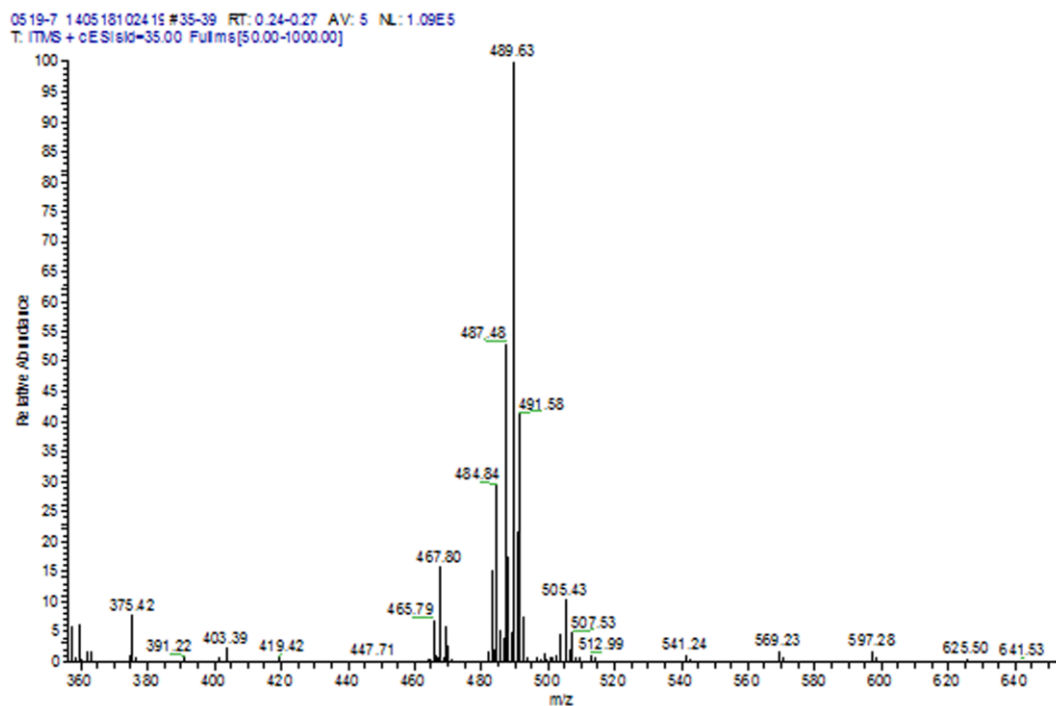
4d. diethyl 2-amino-3-cyano-6-methyl-4H-chromen-4-ylphosphonate



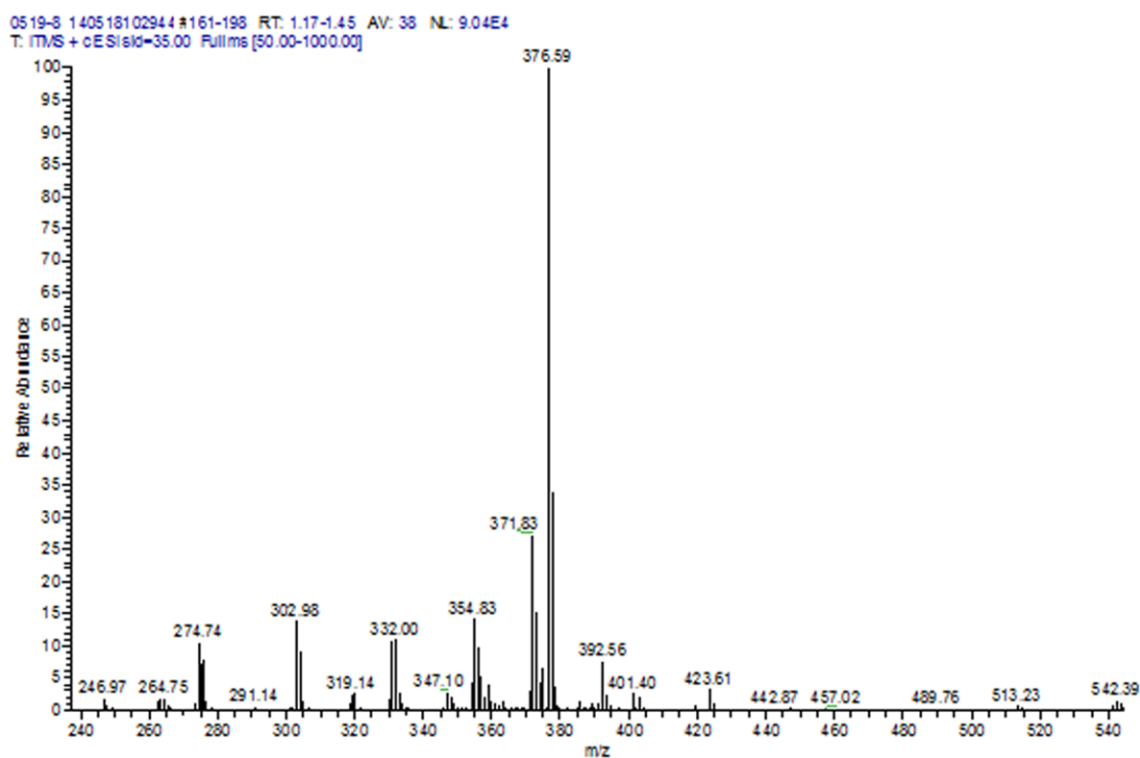
4e. diethyl 2-amino-6-chloro-3-cyano-4H-chromen-4-ylphosphonate



4f. diethyl 2-amino-6-bromo-3-cyano-4H-chromen-4-ylphosphonate



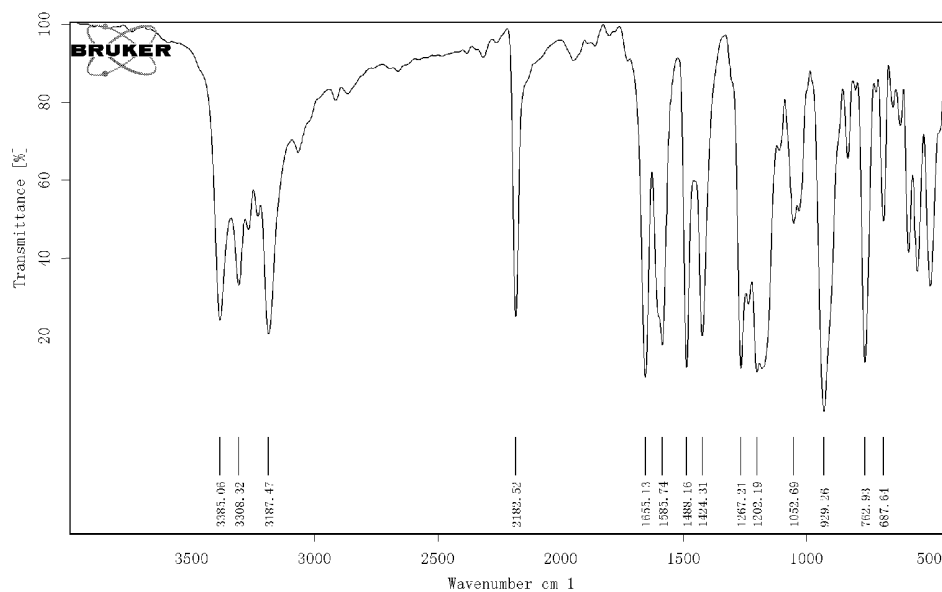
4g. diethyl 2-amino-6, 8-dibromo-3-cyano-4H-chromen-4-ylphosphonate



4h. diethyl 2-amino-3-cyano-6-nitro-4H-chromen-4-ylphosphonate



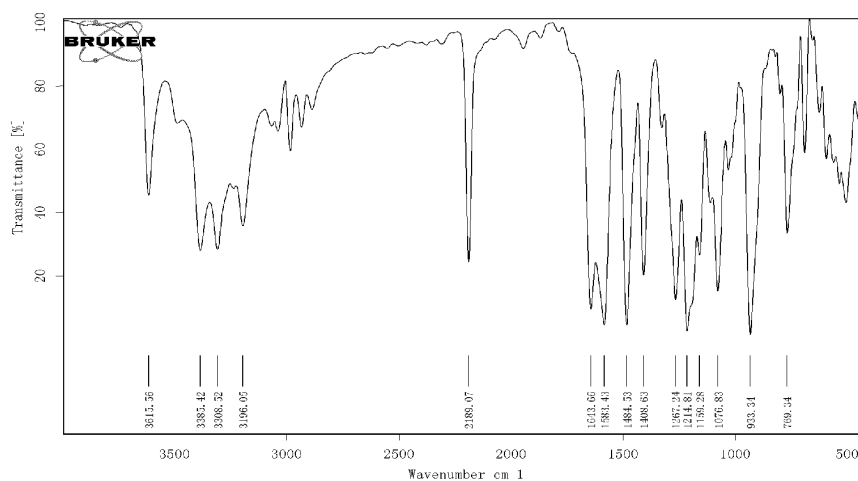
## Copies of IR Spectra for Compounds 7



C:\OPUS 7.0.129\MEAS\Sample description.650	Sample description	Instrument type and / or accessory	2014-5-6
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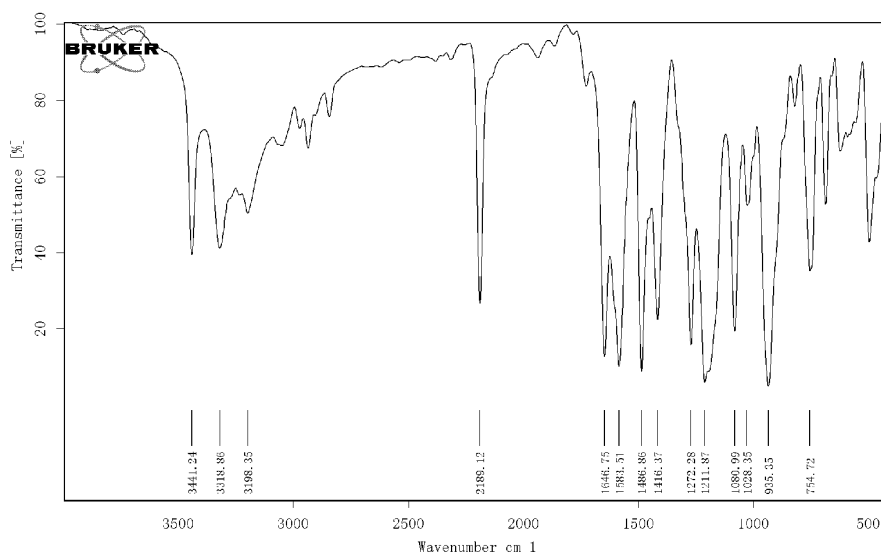
## 7a.diphenyl 2-amino-3-cyano-4H-chromen-4-ylphosphonate



C:\OPUS 7.0.129\MEAS\Sample description.652	Sample description	Instrument type and / or accessory	2014-5-6
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## 7b.diphenyl 2-amino-3-cyano-8-ethoxy-4H-chromen-4-ylphosphonate



