Electronic Supplementary Material (ESI) for RSC Advances.

Regioselective $BF_3 \cdot Et_2O$-catalyzed C-H Functionalization of Indoles and Pyrroles with Reaction of α-Diazophosphonates

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Supporting Information

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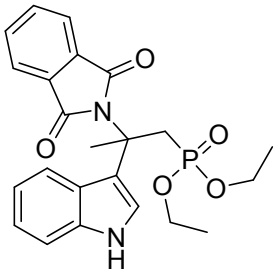
General Comments.

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.

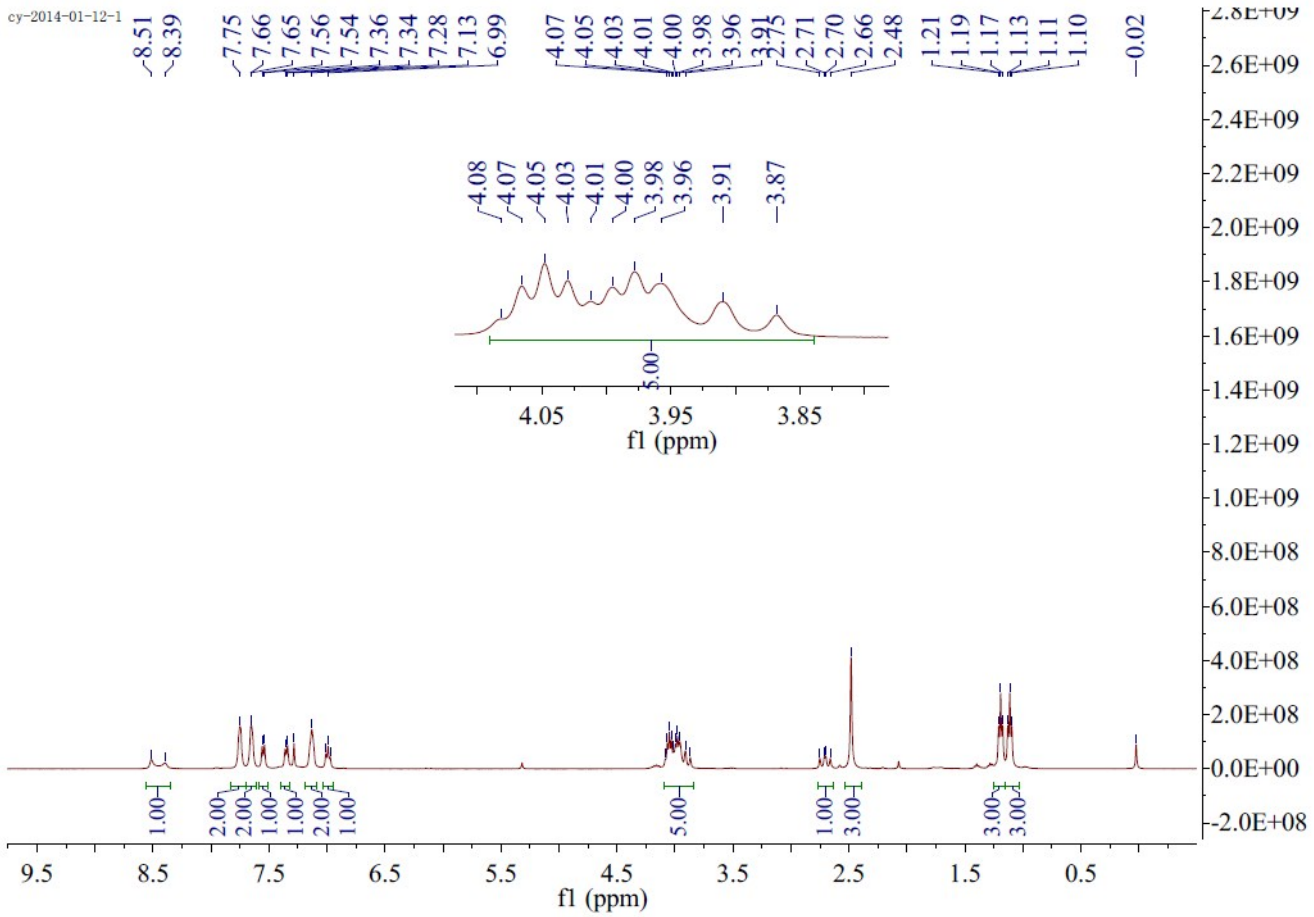
General procedure for the preparation of 3 and 4:

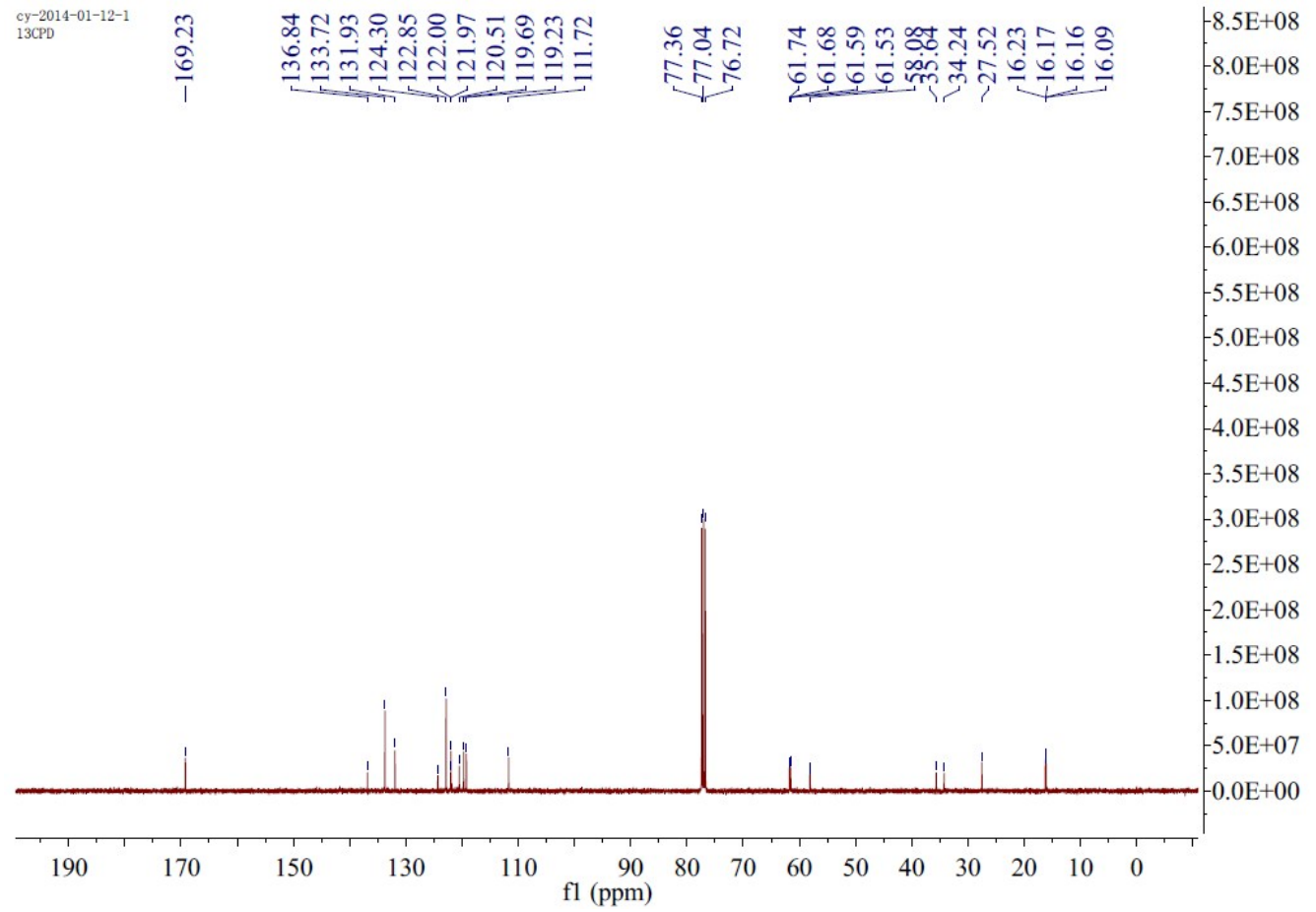
The 7.2 μL $BF_3{\cdot}Et_2O$ (0.056 mmol) and 50 mg indole (0.42 mmol) in an oven-dried Schlenk tube was dissolved in 2 mL of freshly distilled CH_2Cl_2 under nitrogen. Dialkyl α-diazophosphonates **1** (0.28 mmol) was diluted with 2 mL of CH_2Cl_2 and was drawn into a gastight syringe. It was then 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 2 hour 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 (v:v)] to give the corresponding products **3** and **4**.

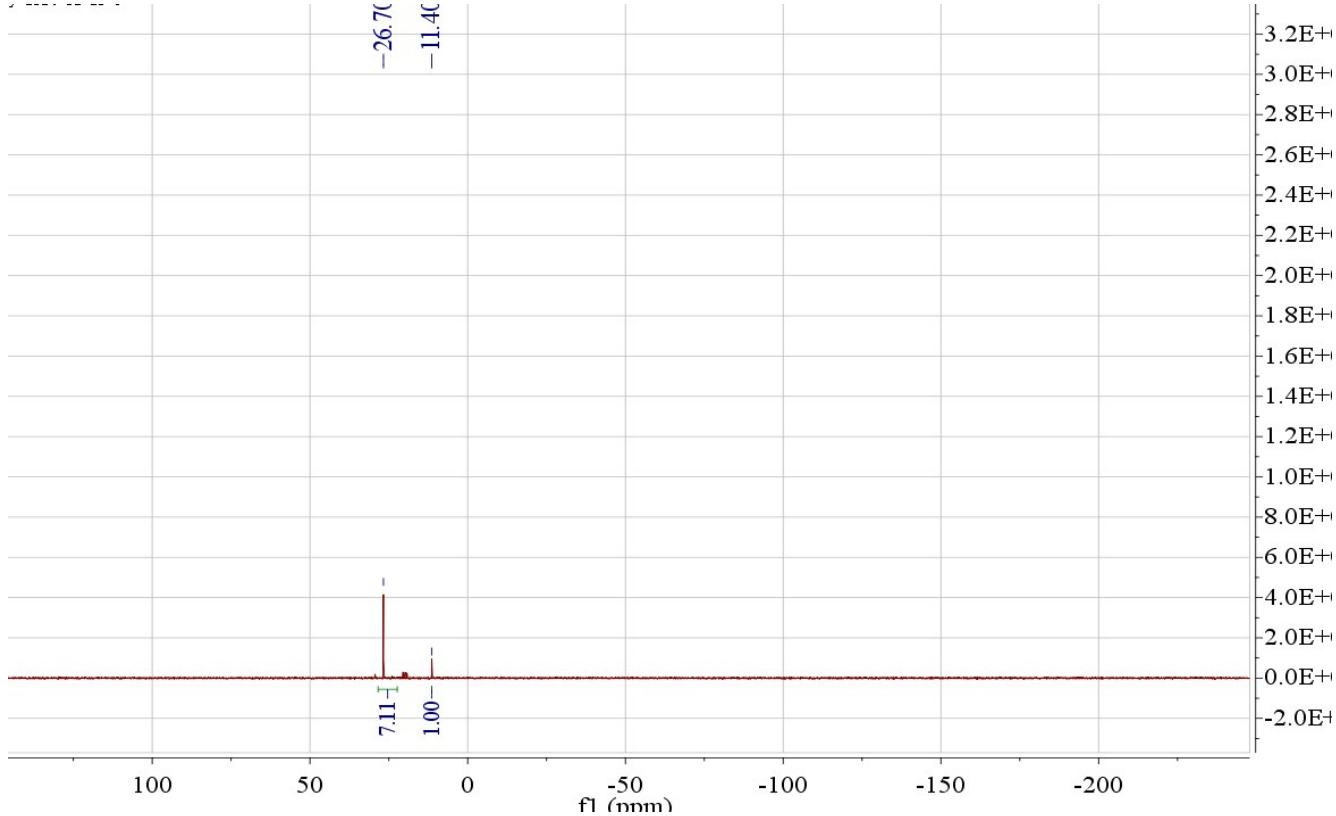
Diethyl (2-(1,3-dioxoisoindolin-2-yl)-2-(1H-indol-3-yl)propyl)phosphonate (3a):



White solid; mp: 146-147 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, *J* = 48.0 Hz, 1H, N-H), 7.70-7.79 (m, 2H, Ph), 7.60-7.68 (m, 2H, Ph), 7.55 (d, *J* = 7.9 Hz, 1H, Ph), 7.35 (d, *J* = 7.9 Hz, 1H, Ph), 7.09-7.17 (m, 2H, Ph, =CH), 6.99 (t, *J* = 7.3 Hz, 1H, Ph), 3.78-4.25 (m, 5H, $2OCH_2$, CH_2P), 2.71 (dd, *J* = 20.4, 15.6 Hz, 1H, CH_2P), 2.48 (s, 3H, CH_3), 1.19 (t, *J* = 6.9 Hz, 3H, CH_3), 1.11 (t, *J* = 6.9 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.23 (s, C=O), 136.84, 133.72, 131.93, 124.30, 122.85 (s, Ph), 122.00 (s, =C), 121.97, 120.51, 119.69, 119.23 (s, Ph), 111.72 (s, =CH), 61.71 (d, *J* = 6.6 Hz, OCH_2), 61.56 (d, *J* = 6.6 Hz, OCH_2), 58.10 (d, *J* = 4.3 Hz, N-C), 34.94 (d, *J* = 141.5 Hz, CH_2P), 27.52 (s, CH_3), 16.20 (d, *J* = 6.7 Hz, CH_3), 16.12 (d, *J* = 6.7 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.75 (s); ESI-HRMS calcd for $[C_{23}H_{25}N_2O_5P, M + Na]^+$: 463.1393, Found: 463.1394.

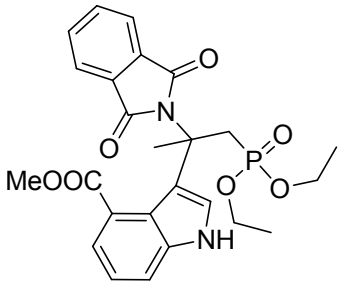




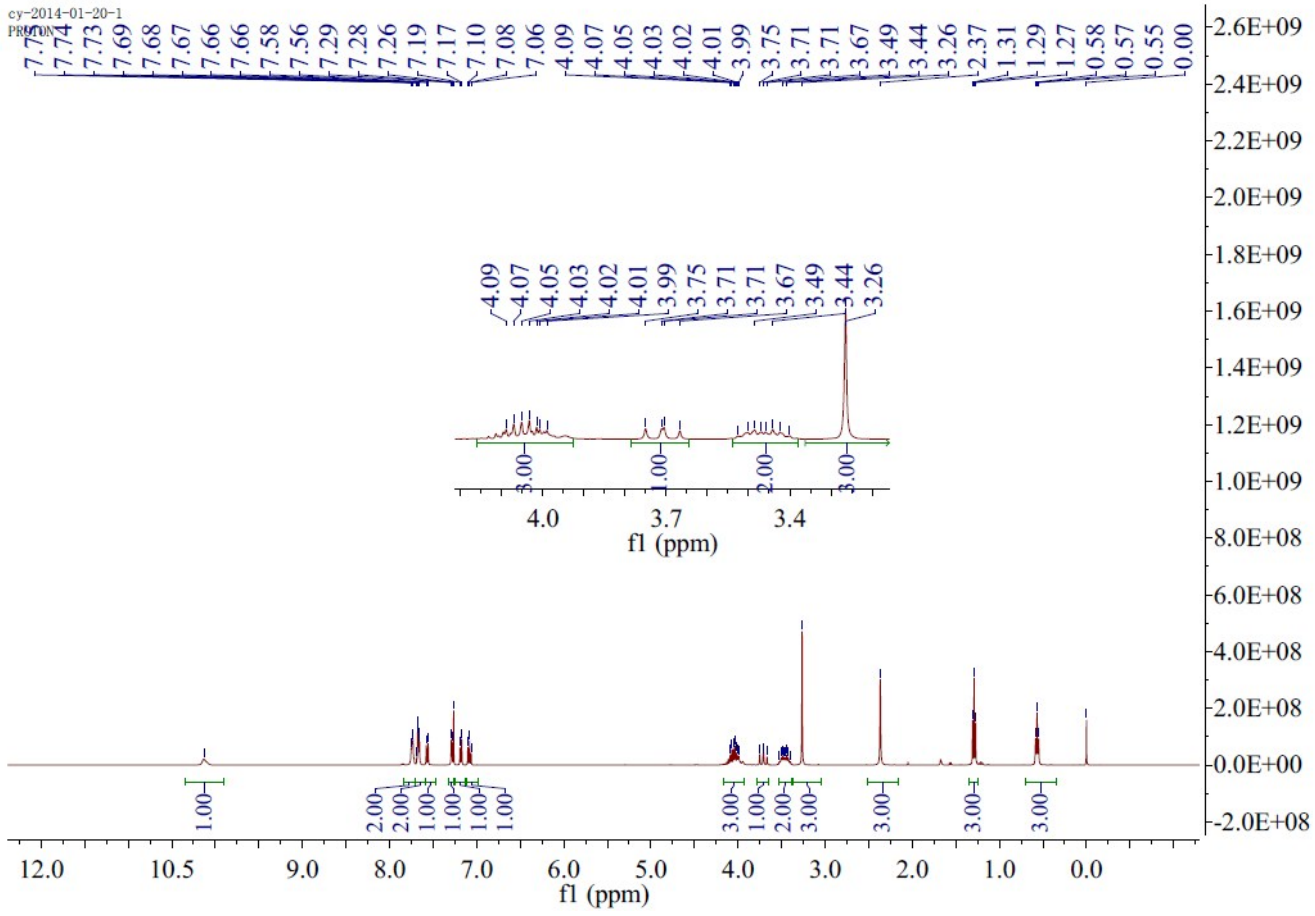


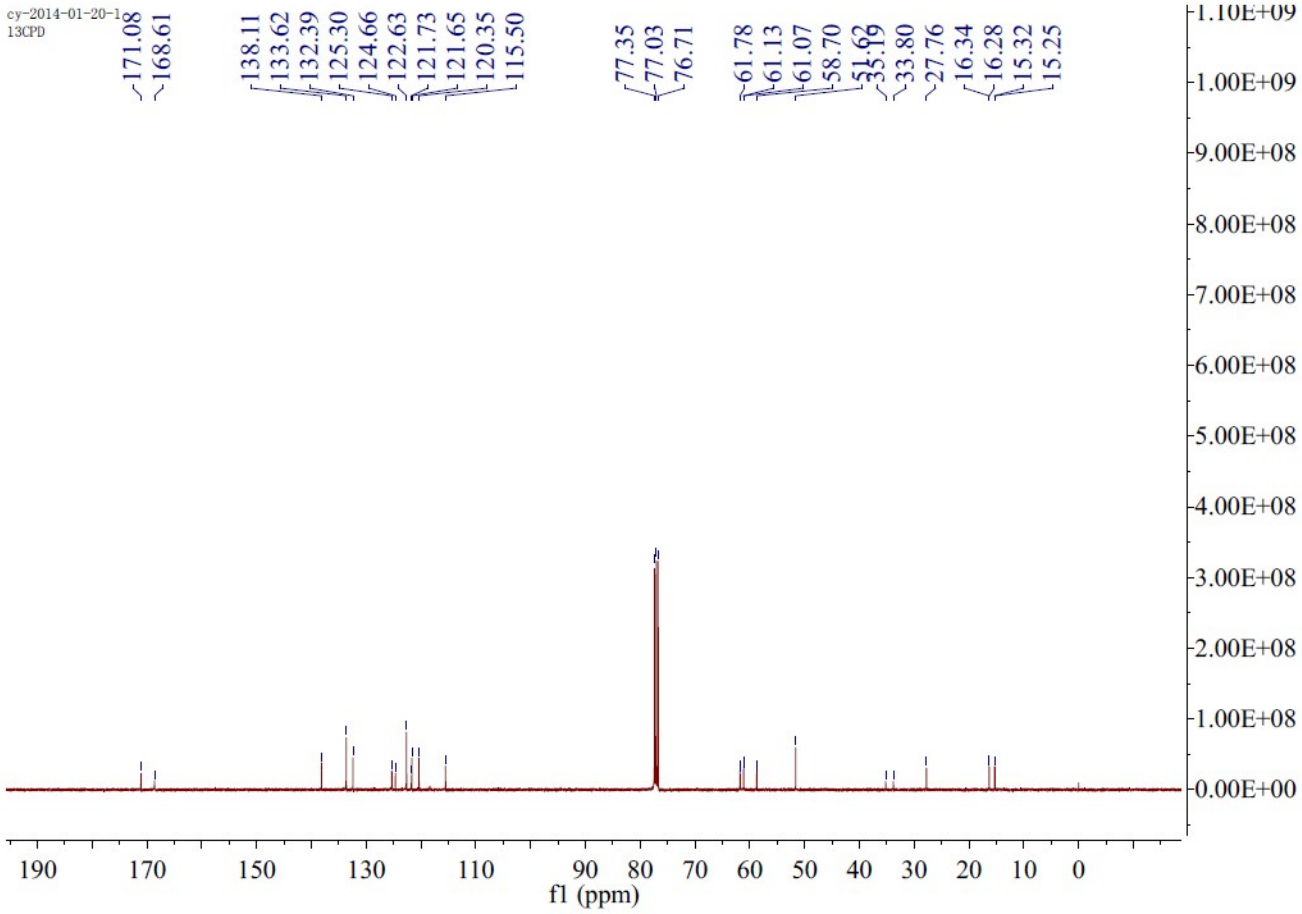
The mole ratio of **3a** and **4a** determined by crude ^{31}P NMR

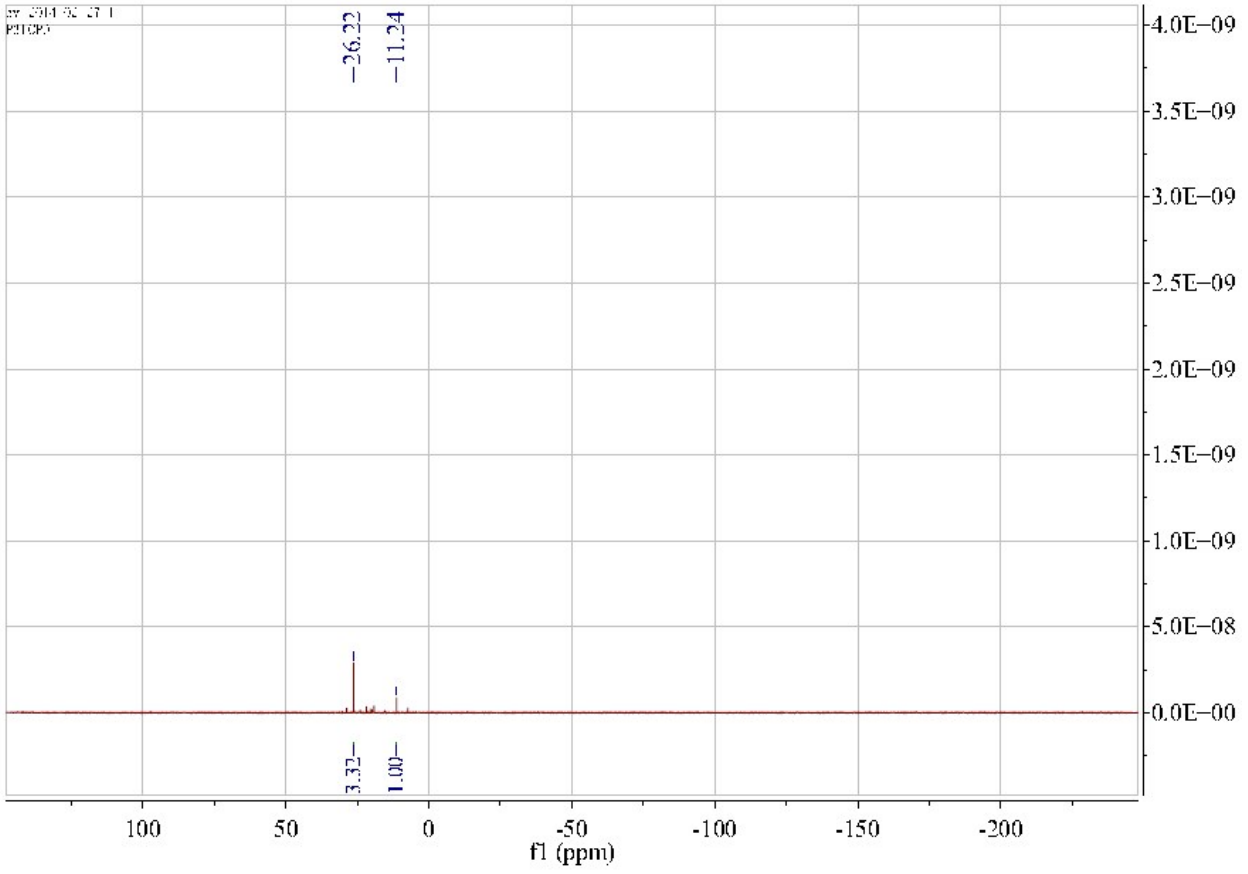
Methyl 3-(1-(diethoxyphosphoryl)-2-(1,3-dioxoisoindolin-2-yl)propan-2-yl)-1H-indole-4-carboxylate (3d):



White solid; mp: 163-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.13 (s, 1H, N-H), 7.71-7.77 (m, 2H, Ph), 7.64-7.69 (m, 2H, Ph), 7.57 (d, *J* = 8.0 Hz, 1H, Ph), 7.29 (d, *J* = 2.6 Hz, 1H, =CH), 7.18 (d, *J* = 6.5 Hz, 1H, Ph), 7.08 (t, *J* = 7.7 Hz, 1H, Ph), 3.90-4.19 (m, 3H, OCH_2, CH_2P), 3.71 (dd, *J* = 17.9, 15.5 Hz, 1H, CH_2P), 3.39-3.56 (m, 2H, OCH_2), 3.26 (s, 3H, OCH_3), 2.37 (s, 3H, CH_3), 1.29 (t, *J* = 7.1 Hz, 3H, CH_3), 0.57 (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.08, 168.61 (s, C=O), 138.11, 133.62, 132.39, 125.30, 124.66, 122.63, 121.73, 121.65, 120.35 (s, Ph), 115.50 (s, =CH), 61.75 (d, *J* = 6.7 Hz, OCH_2), 61.10 (d, *J* = 6.7 Hz, OCH_2), 58.72 (d, *J* = 3.5 Hz, N-C), 51.62 (s, OCH_3), 34.49 (d, *J* = 140.1 Hz, CH_2P), 27.76 (s, CH_3), 16.31 (d, *J* = 6.9 Hz, CH_3), 15.28 (d, *J* = 6.9 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.09 (s); ESI-HRMS calcd for $[C_{25}H_{27}N_2O_7P, M + Na]^+$: 521.1448, Found: 521.1441.

