Electronic Supplementary Material (ESI) for ChemComm.

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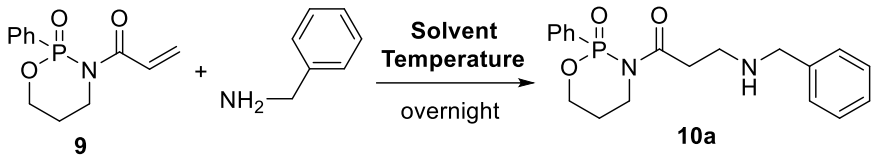
1) General information

Except where stated, all reagents were purchased from commercial sources and used without further purification. Anhydrous CH_2Cl_2 and THF were obtained from an Innovative Technology Inc. PureSolv® solvent purification system. ^{1}H NMR, ^{13}C NMR, and ^{31}P spectra were recorded on a JEOL ECX400 or JEOL ECS400 spectrometer (operating at 400 MHz and 100 MHz). All Spectroscopic data was acquired at 295 K unless stated otherwise. Chemical shifts (δ) are quoted in parts per million (ppm). The residual solvent peaks, δ_H 7.26 and δ_c 77.16 for $CDCl_3$ were used as a reference. Coupling constants (*J*) are reported in Hertz (Hz) to the nearest 0.1 Hz. The multiplicity abbreviations used are: br s broad singlet, s singlet, d doublet, br d broad doublet, t triplet, br t broad triplet, q quartet, p pentet, dd, doublet of doublets, ddd doublet of doublet of doublets, dddd doublet of doublet of doublet of doublets, dt doublet of triplets, ddt doublet of doublet of triplets, td triplet of doublets, m multiplet. Signal assignment was achieved by analysis of DEPT, COSY, HMBC and HSQC experiments where required. In cases where products were formed as a mixture of rotamers, their ratio was determined by integration of signals in the ^{1}H NMR spectrum. Infrared (IR) spectra were recorded on a PerkinElmer UATR 2 spectrometer as a thin film dispersed from either CH_2Cl_2 or $CDCl_3$. Mass spectra (high-resolution) were obtained by the University of York Mass Spectrometry Service, using Electrospray Ionisation (ESI) on a Bruker Daltonics, Micro-tof spectrometer. Melting points were determined using Gallenkamp apparatus. Thin layer chromatography was carried out on Merck silica gel $60F_{254}$ pre-coated aluminium foil sheets and were visualised using UV light (254 nm) and stained with basic aqueous potassium permanganate. Flash column chromatography was carried out using slurry packed Fluka silica gel (SiO_2), 35–70 µm, 60 Å, under a light positive pressure, eluting with the specified solvent system.

2) Optimisation tables

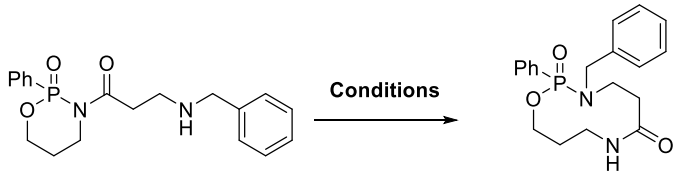
Table S1: Optimization of amine conjugate addition conditions



9 10a

Entry	Conditions	Yield of 10a
1	MeOH, RT	50%
2	THF, RT	81%
3	THF, NEt_3, RT	61%
4	DCM, DBU, RT	72%
5	MeOH, DBU, RT	40%
6	EtOAc, DBU, RT	70%
7	THF, DBU, RT	70%
8	THF, NEt_3, reflux	61%
9	$CHCl_3$, NEt_3, reflux	70%

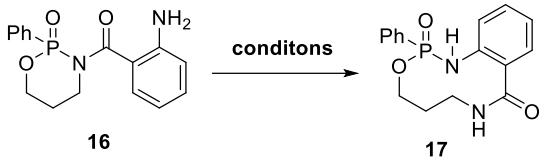
Table S2: Unsuccessful optimization of aliphatic amine ring expansion:



10a 11a

Entry	Conditions	Yield of 11a
1	NaH, THF, –78 °C, overnight	0%
2	NaH, THF, 0 °C, overnight	0%
3	*n*-BuLi, THF, –78 °C, overnight	0%
4	*n*-BuLi, THF, 0 °C, overnight	0%
5	NaH, THF, RT, 1 h	0%

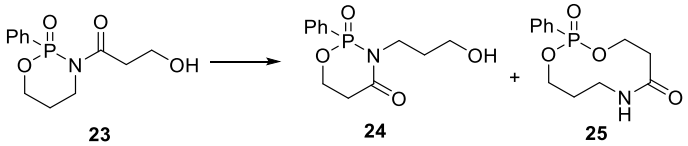
Table S3: Optimisation of the ring expansion conditions from 16 to 17



16 17

Entry	Conditions	Yield of **17**
1	NEt_3 in DCM, RT, overnight	0%
2	DBU in DCM, RT, overnight	0%
3	Pyridine as solvent, reflux, overnight	0%
4	NaH in THF, RT, 1 h	44%

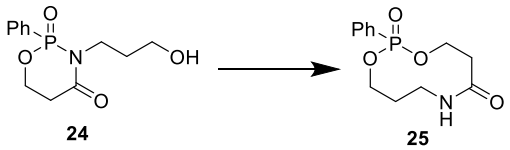
Table S4: Optimisation of the ring expansion conditions from 23 to 25



23 24 25

Entry	conditions	results
1	NMM, THF, RT, 16 h	80% **24**, 0% **25**
2	NEt_3, $CHCl_3$, RT, 16 h	90% **24**, 0% **25**
3	DBU, $CHCl_3$, RT, 16 h	0% **24**, 0% **25**
4	DIPEA, THF, RT, 48 h	60% **24**, 32% **25**
5	DIPEA, THF, reflux, 16 h	11% **24**, 22% **25**
6	DIPEA, $CHCl_3$, RT, 16 h	70% **24**, 20% **25**
7	TBAF, THF, RT, 16 h	87% **23**
8	NaH, THF, RT, 3 h	0% **24**, 68% **25**

Table S5: Optimisation of the ring expansion conditions from 24 to 25

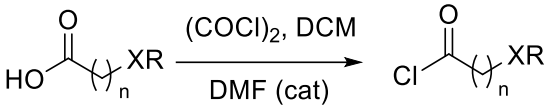


24 25

Entry	conditions	results
1	NEt_3, $CHCl_3$, RT, 16 h	0% **25**
3	DBU, $CHCl_3$, RT, 16 h	0% **25**
4	DIPEA, THF, RT, 16 h	0% **25**
8	NaH, THF, RT, 3 h	0% **25**

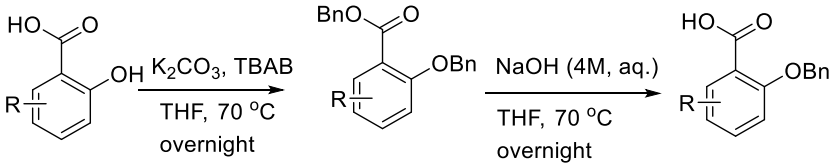
3) General procedures

General procedure for acid chloride formation:



Oxalyl chloride (3 mmol) was added to a suspension of carboxylic acid (1 mmol) in DCM (5 mL), followed by a catalytic amount of DMF (1 drop/mmol of carboxylic acid). The resulting mixture was stirred at RT for 1 h and concentrated *in vacuo* to remove all solvent and excess oxalyl chloride, affording the acid chloride, which was dried with a high vacuum for 1 h at RT before use.

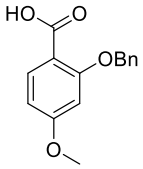
General procedure for OBn-protected carboxylic acids formation:



A mixture of the respective hydroxybenzoic acid (5.0 mmol), anhydrous K_2CO_3 (5.0 mmol), TBAB (10 mol %) and benzyl bromide (10 mmol), in anhydrous THF (25 mL) was stirred at reflux until TLC analysis showed the consumption of the starting materials. The reaction mixture was filtered to remove the solid. Then NaOH (4 M, aq., 5.0 mL, 20.0 mmol) was added to the filtrate and the resulting mixture was heated to reflux. After completion of reaction, the THF was evaporated. Then the crude material was diluted with H_2O (30 mL) and washed with DCM (30 mL). The PH of the aqueous layer was lowered to pH = 2 with 1 M HCl (aq.) and was subsequently extracted three times with DCM (20 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*, purification by flash column chromatography (SiO_2, ethyl acetate) afforded the target compound.[1,2]

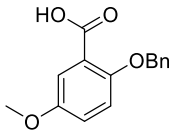
4) Experimental Procedures and spectroscopic data

2-(Benzyloxy)-4-methoxybenzoic acid (S1)



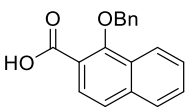
A mixture of the 4-methoxysalicyclic acid (841 mg, 5.0 mmol, 1 equiv), anhydrous K_2CO_3 (691 mg, 5.0 mmol, 1 equiv), TBAB (161.2 mg, 10 mol %) and benzyl bromide (1710 mg, 10.0 mmol, 2 equiv), in anhydrous THF (25 mL) was stirred at ambient temperature until TLC analysis showed the disappearance of the starting materials. The reaction mixture was filtered to remove the solid. NaOH (4 M, aq., 5.0 mL, 20.0 mmol) was added to the filtrate and the resulting mixture was heated to reflux. After completion of reaction, the THF was evaporated. Then the crude material was diluted with H_2O (30 mL) and washed with DCM (30 mL). The pH of the aqueous layer was lowered to pH = 2 with 1 M HCl (aq.) and was subsequently extracted three times with DCM (20 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*, purification by flash column chromatography (SiO_2, ethyl acetate) afforded the *title compound* as a white solid (1060 mg, 82%). m.p. 73 – 75 °C; R_f= 0.62 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3283, 2941, 1726, 1680, 1606, 1442, 1391, 1256, 1166, 1035, 835, 733, 696; δ_H (400 MHz, $CDCl_3$) 8.09 (d, *J* = 8.6 Hz, 1H, Ar-C**H**), 7.45 – 7.31 (m, 5H, Ar-C**H**), 6.62 – 6.57 (m, 2H, Ar-C**H**), 5.20 (s, 2H, OC**H₂**Ph), 3.82 (s, 3H, OC**H₃**); δ_C (100 MHz, $CDCl_3$) 165.9 (**C**O), 165.0 (Ar-**C**), 159.0 (Ar-**C**), 135.4 (Ar-**C**H), 134.5 (Ar-**C**), 129.1 (Ar-**C**H), 129.0 (Ar-**C**H), 127.8 (Ar-**C**H), 110.7 (Ar-**C**), 106.9 (Ar-**C**H), 99.9 (Ar-**C**H), 71.9 (O**C**H_2Ph), 55.7 (O**C**H_3); HRMS (ESI): calcd. for $C_{15}H_{14}NaO_4$, 281.0784. Found: $[MNa]^+$, 281.0785 (–0.2 ppm error). Spectroscopic data are in accordance with those reported in the literature.[3]

2-(Benzyloxy)-5-methoxybenzoic acid (S2)



A mixture of the 5-methoxysalicyclic acid (841 mg, 5.0 mmol, 1 equiv), anhydrous K_2CO_3 (691 mg, 5.0 mmol, 1 equiv), TBAB (161.2 mg, 0.50 mmol, 10 mol %) and benzyl bromide (1.71 g, 10 mmol, 2 equiv), in anhydrous THF (25 mL) was stirred at ambient temperature until TLC analysis showed the disappearance of the starting materials. The reaction mixture was filtered to remove the solid. NaOH (4 M, aq., 5.0 mL, 20.0 mmol) was added to the filtrate and the resulting mixture was heated to reflux. After completion of reaction, the THF was evaporated. Then the crude material was diluted with H_2O (30 mL) and washed with DCM (30 mL). The PH of the aqueous layer was lowered to pH = 2 with 1 M HCl (aq.) and was subsequently extracted three times with DCM (20 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*, purification by flash column chromatography (SiO_2, ethyl acetate) afforded the *title compound* as a white solid (1.08 g, 84%). m.p. 75 – 77 °C; R_f = 0.55 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3247, 1732, 1495, 1426, 1284, 1215, 1039, 814, 732, 697; δ_H (400 MHz, $CDCl_3$) 7.60 (s, 1H, Ar-C**H**), 7.44 – 7.24 (m, 5H, Ar-C**H**), 7.01 (s, 2H, Ar-C**H**), 5.19 (s, 2H, OC**H₂**Ph), 3.73 (s, 3H, OC**H₃**); δ_C (100 MHz, $CDCl_3$) 166.2 (br, **C**O), 154.4 (Ar-**C**), 151.5 (Ar-**C**), 141.0 (Ar-**C**), 134.9 (Ar-**C**), 129.0 (Ar-**C**H), 128.5 (Ar-**C**H), 127.9 (Ar-**C**H), 127.5 (Ar-**C**H), 127.0 (Ar-**C**H), 121.5 (br, Ar-**C**H), 116.2 (Ar-**C**H), 115.3 (br, Ar-**C**H), 72.9 (O**C**H₂Ph), 55.8 (O**C**H₃); HRMS (ESI): calcd. for $C_{15}H_{14}NaO_4$, 281.0784. Found: $[MNa]^+$, 281.0783 (0.4 ppm error). Spectroscopic data are in accordance with those reported in the literature.[4]

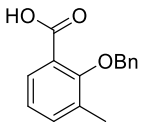
1-(Benzyloxy)-2-naphthoic acid (S3)



A mixture of the 1-hydroxyl-2-naphthoic acid (941mg, 5.0 mmol, 1 equiv), anhydrous K_2CO_3 (691 mg, 5.0 mmol, 1 equiv), TBAB (161.2 mg, 10 mol %) and benzyl bromide

(1.71 g, 10 mmol, 2 equiv), in anhydrous THF (25 mL) was stirred at ambient temperature until TLC analysis showed the disappearance of the starting materials. The reaction mixture was filtered to remove the solid. NaOH (4 M, aq., 5.2 mL, 20.8 mmol) was added to the filtrate and the resulting mixture was heated to reflux. After completion of reaction, the THF was evaporated. Then the crude material was diluted with H_2O (30 mL) and washed with DCM (30 mL). The PH of the aqueous layer was lowered to pH = 2 with 1 M HCl (aq.) and was subsequently extracted three times with DCM (20 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*, purification by flash column chromatography (SiO_2, ethyl acetate) afforded the *title compound* as a white solid (1.01 g, 73%). m.p. 100 – 102 °C; R_f = 0.60 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3065, 1686, 1624, 1467, 1363, 1335, 1289, 1247, 1083, 966, 768, 695; δ_H (400 MHz, $CDCl_3$) 10.87 (brs, 1H, COO**H**), 8.29 (d, *J* = 8.3 Hz, 1H, Ar-C**H**), 8.10 (d, *J* = 8.7 Hz, 1H, Ar-C**H**), 7.90 (d, *J* = 7.8 Hz, 1H, Ar-C**H**), 7.71 (d, *J* = 8.7 Hz, 1H, Ar-C**H**), 7.67 – 7.62 (m, 1H, Ar-C**H**), 7.62 – 7.55 (m, 3H, Ar-C**H**), 7.48 – 7.36 (m, 3H, Ar-C**H**), 5.25 (s, 2H, OC**H₂**Ph); δ_C (100 MHz, $CDCl_3$) 169.6 (**C**O), 157.2 (Ar-**C**), 137.5 (Ar-**C**), 136.0 (Ar-**C**), 129.0 (Ar-**C**H), 128.8 (Ar-**C**H), 128.8 (Ar-**C**H), 128.6 (Ar-**C**H), 128.2 (Ar-**C**H), 128.1 (Ar-**C**), 127.0 (Ar-**C**H), 127.0 (Ar-**C**H), 124.6 (Ar-**C**H), 123.6 (Ar-**C**H), 118.7 (Ar-**C**), 78.7 (O**C**H_2Ph); HRMS (ESI): calcd. for $C_{15}H_{14}NaO_4$, 301.0835. Found: [MNa]+, 301.0838 (–1.0 ppm error). Spectroscopic data are in accordance with those reported in the literature.[1]

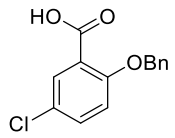
2-(Benzyloxy)-3-methylbenzoic acid (S4)



A mixture of the 3-methylsalicylic acid (761mg, 5.0 mmol, 1 equiv), anhydrous K_2CO_3 (691 mg, 5.0 mmol, 1 equiv), TBAB (161.2 mg, 10 mol %) and benzyl bromide (1710 mg, 10 mmol, 2 equiv), in anhydrous THF (25 mL) was stirred at ambient temperature until TLC analysis showed the disappearance of the starting materials. The reaction mixture was filtered to remove the solid. NaOH (4 M, aq., 5.0 mL, 20.0 mmol) was

added to the filtrate and the resulting mixture was heated to reflux. After completion of reaction, the THF was evaporated. Then the crude material was diluted with H_2O (30 mL) and washed with DCM (30 mL). The pH of the aqueous layer was lowered to pH = 2 with 1 M HCl (aq.) and was subsequently extracted three times with DCM (20 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*, purification by flash column chromatography (SiO_2, ethyl acetate) afforded the *title compound* as a white solid (717 mg, 60%). m.p. 65 – 67 °C; R_f= 0.65 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3039, 1692, 1592, 1466, 1303, 1220, 1088, 981, 765, 696; δ_H (400 MHz, $CDCl_3$) 11.57 (s, 1H, COO**H**), 7.95 (dd, *J* = 7.9, 1.8 Hz, 1H, Ar-C**H**), 7.54 – 7.33 (m, 6H, Ar-C**H**), 7.18 (t, *J* = 7.7 Hz, 1H, Ar-C**H**), 5.00 (s, 2H, OC**H₂**Ph), 2.39 (s, 3H, C**H₃**); δ_C (100 MHz, $CDCl_3$) 168.9 (**C**O), 157.0 (Ar-**C**), 136.8 (Ar-**C**H), 135.8 (Ar-**C**), 132.6 (Ar-**C**), 130.6 (Ar-**C**H), 128.8 (3 × Ar-**C**H), 128.7 (2 × Ar-**C**H), 124.7 (Ar-**C**H), 123.1 (Ar-**C**), 76.9 (O**C**H_2Ph), 16.4 (**C**H_3); HRMS (ESI): calcd. for $C_{15}H_{14}NaO_3$, 265.0835. Found: $[MNa]^+$, 265.0837 (–0.7 ppm error). Spectroscopic data are in accordance with those reported in the literature.[5]

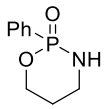
2-(Benzyloxy)-5-chlorobenzoic acid (S5)



A mixture of the 5-chlorosalicyclic acid (863 mg, 5.0 mmol, 1 equiv), anhydrous K_2CO_3 (691 mg, 5.0 mmol, 1 equiv), TBAB (161.2 mg, 10 mol %) and benzyl bromide (1710 mg, 10 mmol, 2 equiv), in anhydrous THF (25 mL) was stirred at ambient temperature until TLC analysis showed the disappearance of the starting materials. The reaction mixture was filtered to remove the solid. NaOH (4 M, aq., 5.0 mL, 20.0 mmol) was added to the filtrate and the resulting mixture was heated to reflux. After completion of reaction, the THF was evaporated. Then the crude material was diluted with H_2O (30 mL) and washed with DCM (30 mL). The pH of the aqueous layer was lowered to pH = 2 with 1 M HCl (aq.) and was subsequently extracted three times with DCM (20 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*,

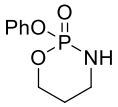
purification by flash column chromatography (SiO_2, ethyl acetate) afforded the *title compound* as a white solid (790 mg, 60%). m.p. 88 – 90 °C; R_f = 0.55 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3034, 1736, 1697, 1599, 1484, 1415, 1274, 1230, 1116, 986, 812, 736, 697; δ_H (400 MHz, $CDCl_3$) 8.10 (d, *J* = 2.8 Hz, 1H, Ar-C**H**), 7.47 (dd, *J* = 8.9, 2.8 Hz, 1H, Ar-C**H**), 7.44 – 7.34 (m, 5H, Ar-C**H**), 7.06 (d, *J* = 8.8 Hz, 1H, Ar-C**H**), 5.26 (s, 2H, OC**H₂**Ph); δ_C (100 MHz, $CDCl_3$) 165.2 (**C**O), 156.2 (Ar-**C**), 134.7 (Ar-**C**H), 134.3 (Ar-**C**), 133.2 (Ar-**C**H), 129.2 (Ar-**C**H), 129.2 (Ar-**C**H), 127.9 (Ar-**C**H), 127.5 (Ar-**C**), 119.6 (Ar-**C**), 114.9 (Ar-**C**H), 72.5 (O**C**H_2Ph); HRMS (ESI): calcd. for $C_{14}H_{11}{}^{35}ClNaO_3$, 285.0289. Found: $[MNa]^+$, 285.0283 (1.9 ppm error). Spectroscopic data are in accordance with those reported in the literature.[6]

2-Phenyl-1,3,2-oxazaphosphinane 2-oxide (8a)



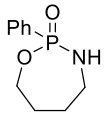
Phenylphosphinic dichloride (3.90 g, 20 mmol) in THF (90 mL) was added dropwise to a solution of 3-amino-1-propanol (1.80 mL, 22 mmol) and triethylamine (5.80 mL, 20 mmol) in THF (30 mL). The mixture was stirred at room temperature for 24 h. The solution was filtered to remove the $NEt_3{\cdot}HCl$ salts and the resulting filtrate was concentrated under reduced pressure to give a clear colorless oil. The crude product was purified by flash chromatography (9:1 ethyl acetate: methanol) to give the product as a thick, clear colorless oil (2.76 g, 70%); R_f 0.48 (ethanol); δ_H (400 MHz, $CDCl_3$) 7.84 – 7.69 (m, 2H, Ar-C**H**), 7.54 – 7.34 (m, 3H, Ar-C**H**), 4.45 – 4.33 (m, 1H, C**H₂**), 4.30 – 4.22 (m, 1H, N**H**), 4.11 – 3.99 (m, 1H, C**H₂**), 3.45 – 3.29 (m, 1H, C**H₂**), 3.20 – 3.03 (m, 1H, C**H₂**), 2.09 – 1.93 (m, 1H, C**H₂**), 1.71 – 1.57 (m, 1H, C**H₂**); δ_C (100 MHz, $CDCl_3$) 131.7 (d, *J* = 3.0 Hz, Ar-**C**H), 131.3 (d, *J* = 10.2 Hz, Ar-**C**H), 131.1 (d, *J* = 170.5 Hz, Ar-**C**), 128.6 (d, *J* = 14.4 Hz, Ar-**C**H), 67.8 (d, *J* = 6.8 Hz, O**C**H_2), 40.9 (d, *J* = 2.7 Hz, **C**H_2), 26.4 (d, *J* = 7.6 Hz, **C**H_2); δ_P (162 MHz, $CDCl_3$) 20.1 (Ph**P**=O); HRMS (ESI): calcd. for $C_9H_{12}NNaO_2P$, 220.0498. Found: $[MNa]^+$, 220.0499 (–0.5 ppm error). Spectroscopic data are in accordance with those reported in the literature.[7]

2-Phenoxy-1,3,2-oxazaphosphinane 2-oxide (8b)



A solution of phosphoric acid phenyl ester dichloride (1.1 g, 5.1 mmol) in DCM (5.0 mL) was added under stirring and cooling at 0 °C to a solution of 3-amino-1-propanol (0.38 g, 5.1 mmol) in 10 mL of DCM. After addition of a solution of triethylamine (1.4 mL, 10.2 mmol) in 10 mL DCM, the reaction mixture was stirred at RT for 1 h and washed with H_2O. The organic solution was dried over $MgSO_4$, the solvent evaporated, and the residue purified by flash chromatography (20:1 dichloromethane: methanol) to give the product as a colorless oil (960 mg, 90%); R_f 0.43 (10:1 dichloromethane: methanol); δ_H (400 MHz, $CDCl_3$) 7.33 – 7.18 (m, 4H, Ar-C**H**), 7.13 – 7.07 (m, 1H, Ar-C**H**), 4.44 – 4.34 (m, 2H, OC**H₂**), 4.32 – 4.24 (m, 1H, N**H**), 3.33 – 3.13 (m, 2H, C**H₂**), 2.08 – 1.91 (m, 1H, C**H**$_2$), 1.62 – 1.54 (m, 1H, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 150.9 (d, *J* = 7.1 Hz, Ar-**C**), 129.6 (Ar-**C**H), 124.5 (d, *J* = 0.7 Hz, Ar-**C**H), 112.0 (d, *J* = 5.0 Hz, Ar-**C**H), 70.0 (d, *J* = 7.6 Hz, O**C**H$_2$), 41.3 (d, *J* = 3.4 Hz, **C**H$_2$), 26.0 (d, *J* = 7.3 Hz, **C**H$_2$); δ_P (162 MHz, $CDCl_3$) – 0.3 (PhO**P**=O); HRMS (ESI): calcd. for $C_9H_{12}NNaO_3P$, 236.0447. Found: $[MNa]^+$, 236.0452 (–2.1 ppm error). Spectroscopic data are in accordance with those reported in the literature.[8]

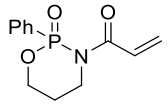
2-Phenyl-1,3,2-oxazaphosphepane 2-oxide (8c)



A solution of phenylphosphinic dichloride (0.995 g, 5.1 mmol) in DCM (5.0 mL) was added under stirring and cooling at 0 °C to a solution of 4-aminobutan-1-ol (0.45 g, 5.1 mmol) in 10 mL of DCM. After addition of a solution of triethylamine (1.40 mL, 10.2 mmol) in 10 mL DCM, the reaction mixture was stirred at RT for 1 h and washed with H_2O. The organic solution was dried over $MgSO_4$, the solvent evaporated, and the residue purified by flash chromatography (10:1 dichloromethane: methanol) to give the product as a colorless oil (350 mg, 33%); R_f 0.31 (10:1 dichloromethane: methanol); δ_H (400 MHz, $CDCl_3$) 7.85 – 7.72 (m, 2H, Ar-C**H**), 7.49 – 7.35 (m, 3H, Ar-C**H**), 4.53 (q, *J* =

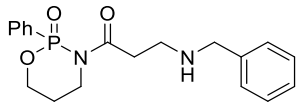
11.5 Hz, 1H, OC**H**$_2$), 4.20 – 4.08 (m, 1H, N**H**), 4.03 (q, *J* = 8.5 Hz, 1H, NHC**H**$_2$), 3.19 – 3.01 (m, 1H, OC**H**$_2$), 2.82 – 2.68 (m, 1H, NHC**H**$_2$), 1.91 – 1.52 (m, 4H, 2 × C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 131.5 (d, *J* = 2.9 Hz, Ar-**C**H), 131.5 (d, *J* = 182.5 Hz, Ar-**C**), 130.9 (d, *J* = 9.6 Hz, Ar-**C**H), 128.3 (d, *J* = 14.6 Hz, Ar-**C**H), 65.4 (d, *J* = 6.7 Hz, O**C**H$_2$), 41.1 (**C**H$_2$), 31.9 (**C**H$_2$), 30.0 (**C**H$_2$); δ_P (162 MHz, $CDCl_3$) 27.7 (Ph**P**=O); HRMS (ESI): calcd. for $C_{10}H_{14}NNaO_2P$, 234.0654. Found: $[MNa]^+$, 234.0656 (–0.6 ppm error).

1-(2-Oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)prop-2-en-1-one (9)



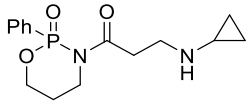
To a solution of 2-phenyl-1,3,2-oxazaphosphinane 2-oxide (2.09 g, 10.6 mmol) in dry THF (50 mL), was added acryl chloride (1.44 g, 15.9 mmol) in a single portion, then NEt_3 (1.61 g, 15.9 mmol) was added to the mixture. The reaction mixture was allowed to stir for 10 min a RT. The reaction mixture was then quenched with sat. aq. $NaHCO_3$ (100 mL) and the mixture was extracted with Et_2O (2 × 100 mL). The organic extracts dried over $MgSO_4$ and concentrated in vacuo. Purification by flash column chromatography (SiO_2, 1:1 hexane: ethyl acetate → ethyl acetate) afforded the title compound as a pale-brown oil (2.37 g, 89%); R_f 0.28 (ethyl acetate); δ_H (400 MHz, $CDCl_3$) 7.73 – 7.65 (m, 2H, Ar-C**H**), 7.59 – 7.51 (m, 1H, Ar-C**H**), 7.51 – 7.40 (m, 2H, Ar -C**H**), 7.06 (dd, *J* = 16.6, 10.3 Hz, 1H, C**H**=CHH'), 6.34 (dd, *J* = 16.6, 1.9 Hz, 1H, CH=C**H**H'), 5.63 (dd, *J* = 10.3, 1.9 Hz, 1H, CH=CH**H'**), 4.62 – 4.46 (m, 2H, 1H from OC**H**$_2$ + 1H from C**H**$_2$), 4.23 (dddd, *J* = 12.6, 10.9, 9.2, 5.3 Hz, 1H, OC**H**$_2$), 3.30 (ddt, *J* = 14.0, 11.0, 3.2 Hz, 1H, C**H**$_2$), 2.29 – 2.16 (m, 1H, C**H**$_2$), 2.07 – 1.95 (m, 1H, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 167.5 (d, *J* = 7.6 Hz, **C**O), 133.1 (d, *J* = 3.1 Hz, Ar-**C**H), 131.1 (d, *J* = 10.8 Hz, Ar-**C**H), 130.3 (CO**C**H=CH$_2$), 129.8 (COCH=**C**H$_2$), 129.1 (d, *J* = 174.8 Hz, Ar-**C**), 129.1 (d, *J* = 15.3 Hz, Ar-**C**H), 67.3 (d, *J* = 8.0 Hz, O**C**H$_2$), 41.3 (d, *J* = 1.0 Hz, **C**H$_2$), 25.8 (d, *J* = 6.1 Hz, **C**H$_2$); δ_P (162 MHz, $CDCl_3$) 15.9; HRMS (ESI): calcd. for $C_{12}H_{14}NNaO_3P$, 274.0604. Found: $[MNa]^+$, 274.0607 (–1.3 ppm error).

3-(Benzylamino)-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)propan-1-one (10a)



To a solution of 1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl) prop-2-en-1-one **9** (125.6 mg, 0.5 mmol) in dry THF (1.0 mL), was added benzylamine (64.3 mg, 0.6 mmol) in a single portion. The reaction mixture was allowed to stir overnight at RT. Purification by flash column chromatography (SiO_2, 10:1 dichloromethane: methanol) afforded the title compound as a colorless oil (145 mg, 81%); R_f 0.22 (10:1 dichloromethane: methanol); ν_{max}/cm^{-1} (thin film) 3480, 3324, 2923, 1677, 1439, 1254, 1130, 1022, 914, 747, 696, 540; δ_H (400 MHz, $CDCl_3$) 7.85 – 7.70 (m, 2H, Ar-C**H**), 7.62 – 7.52 (m, 1H, Ar-C**H**), 7.53 – 7.42 (m, 1H, Ar-C**H**), 7.34 – 7.11 (m, 5H, Ar-C**H**), 4.50 (m, 2H, OC**H**$_2$ + C**H**$_2$), 4.21 (dddd, *J* = 14.1, 11.0, 8.9, 5.4 Hz, 1H, OC**H**$_2$), 3.69 (s, 2H, NHC**H**$_2$Ph), 3.32 (ddd, *J* = 13.5, 8.3, 3.0 Hz, 1H, C**H**$_2$), 3.11 (dt, *J* = 16.2, 5.7 Hz, 1H, C**H**$_2$), 2.95 – 2.71 (m, 2H, C**H$_2$**), 2.58 (ddd, *J* = 16.5, 7.2, 5.6 Hz, 1H, C**H**$_2$), 2.20 (ddp, *J* = 14.7, 10.0, 5.2, 5.1 Hz, 1H, N**H**), 2.08 – 1.94 (m, 2H, C**H$_2$**); δ_C (100 MHz, $CDCl_3$) 174.3 (d, *J* = 7.9 Hz, **C**O), 140.1 (Ar-**C**), 133.0 (d, *J* = 3.1 Hz, Ar-**C**H), 131.2 (d, *J* = 10.7 Hz, Ar-**C**H), 129.1 (d, *J* = 176.7 Hz, Ar-**C**), 129.0 (d, *J* = 15.2 Hz, Ar-**C**H), 128.2 (Ar-**C**H), 128.0 (Ar-**C**H), 126.7 (Ar-**C**H), 66.8 (d, *J* = 8.0 Hz, O**C**H$_2$), 53.5 (NH**C**H$_2$Ph), 44.6 (**C**H$_2$), 41.1 (**C**H$_2$), 37.2 (**C**H$_2$), 25.7 (d, *J* = 6.0 Hz, **C**H$_2$); δ_P (162 MHz, $CDCl_3$) 15.8 (Ph**P**=O); HRMS (ESI): calcd. for $C_{19}H_{24}N_2O_3P$, 359.1519. Found: $[MH]^+$, 359.1526 (–2.1 ppm error).

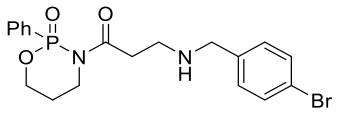
3-(Cyclopropylamino)-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)propan-1-one (10b)



To a solution of 1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)prop-2-en-1-one **9** (125.6 mg, 0.5 mmol) in dry THF (1.0 mL), was added cyclopropylamide (34.3 mg, 0.6 mmol) in a single portion. The reaction mixture was allowed to stir for overnight at RT.

Purification by flash column chromatography (SiO_2, 10: 1 dichloromethane: methanol) afforded the title compound as a colorless oil (73 mg, 47%); R_f 0.26 (9:1 dichloromethane: methanol); ν_{max}/cm^{-1} (thin film) 3478, 2929, 1677, 1439, 1365, 1253, 1130, 1017, 914, 749, 695, 540; δ_H (400 MHz, $CDCl_3$) 7.78 – 7.66 (m, 2H, Ar-C**H**), 7.58 – 7.50 (m, 1H, Ar-C**H**), 7.48 – 7.42 (m, 1H, Ar-C**H**), 4.55 – 4.39 (m, 2H, OC$\mathbf{H}_2$ + C$\mathbf{H}_2$), 4.19 (dddd, *J* = 14.2, 11.0, 8.8, 5.5 Hz, 1H, OC$\mathbf{H}_2$), 3.30 (tq, *J* = 10.6, 3.2 Hz, 1H, C$\mathbf{H}_2$), 3.04 (dt, *J* = 16.3, 6.0 Hz, 1H, C$\mathbf{H}_2$), 2.87 – 2.81 (m, 2H, C$\mathbf{H_2}$), 2.48 (dt, *J* = 16.5, 6.4 Hz, 1H, C$\mathbf{H}_2$), 2.19 – 1.99 (m, 3H, N**H** + C$\mathbf{H_2}$), 1.94 (tt, *J* = 6.6, 3.6 Hz, 1H, NC**H**), 0.31 – 0.15 (m, 4H, 2 × C$\mathbf{H_2}$); δ_C (100 MHz, $CDCl_3$) 174.4 (d, *J* = 7.8 Hz, **C**O), 133.1 (d, *J* = 3.0 Hz, Ar-**C**H), 131.3 (d, *J* = 10.8 Hz, Ar-**C**H), 129.1 (d, *J* = 176.0 Hz, Ar-**C**), 129.0 (d, *J* = 15.2 Hz, Ar-**C**H), 66.8 (d, *J* = 7.9 Hz, **C**H_2), 44.8 (**C**H_2), 41.1 (**C**H_2), 37.0 (**C**H_2), 29.8 (N**C**H), 25.8 (d, *J* = 6.1 Hz, **C**H_2), 6.1 (**C**H_2), 6.1 (**C**H_2); δ_P (162 MHz, $CDCl_3$) 15.7 (Ph**P**=O); HRMS (ESI): calcd. for $C_{15}H_{22}N_2O_3P$, 309.1363. Found: $[MH]^+$, 309.1365 (–0.8 ppm error).

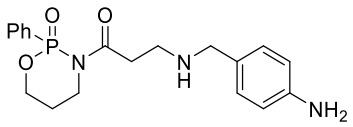
3-((4-Bromobenzyl)amino)-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)propan-1-one (10c)



To a solution of 1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl) prop-2-en-1-one **9** (125.6 mg, 0.5 mmol) in dry THF (1.0 mL), was added 4-bromobenzylamine (111.6 mg, 0.6 mmol) in a single portion. The reaction mixture was allowed to stir for overnight at RT. Purification by flash column chromatography (SiO_2, 20:1 dichloromethane: methanol) afforded the title compound as a colorless oil (186 mg, 85%); R_f 0.45 (10:1 dichloromethane: methanol); ν_{max}/cm^{-1} (thin film) 3321, 2907, 1678, 1486, 1439, 1255, 1181, 1130, 1069, 1011, 913, 787, 749, 695, 540; δ_H (400 MHz, $CDCl_3$) 7.75 – 7.66 (m, 2H, Ar-C**H**), 7.57 – 7.49 (m, 1H, Ar-C**H**), 7.49 – 7.38 (m, 2H, Ar-C**H**), 7.36 – 7.29 (m, 2H, Ar-C**H**), 7.11 – 7.04 (m, 2H, Ar-C**H**), 4.46 (m, 2H, OC$\mathbf{H}_2$ + C$\mathbf{H}_2$), 4.18 (dddd, *J* = 14.0, 11.0, 8.9, 5.4 Hz, 1H, OC$\mathbf{H}_2$), 3.59 (s, 2H, NHC$\mathbf{H}_2$Ph), 3.27 (ddt, *J* = 13.8, 10.6, 3.3 Hz, 1H, C$\mathbf{H}_2$), 3.06 (dt, *J* = 16.6, 6.0 Hz, 1H, C$\mathbf{H}_2$), 2.83 – 2.67 (m, 2H, C$\mathbf{H_2}$), 2.51 (ddd, *J* = 16.5, 7.1, 5.4 Hz, 1H, C$\mathbf{H}_2$), 2.25 – 2.06 (m, 1H, C$\mathbf{H}_2$), 1.97 (dddd, *J* = 14.4, 5.1, 3.6, 1.5 Hz, 1H, N**H**),

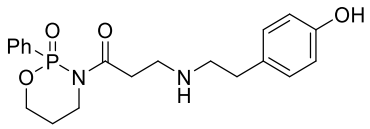
1.84 (s, 1H, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 174.2 (d, *J* = 7.9 Hz, **C**O), 139.3 (Ar-**C)**, 133.0 (d, *J* = 3.1 Hz, Ar-**C**H), 131.3 (Ar-**C**H), 131.2 (Ar-**C**H), 131.1 (Ar-**C**H), 129.7 (Ar-**C**H), 129.0 (d, *J* = 176.7 Hz, Ar-**C**), 129.0 (d, *J* = 15.2 Hz, Ar-**C**H), 120.4 (Ar-**C**), 66.8 (d, *J* = 7.9 Hz, O**C**H$_2$), 52.8 (NH**C**H$_2$Ph), 44.5 (**C**H$_2$), 41.1 (**C**H$_2$), 37.2 (**C**H$_2$), 25.8 (d, *J* = 6.1 Hz, **C**H$_2$); δ_P (162 MHz, $CDCl_3$) 15.8 (Ph**P**=O); HRMS (ESI): calcd. for $C_{19}H_{23}{}^{79}BrN_2O_3P$, 437.0624. Found: $[MH]^+$, 437.0633 (–1.9 ppm error).

3-((4-Aminobenzyl)amino)-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)propan-1-one (10d)



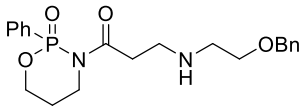
To a solution of 1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl) prop-2-en-1-one **9** (125.6 mg, 0.5 mmol) in dry THF (1.0 mL), was added 4-aminobenzylamine (73.3 mg, 0.6 mmol) in a single portion. The reaction mixture was allowed to stir for overnight at RT. Purification by flash column chromatography (SiO_2, 9:1 dichloromethane: methanol) afforded the title compound as a colorless oil (130 mg, 70%); R_f 0.15 (10:1 dichloromethane: methanol); ν_{max}/cm^{-1} (thin film) 3347, 2922, 1673, 1517, 1439, 1252, 1129, 1019, 727, 694, 538, 506; δ_H (400 MHz, $CDCl_3$) 7.77 – 7.64 (m, 2H, Ar-C**H**), 7.57 – 7.48 (m, 1H, Ar-C**H**), 7.47 – 7.37 (m, 2H, Ar-C**H**), 6.96 (d, *J* = 8.3 Hz, 2H, Ar-C**H**), 6.59 – 6.44 (m, 2H, Ar-C**H**), 4.51 – 4.34 (m, 2H, OC**H**$_2$ + C**H**$_2$), 4.16 (dddd, *J* = 14.1, 10.9, 8.8, 5.4 Hz, 1H, OC**H**$_2$), 3.50 (s, 2H, NHC**H**$_2$Ph), 3.27 (ddt, *J* = 13.6, 10.2, 3.4 Hz, 1H, C**H**$_2$), 3.03 (dt, *J* = 16.3, 5.5 Hz, 1H, C**H**$_2$), 2.82 – 2.66 (m, 2H, C**H$_2$**), 2.51 (ddd, *J* = 16.6, 7.1, 5.7 Hz, 1H, C**H**$_2$), 2.21 – 2.07 (m, 1H, N**H**), 2.02 – 1.88 (m, 1H, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 174.3 (d, *J* = 7.7 Hz, **C**O), 145.4 (Ar-**C)**, 133.0 (d, *J* = 3.1 Hz, Ar-**C**H), 131.2 (d, *J* = 10.7 Hz, Ar-**C**H), 129.6 (Ar-**C**), 129.1 (Ar-**C**H), 129.0 (d, *J* = 176.7 Hz, Ar-**C**), 128.9 (d, *J* = 15.3 Hz, Ar-**C**H), 114.9 (Ar-**C**H), 66.8 (d, *J* = 8.0 Hz, O**C**H$_2$), 53.0 (NH**C**H$_2$Ph), 44.3 (**C**H$_2$), 41.1 (**C**H$_2$), 37.0 (**C**H$_2$), 25.7 (d, *J* = 6.0 Hz, **C**H$_2$); δ_P (162 MHz, $CDCl_3$) 15.8 (Ph**P**=O); HRMS (ESI): calcd. for $C_{19}H_{25}N_3O_3P$, 347.1628. Found: $[MH]^+$, 347.1628 (0.1 ppm error).

3-((4-Hydroxyphenethyl)amino)-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)propan-1-one (10e)



To a solution of 1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl) prop-2-en-1-one **9** (125.6 mg, 0.5 mmol) in dry THF (1.0 mL), was added tyramine (82 mg, 0.6 mmol) in a single portion. The reaction mixture was allowed to stir for overnight at RT. Purification by flash column chromatography (SiO_2, 5:1 dichloromethane: methanol) afforded the title compound as a colorless oil (125 mg, 64%); R_f 0.10 (10:1 dichloromethane: methanol); ν_{max}/cm^{-1} (thin film) 2925, 1677, 1515, 1439, 1252, 1130, 1018, 749, 541; δ_H (400 MHz, $CDCl_3$) 7.76 – 7.62 (m, 2H, Ar-C**H**), 7.56 – 7.47 (m, 1H, Ar-C**H**), 7.46 – 7.35 (m, 2H, Ar-C**H**), 6.94 – 6.84 (m, 2H, Ar-C**H**), 6.68 – 6.60 (m, 2H, Ar-C**H**), 5.70 – 5.00 (br m, 2H), 4.62 – 4.30 (m, 2H, OC**H**$_2$ + C**H**$_2$), 4.19 (dddd, *J* = 14.1, 10.9, 8.6, 5.4 Hz, 1H, C**H**$_2$), 3.36 – 3.22 (m, 1H, C**H**$_2$), 3.06 (dt, *J* = 17.1, 5.9 Hz, 1H, C**H**$_2$), 2.90 – 2.77 (m, 2H, C**H$_2$**), 2.76 – 2.67 (m, 2H, C**H$_2$**), 2.62 (t, *J* = 6.7 Hz, 2H, C**H$_2$**), 2.57 – 2.43 (m, 1H, C**H**$_2$), 2.25 – 2.09 (m, 1H, N**H**), 2.05 – 1.90 (m, 1H, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 174.1 (d, *J* = 7.4 Hz, **C**O), 155.6 (Ar-**C**), 133.2 (d, *J* = 2.9 Hz, Ar-**C**H), 131.3 (d, *J* = 10.9 Hz, Ar-**C**H), 129.9 (Ar-**C**), 129.6 (Ar-**C**H), 129.1 (d, *J* = 15.4 Hz, Ar-**C**H), 128.6 (d, *J* = 176.8 Hz, Ar-**C**), 115.7 (Ar-**C**H), 67.0 (d, *J* = 7.6 Hz, O**C**H$_2$), 50.9 (NH**C**H$_2$), 44.7 (**C**H$_2$), 41.4 (**C**H$_2$), 36.4 (**C**H$_2$), 34.8 (**C**H$_2$), 25.7 (d, *J* = 6.0 Hz, **C**H$_2$); δ_P (162 MHz, $CDCl_3$) 16.1 (Ph**P**=O); HRMS (ESI): calcd. for $C_{20}H_{26}N_2O_4P$, 389.1625. Found: $[MH]^+$, 389.1623 (0.4 ppm error).

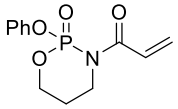
3-((2-(Benzyloxy)ethyl)amino)-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)propan-1-one (10f)



To a solution of 1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl) prop-2-en-1-one **9** (125.6 mg, 0.5 mmol) in dry THF (1.0 mL), was added 2-(benzyloxy)-1-ethanamine (91 mg, 0.6 mmol) in a single portion. The reaction mixture was allowed to stir for

overnight at RT. Purification by flash column chromatography (SiO_2, 10:1 dichloromethane: methanol) afforded the title compound as a colorless oil (158 mg, 78%); R_f 0.30 (10:1 dichloromethane: methanol); ν_{max}/cm^{-1} (thin film) 3468, 2858, 1678, 1439, 1254, 1130, 1021, 914, 748, 697, 540; δ_H (400 MHz, $CDCl_3$) 7.75 – 7.68 (m, 2H, Ar-C**H**), 7.55 – 7.48 (m, 1H, Ar-C**H**), 7.48 – 7.37 (m, 2H, Ar-C**H**), 7.30 – 7.17 (m, 5H, Ar-C**H**), 4.51 – 4.39 (m, 4H, OC**H₂**Ph + OC**H₂** + C**H₂**), 4.16 (dddd, *J* = 14.1, 11.0, 8.8, 5.4 Hz, 1H, OC**H₂**), 3.46 (t, *J* = 5.3 Hz, 2H, OC**H₂**), 3.27 (ddt, *J* = 13.8, 10.3, 3.4 Hz, 1H, C**H₂**), 3.05 (dt, *J* = 16.5, 6.2 Hz, 1H, C**H₂**), 2.85 – 2.76 (m, 2H, C**H₂**), 2.67 (q, *J* = 5.2 Hz, 2H, C**H₂**), 2.51 (ddd, *J* = 16.5, 7.1, 6.1 Hz, 1H, C**H₂**), 2.24 – 2.10 (m, 2H, N**H** + C**H₂**), 1.96 (dddd, *J* = 14.4, 5.1, 3.6, 1.5 Hz, 1H, C**H₂**); δ_C (100 MHz, $CDCl_3$) 174.1 (d, *J* = 7.8 Hz, **C**O), 138.2 (Ar-**C)**, 133.0 (d, *J* = 3.1 Hz, Ar-**C**H), 131.2 (d, *J* = 10.8 Hz, Ar-**C**H), 129.0 (d, *J* = 176.1 Hz, Ar-**C**), 128.9 (d, *J* = 15.2 Hz, Ar-**C**H), 128.3 (Ar-**C**H), 127.6 (Ar-**C**H), 127.5 (Ar-**C**H), 73.0 (O**C**H_2Ph), 69.3 (O**C**H_2), 66.7 (d, *J* = 8.0 Hz, O**C**H_2), 48.9 (**C**H_2), 45.0 (**C**H_2), 41.1 (**C**H_2), 37.1 (**C**H_2), 25.7 (d, *J* = 6.0 Hz, **C**H_2); δ_P (162 MHz, $CDCl_3$) 15.7 (Ph**P**=O); HRMS (ESI): calcd. for $C_{21}H_{28}N_2O_4P$, 403.1781. Found: $[MH]^+$, 403.1788 (–1.8 ppm error).

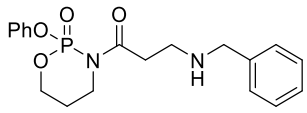
1-(2-Oxido-2-phenoxy-1,3,2-oxazaphosphinan-3-yl)prop-2-en-1-one (12)



To a solution of 2-phenoxy-1,3,2-oxazaphosphinane 2-oxide (213 mg, 1.0 mmol) in dry THF (5.0 mL), was added acryl chloride (136 mg, 1.5 mmol) in a single portion, then NEt_3 (420 µL, 1.5 mmol) was added to the mixture. The reaction mixture was allowed to stir for 10 min a RT. The reaction mixture was then quenched with sat. aq. $NaHCO_3$ (10 mL) and the mixture was extracted with Et_2O (2 × 10 mL). The organic extracts dried over $MgSO_4$ and concentrated in vacuo. Purification by flash column chromatography (SiO_2, 1:1 hexane: ethyl acetate → ethyl acetate) afforded the title compound as a colorless oil (169 mg, 63%); R_f 0.48 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 2970, 1680, 1488, 1406, 1299, 1182, 1058, 1019, 925, 798, 692, 526; δ_H (400 MHz, $CDCl_3$) 7.33 – 7.22 (m, 3H, Ar-C**H**), 7.21 – 7.11 (m, 3H, Ar-C**H** + C**H**=CHH'), 6.34 (dd, *J* = 16.7, 1.9 Hz, 1H, CH=C**H**H'), 5.69 (dd, *J* = 10.4, 1.9 Hz, 1H, CH=CH**H'**), 4.69 – 4.55 (m,

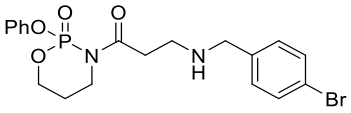
1H, C**H**$_2$), 4.52 – 4.37 (m, 2H, C**H$_2$**), 3.32 (ddt, *J* = 14.1, 11.7, 2.7 Hz, 1H, C**H**$_2$), 2.15 – 1.88 (m, 2H, C**H$_2$**); δ_C (100 MHz, $CDCl_3$) 166.7 (d, *J* = 9.0 Hz, **C**O), 149.8 (d, *J* = 7.2 Hz, Ar-**C**), 130.5 (COCH=**C**H$_2$), 130.0 (CO**C**H=CH$_2$), 129.8 (d, *J* = 1.0 Hz, Ar-**C**H), 125.6 (d, *J* = 1.1 Hz, Ar-**C**H), 119.8 (d, *J* = 4.9 Hz, Ar-**C**H), 70.9 (d, *J* = 8.6 Hz, O**C**H$_2$), 42.2 (**C**H$_2$), 25.7 (d, *J* = 5.2 Hz, **C**H$_2$); δ_P (162 MHz, $CDCl_3$) –8.8 (PhO**P**=O); HRMS (ESI): calcd. for $C_{12}H_{14}NNaO_3P$, 274.0604. Found: $[MNa]^+$, 274.0607 (–1.3 ppm error).

3-(Benzylamino)-1-(2-oxido-2-phenoxy-1,3,2-oxazaphosphinan-3-yl)propan-1-one (13a)



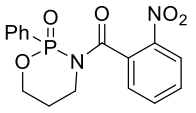
To a solution of 1-(2-oxido-2-phenoxy-1,3,2-oxazaphosphinan-3-yl) prop-2-en-1-one **12** (78 mg, 0.29 mmol) in dry THF (0.6 mL), was added benzylamine (38 mg, 0.36 mmol, 1.2 eq) in a single portion. The reaction mixture was allowed to stir for overnight at RT. Purification by flash column chromatography (SiO_2, 10: 1 dichloromethane: methanol) afforded the title compound as a colorless oil (81 mg, 75%); R_f 0.23 (10:1 dichloromethane: methanol); ν_{max}/cm^{-1} (thin film) 2925, 1687, 1488, 1300, 1202, 1174, 1026, 926, 800, 691, 531; δ_H (400 MHz, $CDCl_3$) 7.34 – 7.15 (m, 10H, Ar-C**H**), 4.65 – 4.53 (m, 1H, C**H**$_2$), 4.48 – 4.35 (m, 2H, OC**H$_2$**), 3.72 (s, 2H, NHC**H$_2$**Ph), 3.34 – 3.12 (m, 2H, C**H$_2$**), 2.90 – 2.70 (m, 3H, C**H**$_2$ + C**H$_2$**), 2.13 – 1.84 (m, 3H, N**H** + C**H$_2$**); δ_C (100 MHz, $CDCl_3$) 173.6 (d, *J* = 9.6 Hz, **C**O), 149.9 (d, *J* = 7.3 Hz, Ar-**C**), 140.2 (Ar-**C**H), 130.1 (Ar-**C**H), 128.3 (Ar-**C**H), 128.0 (Ar-**C**H), 126.8 (Ar-**C**H), 125.6 (Ar-**C**H), 119.9 (d, *J* = 4.9 Hz, Ar-**C**H), 70.8 (d, *J* = 8.6 Hz, O**C**H$_2$), 53.6 (**C**H$_2$), 44.7 (**C**H$_2$), 41.9 (**C**H$_2$), 37.4 (**C**H$_2$), 25.7 (d, *J* = 5.2 Hz, **C**H$_2$); δ_P (162 MHz, $CDCl_3$) –8.4 (PhO**P**=O); HRMS (ESI): calcd. for $C_{19}H_{24}N_2O_4P$, 375.1468. Found: [MH]+, 375.1473 (–1.2 ppm error).

3-((4-Bromobenzyl)amino)-1-(2-oxido-2-phenoxy-1,3,2-oxazaphosphinan-3-yl)propan-1-one (13b)



To a solution of 1-(2-oxido-2-phenoxy-1,3,2-oxazaphosphinan-3-yl) prop-2-en-1-one **12** (150 mg, 0.55 mmol) in dry THF (1.1 mL), was added 4-bromobenzylamine (139.5 mg, 0.66 mmol, 1.2 eq) in a single portion. The reaction mixture was allowed to stir for overnight at RT. Purification by flash column chromatography (SiO_2, 20: 1 dichloromethane: methanol) afforded the title compound as a colorless oil (195 mg, 78%); R_f 0.52 (10:1 dichloromethane: methanol); ν_{max}/cm^{-1} (thin film) 3410, 1591, 1489, 1392, 1265, 1209, 1047, 1025, 1005, 920, 823, 762, 511; δ_H (400 MHz, $CDCl_3$) 7.40 – 7.29 (m, 4H, Ar-C**H**), 7.22 – 7.10 (m, 5H, Ar-C**H**), 4.61 (ddtd, *J* = 15.0, 13.7, 4.2, 1.2 Hz, 1H, C$\mathbf{H}_2$), 4.44 (dddt, *J* = 12.9, 7.1, 3.7, 1.6 Hz, 2H, OC$\mathbf{H_2}$), 3.67 (s, 2H, NHC$\mathbf{H_2}$Ph), 3.30 (ddt, *J* = 14.0, 11.5, 2.8 Hz, 1H, C$\mathbf{H}_2$), 3.23 – 3.12 (m, 1H, C$\mathbf{H}_2$), 2.87 – 2.75 (m, 3H, C$\mathbf{H_2}$ + C$\mathbf{H}_2$), 2.11 – 1.98 (m, 1H, N**H**), 1.95 – 1.81 (m, 2H, C$\mathbf{H_2}$); δ_C (100 MHz, $CDCl_3$) 173.6 (d, *J* = 9.6 Hz, **C**O), 149.9 (d, *J* = 7.2 Hz, Ar-**C**), 139.3 (Ar-**C**), 131.3 (Ar-**C**H), 130.1 (Ar-**C**H), 129.8 (Ar-**C**H), 125.7 (Ar-**C**H), 120.5 (Ar-**C**), 119.9 (d, *J* = 4.9 Hz, Ar-**C**H), 70.8 (d, *J* = 8.5 Hz, O**C**H_2), 52.9 (N**C**H_2Ph), 44.6 (**C**H_2), 42.0 (**C**H_2), 37.4 (**C**H_2), 25.7 (d, *J* = 5.2 Hz, **C**H_2); δ_P (162 MHz, $CDCl_3$) –8.4 (PhO**P**=O); HRMS (ESI): calcd. for $C_{19}H_{23}{}^{79}BrN_2O_4P$, 453.0573. Found: $[MH]^+$, 453.0575 (–0.3 ppm error).

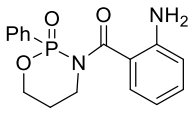
(2-Nitrophenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone (15)



2-Phenyl-1,3,2-oxazaphosphinane 2-oxide **8a** (197.2 mg, 1.0 mmol) was dissolved in THF (5 mL) and the temperature was lowered –78 ℃ (dry ice/acetone bath). *n*-BuLi (2.5 M in hexanes, 0.48 mL, 1.2 mmol, 1.2 eq) was added dropwise by syringe and the reaction was allowed to stir at –78 ℃. After 1 hour, a solution of 2-nitrobenzoyl chloride (1.5 mmol, 1.5 equiv. prepared using the general procedure with 2-

nitrobenzoic acid) in THF (5 mL) was added slowly to the stirring reaction mixture. The reaction was allowed to warm to room temperature overnight before the addition of sat. aq. $NaHCO_3$ solution (20 mL). The aqueous layer was extracted with EtOAc (2 × 10 mL) and the combined organic layers were dried ($MgSO_4$). After filtration, the solvent was then concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the title compound as a colorless oil (308 mg, 89%). R_f= 0.15 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3062, 1667, 1527, 1440, 1346, 1321, 1250, 1129, 1058, 997, 908, 861, 724, 701, 578; δ_H (400 MHz, $CDCl_3$ at 50 °C) 7.91 (d, *J* = 7.7 Hz, 1H, Ar-C**H**), 7.43 – 7.33 (m, 5H, Ar-C**H**), 7.26 – 7.08 (m, 3H, Ar-C**H**), 4.58 – 4.14 (m, 3H, OC**H₂** + C**H**$_2$), 3.78 – 3.45 (m, 1H, C**H**$_2$), 2.42 – 2.23 (m, 1H, C**H**$_2$), 2.16 – 2.01 (m, 1H, C**H**$_2$); δ_C (100 MHz, $CDCl_3$ at 50 °C) 168.5 (d, *J* = 8.0 Hz, **C**O), 145.3 (Ar-**C**), 133.4 (Ar-**C**H), 132.8 (d, *J* = 3.2 Hz, Ar-**C**H), 132.2 (Ar-**C**), 131.5 (d, *J* = 10.7 Hz, Ar-**C**H), 130.1 (Ar-**C**H), 128.8 (br, Ar-**C**H), 128.3 (d, *J* = 15.4 Hz, Ar-**C**H), 128.2 (d, *J* = 180.5 Hz, Ar-**C**), 123.9 (Ar-**C**H), 66.6 (d, *J* = 8.1 Hz, O**C**H$_2$), 41.7 (br, **C**H$_2$), 25.3 (d, *J* = 6.0 Hz, **C**H$_2$); δ_P (162 MHz, $CDCl_3$ at 50 °C) 13.9 (Ph**P**=O); HRMS (ESI): calcd. for $C_{16}H_{15}N_2NaO_5P$, 369.0611. Found: $[MNa]^+$, 369.0608 (0.6 ppm error).

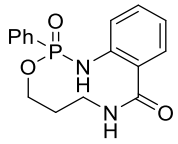
(2-Aminophenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone (16)



(2-Nitrophenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone **15** (200 mg, 0.56 mmol) was dissolved in dry EtOAc (6.0 mL) and placed under an argon atmosphere. Palladium on carbon 60 mg, Pd 10% on carbon) was added and the reaction vessel was backfilled with hydrogen (via balloon) several times, then stirred at RT under a slight positive pressure of hydrogen (balloon) for 3 h. The reaction was then purged with argon, filtered through Celite, washed with ethyl acetate where the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the title compound as a colorless oil (180 mg, 77%). R_f= 0.14 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3465, 3440, 2970, 1649, 1621, 1491, 1440, 1326,

1236, 1129, 1056, 994, 748, 725, 693, 504; δ_H (400 MHz, $CDCl_3$) δ 7.66 – 7.52 (m, 2H, Ar-C**H**), 7.41 – 7.30 (m, 1H, Ar-C**H**), 7.26 – 7.17 (m, 3H, Ar-C**H**), 6.96 (ddd, *J* = 8.5, 7.3, 1.6 Hz, 1H, Ar-C**H**), 6.51 (td, *J* = 7.6, 1.1 Hz, 1H, Ar-C**H**), 6.35 (dd, *J* = 8.2, 1.0 Hz, 1H, Ar-C**H**), 4.63 – 4.44 (m, 3H, N**H₂** + OC**H**$_2$), 4.21 (dddd, *J* = 18.9, 10.7, 8.0, 5.8 Hz, 1H, OC**H**$_2$), 3.92 – 3.75 (m, 2H, C**H₂**), 2.37 – 2.25 (m, 1H, C**H**$_2$), 2.16 – 2.04 (m, 1H, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 173.3 (d, *J* = 5.5 Hz, **C**O), 147.0 (Ar-**C**), 132.3 (d, *J* = 3.1 Hz, Ar-**C**H), 132.2 (Ar-**C**H), 131.5 (d, *J* = 10.7 Hz, Ar-**C**H), 129.2 (Ar-**C**H), 129.2 (Ar-**C**), 128.3 (d, *J* = 181.5 Hz, Ar-**C**), 127.9 (d, *J* = 15.5 Hz, Ar-**C**H), 117.2 (d, *J* = 2.3 Hz, Ar-**C**), 116.2 (d, *J* = 10.7 Hz, Ar-**C**H), 65.8 (d, *J* = 7.6 Hz, O**C**H$_2$), 43.8 (**C**H$_2$), 25.5 (d, *J* = 7.3 Hz, **C**H$_2$); δ_P (162 MHz, $CDCl_3$) 15.7 (Ph**P**=O); HRMS (ESI): calcd. for $C_{16}H_{17}N_2NaO_3P$, 339.0869. Found: [MNa]+, 339.0864 (1.4 ppm error).

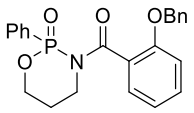
2-Phenyl-1,4,5,6,7-pentahydrobenzo[*d*][1,3,7,2]oxadiazaphosphecin-8-one 2-oxide (17)



(2-Aminophenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone **16** (150 mg, 0.47 mmol) was dissolved in THF (5.0 mL) and NaH (60% in Paraffin oil, 30 mg, 0.75 mmol, 1.5 eq) was added, the mixture was stirred at RT for 1 h. Quenched with sat. NH_4Cl aq. (5 mL), extracted with EtOAc (3 × 10 mL) and the combined organic layers were dried ($MgSO_4$). After filtration, the solvent was then concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, 9:1 ethyl acetate: methanol) afforded the title compound (as a 3:2 mixture of rotamers in solution in $CDCl_3$) as a colorless oil (66 mg, 44%); R_f= 0.15 (9:1 ethyl acetate: methanol); ν_{max}/cm^{-1} (thin film) 3152, 1643, 1537, 1454, 1310, 1207, 1126, 1046, 989, 752, 695, 533; δ_H (400 MHz, $CDCl_3$) 8.29 (t, *J* = 6.4 Hz, 1H, Ar-C**H**, minor rotamer), 7.96 (d, *J* = 6.0 Hz, 1H, Ar-C**H**, minor rotamer), 7.91 – 7.76 (m, 1H, Ar-C**H**, both rotamers), 7.62 – 7.30 (m, 7H, Ar-C**H**, both rotamers), 7.24 – 7.01 (m, 5H, Ar-C**H**, both rotamers), 6.94 (td, *J* = 7.7, 1.7 Hz, 1H, N**H**, minor rotamer), 6.76 (dt, *J* = 7.4, 1.6 Hz, 1H, N**H**, major rotamer), 6.72 (d, *J* = 3.9

Hz, 1H, CON**H**, major rotamer), 6.31 (d, *J* = 8.0 Hz, 1H, CON**H**, minor rotamer), 4.93 (qd, *J* = 10.7, 4.1 Hz, 1H, OC**H**$_2$, minor rotamer), 4.65 (dtd, *J* = 10.6, 9.1, 1.2 Hz, 1H, OC**H**$_2$, major rotamer), 4.33 – 4.16 (m, 1H, OC**H**$_2$, major rotamer), 4.06 – 3.01 (m, 2H, C**H**$_2$ both rotamers + OC**H**$_2$ minor rotamer), 2.66 – 1.64 (m, 2H, C**H**$_2$, both rotamers); δ_C (100 MHz, $CDCl_3$) 173.5 (NH**C**O, minor rotamer), 169.1 (NH**C**O, major rotamer), 136.4 (d, *J* = 4.3 Hz, Ar-**C**, minor rotamer),136.0 (d, *J* = 2.9 Hz, Ar-**C**, major rotamer), 133.6 (Ar-**C**, both rotamers), 132.3 (Ar-C**H**, both rotamers), 132.1 (d, *J* = 3.1 Hz, Ar-C**H**, both rotamers), 131.9 (d, *J* = 9.5 Hz, Ar-C**H**, minor rotamer), 131.3 (Ar-C**H**, both rotamers), 130.9 (d, *J* = 9.6 Hz, Ar-C**H**, major rotamer), 130.8 (d, *J* = 182.0 Hz, Ar-**C**, minor rotamer), 129.7 (d, *J* = 1.9 Hz, Ar-C**H**, both rotamers), 129.2 (Ar-C**H**, both rotamers), 129.1 (d, *J* = 175.8 Hz, Ar-**C**, major rotamer), 128.5 (d, *J* = 14.7 Hz, Ar-C**H**, minor rotamer), 128.2 (d, *J* = 14.6 Hz, Ar-C**H**, major rotamer), 127.7 (d, *J* = 4.8 Hz, Ar-C**H**, major rotamer), 126.5 (Ar-C**H**, minor rotamer), 126.4 (d, *J* = 2.1 Hz, Ar-C**H**, minor rotamer), 125.6 (d, *J* = 1.9 Hz, Ar-C**H**, major rotamer), 65.9 (d, *J* = 7.1 Hz, O**C**H$_2$, major rotamer), 58.7 (d, *J* = 5.7 Hz, O**C**H$_2$, minor rotamer), 39.4 (**C**H$_2$, minor rotamer), 39.1 (**C**H$_2$, major rotamer), 28.8 (d, *J* = 6.6 Hz, **C**H$_2$, minor rotamer), 27.3 (d, *J* = 5.1 Hz, **C**H$_2$, major rotamer); δ_P (162 MHz, $CDCl_3$) 20.7 (Ph**P**=O, major rotamer), 20.8 (Ph**P**=O, minor rotamer); HRMS (ESI): calcd. for $C_{16}H_{17}N_2NaO_3P$, 339.0869. Found: $[MNa]^+$, 339.0866 (1.0 ppm error).

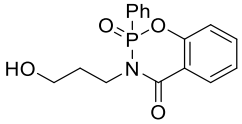
(2-(Benzyloxy)phenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone (18a)



2-Phenyl-1,3,2-oxazaphosphinane 2-oxide **8a** (197.2 mg, 1.0 mmol) was dissolved in dry THF (5 mL) and the temperature was lowered –78 ℃ (dry ice/acetone bath). *n*-BuLi (2.5 M in hexanes, 0.48 mL, 1.2 mmol, 1.2 eq) was added dropwise by syringe and the reaction was allowed to stir at –78 ℃. After 1 hour, a solution of acid chloride (1.5 mmol, 1.5 equiv. prepared using the general procedure with 2-benzyloxybenzoic acid) in dry THF (5 mL) was added slowly to the stirring reaction mixture. The reaction was

allowed to warm to room temperature overnight before the addition of sat. aq. $NaHCO_3$ solution (20 mL). The aqueous layer was extracted with EtOAc (2 × 10 mL) and the combined organic layers were dried ($MgSO_4$). After filtration, the solvent was then concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the title compound as a colorless oil (357 mg, 88%). R_f= 0.25 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3065, 1662, 1599, 1488, 1449, 1344, 1243, 1132, 1059, 996, 746, 724, 694, 583, 502; δ_H (400 MHz, $CDCl_3$ at 50 °C) 7.49 (dd, *J* = 13.8, 7.4 Hz, 2H, Ar-C**H**), 7.41 – 7.23 (m, 7H, Ar-C**H**), 7.22 – 7.04 (m, 3H, Ar-C**H**), 6.84 (t, *J* = 6.7 Hz, 1H, Ar-C**H**), 6.70 – 6.60 (m, 1H, Ar-C**H**), 4.93 – 4.61 (m, 2H, OC**H**$_2$), 4.44 (dq, *J* = 10.8, 5.3 Hz, 1H, C**H**$_2$), 4.22 – 4.04 (m, 1H, C**H**$_2$), 3.95 – 3.67 (m, 2H, C**H$_2$**), 2.23 – 1.91 (m, 2H, C**H$_2$**); δ_C (100 MHz, $CDCl_3$ at 50 °C) 170.7 (d, *J* = 5.8 Hz, **C**O), 154.8 (Ar-**C**), 136.4 (Ar-**C**), 131.9 (Ar-**C**H), 131.7 (Ar-**C**H), 131.2 (Ar-**C**H), 129.7 (Ar-**C**), 129.0 (Ar-**C**H), 128.3 (Ar-**C**H), 127.9 (Ar-**C**H), 127.6 (Ar-**C**H), 127.2 (Ar-**C**H), 125.2 (Ar-**C**), 120.5 (d, *J* = 8.2 Hz, Ar-**C**H), 111.7 (Ar-**C**H), 69.9 (O**C**H$_2$), 65.7 (d, *J* = 5.7 Hz, O**C**H$_2$), 43.0 (**C**H$_2$), 25.5 (d, *J* = 6.5 Hz, **C**H$_2$); δ_P (162 MHz, $CDCl_3$) 14.8 (Ph**P**=O); HRMS (ESI): calcd. for $C_{23}H_{22}NNaO_4P$, 430.1179. Found: $[MNa]^+$, 430.1186 (–1.7 ppm error).

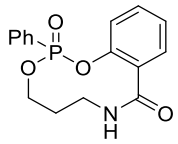
3-(3-Hydroxypropyl)-2-phenyl-3-hydrobenzo[*e*][1,3,2]oxazaphosphinin-4-one 2-oxide (20a)



(2-(Benzyloxy)phenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone **18a** (160 mg, 0.39 mmol) was dissolved in EtOAc (4.0 mL) and placed under an argon atmosphere. Palladium on carbon (40 mg, Pd 10% on carbon) was added and the reaction vessel was backfilled with hydrogen (via balloon) several times, then stirred at RT under a slight positive pressure of hydrogen (balloon) for 2 h. The reaction was then purged with argon, filtered through Celite, washed with ethyl acetate where the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the title compound as a colorless oil (110 mg, 90%). R_f= 0.34

(ethyl acetate); δ_H (400 MHz, $CDCl_3$) 8.11 (dd, *J* = 7.9, 1.7 Hz, 1H, Ar-C**H**), 7.75 – 7.68 (m, 2H, Ar-C**H**), 7.62 – 7.52 (m, 2H, Ar-C**H**), 7.49 – 7.42 (m, 2H, Ar-C**H**), 7.27 (td, *J* = 7.9, 1.0 Hz, 1H, Ar-C**H**), 7.09 (d, *J* = 8.3 Hz, 1H, Ar-C**H**), 3.94 (ddt, *J* = 14.0, 12.0, 5.7 Hz, 1H, NC**H**$_2$), 3.64 (ddd, *J* = 12.1, 8.5, 3.8 Hz, 1H, C**H**$_2$OH), 3.58 – 3.36 (m, 3H, NC**H**$_2$ + C**H**$_2$OH + CH_2O**H**), 1.98 – 1.70 (m, 2H, C**H$_2$**); δ_C (100 MHz, $CDCl_3$) 162.9 (d, *J* = 4.8 Hz, **C**O), 150.7 (d, *J* = 7.4 Hz, Ar-**C**), 135.7 (Ar-**C**H), 134.1 (d, *J* = 3.2 Hz, Ar-**C**H), 131.7 (d, *J* = 11.3 Hz, Ar-**C**H), 130.1 (Ar-**C**H), 129.2 (d, *J* = 15.8 Hz, Ar-**C**H), 126.6 (d, *J* = 178.4 Hz, Ar-**C**), 125.0 (Ar-**C**H), 118.6 (d, *J* = 9.3 Hz, Ar-**C**H), 117.1 (d, *J* = 2.5 Hz, Ar-**C**), 58.3 (**C**H_2OH), 39.3 (d, *J* = 4.6 Hz, N**C**H_2), 31.2 (**C**H_2); δ_P (162 MHz, $CDCl_3$) 17.7 (Ph**P**=O); HRMS (ESI): calcd. for $C_{16}H_{16}NNaO_4P$, 340.0709. Found: [MNa]+, 340.0712 (- 1.0 ppm error).

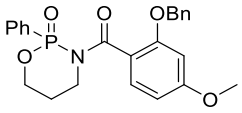
2-Phenyl-4,5,6,7-tetrahydro-8*H*-benzo[*d*][1,3,7,2]dioxazaphosphecin-8-one 2-oxide (21a)



3-(3-Hydroxypropyl)-2-phenyl-3-hydrobenzo[e][1,3,2]oxazaphosphinin-4-one 2-oxide **20a** (150 mg, 0.48 mmol) was dissolved in chloroform (5.0 mL) and triethylamine (700 µL, 5.0 mmol, 10 eq) added, the mixture was stirred for 18 h at RT, then reduced *in vacuo*. Purification by flash column chromatography (SiO_2, 1:1 hexane: ethyl acetate → ethyl acetate) afforded the *title compound* as a colorless oil (126 mg, 84%). R_f= 0.22 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3434, 2938, 1683, 1439, 1337, 1247, 1129, 1025, 995, 750, 727, 694, 540; δ_H (400 MHz, $CDCl_3$) 7.77 – 7.70 (m, 2H, Ar-C**H**), 7.61 (dd, *J* = 7.4, 2.0 Hz, 1H, Ar-C**H**), 7.58 – 7.48 (m, 1H, Ar-C**H**), 7.46 – 7.35 (m, 2H, Ar-C**H**), 7.24 – 7.08 (m, 3H, Ar-C**H** + N**H**CO), 6.77 – 6.62 (m, 1H, Ar-C**H**), 4.74 – 4.55 (m, 1H, OC**H**$_2$), 4.31 (td, *J* = 12.4, 6.5 Hz, 1H, OC**H**$_2$), 3.96 (td, *J* = 13.0, 5.1 Hz, 1H, NHC**H**$_2$), 3.40 (ddt, *J* = 13.9, 9.3, 4.5 Hz, 1H, NHC**H**$_2$), 2.37 – 2.21 (m, 1H, C**H**$_2$), 2.08 – 1.94 (m, 1H, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 167.0 (**C**O), 147.6 (d, *J* = 9.1 Hz, Ar-**C**), 133.0 (d, *J* = 3.1 Hz, Ar-**C**H), 131.7 (Ar-**C**H), 131.2 (d, *J* = 10.2 Hz, Ar-**C**H), 129.9 (d, *J* = 2.5 Hz, Ar-**C**), 129.6 (d, *J* = 1.5 Hz, Ar-**C**H), 128.6 (d, *J* = 15.9 Hz, Ar-**C**H), 127.3 (d, *J* = 196.5 Hz, Ar-**C**), 125.8 (d, *J* = 1.5

Hz, Ar-**C**H), 122.2 (d, *J* = 3.7 Hz, Ar-**C**H), 67.9 (d, *J* = 7.8 Hz, O**C**H_2), 38.9 (**C**H_2), 28.9 (d, *J* = 2.7 Hz, **C**H_2); δ_P (162 MHz, $CDCl_3$) 17.1 (Ph**P**=O); HRMS (ESI): calcd. for $C_{16}H_{16}NNaO_4P$, 340.0709. Found: $[MNa]^+$, 340.0710 (–0.3 ppm error).

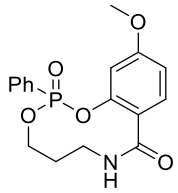
(2-(Benzyloxy)-4-methoxyphenyl) (2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl) methanone (18b)



2-Phenyl-1,3,2-oxazaphosphinane 2-oxide **8a** (197.2 mg, 1.0 mmol) was dissolved in dry THF (5 mL) and the temperature was lowered –78 ℃ (dry ice/acetone bath). *n*-BuLi (2.5 M in hexanes, 0.48 mL, 1.2 mmol, 1.2 eq) was added dropwise by syringe and the reaction was allowed to stir at –78 ℃. After 1 hour, a solution of acid chloride (1.5 mmol, 1.5 equiv. prepared using the general procedure with the acid **S1**) in THF (5 mL) was added slowly to the stirring reaction mixture. The reaction was allowed to warm to room temperature overnight before the addition of sat. aq. $NaHCO_3$ solution (20 mL). The aqueous layer was extracted with EtOAc (2 × 10 mL) and the combined organic layers were dried ($MgSO_4$). After filtration, the solvent was then concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the title compound as a colorless oil (335 mg, 77%). R_f = 0.20 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 2943, 1656, 1608, 1505, 1440, 1341, 1310, 1250, 1166, 1137, 997, 747, 723, 695, 503; δ_H (400 MHz, $CDCl_3$) 7.51 (dd, *J* = 14.4, 7.6 Hz, 1H, Ar-C**H**), 7.44 – 7.31 (m, 7H, Ar-C**H**), 7.25 – 7.14 (m, 2H, Ar-C**H**), 6.43 (d, *J* = 7.9 Hz, 1H, Ar-C**H**), 6.19 (s, 1H, Ar-C**H**), 4.87 (d, *J* = 11.2 Hz, 1H, OC**H**$_2$Ph), 4.76 – 4.63 (m, 1H, OC**H**$_2$Ph), 4.52 (dq, *J* = 10.6, 5.4 Hz, 1H, OC**H**$_2$), 4.18 (dddd, *J* = 18.7, 10.7, 7.8, 5.7 Hz, 1H, OC**H**$_2$), 3.95 – 3.81 (m, 2H, C**H$_2$**), 3.74 (s, 3H, OC**H$_3$**), 2.34 – 2.20 (m, 1H, C**H**$_2$), 2.14 – 1.96 (m, 1H, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 170.9 (d, *J* = 4.8 Hz, **C**O), 162.6 (Ar-**C**), 156.4 (Ar-**C**), 136.2 (Ar-**C**), 132.2 (d, *J* = 2.9 Hz, Ar-**C**H), 131.9 (Ar-**C**H), 131.8 (Ar-**C**H), 131.0 (Ar-**C**), 128.6 (Ar-**C**H), 128.2 (Ar-**C**H), 128.0 (Ar-**C**H), 127.8 (Ar-**C**H), 127.5 (Ar-**C**H), 117.7 (Ar-**C**), 104.7 (Ar-**C**H), 99.2 (Ar-**C**H), 70.0 (O**C**H_2Ph), 66.0 (d, *J* = 7.7 Hz, O**C**H_2), 55.5 (O**C**H_3), 43.4 (**C**H_2),

25.7 (d, *J* = 7.0 Hz, **C**H_2); δ_P (162 MHz, $CDCl_3$) 14.9 (Ph**P**=O); HRMS (ESI): calcd. for $C_{24}H_{24}NNaO_5P$, 460.1284. Found: $[MNa]^+$, 460.1286 (–0.3 ppm error).