C:\VOPUS 7.0.129\MEAS\Sample description.653

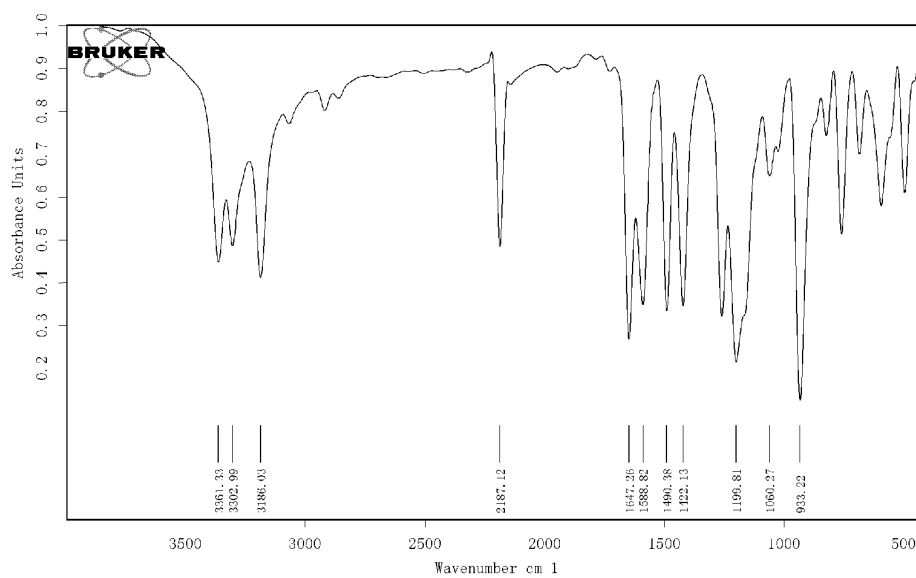
Sample description

Instrument type and / or accessory

2014-5-6

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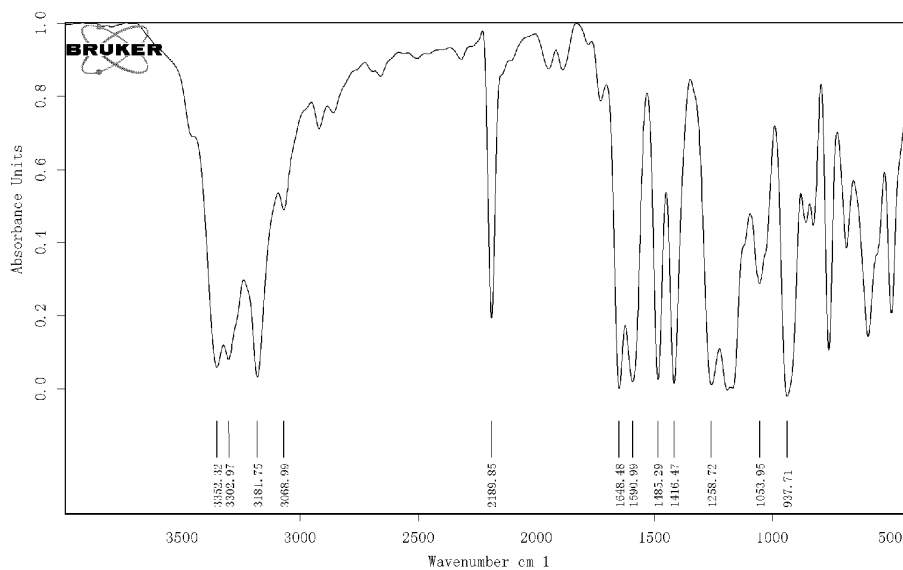
### 7c.diphenyl 2-amino-3-cyano-8-methoxy-4H-chromen-4-ylphosphonate



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Page 1 of 1

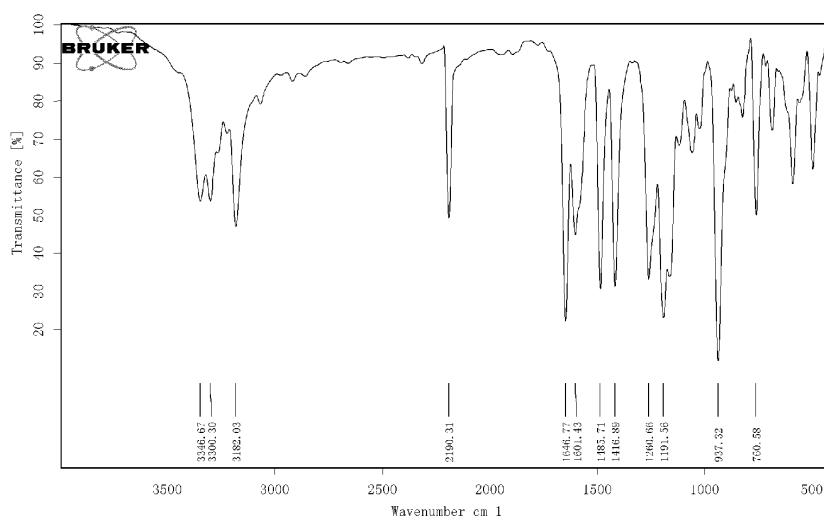
### 7d.diphenyl 2-amino-3-cyano-6-methyl-4H-chromen-4-ylphosphonate



E:\tr\中永存2\5-氨基磷酸二苯酯.dpr

Page 1 of 1

**7e.diphenyl 2-amino-6-chloro-3-cyano-4H-chromen-4-ylphosphonate**



C:\OPUS 7.0.128\WEAS\Sample description.651

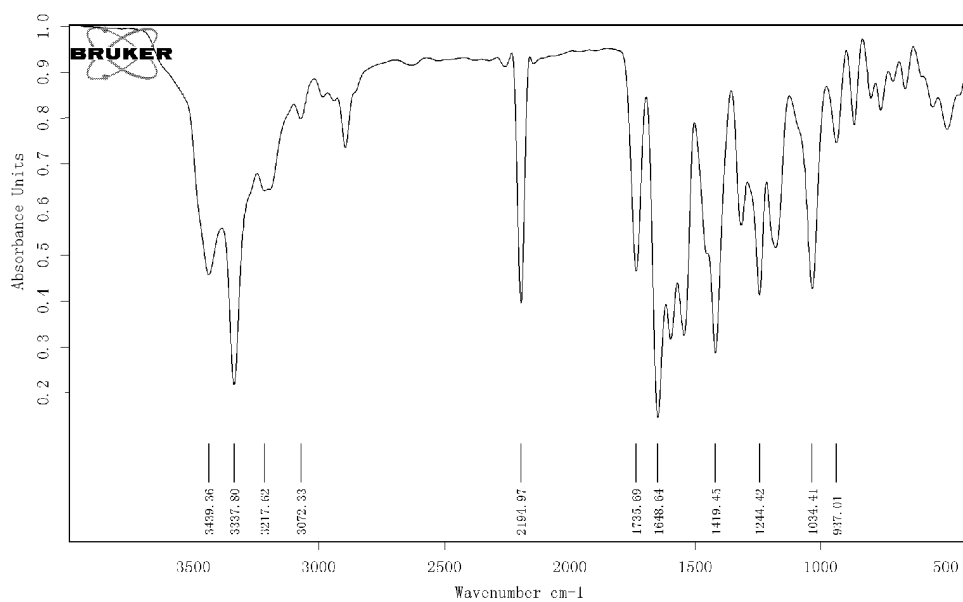
Sample description

Instrument type and / or accessory

2014-5-6

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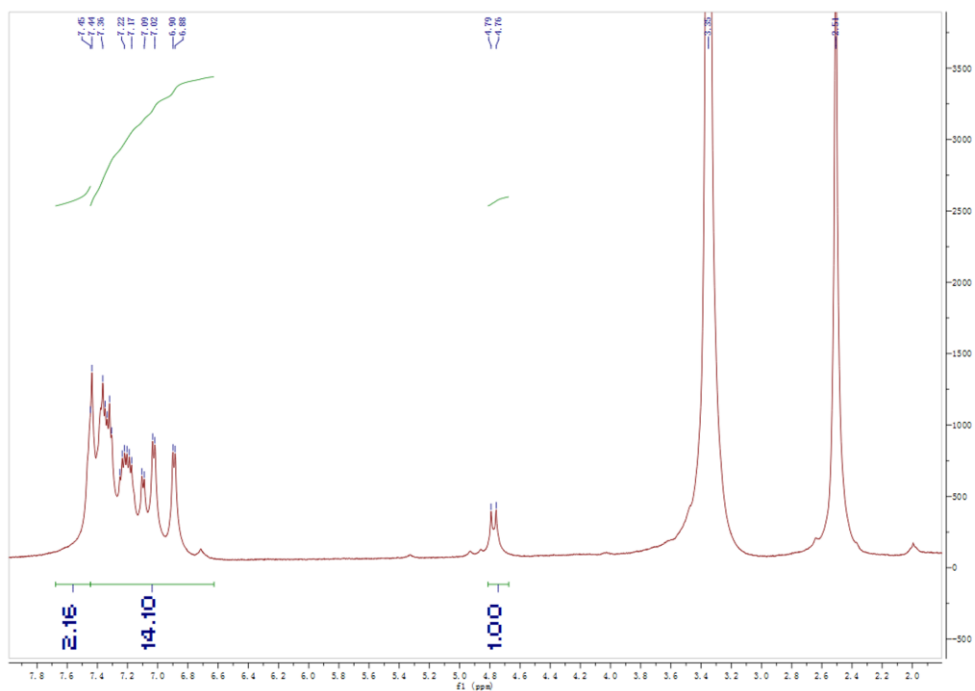
**7f.diphenyl 2-amino-6-bromo-3-cyano-4H-chromen-4-ylphosphonate**