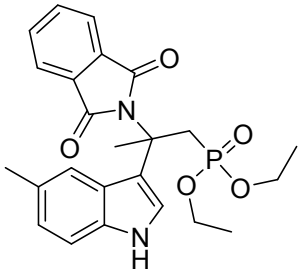




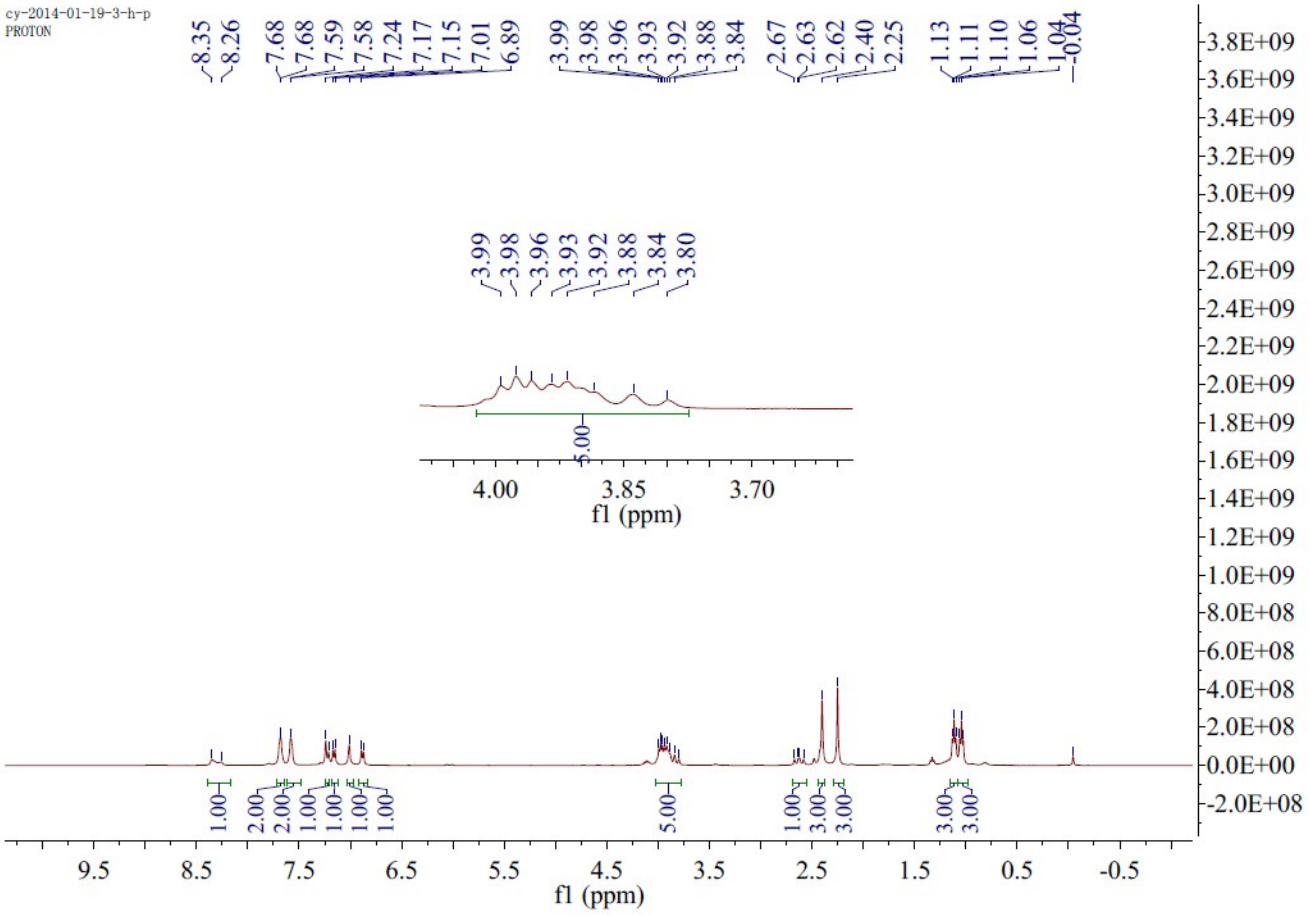


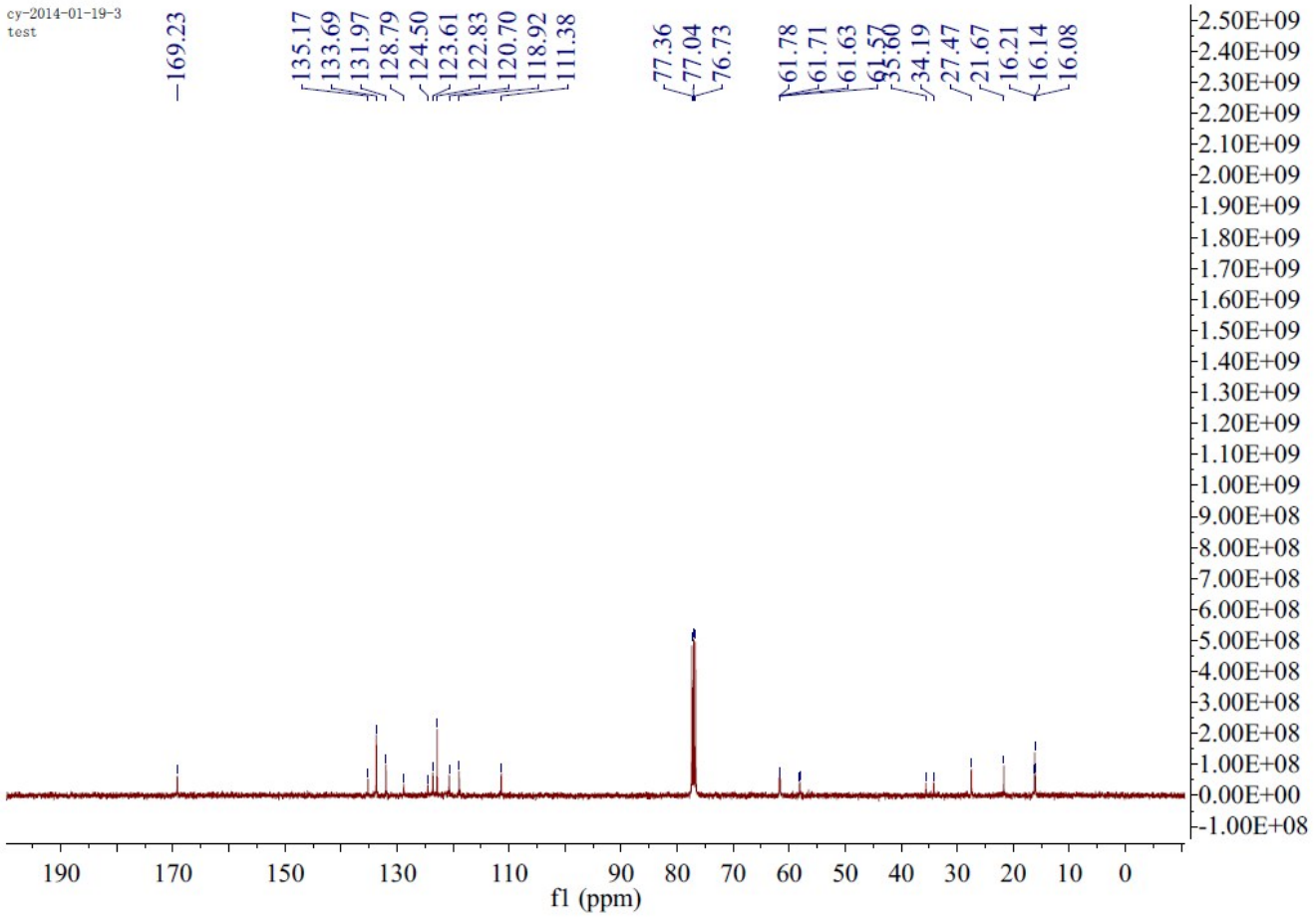
The mole ratio of **3d** and **4a** determined by crude ^{31}P NMR

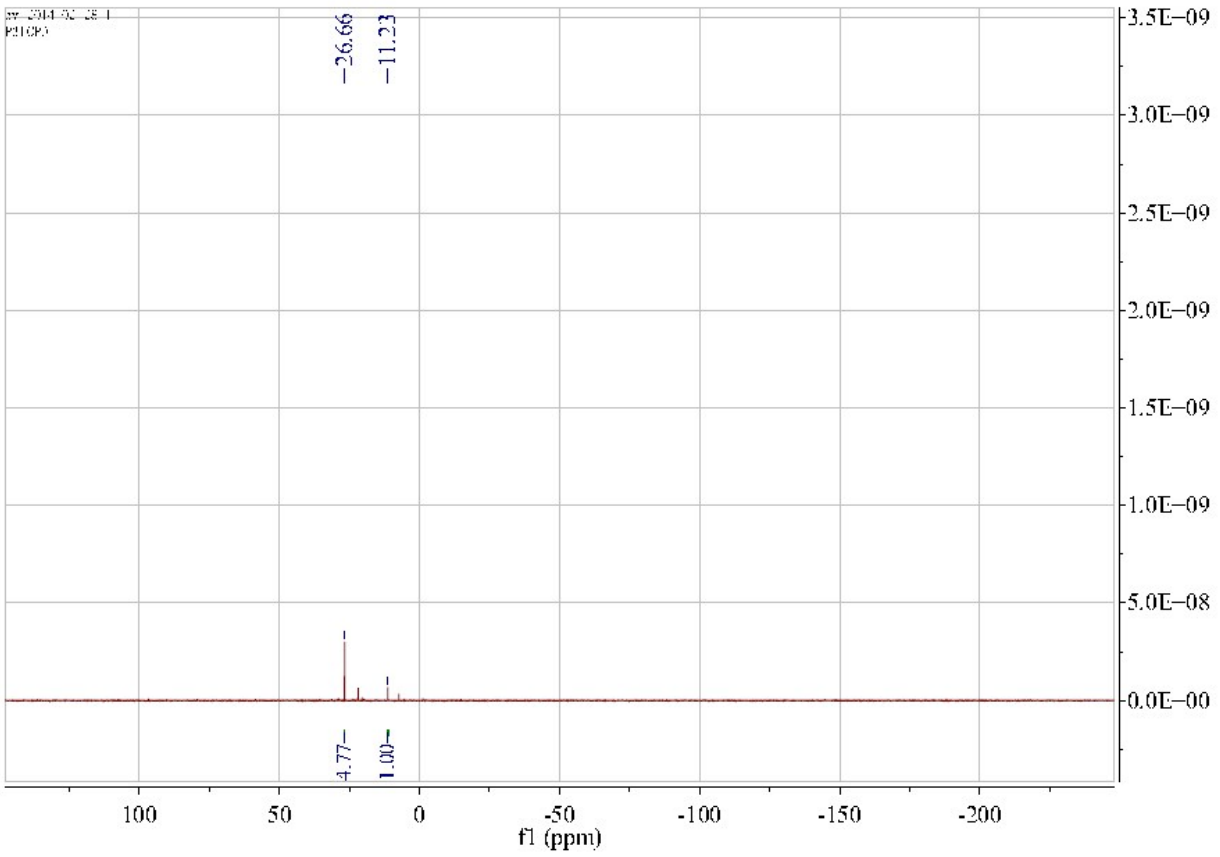
Diethyl (2-(1,3-dioxoisoindolin-2-yl)-2-(5-methyl-1H-indol-3-yl)propyl)phosphonate (3e):



White solid; mp: 118-119 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 37.4 Hz, 1H, N-H), 7.65-7.75 (m, 2H, Ph), 7.53-7.62 (m, 2H, Ph), 7.21 (s, 1H, Ph), 7.16 (d, *J* = 8.2 Hz, 1H, Ph), 7.01 (s, 1H, =CH), 6.88 (d, *J* = 8.2 Hz, 1H, Ph), 3.76-4.04 (m, 5H, $2OCH_2$, CH_2P), 2.63 (dd, *J* = 20.3, 15.6 Hz, 1H, CH_2P), 2.40 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 1.11 (t, *J* = 6.9 Hz, 3H, CH_3), 1.04 (t, *J* = 6.9 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.23 (s, C=O), 135.17, 133.69, 131.97, 128.79, 124.50, 123.61, 122.83, 120.70, 118.92 (s, Ph), 111.38 (s, =CH), 61.74 (d, *J* = 6.6 Hz, OCH_2), 61.60 (d, *J* = 6.6 Hz, OCH_2), 58.11 (d, *J* = 2.4 Hz, N-C), 34.89 (d, *J* = 141.7 Hz, CH_2P), 27.47 (s, CH_3), 21.67 (s, CH_3), 16.17 (d, *J* = 6.5 Hz, CH_3), 16.11 (d, *J* = 6.5 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.86 (s); ESI-HRMS calcd for $[C_{24}H_{27}N_2O_5P, M + Na]^+$: 477.1550, Found: 477.1548.

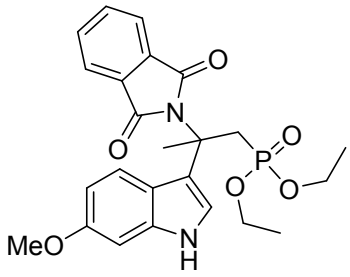




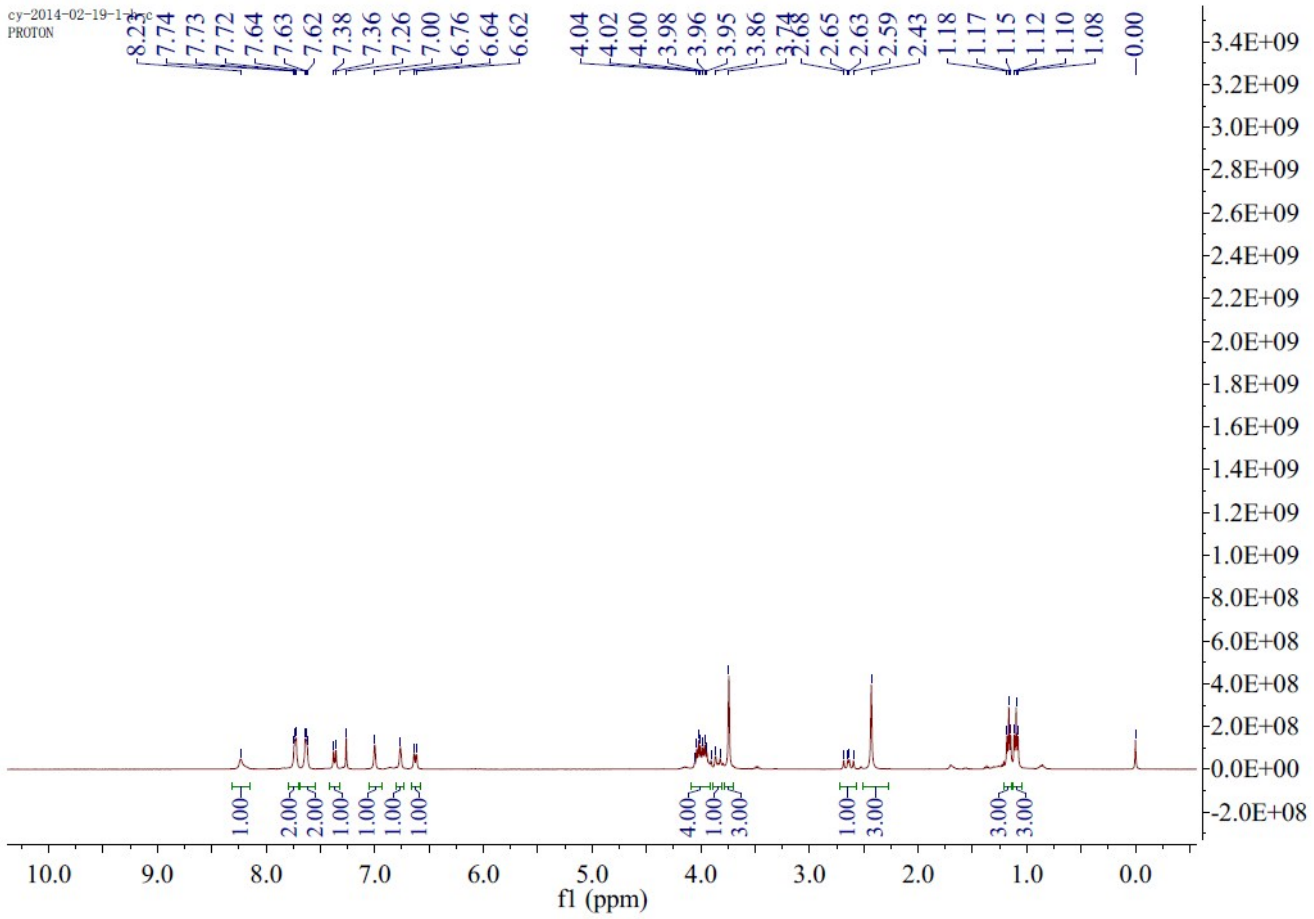


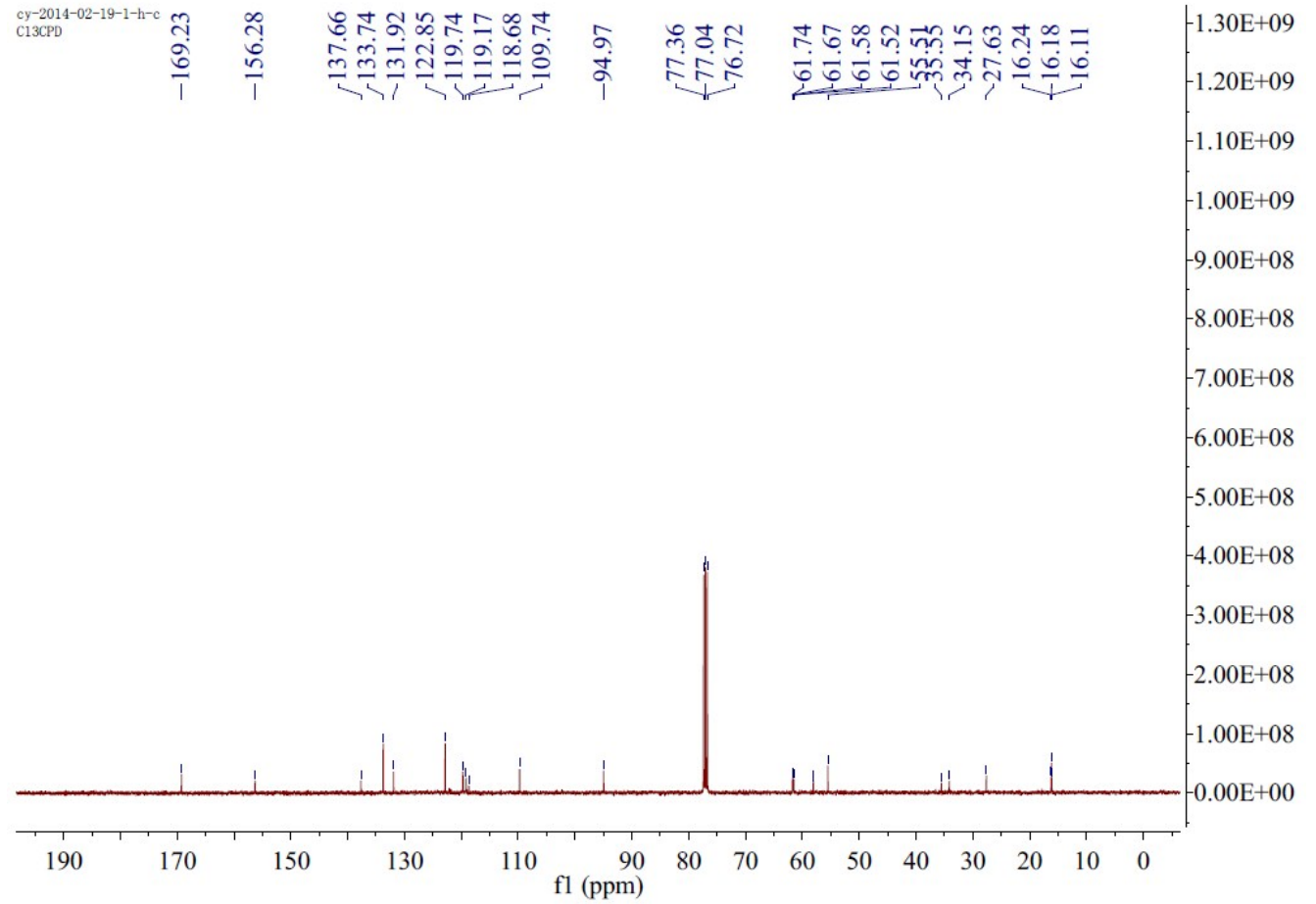
The mole ratio of **3e** and **4a** determined by crude ^{31}P NMR

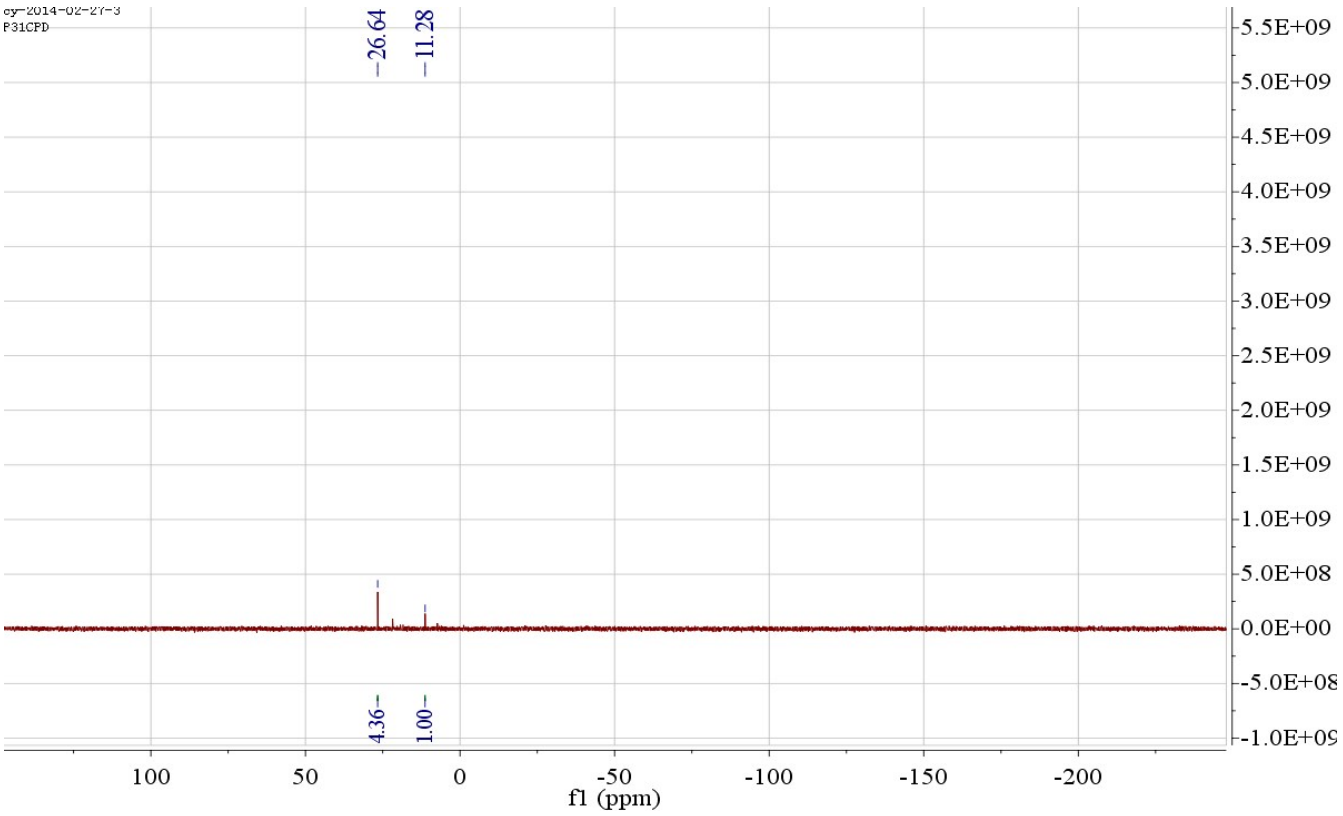
Diethyl (2-(1,3-dioxoisoindolin-2-yl)-2-(6-methoxy-1H-indol-3-yl)propyl)phosphonate (3f):



Faint yellow solid; mp: 129-130 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H, N-H), 7.69-7.80 (m, 2H, Ph), 7.58-7.67 (m, 2H, Ph), 7.37 (d, *J* = 8.7 Hz, 1H, Ph), 7.00 (s, 1H, Ph), 6.76 (s, 1H, =CH), 6.63 (d, *J* = 8.6 Hz, 1H, Ph), 3.92-4.10 (m, 4H, $2OCH_2$), 3.81-3.91 (m, 1H, CH_2P), 3.74 (s, 3H, OCH_3), 2.64 (dd, *J* = 20.7, 15.3 Hz, 1H, CH_2P), 2.43 (s, 3H, CH_3), 1.17 (t, *J* = 7.0 Hz, 3H, CH_3), 1.10 (t, *J* = 7.0 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.23 (s, C=O), 156.28, 137.66, 133.74, 131.92, 122.85, 119.74, 119.17 (s, Ph), 118.68 (s, =C), 109.74 (s, Ph), 94.97 (s, =CH), 61.70 (d, *J* = 6.7 Hz, OCH_2), 61.55 (d, *J* = 6.7 Hz, OCH_2), 58.06 (d, *J* = 4.6 Hz, N-C), 55.51 (s, OCH_3), 34.85 (d, *J* = 141.0 Hz, CH_2P), 27.63 (s, CH_3), 16.21 (d, *J* = 6.2 Hz, CH_3), 16.14 (d, *J* = 6.2 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.80 (s); ESI-HRMS calcd for $[C_{24}H_{27}N_2O_6P, M + Na]^+$: 493.1499, Found: 493.1495.

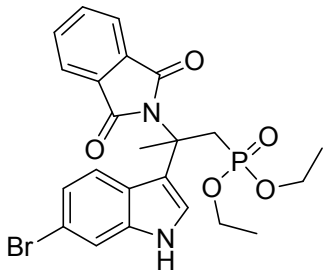




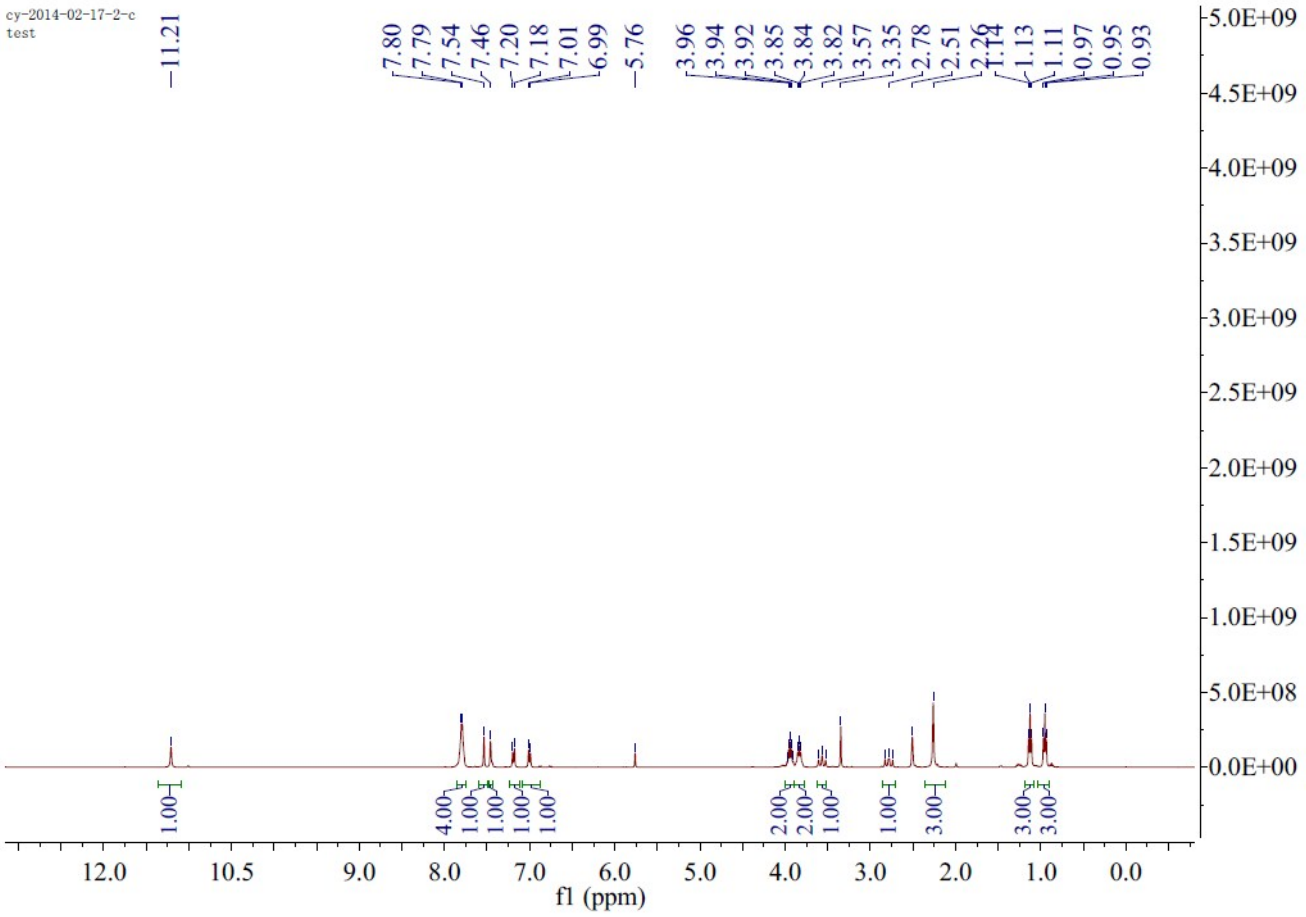


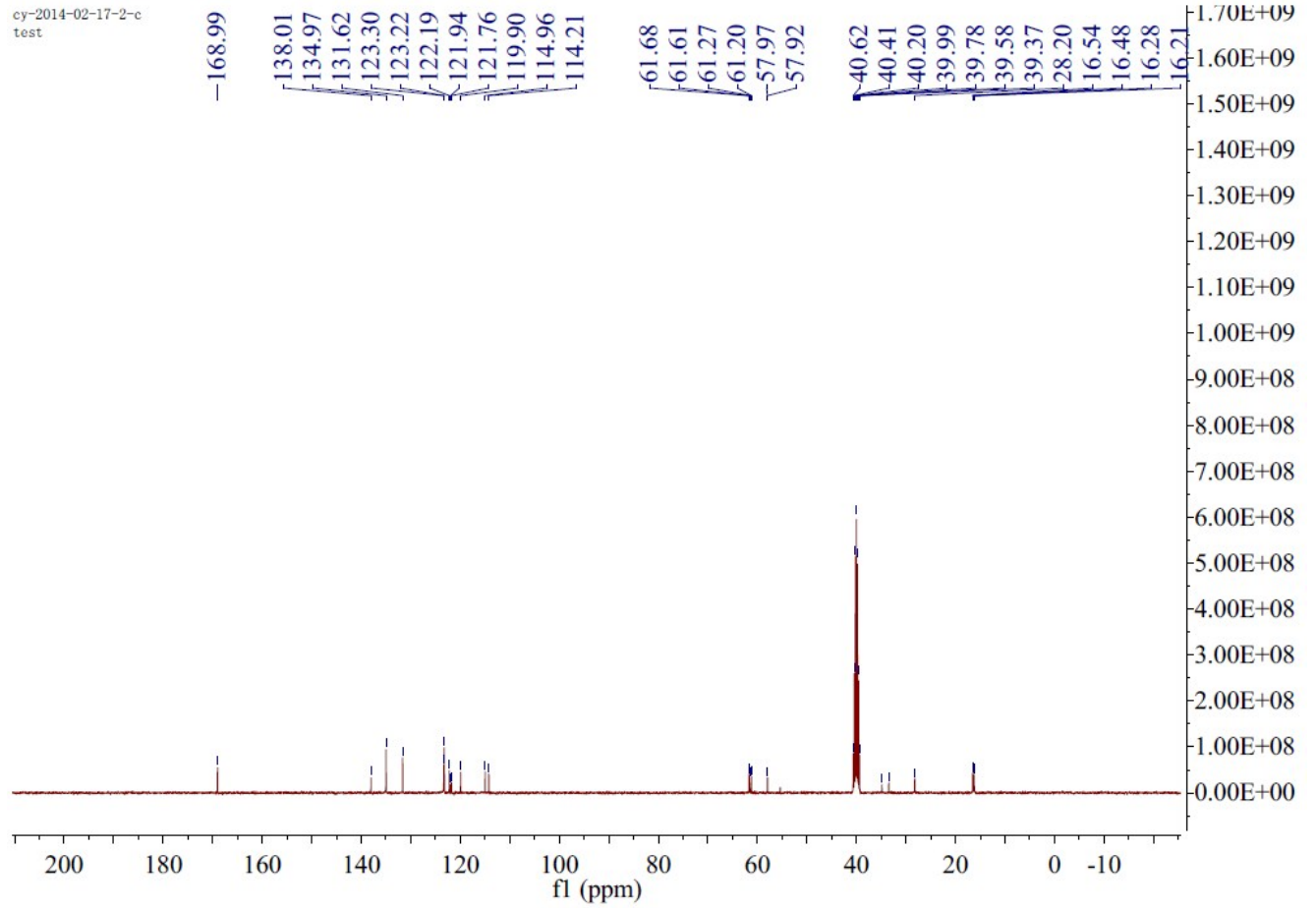
The mole ratio of **3f** and **4a** determined by crude ^{31}P NMR

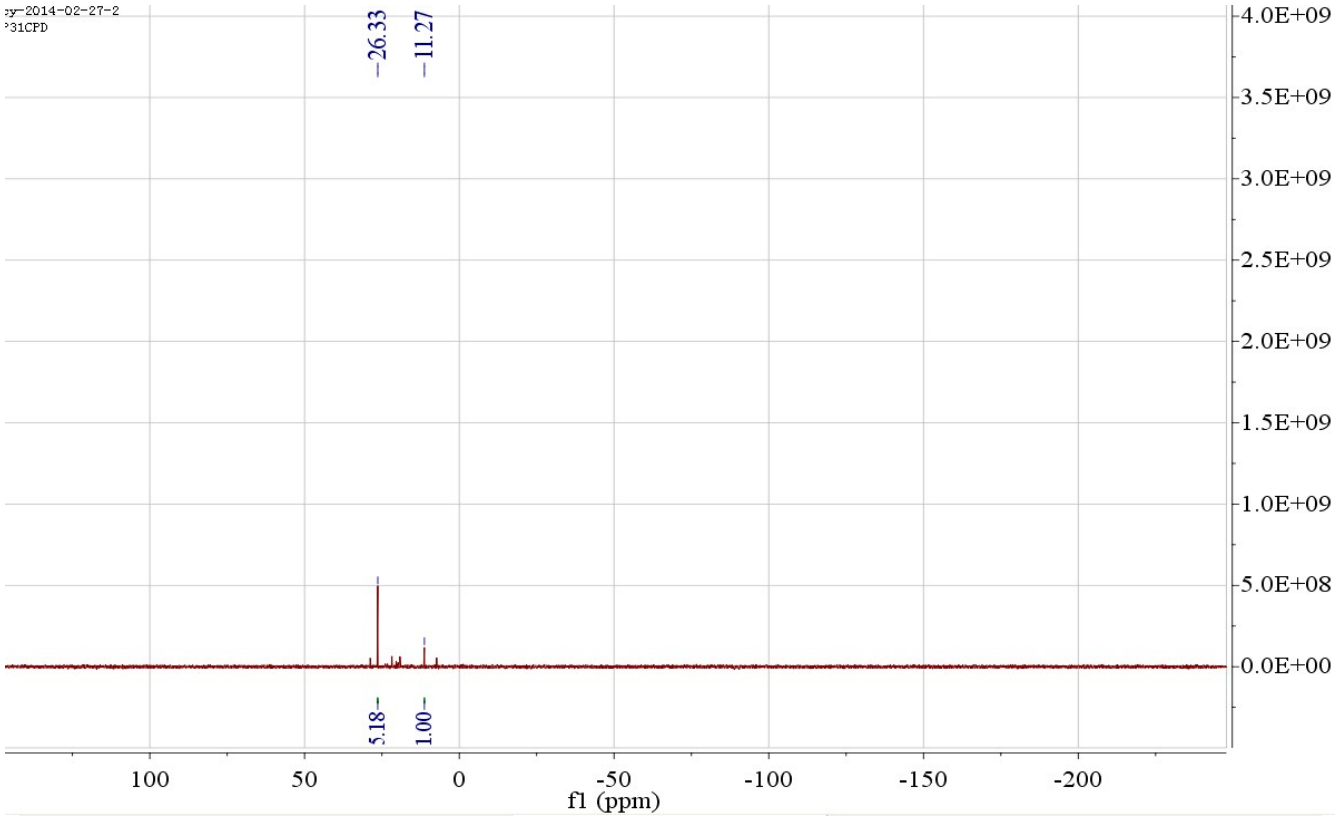
Diethyl (2-(6-bromo-1H-indol-3-yl)-2-(1,3-dioxoisoindolin-2-yl)propyl)phosphonate (3g):



Yellow Solid; mp: 170-172 ^{o}C; ^{1}H NMR (400 MHz, *d*-DMSO): δ 11.21 (s, 1H, N-H), 7.75-7.86 (m, 4H, Ph), 7.54 (s, 1H, Ph), 7.46 (s, 1H, =CH), 7.19 (d, J = 8.5 Hz, 1H, Ph), 7.00 (d, J = 8.5 Hz, 1H, Ph), 3.90-4.01 (m, 2H, OCH_2), 3.77-3.89 (m, 2H, OCH_2), 3.57 (t, J = 16.5 Hz, 1H, CH_2P), 2.78 (dd, J = 19.8, 15.8 Hz, 1H, CH_2P), 2.26 (s, 3H, CH_3), 1.13 (t, J = 6.9 Hz, 3H, CH_3), 0.95 (t, J = 6.9 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, *d*-DMSO): δ 168.99 (s, C=O), 138.01, 134.97, 131.62, 123.30, 123.22, 122.19, 121.94 (s, Ph), 121.76 (s, =C), 119.90, 114.96 (s, Ph), 114.21 (s, =CH), 61.65 (d, J = 6.3 Hz, OCH_2), 61.23 (d, J = 6.3 Hz, OCH_2), 57.94 (d, J = 5.0 Hz, N-C), 34.15 (d, J = 138.8 Hz, CH_2P), 28.20 (s, CH_3), 16.51 (d, J = 6.2 Hz, CH_3), 16.24 (d, J = 6.2 Hz, CH_3); ^{31}P NMR (162 MHz, *d*-DMSO): δ 26.51 (s); ESI-HRMS calcd for $[C_{23}H_{24}BrN_2O_5P, M + Na]^+$: 541.0498, Found: 541.0496.