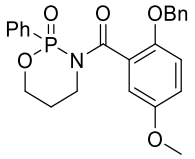
11-Methoxy-2-phenyl-4,5,6,7-tetrahydro-8*H*-benzo[*d*][1,3,7,2]dioxazaphosphecin-8-one 2-oxide (21b)



(2-(Benzyloxy)-4-methoxyphenyl) (2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl) methanone **18b** (270 mg, 0.60 mmol) was dissolved in dry EtOAc (6.0 mL) and placed under an argon atmosphere. Palladium on carbon (60 mg, Pd 10% on carbon) was then added and the reaction vessel was backfilled with hydrogen (via balloon) several times, then stirred at RT under a slight positive pressure of hydrogen (balloon) for 4 h. The reaction was then purged with argon, filtered through Celite, washed with ethyl acetate where the solvent was removed *in vacuo*. The crude was dissolved in chloroform (6.0 mL) and triethylamine (840 µL, 6.0 mmol, 10 eq) added, the mixture was stirred overnight at RT, then reduced *in vacuo*. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the *title compound* as a colorless oil (147 mg, 71%). R_f= 0.16 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3305, 2964, 1656, 1613, 1500, 1441, 1259, 1131, 992, 978, 866, 696, 522; δ_H (400 MHz, $CDCl_3$) 7.77 – 7.70 (m, 2H, Ar-C**H**), 7.65 (d, *J* = 8.7 Hz, 1H, Ar-C**H**), 7.59 – 7.49 (m, 1H, Ar-C**H**), 7.48 – 7.37 (m, 2H, Ar-C**H**), 6.97 (t, *J* = 5.9 Hz, 1H, CON**H**), 6.71 (ddd, *J* = 8.7, 2.5, 1.1 Hz, 1H, Ar-C**H**), 6.13 (dd, *J* = 2.4, 1.5 Hz, 1H, Ar-C**H**), 4.82 – 4.69 (m, 1H, OC$\mathbf{H}_2$), 4.39 – 4.29 (m, 1H, OC$\mathbf{H}_2$), 4.01 – 3.88 (m, 1H, C$\mathbf{H}_2$), 3.61 (s, 3H, OC$\mathbf{H_3}$), 3.55 – 3.40 (m, 1H, C$\mathbf{H}_2$), 2.40 – 2.26 (m, 1H, C$\mathbf{H}_2$), 2.10 – 1.99 (m, 1H, C$\mathbf{H}_2$); δ_C (100 MHz, $CDCl_3$) 166.8 (**C**O), 162.3 (d, *J* = 1.1 Hz, Ar-**C**), 149.1 (d, *J* = 8.9 Hz, Ar-**C**), 133.1 (d, *J* = 3.2 Hz, Ar-**C**H), 131.4 (d, *J* = 10.1 Hz, Ar-**C**H), 131.4 (d, *J* = 1.6 Hz, Ar-**C**H), 128.7 (d, *J* = 15.9 Hz, Ar-**C**H), 127.2 (d, *J* = 196.3 Hz, Ar-**C**), 121.8 (d, *J* = 2.4 Hz, Ar-**C**H), 111.8 (d, *J* = 1.4 Hz, Ar-**C**H), 107.9 (d, *J* = 3.8 Hz, Ar-**C**H), 68.1 (d, *J* = 7.8 Hz, O**C**H_2), 55.6 (O**C**H_3), 39.1 (**C**H_2), 28.8 (d, *J* = 2.5 Hz,

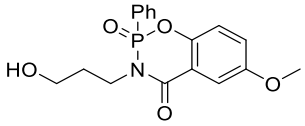
CH_2); δ_P (162 MHz, $CDCl_3$) 16.9 (Ph**P**=O); HRMS (ESI): calcd. for $C_{17}H_{18}NNaO_5P$, 370.0815. Found: $[MNa]^+$, 370.0819 (–1.1 ppm error).

(2-(Benzyloxy)-5-methoxyphenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone (18c)



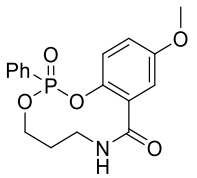
2-Phenyl-1,3,2-oxazaphosphinane 2-oxide **8a** (197.2 mg, 1.0 mmol) was dissolved in dry THF (5 mL) and the temperature was lowered –78 ℃ (dry ice/acetone bath). *n*-BuLi (2.5 M in hexanes, 0.48 mL, 1.2 mmol, 1.2 eq) was added dropwise by syringe and the reaction was allowed to stir at –78 ℃. After 1 hour, a solution of acid chloride (1.5 mmol, 1.5 equiv. prepared using the general procedure with the acid **S2**) in THF (5 mL) was added slowly to the stirring reaction mixture. The reaction was allowed to warm to room temperature overnight before the addition of sat. aq. $NaHCO_3$ solution (20 mL). The aqueous layer was extracted with EtOAc (2 × 10 mL) and the combined organic layers were dried ($MgSO_4$). After filtration, the solvent was then concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the title compound as a colorless oil (335 mg, 77%). R_f = 0.16 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 2937, 2236, 1660, 1498, 1418, 1340, 1247, 1216, 1040, 996, 910, 799, 719, 692, 612, 501; δ_H (400 MHz, $CDCl_3$) 7.57 – 7.45 (m, 2H, Ar-C**H**), 7.38 – 7.22 (m, 6H, Ar-C**H**), 7.19 – 7.07 (m, 2H, Ar-C**H**), 6.95 – 6.62 (m, 3H, Ar-C**H**), 4.90 – 4.56 (m, 2H, OC**H₂**Ph), 4.41 (dq, *J* = 10.6, 5.4 Hz, 1H, OC**H**$_2$), 4.22 – 3.99 (m, 1H, OC**H**$_2$), 3.92 – 3.65 (m, 2H, C**H₂**), 3.61 (s, 3H, OC**H₃**), 2.32 – 2.10 (m, 1H, C**H**$_2$), 2.04 – 1.86 (m, 1H, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 170.5 (br, **C**O), 153.2 (Ar-**C**), 148.5 (Ar-**C**), 136.3 (Ar-**C**), 132.0 (Ar-**C**H), 131.6 (Ar-**C**H), 131.5 (Ar-**C**H), 129.3 (Ar-**C**), 128.3 (Ar-**C**H), 127.7 (Ar-**C**H), 127.6 (Ar-**C**H), 127.3 (Ar-**C**H), 124.8 (Ar-**C**), 117.0 (Ar-**C**H), 113.7 (Ar-**C**H), 112.8 (Ar-**C**H), 70.3 (O**C**H_2Ph), 65.6 (d, *J* = 7.1 Hz, O**C**H_2), 55.4 (O**C**H_3), 43.3 (br, **C**H_2), 25.3 (d, *J* = 7.0 Hz, **C**H_2); δ_P (162 MHz, $CDCl_3$) 14.6 (Ph**P**=O); HRMS (ESI): calcd. for $C_{24}H_{24}NNaO_5P$, 460.1284. Found: $[MNa]^+$, 460.1290 (–1.3 ppm error).

3-(3-Hydroxypropyl)-6-methoxy-2-phenyl-3-hydrobenzo[*e*][1,3,2]oxazaphosphinin-4-one 2-oxide (20c)



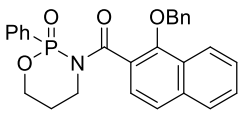
2-(Benzyloxy)-5-methoxyphenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone **18c** (230 mg, 0.53 mmol) was dissolved in dry EtOAc (6.0 mL) and placed under an argon atmosphere. Palladium on carbon (60 mg, Pd 10% on carbon) was then added and the reaction vessel was backfilled with hydrogen (via balloon) several times, then stirred at RT under a slight positive pressure of hydrogen (balloon) for 2 h. The reaction was then purged with argon, filtered through Celite, washed with ethyl acetate where the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the title compound as a colorless oil (170 mg, 92%). R_f = 0.29 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3446, 2942, 1678, 1488, 1428, 1333, 1283, 1247, 1196, 1126, 1029, 916, 728, 717, 692, 576, 558, 507; δ_H (400 MHz, $CDCl_3$) 7.67 (ddd, *J* = 14.5, 8.3, 1.4 Hz, 2H, Ar-C**H**), 7.55 (tdd, *J* = 7.0, 2.9, 1.4 Hz, 1H, Ar-C**H**), 7.50 (d, *J* = 3.1 Hz, 1H, Ar-C**H**), 7.45 – 7.37 (m, 2H, Ar-C**H**), 7.05 (ddd, *J* = 9.0, 3.2, 0.9 Hz, 1H, Ar-C**H**), 6.98 (d, *J* = 9.0 Hz, 1H, Ar-C**H**), 3.90 (ddt, *J* = 14.0, 11.8, 5.7 Hz, 1H, NC$\mathbf{H}_2$), 3.76 (s, 3H, OC$\mathbf{H_3}$), 3.71 – 3.56 (m, 2H, OC$\mathbf{H}_2$ + CH_2O**H**), 3.50 (dt, *J* = 11.8, 5.1 Hz, 1H, OC$\mathbf{H}_2$), 3.41 (dtd, *J* = 14.4, 8.5, 6.0 Hz, 1H, NC$\mathbf{H}_2$), 1.93 – 1.69 (m, 2H, C$\mathbf{H_2}$); δ_C (100 MHz, $CDCl_3$) 162.8 (d, *J* = 4.8 Hz, **C**O), 156.3 (Ar-**C**), 144.5 (d, *J* = 7.2 Hz, Ar-**C**), 134.0 (d, *J* = 3.2 Hz, Ar-**C**H), 131.6 (d, *J* = 11.2 Hz, Ar-**C**H), 129.0 (d, *J* = 15.8 Hz, Ar-**C**H), 126.6 (d, *J* = 178.1 Hz, Ar-**C**), 123.1 (Ar-**C**H), 119.7 (d, *J* = 9.4 Hz, Ar-**C**H), 117.4 (d, *J* = 2.6 Hz, Ar-**C**), 111.7 (Ar-**C**H), 58.2 (**C**H_2OH), 55.8 (O**C**H_3), 39.3 (d, *J* = 4.6 Hz, N**C**H_2), 31.1 (**C**H_2); δ_P (162 MHz, $CDCl_3$) 17.9 (Ph**P**=O); HRMS (ESI): calcd. for $C_{17}H_{18}NNaO_5P$, 370.0815. Found: $[MNa]^+$, 370.0818 (–0.9 ppm error).

10-Methoxy-2-phenyl-4,5,6,7-tetrahydro-8*H*-benzo[*d*][1,3,7,2]dioxazaphosphecin-8-one 2-oxide (21c)



3-(3-Hydroxypropyl)-6-methoxy-2-phenyl-3-hydrobenzo[e][1,3,2]oxazaphosphinin-4-one 2-oxide **20c** (160 mg, 0.46 mmol) was dissolved in chloroform (5.0 mL) and triethylamine (700 µL, 5.0 mmol) added, the mixture was stirred overnight at RT, then reduced *in vacuo*. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the *title compound* as a colorless oil (146 mg, 91%). R_f= 0.15 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3299, 2939, 1655, 1536, 1485, 1249, 1196, 1131, 1033, 993, 919, 730, 695, 526; δ_H (400 MHz, $CDCl_3$) 7.71 – 7.60 (m, 2H, Ar-C**H**), 7.49 – 7.42 (m, 1H, Ar-C**H**), 7.38 – 7.31 (m, 2H, Ar-C**H**), 7.29 – 7.22 (m, 1H, Ar-C**H**), 7.06 (d, *J* = 3.2 Hz, 1H, CON**H**), 6.64 (dd, *J* = 9.0, 3.2 Hz, 1H, Ar-C**H**), 6.52 (dd, *J* = 8.9, 1.6 Hz, 1H, Ar-C**H**), 4.66 – 4.55 (m, 1H, OC**H**$_2$), 4.23 (td, *J* = 12.1, 11.9, 6.5 Hz, 1H, OC**H**$_2$), 3.92 – 3.80 (m, 1H, C**H**$_2$), 3.66 (s, 3H, OC**H**$_3$), 3.37 (ddt, *J* = 14.0, 9.5, 4.8 Hz, 1H, C**H**$_2$), 2.31 – 2.17 (m, 1H, C**H**$_2$), 2.01 – 1.88 (m, 1H, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 166.6 (**C**O), 156.7 (d, *J* = 1.7 Hz, Ar-**C**), 141.0 (d, *J* = 9.2 Hz, Ar-**C**), 132. 8 (d, *J* = 3.1 Hz, Ar-**C**H), 131.1 (d, *J* = 10.0 Hz, Ar-**C**H), 130.1 (d, *J* = 2.5 Hz, Ar-**C**), 128.4 (d, *J* = 15.7 Hz, Ar-**C**H), 127.4 (d, *J* = 195.4 Hz, Ar-**C**), 123.1 (d, *J* = 3.7 Hz, Ar-**C**H), 117.9 (Ar-**C**H), 113.1 (Ar-**C**H), 67.7 (d, *J* = 7.7 Hz, O**C**H$_2$), 55.6 (O**C**H$_3$), 38.7 (**C**H$_2$), 28.6 (d, *J* = 2.9 Hz, **C**H$_2$); δ_P (162 MHz, $CDCl_3$) 17.1 (Ph**P**=O); HRMS (ESI): calcd. for $C_{17}H_{18}NNaO_5P$, 370.0815. Found: $[MNa]^+$, 370.0822 (–2.0 ppm error).

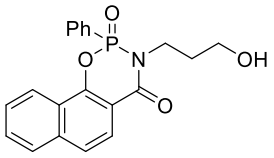
(1-(Benzyloxy)naphthalen-2-yl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone (18d)



2-Phenyl-1,3,2-oxazaphosphinane 2-oxide **8a** (197.2 mg, 1.0 mmol) was dissolved in dry THF (5 mL) and the temperature was lowered –78 °C (dry ice/acetone bath). *n*-BuLi

(2.5 M in hexanes, 0.48 mL, 1.2 mmol, 1.2 eq) was added dropwise by syringe and the reaction was allowed to stir at –78 ℃. After 1 hour, a solution of acid chloride (1.5 mmol, 1.5 equiv. prepared using the general procedure with the acid **S3**) in THF (5 mL) was added slowly to the stirring reaction mixture. The reaction was allowed to warm to room temperature overnight before the addition of sat. aq. $NaHCO_3$ solution (20 mL). The aqueous layer was extracted with EtOAc (2 × 10 mL) and the combined organic layers were dried ($MgSO_4$). After filtration, the solvent was then concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the title compound as a colorless oil (345 mg, 75%). R_f= 0.34 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3061, 1660, 1439, 1358, 1253, 1131, 1060, 998, 745, 722, 694, 623, 533; δ_H (400 MHz, $CDCl_3$) 8.15 – 6.76 (m, 16H, Ar-C**H**), 5.24 – 4.79 (m, 2H, OC**H₂**Ph), 4.60 (dtd, *J* = 11.0, 5.5, 2.6 Hz, 1H, OC**H**$_2$), 4.37 – 4.14 (m, 1H, OC**H**$_2$), 4.08 – 3.60 (m, 2H, C**H₂**), 2.38 – 1.98 (m, 2H, C**H₂**); δ_C (100 MHz, $CDCl_3$) 171.9 (br, **C**O), 151.9 (Ar-**C**), 137.2 (Ar-**C**), 135.7 (Ar-**C**H), 132.5 (d, *J* = 3.0 Hz, Ar-**C**H), 132.1 (d, *J* = 10.9 Hz, Ar-**C**H), 128.5–127.5 (overlapping signals covering 9 carbon atoms), 126.6 (Ar-**C**H), 124.9 (Ar-**C**), 124.5 (Ar-**C**), 122.6 (Ar-**C**H), 77.4 (O**C**H$_2$Ph), 65.8 (d, *J* = 4.9 Hz, O**C**H$_2$), 44.0 (br, **C**H$_2$), 25.9 (d, *J* = 6.6 Hz, **C**H$_2$); δ_P (162 MHz, $CDCl_3$) 14.5 (Ph**P**=O); HRMS (ESI): calcd. for $C_{27}H_{24}NNaO_4P$, 480.1335. Found: $[MNa]^+$, 480.1336 (–0.1 ppm error).

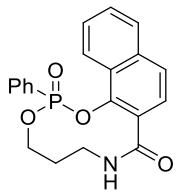
3-(3-Hydroxypropyl)-2-phenyl-3-hydronaphtho[2,1-*e*][1,3,2]oxazaphosphinin-4-one 2-oxide (20d)



(1-(Benzyloxy)naphthalen-2-yl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone **18d** (252 mg, 0.55 mmol) was redissolved in dry EtOAc (6.0 mL) and placed under an argon atmosphere. Palladium on carbon (60 mg, Pd 10% on carbon) was then added and the reaction vessel was backfilled with hydrogen (via balloon) several times, then stirred at RT under a slight positive pressure of hydrogen (balloon) for 4 h. The reaction was then purged with argon, filtered through Celite, washed with

ethyl acetate where the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the *title compound* as a colorless oil (190 mg, 94%). R_f= 0.32 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3457, 1677, 1438, 1383, 1352, 1295, 1265, 1196, 1128, 1089, 928, 822, 761, 732, 693, 567; δ_H (400 MHz, $CDCl_3$) 8.19 (dd, *J* = 8.3, 1.2 Hz, 1H, Ar-C**H**), 8.04 (d, *J* = 8.7 Hz, 1H, Ar-C**H**), 7.83 – 7.73 (m, 3H, Ar-C**H**), 7.64 (dd, *J* = 8.9, 0.9 Hz, 1H, Ar-C**H**), 7.63 – 7.50 (m, 2H, Ar-C**H**), 7.50 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H, Ar-C**H**), 7.46 – 7.39 (m, 2H, Ar-C**H**), 4.12 – 3.95 (m, 1H, NC**H**$_2$), 3.77 – 3.65 (m, 2H, C**H**$_2$OH + CH_2O**H**), 3.62 – 3.44 (m, 2H, C**H**$_2$OH + NC**H**$_2$), 2.07 – 1.77 (m, 2H, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 163.2 (d, *J* = 4.8 Hz, **C**O), 148.5 (d, *J* = 7.5 Hz, Ar-**C**), 137.1 (Ar-**C**), 134.1 (d, *J* = 3.1 Hz, Ar-**C**H), 131.6 (d, *J* = 11.4 Hz, Ar-**C**H), 129.7 (Ar-**C**H), 129.1 (d, *J* = 15.7 Hz, Ar-**C**H), 127.8 (Ar-**C**H), 127.3 (Ar-**C**H), 126.7 (d, *J* = 178.2 Hz, Ar-**C**), 124.4 (Ar-**C**H), 123.8 (Ar-**C**H), 123.7 (d, *J* = 8.1 Hz, Ar-**C**), 122.6 (Ar-**C**H), 111.9 (d, *J* = 2.6 Hz, Ar-**C**), 58.3 (**C**H$_2$OH), 39.3 (d, *J* = 4.5 Hz, N**C**H$_2$), 31.3 (**C**H$_2$); δ_P (162 MHz, $CDCl_3$) 18.9 (Ph**P**=O); HRMS (ESI): calcd. for $C_{20}H_{18}NNaO_4P$, 390.0866. Found: $[MNa]^+$, 390.0868 (–0.6 ppm error).

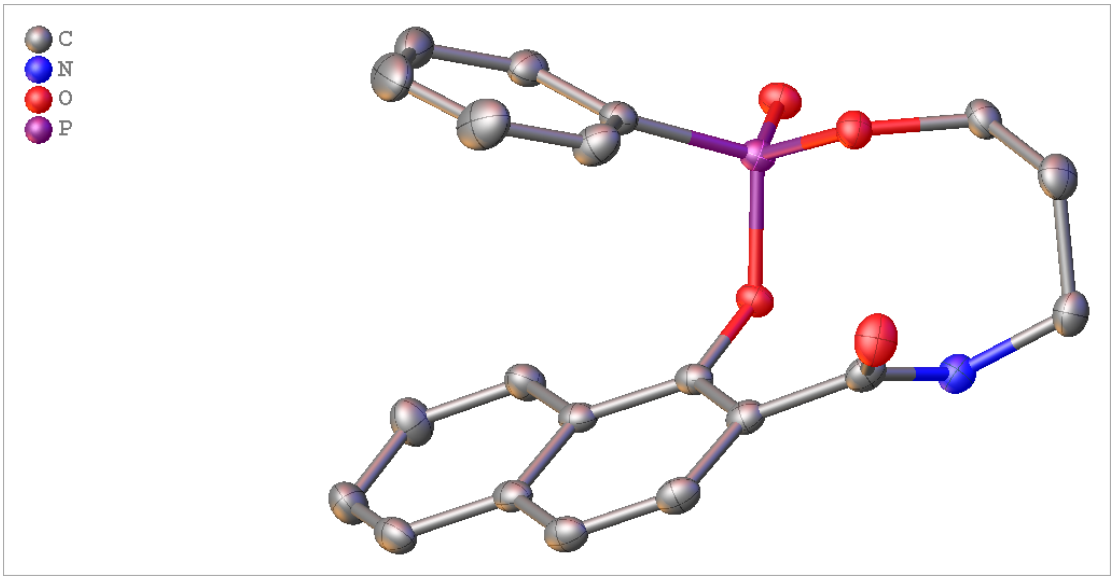
2-Phenyl-4,5,6,7-tetrahydro-8*H*-naphtho[1,2-*d*][1,3,7,2]dioxazaphosphecin-8-one 2-oxide (21d)



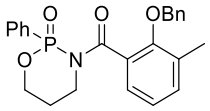
(1-(Benzyloxy)naphthalen-2-yl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone **18d** (230 mg, 0.50 mmol) was redissolved in dry EtOAc (5.0 mL) and placed under an argon atmosphere. Palladium on carbon (50 mg, Pd 10% on carbon) was then added and the reaction vessel was backfilled with hydrogen (via balloon) several times, then stirred at RT under a slight positive pressure of hydrogen (balloon) for 4 h. The reaction was then purged with argon, filtered through Celite, washed with ethyl acetate where the solvent was removed *in vacuo*. The crude was dissolved in chloroform (5.0 mL) and triethylamine (700 µL, 5.0 mmol, 10 eq) added, the mixture

was stirred overnight at RT, then reduced *in vacuo*. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the *title compound* as a colorless oil (110 mg, 60%). R_f= 0.17 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3300, 3065, 2935, 1650, 1536, 1439, 1370, 1252, 1190, 1130, 1039, 993, 907, 814, 749, 695, 512; δ_H (400 MHz, $CDCl_3$) 7.76 – 7.54 (m, 5H, Ar-C**H**), 7.50 – 7.27 (m, 6H, CON**H** + Ar-C**H**), 7.19 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H, Ar-C**H**), 4.73 (dddd, *J* = 11.5, 10.2, 8.8, 1.4 Hz, 1H, OC$\mathbf{H}_2$), 4.37 – 4.21 (m, 1H, OC$\mathbf{H}_2$), 3.95 – 3.82 (m, 1H, NHC$\mathbf{H}_2$), 3.59 – 3.42 (m, 1H, NHC$\mathbf{H}_2$), 2.44 – 2.29 (m, 1H, C$\mathbf{H}_2$), 2.03 – 1.86 (m, 1H, C$\mathbf{H}_2$); δ_C (100 MHz, $CDCl_3$) 167.3 (**C**O), 144.2 (d, *J* = 9.9 Hz, Ar-**C**), 135.4 (Ar-**C**), 132.9 (d, *J* = 3.1 Hz, Ar-**C**), 131.4 (d, *J* = 10.1 Hz, Ar-**C**H), 128.4 (d, *J* = 15.9 Hz, Ar-**C**H), 127.6 (d, *J* = 12.5 Hz, Ar-**C**H), 127.0 (d, *J* = 197.5 Hz, Ar-**C**), 126.8 (d, *J* = 3.6 Hz, Ar-**C**), 126.7 (Ar-**C**H), 125.6 (d, *J* = 1.3 Hz, Ar-**C**H), 125.3 (d, *J* = 1.7 Hz, Ar-**C**H), 125.1 (d, *J* = 3.2 Hz, Ar-**C**H), 122.7 (Ar-**C**H), 67.7 (d, *J* = 7.6 Hz, O**C**H_2), 38.7 (**C**H_2), 28.4 (d, *J* = 2.9 Hz, **C**H_2); δ_P (162 MHz, $CDCl_3$) 16.3 (Ph**P**=O); HRMS (ESI): calcd. for $C_{20}H_{18}NNaO_4P$, 390.0866. Found: $[MNa]^+$, 390.0863 (0.8 ppm error).

X-ray crystallographic data for this compound was recorded; see CCDC2260255 for details.

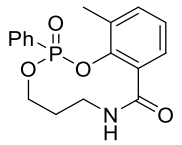


(2-(Benzyloxy)-3-methylphenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone (18e)



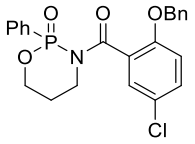
2-Phenyl-1,3,2-oxazaphosphinane 2-oxide **8a** (197.2 mg, 1.0 mmol) was dissolved in dry THF (5 mL) and the temperature was lowered –78 ℃ (dry ice/acetone bath). *n*-BuLi (2.5 M in hexanes, 0.48 mL, 1.2 mmol, 1.2 eq) was added dropwise by syringe and the reaction was allowed to stir at –78 ℃. After 1 hour, a solution of acid chloride (1.5 mmol, 1.5 equiv. prepared using the general procedure with the acid **S4**) in THF (5 mL) was added slowly to the stirring reaction mixture. The reaction was allowed to warm to room temperature overnight before the addition of sat. aq. $NaHCO_3$ solution (20 mL). The aqueous layer was extracted with EtOAc (2 × 10 mL) and the combined organic layers were dried ($MgSO_4$). After filtration, the solvent was then concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the title compound as a colorless oil (220 mg, 52%). R_f= 0.23 (ethyl acetate); ν_{max}/cm^{-1} (neat) 2923, 2237, 1662, 1462, 1440, 1320, 1245, 1215, 1132, 1068, 995, 908, 726, 692, 645, 596; δ_H (400 MHz, $CDCl_3$ at 50 ℃) 7.65 (dd, *J* = 14.5, 7.6 Hz, 2H, Ar-C**H**), 7.46 – 7.09 (m, 10H, Ar-C**H**), 6.98 (t, *J* = 7.5 Hz, 1H, Ar-C**H**), 4.88 – 4.63 (m, 2H, OC**H₂**Ph), 4.53 (dq, *J* = 11.3, 5.7 Hz, 1H, OC**H**$_2$), 4.24 (dddd, *J* = 18.4, 10.9, 7.2, 5.7 Hz, 1H, OC**H**$_2$), 4.02 – 3.56 (m, 2H, C**H₂**), 2.31 – 2.17 (m, 1H, C**H**$_2$), 2.07 (s, 4H, C**H₃** + C**H**$_2$); δ_C (100 MHz, $CDCl_3$ at 50 ℃) 171.5 (br, **C**O), 153.6 (Ar-**C**), 137.5 (Ar-**C**), 133.2 (Ar-**C**H), 132.3 (Ar-**C**H), 132.3 (Ar-**C**H), 132.2 (Ar-**C**H), 132.1 (Ar-**C**H), 131.6 (Ar-**C**), 130.1 (Ar-**C**), 128.3 (Ar-**C**H), 128.0 (Ar-**C**), 127.9 (Ar-**C**H), 127.8 (Ar-**C**H), 127.6 (Ar-**C**H), 126.6 (Ar-**C**), 124.0 (Ar-**C**H), 75.8 (O**C**H_2Ph), 65.7 (d, *J* = 7.8 Hz, O**C**H_2), 43.0 (br, **C**H_2), 25.8 (d, *J* = 6.0 Hz, **C**H_2), 16.0 (**C**H_3); δ_P (162 MHz, $CDCl_3$ at 50 ℃) 14.5 (Ph**P**=O); HRMS (ESI): calcd. for $C_{24}H_{24}NNaO_4P$, 444.1335. Found: $[MNa]^+$, 444.1333 (0.4 ppm error).

12-Methyl-2-phenyl-4,5,6,7-tetrahydro-8*H*-benzo[*d*][1,3,7,2]dioxazaphosphecin-8-one 2-oxide (21e)



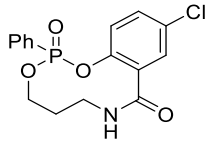
(2-(Benzyloxy)-3-methylphenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone **18e** (167 mg, 0.40 mmol) was redissolved in dry EtOAc (4.0 mL) and placed under an argon atmosphere. Palladium on carbon (40 mg, Pd 10% on carbon) was then added and the reaction vessel was backfilled with hydrogen (via balloon) several times, then stirred at RT under a slight positive pressure of hydrogen (balloon) for 2 h. The reaction was then purged with argon, filtered through Celite, washed with ethyl acetate where the solvent was removed *in vacuo*. The crude was dissolved in chloroform (4.0 mL) and triethylamine (560 µL, 4.0 mmol, 10 eq) added, the mixture was stirred overnight at RT, then reduced *in vacuo*. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the *title compound* as a colorless oil (98 mg, 75%). R_f = 0.20 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3300, 2959, 1649, 1536, 1439, 1315, 1254, 1176, 1130, 1045, 992, 921, 730, 696, 561, 543; δ_H (400 MHz, $CDCl_3$) 7.73 (ddd, *J* = 13.8, 8.2, 1.4 Hz, 2H, Ar-C**H**), 7.50 (td, *J* = 7.4, 1.4 Hz, 1H, Ar-C**H**), 7.43 – 7.32 (m, 3H, Ar-C**H**), 7.11 – 6.99 (m, 3H, CON**H** + Ar-C**H**), 4.59 (dddd, *J* = 11.4, 9.9, 8.5, 1.4 Hz, 1H, OC$\mathbf{H}_2$), 4.24 (dddd, *J* = 13.3, 11.4, 6.8, 1.7 Hz, 1H, OC$\mathbf{H}_2$), 3.96 – 3.81 (m, 1H, NHC$\mathbf{H}_2$), 3.42 (ddt, *J* = 14.2, 9.8, 5.0 Hz, 1H, NHC$\mathbf{H}_2$), 2.34 – 2.20 (m, 1H, C$\mathbf{H}_2$), 2.02 – 1.89 (m, 1H, C$\mathbf{H}_2$), 1.78 (s, 3H, C$\mathbf{H_3}$); δ_C (100 MHz, $CDCl_3$) 167.5 (**C**O), 146.2 (d, *J* = 9.7 Hz, Ar-**C**), 133.2 (Ar-**C**H), 132.8 (d, *J* = 3.3 Hz, Ar-**C**H), 131.2 (d, *J* = 10.1 Hz, Ar-**C**H), 131.0 (d, *J* = 4.2 Hz, Ar-**C**), 130.0 (d, *J* = 2.4 Hz, Ar-**C**), 128.4 (d, *J* = 15.8 Hz, Ar-**C**H), 127.6 (d, *J* = 196.1 Hz, Ar-**C**), 127.1 (d, *J* = 1.8 Hz, Ar-**C**H), 125.4 (d, *J* = 1.7 Hz, Ar-**C**H), 67.5 (d, *J* = 7.7 Hz, O**C**H_2), 38.6 (NH**C**H_2), 28.5(d, *J* = 3.2 Hz, **C**H_2), 17.0 (**C**H_3); δ_P (162 MHz, $CDCl_3$) 15.5 (Ph**P**=O); HRMS (ESI): calcd. for $C_{17}H_{18}NNaO_4P$, 354.0866. Found: $[MNa]^+$, 354.0863 (0.7 ppm error).

(2-(Benzyloxy)-5-chlorophenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone (18f)



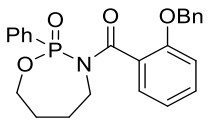
2-Phenyl-1,3,2-oxazaphosphinane 2-oxide **8a** (197.2 mg, 1.0 mmol) was dissolved in dry THF (5 mL) and the temperature was lowered –78 ℃ (dry ice/acetone bath). *n*-BuLi (2.5 M in hexanes, 0.48 mL, 1.2 mmol, 1.2 eq) was added dropwise by syringe and the reaction was allowed to stir at –78 ℃. After 1 hour, a solution of acid chloride (1.5 mmol, 1.5 equiv. prepared using the general procedure with the acid **S5**) in THF (5 mL) was added slowly to the stirring reaction mixture. The reaction was allowed to warm to room temperature overnight before the addition of sat. aq. $NaHCO_3$ solution (20 mL). The aqueous layer was extracted with EtOAc (2 × 10 mL) and the combined organic layers were dried ($MgSO_4$). After filtration, the solvent was then concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the title compound as a colorless oil (255 mg, 58%). R_f = 0.11 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3062, 1663, 1596, 1484, 1407, 1318, 1247, 1127, 1058, 997, 911, 745, 725, 693, 594, 502; δ_H (400 MHz, $CDCl_3$) 7.67 – 7.01 (m, 12H, Ar-C**H**), 6.60 (s, 1H, Ar-C**H**), 5.15 – 4.59 (m, 2H, OC**H₂**Ph), 4.46 (dq, *J* = 11.1, 5.6 Hz, 1H, OC**H**$_2$), 4.16 (dddd, *J* = 18.6, 10.9, 7.8, 5.6 Hz, 1H, OC**H**$_2$), 4.09 – 3.31 (m, 2H, C**H₂**), 2.42 – 1.77 (m, 2H, C**H₂**); δ_C (100 MHz, $CDCl_3$) 168.9 (br, **C**O), 153.1 (br, Ar-**C**), 135.8 (br, Ar-**C**), 132.4 (Ar-**C**H), 131.7 (Ar-**C**H), 131.6 (Ar-**C**H), 130.9 (Ar-**C**H), 128.5 (Ar-**C**H), 128.0 (Ar-**C**H), 127.9 (Ar-**C**H), 127.3 (Ar-**C**H), 125.3 (Ar-**C**), 112.9 (Ar-**C**), 70.2 (O**C**H_2Ph), 65.9 (d, *J* = 7.7 Hz, O**C**H_2), 42.9 (br, **C**H_2), 25.4 (d, *J* = 6.7 Hz, **C**H_2); δ_P (162 MHz, $CDCl_3$) 14.5 (Ph**P**=O); HRMS (ESI): calcd. for $C_{23}H_{21}{}^{35}ClNNaO_4P$, 464.0789. Found: $[MNa]^+$, 464.0798 (–2.0 ppm error).

10-Chloro-2-phenyl-4,5,6,7-tetrahydro-8*H*-benzo[*d*][1,3,7,2]dioxazaphosphecin-8-one 2-oxide (21f)



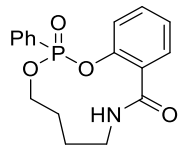
(2-(Benzyloxy)-5-chlorophenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone **18f** (212 mg, 0.48 mmol) was dissolved in dry EtOAc (5.0 mL) and placed under an argon atmosphere. Palladium on carbon (50 mg, Pd 10% on carbon) was then added and the reaction vessel was backfilled with hydrogen (via balloon) several times, then stirred at RT under a slight positive pressure of hydrogen (balloon) for 2 h. The reaction was then purged with argon, filtered through Celite, washed with ethyl acetate where the solvent was removed *in vacuo*. The crude was dissolved in chloroform (5.0 mL) and triethylamine (700 µL, 5.0 mmol, 10 eq) added, the mixture was stirred overnight at RT, then reduced *in vacuo*. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the *title compound* as a colorless oil (100 mg, 60%), contaminated with ≈10% impurity, dechlorinated product **21a**. R_f = 0.19 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3294, 2932, 1653, 1547, 1470, 1439, 1252, 1215, 1131, 1043, 994, 922, 827, 730, 694, 558, 534; δ_H (400 MHz, $CDCl_3$) 7.80 – 7.69 (m, 2H, Ar-C**H**), 7.64 – 7.52 (m, 2H, Ar-C**H**), 7.50 – 7.40 (m, 2H, Ar-C**H**), 7.24 – 7.13 (m, 2H, CON**H** + Ar-C**H**), 6.65 (dd, *J* = 8.7, 1.6 Hz, 1H, Ar-C**H**), 4.78 – 4.56 (m, 1H, OC$\mathbf{H}_2$), 4.42 – 4.25 (m, 1H, OC$\mathbf{H}_2$), 4.03 – 3.86 (m, 1H, NHC$\mathbf{H}_2$), 3.51 – 3.34 (m, 1H, NHC$\mathbf{H}_2$), 2.38 – 2.23 (m, 1H, C$\mathbf{H}_2$), 2.10 – 1.95 (m, 1H, C$\mathbf{H}_2$); δ_C (100 MHz, $CDCl_3$) 165.6 (**C**O), 146.2 (d, *J* = 9.1 Hz, Ar-**C**), 133.3 (d, *J* = 3.3 Hz, Ar-**C**H), 131.7 (Ar-**C**H), 131.4 (d, *J* = 2.2 Hz, Ar-**C**), 131.3 (d, *J* = 10.2 Hz, Ar-**C**H), 129.6 (d, *J* = 1.7 Hz, Ar-**C**H), 129.1 (d, *J* = 15.7 Hz, Ar-**C**), 128.8 (d, *J* = 15.9 Hz, Ar-**C**H), 127.1 (d, *J* = 196.8 Hz, Ar-**C**), 123.7 (d, *J* = 3.8 Hz, Ar-**C**H), 68.2 (d, *J* = 7.8 Hz, O**C**H_2), 39.0 (**C**H_2), 29.0 (d, *J* = 2.7 Hz, **C**H_2); δ_P (162 MHz, $CDCl_3$) 17.5 (Ph**P**=O); HRMS (ESI): calcd. for $C_{16}H_{15}ClNNaO_4P$, 374.0319. Found: $[MNa]^+$, 374.0319 (0.2 ppm error).

(2-(Benzyloxy)phenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphepan-3-yl)methanone (18g)



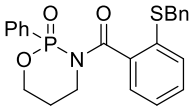
2-Phenyl-1,3,2-oxazaphosphepane 2-oxide **8c** (211.2 mg, 1.0 mmol) was dissolved in dry THF (5 mL) and the temperature was lowered to –78 ℃ (dry ice/acetone bath). *n*-BuLi (2.5 M in hexanes, 0.48 mL, 1.2 mmol, 1.2 eq) was added dropwise by syringe and the reaction was allowed to stir at –78 ℃. After 1 hour, a solution of acid chloride (1.5 mmol, 1.5 equiv. prepared using the general procedure with 2-benzyloxybenzoic acid) in THF (5 mL) was transferred to the stirring reaction mixture slowly. The reaction was allowed to warm to room temperature overnight before the addition of sat. aq. $NaHCO_3$ solution (20 mL). The aqueous layer was extracted with EtOAc (2 × 20 mL), the combined organic layers were dried ($MgSO_4$). After filtration, the solvent was removed by rotary evaporation. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the title compound as a colorless oil (276 mg, 65%). R_f= 0.35 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 2929, 1665, 1599, 1490, 1448, 1326, 1250, 1130, 1019, 955, 747, 721, 695, 579, 542; δ_H (400 MHz, $CDCl_3$ at 50 ℃) 7.73 – 7.53 (m, 2H, Ar-C**H**), 7.48 – 7.38 (m, 1H, Ar-C**H**), 7.34 – 7.18 (m, 8H, Ar-C**H**), 7.18 – 7.01 (m, 1H, Ar-C**H**), 6.93 – 6.78 (m, 2H, Ar-C**H**), 5.04 – 4.74 (m, 2H, OC**H₂**Ph), 4.51 (tt, *J* = 11.7, 5.8 Hz, 1H, OC**H**$_2$), 4.26 (ddd, *J* = 19.5, 14.0, 4.9 Hz, 1H, C**H**$_2$), 4.05 (ddt, *J* = 18.1, 11.1, 3.3 Hz, 1H, OC**H**$_2$), 3.27 – 3.05 (m, 1H, C**H**$_2$), 1.92 – 1.61 (m, 4H, 2 × C**H₂**); δ_C (100 MHz, $CDCl_3$ at 50 ℃) 171.6 (d, *J* = 7.5 Hz, **C**O), 155.1 (Ar-**C**), 136.7 (Ar-**C**), 132.1 (d, *J* = 3.0 Hz, Ar-**C**H), 131.1 (d, *J* = 10.1 Hz, Ar-**C**H), 130.4 (Ar-**C**H), 129.2 (d, *J* = 181.6 Hz, Ar-**C**), 128.2 (Ar-**C**H), 128.0 (d, *J* = 15.3 Hz, Ar-**C**H), 127.6 (Ar-**C**H), 127.2 (Ar-**C** + Ar-**C**H), 120.3 (Ar-**C**H), 112.1 (Ar-**C**H), 70.1 (O**C**H_2Ph), 66.5 (d, *J* = 6.8 Hz, O**C**H_2), 45.5 (br, **C**H_2), 28.5 (**C**H_2), 27.8 (**C**H_2); δ_P (162 MHz, $CDCl_3$ at 50 ℃) 19.6 (Ph**P**=O); HRMS (ESI): calcd. for $C_{24}H_{24}NNaO_4P$, 444.1333. Found: $[MNa]^+$, 444.1335 (0.6 ppm error).

2-Phenyl-5,6,7,8-tetrahydrobenzo[*d*][1,3]dioxa[7]aza[2]phosphacycloundecin-9(4*H*)-one 2-oxide (21g)



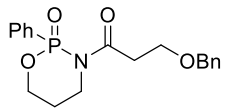
(2-(Benzyloxy)phenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphepan-3-yl)methanone **18g** (118 mg, 0.28 mmol) was redissolved in dry EtOAc (3.0 mL) and placed under an argon atmosphere. Palladium on carbon (30 mg, Pd 10% on carbon) was then added and the reaction vessel was backfilled with hydrogen (via balloon) several times, then stirred at RT under a slight positive pressure of hydrogen (balloon) for 4 h. The reaction was then purged with argon, filtered through Celite, washed with ethyl acetate where the solvent was removed *in vacuo*. The crude was dissolved in chloroform (3.0 mL) and triethylamine (420 µL, 3.0 mmol) added, the mixture was stirred overnight at RT, then reduced *in vacuo*. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the *title compound* as a colorless oil (60 mg, 65%). R_f = 0.19 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3299, 2928, 1645, 1606, 1542, 1481, 1440, 1312, 1252, 1211, 1131, 1008, 993, 923, 741, 695, 531; δ_H (400 MHz, $CDCl_3$) 7.93 – 7.86 (m, 2H, Ar-C**H**), 7.74 (dd, *J* = 7.5, 1.9 Hz, 1H, Ar-C**H**), 7.67 – 7.59 (m, 1H, Ar-C**H**), 7.58 – 7.47 (m, 2H, Ar-C**H**), 7.36 (t, *J* = 5.7 Hz, 1H, CON**H**), 7.33 – 7.27 (m, 1H, Ar-C**H**), 7.25 – 7.19 (m, 1H, Ar-C**H**), 6.80 (dt, *J* = 8.0, 1.1 Hz, 1H, Ar-C**H**), 4.51 – 4.33 (m, 2H, OC**H₂**), 3.86 – 3.68 (m, 1H, NHC**H**$_2$), 3.60 – 3.43 (m, 1H, NHC**H**$_2$), 2.00 – 1.92 (m, 4H, 2 × C**H₂**); δ_C (100 MHz, $CDCl_3$) 165.7 (**C**O), 147.7 (d, *J* = 8.6 Hz, Ar-**C**), 133.3 (d, *J* = 3.1 Hz, Ar-**C**H), 131.9 (d, *J* = 1.4 Hz, Ar-**C**H), 131.7 (d, *J* = 10.4 Hz, Ar-**C**H), 130.5 (d, *J* = 1.3 Hz, Ar-**C**H), 129.3 (d, *J* = 3.2 Hz, Ar-**C**), 128.9 (d, *J* = 15.9 Hz, Ar-**C**H), 127.7 (d, *J* = 196.7 Hz, Ar-**C**), 125.9 (d, *J* = 1.5 Hz, Ar-**C**H), 122.0 (d, *J* = 2.9 Hz, Ar-**C**H), 67.4 (d, *J* = 8.0 Hz, O**C**H_2), 39.7 (**C**H_2), 29.4 (d, *J* = 4.6 Hz, **C**H_2), 24.2 (**C**H_2); δ_P (162 MHz, $CDCl_3$) 17.3 (Ph**P**=O); HRMS (ESI): calcd. for $C_{17}H_{18}NNaO_4P$, 354.0866. Found: $[MNa]^+$, 354.0863 (0.8 ppm error).

(2-(benzylthio)phenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone



2-Phenyl-1,3,2-oxazaphosphinane 2-oxide (197.2 mg, 1.0 mmol) was dissolved in dry THF (5 mL) and the temperature was lowered –78 °C (dry ice/acetone bath). *n*-BuLi (2.5 M in hexanes, 0.48 mL, 1.2 mmol, 1.2 eq) was added dropwise by syringe and the reaction was allowed to stir at –78 °C. After 1 hour, a solution of acid chloride (1.2 mmol, 1.5 equiv. prepared using the general procedure with SBn-acid) in dry THF (5 mL) was added slowly to the stirring reaction mixture. The reaction was allowed to warm to room temperature overnight before the addition of sat. aq. $NaHCO_3$ solution (20 mL). The aqueous layer was extracted with EtOAc (2 × 10 mL) and the combined organic layers were dried ($MgSO_4$). After filtration, the solvent was then concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the title compound as a colorless oil (150 mg, 36%). R_f= 0.17 (ethyl acetate); δ_H (400 MHz, $CDCl_3$) 7.59 (dd, *J* = 14.4, 7.6 Hz, 2H, Ar-C**H**), 7.48 – 7.31 (m, 2H, Ar-C**H**), 7.29 – 7.04 (m, 9H, Ar-C**H**), 6.87 (d, *J* = 7.4 Hz, 1H, Ar-C**H**), 4.56 (dq, *J* = 11.0, 5.4 Hz, 1H, OC**H**$_2$), 4.26 (dddd, *J* = 18.7, 10.9, 7.3, 5.5 Hz, 1H, OC**H**$_2$), 4.01 – 3.56 (m, 4H, SC**H$_2$**Ph + C**H$_2$**), 2.46 – 1.98 (m, 2H, C**H$_2$**); δ_C (100 MHz, $CDCl_3$) 171.2 (d, *J* = 6.8 Hz, **C**O), 137.9 (Ar-**C**), 136.9 (Ar-**C**), 133.2 (Ar-**C**), 132.3 (d, *J* = 3.2 Hz, Ar-**C**H), 131.9 (d, *J* = 10.9 Hz, Ar-**C**H), 131.7 (Ar-**C**H), 129.9 (Ar-**C**H), 128.9 (Ar-**C**H), 128.3 (Ar-**C**H), 128.2 (d, *J* = 181.7 Hz, Ar-**C**), 127.8 (d, *J* = 15.7 Hz, Ar-**C**H), 127.1 (Ar-**C**H), 126.6 (Ar-**C**H), 66.0 (d, *J* = 7.7 Hz, O**C**H$_2$), 43.0 (**C**H$_2$), 39.6 (**C**H$_2$), 25.5 (d, *J* = 6.6 Hz, **C**H$_2$); δ_P (162 MHz, $CDCl_3$) 14.6 (Ph**P**=O); HRMS (ESI): calcd. for $C_{23}H_{22}NNaO_3PS$, 446.0950. Found: $[MNa]^+$, 446.0955 (–1.1 ppm error).

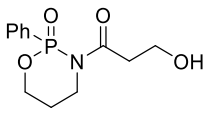
3-(Benzyloxy)-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)propan-1-one (22)



2-Phenyl-1,3,2-oxazaphosphinane 2-oxide **8a** (394.4 mg, 2.0 mmol) was dissolved in THF (10 mL) and the temperature was lowered –78 °C (dry ice/acetone bath). *n*-BuLi

(2.5 M in hexanes, 0.88 mL, 2.2 mmol, 1.1 eq) was added dropwise by syringe and the reaction was allowed to stir at –78 ℃. After 1 hour, a solution of acid chloride (3.0 mmol, 1.5 equiv. prepared using the general procedure with 3-(benzyloxy)propanoic acid) in THF (10 mL) was added slowly to the stirring reaction mixture. The reaction was allowed to warm to room temperature overnight before the addition of sat. aq. $NaHCO_3$ solution (20 mL). The aqueous layer was extracted with EtOAc (2 × 20 mL) and the combined organic layers were dried ($MgSO_4$). After filtration, the solvent was then concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the title compound as a colorless oil (300 mg, 42%). R_f = 0.24 (ethyl acetate); δ_H (400 MHz, $CDCl_3$) 7.80 – 7.66 (m, 2H, Ar-C**H**), 7.57 – 7.50 (m, 1H, Ar-C**H**), 7.46 – 7.36 (m, 2H, Ar-C**H**), 7.31 – 7.20 (m, 5H, Ar-C**H**), 4.56 – 4.45 (m, 2H, OC**H**$_2$ + C**H**$_2$), 4.45 – 4.35 (m, 2H, OC**H$_2$**), 4.24 – 4.13 (m, 1H, OC**H**$_2$), 3.80 – 3.63 (m, 2H, OC**H$_2$**), 3.34 – 3.20 (m, 1H, C**H**$_2$), 3.09 (dt, *J* = 16.5, 5.6 Hz, 1H, C**H**$_2$), 2.86 (ddd, *J* = 16.5, 7.5, 6.0 Hz, 1H, C**H**$_2$), 2.26 – 2.10 (m, 1H, C**H**$_2$), 2.06 – 1.89 (m, 1H, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 173.1 (d, *J* = 7.7 Hz, **C**O), 138.3 (Ar-**C**), 133.0 (d, *J* = 3.1 Hz, Ar-**C**H), 131.3 (d, *J* = 10.9 Hz, Ar-**C**H), 129.0 (d, *J* = 15.4 Hz, Ar-**C**H), 128.9 (d, *J* = 175.1 Hz, Ar-**C**), 128.3 (Ar-**C**H), 127.6 (Ar-**C**H), 127.5 (Ar-**C**H), 72.9 (O**C**H$_2$), 67.1 (d, *J* = 7.9 Hz, O**C**H$_2$), 65.8 (O**C**H$_2$), 41.2 (**C**H$_2$), 37.5 (**C**H$_2$), 25.8 (d, *J* = 5.9 Hz, **C**H$_2$); δ_P (162 MHz, $CDCl_3$) 15.9 (Ph**P**=O); HRMS (ESI): calcd. for $C_{19}H_{22}NNaO_4P$, 382.1179. Found: $[MNa]^+$, 382.1184 (–1.3 ppm error).

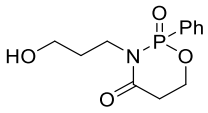
3-Hydroxy-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)propan-1-one (23)



3-(Benzyloxy)-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)propan-1-one **22** (90 mg, 0.25 mmol) was dissolved in dry EtOAc (3.0 mL) and placed under an argon atmosphere. Palladium on carbon (30 mg, Pd 10% on carbon) was then added and the reaction vessel was backfilled with hydrogen (via balloon) several times, then stirred at RT under a slight positive pressure of hydrogen (balloon) for 3 h. The reaction was then purged with argon, filtered through Celite, washed with methanol where the

solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, 9:1 ethyl acetate: methanol) afforded the *title compound* as a colorless oil (50 mg, 56%); R_f= 0.20 (9:1 ethyl acetate: methanol); ν_{max}/cm^{-1} (thin film) 3396, 2890, 1674, 1439, 1381, 1250, 1130, 1018, 912, 749, 727, 695, 539; δ_H (400 MHz, $CDCl_3$) 7.78 – 7.66 (m, 2H, Ar-C**H**), 7.59 – 7.53 (m, 1H, Ar-C**H**), 7.53 – 7.42 (m, 2H, Ar-C**H**), 4.49 (tt, *J* = 10.9, 5.3 Hz, 2H, OC**H**$_2$ + C**H**$_2$), 4.21 (dddd, *J* = 14.1, 11.0, 8.8, 5.4 Hz, 1H, OC**H**$_2$), 3.81 (ddd, *J* = 11.1, 6.9, 4.0 Hz, 1H, C**H**$_2$OH), 3.71 (ddd, *J* = 11.2, 6.9, 4.0 Hz, 1H, C**H**$_2$OH), 3.36 – 3.02 (m, 3H, C**H$_2$** + CH$_2$O**H**), 2.50 (ddd, *J* = 16.7, 6.9, 4.1 Hz, 1H, C**H**$_2$), 2.19 (dtt, *J* = 14.8, 10.3, 5.2 Hz, 1H, C**H**$_2$), 2.07 – 1.94 (m, 1H, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 174.7 (d, *J* = 7.9 Hz, **C**O), 133.3 (d, *J* = 3.1 Hz, Ar-**C**H), 131.2 (d, *J* = 10.8 Hz, Ar-C**H**), 129.1 (d, *J* = 15.3 Hz, Ar-C**H**), 128.7 (d, *J* = 176.1 Hz, Ar-**C**), 67.0 (d, *J* = 7.9 Hz, O**C**H$_2$), 58.6 (O**C**H$_2$), 41.1 (**C**H$_2$), 39.5 (**C**H$_2$), 25.7 (d, *J* = 6.0 Hz, **C**H$_2$); δ_P (162 MHz, $CDCl_3$) 16.3 (Ph**P**=O); HRMS (ESI): calcd. for $C_{12}H_{16}NNaO_4P$, 292.0709. Found: $[MNa]^+$, 292.0710 (–0.3 ppm error).

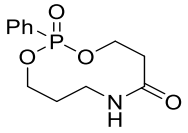
3-(3-Hydroxypropyl)-2-phenyl-1,3,2-oxazaphosphinan-4-one 2-oxide (24)



3-Hydroxy-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)propan-1-one **23** (50 mg, 0.185 mmol) was dissolved in $CHCl_3$ (2.0 mL) and NEt_3 (280 µL, 2.0 mmol, 10 eq) was added, the mixture was stirred at RT overnight. Purification by flash column chromatography (SiO_2, 10:1 ethyl acetate: methanol) afforded the *title compound* as a colorless oil (35 mg, 70%); R_f= 0.40 (9:1 ethyl acetate: methanol); ν_{max}/cm^{-1} (thin film) 3415, 2950, 1683, 1440, 1336, 1282, 1244, 1127, 1024, 994, 943, 725, 693, 539; δ_H (400 MHz, $CDCl_3$) 7.82 – 7.70 (m, 2H, Ar-C**H**), 7.65 – 7.58 (m, 1H, Ar-C**H**), 7.55 – 7.47 (m, 2H, Ar-C**H**), 4.68 (tdd, *J* = 11.5, 8.8, 3.2 Hz, 1H, OC**H**$_2$), 4.36 (dddd, *J* = 22.1, 11.5, 5.5, 3.2 Hz, 1H, OC**H**$_2$), 3.79 – 3.58 (m, 3H, C**H$_2$** + CH$_2$O**H**), 3.58 – 3.47 (m, 1H, C**H**$_2$), 3.18 (dtd, *J* = 14.2, 9.2, 5.1 Hz, 1H, C**H**$_2$), 3.01 (ddd, *J* = 17.0, 11.2, 5.6 Hz, 1H, C**H**$_2$), 2.84 (dt, *J* = 17.9, 3.0 Hz, 1H, C**H**$_2$), 1.84 (tdd, *J* = 14.4, 5.3, 3.5 Hz, 1H, C**H**$_2$), 1.68 (ddq, *J* = 14.1, 9.3, 4.7 Hz, 1H, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 170.2 (d, *J* = 3.9 Hz, **C**O), 133.9 (d, *J* = 3.1 Hz,

Ar-**C**H), 132.4 (d, *J* = 10.8 Hz, Ar-**C**H), 129.1 (d, *J* = 15.4 Hz, Ar-**C**H), 126.4 (d, *J* = 179.9 Hz, Ar-**C**), 61.7 (d, *J* = 6.3 Hz, O**C**H_2), 58.3 (**C**H_2OH), 39.2 (d, *J* = 4.7 Hz, N**C**H_2), 35.2 (**C**H_2), 30.7 (**C**H_2); δ_P (162 MHz, $CDCl_3$) 19.9 (Ph**P**=O); HRMS (ESI): calcd. for $C_{12}H_{16}NNaO_4P$, 292.0709. Found: $[MNa]^+$, 292.0712 (–0.8 ppm error).

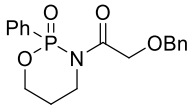
2-Phenyl-1,3,7,2-dioxazaphosphecan-6-one 2-oxide (25)



3-Hydroxy-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)propan-1-one **23** (150 mg, 0.56 mmol) was dissolved in THF (6.0 mL) and NaH (60% in paraffin oil, 36 mg, 0.9 mmol, 1.5 eq) was added, the mixture was stirred at RT for 3 h. Quenched with sat. NH_4Cl aq. (5 mL), extracted with EtOAc (3 × 10 mL) and the combined organic layers were dried ($MgSO_4$). After filtration, the solvent was then concentrated *in vacuo* to give the *title compound* (as a 10:1 mixture of rotamers in solution in $CDCl_3$) as a colorless oil (102 mg, 68%); R_f = 0.15 (9:1 ethyl acetate: methanol); ν_{max}/cm^{-1} (thin film) 3291, 2960, 1654, 1559, 1439, 1235, 1132, 1071, 1006, 936, 748, 697, 562; δ_H (400 MHz, $CDCl_3$) 7.76 – 7.67 (m, 2H, Ar-C**H**, both rotamers), 7.57 – 7.50 (m, 1H, Ar-C**H**, both rotamers), 7.50 – 7.38 (m, 2H, Ar-C**H**, both rotamers), 6.74 (t, *J* = 6.1Hz, 1H, CON**H**, major rotamer), 6.35 (s, 1H, CON**H**, minor rotamer), 4.88 – 4.75 (m, 1H, C**H**$_2$, minor rotamer), 4.73 – 4.44 (m, 2H, OC**H**$_2$, both rotamers), 4.35 – 4.04 (m, 2H, OC**H**$_2$, both rotamers), 3.81 – 3.56 (m, 1H, C**H**$_2$, major rotamer), 3.51 – 3.24 (m, 1H, C**H**$_2$, both rotamers), 2.80 – 2.44 (m, 2H, C**H$_2$**, both rotamers), 2.32 – 2.13 (m, 1H, C**H**$_2$, both rotamers), 1.99 – 1.69 (m, 1H, C**H**$_2$, both rotamers); δ_C (100 MHz, $CDCl_3$) data for major rotamer only: 171.3 (**C**O), 132.6 (d, *J* = 3.0 Hz, Ar-**C**H), 131.1 (d, *J* = 10.1 Hz, Ar-**C**H), 128.7 (d, *J* = 15.6 Hz, Ar-**C**H), 128.6 (d, *J* = 196.3 Hz, Ar-**C**), 67.5 (d, *J* = 7.0 Hz, O**C**H_2), 64.7 (d, *J* = 7.6 Hz, O**C**H_2), 39.2 (**C**H_2), 38.8 (**C**H_2), 28.6 (d, *J* = 4.5 Hz, **C**H_2); Diagnostic ^{13}C NMR resonances for the minor rotamer: 173.4 (**C**O), 132.7 (d, *J* = 3.0 Hz, Ar-**C**H), 131.2 (d, *J* = 9.8 Hz, Ar-**C**H), 128.7 (d, *J* = 15.3 Hz, Ar-**C**H), 64.4 (d, *J* = 7.1 Hz, O**C**H_2), 30.3 (d, *J* = 6.3 Hz, **C**H_2); δ_P (162 MHz, $CDCl_3$) 19.0 (Ph**P**=O, major rotamer), 18.7 (Ph**P**=O,

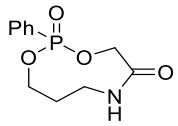
minor rotamer); HRMS (ESI): calcd. for $C_{12}H_{16}NNaO_4P$, 292.0709. Found: $[MNa]^+$, 292.0713 (–1.2 ppm error).

2-(Benzyloxy)-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)ethan-1-one (26)



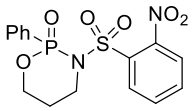
2-Phenyl-1,3,2-oxazaphosphinane 2-oxide **8a** (197.2 mg, 1.0 mmol) was dissolved in dry THF (5 mL) and the temperature was lowered –78 ℃ (dry ice/acetone bath). *n*-BuLi (2.5 M in hexanes, 0.48 mL, 1.2 mmol, 1.2 eq) was added dropwise by syringe and the reaction was allowed to stir at –78 ℃. After 1 hour, a solution of acid chloride (1.5 mmol, 1.5 equiv. prepared using the general procedure with benzyloxyacetic acid) in THF (5 mL) was added slowly to the stirring reaction mixture. The reaction was allowed to warm to room temperature overnight before the addition of sat. aq. $NaHCO_3$ solution (20 mL). The aqueous layer was extracted with EtOAc (2 × 20 mL) and the combined organic layers were dried ($MgSO_4$). After filtration, the solvent was then concentrated *in vacuo*. Purification by flash column chromatography (SiO_2, 1:1 hexane: ethyl acetate → ethyl acetate) afforded the *title compound* as a yellow oil (280 mg, 81%). R_f = 0.22 (ethyl acetate); δ_H (400 MHz, $CDCl_3$) 7.63 – 7.53 (m, 2H, Ar-C**H**), 7.50 – 7.43 (m, 1H, Ar-C**H**), 7.42 – 7.30 (m, 2H, Ar-C**H**), 7.20 – 7.11 (m, 5H, Ar-C**H**), 4.59 – 4.45 (m, 2H, 1 H each from OC**H**$_2$ + C**H**$_2$), 4.45 (s, 2H, OC**H**$_2$), 4.37 (ddt, *J* = 15.5, 10.2, 5.1 Hz, 1H, OC**H**$_2$), 4.25 (d, *J* = 16.1 Hz, 1H, OC**H**$_2$), 4.08 (tdd, *J* = 11.1, 9.5, 4.9 Hz, 1H, OC**H**$_2$), 3.10 (ddt, *J* = 13.9, 11.2, 3.0 Hz, 1H, C**H**$_2$), 2.04 (dtq, *J* = 14.8, 10.2, 5.0 Hz, 1H, C**H**$_2$), 1.84 (dq, *J* = 14.3, 4.5, 3.9 Hz, 1H, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 171.8 (d, *J* = 7.6 Hz, **C**O), 137.0 (Ar-**C**), 132.8 (d, *J* = 3.1 Hz, Ar-**C**H), 130.7 (d, *J* = 10.8 Hz, Ar-**C**H), 128.8 (d, *J* = 173.7 Hz, Ar-**C**), 128.8 (d, *J* = 15.1 Hz, Ar-**C**H), 128.0 (Ar-**C**H), 127.7 (Ar-**C**H), 127.5 (Ar-**C**H), 73.0 (O**C**H$_2$), 70.1 (O**C**H$_2$), 67.3 (d, *J* = 8.0 Hz, O**C**H$_2$), 40.8 (**C**H$_2$), 25.3 (d, *J* = 5.5 Hz, **C**H$_2$); δ_P (162 MHz, $CDCl_3$) 15.4 (Ph**P**=O); HRMS (ESI): calcd. for $C_{18}H_{20}NNaO_4P$, 368.1022. Found: $[MNa]^+$, 368.1023 (–0.2 ppm error).

2-Phenyl-1,3,6,2-dioxazaphosphonan-5-one 2-oxide (27)



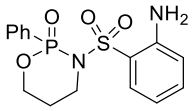
2-(Benzyloxy)-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)ethan-1-one **26** (300 mg, 0.87 mmol) was dissolved in dry EtOAc (9.0 mL) and placed under an argon atmosphere. Palladium on carbon (90 mg, Pd 10% on carbon) was then added and the reaction vessel was backfilled with hydrogen (via balloon) several times, then stirred at RT under a slight positive pressure of hydrogen (balloon) for 4 h. The reaction was then purged with argon, filtered through Celite, washed with methanol where the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, 9:1 ethyl acetate: methanol) afforded the *title compound* (a 5:3:1 mixture of rotamers at RT) as a colorless oil (170 mg, 77%); R_f= 0.22 (9:1 ethyl acetate: methanol); ν_{max}/cm^{-1} (thin film) 3476, 3278, 2963, 1664, 1475, 1439, 1235, 1132, 1078, 1051, 977, 828, 750, 695, 580, 548, 508; δ_H (400 MHz, $CDCl_3$ at 50 ℃, exists in $CDCl_3$ solution as a roughly 3:2 mixture of rotamers based on analysis of the ^{13}C NMR spectrum) 7.84 – 7.37 (m, 11H, Ar-C**H** both rotamers + CON**H** one rotamer), 6.91 (d, *J* = 8.4 Hz, 1H, CON**H** one rotamer), 5.10 (dd, *J* = 14.4, 9.4 Hz, 1H, OC**H**$_2$, one rotamer), 4.78 – 4.36 (m, 4H, C**H$_2$**, both rotamers), 4.29 – 3.79 (m, 5H, C**H$_2$** both rotamers + OC**H**$_2$ one rotamer), 3.53 (td, *J* = 11.8, 5.1 Hz, 1H, C**H**$_2$, one rotamer), 3.16 – 2.25 (m, 2H, C**H**$_2$, both rotamers), 2.00 – 1.43 (m, 3H, C**H**$_2$ both rotamers + C**H**$_2$ one rotamer); δ_C (100 MHz, $CDCl_3$ at 50 ℃, a 3:2 mixture of rotamers) 170.4 (NH**C**O, major rotamer), 169.1 (NH**C**O, minor rotamer), 132.8 (d, *J* = 3.3 Hz, Ar-**C**H, both rotamers), 131.2 (d, *J* = 10.0 Hz, Ar-**C**H, both rotamers), 128.5 (d, *J* = 15.8 Hz, Ar-**C**H, both rotamers), 126.6 (Ar-**C**, both rotamers), 67.7 (brs, O**C**H$_2$, minor rotamer), 67.0 (brs, O**C**H$_2$, minor rotamer), 64.7 (d, *J* = 7.8 Hz, O**C**H$_2$, major rotamer), 62.2 (d, *J* = 7.5 Hz, O**C**H$_2$, major rotamer), 38.8 (**C**H$_2$, minor rotamer), 38.2 (**C**H$_2$, major rotamer), 30.6 (**C**H$_2$, major rotamer), 25.5 (**C**H$_2$, minor rotamer); δ_P (162 MHz, $CDCl_3$) 20.2 (Ph**P**=O): 20.7 (Ph**P**=O): 21.4 (PhP=O) = 5:3:1; HRMS (ESI): calcd. for $C_{11}H_{14}NNaO_4P$, 278.0553. Found: $[MNa]^+$, 278.0551 (0.5 ppm error).

3-((2-Nitrophenyl)sulfonyl)-2-phenyl-1,3,2-oxazaphosphinane 2-oxide (28)



2-Phenyl-1,3,2-oxazaphosphinane 2-oxide **8a** (197.2 mg, 1.0 mmol) was dissolved in dry THF (8 mL) and the temperature was lowered to –78 ℃ (dry ice/acetone bath). *n*-BuLi (2.5 M in hexanes, 0.48 mL, 1.2 mmol, 1.2 eq) was added dropwise by syringe and the reaction was allowed to stir at –78 ℃. After 1 hour, a solution of 2-nitrobenzenesulfonyl chloride (332.4 mg, 1.5 mmol, 1.5 eq) in THF (2.0 mL) was transferred to the stirring reaction mixture dropwise by syringe. The reaction was allowed to warm to room temperature overnight before the addition of sat. aq. $NaHCO_3$ solution (15 mL). The aqueous layer was extracted with EtOAc (2 × 15 mL), the combined organic layers were dried ($MgSO_4$). After filtration, the solvent was removed by rotary evaporation. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the title compound as a colorless oil (93 mg, 25%). R_f= 0.30 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3096, 1542, 1439, 1362, 1249, 1169, 1129, 1056, 987, 845, 782, 745, 694, 582, 511; δ_H (400 MHz, $CDCl_3$) 8.44 – 8.38 (m, 1H, Ar-C**H**), 7.92 – 7.83 (m, 2H, Ar-C**H**), 7.71 – 7.54 (m, 4H, Ar-C**H**), 7.53 – 7.42 (m, 2H, Ar-C**H**), 4.52 – 4.36 (m, 1H, OC**H**$_2$), 4.29 – 4.05 (m, 2H, C**H**$_2$ + OC**H**$_2$), 3.57 (ddt, *J* = 13.8, 9.9, 3.8 Hz, 1H, C**H**$_2$), 2.43 – 2.23 (m, 1H, C**H**$_2$), 2.10 – 1.95 (m, 1H, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 148.0 (Ar-**C**), 134.3 (Ar-**C**H), 133.6 (Ar-**C**), 133.3 (d, *J* = 3.2 Hz, Ar-**C**H), 133.2 (Ar-**C**H), 132.2 (Ar-**C**H), 131.9 (d, *J* = 11.1 Hz, Ar-**C**H), 128.9 (d, *J* = 15.8 Hz, Ar-**C**H), 127.7 (d, *J* = 178.0 Hz, Ar-**C**), 123.7 (Ar-**C**H), 67.5 (d, *J* = 7.8 Hz, O**C**H$_2$), 46.2 (**C**H$_2$), 26.0 (d, *J* = 4.6 Hz, **C**H$_2$); δ_P (162 MHz, $CDCl_3$) 14.5 (Ph**P**=O); HRMS (ESI): calcd. for $C_{15}H_{15}N_2NaO_6PS$, 405.0281. Found: $[MNa]^+$, 405.0291 (–2.5 ppm error).

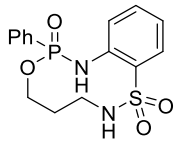
3-((2-Aminophenyl)sulfonyl)-2-phenyl-1,3,2-oxazaphosphinane 2-oxide (28a)



3-((2-Nitrophenyl)sulfonyl)-2-phenyl-1,3,2-oxazaphosphinane 2-oxide **28** (85 mg, 0.22

mmol) was dissolved in dry EtOAc (3.0 mL) and placed under an argon atmosphere. Palladium on carbon (30 mg, Pd 10% on carbon) was added and the reaction vessel was backfilled with hydrogen (via balloon) several times, then stirred at RT under a slight positive pressure of hydrogen (balloon) for 2 h. The reaction was then purged with argon, filtered through Celite, washed with ethyl acetate where the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, ethyl acetate) afforded the title compound as a colorless oil (60 mg, 77%). R_f= 0.44 (ethyl acetate); ν_{max}/cm^{-1} (thin film) 3354, 3241, 2926, 1603, 1485, 1454, 1332, 1246, 1153, 1130, 1092, 994, 902, 850, 749, 696, 595, 508; δ_H (400 MHz, $CDCl_3$) 7.99 – 7.85 (m, 2H, Ar-C**H**), 7.70 (dd, *J* = 8.2, 1.6 Hz, 1H, Ar-C**H**), 7.61 – 7.54 (m, 1H, Ar-C**H**), 7.53 – 7.45 (m, 2H, Ar-C**H**), 7.29 (ddd, *J* = 8.5, 7.1, 1.6 Hz, 1H, Ar-C**H**), 6.72 (dd, *J* = 8.3, 1.1 Hz, 1H, Ar-C**H**), 6.65 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H, Ar-C**H**), 5.69 (s, 2H, N**H₂**), 4.46 – 4.37 (m, 1H, OC**H**$_2$), 4.17 (dddd, *J* = 15.4, 11.1, 7.2, 5.7 Hz, 1H, OC**H**$_2$), 3.64 – 3.43 (m, 2H, C**H₂**), 2.07 – 1.91 (m, 2H, C**H₂**); δ_C (100 MHz, $CDCl_3$) 146.7 (Ar-**C**), 135.3 (Ar-**C**H), 133.0 (d, *J* = 3.3 Hz, Ar-**C**H), 131.8 (d, *J* = 11.3 Hz, Ar-**C**H), 131.1 (Ar-**C**H), 129.5(d, *J* = 183.5 Hz, Ar-**C**), 128.8 (d, *J* = 16.0 Hz, Ar-**C**H), 117.9 (Ar-**C**H), 117.2 (Ar-**C**), 116.0 (Ar-**C**H), 66.0 (d, *J* = 8.1 Hz, O**C**H$_2$), 45.0 (**C**H$_2$), 25.7 (d, *J* = 5.3 Hz, **C**H$_2$); δ_P (162 MHz, $CDCl_3$) 13.7 (Ph**P**=O); HRMS (ESI): calcd. for $C_{15}H_{17}N_2NaO_4PS$, 375.0539. Found: $[MNa]^+$, 375.0530 (2.3 ppm error).

2-Phenyl-1,4,5,6,7-pentahydrobenzo[*d*][1,6,3,7,2]oxathiadiazaphosphecine 2,8,8-trioxide (29)

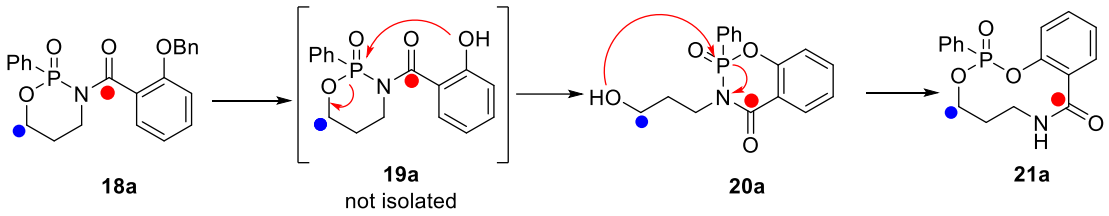


3-((2-Aminophenyl)sulfonyl)-2-phenyl-1,3,2-oxazaphosphinane 2-oxide **28a** (60 mg, 0.17 mmol) was dissolved in THF (2.0 mL) and NaH (60% in Paraffin oil, 12 mg, 0.3 mmol, 1.5 eq) was added, the mixture was stirred at RT for 1 h. Quenched with sat. NH_4Cl aq. (5 mL), extracted with EtOAc (3 × 10 mL) and the combined organic layers were dried ($MgSO_4$). After filtration, the solvent was then concentrated *in vacuo* to give the title compound as a colorless oil (55 mg, 92%); R_f= 0.25 (ethyl acetate);

ν_{max}/cm^{-1} (thin film) 3301, 3135, 2923, 1594, 1481, 1459, 1315, 1273, 1229, 1149, 1127, 1052, 975, 926, 734, 692, 606, 535; δ_H (400 MHz, $CDCl_3$) 7.95 – 7.83 (m, 3H, Ar-C**H**), 7.75 (d, *J* = 8.2 Hz, 1H, Ar-C**H**), 7.64 – 7.57 (m, 1H, Ar-C**H**), 7.55 – 7.44 (m, 3H, Ar-C**H**), 7.18 – 7.09 (m, 1H, Ar-C**H**), 6.15 (d, *J* = 9.3 Hz, 1H, N**H**), 5.38 (dd, *J* = 8.4, 4.1 Hz, 1H, SO_2N**H**), 4.31 – 4.20 (m, 1H, OC**H**$_2$), 3.99 – 3.87 (m, 1H, OC**H**$_2$), 3.68 (dddd, *J* = 14.6, 11.7, 8.4, 3.6 Hz, 1H, C**H**$_2$), 3.35 (dq, *J* = 14.3, 4.2 Hz, 1H, C**H**$_2$), 1.90 – 1.77 (m, 1H, C**H**$_2$), 1.67 – 1.50 (m, 1H, C**H**$_2$); δ_C (100 MHz, $CDCl_3$) 137.8 (d, *J* = 2.5 Hz, Ar-**C**), 134.0 (Ar-**C**H), 133.1 (d, *J* = 3.1 Hz, Ar-**C**H), 132.7 (d, *J* = 5.7 Hz, Ar-**C**), 131.2 (d, *J* = 10.1 Hz, Ar-**C**H), 129.5 (d, *J* = 185.8 Hz, Ar-**C**), 128.9 (Ar-**C**H), 128.8 (d, *J* = 15.0 Hz, Ar-**C**H), 126.1 (Ar-**C**H), 123.6 (Ar-**C**H), 61.8 (d, *J* = 7.0 Hz, O**C**H$_2$), 40.3 (**C**H$_2$), 29.3 (d, *J* = 4.3 Hz, **C**H$_2$); δ_P (162 MHz, $CDCl_3$) 19.3 (Ph**P**=O); HRMS (ESI): calcd. for $C_{15}H_{17}N_2NaO_4PS$, 375.0539. Found: $[MNa]^+$, 375.0532 (1.9 ppm error).