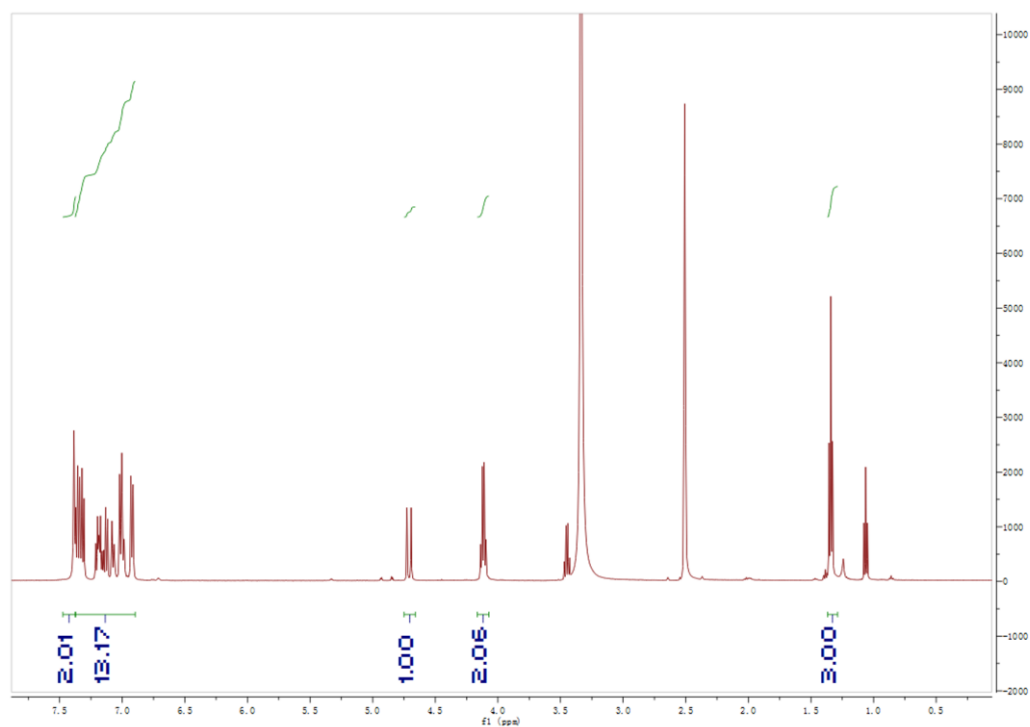
E:\tt\甲水存2\3, 5 二溴水杨醛二甲肼.dpt

Page 1 of 1

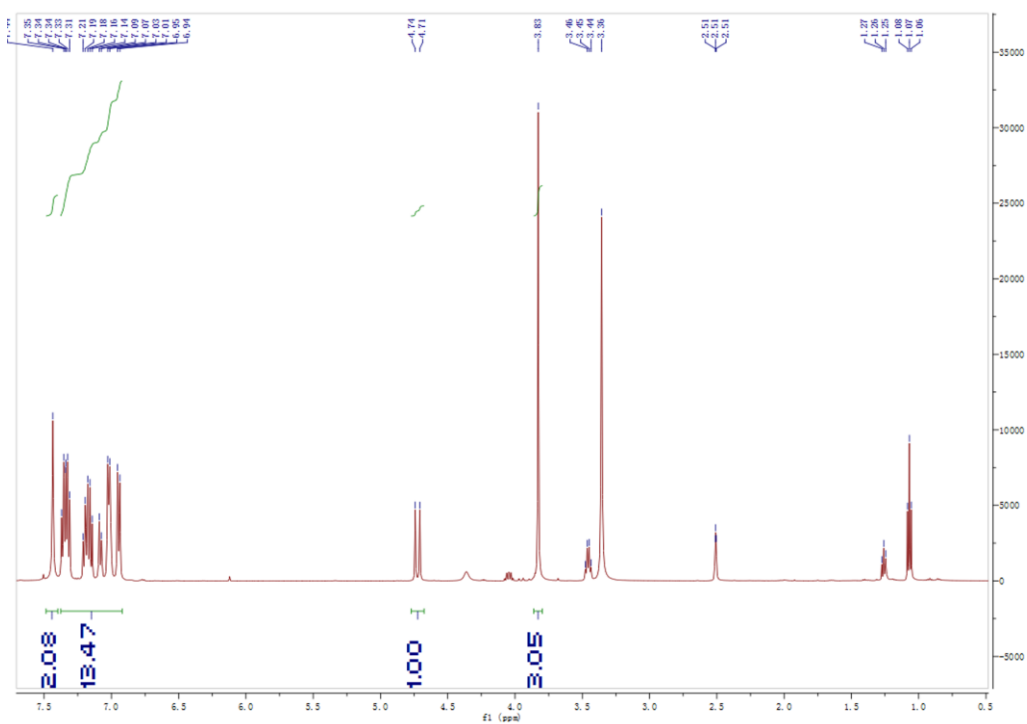
**7g.diphenyl 2-amino-6, 8-dibromo-3-cyano-4H-chromen-4-ylphosphonate**

Copies of  $^1\text{H-NMR}$  Spectra for Compounds 7

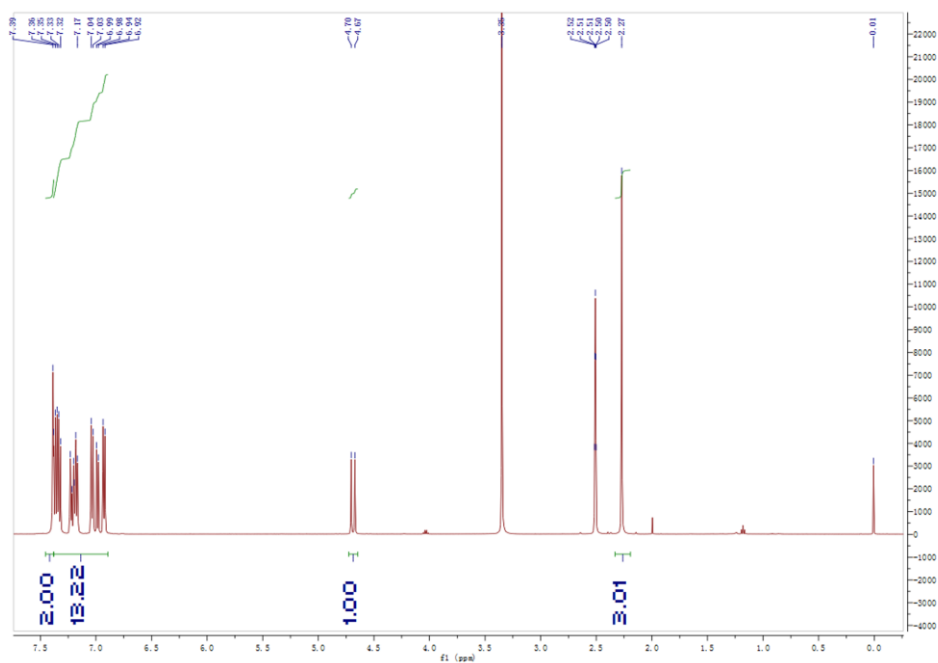
7a.diphenyl 2-amino-3-cyano-4H-chromen-4-ylphosphonate



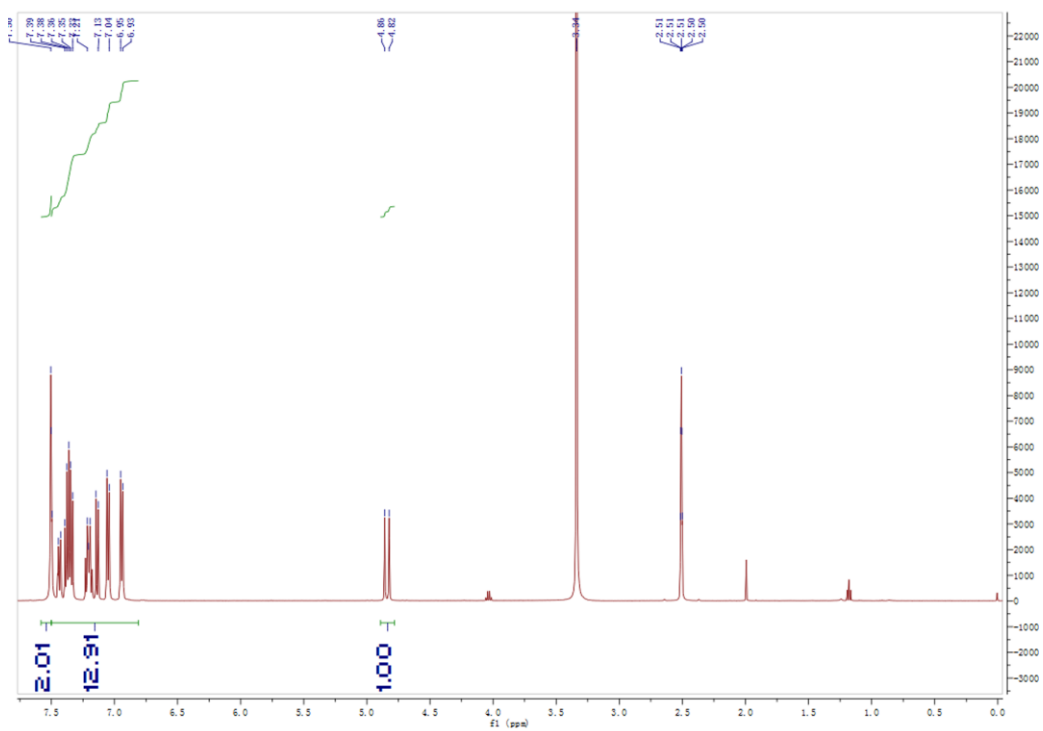
7b.diphenyl 2-amino-3-cyano-8-ethoxy-4H-chromen-4-ylphosphonate



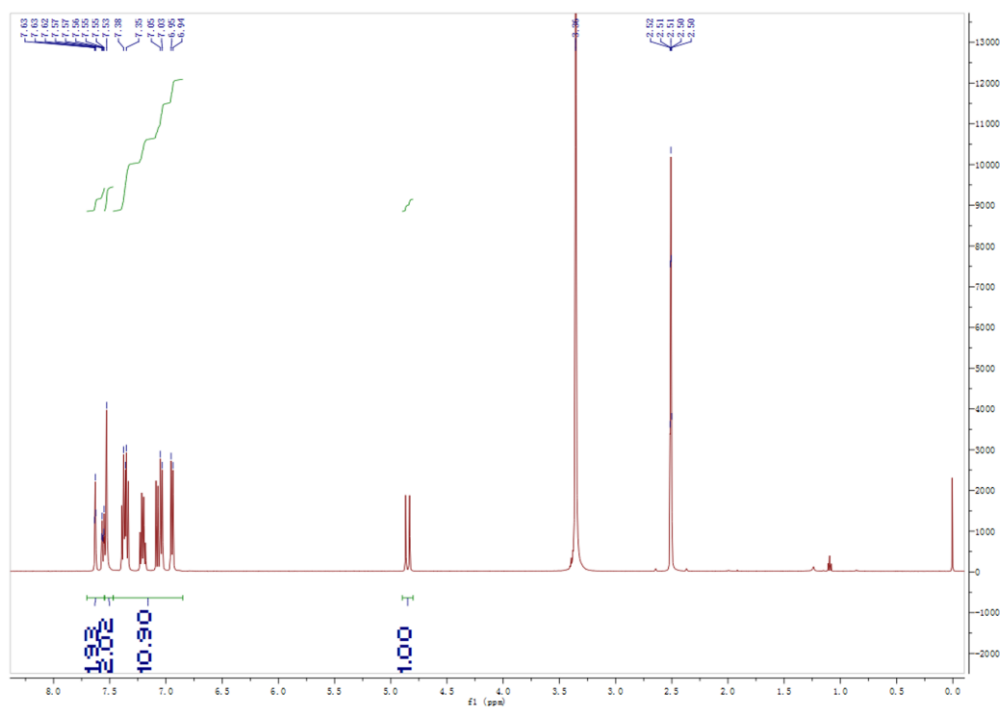
**7c.diphenyl 2-amino-3-cyano-8-methoxy-4H-chromen-4-ylphosphonate**