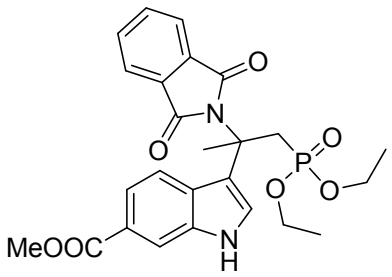




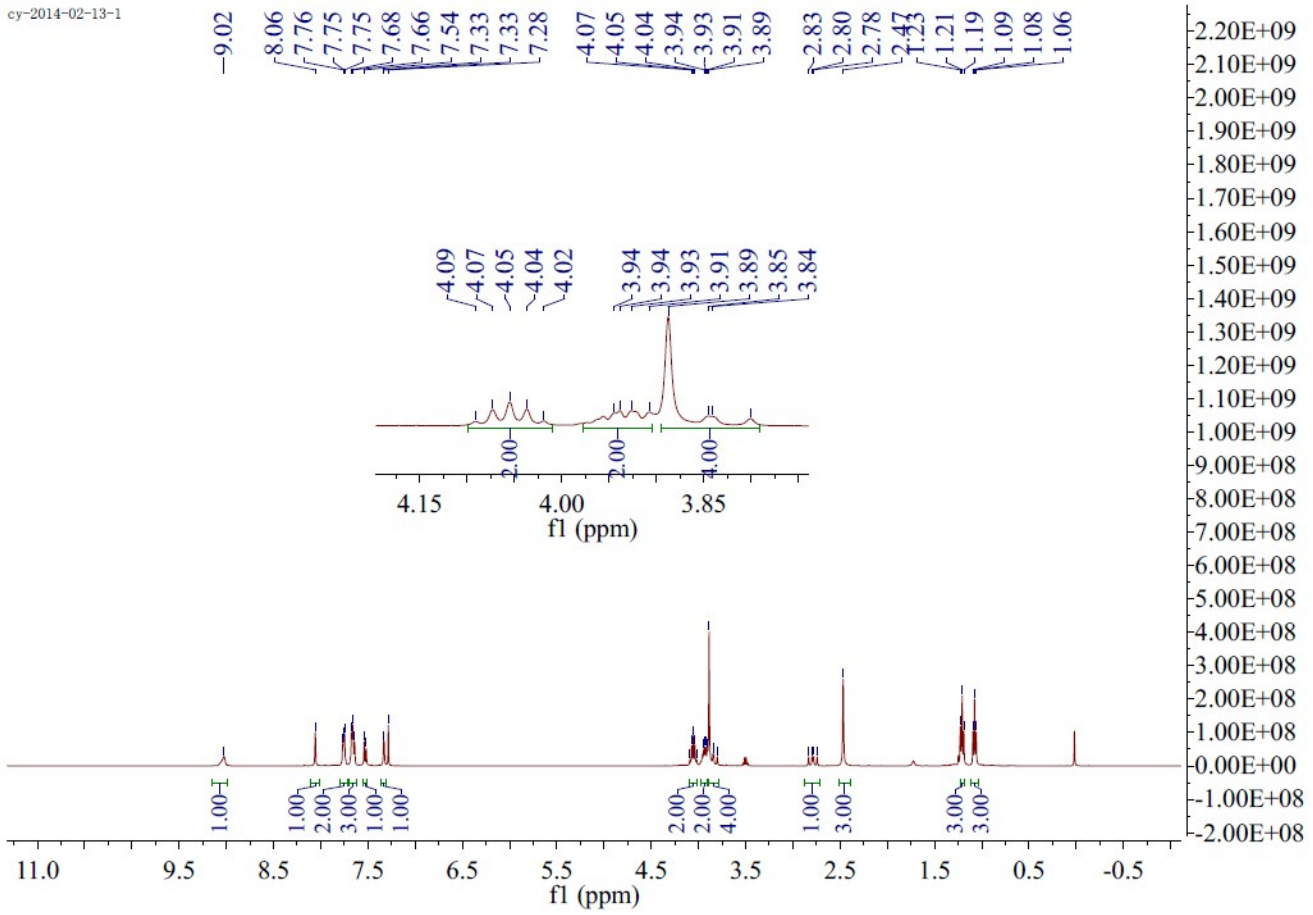


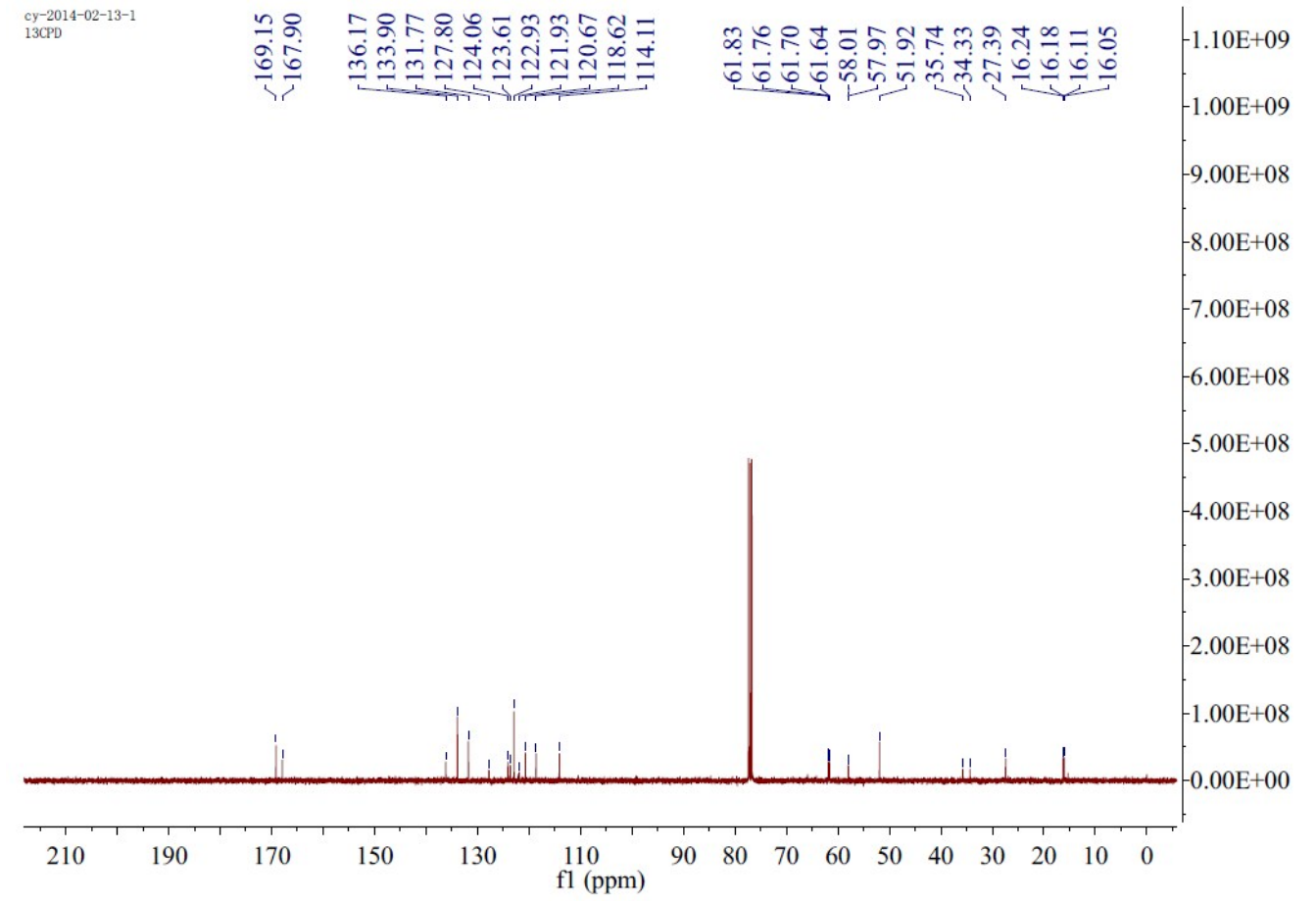
The mole ratio of **3g** and **4a** determined by crude ^{31}P-NMR

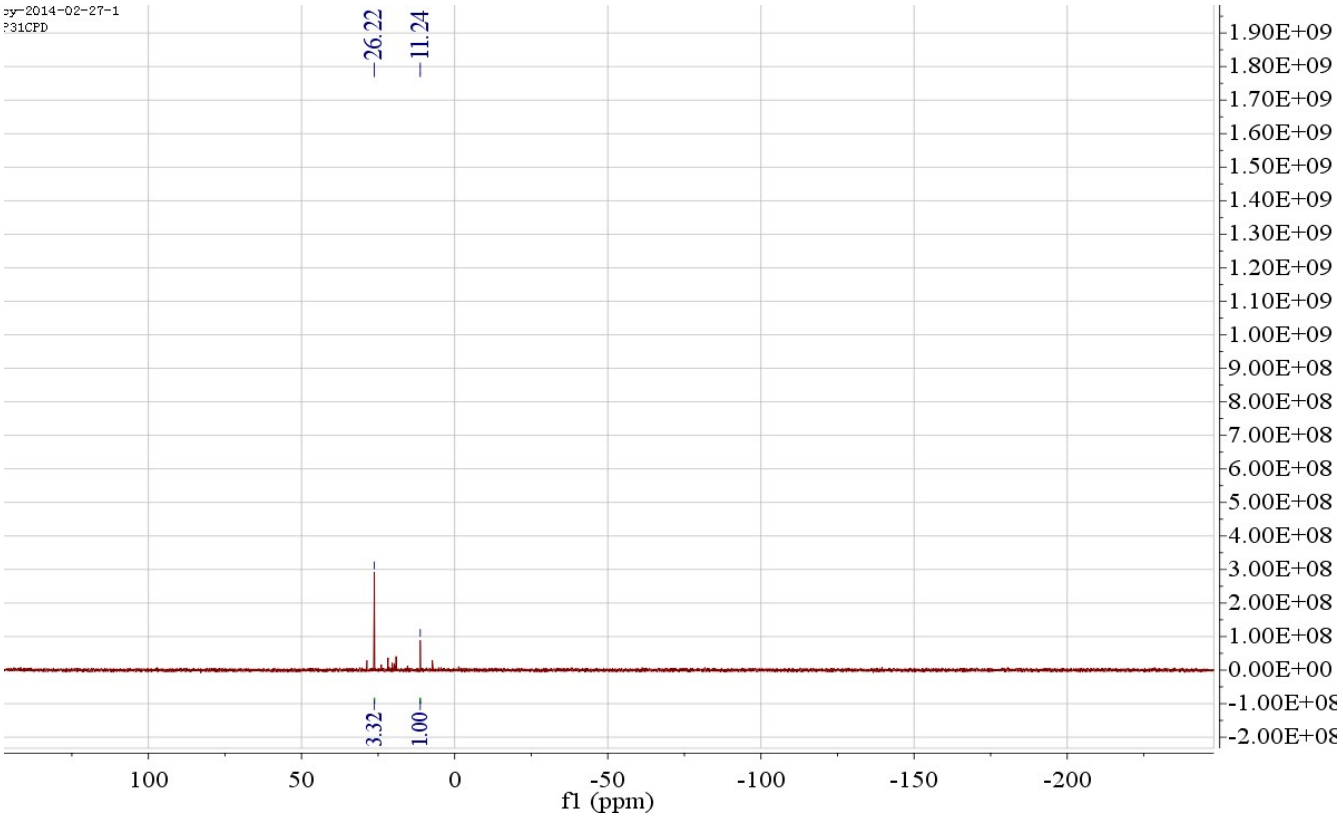
Methyl 3-(1-(diethoxyphosphoryl)-2-(1,3-dioxoisoindolin-2-yl)propan-2-yl)-1H-indole-6-carboxylate (3h):



White solid; mp: 160-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.02 (s, 1H, N-H), 8.06 (s, 1H, Ph), 7.73-7.80 (m, 2H, Ph), 7.62-7.70 (m, 3H, Ph), 7.53 (d, *J* = 8.5 Hz, 1H, Ph), 7.33 (d, *J* = 2.0 Hz, 1H, =CH), 4.01-4.11 (m, 2H, OCH_2), 3.90-3.98 (m, 2H, OCH_2), 3.79-3.90 (m, 4H, OCH_3, CH_2P), 2.79 (dd, *J* = 20.8, 15.2 Hz, 1H, CH_2P), 2.47 (s, 3H, CH_3), 1.21 (t, *J* = 7.1 Hz, 3H, CH_3), 1.08 (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.15, 167.90 (s, C=O), 136.17, 133.90, 131.77, 127.80, 124.06 (s, Ph), 123.61 (s, =C), 122.93, 121.93, 120.67, 118.62 (s, Ph), 114.11 (s, =CH), 61.79 (d, *J* = 6.7 Hz, OCH_2), 61.67 (d, *J* = 6.7 Hz, OCH_2), 57.99 (d, *J* = 3.2 Hz, N-C), 51.92 (s, OCH_3), 35.04 (d, *J* = 142.0 Hz, CH_2P), 27.39 (s, CH_3), 16.21 (d, *J* = 6.4 Hz, CH_3), 16.08 (d, *J* = 6.4 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.26 (s); ESI-HRMS calcd for $[C_{25}H_{27}N_2O_7P, M + Na]^+$: 521.1448, Found: 521.1442.

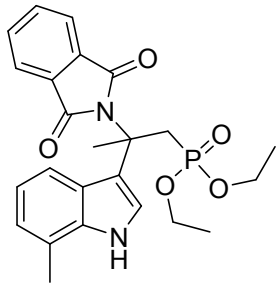




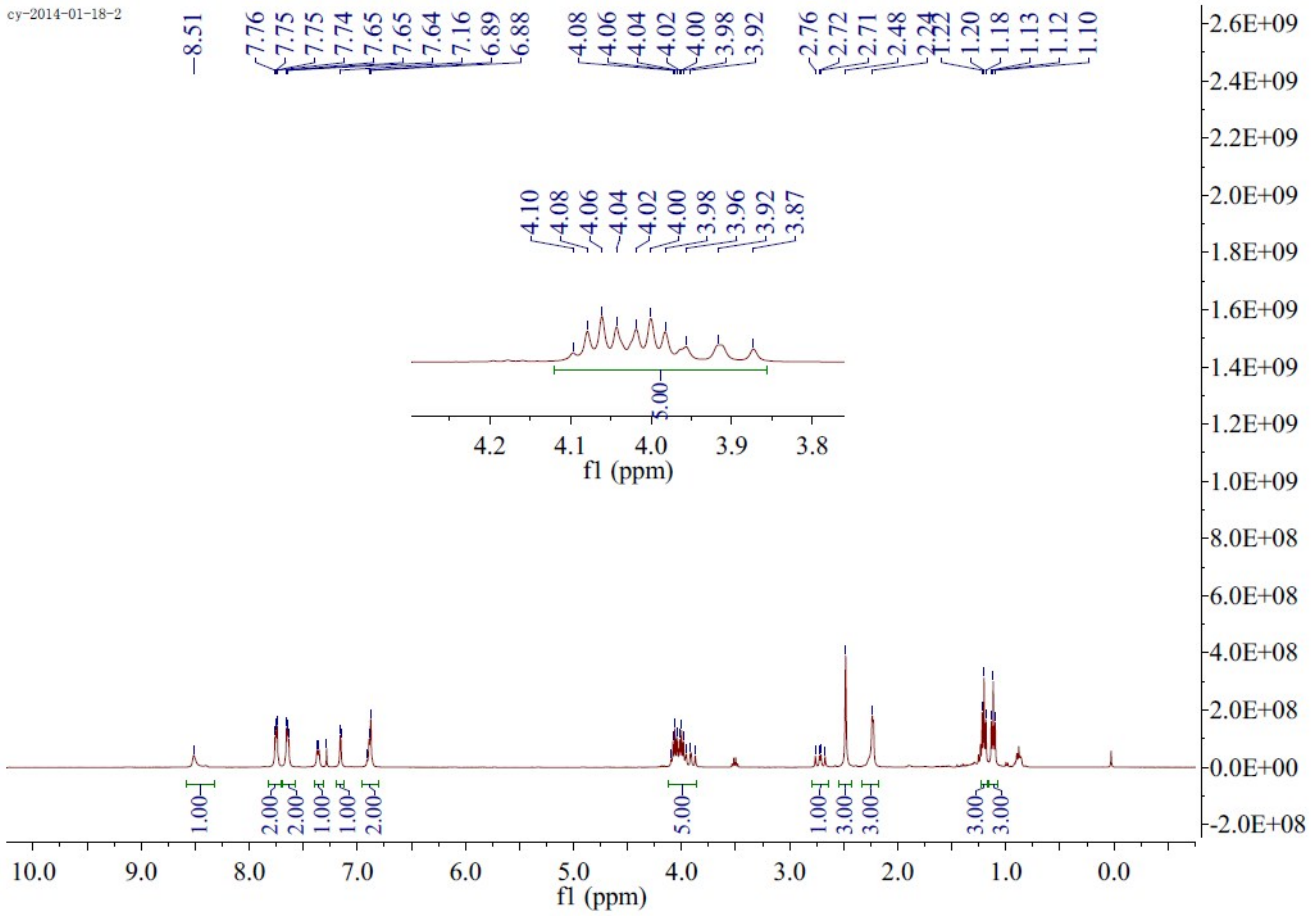


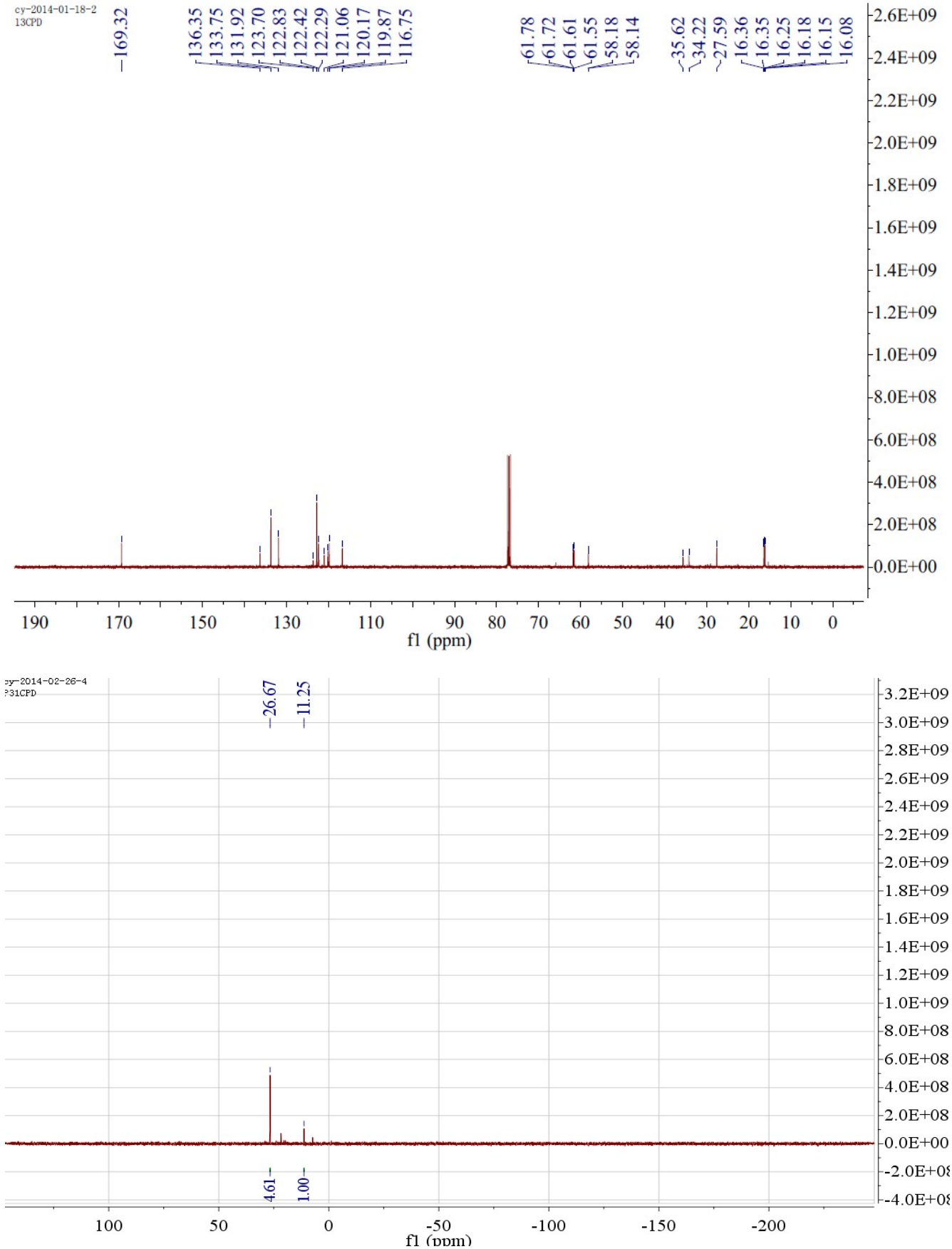
The mole ratio of **3h** and **4a** determined by crude ^{31}P NMR

Diethyl (2-(1,3-dioxoisoindolin-2-yl)-2-(7-methyl-1H-indol-3-yl)propyl)phosphonate (3i):



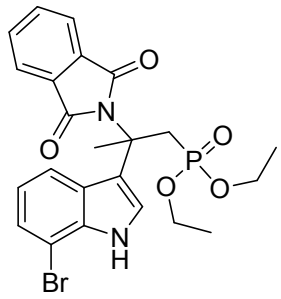
White solid; mp: 125-126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.51 (s, 1H, N-H), 7.70-7.81 (m, 2H), 7.59-7.68 (m, 2H, Ph), 7.36 (d, *J* = 6.0 Hz, 1H, Ph), 7.16 (d, *J* = 2.1 Hz, 1H, Ph), 6.82-6.95 (m, 2H, Ph, =CH), 3.84-4.16 (m, 5H, $2OCH_2$, CH_2P), 2.72 (dd, *J* = 20.7, 15.2 Hz, 1H, CH_2P), 2.48 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 1.20 (t, *J* = 7.0 Hz, 3H, CH_3), 1.12 (t, *J* = 7.0 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.32 (s, C=O), 136.35, 133.75, 131.92, 123.70, 122.83, 122.42 (s, Ph), 122.29 (s, =C), 121.06, 120.17, 119.87 (s, Ph), 116.75 (s, =CH), 61.75 (d, *J* = 6.7 Hz, OCH_2), 61.58 (d, *J* = 6.7 Hz, OCH_2), 58.16 (d, *J* = 4.4 Hz, N-C), 34.92 (d, *J* = 141.3 Hz, CH_2P), 27.59 (s, CH_3), 16.36 (d, *J* = 0.9 Hz, CH_3), 16.22 (d, *J* = 6.5 Hz, CH_3), 16.11 (d, *J* = 6.5 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.79 (s); ESI-HRMS calcd for $[C_{24}H_{27}N_2O_5P, M + Na]^+$: 477.1550, Found: 477.1549.



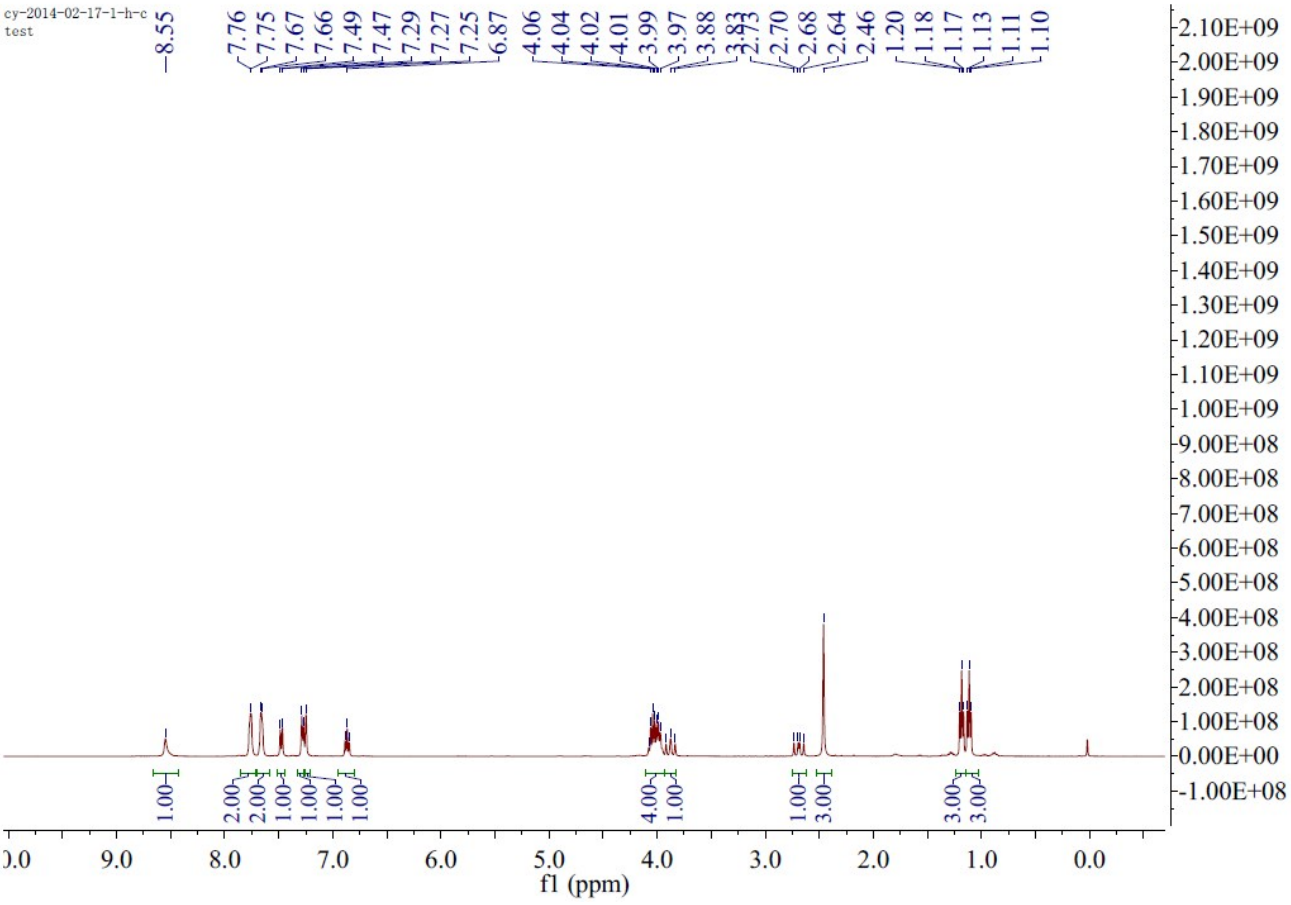


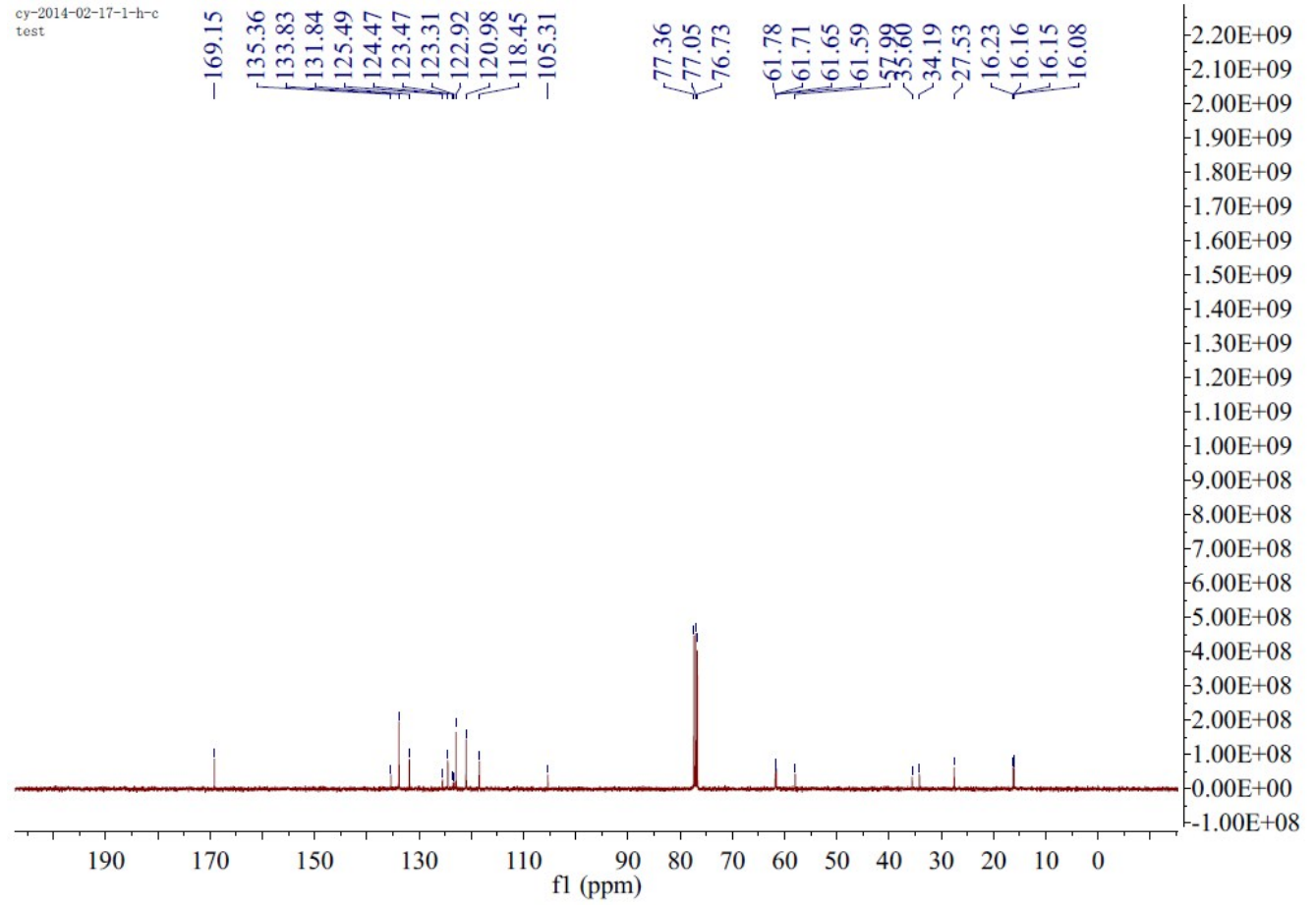
The mole ratio of **3i** and **4a** determined by crude ^{31}P NMR

