Electronic Supplementary Material (ESI) for RSC Advances.

Regiospecific and Highly Stereoselective Synthesis of β-Amino (*Z*)-Enylphosphonates *via* β-Hydrogen Migration Reaction of Dialkyl α-Diazophosphonates Catalyzed by AgOTf

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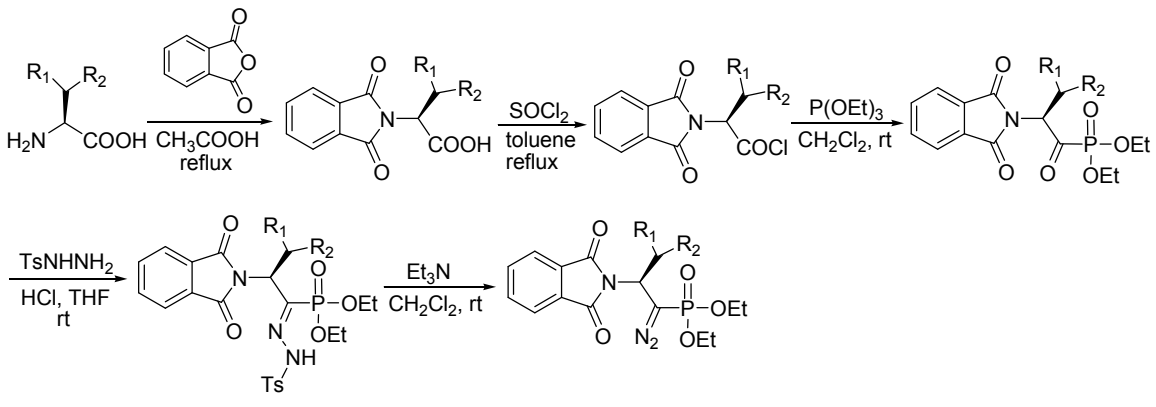
Supporting Information

List of contents (pages)

General Comments.

All reactions and manipulations were performed using standard Schlenk techniques. Solvents were dried and distilled prior to use according to the standard methods. Unless otherwise indicated, all materials were obtained from commercial sources, and used as purchased without dehydration. Flash column chromatography was performed on silica gel (particle size 10-40 μm, Ocean Chemical Factory of Qingdao, China). Nitrogen gas (99.999%) was purchased from Boc Gas Inc. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded in $CDCl_3$ at Bruker 400 MHz spectrometers, TMS served as internal standard (δ = 0 ppm) for ^{1}H NMR and ^{13}C NMR, H_3PO_4 served as internal standard (δ = 0 ppm) for ^{31}P NMR. The crystal structure was determined on a Bruker SMART 1000 CCD diffractometer. Mass spectra were recorded on a LCQ advantage spectrometer with ESI resource. HR-MS were recorded on APEXII and ZAB-HS spectrometer. Melting points were determined on a T-4 melting point apparatus (uncorrected). Optical rotations were recorded on a Perkin Elemer 241 Polarimeter.

The synthesis pathway of α-diazophosphonate 1:[1]

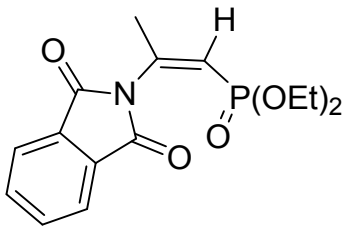


General procedure for the preparation of 2 and 3:

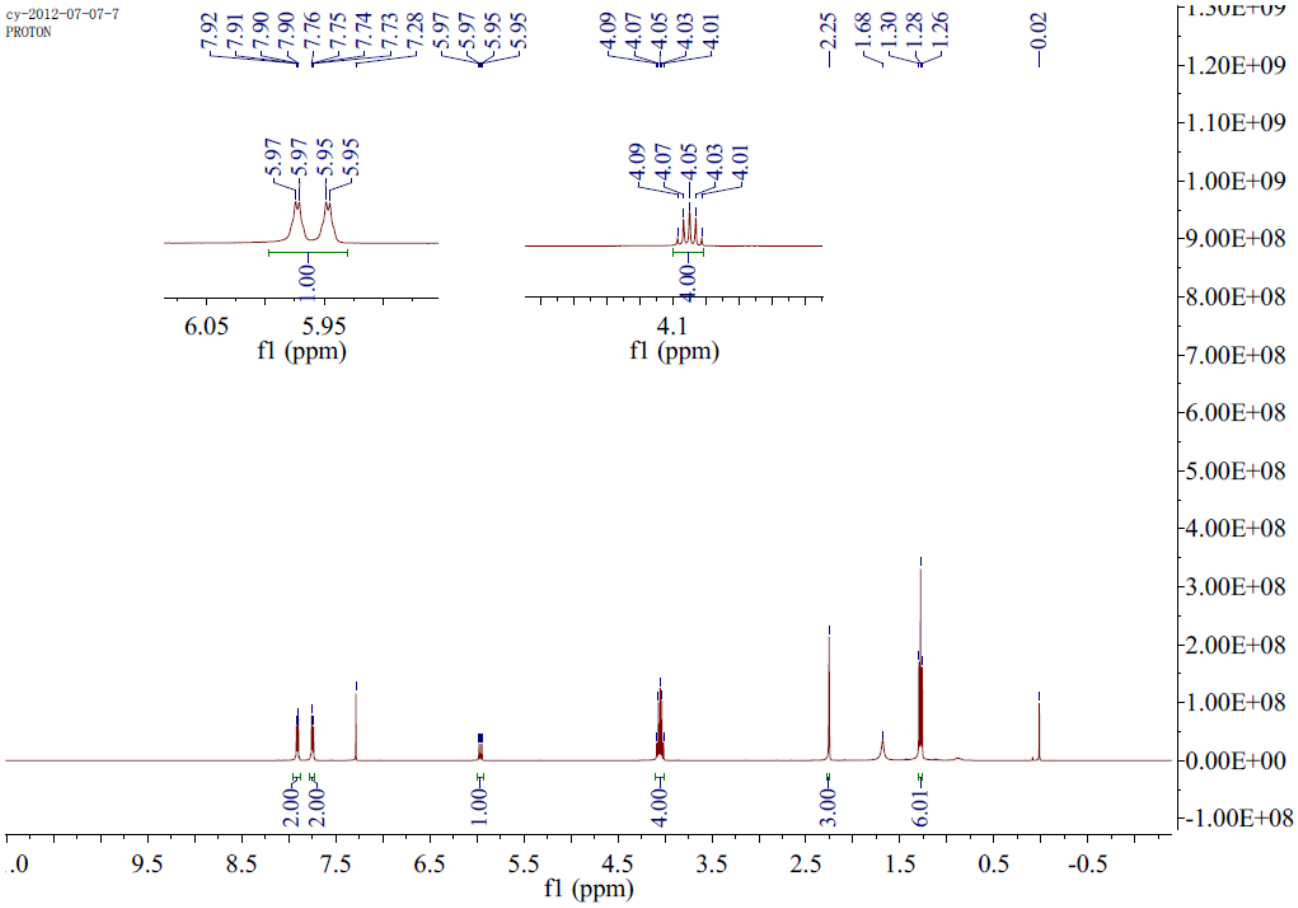
The AgOTf (0.0156 mmol) and $NaBAr_F$ (0.0169mmol) in an oven-dried Schlenk tube was dissolved in 2 mL of MTBE under nitrogen. The solution was stirred for several minutes at 25 °C. Dialkyl α-diazophosphonates **1** (0.28 mmol) was diluted with 4 mL of MTBE and was drawn into a gastight syringe. It was then added to the reaction mixture dropwise over a period of 1.5h with the help of a syringe pump. After the addition was complete, the reaction mixture was stirred for another 6 hours at 25 °C. The solvent was then removed under reduced pressure and the crude residue was purified by silica gel chromatography with the eluent (CH_2Cl_2/EtOAc = 15:1) to afford the corresponding products **2** and **3**.

(*Z*)-Diethyl (2-(1,3-dioxoisoindolin-2-yl)prop-1-en-1-yl)phosphonate (2a):

White solid; mp 140-143°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.94 (m, 2H, Ph), 7.69-7.80 (m, 2H, Ph),



5.96 (dd, *J* = 10.4, 1.2 Hz, 1H, CH), 3.98-4.13 (m, 4H, $2OCH_2$), 2.25 (s, 3H, CH_3), 1.28 (t, *J* = 7.1 Hz, 6H, $2CH_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.63 (C=O), 146.83 (C-N), 134.11, 132.28, 123.71 (Ph), 118.32 (d, *J* = 186.2 Hz, C-P), 62.08 (d, *J* = 5.3 Hz, OCH_2), 24.56 (d, *J* = 17 Hz, CH_3), 16.27 (d, *J* = 6.6 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 11.34 (s). ESI-HRMS calcd for $[C_{15}H_{18}NO_5P, M+Na]^+$: 346.0815, Found: 346.0815.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7.90
7.90
7.76
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7.74
7.73
7.28
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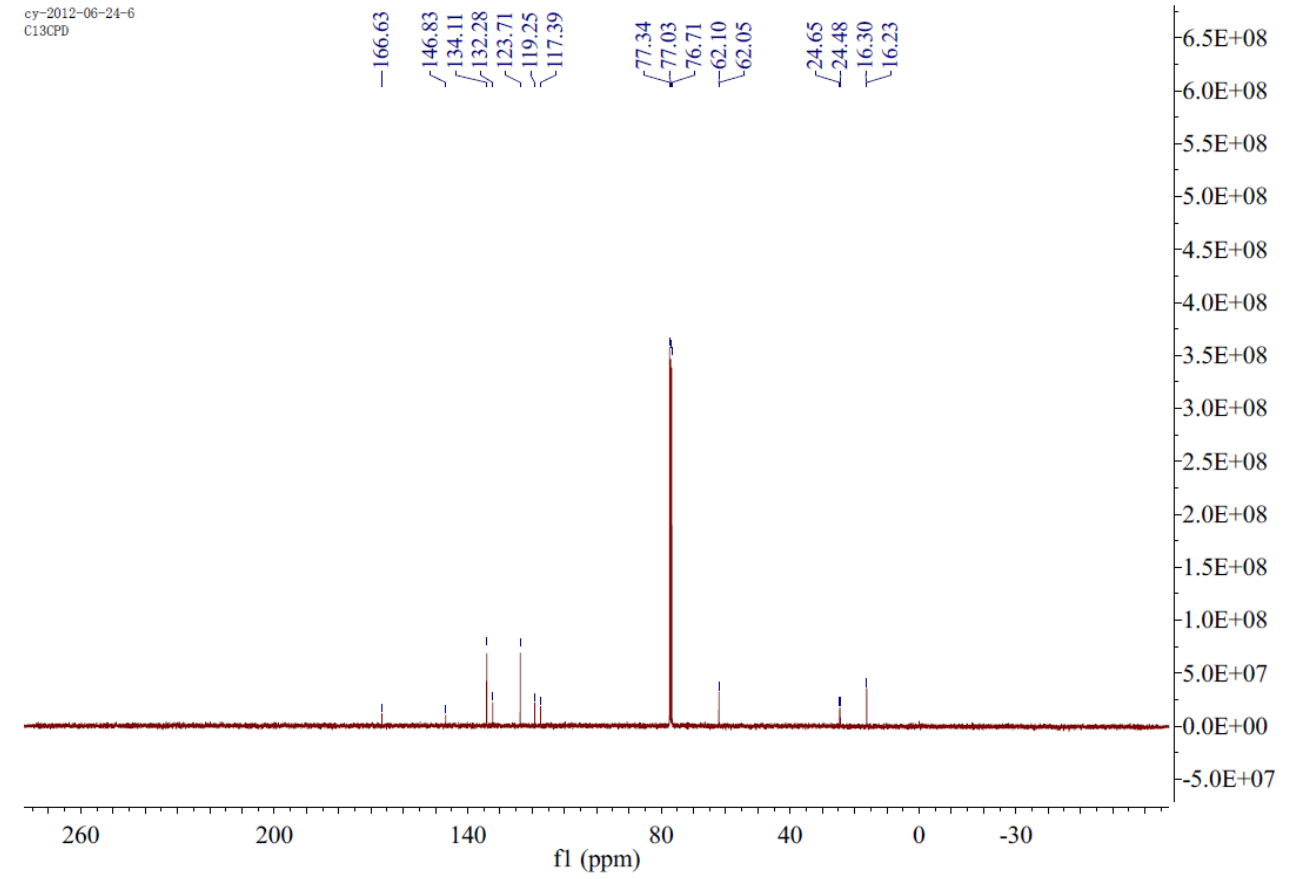
5.97
5.95
5.95
4.09
4.07
4.05
4.03
4.01
2.25
1.68
1.30
1.28
1.26
0.02
1.00
4.00
6.05
5.95
f1 (ppm)
4.1
f1 (ppm)
2.00
2.00
1.00
4.00
3.00
6.01
f1 (ppm)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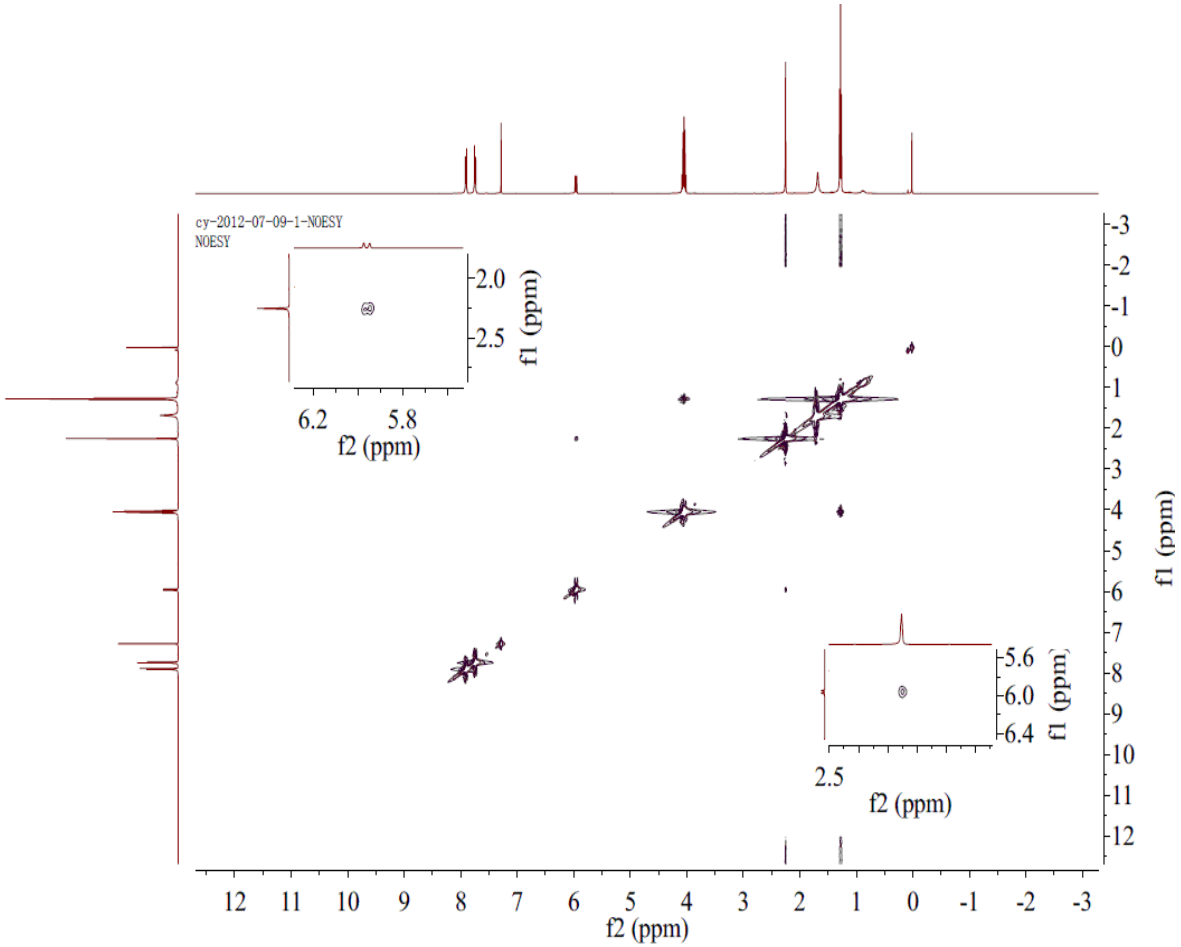
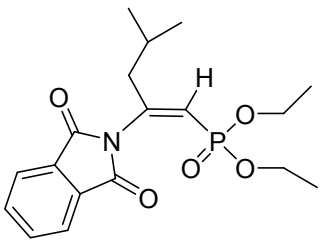
24.65
24.48
16.30
16.23
f1 (ppm)