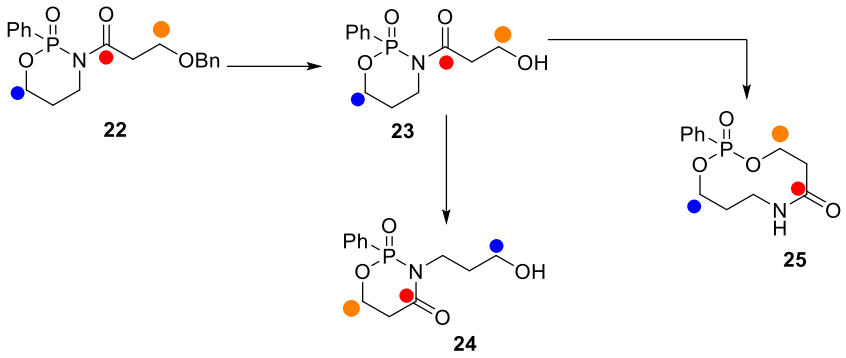
5) Assignment of isomers based on ^{13}C-^{31}P coupling in the ^{13}C NMR

Observing which ^{13}C nuclei couple to ^{31}P in the ^{13}C NMR spectra provided a convenient way to distinguish isomer species in this study, by enabling the proximity of different C-atoms to P to be mapped as the rearrangement progresses. This method is summarised in the Tables below (^{13}C-^{31}P coupling in the ^{13}C NMR in all compounds is also indicated in the induvial data write ups in section 4)



	18a (50 °C)	**20a**	**21a**
^{13}C CO	170.7 d, *J* = 5.8 Hz	162.9 d, *J* = 4.8 Hz	167.0
^{13}C CH_2	69.9 OCH_2Ph		
	65.7 d, *J* = 5.7 Hz, OCH_2	58.3 (CH_2OH)	67.9 d, *J* = 7.8 Hz, OCH_2
	43.0 (CH_2)	39.3 d, *J* = 4.6 Hz, NCH_2	38.9 (CH_2)
	25.5 d, *J* = 6.5 Hz, CH_2	31.2 (CH_2)	28.9 d, *J* = 2.7 Hz, CH_2
^{31}P	14.8	17.7	17.1
^{1}H OH or NH		3.58 – 3.36 (m, 3H, NCH_2 + CH_2OH + CH_2OH)	7.24 – 7.08 (m, 3H, Ar-CH + NHCO)

Table S6

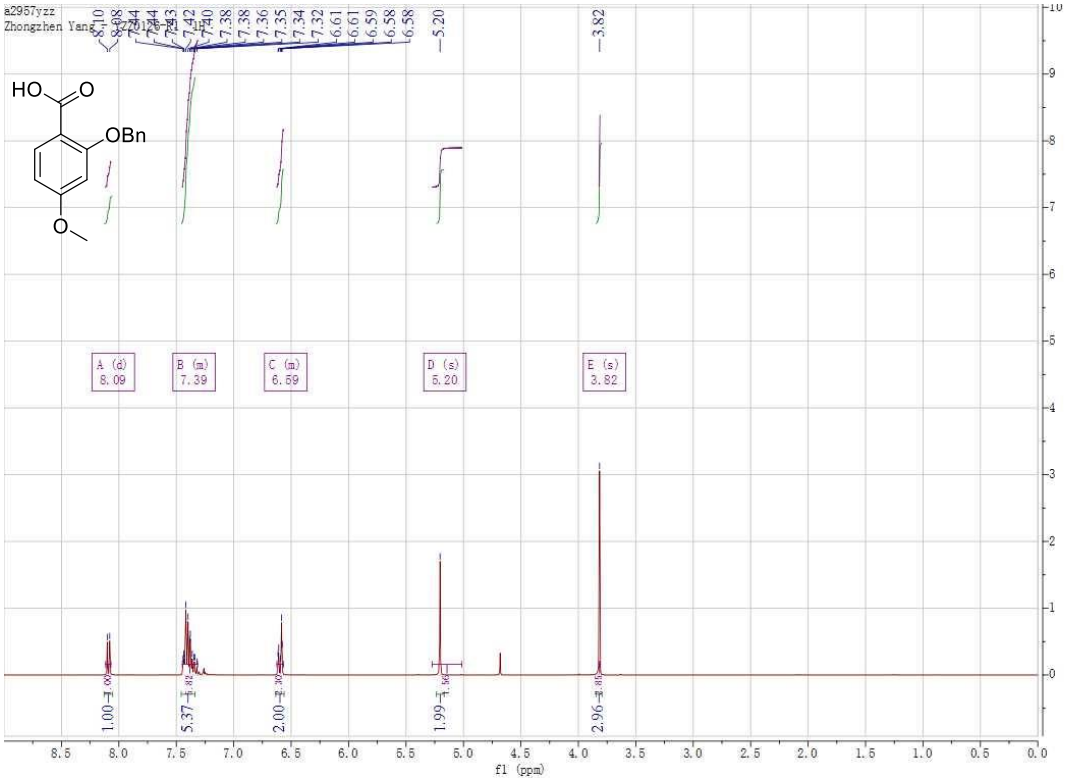


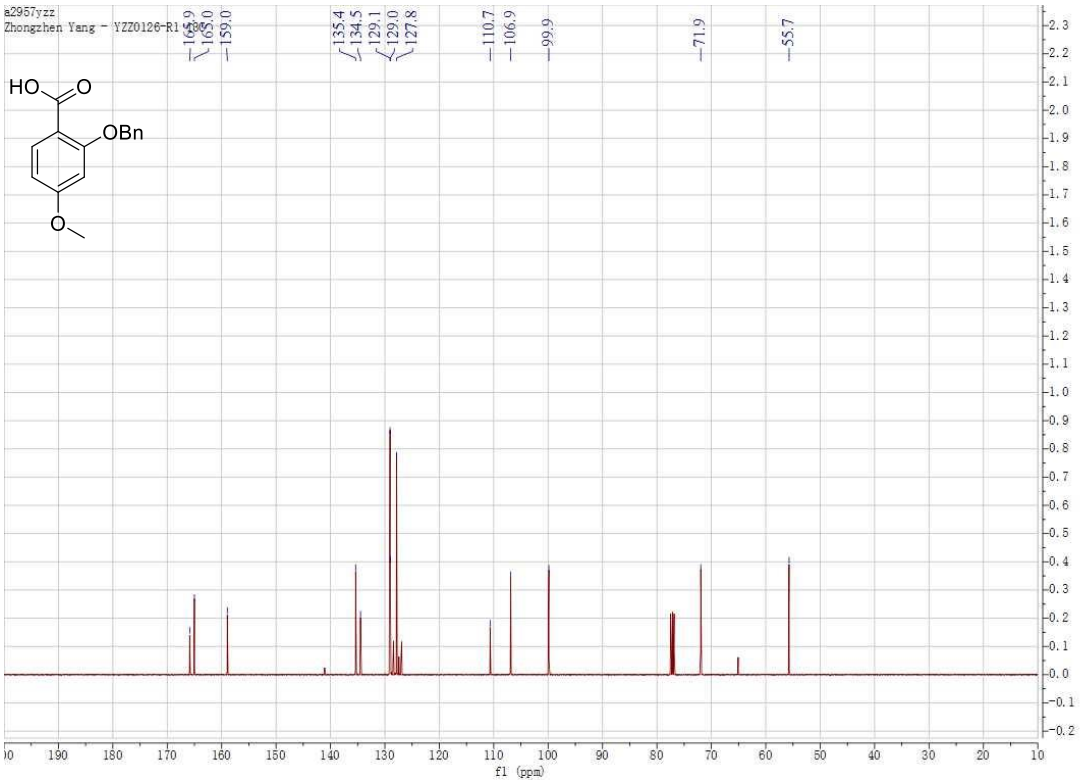
	22	23	24	25
^{13}**C** **C**O	173.1 d, *J* = 7.7 Hz	174.7 d, *J* = 7.9 Hz	170.2 d, *J* = 3.9 Hz	171.3 (major) 173.4 (minor)
^{13}**C** **C**H$_2$	72.9 (O**C**H$_2$Ph),			
	67.1 d, *J* = 7.9 Hz, O**C**H$_2$	67.0 d, *J* = 7.9 Hz, O**C**H$_2$	61.7 d, *J* = 6.3 Hz, O**C**H$_2$	67.5 d, *J* = 7.0 Hz, O**C**H$_2$
	65.8 (O**C**H$_2$),	58.6 (**C**H$_2$OH)	58.3 (O**C**H$_2$)	64.7 d, *J* = 7.6 Hz, O**C**H$_2$
	41.2 (**C**H$_2$)	41.1 (**C**H$_2$)	39.2 d, *J* = 4.7 Hz, **C**H$_2$	39.2 (**C**H$_2$)
	37.5 (**C**H$_2$)	39.5 (**C**H$_2$)	35.2 (**C**H$_2$)	38.8 (**C**H$_2$)
	25.8 d, *J* = 5.9 Hz, **C**H$_2$	25.7 d, *J* = 6.0 Hz, **C**H$_2$	30.7 (**C**H$_2$)	28.6 d, *J* = 4.5 Hz, **C**H$_2$
^{31}**P**	15.9	16.3	19.9	19.0 (major) 18.7 (minor)
^{1}**H** O**H** or N**H**		3.36 – 3.02 (m, 3H, C**H$_2$** + CH$_2$O**H**)	3.79 – 3.58 (m, 3H, C**H**$_2$OH + CH$_2$O**H** + C**H**$_2$)	6.74 (t, *J* = 6.1Hz, 1H, CON**H**, major), 6.35 (s, 1H, CON**H**, minor)

Table S7

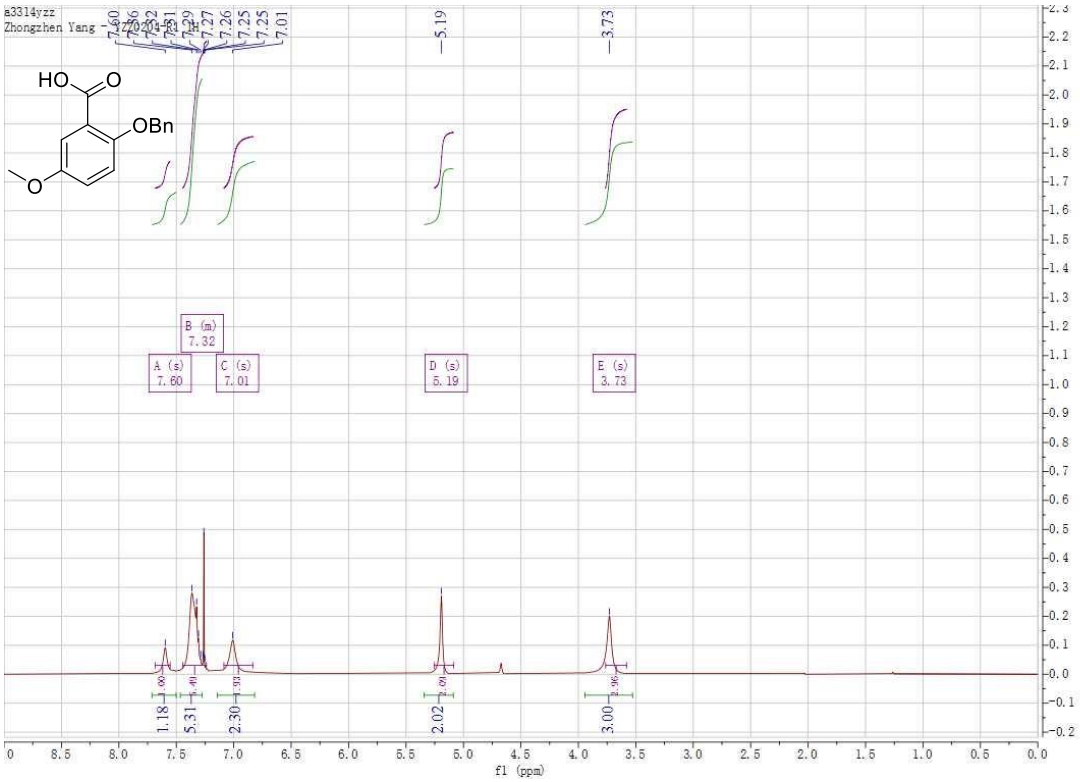
6) ^{1}H, ^{13}C and ^{31}P NMR spectra

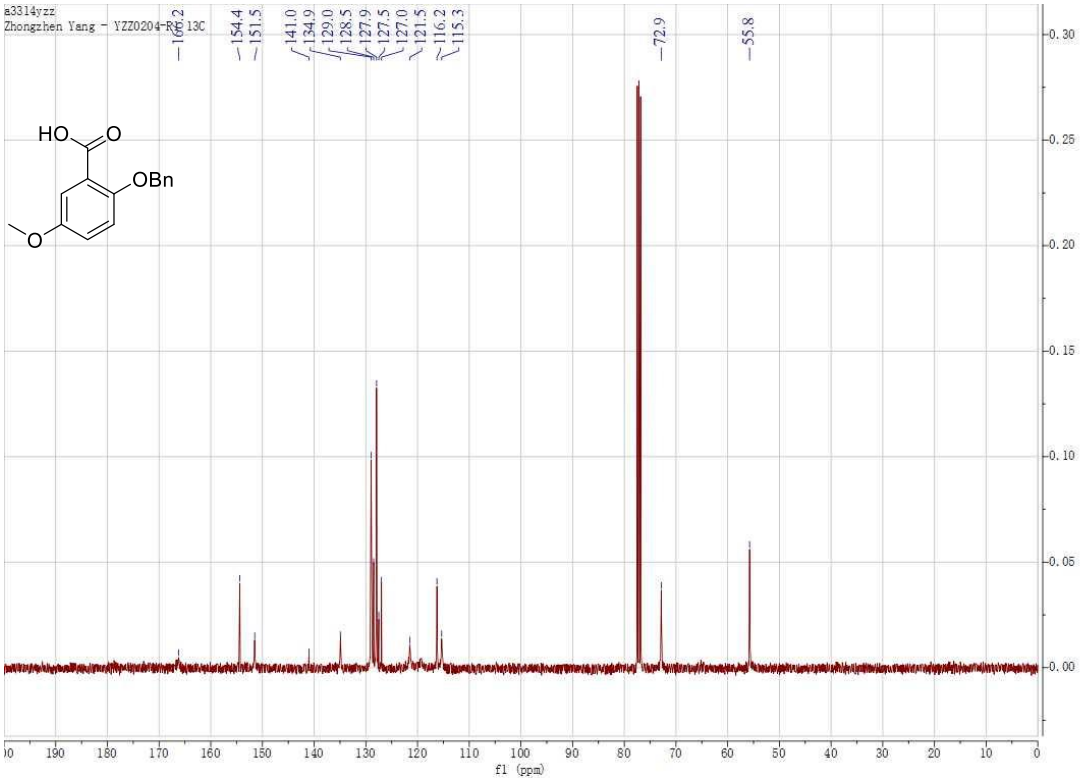
2-(Benzyloxy)-4-methoxybenzoic acid (S1)



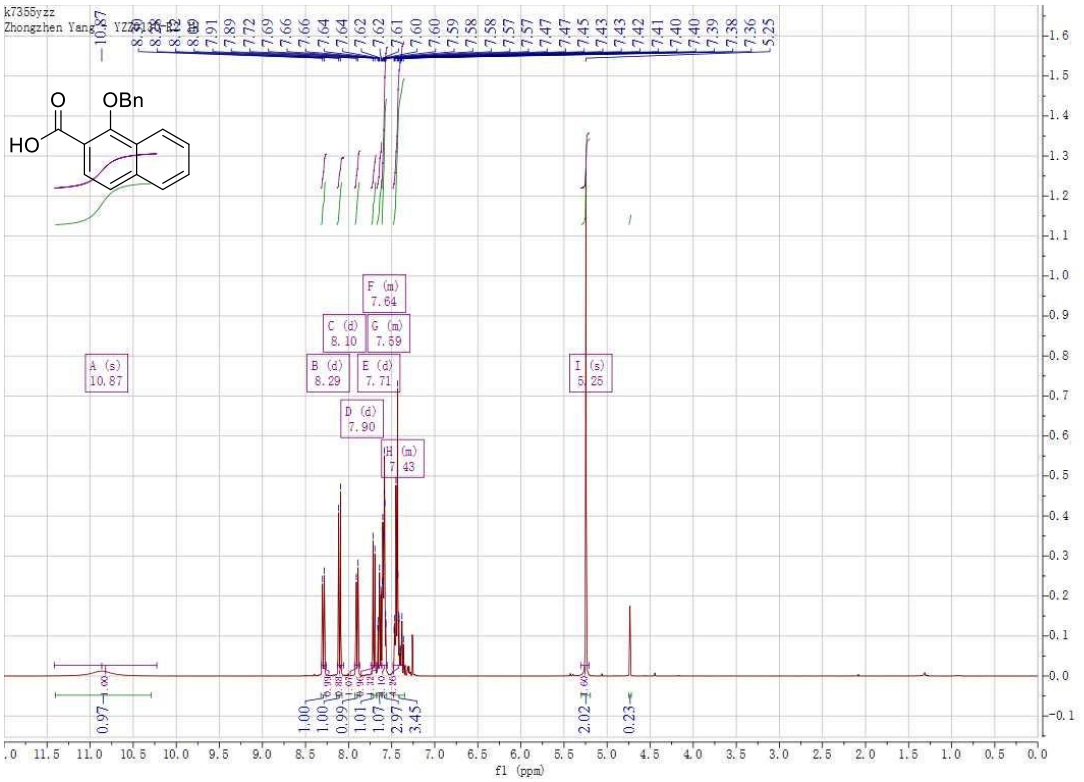


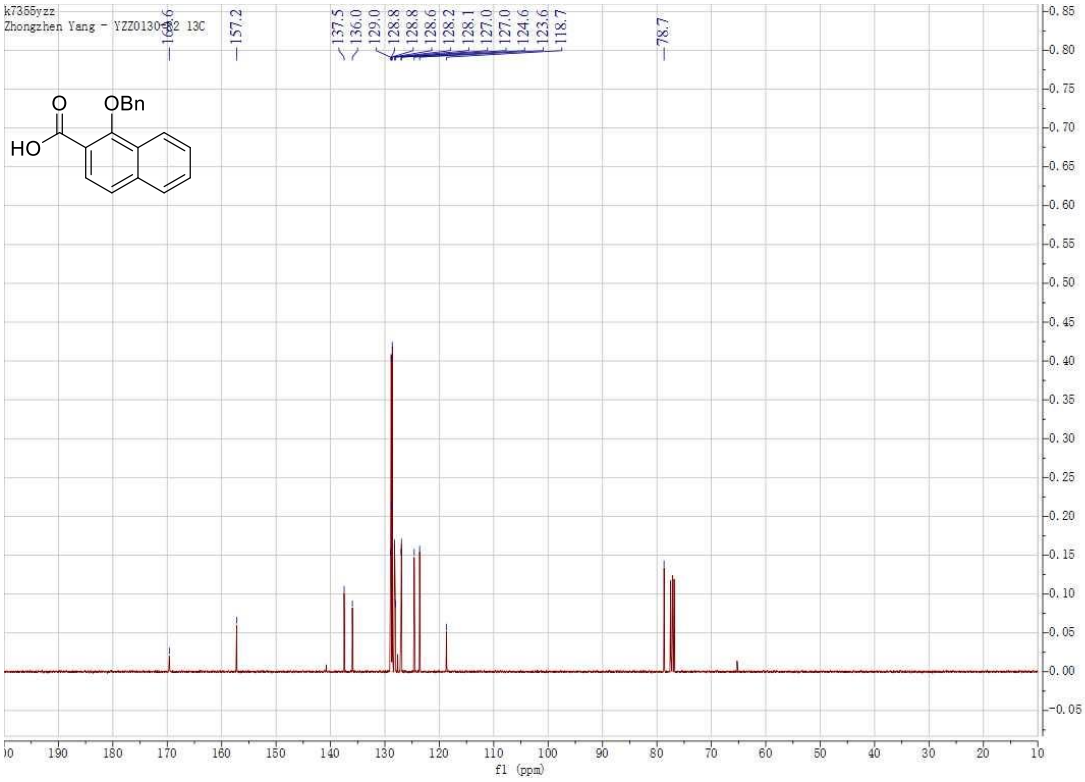
2-(Benzyloxy)-5-methoxybenzoic acid (S2)



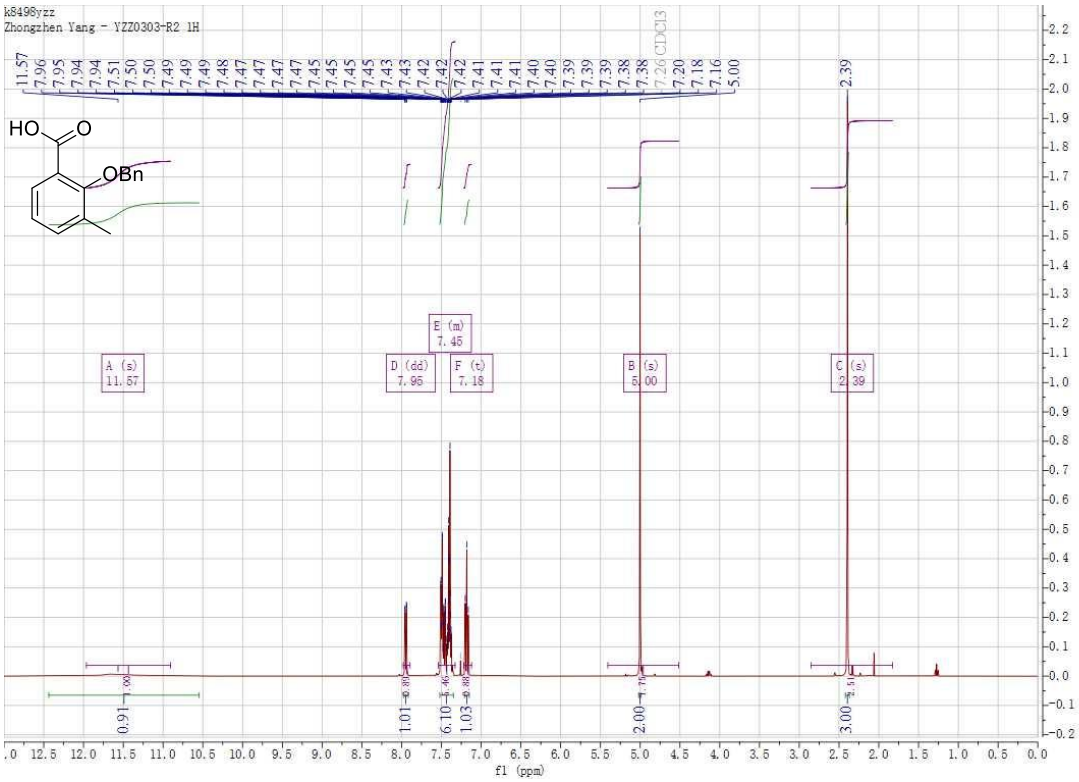


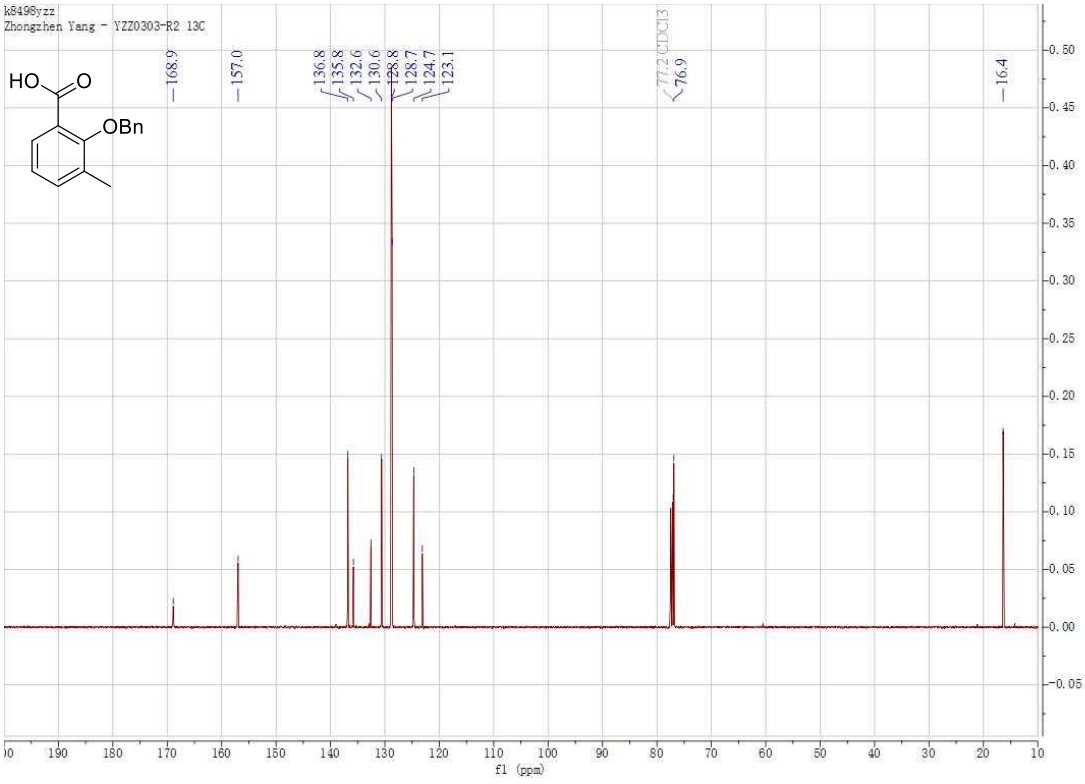
1-(Benzyloxy)-2-naphthoic acid (S3)



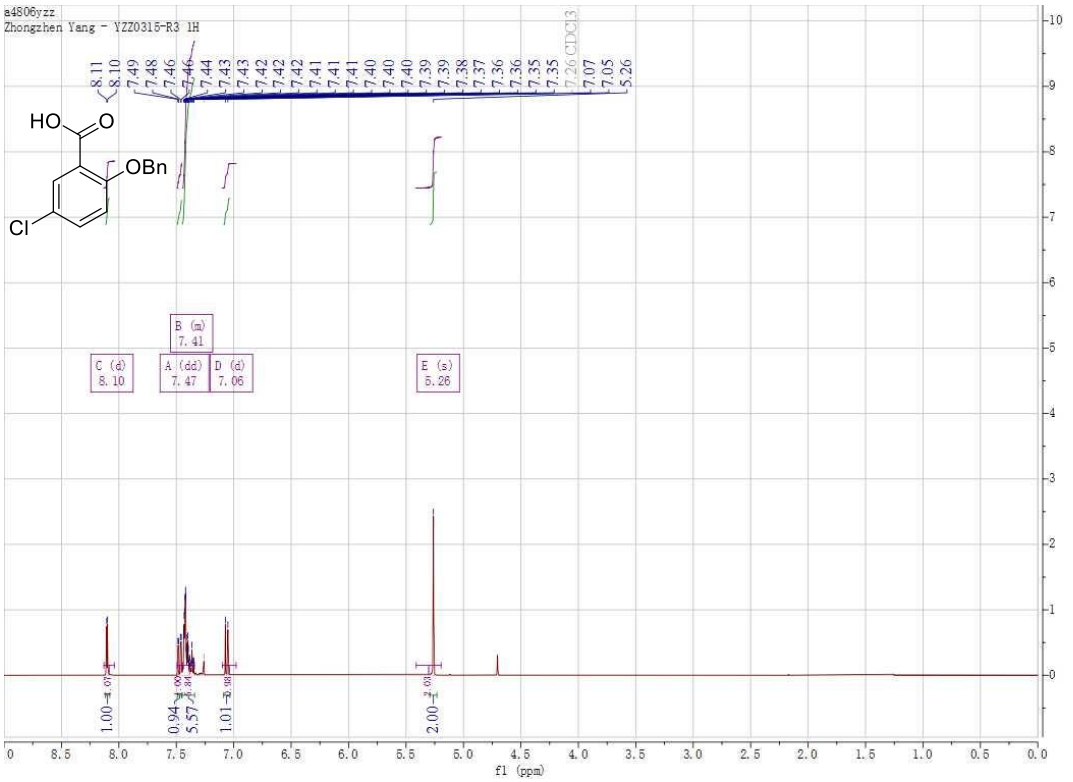


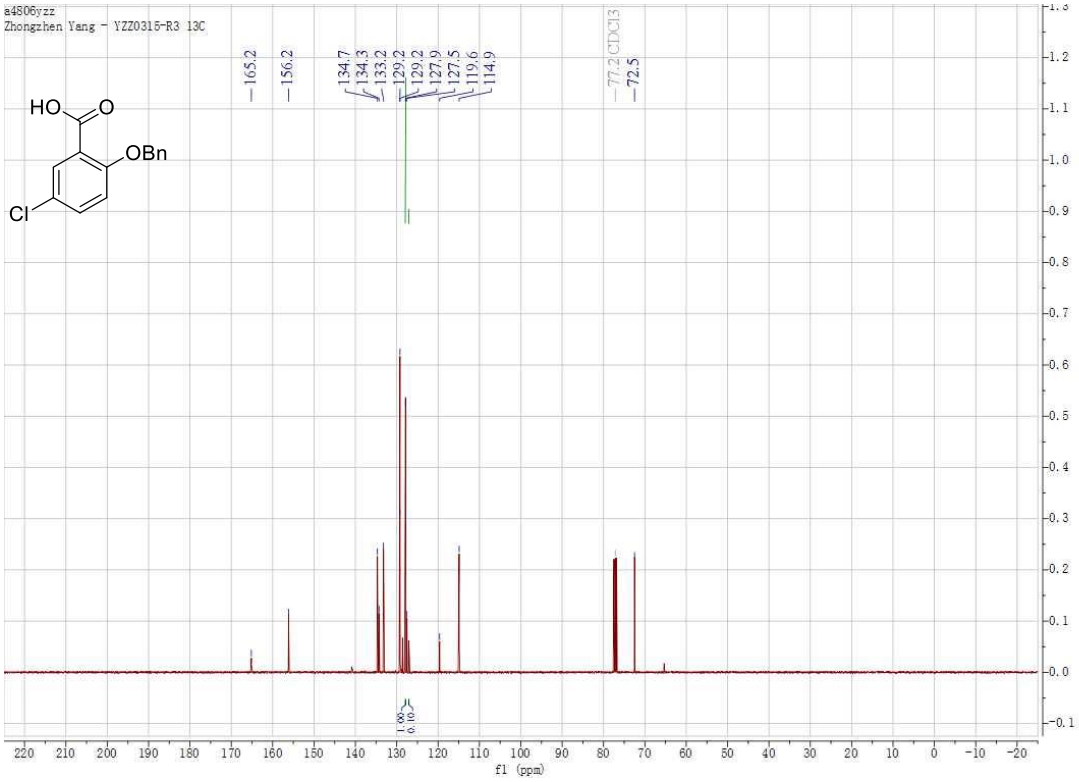
2-(Benzyloxy)-3-methylbenzoic acid (S4)



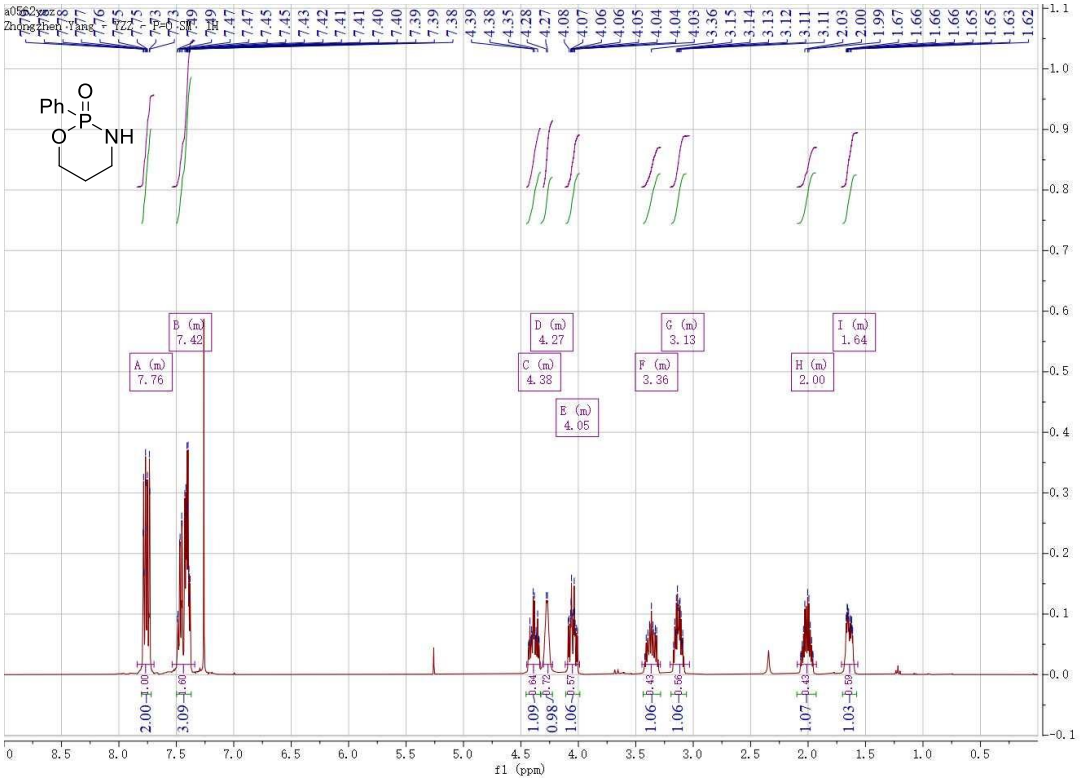


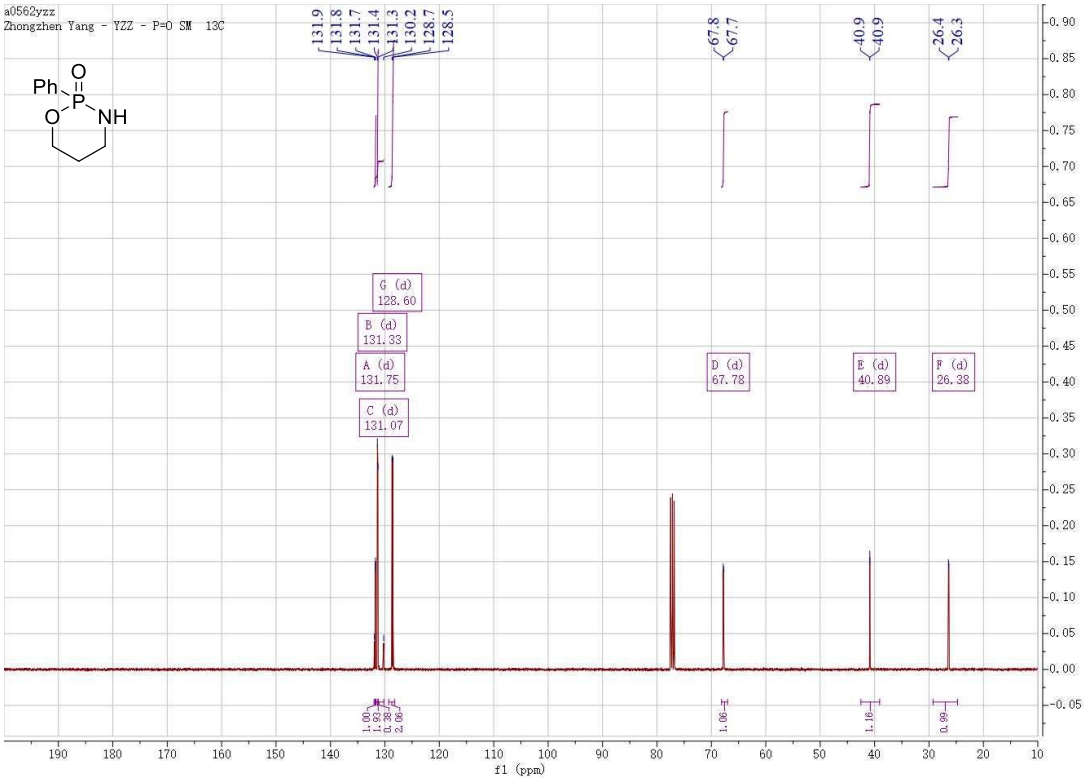
2-(Benzyloxy)-5-chlorobenzoic acid (S5)

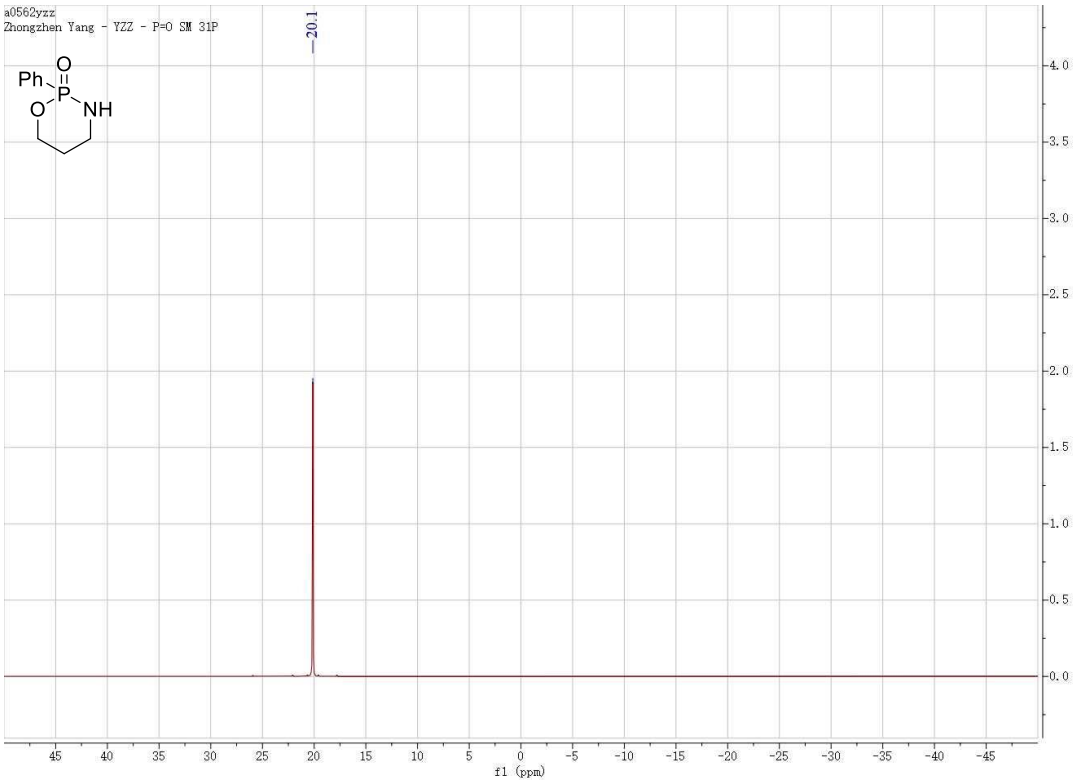




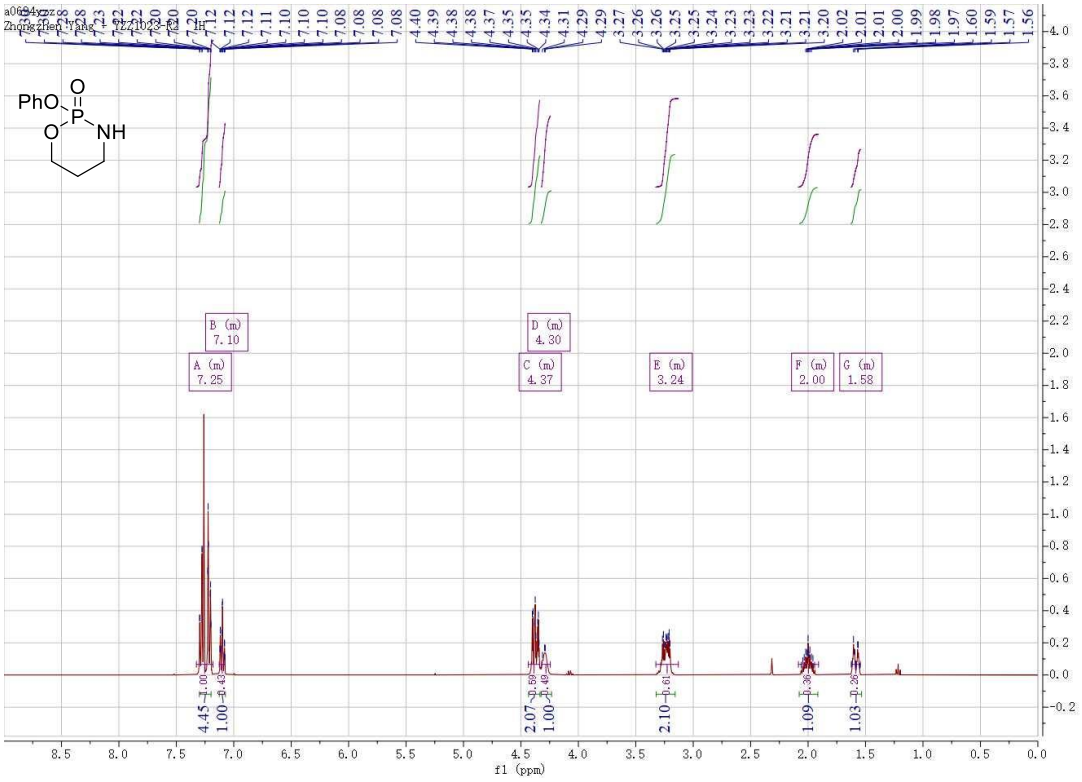
2-Phenyl-1,3,2-oxazaphosphinane 2-oxide (8a)

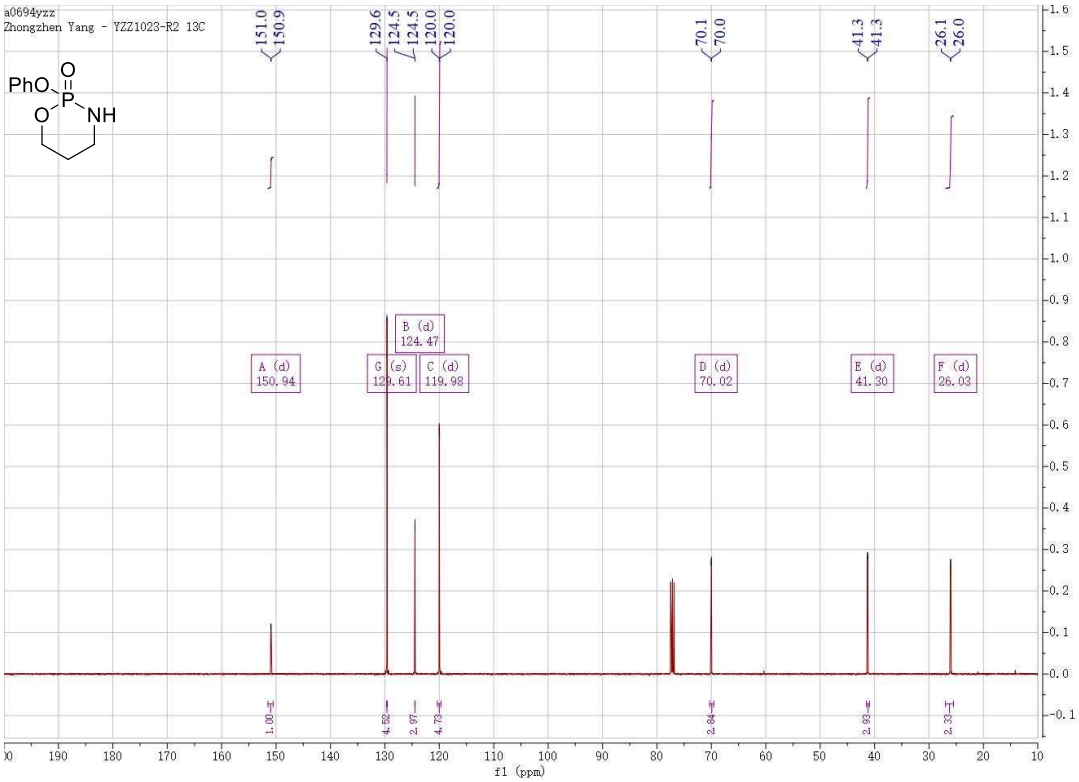


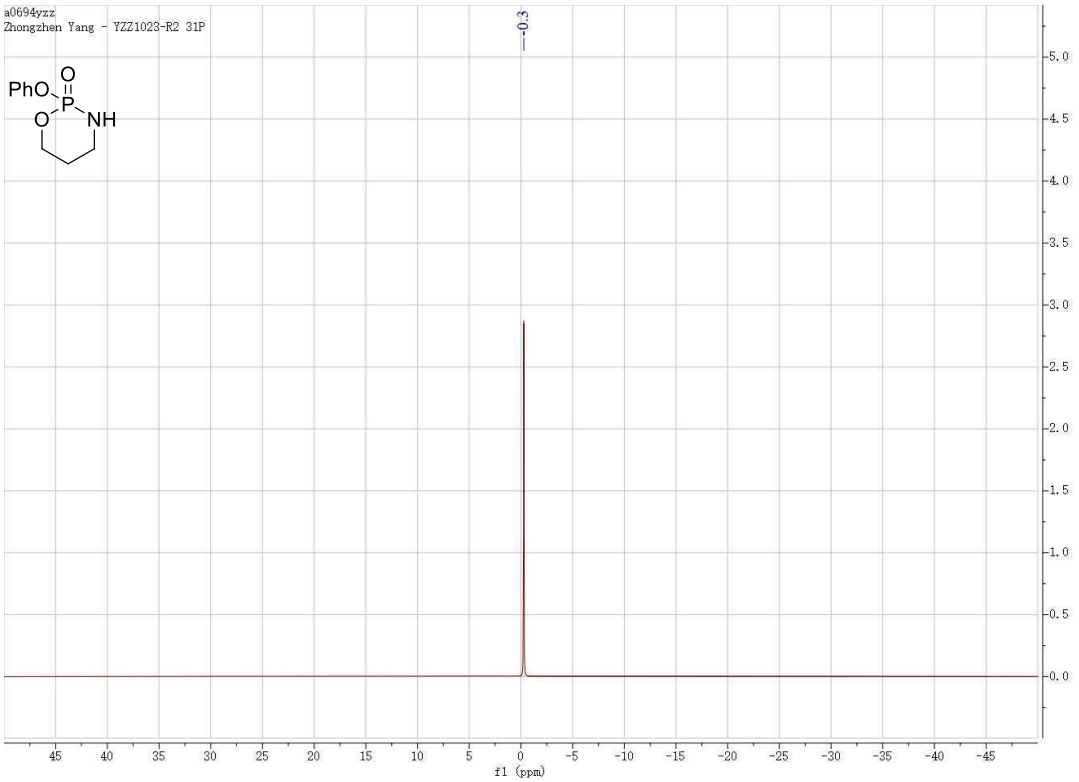




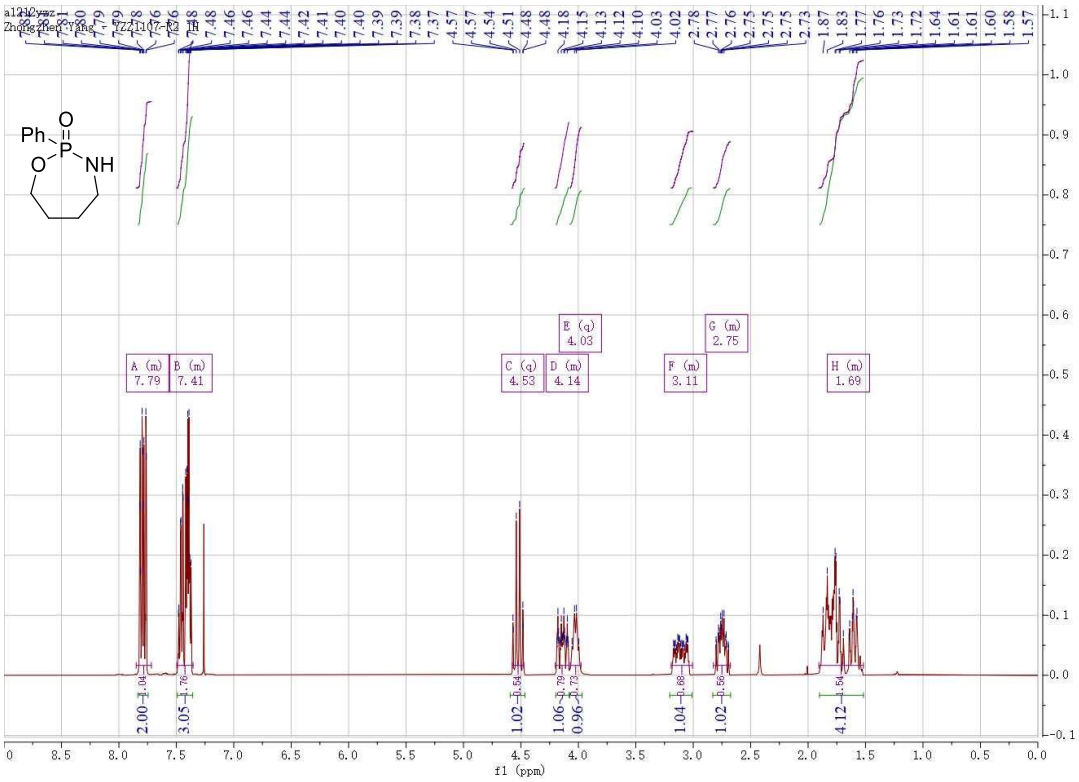
2-Phenoxy-1,3,2-oxazaphosphinane 2-oxide (8b)

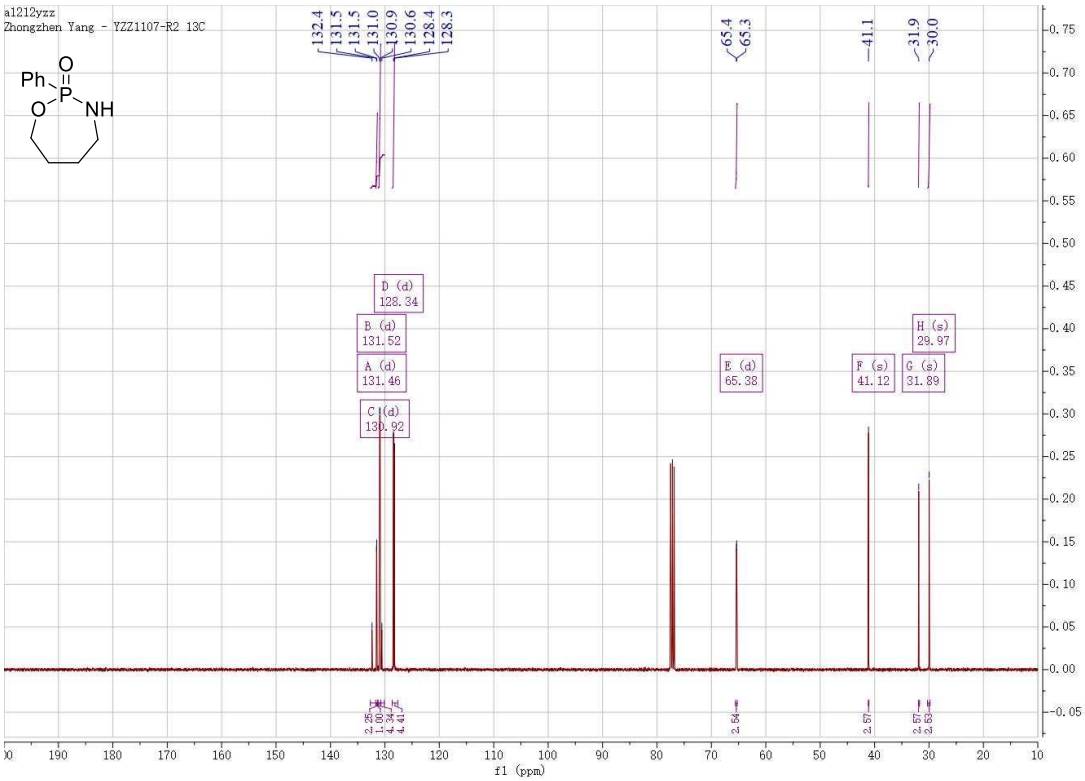


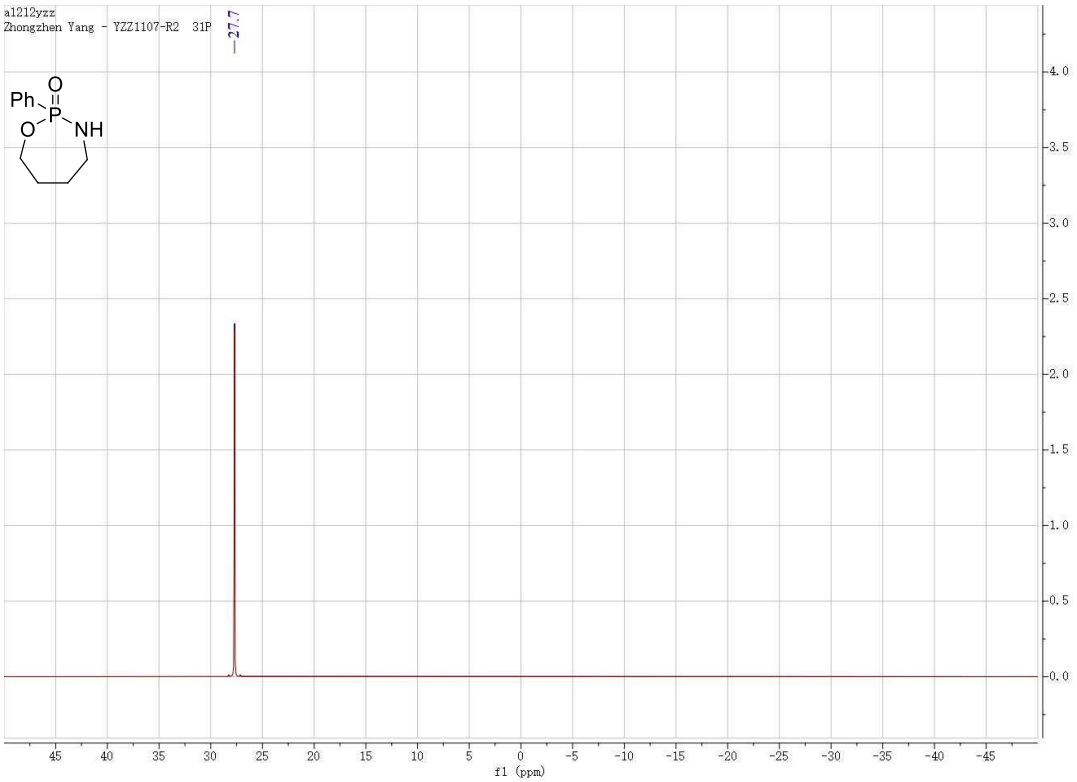

a0694yzz
Zhongzhen Yang - YZZ1023-R2 13C
151.0
150.9
129.6
124.5
124.5
120.0
120.0
70.1
70.0
41.3
41.3
26.1
26.0
B (d)
124.47
A (d)
150.94
G (s)
129.61
C (d)
119.98
D (d)
70.02
E (d)
41.30
F (d)
26.03
f1 (ppm)


a0694yzz
Zhongzhen Yang - YZZ1023-R2 31P
-0.3
f1 (ppm)

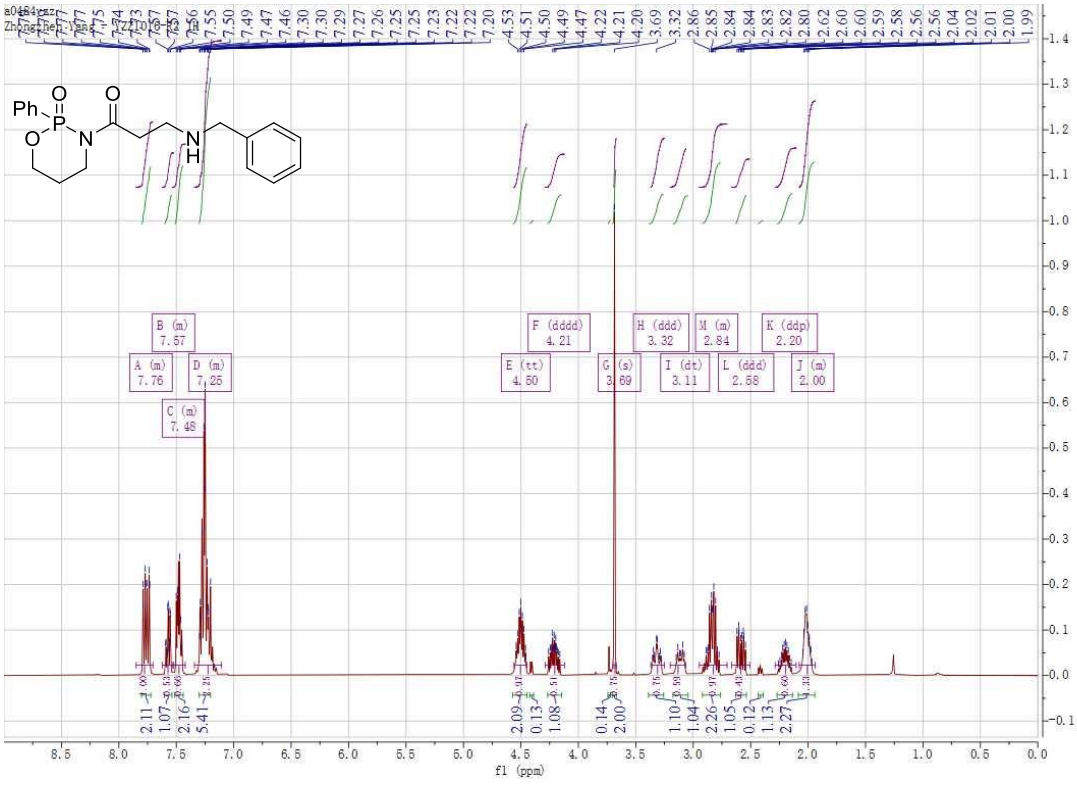
2-Phenyl-1,3,2-oxazaphosphepane 2-oxide (8c)

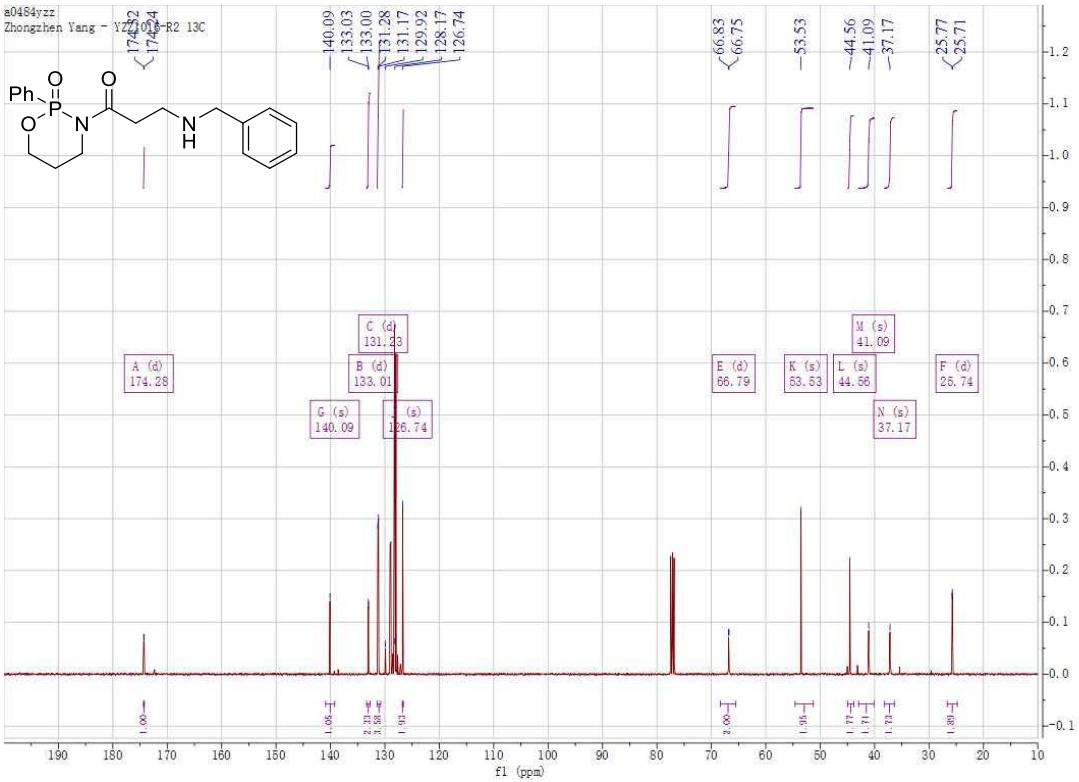


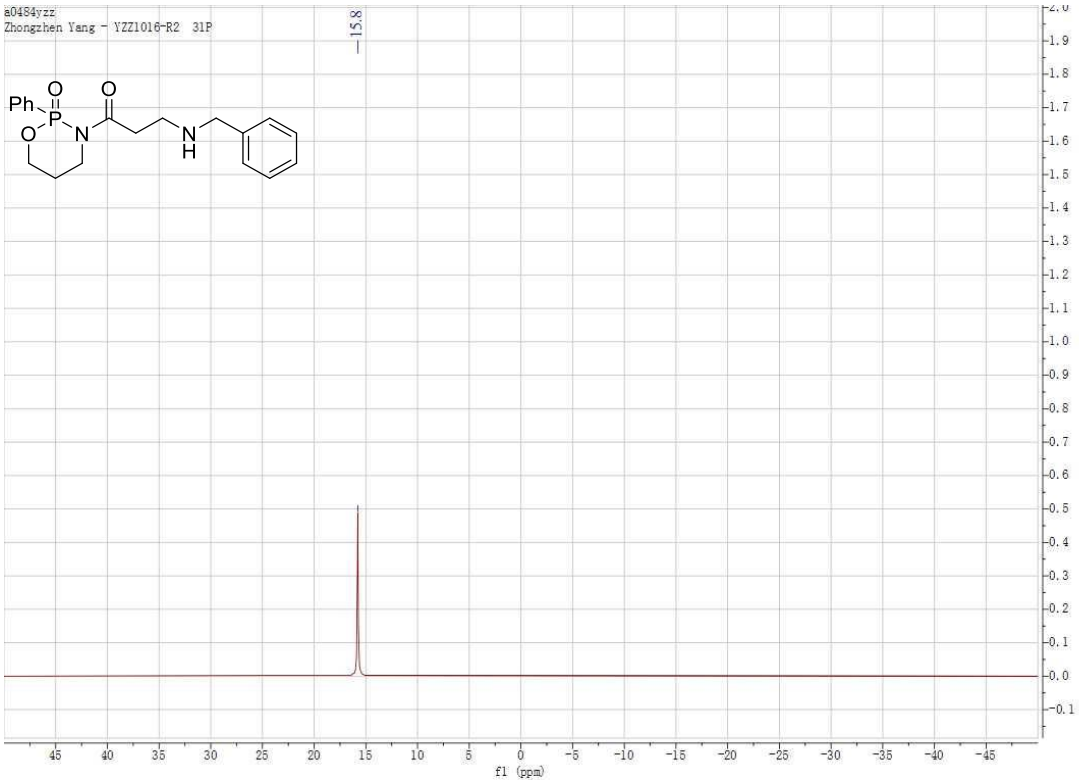




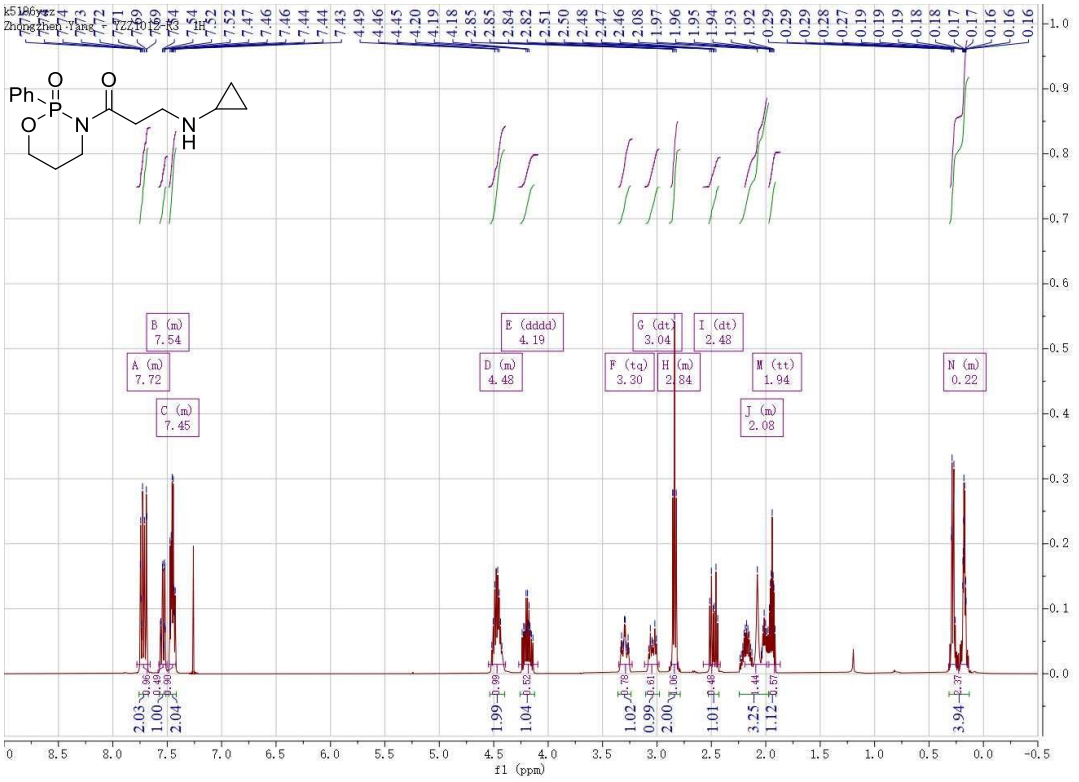
3-(Benzylamino)-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)propan-1-one (10a)

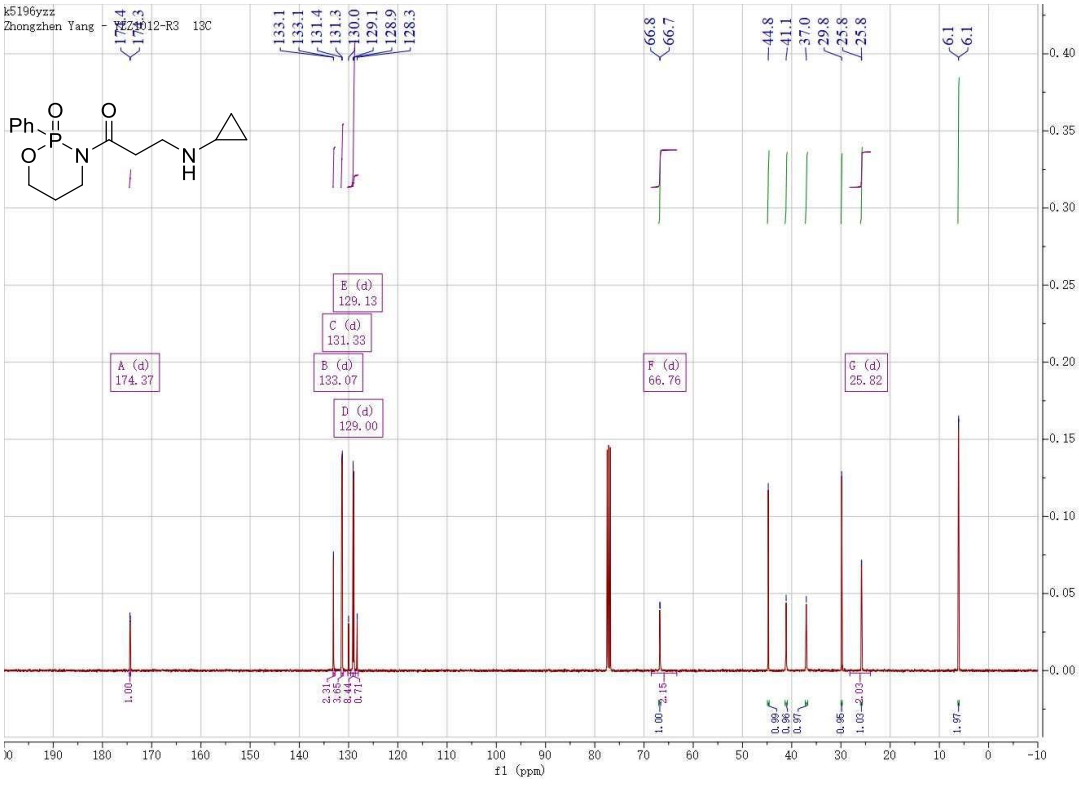


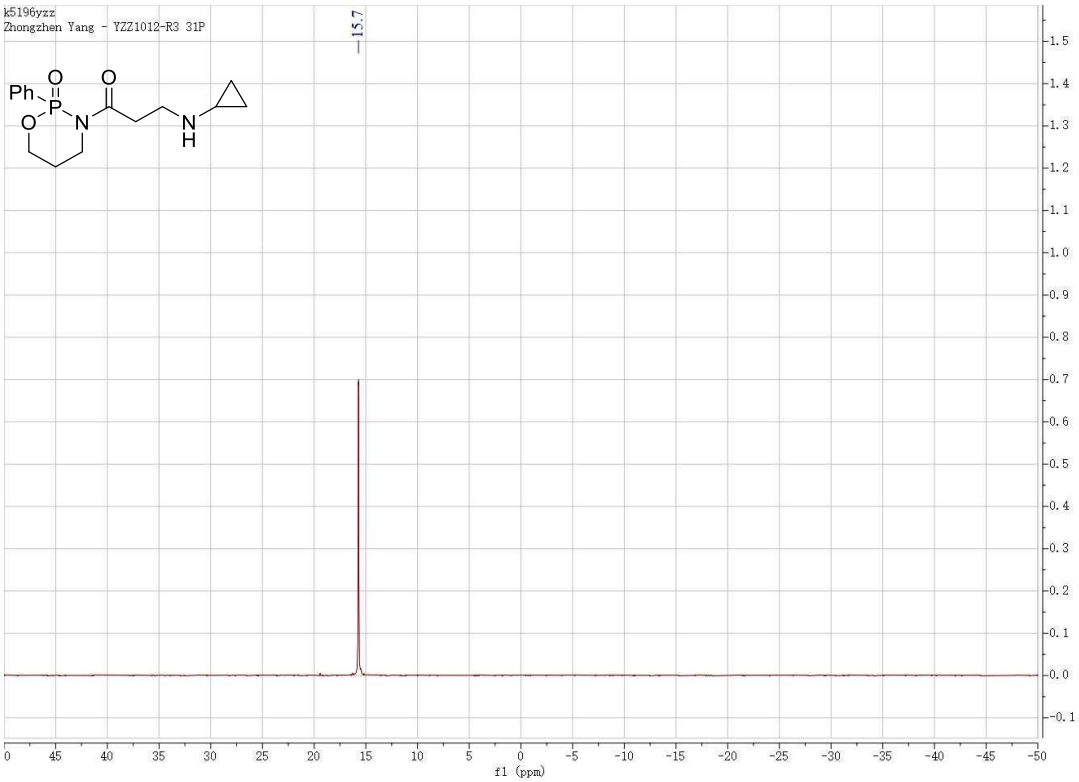

a0484yzz
Zhongzhen Yang - YZZ1016-R2 13C
174.32
174.24
140.09
133.03
133.00
131.28
131.17
129.92
128.17
126.74
66.83
66.75
53.53
44.56
41.09
37.17
25.77
25.71
A (d) 174.28
B (d) 133.01
C (d) 131.23
E (d) 66.79
K (s) 53.53
L (s) 44.56
M (s) 41.09
F (d) 25.74
G (s) 140.09
N (s) 37.17
f1 (ppm)


a0484yzz
Zhongzhen Yang - YZZ1016-R2 31P
15.8
f1 (ppm)

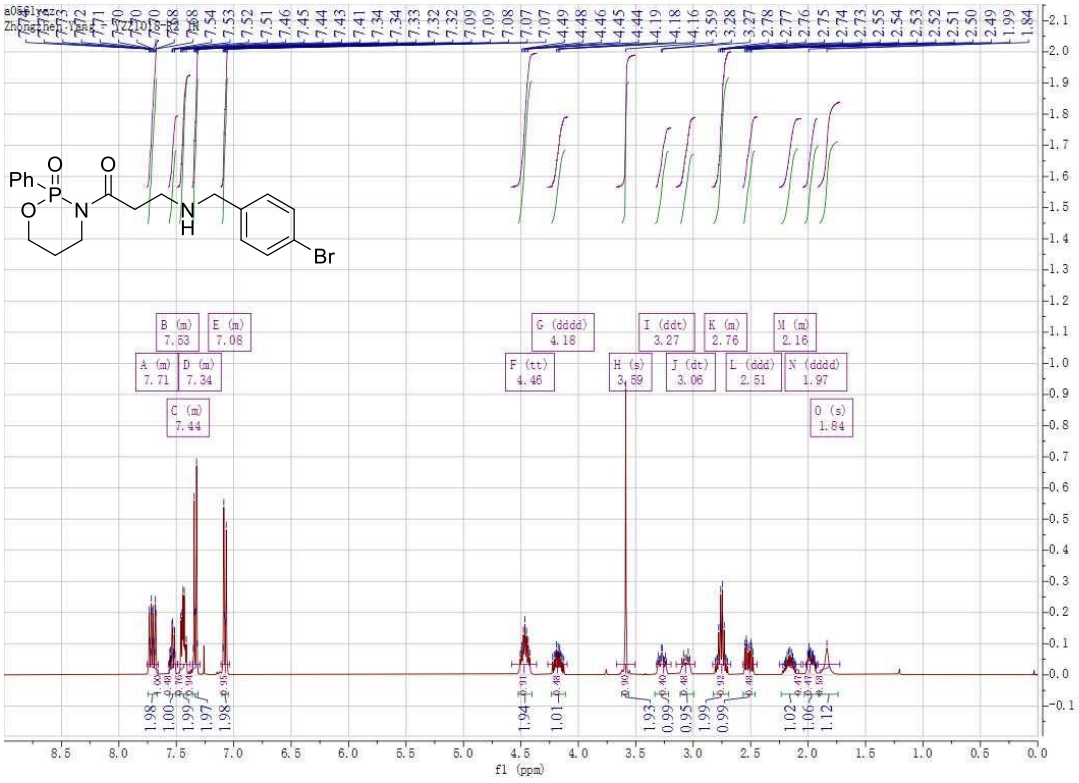
3-(Cyclopropylamino)-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)propan-1-one (10b)

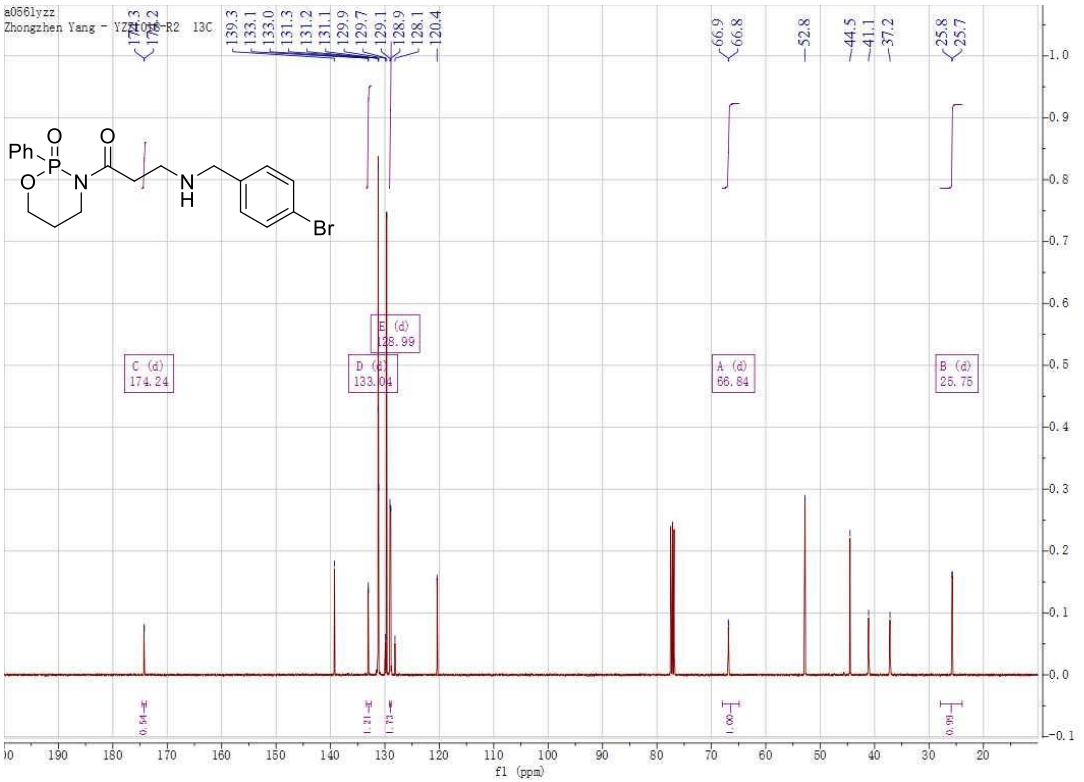


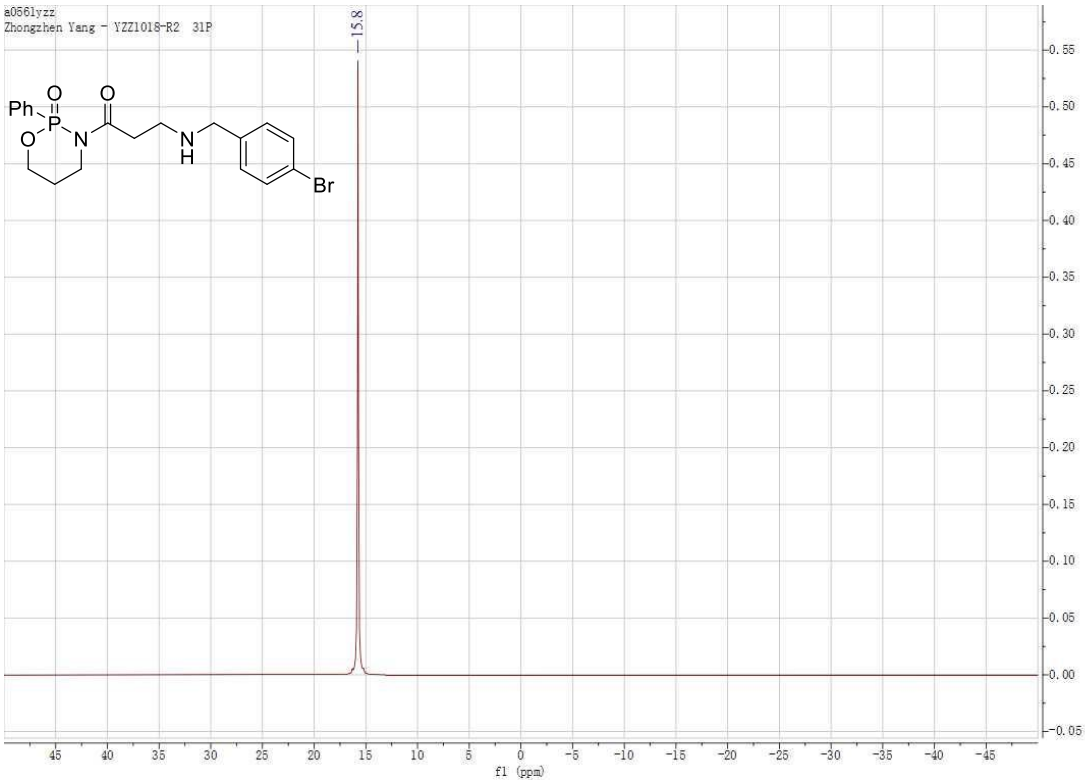




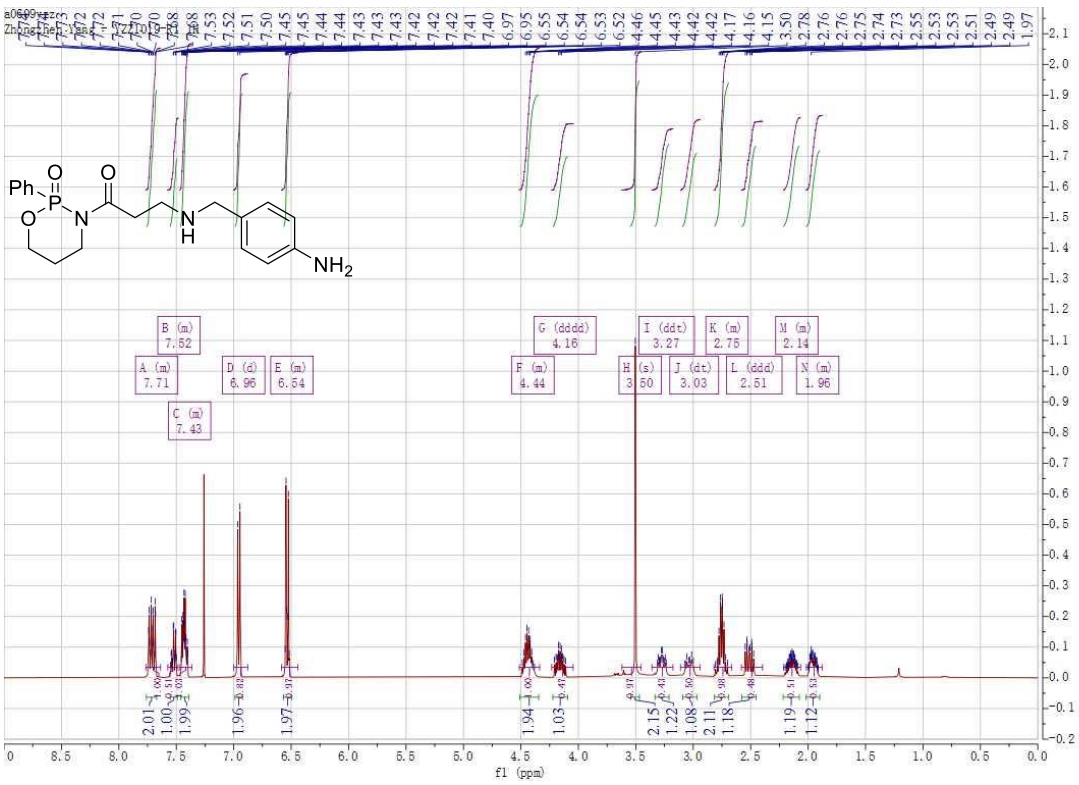
3-((4-Bromobenzyl)amino)-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)propan-1-one (10c)

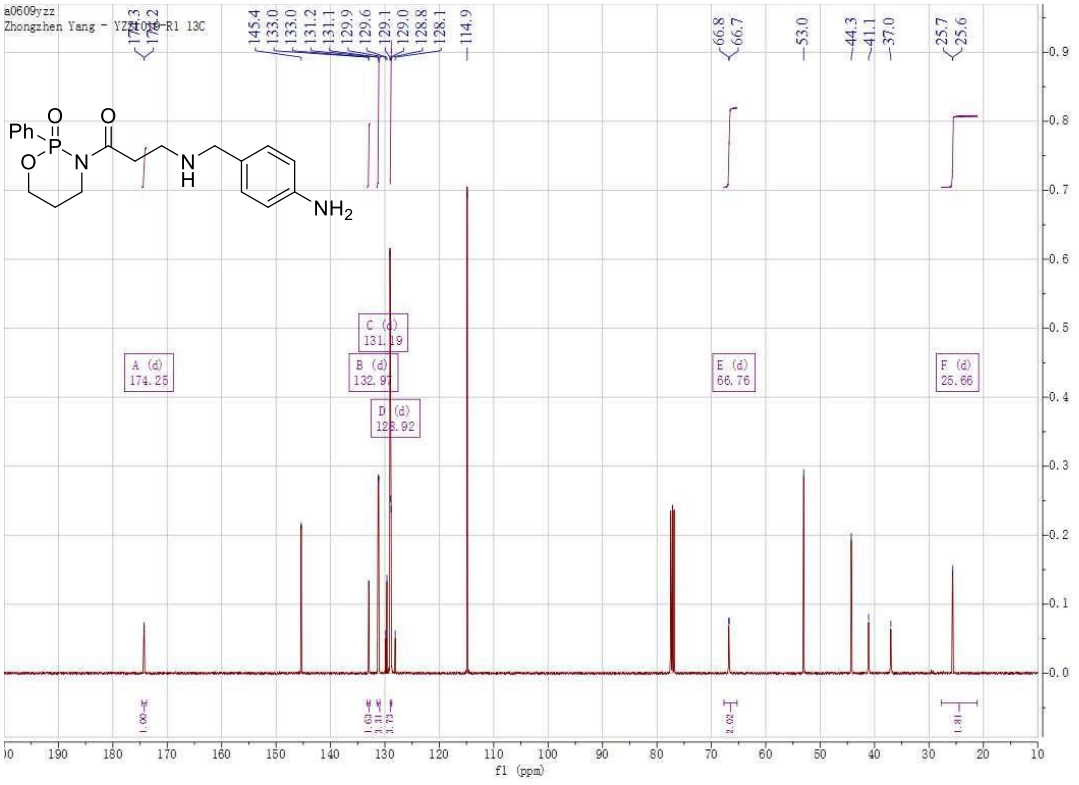



a0661yzz
Zhongzhen Yang - YZZ1018-R2 13C
174.3
174.2
139.3
133.1
133.0
131.3
131.2
131.1
129.9
129.7
129.1
128.9
128.1
120.4
66.9
66.8
52.8
44.5
41.1
37.2
25.8
25.7
Ph
O
P
O
N
O
N
H
Br
E (d)
128.99
C (d)
174.24
D (d)
133.04
A (d)
66.84
B (d)
25.75
f1 (ppm)