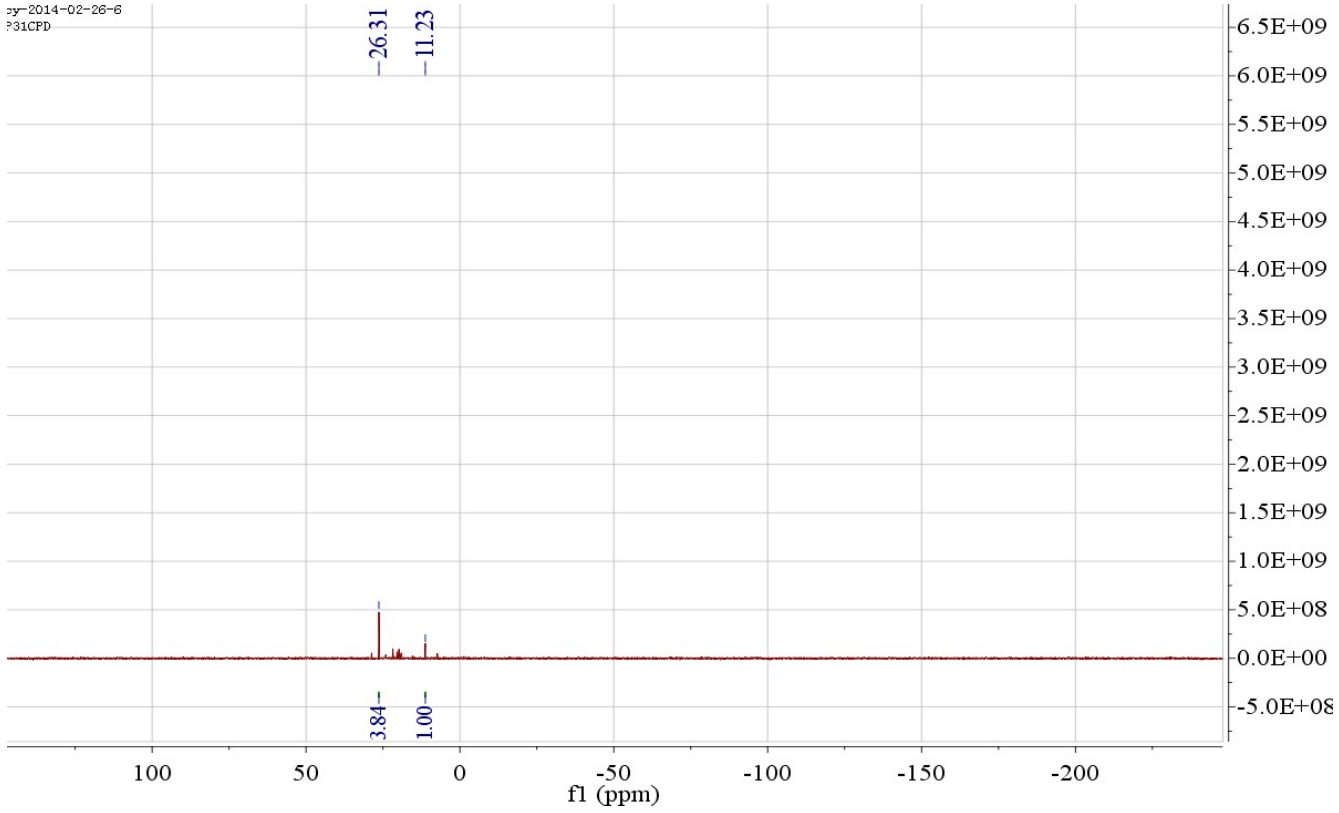
Diethyl (2-(7-bromo-1H-indol-3-yl)-2-(1,3-dioxoisoindolin-2-yl)propyl)phosphonate (3j):



White solid; mp: 159-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (s, 1H, N-H), 7.73-7.83 (m, 2H, Ph), 7.59-7.71 (m, 2H, Ph), 7.48 (d, *J* = 8.0 Hz, 1H, Ph), 7.28 (d, *J* = 6.3 Hz, 1H, Ph), 7.25 (s, 1H, =CH), 6.87 (t, *J* = 7.8 Hz, 1H, Ph), 3.94-4.10 (m, 4H, $2OCH_2$), 3.82-3.93 (m, 1H, CH_2P), 2.69 (dd, *J* = 20.7, 15.3 Hz, 1H, CH_2P), 2.46 (s, 3H, CH_3), 1.18 (t, *J* = 7.0 Hz, 3H, CH_3), 1.11 (t, *J* = 7.0 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.15 (s, C=O), 135.36, 133.83, 131.84, 125.49, 124.47, 123.47 (s, Ph), 123.31 (s, =C), 122.92, 120.98, 118.45 (s, Ph), 105.31 (s, =CH), 61.75 (d, *J* = 6.6 Hz, OCH_2), 61.62 (d, *J* = 6.6 Hz, OCH_2), 57.97 (d, *J* = 4.8 Hz, N-C), 34.89 (d, *J* = 141.4 Hz, CH_2P), 27.53 (s, CH_3), 16.19 (d, *J* = 6.8 Hz, CH_3), 16.11 (d, *J* = 6.8 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.33 (s); ESI-HRMS calcd for $[C_{23}H_{24}BrN_2O_5P, M + Na]^+$: 541.0498, Found: 541.0492.

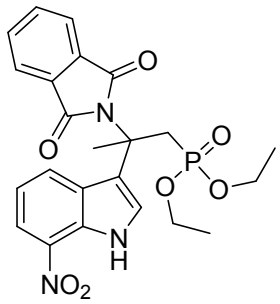




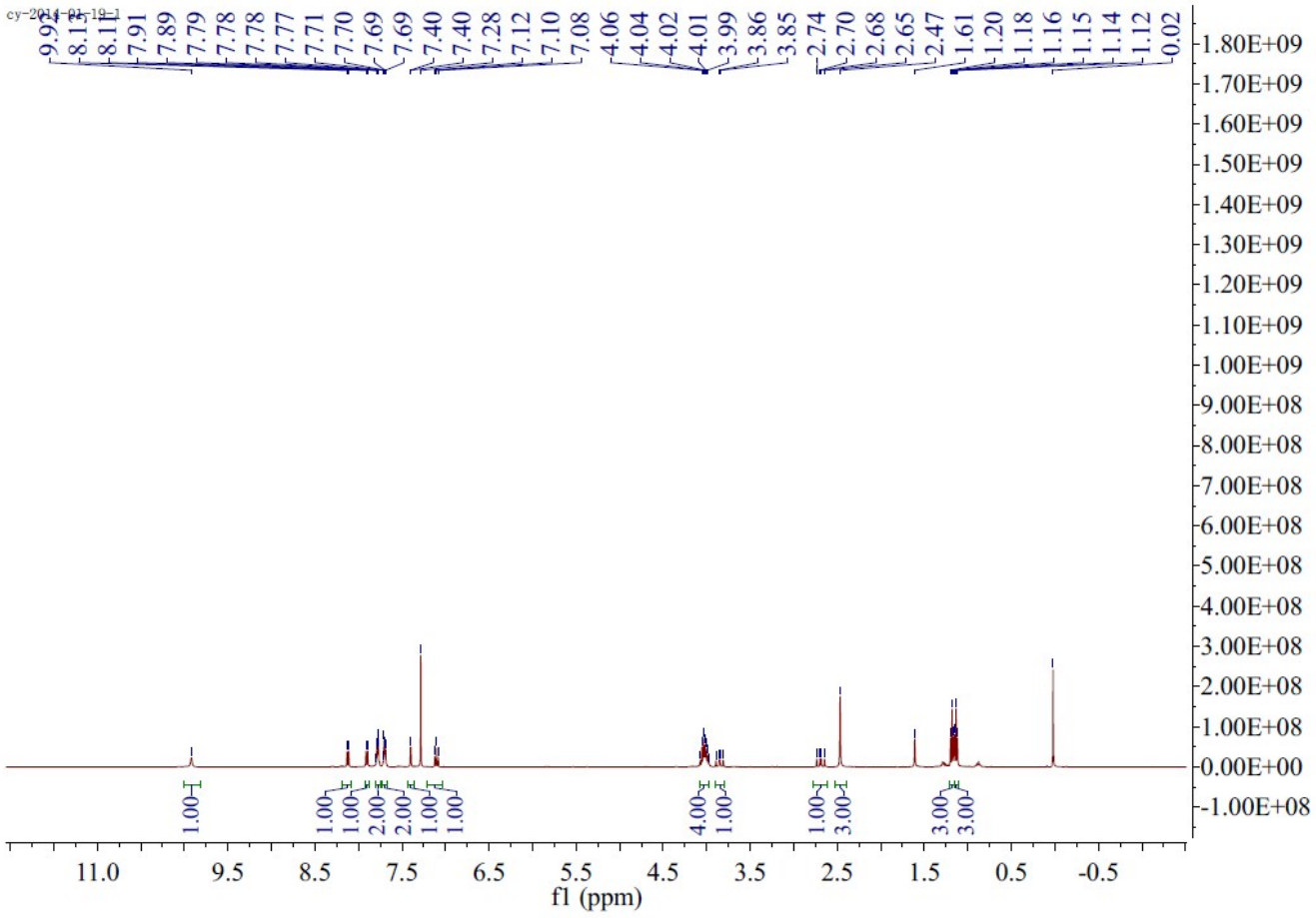


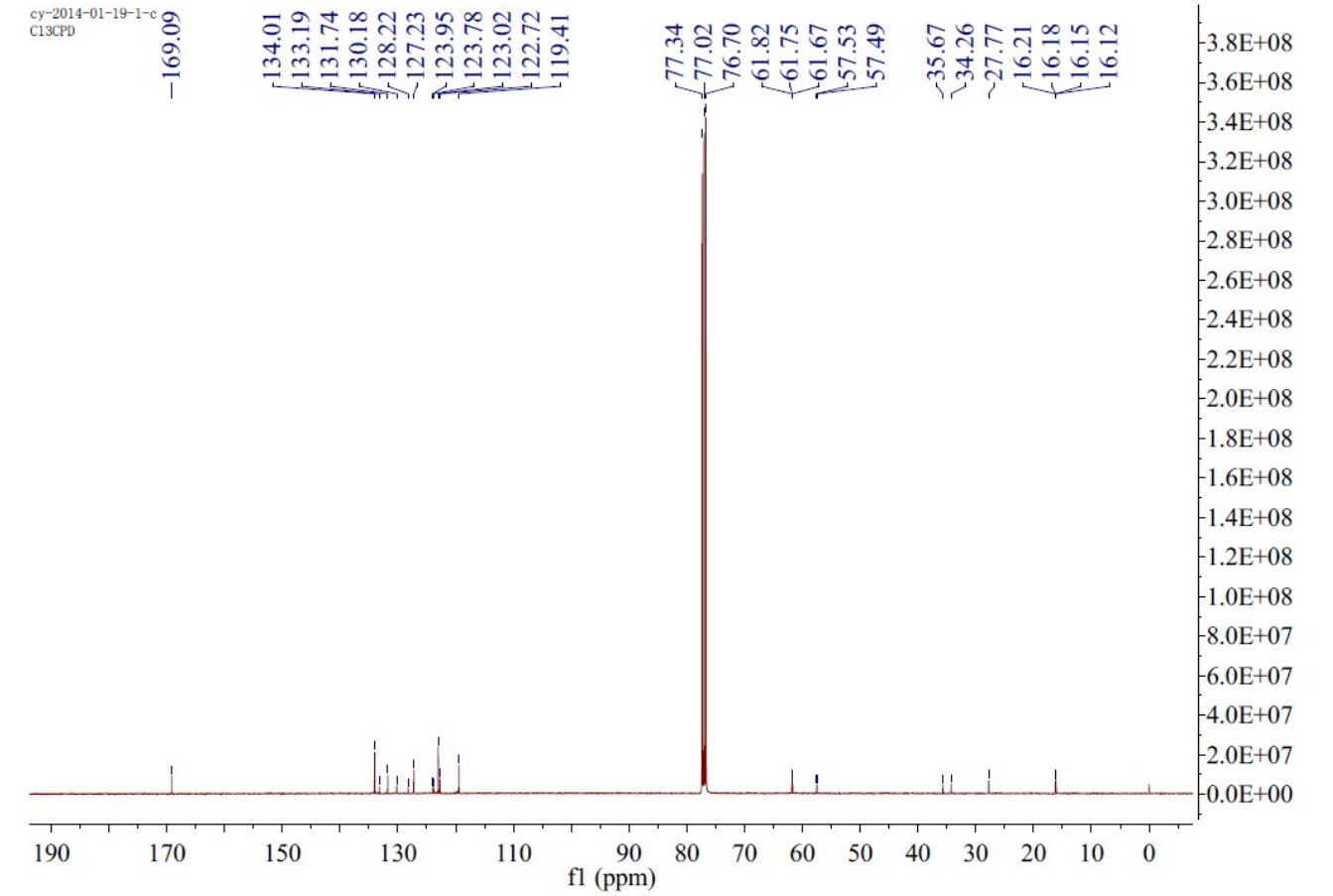
The mole ratio of **3j** and **4a** determined by crude ^{31}P NMR

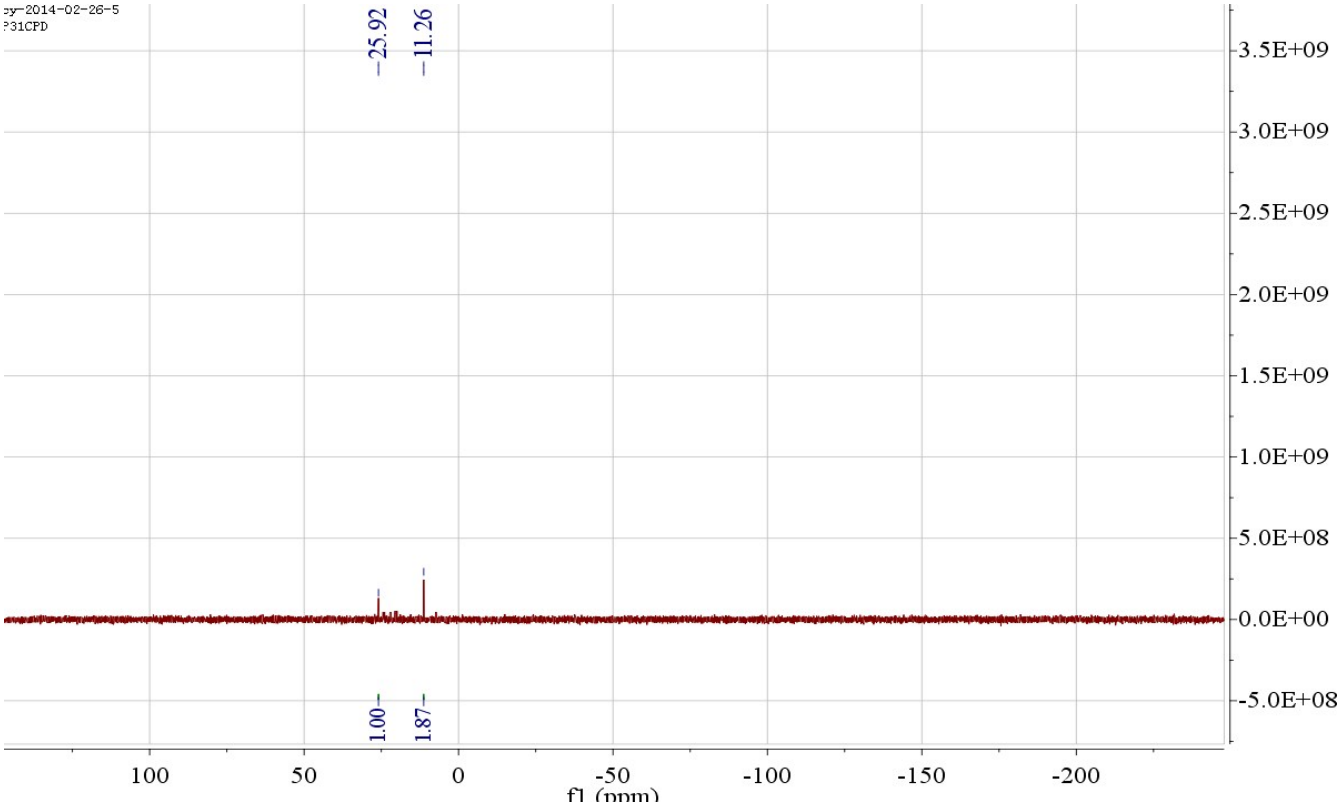
Diethyl (2-(1,3-dioxoisoindolin-2-yl)-2-(7-nitro-1H-indol-3-yl)propyl)phosphonate (3k):



Yellow solid; mp: 178-179 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.92 (s, 1H, N-H), 8.12 (d, *J* = 8.0 Hz, 1H, Ph), 7.90 (d, *J* = 8.0 Hz, 1H, Ph), 7.75-7.81 (m, 2H, Ph), 7.66-7.73 (m, 2H, Ph), 7.40 (d, *J* = 2.3 Hz, 1H, =CH), 7.10 (t, *J* = 8.0 Hz, 1H, Ph), 3.96-4.09 (m, 4H, $2OCH_2$), 3.85 (dd, *J* =21.0, 15.1 Hz, 1H, CH_2P), 2.69 (dd, *J* =21.0, 15.1 Hz, 1H, CH_2P), 2.47 (s, 3H, CH_3), 1.18 (t, *J* = 7.1 Hz, 3H, CH_3), 1.14 (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.09 (s, C=O), 134.01, 133.19, 131.74, 130.18, 128.22, 127.23, 123.95 (s, Ph), 123.78 (s, =C), 123.02, 122.72 (s, Ph), 119.41 (s, =CH), 61.78 (d, *J* = 7.4 Hz, OCH_2), 61.71 (d, *J* = 7.4 Hz, OCH_2), 57.51 (d, *J* = 4.2 Hz, N-C), 34.97 (d, *J* = 142.0 Hz, CH_2P), 27.77 (s, CH_3), 16.19 (d, *J* = 3.1 Hz, CH_3), 16.13 (d, *J* = 3.1 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.81 (s); ESI-HRMS calcd for $[C_{23}H_{24}N_3O_7P, M + Na]^+$: 508.1244, Found: 508.1237.

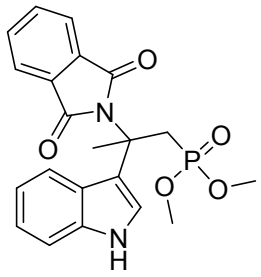




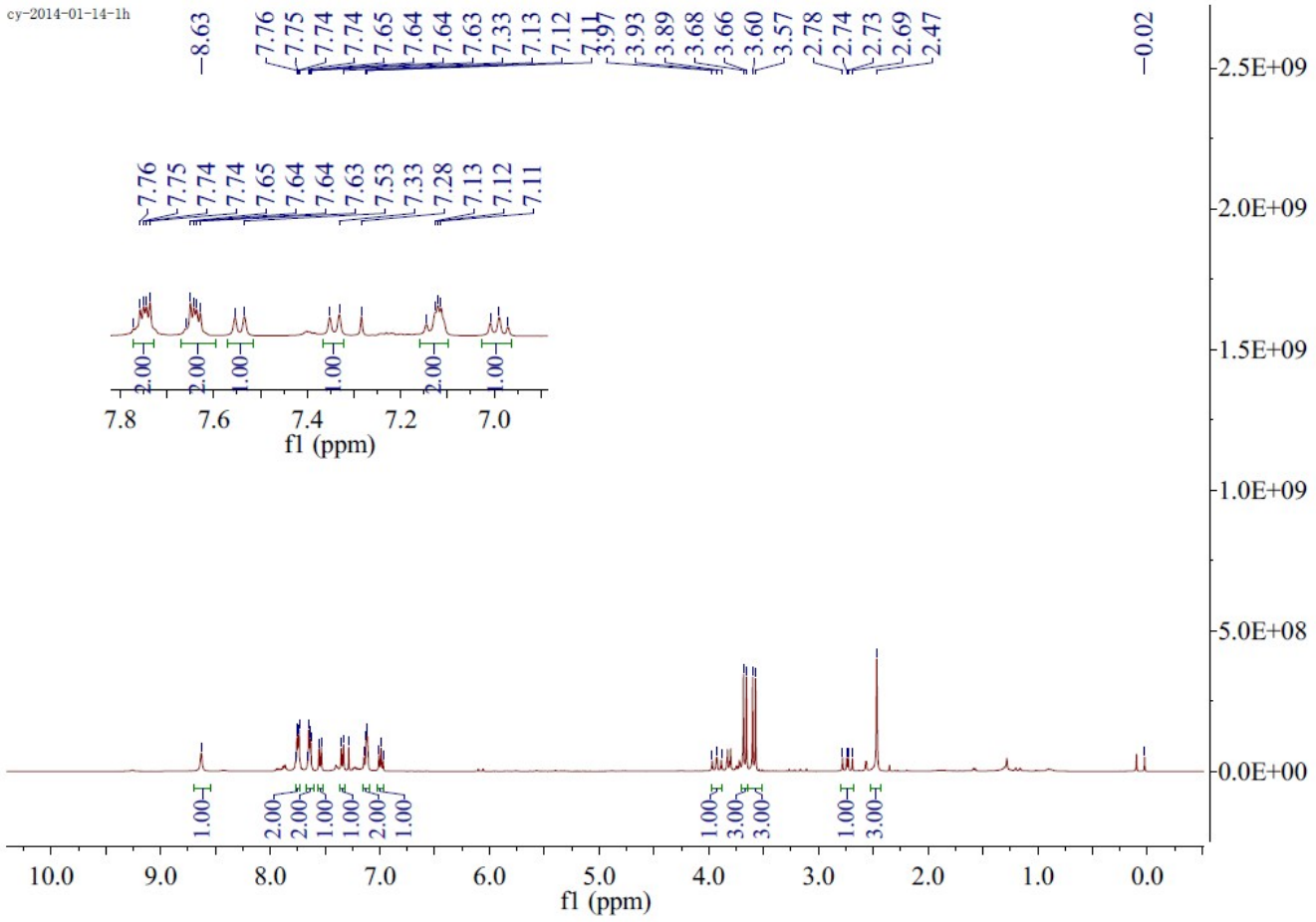


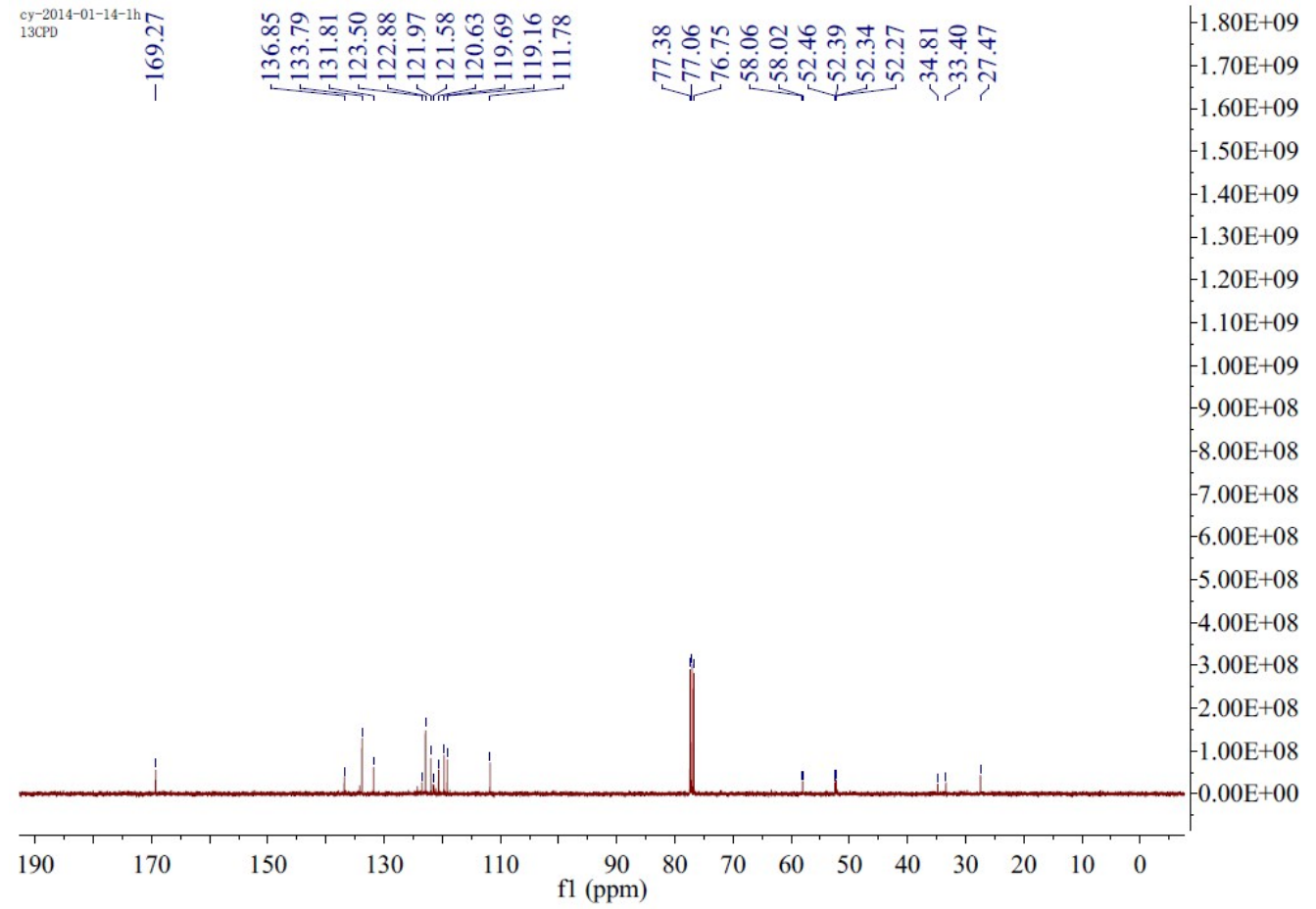
The mole ratio of **3k** and **4a** determined by crude ^{31}P NMR

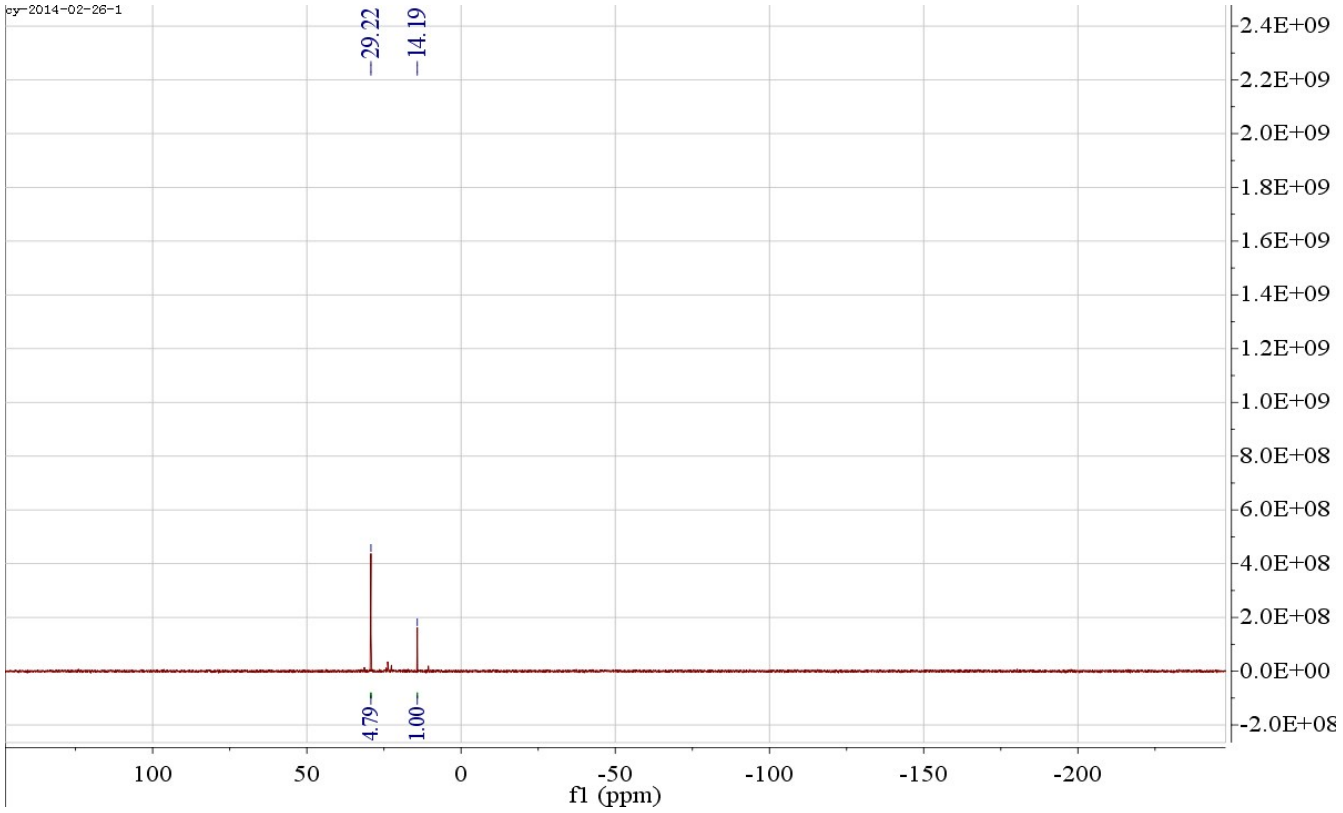
Dimethyl (2-(1,3-dioxoisoindolin-2-yl)-2-(1H-indol-3-yl)propyl)phosphonate (3m):



Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (s, 1H, N-H), 7.72-7.80 (m, 2H, Ph), 7.60-7.67 (m, 2H, Ph), 7.54 (d, *J* = 8.0 Hz, 1H, Ph), 7.34 (d, *J* = 8.0 Hz, 1H, Ph), 7.09-7.16 (m, 2H, Ph, =CH), 6.99 (t, *J* = 7.5 Hz, 1H, Ph), 3.87-3.99 (m, 1H, CH_2P), 3.67 (d, *J* = 11.0 Hz, 3H, OCH_3), 3.59 (d, *J* = 11.0 Hz, 3H, OCH_3), 2.74 (dd, *J* = 20.7, 15.3 Hz, 1H, CH_2P), 2.47 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.27 (s, C=O), 136.85, 133.79, 131.81, 123.50, 122.88, 121.97 (s, Ph), 121.58 (s, =C), 120.63, 119.69, 119.16 (s, Ph), 111.78 (s, =CH), 58.04 (d, *J* = 3.8 Hz, N-C), 52.42 (d, *J* = 6.8 Hz, OCH_3), 52.30 (d, *J* = 6.8 Hz, OCH_3), 34.10 (d, *J* = 141.5 Hz, CH_2P), 27.47 (s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.41 (s); ESI-HRMS calcd for $[C_{21}H_{21}N_2O_5P, M + Na]^+$: 435.1080, Found: 435.1081.