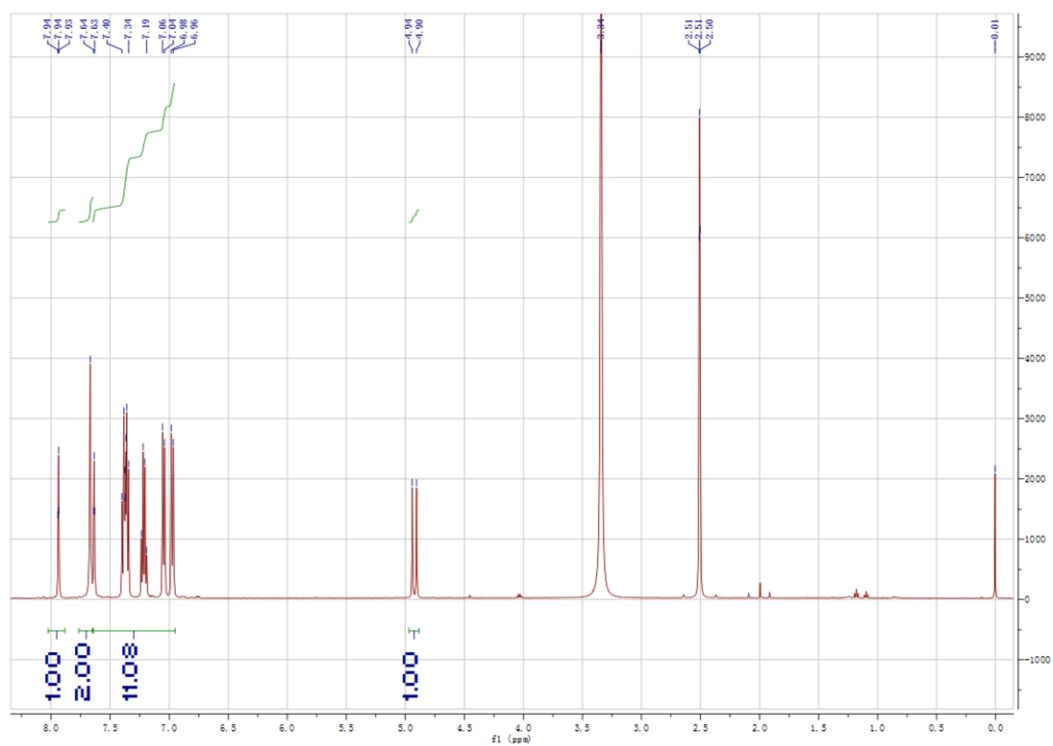
**7d.diphenyl 2-amino-3-cyano-6-methyl-4H-chromen-4-ylphosphonate**



**7e.**diphenyl 2-amino-6-chloro-3-cyano-4H-chromen-4-ylphosphonate

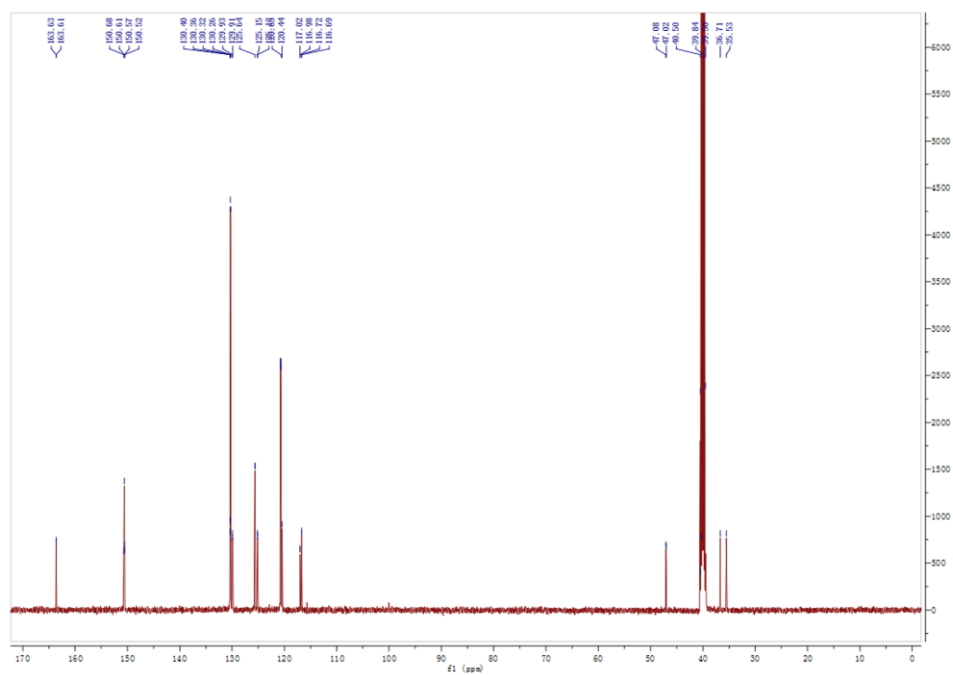


**7f.**diphenyl 2-amino-6-bromo-3-cyano-4H-chromen-4-ylphosphonate

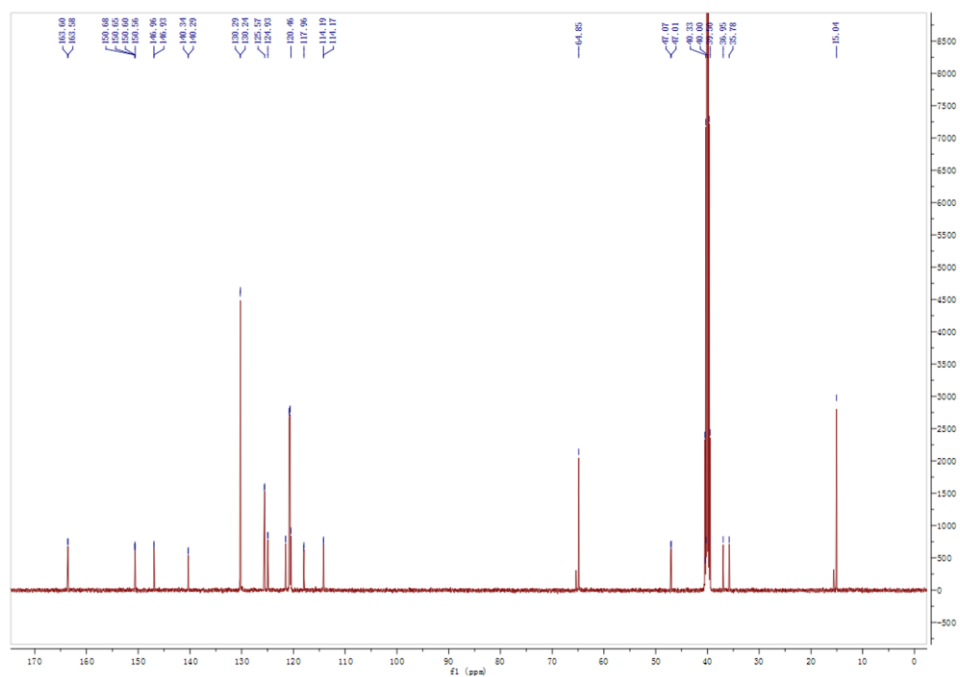


**7g**.diphenyl 2-amino-6, 8-dibromo-3-cyano-4H-chromen-4-ylphosphonate

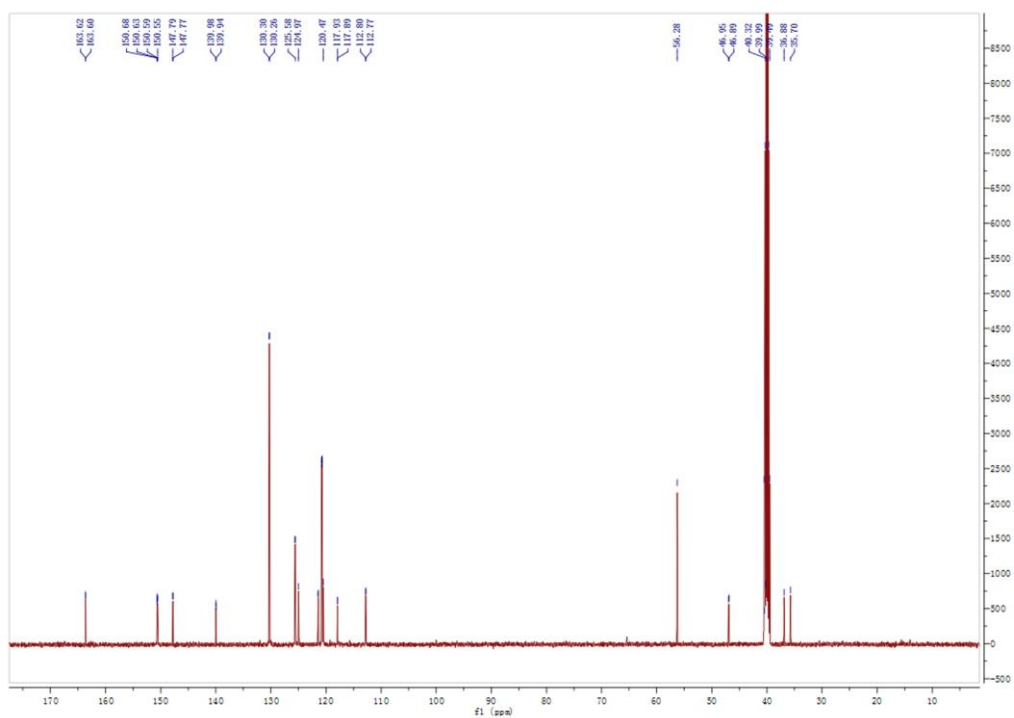


Copies of  $^{13}\text{C}$ -NMR Spectra for Compounds 7

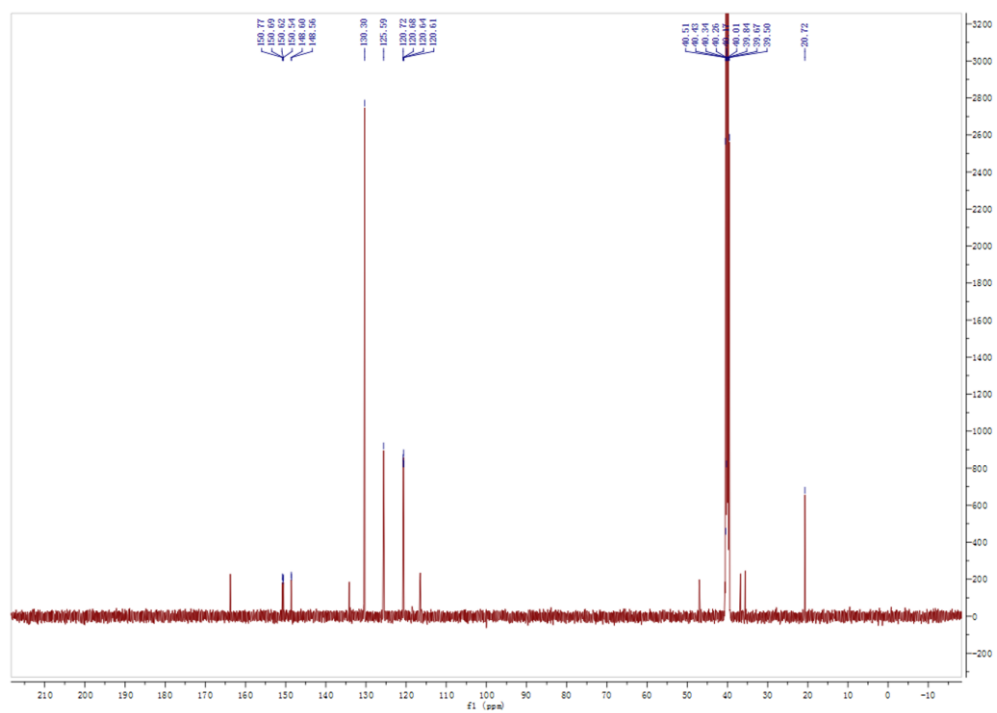
7a.diphenyl 2-amino-3-cyano-4H-chromen-4-ylphosphonate