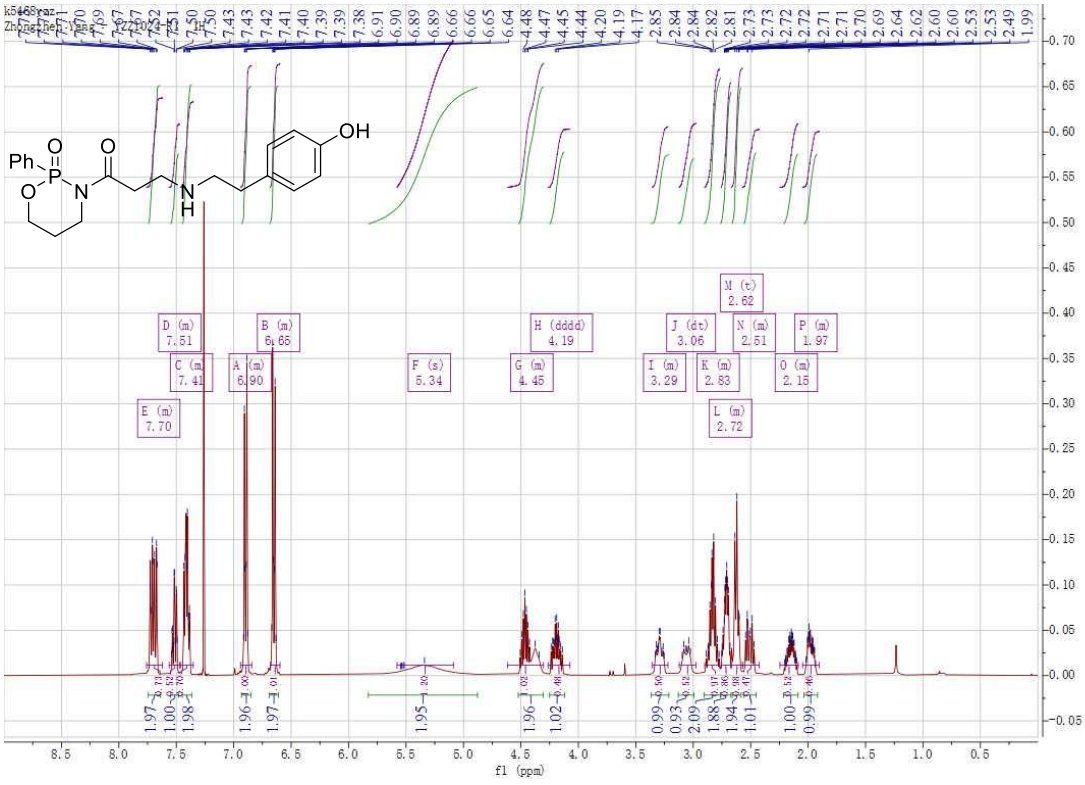

a0661yzz
Zhongzhen Yang - YZZ1018-R2 31P
15.8
Ph
O
P
O
N
O
N
H
Br
f1 (ppm)

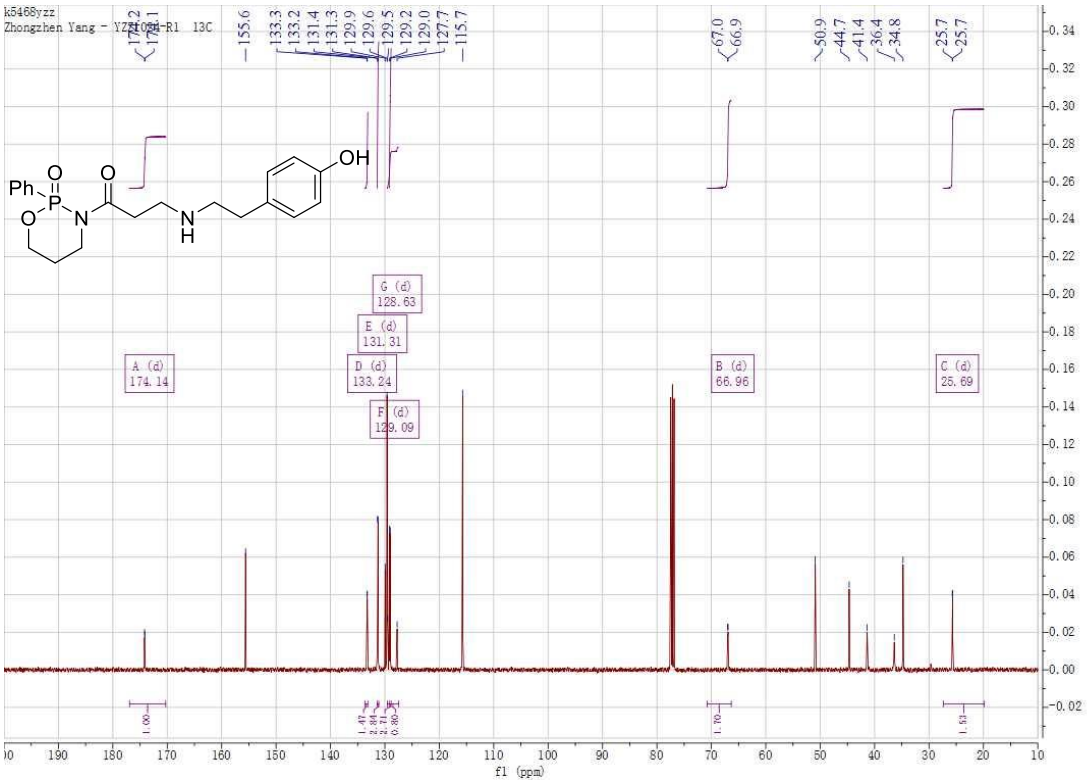
3-((4-Aminobenzyl)amino)-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)propan-1-one (10d)

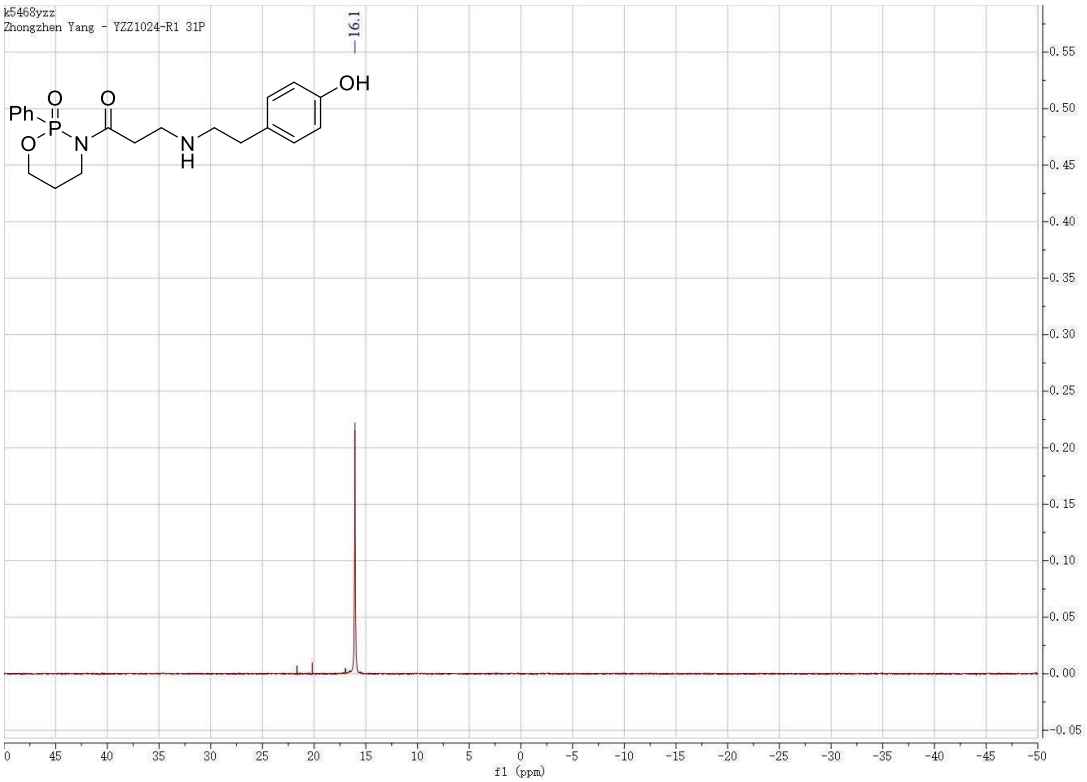




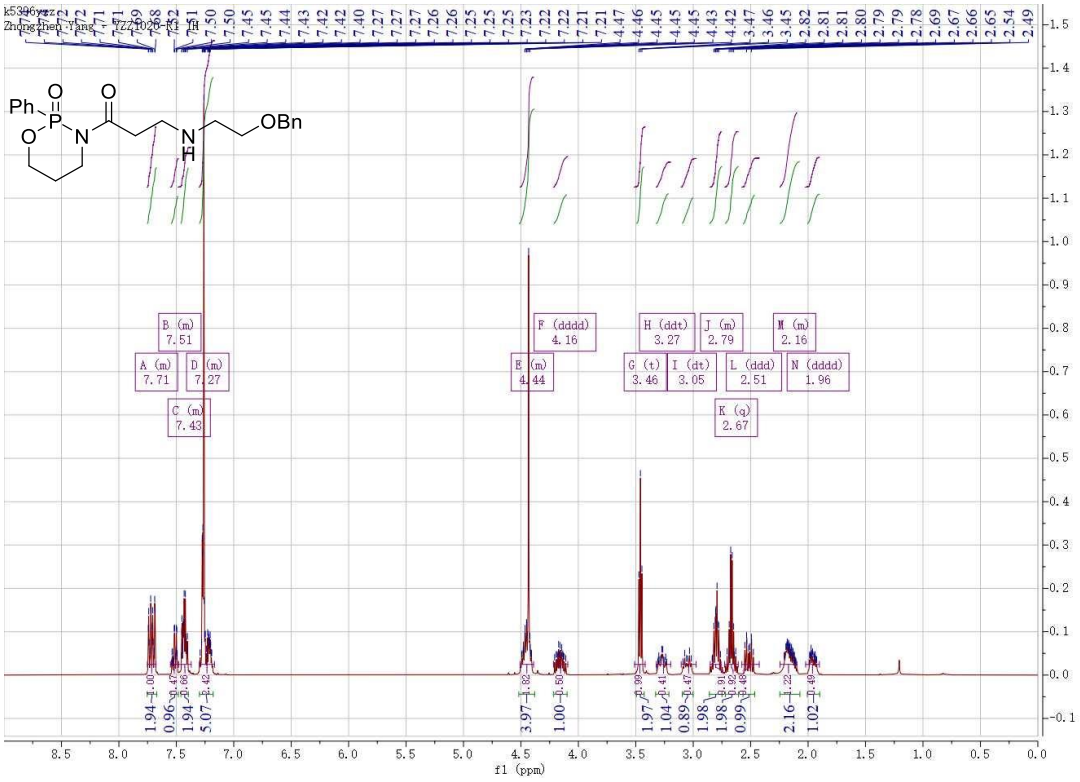
3-((4-Hydroxyphenethyl)amino)-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)propan-1-one (10e)

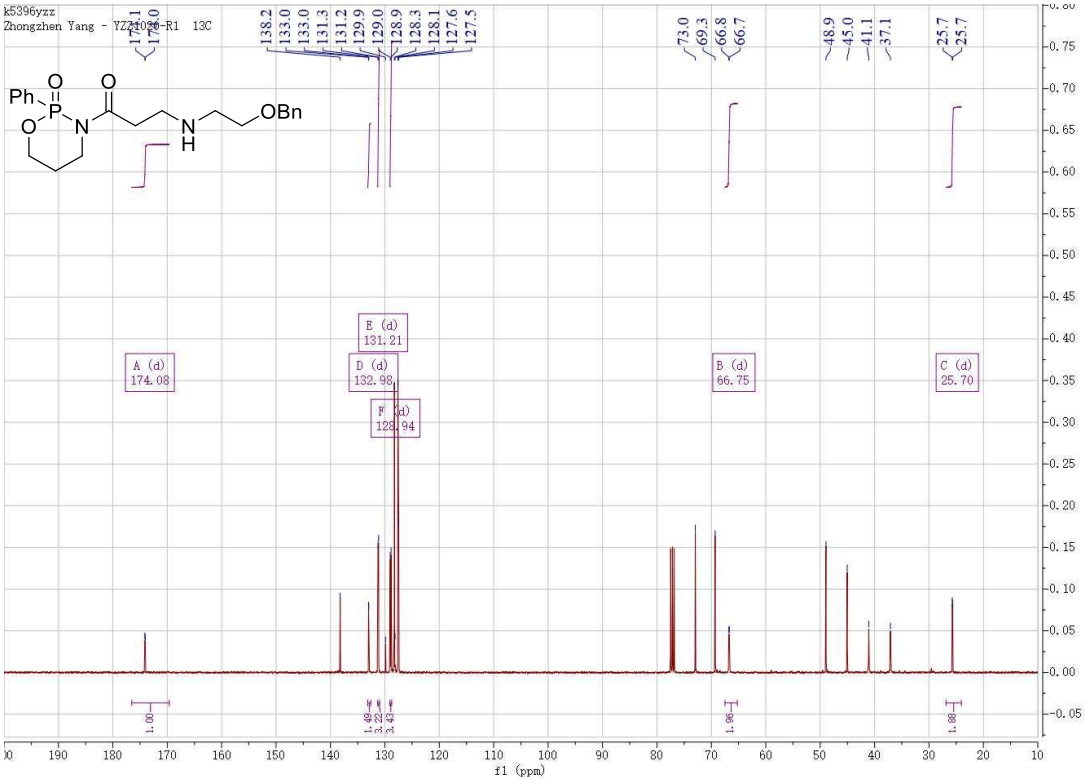


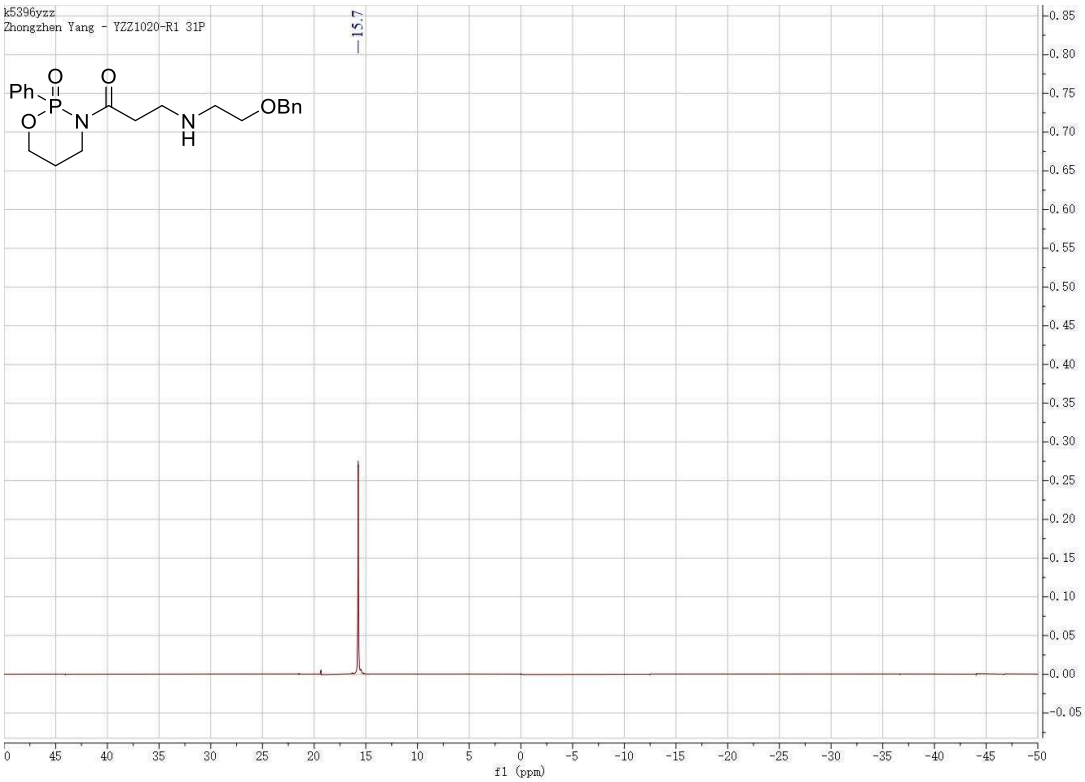

k5468yzz
Zhongzhen Yang - YZZ1024-R1 13C
174.2
174.1
155.6
133.3
133.2
131.4
131.3
129.9
129.6
129.5
129.2
129.0
127.7
115.7
67.0
66.9
50.9
44.7
41.4
36.4
34.8
25.7
25.7
OH
Ph
O
P
N
H
G (d)
128.63
E (d)
131.31
A (d)
174.14
D (d)
133.24
F (d)
129.09
B (d)
66.96
C (d)
25.69
f1 (ppm)


k5468yzz
Zhongzhen Yang - YZZ1024-R1 31P
16.1
OH
Ph
O
P
N
H
f1 (ppm)

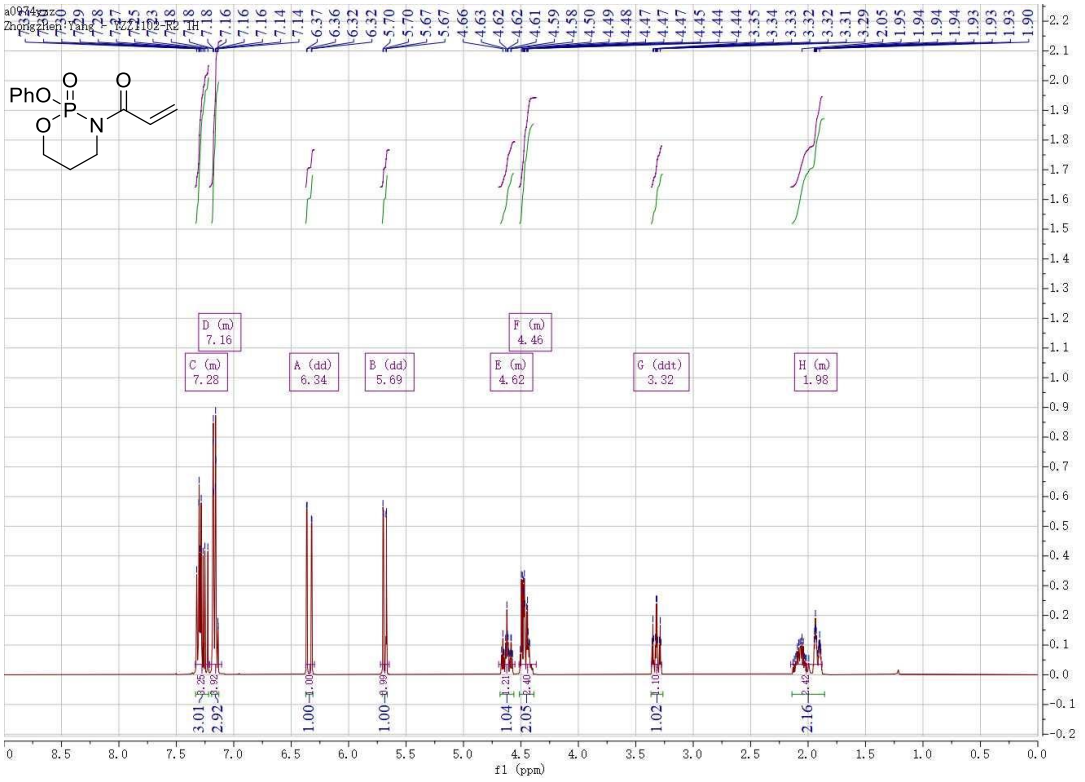
3-((2-(Benzyloxy)ethyl)amino)-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)propan-1-one (10f)

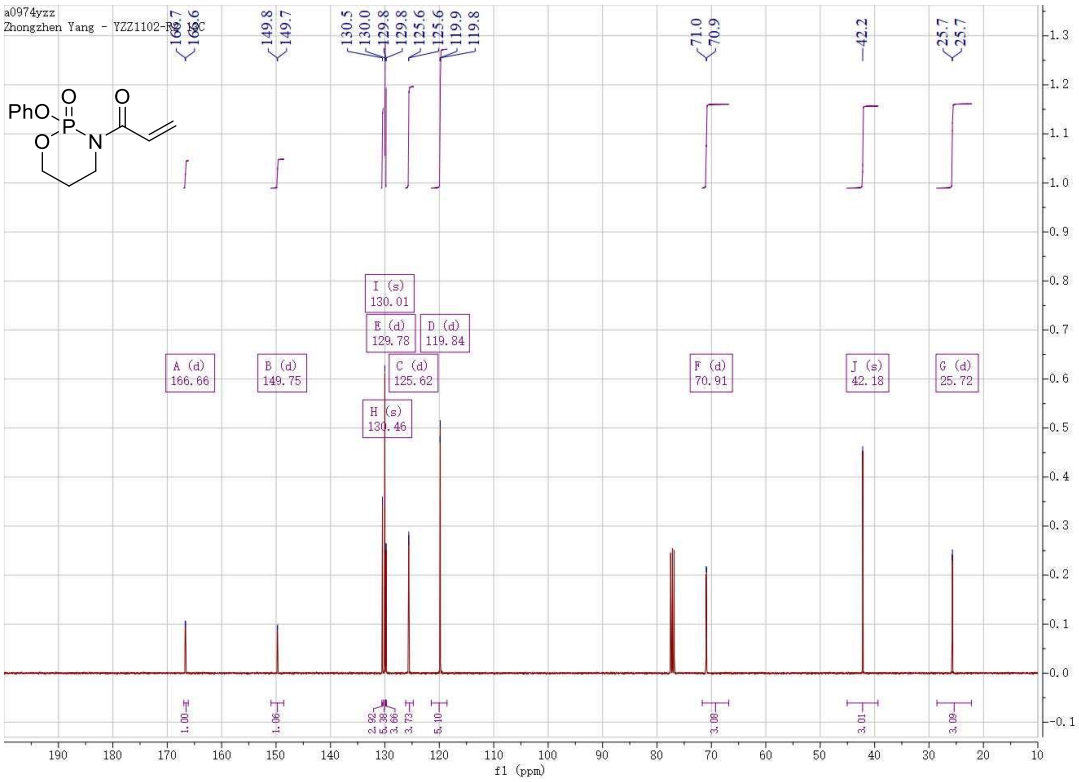


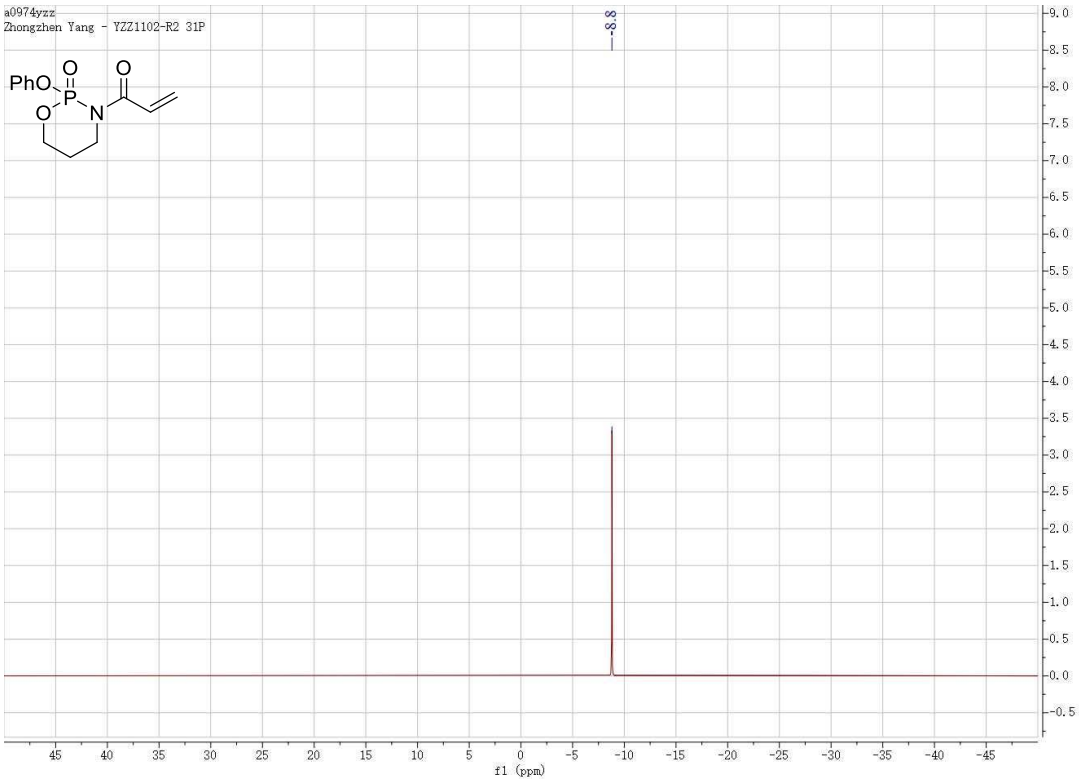




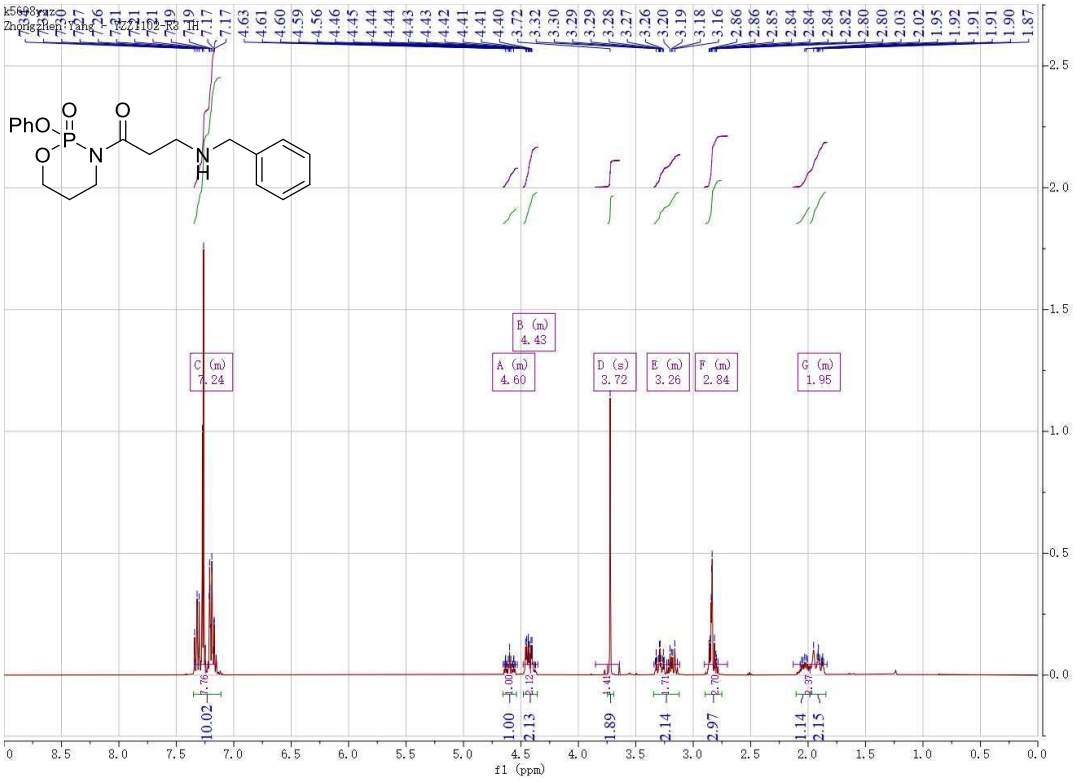
1-(2-Oxido-2-phenoxy-1,3,2-oxazaphosphinan-3-yl)prop-2-en-1-one (12)

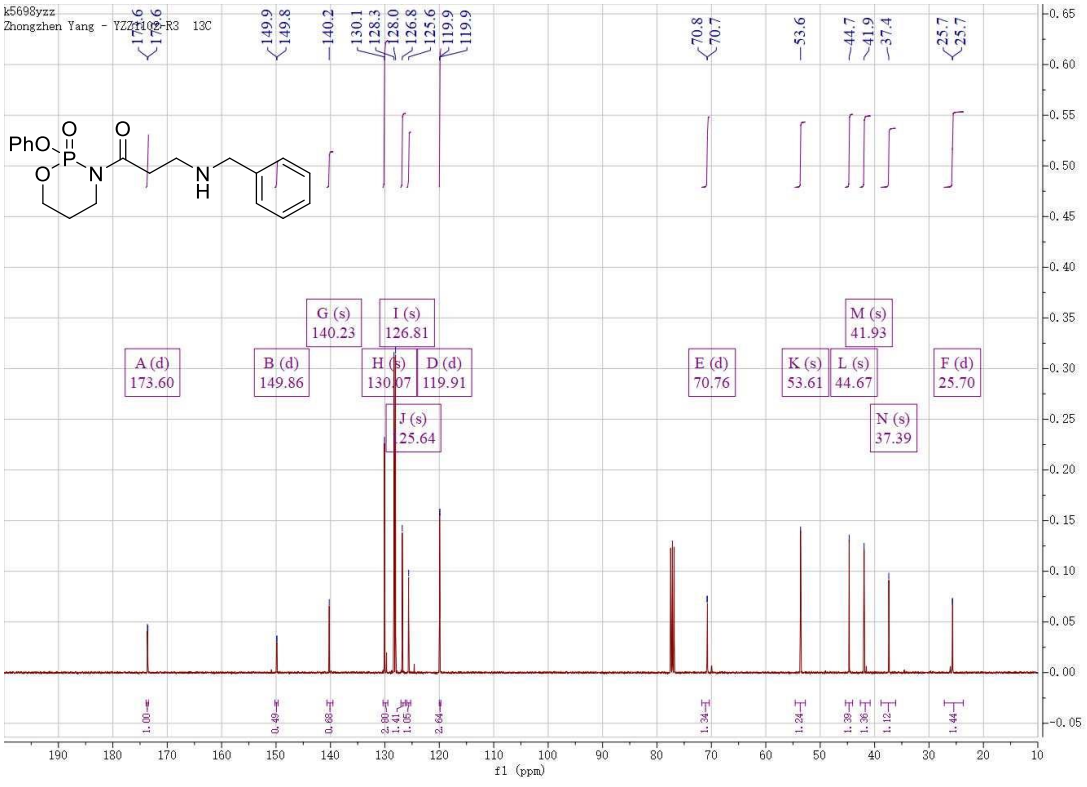


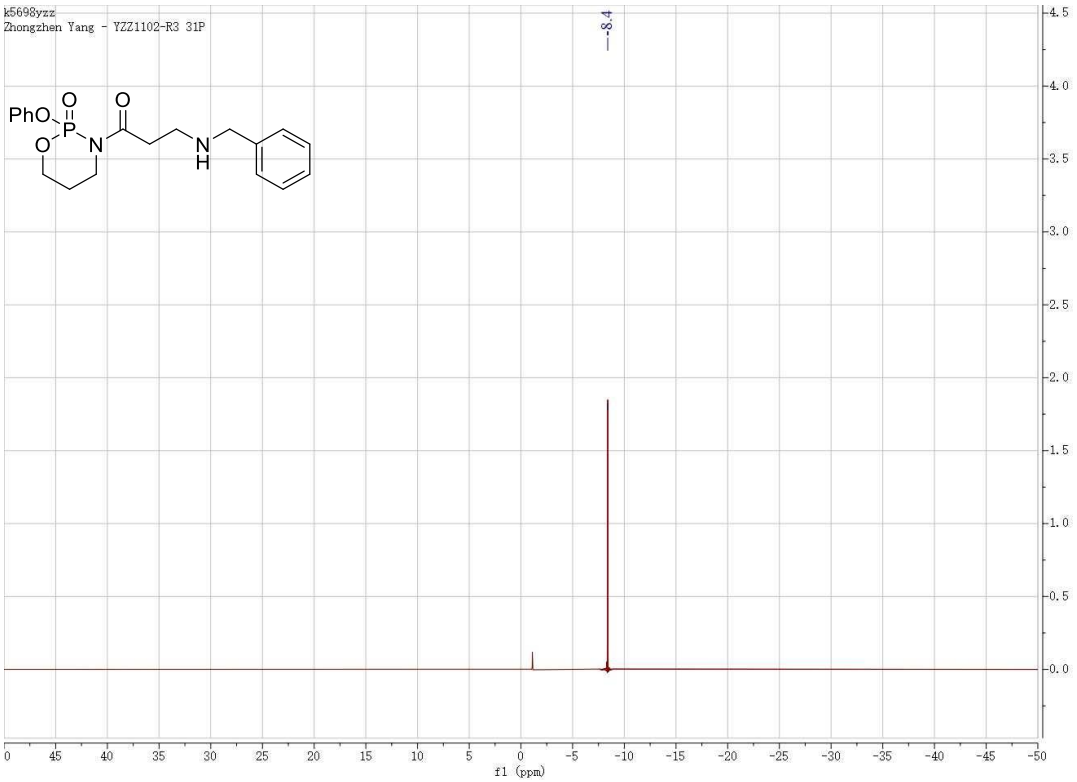

a0974yzz
Zhongzhen Yang - YZZ1102-R2 13C
166.7
166.6
149.8
149.7
130.5
130.0
129.8
129.8
125.6
125.6
119.9
119.8
71.0
70.9
42.2
25.7
25.7
I (s)
130.01
E (d)
129.78
D (d)
119.84
A (d)
166.66
B (d)
149.75
C (d)
125.62
F (d)
70.91
J (s)
42.18
G (d)
25.72
H (s)
130.46
1.00
1.06
2.82
5.38
3.86
3.73
5.10
3.08
3.01
3.09
f1 (ppm)


a0974yzz
Zhongzhen Yang - YZZ1102-R2 31P
-8.8
f1 (ppm)

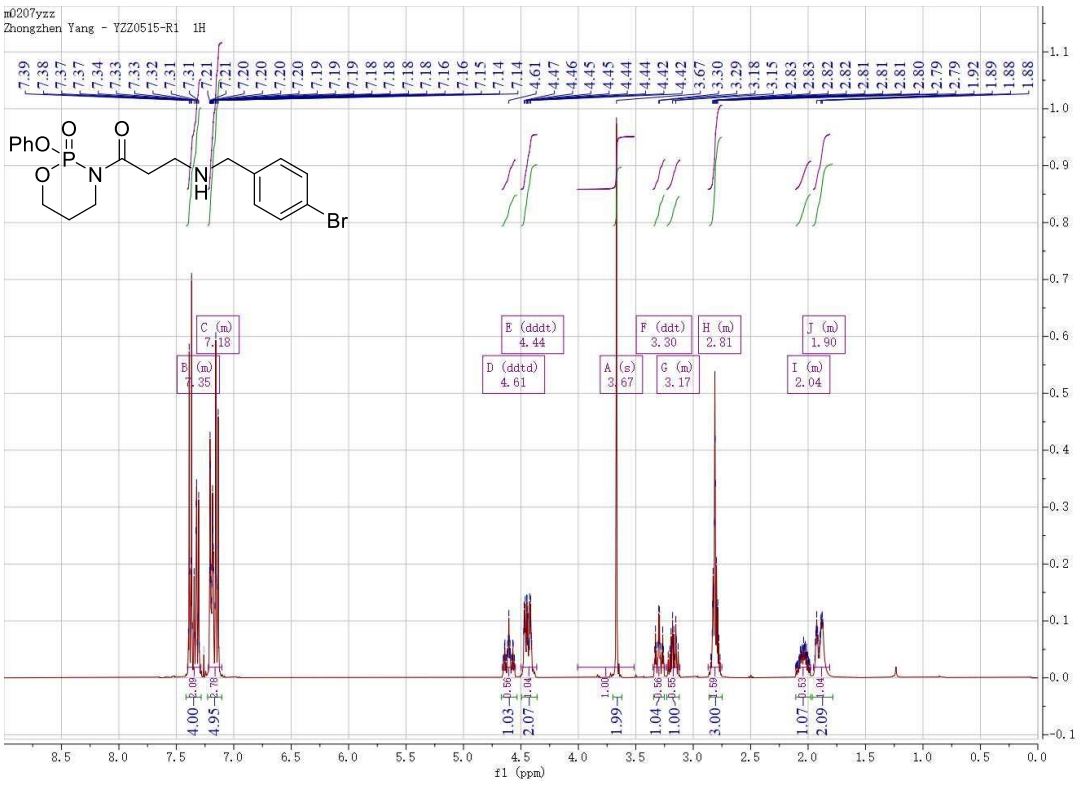
3-(Benzylamino)-1-(2-oxido-2-phenoxy-1,3,2-oxazaphosphinan-3-yl)propan-1-one (13a) (The tract impurity in these spectra is the starting lactam **8b**)

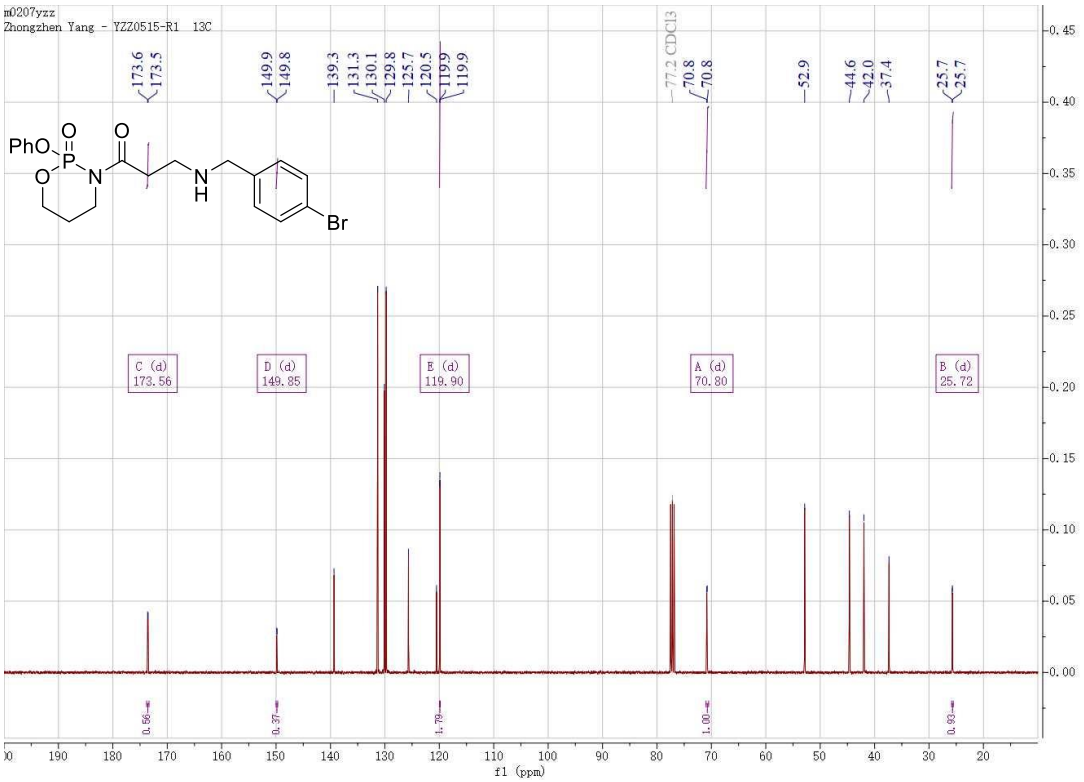






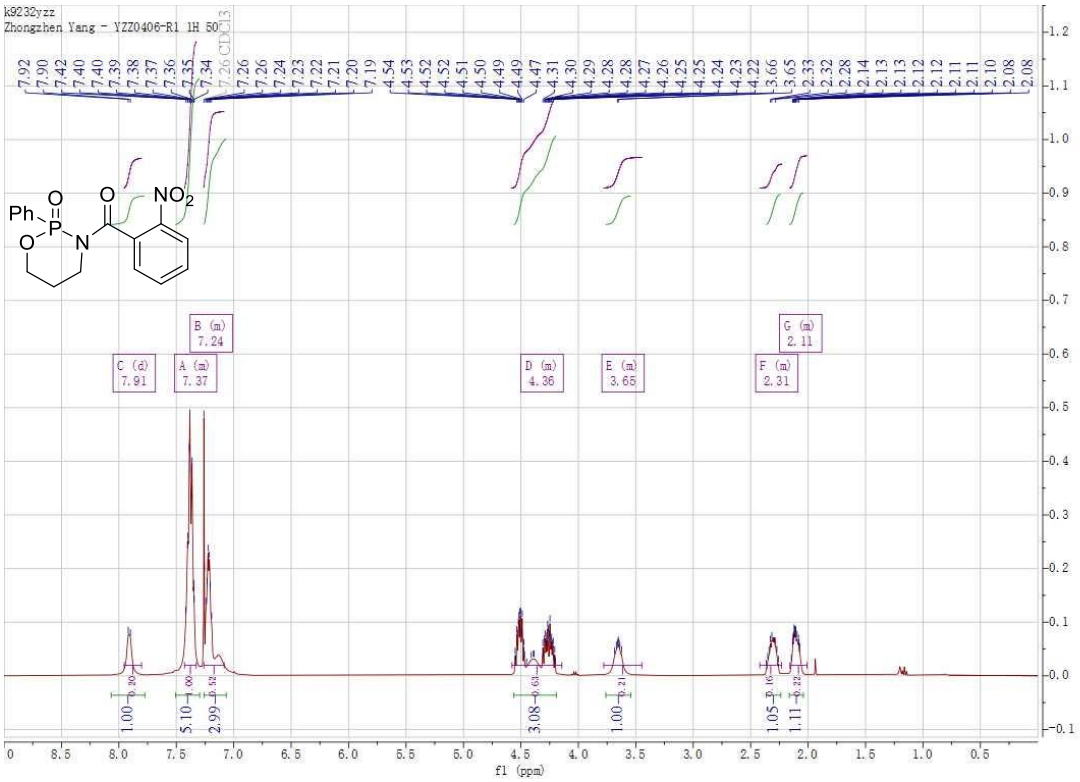
3-((4-Bromobenzyl)amino)-1-(2-oxido-2-phenoxy-1,3,2-oxazaphosphinan-3-yl)propan-1-one (13b)

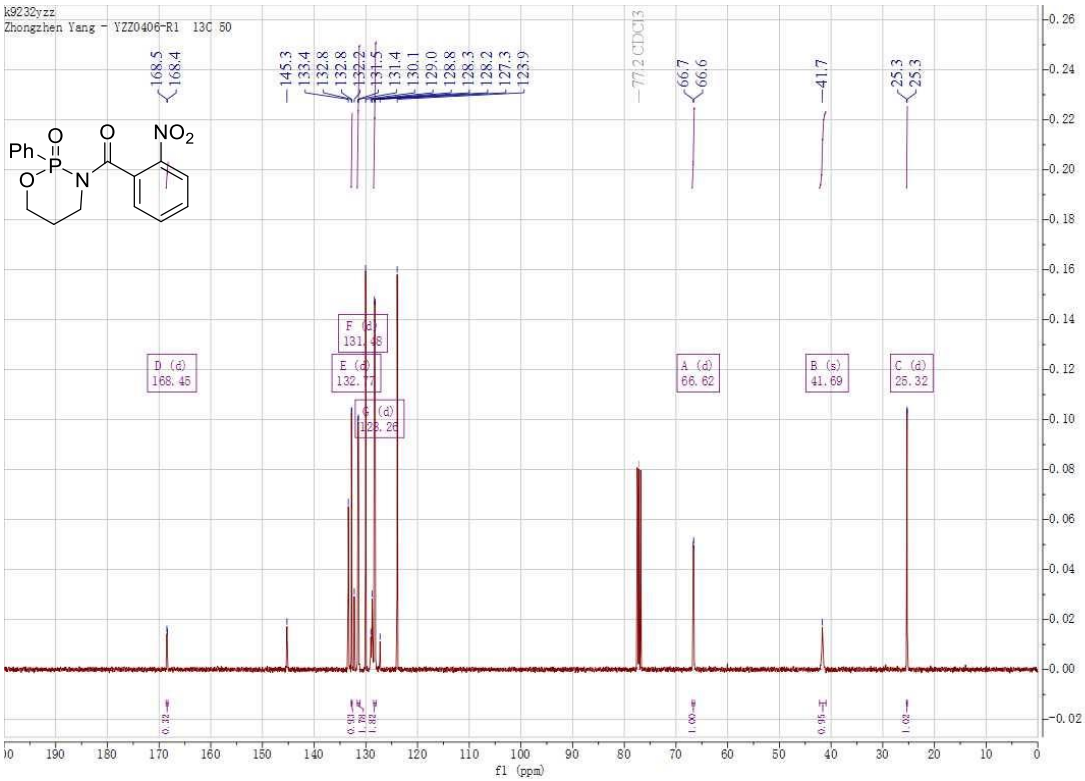


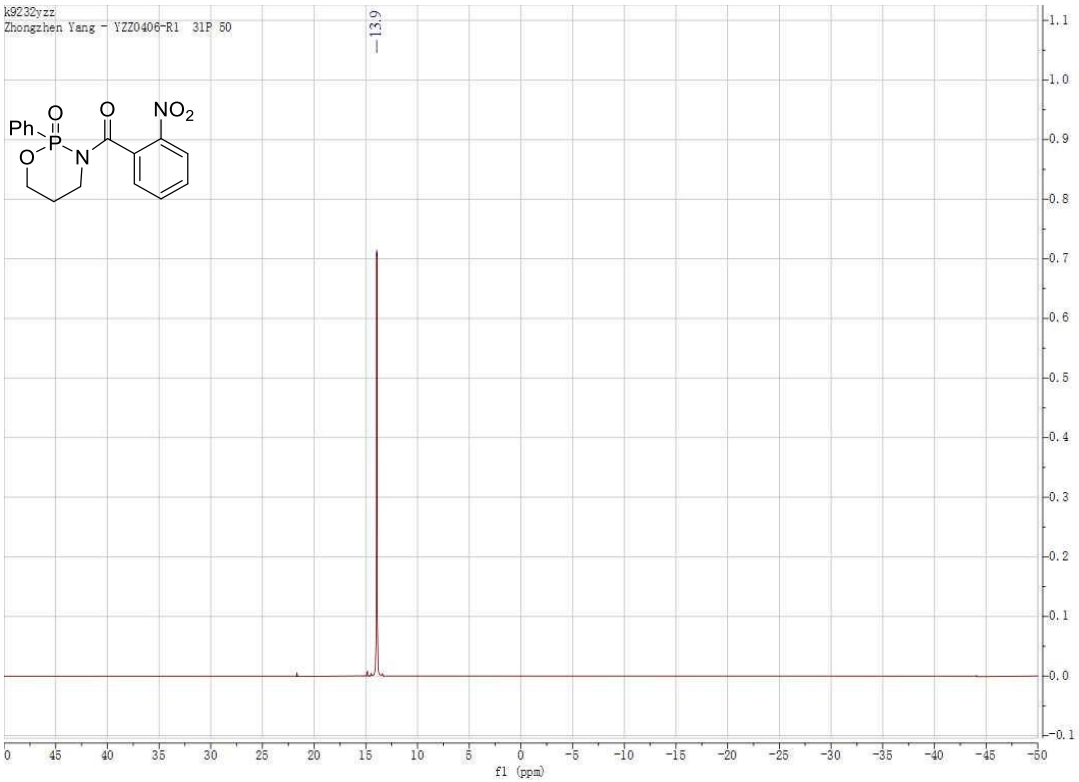

m0207yzz
Zhongzhen Yang - YZZ0515-R1 13C
173.6
173.5
149.9
149.8
139.3
131.3
130.1
129.8
125.7
120.5
119.9
119.9
77.2 CDCl3
70.8
70.8
52.9
44.6
42.0
37.4
25.7
25.7
PhO
O
P
O
N
O
N
H
Br
C (d)
173.56
D (d)
149.85
E (d)
119.90
A (d)
70.80
B (d)
25.72
0.56
0.37
1.79
1.00
0.93
f1 (ppm)


m0207yzz
Zhongzhen Yang - YZZ0515-R1 31P
-8.4
PhO
O
P
O
N
O
N
H
Br
f1 (ppm)

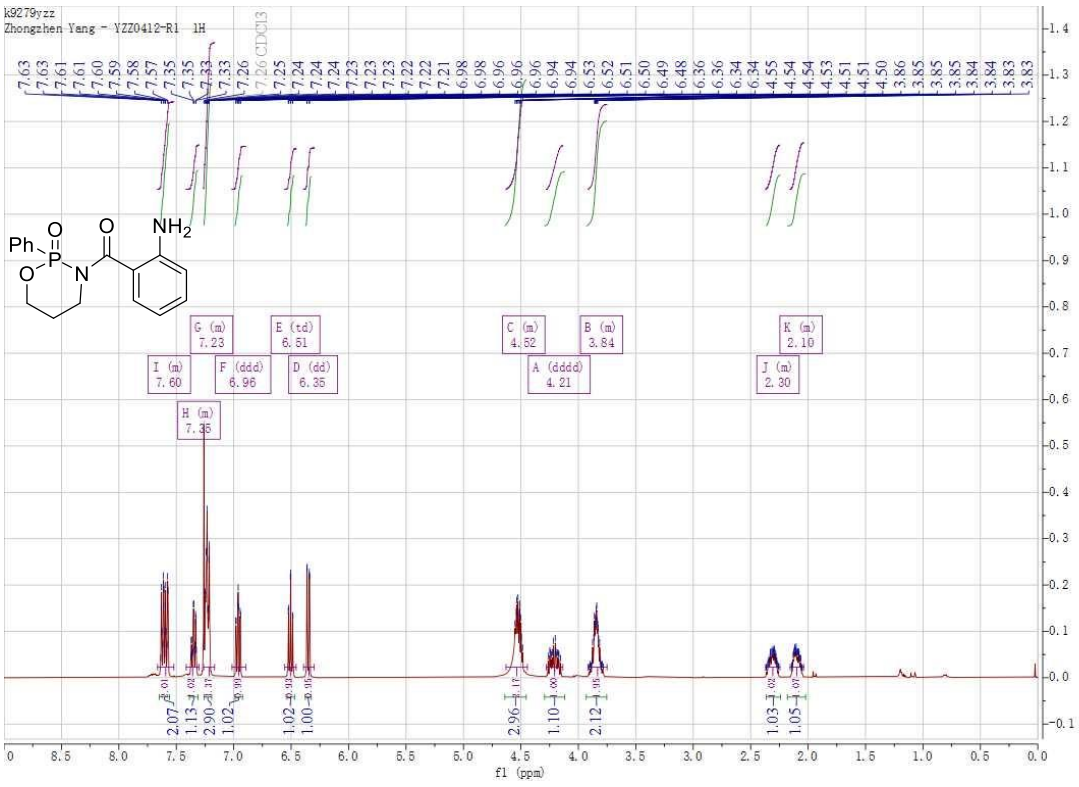
(2-Nitrophenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone (15)

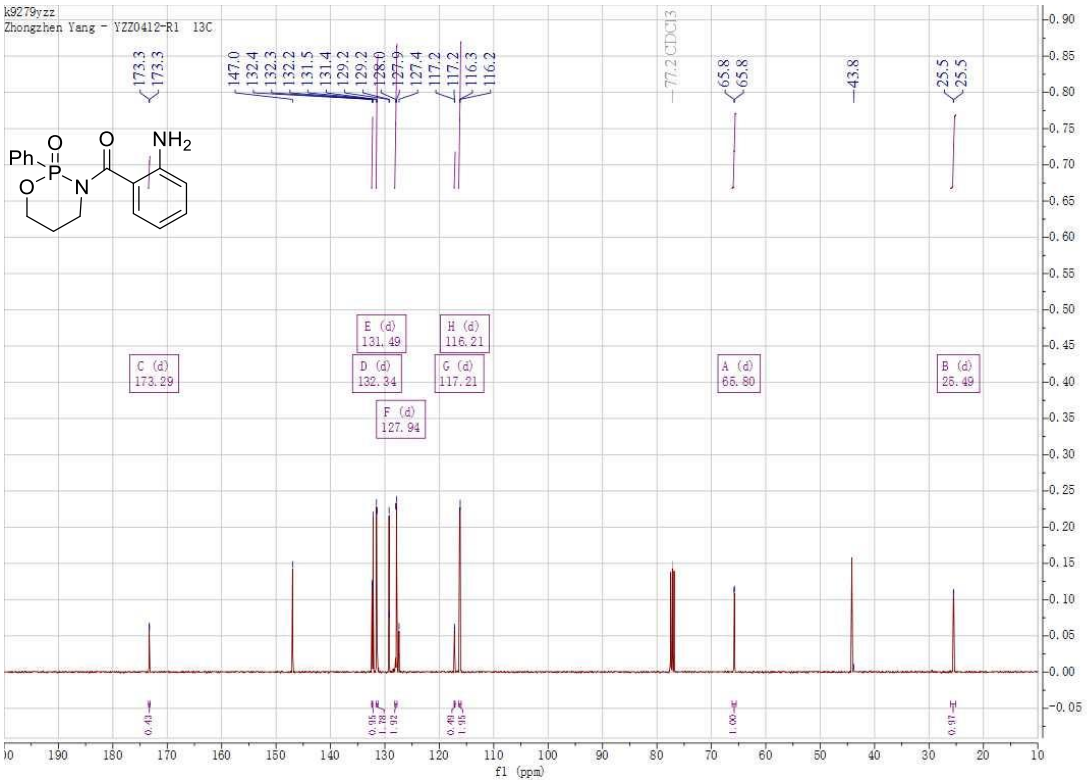


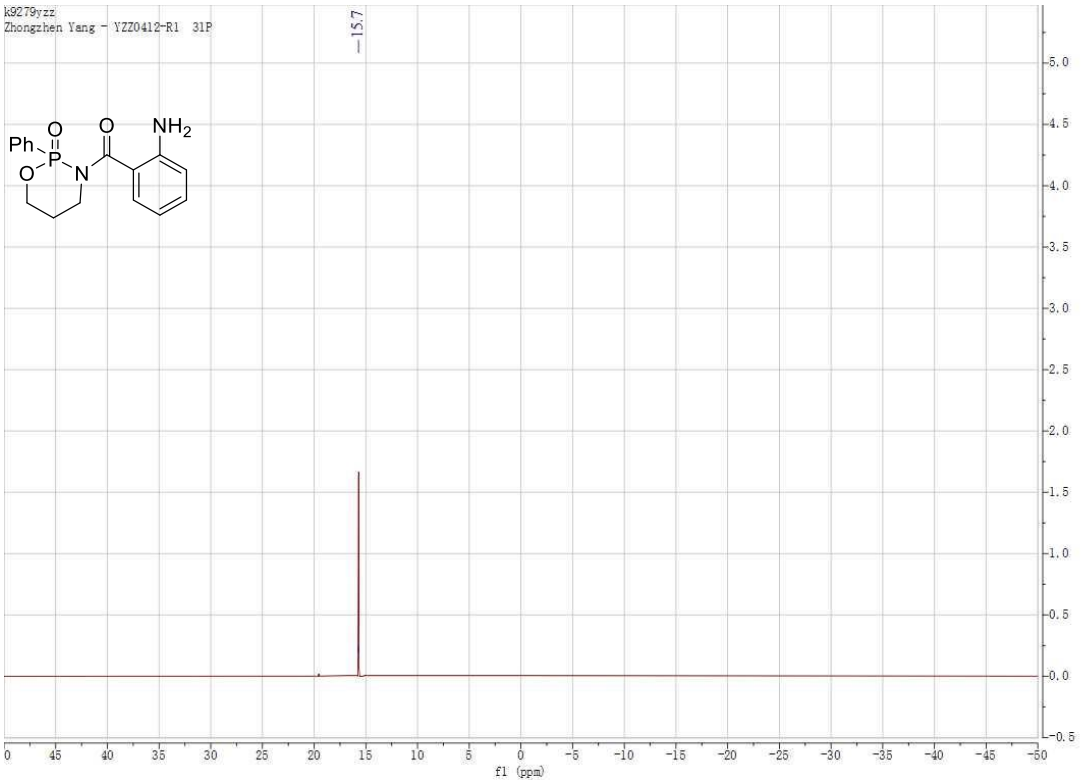




(2-Aminophenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone (16)

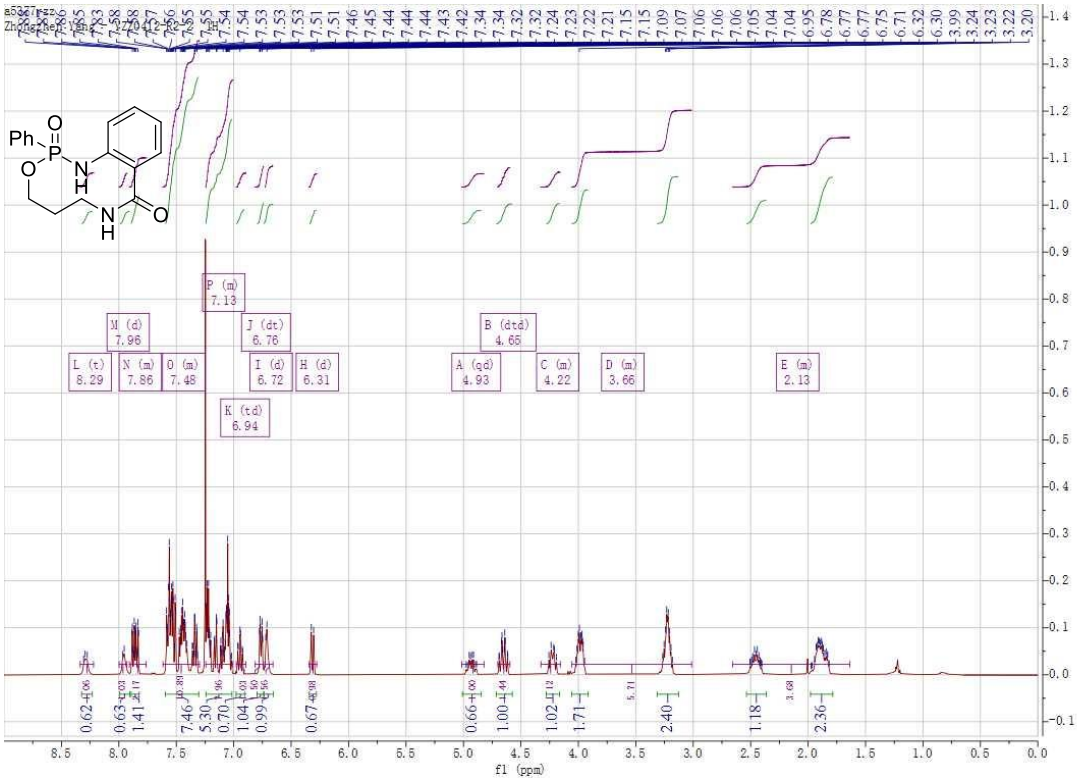


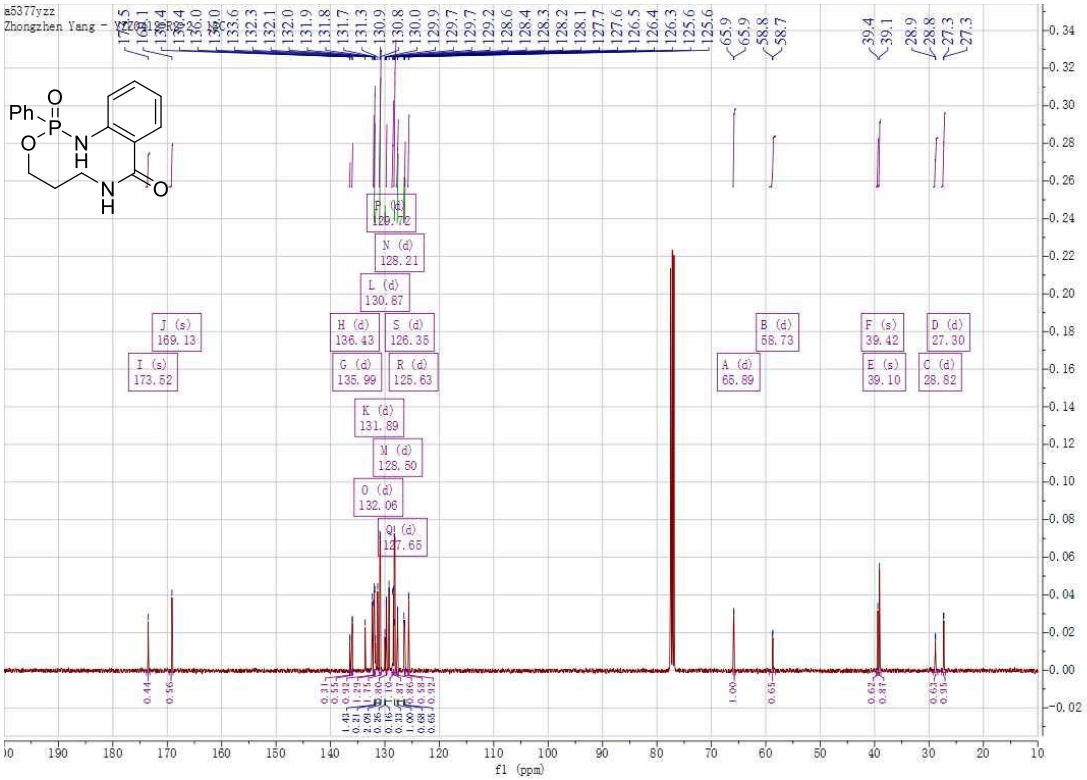

k9279yzz
Zhongzhen Yang - YZZ0412-R1 13C
173.3
173.3
147.0
132.4
132.3
132.2
131.5
131.4
129.2
129.2
128.6
127.9
127.4
117.2
117.2
116.3
116.2
77.2 CDCl3
65.8
65.8
43.8
25.5
25.5
E (d) 131.49
H (d) 116.21
C (d) 173.29
D (d) 132.34
G (d) 117.21
A (d) 65.80
B (d) 26.49
F (d) 127.94
f1 (ppm)

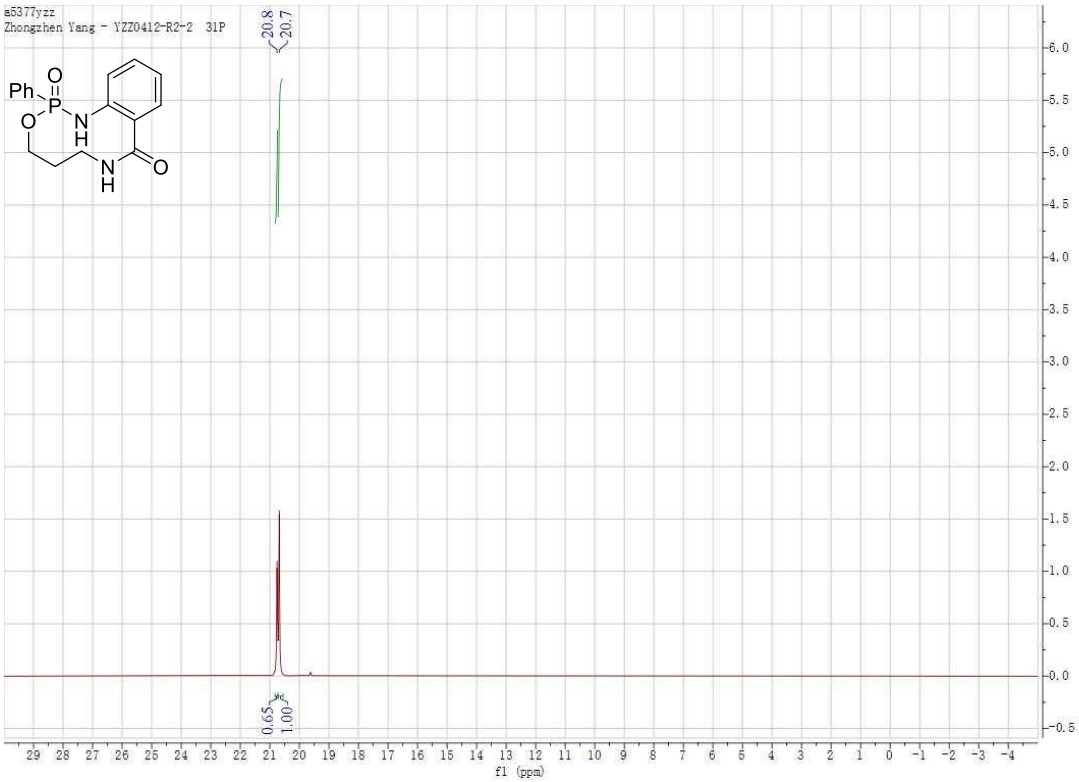

k9279yzz
Zhongzhen Yang - YZZ0412-R1 31P
15.7
f1 (ppm)

2-Phenyl-1,4,5,6,7-pentahydrobenzo[*d*][1,3,7,2]oxadiazaphosphecin-8-one 2-oxide (17)

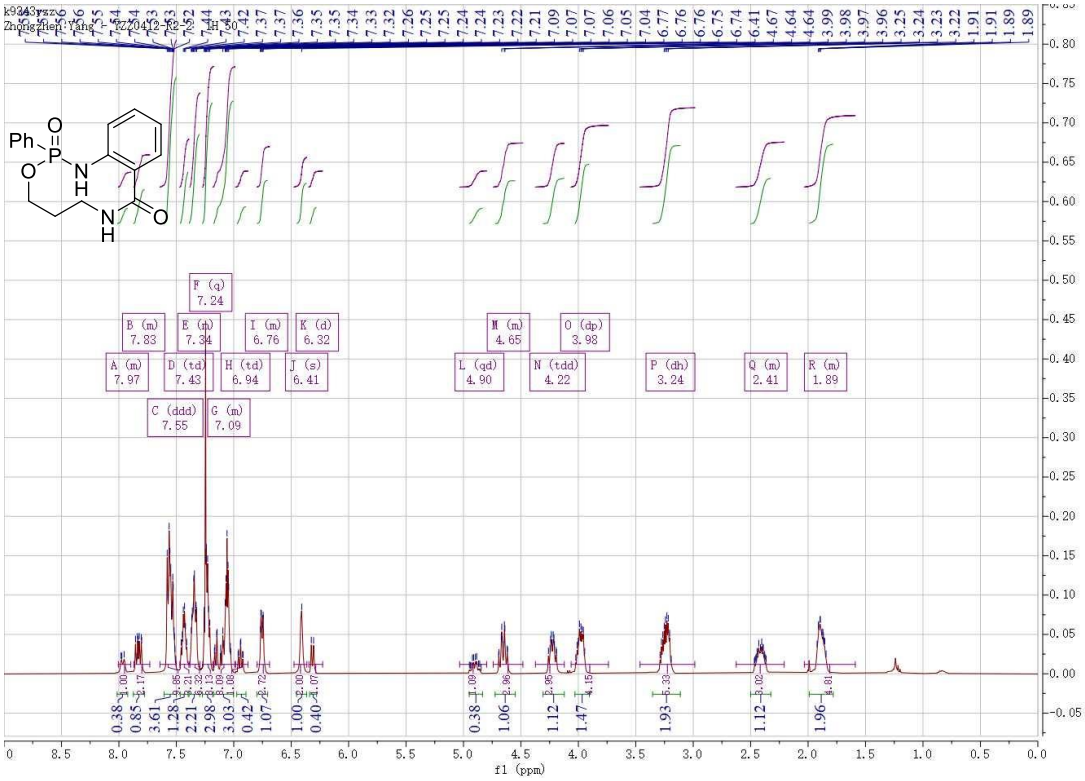
NMRs at RT

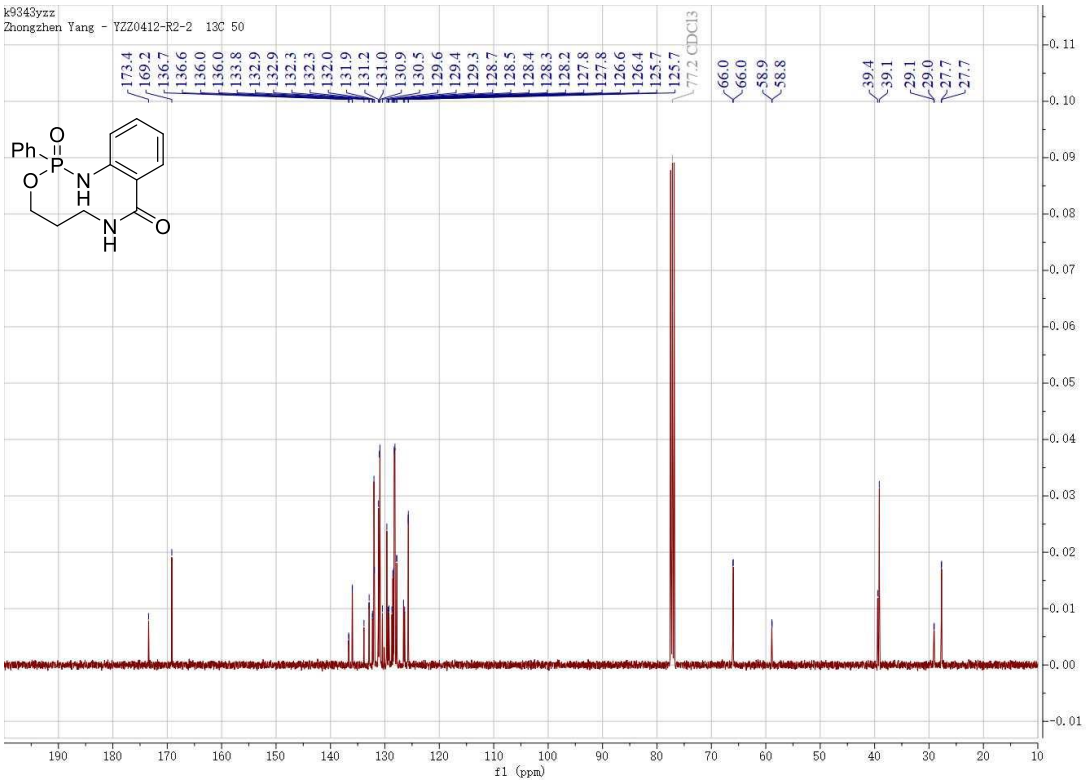


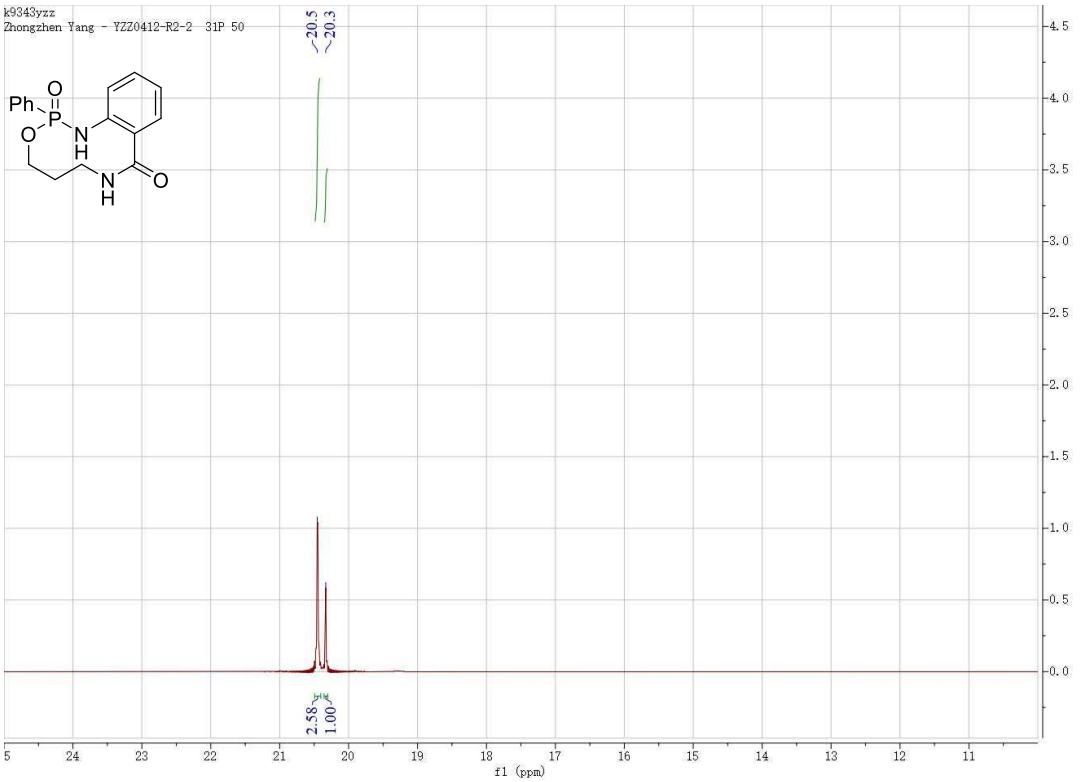



a5377yzz
Zhongzhen Yang - YZZ0412-R2-2 31P
20.8
20.7
0.65
1.00
f1 (ppm)

17 NMRs at 50 ℃

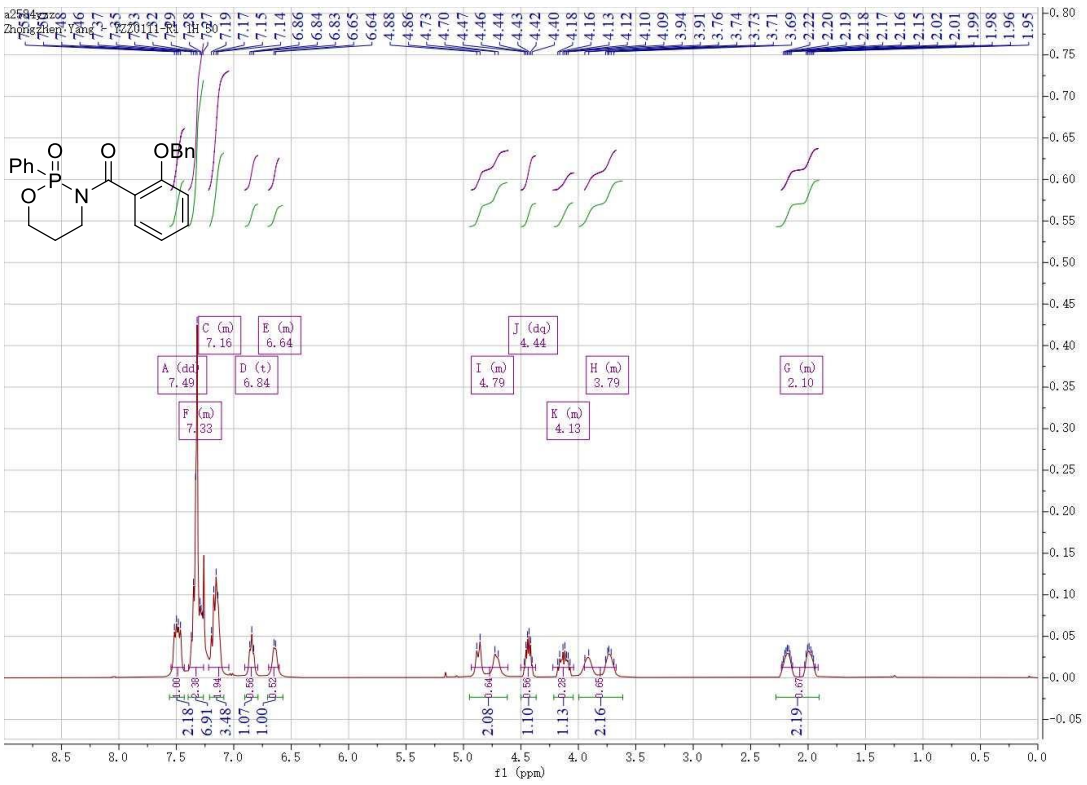

F (q) 7.24
B (m) 7.83
E (q) 7.34
I (m) 6.76
K (d) 6.32
M (m) 4.65
O (dp) 3.98
A (m) 7.97
D (td) 7.43
H (td) 6.94
J (s) 6.41
L (qd) 4.90
N (tdd) 4.22
P (dh) 3.24
Q (m) 2.41
R (m) 1.89
C (ddd) 7.55
G (m) 7.09
f1 (ppm)

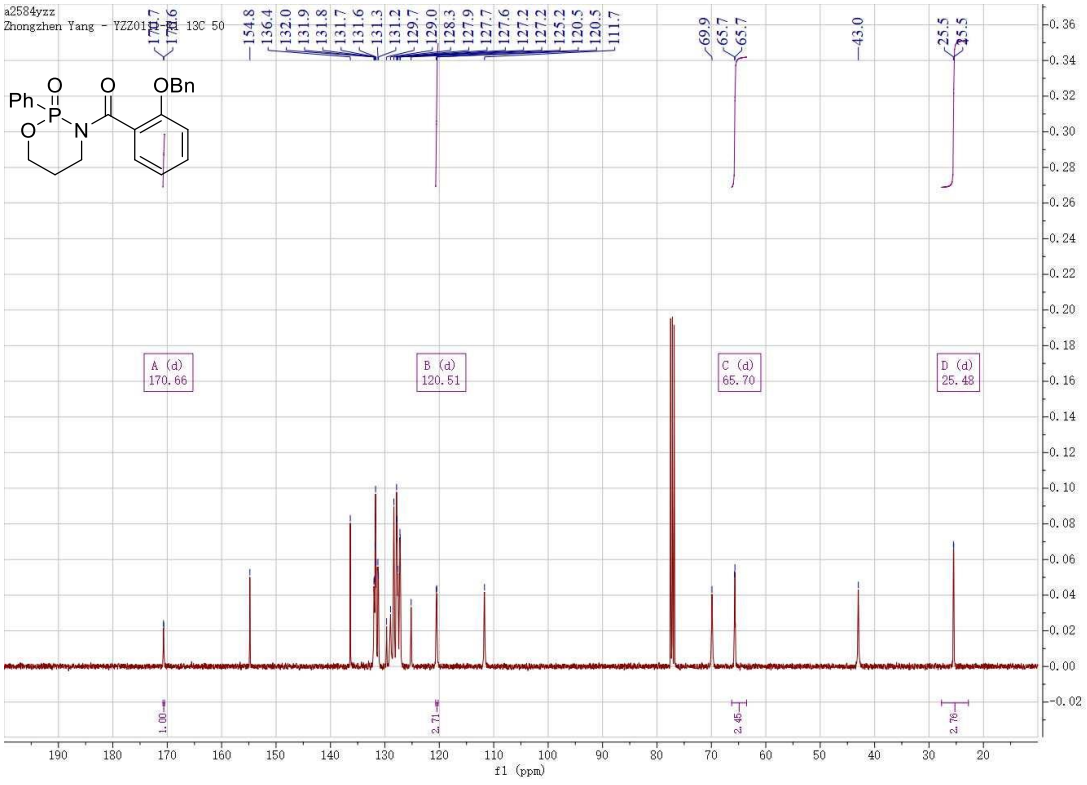

k9343yzz
Zhongzhen Yang - YZZ0412-R2-2 13C 50
173.4
169.2
136.7
136.6
136.0
136.0
133.8
132.9
132.9
132.3
132.3
132.0
131.9
131.2
131.0
130.9
130.5
129.6
129.4
129.3
128.7
128.5
128.4
128.3
128.2
127.8
127.8
126.6
126.4
125.7
125.7
77.2 CDCl3
66.0
66.0
58.9
58.8
39.4
39.1
29.1
29.0
27.7
27.7
Ph
O
P
O
N
H
N
H
O
f1 (ppm)

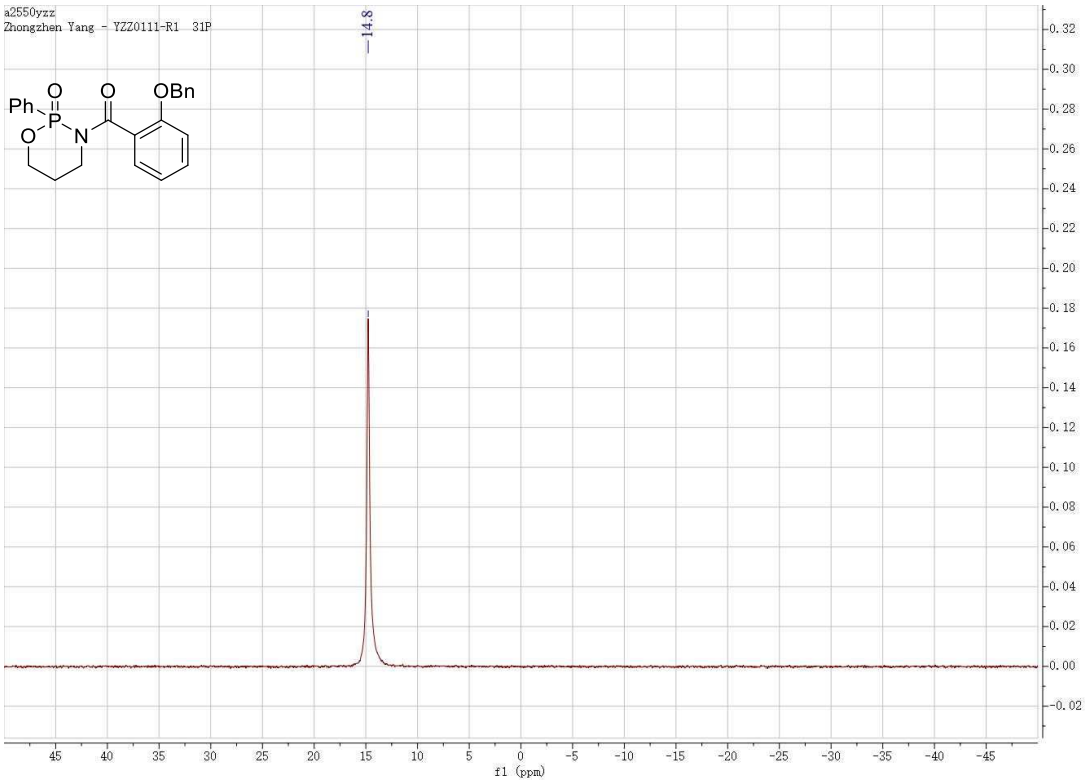

k9343yzz
Zhongzhen Yang - YZZ0412-R2-2 31P 50
20.5
20.3
2.58
1.00
Ph
O
P
O
N
H
N
H
O
f1 (ppm)