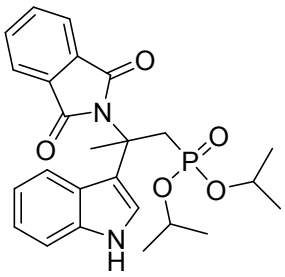




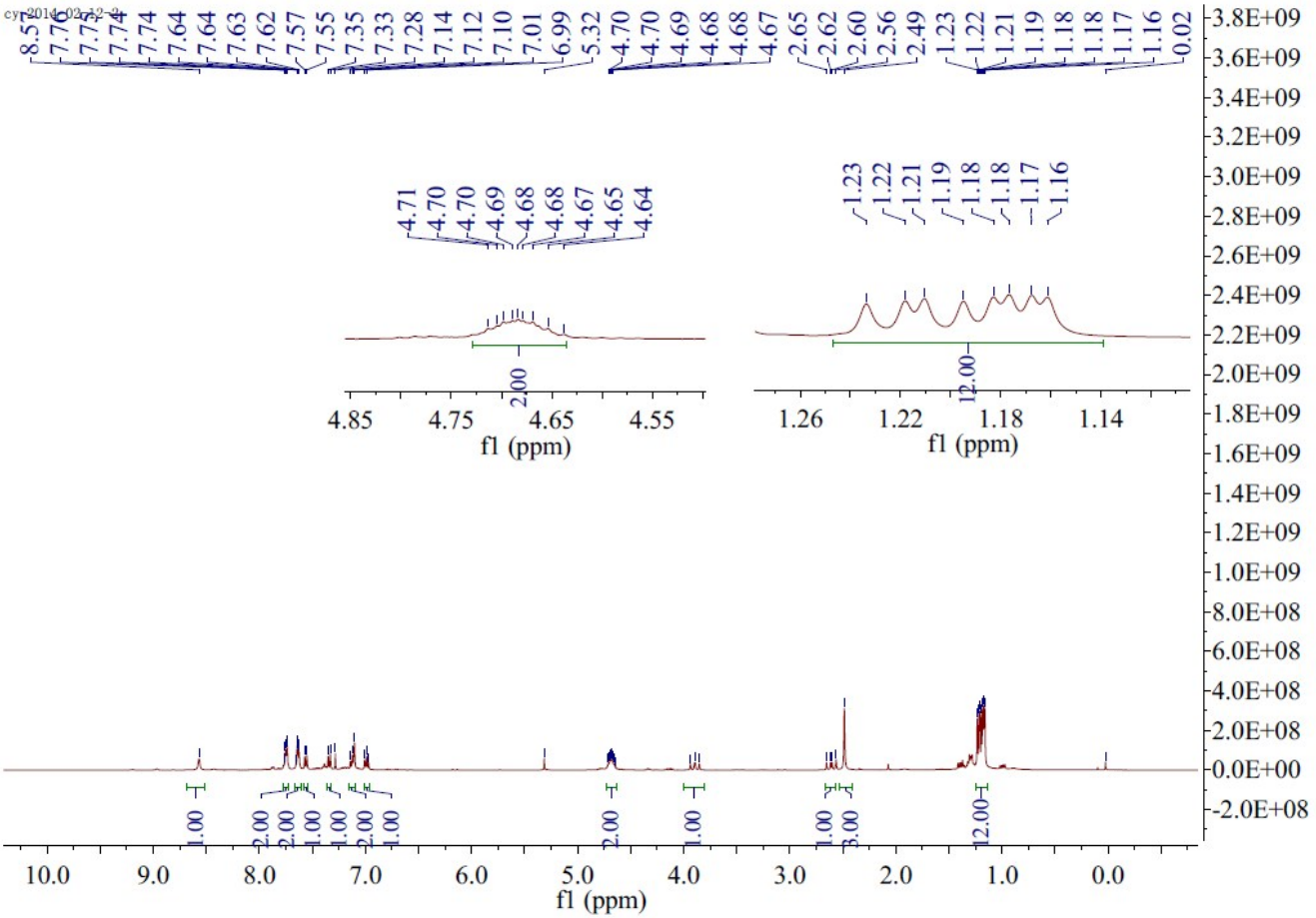


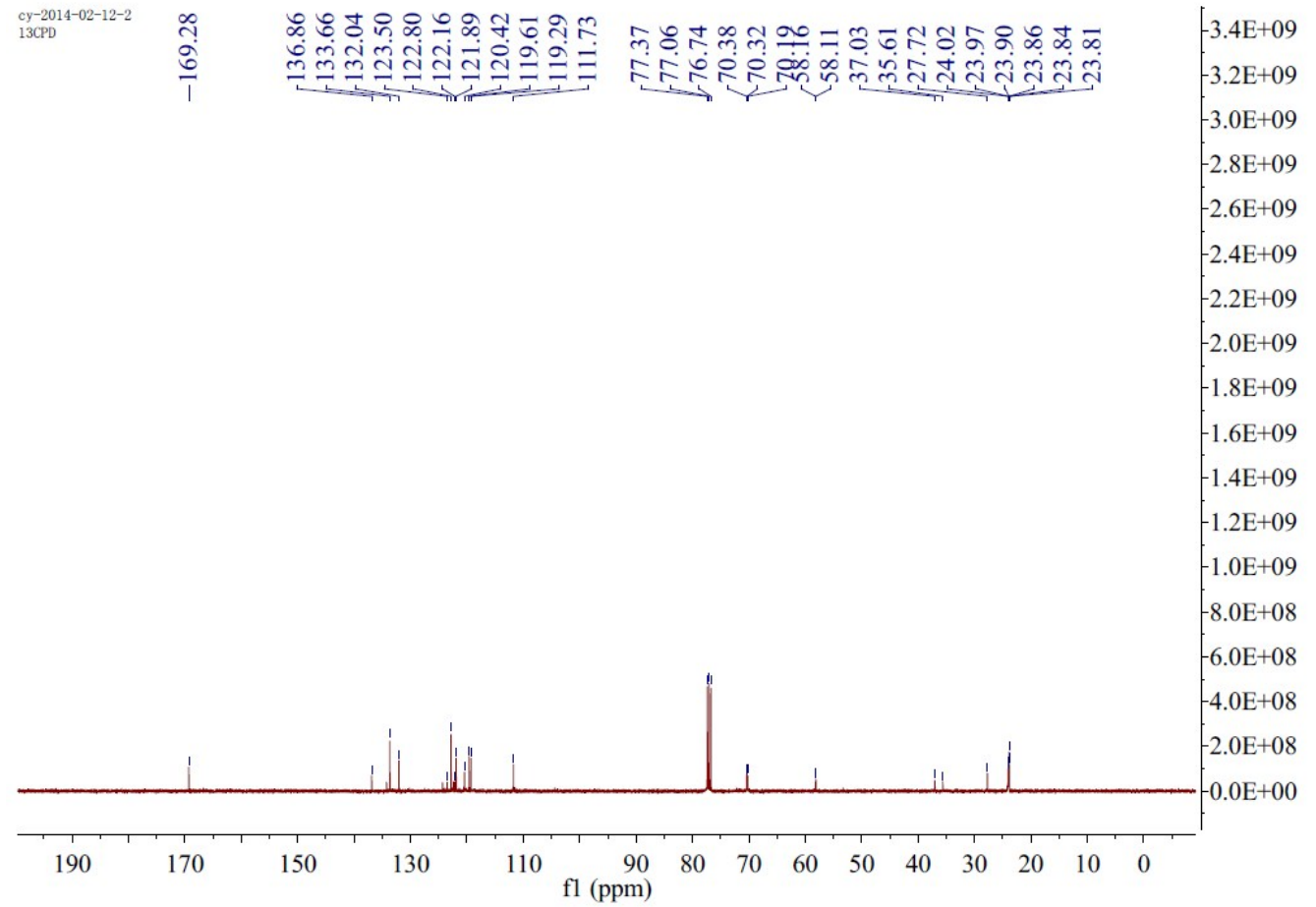
The mole ratio of **3m** and **4m** determined by crude ^{31}P NMR

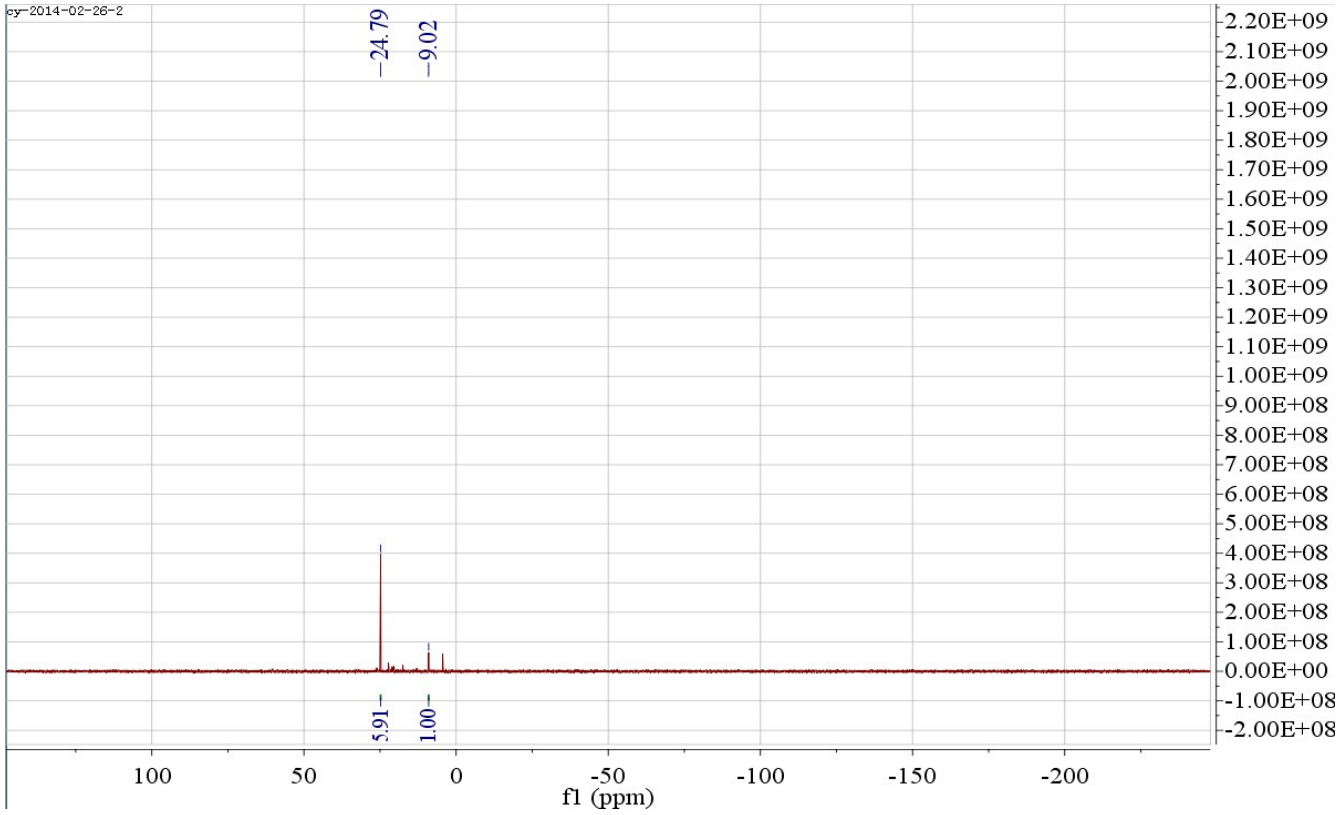
Diisopropyl (2-(1,3-dioxoisoindolin-2-yl)-2-(1H-indol-3-yl)propyl)phosphonate (3n):



Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 1H, N-H), 7.71-7.79 (m, 2H, Ph), 7.61-7.67 (m, 2H, Ph), 7.56 (d, *J* = 8.1 Hz, 1H, Ph), 7.34 (d, *J* = 8.1 Hz, 1H, Ph), 7.08-7.17 (m, 2H, Ph, =CH), 6.99 (t, *J* = 7.5 Hz, 1H, Ph), 4.63-4.74 (m, 2H, 2OCH), 3.89 (dd, *J* = 17.7, 15.6 Hz, 1H, OCH_2P), 2.61 (dd, *J* = 17.7, 15.6 Hz, 1H, OCH_2P), 2.49 (s, 3H, CH_3), 1.15-1.25 (m, 12H, $4CH_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.28 (s, C=O), 136.86, 133.66, 132.04, 123.50, 122.80 (s, Ph), 122.16 (s, =C), 121.89, 120.42, 119.61, 119.29 (s, Ph), 111.73 (s, =CH), 70.35 (d, *J* = 6.9 Hz, OCH), 70.23 (d, *J* = 6.9 Hz, OCH), 58.14 (d, *J* = 5.0 Hz, N-C), 36.32 (d, *J* = 142.1 Hz, CH_2P), 27.72 (s, CH_3), 23.99 (d, *J* = 4.1 Hz, CH_3), 23.88 (d, *J* = 4.1 Hz, CH_3), 23.83 (d, *J* = 4.1 Hz, CH_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 24.94 (s); ESI-HRMS calcd for $[C_{25}H_{29}N_2O_5P, M + Na]^+$: 491.1706, Found: 491.1705.

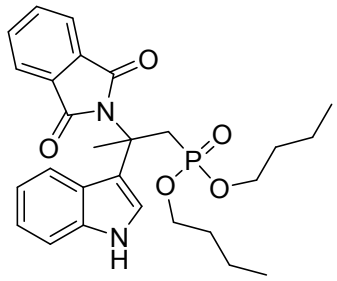




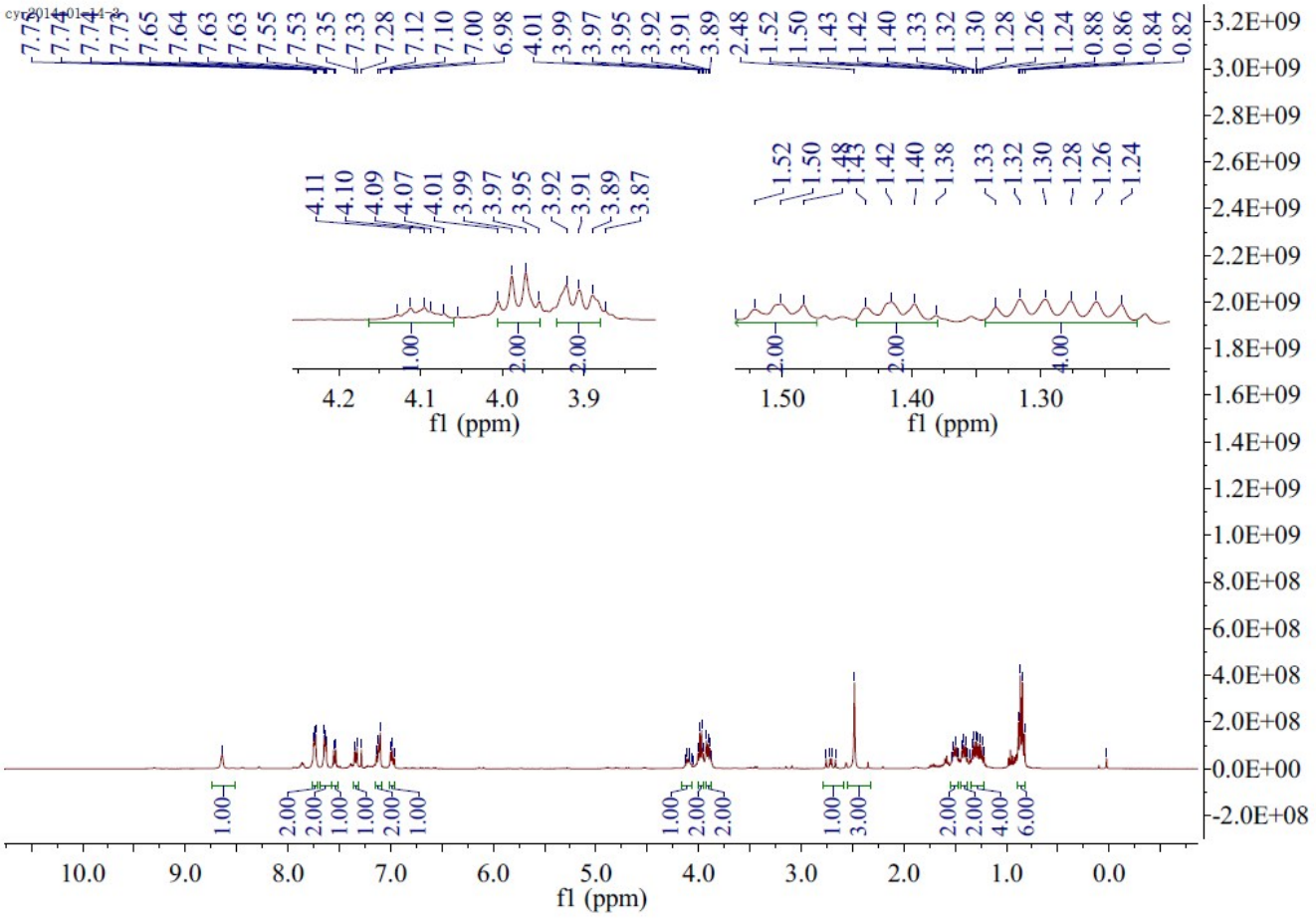


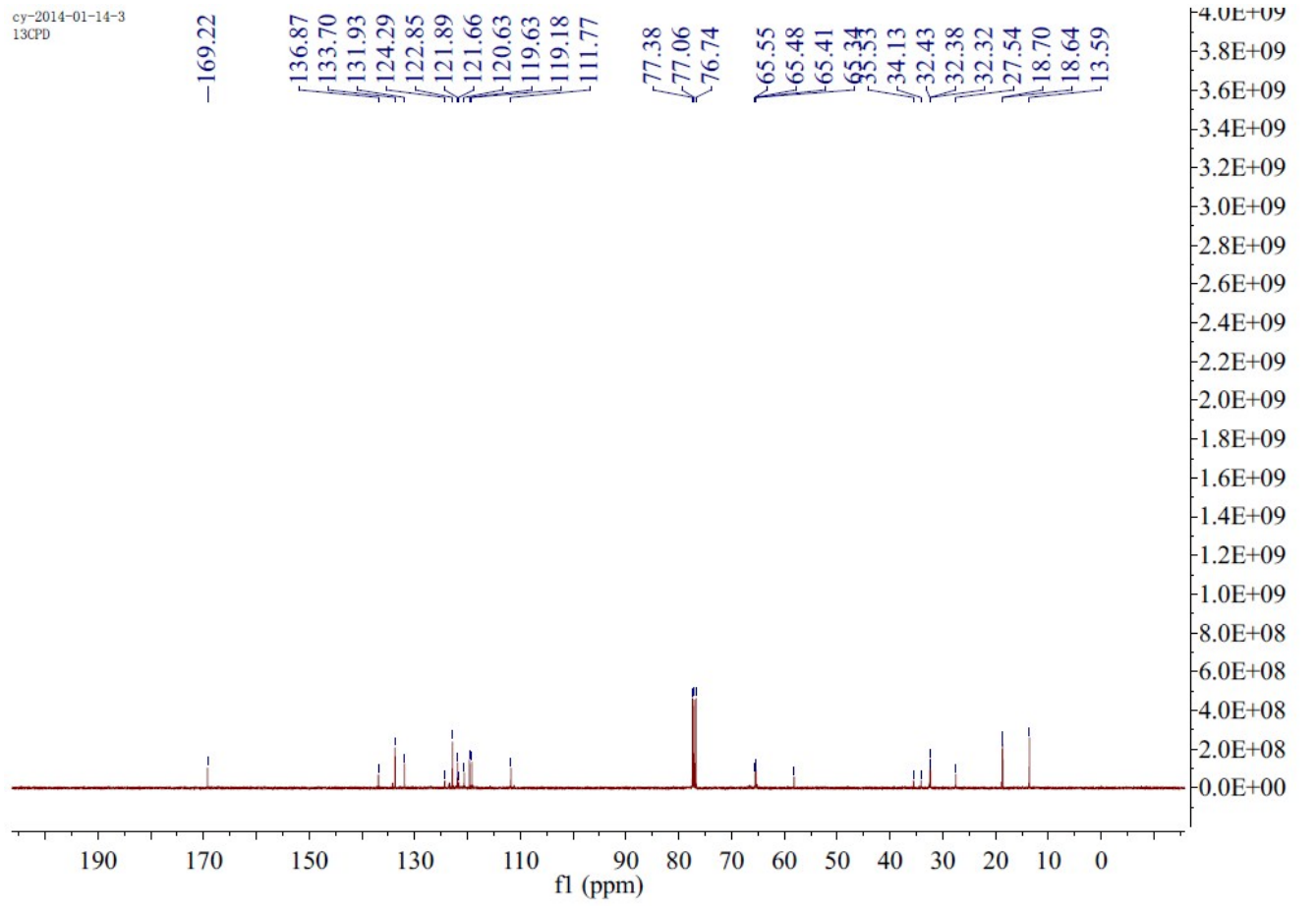
The mole ratio of **3n** and **4n** determined by crude ^{31}P NMR

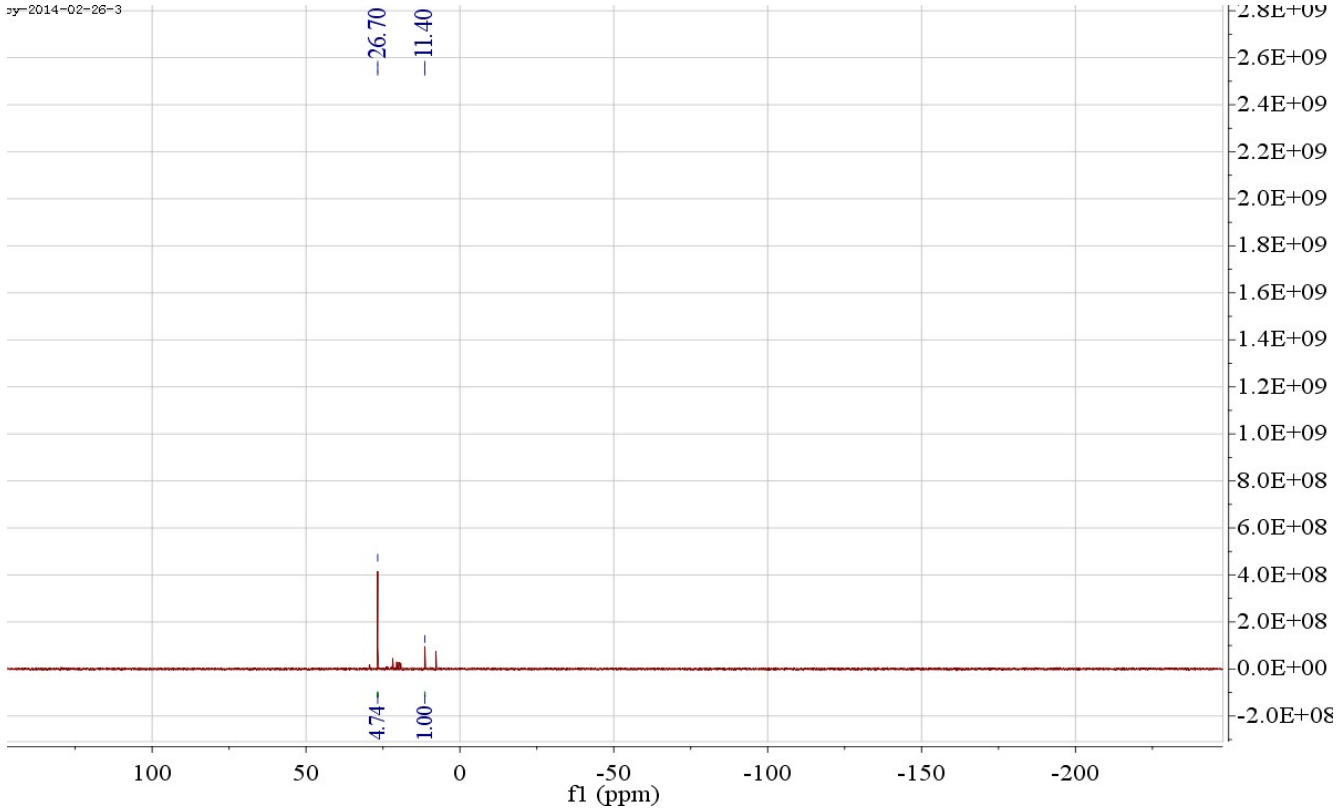
Dibutyl (2-(1,3-dioxoisoindolin-2-yl)-2-(1H-indol-3-yl)propyl)phosphonate (3o):



Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (s, 1H, N-H), 7.71-7.77 (m, 2H, Ph), 7.62-7.66 (m, 2H, Ph), 7.54 (d, *J* = 8.1 Hz, 1H, Ph), 7.34 (d, *J* = 8.1 Hz, 1H, Ph), 7.09-7.15 (m, 2H, Ph, =CH), 6.98 (t, *J* = 7.4 Hz, 1H, Ph), 4.06-4.17 (m, 1H, CH_2P), 3.95-4.02 (m, 2H, OCH_2), 3.87-3.94 (m, 2H, OCH_2), 2.71 (dd, *J* = 20.7, 15.2 Hz, 1H, CH_2P), 2.48 (s, 3H, CH_3), 1.47-1.55 (m, 2H, CH_2), 1.37-1.45 (m, 2H, CH_2), 1.22-1.36 (m, 4H, $2CH_2$), 0.85 (dd, *J* = 16.1, 7.5 Hz, 6H, $2CH_3$); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.22 (s, C=O), 136.87, 133.70, 131.93, 124.29, 122.85, 121.89 (s, Ph), 121.66 (s, =C), 120.63, 119.63, 119.18 (s, Ph), 111.77 (s, =CH), 65.51 (d, *J* = 6.8 Hz, OCH_2), 65.38 (d, *J* = 6.8 Hz, OCH_2), 58.14 (d, *J* = 4.3 Hz, N-C), 34.83 (d, *J* = 140.5 Hz, CH_2P), 32.40 (d, *J* = 6.0 Hz, CH_2), 32.35 (d, *J* = 6.0 Hz, CH_2), 27.54 (s, CH_3), 18.67 (d, *J* = 6.2 Hz, CH_2), 13.59 (s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.90 (s); ESI-HRMS calcd for $[C_{27}H_{33}N_2O_5P, M + Na]^+$: 519.2019, Found: 519.2023.