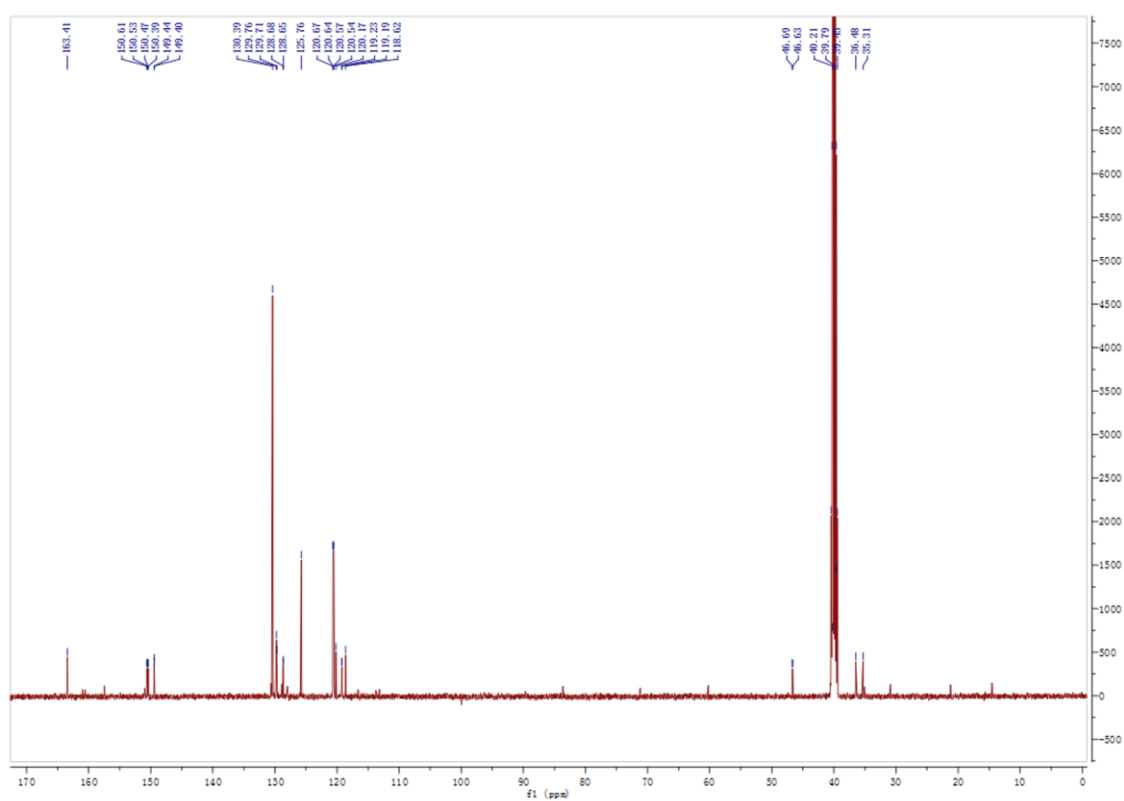
7b.diphenyl 2-amino-3-cyano-8-ethoxy-4H-chromen-4-ylphosphonate



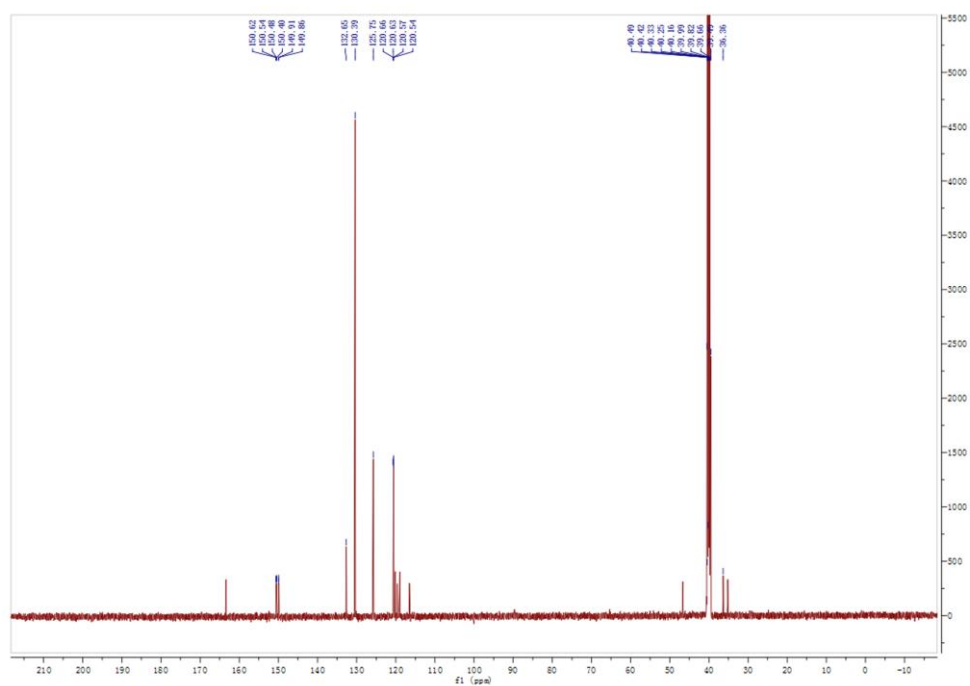
7c.diphenyl 2-amino-3-cyano-8-methoxy-4H-chromen-4-ylphosphonate



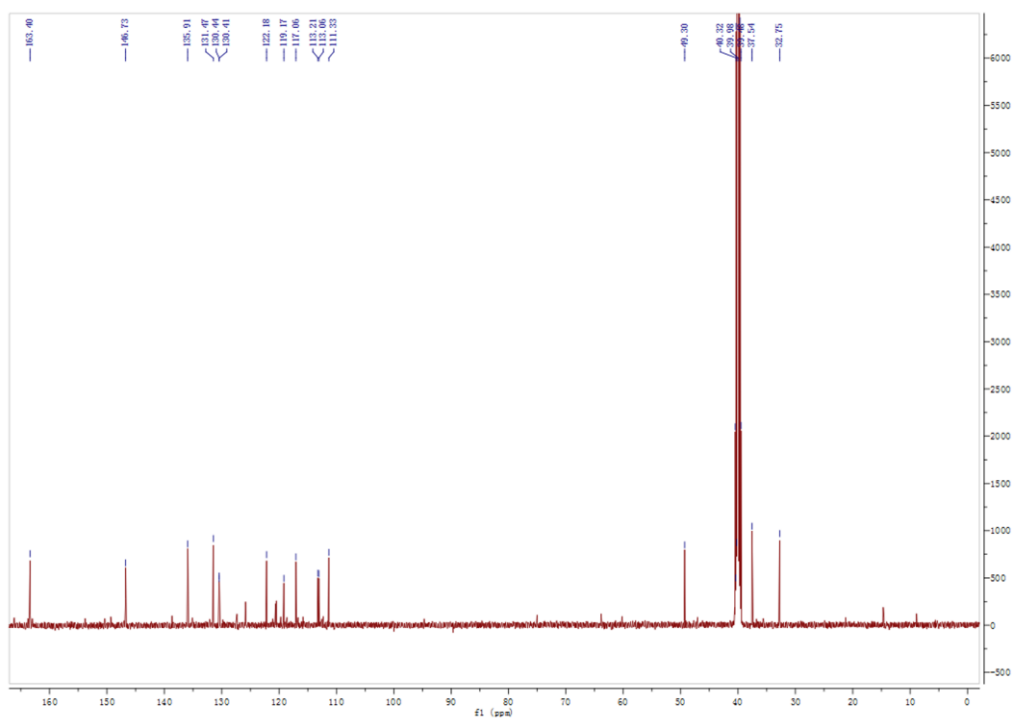
7d.diphenyl 2-amino-3-cyano-6-methyl-4H-chromen-4-ylphosphonate



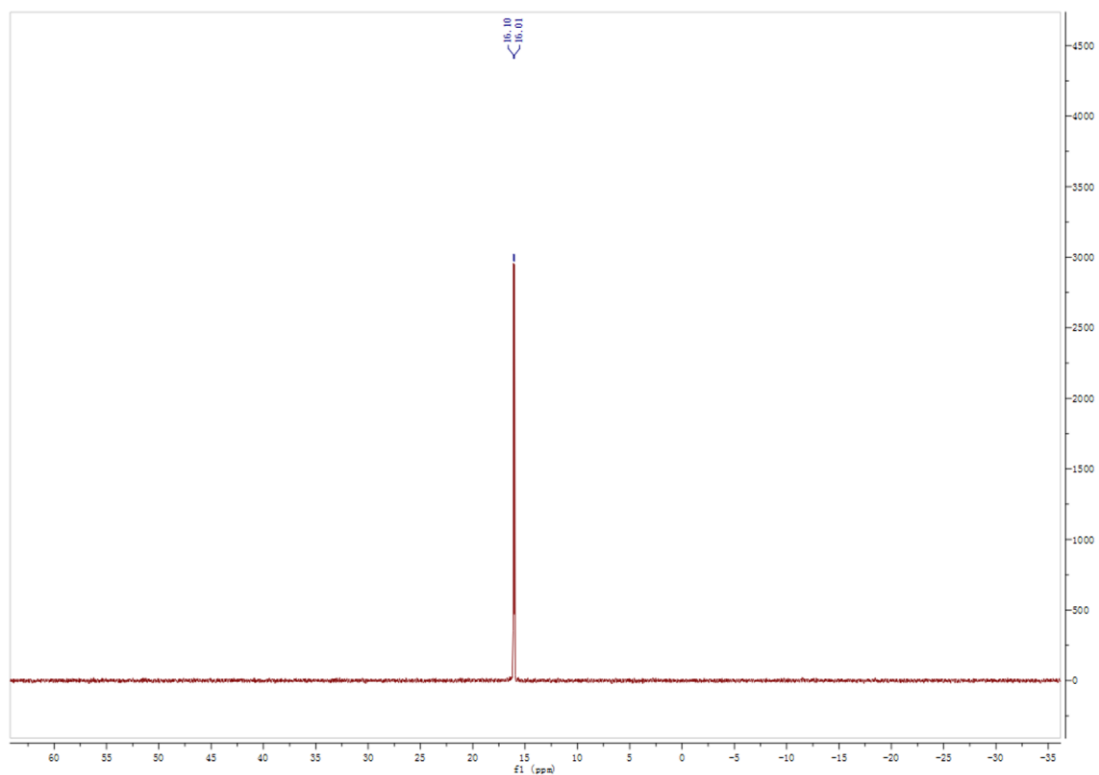
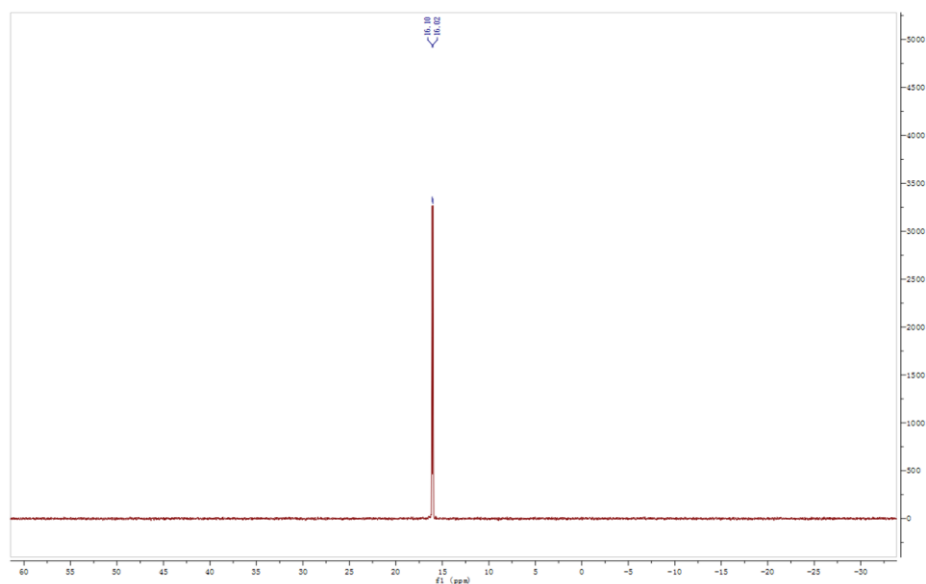
7e. diphenyl 2-amino-6-chloro-3-cyano-4H-chromen-4-ylphosphonate