(2-(Benzyloxy)phenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone

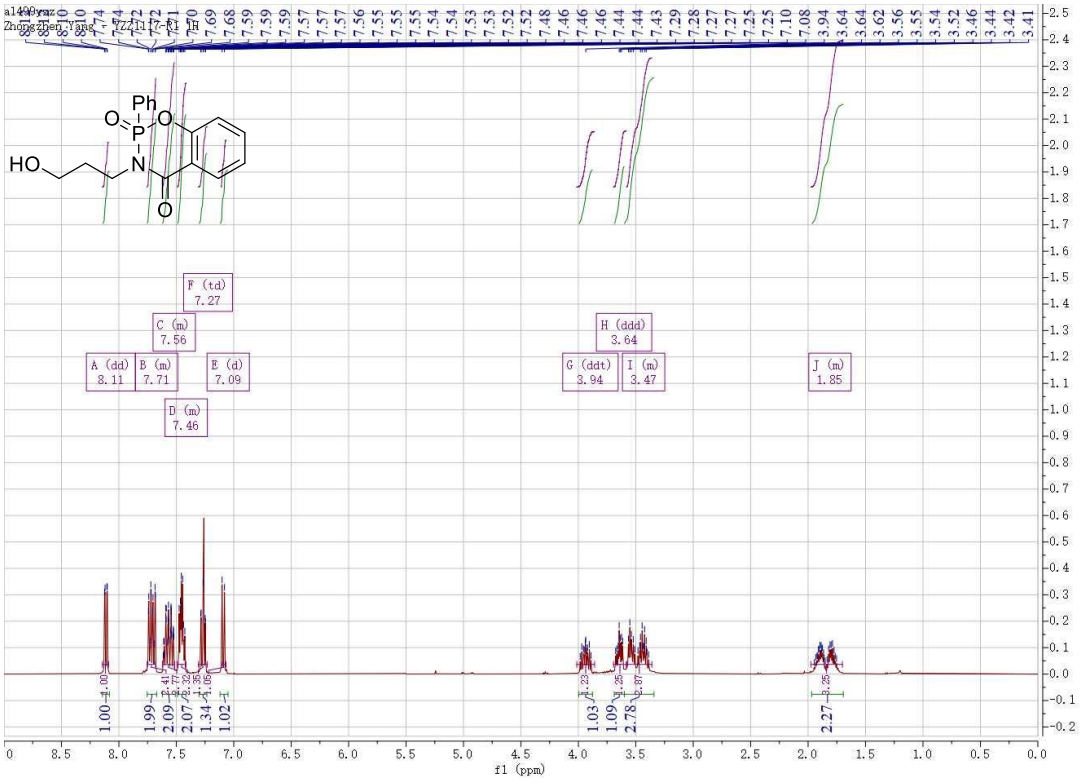
(18a)

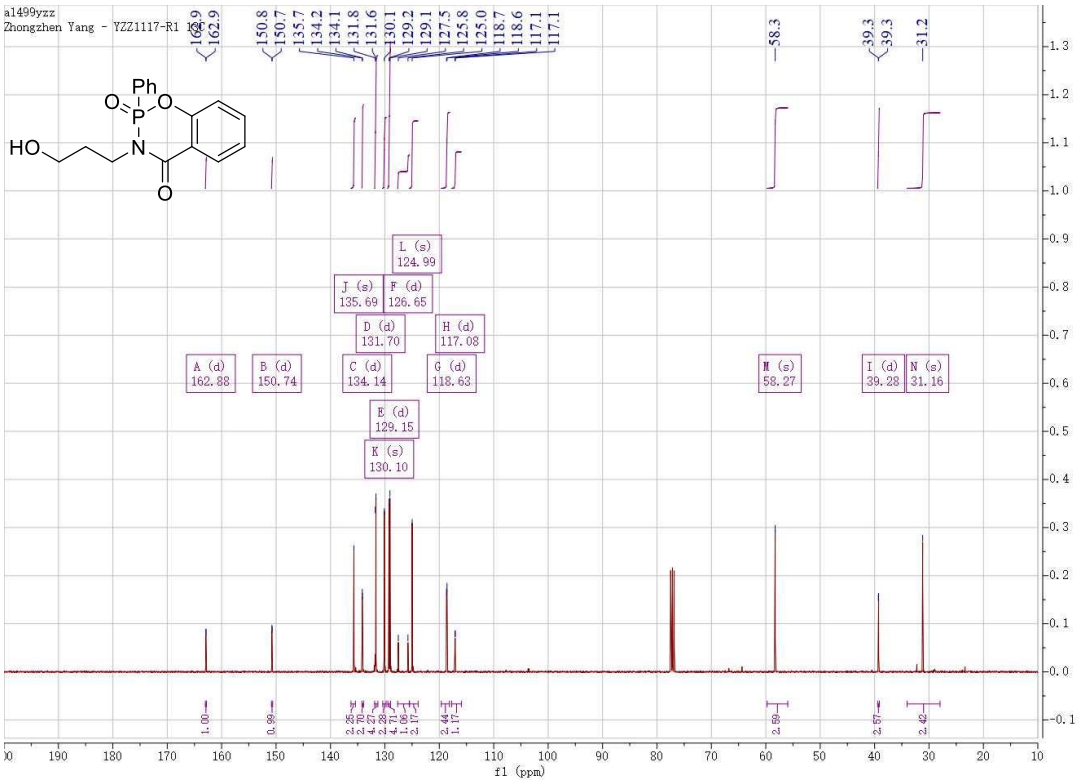


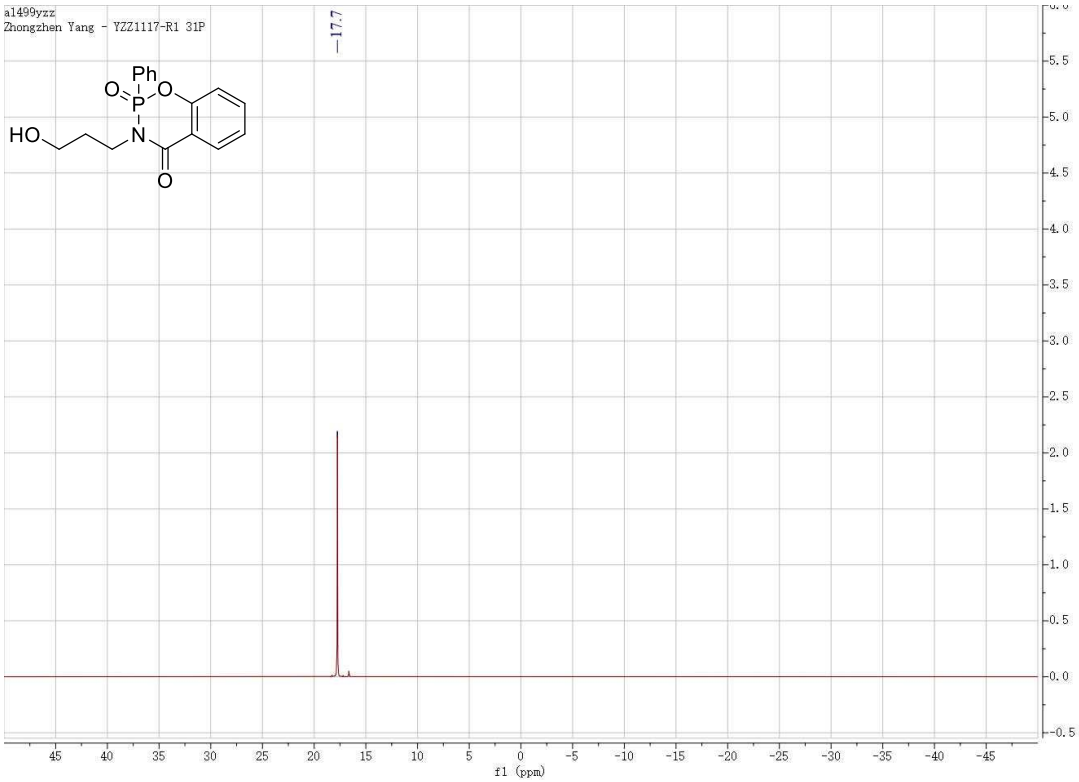




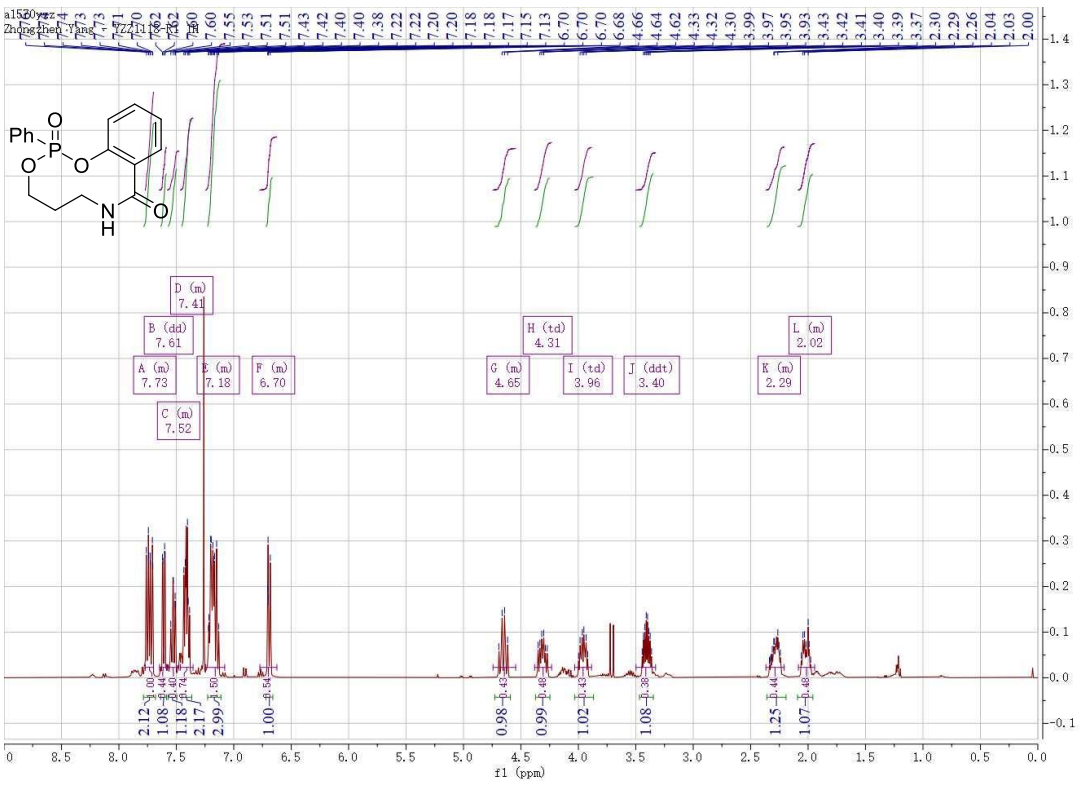
3-(3-Hydroxypropyl)-2-phenyl-3-hydrobenzo[*e*][1,3,2]oxazaphosphinin-4-one 2-oxide (20a)

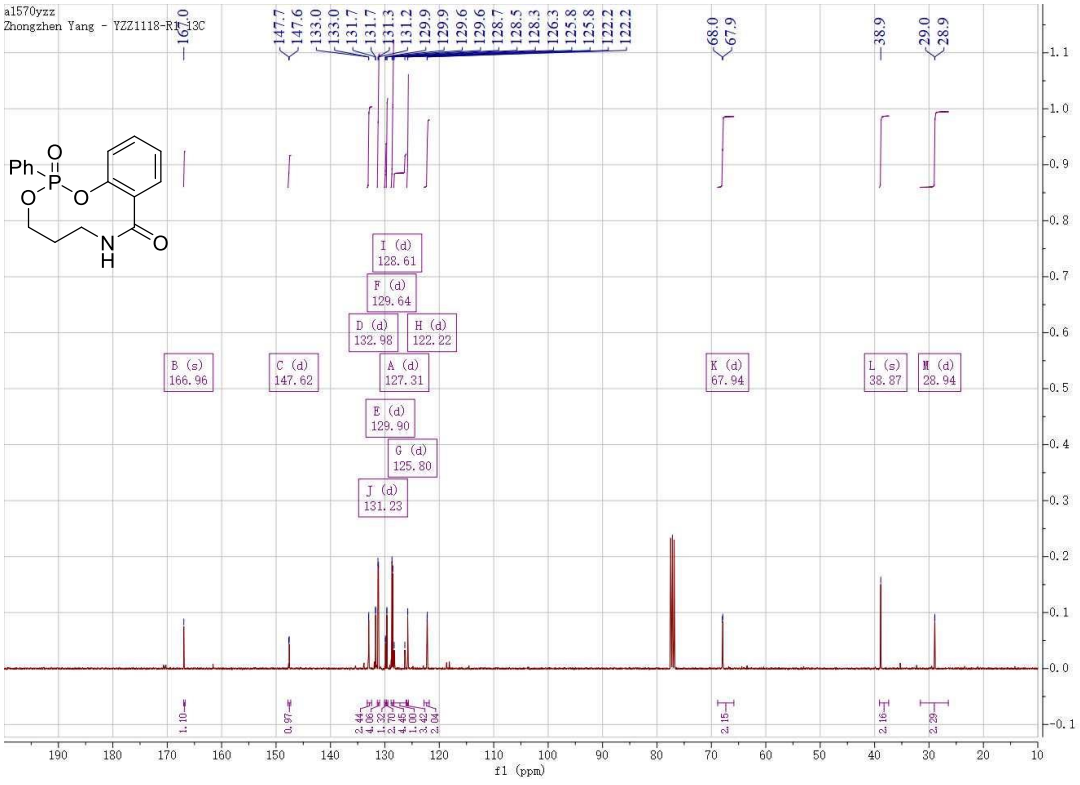


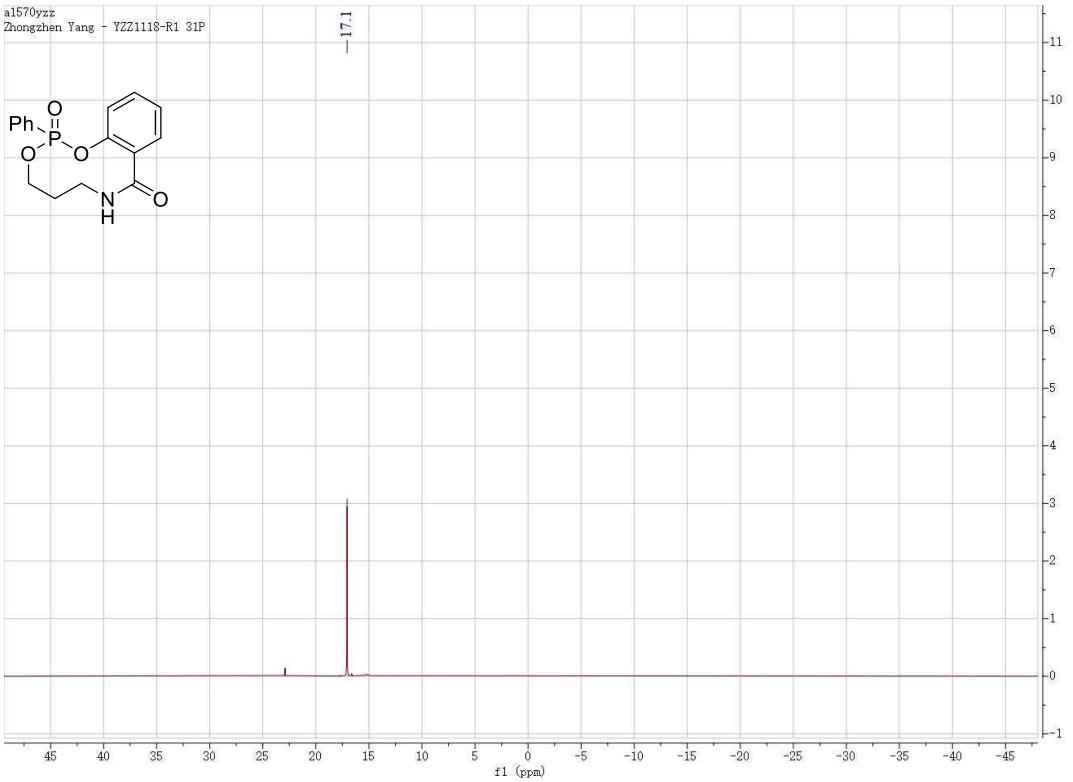

a1499yzz
Zhongzhen Yang - YZZ1117-R1 13C
Ph
O
P
O
N
HO
O
A (d) 162.88
B (d) 150.74
C (d) 134.14
D (d) 131.70
E (d) 129.15
F (d) 126.65
G (d) 118.63
H (d) 117.08
I (d) 39.28
J (s) 135.69
K (s) 130.10
L (s) 124.99
M (s) 58.27
N (s) 31.16
f1 (ppm)


a1499yzz
Zhongzhen Yang - YZZ1117-R1 31P
17.7
Ph
O
P
O
N
HO
O
f1 (ppm)

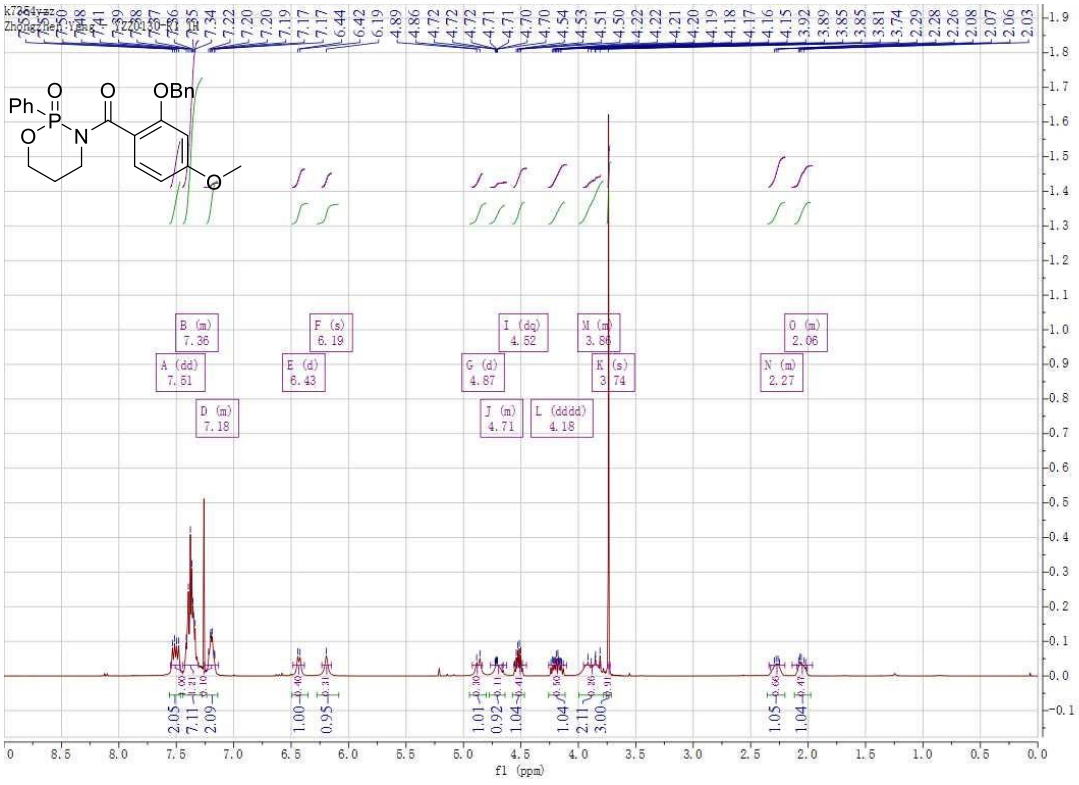
2-Phenyl-4,5,6,7-tetrahydro-8*H*-benzo[*d*][1,3,7,2]dioxazaphosphecin-8-one 2-oxide (21a)

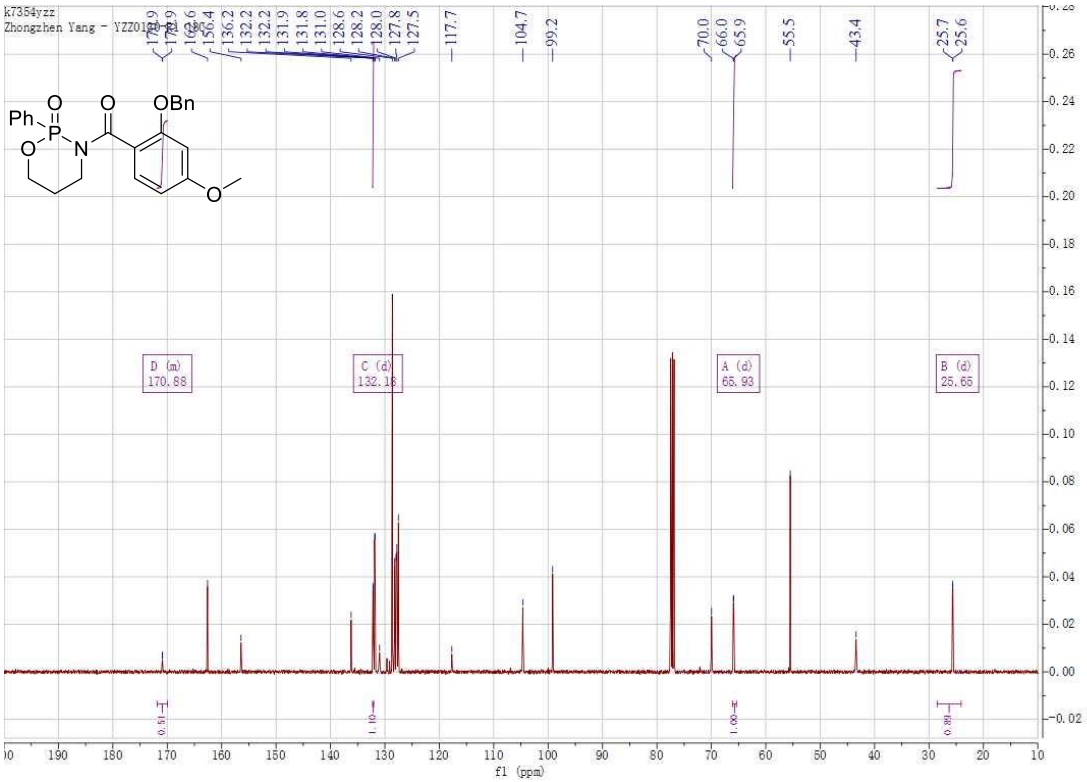


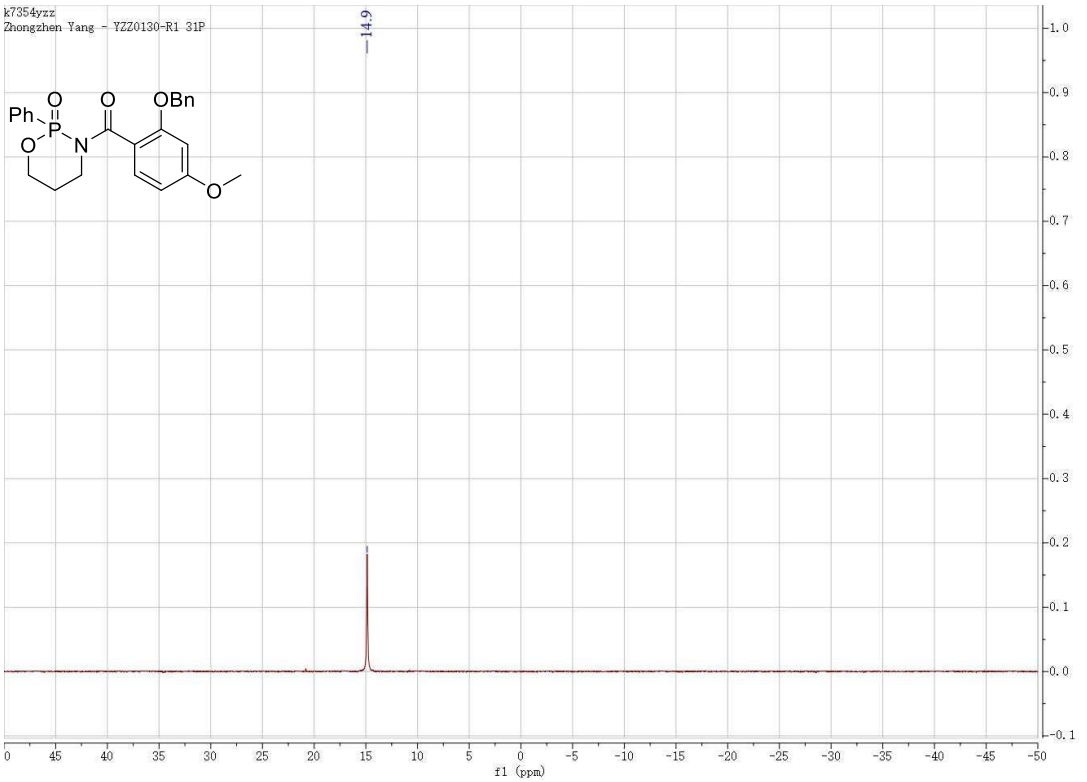




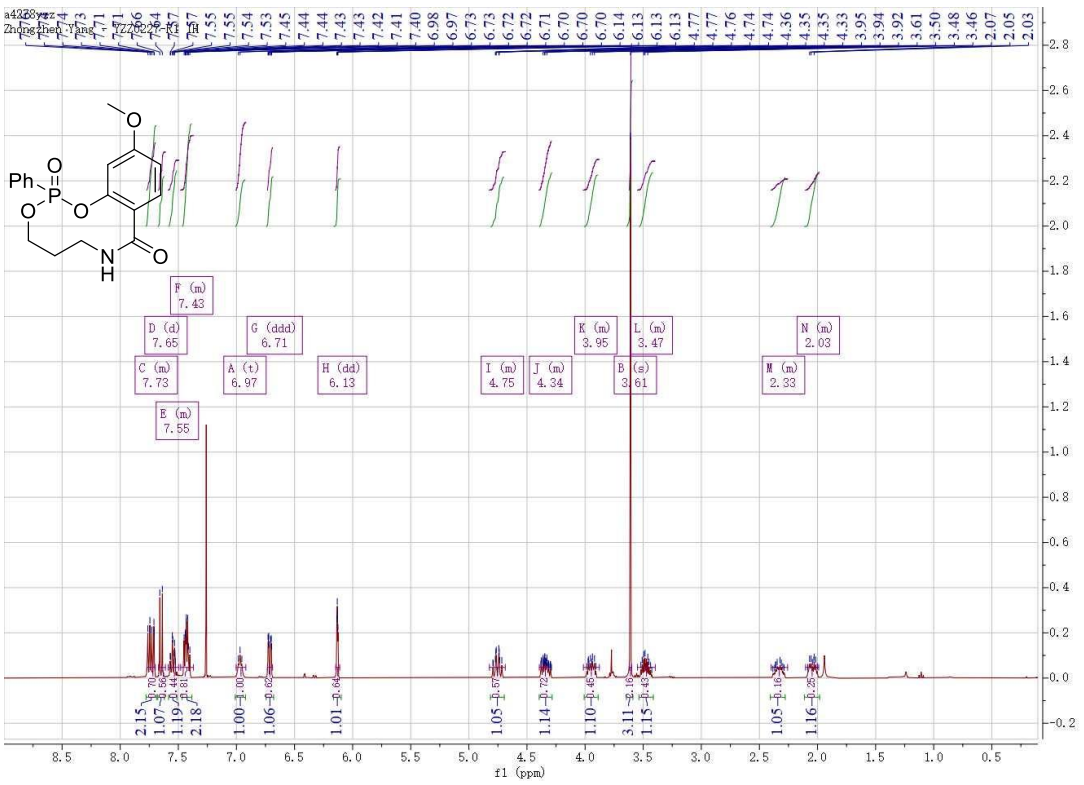
(2-(Benzyloxy)-4-methoxyphenyl) (2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl) methanone (18b)

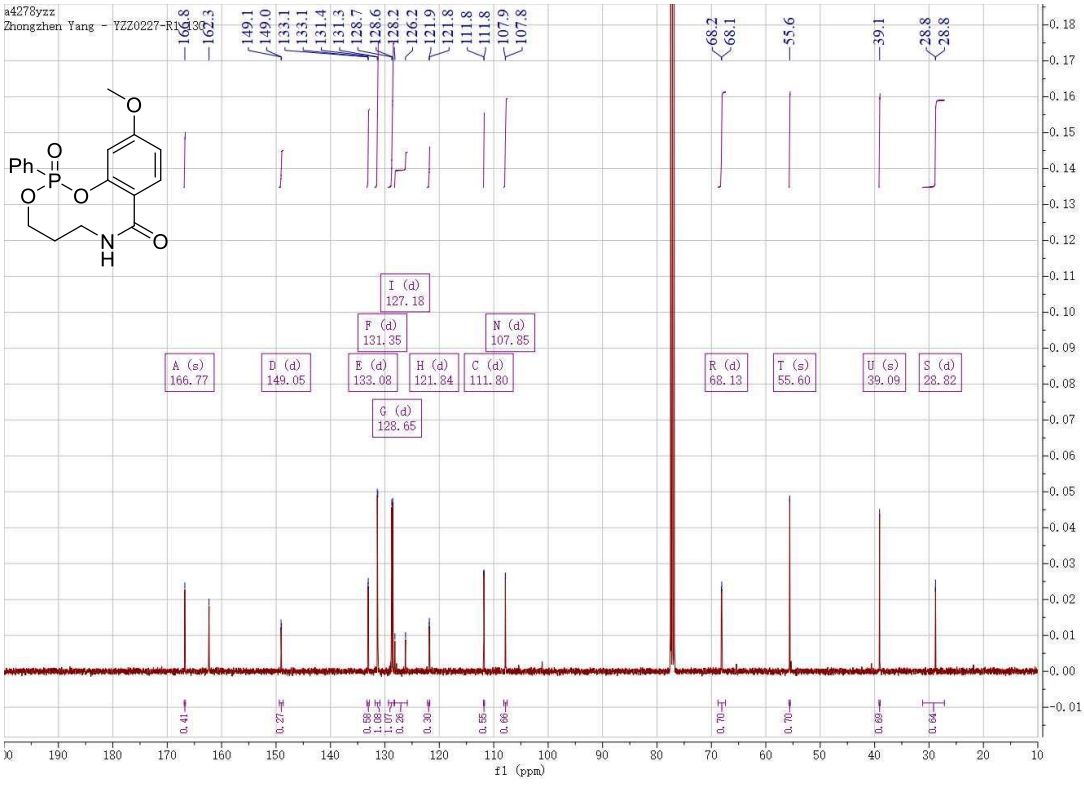


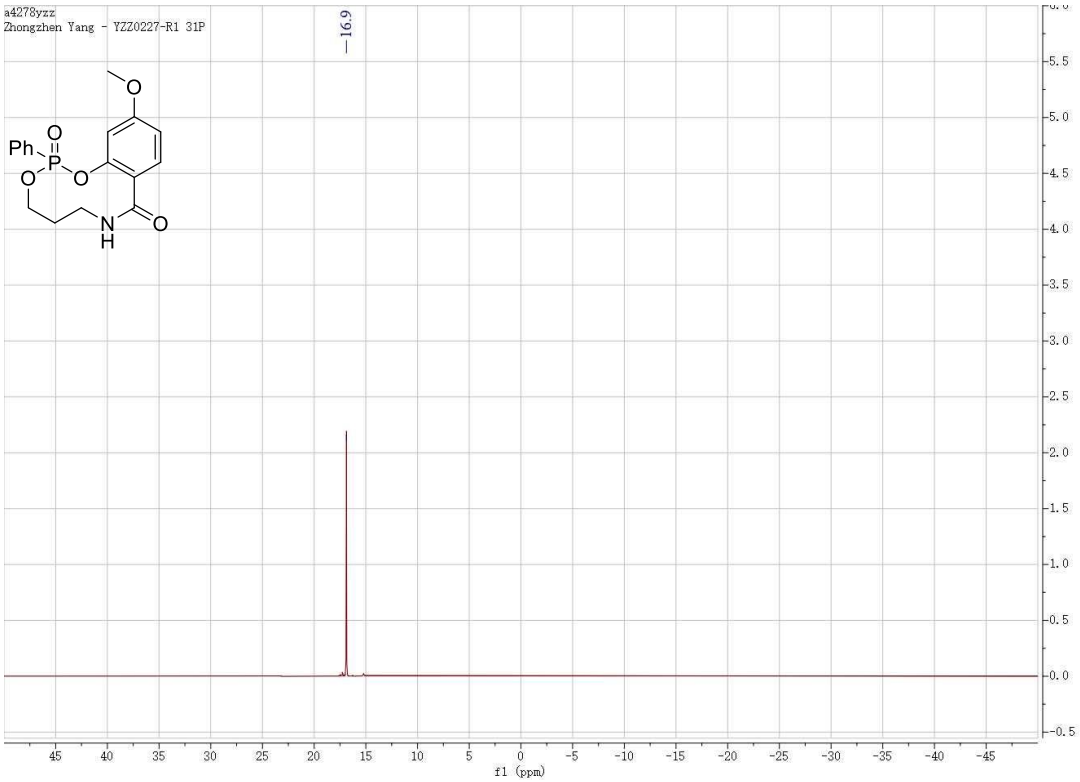

k7354yzz
Zhongzhen Yang - YZZ0130-R1
170.9
132.2
131.9
131.8
131.0
128.6
128.2
128.0
127.8
127.5
117.7
104.7
99.2
70.0
66.0
65.9
55.5
43.4
25.7
25.6
Ph
O
O
OBn
P
N
O
O
D (m)
170.88
C (d)
132.18
A (d)
65.93
B (d)
25.65
fl (ppm)


k7354yzz
Zhongzhen Yang - YZZ0130-R1 31P
14.9
Ph
O
O
OBn
P
N
O
O
fl (ppm)

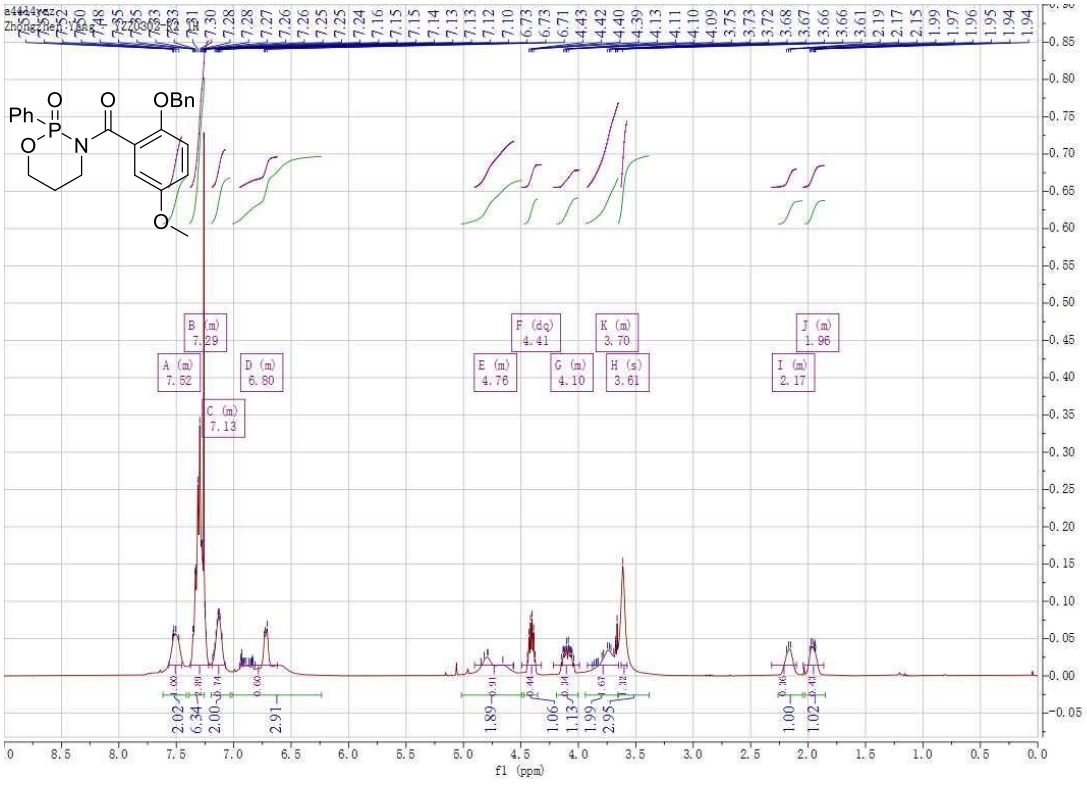
11-Methoxy-2-phenyl-4,5,6,7-tetrahydro-8*H*-benzo[*d*][1,3,7,2]dioxazaphosphecin-8-one 2-oxide (21b)

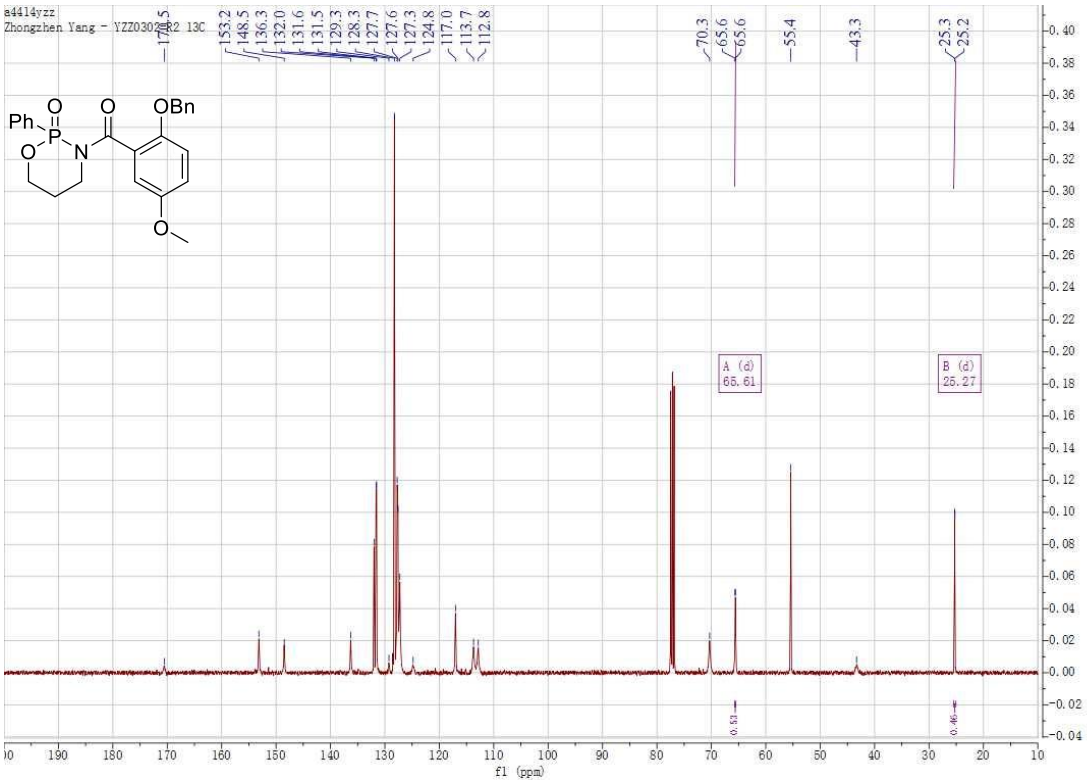


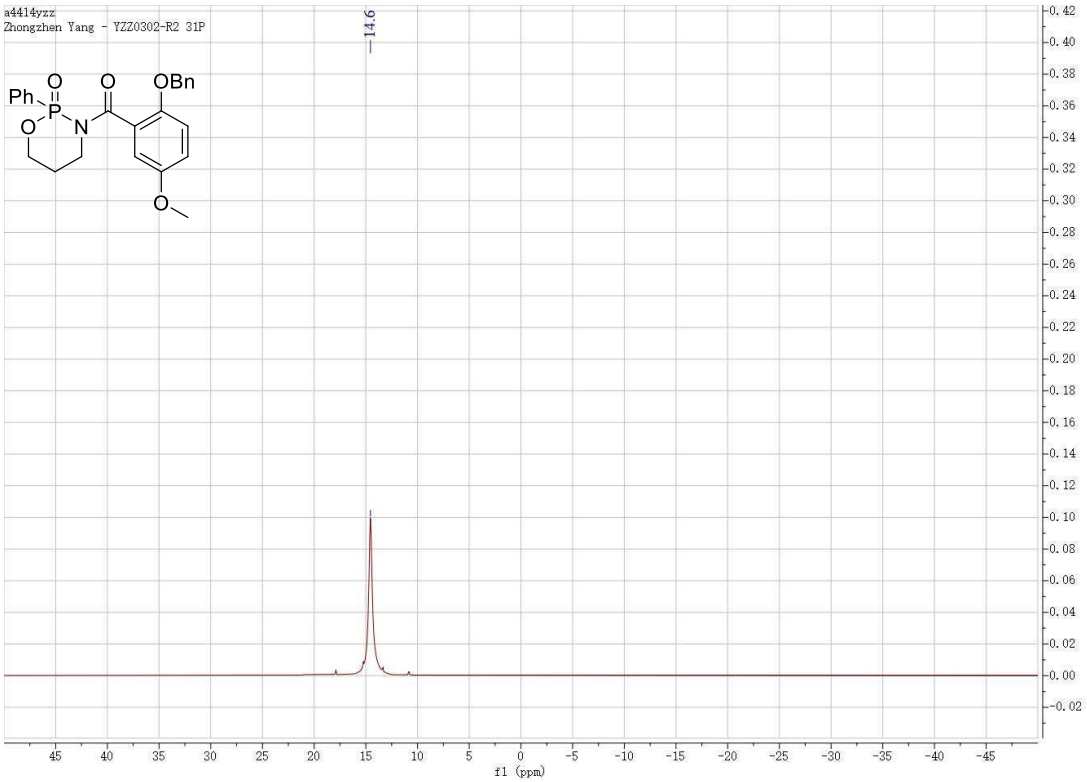




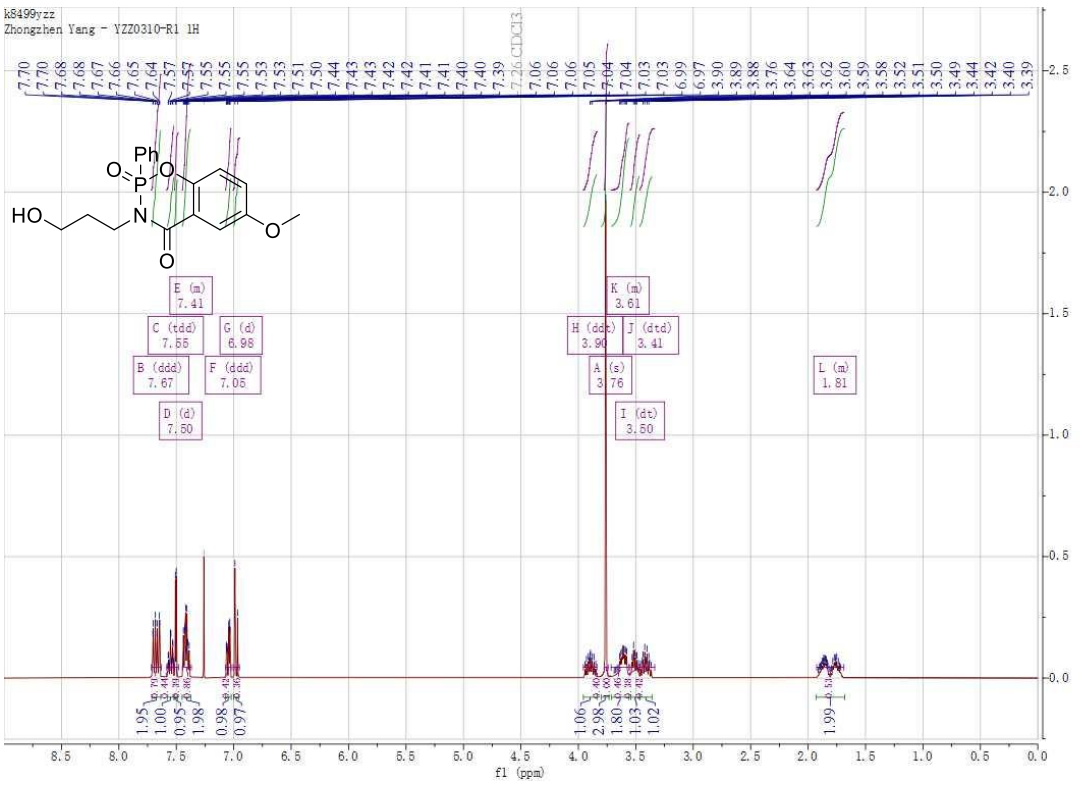
(2-(Benzyloxy)-5-methoxyphenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone (18c)

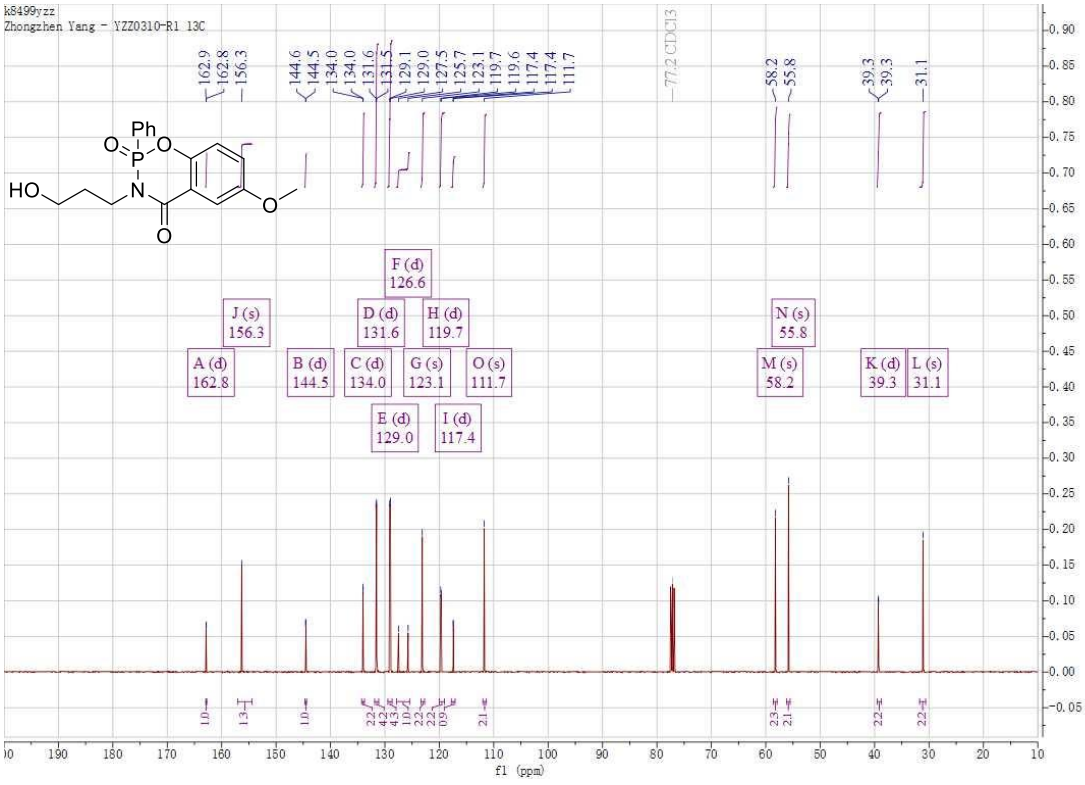


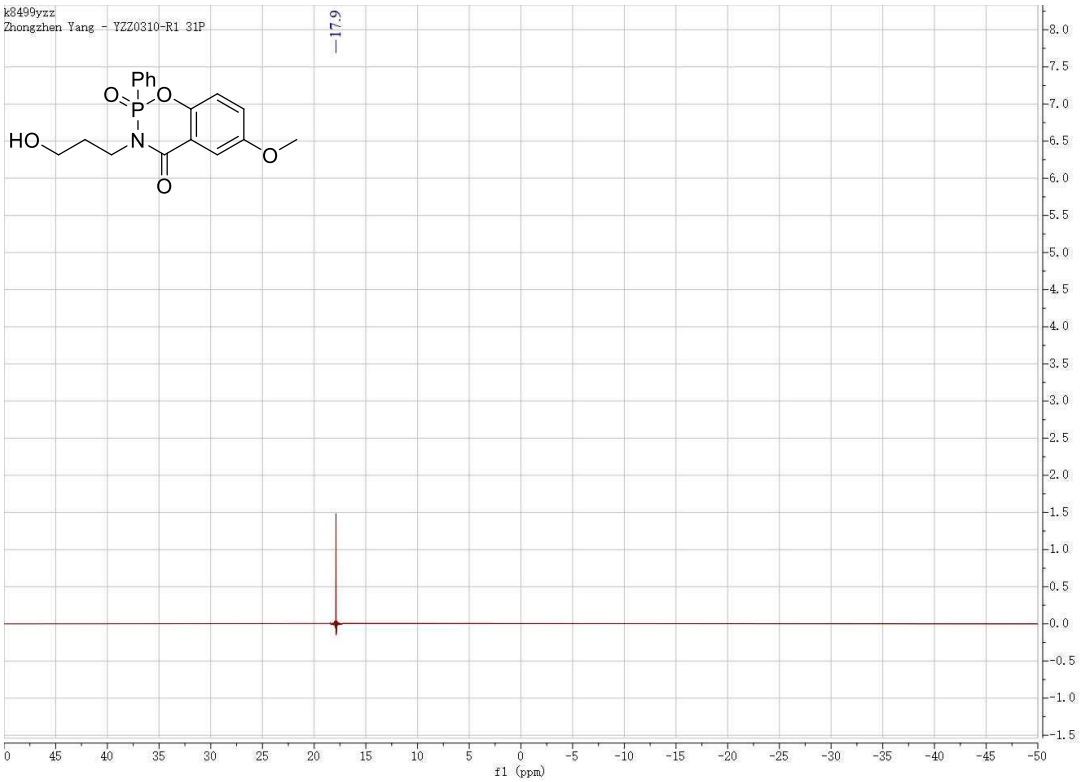

a4414yzz
Zhongzhen Yang - YZZ0302-R2 13C
153.2
148.5
136.3
132.0
131.6
131.5
129.3
128.3
127.7
127.6
127.3
124.8
117.0
113.7
112.8
70.3
65.6
65.6
55.4
43.3
25.3
25.2
A (d)
65.61
B (d)
26.27
Ph
O
P
N
O
O
OBn
O
f1 (ppm)


a4414yzz
Zhongzhen Yang - YZZ0302-R2 31P
14.6
Ph
O
P
N
O
O
OBn
O
f1 (ppm)

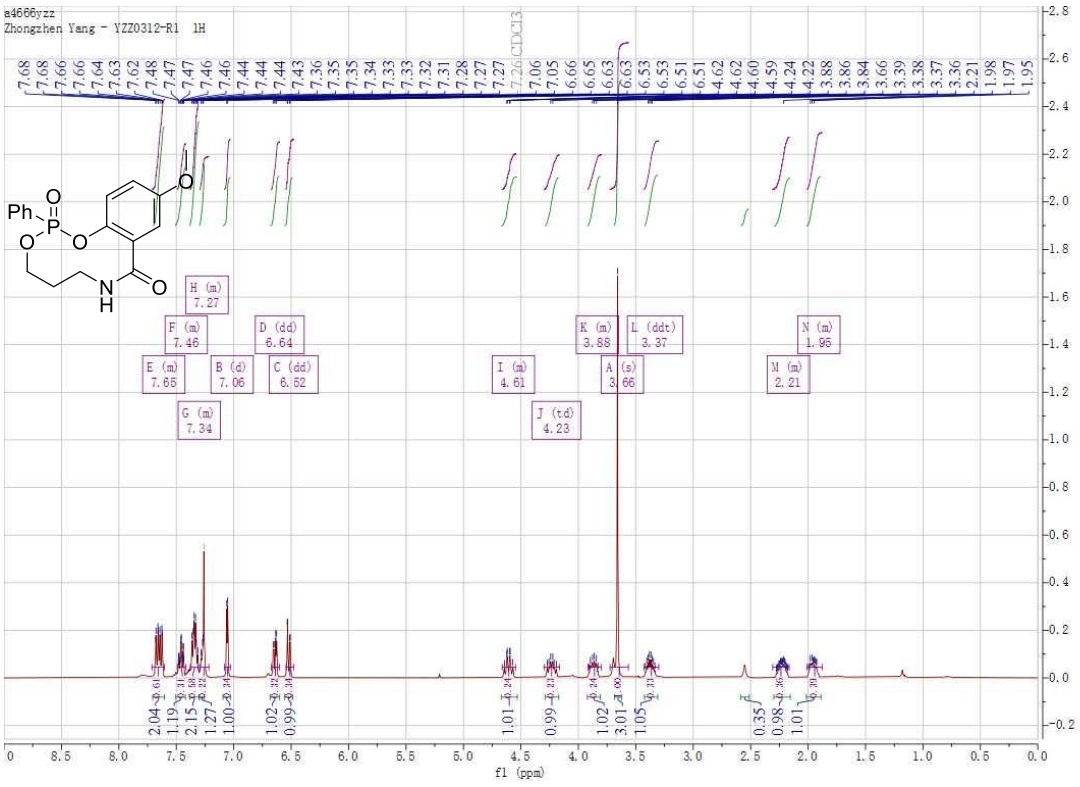
3-(3-Hydroxypropyl)-6-methoxy-2-phenyl-3-hydrobenzo[*e*][1,3,2]oxazaphosphinin-4-one 2-oxide (20c)

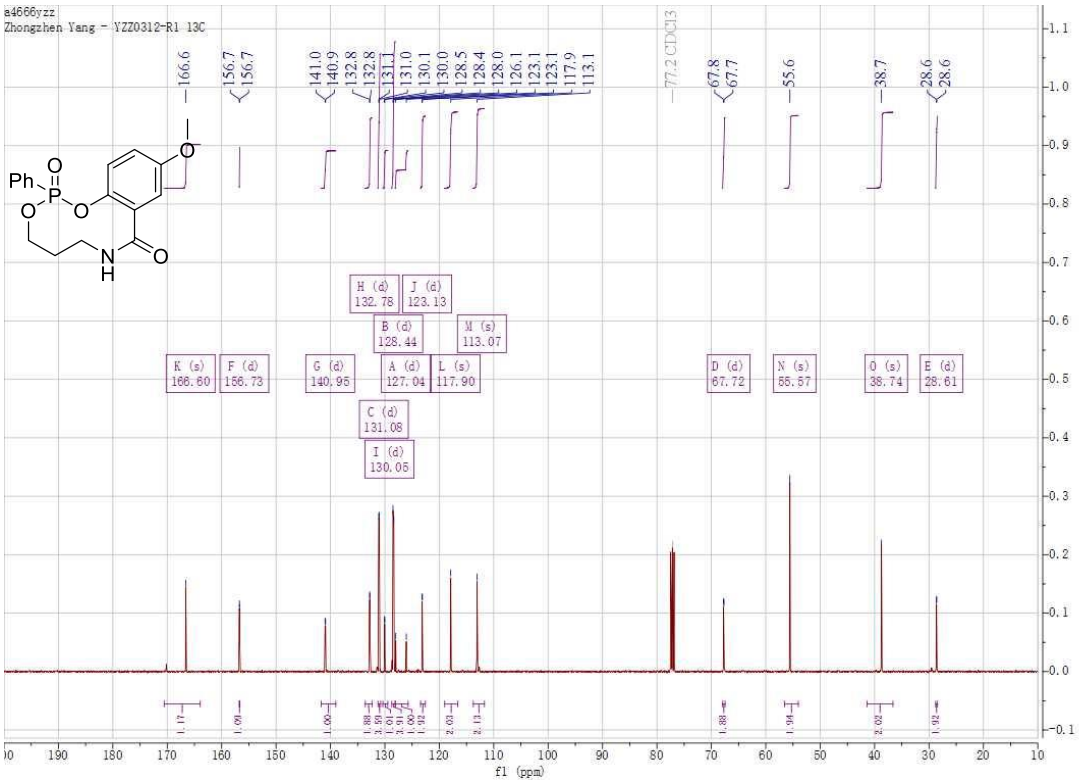


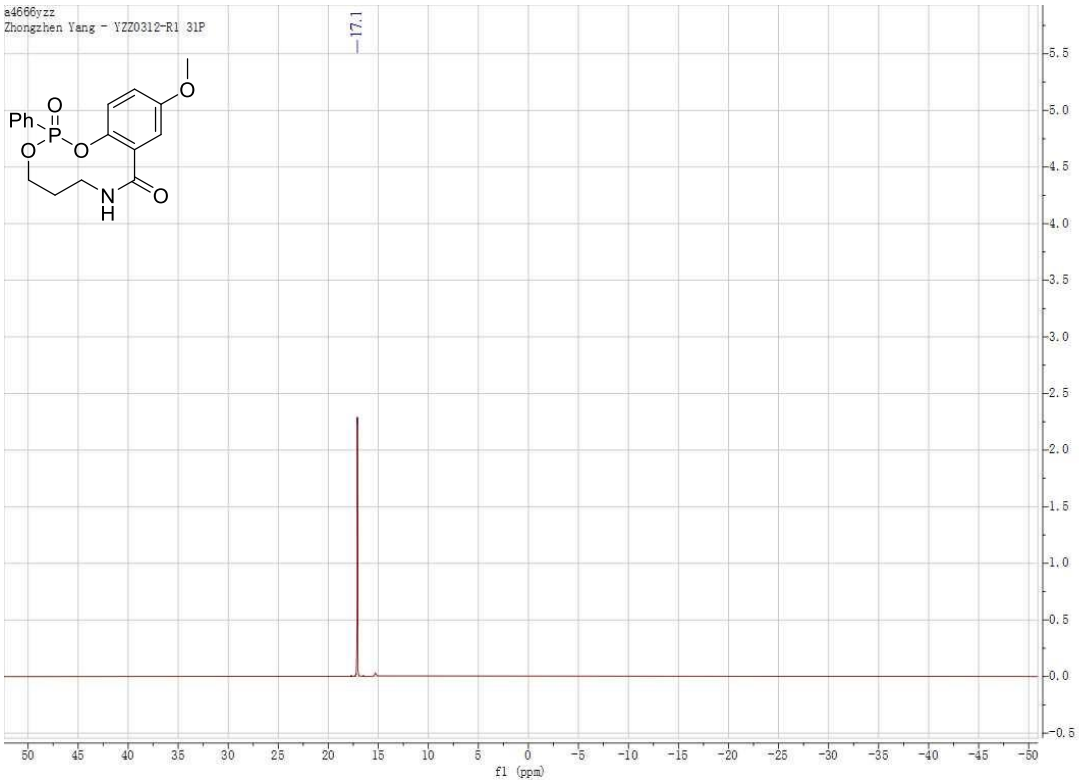




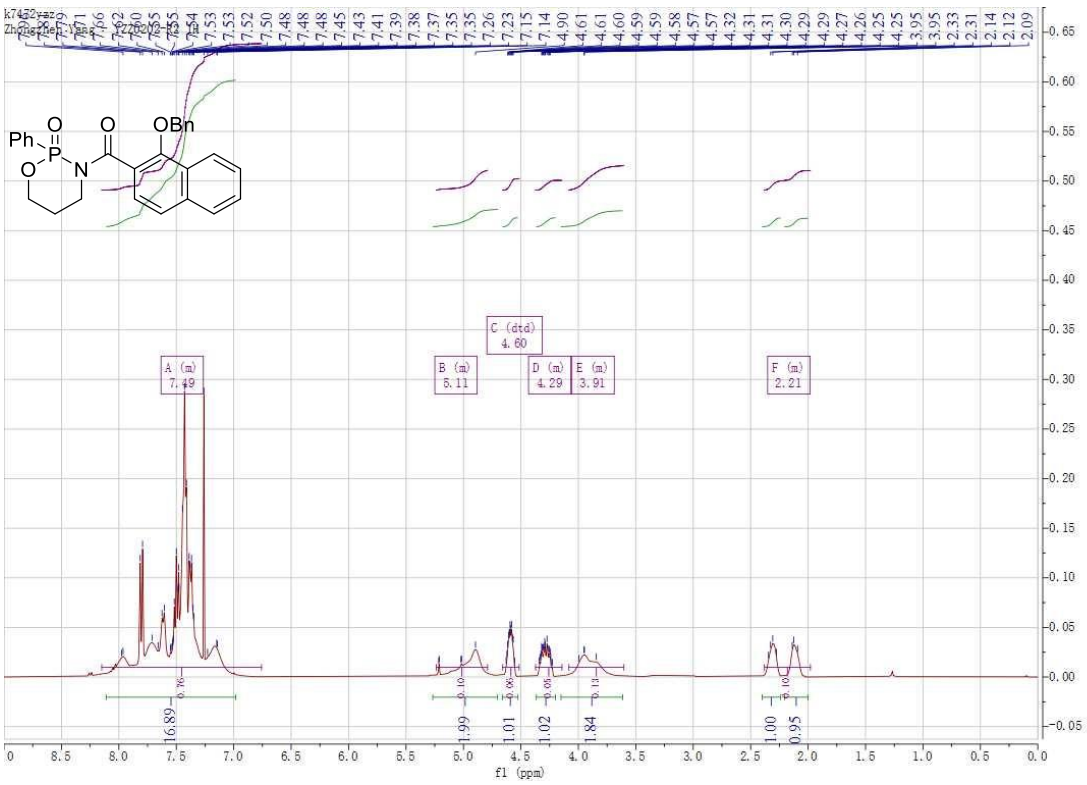
10-Methoxy-2-phenyl-4,5,6,7-tetrahydro-8*H*-benzo[*d*][1,3,7,2]dioxazaphosphecin-8-one 2-oxide (21c)

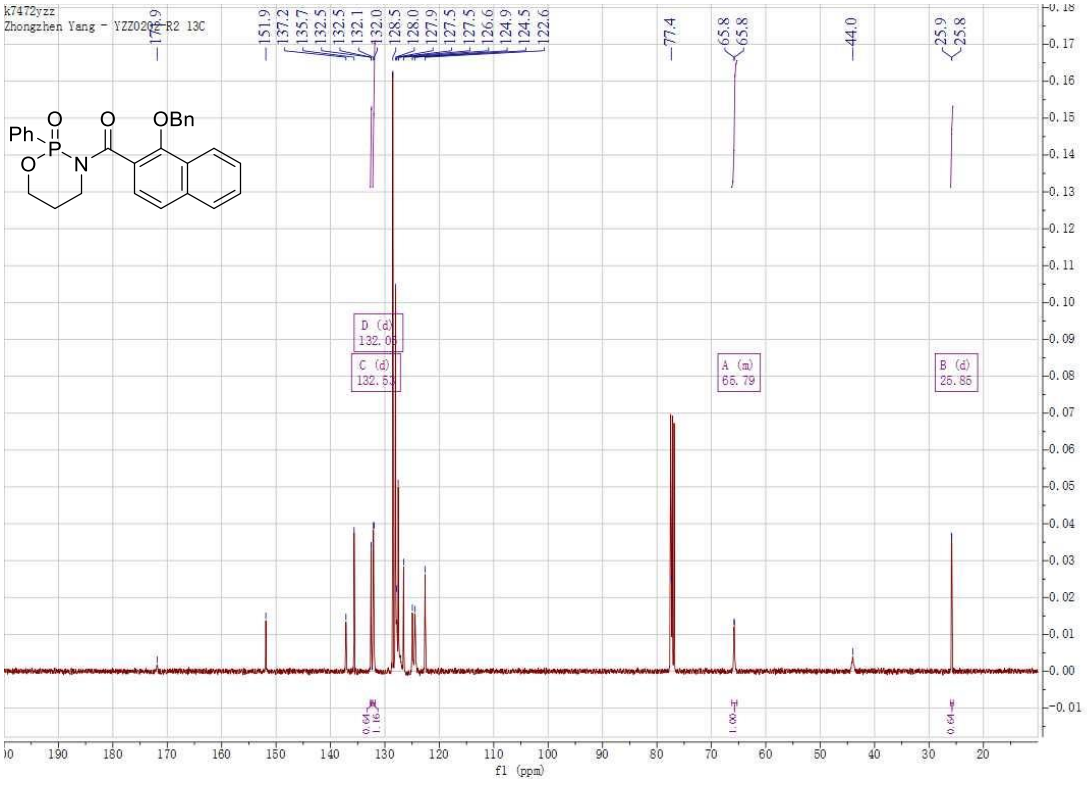


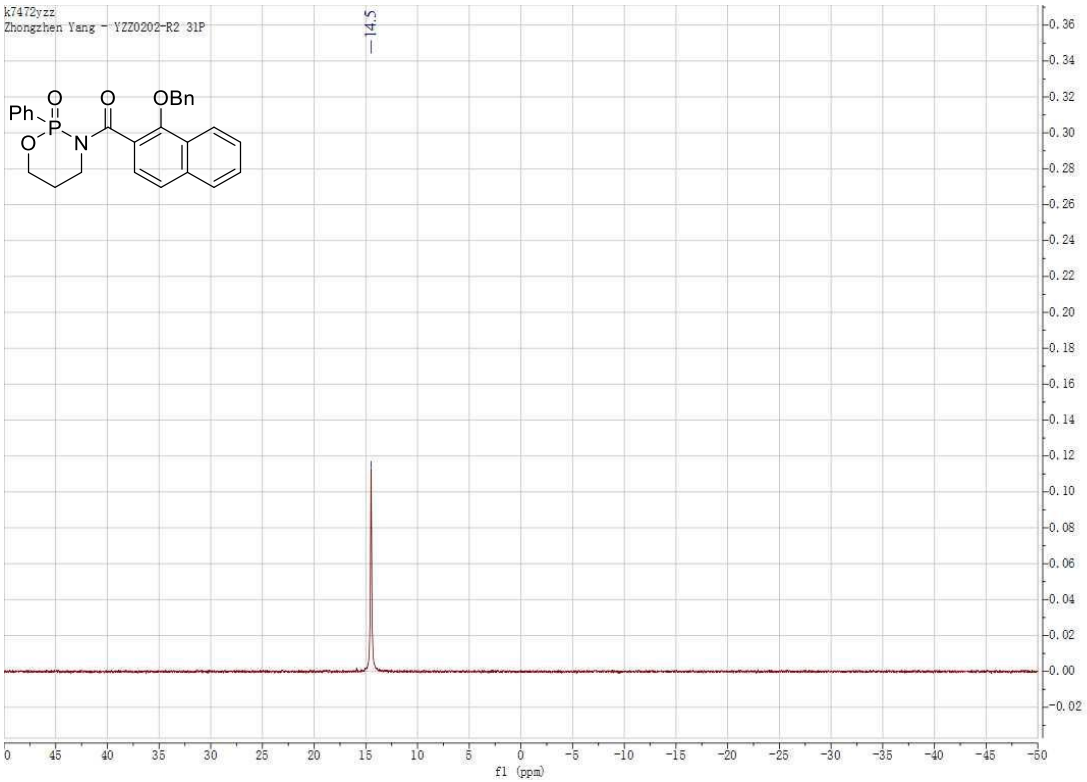

a4666yzz
Zhongzhen Yang - YZZ0312-R1 13C
166.6
156.7
156.7
141.0
140.9
132.8
132.8
131.1
131.0
130.1
130.0
128.5
128.4
128.0
126.1
123.1
123.1
117.9
113.1
77.2 CDCl3
67.8
67.7
55.6
38.7
28.6
28.6
H (d) 132.78
J (d) 123.13
B (d) 128.44
M (s) 113.07
K (s) 166.60
F (d) 156.73
G (d) 140.95
A (d) 127.04
L (s) 117.90
C (d) 131.08
I (d) 130.05
D (d) 67.72
N (s) 55.57
O (s) 38.74
E (d) 28.61
f1 (ppm)


a4666yzz
Zhongzhen Yang - YZZ0312-R1 31P
17.1
f1 (ppm)

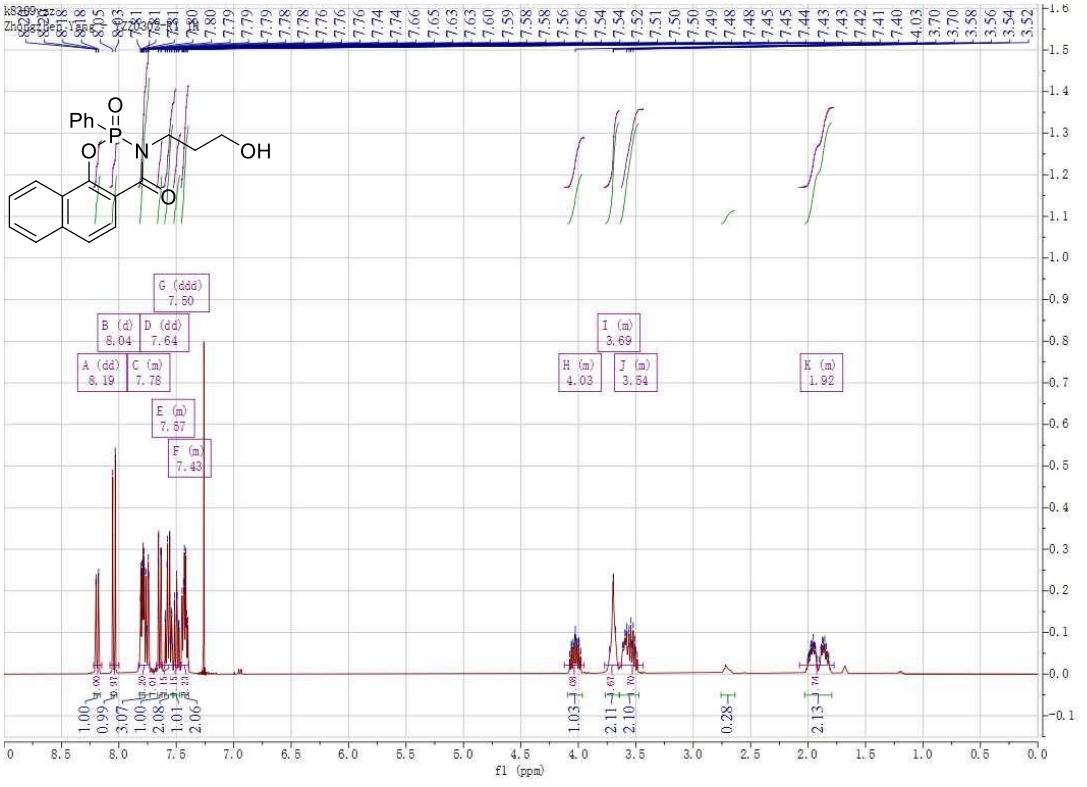
(1-(Benzyloxy)naphthalen-2-yl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone (18d)

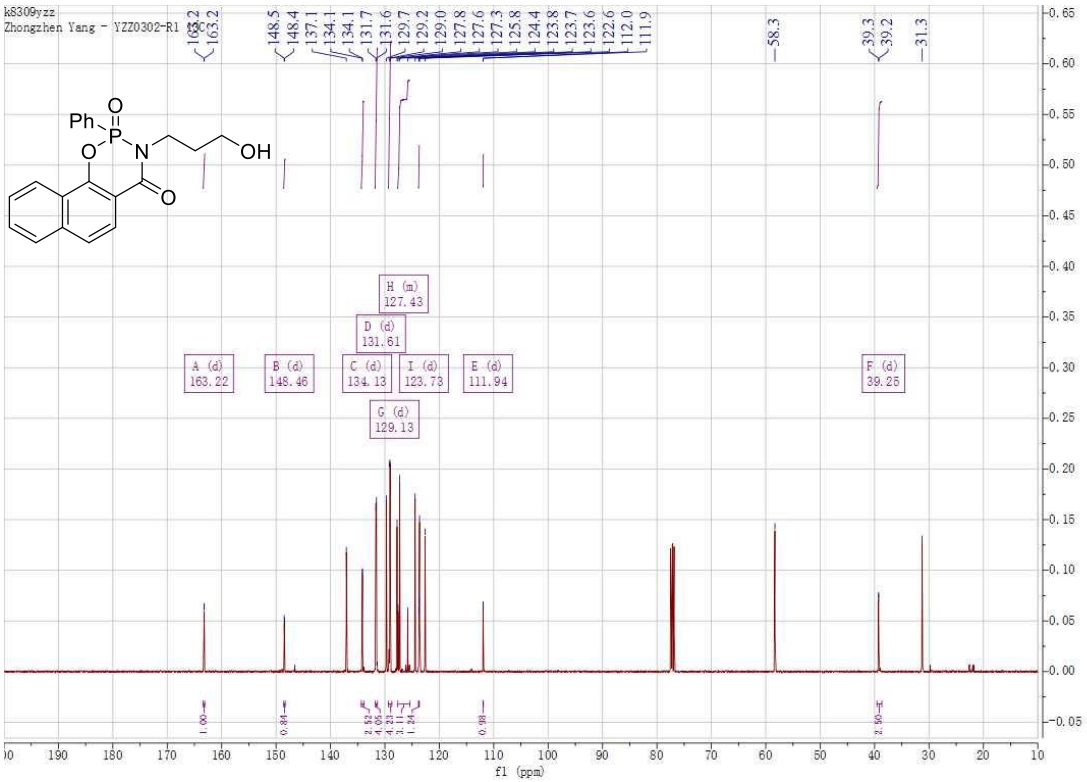


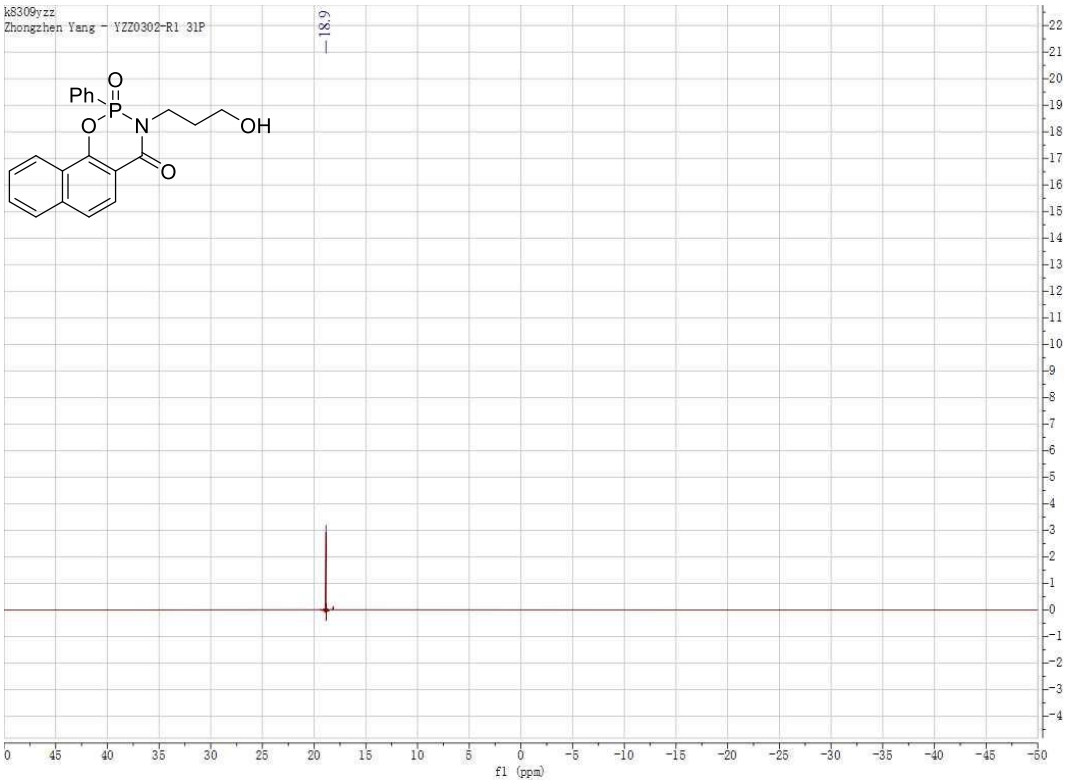




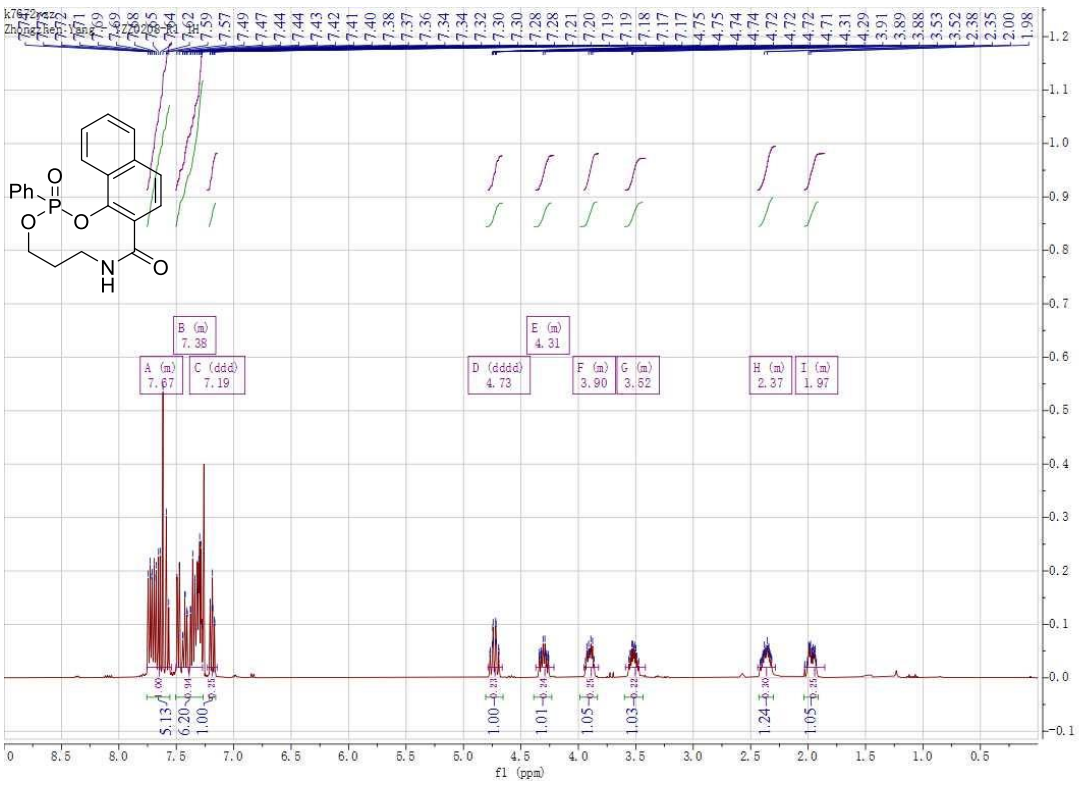
3-(3-Hydroxypropyl)-2-phenyl-3-hydronaphtho[2,1-*e*][1,3,2]oxazaphosphinin-4-one 2-oxide (20d)