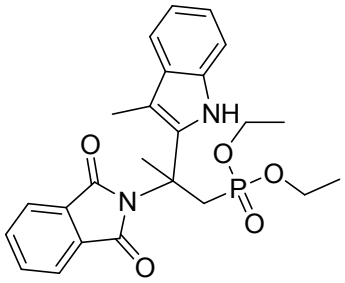




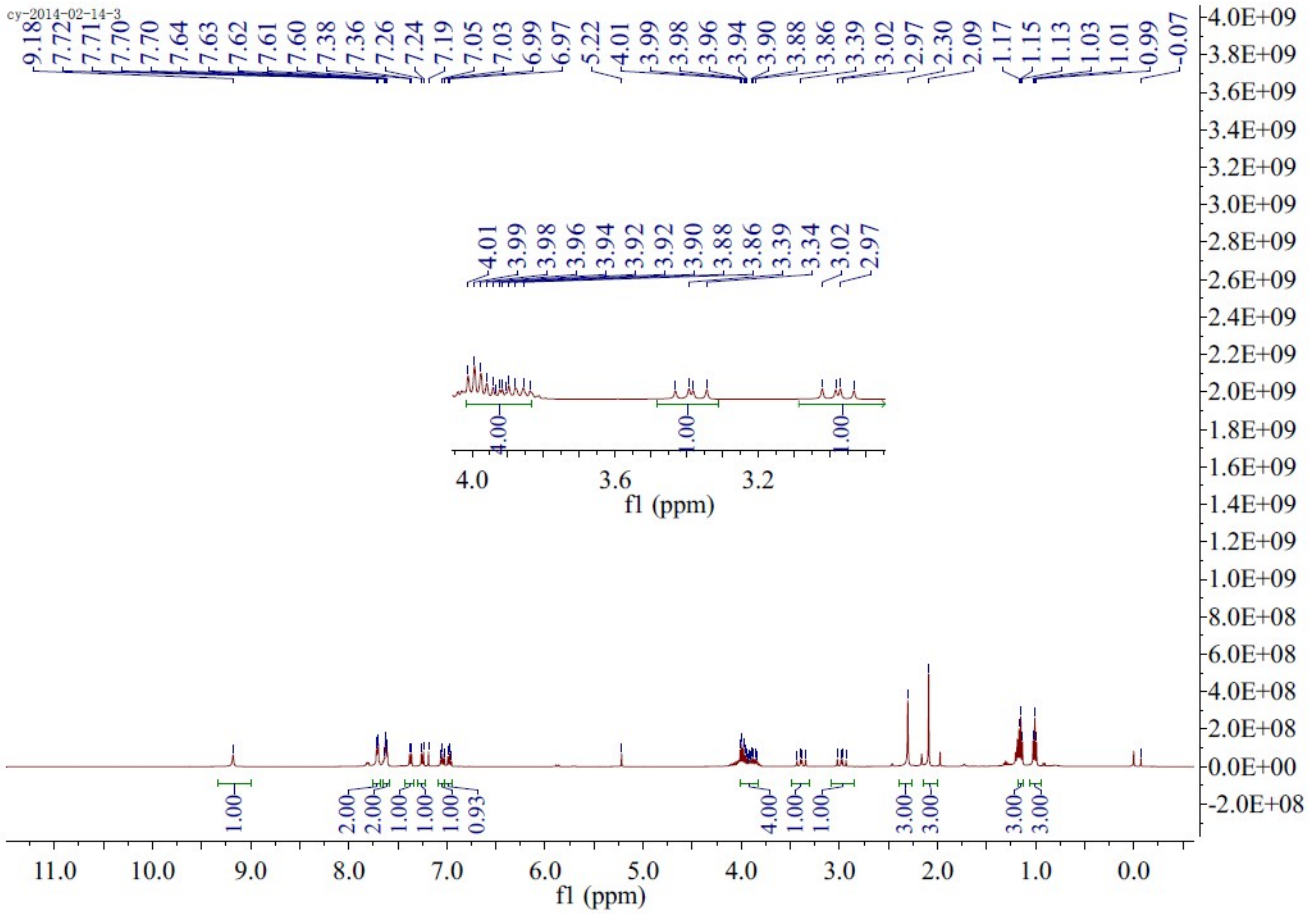


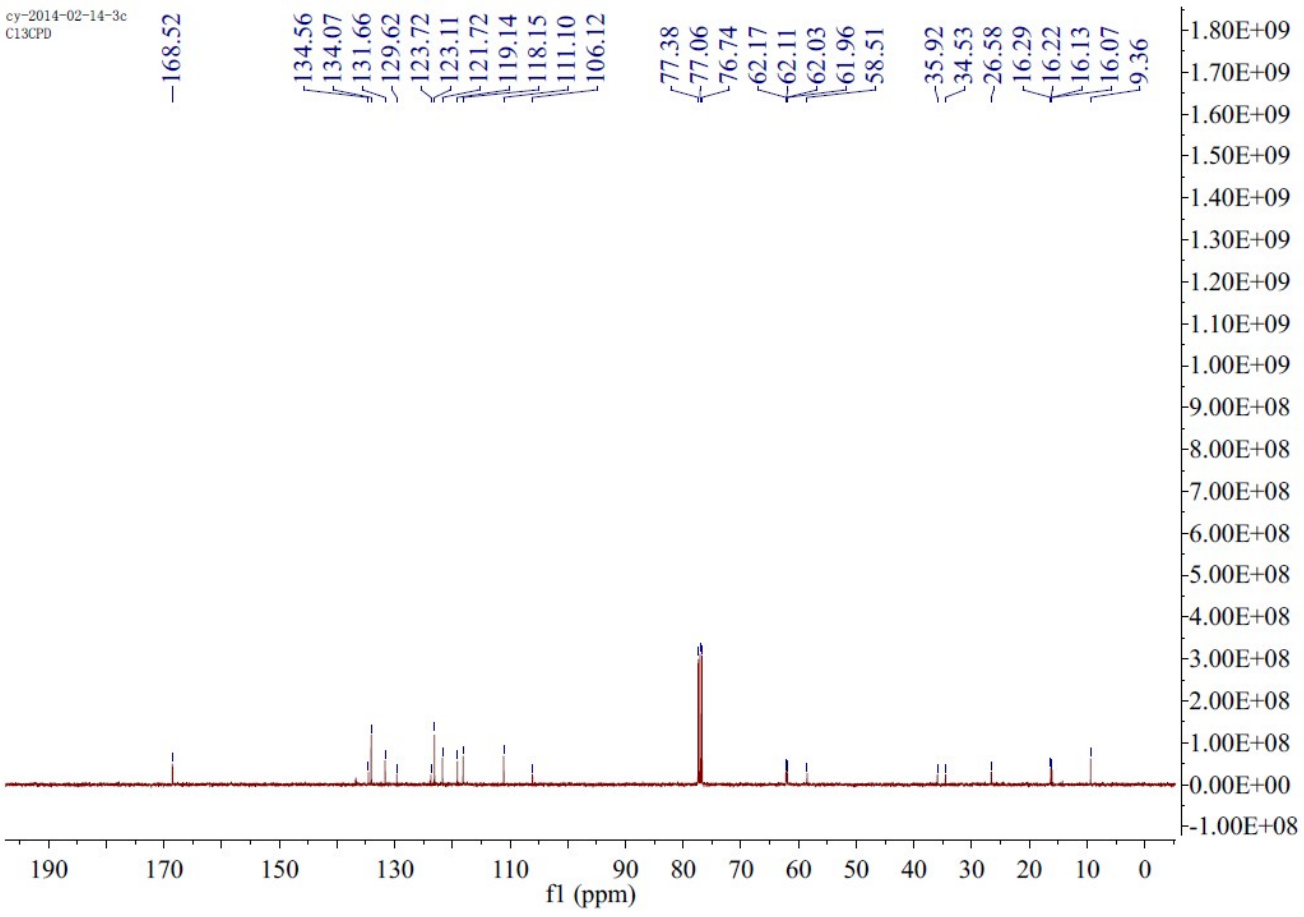
The mole ratio of **3o** and **4o** determined by crude ^{31}P NMR

Diethyl (2-(1,3-dioxoisoindolin-2-yl)-2-(3-methyl-1H-indol-2-yl)propyl)phosphonate (3p):

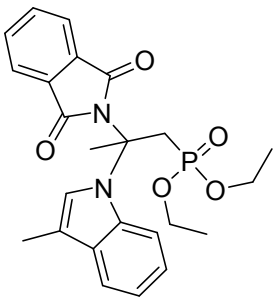


Yellow solid; mp: 182-183 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.18 (s, 1H, N-H), 7.68-7.75 (m, 2H, Ph), 7.59-7.65 (m, 2H, Ph), 7.37 (d, *J* = 7.9 Hz, 1H, Ph), 7.25 (d, *J* = 7.9 Hz, 1H, Ph), 7.05 (t, *J* = 7.5 Hz, 1H, Ph), 6.97 (t, *J* = 7.5 Hz, 1H, Ph), 3.82-4.05 (m, 4H, $2OCH_2$), 3.39 (dd, *J* = 19.9, 15.2 Hz, 1H, CH_2P), 2.98 (dd, *J* = 19.9, 15.2 Hz, 1H, CH_2P), 2.30 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 1.15 (t, *J* = 7.1 Hz, 3H, CH_3), 1.01 (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.52 (s, C=O), 134.56, 134.07, 131.66, 129.62 (s, Ph), 123.72 (s, =C-N), 123.11, 121.72, 119.14, 118.15, 111.10 (s, Ph), 106.12 (s, =CH), 62.14 (d, *J* = 6.8 Hz, OCH_2), 61.99 (d, *J* = 6.8 Hz, OCH_2), 58.51 (s, N-C), 35.23 (d, *J* = 139.9 Hz, CH_2P), 26.58 (s, CH_3), 16.25 (d, *J* = 6.4 Hz, CH_3), 16.10 (d, *J* = 6.4 Hz, CH_3), 9.36 (s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.03 (s); ESI-HRMS calcd for $[C_{24}H_{27}N_2O_5P, M + Na]^+$: 477.1550, Found: 477.1558.

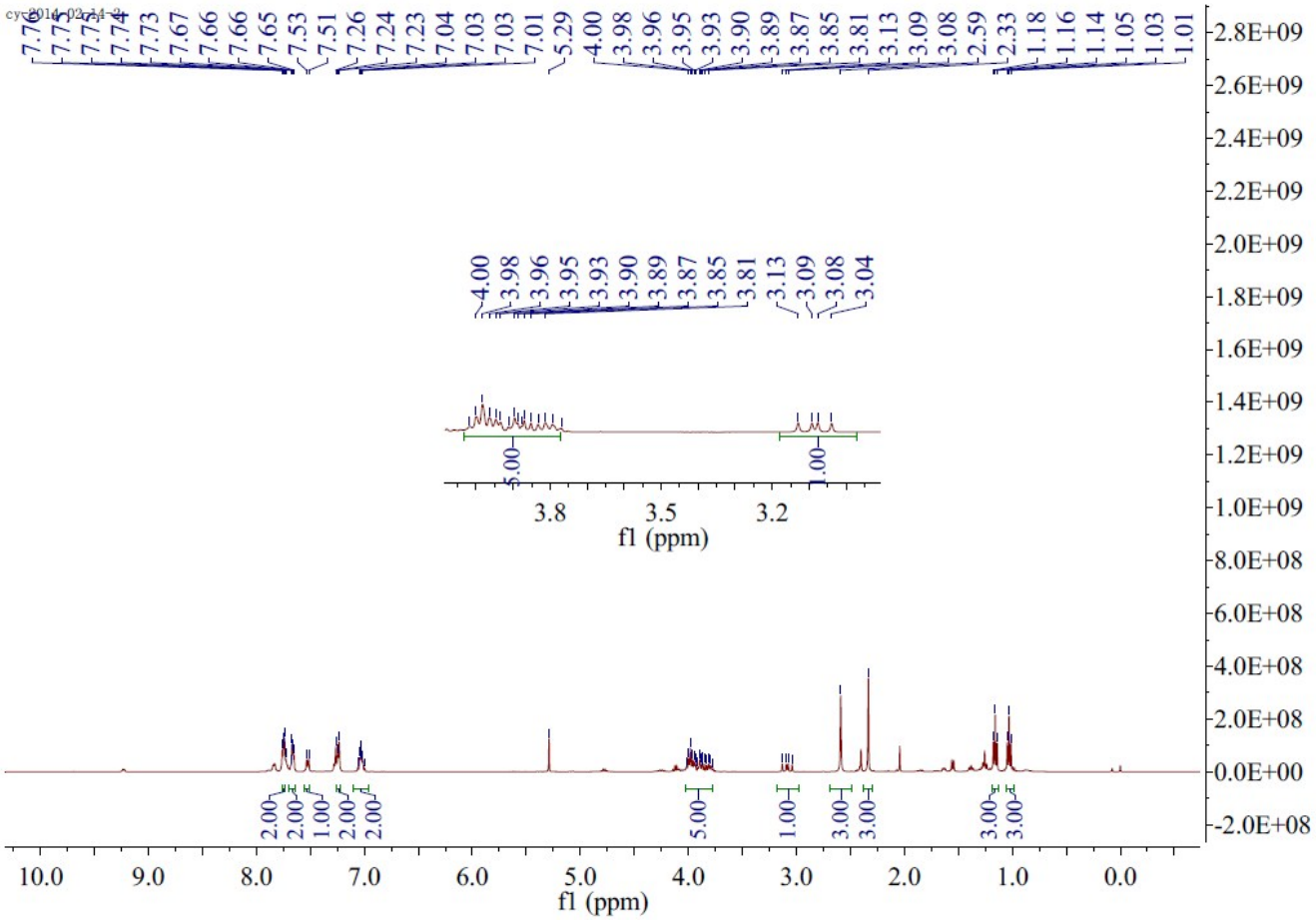


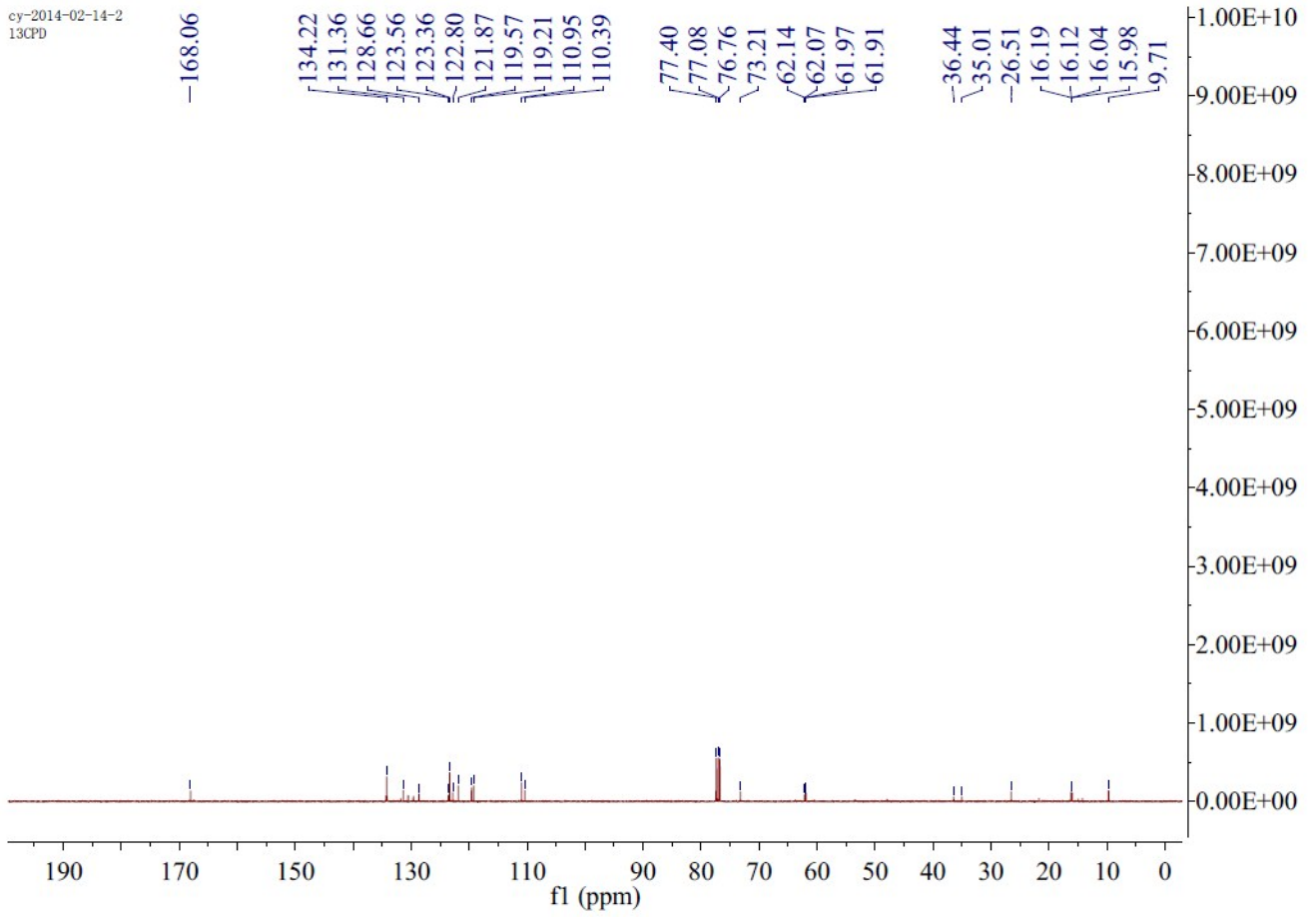


Diethyl (2-(1,3-dioxoisoindolin-2-yl)-2-(3-methyl-1H-indol-1-yl)propyl)phosphonate (3p'):



Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71-7.80 (m, 2H, Ph), 7.63-7.69 (m, 2H, Ph), 7.52 (d, *J* = 8.2 Hz, 1H, Ph), 7.20-7.27 (m, 2H, Ph, =CH), 6.98-7.10 (m, 2H, Ph), 3.76-4.03 (m, 5H, 2OCH_2, CH_2P), 3.08 (dd, *J* = 21.3, 14.9 Hz, 1H, CH_2P), 2.59 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 1.16 (t, *J* = 7.1 Hz, 3H, CH_3), 1.03 (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.06 (s, C=O), 134.22, 131.36, 128.66, 123.56, 123.36 (s, Ph), 122.80 (s, =C), 121.87, 119.57, 119.21, 110.95 (s, Ph), 110.39 (s, =CH), 73.21 (s, N-C), 62.10 (d, *J* = 6.7 Hz, OCH_2), 61.94 (d, *J* = 6.7 Hz, OCH_2), 35.73 (d, *J* = 143.5 Hz, CH_2P), 26.51 (s, CH_3), 16.15 (d, *J* = 6.5 Hz, CH_3), 16.01 (d, *J* = 6.5 Hz, CH_3), 9.71 (s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 23.38 (s); ESI-HRMS calcd for $[C_{24}H_{27}N_2O_5P, M + Na]^+$: 477.1550, Found: 477.1551.

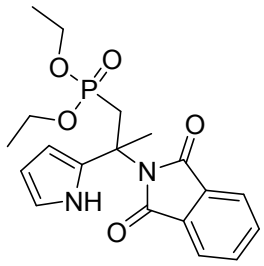

7.76 7.75 7.75 7.74 7.73 7.67 7.66 7.66 7.65 7.53 7.51 7.26 7.24 7.23 7.04 7.03 7.03 7.01 5.29 4.00 3.98 3.96 3.95 3.93 3.90 3.89 3.87 3.85 3.81 3.13 3.09 3.08 2.59 2.33 1.18 1.16 1.14 1.05 1.03 1.01
4.00 3.98 3.96 3.95 3.93 3.90 3.89 3.87 3.85 3.81 3.13 3.09 3.08 3.04
5.00 1.00
3.8 3.5 3.2
f1 (ppm)
2.00 2.00 1.00 2.00 2.00 5.00 1.00 3.00 3.00 3.00 3.00
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)
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 -2.0E+08


cy-2014-02-14-2
13CPD
168.06
134.22 131.36 128.66 123.56 123.36 122.80 121.87 119.57 119.21 110.95 110.39
77.40 77.08 76.76 73.21 62.14 62.07 61.97 61.91
36.44 35.01 26.51 16.19 16.12 16.04 15.98 9.71
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
1.00E+10 9.00E+09 8.00E+09 7.00E+09 6.00E+09 5.00E+09 4.00E+09 3.00E+09 2.00E+09 1.00E+09 0.00E+00

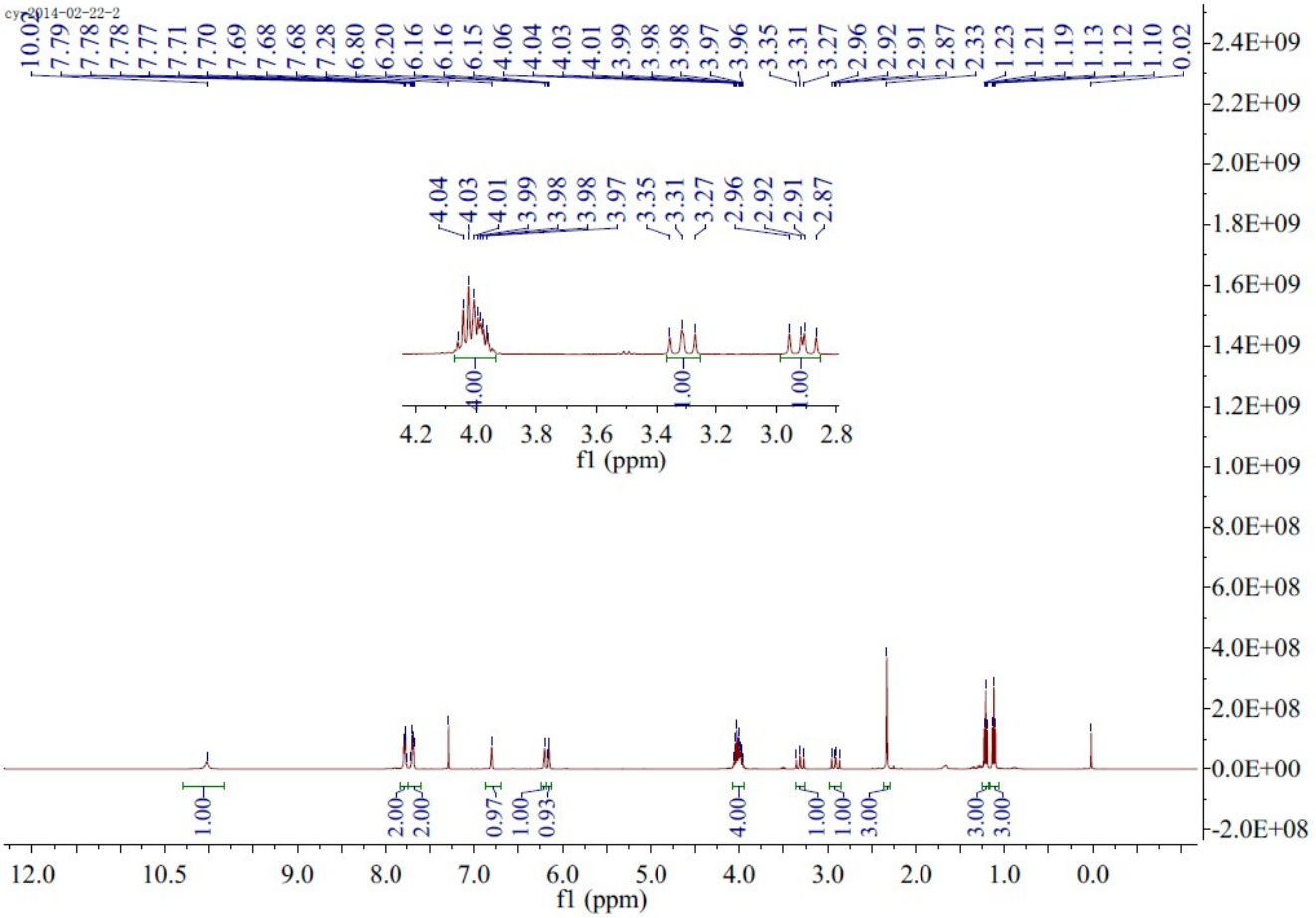
General procedure for the preparation of 6 and 4:

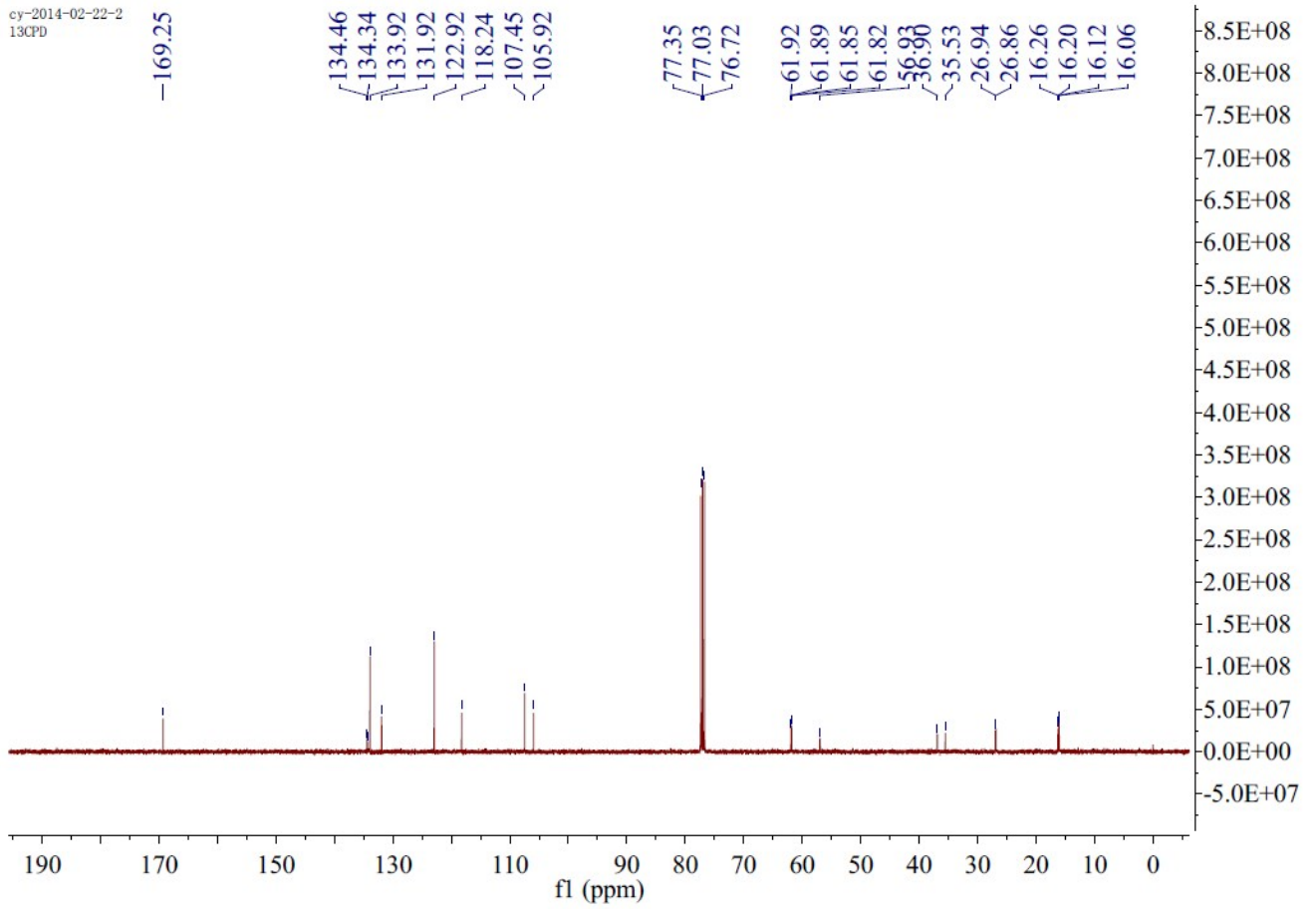
The 7.2 μL $BF_3{\cdot}Et_2O$ (0.056 mmol) and 28 mg pyrrole (0.42 mmol) in an oven-dried Schlenk tube was dissolved in 2 mL of freshly distilled CH_2Cl_2 under nitrogen. Dialkyl α-diazophosphonates **1** (0.28 mmol) was diluted with 2 mL of CH_2Cl_2 and was drawn into a gastight syringe. It was then 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 2 hour 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 (v:v)] to give the corresponding products **6** and **4**.

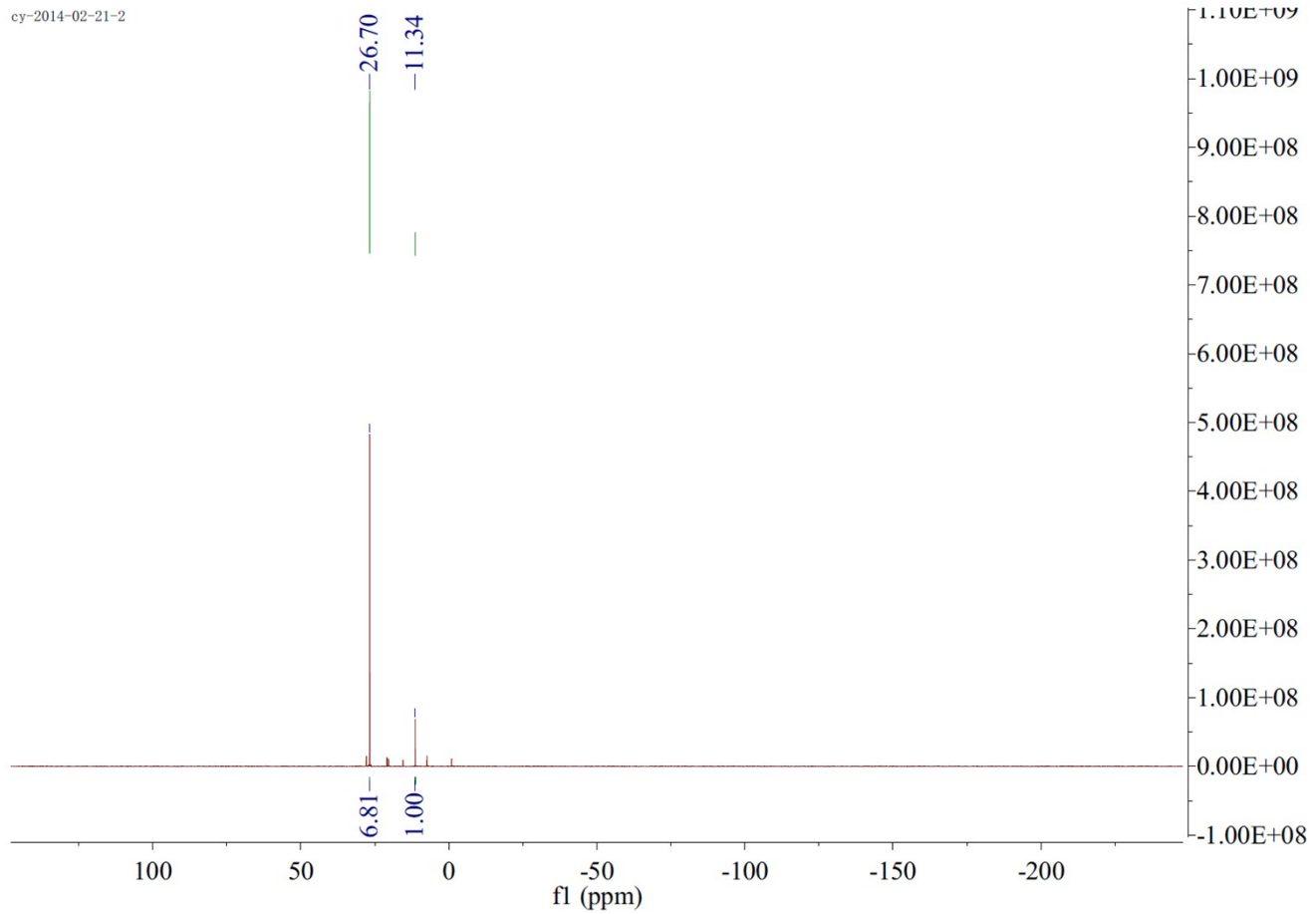
Diethyl (2-(1,3-dioxoisoindolin-2-yl)-2-(1H-pyrrol-2-yl)propyl)phosphonate (6a):



White solid; mp: 111-112 ^oC; ^1H NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 1H, N-H), 7.74-7.87 (m, 2H, Ph), 7.64-7.72 (m, 2H, Ph), 6.80 (s, 1H, =CH), 6.20 (s, 1H, =CH), 6.11-6.19 (m, 1H, =CH), 3.92-4.11 (m, 4H, $2OCH_2$), 3.21-3.44 (m, 1H, CH_2P), 2.91 (dd, J = 19.9, 15.6 Hz, 1H, CH_2P), 2.33 (s, 3H, CH_3), 1.21 (t, J = 7.1 Hz, 3H, CH_3), 1.12 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.25 (s, C=O), 134.40 (d, J = 11.4 Hz, =C), 133.92, 131.92, 122.92 (s, Ph), 118.24, 107.45, 105.92 (s, =CH), 61.90 (d, J = 2.9 Hz, OCH_2), 61.84 (d, J = 2.9 Hz, OCH_2), 56.95 (d, J = 4.6 Hz, N-C), 36.21 (d, J = 137.8 Hz, CH_2P), 26.90 (d, J = 7.8 Hz, CH_3), 16.23 (d, J = 6.3 Hz, CH_3), 16.09 (d, J = 6.3 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.74 (s); ESI-HRMS calcd for $[C_{19}H_{23}N_2O_5P, M + Na]^+$: 413.1237, Found : 413.1229.