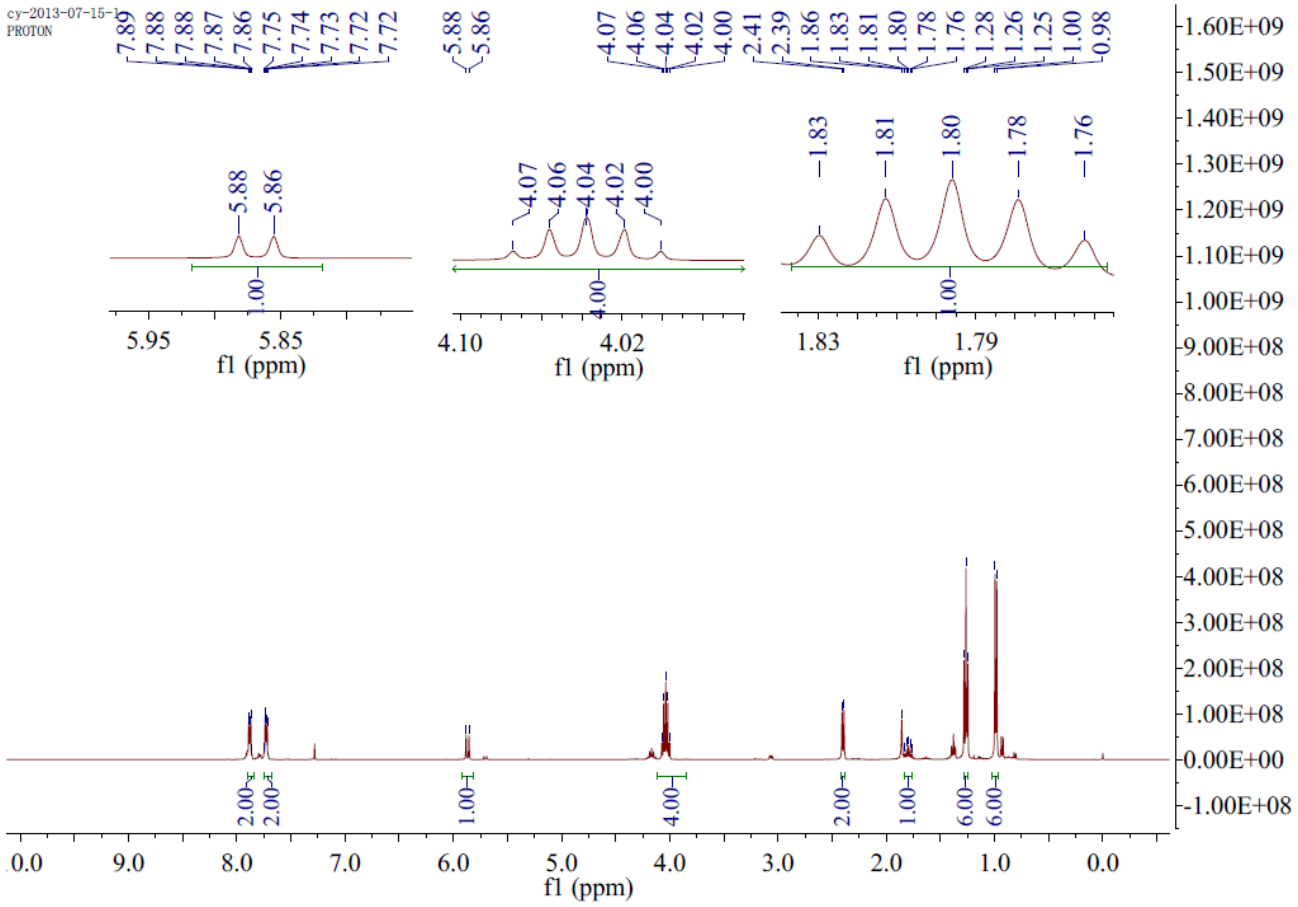


^{1}H-^{1}H NOESY spectrum

(*Z*)-Diethyl (2-(1,3-dioxoisoindolin-2-yl)-4-methylpent-1-en-1-yl)phosphonate (2b):



Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.90 (m, 2H, Ph), 7.71-7.75 (m, 2H, Ph), 5.87 (d, *J* = 10.6, Hz, 1H, CH), 3.98-4.10 (m, 4H, $2OCH_2$), 2.40 (d, *J* = 7.1 Hz, 2H, CH_2), 1.74-1.84 (m, 1H, CH), 1.26 (t, *J* = 7.1 Hz, 6H, $2CH_3$), 0.99 (d, *J* = 6.6 Hz, 6H, $2CH_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.99 (C=O), 150.06 (N-C), 134.08, 132.20, 123.66 (Ph), 118.14 (d, *J* = 184.1 Hz, C-P), 62.06 (d, *J* = 5.1 Hz, OCH_2), 47.20 (d, *J* = 15.3 Hz, CH_2), 25.76 (CH), 22.36 (CH_3), 16.27 (d, *J* = 6.5 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 11.59 (s). ESI-HRMS calcd for $[C_{18}H_{24}NO_5P, M+H]^+$: 366.1465, Found: 366.1468.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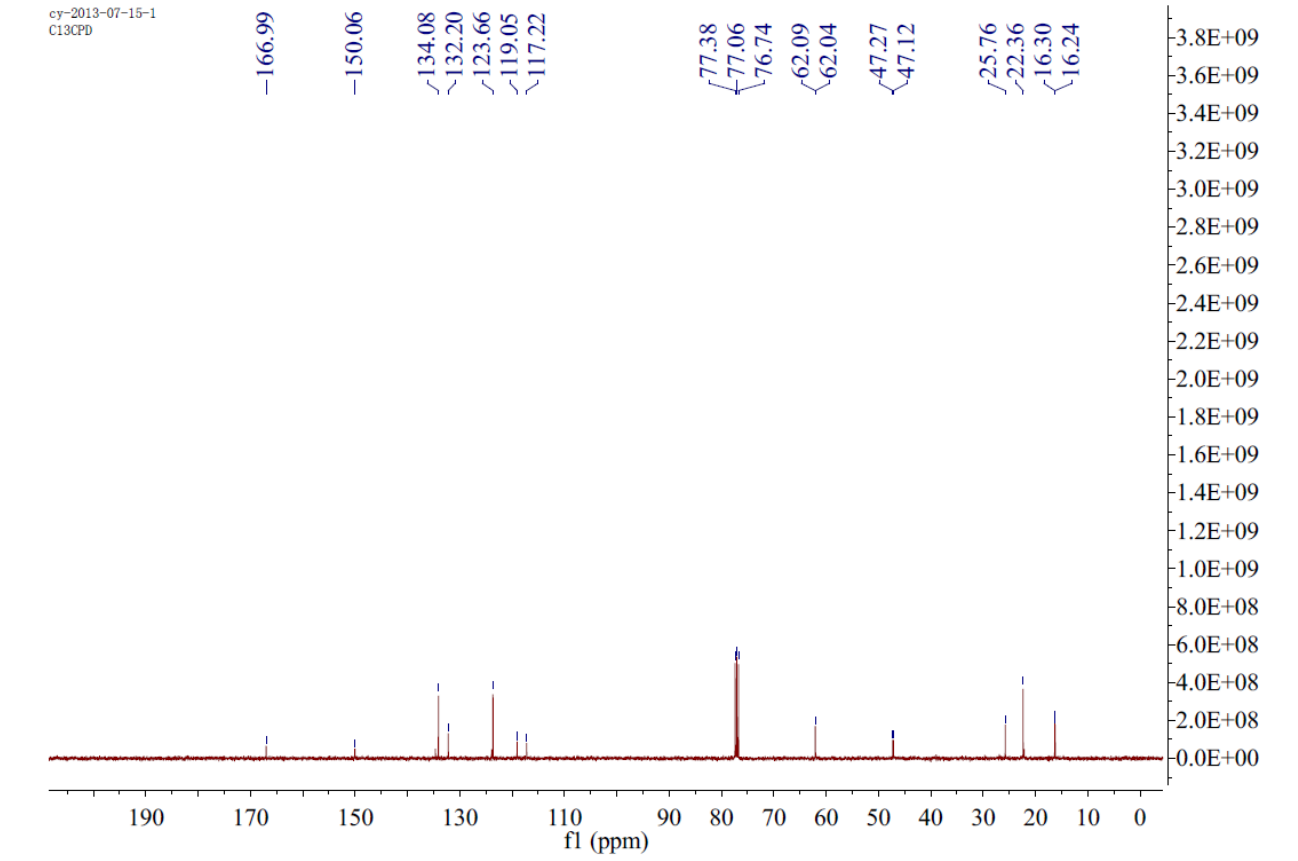
2.41 2.39 1.86 1.83 1.81 1.80 1.78 1.76 1.28 1.26 1.25 1.00 0.98
5.88 5.86
1.00
5.95 5.85
f1 (ppm)
4.07 4.06 4.04 4.02 4.00
4.00
4.10 4.02
f1 (ppm)
1.83 1.81 1.80 1.78 1.76
1.00
1.83 1.79
f1 (ppm)
2.00 2.00 1.00 4.00 2.00 1.00 6.00 6.00
0.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)
1.60E+09 1.50E+09 1.40E+09 1.30E+09 1.20E+09 1.10E+09 1.00E+09 9.00E+08 8.00E+08 7.00E+08 6.00E+08 5.00E+08 4.00E+08 3.00E+08 2.00E+08 1.00E+08 0.00E+00 -1.00E+08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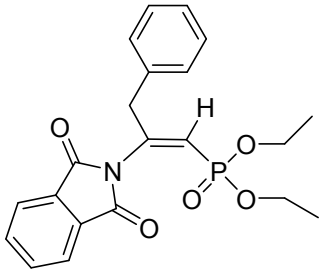
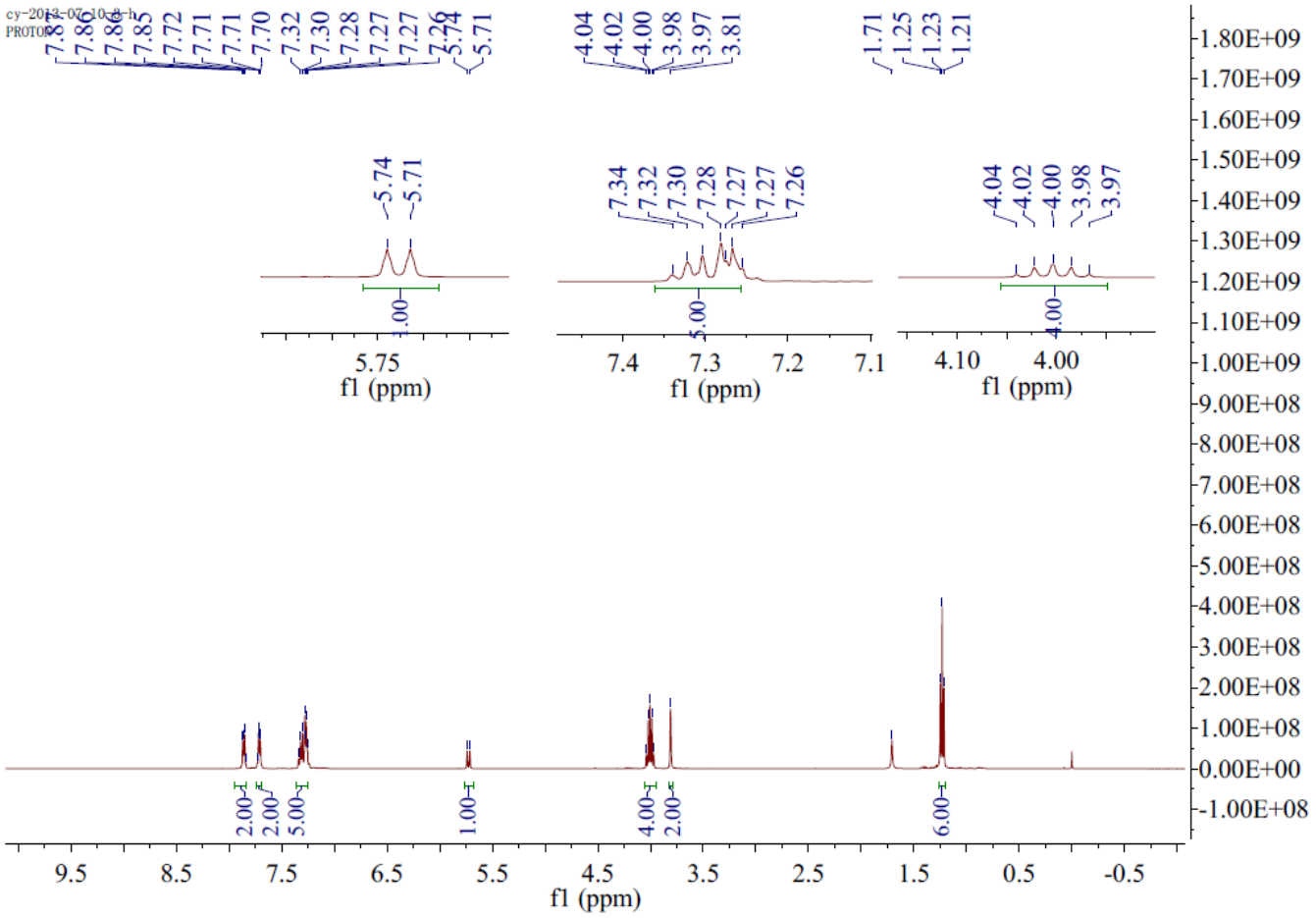
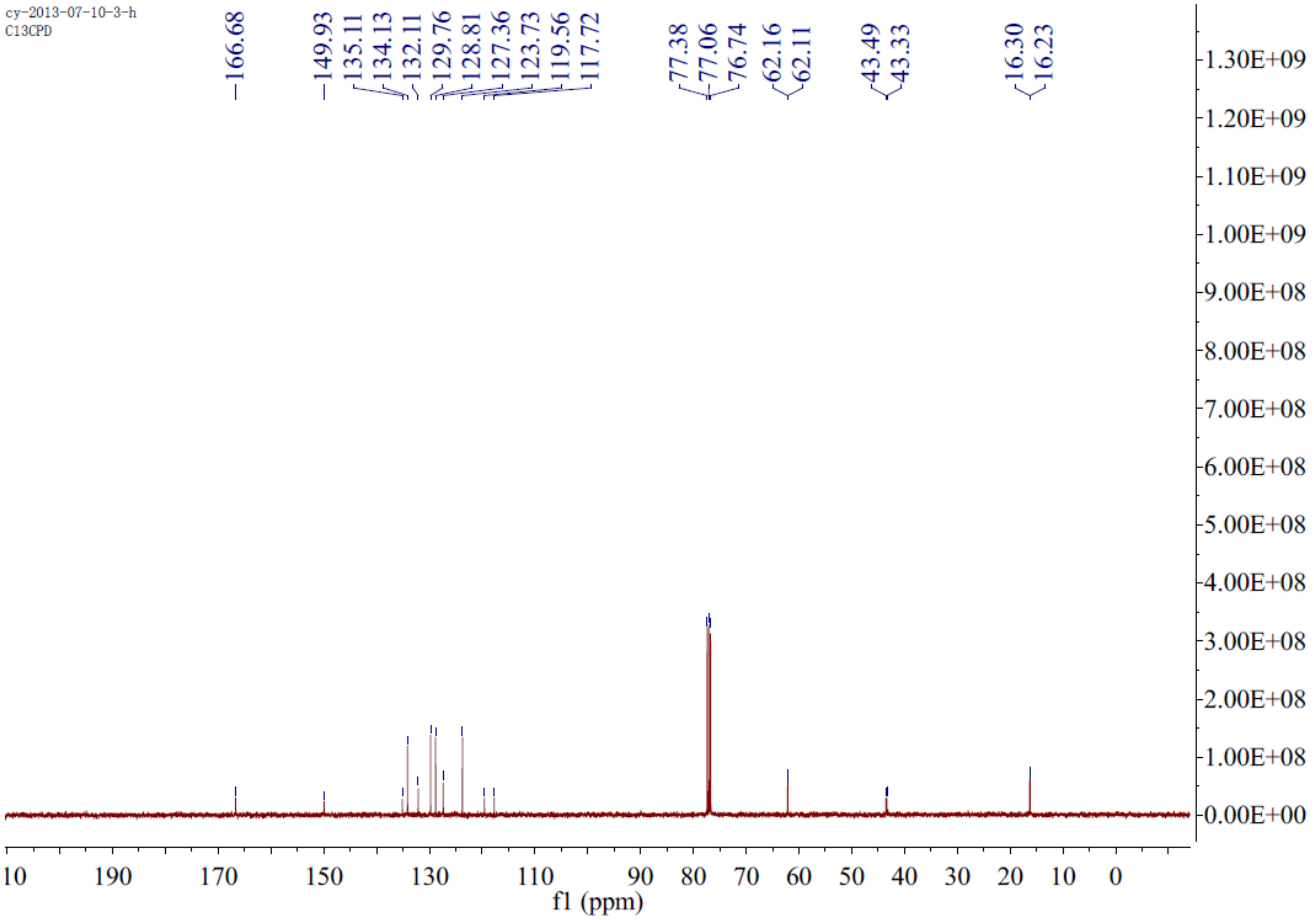
77.38 77.06 76.74 62.09 62.04 47.27 47.12 25.76 22.36 16.30 16.24
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
3.8E+09 3.6E+09 3.4E+09 3.2E+09 3.0E+09 2.8E+09 2.6E+09 2.4E+09 2.2E+09 2.0E+09 1.8E+09 1.6E+09 1.4E+09 1.2E+09 1.0E+09 8.0E+08 6.0E+08 4.0E+08 2.0E+08 0.0E+00

(*Z*)-Diethyl (2-(1,3-dioxoisoindolin-2-yl)-3-phenylprop-1-en-1-yl)phosphonate (2c):