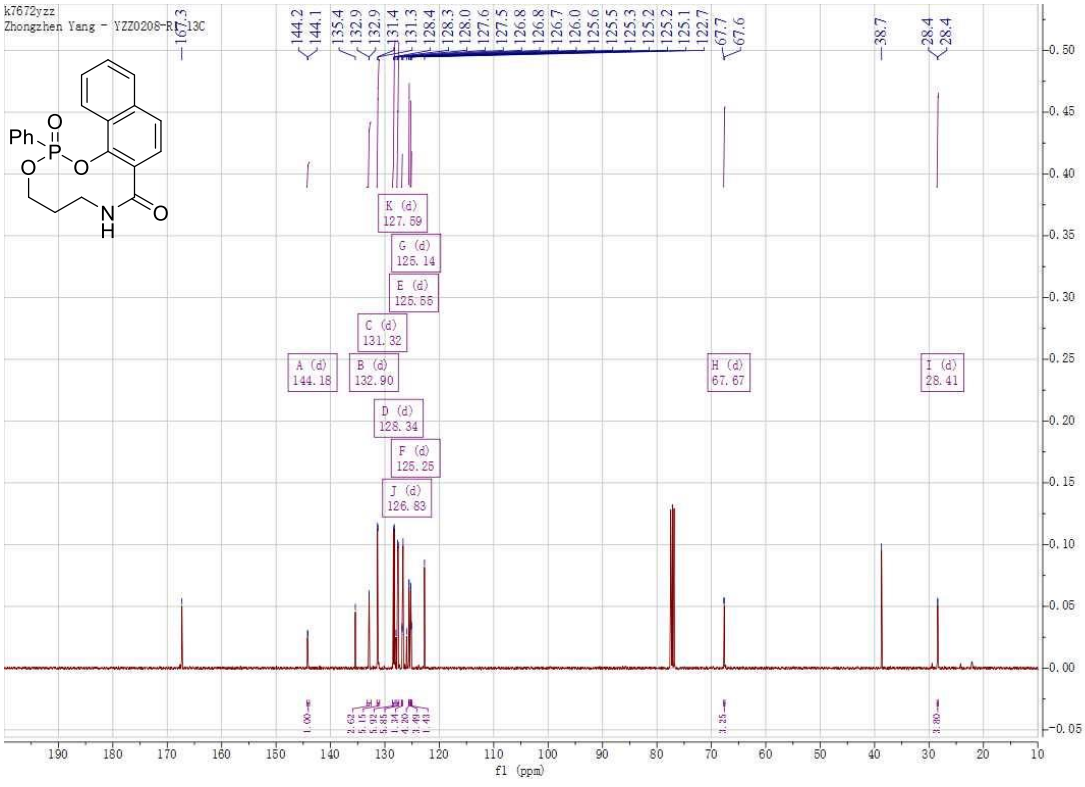


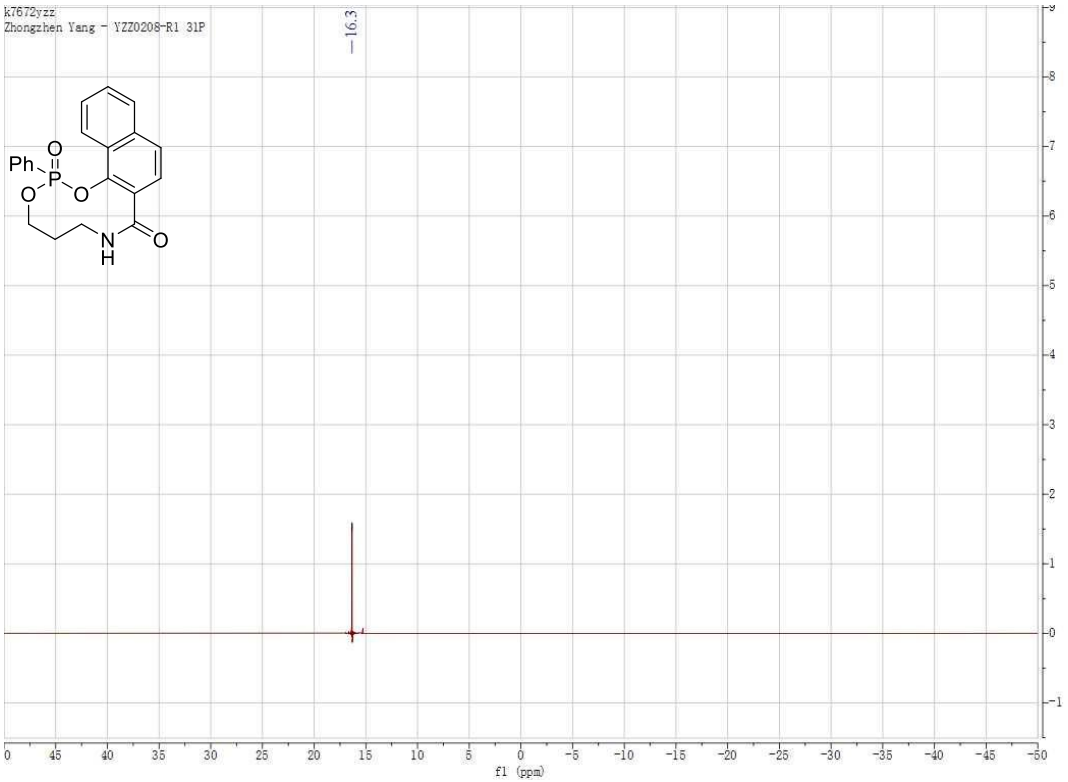

k8309yzz
Zhongzhen Yang - YZZ0302-R1 13C
163.2
148.5
148.4
137.1
134.1
131.7
131.6
129.7
129.2
129.0
127.8
127.6
127.3
125.8
124.4
123.8
123.7
123.6
122.6
112.0
111.9
58.3
39.3
39.2
31.3
Ph
O
P
N
OH
O
O
H (m)
127.43
D (d)
131.61
A (d)
163.22
B (d)
148.46
C (d)
134.13
I (d)
123.73
E (d)
111.94
G (d)
129.13
F (d)
39.25
f1 (ppm)


k8309yzz
Zhongzhen Yang - YZZ0302-R1 31P
18.9
Ph
O
P
N
OH
O
f1 (ppm)

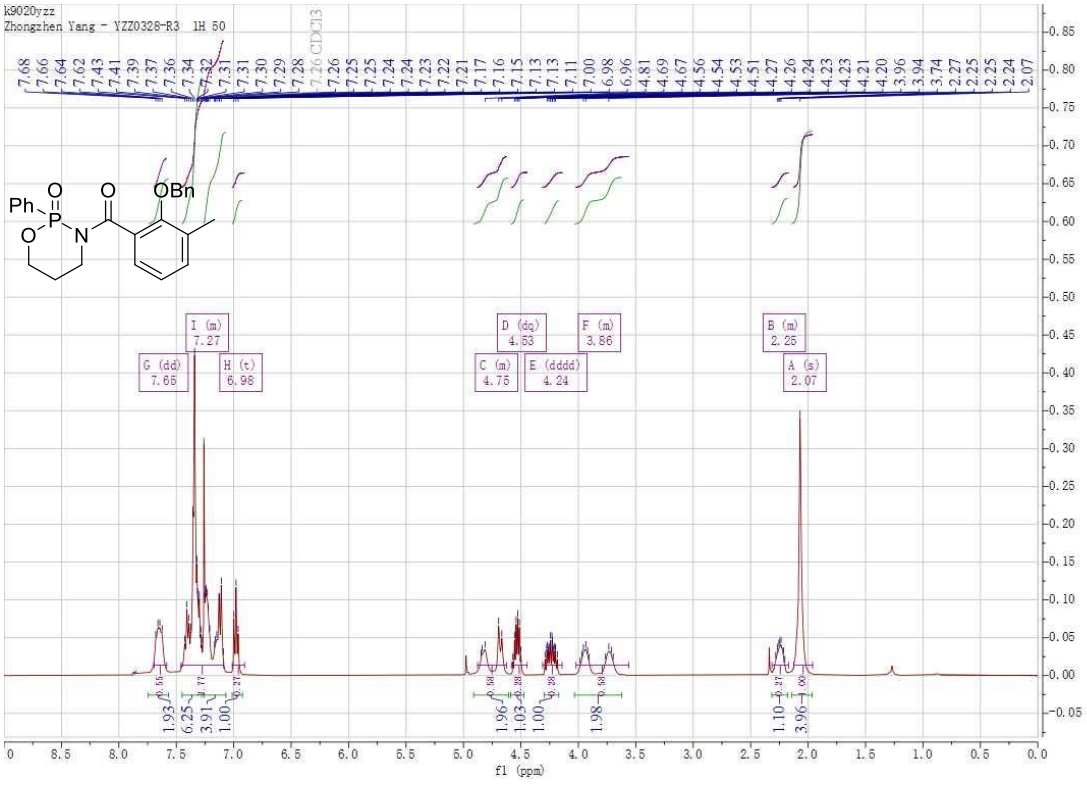
2-Phenyl-4,5,6,7-tetrahydro-8*H*-naphtho[1,2-*d*][1,3,7,2]dioxazaphosphecin-8-one 2-oxide (21d)

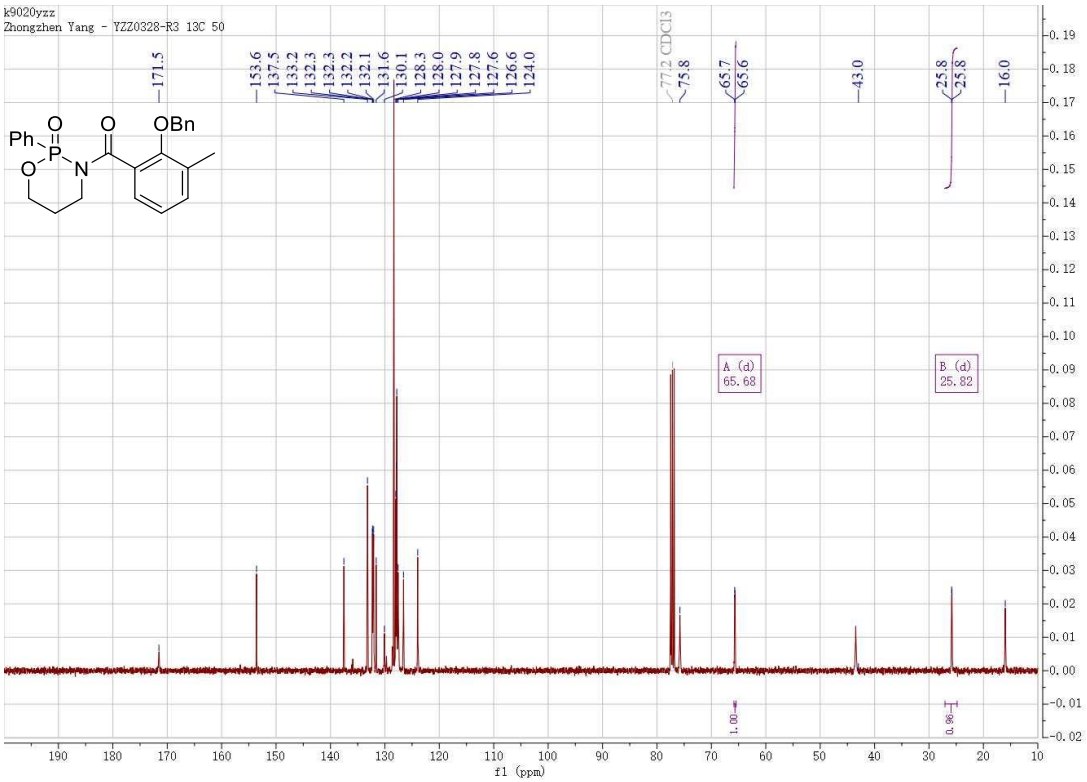


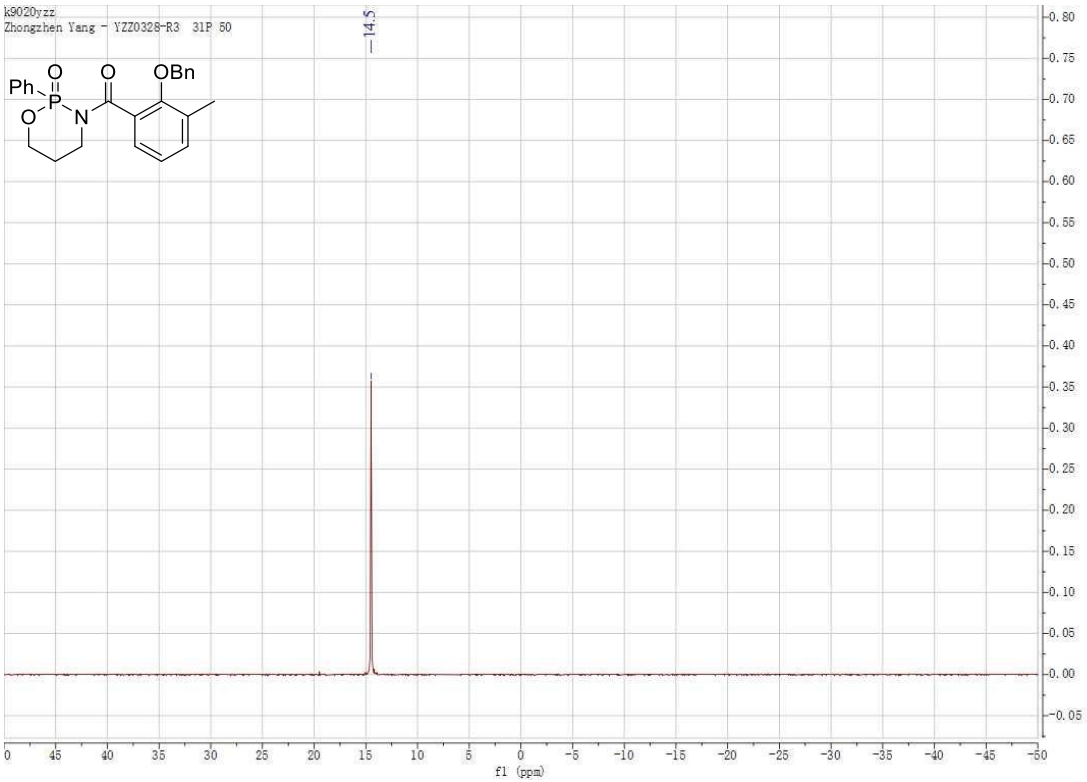




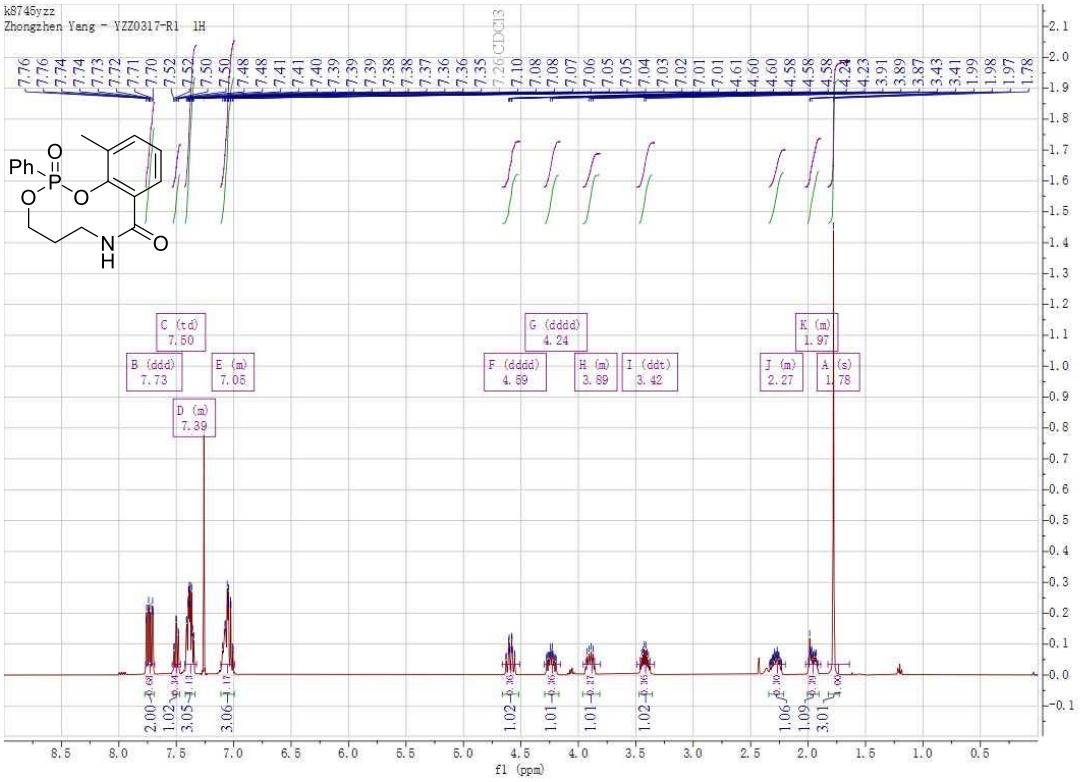
(2-(Benzyloxy)-3-methylphenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone (18e)

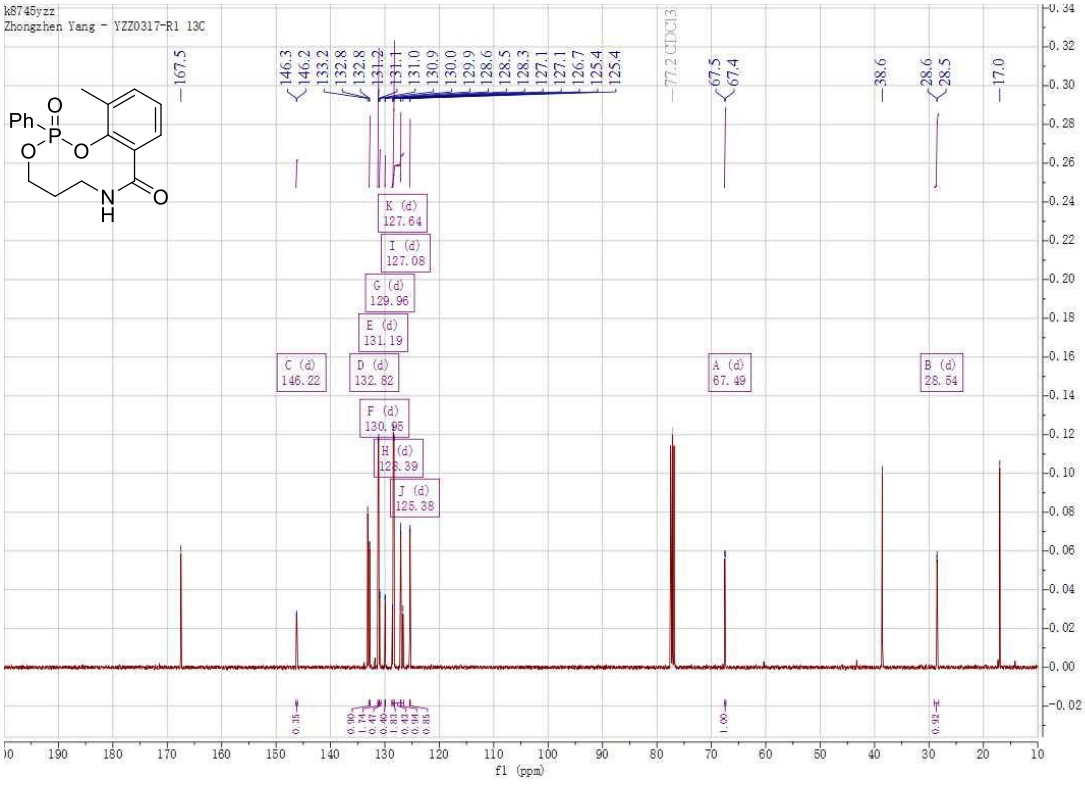


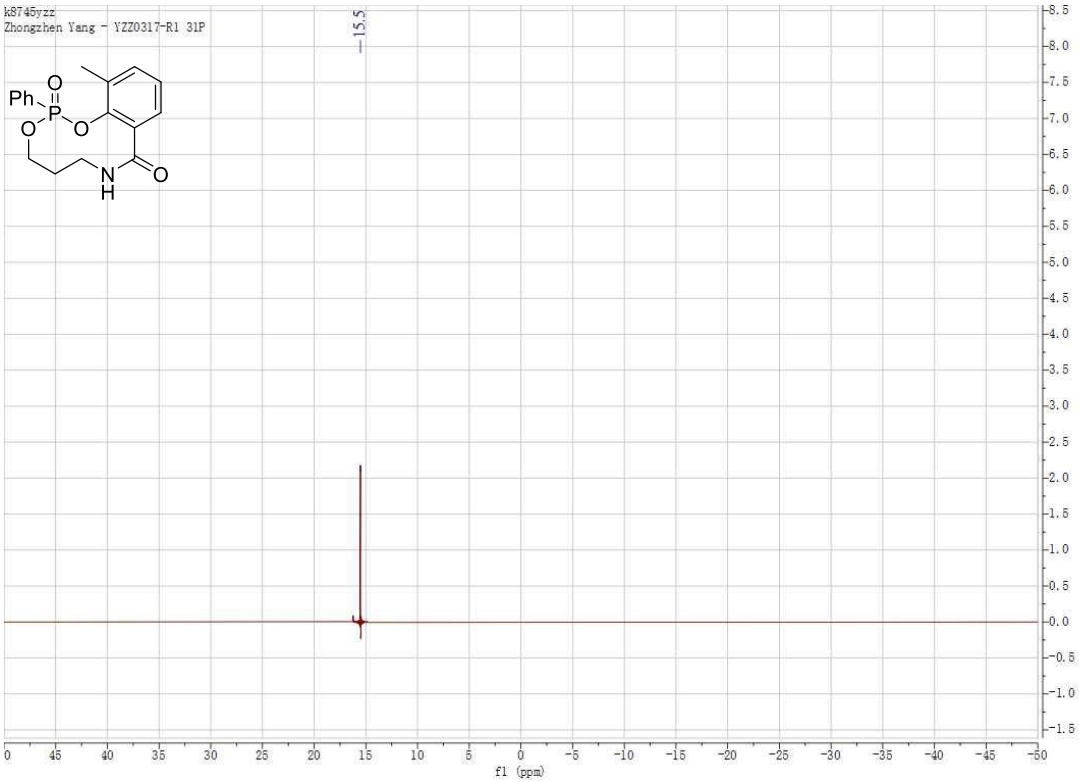

k9020yzz
Zhongzhen Yang - YZZ0328-R3 13C 50
171.5
153.6
137.5
133.2
132.3
132.2
132.1
131.6
130.1
128.3
128.0
127.9
127.8
127.6
126.6
124.0
77.2 CDCl3
75.8
65.7
65.6
43.0
25.8
25.8
16.0
A (d)
65.68
B (d)
25.82
1.00
0.96
f1 (ppm)


k9020yzz
Zhongzhen Yang - YZZ0328-R3 31P 50
14.5
f1 (ppm)

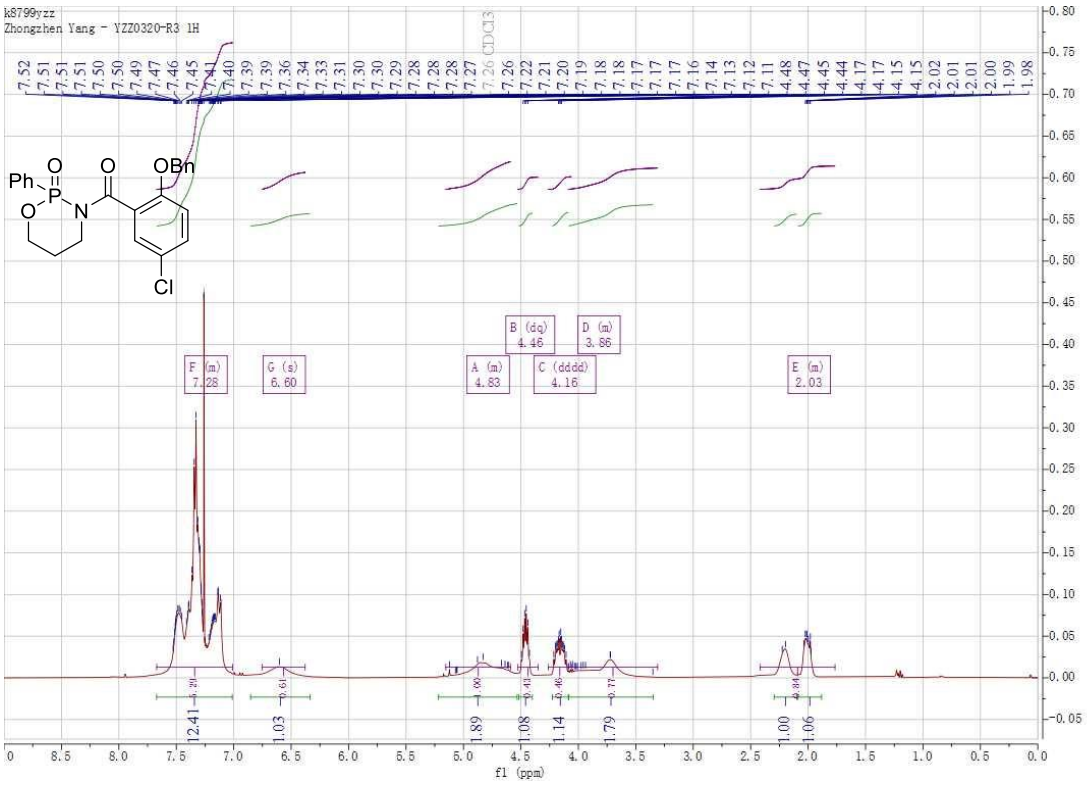
12-Methyl-2-phenyl-4,5,6,7-tetrahydro-8*H*-benzo[*d*][1,3,7,2]dioxazaphosphecin-8-one 2-oxide (21e)

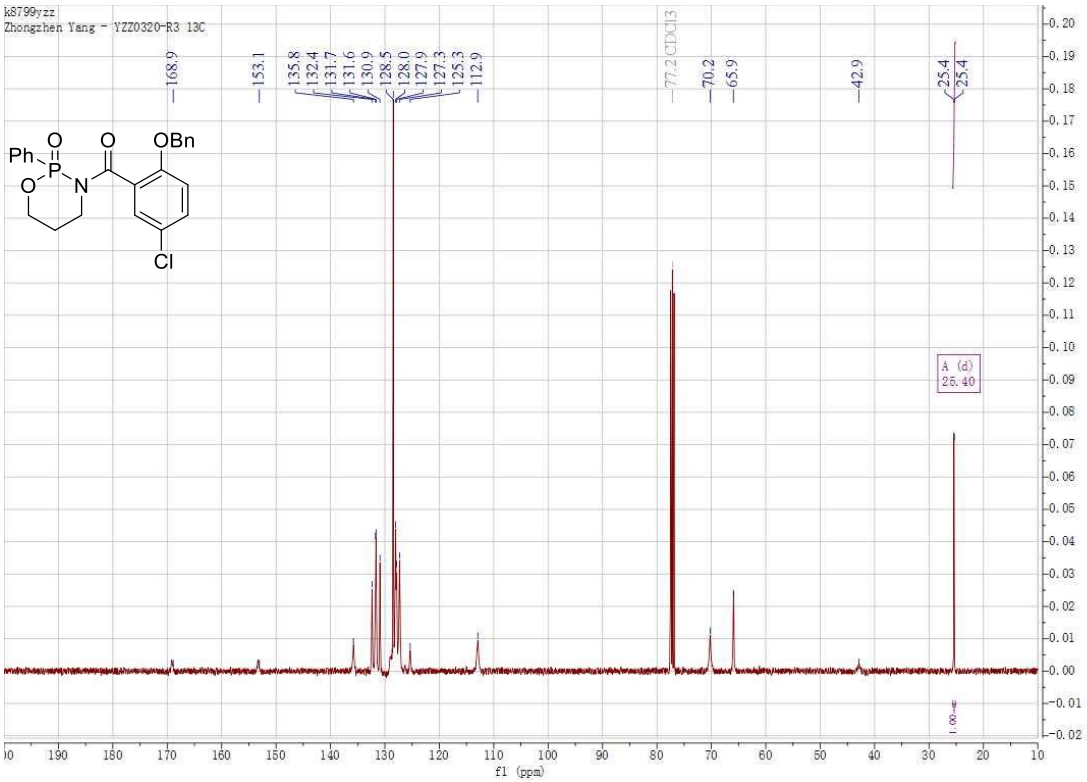


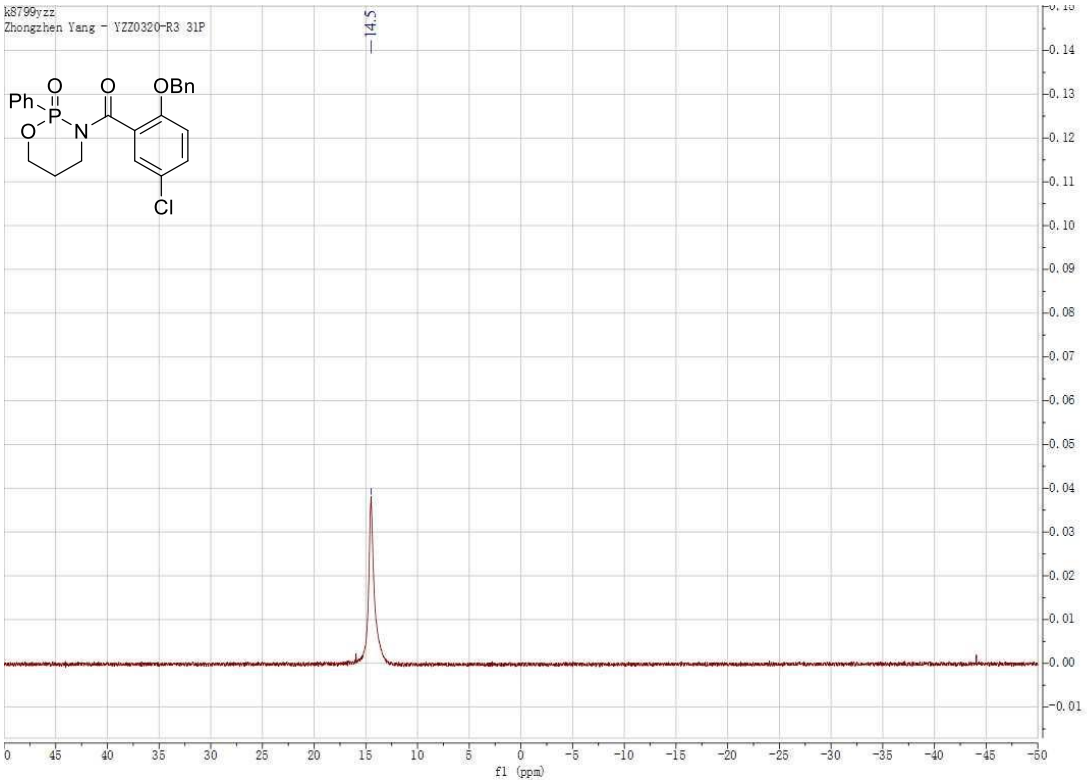




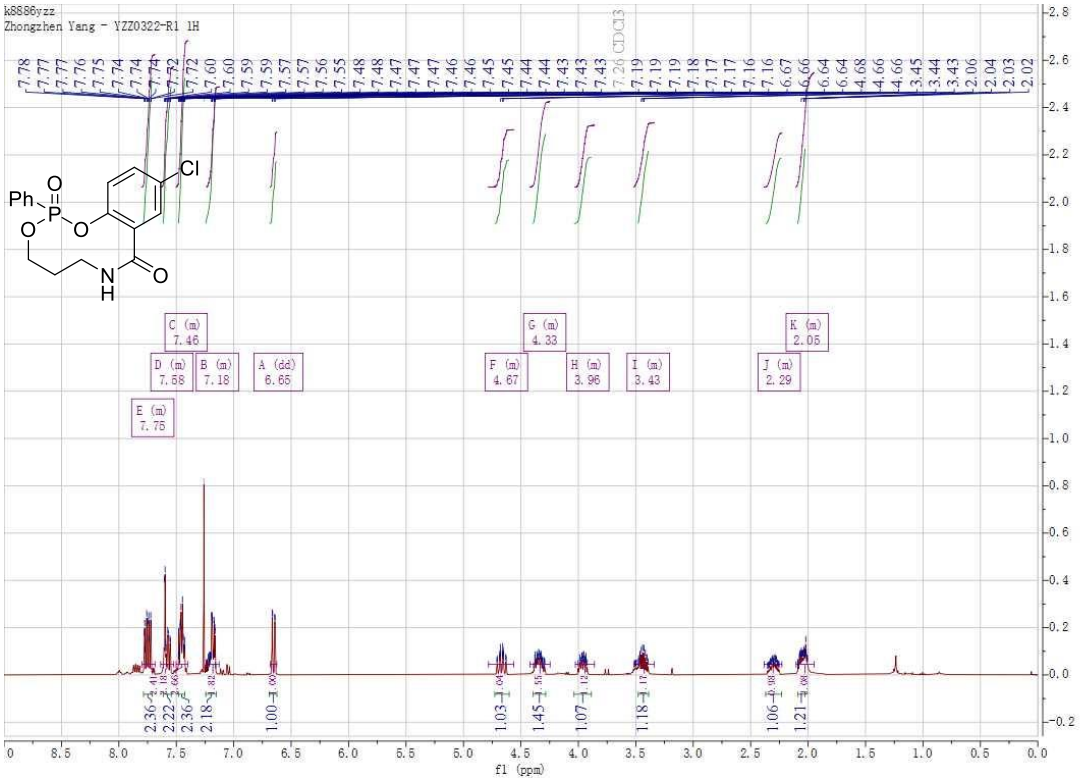
(2-(Benzyloxy)-5-chlorophenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone (18f)

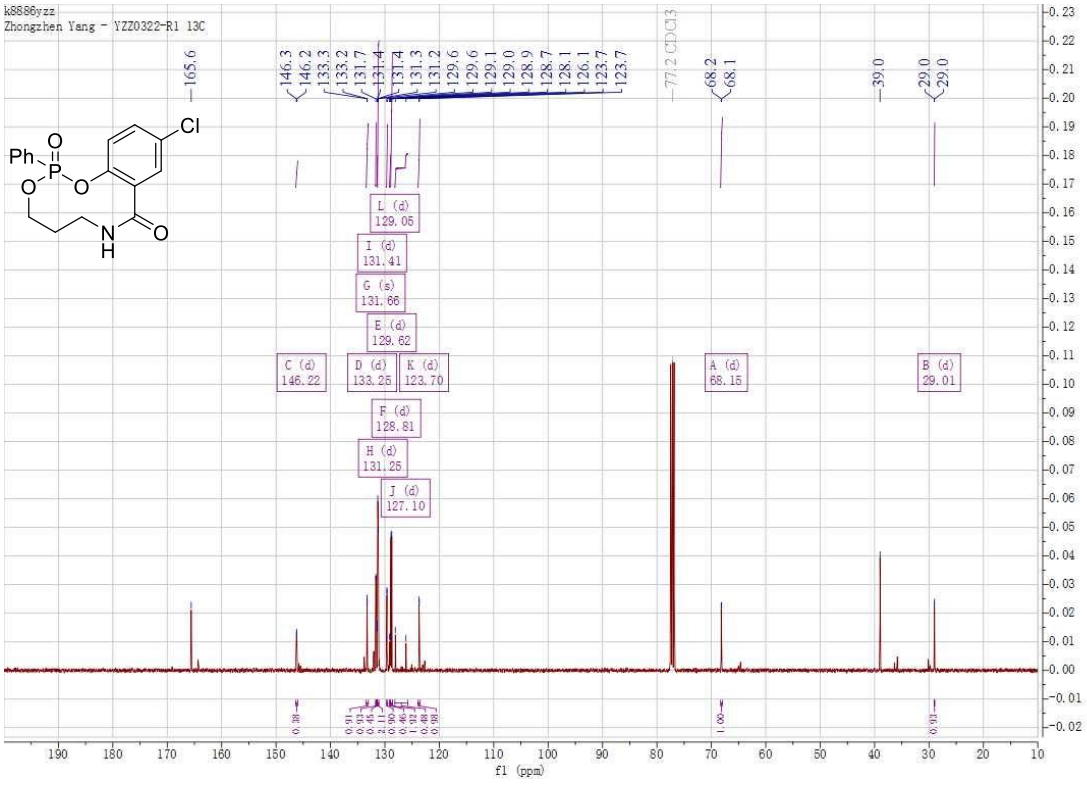


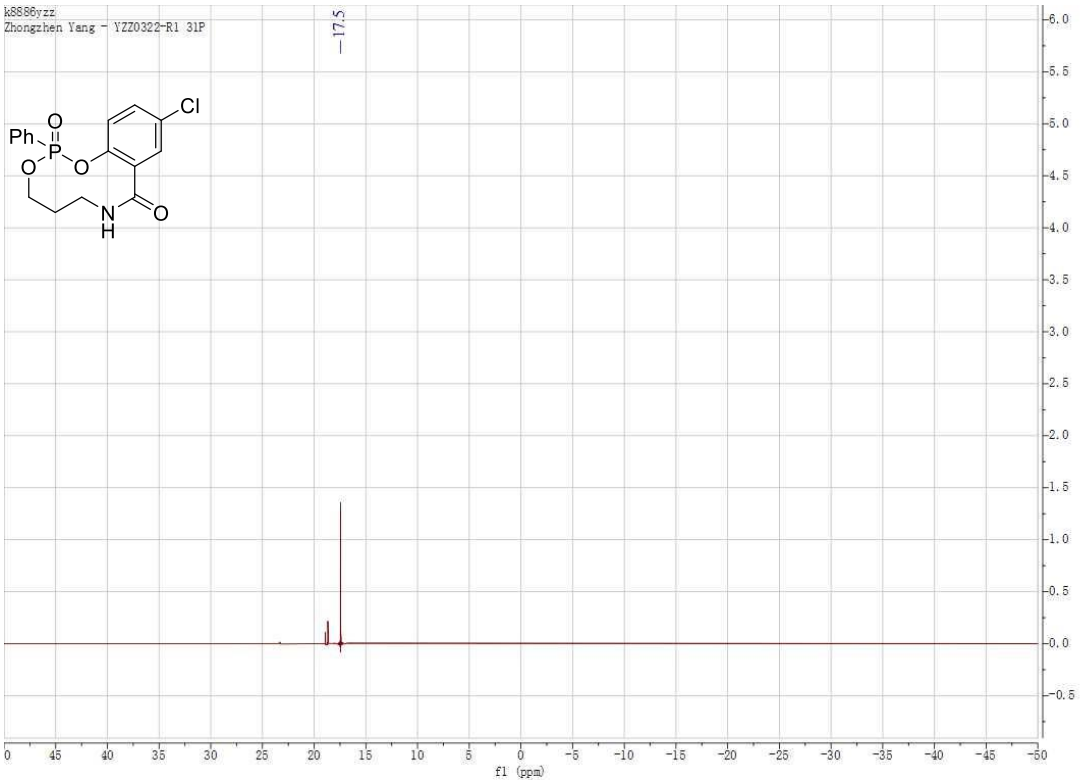

k8799yzz
Zhongzhen Yang - YZZ0320-R3 13C
168.9
153.1
135.8
132.4
131.7
131.6
130.9
128.5
128.0
127.9
127.3
125.3
112.9
77.2 CDCl3
70.2
65.9
42.9
25.4
25.4
A (d)
26.40
Ph
O
P
O
N
O
OBn
Cl
f1 (ppm)


k8799yzz
Zhongzhen Yang - YZZ0320-R3 31P
14.5
Ph
O
P
O
N
O
OBn
Cl
f1 (ppm)

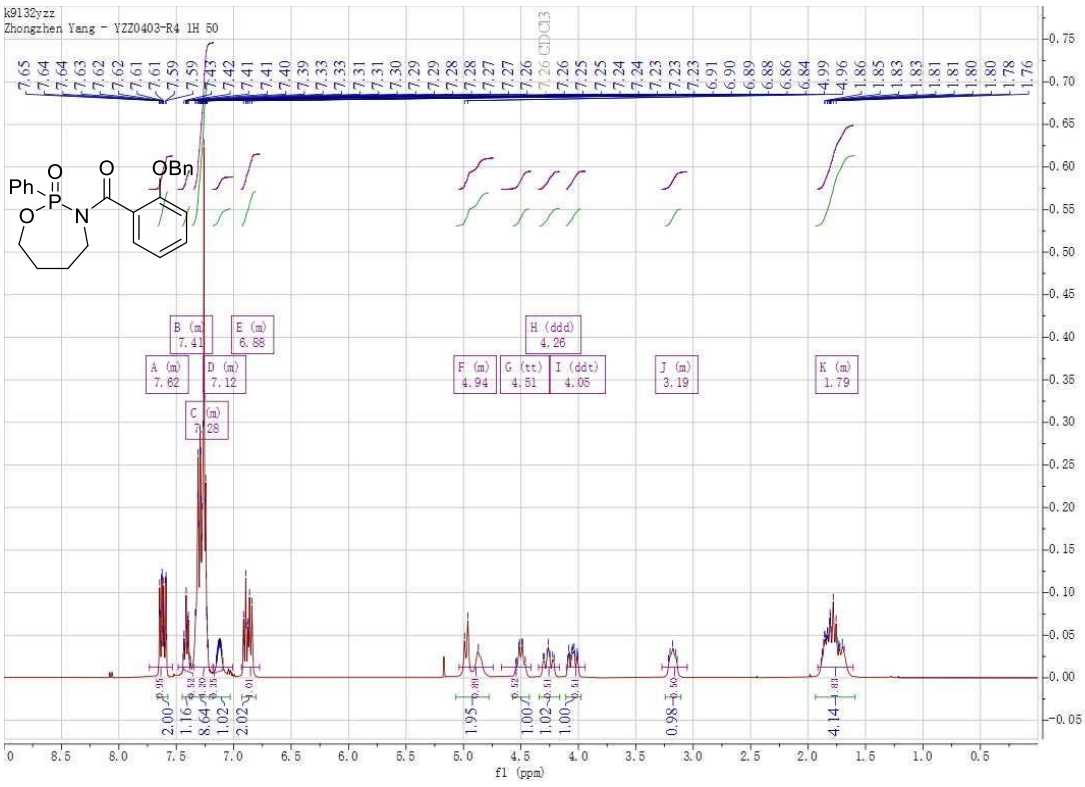
10-Chloro-2-phenyl-4,5,6,7-tetrahydro-8*H*-benzo[*d*][1,3,7,2]dioxazaphosphecin-8-one 2-oxide (21f) (contains a small amount of impurity - Cl-cleaved product **21a**)

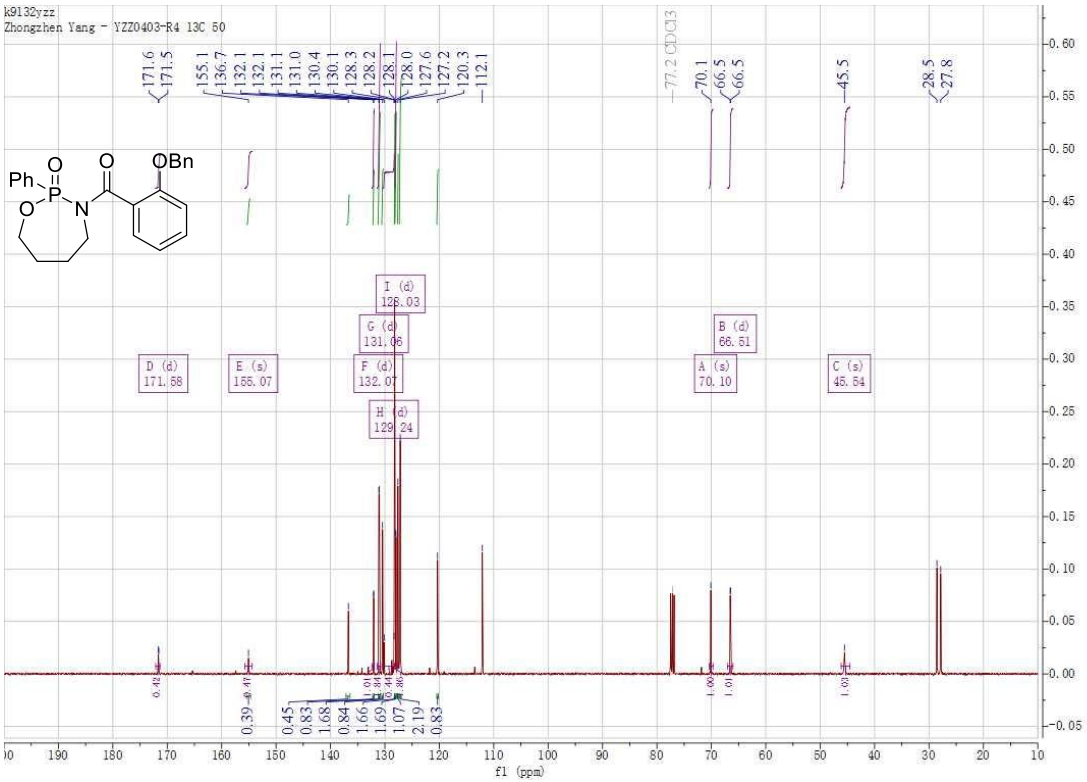


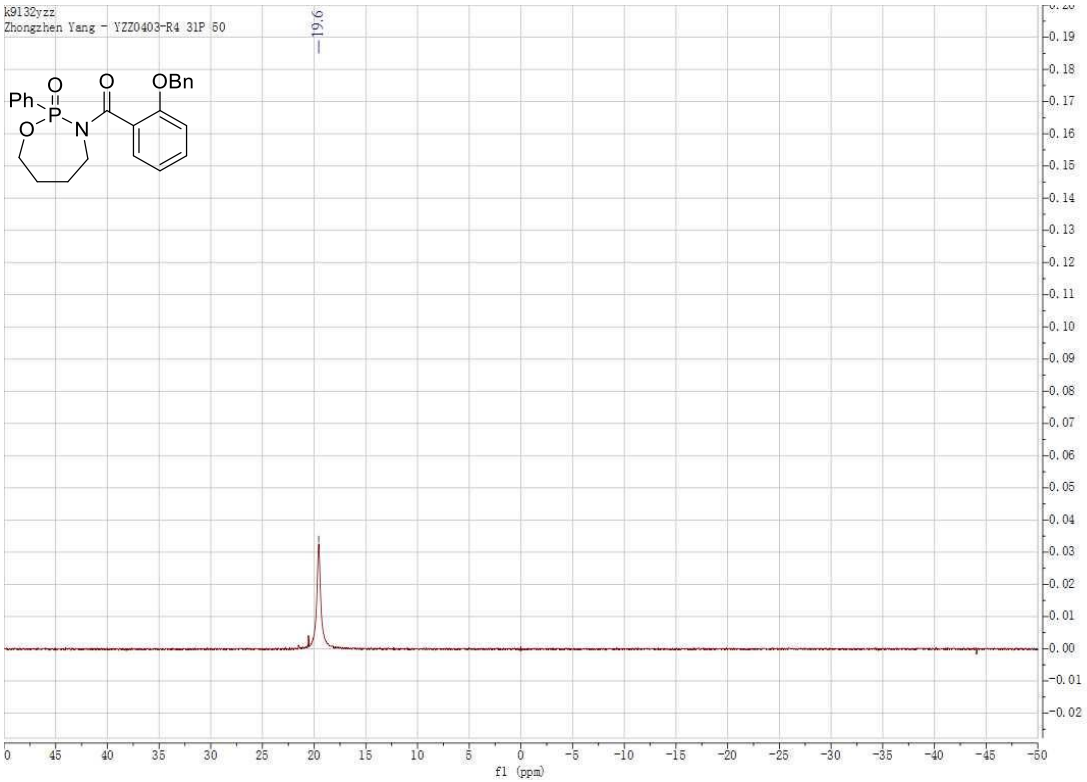




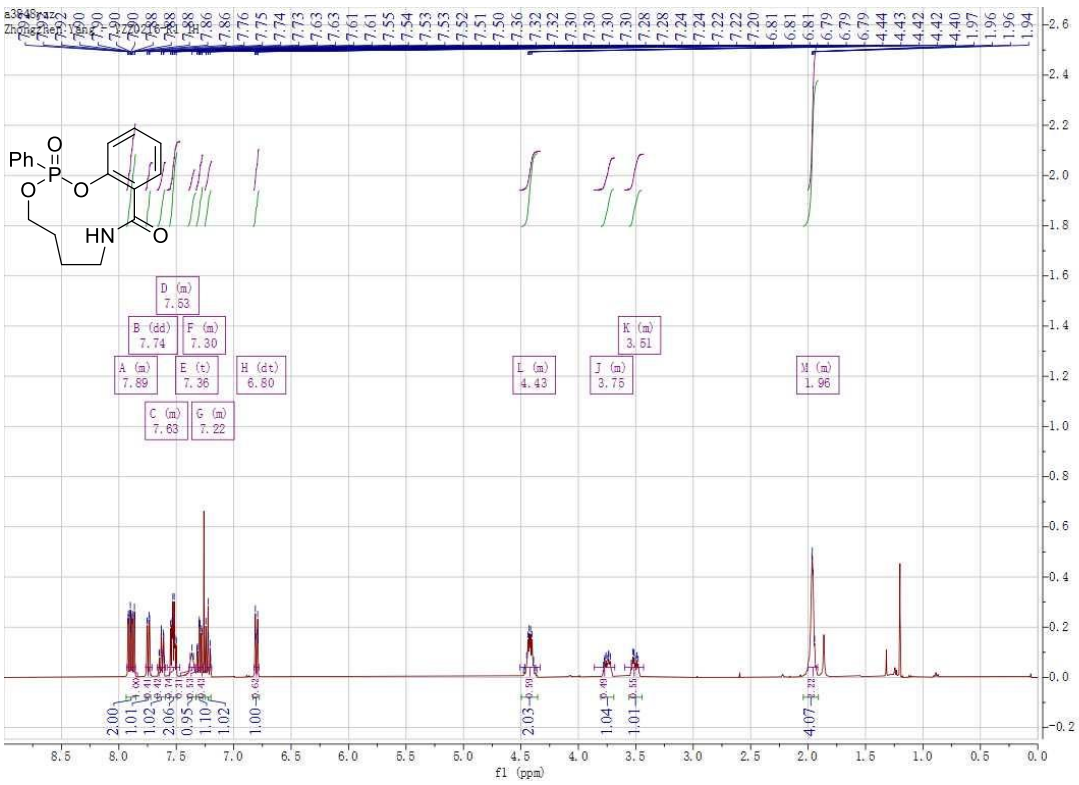
(2-(Benzyloxy)phenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphepan-3-yl)methanone (18g)

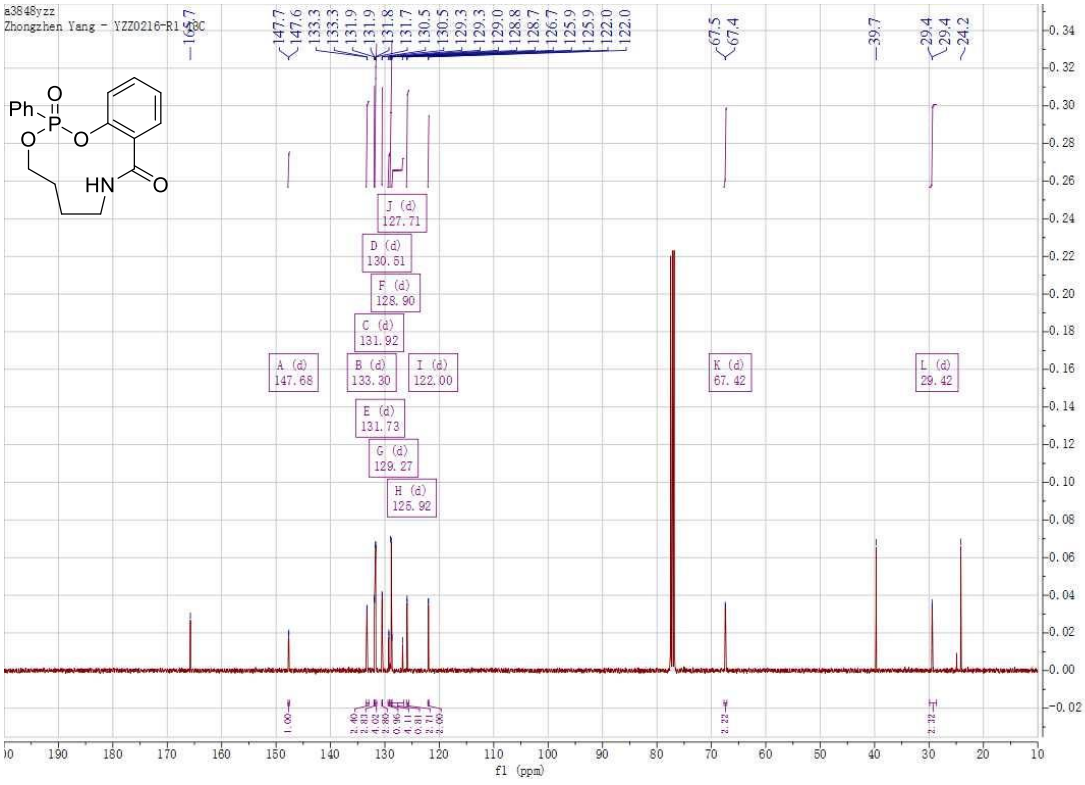


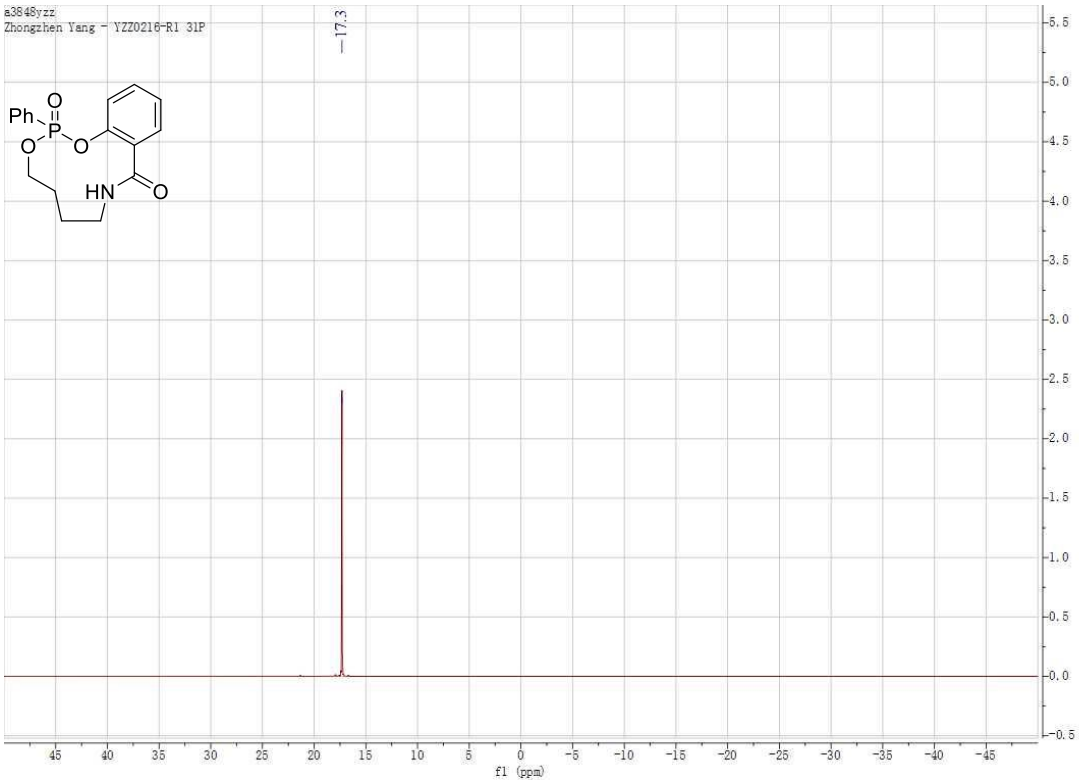

k9132yzz
Zhongzhen Yang - YZZ0403-R4 13C 50
171.6
171.5
155.1
136.7
132.1
132.1
131.1
131.0
130.4
130.1
128.3
128.2
128.1
128.0
127.6
127.2
120.3
112.1
77.2 CDCl3
70.1
66.5
66.5
45.5
28.5
27.8
Ph
O
P
O
N
O
OBn
I (d) 128.03
G (d) 131.06
F (d) 132.07
H (d) 129.24
D (d) 171.58
E (s) 155.07
B (d) 66.51
A (s) 70.10
C (s) 45.54
f1 (ppm)


k9132yzz
Zhongzhen Yang - YZZ0403-R4 31P 50
19.6
Ph
O
P
O
N
O
OBn
f1 (ppm)

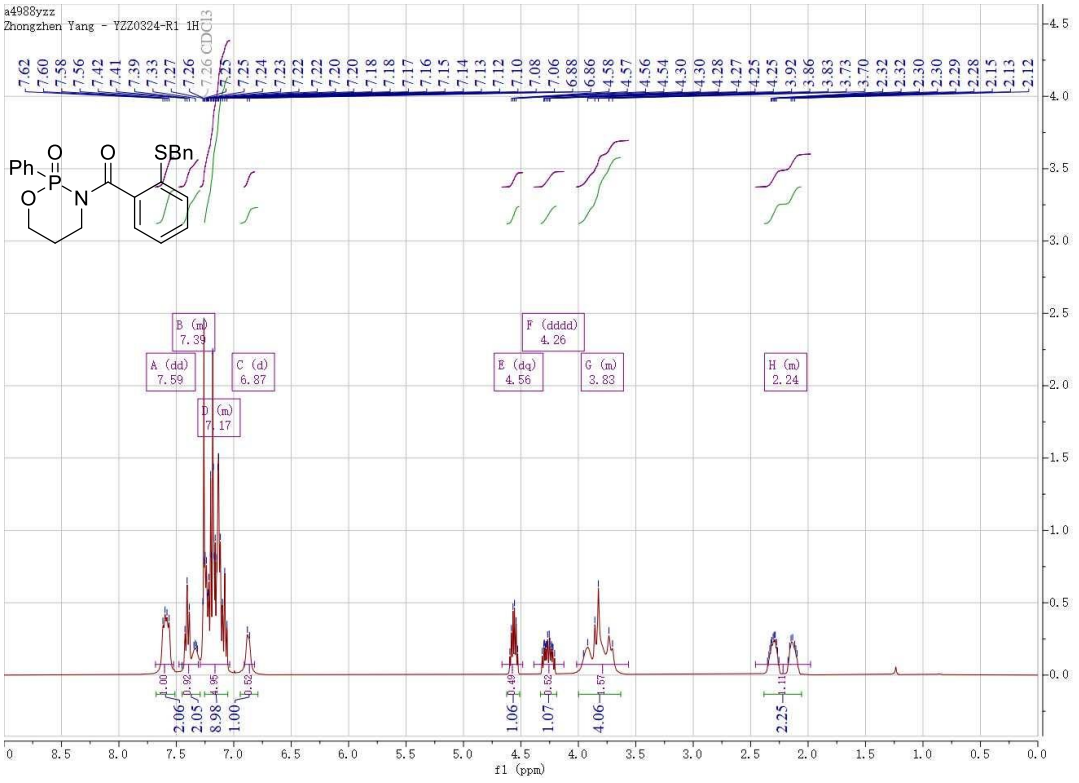
2-Phenyl-5,6,7,8-tetrahydrobenzo[*d*][1,3]dioxa[7]aza[2]phosphacycloundecin-9(4*H*)-one 2-oxide (21g)

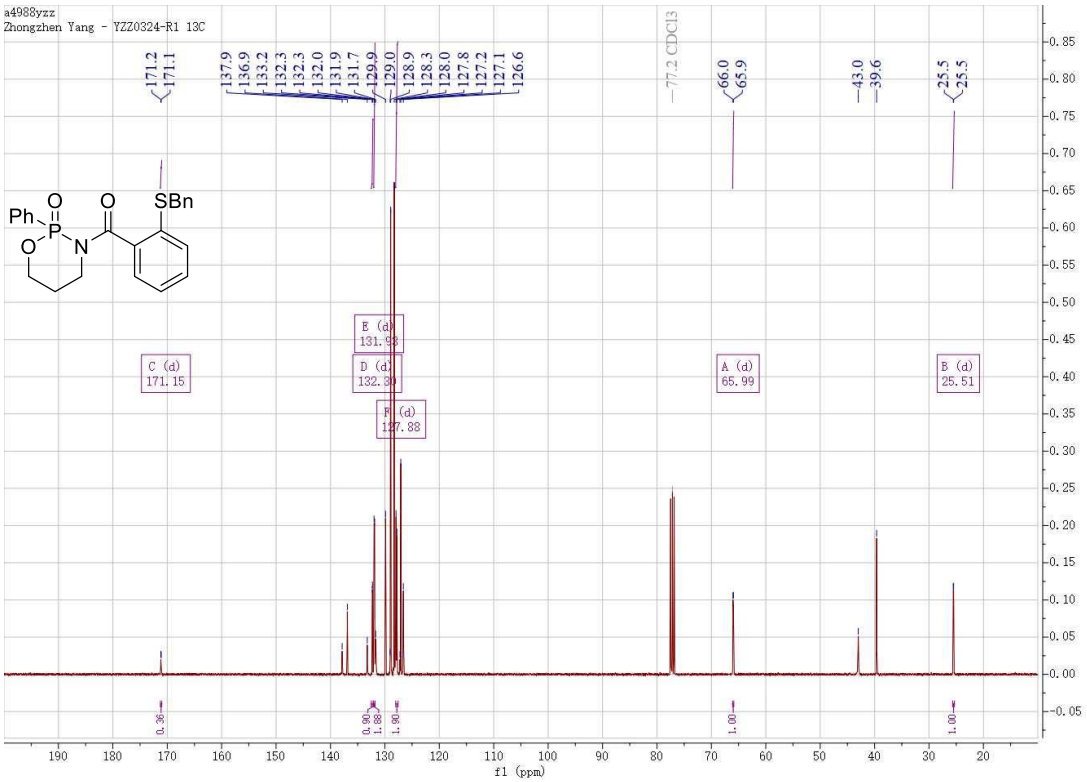


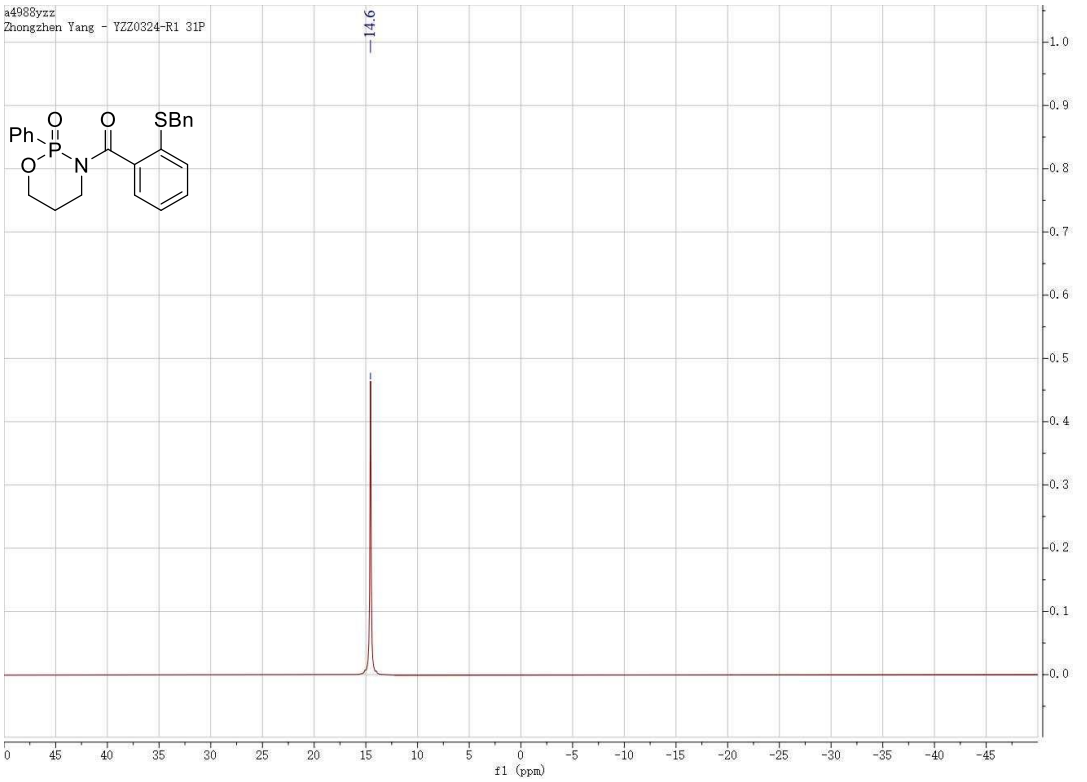




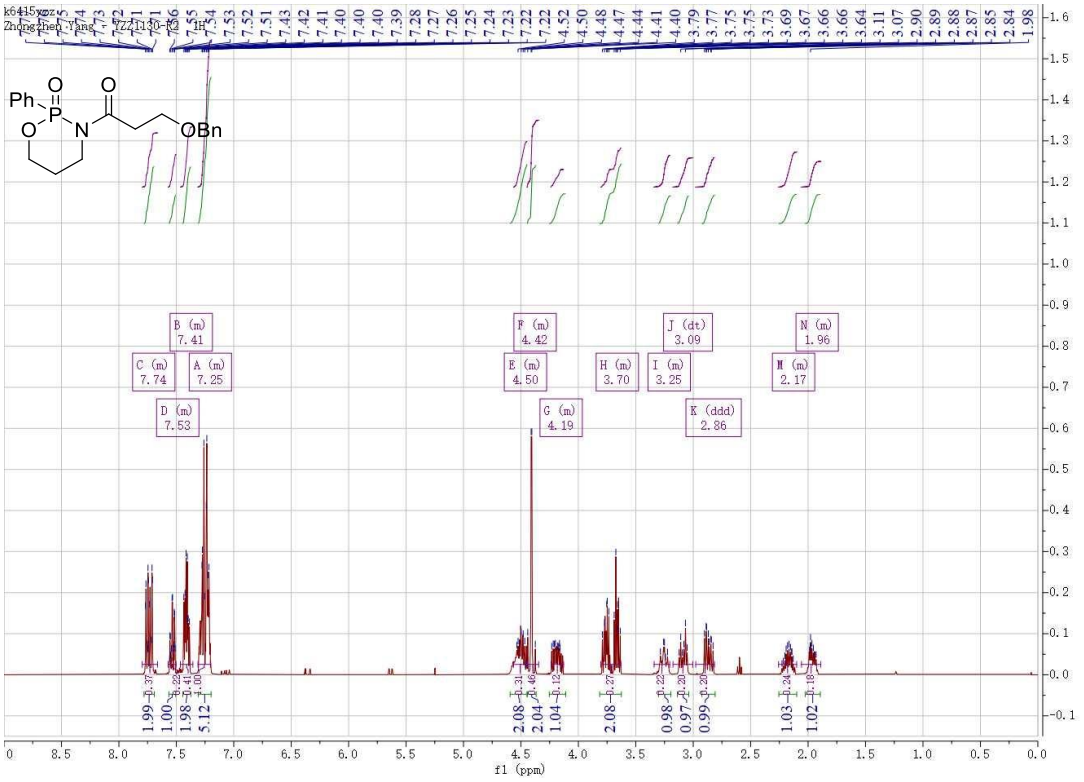
(2-(benzylthio)phenyl)(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)methanone

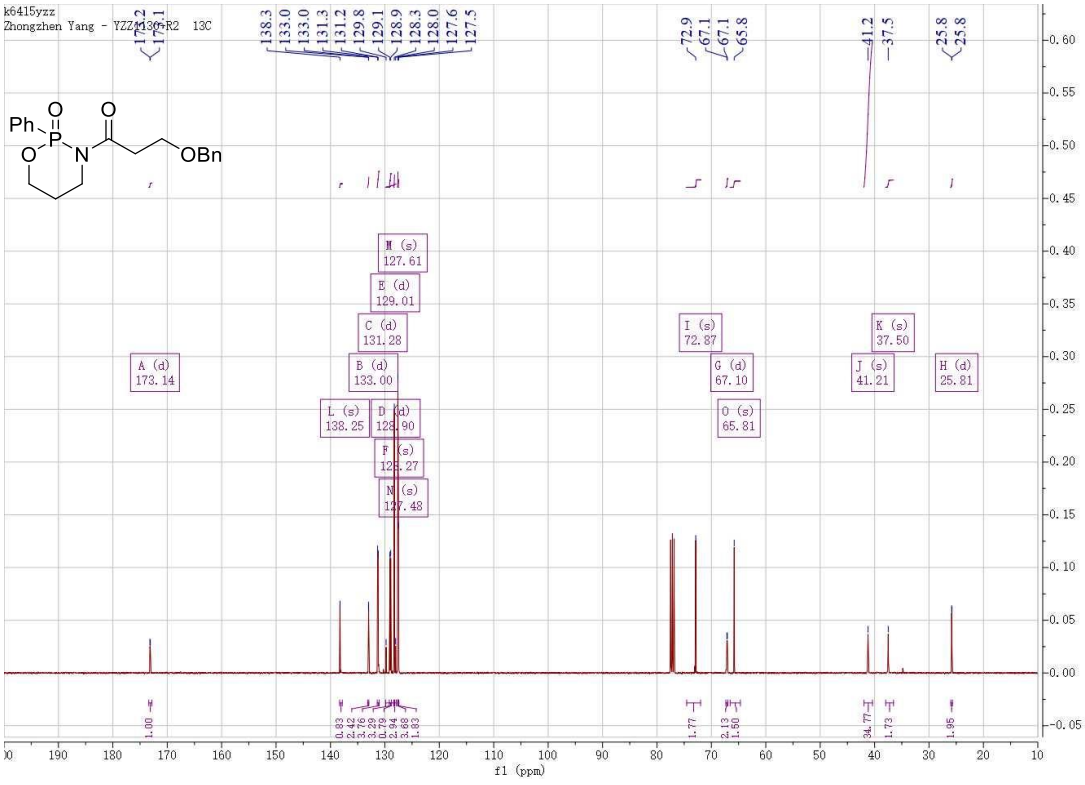


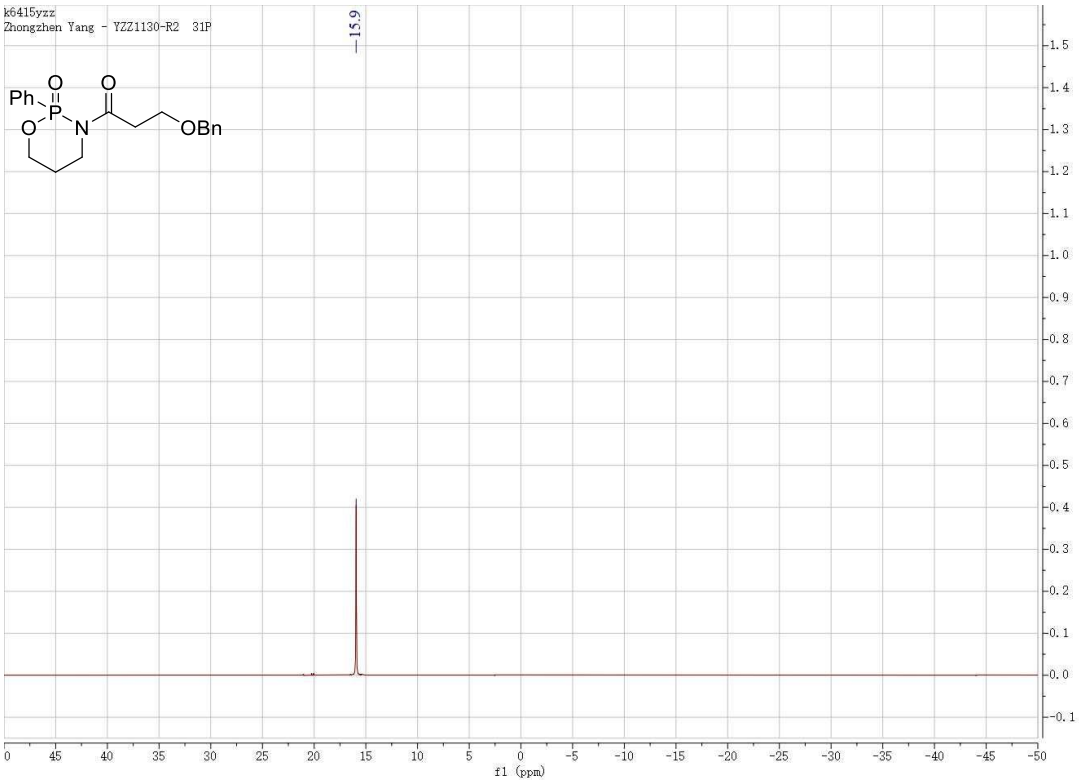

a4988yzz
Zhongzhen Yang - YZZ0324-R1 13C
171.2
171.1
137.9
136.9
133.2
132.3
132.3
132.0
131.9
131.7
129.9
129.0
128.9
128.3
128.0
127.8
127.2
127.1
126.6
77.2 CDCl3
66.0
65.9
43.0
39.6
25.5
25.5
Ph
O
P
O
N
O
O
SBn
C (d)
171.15
E (d)
131.93
D (d)
132.39
F (d)
127.88
A (d)
65.99
B (d)
25.51
0.36
0.90
1.88
1.90
1.00
1.00
f1 (ppm)


a4988yzz
Zhongzhen Yang - YZZ0324-R1 31P
14.6
Ph
O
P
O
N
O
O
SBn
f1 (ppm)

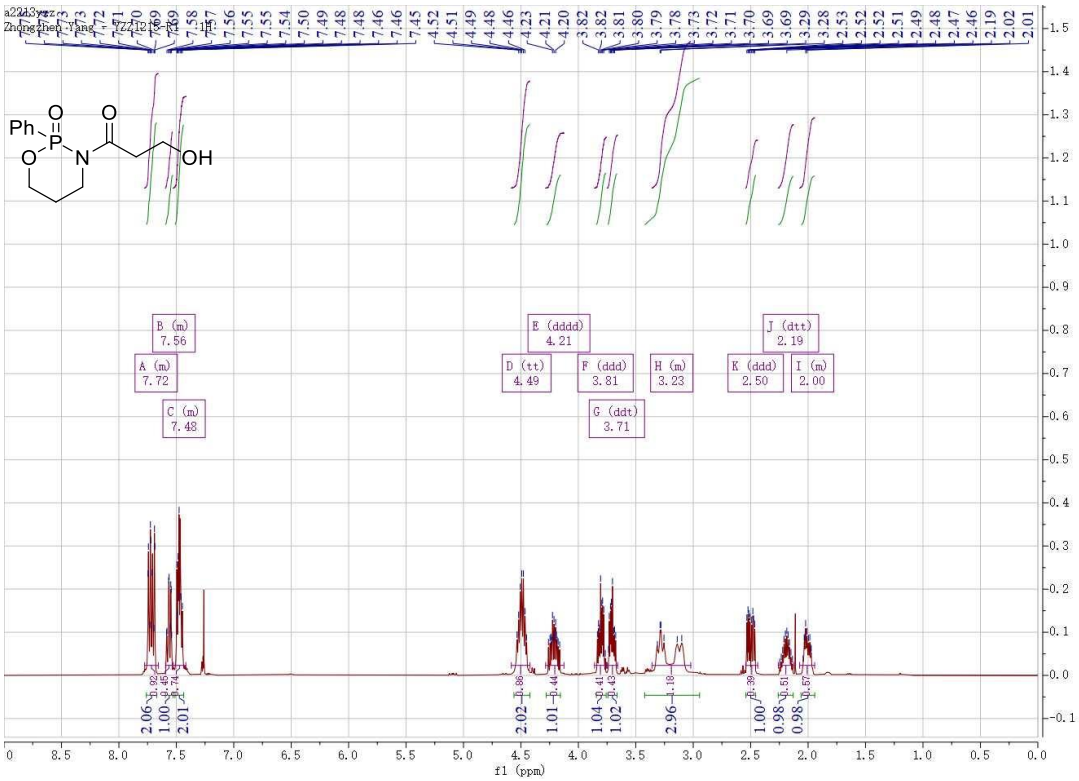
3-(Benzyloxy)-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)propan-1-one (22)

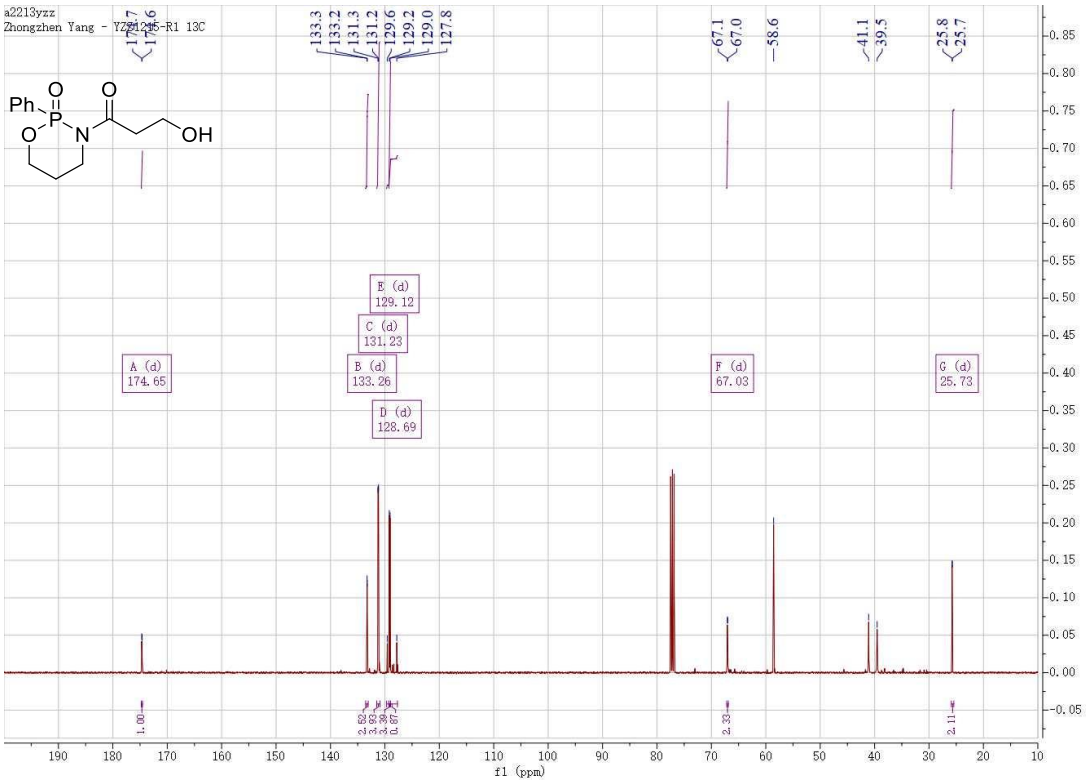


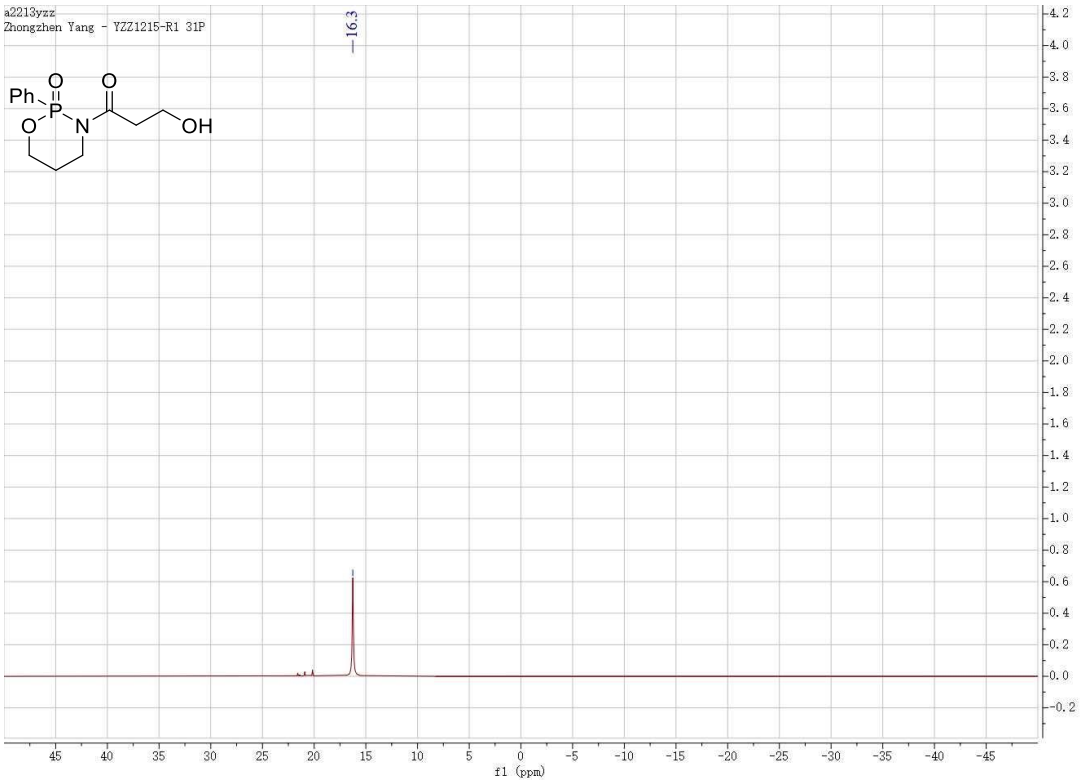




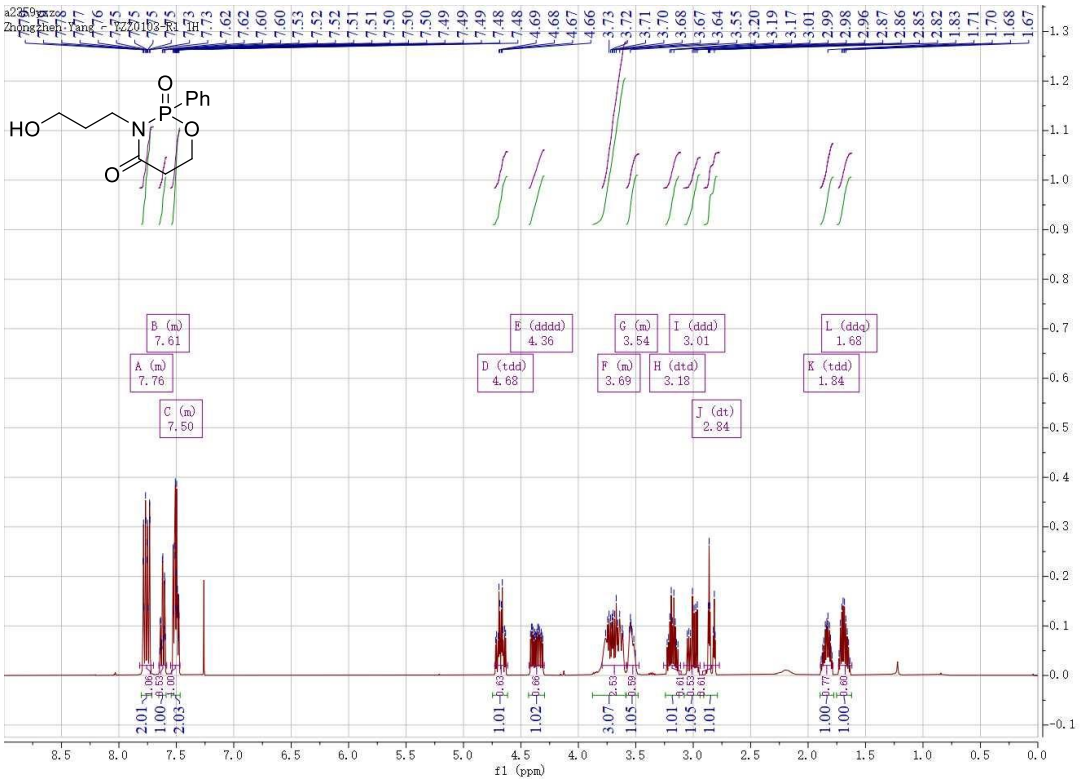
3-Hydroxy-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)propan-1-one (23)