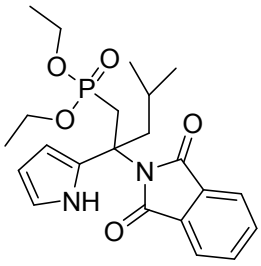

cy-2014-02-22-2
10.02
7.79
7.78
7.78
7.77
7.71
7.70
7.69
7.68
7.68
7.28
6.80
6.20
6.16
6.16
6.15
4.06
4.04
4.03
4.01
3.99
3.98
3.98
3.97
3.96
3.35
3.31
3.27
2.96
2.92
2.91
2.87
2.33
1.23
1.21
1.19
1.13
1.12
1.10
0.02
4.04
4.03
4.01
3.99
3.98
3.98
3.97
3.35
3.31
3.27
2.96
2.92
2.91
2.87
4.00
1.00
1.00
4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8
f1 (ppm)
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
-2.0E+08
1.00
2.00
2.00
0.97
1.00
0.93
4.00
1.00
1.00
3.00
3.00
3.00
12.0 10.5 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)


cy-2014-02-22-2
13CPD
169.25
134.46
134.34
133.92
131.92
122.92
118.24
107.45
105.92
77.35
77.03
76.72
61.92
61.89
61.85
61.82
56.93
56.90
35.53
26.94
26.86
16.26
16.20
16.12
16.06
8.5E+08
8.0E+08
7.5E+08
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

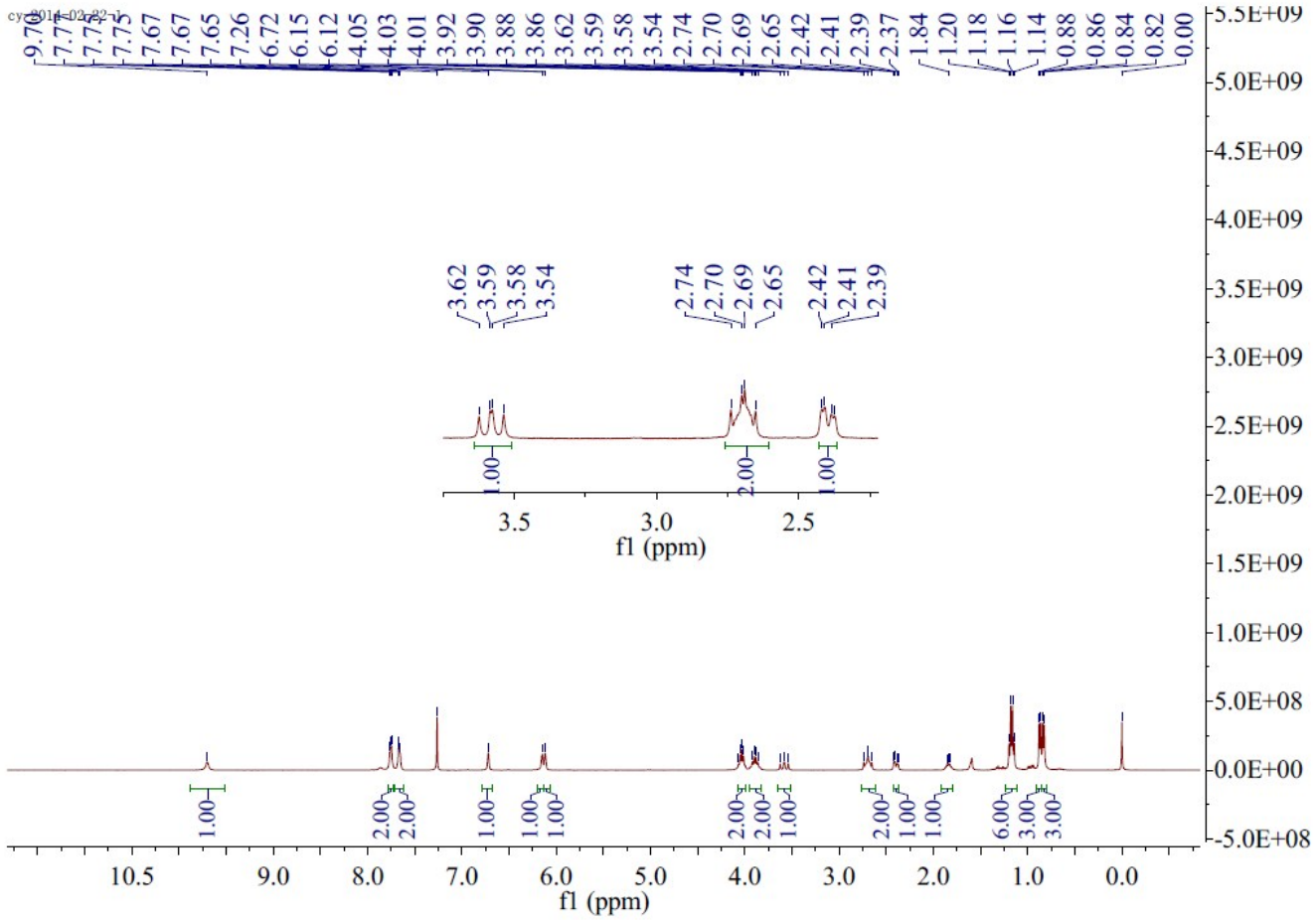


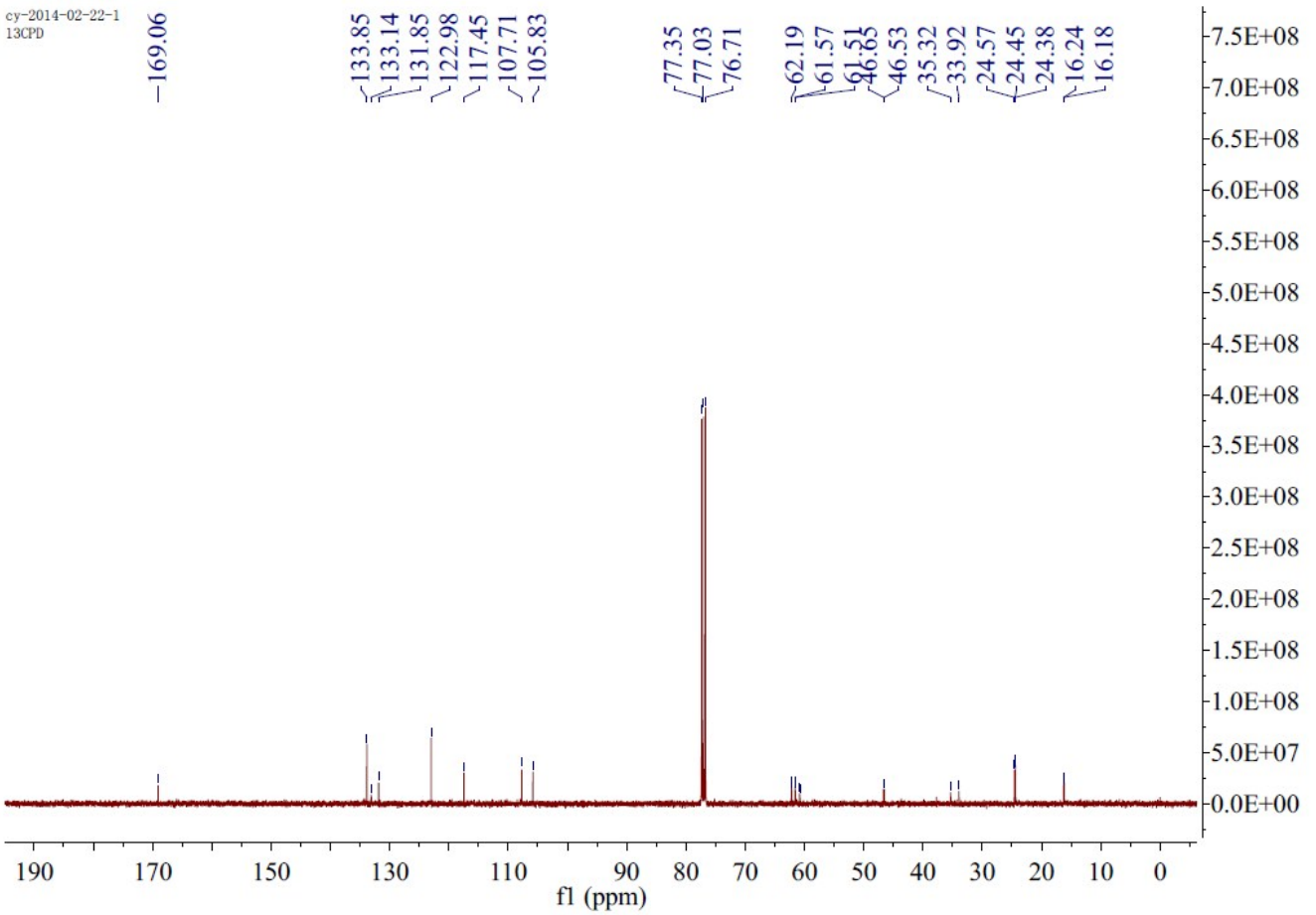
The mole ratio of **6a** and **4a** determined by crude ^{31}P NMR

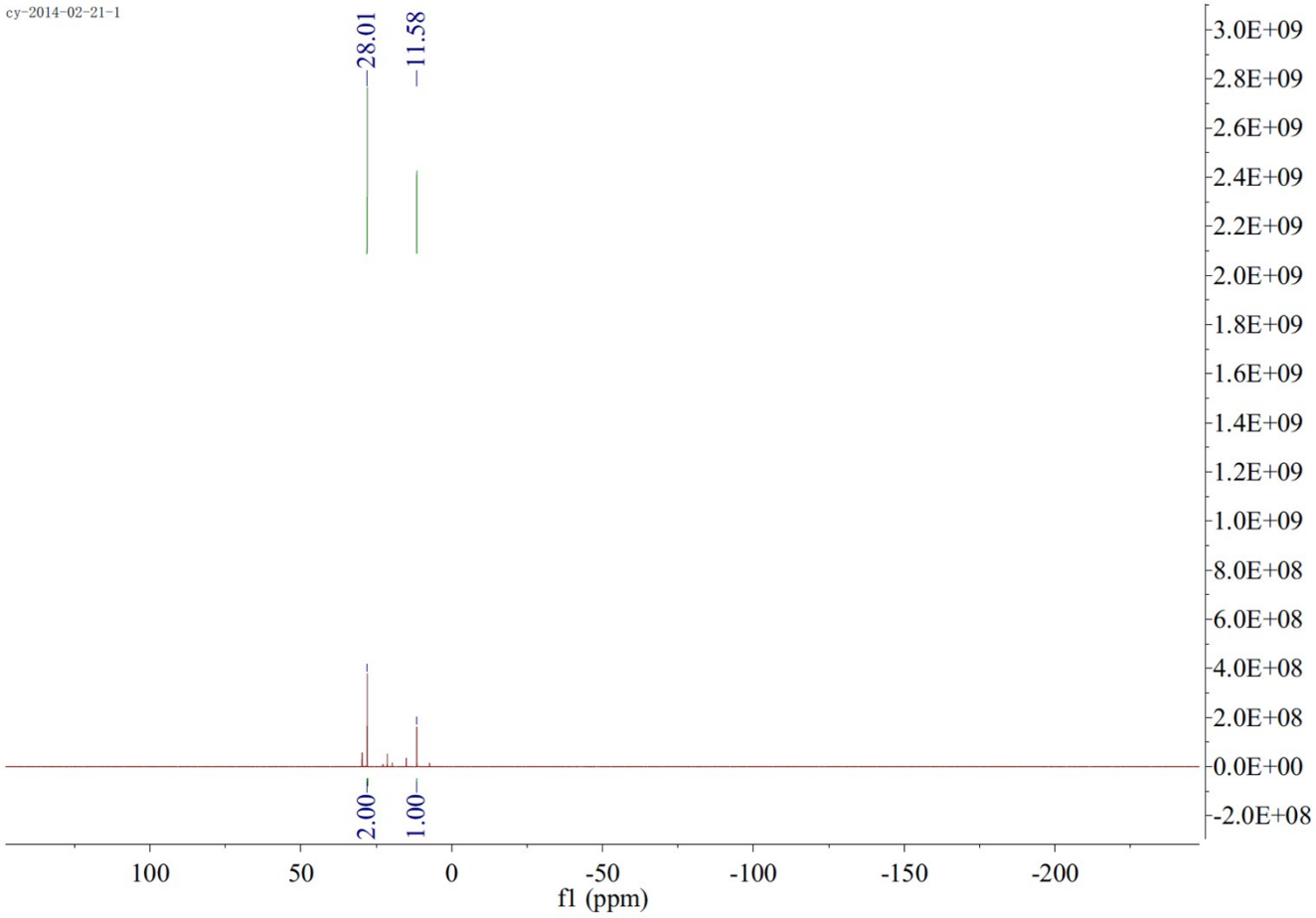
Diethyl (2-(1,3-dioxoisoindolin-2-yl)-4-methyl-2-(1H-pyrrol-2-yl)pentyl)phosphonate (6b):



White solid; mp: 119-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.70 (s, 1H, N-H), 7.73-7.83 (m, 2H, Ph), 7.63-7.69 (m, 2H, Ph), 6.72 (s, 1H, =CH), 6.15 (s, 1H, =CH), 6.12 (s, 1H, =CH), 3.99-4.10 (m, 2H, OCH_2), 3.83-3.95 (m, 2H, OCH_2), 3.58 (dd, *J* = 18.8, 15.7 Hz, 1H, CH_2P), 2.61-2.78 (m, 2H, CH_2, CH_2P), 2.40 (dd, *J* = 13.5, 4.3 Hz, 1H, CH_2), 1.78-1.93 (m, 1H, CH), 1.17 (dd, *J* = 15.1, 7.3 Hz, 6H, $2CH_3$), 0.87 (d, *J* =6.6 Hz, 3H, CH_3), 0.83 (d, *J* =6.6 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.06 (s, C=O), 133.85 (s, Ph), 133.14 (s, =C), 131.85, 122.98 (s, Ph), 117.45, 107.71, 105.83 (s, =CH), 62.16 (d, *J* = 6.7 Hz, OCH_2), 61.54 (d, *J* = 6.7 Hz, OCH_2), 60.77 (d, *J* = 4.9 Hz, N-C), 46.59 (d, *J* = 11.3 Hz, CH_2), 34.62 (d, *J* = 141.1 Hz, CH_2P), 24.57 (s, CH), 24.45 (s, CH_3), 24.38 (s, CH_3), 16.21 (d, *J* = 6.1 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.16 (s); ESI-HRMS calcd for $[C_{22}H_{29}N_2O_5P, M + Na]^+$: 455.1706, Found : 455.1714.

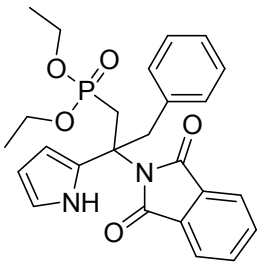

9.70
7.77
7.75
7.67
7.65
7.26
6.72
6.15
6.12
4.05
4.03
4.01
3.92
3.90
3.88
3.86
3.62
3.59
3.58
3.54
2.74
2.70
2.69
2.65
2.42
2.41
2.39
2.37
1.84
1.20
1.18
1.16
1.14
0.88
0.86
0.84
0.82
0.00
1.00
2.00
2.00
1.00
1.00
1.00
2.00
2.00
1.00
2.00
1.00
1.00
6.00
3.00
3.00
f1 (ppm)


cy-2014-02-22-1
13CPD
169.06
133.85
133.14
131.85
122.98
117.45
107.71
105.83
77.35
77.03
76.71
62.19
61.57
61.51
46.85
46.53
35.32
33.92
24.57
24.45
24.38
16.24
16.18
f1 (ppm)

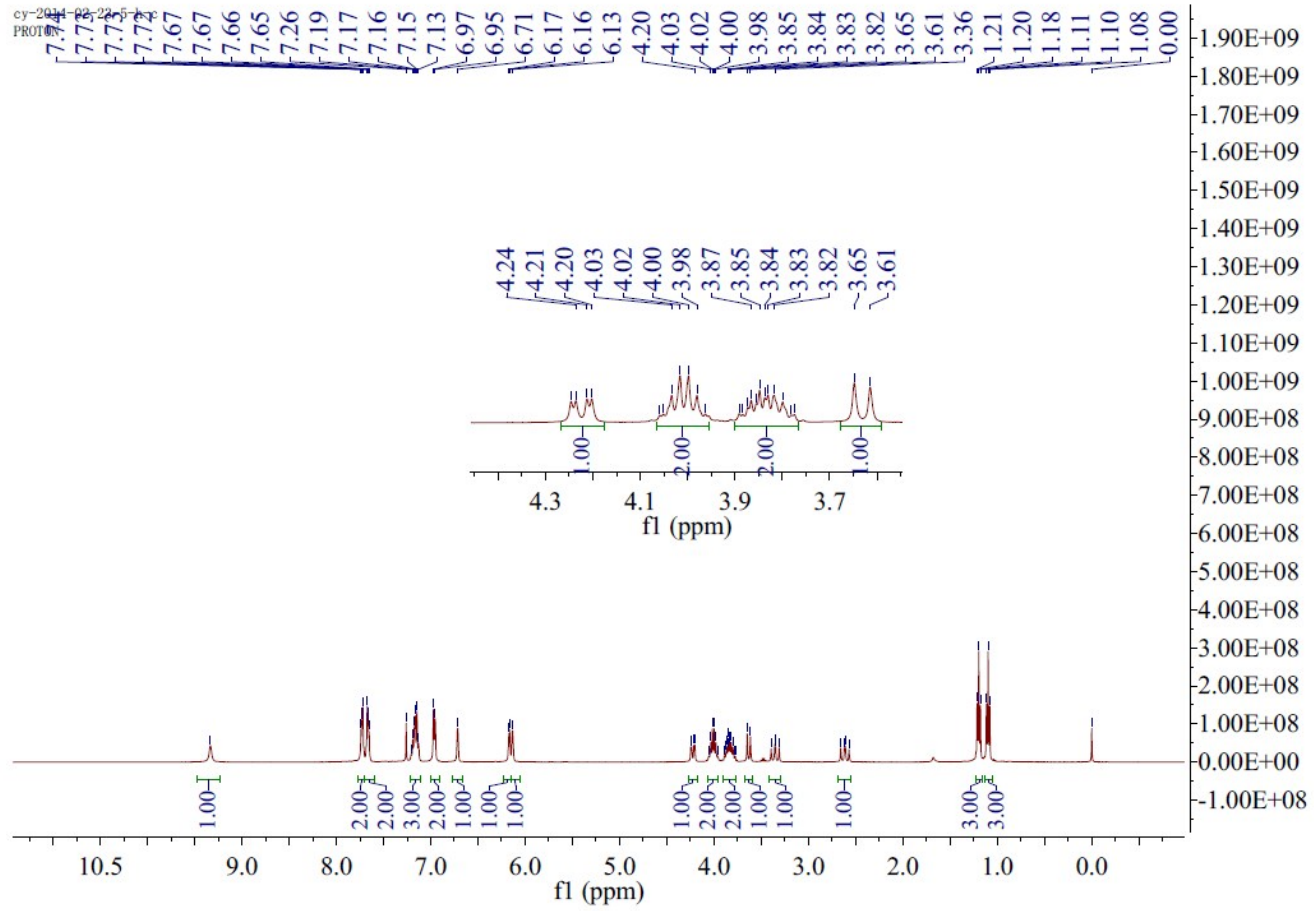


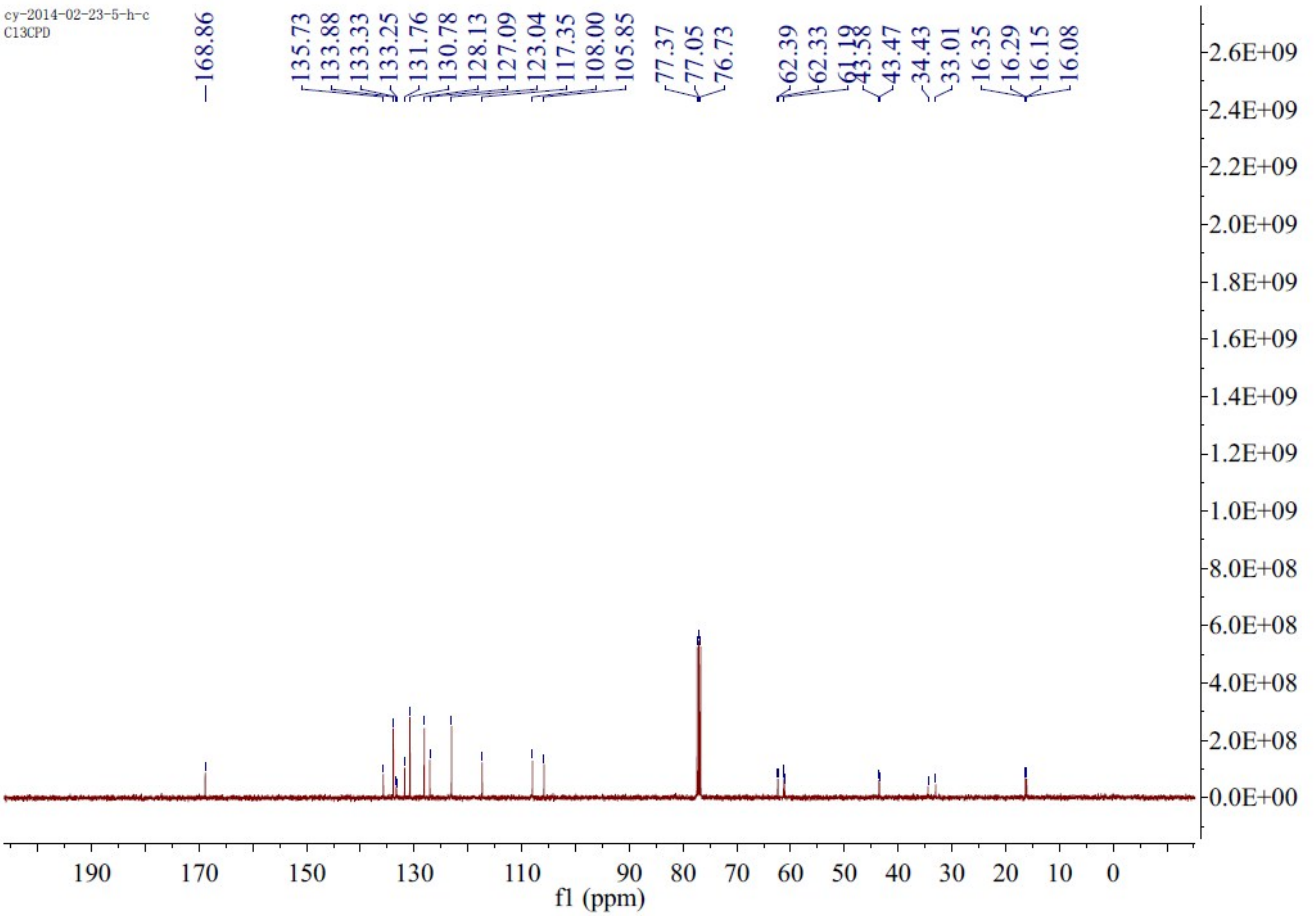
The mole ratio of **6b** and **4b** determined by crude ^{31}P NMR

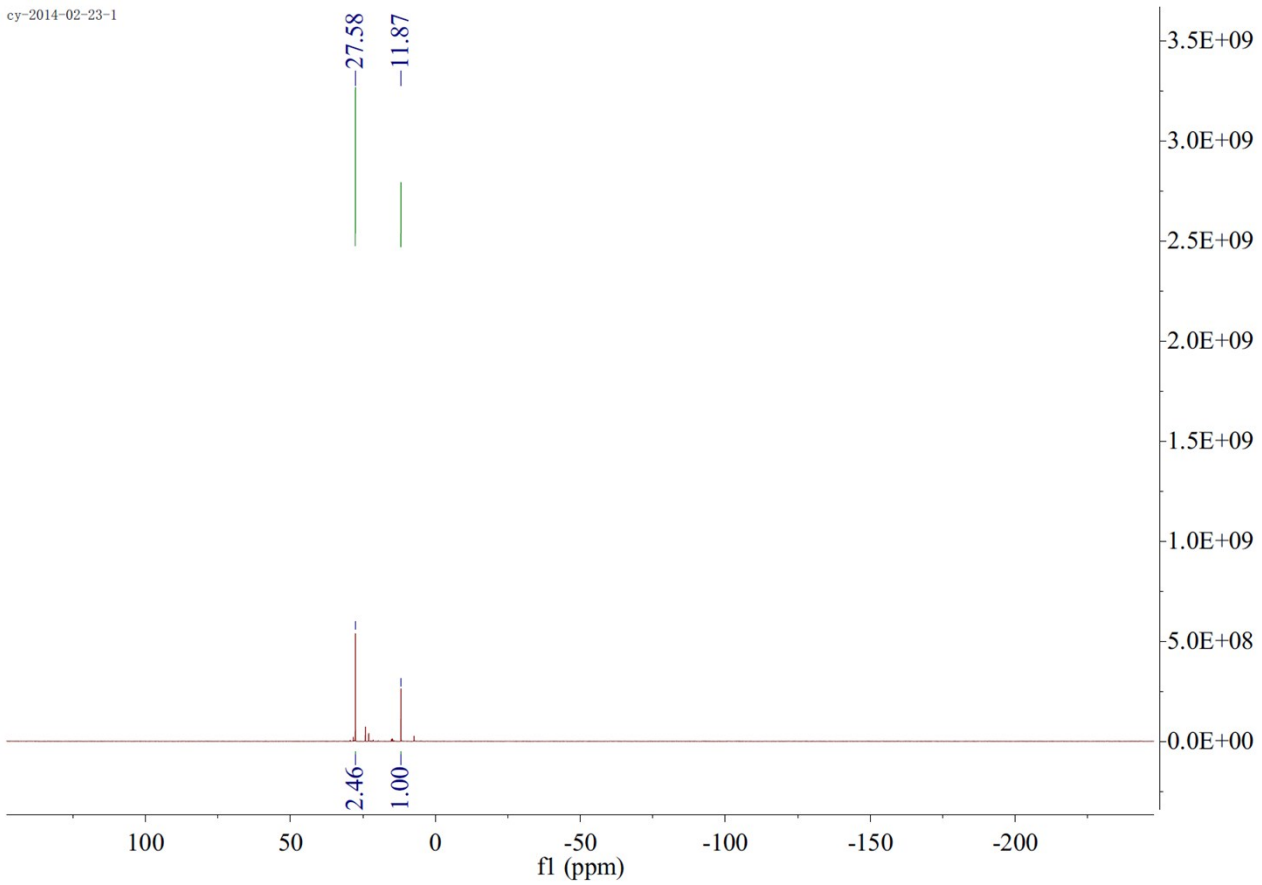
Diethyl (2-(1,3-dioxoisoindolin-2-yl)-3-phenyl-2-(1H-pyrrol-2-yl)propyl)phosphonate (6c):



White solid; mp: 152-154 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.33 (s, 1H, N-H), 7.70-7.77 (m, 2H, Ph), 7.64-7.70 (m, 2H, Ph), 7.11-7.23 (m, 3H, Ph), 6.96 (d, *J* = 6.9 Hz, 2H, Ph), 6.71 (s, 1H, =CH), 6.17 (d, *J* = 2.7 Hz, 1H, =CH), 6.13 (s, 1H, =CH), 4.22 (dd, *J* = 13.4, 4.0 Hz, 1H, CH_2), 3.95-4.09 (m, 2H, OCH_2), 3.76-3.91 (m, 2H, OCH_2), 3.63 (d, *J* = 13.4 Hz, 1H, CH_2), 3.35 (dd, *J* = 19.4, 15.4 Hz, 1H, CH_2P), 2.61 (dd, *J* = 19.4, 15.4 Hz, 1H, CH_2P), 1.20 (t, *J* = 7.1 Hz, 3H, CH_3), 1.10 (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.86 (s, C=O), 135.73 (s, Ph), 133.88 (s, Ph), 133.29 (d, *J* = 9.0 Hz, =C), 131.76, 130.78, 128.13, 127.09, 123.04 (s, Ph), 117.35, 108.00, 105.85 (s, =CH), 62.36 (d, *J* = 6.4 Hz, OCH_2), 61.23 (d, *J* = 6.4 Hz, OCH_2), 61.13 (d, *J* = 4.2 Hz, N-C), 43.52 (d, *J* = 10.8 Hz, CH_2), 33.72 (d, *J* = 142.6 Hz, CH_2P), 16.32 (d, *J* = 6.1 Hz, CH_3), 16.12 (d, *J* = 6.1 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.81 (s); ESI-HRMS calcd for $[C_{25}H_{27}N_2O_5P, M + Na]^+$: 489.1550, Found : 489.1546.