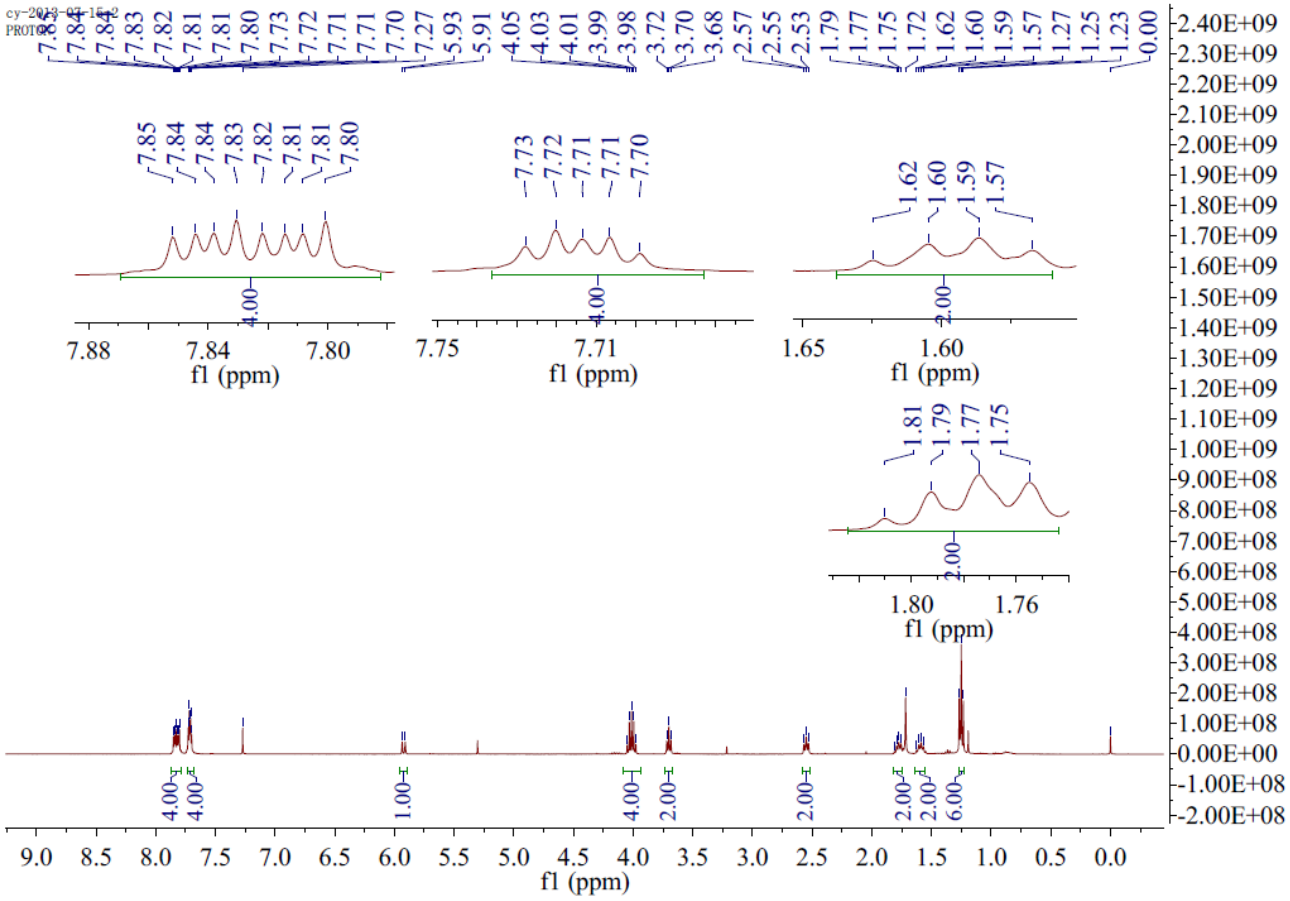
Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.89 (m, 2H, Ph), 7.69-7.74 (m, 2H, Ph), 7.25-7.37 (m, 5H, Ph), 5.73 (d, *J* = 10.1 Hz, 1H, CH), 3.94-4.07 (m, 4H, $2OCH_2$), 3.81 (s, 2H, CH_2), 1.23 (t, *J* = 7.1 Hz, 6H, $2CH_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.68 (C=O), 149.93 (N-C), 135.11, 134.13, 132.11, 129.76, 128.81, 127.36, 123.73 (Ph), 118.64 (d, *J* = 185.2 Hz, C-P), 62.13 (d, *J* = 5.1 Hz, OCH_2), 43.41 (d, *J* = 16.0 Hz, CH_2), 16.26 (d, *J* = 6.4 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 11.90 (s). ESI-HRMS calcd for $[C_{21}H_{22}NO_5P, M+H]^+$: 400.1308, Found: 400.1313.





(*Z*)-Diethyl (2,6-bis(1,3-dioxoisoindolin-2-yl)hex-1-en-1-yl)phosphonate (2d):

White solid; mp 143-145°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.87 (m, 4H, Ph), 7.69-7.74 (m, 4H, Ph), 5.92 (d, *J* = 10.2 Hz, 1H, CH), 3.96-4.07 (m, 4H, 2OCH_2), 3.70 (t, *J* = 7.0, 2H, CH_2), 2.55 (t, *J* = 7.5 Hz, 2H, CH_2), 1.74-1.83 (m, 2H, CH_2), 1.56-1.63 (m, 2H, CH_2), 1.25 (t, *J* = 7.1 Hz, 6H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.41, 166.95 (C=O), 150.19 (N-C), 134.07, 133.91, 132.22, 132.13, 123.69, 123.22 (Ph), 117.83 (d, *J* = 185.0 Hz, C-P), 62.12 (d, *J* = 5.1 Hz, OCH_2), 37.35 (CH_2), 37.12 (d, *J* = 15.9 Hz, CH_2), 27.78, 23.44 (CH_2), 16.26 (d, *J* = 6.5 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 11.60 (s). ESI-HRMS calcd for $[C_{26}H_{27}N_2O_7P, M+H]^+$: 511.1629, Found: 511.1631.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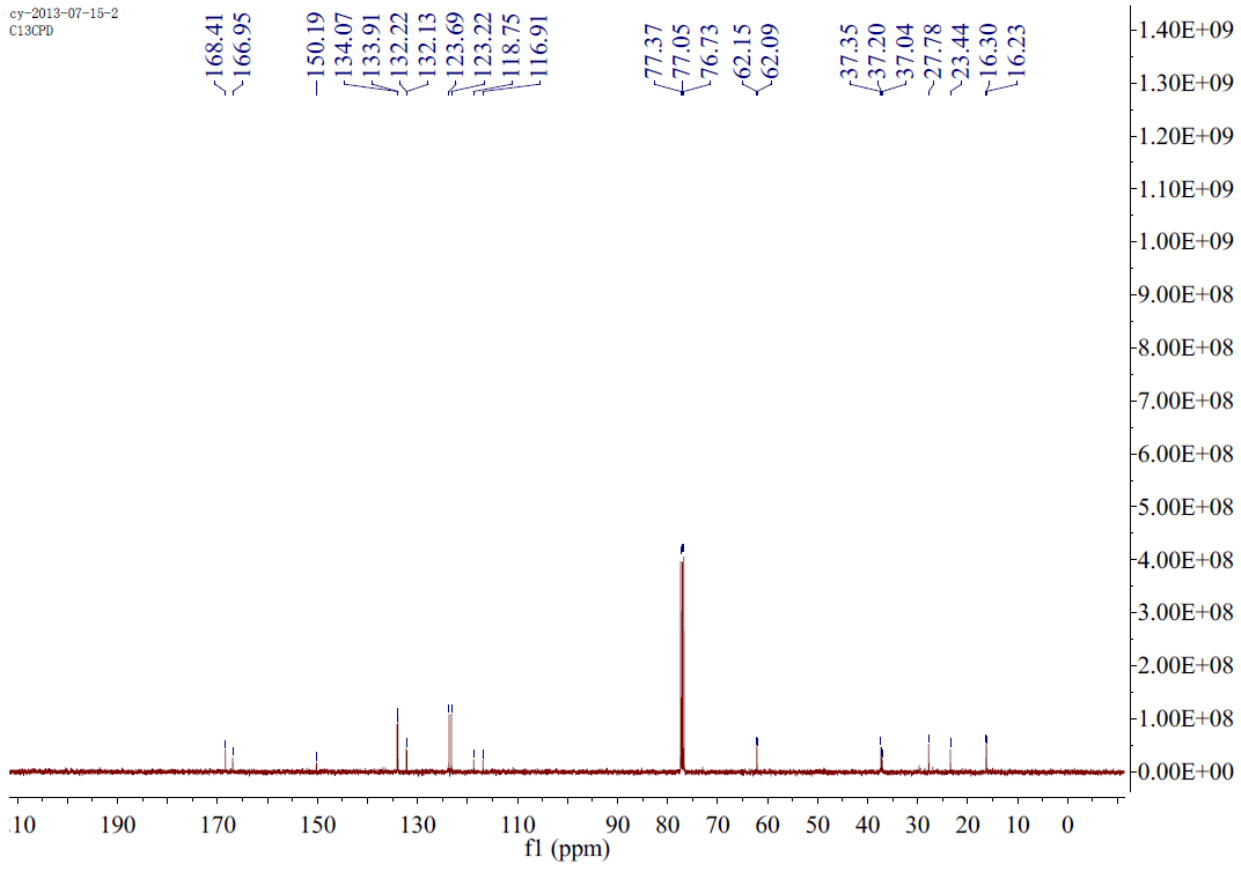
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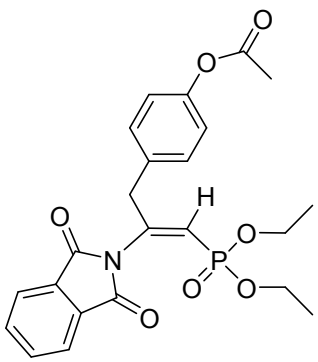
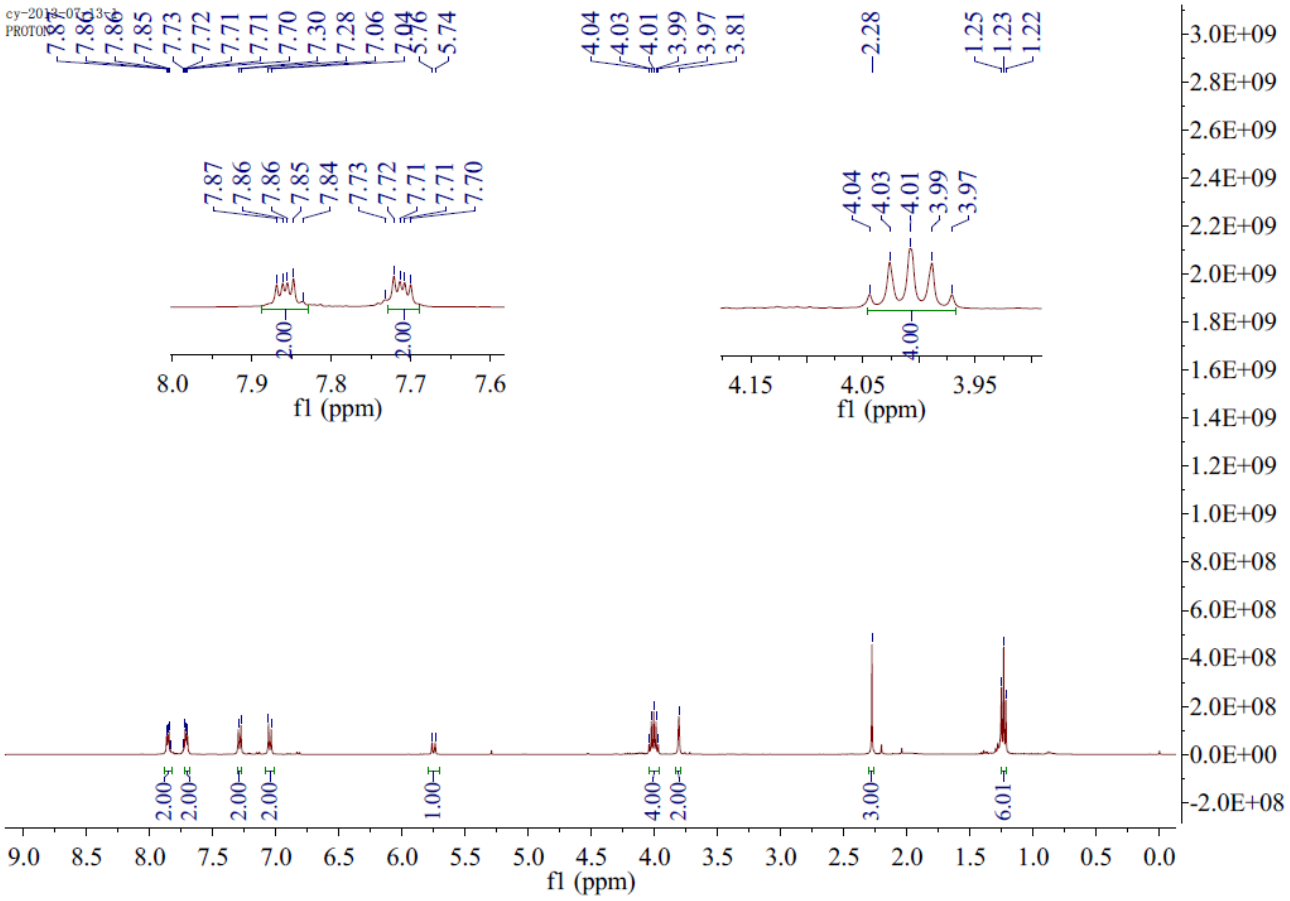
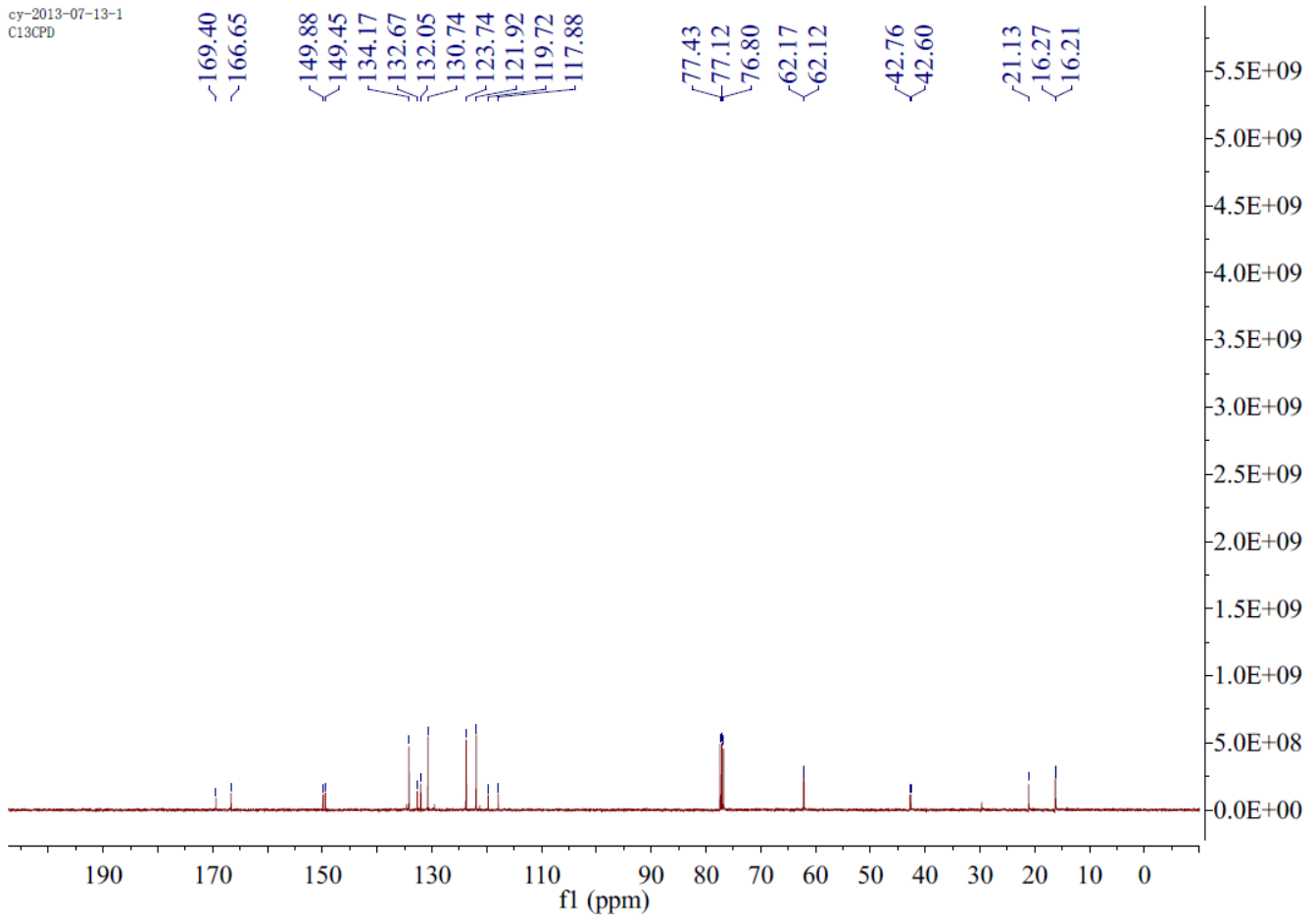
116.91
77.37
77.05
76.73
62.15
62.09
37.35
37.20
37.04
27.78
23.44
16.30
16.23
fl (ppm)

(*Z*)-4-(3-(Diethoxyphosphoryl)-2-(1,3-dioxoisoindolin-2-yl)allyl)phenyl acetate (2e):



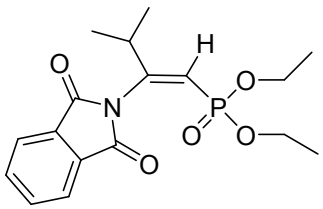
Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.89 (m, 2H, Ph), 7.68-7.74 (m, 2H, Ph), 7.29 (d, *J* = 8.4 Hz, 2H, Ph), 7.05 (d, *J* = 8.4 Hz, 2H, Ph), 5.75 (d, *J* = 9.9 Hz, 1H, CH), 3.95-4.07 (m, 4H, $2OCH_2$), 3.81 (s, 2H, CH_2), 2.28 (s, 3H, CH_3), 1.23 (t, *J* = 7.1 Hz, 6H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.40, 166.65 (C=O), 149.88 (N-C), 149.45 (Ph), 134.17, 132.67, 132.05, 130.74, 123.74, 121.92 (Ph), 118.80 (d, *J* = 185.6 Hz, C-P), 62.15 (d, *J* = 5.0 Hz, OCH_2), 42.68 (d, *J* = 16.2 Hz, CH_2), 21.13 (CH_3), 16.24 (d, *J* = 6.4 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 11.67 (s). ESI-HRMS calcd for $[C_{23}H_{24}NO_7P, M+H]^+$: 458.1363, Found: 458.1366.