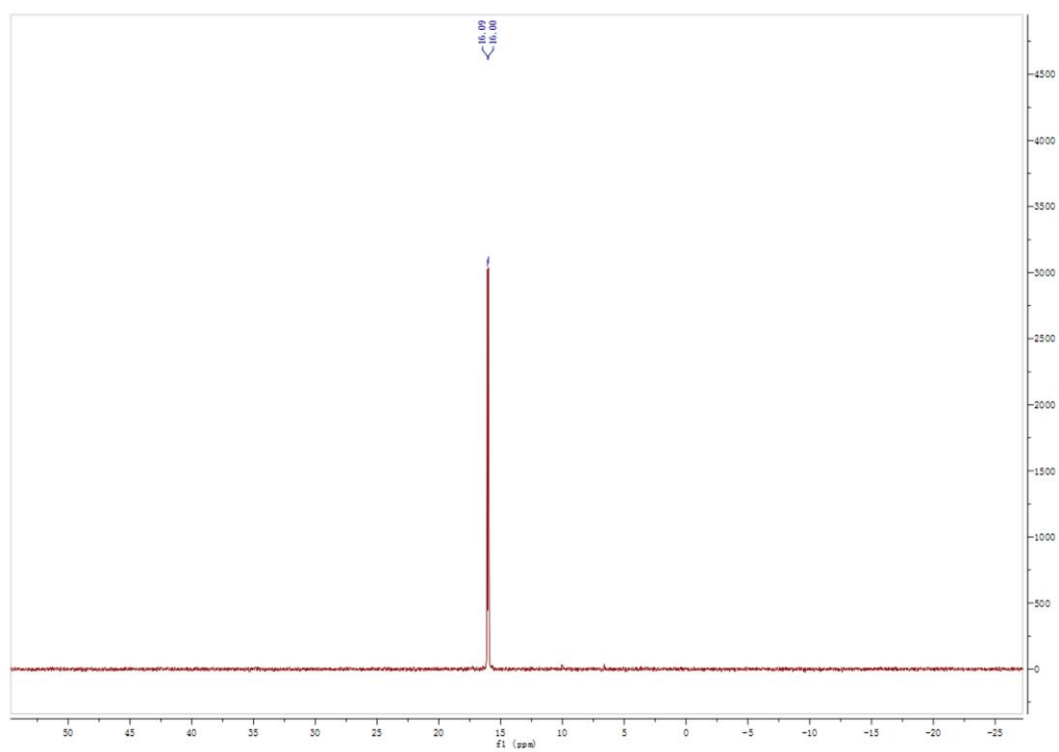


7f. diphenyl 2-amino-6-bromo-3-cyano-4H-chromen-4-ylphosphonate

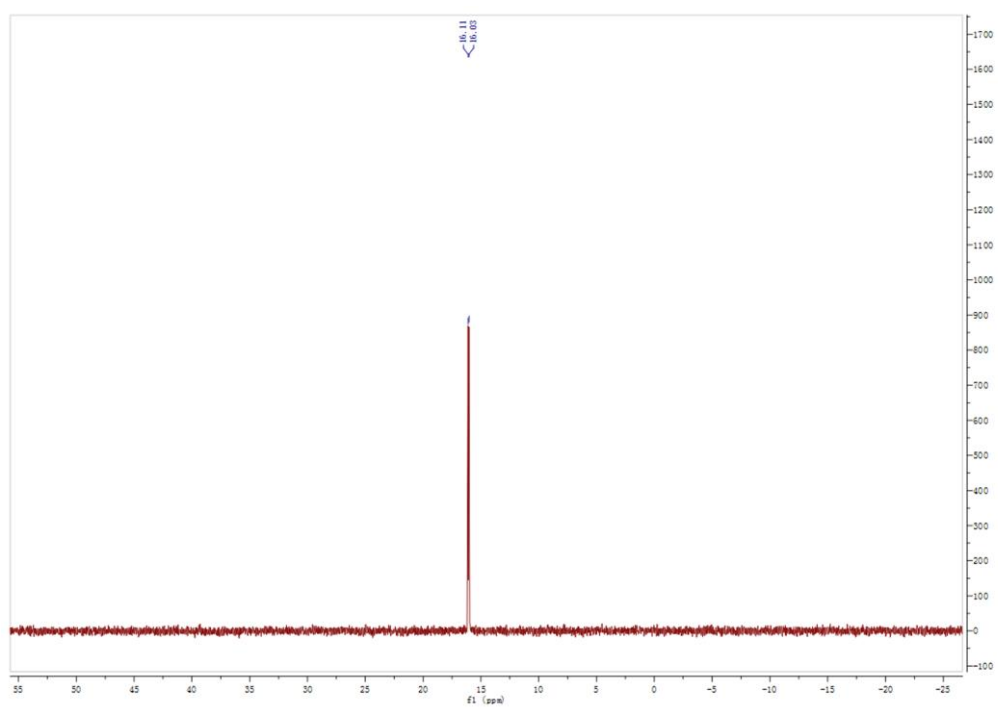


**7g, diphenyl 2-amino-6,8-dibromo-3-cyano-4H-chromen-4-ylphosphonate**

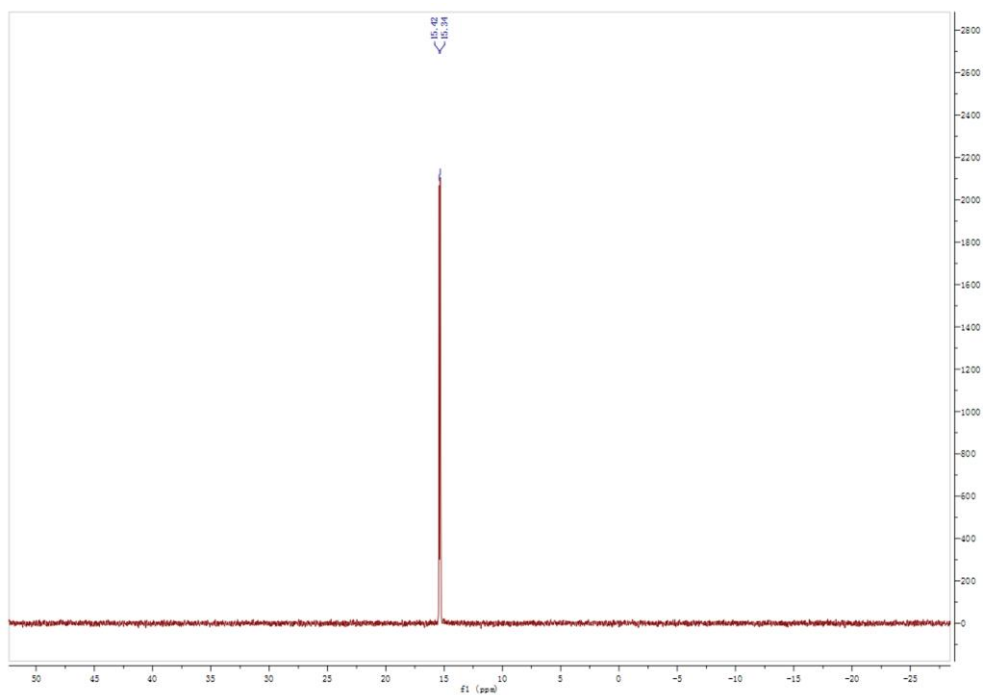
Copies of  $^{31}\text{P}$ -NMR Spectra for Compounds 7**7a.diphenyl 2-amino-3-cyano-4H-chromen-4-ylphosphonate****7b.diphenyl 2-amino-3-cyano-8-ethoxy-4H-chromen-4-ylphosphonate**



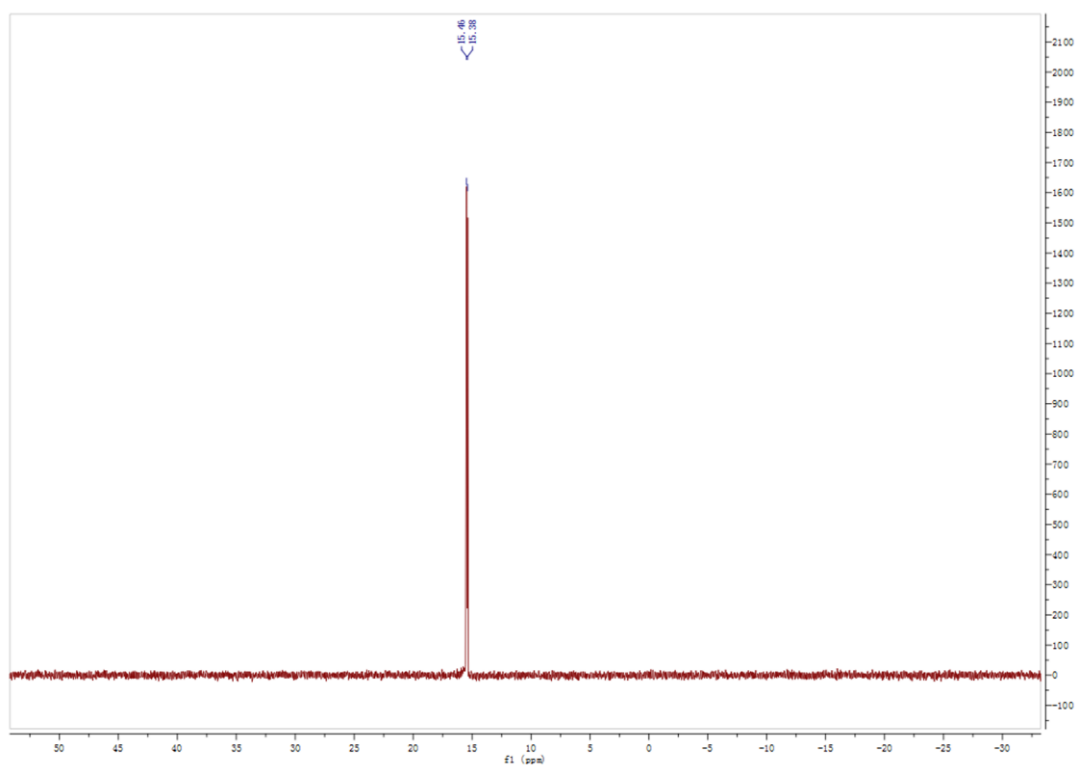
**7c.diphenyl 2-amino-3-cyano-8-methoxy-4H-chromen-4-ylphosphonate**