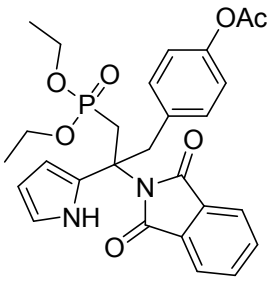

PROTON
7.77 7.75 7.74 7.67 7.67 7.66 7.65 7.26 7.19 7.17 7.16 7.15 7.13 6.97 6.95 6.71 6.17 6.16 6.13 4.20 4.03 4.02 4.00 3.98 3.85 3.84 3.83 3.82 3.65 3.61 3.36 1.21 1.20 1.18 1.11 1.10 1.08 0.00
4.24 4.21 4.20 4.03 4.02 4.00 3.98 3.87 3.85 3.84 3.83 3.82 3.65 3.61
1.00 2.00 2.00 1.00
4.3 4.1 3.9 3.7
f1 (ppm)
1.00 2.00 2.00 3.00 2.00 1.00 1.00 1.00 1.00 2.00 2.00 1.00 1.00 1.00 3.00 3.00
10.5 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)
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-2014-02-23-5-h-c
C13CPD
168.86
135.73 133.88 133.33 133.25 131.76 130.78 128.13 127.09 123.04 117.35 108.00 105.85
77.37 77.05 76.73
62.39 62.33 61.19 43.58 43.47 34.43 33.01 16.35 16.29 16.15 16.08
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
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

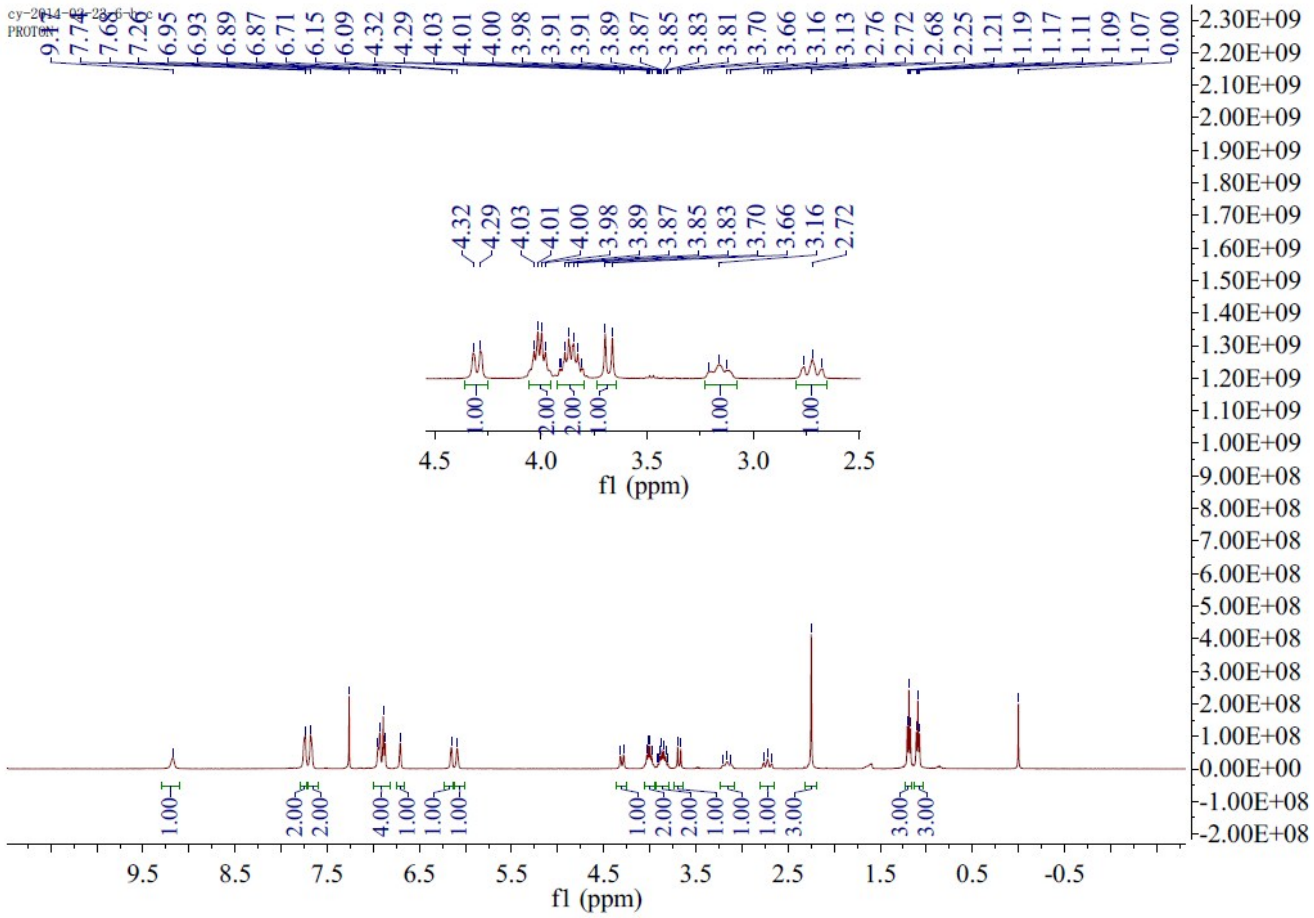


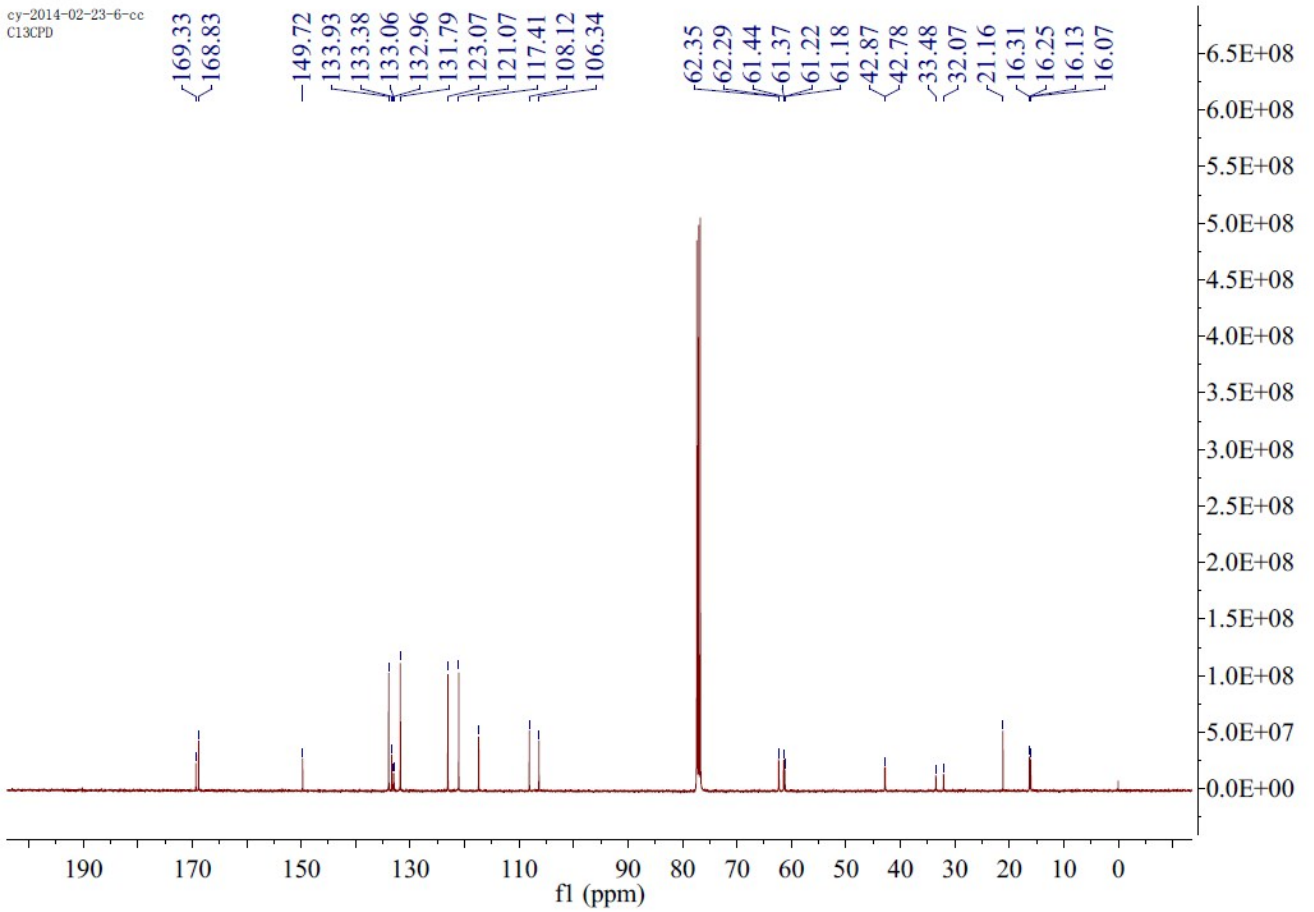
The mole ratio of **6c** and **4c** determined by crude ^{31}P NMR

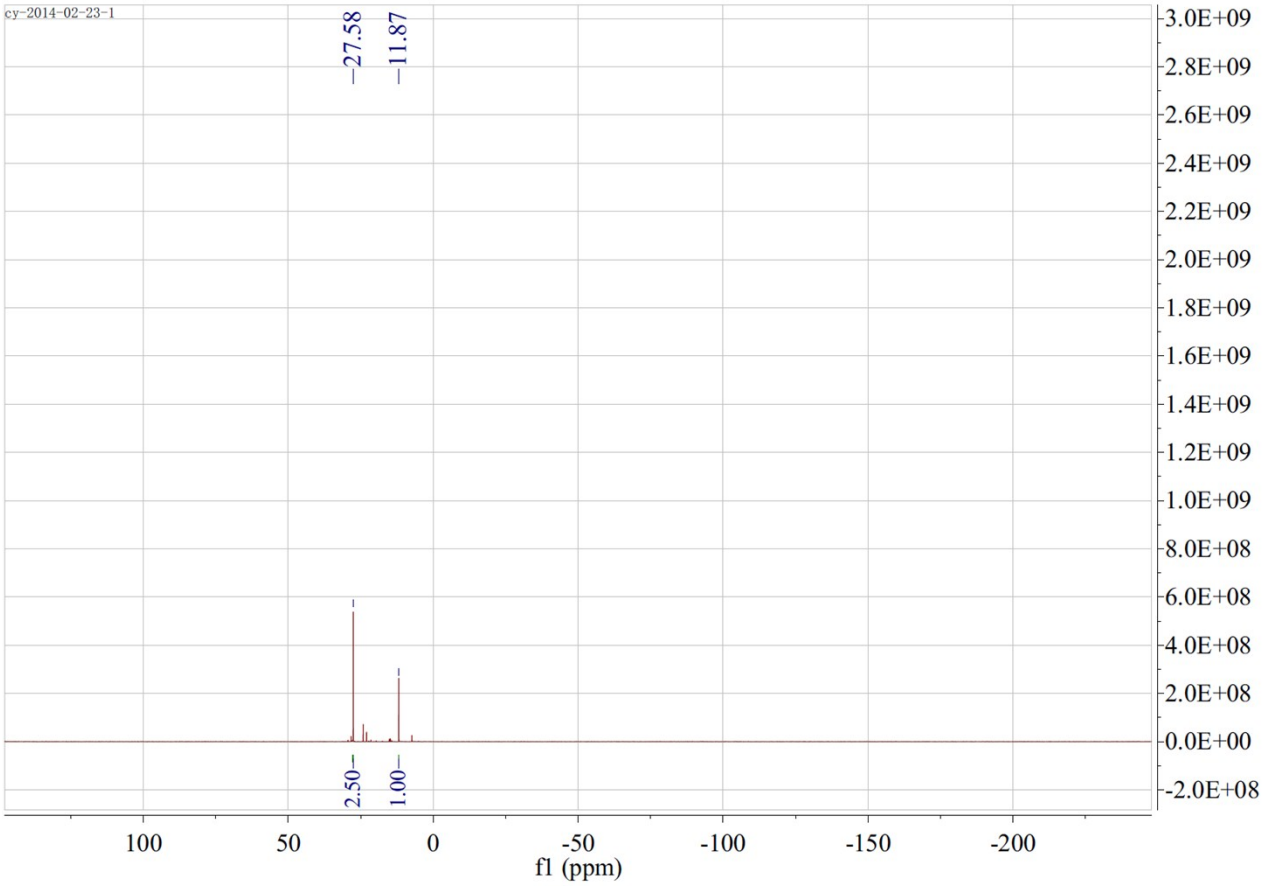
4-(3-(diethoxyphosphoryl)-2-(1,3-dioxoisoindolin-2-yl)-2-(1H-pyrrol-2-yl)propyl)phenyl acetate (6d):



White solid; mp: 153-154 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.17 (s, 1H, N-H), 7.72-7.80 (m, 2H, Ph), 7.63-7.70 (m, 2H, Ph), 6.83-6.99 (m, 4H, Ph), 6.71 (s, 1H, =CH), 6.15 (s, 1H, =CH), 6.09 (s, 1H, =CH), 4.30 (d, J = 13.5 Hz, 1H, CH_2), 3.95-4.09 (m, 2H, OCH_2), 3.79-3.93 (m, 2H, OCH_2), 3.68 (d, J = 13.5 Hz, 1H, CH_2), 3.17 (t, J = 16.9 Hz, 1H, CH_2P), 2.72 (t, J = 16.9 Hz, 1H, CH_2P), 2.25 (s, 3H, CH_3), 1.19 (t, J = 7.1 Hz, 3H, CH_3), 1.09 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.33, 168.83 (s, C=O), 149.72, 133.93, 133.38, 133.06 (s, Ph), 132.96 (s, =C), 131.79, 123.07, 121.07 (s, Ph), 117.41, 108.12, 106.34 (s, =CH), 62.32 (d, J = 6.6 Hz, OCH_2), 61.40 (d, J = 6.6 Hz, OCH_2), 61.20 (d, J = 4.1 Hz, N-C), 42.82 (d, J = 9.0 Hz, CH_3), 32.78 (d, J = 142.4 Hz, CH_2P), 21.16 (s, CH_2), 16.28 (d, J = 6.3 Hz, CH_3), 16.10 (d, J = 6.3 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.34 (s); ESI-HRMS calcd for $[C_{27}H_{29}N_2O_7P, M + Na]^+$: 547.1605, Found : 547.1606.

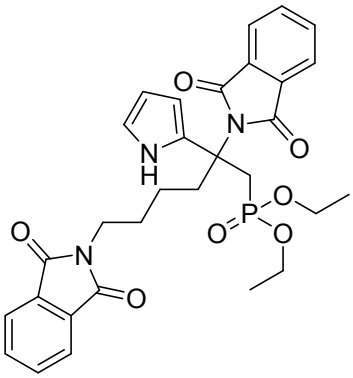

f1 (ppm)


cy-2014-02-23-6-cc
C13CPD
f1 (ppm)

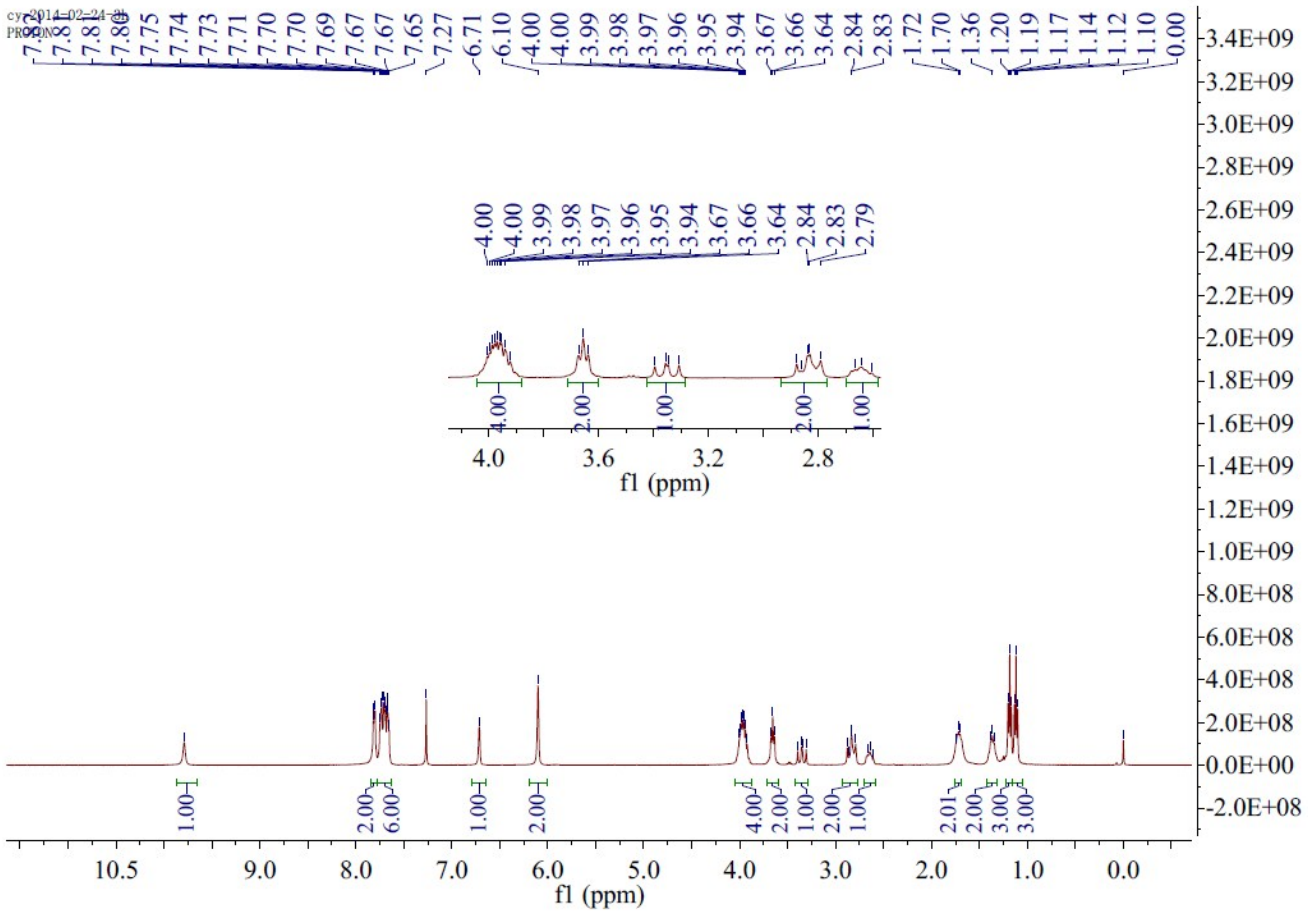


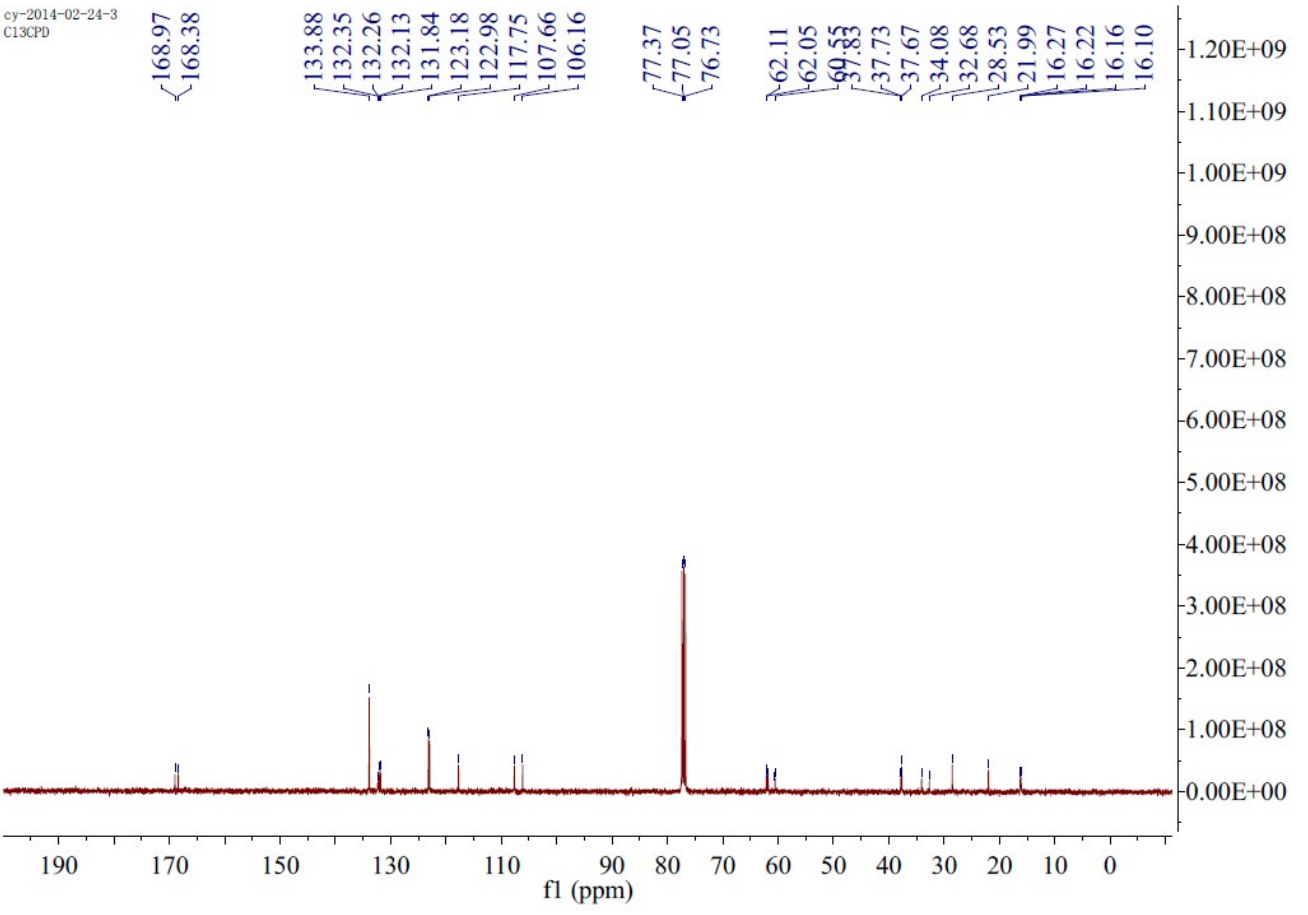
The mole ratio of **6d** and **4d'** determined by crude ^{31}P NMR

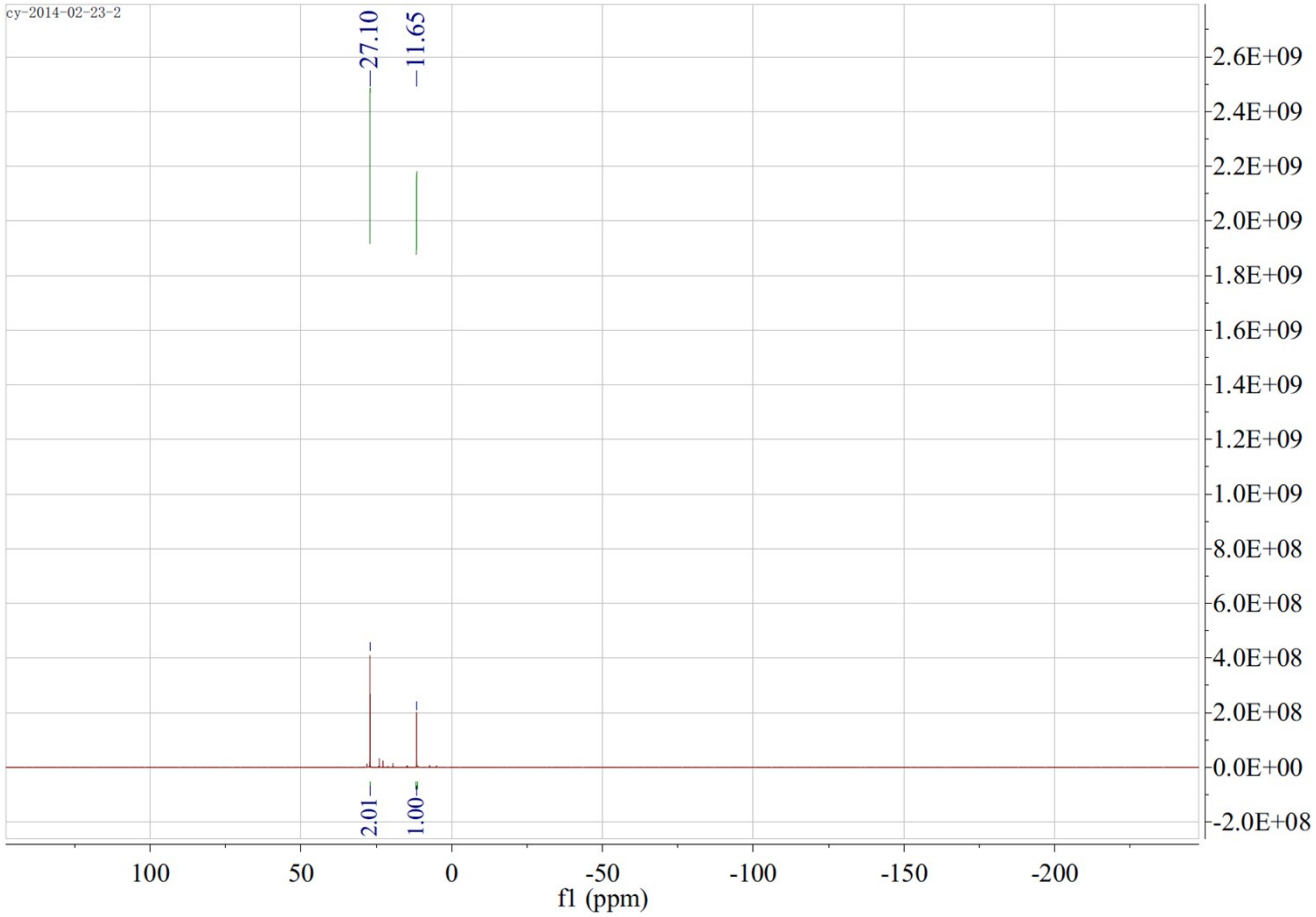
Diethyl (2,6-bis(1,3-dioxoisoindolin-2-yl)-2-(1H-pyrrol-2-yl)hexyl)phosphonate (6e):



White solid; mp: 101-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.79 (s, 1H, N-H), 7.78-7.87 (m, 2H, Ph), 7.62-7.77 (m, 6H, Ph), 6.71 (s, 1H, =CH), 6.10 (s, 2H, =CH), 3.84-4.10 (m, 4H, $2OCH_2$), 3.65 (t, J = 7.0 Hz, 2H, CH_2), 3.35 (dd, J = 19.5, 15.7 Hz, 1H, CH_2P), 2.75-2.97 (m, 2H, CH_2, CH_2P), 2.64 (m, 1H, CH_2), 1.66-1.80 (m, 2H, CH_2), 1.33-1.44 (m, 2H, CH_2), 1.19 (t, J = 7.0, 3H, CH_3), 1.12 (t, J = 7.0, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.97, 168.38 (s, C=O), 133.88 (s, Ph), 132.30 (d, J = 9.5 Hz, =C), 132.13, 131.84, 123.18, 122.98 (s, Ph), 117.75, 107.66, 106.16 (s, =CH), 62.08 (d, J = 6.4 Hz, OCH_2), 61.82 (d, J = 6.4 Hz, OCH_2), 60.56 (d, J = 3.9 Hz, N-C), 37.78 (d, J = 10.1 Hz, CH_2), 37.67 (s, CH_2), 33.38 (d, J = 140.8 Hz, CH_2P), 28.53 (s, CH_2), 21.99 (s, CH_2), 16.25 (d, J = 6.2 Hz, CH_3), 16.13 (d, J = 6.2 Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.77 (s); ESI-HRMS calcd for $[C_{30}H_{32}N_3O_7P, M + Na]^+$: 600.1870, Found: 600.1865.


f1 (ppm)

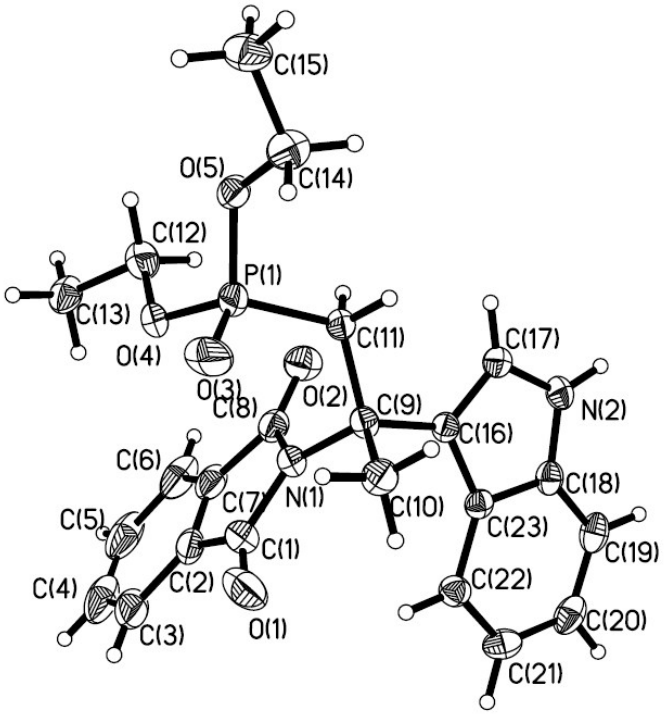

cy-2014-02-24-3
C13CPD
f1 (ppm)



The mole ratio of **6e** and **4e'** determined by crude ^{31}P NMR

X-ray crystal structure of 3a and 6a:

Single Crystal X-Ray Analysis **3a** (CCDC 982309) and 6a (CCDC 992526) 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.

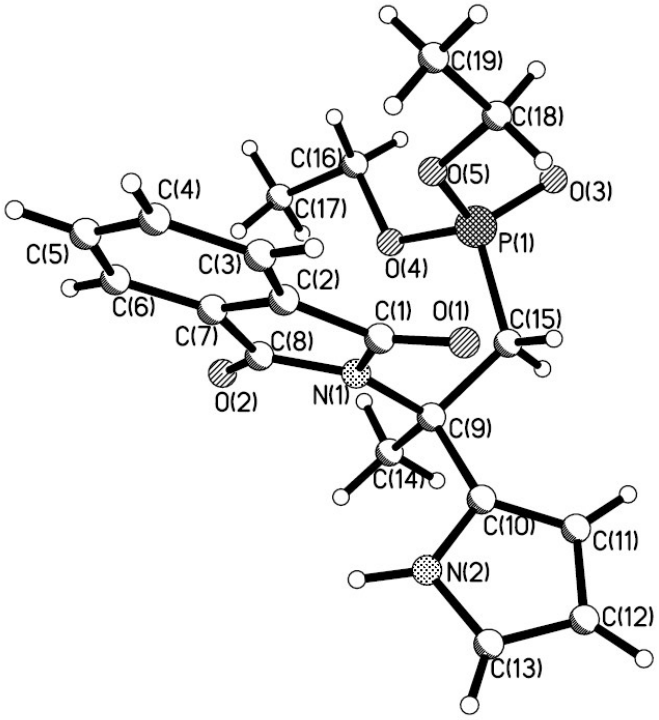


X-ray crystal structure of **3a**

Table 1. Crystal data and structure refinement for R140114A1.

Identification code	R140114A1
Empirical formula	$C_{23}H_{25}N_2O_5P$
Formula weight	440.42
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 14.067(3) A α = 90°
	b = 17.217(3) A β = 90°

	c = 18.001(4) A γ = 90°
Volume	4359.7(15) A^3
Z, Calculated density	8, 1.342 Mg/m^3
Absorption coefficient	0.164 mm^-1
F(000)	1856
Crystal size	0.20 x 0.18 x 0.12 mm
Theta range for data collection	2.19 to 25.02°
Limiting indices	-16 <= h <= 16, -20 <= k <= 20, -21<= l <= 21
Reflections collected / unique	33067/3797 [R(int) = 0.1935]
Completeness to theta = 25.01	98.7%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9806 and 0.9680
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3797/103/312
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0992, wR2 = 0.2308
R indices (all data)	R1 = 0.1314, wR2 = 0.2509
Extinction coefficient	0.0096(15)
Largest diff. peak and hole	0.301 and -0.416 e.A^-3



X-ray crystal structure of **6a**

Table 1. Crystal data and structure refinement for SA.

Identification code	sa
Empirical formula	$C_{19}H_{23}N_2O_5P$
Formula weight	390.36
Temperature	113(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 12.744(3) A α = 90°
	b = 7.7256(15) A β = 109.09(3)°
	c = 20.770(4) A γ = 90°
Volume	1932.4(7) A^3
Z, Calculated density	4, 1.342 Mg/m^3
Absorption coefficient	0.175 mm^-1
F(000)	824

Crystal size	0.20 x 0.18 x 0.12 mm
Theta range for data collection	1.69 to 28.04°
Limiting indices	-16 <= h <= 16, -10 <= k <= 10, -16<= l <= 27
Reflections collected / unique	4619/4619 [R(int) = 0.0000]
Completeness to theta = 25.01	98.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9793 and 0.9659
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4619/0/254
Goodness-of-fit on F^2	1.878
Final R indices [I>2sigma(I)]	R1 = 0.1972, wR2 = 0.5345
R indices (all data)	R1 = 0.2171, wR2 = 0.5409
Extinction coefficient	0.0000(10)
Largest diff. peak and hole	1.148 and -1.073 e.A^-3