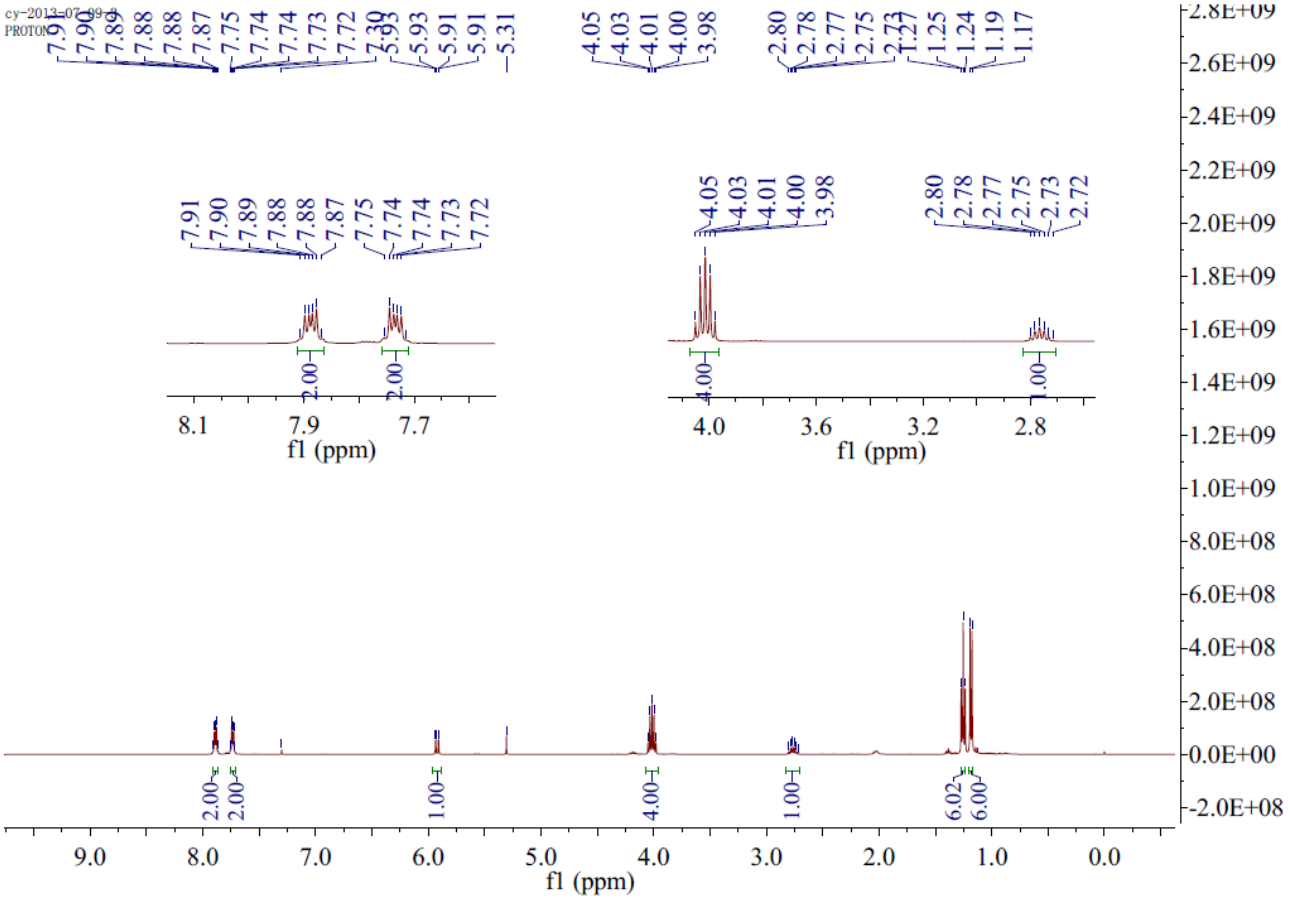


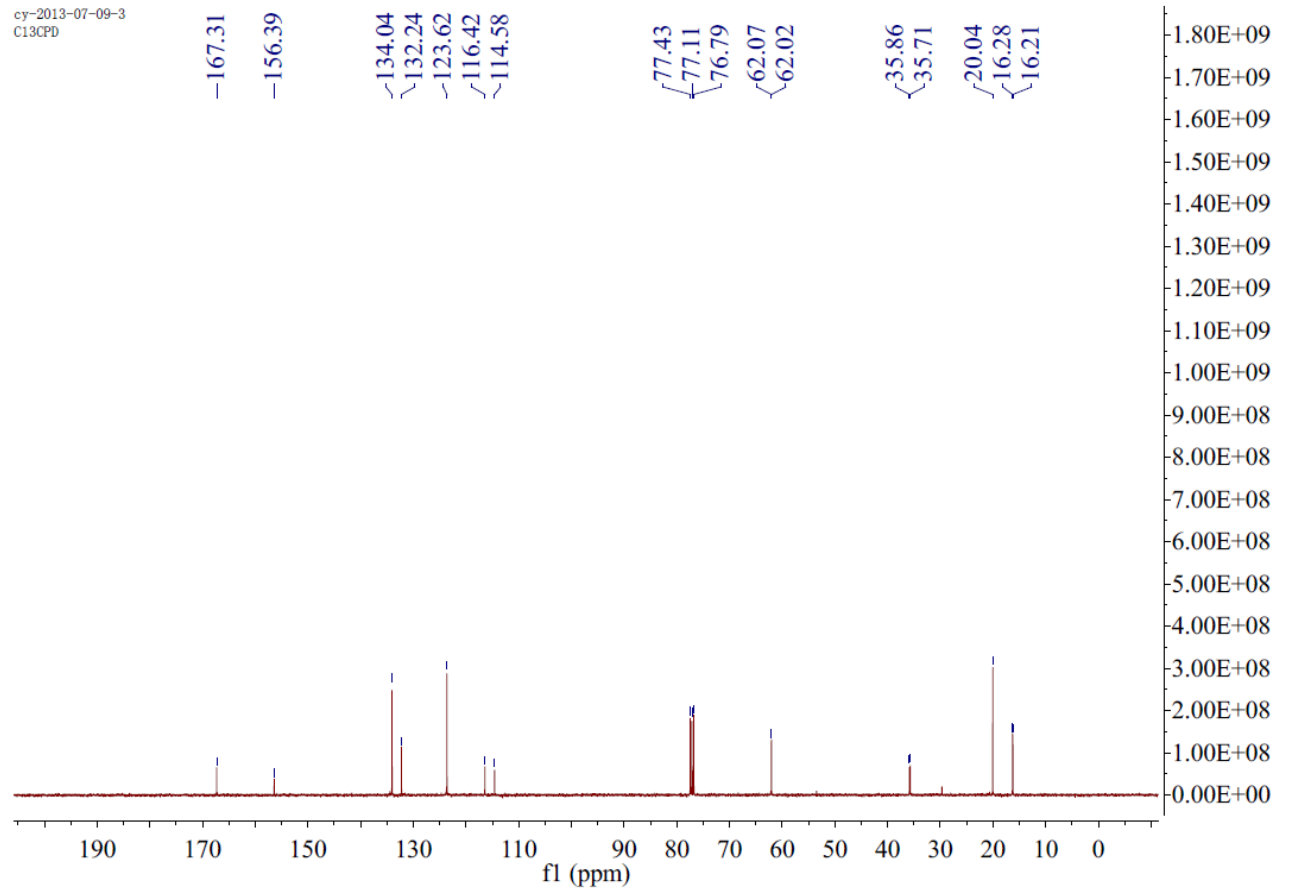


(*Z*)-Diethyl (2-(1,3-dioxoisoindolin-2-yl)-3-methylbut-1-en-1-yl)phosphonate (2f):

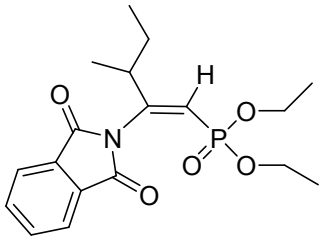
Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.95 (m, 2H, Ph), 7.70-7.76 (m, 2H, Ph), 5.92 (dd, *J* = 9.9, 1.0 Hz, 1H, CH), 3.96-4.07 (m, 4H, $2OCH_2$), 2.71-2.83 (m, 1H, CH), 1.25 (t, *J* = 7.1 Hz, 6H, $2CH_3$), 1.18 (d, *J* = 6.9 Hz, 6H, $2CH_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.31 (C=O), 156.39 (N-C), 134.04, 132.24, 123.62 (Ph), 115.50 (d, *J* = 185.5 Hz, C-P), 62.04 (d, *J* = 5.0 Hz, OCH_2), 35.79 (d, *J* = 14.7 Hz, CH), 20.04 (CH_3), 16.25 (d, *J* = 6.5 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 12.74 (s). ESI-HRMS calcd for $[C_{17}H_{22}NO_5P, M+H]^+$: 352.1308, Found: 352.1315.



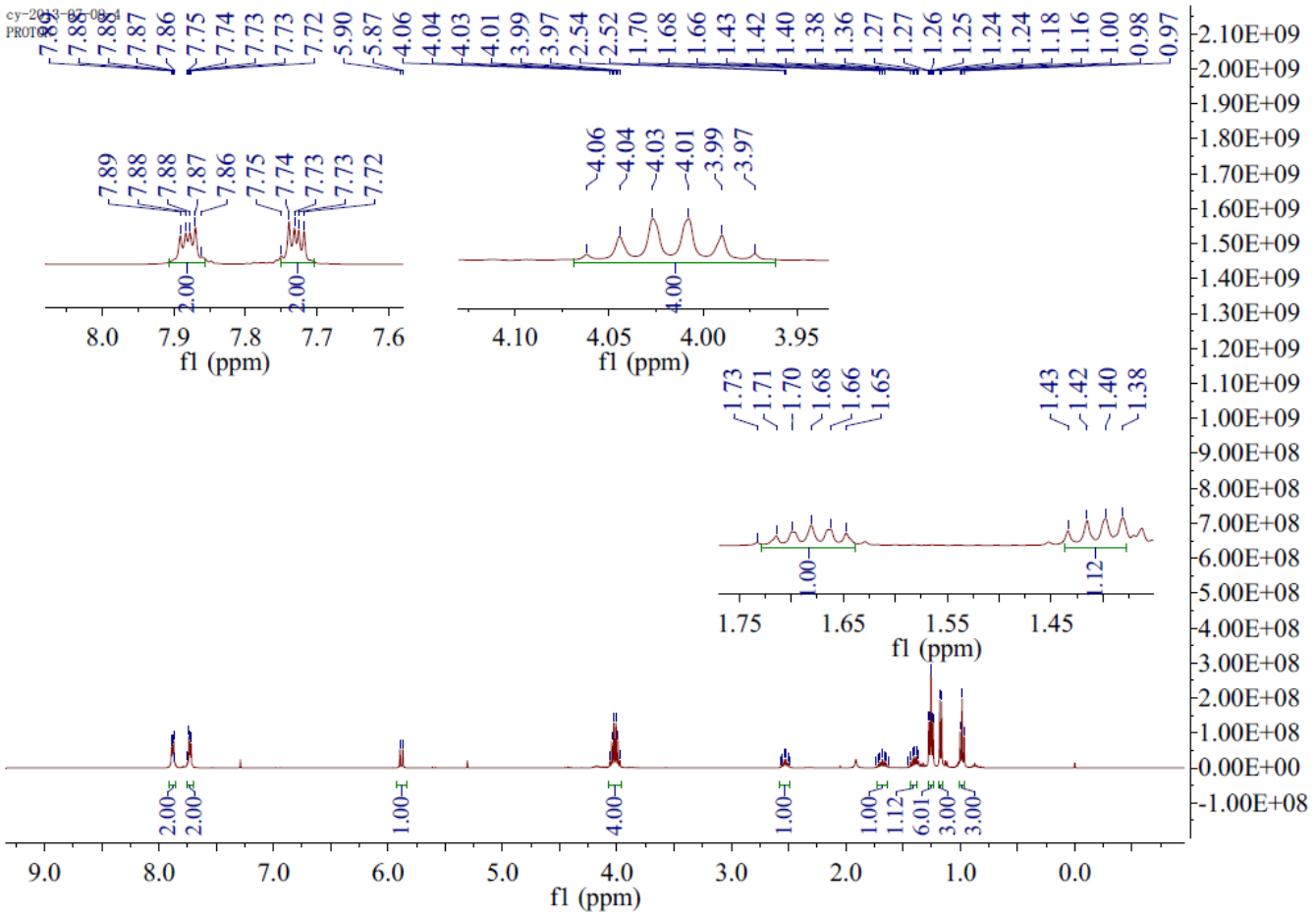

fl (ppm)

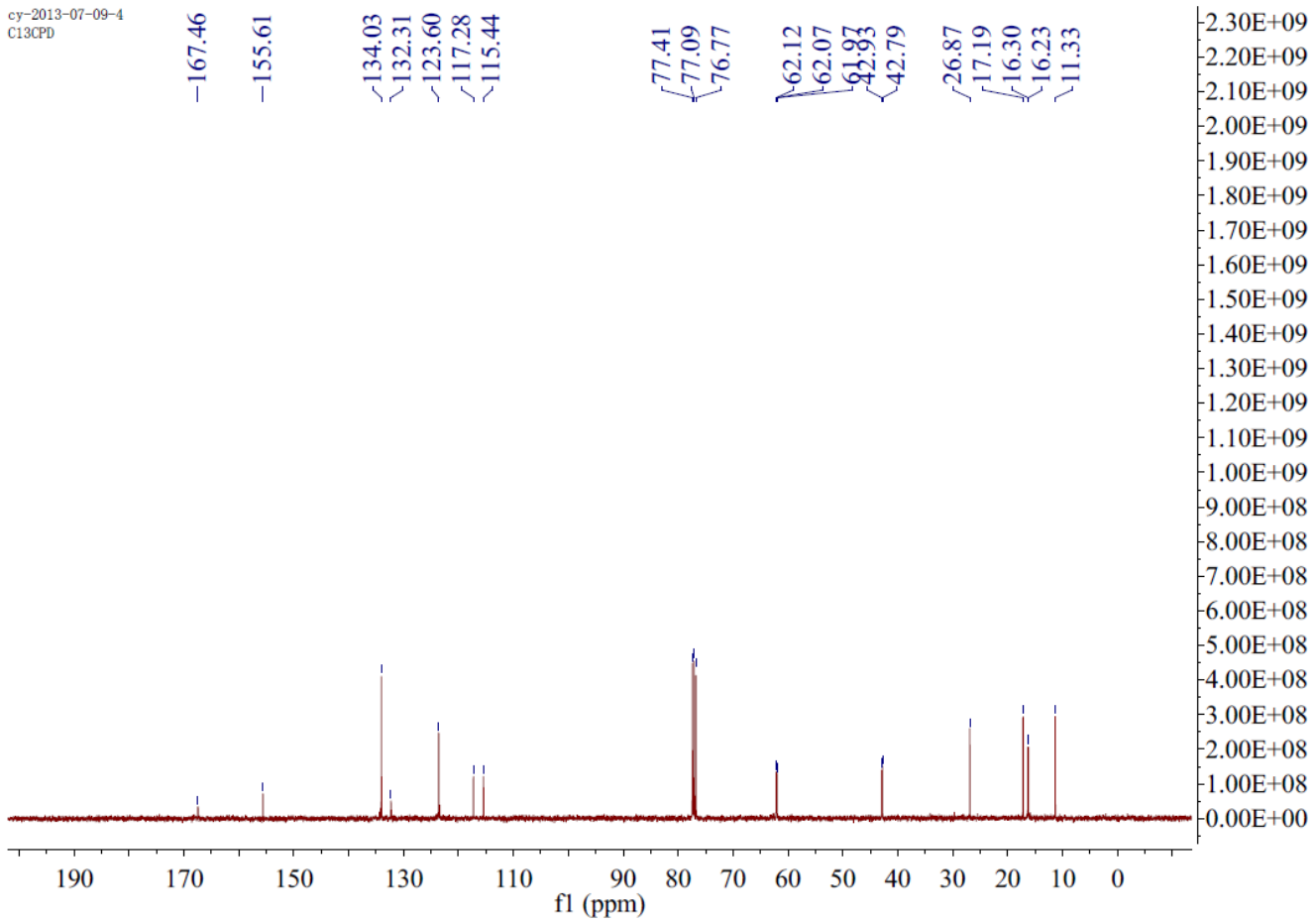

fl (ppm)