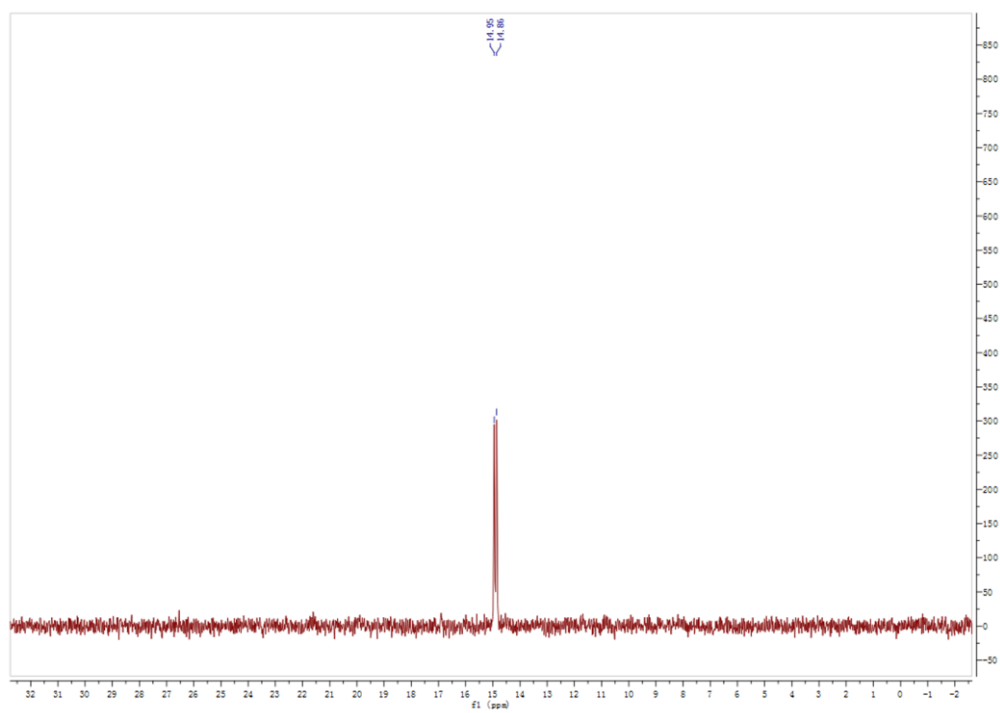
**7d.diphenyl 2-amino-3-cyano-6-methyl-4H-chromen-4-ylphosphonate**



**7e.diphenyl 2-amino-6-chloro-3-cyano-4H-chromen-4-ylphosphonate**



**7f.diphenyl 2-amino-6-bromo-3-cyano-4H-chromen-4-ylphosphonate**

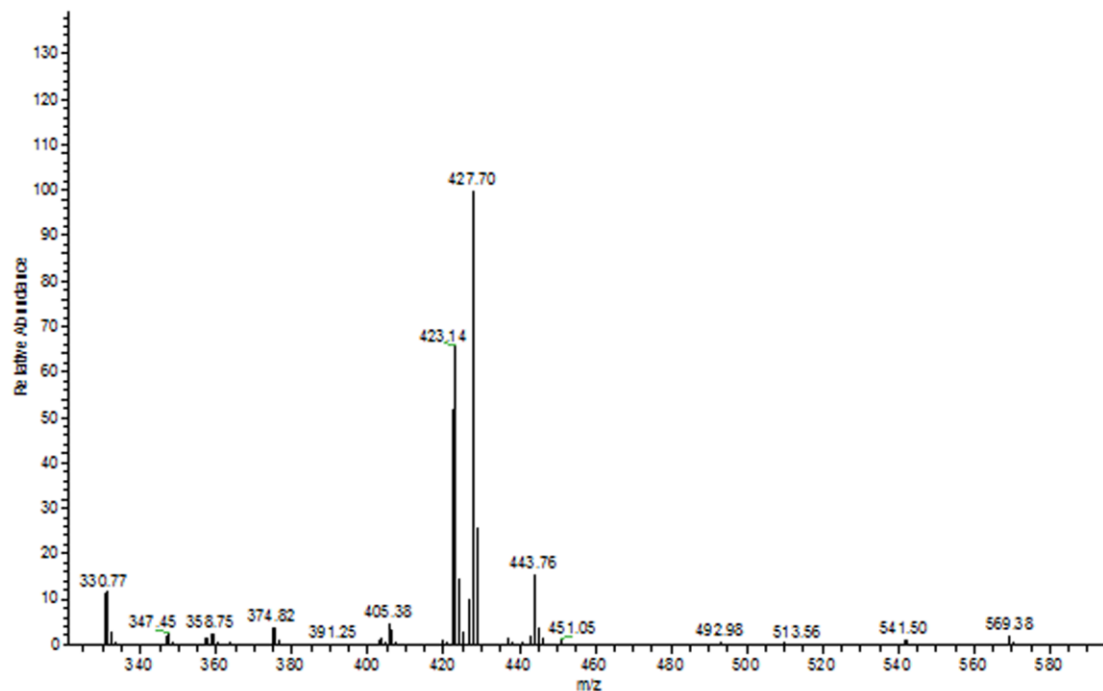


**7g.diphenyl 2-amino-6, 8-dibromo-3-cyano-4H-chromen-4-ylphosphonate**



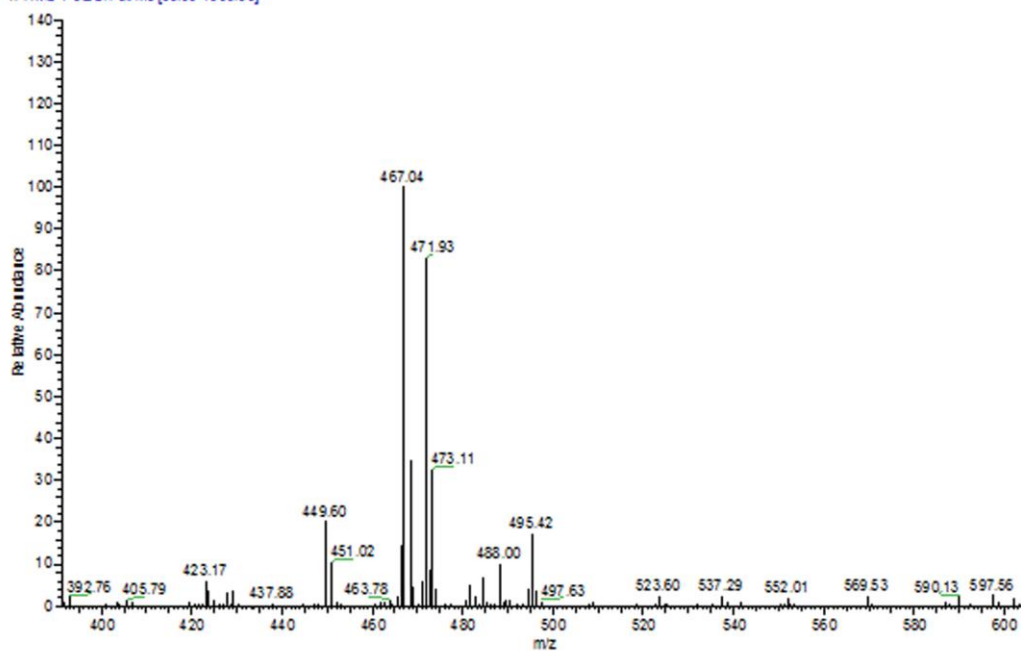
## Copies of MS Spectra for Compounds 7

0519-9 140518103937 #71 RT: 0.52 AV: 1 NL: 3.39E4  
T: ITMS + cESI:slid=35.00 Fullms[50.00-1000.00]



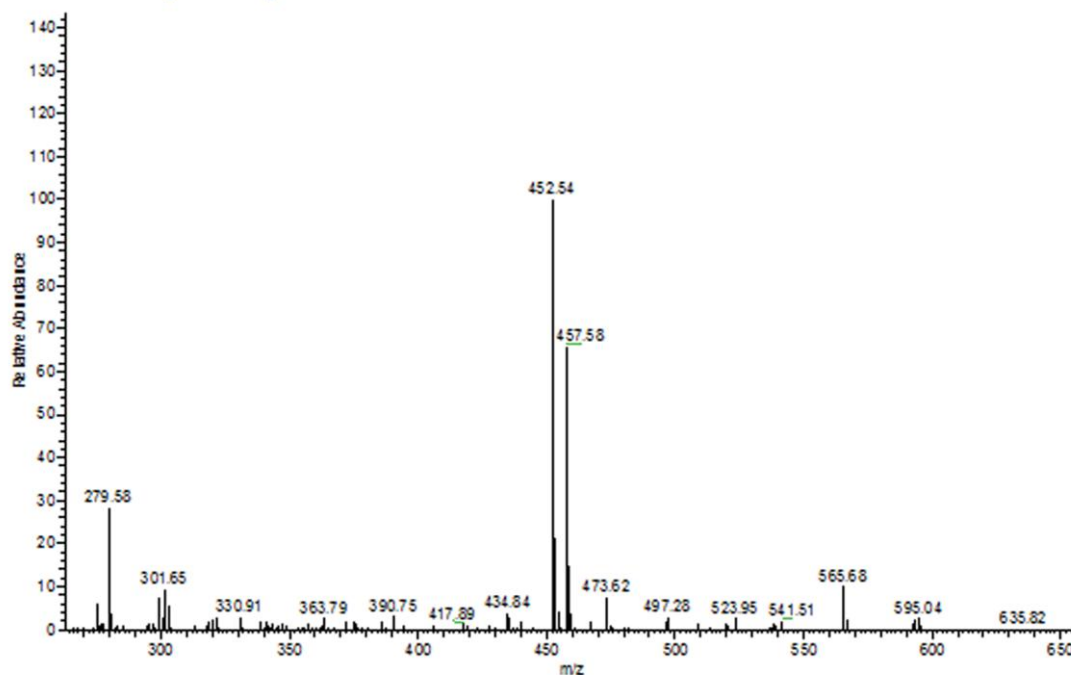
7a.diphenyl 2-amino-3-cyano-4H-chromen-4-ylphosphonate

0519-1C #4-7 RT: 0.02-0.04 AV: 4 NL: 4.03E4  
T: ITMS + cESI:Full ms [50.00-1000.00]