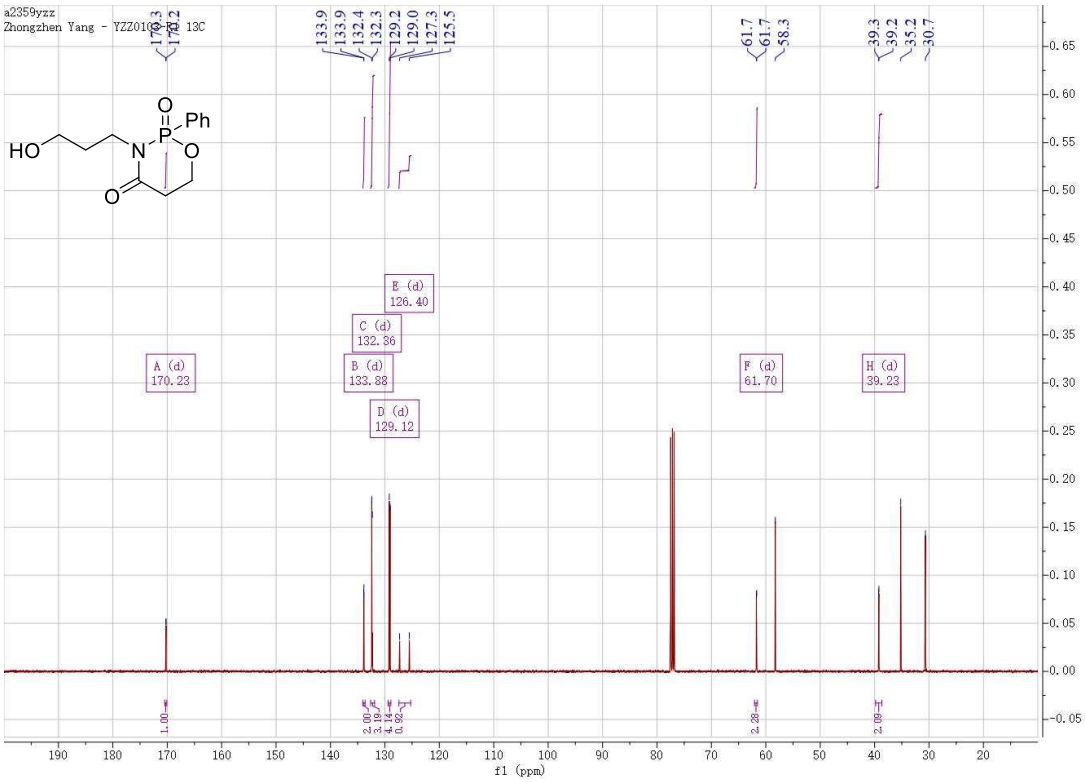


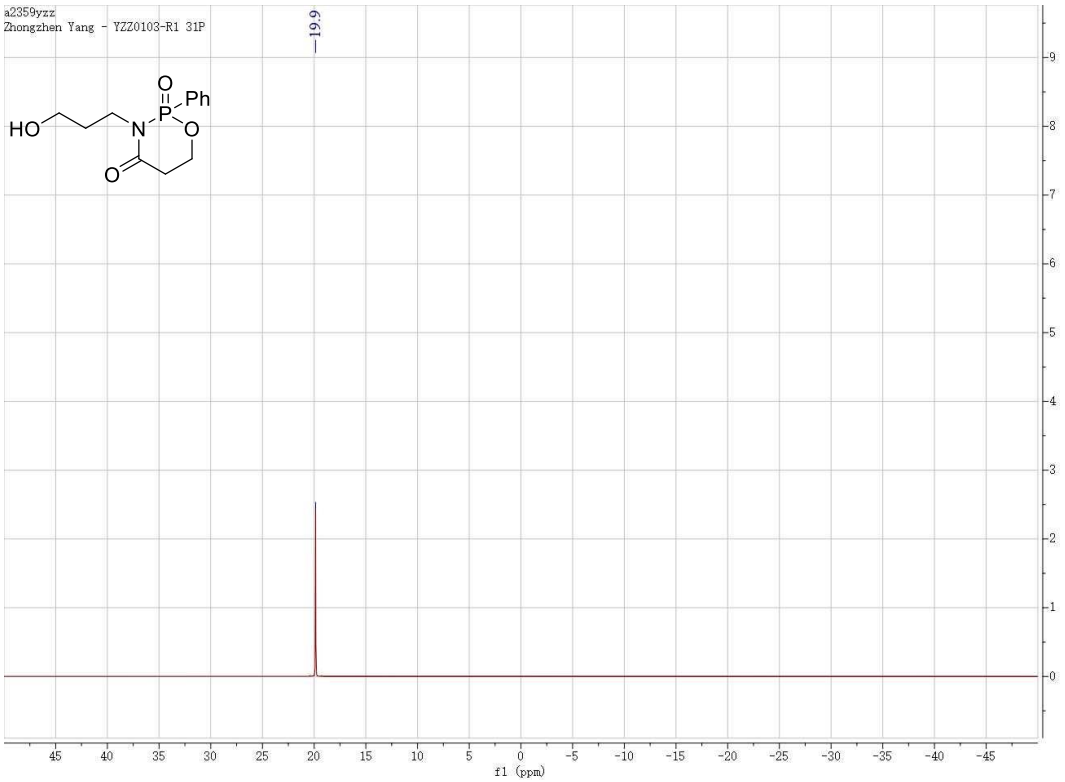

a2213yzz
Zhongzhen Yang - YZZ1215-R1 13C
Ph
O
P
N
O
O
OH
A (d)
174.65
B (d)
133.26
C (d)
131.23
D (d)
128.69
E (d)
129.12
F (d)
67.03
G (d)
25.73
f1 (ppm)


a2213yzz
Zhongzhen Yang - YZZ1215-R1 31P
16.3
Ph
O
P
N
O
O
OH
f1 (ppm)

3-(3-Hydroxypropyl)-2-phenyl-1,3,2-oxazaphosphinan-4-one 2-oxide (24)

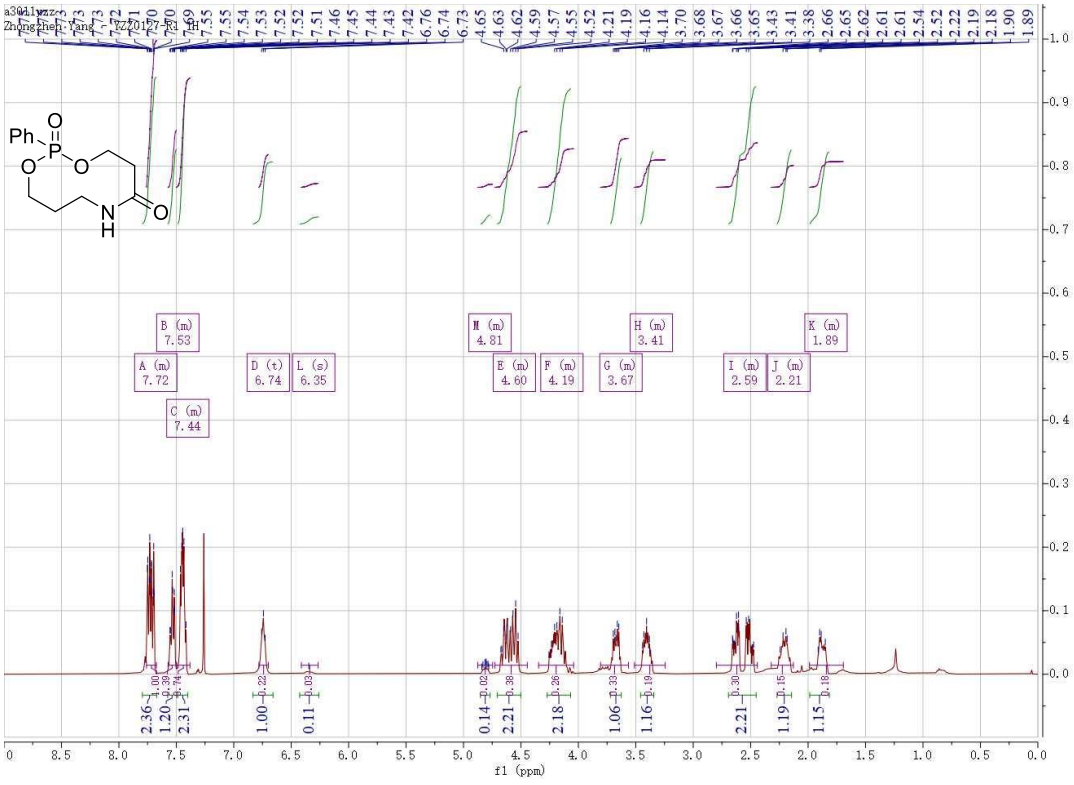


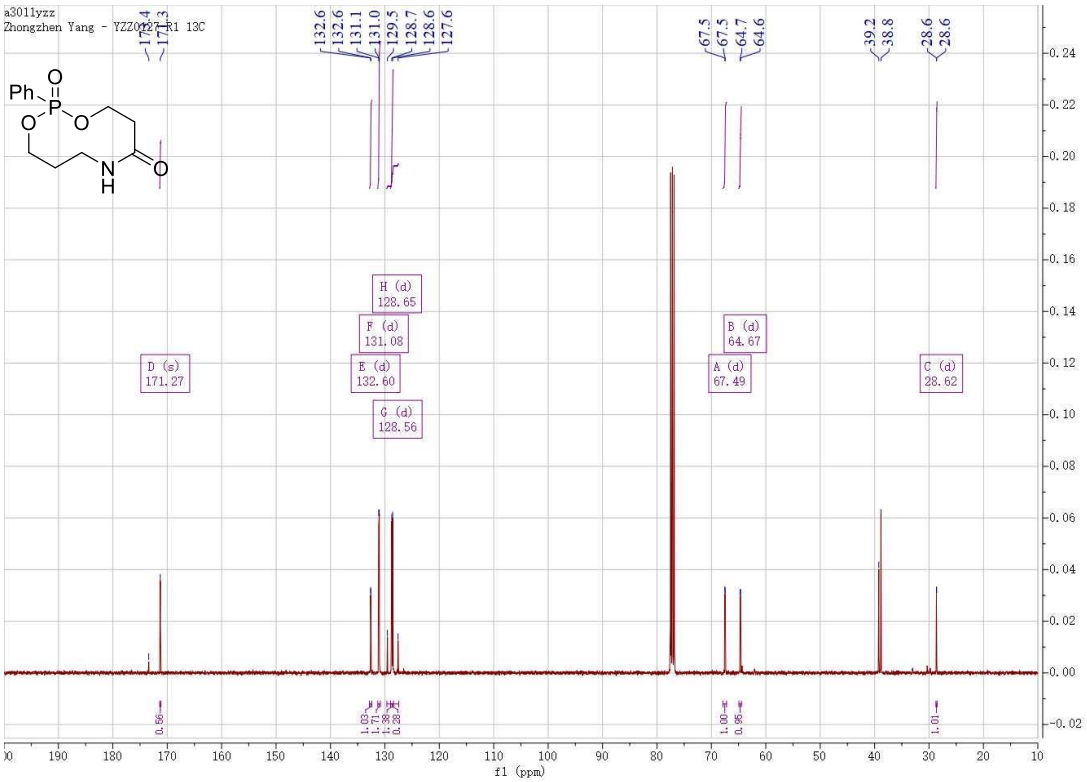


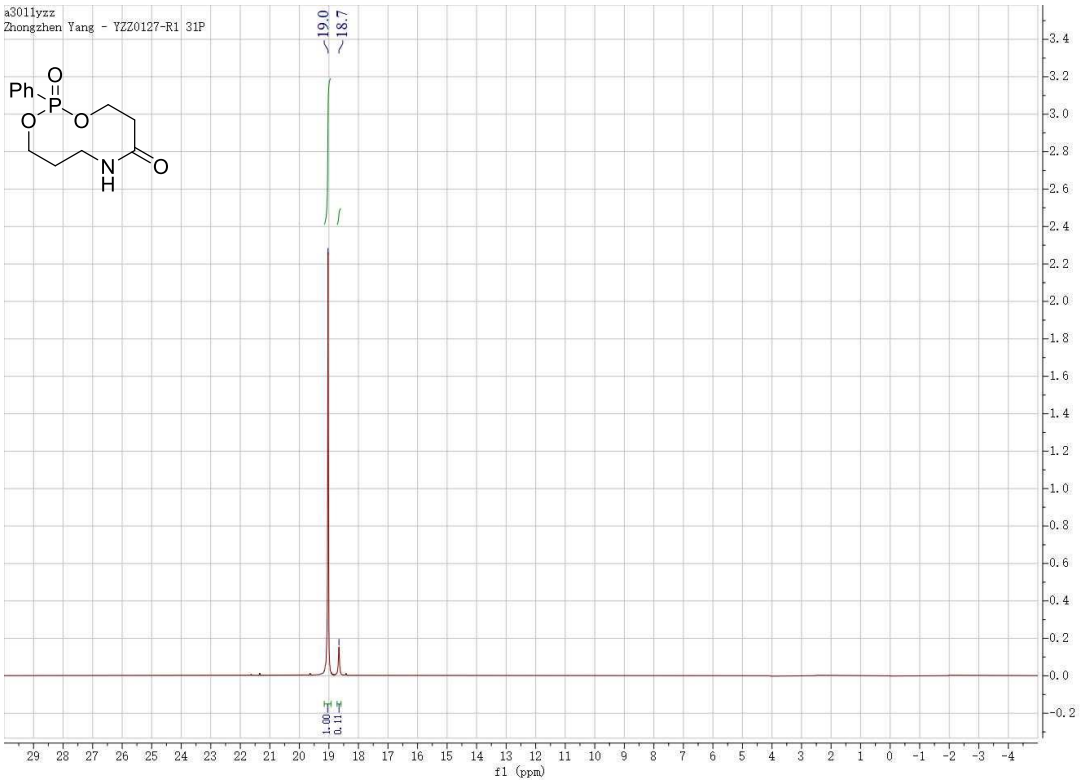


2-Phenyl-1,3,7,2-dioxazaphosphecan-6-one 2-oxide (25) (10:1 mixture of rotamers)

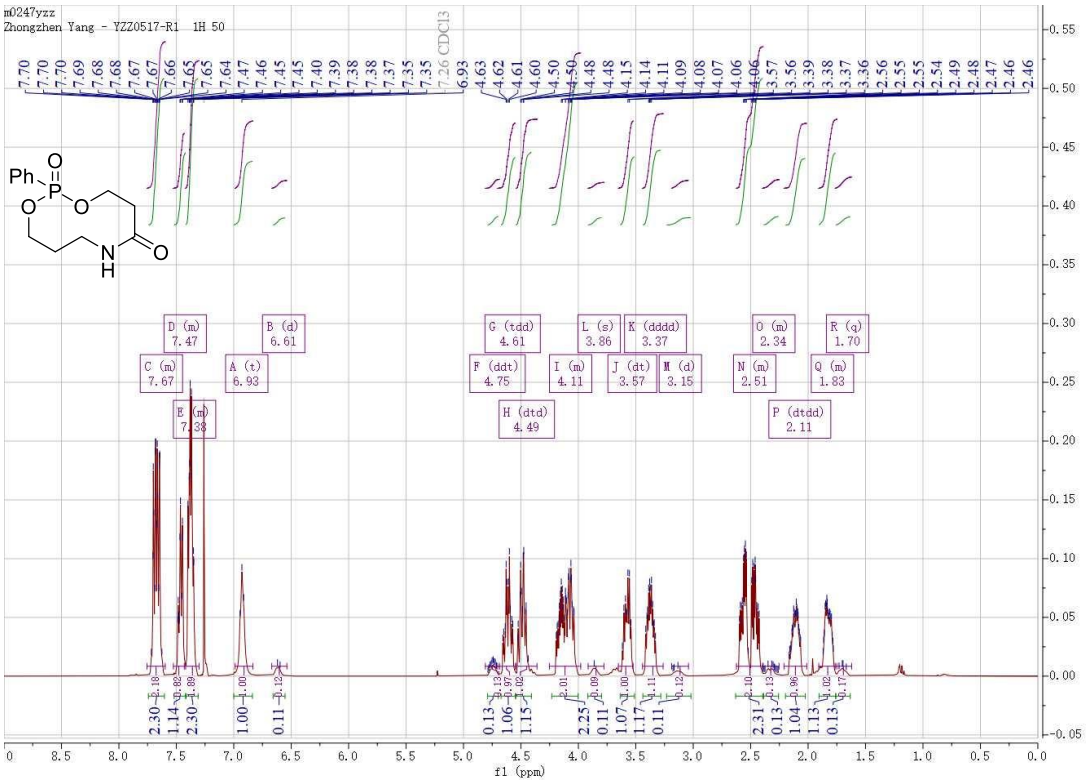
NMRs at RT

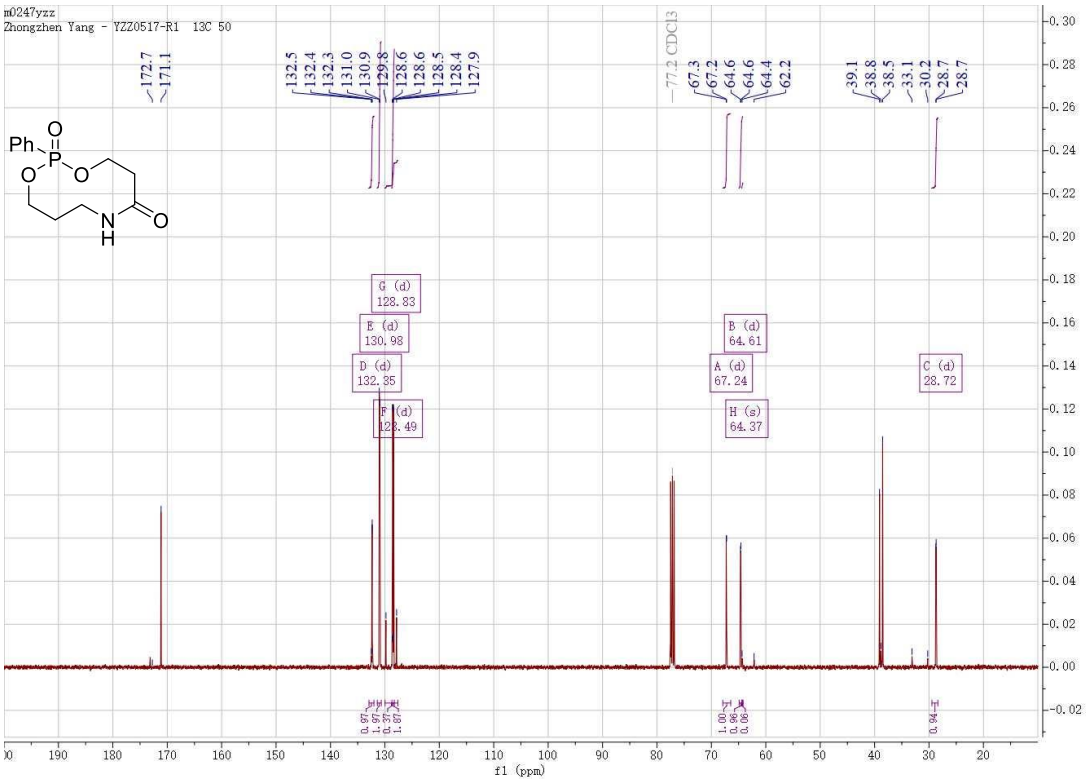


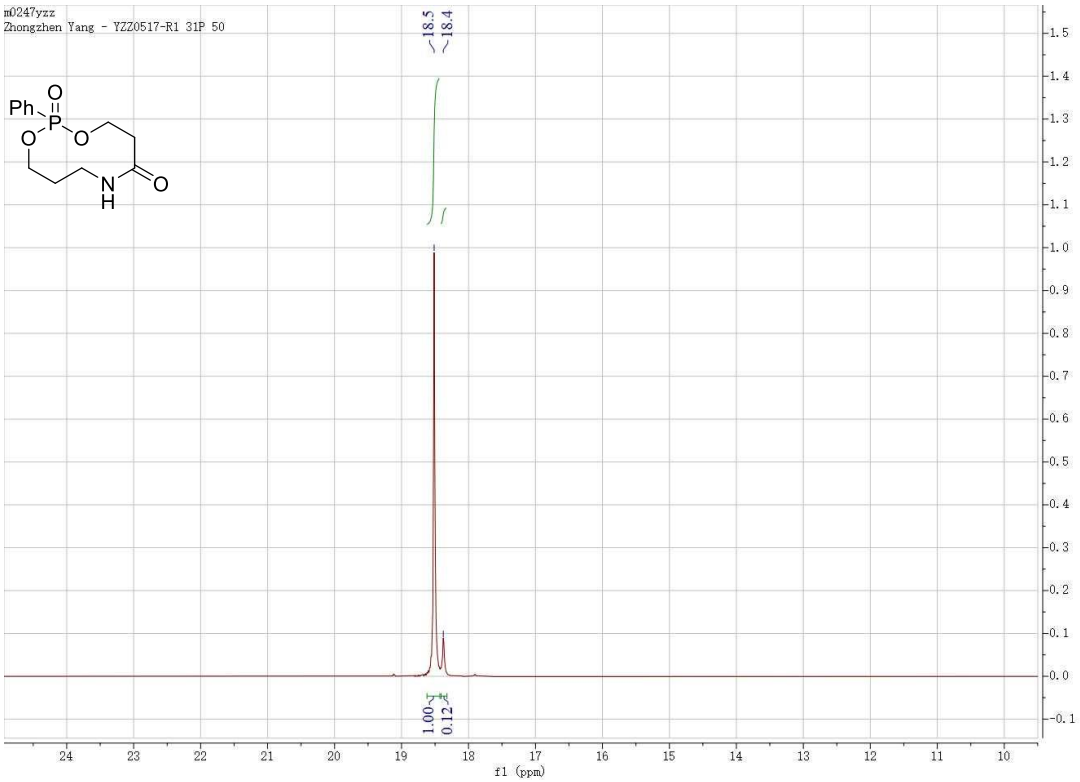

a3011yzz
Zhongzhen Yang - YZZ0127-R1 13C
Ph
O
P
O
O
N
H
O
132.6
132.6
131.1
131.0
129.5
128.7
128.6
127.6
67.5
67.5
64.7
64.6
39.2
38.8
28.6
28.6
H (d)
128.65
F (d)
131.08
E (d)
132.60
G (d)
128.56
D (s)
171.27
B (d)
64.67
A (d)
67.49
C (d)
28.62
f1 (ppm)


a3011yzz
Zhongzhen Yang - YZZ0127-R1 31P
Ph
O
P
O
O
N
H
O
19.0
18.7
f1 (ppm)

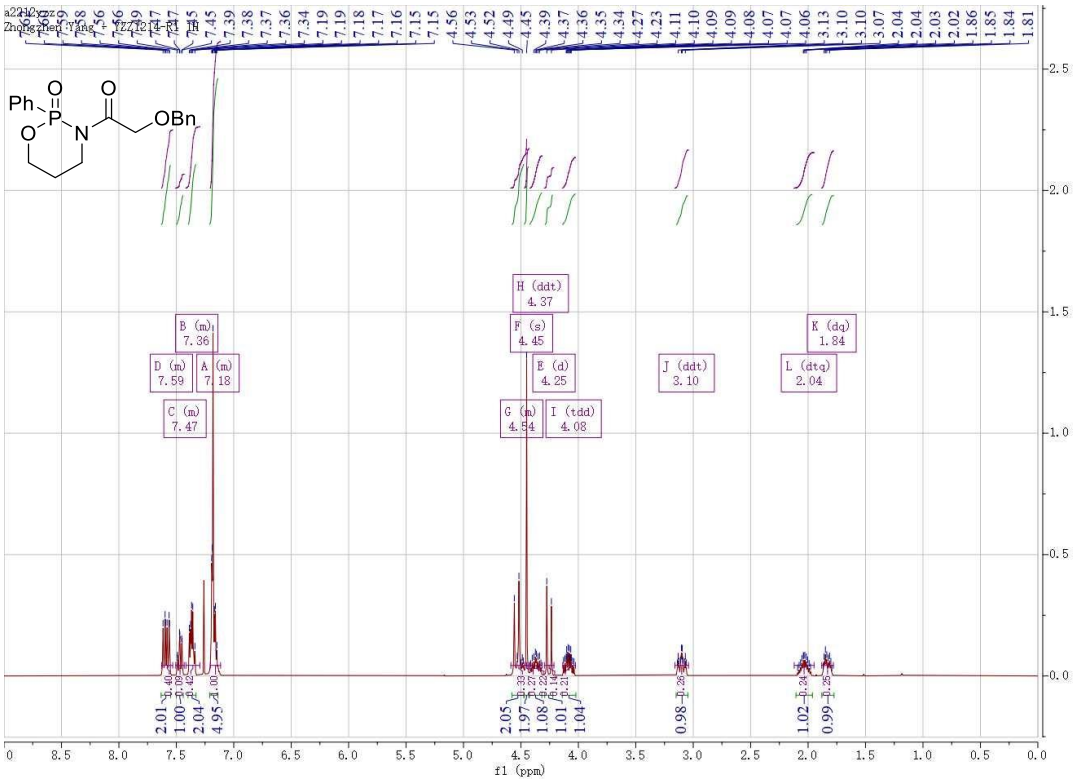
25 NMRs at 50 ℃

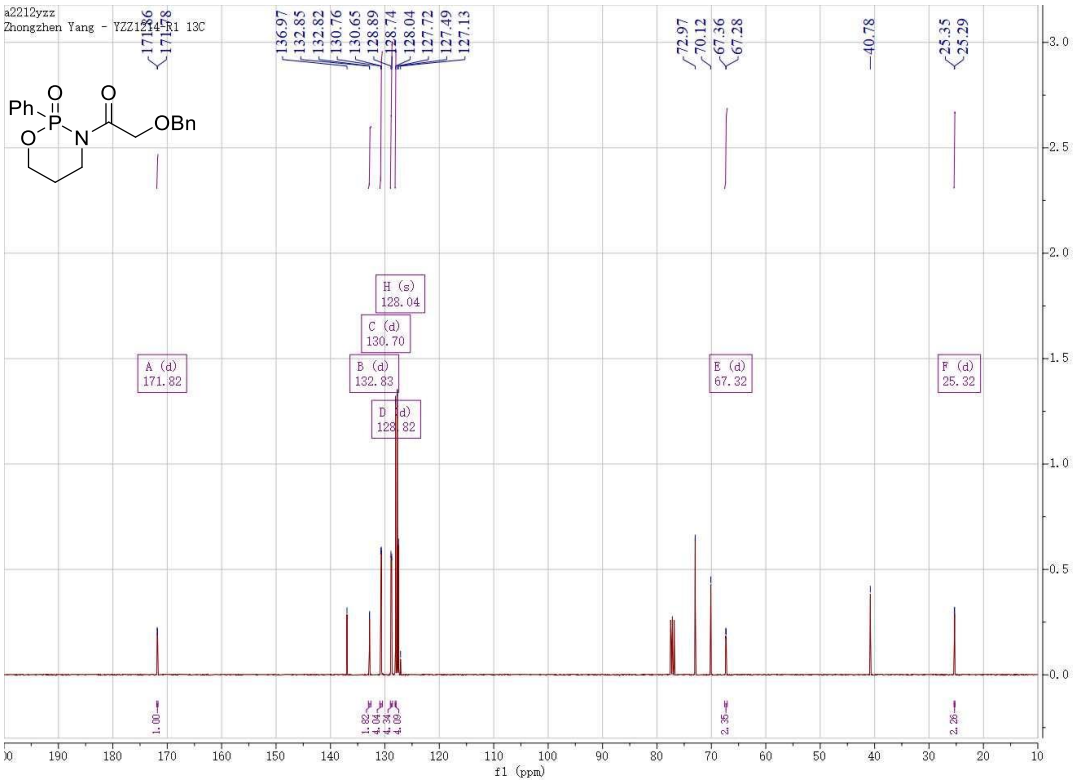

m0247yzz
Zhongzhen Yang - YZZ0517-R1 1H 50
CDCl3
D (m) 7.47
B (d) 6.61
C (m) 7.67
A (t) 6.93
E (m) 7.33
G (tdd) 4.61
L (s) 3.86
K (dddd) 3.37
F (ddt) 4.75
I (m) 4.11
J (dt) 3.57
M (d) 3.15
H (dtd) 4.49
O (m) 2.34
R (q) 1.70
N (m) 2.51
Q (m) 1.83
P (dtdd) 2.11
f1 (ppm)

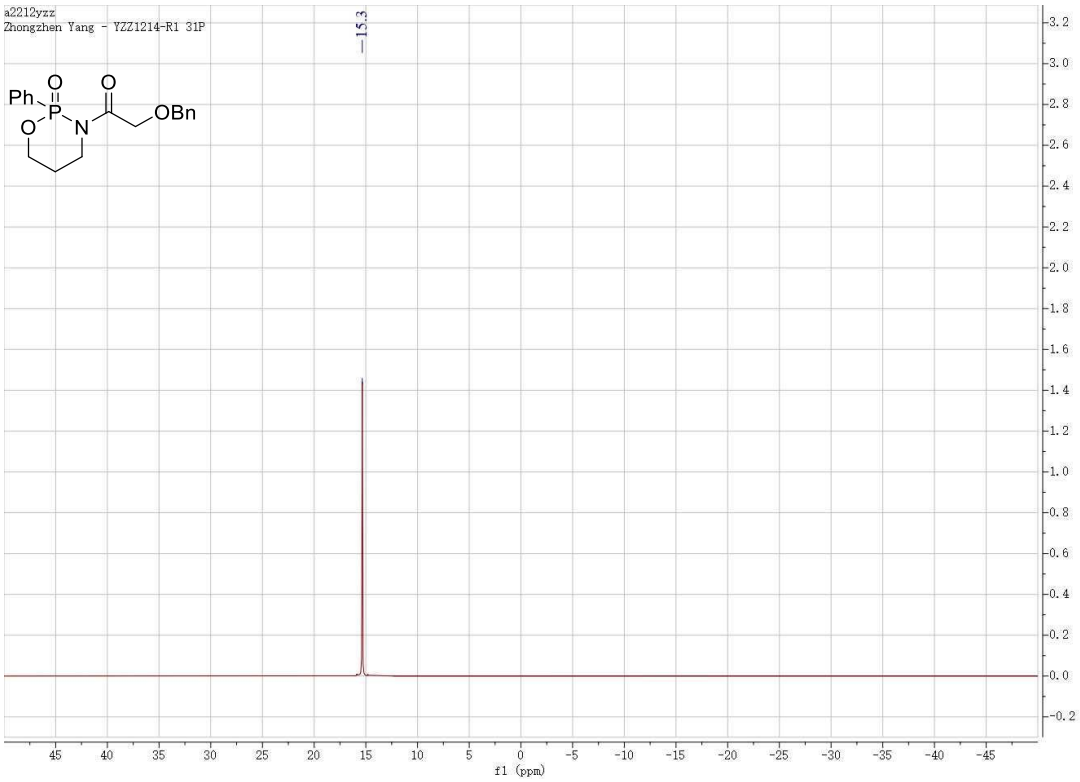

m0247yzz
Zhongzhen Yang - YZZ0517-R1 13C 50
CDCl3
G (d) 128.83
E (d) 130.98
D (d) 132.35
F (d) 128.49
B (d) 64.61
A (d) 67.24
H (s) 64.37
C (d) 28.72
f1 (ppm)



2-(Benzyloxy)-1-(2-oxido-2-phenyl-1,3,2-oxazaphosphinan-3-yl)ethan-1-one (26)

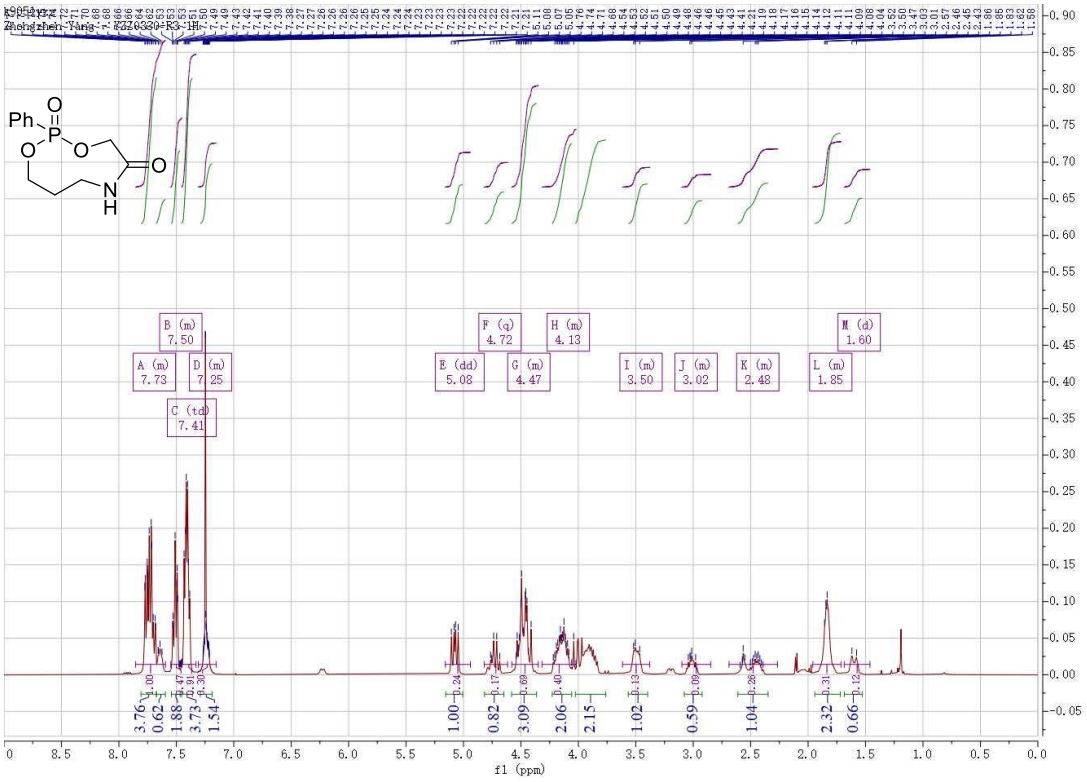


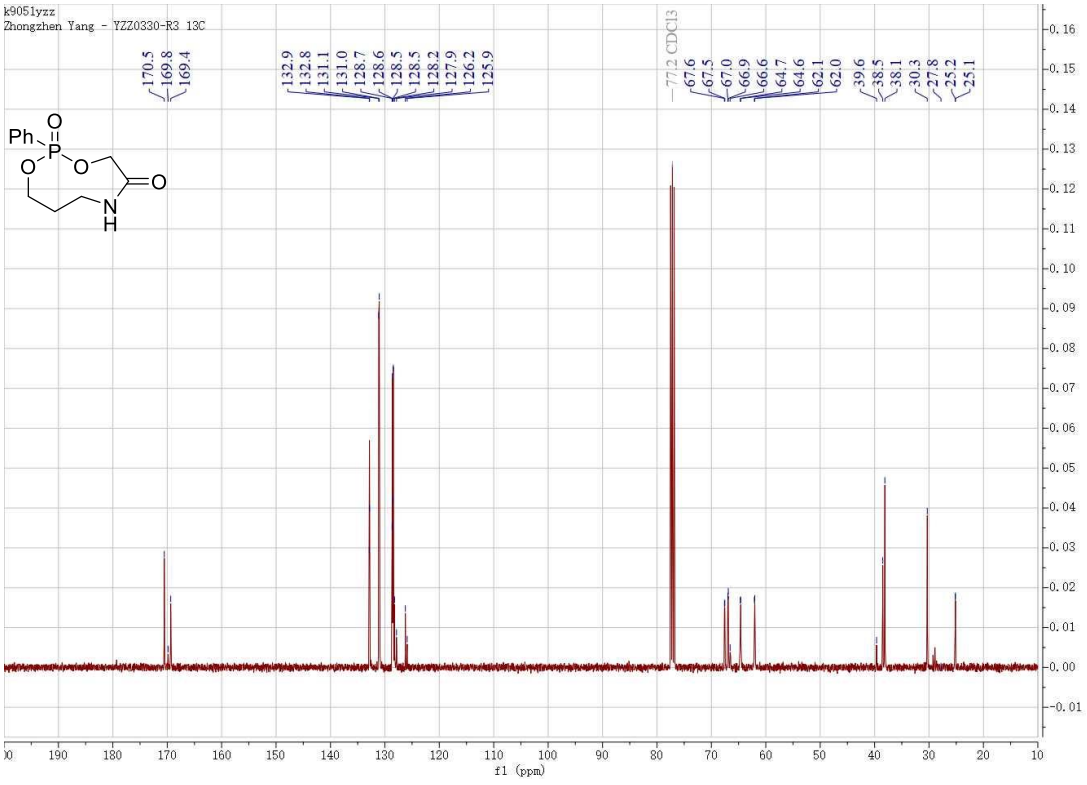

a2212yzz
Zhongzhen Yang - YZZ1214-R1 13C
171.96
171.18
136.97
132.85
132.82
130.76
130.65
128.89
128.74
128.04
127.72
127.49
127.13
72.97
70.12
67.36
67.28
40.78
25.35
25.29
Ph
O
O
O
P
N
OBn
H (s)
128.04
C (d)
130.70
A (d)
171.32
B (d)
132.83
D (d)
128.82
E (d)
67.32
F (d)
25.32
1.00
1.82
4.04
4.34
4.09
2.35
2.26
f1 (ppm)

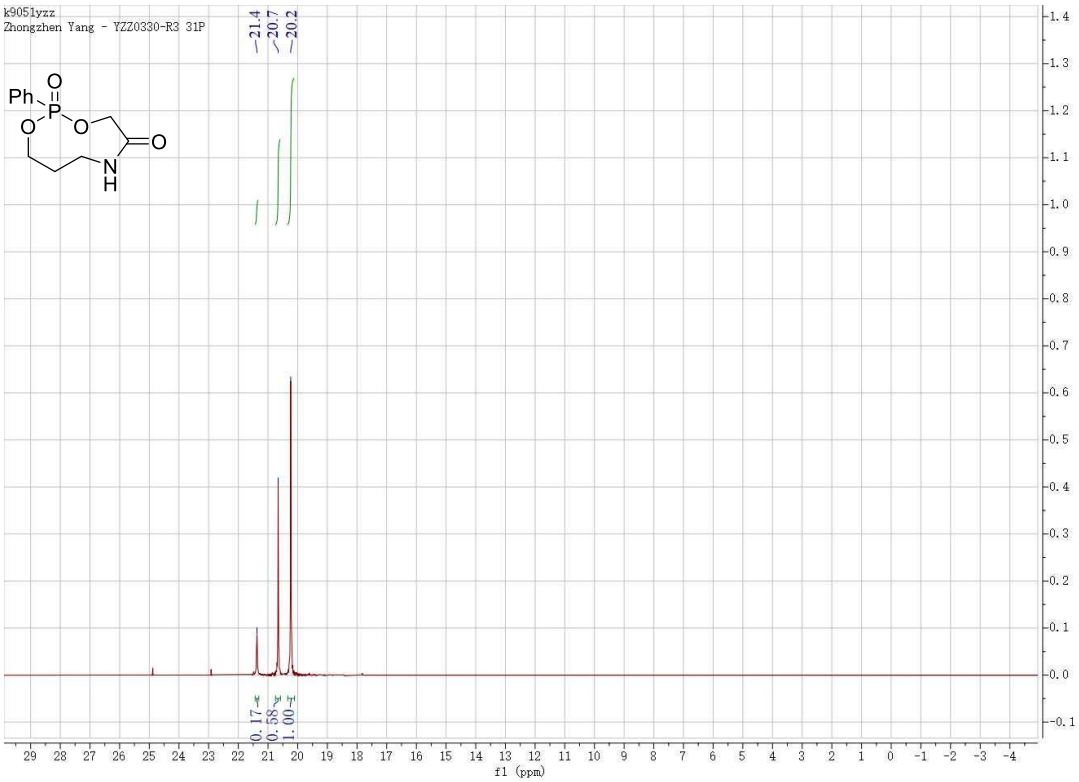

a2212yzz
Zhongzhen Yang - YZZ1214-R1 31P
15.3
Ph
O
O
O
P
N
OBn
f1 (ppm)

2-Phenyl-1,3,6,2-dioxazaphosphonan-5-one 2-oxide (27)

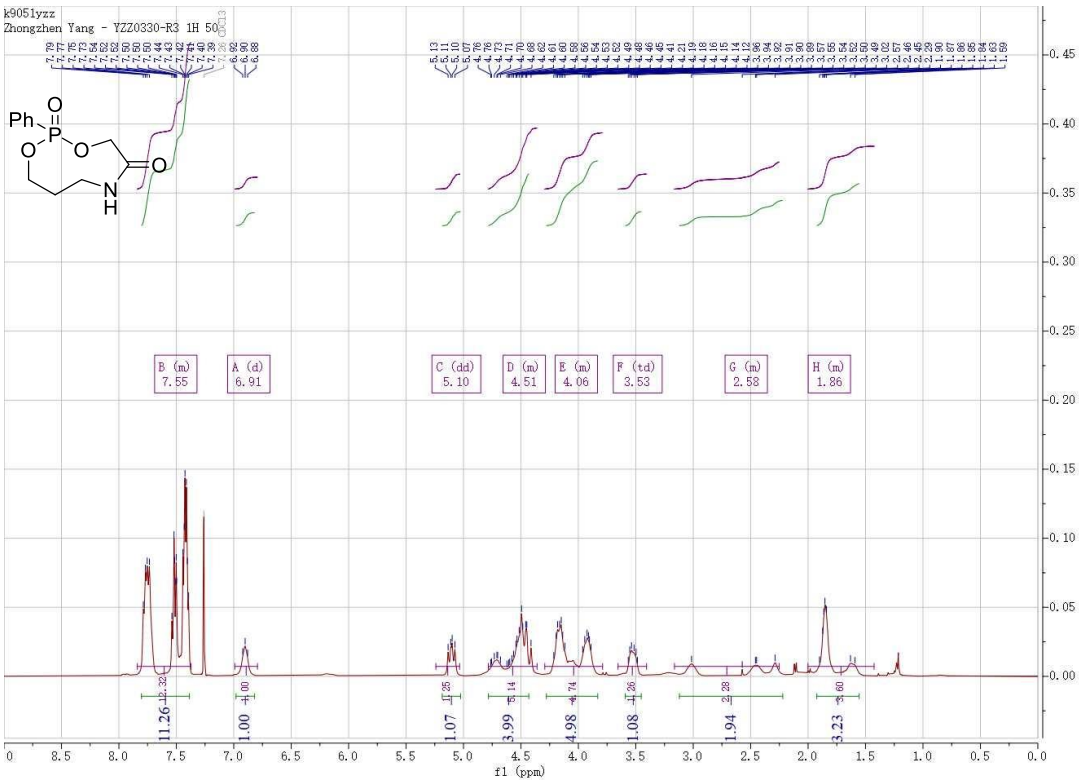
NMRs at RT

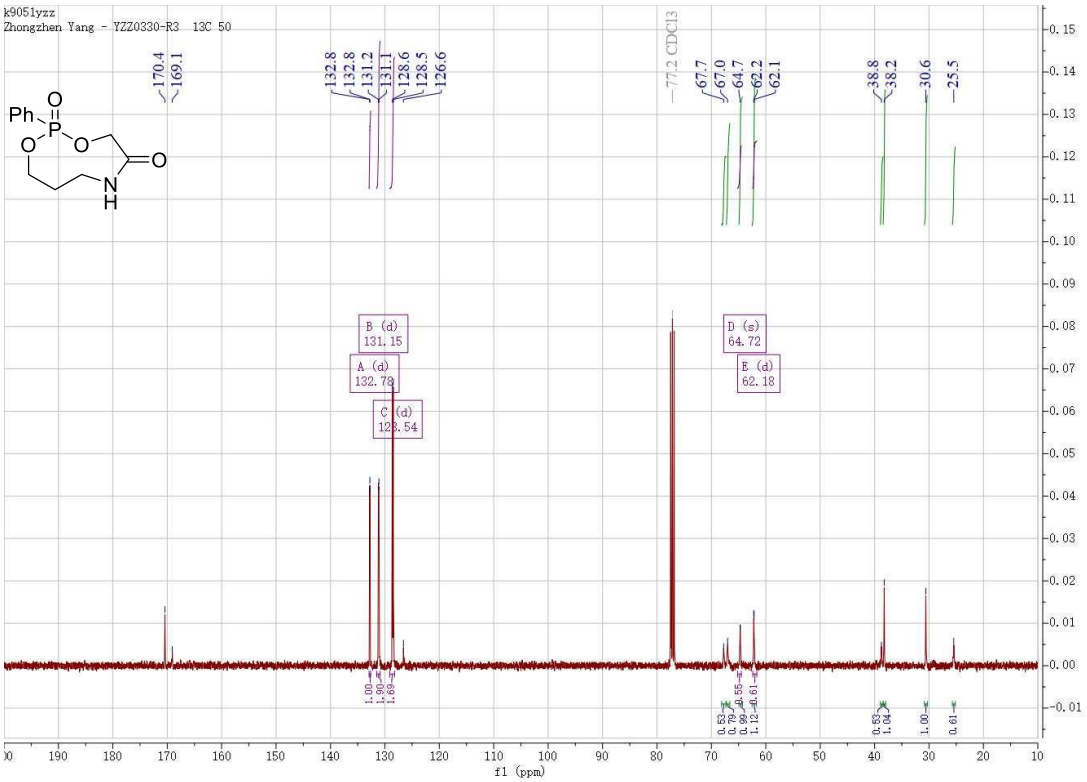


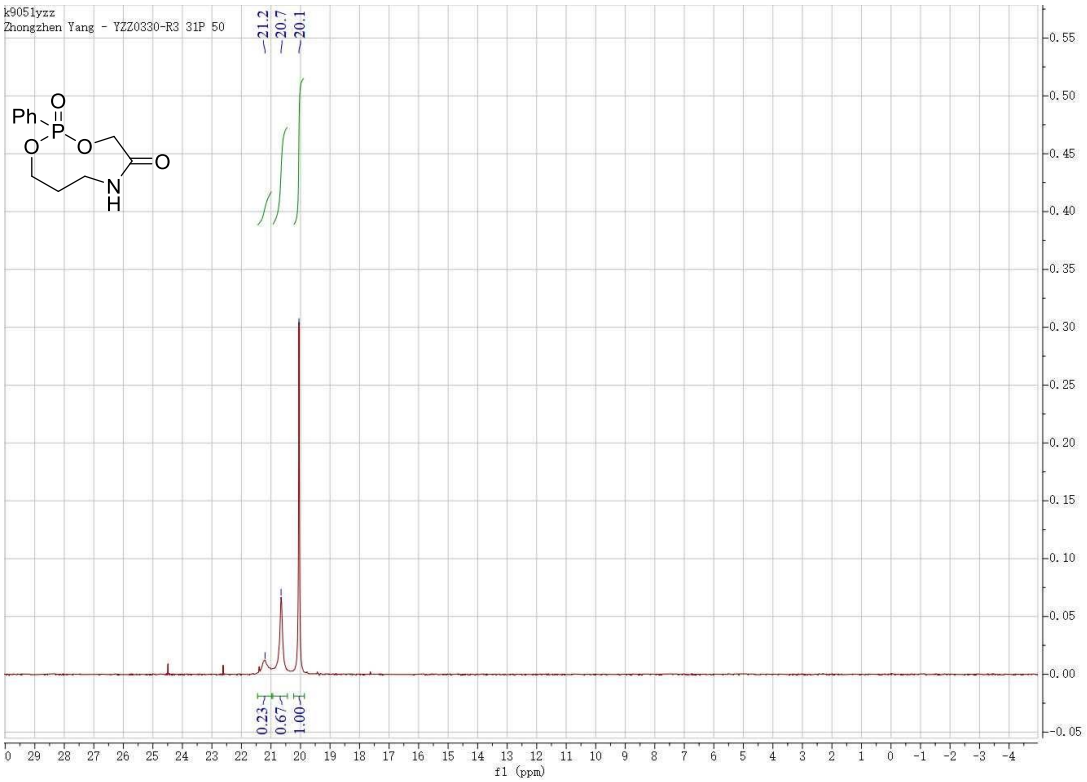



k9051yzz
Zhongzhen Yang - YZZ0330-R3 31P
21.4
20.7
20.2
0.17
0.58
1.00
f1 (ppm)

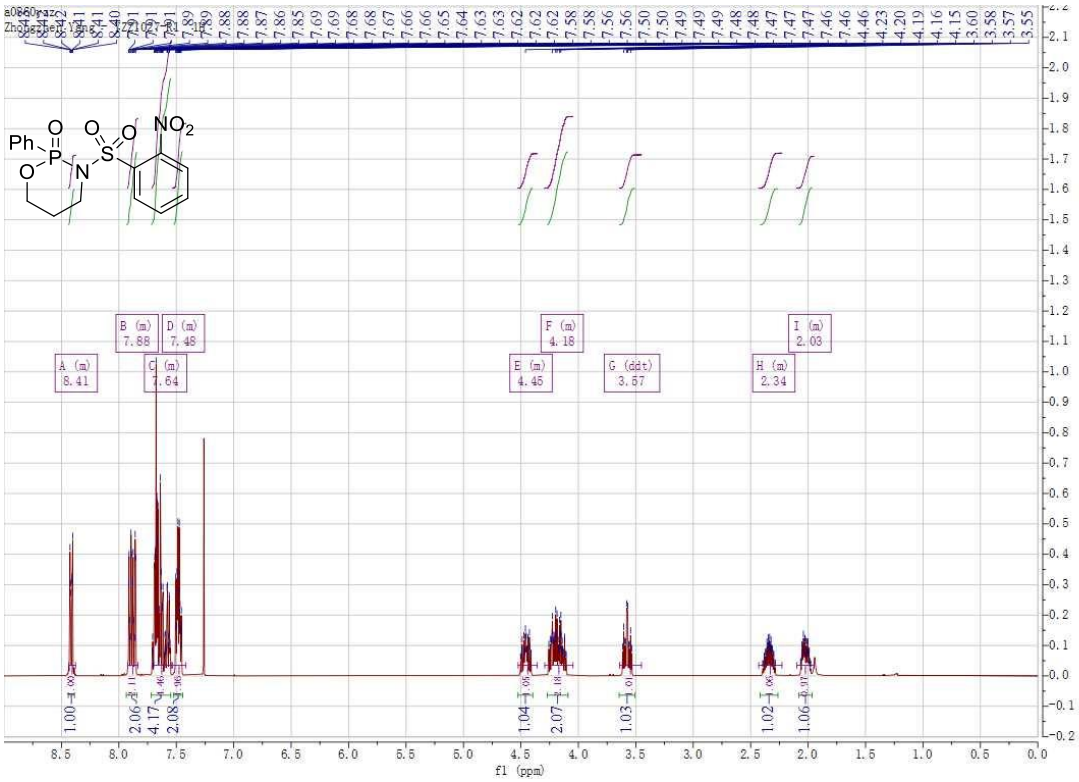
27 NMRs at 50 ℃

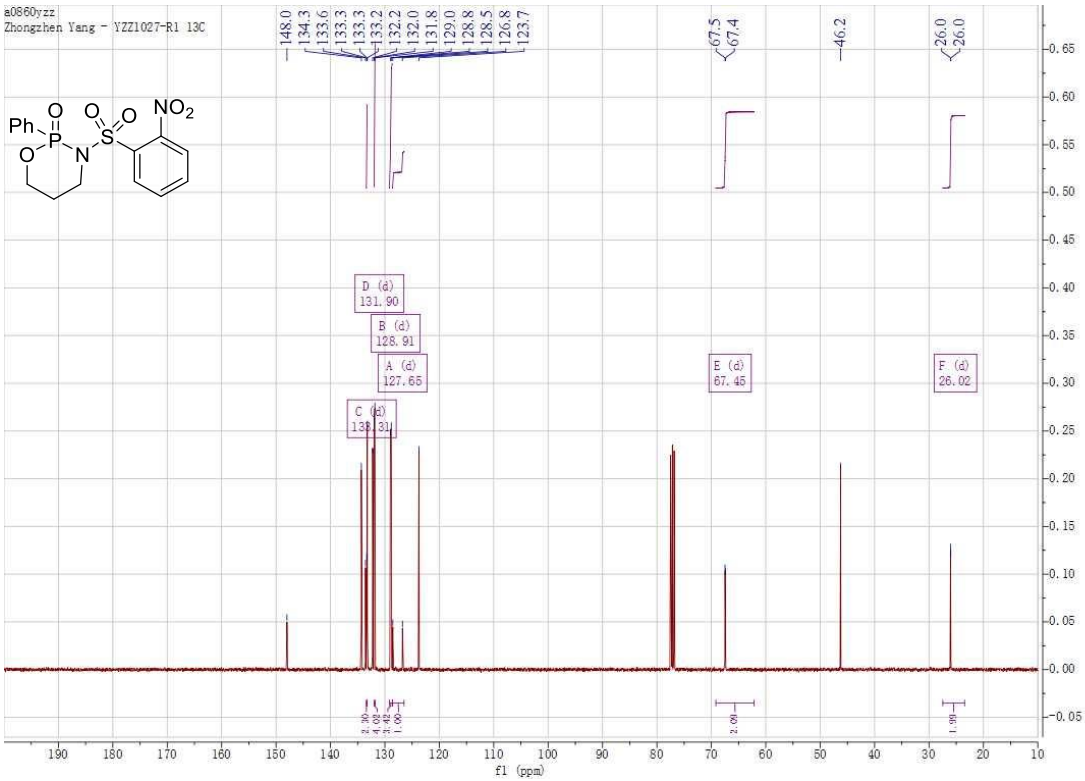

k9051yzz
Zhongzhen Yang - YZZ0330-R3 1H 50
B (m) 7.55
A (d) 6.91
C (dd) 5.10
D (m) 4.51
E (m) 4.06
F (td) 3.53
G (m) 2.58
H (m) 1.86
11.26
1.00
1.07
3.99
4.98
1.08
1.94
3.23
f1 (ppm)

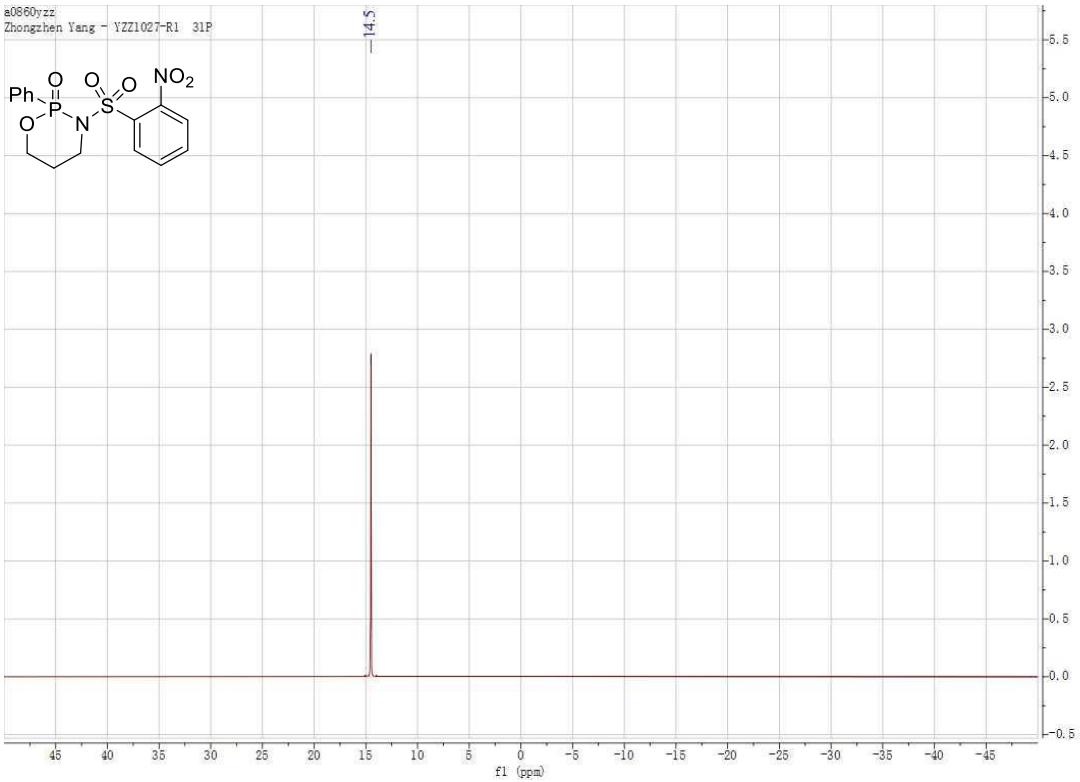

k9051yzz
Zhongzhen Yang - YZZ0330-R3 13C 50
170.4
169.1
132.8
132.8
131.2
131.1
128.6
128.5
126.6
77.2 CDCl3
67.7
67.0
64.7
62.2
62.1
38.8
38.2
30.6
25.5
B (d)
131.15
A (d)
132.78
C (d)
128.54
D (s)
64.72
E (d)
62.18
fl (ppm)


k9051yzz
Zhongzhen Yang - YZZ0330-R3 31P 50
21.2
20.7
20.1
0.23
0.67
1.00
fl (ppm)

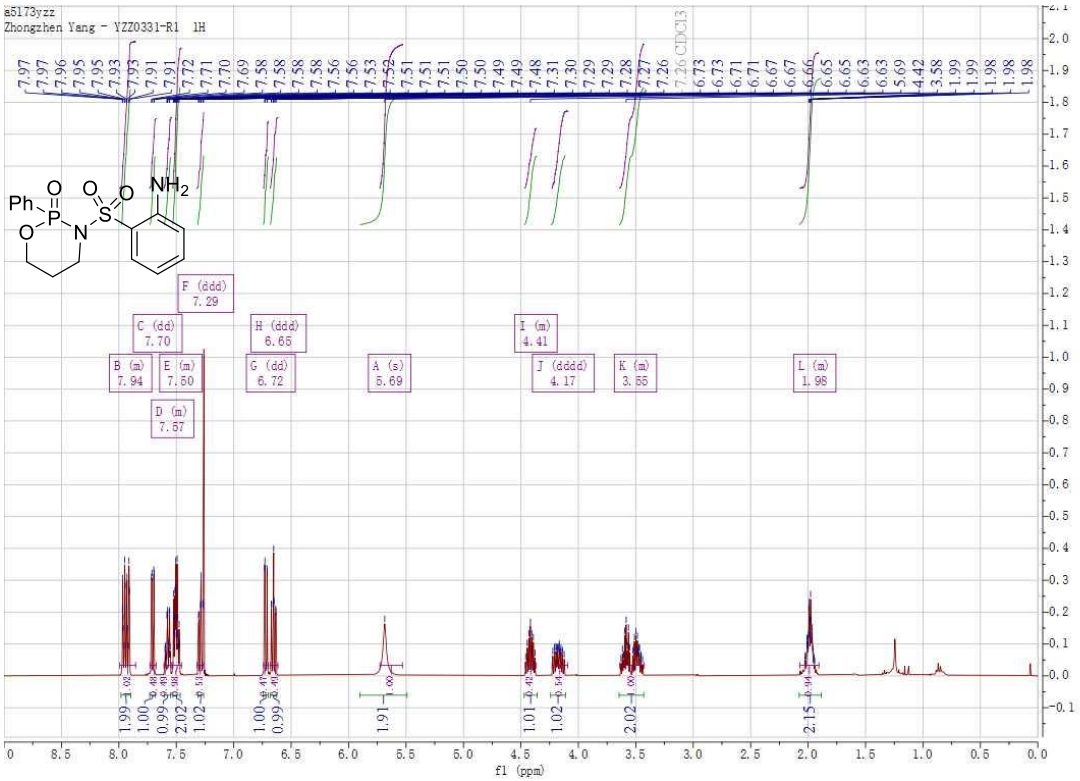
3-((2-Nitrophenyl)sulfonyl)-2-phenyl-1,3,2-oxazaphosphinane 2-oxide (28)

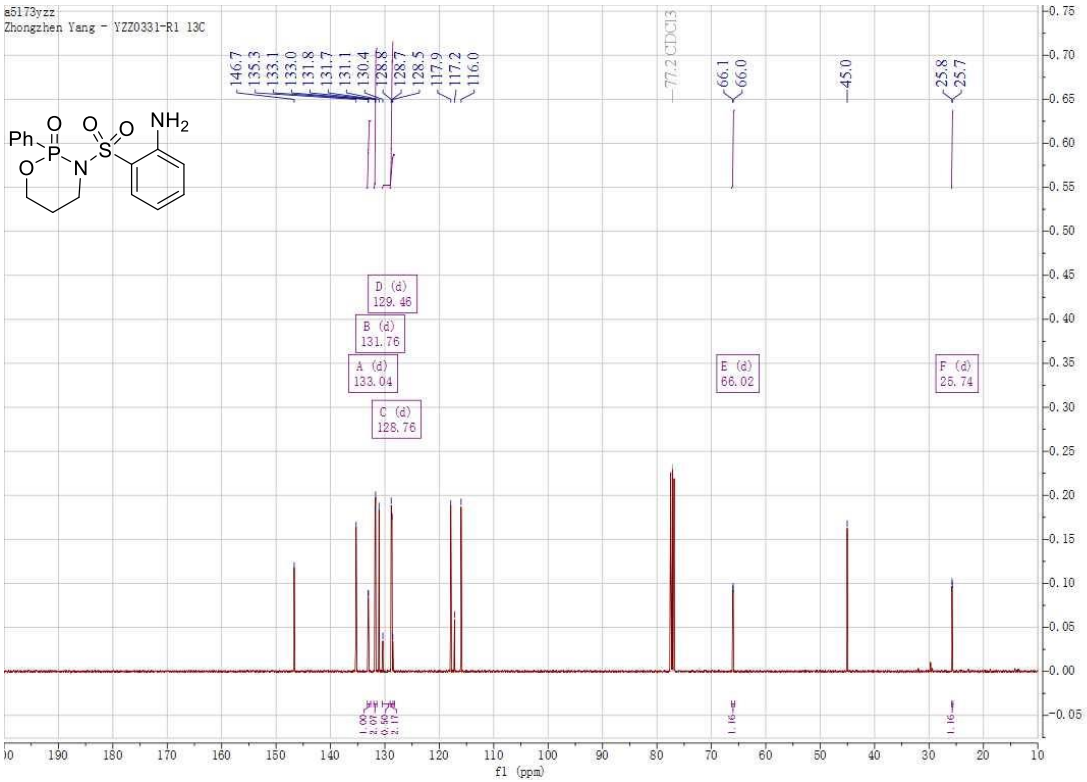


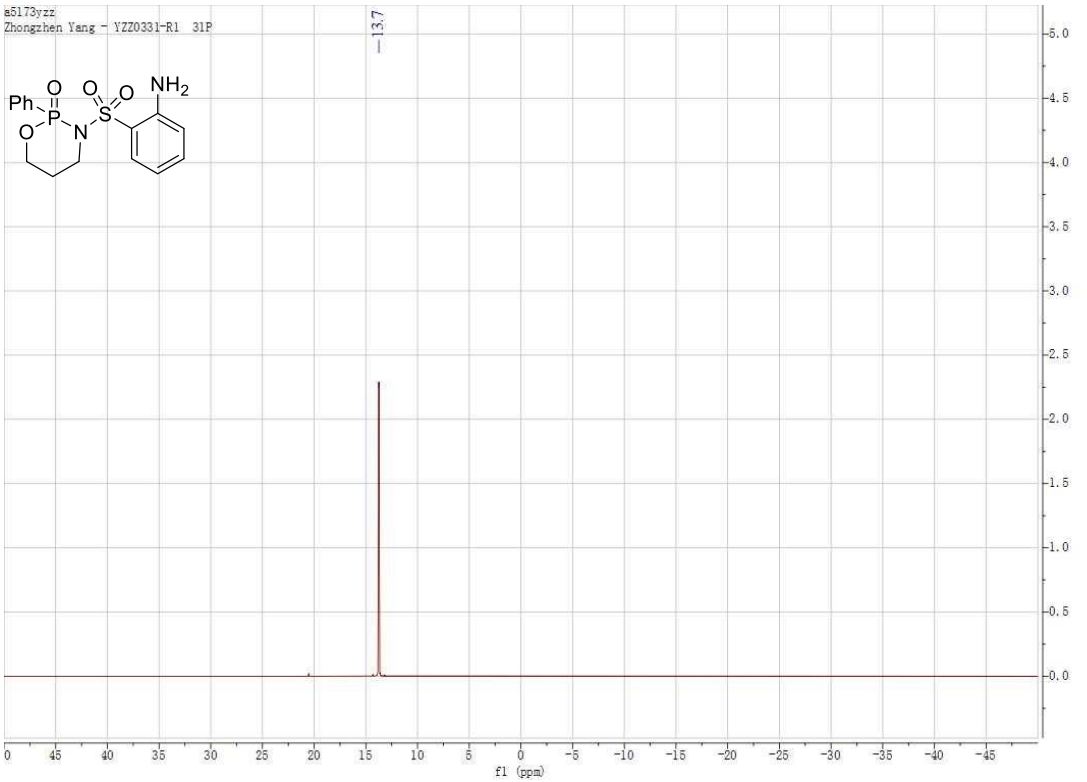




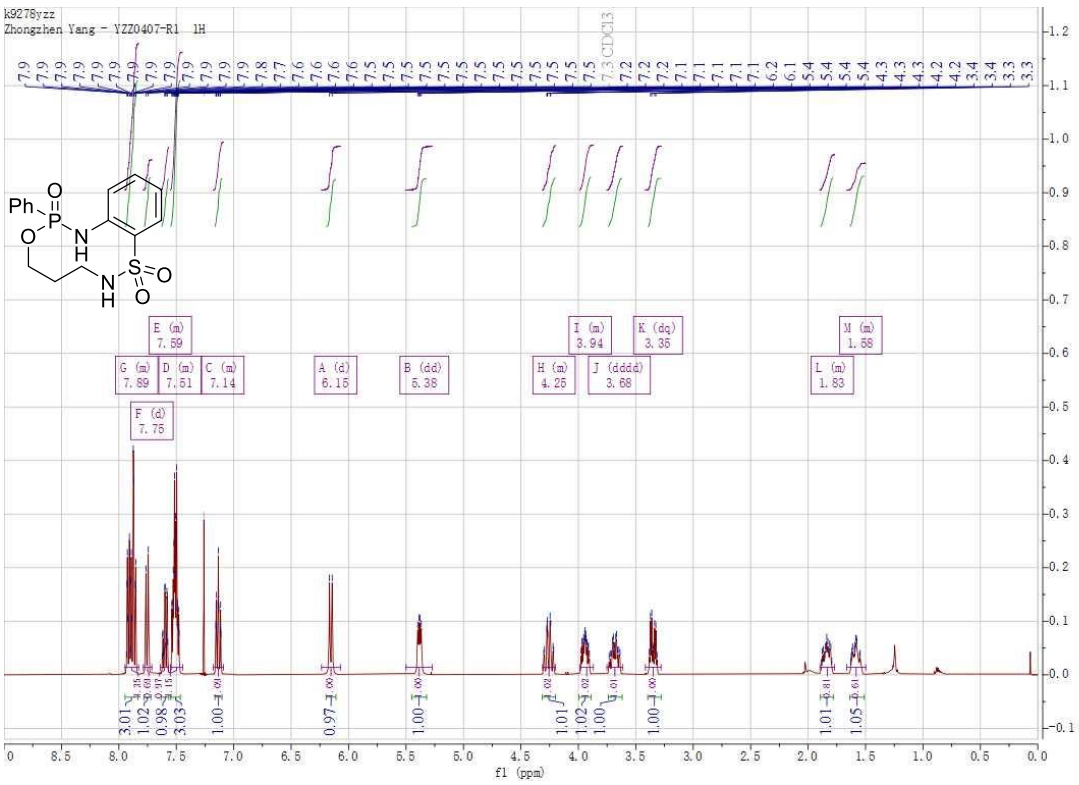
3-((2-Aminophenyl)sulfonyl)-2-phenyl-1,3,2-oxazaphosphinane 2-oxide (28a)

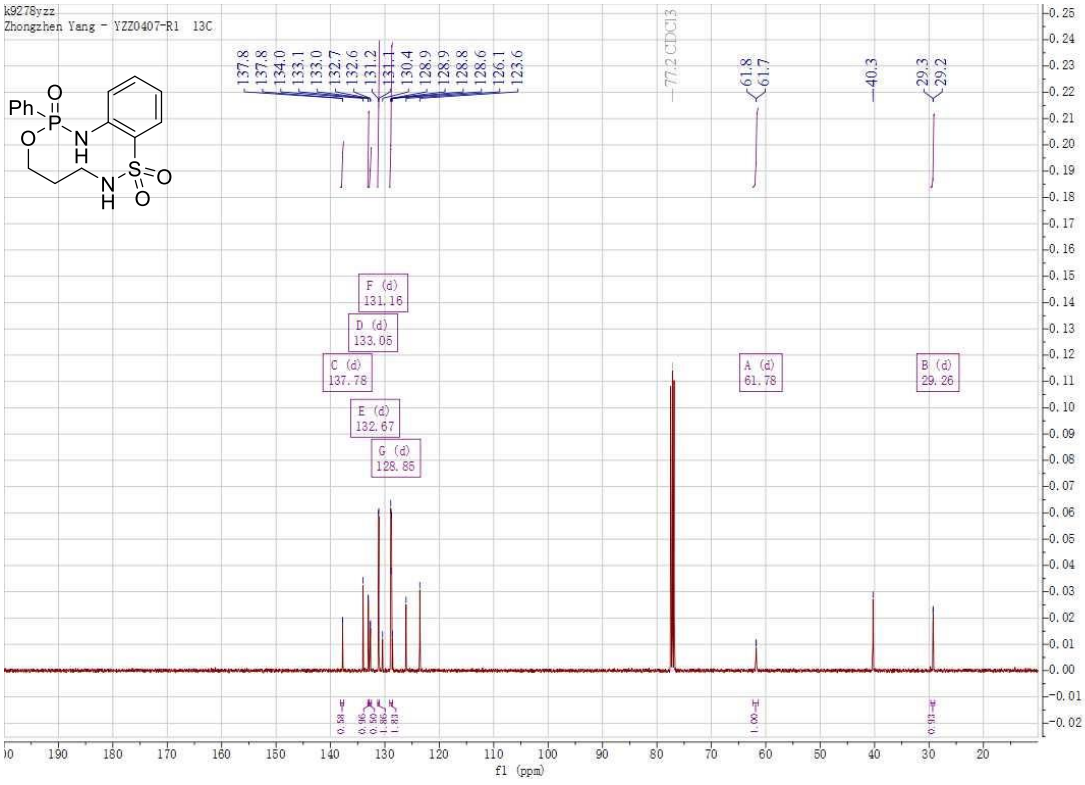


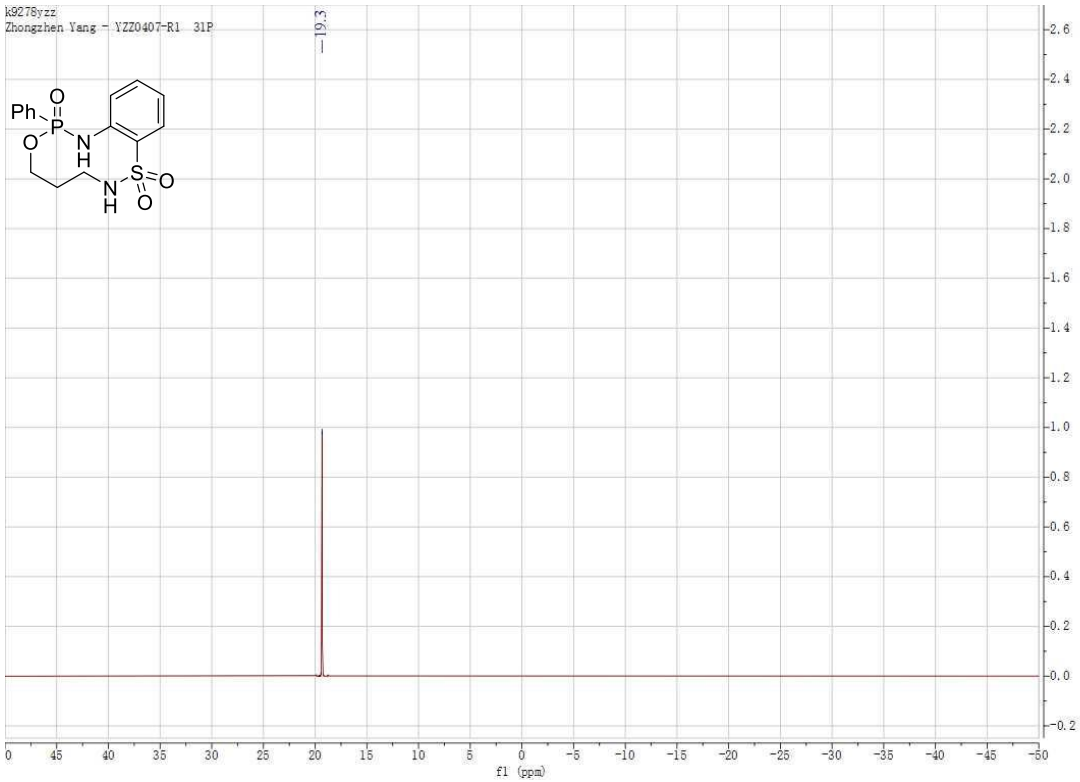

a5173yzz
Zhongzhen Yang - YZZ0331-R1 13C
146.7
135.3
133.1
133.0
131.8
131.7
131.1
130.4
128.8
128.7
128.5
117.9
117.2
116.0
77.2 CDCl3
66.1
66.0
45.0
25.8
25.7
D (d)
129.46
B (d)
131.76
A (d)
133.04
C (d)
128.76
E (d)
66.02
F (d)
25.74
f1 (ppm)


a5173yzz
Zhongzhen Yang - YZZ0331-R1 31P
13.7
f1 (ppm)

2-Phenyl-1,4,5,6,7-pentahydrobenzo[*d*][1,6,3,7,2]oxathiadiazaphosphecine 2,8,8-trioxide (29)






k9278yzz
Zhongzhen Yang - YZZ0407-R1 31P
19.3
f1 (ppm)

7) Computational Chemistry

The structures were loaded in PCModel,[9] and a conformational analysis was performed using the Molecular Mechanics Force Field (MMFF94) level of theory.[10–14] The structures within 3.5 kcal mol^{-1} of the lowest energy conformation were kept and the geometry of each structure was optimised using the Gaussian 16, Revision A.03 package,[15] at the B3LYP/6-31G* or B3LYP/6-31+G* level of theory.[16-21] The lowest energy structure was then reoptimised with tight convergence criteria followed by frequency calculations, which confirmed the structures were minima due to the absence of imaginary frequencies.

For the methodology screening, single point calculations were carried out on the B3LYP/6-31G* optimised structures using the stated functional (B3LYP, M06-2X[22] or PBE0[23,24]) and basis set (6-31G*, 6-31+G* or def2-TZVPP[25–28]). All minima were again confirmed as such by the absence of imaginary frequencies. The SCF energies were corrected for their zero-point energies, thermal energies and entropies at 298 K, obtained from the frequency calculations. Optimisations were performed with tight convergence criteria and no symmetry constraints were applied. An ultrafine integral grid was used for all calculations. Where used, solvent corrections were applied with the SMD model.[29] Where used, dispersion effects were modelled with Grimme's D3 method with additional Becke–Johnson damping.[30] Energies in Hartrees and xyz coordinates are reported.

Transition states were located by performing a scan of the bond length of the relevant bond being formed/broken. The highest energy structures from the scans were retained and optimised to a transition state using the Berny algorithm[31] at the B3LYP/6-31+G* level of theory. This was followed by a frequency calculation to confirm there was a single imaginary frequency. Intrinsic Reaction Coordinate (IRC) analysis[32–34] confirmed that the transition states were connected to the appropriate minima.

Methodology Screening

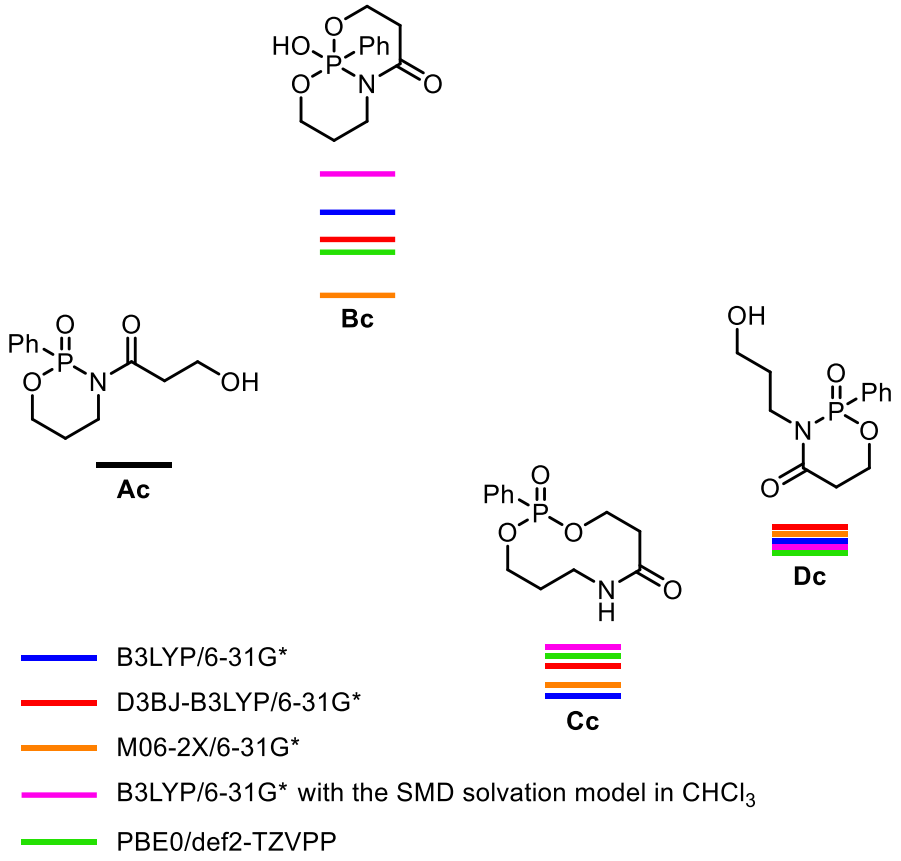


Figure S1. Relative energies of isomeric species in the ring expansion of **Ac** using various levels of theory.

Functional	Basis set	Solvent correction	Empirical dispersion correction	Ac	Bc	Cc	Dc
B3LYP	6-31G*	N	N	0	16.0	–14.6	–4.8
B3LYP	6-31G*	N	D3BJ	0	14.3	–13.1	–4.1
M06-2X	6-31G*	N	N	0	10.5	–14.1	–4.5
B3LYP	6-31G*	SMD ($CHCl_3$)	N	0	18.6	–11.5	–5.0
PBE0	def2-TZVPP	N	N	0	13.6	–12.4	–5.3

Table S8 DFT calculated relative energies of isomeric species in the ring expansion of **Ac** at various levels of theory. Energies are Gibbs free energies at 298 K in kcal mol^{-1}.