(*Z*)-Diethyl (2-(1,3-dioxoisoindolin-2-yl)-3-methylpent-1-en-1-yl)phosphonate (2g):



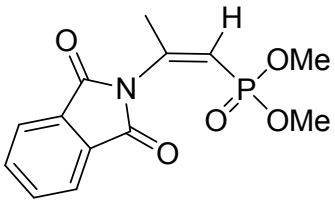
Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.91 (m, 2H, Ph), 7.70-7.76 (m, 2H, Ph), 5.88 (d, *J* =10.0 Hz, 1H, CH), 3.96-4.07 (m, 4H, $2OCH_2$), 2.49-2.59 (m, 1H, CH), 1.63-1.75 (m, 1H, CH_2), 1.38-1.46 (m, 1H, CH_2), 1.26 (td, *J* = 7.1 , 1.2, Hz, 6H, $2CH_3$), 1.17 (d, *J* = 6.9 Hz, 3H, CH_3), 0.98 (t, *J* = 7.4 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.46 (C=O), 155.61 (N-C), 134.03, 132.31, 123.60 (Ph), 116.36 (d, *J* = 184.9 Hz, C-P), 62.10 (d, *J* = 5.0 Hz, OCH_2), 62.00 (d, *J* = 5.0 Hz, OCH_2), 42.86 (d, *J* = 14.3 Hz, CH), 26.87 (CH_2), 17.19 (CH_3), 16.26 (d, *J* = 6.5 Hz, CH_3), 11.33 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 12.59 (s). ESI-HRMS calcd for $[C_{18}H_{24}NO_5P, M+H]^+$: 366.1465; Found: 366.1467.

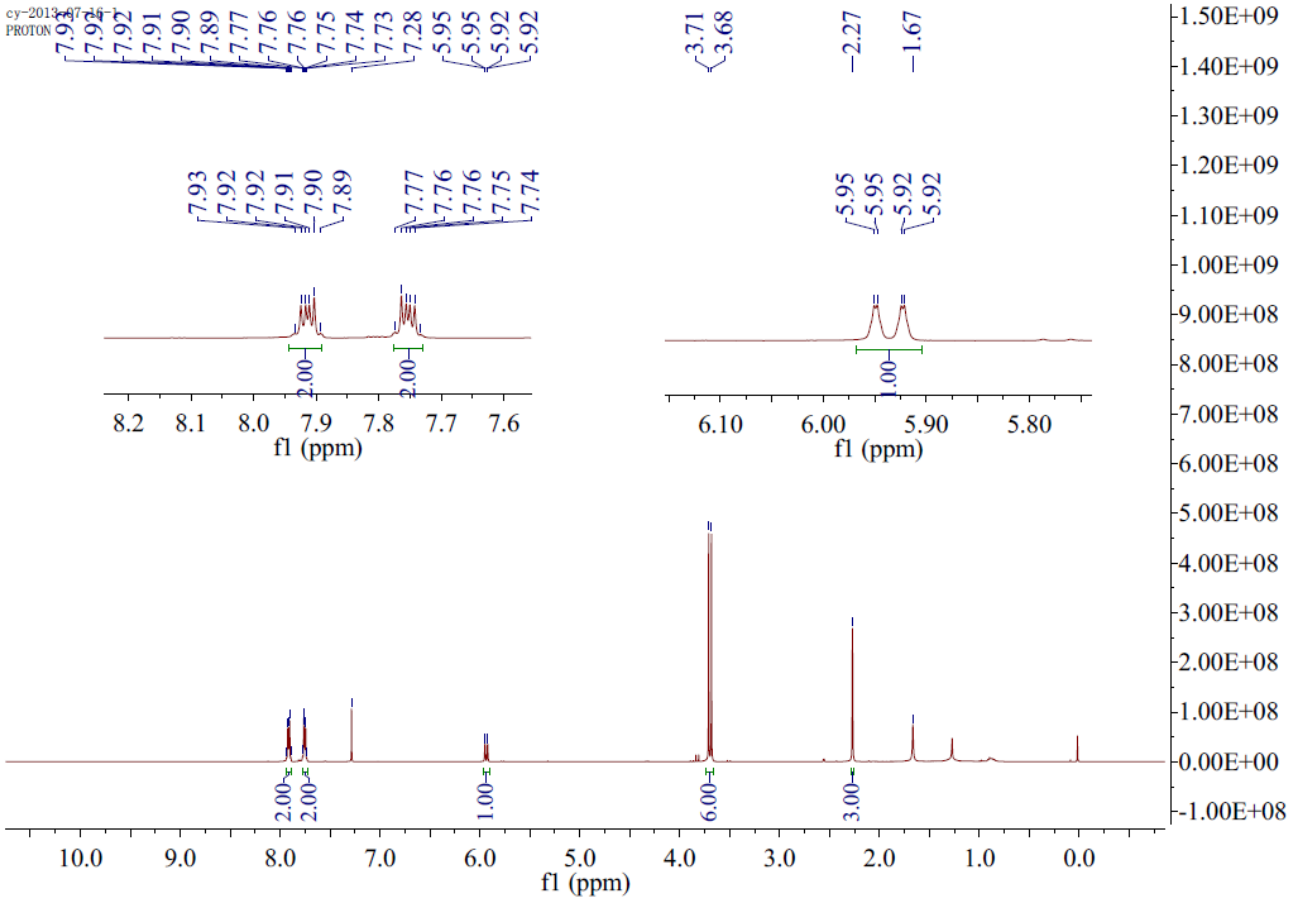


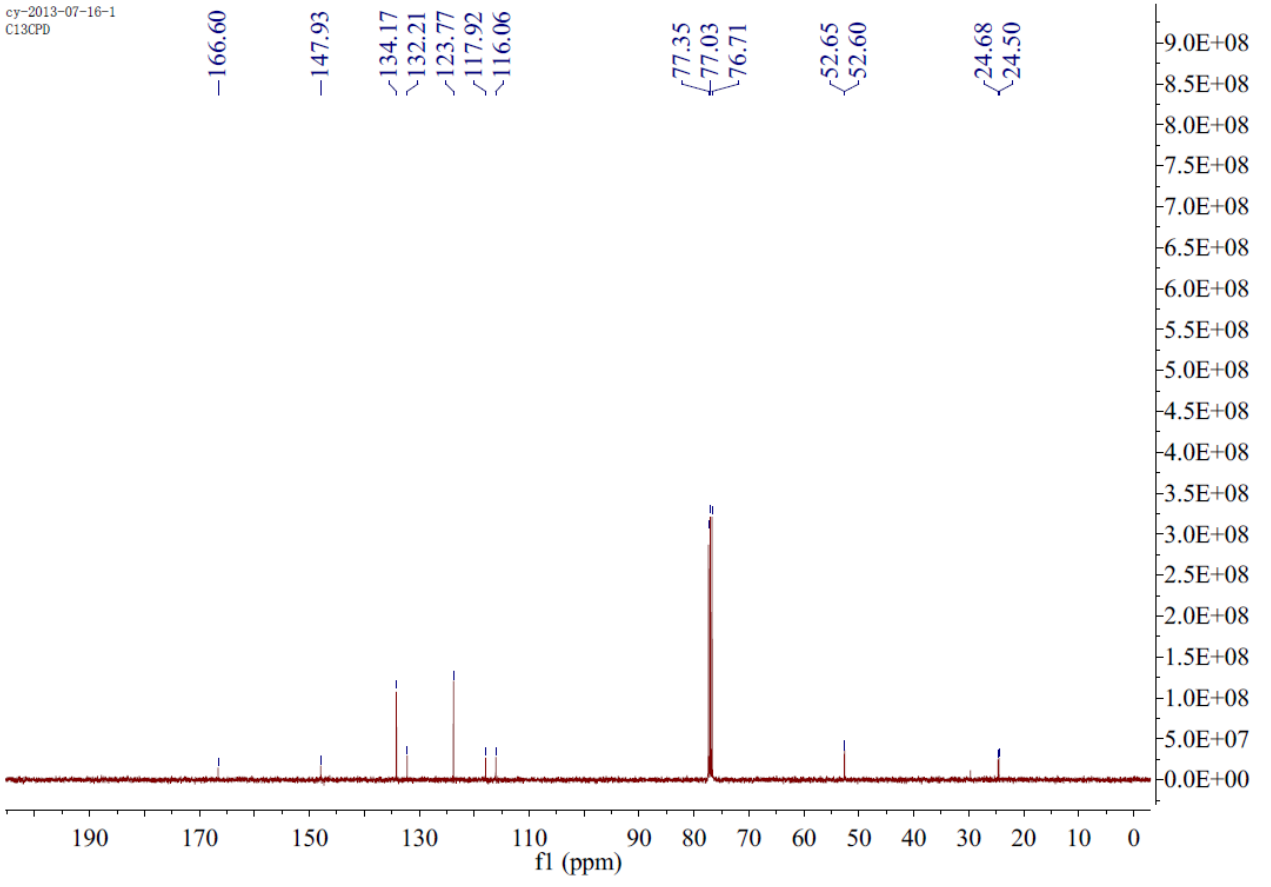


(*Z*)-Dimethyl (2-(1,3-dioxoisoindolin-2-yl)prop-1-en-1-yl)phosphonate (2i):

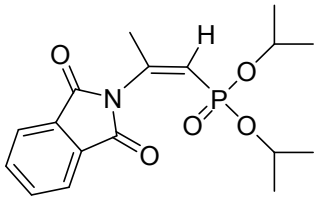
Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.95 (m, 2H, Ph), 7.73-7.79 (m, 2H, Ph), 5.94 (dd, *J* = 10.5, 1.2 Hz, 1H, CH), 3.70 (d, *J* = 11.3 Hz, 6H, $2CH_3$), 2.27 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.60 (C=O), 147.93 (N-C), 134.17, 132.21, 123.77 (Ph), 116.99 (d, *J* = 187.1 Hz, C-P), 52.63 (d, *J* = 5.1 Hz, OCH_3), 24.59 (d, *J* = 17.4 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 14.25 (s); ESI-HRMS calcd for $[C_{13}H_{14}NO_5P, M+H]^+$: 296.0682, Found: 296.0682.



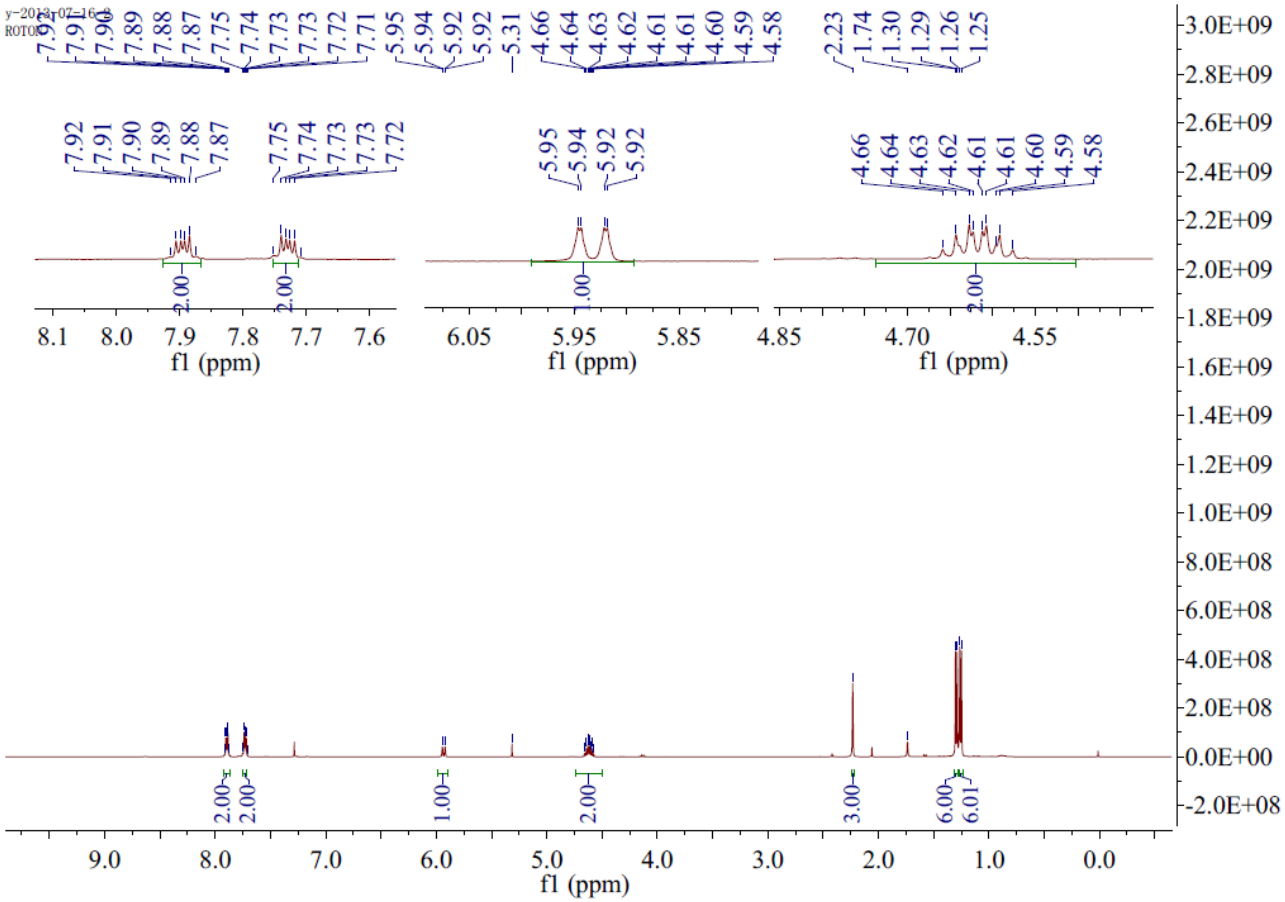

cy-2013-07-16-1
PROTON
7.93 7.92 7.92 7.91 7.90 7.89 7.77 7.76 7.76 7.75 7.74 7.73 7.28 5.95 5.95 5.92 5.92
3.71 3.68 2.27 1.67
2.00 2.00 1.00
fl (ppm)
2.00 2.00 1.00 6.00 3.00
fl (ppm)

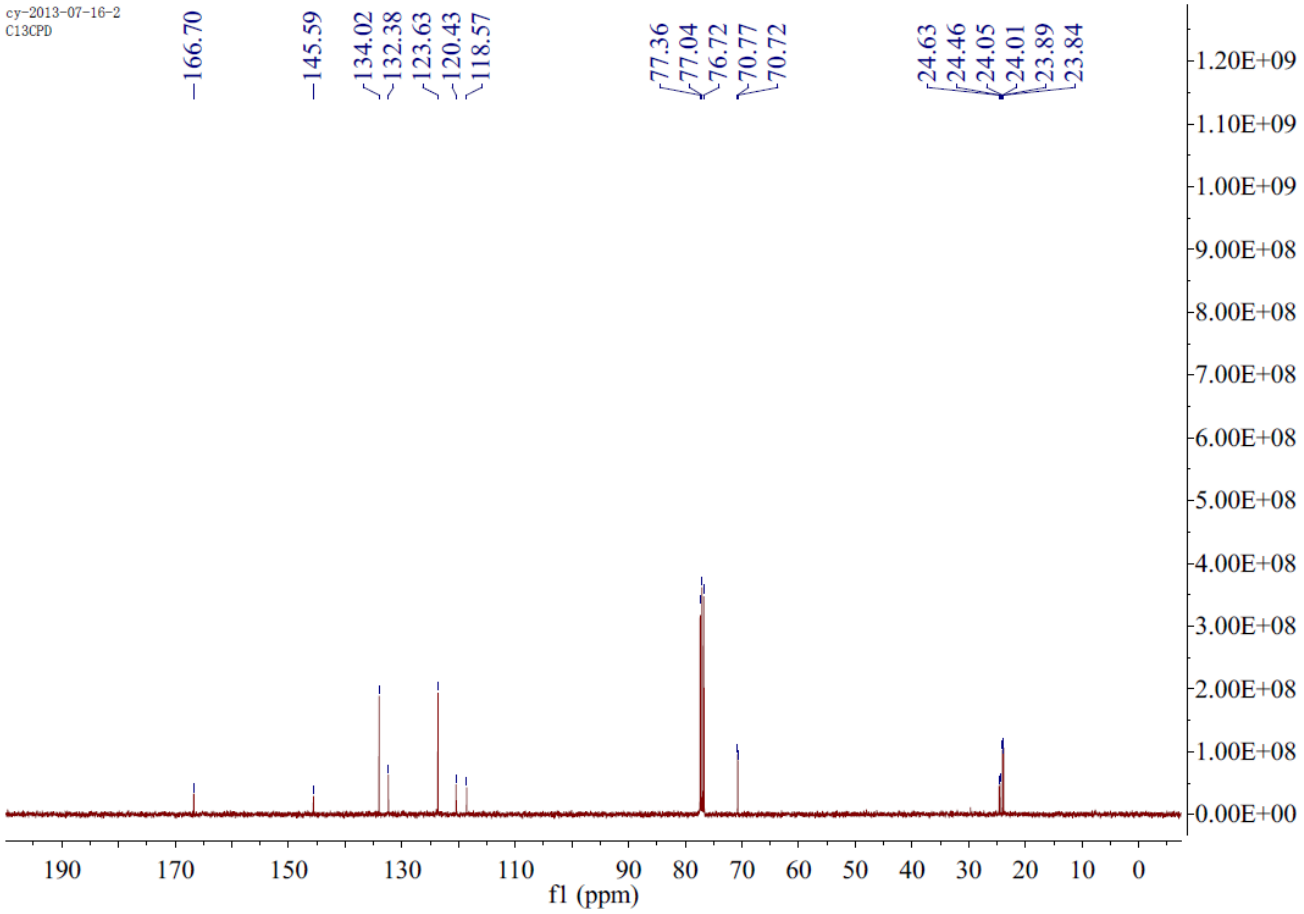

cy-2013-07-16-1
C13CPD
166.60 147.93 134.17 132.21 123.77 117.92 116.06
77.35 77.03 76.71 52.65 52.60 24.68 24.50
fl (ppm)