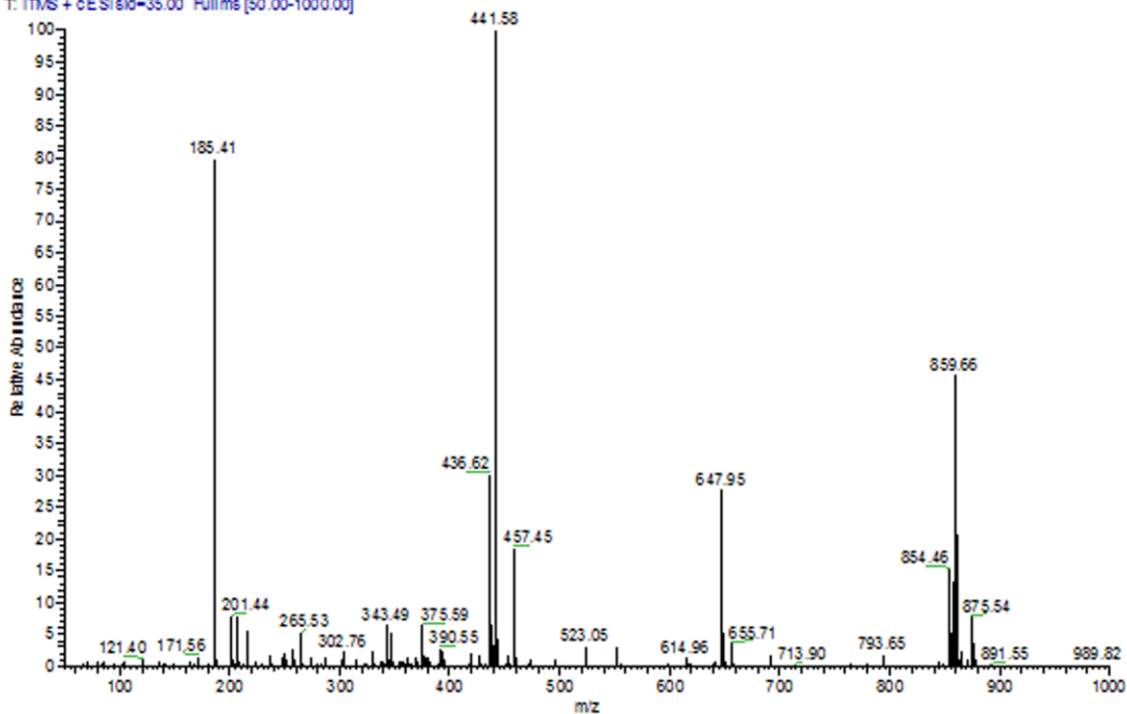
7b.diphenyl 2-amino-3-cyano-8-ethoxy-4H-chromen-4-ylphosphonate

0519-11 140518104834 #77 RT: 0.55 AV: 1 NL: 2.89E4  
T: ITMS + cESI Full ms [50.00-1000.00]



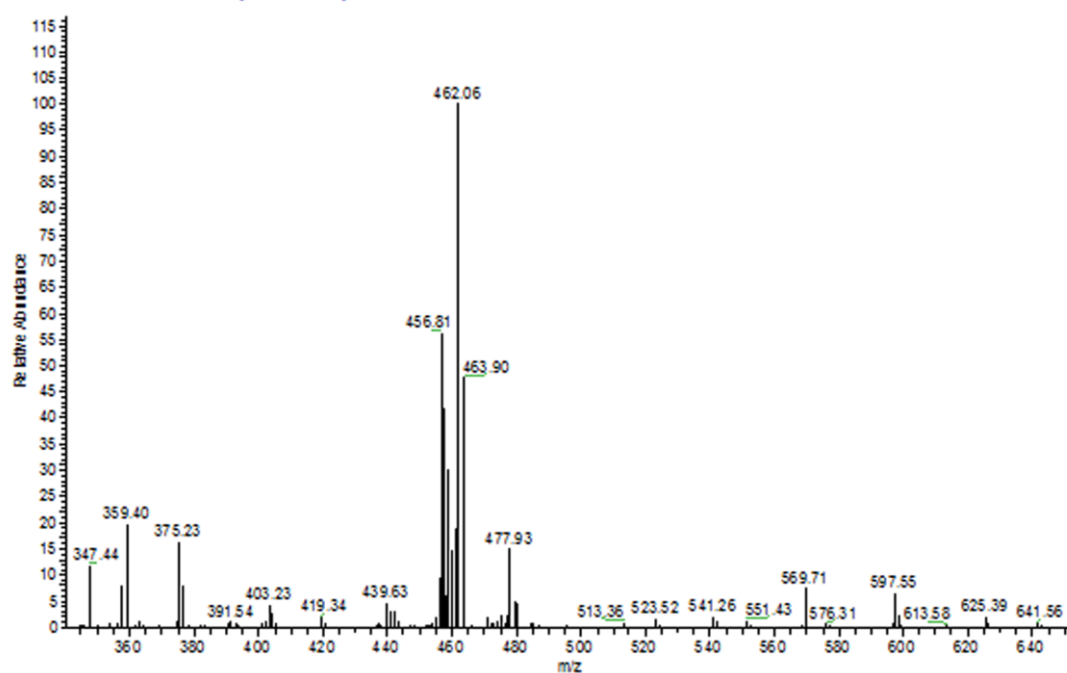
7c.diphenyl 2-amino-3-cyano-8-methoxy-4H-chromen-4-ylphosphonate

0519-12 140518105907 #20 RT: 0.14 AV: 1 NL: 4.54E4  
T: ITMS + cESI Full ms [50.00-1000.00]



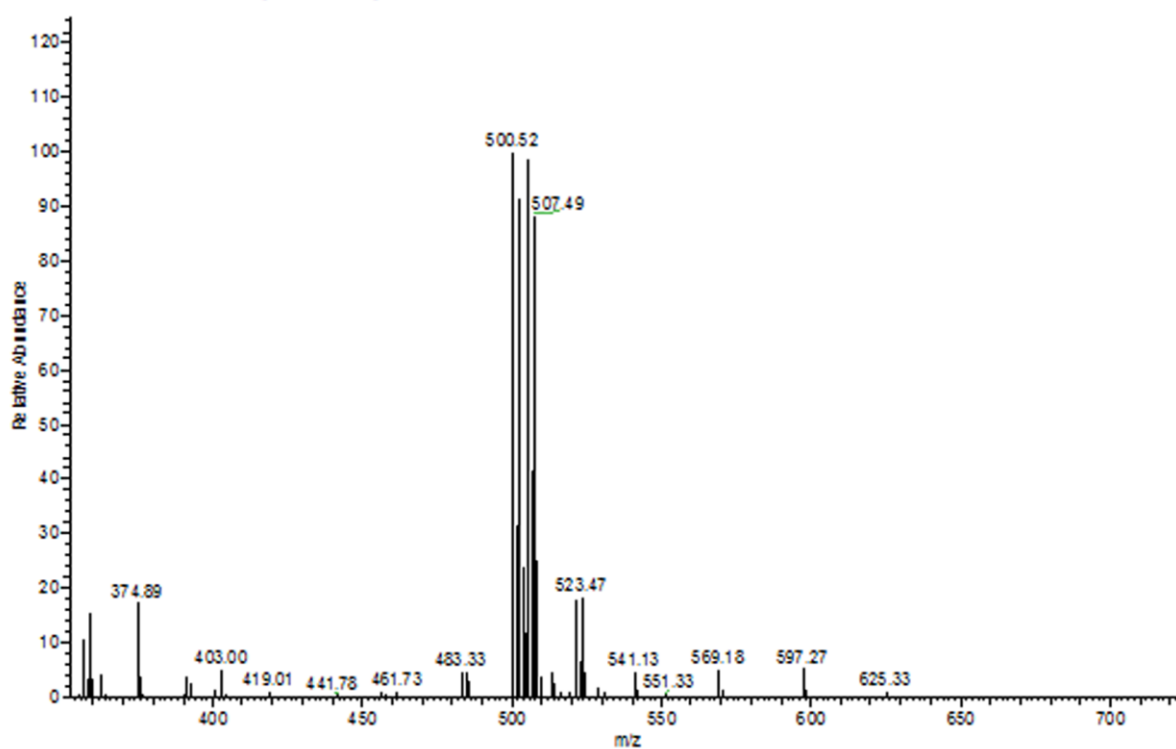
7d.diphenyl 2-amino-3-cyano-6-methyl-4H-chromen-4-ylphosphonate

0519-13 140518105907 #412 RT: 3.04 AV: 1 NL: 4.98E4  
T: ITMS + cESI:slid=35.00 Fullms[50.00-1000.00]



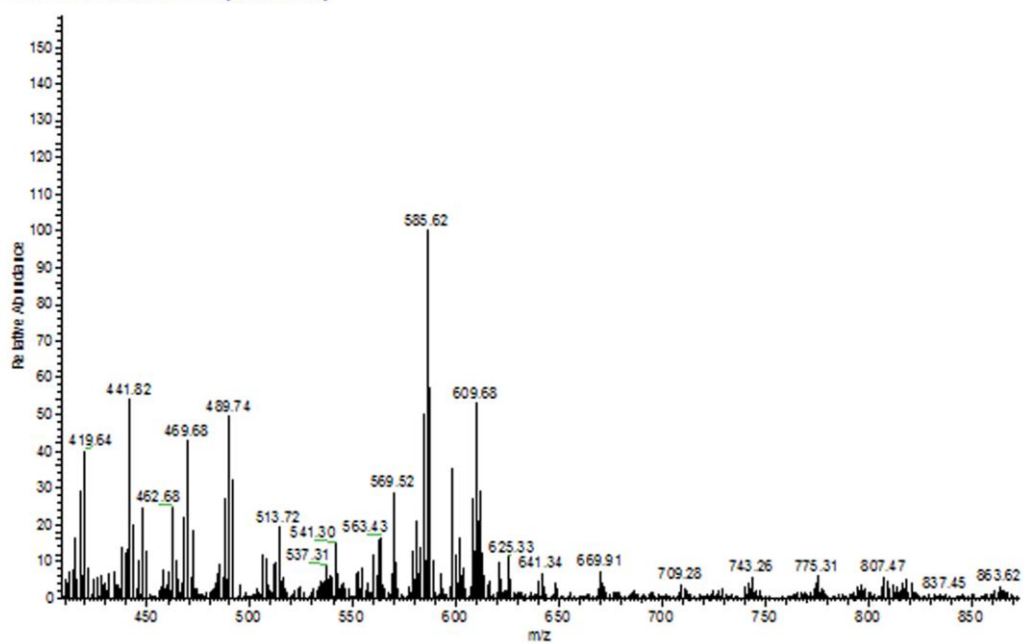
7e.diphenyl 2-amino-6-chloro-3-cyano-4H-chromen-4-ylphosphonate

0519-14 140518110505 #240 RT: 1.93 AV: 1 NL: 1.75E4  
T: ITMS + cESI:slid=35.00 Fullms [50.00-1200.00]



7f.diphenyl 2-amino-6-bromo-3-cyano-4H-chromen-4-ylphosphonate

05-19-15 140518111732 #201 RT: 1.76 AV: 1 NL: 1.98E4  
T: ITMS + cESI/sld=35.00 Fullms[50.00-1500.00]



**7g.diphenyl 2-amino-6, 8-dibromo-3-cyano-4H-chromen-4-ylphosphonate**