Energies and xyz coordinates

Aa

B3LYP/6-31G*

SCF Done: E(RB3LYP) = -1183.41051392

Zero-point correction= 0.317570

Thermal correction to Gibbs Free Energy= 0.268946

C	-2.10887900	-2.56498900	-0.33314600
C	-0.15357400	-1.53268400	-1.54770900
C	-0.90850900	-2.82575500	-1.23344800
H	-2.60368400	-3.49051900	-0.02943800
H	-2.84624300	-1.92601300	-0.83728500
H	0.71367200	-1.72278900	-2.17940300
H	-0.81111500	-0.82749900	-2.07318600
H	-1.25658000	-3.27807600	-2.17075100
H	-0.23155300	-3.53925200	-0.74981200
P	-0.80032700	-0.57995800	0.91242800
C	-1.88513900	0.70602500	0.23134200
C	-3.23626500	0.73566900	0.61224600
C	-1.38020800	1.72154600	-0.59376300
C	-4.06695800	1.76508800	0.17127800
H	-3.63284300	-0.04534100	1.25456000
C	-2.21393200	2.75044000	-1.03190500
H	-0.33655800	1.70774900	-0.89530100
C	-3.55688400	2.77258500	-0.65059100
H	-5.11155200	1.78135000	0.46960300
H	-1.81471800	3.53333600	-1.67060400
H	-4.20546500	3.57415100	-0.99344300
O	-0.24981100	-0.30385400	2.25937300
O	-1.69953100	-1.92976200	0.89836900
N	0.36698500	-0.88417000	-0.31613400
C	1.75109400	-0.61889100	-0.27522000
C	2.31899900	0.10770900	0.93366200
H	1.81772400	1.07744200	1.03450400
H	2.06139800	-0.44882200	1.83930400
C	3.83000100	0.32385700	0.83556700
H	4.16201400	0.77307100	1.78046500
H	4.33969600	-0.65404600	0.75242300
O	2.45988100	-0.95747500	-1.21469400
N	4.18061800	1.24206700	-0.24491100
H	3.92984100	0.78283300	-1.11845500
C	5.60291800	1.56247300	-0.26852400
H	5.86653100	2.13112700	0.63198700

H	6.27057900	0.68061900	-0.31139300
H	5.82023100	2.19506500	-1.13599300

Ba

B3LYP/6-31G*

SCF Done: E(RB3LYP) = -1183.35259598

Zero-point correction= 0.317883

Thermal correction to Gibbs Free Energy= 0.273832

C	-1.03294300	2.45018200	1.38175800
C	-1.16943100	2.27007400	-0.13060400
C	0.09386500	1.56383600	1.90677200
H	-0.26648000	2.62819200	-0.64168900
H	-2.02535800	2.81348500	-0.53366200
H	-0.82539200	3.50229400	1.61773600
H	-1.97785700	2.17677700	1.86611600
H	0.14862800	1.59966300	3.00167200
H	1.06086100	1.92357100	1.51876100
P	-0.16520300	-0.34105500	-0.10686400
O	-0.11395100	0.20187100	1.55420000
O	-0.29111100	-0.81284800	-1.76970200
C	1.67340500	-0.12783200	-0.26988900
C	2.52604000	-0.30061300	0.83566400
C	2.24245100	0.20060500	-1.51258100
C	3.90806800	-0.17797300	0.69318300
H	2.10022200	-0.52631700	1.80543500
C	3.62219700	0.36250700	-1.64156700
H	1.59501300	0.31816300	-2.37264000
C	4.45940400	0.16271100	-0.54314900
H	4.55282600	-0.33792100	1.55329900
H	4.04260200	0.63449100	-2.60609200
H	5.53552300	0.27286900	-0.64908700
H	0.03372800	-1.72571000	-1.83764800
N	-1.38267100	0.85470700	-0.47769200
C	-2.65731500	0.44562800	-0.85408700
C	-2.91212300	-1.06299300	-0.88577500
H	-2.55721700	-1.46221600	-1.83821400
H	-3.99916700	-1.17765600	-0.85127400
C	-2.31104000	-1.84680500	0.29467600
H	-2.72534600	-1.43460500	1.23082600
H	-2.64217700	-2.89135800	0.23028900
O	-3.55098900	1.24780800	-1.08735200
N	-0.83012400	-1.85908600	0.37888400
C	-0.38340400	-2.48296800	1.62666400
H	-0.75398800	-3.51538000	1.63526700
H	0.70817000	-2.52026200	1.65718100

H	-0.74361800	-1.96440100	2.52477400

Ca
B3LYP/6-31G*
SCF Done: E(RB3LYP) = -1183.42209988

Zero-point correction= 0.318995
Thermal correction to Gibbs Free Energy= 0.272769

P	-0.36766900	0.07083600	0.32302300
O	0.36718100	-0.77467900	-0.85007000
C	0.77307200	-2.15447100	-0.62373300
H	0.29385500	-2.73354600	-1.41882700
H	0.38590400	-2.49841200	0.34124400
C	2.29101700	-2.30931400	-0.69562000
H	2.50472800	-3.37671300	-0.84877600
H	2.66374700	-1.77892500	-1.57761800
C	3.07366500	-1.83804500	0.54507900
H	4.14232000	-1.98459500	0.36429500
H	2.79510300	-2.43286600	1.42152900
N	2.84965800	-0.43614700	0.88521700
H	2.04082300	-0.25346600	1.47627800
C	3.24994800	0.53999500	0.01935500
C	1.32248600	1.97665100	-0.76554500
H	1.21843000	3.00370100	-1.13271500
H	1.48739700	1.34048700	-1.63780200
C	2.56511200	1.89530800	0.17084000
H	2.27616500	2.10660000	1.20685200
H	3.29356400	2.64939200	-0.14079400
O	4.05554500	0.33877900	-0.88677300
O	0.01172800	-0.35311700	1.71322400
C	-2.15385700	-0.08839900	0.05761400
C	-2.74688000	0.28946200	-1.15717700
C	-2.94530400	-0.64127400	1.07386600
C	-4.11583000	0.11430000	-1.35022300
H	-2.13560600	0.72473500	-1.94236900
C	-4.31652300	-0.81337400	0.87714700
H	-2.47643100	-0.92751700	2.01023600
C	-4.90089000	-0.43707500	-0.33321600
H	-4.57204600	0.40850700	-2.29155000
H	-4.92724700	-1.23940900	1.66848300
H	-5.96859900	-0.57124600	-0.48570700
N	0.02164100	1.63461000	-0.16524400
C	-0.57295600	2.70705100	0.64176000
H	-0.67766100	3.60533700	0.02257400
H	-1.57042900	2.41508600	0.98061400

H	0.02794300	2.95831600	1.52696200

Da

B3LYP/6-31G*

SCF Done: E(RB3LYP) = -1183.40715174

Zero-point correction= 0.317571

Thermal correction to Gibbs Free Energy= 0.270097

C	-1.14699300	2.62252400	0.72073000
C	-1.51951700	2.55459500	-0.75492600
H	-1.96950700	2.25355100	1.35392900
H	-0.96952500	3.66541700	1.00406700
H	-2.46359400	3.07263400	-0.94751200
H	-0.74823400	3.06194800	-1.34912900
P	0.06323600	0.22319400	0.67609900
O	-0.30539700	-0.67211400	1.82342800
C	1.70714100	-0.20261200	0.03568800
C	2.32628200	0.55978900	-0.96699500
C	2.35853600	-1.33294200	0.54943200
C	3.57972900	0.19178400	-1.45121900
H	1.83026300	1.44267400	-1.35968100
C	3.61414900	-1.69838000	0.06130700
H	1.87555600	-1.91233200	1.32997000
C	4.22333900	-0.93823000	-0.93792800
H	4.05578600	0.78477400	-2.22724500
H	4.11496600	-2.57511100	0.46226000
H	5.20079200	-1.22360300	-1.31756600
N	-1.03990600	0.10777400	-0.63760500
C	-1.67659600	1.14805200	-1.31429200
O	-2.33325700	0.94027800	-2.32157200
C	-1.25526700	-1.26432900	-1.18092900
H	-1.08426400	-1.21397600	-2.25901900
H	-0.49521200	-1.91781700	-0.74527500
C	-2.64234300	-1.84869600	-0.89498800
H	-3.40816700	-1.22976200	-1.37568100
H	-2.66958200	-2.83362500	-1.38004500
C	-2.97101000	-2.02856100	0.59277000
H	-3.07356600	-1.04573000	1.07682300
H	-3.94441800	-2.52876200	0.67631900
O	-2.01798900	-2.82816100	1.27013500
H	-1.34747400	-2.21169400	1.62468300
N	0.10345700	1.88525700	0.95128400
C	0.86053600	2.29705500	2.14121200
H	1.09289800	3.36412900	2.05882200
H	0.31032500	2.12021800	3.07539500

H	1.80478500	1.74761900	2.18654700

Ab

B3LYP/6-31G*

SCF Done: E(RB3LYP) = -1335.84501508

Zero-point correction= 0.340927

Thermal correction to Gibbs Free Energy= 0.290024

C	-1.99407100	-0.41207600	2.68099100
C	-1.17868400	-1.11392900	0.48953100
C	-3.26498100	-0.21971600	2.13398000
H	-1.80464600	-0.22338100	3.73286700
C	-2.49824200	-0.97746100	-0.05486800
C	-3.51731800	-0.49639700	0.79587300
H	-4.08002600	0.13348400	2.76139900
H	-4.51899200	-0.36138200	0.40354300
C	-0.96753800	-0.85439500	1.85373200
H	0.02095400	-1.00421100	2.27140600
C	-0.07909700	-1.62065700	-0.36793700
O	-0.27847700	-2.41617400	-1.29327500
C	2.28396100	-2.02927300	-0.79318100
C	3.63239000	-1.87215500	-0.08609500
H	2.36005000	-1.74451700	-1.85040600
H	1.94932000	-3.06726400	-0.76551700
C	4.17916200	-0.45145800	-0.26088000
H	4.34835300	-2.59193300	-0.49951000
H	3.50847000	-2.10774800	0.97692500
H	4.84074700	-0.16299300	0.56175000
H	4.72371000	-0.34863900	-1.20360600
N	1.24036100	-1.21772900	-0.11425500
O	3.10360200	0.51198100	-0.35824000
P	1.76395200	0.30746200	0.53737700
C	0.70193800	1.60533100	-0.12465600
C	0.17200800	2.54614500	0.76725200
C	0.43730200	1.71323900	-1.49756000
C	-0.62139800	3.58802600	0.28683400
H	0.38390300	2.45012900	1.82722200
C	-0.35653600	2.75533800	-1.97164400
H	0.85048100	0.98721300	-2.19163900
C	-0.88570200	3.69218500	-1.07968500
H	-1.03423900	4.31605300	0.97952500
H	-0.56259900	2.83749400	-3.03520700
H	-1.50516200	4.50384700	-1.45214100
O	1.95837400	0.34002400	2.01222400
N	-2.75286500	-1.27559100	-1.36956500

H	-2.05926000	-1.88056500	-1.79301600
C	-4.08420300	-1.27812000	-1.93426400
H	-4.01580800	-1.60058200	-2.97621300
H	-4.77564700	-1.95562300	-1.40792000
H	-4.52330400	-0.27247900	-1.92358600

Bb

B3LYP/6-31G*

SCF Done: E(RB3LYP) = -1335.80909524

Zero-point correction= 0.342315

Thermal correction to Gibbs Free Energy= 0.295451

C	1.23341200	3.23726100	0.02174400
C	0.60612300	2.31019700	-1.01067800
C	2.11077900	2.40996300	0.94646500
H	1.39406600	1.80261300	-1.58085000
H	-0.02633200	2.85976100	-1.70578100
H	1.83106600	4.00330400	-0.48939800
H	0.44701000	3.74552800	0.59133000
H	2.51004500	3.00429900	1.77690000
H	2.96790400	2.00225500	0.38721900
P	0.41622000	0.13354100	0.68728400
O	1.35530400	1.36035100	1.53067000
O	-0.12805000	-0.19772900	2.21087400
C	1.92173300	-0.63370800	-0.04078400
C	1.90968500	-1.06237300	-1.37675900
C	3.09868000	-0.76728100	0.70937500
C	3.05721600	-1.60825200	-1.95222600
H	0.99636200	-0.97621900	-1.95654700
C	4.23669800	-1.33998800	0.13922100
H	3.12105000	-0.41933200	1.73643200
C	4.22017600	-1.75532500	-1.19331000
H	3.03933400	-1.92588100	-2.99121500
H	5.13825400	-1.45295200	0.73519000
H	5.11033600	-2.19078900	-1.63928800
H	0.29912300	0.44533000	2.80820100
N	-0.27444400	1.26899600	-0.41670400
C	-1.64480600	1.39945600	-0.72126300
O	-2.05384500	2.40312500	-1.29829600
C	-2.53668000	0.28983000	-0.35098700
C	-2.04301400	-0.98363300	0.02540700
C	-3.91540700	0.51546800	-0.47923000
H	-4.22951200	1.50769500	-0.78476100
C	-2.99769700	-2.00374300	0.25113500
C	-4.35901600	-1.75765800	0.11925500
H	-5.05797800	-2.56900800	0.30837000
C	-4.83587800	-0.49332000	-0.24104000
H	-5.90103600	-0.30690700	-0.33809500
H	-2.67892100	-2.99550000	0.54209000

N	-0.67134500	-1.21125300	0.12603800
C	-0.29604400	-2.54957800	0.59582900
H	-0.72389700	-2.77978400	1.58031600
H	-0.63001500	-3.30500700	-0.12452300
H	0.78735300	-2.62659900	0.67088900

Cb

B3LYP/6-31G*

SCF Done: E(RB3LYP) = -1335.84355294

Zero-point correction= 0. 341772

Thermal correction to Gibbs Free Energy= 0. 292028

C	-0.44420700	3.89500100	-0.23098100
C	-1.41871700	1.67022600	0.00594800
C	0.62296600	3.51795200	0.58562500
H	-0.49579100	4.89933200	-0.64184300
C	-0.33221700	1.28848400	0.82665700
C	0.67874300	2.22390200	1.09508900
H	1.41852400	4.22180100	0.81485000
H	1.52566900	1.92286000	1.70336800
C	-1.43978000	2.97009100	-0.52273400
H	-2.26925200	3.22569800	-1.17337300
C	-2.56841100	0.78760100	-0.43157900
O	-3.18922600	1.03769700	-1.46303000
C	-3.61252700	-1.40227600	-0.17217900
C	-2.80988500	-2.16776300	-1.23992100
H	-4.54569200	-1.03865400	-0.60995600
H	-3.86853100	-2.06275600	0.66398200
C	-1.43253900	-2.65046600	-0.79502400
H	-2.69739300	-1.53543500	-2.12658000
H	-3.38705100	-3.05156300	-1.54544900
H	-1.02222800	-3.35232000	-1.52757500
H	-1.46306500	-3.15698300	0.17520000
N	-2.88446300	-0.26410300	0.37906000
O	-0.48946200	-1.54005600	-0.73145600
P	0.48227200	-1.33554500	0.54657300
C	2.01103200	-0.77084200	-0.23997800
C	3.22087500	-1.11120400	0.38353400
C	2.02589500	-0.01377000	-1.42149500
C	4.43266700	-0.68980100	-0.16457900
H	3.20448900	-1.72205300	1.28120800
C	3.24036900	0.40334900	-1.96456900
H	1.09425800	0.23739000	-1.91786600
C	4.44271200	0.06907900	-1.33629500
H	5.36754900	-0.96143800	0.31804600
H	3.24818400	0.98659500	-2.88127100
H	5.38711400	0.39446200	-1.76460700
O	0.64614200	-2.50995100	1.44819200
H	-2.18765600	-0.46978900	1.08723500

N	-0.23267400	-0.02936200	1.41800900
C	-0.03105600	-0.04906100	2.88333000
H	0.95213000	0.33107100	3.19041200
H	-0.80312500	0.57145800	3.34826600
H	-0.12740100	-1.07678300	3.23312900

Db

B3LYP/6-31G*

SCF Done: E(RB3LYP) = -1335.84439881

Zero-point correction= 0.341296

Thermal correction to Gibbs Free Energy= 0.290362

C	-4.67076800	-0.81178500	-0.52456200
C	-2.36089500	-0.04386800	-0.52016200
C	-4.34400200	-1.74760900	0.45909500
H	-5.68424400	-0.73909100	-0.90642300
C	-2.02915400	-0.99795800	0.46911400
C	-3.04616100	-1.84317400	0.95185200
H	-5.10574300	-2.41444200	0.85437600
H	-2.82997800	-2.57748300	1.71710200
C	-3.67567800	0.02954000	-1.00202400
H	-3.88067100	0.77439600	-1.76313900
C	-1.39220700	0.91940300	-1.09889400
O	-1.68879000	1.66474200	-2.02474600
C	0.81001500	2.01288200	-1.09385700
C	0.47708400	3.45005700	-0.68047000
H	0.77871200	1.91810000	-2.18175600
C	0.53254000	3.71683700	0.82896000
H	-0.50712800	3.72719600	-1.07288700
H	1.21799400	4.09097900	-1.17707000
H	0.37339000	4.78967400	0.99841300
H	-0.28668300	3.18732200	1.33611900
N	-0.11000800	0.97607900	-0.54100700
O	1.78514000	3.36872300	1.39623100
P	0.53294700	-0.00917600	0.68303600
C	1.89128900	-0.94929600	-0.06928700
C	1.68492300	-1.72752700	-1.21924000
C	3.16597300	-0.89169200	0.51120300
C	2.74318700	-2.43912800	-1.77998300
H	0.69962100	-1.77542600	-1.67557200
C	4.22348000	-1.60667000	-0.05383500
C	4.01264500	-2.37876100	-1.19698100
H	2.58026700	-3.03909800	-2.67093000
H	5.21023900	-1.55825800	0.39798700
H	4.83685200	-2.93380100	-1.63684400
O	1.00762400	0.70841400	1.90902800
H	1.68185100	2.46527100	1.75171700
H	1.82135100	1.76825600	-0.75893800
H	3.31593700	-0.28549000	1.39902200

N	-0.71322700	-1.13049500	0.93915000
C	-0.40972500	-2.16247200	1.94009600
H	-0.94139500	-1.97559600	2.87954800
H	-0.67988100	-3.15147500	1.55629600
H	0.66087400	-2.16018200	2.15017800

Ac

B3LYP/6-31G*

SCF Done: E(RB3LYP) = -1163.97119426

Zero-point correction= 0.277674

Thermal correction to Gibbs Free Energy= 0.232636

C	-0.28880300	2.72883100	-0.20192200
C	0.51654500	1.24187800	1.66950900
C	0.65960800	2.60275700	0.98341900
H	-0.12364800	3.64985400	-0.76537000
H	-1.33589700	2.70450100	0.12807900
H	1.19286900	1.15419900	2.51948400
H	-0.51098500	1.09699300	2.02636500
H	0.43473500	3.40042100	1.70274400
H	1.69451700	2.73430400	0.64867600
P	-0.02482500	0.10615700	-0.71023300
C	-1.72242600	-0.31240400	-0.23161400
C	-2.79237900	0.19928400	-0.98291400
C	-1.98118500	-1.20336200	0.81997400
C	-4.10128400	-0.17626300	-0.68289200
H	-2.59756700	0.88722700	-1.80048300
C	-3.29182800	-1.57694000	1.11635800
H	-1.15814500	-1.60032900	1.40745900
C	-4.35175400	-1.06376100	0.36600000
H	-4.92512900	0.22340000	-1.26755400
H	-3.48504000	-2.26684800	1.93300900
H	-5.37240800	-1.35476400	0.59886400
O	0.52901600	-0.74128700	-1.80305100
O	-0.07923800	1.65980500	-1.15564700
N	0.87028400	0.12831400	0.74997000
C	2.01591300	-0.62947900	1.09644200
C	2.46126000	-1.76433300	0.19461300
H	2.84605200	-2.54540300	0.85880200
H	1.64153900	-2.17203300	-0.39752500
C	3.60500200	-1.31153400	-0.74142700
H	4.46299500	-1.00311200	-0.13511800
H	3.91533700	-2.18234900	-1.34220700
O	2.63350400	-0.36552500	2.11465000
O	3.26859500	-0.20516700	-1.55129100
H	2.41414100	-0.40726900	-1.98206700

D3(BJ)-B3LYP/6-31G*

SCF Done: E(RB3LYP) = -1164.04984547

Zero-point correction= 0.277822

Thermal correction to Gibbs Free Energy= 0.233106

C	-0.28880300	2.72883100	-0.20192200
C	0.51654500	1.24187800	1.66950900
C	0.65960800	2.60275700	0.98341900
H	-0.12364800	3.64985400	-0.76537000
H	-1.33589700	2.70450100	0.12807900
H	1.19286900	1.15419900	2.51948400
H	-0.51098500	1.09699300	2.02636500
H	0.43473500	3.40042100	1.70274400
H	1.69451700	2.73430400	0.64867600
P	-0.02482500	0.10615700	-0.71023300
C	-1.72242600	-0.31240400	-0.23161400
C	-2.79237900	0.19928400	-0.98291400
C	-1.98118500	-1.20336200	0.81997400
C	-4.10128400	-0.17626300	-0.68289200
H	-2.59756700	0.88722700	-1.80048300
C	-3.29182800	-1.57694000	1.11635800
H	-1.15814500	-1.60032900	1.40745900
C	-4.35175400	-1.06376100	0.36600000
H	-4.92512900	0.22340000	-1.26755400
H	-3.48504000	-2.26684800	1.93300900
H	-5.37240800	-1.35476400	0.59886400
O	0.52901600	-0.74128700	-1.80305100
O	-0.07923800	1.65980500	-1.15564700
N	0.87028400	0.12831400	0.74997000
C	2.01591300	-0.62947900	1.09644200
C	2.46126000	-1.76433300	0.19461300
H	2.84605200	-2.54540300	0.85880200
H	1.64153900	-2.17203300	-0.39752500
C	3.60500200	-1.31153400	-0.74142700
H	4.46299500	-1.00311200	-0.13511800
H	3.91533700	-2.18234900	-1.34220700
O	2.63350400	-0.36552500	2.11465000
O	3.26859500	-0.20516700	-1.55129100
H	2.41414100	-0.40726900	-1.98206700

M06-2X/6-31G*

SCF Done: E(RM062X) = -1163.60197844

Zero-point correction= 0.280020

Thermal correction to Gibbs Free Energy= 0.236355

C	-0.28880300	2.72883100	-0.20192200
C	0.51654500	1.24187800	1.66950900
C	0.65960800	2.60275700	0.98341900
H	-0.12364800	3.64985400	-0.76537000
H	-1.33589700	2.70450100	0.12807900
H	1.19286900	1.15419900	2.51948400
H	-0.51098500	1.09699300	2.02636500
H	0.43473500	3.40042100	1.70274400
H	1.69451700	2.73430400	0.64867600
P	-0.02482500	0.10615700	-0.71023300
C	-1.72242600	-0.31240400	-0.23161400
C	-2.79237900	0.19928400	-0.98291400
C	-1.98118500	-1.20336200	0.81997400
C	-4.10128400	-0.17626300	-0.68289200
H	-2.59756700	0.88722700	-1.80048300
C	-3.29182800	-1.57694000	1.11635800
H	-1.15814500	-1.60032900	1.40745900
C	-4.35175400	-1.06376100	0.36600000
H	-4.92512900	0.22340000	-1.26755400
H	-3.48504000	-2.26684800	1.93300900
H	-5.37240800	-1.35476400	0.59886400
O	0.52901600	-0.74128700	-1.80305100
O	-0.07923800	1.65980500	-1.15564700
N	0.87028400	0.12831400	0.74997000
C	2.01591300	-0.62947900	1.09644200
C	2.46126000	-1.76433300	0.19461300
H	2.84605200	-2.54540300	0.85880200
H	1.64153900	-2.17203300	-0.39752500
C	3.60500200	-1.31153400	-0.74142700
H	4.46299500	-1.00311200	-0.13511800
H	3.91533700	-2.18234900	-1.34220700
O	2.63350400	-0.36552500	2.11465000
O	3.26859500	-0.20516700	-1.55129100
H	2.41414100	-0.40726900	-1.98206700

B3LYP/6-31G* with Solvent Correction

SCF Done: E(RB3LYP) = -1163.99381962

Zero-point correction= 0.277209

Thermal correction to Gibbs Free Energy= 0.231365

C	-0.28880300	2.72883100	-0.20192200
C	0.51654500	1.24187800	1.66950900
C	0.65960800	2.60275700	0.98341900
H	-0.12364800	3.64985400	-0.76537000
H	-1.33589700	2.70450100	0.12807900
H	1.19286900	1.15419900	2.51948400
H	-0.51098500	1.09699300	2.02636500
H	0.43473500	3.40042100	1.70274400
H	1.69451700	2.73430400	0.64867600
P	-0.02482500	0.10615700	-0.71023300
C	-1.72242600	-0.31240400	-0.23161400
C	-2.79237900	0.19928400	-0.98291400
C	-1.98118500	-1.20336200	0.81997400
C	-4.10128400	-0.17626300	-0.68289200
H	-2.59756700	0.88722700	-1.80048300
C	-3.29182800	-1.57694000	1.11635800
H	-1.15814500	-1.60032900	1.40745900
C	-4.35175400	-1.06376100	0.36600000
H	-4.92512900	0.22340000	-1.26755400
H	-3.48504000	-2.26684800	1.93300900
H	-5.37240800	-1.35476400	0.59886400
O	0.52901600	-0.74128700	-1.80305100
O	-0.07923800	1.65980500	-1.15564700
N	0.87028400	0.12831400	0.74997000
C	2.01591300	-0.62947900	1.09644200
C	2.46126000	-1.76433300	0.19461300
H	2.84605200	-2.54540300	0.85880200
H	1.64153900	-2.17203300	-0.39752500
C	3.60500200	-1.31153400	-0.74142700
H	4.46299500	-1.00311200	-0.13511800
H	3.91533700	-2.18234900	-1.34220700
O	2.63350400	-0.36552500	2.11465000
O	3.26859500	-0.20516700	-1.55129100
H	2.41414100	-0.40726900	-1.98206700

PBE0/def2-TZVPP

SCF Done: E(RPBE1PBE) = -1163.27640987

Zero-point correction= 0.275841
Thermal correction to Gibbs Free Energy= 0.233244

C	-0.28880300	2.72883100	-0.20192200
C	0.51654500	1.24187800	1.66950900
C	0.65960800	2.60275700	0.98341900
H	-0.12364800	3.64985400	-0.76537000
H	-1.33589700	2.70450100	0.12807900
H	1.19286900	1.15419900	2.51948400
H	-0.51098500	1.09699300	2.02636500
H	0.43473500	3.40042100	1.70274400
H	1.69451700	2.73430400	0.64867600
P	-0.02482500	0.10615700	-0.71023300
C	-1.72242600	-0.31240400	-0.23161400
C	-2.79237900	0.19928400	-0.98291400
C	-1.98118500	-1.20336200	0.81997400
C	-4.10128400	-0.17626300	-0.68289200
H	-2.59756700	0.88722700	-1.80048300
C	-3.29182800	-1.57694000	1.11635800
H	-1.15814500	-1.60032900	1.40745900
C	-4.35175400	-1.06376100	0.36600000
H	-4.92512900	0.22340000	-1.26755400
H	-3.48504000	-2.26684800	1.93300900
H	-5.37240800	-1.35476400	0.59886400
O	0.52901600	-0.74128700	-1.80305100
O	-0.07923800	1.65980500	-1.15564700
N	0.87028400	0.12831400	0.74997000
C	2.01591300	-0.62947900	1.09644200
C	2.46126000	-1.76433300	0.19461300
H	2.84605200	-2.54540300	0.85880200
H	1.64153900	-2.17203300	-0.39752500
C	3.60500200	-1.31153400	-0.74142700
H	4.46299500	-1.00311200	-0.13511800
H	3.91533700	-2.18234900	-1.34220700
O	2.63350400	-0.36552500	2.11465000
O	3.26859500	-0.20516700	-1.55129100
H	2.41414100	-0.40726900	-1.98206700

Bc

B3LYP/6-31G*

SCF Done: E(RB3LYP) = -1163.94822354

Zero-point correction= 0.277921

Thermal correction to Gibbs Free Energy= 0.235153

C	-0.86394900	2.84050500	-0.49693100
C	-1.11726900	1.58722100	-1.32826200
C	0.30313700	2.59760300	0.45041900
H	-0.24044100	1.36881700	-1.95271400
H	-1.97666900	1.70112000	-1.98960900
H	-0.64018000	3.68279900	-1.16464800
H	-1.76391400	3.09445300	0.07562100
H	0.46039300	3.44729200	1.12492000
H	1.23162700	2.45402200	-0.12355100
P	-0.23384200	-0.15292500	0.67986300
O	0.04959600	1.46877600	1.27559700
O	-0.70181300	-0.46655800	2.22486500
C	1.49247000	-0.33521400	0.07845400
C	1.76686400	-1.02693000	-1.11165500
C	2.55793300	0.20852900	0.81142800
C	3.07907200	-1.15528400	-1.56617000
H	0.95267500	-1.47201000	-1.67147900
C	3.87215500	0.04996500	0.37054800
H	2.35471300	0.75351600	1.72638500
C	4.13478500	-0.62408900	-0.82292000
H	3.27671300	-1.68199900	-2.49587300
H	4.68942000	0.46047000	0.95743200
H	5.15793000	-0.73623300	-1.17192300
H	-0.66000500	0.38018900	2.70626600
N	-1.41309200	0.40795900	-0.48255600
C	-2.60718700	-0.27435200	-0.73589700
C	-2.93439200	-1.38085600	0.25115200
H	-3.84428600	-1.87669200	-0.09400100
H	-3.14845900	-0.91271300	1.21900000
C	-1.78174100	-2.38514600	0.41042600
H	-1.83351500	-3.14443700	-0.37836700
H	-1.85949300	-2.89244100	1.37937800
O	-0.50536700	-1.77530300	0.28513700
O	-3.36348000	0.04812100	-1.63940400

D3(BJ)-B3LYP/6-31G*

SCF Done: E(RB3LYP) = -1164.02921690

Zero-point correction= 0.278052

Thermal correction to Gibbs Free Energy= 0.235472

C	-0.86394900	2.84050500	-0.49693100
C	-1.11726900	1.58722100	-1.32826200
C	0.30313700	2.59760300	0.45041900
H	-0.24044100	1.36881700	-1.95271400
H	-1.97666900	1.70112000	-1.98960900
H	-0.64018000	3.68279900	-1.16464800
H	-1.76391400	3.09445300	0.07562100
H	0.46039300	3.44729200	1.12492000
H	1.23162700	2.45402200	-0.12355100
P	-0.23384200	-0.15292500	0.67986300
O	0.04959600	1.46877600	1.27559700
O	-0.70181300	-0.46655800	2.22486500
C	1.49247000	-0.33521400	0.07845400
C	1.76686400	-1.02693000	-1.11165500
C	2.55793300	0.20852900	0.81142800
C	3.07907200	-1.15528400	-1.56617000
H	0.95267500	-1.47201000	-1.67147900
C	3.87215500	0.04996500	0.37054800
H	2.35471300	0.75351600	1.72638500
C	4.13478500	-0.62408900	-0.82292000
H	3.27671300	-1.68199900	-2.49587300
H	4.68942000	0.46047000	0.95743200
H	5.15793000	-0.73623300	-1.17192300
H	-0.66000500	0.38018900	2.70626600
N	-1.41309200	0.40795900	-0.48255600
C	-2.60718700	-0.27435200	-0.73589700
C	-2.93439200	-1.38085600	0.25115200
H	-3.84428600	-1.87669200	-0.09400100
H	-3.14845900	-0.91271300	1.21900000
C	-1.78174100	-2.38514600	0.41042600
H	-1.83351500	-3.14443700	-0.37836700
H	-1.85949300	-2.89244100	1.37937800
O	-0.50536700	-1.77530300	0.28513700
O	-3.36348000	0.04812100	-1.63940400

M06-2X/6-31G*

SCF Done: E(RM062X) = -1163.58756334

Zero-point correction= 0.280414
Thermal correction to Gibbs Free Energy= 0.238625

C	-0.86394900	2.84050500	-0.49693100
C	-1.11726900	1.58722100	-1.32826200
C	0.30313700	2.59760300	0.45041900
H	-0.24044100	1.36881700	-1.95271400
H	-1.97666900	1.70112000	-1.98960900
H	-0.64018000	3.68279900	-1.16464800
H	-1.76391400	3.09445300	0.07562100
H	0.46039300	3.44729200	1.12492000
H	1.23162700	2.45402200	-0.12355100
P	-0.23384200	-0.15292500	0.67986300
O	0.04959600	1.46877600	1.27559700
O	-0.70181300	-0.46655800	2.22486500
C	1.49247000	-0.33521400	0.07845400
C	1.76686400	-1.02693000	-1.11165500
C	2.55793300	0.20852900	0.81142800
C	3.07907200	-1.15528400	-1.56617000
H	0.95267500	-1.47201000	-1.67147900
C	3.87215500	0.04996500	0.37054800
H	2.35471300	0.75351600	1.72638500
C	4.13478500	-0.62408900	-0.82292000
H	3.27671300	-1.68199900	-2.49587300
H	4.68942000	0.46047000	0.95743200
H	5.15793000	-0.73623300	-1.17192300
H	-0.66000500	0.38018900	2.70626600
N	-1.41309200	0.40795900	-0.48255600
C	-2.60718700	-0.27435200	-0.73589700
C	-2.93439200	-1.38085600	0.25115200
H	-3.84428600	-1.87669200	-0.09400100
H	-3.14845900	-0.91271300	1.21900000
C	-1.78174100	-2.38514600	0.41042600
H	-1.83351500	-3.14443700	-0.37836700
H	-1.85949300	-2.89244100	1.37937800
O	-0.50536700	-1.77530300	0.28513700
O	-3.36348000	0.04812100	-1.63940400

B3LYP/6-31G* with Solvent Corrections

SCF Done: E(RB3LYP) = -1163.96706351

Zero-point correction= 0.277443

Thermal correction to Gibbs Free Energy= 0.234360

C	-0.86394900	2.84050500	-0.49693100
C	-1.11726900	1.58722100	-1.32826200
C	0.30313700	2.59760300	0.45041900
H	-0.24044100	1.36881700	-1.95271400
H	-1.97666900	1.70112000	-1.98960900
H	-0.64018000	3.68279900	-1.16464800
H	-1.76391400	3.09445300	0.07562100
H	0.46039300	3.44729200	1.12492000
H	1.23162700	2.45402200	-0.12355100
P	-0.23384200	-0.15292500	0.67986300
O	0.04959600	1.46877600	1.27559700
O	-0.70181300	-0.46655800	2.22486500
C	1.49247000	-0.33521400	0.07845400
C	1.76686400	-1.02693000	-1.11165500
C	2.55793300	0.20852900	0.81142800
C	3.07907200	-1.15528400	-1.56617000
H	0.95267500	-1.47201000	-1.67147900
C	3.87215500	0.04996500	0.37054800
H	2.35471300	0.75351600	1.72638500
C	4.13478500	-0.62408900	-0.82292000
H	3.27671300	-1.68199900	-2.49587300
H	4.68942000	0.46047000	0.95743200
H	5.15793000	-0.73623300	-1.17192300
H	-0.66000500	0.38018900	2.70626600
N	-1.41309200	0.40795900	-0.48255600
C	-2.60718700	-0.27435200	-0.73589700
C	-2.93439200	-1.38085600	0.25115200
H	-3.84428600	-1.87669200	-0.09400100
H	-3.14845900	-0.91271300	1.21900000
C	-1.78174100	-2.38514600	0.41042600
H	-1.83351500	-3.14443700	-0.37836700
H	-1.85949300	-2.89244100	1.37937800
O	-0.50536700	-1.77530300	0.28513700
O	-3.36348000	0.04812100	-1.63940400

PBE0/def2-TZVPP

SCF Done: E(RPBE1PBE) = -1163.25665358

Zero-point correction= 0.276233
Thermal correction to Gibbs Free Energy= 0.235258

C	-0.86394900	2.84050500	-0.49693100
C	-1.11726900	1.58722100	-1.32826200
C	0.30313700	2.59760300	0.45041900
H	-0.24044100	1.36881700	-1.95271400
H	-1.97666900	1.70112000	-1.98960900
H	-0.64018000	3.68279900	-1.16464800
H	-1.76391400	3.09445300	0.07562100
H	0.46039300	3.44729200	1.12492000
H	1.23162700	2.45402200	-0.12355100
P	-0.23384200	-0.15292500	0.67986300
O	0.04959600	1.46877600	1.27559700
O	-0.70181300	-0.46655800	2.22486500
C	1.49247000	-0.33521400	0.07845400
C	1.76686400	-1.02693000	-1.11165500
C	2.55793300	0.20852900	0.81142800
C	3.07907200	-1.15528400	-1.56617000
H	0.95267500	-1.47201000	-1.67147900
C	3.87215500	0.04996500	0.37054800
H	2.35471300	0.75351600	1.72638500
C	4.13478500	-0.62408900	-0.82292000
H	3.27671300	-1.68199900	-2.49587300
H	4.68942000	0.46047000	0.95743200
H	5.15793000	-0.73623300	-1.17192300
H	-0.66000500	0.38018900	2.70626600
N	-1.41309200	0.40795900	-0.48255600
C	-2.60718700	-0.27435200	-0.73589700
C	-2.93439200	-1.38085600	0.25115200
H	-3.84428600	-1.87669200	-0.09400100
H	-3.14845900	-0.91271300	1.21900000
C	-1.78174100	-2.38514600	0.41042600
H	-1.83351500	-3.14443700	-0.37836700
H	-1.85949300	-2.89244100	1.37937800
O	-0.50536700	-1.77530300	0.28513700
O	-3.36348000	0.04812100	-1.63940400

Cc

B3LYP/6-31G*

SCF Done: E(RB3LYP) = -1163.99524323

Zero-point correction= 0.278444

Thermal correction to Gibbs Free Energy= 0.233588

P	-0.37598600	0.17346300	0.33716400
O	0.34502700	-0.64514300	-0.86256500
O	-0.08304900	1.69320300	-0.09324900
C	0.79979700	-2.01720300	-0.69488100
H	0.28899100	-2.59386100	-1.47174900
H	0.48268900	-2.39248900	0.28412800
C	2.31533900	-2.11599100	-0.86774200
H	2.55737200	-3.15713700	-1.12270000
H	2.61138700	-1.49853100	-1.72160700
C	3.15250800	-1.71769000	0.36341700
H	4.21269300	-1.74612000	0.09652300
H	2.99273100	-2.43057800	1.17964800
N	2.84051000	-0.39045500	0.88439600
H	2.04774800	-0.33675400	1.52169000
C	3.09594100	0.71224300	0.12597000
C	1.19517100	2.28083100	-0.44629100
H	0.98145800	3.35137900	-0.46523700
H	1.46459100	1.95586700	-1.45560100
C	2.35123500	1.98812900	0.52523100
H	1.98102000	1.97198900	1.55521600
H	3.06986200	2.80895600	0.43086300
O	3.83396800	0.70220200	-0.85603800
O	0.05545500	-0.25183400	1.70388700
C	-2.15707800	0.06168700	0.09235200
C	-2.74922000	0.38501400	-1.13785700
C	-2.95365600	-0.38212900	1.15597300
C	-4.12786600	0.26515900	-1.29819100
H	-2.13353700	0.73176200	-1.96249800
C	-4.33439000	-0.49981500	0.99004400
H	-2.48400100	-0.62703800	2.10339200
C	-4.92037500	-0.17704200	-0.23467600
H	-4.58578500	0.51755400	-2.25061700
H	-4.95095900	-0.84158700	1.81676800
H	-5.99569500	-0.26874400	-0.36282300

D3(BJ)-B3LYP/6-31G*

SCF Done: E(RB3LYP) = -1164.07192846

Zero-point correction= 0.278602

Thermal correction to Gibbs Free Energy= 0.234225

P	-0.37598600	0.17346300	0.33716400
O	0.34502700	-0.64514300	-0.86256500
O	-0.08304900	1.69320300	-0.09324900
C	0.79979700	-2.01720300	-0.69488100
H	0.28899100	-2.59386100	-1.47174900
H	0.48268900	-2.39248900	0.28412800
C	2.31533900	-2.11599100	-0.86774200
H	2.55737200	-3.15713700	-1.12270000
H	2.61138700	-1.49853100	-1.72160700
C	3.15250800	-1.71769000	0.36341700
H	4.21269300	-1.74612000	0.09652300
H	2.99273100	-2.43057800	1.17964800
N	2.84051000	-0.39045500	0.88439600
H	2.04774800	-0.33675400	1.52169000
C	3.09594100	0.71224300	0.12597000
C	1.19517100	2.28083100	-0.44629100
H	0.98145800	3.35137900	-0.46523700
H	1.46459100	1.95586700	-1.45560100
C	2.35123500	1.98812900	0.52523100
H	1.98102000	1.97198900	1.55521600
H	3.06986200	2.80895600	0.43086300
O	3.83396800	0.70220200	-0.85603800
O	0.05545500	-0.25183400	1.70388700
C	-2.15707800	0.06168700	0.09235200
C	-2.74922000	0.38501400	-1.13785700
C	-2.95365600	-0.38212900	1.15597300
C	-4.12786600	0.26515900	-1.29819100
H	-2.13353700	0.73176200	-1.96249800
C	-4.33439000	-0.49981500	0.99004400
H	-2.48400100	-0.62703800	2.10339200
C	-4.92037500	-0.17704200	-0.23467600
H	-4.58578500	0.51755400	-2.25061700
H	-4.95095900	-0.84158700	1.81676800
H	-5.99569500	-0.26874400	-0.36282300

M06-2X/6-31G*

SCF Done: E(RM062X) = -1163.62548505

Zero-point correction= 0.280708

Thermal correction to Gibbs Free Energy= 0.237488

P	-0.37598600	0.17346300	0.33716400
O	0.34502700	-0.64514300	-0.86256500
O	-0.08304900	1.69320300	-0.09324900
C	0.79979700	-2.01720300	-0.69488100
H	0.28899100	-2.59386100	-1.47174900
H	0.48268900	-2.39248900	0.28412800
C	2.31533900	-2.11599100	-0.86774200
H	2.55737200	-3.15713700	-1.12270000
H	2.61138700	-1.49853100	-1.72160700
C	3.15250800	-1.71769000	0.36341700
H	4.21269300	-1.74612000	0.09652300
H	2.99273100	-2.43057800	1.17964800
N	2.84051000	-0.39045500	0.88439600
H	2.04774800	-0.33675400	1.52169000
C	3.09594100	0.71224300	0.12597000
C	1.19517100	2.28083100	-0.44629100
H	0.98145800	3.35137900	-0.46523700
H	1.46459100	1.95586700	-1.45560100
C	2.35123500	1.98812900	0.52523100
H	1.98102000	1.97198900	1.55521600
H	3.06986200	2.80895600	0.43086300
O	3.83396800	0.70220200	-0.85603800
O	0.05545500	-0.25183400	1.70388700
C	-2.15707800	0.06168700	0.09235200
C	-2.74922000	0.38501400	-1.13785700
C	-2.95365600	-0.38212900	1.15597300
C	-4.12786600	0.26515900	-1.29819100
H	-2.13353700	0.73176200	-1.96249800
C	-4.33439000	-0.49981500	0.99004400
H	-2.48400100	-0.62703800	2.10339200
C	-4.92037500	-0.17704200	-0.23467600
H	-4.58578500	0.51755400	-2.25061700
H	-4.95095900	-0.84158700	1.81676800
H	-5.99569500	-0.26874400	-0.36282300

B3LYP/6-31G* with Solvent Corrections

SCF Done: E(RB3LYP) = -1164.01581019

Zero-point correction= 0.277976

Thermal correction to Gibbs Free Energy= 0.234931

P	-0.37598600	0.17346300	0.33716400
O	0.34502700	-0.64514300	-0.86256500
O	-0.08304900	1.69320300	-0.09324900
C	0.79979700	-2.01720300	-0.69488100
H	0.28899100	-2.59386100	-1.47174900
H	0.48268900	-2.39248900	0.28412800
C	2.31533900	-2.11599100	-0.86774200
H	2.55737200	-3.15713700	-1.12270000
H	2.61138700	-1.49853100	-1.72160700
C	3.15250800	-1.71769000	0.36341700
H	4.21269300	-1.74612000	0.09652300
H	2.99273100	-2.43057800	1.17964800
N	2.84051000	-0.39045500	0.88439600
H	2.04774800	-0.33675400	1.52169000
C	3.09594100	0.71224300	0.12597000
C	1.19517100	2.28083100	-0.44629100
H	0.98145800	3.35137900	-0.46523700
H	1.46459100	1.95586700	-1.45560100
C	2.35123500	1.98812900	0.52523100
H	1.98102000	1.97198900	1.55521600
H	3.06986200	2.80895600	0.43086300
O	3.83396800	0.70220200	-0.85603800
O	0.05545500	-0.25183400	1.70388700
C	-2.15707800	0.06168700	0.09235200
C	-2.74922000	0.38501400	-1.13785700
C	-2.95365600	-0.38212900	1.15597300
C	-4.12786600	0.26515900	-1.29819100
H	-2.13353700	0.73176200	-1.96249800
C	-4.33439000	-0.49981500	0.99004400
H	-2.48400100	-0.62703800	2.10339200
C	-4.92037500	-0.17704200	-0.23467600
H	-4.58578500	0.51755400	-2.25061700
H	-4.95095900	-0.84158700	1.81676800
H	-5.99569500	-0.26874400	-0.36282300

PBE0/def2-TZVPP

SCF Done: E(RPBE1PBE) = -1163.29730696

Zero-point correction= 0.276557

Thermal correction to Gibbs Free Energy= 0.234336

P	-0.37598600	0.17346300	0.33716400
O	0.34502700	-0.64514300	-0.86256500
O	-0.08304900	1.69320300	-0.09324900
C	0.79979700	-2.01720300	-0.69488100
H	0.28899100	-2.59386100	-1.47174900
H	0.48268900	-2.39248900	0.28412800
C	2.31533900	-2.11599100	-0.86774200
H	2.55737200	-3.15713700	-1.12270000
H	2.61138700	-1.49853100	-1.72160700
C	3.15250800	-1.71769000	0.36341700
H	4.21269300	-1.74612000	0.09652300
H	2.99273100	-2.43057800	1.17964800
N	2.84051000	-0.39045500	0.88439600
H	2.04774800	-0.33675400	1.52169000
C	3.09594100	0.71224300	0.12597000
C	1.19517100	2.28083100	-0.44629100
H	0.98145800	3.35137900	-0.46523700
H	1.46459100	1.95586700	-1.45560100
C	2.35123500	1.98812900	0.52523100
H	1.98102000	1.97198900	1.55521600
H	3.06986200	2.80895600	0.43086300
O	3.83396800	0.70220200	-0.85603800
O	0.05545500	-0.25183400	1.70388700
C	-2.15707800	0.06168700	0.09235200
C	-2.74922000	0.38501400	-1.13785700
C	-2.95365600	-0.38212900	1.15597300
C	-4.12786600	0.26515900	-1.29819100
H	-2.13353700	0.73176200	-1.96249800
C	-4.33439000	-0.49981500	0.99004400
H	-2.48400100	-0.62703800	2.10339200
C	-4.92037500	-0.17704200	-0.23467600
H	-4.58578500	0.51755400	-2.25061700
H	-4.95095900	-0.84158700	1.81676800
H	-5.99569500	-0.26874400	-0.36282300

Dc

B3LYP/6-31G*

SCF Done: E(RB3LYP) = -1163.97767018

Zero-point correction= 0.277095

Thermal correction to Gibbs Free Energy= 0.231306

C	-1.16525700	-2.29020000	-1.56740800
C	-1.57598100	-2.67366500	-0.15597800
H	-1.91473500	-1.65766700	-2.05704800
H	-0.99046500	-3.16690800	-2.19370500
H	-2.55152600	-3.16957800	-0.14792500
H	-0.85180900	-3.38824200	0.25611300
P	0.09319600	-0.11632700	-0.84592600
O	-0.29033900	1.02168600	-1.73231000
C	1.76234400	0.04404800	-0.18638900
C	2.30041000	-0.90566000	0.69534000
C	2.52905600	1.15195500	-0.57293100
C	3.59455300	-0.74617200	1.18454300
H	1.71076400	-1.76634300	0.99797900
C	3.82493100	1.30721300	-0.07928600
H	2.10374100	1.87912700	-1.25717200
C	4.35629400	0.36047900	0.79747300
H	4.00978000	-1.48234500	1.86696700
H	4.41741700	2.16666000	-0.37961100
H	5.36526000	0.48314800	1.18184300
O	0.09949900	-1.59091500	-1.50523300
N	-0.98601800	-0.32620300	0.47629700
C	-1.67111100	-1.49569200	0.81131000
O	-2.32242300	-1.57911000	1.83864200
C	-1.15998300	0.83743100	1.39117100
H	-0.99121400	0.47567300	2.40853800
H	-0.37709700	1.56260300	1.15345700
C	-2.52628500	1.52374400	1.29616200
H	-3.31257800	0.82246200	1.59726600
H	-2.51661800	2.33658800	2.03439800
C	-2.85305800	2.11688200	-0.08043200
H	-2.99941500	1.30958300	-0.81325400
H	-3.80448600	2.65940500	-0.00916600
O	-1.86722300	3.03137300	-0.52722900
H	-1.24442300	2.51769800	-1.07628300

D3(BJ)-B3LYP/6-31G*

SCF Done: E(RB3LYP) = -1164.05512395

Zero-point correction= 0.277245

Thermal correction to Gibbs Free Energy= 0.231923

C	-1.16525700	-2.29020000	-1.56740800
C	-1.57598100	-2.67366500	-0.15597800
H	-1.91473500	-1.65766700	-2.05704800
H	-0.99046500	-3.16690800	-2.19370500
H	-2.55152600	-3.16957800	-0.14792500
H	-0.85180900	-3.38824200	0.25611300
P	0.09319600	-0.11632700	-0.84592600
O	-0.29033900	1.02168600	-1.73231000
C	1.76234400	0.04404800	-0.18638900
C	2.30041000	-0.90566000	0.69534000
C	2.52905600	1.15195500	-0.57293100
C	3.59455300	-0.74617200	1.18454300
H	1.71076400	-1.76634300	0.99797900
C	3.82493100	1.30721300	-0.07928600
H	2.10374100	1.87912700	-1.25717200
C	4.35629400	0.36047900	0.79747300
H	4.00978000	-1.48234500	1.86696700
H	4.41741700	2.16666000	-0.37961100
H	5.36526000	0.48314800	1.18184300
O	0.09949900	-1.59091500	-1.50523300
N	-0.98601800	-0.32620300	0.47629700
C	-1.67111100	-1.49569200	0.81131000
O	-2.32242300	-1.57911000	1.83864200
C	-1.15998300	0.83743100	1.39117100
H	-0.99121400	0.47567300	2.40853800
H	-0.37709700	1.56260300	1.15345700
C	-2.52628500	1.52374400	1.29616200
H	-3.31257800	0.82246200	1.59726600
H	-2.51661800	2.33658800	2.03439800
C	-2.85305800	2.11688200	-0.08043200
H	-2.99941500	1.30958300	-0.81325400
H	-3.80448600	2.65940500	-0.00916600
O	-1.86722300	3.03137300	-0.52722900
H	-1.24442300	2.51769800	-1.07628300

M06-2X/6-31G*

SCF Done: E(RM062X) = -1163.60832332

Zero-point correction= 0.279449
Thermal correction to Gibbs Free Energy= 0.235520

C	-1.16525700	-2.29020000	-1.56740800
C	-1.57598100	-2.67366500	-0.15597800
H	-1.91473500	-1.65766700	-2.05704800
H	-0.99046500	-3.16690800	-2.19370500
H	-2.55152600	-3.16957800	-0.14792500
H	-0.85180900	-3.38824200	0.25611300
P	0.09319600	-0.11632700	-0.84592600
O	-0.29033900	1.02168600	-1.73231000
C	1.76234400	0.04404800	-0.18638900
C	2.30041000	-0.90566000	0.69534000
C	2.52905600	1.15195500	-0.57293100
C	3.59455300	-0.74617200	1.18454300
H	1.71076400	-1.76634300	0.99797900
C	3.82493100	1.30721300	-0.07928600
H	2.10374100	1.87912700	-1.25717200
C	4.35629400	0.36047900	0.79747300
H	4.00978000	-1.48234500	1.86696700
H	4.41741700	2.16666000	-0.37961100
H	5.36526000	0.48314800	1.18184300
O	0.09949900	-1.59091500	-1.50523300
N	-0.98601800	-0.32620300	0.47629700
C	-1.67111100	-1.49569200	0.81131000
O	-2.32242300	-1.57911000	1.83864200
C	-1.15998300	0.83743100	1.39117100
H	-0.99121400	0.47567300	2.40853800
H	-0.37709700	1.56260300	1.15345700
C	-2.52628500	1.52374400	1.29616200
H	-3.31257800	0.82246200	1.59726600
H	-2.51661800	2.33658800	2.03439800
C	-2.85305800	2.11688200	-0.08043200
H	-2.99941500	1.30958300	-0.81325400
H	-3.80448600	2.65940500	-0.00916600
O	-1.86722300	3.03137300	-0.52722900
H	-1.24442300	2.51769800	-1.07628300

B3LYP/6-31G* with Solvent Corrections

SCF Done: E(RB3LYP) = -1164.00067701

Zero-point correction= 0.276752

Thermal correction to Gibbs Free Energy= 0.230396

C	-1.16525700	-2.29020000	-1.56740800
C	-1.57598100	-2.67366500	-0.15597800
H	-1.91473500	-1.65766700	-2.05704800
H	-0.99046500	-3.16690800	-2.19370500
H	-2.55152600	-3.16957800	-0.14792500
H	-0.85180900	-3.38824200	0.25611300
P	0.09319600	-0.11632700	-0.84592600
O	-0.29033900	1.02168600	-1.73231000
C	1.76234400	0.04404800	-0.18638900
C	2.30041000	-0.90566000	0.69534000
C	2.52905600	1.15195500	-0.57293100
C	3.59455300	-0.74617200	1.18454300
H	1.71076400	-1.76634300	0.99797900
C	3.82493100	1.30721300	-0.07928600
H	2.10374100	1.87912700	-1.25717200
C	4.35629400	0.36047900	0.79747300
H	4.00978000	-1.48234500	1.86696700
H	4.41741700	2.16666000	-0.37961100
H	5.36526000	0.48314800	1.18184300
O	0.09949900	-1.59091500	-1.50523300
N	-0.98601800	-0.32620300	0.47629700
C	-1.67111100	-1.49569200	0.81131000
O	-2.32242300	-1.57911000	1.83864200
C	-1.15998300	0.83743100	1.39117100
H	-0.99121400	0.47567300	2.40853800
H	-0.37709700	1.56260300	1.15345700
C	-2.52628500	1.52374400	1.29616200
H	-3.31257800	0.82246200	1.59726600
H	-2.51661800	2.33658800	2.03439800
C	-2.85305800	2.11688200	-0.08043200
H	-2.99941500	1.30958300	-0.81325400
H	-3.80448600	2.65940500	-0.00916600
O	-1.86722300	3.03137300	-0.52722900
H	-1.24442300	2.51769800	-1.07628300

PBE0/def2-TZVPP

SCF Done: E(RPBE1PBE) = -1163.28417018

Zero-point correction= 0.275535

Thermal correction to Gibbs Free Energy= 0.232702

C	-1.16525700	-2.29020000	-1.56740800
C	-1.57598100	-2.67366500	-0.15597800
H	-1.91473500	-1.65766700	-2.05704800
H	-0.99046500	-3.16690800	-2.19370500
H	-2.55152600	-3.16957800	-0.14792500
H	-0.85180900	-3.38824200	0.25611300
P	0.09319600	-0.11632700	-0.84592600
O	-0.29033900	1.02168600	-1.73231000
C	1.76234400	0.04404800	-0.18638900
C	2.30041000	-0.90566000	0.69534000
C	2.52905600	1.15195500	-0.57293100
C	3.59455300	-0.74617200	1.18454300
H	1.71076400	-1.76634300	0.99797900
C	3.82493100	1.30721300	-0.07928600
H	2.10374100	1.87912700	-1.25717200
C	4.35629400	0.36047900	0.79747300
H	4.00978000	-1.48234500	1.86696700
H	4.41741700	2.16666000	-0.37961100
H	5.36526000	0.48314800	1.18184300
O	0.09949900	-1.59091500	-1.50523300
N	-0.98601800	-0.32620300	0.47629700
C	-1.67111100	-1.49569200	0.81131000
O	-2.32242300	-1.57911000	1.83864200
C	-1.15998300	0.83743100	1.39117100
H	-0.99121400	0.47567300	2.40853800
H	-0.37709700	1.56260300	1.15345700
C	-2.52628500	1.52374400	1.29616200
H	-3.31257800	0.82246200	1.59726600
H	-2.51661800	2.33658800	2.03439800
C	-2.85305800	2.11688200	-0.08043200
H	-2.99941500	1.30958300	-0.81325400
H	-3.80448600	2.65940500	-0.00916600
O	-1.86722300	3.03137300	-0.52722900
H	-1.24442300	2.51769800	-1.07628300

Ad

B3LYP/6-31G*

SCF Done: E(RB3LYP) = -1316.40558180

Zero-point correction= 0.300406

Thermal correction to Gibbs Free Energy= 0.252149

C	-2.59531000	-0.64550400	2.13837400
C	-1.36523800	-1.27172100	0.13012700
C	-3.79198100	-0.67286500	1.41014700
H	-2.59834300	-0.40052700	3.19591700
C	-2.59755800	-1.36639600	-0.57833700
C	-3.79578700	-1.02972100	0.06913700
H	-4.73220900	-0.43385300	1.90075700
H	-4.71605200	-1.08813900	-0.50319600
C	-1.39895600	-0.94196900	1.50006200
H	-0.47642200	-0.92648500	2.06878300
C	-0.11989900	-1.60531600	-0.59505900
O	-0.15188600	-2.31238800	-1.61822000
C	2.29109500	-1.87103400	-0.74455400
C	3.52378500	-1.72574100	0.15096100
H	2.48952000	-1.48754700	-1.75306800
H	2.01004100	-2.91965900	-0.84961300
C	4.01994500	-0.27624800	0.16591500
H	3.27071500	-2.05665600	1.16446000
H	4.32113200	-2.38121300	-0.21758600
H	4.54120900	-0.02940600	1.09562900
H	4.68582600	-0.07389700	-0.67717900
N	1.12551500	-1.16606900	-0.14359800
O	2.91983400	0.64848600	-0.01499500
P	1.48727600	0.33180000	0.67463100
C	0.45473400	1.62358000	-0.03954600
C	0.34258600	1.79474000	-1.42713500
C	-0.21458200	2.49319000	0.83093300
C	-0.43980000	2.82816000	-1.93756000
H	0.86356800	1.12428100	-2.10450400
C	-0.99467800	3.52756000	0.31397000
H	-0.11941100	2.34952500	1.90242800
C	-1.10820000	3.69371900	-1.06716500
H	-0.52950100	2.95838600	-3.01227400
H	-1.51548300	4.20054900	0.98919500
H	-1.71913400	4.49796800	-1.46825100
O	1.47982600	0.25913600	2.16073400
O	-2.67770700	-1.76492300	-1.86088200

H	-1.78468200	-2.11693400	-2.10049500

Bd

B3LYP/6-31G*

SCF Done: E(RB3LYP) = -1316.39012359

Zero-point correction= 0.301072

Thermal correction to Gibbs Free Energy= 0.255562

C	1.13668400	3.22665800	-0.16765600
C	0.44685400	2.28285600	-1.14506200
C	2.06449400	2.42305500	0.72923100
H	1.19802700	1.79143000	-1.77772300
H	-0.24972400	2.81657200	-1.79041000
H	1.70606700	3.97882800	-0.72891600
H	0.38775600	3.75119500	0.43686600
H	2.52355100	3.04273400	1.50763500
H	2.87678300	1.97596800	0.13562600
P	0.40757900	0.15299500	0.64652300
O	1.33012000	1.41003500	1.40554100
O	-0.22698900	-0.08622900	2.13843700
C	1.88629700	-0.73172900	0.02535800
C	1.85987000	-1.38212500	-1.21806600
C	3.06253500	-0.76425800	0.78916200
C	2.99469900	-2.03879600	-1.69282300
H	0.94956600	-1.37955400	-1.80640500
C	4.18606700	-1.44816300	0.32403100
H	3.09337600	-0.25671600	1.74663700
C	4.15695200	-2.07946100	-0.92027600
H	2.96597900	-2.52851400	-2.66231300
H	5.08558600	-1.48118000	0.93264400
H	5.03644500	-2.60232600	-1.28656900
H	0.13586000	0.61405400	2.71102900
N	-0.35599500	1.22575900	-0.47984100
C	-1.74224800	1.24094700	-0.75408000
O	-0.56017900	-1.19350700	0.12830000
O	-2.24567200	2.17282400	-1.37095100
C	-2.53906400	0.08633600	-0.29071700
C	-1.91170400	-1.10398800	0.10578600
C	-3.93998200	0.14341200	-0.35149100
H	-4.39899400	1.07125400	-0.67679800
C	-2.67709600	-2.23173900	0.42478800
C	-4.06439400	-2.15628900	0.36393100
H	-4.65742900	-3.03055900	0.62019100
C	-4.70326000	-0.96729400	-0.01777800
H	-5.78729600	-0.91858700	-0.05957500

H	-2.16575300	-3.14135600	0.72247300

Cd
B3LYP/6-31G*
SCF Done: E(RB3LYP) = -1316.41850319

Zero-point correction= 0.300703
Thermal correction to Gibbs Free Energy= 0.252340

C	-2.66079300	3.52399900	0.31242900
C	-2.33620500	1.14735200	-0.07463800
C	-1.29350900	3.74568300	0.13294900
H	-3.32429600	4.35446700	0.53544800
C	-0.97086600	1.39457300	-0.27166500
C	-0.44596300	2.68155800	-0.17341400
H	-0.88566300	4.74921400	0.21553100
H	0.61267800	2.83694200	-0.35564300
C	-3.17531000	2.23443800	0.19389000
H	-4.23938500	2.04977900	0.30719500
C	-2.92753800	-0.23320900	-0.22981300
O	-3.82266300	-0.46470400	-1.03622500
C	-2.60056300	-2.59451000	0.40508200
C	-1.53859100	-3.25482300	-0.49470700
H	-3.58773900	-2.72145900	-0.04600400
H	-2.61221800	-3.08117700	1.38780300
C	-0.08827400	-3.16658700	-0.00171200
H	-1.59343400	-2.83566400	-1.50571500
H	-1.79344800	-4.32055800	-0.57987800
H	-0.03074300	-3.17076300	1.09216400
H	0.49009500	-4.01214700	-0.38104200
N	-2.39220900	-1.17036100	0.60429000
O	0.63188200	-2.00777300	-0.50723900
P	0.73502700	-0.61047700	0.28498100
C	2.43800100	-0.08438200	0.03703100
C	2.94537000	0.19939300	-1.24022500
C	3.26507800	0.03254900	1.16218100
C	4.27484400	0.59058200	-1.38567100
H	2.30249000	0.11957300	-2.11168300
C	4.59485500	0.42684500	1.00903500
H	2.85854400	-0.17779400	2.14650400
C	5.09939000	0.70346300	-0.26244400
H	4.66795500	0.81013000	-2.37440900
H	5.23433300	0.52016700	1.88232900
H	6.13504300	1.01091200	-0.38018500
O	0.28663400	-0.63363900	1.70720200
O	-0.13641700	0.35875500	-0.70213200

H	-1.66920500	-0.88459300	1.26013500

Dd
B3LYP/6-31G*
SCF Done: E(RB3LYP) = -1316.41155983

Zero-point correction= 0.300121
Thermal correction to Gibbs Free Energy= 0.251415

C	-4.64701400	-1.13130300	0.13367200
C	-2.39890200	-0.25653400	0.39998900
C	-4.17114900	-2.06792300	-0.79198300
H	-5.70187900	-1.10354000	0.38885800
C	-1.94831100	-1.20186600	-0.52755200
C	-2.81981600	-2.10971900	-1.12533400
H	-4.85640900	-2.77074100	-1.25739500
H	-2.42588900	-2.82863900	-1.83572900
C	-3.76387100	-0.23622400	0.72465600
H	-4.09786400	0.49849700	1.44944300
C	-1.49328500	0.71956300	1.06355800
O	-1.86995600	1.42807800	1.98664700
C	0.68191500	1.86983900	1.18011300
C	0.30509800	3.30759400	0.80621100
H	0.63564700	1.74088900	2.26448200
C	0.32350800	3.60846300	-0.69701900
H	1.03895200	3.95459000	1.30524500
H	-0.67848200	3.55214100	1.22083800
H	-0.50001300	3.08041000	-1.19712400
H	0.14853700	4.68302900	-0.83954700
N	-0.18239300	0.81342200	0.57974200
O	1.56808700	3.27936900	-1.29639400
P	0.47272200	-0.09690300	-0.70635200
C	1.93599100	-0.94145000	-0.08473300
C	1.89848000	-1.68863400	1.10276400
C	3.12657600	-0.85128200	-0.81879700
C	3.04580300	-2.33919800	1.54993600
H	0.97768800	-1.75935900	1.67497700
C	4.27285200	-1.50469800	-0.36513700
C	4.23235100	-2.24662300	0.81620200
H	3.01645000	-2.91728000	2.46912500
H	5.19542100	-1.43319100	-0.93390400
H	5.12631300	-2.75404300	1.16851400
O	0.72579400	0.65967700	-1.96542100
O	-0.60662200	-1.31527500	-0.83919100
H	1.43748500	2.42417100	-1.74630500
H	1.70693900	1.67032200	0.85785900

H	3.14324200	-0.27248900	-1.73663900

E

B3LYP/6-31+G*

SCF Done: E(RB3LYP) = -1163.42127361

Zero-point correction= 0.260284

Thermal correction to Gibbs Free Energy= 0.215872

C	0.56190200	2.91935200	-0.44830400
C	-0.98936300	1.23350200	-1.48420800
C	-0.69342700	2.72233600	-1.29034600
H	0.73534600	3.97366100	-0.20730000
H	1.44528200	2.53718000	-0.98124600
H	-1.89641800	1.09115800	-2.07241300
H	-0.15570900	0.74521800	-2.00893500
H	-0.54461700	3.19994600	-2.26987500
H	-1.55038100	3.20510000	-0.80457900
P	0.03887300	0.65977700	0.93783500
C	1.49403300	-0.20518600	0.26787200
C	2.77469100	0.34697900	0.44985300
C	1.34192400	-1.45734400	-0.35202100
C	3.90527000	-0.34037400	0.00407700
H	2.88466600	1.30934100	0.94393400
C	2.48638900	-2.13485400	-0.79259000
H	0.33918500	-1.91542700	-0.46458600
C	3.75948600	-1.58457400	-0.62216900
H	4.89445300	0.09059900	0.14689400
H	2.36837700	-3.10600000	-1.26808500
H	4.63984500	-2.12259800	-0.97066100
O	-0.30057000	0.34304800	2.35105400
O	0.45017800	2.25173700	0.82031700
N	-1.21991800	0.53222800	-0.20290800
C	-2.49490300	-0.09713600	-0.04410500
C	-2.61522100	-1.25840400	0.87935100
H	-1.86675200	-1.24956400	1.67143200
H	-3.62238700	-1.24729300	1.31445200
C	-2.44550400	-2.62171100	0.03093500
H	-2.67855700	-3.40715500	0.80466200
H	-3.32574600	-2.61960600	-0.66375000
O	-3.41564900	0.26721800	-0.77460200
O	-1.26170100	-2.76729500	-0.57266500

TS_{EF}
B3LYP/6-31+G*
SCF Done: E(RB3LYP) = -1163.41797840

Zero-point correction= 0.260566
Thermal correction to Gibbs Free Energy= 0.217933

Imaginary frequency -- –71.52

C	-0.68911900	2.77675000	-0.99939300
C	-0.96241400	1.34056900	-1.45089300
C	0.47307900	2.81389400	-0.01198800
H	-0.07860500	0.93076300	-1.95982200
H	-1.80590200	1.29674900	-2.14103300
H	-0.44355500	3.39933800	-1.87266700
H	-1.59192400	3.18956100	-0.53192600
H	0.61132900	3.81333600	0.41717800
H	1.40897500	2.52799300	-0.51722800
P	-0.12580800	0.32361000	0.91368800
O	0.24141000	1.94377300	1.09894600
O	-0.52274700	-0.15535300	2.26336300
C	1.45982100	-0.27182300	0.21030200
C	1.54052600	-1.26318300	-0.77947800
C	2.64236600	0.28707800	0.72867400
C	2.79323000	-1.65959900	-1.25961000
H	0.61454300	-1.75254200	-1.08856000
C	3.88982900	-0.12709200	0.25519000
H	2.58399700	1.04547100	1.50455100
C	3.96715500	-1.09679600	-0.74996200
H	2.84837600	-2.43352500	-2.02274800
H	4.79741000	0.30746800	0.67016400
H	4.93784400	-1.41898400	-1.12365300
N	-1.31908500	0.46265700	-0.31690100
C	-2.59276300	-0.14934500	-0.36008600
C	-2.88747300	-1.23211300	0.62244300
H	-3.97424000	-1.37666200	0.64456300
H	-2.50933300	-0.99304700	1.61716800
C	-2.15552400	-2.56892300	0.15065200
H	-2.71372700	-2.90545400	-0.76347700
H	-2.42622000	-3.31092200	0.95008200
O	-0.83596800	-2.40440000	-0.03680300
O	-3.38401100	0.17738100	-1.25109600

F

B3LYP/6-31+G*

SCF Done: E(RB3LYP) = -1163.43911549

Zero-point correction= 0.262460

Thermal correction to Gibbs Free Energy= 0.219632

C	-0.80991700	2.88527800	-0.25844000
C	-1.22813600	1.69308800	-1.11446500
C	0.41354400	2.50769600	0.57348200
H	-0.42452500	1.46673100	-1.83382800
H	-2.13201900	1.90452100	-1.68963200
H	-0.58565600	3.74212800	-0.91401300
H	-1.63450400	3.17075300	0.40810500
H	0.70551800	3.33401400	1.24133400
H	1.27034500	2.32504700	-0.10522400
P	-0.24748900	-0.24671000	0.77030500
O	0.14052800	1.39344900	1.38184400
O	-0.62068000	-0.76274800	2.14294200
C	1.47522700	-0.34520000	0.06188000
C	1.75030200	-0.61799100	-1.28531500
C	2.55346700	-0.15415100	0.93964200
C	3.06923900	-0.68125000	-1.74938100
H	0.92645000	-0.80346300	-1.96692100
C	3.87210400	-0.24545800	0.48542600
H	2.34641800	0.06585600	1.98271000
C	4.13643300	-0.50098400	-0.86482000
H	3.26129100	-0.88564300	-2.80156500
H	4.69469500	-0.10966900	1.18586000
H	5.16307600	-0.56125200	-1.22225200
N	-1.51318100	0.49131300	-0.31270600
C	-2.69020500	-0.16927300	-0.57299800
C	-2.91118400	-1.42996500	0.24005500
H	-3.86373600	-1.87003100	-0.07108200
H	-2.96926900	-1.15359800	1.29797700
C	-1.73874200	-2.42758000	0.05852100
H	-1.92346200	-3.05539000	-0.82768400
H	-1.69713400	-3.08440400	0.94188000
O	-0.51045800	-1.77862900	-0.14271000
O	-3.53260100	0.23425200	-1.39118000

G

B3LYP/6-31+G*

SCF Done: E(RB3LYP) = -1163.45467638

Zero-point correction= 0.262562

Thermal correction to Gibbs Free Energy= 0.219339

P	-0.36152300	-1.26354900	0.44005900
O	0.64055400	-1.06327800	-0.80769700
O	0.31480500	-0.59630400	1.75044600
C	1.95426900	-1.69197700	-0.80077800
H	1.81939400	-2.74499600	-1.07791600
H	2.36902300	-1.62248000	0.20679100
C	2.88492000	-0.97392300	-1.77134400
H	3.85744500	-1.48176100	-1.67148800
H	2.54676000	-1.12632200	-2.80772000
C	3.04213500	0.54357000	-1.47676200
H	2.23217700	1.09419300	-1.97683700
H	3.99122400	0.87894900	-1.93198900
N	3.03804300	0.76105100	-0.04378000
C	2.05102100	1.51388900	0.40297300
C	0.41291300	0.79838800	2.16205900
H	0.17691900	0.77344700	3.23233900
H	-0.34561000	1.39157900	1.64419000
C	1.79492900	1.39784500	1.91376900
H	2.56865300	0.79285100	2.39903900
H	1.78390500	2.39922100	2.37221500
O	1.21873000	2.23870300	-0.24182700
O	-0.72719700	-2.68031900	0.74726800
C	-1.77725000	-0.25187100	-0.08885600
C	-1.62522800	1.01508100	-0.67846700
C	-3.06070500	-0.79076900	0.09327000
C	-2.76192700	1.72767800	-1.07485100
H	-0.63016600	1.44837700	-0.79999900
C	-4.18962700	-0.07085400	-0.30601600
H	-3.15985800	-1.77822500	0.53573000
C	-4.04001600	1.19033300	-0.89258000
H	-2.64140700	2.71006800	-1.52616900
H	-5.18158500	-0.49581500	-0.16565700
H	-4.91806200	1.75203700	-1.20699200

TS_{FH}
B3LYP/6-31+G*
SCF Done: E(RB3LYP) = -1163.40997148

Zero-point correction= 0.259649
Thermal correction to Gibbs Free Energy= 0.215376

Imaginary frequency -- –68.57

C	-1.04618100	2.82282100	-0.40493200
C	-0.79512800	1.48254400	-1.12619200
C	0.29380100	3.40663900	0.12474500
H	0.28068900	1.34701300	-1.25797500
H	-1.28751300	1.44992500	-2.10186700
H	-1.54891700	3.52796000	-1.08941200
H	-1.71890500	2.65360600	0.44549000
H	0.02649400	4.35696700	0.66811400
H	0.85543800	3.76744500	-0.79181400
P	-0.30225000	-0.63959300	0.70556500
O	0.98374400	2.51244400	0.86391900
O	-0.54070600	-0.39841400	2.15560300
C	1.40803100	-0.65656100	0.12330900
C	1.80718900	-1.50034700	-0.92654100
C	2.34866000	0.15892800	0.77376700
C	3.14569600	-1.53723700	-1.32454200
H	1.07476500	-2.13108600	-1.42041100
C	3.68866900	0.10345400	0.37487400
H	2.01707300	0.85874400	1.53191700
C	4.08758700	-0.73607600	-0.66813800
H	3.45122100	-2.19058200	-2.13925500
H	4.41446100	0.74416700	0.86956100
H	5.13137700	-0.76307600	-0.97699700
N	-1.28937800	0.28431200	-0.39490800
C	-2.61594700	-0.05921400	-0.53392500
C	-3.07104400	-1.24267800	0.31696000
H	-4.09461800	-1.49032700	0.02174800
H	-3.07517000	-0.93577300	1.36993100
C	-2.16578800	-2.46832600	0.14411400
H	-2.32049300	-2.91904700	-0.84464500
H	-2.39500500	-3.22159800	0.90756400
O	-0.76892800	-2.15605200	0.23325400
O	-3.39470800	0.53023300	-1.28428300

H

B3LYP/6-31+G*

SCF Done: E(RB3LYP) = -1163.41674910

Zero-point correction= 0.260351

Thermal correction to Gibbs Free Energy= 0.215714

C	2.39768300	-2.19048800	0.68094800
C	3.03027300	-1.52559900	-0.53155400
H	2.70340900	-1.70919200	1.61863800
H	2.65381100	-3.25277400	0.73721400
H	2.85294400	-2.14200600	-1.42331400
H	4.11596100	-1.44536300	-0.40890200
P	0.35215500	-0.62199900	0.77090300
O	0.47017700	-0.11496600	2.16683100
C	-1.33264800	-0.80325300	0.13658400
C	-1.77382700	-2.04085000	-0.36707200
C	-2.21490400	0.29133500	0.21318200
C	-3.09636000	-2.19192100	-0.78642700
H	-1.08734900	-2.87972800	-0.42218100
C	-3.53356200	0.12326000	-0.22713100
H	-1.88676000	1.30045700	0.52322500
C	-3.97876600	-1.10692900	-0.71502200
H	-3.43518800	-3.15231200	-1.16991900
H	-4.20229800	0.97943400	-0.19147600
H	-5.00893300	-1.22298100	-1.04808700
O	0.96533700	-2.12806200	0.55570800
N	1.29621600	0.28128000	-0.37564600
C	2.51903600	-0.12142400	-0.87314600
O	3.19705400	0.57680200	-1.62624100
C	0.78208800	1.63910200	-0.75764200
H	1.32341600	1.91153700	-1.66455000
H	-0.27728700	1.52886300	-1.00412700
C	0.89342500	2.72858400	0.31575400
H	0.79953200	2.28229500	1.31186000
H	1.87390500	3.23060800	0.25660000
C	-0.28960600	3.74126500	0.14420400
H	-0.11447400	4.52696400	0.93108700
H	-0.10431700	4.28524300	-0.82964800
O	-1.50496800	3.14891200	0.21038900

8) Reference

1 J. Pandey, M. Mishra, S. S. Bisht, A. Sharma and R. P. Tripathi, *Tetrahedron Lett.*, 2008, **49**, 695–698.

2 C. Courtens, F. van Charante, T. Quennesson, M. Risseeuw, P. Cos, G. Caljon, T. Coenye and S. Van Calenbergh, *Eur. J. Med. Chem.*, 2023, **245**, 114924.

3 A. J. Foster, M. Nagata, X. Lu, A. T. Lynch, Z. Omahdi, E. Ishikawa, S. Yamasaki, M. S. M. Timmer and B. L. Stocker, , DOI:10.1021/acs.jmedchem.7b01468.

4 J. R. Davies, P. D. Kane and C. J. Moody, *Tetrahedron*, 2004, **60**, 3967–3977.

5 J. B. Laursen, P. C. De Visser, H. K. Nielsen, K. J. Jensen and J. Nielsen, *Bioorganic Med. Chem. Lett.*, 2002, **12**, 171–175.

6 X. Ding, X. Dai, K. Long, C. Peng, D. Andreotti, P. Bamborough, A. J. Eatherton, C. Edge, K. S. Jandu, P. L. Nichols, O. J. Philps, L. P. Stasi, Z. Wan, J. N. Xiang, K. Dong, P. Dossang, M. H. Ho, Y. Li, L. Mensah, X. Guan, A. D. Reith and F. Ren, *Bioorganic Med. Chem. Lett.*, 2017, **27**, 4034–4038.

7 W. L. Benoit, M. Parvez and B. A. Keay, *Tetrahedron Asymmetry*, 2009, **20**, 69–77.

8 V. Gilard, R. Martino, M. C. Malet-Martino, B. Kutscher, A. Müller, U. Niemeyer, J. Pohl and E. E. Polymeropoulos, *J. Med. Chem.*, 1994, **37**, 3986–3993.

9 PCModel 10.075, K. E. Gilbert, Serena Software, Bloomington IN, 2020.

10 T. A. Halgren, *J. Comput. Chem.*, 1996, **17**, 490–519.

11 T. A. Halgren, *J. Comput. Chem.*, 1996, **17**, 520–552.

12 T. A. Halgren, *J. Comput. Chem.*, 1996, **17**, 553–586.

13 T. A. Halgren and R. B. Nachbar, *J. Comput. Chem.*, 1996, **17**, 587–615.

14 T. A. Halgren, *J. Comput. Chem.*, 1996, **17**, 616–641.

15 Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

16 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.

17 A. D. Becke, *J. Chem. Phys.*, 1992, **97**, 9173–9177.

18 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213–222.

19 M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654–3665.

20 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.
21 T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. V. R. Schleyer, *J. Comput. Chem.*, 1983, **4**, 294–301.
22 Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241.
23 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
24 C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158–6170.
25 A. Schäfer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571–2577.
26 A. Schäfer, C. Huber and R. Ahlrichs, *J. Chem. Phys.*, 1994, **100**, 5829–5835.
27 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.
28 F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057.
29 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378–6396.
30 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.
31 H. B. Schlegel, *J. Comput. Chem.*, 1982, **3**, 214–218.
32 K. Fukui, *Acc. Chem. Res.*, 1981, **14**, 363–368.
33 H. P. Hratchian and H. B. Schlegel, *J. Chem. Phys.*, 2004, **120**, 9918–9924.
34 H. P. Hratchian and H. B. Schlegel, *J. Chem. Theory Comput.*, 2005, **1**, 61–69.