(*Z*)-Diisopropyl (2-(1,3-dioxoisoindolin-2-yl)prop-1-en-1-yl)phosphonate (2j):



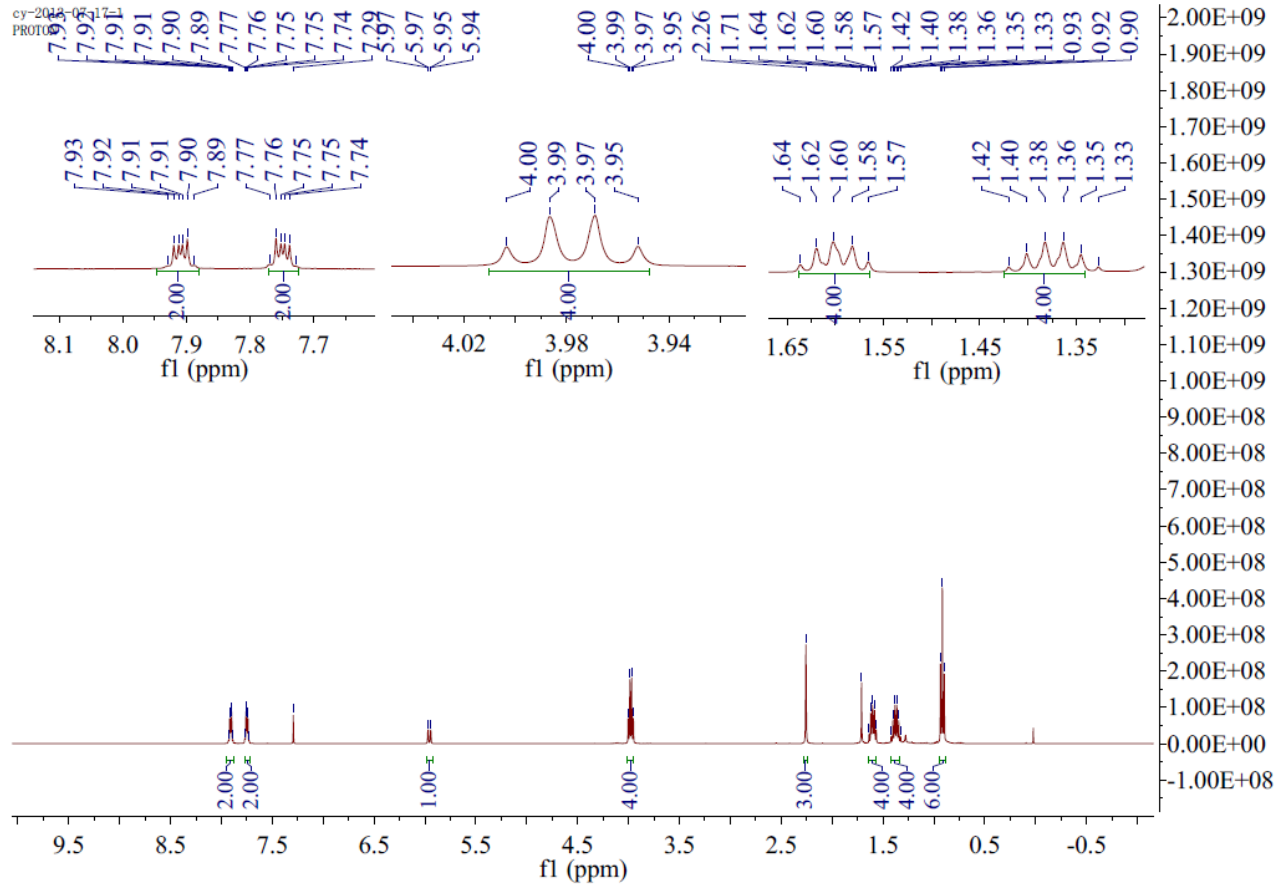
Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86-7.92 (m, 2H, Ph), 7.71-7.76 (m, 2H, Ph), 5.93 (dd, *J* = 10.0, 1.2 Hz, 1H, CH), 4.55-4.68 (m, 2H, 2OCH), 2.23 (s, 3H, CH_3), 1.29 (d, *J* = 6.2 Hz, 6H, $2CH_3$), 1.26 (d, *J* = 6.2 Hz, 6H, $2CH_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.70 (C=O), 145.59 (N-C), 134.02, 132.38, 123.63 (Ph), 119.50 (d, *J* = 186.6 Hz, C-P), 70.74 (d, *J* = 5.3 Hz, OCH), 24.54 (d, *J* = 17.3 Hz, CH_3), 24.03 (d, *J* = 3.8 Hz, CH_3), 23.87 (d, *J* = 5.0 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 9.09 (s). ESI-HRMS calcd for $[C_{17}H_{22}NO_5P, M+H]^+$: 352.1308, Found: 352.1313.

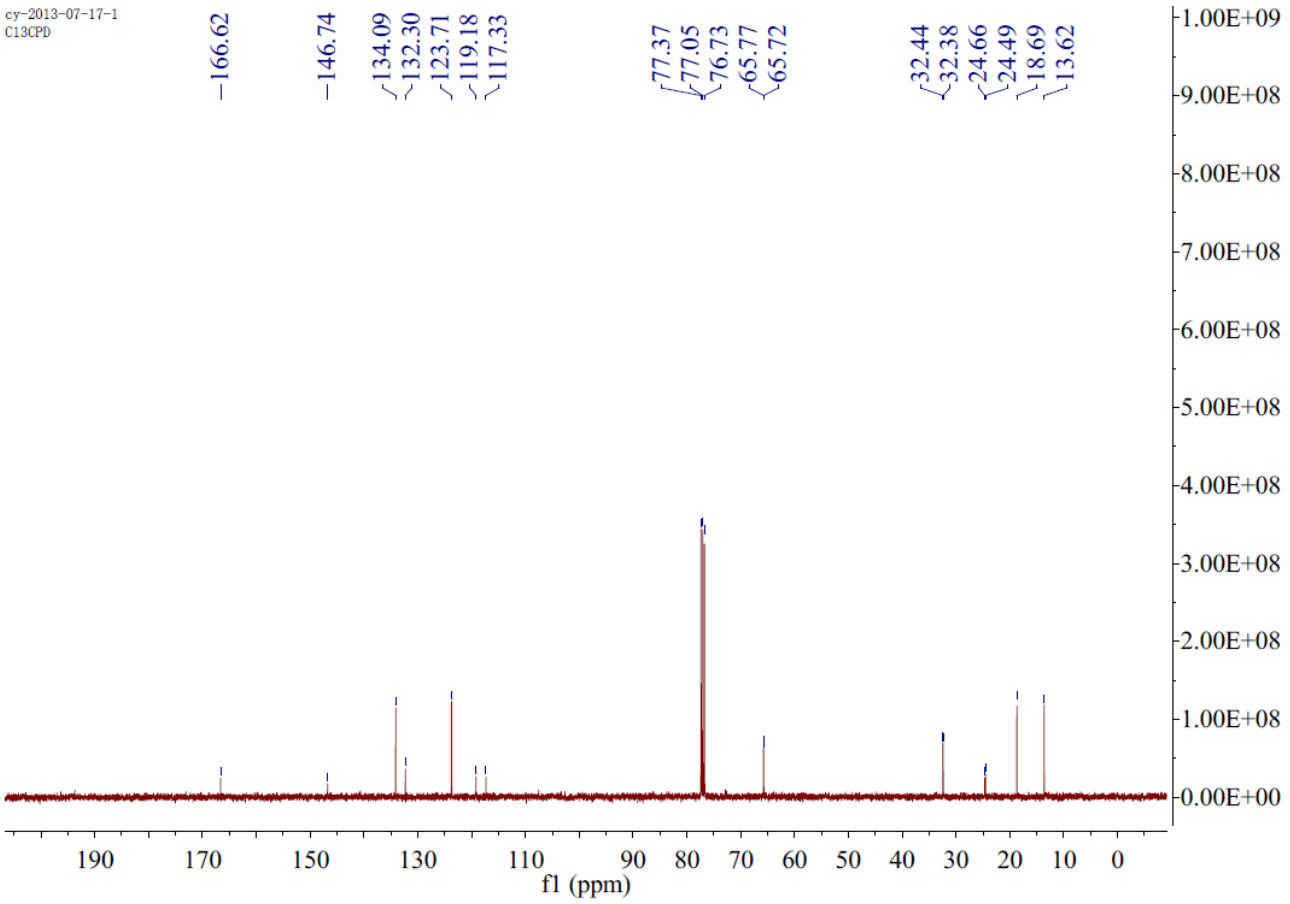




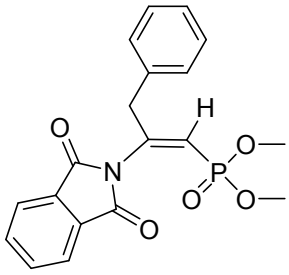
(*Z*)-Dibutyl (2-(1,3-dioxoisoindolin-2-yl)prop-1-en-1-yl)phosphonate (2k):

Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.94 (m, 2H, Ph), 7.72-7.78 (m, 2H, Ph), 5.96 (dd, *J* = 10.3, 1.2 Hz, 1H, CH), 3.98 (q, *J* = 6.7 Hz, 4H, $2OCH_2$), 2.26 (s, 3H, CH_3), 1.55-1.65 (m, 4H, $2CH_2$), 1.31-1.44 (m, 4H, $2CH_2$), 0.92 (t, *J* = 7.4 Hz, 6H, $2CH_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.62 (C=O), 146.74 (N-C), 134.09, 132.30, 123.71 (Ph), 118.25 (d, *J* = 186.5 Hz, C-P), 65.75 (d, *J* = 5.4 Hz, OCH_2), 32.41 (d, *J* = 6.5 Hz, CH_2), 24.57 (d, *J* = 16.9 Hz, CH_3), 18.69 (CH_2), 13.62 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 11.50 (s). ESI-HRMS calcd for $[C_{19}H_{26}NO_5P, M+H]^+$: 380.1621, Found: 380.1629.

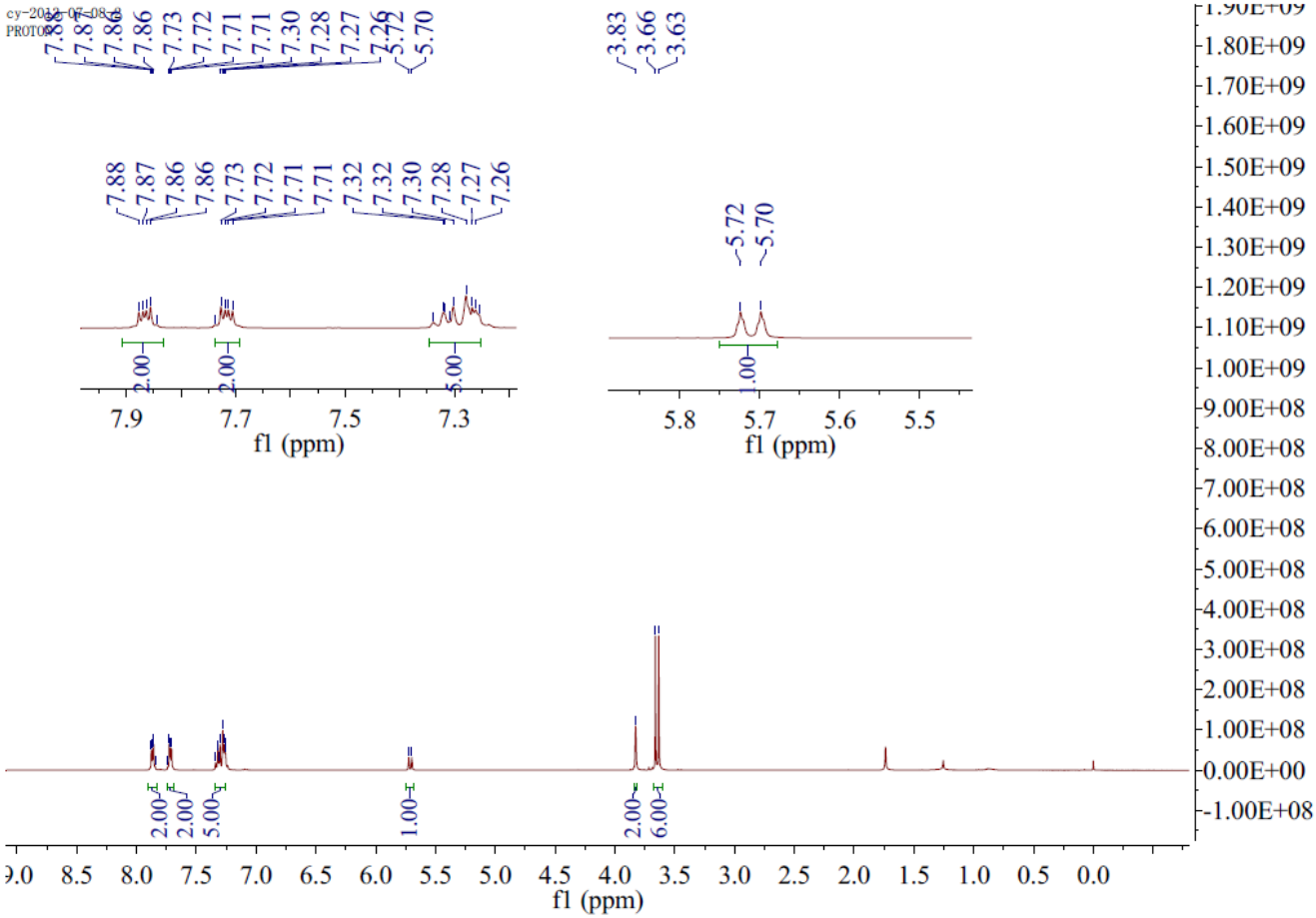

cy-2013-07-17-1
PROTON
7.93 7.92 7.91 7.91 7.90 7.89 7.77 7.76 7.75 7.75 7.74 7.29 5.97 5.95 5.94
4.00 3.99 3.97 3.95 2.26 1.71 1.64 1.62 1.60 1.58 1.57 1.42 1.40 1.38 1.36 1.35 1.33 0.93 0.92 0.90
2.00 2.00 4.00 4.00 4.00 4.00
8.1 8.0 7.9 7.8 7.7 4.02 3.98 3.94 1.65 1.55 1.45 1.35
fl (ppm)
2.00 2.00 1.00 4.00 3.00 4.00 4.00 6.00
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
fl (ppm)
2.00E+09 1.90E+09 1.80E+09 1.70E+09 1.60E+09 1.50E+09 1.40E+09 1.30E+09 1.20E+09 1.10E+09 1.00E+09 9.00E+08 8.00E+08 7.00E+08 6.00E+08 5.00E+08 4.00E+08 3.00E+08 2.00E+08 1.00E+08 0.00E+00 -1.00E+08

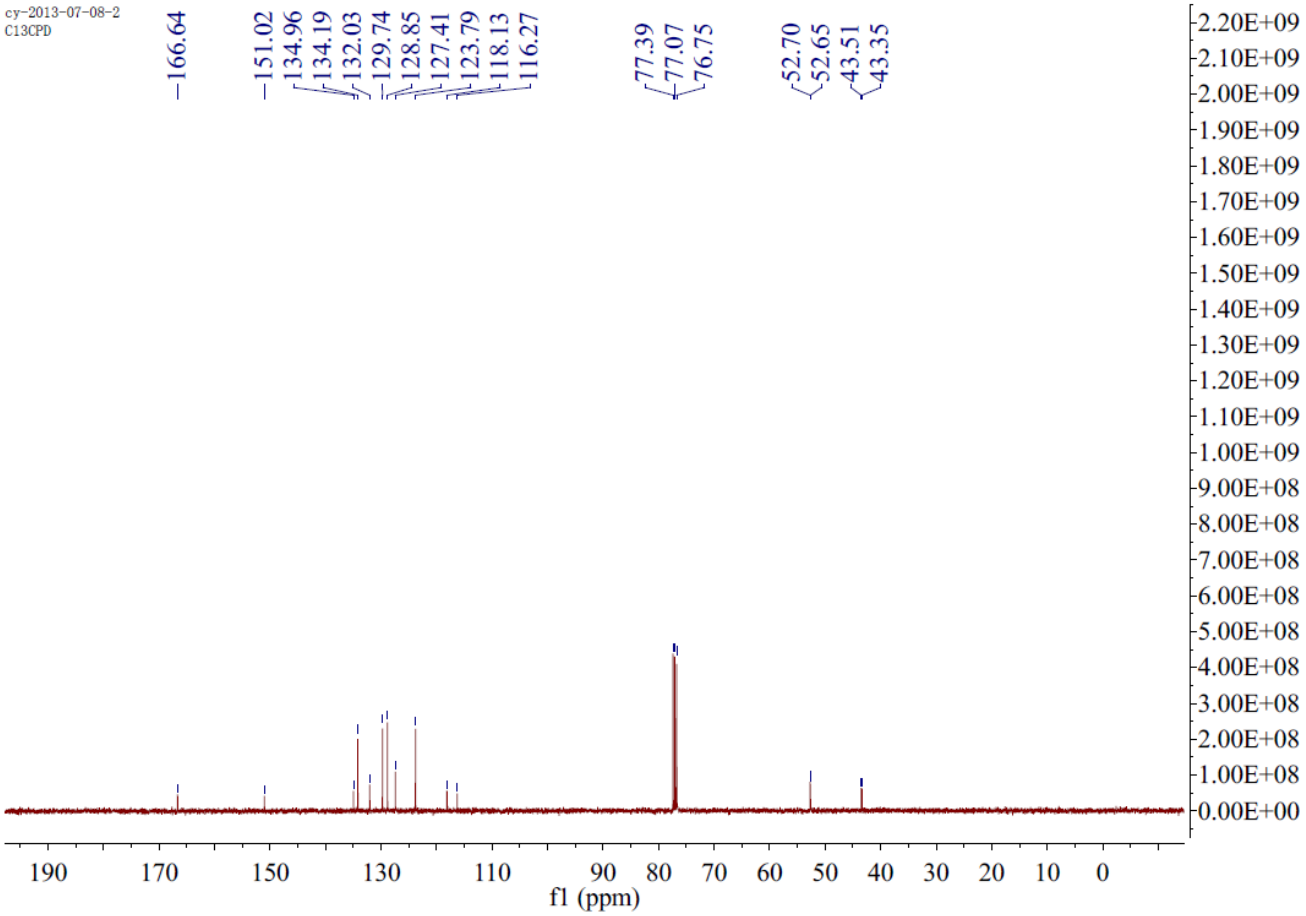

cy-2013-07-17-1
C13CPD
166.62 146.74 134.09 132.30 123.71 119.18 117.33 77.37 77.05 76.73 65.77 65.72 32.44 32.38 24.66 24.49 18.69 13.62
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
fl (ppm)
1.00E+09 9.00E+08 8.00E+08 7.00E+08 6.00E+08 5.00E+08 4.00E+08 3.00E+08 2.00E+08 1.00E+08 0.00E+00

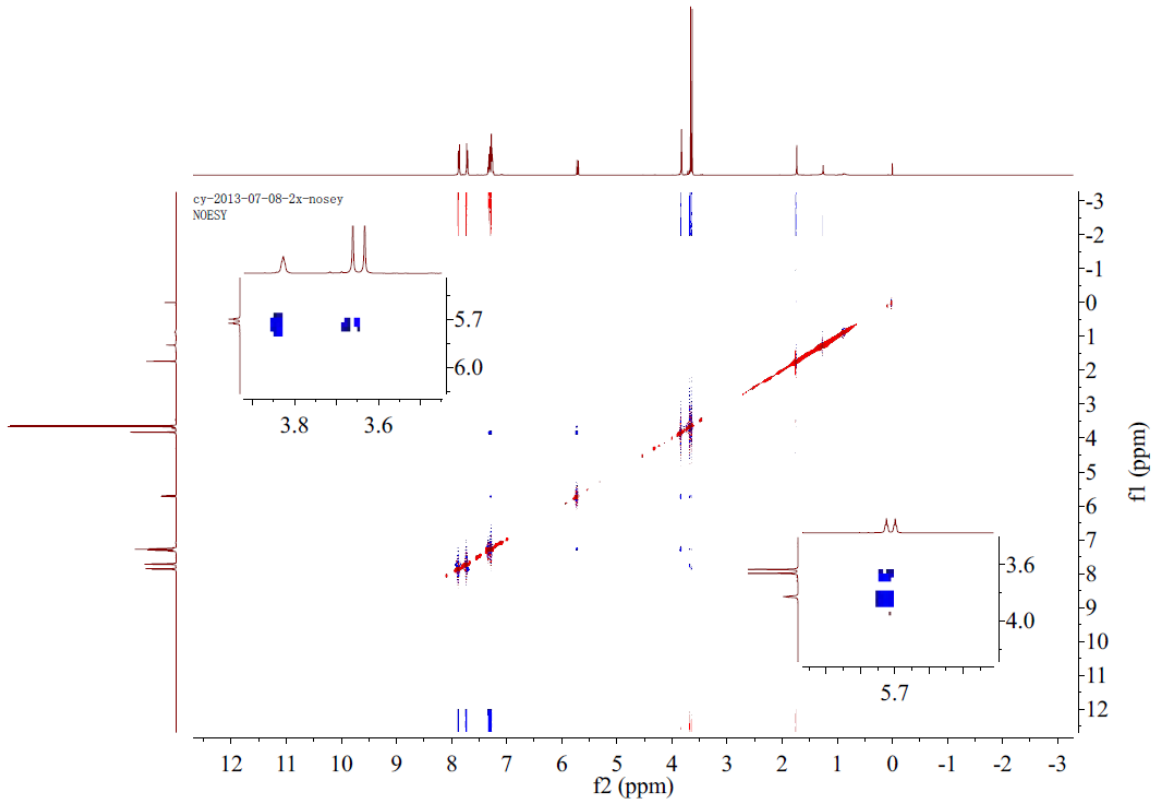
(*Z*)-Dimethyl (2-(1,3-dioxoisoindolin-2-yl)-3-phenylprop-1-en-1-yl)phosphonate (2l):



Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.92 (m, 2H, Ph), 7.65-7.77 (m, 2H, Ph), 7.25 – 7.35 (m, 5H, Ph), 5.71 (d, *J* = 10.2 Hz, 1H, CH), 3.83 (s, 2H, CH_2), 3.65 (d, *J* = 11.3 Hz, 6H, $2OCH_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.64 (C=O), 151.02 (N-C), 134.96, 134.19, 132.03, 129.74, 128.85, 127.41, 123.79 (Ph), 117.20 (d, *J* = 186.7 Hz, C-P), 52.67 (d, *J* = 5.1 Hz, OCH_3), 43.43 (d, *J* = 16.2 Hz, CH_2); ^{31}P NMR (162 MHz, $CDCl_3$): δ 14.83 (s). ESI-HRMS calcd for [$C_{19}H_{18}NO_5P$, M+H]$^{+}$: 372.0995, Found: 372.1000.

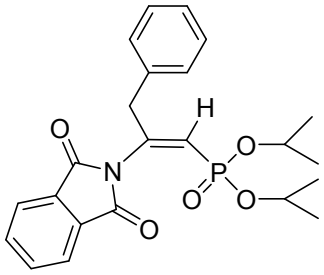




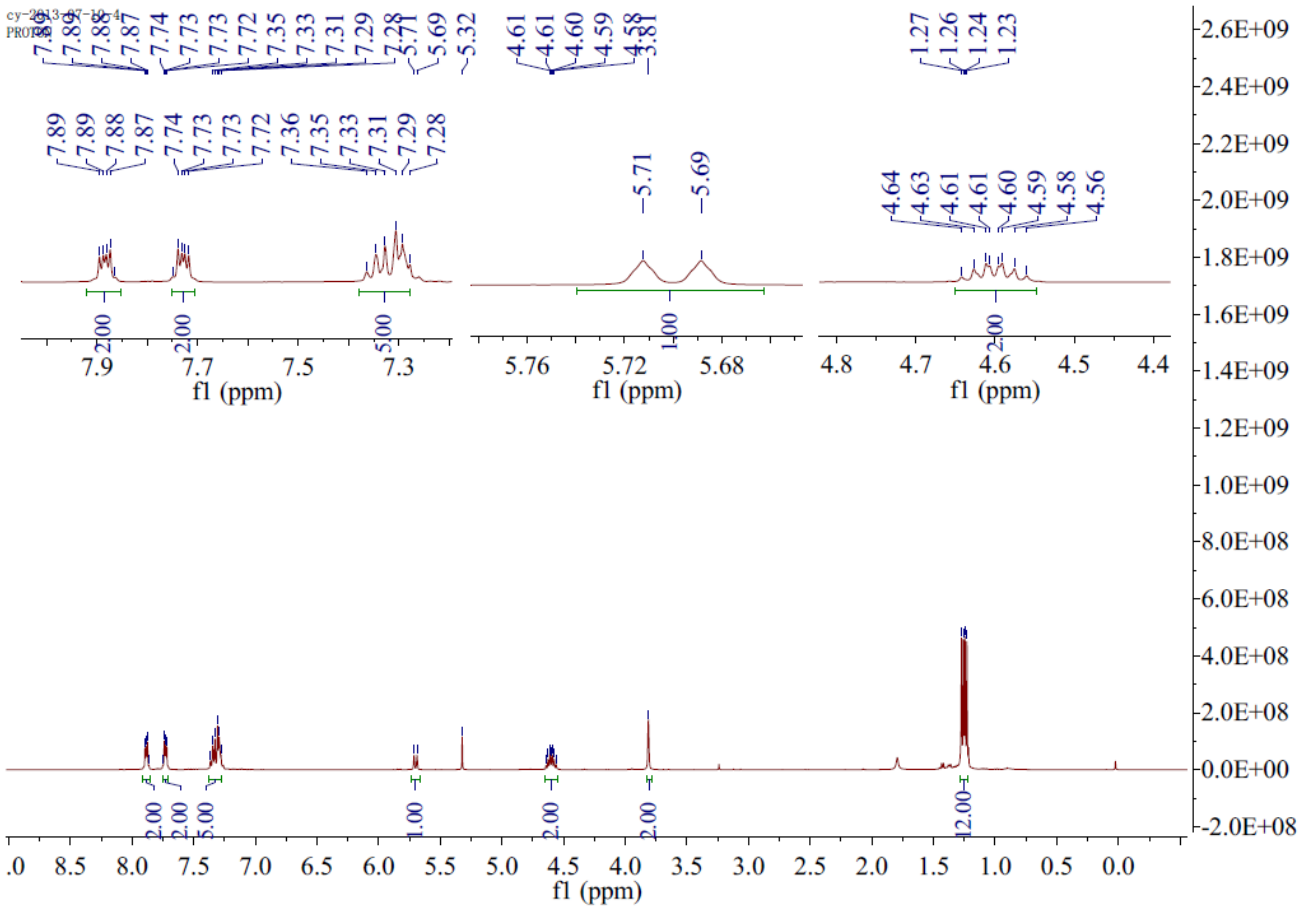


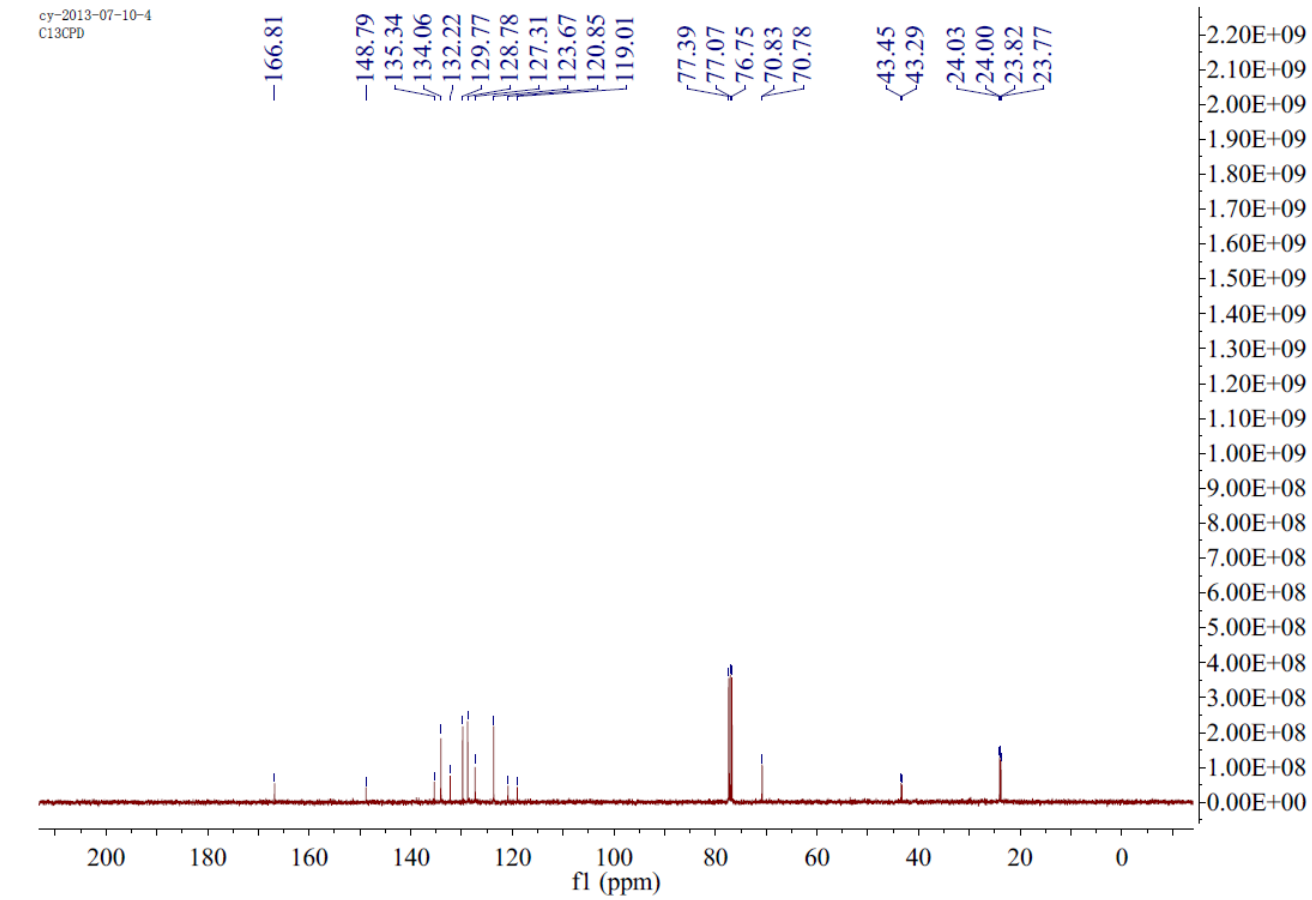
^{1}H-^{1}H NOESY spectrum

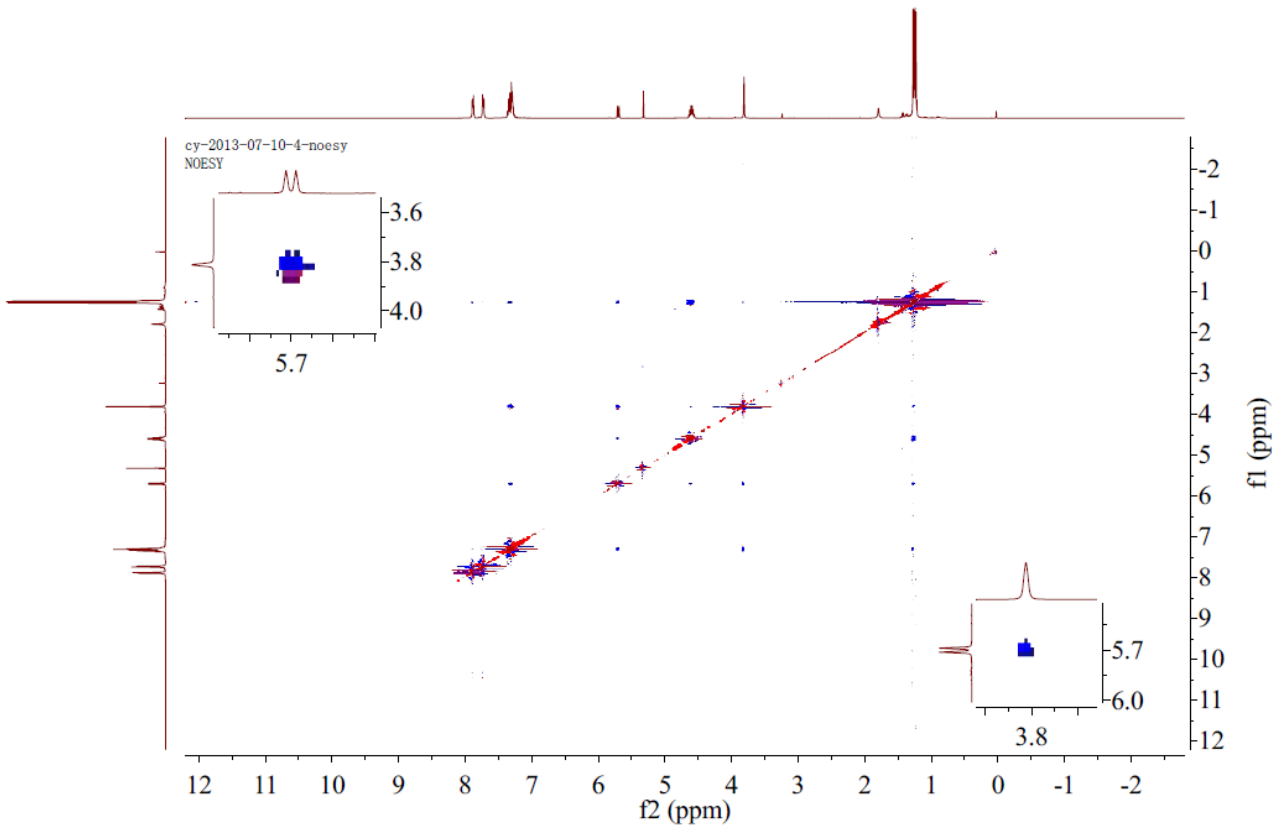
(*Z*)-Diisopropyl (2-(1,3-dioxoisoindolin-2-yl)-3-phenylprop-1-en-1-yl)phosphonate (2m):



Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-7.92 (m, 2H, Ph), 7.71-7.76 (m, 2H, Ph), 7.27-7.37 (m, 5H, Ph), 5.70 (d, *J* = 9.5 Hz, 1H, CH), 4.54-4.66 (m, 2H, 2OCH), 3.81 (s, 2H, CH_2), 1.25 (dd, *J* = 11.3, 6.2 Hz, 12H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.81 (C=O), 148.79 (N-C), 135.34, 134.06, 132.22, 129.77, 128.78, 127.31, 123.67 (Ph), 119.93 (d, *J* = 185.2 Hz, C-P), 70.80 (d, *J* = 5.1 Hz, OCH), 43.37 (d, *J* = 16.0 Hz, CH_2), 24.02 (d, *J* = 3.9 Hz, CH_3), 23.80 (d, *J* = 4.9 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 9.58 (s). ESI-HRMS calcd for $[C_{23}H_{26}NO_5P, M+H]^+$: 428.1621, Found: 428.1624.

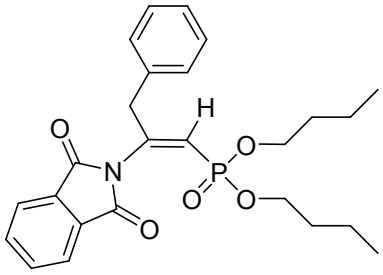




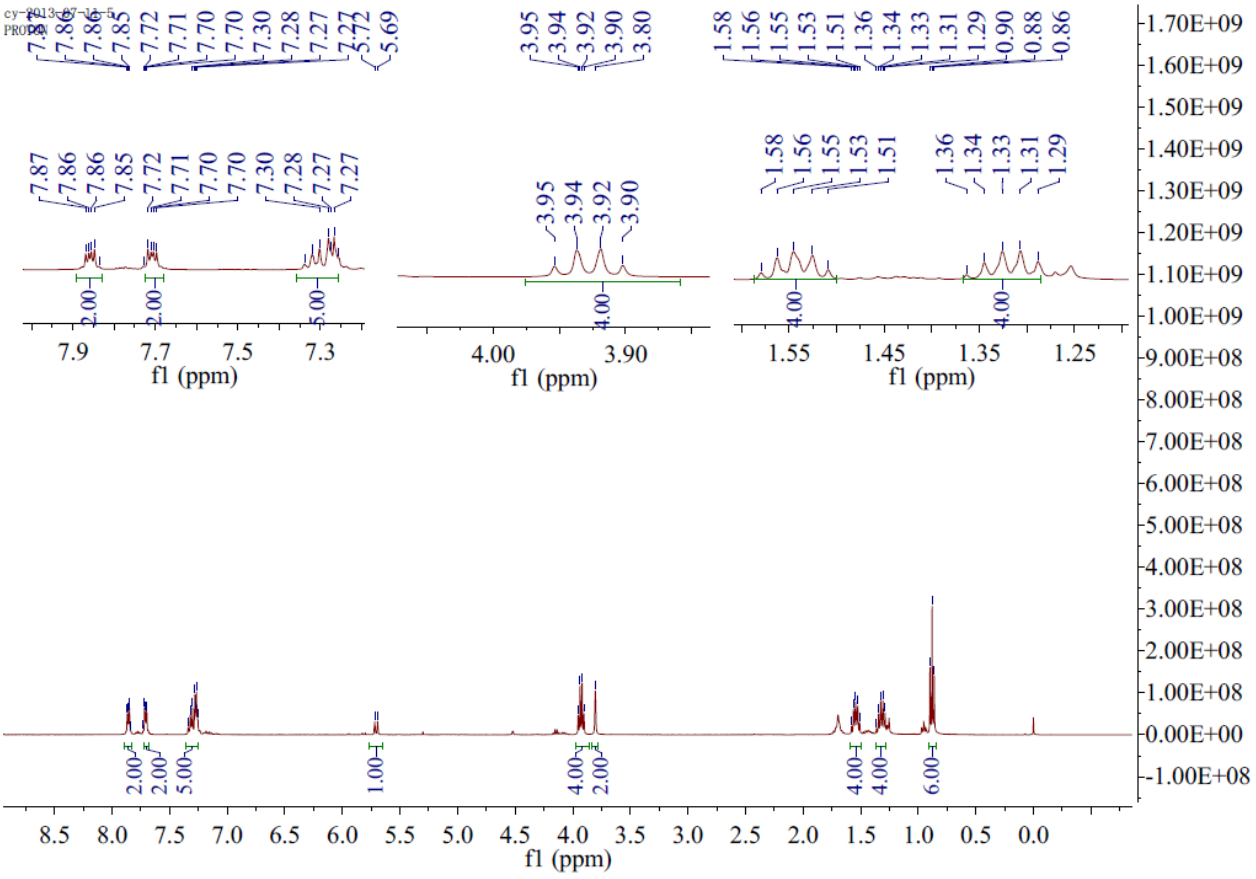


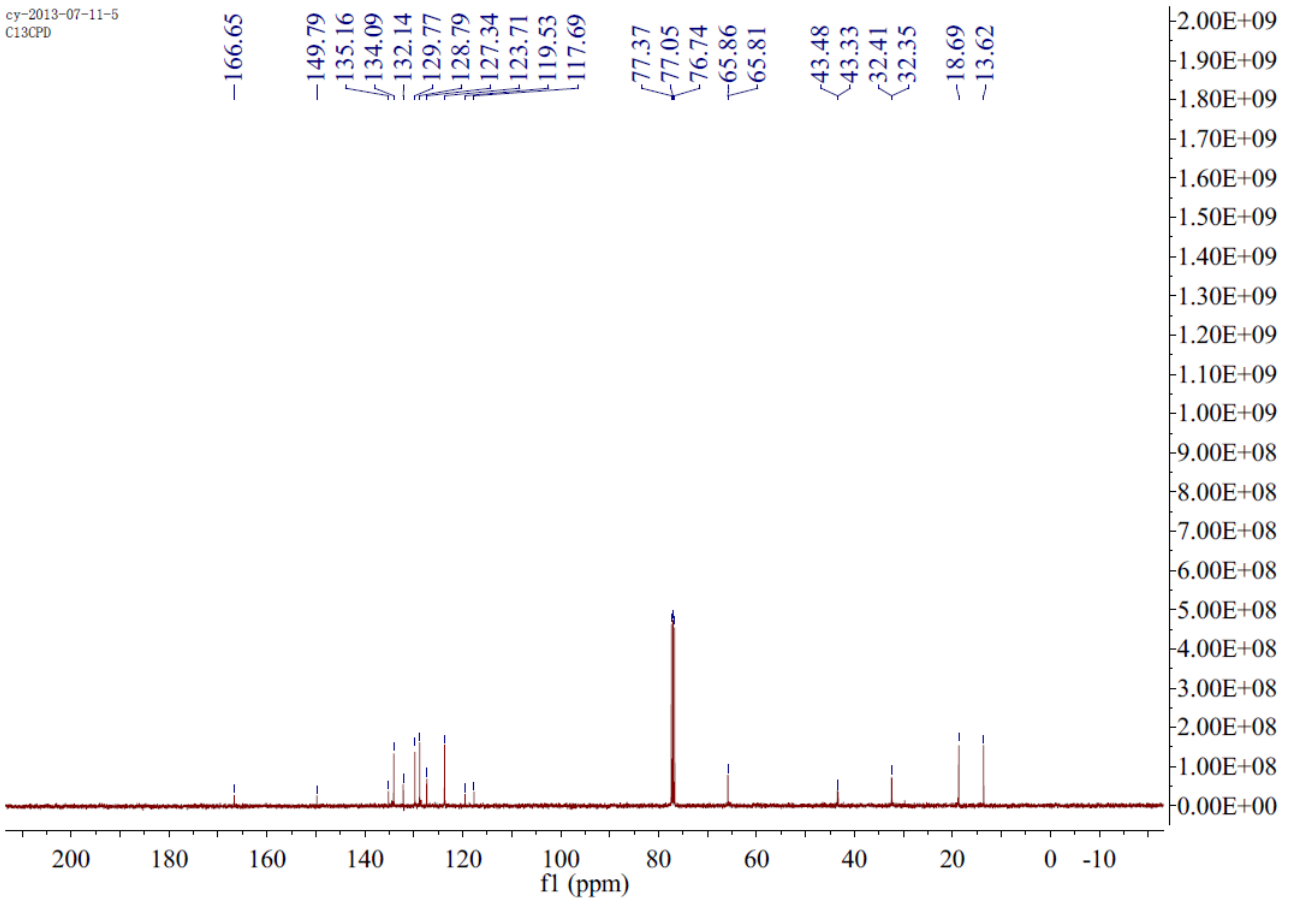
^{1}H-^{1}H NOESY spectrum

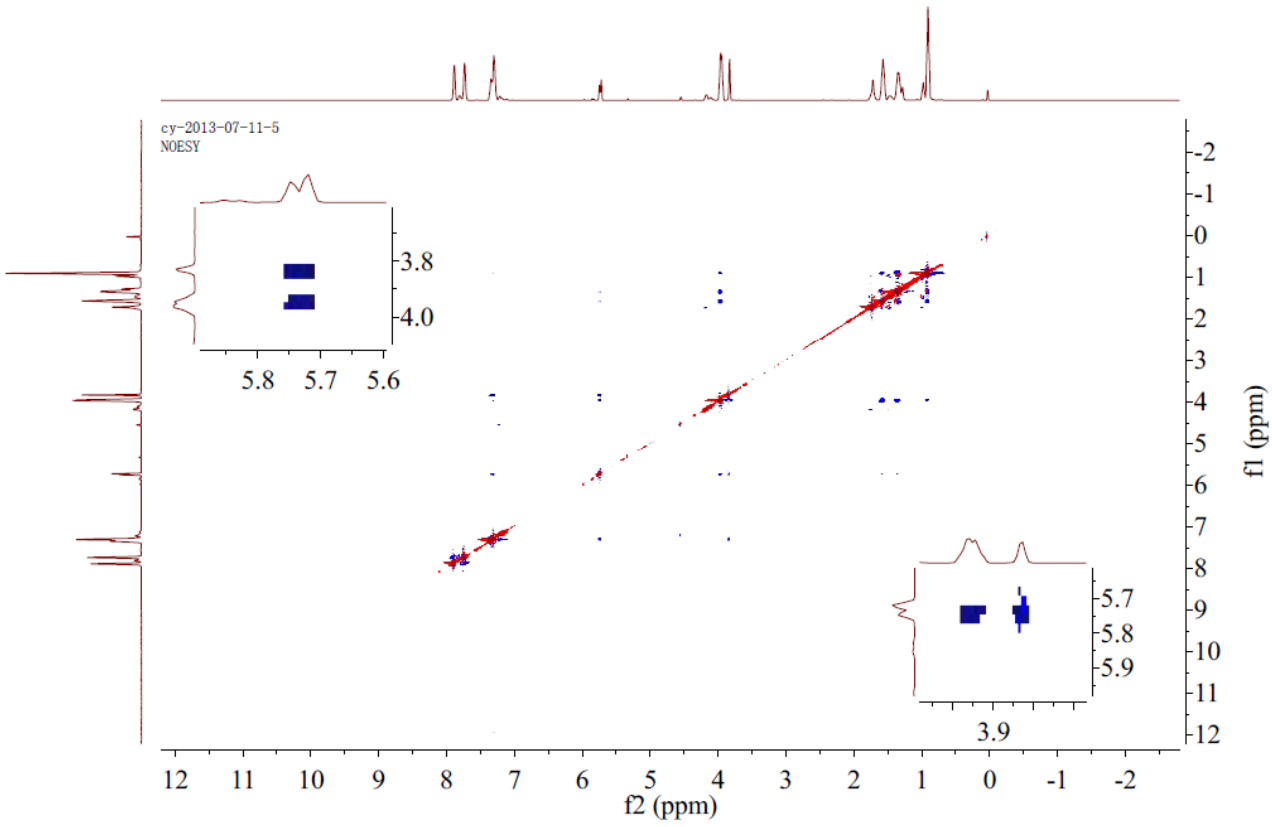
(*Z*)-Dibutyl (2-(1,3-dioxoisoindolin-2-yl)-3-phenylprop-1-en-1-yl)phosphonate (2n):



Colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.89 (m, 2H, Ph), 7.68-7.74 (m, 2H, Ph), 7.25-7.35 (m, 5H, Ph), 5.71 (d, *J* = 10.0 Hz, 1H, CH), 3.93 (dd, *J* = 13.9, 6.7 Hz, 4H, $2OCH_2$), 3.80 (s, 2H, CH_2), 1.49-1.60 (m, 4H, CH_2), 1.28-1.38 (m, 4H, CH_2), 0.88 (t, *J* = 7.4 Hz, 6H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.65 (C=O), 149.79 (N-C), 135.16, 134.09, 132.14, 129.77, 128.79, 127.34, 123.71 (Ph), 118.61 (d, *J* = 185.5 Hz, C-P), 65.83 (d, *J* = 5.4 Hz, OCH_2), 43.40 (d, *J* = 15.8 Hz, CH_2), 32.38 (d, *J* = 6.3 Hz, CH_2), 18.69 (CH_2), 13.62 (CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 12.06 (s). ESI-HRMS calcd for $[C_{25}H_{30}NO_5P, M+H]^+$: 456.1934, Found: 456.1934.







^{1}H-^{1}H NOESY spectrum

Single Crystal X-Ray Analysis **2a** (CCDC 893994 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk.)

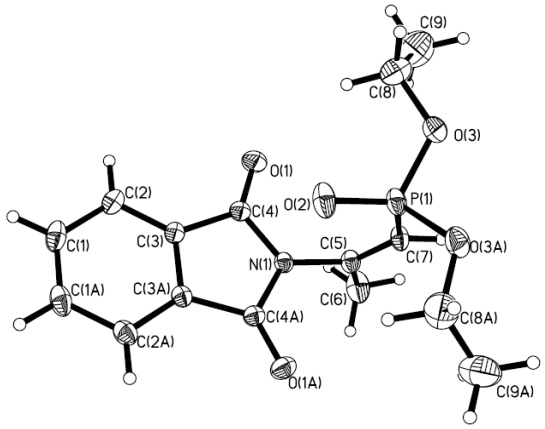


Table 1. Crystal data and structure refinement for shelx.

Identification code	shelx
Empirical formula	C15 H18 N O5 P
Formula weight	323.27
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pnma
Unit cell dimensions	a = 14.554(3) A α = 90°
	b = 12.849(3) A β = 90°
	c = 8.6466(17) A γ = 90°
Volume	1617.0(6) A^3
Z, Calculated density	4, 1.328 Mg/m^3
Absorption coefficient	0.192 mm^-1
F(000)	680.0
Crystal size	0.20 x 0.18 x 0.10 mm
Theta range for data collection	2.80 to 27.86°
Limiting indices	-19 <= h <= 19, -16 <= k <= 16, -11<= l <= 11
Reflections collected / unique	15501/2001 [R(int) = 0.0374]
Completeness to theta = 27.87	99.3%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9811 and 0.9626
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	2001/13/112
Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0501, wR2 = 0.1450
R indices (all data)	R1 = 0.0616, wR2 = 0.1570
Absolute structure parameter	0.072(12)
Largest diff. peak and hole	0.229 and -0.265 e.A^-3

Reference:

1. Y. Cai, Y. C. Lu, C. B. Yu, H. R. Lyu, Z. W. Miao *Org. Biomol. Chem.* **2013**, *11*, 5491.